BINOL: A Versatile Chiral Reagent

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1. Introduction

Over the last 20 years an explosive growth of research in the field of asymmetric synthesis has

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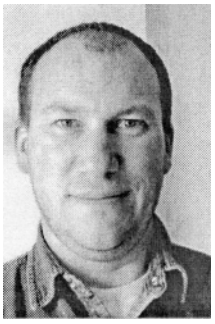


Jean Michel Brunel was born in 1968 in Marseille, France. He was graduated from the School of Chemistry (Ecole Supérieure de Chimie de Marseille, ESCM) in 1991. He obtained his Ph.D. degree in 1994 from Université Aix Marseille III in the field of enantioselective synthesis and organophosphorus chemistry. In 1994, he joined the group of Pr. H. B. Kagan (Université Paris Sud) as a postdoctoral fellow working on the enantioselective catalytic oxidation of sulfides (1994–1996). In 1997, he joined the CNRS as Chargé de Recherche and is now working in the Institut Méditerranéen de Recherche en Nutrition (IMRN INRA 1111). His research program is focused on the development of novel synthetic methods in asymmetric catalysis as well as the synthesis of a new class of antifungal agents.

occurred.[1−9] The aim of enantioselective synthesis or catalysis is to produce chiral products (a single enantiomer as the ultimate goal) starting from achiral substrates by exploiting the presence of chiral reagents. The role of these latter is to generate diastereomeric transition states leading to the two enantiomers so that one of them is preferentially formed. In such a schematic representation, only two competitive pathways are present, one leading to the *R* enantiomer and the other giving rise to the *S* one. Actually, the situation can be more complex. For instance, both the substrate and the reagent can exist as a mixture of conformational isomers, several conformations can be significantly populated, and they can also exist in different states of aggregation or solvation, each of these species showing its own reactivity. The final result is a weighted average depending on the distribution and reactivity of the species involved, and a low stereoselectivity is generally obtained. A rational approach to the control of stereoselectivity is based on the use of molecules possessing only symmetry elements of pure rotation and belonging to the C_n or D_n symmetry groups, allowing the prediction of the enantioselectivity due to the presence in solution of only a single defined reactive species. Under these assumptions, interest in the applications of chiral atropoisomers, especially binaphthalene systems, has blossomed.[10,11] This review deals exclusively with the synthesis and resolution of BINOL, as well as its use as chiral reagent or ligand, and does not cover its substituted derivatives.[12,13]

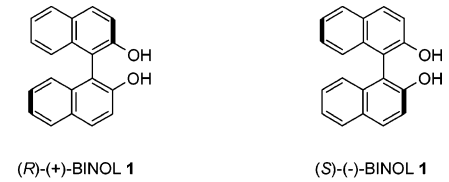
Since 1990 the enantiomeric atropoisomers of 1,1′-binaphthyl-2,2′-diol (BINOL) have become among the most widely used ligands for both stoichiometric and catalytic asymmetric reactions. In the first part of this review, we will describe the different methods of preparation of racemic and enantiopure BINOL **1** and its application as a ligand or chiral auxiliary in enantioselective reduction or oxidation reactions. In the second part, the C−C bond forming reactions, catalyzed or not, involving BINOL **1** as reagent or ligand will be discussed.

2. BINOL Synthesis and BINOL-Mediated Asymmetric Oxidation and Reduction Reactions

2.1. Properties and Synthesis of Racemic BINOL

2,2′-Disubstituted derivatives of 1,1′-binaphthyl have been widely used in organic synthesis. The stability of the enantiomers, with barriers of rotation ranging from 23.8 kcal/mol for 1,1′-binaphthyl to more than 46 kcal/mol for 2,2′-diiodo-1,1′-binaphthyl, enables their use as chirality inducers in asymmetric reactions. The most important compound of this type is 1,1′-binaphthyl-2,2′-diol (BINOL, $C_{20}H_{14}O_2$, mp 215−217 °C) the chiral atropoisomers (*R*)-**1** ($[\alpha]^{20}_D$ = +35.5 (THF, $c = 1$), mp 205−211 °C) and (*S*)-**1** ($[\alpha]^{20}_D$ = −34.5 (THF, $c = 1$), mp 205−211 °C) of which are stable at high temperature[14] and allow numerous asymmetric reactions under various experimental conditions (Scheme 1).

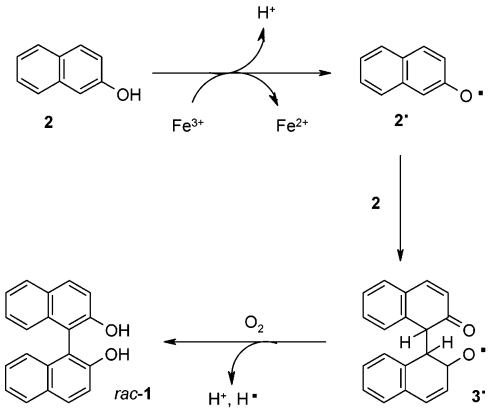
Scheme 1



(*R*)-(+)-BINOL **1** (*S*)-(-)-BINOL **1**

BINOL **1** is the best known representative of axially chiral molecules[15] and was first prepared as a racemate in 1873 by von Richter.[16] Since this date, the preparation of racemic BINOL **1** has been widely studied, and a well-established method is the oxidative coupling of 2-naphthol using $FeCl_3$,[17−20] $K_3Fe(CN)_6$,[21] $Mn(acac)_3$ (acac = acetylacetone),[22,23] Cu−amine complexes,[24−26] or $TiCl_4$ [27]as coupling agents with chemical yields up to 90% being commonly reached. A mechanistic rationale implying that the formation of one molecule of **1** requires 1 equiv of Fe^{3+} has been proposed. This suggests that the radical species **2**•, resulting from a one-electron oxidation of **2** with Fe^{3+}, adds to another neutral **2** to form a new C−C bond and generates carbinyl radical **3**•, which eliminates H• and is further oxidized by O_2 to release H^+ and regain aromaticity (Scheme 2).[17,28,29]

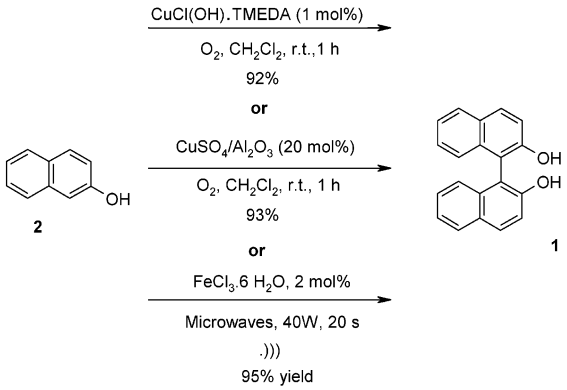
Scheme 2



These coupling reactions are not catalytic processes and require more than stoichiometric amounts of the metal salts. A few exceptions are the coupling that

proceeds catalytically under ultrasonic irradiation of aerated powder mixtures of 2-naphthol and $FeCl_3 \cdot 6H_2O$ (2 mol %) at 50 °C,[19,30,31] $FeCl_3/Al_2O_3$,[32,33] the use of Cu(II)−amine complex (1 mol %),[26,34−36] $VO(acac)_2$,[37] methyltrioxo rhenium,[38] an alumina-supported copper(II) sulfate catalyst (20 mol %) under aerated conditions,[39−41] a vanadyl phosphate (VOPC),[42] and mesoporous molecular sieves[43] (Scheme 3).

Scheme 3



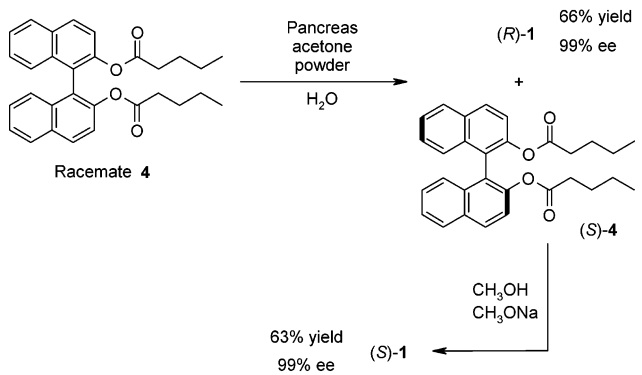
2.2. Preparation of (*R*)- and (*S*)-Binol

The synthesis of enantiomerically pure (*R*)- or (*S*)-BINOL **1** has been extensively studied, and two major different approaches have been developed, enzymatic or chemical resolution of racemic BINOL **1** and direct stoichiometric or catalytic oxidative coupling synthesis.

2.2.1. Resolution of Racemic BINOL

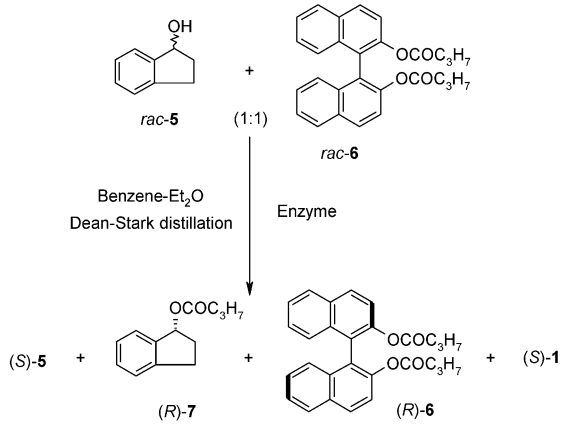
2.2.1.1. Enzymatic Resolution of Racemic BINOL. The recent development of enzyme catalysis in organic synthesis for kinetic resolution of racemates has attracted the attention of organic chemists because of its synthetic utility. One of the first efficient methods for enzymatic resolution of *rac*-BINOL **1** was described in 1989 by Kazlaukas. It is based on the cholesterol esterase-catalyzed enantiospecific hydrolysis of binaphthol esters.[44−48] A simple synthetic scale (200 g) procedure has been detailed for hydrolysis of the dipentanoate ester catalyzed by crude, inexpensive enzyme (bovine pancreatic acetone powder (PAP)). Each enantiomer was obtained in more than 60% theoretical yield and 99% enantiomeric purity (Scheme 4).

Scheme 4



Furthermore, an enantioselective enzyme-catalyzed transacylation reaction has been reported by Lin et al.[49,50] In this case, the enantioselective transacylation of *rac*-1-indanol **5** with *rac*-1,1′-binaphthyl-2,2′-dibutyrate **6** afforded (*S*)-1-indanol **5**, (*R*)-1-indanylbutyrate **7**, (*S*)-1,1′-binaphthyl-2,2′-diol **1**, and (*R*)-1,1′-binaphthyl-2,2′-dibutyrate **6**. Among many enzymes tested, porcine pancreatic lipase (PPL) showed the best results in both chemical yield and enantioselectivity. Porcine pancreatin (PN) and crude cholesterol esterase from PAP had moderate reaction rates and high enantioselectivities (Table 1).

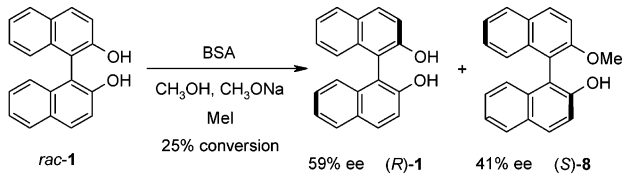
Table 1. Enzyme-Catalyzed Enantioselective Transacylation



enzymes	relative rate	yield ratio (%) of (*S*)-**5**/(*R*)-**7**/(*R*)-**6**/(*S*)-**1**	ee of (*S*)-**5**	ee of (*R*)-**7**	ee of (*R*)-**6**	ee of (*S*)-**1**
PPL	1	24:23:23:23	>99	>99	98	98
PN	0.3	21:23:21:23	99	>99	97	98
PAP	0.5	23:22:21:22	98	97	95	95

Cavazza et al. reported an enzymatic resolution of *rac*-BINOL **1** based on a monomethyl etherification reaction promoted by a transport protein, bovine serum albumin (BSA).[51−53] In this case, enantiomeric excesses only up to 59% and 41% have been encountered, respectively, for (*R*)-BINOL **1** and the methylated (*S*)-product **8** (Scheme 5).

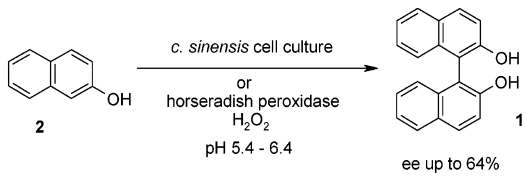
Scheme 5



On the other hand, better results have been obtained using lipoprotein lipase enzymes from *Pseudomonas sp.* and *Pseudomonas fluorescens* for the enantioselective resolution and desymmetrization of racemic BINOL **1** leading to enantioselectivities up to 80% ee.[54]

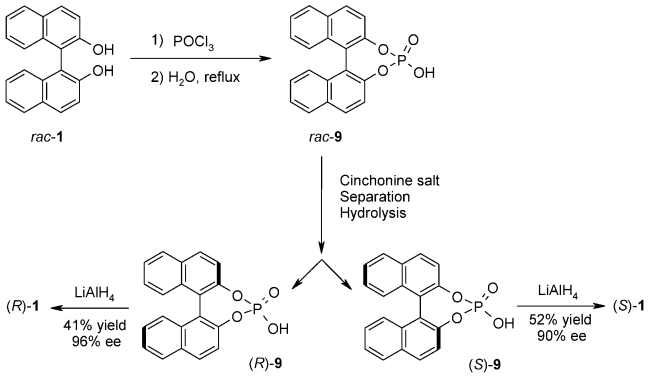
More recently, optically active 1,1′-binaphthyl-2,2′-diol **1** was synthesized by oxidative coupling of 2-naphthol using *Camellia sinensis* cell culture[55] or horseradish peroxidase[56,57] as catalytic systems. In these cases, enantiomeric excesses of up to 64% have been encountered (Scheme 6).

Scheme 6



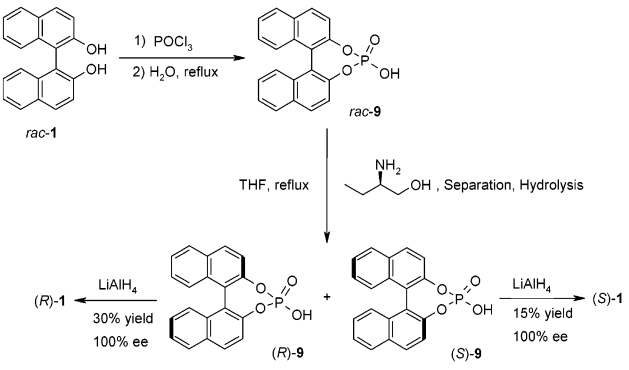
2.2.1.2. Chemical Resolution of Racemic BINOL. The chemical resolution of *rac*-BINOL **1** has been extensively reported in the literature, and in all cases the methods are based on the easy separation of the pair of diastereomers derived from the reaction of *rac*-BINOL **1** with a chiral auxiliary. Thus, Jacques et al. were the first to describe the synthesis of cyclic binaphthyl phosphoric acids **9** from *rac*-BINOL **1** and their successful resolution via their cinchonine salts.[58−60] The (*R*)- and (*S*)-enantiomers of BINOL **1** were obtained in, respectively, 24% (96% ee) and 26% isolated yield (90% ee) (Scheme 7).

Scheme 7



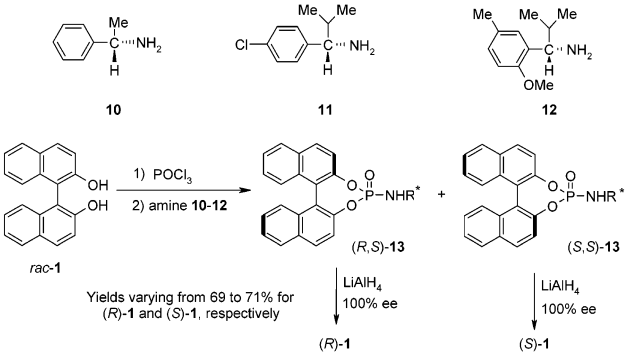
Nevertheless, the overall resolved yield is only moderate, and the enantiomeric purity is not satisfactory (respectively, 96% and 90% ee for (*R*)-**1** and (*S*)-**1**). Moreover, cinchonine is expensive and often recovered in contaminated form. In 1990, a similar method was reported by Miyano et al. by replacement of the cinchonine salt with the less expensive (*R*)-2-aminobutanol.[61] In this case, although both enantiomers are pure, they are obtained in even lower yield (respectively, 30% and 15% for (*R*)-**1** and (*S*)-**1**) (Scheme 8).

Scheme 8



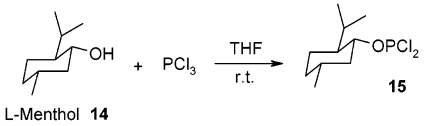
On the other hand, Hu et al.[62,63] and De Lucchi et al.[64,65] have reported independently the resolution of *rac*-BINOL **1** via the formation of phosphoramidates derived from optically active phenethylamines **10**−**12**, which are readily accessible and widely used basic resolving agents. Compared to the above-mentioned methods, a significant enhancement of overall yield (up to 69% for (*R*)-**1** and 71% for (*S*)-**1**) and enantiomeric purity (100% for both enantiomers) has been achieved with all three amines, **10**−**12**. Moreover, the resolving agents can be recovered in 80% yield with their original enantiomeric purity (Scheme 9).

Scheme 9



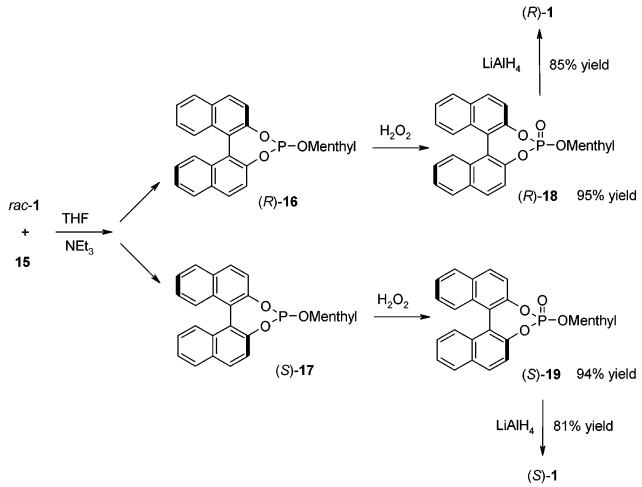
Another efficient, practical, and inexpensive method described in 1993 by Brunel et al.[66] involves the tricoordinated compound **15**, easily prepared from phosphorus trichloride and L-menthol (Scheme 10). This methodology has been recently reproduced and improved by Tang et al.[67,68]

Scheme 10



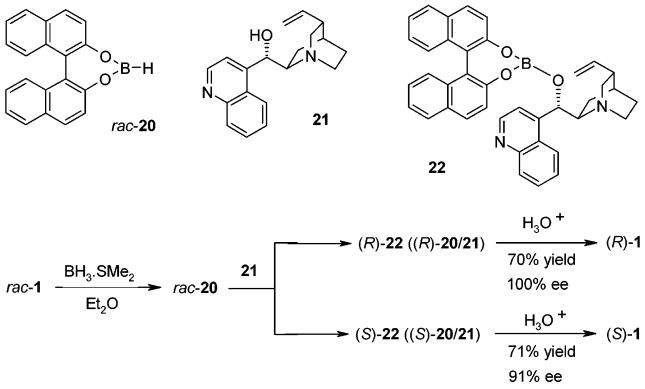
Compound **15** reacts with *rac*-BINOL **1** leading to a 1:1 mixture of diastereomers **16** and **17** in quantitative yield. Complete separation of the two diastereomers was achieved in a single recrystallization from diethyl ether. Oxidation with 30% hydrogen peroxide led to the expected compounds **18** and **19**, which were reduced with $LiAlH_4$ to afford enantiomerically pure (*R*)-**1** and (*S*)-**1** in 81% and 85% overall yield, respectively (Scheme 11).

Scheme 11



The preparation of enantiomerically pure BINOL **1** has also been achieved from *rac*-BINOL **1** via cyclic borate ester **22** formed from the reaction of racemic 1,1′-binaphtholborane **20** with cinchonine **21** in THF.[69−71] Thus, under the chosen experimental conditions, one diastereomer is soluble, while the other precipitates (Scheme 12).

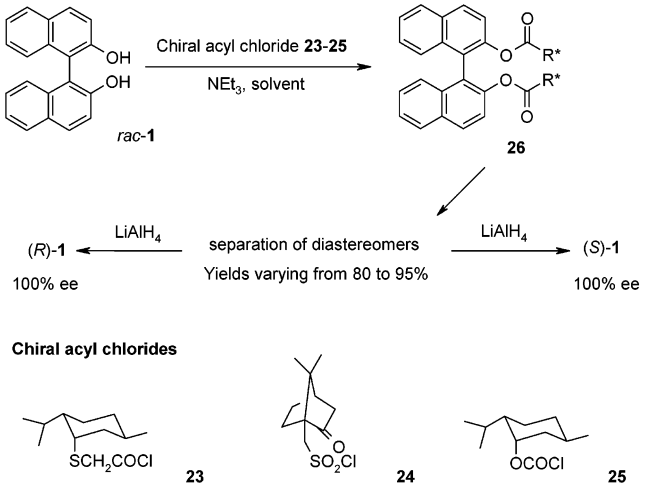
Scheme 12



The same methodology has been applied using (*S*)-proline instead of cinchonine but a decrease of enantioselectivity (down to 86% ee) was noticed.[72−74]

Recently, methods of resolution using chiral acyl chlorides for a simple two-step separation of pure enantiomers of BINOL **1** in 80−95% yield have appeared in the literature (Scheme 13).[65,75−77]

Scheme 13



Simple and convenient methods of resolution of *rac*-BINOL **1** have been widely developed through selective crystallization of diastereomeric complexes obtained using various chiral auxiliaries. Thus, chiral *m*-tolyl methyl sulfoxide **27**,[78,79] chiral tartaric acid derivative **28**,[80,81] (1*R*,2*R*)-diaminocyclohexane **29**,[82−84] (*S*)-proline derivatives **30a** and **30b**,[85−88] and more recently, chiral *N*-benzylcinchonidinium chloride **31**[89−95] and (*R*)-α-methylbenzylamine[69,96] proved to be efficient (Scheme 14).

In all cases, the resolution was achieved in moderate to very good chemical yields (38−99%) and in enantiomeric excesses varying from 66% to 99% ee depending on the nature of the chiral auxiliary used (Table 2).

Scheme 14

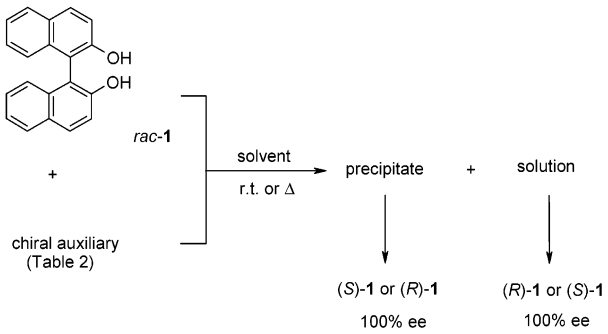
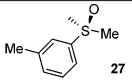
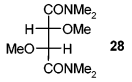
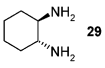
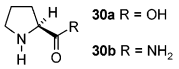
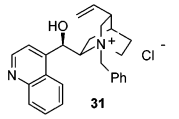
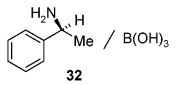


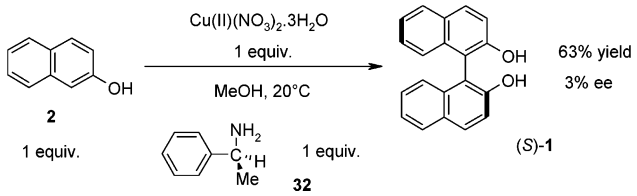
Table 2. Resolution of BINOL 1 Using Various Resolving Agents

Entry	Chiral auxiliary	(*R*)-**1** Yield (%)	(*R*)-**1** ee (%)	(*S*)-**1** Yield (%)	(*S*)-**1** ee (%)
1	 **27**	86	85	83	100
2	 **28**	59	100	72	100
3	 **29**	86	94	57	67
4	 **30a** R = OH **30b** R = NH_2	38 74	63 70	52 75	66 39
5	 **31**	95	>99.8	99	99
6	 **32**	53	56	58	99

*2.2.2. Enantioselective Synthesis of BINOL **1** by Oxidative Coupling of 2-Naphthol*

Although enantioselective oxidative coupling of 2-naphthol with chiral catalysts provides one of the simplest routes to optically active BINOL **1**, only a few attempts to develop such an approach have been reported. Wynberg et al. were the first to describe an oxidative coupling of 2-naphthol by stirring a mixture of cupric-(*S*)-phenylethylamine **32** complex and 2-naphthol **2** in equimolar quantities at room temperature under a nitrogen atmosphere (Scheme 15).[25]

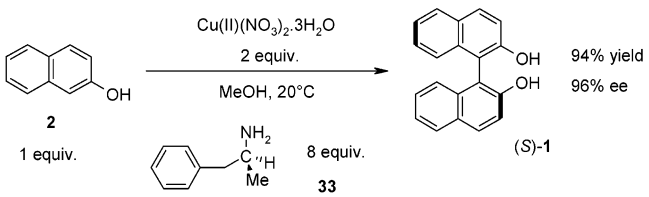
Scheme 15



Although BINOL **1** was obtained in 63% yield, only 3% ee was obtained. On the basis of these results, Brussee et al. found that the replacement of (*S*)-phenylethylamine **32** by (*S*)-α-methyl-phenylethyl-

amine (amphetamine) **33** led to a beneficial increase of enantioselectivity.[97,98] Under these conditions, (*S*)-BINOL **1** was obtained in 94% yield and an enantiomeric excess up to 96% ee (Scheme 16).

