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[2+1]-TYPE CYCLOPROPANATION REACTIONS

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1.1 INTRODUCTION

Cyclopropane is often present in natural and biologically active products. Alternatively, the cyclopropane structure has been used as parts for the modification of such products. It has a high ring strain because of its bond angle, and this property facilitates unique reactions. The formation of cyclopropanes has been the focus of considerable study and many reviews are available [1]. Among the methods reported in these reviews, [2+1]-type cycloaddition by carbenoids is a representative strategy [2]. In this chapter, we collected recent representative examples of [2+1]-type cyclopropanation reactions. We reviewed and classified the literature from the past decade into six categories: Michael-induced ring closure (MIRC), the Simmons–Smith reaction, reactions by carbenes from diazoalkanes catalyzed/noncatalyzed by transition metals, cycloisomerization reactions by transition metal catalysts, the Kulinkovich reaction, and miscellaneous reactions. Since this chapter focuses on [2+1]-type cycloaddition, we excluded γ-elimination-type cyclopropanations from a single molecule. The asymmetric synthesis of cyclopropanes, which is a topic of interest among synthetic chemists, is discussed in each category. Although we carefully reviewed the literature, it could be possible we may have missed some citations owing to the significant amount of related studies.

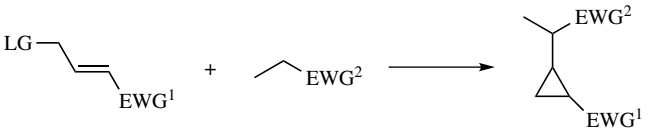
1.2 CYCLOPROPANATION REACTION VIA MICHAEL-INDUCED RING CLOSURE REACTION

1.2.1 Introduction

Cyclopropanes are prepared by the nucleophilic attack on electron-deficient alkenes followed by intramolecular

Methods and Applications of Cycloaddition Reactions in Organic Syntheses, First Edition. Edited by Nagatoshi Nishiwaki.

nucleophilic substitution. This occurs when the nucleophile or electron-deficient alkene contains a leaving group at an appropriate position. This type of reaction is called the MIRC [3] and is frequently employed for cyclopropanation. There are two types of MIRC reactions, which are expressed by Equations 1.1 and 1.2.



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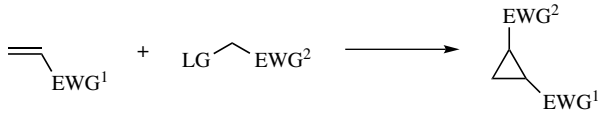


(1.2)

Equation 1.1 shows an MIRC reaction with an electron-drawing alkene containing a leaving group, which reacts with a nucleophile that is generated under reaction conditions. In this case, all carbons in cyclopropane originate from the alkene. Equation 1.2 is an MIRC reaction with a nucleophile containing a leaving group. Cyclopropane formed in this sequence contains two carbons from the alkene and one carbon from the nucleophile. Because this chapter focuses on [2+1] cycloaddition, we will concentrate on the latter case of MIRC cyclopropanation.

The leaving group is typically halogen if the nucleophile is derived from active methylene compounds or nitro compounds. α-Halo enolates are used for this reaction. The reaction is usually performed in a one-pot procedure; however, a two-step sequence with the oxidation of conjugate adducts, intermediates for cyclopropanation, can occasionally afford good results. Recently, organocatalysts have been employed in catalytic asymmetric cyclopropanation. Ylides are another species frequently used in MIRC cyclopropanation. Sulfur ylides are most frequently used; however, phosphorous, arsenic, selenium, tellurium, and iodonium ylides are also useful.

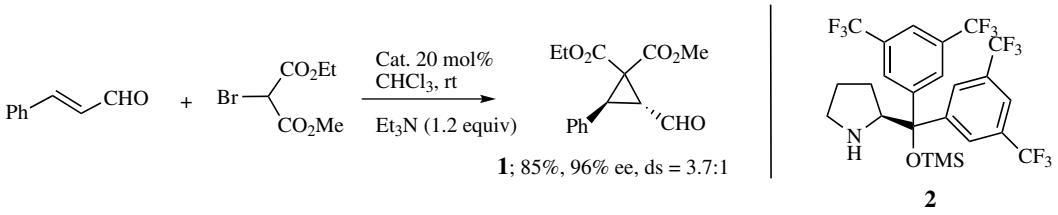
1.2.2 Halo-Substituted Nucleophiles in MIRC Reaction

Active methylene compounds are very reactive nucleophiles and their halo-derivatives are actively used for catalytic asymmetric cyclopropanation through the MIRC process. Rios and coworkers demonstrated catalytic asymmetric cyclopropanation between 2-bromo malonate and unsaturated aldehydes in the presence of proline-derived organocatalyst **2** (Scheme 1.1) [4]. The reaction smoothly progressed in chloroform at room temperature (rt) and highly enantioselective cyclopropanation was achieved.

Similarly, catalyst **3** works well for cyclopropanation, and a chiral cyclopropane was obtained in good enantiomeric excesses (Scheme 1.2) [5].

A proline-derived catalyst effectively works for the asymmetric synthesis of cyclopropanes from α-chloroketones. Ye and coworkers reported that α-chloroacetophenone derivatives underwent asymmetric MIRC cyclopropanation by treatment with substituted cinnamaldehyde in the presence of chiral pyrrolidine **3** and that optically active cyclopropanes **5** were obtained in good yields (Scheme 1.3) [6].

Nitroalkenes are regarded as good electrophiles toward conjugate addition. Chiral organocatalysts effectively promoted an asymmetric MIRC reaction. Connon and coworkers reported that the enantioselective asymmetric cyclopropanation of nitrostyrenes was achieved in the presence of quinine-derived thiourea **6**. The enantiomeric excesses reached up to 47% ee (Scheme 1.4) [7].



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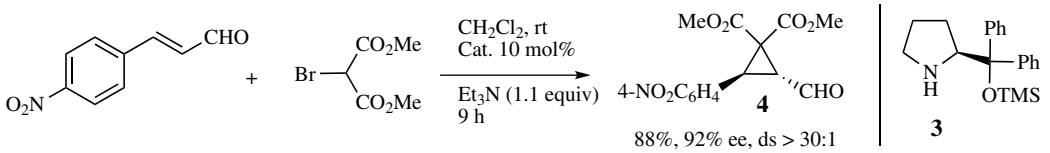

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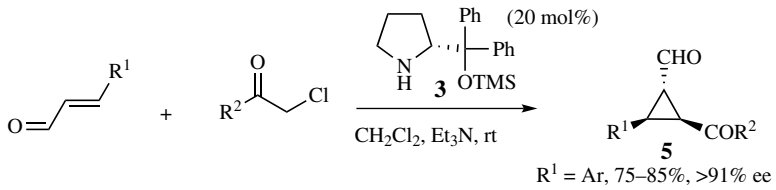

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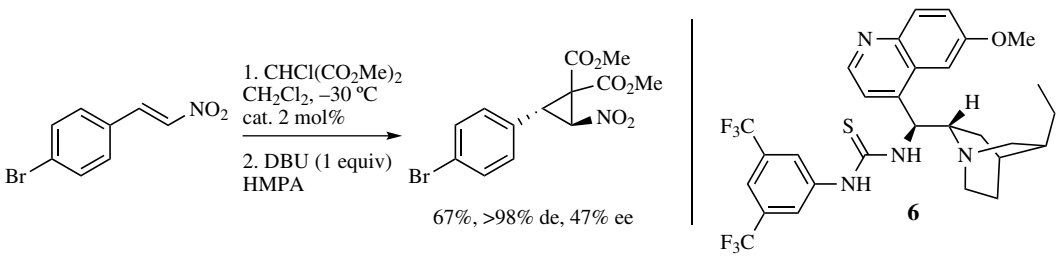

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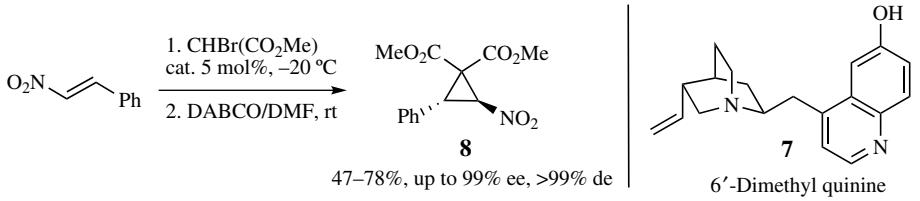
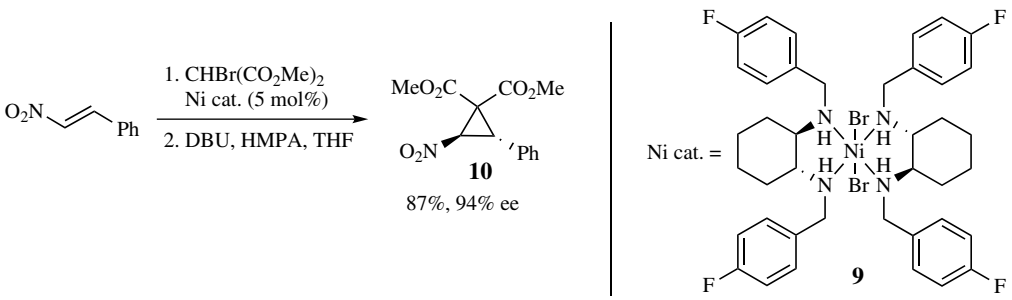


SCHEME 1.5

Yan and coworkers reported that quinine derivative **7** serves as an effective catalyst for asymmetric MIRC cyclopropanation. They obtained nitrocyclopropanes **8** derived from substituted nitrostyrenes as an almost single enantiomer (Scheme 1.5) [8].

Recently, Kim and coworkers revealed that chiral Ni(II) complex **9** catalyzed an MIRC reaction with bromomalonate and nitrostyrene. Nitrocyclopropane **10** was obtained in 87% yield. The enantiomeric excess reached 94% ee (Scheme 1.6) [9].

α-Bromonitromethane serves as a good nucleophile for MIRC cyclopropanation, and asymmetric modification has been examined using various chiral catalysts. Ley and coworkers examined chiral tetrazole catalyst **10** for the cyclopropanation with bromonitromethane. Cyclopropanation of cyclohexenone successfully progressed to give bicyclic



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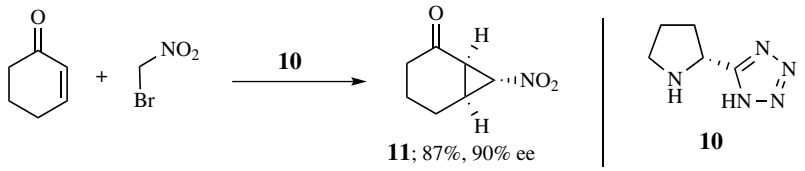

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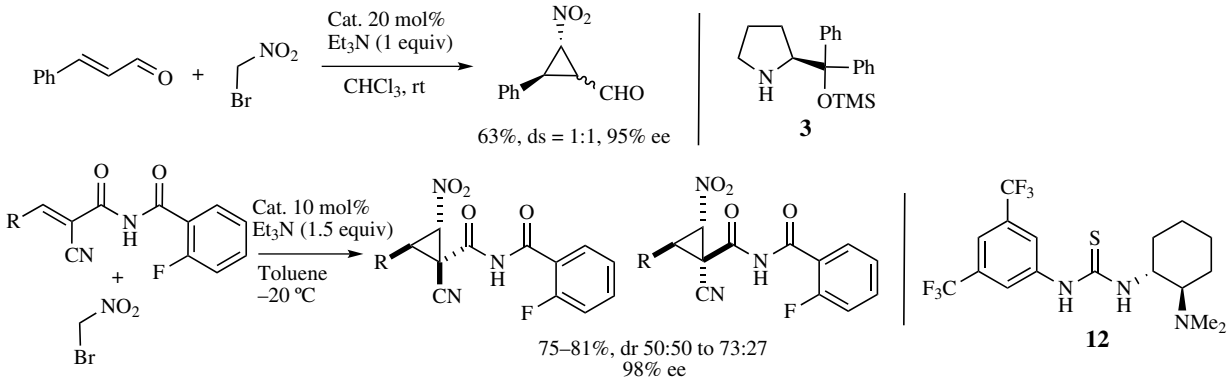

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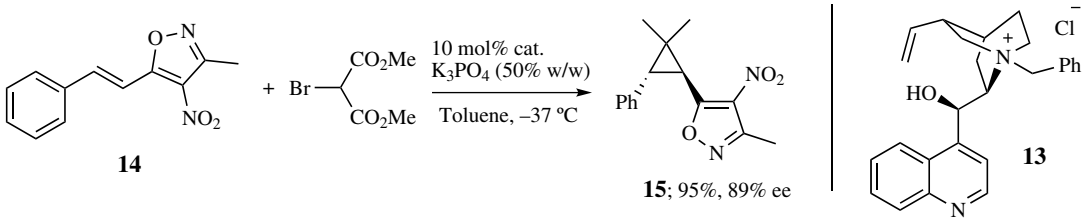


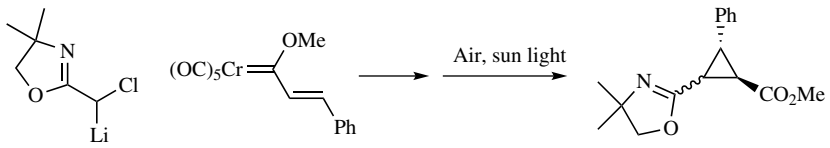
SCHEME 1.9

cyclopropane **11** in high enantiomeric excess (Scheme 1.7) [10].

Chiral proline **3** and thiourea **12** also afforded chiral cyclopropanes in high enantiomeric excess [11, 12]. For example, Takemoto and coworkers reported that efficient MIRC cyclopropanation occurred with α-cyano-α,β-unsaturated amides in the presence of 10 mol% of chiral catalyst **12** (Scheme 1.8).

The MIRC reaction also occurs with α,β-unsaturated isoxazole derivatives. For example, Adamo and coworkers prepared optically active cyclopropanes **13** from α,β-unsaturated isoxazoles **14** in the presence of chiral phase-transfer catalysts (PTCs) **15** (Scheme 1.9) [13].

Organometallic nucleophiles are also useful for MIRC cyclopropanation. The treatment of chloroalkyl oxazoline with LDA generated an oxazoline anion, which underwent cyclopropanation with alkenes through conjugate addition followed by intramolecular substitution [14]. The unsaturated Fischer carbene complex was also useful (Scheme 1.10) [15]. MIRC reactions to heterocyclic compounds have also been reported [16].



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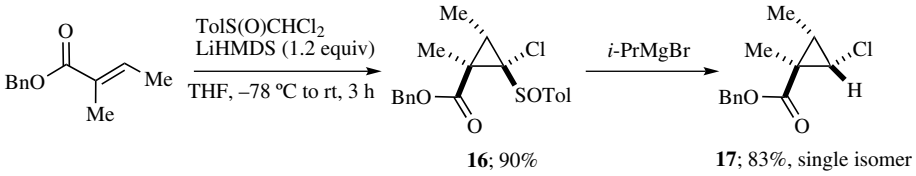

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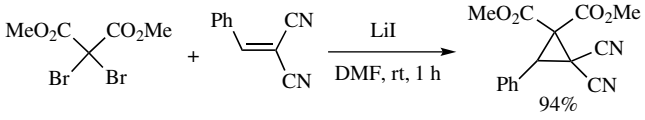


SCHEME 1.12

α-Lithio chlorosulfoxides underwent stereoselective cyclopropanation with α,β-unsaturated esters to give cyclopropane **16** that was substituted by the sulfoxide unit, which was readily converted to hydrogen to give **17** by treatment with isopropyl magnesium bromide (Scheme 1.11) [17]. Cyclopropane was a useful synthetic block because it served as an allene precursor [18]. Grignard reagents as well as organocopper zinc reagents also work well for MIRC reactions to give cyclopropanes [19]. It is interesting to note that no metallic activation is necessary for cyclopropanation with dibromomalonate (Scheme 1.12) [20].

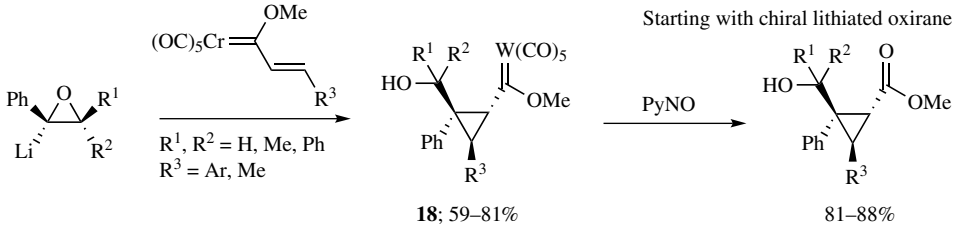
Epoxides are another good candidate for MIRC cyclopropanation. For example, α-lithioepoxide attacked electron-deficient alkenes activated by the Fischer carbene complex to give an enolate intermediate, which then served as a nucleophile to open the epoxide ring. Cyclopropanes **18** were isolated in good yields (Scheme 1.13) [21]. Starting with chiral oxiranes, the MIRC reaction provided optically active cyclopropanes.

Cyclopropanes are obtained by the electrolysis of a mixture of activated alkenes and a malonate nucleophile (Scheme 1.14) [22]. Electrolysis is also useful for one-pot cyclopropanation from an aromatic aldehyde, malononitrile, and a malonate ester [23].

Conjugate addition followed by oxidation gave cyclopropanes. Although this requires a stepwise procedure, it sometimes makes it possible an efficient synthesis. Bromine [24], iodine [25], and phenyliodonium acetate [26] are used as the oxidants (Scheme 1.15).

1.2.3 Ylides for Cyclopropanation

Sulfur ylides are usually used for cyclopropanation [27]. Recently, chiral cyclopropane synthesis has been actively investigated. Chiral S-ylide **19** serves as a chiral donor for



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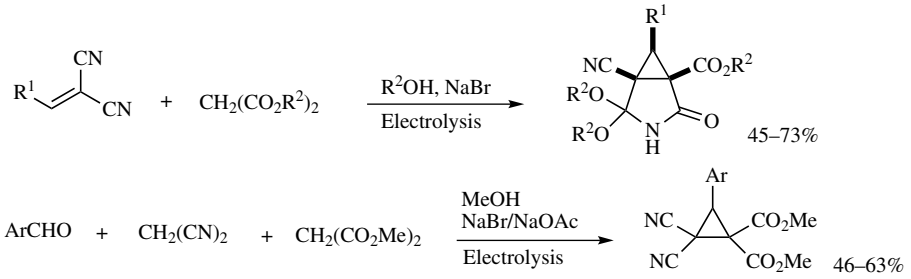

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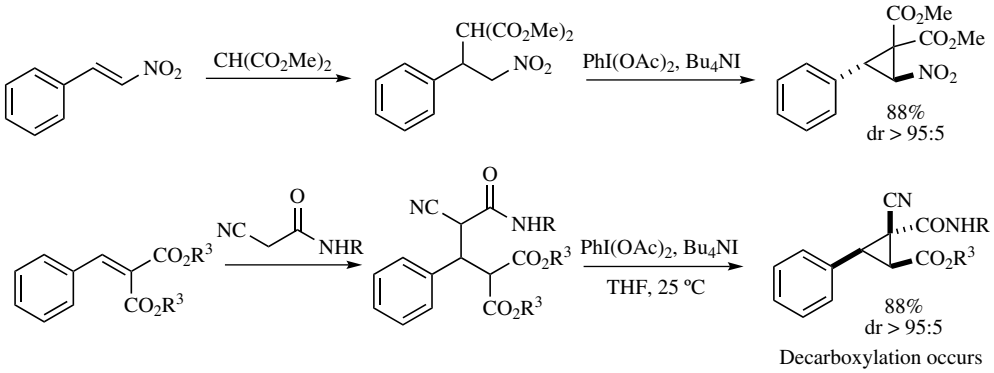

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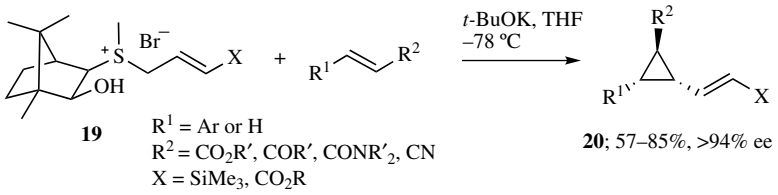

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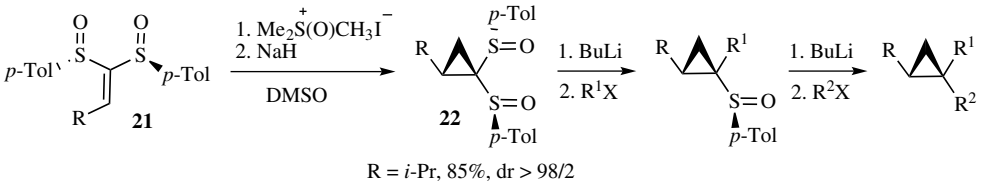
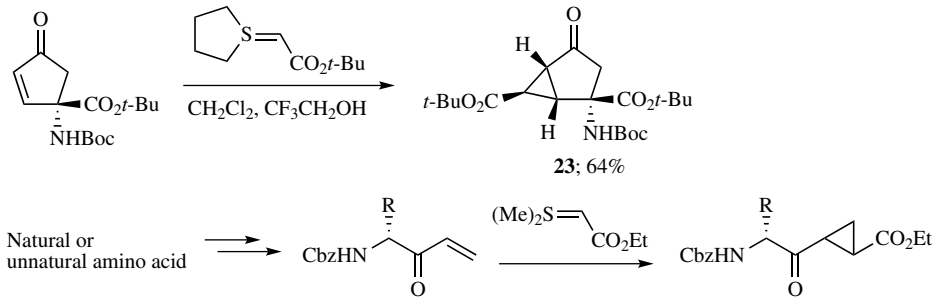


SCHEME 1.17

MIRC cyclopropanation to give optically active cyclopropanes **20** in high enantiomeric excesses (Scheme 1.16) [28].

Chiral Michael acceptors underwent asymmetric cyclopropanation. Chiral unsaturated sulfoxide **21** controlled the nucleophilic addition of S-ylides to give chiral cyclopropanes **22** (Scheme 1.17) [29]. The sulfoxide group in **22** was converted into alkyl groups by treatment with alkyllithium. Phospholyl sulfoxides also gave chiral cyclopropanes [30].

Chiral cyclopentenone effectively gave bicyclic cyclopropanes in high enantiomeric excesses. Product **23** was a useful precursor for the improved synthesis of C4α and C4β-methyl analogues of 2-aminobicyclo[3.1.0]hexanes (Scheme 1.18) [31]. Amino acid-derived vinylketones



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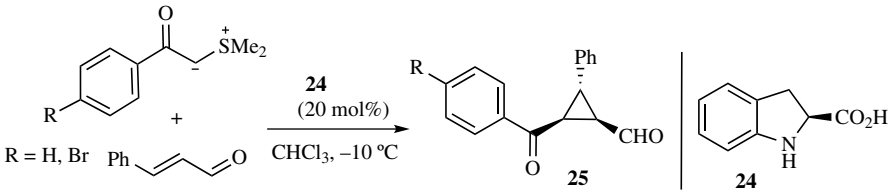

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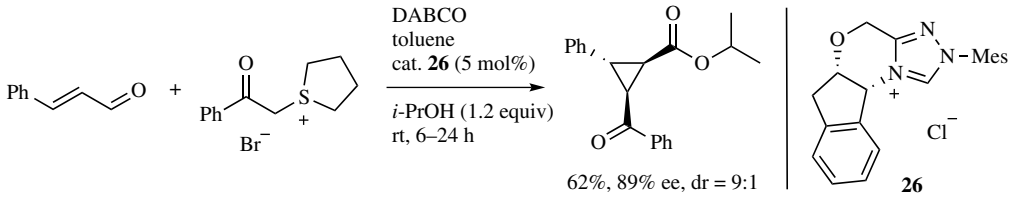


SCHEME 1.20

afforded chiral cyclopropanes in good yields [32]. This procedure provided a useful synthesis of a cyclopropyl peptidomimetic from amino acids in three steps.

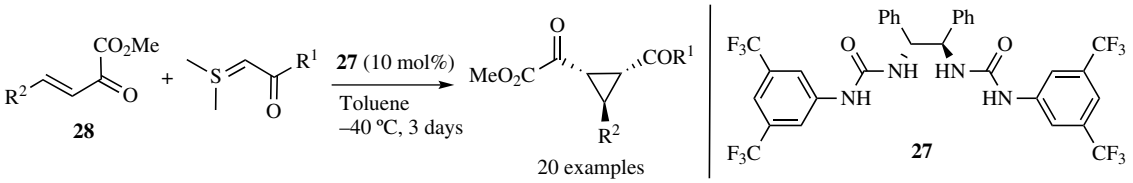
Organocatalysts successfully promoted catalytic asymmetric cyclopropanation. A pioneering study by Kunz and MacMillan showed that chiral benzo-fused proline **24** gave chiral cyclopropane **25** from an α,β-unsaturated aldehyde and sulfonium ylides (Scheme 1.19) [33]. Kinetic studies to rationalize the asymmetric induction were also performed [34].

Studer and coworkers reported that chiral aminoalcohol derivative **26** works well for asymmetric cyclopropanation with sulfonium ylides (Scheme 1.20) [35].

Diurea derived from chiral C2-symmetric diamine **27** catalyzed asymmetric cyclopropanation of α,β-unsaturated keto esters **28** with sulfonium ylides (Scheme 1.21) [36].

Chiral biaryl-derived lanthanum complex **29** promoted the chiral formation of cyclopropanes **30** (Scheme 1.22) [37]. A catalyst loading of 10 mol% achieved up to 97% ee of cyclopropane.

Sulfonium ylides were generated by treatment with a cyclic or an acyclic sulfide in the presence of a base. For example, Tang and coworkers generated a sulfonium ylide from corresponding benzylic halide **31** and tetrahydrothiophene **32**, and effectively formed bicyclic cyclopropanes



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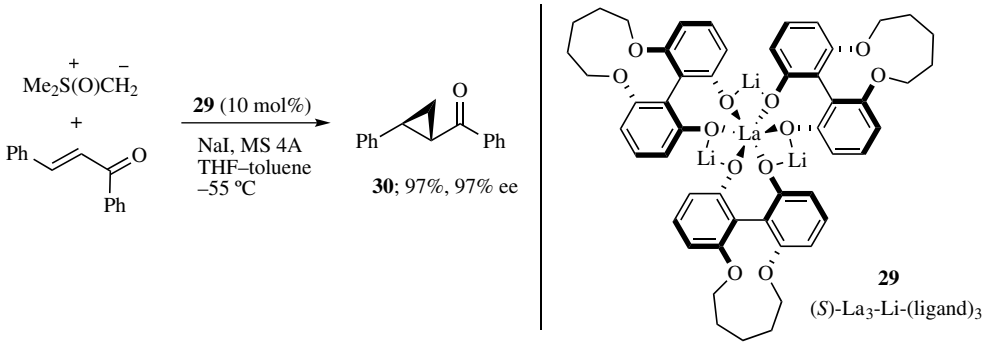

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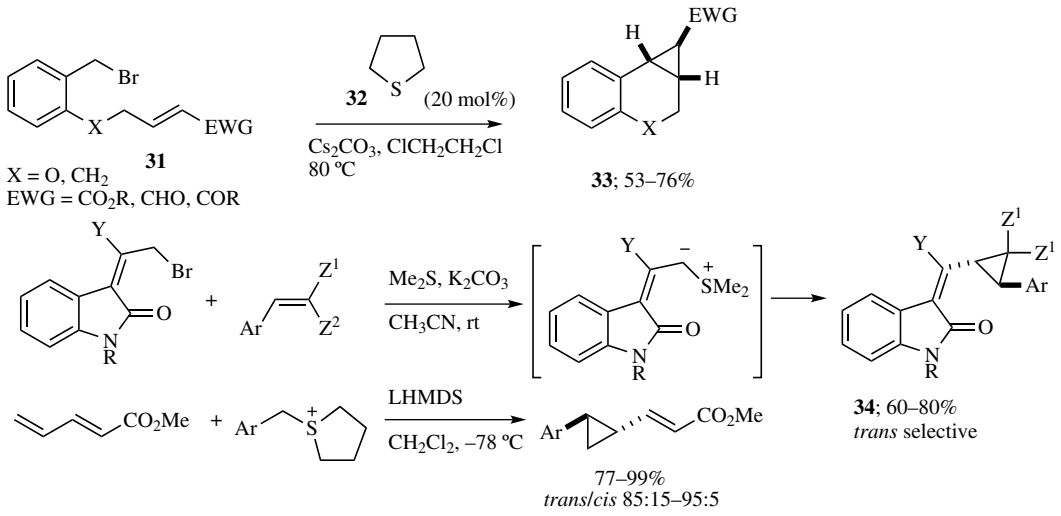
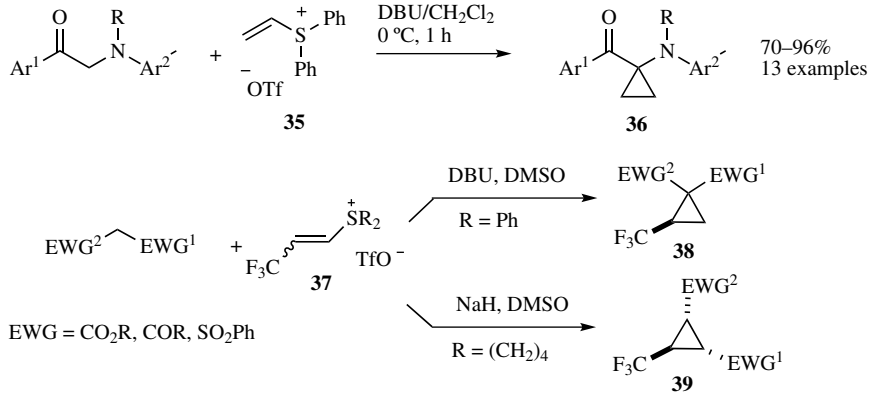


SCHEME 1.23

33 [38]. Dimethyl sulfide successfully generated sulfonium ylides in a similar manner and cyclopropanes **34** were obtained (Scheme 1.23) [39]. Dienyl carboxylate underwent cyclopropanation in a 1,6-addition manner by treatment with benzylic sulfur ylides, and *trans*-selective cyclopropanation proceeded at the terminal carbon–carbon double bond position to give vinylcyclopropanes [40].

Vinylsulfonium salts serve as an electron-deficient alkene and conjugate addition to the alkene generates sulfonium ylides. Thus, conjugate addition to vinylsulfonium compounds provides another preparation of cyclopropanes. For example, Lin and coworkers prepared 1,1-cyclopropane aminoketones **36** in good yields from diphenyl vinylsulfonium triflate **35** by the treatment of aminoketones in the presence of DBU (Scheme 1.24) [41]. Diphenyl vinylsulfonium salt **37** was also useful for the preparation of trifluoromethyl-substituted cyclopropanes **38** and **39** [42]. The multigram-scale preparation of CF_3-substituted cyclopropane has also been reported [43].

A similar cyclopropanation reaction was reported by the treatment of β-bromosulfonium salt **40** with active methylene compounds in the presence of a base (Scheme 1.25) [44].



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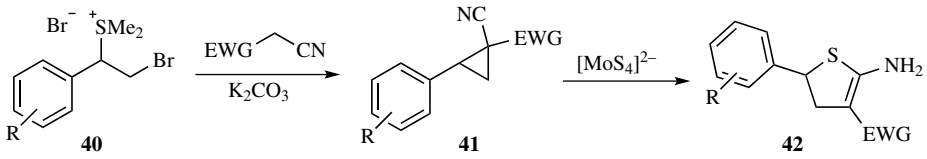

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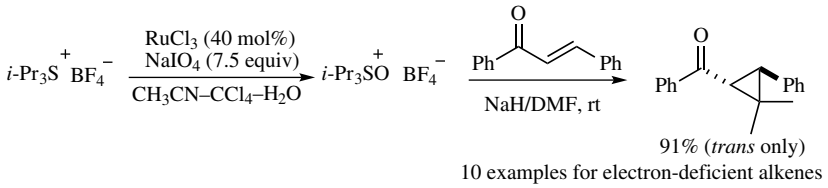

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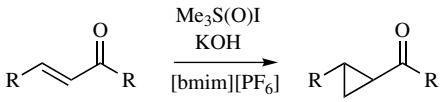


SCHEME 1.27

The obtained cyclopropanes **41** were effectively converted to dihydrothiophenes **42** by treatment with tetrathiomolybdate $[MoS_4]^{2-}$.

