

Saturated and partially unsaturated carbocycles

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Reviewing the literature published between May 1995 and April 1996

Continuing the coverage in *Contemporary Organic Synthesis*, 1996, 3, 19

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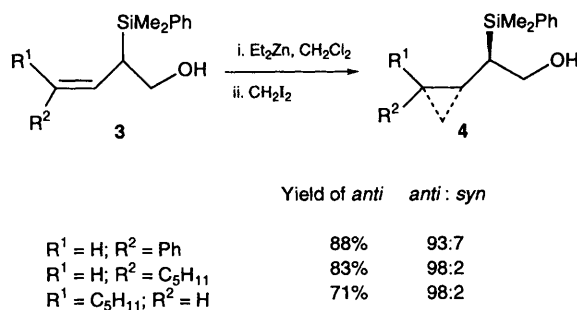
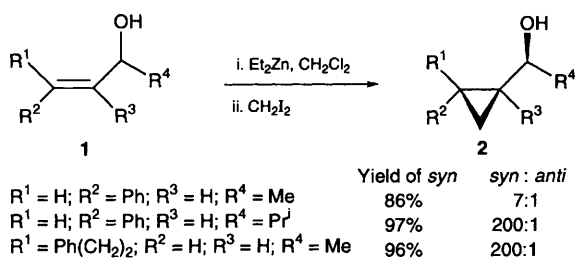
1 Three-membered rings

1.1 Metal carbenoid-based methods

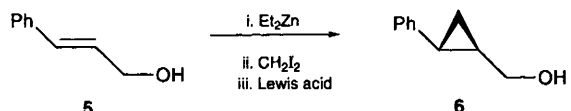
1.1.1 From dihaloalkanes

The zinc carbenoid Simmons–Smith cyclopropanation remains one of the most useful methods available for the construction of the three-membered ring. Recent work has concentrated on the use of allylic or homoallylic alcohols to facilitate asymmetric induction; this coupled with the use of a chiral auxiliary has resulted in the preparation of

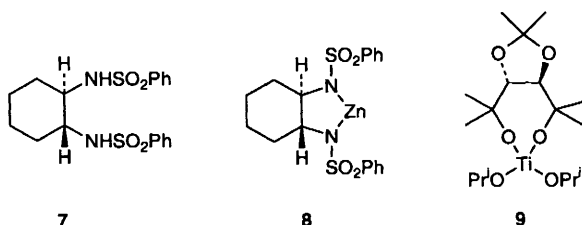
optically active cyclopropanes. For example, Charette and Lebel¹ have reported the diastereo-selective cyclopropanation of allylic alcohols **1** using the modified Simmons–Smith reagent of diethylzinc and diiodomethane to give the desired products **2** in high yields and very high diastereomeric excesses superior to those obtained using the corresponding samarium-based cyclopropanation. Landais and Parra-Rapado² have used the same reagent to study 1,2-asymmetric induction in 2-silylalk-3-enols **3**; similarly the resulting cyclopropanes **4** were obtained in high yields and high diastereomeric excesses.



Two research groups (Kobayashi³ and Charette⁴) have reported the Lewis acid-catalysed cyclopropanation of the allylic alcohol **5**; in both cases titanium tetrachloride was used as the Lewis acid and a good yield of the cyclopropylmethanol **6** was obtained. This principle was extended by both research groups to give enantioselection by the use of a chiral Lewis acid. Kobayashi used the Lewis acid **8** which was formed *in situ* from the C₂ symmetric disulfonamide **7**, whereas Charette used the titanium derivative **9**. High yields of **6** were obtained with moderate to good enantiomeric excesses.

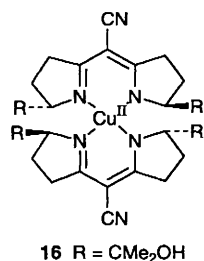
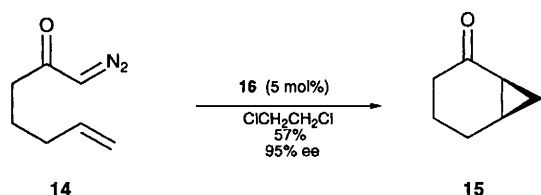
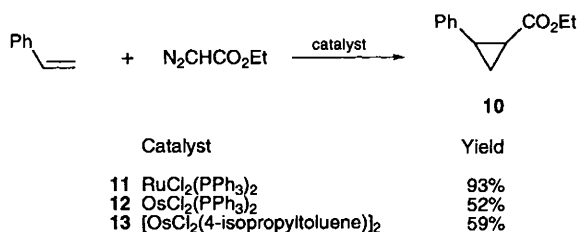


Lewis acid	Yield	ee
8	75%	68%
9	80%	90%

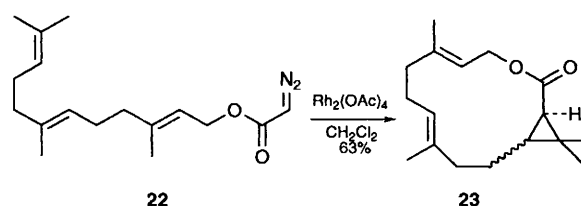
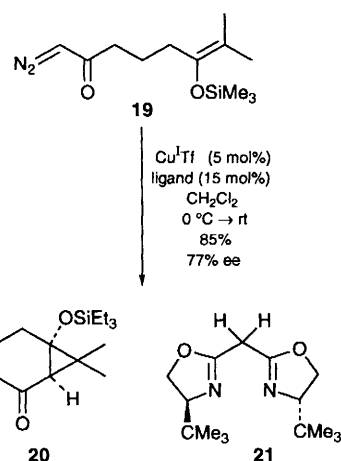
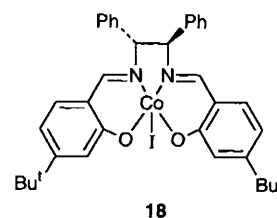
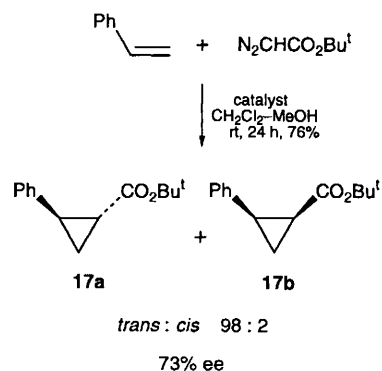


1.1.2 From diazocarbonyl compounds

The second metal carbenoid-based method of cyclopropanation is by the treatment of an alkene with diazocarbonyl compounds in the presence of a metal catalyst. Démonceau and co-workers have demonstrated the use of the ruthenium–phosphine complex **11** and the osmium–phosphine complex **12** as catalysts^{5,6} as well as the osmium–aryl complex **13**⁷. Good yields of the product **10** were only achieved using styrene systems. Various research groups have been active in the development of chiral catalysts for both intra- and inter-molecular enantioselective alkene–diazocarbonyl cyclopropanations. The semicorrin–copper complex **16** has been reported⁸ to effect the conversion of substrate **14** into the cyclopropyl ketone **15** in moderate yield with very good enantiomeric



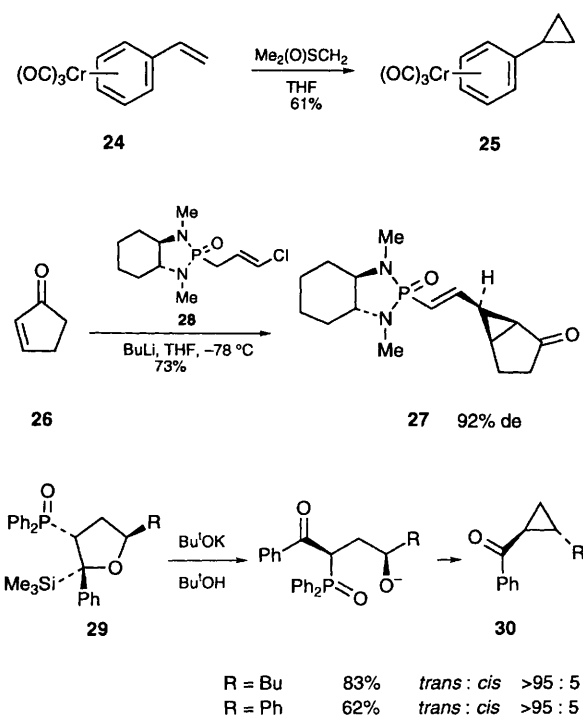
excesses. A cobalt–salen complex, viz **18**, has been reported⁹ to catalyse the reaction between styrene and *tert*-butyl diazoacetate giving cyclopropanes **17a,b** in good yield with good ee; a similar reaction has been described¹⁰ using an iron porphyrin as the catalyst. Shibasaki *et al.*¹¹ in their synthesis of the phorbol CD-ring skeleton have demonstrated an asymmetric intramolecular cyclopropanation of the enol silyl ether **19** using the chiral ligand **21** coupled with a copper catalyst to give the desired bicyclo-[4.1.0]heptane system **20** in very good yield and good ee. Doyle and Protopopova¹² have used the standard dirhodium tetraacetate catalyst in macrocyclic lactone formation (**22**→**23**). Finally, all four



diastereomers of 4-(carboxymethyl)proline have been prepared *via* a dirhodium tetraacetate-induced cyclopropanation¹³.

1.2 Anion-based and related methods

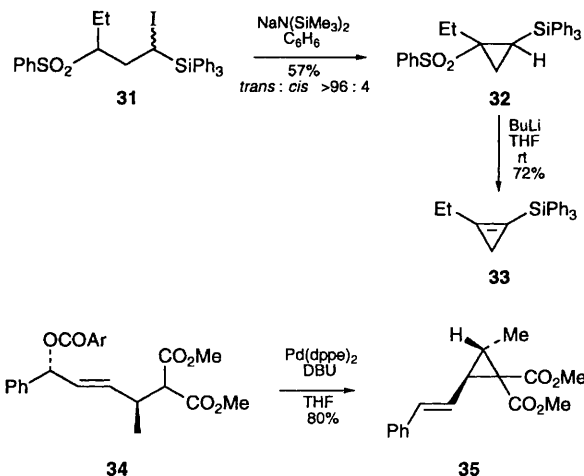
The familiar trimethylsulfoxonium ylide has been used by Gibson and co-workers¹⁴ as a reagent to convert the Cr⁰ complex **24** into the cyclopropane **25** in moderate yield. As a chiral alternative to the more usual trimethylsulfoxonium ylide, Hanessian *et al.*¹⁵ have developed the new reagent **28** to prepare diastereomerically pure cyclopropyl ketones **27** from α,β -unsaturated ketones such as **26**. In the field of intramolecular anion reactions Nelson and Warren¹⁶ have prepared cyclopropyl ketones **30** stereoselectively from phosphine oxides **29**. An intra-



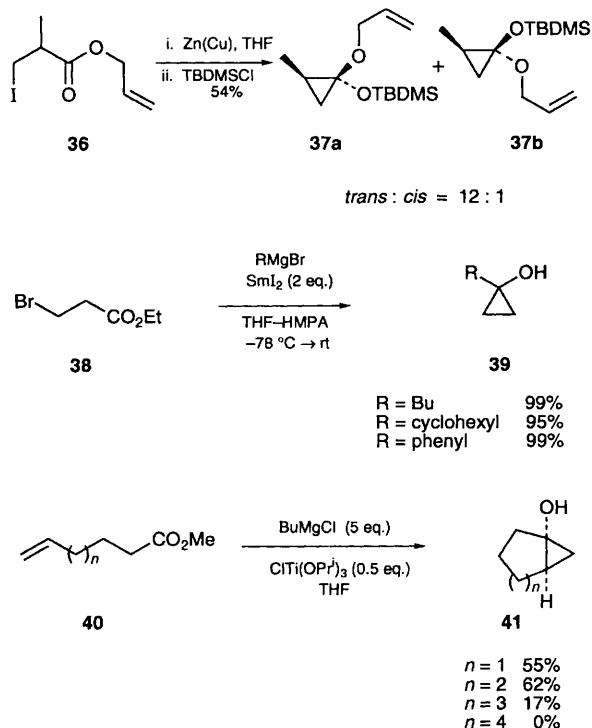
molecular nucleophilic displacement has been used by Wicha *et al.*¹⁷ to produce functionalised cyclopropanes such as **32** from the iodide **31**; elimination of benzenesulfinic acid from **32** then gave the cyclopropene **33** in good yield. An intramolecular epoxide-ring opening has been reported¹⁸ in the enantioselective synthesis of cyclopropane α -amino acids, and a novel anion-induced ring contraction of cyclobutanes has been used as the key step in a preparation of an unusual cyclopropane nucleoside.¹⁹ Finally, Genêt and co-workers²⁰ have reported an asymmetric synthesis of the *cis*- and *trans*-vinylcyclopropanes **35** from the corresponding allylic esters **34**.

1.3 Other methods

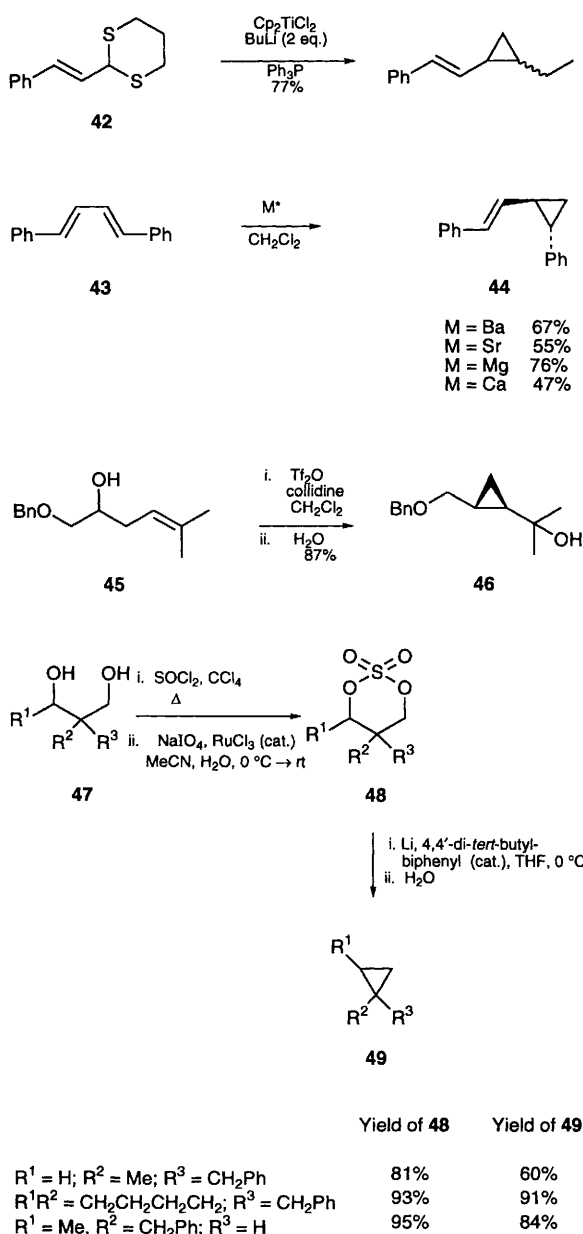
Two novel methods of cyclopropane ring formation starting from β -haloesters have recently been



reported. Thus, Tamaru *et al.*²¹ have developed a synthesis of the cyclopropane ketals **37a,b** *via* a silyl chloride promoted cyclisation from β -iodo esters such as **36** (moderate yields and stereoselectivities are obtained). Along similar lines, Fukuzawa *et al.*²² found that treatment of 3-bromo esters **38** with a Grignard reagent–samarium iodide couple led to cyclopropanols **39** in excellent yield (this method has been adapted with less success to the preparation of other cycloalkanols). Two other closely related methods of cyclopropanol formation, both utilising a titanium reagent, have recently been reported.²³ For example Cha and co-workers²⁴ prepared the fused ring systems **41** from ω -vinyl esters **40** *via* an intramolecular Kulinkovich hydroxycyclopropanation. The same research group has also reported²⁵ the diastereoselective synthesis