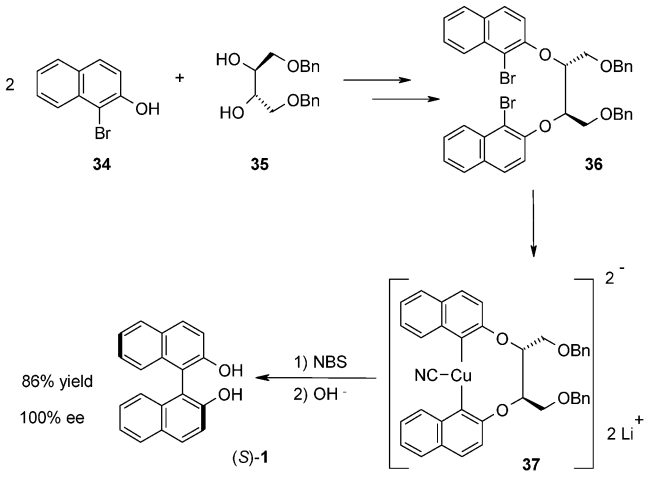
Scheme 16



Nevertheless, this system requires a large amount of chiral amine **33**, up to 8 equiv with respect to 2-naphthol **2**. Recently, Kocovsky et al. improved this reaction using a $CuCl_2$−sparteine complex (1/1 ratio) in stoichiometric amounts leading to the formation of the expected chiral BINOL **1** in very high enantiomeric excesses but in only 36% chemical yield.[99−104]

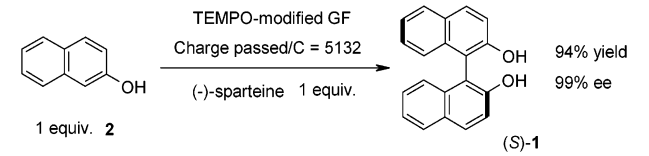
Lipshutz et al. reported in 1994 an asymmetric synthesis of BINOL **1** involving an intramolecular oxidative coupling of cyanocuprate intermediates.[105] In this approach, inexpensive 1-bromo-2-naphthol **34** was converted to dibromide **36** with chiral diol **35**. Subsequent treatment with *tert*-BuLi followed by addition of solubilized CuCN presumably led to the in situ formation of a cyanocuprate **37**, which produced enantiomerically pure (*S*)-BINOL **1** in 86% yield upon exposure to *N*-bromosuccinimide (NBS) (Scheme 17).

Scheme 17



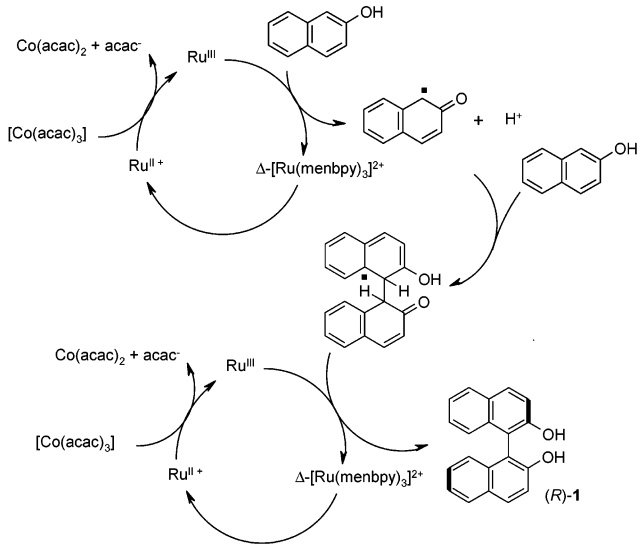
A remarkable result was obtained using an enantioselective electrocatalytic oxidative coupling of 2-naphthol **2** on a 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO)-modified graphite felt electrode in the presence of (−)-sparteine. It allowed the synthesis of (*S*)-BINOL **1** in 94% yield and 99% ee (Scheme 18).[106]

Scheme 18



On the other hand, Ohkubo et al. reported a novel photoaccelerated asymmetric synthesis of an (*R*)-BINOL catalyzed by Δ-$[Ru(menbpy)_3]^{2+}$ with $Co(acac)_3$ as oxidant. Because the one-electron oxidation potential of 2-naphthol is +1.34 V vs. SCE in MeCN, Δ-$[Ru(menbpy)_3]^{3+}$ formed by an oxidative quenching of Δ-$[Ru(menbpy)_3]^{2+}$ with $Co(acac)_3$ can oxidize 2-naphthol **2** efficiently so as to generate the corresponding radical, which produces a precursor of (*R*)-BINOL **1** (Scheme 19).[107,108]

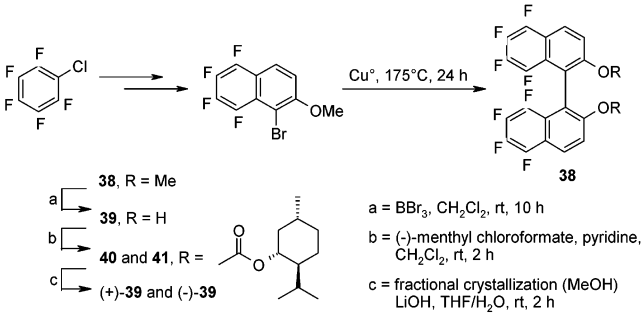
Scheme 19



In the same area, Katsuki et al. reported the enantioselective synthesis of (*R*)-BINOL **1** with moderate to good enantioselectivity (65% ee) via aerobic oxidative coupling of 2-naphthol using chiral (NO)-Ru(II)−salen complex as a catalyst under irradiation of visible light.[109]

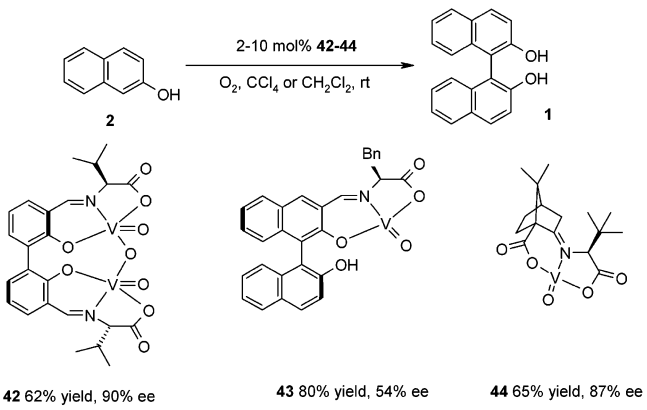
Among the numerous syntheses of BINOL derivatives described in the literature, we have decided to focus our interest on slightly modified BINOLs. In this context, we only report the synthesis of F_8BINOL derivative, an electronically perturbed version of BINOL with remarkable configurational stability. Thus, the electron-deficient nature of the aromatic rings raises the oxidative stability of **39** compared to **1**, as well as increases the acidity of the hydroxyl groups. Racemic **39** was prepared from commercially available starting materials and resolved by fractional crystallization of diastereomeric bis[(−)menthoxycarbonyl] derivatives **40** and **41** (Scheme 20).[110]

Scheme 20



More recently, several novel chiral oxovanadium(IV) complexes **42**−**44** have been designed and prepared for the asymmetric catalytic oxidative coupling of 2-naphthols with high enantioselectivities of up to 80% ee depending on the nature of the catalyst considered (Scheme 21).[111−116]

Scheme 21



3. BINOL-Mediated Asymmetric Oxidation and Reduction Reactions

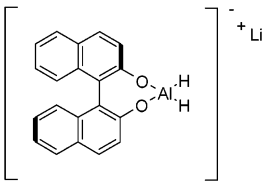
3.1. Enantioselective Reduction Reactions

3.1.1. Reduction of Ketones

Among a wide variety of asymmetric reactions, enantioselective reduction of prochiral carbonyl compounds is one of the most extensively studied transformations.[117] A standard method to this end stems from the use of complex metal hydride reagents bearing chiral alkoxyl or amino ligands. In this area, a number of reagents have been elaborated by modification of lithium aluminum hydride ($LiAlH_4$) with alkaloids, sugars, etc. Nevertheless, the general difficulty in obtaining a high level of stereoselectivity was attributed to the presence of multiple reactive species that are placed in different chemical and chiral environments. In this context, only Al reagents bearing a ligand with a C_2 axis (such as BINOL **1**) led to high enantiomeric excesses in the enantioselective reduction of aromatic ketones.

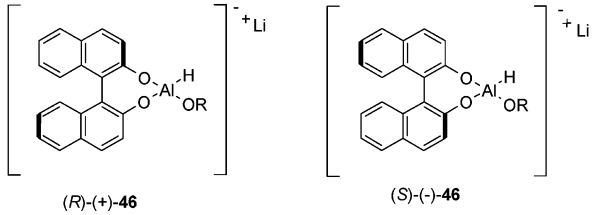
A reducing agent called (*R*)-BINAL-H **45** was prepared by mixing $LiAlH_4$ and an equimolar amount of enantiomerically pure BINOL **1** in THF (Scheme 22).[118−122] However, this initial attempt failed to

Scheme 22



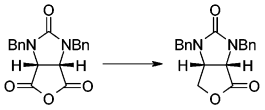
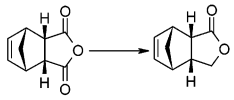
reduce prochiral acetophenone in significant enantiomeric excess (2% ee). This result prompted Noyori et al. to examine a further modification of the reagent by adding a second simple alcohol (EtOH): replacement of either hydrogen by an EtO moiety produces an identical single aluminum hydride reagent (Scheme 23).[123]

Scheme 23



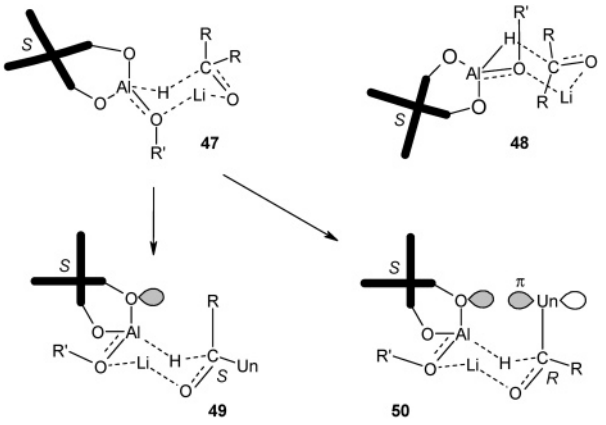
A series of prochiral alkyl phenyl ketones were reduced with 3 equiv of (*R*)-**46** or (*S*)-**46** at low temperature (−100 to −78 °C) and gave the corresponding carbinols in high enantiomeric excess with generally good enantioface differentiation as shown in Table 3, entries 10 and 11. This methodology was recently applied to the synthesis of chiral lactones through enantioselective reduction of a carbonyl group in *meso*-1,2-dicarboxylic anhydrides.[124,125]

Table 3. Enantioselective Reduction of Carbonyl Group with BINAL-H 46

Entry	Ketone	BINOL **1** confign in **46**	Yield (%)	ee (%)
1	$C_6H_5COCH_3$	*R*	61	95 (*R*)
2	$C_6H_5COC_2H_5$	*S*	62	98 (*S*)
3	C_6H_5CO-*n*-C_3H_7	*S*	92	>99 (*S*)
4	C_6H_5CO-*n*-C_4H_9	*S*	64	>99 (*S*)
5	$C_6H_5COCH(CH_3)_2$	*S*	68	71 (*S*)
6	$C_6H_5COC(CH_3)_3$	*R*	80	44 (*R*)
7	α-tetralone	*R*	91	74 (*R*)
8	$C_6H_5COCH_2Br$	*R*	97	95 (*S*)
9	(*E*)-*n*-C_4H_9CH=$CHCOCH_3$	*R*	47	79 (*R*)
10	(*E*)-*n*-C_4H_9CH=$CHCO$-*n*-C_5H_{11}	*R*	91	91 (*R*)
11	(*E*)-*cyclo*-C_5H_9CH=$CHCO$-*n*-C_5H_{11}	*R*	91	92 (*R*)
12		*R*	76	90
13		*R*	69	84

Reactivity of the carbonyl substrates toward BINAL-H reduction seems to be greatly influenced by steric effects, various electronic factors including LUMO level and electron density at the carbonyl carbon, flexibility of the molecule, etc. Thus, the early or late nature of the transition state (energy, shape, tightness, atomic distances, etc.) varies subtly from reaction to reaction. Although it is not easy to present a unifying view, the stereochemistry of carbonyl group reduction may be rationalized as proceeding through the pathway depicted in Scheme 24.

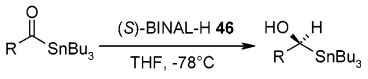
Scheme 24



The reaction is initiated by the complexation of the Li^+ cation to the oxygen atom of the C=O group, which is thus activated. The product-determining hydride transfer then occurs from Al to the carbonyl carbon by way of a six-membered ring transition state (Zimmerman−Traxler). In this case, the two binaphthoxy oxygens of (*S*)-BINAL-H **46** are diastereotopic, and therefore, two types of chairlike transition states, **47** and **48**, are possible. When a prochiral unsaturated ketone, UnCOR, for example, is put into **47**, there emerge two diastereomeric transition states, **49** and **50**. A series of (*S*)-BINAL-H reductions giving *S* products selectively indicates that transition state **49** is generally favored over the *R*-generating transition state **50**. This **49** versus **50** relative stability would be controlled primarely by interactions between the axially located groups. Thus, transition state **50** possessing axial-Un and equatorial R groups is destabilized by the substantial n/π-type electronic repulsion between the axially oriented binaphthoxyl oxygen and the unsaturated moiety.

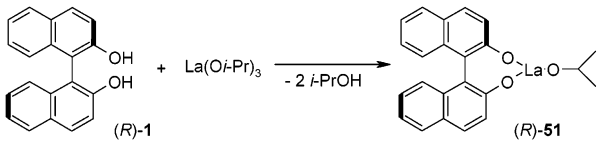
It is noteworthy that, in 1988, Chong et al. have already mentioned this methodology to the asymmetric reduction of acylstannanes to prepare enantiomerically enriched α-alkoxystannanes[126] in enantiomeric excesses up to 94% ee (Scheme 25).

Scheme 25



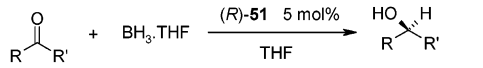
Among all the enantioselective methods described in the literature, borane reduction of C=O or C=N groups has appeared to be one of the most convenient. Thus, examples have recently been described using **51**, a chiral catalyst obtained from lanthanum triisopropoxide, and (*R*)-BINOL **1** (Scheme 26).[127]

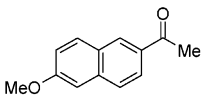
Scheme 26



Some typical results are summarized in Table 4.

Table 4. Ketone Reduction with Borane and (*R*)-51 Catalyst

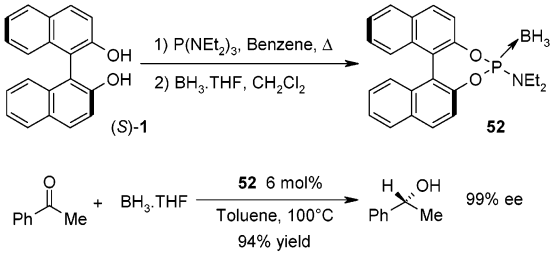


Entry	Ketone	Yield (%)	ee (%)
1	$PhCOCH_3$	95	39 (*S*)
2	$PhCOC_3H_7$	95	24 (*S*)
3	*tert*-$BuCOCH_3$	70	24 (*S*)
4	2-Octanone	73	23 (*S*)
5		95	62 (*S*)

As an extension of this catalytic system, Uang et al. have used a chiral aluminum complex generated in situ from aluminum isopropoxide and (*R*)-BINOL **1**. Under these conditions, alcohols were obtained in high yields and ee's of up to 83%.[128,129]

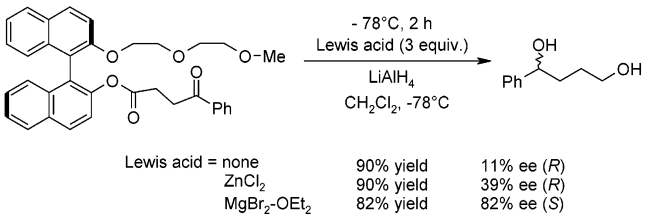
Recently, Tang et al. reported the synthesis of a new 2,2′-*O*,*O*-(1,1′-binaphthyl)-dioxo-*N*,*N*-diethylphospholidine borane complex **52** and its use as a catalyst in the enantioselective borane reduction of acetophenone leading to the expected alcohol in 99% ee at 100 °C (Scheme 27).[130]

Scheme 27



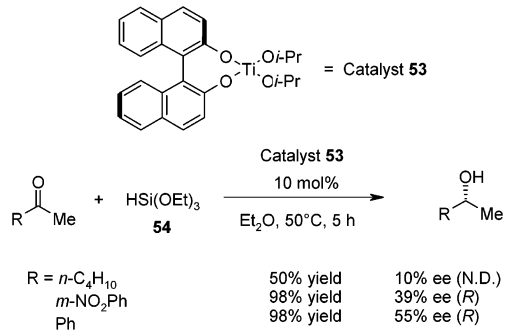
The diastereoselective reduction of chirally modified keto acids is a practical asymmetric method for the synthesis of hydroxy acid derivatives. Thus, using (*R*)-BINOL **1** as chiral auxiliary in the diastereoselective reduction of γ-keto acid esters led to enantiomeric excesses up to 82% ee (Scheme 28).[131]

Scheme 28



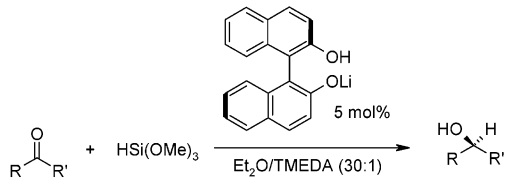
An enantioselective synthesis of chiral alcohols has been developed by Nakai et al. It involves an asymmetric catalytic hydrosilylation of prochiral ketones with $HSi(OEt)_3$ using (*R*)-BINOL-Ti(O*i*-Pr)$_2$ **53** complex. Moderate enantioselectivities ranged from 10% to 55% ee depending on the nature of the ketones (Scheme 29).[132]

Scheme 29



The catalytic asymmetric reduction of different ketones with transient hypervalent silicon hydrides has been also described (Table 5).[133] Trialkoxysilanes,

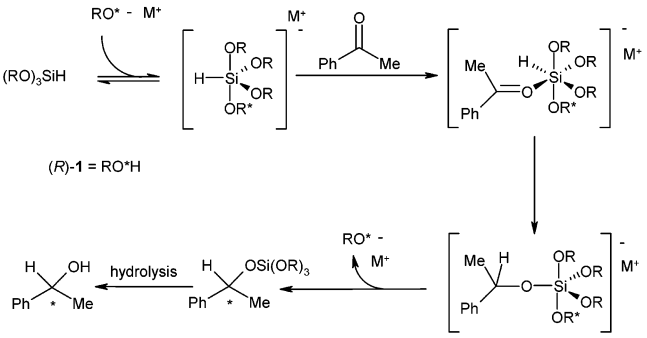
Table 5. Enantioselective Reduction of Ketones with BINOL-Modified Silicon Hydrides



entry	ketone	conditions	yield (%)	ee (%)
1	acetophenone	6 h, 0 °C	80	61 (*S*)
2	isobutyrophenone	24 h, 0 °C	60	90 (*R*)
3	α-tetralone	24 h, 0 °C	39	93 (*R*)
4	methyl benzoylpropionate	24 h, 0 °C	63	65 (*S*)
5	4′-methylbenzophenone	24 h, 0 °C	74	0
6	2′-bromoacetophenone	24 h, 0 °C	91	66 (*S*)

upon activation by a small amount of a chiral nucleophile such as BINOL **1**, underwent addition to the carbonyl group, forming the corresponding silyl-protected alcohols, which were cleaved during the workup to give the enantiomerically enriched product alcohols (Scheme 30).

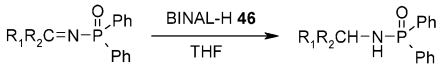
Scheme 30



3.1.2. Reduction of Imines

In contrast to the various studies dealing with the asymmetric reduction of the carbonyl group using chiral BINOL reagents, few examples dealing with the asymmetric reduction of the C=N group are known.[134] To our knowledge, the first example using a BINAL-H **46** reagent was described in 1987 by Hutchins et al. where prochiral diphenylphosphinylimines have been asymmetrically reduced to chiral diphenylphosphinylamines in quite good yields and moderate enantioselectivities (Table 6).[135]

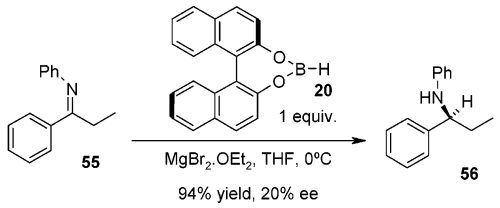
Table 6. Asymmetric Reduction of Diphenylphosphimylimines Using Reagent BINAL-H 46



entry	R_1	R_2	reagent	T (°C)	yield (%)	ee (%)
1	Me	Ph	(*S*)-**46**	−78	84	13
2	Me	Ph	(*S*)-**46**	25	35	77
3	Me	β-naphthyl	(*S*)-**46**	25	16	98
4	Me	α-naphthyl	(*R*)-**46**	−78	66	52
5	Me	Et	(*S*)-**46**	−40	63	40
6	Me	*c*-C_6H_{11}	(*R*)-**46**	−78	56	52

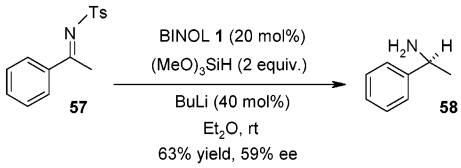
In 1992, Hino et al. reported a preliminary communication on the asymmetric reduction of imine **55** promoted by stoichiometric chiral dialkoxyborane reagent **20** (Scheme 31).[136] However, although the reduction was achieved in a good chemical yield, amine **56** was obtained in low enantiomeric excess (20% ee).

Scheme 31



Recently, an optically active lithium-alkoxide-catalyzed asymmetric reduction of imines with trimethoxyhydrosilane was reported by Hosomi et al. affording the expected amines in moderate ee (up to 72% ee) (Scheme 32).[137]

Scheme 32



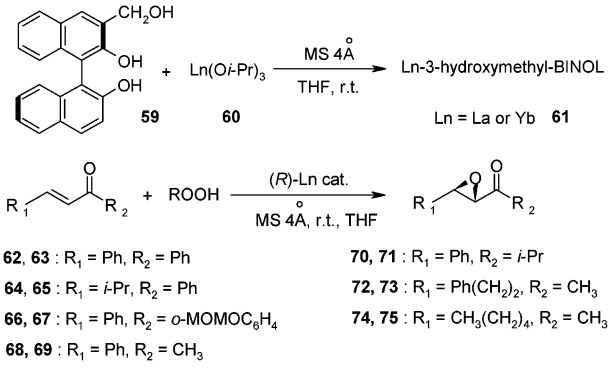
3.2. Enantioselective Oxidation Reactions

3.2.1. Epoxidation of Olefins

The asymmetric epoxidation of olefins is one of the most useful and challenging reactions in modern organic chemistry. In this area, chiral BINOL **1** has been extensively used to develop catalytic or stoichiometric methods of enantioselective epoxidation. Recently, Shibasaki et al. used lanthanum- or ytterbium-modified BINOL derivatives as catalysts in the asymmetric epoxidation of enones using hydroperoxides such as *tert*-butyl hydroperoxide (TBHP) (Table 7).[138−141]

It appears that the enones were best converted to the corresponding epoxides by using the ytterbium

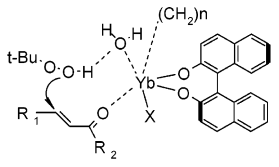
Table 7. Enantioselective Epoxidation of Enones Using (*R*)-Ln Catalysts



entry	enone	epoxide	Ln catal (mol %)	time (h)	yield (%)	ee (%)
1	**62**	**63**	La (5)	7	93	91
2	**62**	**63**	La (1)	44	95	89
3	**64**	**65**	La (5)	7	95	94
4	**66**	**67**	La (5)	96	78	83
5	**68**	**69**	Yb (5)	96	83	94
6	**70**	**71**	Yb (5)	159	55	88
7	**72**	**73**	Yb (8)	118	91	88
8	**74**	**75**	Yb (8)	67	71	91
9	**62**	**63**	La (8) + 15 mol % Ph_3PO	0.5	99	96
10	**68**	**69**	Yb (5) + H_2O (5 equiv/Yb)	48	92	94

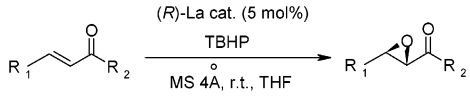
complex generated from Yb(O*i*-Pr)$_3$, BINOL derivative **59**, and molecular sieves (MS) 4 Å in THF. It seems likely that the difference in ionic radius between lanthanum and ytterbium, as well as the difference in Lewis acidities, account for the observed metal effects. It is noteworthy that the enantioselective epoxidation of α,β-unsaturated ketones catalyzed by (*R*)-Ln−BINOL complexes was greatly improved (up to 98% ee) by adding of a small amount of triphenylphosphine oxide[142,143] or water (ca 5 equiv to Ln).[144] In the latter case, the role of water can be explained in the following way. Water molecules coordinate to the Yb (atoms) and thereby control the orientation of the hydroperoxide to form appropriate asymmetric environment for epoxidation (Scheme 33).

