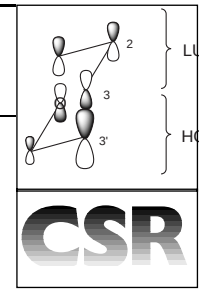
Asymmetric Claisen rearrangement



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Development of the asymmetric Claisen rearrangement is one of the challenging tasks in synthetic organic chemistry. There have been numerous reports of the asymmetric Claisen rearrangement based on the intramolecular chirality transfer using chiral substrates. On the other hand, reactions of achiral substrates with an external chiral activator have been studied during the last decade. In this review article, recent advances in the asymmetric Claisen rearrangement are described.

1 Introduction

Recent advances of asymmetric reactions in synthetic organic chemistry have been well documented and excellent enantioselective reactions successfully established. Among these, epoxidation of allylic alcohols, dihydroxylation of a carbon–carbon double bond, hydrogenation of multiple bonds (C=C, C=O, and C=N) and carbon–carbon bond forming reactions through the addition of organometallics to a carbonyl functionality are the typical reactions in which a high level of asymmetric catalysis has been realized.[1] The Claisen rearrangement has been one of the most useful tools for the formation of carbon–carbon bonds.[2] Since the discovery by Claisen in 1912, development of the Claisen rearrangement, the [3,3] sigmatropic rearrangement of allyl vinyl ethers which now involves a variety of modified variants, has made this reaction widely applicable to the synthesis of organic molecules, in particular to natural product synthesis.[3,4] An extension of the Claisen rearrangement to an asymmetric version is, however, a challenging task. The asymmetric Claisen rearrangement can be classified into two types: a diastereoselective reaction or an enantioselective reaction (Scheme 1). The diastereoselective Claisen rearrangement of a substrate having a chiral center has been extensively studied. Although the substrate can have a chiral center at the 1-position in the rearrangement system or at any other position near to the rearrangement system, usually a chiral center at the 1-position is quite efficient for the intramolecular chirality transfer and such a rearrangement system can be constructed by using a chiral secondary or tertiary allylic alcohol. These chiral alcohols are available in enantiomerically enriched forms, for example, by asymmetric reduction of an α,β-unsaturated carbonyl compound, kinetic resolution of a racemic alcohol by using the Sharpless epoxidation, and by addition of a vinylmetal to a chiral carbonyl compound. While this type of internal chirality transfer reaction has been successfully employed for the total synthesis of natural products, this extensive literature will not be discussed here.

Asymmetric induction based on the incorporation and subsequent cleavage of a chiral auxiliary within an otherwise achiral substrate may be regarded as a second group of diastereoselective Claisen rearrangements. As an alternative, a chiral auxiliary may be temporarily incorporated on the achiral substrate not only to induce a chirality transfer but also to activate the reaction. In such a system, the chiral auxiliary can be detached from the product so readily, for example by simple workup procedure, that this process does not involve formal introduction and removal of the chiral auxiliary. The most advanced variant of this concept is the enantioselective reaction involving a chiral Lewis acid as mediator. An enantioselective reaction employing a catalytic amount of chiral Lewis acid has

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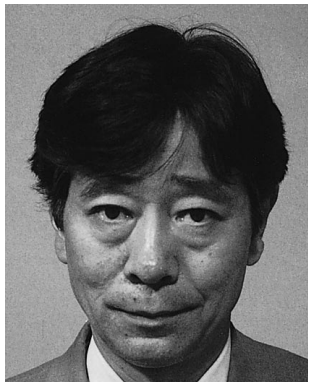

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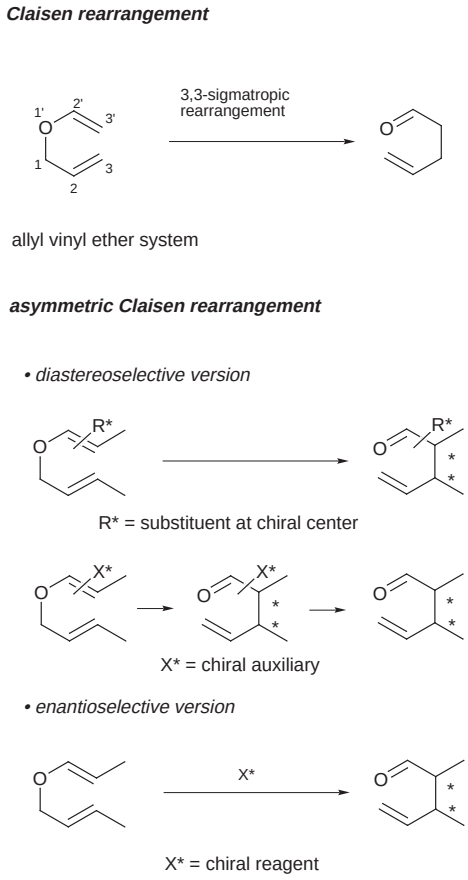


