Review

Recent Advances in Substrate-Controlled Asymmetric Cyclization for Natural Product Synthesis

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Abstract: Asymmetric synthesis of naturally occurring diverse ring systems is an ongoing and challenging research topic. A large variety of remarkable reactions utilizing chiral substrates, auxiliaries, reagents, and catalysts have been intensively investigated. This review specifically describes recent advances in successful asymmetric cyclization reactions to generate cyclic architectures of various natural products in a substrate-controlled manner.

Keywords: asymmetric cyclization; substrate-controlled manner; total synthesis; natural product

1. Introduction

Asymmetric construction of structurally diverse ring architectures has always been considered a formidable task in natural product synthesis. Various natural sources have provided an enormous number of enantiomerically enriched carbo- and heterocycles [1–5]. Their ring systems include monocycles, such as small-sized, medium-sized, and large-sized rings and polycycles, such as spiro-, fused-, bridged-, and ansa-rings. These intriguing structures have attracted considerable attention from the organic synthesis communities. Many synthetic chemists have explored fascinating tactics to construct chiral ring frameworks using chiral substrates, auxiliaries, reagents, and catalysts [6–8]. In particular the substrate-controlled cyclization strategy, which utilizes the nature of the built-in chiral environment in the starting material, is a very powerful method. In addition, this strategy is more environmentally and economically attractive than using chiral auxiliaries or catalysts [9,10].

The aim of this review is to highlight outstanding achievements in the construction of enantioenriched rings in the field of total synthesis from 2010 to April 2017. Selected original articles in this review contain various substrate-controlled cyclization strategies. The cyclization reactions are categorized by reaction type, such as anionic, cationic, transition metal-mediated, pericyclic, and radical reactions.

2. Anionic Cyclizations

Recently, a wide range of natural product syntheses via anionic cyclization in a substrate-controlled manner have been reported. Carreira et al. accomplished the total synthesis of (∼)-dendrobine (8) [11], which was isolated from the ornamental orchid Dendrobium nobile Lindl [12,13]. To construct the core of 8, they utilized a special cascade sequence including enamine conjugate addition and stereoselective protonation as shown in Scheme 1. Highly advanced precursor 2 was readily prepared from ester 1 [14] in twelve steps. Treatment of 2 with N-methylbenzylamine followed by exposure to H2 and Pd/C led to bicycle 7 in 68% yield. High diastereoselectivity was obtained...
by a substrate-controlled cascade process involving the conjugate addition of enamine 3, enamine formation by proton loss of 4 and the convex protonation of enamine 5. This transformation allowed the asymmetric formations of the important C–C bond and the desired pendant amine.

Another substrate-controlled asymmetric cyclization is summarized in Scheme 2 which depicts the total synthesis reported by Tomioka et al. [15] of (−)-kopsinine (17), a Kopsia alkaloid isolated from Kopsia longiflora Merr. in 1955 [16,17]. Key precursor 11 was smoothly formed via a high-yielding process including the asymmetric one-pot [N+2+3] cyclization of tert-butyl N-Boc-indole-3-propenoate (9) and lithium N-benzyltrimethylsilylamide (10). Having successfully inserted two stereocenters onto 11, the three stereocenters of pentacyclic intermediate 16 were generated in a substrate-controlled manner. Mesylation of β-ketoester 11 and subsequent anionic cyclization of the resulting tetracycle 14 gave optically pure 16, presumably through transition states 12 and 15. The bridged ring of 17 was later introduced by Diels-Alder cyclization.
An elegant anionic polycyclization strategy of Deslongchamps et al. led to the total synthesis of (+)-cassaine (23) as shown in Scheme 3 [18]. (+)-Cassaine was isolated from *Erythrophleum guineense* in 1935 and reported as a nonsteroidal Na\(^{+}\)-K\(^{+}\)-ATPase inhibitor [19]. (+)-Carvone (18) was selected as the starting building block to synthesize the pharmacologically interesting natural product. The authors successfully prepared cyclization precursor 19 based on their previous synthetic route [20]. With the asymmetric formation of the trans-decalin system of 19, the desired anionic cyclization was performed using Nazarov reagent 20. Thus, treatment with cesium carbonate in EtOAc gave rise to diastereomerically pure tricycle 21 via Michael adduct 21 in 62\% yield. The newly created stereocenters originated from the α-face attack of 20 toward 19, which was controlled by the steric repulsion of the angular methyl group in the ring junction of 19. Synthesis of (+)-cassaine (23) was completed through multiple chemical reactions.

