

# Chapter 4: Synthesis and applications of tartaric acid in asymmetric catalysis

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**Abstract:** This chapter presents recent advances in the synthesis and application of tartaric acid derivatives in asymmetric catalysis. Tartaric acid, a naturally occurring C<sub>2</sub>-symmetric diol, serves as a versatile chiral pool compound for the preparation of diverse ligands and catalysts. Dimethyl (2R,3R)-tartrate and its modified derivatives are employed as key chiral building blocks in the development of enantioselective catalytic systems. Their functionalized forms have been utilized in a variety of asymmetric transformations, including aldol reactions, epoxidations, Diels–Alder reactions, and hydrogenations. Structural modifications at the carboxylic acid and hydroxyl positions of tartaric acid have led to highly selective chiral auxiliaries, organocatalysts, and metal–ligand complexes. These derivatives offer efficient access to enantiomerically pure compounds and continue to play a critical role in modern stereoselective synthesis.

**Keywords:** Asymmetric catalysis, chirality, enantioselective synthesis, resolving agents, stereoselective reactions, tartaric acid.

## 1 Introduction

The concept of molecular chirality, a cornerstone of stereochemistry, was first discovered by Louis Pasteur in 1848 through the manual separation of enantiomorphic crystals of (±)-ammonium tartrate (Gal, 2011). This seminal discovery not only laid the foundation for stereochemical understanding in organic chemistry but also underscored the critical role of molecular asymmetry in biological systems. Chirality has since emerged as a central concept in synthetic organic chemistry, materials science, and pharmaceutical development (Eliel & Wilen, 1994).

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Tartaric acid is one of the most significant naturally occurring chiral compounds, renowned for its structural simplicity, commercial availability, and high enantiomeric purity (Seebach & Kalinowski, 1984). It exists in two enantiomeric forms—(2R,3R)-(+)-tartaric acid and (2S,3S)-(-)-tartaric acid as well as in the achiral meso form (Clayden, Greeves, & Warren, 2012). The (2R,3R)-enantiomer is commonly found in nature, particularly in grapes and tamarind, and is biosynthesized *via* the ascorbic acid pathway (Davies & Morton, 2011). With its C<sub>2</sub> symmetry, two stereocenters, and multiple functional groups (dihydroxyl and dicarboxylic acid), tartaric acid provides a versatile scaffold for asymmetric catalysis (Noyori, 2002).

Asymmetric catalysis has become an essential tool in modern organic synthesis, enabling the preparation of enantiomerically enriched compounds with high atom economy and selectivity (Ojima, 2010). Early approaches to chirality induction involved chiral auxiliaries and optical resolution of racemates (Oppolzer, 1987). While effective, these methods are often inefficient and wasteful, requiring stoichiometric amounts of chiral reagents and generating undesired by-products (Sheldon, 2007). Catalytic asymmetric methodologies—particularly those utilizing chiral ligands and organocatalysts have thus become the preferred strategy for constructing complex chiral molecules (Mikami & Lautens, 2007).

Tartaric acid-derived compounds have played a pivotal role in this transformation. Their ability to form stable chelating ligands and coordinate with various transition metals has enabled the development of a wide range of chiral catalysts (Tang & Zhang, 2003). For example, tartaric acid-derived esters and amides are widely used in Sharpless asymmetric epoxidation (Katsuki & Sharpless, 1980), asymmetric dihydroxylation (Kolb et al., 1994), and hydrogenation reactions (Knowles, 2002). These systems typically rely on the precise configuration of the tartaric acid backbone to induce chirality in the substrate (Noyori, 2008).

One of the earliest and most influential uses of tartaric acid in catalysis is the modification of heterogeneous metal surfaces. (R,R)-Tartaric acid-modified nickel or Raney nickel catalysts have shown excellent performance in the enantioselective hydrogenation of  $\beta$ -ketoesters such as methyl acetoacetate (Blaser & Schmidt, 2010). These systems are industrially relevant and serve as models for heterogeneous enantioselective catalysis (Mallat & Baiker, 2004).

Tartaric acid has also been used to generate highly effective C<sub>2</sub>-symmetric diphosphine ligands, which have enabled high enantioselectivity in palladium-, ruthenium-, and rhodium-catalyzed reactions (Togni & Grützmacher, 1998). These ligands have been employed in asymmetric additions, hydrogenations, and carbon–carbon coupling

reactions (Trost, 1991). Their structural rigidity, resulting from chelation, provides a highly defined chiral environment around the metal center (Xie & Zhou, 2012).

In organocatalysis, tartaric acid-derived scaffolds have been used to develop chiral Brønsted acids, such as chiral phosphoric acids (Akiyama & Mori, 2015), which are among the most versatile catalysts for enantioselective transformations including Mannich reactions, imine additions, and transfer hydrogenations (Terada, 2008). The dual functionalization of tartaric acid also allows for the introduction of bifunctional catalytic motifs, enhancing both reactivity and stereocontrol (Schreiner, 2003).