Sulfur ylides are usually used in methylene-transfer cyclopropanation, and an alkylidene-transfer reaction is rather difficult because the generation of an alkylidene ylide is typically difficult. Taylor and coworkers developed a new alkylidene-transfer cyclopropanation reaction using a triisopropylsulfoxonium ylide, which was readily generated from triisopropylsulfoxonium tetrafluoroborate (Scheme 1.26) [45]. They successfully prepared *gem*-dimethylcyclopropanes from electron-deficient alkenes. The obtained cyclopropanes usually contained *trans*-configuration.

Recently, ionic liquids have been reported as another solvent for the cyclopropanation using sulfonium ylides (Scheme 1.27) [46].

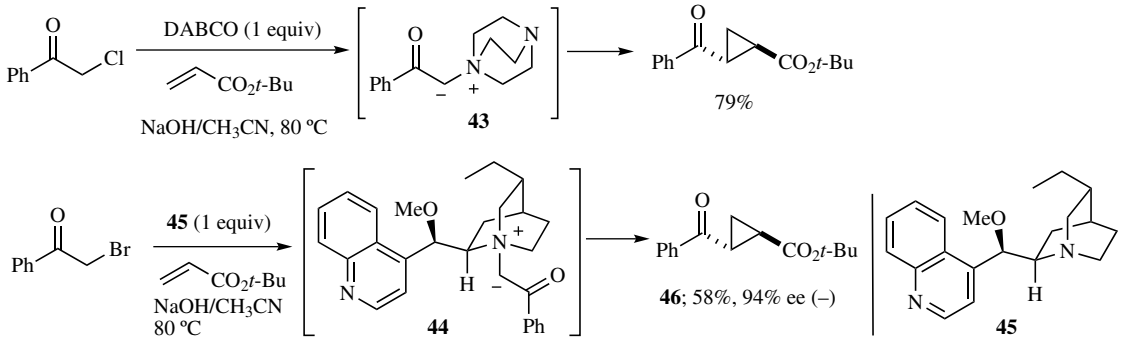
Other ylides have also been used for cyclopropanation. Ley and coworkers reported effective cyclopropanation using chloroketones and an acrylate ester in the presence of DABCO (Scheme 1.28) [47]. In the reaction, N-ylide **43** or **44** was assumed to be generated as an active reaction intermediate. A chiral amine derived from quinidine **45** catalyzed asymmetric cyclopropanation to give **46** in 94% ee.

They initially developed the method that required stoichiometric amounts of chiral amine. They then published an improved method in which reduced amounts of chiral amine achieved asymmetric cyclopropanation in an intermolecular [48] or intramolecular manner [49] (Scheme 1.29). Note that absolute stereochemistry in the cyclopropanes obtained by this method depended on the chiral catalysts derived from either quinine or quinidine [50]. For example, Me-MQ **47** catalyzed the reaction to give (+)-**49** in 84% with 97% ee, while Me-MQD **48** promoted the reaction from the same starting material to give (−)-**49** in 88% with 97% ee.

Pyridinium ylides containing a chiral auxiliary served as a good precursor for cyclopropane synthesis (Scheme 1.30). Ohkata and coworkers reported that α-pyridinium 8-phenylmenthylamide **50** achieved asymmetric cyclopropanation to give cyclopropane in up to a 98:2 diastereomeric ratio [51]. Yamada's group devised chiral pyridinium salts **51**, which underwent asymmetric cyclopropanation [52]. Kanomata's group used planner chiral pyridinium ylides **52** for successful asymmetric cyclopropanation [53].

Selenium and tellurium ylides other than sulfonium have also been reported to be useful for the cyclopropanation. Selenium ylides were studied by Kataoka and coworkers, and cyclopropane formation was observed. Diphenyl vinyl or allenyl selenium triflate serves as an electron-deficient alkene, and selenium ylides can be generated by the conjugate addition. The resulting ylides underwent cyclopropane formation by an MIRC reaction (Scheme 1.31) [54].

Tellurium ylides were used by Tang and coworkers, and its allylic ylides reacted with α,β-unsaturated esters or imines to



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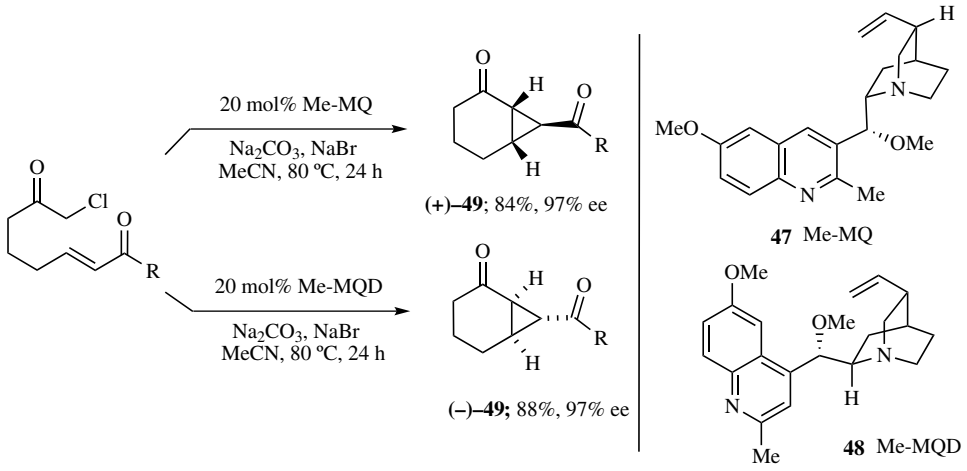

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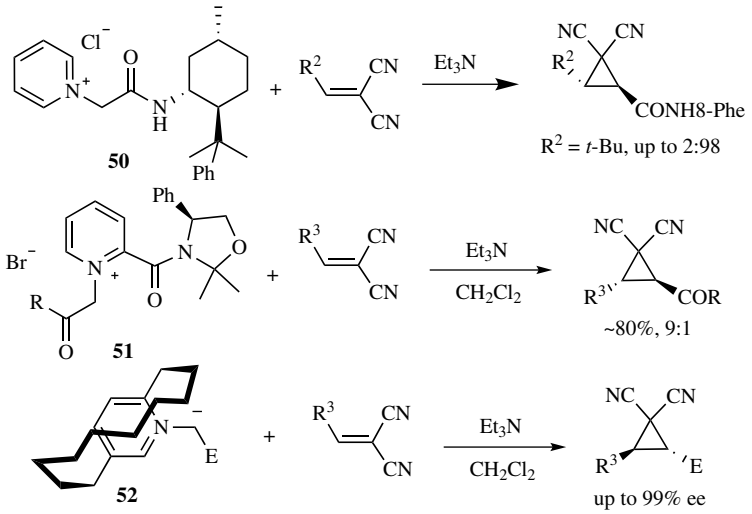
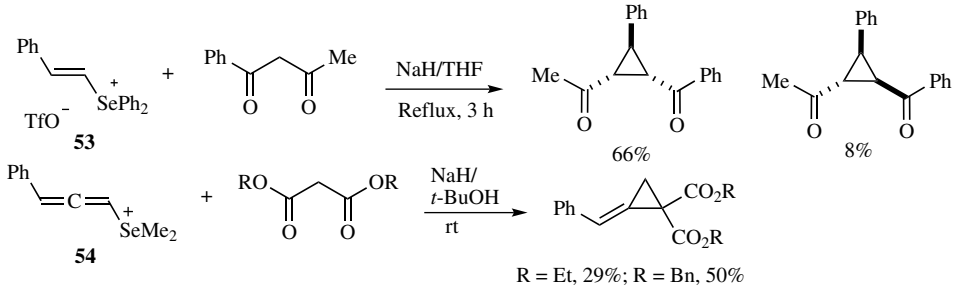


SCHEME 1.30

give allylcyclopropane carboxylates **56** or aldehydes **57** in good yields. Cyclopropanation occurred in a highly stereoselective manner (Scheme 1.32) [55]. Optically active tellurium ion **55** generated tellurium ylides by treatment with a base, giving chiral cyclopropane in high optical purity. Cyclopropyl aziridines **58** were also obtained stereoselectively.

Arsenic analogues gave cyclopropanes in a similar manner (Scheme 1.33). The basic treatment of arsenium salts **59**



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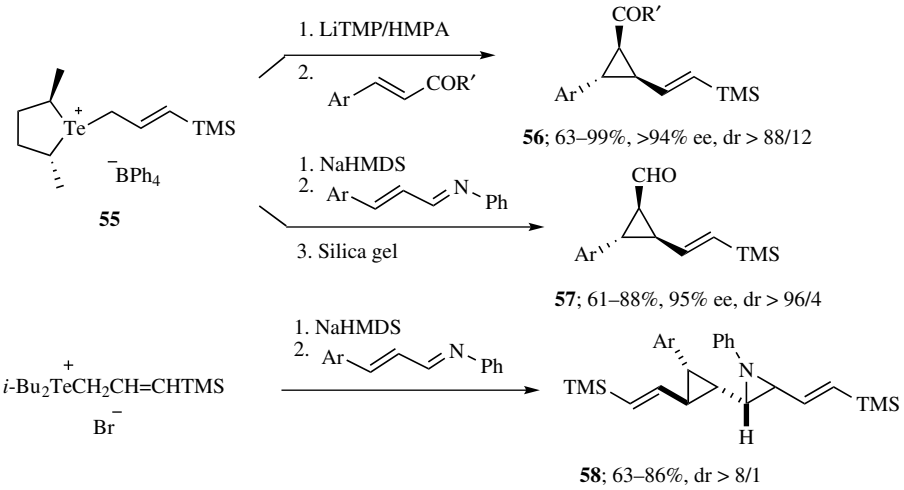

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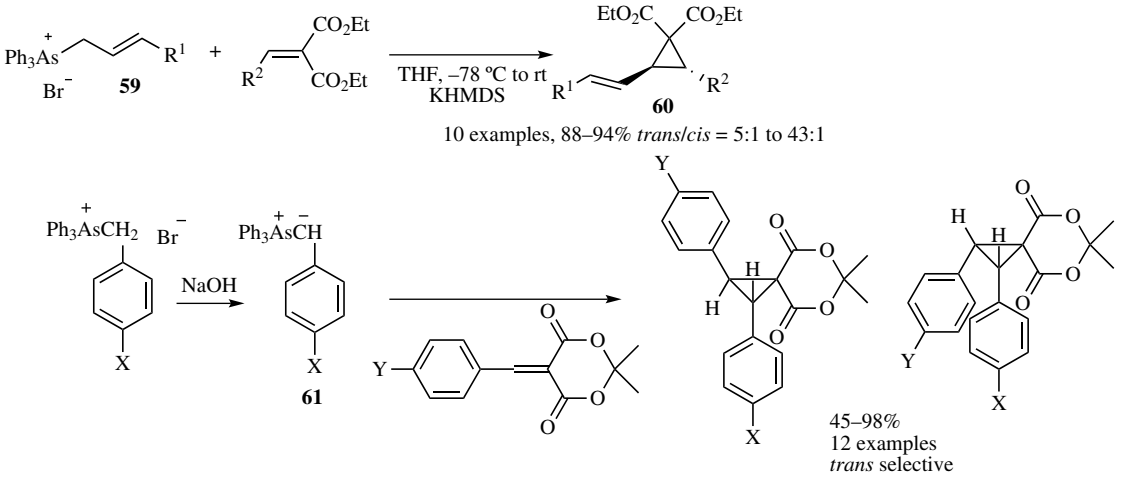

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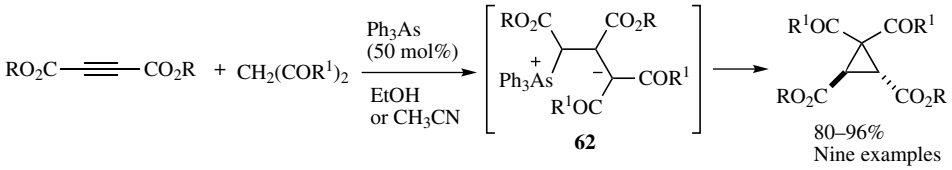
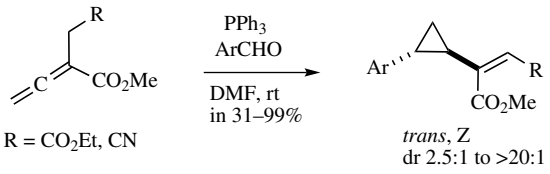


SCHEME 1.34

provided arsenium ylides, which underwent an MIRC reaction with alkylidene malonates to give vinylcyclopropane **60** in good yields [56]. The stereoselectivity of the reaction was usually high. Stereoselective cyclopropanation was achieved using benzylarsenium ylides **61** [57]. Arsenium ion intermediate **62** was used for cyclopropane formation from acetylene carboxylates and malonate (Scheme 1.34) [58]. Phosphonium ions were used in a similar manner in the reaction of allenic esters and aromatic aldehydes (Scheme 1.35) [59].



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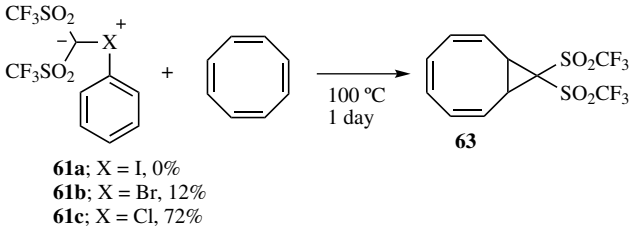


SCHEME 1.36

Halonium ylides afforded cyclopropanes. Ochiai et al. synthesized halonium ylides and examined cyclopropanation with cyclooctatetraene [60]. Chloronium ylides **61c** smoothly underwent progress of cyclopropanation and bicyclic cyclopropane **63** was obtained in 72% yield (Scheme 1.36).

1.3 SIMMONS–SMITH CYCLOPROPANATION AND RELATED REACTIONS

1.3.1 Introduction

The Simmons–Smith reaction was first reported in the late 1950s [61]. Since then, it has been one of the representative reactions for the formation of cyclopropanes. The active species $IZnCH_2I$ is generated from a Zn/Cu couple and CH_2I_2. Several years later, Furukawa et al. reported an alternative generation of the zinc carbenoid species from Et_2Zn and CH_2I_2, which offered a more convenient procedure for the cyclopropanation [62]. An asymmetric modification using a chiral auxiliary was developed in the1980s. The use of a C2 chiral vinyl acetal successfully promoted the asymmetric Simmons–Smith reaction to give chiral cyclopropanes [63], and the reaction has been applied to natural product synthesis [64]. Ligand-controlled asymmetric induction has been reported since 1990 [65]. The reactivity of the reagent depends on zinc complexes with appropriate ligands. Shi and coworkers reported that reactivity dramatically changed when CF_3CO_2H was added to the reaction [66]. This modification was observed while generating $CF_3CO_2ZnCH_2I$. In this section, we reviewed several new developments in this field.

1.3.2 The Simmons–Smith Reaction with Zinc Reagents

Although the Simmons–Smith reagent is usually generated by treatment with CH_2I_2 and Zn/Cu or Et_2Zn, its reactivity is modified when an additive is used. The addition of CF_3CO_2H was regarded to generate $CF_3CO_2ZnCH_2I$. For example, the addition of CF_3CO_2H modifies the reactivity [67]. Also, the acceleration of the reaction by adding CF_3CO_2H and Et_2AlCl to the Simmons–Smith reagent was observed (Scheme 1.37) [68]. Also, asymmetric cyclopropanation of nonallylic alcohol was attempted, and a moderate level of asymmetric induction was achieved.

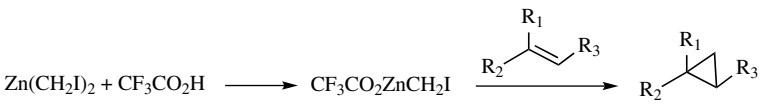
$CF_3CO_2ZnCH_2I$ showed different reactivity/selectivity to cyclopropanation. Davies and coworkers examined the comparative chemistry (Scheme 1.38) [69]. For example, cyclic allylic amines **64** underwent stereoselective cyclopropanation by exposure to $CF_3CO_2ZnCH_2I$. Stereoselectivity depended on the ring size. Thus, **65** was preferentially formed when $n = 0$ or 1, while **66** was selectively obtained when $n = 2$ or 3. In addition, the protective group on the amino group affected the selectivity. The use of the original ICH_2ZnI reagent achieved *cis*-selective cyclopropanation to give **67** by chelation control to the carbamoyl group, while $CF_3CO_2ZnCH_2I$ promoted *trans*-selective cyclopropanation to give **68**. This is explained by the external delivery of the cyclopropanation reagent. Allylic strain is important to control the stereochemistry in the cyclopropanation to form acyclic allylic amines.

The addition of dibutylphosphoric acid gave $(BuO)_2P(O)OZnCH_2I$ **69**, which is a more reactive reagent and can be stored. The zinc reagent **69** maintains reactivity for one week when stored at $-22\,^{\circ}C$ (Scheme 1.39) [70].

Methylene bis(iodozinc) [$CH_2(ZnI)_2$] is another cyclopropanation reagent. Fournier and Charette improved its generation by adding ZnI_2 (Scheme 1.40) [71].

Walsh and coworkers reported that the reagent achieved direct cyclopropanation from α-chloroaldehydes **70** (Scheme 1.41) [72]. High *trans*-selectivity was observed.

Matsubara and coworkers reported that the bis(iodozinc) reagent **71** reacts with α,β-unsaturated ketones to give enol cyclopropane **72**, which underwent further carbon–carbon bond formation with an imine to give multifunctionalized aminoesters **73** (Scheme 1.42) [73]. The reaction with epoxy ketone **74** and iminoketones **76** gave hydroxycyclopropanes **75** and aminocyclopropanes **77**, respectively [74].



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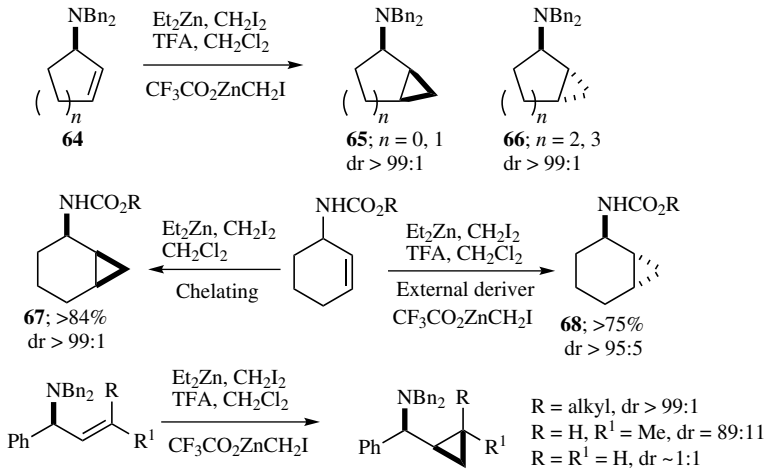

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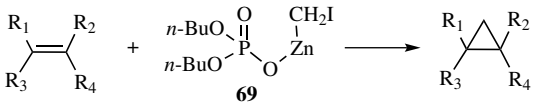

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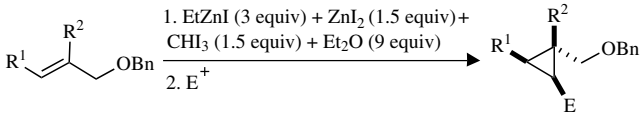

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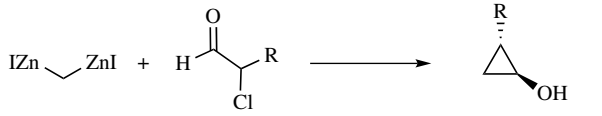
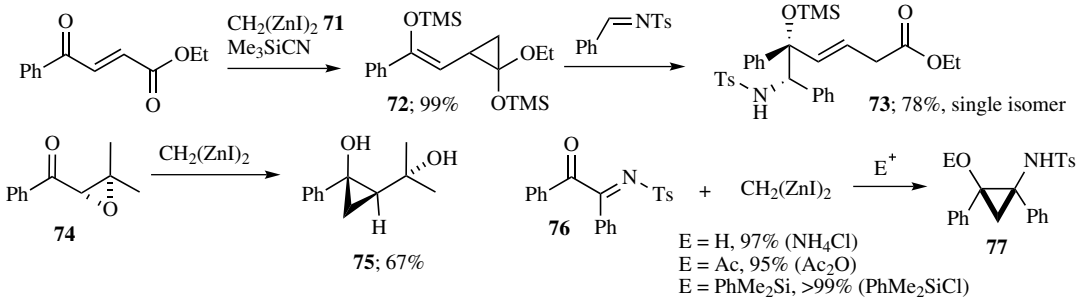


SCHEME 1.41

Chelation control in the cyclopropanation was observed for this reagent. Charette and coworkers reported the stereoselective cyclopropanation of the reagent using vinylsilanol acceptors **78** (Scheme 1.43) [75]. The resulting silyl group attached to cyclopropane in **79** was converted to an aryl group by a palladium-catalyzed coupling reaction to give **80**.

One of the drawbacks of the Simmons–Smith reaction is that it is usually difficult to generate alkylidene-transfer reagents. Bull and Charette reported intramolecular alkylidene transfer by the zinc reagent generated from the terminal diiodomethyne group and the efficient formation of bicyclic cyclopropanes (Scheme 1.44) [76]. The synthesis of five- and six-membered ring fused by cyclopropane **81** effectively progressed, but the formation of a seven-membered ring was less efficient.

Motherwell et al. reported the formation of a nitrogen-substituted methylene-transfer reagent from amide acetal **82** using zinc and cupric chloride or zinc chloride (Scheme 1.45) [77]. Aminocyclopropanes **83** were isolated in good yields. Asymmetric induction using chiral oxazolidinone **84** was examined [78]. Intramolecular cyclopropanation progressed, and β-lactam-fused multicarbocyclic cyclopropanes **85** were obtained [79].



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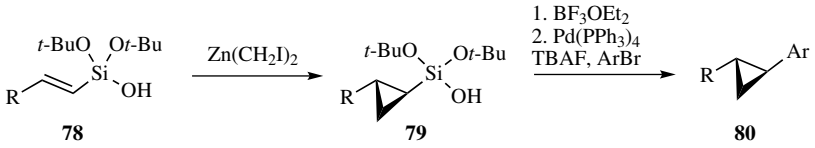

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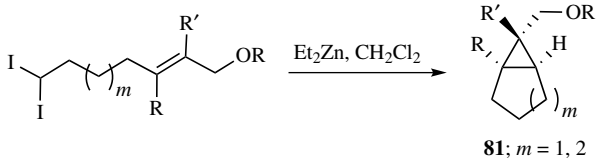

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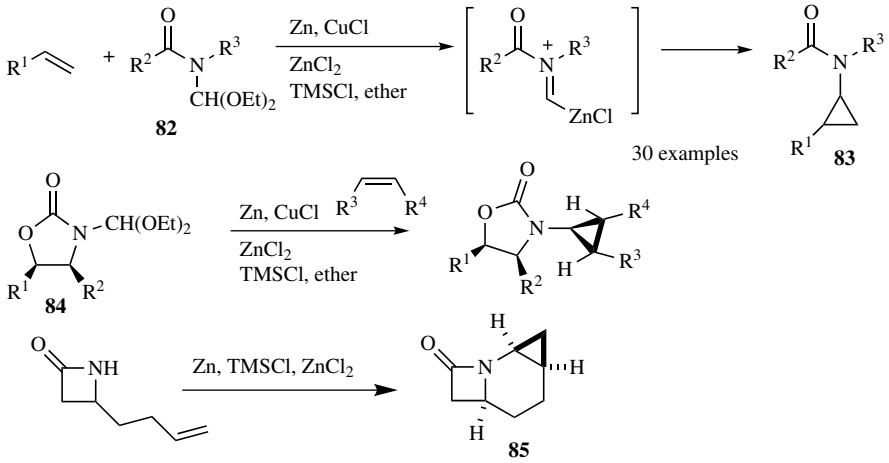

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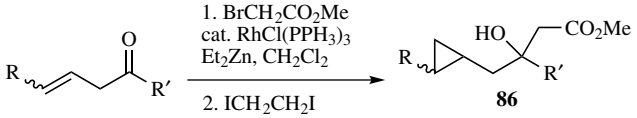
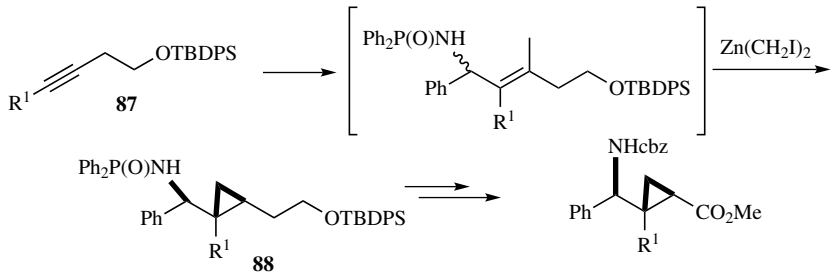


SCHEME 1.46

The Reformatsky reaction in combination with another reaction provides a one-pot cascade cyclopropanation process. Cossy and coworkers reported the efficient synthesis of **86** using the cascade strategy (Scheme 1.46) [80].

Homopropargyl ether **87** underwent a multicomponent coupling reaction to give cyclopropylalkylamides **88** in good yields by successive treatment with Cp_2ZrHCl, Me_2Zn, imine, and CH_2I_2 (Scheme 1.47) [81].



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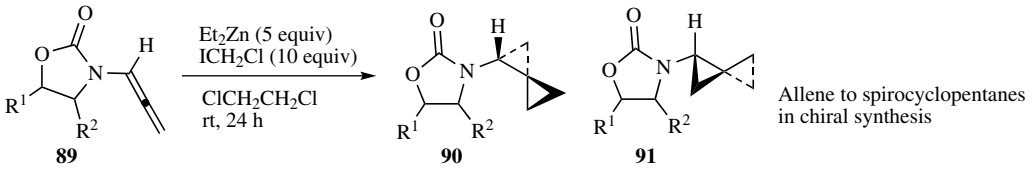
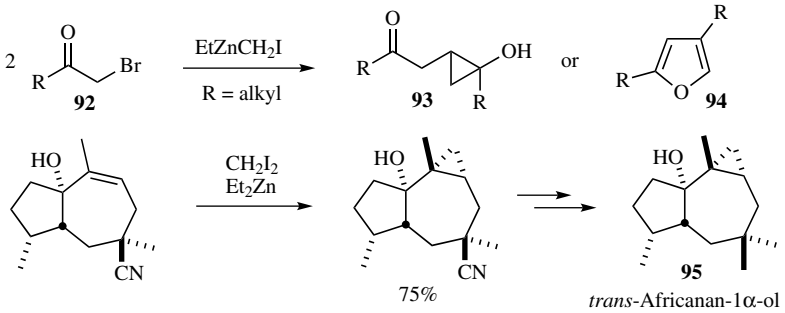


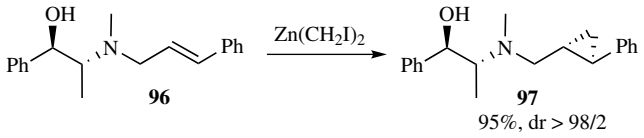
89 90 91

SCHEME 1.48



92 93 94 95

SCHEME 1.49



96 97

95%, dr > 98/2

SCHEME 1.50

The use of the Simmons–Smith reaction of allenes provides an efficient synthesis of novel spiro cyclopropanes. The use of chiral oxazolidinone-attached allenes **89** afforded chiral spiro[2.2]pentanes **90** and **91** (Scheme 1.48) [82].

Cyclopropanation from 2 equiv of bromoketone **92** gave cyclopropane **93** or furan **94** in good yield (Scheme 1.49) [83]. Taber et al. recently applied cyclopropanation for the synthesis of *trans*-Africanan-1α-ol **95** [84].

The stereoselectivity of cyclopropanation is highly affected by the stereogenic centers close to the alkene unit. Aggarwal et al. reported that *N*-chiral allylic amine **96** underwent stereoselective cyclopropanation to give **97** in 95% yield (Scheme 1.50) [85]. The obtained product **97** was almost a single isomer.

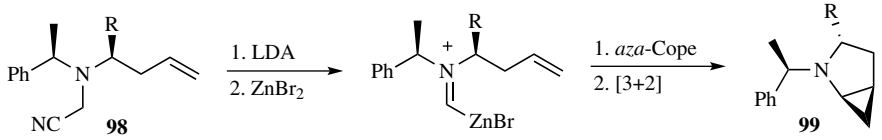
N-Cyanomethylhomoallylic amine **98** underwent direct cyclization and cyclopropanation in a stereoselective manner and azabicyclo[3.1.0]hexanes **99** were prepared in good yields (Scheme 1.51) [86].

Charette and coworkers investigated the stereoselectivity of *gem*-zinc carbenoids in the reaction with allylic alcohols **100** and **101** (Scheme 1.52). Configuration at the allylic stereogenic center and alkene geometry affected the stereoselectivity of cyclopropanation [87].

Chiral oxazolidinone also controlled the stereochemistry of cyclopropanation of enamides **102** (Scheme 1.53) [88]. Cyclopropane **103** was obtained in good yields with high diastereomeric excesses.

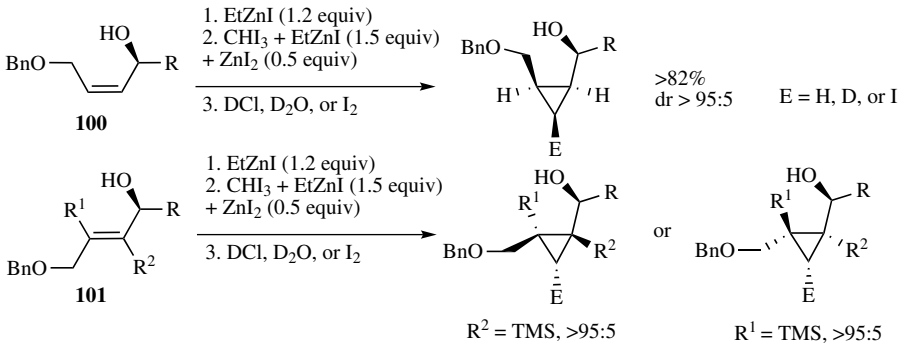
A chiral aldol-retro-aldol-type introduction of a chiral auxiliary was applied to the cyclopropanation (Scheme 1.54) [89]. Chiral aldol **104** was first formed and then underwent stereoselective cyclopropanation to give **105**. The basic treatment of **105** afforded chiral cyclopropane **106** in good yields with high enantiomeric excess. The three-step synthesis achieved enantiomerically pure cyclopropane. (1*S*,2*R*)-Cascarillic acid **107** was synthesized by this route. The asymmetric synthesis of aminocyclopropane carboxylic acid **108** has also been reported [90].

Catalytic asymmetric cyclopropanation has been actively investigated. Shi and coworkers developed Val–Pro dipeptide catalysts **109**, which effectively catalyzed cyclopropanation of



98 99

SCHEME 1.51



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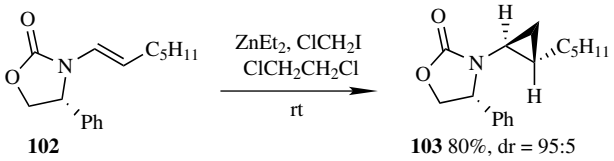
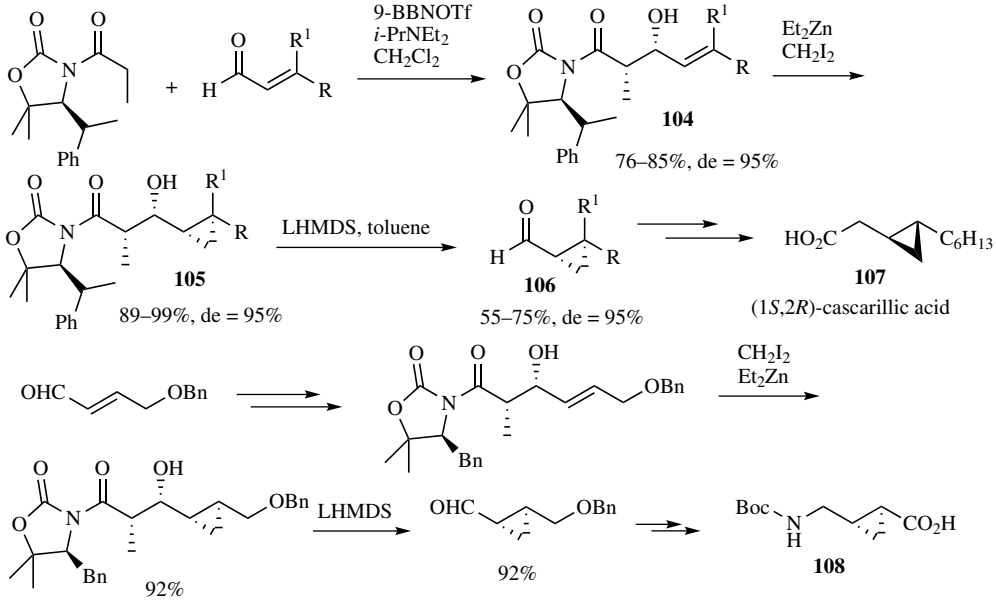


SCHEME 1.53

unfunctionalized alkenes **110**, although more than 1 equiv of a chiral dipeptide was necessary (Scheme 1.55) [91]. The mechanistic study revealed that the dipeptide **111** chelating on the zinc reagent promoted the stereoselective formation of the cyclopropanes **112** [92]. This method was useful for cyclopropanation of enol ethers [93] and cyclic alkenes [94].