![Scheme 3. Total syntheses of (+)-cassaine (23).](image)

Stereoselective double Michael reactions have also been adopted for the construction of unique ring systems. Shenvi et al. completed the impressive synthesis of (−)-jiadifenolide (31) [21], which is one of the *Illicium* terpenes [22], as shown in Scheme 4. Key precursors butenolides 25 and 26 were quickly synthesized through three- and two-step routes, respectively. The first intermolecular Michael reaction of chiral butenolide 25 with achiral butenolide 26 in the presence of lithium diisopropylamide (LDA) provided stable intermediate 28. The stereochemistry of the process derived from a chelated transition state 27 and the newly created stereocenters of 28 were controlled by the chiral methyl group of 25. Subsequent exposure of the resulting 28 to titanium(IV) isopropoxide and additional LDA finally furnished ketolactone 30 via enolate 29 in 70\% yield. The second intramolecular Michael reaction enabled the construction of the entire skeleton of 31 in a substrate-controlled manner.

![Scheme 4. Total synthesis of (−)-jiadifenolide (31).](image)
3. Cationic Cyclizations

Cation-induced cyclization has been a powerful tool for controlling the stereochemistry of various ring structures in natural product synthesis. The total synthesis of (+)-sieboldine A (37), which is an alkaloid of club moss *Lycopodium sieboldii* [23], was firstly reported by Overman et al. [24,25]. This landmark synthesis was accomplished with a pinacol-terminated cyclization cascade as depicted in Scheme 5. Cyclization precursor 33 was built from the readily available allylic lactone 32 [26,27] in 9 steps. Initially, an increased cationic environment of gold alkyne species 34 enabled 1,6-enyne cyclization. The subsequent pinacol shift of cyclized cationic intermediate 35 afforded the desired cis-hydrindanone 36 as a single stereoisomer. The stereochemistry of enyne 33 was efficiently reorganized in a substrate-controlled manner.

![Scheme 5. Total synthesis of (+)-sieboldine A (37).](image)

Another interesting example of substrate-controlled cyclization is the total synthesis of (−)-zampanolide (42) published by Ghosh et al. [28,29] (Scheme 6). (−)-Zampanolide was initially separated from the marine sponge *Fasciospongia rimosa* and exhibited a potent microtubule-stabilizing activity [30,31]. Synthesis of interesting macrolide 42 commenced from the known ester 38, which was effectively prepared by the Noyori hydrogenation procedure [32]. Optically active starting material 38 was converted to allylsilane 39 in three steps. With the desired starting material 39 in hand, the authors carried out an oxidative Sakurai type cyclization using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with mild Brønsted acid pyridinium -toluenesulfonate (PPTS). Cyclized product 41 was obtained diastereoselectively through the Zimmerman-Traxler transition state 40. The cis-stereochemistry of tetrahydropyran ring 41 was caused by the equatorial orientations of all substituents in 40. Having successfully assembled the core ring, macrocycle 42 was successfully constructed via cross and ring-closing metatheses.

![Scheme 6. Total synthesis of (−)-zampanolide (42).](image)
Natural product clusianone is one of the polyprenylated polycyclic acylphloroglucinols (PPAPs) possessing a structurally unique bicyclo[3.3.1]nonane-2,4,9-trione core [33]. A biomimetic cationic cyclization was applied to construct the bicyclic template of (−)-clusianone (48) as shown in Scheme 7 [34]. Porco Jr. et al. were interested in the synthesis and structure-activity relationship of PPAP natural products and derivatives. Cyclization precursor 44 was accessible from starting material 43 via an unprecedented alkylative dearomatization strategy. Thus, when optically active 44 was subjected to neat formic acid, a tertiary carbocation was initially formed, which led to the intramolecular attack of the methyl enol ether to stereoselectively furnish the desired bicycle 47 in 72% yield. The authors proposed the transition states 45 and 46 due to the observation of formate adduct from ultrahigh performance liquid chromatography (UPLC) measurements. A final olefin metathesis produced (−)-clusianone (48).