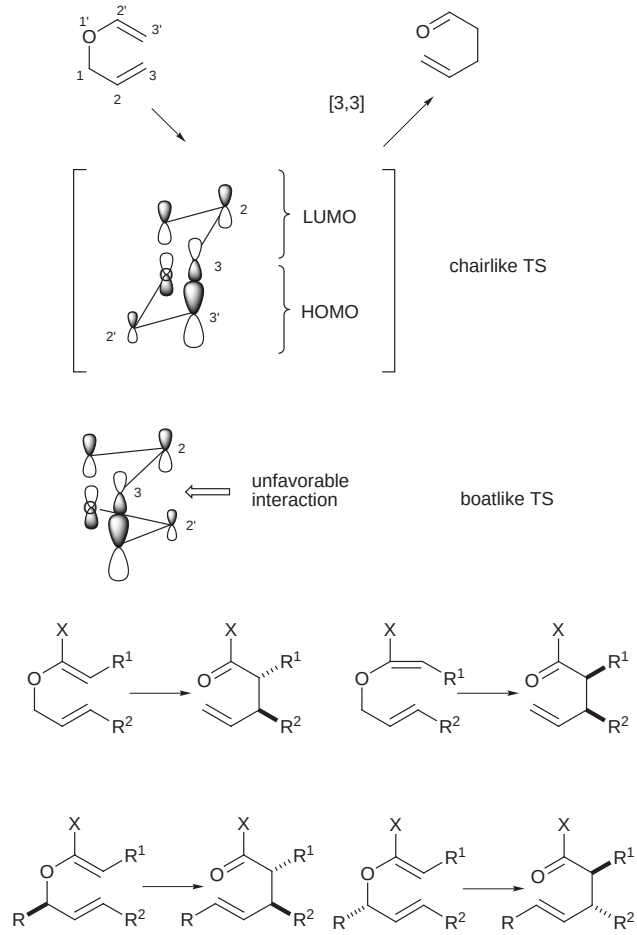
Scheme 1

not, however, been reported, because the resulting carbonyl group in the product shows a higher Lewis basicity than the ethereal oxygen in the substrate. That is, the Lewis acid coordinates to the product more tightly than to the starting material. We will review here recent advances in the asymmetric Claisen rearrangement of allyl vinyl ether derivatives. Regarding the aza- and thia-Claisen rearrangements, readers are recommended to see a recent review by Enders *et al*.[5]

The Claisen rearrangement of the parent substrate, allyl vinyl ether, is a symmetry-allowed and concerted pericyclic reaction involving a suprafacial pathway which proceeds through a high preference for a chairlike transition state. In the boatlike transition state, an anti-bonding interaction between $LUMO_{C(2)}$ and $HOMO_{C(2')}$ makes it an unfavorable pathway. Introduction of a substituent onto the carbon chain of the rearrangement system is possible at every position resulting in different effects involving the reactivity and the stereochemical outcome of the rearranged products. In the Claisen rearrangement, in particular those of acyclic systems, the relative stereochemistry (*syn*/*anti*) at the newly formed adjacent chiral centers is highly controlled by the geometry of the double bonds (*E*/*Z*) when substituted at the 3- and 3'-positions. If the substrate is a chiral molecule due to a substituent at the 1-position, this chirality can be transferred to the 3- and/or 3'-position through the highly ordered transition state. These variations are illustrated in Scheme 2 in those cases where the rearrangement proceeds *via* a chairlike transition state.

2 Asymmetric aliphatic Claisen rearrangement

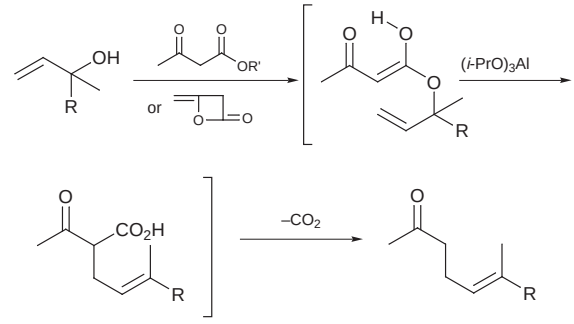
We summarize here the asymmetric aliphatic Claisen rearrangements, the diastereoselective Claisen rearrangements of the substrates having a chiral auxiliary and the enantioselective Claisen rearrangements mediated by chiral reagents.



Scheme 2

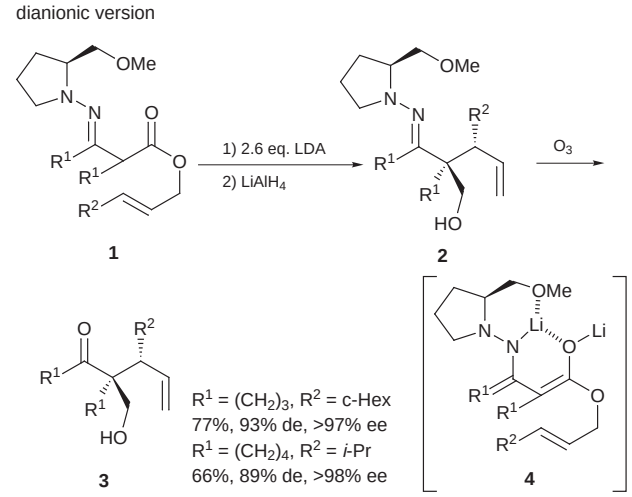
2.1 Asymmetric Carroll rearrangement

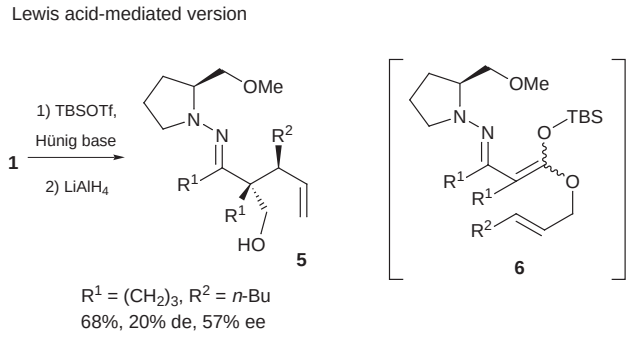
The [3,3]-sigmatropic rearrangement of the allylic ester of a β-keto acid giving rise to a γ,δ-unsaturated ketone *via* decarboxylation of the rearranged β-keto acid is known as the Carroll rearrangement.[3] In particular, this has been an important process in a commercial scale production of geranylacetone and β-ionone (Scheme 3).



