REVIEW

Catalytic asymmetric processes

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1 Introduction

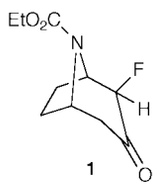
This review covers developments in catalytic asymmetric processes for the calendar year 1998. As in previous years the volume of publications in this area is increasing apace. Accordingly it has been necessary to focus on significant new developments with the emphasis being placed on synthetic methods rather than structural or mechanistic aspects. Some aspects of solid phase chemistry and high throughput screening methods have also been included but are by no means comprehensively covered.

2 Synthetic organic catalysts

2.1 Oxidations

2.1.1 Epoxidation and aziridination

Shi has extended the use of chiral dioxirane catalysts (generated *in situ*) for the epoxidation of silyl enol ethers and enol esters giving up to 95% ee in some cases.[1] This methodology has been extended to the chemoselective epoxidation of enynes giving epoxy alkynes of 96% ee.[2] Armstrong has also published in this area, describing a tropinone derived chiral ketone **1** which gives stilbene oxide with up to 76% ee.[3] Here careful modification of the catalyst was required to ensure that competing



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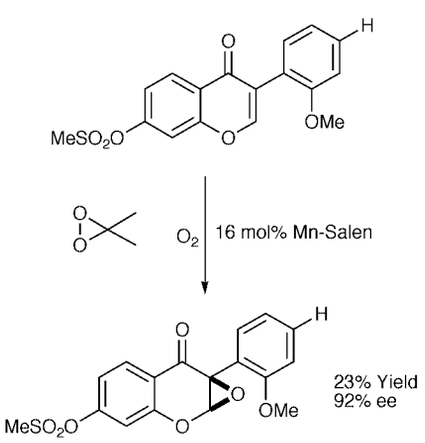
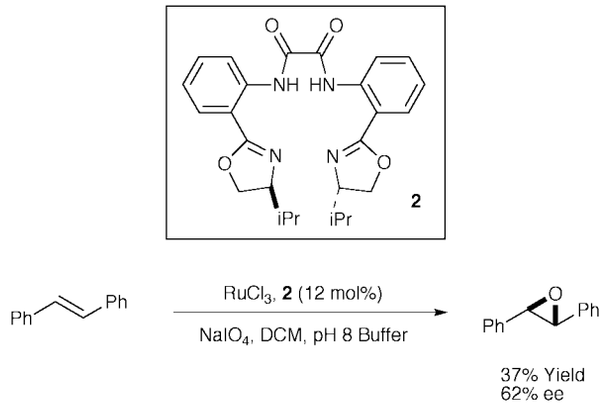
Baeyer–Villiger rearrangement of the catalyst did not occur. A related method of epoxidation using an *in situ* generated chiral oxaziridinium species has been described by Bulman-Page.[4]

Numerous variations on the Jacobsen–Katsuki epoxidation reaction have been reported. Linker described a resolution of 1,2-dihydroxynaphthalene derivatives using a Mn–Salen complex as catalyst with MCPBA as terminal oxidant.[5] The epoxidation of a range of di- and tri-substituted olefins, employing ammonium acetate as an additive in the Salen catalysed reaction, was reported to give epoxides of 64–96% ee, although the exact role of the additive is not well understood.[6] Another variation on the Salen catalysed reaction was described by Adam. In this case the use of dimethyldioxirane, in an oxygen atmosphere as the terminal oxidant, resulted in the epoxidation of a range of isoflavin derivatives giving high ee's (92%) but in only moderate yield (23%) (Scheme 1).[7] The use of Co–Salen complexes for the kinetic resolution of terminal epoxides has been demonstrated to good effect for a range of substrates providing epoxides of up to 95% ee.[8] Pfaltz has prepared a new oxalamide bisoxazoline ligand **2**, the ruthenium complex of which was used to catalyse the epoxidation of stilbene in up to 69% ee under biphasic reaction conditions using sodium periodate as cooxidant (Scheme 2).[9,10]

The lanthanide–BINOL catalysts previously described for the epoxidation of chalcone have been extended for use with a

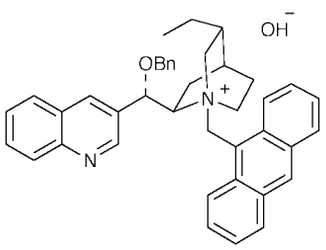


Scheme 1

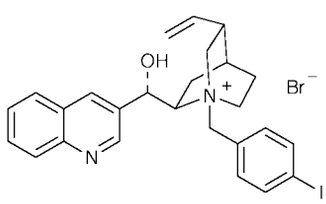


Scheme 2

range of related *trans* enones with excellent results. Shibasaki has developed the Yb catalysed reaction where it was noted that the addition of controlled quantities of water to the reaction resulted in an enhanced ee of the product.[11] Daikai described another additive effect in the La catalysed reaction where addition of 15 to 30 mol% of triphenylphosphine oxide gave increased enantioselectivity.[12] Two groups have independently reported the use of chiral phase transfer catalysts **3** and **4**, derived from Cinchona alkaloid, for the epoxidation of enones.[13,14] The group of Roberts has continued interest in the polyleucine catalysed epoxidation of enones.[15–17] The method has been applied to the synthesis of epoxide precursors to 1,2,3,4-tetrahydro-4-quinolines with up to 98% ee (Scheme 3) and solid phase immobilised polyleucine has been shown to give epoxyketones of up to 98% ee which were subsequently used in the synthesis of naturally occurring lactams such as (+)-clausenamide.

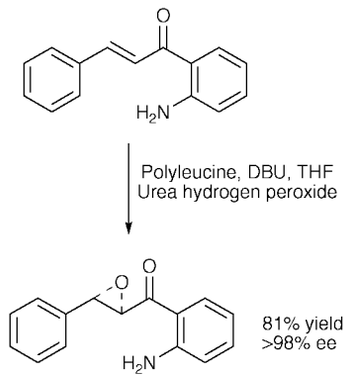


3 (ref. 13)

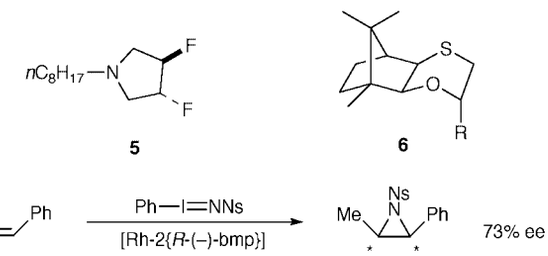


4 (ref. 14)

Marson has reported a variation on the Sharpless epoxidation of allylic alcohols using a difluoropyrrolidine **5** as a chiral ligand. In the case of Geraniol as substrate this leads to the formation of epoxide with 66% ee.[18] Aggarwal has developed a new 1,4-oxathiane ligand **6** for the Cu catalysed addition of sulfur ylides to aldehydes resulting in the formation of stilbene oxide with good *trans* to *cis* selectivity and in up to 64% ee.[19] Finally in this section one notable example of asymmetric aziridination has been reported by Muller, utilising a hypervalent iodine nitrene source to give nosyl protected aziridines of up to 73% ee (Scheme 4).[20]



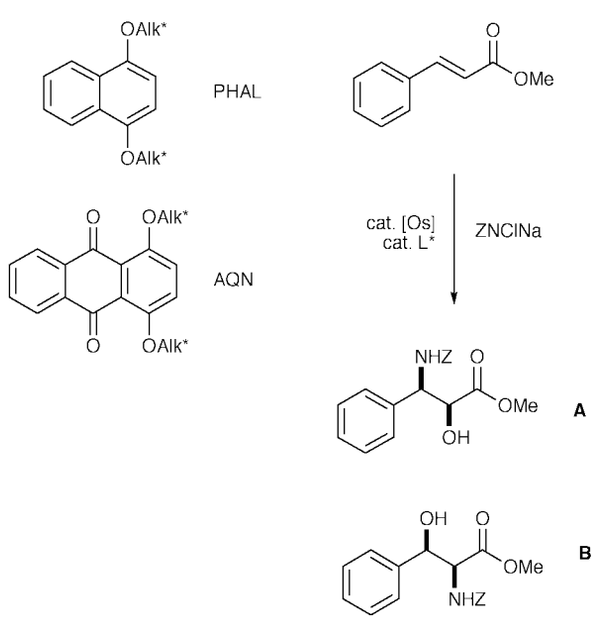
Scheme 3



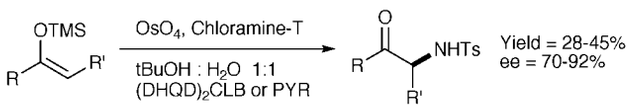
Scheme 4

2.1.2 Dihydroxylation and aminohydroxylation

Although a few examples of Sharpless dihydroxylation[21,22] have appeared in 1998, however, there has been a marked shift in interest towards the related aminohydroxylation reaction. Sharpless reported a new anthraquinone derived ligand (AQN) which shows a reversal in regioselectivity in the aminohydroxylation of cinnamates when compared to the traditional phthalazine (PHAL) derived ligands (Scheme 5).[23] A number of new nitrogen sources have been developed including *N*-chloro-*N*-sodio-2-(trimethylsilyl)ethyl carbamate[24] and the corresponding *tert*-butyl carbamate.[25] Li has developed a new method for the synthesis of Evans oxazolidinones using the aminohydroxylation reaction to generate aryl amino alcohols of up to 91% ee.[26] Finally Phuka has reported the first example of aminohydroxylation of silyl enol ethers to give *N*-tosyl α-amino ketones of up to 92% ee (Scheme 6).[27]



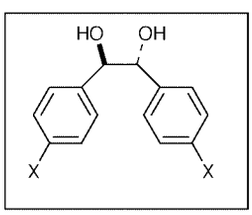
Scheme 5

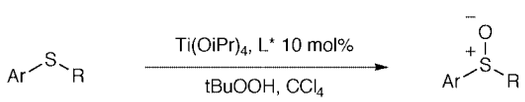


Scheme 6

2.1.3 Sulfoxidation, allylic oxidation and other oxidations

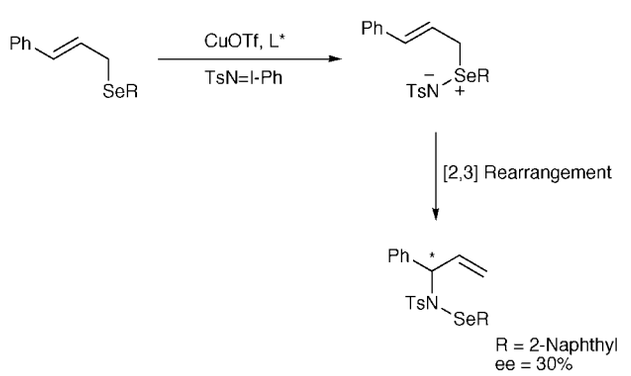
The oxidation of sulfides to sulfoxides remains an area of interest. Superchi has described a new diol ligand for use in the Kagan type oxidation of aryl alkyl sulfides. In this case a notable substituent effect was observed to give reversal of the sense of induction upon sulfoxidation (Scheme 7).[28] The monooxidation of dithianes has also been reported using the Kagan system under anhydrous conditions.[29] Berkessel and Bolm have independently reported the use of Schiff base ligands for the $VO(acac)_2$ catalysed sulfoxidation of aryl alkyl sulfides and dithianes respectively.[30,31] The historically difficult imidation of sulfides and selenides has also shown some promise. Miyake has demonstrated the use of a Cu bisoxazoline catalyst for the imidation of dithianes and aryl alkyl selenides in good yield and up to 40% ee.[32,33] In the case of selenimidation of allylic substrates a concomitant [2,3] sigmatropic rearrangement was observed giving allylic amines of up to 30% ee (Scheme 8).





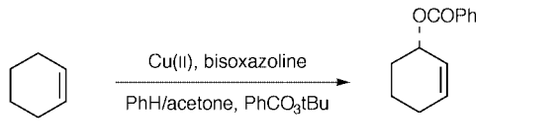
X = H, Ar = Tol, R = Me, Yield = 62%, 80% ee (*S*)
X = CF_3, Ar = Tol, R = Me, Yield = 70%, 26% ee (*R*)

Scheme 7



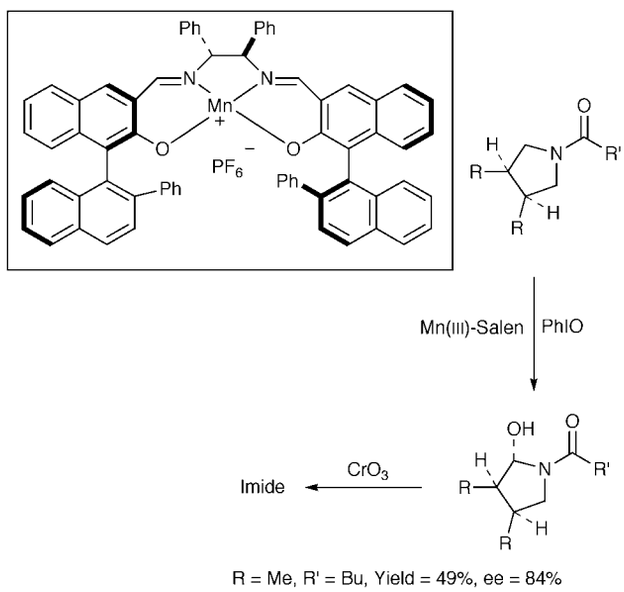
Scheme 8

Allylic oxidation catalysed by Cu(I) bisoxazoline or pybox complexes has been a popular theme this year. Schulz reported the oxidation of methylcyclohexene with *tert*-butyl peroxide to give allylic peroxides with moderate regioselectivity in up to 84% ee.[34] Sekar and Clark have both reported the oxidation of cyclohexene with peresters to give allylic esters in 86 and 78% ee respectively (Scheme 9).[35,36] Clark has also extended this methodology to the oxidation of propargylic (prop-2-ynyl) systems giving alkynyl esters in up to 46% ee.[37] Katsuki and Murahashi have independently described the use of Mn–Salen complexes for the desymmetrisation of pyrrolidines and indan-2-ols respectively using hypervalent iodine reagents as



Sekar: Yield = 88%, ee = 86%
Clark: Yield = 48%, ee = 78%

Scheme 9



R = Me, R' = Bu, Yield = 49%, ee = 84%

Scheme 10

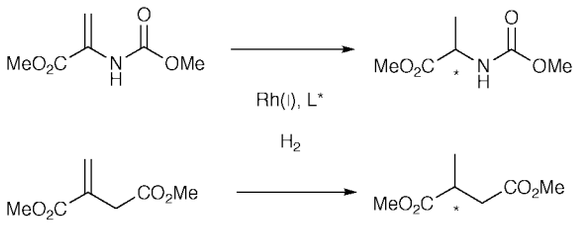
oxidants (Scheme 10).[38,39] Finally Kanger has reported a Ti–TADDOL catalysed Baeyer–Villiger oxidation of ketones to give esters of up to 44% ee.[40]

2.2 Reductions

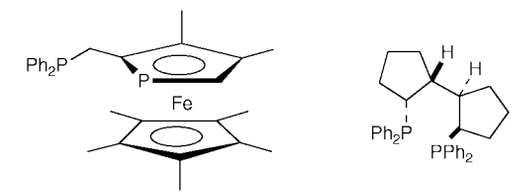
2.2.1 Hydrogenation

Catalytic asymmetric hydrogenation remains an area of great interest with many new ligands being developed, as well as the application of existing methodologies to diverse substrate types. In most cases the ee's are generally good (>90%) and the catalytic turnovers achieved are among the highest of any asymmetric process. Because of the volume of references to be covered in this section not all examples can be discussed in detail, however some attempt has been made to group ligand types and reactions together to aid the reader's evaluation of the material presented.