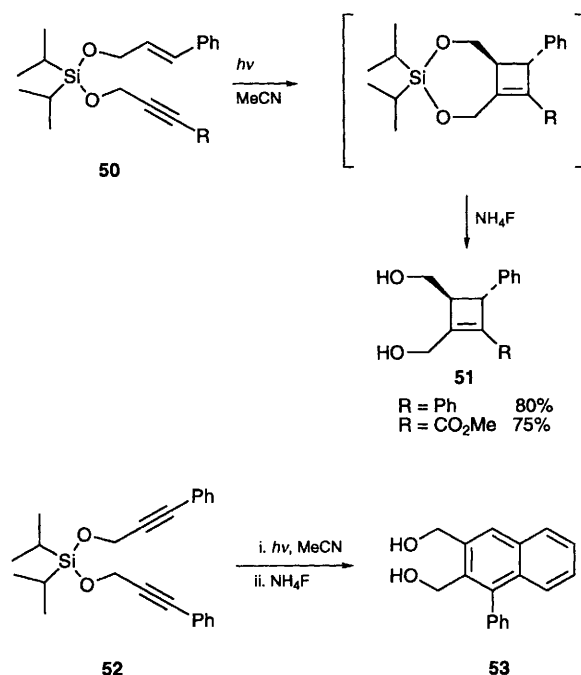
of *cis*-1,2-dialkenylcyclopropanols using an intermolecular variation. The Cp_2TiCl_2 complex has been used by Takeda *et al.*²⁶ in the desulfurative cyclopropanation of substituted 1,3-dithianes such as **42**. A general method of small ring formation has been reported by Rieke and Sell²⁷ in which, for example the cyclopropane **44** is prepared in good yield by reaction between Rieke barium, strontium, magnesium or calcium, the butadiene **43** and dichloromethane. A very neat synthesis of the cyclopropane **46** has been described by Suzuki and co-workers²⁸ starting from the homoallylic alcohol **45**. This methodology has been used in the synthesis of a cyclopropane-containing icosanoid.²⁹ Finally, a novel and highly efficient cyclopropane ring synthesis has been reported by Yus and Guijarro³⁰ in which a 1,3-diol **47** is converted into a substituted cyclopropane **49** through the corresponding cyclic sulfate **48**.

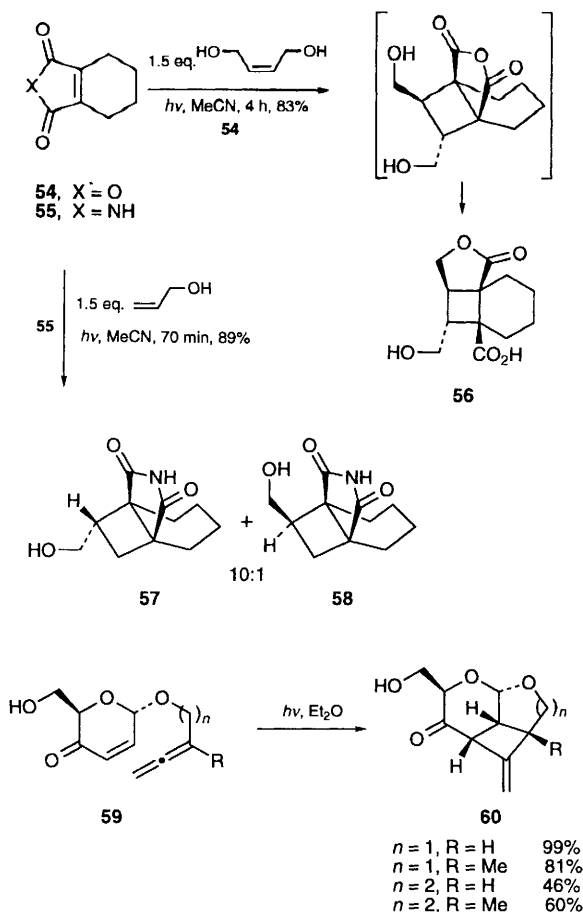


2 Four-membered rings

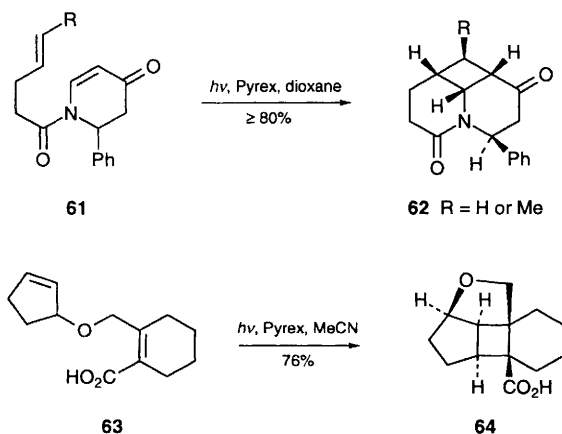
2.1 Photochemical methods

The temporary silicon tether has again been used to good effect in [2+2] photocycloadditions. For example, Fleming *et al.* found that irradiation of the tethered enyne alkoxyasilanes **50** followed by desilylation of the photoadducts led to high yields of the functionalised cyclobutene diols **51** with excellent levels of regio- and stereo-control.³¹ Overall the temporary silicon tether allows the synthesis of 'intermolecular' [2+2] photocycloadducts with the regio- and stereo-control normally associated with the intramolecular variant. Interestingly the diphenyl diyne **52** gave the naphthalene derivative **53** via an alternative cycloaddition involving one of the phenyl moieties. Booker-Milburn *et al.*³² have reported that 3,4,5,6-tetrahydrophthalic anhydride **54** and the corresponding imide **55** underwent highly stereo-selective intermolecular [2+2] photocycloadditions with a variety of alkenols. For example irradiation of **54** with but-2-ene-1,4-diol gave the cyclobutane lactone **56** as a single product in excellent yield via spontaneous lactonisation of the initially formed cyclobutane anhydride. Irradiation of **55** with allyl alcohol for example gave the diastereomeric cyclobutane imides **57** and **58** with a high de of 10:1. Similarly, a number of cyclobutene-anhydrides and imides were prepared in good yield by [2+2] photocycloadditions of **54** and **55** with a variety of acetylenic alcohols. Studies of the scope for intramolecular [2+2] photocycloadditions in synthesis have continued in earnest and a number of interesting examples have been reported over the review period. For example, Tenaglia and Barillé³³ found that irradiation of the allenyl pyrone acetals **59** gave the corresponding *exo*-methylenecyclo-



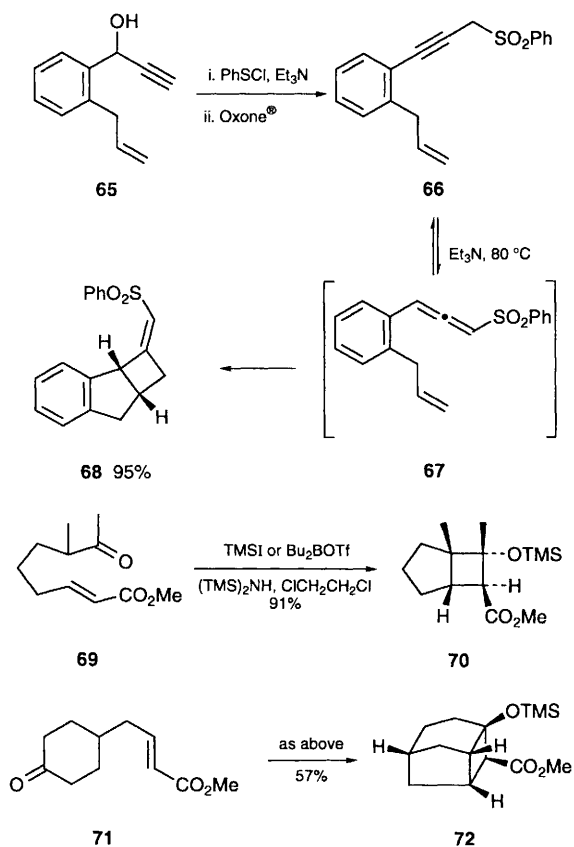


butanes **60** in good yield with excellent stereo-selectivity. In a study of the radical fragmentation of cyclobutanes, Beckwith and co-workers³⁴ found that irradiation of the pyridone **61** gave the highly functionalised cyclobutane **62**, as a single diastereomer, in excellent yield. In their studies towards asteriscanolide Booker-Milburn and Cowell³⁵ found that intramolecular photocycloaddition of the α,β -unsaturated acid **63** gave the fused cyclobutane **64** with complete stereocontrol. Finally, Haddad and Abramovich³⁶ have reported moderate to good diastereocontrol on irradiation of alkenyl tethered cyclic acetals.



2.2 Other methods

Padwa *et al.*³⁷ have reported a very useful thermal [2 + 2] cycloaddition reaction involving prop-2-ynyl sulfones. For example reaction of the alcohol **65** with benzenesulfonyl chloride gave the corresponding prop-2-ynyl sulfoxide which was then oxidised to the sulfone **66**. Heating **66** with triethylamine led to the methylenecyclobutane **68** in excellent yield *via* thermal [2 + 2] cycloaddition of the transient allenyl sulfone **67**. The Lewis acid promoted tandem intramolecular Michael–aldol reactions of keto esters have been further investigated by Fukumoto³⁸ and a number of new examples reported (**69**→**70** and **71**→**72**). Jun has reported³⁹ an interesting new

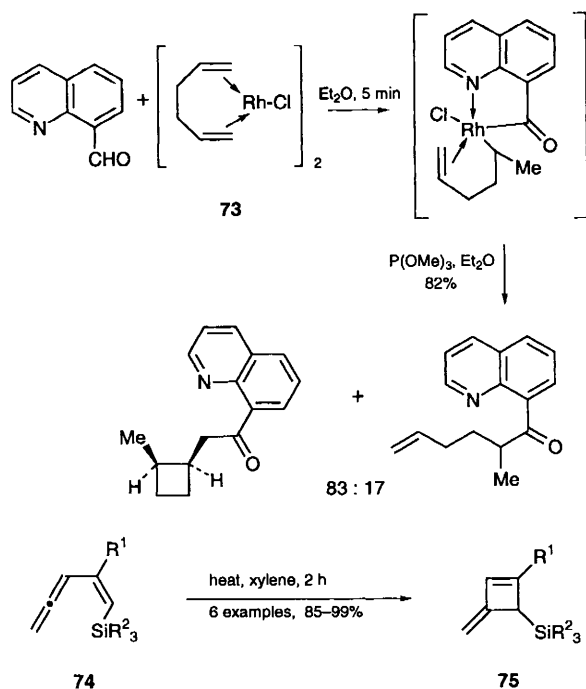


cyclobutane ring-forming process involving the reaction of quinoline-7-carbaldehyde with the Rh^I bis-alkene dimer **73**. The reaction probably proceeds by oxidative insertion of Rh into the aldehyde C–H bond followed by reductive cyclisation on treatment with trimethyl phosphite. Silyl substitution of vinyl allenes has been found to have a remarkable effect on the rate and equilibrium of electrocycloaddition; thus Ito *et al.*⁴⁰ have found that a number of silyl substituted methylenecyclobutenes can be prepared in good yield under mild conditions (**74**→**75**).

3 Five-membered rings

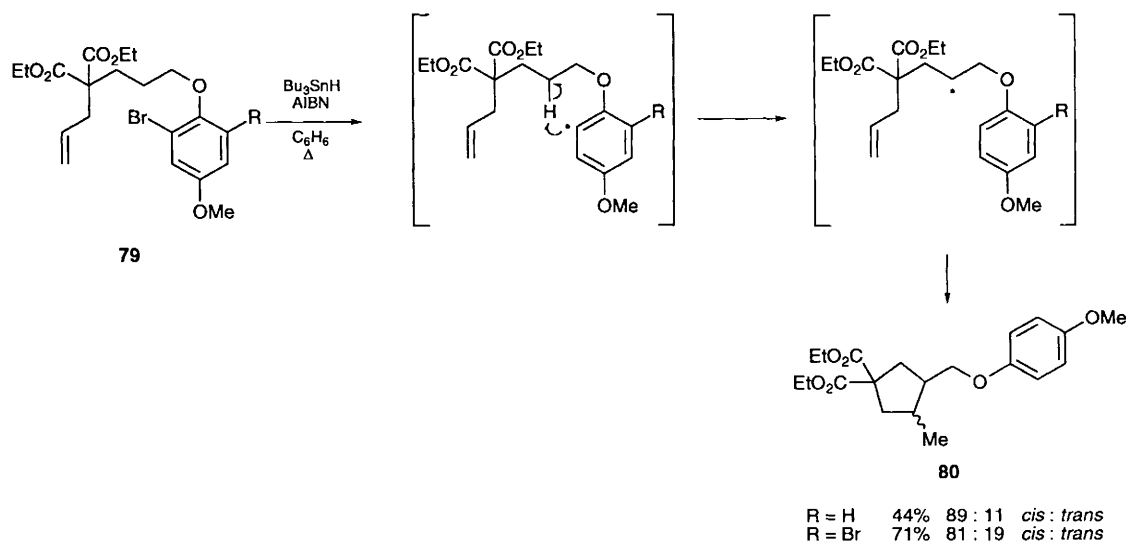
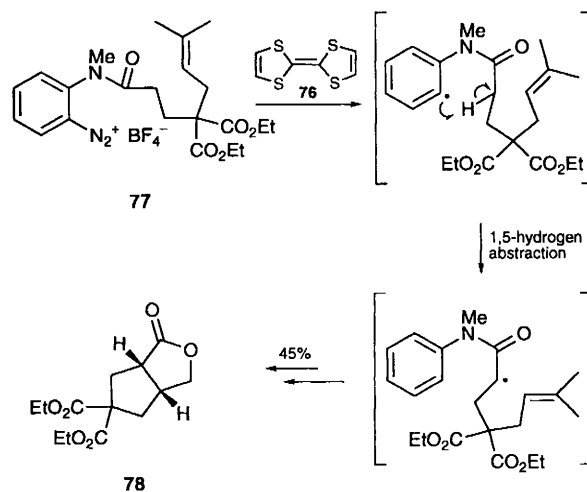
3.1 Free radical methods

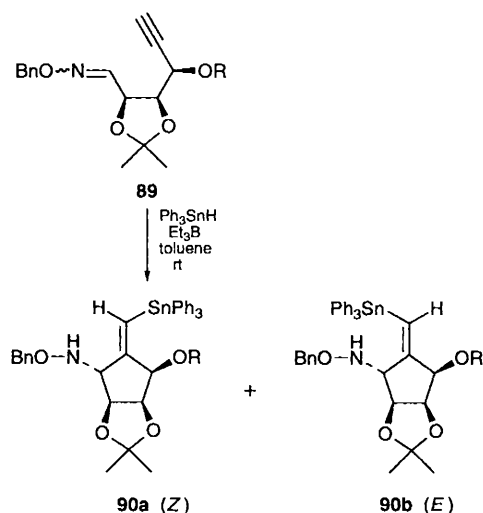
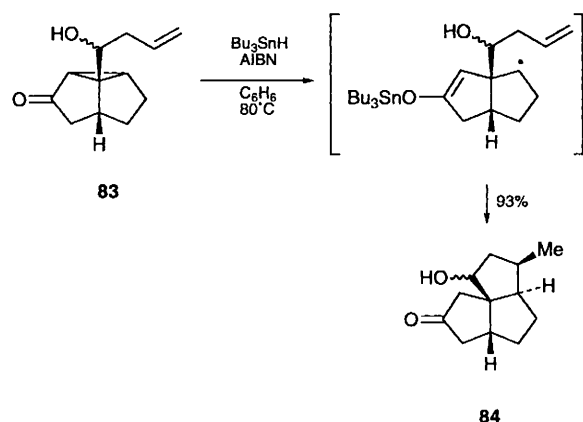
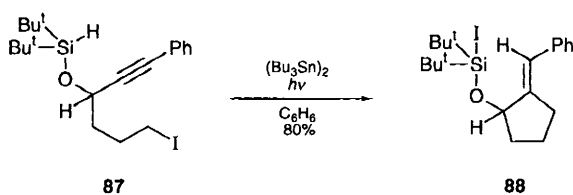
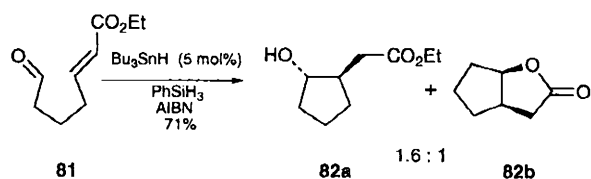
Free radical cyclisations remain a very popular method of five-membered ring synthesis; new work