As depicted in Scheme 8, another biomimetic cationic cyclization study was performed by Takayama et al. [35]. *Lycopodium* alkaloids (+)-flabellidine (55) and (−)-lycodine (56) were reported from *Lycopodium complanatum* in 1942 and *Lycopodium annotinum* in 1958, respectively [36,37]. The methyl group of linear precursor 50 was diastereoselectively introduced by Hosomi-Sakurai allylation of commercially available crotonamide 49 [38]. With linear substrate 50 in hand, the authors examined the designed cationic cascade cyclization to form the tetracyclic backbone. Exposure of 50 in CH₂Cl₂ to an excess amount of (+)-camphorsulfonic acid (CSA) provided tetracycle 54 as the major product, presumably through conjugate addition of ene-iminium intermediate 51 and olefin migration of 52, Mannich-like reaction of 53. The diastereoselectivity was dominantly controlled by the stereocenter of the methyl group. After protecting group manipulation a minor diastereomer of the cationic cascade cyclization could be removed, and syntheses of (+)-flabellidine (55) and (−)-lycodine (56) were completed by a chemoselective acetylation and selective IBX oxidation, respectively.

![Scheme 7. Total synthesis of (−)-clusianone (48).](image-url)

![Scheme 8. Total syntheses of (+)-flabellidine (55) and (−)-lycodine (56).](image-url)
More recently, a protecting-group-free total synthesis of (−)-lycopodine (63) was described (Scheme 9). (−)-Lycopodine is one of the Lycopodium alkaloids and was originally isolated from Lycopodium complanatum in 1881 [39]. To construct its polycyclic architecture, She et al. employed an acid-promoted aza-Prins cyclization [40]. Cyclization substrate 58 was smoothly synthesized from (R)-pulegone (57) via Wade’s enone synthesis, a one-pot amidation, and cyclization [41]. Alkyne-enamide 58 was subjected to a phosphoric acid-promoted cyclization and the desired product 62 was obtained in almost quantitative yield. Initially, enamine 58 was protonated stereoselectively to furnish N-acyliminium 59. Subsequent intramolecular 6-exo-trig cyclization provided unstable carbocation species 60, which was quickly transformed to enol 61 via the capture of water. Further manipulation, including an intramolecular aldol cyclization, led to completion of the synthesis of (−)-licopodine (63).

4. Transition Metal-Mediated Cyclizations

Transition metals have been used as powerful reagents for cyclization in the synthesis of complex natural products. The enantioselective total synthesis of (+)-isolysergol (69) [42], one of the biologically important ergot alkaloids [43], was completed by Fujii and Ohno et al. The authors examined a special palladium-catalyzed domino cyclization to build the ergot alkaloid backbone (Scheme 10). Allenic amide 65, required for the cyclization, was prepared from commercially available 4-bromoindole (64). Successful substrate-controlled cyclization of allene 65 in the presence of 5 mol % of Pd(PPh3)4 and K2CO3 was achieved leading to the desired product 68 in 76% yield with high diastereoselectivity. After oxidative addition, aminopalladation of the indolypalladium halide proceeded via the conformation 66 to provide allenypalladium(II) intermediate 67. The stereochemistry of the ring junction in 68 ultimately derived from chiral allene 65.
The nickel-mediated carboxylative cyclization of enyne precursor is another example of a transition-metal mediated cyclization as depicted in Scheme 11. Sato et al. described the total synthesis of indole alkaloid (−)-corynantheidine (76) [44], which was first reported in 1944 from the African plant Pseudocinchona africana [45]. Desired enyne 71 was readily accessible from 1-tryptophan (70) in an optically active form through a sequence of usual transformations involving a cis-selective Pictet-Spengler reaction [46]. Upon treatment of precursor 71 with a stoichiometric amount of Ni(cod)2 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under an atmosphere of gaseous CO2, the crude materials were obtained. Hydrolysis and methylation of the crude nickelacycle 73 stereoselectively led to the desired tetracycle 75 in 73% yield. The fourth ring was formed through oxidative cycloaddition of 71 and subsequent insertion of CO2 between the Csp3–nickel bond in 73. The new stereogenic center of the ring junction in 75 was created by an asymmetric formation of the nickelacycle in a substrate-controlled manner.

