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# Epoxides: methods of synthesis, reactivity, practical significance

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This review systematically summarizes recent literature data on the chemistry of epoxides published from 2010 to 2021 and, in part, in 2022. Epoxides are an important class of compounds, which are valuable building blocks in the design of new structures serving as the basis for many practically important compounds. Epoxy derivatives have long attracted the attention of synthetic chemists, as confirmed by a number of name reactions associated with their synthesis. The review describes methods for the synthesis of epoxy compounds, including both improved classical and new approaches, considers chemical reactions involving epoxides, discusses the practical significance of such compounds in relation to the synthesis of natural products, drugs and polymer structures and the CO and $CO_2$ utilization. Much attention is paid to the issues of asymmetric synthesis, which enable one to get a general idea on the current trends in the chemistry of epoxides. The most unexpected rearrangements of functionalized epoxides are considered and the role of epoxy compounds in the synthesis of various carbo- and heterocyclic systems is discussed.
The bibliography includes 555 references.

## Contents

1. Introduction 2
2. Methods for the synthesis of epoxides 3
2.1. Darzens condensation 3
2.2. Büchner – Curtius – Schlotterbeck reaction 4
2.3. Prilezhaev epoxidation 5
2.4. Weitz – Scheffer epoxidation 5
2.5. Johnson – Corey – Chaykovsky method 8
2.6. Sharpless epoxidation 9
2.7. Juliá – Colonna epoxidation 11
2.8. Jacobsen – Katsuki epoxidation 11
2.9. Shi epoxidation 11
2.10. Biocatalysis in the synthesis of epoxides 12
2.11. Miscellaneous methods of synthesis of epoxides 12
3. Chemical transformations of epoxide compounds 14
3.1. Nucleophilic epoxide ring-opening 14
3.2. Rearrangements in the chemistry of epoxides 20
3.2.1. Meinwald rearrangement 20
3.2.2. Payne rearrangement 21
3.2.3. Semipinacol rearrangement 21
3.2.4. New rearrangements of epoxy compounds 21
3.3. Tandem and one-pot reactions 23
3.3.1. Meinwald rearrangement in tandem and one-pot reactions 24
3.3.2. Construction of new carbo- and heterocyclic structures from functionalized epoxides 27
3.3.3. Intramolecular Friedel – Crafts reaction involving functionalized epoxides 30
3.3.4. Tandem reactions involving epoxide and another reagent 32
3.3.5. Intermolecular Friedel – Crafts reactions involving epoxides 40
3.3.6. Multicomponent reactions in the chemistry of epoxides 42
3.4. Miscellaneous transformations of epoxides 45
4. Practical applications of epoxides 47
4.1. Natural products and drugs based on epoxy derivatives 47
4.2. Epoxy derivatives in the synthesis of natural products 48
4.3. Epoxy derivatives in the synthesis of drugs 62
4.4. Epoxide carbonylation 64
4.5. Epoxide carboxylation 65
4.6. Epoxide polymerization 67
5. Conclusion 67
6. List of abbreviations and designations 67
7. References 68

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## 1. Introduction

Epoxides are an important class of organic compounds with great synthetic potential. The synthesis, reactivity and fields of practical applications of these derivatives were described in numerous publications, including reviews, as evidenced by the reference list in the present review. However, most reviews published from 2010 to 2022 cover selected issues in this research area. Prior to considering the data on the chemistry of epoxy compounds, let us only mention the most recent reviews, indicating their specifics, while other reviews published during this period of time, will be referred to when appropriate. Thus, the review by Meninno and Lattanzi,[1] published in 2017, focuses on the organocatalysis in the synthesis of epoxides. In 2016, these authors [2] wrote a review on organocatalytic asymmetric reactions of epoxides. There are reviews on the nucleophilic epoxide ring-opening,[3] intramolecular reactions of epoxides with arenes and hetarenes [4] and multicomponent reactions involving epoxides.[5] In 2020, Gomes *at al*.[6] published a review titled 'Epoxide containing molecules: a good or a bad drug design approach'. The review by Werner and co-workers,[7] published in 2017, is devoted to the synthesis of cyclic carbonates from epoxides and $CO_2$. In 2018, Wang and Darensbourg [8] discussed the issues of the copolymerization of epoxides with $CO_2$. In 2016, Herzberger *et al.* [9] published a review in the *Chemical Reviews*, where they considered the issues of epoxide polymerization. Despite the abundance of data on the chemistry of epoxides, they are scattered. To better navigate the world of scientific publishing and reveal the important issues and challenges, it has become essential to summarize current advances in this area of organic synthesis. In the present review, we use the data from the previous reviews, which are presented in a new perspective and are supplemented with recent studies. Our goal is to survey the new literature data on epoxides as complete and accessible as possible, classifying the available data according to selected features. In the case of highly specialized issues, we consider the general characteristics, without complete analysis of all the available literature on the chosen topic. This applies, for example, to the enzyme catalysis of the oxidation of unsaturated compounds or polymerization of epoxides. The review is divided into three main parts: the synthesis, transformations and applications of epoxides. The methods of synthesis are classified according to the commonly accepted names of reactions (Darzens, Büchner – Curtius – Schlotterbeck, Prilezhaev, Weitz – Scheffer, Johnson – Corey – Chaykovsky, Sharpless, Juliá – Colonna, Jacobsen – Katsuk, Shi reactions) or are included in a special section, if the known name reactions are not used in the synthesis. The transformations of epoxy compounds, in which the epoxide ring remains intact, are beyond the scope of this review if they are not involved in one-pot or tandem strategies along with the epoxide ring formation.

The chemistry of epoxy compounds is very diverse. Therefore, the classification of their transformations is a rather difficult problem. We begin the description of chemical reactions with the well-known nucleophilic epoxide ring-opening reactions, drawing the attention to current trends in the asymmetric synthesis of valuable chiral reagents. These reactions occurring in the presence of various nucleophilic reagents have been extensively studied. Therefore, we consider only studies, which were not included in the previous reviews. The trends in the development of this research area are discussed mainly in relation to the reactions with amines as nucleophilic reagents. Then we present examples of rearrangements, which are addressed by the authors of modern studies, such as the Meinwald, Payne and semipinacol rearrangements. Particular attention is given to new rearrangements of epoxides, for which the putative mechanisms were proposed. The Section devoted to tandem and one-pot reactions includes complex transformations, which occur in one pot and which can be divided into several steps. These reactions are typical of functionalized epoxides. For example, the Meinwald rearrangement product undergoes the subsequent *in situ* transformation. Tandem reactions, including multicomponent reactions, are considered in both intramolecular and intermolecular fashions. Due to a great importance of the Friedel – Crafts reaction in the chemistry of epoxides and an insufficient systematic review on this issue, intramolecular and intermolecular tandem reactions involving this transformation are discussed in a special Section. Evidently, numerous new rearrangements can be ranked among tandem reactions, but they are described separately because it is difficult to assign them to a particular known process. The reactions, which do not fit into the proposed classification, are discussed in the Section titled 'Miscellaneous transformations of epoxides'. The reactions, in which epoxy compounds are intermediates in tandem reactions or are used *in situ* are beyond the scope of the present review. Besides, we did not aim to consider the whole chain of transformations starting with epoxides and resulting in the formation of interesting structures through numerous steps. Hence, we present only reactions directly involving the epoxide ring.

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Translation: T.N.Safonova

The discussion of the practical significance of epoxides begins with the brief consideration of their role as drugs and natural products, where we partially employ the data summarized in the review[6] published in 2020. Then we present parts of the syntheses of natural products and drugs involving epoxides. These data are summarized and analyzed for the first time. Rather recently, the fields of practical applications of epoxides were extended by the addition of their use for the utilization of the industrial waste gases, carbon monoxide and carbon dioxide, resulting in the simultaneous formation of valuable materials and reagents for organic chemistry such as β-lactones, polymeric and cyclic carbonates, cyclic and acyclic carbamates, *etc*. Unusual and conventional polymerization reactions and new trends in their development are briefly considered relying on the reviews.[7–9]

## 2. Methods for the synthesis of epoxides

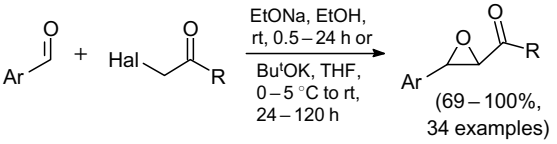
Currently, the synthesis of epoxides is most commonly based on conventional methods or their modifications. Meanwhile, new reactions, which are difficult to assign to a particular known method, were also discovered. This Section presents recent studies of name reactions, although this assignment is often very conditional. Subsections are titled according to the reactions used in the synthesis of epoxy compounds and are arranged in chronological order according to the date of their discovery. Unique methods, which do not fit into the proposed classification, are included in a special Subsection. Recent review studies on each method for the synthesis of epoxides (if they are available) are presented. The methods for the synthesis of epoxides published in 2015, 2016 and 2017 were systematically considered by Badenock in the reviews,[10–12] respectively.

### 2.1. Darzens condensation

The Darzens condensation is the reaction of aldehydes or ketones with α-mono- or dihalocarbonyl compounds in the presence of bases giving epoxides or dicarbonyl compounds.

This condensation reaction of aromatic aldehydes with α-halocarbonyl compounds in the presence of sodium ethoxide afforded *trans* isomers of 2-aryl epoxy aryl ketones[13] and also esters[14] and amides[15–17] of 3-arylglycidic acid (Scheme 1).

**Scheme 1**

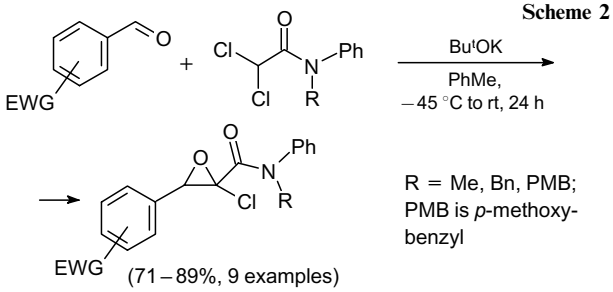



Hal = Cl, Br; R = Ar, NHAr, $NH_2$, OMe

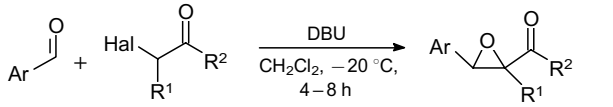
2-Chloro-3-arylglycidic acid anilides can be prepared from aromatic aldehydes and dichloroacetic acid anilides under Darzens condensation conditions only if the aldehyde contains an electron-withdrawing group (EWG) and the anilide contains the protectimg group at the nitrogen atom (Scheme 2).[17]

Tang and co-workers[18] used 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base in the condensation of aromatic aldehydes with cyclic and acyclic α-chloroketones to prepare 2-aryl epoxy aryl ketones (Scheme 3).

**Scheme 2**



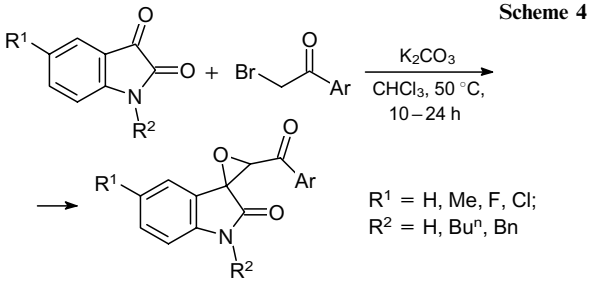

**Scheme 3**




Hal = Cl, Br; $R^1$ = H, Me; $R^2$ = Alk, Ph

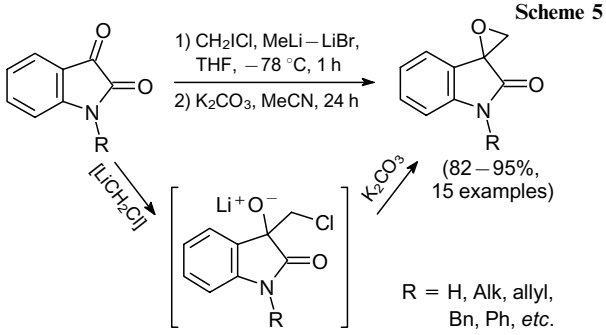
Fu and Yan[19] synthesized spiro epoxyoxindoles from isatin derivatives and α-bromoacetophenones in the presence of potassium carbonate as a base catalyst (Scheme 4).

**Scheme 4**




The reaction of N-protected isatins with $LiCH_2Cl$, generated *in situ* from chloroiodomethane and a mixture of MeLi and LiBr, in the presence of potassium carbonate affords spiro epoxyoxindoles also *via* the Darzens condensation (Scheme 5).[20]

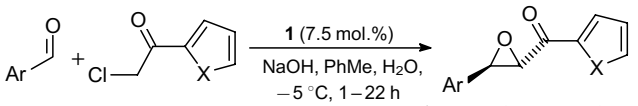
**Scheme 5**



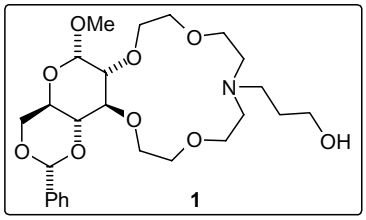

In modern organic chemistry, great attention is paid to the Darzens condensation involving chiral organic and organometallic catalysts, which are applied to prepare enantiopure epoxy compounds.[21] Examples of these reactions are given below.

Bako and co-workers used chiral crown ether **1** as the phase transfer catalyst in the condensation of aromatic

**Scheme 6**




X = O, S, NH, NMe

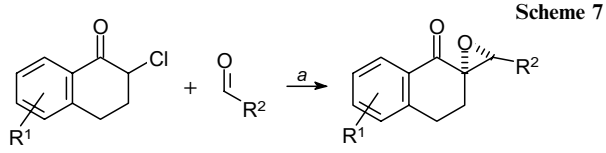


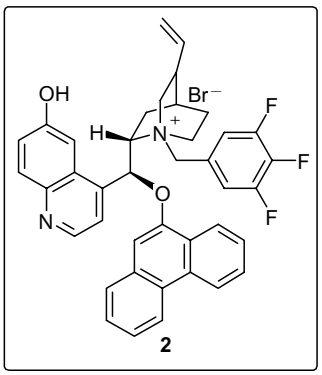

*ee* is enantiomeric excess

aldehydes with aromatic[22−24] and heteroaromatic (Scheme 6)[25,26] chloromethyl ketones giving the corresponding chiral epoxy compounds.

Deng and co-workers[27] (Scheme 7) and Siva and co-workers[28] performed the condensation of aldehydes with cyclic chlorocarbonyl compounds in the presence of quinone derivative **2** as the chiral catalyst to form spiroepoxy compounds with good enantioselectivity.

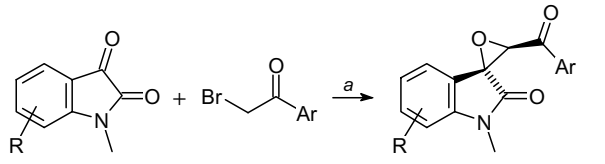
**Scheme 7**



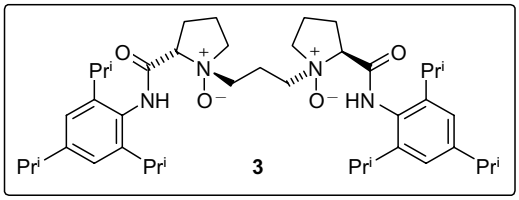




(*a*) **2** (10 mol.%), LiOH, $H_2O$, $CH_2Cl_2$, 0 °C, 72 h;
$R^1$ = H, 4-OMe;
$R^2$ = Alk, Ar, 1- and 2-naphthyl (Naph)

**Scheme 8**



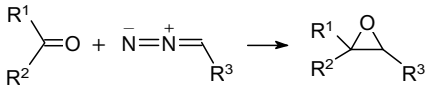

(*a*) $Co(acac)_2$−**3** (10 mol.%), $K_3PO_4$, $K_2HPO_4$, THF, $Me_2CO$, −30 °C, 48−72 h; acac is acetylacetonate;
R = H, 5-Me, 7-Me, 5,7-$Me_2$, 5-OMe, 5-F, 7-F, 7-Cl, 6-Br, 7-Br, 6,7-$(CH_2)_4$




## 2.2. Büchner–Curtius–Schlotterbeck reaction

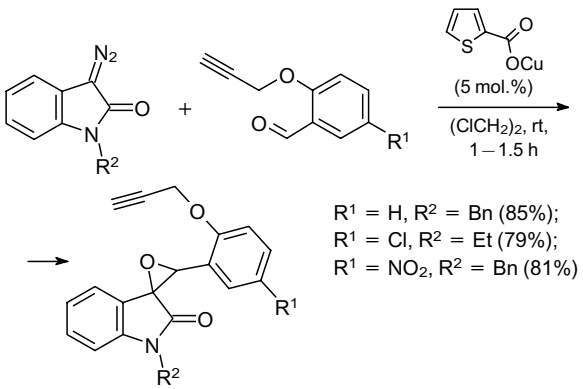
The Büchner–Curtius–Schlotterbeck reaction is the reaction of aldehydes or ketones with diazo derivatives giving epoxides (Scheme 9) or carbonyl compounds.[30]

**Scheme 9**




Muthusamy *et al.*[31] synthesized spiro epoxyoxindoles from N-protected 3-diazoindolin-2-ones with 2-propoxybenzaldehyde (Scheme 10).

**Scheme 10**

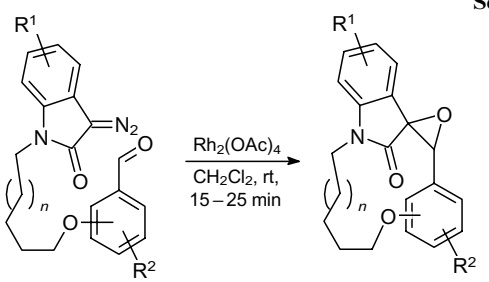



$R^1$ = H, $R^2$ = Bn (85%);
$R^1$ = Cl, $R^2$ = Et (79%);
$R^1$ = $NO_2$, $R^2$ = Bn (81%)

This research group[32] also performed the rhodium acetate-catalyzed intramolecular Büchner–Curtius–Schlotterbeck reaction and prepared macroheterocycles containing the epoxide moiety (Scheme 11).

This reaction is successfully used in the asymmetric synthesis catalyzed by complexes with chiral ligands. Thus, Wong and co-workers[33] prepared chiral 3-substituted glycidic acid anilides from aldehydes and diazoacetic acid

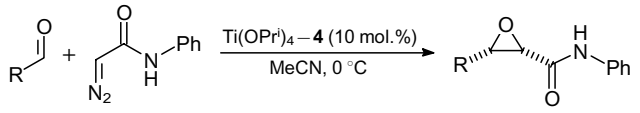
**Scheme 11**



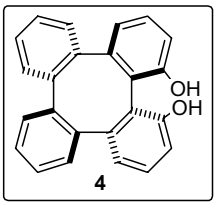

*n* = 2, 4, 5, 6, 8

(59−71%, 10 examples)

**Scheme 12**



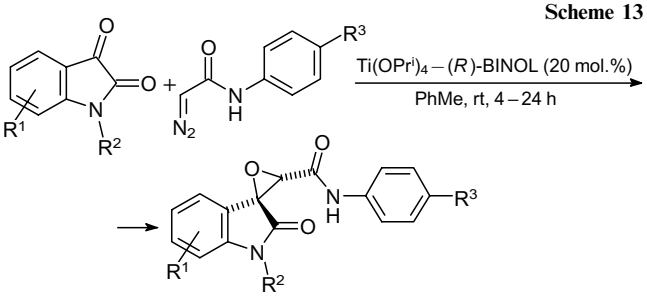

R = Alk, Cy, Bn, vinyl, 1- and 2-Naph, 2-Py; Cy is cyclohexyl, Py is pyridyl




anilides in the presence of a titanium complex with chiral tetraphenylenediol ligand **4** (Scheme 12).

This research group [34] applied a titanium complex with (*R*)-1,1′-binaphthyl-2,2′-diol [(*R*)-BINOL] in the synthesis of spiro epoxyoxindoles from isatins and diazoacetic acid anilides (Scheme 13). Gong and co-workers [35] carried out similar reactions in the presence of a chiral zirconium complex catalyst.

**Scheme 13**




$R^1$ = H, 5-Me, 5-OMe, 5-$NO_2$, 5-$OCF_3$, 5-Hal (F, Cl, Br, I), 6-Br, 7-Br, 7,5-$Me_2$, Cl; $R^2$ = Me, Bn, PMB, $CH_2C_6H_4F$-4; $R^3$ = H, OMe

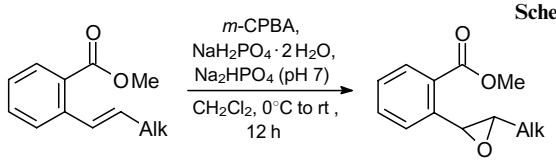
The Büchner – Curtius – Schlotterbeck reaction, like the Darzens reaction, is generally employed to prepare functionalized epoxy compounds and in the asymmetric synthesis catalyzed by complexes with chiral ligands.

## 2.3. Prilezhaev epoxidation

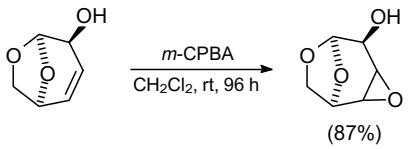
The double bond oxidation with peroxy acids is known as the Prilezhaev reaction. *m*-Chloroperoxybenzoic acid (*m*-CPBA) is most commonly used for the epoxidation of unsaturated compounds. Examples of the oxidation of *o*-vinyl benzoates,[36] levoglucosenol,[37] chiral cyclohexenol [38] and glycosylated allylic alcohol [39] under these conditions are presented in Schemes 14 – 17, respectively.

Wipf and co-workers [40] reported a one-pot synthesis, involving the ring closing metathesis (RCM) in the presence of a Grubbs catalyst and the oxidation of a double bond in

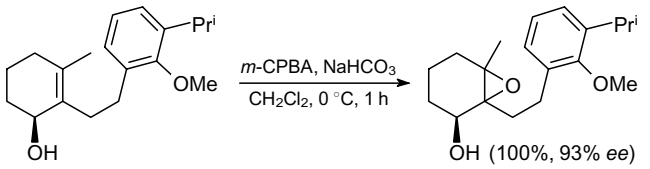
**Scheme 14**



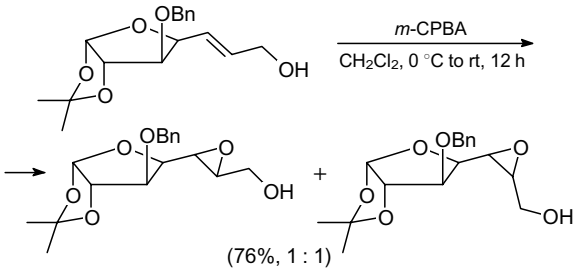

**Scheme 15**



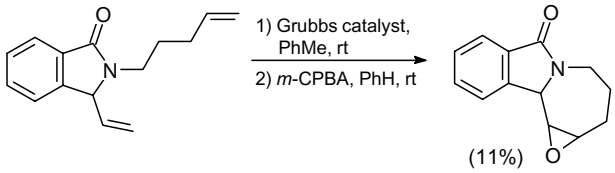

**Scheme 16**




**Scheme 17**




**Scheme 18**




the tetrahydroazepine moiety of the resulting fused tricyclic compound with *m*-chloroperoxybenzoic acid (Scheme 18).

Salmi and co-workers [41] performed the kinetic modeling of the epoxidation of oleic acid with peracetic acid in a recycled reactor system under conventional heating and microwave irradiation (MW).

An analysis of the recent studies demonstrated that the Prilezhaev reaction is extensively used for the selective double bond oxidation in polyfunctionalized unsaturated compounds.

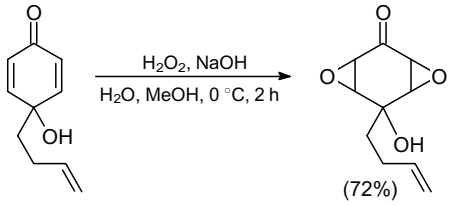
## 2.4. Weitz – Scheffer epoxidation

The oxidation of electron-deficient unsaturated compounds (generally α,β-unsaturated ketones or aldehydes) with hydrogen peroxide in a basic medium is one of the most commonly applied approaches to the epoxide ring formation, which was first described by Weitz and Scheffer.[42] Recent modifications of this method are based on the use of various electron-deficient unsaturated compounds, other peroxide compounds, including optically active ones, and chiral catalysts in this reaction and variations of the reaction conditions. The reviews published in 2011 (see Ref. 43) and 2012 (see Ref. 44) were devoted to the double bond oxidation with hydrogen peroxide under environmentally benign conditions, involving eco-friendly oxidants, *e.g.*, $H_2O_2$, in the presence of organocatalysts instead of metal complexes. The applications of chiral organocatalysts in the asymmetric epoxidation, in particular in the Weitz –

Scheffer epoxidation, are covered in a number of reviews.[1,42,45,46] The data reported since 2010, which are partially referred to in these reviews, are considered below.

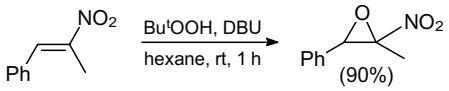
Thus, Wipf and co-workers[47] accomplished the selective epoxidation of 4-(but-3-en-1-yl)-4-hydroxycyclohexa-2,5-dien-1-one giving 4-(buten-3-enyl)-4-hydroxycyclohexadiene 2,5-diepoxide as the Weitz–Scheffer reaction product in good yield (Scheme 19).

**Scheme 19**



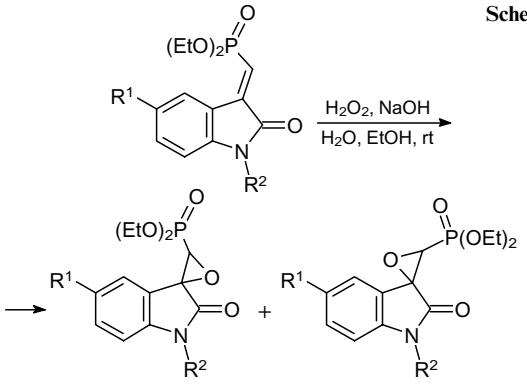

Tsogoeva's research group[48] used 2-nitro-1-phenylprop-1-ene as the electron-deficient unsaturated compound, *tert*-butyl hydroperoxide as the oxidant and DBU as the base (Scheme 20).

**Scheme 20**




Loreto and co-workers[49] performed the epoxidation of phosphonate derivatives of *trans*-ylidene oxindoles with hydrogen peroxide giving phosphonate derivatives of spiro epoxyoxindoles as a mixture of isomers with the *trans* isomer predominating (78–96% yield, the ratio from 3 : 1 to 11 : 1, 6 examples) (Scheme 21).

**Scheme 21**

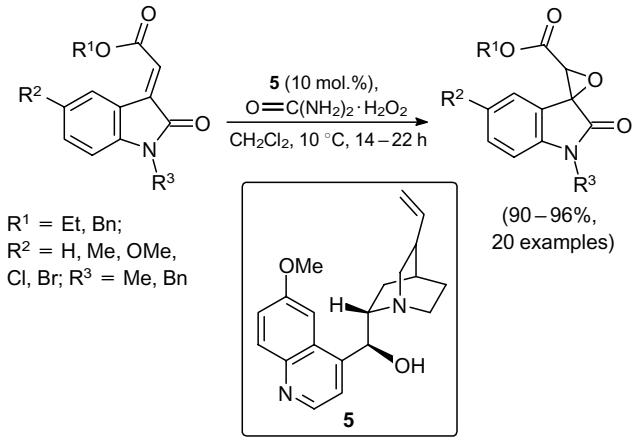



$R^1$ = H, OMe, Pr$^i$; $R^2$ = Me, Ph, Bn

Nair and co-workers[50] reported the regioselective epoxidation of alkoxycarbonyl derivatives of *trans*-ylidene oxindoles with hydroperite (hydrogen peroxide clathrate with urea) in the presence of quinine (**5**), a readily available alkaloid derived from the bark of the Cinchona tree (Scheme 22).

Dandia *et al.*[51] used cetrimonium bromide as a phase transfer catalyst under ultrasound treatment (US) for the regioselective epoxidation of *trans*-ylidene oxindole derivatives with hydrogen peroxide (Scheme 23).

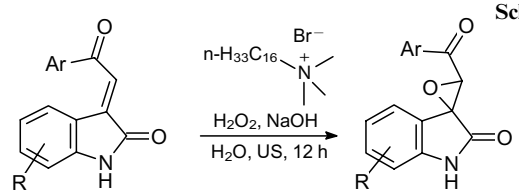
**Scheme 22**




$R^1$ = Et, Bn;
$R^2$ = H, Me, OMe, Cl, Br; $R^3$ = Me, Bn

(90–96%, 20 examples)

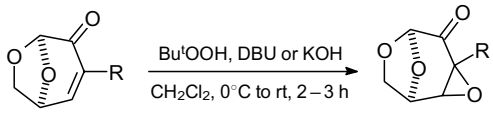
**Scheme 23**




(91–96%, 7 examples)

Ledingham and Greatrex[52] successfully applied the Weitz–Scheffer reaction to perform the epoxidation of (−)-levoglucosenone and its aryl derivatives with *tert*-butyl hydroperoxide in the presence of DBU or KOH as the base (Scheme 24).

**Scheme 24**

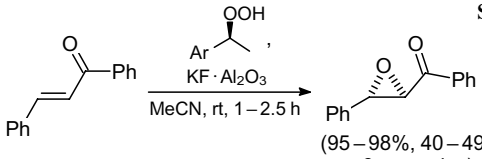



(56–93%, 6 examples)

R = H ((−)-levoglucosenone), Ar

Zilbeyaz *et al.*[53] reported the asymmetric oxidation of chalcone using enzymatically prepared chiral hydroperoxides (Scheme 25).

**Scheme 25**

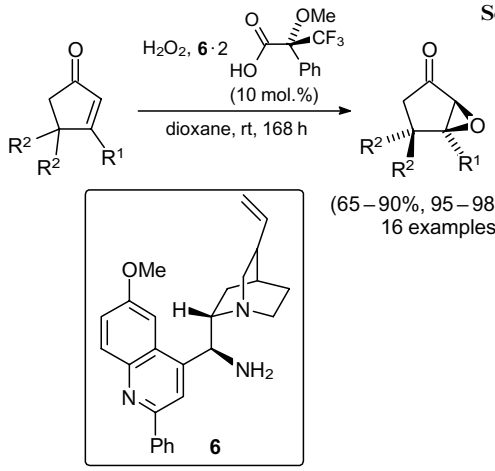



(95–98%, 40–49% *ee*; 6 examples)

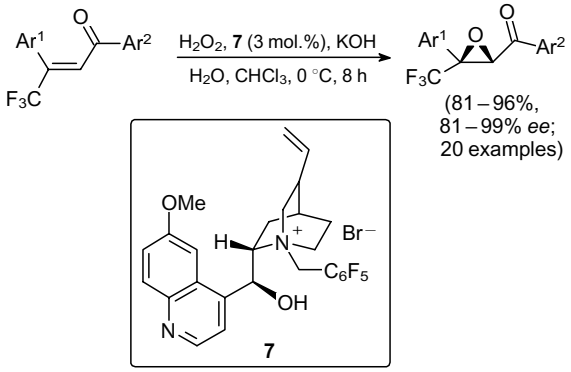
Numerous recent studies were dedicated to the asymmetric variant of the Weitz–Scheffer reaction using chiral catalysts. For this purpose, researchers employed quinine derivatives combined with trifluoroacetic acid (TFA),[54,55] Mosher acid (Scheme 26, exemplified by quinine catalyst **6**)[56] or a binaphthol phosphoric acid derivative,[54,57] as well as a thiourea derivative of this alkaloid.[58]

Chen and co-workers[59] and Shibata and co-workers[60] used quinine derivative **7** as the quaternary ammonium salt for the asymmetric epoxidation of electron-deficient alkenes (Scheme 27). In the latter study, hydrogen peroxide was

**Scheme 26**



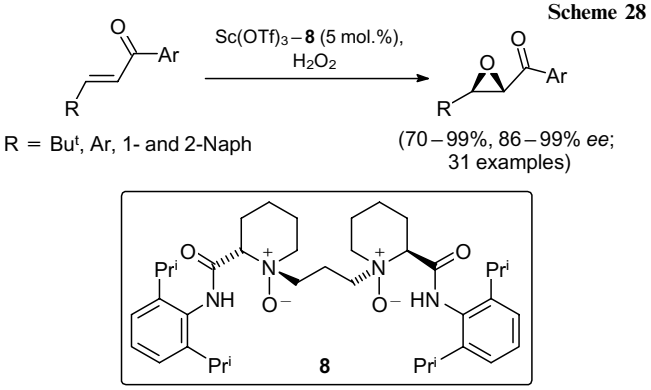

**Scheme 27**




generated *in situ* in a basic medium from methylhydrazine and atmospheric oxygen.

Feng and co-workers[61] performed the epoxidation of chalcones with hydrogen peroxide in the presence of a scandium triflate complex catalyst with chiral ligand **8** (Scheme 28).

**Scheme 28**

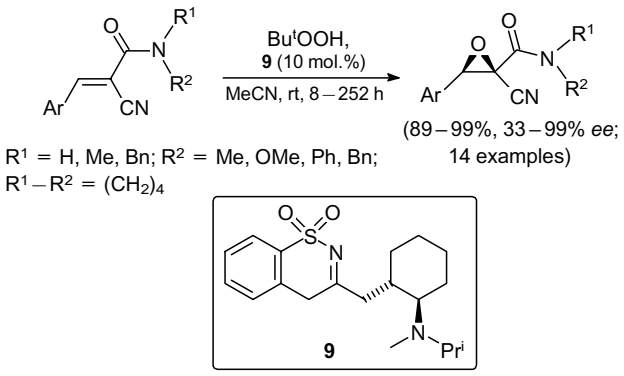



Chiral organocatalysts, *e.g.*, compound **9**, were applied by research groups headed by Takemoto (Scheme 29)[62] and Bako[25] to perform the epoxidation of *tert*-butyl hydroperoxide with various electron-deficient alkenes.

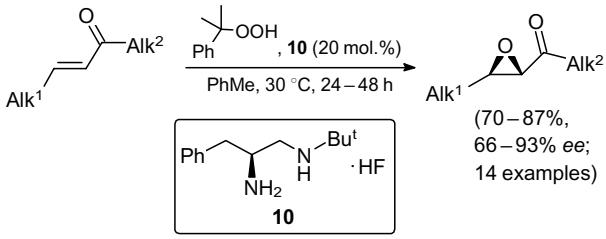
The epoxidation of acrolein derivatives[63] and α,β-unsaturated ketones (Scheme 30)[64] was successfully carried out using cumene hydroperoxide in the presence of chiral diimine catalysts, *e.g.*, salt **10**.

In recent years, catalysts based on the chiral amino alcohol prolinol were extensively used in the Weitz–

**Scheme 29**

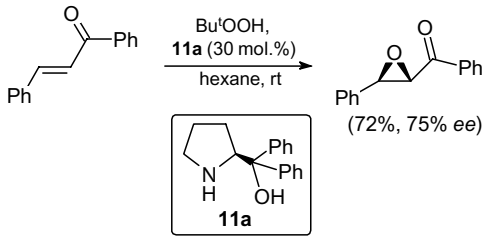



**Scheme 30**

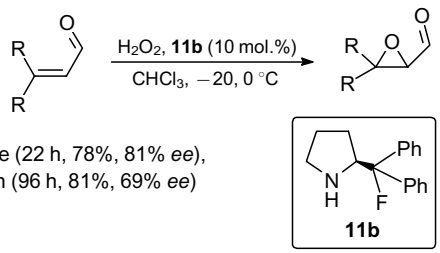



Scheffer reaction. In 2005, Jorgensen and co-workers[65] applied this catalyst for the first time for the asymmetric epoxidation of α,β-unsaturated aldehydes with hydrogen peroxide. Since then, the epoxidation of electron-deficient alkenes with hydrogen peroxide[66–69] or *tert*-butyl hydroperoxide[70–74] was accomplished in the presence of prolinol derivatives.[66,67,69–74] Scheme 31 presents an example of the epoxidation of chalcone catalyzed by prolinol **11a**;[70] epoxy derivatives of unsaturated aldehydes were prepared in the presence of its fluorine analogue, (*S*)-2-(fluorodiphenylmethyl)pyrrolidine (**11b**) (Scheme 32).[68]

**Scheme 31**



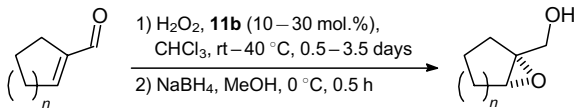

**Scheme 32**




Proline catalysts are successfully used in one-pot syntheses. Gilmour and co-workers[68] epoxidized cycloalkene aldehydes in the presence of fluoride **11b** as the catalyst followed by the reduction of the aldehyde group to an alcoholic moiety (Scheme 33).

The one-pot synthesis involving the epoxidation of α,β-acroleins in the presence of prolinol silyl ether deriva-

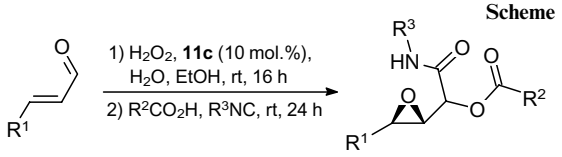
**Scheme 33**




(43–68%, 83–98% *ee*; 5 examples)

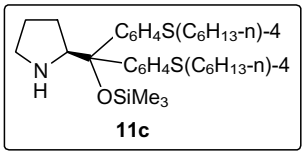
$n$ = 1–4, 10

**Scheme 34**




$R^1$ = n-$C_7H_{15}$, $C_6H_4NO_2$-2;
$R^2$ = Pr, Ar, pyrrolidin-2-yl;
$R^3$ = Bu$^t$, Cy, Bn

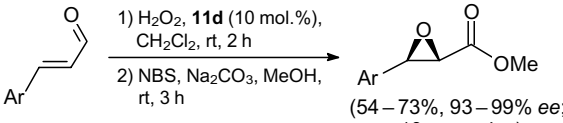
(53–75%, up to 98% *ee*; 6 examples)




tive **11c** followed by the Passerini reaction (Scheme 34) was described in the studies.[66, 75]

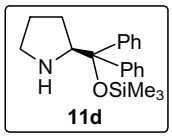
Xuan *et al.*[76] accomplished the epoxidation of aldehydes with hydrogen peroxides in the presence of catalyst **11d** and esterification in a one-pot fashion (Scheme 35).

**Scheme 35**




(54–73%, 93–99% *ee*; 10 examples)

NBS is *N*-bromosuccinimide



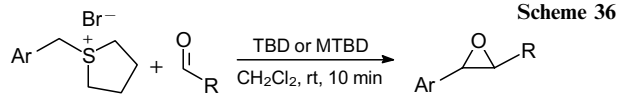

As can be seen from the literature data, the current trends in the use of the Weitz–Scheffer reaction are aimed at the improvement of environmental friendliness and the increase in the enantioselectivity of asymmetric synthesis by selecting the appropriate organocatalysts.

## 2.5. Johnson–Corey–Chaykovsky method

The Johnson–Corey–Chaykovsky method is based on the reaction of carbonyl compounds with sulfonium and sulfoxonium ylides, which are often derived *in situ* from sulfonium or sulfoxonium halides containing the mono- or disubstituted methyl group. The substituents at the methyl groups become substituents on the epoxide ring, and the adjacent position bears substituents of the carbonyl compound. In modern modifications of the Johnson–Corey–Chaykovsky reaction, sulfonium and sulfoxonium ylides are generated *in situ* from halides and other sulfonium and sulfoxonium salts in the presence of bases.

Graham and co-workers[77] reported the regioselective synthesis of *trans*-epoxides, promoted by the guanidine bases 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), starting from benzyltetrahydrothiophenium bromide and aldehydes (Scheme 36)[77, 78] or alcohols, which are oxidized *in situ* to aldehydes using manganese(IV) oxide or barium manganate (Scheme 37).

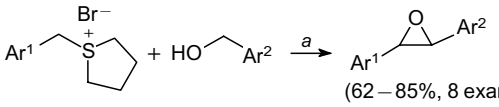
**Scheme 36**




R = Alk, Ar, 2-Fu; Fu is furyl

(38–100%, 10 examples)

**Scheme 37**

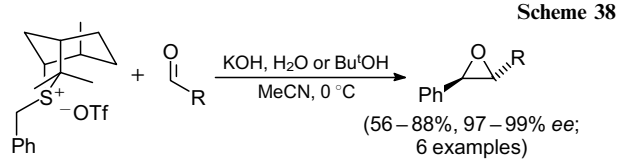


(*a*) $MnO_2$, TBD, $CHCl_3$, Δ, 6 h or $BaMnO_4$, TBD, MeCN, 60 °C, 30 min

(62–85%, 8 examples)

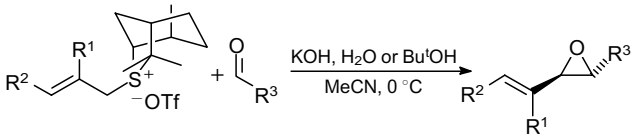
Aggarwal and co-workers[79] performed the Johnson–Corey–Chaykovsky reaction with sulfonium salts based on chiral isothiocineole containing benzyl or allyl groups. This reaction afforded epoxides with good regio- and enantioselectivity (Scheme 38).

**Scheme 38**




(56–88%, 97–99% *ee*; 6 examples)

R = Alk, vinyl derivatives, Ph




$R^1$ = H, Me; $R^2$ = H, Ph; $R^3$ = Cy, Ph

(77–97%, 85–99% *ee*; 5 examples)

Teran and co-workers[80–82] synthesized *trans* isomers of glycidic acid amides with retention of asymmetric centers by the reaction of sulfonium salts containing various chiral amide moieties (Scheme 39).

Sarabia *et al.*[83] employed chiral cyclic sulfone annulated to the oxazolidine ring in the Johnson–Corey–Chaykovsky reaction (Scheme 40).

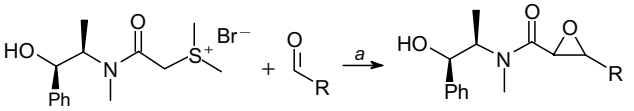
Zefirova's research group[84] converted the cyclohexanone moiety into the spiro-fused epoxycyclohexane moiety under these reaction conditions (Scheme 41).

Spiro epoxyoxindoles bearing the trifluoromethyl group, which is delivered to the product from the sulfonium ion, were characterized in the study[85] (Scheme 42).

The asymmetric synthesis of spiro epoxyoxindoles from *N*-methylisatins and camphor-derived chiral sulfonium salts was accomplished by Xiao and co-workers[86] (Scheme 43).

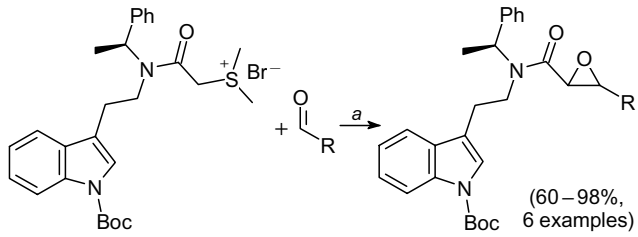
Two research groups performed three-component reactions, in which sulfonium and sulfoxonium ylides were generated *in situ* from *o*-(trimethylsilyl)phenyl triflate and sulfoxide or thioester.[87, 88] Wang and co-workers[87] used aromatic aldehydes or *N*-methylisatin as the third component in these reactions (Scheme 44). Shen and co-workers[88] synthesized a series of spiro epoxyoxindoles containing a

**Scheme 39**



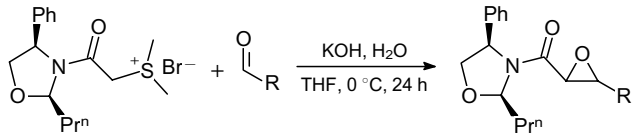

(73–93%, 9 examples)

(*a*) DBU, $CH_2Cl_2$, 0 °C to rt, 12 h; R = Alk, Ar




(60–98%, 6 examples)

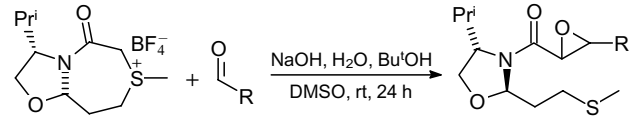
(*a*) DBU, $CH_2Cl_2$, 0 °C to rt, 8–12 h; R = Alk, Ar; Boc is *tert*-butoxycarbonyl




R = Alk, Ar

(75–95%, 15 examples)

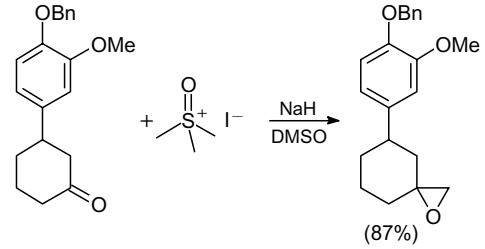
**Scheme 40**




R = Alk, Ar

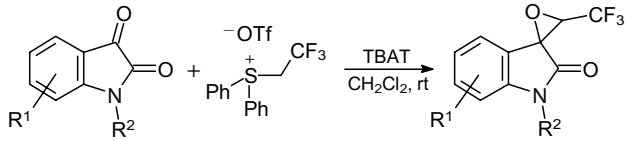
(41–89%, 14 examples)

**Scheme 41**




(87%)

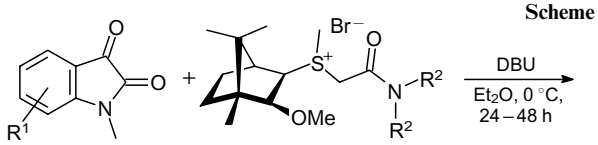
**Scheme 42**

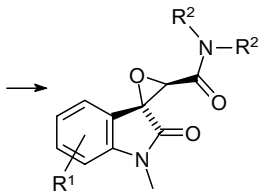



(51–95%, 14 examples)

R$^1$ = H, 5-Me, 5-OMe, 5-Hal (F, Cl, Br, I), 5-$NO_2$, *etc*;
R$^2$ = Me, Bn; TBAT is tetra-n-butylammonium difluorotriphenylsilicate

**Scheme 43**

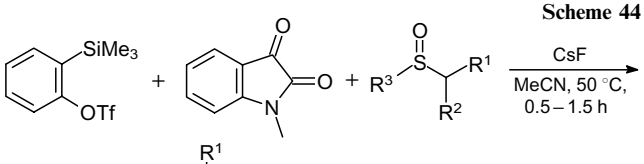


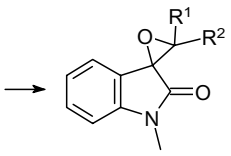




R$^1$ = H, 5-Me, 5-OMe, 7-Hal (F, Cl, Br), 7-$CF_3$, 5-$NO_2$, *etc*;
R$^2$ = Et, allyl

(70–99%, 90–96% *ee*; 14 examples)

**Scheme 44**

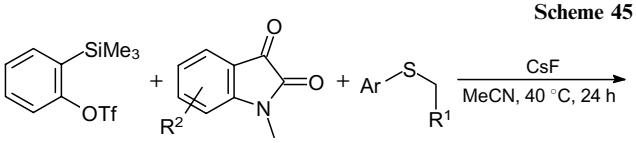


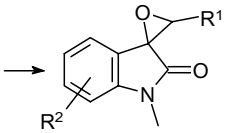




R$^1$ = H, Me; R$^2$ = Alk, Ar; R$^3$ = Pr$^i$, Ph, $C_6H_4Me$-4; Tf is trifluoromethanesulfonyl (triflyl)

(21–59%, 19 examples)

**Scheme 45**




R$^1$ = vinyl, Ar; R$^2$ = H, 5-Me, 5-OMe, 5-Hal (F, Cl, Br), 6-Hal, 7-Cl, 5-$NO_2$

(31–99%, 20 examples)

substituted benzene ring from substituted isatins (Scheme 45).

It is worth noting that the Johnson–Corey–Chaykovsky reaction allows the regioselective synthesis of epoxides bearing various substituents under mild conditions; when using chiral methyl sulfonium or methyl sulfoxonium salts, one can introduce a chiral moiety into the epoxide molecule (see Schemes 39 and 40). If a chiral moiety is directly bound to the sulfur atom, the reaction occurs in an asymmetric fashion and affords epoxy compounds containing asymmetric carbon atoms in the epoxide ring with good enantioselectivity (see Schemes 38 and 43).

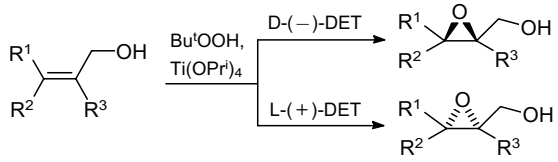
## 2.6. Sharpless epoxidation

The classical version of the Sharpless epoxidation is the enantioselective epoxidation of allylic alcohols with *tert*-butyl hydroperoxide in the presence of titanium isopropoxide and chiral diethyl tartrate (DET). The configuration of the resulting epoxide can easily be predicted according to the Sharpless rule: it correlates with the enantiomer of the tartrate used (Scheme 46).[89,90]

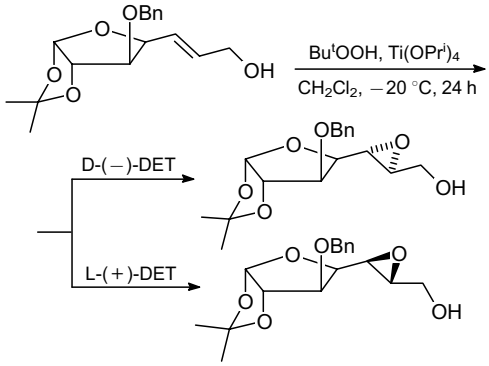
This rule is also true for the reactions with more complex systems,[39,91] in particular, with glycosylated allylic alcohol (Scheme 47).[39]

The asymmetric Sharpless epoxidation is widely used to synthesize unsaturated epoxy alcohols by the selective oxidation of the allylic double bonds in compounds containing other multiple, *e.g.* double, bonds (Scheme 48).[91]

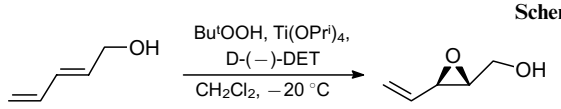
**Scheme 46**




**Scheme 47**



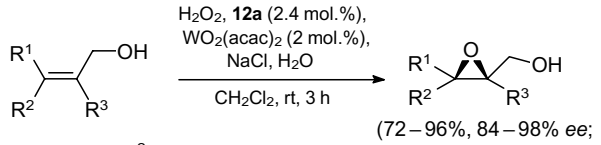

**Scheme 48**




Recent modifications of the Sharpless reaction include the use of new catalytic systems for the asymmetric epoxidation of allylic alcohols.[92–94] Below we give a number of examples, in which not only chiral catalysts but also oxidants are varied and the reactions are performed with both allylic alcohols and related structures.

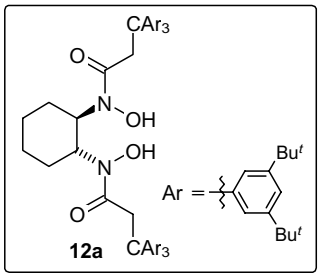
Scheme 49 demonstrates the epoxidation of allylic alcohols with hydrogen peroxide in the presence of a tungsten complex with chiral bishydroxamic acid derivative **12a**.[94]

**Scheme 49**



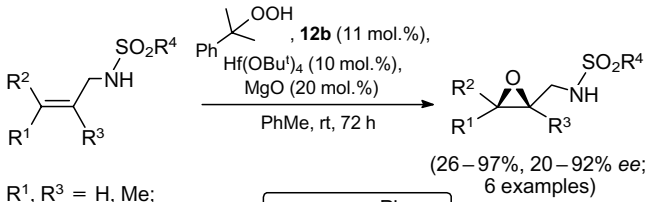

(72–96%, 84–98% *ee*; 14 examples)

$R^1$ = H, Alk, Ar; $R^2$ = H, Alk;
$R^3$ = H, Me



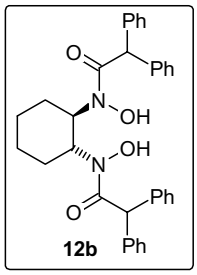

The epoxidation of allylic amines containing a sulfonyl group with cumene hydroperoxide in the presence of a hafnium complex with chiral bihydroxamic acid derivative **12b** is shown in Scheme 50.[95] The epoxidation of homoallylic amines containing an additional methylene bridge between the double bond and the functional group was performed under the same conditions.[95] Homoallylic alcohols were also epoxidized with cumene hydroperoxide in the presence of hafnium and zirconium catalysts.[96]

**Scheme 50**



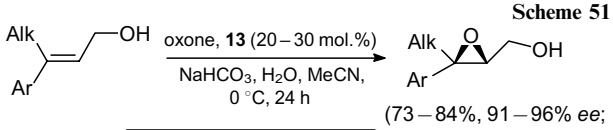

(26–97%, 20–92% *ee*; 6 examples)

$R^1$, $R^3$ = H, Me;
$R^2$ = H, Alk;
$R^4$ = Ar, $CH_2CH_2SiMe_3$

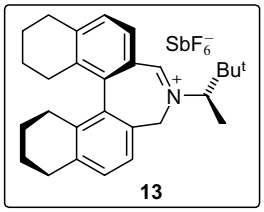



Novikov and Lacour[97] reported the enantioselective epoxidation of allylic alcohols with oxone ($KHSO_5 \cdot 0.5\,KHSO_4 \cdot 0.5\,K_2SO_4$) in the presence of chiral iminium salt **13** as the catalyst (Scheme 51).