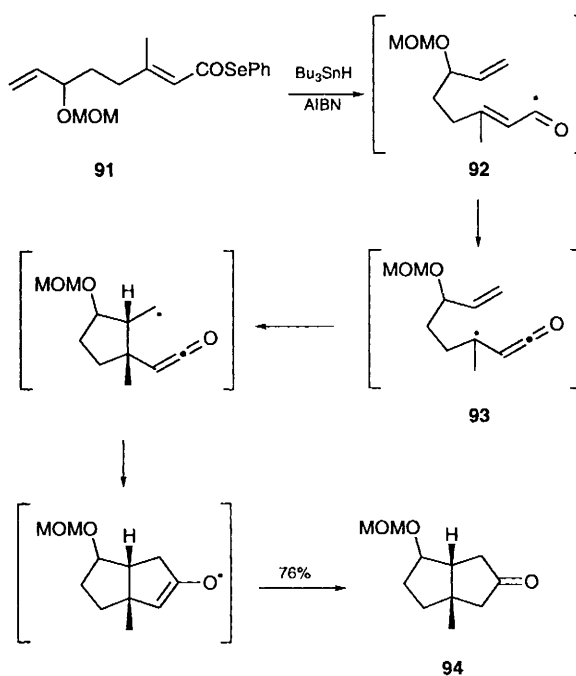
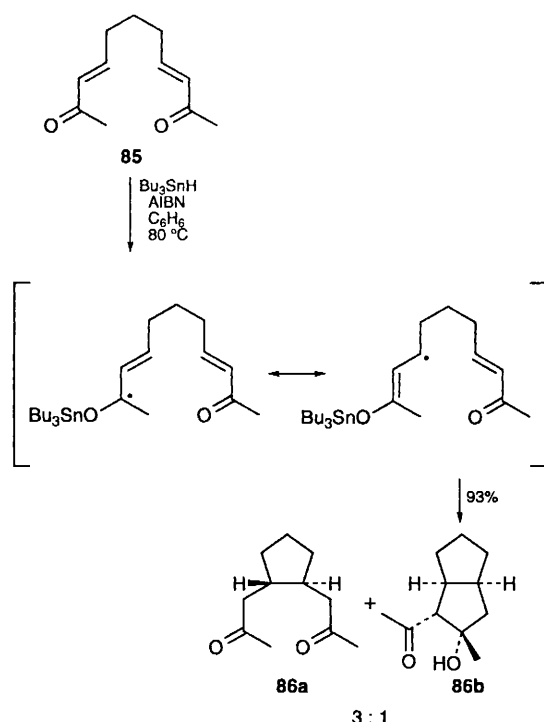
cyclisations of enals and enones, such as **81**, giving good yields of cyclopentanes, e.g. **82a,b**. As alternative radical-generating methods, Chuang and Wang⁴⁴ have reported the use of sodium toluene-*p*-sulfinate, while Hatem *et al.*⁴⁵ have proposed the use of toluene-*p*-sulfonyl bromide in the cyclisations of allylallenenes. Booker-Milburn and Thompson⁴⁶ have published full experimental details of their iron(III)-mediated ring expansion–cyclisation technique for the formation of [*n*.3.0] systems from cyclopropyl ethers. Enholm and Jia⁴⁷ have also made use of the radical ring openings of functionalised cyclopropanes; thus generation of the *O*-stannyl radical from the cyclopentanone **83** results in a fragmentation–cyclisation sequence of reactions to produce the angular triquinane skeleton **84**. The same research group⁴⁸ has also studied the reactions of allylic *O*-stannyl radicals and excellent yields of cyclisation products **86a,b** were achieved using tributyltin hydride radical-generation from the α,β -unsaturated ketone **85**. Two examples of stereoselective radical cyclisations using a chiral aluminium-based Lewis acid have been reported by Nishida and co-workers.^{49,50} Curran and Martinez-

in this area comprises novel methodology, the use of chiral reagents to confer stereoselectivity and the application of existing methods to natural product synthesis. Two interesting developments reported recently involve the translocation *via* a 1,5-hydrogen abstraction by an aryl radical to form an alkyl radical which then undergoes cyclisation. For example Murphy and Roome⁴¹ have generated aryl radicals from arenediazonium salts, such as **77**, in the presence of tetrathiofulvalene **76** to afford ring systems, such as **78**, in good yields. Curran and Xu⁴² have demonstrated the viability of a protecting–translocating group that generates a radical in the β -position relative to a protected alcohol, such that *o*-bromo-*p*-methoxyphenyl ethers **79** are converted successfully into cyclopentanes **80**. Fu and Hays⁴³ have described the use of catalytic tributyltin hydride for the radical-mediated reductive



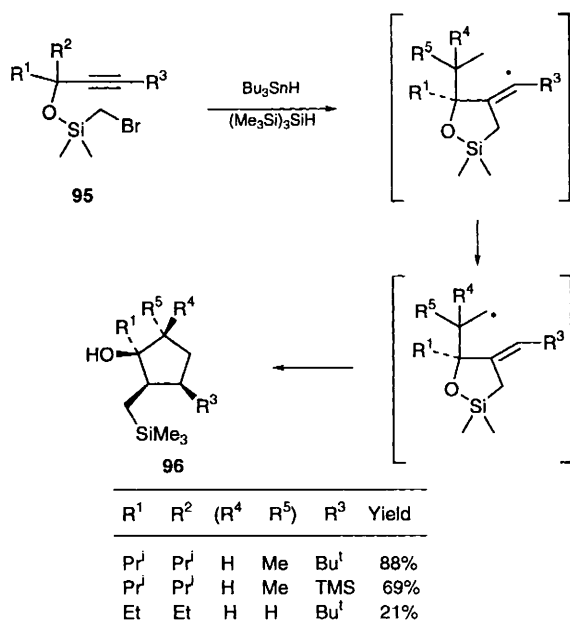


R = H	69%	3%
R = Ac	70%	
R = TBDMS	45%	14%



Grau⁵¹ have used the unimolecular chain reactions of silicon hydrides such as **87** to give exclusively the *E*-alkene cyclisation product **88** (this methodology has also been applied to the synthesis of six-membered rings). The same principle⁵² has been utilised to prepare alkenes **90a,b** predominantly as the *Z*-isomer **90a** from the enantiomerically pure alkyne-tethered oxime ethers **89**. The final area of research involving free radicals that has attracted much interest is tandem cyclisations and cascade reactions. Pattenden and Hayes⁵³ have devised elegant methodology in which the selenoester **91** is converted into the bicyclic ketone **94** in very good yield via the α,β -unsaturated acyl radical **92** and the

α -ketene alkyl radical **93**. This is the first reported example of radical cyclisation onto a ketene. An example of the unusual 5-*endo-trig* cyclisation in a radical cascade has been demonstrated by Malacrie and Bogen⁵⁴ in which alkynes **95** are converted into cyclopentanols **96** in very good yield. The uses of tandem radical cyclisations in natural product synthesis have been reported in the synthesis of (\pm)- α - and β -biotol,⁵⁵ and by Hoffmann and

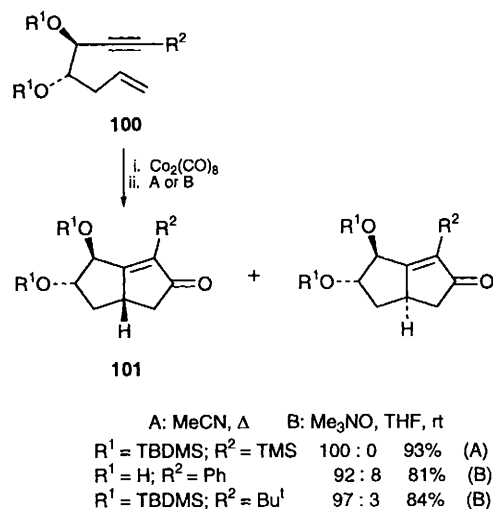
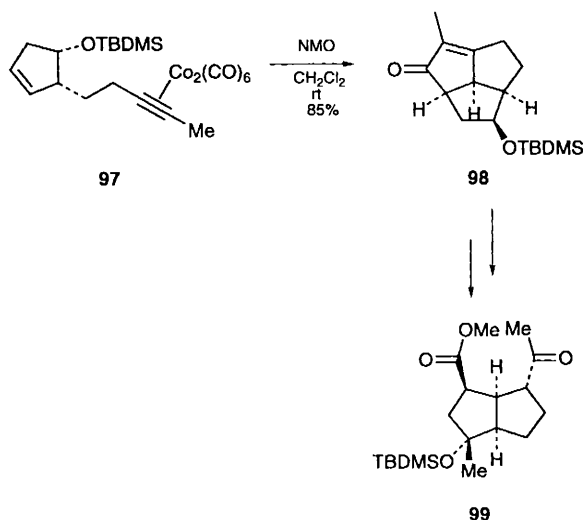


Woltering⁵⁶ in their synthesis of dioxatriquinanes and doubly annulated glycosides.

3.2 Metal-based methods

3.2.1 Cobalt

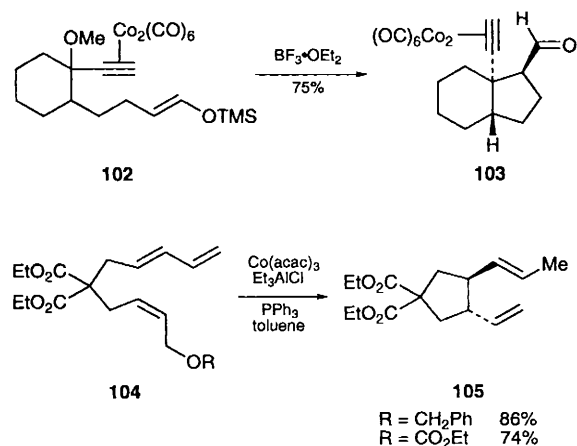
As in previous years the most commonly reported cobalt-based cyclisation method has been the Pauson–Khand reaction (PKR). Perhaps the most important recent development in the PKR has been reported by Livinghouse and Pagenkopf⁵⁷ who have found that under photochemical conditions the reaction can be made catalytic in cobalt with only 5 mol% $\text{Co}_2(\text{CO})_8$ required. Cazes *et al.*⁵⁸ have studied the intermolecular PKR with allenic compounds, and Veretenov and co-workers⁵⁹ have used the PKR to synthesise linearly fused triquinanes. Paquette and Borelly⁶⁰ have prepared the angularly fused triquinane **98** from the cyclopentene **97** in their approach to the CD diquinane substructure **99** of

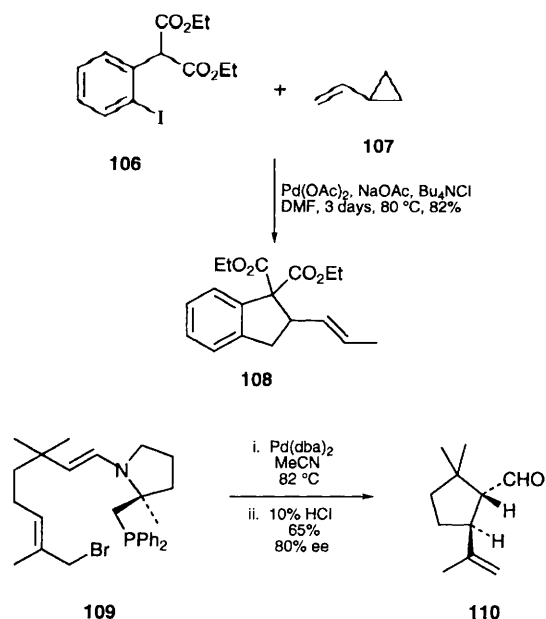


kalmanol. A highly diastereoselective construction of optically active bicyclo[3.3.0]octenones **101** from enynes **100** by an intramolecular PKR has been reported by Mukai *et al.*⁶¹ Other uses of cobalt have been reported by Tyrrell and co-workers⁶² who have utilized the intramolecular Nicholas reaction in an approach to fused carbocycles such as **103** from the alkynyl enol ether **102**. Takacs and Mehrman⁶³ have developed the cobalt-mediated reductive cyclisation of ene dienes **104** to cyclopentanes, *e.g.* **105**.

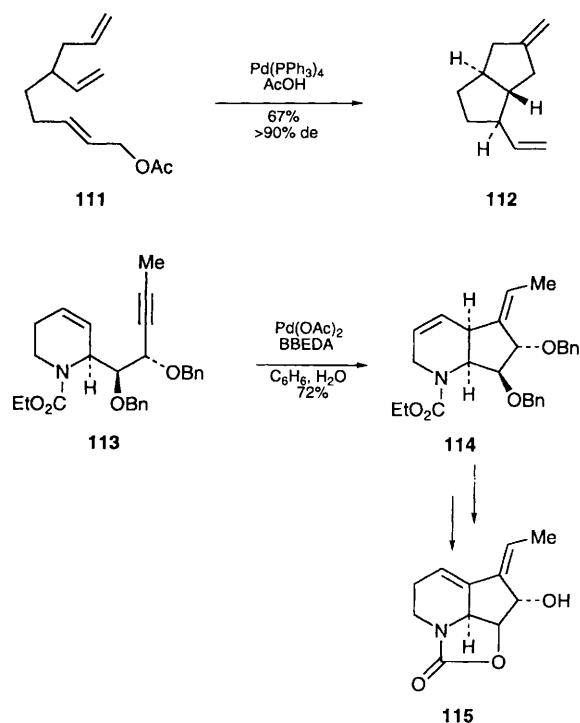
3.2.2 Palladium and nickel

The familiar palladium-catalysed coupling of alkenes has been well represented in the literature recently, particularly in the area of natural product synthesis. On the methodology side, Larock and Guo⁶⁴ have studied the annulation of oxygen-substituted dienes with aryl iodides leading to benzo-fused cyclopentanes in excellent yield. The same research group⁶⁵ has also reacted aryl iodides **106** with vinylic cyclopropanes, including **107**, to give benzo-fused cyclopentanes such as **108**. The stereochemistry of the product **110** resulting from intramolecular asymmetric allylation of the chiral enamine **109** has been investigated with some success by Hiroi and co-workers,⁶⁶ and Yamamoto

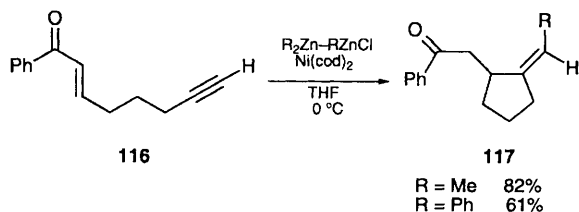




*et al.*⁶⁷ have demonstrated a tandem palladium(0)-catalysed cyclization of 6-(alk-2-enyl)octa-2,7-dienyl acetate **111** giving the diquinane **112** with high diastereoselectivity. Palladium-catalysed cyclisation reactions directed towards the synthesis of natural products have been reported from the research groups of Fukumoto,^{68,69} Shirahama⁷⁰ (in their synthesis of kainic acid analogues) and Kibayashi⁷¹ in which under controlled conditions the enyne **113** was found to give predominantly the single isomer **114**, a key intermediate used in their synthesis of (+)-streptazolin **115**. Two research groups have studied organozinc/catalytic nickel(0)-promoted cyclisations. Thus, Knochel and Stadtmüller⁷² have

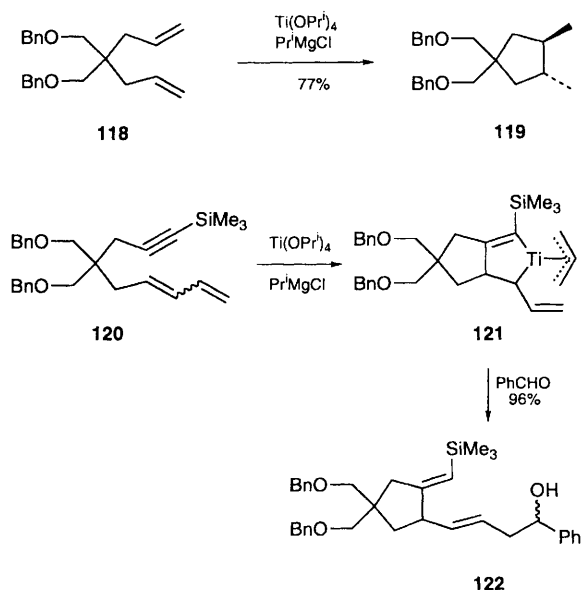


utilized this methodology in asymmetric syntheses of (+)-methyl epijasmonate and (–)-methyl cucurbitate, whereas Montgomery and Sauchenko^{73,74} have examined the cyclizations of bis-enones and the alkynyl enones **116** leading to products **117** in which the substituted double bonds have been introduced in a stereoselective manner.