Recent studies have expanded the applications of tartaric acid derivatives beyond traditional asymmetric synthesis into the development of advanced chiral polymers that exhibit high enantioselectivity and mechanical robustness (Rajca, 1994). These chiral polymers have shown promising utility in areas such as enantioselective separation and catalysis, thereby broadening the scope of tartaric acid as a versatile monomeric unit. Additionally, tartaric acid-based frameworks have been integral in designing optically active materials with tailored electronic and photophysical properties, contributing to innovations in chiral optoelectronics and molecular recognition (Han, Zhao, & Yang, 2017). These materials demonstrate enhanced chiroptical responses and stability, which are essential for practical applications in sensing and asymmetric catalysis. Furthermore, the supramolecular assembly of tartaric acid derivatives has been exploited in the construction of highly selective and recyclable catalysts, harnessing noncovalent interactions to achieve substrate specificity and catalytic efficiency (Bräse, Höfener, & Zimmermann, 2010). The ability of these supramolecular systems to mimic enzyme-like behavior while maintaining operational simplicity under mild conditions underscores the importance of tartaric acid in sustainable catalyst design. Collectively, these advances highlight tartaric acid's expanding role as a foundational scaffold in the synthesis of environmentally benign and highly selective catalytic systems.

This review aims to provide a comprehensive overview of tartaric acid derivatives in asymmetric catalysis, including their synthesis, structural modifications, and catalytic applications across various reaction classes such as aldol condensations, Michael additions, Mannich reactions, Diels–Alder cycloadditions, asymmetric reductions, and epoxidations. The enduring utility of tartaric acid-based systems underscores their role as indispensable tools in stereoselective synthesis.

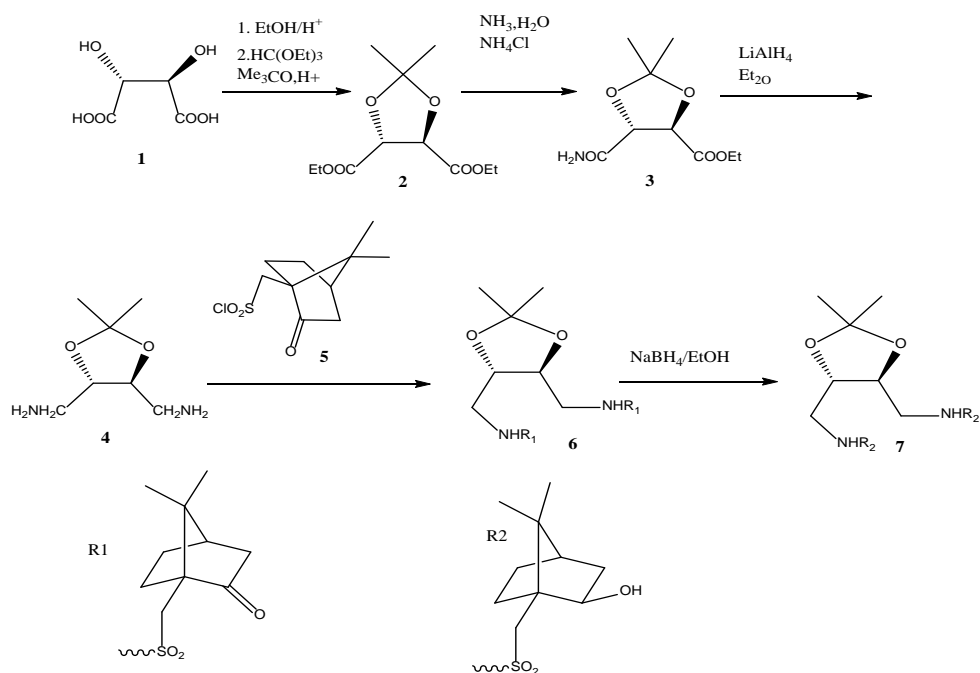
## 2 Tartaric acid derivatives and their applications in asymmetric synthesis

### Enantioselectivity in the presence of tartaric acid derivatives

Enantioselective reactions are those reactions where one of the isomer forms predominantly. Enantioselective addition of alkylation group is fundamentally important transformation in organic synthesis.

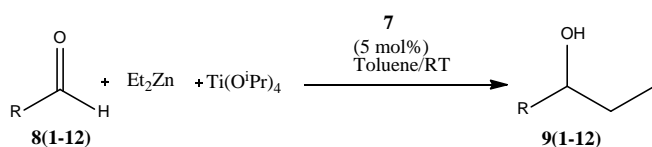
In order to apply the enantioselective addition of diethyl zinc to aldehydes and ketones, Ailing hui and coworkers (Hui, Zhang, Fan, & Wang, 2006) created chiral sulfonamide-based ligands on tartaric acid (**6** & **7**) in 2006. Diethylzinc was added to

*p*-chlorobenzaldehyde using a typical enantioselective addition process using the synthesised ligands **6** and **7**, which had a 5 mol% toluene ligand loading. With ligand **6** they obtained a poor enantiomeric excess of 20% ee, while ligand **9** achieved moderate enantioselectivity of 70% ee under the same condition.