**Scheme 51**

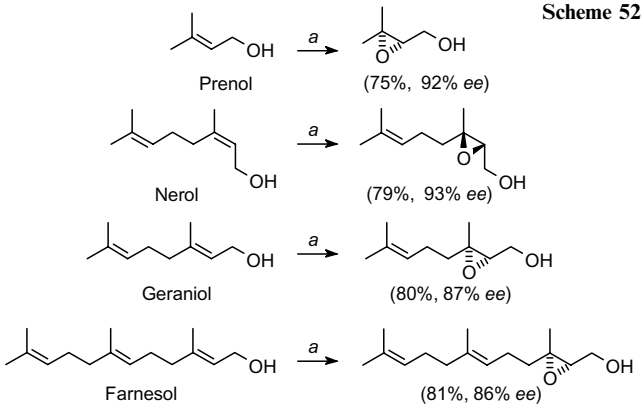



(73–84%, 91–96% *ee*; 5 examples)




Lichtor and Miller[98] accomplished the oxidation of a series of terpene alcohols with hydrogen peroxide in the presence of a peptide-based catalyst and equivalent amounts of *N*,*N*′-di(isopropyl)carbodiimide (DIC), 4-(dimethylamino)pyridine (DMAP) and 1-hydroxybenzotriazole (HOBt) comparable in the regio- and enantioselectivity with the Sharpless epoxidation (Scheme 52). Katsuki's research group[99] oxidized these terpene alcohols with hydrogen peroxide in the presence of a niobium complex catalyst.

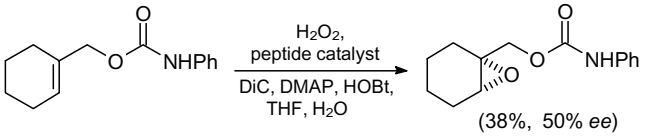
**Scheme 52**




(*a*) $H_2O_2$, peptide catalyst (10 mol.%), DIC, DMAP, HOBt, $CH_2Cl_2$, 4 °C, 7 h

A peptide catalyst was also employed in the oxidation of a double bond in cyclohex-1-en-1-ylmethyl phenylcarbamate with hydrogen peroxide (Scheme 53).[100]

**Scheme 53**

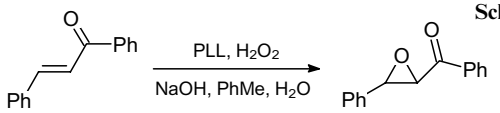



Therefore, the asymmetric Sharpless epoxidation of allylic alcohols can be applied to other structures, in particular to allylic amines and homoallylic alcohols. Currently, this reaction is performed in the presence of not only diethyl tartrate proposed by Sharpless but also other chiral organocatalysts, for example peptides, using *tert*-butyl hydroperoxide along with other oxidants, such as hydrogen peroxide (see Schemes 49, 52, 53), cumene hydroperoxide (see Scheme 50) and oxone (see Scheme 51). The selectivity of the oxidation of the allylic double bond was demonstrated for a series of terpnene alcohols (see Scheme 52).

### 2.7. Juliá – Colonna epoxidation

The Juliá – Colonna epoxidation is the asymmetric epoxidation catalyzed by chiral polyamino acids, generally by poly(L-leucine) (PLL), electron-deficient alkenes, generally chalcones, and peroxy compounds in a basic medium (Scheme 54).[44] The compound to be oxidized is dissolved in an organic solvent, most often in toluene, and the peroxide oxidant is dissolved in an aqueous alkaline medium; the reaction occurs in an insoluble polymer layer at the interface. Recent studies of this reaction were aimed mainly at the investigation of the mechanism of the catalytic effect [101–103] and modifications of catalysts.[102–106]

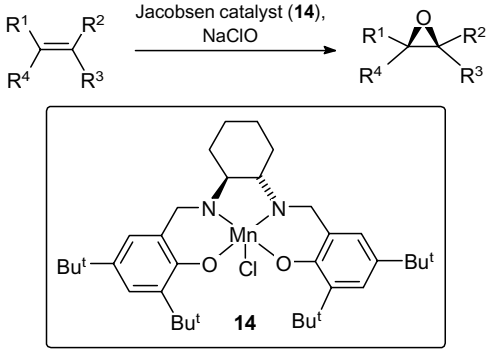
**Scheme 54**




### 2.8. Jacobsen – Katsuki epoxidation

The works by Jacobsen and Katsuki † on the epoxidation of alkenes were aimed at preparing chiral epoxy compounds. By that time, the asymmetric synthesis was not only of fundamental interest but also of practical significance because the medical industry was interested in enantiopure compounds if pharmacological agents contain a chiral center. The Jacobsen – Katsuki epoxidation was a significant supplement to the Sharpless method, which was designed for allylic alcohols and, in the classical version, is unsuitable for the epoxidation of unfunctionalized alkenes. The oxidation of alkenes with sodium hypochlorite in the presence of manganese complexes with chiral salen-type ligands (Jacobsen catalyst, **14**) is known as the Jacobsen – Katsuki epoxidation (Scheme 55).[107]

**Scheme 55**




Freire and co-workers [108, 109] and Huang and co-workers [110–113] extensively used Jacobsen catalyst for the epoxidation of alkenes. Although this catalyst provided the desired enantioselectivity of the reaction, there were problems with its regeneration, as in the case of any homogeneous catalyst. In order to overcome this drawback, heterogeneous catalysts on solid substrates (organic polymers or inorganic materials) with different porosity were developed based on Jacobsen catalyst. These catalysts also showed good catalytic activity in the enantioselective epoxidation of alkenes.[109–111, 113–117] Currently, studies are being continued on the design of new salen [118] and other ligands,[119–124] which can be coordinated to Mn, in order to use them in epoxidation reactions.‡ Iron-based complex catalysts are widely used in this reaction, which utilizes, apart from sodium hypochlorite,[125] oxone [126] and dioxygen [127–129] as oxidizing agents. Kuhn and co-workers [130] applied molybdenum complexes as catalysts for the epoxidation of alkenes; Notestein and co-workers,[131] heterogeneous catalysts based on calixarene complexes of Group IV and V metals (hydrogen peroxide served as the oxidizing agent). Moghadam and co-workers [132] performed the epoxidation of alkenes with sodium periodate in the presence of a zeolite-encapsulated ruthenium complex. The $Co(OAc)_2$-catalyzed oxidation of alkenes with hydrogen peroxide in ionic liquids was described in the study.[133] Katsuki and co-workers [134, 135] used ruthenium catalysts with a chiral salen ligand of complex structure for the asymmetric aerobic oxidation of alkenes conjugated with an aromatic system.

### 2.9. Shi epoxidation

Shi § proposed a D-fructose derivative (Shi ketone, **15**) for the catalysis of the asymmetric oxidation of alkenes with oxone (Scheme 56).

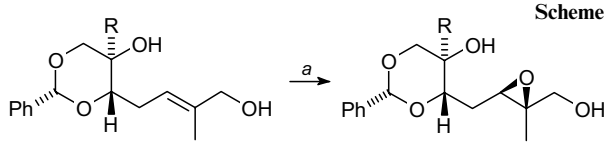
As opposed to the Jacobsen – Katsuki method, which gave products in good yields with good enantioselectivity in the epoxidation of *cis*-olefins, often being inefficient with respect to the *trans* isomers, the Shi method and its modifications allowed the epoxidation of *trans*-alkenes, allylic and homoallylic alcohols, conjugated dienes and enynes, unsaturated esters and ethers giving products in high yields with high enantioselectivity. This reaction proved to be sensitive to the pH of the medium, and one should pay special attention to this parameter when choosing the reaction conditions in order to avoid decomposition

† E.N.Jacobsen, W.Zhang, A.R.Muci, J.R.Ecker, L.Deng. *J. Am. Chem. Soc.*, **113**, 7603 (1991); E.N.Jacobsen. In *Catalytic Asymmetric Synthesis*. (Ed. I.Ojima). (1st Edn). (New York: Wiley-VCH, 1993). Ch. 4.2; T.Katsuki. In *Catalytic Asymmetric Synthesis*. (Ed. I.Ojima). (2nd Edn). (New York: Wiley-VCH, 2000). Ch. 6B.

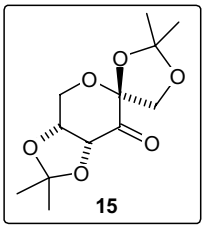
‡ The references are given on the studies of metal-containing complex catalysts for the epoxidation, even if the ligand in these complexes is not chiral.

§ Z.X.Wang, Y.Tu, M.Frohn, J.R.Zhang, Y.Shi. *J. Am. Chem. Soc.*, **119**, 11224 (1997).

**Scheme 56**



(*a*) oxone, Shi ketone (**15**) (25 mol.%), pH 9.3, $K_2CO_3$, AcOH, KOH, $CH_2(OMe)_2$, MeCN, −10 °C, 3 h; R = H, Me

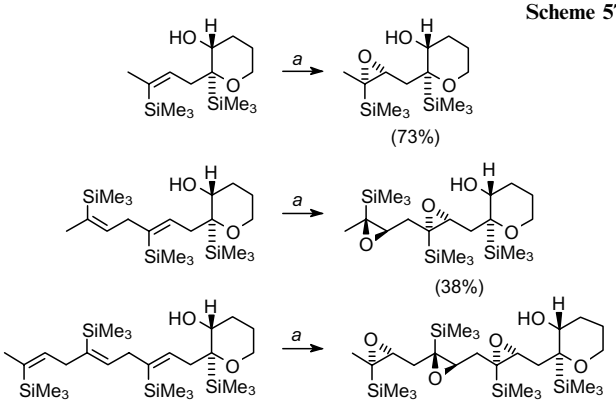


**15**

of the catalyst and prevent side reactions. A mixture of dimethoxymethane and acetonitrile is most often used as the solvent for the catalyst and the reagent, while oxone is dissolved in water and is transferred to the organic phase by tetra-*n*-butylammonium sulfate.[107]

The Shi epoxidation is often applied in the synthesis of ladder polyethers of natural origin (see the Section on the synthesis of natural products). Scheme 57 presents the epoxidation step in the path to such products.[136, 137]

**Scheme 57**

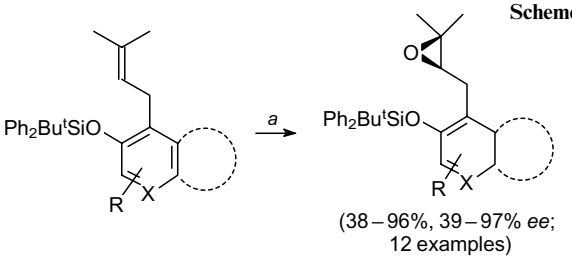


(*a*) oxone, Shi ketone (**15**), buffer, $Bu^n_4NHSO_4$, $CH_2(OMe)_2$, MeCN, rt, 20 min

Hamada's research group[138] used this reaction to oxidize allylic aromatic and heteroaromatic compounds containing a protected hydroxy group in the *ortho* position (Scheme 58).

The Shi epoxidation gave rise to the development of organocatalysis in the asymmetric synthesis of epoxides, which is described, for example, in the reviews.[2, 44, 46] Recent original studies, which are referred to in these reviews and were concerned with the organocatalyzed asymmetric epoxidation of allylic alcohols and related

**Scheme 58**

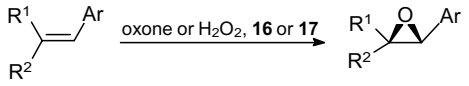


(38–96%, 39–97% *ee*; 12 examples)

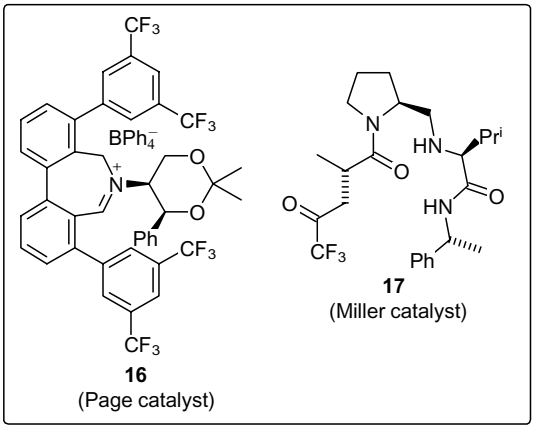
(*a*) oxone, Shi ketone (**15**) (15 mol.%), pH 6, $Bu^n_4NHSO_4$, $CH_2(OMe)_2$, MeCN, 0 °C, 24 h; X = CH, N; R = H, Cl, $Bu^t$, NHBoc, *etc.*

structures, supplement the data in Section 2.6 devoted to the Sharpless epoxidation. In this Subsection, mention should be made of the following studies, in which chiral organocatalysts (apart from the Shi catalyst) are employed in the epoxidation reactions of unfunctionalized alkenes. Thus, Page and co-workers[139, 140] proposed iminium salts **16** as catalysts for the asymmetric oxidation of alkenes with oxone. Romney and Miller[141] performed the epoxidation of alkenes with hydrogen peroxide in the presence of chiral peptide catalyst **17** bearing the trifluoromethylcarbonyl moiety (Scheme 59).

**Scheme 59**



$R^1$ = H; $R^2$ = H, Me, Ph; $R^1-R^2$ = $(CH_2)_n$ (*n* = 3, 4)



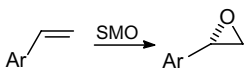
**16** (Page catalyst)

**17** (Miller catalyst)

## 2.10. Biocatalysis in the synthesis of epoxides

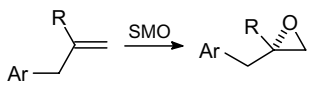
Biocatalysis described in the review papers[142, 143] is a version of the asymmetric synthesis of epoxides. Without going into detail of this highly specialized research area, we will give only examples of these reactions reported by Wu and co-workers.[144, 145] In these studies, olefins conjugated with an aromatic system (Scheme 60) and non-conjugated olefins (Scheme 61) were oxidized with styrene monooxygenase (SMO). It was found that the yields and enantioselectivity of the reactions is higher in the case of conjugated systems.

**Scheme 60**



(77–100%, > 99% *ee*; 4 examples)

**Scheme 61**



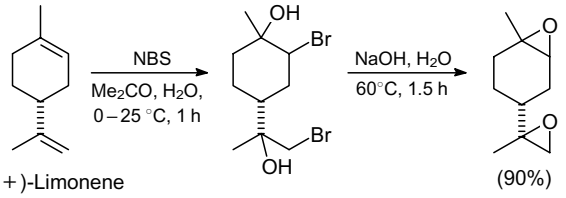
R = H, Me

(5–38%, 13–86% *ee*; 5 examples)

## 2.11. Miscellaneous methods of synthesis of epoxides

This Subsection presents the data on unique reactions giving epoxy compounds radically different from those described above. For example, Saleem and co-workers[146] synthesized a diepoxide compound by the reaction of

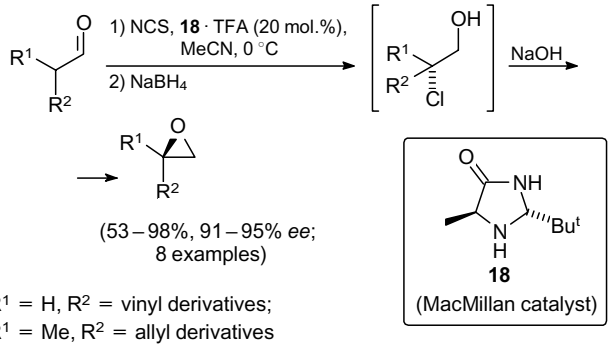
**Scheme 62**




(*R*)-(+)-limonene with *N*-bromosuccinimide followed by the treatment of the reaction mixture with a sodium hydroxide solution (Scheme 62).

Christmann and co-workers [147] performed the one-pot asymmetric synthesis of epoxides from acetaldehydes. This synthesis combines the chlorination of acetaldehydes with *N*-chlorosuccinimide (NCS) in the presence of chiral MacMillan catalyst (**18**), the reduction of the carbonyl group with sodium borohydride and the dehydrochlorination with NaOH (Scheme 63).

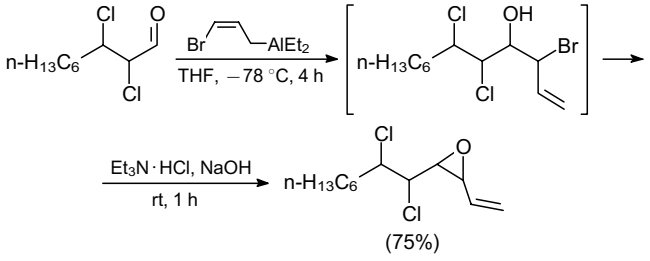
**Scheme 63**




$R^1$ = H, $R^2$ = vinyl derivatives;
$R^1$ = Me, $R^2$ = allyl derivatives

The regioselective one-pot synthesis of vinyl-containing epoxide described by Vanderwal and co-workers [148] involves the bromoallylation of aldehyde with (3-bromoallyl)diethylaluminium and the dehydrobromination of the corresponding intermediate (Scheme 64).

**Scheme 64**

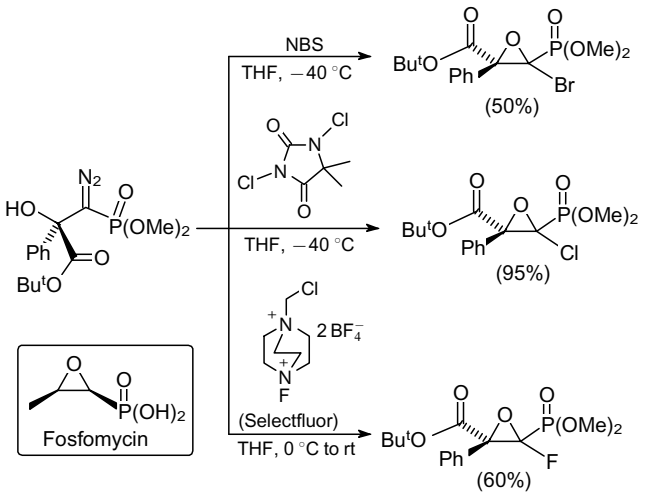



Peng and co-workers [149] developed synthetic routes to halogenated analogues of the broad-spectrum antibiotic fosfomycin from chiral β-hydroxy-α-diazophosphonate by the reaction with various halogenating agents (Scheme 65).

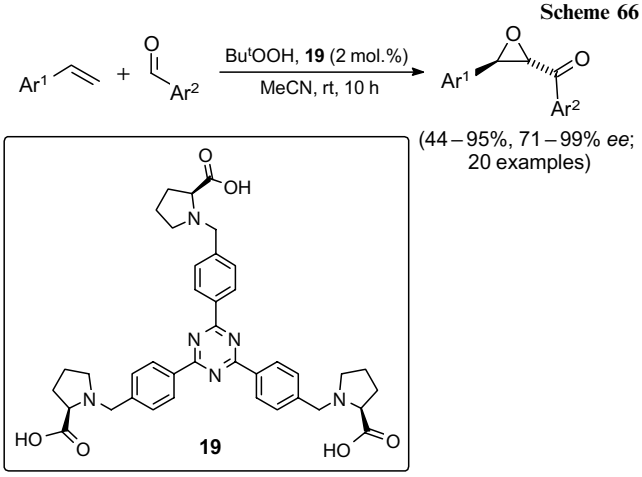
Ashokkumar and Siva [150] reported the tandem oxidative coupling of styrenes with aromatic aldehydes in the presence of chiral organocatalyst **19** containing three proline residues, resulting in the formation of epoxides in a regio- and enantioselective fashion (Scheme 66).

Biju and co-workers [151] synthesized trisubstituted *N*-aryl-α-amino epoxides by the three-component reaction

**Scheme 65**



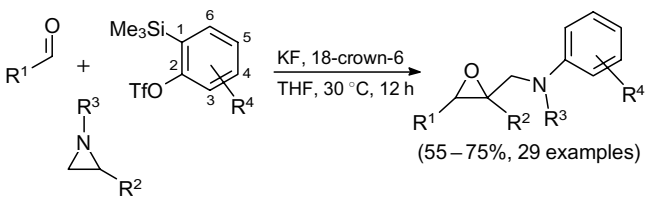

**Scheme 66**




of aldehydes with N-protected aziridines containing an electron-withdrawing substituent and *o*-(trimethylsilyl)-phenyl triflates (Scheme 67). The related reactions using N-substituted isatins instead of aldehydes diastereoselectively afford spiro epoxyoxindoles containing the amino moiety in the α position with respect to the epoxide ring (Scheme 68). The mechanism of these reactions involving dehydrobenzenes (benzynes) generated from *o*-(trimethylsilyl)phenyl triflates is presented in Scheme 69.

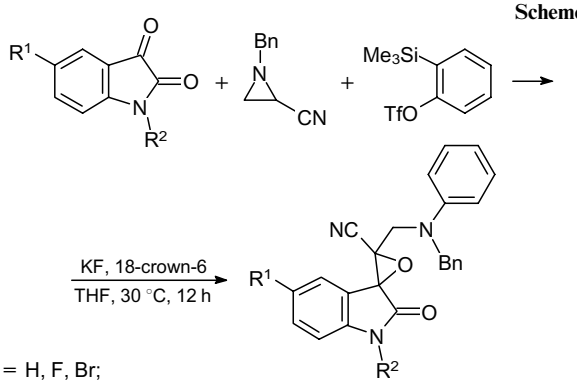
An unusual method for the synthesis of a wide range of functionalized epoxy compounds in the presence of tris(dimethylamino)phosphine was developed by Zhou and Gao.[152] Various dicarbonyl compounds, including isatins and α-keto esters, served as one reagent; ketones or alde-

**Scheme 67**

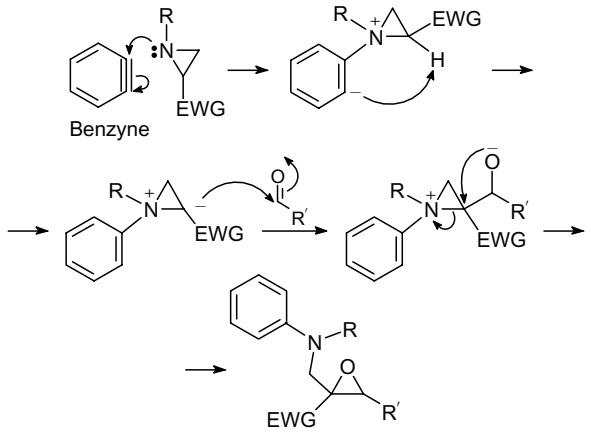



$R^1$ = Alk, Cy, Bn, Ar; $R^2$ = CN, $CO_2$Alk; $R^3$ = Alk, Cy, Bn;
$R^4$ = H, 3-Me, 4-F, 4,5-$Me_2$, 4,5-$F_2$, 4,5-$(CH_2)_3$, 4,5-$OCH_2O$

**Scheme 68**

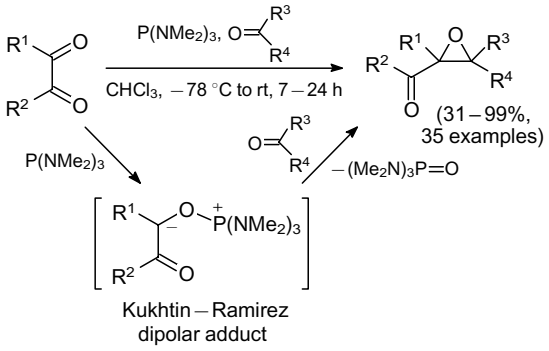



**Scheme 69**




hydes, as another one. The reaction occurs through the formation of the dipolar Kukhtin–Ramirez adduct and is accompanied by the conversion of the phosphorus atom into the pentavalent state *via* the abstraction of an oxygen atom from the adduct in the reaction with aldehyde or ketone (Scheme 70). The reaction with isatin derivatives as dicarbonyl compounds afforded spiro epoxyoxindoles. This reaction was tested using a wide variety of both carbonyl reagents and is versatile for the synthesis of functionalized epoxides.

**Scheme 70**




Summarizing the data presented in this Section, it is worth noting that epoxides can be synthesized using, apart from the classical name reactions, other methods, which often involve several reactions occurring in a tandem or one-pot fashion.

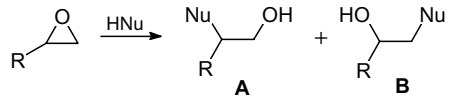
## 3. Chemical transformations of epoxide compounds

The transformations of epoxy compounds, as well as their synthesis, are summarized in a number of review publications. For example, three reviews by Badenock [10–12] cover the studies on these issues published in 2015–2017. Other review studies will be mentioned in the course of this review. This Section begins with the data on the nucleophilic epoxide ring-opening, the discussion of the regioselectivity of the formation of 1,2-bifunctional compounds and the considerations of examples of the asymmetric synthesis, desymmetrization of *meso* structures and kinetic resolution. Then rearrangements commonly encountered in the chemistry of epoxy compounds, such as tandem and one-pot reactions, both intramolecular reactions for functionalized epoxides and intermolecular reactions, are discussed. Particular attention is given to the Meinwald rearrangement and the Friedel–Crafts reaction, which play a great role in the chemistry of epoxy compounds. The role of epoxide derivatives in the construction of carbo- and heterocyclic structures is demonstrated and multicomponent reactions involving epoxides are considered. The reduction, oxidation, deoxygenation and electrophilic epoxide ring-opening reactions will be discussed at the end of the Section.

### 3.1. Nucleophilic epoxide ring-opening

The epoxide ring-opening with nucleophiles (NuH) in unsymmetrically substituted epoxides can afford two regioisomeric products (Scheme 71). The reaction pathway depends on numerous factors, such as the nature of substituents and the nucleophile, the reaction medium and the catalyst used. Despite a long history of investigation of this reaction, it still attracts the attention of researches, and this reaction with epoxides has been extensively studied in the past decade.

**Scheme 71**




In order to gain insight as to which aspects of these well-known reactions have attracted attention, the epoxide ring-opening with amines will be considered in more detail. This issue is covered in the review [153] published in 2016. When an analyzing the recent publications on this issue, the first thing to note are the efforts to select catalysts for aminolysis and with the aim of increasing the regioselectivity of this reactions. In the presence of various catalysts, the reactions of aryl epoxides with anilines afford products **A** (see Scheme 71).[154–169] However, in most studies it was noted that the reactions can give products **B** when using other reagents. For example, these products can be prepared by the reactions of aniline with phenoxymethyl epoxide,[154, 155, 157, 161, 170] isopropoxymethyl epoxide,[155, 157, 163] methyl epoxide,[156, 163] chloromethyl epoxide (epichlorohydrin) [156, 163, 165] and allyloxymethyl epoxide.[165] The effect of the substituents in epoxide and aniline on the regioselectivity of the reactions was investigated by Halimehjani's [171] and Chimni's research groups.[172] The regioselectivity and the pathway of the reactions depend on the type of the catalyst. For example, the reaction using a bismuth complex catalyst in the epoxide ring-opening of methyl epoxide and

epichlorohydrin with aniline affords a mixture of products **A** and **B** in an approximately equal ratio.[156] Gao and co-workers[169] proposed a Zr triflate catalyst grafted onto a mesoporous silicon substrate, which provides predominant formation of products **A** *via* the epoxide ring-opening of phenoxymethyl and allyloxymethyl epoxides, as well as of epichlorohydrin, with anilines.

In a number of studies, it was demonstrated that the nature of the substituent in anilines affects the regioselectivity of the epoxide ring-opening of phenyl epoxide giving products **A**.[154, 166–168] A similar result was obtained in the reaction with diethylamine.[154] However, the reactions with cycloxehyl-, piperidine- or morpholineamines lead to the epoxide ring-opening of phenyl epoxide giving products **B**,[161] although the reaction with morpholine under other conditions can afford product **A** as well.[173]

Narsaiah *et al.*[174] examined the effect of diverse amines, including heterocyclic amines, on 2-phenoxymethyl and 2-(1-maphthyloxymethyl) epoxides in the presence of cerium chloride ($CeCl_3 \cdot 7H_2O$) in glycerol. In all cases, products **B** were isolated in good yields. The epoxide ring-opening of spiro epoxyoxindoles with ammonia, aliphatic amines or anilines gives products **B**.[175, 176] However, the aminolysis of fatty acid esters containing a terminal epoxide moiety affords products **A**.[177]

The selection of conditions for the epoxide ring-opening is aimed in particular at ensuring the environmental friendliness of the reaction, *i.e.*, the possibility of the catalyst recycling and the performance of the reactions in aqueous media or under solvent-free conditions. Aghapoor and co-workers[167] developed a green version of the microwave-assisted aminolysis of epoxides under solvent-free conditions with the re-use of the catalyst, allowing a decrease in the reaction time. Many research teams carried out the aminolysis under solvent-free conditions[159, 161–168, 170, 172, 175, 178, 179] or in water.[154, 169, 174, 179, 180] The epoxide ring-opening reactions in aqueous media are considered in the review[181] published in 2011. Jamison and co-workers[182] and Jensen and co-workers[183] explored the aminolysis of epoxides in microreactor systems, which provided a significant decrease in the reaction time.

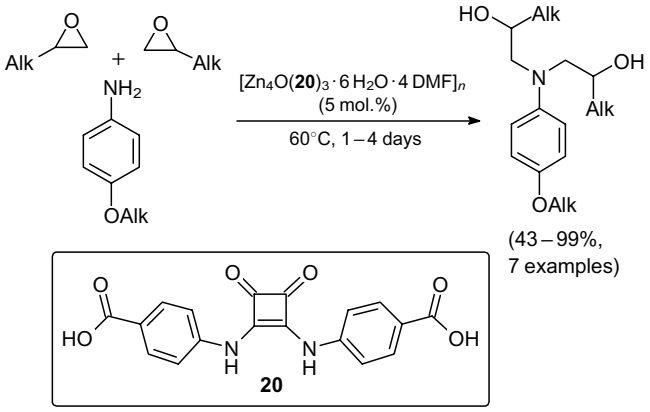
Several studies of the epoxide ring-opening with amines, which were not included in the reviews[153, 181] and the more recent review[3] published in 2018, are considered below.

Vignatti *et al.*[184] reported the ring-opening of two epoxide molecules with one aniline molecule in the presence of a metal-organic framework (MOF) based on zinc and squaramide (**20**) as the ligand (Scheme 72).

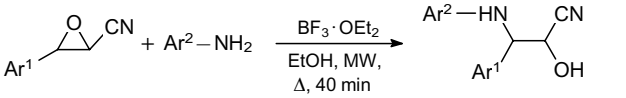
Xu and co-workers[185] performed the regio- and diastereoselective epoxide ring-opening of *trans*-3-arylglycidic acid nitriles with anilines in the presence of boron trifluoride etherate giving *anti* diastereomers of 3-anilino-3-aryl-2-hydroxypropionic acid (Scheme 73). The reaction with *cis*-3-arylglycidic acid nitriles affords a diastereomeric *syn*-configured product.

Fujinaga *et al.*[186] reported the regioselective epoxide ring-opening of $^{18}F$-isotope-labeled epifluorohydrin. The reactions with anilines, 3-aminopyridine and 3-aminoquinoline produced [$^{18}F$]-fluoroalkylated aryl- and heteroarylamines, which are valuable radionuclides for positron emission tomography imaging (Scheme 74). The synthesis using chiral [$^{18}F$]-epifluorohydrins yielded chiral products with high enantioselectivity.

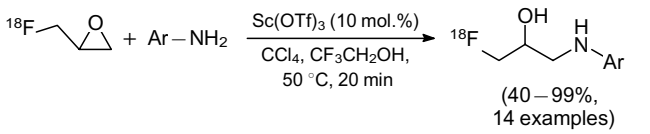
**Scheme 72**



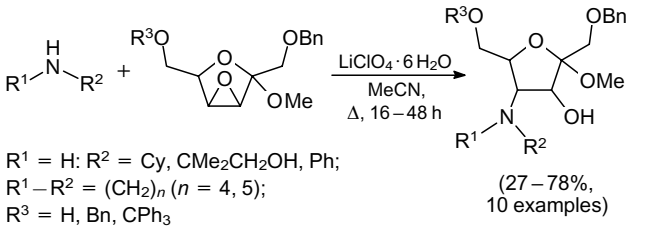

**Scheme 73**



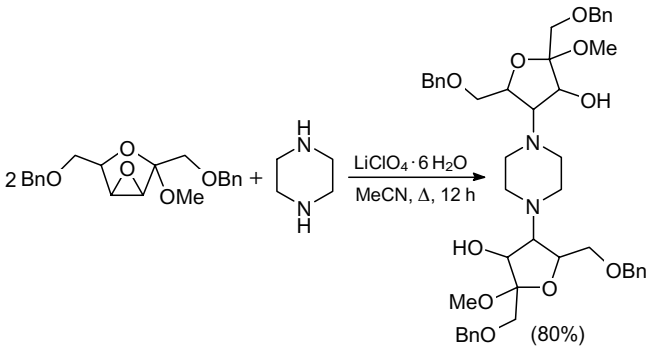

**Scheme 74**




**Scheme 75**




**Scheme 76**



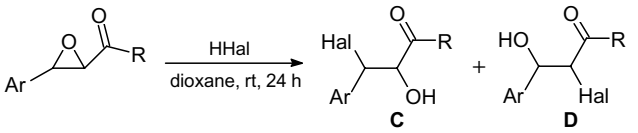

Pathak and co-workers[187] explored the epoxide ring-opening of epoxy derivatives of D-fructose with different amines (Scheme 75) and found that piperazine reacts with two epoxide molecules (Scheme 76).

Kumar and Panda[188] reported the magnesium chloride-catalyzed regioselective epoxide ring-opening of 2,3-epoxy alcohols with anilines and azides giving α-diols.

The data on the epoxide ring-opening with different nucleophiles (azides, thiocyanates, cyanides, halides, nitrates, nitrites, amines, water, alcohols and acetic acid) are summarized in the review,[3] which was published in 2018 and which covers the literature up to 2017. Besides, the thiolysis of epoxides is highlighted in two reviews [189, 190] published in the same year. More recent reviews consider the catalytic epoxide ring-opening with alcohols,[191] sodium azide,[192] thiocyanate [193] and acetone cyanohydrin [193] giving products **B** (see Scheme 71). Two such reactions that occur in the presence of hydrogen halides are given below.

The reactions of hydrochloric and hydrobromic acids with 3-arylglycidic acid amides [15, 194, 195] and 2-arylepoxy aryl ketones [196] were investigated (Scheme 77). It was demonstrated that in the case of R = $NH_2$, the epoxide ring-opening affords product **C**;[15, 195] in the case of R = NHPh, the reaction pathway depends on the substituent in the aryl group (electron-withdrawing substituents are favourable for the formation of product **D**);[194] in the case of R = Ar, the reaction gives exclusively product **D**.[196]

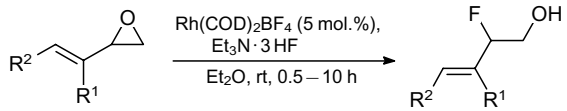
**Scheme 77**




R = $NH_2$, NHPh, Ar; Hal = Cl, Br

Zhang and Nguyen [197] reported the rhodium-catalyzed epoxide ring-opening of vinyl epoxides with triethylamine trihydrogen fluoride (Scheme 78).

**Scheme 78**



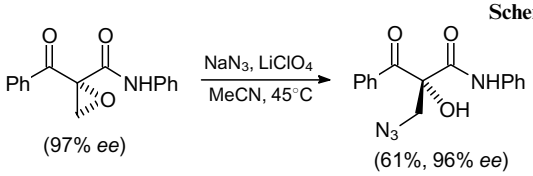

$R^1$ = H, Me, Ph; $R^2$ = H, Alk, Ar;
COD is cycloocta-1,5-diene

(50 – 82%, 11 examples)

The below examples of the epoxide ring-opening with nucleophilic reagents are related to the asymmetric synthesis involving chiral reagents or catalysts and giving chiral β-functionalized alcohols.

The regio- and enantioselective epoxide ring-opening of an enantiopure epoxide compound with sodium azide in the presence of $LiClO_4$ (Scheme 79) was accomplished by Lattanzi and co-workers.[58]

**Scheme 79**



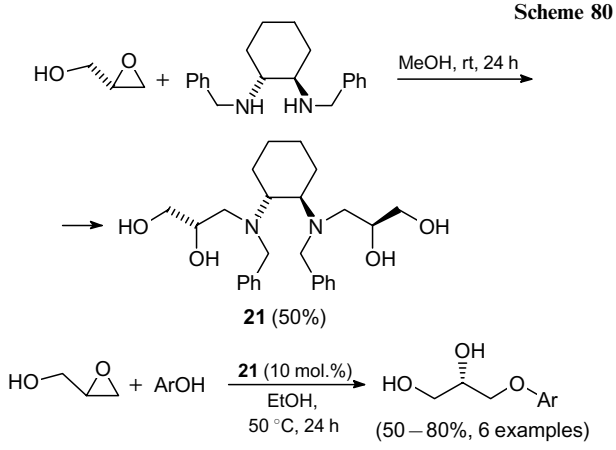

(97% *ee*)

(61%, 96% *ee*)

Sarabia *et al.*[91] used the chiral epoxide ring-opening with methylamine to synthesize the structural core of the natural antibiotics of the liposidomycin and caprazamycin series.

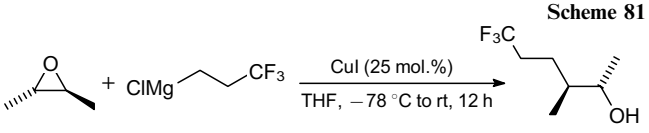
The epoxide ring-opening of (*S*)-2-(hydroxymethyl)oxirane with (1*R*,2*R*)-1,2-dibenzylaminocyclohexane afforded chiral diamine **21** containing two β-amino alcohol moieties.[198] Aral *et al.*[198] quite successfully employed compound **21** as the catalyst in the asymmetric epoxide ring-opening with phenols (Scheme 80).

**Scheme 80**




Jouffroy *et al.*[199] performed the epoxide ring-opening of chiral 1,2-dimethyloxirane using an organomagnesium reagent (Scheme 81).

**Scheme 81**

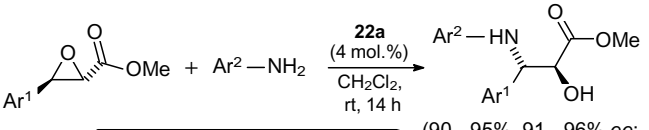


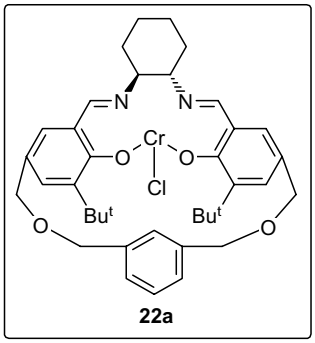

Yamamoto and co-workers [92, 200 – 203] applied an asymmetric version of this reaction to synthesize various aminodiols in the presence of Ni, W, Gd, Ti or Hf catalysts with chiral ligands in good yields with high regio-, diastereo- and enantioselectivity.

Kureshy and co-workers [204] reported the regio-, diastereo- and enantioselective aminolysis of methyl 3-arylglycidates in the presence of chromium(III) complexes with the chiral salen ligand (*e.g.*, compound **22a**) (Scheme 82).

The desymmetrization of *meso* epoxides, symmetrically substituted epoxides with two chiral centres, takes a special place in the chemistry of epoxides and the asymmetric

**Scheme 82**



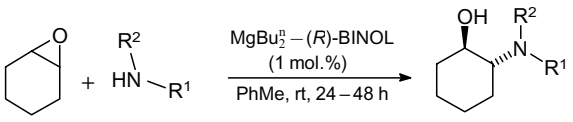



**22a**

synthesis. These compounds have an internal mirror plane and are not optically active, but the nucleophilic epoxide ring-opening introduces the chirality in these compounds. In recent years, great attention has been paid to the desymmetrization of *meso* epoxides containing prochiral carbon atoms in the oxirane ring using chiral catalysts. The problems of the desymmetrization of *meso* epoxides are covered in the reviews published in 2012,[205] 2013 (see Ref. 206) and 2016.[2] In view of the importance of this issue, selected studies referred to in these reviews are considered in this Section along with the new data.

Schemes 83 (see Ref. 207) and 84 (see Ref. 208) display the epoxide ring-opening reactions of *meso* epoxides with amines in the presence of chiral complex catalysts with binol and bipyridine (**23**) ligands, respectively.

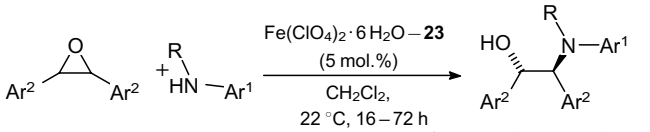
**Scheme 83**




$R^1$ = H: $R^2$ = $Pr^i$, $Bu^t$, Bn,
$R^1-R^2$ = $(CH_2)_5$

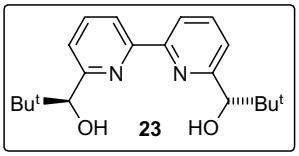
(55 – 92%, 47 – 94% *ee*;
16 examples)

**Scheme 84**




R = H, Me

(70 – 95%, 82 – 96% *ee*;
15 examples)




Zhao and co-workers[209] utilized chiral MOF for the similar ring-opening of *meso* epoxides with anilines.

Organocatalysts are widely employed in the desymmetrization of *meso* epoxides.[206, 210 – 212] Examples of the reactions involving organocatalysts are shown in Schemes 85 and 86. Thus, chiral orthophosphoric acid derivative **24** served as the catalyst for the ring-opening of *meso* epoxides with heteroaromatic thiols (see Scheme 85).[213]

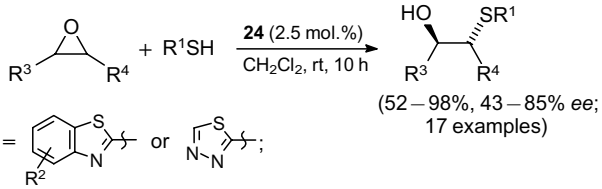
Antilla and co-workers[214] used a lithium salt of the related chiral orthophosphoric acid derivative for the desymmetrization of *meso* epoxides with aromatic thiols and selenols.

Nakajima and co-workers[215] prepared 1,2-chlorohydrins by the ring-opening of *meso* epoxides with silicon tetrachloride in the presence of the chiral catalyst (*S*)-BINAPO (see Scheme 86).

Kalow and Doyle[216] reported the desymmetrization of cyclic *meso* epoxides with benzoyl fluoride promoted by (–)-tetramisole (**25**) and cobalt complex **26** with the chiral salen ligand (Scheme 87).

The kinetic resolution is another method for the preparation of chiral β-functionalized alcohols and simultaneously chiral epoxides from racemic epoxy compounds. This method was first applied by Jacobsen[¶] to prepare chiral

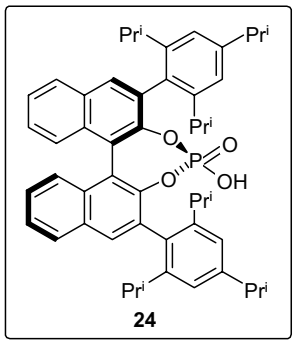
**Scheme 85**




(52 – 98%, 43 – 85% *ee*;
17 examples)

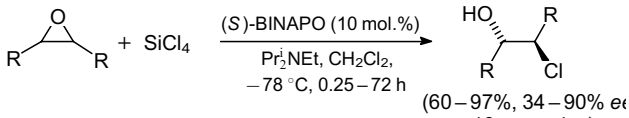
$R^1$ =  ;

$R^2$ = H, 5-Cl, 5-OMe, 6-OEt; $R^3$ = $R^4$ = $Pr^n$, Ar;
$R^3-R^4$ = $(CH_2)_n$ ($n$ = 3, 4, 6), $CH_2OCH_2$, $CH_2N(Boc)CH_2$



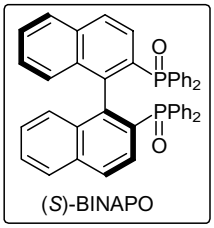

**24**

**Scheme 86**



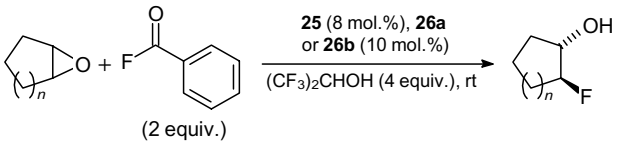

(60 – 97%, 34 – 90% *ee*
10 examples)

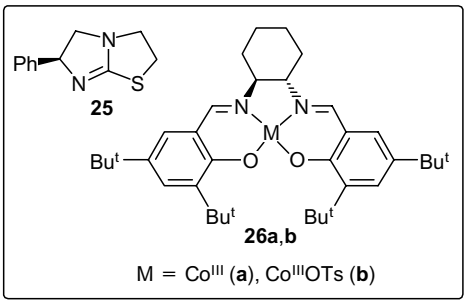
R = Ar, $CH_2OBn$;
R–R = $(CH_2)_n$
($n$ = 4, 6), *etc.*




(*S*)-BINAPO

**Scheme 87**



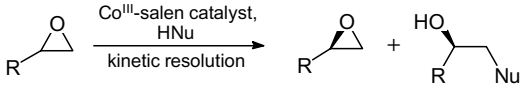




Ts is *p*-toluenesulfonyl (tosyl)

| *n* | 1 | 2 | 3 |
|---|---|---|---|
| Catalyst | **26a** | **26b** | **26a** |
| Solvent | $Et_2O$ | tert-$C_5H_{11}OH$ | $Bu^tOMe$ |
| *t*, h | 72 | 24 | 72 |
| Yield (%) | 77 | 65 | 82 |
| *ee* (%) | 85 | 93 | 90 |

¶ M.Togunaga, J.F.Larrow, F.Kakiuchi, E.N.Jacobsen. *Science*, **277**, 936 (1997).

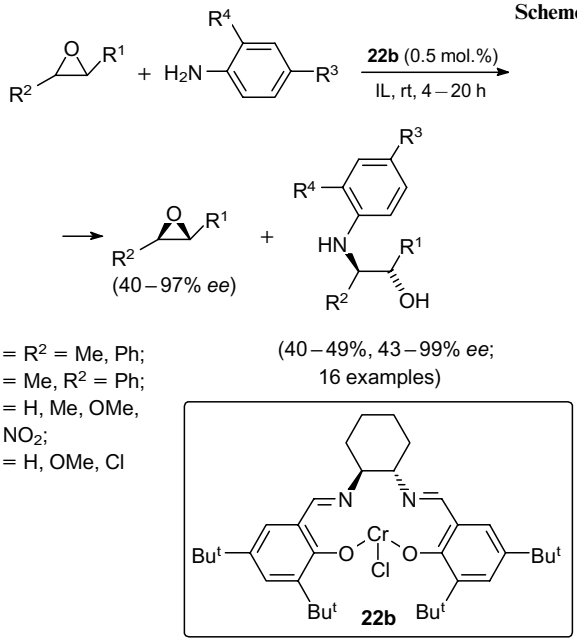
**Scheme 88**




terminal epoxides (Scheme 88), which are difficult to synthesize by the Jacobsen–Katsuki epoxidation. Subsequently, this method was widely applied to prepare enantiopure β-functionalized alcohols and epoxides difficultly accessible by other methods.[140, 208, 217–219]

Kureshy *et al.*[220] explored the kinetic resolution of racemates of 1,2-disubstituted *trans*-epoxy compounds with anilines in the presence of a chromium catalysts with the salen ligand in an ionic liquid (IL) as a benign medium. One enantiomer of the starting racemate of the epoxide was isolated in the enantiopure form; another enantiomer was converted into *anti*-β-amino alcohol in a diastereo- and enantioselective fashion (Scheme 89).

**Scheme 89**



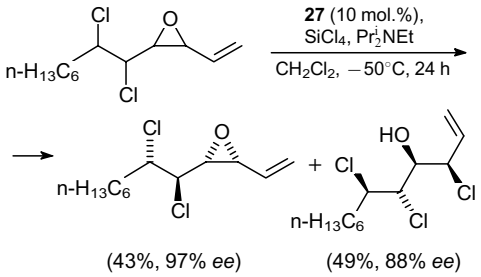

Vanderwal and co-workers[148] utilized dimeric phosphoramide derivative **27** as the catalyst for the kinetic resolution of vinyl epoxides (Scheme 90).

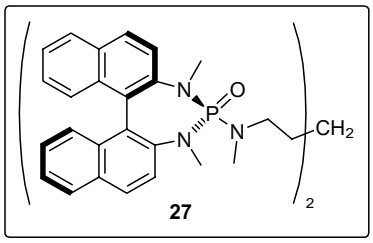
Kalow and Doyle[216] observed the effect of kinetic resolution in the reaction of monosubstituted racemic epoxides with benzoyl fluoride in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene (**28**) and chiral salen-type catalyst **26a** (Scheme 91).

The role of epoxide hydrolases (EHs), which are ubiquitously expressed in all living organisms, in the synthesis of vicinal diols was discussed in a number of studies.[143, 221–230] For example, Lou and co-workers[222] explored the effect of EHs on the hydrolysis of racemic epoxymethyl phenyl ethers. In the kinetic resolution, the *R* enantiomer remained non-hydrolyzed, while the *S* enantiomer served as the source of chiral diol (Scheme 92).

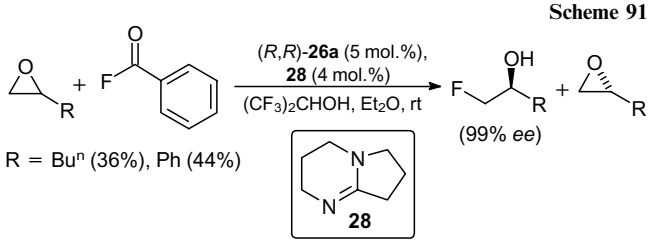
Wu and co-workers[226, 227] demonstrated the stereoconvergence of the hydrolysis of *p*-chlorophenyl epoxide. Thus, EHs convert both enantiomers into the same enantiomer of diol, one enantiomer being converted with inversion of configuration at the chiral centre, while another being converted with retention of configuration (Scheme 93).

**Scheme 90**

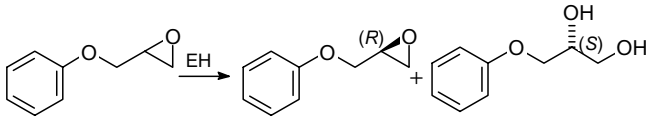


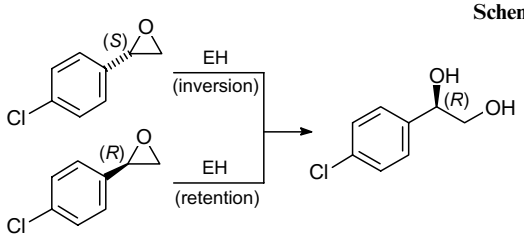

**Scheme 91**




**Scheme 92**

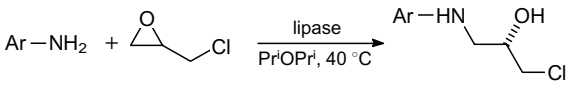



**Scheme 93**



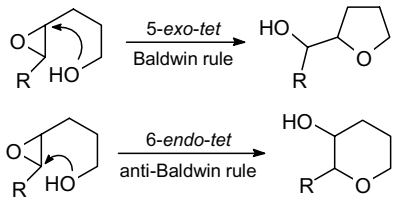

Prasad and co-workers[231] used lipases as biocatalysts for the asymmetric aminolysis of epichlorohydrin (Scheme 94).

**Scheme 94**




In recent years, great attention has been paid to the formation of tetrahydrofuran or tetrahydropyran rings *via* the intramolecular nucleophilic epoxide ring-opening with a hydroxy group in the γ position followed by the 5-*exo*-*tet* or 6-*endo*-*tet* ring closure. According to the Baldwin rules, the 5-*exo*-*tet* ring closure is favourable. However, natural ladder polyethers derived from polyepoxide compounds bearing hydroxy functions more often contain tetrahydro-

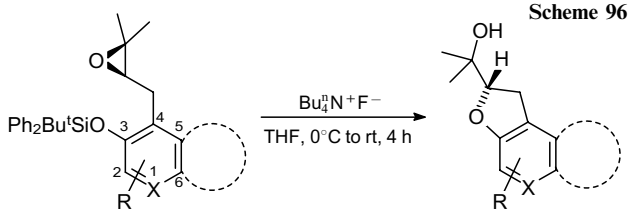
**Scheme 95**




pyran rings, the formation of which requires the anti-Baldwin selectivity (Scheme 95).[232–236]

Hamada and co-workers[138] reported the synthesis of dihydrofuran derivatives of chiral epoxides substituted with a benzyl or related heterocyclic moiety containing the protected hydroxy group at the *ortho* position (*i.e.*, at the γ position with respect to the epoxide ring) (Scheme 96).