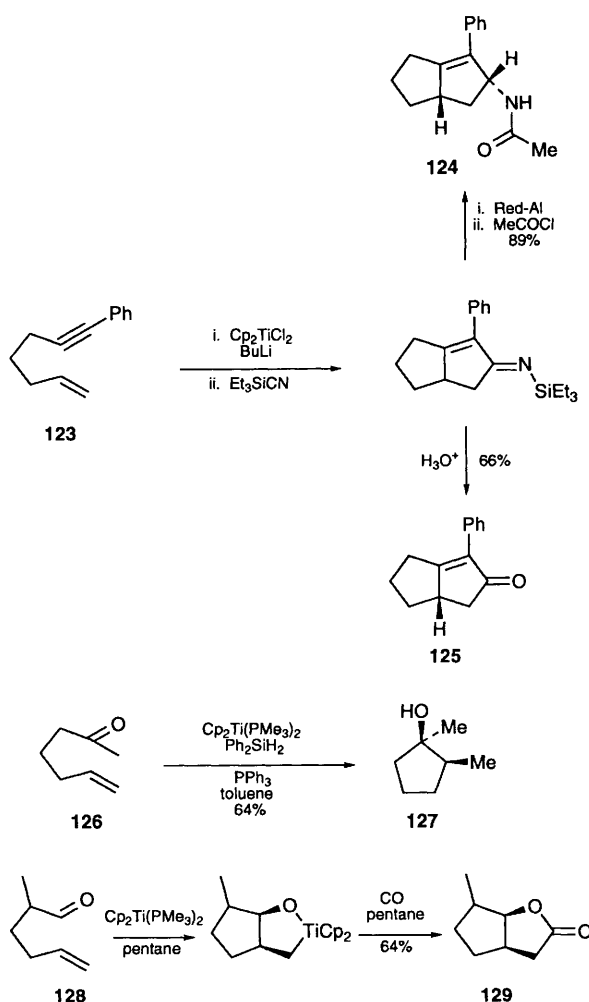


3.2.3 Zirconium and titanium

The zirconium-mediated intramolecular cyclisation of 1,6-dienes, enynes and diynes is a well-known method for the formation of cyclopentanes proceeding *via* zirconobicycles. Recently new methodology has been developed by Sato and co-workers⁷⁵ in which the established zirconium reagent is replaced by a new titanium reagent, *viz.* a titanobicycle. Thus the diene **118** is converted in high yield into the cyclopentane **119** upon treatment with titanium tetrakisopropoxide and iso-propylmagnesium chloride. As with zirconium, the intermediate metallobicycle can be reacted with carbon monoxide to give a bicyclo[3.3.0]octanone; one advantage over zirconium is that single terminal alkynes can be used in the cyclisation. Sato's group have extended this work to include the stereoselective synthesis of cycloalkylamines from unsaturated imines⁷⁶ as well as to the cyclisation of conjugated dienes with alkynes;⁷⁷ in the latter case it was found that the intermediate titanobicycle **121** derived from **120** reacts exclusively with electrophiles such as benzaldehyde through the allylic double bond to give the corresponding cyclopentane



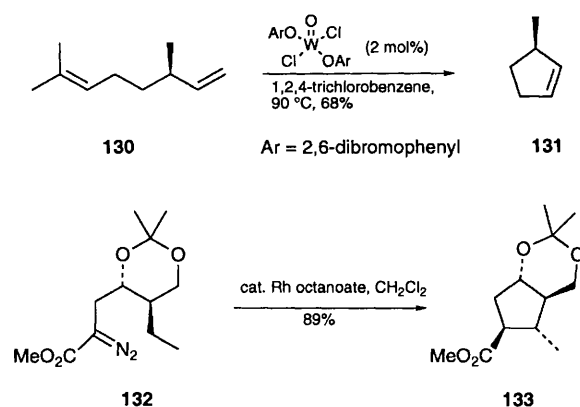
122 in excellent yield. Along similar lines, Buchwald and co-workers⁷⁸ have shown that dicyclopentene-titanium dichloride and butyllithium form a suitable alternative catalyst for the synthesis of bicyclic cyclopentenones and allylic amides; thus the enyne **123** can be converted into the amide **124** or the α,β -unsaturated ketone **125**. Zirconium-based cyclisations in conjunction with the zircon-ene-allene reaction have been used to synthesise linear and angular triquinane skeletons stereoselectively.⁷⁹ Returning to titanium-based methods, two research groups have studied the reductive cyclisations of δ,ε -unsaturated ketones and aldehydes. Buchwald and Kablaoui^{80,81} for instance have used a titanium catalyst with diphenylphosphine to prepare the cyclopentanol **127** from the enone **126**, whereas Crowe and co-workers^{82,83} have developed similar methodology that includes a carbon monoxide insertion reaction to synthesise fused bicyclic γ -butyrolactones, such as **129**, from enones *e.g.* **128**.



3.2.4 Other metals

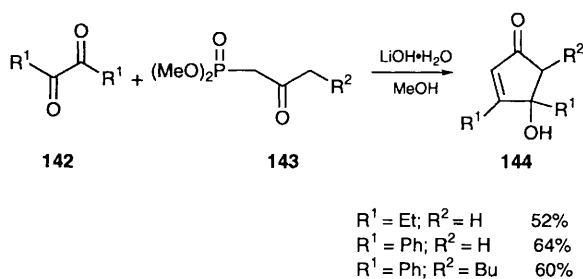
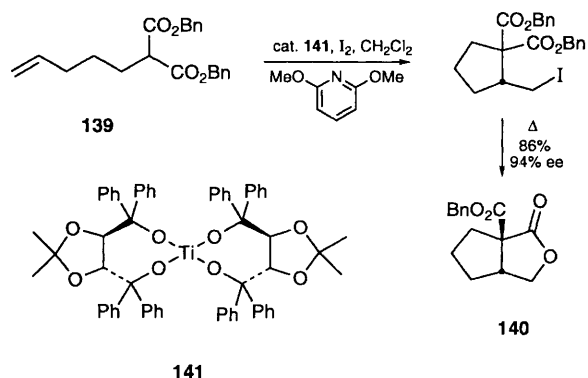
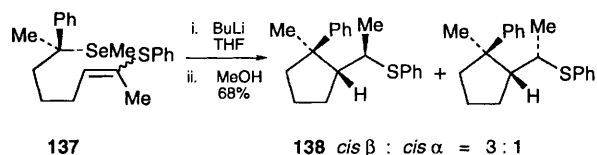
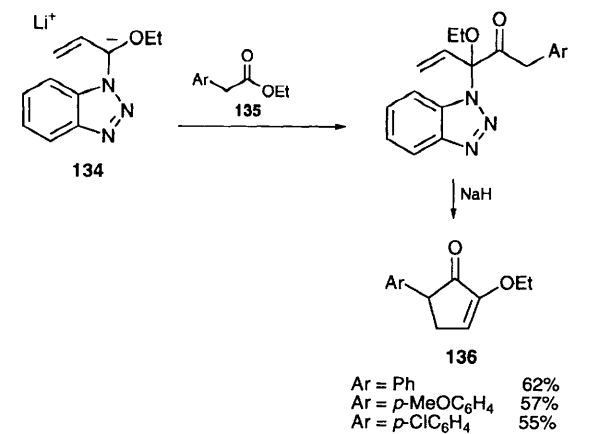
The familiar samarium diiodide coupling reactions of aldehydes and ketones with alkenes have been used for the synthesis of cyclopentanols notably by Holzaffel *et al.*⁸⁴ in their stereoselective synthesis

from carbohydrates; this methodology has been extended to oxime ethers for the synthesis of aminocyclopentenols.⁸⁵ Bennett and co-workers⁸⁶ have used samarium diiodide to effect the transformation of alkynyl bromides to cyclopentanes in very good yields. Forsyth and Huang⁸⁷ have reported the spirocarbomercuration of a silyl enol ether in their synthesis of the spirocyclic sesquiterpenes erythrodiene and spirojatamol. Rieke *et al.*⁸⁸ have reacted substituted (but-2-ene-1,4-diyl)magnesium complexes with carboxylic esters and lactones to generate cyclopentanols. In the field of alkene metathesis, Nugent *et al.*⁸⁹ have used a tungsten catalyst to synthesize enantiomerically pure cycloalkenes *e.g.* **131** from the simple dienes **130**, and Grubbs and Fuyimura⁹⁰ have had modest success with asymmetric ring-closure reactions using a chiral molybdenum catalyst. Finally, Taber and You⁹¹ have used a diastereoselective rhodium carbenoid C–H insertion reaction (**132** \rightarrow **133**) in their approach to the synthesis of the dendrobatid alkaloid 251F.



3.3 Anion-based methods

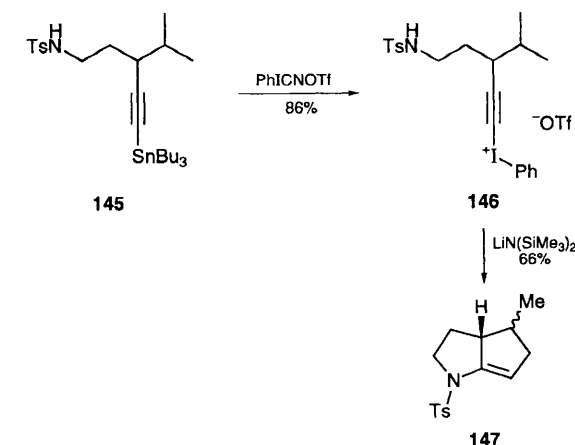
Once again there have been many reports of five-membered ring synthesis using anion-based methods, including the standard aldol, Michael and Dieckman-like reactions, those of note leading to the syntheses of (\pm)-laurene⁹² and (\pm)-axamide.^{93,94} There have also been a number of more novel methods including the reagent **134** devised by Katritzky *et al.*⁹⁵ to effect the transformation of esters **135** into 2-ethoxycyclopent-2-enones **136**. Krief and co-workers⁹⁶ have reported the stereoselective synthesis of 1,2-dialkyl-1-phenylcyclopentanes **138** by intramolecular carbolithiation of vinyl sulfides **137**, and Taguchi *et al.*⁹⁷ have used the chiral titanium reagent **141** to effect the catalytic asymmetric iodocarbocyclisation of diesters **139** to cyclopentane lactones **140**, both in very good yield and with high ees. There have been several reports of anion-based annulations, including two based on aldol condensations coupled with Wittig or Horner–Emmons reactions to make 4-hydroxycyclopent-2-en-1-ones **144**. Thus, Bonadies *et al.*⁹⁸ have reacted diketones **142** with phosphonates **143** to achieve this



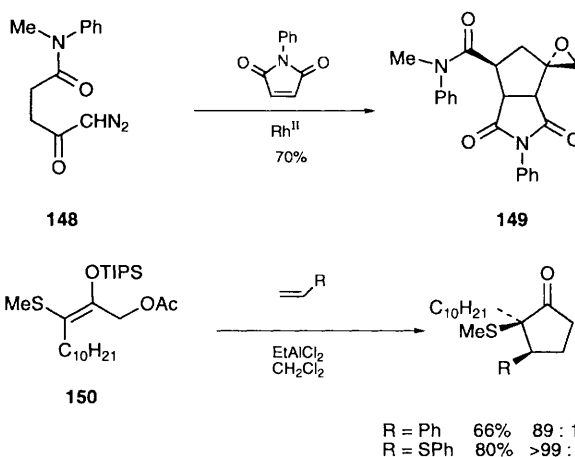
end, whereas Hatanaka and co-workers⁹⁹ have reacted a phosphorane with chiral glyoxals. Another annulation reaction leading to the synthesis of bicyclic conjugated enediones has been described by Ghera and co-workers.¹⁰⁰ Finally, in a carbene-based cyclisation, Feldman *et al.*¹⁰¹ have reacted the alkynylidonium salt **146** (derived from the alkynylstannane **145**) with base to produce the nitrogen-containing bicycle **147**.

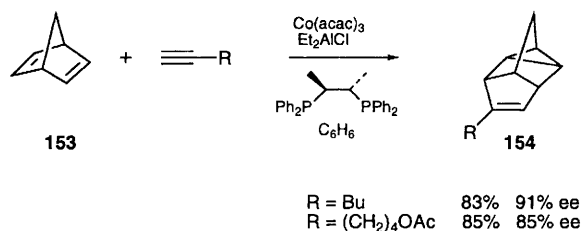
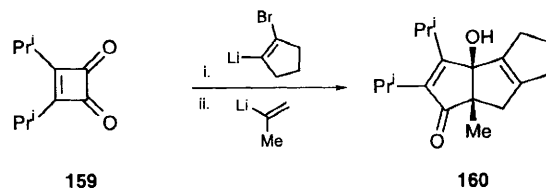
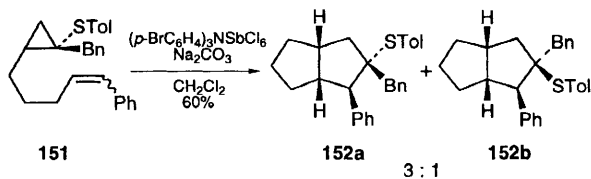
3.4 Cycloadditions, rearrangements and ring expansions

Many research groups have been active in the area of five-membered ring formation *via* cycloadditions.