Scheme 33



Despite excellent yields and enantiomeric excesses, this catalytic process is still unsatisfactory in terms of its rather low reactivity. This catalytic process has been improved using a novel multifunctional asymmetric catalyst, the La−BINOL−triphenyl arsine oxide ($Ph_3As{=}O$) complex exhibiting higher activity and selectivity compared to those of Ln−BINOL complexes and affording optically active epoxy ketones with broad generality in up to 99% yield and more than 99% ee (Table 8).[145]

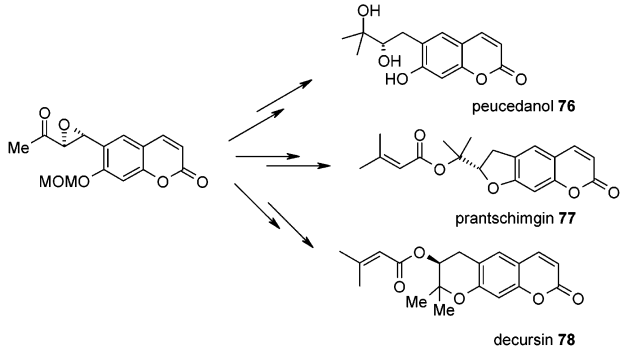
Table 8. Enantioselective Epoxidation of Enones Using (*R*)-La Catalysts



entry	R_1	R_2	time (h)	yield (%)	ee (%)
1	Ph	Ph	0.25	99	96
2	*i*-Pr	Ph	1.5	95	94
3	Ph	*t*-Bu	7	94	98
4	Ph	Me	6	92	99
5	Me	C_5H_{11}	1.5	89	95

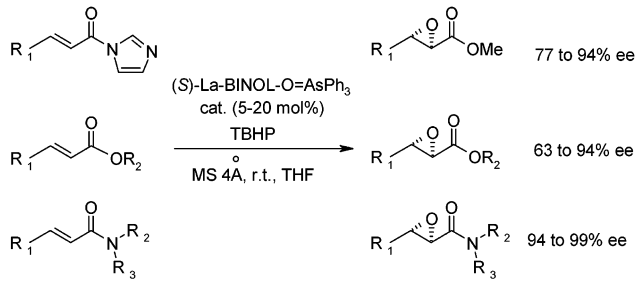
This catalytic system has been successfully applied in the enantioselective total syntheses of protein kinase C activator (+)-decursin **78** and its derivatives, peucedanol **76** and prantschimgin **77** (Scheme 34).[146,147]

Scheme 34



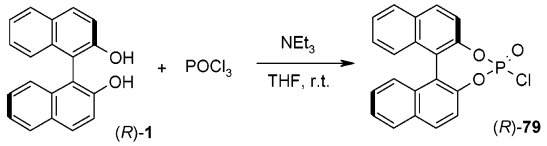
As an extension of this study, the catalytic asymmetric synthesis of α,β-epoxy esters, aldehydes, amides, and γ,δ-epoxy-β-ketoesters has been investigated with high enantioselectivities. This methodology is illustrated in Scheme 35, the reaction proceeding smoothly with high substrate generality (Scheme 35).[148−151]

Scheme 35



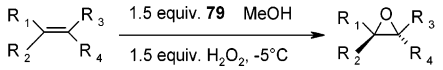
Another example of epoxidation of olefins using a stoichiometric amount of a chiral reagent (*R*)-**79** generated from phosphoryl chloride and (*R*)-BINOL **1** has been described by Berkessel et al. (Scheme 36).[152] Only low enantiomeric excesses were obtained

Scheme 36



(maximum 22% ee) (Table 9). A possible mechanistic interpretation involving a chiral $(RO)_2P(O)-OOH$ intermediate has been suggested.

Table 9. Enantioselective Epoxidation of Olefins Using Hydroperoxide Generated from 79

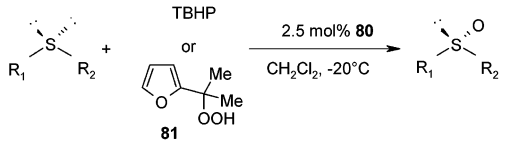


entry	olefin	reaction time (h)	yield (%)	ee (%)
1	1,2-dihydronaphthalene	4	55	20
2	1-methylcyclohexene	2	60	0
3	(*E*)-β-methylstyrene	4	40	16
4	styrene	6	16	22
5	(*E*)-stilbene	12	5	0
6	1-octene	24	20	10

3.2.2. Oxidation of Sulfides

The catalytic asymmetric oxidation of sulfides to chiral sulfoxides in moderate yield with *tert*-butyl hydroperoxide and renewable furylhydroperoxide **81** was achieved using titanium complex **80** produced in situ from a titanium alkoxide and (*R*)-BINOL **1** (Table 10).[153−159] The highest enantioselectivities (up to 93% ee) were obtained with 2.5 mol % of catalyst **80**. The presence of more than 1 equiv of water with respect to sulfide was essential for the oxidation, and it was found that the water was necessary not only to produce an effective catalyst for a highly enantioselective oxidation but also to maintain the catalytic activity of complex **80** for a longer period of time. A moderate level of asymmetric amplification was observed with this catalytic system. From a mechanistic standpoint, it was revealed that the initial asymmetric oxidation to the chiral sulfoxide is followed by the kinetic resolution of the sulfoxide. The nature of the active species involved in this process has not yet been clearly established.

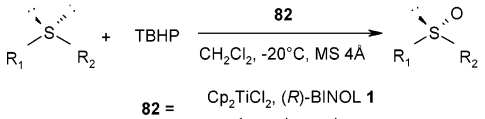
Table 10. Enantioselective Oxidation of Sulfides Using Catalyst 80



entry	R_1	R_2	oxidant	yield (%)	ee (%)
1	*p*-tolyl	Me	TBHP	67	93
2	*p*-tolyl	Me	**81**	71	49
3	Ph	Me	TBHP	80	65
4	Ph	Me	**81**	69	85
5	*p*-bromophenyl	Me	TBHP	57	93
6	*p*-bromophenyl	Me	**81**	79	51
7	2-naphthyl	Me	TBHP	73	51
8	*n*-octyl	Me	TBHP	64	69

Investigations were also carried out on the oxidation of sulfides to sulfoxides by Scettri et al. using Cp_2TiCl_2 as transition metal catalyst in the presence of (*R*)-BINOL **1** as chiral ligand and activated 4 Å molecular sieves. In this case, methyl aryl sulfoxides are isolated in good yields and moderate ee's (Table 11).[160]

Table 11. Enantioselective Oxidation of Sulfides Using Cp_2TiCl_2/BINOL System 82



entry	R_1	R_2	yield (%)	ee (%)
1	*p*-tolyl	Me	95	45
2	Ph	Me	65	39
3	*p*-bromophenyl	Me	83	37
4	*p*-chlorophenyl	Me	81	38
5	*p*-methoxyphenyl	Me	80	40

4. BINOL-Mediated Asymmetric C–C Bond Forming Reactions

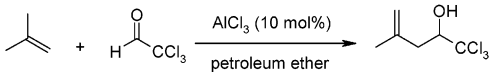
4.1. Ene Reaction

4.1.1. Introduction

The ene reaction, initially known as the "Alder-ene reaction" goes back to 1943 when Alder found that propene reacts with maleic anhydride in benzene at high temperature and pressure to give allylic succinic anhydride.[161] The first example of an intramolecular ene reaction (actually a carbonyl ene reaction) was even described earlier by Schmidt in 1927 with the thermal cyclization of citronellal into isopulegol.[162] However, because of high activation energy (higher than the corresponding Diels−Alder reaction),[163] ene reactions generally require high temperature and pressure, a fact that has limited the widespread use of this reaction in its uncatalyzed version.

The first Lewis acid-catalyzed ene reaction was due to Colonge[164] and Normant[165] in the mid-1950s. It involved chloral, isobutene, and $AlCl_3$ (Scheme 37).

Scheme 37

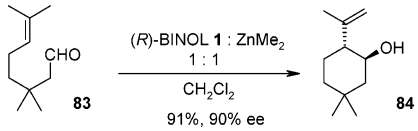


Blomquist[166] (limonene, formaldehyde, and BF_3-dihydrate) and Snider[167] (β-pinene, acrolein, methyl acrylate, or methyl vinyl ketone, and $AlCl_3$) then provided examples that proved the usefulness and efficiency of Lewis acid catalysis for the ene reaction. Over the years, examples of Lewis acid-promoted ene reactions became more and more frequent, and several reviews can be found in the literature.[168−172] One of the big advantages of this reaction over the addition of allylmetals to carbonyl compounds is atom economy.

With respect to the use of BINOL, nearly all reported examples involve Ti-centered Lewis acids. However, the first successful example of asymmetric induction, which deals with a cyclization, was reported by Yamamoto with a BINOL−Al catalyst.[173,174] Indeed, a catalyst prepared in situ from dimethyl zinc and optically pure (*R*)-(−)-BINOL **1** promoted the

cyclization of 3-methylcitronellal **83** into methylisopulegol **84** as a single isomer of 90% ee but was required to be used in excess (Scheme 38).

Scheme 38



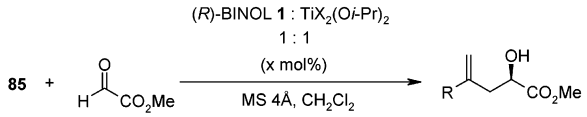
The same catalyst cyclized (*Z*)-methylfarnesal in 91% ee, but (*E*)-methylfarnesal only gave 32% ee and 3-dimethylcitronellal gave 0% ee.[175,176] Finally, Yamamoto reported the first example of an asymmetric intermolecular ene reaction promoted by chiral catalysts that were prepared from both enantiomers of 3,3′-bis(triphenylsilyl)-BINOL and Me_3Al.[177]

Ti-centered Lewis acids have had a major impact on the development of asymmetric carbonyl-ene reaction.

4.1.2. Addition of Enes to Glyoxylate Esters and Fluoral

The greatest contribution in the field is due to Nakai and Mikami[178] who, since 1989, studied the glyoxylate−ene reaction in great detail. Extensive screening of various chiral catalysts derived from optically active diols indicated that BINOL−Ti catalysts provided the best levels of enantiocontrol (Table 12).[179−182]

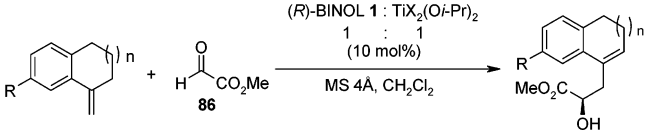
Table 12. Catalytic Enantioselective Addition of Enes to Glyoxylate Esters



Entry	Ene **85**	X	Catalyst amount (mol%)	Yield (%)	Ee (%)
1	Ph, Me	Cl	1	97	97
2		Br	1	98	94
3	Me, Me	Cl	10	72	95
4		Br	10	87	94
5		Cl	10	82	97
6		Br	5	89	98

Feringa showed that optically active α-hydroxy propionic ester-substituted indenes and naphthalenes can be produced under similar conditions (Table 13).[183]

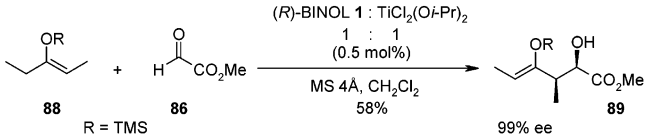
Table 13. Enantioselective Synthesis of α-Hydroxy Propionic Ester Substituted Indenes and Naphthalenes



entry	R	*n*	X	yield (%)	ee (%)
1	H	1	Cl	66	94
2	H	1	Br	69	94
3	H	0	Cl	62	18
4	H	0	Br	60	63
5	OMe	1	Br	52	>99

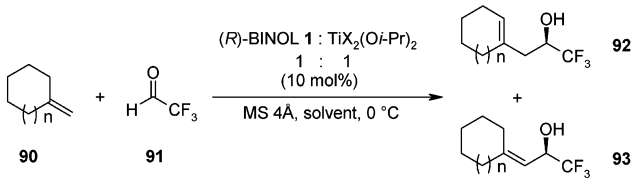
Mikami also showed that under BINOL−$TiCl_2$ catalysis, ketene silyl enol ethers and glyoxylate esters do not lead to a Mukaiyama aldol adduct but rather to the ene adduct, which is formed with complete control of absolute and relative stereochemistry (Scheme 39).[184]

Scheme 39



To expand the scope of the reaction and its applicability in synthesis, Mikami developed a fluoral−ene reaction, which led to the expected homoallylic alcohols with enantioselectivity above 95% ee and the Friedel−Crafts adducts, also with excellent enantioselectivity.[185] The sense of induction was the same as the one observed with glyoxylate esters: (*R*)-BINOL−Ti leads to (*R*)-α-CF_3-alcohols. Results with chloral were not as good both with respect to regioselectivity and enantiocontrol (Table 14).

Table 14. Asymmetric Synthesis of Homoallylic Alcohols

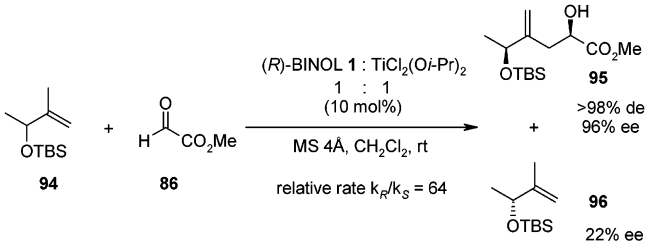


entry	*n*	X	solvent	yield (%)	**92** (ee, %)/**93** (ee, %)
1	0	Cl	CH_2Cl_2	78	62 (>95):38 (>95)
2	0	Cl	toluene	82	77 (>95):23 (>95)
3	1	Cl	CH_2Cl_2	93	76 (>95):24 (>95)
4	1	Br	CH_2Cl_2	95	79 (>95):21 (>95)

4.1.3. Kinetic Optical Resolution, Double Asymmetric Induction, and Asymmetric Desymmetrization

The kinetic optical resolution of a racemic compound can be regarded as an intermolecular desymmetrization process (vide infra) exemplified by the ene-reaction depicted in Scheme 40. Thus, the syn ene-adduct was obtained almost exclusively with an excellent level of optical purity by Mikami (Scheme 40).[186]

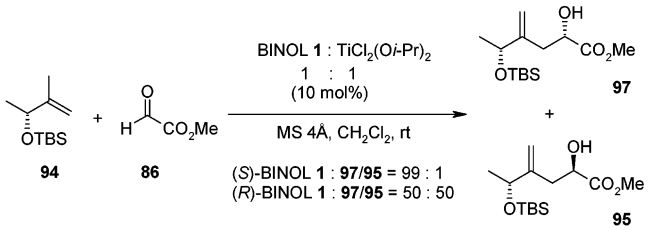
Scheme 40



Moreover, the double asymmetric induction involving the "matched" pair [(*S*)-BINOL/(*R*)-ene] led to a

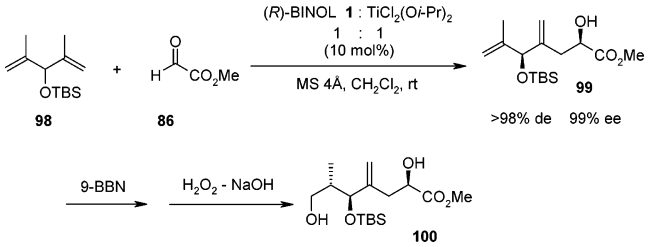
single diastereoisomer in high yield, whereas the "mismatched" pair [(*R*)-BINOL/(*R*)-ene] resulted in the formation of a 1:1 mixture of diastereomers in low yield (Scheme 41).

Scheme 41



The same group also performed the asymmetric desymmetrization of the following symmetrical bis-allylic ether under the same experimental conditions. A single ene-adduct was obtained with very high diastereoselection and optical purity (Scheme 42).

Scheme 42



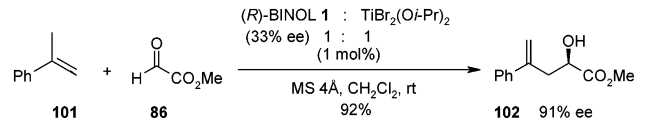
Finally, double asymmetric induction is also described with chiral ene such as (−)-β-pinene or (+)-α-fenchene under (+)- or (−)-BINOL−Ti complex catalysis,[187] and other examples of desymmetrization were described by Mikami using formaldehyde and vinyl or alkynyl analogues of glyoxylates.[186]

4.1.4. Nonlinear Effect (NLE) and Structure of the Active Species

The fact that the optical purity of the products of a given reaction can exceed the optical purity of the catalysts (or chiral auxiliaries) involved has been known since Kagan's pioneering work in the field.[188,189] It is commonly referred to as a "positive nonlinear effect [(+)-NLE]"[190−194] or "asymmetric amplification".[195,196]

Mikami and Nakai reported a remarkable level of positive NLE for the ene reaction between methylstyrene and methylglyoxylate.[190,197] Thus, the graph in Figure 1 shows the variation of ee of the ene adduct **102** as a function of the ee of the BINOL ligand. It clearly indicates that the use of BINOL of only 35−40% ee is good enough to provide the same level of enantiomeric excess for the ene adduct as when prepared from enantiomerically pure BINOL (Scheme 43, Figure 1).

Scheme 43



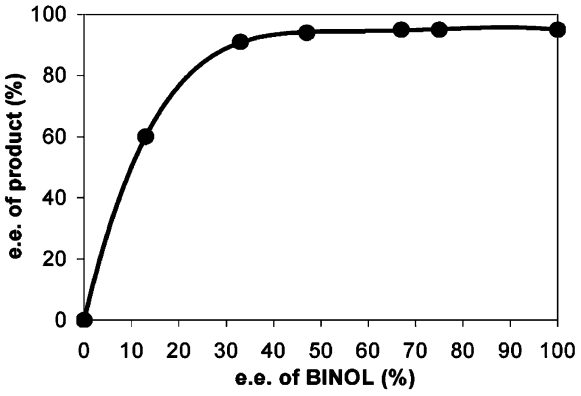
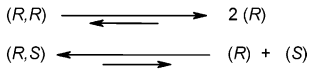


Figure 1.

Considering that the chiral Ti complex derived from a 100% ee BINOL reacted 35 times faster than the counterpart derived from *rac*-BINOL, the authors proposed that this remarkable effect resulted from a marked difference in the stability of the diastereomeric dimer forms of the catalyst [(*R,R*) vs (*R,S*)]. The meso dimer (*R,S*) is the most stable and hence the less reactive and therefore acts as a trap toward the minor (*S*)-enantiomer of the ligand (Scheme 44).

Scheme 44



These results on NLE and their interpretation in terms of dimeric forms of the catalyst initiated further studies on the structure of the active species. Thus, Mikami[198,199] and Nakai[200] independently reported the activity of a complex obtained in the absence of 4 Å molecular sieves. A dimeric Ti-μ_3-oxo structure was proposed for this complex, which displayed a high level of positive nonlinear effect.

4.1.5. Asymmetric Activation

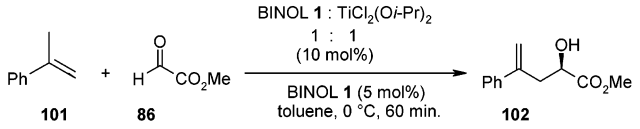
The asymmetric activation of catalysts can occur according to several different strategies: (a) starting from a racemic catalyst, it is possible to introduce a chiral de-activating catalyst or (b) a chiral activating ligand, or (c) starting from a chiral catalyst, it is possible to add a racemic or chiral activating ligand.

The first approach, known as the chiral poisoning strategy, was used successfully by Faller. Starting from chloral, he established that a *rac*-BINOL/$TiCl_2$-(O*i*-Pr)$_2$ catalyst can be poisoned by an inactive enantiopure catalyst [$TiCl_2$(O*i*-Pr)$_2$/(D)-DIPT] to yield a catalyst capable of a better asymmetric induction than the one obtained from catalysts directly prepared from enantiopure BINOL.[201,202]

Mikami applied the second and third strategies to the ene reaction. Indeed, he established that the reaction of methylstyrene with methylglyoxylate under a *rac*-BINOL/$TiCl_2$(O*i*-Pr)$_2$ catalyst could be improved by adding (*R*)-BINOL as a chiral ligand. The same group also showed through kinetic studies that the catalyst prepared from (*R*)-BINOL and $TiCl_2$-(O*i*-Pr)$_2$ could be activated by adding (*R*)-BINOL, *rac*-BINOL, or other chiral diols (Table 15).[203,204]

Finally, Vallée recently obtained similar results with conformationally flexible biphenols and (*R*)-

Table 15. Asymmetric Activation of Catalysts in the Ene Reaction



entry	BINOL (catal)	BINOL (ligand)	yield (%)	ee (%)
1	rac	(*R*)	52	90
2	(*R*)	none	20	95
3	(*R*)	(*R*)	82	97
4	(*R*)	rac	69	96

BINOL−Ti(O*i*-Pr)$_2$. He proposed that a new catalytic species is responsible for the high enantiomeric excesses found.[205]

4.1.6. Ene Cyclization

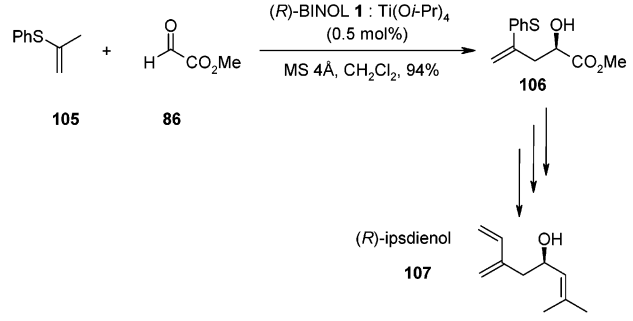
Although examples of ene cyclization are numerous in the literature, examples of intramolecular ene reaction promoted by chiral Lewis acids are scarce, and this is even more true for BINOL−Lewis acids. Mikami reported the efficient synthesis of six- and seven-membered ring carbocycles and heterocycles by using a BINOL-derived titanium perchlorate catalyst.[206,207] The triflate catalyst also gave a high level of enantioselectivity, but the tetrafluoroborate counterpart provided only moderate optical purity and very low yield (Table 16).

Table 16. Asymmetric Ene Cyclization by Various Chiral Lewis Acids

entry	AgY	*T* (°C)	yield (%)	ee (%)
1	none	0	64	88
2	$AgClO_4$	rt	43	91
3	AgOTf	rt	40	92
4	$AgBF_4$	rt	16	55

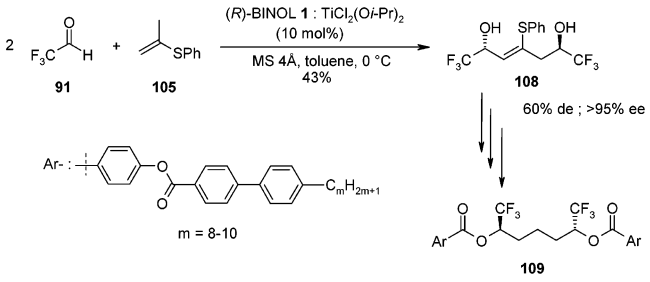
Finally, ene cyclization has been applied to the preparation of natural product precursors (vide infra). Two syntheses of (−)-ipsdienol **107**, an aggregation pheromone of bark beetles, involving a glyoxylate ene reaction were reported by Mikami.[208,209] One takes advantage of the reactivity of vinylsulfides and allows the obtention of the target molecule (Scheme 45).