Scheme 3

In 1995, Enders *et al*. reported the highly efficient asymmetric Carroll rearrangement to generate a chiral quaternary carbon by employing (*S*)- or (*R*)-1-amino-2-methoxymethylpyrrolidine (SAMP or RAMP, respectively) as a chiral auxiliary (Scheme 4).[6,7] The SAMP (or RAMP) hydrazone **1** is readily prepared by treating the allylic ester of a β-keto acid with SAMP in the presence of toluenesulfonic acid. A good chirality transfer could be realized in the dianion-mediated rearrangement, which may involve control of the enolate geometry and a conformationally restricted transition state due to the formation of the intramolecularly chelated intermediate **4**. For example, dianions of SAMP hydrazones **1**, generated by treatment with 2.6 equiv.



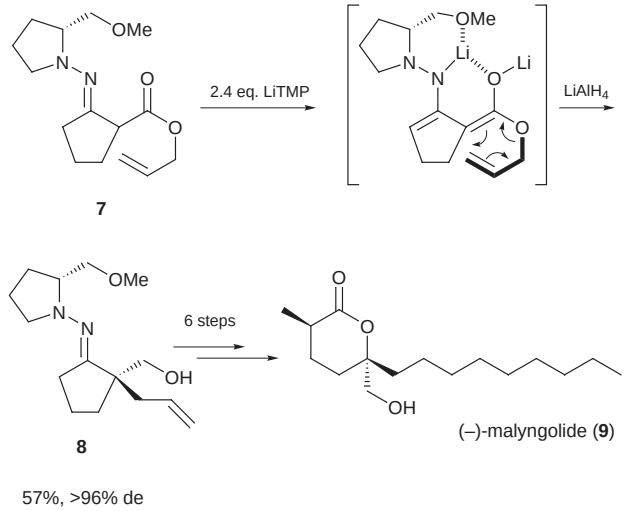


Scheme 4

of LDA at −78 °C in THF–*N*,*N*,*N'*,*N'*-tetramethylethylenediamine, rearranged at room temperature and the following reduction of the rearranged acid with lithium aluminum hydride provided the β-hydroxyhydrazones **2** in good diastereomeric excess (88–98% de, 59–83% yield). β-Hydroxyketones **3** (82 to > 98% ee) were obtained by treating the β-hydroxy hydrazones **2** with ozone.

The Carroll rearrangement of SAMP hydrazones **1** *via* their silyl ketene acetals **6** also proceeded at room temperature in the presence of a Lewis acid, such as *tert*-butyldimethylsilyl triflate (TBSOTf), while this process showed low diastereoselectivity and low asymmetric induction. Thus, a mixture of the SAMP hydrazones **1**, 1.3 equiv. of TBSOTf and 1.5 equiv. of Hünig base was allowed to react at room temperature leading to the rearranged products which, in turn, reacted with lithium aluminum hydride to give β-hydroxy hydrazones **5** as a mixture of the four possible diastereomers in moderate selectivity. Interestingly, the major diastereomer had the opposite configuration at the newly formed chiral center to that from the dianion-mediated reaction.

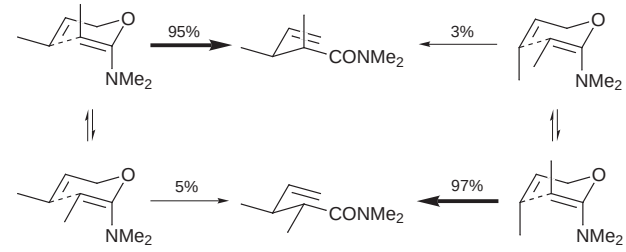
Enders has also applied this process to the total synthesis of (−)-malyngolide (**9**) (Scheme 5)[8] using the dianionic asymmetric Carroll rearrangement as a key step. Upon treatment of the RAMP hydrazone **7** with 2.4 equiv. of lithium 2,2,6,6-tetramethylpiperidide (LiTMP), the rearrangement proceeded smoothly and the following reduction with lithium aluminum hydride gave the β-hydroxy hydrazone **8** with high diastereoselectivity (> 96% de) in moderate yield (57%), which was converted in 6 steps to (−)-malyngolide (**9**) (96% ee).



Scheme 5

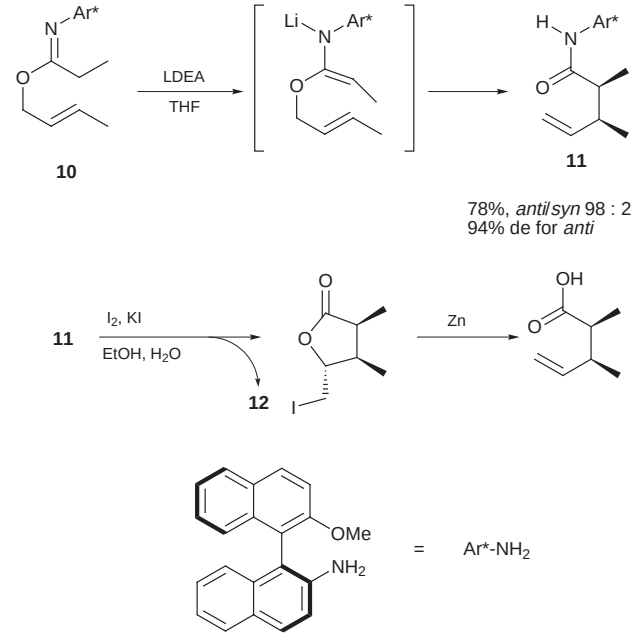
2.2 Asymmetric Eschenmoser–Claisen rearrangement

The [3,3]-sigmatropic rearrangement of ketene *N*,*O*-acetals, first developed by Eshenmoser,[3] involves several variants to generate the rearrangement precursors, such as the reaction of an allylic alcohol with an ynamine or the dimethyl acetal of an *N*,*N*-dimethyl carboxamide. The stereochemical outcome of the rearrangement of the dimethyl acetal of an *N*,*N*-dimethylpropionamide with (*E*)- and (*Z*)-crotyl alcohol under thermodynamic conditions was explained by an axial orientation of the C(1)-methyl group of the ketene *N*,*O*-acetal based on the assumption of a chairlike transition state, in which (*Z*)-ketene *N*,*O*-acetals are predominant (Scheme 6).[9,10]