Chiral dioxaborolane **113** achieved asymmetric cyclopropanation; however, more than 1 equiv of this chiral source was required for efficient asymmetric induction (Scheme 1.56). Goudreau and Charette reported that an aryl-substituted zinc carbenoid underwent effective cycloaddition to allylic alcohol, and *cis*- and *trans*-aryl-substituted chiral cyclopropanes **114** and **115** were formed in highly enantiomeric excesses [95].

The use of catalytic amounts of a chiral source is important to improve the efficiency of asymmetric induction. Charette and coworkers used 10 mol% of chiral phosphoric acid **116**, derived from a binaphthol derivative, and achieved catalytic asymmetric cyclopropanation to form allylic alcohols **117** (Scheme 1.57) [96]. Walsh and coworkers reported that the efficient asymmetric synthesis of cyclopropylmethyl alcohol **118** was achieved through a tandem addition/cyclopropanation process in the presence of 5 mol% of chiral amino alcohol **119** [97]. Catalytic amounts of chiral diamine derivative **120** promoted asymmetric cyclopropanation to give **121** [98]. The catalyst **120** was recovered and recycled three times.



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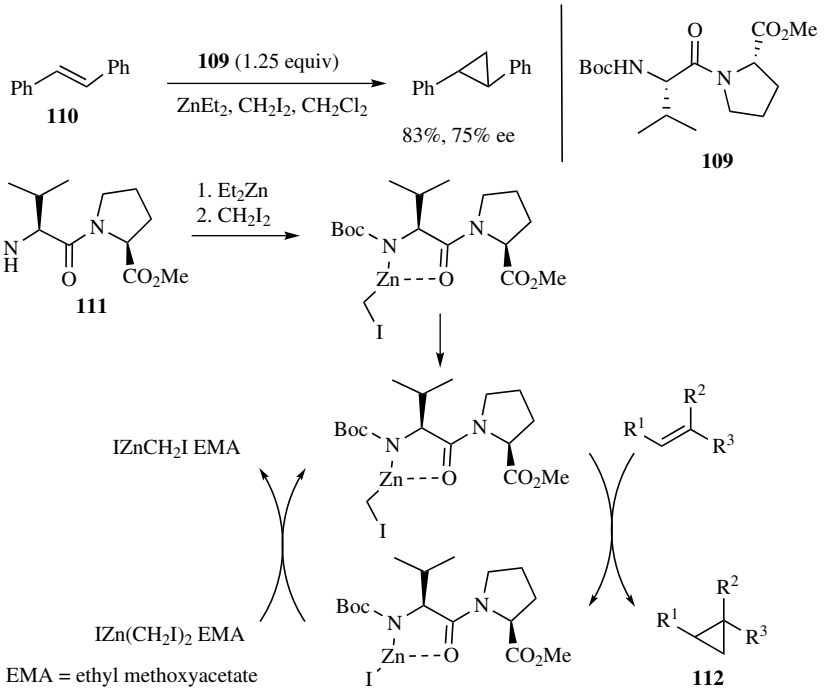


SCHEME 1.55

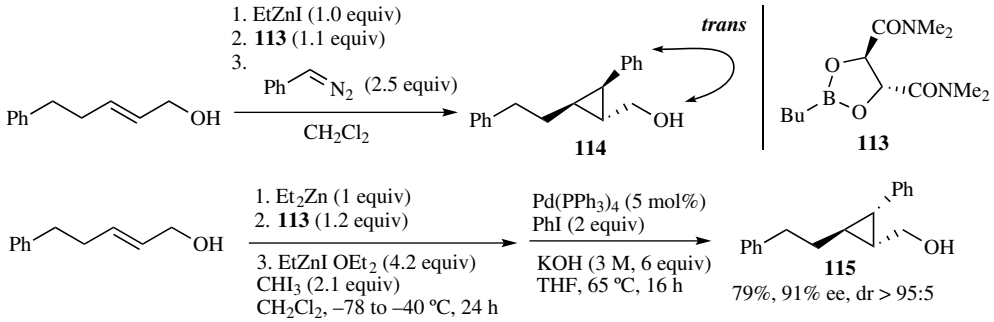
The Simmons–Smith-type cyclopropanation reaction proceeded using other organometallic reagents. Takai et al. developed the cyclopropanation by the reagents generated from Cr(II) and CHI_3 (Scheme 1.58) [99]. They also investigated the mechanism of low-valent chromium reagents.

Stereospecific cyclopropanation of α,β-unsaturated amides **122** was achieved using these reagents generated from Cr(II) and CHI_3 [100]. This is a useful strategy for the preparation of trisubstituted cyclopropanes **123** and **124** in a stereoselective manner (Scheme 1.59) [101].

Samarium reagents are also useful for the Simons–Smith-type cyclopropanation reaction. α,β-Unsaturated amides and carboxylic acids underwent cyclopropanation with the equivalent samarium reagent $ISmCH_2I$ **125**, generated from samarium metal and CH_2I_2, to give **126** and **127**, respectively (Scheme 1.60) [102].

A magnesium carbenoid was readily generated from CH_2Br_2 and *t*-BuMgBr, and cyclopropanation of allylic alkoxides occurred to give cyclopropyl carbinol **128** (Scheme 1.61) [103]. Trialkyl aluminum and CH_2I_2 promoted cyclopropanation of alkynes or allenes, which gave spiro cyclopentanes **129** or **130**, respectively in good yields (Scheme 1.62) [104].

Indium metal generated a carbenoid reagent in a similar manner giving cyclopropanes [105]. A combined use of Cp_2ZrCl_2/2EtMgBr/2$AlCl_3$ achieved cyclopropanation by reaction with alkynylphosphonate **131** (Scheme 1.63) [106]. Zirconacyclopentenylphosphonate **132** was regarded as the reaction intermediate.



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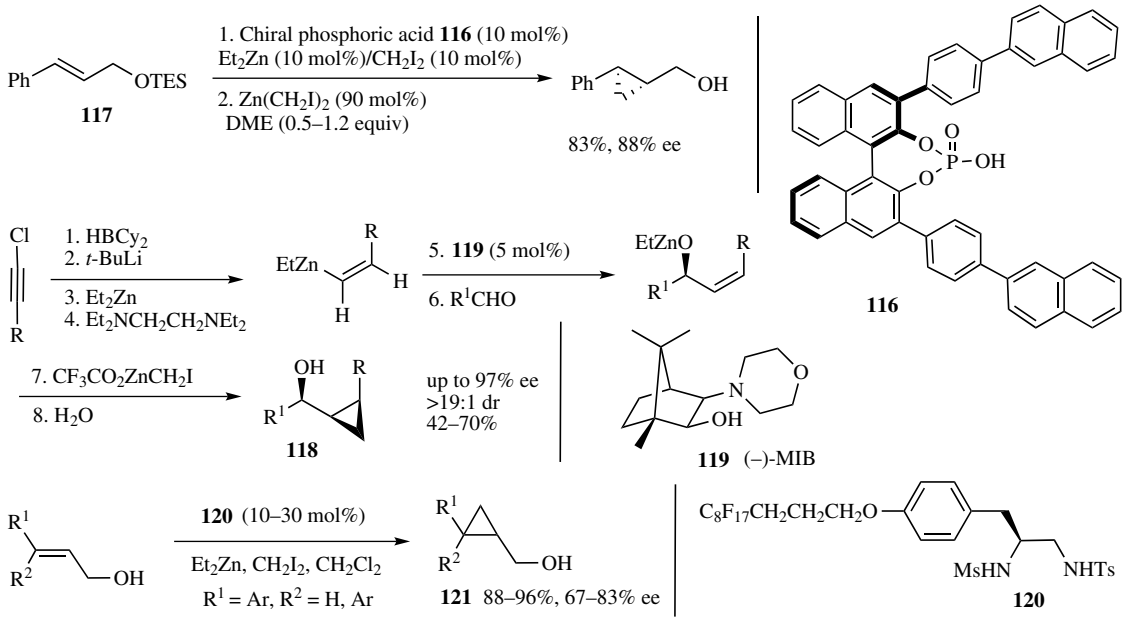

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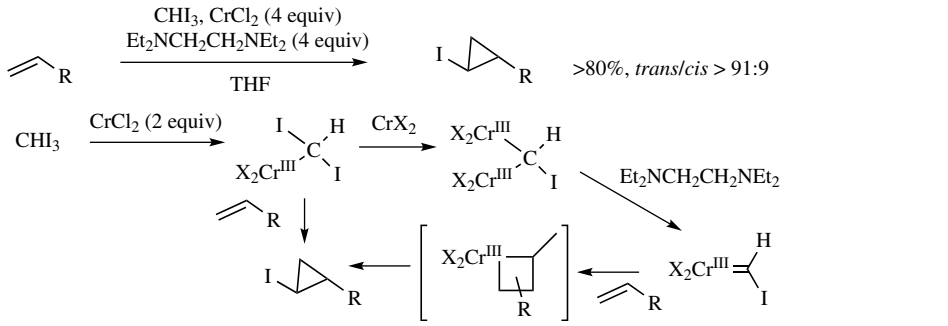
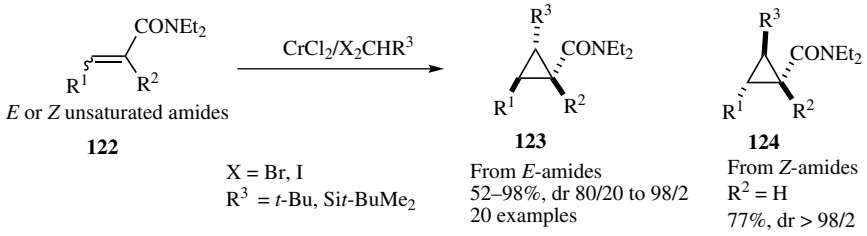


SCHEME 1.58



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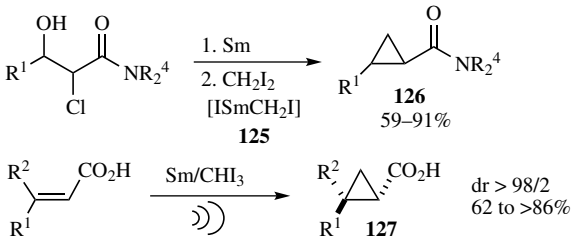

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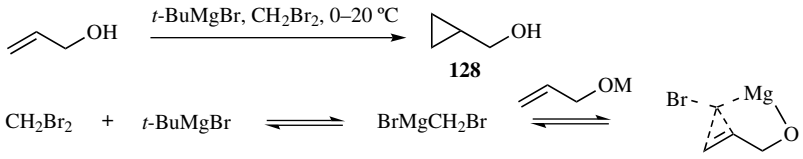

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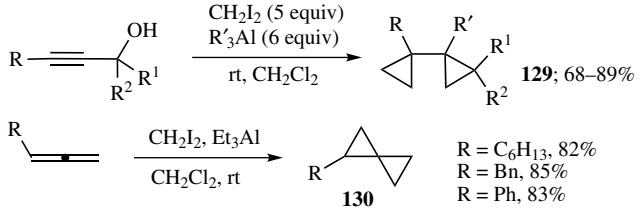

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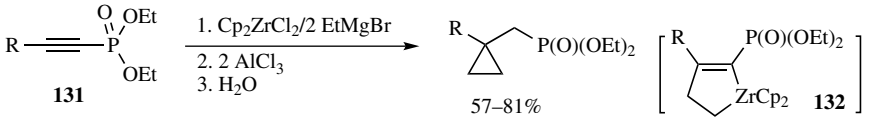


SCHEME 1.63

1.4 DIAZOALKANES WITH TRANSITION METAL CATALYSTS

1.4.1 Introduction

Cyclopropanation by diazoalkane in the presence or absence of transition metal catalysts is widely used in organic synthesis [107]. The recent explosion of research reports has enabled many types of formation of cyclopropanes in a diastereo- and enantioselective manner. The most commonly used transition metals are rhodium, copper, and ruthenium; however, other metals, such as palladium and cobalt, are also used. It may not be possible to report all of the results in this chapter, because numerous papers have been published so far. We selected recent representative examples.

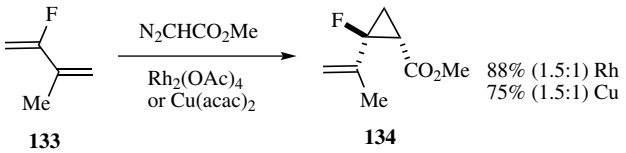
1.4.2 Rhodium-Catalyzed Reactions

Diazoalkanes were readily decomposed and underwent [2+1]-type cycloaddition to alkenes in the presence of catalytic amounts of rhodium complexes. $Rh_2(OAc)_4$ is the simplest complex for the reaction. For example, fluorocyclopropane **134** was prepared by the carbene addition to fluoroalkene **133** (Scheme 1.64) [108]. A copper catalyst also catalyzed the addition reaction.

Trifluoromethyl-substituted cyclopropane **136** was readily available when trifluoromethyldiazomethane **135** was exposed to $Rh_2(OAc)_4$ in the presence of acceptor alkenes (Scheme 1.65) [109]. The yield of cyclopropanes **136** was good while the diastereoselectivity remained at a 2:1 level.

Intramolecular cyclopropanation was useful for the construction of multicyclic compounds in a diastereoselective manner. The carbene species in **137** attacked the aromatic double bond to give fused cyclopropane **138** in good yield [110]. The obtained cyclopropane **138** underwent irreversible ring cleavage to give naphthopyranes (Scheme 1.66).

Vacher and coworkers utilized the intramolecular cyclopropanation of **139** to prepare bicyclo[3.1.0]hexane units **140** (Scheme 1.67) [111]. The bicyclo compounds **140** was converted to compound 141, which was a conformationally restricted analogue of atipamezole **141**. Dihydroquinoline **142** underwent the [2+1] cycloaddition catalyzed by $Rh_2(OAc)_4$ (Scheme 1.68) [112].



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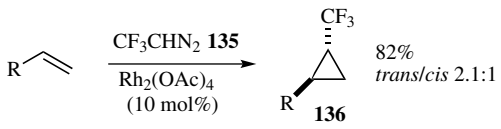

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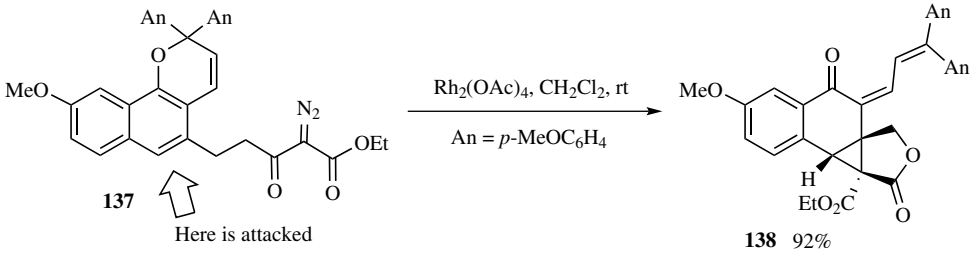

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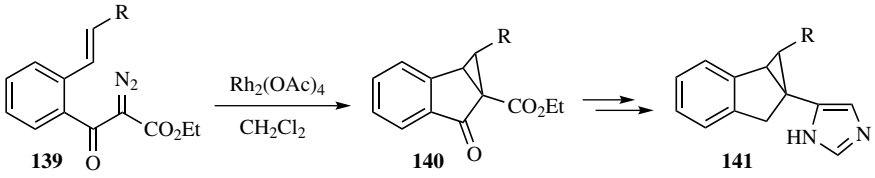

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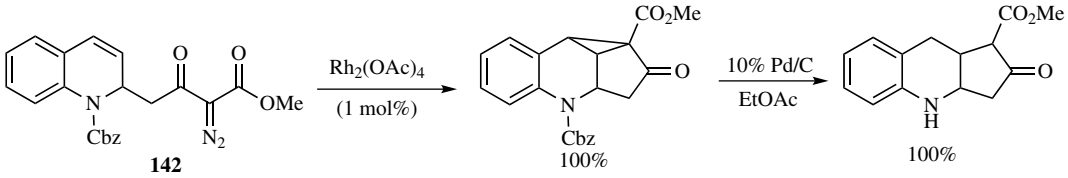
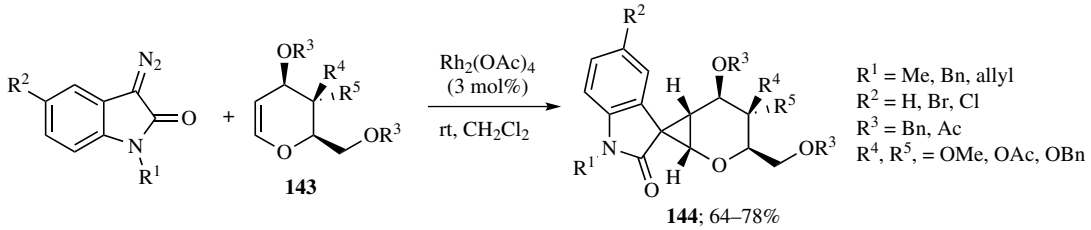


SCHEME 1.68

Diastereoselective cyclopropanation progressed in the reaction with sugar-derived glycals **143** (Scheme 1.69) [113]. A new type of spiro cyclopropanes **144** were formed in a highly stereoselective manner. Optically active enamide **145** underwent stereo-controlled cyclopropanation, and amide cyclopropanes **146** were prepared in more than 95:5 selectivity (Scheme 1.70) [114]. Cyclopropanation of 8-oxabicyclo[3.2.1]octane **147** with diazoalkanes smoothly occurred in the presence of a rhodium or copper catalyst, and *exo*,*exo* adduct **148** was isolated in a highly stereoselective manner (Scheme 1.71) [115].

The nitro group is a strong electron-withdrawing group that has versatile synthetic use. Nitrodiazoacetates **149** yielded nitrocyclopropanes **150** when treated with rhodium complexes in the presence of alkenes (Scheme 1.71). Wurz and Charette examined the intermolecular and intramolecular cyclopropanation of nitrodiazoacetate **149** and ketones. Nitrocyclopropanes were obtained in good yields through intermolecular cyclopropanation and they were readily converted to dihydropyrroles **151** and aminocyclopropanes **152** (Scheme 1.72) [116].

The intramolecular cyclopropanation of nitroester **153** progressed in a stereoselective manner, and cyclopropane-fused lactone **154** served as a useful precursor for nitrocyclopropanes **155** (Scheme 1.73) [117]. The enantiomeric excess of fused-cyclopropane **154** exceeded 95% ee. Cyclopropanation was also possible using nitroacetate and $PhI(OAc)_2$ [118].



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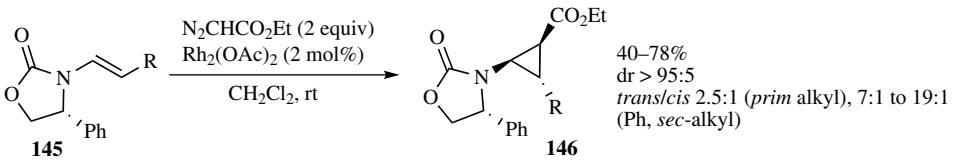

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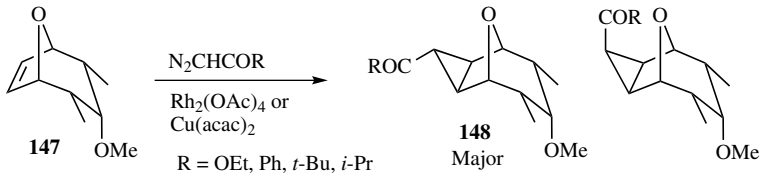

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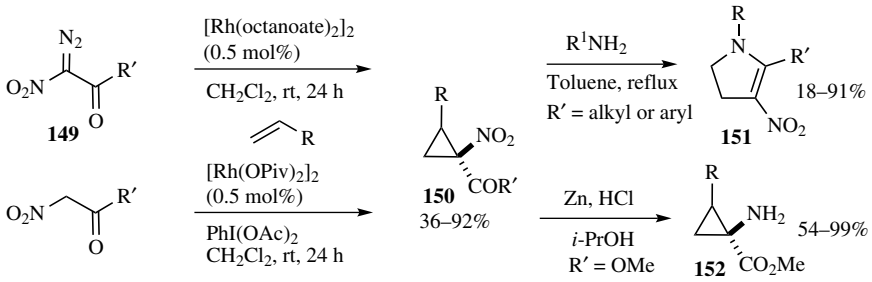
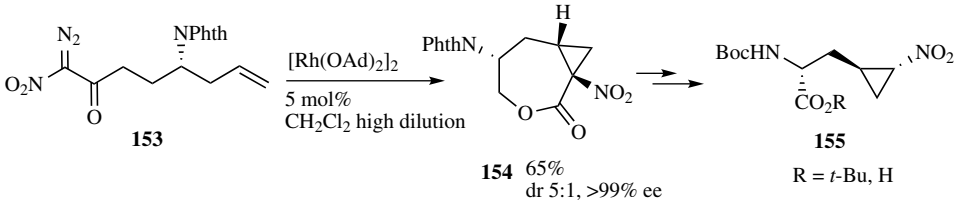


SCHEME 1.72

Rhodium porphyrin **156** was also a useful catalyst for cyclopropanation with diazoalkanes. Furuta and coworkers reported that N-confused rhodium porphyrin served as a good catalyst for the cyclopropanation (Scheme 1.74) [119]. *trans*-Cyclopropane **157** was produced predominantly.

The rhodium complex also catalyzed the cyclopropanation of iodonium ylides **159** that was prepared from malonic esters (Scheme 1.75) [120]. The treatment of a malonic ester with phenyliodonium diacetate gave corresponding iodonium ylides, which underwent smooth cyclopropanation with various alkenes. It was shown that these two steps could be combined. Asymmetric cyclopropanation was examined using a $Rh_2(esp)_2$ catalyst.

Asymmetric cyclopropanation was actively investigated in the last 10 years and an enormous number of reports were published. For example, proline-derived Rh_2(*S*-DOSP)$_4$ **160** was used for asymmetric cyclopropanation. Asymmetric cyclopropanation of *N*-Boc-pyrrole **161** and furan **162** was carried out by Davies and coworkers (Scheme 1.76) [121]. Face selectivity was influenced by steric and electronic effects on the acceptor unit. *N*-Boc-pyrrole **161** underwent asymmetric double cyclopropanation to give chiral azatricycloheptane



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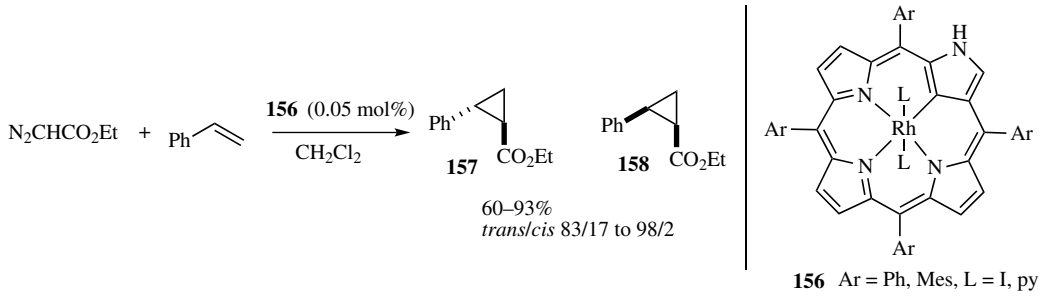

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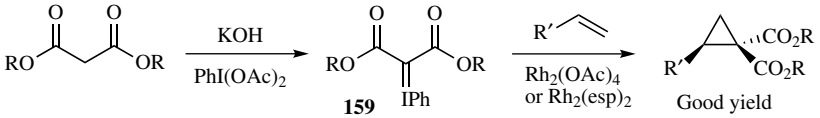

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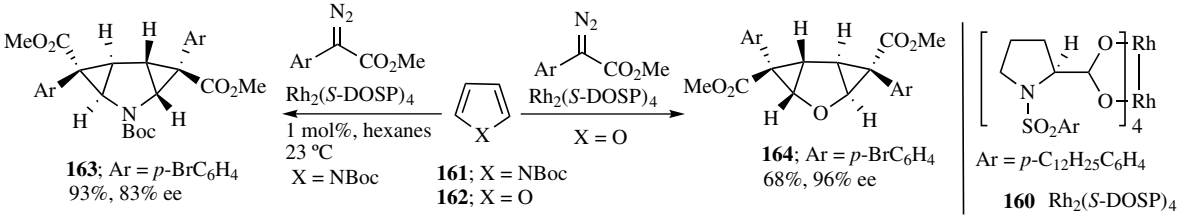


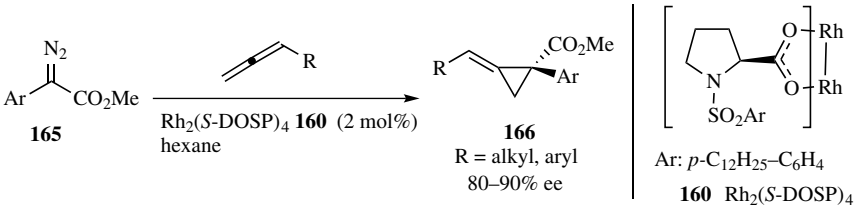
SCHEME 1.76

163 in good yield. The enantiomeric excess reached 93% ee. On the other hand, the same catalyst and diazoacetate with pyrrole showed different selectivity, giving oxatricycloheptane **164** in 68% yield in 96% ee.

Asymmetric cyclopropanation with allenes was studied by Gregg et al. Aryldiazoacetate **165** underwent asymmetric cyclopropanation with monosubstituted allenes in the presence of Rh_2(*S*-DOSP)$_4$ **160** and vinylcyclopropanes **166** were obtained in 80–90% ee (Scheme 1.77) [122]. The Hammett plots of the reaction revealed that the reaction rate depended on allene substituents, and the ρ value was estimated to be -0.25 [123].

Azido cyclopropanes **167** were prepared from azidoalkenes in the presence of Rh_2(*S*-DOSP)$_4$ **160** (Scheme 1.78) [124]. *cis*-Cyclopropanes were formed in a diastereoselective manner and high enantiomeric selectivity was achieved.

The C—H insertion of diazoalkanes to the allylic position is a competitive reaction to cyclopropanation. For example, the reaction of aryldiazoacetate **168** to silyl enol ether **169** catalyzed by Rh_2(*S*-DOSP)$_4$ **160** gave chiral cyclopropane **171** selectively in 95% ee, while the use of Rh_2(*S*-PTAD)$_4$ **170** led to a C—H insertion reaction to the same alkene to give **172** (Scheme 1.79) [125]. On the other hand, the reverse phenomena were observed in the reaction of dihydronaphthalene **173**, where Rh_2(*S*-DOSP)$_4$ **160** efficiently catalyzed asymmetric cyclopropanation to give **174**, while Rh_2(*S*-PTAD)$_4$ **170** promoted a C—H insertion reaction to give **175** (Scheme 1.80) [126].



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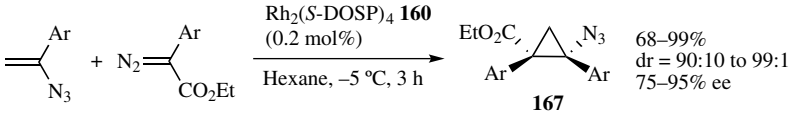

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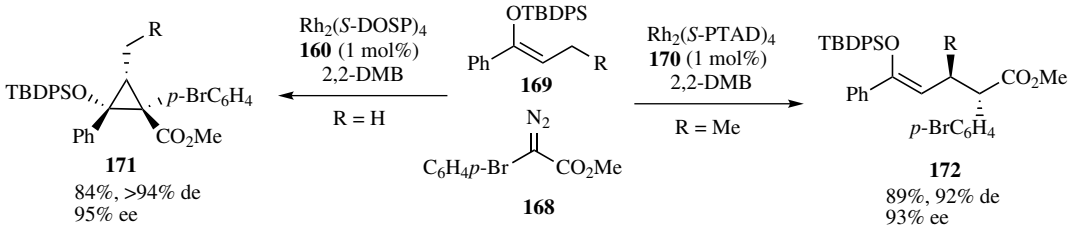

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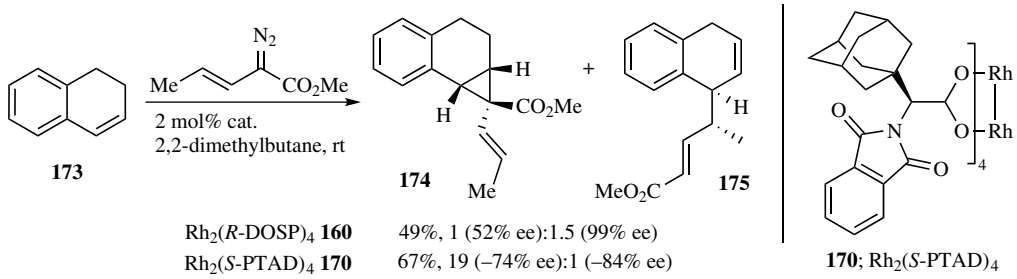


SCHEME 1.80

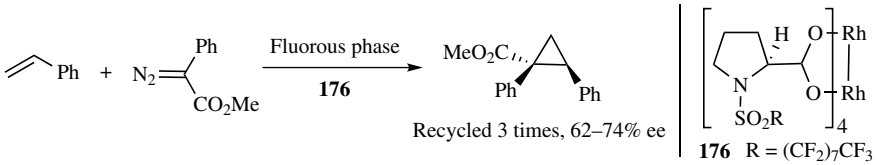
Perfluoroalkyl-substituted Rh_2(*S*-DOSP)$_4$ **176** achieved not only efficient asymmetric cyclopropanation but also convenient recovery and recycling of the catalyst (Scheme 1.81) [127].

Rh_2(*S*-NTTL)$_4$ **177** was also used as a catalyst for the asymmetric cyclopropanation of diazoacetate derivatives. Charette and coworkers examined complex **177** for the cyclopropanation of diazoamide acetate **178**, and diastereo- and enantioselective cyclopropane formation was achieved to give **179** (Scheme 1.82) [128]. They obtained the cyclopropanes **179** in more than 84% ee. The amide group was located at the *trans*-position and the diastereoselectivity reached over 30:1. The addition of $TfNH_2$ was effective to progress the asymmetric cyclopropanation of cyanodiazoacetoamide **180** to give **181** (Scheme 1.83) [129].

(Silanyloxyvinyl)diazoacetate **182** underwent asymmetric cyclopropanation of styrenes in the presence of Rh_2(*S*-NTTL)$_4$ **177**, and vinylcyclopropanes **183** were prepared in good yields (Scheme 1.84) [130]. The ester group in **183** primarily occupied the *trans*-position, and the enantiomeric excess of **183** was approximately 98% ee.

Rh_2(*S*-NTTL)$_4$ **177** was useful for the cyclopropanation of 1,2,3-triazoles **184** (Scheme 1.85) [131].

Halogenated ligands were also employed in the asymmetric cyclopropanation reaction. For example, a rhodium complex with brominated TTL ligand **185** promoted the chiral synthesis of cyclopropanes from active methylene compounds in the presence of iodosylbenzene (Scheme 1.86) [132]. Cyclopropanes **186** were obtained in good optical purity.