**Scheme 96**

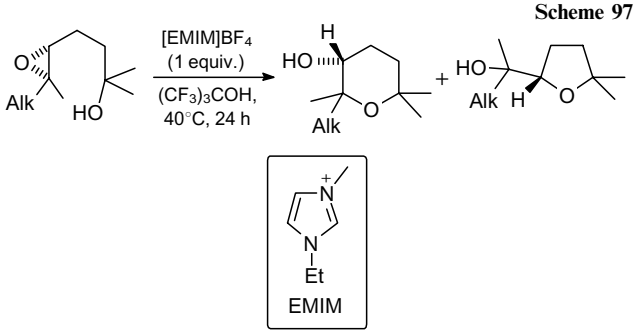



X = CH, N;
R = H, Cl, Bu$^t$, NHBoc, *etc*.

(38–96%, 39–97% *ee*; 12 examples)

Qu and co-workers[232] found the optimal conditions for the predominant formation of the tetrahydropyran ring from γ-hydroxy epoxides by combining perfluoro-*tert*-butyl alcohol with methylimidazolium tetrafluoroborate ([EMIM]$BF_4$) (Scheme 97). Under these conditions, the reaction affords a mixture of tetrahydropyrans and -furans in an overall yield from 60 to 73%; the ratio of the products was from 2.8 : 1 to 18 : 1 (4 examples).

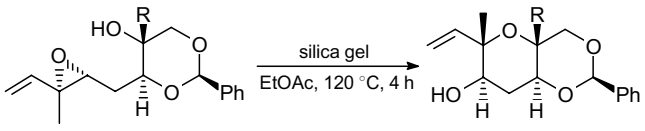
**Scheme 97**




Torikai and co-workers[136] described the selective ring closure of γ-hydroxy epoxides to form tetrahydropyrans (Scheme 98).

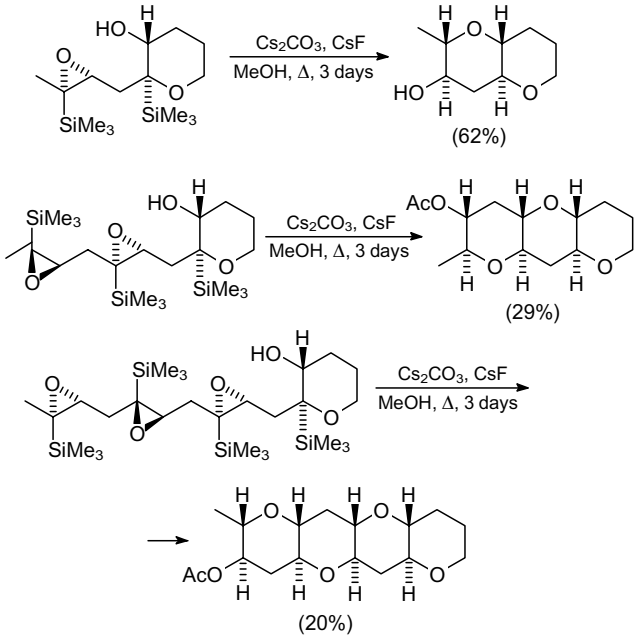
Jamison and co-workers[137,235] converted the above-mentioned mono-, di- and triepoxy compounds (see Scheme 57) into tetrahydropyran ladder polyethers (Scheme 99).

**Scheme 98**



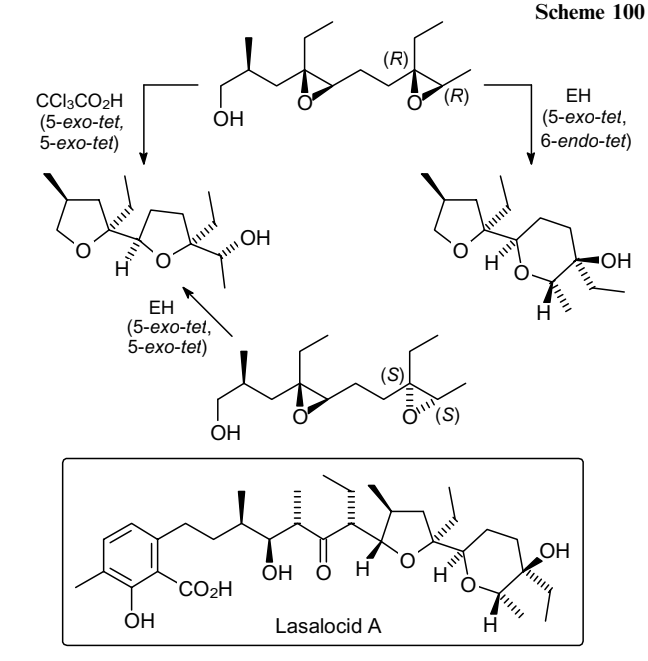

R = H, Me

**Scheme 99**



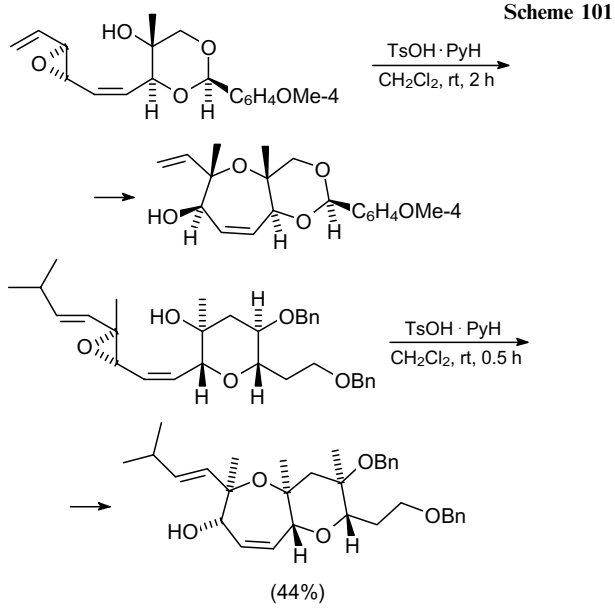

Oikawa and co-workers[236] demonstrated the possibility of performing the cyclization of the same diepoxy alcohol both according to the Baldwin rules and against these rules depending on the reaction conditions. The reaction using trichloroacetic acid affords a product containing two tetrahydrofuran rings; however, in the presence of epoxide hydrolases, the reaction can give a product containing the tetrahydropyran ring. The outcome of the cyclization depends on the configuration of the carbon atoms in the terminal epoxide ring. Thus, the *R*,*R* configuration provided the formation of the tetrahydropyran ring, and the resulting product corresponded to the left segment of the natural antibiotic lasalocid A, whereas the *S*,*S* configuration facilitated the formation of the tetrahydrofuran ring (Scheme 100).

**Scheme 100**



Mori and co-workers[237] prepared 2,3,6,7-tetrahydrooxepine derivatives *via* the 7-*endo* cyclization of δ-hydroxy epoxide derivatives (Scheme 101).

**Scheme 101**




Therefore, the known epoxide ring-opening reaction with nucleophilic reagents is extensively used because it affords reactive polyfunctional products, which are in high demand for the subsequent use. The research efforts are focused on the proper choice of conditions and reagents to increase the regioselectivity of the reactions. Besides, studies aimed at finding new chiral reagents (see Schemes 79–81) and catalysts (see Schemes 82–84) for the asymmetric version of this reaction are continued. Great attention is paid to the desymmetrization of *meso* epoxides *via* the nucleophilic epoxide ring-opening in the presence of chiral catalysts (see Schemes 85–87) and to the kinetic resolution and stereoconvergence (see Schemes 88–94), including enzymatic resolution (see Schemes 92, 93). Intramolecular epoxide ring-opening reactions involving hydroxy groups (see Schemes 95–101) are also an interesting and promising field of chemistry of epoxides.

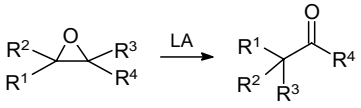
## 3.2. Rearrangements in the chemistry of epoxides

Rearrangements play a great role in the chemistry of epoxides. These rearrangements often serve as the first step of complex tandem reactions or are involved in their due course. This Section demonstrates the applications of classical rearrangements in modern studies and presents new rearrangements discovered in recent years.

### 3.2.1. Meinwald rearrangement

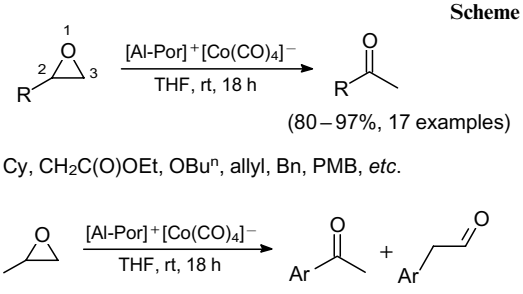
The Meinwald rearrangement plays an important role in the chemistry of epoxides. It involves the migration of one of the substituents on the epoxide ring to the adjacent carbon atom in the presence of Lewis acid (LA) and is accompanied by the ring-opening (Scheme 102).[238]

**Scheme 102**



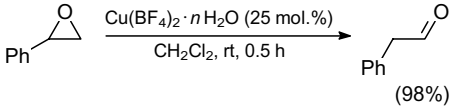

The studies[238–255] were aimed at finding the optimum conditions and catalysts for the Meinwald rearrangement, which affect not only the reaction rate but also the selectivity dictated by the predominant migration of a particular substituent. For example, the migration of a hydrogen atom from the C(2) atom of epoxide in the presence of the catalyst $[Al\text{-}Por]^+[Co(CO)_4]^-$ (Por is porphyrin) selectively affords ketone for a wide range of substituents in the epoxide (Scheme 103). Exceptions are aryl substituents; in this case, the reaction gives a mixture of two Meinwald rearrangement products, ketone and aldehyde, in a ratio of 1 : 1.6 in good yields (up to 90%). The second product is generated through the migration of a hydrogen atom from the C(3) atom (see Scheme 103).[246]

**Scheme 103**



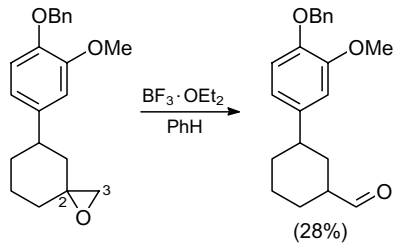

The use of copper tetrafluoroborate instead of the porphyrin catalyst leads to the selective transformation of phenyl epoxide into phenylacetaldehyde (Scheme 104).[239]

**Scheme 104**




Zefirova's research group[84] demonstrated that aldehyde is formed *via* migration of a hydrogen atom from C(3) to C(2) in the spiro-fused epoxide moiety in the presence of boron trifluoride etherate (Scheme 105).

**Scheme 105**

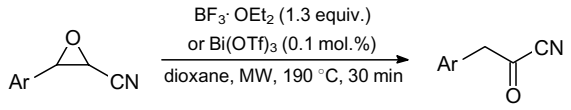



Arylglycidic acid nitriles undergo the microwave-assisted Meinwald rearrangement in the presence of $BF_3 \cdot OEt_2$ or bismuth triflate (Scheme 106).[254]

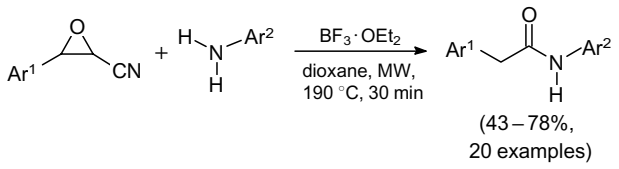
In the presence of water, alcohols or anilines in the reaction mixture, the cyano group is replaced by the hydroxy, alkoxy or aniline group, respectively. Scheme 107 presents the two-component synthesis involving anilines.[254]

It was found that in many cases, the Meinwald rearrangement does not require the presence of LA in the reaction medium. For example, it was demonstrated[14] that the Meinwald rearrangement of 3-arylglycidates containing

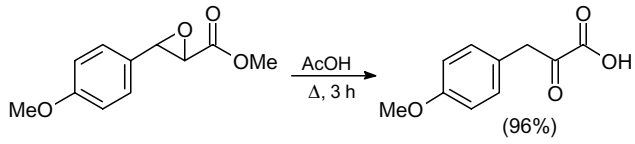
**Scheme 106**




**Scheme 107**



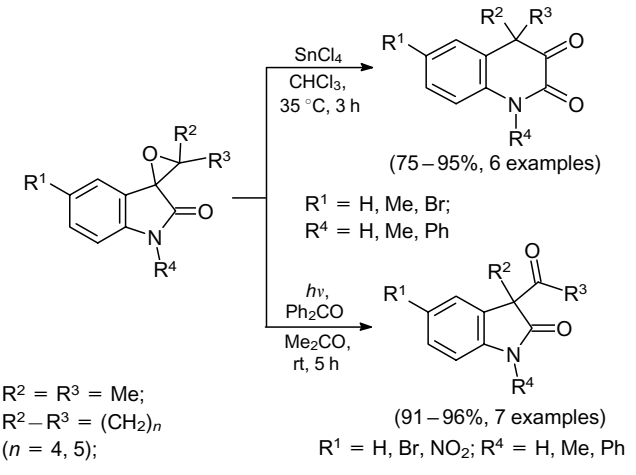

**Scheme 108**




electron-donating substituents on the aryl moiety (*e.g.*, the 4-methoxy group) occurs under reflux of the reagents in acetic acid, the reaction being accompanied by the hydrolysis of the methoxycarbonyl group (Scheme 108).

Zhang and co-workers[255] found that spirooxindole epoxides undergo the Meinwald rearrangement accompanied by the migration of different groups in the presence of tin(IV) chloride under photosensitized conditions. The irradiation affords 3-acylindol-2-ones *via* migration of the substituent $R^2$ to the spiro-fused carbon centre. The $SnCl_4$-catalyzed rearrangement gives 4,4-dialkylquinoline-2,3-diones through aryl migration in the indolone (Scheme 109).

**Scheme 109**



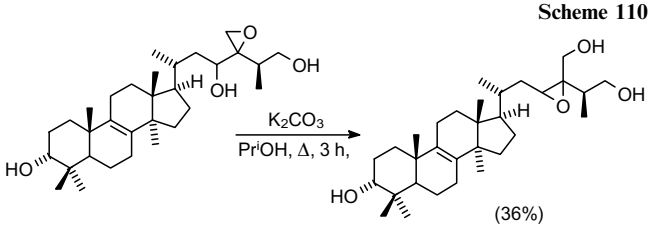

The enzymatic transformation of phenyl epoxide into phenylacetaldehyde was accomplished in the study.[256]

The Meinwald rearrangement provides the basis of many tandem reactions considered below.

### 3.2.2. Payne rearrangement

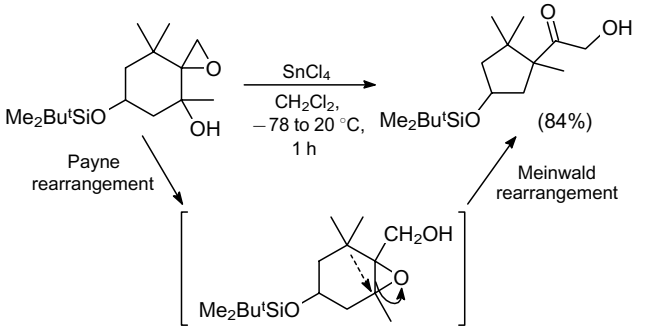
The Payne rearrangement involving the epoxide ring and the hydroxy group at the α position with respect to this ring was described for a triterpene derivative (Scheme 110).[257]

**Scheme 110**



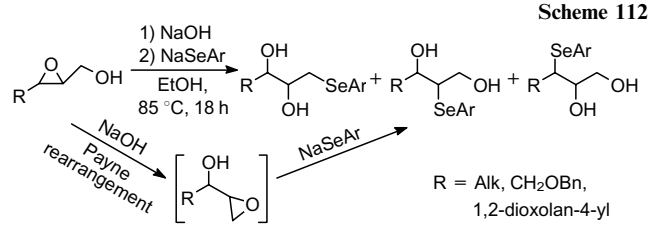

Gosselin and co-workers[258] performed the tandem Payne – Meinwald rearrangement of protected α-hydroxy-spiro epoxide cyclohexane in the presence of $SnCl_4$ (Scheme 111).

**Scheme 111**




A combination of the Payne rearrangement and the ring-opening with aryl selenides was described by Jung and Sun[259] (Scheme 112). The overall yield of isomeric selenated diols varied from 76 to 99% (7 examples).

**Scheme 112**




### 3.2.3. Semipinacol rearrangement

Panda and co-workers[260] converted diaryl epoxides containing a hydroxymethyl group into β-diols using the Grignard reagent. The reaction occurred through the semipinacol rearrangement (Scheme 113).

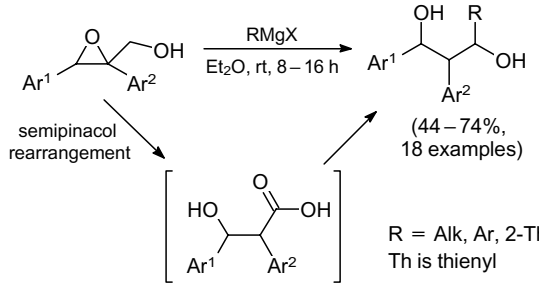
Rearrangements, which significantly differ from the classical rearrangements, are considered below.

### 3.2.4. New rearrangements of epoxy compounds

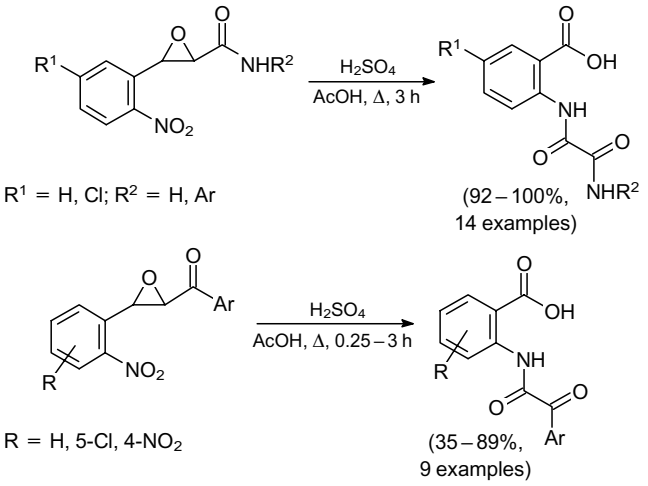
This Section covers the rearrangements, which do not fit into the schemes of rearrangements known for epoxides. Due to the unusual character of these transformations, it is appropriate to consider the proposed mechanisms in detail.

Mamedov's research group discovered a new rearrangement of 3-(2-nitrophenyl)glycidic acid amides[261 – 263] and 3-(2-nitrophenyl)epoxy aryl ketones[261,264] giving anthra-

**Scheme 113**




**Scheme 114**




nilic acid derivatives without changes in the molecular weight (Scheme 114).

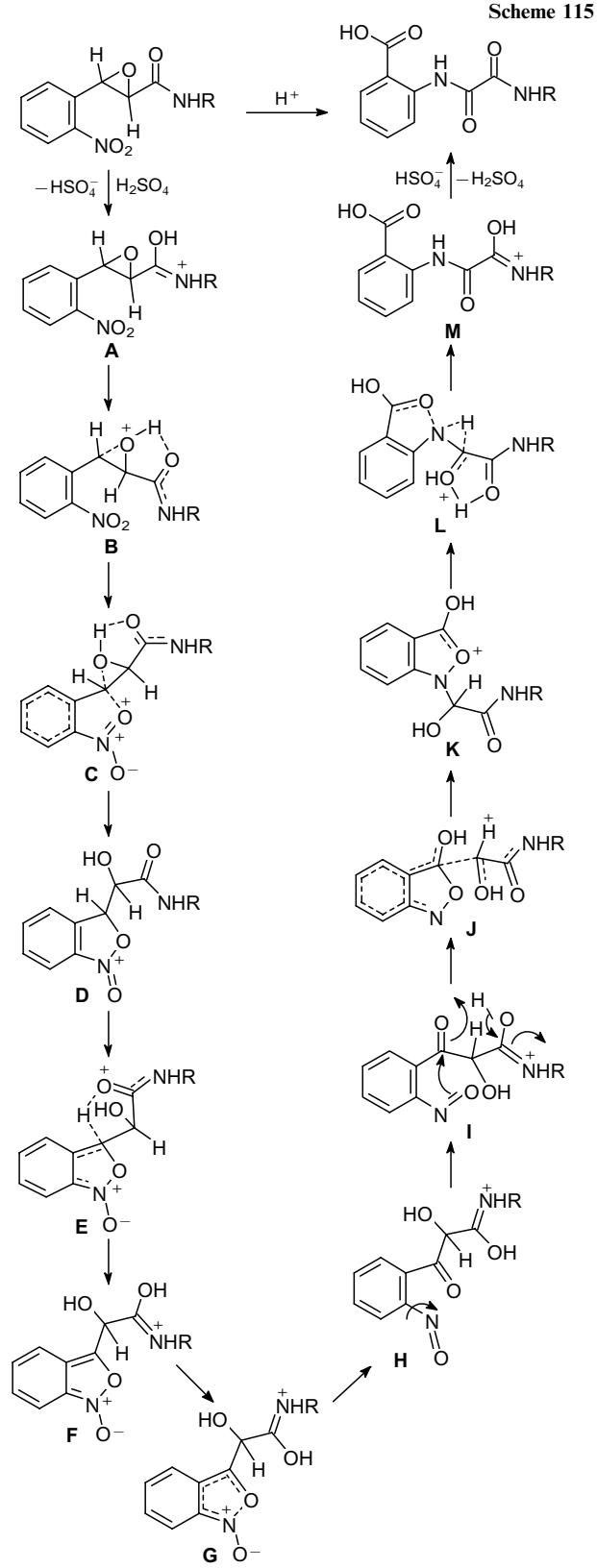
This unusual rearrangement starts with the formation of intermediates **A** and **B** with the special participation of the nitro group, which alternately supplies oxygen atoms through the formation of benzisoxazole systems **C**–**G** (Scheme 115) to form first the oxamoyl moiety [C(O)C(O)NHR] and then the carboxyl function in the final product. The main steps giving rise to the carboxyl group are accompanied by the attack of the nitroso oxygen atom on the carbonyl group of intermediate **I** and the migration of the dihydrooxamoyl moiety from the carbon atom to the nitrogen atom of benzisoxazole system **J**. These reactions afford N-substituted benzisoxazole **K**. The subsequent ring-opening of the latter through intermediates **L** and **M** gives the final product.[263]

It was demonstrated[264] that another rearrangement product, 3-hydroxy-2-phenylquinolin-4-one, can be generated under similar conditions from 3-(2-nitrophenyl)epoxy phenyl ketone *via* the loss of molecular oxygen (Scheme 116). However, the mechanism of the formation of this compound remains unclear.

Complex rearrangements of N-protected 2-chloro-3-arylglycidic acid anilides into cyclohepta[*b*]pyrrole-2,3-diones (Scheme 117) and 1-azaspiro[4,5]deca-3,6,9-trien-2-ones (Scheme 118) were discovered in the study.[265]

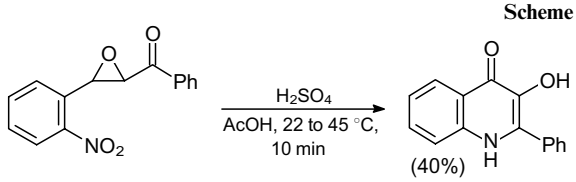
The mechanism of the formation of cyclohepta[*b*]pyrrole-2,3-diones is shown in Scheme 119. The reaction involves the 5-*exo*-*trig* cyclization of salt **A** as the first step giving σ-complex **B**. The elimination of the chloride ion and HCl from the latter affords intermediate **C** stabilized by a chloride ion as neutral tricyclic adduct **D**. The subsequent

**Scheme 115**

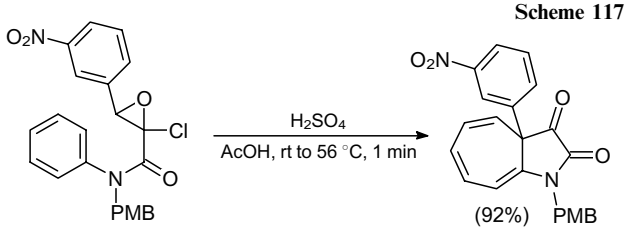



reaction of the amide group with HCl can follow several pathways: the expansion of the cyclohexadiene moiety and the formation of cycloheptapyrrole-2,3-dione through intermediate **G** or the expansion of the pyrrole-2,3-dione ring and the formation of 3-hydroxyquinolin-2-one through

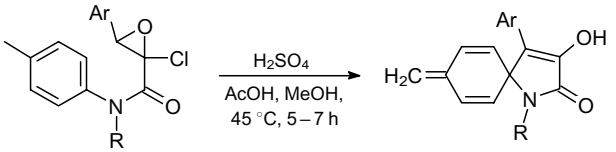
**Scheme 116**




**Scheme 117**



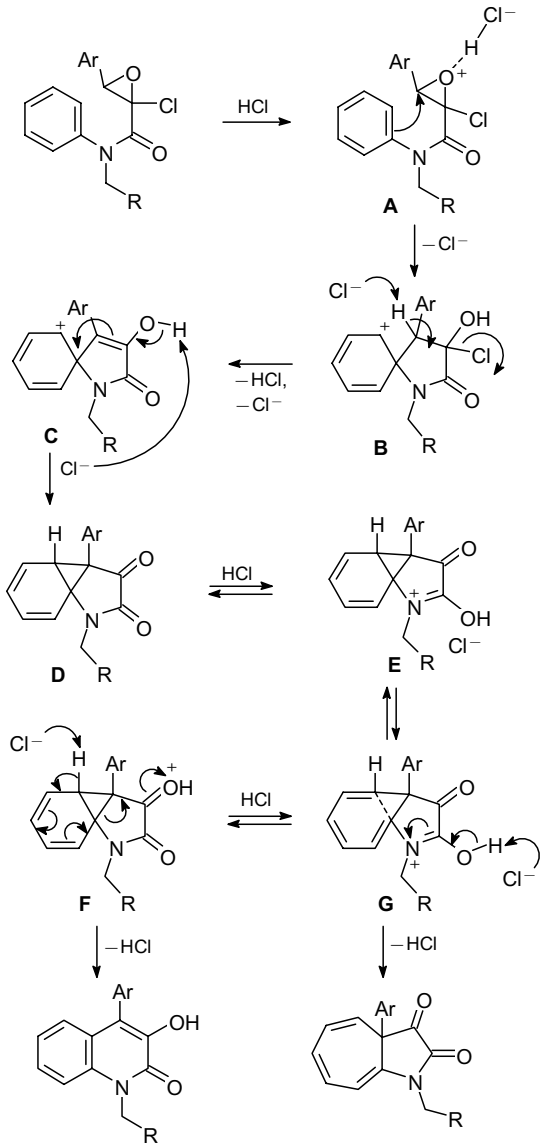

**Scheme 118**




(71–96%, 10 examples)

R = Ph, PMB, $C_6H_4Cl$-4, $C_6H_4Br$-4

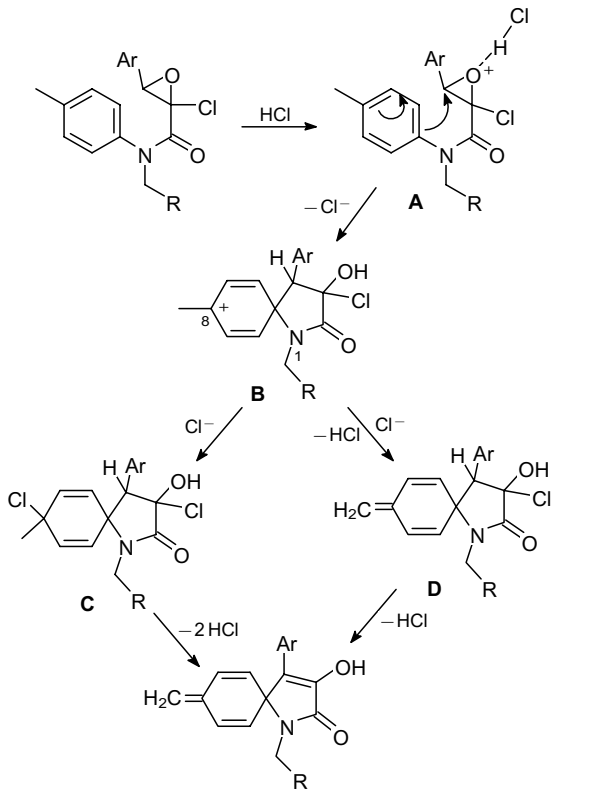
**Scheme 119**




intermediate **F**. The equilibrium **G** ⇄ **F** is reversible and is controlled by the reaction temperature.

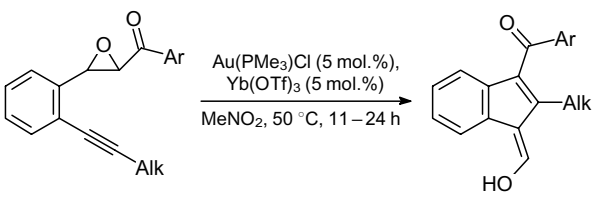
In the presence of the *p*-tolyl group in the amide moiety of the epoxide derivative (see Scheme 118), the corresponding σ-complex **B** (Scheme 120) can be stabilized through the attack of the chloride ion either on the carbon atom C(8) of the cationic centre of complex **B** or on the methyl proton. Correspondingly, these reactions afford neutral molecules **C** and **D**, the dehydrochlorination of which gives the final product.[265]

**Scheme 120**




Dai and Shi[266] reported the intramolecular transformation of the α,β-epoxy ketone and alkyne moieties giving functionalized indenes (Scheme 121). The reaction mechanism proposed by the authors (Scheme 122) involves two catalysts, $Au(PMe_3)Cl$ and $Yb(OTf)_3$.

**Scheme 121**



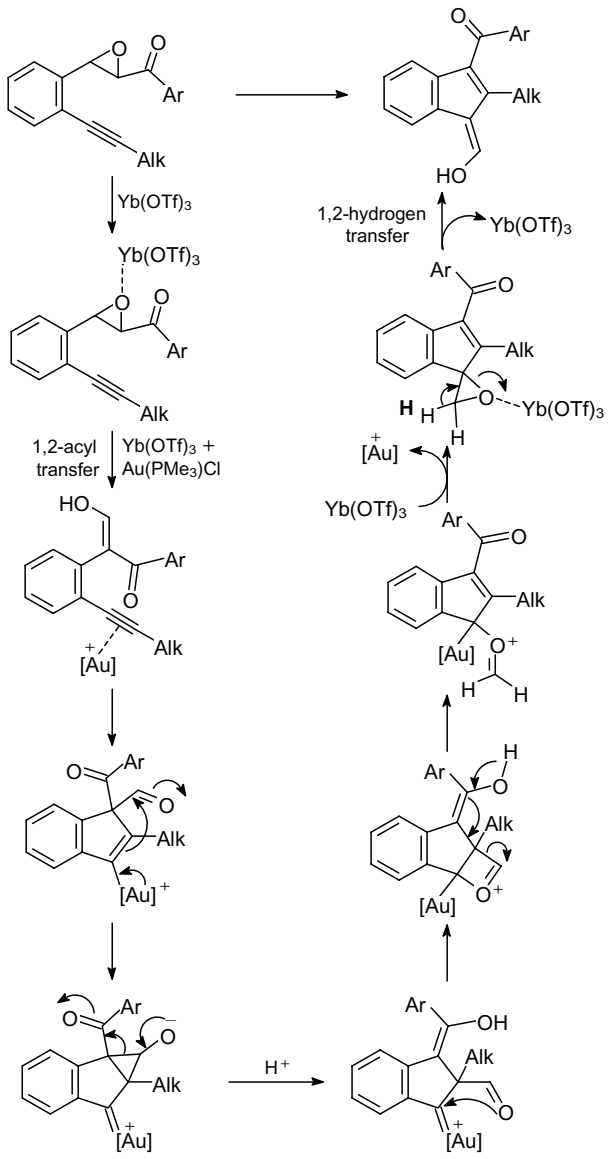

(53–86%, 9 examples)

The data summarized in this Subsection clearly demonstrate the great potential of the chemistry of epoxides with many unexpected and unpredictable issues, which is always attractive for researchers and moves science forward.

### 3.3. Tandem and one-pot reactions

The terms tandem reactions,[238] one-pot reactions[267] and multicomponent reactions[5] are not synonyms. However,

**Scheme 122**



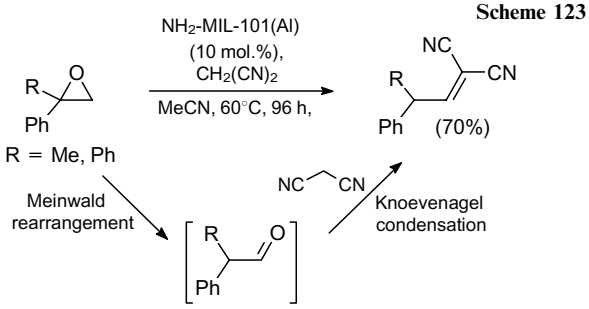

they are similar in many ways because they imply that several synthetic transformations and bond-forming steps proceed in one pot, thereby avoiding several purification steps, minimizing chemical waste and saving time and resources. These transformations were characterized by Hayashi [268] as pot-economy reactions.

Many tandem processes using epoxides involve the Meinwald rearrangement as the first step.[238] This Section begins with such processes followed by the consideration of tandem reactions of functionalized epoxides, which result in the formation of carbo- and heterocyclic structures but which do not involve the Meinwald rearrangement. Tandem reactions involving the intramolecular Friedel–Crafts reaction are considered separately. Then the data on intermolecular tandem reactions, including cycloaddition reactions, and intermolecular Friedel–Crafts-type transformations are presented. In conclusion of this section, we give the data on multicomponent reactions involving more than two reagents.

### 3.3.1. Meinwald rearrangement in tandem and one-pot reactions

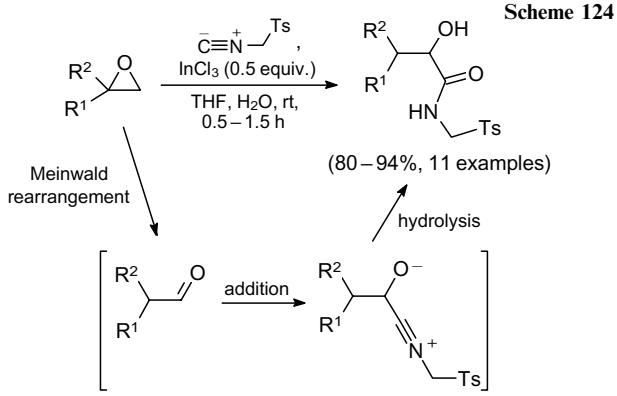
Kim and co-workers [269] reported the tandem catalytic Meinwald rearrangement–Knoevenagel condensation reaction (Scheme 123). The bifunctional metal-organic framework $NH_2$-MIL-101(Al) was used as the catalyst, which acted as Lewis acid in the $Al^{3+}$ form responsible for the first step of the synthesis, and Brønsted base as a $NH_2$ substituent in the ligand responsible for the second step.

**Scheme 123**




Indium chloride was employed as the catalyst for the tandem synthesis involving the Meinwald rearrangement, the addition of tosylmethyl isocyanide to the carbonyl group of the intermediate aldehyde and the hydrolysis (Scheme 124).[270]

**Scheme 124**

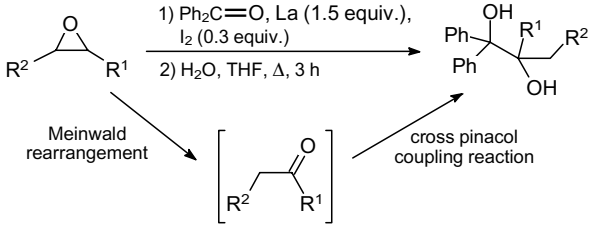



$R^1$ = H, Alk, Ph; $R^2$ = Alk, Ar

1,2-Diols were synthesized by the lanthanum metal-assisted reaction of epoxides with benzophenone in the presence of iodine as the catalyst (Scheme 125).[271]

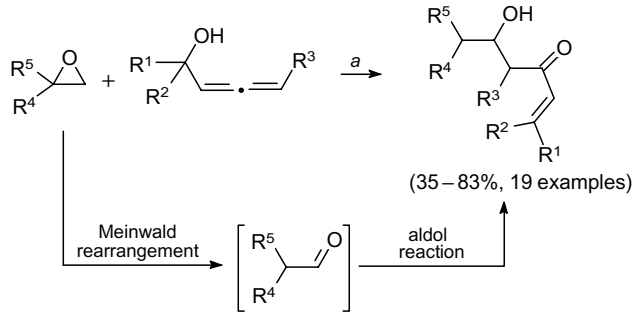
Trost and Tracy [272] used a combination of Lewis acid for the Meinwald rearrangement of the epoxide reagent and

**Scheme 125**




$R^1$ = H, $R^2$ = n-$C_8H_{17}$ (52%); $R^1$ = $R^2$ = Me (44%);
$R^1$–$R^2$ = $(CH_2)_4$ (45%)

**Scheme 126**

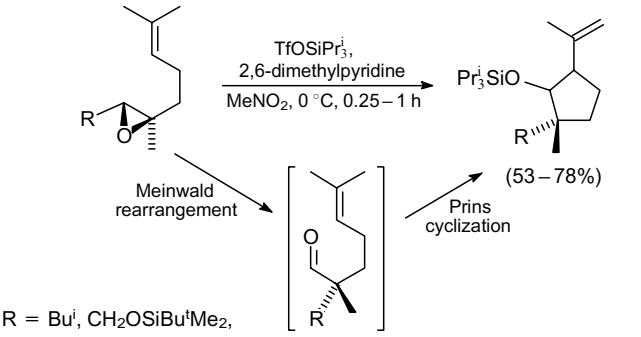



(*a*) $La(OTf)_3$ (16 mol.%), $O{=}V[OSi(C_6H_4Cl\text{-}4)_3]_3$ (5 mol.%), $(ClCH_2)_2$, rt, 10 h;
$R^1$ = H, Me; $R^2$ = Me, Et, Ph, $R^1 - R^2 = (CH_2)_4$;
$R^3$ = H, Me, $Pr^i$; $R^4$ = H, Me; $R^5$ = vinyl derivatives, Ar, 2-Fu

a vanadium catalyst for the aldol condensation of aldehyde with allenol (Scheme 126).

The Meinwald rearrangement followed by the Prins-type cyclization was performed for chiral epoxy compounds (Scheme 127) by Morimoto's research group.[273]

**Scheme 127**

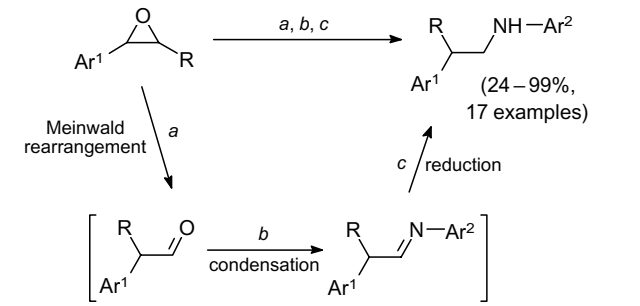



R = $Bu^i$, $CH_2OSiBu^tMe_2$, vinyl, allyl, *etc*.

Otte and co-workers[274] reported the one-pot reaction, involving the $B(C_6F_5)_3$-catalyzed Meinwald rearrangement, the condensation of the rearrangement product with anilines and naphthylamines and the reduction of intermediate imino compounds (Scheme 128).

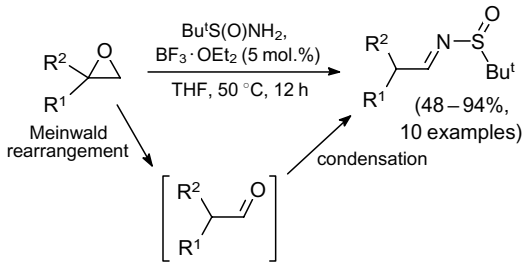
The tandem transformation of epoxides into *N*-(*tert*-butylsufinyl)imines using *tert*-butylsulfinamide in the presence of $BF_3 \cdot OEt_2$ is shown in Scheme 129.[275]

**Scheme 128**




(*a*) $B(C_6F_5)_3$ (5 mol.%), rt, 10 min; (*b*) $Ar^2NH_2$, rt, 5 min;
(*c*) $Me_2PhSiH$, 100 °C, 3 h; R = H, Me, Ph

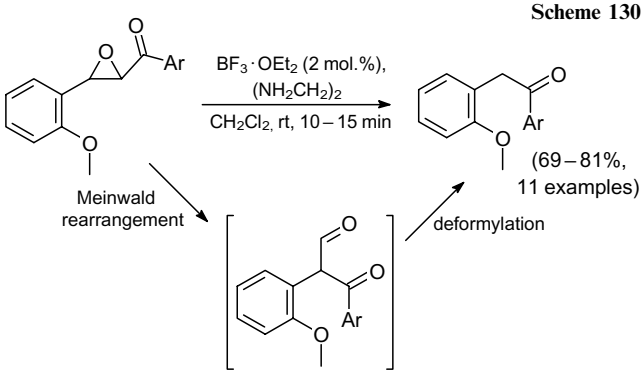
**Scheme 129**




$R^1$ = H, Me, n-$C_5H_{11}$; $R^2$ = Me, n-$C_5H_{11}$, n-$C_6H_{13}$, *etc*.

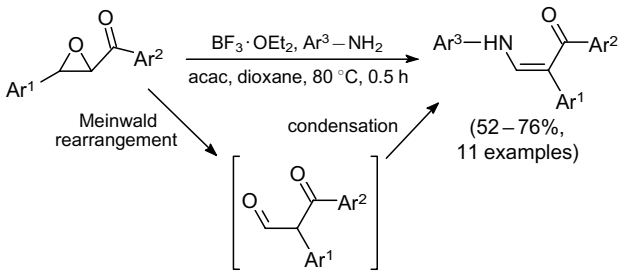
The Meinwald rearrangement accompanied by aroyl migration in 2-(2-methoxyphenyl)epoxy aryl ketones and the deformylation of the intermediate were accomplished in a $BF_3 \cdot OEt_2$-catalyzed one-pot procedure by Ruan *et al*.[276] (Scheme 130).

**Scheme 130**




The $BF_3 \cdot OEt_2$-assisted tandem reaction through aryl migration in 2-arylepoxy aryl ketones followed by the condensation of intermediate aldehyde with aniline was accomplished by Li and co-workers[277] (Scheme 131).

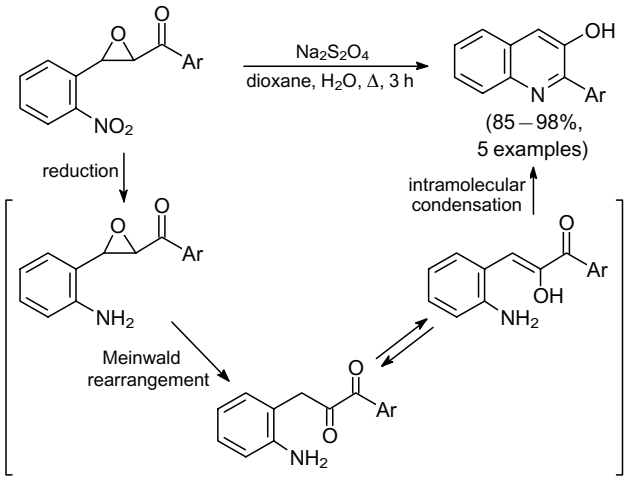
**Scheme 131**



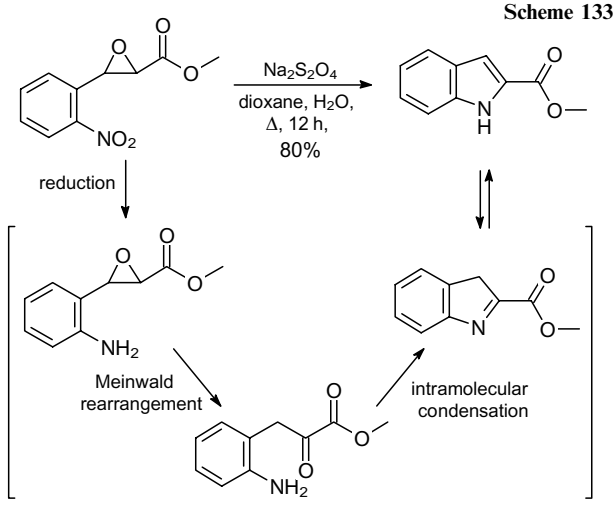

3-Hydroxy-2-arylquinolines were synthesized from 2-(2-nitrophenyl)epoxy aryl ketones using a reaction sequence involving the reduction of the nitro group, the Meinwald rearrangement and the intramolecular condensation (Scheme 132).[13,278] 3-(2-Nitrophenyl)glycidic acid methyl ester was transformed into 2-methoxycarbonylindole in a similar way by treatment with sodium dithionite (Scheme 133).[279]

It was demonstrated that the reaction of methyl 3-arylglycidates containing electron-donating substituents in the aryl moiety with *o*-phenylenediamines in refluxing acetic acid afforded 3-benzylquinoxalin-2-ones (Scheme 134).[14]

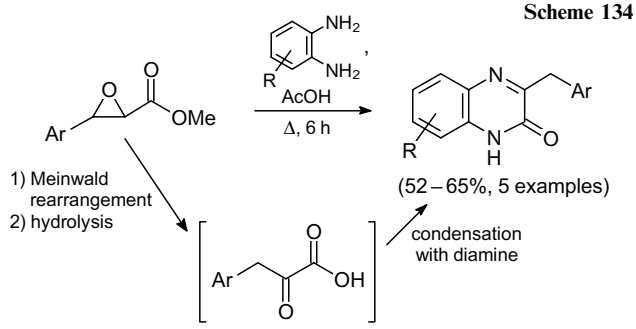
**Scheme 132**




**Scheme 133**




**Scheme 134**

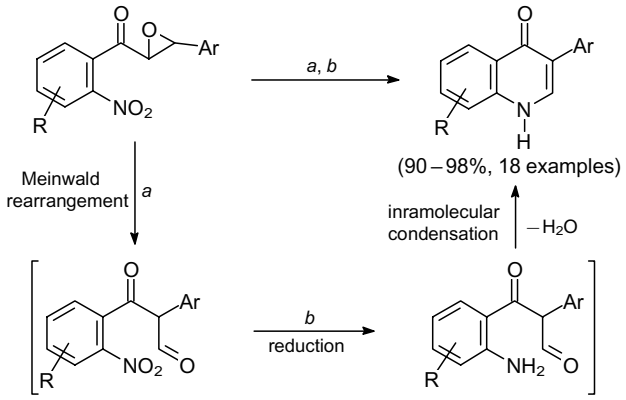



Ar = $C_6H_4Me$-4, $C_6H_4OMe$-4; R = H, Me, Cl, F

Tang and co-workers[280] reported the one-pot synthesis of 3-arylquinolin-2-ones from 2-arylepoxy 2-nitrophenyl ketones involving the $BF_3 \cdot OEt_2$-catalyzed Meinwald rearrangement through aryl migration, the reduction of the nitro group with iron and the intramolecular condensation (Scheme 135).

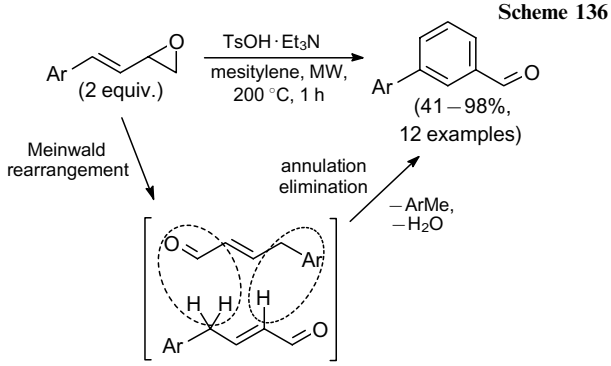
Xu's research group[281] performed the tandem transformation of 2-styryloxiranes into 1,1′-biaryl 3-carbaldehydes. The reaction sequence consists of the *p*-toluenesulfonic acid-catalyzed Meinwald rearrangement

**Scheme 135**




(*a*) $BF_3 \cdot OEt_2$ (5 mol.%), $CH_2Cl_2$, rt, 30 min;
(*b*) Fe, AcOH, 80 °C, 20 min; R = H, 5-Me, 4-Cl, 5-Cl

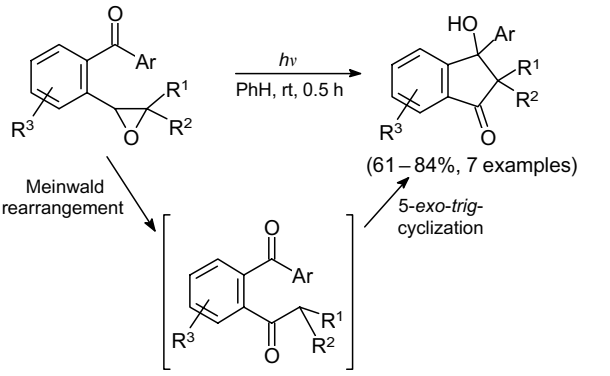
**Scheme 136**




and triethylamine-catalyzed reactions of intermediate 3-benzylacroleins, as illustrated by Scheme 136.

Xiao and co-workers[282] demonstrated that 2-aroylphenyl epoxides undergo the Meinwald rearrangement under irradiation followed by the *5-exo-trig* cyclization to form a cyclopentanone moiety (Scheme 137).

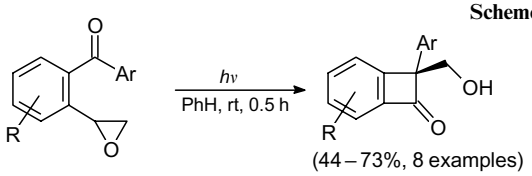
**Scheme 137**




R¹ = H, Me; R² = Me, Et; R³ = H, 4-Cl, 5-Cl

An exception are terminal epoxides, which are transformed under similar conditions into benzocyclobutanones *via* the intramolecular cyclization and the semipinacol rearrangement (Scheme 138).[282]

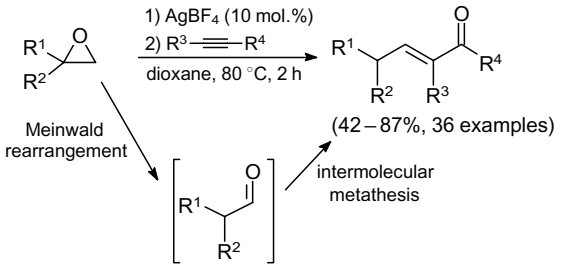
**Scheme 138**




R = H, 5-Me, 4-Cl, 5-Cl

Zhu *et al.*[283] reported the regioselective metathesis (fragmentary exchange between reactant molecules) involving the *in situ* generated aldehydes and alkynes containing heteroatoms in the α position to form acrylic acid derivatives (Scheme 139).

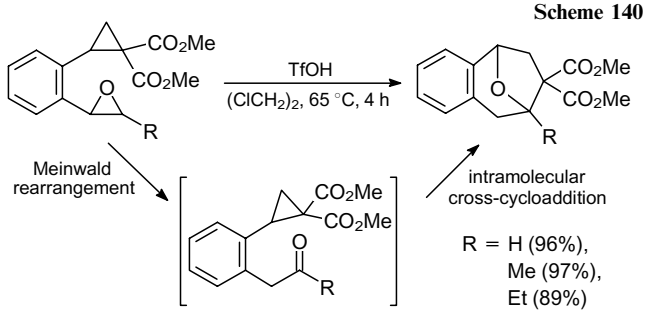
**Scheme 139**




$R^1$ = H, Me; $R^2$ = Alk, vinyl derivatives, allyl, 2-phenylacetylenyl, Ar;
$R^3$ = H, Alk, vinyl derivatives, allyl, Ar;
$R^4$ = N($SO_2$Me)Alk, OMe, OEt, $OC_6H_4$Me-4, SEt, *etc.*

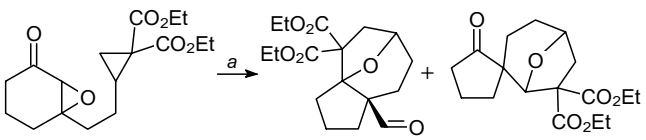
The intramolecular [3 + 2]-cross-cycloaddition of the carbonyl group with the cyclopropane moiety in intermediates, which are generated from the corresponding epoxide derivatives *via* the Meinwald rearrangement, affords a fused bicyclic system in good yield (Scheme 140).[284]

**Scheme 140**



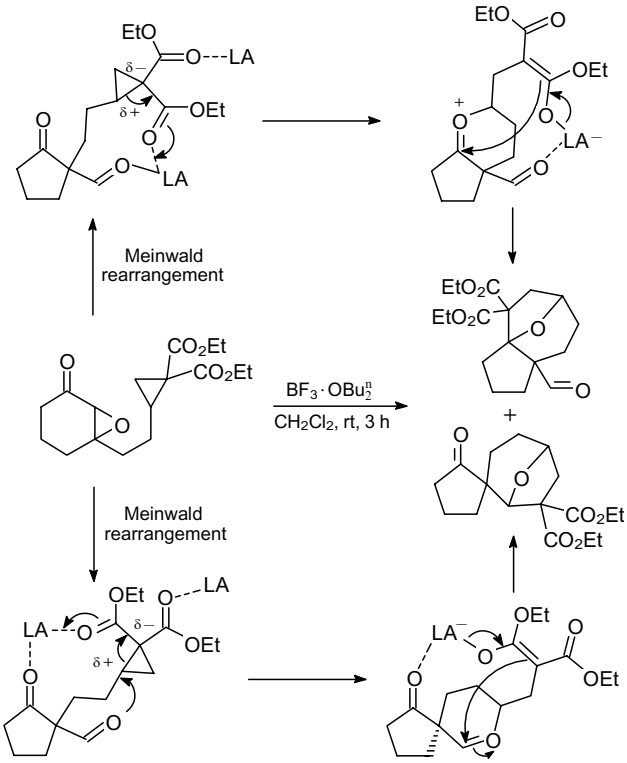

A similar process was accomplished by Shi's research group[285] (Scheme 141). They obtained a mixture of two products, the condensed and spirobicyclic compounds, in an equimolar ratio in 86% yield from condensed 2,3-epoxycyclohexanones containing the 3-cyclopropanepropyl substituent in the γ position (Scheme 142).