Scheme 6

Metz *et al*. have reported a chiral auxiliary induced imidate Claisen rearrangement, based on an axially chiral binaphthylamine derivative **12** (Scheme 7).[11,12] The requisite

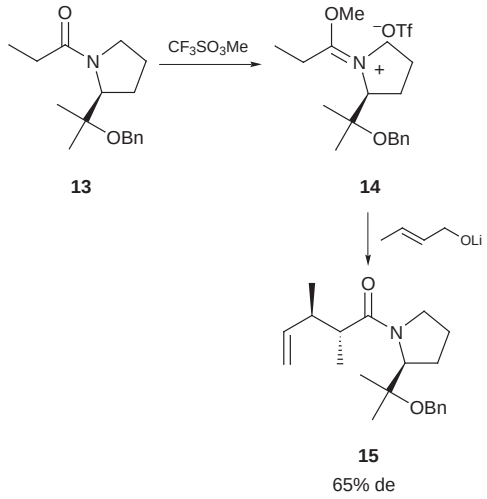


Scheme 7

lithium enolate was prepared by treatment of the imino ether **10** with lithium diethylamide (LDEA). Although the Claisen

rearrangement of the corresponding *N*-TMS azaenol ether did not proceed, the lithium azaenolate rearranged at 0 °C to afford the γ,δ-unsaturated amide **11** with high 2,3-*anti* selectivity (*anti*/*syn*, 98:2) and excellent chiral induction (94% de for the *anti*-isomer). This high selectivity was explained by considering the chairlike transition state, the preferable (*Z*)-configuration of the azaenolate and an efficient chiral environment constructed by the chelation of the methoxy group to lithium atom in the azaenolate intermediate. Conversion of the rearranged amide to carboxylic acid and quantitative recovery of the chiral auxiliary **12** were both efficiently achieved by iodolactonization of the amide **11** followed by the reductive olefination of the iodolactone with zinc powder. During these procedures, no epimerization was observed.

The asymmetric amide acetal Claisen rearrangement using a chiral 2-substituted or 2,5-disubstituted pyrrolidine was reported by Welch *et al*. (Scheme 8).[13] Treatment of the proline-derived *N*-propionyl amide **13** with methyl trifluoromethanesulfonate gave the iminium salt **14**, which was then reacted with lithium alkoxide of allylic alcohols to result directly in the formation of the rearranged amide **15** with moderate chiral induction (65% de). In these reactions, rearrangement proceeded at room temperature in a stereospecific manner with respect to the configuration of the carbon–carbon double bond of the allylic alcohol.



13 **14** **15**

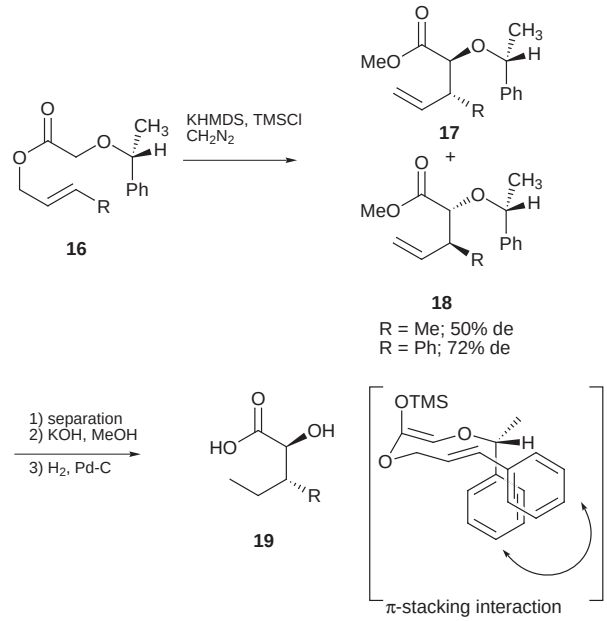
65% de

Scheme 8

2.3 Asymmetric Ireland–Claisen rearrangement

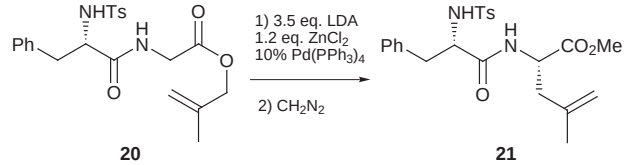
The Ireland–Claisen reaction, the rearrangement of a ketene silyl acetal derived from an allylic ester first reported in 1972, has been widely applied in organic synthesis, in particular to bioactive and natural product synthesis.[3] The versatility of this variant possibly involves the use of a substrate composed of a stoichiometric assembly of allylic alcohol and acid components, relatively low temperature of the rearrangement process, an efficient control of ketene silyl acetal geometry, a highly reliable and predictable transfer of stereochemistry from the starting material to the product through a highly ordered transition state. As for the asymmetric versions, there have been reported a number of examples using substrates having a chiral center in allylic alcohol component, which showed high degree of chirality transfer. Development of new variants of the Ireland–Claisen rearrangement will be focused upon here.

Kallmerten *et al*. reported the diastereoselective asymmetric Ireland–Claisen rearrangement using a chiral phenethyl ether as an auxiliary (Scheme 9).[14] The auxiliary was connected to the α-position of the allylic ester moiety in the substrate **16**. Although the high *syn* selectivity could be achieved, the intramolecular chirality transfer was not so high (R = Me; 50% de, Ph; 72% de). In the case of the substrate having a phenyl group in the allylic moiety, slightly higher diastereoselectivity was rationalized by the π-stacking interaction between both phenyl groups as shown below. Chromatographic separation of the resulting diastereomers **17**, **18** and removal of the chiral auxiliary by hydrogenolysis gave the hydroxy acid **19** with high enantiomeric purity.