Traditionally, new ligands for hydrogenation have been tested on two key reactions; the hydrogenation of *N*-acylamino acrylates to give amino acid derivatives and the hydrogenation of itaconate derivatives (Scheme 11). Several examples of ferrocene bridged ligands have been reported to give excellent levels of asymmetric induction in Rh(I) catalysed hydrogenations.[41–43] Of particular note is the introduction of a phosphorus heterocycle-ferrocene derivative **7** with planar chirality which has been demonstrated to give up to 96% ee in the hydrogenation of *N*-acylamino acrylates.[44] Togni has made an interesting entry into the area of immobilised catalysts, reporting dendrimer bound Josiphos analogues for the Rh(I) catalysed hydrogenation of dimethyl itaconate in up to 98.7% ee which compares well to the level of induction achieved using Josiphos alone (99% ee).[45] New diphosphine ligands bearing chiral backbones (usually C_2 symmetric) have also been introduced.[46–48] Zhu has introduced a new C_2 symmetric dicyclopentane diphosphine **8** for the Rh(I) catalysed hydrogen-



Scheme 11



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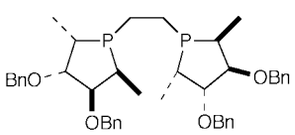

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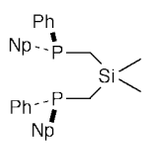

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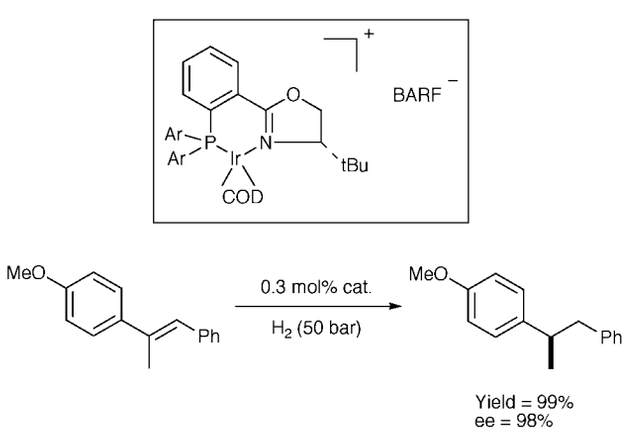
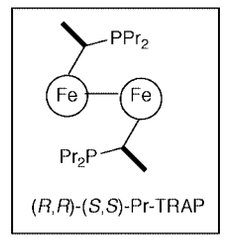
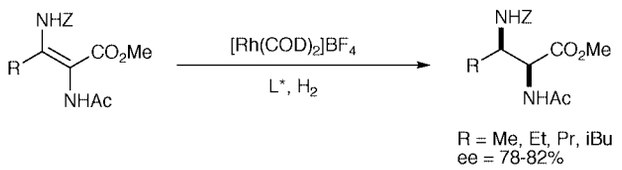
ation of amino acrylates and enamides.[49,50] In the case of amino acrylate hydrogenations the corresponding diphosphonite version of the ligand gave improved enantioselectivities of up to 96% ee. An interesting mimic of Burk's Duphos ligand derived from D-mannitol **9** (termed RoPhos by the authors) provides an excellent catalyst for amino acrylate hydrogenation.[51] Examples of *P*-chiral diphosphines are generally less common due to the complexity of their synthesis, however this type of ligand has been shown to be of value in amino acrylate hydrogenation.[52] One such example is a diphosphine **10** linked by a silicon tether which gives amino acid derivatives of up to 97.7% ee in some cases.[53] Other ligands include bis-aminophosphines derived from a (*R*)-(8*H*)-binaphthyl diamine[54] and an amino phosphonite.[55] Pfaltz has demonstrated the utility of his oxazoline-phosphine ligand for the iridium catalysed hydrogenation of stilbene derivatives (Scheme 12). It is noteworthy that careful choice of counterion (in this case tetrakis{3,5-trifluoromethyl}-phenyl borate abbreviated as BARF) results in increased enantioselectivities compared to more traditional counterions such as tetrafluoroborate.[56] Another example of an Ir catalysed reaction has been demonstrated using a pyrrolidine derived dithiol ligand, giving amino acid derivatives of up to 68% ee.[57]



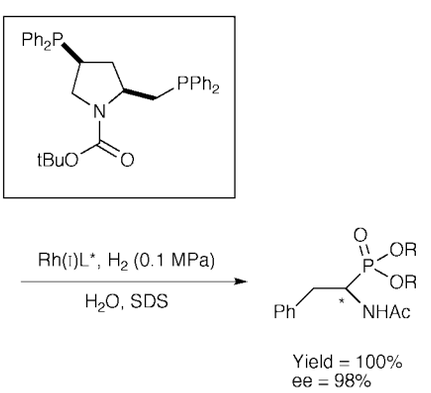
Scheme 12





Scheme 13

Other reactions employing well established ligands for the hydrogenation of novel substrates have been developed. The preparation of β-(2*R*,3*S*)-methyltryptophan in 97% ee by (*R*,*R*)-Me-Duphos-Rh catalysed hydrogenation was reported by Hoerrner.[58] Burk has developed a new route to enamides which can then be utilised in the Me-BPE-Rh catalysed hydrogenation reaction. This more versatile route, involving the reductive amidation of ketones, opens the door to a wider range of substrates for this type of reaction than was previously available.[59] A method for the hydrogenation of (*E*)-α,β-bis(*N*-acylamino)acrylates possessing differently protected amino groups has been demonstrated by Ito using the (*R*,*R*)-(*S*,*S*)-PrTRAP ligand to give amino acid derivatives in up to 82% ee (Scheme 13).[60] Zhang has employed the Me-Duphos-Rh catalyst for the hydrogenation of enol ethers to give β-amino alcohols with excellent levels of stereoselectivity.[61] A similar example utilising enol acetates as substrates, resulting in the formation of secondary acetates, with alkenyl and alkynyl residues remaining untouched, has been reported by Boaz.[62] α,β-Unsaturated phosphinic acids and esters have proven to be useful substrates for asymmetric hydrogenation.[63,64] One particularly striking example is the use of sodium dodecyl sulfate to generate micelle amphiphiles for the hydrogenation of dialkyl 1-benzamido-2-phenylethylphosphonates in aqueous media giving amino phosphonic acid derivatives of up to 98% ee (Scheme 14).[65]

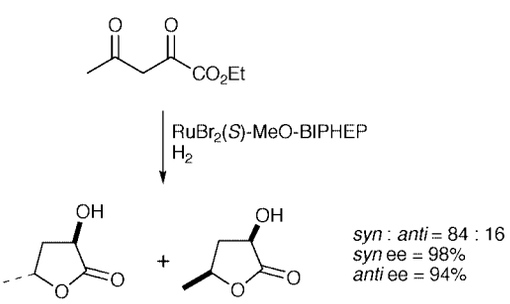


Scheme 14

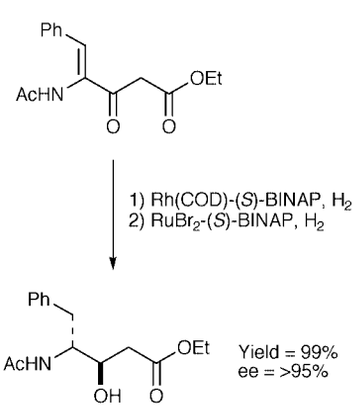
Thus far only examples of C=C bond hydrogenation have been described. In addition, there are a number of examples of catalysts for C=O and C=N hydrogenations which should be mentioned. The sequential hydrogenation of substrates containing more than one keto functionality has shown some promise. Blandin utilised a Ru-complex of the axially chiral biaryl diphosphine (*S*)-MeO-BIPHEP as catalyst for the hydrogenation of ethyl 2,4-dioxovalerate resulting in the formation of lactones with moderate diastereoselectivity and excellent

enantioselectivity (Scheme 15).[66] A remarkably selective one-pot procedure for sequential Rh catalysed C=C and Ru catalysed C=O hydrogenation has been reported by Takahashi allowing the preparation of amino alcohols with >95% ee (Scheme 16).[67] Genet has described a dynamic kinetic resolution of racemic β-oxo amino acid derivatives to give β-hydroxy amino acids with a de and ee of >99% using Ru–(*S*)-MeO-BIPHEP as catalyst.[68] Agbossou has described a number of amidophosphine–phosphinite ligands for the Rh or Ru catalysed hydrogenation of ketones including ketopantolactone.[69–71] Zhang has demonstrated the use of the Rh–PennPhos catalyst for the hydrogenation of aryl alkyl and, more significantly, alkyl methyl ketones with excellent levels of stereoinduction.[72] Noyori has described a series of "shelf stable" Ru–BINAP–Dpen catalysts **11** which are extremely effective for the selective hydrogenation of the keto group in enones and trifluoromethyl ketones.[73,74] Not only do these catalysts give exceedingly high levels of enantioselectivity but they also achieve excellent turnover numbers making them applicable for use in ton scale procedures. A similar Rh catalyst comprising of DIOP and a pyrrole-Schiff base ligand **12** has been employed in the hydrogenation of ketopantolactone giving moderate levels of stereoinduction.[75] Related examples of C=N hydrogenation are less common and in general focus on the use of iridium based catalysts. Schmidt has demonstrated the use of a *tert*-leucine derived iminophosphine phosphonite ligand for Ir catalysed hydrogenation of imines with good levels of stereoinduction (Scheme 17).[76] Kanai has utilised imine hydrogenation in a synthesis of Levofoxacin using an Ir-complex of a proline derived diphosphine. In this case the use of BiI_3 as an additive was important for catalysis.[77] Guiry has designed a novel ligand derived from a C_2 symmetric pyrrolidine for the Ir-catalysed hydrogenation of imines with moderate success (up to 52% ee).[78]

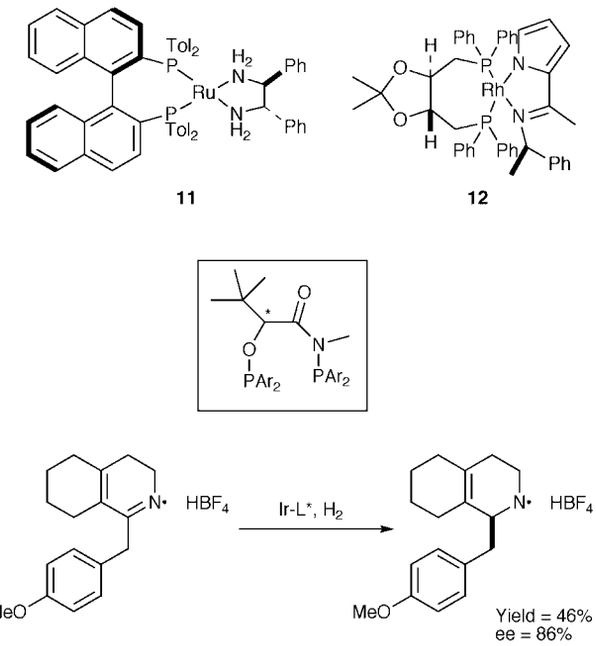
Finally in this section, several examples of asymmetric transfer hydrogenation have been described. In general most of the systems reported utilised isopropyl alcohol as the reductant in combination with an isopropoxide or hydroxide base. Two examples of amino alcohol ligands for use in the transfer hydrogenation of ketones and keto esters have been reported by



Scheme 15



Scheme 16

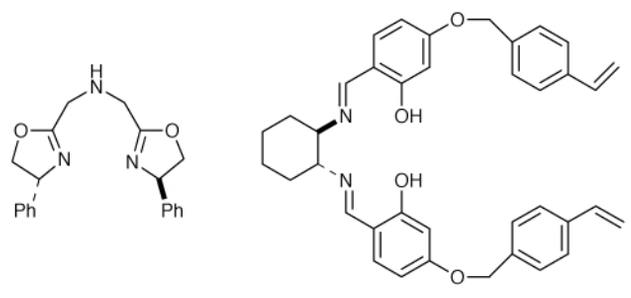


Scheme 17

Andersson and Bulliard respectively.[79,80] Zhang has demonstrated the use of a (bisoxazolinylmethyl)amine ligand **13** for the Ru catalysed transfer hydrogenation of acetophenone with up to 97% ee.[81] de Bellefon has reported the use of *N*,*N*′-dimethyl-1,2-diphenylethylenediamine as a ligand for transfer hydrogenation of ketones in which the addition of acetone to the reaction mixture gives enhanced levels of enantioselectivity.[82] A ferrocene bridged diamine ligand has been reported by Knochel to give up to 90% ee for the Ru catalysed transfer hydrogenation of aryl alkyl ketones.[83] Finally two examples of the solid phase immobilisation of ligands for transfer hydrogenations have been described. The first of these is a heterogenised dialdimine complex **14** of iridium which gives enantioselectivities of up to 70% using acetophenone as substrate.[84] The second example is the use of polystyrene bound Noyori's catalyst **15** for the transfer hydrogenation of ketones with comparable selectivities to those achieved for solution phase catalysis.[85]