**Scheme 1:** Synthesis of chiral sulfonamide based ligands

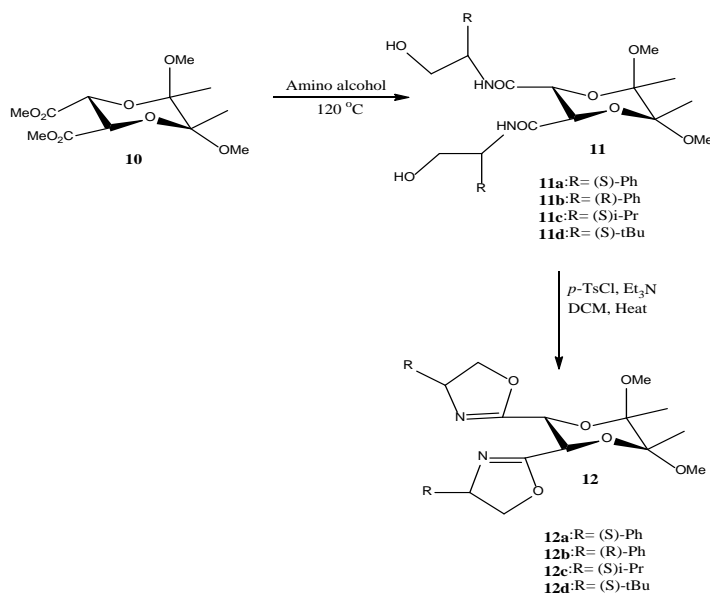
**Table 1.** Addition of diethylzinc to aldehydes in the presence of ligand



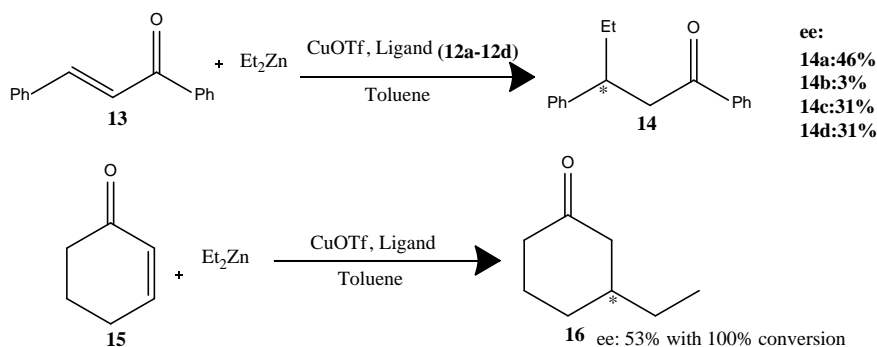
Sr. No.	R	Yields in (%)	Time (h)	ee (%)
1	4-MeC <sub>6</sub> H <sub>4</sub>	81	12	60
2	4-ClC <sub>6</sub> H <sub>4</sub>	95	1	70
3	C <sub>6</sub> H <sub>5</sub>	90	2	65
4	4-FC <sub>6</sub> H <sub>4</sub>	93	1	75
5	4-MeOC <sub>6</sub> H <sub>4</sub>	83	12	58

6	4-MeOC <sub>6</sub> H <sub>4</sub>	97	2	63
7	2-ClC <sub>6</sub> H <sub>4</sub>	92	3	38
8	2-MeC <sub>6</sub> H <sub>4</sub>	96	2	81
9	2-MeOC <sub>6</sub> H <sub>4</sub>	90	3	54
10	2-MeOC <sub>6</sub> H <sub>4</sub>	95	2	63
11	1-Naphthyl	85	3	83
12	Cinnamyl	95	3	31

A method for synthesising chiral bis(oxazolines) generated from tartaric acid was published by M T. Barros et al (Barros, Phillips, & Ventura, 2005). In order to create the bis(hydroxy) amide derivatives, cyclic diacetal diester (**10**) must condense with the appropriate 1,2-amino alcohols. The hydroxyl groups in the bis(hydroxy) amides (**11a-d**) were then activated as tosylates using *p*-toluenesulfonyl chloride in the presence of a significant excess of base (Et<sub>3</sub>N). The activation and cyclization occur in one pot, allowing for the direct production of the bis(oxazolines) in equal or better yields when heated. The copper-catalyzed addition of diethylzinc to an acyclic and a cyclic enone was used to examine their ability to function as chiral ligands in metal-catalyzed processes (Scheme 2). Out of these four ligands, the ligand **12a** exhibit good enantioselective addition of diethyl zinc on chalcone with 46% ee. Additions to the cyclic enone i.e., 2-cyclohexenone (**15**) was also found to be more efficient with 53% ee with 100% reaction conversion.

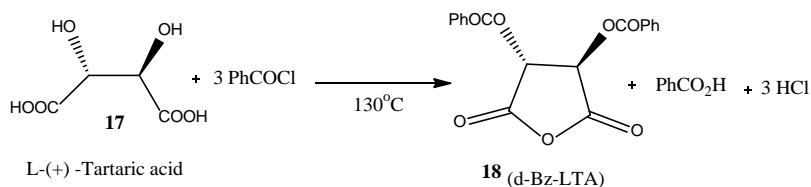


**Scheme 2: Synthesis of bis(oxazolines)**

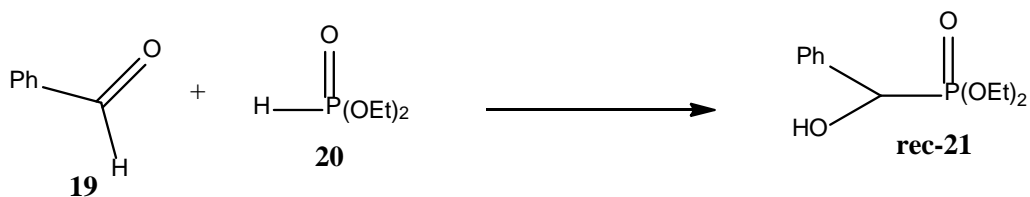


**Scheme 3:** Enantioselective addition of diethylzinc to chalcone and cyclohex-2-enone catalyzed by  $\text{Cu}(\text{OTf})_2$ : chiral bis (oxazoline) ligands