Scheme 9

Kazmaier reported the diastereoselective Ireland–Claisen rearrangement of allylic glycinate **20** having an *N*-protected amino acid as a chiral auxiliary (Scheme 10).[15] To achieve control of enolate geometry, the allylic ester **20** was treated with an excess LDA in the presence of a metal salt such as zinc chloride, tin(II) chloride or cobalt(II) chloride to form the chelated enolate. The palladium(0) catalyzed Claisen rearrangement of the chelated enolate proceeded through intermolecular allylic alkylation *via* a π-allylpalladium intermediate to give the dipeptide derivative **21** in 85% yield with moderate diastereoselectivity (65% de).

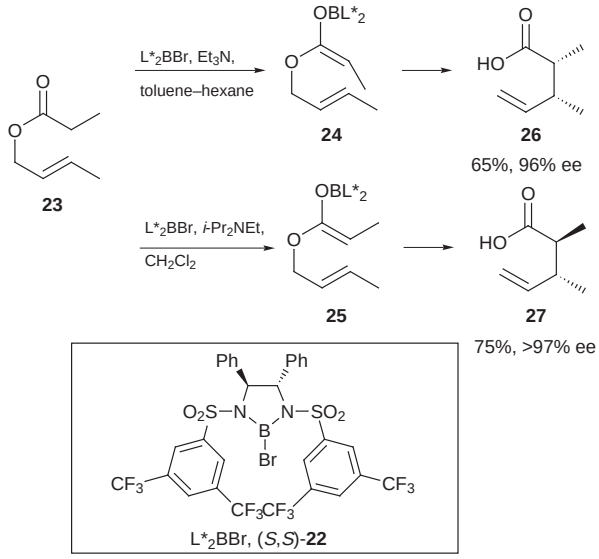


20 **21**

85%, 65% de

Scheme 10

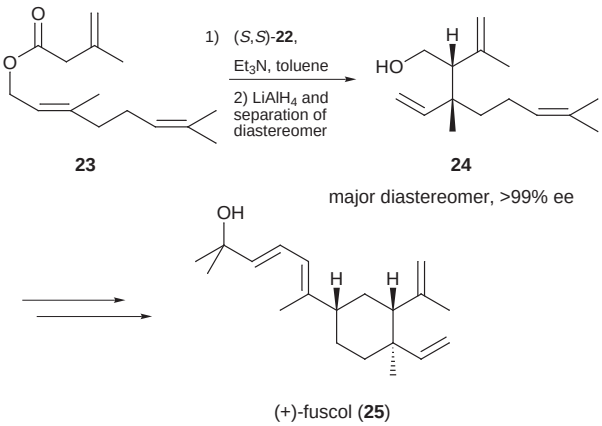
In 1991, Corey and co-workers reported the first enantioselective Ireland–Claisen rearrangement of achiral allylic esters **23**.[16] They employed the chiral boron reagent **22**, which has the C_2-symmetric bissulfonamide, for the formation of a boron enolate within a chiral environment (Scheme 11). It is noteworthy that the geometry of the boron–enolate could be controlled by the choice of tertiary amine and solvent system. Thus, on using triethylamine and a toluene–hexane system, reaction of (*E*)-crotyl propionate **23** with the chiral boron reagent **22** led to the selective formation of (*E*)-enolate **24**, and the following Claisen rearrangement proceeded at −20 °C for 14 days to afford the *anti* isomer **26** with excellent diastereo- and enantioselectivity in 65% yield (96% ee). On the other hand, (*Z*)-enolate **25** could be selectively formed by using diisopropylethylamine in dichloromethane and this rearranged



Scheme 11

to the *syn* isomer **27** in 75% yield (> 97% ee). The high diastereoselectivities (*anti* **26** *vs*. *syn* **27**) are rationalized by the efficient control of the enolate geometry and the preferred chairlike transition state. In the case of allyl propionate, the enantioselectivity of the rearranged product markedly decreased. The chiral bissulfonamide could be easily recovered from the reaction mixture.

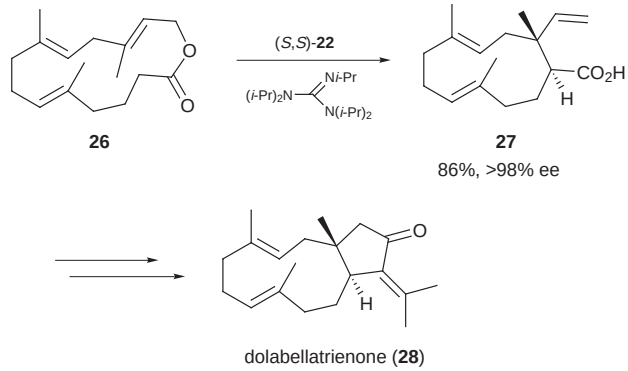
The efficiency of this rearrangement method was further demonstrated by the application to the synthesis of natural products, (+)-fuscol (**25**)[17] and dolabellatrienone (**28**).[18] In the synthesis of fuscol (**25**), the Claisen rearrangement of 3-methylenebutanoic acid geranyl ester (**23**) by using chiral boron reagent (*S*,*S*)-**22** and triethylamine in toluene gave the compound **24** after lithium aluminum hydride reduction of the carboxy group of the rearrangement product (Scheme 12).



Scheme 12

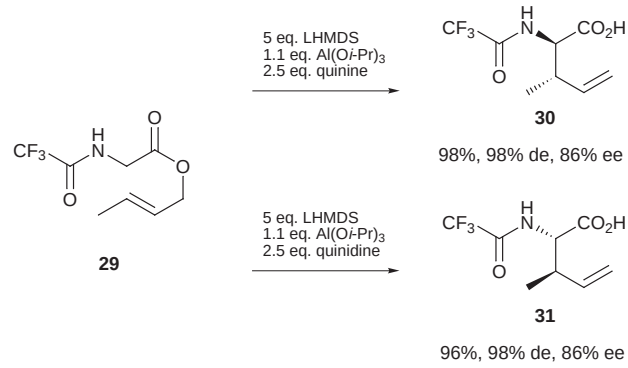
Although the diastereoselectivity was not so high (3 : 1), the enantioselectivity of the major product **24** was excellent (> 99% ee).