**Scheme 141**




(*a*) $BF_3 \cdot OBu^n_2$, $CH_2Cl_2$, rt, 3 h

**Scheme 142**




Scheme 142 presents the mechanisms of the formations of these compounds; in both cases, the first steps involve the Meinwald rearrangement through migration of the carbonyl group of cyclohexanone.

As is evident from the above data, the Meinwald rearrangement is rather popular in the chemistry of epoxides. In this reaction, the epoxide function is transformed into an aldehyde (see Schemes 123, 124, 126 – 129, 131, 135, 136, 139, 142) or ketone (see Schemes 122, 130, 132 – 134, 137, 140) group, and the high reactivity of these groups is generally favourable for the *in situ* formation of new structures. If a carbonyl compound, which is generated *via* the Meinwald rearrangement, is stable, it is the final reaction product (see Section 3.2.1).

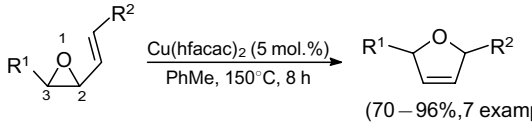
### 3.3.2. Construction of new carbo- and heterocyclic structures from functionalized epoxides

Tandem reactions involving functionalized epoxides, which occur through the C—C or C—O bond cleavage of the epoxide ring, may allow the construction of new carbo- and heterocyclic structures. The reactive functional groups of epoxide compounds often continue the chain of transformations, which begins with the cleavage of one bond in the epoxide ring and ends with the formation of a new heterocyclic system. The bond cleavage of the epoxide ring can be initiated by bases, acids or specially designed catalysts. Double and triple bonds, amine, amide and hydroxy groups or a halogen atom facilitate the ring closure. The Meinwald rearrangement considered above is also accompanied by the C—O bond cleavage of the epoxide ring and it could be discussed in this Section. However, first, this rearrangement has a special place in the chemistry of epoxides and it is appropriate to consider it separately (see Sections 3.2.1 and 3.3.1) and, second, in this case the bond cleavage is necessarily accompanied by the migration of atoms or

groups from one side of the epoxide ring to the other. Radically different reactions are discussed below.

Njardarson and co-workers [286, 287] converted substituted vinyl epoxides into 2,5-dihydrofuran derivatives. The reaction occurred through the C(2)–O bond cleavage of the epoxide and resulted in the formation of a new O–C bond with the participation of the vinyl moiety (Scheme 143). It is worth noting that Njardarson is a co-author of three reviews [288–290] on the small ring expansion, in particular the epoxide ring expansion, in the presence of metal catalysts. The role of vinyl epoxides in organic synthesis is covered in the review by Chiu and co-workers.[291]

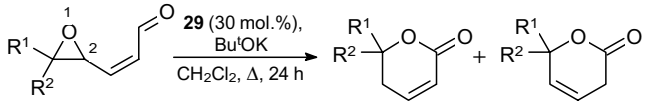
**Scheme 143**



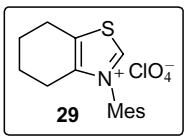

$R^1$ = Me, CH=CHMe, $CH_2OBn$, Ph; $R^2$ = $CH_2CO_2Me$, $CH_2CO_2Et$, OBn; hfacac is hexafluoroacetylacetonate

She and co-workers [292] prepared a mixture of regioisomeric dihydropyrons, with the product containing conjugated bonds predominating (the ratio from 1.5:1 to 4:1, the overall yield was 45–58%, 14 examples), by the reaction of 3-epoxy vinyl aldehydes with potassium *tert*-butoxide and thiazolium salt **29**. This process involved the C(2)–O bond cleavage of the epoxide ring and the formation of a new C–O bond with the carbonyl moiety (Scheme 144).

**Scheme 144**

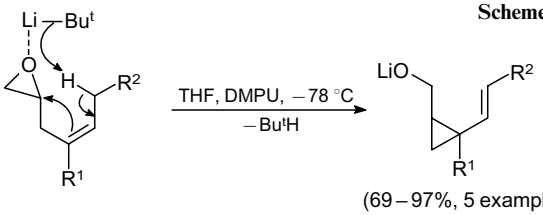



$R^1$ = H, Me;
$R^2$ = Ar, phenylethynyl




The cleavage of the heterocycle in allylic epoxides with lithium n-butoxide can be followed by the double bond migration and the formation of the cyclopropane moiety (Scheme 145).[147]

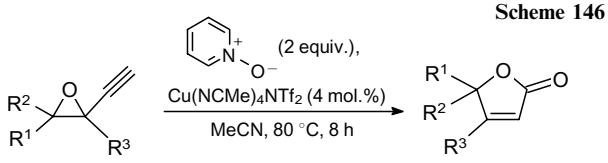
**Scheme 145**




$R^1$ = H, Me; $R^2$ = vinyl, Ph; DMPU is dimethylpropyleneurea

Gagosz and co-workers [293] synthesized α,β-unsaturated δ-lactones from ethynyl epoxides. The reaction occurred through the epoxide C–O bond cleavage followed by the oxidative cyclization involving the triple bond (Scheme 146).

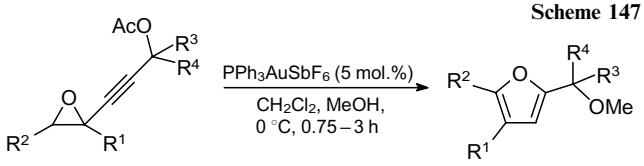
**Scheme 146**




$R^1$ = H, Me, $CH_2OR^4$ ($R^4$ = H, $SiPr^i_3$, C(O)But), NTsPh;
$R^2$ = H, Me, $(CH_2)_2Ph$, $CH_2OCH_2CCH$, *etc.*;
$R^3$ = H, Ar; $R^2–R^3$ = $(CH_2)_n$ ($n$ = 4, 5), *etc.*

Pale and co-workers [294] developed an approach to the synthesis of furan derivatives from epoxides containing the acetoxyalkynyl substituent in the presence of a gold-containing catalyst (Scheme 147).

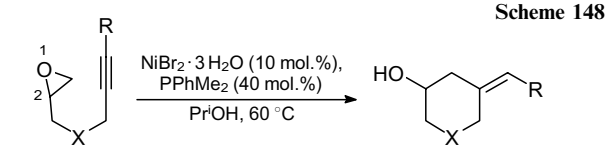
**Scheme 147**




$R^1$ = H, $R^2$ = $R^3$ = Me, $R^4$ = $(CH_2)_2Ph$ (85%);
$R^1$ = H, $R^2$ = Me, $R^3–R^4$ = $(CH_2)_5$ (92%);
$R^1–R^2$ = $(CH_2)_4$, $R^3$ = H, $R^4$ = $(CH_2)_2SiPr^i_3$ (74%);
$R^1–R^2$ = $(CH_2)_4$, $R^3$ = H, $R^4$ = $C_6H_4NO_2$-2 (59%)

Beaver and Jamison [295] described the $Ni^{II}$-catalyzed tandem reaction involving the epoxide ring and the triple bond of the substituent. This process occurred through the C(2)–O bond cleavage of the epoxide ring, reduction and intramolecular addition to the triple bond (Scheme 148).

**Scheme 148**




X = $CH_2$, NBn, O

X = $CH_2$, R = Ph (70%);
X = $C(CO_2Me)_2$, R = Ph (76%);
X = NBn, R = Ph (74 %);
X = O, R = H (55%);
X = O, R = n-$C_5H_{11}$ (75%)

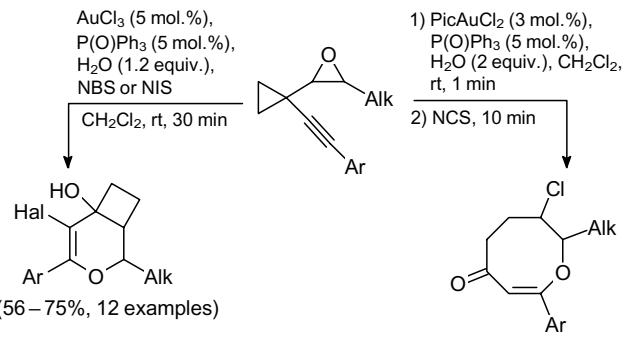
Liao and Liu [296] reported the ring expansion of 1-oxiranyl-1-alkynylcyclopropanes. Two types of transformation, involving the epoxide ring, the cyclopropane moiety and the alkynyl group, followed by the participation of water and a halogenating reagent were described (Scheme 149).

Muthusamy *et al.*[31] demonstrated that spiro epoxyoxindoles functionalized with the propargyl benzoate moiety undergo the C–C bond cleavage of the epoxide ring and intramolecular [3+2]-cycloaddition of the propargyl moiety under prolonged reflux in toluene (Scheme 150).

The intramolecular reaction involving the vinyl epoxide and propargyl moieties, described by Feng and Zhang,[297] occurred in the presence of a rhodium N-heterocyclic carbene catalyst and consisted of the [5+2]-cycloaddition and the subsequent Claisen rearrangement (Scheme 151).

Yeh and co-workers [298] performed the tandem semipinacol rearrangement/alkyne–aldehyde metathesis (Scheme 152).

**Scheme 149**

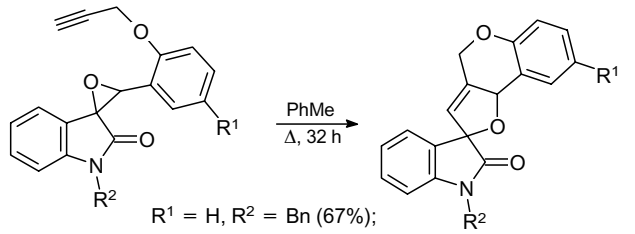



(56 – 75%, 12 examples)

(47 – 83%, 12 examples)

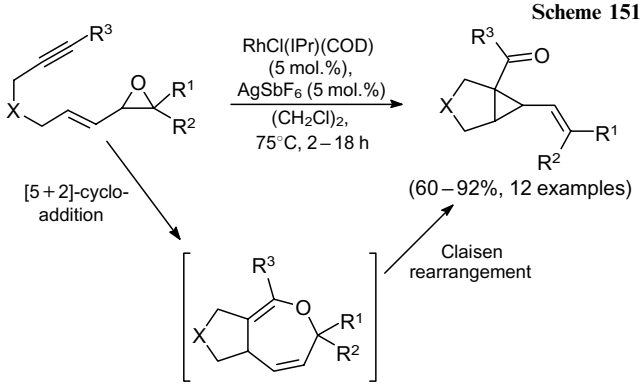
Hal = Br, I; NIS is *N*-iodosuccinimide, Pic is picolate

**Scheme 150**




$R^1$ = H, $R^2$ = Bn (67%);
$R^1$ = Cl, $R^2$ = Et (59%);
$R^1$ = $NO_2$, $R^2$ = Bn (64%)

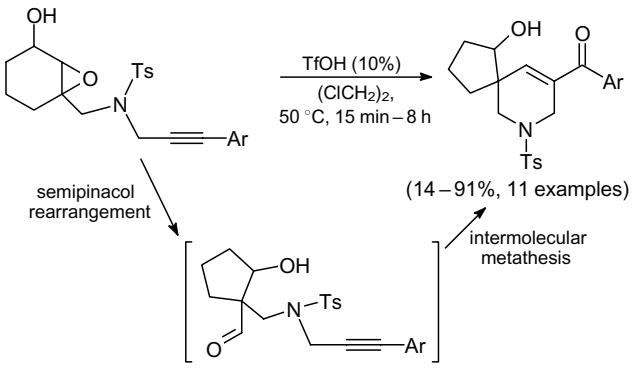
**Scheme 151**




(60 – 92%, 12 examples)

X = $C(CO_2Me)_2$, NTs, O; $R^1$ = H, Me; $R^2$ = Me, Ph;
$R^3$ = Me, Ph, $C_6H_4OMe$-4, $C_6H_4NO_2$-4;
IPr is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene

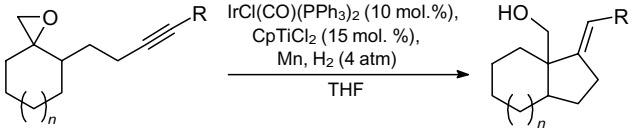
**Scheme 152**




(14 – 91%, 11 examples)

Gansauer *et al.*[299, 300] (Scheme 153) and Chakraborty *et al.*[301] (Scheme 154) explored metal-catalyzed intramolecular reactions giving new carbocycles through the epoxide ring-opening.

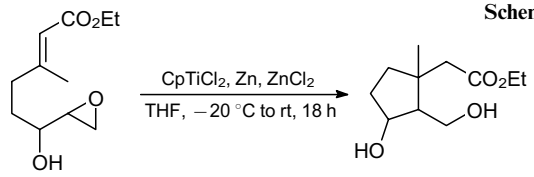
**Scheme 153**




R = Me, Ph; *n* = 1, 2;
Cp is cyclopentadienyl

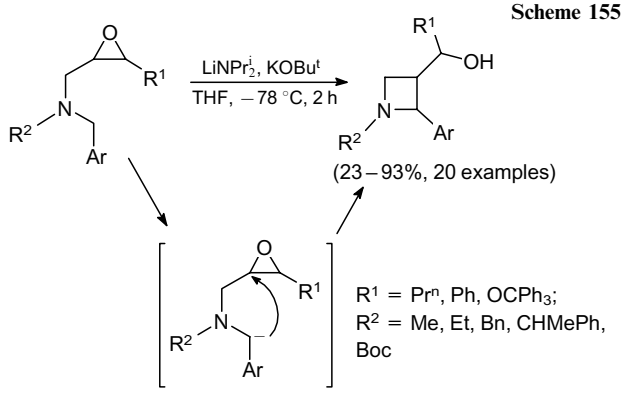
(68 – 91%, 3 examples)

**Scheme 154**




Kovacs *et al.*[302] reported the regio- and diastereoselective transformation of *N*-benzylaminomethyl epoxides into azetidines using a mixture of lithium diisopropylamide and potassium *tert*-butoxide. This reaction proceeds through the epoxide ring-opening of the intermediate carbanion accompanied by the 4-*exo-tet* cyclization (Scheme 155).

**Scheme 155**



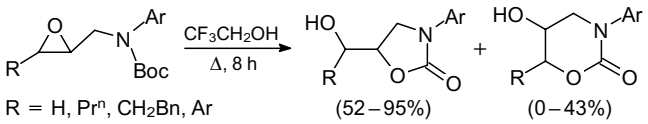

(23 – 93%, 20 examples)

$R^1$ = $Pr^n$, Ph, $OCPh_3$;
$R^2$ = Me, Et, Bn, CHMePh, Boc

Das and co-workers[303] converted amidomethyl epoxides into 1,3-oxazolidinone and 1,3-oxazinan-2-one derivatives (Scheme 156, 9 examples). Oxazolidinones annulated with the five-membered carbocycle were also synthesized from epoxy compounds by Ponticelli's research group[304] (Scheme 157).

Teran and co-workers[305] described the intramolecular 6-*exo-ter* or 7-*endo-tet* cyclization of *N*-hydroxyethylglycidic acid amides. Depending on the reaction conditions,

**Scheme 156**

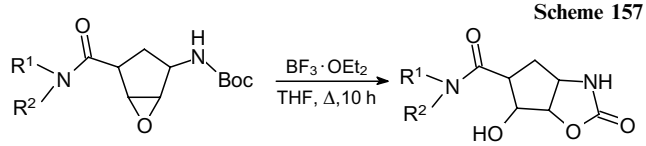



R = H, $Pr^n$, $CH_2Bn$, Ar

(52 – 95%)

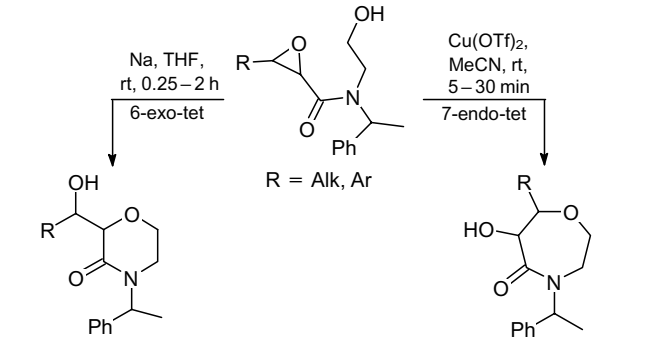
(0 – 43%)

**Scheme 157**




$R^1$ = H, Et; $R^2$ = Et, $(CH_2)_3OH$, Ph, *etc.* (78–93%, 5 examples)

**Scheme 158**



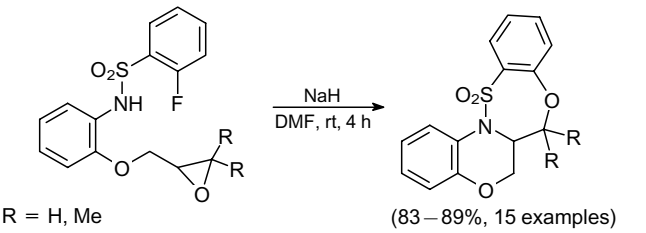

R = Alk, Ar

(78–98%, 10 examples) (40–95%, 10 examples)

either the morpholin-3-one or 1,4-oxazepan-5-one core is formed (Scheme 158).

The tandem epoxide ring-opening–double cyclization reaction of sulfanilamides containing an *ortho*-epoxymethoxy-substituted aryl moiety at the nitrogen atom and the *ortho*-fluorophenyl moiety at the sulfur atom was described by Das *et al.*[306] (Scheme 159).

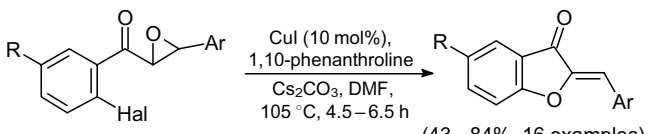
**Scheme 159**




R = H, Me (83–89%, 15 examples)

The transformation of 2-arylethoxy 2-haloaryl ketones into 2-benzylidenebenzofuran-3(2*H*)-ones (aurones), in particular into natural products, catalyzed by monovalent copper iodide was carried out by Su's research group[307] (Scheme 160).

**Scheme 160**




R = H, OMe; Hal = Cl, Br, I (43–84%, 16 examples)

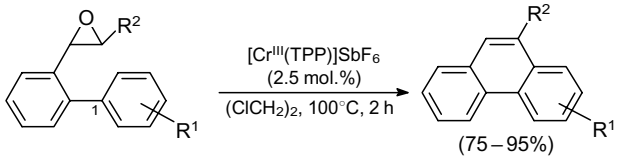
This part of the review covers the data on intramolecular tandem reactions of functionalized epoxides, which do not involve in the Meinwald rearrangement (see Section 3.3.1). These transformations occur through the C–O or C–C bond cleavage and afford diverse carbo- or heterocyclic structures. The next Section of the review is devoted to the intramolecular Friedel–Crafts reaction using epoxide compounds functionalized with aromatic systems and it supplements the data presented in Sections 3.3.1 and 3.3.2. The data on the Friedel–Crafts reaction are summarized in a separate Section because of their abundance and significance for the chemistry of epoxides.

### 3.3.3. Intramolecular Friedel–Crafts reaction involving functionalized epoxides

The Friedel–Crafts reaction is of great importance in the construction of carbo- and heterocyclic structures, which is highlighted in the review[4] published in 2017. The studies dealing with the use of this reaction in the chemistry of epoxides, which were published in 2010–2022, are considered below.

The research groups under the direction of Matsubara,[308] Zondlo[309] and Chiu[310] investigated the formation of benzannulated carbocycles from different epoxide derivatives containing phenyl substituents (Schemes 161–163, respectively).

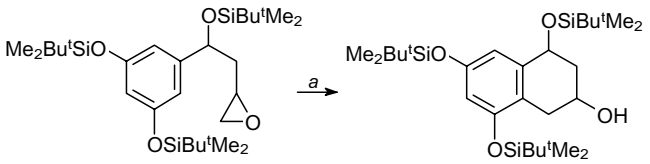
**Scheme 161**




(75–95%)

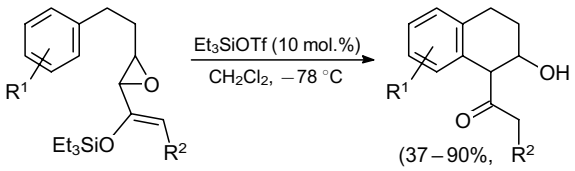
$R^1$ = H, 2-Me, 3-Me, 4-Me, 3-OMe; $R^2$ = H, Ph; TPP is 5,10,15,20-tetraphenylporphyrin

**Scheme 162**




(*a*) $MgBr_2 \cdot OEt_2$ (20 mol.%), $CH_2Cl_2$, 24 h, rt, 65%

**Scheme 163**




(37–90%, 9 examples)

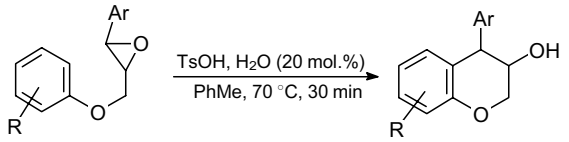
$R^1$ = H, 3-Pr$^i$, 3-OMe, 3-OBn, 3-Br, 2,4-$Me_2$; $R^2$ = H, Me

Chroman-3-ols were synthesized from aryloxymethyl epoxides by Das and co-workers[311,312] and by Qu and Li[313] (Schemes 164 and 165, respectively).

Wei and Zhang[314] developed a procedure for the ytterbium triflate-catalyzed synthesis of isochromanones from (het)aroyl-containing epoxy compounds (Scheme 166).

Wei *et al.*[315] described the scandium triflate-catalyzed intramolecular alkylation of the indole and pyrrole rings epoxycarbonyl-substituted at the nitrogen atom. These reactions produced 1,4-oxazino[4,3-*a*]indoles (Scheme 167) or related pyrroles.

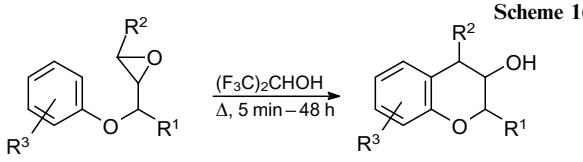
**Scheme 164**




(50–88%, 15 examples)

R = 4-Me, 2,4-$Me_2$, 4-$Bu^t$, 3-OMe, 3-Br, 3-I, 2,4-$(OMe)_2$, 3,4-$(OMe)_2$, 2,3,4-$(OMe)_3$, 2,3-benzo, 3,4-benzo; Ar = Ph, $C_6H_4Br$-4

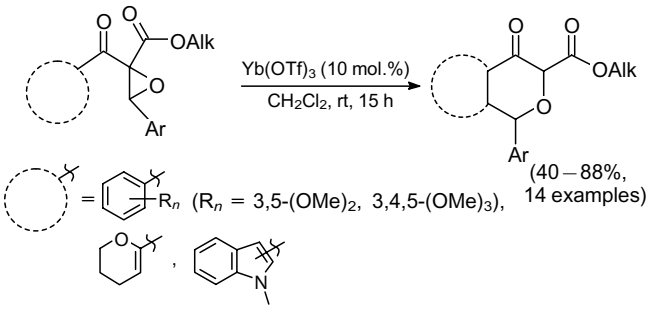
**Scheme 165**




(51–99%, 10 examples)

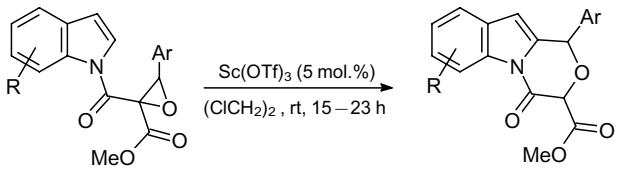
$R^1$ = H, Ph; $R^2$ = H, Me, Ph;
$R^3$ = H, 4-$Bu^t$, 3,5-$(OMe)_2$, 4-Br, 4-I, 3,4-benzo

**Scheme 166**




(40–88%, 14 examples)

**Scheme 167**



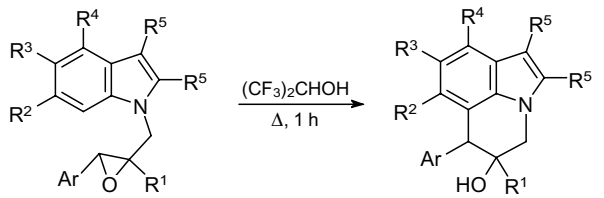

(26–95%, *dr* = 2 : 1–4 : 1; 10 examples)

R = H, 2-Me, 3-Me, 5-Me;
*dr is diastereomeric excess*

Das *et al.*[316] reported the intramolecular ring closure at the 7 position of the indole system for epoxymethyl-*N*-tethered indoles (Scheme 168).

Chakraborty and Khan[317] performed the cyclization of related compounds at the 2 position of indole. This radical-induced reaction was promoted by cyclopentadienyltitanium chloride and occurred in the presence of *sym*-collidine (2,4,6-trimethylpyridine) and trimethylsilyl chloride (Scheme 169).

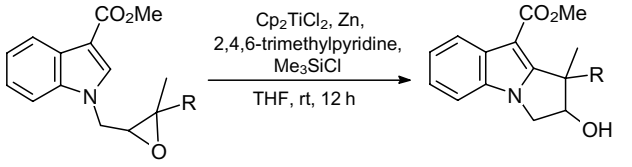
**Scheme 168**




(66–79%, 14 examples)

$R^1$ = H, Me; $R^2$ = H, Me, OMe;
$R^3$ = H, OMe; $R^4$ = Me, OMe, OBn;
$R^5$ = H, Me; $R^5$–$R^5$ = benzo

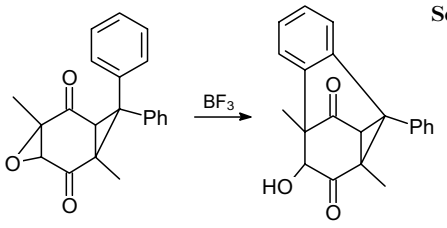
**Scheme 169**




R = Me (86%), $CH_2OSiBu^tMe_2$ (74%), Ph (27%)

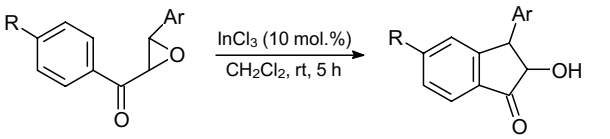
The unusual intramolecular Friedel–Crafts alkylation involving the epoxide moiety was described by Oshima and co-workers[318, 319] (Scheme 170).

**Scheme 170**




Ahmed and co-workers synthesized 2-hydroxyindan-1-ones from 2-arylethoxy aryl ketones using tin chloride,[320, 321] titanium chloride[321] or indium chloride as the catalyst (Scheme 171).[322]

**Scheme 171**

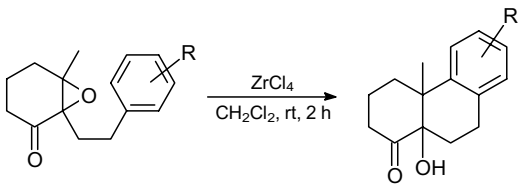



R = H, Cl, Br

(81–95%, 16 examples)

The diastereoselective synthesis of decalinol derivatives, containing the structural moiety of many natural products, from epoxides was developed by Baati and co-workers[38] (Scheme 172).

**Scheme 172**

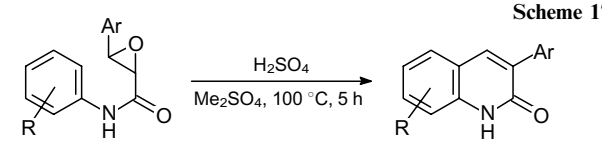



R = 3-Me (90%), 3-OMe (91%), 3-NHBoc (74%), 3,4-$OCH_2O$ (89%)

3-Aryl-2,3-epoxypropionic acid anilides were transformed into 3-arylquinolin-2-ones, the intramolecular Friedel–Crafts alkylation being accompanied by aryl migration and dehydration (Scheme 173).[15]

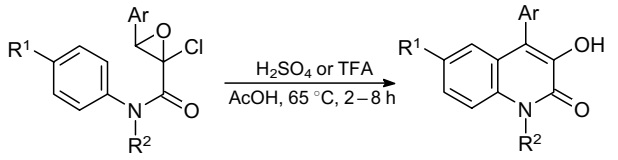
4-Aryl-3-hydroxyquinolin-2-ones were derived from 2-chlorine-containing analogues of such substrates; the

**Scheme 173**




R = H, 3-Me, 4-OMe, 3-Br, 4-Br (68–100%, 14 examples)

**Scheme 174**




$R^1$ = H, Me; $R^2$ = Me, Bn, PMB (75–99%, 24 examples)

intramolecular alkylation of the benzene ring was accompanied by dehydrochlorination (Scheme 174).[17,265]

The Friedel–Crafts cyclization of chiral 2-carbamido-3-(4-bromophenyl)glycidic acid *N*-methylanilide, which is not accompanied by dehydration and aromatization of the system, was accomplished by Takemoto and co-workers[62] (Scheme 175).

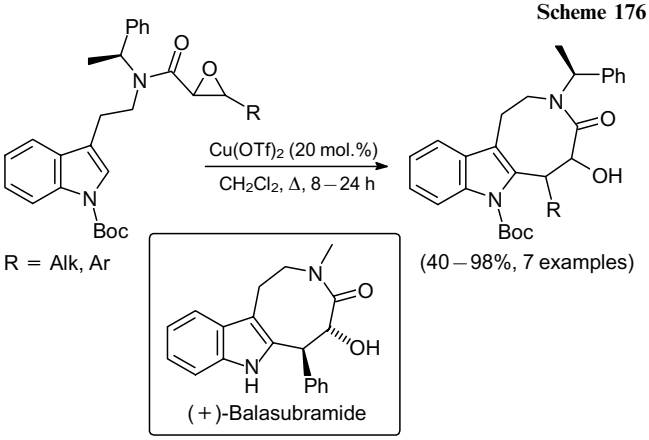
**Scheme 175**




(67%, 96% *ee*)

Teran and co-workers[81] constructed the core of the natural product balasubramide *via* 7-*endo-tet* cyclization of *N*-[2-(indol-3-yl)ethyl]anilides of 3-substituted glycidic acids (Scheme 176).

**Scheme 176**




R = Alk, Ar (40–98%, 7 examples)

A tricyclic compound containing annulated tetrahydrobenzazepinone and oxazole rings was synthesized from chiral oxazole bearing the epoxide moiety in the substituent at the nitrogen atom and the phenyl group at the 4 position (Scheme 177).[323]

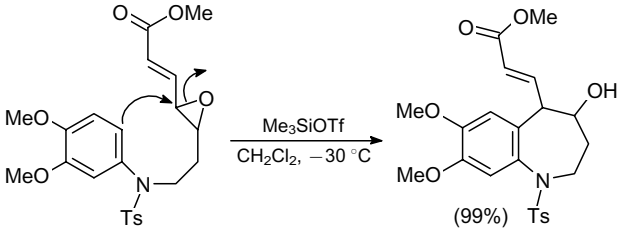
Nagumo and co-workers[324] reported the formation of tetrahydrobenzo-1(or 2)-azepines from functionalized epoxides *via* selective 7-*endo-tet* Friedel–Crafts cyclization in

**Scheme 177**




R = Ar, Alk (80–93%, 8 examples)

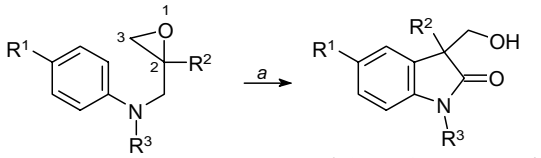
**Scheme 178**




the presence of trimethylsilyl triflate (Scheme 178 by an example of the benzo-1-azepine derivative).

Flowers and co-workers[325–327] described the titanium-catalyzed intramolecular radical transformation of glycidic acid anilides into 3-hydroxymethyl oxindoles (Scheme 179, see Ref. 325). In the presence of an additional methylene unit between the epoxide ring and the N atom or in the case when the methyl substituent on the epoxide ring is at the C(3) atom, the reactions performed under these conditions afforded tetrahydroquinoline derivatives.[325]

**Scheme 179**




(70–92%, 6 examples)

(*a*) $(C_5H_4Cl)_2TiCl_2$ (5 mol.%),
Mn, 2,4,6-trimethylpyridin·HCl, THF, Δ, 0.5–2 h;
$R^1$ = H, Cl, Br, $CO_2Me$, CN; $R^2$ = H, Me; $R^3$ = Me, Ar, *etc.*

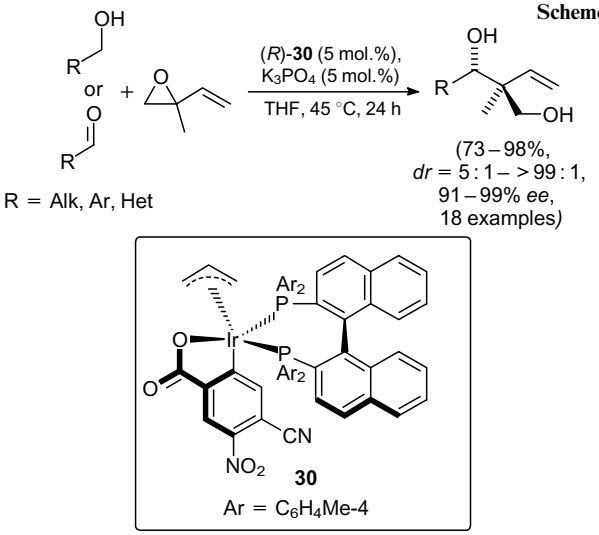
Therefore, functionalized epoxides proved to be useful substrates for the synthesis of various cyclic structures.

### 3.3.4. Tandem reactions involving epoxide and another reagent

The reactions of epoxides with other compounds often begin with the C–O or C–C bond cleavage of the oxirane ring and, depending on the nature of the reagent, involve either the coupling or cycloaddition, resulting in the formation of a new C–C bond, and the functionalization of the epoxide. If the epoxide already contains a functional group, it can be involved in the reaction with another reagent along with the epoxide function, thereby initiating or continuing the tandem process. The metal-catalyzed C–C bond forming reactions are covered in the review[328] published in 2016. The tandem processes considered in this Section involve, along with other steps, the Meinwald rearrangement, the Friedel–Crafts reaction and the nucleophilic epoxide ring-opening.

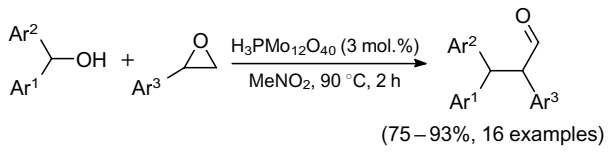
Thus, the coupling of primary alcohols or aldehydes with 1-methyl-1-vinyl epoxide catalyzed by chiral iridium complex **30** was studied by Krische and co-workers [329] (Scheme 180). Under these conditions, the reactions afforded β-diol derivatives in good yields with high diastereo- and enantioselectivity.

**Scheme 180**



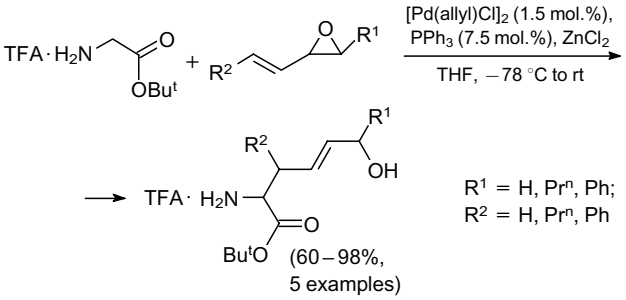

The coupling of diarylmethanols with aryl epoxides in the presence of heteropoly acid was accomplished by the research group under the direction of Hu and Yu [330] (Scheme 181).

**Scheme 181**



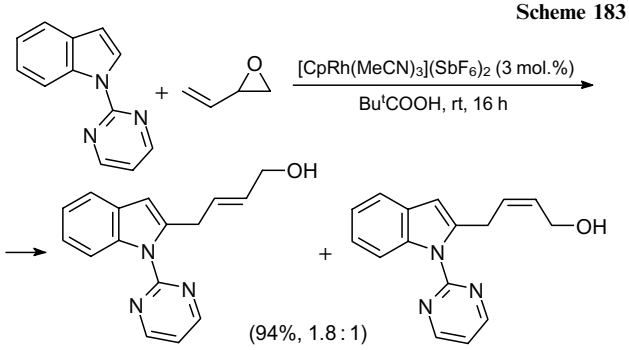

Thies and Kazmaier [331] demonstrated that the palladium-catalyzed coupling of amino acids at the double bond of vinyl epoxides is accompanied by the double bond migration, like the coupling with conjugated diene systems (Scheme 182). The ratio of the *trans*- and *cis*-isomeric products varied from 4 : 1 to 9 : 1; *dr*, from 1 : 1 to 7 : 1.

**Scheme 182**



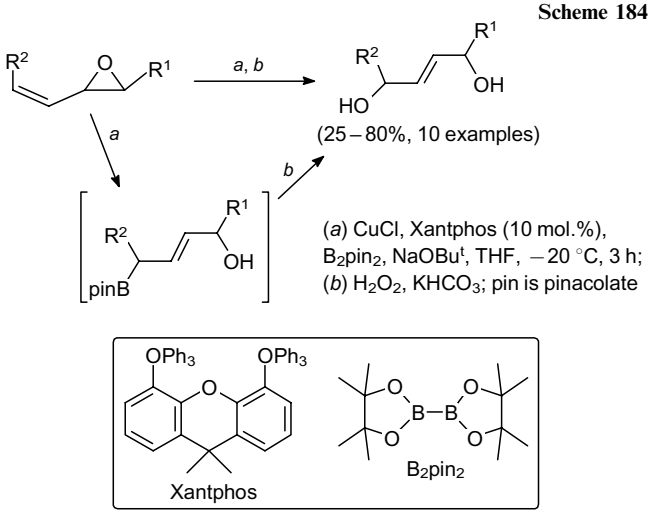

The rhodium-catalyzed reactions of aromatic or heteroaromatic compounds with vinyl epoxides giving allylated aromatic systems were explored by Li and Yu.[332] An example of one of the numerous reactions is presented in Scheme 183.

**Scheme 183**



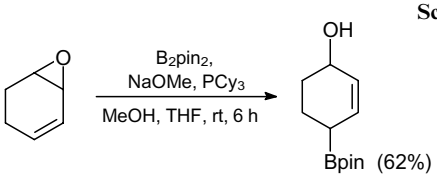

The phosphorus-catalyzed reaction between vinyl epoxides, containing substituents *cis*-oriented with respect to the double bond, and bis(pinacolato)diboron allowed the diastereoselective synthesis of vinyl diols bearing *syn*-oriented hydroxy groups (Scheme 184).[333]

**Scheme 184**




The similar reaction of cyclic vinyl epoxide afforded the diastereomeric *anti*-configured product (Scheme 185).[334]

**Scheme 185**

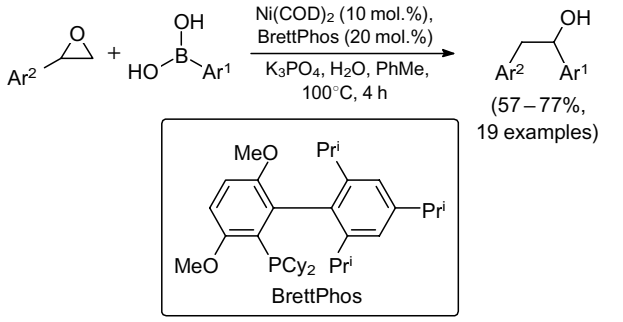



Schemes 186 and 187 show the coupling of organoboron compounds with aryl epoxides followed by the hydrolysis of the coupling products.[335, 336] The epoxide ring-opening reactions with organoboranes are covered in the review by Pineschi [337] published in 2014.

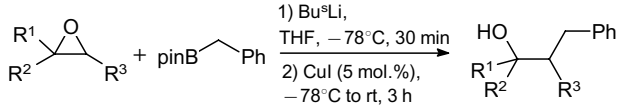
Vile's research group [338] reported the tandem synthesis of azetidinium salts *via* the epoxide ring-opening of epichlorohydrin with secondary amines and the intramolecular N-ring closure performed in batch (Scheme 188).

Zhang and co-workers [339–343] published a series of studies on the construction of heterocyclic structures using intermolecular reactions with epoxy compounds. It was demonstrated that the reactions of epoxide derivatives with aldehydes can follow two pathways depending on the conditions and the nature of substituents on the epoxide

**Scheme 186**

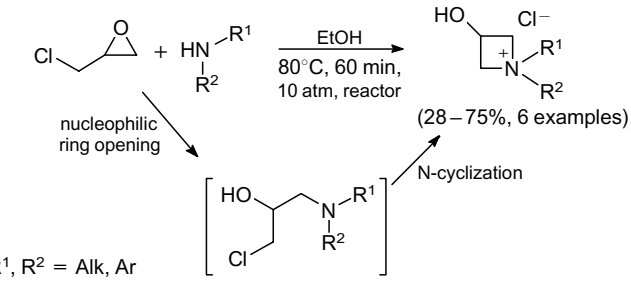



**Scheme 187**



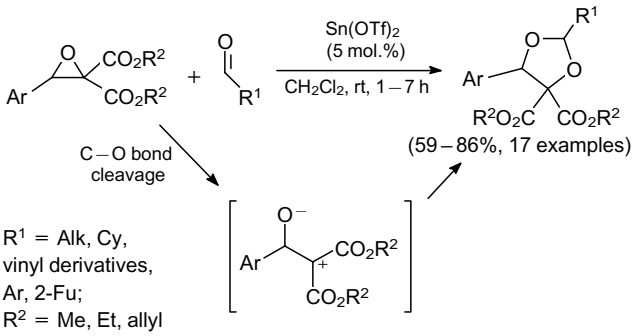

$R^1$ = H, Me;
$R^2$ = Me, $Bu^n$, $CH_2OPh$, $C_6H_4Br$-4, *etc.*;
$R^3$ = H; $R^3-R^2 = (CH_2)_4$

**Scheme 188**



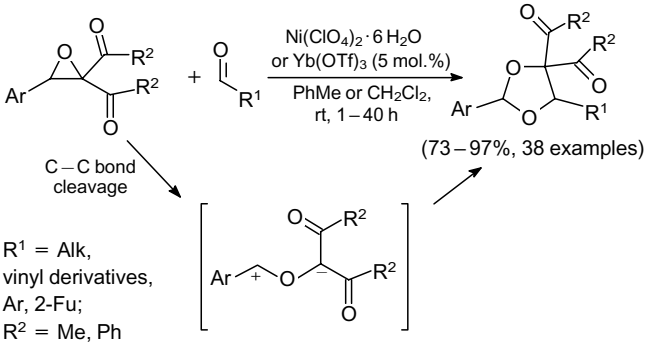

$R^1$, $R^2$ = Alk, Ar

**Scheme 189**




$R^1$ = Alk, Cy,
vinyl derivatives,
Ar, 2-Fu;
$R^2$ = Me, Et, allyl

**Scheme 190**

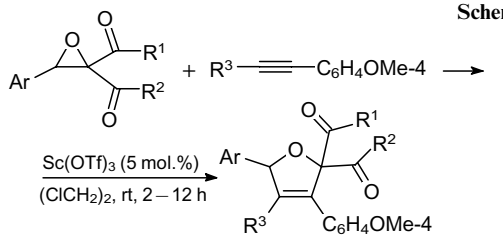



$R^1$ = Alk,
vinyl derivatives,
Ar, 2-Fu;
$R^2$ = Me, Ph

ring: through the initial C–O (Scheme 189)[339] or C–C bond cleavage (Scheme 190).[339,340] These reactions afforded 1,3-dioxolanes containing substituents in different positions. In the latter case (see Scheme 190), the reactions occurred in a diastereoselective fashion regardless of the aldehyde use and gave *syn* diastereomers as the major products.

The [3 + 2]-cycloaddition of epoxides with *p*-methoxyphenylacetylenes in the presence of scandium triflate produces 2,5-dihydrofurans (Scheme 191).[341]

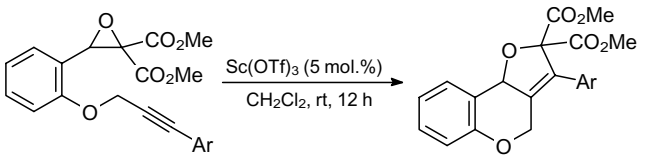
**Scheme 191**




$R^1$ = Me, Ph, OMe;
$R^2$ = Me, Ph, OMe, OEt; $R^3$ = Alk, Ar, Br, 1-Naph

Apart from the Lewis acid-promoted intermolecular [3 + 2]-cycloaddition, an intramolecular version of this transformation was also described (Scheme 192).[341]

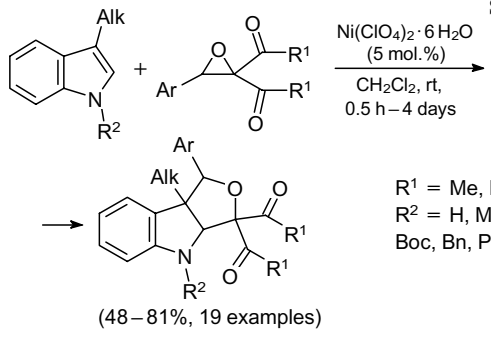
**Scheme 192**




Ar = Ph (43%), $C_6H_4OMe$-4 (76%)

The nickel perchlorate-catalyzed [3 + 2]-cycloaddition of epoxides with indoles affords benzannulated tetrahydrofuroindoles in a diastereoselective fashion (Scheme 193).[342]

**Scheme 193**

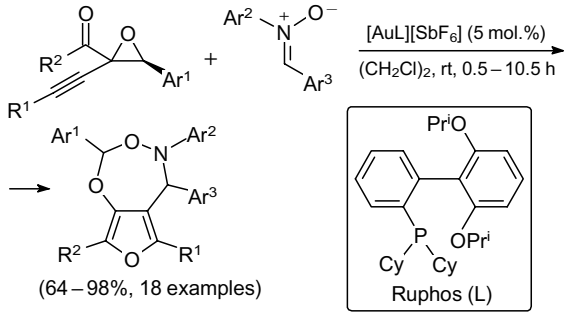



$R^1$ = Me, Ph, OAlk;
$R^2$ = H, Me, allyl,
Boc, Bn, Ph

Biheterocyclic compounds were synthesized by the [4 + 3]-cycloaddition of 1-alkynyl epoxy ketones with nitrones in the presence of a gold-containing catalyst with phosphine ligands (Scheme 194).[343]

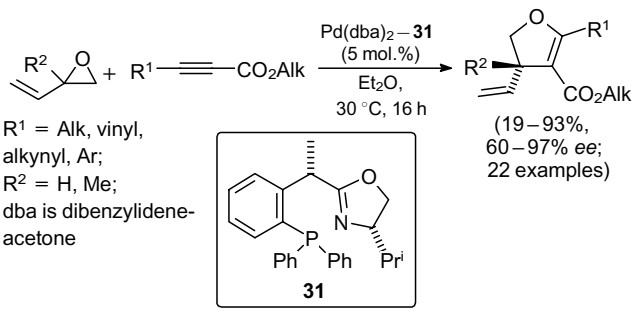
Hou and co-workers[344] synthesized 3-alkoxycarbonyl-4-vinyl-4,5-dihydrofurans by employing the [3 + 2]-cycloaddition of epoxides with alkoxycarbonylacetylenes catalyzed by a Pd complex with chiral ligand **31** (Scheme 195).

**Scheme 194**



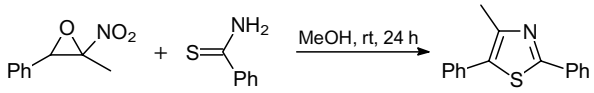

$R^1$ = Alk, Ar; $R^2$ = Me, Ar

**Scheme 195**



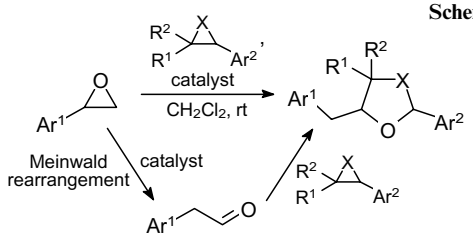

Tsogoeva's research group [48] reported the synthesis of 4-methyl-2,5-diphenylthiazole in 80% yield from 1-methyl-1-nitro-2-phenyloxirane and thiobenzamide (Scheme 196).

**Scheme 196**




The reactions of aryl epoxides with cyclopropanes, aziridines or epoxides in the presence of $InCl_3$, $BF_3 \cdot OEt_2$ or $Ni(ClO_4)_2 \cdot 6H_2O$ afforded of 2,5-disubstituted tetrahydrofurans,[345] 1,3-oxazolidines [346] or 1,3-dioxolanes,[347] respectively, in a diastereoselective fashion (Scheme 197).

**Scheme 197**

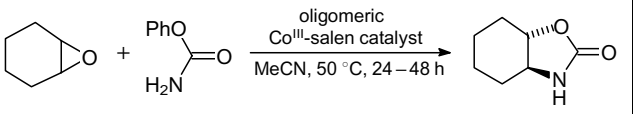



X = $CH_2$, $R^1$ = $R^2$ = $CO_2Et$ (50–88%, 8 examples);
X = NTs, $R^1$ = H: $R^2$ = Bu$^i$, Ph (30–92%, 13 examples);
X = O, $R^1$ = H: $R^2$ = $CO_2Alk$, $CO_2allyl$ (60–75%, 9 examples)

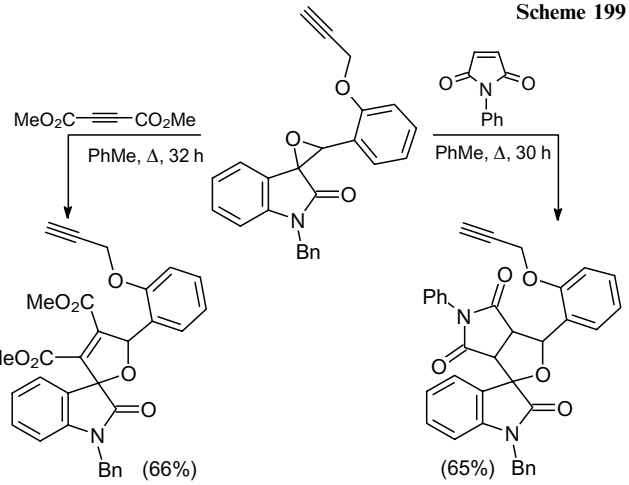
Birrell and Jacobsen [348] described the enantioselective addition of phenyl carbamate to *meso* epoxides promoted by an oligomeric cobalt catalyst with the chiral salen ligand (Scheme 198).

Muthusamy *et al.*[31] demonstrated that the intermolecular [3 + 2]-cycloaddition (Scheme 199) rather than the intramolecular [3 + 2]-cycloaddition involving the propargyl moiety and the epoxide ring (see Scheme 150 in Section 3.3.2) predominates in a mixture of spiro epoxyoxindole functionalized with the propargylic benzoate moiety and dimethyl acetylenedicarboxylate or *N*-phenylmaleimide.

**Scheme 198**

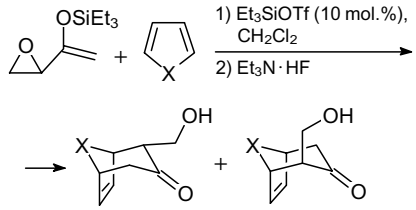



**Scheme 199**




The [4 + 3]-cycloaddition of epoxy enol silanes, including chiral reagents, with cyclopentadiene and furan was explored by Chiu's research group [349–352] (Scheme 200).

**Scheme 200**




X = O, $CH_2$

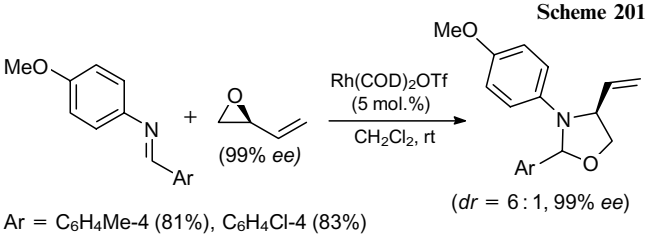
Jarvo and co-workers [353] synthesized substituted 1,3-oxazolidines from arylimines and vinyl epoxides in the presence of a rhodium catalyst. The process occurred with retention of chirality when using a chiral epoxy compound (Scheme 201). The reactions using racemates of epoxides in the presence of a palladium [354] or rhodium [355] catalyst with chiral ligands afforded enantiopure products, the configuration of the chiral carbon atoms in which depended on the configuration of the chiral atoms in the ligand.