2.2.2 Hydrosilylation

The hydrosilylation of C=O bonds provides an alternative means for the production of secondary alcohols, initially formed as their silyl ether derivatives. As for hydrogenation the hydrosilylation reaction is generally rhodium catalysed, utilising chiral ligands containing P or N donor groups. The groups of Rettig and Brunner have reported two different pyridyl oxazoline ligands **16** and **17** which give rise to enantiomeric excesses of 42% and 79% for the hydrosilylation of acetophenone with diphenylsilane.[86,87] A chiral thiazolidine ligand has also been reported by Li.[88] An example of a P donor ligand in the form of a sterically crowded phosphite ligand **18** possessing three branches linked by an amine core (termed TRISPHOS by the authors) has been shown to give 81% ee for the hydrosilylation of acetophenone using 2 mol% of catalyst.[89] The related hydrosilylation of C=N bonds has been extensively investigated by Buchwald who uses polymethylhydroxysilane (PMSH) in combination with his ethylene bridged chiral titanocene catalyst ({EBTHI}TiF_2) for the reduction of imines with up to 98% ee.[90] It is noted that the addition of primary amines to the reaction mixture assists in the release of product from the catalyst and thus improves the scope of this transformation. Buchwald has applied the EBTHI ligand in the Ti-catalysed hydrosilylation of an imine precursor to (*S*)-coniine



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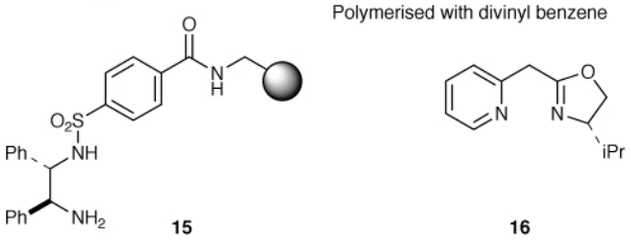
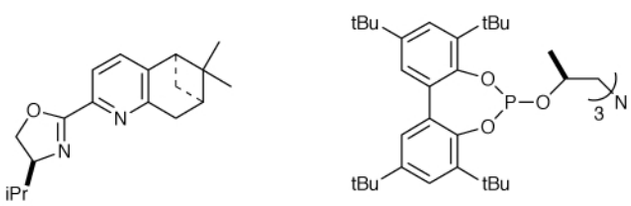
Polymerised with divinyl benzene

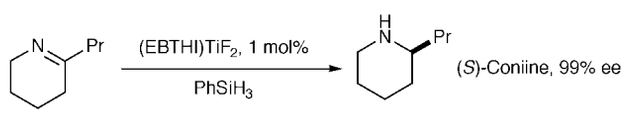


15 16

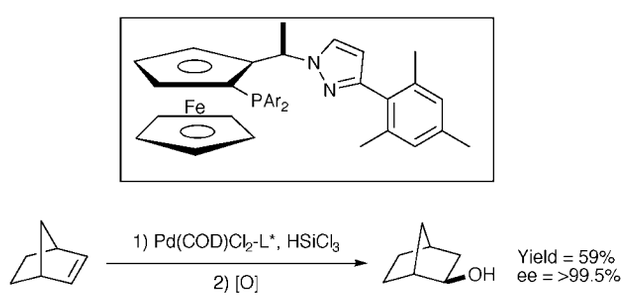


17 18

to good effect giving the natural product in 99% ee (Scheme 18).[91] The hydrosilylation of C=C bonds is best achieved using Pd catalysts. Gladiali has reported the use of a BINAP monooxide (BINAPO) as a P,O chelate for Pd in the hydrosilylation of styrene to give phenylmethyl alcohol of up to 72% ee after oxidative work up.[92] The hydrosilylation of norbornene† with trichlorosilane has been demonstrated by Togni (Scheme 19).[93] The use of a ferrocene derived P,N ligand for Pd enabled the production of the alcohol product in up to 99.5% ee. It was found that steric and electronic factors played an important role in determining the level of stereoinduction, a bulky pyrazole and π-acidic phosphine combination giving the best results.



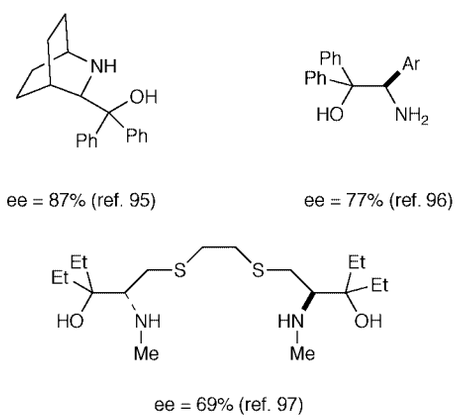
Scheme 18



Scheme 19

2.2.3 Other reductions

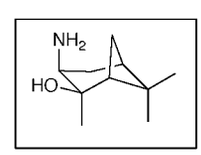
A first example of the use of oxazaborolidines for the synthesis of 1,2-diols has been reported.[94] In this case the Corey oxazaborolidine derived from prolinol was utilised in combination with BH_3·THF for the reduction of a range of α-keto silyl ethers. A few new amino alcohol ligands for use in the reduction of aryl alkyl ketones are shown in Fig. 1 along with the ee's achieved for the reduction of acetophenone.[95–97] The reduction of more complex ketone substrates has been demonstrated by Fujisawa (reduction of an aryl trifluoromethyl ketone) and Wald (reduction of an aryl bromomethyl ketone in a synthesis of (*R*,*R*)-formoterol).[98,99] The double reduction of α-oxoketoximes has been achieved using an amino alcohol ligand derived from α-pinene (Scheme 20).[100,101] The reduction resulted in the formation of 1,2-amino alcohols with moderate *anti*:*syn* selectivity of 82:18 and ee's of up to 99%. Thioxaborolidines have also shown some promise in the area of ketone reductions. Kagan and Dai have reported the use of mercapto alcohols derived from camphor for the reduction of acetophenone with up to 70% ee.[102,103] Finally Wills has developed a phosphinamide derived catalyst **19** for the borane mediated reduction of aryl alkyl ketones with good levels of enantioselectivity (up to 94.4% ee in the case of α-chloroacetophenone).[104]

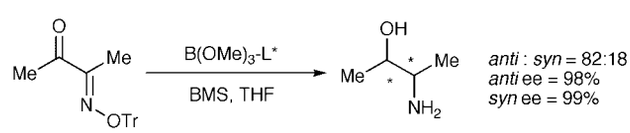


ee = 87% (ref. 95) ee = 77% (ref. 96)

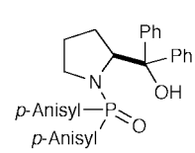
ee = 69% (ref. 97)

Fig. 1 New ligands for borane mediated reductions.





Scheme 20



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2.3 Carbon–carbon bond forming reactions

2.3.1 Addition of carbon nucleophiles to C=O and C=N bonds

The addition of diethylzinc to benzaldehyde remains a proving ground for many new amino alcohol and related ligands. As in previous years the number of examples precludes any detailed discussion of this reaction. Nevertheless, the interested reader is directed to Fig. 2 showing the new ligands reported and the enantiomeric excesses achieved for this reaction. In some cases other aldehydes were also employed but the selectivity achieved using benzaldehyde provides a useful bench mark

† The IUPAC name for norbornene is bicyclo[2.2.1]hept-2-ene.

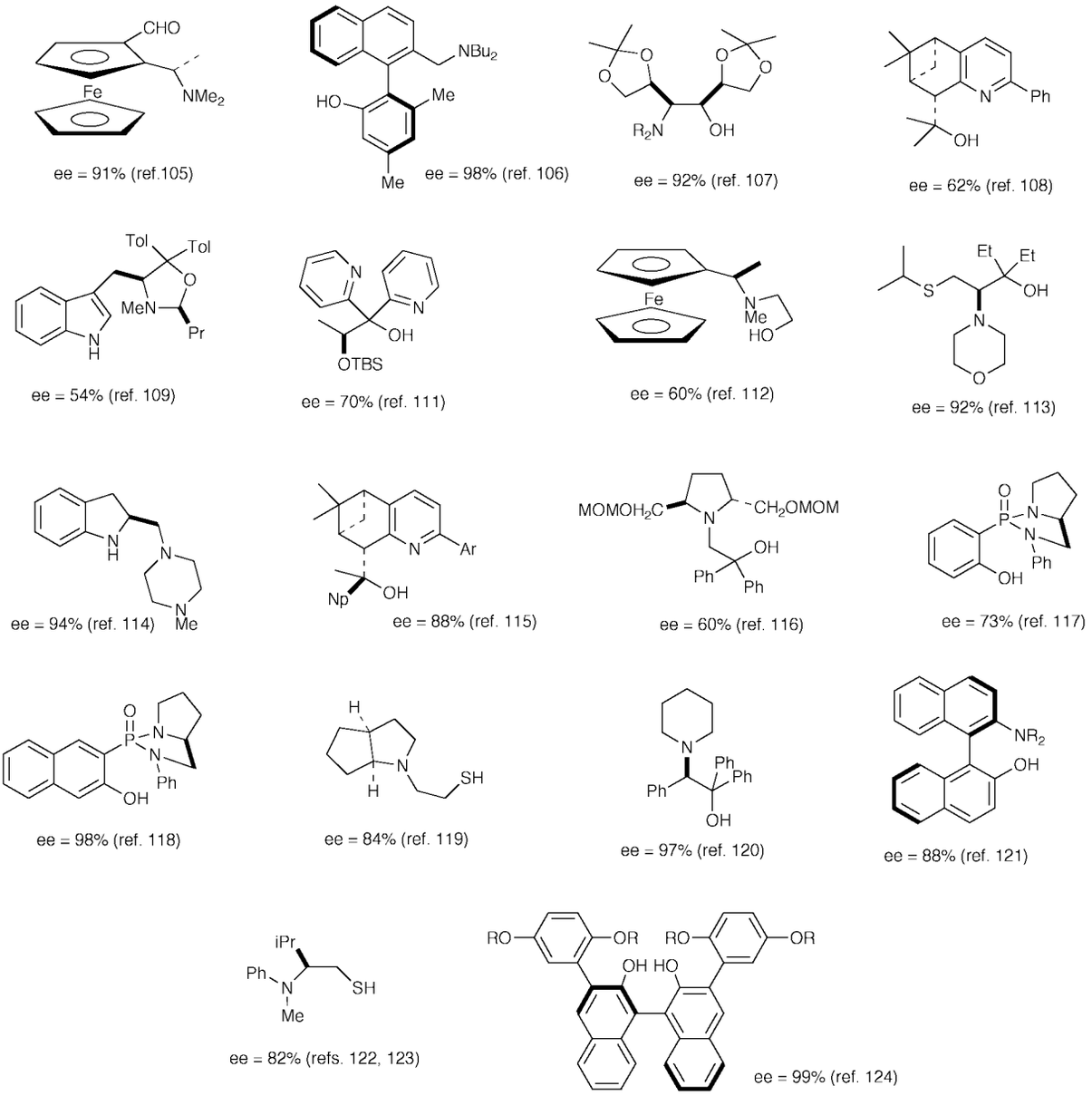
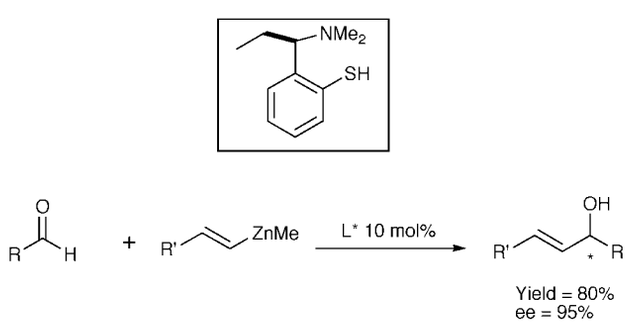


Fig. 2 New ligands for Et_2Zn addition to aldehydes.

for comparisons.[105–124] The reaction has been extended to zinc reagents other than diethylzinc. Wipf has demonstrated the use of a vinylzinc reagent to prepare vinylic alcohols of up to 95% ee (Scheme 21).[125] In this case the zinc reagent was generated from an acetylene precursor using Schwartz chemistry to form the vinylzirconocene which was transmetallated with dimethylzinc to form a mixed vinylmethylzinc reagent. It is noteworthy that only transfer of the vinyl ligand was observed in the subsequent alkylation reaction. Dosa and Fu utilised the DAIB ligand, pioneered by Noyori, for the addition of diphenylzinc to ketones giving tertiary alcohols with excellent levels of stereoinduction (up to 91% ee).[126] The authors noted that the addition of 1.5 equivalents of methanol to the reaction mixture was required to achieve good catalyst turnover (as little as 15 mol% of DAIB could be used successfully.)

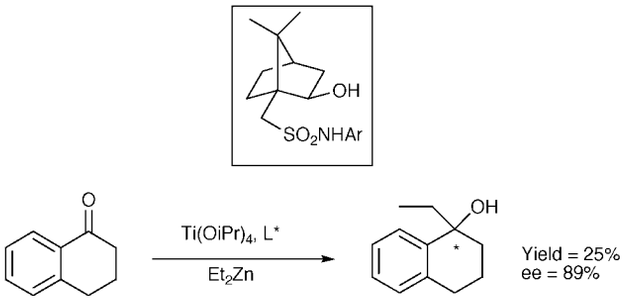
The related Ti(IV) catalysed addition of dialkylzinc to aldehydes has received somewhat less attention during 1998.[127–131] Two examples stand out, the first being the addition of dicyclopropylzinc to benzaldehyde reported by Shibata using amino alcohol derived ligands in conjunction with titanium tetraisopropoxide to give cyclopropyl alcohols with up to 96% ee.[132] The second example, reported by Ramon, demonstrated the addition of diethylzinc to ketones catalysed by a camphor derived sulfonamide ligand (Scheme 22).[133,134] This led to the



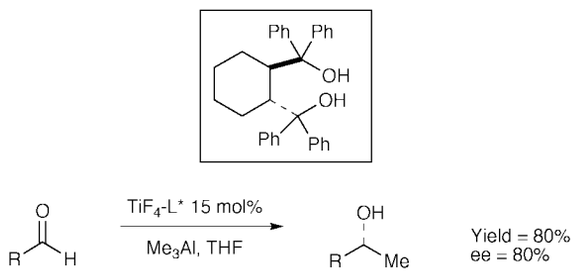
Scheme 21

formation of tertiary alcohols of up to 89% ee although in moderate yield. A related titanium catalysed reaction of trimethylaluminium with benzaldehyde using a C_2 symmetric diol in combination with titanium tetrafluoride was shown to give good levels of stereoinduction.[135] Complexation of aluminium to a titanium bound fluoride is thought to play a key role in the reaction (Scheme 23).