In order to separate racemic alcohols and amines, Kaboudin reported that L-Tartaric anhydride and O,O'-dibenzoyl-L-tartaric anhydride (**18**, d-Bz-LTA) (Scheme 4) were used as effective chiral resolving agents. By reacting benzaldehyde with diethyl phosphite in the presence of magnesium oxide, racemic diethyl 1-hydroxy-1-phenylmethylphosphonate (rec-**23**) was produced in a quantifiable yield (Scheme 5).

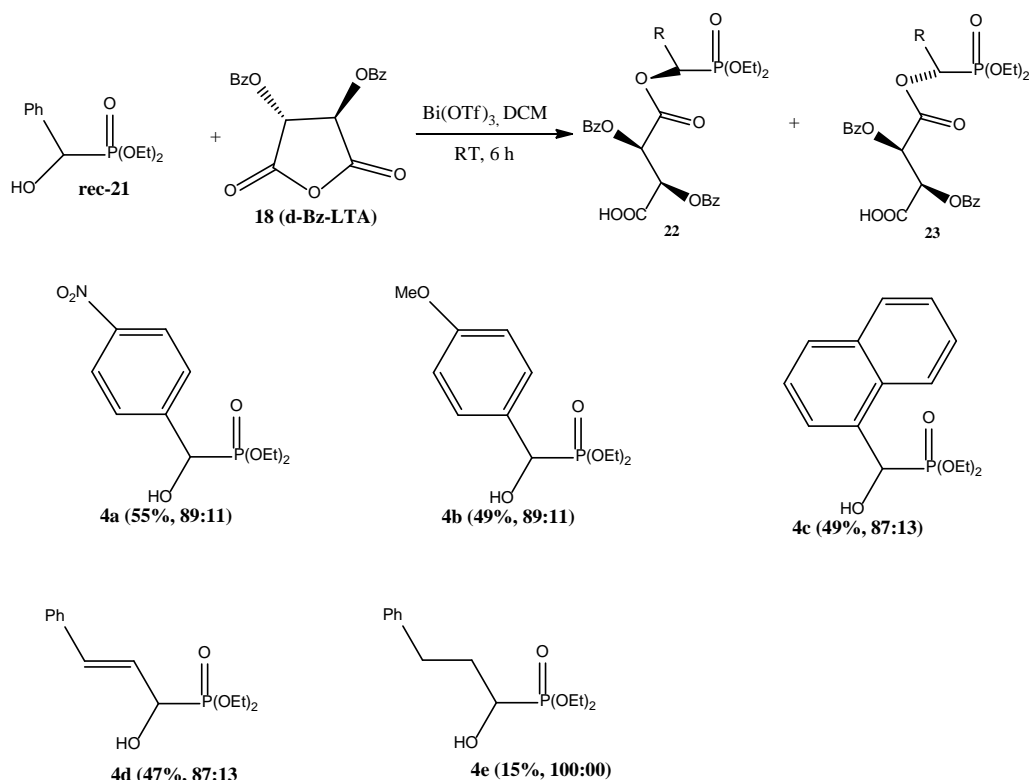


**Scheme 4:** Synthesis of O,O'-dibenzoyl-L-tartaric anhydride



**Scheme 5:** Synthesis of racemic alcohol

Thermal heating of a combination of L-tartaric acid and benzoyl chloride was used to create d-Bz-LTA (**18**). Racemic diethyl treatment in the presence of bismuth triflate (15 mol%) in an 86:14 ratio, 1-hydroxy-1-phenylmethylphosphonate (**21**) and (+)-dibenzoyl-L-tartaric anhydride (**18**) yielded two diastereomeric esters **22** and **23** (Scheme 6).