A particularly interesting and unusual example has been devised by Padwa and co-workers¹⁰² in which an α -diazo- γ -amido ketone such as **148** is treated with rhodium(II) acetate and an electron-deficient alkene or alkyne to give a spiro-epoxy cyclopentane such as **149**. Lu and Zhang¹⁰³ have developed a phosphine-catalysed cycloaddition reaction between buta-2,3-dienoate and electron-deficient alkenes, while Kurajima *et al.*¹⁰⁴ have used the silyl enol ether **150** to prepare cyclopentanones from alkenes. A synthesis of diquinanes has been achieved by Iwato *et al.*¹⁰⁵ using a novel cation radical-mediated intramolecular [3 + 2] cycloaddition of cyclopropyl sulfides (**151** \rightarrow **152a,b**). Motherwell *et al.*¹⁰⁶ have continued to develop their intramolecular [3 + 2] cycloadditions involving cyclopropanes which under palladium catalysis are converted into bicyclic systems. Lautens and co-workers^{107,108} have made extensive studies on cobalt- and nickel-catalysed [2 π + 2 π + 2 π] cycloadditions; thus for instance bicyclo[2.2.1]hepta-2,5-diene **153** is converted into the enantiomerically pure cycloadducts **154** using Co(acac)₃ in conjunction with a chiral phosphine ligand. Weinreb and co-workers¹⁰⁹ have reported a novel ene reaction involving allenylsilanes to synthesise cyclopentanols and cyclohexanols, while Normant *et al.*⁷⁹ have used a similar zinc-ene-allene reaction to prepare, for example, the cyclopentane **156** from the silylalkyne **155** in very good yield; this



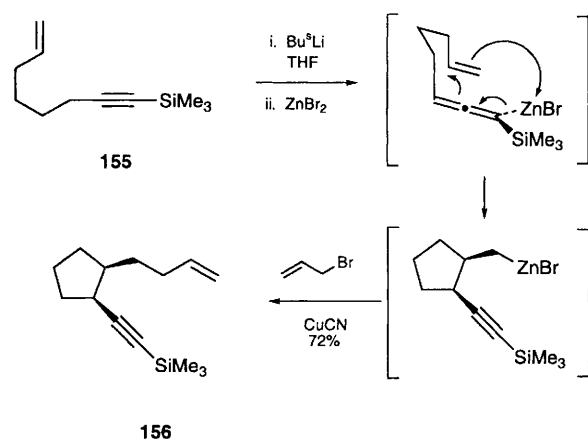


developed a facile conversion of cyclobutanones into cyclopentanones using samarium diiodide and diiodomethane. Finally, Fukumoto *et al.*^{114,115} have prepared cyclopentanones from vinyl cyclobutanols.

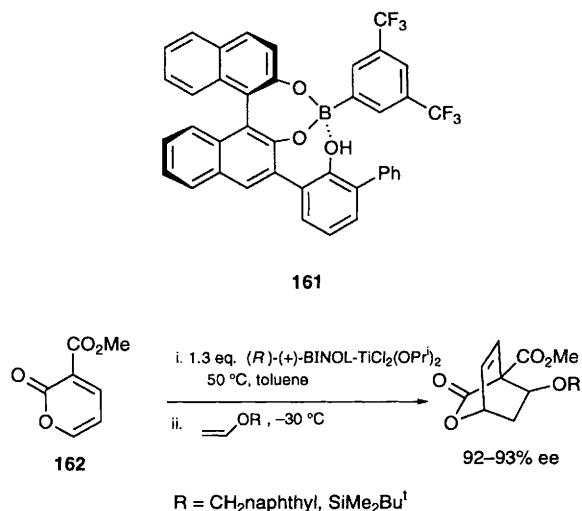
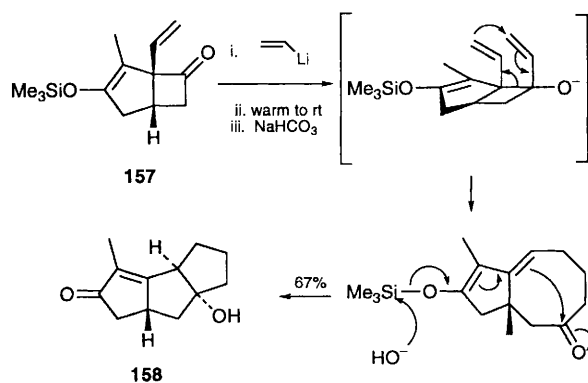
4 Six-membered rings

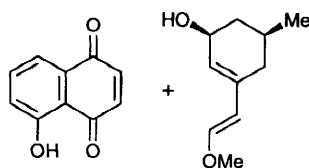
4.1 Diels–Alder reactions

The Diels–Alder reaction has continued to be the premier method for the formation of six-membered carbocycles, and again much work has been focused towards developing new methods for the construction of enantiomerically pure cyclohexenes. The interest in asymmetric catalysis using binaphthol ligands has continued.¹¹⁶ For example the cycloadditions of eight different dienophiles were found to give very high ees with the boron-derived catalyst **161** and a number of cyclic and acyclic dienes.¹¹⁷ Posner *et al.*¹¹⁸ have reported that the pyrone **162** undergoes enantioselective cycloaddition using a BINOL [1,1'-bi(2-naphthol)]–Ti catalyst. A very interesting kinetic resolution was reported by Larsen *et al.*¹¹⁹ during the synthesis of angucyclinone antibiotics. It was found that brief exposure (< 2 min) of 5-hydroxy-naphtho-1,4-quinone and the *racemic* diene **163**, to a catalyst prepared from (*S*)-3,3'-diphenyl-1,1'-binaphthalene-2,2'-diol and borane, gave the Diels–Alder adduct **164** in good yield and greater than 98% ee. The use of chiral auxiliaries and diastereocontrol has continued to attract attention. For example Sommakia and Berliner have demonstrated¹²⁰ that treatment of the acetals **165** with fluoroboric acid yields the cyclohexenes **167** via highly diastereoselective Diels–Alder cycloaddition of the vinyloxocarbenium ions **166**. The continued interest of Aggarwal *et al.*¹²¹ in chiral

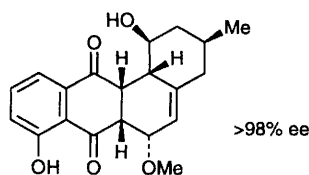
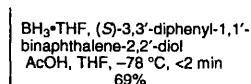


sequence in conjunction with zirconium chemistry has led to the synthesis of linear and angular triquinane carbon skeletons. An alternative synthesis of triquinanes has been devised by Moore and Santora¹¹⁰ which features a novel tandem oxy-Cope–transannular ring closure to prepare, for example, the triquinane **158** from the ketone **157**. Paquette and Doyen¹¹¹ have continued to explore the fascinating chemistry of squarate esters to achieve full control of regioselectivity in their synthesis of linear and angular polyquinanes (**159**→**160**). In the field of ring expansions, Fitjer *et al.*¹¹² have successfully prepared cyclopentanones from cyclobutyl phenyl sulfides (an asymmetric method has also been described), and Fukuzawa and Tsuchimoto¹¹³ have

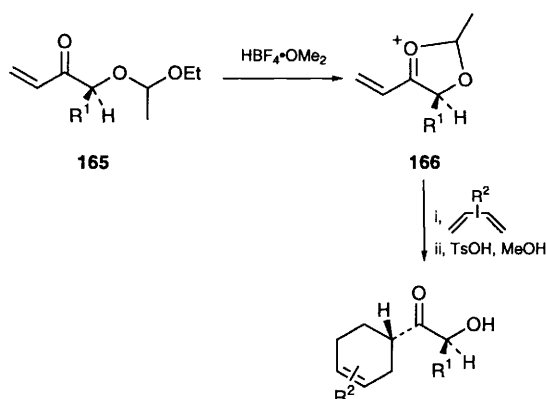




(±)-163

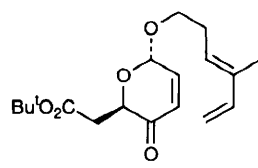
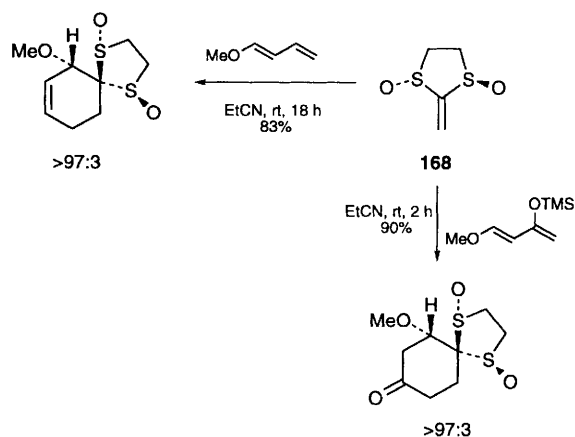


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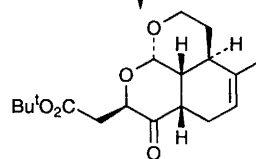
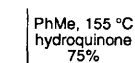


167 40–74%
high des (20–200:1)

sulfoxides has led to some promising results with the use of the enantiomerically pure sulfoxide **168** as a chiral ketene equivalent in diastereoselective Diels–Alder reactions. An entry to enantiomerically pure decalin structures has been reported by Chapleur and co-workers¹²² via the diastereoselective intramolecular reaction of the carbohydrate derived triene **169**. An interesting use of the retro Diels–

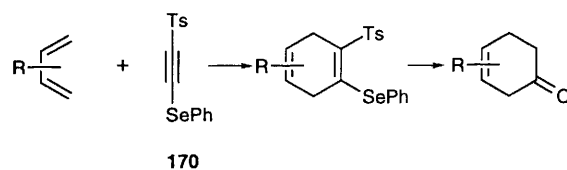


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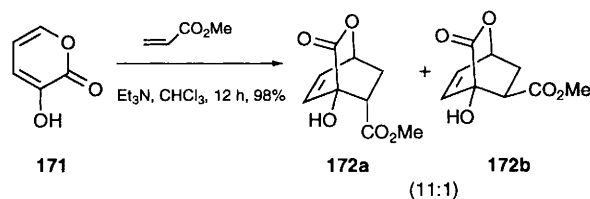


Alder reaction has been described in an enantioselective synthesis¹²³ of calcitriol.

The toluene-*p*-sulfonyl selenoacetylene **170** has proved to be a useful masked ketene equivalent in a number of Diels–Alder reactions with unactivated dienes, leading to excellent yields of cycloadducts under mild conditions.¹²⁴ Grieco *et al.*^{125,126} have continued to report on the excellent results obtained with lithium perchlorate-accelerated Diels–Alder reactions. Of particular note is the use of LiNTf_2 as a safer and equally efficient alternative to LiClO_4 .¹²⁷ Okamura *et al.*¹²⁸ have demonstrated that 3-hydroxy-2-pyrone undergoes a base-catalysed Diels–Alder reaction with a number of dienophiles without the need for high pressure *e.g.* **171** → **172a,b**. Furthermore, the resulting cycloadducts can be isolated without extrusion of CO_2 . Funk and Yost have shown that 2-acyloxyacroleins are excellent dienophiles for a number of different diene systems. Most importantly the tetrasubstituted dienes **173** lead to excellent yields of Diels–Alder cycloadducts under SnCl_4 catalysis, thus providing rapid access to functionalised Taxol A ring synthons.¹²⁹



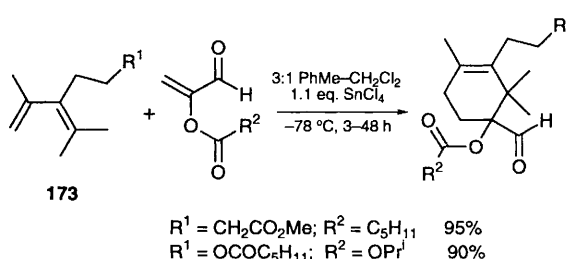
170



171

172a

172b

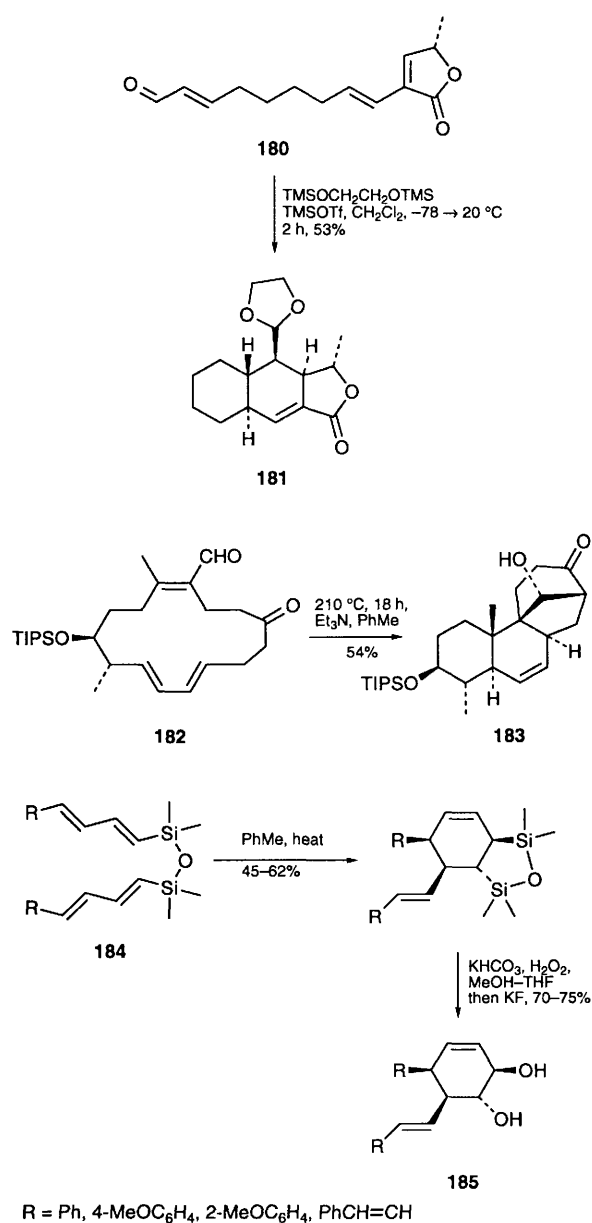
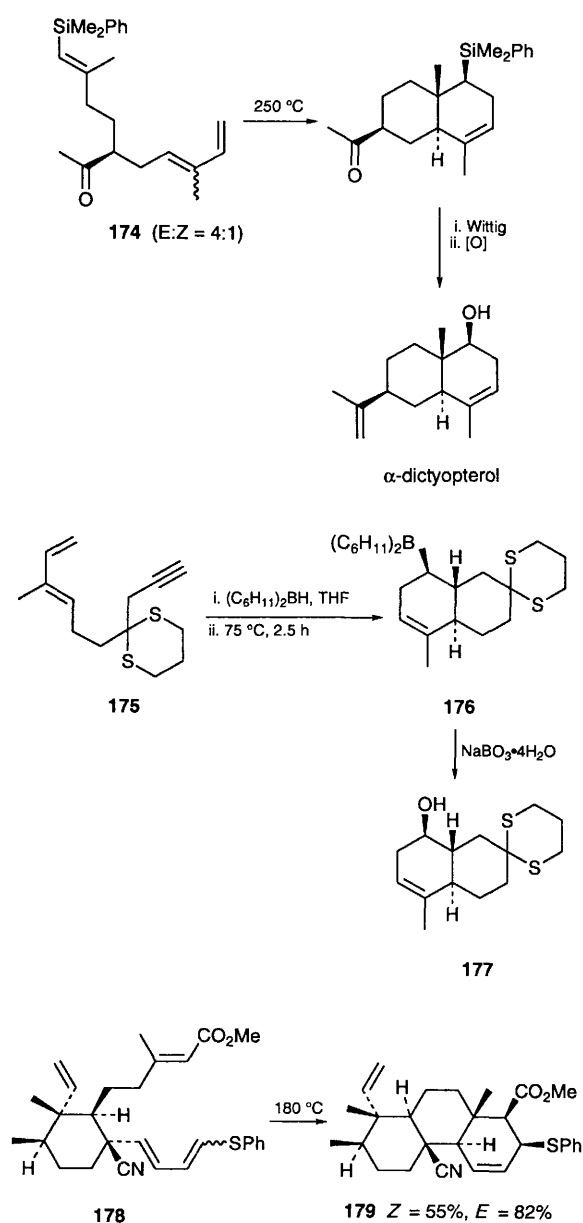