![Scheme 11. Total synthesis of (−)-corynantheidine (76).](image-url)

The asymmetric synthesis of incarvillea alkaloids was studied by using palladium(0)-catalyzed cyclization. Suh et al. completed an enantioselective synthesis of 7-epi-incarvilline (77) [47], which is an advanced architecture for the formal syntheses of (−)-incarvilline (78), (+)-incarvine C (79), and (−)-incarvillatine (80) (Scheme 12). Structurally, they consist of a common bicyclic piperidine skeleton including five contiguous stereocenters [48–50]. The authors focused on the diastereoselective construction of key intermediate 85, a highly functionalized bicyclic lactone containing three stereocenters. The desired precursor 82 of the reaction was easily obtained from the known chiral tosylate 81 [51]. Exposure of 82 in THF to Pd(dpbb)2 resulted in the desired bicyclic lactone 85 in 90% yield and with excellent diastereoselectivity (>29:1). The two transition states, 83 and 84, were controlled by the built-in chirality of lactone 82 and the high diastereoselectivity likely occurred due to the steric repulsion between the benzenesulfonyl group and the R substituent in Pd−π-allyl complex of 83. With the bicyclic lactone 85 in hand, 7-epi-incarvilline (77) was synthesized using further manipulations such as a substrate-controlled catalytic hydrogenation and a 1,4-addition.
Metal-catalyzed carbenoid transfer is also a useful method for asymmetric cyclizations. Bolivianine was isolated from *Hedyosmum angustifolium* (Chloranthaceae) in 2007 [52]. The sesterterpenoid natural product consists of a highly complex heptacyclic skeleton and nine stereocenters. Liu et al. reported a bioinspired total synthesis of bolivianine (90), which is summarized in Scheme 13. [53,54]. Precursor tosylhydrazone 87 was well designed for the formation of the chiral cyclopropyl moiety in 89 and produced from commercially available (+)-verbenone (86). The programmed intramolecular cyclopropanation of 87 with a palladium catalyst and a sodium salt afforded the desired product 89 as the sole isolable diastereomer in 65% yield. The stereochemistry of the chiral cyclopropane was substrate-controlled via allylic metal carbene species 88, which its conformation was caused by an equatorial positioning of two alkyl chains in chair-like transition state.

**Scheme 13.** Total synthesis of bolivianine (90).

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**Scheme 12.** Synthesis of 7-epi-incarvilline (77).
5. Pericyclic Reactions

Diverse types of pericyclic reactions have been used as an attractive tactic for substrate-controlled asymmetric cyclizations. Structurally interesting fluvirucins were isolated from actinomycetes by scientists from Bristol-Myers Squibb [55–58] and Schering-Plough [59,60] independently. Suh et al. employed a stereoselective aza-Claisen rearrangement-promoted ring expansion in the total synthesis of antibiotic macrolactam fluvirucinine A₁ (95), an aglycon of fluvirucine A₁ (Scheme 14) [61]. The key precursor, 10-membered α-alkoxyvinyl acylazacycle 92, was obtained from piperidine 91 by a diastereoselective α-alkylation of an iminium ion generated from an N,O-acetal TMS ether [62]. With the functionalized precursor 92 in hand, the projected aza-Claisen reorganization was executed in the presence of lithium bis(trimethylsilyl)amide (LHMDS) in refluxing toluene, to affording 14-membered macrolactam 94. The origin of the stereoselectivity could be explained based on a selective (Z)-lactam enolate formation and an equatorial positioning of the alkoxyvinyl substituent in chair-like transition state 93.

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\text{Scheme 14. Total synthesis of fluvirucinine A₁ (95).}
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(−)-Lingzhiol and its enantiomer were separated from Ganoderma lucidum in 2013 and found to inhibit selectively p-Smad3 [63]. The architecture of lingzhiol is composed of a carbocyclo[4.3.0]nonane skeleton and two quaternary bridgehead carbons (Scheme 15). Long et al. achieved the total synthesis of (−)-lingzhiol (99) via a rhodium-catalyzed intramolecular [3 + 2] cycloaddition [64]. Important precursor 97 was easily generated from 5,8-dimethoxy-3,4-dihydronaphthalen-1(2H)-one (96) in 10 steps by a ring expansion reaction employing Koser’s reagent [65] and an alkynylation using Waser’s reagent [66]. Treatment of compound 97 with the rhodium catalyst in the presence of CO in DCE gave rise to tricycle 98 in a diastereoselective manner. The catalytic cycle underwent a retro-propargylation, Michael reaction, Conia-ene type reaction, and protonolysis. The stereochemistry of the product was transferred stereospecifically from the chirality of the substrate. Further six steps completed the synthesis of (−)-lingzhiol (99).