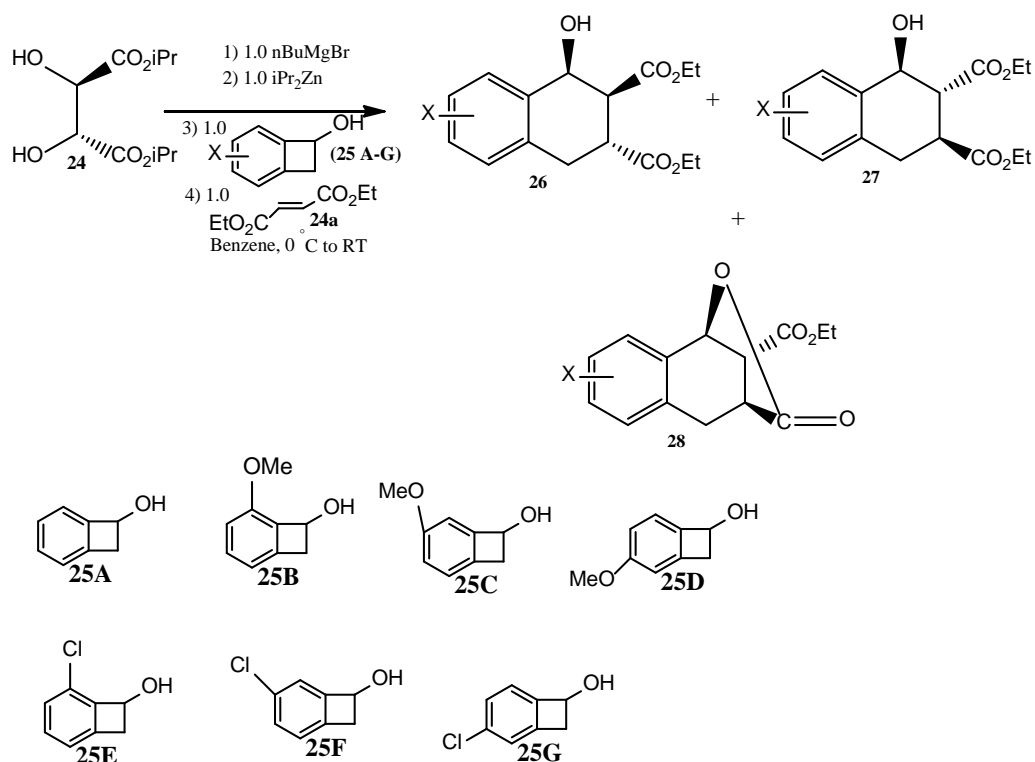
in parenthesis (conversion %, ratio of **21:22**)

**Scheme 6:** Diastereoselective reaction of compound **rec-21** with **18 (d-Bz-LTA)** in the presence of  $\text{Bi}(\text{OTf})_3$

Using tartaric acid ester, M. Takinami et al. (Takinami, Ukaji, & Inomata, 2006) have created optically active tetrahydronaphthalene. A magnesium and zinc bridging intermediate is created when diisopropyl (R,R)-tartrate **24** is progressively treated with butylmagnesium bromide, dialkylzinc, and benzocyclobutenol **25A**. Fumaric acid ester was added after. **24a** by electrocyclic ring-opening process, *o*-quinodimethane is produced, and then Diels-Alder reaction is used to produce the equivalent optically active tetrahydronaphthalene(s) **26** and/or **27**. Initially, the first, dimethylzinc was used to analyse the Diels-Alder reaction with diethyl fumarate **24a** in  $\text{CH}_2\text{Cl}_2$ . At room temperature, the cycloaddition slowly produced primarily 1,2-cis-tetrahydronaphthalene **26**, as well as 1,2-trans-isomer **27** and cyclized lactone **28**.

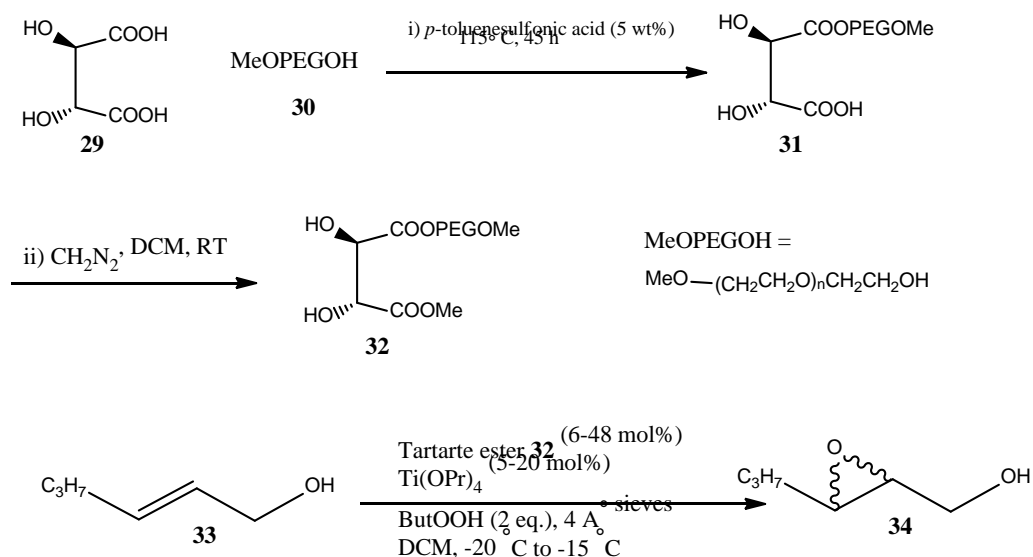
According to HPLC analysis, of the **28** produced, diisopropylzinc provided the greatest yields and enantioselectivities among the dialkylzincs studied. Solvent effects were also investigated. Higher enantioselectivities were obtained by the reaction in aromatic

solvents than in ether solvents. Finally, when the reaction was carried out in benzene, the 1, 2-cis-tetrahydronaphthalene **26** was generated in 83% ee.