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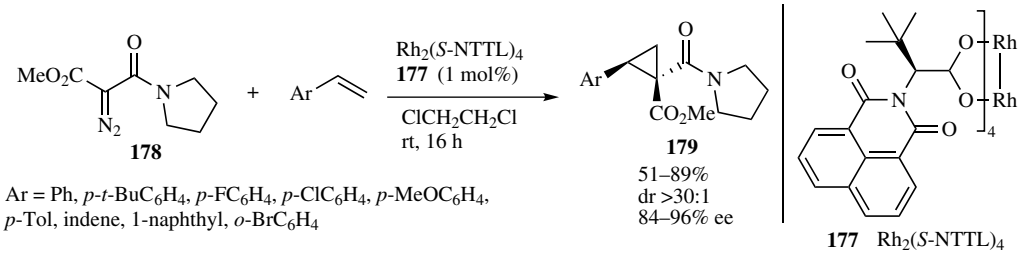

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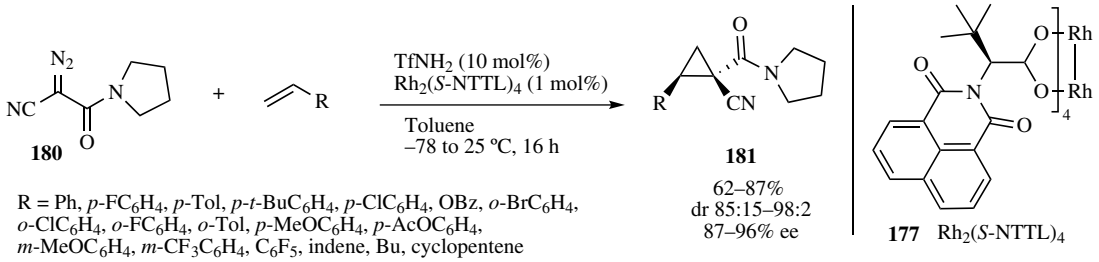
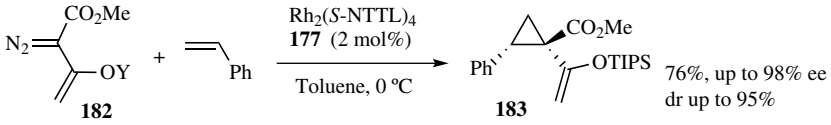
SCHEME 1.82



R = Ph, *p*-FC_6H_4, *p*-Tol, *p*-*t*-BuC_6H_4, *p*-ClC_6H_4, OBz, *o*-BrC_6H_4, *o*-ClC_6H_4, *o*-FC_6H_4, *o*-Tol, *p*-MeOC_6H_4, *p*-AcOC_6H_4, *m*-MeOC_6H_4, *m*-$CF_3C_6H_4$, C_6F_5, indene, Bu, cyclopentene

SCHEME 1.83



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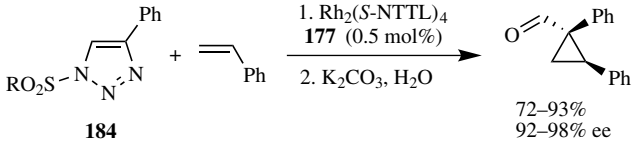
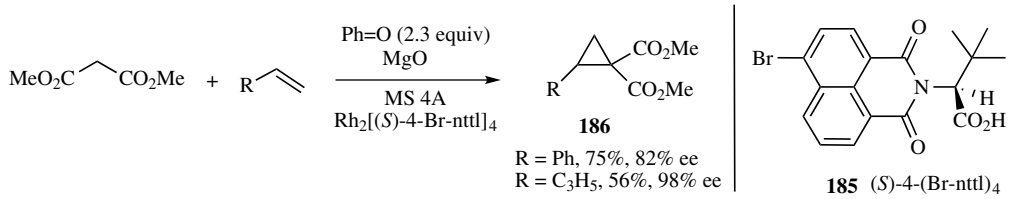


SCHEME 1.85

α-Alkyl-α-diazocarboxylates **187** undergo β-elimination in the presence of $Rh_2(OAc)_4$; however, sterically demanding ligands prevent it, and cyclopropanation progressed in the presence of alkene. Rh_2TPA_4 **188** achieved stereoselective cyclopropanation to give **189** (Scheme 1.87) [133]. Polybrominated nnl complex Rh_2(*S*-TBPTTL)$_4$ **190** was used for the reaction with diazopropionate **191** [134]. Cycloaddition progressed with high diastereoselectivity and enantioselectivity and cyclopropane **192** was obtained in a *trans*-selective manner. The reaction progressed in a one-pot procedure and provided a convenient preparation of chiral cyclopropanes.

Polychlorinated TTL ligand was useful for the cyclopropanation of α-nitro- and α-cyanodiazoacetates **193** and **194**, respectively, as well as diazomalonoacetate **195** (Scheme 1.88) [135]. Cyclopropanation promoted by Rh_2(*S*-TBCTTL)$_4$ **196** gave cyclopropanes **197** in good enantioselectivity. A conformational study on the ligand during the reaction was also carried out [136].

The adamantyl analogue of ligand TTL-containing rhodium complex Rh_2(*S*-PTAD)$_4$ **170** was reported for the



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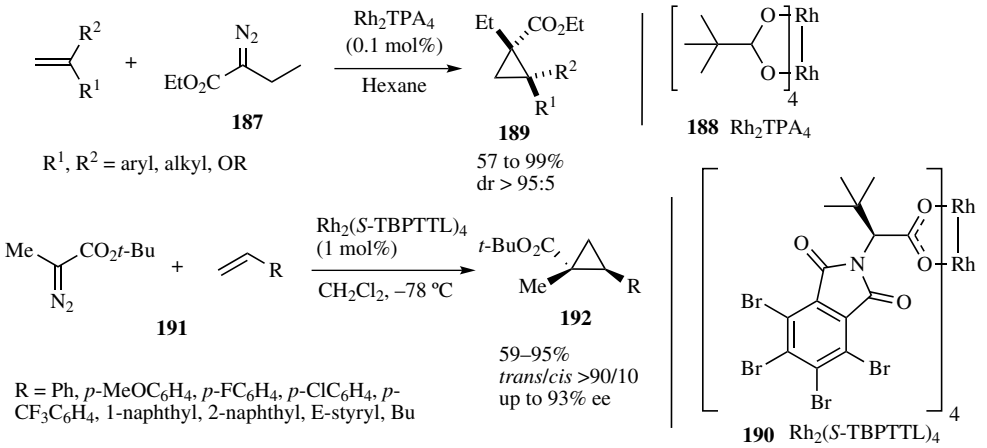

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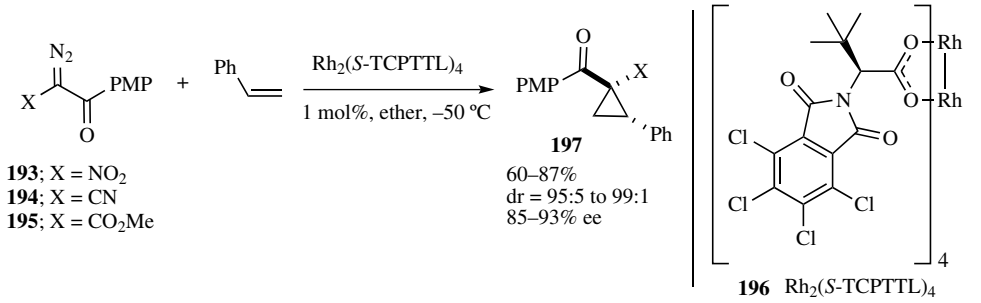
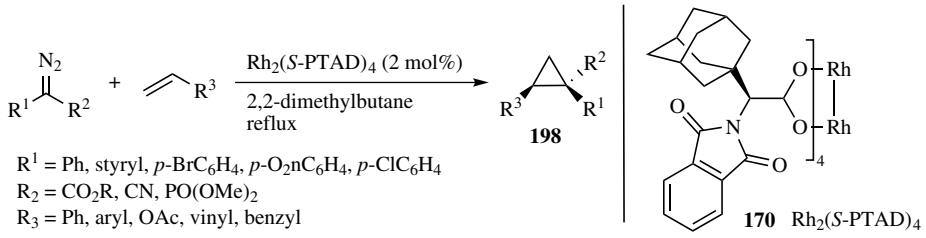


SCHEME 1.88

catalytic asymmetric reaction. Davies and coworkers reported that diazoarylacetate [137], diazoarylacetonitrile [138], and diazobenzylphophonate [139] underwent asymmetric cyclopropanation to give corresponding arylcyclopropanes **198** in good yields (Scheme 1.89). The enantioselectivity reached up to 98% ee for the reaction of diazoarylacetates and 99% ee for diazobenzylphosphonate. Trifluoromethyl-substituted chiral cyclopropanes **200** were prepared from corresponding hydrazone **199** in the presence of Rh_2(*S*-PTAD)$_4$ (Scheme 1.90) [140].

$Rh_2(esp)_2$ **201** was used as an efficient catalyst for cyclopropane formation from diazoalkanes. For example, Davies



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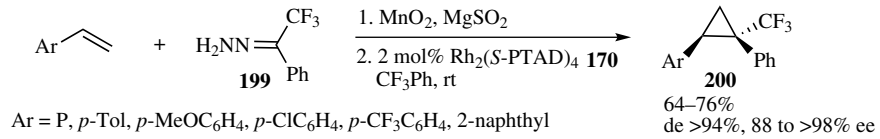

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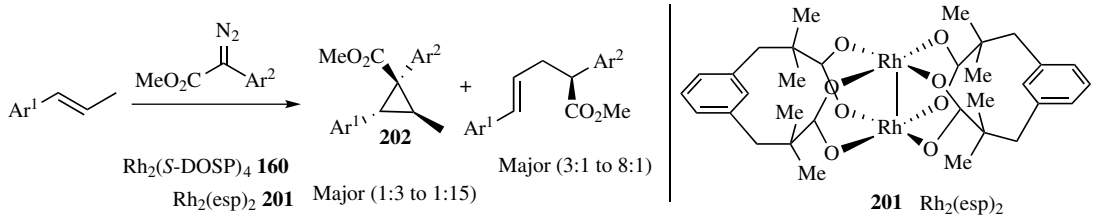
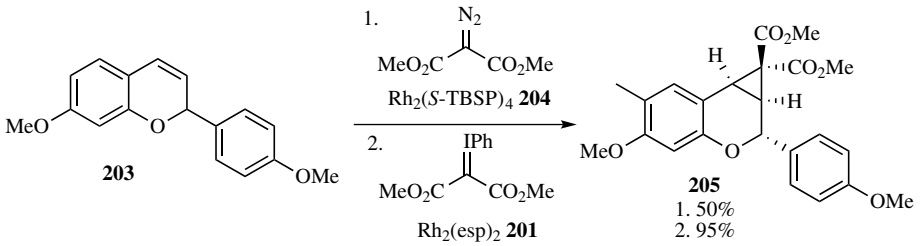


SCHEME 1.91



SCHEME 1.92

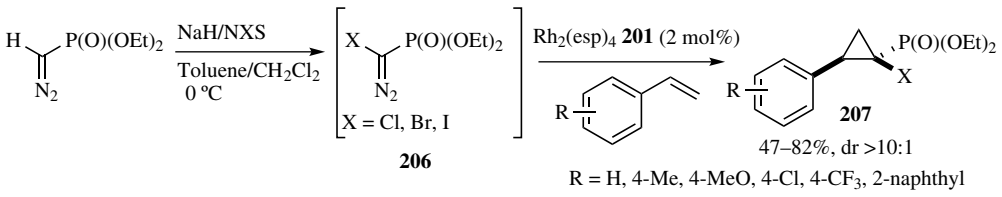
et al. successfully prepared polysubstituted cyclopropanes **202** from α,β-disubstituted styrenes (Scheme 1.91) [141].

In these cases, the C—H insertion reaction of an allylic methyl group is a significant side reaction. $Rh_2(esp)_2$ **201** predominantly promoted cyclopropanation while Rh_2(*S*-DOSP)$_4$ **160** gave C—H insertion adducts as the major products. A theoretical study of the $Rh_2(esp)_2$ **201** has been reported [142]. The efficiency of the catalyst was also shown in a study that reported that cyclopropanation of 2*H*-chromene **203** efficiently progressed in the presence of $Rh_2(esp)_2$ **201** (Scheme 1.92) [143]. The reaction catalyzed by Rh_2(*S*-TBSP)$_4$ **204** gave the same cyclopropane **205** in moderate yield.

Halogen-substituted cyclopropanes were prepared by the reaction of halodiazophosphonate **206** catalyzed by $Rh_2(esp)_2$ **201** (Scheme 1.93) [144]. The diastereoselectivity of the formation of **207** was better than 10:1. The catalyst loading could be reduced to 0.1 mol% for the reaction. Trifluoromethyl-substituted cyclopropenes **208** were prepared by Morandi and Carreira (Scheme 1.94) [145].

A chiral analogue of the bidentate ligand biTISP was utilized for asymmetric cyclopropanation. Rh_2(*S*-biTISP)$_2$ **209** catalyzed the reaction of phenyldiazoacetate [146] and phenyldiazophosphonate [147] with styrene, giving chiral cyclopropanes **210** in good yields with high enantiomeric excesses (Scheme 1.95). The substrate/catalyst (S/C) ratio reached 92,000. Thus, a very high turnover number (TON) was achieved, and turnover frequency reached 4000 l/h.

Rh_2(5-S-MEPY)$_4$ **211** catalyzed intramolecular cyclopropanation to give fused lactone **212** (Scheme 1.96) [148]. The lactone was converted to eight-membered ring **213**.



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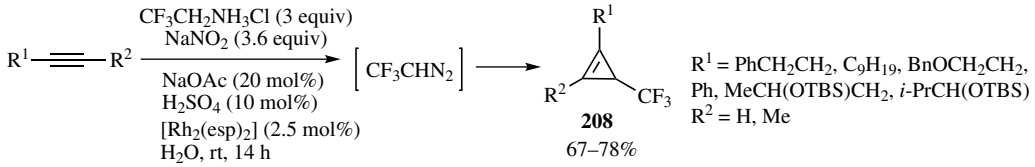

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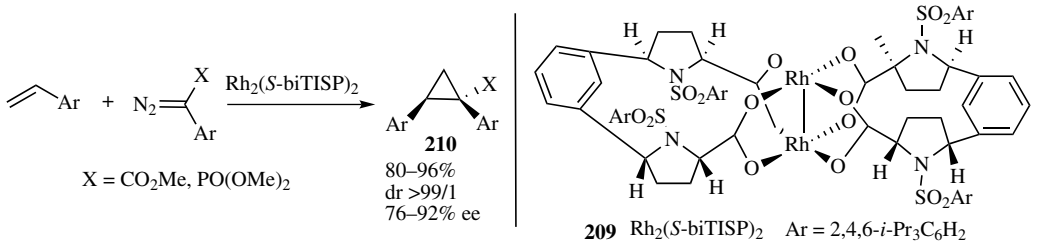

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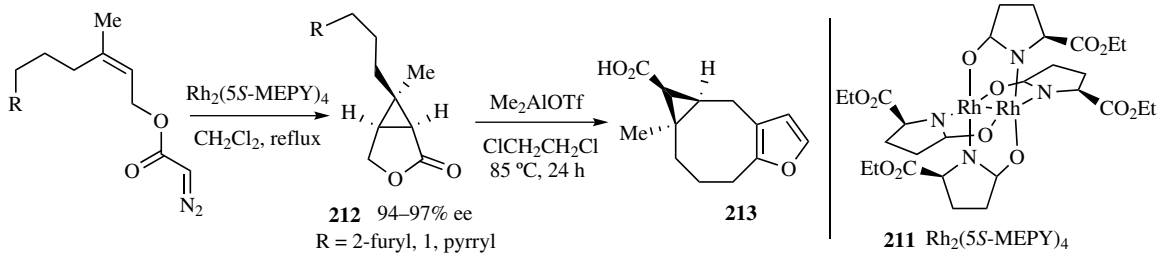

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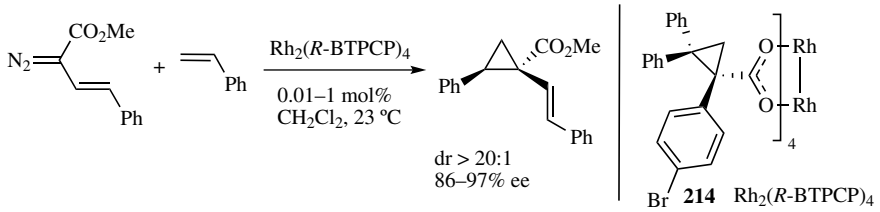


SCHEME 1.97

The cyclopropane-containing ligand R-BTPCP forms Rh_2(RBTPCP)$_4$ **214** and it catalyzed asymmetric cyclopropanation (Scheme 1.97) [149].

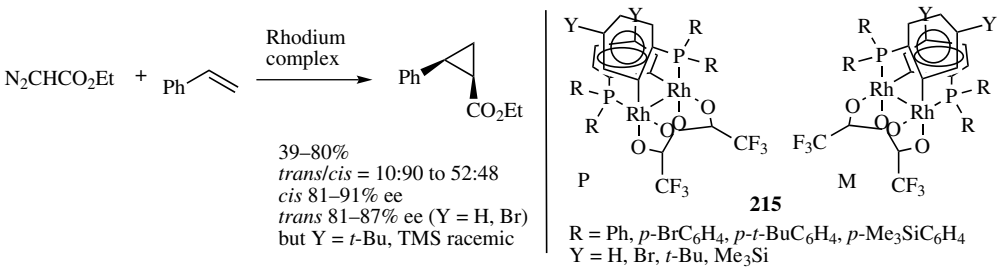
Bulky *ortho*-methylated phosphine-ligand-coordinating rhodium complex **215** was used for enantiocontrolled and diastereocontrolled cyclopropanation with styrene (Scheme 1.98) [150]. The diastereoselectivity and enantioselectivity of the reaction depended on a substituent on the aromatic ring of the ligand.

The rhodium complex of *N*-heterocyclic carbene **216** was developed as a new catalyst for the cyclopropanation of diazoacetate (Scheme 1.99) [151]. High *cis*-selectivity was achieved. The use of NaBArf **217** rather than AgOTf improved catalyst loading and *cis*-selectivity.

Hayashi and coworkers used chiral diene-rhodium complex **218** for the cyclopropanation of diazomalonate (Scheme 1.100) [152]. The optical purity of the product **219** was more than 80% ee.

1.4.3 Copper-Catalyzed Reactions

Copper is the most widely used transition metal in asymmetric cyclopropanation. In particular, its use in combination



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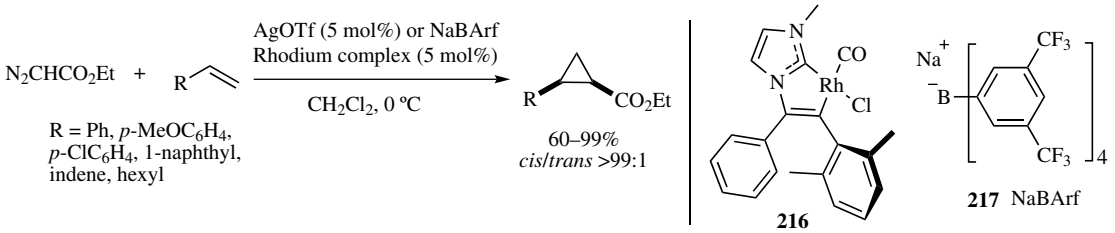

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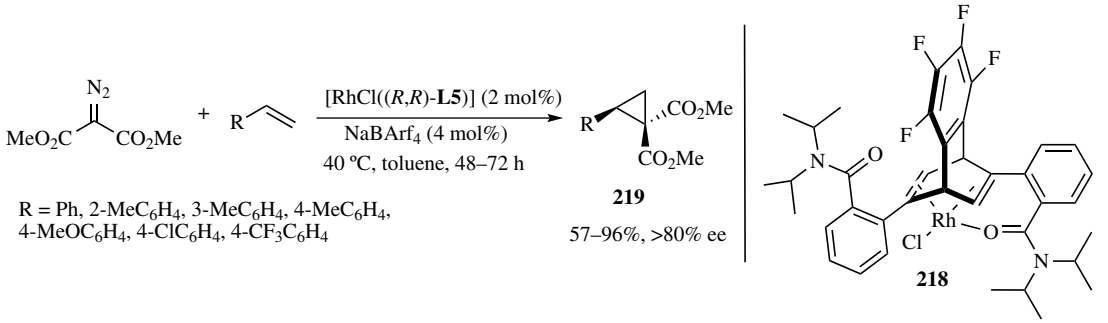


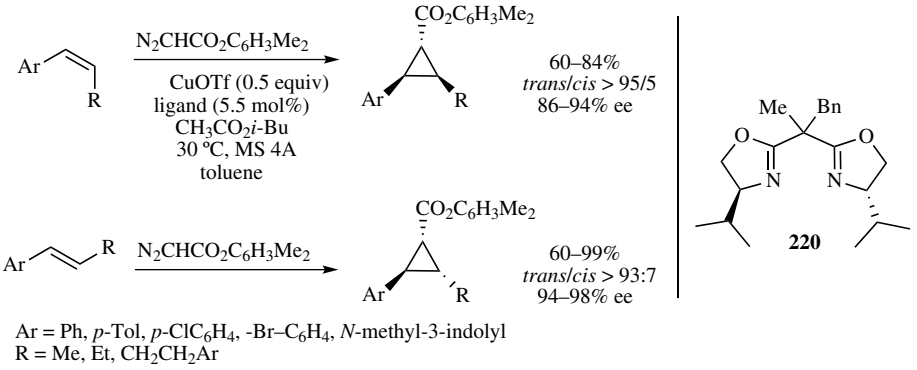
SCHEME 1.100

with a chiral bisoxazoline (BOX) ligand is well established [153]. We selected a number of examples, described below.

Sun and coworkers reported that a BOX ligand **220** that broke C2 symmetry served as an effective catalyst for enantioselective cyclopropanation of 1,2-disubstituted alkenes (Scheme 1.101) [154]. Good diastereoselectivity was observed for the cycloaddition reaction.

Cyclopropane-substituted BOX ligand complex **221** was used for the asymmetric cyclopropanation of diazoacetate (Scheme 1.102) [155]. Nitrodiazoacetate [156] and trimethylsilyldiazomethane [157] underwent asymmetric cyclopropanation catalyzed by chiral copper BOX complex **222** (Scheme 1.103). Stereocontrol was primarily controlled by BOX ligand **227** if an extra stereogenic center existed in the alkene unit (Scheme 1.104) [158]. Thus, two chiral unsaturated morpholines **223** and **224** were examined. The configuration of the cyclopropane unit **225** and **226** in the major products was the same regardless of the configuration of the carboxylate unit.

Polyfluorinated BOX ligand **228** provides a useful copper complex catalyst, which can be recovered easily from the reaction mixture by a fluorous solvent system [159]. Benaglia and coworkers reported that an F-BOX ligand with CuOTf catalyzed the asymmetric cyclopropanation of diazoacetate in a C_8F_{18}/CH_3CN biphasic mixture; the F-BOX ligand was readily separated from products by phase separation and recovered from the reaction mixture (Scheme 1.105).



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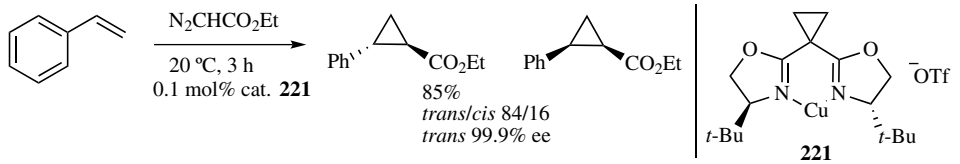

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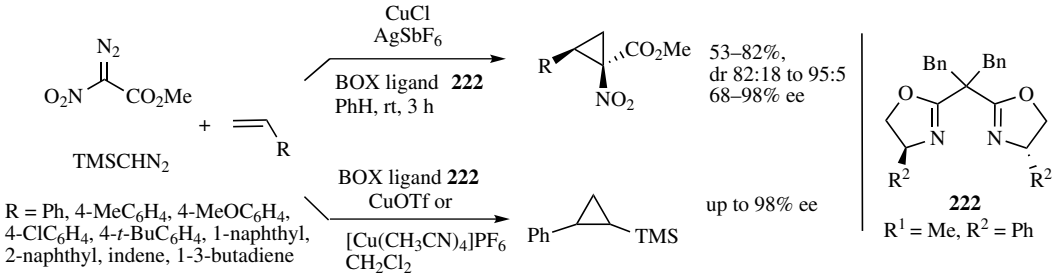

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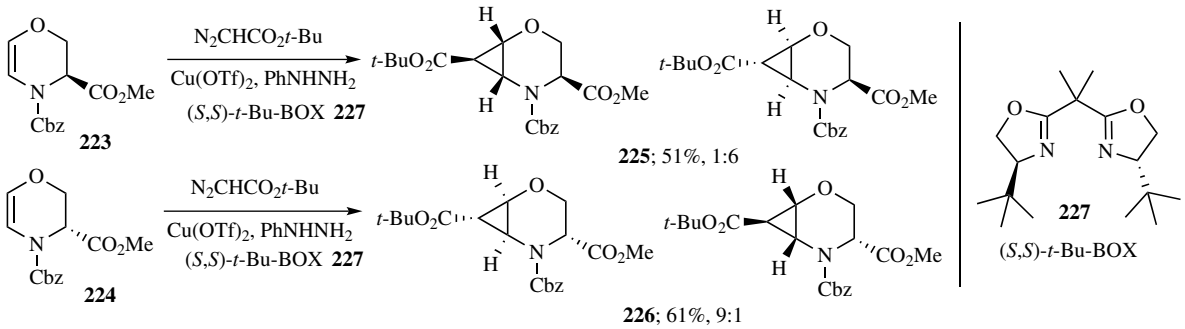
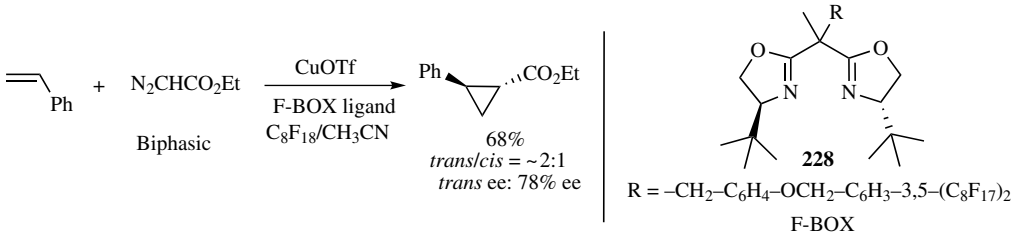


SCHEME 1.104

A polymer-supported chiral BOX ligand served as a good catalyst for the asymmetric cyclopropanation. For example, Salvadori and coworkers reported a chiral BOX containing polystyrene **229** promoted the asymmetric cyclopropanation reaction to give optically active cyclopropanes **230** in good yields with high enantioselectivity (Scheme 1.106) [160]. Polymer **229** was not soluble in reaction solvent; therefore, it was readily separated from the reaction mixture. The polymer-supported catalyst **229** was useful at least five times.

Asymmetric cyclopropanation in ionic liquids was examined (Scheme 1.107) [161]. Ionic liquids [emim][OTf] were recovered and could be reused.

Desymmetrization using PyBOX ligand **231** was carried out by Landais and coworkers (Scheme 1.108) [162]. Cyclopentadiene **232** was monocyclopropanated by diazoacetate in the presence of CuOTf and PyBOX catalysts. Optically active bicyclo[3.1.0]hexene **233** was obtained with up to 72% ee.



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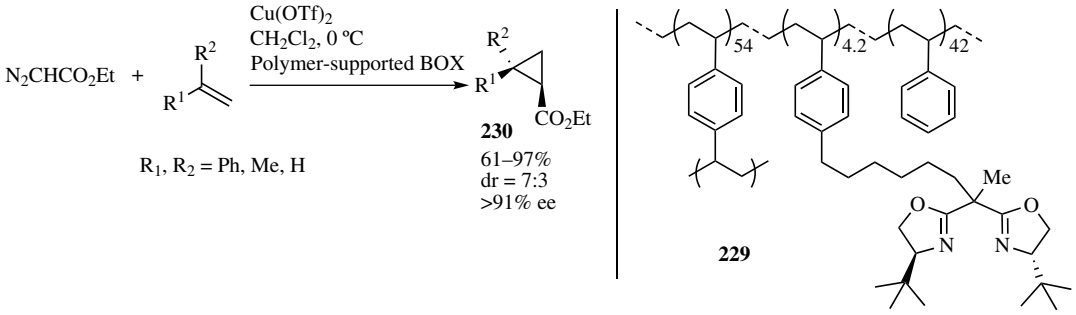

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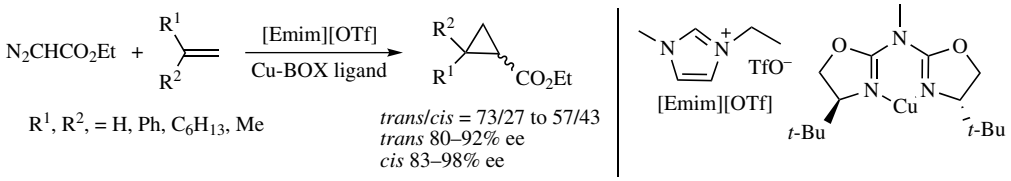

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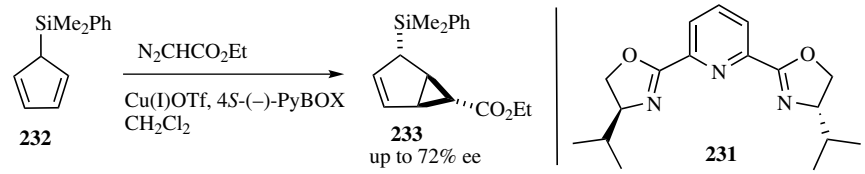
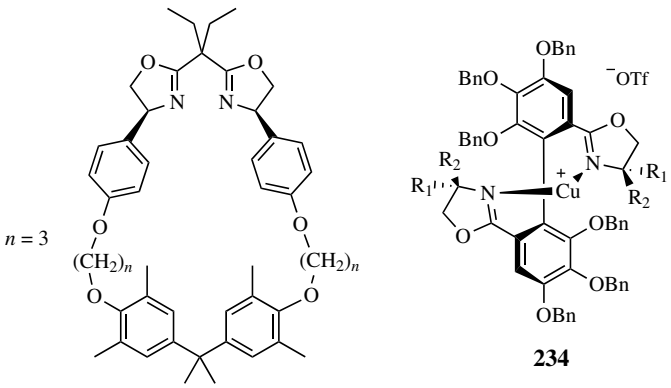


SCHEME 1.108

Cyclic BOX catalysts were examined to probe mechanistic studies (Scheme 1.109) [163]. C2-symmetric chiral ligand **234** was employed for asymmetric cyclopropanation using diazoacetate [164].

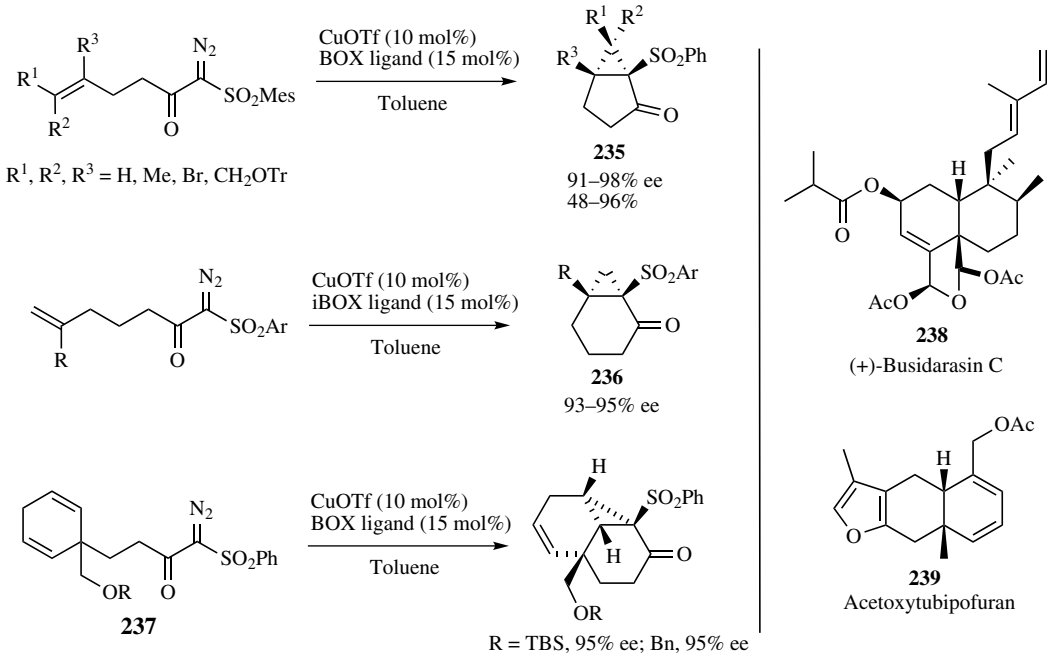
Intramolecular cyclopropanations catalyzed by Cu-BOX catalysts have been frequently used for the synthesis of multicyclic compounds. For example, Nakada and coworkers examined intramolecular cyclopropanation to prepare bicyclo[3.1.0]hexanone **235** and bicyclo[4.1.0]heptanone **236** systems in a highly enantioselective manner (Scheme 1.110) [165]. This was applied for the desymmetrization of 1,4-cyclohexadiene **237** for the acceptor unit. They examined these methodologies for the preparation of (−)-platencin [166], (+)-busidarasin C **238**, and acetoxytubipofuran **239** [167]. Diastereoselectivity for the intramolecular cyclopropanation of **240** was also examined (Scheme 1.111) [168].