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\text{Scheme 15. Total synthesis of (−)-lingzhiol (99).}
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Vanderwal et al. recently described the total synthesis of alsmaphorazine B (108) by an intramolecular nitrone/alkene dipolar cycloaddition (Scheme 16) [67]. Alsmaphorazine B possesses a highly dense, oxidized, and cage-like hexacyclic structure with a rare endo N–O bond [68]. The authors analyzed the structure of 108 and then proposed an alternative biogenetic hypothesis of multiple oxidations from akuammicine (109). Akuammicine-derived pivotal substrate 101 was prepared from tryptamine (100) by applying a scalable process involving a Diels-Alder reaction and a Heck reaction. Firstly, deoxygenation of α-ketol 101 with samarium iodide furnished two diastereomers, 102 and 103, in 1:1.5 ratio. Subsequent DMDO oxidation of the mixture of tertiary amines 102 and 103 readily led to the corresponding N-oxides, 104 and 105. Then, treatment of the obtained N-oxide mixture, 104 and 105, with DBU liberated a hydroxylamine and an enone. Finally, the desired cycloadduct 107 was spontaneously produced in 49% yield for 3 steps. This surprising sequence proceeded stereoselectively in a substrate-controlled manner.

Scheme 16. Total synthesis of alsmaphorazine B (108).

Intramolecular nitrile oxide-olefin cycloaddition (INOC) was utilized to form the macroyclic moiety of (−)-11β-hydroxycurvularin (115) (Scheme 17). This polyketide was isolated from Alternaria tomato and contains a 3,5-dihydroxyphenylacetic acid skeleton [69]. Lee et al. described a remote stereoinductive fashion of the key cyclization to synthesize the natural product [70]. Oxime 112, the substrate of nitrile oxide 113, was efficiently prepared from commercially available 110 by esterification, formylation, and oxime formation. Then oxime 112 was subjected to an intramolecular nitrile oxide cycloaddition reaction. It is well known that isolated alkene group has decreased reactivity compared to enone group and that regio- and stereoselectivity can be problematic in large ring formation with remote stereocenter [71]. Unexpectedly, the desired isomer 114 was produced in 79% yield with good diastereoselectivity. This reaction was an example of unprecedented remote stereoinduction and concomitant macrocyclization.
6. Radical Cyclizations

Radical cyclizations have served as a useful strategy to create various ring systems. As shown in Scheme 19, a total synthesis of the akuammiline alkaloid (+)-scholarisine A (127) was completed by Snyder et al. [76]. The structurally unique alkaloid, which was isolated from *Alstonia scholaris*, contains an indolenine fused to a strained carbocyclic cage and several tertiary and quaternary stereogenic centers [77]. To access the cage architecture of 126, a tandem 6-exo-trig radical cyclization/Keck alkylation was explored. The key precursor 122 of the tandem reaction was efficiently prepared in three steps from acrylate 121 [78]. Substrate 122 was smoothly cyclized using allyltributylstannane and the radical initiator Et$_3$B [79] in benzene at 75 $^\circ$C, providing the desired 126 in 59% yield as a single

More recently, unified syntheses of denudatine-type diterpenoid alkaloids were disclosed by Sarpong et al. [72]. Among these alkaloids, cochlearenine (120) consists of a highly complex bicyclo[2.2.2] structural architecture and exhibits a bradycardic activity in guinea pig atria [73,74]. Synthesis of cyclization precursor 117 began with the known bicycle 116, which was effectively prepared using Diels-Alder cycloaddition [75] (Scheme 18). Subjecting a solution of dienone 117 in $p$-xylene to heat resulted in the exclusive formation of hexacycle 119, which contains the whole ring backbone of 120. The excellent diastereoselectivity was determined by a substrate-controlled transition state. Total synthesis of cochlearenine (120) was completed in seven steps from hexacycle 119.

![Scheme 17. Total synthesis of (−)-11β-hydroxycurvularin (115).](image)

![Scheme 18. Total synthesis of cochlearenine (120).](image)
diastereomer. The transformation likely progressed in the mechanistic fashion shown in Scheme 19 through the initial radical formation of 123, 6-exo-trig cyclization onto the Michael accepter of 124, and allylation of the resulting 125. The newly incorporated stereogenic centers were influenced by the asymmetric geometry of bicyclic lactone 122.