**Scheme 7:** Asymmetric Diels-Alder reaction of several *o*-quinomethanes generated from the corresponding benzocyclobutenols **27A-G**

H. Gau and coworkers (Fan, et al., 2002) synthesized Tartrate esters **31** and **32**. The  $\text{Ti}(\text{O}^i\text{Pr})_4$ /*tert*-butyl hydroperoxide was utilised to epoxidize trans-hex-2-en-1-ol. When trans-hex-2-en-1-ol is oxidised using  $\text{Ti}(\text{O}^i\text{Pr})_4$  and *tert*-butyl hydroperoxide, significant chemical yields and good enantiomeric excesses up to 98% are achieved (Scheme 8).



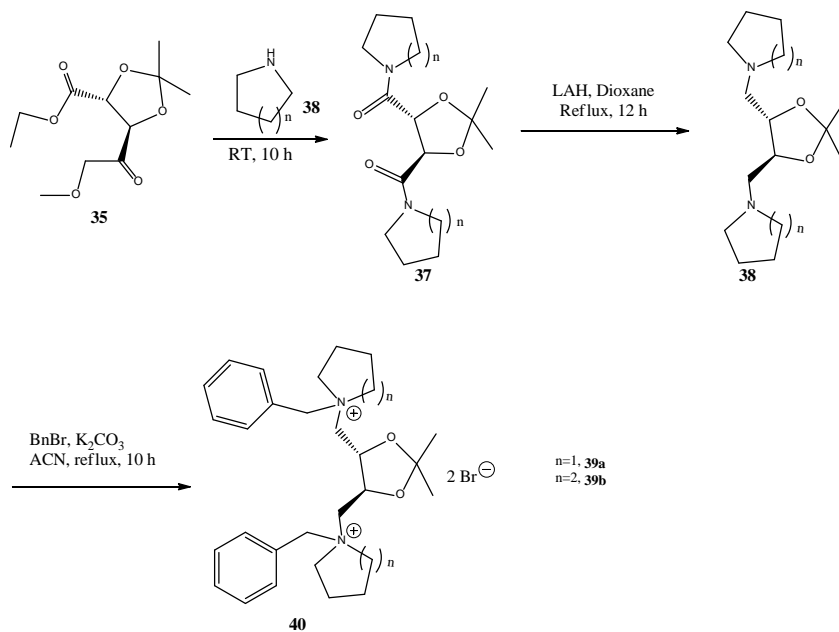
**Scheme 8:** Epoxidation of trans-hex-2-ene-1-ol with t-BHP catalysed by –(+)-tartrate ester and  $\text{Ti}(\text{OPr})_4$

Ca-Jie Zhu and coworkers (Zhu et al., 2013) have synthesized chiral cyclic phase transfer catalyst **39a** and **39b** using dimethyl acetal tartaric acid ester **35** (Scheme 9). Various malonate esters (**41a-e**) were subjected to Michael addition to benzalacetophenone **40** by using 5 to 10 mol% of chiral PTC (**39a** & **39b**) in the presence of  $\text{K}_2\text{CO}_3$  in toluene to get the Michael adduct (**42a-e**) (Scheme 10). Effective phase transfer catalysis was achieved with 95% yield and 84% ee for enantioselective Michael additions (Table 2).

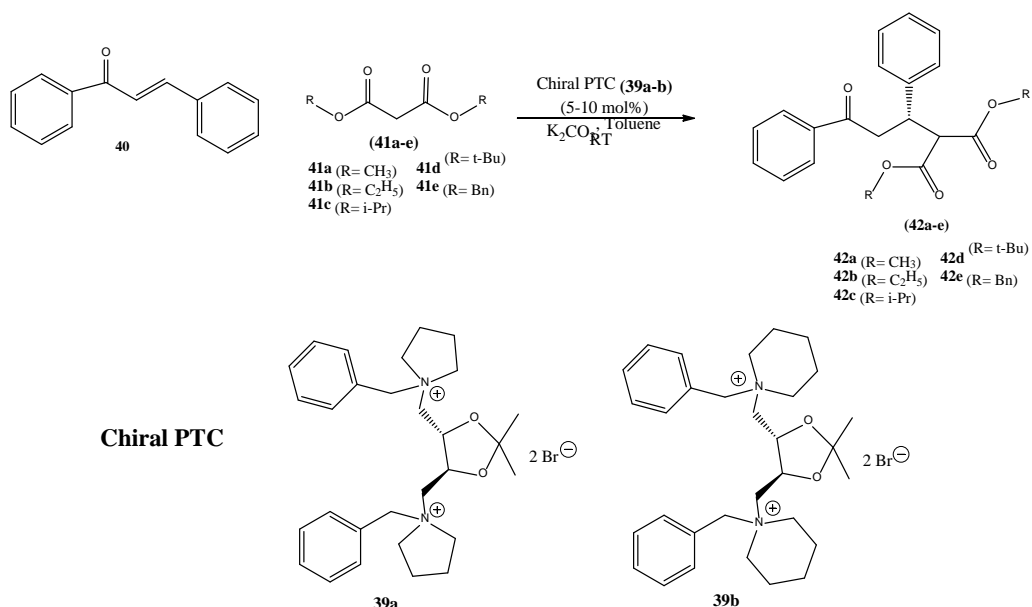
**Table 2:** Michael addition of malonate esters (**41a-e**) to benzalacetophenone **40** by using 5 to 10 mol% of chiral PTC (**39a** and **39b**) in the presence of  $\text{K}_2\text{CO}_3$  in toluene to get Michael adduct (**42a-e**)