The enantioselective synthesis of the marine diterpenoid dolabellatrienone (**28**) was achieved by the rearrangement of the achiral 15-membered lactone **26** leading, *via* a ring contraction, to the stereochemically defined 11-membered carbocyclic acid **27** (Scheme 13).[18] In this reaction, the choice of amine was found to affect the chemical yield of the rearrangement product. Treatment of the lactone **26** with the chiral boron reagent (*S*,*S*)-**22** and pentaisopropylguanidine at −78 °C to form the boron–enolate and the following rearrangement at 4 °C for 48 h gave the acid **27** in excellent diastereo- and enantioselectivity (86% yield, > 96% de, > 98% ee). Construction of the α-isopropylidene cyclopentanone skeleton by several steps led to the first enantioselective synthesis of this diterpene **28**, by which the absolute stereochemistry was unambiguously revised from that previously reported.



Scheme 13

Kazmaier *et al*. described a highly efficient enantioselective Ireland–Claisen rearrangement of the chelated enolate of *N*-trifluoroacetylglycinate **29** in the presence of a chiral bidentate ligand (Scheme 14).[19–21] The best results were obtained in the

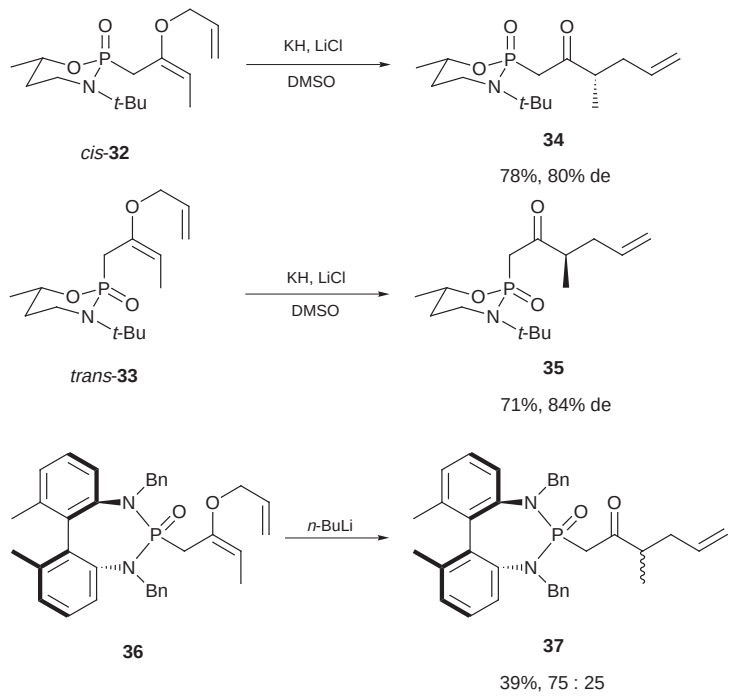


Scheme 14

combined use of a lithium hexamethyldisilylamide (LHMDS)–aluminum isopropoxide system and quinine or quinidine as the chiral amino alcohol ligand. Thus, the chelated enolate generated by treating **29** with 5 equiv. of LHMDS in the presence of 1.1 equiv. of aluminum isopropoxide and 2.5 equiv. of quinine underwent the rearrangement at −78 °C–room temperature to give the (2*R*, 3*S*)-γ,δ-unsaturated amino acid **30** in good yield with high diastereo- and enantioselectivity (98% de, 86% ee). With the same substrate, the antipode **31** could be obtained in almost the same degree of chiral induction by using quinidine as a chiral ligand (98% de, 86% ee).

2.4 Asymmetric Claisen rearrangement

The asymmetric carbanion-accelerated Claisen rearrangement of the substrate having a phosphonomethyl substituent at 2-position was reported by Denmark *et al*. in 1987.[22,23] The accelerating effect of phosphorus-stabilized carbanions in the rearrangement is so remarkable that the reaction proceeds at −20 to 20 °C within a short period, while the parent compound rearranged at much higher temperature. They designed a chiral 1,3,2-oxazaphosphorinane moiety not only as a chiral auxiliary but also as an anion stabilizing agent. Typical examples are shown in Scheme 15. When the compound **32** was treated with KH–DMSO in the presence of LiCl, the reaction proceeded under mild conditions to give the γ,δ-unsaturated ketone **34** with high diastereoselectivity (80% de) in 78% yield. The use of lithium as the counter cation is crucial for the coordination to construct an efficient chiral environment and in the absence of

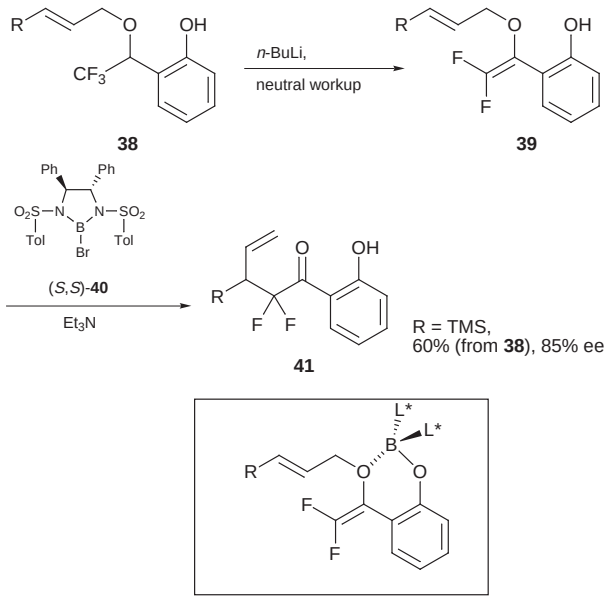


Scheme 15

LiCl, chiral transfer was not observed (0% de, 62% yield). Under the thermal conditions, in the absence of KH–DMSO and LiCl, the rearrangement of **32** took place above 100 °C and the diastereoselectivity was found to be relatively poor (32% de).

