Saturated and unsaturated hydrocarbons

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Reviewing the literature published between September 1993 and December 1994

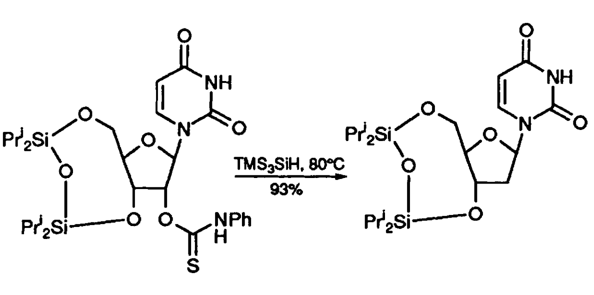
Continuing the coverage in *Contemporary Organic Synthesis*, 1994, **1**, 173

1 Introduction

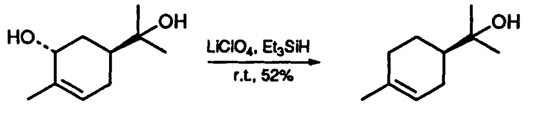
This review covers new methods for the synthesis of saturated and unsaturated hydrocarbons, with the emphasis being placed on practical and stereoselective methodologies.

2 Saturated hydrocarbons

The development of radical deoxygenations, dehalogenations, and deaminations continues, with methods using dialkyl phosphates and hypophosphorus acid as hydrogen sources[1] along with a new approach using *N*-phenylthioxocarbamate derivatives applied to sugars and nucleosides (**Scheme 1**)[2,3] being reported. The direct reductions of alcohols to alkanes using borohydride can be accomplished after initial phosphonium anhydride activation,[4] whilst selective deoxygenations of secondary allylic alcohols and acetates using triethylsilane in the presence of ethereal lithium perchlorate leave esters, isolated olefins, ketals, and tertiary alcohols unaffected (**Scheme 2**).[5]



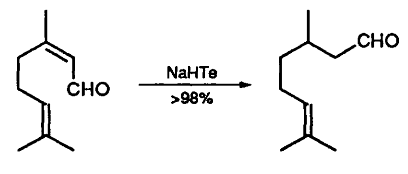
Scheme 1



Scheme 2

In an alternative approach to direct one-step deoxygenations of primary and secondary alcohols, constant current electrolysis of a mixture of alcohol, a phosphine, and tetraethylammonium bromide is found to give moderate yields of the corresponding alkane.[6] Samarium iodide has been applied to a number of different structural classes to effect reductive transformations such as α-deoxygenations of unprotected aldonolactones,[7] deoxygenations of Taxol$^{\text{TM}}$[8,9] and hydrodehalogenations of alkyl halides.[10] Other hydrodehalogenation methodologies which have been reported include the use of borohydride exchange resin with nickel acetate,[11] the application of tri-n-butyltinhydride in aqueous media,[12] the use of palladium mounted on poly(*N*-vinyl-2-pyrrolidine) with atmospheric pressure hydrogen in the presence of a base,[13] and the utilization of aminoborohydride at room temperature in tetrahydrofuran.[14]

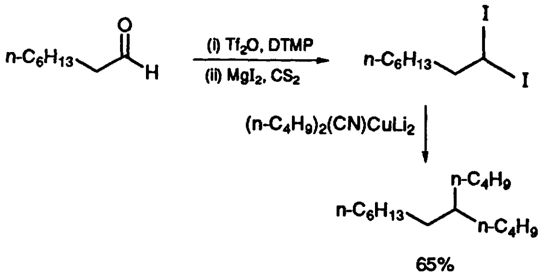
The 1,4-hydrogenation of α,β-unsaturated ketones and aldehydes can be affected with hydrogen in the presence of *in situ* generated nickel boride,[15] whilst sodium hydrogen telluride is found to be effective in 1,4-reductions on a range of substrates (**Scheme 3**).[16] The hydrogenation of α,β-unsaturated sulfones and phosphonates has been achieved with the activated binuclear palladium complex $[(Bu^t_2PH)PdPBu^t_2]$ in



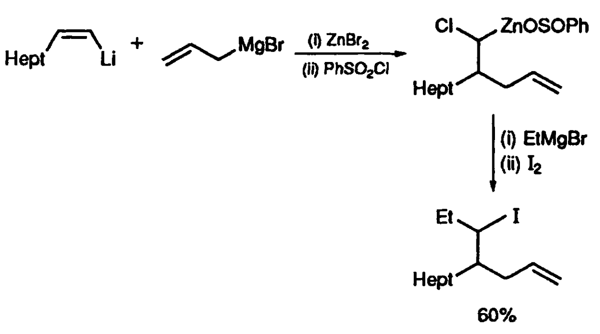
Scheme 3

moderate to good yields,[17] and the asymmetric hydrogenation of unfunctionalized trisubstituted olefins has been realized, in good yield and with high stereocontrol, through the use of a chiral C_2-symmetric titanocene catalyst.[18]