Finally on the subject of dialkylzinc additions to carbonyl compounds, several examples of solid supported catalysts have been reported.[136–138] Kurth has shown that a polymer bound



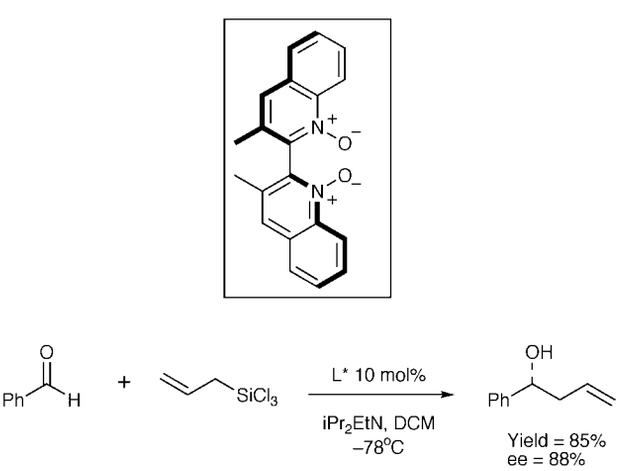
Scheme 22



Scheme 23

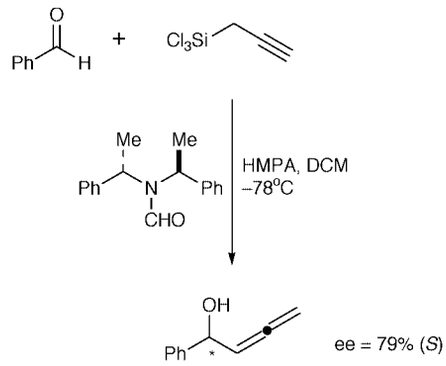
C_2 symmetric bis-sulfonamide gives excellent levels of stereoselectivity (up to 98%) when using only 1–2 mol% of ligand under Ti(IV) catalysed conditions.[139]

The addition of allyl groups to aldehydes can be achieved using either allylstannanes or silanes. Two examples of allylstannane addition utilising BINOL as the chiral ligand have been reported independently by Yasuda (tetra-allylSn–BINOL) and Mikami (Zr–BINOL).[140,141] The use of more environmentally friendly silicon reagents has seen some preference during 1998. Hashimoto has developed a Sakurai reaction in which a biquinoline-*N*,*N*′-dioxide is very effective as a catalyst leading to the formation of allylic alcohols in up to 88% ee (Scheme 24).[142] A chiral formamide has been employed in the allylation and crotylation of cyclohexylaldehyde giving alcohols with remarkable levels of enantioselectivity (98% ee).[143] However, the reaction was observed to be very sluggish, taking up to 21 days to run to completion at −78 °C when 20 mol% of catalyst was used. The same group reported an analogous allenylation of aldehydes to give allenic alcohols with up to 79% ee (Scheme 25).[144]



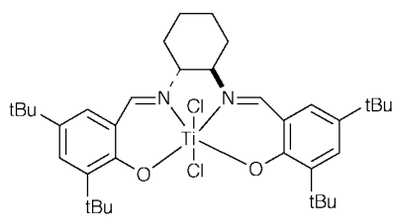
Scheme 24

Progress continues in the area of addition of cyanide to aldehydes.[145–147] The groups of Belokon and North have demonstrated that use of a Salen type catalyst **20** at loadings of as low as 0.1 mol% is effective for the titanium catalysed



Scheme 25

addition of TMSCN to benzaldehyde at room temperature.[148] Even lower catalyst loadings were reported by Yang for the Sm(III) catalysed reaction using a biphosphoramidate ligand **21**, however, slightly lower temperatures are required to achieve comparable levels of enantioselectivity.[149] In the related area of cyanide addition to imines (the asymmetric Strecker reaction) Jacobsen has utilised a high throughput screening method to find the optimal Schiff base–peptide ligand for the cyanation of allyl protected imines in up to 85% ee.[150] Even greater selectivities (up to 95% ee) could be achieved employing a new Al–Salen complex.[151] Kobayashi has also utilised his Zr–BINOL catalysts in the addition of tributylstannylcyanide to imines giving ee's of up to 91%.[152]



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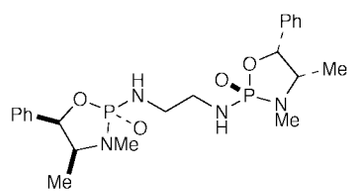
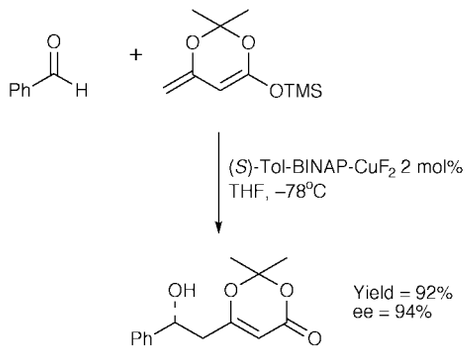


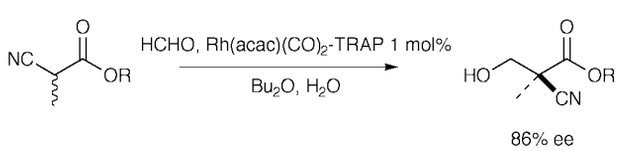
21

The aldol reaction between silyl enol ethers/ketene acetals and aldehydes has remained an area of interest.[153,154] Denmark has extended the use of phosphoramide Lewis bases to the addition of trichlorosilyl enol ethers to aldehydes, giving high yields and good levels of enantioselectivity (92% ee).[155] The use of a "soft" copper Lewis acid has been demonstrated by Carreira for the addition of a dienolate species to a range of aldehydes, possessing aromatic, heteroaromatic and vinyl groups, giving up to 94% ee in some cases, using only 2 mol% of catalyst (Scheme 26).[156] Yamamoto has utilised Evans' pybox ligand for the $Cu(OTf)_2$ catalysed addition of tin enolates to aldehydes giving up to 84% ee for the *syn* product, although with only moderate diastereoselectivity.[157] The authors noted that the reaction failed completely in the case of the analogous silyl enol ethers. A somewhat more unusual aldol reaction employing a Ba(II)–BINOL catalyst for the reaction between ketones and aldehydes (presumably *via* a barium enolate) was reported by Shibasaki, giving moderate levels of selectivity (up to 67% ee in the reaction of acetophenone with pivaldehyde).[158] Ito has demonstrated the use of the ferrocene derived TRAP ligand for the Rh catalysed addition of 2-cyanopropionates to

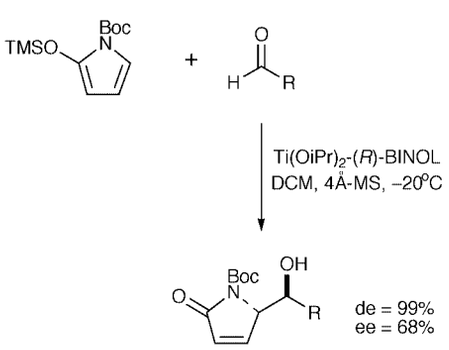


Scheme 26

aldehydes giving the product in up to 86% ee (Scheme 27).[159] The reaction is believed to proceed by coordination of the nitrile group to rhodium. A similar reaction employing a palladium catalyst has been reported by Longmire, in this case giving oxazoline products, although with much reduced levels of enantioselectivity.[160] A pyrrole derivative has been employed in an aldol-like addition to an alkyl aldehyde catalysed by a Ti(IV)–BINOL species (Scheme 28).[161] The product lactam was further utilised in a synthesis of (+)-aminomuricaticin. Finally, on the subject of asymmetric aldol reactions, Salvadori has described the use of a polymer bound salicylaldimine ligand (derived from Carreira's work) for the addition of silyl ketene acetals to aldehydes, giving β-hydroxy esters of up to 53% ee at 48% conversion.[162] A single example of an asymmetric Baylis-Hillman reaction has been described by Hayase. The reaction was catalysed by (*S*)-BINAP at atmospheric pressure to give the desired adduct in 49% yield and 44% ee (Scheme 29).[163]

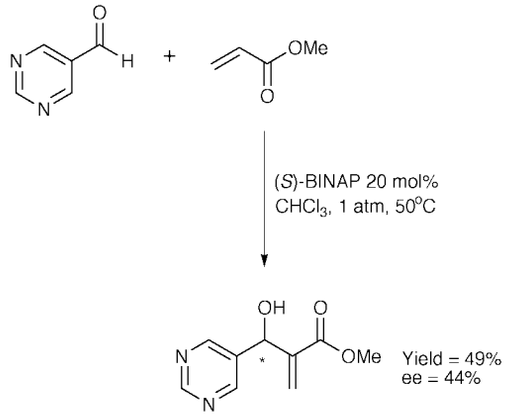


Scheme 27



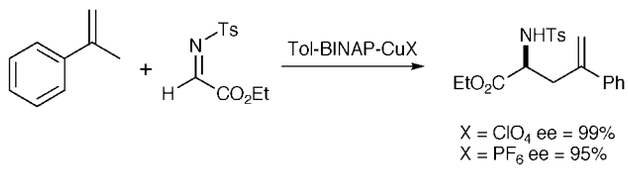
Scheme 28

Intermolecular ene reactions have seen some advances during 1998. Evans has published a nice example of the use of a bisoxazoline–$Cu(H_2O)_2(SbF_6)_2$ catalyst for the ene reaction between olefins and glyoxalates giving up to 97% ee using as little as 1 mol% of catalyst.[164] A key complex was proposed to be a copper chelate between the substrate carbonyl groups. Chavarot has reported a similar reaction catalysed by a Ti(IV) complex of (*R*)-BINOL and a flexible achiral biphenol ligand, giving adducts of 97% ee.[165] Two groups have published an analogous reaction between olefins and imino esters to form amino acid derivatives. In both cases Cu(I)–BINAP complexes were utilised, the only variation being the counterion (Scheme 30).[166,167] Lectka utilised a perchlorate complex (5 mol%) to give



Scheme 29

ee's of up to 99% whereas Jorgensen used a PF_6 complex (0.1 mol%) giving up to 95% ee.



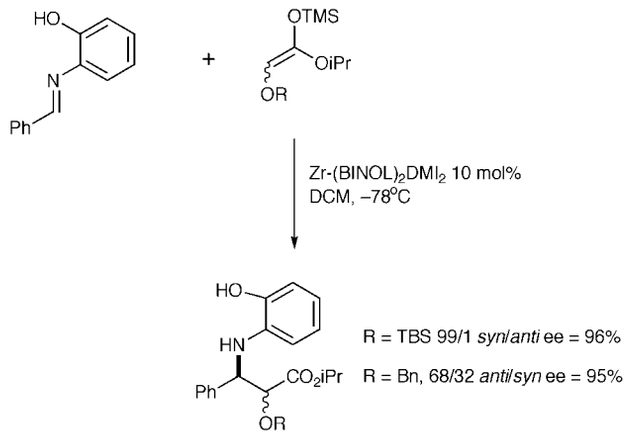
Scheme 30

The addition of carbon nucleophiles to imines has seen such a growth in interest that it almost warrants its own section. Kobayashi has extended the use of his Zr–BINOL catalyst to the addition of *E* or *Z* silyl ketene acetals, bearing silyl or benzyl ether groups to imines.[168] In the case of the silyl ether substrates the *E* or *Z* isomers gave >99 : 1 in favour of the *syn* product with up to 96% ee. However the *E* or *Z*-benzyl ether substrates gave much reduced diastereoselectivity (32 : 68 *syn* : *anti*) with 95% ee for the *anti* isomer (Scheme 31). Kobayashi has also utilised this catalyst system for the addition of silyl enol ethers to *N*-acyl hydrazones, subsequent cleavage of the N–N bond being possible using SmI_2.[169] The groups of Sodeoka and Lectka have used a slightly different approach, employing BINAP derived catalysts for the addition of enol ethers to imino esters either with Pd(II) or Cu(I) as the Lewis acidic species.[170–172] The allylation of *N*-benzyl imines with allyl tributyltin has been accomplished using a β-pinene derived allyl palladium chloride dimer as catalyst giving ee's of up to 81%.[173] The addition of diethylzinc to a phosphinamide protected imine using a novel amino alcohol as catalyst has been reported to proceed in up to 85% ee using 25 mol% of the ligand.[174]

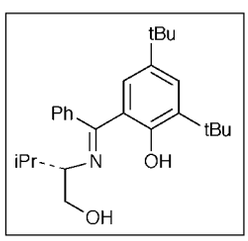
Finally within this section some rather unique examples of carbon nucleophile addition to C=O bonds will be discussed. Oguni has published an example of the addition of diketene to aldehydes catalysed by a Ti(IV) Schiff base complex (Scheme 32).[175] The reaction using 20 mol% of catalyst gives up to 92% ee for the δ-hydroxy-β-oxo ester formed during the reaction. A chiral triazolium salt has been used in combination with triethylamine to effect an asymmetric benzoin condensation giving up to 80% ee when 30 mol% of catalyst was used (Scheme 33).[176] The related thiazolium catalysts gave somewhat reduced enantioselectivities. Asymmetric Darzens condensations have been described by Shioiri using a *Cinchona* derived phase transfer catalyst.[177,178] The addition of α-chloro ketones or sulfones to aldehydes resulted in the formation of epoxides with 80% ee (Scheme 34).