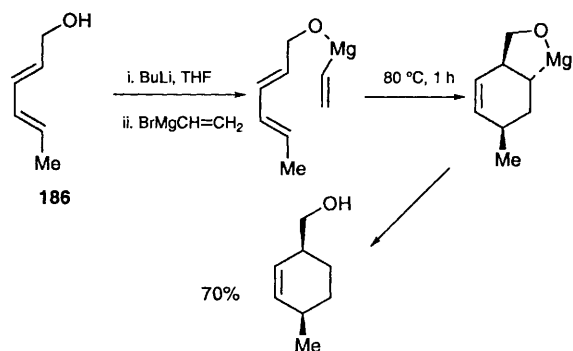
173

$\text{R}^1 = \text{CH}_2\text{CO}_2\text{Me}$; $\text{R}^2 = \text{C}_5\text{H}_{11}$ 95%
 $\text{R}^1 = \text{OCOC}_5\text{H}_{11}$; $\text{R}^2 = \text{OPr}^i$ 90%

The intramolecular Diels–Alder (IMDA) reaction continues to be one of the most useful strategies in target molecule synthesis and a number of significant examples have been reported over the review period. Taber's synthesis of α -dictyopterol involved an efficient construction of the decalin framework via IMDA reaction of the vinylsilane **174** followed by Wittig olefination and oxidative desilylation.¹³⁰ Singleton and Lee¹³¹ have continued their studies on the use of vinylboranes in the Diels–Alder reaction and have found that hydroboration of the acetylene **175** followed by IMDA of the intermediate vinylborane **176** yields the hydroxylated decalin **177** after oxidative work-up, all in a one pot reaction. It is interesting to note that **175** itself is constructed in good yield in a one pot reaction. In an approach towards the diterpene skeleton of the radarins either geometrical isomer of the tetraene **178** was found to undergo IMDA leading to the highly functionalised skeleton **179**.¹³² Baldwin and

co-workers¹³³ have demonstrated the viability of an IMDA in the proposed biosynthesis of himgravin (**180**→**181**), and Deslongchamps and Hall¹³⁴ have used a tandem transannular Diels–Alder–aldol cyclisation sequence to good effect in a stereocontrolled approach towards (+)-aphidicolin (**182**→**183**). The temporary silicon connection has again been used as a powerful tool in the stereocontrolled formation of highly functionalised cyclohexenes.¹³⁵ For example Luh *et al.*¹³⁶ found that the siloxane tethered bis-dienes **184** underwent IMDA reaction followed by oxidative desilylation to yield the highly functionalised *trans*-cyclohex-3-ene-1,2-diols **185** with complete stereocontrol. Finally, Stork and Chan¹³⁷ have reported the remarkable observation that a magnesium or aluminium atom can serve as a temporary connection in an IMDA reaction, leading to good yields and stereoselectivities. One of the fascinating features of this reaction is that it allows for the cycloaddition of unactivated

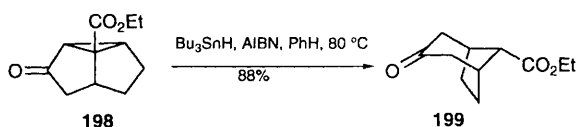
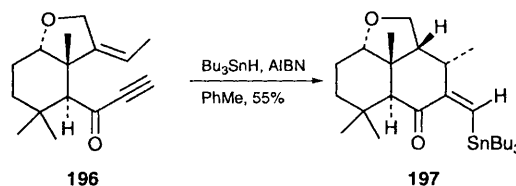
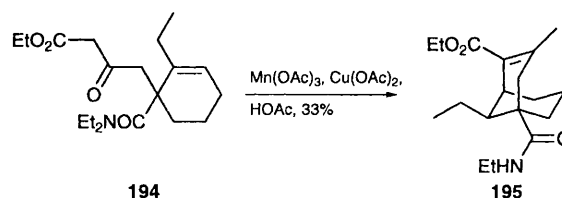
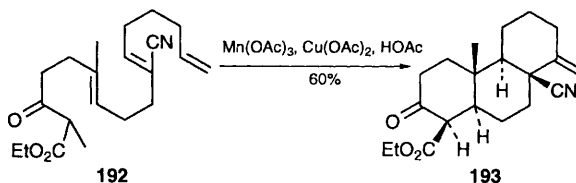
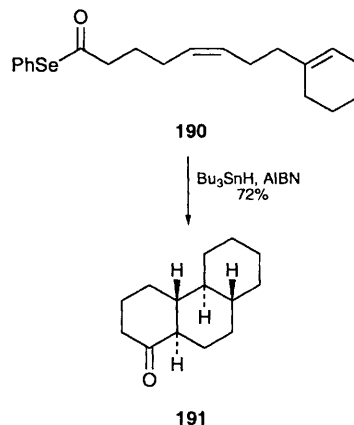
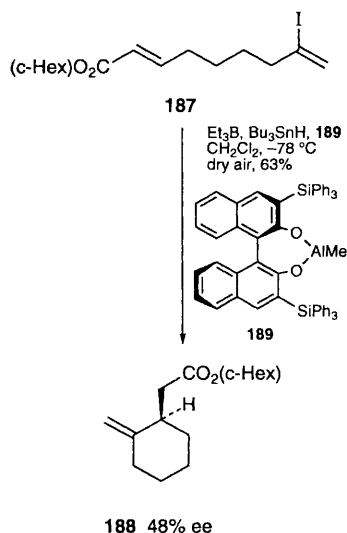




dienes and dienophiles under mild conditions. The reaction of **186** with vinylmagnesium bromide is illustrative.

4.2 Free radical cyclisation

Nishida and co-workers¹³⁸ have reported the first example of an enantioselective radical cyclisation controlled by a chiral aluminium reagent. For example treatment of the vinyl iodide **187** with tributyltin hydride and triethylborane in the presence of the binaphthol catalyst **189** gave the methylenecyclohexene **188** in 63% yield with an ee of 48%. Although in absolute terms this ee is moderate, the fact that enantioselectivity in a prochiral 6-*exo* radical cyclisation ($k_c \sim 5.4 \times 10^3 \text{ s}^{-1}$) can be controlled by added external Lewis acid is impressive. Chelation controlled 6-*exo* radical cyclisations of chiral oxazolidinone-derived alk-2-enamides were found to proceed in good yield with moderate diastereoselection.¹³⁹ Pattenden and co-workers^{140–142} have published a series of full papers on their successful 6-*endo* multiple radical cyclisation reactions of polyenes (e.g. **190** → **191**). In a similar vein Zoretic *et al.*¹⁴³ have shown that the Mn^{III} oxidative cyclisation of the polyene **192** gives the tricyclic system **193** with excellent stereoselectivity. In an approach towards the huperzine skeleton White and Jeffrey¹⁴⁴ found that Mn^{III} oxida-

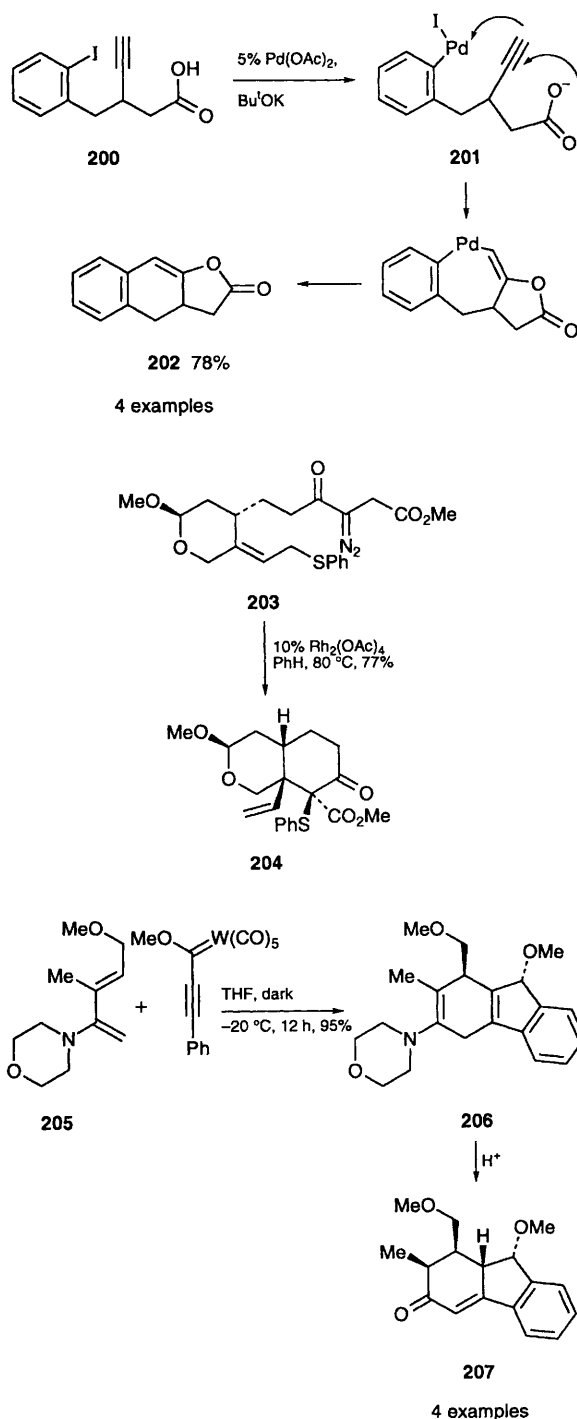


tive cyclisation of the amide **194** gave the [3.3.1] bicyclic system **195**. The rather unusual deethylation was a result of a sequence involving 1,5-hydrogen abstraction, oxidation, hydroxylation and loss of acetaldehyde. A 6-*endo* radical cyclisation, initiated by addition of the tributylstannyl radical to an acetylene, has been used in an approach to forskolin (**196** → **197**).¹⁴⁵ Addition of $\text{Bu}_3\text{Sn}^\bullet$ to the carbonyl oxygen of the diquinane **198** followed by β -scission of the adjacent cyclopropane bond has been shown to provide novel access to the [3.2.1] ring system **199**.¹⁴⁶

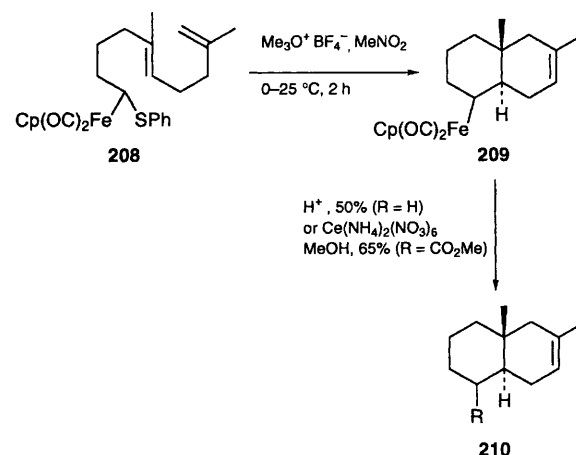
4.3 Transition metal mediated cyclisations

Balme *et al.*¹⁴⁷ have reported a useful palladium terminated carbocyclisation for the formation of functionalised lactones. For example, treatment of

the carboxylic acid **200** with palladium acetate in the presence of base leads to the lactone **202** via cyclisation of the Pd^{II} intermediate **201**. Malacria and co-workers^{148,149} have used the Vollhardt cobalt mediated cycloaddition to good effect in the rapid construction of complex terpene skeletons. The rhodium-catalysed generation of sulfonium ylides from diazo esters, and the subsequent [2,3] sigma-tropic rearrangement¹⁵⁰ have proved useful in the synthesis of highly functionalised cyclohexanones, as well as in a key step (**203**→**204**) in an approach to vernolepin¹⁵¹. A novel and very useful annulation (**205**→**207**) reaction involving Fischer carbene

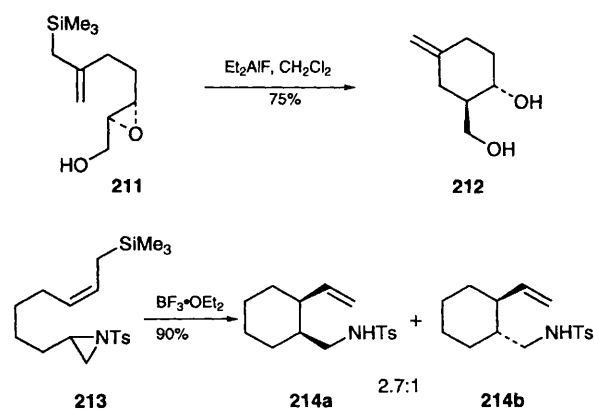


complexes and dienes leads to highly functionalised tricyclic ring systems in a one pot sequence.¹⁵² The reaction is thought to proceed *via* an initial [4 + 2] cycloaddition followed by benzannulation to yield the enamine **206**. Grubbs *et al.*¹⁵³ have continued to report on the success of their ruthenium-catalysed metathesis reaction for the formation of fused 6,5- and 6,6-systems. Helquist *et al.*¹⁵⁴ have demonstrated that iron carbene complexes undergo cationic polyene cyclisations leading to fused 6,6-systems (**208**→**210**). A useful feature of these reactions is that the intermediate iron complex **209** can be used to introduce further functionality into the cyclised products.

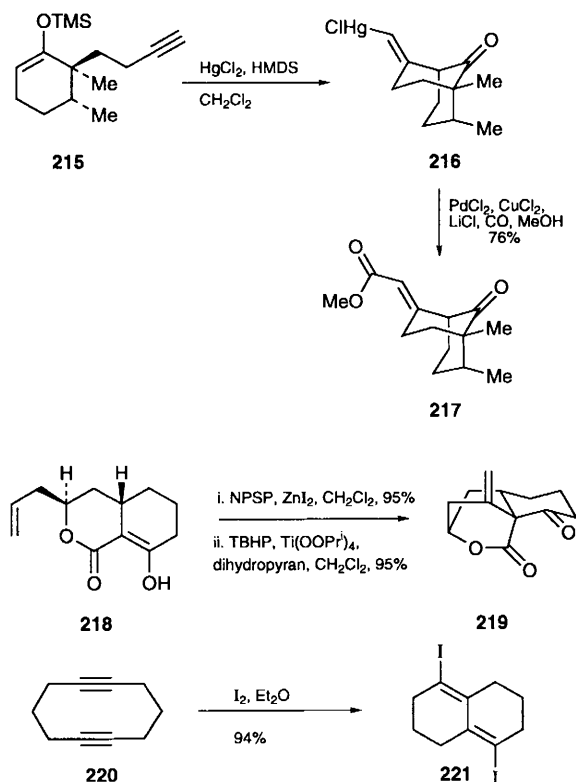


4.4 Cationic cyclisations

Lewis acid-catalysed cyclohexane ring formation reactions have continued to attract interest and a number of research groups have reported significant results over the review period. For example, Jung *et al.*¹⁵⁵ have shown that the allylsilane cyclisation of the Sharpless derived epoxy alcohol **211** leads to the enantiomerically pure diol **212** in good yield upon treatment with diethylaluminium fluoride. A similar BF₃-catalysed allylsilane ring-opening reaction of an aziridine **213** was used to construct the amino substituted cyclohexanes **214a,b**.¹⁵⁶ Majetich and Siesel¹⁵⁷ have used a BF₃-catalysed cyclisation in their synthesis of nimbiol.