Scheme 45



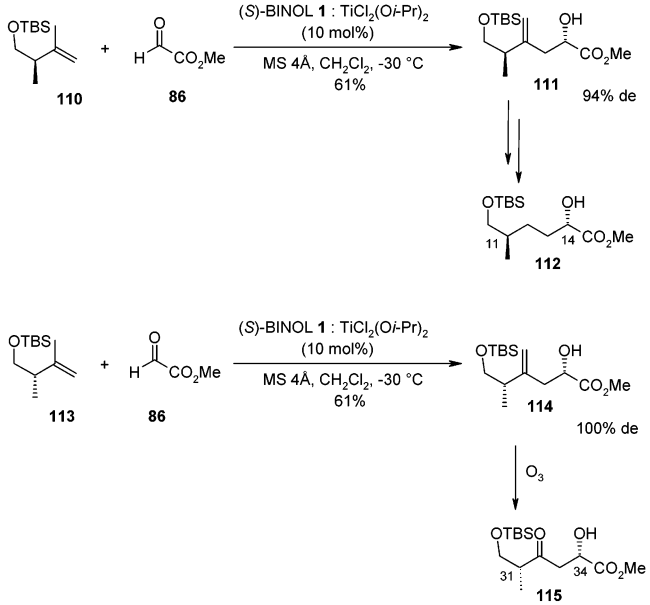
Vinylsulfides were also involved in a very nice application of a tandem and two directional asymmetric fluoral ene reaction to the synthesis of a new antiferroelectric liquid crystalline molecule **109** (Scheme 46).[210,211]

Scheme 46



The carbonyl−ene reaction was also useful for the construction of more complex natural products such as the $C_{10}-C_{15}$ and $C_{30}-C_{35}$ fragments of rapamycin in which the 1,4 remote stereocontrol was ensured by a double asymmetric induction (Scheme 47).[212]

Scheme 47

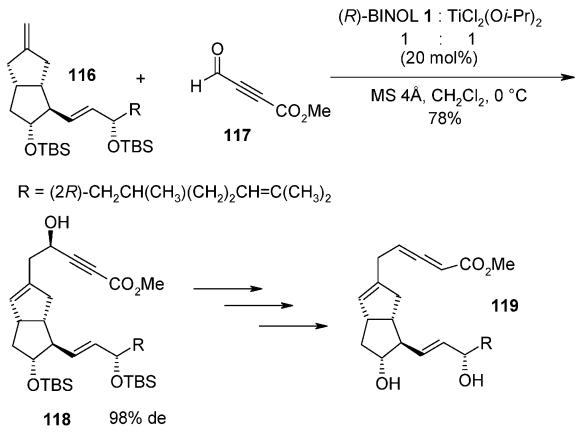


The same group also applied the reaction to alkynylogous and vinylogous glyoxylates and proposed, starting from a chiral ene, a double asymmetric synthesis of isocarbacyclin analogues **119** bearing a 2-allenyl side chain (Scheme 48).[213]

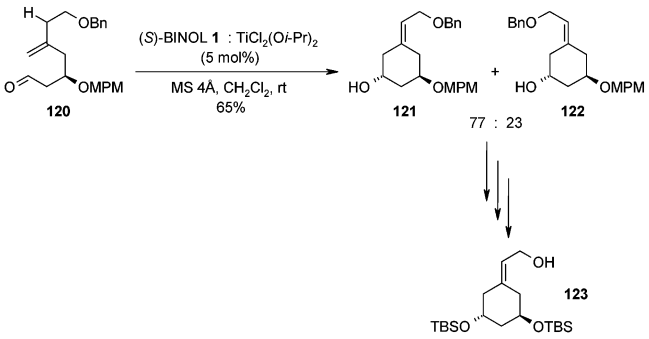
The synthesis of the A ring of vitamin D was also proposed by Mikami based on a regioselective propiolate ene reaction/enantioselective epoxidation/BINOL−Ti-catalyzed carbonyl ene cyclization sequence.[214,215] A more recent paper established the superiority of 6,6′-Br_2−BINOL over BINOL in that specific case (Scheme 49).[216]

Although less efficient, the cyclization of malondialdehyde is also noteworthy. Indeed, the major isomer is an intermediate in the synthesis of the highly functionalized carbon ring skeleton of the trichlothecene anguidine **127** (Scheme 50).[217]

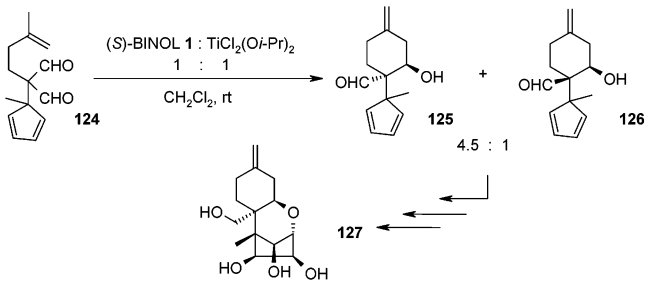
Scheme 48



Scheme 49



Scheme 50

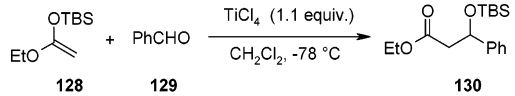


4.2. Aldol and Related Reactions

4.2.1. Introduction

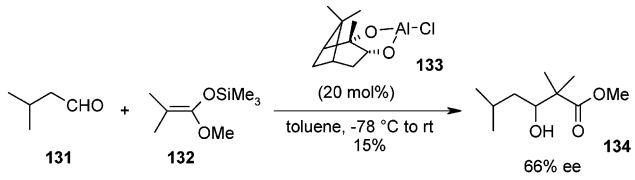
Although the Lewis acid-promoted aldol-type reaction of nucleophilic alkenes with carbonyl compounds has been known since the late 1930s, the introduction of silyloxyalkenes by Mukaiyama in 1973 marked a major breakthrough. Indeed, under $TiCl_4$ catalysis, silyl ketene acetal **128** reacts with benzaldehyde **129** to give the corresponding aldol adduct **130**.[218–221] The versatility of the Mukaiyama reaction, as it is commonly referred to, has since then been widely recognized and discussed in a number of reviews (Scheme 51).[222–224]

Scheme 51



The first successful enantioselective Mukaiyama reaction with substoichiometric amounts of a chiral Lewis acid was reported in 1986 by Reetz.[225] The best enantiomeric excess (66% ee) was obtained with a pinanediol–Al(III) **133** catalyst, but the yield remained low (15%) (Scheme 52).

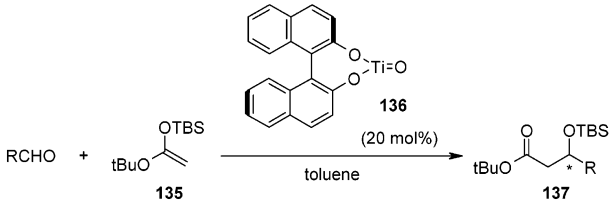
Scheme 52



A BINOL–Ti(IV) catalyst, prepared from (*S*)-BINOL bis-lithium alkoxide and $TiCl_4$, had also been tried by the same authors, but the results were disappointing (enol ether **132** and isobutyraldehyde **131**, 8% ee).

However, a few years later Mukaiyama reported more encouraging results with a closely related BINOL–Ti complex.[226] Up to 85% ee's were reported with a complex formed from (*R*)-BINOL and (*i*-PrO)$_2$-Ti(O) and for which structure **136** was proposed (Table 17).

Table 17. Enantioselective Mukaiyama Reaction Catalyzed by 136



entry	R	*T* (°C)	yield (%)	ee (%)
1	Ph	−43	91	60
2	*p*-ClPh	−78	91	44
3	*β*-naphthyl	−78	98	80
4	(*E*)-PhCH=CH	−78	98	85

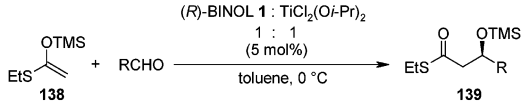
These two results underline an important observation pointed out by Nelson in his excellent review[222] on catalyzed enantioselective aldol additions of latent enolate equivalents, which we have already mentioned: *enantiomeric excesses are highly sensitive to minor variations in Ti-based catalyst preparation*.

The Mukaiyama group[227–230] also studied other types of catalysts principally based on Sn(II) that do not use BINOL as ligand and are therefore beyond the scope of the present review.

4.2.2. Titanium-Catalyzed Aldol Reaction

Mikami studied the addition of ketene silyl acetals of esters or thioesters to various aldehydes catalyzed by 5 mol % of a complex prepared from (*R*)-BINOL and $TiCl_2(Oi\text{-}Pr)_2$. The reaction led to the silyl ether of the expected aldol product in good yield and enantiomeric excesses. A series of crossover experiments involving "labeled" ketene acetals allowed the authors to propose a silatropic ene mechanism in which the silyl group undergoes a [1,3] O–O migration (Table 18).[231]

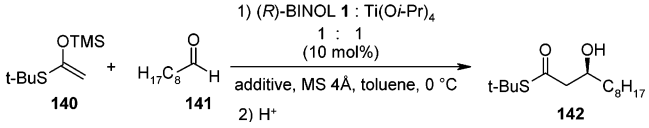
Table 18. Enantioselective Aldol Reaction Catalyzed by the $TiCl_2(Oi\text{-}Pr)_2$/1 System



entry	R	yield (%)	ee (%)
1	$BnOCH_2$	81	94
2	n-C_8H_{17}	60	91
3	i-Pr	61	85
4	(E)-CH_3CH=CH	60	81
5	n-BuO_2C	84	95

Further studies showed that the introduction of alcohols as additives often resulted in an increase in the optical yields of the reaction. Best results were obtained with phenols (Table 19).[232,233]

Table 19. Effects of Additives in the Enantioselective Aldolization Reaction Catalyzed by the Ti(O*i*-Pr)$_4$/1 System



entry	additive	equiv/Ti	yield (%)	ee (%)
1	none		53	91
2	$(CF_3)_2CHOH$	2	56	92
3	C_6F_5OH	1	62	97
4	C_6H_5OH	1	61	96

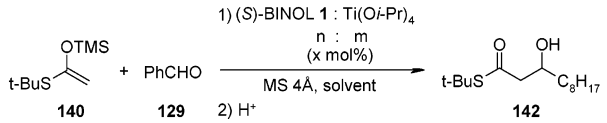
In the same paper, Mikami also showed that enoxysilacyclobutane is more effective as a silyl nucleophile than the usual trimethylsilyl enol ether in the enantioselective catalysis of the reaction. Furthermore, the same group then established that the observed anomalous nonchelation complexation with benzyloxyaldehydes resulted from the steric hindrance of this particular silyl group.[234]

Almost contemporaneously with Mikami's initial study on the silatropic ene mechanism, Keck reported results that highlight the sensitivity of enantiomeric excesses to reaction variables on a very similar system, the addition of 1-(*tert*-butylthio)-1-((trimethylsilyl)oxy)ethene **140** to aldehydes under catalysis by different BINOL−Ti complexes.[235] Both the stoichiometry of the catalyst components and the solvent had a significant effect on the results of the reaction (Table 20).

The conditions reported in entry 4 were then successfully applied to various aldehydes (Table 21).

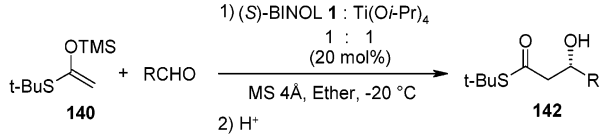
The same group then studied the condensation of the Danishefsky diene with a selection of different aldehydes under the catalysis of the 2:1 BINOL/Ti(O*i*-Pr)$_4$ complex and in the presence of catalytic amounts of CF_3CO_2H. The β-hydroxy vinylogous esters could then be transformed into the corresponding dihydropyrone derivatives in the presence of trifluoro acetic acid (see hetero Diels−Alder section).[236]

Table 20. Enantioselective Catalyzed Aldolization of Benzaldehyde under Keck's Conditions



	catalyst					
entry	n/m	mol %	solvent	T (°C)	yield (%)	ee (%)
1	1:1	10	CH_2Cl_2	0	27	36
2	2:1	10	CH_2Cl_2	0	45	62
3	2:1	20	toluene	0	54	95
4	1:1	20	diethyl ether	−20	90	97
5	2:1	20	diethyl ether	−20	86	91

Table 21. Enantioselective Catalyzed Aldolization of Various Aldehydes under Keck's Conditions

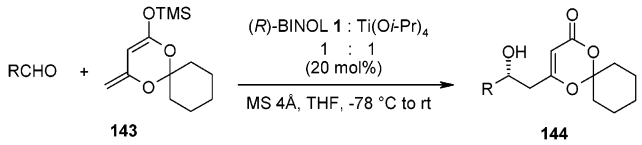


entry	R	yield (%)	ee (%)
1	Ph	90	97
2	n-C_8H_{17}	74	98
3	furyl	88	>98
4	cyclohexyl	70	89
5	PhCH=CH	76	89

4.2.3. Titanium-Catalyzed Vinylogous and Homoaldol Reactions

BINOL complexes have also been used in various vinylogous aldol reactions involving acyclic[237] or cyclic enol ethers. Thus, in the presence of BINOL−Ti catalyst, silyoxydioxine **143** and benzaldehyde led to the corresponding alcohol **144** with very good yield and enantiomeric excess.[238] Yields obtained with cinnamaldehyde and pentanal were lower although the enantiomeric excess remained good (Table 22).[239−247]

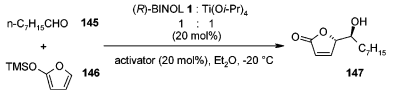
Table 22. Vinylogous Catalyzed Aldol Reaction Using Acyclic and Cyclic Enol Ethers



entry	R	yield (%)	ee (%)
1	Ph	93	92
2	(E)-PhCH=CH	58	79
3	n-Bu	37	76

Figadère studied the condensation of 2-trimethylsilyloxyfuran **146** on various aldehydes in the presence of a BINOL−Ti catalyst and different activators,[248−250] including the product of the reaction. As the result of a careful study, he was able to report the first example of a catalytic asymmetric autoinductive aldol reaction (Table 23).

Table 23. Catalytic Asymmetric Autoinductive Aldol Reaction

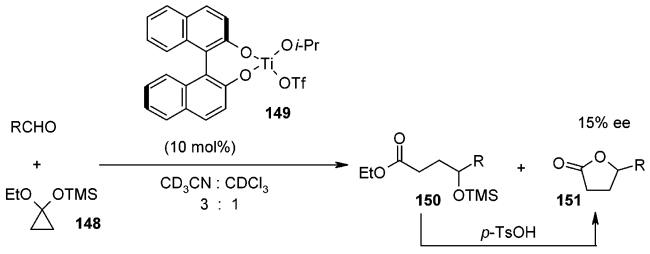


entry	activator	yield (%)	*syn*/*anti*	*syn* ee (%)
1	none	99	70/30	70 (*S*,*S*)
2	(*S*,*S*)-**147**	99	70/30	>96 (*S*,*S*)
3	(*R*,*R*)-**147**	99	70/30	40 (*S*,*S*)
4	(+)-TADDOL	99	70/30	82 (*S*,*S*)

2-Trialkylsilyloxyfurans were also added to aldimines in the presence of a BINOL−Ti(O*i*-Pr)$_4$ catalyst by Martin: yields were good with diastereomeric excesses (*erythro*/*threo*) between 42% and 92% and enantiomeric excesses up to 54%.[251]

Finally, 1-ethoxy-1-trimethylsilyloxy cyclopropane **148** was recently added to different aldehydes in the presence of two BINOL−Ti(X)(OTf) catalysts (X = O*i*-Pr or OTf).[252] Yields of the homoaldol adducts and corresponding lactones were good to excellent but enantiomeric excesses, measured on the experiments on benzaldehyde, were low with both catalysts (X = OTf, 17% ee; X = O*i*-Pr, 15% ee) (Table 24).[253]

Table 24. Homoaldol Adducts and Lactones Synthesis Catalyzed by 149

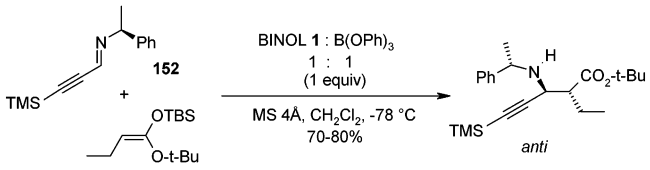


entry	R	*T* (°C)	lactone yield (%)
1	Ph	0	99
2	*p*-ClPh	0	84
3	TMS−C≡C	0	82
4	*t*-Bu	45−50	52

4.2.4. Other Metals

4.2.4.1. Boron Lewis Acids. In 1993, Yamamoto proposed the diastereoselective synthesis of anti β-amino esters from optically active aldimines, under the catalysis of complexes formed from (*R*)- or (*S*)-BINOL and triphenyl borate at room temperature in CH_2Cl_2.[254,255] The products were then converted into β-lactams (Table 25).

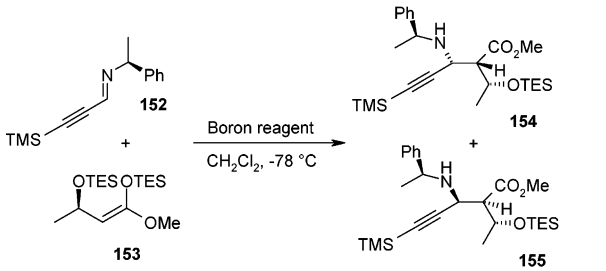
Table 25. Synthesis of *anti*-β-Aminoesters



entry	catalyst	*anti*/*syn*	*anti* de (%)
1	(*R*)-BINOL−B(OPh)$_3$	40/1	98
2	(*S*)-BINOL−B(OPh)$_3$	2/1	88

It is interesting to note that when a chiral silylketene acetal, **153**, was used, the stereoselectivity could be reversed and syn adducts were obtained predominantly (Table 26).

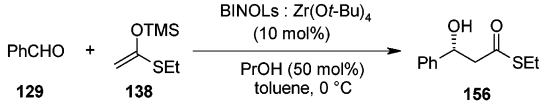
Table 26. Stereoselective Synthesis of *syn*-β-Aminoesters Using Chiral Silylketene Acetal 153



entry	catalyst	yield (%)	*syn*/*anti*	**154/155**
1	B(OPh)$_3$	75	92/8	98/2
2	(*R*)-BINOL-B(OPh)$_3$	53	100/0	33/67
3	(*S*)-BINOL-B(OPh)$_3$	83	100/0	2/98

4.2.4.2. Zr Lewis Acids. Recently, Kobayashi reported the use of chiral zirconium catalysts prepared from (*R*)-BINOLs and Zr(O*t*-Bu)$_4$. The reactions were carried out with 10 mol % catalyst and in the presence of an additive (propanol in most examples).[256] Enantiomeric excesses with (*R*)-BINOL were modest but increased when (*R*)-3,3′-diiodo-BINOL was used. The catalyst prepared from this ligand also allowed the preparation of anti aldol adduct (up to 90% de), while aldol reactions are generally syn stereoselective (Table 27).

Table 27. Zirconium−BINOL-Catalyzed Synthesis of Aldol Adduct 156



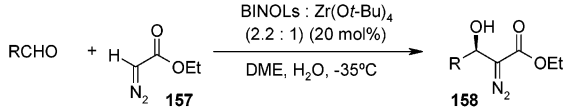
entry	ligand	yield (%)	ee (%)
1	(*R*)-BINOL	72	57
2	(*R*)-3,3′-I$_2$-BINOL	81	92
3	(*R*)-3,3′-Br$_2$-BINOL	54	61
4	(*R*)-3,3′-Cl$_2$-BINOL	48	35

In the same area, Wang et al. have recently demonstrated that the direct aldol-type condensation of aldehydes with ethyl diazoacetate catalyzed by the chiral complex of BINOL derivatives−Zr(O*t*-Bu)$_4$ gave β-hydroxy α-diazo compounds with moderate enantioselectivities (53−87% ee) (Table 28).[257]

A mechanism of this enantioselective condensation is outlined in Scheme 53. In this case, it has been postulated that the Zr(IV) catalyst acts as a Lewis acid activating the aldehyde (Scheme 53).

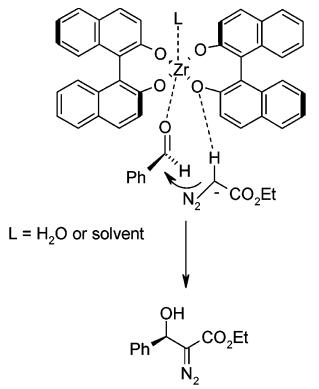
Two syntheses of natural products benefit from an application of a vinylogous aldol reaction. Figadère proposed a synthesis of (+)-muricatacin[249] and (+)-amino muricatacin[258] as direct applications of his study on the reactivity of 2-trimethylsilyloxyfuran under BINOL−Ti catalysis. Scettri reported a study on the synthesis of a nonracemic 6-(furan-3-yl)-5,6-dihydropyran-2-ones[242] and its implementation to the

Table 28. Zirconium−BINOL-Catalyzed Aldol-Type Condensation of Aldehydes with Ethyl Diazoacetate



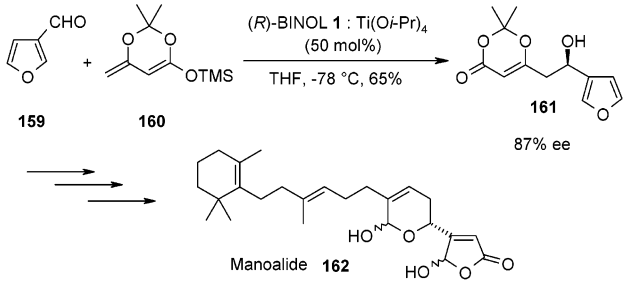
entry	aldehyde	yield (%)	ee (%)
1	PhCHO	40	65
2	3-$F_3CC_6H_4CHO$	61	65
3	4-ClC_6H_4CHO	59	72
4	3-BrC_6H_4CHO	47	78
5	*n*-C_3H_7CHO	82	57
6	furylCHO	82	57

Scheme 53



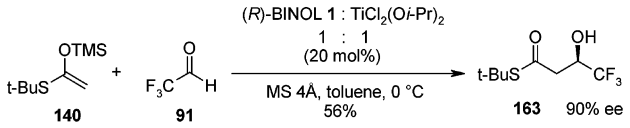
synthesis of manoalide **162**, a sesquiterpene of marine origin (Scheme 54).[245,259]

Scheme 54



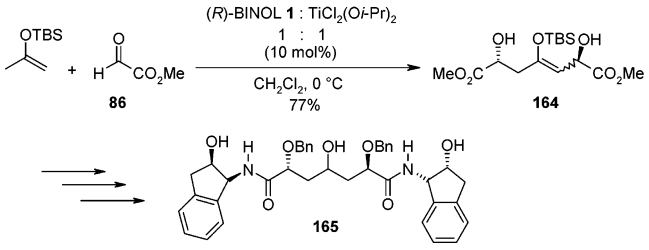
Mikami also showed that the reaction involving ketene silyl acetal of thioesters could be applied to fluoral **91** allowing an enantioselective synthesis of CF_3-substituted aldol **163** of biological importance (Scheme 55).[185,260]

Scheme 55



Finally, a particularly attractive version of the reaction was proposed by the same group: a tandem and two directional enantioselective aldolization. The pseudo-C_2 symmetric product of the condensation between the silyl enol ether and two molecules of the methyl glyoxylate led, through five steps, to a potentially powerful analogue of HIVP inhibitor **165** (Scheme 56).[261]

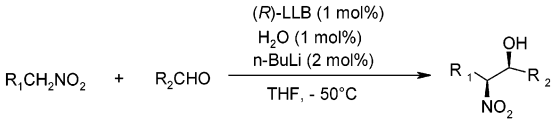
Scheme 56



4.2.5. Catalytic Asymmetric Nitroaldol Reaction

The concept of heterobimetallic chiral catalysts has been applied in asymmetric nitroaldol reactions. In this case, the most efficient catalyst was found to be the lanthanum−lithium−BINOL complex (LaLi−BINOL (**LLB**)) leading to enantiomeric excesses varying from 40% to 96% ee (Table 29).[262−264]

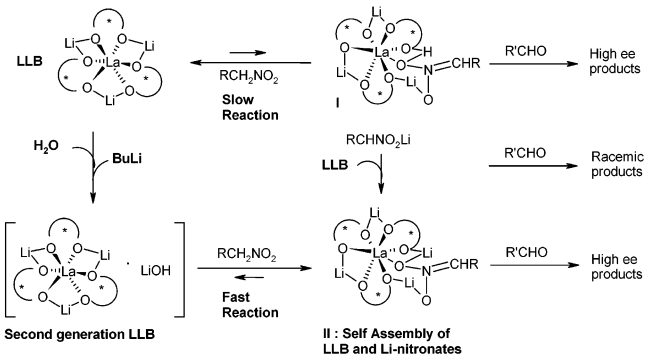
Table 29. Catalytic Asymmetric Nitroaldol Reaction



entry	R_1	R_2	yield (%) (*syn*/*anti*)	ee (%) of *syn*
1	H	C_6H_{11}	94	40
2	Me	CH_2Bz	83 (89/11)	94
3	Et	CH_2Bz	84 (95/5)	95
4	CH_2OH	CH_2Bz	76 (94/6)	96

A proposed reaction course for an improved catalytic asymmetric nitroaldol reaction is shown in Scheme 57.

Scheme 57



First, the tight complex of LaLi−BINOL and LiOH or the high rate of aggregation between LaLi−BINOL and lithium nitronates results in the formation of products with high enantiomeric excesses. Second, much higher reaction rates were observed in all cases; this suggests that heteropolymetallic intermediates such as **II** react with carbonyl compounds much more quickly than heterobimetallic intermediates such as **I** or that the rate of reverse reactions of the type **II** to LaLi−BINOL is much lower than the rate of reactions of the type **I** to LaLi−BINOL.

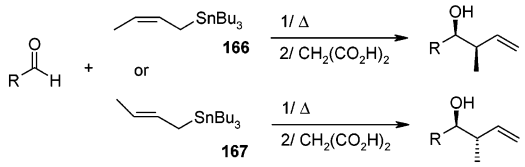
4.3. Allylation

4.3.1. Introduction

The allylation of carbonyl compounds with allyltin or allylsilane derivatives is a fairly recent reaction.

Indeed, the first example of a thermal reaction between allyltin and aldehydes to produce homoallylic alcohols was reported by König and Neumann in 1967.[265] In the same paper, they also established that the reaction rate could be enhanced by adding $ZnCl_2$ to the reactants. Pereyre then showed that the thermal reaction occurs with allylic rearrangement and remarkable stereospecificity in the case of both isomers of crotyl tri-*n*-butyltin **166** and **167** (Scheme 58).[266,267]

Scheme 58



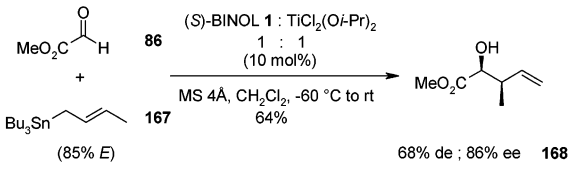
Calas[268,269] showed that the same kind of reaction could be performed with allylsilane derivatives if Lewis acids such as $AlCl_3$ or $TiCl_4$, respectively, were used. With respect to enantioselective catalysis, the first breakthrough is due to Seebach who prepared optically active dichlorodialkoxytitanium derivatives from (*S*)-(−)-1-phenylethanol.[270]

Once again, BINOL−Ti Lewis acids dominate the literature in the field.

4.3.2. Titanium-Catalyzed Allylation Using Allyltin Reagent

In 1993, after Yamamoto had obtained respectable enantiomeric excesses by using chiral acyloxyborane complexes,[271] three groups discovered simultaneously that tri-*n*-butylallyltin undergoes enantioselective reactions with a wide variety of aldehydes provided optically active BINOL−Ti(O*i*-Pr)$_2$ or BINOL−$TiCl_2$ was used. Thus, Mikami and Nakai used a complex prepared in situ from (*S*)-BINOL and $TiCl_2$(O*i*-Pr)$_2$ in the presence of 4 Å molecular sieves. Such a complex used in 10 mol % catalyzes the condensation of various tri-*n*-butylallyltins on glyoxylates with both good diastereoselectivity and good enantioselectivity.[272,273] Condensations also occur with different substituted allylsilanes but yields were lower (vide infra) (Scheme 59).