Malonate ester	Catalyst	Mol%	Time (h)	Yield (%)	Optical purity (ee)
Dimethyl malonate ( <b>41a</b> )	<b>39a</b>	5	3	95	83.5%
		10	2	94	83.4%
	<b>39b</b>	5	3	95	84.0%
		10	2	95	84.3%
Dimethyl malonate ( <b>41b</b> )	<b>39a</b>	5	5	93	84.7%
		10	3	93	84.6%
	<b>39b</b>	5	5	94	85.2%
		10	3	93	85.3%
Dimethyl	<b>39a</b>	5	11	89	85.7%

malonate ( <b>41c</b> )		10	8	90	85.9%
	<b>39b</b>	5	11	90	86.2%
		10	8	89	86.4%
Dimethyl malonate ( <b>41d</b> )	<b>39a</b>	5	38	85	87.6%
		10	31	84	87.8%
	<b>39b</b>	5	38	85	89.2%
		10	30	85	89.0%
Dimethyl malonate ( <b>41e</b> )	<b>39a</b>	5	4	94	86.3%
		10	3	93	86.5%
	<b>39b</b>	5	4	93	88.0%
		10	3	94	87.9%



**Scheme 9:** Synthesis of chiral phase transfer catalyst using tartaric acid (**39a** & **39b**)

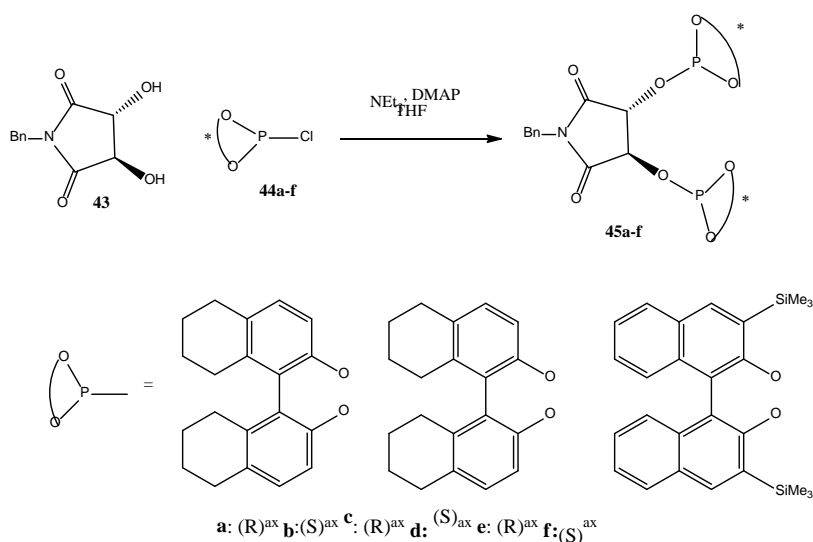


**Scheme 10:** Michael addition of malonates (**41a-e**) to benzalacetophenone (**40**) to get Michael adduct (**42a-e**)

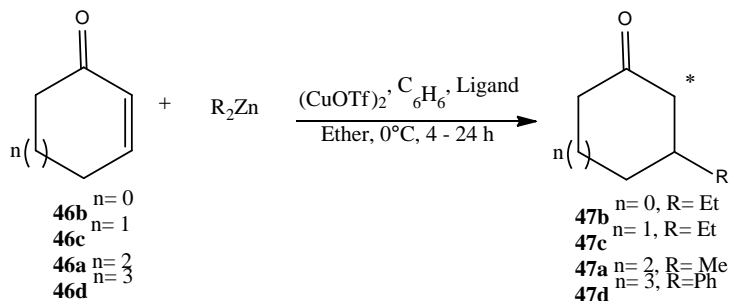
A-P Xing et al (Xing et al., 2013) synthesized diphosphate ligands (**45a-f**) from the reaction of (3R,4R)-*N*-benzyltartaric acid derivative and various chlorophosphoric acid diaryl ester (i.e., R or S 8H binaphthol, R or S binaphthol, Me<sub>3</sub>Si-binaphthol) under triethylamine/DMAP condition (Scheme 11). The synthesized ligands were employed for the Cu-catalyzed asymmetric 1,4-conjugate addition (ACA) of organozincs to 2-cyclopentenone and 2-cyclohexenone. The R<sup>ax</sup> binaphthol based ligand (**45c**) showed the highest enantioselectivity (up to 95% ee) in Cu catalysed reaction of cyclic enones (Scheme 12). The excellent ee was obtained because of synergic effect of L-(+) tartaric acid skeleton and the axially chiral binaphthol moiety of the ligand (**45c**) (Table 3).