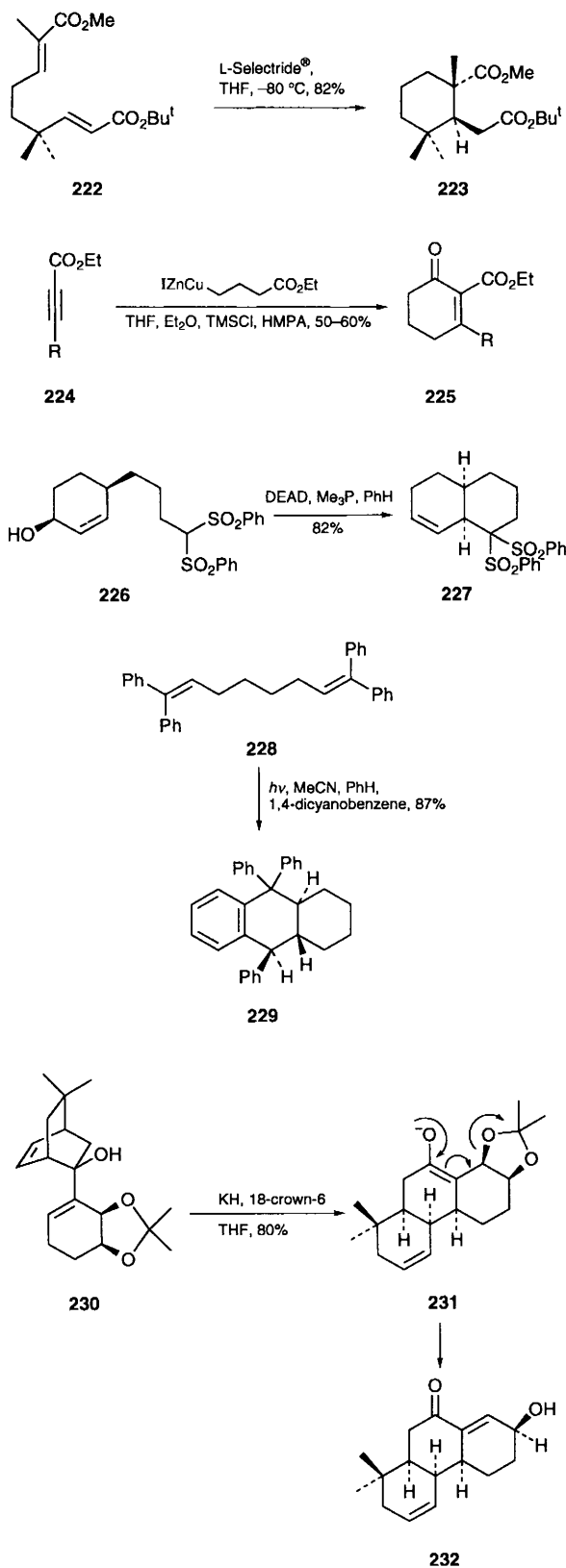


the silyl enol ether **215** gave the intermediate vinyl-mercury species **216** which underwent transmetalation with palladium followed by carbonylation to yield the [3.3.1] bicyclic ketoester **217**.¹⁵⁸ Ley and co-workers¹⁵⁹ have again used the selenium mediated cationic cyclisation to good effect in an approach towards the insect antifeedant jodrellin (**218**→**219**). A high yielding iodine mediated transannular cyclisation of the bis-acetylene **220** has been shown to lead to the symmetrically functionalised¹⁶⁰ decalin system **221**.

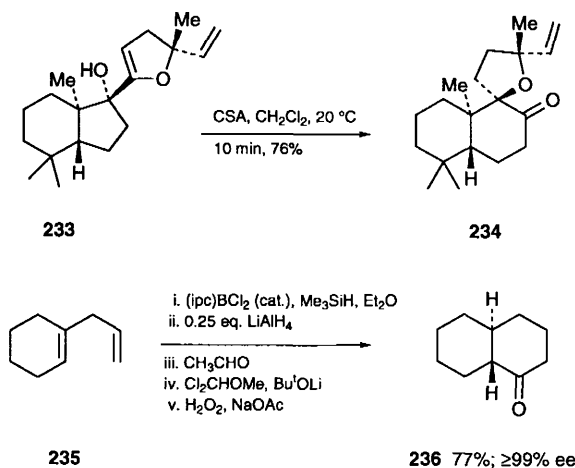


4.5 Other routes

Yamaguchi *et al.*¹⁶¹ have found that conjugate addition of hydride to the bis- α,β -unsaturated ester **222** promotes a Michael ring closure to form the cyclohexane diester **223** in good yield. In a similar vein Crimmins and co-workers¹⁶² have reported on a useful annulation reaction involving the conjugate addition of zinc-copper reagents to acetylenic esters (**224**→**225**). Functionalised 6,6-bicyclic systems have been constructed using a novel dehydrative cyclisation of allylic alcohols under Mitsunobu conditions (**226**→**227**).¹⁶³ Mangion *et al.*¹⁶⁴ have demonstrated that the diene **228** undergoes a stereoselective photosensitised [4+2] cycloaddition to give the tricyclic system **229** in excellent yield. Paquette and Tsui¹⁶⁵ have once again demonstrated the power of the anionic oxy Cope-rearrangement for the construction of complex carbocyclic structures from simple precursors. Thus, in their approach to the diterpene kaurane, the requisite dienol **230** was readily available in enantiomerically pure form and



underwent smooth rearrangement to the enone **232** via elimination from the intermediate enolate **231**. The same research group reported the use of a stereocontrolled oxonium ion-activated pinacol ring expansion (**233**→**234**) as the key step in the construction of (+)-grindelic acid.¹⁶⁶ Finally, Brown

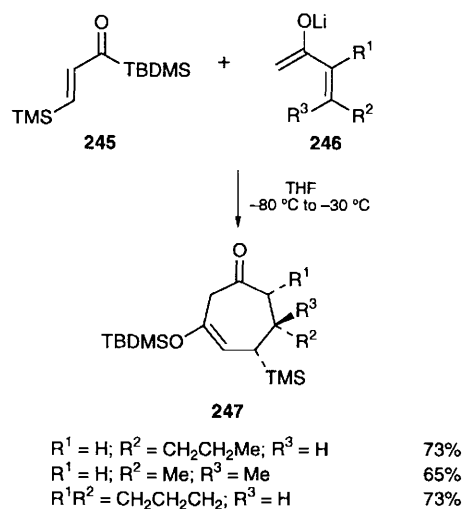
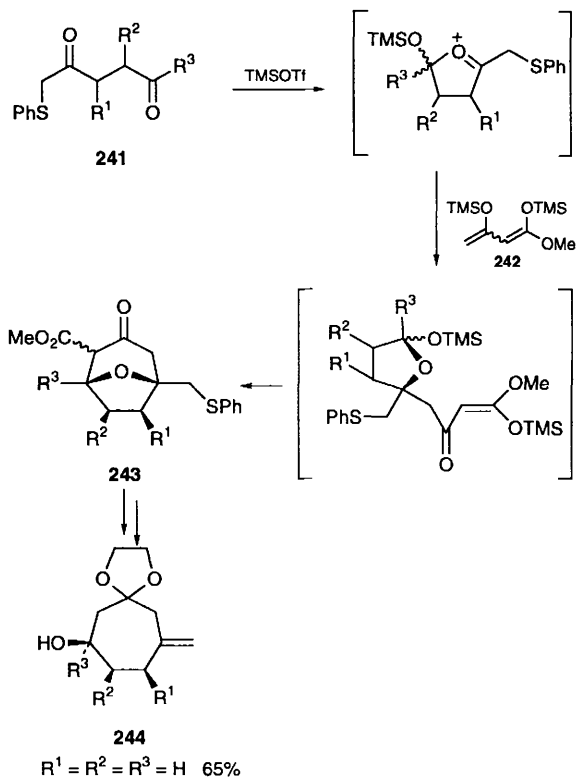
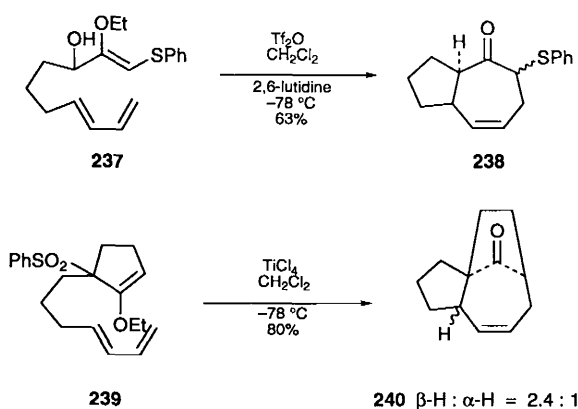


and colleagues¹⁶⁷ have reported a practical enantioselective synthesis of *trans*-decalone **236**, which involves treatment of the allylcyclohexene **235** with a remarkable succession of five different reagents resulting in an overall yield of 76% and an ee $\geq 99\%$.

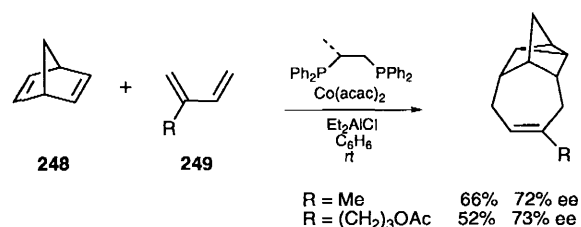
5 Seven-membered rings

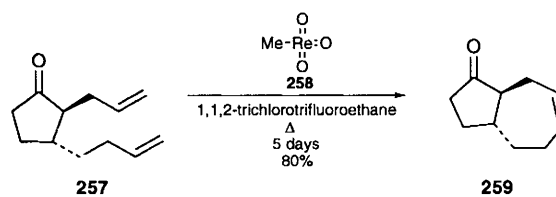
5.1 Cycloadditions and annulations

The most frequently reported method for the synthesis of seven-membered rings has been via [3+4] cycloadditions or annulations. Harmata *et al.*^{168–170} have been particularly prolific in the field of intramolecular cycloadditions; for example treatment of the allyl alcohol **237** with trifluoromethanesulfonic anhydride and 2,6-lutidine resulted in the formation of the bicycle **238** via cycloaddition of the intermediate vinylthionium ion. The tricycle **240** was prepared in high yield by Lewis acid-induced formation of the alkoxyallylic cation from the enol ether **239**. Molander and Eastwood¹⁷¹ have reported that the reaction of diones **241** with the bis(trimethylsilyl)enol ether **242** gives the familiar oxygen-bridged carbocycle **243** which can then be readily converted into the cycloheptane **244**. This method has also been adapted to [3+5] annulations. Takeda and co-workers¹⁷² have described the reaction of the silane **245** with the lithium enolates of α, β -unsaturated ketones **246** to give the desired

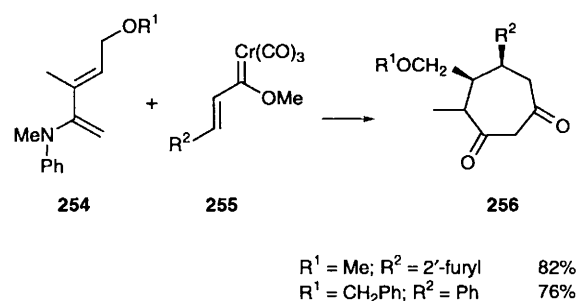
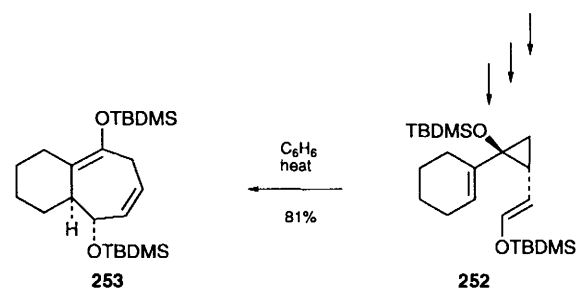
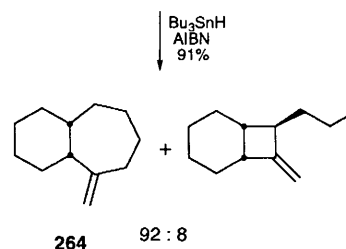
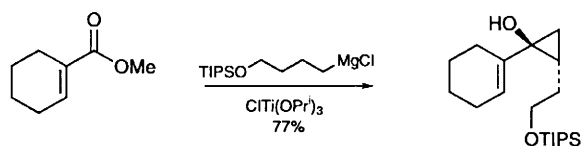
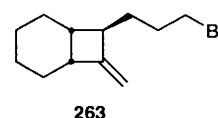
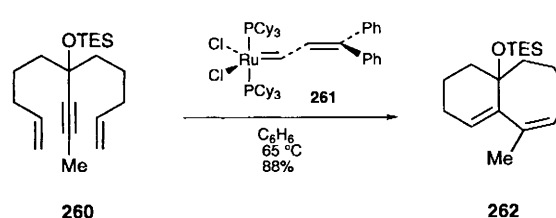


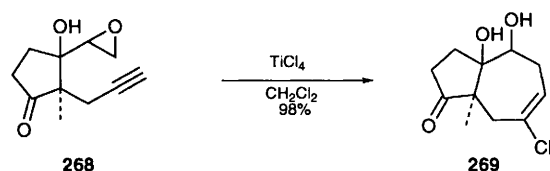
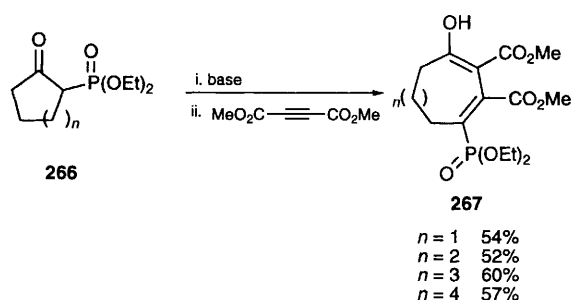
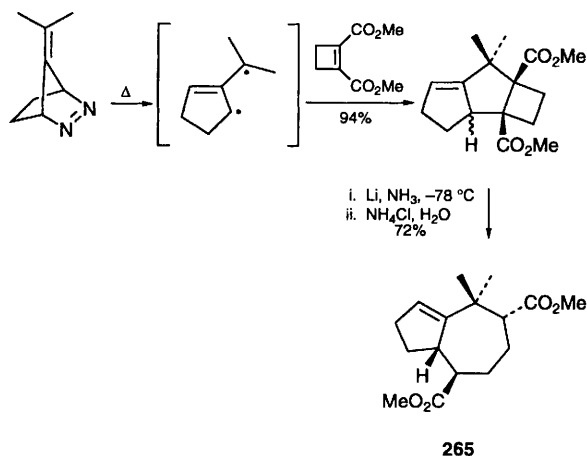
products **247** in good yield. Higher order cycloadditions have also featured in the preparation of seven-membered rings. Lautens *et al.*¹⁰⁷ in their studies of the reactions of bicyclo[2.2.1]hepta-2,5-diene **248** have demonstrated the asymmetric $[2\pi + 2\pi + 4\pi]$ cycloaddition with dienes **249** using a cobalt catalyst and the chiral ligand *R*-1,2-bis(diphenylphos-



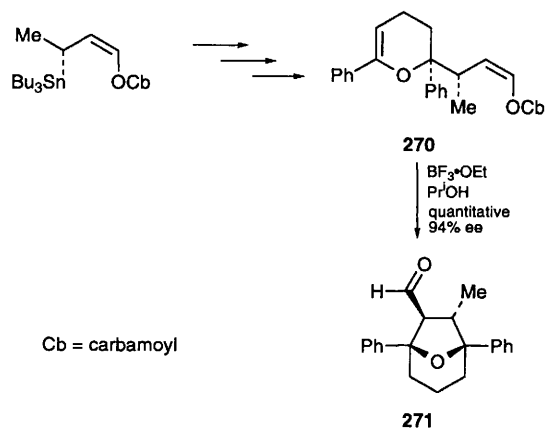


cyclopentane **257**. Grubbs *et al.*¹⁵³ have also used the ruthenium catalyst **261** in their studies on the metathesis of diynes, such as **260**, to give fused bicyclic $[n.m.0]$ rings (e.g. **262**) in very good yields. Using an alternative strategy, Dowd and Zhang¹⁷⁷ have extended their work on free radical ring expansions of fused cyclobutanones to fused methylenecyclobutanes; for example **263** gave the