They also examined the 1,3,2-diazaphospholidine derivatives **36** having the C_2-symmetric chiral auxiliary.[24] However, the diastereoselectivity was not as high as observed in the formation of **34** or **35**.

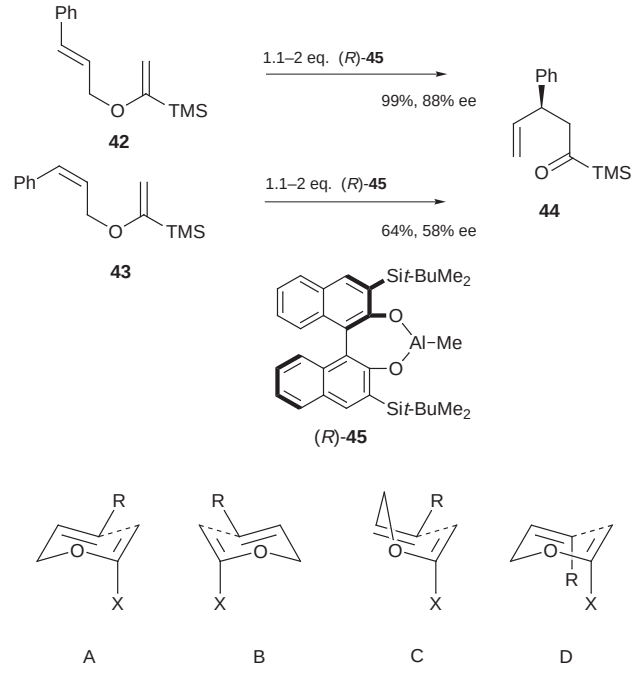
Very recently, we examined the enantioselective Claisen rearrangement of difluorovinyl allyl ether derivatives **39** having a phenol moiety (Scheme 16).[25] By treating substrate **39**,



Scheme 16

preparated by dehydrofluorination of the trifluoromethylated ether **38**, with chiral boron reagent (*S*,*S*)-**40**, the Claisen rearrangement proceeded smoothly to give the β-substituted-α,α-difluoroketone **41** with moderate to good enantioselectivity. The formation of a covalent bond between a chiral boron reagent and the phenolic hydroxy group and following coordination of ethereal oxygen to the boron atom should result in an efficient chiral environment.

In 1990, Yamamoto *et al*. reported the first example of a chiral Lewis acid catalyzed enantioselective Claisen rearrangement (Scheme 17).[26–28] They used 1.1–2 equiv. of the modified

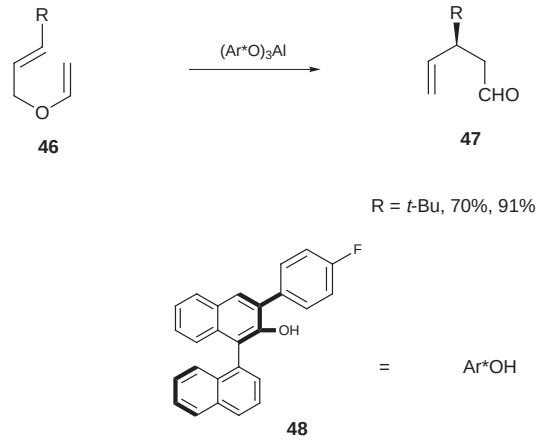


Scheme 17

chiral binaphthol–aluminum complex [(*R*)-**45**] as an activating reagent. In the case of the silylated (*E*)-substrate **42**, the Lewis acid promoted Claisen rearrangement proceeded smoothly *via* the chairlike transition state to give the silyl ketone **44** with high enantioselectivity (88% ee). The chiral aluminum reagent **45** efficiently discriminated between the two enantiotopic chairlike transition states. In the case of the (*R*)-**45** reagent, the transition state **A** should be more favorable as compared with transition state **B**. It is noteworthy that the absolute stereochemistry of the product from (*Z*)-substrate **43** was the same as that of (*E*)-substrate **42**. They explained this result by the fact that the boatlike transition state **C** is favorable in the case of (*Z*)-substrate **43** due to the steric repulsion between the allylic

substituent and bulky silyl group in the chairlike transition state **D**. The substrate having a germyl group instead of a silyl group underwent the rearrangement with a higher enantioselectivity.

Further development of chiral Lewis acids for the enantioselective Claisen rearrangement by the same group have been studied based on the monomeric aluminum alkoxide composed of an extremely bulky and axially chiral phenol derivative (Scheme 18).[29] To this end, C_3-symmetric aluminum tris-

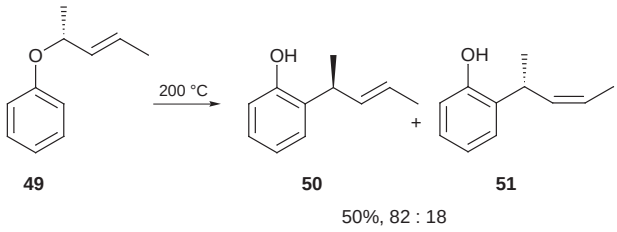


Scheme 18

phenoxide derived from the naphthol derivative **48** was found to work nicely for the rearrangement of non-silylated achiral allylic vinyl ethers **46** to give the γ,δ-unsaturated aldehydes **47** having a newly formed chiral center at the β-position in high enantioselectivities (61–92% ee). On the basis of X-ray analysis of the aluminum trisphenoxide–DMF complex, they discussed the mechanism of chiral induction in the rearrangement reaction.