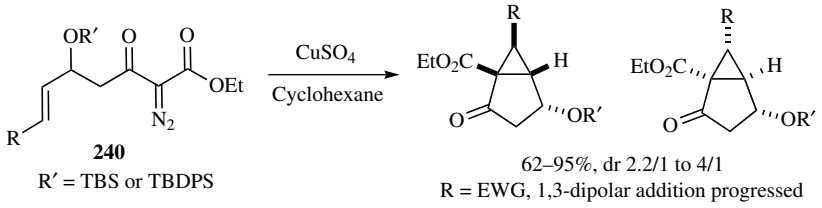
SCHEME 1.109

Intramolecular cyclopropanation has been applied for the synthesis of natural or bioactive compounds. For example, Qin and coworkers examined the intramolecular cyclopropanation of **241** for the synthesis of a pentacyclic indoline structure **242**, which was a key intermediate toward the total synthesis of perophoramidine and communesin (Scheme 1.112) [169]. Reisman and coworkers reported that the main core of salvileucalin B **243** was synthesized by intramolecular cyclopropanation (Scheme 1.113) [170]. Catalytic C—H insertion of rhodium was preferred.

Schiff-base-copper complex **244** catalyzed intramolecular cyclopropanation to give cyclopropane-fused lactone **245** (Scheme 1.114) [171]. Chiral Schiff base **246** was employed for asymmetric cyclopropanation of dienes (Scheme 1.115)



SCHEME 1.110



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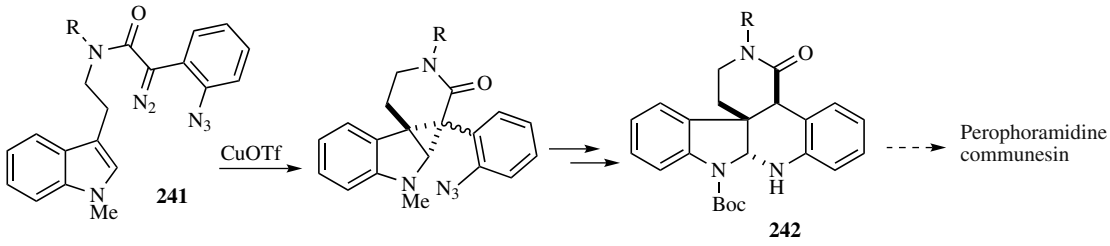

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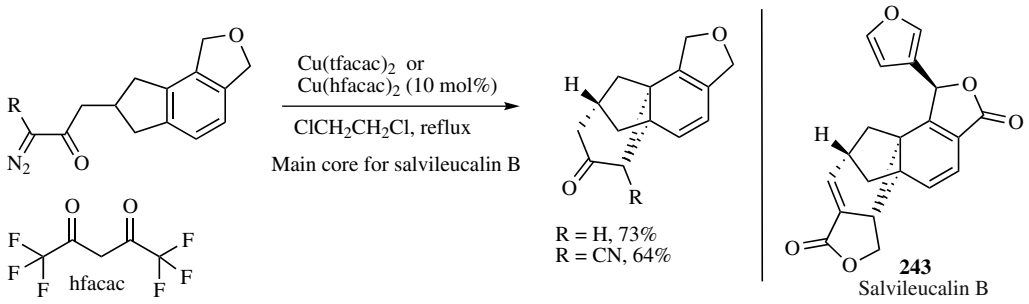

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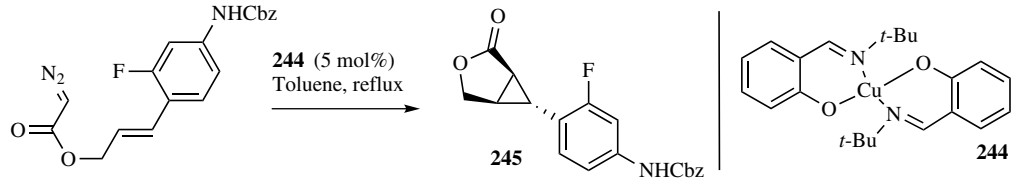

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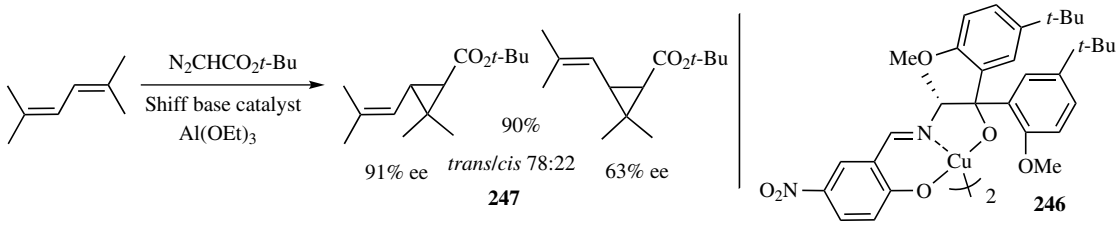


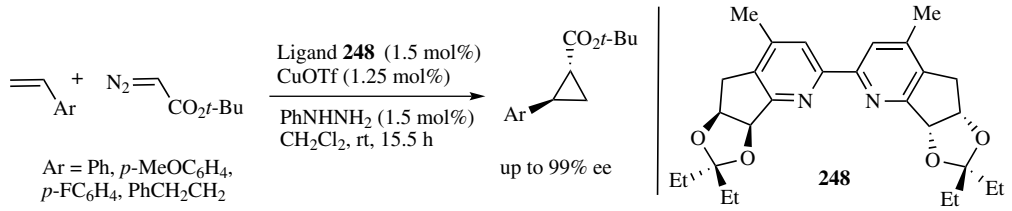
SCHEME 1.115

[172]. A diastereomeric mixture of **247** was obtained; the *trans*/*cis* ratio was approximately 4:1. The *trans*-isomer was prepared with good selectivity; the enantiomeric excess for the *cis*-isomer was moderate.

Chiral bipyridine ligands have been explored for the asymmetric cyclopropanation of diazoacetate. For example, Lyle and Wilson reported that optically active C2-symmetric 2,2′-bipiridyl **248** served as a good ligand for asymmetric cyclopropanation in the presence of CuOTf and phenyl hydrazine (Scheme 1.116) [173]. Boyd et al. showed that a similar 2,2′-bipyridyl **249** also worked as an effective catalyst (Scheme 1.117) [174]. Mono-oxazoline-substituted 2,2′-bipyridyl derivatives **250–252** have been examined (Scheme 1.118) [175]. Chiral double helical oligopyridine **253** showed good activity toward asymmetric cyclopropanation (Scheme 1.119) [176]. Low catalyst loading and high TON were achieved.

Diamine-derived chiral copper complex **254** was used in the asymmetric cyclopropanation (Scheme 1.120) [177]. Perfluorinated diamine ligand **255** was developed and showed moderate levels of enantioselectivity for the cyclopropanation of diazoacetate (Scheme 1.121) [178]. The fluorous ligand was readily separated by the simple decantation of the fluorous phase. Although the recycling of the catalyst was expected, reuse was difficult because of its partial decomposition.

New types of copper complexes have been used as catalysts for cyclopropanation. For example, the diiminophosphorane



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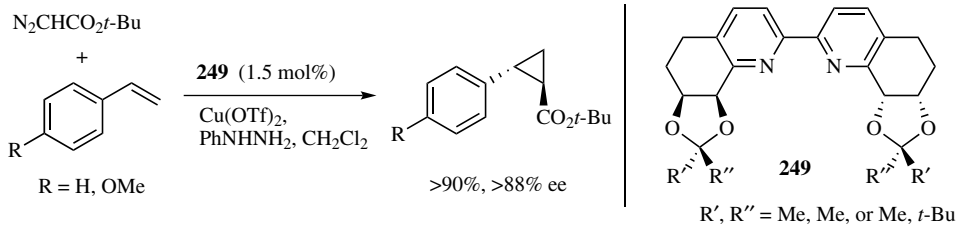

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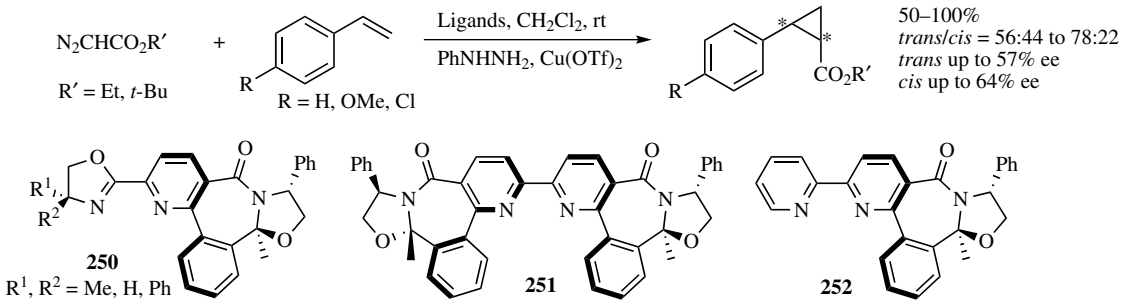

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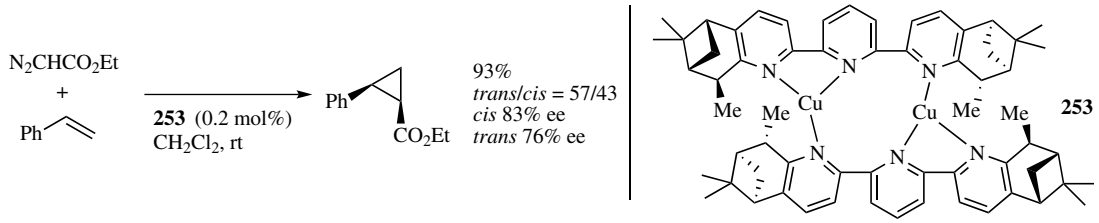

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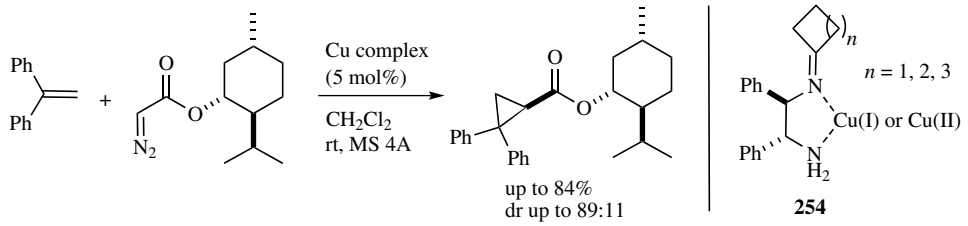


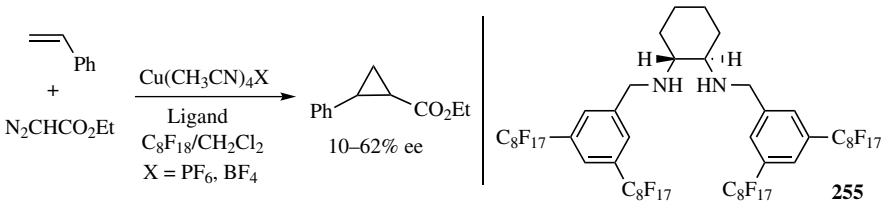
SCHEME 1.120

and triiminophosphorane copper complex of **256** catalyzed the cyclopropanation of diazoacetate to give cyclopropanecarboxylate **257** in good yield (Scheme 1.122) [179].

Hydrotris(3,4,5-tribromopyrazolyl)borate ligand **258**, $TpBr_3$, was examined for the cyclopropanation reaction of diazoacetate (Scheme 1.123) [180]. This complex worked in fluorous media and was readily recovered and recycled. Surface hydroxyl groups on metal–organic polyhedron **259** were used as the cyclopropanation catalyst (Scheme 1.124) [181].

1.4.4 Ruthenium-Catalyzed Reactions

Ruthenium complexes serve as catalysts for the cyclopropanation in a manner similar to rhodium complexes. For example, the ruthenium complex of bisoxiazolinyl thiophene **260** was examined for asymmetric cyclopropanation (Scheme 1.125) [182]. PyBOX-ruthenium catalyst **261** promoted the asymmetric cyclopropanation of diazoacetate and good *trans*-selectivity was observed (Scheme 1.126) [183]. The cycloadduct was converted to BMS-505130 **262**, a potential serotonin reuptake inhibitor.



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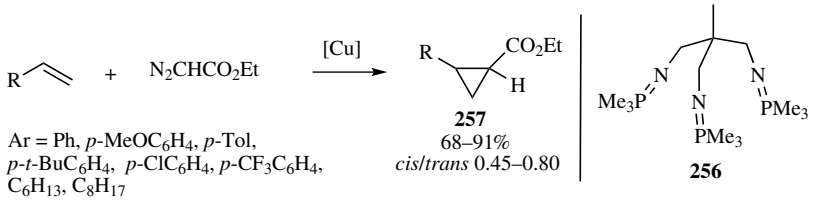

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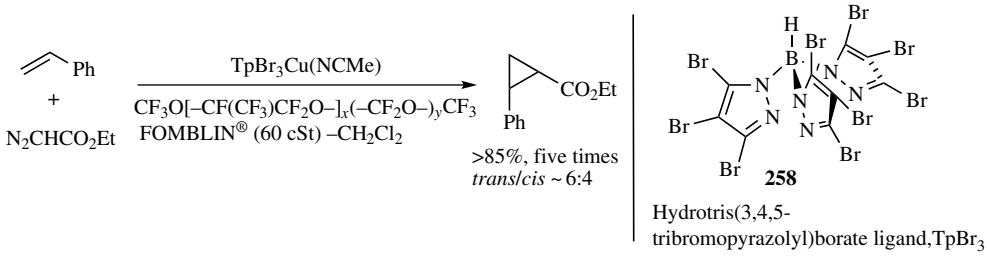

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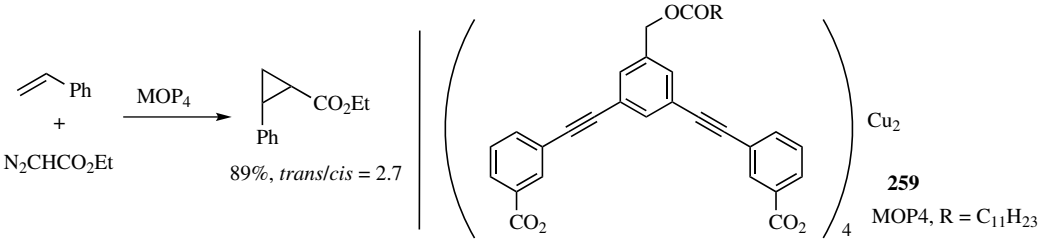

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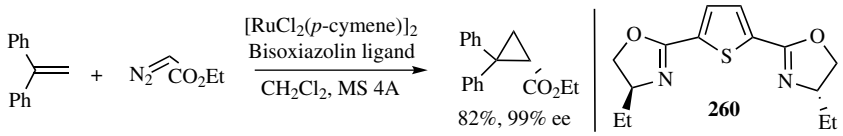

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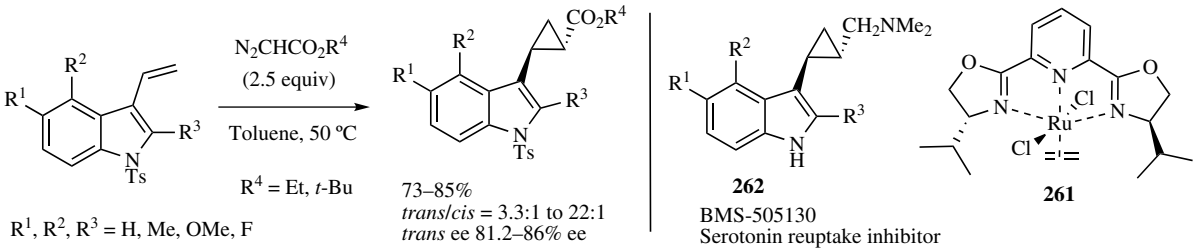
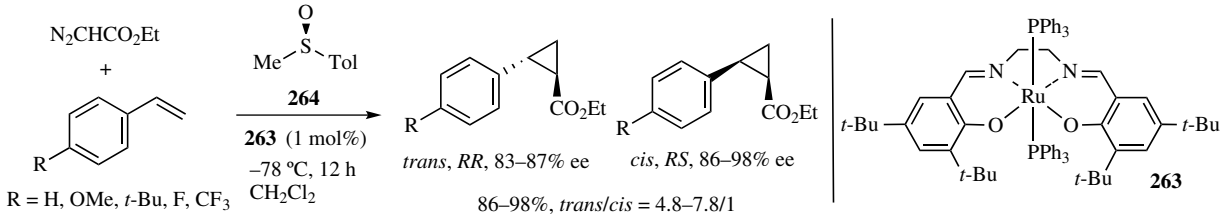


SCHEME 1.126



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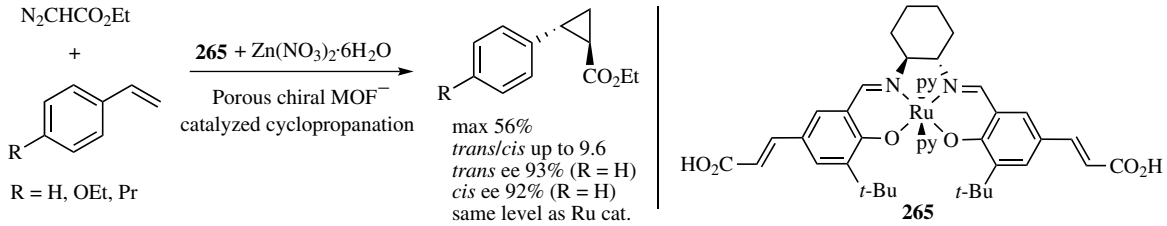


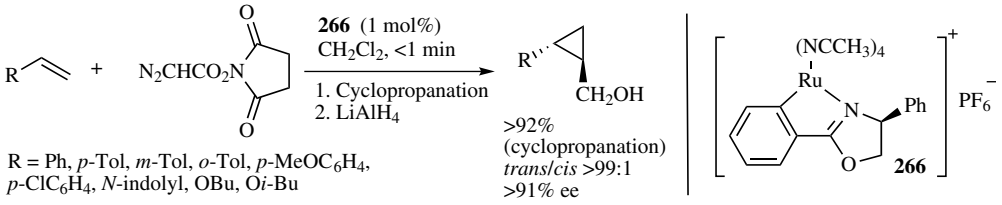
SCHEME 1.128

Ruthenium-salen complex **263** was examined. Achiral salen complex **263** in the presence of chiral sulfoxide **264** progressed the cyclopropanation of diazoacetate in a highly enantioselective manner (Scheme 1.127) [184]. Chiral sulfoxide served as an axial ligand that showed good asymmetric induction. C2-symmetric chiral ruthenium-salen complex **265** contained in metal–organic frameworks worked as a chiral catalyst for cyclopropanation (Scheme 1.128) [185].

Ruthenium-phenyloxazoline (Pheox) complex **266** was a useful catalyst for the cyclopropanation of terminal alkenes (Scheme 1.129) [186]. The reaction progressed in a *trans*-selective manner and was completed within 1 min. This catalyst was applied to polymer-supported catalyst **267**, which achieved high enantioselectivity for the reaction of diazoacetate to styrene derivatives (Scheme 1.130) [187].

Ruthenium porphyrin **268** catalyzed cyclopropanation (Scheme 1.131) [188]. Aryldiazomethane was generated *in situ* from tosylhydrazone, and cyclopropanation smoothly progressed to give cyclopropanes **269** in a *trans*-selective manner.

Simonneaux and coworkers reported that chiral ruthenium porphyrin **270** was used for the asymmetric cyclopropanation of diisopropyl diazomethylphosphonate [189] or



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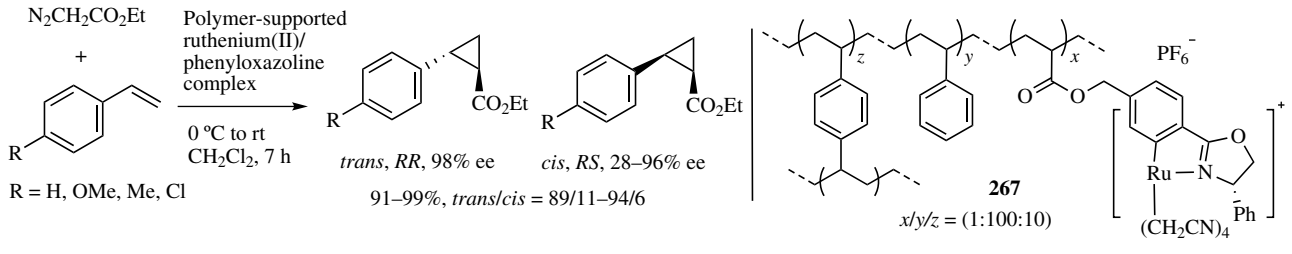

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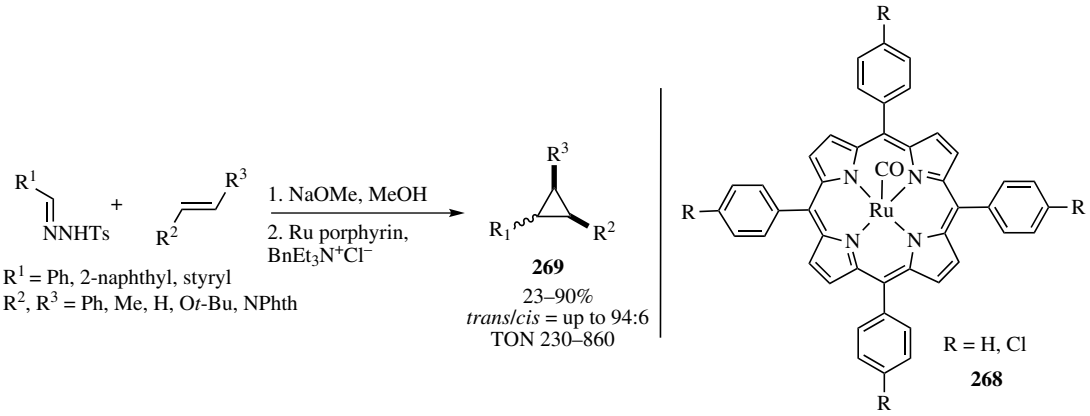

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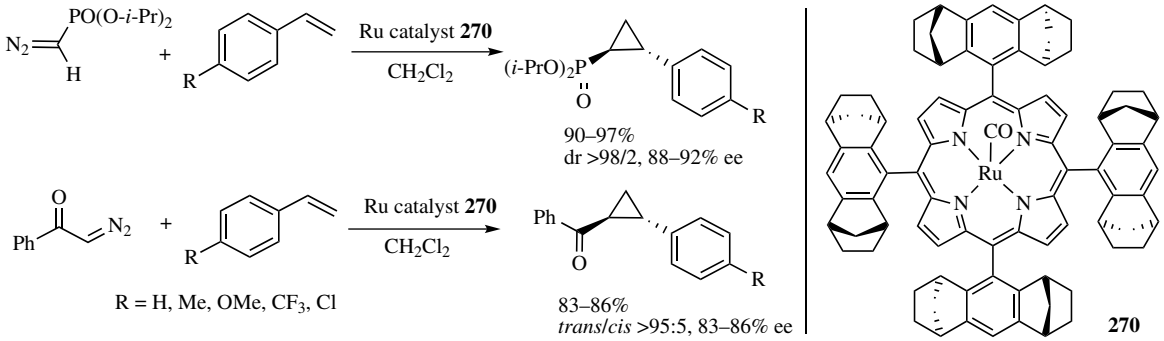
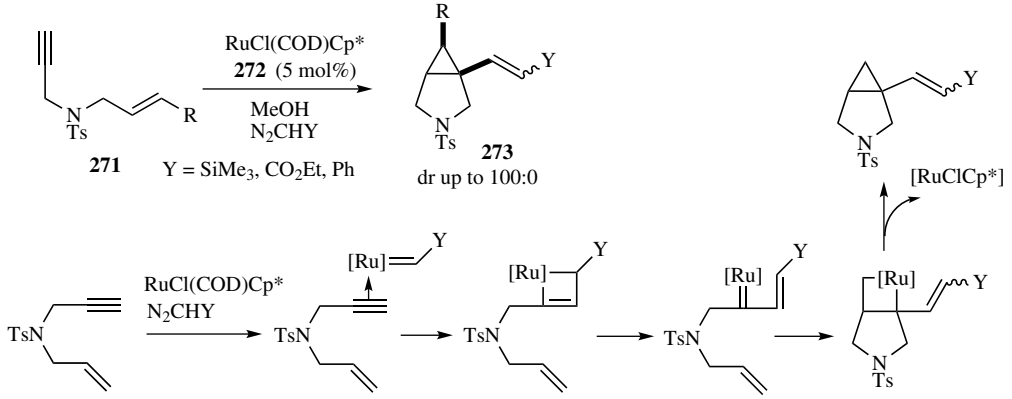


SCHEME 1.132

diazoacetophenone [190] with styrene and styrene-substituted compounds (Scheme 1.132). Usually, the *trans*-isomer was predominantly formed, and the enantiomeric excesses reached about 83% ee.

Trimethylsilyldiazomethane underwent the reaction with 1,6-ene-yne compounds **271** in the presence of ruthenium complex **272** (Scheme 1.133) [191]. Fused cyclopropane **273** was formed in a diastereoselective manner. A mechanistic study including theoretical calculation was reported.

A combination of cross-metathesis and cyclopropanation gave vinylcyclopropanes **274** (Scheme 1.134) [192]. Three-component coupling progressed with high efficiency.



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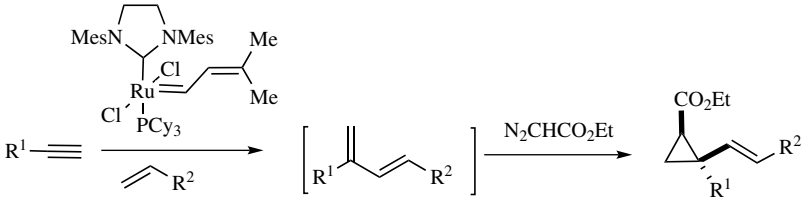


R^1 = Ph, 6-MeO-2-naphth, *p*-$CF_3C_6H_4$, Bu
R^2 = C_6H_{13}, $(CH_2)_8OTBS$, $(CH_2)_6OBn$, Ph

274
46–66% (*E*/*Z* = 1:1 to 1.9:1)

SCHEME 1.134

1.4.5 Cobalt- and Iron-Catalyzed Reactions [193]

Zhang and coworkers reported that D2-symmetric cobalt porphyrin **275** was examined for the asymmetric cyclopropanation of diazoacetate with styrenes and electron-deficient alkenes (Scheme 1.135) [194]. Good *trans*-selectivity was observed. Corresponding iron porphyrin yielded poor results; therefore, cobalt porphyrin was very advantageous for the selective cycloaddition reaction. The cobalt porphyrin complex also catalyzed the asymmetric cyclopropanation of tosyldiazomethane [195], nitrodiazoacetate **277** [196], and cyanodiazoacetate **276** with styrene derivatives [197]. After cyclopropanation, the nitro group of nitrodiazoacetate **277** was located *cis* to the aryl group in the product, while the cyano group of cyanodiazoacetate **276** was located *trans* to the aryl group in the product.

Chiral salen **278** [198] and bispyridyliminoisoindole **279** [199] complex of cobalt catalyzed the cyclopropanation reaction of diazoacetate (Scheme 1.136).

Trifluorodiazomethane **280** was generated *in situ* from trifluoroethylamine hydrochloride **281** in the presence of FeTPP **282** [200] or chiral salen-cobalt complex **283**. Chiral trifluoromethyl-substituted cyclopropane **284** was isolated in good yield with high optical purity (Scheme 1.137) [201]. This procedure for the cyclopropanation was also applicable to glycine ethyl ester **285** in the presence of FeTPPCl and $NaNO_2$, and cyclopropanes **286** were prepared in good yields [202]. This is useful for the synthesis of cyclopropanes without preparation of potentially hazardous diazoacetate intermediate.

1.4.6 Other Transition Metal-Catalyzed Reactions

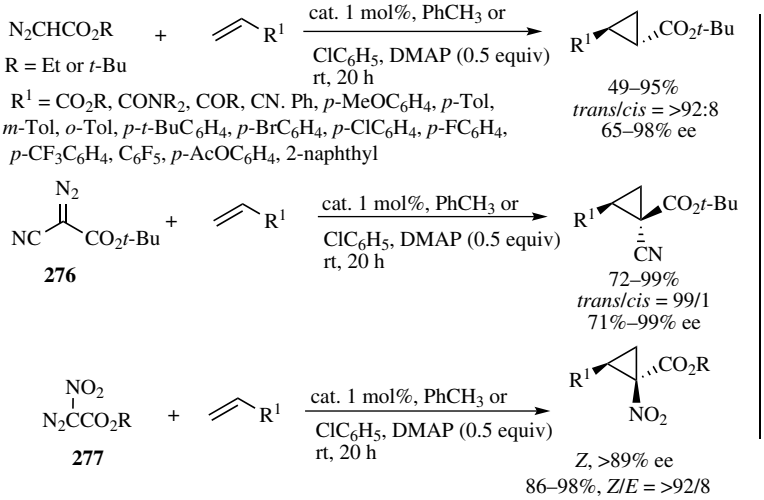
Palladium acetate catalyzes cyclopropanation with diazomethane and aryldiazoacetate (Scheme 1.138) [203].

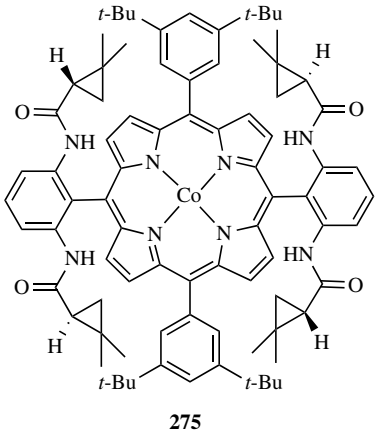
D2-symmetric iron porphyrin **287** promoted the asymmetric cyclopropanation of diazoketone (Scheme 1.139) [204]. The enantiomeric excesses of the products were approximately 60–80%.

Dötz and coworkers employed chromium complex **288** for the cyclopropanation of 1-alkoxy-1,3-dienes **289** (Scheme 1.140) [205]. High regio- and *trans*-selectivity was observed.

Rhenium(I) complex **290** was examined for the asymmetric cyclopropanation of diazoacetate (Scheme 1.141) [206]. A moderate level of asymmetric induction was observed.