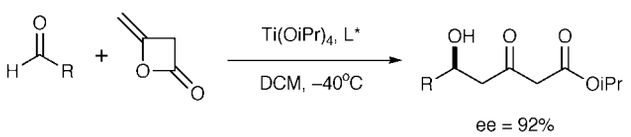
2.3.2 Palladium catalysed allylic substitution

The well known reaction of an acyclic allylic acetate or carbon-

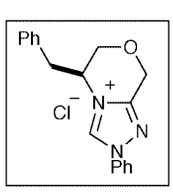


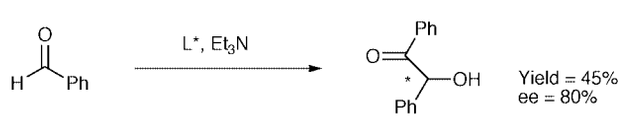
Scheme 31



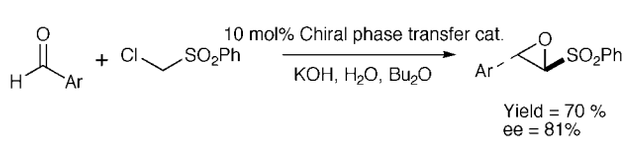


Scheme 32



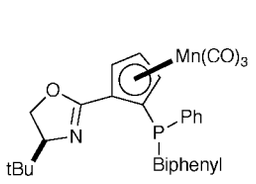


Scheme 33



Scheme 34

ate with dimethyl malonate remains a popular test reaction for new chiral palladium catalysts. The enormous number of new ligands cannot be discussed in detail and the reader is thus directed to Fig. 3, where the ligands are shown, along with the optimal ee's for the alkylation reaction (note that the reaction conditions vary and thus it is necessary to refer to the original paper for more details).[179–200] The less commonly explored reaction of cyclic allylic acetates has been investigated by Helmchen with great success. The use of a facially chiral oxazoline phosphine manganese tricarbonyl ligand **22** was shown to give ee's of >99% for the addition of dimethyl malonate anion to an allylic acetate derived from cycloheptenone.[201] Remarkably the



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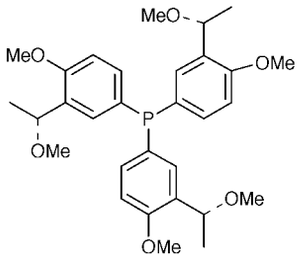

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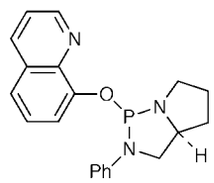
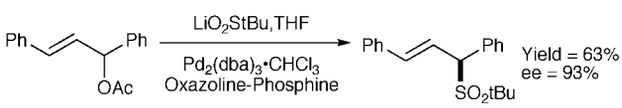


24

ligand contains three chiral features: a stereogenic centre in the oxazoline, a stereogenic centre at phosphorus and facial chirality of the cyclopentadienyl group, all of which are matched to give optimal enantioselectivity. Burgess has developed a C_3 symmetric phosphine ligand **23** for the related amination of cyclic allylic carbonates, the reaction with phthalimide proceeding with up to 82% ee.[202]

Amines have long been popular nucleophiles for allylic substitution. Buono has employed a P-chiral ligand **24** for the reaction of a range of amines with acyclic allylic acetates.[203] In the case of benzylamine addition an ee of 93% was achieved using only 2 mol% of Pd. Gais has demonstrated the use of sulfur nucleophiles with remarkable success. Using Trost's diphosphine ligand the addition of thiols to cyclic and acyclic allylic carbonates was achieved in up to 87% yield and 96% ee.[204] A similar addition of $LiSO_2tBu$ was achieved using an oxazoline phosphine ligand giving up to 93% ee (Scheme 35).[205] During the course of the reaction a kinetic resolution of the starting allylic carbonate was observed, giving recovered starting material which was enantiomerically enriched. A silyl ketene acetal has also been employed as a nucleophile in an addition to an allylic carbonate catalysed by a chiral amidine phosphine complex, with up to 81% ee being achieved in this case.[206]



Scheme 35

Trost has pushed back the frontiers of the allylic substitution reaction even further with the advent of a new reaction of phenols with allylic carbonates followed by an O to C migration occurring with retention of configuration.[207] The result is an allylic arylation reaction which proceeds in up to 97% ee (Scheme 36). This new methodology has been successfully applied to the synthesis of (−)-calanolides A and B and of the vitamin E nucleus.[208] Trost has also developed a novel two component catalyst system for the addition of alcohol nucleophiles to allylic epoxides derived from isoprene or butadiene. The use of 1 mol% of a trialkyl borane in conjunction with 1 mol% of a chiral Pd catalyst gave rise to an allyl palladium borate complex which then underwent a migration of alkoxide from B to C giving products of up to 98% ee (Scheme 37).[209] A synthesis of huperazine A was reported by Bai utilising a bicycloannulation reaction catalysed by a ferrocene bridged diphosphine ligand giving the cyclised adduct in 52% ee.[210] The application of solid phase methods in the Pd catalysed allylic substitution reaction has been demonstrated by

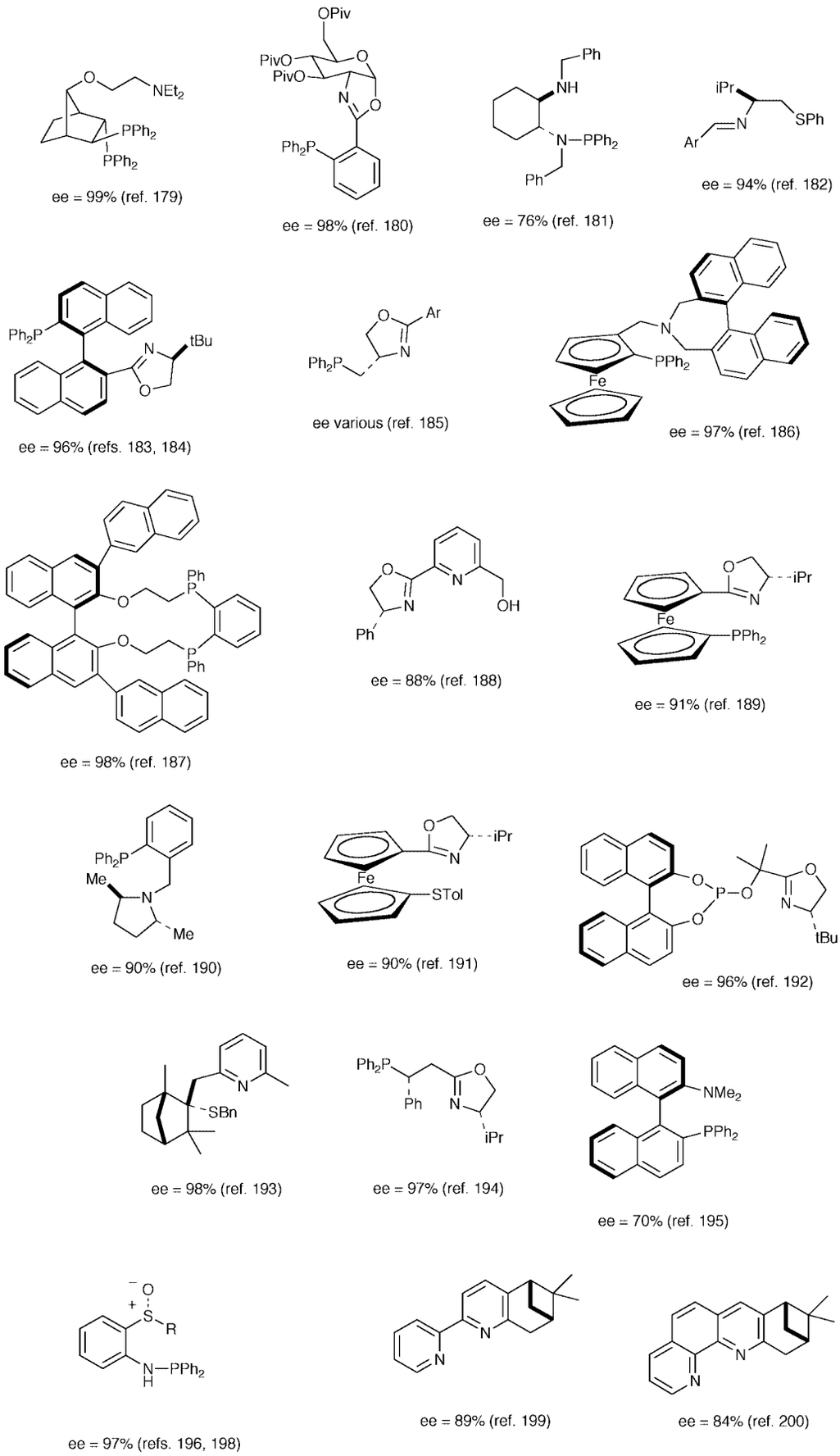
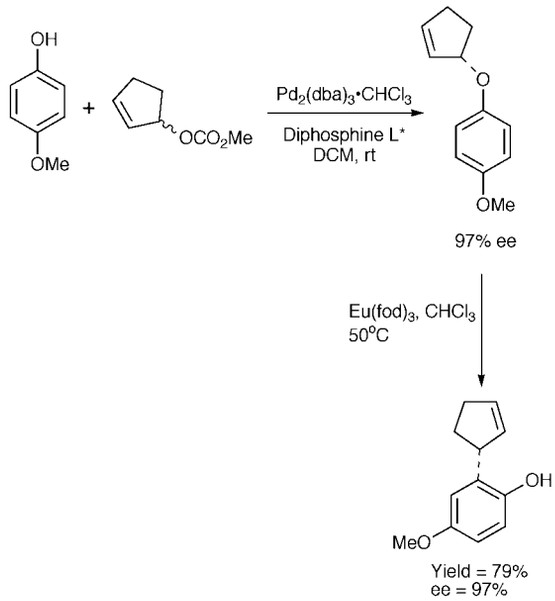
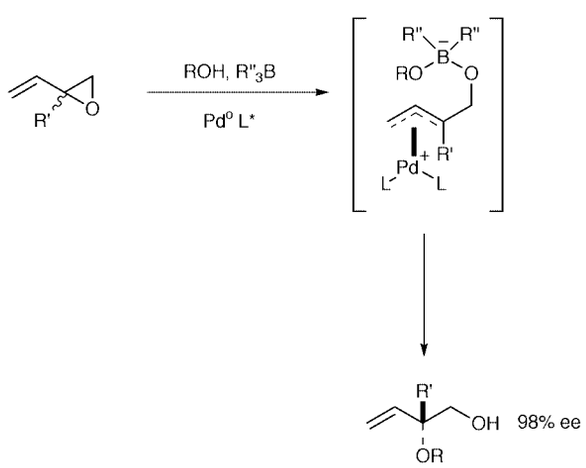


Fig. 3 New ligands for Pd catalysed allylic substitution.

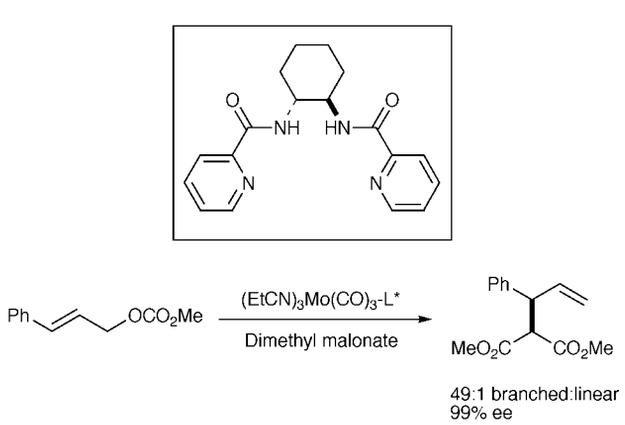
Hayashi using a polymer bound monodentate phosphine ligand.[211] Enantioselectivities of up to 84% were achieved when 2 mol% of the catalyst was employed. Finally within this section a molybdenum catalyst has been developed by Trost for the addition of malonate anion to terminal allylic acetates giving good branched to linear selectivity (49 : 1) and excellent ee's



Scheme 36



Scheme 37

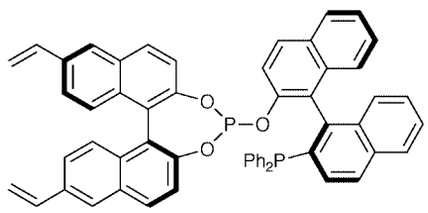


Scheme 38

(99%) for which a C_2 symmetric bis-pyridyl amide ligand was developed especially (Scheme 38).[212]

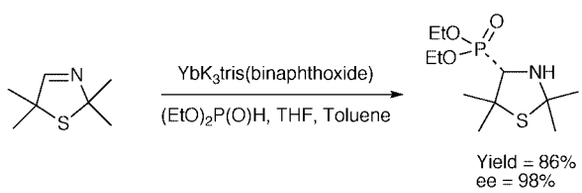
2.3.3 Hydroformylation, Heck and related reactions

The hydroformylation of styrene remains a subject of interest, with a few examples of new ligands for this reaction being reported.[69,213,214] The related hydroformylation of vinyl acetate has been studied by Selke using bis-phosphite ligands derived from β-D-glucopyranoside in the Rh(I) or Pt(II) catalysed hydroformylation reaction, giving greater than 90% of the branched product although in only moderate ee (36%).[215] A solid phase version of this reaction using a phosphine-phosphite ligand **25**, with BINOL units providing the chirality, enables catalysis of the reaction using Rh(I) to give 90% branched product of up to 93% ee.[216] A nickel catalysed hydrovinylation of a styrene derivative using the MOP ligand gave up to 62% ee of product olefin using only 0.7 mol% of the catalyst in an atmosphere of ethene.[217]



Polymerised with divinyl benzene **25**

Hydrophosphonylation of aldehydes to give α-hydroxy phosphonates was reported by Sun using a La(III)–BINOL catalyst.[218] A range of aromatic aldehydes were phosphonylated in up to 74% ee. A similar hydrophosphonylation of a C=N bond was reported by Shibasaki using a YbK_3tris(binaphthoxide) catalyst which gave cyclic amino phosphonates of up to 98% ee (Scheme 39).[219]

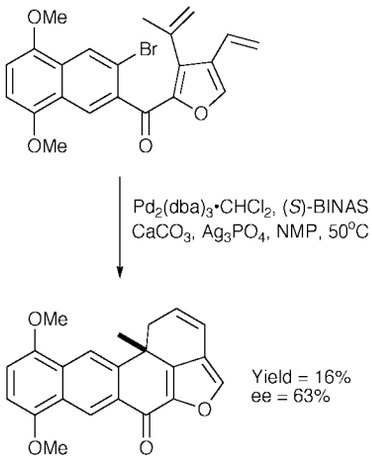


Scheme 39

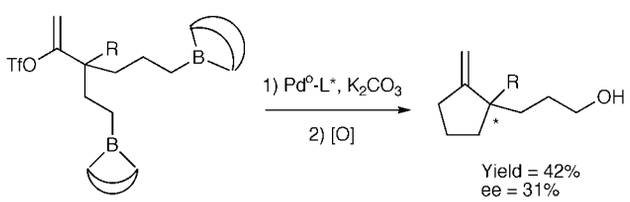
Intramolecular Heck reactions have been reported by Overman for the synthesis of a number of spirocyclic compounds possessing quaternary chiral centres.[220–222] Shibasaki has employed the BINAPAS ligand for intramolecular Heck reactions.[223] The related BINAS ligand was also utilised in a tandem cyclisation reaction to prepare (+)-xestoquinone in 63% ee (Scheme 40).[224] The authors noted that a careful choice of Ag co-catalysts was required, with Ag_3PO_4 performing better than Ag–zeolite. Charpentier has reported the use of a Pd–BINAP complex to catalyse the tandem Heck reaction–hydride capture reaction in a synthesis of retinoid analogues.[225] In this case the use of Ag–zeolite as co-catalyst gave good results with products being formed in up to 81% ee. Finally, Shibasaki has employed a ferrocene bridged P–N ligand in an asymmetric Suzuki–Miyaura reaction giving cyclic products of 31% ee (Scheme 41).[226]