3 Asymmetric aromatic Claisen rearrangement

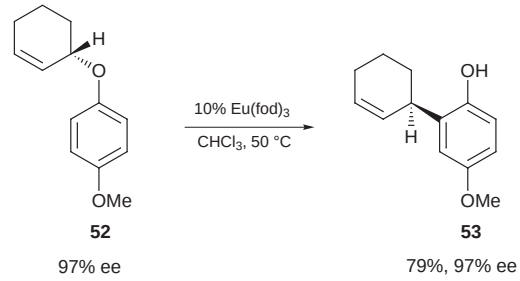
Only a few examples of an asymmetric aromatic Claisen rearrangement have been reported. For example, (*R*)-(*E*)-ether **49**, upon heating, rearranged to give a mixture of (*S*)-(*E*)-**50** and (*R*)-(*Z*)-**51** in a ratio of 82 : 18, although the optical purity of each product was not reported (Scheme 19).[30]



Scheme 19

In general, several problems found in the aromatic Claisen rearrangement have retarded the development of its asymmetric variant.[4] These involve the *ortho*, *para*-selectivity of migration, abnormal Claisen rearrangement based on the 1,5-sigmatropic hydrogen shift, and the rearrangement *via* an allylic cation mechanism resulting in a loss of regioselectivity and stereospecificity with respect to the geometry of the parent allylic moiety particularly in the case of Lewis acid-mediated conditions. Therefore, finding an efficient activating agent for aromatic Claisen rearrangement is an important goal.

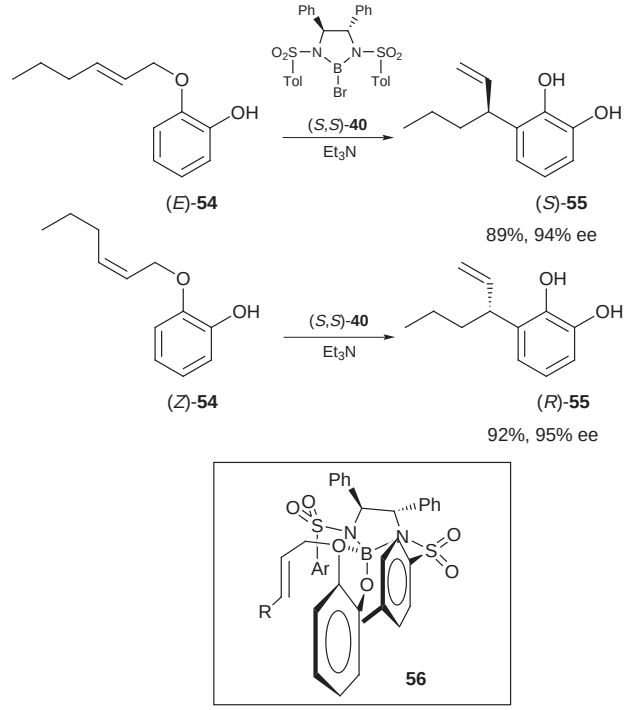
Very recently, Trost *et al*. succeeded in achieving an asymmetric aromatic Claisen rearrangement by an intramolecular chirality transfer of the *para*-protected chiral substrate (Scheme 20).[31] They synthesized chiral allyl aryl ethers



Scheme 20

such as **52** by enantioselective *O*-alkylation of hydroquinone monomethyl ether using a chiral palladium catalyst. Upon treatment of the substrate **52** with a catalytic amount (10% mol) of Eu(fod)$_3$ as Lewis acid, an excellent intramolecular chirality transfer could be achieved.

We reported the first enantioselective aromatic Claisen rearrangement using an *O*-allyloxy phenol derivative and a chiral boron reagent (Scheme 21).[32] Upon treatment of the



Scheme 21

substrate (*E*)-**54** with 1.5 equiv. of the chiral boron reagent (*S*,*S*)-**40** and triethylamine at low temperature, a boron–phenoxide intermediate was formed, which underwent the *ortho*-rearrangement at −45 °C to give the product (*S*)-**55** in 89% yield with excellent enantioselectivity (94% ee) without the formation of by-products such as the *para*-rearranged or abnormal Claisen products. Reaction of (*Z*)-**54** and (*S*,*S*)-**40** gave the rearrangement product having the (*R*)-configuration with excellent selectivity (*R*-**55**, 92%, 95% ee). The selective *ortho*-rearrangement observed in the boron-mediated reaction could be rationalized by considering the catechol borate structure in the product, since *para*-rearrangement takes place *via* Cope-rearrangement of the *ortho*-rearranged dienone intermediate, which, in the present case, readily isomerizes to the catechol form. Furthermore, the catechol borate structure in the product would be unfavorable for a 1,5-hydrogen shift leading to abnormal Claisen rearrangement. The importance of the boron–phenoxide intermediate should be also noted for the rearrangement reaction to proceed regioselectively and to achieve a high enantioselectivity, since the substrates without a

phenolic hydroxy group (allyl phenyl ethers and allyl *ortho*-methoxyphenyl ethers) or an *ortho*-hydroxymethylated substrate did not rearrange when treated with the boron reagent at room temperature. The mechanism of asymmetric induction can be explained by considering the 5-membered cyclic intermediate **56** formed by a covalent bond between the boron reagent and the phenolic hydroxy group and following coordination of the ethereal oxygen to the boron atom. In this cyclic intermediate, one of the arenesulfonyl groups would effectively shield one face of the benzene ring, therefore the allylic moiety approaches its other face resulting in the enantiotopic facial selection of the allylic double bond.

4 Conclusion

The diastereoselective Claisen rearrangements of the substrates having chiral auxiliary and enantioselective variants of achiral substrates were well studied during the last decade as summarized in this article. Numerous successful achievements have been reported in the aliphatic Claisen rearrangement, while only a limited number of examples of enantioselective aromatic Claisen rearrangements have appeared. Development of an enantioselective Claisen rearrangement by using a catalytic amount of a chiral source still remains as one of the future objectives in this field.

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