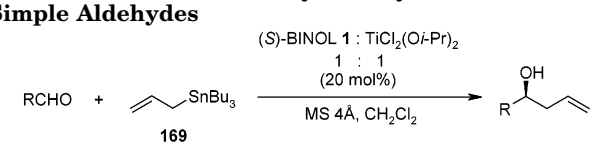
Scheme 59



The same catalyst, used by Tagliavini and Umani-Ronchi in 20 mol %, also in the presence of activated 4 Å MS, promotes the allylation of simple achiral aldehydes with good chemical yields and excellent enantiomeric excesses (Table 30).[274]

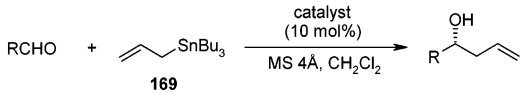
Keck prepared a similar chiral catalyst by two different methods: first (method A), by heating a mixture of (*R*)-BINOL and Ti(O*i*-Pr)$_4$ (1:1) with powdered 4 Å MS; second (method B), by heating a 2:1 mixture of (*R*)-BINOL/Ti(O*i*-Pr)$_4$ in the presence of catalytic amounts of CF_3CO_2H (3 mol % relative to Ti). Both catalysts were then employed successfully at 10 mol % (Table 31).[275,276]

Table 30. Ti−BINOL-Catalyzed Allylation of Achiral Simple Aldehydes



entry	R	*T* (°C)	yield (%)	ee (%)
1	C_7H_{15}	−20	83	97
2	C_5H_{11}	−20	75	98
3	PhCH=CH	−20	38	94
4	Ph	rt	96	82

Table 31. Ti−BINOL-Catalyzed Allylation of Aldehydes under Keck's Conditions

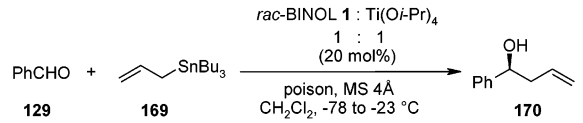


entry	R	catal (method)[a]	yield (%)	ee (%)
1	Ph	A	88	95
2	Ph	B	98	92
3	cyclohexyl	A	66	94
4	cyclohexyl	B	95	92
5	(*E*)-Ph-CH=CH	B	78	77

[a] A = (*R*)-BINOL/Ti(O*i*-Pr)$_4$ (1:1), MS 4 Å; B = (*R*)-BINOL/Ti(O*i*-Pr)$_4$ (2:1), CF_3CO_2H, 3 mol % relative to Ti.

Keck also noticed a case of chiral amplification (positive NLE): in one case, the use of an (*R*)-BINOL of only 50% ee gave the homoallylic alcohol with 88% ee.[277] This observation was confirmed later by Faller who proposed an explanation similar to the one put forward by Mikami for the glyoxylate−ene reaction (vide supra). The fact that the positive NLE could result from the formation of a rather inactive *meso* dimeric catalyst led Faller to propose a chiral poisoning strategy.[201] Thus, a racemic BINOL−Ti(O*i*-Pr)$_2$ catalyst was poisoned by an enantiopure D-DIPT−Ti(O*i*-Pr)$_2$ catalyst (which is inactive). Results reported clearly show the effectiveness of this approach (Table 32).

Table 32. Influence of Poison Amount on the Enantioselectivity in the Ti−BINOL-Catalyzed Allylation of Benzaldehyde

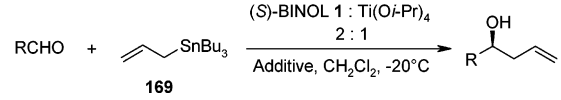


entry	poison (mol %) D-DIPT	poison (mol %) Ti(O*i*-Pr)$_4$	yield (%)	ee (%)
1	0	0	65	0
2	15	10	40	39
3	20	10	47	81
4	30	10	63	91

Always with the goal of reaction rate enhancing and greater selectivity, Yu proposed various accelerators of general structure R_nMSR' (M = Si, B, Al).[278−283]

The key to this approach, which proved to be efficient, is the strong Sn−S and M−O bonds relative to the weaker M−S bond (Table 33).

Table 33. Influence of "Accelerator" Amount on the Enantioselectivity in the Ti−BINOL-Catalyzed Allylation of Benzaldehyde

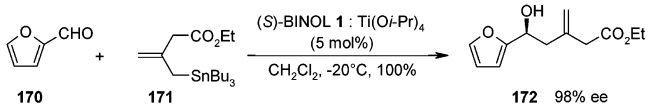


entry	R	catal (%)	additive	yield (%)	ee (%)
1	$PhCH_2CH_2$	10	*i*-PrSSiMe$_3$	87	94
2	$PhCH_2CH_2$	10	Et_2BS-*i*-Pr	93	97
3	*n*-C_6H_{13}	10	*i*-PrSSiMe$_3$	83	92
4	*n*-C_6H_{13}	10	Et_2BS-*i*-Pr	87	97
5	Ph	10	*i*-PrSSiMe$_3$	91	97
6	Ph	10	Et_2B-*i*-Pr	89	96

The same authors also proposed an approach involving the use of a Lewis acid, $B(OMe)_3$.[280]

Allylation with functionalized allyltin under BINOL−Ti catalysis is rare. Thomas reported the reactivity of a chiral silyloxy reactant[284] and Keck the use of allyltin derivatives with various aldehydes including furaldehyde, benzaldehyde, and benzyloxyethanal. All enantiomeric excesses were excellent (93−99%); the most spectacular was obtained with furaldehyde **170** with only 5 mol % catalyst (Scheme 60).[285]

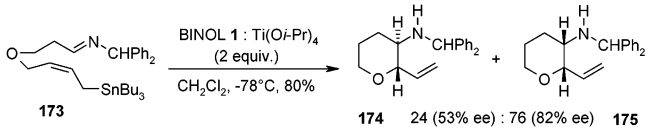
Scheme 60



Since these works, numerous studies have appeared in the literature increasing the performance of the catalyst by using numerous additives.[286−297]

Finally, the only example of cyclization promoted by a BINOL−Ti catalyst that we are aware of was performed by Yamamoto on the following iminoallyltin reactant **173**. Unfortunatly, the Ti complex had to be used in excess to achieve good enantioselectivity (Scheme 61).[298]

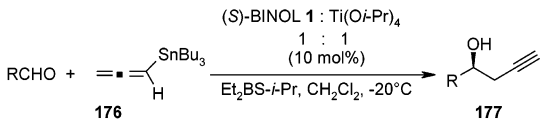
Scheme 61



4.3.3. Titanium-Catalyzed Allylation Using Propargyl and Allenyltin Reagents

The substitution of allyltin reagents by allenyl tri-*n*-butyltin **176** in an enantioselective transformation involving BINOL was proposed by Keck in 1994.[299] Good to excellent ee's (82−99%) were obtained on various aldehydes, but 50−100 mol % catalyst was to be used, and reaction times were all over 72 h. These drawbacks were overcomed by Yu who applied his accelerator strategy to this problem. Indeed, by using R_nMSR' accelerators, the BINOL−Ti could be reduced to 10 mol % and reaction times to 10−20 h (Table 34).[278]

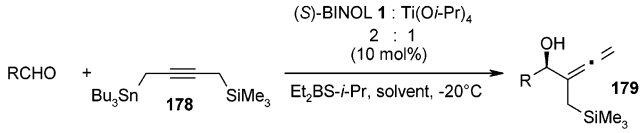
Table 34. "Accelerator" Influence on the Enantioselectivity in the Ti−BINOL Catalyzed Allenyltin Addition to Aldehydes



entry	R	time (h)	yield (%)	ee (%)
1	$PhCH_2CH_2$	9	86	94
2	*n*-C_6H_{13}	9	75	92
3	Ph	15	52	92

The same approach proved also to be efficient when applied to propargyltin. Indeed, optically active allenyl alcohols were obtained in that way.[300,301] Finally, when 1,4-bis(tri-*n*-butyltin)but-2-yne or 1-trimethylsilyl-4-tri-*n*-butyltin-but-2-yne **178** were used, alcohols **179** were prepared in good yields and excellent enantiomeric excesses (Table 35).[294,302−305]

Table 35. Ti−BINOL-Catalyzed Propargyltin Addition to Aldehydes



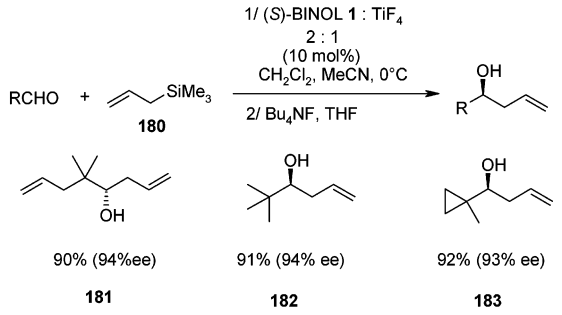
entry	R	time (h)	solvent	yield (%)	ee (%)
1	*n*-C_6H_{13}	18	CH_2Cl_2	60	90
2	*n*-C_6H_{13}	18	$PhCF_3$	83	97
3	$PhCH_2CH_2$	18	CH_2Cl_2	62	92
4	$PhCH_2CH_2$	18	$PhCF_3$	78	97

4.3.4. Other Allylmetal Reagents

Examples of enantioselective allylation using allyltrimethylsilane are scarce since the addition of this reagent results in 10^3−10^4 times slower allylation than with allyl tri-*n*-butyltin.[306] Therefore the abovementioned catalysts are not sufficiently Lewis acidic to promote the reaction with good results. For example, the use of (*S*)-BINOL−$TiBr_2$ only enabled the preparation of homoallylic alcohols with 40% yield and 30% ee. Carreira overcame the problem by using a catalyst prepared from enantiopure BINOL and TiF_4. Yields and ee increased to 90−94% on various aldehydes[293,307] owing to the greater electronegativity of fluorine compared to chlorine or bromine and the strong Ti−F bond (E_{diss} = 140 kcal/mol), which prevents desilylation of the formed trimethylsilyl ethers to give trimethylsilylfluoride (Si−F bond, E_{diss} = 135 kcal/mol) (Scheme 62).

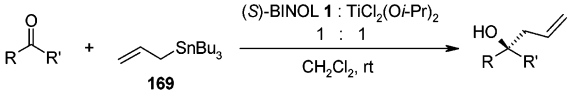
Majundar explored the reactivity of various aldehydes in a Sn(II)-mediated Barbier-like reaction under BINOL−Ti(O*i*-Pr)$_2$ catalysis. The ee of the resulting homoallylic alcohols ranged from 18% to 63%.[308]

Scheme 62



Finally, Tagliavini expanded the scope of the reaction to ketones by using tetraallyltin as allylating reactant in the presence of a BINOL−Ti(O*i*-Pr)$_2$ catalyst. Enantiomeric excesses are moderate to good with aromatic and α,β-unsaturated ketones but remain low with aliphatic ones (Table 36).[309]

Table 36. Catalyzed Allylation of Ketones Using TiCl$_2$(O*i*-Pr)$_2$/BINOL System

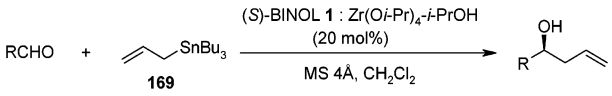


entry	R	R′	catal (%)	time (h)	yield (%)	ee (%)
1	Ph	Me	20	20	75	52
2	2-naphthyl	Me	40	4	94	80
3	(*E*)-PhCH=CH	Me	20	1	83	51
4	*n*-C$_6$H$_{13}$	Me	20	3	89	29

4.3.5. Zr Lewis Acids

Although the synthesis of homoallylic alcohols is very efficient with BINOL−Ti catalysts, reaction times are often very long when no activator is used. This observation led Bedeschi et al. to study a Lewis acid catalyst obtained from Zr(O*i*-Pr)$_4$−*i*-PrOH and BINOL. Results were very satisfying for aromatic aldehydes (good yields and ee, along with a dramatic reduction in reaction times) but not as good for aliphatic aldehydes (lower yields) (Table 37).[289,310]

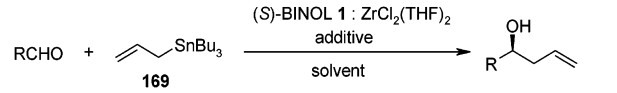
Table 37. Catalyzed Allylation of Aldehydes Using the Zr(O*i*-Pr)$_4$/*i*-PrOH/BINOL System



entry	R	*T* (°C)	time (h)	yield (%)	ee (%)
1	*n*-C$_7$H$_{15}$	0	6	58	87
2	*n*-C$_5$H$_{11}$	0	10	84	89
3	(*E*)-PhCH=CH	−20	3	81	91
4	Ph	−40	6	79	93

Although 4 Å MS are not necessary for the catalyst preparation, their inclusion is essential to achieve good enantioselectivity and in a reasonable time.[288] Later, the same authors showed that the reaction could also be performed with ee up to 85−87% with a catalyst obtained from ZrCl$_4$ and BINOL. The introduction of 4-*tert*-butylcalix[4]arene allowed a diminution of the catalyst and an enhancement of the ee (Table 38).[311]

Table 38. Catalyzed Allylation of Aldehydes Using ZrCl$_2$(THF)$_2$/BINOL System



entry	R	BINOL/Zr	additive (%)	yield (%)	ee (%)
1[a]	*n*-C$_7$H$_{15}$	2:1	none	65	85
2[a]	Ph	2:1	none	40	87
3[b]	*n*-C$_7$H$_{15}$	1:1	calix[4]arene (5)	65	96
4[b]	Ph	1:1	calix[4]arene (5)	85	85

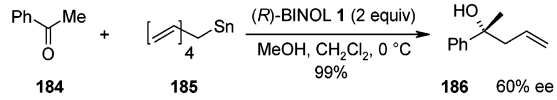
[a] Reaction performed using 10 mol % of catalyst in Et$_2$O. [b] Reaction performed using 5 mol % of catalyst in CH$_2$Cl$_2$.

Finally, Mikami proposed to use a catalyst prepared from BINOL and Zr(O*t*-Bu)$_4$ associated with a product-like activator, (*R*)-(+)-α-methyl-2-naphthalenemethanol. Although the ee remained moderate (40−57%), the influence of the activator is clear.[312]

4.3.6. Other Complexes

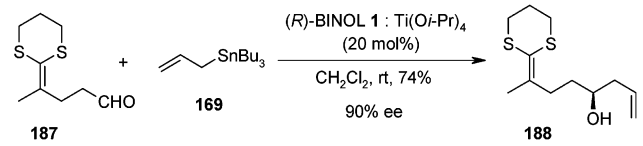
Baba showed that a tetraallyltin/(*R*)-BINOL system associated with methanol as an additive could lead from acetophenone **184** to the obtention of the corresponding homoallylic alcohol **186** with up to 60% ee (Scheme 63).[313]

Scheme 63



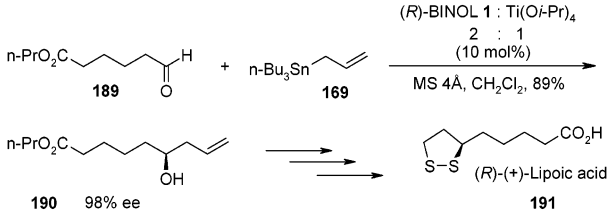
In 1996, Kocienski reported a synthesis of the C$_1$−C$_{21}$ fragment of the immunosuppressant rapamycin, which involved an asymmetric allylation to introduce the first stereogenic center of the target molecule. The reaction was run on a 350 mmol scale, and (*R*)-BINOL was recycled (Scheme 64).[314]

Scheme 64



More recently, Zimmer achieved a formal synthesis of (*R*)-α-lipoic acid **191** and its (*S*)-antipode based on the asymmetric synthesis (98% ee) of both enantiomers of 6-hydroxy-8-nonene carboxylates under (*R*)- or (*S*)-BINOL−Ti(O*i*-Pr)$_2$ catalysis (Scheme 65).[315]

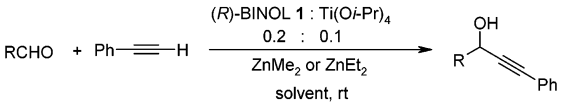
Scheme 65



4.4. Alkynylation

Optically active propargylic alcohols are versatile precursors for the synthesis of many chiral organic compounds. Thus, the asymmetric addition of alkynylzinc to aldehydes is an important method of synthesizing such compounds.[316−320] Nevertheless, a single and pratical method to make chiral propargylic alcohols from aromatic aldehydes has been developed in the presence of a titanium alkoxide catalyst prepared in situ from Ti(O*i*-Pr)$_4$ and (*R*)-BINOL **1** leading to excellent enantioselectivity of up to 96% ee (Table 39).[303,321−324]

Table 39. Enantioselective Addition of Phenylacetylene to Aromatic Aldehydes Promoted by the BINOL−Ti Complex

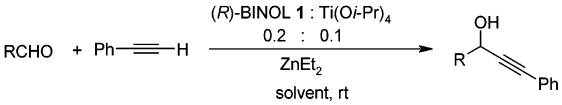


entry	R	yield (%)	ee (%)
1	Ph	77	96
2	*p*-F-Ph	74	96
3	*p*-NO_2-Ph	79	97
4	*p*-Cl-Ph	81	92
5	*p*-Me-Ph	93	97
6	*o*-Me-Ph	81	96
7	*m*-Me-Ph	77	94
8	*p*-MeO-Ph	97	94

It is noteworthy that activation of chiral titanium(IV) complexes with chiral or achiral activators has been found to provide higher levels of enantioselectivities than those attained with an enantiopure catalyst

Since these pioneering studies, Pu et al. have extended the scope of this reaction demonstrating that the BINOL−Ti(O*i*-Pr)$_4$ catalyst system is also highly enantioselective for the phenylacetylene addition to aliphatic aldehydes as well as α,*β*-unsaturated aldehydes (Table 40).[325,326]

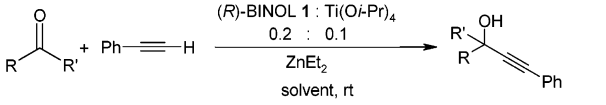
Table 40. Enantioselective Addition of Phenylacetylene to Aliphatic and α,*β*-Unsaturated Aldehydes Promoted by the BINOL−Ti Complex



entry	aldehyde	yield (%)	ee (%)
1	Me-$(CH_2)_7$−CHO	96	91
2	Me-$(CH_2)_6$−CHO	70	93
3	Me-$(CH_2)_3$−CHO	91	93
4	Me-CH_2−CHO	60	94
5	Ph-CH_2−CHO	93	91
6	allyl-CHO	92	96
7	cinnamaldehyde	89	97

Recently, this reaction was successfully applied to the phenylacetylene additions to ketones. In this case, most of the chiral tertiary propargyl alcohols that were generated from aromatic ketones were obtained with 85−92% ee at room temperature (Table 41).[327]

Table 41. Enantioselective Addition of Phenylacetylene to Ketones Promoted by the BINOL−Ti Complex



entry	ketone	yield (%)	ee (%)
1	acetophenone	67	85
2	3′-methoxyacetophenone	81	92
3	3′-methylacetophenone	66	90
4	3′-bromoacetophenone	68	86
5	1′-naphthacetophenone	71	91
6	4-methyl-2-pentanone	91	63
7	benzalacetone	88	73

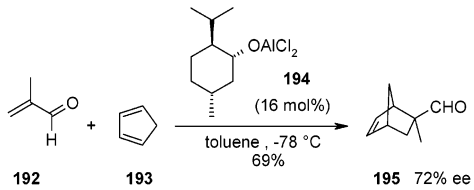
4.5. Diels−Alder Reaction

4.5.1. Titanium-Catalyzed Diels−Alder Reaction

Since the landmark publication of Yates and Eaton[328] on the Lewis acid-catalyzed Diels−Alder reaction,[329] the use of these catalysts has become very popular. Inded, they both accelerate the reaction and enhance its selectivity. As one of the consequences of this success, a number of reviews are devoted to this area of research.[330−334]

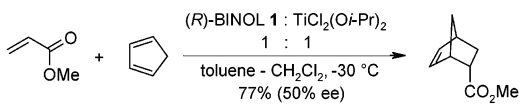
The use of chiral Lewis acids to induce enantioselectivity is only 25 years old. The first report by Guseinov[335] in 1976 cited a poor enantiomeric excess, but three years later, Koga obtained bicyclic derivatives with up to 72% ee when using chiral alkoxyaluminum dichlorides **194** as Lewis acids (Scheme 66).[336]

Scheme 66



As for the use of BINOL as chiral ligand, early studies are due to Seebach[337] and Reetz[225] who both used BINOL−Ti complexes, BINOL−Ti(O*i*-Pr)$_2$ and BINOL−$TiCl_2$ respectively. The most encouraging results were obtained with the latter (Scheme 67).

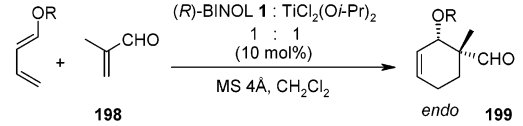
Scheme 67



Mikami and Nakai extended their studies on catalysts such as BINOL−TiX_2 (X = Cl, Br), which were prepared in situ from Ti(O*i*-Pr)$_2X_2$, (*R*)-BINOL, and molecular sieves 4 Å, to the Diels−Alder cycloaddition of 1,3-dienol derivatives added to methacrolein.[208,338] The *endo*/*exo* ratios were very high, and enantiomeric excesses were in the 71−86% range. A few years later, Mikami reported that endo- and enantioselectivity could be enhanced by using a MS-free BINOL−Ti catalyst (i.e., the catalyst is prepared in the presence of molecular sieves, which are then

removed by centrifugation).[339] The same catalyst also exhibits a significant positive nonlinear effect (NLE) (Table 42).

Table 42. Influence of the Catalyst Preparation on the Diels–Alder Cycloaddition of 1,3-Dienol Derivatives with Methacrolein

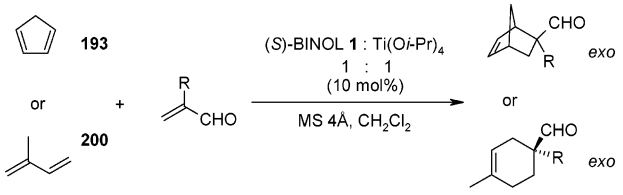


entry	R	MS 4 Å	*T* (°C)	yield (%)	*endo* (%)	ee (%)
1	Me	yes	−30	43	87	71
2	Me	removed	−30	40	93	85
3	COMe	yes	rt	69	97	78
4	COMe	removed	rt	63	99	94

Mikami also showed that the use of 6,6′-Br_2-BINOL–$TiCl_2$ leads to improvement of endo- and enantioselectivity with respect to the parent BINOL complex when methacrolein was involved but not when 2-bromoacrolein was used.[340]

Finally, Keck studied the selectivity of the reaction between cyclopentadiene **193** or isoprene **200** and methacrolein or 2-bromoacrolein in the presence of (*S*)-BINOL–Ti(O*i*-Pr)$_2$ [prepared from (*S*)-BINOL, Ti(O*i*-Pr)$_4$, and MS 4 Å]. Exo selectivity ranged from 10:1 to 17:1, and enantiomeric excesses were up to 94% in the case of cyclopentadiene **193** and 2-bromoacrolein (Table 43).[341]

Table 43. Selectivity of the Diels–Alder Reaction Catalyzed by the Ti(O*i*-Pr)$_4$/BINOL/MS 4 Å System

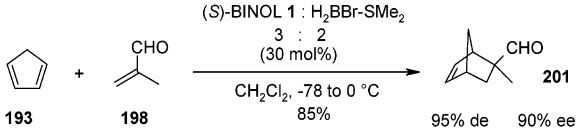


entry	diene	R	*T* (°C)	yield (%)	*exo*/*endo*	ee (%)
1	**193**	Br	−78	94	17/1	94
2	**200**	Br	−20	75	10/1	80
3	**193**	Me	−20	75	10/1	58

4.5.2. B– and Al–BINOL Complexes

In 1990, Kaufmann reported the synthesis and X-ray structure of a C_3-symmetric tetradecacyclic diborate complex (propeller complex), which efficiently catalyzed the reaction between cyclopentadiene **193** and methacrolein **198**. The catalyst is obtained from (*S*)-BINOL (3 equiv) and bromoborane–dimethyl sulfide complex (2 equiv) (Scheme 68).[342,343]

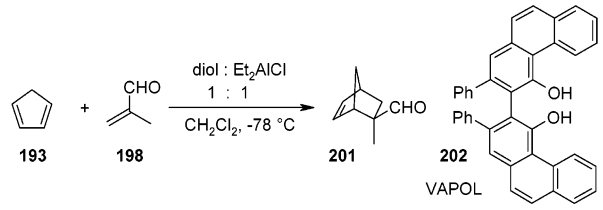
Scheme 68



The same reaction was studied by Wulff with similar catalysts obtained from vaulted biaryls[344] and by Oh with catalysts prepared from 1,8-naphthalenediyl bis(dichloroborane), a bidentate Lewis acid,[345] and various chiral ligands including BINOL.

Wulff also worked on the influence of catalysts obtained from diethylaluminum chloride and BINOL (or various vaulted biaryls).[346] Although good to excellent exo selectivities were obtained in all cases, enantiomeric excesses were only modest with BINOL (13–41%) compared to the ones reached with a vaulted biphenanthrol (VAPOL) **112**, 88–98% (Table 44).