![Scheme 19. Total synthesis of (+)-scholarisine (127).](image)

Another remarkable radical cyclization was reported by Zakarian et al. (Scheme 20) [80]. Maoecrystal V (133), a cytotoxic diterpenoid, was discovered in 2004 from *Isodon eriocalyx*, a Chinese medicinal herb [81]. Structurally, three contiguous quaternary stereocenters are compactly arranged on a pentacyclic framework; the complex molecular architecture provides an intriguing synthetic challenge. Key precursor 129, having two quaternary stereocenters, was synthesized from alcohol 128 through a C–H-insertion and a [4 + 2] cycloaddition. With phenylselenocarbonate 129 in hand, a substrate-controlled radical cyclization was explored. To a solution of substrate 129 in benzene at 80 °C was slowly added a mixture of TMS$_3$SiH, as a less efficient hydrogen atom donor reagent, and AIBN, resulting in the formation of lactone 132 (55% yield). The asymmetric cyclization successfully generated the third quaternary stereocenter of 132 through the initially generated formyl radical 130.

![Scheme 20. Total synthesis of maoecrystal V (133).](image)
Ma et al. described the total syntheses of leucosceptroids A (139) and B (138) by applying a SmI$_2$-mediated intramolecular ketyl-olefin radical cyclization (Scheme 21) [82]. These two sesterterpenoids were separated from glandular trichomes of *Leucosceptrum canum* [83]. These intriguing compounds contain a common tricyclic hydrindane ring skeleton and eight contiguous stereogenic centers. Advanced intermediate 135 was smoothly accessed from commercially available enynol 134. Exposure of 135 to samarium(II) iodide gave rise to fused tricycle 137 through ketyl radical species 136 in a substrate-controlled manner. The α-OTMS unit of 136 played a critical role to promote selective 6-exo-cyclization, which competed with 7-endo-cyclization, by blocking the chelation of the free hydroxy group to SmI$_2$, and high diastereoselectivity by decreasing the steric repulsion with the olefin. Further transformations efficiently led to completion of the syntheses of leucosceptroids A (139) and B (138).

![Scheme 21. Total syntheses of leucosceptroids A (139) and B (138).](image)

More recently, a remarkable photochemical C–H acylation was utilized to cyclize a complicated ring system (Scheme 22). Inoue et al. presented a total synthesis of zaragozic acid C (145) [84], a potent inhibitor of mammalian squalene synthase [85]. Natural acid 145 is characterized by a dioxabicyclo[3.2.1]octane architecture with an array of six stereocenters. Pivotal radical cyclization precursor 141 was produced from commercially available gluconolactone derivative 140. Irradiation of highly oxygenated substrate 141 with violet LED light excited the 1,2-diketone moiety and the resulting 1,2-biradical 142 spontaneously generated 1,4-biradical 143 via a hydrogen atom abstraction of the proximal ethereal C–H bond. The facile C–C bond formation of the 1,4-biradical 143 stereoselectively afforded the desired bicycle 144 (54% yield) by avoiding steric repulsions between the bulky substituents. Careful functional group transformations provide final product 145.

![Scheme 22. Total synthesis of zaragozic acid C (145).](image)
7. Conclusions

Substrate-controlled asymmetric cyclizations provide organic chemists with a powerful tool for the construction of optically active ring frameworks of natural products. In this review, a remarkable variety of cyclizations were classified by reaction type, such as anionic, cationic, transition metal-mediated, pericyclic, and radical reaction and discussed in detail. Various ring systems of natural products and their newly generated stereocenters were successfully established and defined. To conclude, asymmetric cyclization induced by the chiral nature of the substrate is in continuous development for the synthesis of natural products and related compounds.

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Abbreviations

The following abbreviations are used in this manuscript:

| Abbreviation | Definition |
|--------------|------------|
| Ac           | Acetyl     |
| AIBN         | Azobisisobutyronitrile |
| Bn           | Benzyl     |
| Boc          | t-Butyloxycarbonyl |
| Bu           | Butyl      |
| Bz           | Benzoyl    |
| cod          | 1,5-Cyclooctadiene |
| CSA          | Camphorsulfonic acid |
| dba          | Dibenzyldieneacetone |
| DBU          | 1,8-Diazabicyle[5.4.0]undec-7-ene |
| DCE          | 1,2-Dichloroethane |
| DDQ          | 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone |
| DMDO         | Dimethylidioxidirane |
| DMF          | N,N-Dimethylformamide |
| dppb         | 1,4-Bis(diphenylphosphino)butane |
| Et           | Ethyl      |
| HMPA         | Hexamethylphosphoramid |
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