2.3.4 Cyclopropanations

A number of new ligands for the cyclopropanation of styrene using diazo acetates as carbenoid precursors have been reported.[227–232] Most of these new ligands use Cu as the catalytic metal, although a few employ Ru equally effectively. In many cases the levels of *cis*:*trans* selectivity as well as enantioselectivity are moderate to good (Fig. 4). An interesting example of a heterogenised catalyst system was reported by Fraile who used a clay supported bisoxazoline Cu complex. It was noted that the type of clay employed had a marked affect on the *cis:trans* selectivity with Laponite giving the most favourable results.[233] An example of the extension of the bisoxazoline Cu catalyst system to substrates other than styrene has been demonstrated by Andersson who performed the



Scheme 40



Scheme 41

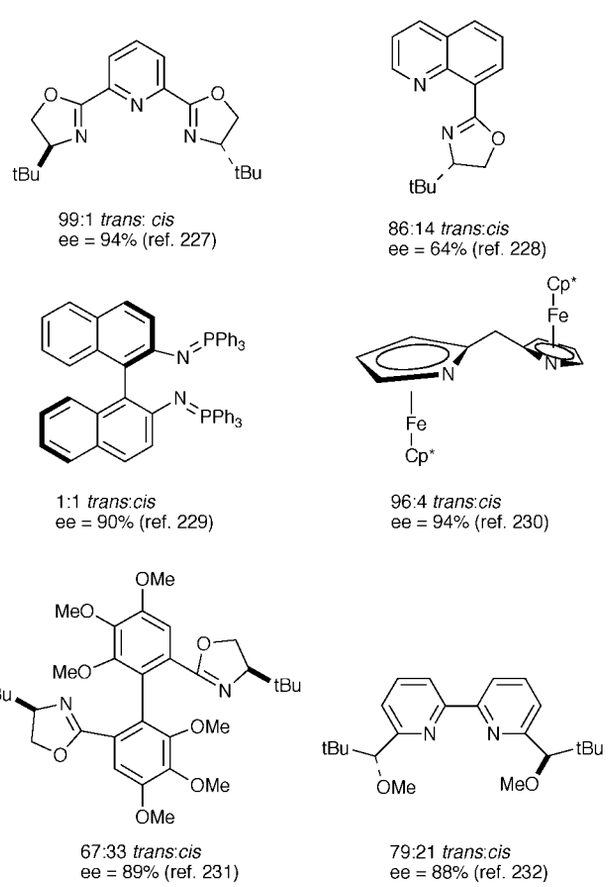
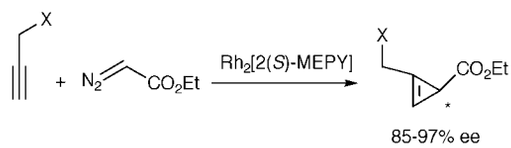


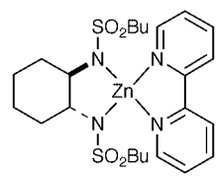
Fig. 4 New ligands for the cyclopropanation of styrene.

cyclopropanation of a cyclic enol ether as part of a total synthesis of (+)-quebrachamine.[234] The cyclopropanation of 1,1-diphenylethene using menthyl diazoacetate as a carbenoid precursor proceeded with excellent stereoselectivity (98% ee) when catalysed by a Cu complex of a binaphthyl derived bis-imine ligand.[235]

Muller has reported two examples of an analogous cyclopropenation reaction.[236,237] In both cases Rh complexes of Doyle's 2-oxopyrrolidin-5-carboxylate (MEPY) ligand were employed for the cyclopropenation of propargyl amines and propargyl acetals in >95% ee and 88–95% ee respectively (Scheme 42). Finally Denmark has described a Simmons-Smith type cyclopropanation of allylic alcohols using a mixed ligand complex **26** comprising of a C_2 symmetric bis-sulfonamide, an achiral bipyridine and zinc.[238] The reaction gives up to 84% ee when 10 mol% of the preformed catalyst is employed, some mechanistic discussion is also included to give an insight into the stereocontrolling factors. Kurth presents an example of a similar Simmons-Smith reaction in which the catalyst is a polymer bound bis-sulfonamide Zn complex.[139]



Scheme 42

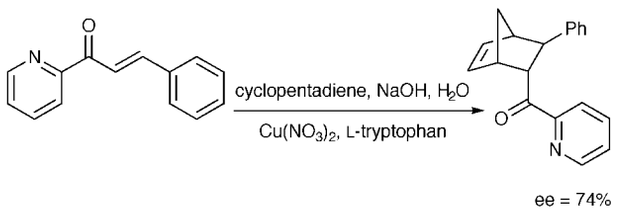


26

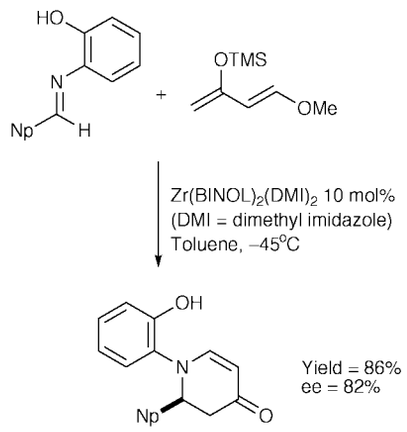
2.3.5 Cycloaddition reactions

The majority of cycloaddition reactions to be discussed here fall into the general category of Diels–Alder reactions. By far the most popular are those utilising an oxazolidinone derived acrylate along with cyclopentadiene as the cyclisation partner. Some examples of Cu(II) catalysed reactions employing bis-oxazolines, quinoline-phosphites or oxazoline-phosphines have been shown to give high preference for the *endo* adduct along with 97–99% ee's.[239–241] Other examples include the use of a Pd(II)–BINAP catalyst giving up to 99% ee for the *endo* isomer,[242] a heterobimetallate LLB catalyst giving a moderate ee of 63% for the *endo* isomer,[243] and an unusual cationic silicon catalyst giving good *endo* selectivity (>95%) but poor enantioselectivity (10%) for the reaction of cyclohexadiene with an oxazolidinone derived acrylate.[244] Aggarwal has demonstrated the utility of Evans's Cu–bisoxazoline catalysts for the [4 + 2] addition of α-thioacrylates with cyclopentadiene as a route to (1*S*,4*S*)-norbornenone, giving 88% de in favour of the *endo* isomer which was formed in >95% ee.[245] The use of a pyridyl enone as a substrate for cycloaddition was described by Engberts who used a Cu(II) complex of the amino acid L-tryptophan to catalyse the reaction. The reaction was carried out in aqueous solvent and gave up to 74% ee of product when 10 mol% of catalyst was used (Scheme 43).[246] Two groups have described the Diels–Alder reaction of methacrolein with cyclopentadiene, the first utilising an imino–Ir(III) catalyst **27** to give an *exo* selective reaction [although in moderate ee (46%)] and the second using an aluminium complex of a facially chiral diol **28** to give similar *exo* selectivity but with an increased level of enantioselectivity (61%).[247,248] An unusual example of the use of a chiral dichloroborane as catalyst for the cycloaddition of methacrylate to cyclopentadiene was reported by Yamamoto giving exclusively the *endo* isomer in 73% ee (corrected for the enantiopurity of the catalyst).[249]

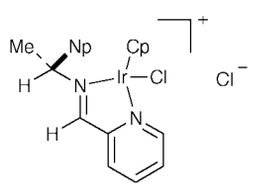
There has been an increased degree of interest in the catalysis of asymmetric hetero-Diels–Alder reactions. In particular several examples of aza-Diels–Alder reactions have appeared. Kobayashi has utilised his Zr–BINOL catalyst for the reaction between an imine and Danishefsky's diene giving the cyclo-



Scheme 43



Scheme 44



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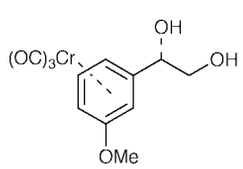
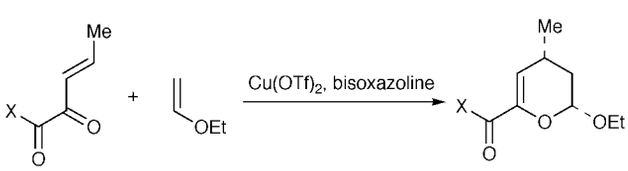


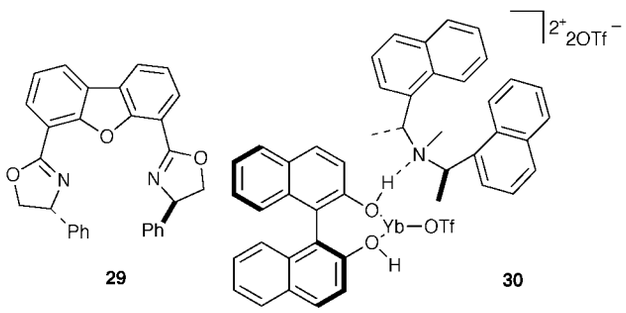
28

adduct in 82% ee (Scheme 44).[250] Similar reactions have been reported by Jorgensen (using a Cu(I)–BINAP catalyst) and Whiting (using a Mg(II)–diamine catalyst optimised using high throughput screening methods).[251,252] Hetero-Diels–Alder reactions of aldehydes with the Danishefsky diene have been reported by Jacobsen and Wu who used Cr(III) and Co(II) Salen complexes respectively.[253,254] Jacobsen achieved 87% ee for the reaction with benzaldehyde and Wu used ethyl glyoxalate, giving a lower ee of 52%. Both Evans and Jorgensen reported essentially the same inverse electron demand Diels–Alder reaction using an enol ether as the dienophile. Both groups utilised the Cu–bisoxazoline catalyst pioneered by Evans to give cycloadducts in 99 and 96% ee respectively (Scheme 45).[255,256] Evans has extended this reaction to use with α,β-unsaturated acyl phosphonates giving cycloadducts of 99% ee.[257]



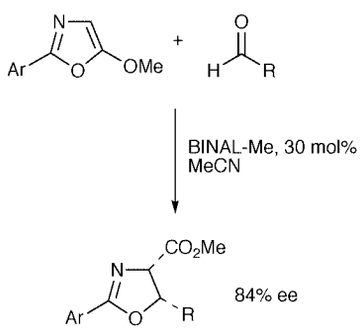
Scheme 45

Another cycloaddition reaction that has been tackled using bisoxazoline ligands is the 1,3-dipolar cycloaddition reaction of a nitrone to an acrylate derivative. Wada has developed a novel dibenzofuran linked bisoxazoline **29** which catalyses this reaction giving excellent levels of *endo* selectivity (98%) and enantioselectivity (>99%).[258] A similar cycloaddition catalysed by an Yb(III) complex **30** of BINOL and a C_2 symmetric amine has been reported by Kobayashi giving up to 98% *endo* product with 96% ee.[259] The amine is thought to hydrogen bond to



29 **30**

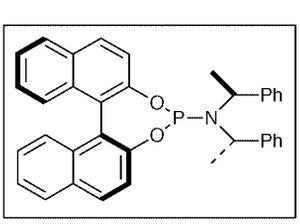
the phenolic hydrogens of the BINOL within the complex and the authors present some IR evidence to support this idea. A BINOL–Al complex has been employed as a catalyst in a [3 + 2] cycloaddition of 5-alkoxyoxazoles with a range of aldehydes giving good levels of diastereoselectivity and up to 84% ee (Scheme 46).[260] Finally a [2 + 2] cycloaddition of ketenes with aldehydes to give butyrolactones has been described using a Ti(IV)–TADDOL complex as the catalyst, although only moderate levels of enantioselectivity were achieved.[261]

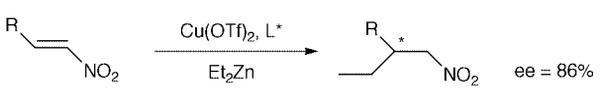


Scheme 46

2.3.6 Addition of carbon nucleophiles to C=C bonds

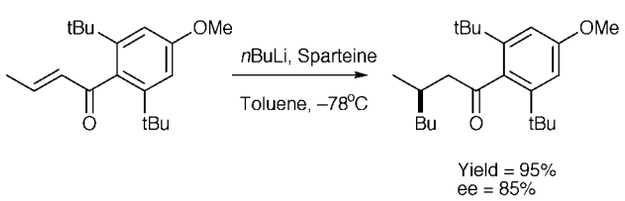
Recent success in catalysing the addition of diethylzinc to cyclohexenone has prompted a number of reports in this area. Both Alexakis and Feringa have described the use of TADDOL derived ligands for such a reaction.[262,263] Alexakis's group reported a phosphite which gave up to 96% ee when using only 1 mol% of the chiral ligand in combination with $Cu(OTf)_2$ as the copper source. Feringa presented the use of a related phosphoramidite ligand which gave 71% ee for the addition to cyclohexenone and up to 62% ee when cyclopentenone was used as the substrate (this was an improvement on his previously reported BINOL derived ligand for the same substrate). Other phosphoramidite and amino phosphine ligands which have been used for analogous Michael reaction have been reported by Mori and Chan.[264,265] Sewald has employed Feringa's original BINOL derived phosphoramidite ligand to the conjugate addition of diethylzinc to nitro olefins giving good levels of stereoinduction (Scheme 47).[266]



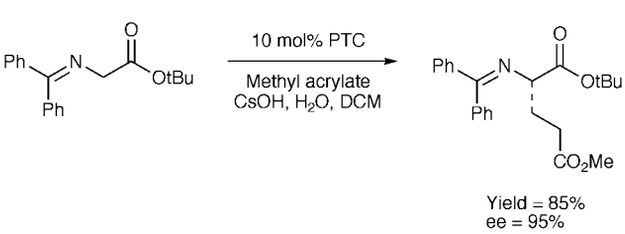


Scheme 47

The addition of other types of organometallic to α,β-unsaturated carbonyl compounds has been demonstrated by Hoveyda who has utilised a Ni(II)–diphosphine catalyst for the addition of butylmagnesium chloride to the dimethyl-acetal of cyclohexenone in up to 82% ee.[267] The conjugate addition of an alkyllithium, in the presence of 30 mol% of sparteine, to a hindered α,β-unsaturated ester gave a remarkable 95% yield and 85% ee of the desired product. Reduction of the sparteine content to 10 mol% resulted in only a small drop in ee to 72% (Scheme 48).[268] Hayashi has pioneered the 1,4-addition of boronic acids and esters, to enones catalysed by a Rh(I)–BINAP complex. The reaction of vinyl boronic acids/esters generated by the hydroboration of an acetylene precursor, with cyclic and acyclic enones has been shown to proceed in 91–99% ee for a wide range of substrates giving access to a variety of γ,δ-unsaturated ketones.[269,270] Shibasaki has reported the addition of dimethyl malonate and a related phosphate ester analogue to cyclohexenone in a conjugate manner using AlLi–binaphthoxide (ALB) complexes as amphoteric catalysts giving adducts with 95–99% ee using as little as 0.3 mol% of catalyst.[271,272] This methodology was subsequently utilised in a synthesis of 11-deoxy-$PGF_{1\alpha}$ in 92% ee.[273] Pfaltz has described a similar conjugate addition of malonate to chalcone catalysed by a Co(II) complex of oxalamide bisoxazoline **2** (see Scheme 2). Diisopropylethyl-amine was employed as base in ethanol as solvent, giving up to 89% ee however in a very low yield of only 13%.[10] The Michael addition of nitroalkanes to chalcone derivatives has been reported independently by two groups. Shibasaki has employed a LaK_3–trisbinaphthoxide catalyst giving up to 97% ee and Bako has utilised a D-glucose derived azacrown ether in combination with NaOtBu to give up to 82% ee for a similar reaction.[274,275] Corey has reported the use of a chiral phase transfer catalyst, derived from Cinchona alkaloid, for the 1,4-addition of a glycine anion equivalent to methyl acrylate to give novel amino acid derivatives in 95% ee (Scheme 49).[276]