Table 44. Selectivity of the Diels–Alder Reaction Catalyzed by the Et_2AlCl/Diol System



entry	diol	catal (mol %)	yield (%)	*exo*/*endo*	ee (%)
1	(*S*)-BINOL	10	99	97/3	23
2	(*S*)-VAPOL	10	100	98/2	98
3	(*S*)-VAPOL	0.5	98	97/3	88

Recently, as part of a study directed toward the Diels–Alder reaction between "noncompatible" dienes and dienophiles by means of a temporary Al or Zr tethering, Olson reported an interesting result.[347] Noteworthy is the fact that (−)-menthol and (−)-8-phenylmenthol did not lead to any enantiomeric excess (Scheme 69).

Scheme 69

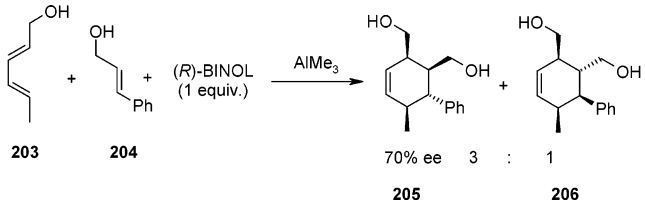
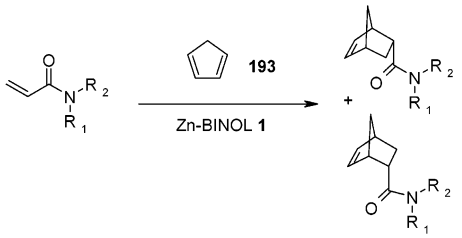


Table 45. Reaction of *N*-Alkoxyacrylamides with Cyclopentadiene Catalyzed by (*R*)-Zn-1



entry	R_1	R_2	*endo*/*exo*	ee (*endo*) (%)
1	Me	OMe	7:1	89
2	*t*-Bu	OMe	*a*	60
3	Ph	OMe	54:1	96
4	Ph	OMe	41:1	90
5	Ph	OEt	29:1	86
6	Ph	O*i*-Pr	14:1	76

[a] Not determined.

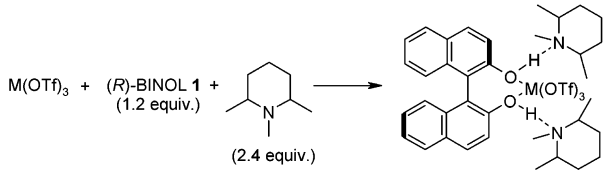
Dialkylzinc represents an attractive alternative to trialkylaluminum for preparation of mild Lewis acids.[348] The Lewis acid obtained from dimethylzinc and BINOL **1** was investigated for the Diels−Alder reaction of *N*-alkylacrylamides providing good results in terms of enantioselectivity (Table 45).

Thus, the superiority of the Zn−BINOL experimental procedure makes it very attractive from a synthetic point of view.[349,350]

4.5.3. BINOL−Lanthanide Complexes

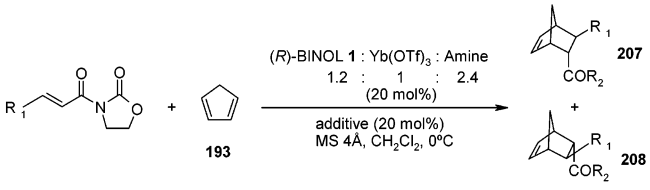
As part of his systematic study of lanthanide triflates as Lewis acids, Kobayashi published in 1993 and 1994 a series of papers describing the enantioselectivity induced by BINOL−ytterbium[351] (or scandium[352]) triflates in the reaction between cyclopentadiene and various acyl-1,3-oxazolidin-2-ones. Both catalysts were prepared by mixing the metal triflate with BINOL in the presence of molecular sieves 4 Å and then adding 2.4 equiv of a tertiary amine. The proposed structure, based on ^{13}C NMR and IR data, involves a Lewis acid−Lewis base interaction between the metal and the oxygen and hydrogen bonds between the nitrogen of the tertiary amine and the proton of the hydroxy functions (Scheme 70).[353]

Scheme 70



Different groups also showed that both enantiomers of the cycloadduct could be obtained by using the same enantiomer of BINOL and only changing an achiral ligand (3-phenylacetylacetone, PAA) (Table 46).[354−356]

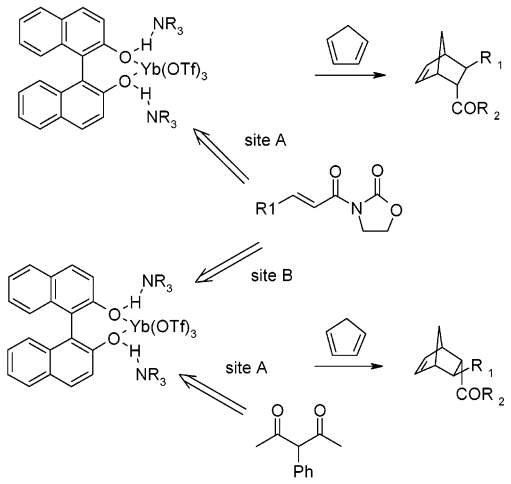
Table 46. Diels−Alder Reaction Catalyzed by the Yb(OTf)$_3$/1/Additive System



entry	additive	R_2	yield (%)	*endo*/*exo*	**207/208**	ee (%)
1	none	Me	77	89/11	97.5/2.5	95
2	PAA	Me	83	93/7	9.5/90.5	81
3	none	*n*-Pr	81	80/20	91.5/8.5	83
4	PAA	*n*-Pr	81	91/9	10/90	80

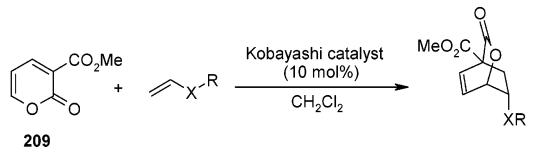
This result was accounted for in the following way by the authors: in the absence of PAA, the dienophile approaches on site A, while when PAA is present it preferentially binds to site A, forcing the dienophile to approach on site B (Scheme 71).

Scheme 71



Marko then used the same catalysts in an inverse electron demand Diels−Alder reaction between vinyl ethers or vinyl sulfides and 3-carbomethoxy-2-pyrone. The enantiomeric excess reached 85% with vinyl ethers and 95% with vinyl sulfides (Table 47).[357,358]

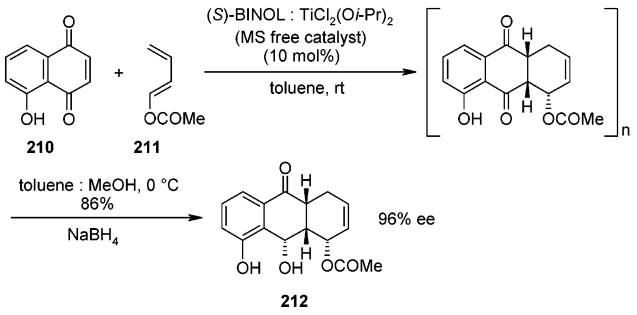
Table 47. Diels−Alder Reaction between Vinyl Ethers or Vinyl Sulfides and 3-Carbomethoxy-2-pyrone Using the Kobayashi Catalyst



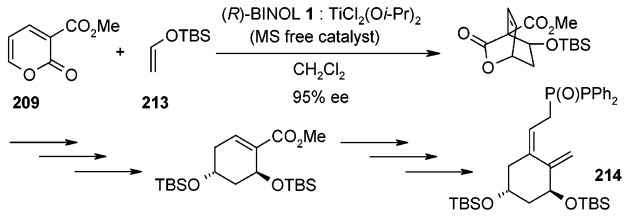
entry	X	R	yield (%)	ee (%)
1	O	Et	90	27
2	O	cyclohexyl	91	82
3	O	adamantyl	97	85
4	S	Et	96	30
5	S	cyclohexyl	88	86
6	S	Ph	91	>95

Mikami reported the reaction of juglone with butadienyl acetate using a MS-free BINOL−Ti catalyst. The use of the MS-free catalyst was crucial since with the classical one, the enantiomeric excess dropped to 9%. The obtention of the cycloadduct provided an efficient entry to the asymmetric synthesis of anthracycline and tetracycline antibiotics (Scheme 72).[359]

Scheme 72



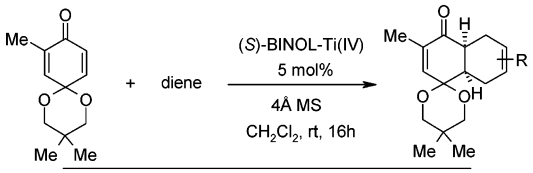
Scheme 73

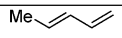
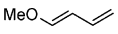


Posner applied the inverse electron demand approach to the synthesis of the A ring of vitamin D derivatives (Scheme 73).[360,361]

As an extension of this methodology, Corey et al. have found that achiral 1,4-quinone monoketals function well as dienophiles in enantioselective Diels–Alder reactions catalyzed by a chiral Ti(IV) Lewis acid. The results are excellent as shown in Table 48.

Table 48. Enantioselective Diels–Alder Reactions of Quinone Monoketal 215 with Various Dienes Catalyzed by (*S*)-BINOL–Ti(IV)–MS 4 Å



Entry	Diene	Yield (%)	Ee (%)
1		90	99
2		90	99
3		95	95
4		95	90
5		91	96

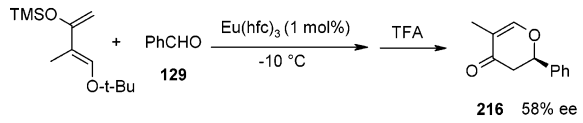
Nevertheless, although the Mikami catalyst system is very useful in this connection, there is a need for the development of more clearly defined, more structurally homogeneous, and more efficacious catalysts.[362]

4.6. Hetero Diels–Alder Reaction

4.6.1. Introduction

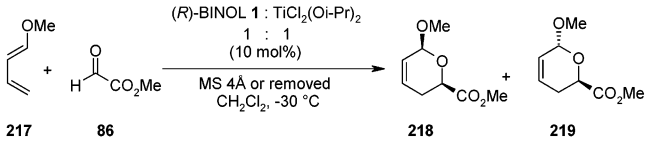
Although less studied than the all-carbon version of the reaction, the hetero Diels–Alder reaction has attracted over the past decades a greater attention. It provides a versatile regio- and stereoselective approach toward heterocyclic compounds from heterodienes[363] or heterodienophiles.[364] The use of Lewis acid catalysis in these reactions is overwhelmingly associated with heterodienophiles, the most known example being the cyclocondensation developed by Danishefsky between activated dienes and aldehydes.[365,366] The first successful use of a chiral Lewis acid is precisely due to Danishefsky who obtained a very promising result with catalytic amounts of chiral shift reagent (Scheme 74).[367]

Scheme 74



As for BINOL, the first example of its use in such a reaction was reported by Nakai and Mikami in 1991. They prepared dihydropyran dicarboxylates with high enantiomeric excess from methoxy butadiene and methyl glyoxylate in the presence of an (*R*)-BINOL–$TiCl_2$ catalyst.[208] A few years later, Mikami showed that, as in the case of the all-carbon version of the reaction, the use of molecular sieves-free catalyst improves the endo- and enantioselectivity of the reaction between glyoxylates and methoxydienes (Table 49).[339]

Table 49. Hetero Diels–Alder Reaction Catalyzed by the $TiCl_2$(O*i*-Pr)$_2$/BINOL System

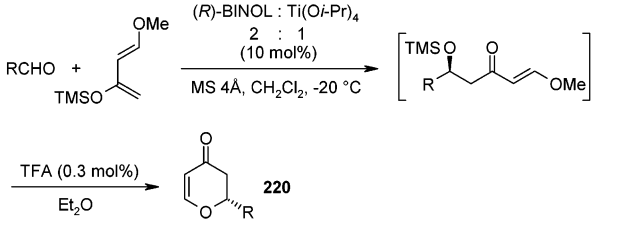


entry	MS 4 Å	yield (%)	**218** (ee)	**219** (ee)
1	yes	77	78 (94)	22 (>90)
2	removed	78	88 (96)	12 (>90)

Similarly, the use of 6,6′-Br_2-BINOL–Ti catalyst also enhanced the selectivities of the reaction.[340]

Attempts were also made with Danishefsky's diene and various aldehydes with catalysts prepared from BINOL and Ti(O*i*-Pr)$_4$. Thus, Keck showed that enantiomeric excess up to 97% could be obtained provided the catalyst was prepared using a 2:1 BINOL/Ti(O*i*-Pr)$_4$ stoichiometry in the presence of 4 Å molecular sieves and 0.003 equiv of trifluoroacetic acid (TFA). TFA is necessary to induce the cyclization step since the chiral Lewis acid only induces the formation of the Mukaiyama aldol product **220** (Table 50).[236,368,369]

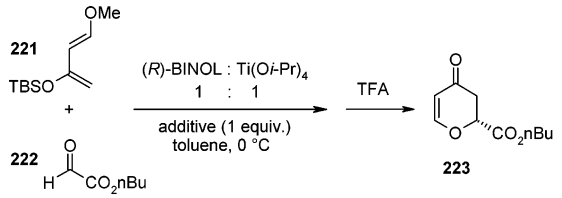
Table 50. Hetero Diels–Alder Reaction Catalyzed by the Ti(O*i*-Pr)$_4$/1/MS 4 Å System



entry	R	yield (%)	ee (%)
1	Ph	40	55
2	$BnOCH_2$	60	97
3	furyl	61	97
4	n-C_8H_{17}	88	97

Mikami then showed that the addition of chiral activators, including BINOL itself, could enhance the level of enantioselectivity promoted by a 1:1 BINOL/Ti(O*i*-Pr)$_4$ catalyst between Danishefsky's dienes and butylglyoxylate (Table 51).[370]

Table 51. Influence of the Additive in the Hetero Diels–Alder Reaction Catalyzed by the Ti(O*i*-Pr)$_4$/1 System

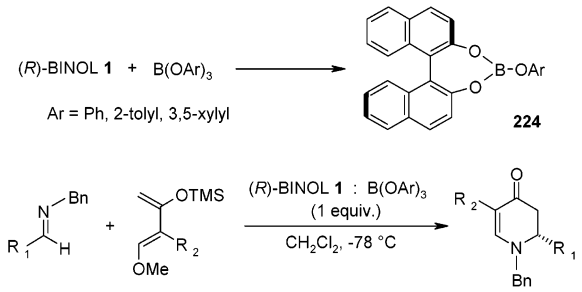


entry	additive	yield (%)	ee (%)
1	none	40	5
2	(*R*)-BINOL	50	84
3	(*R*)-5-Cl-BIPOL	53	26
4	(*R*)-6-Br-BINOL	25	43

4.6.2. BINOL–B and –Al Complexes

To the best of our knowledge, boron Lewis acids have been widely dedicated to aza-Diels–Alder reaction. Yamamoto reported in 1992 the preparation of chiral Lewis acids from (*R*)-BINOL and triarylborates, B(OAr)$_3$.[371] Enantiomeric excesses, up to 90%, were obtained for the aza-Diels–Alder cycloaddition between Danishefsky's dienes and aldimines (Table 52).[372]

Table 52. Aza-Diels–Alder Reaction Catalyzed by the B(OAr)$_3$/1 System

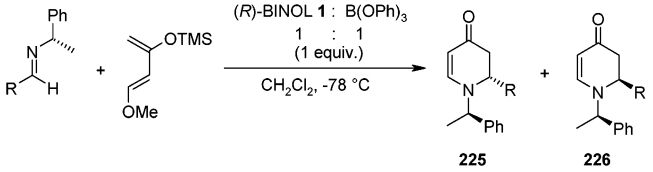


entry	R_1	R_2	Ar	yield (%)	ee (%)
1	Ph	H	Ph	75	82
2	Ph	H	2-tolyl	76	84
3	Ph	H	3,5-xylyl	75	86
4	Ph	Me	Ph	72	81
5	3-pyr	H	Ph	71	90

In further publications, the same authors also studied the double asymmetric induction (chiral Lewis acid and chiral aldimines) of the reaction. The approach was successful for both aliphatic and aromatic aldimines, and diastereomeric excesses up to 98% were reached (Table 53).[373,374]

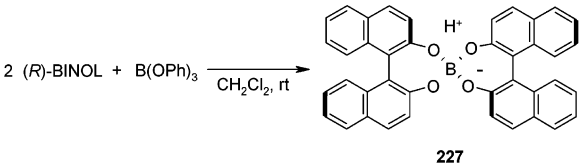
Finally, Yamamoto also showed that, provided a 2:1 mixture of BINOL and trialkylborate was used, a Bronsted acid-assisted chiral Lewis acid (BLA) **227** could be obtained (Scheme 75).[375–378]

Table 53. Aza-Diels–Alder Reaction Catalyzed by the B(OPh)$_3$/1 System



entry	R	yield (%)	**225/226**
1	Ph	61	99/1
2	3-pyridyl	63	99/1
3	cyclohexyl	31	99/1
4	*n*-propyl	49	95/5

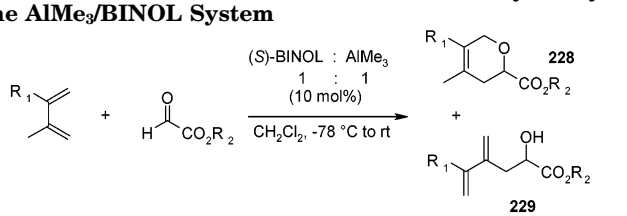
Scheme 75



This BLA was likewise efficient for the double asymmetric induction of the aza-Diels–Alder reaction of a chiral aldimine and Danishefsky's diene (up to 99% de). It is worth noting that in all these aza-Diels–Alder reactions, the boron Lewis acid was used in stoichiometric quantities.

A BINOL–AlMe catalyst, obtained from (*S*)-BINOL and AlMe$_3$, has been used by Jorgensen to promote preferentially the hetero Diels–Alder cycloadduct (vs the ene adduct) in the reaction between conjugated dienes having allylic C–H bonds, such as isoprene and glyoxylate esters (Table 54).[379]

Table 54. Hetero Diels–Alder Reaction Catalyzed by the AlMe$_3$/BINOL System

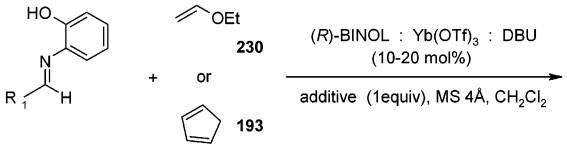


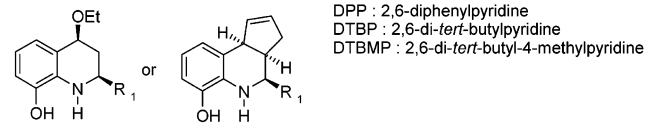
			228		**229**	
entry	R_1	R_2	yield (%)	ee (%)	yield (%)	ee (%)
1	Me	Me	37	94	12	56
2	H	Me	13	70	3	27
3	Me	Et	73	97	9	88
4	H	Et	29	97	14	88

4.6.3. BINOL–Ln Complexes

A significant improvement in the asymmetric aza-Diels–Alder reaction was made with the introduction of chiral lanthanide Lewis acids. Kobayashi reported the first examples of such reactions promoted with substoichiometric quantities of Lewis acid.[380] It must also be noted that the reaction involves an azadiene and not, as in all other cases reported so far, an azadienophile. The chiral catalyst is prepared from Yb(OTf)$_3$, (*R*)-BINOL, and DBU and is used in 10–20 mol % in the presence of 1 equiv of an additive (Table 55).

Table 55. Aza-Diels–Alder Reaction Catalyzed by the Yb(OTf)$_3$/1/DBU System



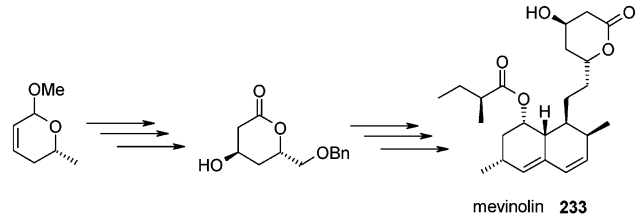


entry	R_1	alkene	additive	yield (%)	cis/ trans	ee (%)
1	Ph	**230**	DTBP	52	94/6	77
2	α-naphthyl	**230**	DPP	65	99/1	91
3	α-naphthyl	**230**	DTBMP	74	>99/1	91
4	α-naphthyl	**193**	DTBMP	69	>99/1	68
5	cyclohexyl	**193**	DTBMP	58	>99/1	73

Yb(OTf)$_3$, associated with (*R*)-BINOL and 2,6-lutidine, was also used in 10 mol % to promote the cycloaddition between Danishefsky's diene and aldimines. However, the best enantiomeric excess with this combination (41%) exceeded the ones obtained with Cu- and Mg-centered Lewis acids associated with chiral diamines.[381]

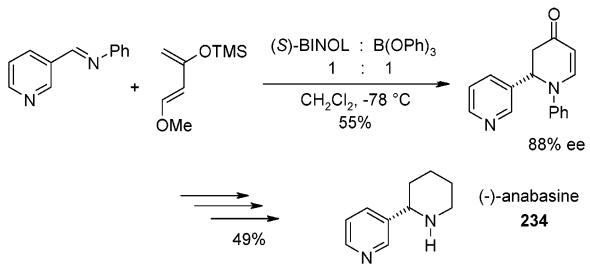
Mikami and Nakai applied their methodology to the synthesis of the lactone portion of mevinolin **233** (Scheme 76).[208,382]

Scheme 76



Piperidine alkaloids (−)-anabasine **234** and (+)-coniine were synthesized by Yamamoto as an application of the aza-Diels–Alder reaction promoted by the BINOL–B(OPh) catalyst (Scheme 77).[373]

Scheme 77

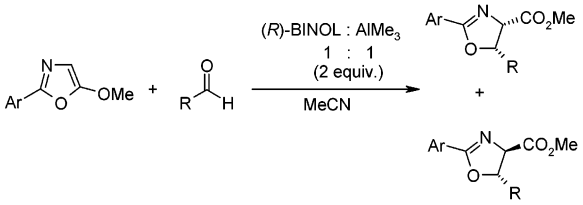


4.7. Miscellaneous

4.7.1. [3+2] Cycloadditions and 1,3-Dipolar Cycloadditions

4.7.1.1. [3+2] Cycloadditions. Racemic BINOL, associated with aluminum, was first used in 1991 by Suga to catalyze the [3+2] cycloaddition between 2-aryl-5-methoxyoxazoles and aldehydes.[383,384] 2-Oxazoline-4-carboxylates, which are useful building blocks, were obtained with high cis selectivity. Only recently, the same authors reported results obtained with a chiral catalyst that was prepared in situ from (*R*)- or (*S*)-BINOL and Me_3Al in hexane: four different oxazoles were involved with various substituted benzaldehydes. The resulting *cis*-2-oxazoline-4-carboxylates were obtained with up to 90% ee.[385,386] It is however worth noting that the catalyst is used in excess (2 equiv) in most examples (Table 56).

Table 56. [3+2] Cycloaddition between 2-Aryl-5-methoxyoxazoles and Aldehydes Catalyzed by the AlMe$_3$/1 System

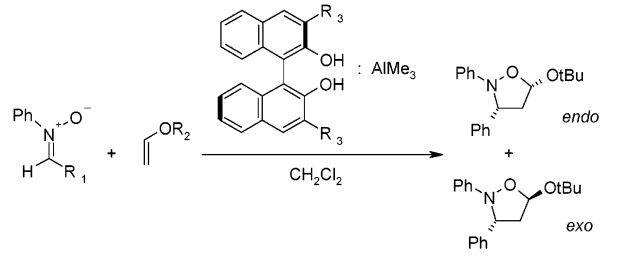


entry	Ar	R	*T* (°C)	yield (%)	cis/ trans	cis ee (%)
1	*p*-MeOPh	Ph (1 equiv)	20	40	60/40	90
2	*p*-MeOPh	Ph (3 equiv)	−10	81	92/8	88
3	*p*-MeOPh	*p*-NO_2Ph (3 equiv)	−10	81	82/18	73
4	p-MeOPh	*p*-ClPh (3 equiv)	−10	93	87/13	51
5	*o*-MeOPh	*p*-ClPh (3 equiv)	5	89	87/13	87
6	*o*-MeOPh	*m*-MePh	5	51	88/12	88
7	*o*-MeOPh	*m*-MeOPh	5	70	87/13	90

4.7.1.2. 1,3-Dipolar Cycloadditions. Among this class of reactions, the 1,3-dipolar cycloaddition between nitrones and alkenes leading to isoxazolidine derivatives is of particular interest. Indeed, these molecules can be converted to 1,3-amino alcohol equivalents under mild conditions. The first attempt to prepare optically active isoxazolidines by means of a chiral catalyst is due to Jorgensen in 1994 who studied the reaction between nitrones and 3-crotyloxazolidinone in the presence of catalytic amounts of various chiral titanium catalysts generated in situ from Ti(O*i*-Pr)$_2$Cl$_2$ and chiral diols.[387,388] Up to 62% ee was obtained with TADDOL, but results with BINOL were disappointing (8% ee). More recently, the same authors studied the formation of isoxazolidines through an inverse electron demand 1,3-dipolar cycloaddition between aromatic nitrones and vinyl ethers under catalysis of different BINOL–AlMe complexes. Although the ee remained very low (<5%) with parent BINOL, up to 97% was obtained with 3,3′-bisphenyl-BINOL (Table 57).[389]

Isoxazolidines can also be prepared diastereo- and enantioselectively in the presence of chiral lanthanide catalysts. Indeed, Kobayashi, as part of his exploration of the potentialities of lanthanide triflates as Lewis acids, discovered a heterochiral catalyst that combines the chirality of BINOL and of an amine, (*R*)-methyl-bis[1-(1-naphthyl)ethyl]amine ((*R*)-MNEA) **235**, and leads to an excellent *endo*/*exo* ratio and up to 96% ee (Table 58).[390,391]

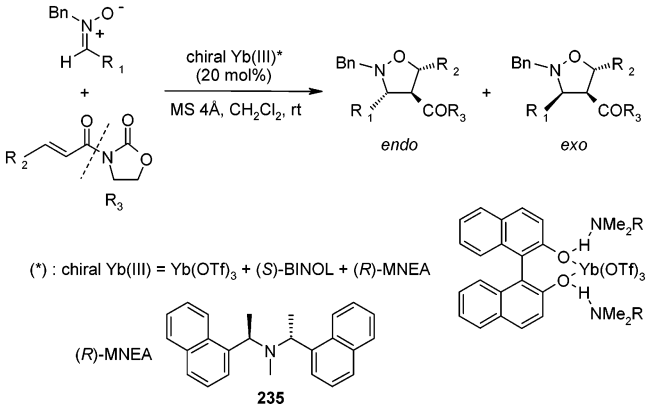
Table 57. 1,3-Dipolar Cycloaddition between Nitrones and Alkenes Catalyzed by the $AlMe_3$/1 System



entry	R_1	R_2	R_3	catal (mol %)	yield (%)	*endo*/*exo*	*endo* ee (%)
1	Ph	*t*-Bu	H	20	90[a]	27/73	<5
2	Ph	*t*-Bu	Ph	20	95[a]	95/5	89
3	*p*-ClPh	*t*-Bu	Ph	10	74	83/17	78
4	*p*-ClPh	Et	Ph	10	66	95/5	97

[a] Conversion.