Substituted 3-vinyl-1-oxa-4-azaspiro[4.5]deca-6,9-dienes were synthesized by the research group under the direction of Zhou and He [355] using palladium-catalyzed reactions of vinyl epoxide with 4-alkoxycyclohexadienimines (Scheme 202).

A large series of 1,3-oxazolidin-2-ones were synthesized from epoxides and isocyanates in the presence of pyridinium iodide **32** (Scheme 203).[356]

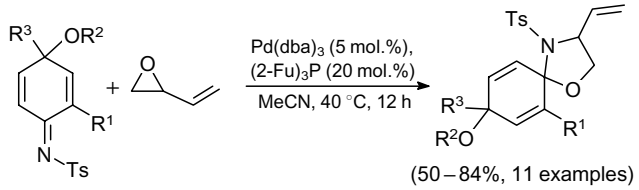
The reaction of 1-methyl-1-vinyloxirane with nitroalkenes in the presence of ferrocene (**33**) and palladium

**Scheme 201**




Ar = $C_6H_4Me$-4 (81%), $C_6H_4Cl$-4 (83%)

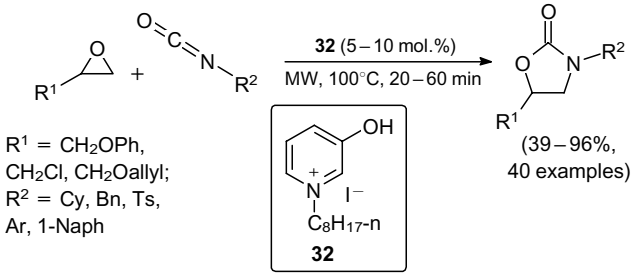
**Scheme 202**




(50 – 84%, 11 examples)

$R^1$ = H, Me, Cl, *etc.*; $R^2$ = Me, $CH_2CF_3$; $R^3$ = Me, $Bu^n$

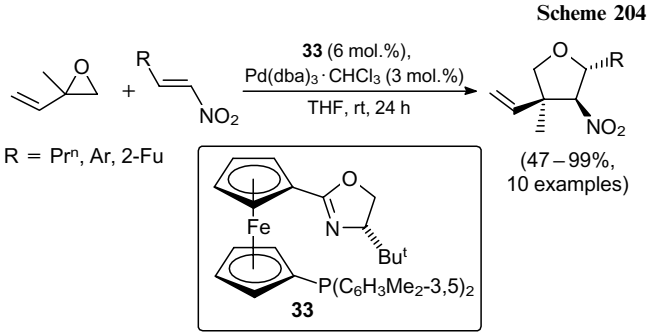
**Scheme 203**




$R^1$ = $CH_2OPh$, $CH_2Cl$, $CH_2Oallyl$;
$R^2$ = Cy, Bn, Ts, Ar, 1-Naph

(39 – 96%, 40 examples)

**Scheme 204**




R = $Pr^n$, Ar, 2-Fu

(47 – 99%, 10 examples)

catalysts produces nitro-substituted tetrahydrofurans (Scheme 204).[357] The diastereomeric ratio in the products varies from 2 : 1 to 20 : 1, and the enantiomeric excess is 4 – 72%.

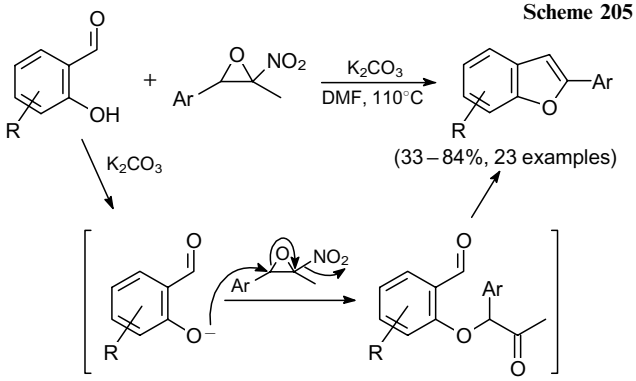
Ranjbari and Tavakol[358] synthesized benzofuran derivatives *via* the tandem reaction of nitro epoxides with salicylaldehyde and its analogues (Scheme 205).

Cyclic epoxy compounds react with acetates to form fused bicyclic compounds containing the tetrahydrofuran-2-one moiety (Scheme 206).[359]

Pizzo and co-workers[360] reported the synthesis of 1,3-dioxolanes by the reactions of epoxides with compounds containing the activated methylene group, *e.g.*, with acetylacetone, promoted by polymer-supported bases (Scheme 207).

Various reactions of spiro epoxyoxindoles have been extensively studied. Thus, Kumar and co-workers[361] synthesized spirotetrahydrofuranoxindoles by the reactions of

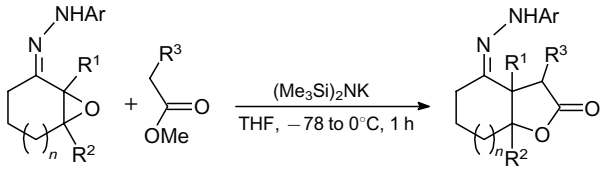
**Scheme 205**




(33 – 84%, 23 examples)

R = H, 2-OMe, 4-$NEt_2$, 5-Hal (F, Cl, Br)

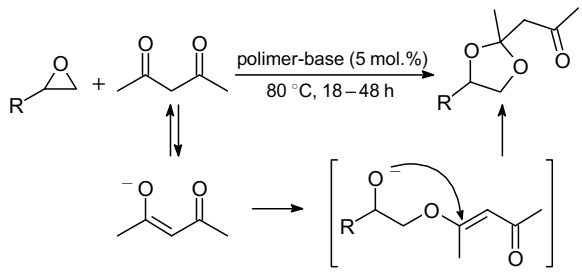
**Scheme 206**




(51 – 92%, 20 examples)

$R^1$, $R^2$ = H, Me; $R^3$ = Me, Et, $CO_2Me$, Ar, 2-Naph, 2-Th; *n* = 1, 2

**Scheme 207**




R = $CH_2Oallyl$ (28%), $CH_2Cl$ (37%), $CH_2OBn$ (34%), $CH_2OPh$ (29%), $CH_2Fu$-2 (36%)

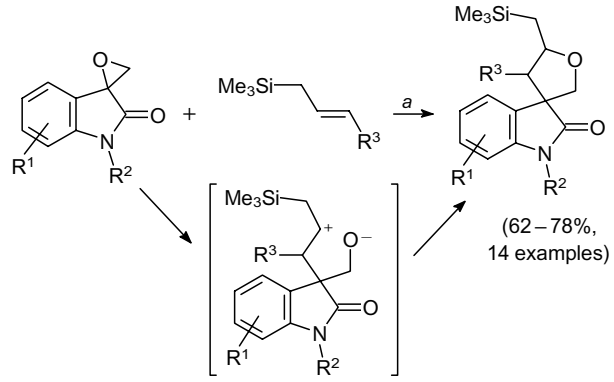
such compounds with allylsilanes in the presence of $BF_3 \cdot OEt_2$ (Scheme 208).

An increase in the amount of $BF_3 \cdot OEt_2$ and in the reaction time and the rise in the reaction temperature to room temperature led to further transformations giving 1-allyl-1-hydroxymethyl-substituted oxindoles (Scheme 209). The reaction product with R = Me was used in the formal[††] synthesis of the natural product physovenine.[361]

Hajra *et al.*[362] successfully used scandium triflate as the catalyst in related reactions. Wang *et al.*[363] demonstrated that the reaction with styrenes in the presence of 2,4,6-triphenylpyrylium tetrafluoroborate (**34**) as the catalyst was accompanied by the epoxide ring-expansion of spiro epoxyoxindoles (Scheme 210). Zhai and co-workers[85] explored similar reactions with spiro epoxyoxindoles containing the trifluoromethyl group on the oxirane ring.

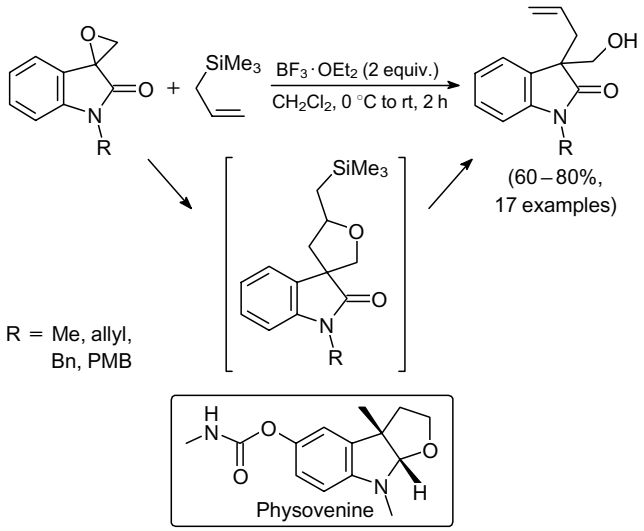
†† In the chemistry of natural products, the term formal synthesis defines the sequence of transformations up to the step giving the product, from which this compound has been synthesized previously.

**Scheme 208**

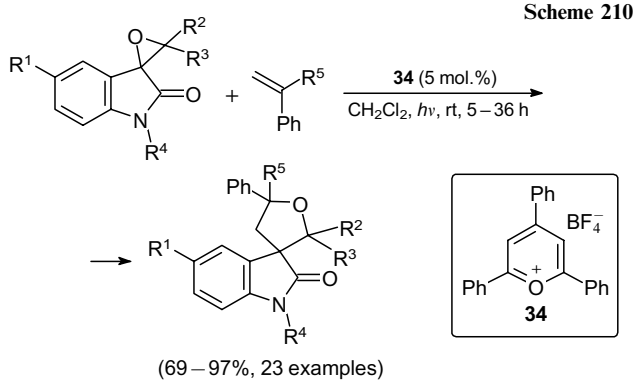



(*a*) $BF_3 \cdot OEt_2$ (20 mol.%), $CH_2Cl_2$, 0 °C, 30 min;
$R^1$ = H, 5-Me, 5-OMe, 5-$OCF_3$, 5-Hal, 7-F;
$R^2$ = Me, allyl, PMB, Bn; $R^3$ = H, Ph

**Scheme 209**



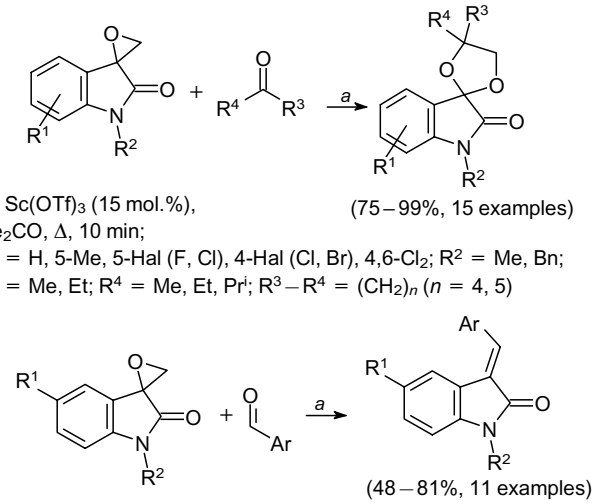

**Scheme 210**




$R^1$ = H, Me. OMe, Br, $NO_2$; $R^2$ = H: $R^3$ = $CO_2$Et, Ph;
$R^2$–$R^3$ = $(CH_2)_n$ ($n$ = 4, 5); $R^5$ = H, Me, Ph

Li and co-workers [364] performed the reactions of spiro epoxyoxindoles with ketones and aldehydes in the presence of scandium triflate giving spiro dioxolane oxindoles and alkylidene oxindoles, respectively (Scheme 211). The latter reaction accompanied by the elimination of two oxygen atoms was called by the authors an 'unexpected rearrangement'.

**Scheme 211**

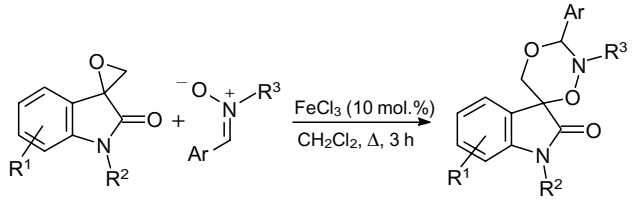



(*a*) $Sc(OTf)_3$ (15 mol.%), $Me_2CO$, Δ, 10 min;
$R^1$ = H, 5-Me, 5-Hal (F, Cl), 4-Hal (Cl, Br), 4,6-$Cl_2$; $R^2$ = Me, Bn;
$R^3$ = Me, Et; $R^4$ = Me, Et, Pr$^i$; $R^3$–$R^4$ = $(CH_2)_n$ ($n$ = 4, 5)

(*a*) $Sc(OTf)_3$ (15 mol.%), PhMe, 100 °C;
$R^1$ = Me, OMe, F, Cl; $R^2$ = Me, Bn, Boc

Yu and Cai [365] converted spiro epoxyoxindoles into spiro[1,4,2-dioxazinan]oxindoles by the treatment with nitrones in the presence of iron(III) chloride (Scheme 212).

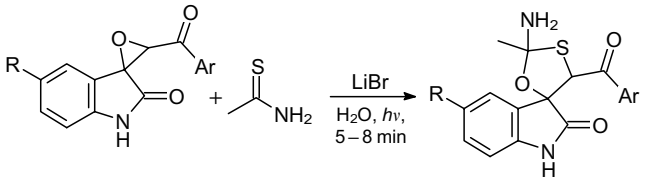
**Scheme 212**




$R^1$ = H, 5-Me, 7-F, 6-Cl; $R^2$, $R^3$ = Me, Bn

Dandia *et al.* [366] synthesized spiro oxathiolane oxindoles from spiro epoxyoxindoles, thioacetamide and LiBr (Scheme 213).

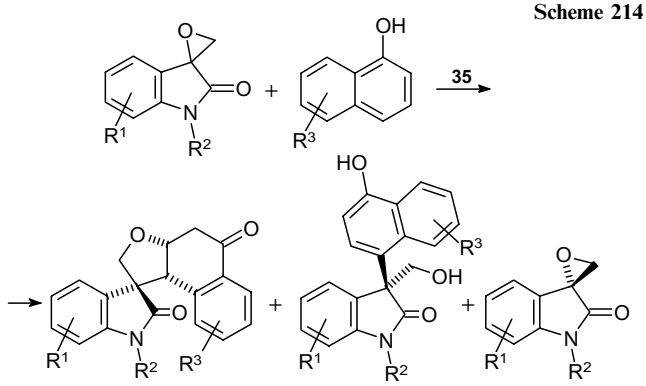
**Scheme 213**



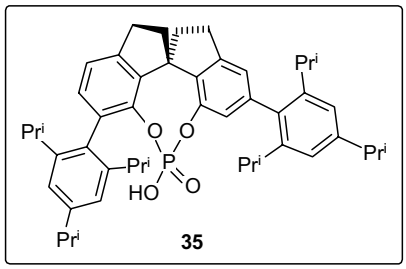

R = H, Me, Hal (F, Cl, Br)

Zhu *et al.* [367] performed the asymmetric transformation of spiro epoxyoxindoles by treating with 1-naphthols in the presence of chiral organophosphorus acid **35** as the catalyst. The reaction gave two products, the ratio of which depended on the reaction conditions, and simultaneously resulted in the kinetic resolution, with the isolation of one enantiomer of the starting spiro epoxyoxindole in the pure form (Scheme 214).

**Scheme 214**

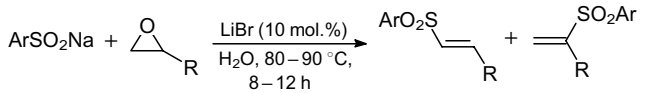



$R^1$ = H, 5-Me, 7-Me, 5-OMe, 5-Hal (F, Cl), 7-Cl, 6-Br;
$R^2$ = Me, allyl, $CH_2OMe$, Ac, Boc, $SiMe_2Bu^t$, Bn, PMB;
$R^3$ = H, 6-Me, 6-OMe, 7-OMe, 6-Hal (Cl, Br), 7-Cl, 6-Ph, 6,7-benzo




Yadav and co-workers [368] converted monosubstituted epoxides into vinyl sulfones by the treatment with sodium sulfinate in an aqueous medium in the presence of lithium bromide. This tandem catalytic process involves the epoxide ring-opening and water elimination from the sulfinated intermediate (Scheme 215).

**Scheme 215**



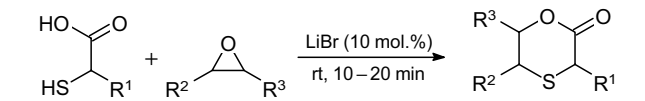

R = Me, $CH_2OPh$, Ar

This research group also explored the lithium bromide-catalyzed reactions of epoxides with α-sulfanylcarboxylic acids giving 1,4-oxathian-2-ones (Scheme 216) [369] and the pyrrolidine-catalyzed reaction of epoxides with cyclohexane-1,3-diones (Scheme 217).[370]

Wang and co-workers [371] demonstrated that the reactions of aryl epoxides with anilines in the presence of iron chloride afford 3-arylquinolines (Scheme 218).

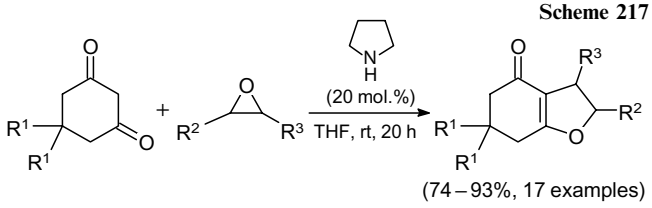
Two research groups reported the tandem synthesis of quinolines from epoxides and anilines catalyzed by scandium triflate [372] or ytterbium triflate.[373] This transformation involved the epoxide ring-opening, the dehydration, the intermolecular Mannich reaction with tautomers of intermediate vinylaniline, the intramolecular electrophilic substitution and the aromatization of the resulting quinoline system accompanied by the elimination of aniline (Scheme 219, see Ref. 373).

**Scheme 216**



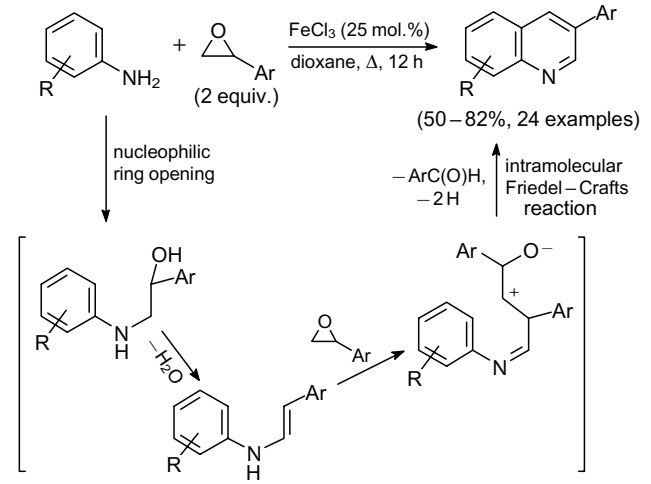

$R^1$ = H, Me; $R^2$ = Me, Ar; $R^2 – R^3 = (CH_2)_n$ ($n$ = 3, 4)

**Scheme 217**




$R^1$, $R^2$ = H, Me; $R^3$ = Me, $CH_2OPh$, Ar; $R^2 – R^3 = (CH_2)_4$

**Scheme 218**




R = H, 2-Me, 3-Me, 4-Me, 2,3-$Me_2$, 2,4-$Me_2$, 2,5-$Me_2$, 3,5-$Me_2$, 4-Et, 4-$Pr^i$, 4-$CF_3$, 4-OMe, 4-F, 2-Cl, 3-Cl, 3,4,5-$Cl_3$, 2-Br, 4-Br, 2,3-benzo

Beller and co-workers [374] reported the two-step synthesis of indoles from epoxides and anilines (Scheme 220).

Under more accessible conditions, indoles were derived from cyanoepoxides and anilines (Scheme 221).[375]

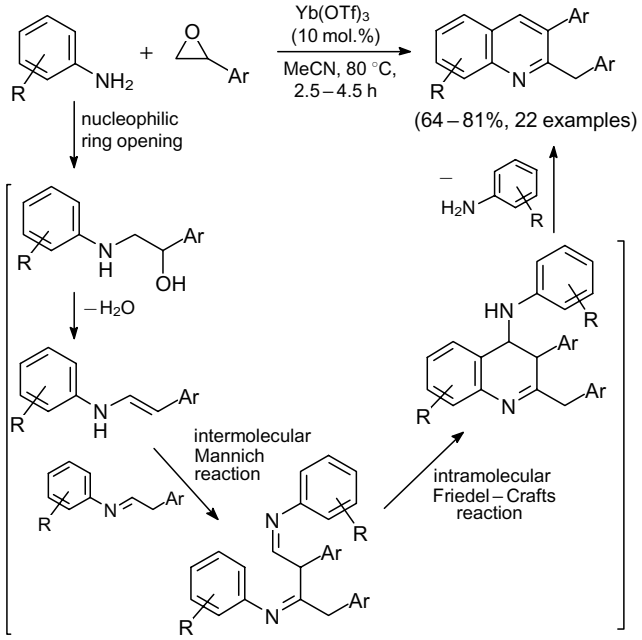
Das and co-workers [376 – 378] demonstrated the possibility of forming various fused biheterocyclic systems in the reactions using epoxides (Schemes 222 – 224).

The nucleophilic epoxide ring-opening of methyl 3-arylglycidates with phenylenediamines followed by the 7-*exo-trig* cyclization to diazepin-2-one derivatives was accomplished by the research group under the direction of Mamedov [14] (Scheme 225). This reaction has a high tolerance towards 3-aryglycidates except for those containing an electron-donating substituent on the aryl moiety (such examples are considered in Section 3.3.1, see Scheme 134).

Kumar *et al.*[379] described the asymmetric conversion of chiral epoxides into cyclopropane derivatives using triethyl phosphonoacetate (Scheme 226).

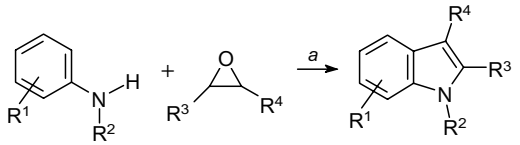
Battula and co-workers [380] performed the tandem synthesis using aryl epoxides and acetylenes. It involved the trifluoromethanesulfonic acid-promoted Meinwald rearrangement, the electrophilic addition of the resulting aldehyde to the acetylenic triple bond and the Friedel – Crafts-type ring closure of the intermediate giving naphthalene derivatives (Scheme 227).

**Scheme 219**




R = H, 2-Me, 3-Me, 4-Et, 2,4-$Me_2$, 3,4-$Me_2$, 3,5-$Me_2$, 3-OMe, 4-OMe, 3,4-$(OMe)_2$, 3,5-$(OMe)_2$, 3,4,5-$(OMe)_3$, 2,3-benzo, 4,5-benzo, 3,4-$(CH_2)_3$, 3,4-$OCH_2O$

**Scheme 220**

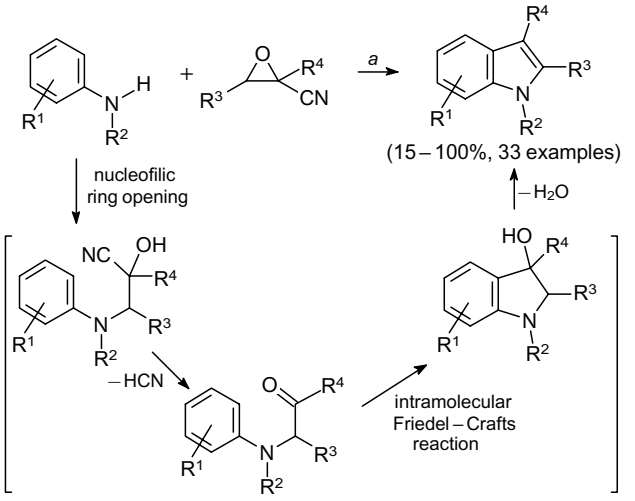



(*a*) 1) $Zn(OTf)_2$ (2 mol.%), rt, 1 h; 2) $Ru_3(CO)_{12}$ (1 mol.%), dppf (3 mol.%), TsOH (10 mol.%), dioxane, Δ, 22 h;
$R^1$ = H, 2-Me, 3-Me, 4-Me, 2,5-$Me_2$, 4-OMe, 4-OH, 4-$NMe_2$, 4-F, 4-Ac;
$R^2$, $R^3$ = H, Me; $R^4$ = $Bu^n$, Ar;
$R^3 – R^4$ = $(CH_2)_n$ (*n* = 3, 4); dppf is 1,1′-bis(diphenylphosphino)-ferrocene

Baskaran and co-workers[381] synthesized triarylcyclopentenones by the reactions of epoxides with aldehydes (Scheme 228).

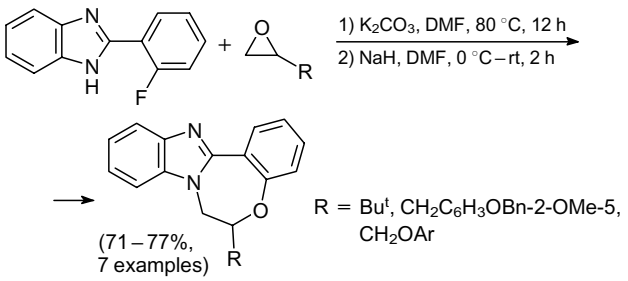
Diverse transformations of epoxy compounds using miscellaneous reagents are summarized in this Section. For example, Schemes 180, 181, 186 and 187 present the C – C bond formation *via* the coupling of epoxides; Schemes 189 – 195, 197, 199, 200, 204, 210 and 212, cycloaddition reactions using such substrates. The addition at the double bond of vinyl epoxides followed by the participation of the epoxide moiety in the transformation is shown in Schemes 182 – 185. The nucleophilic epoxide ring-opening and subsequent cyclization are displayed in Schemes 188, 196, 198, 201 – 203, 207, 213, 215, 216, 218 – 222, 224 and 225. Many tandem processes using epoxides and the second reagent catalyzed by Lewis or mineral acids begin with the Meinwald rearrangement (Schemes 197, 227, 228). In some cases, the functionalized intermediate in the tandem sequence favours the intramolecular Friedel – Crafts reaction (see the second product in Scheme 214 and Schemes 218 – 221,

**Scheme 221**

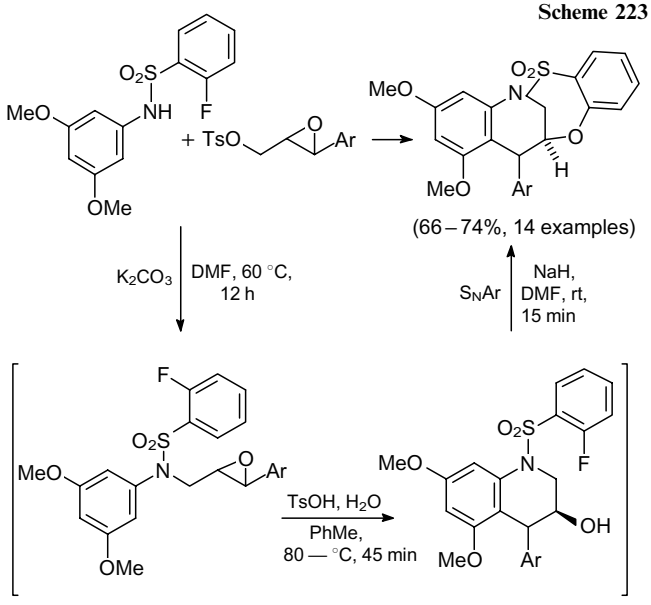



(*a*) $BF_3 \cdot OEt_2$ or $AlCl_3$, EtOH – $CF_3CH_2OH$ or $CF_3CH_2OH$, Δ, 20 – 30 h;
$R^1$ = H, 2-Me, 2,4-$Me_2$, 3,4-$Me_2$, 4-Alk (Et, $Pr^i$, $Bu^t$), 4-OMe, 3,5-$(OMe)_2$, 3,4,5-$(OMe)_3$, 4-OH, 2,3-benzo, 4,5-benzo;
$R^2$ = H, Me, $Pr^n$, $Pr^i$; $R^3$ = $Bu^n$, $(CH_2)_2Ph$, Ar; $R^4$ = H, Me

**Scheme 222**

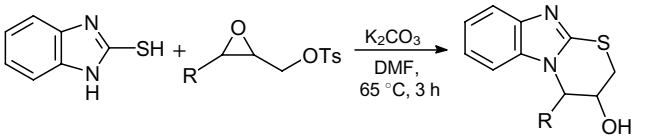



**Scheme 223**



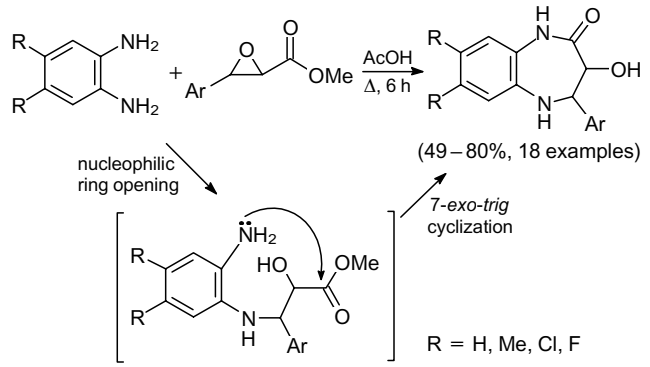

227). These reactions can be accompanied by the nucleophilic substitution of fluorine in the benzene ring (see Schemes 222, 223). The intermolecular Friedel – Crafts reac-

**Scheme 224**

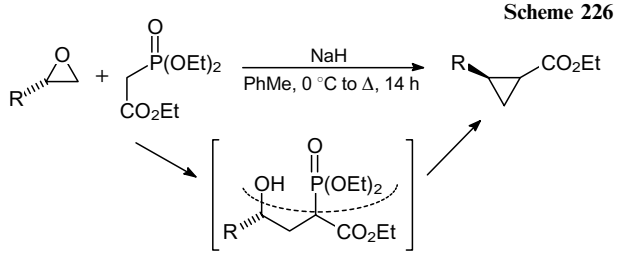



R = $Pr^n$, $(CH_2)_2Ph$, Ar (70–86%, 15 examples)

**Scheme 225**

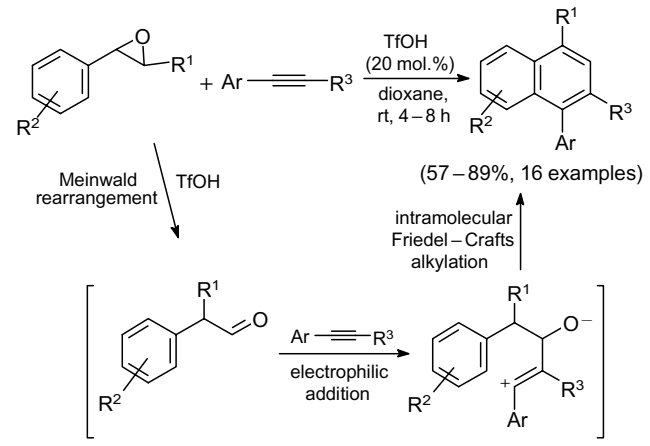



**Scheme 226**




R = n-$C_6H_{13}$ (85%), n-$C_7H_{15}$ (83%), OPMB Ph (75%)

**Scheme 227**



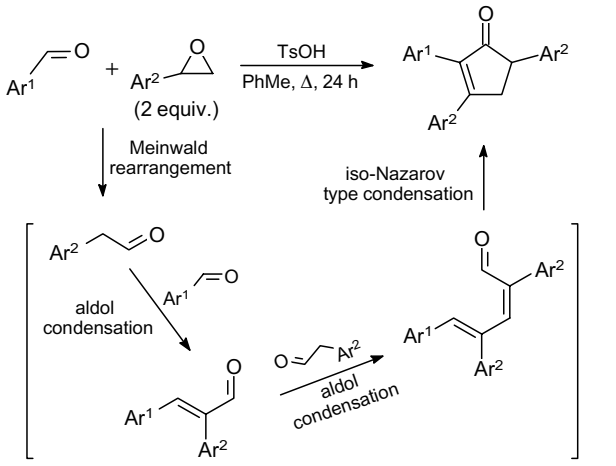

$R^1$ = H, Me, Ph; $R^2$ = H, 4-Hal (F, Cl), 3,5-$OCH_2O$; $R^3$ = H, Alk

tions with epoxides are considered in detail in the next Section.

### 3.3.5. Intermolecular Friedel–Crafts reactions involving epoxides

As mentioned above, the Friedel–Crafts reaction plays a significant role in the chemistry of epoxides. Intramolecular

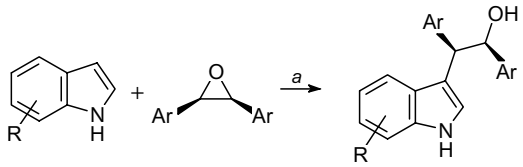
**Scheme 228**




versions of this reaction are considered in Section 3.3.3. This Section covers the tandem intermolecular reactions with epoxides, involving the electrophilic substitution of the aromatic ring. The intra- and intermolecular reactions of epoxides with π-nucleophilic reagents, including aromatic and heteroaromatic compounds, are described in detail in the review [382] published in 2010. The recent studies are discussed below.

Ollevier and co-workers [383] performed the electrophilic substitution in indoles accompanied by the desymmetrization of *meso* epoxides in the presence of a $Fe^{II}$ complex with chiral ligand **23** (Scheme 229).

**Scheme 229**




(64–99%, 96–>99% *ee*; 13 examples)

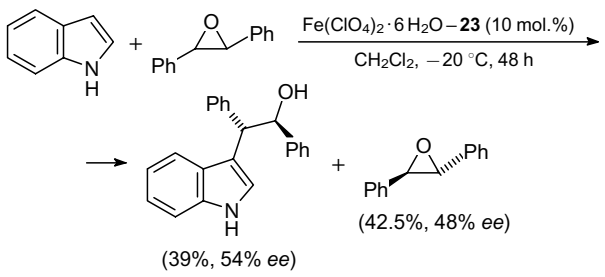
(*a*) $Fe(ClO_4)_2 \cdot 6H_2O$–**23** (10 mol.%), $CH_2Cl_2$, rt, 1–48 h; R = H, 5-Me, 5-OMe, 6-F, 4-Cl, 5-Br, 5-$NO_2$, 7-Me, 6,7-benzo

This reaction using a racemate of *trans*-stilbene oxide leads to the kinetic resolution giving substituted indole and the enantiopure substrate (Scheme 230).[383] The introduction of substituents containing the β-hydroxy group at the 3 position of indole *via* the reaction with epoxides was explored by several research groups.[384–389]

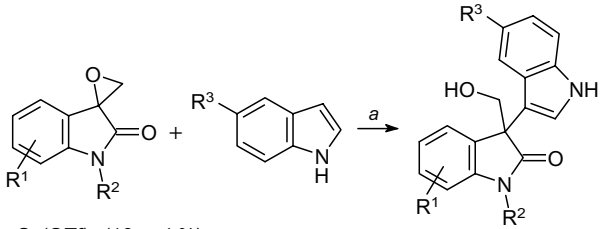
The reactions of spiro epoxyoxindoles with indoles in the presence of Lewis acids (Scheme 231) [390] or Brønsted acids [391, 392] afford 3,3′-bisindole derivatives. This reaction provided the basis for the synthesis of the natural alkaloid gliocladin C.[390]

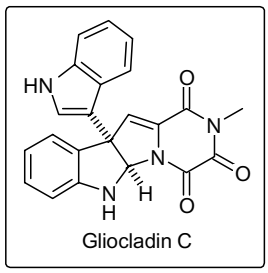
The intermolecular Friedel–Crafts reactions of spiro epoxyoxindoles were accomplished using, apart from indoles, other (hetero)aromatic compounds, such as benzofuran,[392] pyrrole,[392] phenols [392, 393] and naphthols,[393] as the aromatic component. Wei and co-workers [393] performed the reactions with phenols (Scheme 232) and naphthols (Scheme 233) in the presence of iron(III) chloride as the catalyst. In the case of naphthols, the intermediate Frie-

**Scheme 230**

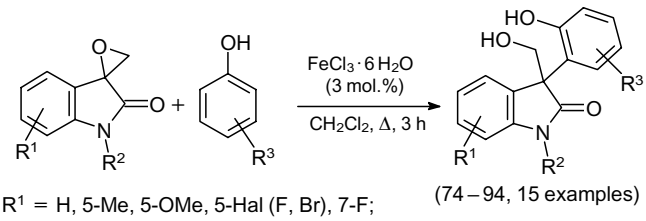



**Scheme 231**

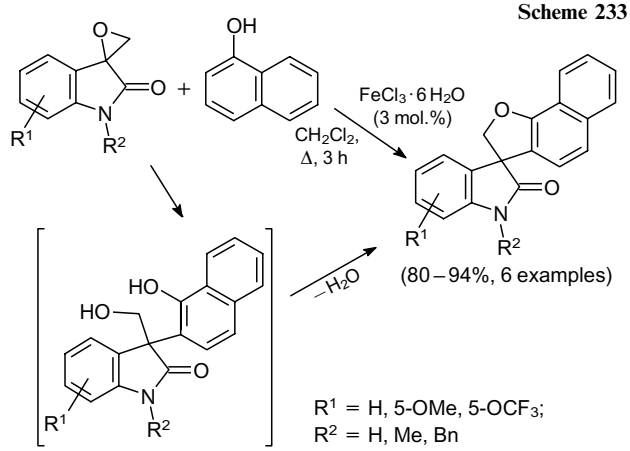



**Scheme 232**



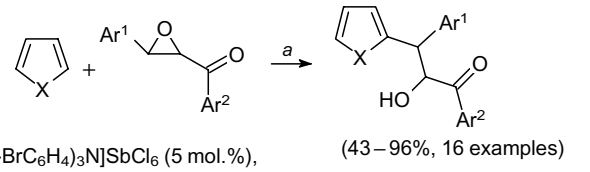

**Scheme 233**




del – Crafts substitution product underwent intramolecular cyclization to form the tetrahydrofuran ring.

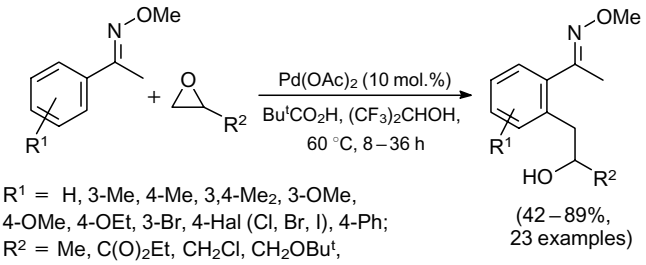
The reactions of 2-arylethoxy aryl ketones with furans, pyrroles or indoles in the presence of triarylammonium salts gave the corresponding heterocyclic derivatives containing a substituent in the 2 position (in the case of furans and pyrroles) (Scheme 234) or the 3 position (in the case of indoles).[394]

**Scheme 234**



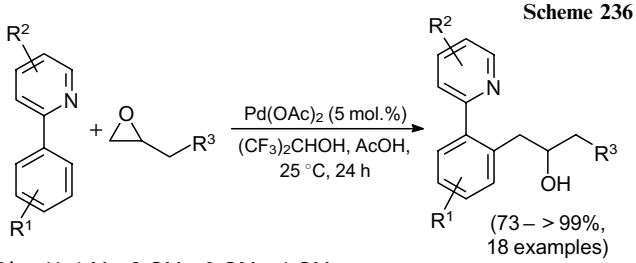

The Catellani reaction is a variant of the Friedel – Crafts reaction. It is the metal-catalyzed selective *ortho*-alkylation of aryl iodides. Its modified version is extended to other substituents, apart from the iodine atom. For example, Li *et al.*[395] performed the *ortho*-alkylation of acetophenone *O*-methyloximes with epoxides (Scheme 235).

**Scheme 235**



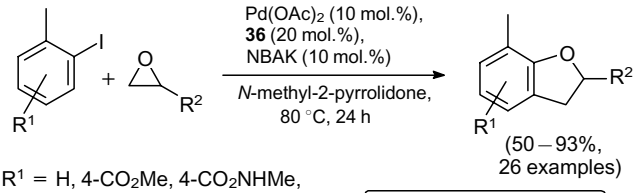

2-Arylpyridines behave in a similar way in the reactions with epoxides (Scheme 236).[396, 397]

**Scheme 236**

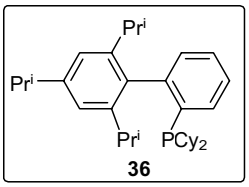



Under certain conditions, the Catellani reaction can be accompanied by the 2,3-dihydrobenzofuran ring closure, for example, in the presence of a palladium catalyst, ligand **36** and potassium 5-norbornene-2-carboxylate (NBAK) (Scheme 237).[398, 399]

**Scheme 237**

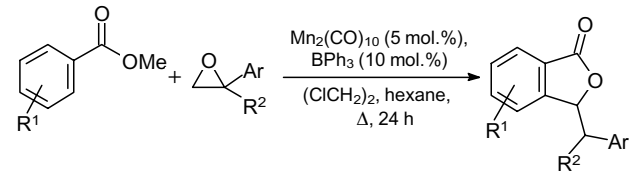



$R^1$ = H, 4-$CO_2$Me, 4-$CO_2$NHMe, 4-$NO_2$, 3-Cl, 3-F;
$R^2$ = H, Alk, $CH_2OMe$, $CH_2OH$, $CH_2OPh$,$CH_2OBn$, *etc.*;
NBAK is potassium 5-norbornene-2-carboxylate



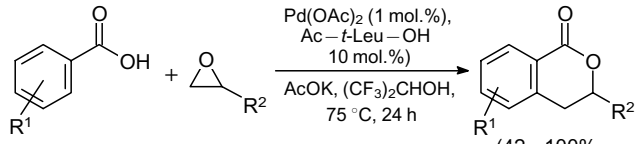

Kuninobu's research group[400] synthesized isobenzofuranones by the reactions of benzoates with epoxides (Scheme 238). Yu and co-workers[401] prepared isochroman-1-ones from benzoic acids and epoxides (Scheme 239).

**Scheme 238**




$R^1$ = H, 3-Me, 4-OMe, 4-$NMe_2$, 4-SMe, 4-$CO_2$Me, *etc.*; $R^2$ = H, Ph;

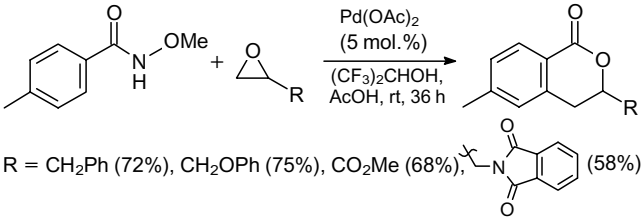
**Scheme 239**




$R^1$ = Me, $Bu^t$, OMe, $CF_3$, Hal, *etc.*;
$R^2$ = Alk, $CH_2Cl$, $CH_2OAlk$, $CH_2OAr$, *etc.*;
Leu is leucine

Isochroman-1-ones were also synthesized by the palladium acetate-catalyzed reaction of *N*-methoxybenzamides with epoxides (Scheme 240).[397,402] One of these products served as the basis for the production of natural (−)-berkelic acid.[402]

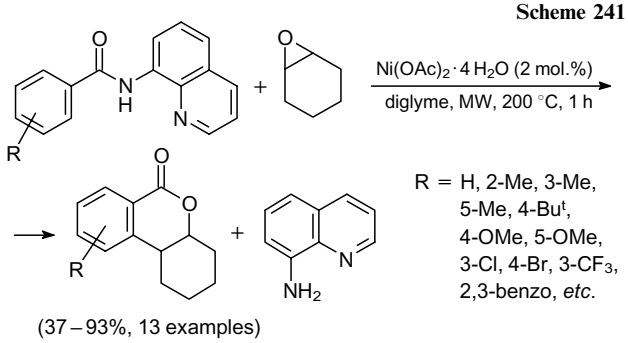
**Scheme 240**




R = $CH_2Ph$ (72%), $CH_2OPh$ (75%), $CO_2Me$ (68%),

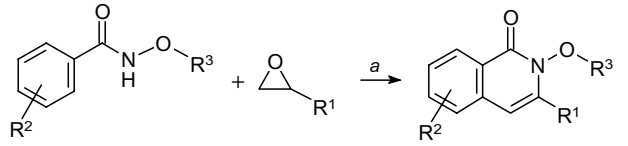
Isochromanone derivatives were synthesized by the reactions of *N*-(quinolin-8-yl)amides of benzoic (Scheme 241), α-naphthoic and β-thiophenic acids with cyclohexene oxides; these reactions are accompanied by the elimination of 8-aminoquinoline from the substrates.[403]

**Scheme 241**




*N*-Alkoxybenzamides react with epoxides to give isoquinolinones (Scheme 242), which were used to synthesize the natural alkaloids rupreschstyril, siamine and cassiarin A.[404]

**Scheme 242**




(*a*) $Pd(OAc)_2$ (10 mol.%), $CF_3COOK$, $N(C_2H_4OH)_3$ (20 mol.%), air, $(CF_3)_2CHOH$, 100 °C, 24 h; $R^1$ = Alk, $CH_2OBu^t$, $CH_2OH$, $CH_2Bn$, *etc.*

The above data clearly demonstrate that various epoxy compounds are often used as the electrophilic reagent in the electrophilic substitution of the (hetero)aromatic ring (see Schemes 229 – 231, 234). If the aromatic system contains an appropriate functional group, the substitution is accompanied by the closure of a new heterocycle (see Schemes 233, 237 – 242).

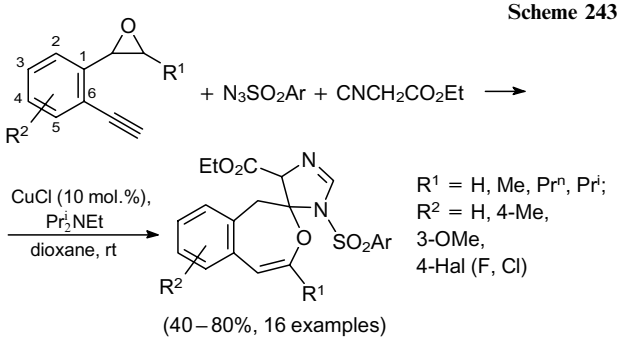
### 3.3.6. Multicomponent reactions in the chemistry of epoxides

Multicomponent reactions are reactions that combine three or more starting materials in one pot. In many cases, researchers, when designing these syntheses, initially performed the reactions of two reactants and then the isolated product is reacted with the third component under the same conditions. In some cases, this control experiment can provide a proof of the three-component reaction pathway. Compared to stepwise reactions, multicomponent processes minimize chemical waste, save time and simplify the loading of reagents and the isolation of products, thereby better complying with the green chemistry principles. Stereoselective multicomponent reactions involving epoxides and aziridines are covered in the review[5] published in 2019. We refer to the literature 2010 – 2018 cited in this review and add more recent data.

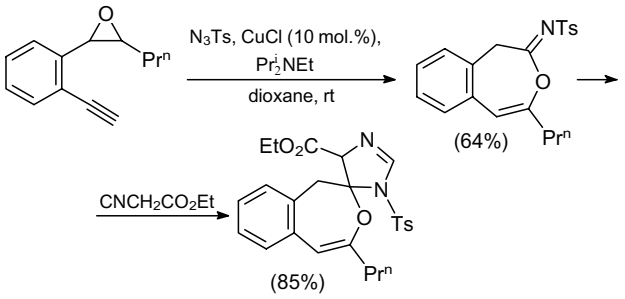
Li and Wu[405] synthesized spiro compounds containing dihydrobenzoxepine and dihydroimidazole heterocycles by the monovalent copper chloride-catalyzed reaction of 2-ethynylaryl epoxides with sulfonyl azides and 2-isocyanoacetate (Scheme 243). The control experiment demonstrated that the synthesis begins with the reaction of epoxide with sulfonyl azides (Scheme 244).

Mamedov's research group[16,195,279] accomplished the three-component synthesis using 3-arylglycidic acid amides, HBr (or HCl) and acetone and prepared 5-(α-

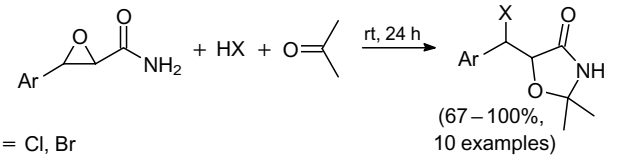
**Scheme 243**




**Scheme 244**



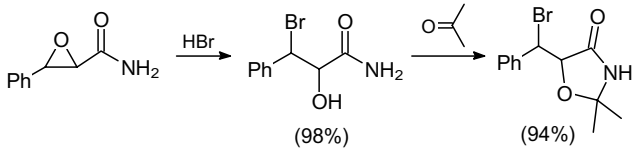

**Scheme 245**




bromo(or chloro)benzyl)-2,2-dimethyl-1,3-oxazolidin-4-ones (Scheme 245).

The synthesis involves the epoxide ring-opening with hydrohalic acids and the intermediate formation of 3-halo-2-hydroxy-3-arylproionic acid amides followed by the reaction of the latter with acetone (Scheme 246).

**Scheme 246**

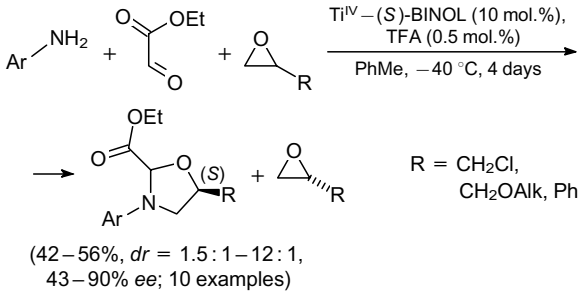



The three-component reaction of anilines with ethyl glyoxylate and the racemic form of a monosubstituted epoxy compound catalyzed by a (*S*)-binaphthol-derived titanium complex was described by Hong *et al.*[406] This reaction not only afforded two diastereomers of 1,3-oxazolidines containing an *S*-configured carbon atom at the 5 position of the heterocycle but also involved the kinetic resolution of the racemate with the isolation of the *R*-stereoisomer of the epoxide (Scheme 247).

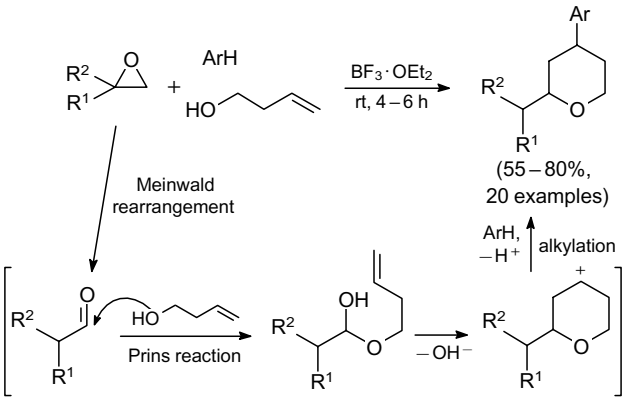
The three-component tandem Meinwald rearrangement–Prins cyclization–Friedel–Crafts alkylation gave tetrahydropyran derivatives (Scheme 248).[407]

1-(Ethoxycarbonylmethyl)-8-methylisochromane was synthesized also by the catalytic transformation involving

**Scheme 247**

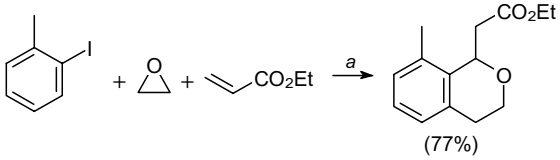



**Scheme 248**




2-iodotoluene, epoxyethane and ethyl acrylate *via* the Catellani reaction and oxa-Michael addition (Scheme 249).[408]

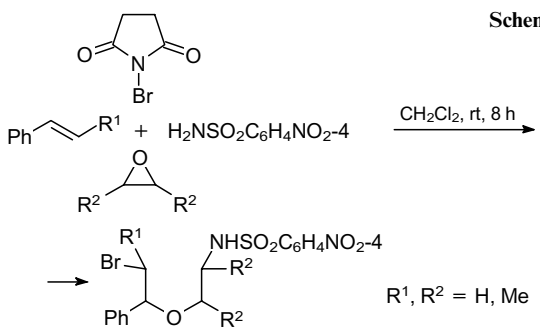
**Scheme 249**




(*a*) 1) $Pd(OAc)_2$ (1 mol.%), **36** (2.4 mol.%), NBAK (50 mol.%), *N*-methyl-2-pyrrolidone, 0 °C, 10 h; 2) $Cs_2CO_3$, 4 h

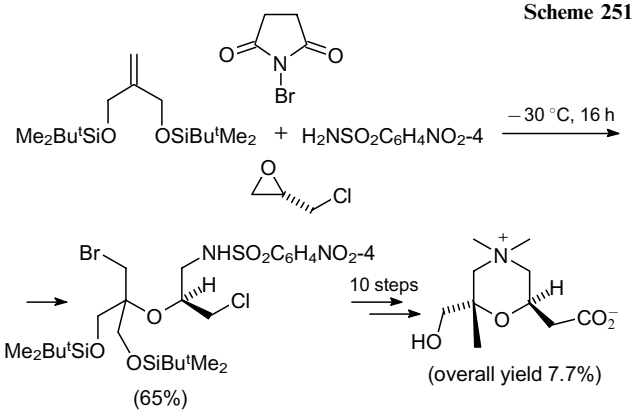
Yeung and co-workers[409,410] explored the four-component reactions of alkenes, epoxides, *p*-nitronenzenesulfonic acid amide and *N*-bromosuccinimide (Scheme 250, see Ref. 409).