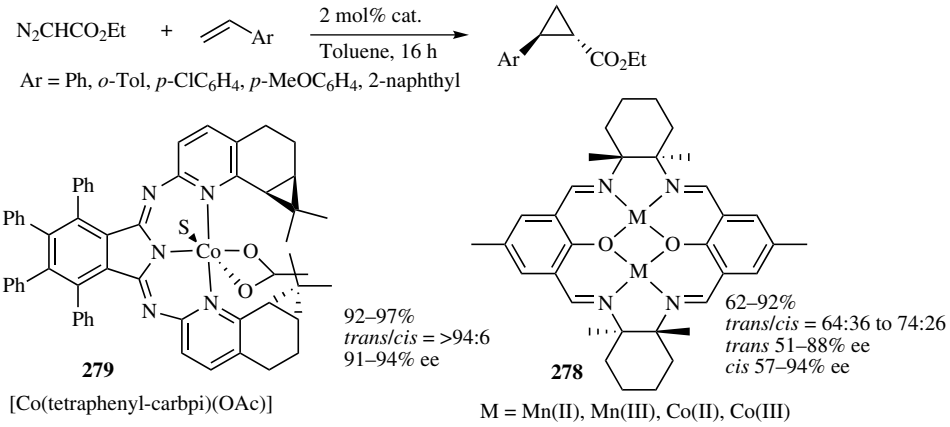
Katsuki and coworkers reported that the iridium complex of chiral salen **291** served as a good catalyst for





275

SCHEME 1.135



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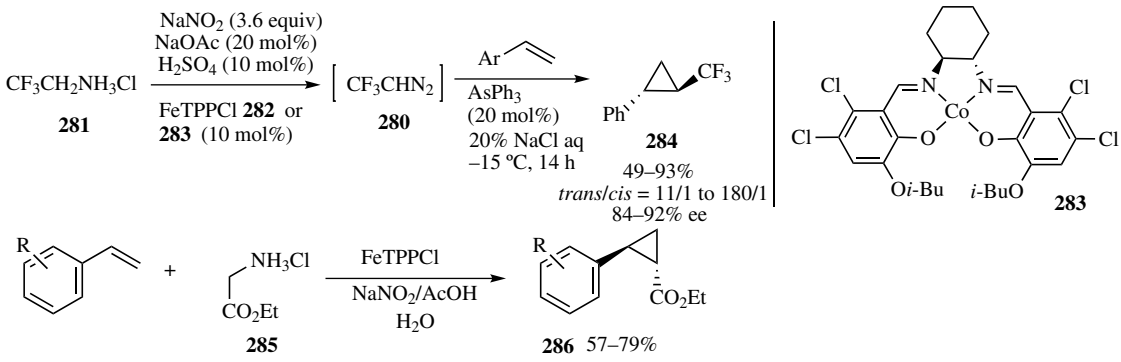

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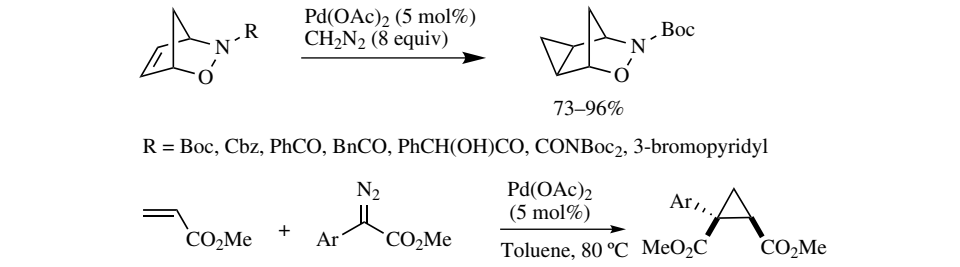

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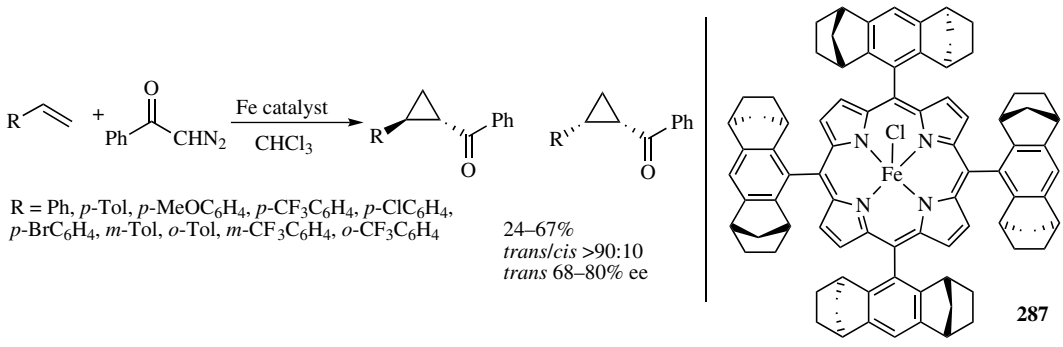

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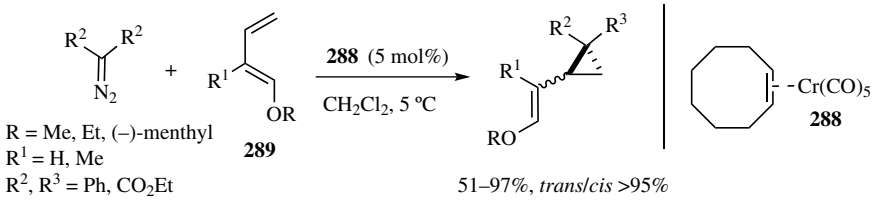

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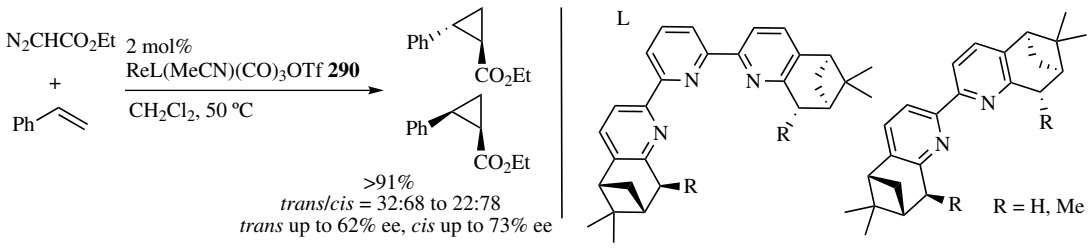

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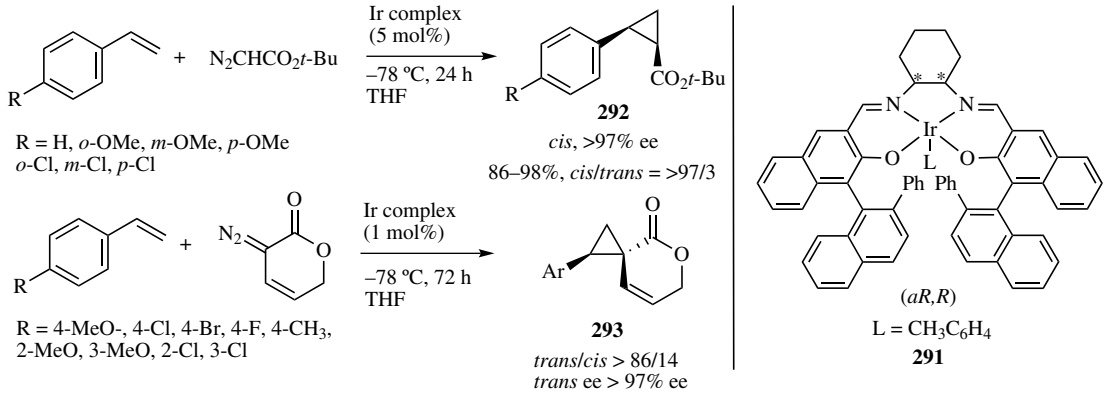


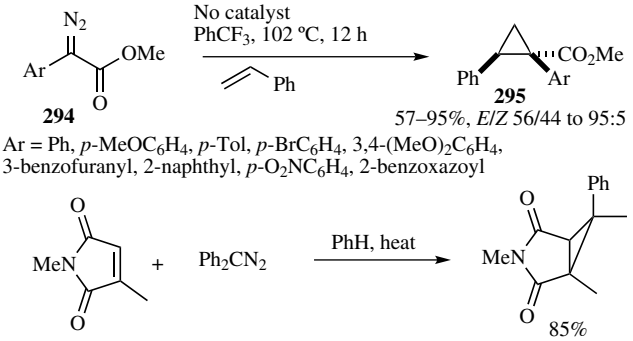
SCHEME 1.142

cyclopropanation (Scheme 1.142) [207]. Cyclopropanes **292** were formed *trans*-selectively. Diazolactone gave optically active spiro cyclopropanes **293**.

1.4.7 Cyclopropanation Without Transition Metal Catalysts

Diazoalkanes are reactive; consequently, cycloaddition occurs without transition metal catalysts. Davies and coworkers reported that aryldiazoacetate **294** underwent the formation of cyclopropanes with styrenes to give trisubstituted cyclopropanes **295** in good yields (Scheme 1.143) [208]. The active carbene was generated under thermal conditions.

Iodonium ylide **296** promoted intramolecular cycloaddition without a catalyst to give polycyclic cyclopropane **297** in good yield (Scheme 1.144) [209].



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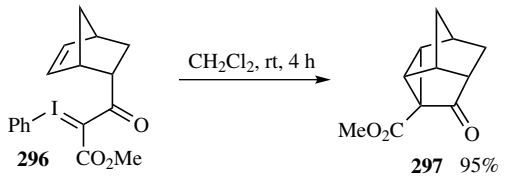


SCHEME 1.144

Cyclopropanation was induced under acid-catalyzed conditions (Scheme 1.145) [210]. Organocatalyst **298** promoted the catalytic asymmetric cyclopropanation of aryldiazoacetates [211]. High enantioselectivity was achieved.

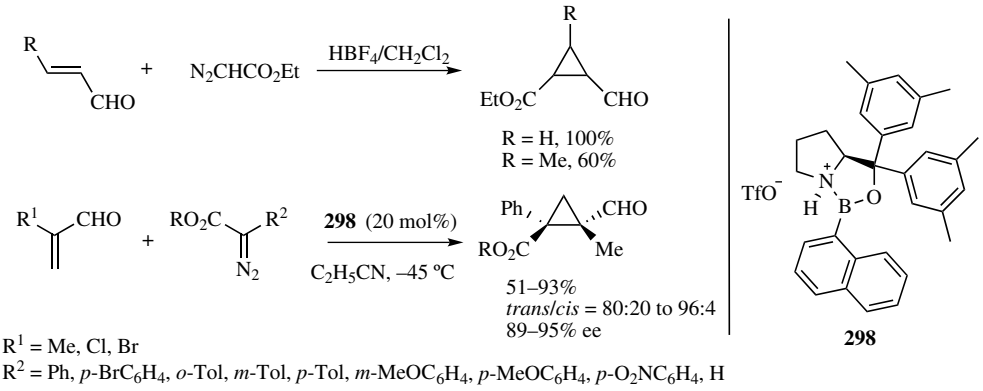
1.4.8 Cyclopropanation of Dihalocarbenes

Dichlorocarbene is readily generated from chloroform. Since NaOHaq is usually used as the base, the reaction becomes biphasic, and a good PTC is needed. Tetraalkylammonium salts **299** and **300** are usually used as the PTC catalyst (Scheme 1.146) [212].

Cyclopropanation of iron complex **301** also progressed but the stereoselectivity was moderate (Scheme 1.147) [213]. Iron complex **301** was also useful for the Simmons–Smith cyclopropanation reaction.

Dibromocarbene **302** was generated by the reductive treatment of CBr_4. For example, the treatment of CBr_4 with iron and copper resulted in two single-electron reductions of CBr_4 to give dibromocarbene, which underwent cycloaddition to alkenes to afford cyclopropane **303** (Scheme 1.148) [214].

Difluorocarbene is an important active species for the generation of difluorocyclopropanes; however, its generation requires a special strategy. Trimethylsilyl 2,2-difluoro-2-(fluorosulfonyl)acetate (TFDA) **304** was frequently used



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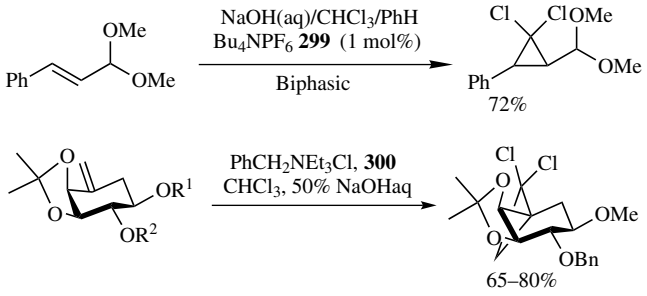

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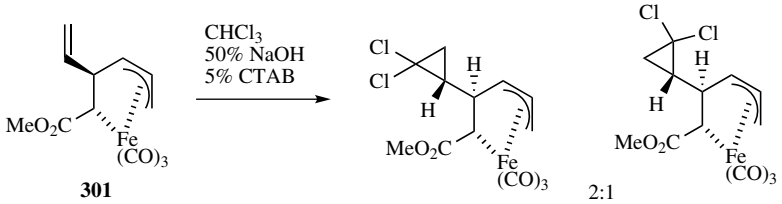

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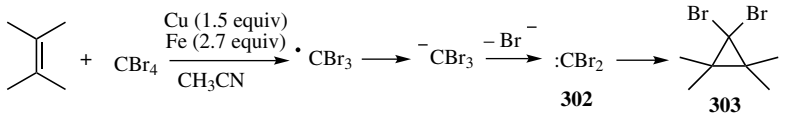

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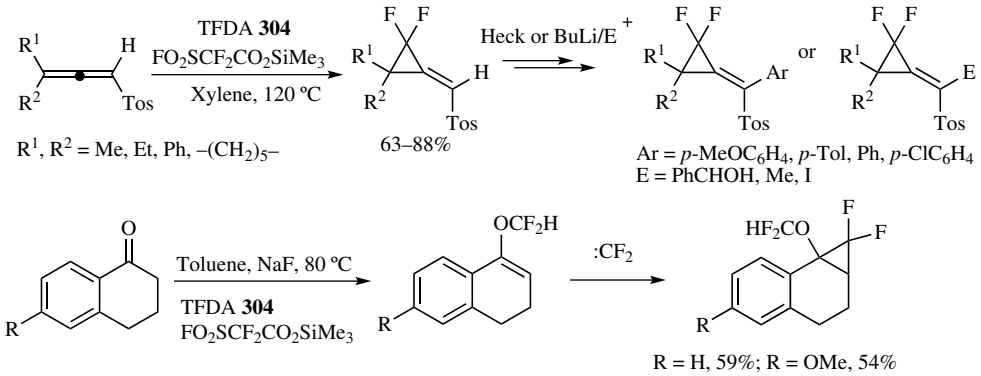

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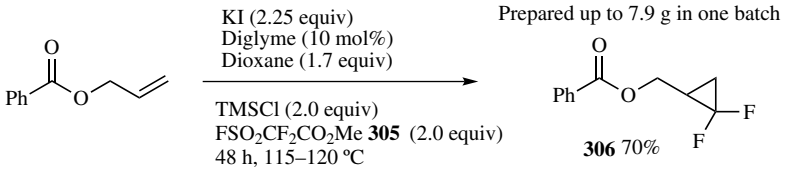

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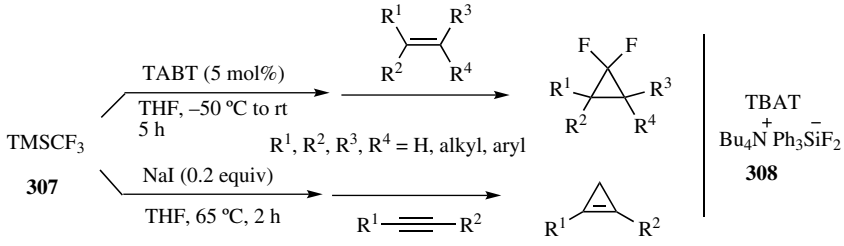


SCHEME 1.151

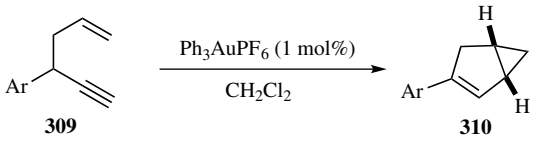
as the difluorocarbene precursor (Scheme 1.149) [215]. Methyl 2,2-difluoro-2-(fluorosulfonyl)acetate (MDFA) **305** and TMSCl serve as efficient sources of difluorocarbene. The large-scale preparation of difluorocyclopropane **306** was examined (Scheme 1.150) [216].

Trimethylsilyl trifluoromethane **307** was another source of difluorocarbene when it was treated with catalytic amounts of tetrabutylammonium triphenyldifluorosilicate **308** (TBAT) or NaI (Scheme 1.151) [217].

1.5 CYCLOISOMERIZATION WITH TRANSITION METAL CATALYSTS

1.5.1 Introduction

The intramolecular cycloisomerization of enyne compounds is an actively developing area for cyclopropanation. In this strategy, a metal–carbene complex is generated during the reaction process and it undergoes cyclopropanation with an alkene unit in an intramolecular manner. Gold and ruthenium



SCHEME 1.152

complexes mainly catalyzed the reaction, but other transition metal complexes are also employed for this type of reaction. Some intermolecular reactions between alkenes and alkynes have been reported. We will present some recent examples of this strategy.

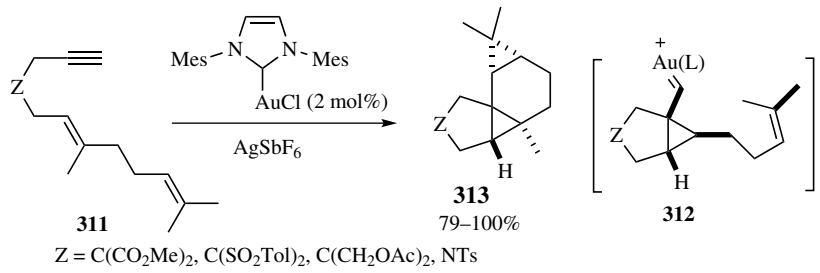
1.5.2 Gold Complex-Catalyzed Reactions

Gold complexes are the most useful catalyst for the cyclopropanation reaction. A recent minireview is available [218]. Toste and coworkers reported that a gold complex catalyzed the intramolecular cyclopropanation of enyne compounds (Scheme 1.152) [219]. They successfully obtained bicyclo [3.1.0]hexane **310** from 1,5-enyne compound **309** in good yields in the presence of catalytic amounts of a gold(I) complex.

Cyclopropanation progressed through a cyclopropyl methyl carbene complex of gold **312**, which is active toward further cyclopropanation with an intramolecular alkene unit. Echavarren and coworkers reported that dienyne compounds **311** gave tricyclic cyclopropanes **313** in good yields (Scheme 1.153) [220].

The use of cyclic alkenes **314** also gave tricyclic cyclopropanes **315** (Scheme 1.154) [221]. Cyclopropanation progressed from 1,6-enynes **316** with oxidative treatment [222]. Asymmetric cyclopropanation was examined and applied to the preparation of GSK1360707F **317** [223].

This methodology was used for the asymmetric preparation of a medium-sized ring (Scheme 1.155) [224]. Toste and coworkers obtained optically active tricyclic cyclooctane **318** and cycloheptanes from benzo-fused enyne compounds by



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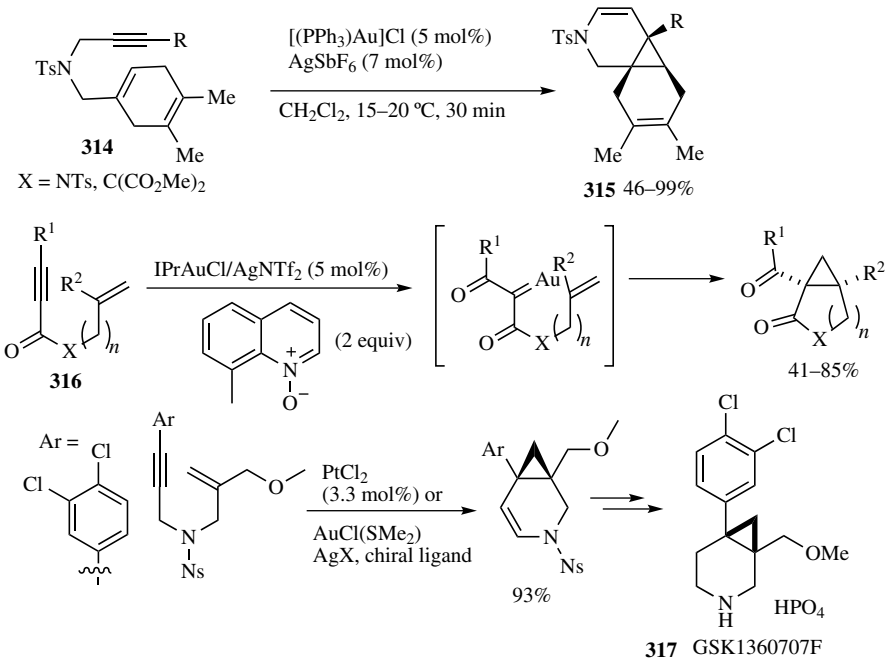

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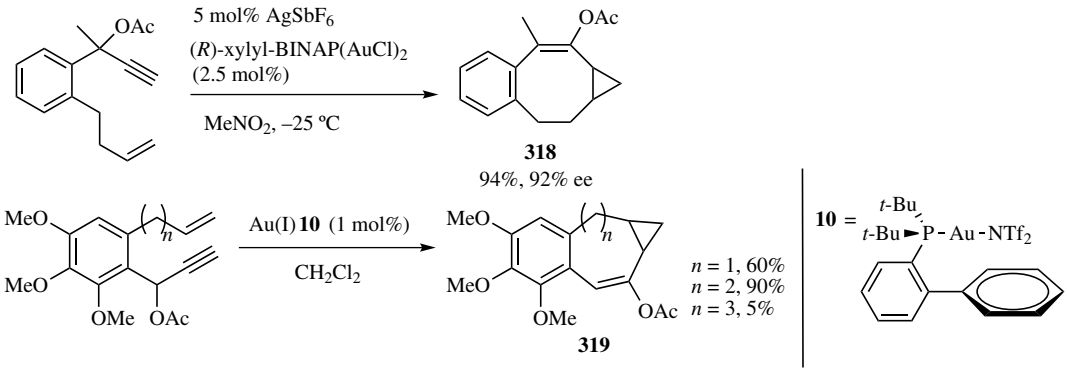


SCHEME 1.155

the presence of a chiral gold catalyst. Hanna and coworkers explored cyclopropanation for the synthesis of allocolchicinoids to give **319** [225].

The C—H insertion of a gold carbene complex provided the formation of tetracyclic cyclopropanes **320** (Scheme 1.156) [226].

This type of cyclopropanation reaction catalyzed by a gold(I) complex produced cyclopropylmethyl carbene complex **321**, which is reactive toward external alkenes or nucleophiles. The reaction depended on the ligand of the gold complex as well as the substituted patterns of enyne compounds. Echavarren and coworkers reported a cyclopropanation reaction mechanism. The cyclopropane gold complex intermediates **322** and **323** were trapped by external alkenes to give cyclopropanes **324** and **325**, respectively (Scheme 1.157) [227].

The gold complex intermediates were also trapped by active methylene compounds or aldehydes (Scheme 1.158). The reaction pathway depended on the gold catalysts; NHC–gold complex **326** gave cyclopropanes **327** in good yields in a chemoselective manner, while alkoxy–gold complex **328** formed *exo*-methylene compounds **329** [228].

The presence of an aldehyde gave tetrahydrofuran-fused cyclopropanes **330** (Scheme 1.159) [229]. This reaction passed through a gold complex intermediate **331**, which was trapped by aldehyde to give cationic intermediate **332**. Finally, nucleophilic attack afforded cyclopropanes. This type of trapping by aldehydes occurred in an intramolecular manner to give **333** in good yields (Scheme 1.160) [230].

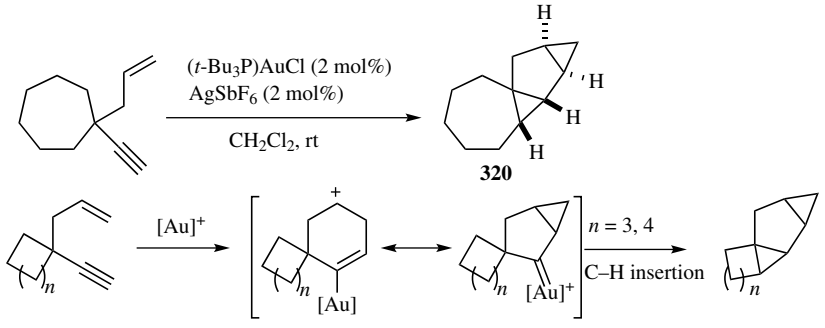
Combining this cycloisomerization reaction with metalla-Nazarov rearrangement gave tetracyclic cyclopropanes **334** in good yield. The stereoselectivity was very high, and a single isomer was isolated (Scheme 1.161) [231].

Cycloisomerization progressed from cyclopropenyl alkene **335** in the presence of a gold(I) catalyst (Scheme 1.162) [232]. *Exo*-methylene cyclopropane **336** was produced in a stereoselective manner.

Intermolecular reactions between alkyne and alkenes have also been reported. Vinylcyclopropanes **337** and **338** were prepared by these reactions (Scheme 1.163) [233]. The use of DTBM-SEGPHOS($AuCl_2$) achieved asymmetric cyclopropanation and chiral cyclopropanes were obtained with up to 81% ee.

1.5.3 Palladium Complex-Catalyzed Reactions

Cyclopropanation from the intermolecular or intramolecular cycloisomerization of enyne compounds has been reported. Intermolecular cyclopropanation between norbornadiene **339** and styrene was achieved by palladium(II) complex **340** (Scheme 1.164) [234].



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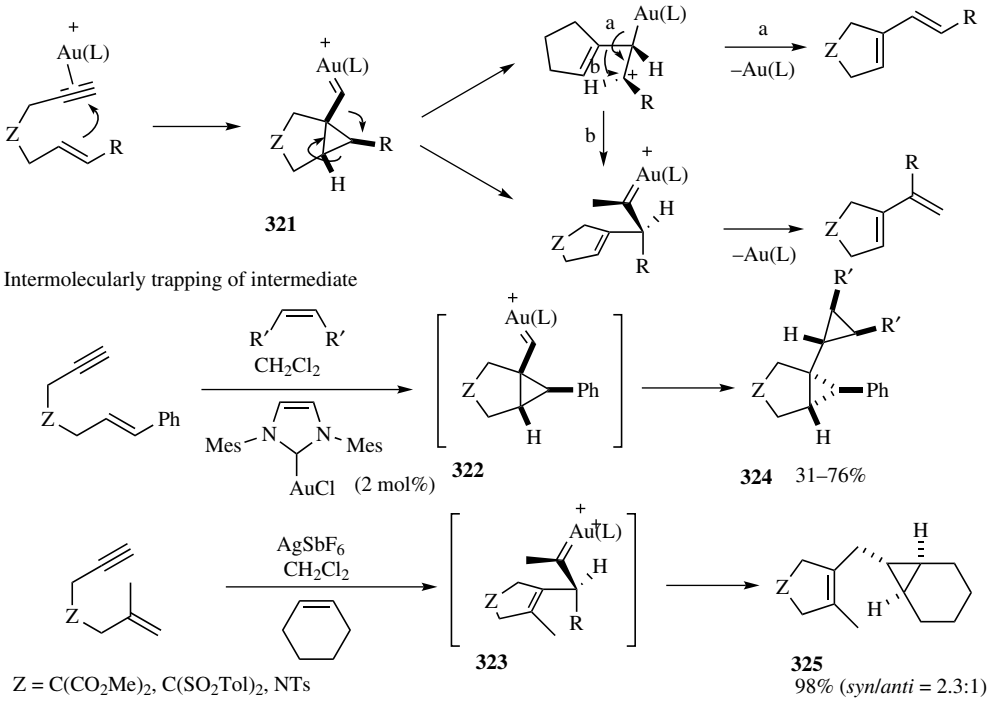
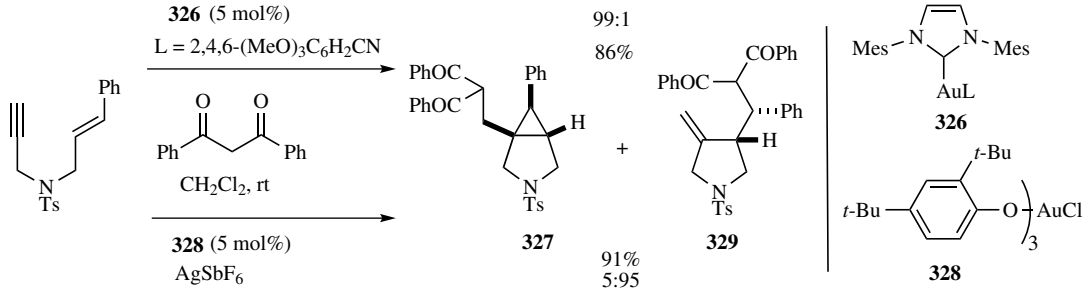


SCHEME 1.157



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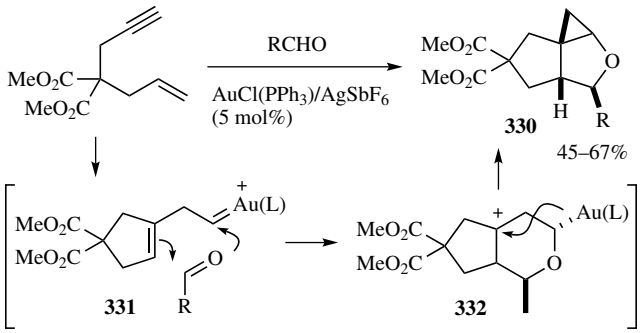
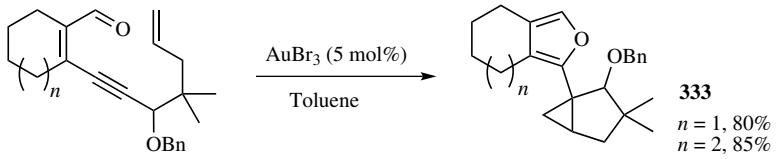


SCHEME 1.159

The allyl ester of acetylene carboxylate **341** was employed as a good precursor for the preparation of cyclopropane-fused γ-butyrolactones **342** (Scheme 1.165) [235]. The reaction progressed in the presence of catalytic amounts of $Pd(OAc)_2$ and stoichiometric amounts of an oxidant such as $PhI(OAc)_2$. Palladium(II) and palladium(IV) were presumed to be a catalytic cycle of the reaction. Amide derivative **343**, which was readily prepared by the Ugi reaction, gave corresponding cyclopropane-fused γ-butyrolactam **344** in moderate yields (Scheme 1.166) [236].

Nucleophilic attack of a π-allyl palladium complex gave cyclopropanes. Intramolecular cyclopropanation was achieved



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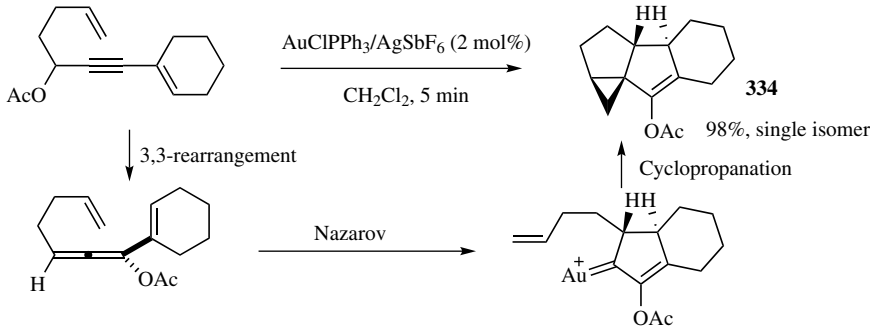

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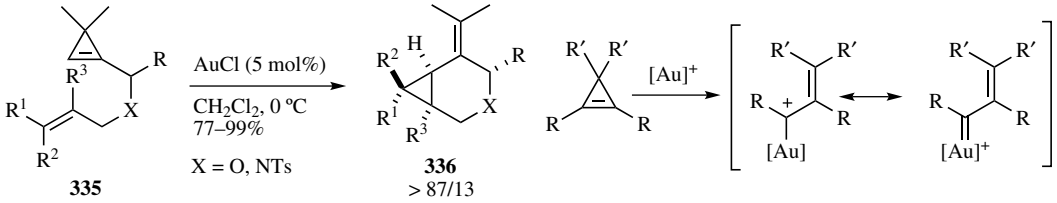

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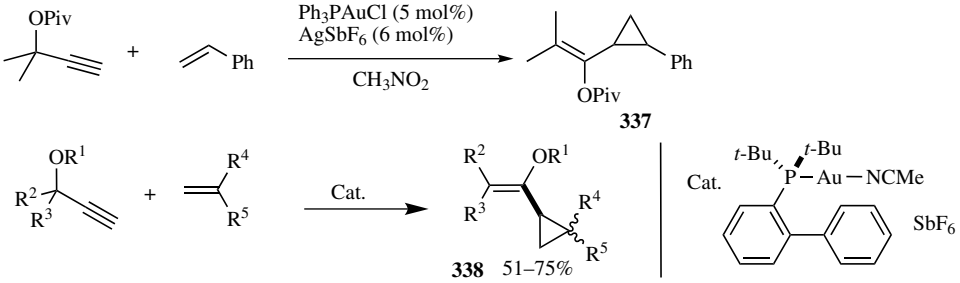

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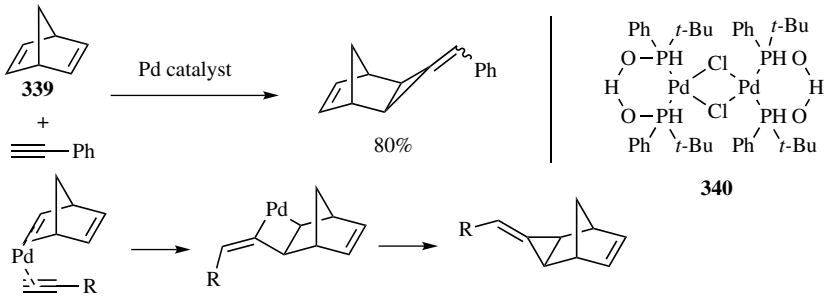

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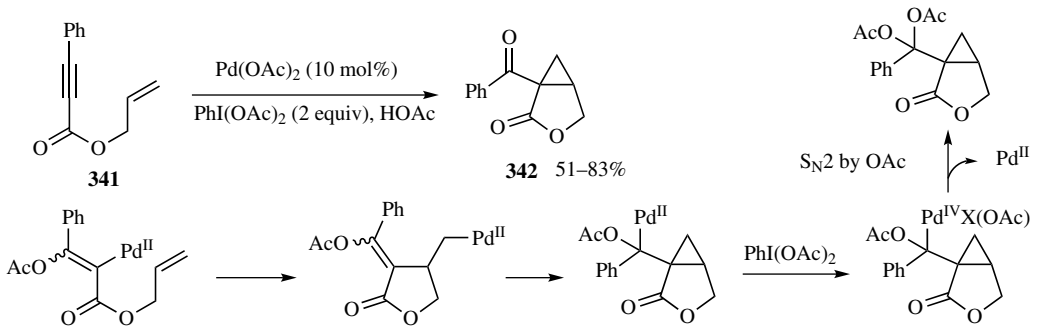

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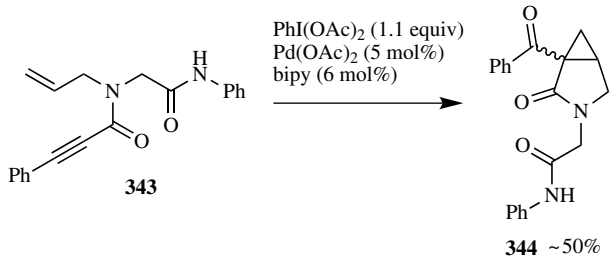
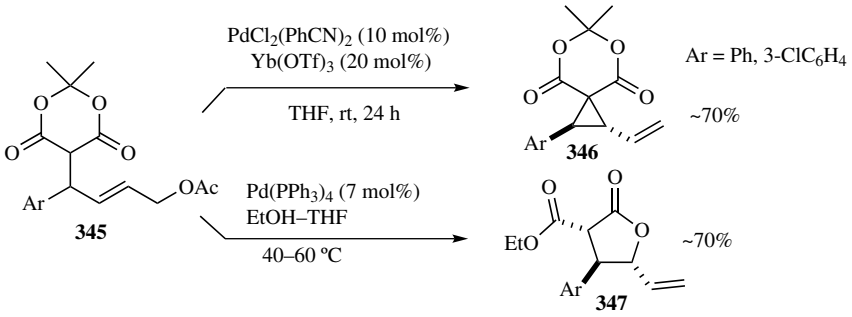


SCHEME 1.166

from an allylic maleic ester **345** to give spiro cyclopropane **346** and **347** in 70% yields (Scheme 1.167) [237]. The reaction pathway depended on the catalyst, and C-alkylation was selectively promoted in the presence of $PdCl_2(PhCN)_2$. Enantioselective intermolecular cyclopropanation between allyl carbonates and diphenylamide catalyzed by a palladium complex attached by ferrocenyl chiral ligand **348** has been reported (Scheme 1.168) [238].