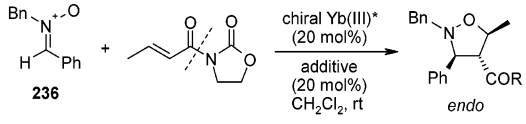
Table 58. Preparation of Isoxazolidines Using $Yb(OTf)_3$/1/MNEA Catalyst



entry	R_1	R_2	yield (%)	*endo*/*exo*	*endo* ee (%)
1	Ph	Me	92	99/1	96
2	*p*-ClPh	Me	93	99/1	92
3	2-furyl	Me	89	95/5	89
4	Ph	H	91	>99/1	79
5	Et	Me	88	53/47	96

Later the same authors reported that molecular sieves 4 Å (MS 4 Å) were essential to secure high enantioselectivity.[392] Suprisingly, the absence of MS led to an inversion of enantioselectivity, which was not the case for the Diels−Alder reaction. In the absence of MS, additives such as NMO, pyridine oxide, or even the starting nitrone **236**, helped to reach ee around 65−83% (Table 59).

Table 59. Influence of the Additives in the Preparation of Isoxazolidines Using $Yb(OTf)_3$/1/MNEA Catalyst

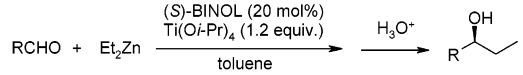


entry	additive	yield (%)	*endo*/*exo*	*endo* ee (%)
1	none	83	98/2	50
2	NMO	68	98/2	81
3	pyridine oxide	78	99/1	65
4	nitrone **236**	90	99/1	83

4.7.2. Addition of Dialkylzinc and Trialkylaluminium to Aldehydes and Ketones

Nakai[393] and Chan[394] independently reported in 1997 the asymmetric alkylation of aldehydes with diethylzinc catalyzed by BINOL−Ti complexes (obtained from (*S*)-BINOL and $Ti(O\textit{i}\text{-}Pr)_4$). Nakai used a large excess of $Ti(O\textit{i}\text{-}Pr)_4$ (vs BINOL) and 3 equiv of Et_2Zn; thus, the typical proportions were $RCHO/Et_2Zn/BINOL/Ti(O\textit{i}\text{-}Pr)_4$ = 1:3:0.2:1.2 (Table 5) (Table 60). It is noteworthy that structures of binolate titanium complexes as well as mechanistic studies of the asymmetric addition of alkyl groups to aldehydes have been reported by Walsh et al.[395−397]

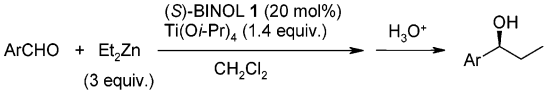
Table 60. Addition of Diethylzinc to Aldehydes Catalyzed by the $Ti(O\textit{i}\text{-}Pr)_4$/1 System



entry	R	*T* (°C)	yield (%)	ee (%)
1	n-C_8H_{17}	−30	94	86
2	cyclohexyl	−30	75	85
3	(*E*)-Ph-CH=CH	0	97	82
4	TBS−C≡C−	0	98	79

Chan studied the influence of the BINOL/$Ti(O\textit{i}\text{-}Pr)_4$ ratio and of the temperature on the enantioselectivity of the addition of Et_2Zn on aromatic aldehydes. The conclusions were in agreement with those reported by Nakai (Table 61).

Table 61. Addition of Diethylzinc to Various Aldehydes Catalyzed by the $Ti(O\textit{i}\text{-}Pr)_4$/1 System

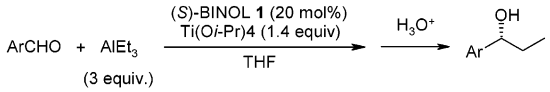


entry	Ar	*T* (°C)	conv (%)	ee (%)
1	Ph	−78	64	96
2	Ph	−20	87	93
3	Ph	0	100	92
4	*m*-MeOPh	0	100	94
5	*p*-FPh	0	100	86
6	*p*-MePh	0	99	88

These authors then established that all ee's were increased if the BINOL−Ti complex was substituted by a H_8-BINOL−Ti catalyst.[398] The same observation was also made during the study of the asymmetric alkylation of aromatic aldehydes with triethylaluminum under titanium catalysis (Table 62).[399]

Finally, the enantioselective addition under Ti catalysis of dimethylzinc and diethylzinc to prostereogenic ketones has been studied by Yus.[400] The best results were obtained with camphorsulfonamide titanium alkoxide derivatives (up to 89% ee). In contrast, BINOL complexes led to poor yields and modest ee (35%).

Table 62. Addition of $AlEt_3$ to Various Aldehydes Catalyzed by the Ti(O*i*-Pr)$_4$/1 System

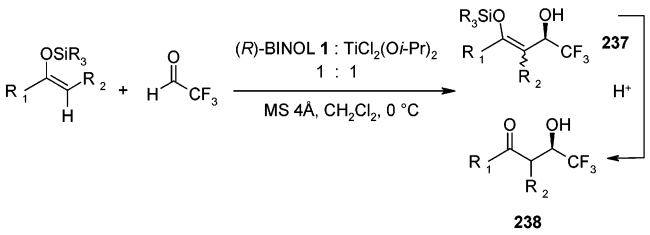


entry	Ar	yield (%)	ee (%) (*R*) with (*S*)-BINOL	ee (%) (*S*) with (*S*)-H_8-BINOL
1	Ph	100	81	96
2	*o*-FPh	82	52	91
3	*o*-ClPh	83	62	91
4	*p*-FPh	90	78	94
5	*p*-ClPh	93	81	90

4.7.3. Friedel–Crafts Reaction

Although the Friedel−Crafts reaction is both one of the oldest Lewis acid-catalyzed reactions and one of the most important carbon−carbon bond-forming reactions in organic synthesis, its application to catalytic asymmetric synthesis has been quite limited. With respect to BINOL, reports are even more recent. Thus, Mikami showed in 1999 that such a reaction was occurring, under Mukaiyama reaction conditions, between fluoral and silyl enol ethers under BINOL−Ti complex catalysis.[401] The Friedel−Crafts product, which was obtained in good yield and high ee (up to 98%), along with the classical aldol adduct, could be further transformed into the latter. This observation led Mikami to propose a Friedel−Crafts mechanism for the Mukaiyama aldol reaction with fluoral (Table 63).

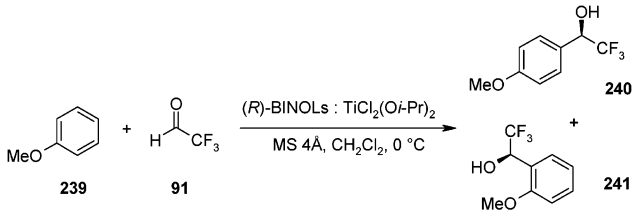
Table 63. Friedel−Crafts Reaction Catalyzed by the TiCl$_2$(O*i*-Pr)$_2$/1 System



entry	SiR_3	R_1	R_2	catal (%)	yield (%) **237** (*e*/*z*)	(*Z*) ee (%)	yield (%) **238**
1	$SiMe_2$*t*-Bu	Ph	H	5	67 (1/5)	98	14
2	Si(*i*-Pr)$_3$	Ph	H	1	90 (1/5)	96	4
3	$SiMe_2$*t*-Bu	*p*-MePh	Me	20	77 (1/6)	94	10
4	$SiMe_2$*t*-Bu	*p*-MeOPh	Me	20	68 (1/5)	95	22

A few years latter, the same group extended the reaction of fluoral to aromatic substrates.[402] The sense of asymmetric induction was identical to the one observed in BINOL−Ti-catalyzed carbonyl−ene or Mukaiyama reactions. Although the ee's were not improved by using a H_8-BINOL−Ti complex, they could be enhanced with a 6,6′-Br_2-BINOL−Ti complex (Table 64).

Table 64. Reaction of Fluoral to Aromatic Substrates Catalyzed by TiCl$_2$(O*i*-Pr)$_2$/1 System

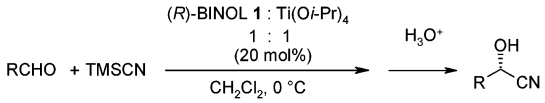


entry	ligand	catal (%)	yield (%)	**240**/**241**	**240** ee (%)
1	(*R*)-BINOL	30	82	4/1	73
2	(*R*)-H_8−-BINOL	5	11	4/1	22
3	(*R*)-6,6′-Br_2-BINOL	5	94	4/1	84

4.7.4. Addition of Trimethylsilyl Cyanide to Carbonyl Compounds and Imines (Strecker Reaction)

Nakai studied the addition of trimethylsilyl cyanide to aldehydes and imines under BINOL−Ti(O*i*-Pr)$_2$ catalysis.[403,404] Good results were obtained with aliphatic aldehydes (up to 75% ee) when the reaction was carried out in CH_2Cl_2 at 0 °C, while ee's were disappointingly low with aromatic aldehydes (<10%) and an aromatic imine (30%) (Table 65).

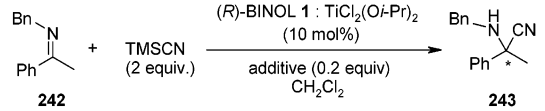
Table 65. Enantioselective Addition of Trimethylsilyl Cyanide to Aldehydes Catalyzed by the Ti(O*i*-Pr)$_4$/1 System



entry	R	yield (%)	ee (%)
1	*n*-C_8H_{17}	92	72
2	*t*-Bu	>90	75
3	Et	>90	<10
4	Ph	>90	<10
5	*p*-MeOPh	>90	<10

^{1}H NMR experiments led the authors to propose that the active catalyst in this reaction is a BINOL−Ti(CN)$_2$ complex. In 2000, Vallée reported the condensation of TMSCN on ketimines under TADDOL− and BINOL−Ti complex catalysis in the presence of various activators (diols, ethers, amines).[405] The best result was obtained with BINOL−Ti(O*i*-Pr)$_2$ as catalyst (10 mol %) and tetramethylethylenediamine (TMEDA) as activator (20 mol %) (Table 66).

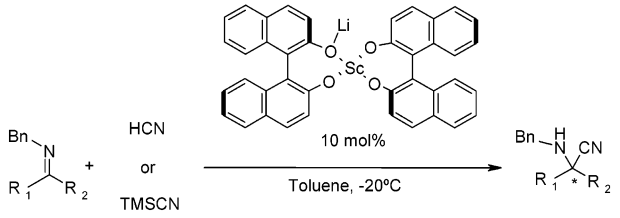
Table 66. Enantioselective Addition of Trimethylsilyl Cyanide to Imines Catalyzed by the TiCl$_2$(O*i*-Pr)$_2$/1 System



entry	additive	conv (%)	ee (%)
1	(*R*)-BINOL	80	33
2	Et_2O	85	37
3	TMEDA	80	56
4	Et_3N	66	50

The same group improved this system preparing a new chiral heterobimetallic complex Sc(BINOL)$_2$Li affording the expected cyanohydrins in good yields and high ee's (Table 67).[406]

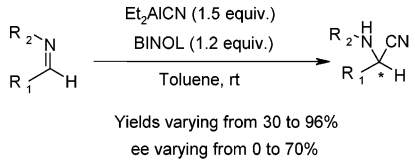
Table 67. Enantioselective Addition of TMSCN or HCN to Imines Using Sc(BINOL)$_2$Li Catalyst



entry	XCN	R_1	R_2	conv (%)	ee (%)
1	TMSCN	Ph	Me	95	88
2	HCN	Ph	Me	95	81
3	TMSCN	β-naphthyl	H	45	65
4	HCN	β-naphthyl	H	80	86

Very recently, an enantioselective Strecker-type reaction of imines with Et$_2$AlCN in the presence of chiral additives such as BINOL has been examined by Toru et al. The enantioselectivity varied depending on the substituents of the imino group as well as the chiral additives used. Thus, α-aminonitriles were obtained in good yields with good enantioselectivities of up to 70% ee in the reaction of *N*-benzylidenebenzhydrylamine with Et$_2$AlCN and BINOL (Scheme 78).[407]

Scheme 78

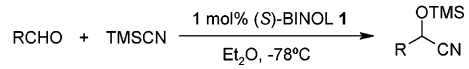


Kagan and Holmes have investigated the addition of TMSCN to aldehydes catalyzed by lithium salts of chiral phenols. Taking advantage of the propensity of silicon to form strongly Lewis acidic complexes with valences of 5 and 6, templated asymmetric additions have been performed. This process is of note because it removes the need for a transition metal, using the metalloid silicon inherent in the reaction, instead. (*S*)-(−)-BINOL **1** has been identified as a precursor to active enantioselective catalysts which, after optimization of the reaction conditions, were used to convert a range of aldehydes to their corresponding cyanohydrins with ee's of up to 56% (Table 68).[408]

While this procedure is interesting from a mechanistic point of view, the highly exothermic nature of the reaction and the poor substrate tolerance render it currently only of academic interest. Also, it is unclear whether hypervalent silicon intermediates are responsible for the observed reactions or whether lithium is acting as a Lewis acid.

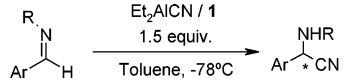
Recently, a new approach to enantioselective cyanation of imines with Et$_2$AlCN in the presence of various chiral additives has been examined. The enantioselectivity varied depending on the substituents of the imino group as well as the chiral additives used. Thus, α-aminotriles were obtained in good yields with good enantioselectivities of up to 70% ee in the reaction of *N*-benzylidenebenzhydrylamine with Et$_2$AlCN and BINOL **1** (Table 69).[409]

Table 68. Enantioselective Addition of TMSCN to Aldehydes Using Hypervalent Silicon Species



entry	aldehyde	yield (%)	ee (%)
1	benzaldehyde	96	56 (*S*)
2	*p*-anisaldehyde	95	54 (*S*)
3	cyclohexanecarbaldehyde	94	30 (*S*)
4	pivaldehyde	62	26 (*S*)

Table 69. Enantioselective Cyanation of Imines with Et$_2$AlCN in the Presence of BINOL 1 as Chiral Additive

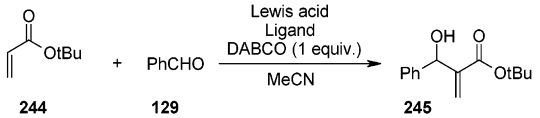


entry	Ar	R	yield (%)	ee (%)
1	Ph	Ph	96	61
2	Ph	Flu	93	22
3	Ph	Ph_2CH	98	70
4	1-Naph	Ph_2CH	99	70
5	*p*-ClC_6H_4	Ph_2CH	99	64

4.7.5. Baylis–Hillman Reaction

The Baylis−Hillman reaction (reaction between an unsaturated ester and an aldehyde catalyzed by 1,4-diazabicyclo[2.2.2]octane (DABCO), for example) is useful in organic synthesis but suffers from low reaction rates. Aggarwal investigated the Lewis acid catalysis of the reaction and found that the use of lanthanide triflates (5 mol %) induced a significant rate acceleration (4.5−5-fold).[410−412] Noteworthy is the fact that more classical Lewis acids, such as BF_3−OEt_2 or $TiCl_4$, induced a decceleration of the reaction presumably because of the formation of a too stable amine−Lewis acid complex. Although this problem is less serious with lanthanide Lewis acids, the authors also established that the addition of ligands would increase the rate of the reaction. Among these ligands, (+)-BINOL (5 mol %) gave one of the largest rate accelerations observed but no

Table 70. Baylis−Hillman Reaction Catalyzed by Different Lewis Acid/1 Systems



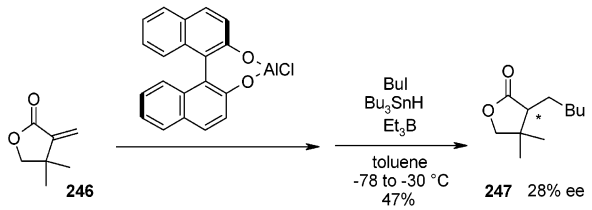
entry	lewis acid (5 mol %)	ligand (5 mol %)	relative rate
1	none	none	1
2	BF_3−OEt_2	none	<0.1
3	$TiCl_4$	none	<0.1
4	Yb(OTf)$_3$	none	3.6
5	La(OTf)$_3$	none	4.7
6	Yb(OTf)$_3$	(*R*)-BINOL	14.4
7	La(OTf)$_3$	(*R*)-BINOL	14.6

significant asymmetric induction (however the authors observed that racemic BINOL had no influence on the rate of the reaction) (Table 70).

4.7.6. Radical Addition and Cyclization

Over the past decade remarkable progress has been made on the stereoselectivities of radical carbon−carbon bond formation, and Lewis acids have played an important role via the formation of chelates that induce facial differentiation.[413−416] Examples in which the Lewis acid has also a radical acceptor activation role are more rare. The first paper on the topic is due to Sato who studied the Lewis acid-enhanced reactivity of α,β-unsaturated ester and amide toward radical addition.[417] In the same paper, the authors also reported the first example of asymmetric radical addition controlled by a chiral BINOL−Al Lewis acid (Scheme 79).

Scheme 79

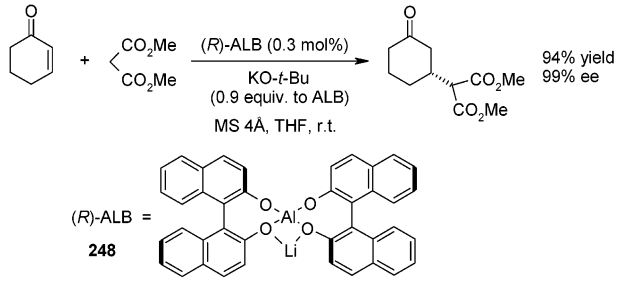


Nishida then studied the influence of chiral Lewis acids prepared from various BINOLs and trimethylaluminum, on a 5-exo-trig radical cyclization. Enantiomeric excesses were poor with (*R*)-BINOL−AlMe (2%) and modest with 3,3′-bis(triphenylsilyl)−BINOL−AlMe (36−18%), provided the latter was used in excess (4 equiv).[418]

4.7.7. Catalytic Asymmetric Michael Addition

In 1998, Shibasaki et al. described the use of a heterobimetallic asymmetric complex as catalyst in a Michael addition reaction. Thus, Albis(binaphthoxide) complex (ALB) was the most effective catalyst in the presence of 1 equiv of base such as BuLi or KO-*t*-Bu, which accelerates the reaction rate (Scheme 80).[419−421]

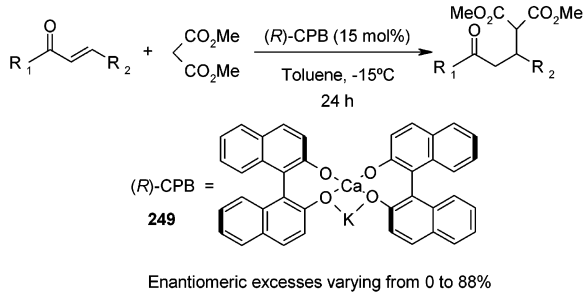
Scheme 80



Immobilization of this multifunctional catalyst on an insoluble polymer led to similar results in terms of enantioselectivity (88% ee instead of 99% ee in the homogeneous case). Nevertheless, in this case easy separation, reusability, stability, and less toxicity of immobilized species may be noticed.[422] It is noteworthy that this reaction has been also performed using microwaves with comparable enantioselectivities in a remarkably lesser reaction time.[423]

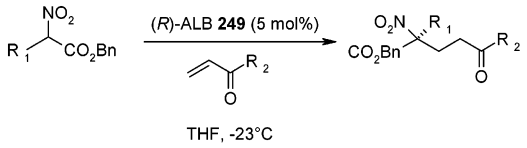
Recently, a new calcium−BINOL catalyst has been developed for asymmetric Michael addition reactions of enones and enals in good yields but with moderate enantioselectivities of up to 87% ee (Scheme 81).[424]

Scheme 81



In the same area, enantioselective Michael additions of α-nitroesters with α,β-unsaturated ketones were carried out in the presence of a catalytic amount of (*R*)-ALB **248**. The enantioselectivity proved to be extremely temperature dependent with a maximum of enantiomeric excess obtained at −23 °C. Numerous examples have been investigated with enantiomeric excesses varying from 5% to 80% ee depending on the nature of the considered substrates (Table 71).[425,426]

Table 71. Enantioselective Michael Additions of α-Nitroesters with α,β-Unsaturated Ketones

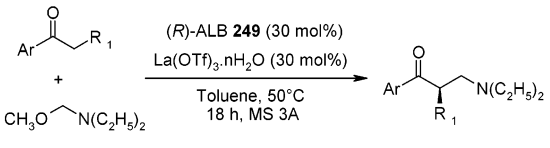


entry	R_1	R_2	yield (%)	ee (%)
1	Me	Me	81	80
2	Me	Et	86	55
3	Et	Et	84	33
4	Me	Ph	86	5
5	Me	OEt	<5	<5

4.7.8. Catalytic Asymmetric Mannich-Type Reaction

Using the same heterobimetallic chiral complex (ALB), Shibasaki et al. achieved the first direct catalytic asymmetric Mannich-type reaction leading to moderate enantiomeric excesses up to 44% ee (Table 72).[427,428]

Table 72. Direct Catalytic Asymmetric Mannich-Type Reaction

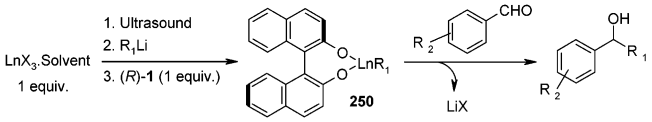


entry	Ar	R_1	yield (%)	ee (%)
1	Ph	Me	65	40
2	Ph	Et	69	34
3	4-anisyl	Me	76	31
4	2-naphthyl	Me	61	44
5	6-MeO-2-naphthyl	Me	69	44

4.7.9. Asymmetric Addition of Alkyl Groups to Aldehydes

In 1993, Greeves et al. reported the use of homochiral organolanthanide (Ln = Ce, Yb) reagents in enantioselective additions of alkyl groups to aldehydes to produce secondary alcohols in moderate to high enantiomeric excesses. The reagents were prepared by reaction of (*R*)-**1** with the desired trialkyllanthanide species, which was generated from 2.8 equiv of alkyllithium and 1 equiv of anhydrous lanthanide(III) chloride or triflate. This stoichiometry was essential to ensure that no unreacted organolithium precursor, which would be detrimental to the enantiomeric excess, was present (Table 73).[429−433]

Table 73. Generation of Reagents and Their Reaction with Aromatic Aldehydes

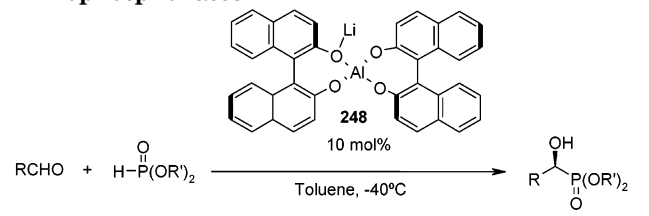


entry	LnX_3	R_1	R_2	yield (%)	ee (%)
1	$Yb(OTf)_3$	*n*-Bu	H	87	33
2	$CeCl_3$	*n*-Bu	4-OMe	87	52
3	$CeCl_3$	Me	4-OMe	75	68
4	$CeCl_3$	Me	4-Cl	53	75
5	$CeCl_3$	*n*-Bu	4-Me	71	85
6	$Ce(OTf)_3$	Me	4-Me	62	57
7	$Yb(OTf)_3$	Me	4-Me	56	65

4.7.10. Synthesis of α-Hydroxy- and Aminophosphonates

$LaLi_3$tris(binaphthoxide) catalyst (LLB), which is prepared from $LaCl_3 \cdot 7H_2O$, (*R*)-BINOL **1** dilithium salt, and NaO-*t*-Bu, is effective for the hydrophosphonylation of various aldehydes.[434−437] Thus, despite all the different catalysts teted, the desired α-hydroxyphosphonates are obtained in up to 95% ee and 88% yield using the Al−Li−BINOL complex (Table 74).[438−440]