**Scheme 250**



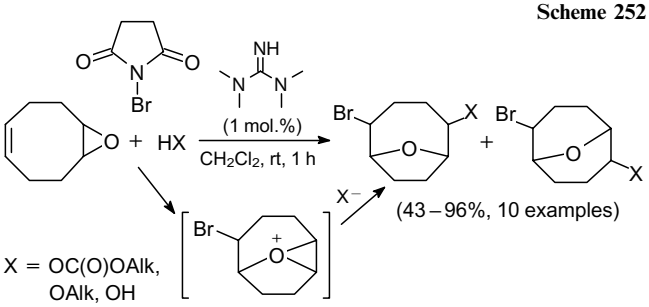
Under the optimized conditions, this reaction allowed the synthesis of a substituted morpholine salt that inhibits carnitine acetyltransferase (Scheme 251).[411]

**Scheme 251**



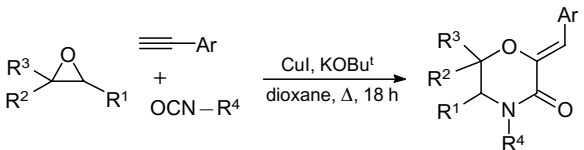

Braddock and co-workers[412] accomplished the three-component reaction involving 9-oxabicyclo[6.1.0]non-4-ene, *N*-bromosuccinimide and a source of the anion (water, alcohol, ester). This synthesis occurred through the intermediate oxonium ion and gave the previously unknown systems, 9-oxabicyclo[4.2.1]- and 9- oxabicyclo[3.3.1]nonanes (Scheme 252).

**Scheme 252**




The synthesis of morpholine derivatives from epoxides, arylacetylenes and isocyanates in the presence of copper iodide as the catalyst and potassium *tert*-butoxide as the base was performed by Homami and co-workers[413,414] (Scheme 253).

**Scheme 253**

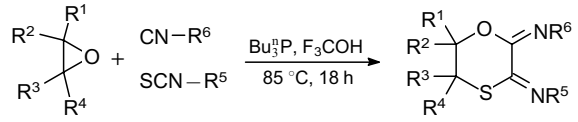



$R^1$ = H, Ar; $R^2$ = H, Me;
$R^1 - R^2$ = $(CH_2)_4$;
$R^3$ = H, Me, Bn, $CH_2OPr^i$, $CH_2OBn$, $CO_2Me$

Samzadeh-Kermani's research group[415] prepared 1,4-oxathianes from epoxides, isocyanides and isothiocyanates (Scheme 254).

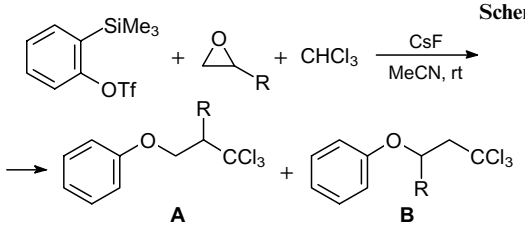
Okuma *et al.*[416] developed the three-component reaction of terminally substituted epoxide with *o*-(trimethylsilyl)-phenyl triflate and chloroform giving positional regioisomers of ethers (Scheme 255).

**Scheme 254**




$R^1$ = H, $CO_2Me$;
$R^2$ = H, Alk, $CH_2OPr^i$, $CH_2OPh$;
$R^3$ = H, Ph, $C_6H_4Me$-4; $R^2 - R^3$ = $(CH_2)_4$;
$R^4$ = H, Me; $R^5$ = $Pr^i$, Ar; $R^6$ = $Bu^t$, Cy, $C_6H_3Me_2$-2,6

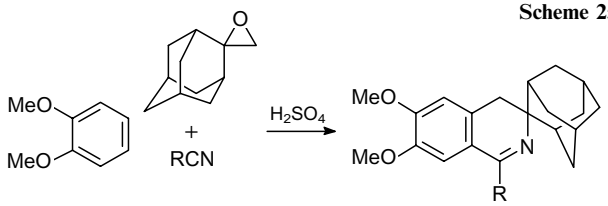
**Scheme 255**




| R | *t*, h | **A** (%) | **B** (%) |
|---|---|---|---|
| Me | 16 | 48 | 24 |
| Et | 24 | 39 | 26 |
| $Bu^n$ | 16 | 37 | 25 |
| n-$C_6H_{13}$ | 24 | 19 | 6 |

Shklyaev's research group[417] performed the three-component reaction involving 2-epoxymethyleneadamantane, 1,2-dimethoxybenzene and nitriles and synthesized spiro[adamantaneisoquinolines] (Scheme 256).

**Scheme 256**




R = SMe (70%), Me (43%), Ph (49%), $CH_2CO_2Et$ (48%), $CH_2C(O)NH_2$ (38%)

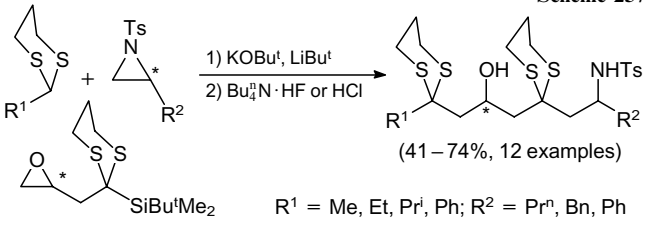
Smith *et al.*[418] explored the three-component reaction between dithiane, chiral dithiane-containing epoxide and chiral aziridine accompanied by the oxirane and aziridine ring-opening to form a product containing two chiral centres (Scheme 257).

Yousefi and Ghashang[419] reported the reactions of ethyl 3-phenylglycidate with anilines and dimethylformamide in the presence of silica-supported $POCl_3$ giving dihydrooxazole derivatives (Scheme 258).

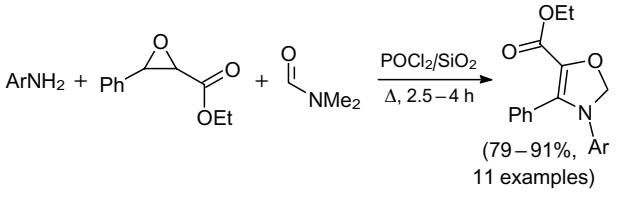
The three-component catalytic synthesis of β-hydroxytriazoles in the presence of reduced graphene oxide (rGO)-supported copper(I) and titanium oxides as the photocatalyst is presented in Scheme 259.[420] The product yields for 5 examples varied from 60 to 80%.

Meek and co-workers[421] performed the three-component reaction of a pinacolate derivative of lithium diborylmethane with epoxides and allyl bromides; two reagents were first mixed and then the third component was added

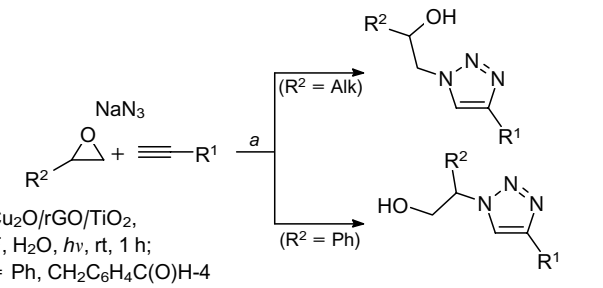
**Scheme 257**



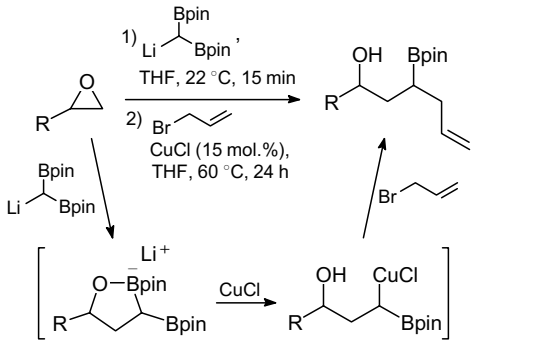

**Scheme 258**




**Scheme 259**




**Scheme 260**




(it is more appropriate to name this sequence as a one-pot process) (Scheme 260).

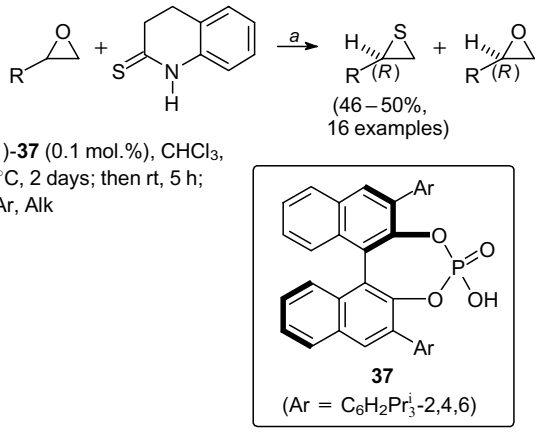
As mentioned above, multicomponent reactions are more atom-economical compared to stepwise reactions and, consequently, they continue to attract great interest of synthetic chemists. The use of epoxides in these processes was described in the recent studies[413–415,419,420] reported after 2019, the year when the review on the multicomponent reactions involving epoxides and aziridines[5] was published.

### 3.4. Miscellaneous transformations of epoxides

The oxygen-by-sulfur replacement in the epoxide ring, the electrophilic epoxide ring-opening, reduction, oxidation, deoxygenation and some other reactions of epoxides, which are not included in the above Sections, are considered below.

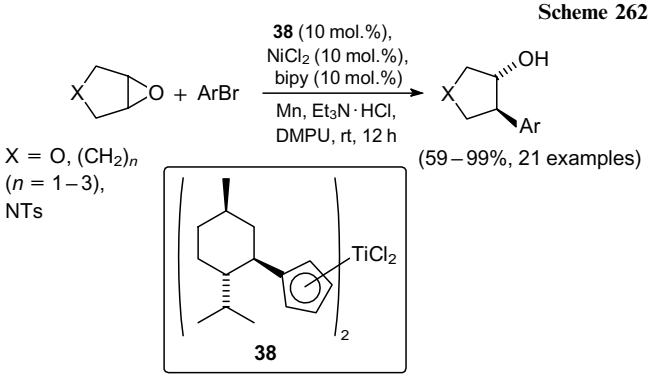
List and co-workers[422] reported the conversion of epoxides into thiiranes by the reaction with sulfur donors, among which 3,4-dihydroquinoline-2(1*H*)-thione proved to be the most efficient. In the presence of chiral catalyst **37** based on phosphoric acid, the reaction afforded chiral thiirane and gave the enantiopure substrate *via* kinetic resolution of racemic epoxide (Scheme 261).

**Scheme 261**




Zhao and Weix[423,424] explored the electrophilic epoxide ring-opening reactions with aryl halides in the presence of nickel complex catalysts. Scheme 262 presents the desymmetrization of *meso* epoxides with aryl bromides catalyzed by a combination of a nickel chloride complex with 2,2′-bipyridine (bipy) and chiral titanocene **38**.[424] The electrophilic ring-opening reactions of small heterocycles, including epoxides, are considered in the review[425] published in 2017.

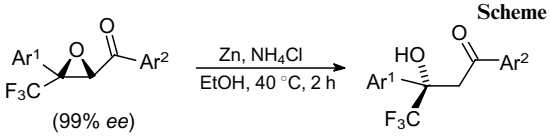
**Scheme 262**



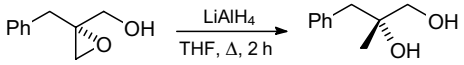

Chen and co-workers[59] accomplished the regio- and enantioselective reduction of chiral 2-trifluoromethyl-2-arylephoxy aryl ketones with zinc giving optically active trifluoromethyl-containing alcohols (Scheme 263).

The asymmetric reduction of chiral (*R*)-(2-benzyloxiran-2-yl)methanol with lithium aluminium hydride to the corre-

**Scheme 263**



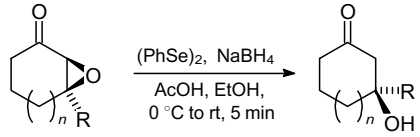
**Scheme 264**




sponding 1,2-diol was performed under the direction of Luo [63] (Scheme 264).

List and co-workers [54] reduced chiral cyclic α,β-epoxy ketones with sodium borohydride to chiral cyclic β-hydroxy ketones (Scheme 265).

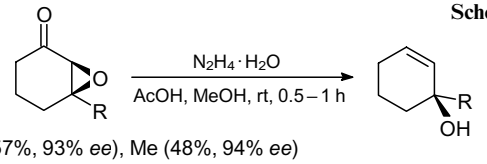
**Scheme 265**




R = H, Me; *n* = 1–3 (53–94%, 86–99% *ee*; 4 examples)

The conversion of chiral α,β-epoxycyclohexanones into chiral β-hydroxycyclohexenes (Wharton reaction) using hydrazine hydrate was accomplished by Jorgensen and co-workers [55] (Scheme 266).

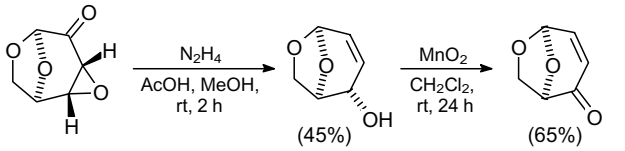
**Scheme 266**




R = H (57%, 93% *ee*), Me (48%, 94% *ee*)

The Wharton reaction was also used to prepare isolevoglucosenone from easily accessible levoglucosenone (Scheme 267).[37]

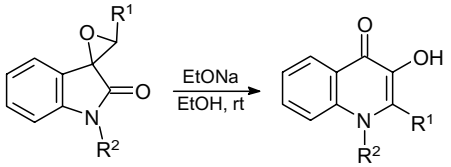
**Scheme 267**




Blanco and co-workers [426] described the sodium ethoxide-promoted conversion of spiro epoxyoxindoles into 3-hydroxyquinolin-4-ones under prolonged storage of the reaction mixtures at room temperature (Scheme 268).

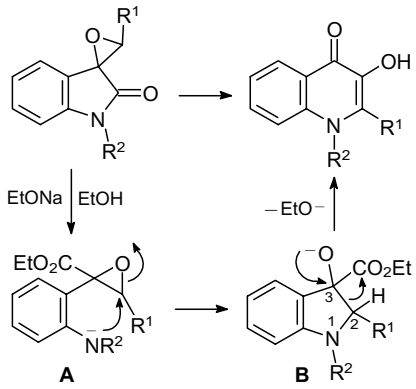
The mechanism of this reaction involves the amide bond cleavage of the indolinone ring *via* the Pfitzinger reaction to form intermediate **A**, which undergoes the ring closure followed by the ring expansion by the C(2)–C(3) bond migration to the carbonyl carbon atom of the ester group of intermediate **B**. The elimination of the ethoxy group from the latter affords the final product (Scheme 269).

**Scheme 268**

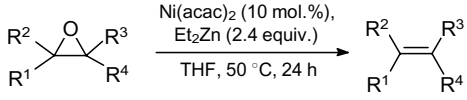



$R^1$ = C(O)Ar: $R^2$ = H, Me; $R^1$ = C(O)Alk, $R^2$ = H (70–95%, 8 examples)

**Scheme 269**



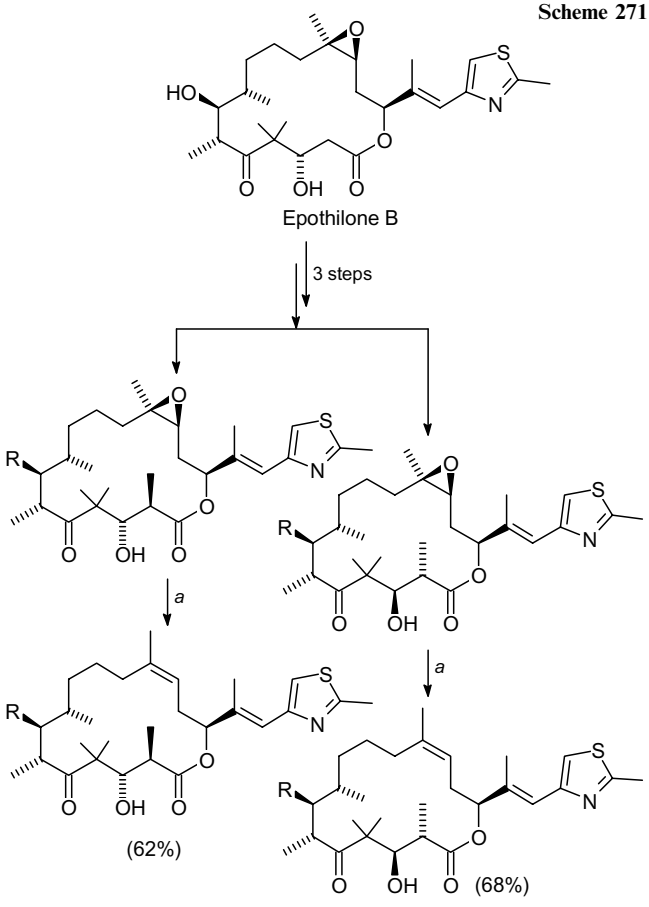

**Scheme 270**




(70–99%, 13 examples)

$R^1$ = H, Me; $R^2$ = Alk, Ar;
$R^3$ = $Bu^t$, Ph, $CO_2Et$; $R^2–R^3$ = $(CH_2)_n$ (*n* = 4, 6), *etc.*;
$R^4$ = H, Me, Ph

**Scheme 271**



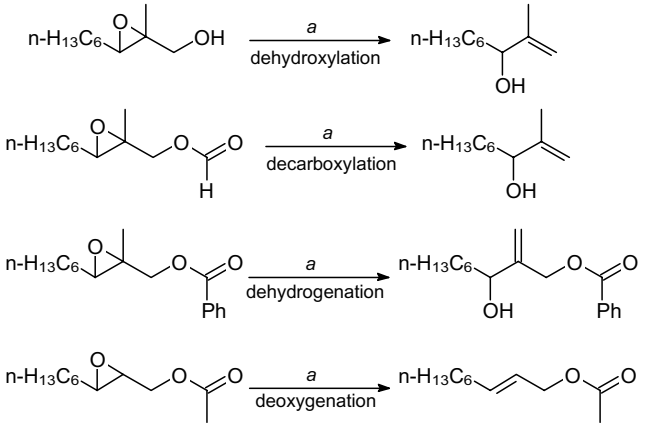

(*a*) $WCl_6$, $Bu^nLi$, THF, –20 °C (deoxygenation); R = $OSiEt_3$

Deoxygenation reactions of epoxides giving alkenes, of which they are formally protected analogues (Scheme 270), play a significant role in the chemistry of epoxides.[427]

Nicolaou *et al.*[428] applied the deoxygenation to convert the natural product epothilone B (Scheme 271).

The reactions of 2,3-epoxy alcohols with the corresponding formates, acetates and benzoates are induced by a titanocene catalyst, which provides the homolytic C–O bond cleavage of the epoxide ring. Depending on the substituents, the reactions result in the dehydroxylation, decarboxylation, dehydration giving allylic alcohols or deoxygenation with the formation of a double bond at the place of the oxirane ring (Scheme 272).[429]

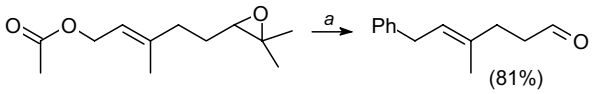
**Scheme 272**




(*a*) $Cp_2TiCl_2$, Zn, THF, rt, 0.5 h

Christmann and co-workers[430] synthesized 4-methyl-6-phenylhex-4-enal from the terpene derivative, epoxy geranyl acetate. The one-pot process involved the replacement of the acetate group with the phenyl moiety using an organomagnesium reagent and the oxidation of the epoxide moiety with sodium periodate (Scheme 273).

**Scheme 273**




(*a*) 1) $Li_2CuCl_4$, PhMgCl, THF, 0 °C; 2) $NaIO_4$, THF, $H_2O$, 20 °C

As can be seen from the data on the transformations of epoxides, the chemistry of epoxy compounds is very diverse and its classification is difficult. These studies are still in progress, and the above data may be completed with new reactions in the nearest future. Besides, each Section can serve as the basis for specialized surveys, including the detailed analysis of specific features and mechanisms of the corresponding reactions.

## 4. Practical applications of epoxides

The epoxide ring is involved in many natural products with valuable properties, including biological activity. The production of epoxy resins and other polymeric and oligomeric materials is based on the application of epoxide derivatives. These compounds serve as reactants for organic synthesis. The known methods for the synthesis and chemical transformations of epoxides are often used to prepare natural products and drugs. Carbonylation and carboxylation reactions of epoxides, which use available starting materials, utilize industrial waste and afford valuable cyclic compounds and polymeric materials, have been extensively developed in recent years. New approaches to the synthesis of natural products, drugs, polymers and other practically useful compounds based on conversions of epoxides were described in recent publications. This Section presents natural products and pharmacologically important compounds containing epoxide rings. The steps of the synthesis of natural products and drugs involving epoxides are considered, and the carbonylation, carboxylation and polymerization reactions of epoxide derivatives are described.

### 4.1. Natural products and drugs based on epoxy derivatives

Epoxy compounds are widespread in nature and are of particular interest for the design of pharmaceuticals because ~65% of the currently used drugs are based on natural products.[6] Among natural products is, for example, the tetrapeptide epoxomicin containing the terminal epoxy ketone group. An analogue of this compound with improved pharmacological properties, the drug carfilzomib, is commonly used in cancer therapy to treat myeloma (Fig. 1).[431–433]

The pharmacological significance of epoxy compounds is discussed in the review[6] published in 2020. The review[434] published in 2019 presents the data on α,β-diepoxy compounds of natural origin (> 80 examples, incliuding lipids, terpenoids, alkaloids, quinones and pyrones; see Fig. 2), which exhibit anticancer, antifungal, anti-inflammatory, antibacterial, antiviral and antiallergic activities and serve as regulators of lipid metabolism.

The review[435] published in 2014 is concerned with epoxy acetylenic lipids, which are released by microorganisms in a wide variety (their number approaches 250) and exhibit anticancer, cytotoxic, antibacterial, antiviral and other biological activities. Several structures of epoxy acetylenic lipids are shown in Fig. 3.

The routes to naturally occurring and pharmaceutical epoxy compounds considered below (Schemes 274, 275) were taken from the original studies,[436–438] but hereinafter the reaction conditions and the product yields are given only for the steps, in which the epoxide ring is formed or is involved in transformations.

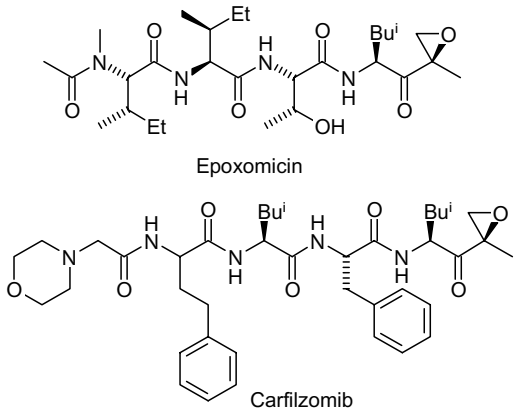



**Figure 1.** Naturally occurring epoxide and the drug based on this epoxide.[433]

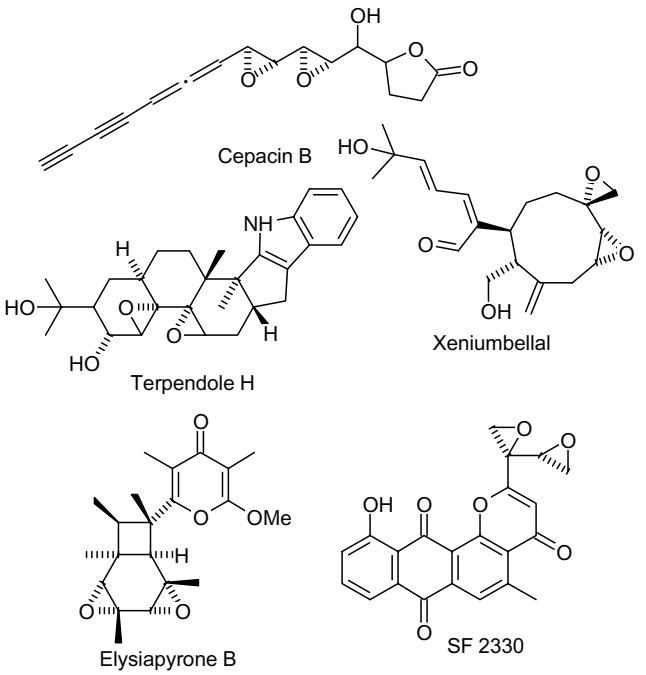


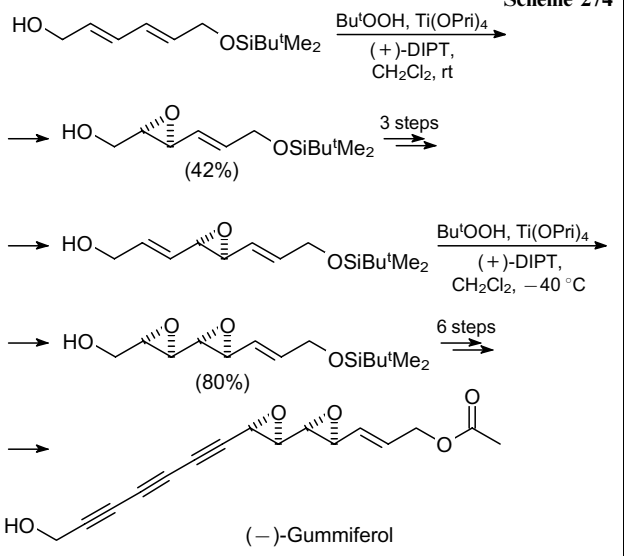

**Figure 2.** α,β-Diepoxy compounds of natural origin.[434]

Thus, Kadota and co-workers[436, 437] developed a multistep synthesis of the naturally occurring α,β-diepoxy compound (−)-gummiferol from the appropriate diene in an overall yield of 10.5% twice using the Sharpless epoxidation (see Scheme 274).

Yadav *et al.*[438] accomplished the synthesis of naturally occurring oploxyne A from 2,3-*O*-isopropylidene-D-ribose in an overall yield of 26.5% (Scheme 275).

The development of approaches to the synthesis of practically significant natural products is a challenging but attractive target for synthetic chemists, who either improve the available methods or disclose new approaches. The development of new routes to otherwise difficult-to-synthesize natural products is of particular importance. It should be noted that the synthesis of natural products containing epoxide rings has received little attention in the past decade, while much research has been undertaken regarding the methods for the synthesis of natural products, which utilize epoxides in one of the steps. Despite the abundant data, they have not been surveyed before. In the next Section, the relevant data are summarized.

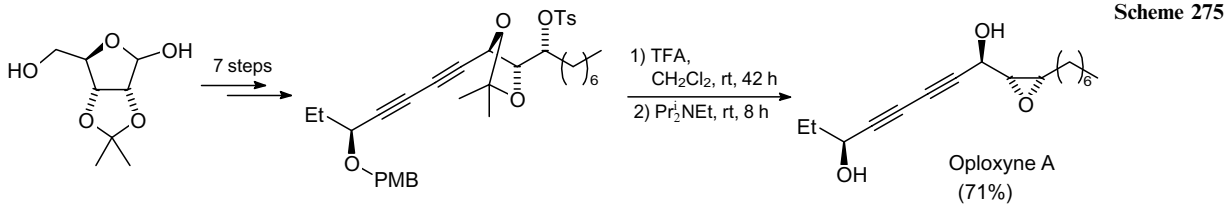
**Scheme 274**




## 4.2. Epoxy derivatives in the synthesis of natural products

The development of synthetic routes to natural products has attracted attention of chemists due to biological activity of these compounds, in particular their potential use in pharmacology. Although the nature continuously produces new sources of biologically active compounds, the isolation of

**Scheme 275**



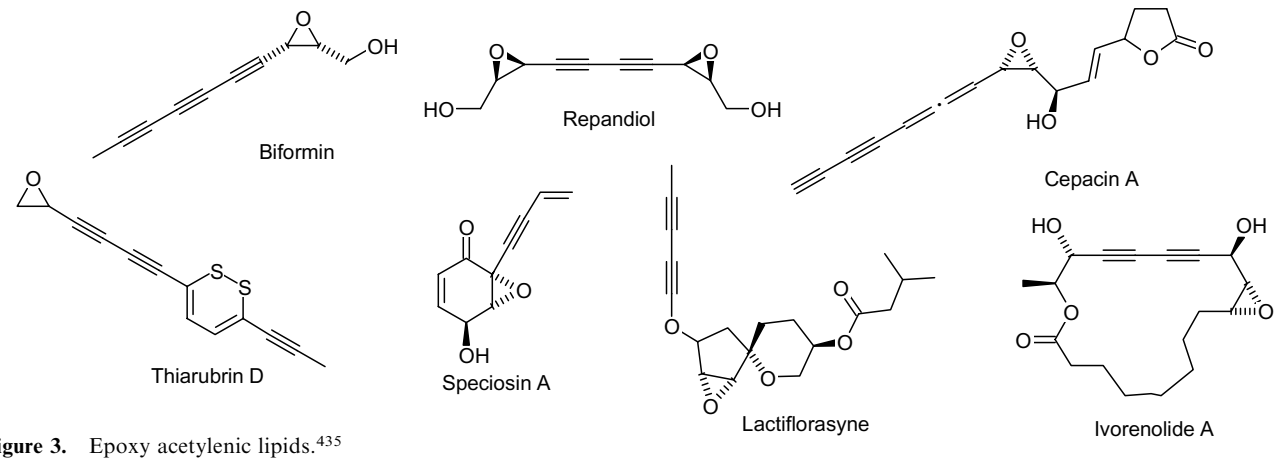




**Figure 3.** Epoxy acetylenic lipids.[435]

these compounds is often a time-consuming and expensive procedure, thereby making it difficult to accumulate them for research purposes and, all the more, for their use in other fields of human activities. Many chemists focused their efforts on both the total synthesis of natural products and the construction of their analogues. The data on the modern synthetic approaches to natural products with valuable properties, most often with broad-spectrum pharmacological activities, using the epoxide ring formation and its transformations are considered below.

Nanda and co-workers [439] reported the synthesis of the cyclopentane sesquiterpenes (*R*)-α-cuparenone (8% overall yield) and (*S*)-cuparene (6% overall yield). The key steps were the Sharpless asymmetric epoxidation of allylic alcohol and the methylaluminium bis(2,6-di-tert-butyl-4-methylphenoxide) (MAD)-catalyzed Meinwald rearrangement accompanied by the migration of the methyl group on the epoxide ring to form aldehyde (Scheme 276).

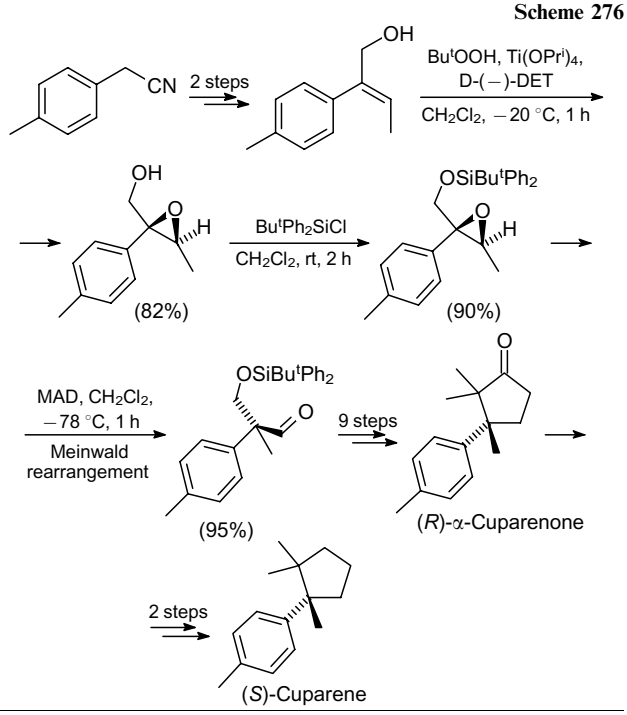
Thorimbert and co-workers [440] proposed an approach to the synthesis of the epimer of naturally occurring deoxynojirimycin, namely deoxymannojirimycin, using the Sharpless epoxidation and the reduction of the epoxide ring (Scheme 277).

Anderson *et al.*[441] synthesized structural analogues of catechins belonging to the flavonoid class (Scheme 278). The synthesis occurred through the Sharpless epoxidation and the epoxide ring-opening with 3,5-dibenzoxyphenol to form vicinal diol. The new epoxide ring was constructed from the diol in a one-pot process, involving the tosylation of the OH group, the subsequent removal of the Ts protection with $K_2CO_3$ and the intramolecular Friedel–Crafts cyclization to form the tetrahydropyran ring.

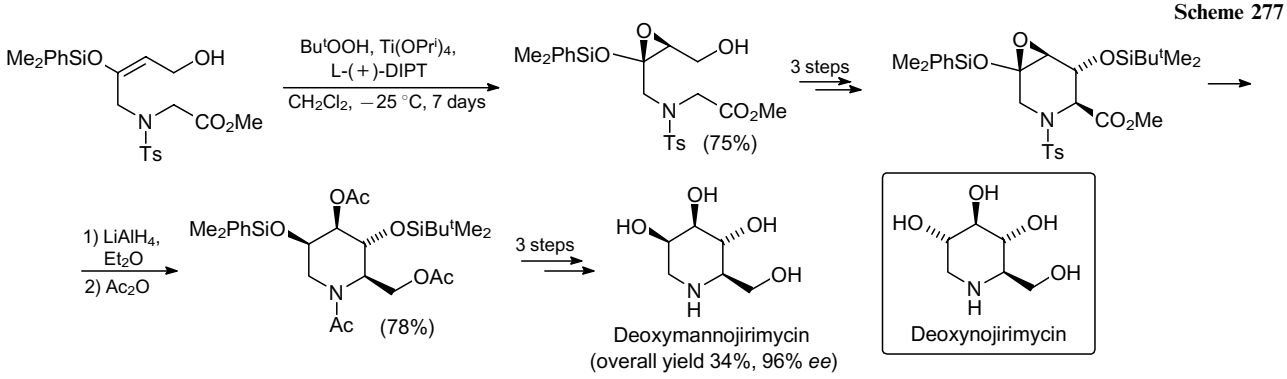
Yang and co-workers [442] improved the method for the synthesis of naturally occurring (+)-gallocatechin and (−)-epigallocatechin and developed the first total synthesis of 8-C-ascorbyl-(−)-epigallocatechin. In these transformations, the epoxide ring was built up through the dehydration and was involved in the intramolecular Friedel–Crafts reaction (Scheme 279).

Vyvyan and co-workers [443] synthesized the alkaloid cananodine as an epimeric mixture (in a ratio of 1 : 1) in an overall yield of 4.4%. In this case, the epoxy compound was

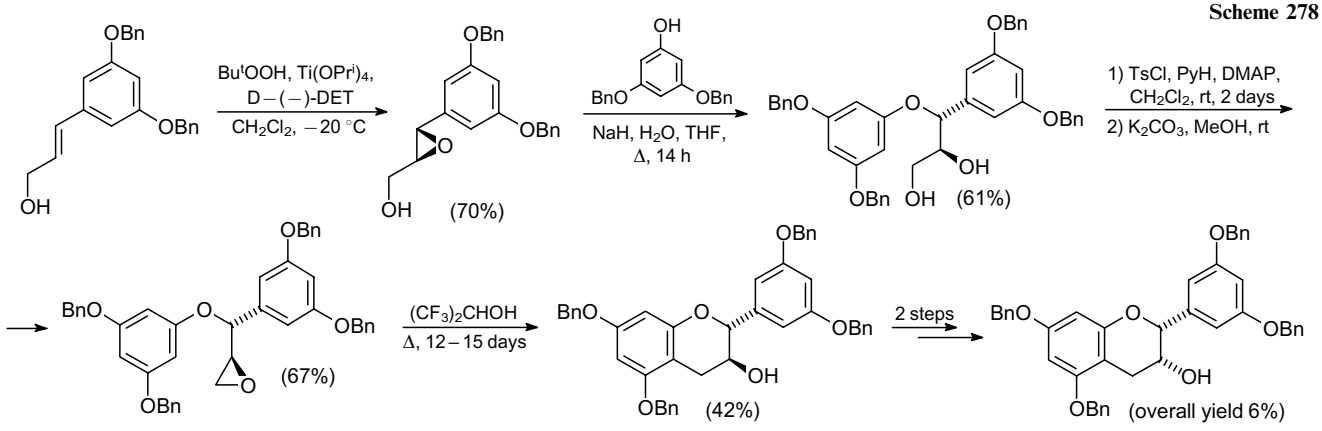
**Scheme 276**



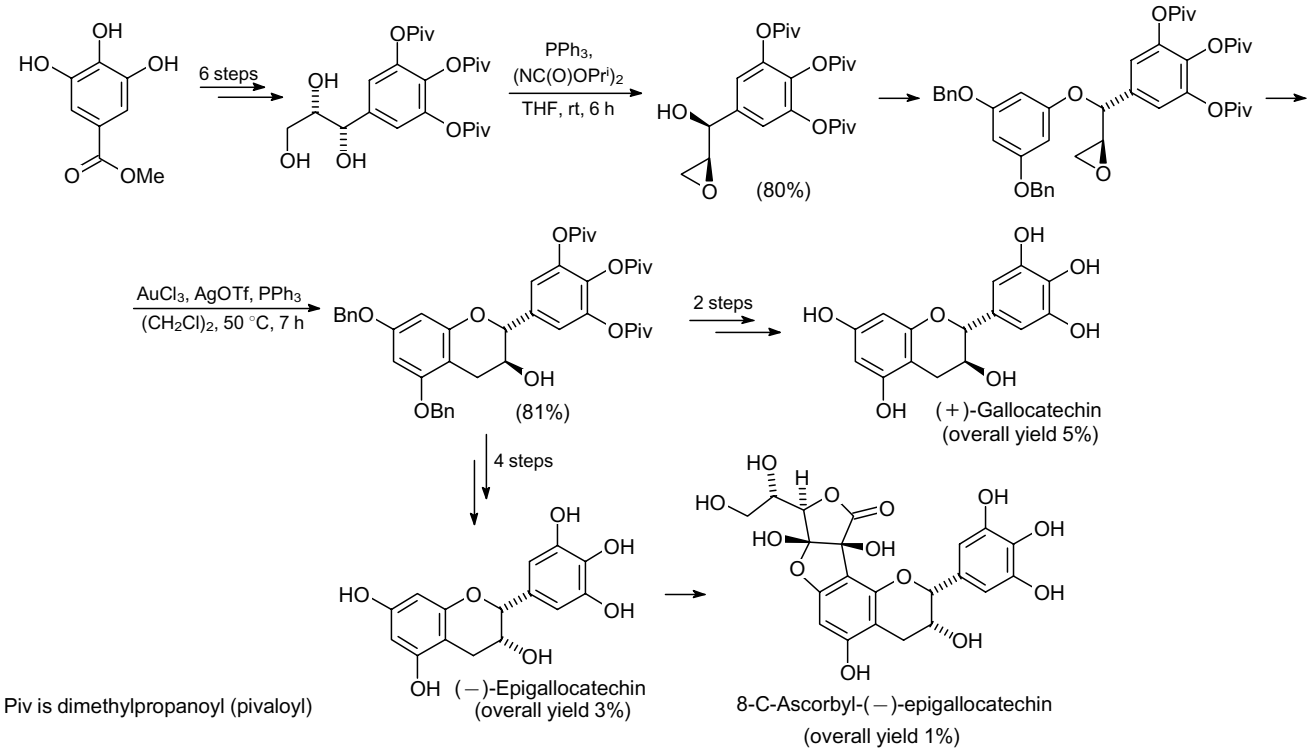

**Scheme 277**




**Scheme 278**



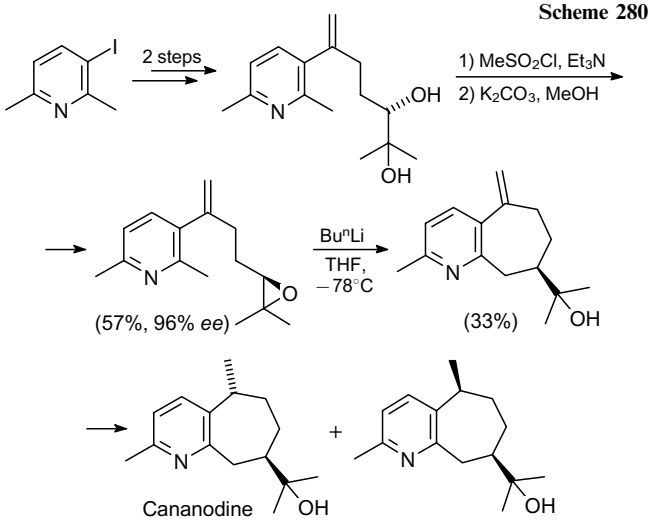
**Scheme 279**




generated *via* elimination of $H_2O$ from vicinal diol followed by the intramolecular epoxide ring-opening with lithium butoxide accompanied by the formation of the seven-membered carbocycle (Scheme 280).

Two research groups optimized the method for the synthesis of (−)-irciniastatin A (a.k.a. psymberin), a member of the pederin natural product family.[444–446] One of the key steps in the multistep synthesis is the camphorsulfonic acid (CSA)-promoted conversion of the epoxide moiety into tetrahydropyran (Scheme 281, Ref. 445).

**Scheme 280**




The research group under the direction of Miyashita and Tanino[447] synthesized the triterpenoid solanoeclepin A *via* a multistep process involving the Prilezhaev epoxidation, the Meinwald rearrangement and the epoxide ring-opening (Scheme 282).

This research group[448] also synthesized the right-hand segment of the triterpenoid tubiferal A *via* the selective epoxidation of the allylic moiety with *tert*-butyl hydroperoxide and the semipinacol rearrangement (Scheme 283).

Ishigami's research group[449] developed the formal synthesis of cochlearol A *via* the conversion of the carbonyl group on the cyclohexane moiety into the spiroepoxide moiety followed by its subsequent rearrangements (Scheme 284).

Marshall *et al.*[450] synthesizes the diastereomer of naturally occurring uprolide D acetate using the epoxide ring-opening with an acetylenic derivative, the Sharpless and Shi asymmetric epoxidation and intramolecular cyclization involving the epoxide ring to form the tetrahydrofuran ring (Scheme 285).

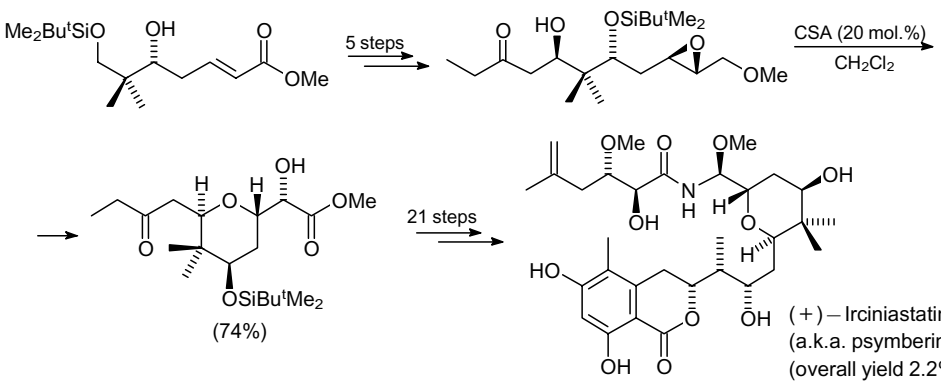
Siegel and co-workers[451,452] synthesized the isomeric natural products caryolanemagnolol (**39a**) and clovanemagnolol (**39b**) starting from commercially available (−)-caryophyllene. The Prilezhaev or Shi epoxidation of (−)-caryophyllene afforded α- and β-caryophyllene oxides, which were subjected, under certain conditions, to complex tandem reactions involving the epoxide ring (Scheme 286).

The authors also described the one-step synthesis of target products **39a**,**b** from magnolol and diphenyl phosphate (Scheme 287).[451]

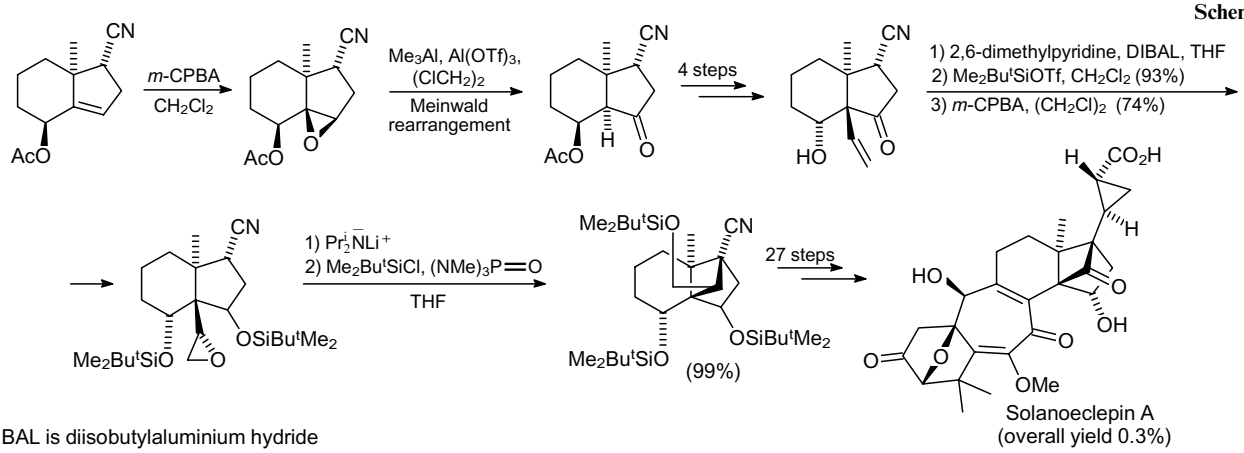
Yang *et al.*[453,454] developed a method for the synthesis of the lycopodium alkaloid (−)-8-deoxyserratinine *via* the Shi epoxidation and the epoxide ring-opening (Scheme 288).

The multistep synthesis of the natural polyether teurilene from 2,5-dimethoxytetrahydrofuran involved the Sharpless and Shi epoxidation, the formation of tetrahydrofuran rings from epoxide rings, the formation of epoxide rings from vicinal diol moieties and the cleavage of terminal epoxides with Grignard reagent (Scheme 289).[455]

**Scheme 281**

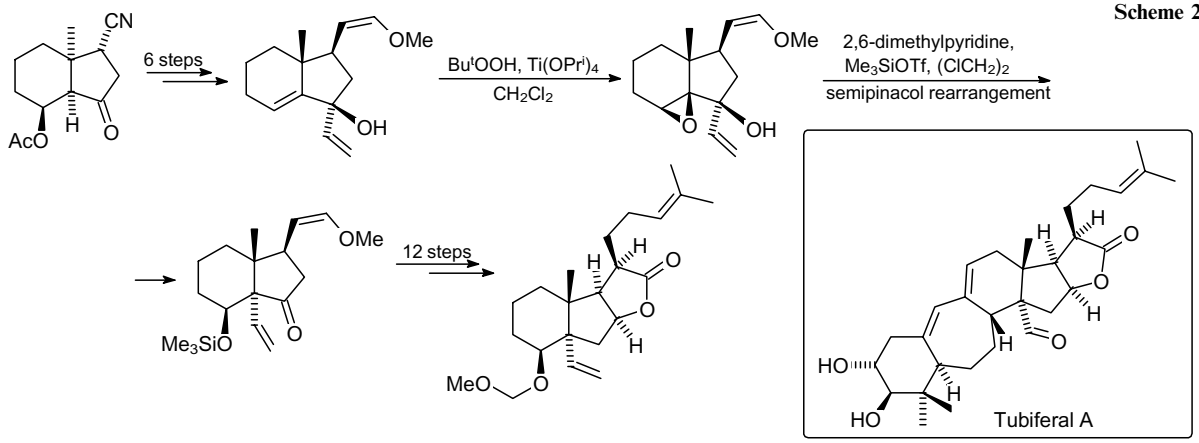



**Scheme 282**

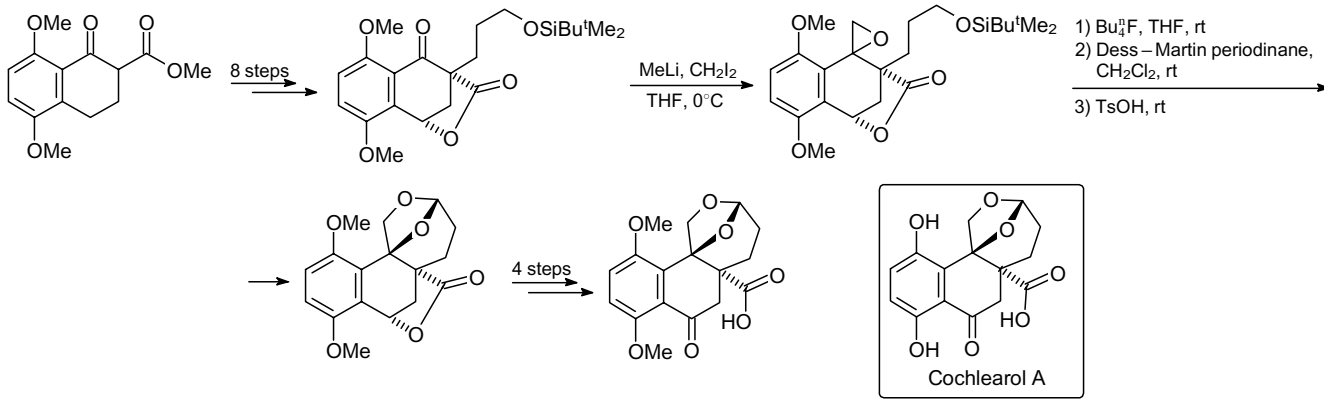



DIBAL is diisobutylaluminium hydride

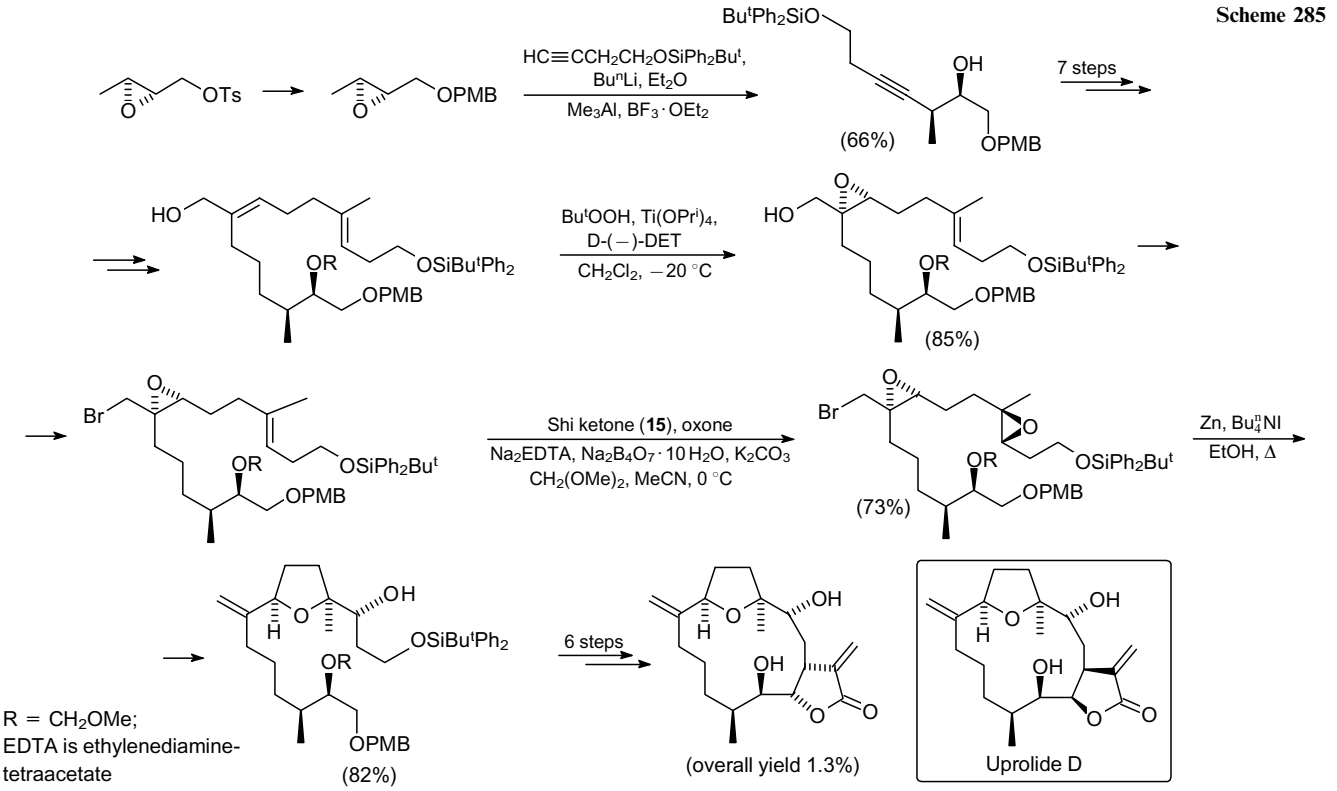
**Scheme 283**



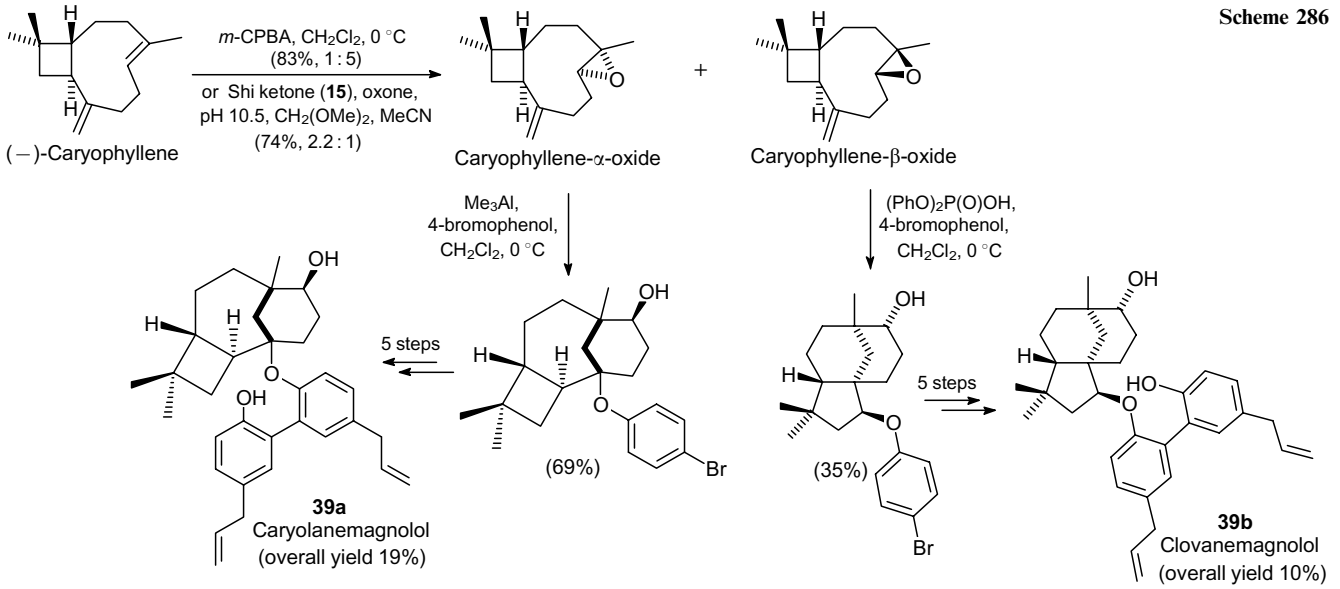

**Scheme 284**



**Scheme 285**




**Scheme 286**

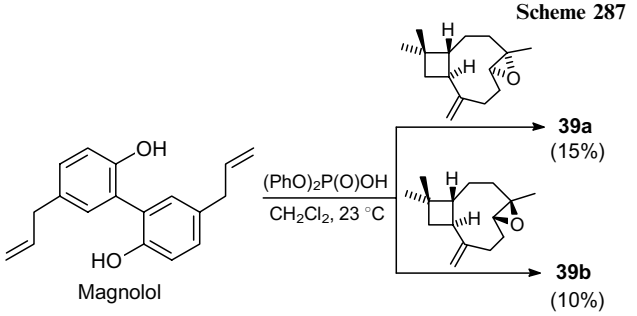



Coster and co-workers [456] proposed an approach to the synthesis of the naturally occurring dihydrobenzofuran methyl (+)-7-methoxyanodendroate from commercially available methyl vanillate. The reaction sequence consisted of the Shi epoxidation and the tetra-n-butylammonium fluoride-promoted intramolecular cyclization involving the epoxide moiety (Scheme 290).