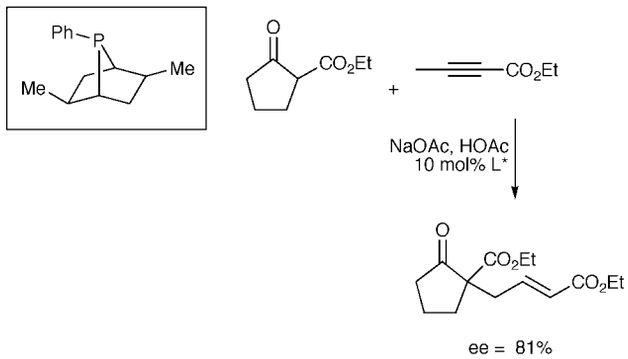


Scheme 48



Scheme 49

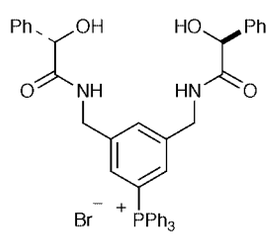
Finally within this section are shown some more unusual examples of asymmetric addition of a range of nucleophiles to C–C double/triple bonds. Katsuki has reported the addition of 2-trimethylsilyloxyfuran to 3-crotyl-1,3-oxazolidinone using a Cu(II)–bisoxazoline catalyst.[277] The resulting 4-substituted butenolide was formed in 95% ee with a preference of 8.5 : 1 for the *anti* diastereomer. This adduct was then converted into *trans*-whisky lactone. Zhang has described an unusual γ-addition of enolates to acetylenic and allenic esters catalysed by a C_2 symmetric phosphine in the presence of sodium acetate (Scheme 50).[278]



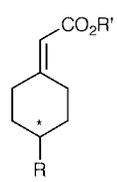
Scheme 50

2.3.7 Other C–C bond forming reactions

This section deals with C–C bond forming reactions which do not readily fit into the previous sections. There has been a surge of interest in chiral phase transfer catalysts for alkylation reactions, many of which are derived from *Cinchona* alkaloids. O'Donnell has used a *Cinchona* derived catalyst for the alkylation of glycine anion equivalents in conjunction with Schwesinger bases.[279] Alkylation was observed to proceed in good yield with ee's ranging from 56–97% depending on the nature of the electrophile. A similar catalyst was employed by Corey for use in CsOH mediated alkylation of β,γ-unsaturated esters to give products of up to 98% ee.[280] Belokon has utilised TADDOL as a phase transfer catalyst for the alkylation of an alanine derivative to produce α,α-dialkyl amino acid derivatives of up to 82% ee.[281] Another reaction which has been shown to be amenable to phase transfer catalysis is the alkylation of enolates. Manabe has designed a new C_2 symmetric phosphonium salt **31** which functions very effectively in the alkylation of keto esters.[282] The author has shown that both arms of the catalyst are required for good levels of stereoinduction (up to 50% ee); when a single arm is present the product is formed with only 1% ee. Shioiri has presented an interesting example of an asymmetric Horner–Wadsworth–Emmons reaction using a Cinchona derived phase transfer catalyst in combination with RbOH.[283] For example 4-substituted cyclohexenones react with a stabilised ylide to give an olefin product **32** of up to 57% ee.



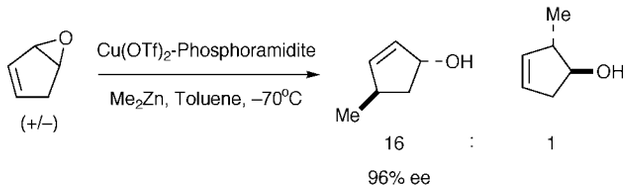
31



32

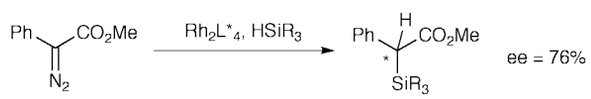
The addition of nucleophiles to *meso* epoxides is a powerful method for the formation of chiral alcohols. In this context Oguni has described the use of a chiral Schiff base for the addition of phenyllithium to cyclohexene oxide giving an α-aryl alcohol of up to 90% ee.[284] An unusual example of a resolution of vinyl epoxides by the S_N2' addition of dimethylzinc under Cu catalysed conditions has been reported by Feringa.[285] The reaction proceeds with a 16 : 1 preference for the S_N2' *vs.* S_N2 reaction with the major isomer being formed with up to 96% ee albeit in a moderate yield of 38% (Scheme 51).

Carbene insertion reactions catalysed by Rh-carboxylates remain an area of interest. For example Hashimoto has demonstrated the use of catalysts derived from *N*-phthaloyl amino acids for the intramolecular insertion reactions to generate pyrrolidinones and azetidinones (for use in carbapenem syn-

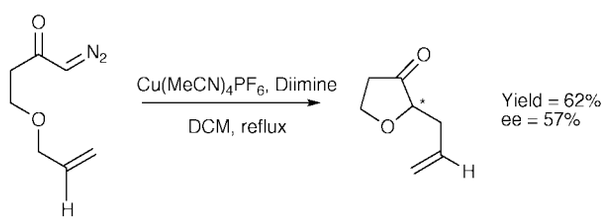


Scheme 51

thesis) with excellent levels of enantioselectivity.[286,287] Moody has described the use of a valine sulfonamide as a catalyst for the intermolecular insertion of carbenoids generated from diazo acetates into Si–H bonds, resulting in the formation of chiral silanes of up to 76% ee (Scheme 52).[288] A very similar transformation has been described by Jacobsen who utilised a Cu–diimine catalyst to give silanes of up to 86% ee.[289] Clark has used a Cu–diimine complex as catalyst for the generation, and subsequent rearrangement of, an oxonium ylide, giving chiral ethers with a respectable 57% ee (Scheme 53).[290]

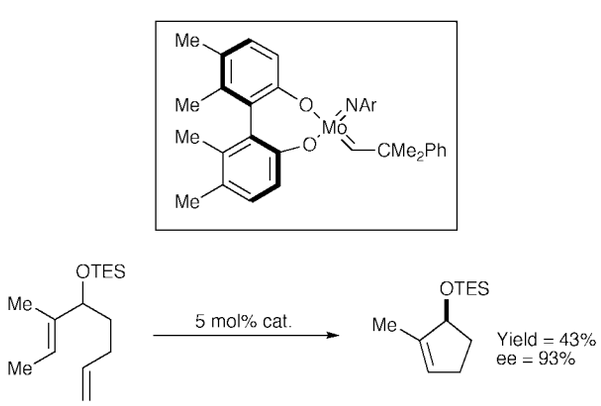


Scheme 52



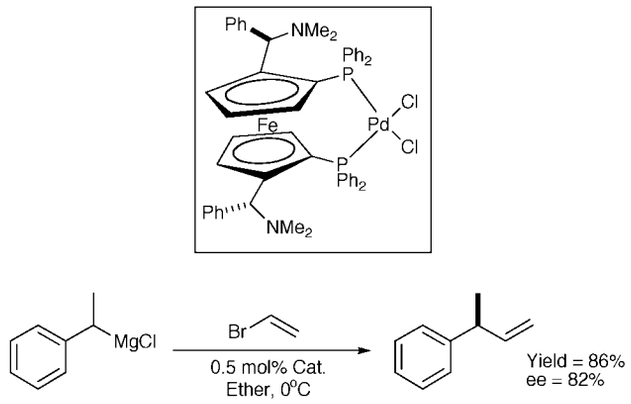
Scheme 53

Asymmetric ring closing metathesis reactions involving the kinetic resolution of racemic substrates or desymmetrisation of *meso* substrates have been reported by Hoveyda who utilised a chiral version of Schrock's molybdenum catalyst.[291,292] The metathesis of a racemic silyl ether led to the formation of cyclic products in 43% yield with an ee of 93%. Unreacted starting material (19%) was recovered in essentially enantiomerically pure form (Scheme 54).



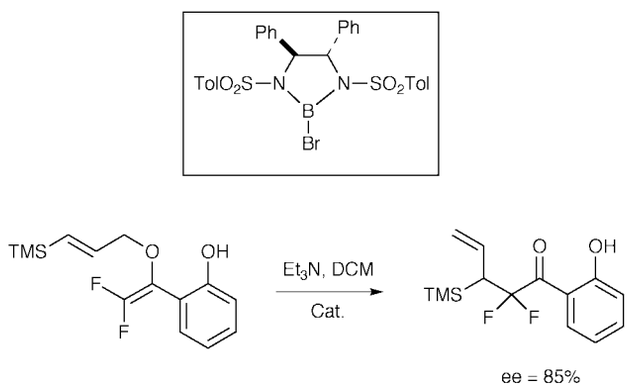
Scheme 54

Several miscellaneous C–C bond forming reactions have also been described. Buchwald demonstrated the asymmetric arylation of ketone enolates using a Pd–BINAP catalyst to generate ketones with quaternary α-centres in up to 88% ee.[293] Knochel reported a Grignard cross coupling reaction in which 0.5 mol% of a ferrocene bridged diphosphine ligand was shown to give stereoinduction of up to 82% ee (Scheme 55).[294] Gilbertson has utilised a Rh–BINAP catalyst for the [4 + 2] cyclo-

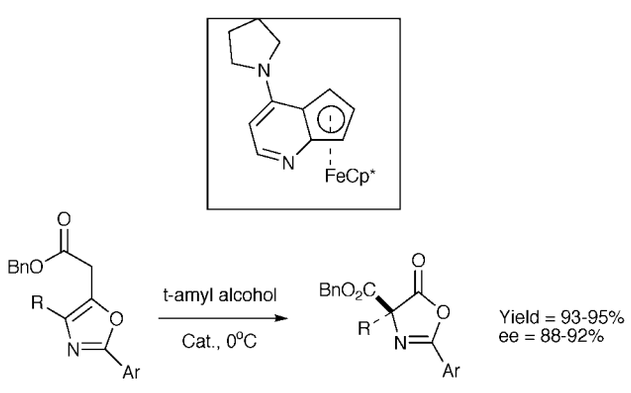


Scheme 55

isomerisation of an ether tethered triene to give dihydrofuran adducts in an impressive 98% ee.[295] An asymmetric Claisen rearrangement has been reported by Ito (Scheme 56).[296] The reaction was catalysed by a boron–bissulfonamide Lewis acid to give α,α-difluoroketone derivatives in 85% ee. Finally, an asymmetric O–C migration reaction has been reported, in which amino acid derivatives possessing α,α-disubstitution have been prepared from *O*-acylated azlactones using a chiral 4-pyrrolidino pyridine analogue (Scheme 57).[297] Products were formed in excellent yields and with 88–92% ee.



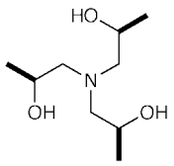
Scheme 56



Scheme 57

2.4 Miscellaneous applications of synthetic asymmetric catalysts

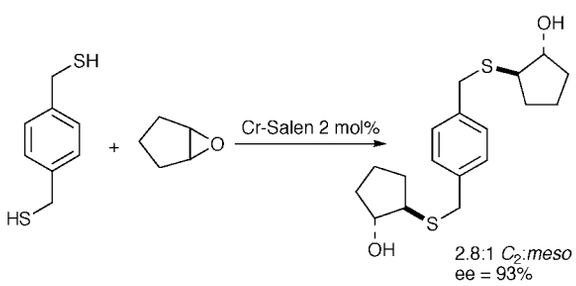
The addition of non-carbon nucleophiles to *meso* epoxides has been described by Nugent, who has utilised allyl iodide as an iodide source that reacts competitively with azide, to form halohydrins in excellent yield (96%) and high ee (95%).[298] The catalyst, a C_3 symmetric triol **33** complexed with Zr(IV), is effective even at only 5 mol% loading. Denmark has reported a chlorohydrin synthesis using tetrachlorosilane as the chloride



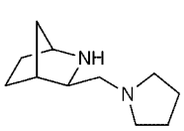
33

source in the presence of a chiral phosphoramide (as Lewis base) giving ee's of up to 93%.[299] Shibasaki has developed a GaLi–BINOL catalyst for the ring opening of epoxides using phenoxides as nucleophiles. The resultant α-hydroxy ethers are produced with ee's ranging from 67–93%.[300]

Various methods for the desymmetrisation of *meso* epoxides have been developed. Chiral β-amino alcohols have been prepared in 80% ee by the Yb–BINOL catalysed addition of anilines to *meso* epoxides.[301] Thiols have also been used as nucleophiles in similar ring opening reactions, catalysed by a Ti–Salen complex, to give hydroxy thiols in excellent yields and moderate ee's.[302] Jacobsen has reported a related example (using a Cr–Salen catalyst) in which enantiomeric enrichment could be achieved by using a bifunctional thiol as the nucleophile (Scheme 58).[303] Jacobsen has also utilised a Co–Salen catalyst for the hydrolytic resolution of racemic epoxides.[304] In one example a dynamic kinetic resolution could be achieved giving the diol product in 93% yield and 96% ee. A novel chiral base **34** for the ring opening desymmetrisation of *meso* epoxides to give allylic alcohols has been reported by Andersson.[305] In the case of cyclohexene oxide the allylic alcohol was formed in 91% yield, 96% ee using only 5 mol% of the chiral ligand.