Hayashi and coworkers reported that 2-alkylidene-1,3-propandiol carbonates **349** underwent cascade-type cyclopropanation in the presence of isocyanate (Scheme 1.169) [239]. In this reaction, a π-allyl complex **350** underwent decarboxylation and esterification with isocyanate to give **351**, which then underwent nucleophilic attack by an amide anion to afford spirocyclopropane **352** in good yields. The diastereoselectivity of the reaction was generally high. A similar type of the reaction progressed between methylene δ-lactones **353** and aromatic aldehydes to give spiro cyclopropanes **354** [240]. *N*-Allyl-*N*-allenyl amine gave cyclopropane-fused pyrrolidines **355** (Scheme 1.170) [241]. Allenyl malonate **356** and aryl halide also gave cyclopropanes **35**7 in a stereoselective manner (Scheme 1.171) [242].

A C—H activation process was employed during an intramolecular cyclopropanation (Scheme 1.172) [243].



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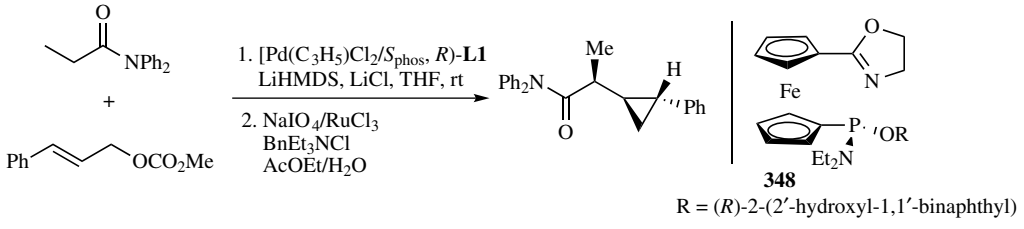

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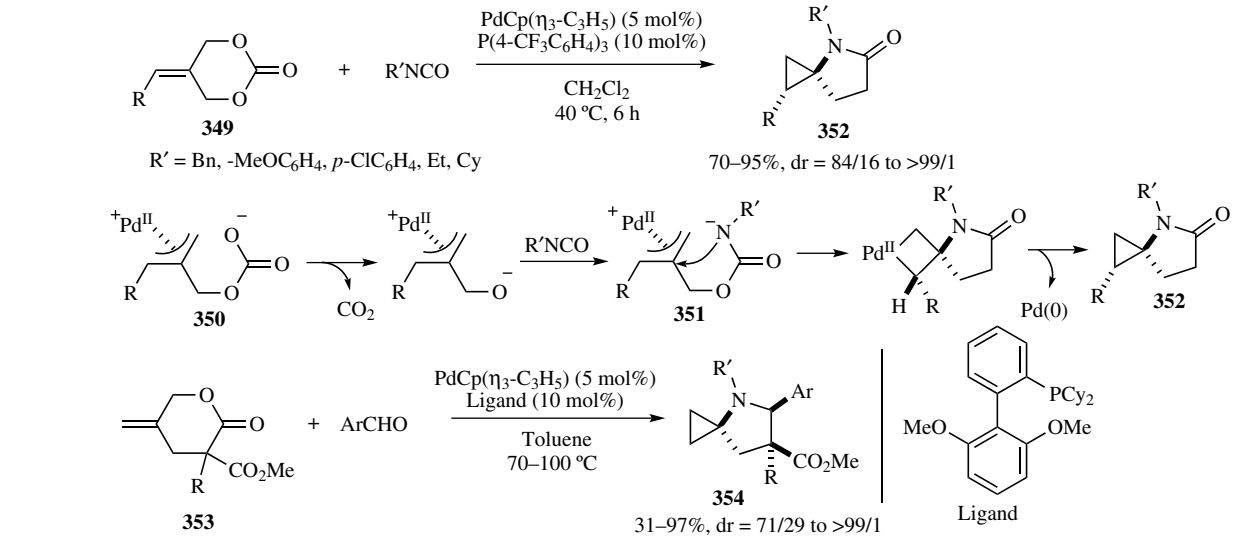

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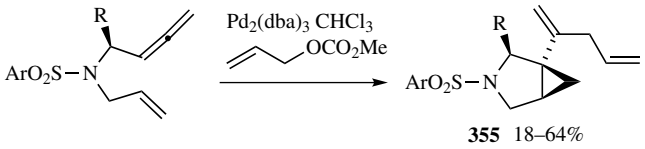
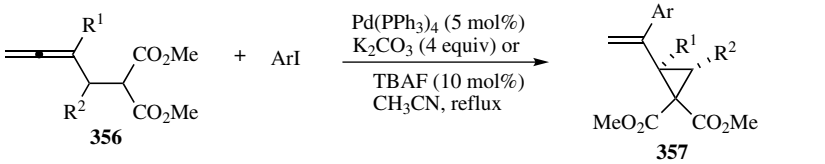


SCHEME 1.170

Liron and Knochel reported the preparation of cyclopropane-fused indanes **359** from 1-bromo-2-crotylbenzenes **358** in the presence of $Pd(OAc)_2$. C—H activation progressed during the cyclopropane formation. 1-Bromo-2-allyloxybenzenes **360** also underwent a similar reaction to give **361** in 77% yield [244].



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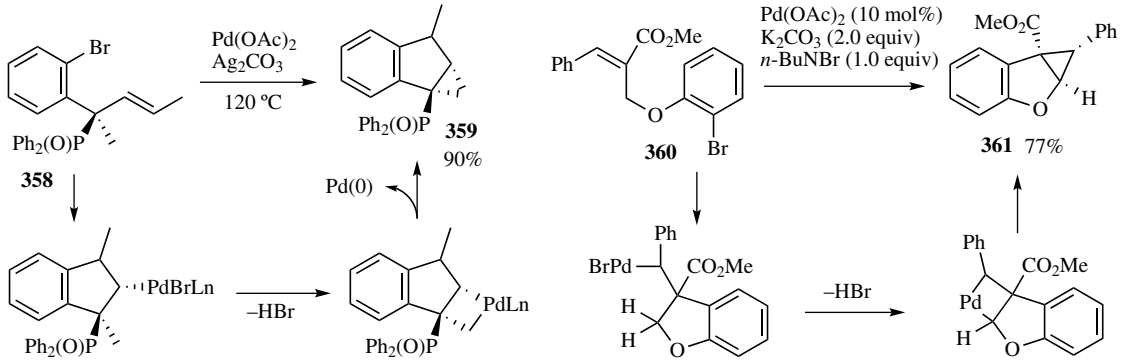

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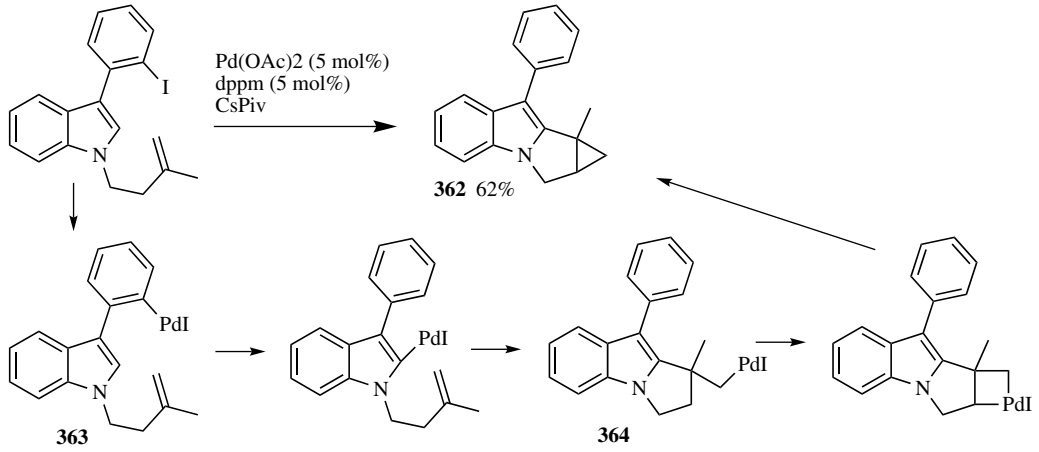


SCHEME 1.173

Huang and Larock reported a similar cyclopropanation reaction to prepare cyclopropane-fused indole **362** (Scheme 1.173) [245]. The initial phenyl palladium complex **363** rearranged to indole-palladium **364**, which underwent the cyclopropanation reaction.

1.5.4 Platinum Complex-Catalyzed Reactions

1,5-Enyne compounds underwent the cyclopropanation reaction in the presence of catalytic amounts of $PtCl_2$. Malacria and coworkers reported that intramolecular cyclization/cyclopropanation progressed from 1,5-enyne-containing medium-sized rings **365** and **366** to give tricyclic cyclopropanes **367** and **368**, respectively (Scheme 1.174) [246].

1,3-Diyne-6-enes **369** also gave bicyclic cyclopropanes **370** by a $PtCl_2$-catalyzed reaction (Scheme 1.175) [247]. The reaction intermediate **371** underwent a 1,3-shift of the platinum carbene complex.

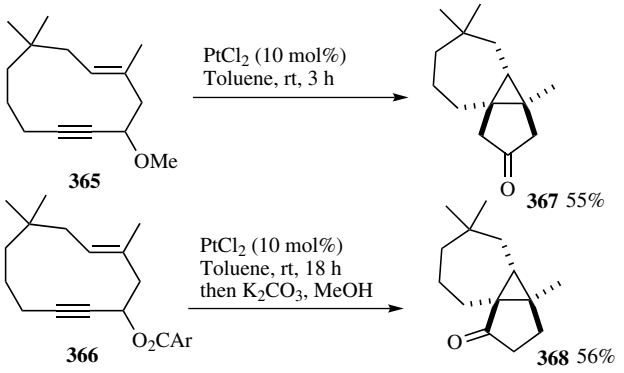
The reaction started from the complexation of $PtCl_2$ with the alkyne unit in **372** to give vinyl platinum **373**. An intermediate **373** was attacked by carbonyl oxygen if the enyne compounds contained the oxygen atom at an appropriate position. This process caused a shift of the acetate unit and provided vinyl platinum carbene complex **374**, which gave cyclohexane-fused cyclopropane **375** (Scheme 1.176) [248].

The dihydropyranyl unit in **376** cyclized to a platinum alkyne complex in a 6-*endo*-selective manner, and tricyclic cyclopropanes **377** were prepared in good yields (Scheme 1.177) [249].

1,6-Dienes **378** also cyclized to give cyclopropanes **380** in the presence of Pt(PPP) complex **379** (Scheme 1.178) [250]. Chiral ligand **381** achieved asymmetric cyclopropanation (Scheme 1.179) [251].

1.5.5 Ruthenium Complex-Catalyzed Reactions

The treatment of 1,6-enynes with 5 mol% amounts of cp*RuCl(cod) **382** in the presence of diazoalkanes resulted in the formation of bicyclic cyclopropanes **383** in good yields (Scheme 1.180) [252]. The reaction progressed through the formation of ruthenacyclobutene **384**, which cleaved to give a ruthenium carbene complex **385**. A [2+2] cycloaddition of the complex **385** with the internal alkene



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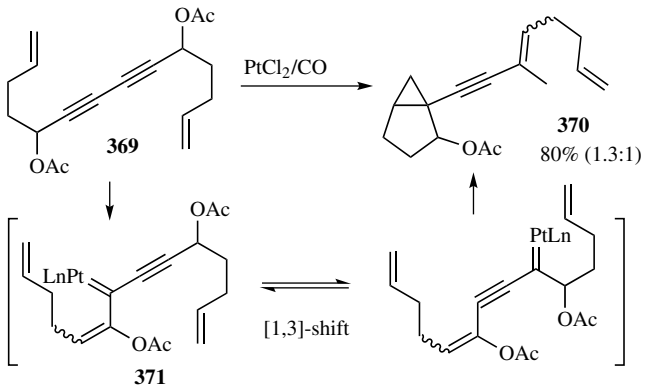

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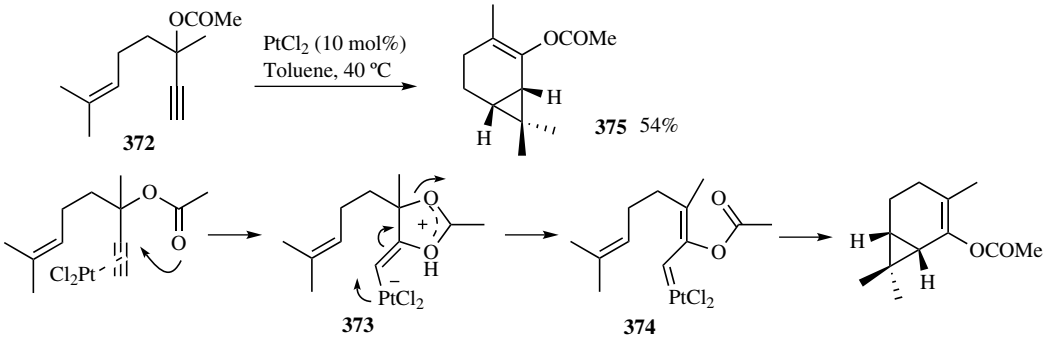

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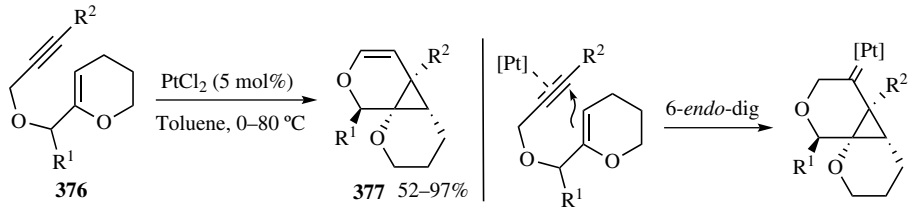

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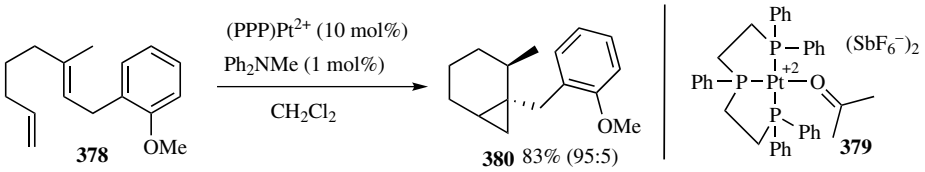
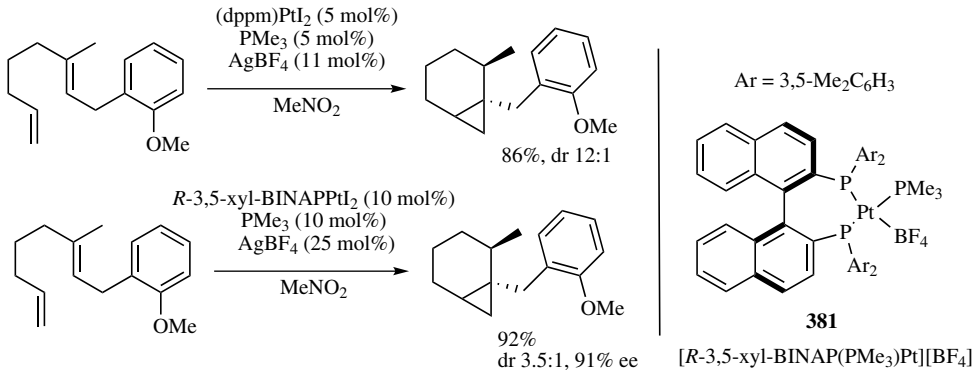


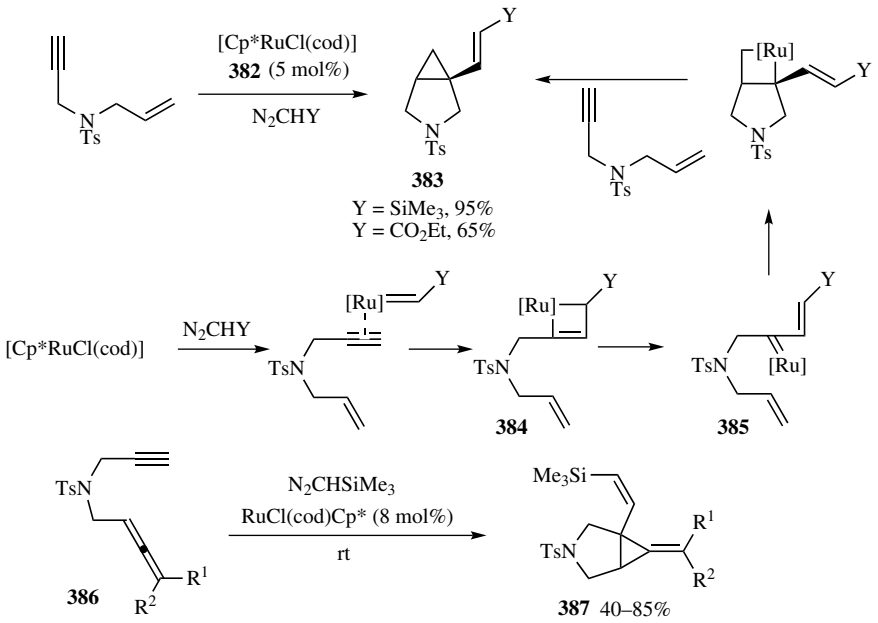
SCHEME 1.178

unit and subsequent elimination of the ruthenium unit gave cyclopropanes **383** in good yields. Allene derivatives **386** also underwent a similar reaction to give methylene cyclopropanes **387** [253].

Propargyl alcohols and esters underwent intermolecular or intramolecular cyclopropanation catalyzed by ruthenium complexes. For example, Uemura and coworkers reported that intermolecular cyclopropanation was achieved from propargyl ester **388** and styrene to give vinylcyclopropanes **389** in good yield (Scheme 1.181) [254]. The ester unit at the propargylic position assisted in the coordination of ruthenium, which promoted the reaction. Tenaglia and Marc reported a similar reaction between propargylic ester and norbornadiene catalyzed by $CpRuCl(PPh_3)_2$ [255].



SCHEME 1.179



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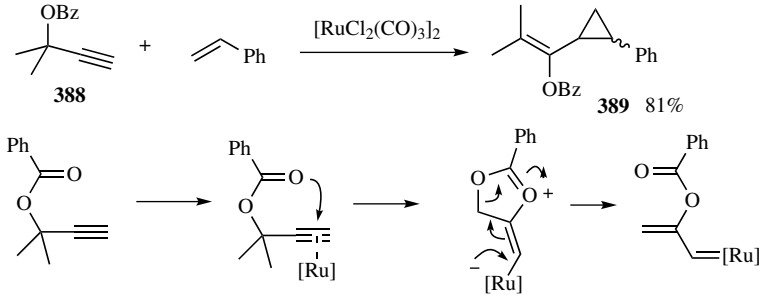


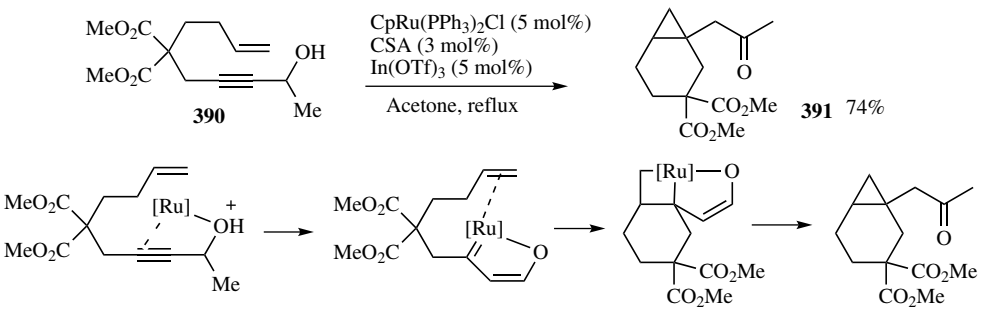
SCHEME 1.181

Trost et al. reported the intramolecular cyclopropanation of 1,7-enyne compounds **390** (Scheme 1.182) [256]. A hydroxyl group at the propargylic position assisted in the complexation of ruthenium. Bicyclic cyclopropane **391** was obtained in good yields.

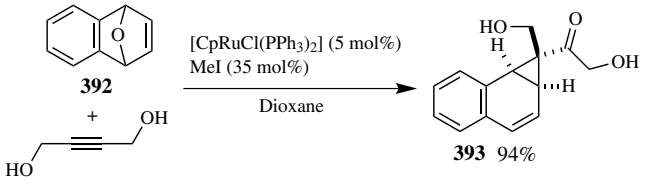
Oxabenzonorbornadiene **392** underwent a similar cyclopropanation reaction catalyzed by $CpRuCl(PPh_3)_2$ to give benzonorcaradienes **393** (Scheme 1.183) [257].

Ring-closing metathesis of **394** followed by further treatment with diazoalkanes or carbenoid gave cyclopropanes **395** or **396**, respectively (Scheme 1.184) [258].

A ruthenium complex is also useful for generating a radical species, which undergoes an addition reaction. Combined with manganese metal as a reducing agent, the ruthenium complex gave cyclopropanes **397** in a *cis*-selective manner (Scheme 1.185) [259].



SCHEME 1.182

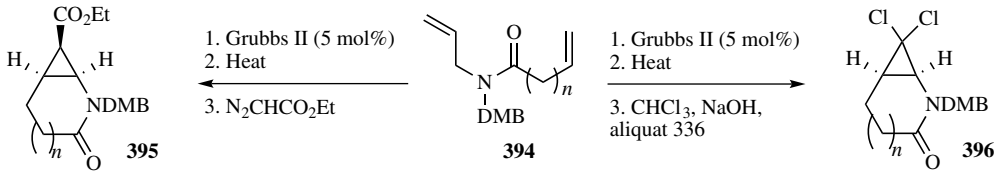


SCHEME 1.183

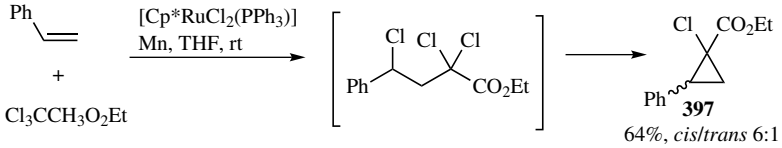
Uemura and coworkers reported novel sequential catalytic cyclopropanation from enyne compounds **398** catalyzed by a ruthenium complex and $PtCl_2$ (Scheme 1.186) [260]. Other metallic salts such as $PtCl_4$, $PdCl_2$, $AuCl_3$, and $Rh_2(OAc)_4$ were not useful for the reaction. The reaction progressed in a *syn*-selective manner. First, the ruthenium complex generated ruthenium allene complex **399**, which promoted a cyclization reaction to give 1,5-enyne intermediate **400**. Then the intermediate **400** was catalyzed by $PtCl_2$ to give cyclopropanes **401** in good yields.

1.5.6 Other Metal Complex-Catalyzed Reactions

Optically active furyl cyclopropane **402** was prepared from acetylene dicarboxylate and alkenes (Scheme 1.187) [261]. The acetylene dicarboxylate underwent dimerization to form metallocyclopentadiene **403**, which decomposes to give cyclopropanes containing rhodium carbene complex **404**. A good level of chiral induction was achieved using Segphos® ligand with $Rh(cod)_2BF_4$.



SCHEME 1.184



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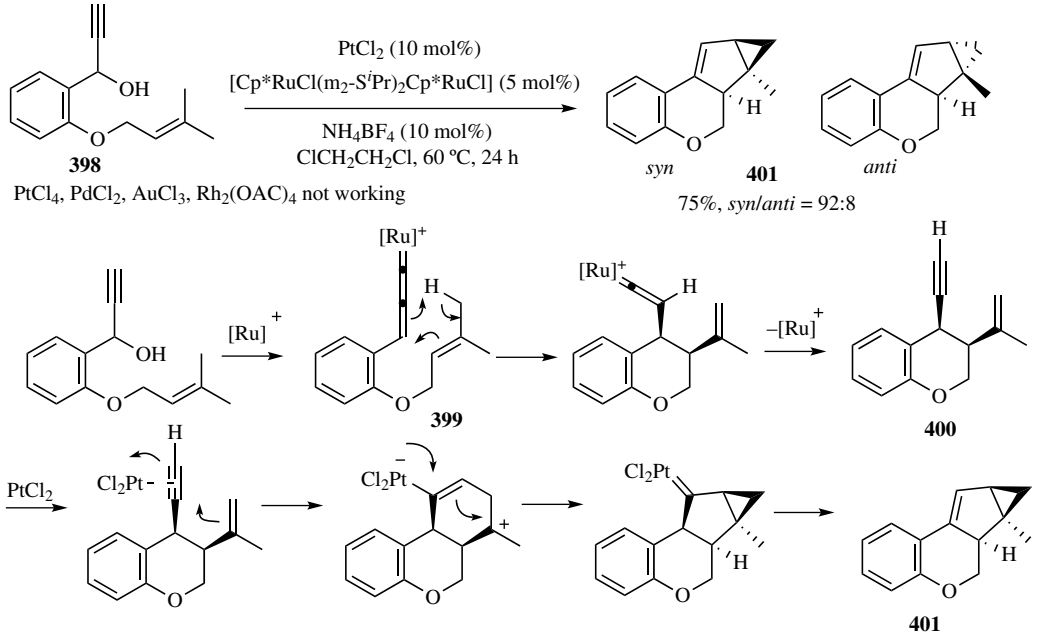
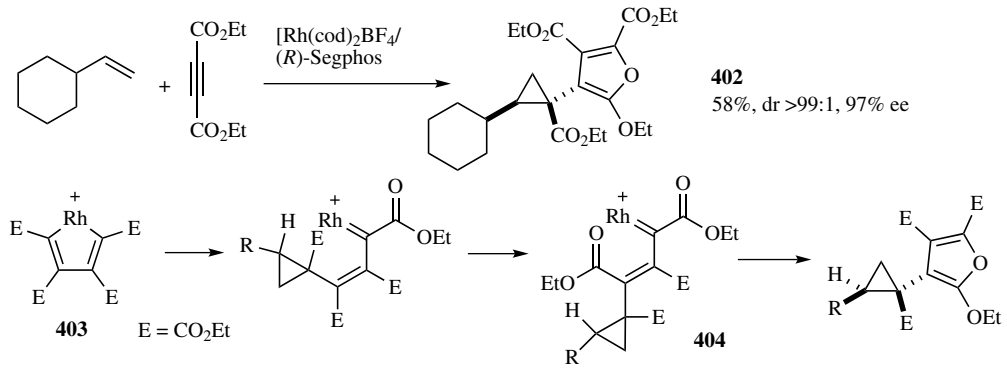
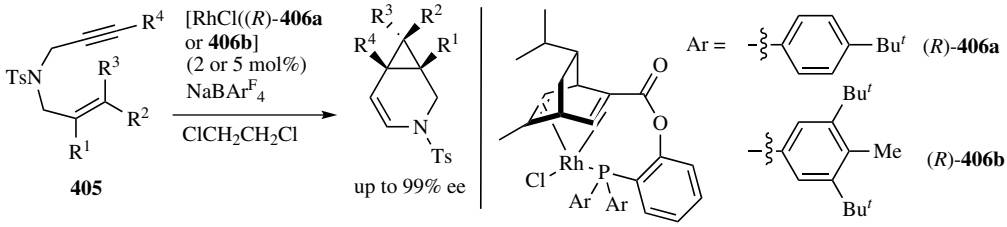


SCHEME 1.186



SCHEME 1.187



SCHEME 1.188

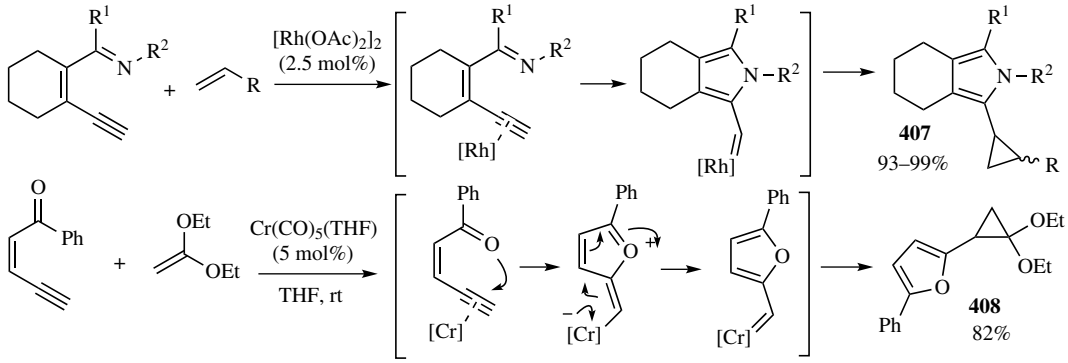
Hayashi and coworkers achieved an asymmetric 1,6-enyne isomerization reaction of **405** using chiral rhodium complexes **406** (Scheme 1.188) [262]. Enantioselectivity reached up to 99% ee.

Uemura and coworkers reported the preparation of pyrrolo cyclopropane **407** using a rhodium catalyst (Scheme 1.189) [263]. Furanyl cyclopropanes **408** were also prepared in a similar manner to this reaction catalyzed by a chromium complex [264].

Chromium Fischer carbene complexes **409** and **410** underwent intermolecular or intramolecular cyclopropanation. The treatment of the carbene complex with lithium enolates resulted in the formation of a cyclopropane in good yield (Scheme 1.190) [265]. An intramolecular reaction for **410** was also reported [266].

The cycloisomerization reaction was also catalyzed by copper(I) complexes. The examples were well reviewed by Fehr [267]. Cycloisomerization of 1,5-enyne compounds **411** was explored using transition metal-catalyzed conditions (Scheme 1.191) [268]. Among the metal complexes examined, $Cu(CH_3CN)_4BF_4$ provided the best results for the formation of tricyclic cyclopropanes **412**. 1,6-Enyne **413** also underwent a similar cycloisomerization reaction to give polycyclic cyclopropanes **414** (Scheme 1.192) [269].

Ito and coworkers reported a new type of cyclopropanation from *Z*-allylic phosphonates **415** (Scheme 1.193) [270]. The reaction proceeded in the presence of catalytic amounts of CuCl and bispinacolate borane. Good diastereoselectivity and enantioselectivity were achieved using the (*R*,*R*)-*i*-PrDuPhos ligand.