Mack and Njardarson [457] synthesized the epimeric forms of labdane diterpenoid in good yields from available natural materials using ketone (**15**) and its L form in the Shi epoxidation steps to convert the vinyl epoxide moieties into 2,5-dihydrofurans (Scheme 291).

The conversion of the vinyl epoxide moiety into 2,5-dihydrofuran was one of the key steps in the synthesis of

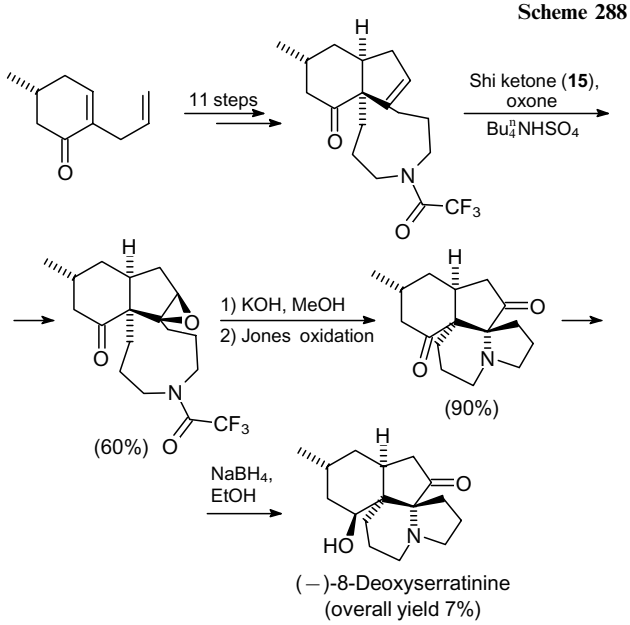
**Scheme 287**



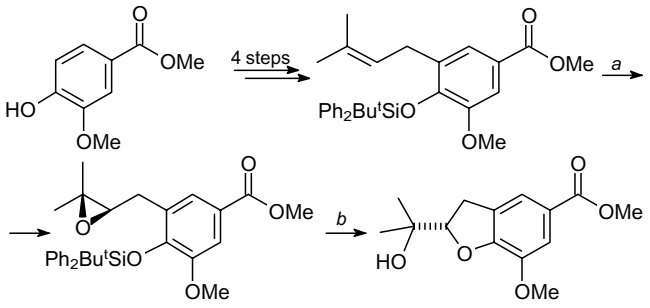
(+)-varitriol (Scheme 292),[458] pachastrissamine and jaspine A (Scheme 293).[459]

Xiong *et al.*[460] synthesized (+)-omaezakianol from available racemic 2,3-oxidosqualene, the epoxide ring of which was opened with hydrogen chloride (Scheme 294) to form two regioisomeric products **40** and **41** in a ratio of 1 : 1 (92% overall yield). The mixture was separated and compound **40** containing the hydroxy group at the γ position to the double bond was subjected to the Shi asymmetric epoxidation to prepare pentaepoxide. The latter contained the hydroxy group at the γ position to the epoxide ring and it was involved first in the reaction sequence resulting in the construction of tetrahydropyran rings of the ladder polyether. The latter was converted into the target product in one step.

**Scheme 288**




**Scheme 290**

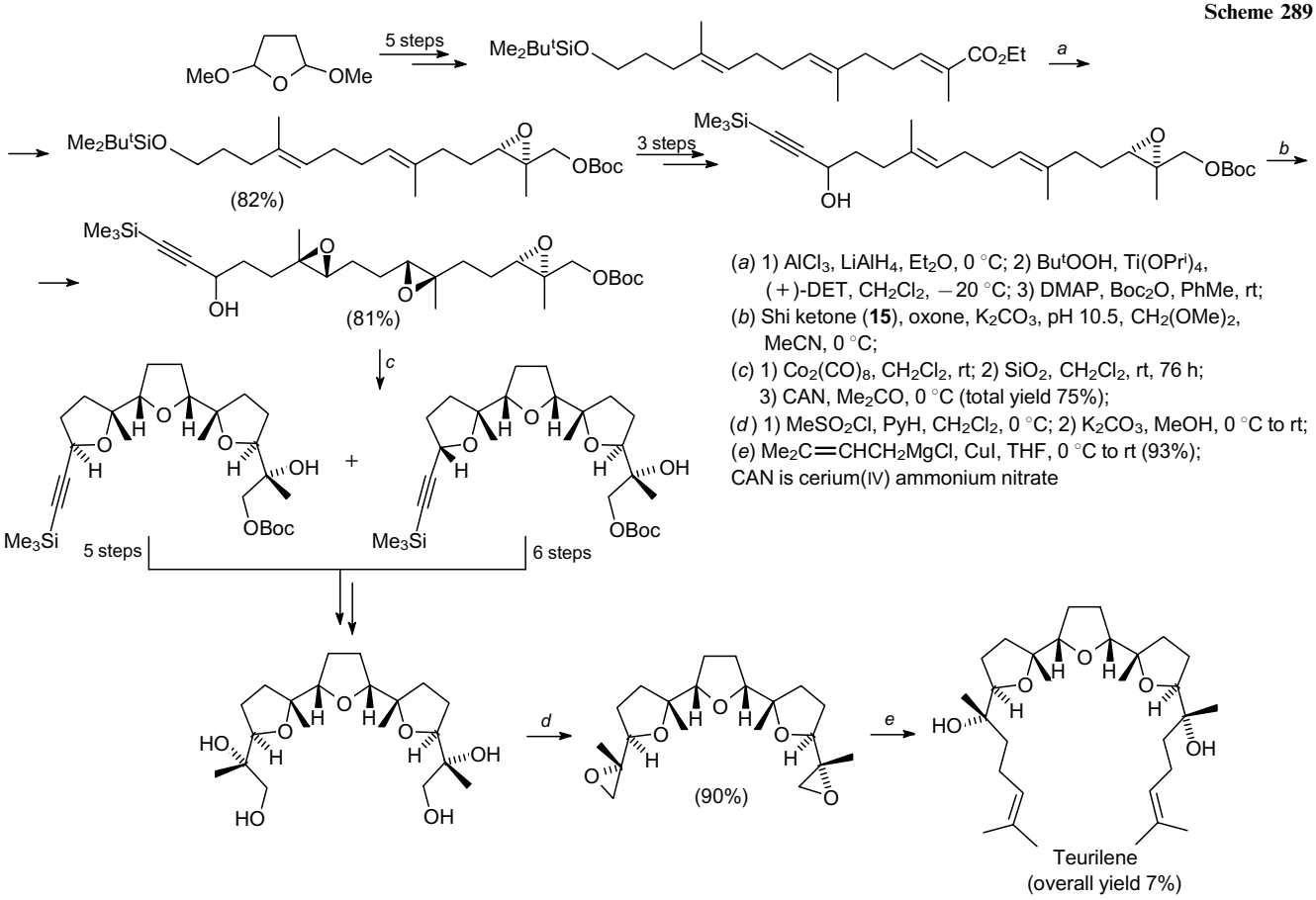



(*a*) Shi ketone (**15**), oxone, $Bu^n_4HSO_4$, $K_2CO_3$, KOH, $KHPO_4$, $H_2O$ (pH 6), $CH_2(OMe)_2$, MeCN, 0 °C, 22 h;
(*b*) $Bu^n_4NF$, THF, 0 °C to rt, 75 min

The total synthesis of related ladder polyethers was described in a number of studies. Thus, Qu and co-workers[461] synthesized (−)-glabrescol from the triterpene hydrocarbon squalene (Scheme 295).

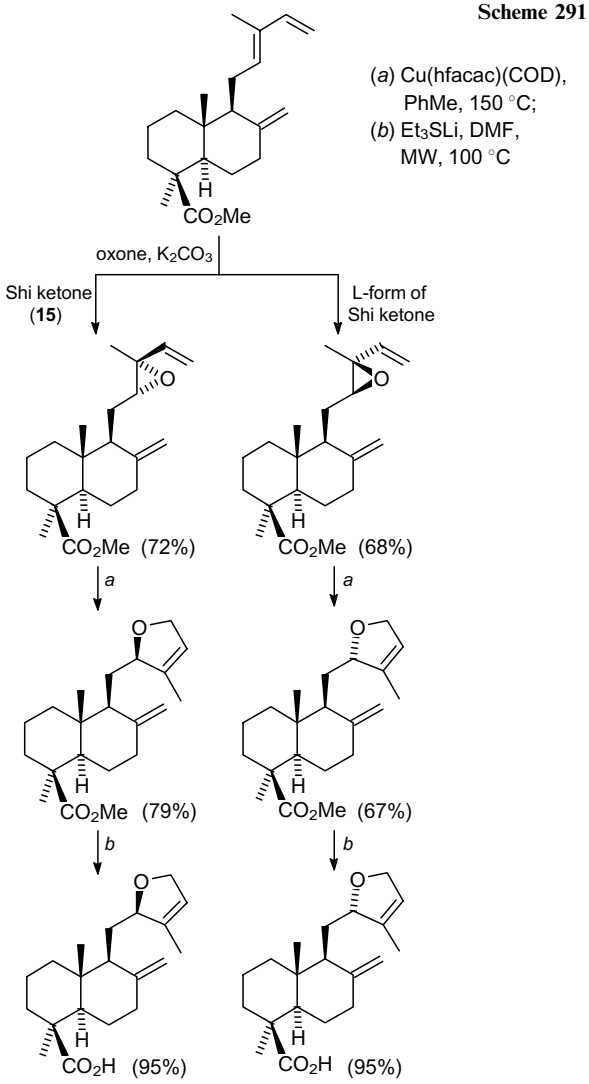
Schmidt and Stark[462] proposed a method for the synthesis of a diastereomer of the natural ladder polyether heronapyrrole C (Scheme 296).

**Scheme 289**

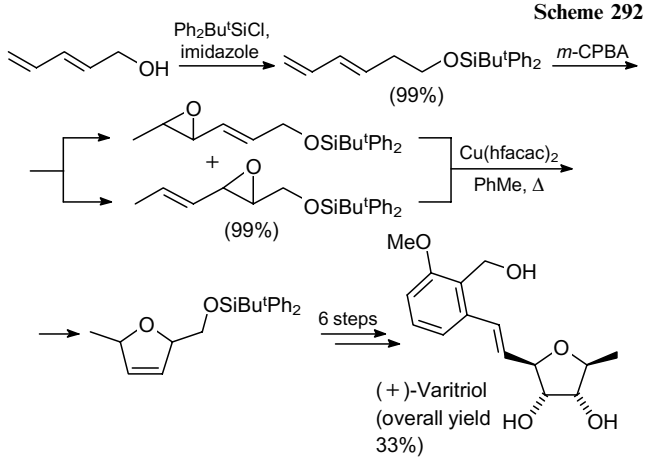



(*a*) 1) $AlCl_3$, $LiAlH_4$, $Et_2O$, 0 °C; 2) $Bu^tOOH$, $Ti(OPr^i)_4$, (+)-DET, $CH_2Cl_2$, −20 °C; 3) DMAP, $Boc_2O$, PhMe, rt;
(*b*) Shi ketone (**15**), oxone, $K_2CO_3$, pH 10.5, $CH_2(OMe)_2$, MeCN, 0 °C;
(*c*) 1) $Co_2(CO)_8$, $CH_2Cl_2$, rt; 2) $SiO_2$, $CH_2Cl_2$, rt, 76 h; 3) CAN, $Me_2CO$, 0 °C (total yield 75%);
(*d*) 1) $MeSO_2Cl$, PyH, $CH_2Cl_2$, 0 °C; 2) $K_2CO_3$, MeOH, 0 °C to rt;
(*e*) $Me_2C{=}CHCH_2MgCl$, CuI, THF, 0 °C to rt (93%);
CAN is cerium(IV) ammonium nitrate

**Scheme 291**



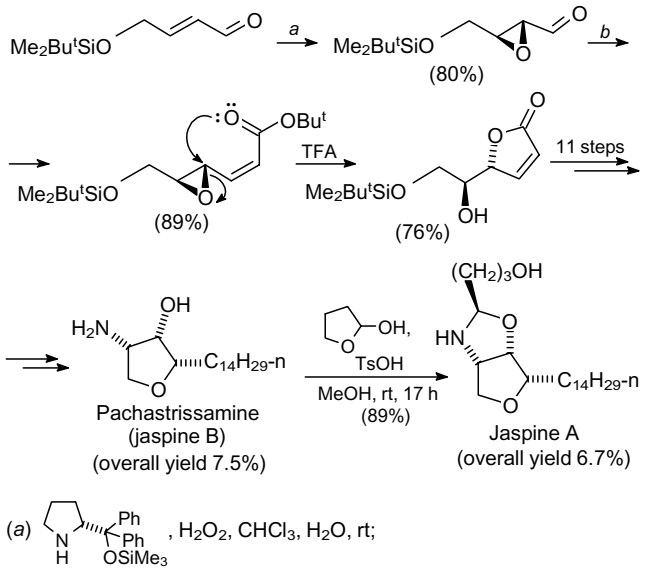

**Scheme 292**




Morimoto *et al.*[463] synthesized the polyethers teurilene, glabrescol and (+)-omaezakianol from squalene polyepoxides (Scheme 297).

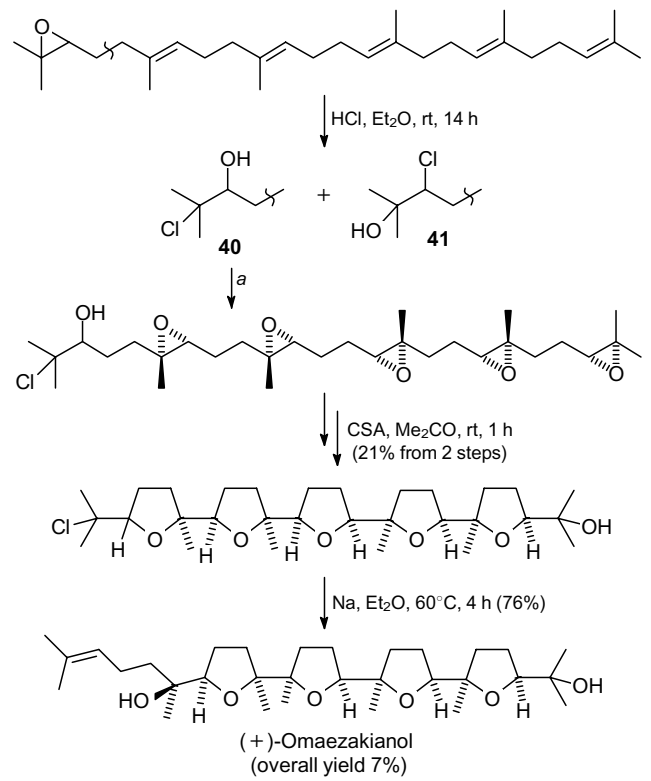
Fragments of the ladder polyethers hemibrevetoxin B and brevcnal were synthesized from appropriate chiral polyepoxy alcohols by Qu's research group[232] (Scheme 298).

**Scheme 293**




(*a*) , $H_2O_2$, $CHCl_3$, $H_2O$, rt;
(*b*) $KN(SiMe_3)_2$, $(PhO)_2P(O)CH_2CO_2Bu^t$, 18-crown-6

**Scheme 294**

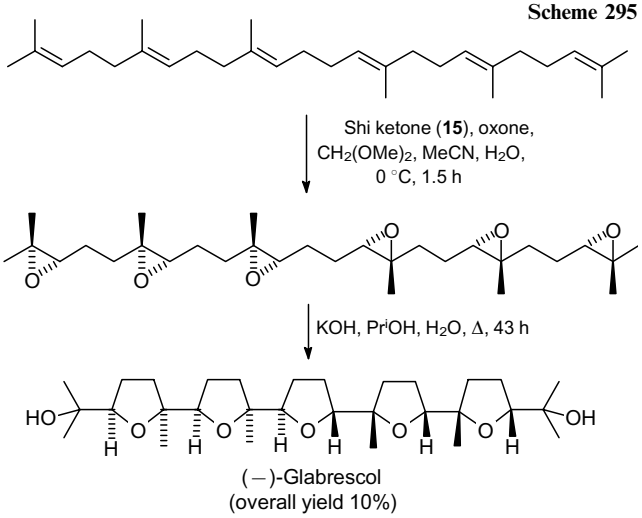



(*a*) Shi ketone (**15**), oxone, $Bu^n_4NHSO_4$, pH 10.5, $CH_2(OMe)_2$, MeCN, $H_2O$, 0°C, 1.5 h; CSA is camphorsulfonic acid

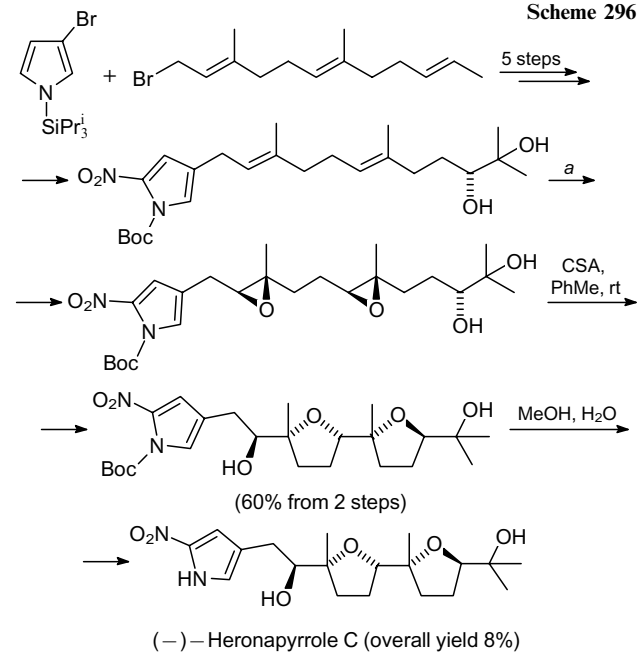
The convergent‡‡ methodology for the synthesis of fragments of natural ladder polyethers involving epoxy compounds was developed by the research group under the direction of Mori.[464–466] Scheme 299 presents the steps of

‡‡ The term convergent in relation to multistep synthesis of complex molecules, in which two individual pieces of the molecule are synthesized in the first step and then these pieces are combined in the second step.

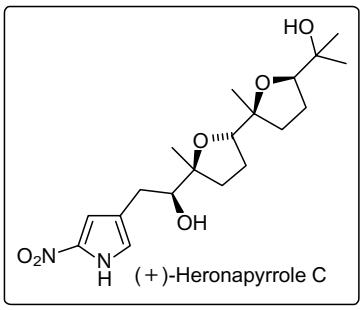
**Scheme 295**




**Scheme 296**



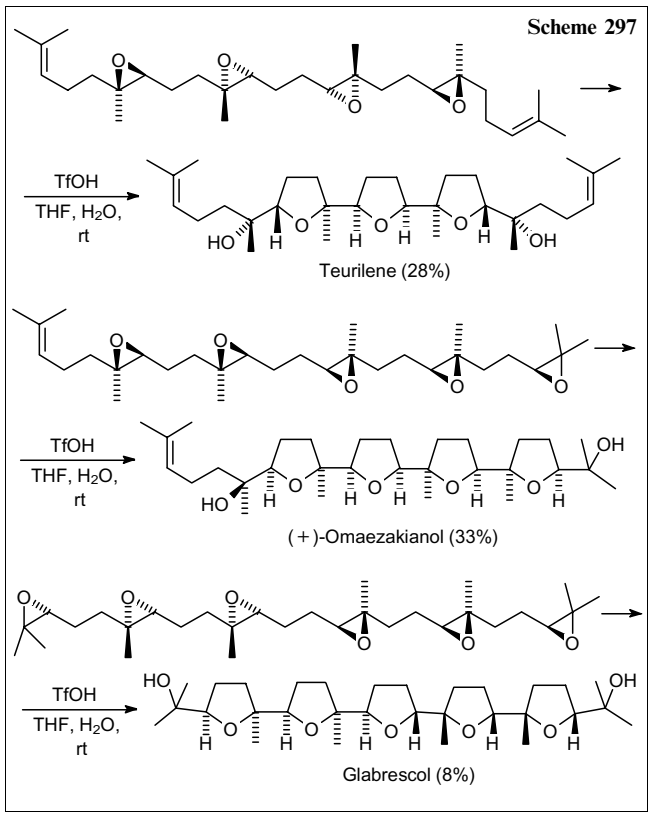

(*a*) L-form of Shi ketone (**15**), oxone, $K_2CO_3$, buffer, $CH_2(OMe)_2$, MeCN, 0 °C




the synthesis of the left-hand fragment of gymnocin A using epoxy compounds.[466]

Floreancig and co-workers[467] synthesized the natural polyether lactodehydrothyrsiferol from pent-4-yn-1-ol using two catalysts with different configurations of chiral atoms, compounds **15′** and **42**, in the Shi epoxidation. In the next step, tetrahydrofuran and tetrahydropyran subunits were

**Scheme 297**




constructed from epoxide rings accompanied by spirocyclization to form a tricyclic system (Scheme 300).

Yaragorla and Muthyala[468] proposed the Shi epoxidation and the epoxide ring-opening with trimethylsilyl azide to accomplish the formal synthesis of the natural protein kinase inhibitor (−)-balanol (Scheme 301).

Hamada s research group[138] synthesized natural coumarins (+)-marmesin, (−)-decursinol and (+)-lomatin from the corresponding chiral epoxy compounds (Scheme 302).

Devi and co-workers[469] synthesized naturally occurring 1-aminoundecan-2-ol and clavaminol G from undec-10-enoic acid using the Prilezhaev epoxidation and the epoxide ring-opening with sodium azide as the key steps (Scheme 303).

The synthesis of (−)-isoglaziovianol, an epimer of natural meroterpenoid glaziovianol, was developed by Trauner and co-workers.[470] The first step was the epoxide ring-opening with *p*-methoxybenzyl alcohol in the presence of a palladium complex catalyst with chiral ligand **43** (Scheme 304).

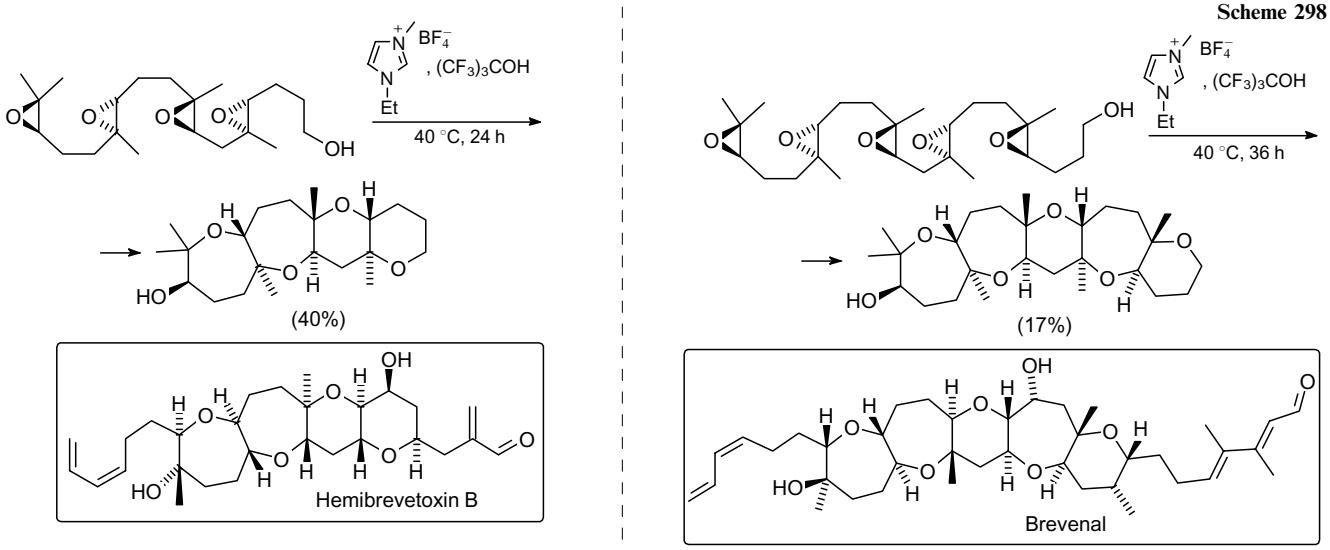
The epoxidation of cinnamaldehyde in the presence of chiral prolinol catalyst **11d** and the azepine ring construction *via* intramolecular Friedel–Crafts cyclization served as the basis for the synthesis of the alkaloid (+)-balasubramide (Scheme 305).[471]

The synthesis of the steroid withanolide A from pregnenolone involved, along with the epoxidation, the Wharton reaction (Scheme 306).[472]

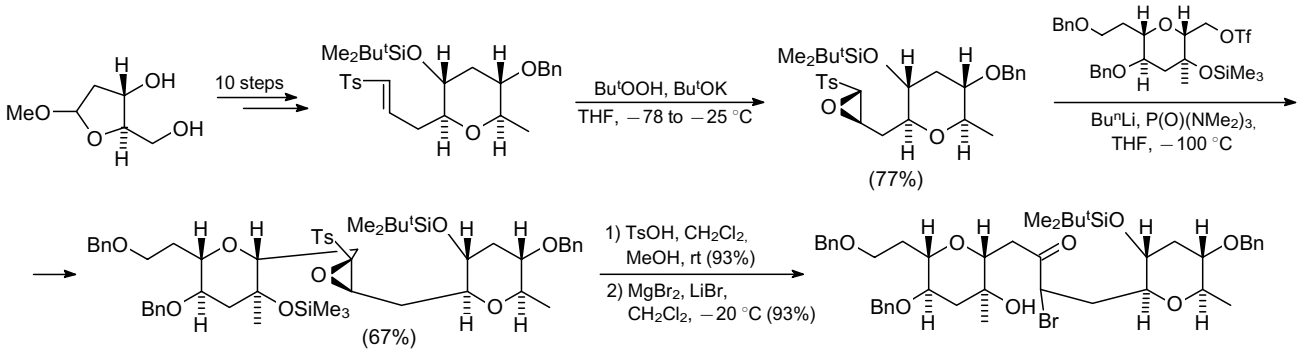
The racemic form of the *cis* isomer of the 12-membered lactone recifeiolide, a geometric isomer of the natural antibiotic, was derived from cyclooctanone (Scheme 307).[473]

The natural antibiotic frydamycin E was synthesized from commercially available anthrarufin through the carbonylation of the epoxide ring, on which the β-lactone ring was formed (Scheme 308).[474]

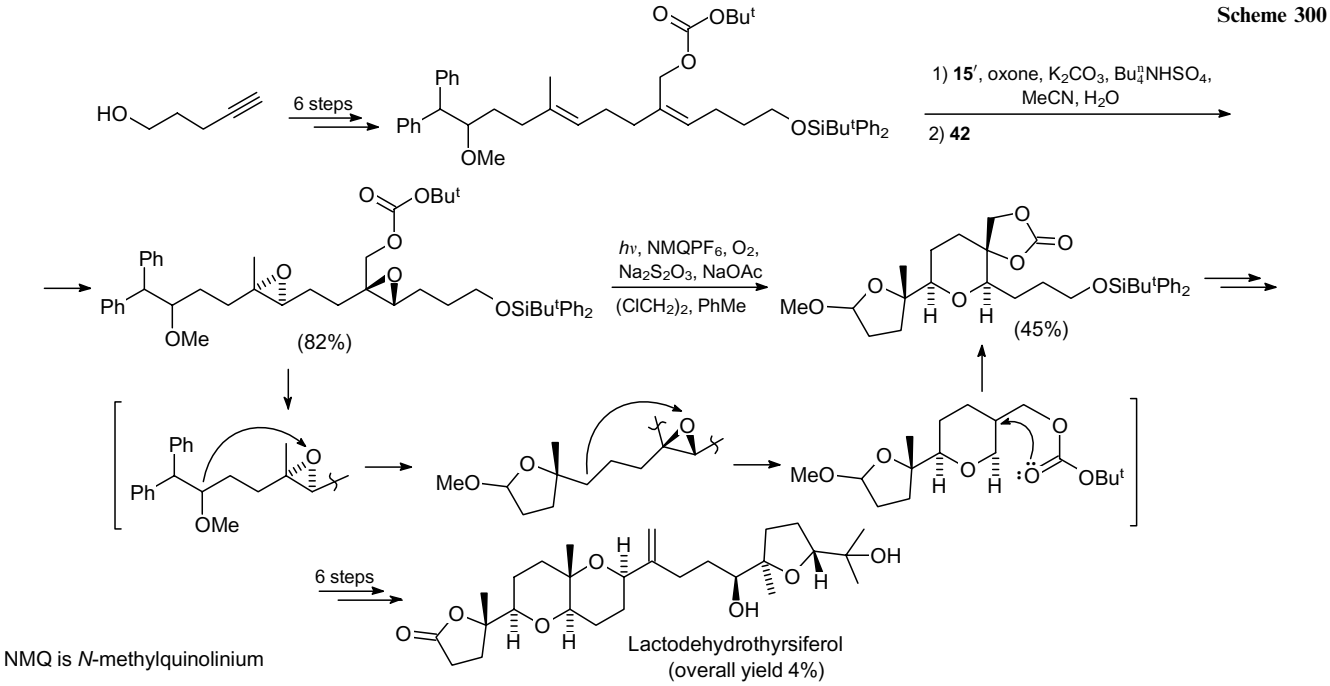
**Scheme 298**



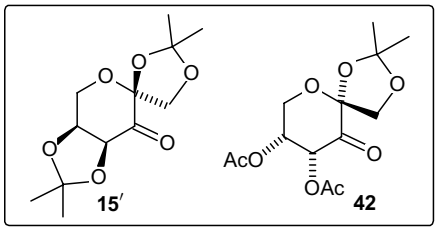

**Scheme 299**



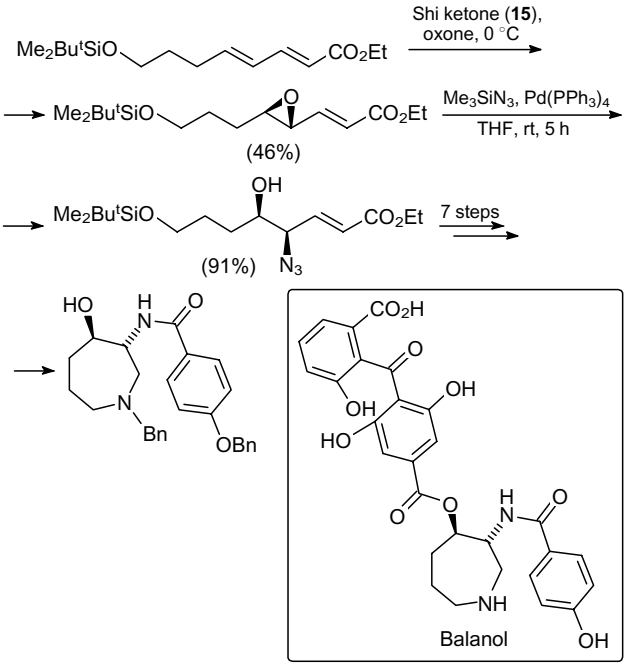

**Scheme 300**



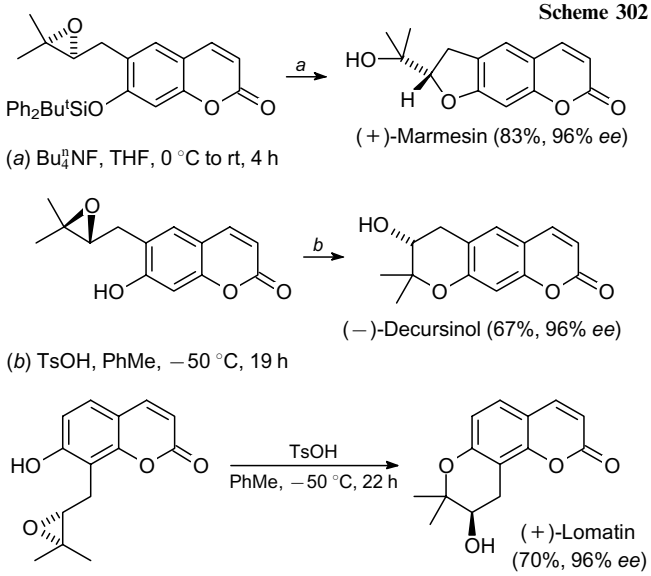

NMQ is *N*-methylquinolinium



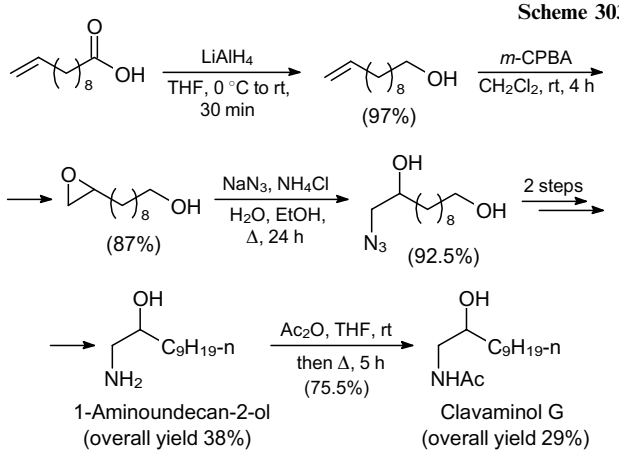
**Scheme 301**



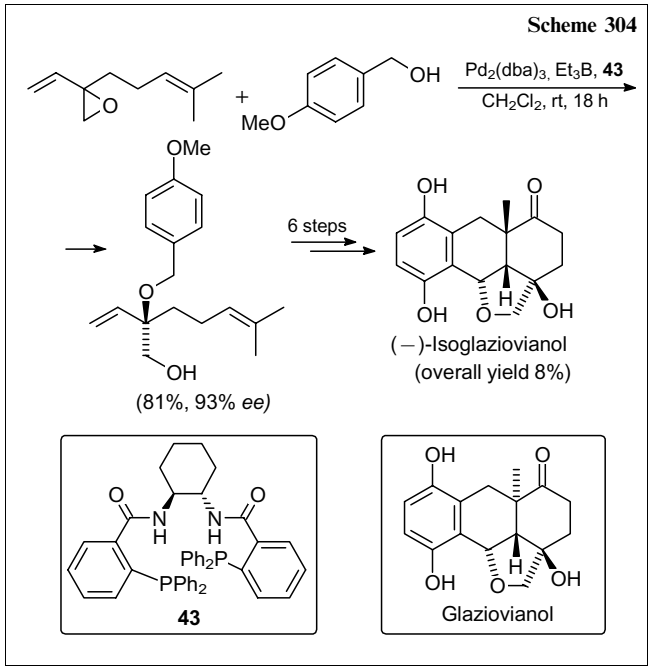

**Scheme 302**



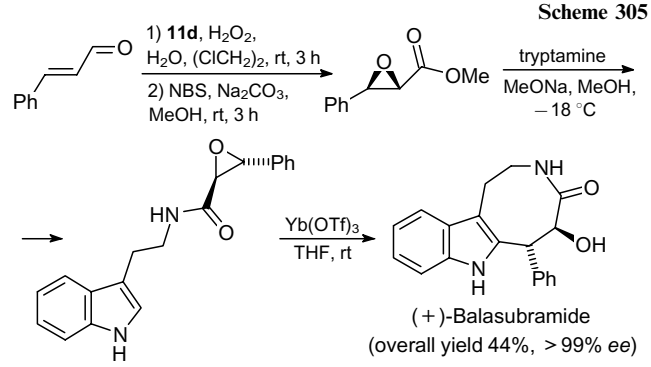

**Scheme 303**




**Scheme 304**




**Scheme 305**




The carbonylation of the epoxide ring was used also in the synthesis of tetrahydrolipstatin, a saturated analogue of lipstatin, which was isolated for the first time from the actinobacteria *Streptomyces toxytricini* (Scheme 309).[475]

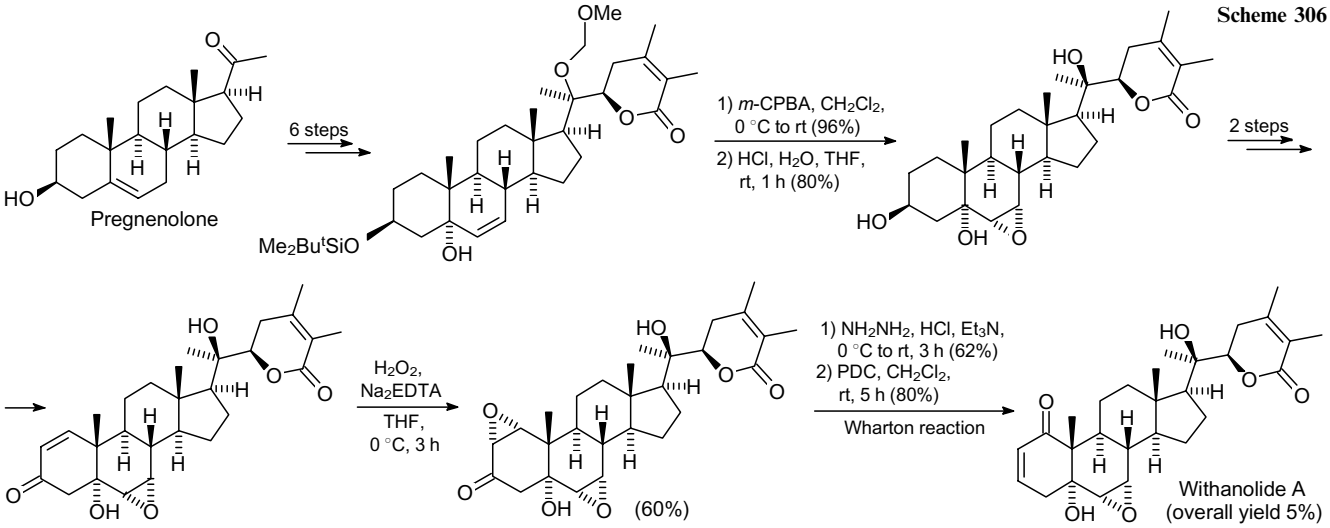
Lindsley and co-workers[476] prepared the natural 13-membered macrolide (−)-melearoride A from (*R*)-epichlorohydrin by the asymmetric synthesis (Scheme 310).

Williams *et al.*[477] used chiral epoxide containing the protected 2-hydroxyethyl group in the side chain as the reagent in the initial steps of the multistep formal synthesis of the macrocyclic natural product leucascandrolide A (Scheme 311).

Vanderwal and co-workers[148,478,479] synthesized naturally occurring chlorosulfolipid mytilipin A (Scheme 312). The transformation sequence involved the bromoallylation of aldehyde followed by the elimination of HBr, the kinetic resolution of the resulting epoxide using chiral dimer **27**, the orthophosphoric acid derivative, and the epoxide ring-opening of the chiral epoxy compound. Similar reactions provided the basis for the synthesis of chlorosulfolipid danicalipin A.[148]

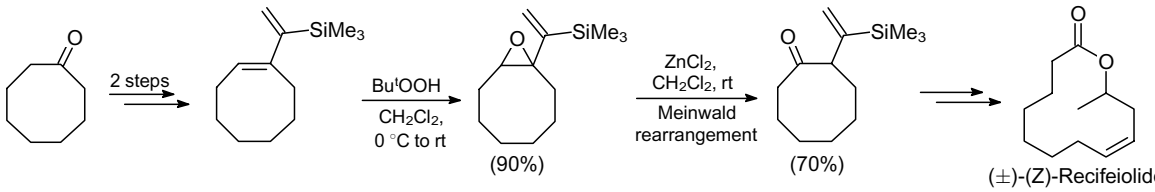
The research group under the direction of Mamedov developed procedures for the synthesis of the alkaloids viridicatol (Scheme 313)[17] and viridicatin (Scheme 314)[265] using the Darzens condensation and the intramolecular Friedel–Crafts cyclization.

**Scheme 306**

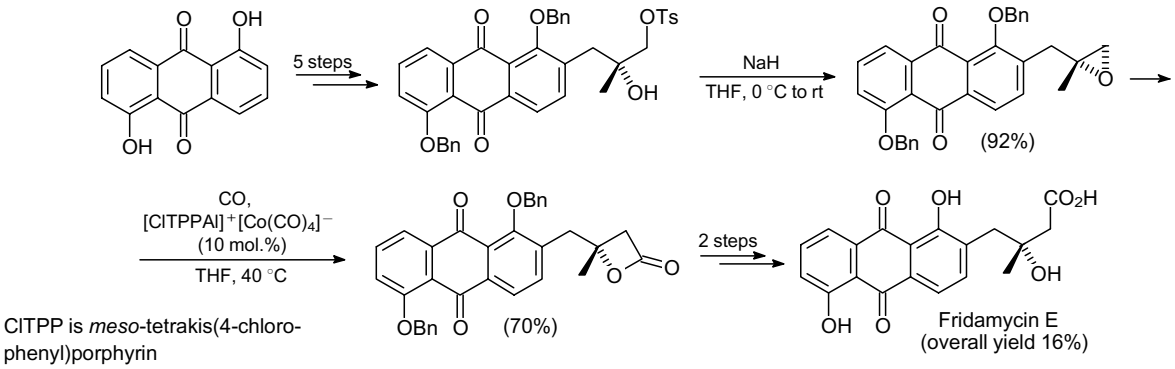



PDS is pyridinium dichromate

**Scheme 307**

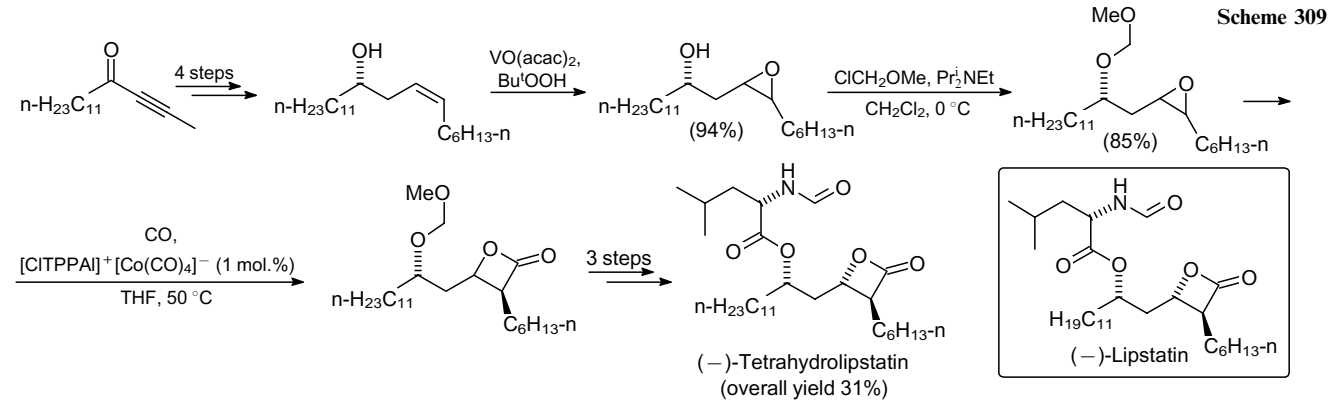



**Scheme 308**

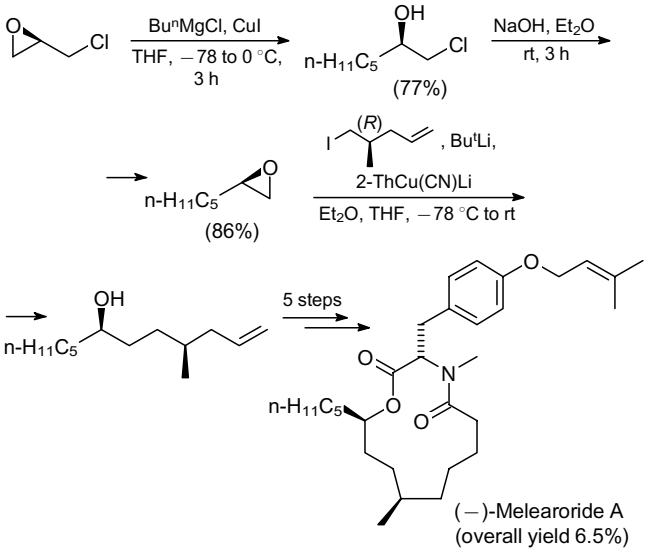



ClTPP is *meso*-tetrakis(4-chlorophenyl)porphyrin

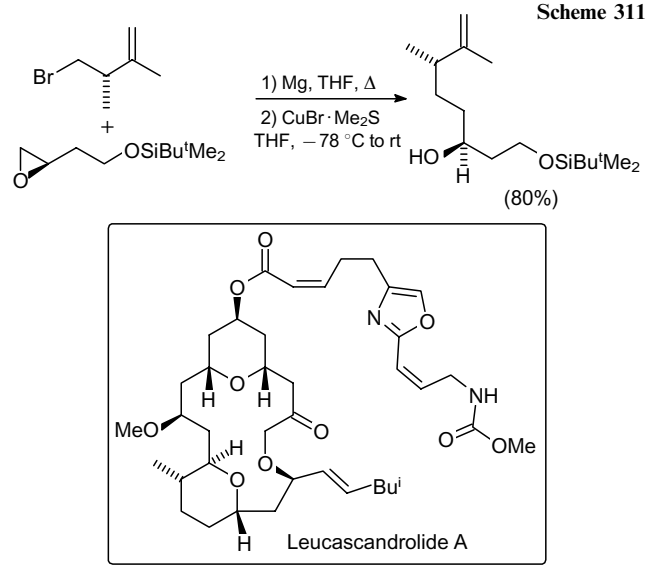
**Scheme 309**



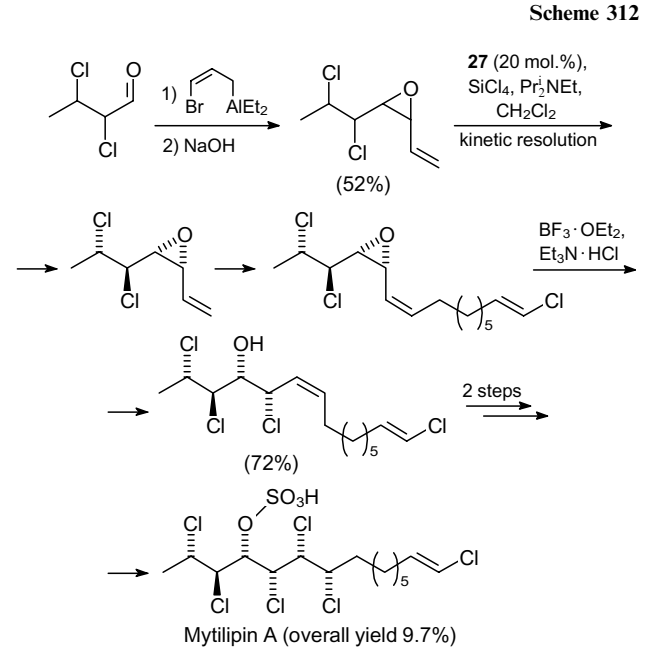
**Scheme 310**



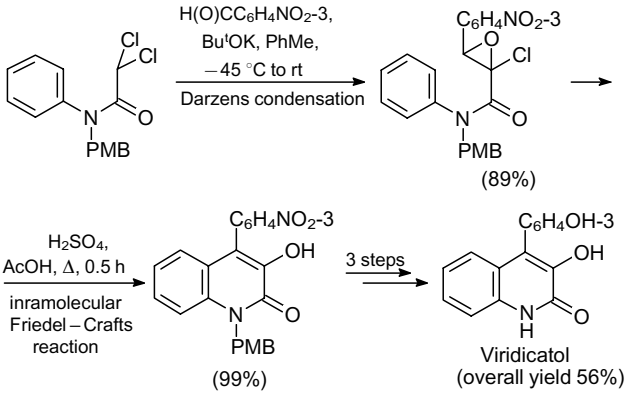

**Scheme 311**



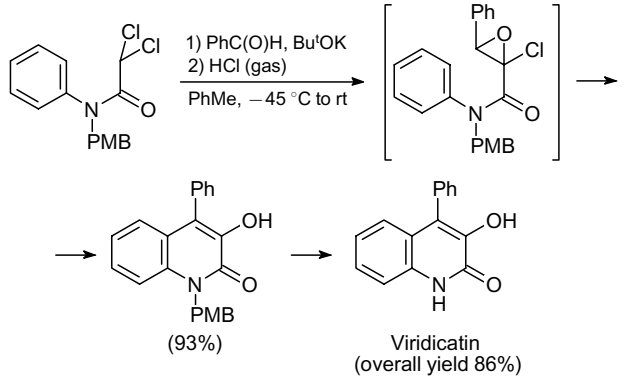

**Scheme 312**




**Scheme 313**

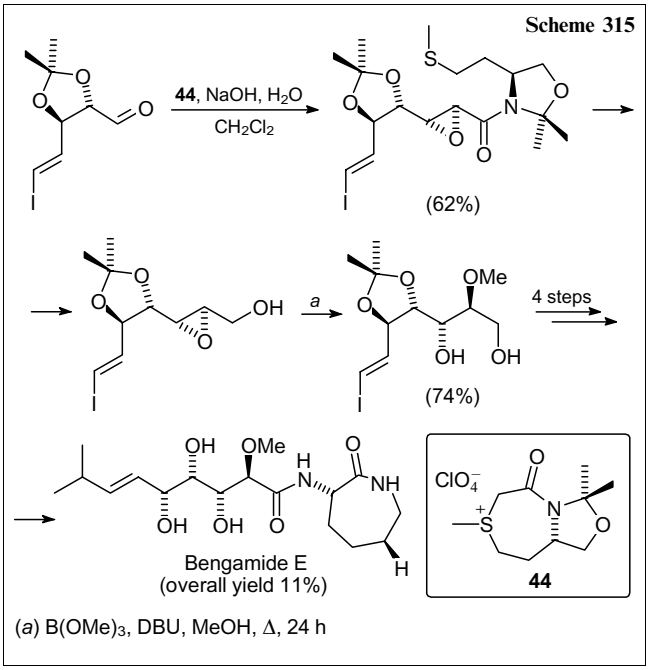



**Scheme 314**



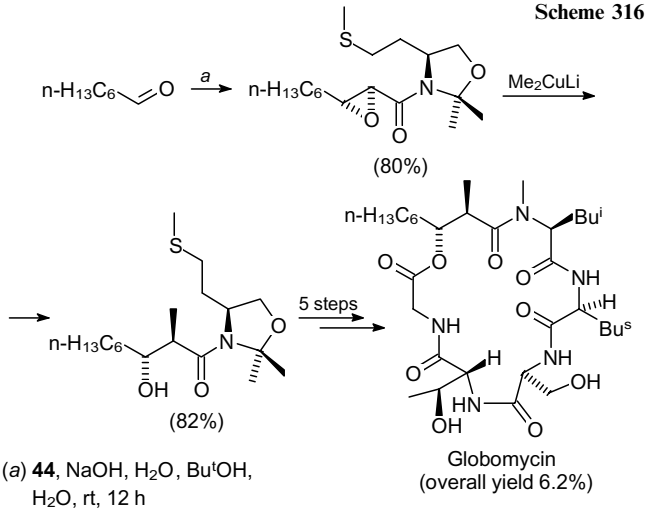

Sarabia *et al.*[480] applied the Corey–Chaykovsky method involving sulfonium salt **44** and the epoxide ring-opening with methanol to synthesize the natural product bengamide E (Scheme 315).