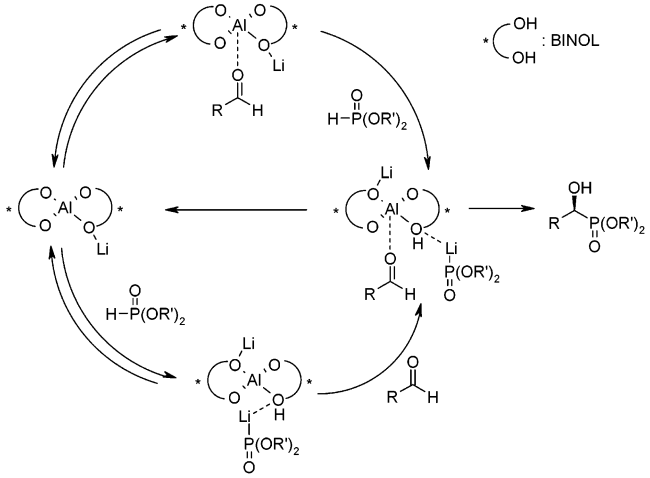
Table 74. Asymmetric Synthesis of α-Hydroxy- and Aminophosphonates



entry	R	R′	yield (%)	ee (%)
1	Ph	Et	39	73
2	Ph	Me	90	85
3	*p*-Cl-Ph	Me	80	83
4	*p*-Me-Ph	Me	82	86
5	*p*-MeO−Ph	Me	88	78
6	(*E*)-PhCH=CH	Me	85	82
7	$(CH_3)_2C$=CH	Me	72	68
8	(*E*)-$CH_3(CH_2)_2CH$=CH	Me	53	55

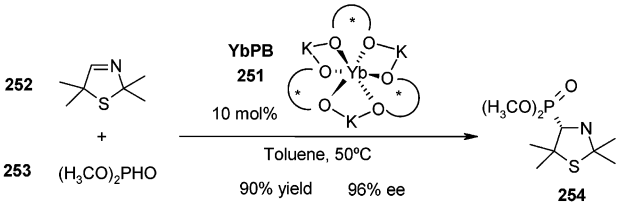
On the basis of numerous experiments, a mechanism involving the activation of both the nucleophile and the electrophile by the heterobimetallic catalyst was proposed (Scheme 82).[441−443]

Scheme 82



As an extension of this work, Shibasaki et al. have described the catalytic and enantioselective hydrophosphonylation of imines using YbPB catalyst. In this area, excellent results have been obtained on cyclic imines with up to 96% ee and up to 90% yield (Scheme 83).[444]

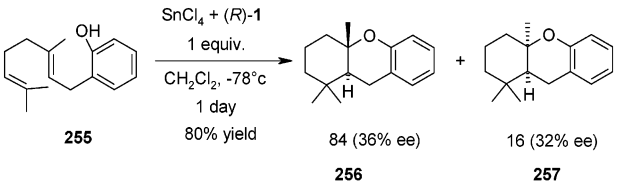
Scheme 83



4.7.11. Enantioselective Cyclization of Polyprenoids

A selective formation of polycyclic terpenoids has been described using the $SnCl_4$−BINOL. Thus, the cyclization occurred in CH_2Cl_2 at −78 °C and afforded the trans-fused tricyclic compound in 67% yield and 36% ee (Scheme 84).[445,446]

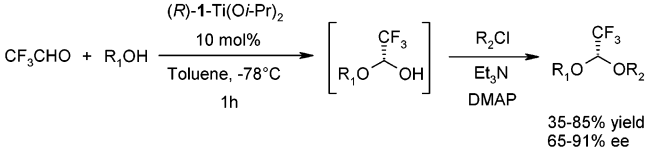
Scheme 84



4.7.12. Asymmetric Synthesis of 1-Alkoxy-2,2,2-trifluoroethanol Derivatives

Reaction of trifluoroacetaldehyde with an alcohol in the presence of a catalytic amount of (*R*)-BINOL−$Ti(O\textit{i}\text{-}Pr)_2$ gives 1-alkoxy-2,2,2-trifluoroethanol with enantiomeric excesses varying from 65% to 91% ee depending on the nature of the substrate (Scheme 85).[447]

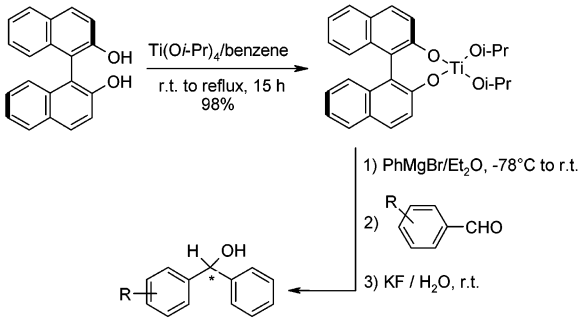
Scheme 85



4.7.13. Asymmetric Synthesis of Substituted Chiral Benzhydrols

On the other hand, a series of substituted chiral benzhydrols were synthesized by reaction of aromatic aldehydes with the chiral intermediates formed from arylmagnesium halides and chiral titanates generated from (*R*)-BINOL **1**. The effect of substituents on the enantioselectivity of the reaction has been studied, and enantiomeric excesses varying from 24% to 100% ee have been encountered (Table 75).[448]

Table 75. Asymmetric Synthesis of Substituted Chiral Benzhydrols

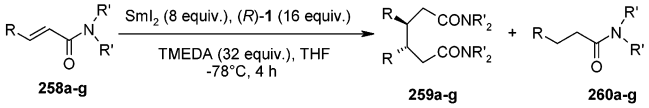


entry	R	yield (%)	ee (%)
1	4-NO_2	73	90
2	3-Br	81	95
3	2,4-di-OMe	83	24
4	4-Cl	57	100

4.7.14. Hydrodimerization of β-Monosubstituted Acrylic Acid Amides

The chiral samarium(II) complex prepared from SmI_2, (*R*)-BINOL **1**, and an achiral tertiary amine promoted the reductive homo-coupling reaction of β-monosubstituted acrylic acid amides **258a**−**g** to give the corresponding 3,4-*trans*-disubstituted adipamides **259a**−**g** with high enantioselectivities (up to 85% ee) (Table 76).[449,450]

Table 76. Hydrodimerization of β-Monosubstituted Acrylic Acid Amides

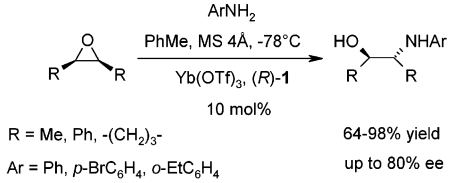


	substrate		product/yield (%)		**259a**−**g**	
entry	R	R′	**259a**−**g**	**260a**−**g**	*dl*/*meso*	ee (%)
1	Me	Bn	70	20	*dl* only	71 (+)
2	Et	Bn	45	42	*dl* only	82 (+)
3	*n*-Pr	Bn	35	46	*dl* only	82 (+)
4	$BnCH_2$	Bn	20	52	*dl* only	85 (+)
5	*i*-Pr	Bn		95		
6	*t*-Bu	Bn		99		
7	Me	Ph	55	44	63:37	44 (−)

4.7.15. Catalytic Enantioselective meso-Epoxide Ring Opening Reaction

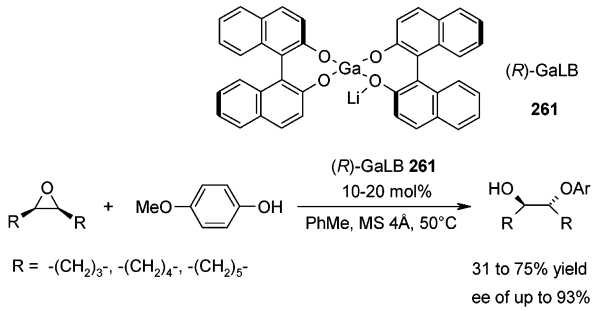
In 1998, Hou et al. reported a simple route to chiral β-amino alcohols by ring opening of *meso*-epoxides catalyzed by $Yb(OTf)_3$ and (*R*)-BINOL **1**. The reaction proceeds smoothly at −78 °C affording the desired amino alcohols in good to high chemical yields and ee up to 80% (Scheme 86).[451,452]

Scheme 86



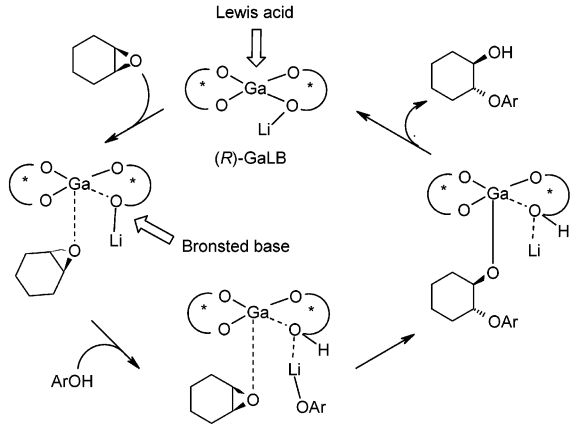
On the other hand, Shibasaki et al. recently described the first catalytic enantioselective *meso*-epoxide ring opening reaction with phenolic oxygen nucleophile promoted by praesidium[453] or gallium heterobimetallic multifunctional complexes such as (*R*)-GaLB **261** (Ga = gallium, L = lithium, B = (*R*)-BINOL).[422,454] Thus, with 10−20 mol % of (*R*)-GaLB catalyst, a variety of epoxides were smoothly cleaved with phenolic oxygen nucleophiles, and the expected products were obtained in enantiomeric excesses varying from 67% to 93% ee and with modest to good yields (31−75%) (Scheme 87).

Scheme 87



On the basis of mechanistic studies of other asymmetric reactions catalyzed by various heterobimetallic complexes, the authors have envisioned that group 13 element Ga could act as a Lewis acid in a similar manner as Al to activate epoxides and lithium binaphthoxide could function as a Bronsted base to activate 4-methoxyphenol (Scheme 88).

Scheme 88

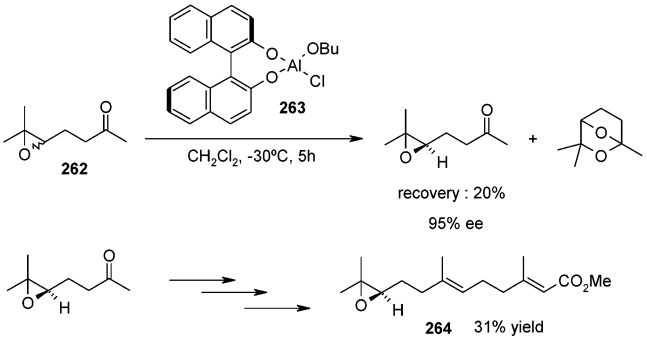


4.7.16. Kinetic Resolution

In 1988, Yamamoto et al. reported for the first time the use of chiral organoaluminum reagent **263** as a

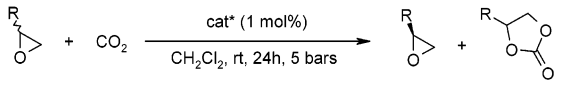
catalyst to resolve simple ketoepoxides. Thus, the optically pure ketoepoxide **262** was recovered after 80% conversion and was found to be a useful chiral building block for a short asymmetric synthesis of the juvenile hormone **264** in 31% overall yield (Scheme 89).[455,456]

Scheme 89



More recently, the kinetic resolution of oxiranes by use of chiral Lewis acids has been described proceeding with moderate enantioselectivities up to 39% in the insertion of CO_2 (Table 77).[457,458]

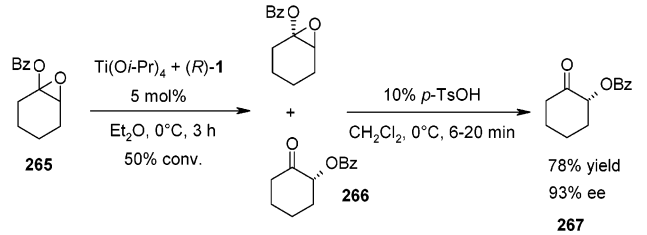
Table 77. Kinetic Resolution of Oxiranes Using Various Lewis Acid/1 Catalysts



entry	R	catalyst	sel (%)	conv (%)	ee (%)	*s*
1	CH_2Cl	Ti(O*i*-Pr)$_4$/BINOL	98	48	17	1.7
2	CH_2Cl	$CpTiCl_3$/Li_2binolate	100	22	9	2.3
3	CH_2Cl	Zr(O*t*-Bu)$_4$/BINOL	100	20	10	2.5
4	Ph	Ti(O*i*-Pr)$_4$/BINOL	83	41	24	2.6
5	Ph	$CpZrCl_3$/Li_2binolate	97	66	27	1.5

Kinetic resolution of racemic enol ester epoxides catalyzed by (*R*)-**1**/Ti(O*i*-Pr)$_4$ has been achieved by Shi et al.[459−461] High resolution efficiency was obtained for a number of cyclic systems. Both enantiomerically enriched enol ester epoxides and α-acyloxy ketones were obtained through this resolution. Thus, a racemic enol ester epoxide can be completely converted into an enantiomerically enriched α-acyloxy ketone by sequential treatment with a catalytic amount of a chiral Lewis acid and a catalytic amount of an achiral acid (Scheme 90).

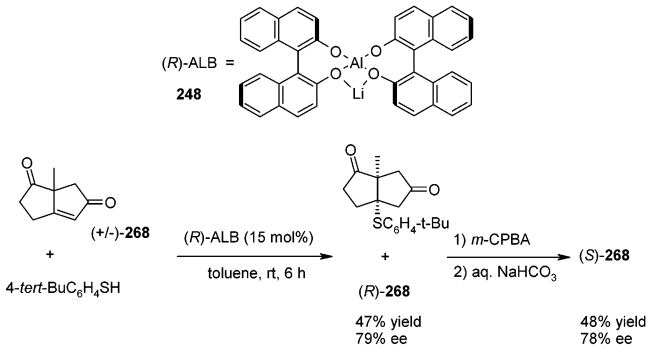
Scheme 90



Numerous examples have been reported with enantioselectivities varying from 38% to 93% ee and excellent chemical yields. As an extension of such a study, Tu et al. have investigated a new method for the enantioselective preparation of β-hydroxy ketones containing a stereogenic quaternary carbon center and tertiary α-hydroxy epoxides. Although the maximum possible yield is 30−40%, the method uses easily accessible racemic starting materials, and conversion levels can be manipulated so that completely enantiopure samples of substrate enantiomers are obtained with enantiomeric excesses of up to 60%.[462]

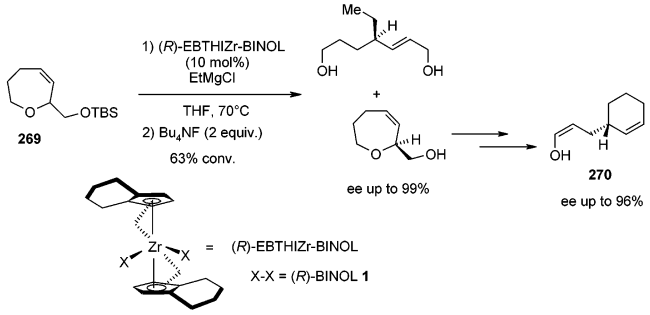
The kinetic resolution of racemic 5-methylbicyclo-[3.3.0]oct-1-ene-3,3-dione catalyzed by AlLibis(*R*)-BINOL with Michael addition of 4-*tert*-butyl(thiophenol) has been developed leading to the two enantiomers (*R*)-**268** and (*S*)-**268** in enantiomeric excesses up to 79% ee (Scheme 91).[463,464]

Scheme 91



Recently, Hoveyda et al. reported that various medium-ring heterocycles bearing a C2-substituent that contains an accessible Lewis basic heteroatom may react with Grignard reagents with high levels of regio- and stereochemical control. The key substrates were prepared enantiomerically pure through the Zr-catalyzed kinetic resolution (Scheme 92).[465]

Scheme 92

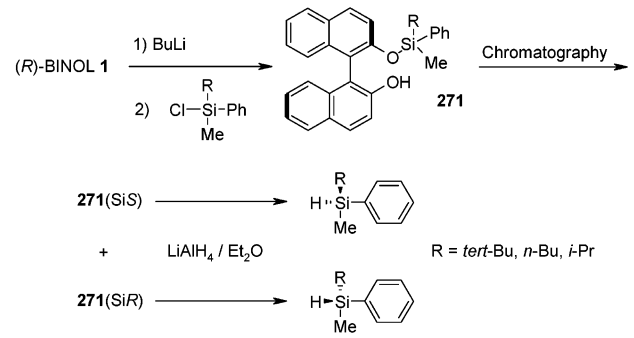


4.7.17. Synthesis of Silane Derivatives and Use of Chiral Proton Donor Reagents

Recently, Asztemborska et al. have performed the resolution of chiral silanes from the corresponding racemic silyl chlorides via diastereomeric derivatives **271** (Scheme 93).[466]

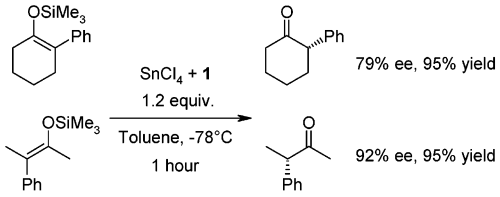
Enantioselective protonation of prochiral enol derivatives is a very simple and attractive route for the preparation of optically active carbonyl compounds.[467] In 1994, Yamamoto et al. reported a new Lewis acid-assisted chiral Bronsted acid for enantioselective protonation of prochiral silyl enol ethers and ketene

Scheme 93



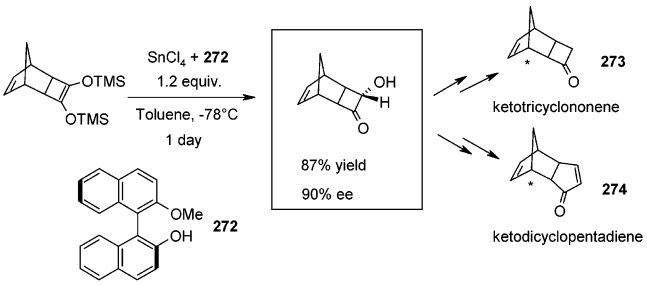
bis(trialkylsilyl)acetals with high enantioselectivities and in quantitative yield (Scheme 94).[468,469]

Scheme 94



In the same area, an asymmetric protonation of a *meso*-1,2-enediol bis(trimethylsilyl)ether using an (*S*)-BINOL monomethyl ether **272**−$SnCl_4$ complex has been described by Ogasawara et al. to realize an alternative route to chiral (−)-ketodicyclopentadiene and (−)-ketotricyclononene (Scheme 95).[470]

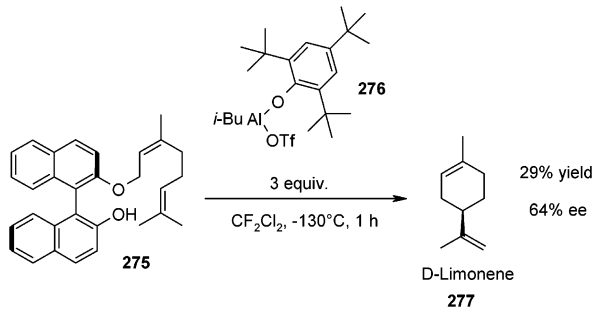
Scheme 95



4.7.18. Use of BINOL as Chiral Auxiliary

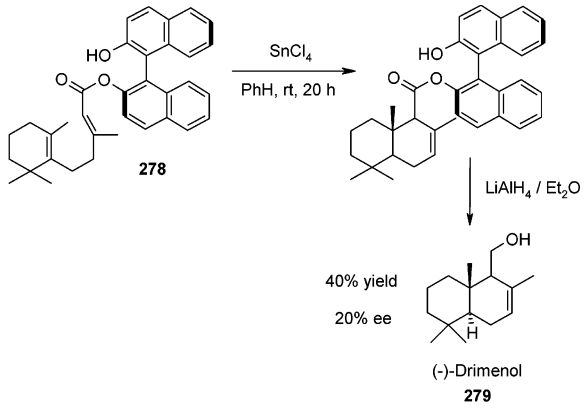
(*R*)-BINOL **1** has been used as chiral leaving group for the asymmetric synthesis of monocyclic terpenes such as limonene. Whatever the experimental conditions, low yields (29% yield) and moderate enantiomeric excesses up to 64% ee were reached (Scheme 96).[173−176]

Scheme 96



A similar approach has been developed by Lee et al. for the asymmetric synthesis of (−)-drimenol (Scheme 97). In this case, use of (*R*)-BINOL **1** in the

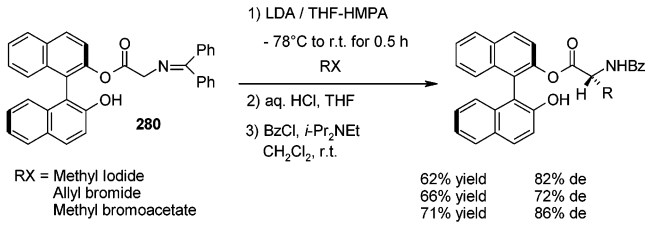
Scheme 97



acid-catalyzed cyclization of monocyclofarnesate resulted in low chiral induction, (20% ee).[471]

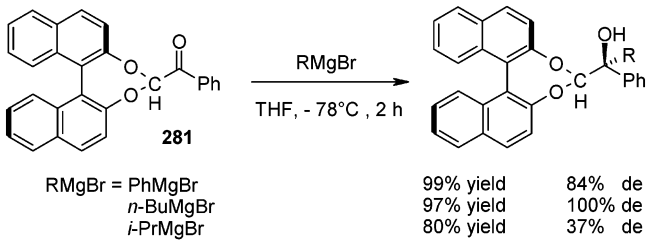
In another context, the preparation of a variety of enantiomerically pure uncommon α-amino acids by alkylation of chiral glycine derivatives possessing axially chiral BINOL as an auxiliary has been depicted by Fuji et al. Thus, depending on the nature of the electrophile, enantiomeric excesses varying from 69% to 86% ee were obtained (Scheme 98).[472]

Scheme 98



Arylglyoxals, protected at the aldehyde function with (*R*)-BINOL **1** and readily prepared by direct nucleophilic substitution of BINOL-salt on dibromoacetophenone, react diastereoselectively with Grignard reagents to afford protected atrolactaldehyde and related compounds in high yields (Scheme 99).[473]

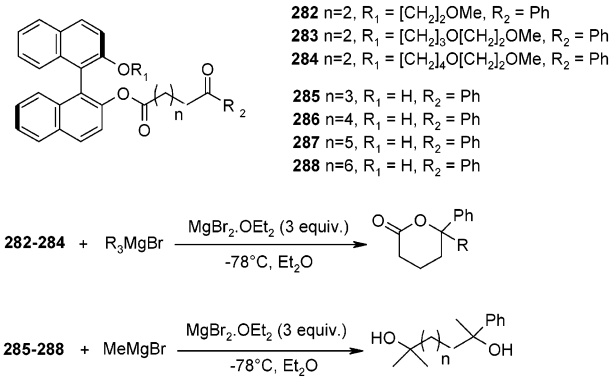
Scheme 99



On the other hand, Tamai et al. have widely studied 1,8 to 1,12-asymmetric induction in Grignard reactions of ω-keto esters. Thus, efficient diastereoselective alkylation of δ- and ϵ-keto acids with Grignard reagents was achieved in up to 97% enantiomeric excess by conversion into the 2′-[3-(2-methoxyethoxy)propoxyl]-(1,1′-binaphthyl)-2-ol esters, while the corresponding alkylation of ζ- to θ-keto acids

could effectively be carried out in up to 88% ee (Table 78).[474,475]

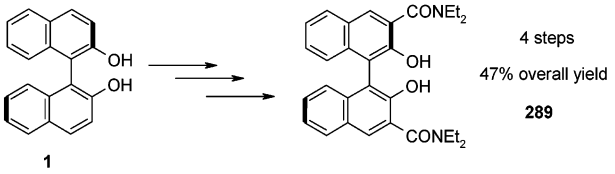
Table 78. Diastereoselective Alkylation of δ- and ϵ-Keto Acids with Grignard Reagents



entry	substrate	R_3MgBr	yield (%)	ee (%)
1	**282**	MeMgBr	73	59
2	**283**	MeMgBr	80	93
3	**283**	$C_9H_{19}MgBr$	82	97
4	**284**	MeMgBr	79	74
5	**285**	MeMgBr	91	61
6	**286**	MeMgBr	92	88
7	**287**	MeMgBr	86	85
8	**288**	MeMgBr	88	81

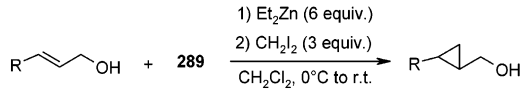
Optically active *N*,*N*,*N*′,*N*′-tetraalkyl-2,2′-dihydroxy-1,1′-binaphthyl-3,3′-dicarboxamides easily prepared from (*R*)-BINOL **1** (Scheme 100) were found to be

Scheme 100



efficient auxiliaries for the asymmetric Simmons–Smith cyclopropanation of allylic alcohols with enantioselectivities up to 94% ee (Table 79).[476,477]

Table 79. Asymmetric Simmons–Smith Cyclopropanation of Allylic Alcohols



entry	R	yield (%)	ee (%)
1	Ph	44	92
2	*p*-MeOPh	78	94
3	*p*-ClPh	59	90
4	$PhCH_2$–	65	89
5	$TBDPSOCH_2$–	88	88

4.7.19. Synthesis of Chiral Organophosphorus Ligands from BINOL

A wide variety of chiral organophosphorus ligands, such as BINAP, have been developed from BINOL **1** and sucessfully used in numerous asymmetric reactions. Nevertheless, this point will not be discussed here since it is beyond the scope of the present review and would deserve a coverage of its own.[478]

5. References

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