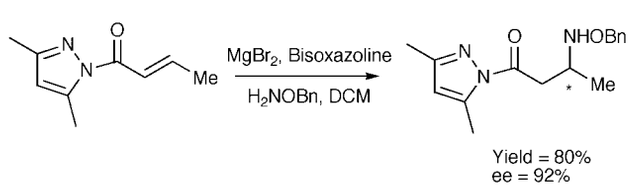


Scheme 58



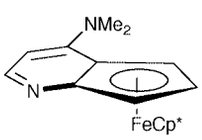
34

The Michael addition of amines to enamide derivatives has been described by Jasperse. The Mg–bisoxazoline catalysed addition of benzyl hydroxylamine to enamides resulted in the formation of β-amino amides of up to 92% ee (Scheme 59).[306] Thiols have also been utilised as nucleophiles by Shibasaki in $LaNa_3$tris(binaphthoxide) catalysed reaction with enones giving, tertiary thiol adducts of 90% ee.[307] Tomioka has reported the addition of thiophenols to α,β-unsaturated esters, catalysed by an ephedrine derivative, to give sulfides of 75% ee.[308]



Scheme 59

A moderate number of non-enzymatic methods for the kinetic resolution or desymmetrisation of alcohols and amines have been described during the course of 1998. The use of chiral proline derivatives as bases for the desymmetrisation of *meso* diols by stereoselective acylation has been reported by Oriyama.[309,310] Initial problems of competitive bis-acylation were solved by the addition of 1 equivalent of triethylamine to the reaction mixture, resulting in the formation of mono-acylated product in 92% yield and 94% ee. Fu has developed the use of a chiral DMAP equivalent **35** for use in the kinetic resolution of racemic secondary alcohols and racemic azlactones.[311,312] The use of a synthetic minimal acylase **36** for the resolution of racemic acylamino alcohols has been reported by Miller.[313] The β-turn geometry of the peptide sequence was observed to play a key role in controlling the enantioselectivity achieved and the sense of induction.



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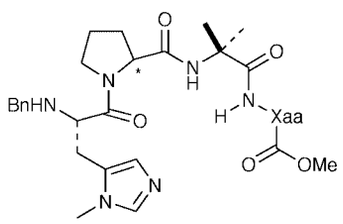

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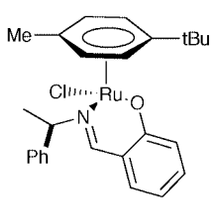


37

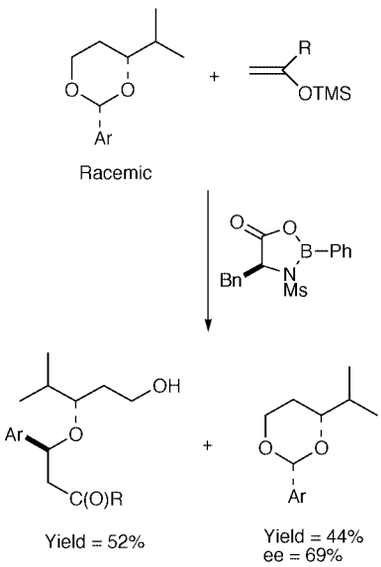
The resolution of racemic acetals of alkane-1,3-diols has been achieved by reaction with a silyl enol ether in the presence of an oxazaborolidine catalyst. At 60% conversion the remaining acetal was isolated in 69% ee and the product alcohol was isolated in 52% yield in an essentially enantiopure form (Scheme 60).[314,315] Double bond isomerisation has proved a useful strategy for the resolution of *meso* 1,3-dioxepins. Frauenrath has reported the use of a Ni–chiraphos catalyst in combination with super hydride to generate isomerised products of up to 67% ee (Scheme 61).[316] Brunner has reported an essentially identical transformation using sodium borohydride in conjunction with a Ru catalyst **37** to give isomerised products with a respectable 60% ee and in good yield.[317]

Two examples of aza-Claisen rearrangements of imidates have been reported. Hayashi employed a Pd(II) cationic complex of a Pfaltz–Helmchen–Williams type oxazoline–phosphine ligand to form the rearranged allylic amine in a modest 30% yield but with 81% ee.[318] Overman performed a similar transformation utilising a ferrocenyl imine Pd complex to give allylic amines in an improved 78% yield with 73% ee (Scheme 62).[319] Asymmetric protonation of an amide enolate was reported by Vedejs giving up to 94% ee for the product amide in the presence of 10 mol% of a chiral diamine.[320] The dynamic kinetic resolution of a racemic enol ether was reported by Yamamoto using a Sn–BINOL complex as catalyst and 2,6-dimethylphenol as proton source to give a chiral ketone in 85% yield and 87% ee.[321]

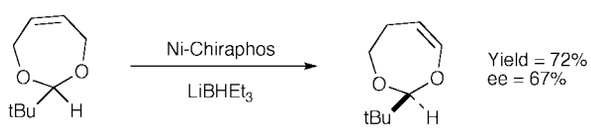
3 Enzymes and antibodies

3.1 Reductions and oxidations

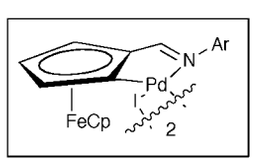
The reduction of ketones to give chiral alcohols using Baker's yeast remains a popular area of interest.[322–331] Reduction of C=C bonds using Baker's yeast has been reported by Kawai.

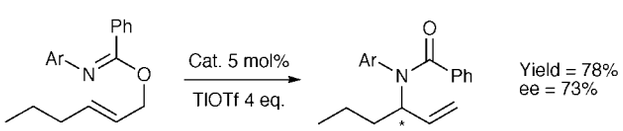


Scheme 60



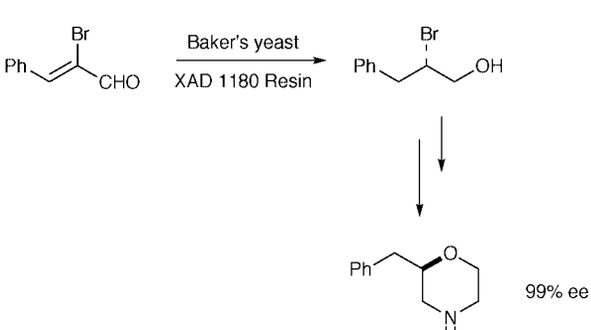
Scheme 61





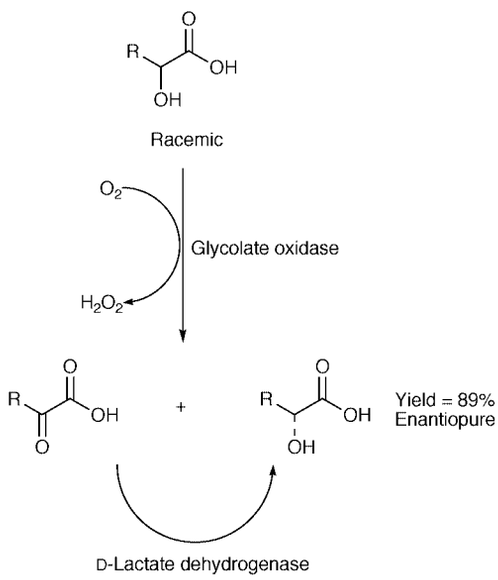
Scheme 62

Enone substrates were selectively reduced to give chiral ketones in >99% ee.[332] The double reductions of α-bromo enones and enals have been reported by Aleu and D'Arrigo respectively.[333,334] The reduction of α-bromo indenone led to the formation of an enantiopure halohydrin in 85% yield, which was then used in a synthesis of Indinavir. The reduction of (*Z*)-α-bromocinnamaldehyde gave a bromohydrin precursor to (*R*)-2-benzylmorpholine (an appetite suppressant) with 99% ee (Scheme 63).



Scheme 63

Other enzymes have also been utilised for ketone reduction giving alcohols with high levels of stereoselectivity.[335,336] Reductases have been employed in the kinetic resolution of 1,2-diols using *Bacillus stearothermophilus* coupled with lactate dehydrogenase (to recycle the NADH reductant) to give enantiomerically pure diols at 50% conversion.[337] A coupled resolution–reduction system was employed in the preparation of enantiomerically pure 2-hydroxy acids in 89% yield.[338] Glycolate oxidase was employed in combination with D-lactate dehydrogenase to produce the *R* enantiomer of the hydroxy acid selectively (Scheme 64).

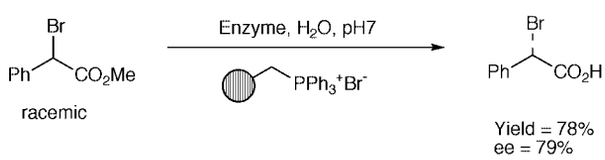


Scheme 64

Oxidation of sulfides has been reported by van de Velde using a phytase, in the presence of vanadate salts and hydrogen peroxide, to yield sulfoxides of up to 66% ee.[339] Other substrates for oxidation include aromatics and heteroaromatics, which can be dihydroxylated using *Pseodomonas putida* to give diols in enantiomerically pure form, albeit in rather low yields.[340,341] Other oxidation reactions include a Baeyer–Villiger reaction for the resolution of substituted cyclopentanones using a new strain of Baker's yeast (*Saccharomyces cerevisiae*), giving unreacted ketone and lactone in moderate yields but in essentially enantiomerically pure form,[342] and a cytochrome P_{450} monooxygenase catalysed oxidation of pentadecanoic acid to give the 14-hydroxy acid in 95% ee.[343]

3.2 Lipases

An enormous number of lipase mediated kinetic resolution reactions have been reported.[344–369] Substrates of particular interest in this area include phosphonyl/phosphoryl acetates,[370,371] fluorinated acyloxy acetonitriles[372] and fluorocyclopropyl carboxylates[373] (Fig. 5). Williams has reported a remarkable dynamic kinetic resolution of bromo esters, in which a polymer-bound phosphonium bromide serves to racemise the slower reacting enantiomer leading to the formation of the bromo acid in 78% yield and 79% ee (Scheme 65).[374] The use of lipases to desymmetrise *meso* substrates has also been heavily utilised during 1998 and the reader is directed to Fig. 6 for some representative examples.[375–385]



Scheme 65

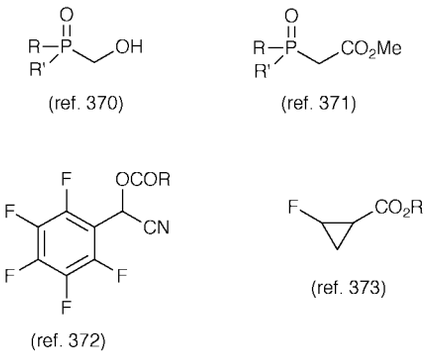


Fig. 5 Substrates for lipase mediated kinetic resolution.

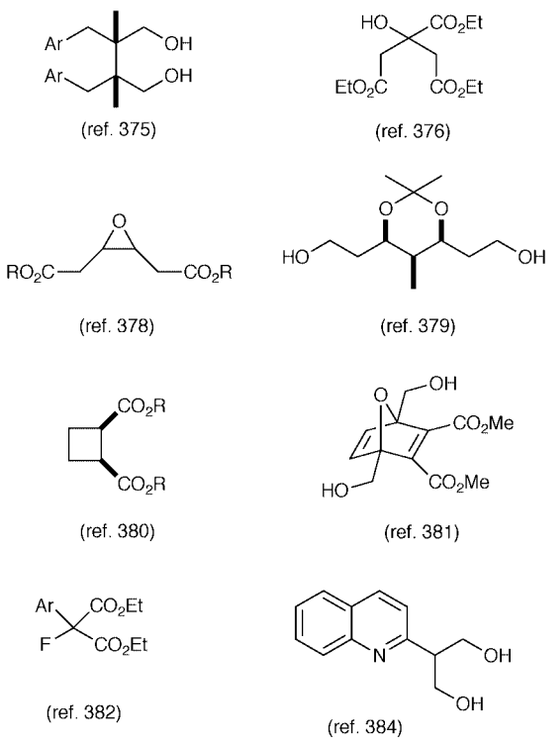
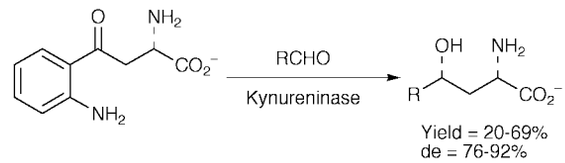


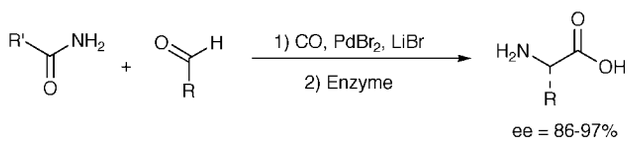
Fig. 6 *meso* Substrates for lipase mediated desymmetrisation.

3.3 Miscellaneous biotransformations

Kynureninase has been used to catalyse the trans-aldolisation between aldehydes and kynurenine to yield γ-hydroxy-α-amino acids in up to 69% yield and 92% de (Scheme 66).[386] Lerner has developed a kinetic resolution of β-hydroxyketones using an antibody aldolase to catalyse the retro aldol reaction giving enatiomerically pure products at 52% conversion.[387] This type of methodology has been applied to the synthesis of natural products such as epothilones and brevicomins.[388,389] An oxynitrilase isolated from almonds has been shown to effect an asymmetric hydrocyanation of aldehydes in quantitative yield and >99% ee.[390] Beller has reported a tandem Pd catalysed amido carbonylation and enzyme resolution reaction for the synthesis of enantiomerically enriched α-amino acids with the choice of enzyme used being dependent on the nature of the substrate (Scheme 67).[391] An enzyme mediated Diels–Alder-resolution reaction was reported by Kita using racemic α-hydroxy furans as the diene substrate.[392] The reaction proceeded with complete control of diastereoselectivity giving exclusively the *syn* isomer with an ee of 84% (Scheme 68). An enantioselective phosphorylation mediated by glycerol kinase was employed in the resolution of 1,2-diols. The L-diol was isolated in 42% yield (70% ee) and the D-monophosphate in 36% yield (>99% ee). This could subsequently be converted into the D-diol using a phosphatase enzyme.[393] A kinetic resolution

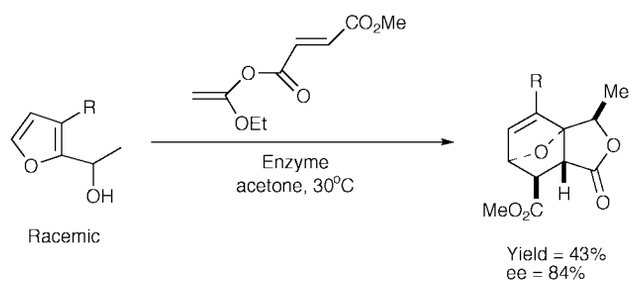


Scheme 66



Scheme 67

of alicyclic nitriles and amides was reported by Matoishi using a nitrile hydrolase derived from *Rhodococcus rhodochrous*.[394] Finally, two examples of epoxide resolution using epoxide hydrolases have been reported independently by Kellogg and Weijers.[395,396]



Scheme 68

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