**Table 3.** The Cu-catalyzed enantioselective 1,4-addition of R<sub>2</sub>Zn to cyclic enones

Entry	Subs.	Product	Time (h)	Conc. (%)	Yield (%)	ee (%)
1	<b>46b</b>	<b>47b</b>	4	>99	21	95(R)
2	<b>46c</b>	<b>47c</b>	4	39	25	63(R)
3	<b>46a</b>	<b>47a</b>	24	30	21	67(R)
4	<b>46b</b>	<b>47d</b>	24	99	34	22(R)

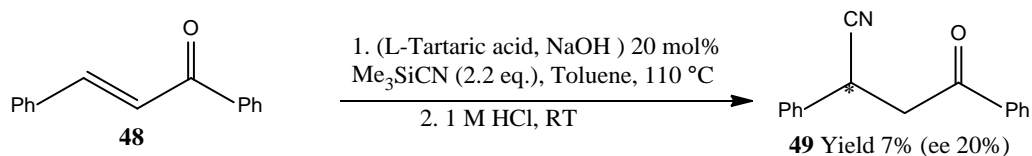


**Scheme 11:** Synthesis of diphosphite ligands



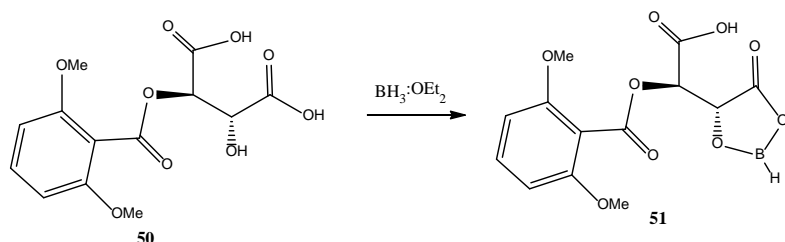
**Scheme 12:** Enantioselective 1,4-addition of  $\text{R}_2\text{Zn}$  to cyclic enones by Cu-catalyst

Jingya Yang et al (Yang, Wu, & Chen, 2010) used disodium salt of L-tartaric acid (which was *in situ* generated by the reaction of L-tartaric acid with NaOH in toluene) for enantioselective 1,4-addition of  $\text{TMSCN}$  to aromatic enones. The disodium salt of L-tartaric acid bearing two chiral centres yielded the product **49** in low yield with 20% ee (Scheme 13).

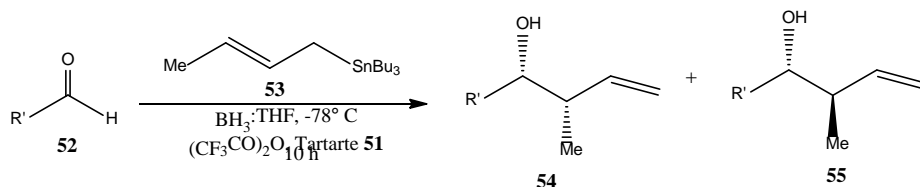


**Scheme 13:** 1,4-Addition of  $\text{TMSCN}$  to aromatic enones

A modified Yamamoto Lewis acid (CAB, **53**) was created by James A. Marshall et al. (Marshall & Liao, 1998) by combining tartaric acid's 2,6-dimethoxybenzoic ester with 1.5 equiv. of  $\text{BH}_3$  (Scheme 13). In the presence of 2 equiv. of CAB, crotylstannane (**53**) undergoes addition with typical achiral aldehydes (Scheme 14). The syn adducts **54** and trans adducts **55**, had enantioselectivity and diastereoselectivity of good to exceptional (78:22-92:8). Authors conclude that the strongly complex-controlled CAB-promoted additions effectively override the aldehyde substrate's natural facial preference. When enantioselective additions to specific aldehyde-Lewis acid complexes were made, Corey's theory of H-bonded transition states led to the production of syn-selective addition to such a complex, which is what caused the stereochemical outcome that was observed. Different aldehydes **52a-e** were screened for this addition reaction under optimized reaction condition corresponding data are summarized in Table 4.



**Scheme 13:** Synthesis a modified Yamamoto Lewis acid (CAB, **53**)



**Scheme 14:** Addition of crotyl stannane **53** to achiral aldehydes (**52a-e**)

**Table-4:** CAB-Promoted addition of crotyl stannane to achiral aldehydes

R'	Yield (%)	<b>54:55</b>	ee% of <b>54</b>
$\text{C}_6\text{H}_{11}$ ( <b>52a</b> )	70	92:8(97:3)	91
$\text{C}_6\text{H}_{13}$ ( <b>52b</b> )	74	91:9(88:12)	92
E-PrCH=CH ( <b>52c</b> )	71	78:22(86:14)	89
$\text{C}_6\text{H}_{13}\text{C}=\text{C}$ ( <b>52d</b> )	70	79:21 (79:21)	71

DPSOCH <sub>2</sub> CH <sub>2</sub> (52e)	73	88:12 (96:4) <sup>c</sup>	70
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## Conclusions

One of the most prevalent naturally occurring chiral chemical is tartaric acid. While its use in creating chiral ligands for metal-catalyzed processes has received extensive different research modifications on tartaric acid leading to formation of new chiral ligand which gives unique selectivity in chiral synthesis. Several recent reports including development of chiral ligand synthesis based on tartaric acid and its applications mainly in 1,2-additions, 1,4-additions, chiral reductions, Diels-Alder reactions have been described in respective schemes. Chiral tartaric acid derivatives play a vital role in chiral resolution and asymmetric synthesis and having tremendous scope in the field of pharmaceuticals, agrochemicals, flavour and perfumes.

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