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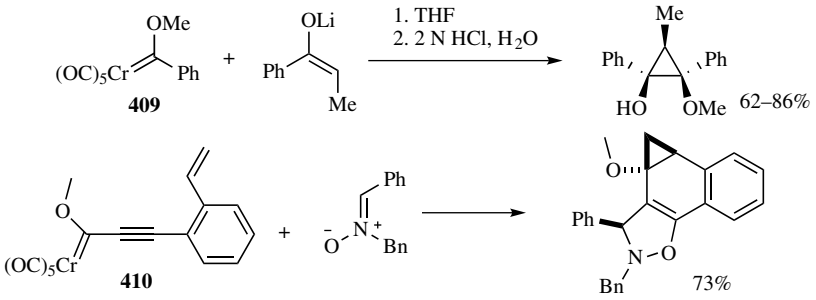

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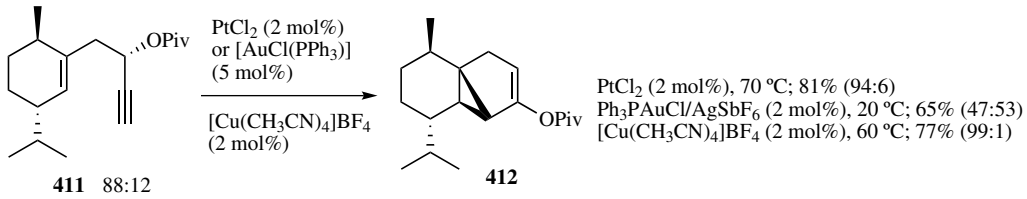
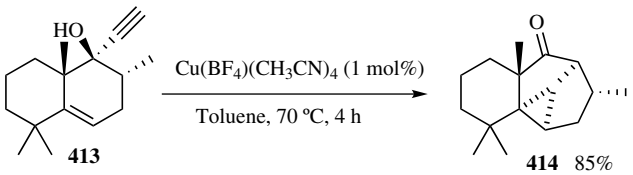


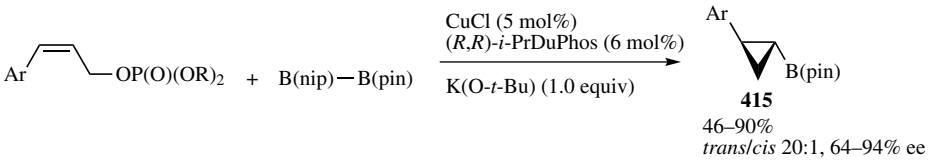
SCHEME 1.191



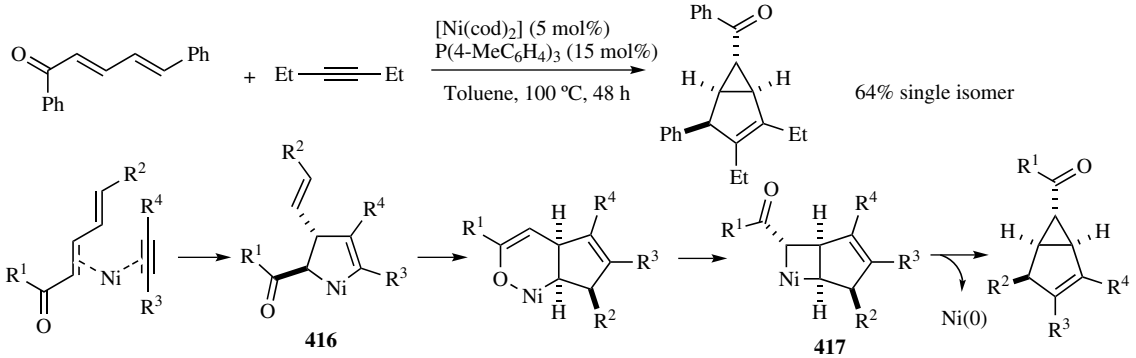
SCHEME 1.192

Ni(cod)-catalyzed intermolecular cyclopropanation between alkene and unsaturated dienes progressed through metallocyclobutane **416**, which isomerized to form metallocyclobutane **417** (Scheme 1.194) [271].

Iron-mediated cyclopropane synthesis was reported (Scheme 1.195) [272]. A mechanistic study was also performed.



SCHEME 1.193



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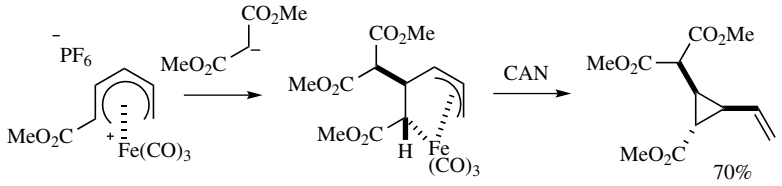


SCHEME 1.195

1.6 KULINKOVICH REACTIONS

1.6.1 Introduction

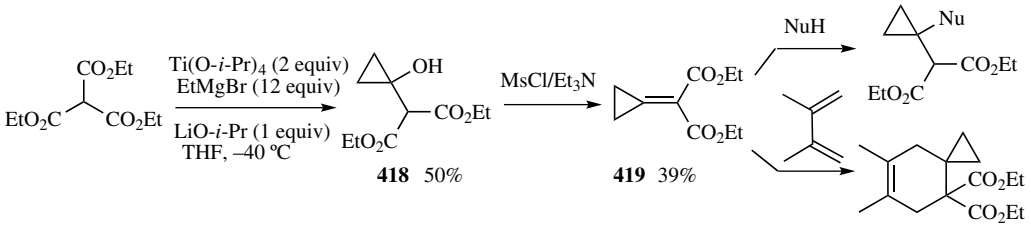
The Kulinkovich reaction is a unique reaction, in which cyclopropane derivatives are formed by a reaction between titanacyclopropanes and ester derivatives. The reaction was established by Kulinkovich in 1989 [273], and a recent review has been published [274, 275]. Titanacyclopropanes were generated from a Grignard reagent and Ti(O-*i*-Pr)$_4$, and the reaction with esters gave cyclopropanol in good yields. When amides are used instead, cyclopropane amine is formed. The mechanistic study on the Kulinkovich reaction was performed [276].

1.6.2 The Kulinkovich Reaction to Esters, Ketones, and Amides

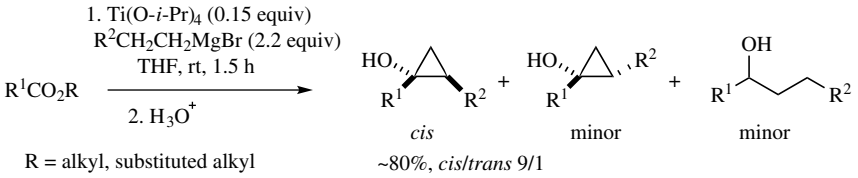
Activated methylene cyclopropane was prepared by de Meijere's group using Kulinkovich's method (Scheme 1.196) [277]. Triester was treated with excess amounts of Grignard reagent in the presence of Ti(O-*i*-Pr)$_4$, and cyclopropanol **418** was obtained in 50% yield. A dehydration reaction converted **418** to methylene cyclopropane **419**, which was a potentially useful synthetic building block for conjugate addition and the Diels–Alder reaction. Methylene cyclopropane **419** was somewhat unstable because of its strong reactivity; however, a combined method for the generation of the methylene cyclopropane and the following reaction gave good results.

Kulinkovich and Kananovich examined ways to reduce the amounts of Ti(O-*i*-Pr)$_4$ (Scheme 1.197) [278]. They improved the reaction procedure and reduced the amounts of Ti(O-*i*-Pr)$_4$ to catalytic amounts.

An intramolecular Kulinkovich reaction afforded bicyclic cyclopropanes **420** from an optically active natural amino acid (Scheme 1.198) [279]. The preparation of optically active azabicyclo[3.1.0]hexanols **420** from natural aspartic or glutamic acid was demonstrated.



SCHEME 1.196



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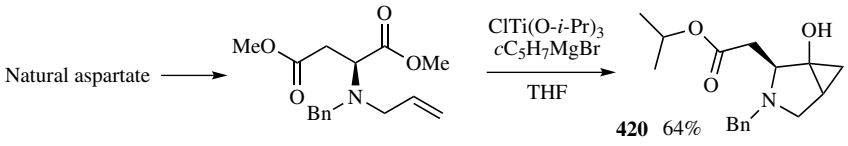

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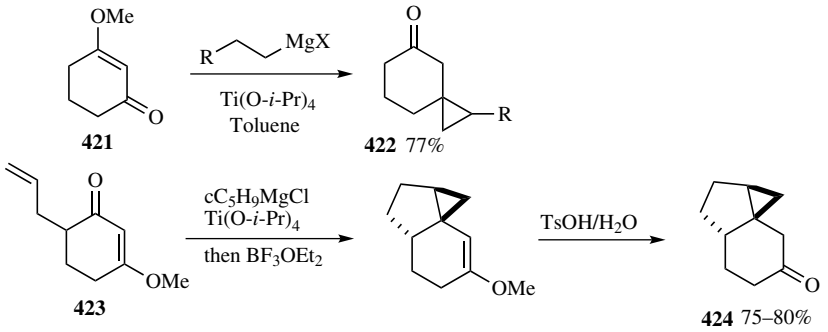
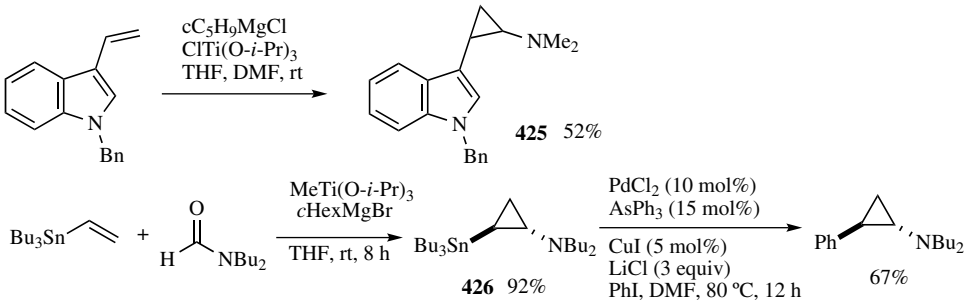


SCHEME 1.199



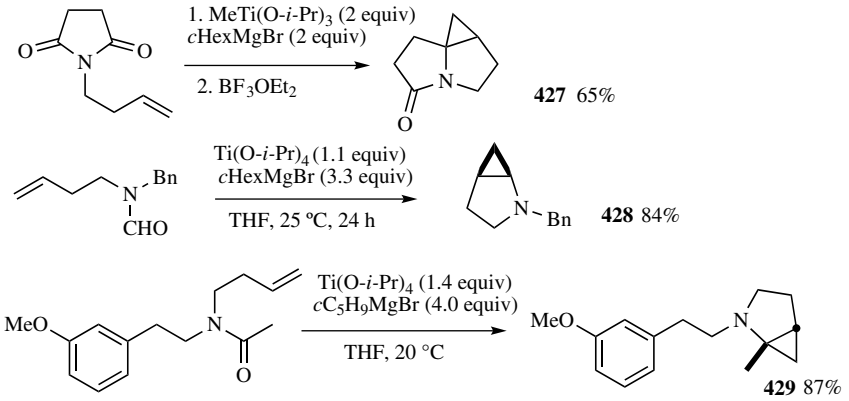
SCHEME 1.200

Unsaturated cyclic ketones also underwent the Kulinkovich reaction (Scheme 1.199) [280]. Cha and coworkers reported that methoxycyclohexene **421** underwent to form spiro cyclopropane **422** in good yield by treatment with Grignard reagent and Ti(O-*i*-Pr)$_4$. Tricyclic cyclopropanes **424** were successfully prepared from vinylic cyclohexene derivatives **423**.

Amides are another useful substrate for the Kulinkovich reaction to give cyclopropyl amines. Tertiary amides are usually used for the reaction. For example, *N*,*N*-dialkyl formamides served as a good aminomethylene-transfer reagent to give amino cyclopropanes **425** and **426** from alkenes in good yields (Scheme 1.200) [281].

N-Alkenyl amides serve as a good precursor for cyclopropane-fused pyrrolidines or piperidines (Scheme 1.201) [282]. Cyclopentyl or cyclohexyl Grignard reagents generate titanocyclopropane with the alkene unit, which reacted with the terminal amide unit to give bicyclic pyrrolidines **427**, **428**, and **429**.

The stereoselectivity of the reaction depended on the substituent pattern. For example, Joullié's group revealed that a stereogenic center located on a pyrrolidine ring **430** gave a good bias for a stereoselective synthesis of bicyclic cyclopropanes (Scheme 1.202) [283]. The selectivity for the formation of **431** was enhanced when a CF_3 group was attached to the stereogenic center [284].



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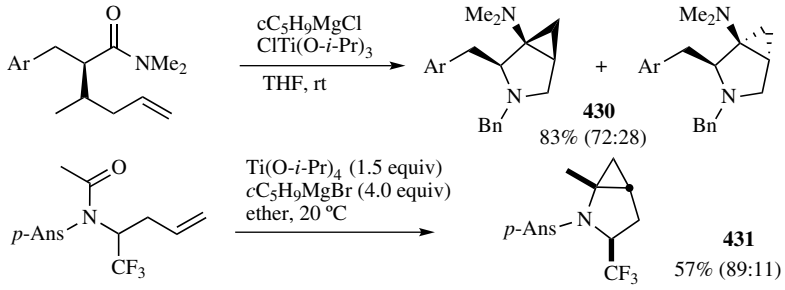

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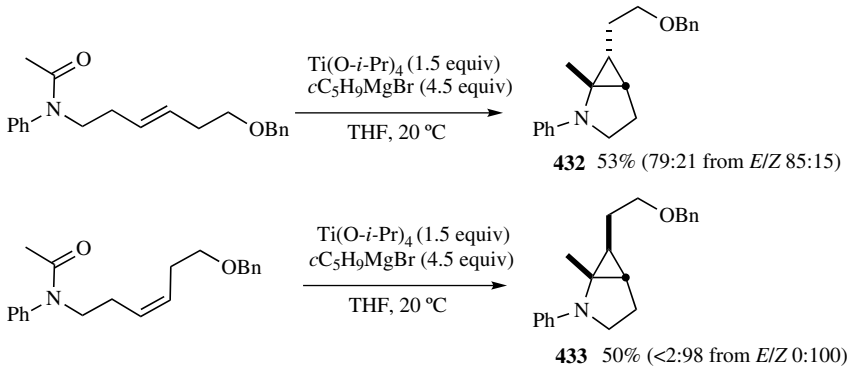


SCHEME 1.203

The geometry of the alkene unit served as good control for the stereochemical course of the reaction. For example, Six and coworkers reported that the stereochemistry of cyclopropanes **432** and **433** was controlled by the geometry of the alkene unit, and a stereospecific reaction progressed (Scheme 1.203) [285].

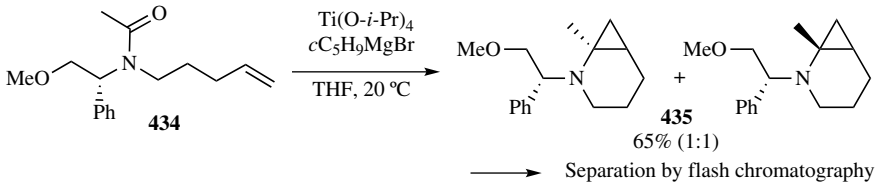
On the other hand, a stereogenic center located outside of the ring offered almost no steric bias for ring formation (Scheme 1.204) [286]. *N*-Chiral amide **434** was examined for the intramolecular Kulinkovich reaction; a 1:1 mixture of the two diastereomers of **435** was obtained. However, the two diastereomers were readily separated by flash chromatography.

1.6.3 Kulinkovich Reaction to Nitriles

Although amides served as a good substrate for the Kulinkovich reaction to give aminocyclopropanes, tertiary amides were also useful for the reaction, and tertiary aminocyclopropanes were obtained from the process. Nitriles were also good substrates for the Kulinkovich reaction, giving primary aminocyclopropanes. Alkenylnitriles afforded aminocyclopropanes **436**, **437**, and **438** by treatment with Grignard reagent and $Ti(O\text{-}i\text{-}Pr)_4$ or $TiCl(O\text{-}i\text{-}Pr)_3$ (Scheme 1.205) [287]. The titanium reagent was reduced to catalytic amounts. Alkenic geometry affected the stereochemistry of aminocyclopropanes, and a stereospecific reaction was observed.

The intermolecular reaction smoothly progressed and aminocyclopropanes **439** were prepared in good yields (Scheme 1.206) [288]. The addition of a Lewis acid was necessary for the formation of aminocyclopropanes. A similar reaction was also promoted by using Et_2Zn rather than using a Grignard reagent [289].

The use of β-cyanoesters provided bicyclic lactams in a one-pot process (Scheme 1.207) [290]. The reaction occurred in a highly stereoselective manner. The use of ethyl or isopropyl esters **440** was useful to reduce the amounts of



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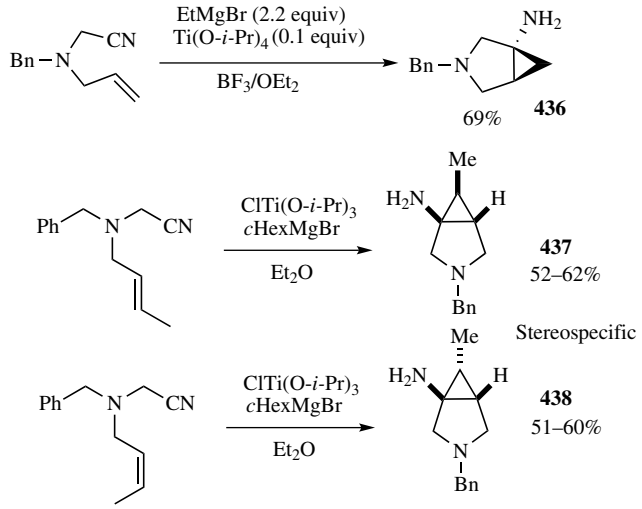

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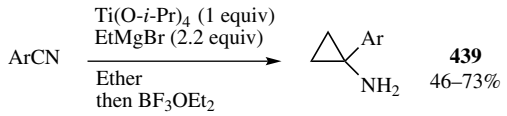


SCHEME 1.206

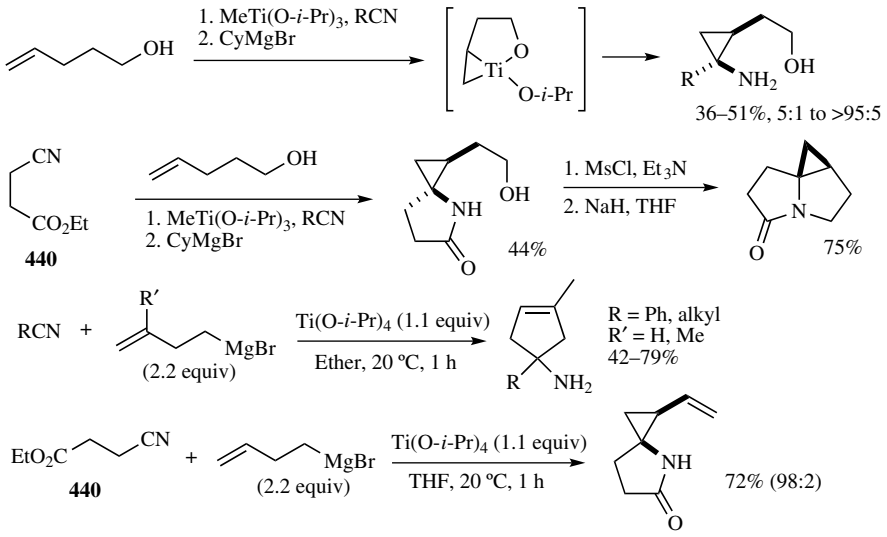
$Ti(O\text{-}i\text{-}Pr)_4$ to catalytic amounts [291]. When homoallylic alcohols **441** were used as a coupling partner, stereoselective cyclopropanation was achieved; however, the homoallylic stereogenic center had no effect on diastereoselectivity (Scheme 1.208) [292].

The Kulinkovich reaction was applied to prepare aminocyclopropanes attached to sugars **442** and **443** or the polyhydroxylated structure **444**. Cyclopropanation occurred in a stereoselective manner (Scheme 1.209) [293].

1.6.4 Other Ti-Mediated Cyclopropanation Reactions

A titanium-methylene complex was readily generated from CH_2Cl_2 by treatment with $TiCl_4$ and magnesium metal. This generation of active titanium-methylene complex **445** was useful for cyclopropane formation with enamines **446** or amides **447** to give aminocyclopropanes **448** and **449**, respectively, in good yields (Scheme 1.210) [294]. $TiCl_4$ worked catalytically in the reaction with enamines **446**, while substoichiometric amounts of $TiCl_4$ were necessary for the reaction with amides **447**.

A titanium-methylene complex was also generated from $Cp_2Ti[P(OEt)_3]_2$ and dithioacetal **450** (Scheme 1.211) [295]. Deuterium was delivered at the *trans*-position of the cyclopropane **451** when the reaction was quenched by deuterium



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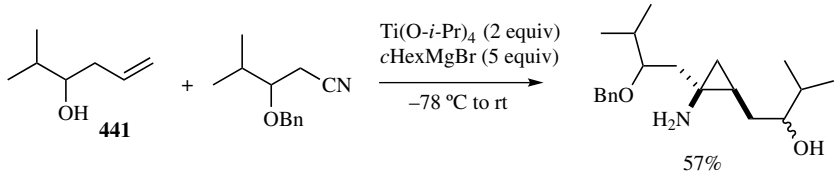

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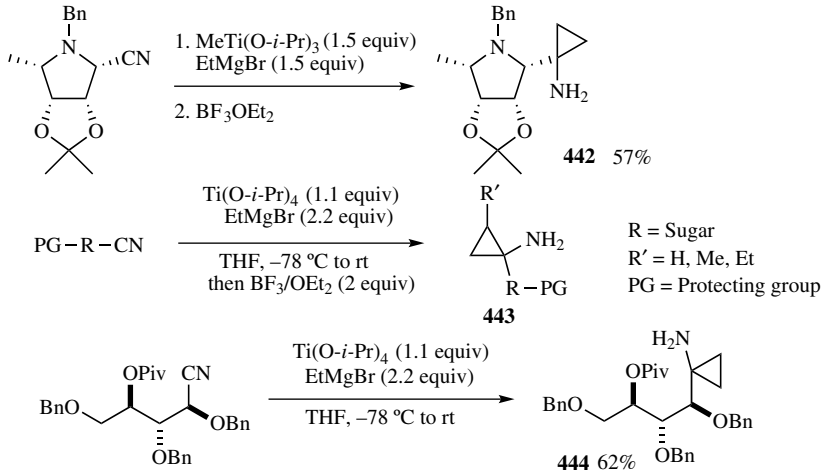

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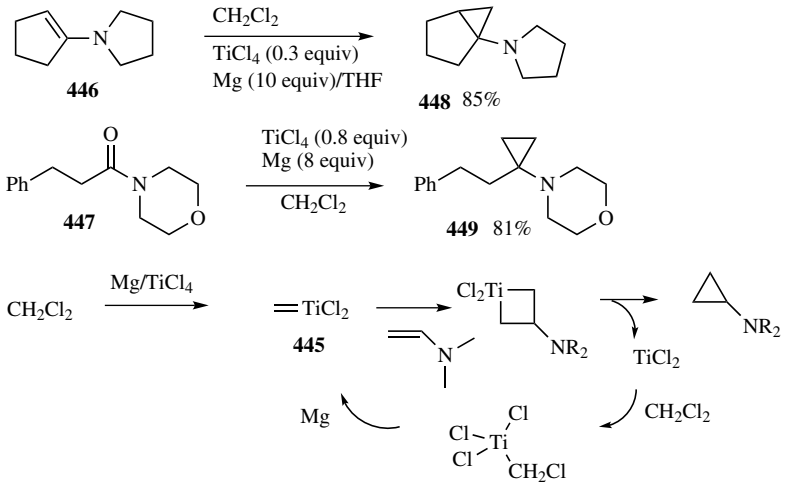

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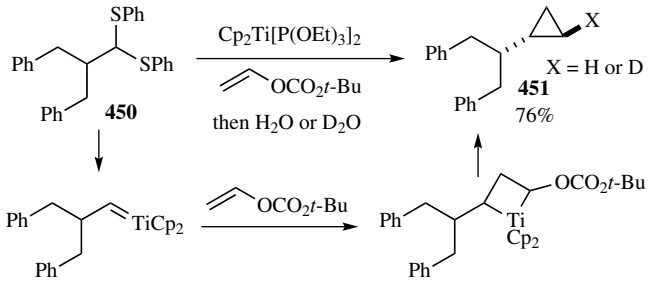


SCHEME 1.211

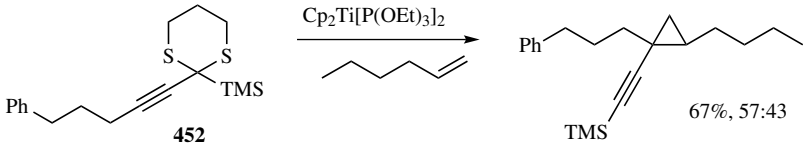
oxide. Dithioacetal **452** also underwent cyclopropanation by treatment with $Cp_2Ti[P(OEt_3)_2]$ (Scheme 1.212) [296].

A similar cyclopropanation to the Kulinkovich reaction was achieved by the use of zirconium aluminum complexes in the presence of magnesium (Scheme 1.213) [297].

1.7 MISCELLANEOUS [2+1]-TYPE OF CYCLOPROPANATION REACTIONS

Epoxide is a good precursor for cyclopropane formation. For example, the treatment of epoxide **453** with a strong base, such as *t*-BuLi or $LiNCy_2$, resulted in the conversion to cyclopropanes **454** in good yields (Scheme 1.214) [298]. The abstract of the terminal proton of the epoxide unit followed by the coordination of lithium metal in the intermediate **455** promoted intramolecular cyclopropanation. Aziridines also underwent a similar conversion to give aminocyclopentanes fused with cyclopropane [299].

Epoxide **456** was readily converted to cyclopropane **457** by treatment with $La(OTf)_3$ (Scheme 1.215) [300]. The reaction progressed with Lewis acid-induced epoxide opening followed by a semipinacol rearrangement.



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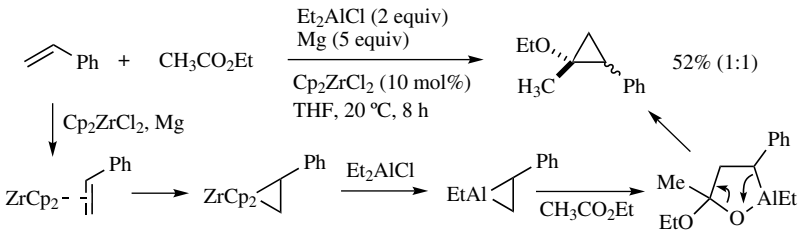

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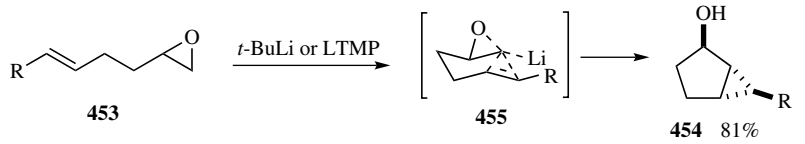
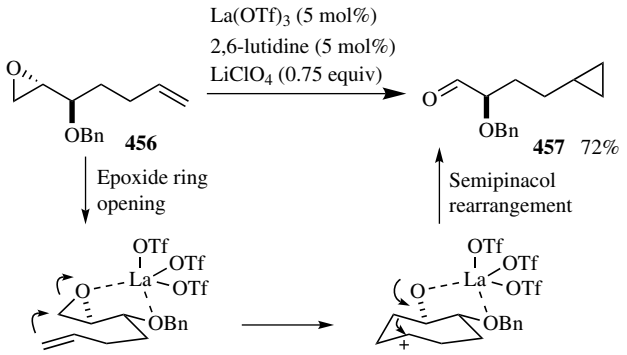


SCHEME 1.214



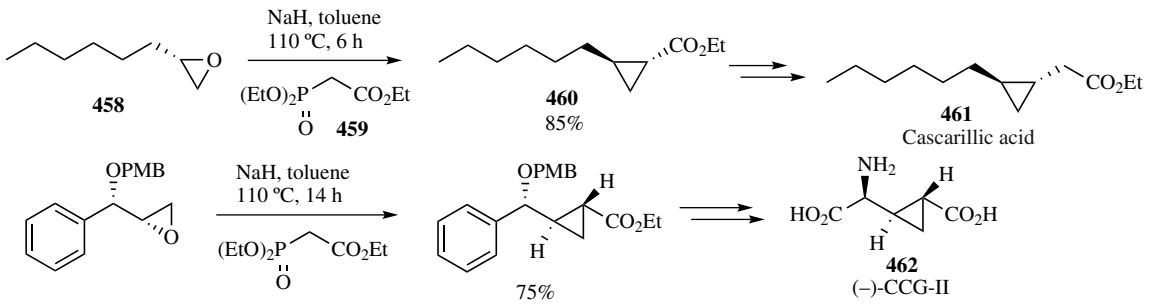
SCHEME 1.215

The reaction of epoxide **458** with diethylphosphonoacetate **459** gave cyclopropane carboxylates **460** in good yields (Scheme 1.216) [301]. The conversion was applied to the preparation of cascarillic acid **461**, grenadamide, and L-(−)-CCG-II **462**. The corresponding sulfone derivative gave cyclopropylsulfones [302].

Di(trifluorimethyl)mercury gave tetrafluorocyclopropane **463** from ketones in one step (Scheme 1.217) [303].

Bridged bicyclic polyene **464** formed cyclopropane (Scheme 1.218) [304]. Aromatic aldehyde **465**, maleic ester **466**, and thiocyanoketone **467** were combined in one step to give cyclopropane **468** in good yield (Scheme 1.219) [305].

Primary nitro compounds **469** served as a precursor for nitrobicyclo[3.1.0]hexanes **470** or [4.1.0]heptanes **471** in one



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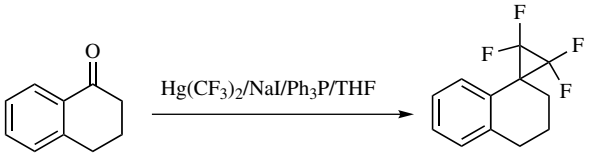
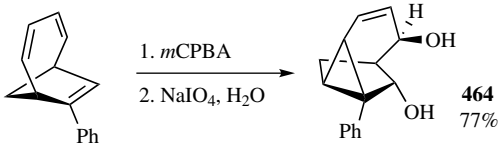


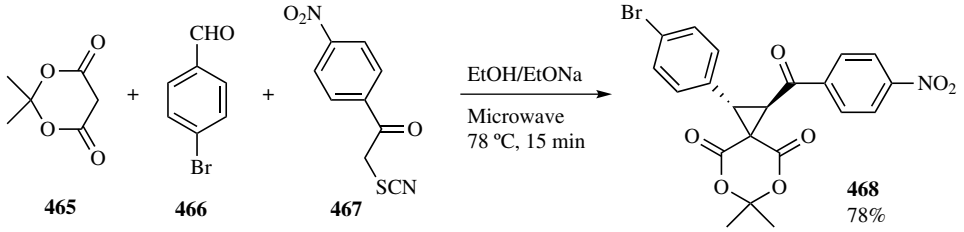
463 49%

SCHEME 1.217



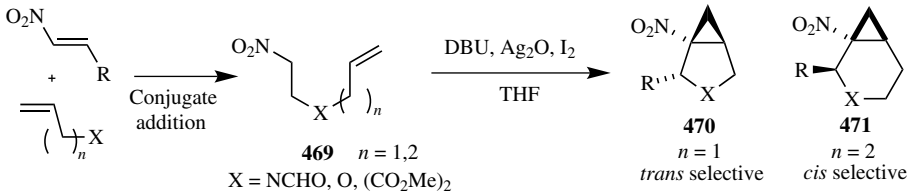
464 77%

SCHEME 1.218



465 **466** **467** **468** 78%

SCHEME 1.219



469 n = 1,2
X = NCHO, O, $(CO_2Me)_2$

470 n = 1 *trans* selective

471 n = 2 *cis* selective

SCHEME 1.220

step (Scheme 1.220) [306]. The treatment of nitro compounds with Ag_2O, DBU, and iodine resulted in bicyclic cyclopropanes **470** and **471** in good yields. The stereoselectivity was generally high. The stereoselectivity depended on the size of the formed ring. The precursors **469** were readily prepared by the conjugate addition of allylic or homoallylic nucleophiles to nitroalkenes. A similar cyclopropanation has also been reported [307].

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