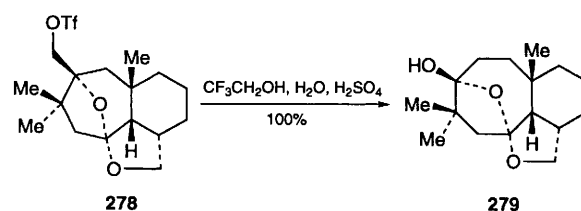
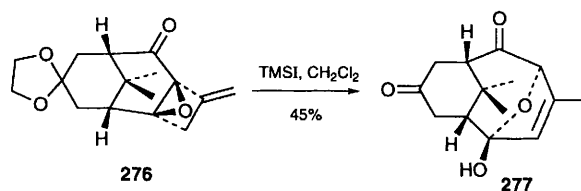
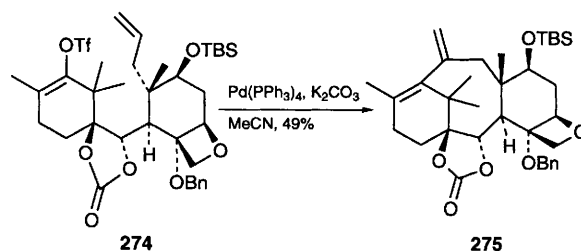
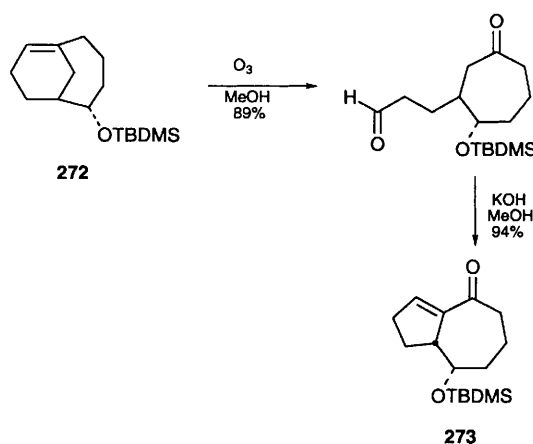


bicyclic tetrahydrofurancarbaldehydes from chiral 3-stannylbut-1-enyl carbamates by tandem homoaldol–aldol reaction has been reported by Hoppe and co-workers (**270**→**271**).¹⁸² Finally, Shea *et al.*¹⁸³ have developed a simple fused cycloheptane and cyclooctane synthesis by subjecting **272** to ozonolysis followed by an intramolecular aldol condensation to give, for example, the [5.3.0] bicyclic system **273** in excellent overall yield. This bridged-to-fused ring interchange methodology has been used in a neat total synthesis of the sesquiterpene ledol.¹⁸⁴

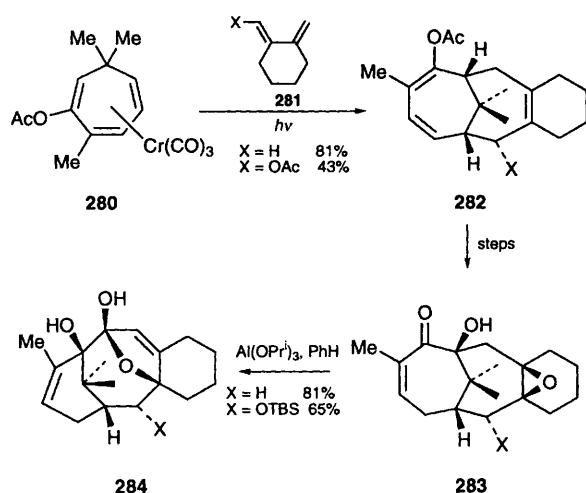


6 Eight-membered rings

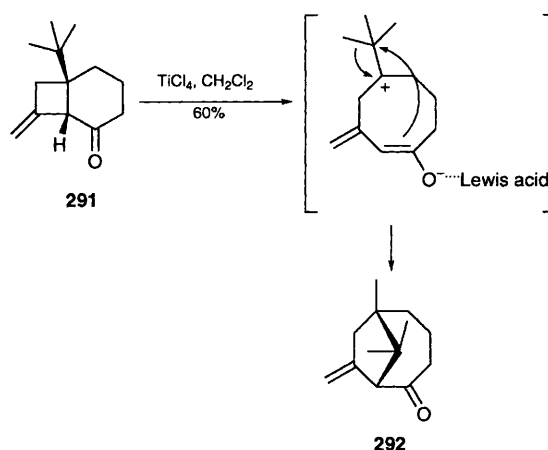
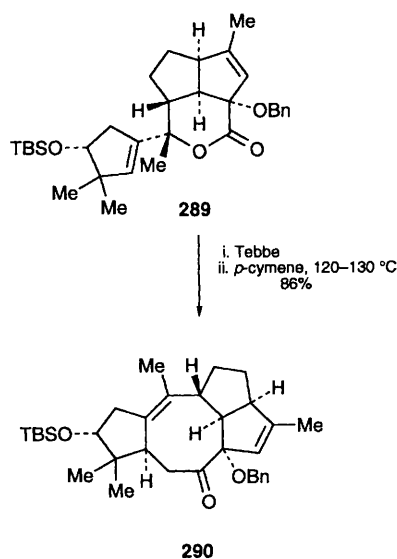
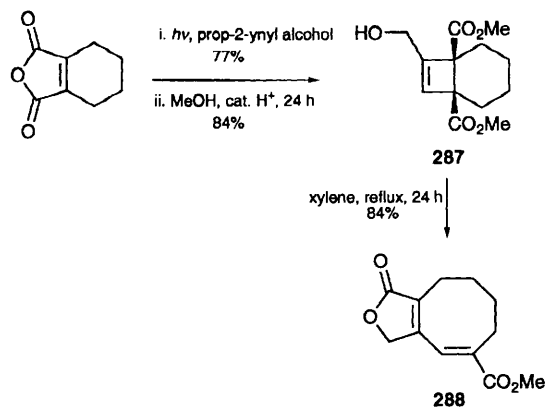
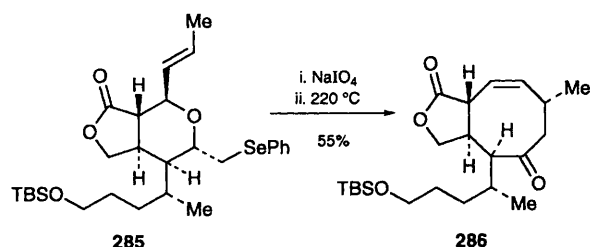
Once again, this year has seen a heightened level of interest in eight-membered carbocycle constructions due to the intense synthetic activity towards Taxol and its congeners. Thus Danishefsky *et al.* have described the total synthesis of baccatin III¹⁸⁵ and constructs¹⁸⁶ using an intramolecular Heck reaction to construct the eight-membered B-ring (**274**→**275**). Blechert *et al.*¹⁸⁷ have used a novel TMSI-promoted ring enlargement process (**276**→**277**) for the formation of the taxane A,B-ring system. Swindell and his co-workers^{188–190} have continued to publish promising results towards the taxanes using Ti- or Sm-mediated pinacol ring closure. Magnus *et al.*¹⁹¹ have constructed the B,C-ring of the taxanes using an extremely efficient semi-pinacol type ring expansion under acid conditions (**278**→**279**). The seven-membered precursor **278** was readily constructed by pyrylium ylide cycloaddition. The cycloaddition chemistry of chromium carbonyl complexes has



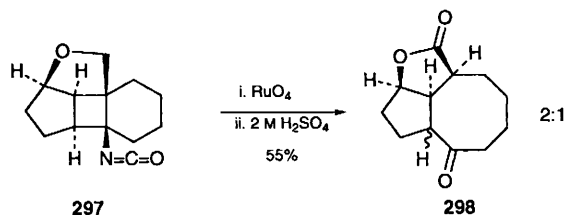
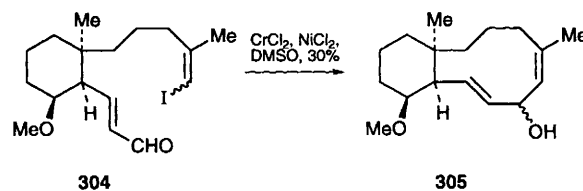
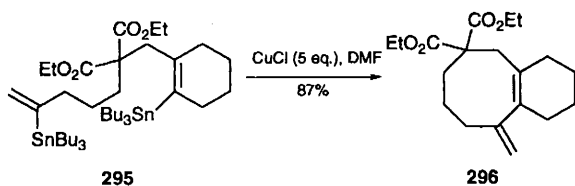
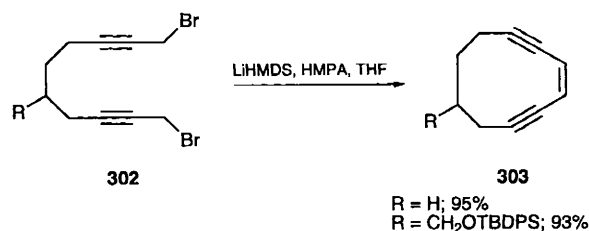
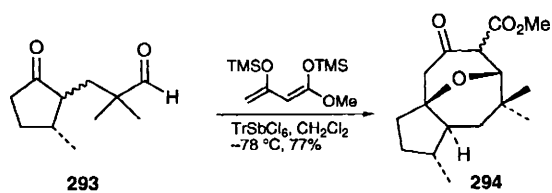
been admirably demonstrated by Rigby *et al.* over the past few years and has recently been used to great effect in the construction of the taxane skeleton. For example, the photochemical [6 + 4] cycloaddition between the chromium tricarbonyl complex **280** and the diene **281** led to the adduct **282** which after some functional group interconversions gave the ketol epoxide **283**. This epoxide was then subjected to an α -ketol rearrangement by treatment with aluminium isopropoxide which resulted in the formation of the taxane A,B-rings **284** in good yield.¹⁹² Other contributions to the formation of the taxane B-ring have come from a number of laboratories including those of Wender,¹⁹³ Kumar,¹⁹⁴ Miesch,¹⁹⁵ Paquette¹⁹⁶ and Magnus.¹⁹⁷ Finally, Nicolaou and Gray¹⁹⁸ have published a highly readable and personal account of their successful Taxol synthesis.



A number of other cyclooctane-containing natural products have been investigated over the review period. For example Paquette and co-workers¹⁹⁹ reported full details of their (+)-acetoxycrenulide synthesis which involved an oxidation–Claisen sequence as the key step (**285**→**286**). Booker-Milburn and Sharpe²⁰⁰ have described an approach to the related pachylactone skeleton where the key step involved an electrocyclic ring opening of the cyclobutene **287** followed by spontaneous lactonisation to yield the cyclooctane **288**. Borrelly and Paquette²⁰¹ also described a very neat Tebbe–Claisen sequence for the rapid construction of the kalmanol skeleton (**289**→**290**). An interesting Lewis acid mediated fragmentation–cyclisation sequence has been used as the key step in the synthesis of (±)-tetramethylmediterraneol B (**291**→**292**).²⁰²



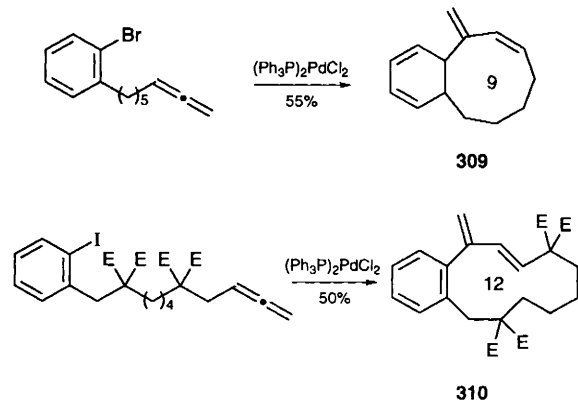
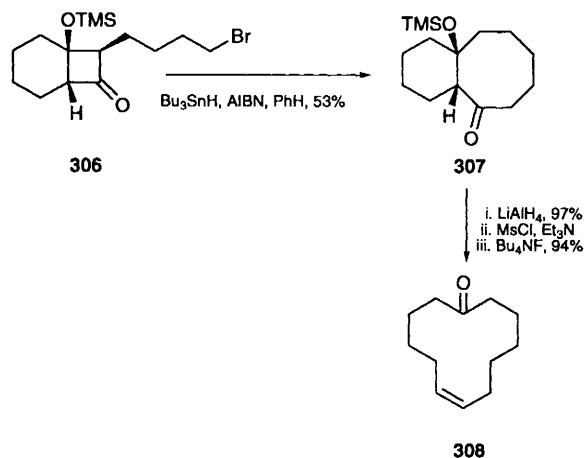
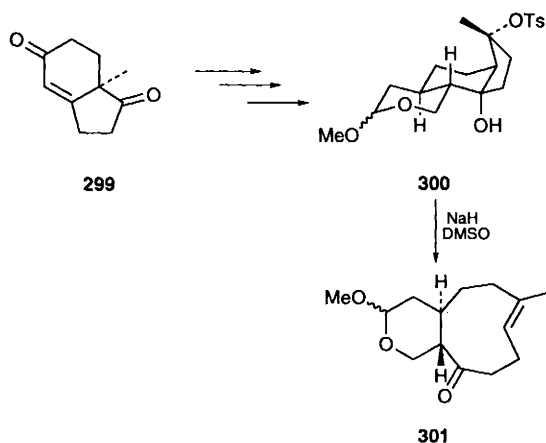
Molander and Eastwood²⁰³ have used a [3 + 5] cycloaddition (**293**→**294**) as the key step in their total synthesis of (+)-dactyol. Piers and Romero²⁰⁴ have reported a useful oxidative cyclisation of bis-alkenylstannanes for the formation of carbocycles of various sizes. For example the bis-alkenylstannane **295** underwent oxidative coupling on treatment with CuCl in DMF to give the 6,8-system **296** in excellent yield. Booker-Milburn and Cowell³⁵ used a novel aza deMayo reaction in their approach towards the

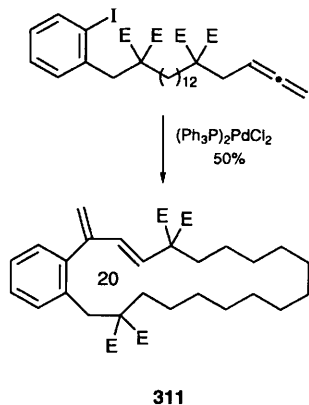


ten-membered ring of the potent anti-inflammatory marine diterpenoid solenolide **F** (**304**→**305**). Dowd and Zhang²¹⁰ have described a useful double ring expansion procedure for the formation of 11- and 12-membered rings. For example reductive cyclisation ring expansion of the cyclobutanone **306** leads to the 6,8-system **307**, which after Grob fragmentation gives the 12-membered enone **308**. Finally, Ma and Negishi²¹¹ have disclosed exciting results on the cyclic carbopalladation of ω -haloallenes. This promises to be a general route towards aryl fused medium and large rings and provides ready access

7 Nine-membered and larger rings

Pfander *et al.*²⁰⁷ have used a Grob fragmentation of the toluene-*p*-sulfonate **300** [derived from (–)-Hajos Parrish ketone **299**] in their synthesis of the optically active *trans*-cyclononene **301**. Continued studies towards the enediyne antitumour agents have yielded a number of new methods for ring closure. For example, Jones *et al.*²⁰⁸ have reported a useful intramolecular carbenoid coupling protocol for the formation of ten-membered enediynes from bis-prop-2-ynyl bromides under basic conditions (**302**→**303**). Procter and co-workers²⁰⁹ have used a Cr^{II} -mediated cyclisation of an aldehyde vinyl iodide precursor to form the





to compounds such as **309**, **310** and **311** from easily prepared starting materials.

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