**Scheme 315**




This research group[481] also synthesized the natural antibiotic globomycin (Scheme 316).

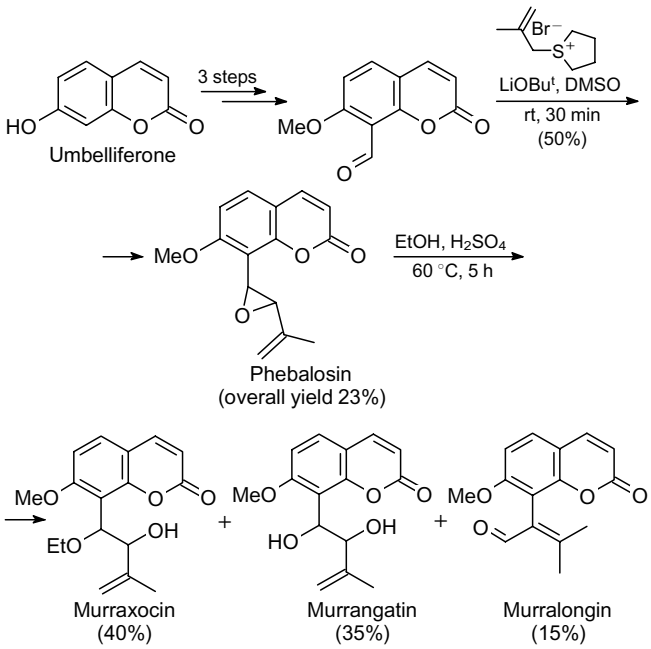
**Scheme 316**




The epoxide ring formation by the Corey–Chaykovsky method involving sulfonium salt **45** and the epoxide ring-opening with sodium bromide were used to synthesize the core structure of the naturally occurring nucleoside antibiotics muraymycin (Scheme 317) and caprazamycin from the corresponding uridine derivative.[482]

Pal and co-workers[483] prepared phebalosin from commercially available umbelliferone by the Corey–Chaykovsky method; the epoxide ring of phebalosin was opened with ethanol or underwent the Meinwald rearrangement in ethanol in the presence of $H_2SO_4$ to give the easily separable mixture of three natural products, murraxocin, murrangatin and murralongin (Scheme 318).

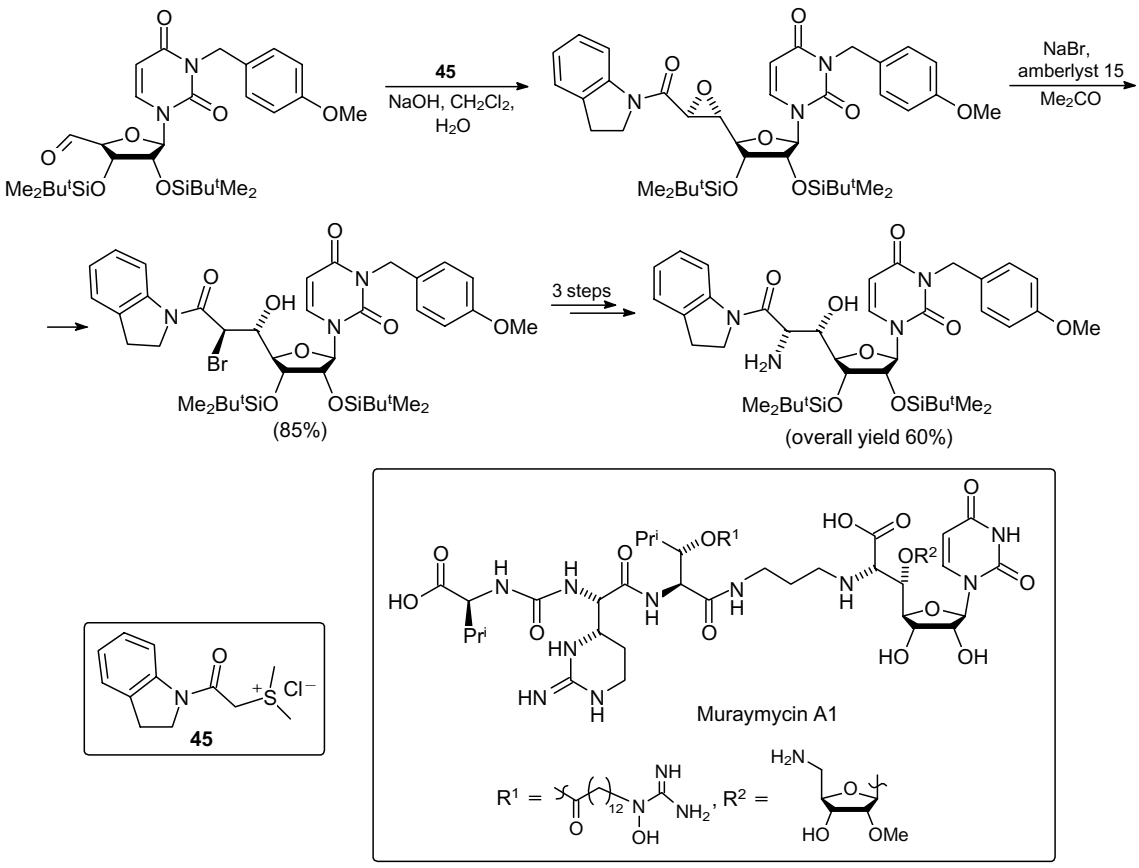
**Scheme 318**



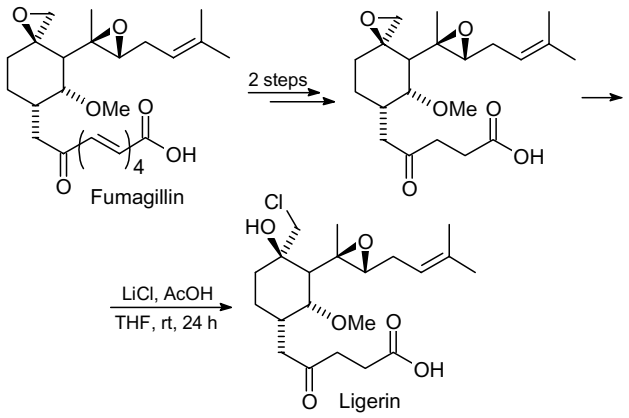

Grovel and co-workers[484] converted the terpenoid fumagillin containing two epoxide rings into its analogue ligerin containing one epoxide ring *via* the spiroepoxide ring-opening with lithium chloride in acetic acid (Scheme 319).

Kumar *et al.*[379] synthesized the naturally occurring cyclopropane-containing fatty acid derivatives, cascarillic

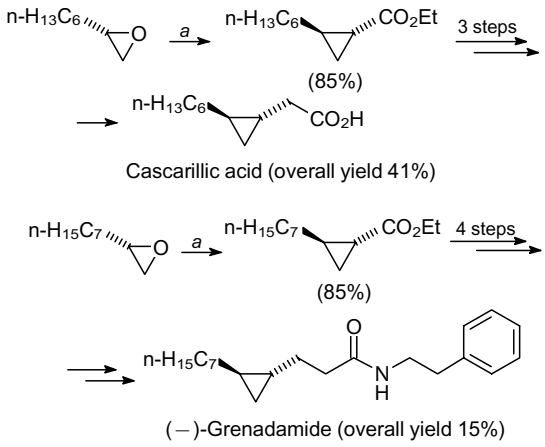
**Scheme 317**



**Scheme 319**




**Scheme 320**

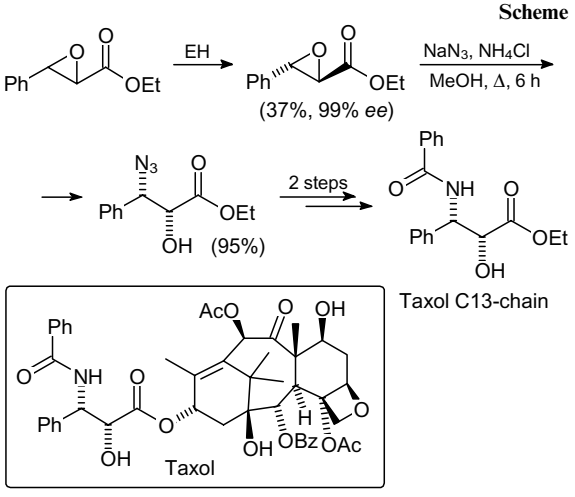



(*a*) $(EtO)_2P(O)CH_2CO_2Et$, NaH, PhMe, 80 to 110°C, 14 h

acid and grenadamide, from commercially available (*S*)-2-hexyl and (*S*)-2-heptyl oxides, respectively (Scheme 320).

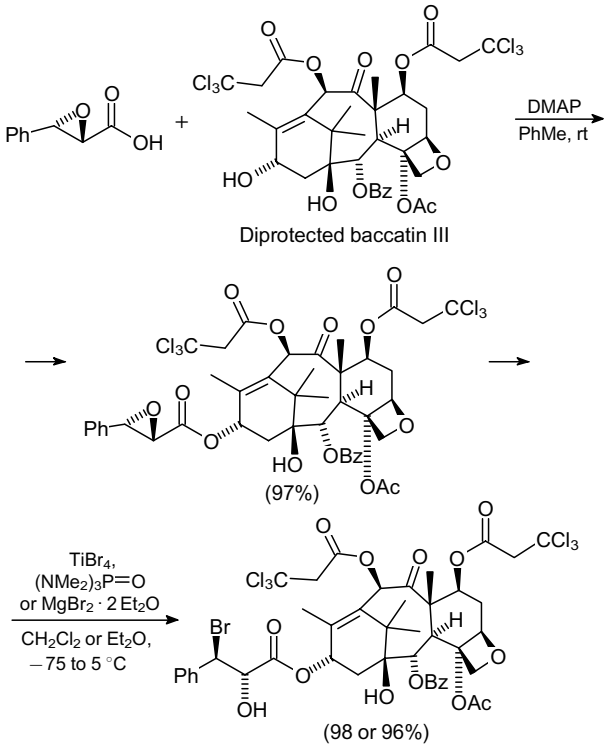
Zhu and co-workers[485] used the kinetic resolution of racemic epoxides with epoxide hydrolases and the epoxide ring-opening with sodium azide as the first steps in the synthesis of the side chain of the naturally occurring anticancer agent taxol (Scheme 321).

**Scheme 321**




Afon'kin *et al.*[486] synthesized the taxol core through esterification of chiral 3-phenylglycidic acids with a beccatin III derivative and the epoxide ring-opening (Scheme 322).

**Scheme 322**




The data summarized in this Section demonstrate that the formation of an epoxide ring and its involvement in chemical transformations are widely used in the synthesis of natural products. The epoxide ring formation is generally accomplished by methods described in Section 2. The application of a particular method depends on the target, the available substrate and the desired product. The Sharpless method is employed in the asymmetric synthesis if it is necessary to oxidize the double bond containing the vicinal hydroxy group (see Schemes 276–278, 283, 285, 289). This method is highly selective and unreactive towards other double bonds of the compound, which, if necessary, can be subjected to Shi epoxidation (see Schemes 285, 286, 288–291, 295, 296, 300, 301). The following reactions are applied in different steps of the synthesis of natural products: the Prilezhaev oxidation of alkenes with *m*-chloroperoxybenzoic acid (see Schemes 282, 286, 292, 303, 306), oxidation of unsaturated ketones and aldehydes with hydrogen peroxide (see Scheme 306), in particular in the presence of a chiral proline catalyst (see Schemes 293, 305), oxidation with *tert*-butyl hydroperoxide (see Schemes 299, 307, 309), dehydration (see Schemes 278–280), dehydrohalogenation (see Schemes 310, 312), the Darzens reaction (see Schemes 313, 314) and the Corey–Chaykovsky reaction (see Schemes 315–318).

The transformations of the epoxide ring are more diverse than the epoxide ring formation reactions. The reactions described in Section 3 are often used for the development of methods for the synthesis of natural products or their analogues, such as the nucleophilic epoxide ring-opening (see Schemes 278, 285–288, 301, 303, 304, 310–312, 315, 317, 318, 319, 321, 322), including intra-

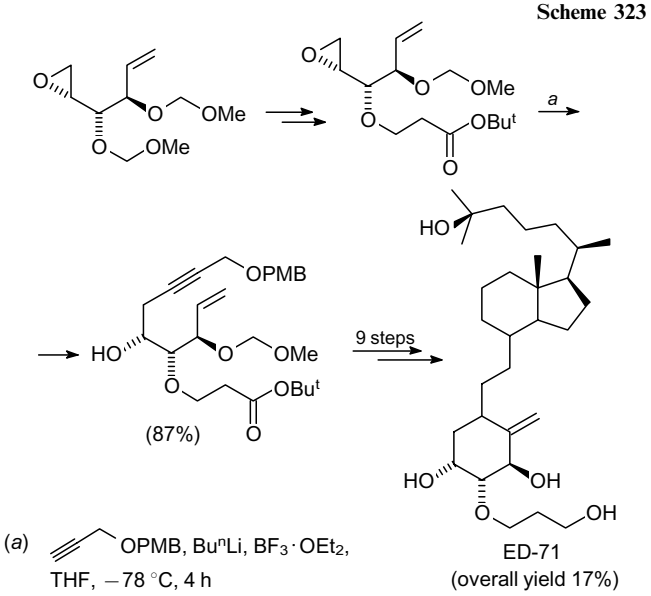
molecular processes (see Schemes 290, 294–298, 302), the intramolecular Friedel–Crafts reaction (see Schemes 278, 279, 305, 313, 314), the Meinwald rearrangement (see Schemes 276, 282, 307), the semipinacol rearrangement (see Scheme 283), the Wharton reaction (see Scheme 306), the reduction (see Scheme 277) and carbonylation (see Schemes 308–309) of the epoxide ring, intramolecular reactions of vinyl epoxides to form 2,5-dihydrofurans (see Schemes 291–293) and other intramolecular reactions (see Scheme 278).

### 4.3. Epoxy derivatives in the synthesis of drugs

This Section covers new approaches to the synthesis of known drugs, which involve epoxy derivatives in the initial or intermediate steps.

Wang and co-workers [487] proposed a method for the synthesis of the vitamin D analogue ED-71, which is used for the treatment of osteoporosis. Chiral epoxide, an intermediate in this synthesis, is generated from D-mannitol; protected propargyl alcohol is employed in the step of epoxide ring-opening (Scheme 323).

**Scheme 323**




Yu and Yao [488] reported the epoxide ring-opening with acetylene derivative **46**. This reaction served as a step in the synthesis of the potent anticancer agent structurally similar to the natural lactone bullatacin isolated from some plants and fruits (Scheme 324).

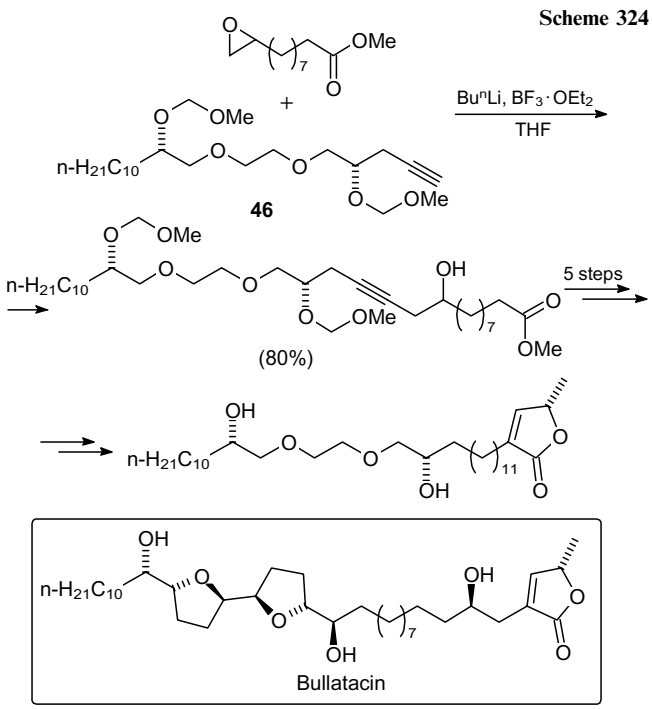
Chakraborti's research group [489] developed an approach to the synthesis of the anti-anginal drug ranolazine through the epoxide ring-opening of epichlorohydrin with piperazine **47** in an aqueous medium (Scheme 325).

This research group also synthesized the sodium channel blocker lubeluzole from chiral epichlorohydrin, 4-piperidone and 3,4-difluorophenol (Scheme 326).[490]

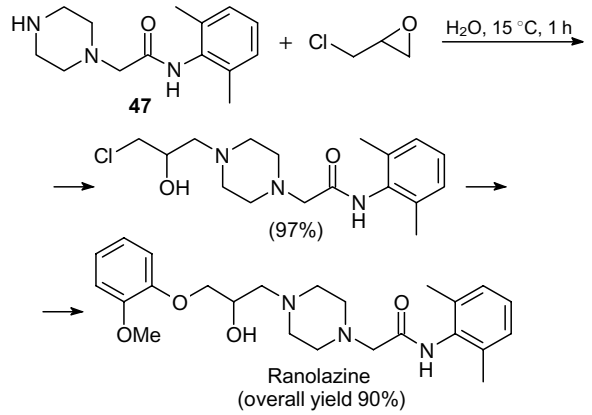
Muthukrishnan and co-workers [491] proposed a method for the synthesis of the appetite suppressant (*R*)-2-benzylmorpholine employing the Sharpless epoxidation and epoxide ring-opening of intermediate azide (Scheme 327).

The synthesis of ambrisentan was achieved *via* the Shi epoxidation and the epoxide ring-opening with methanol.[492] Ambrisentan is widely used in clinical practice for the treatment of pulmonary arterial hypertension (Scheme 328).

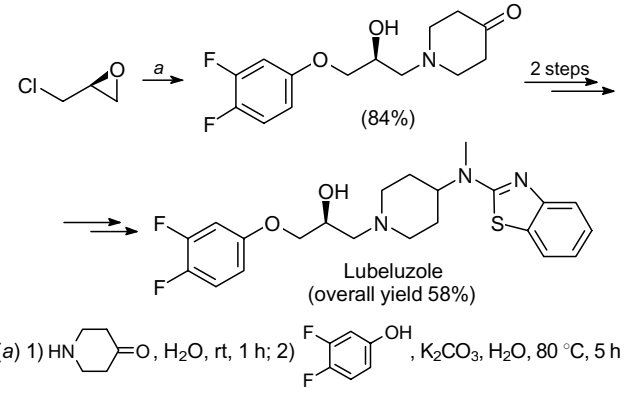
**Scheme 324**




**Scheme 325**

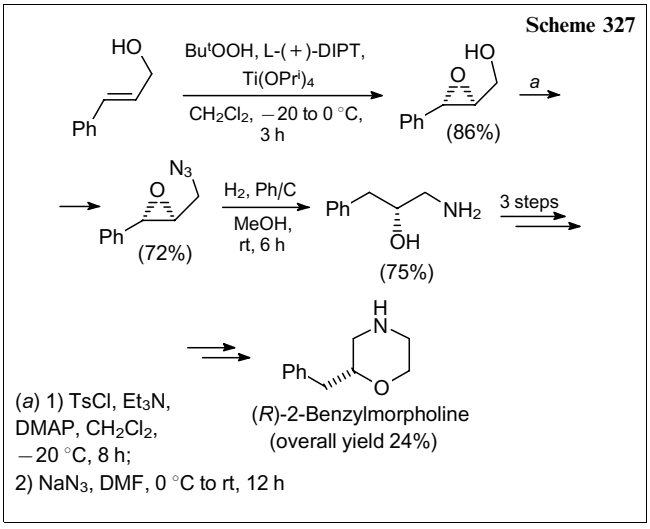



**Scheme 326**

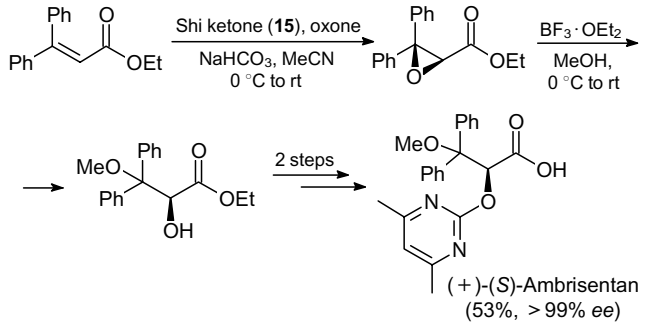



The synthesis of the anticancer agent enigmol through the epoxidation and epoxide ring-opening was proposed by McDonald and Pereira [493] (Scheme 329).

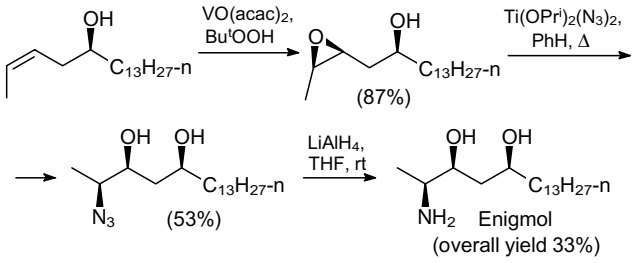
**Scheme 327**



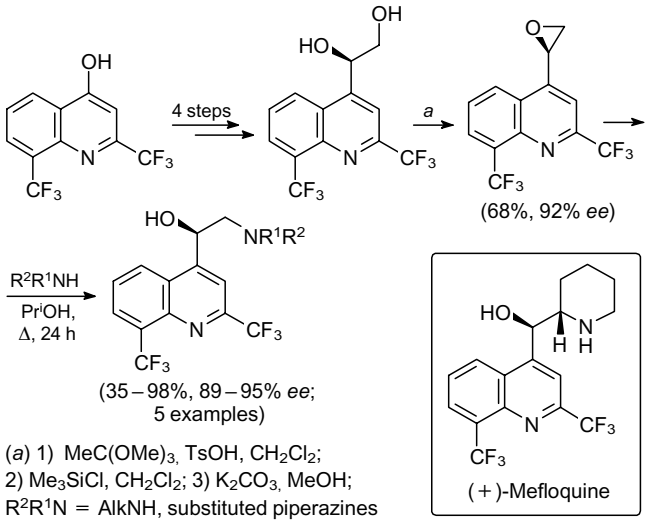

**Scheme 328**




**Scheme 329**



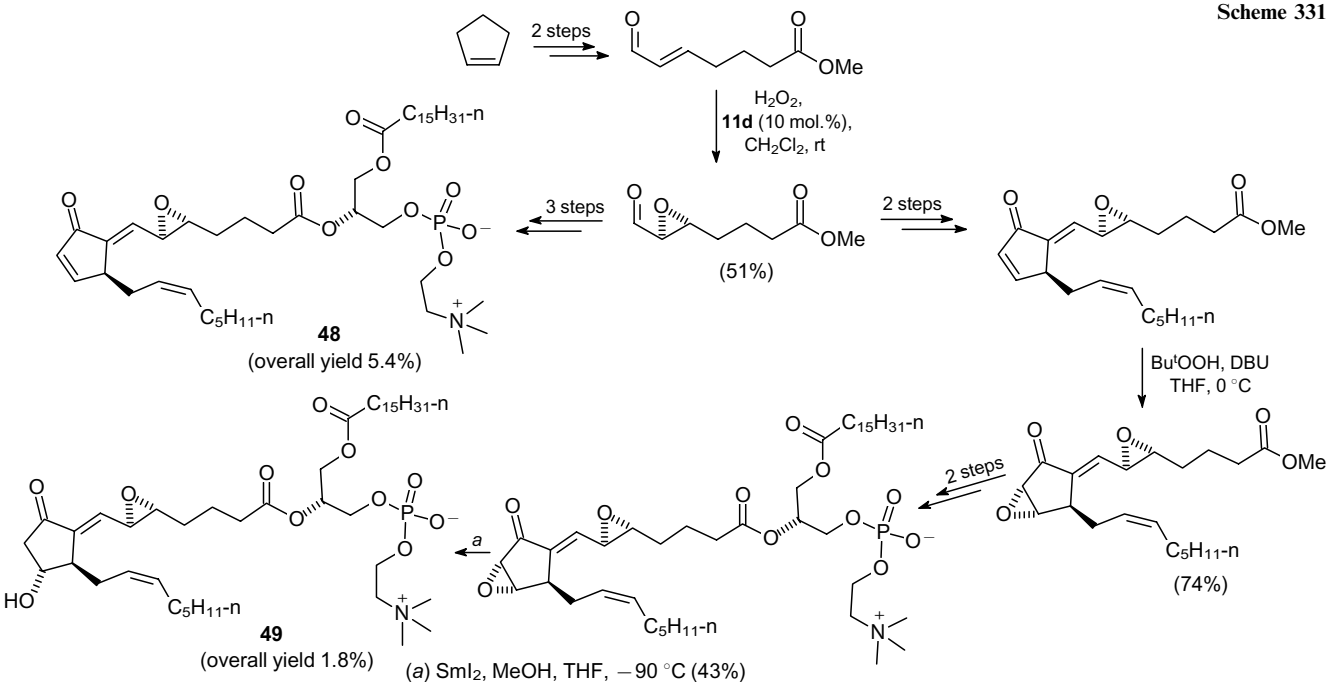

**Scheme 330**




Sonnet and co-workers [494] developed an approach to the synthesis of the (+)-enantiomer of the antimalarial drug mefloquine. In clinical practice, mefloquine is used in the racemic form; however, it is known that the (+)-enantiomer is more effective and less toxic compared to the (−)-form. The method proposed by the authors for the synthesis of (+)-enantiomers of mefloquine analogues is shown in Scheme 330.

Carreira and co-workers [495] synthesized oxidized phospholipids **48** and **49**, which are generated in the human body in response to oxidative stress, and demonstrated their pharmacological effect. These processes employed the epoxidation with hydrogen peroxide in the presence of prolinol

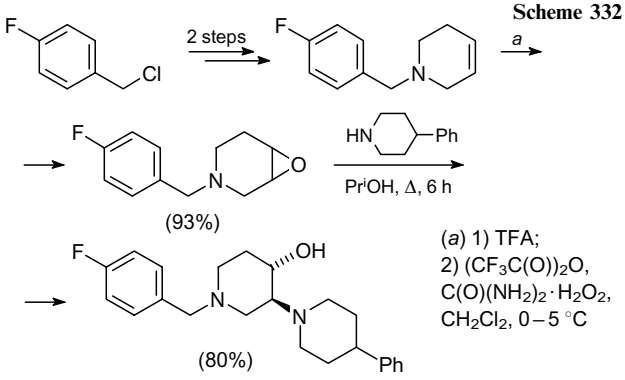
**Scheme 331**



catalyst **11d**, the epoxidation with *tert*-butyl hydroperoxide mediated by DBU and the selective epoxide ring-opening with methanol in the presence of samarium iodide (Scheme 331).

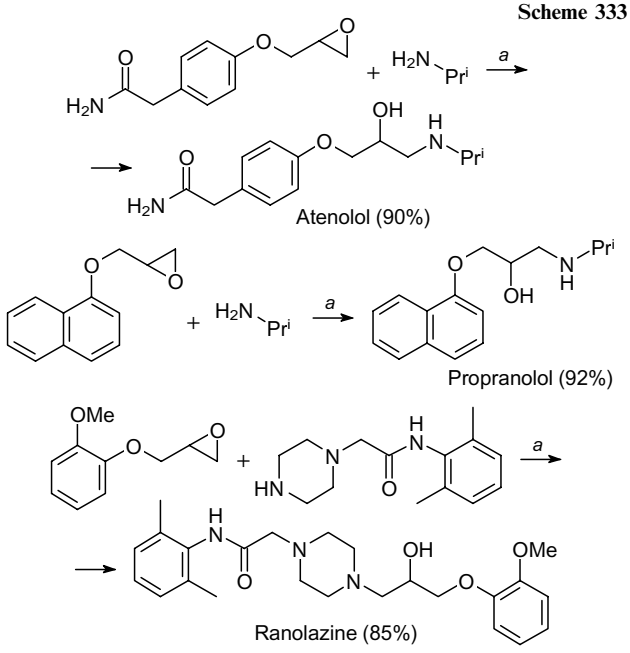
Scheunemann *et al.*[496] developed a procedure for the epoxidation of aminoalkenes using a combination of hydroperite and trifluoroacetic acid, which provides the salt form of the amine, and used it to synthesize 4-fluorobenzyltrozamicol (Scheme 332). 4-Fluorobenzyltrozamicol labeled with the fluorine-18 isotope is employed as a radiotracer for positron emission tomography imaging of the vesicular acetylcholine transporter.

**Scheme 332**



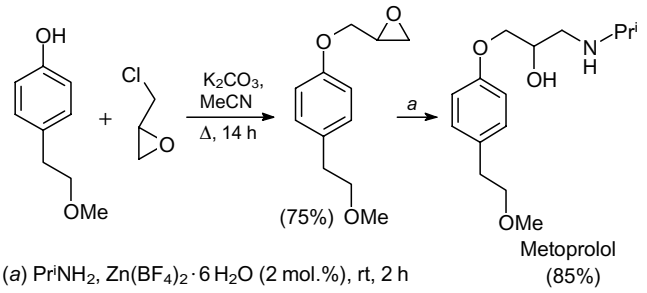

The regioselective epoxide ring-opening with amines under heterogeneous catalysis with tungstates (sulfated tungstate) giving β-amino alcohols served as the basis for the synthesis of the commonly used antihypertensive agents atenolol and propranolol and the antianginal drug ranolazine (Scheme 333).[497]

**Scheme 333**




Chakraborti and co-workers[498] applied the regioselective epoxide ring-opening with isopropylamine in the presence of zinc tetrafluoroborate to synthesize the antihypertensive drug metoprolol (Scheme 334). The use of

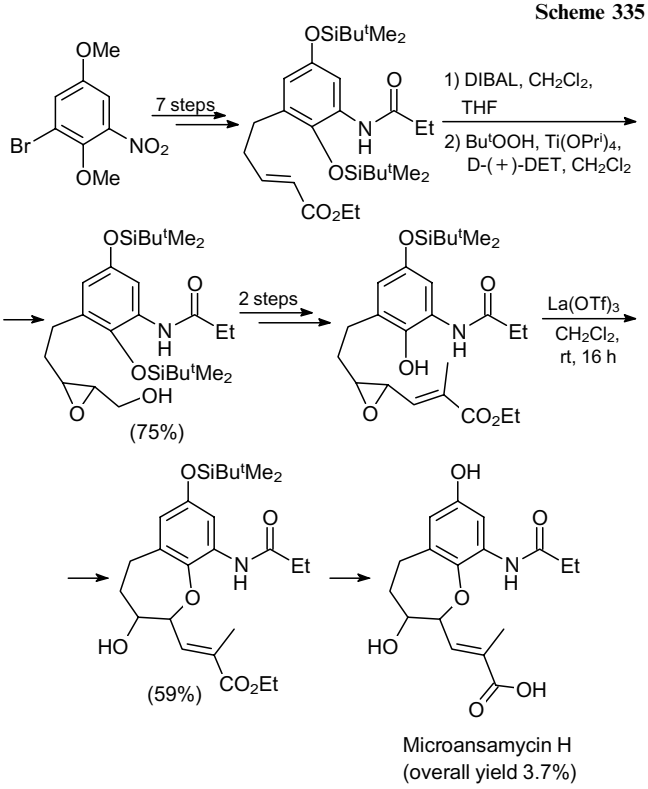
**Scheme 334**




chiral forms of epichlorohydrin in the first step of the synthesis resulted in the formation of the *S* and *R* forms of the drug.

Sittihan and Ruchirawat[499] developed a procedure for the synthesis of the promising gantitubercular agent microansamycin H. This method involved the Sharpless epoxidation and the intramolecular epoxide ring-opening with the phenol moiety of the molecule to form the benzoxepane moiety (Scheme 335).

**Scheme 335**




Therefore, the chemistry of epoxides is currently used to develop new methods for the synthesis of conventional drugs or compounds with known pharmacological activity.

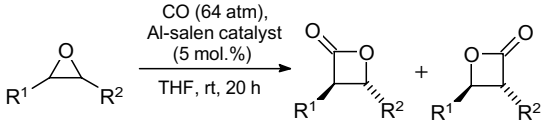
### 4.4. Epoxide carbonylation

The reactions involving epoxides and carbon monoxide, referred to as epoxide carbonylation, are widely employed in synthetic organic chemistry due to the availability of the reagents and high synthetic potential of the products. This type of reactions are briefly described in two reviews[500, 501] published in 2014. The carbonylation reactions involving only two components afford β-lactones. In the presence of alcohols or amines, the reactions give carboxylic acid

β-hydroxyesters or β-hydroxyamides. β-Hydroxyaldehydes are produced in the reactions in the presence of hydrogen.[500] The prospects of the practical use of these reactions are related to the utilization of carbon monoxide and the simultaneous creation of valuable products.

Coates and co-workers [502–504] explored in the detail the catalytic carbonylation of disubstituted epoxides. Generally, these reactions produce two regioisomeric β-lactones or methyl ethers [502] enantioenriched in the presence of chiral salen-type Al catalysts (Scheme 336, see Ref. 503).

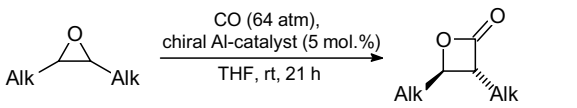
**Scheme 336**




$R^1$ = Me, Et; $R^2$ = n-$C_nH_{2n+1}$ ($n$ = 2–6), iso-$C_5H_{11}$, $(CH_2)_3OSiBu^tMe_2$

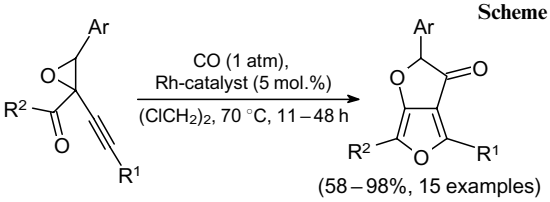
The desymmetrization of *meso* epoxides, accomplished by the same research group,[504] in the presence of a chiral aluminium complex catalyst afforded *trans*-β-lactones with high enantioselectivity (Scheme 337). Ibrahim and co-workers [505, 506] were the first to perform the desymmetrizaton of *meso* epoxides with carbon monoxide giving β-lactones under catalysis with a $Cr^{III}(Cl)$ chiral porphyrin complex in conjunction with $Co_2(CO)_8$.

**Scheme 337**




The rhodium-catalyzed carbonylation of functionalized epoxides containing geminal alkynyl and acyl (or aroyl) substituents afforded the fused biheterocyclic system furo[3,4-*b*]furan-3(2*H*)-one through a tandem process (Scheme 338).[507]

**Scheme 338**

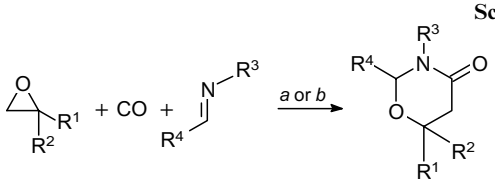



$R^1$ = Bu$^n$, cyclohexenyl, Ar; $R^2$ = Me, Ar

In 2014, two research groups [508, 509] almost simultaneously reported the synthesis of 1,3-oxazinan-4-ones by the Co-catalyzed three-component reaction of epoxide with imine and carbon monoxide (Scheme 339 combines the data from two studies).

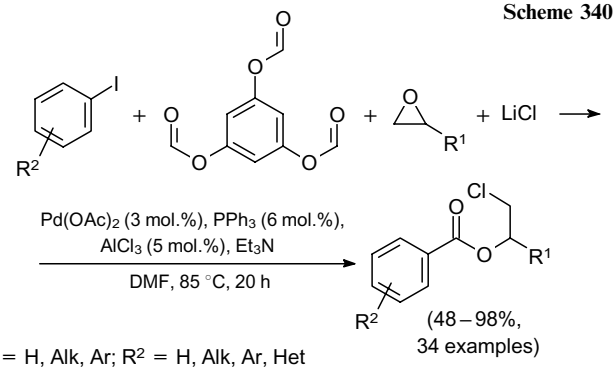
Wu s research group [510] used carbon monoxide, generated *in situ* from benzene-1,3,5-triyl triformate, in the reaction with epoxide, aryl iodide and lithium chloride (the latter served as a source of chlorine) giving 2-chloroethyl benzoate. The tandem process involved the aluminium

**Scheme 339**




(*a*) $Co_2(CO)_8$ (5 mol.%), LiCl (10 mol.%), dioxane, 70 °C, 24 h, 57 atm (50–98%, 9 examples);
(*b*) $Ph_3SiCo(CO)_4$ (5 mol.%), MeOH (5 mol.%), PhMe, 50 °C, 19–96 h, 60 atm (55–94%, 20 examples);
$R^1$ = H: $R^2$ = Me, Ph; $R^1$ = $R^2$ = Me; $R^3$ = Me; $R^4$ = Ar, Het

**Scheme 340**




$R^1$ = H, Alk, Ar; $R^2$ = H, Alk, Ar, Het

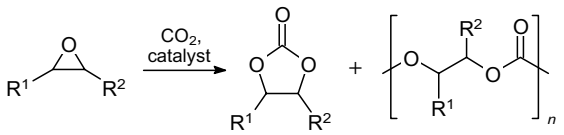
chloride-catalyzed epoxide ring-opening, the palladium-catalyzed coupling of CO with aryl iodide and the cross-coupling of the resulting intermediates (Scheme 340).

The analysis of the literature demonstrated that the carbonylation of epoxides is attractive not only due to the availability of the starting materials but also the valuable products, which can be prepared directly by this reaction or by adding other compounds to the reaction mixture.

### 4.5. Epoxide carboxylation

The carboxylation of epoxides is their reaction with $CO_2$. Generally, these reactions are catalytic and afford cyclic and polymeric carbonates (Scheme 341).

**Scheme 341**

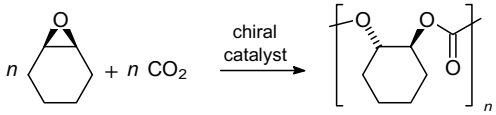



This area of chemistry became in high demand in the beginning of the 21st century due to acute challenges of utilizing industrial and domestic waste, including carbon monoxide. Besides, these reactions provide the basis for the preparation of practically important materials and valuable reagents for organic synthesis. The carboxylation of epoxides was covered in numerous reviews in 2010–2021, where the importance of such processes is demonstrated and the difficulties of their implementation are discussed.[7, 8, 511–515] Recent studies were mostly focused on the selection of catalysts increasing the selectivity of transformations, *i.e.*, directing the reactions towards the copolymerization [516–526] or coupling of epoxides with $CO_2$.[527–538] The reactions in question were generally performed under metal-catalyzed

conditions;[512–529] however, the reactions giving cyclic carbonates in the presence of organocatalysts were explored in some studies.[530–538] Several such transformations, both discussed in the cited reviews and those, which are not included in these reviews, are considered below.

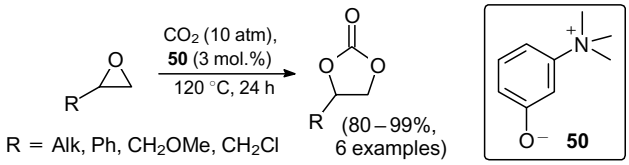
Rieger and co-workers[516,517] investigated chromium-containing complex catalysts in the polymerization of propylene oxide with $CO_2$. For these purposes, Nozaki and co-workers[518] used a cobalt salen complex. Zinc-containing complexes facilitate the copolymerization of cyclohexane oxide and its derivatives with $CO_2$.[519,520] The asymmetric copolymerization of *meso* epoxides, for example, of cyclohexane oxide, with $CO_2$ was performed also in the presence of cobalt,[521,522] zinc[523–525] or aluminium[526] chiral complex catalysts (Scheme 342).

**Scheme 342**




Manganese complexes with ONO-tridentate Schiff bases combined with tetra-n-butylammonium chloride as the co-catalyst were successfully applied in the carboxylation of propylene oxide giving cyclic carbonate.[527] The carboxylation of other epoxides was accomplished using titanium[528] and silver complexes.[529] Metal-organic frameworks were applied as heterogeneous catalysts for the carboxylation of epoxides affording cyclic carbonates.[530–532] The quantum chemical study of the mechanism of the $Re(CO)_5Br$-catalyzed formation of cyclic carbonate from epichlorohydrin and $CO_2$ was performed by Wu and co-workers.[533] Heterogeneous catalysts containing carbene-supported organic molecules,[534] complex polymer structures combined with ionic liquids[535] and more simple organic compounds,[536–538] *e.g.*, 3-(trimethylammonium)phenolate **50** (Scheme 343),[537] were characterized as organocatalysts for the cyclization of epoxides with $CO_2$.

**Scheme 343**

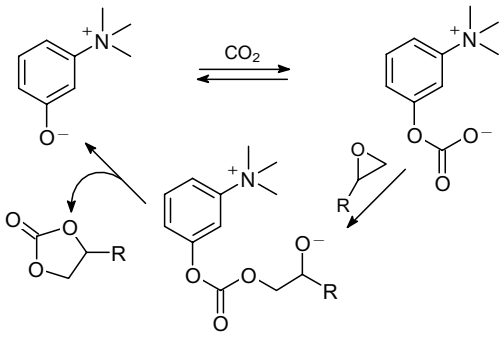



Scheme 344 presents the mechanism of catalysis of this reaction with betaine structure **50**.[537]

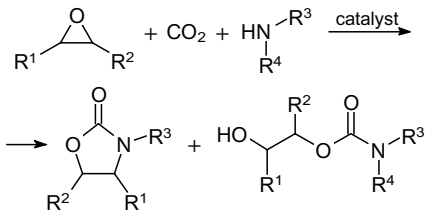
The carboxylation in three-component systems in the presence of amino derivatives affords cyclic or acyclic carbamates (Scheme 345). These transformations are discussed in the review[539] published in 2018. Each product can be prepared in another regioisomeric form. Depending on the site of epoxide ring-opening, these reactions can give mixtures of regioisomers.

Shang *et al.*[540] prepared mixtures of regioisomeric hydroxycarbamates **51** and **52** or compound **51** in the individual state (Scheme 346, the yield from 38 to 98%, 17 examples) by the reaction of monosubstituted epoxides with amines and $CO_2$ in the presence of iron(III) oxide with the addition of gold. Sadeghzadeh and co-workers[541] used

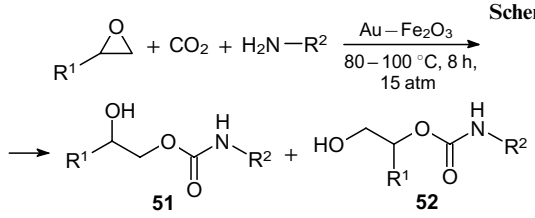
**Scheme 344**




**Scheme 345**




**Scheme 346**

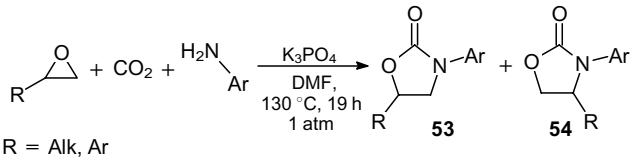



$R^1$ = H, Me, $ClCH_2$, Ph; $R^2$ = Alk, Ar

iron(III) oxide combined with ionic liquid to catalyze a similar reaction.

Regioisomeric cyclic carbamates **53** and **54** as a mixture or the first isomer (Scheme 347, 38–99% yields, 25 examples) are produced in the reaction of monosubstituted epoxides with anilines and $CO_2$ in the presence of potassium phosphate.[542]

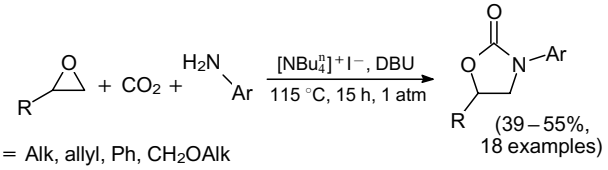
**Scheme 347**




R = Alk, Ar

Only one carbamate **53** was isolated in the reaction of monosubstituted epoxides with anilines and $CO_2$ in the presence of DBU as the base and tetra-n-butylammonium

**Scheme 348**




R = Alk, allyl, Ph, $CH_2OAlk$

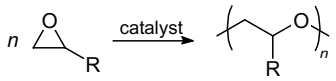
iodide as the catalyst (Scheme 348).[543] The application of ionic liquids in the reactions giving carbamates from ethylene oxide, amines and $CO_2$ has attracted great attention in recent years.[544–548]

Undoubtedly, this field of application of epoxy compounds deserves a great deal of attention because these reactions not only afford practically valuable products but also comply with the green chemistry principles associated with the utilization of carbon monoxide as domestic and industrial waste.

### 4.6. Epoxide polymerization

The epoxide polymerization (Scheme 349) has long been known, is widely used and continues to attract great interest due to the widespread application of polymer materials.

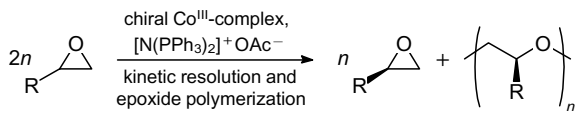
**Scheme 349**




The polymerization of ethylene oxide in the presence of alkali metal hydroxides or zinc chloride was reported by Wurtz as early as 1863. In 1930, polymer materials based on ethylene oxide began to be produced on an industrial scale for pharmaceutical and cosmetic industries and for the manufacture of lubricants, adhesives and detergents. Depending on the molecular weight, these polymers are named polyethylene glycols (PEG, up to 30 000 g $mol^{-1}$) or polyethylene oxides (PEO, > 30 000 g $mol^{-1}$). Polyethylene glycols are the gold standard for water-soluble and biocompatible polymers applied in pharmaceutical, cosmetic, medical and food industries. In recent years, the covalent attachment of PEG to biomolecules, nanocontainers and drugs, so-called PEGylation, has emerged as an independent and promising research area. Thus, PEGylated drugs cannot be recognized by the immune system due to which they serve as drugs with prolonged action.[9]

The epoxide polymerization was covered in many review papers, including recent publications, which highlight the advances in this research area. The literature considered in this Section largely reflects the past decade and discusses the functionalization of PEG,[9, 549–551] the selection of catalysts for the polymerization of epoxides with different substituents,[549, 550, 552] copolymerization, for example, with cyclic anhydrides,[552–554] the stereoselectivity of polymerization and copolymerization, including kinetic resolution (Scheme 350), and desymmetrization of *meso* epoxides using chiral catalysts.[555]

**Scheme 350**




A vast amount of literature on the polymerization of epoxides, like on the carboxylation, confirms the prospects of the further development of this field of chemistry.

## 5. Conclusion

To sum up, the analysis of the recent literature on the methods of synthesis, transformations and practical applications of epoxides demonstrated unlimited possibilities for investigation of this class of compounds despite a vast amount of data. Researches developed new methods and conventional approaches to the synthesis of epoxy compounds are widely used. There is no limit to creative thinking towards the synthesis of heterocyclic structures from functionalized epoxides. The challenge in the pharmaceutical industry is the asymmetric synthesis involving epoxides. The development of the chemistry of epoxides related to the utilization of carbon monoxide and carbon dioxide is needed to comply with the green chemistry principles. Researchers engaged in studies of the epoxide polymerization are interested in designing biomolecules, nanocontainers and drugs with prolonged action.

Despite a large number of review articles devoted to these issues, up to now there was no generalizing analysis of the recent studies, which would represent this class of compounds in its chemical diversity and its practical significance and disclose its prospects. We pursued this goal since we gave great attention to the chemistry of epoxides and contributed significantly to the progress in this area. Many issues considered in the review, have to be discussed in more detail and can stimulate the writing of new reviews on particular issues. In our opinion, the rearrangements in the chemistry of epoxides, the potential of functionalized epoxides in the construction of carbo- and heterocyclic structures and the role of epoxides in the synthesis of natural products and drugs are insufficiently covered in the literature reviews. These issues are briefly considered in our review, but they require deeper understanding. The reactions involving epoxides as intermediates are beyond the scope of this review because of a vast amount of the literature, and these data may be the subject of future surveys.

The abundance of literature on the chemistry of epoxides, does not in any way indicate that these investigations are being completed; on the contrary, these data are evidence that these compounds continue to attract interest. First of all, it is necessary to develop such areas as the heterocyclization and asymmetric synthesis of epoxides, not only in the presence of chiral catalysts but also using chiral reagents. The research in the polymer chemistry and on the conversions involving carbon oxides is of particular importance and highly promising.

We would like to end with the words of the synthetic chemist, Professor Dieter Seebach: 'If carbonyl compounds have been said to be virtually the backbone of organic synthesis, the epoxides correspond to at least one of the main muscles'.[§§]

This review was written in part with the financial support of the Russian Science Foundation (Project No. 18-13-00315-p).

## 6. List of abbreviations and designations

acac — acetylacetonate;
BINOL — 1,1′-binaphthyl-2,2′-diol;
bipy — 2,2′-bipyridine;
Boc — *tert*-butoxycarbonyl;
CAN — cerium(IV) ammonium nitrate;
ClTPP — *meso*-tetrakis(4-chlorophenyl)porphyrin;
COD — cycloocta-1,5-diene;
Cp — cyclopentadienyl;
CSA — camphorsulfonic acid;

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Cy — cyclohexyl;
dba — dibenzylideneacetone;
DBU — 1,8-diazabicyclo[5.4.0]undec-7-ene;
DET — diethyl tartrate;
DIBAL — diisobutylaluminium hydride;
DIC — *N*,*N*′-di(isopropyl)carbodiimide;
DIPT — diisopropyl tartrate;
DMAP — 4-(dimethylamino)pyridine;
DMPU — dimethylpropyleneurea;
dppf — 1,1′-bis(diphenylphosphino)ferrocene;
*dr* — diastereomeric excess;
EDTA — ethylenediaminetetraacetate;
*ee* — enantiomeric excess;
EHs — epoxide hydrolases;
EMIM — methylimidazolium;
EWG — electron-withdrawing group;
Fu — furyl;
hfacac — hexafluoroacetylacetonate;
HOBt — 1-hydroxybenzotriazole;
IL — ionic liquid;
IPr — 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene;
LA — Lewis acid;
Leu — leucine;
MAD — methylaluminum bis(2,6-di-tert-butyl-4-methylphenoxide);
*m*-CPBA — *m*-chloroperoxybenzoic acid;
MOF — metal-organic framework;
MTBD — 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene;
MW — microwave irradiation;
Naph — naphthyl,
NBAK — potassium 5-norbornene-2-carboxylate;
NBS — *N*-bromosuccinimide;
NCS — *N*-chlorosuccinimide;
NIS — *N*-iodosuccinimide;
NMQ — *N*-methylquinolinium;
NuH — nucleophile;
PDS — pyridinium dichromate;
PEG — polyethylene glycol;
PEO — polyethylene oxide;
Pic — picolate;
pin — pinacolate;
Piv — dimethylpropanoyl (pivaloyl);
PLL — poly(L-leucine);
PMB — *p*-methoxybenzyl;
Por — porphyrin;
Py — pyridyl;
rt — room temperature;
RCM — ring closing metathesis;
SMO — styrene monooxygenase;
TBAT — tetra-n-butylammonium difluorotriphenylsilicate;
TBD — 1,5,7-triazabicyclo[4.4.0]dec-5-ene;
Tf — trifluoromethanesulfonyl (triflyl);
TFA — trifluoroacetic acid;
Th — thienyl;
TPP — 5,10,15,20-tetraphenylporphyrin;
Ts — *p*-toluenesulfonyl (tosyl);
US — ultrasound treatment.

## 7. References

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