A simple, two-step reductive geminal dialkylation of α-unbranched aliphatic aldehydes via the corresponding geminal dihalide, using higher-order dialkyl-lithium cyanocuprates proceeds in good yield (**Scheme 4**).[19] The carbozincation of alkenyllithiums leads to α-chloro-triorganozincates, which can then be monoalkylated selectively via an intramolecular nucleophilic substitution process in good yield in a one-pot reaction (**Scheme 5**).[20]



Scheme 4

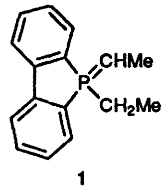


Scheme 5

3 Olefinic hydrocarbons

A study of the Wittig ethylidenations of a number of different ketonic substrates has demonstrated that reagents **1** and **2** are always (*E*)-selective, and these reagents have overcome some of the difficulties in the use of Wittig olefination procedures leading to trisubstituted double bonds.[21] (*E*)-Selective alkylidenations of aldehydes using reagents derived from α-acetoxy bromides, zinc, and $CrCl_3$ are reported to proceed in moderate yields with variable selectivity (**Scheme 6**).[22]

The stereoselectivity of the Peterson olefination procedure has been shown to be influenced by the choice of base and the silyl group in the synthesis of the anti-bacterial BRL49467, where a highly (*E*)-selective protocol is required (**Scheme 7**).[23]



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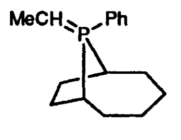

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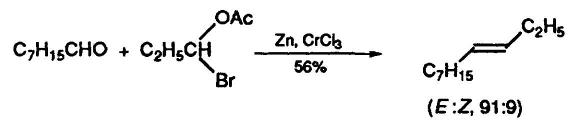
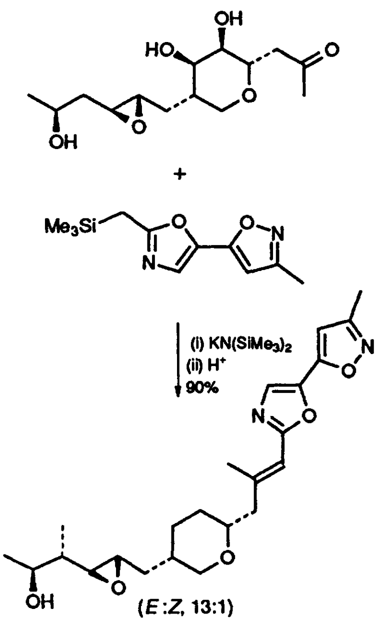
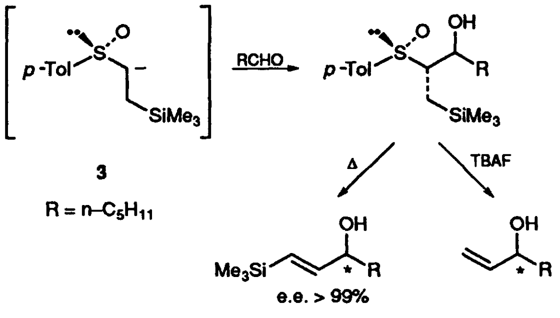


Scheme 6



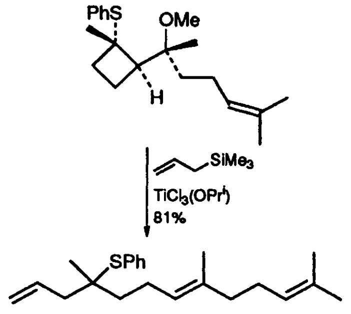
Scheme 7

The methylenation of carbonyl compounds using a CH_2I_2, zinc, and $TiCl_4$ system can be accelerated considerably with the addition of catalytic $PbCl_2$, as it promotes the formation of the reactive geminal dizinc intermediate $CH_2(ZnI)_2$.[24] The asymmetric preparation of allylic alcohols can be achieved by the addition of the vinyl anion equivalent **3** to aldehydes, followed by fluoride-initiated desilylsulfinylation or thermal desulfinylation (**Scheme 8**).[25]

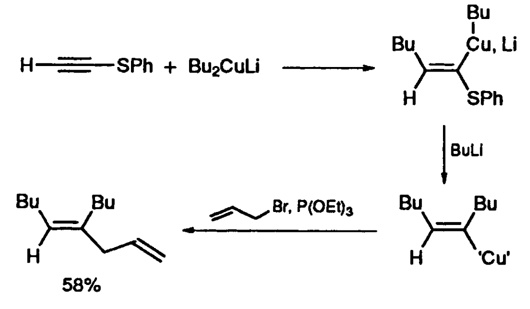


Scheme 8

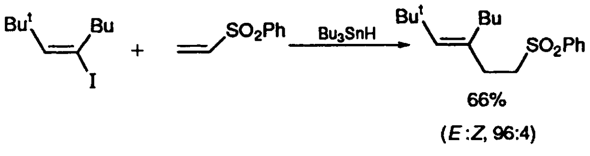
A number of methodologies for the stereoselective synthesis of trisubstituted olefins have been reported. Thus, reacting silyl nucleophiles with (2-phenylthiocyclobutyl)methyl benzoates or methyl ethers generates olefins in moderate yields with a high stereoselectivity (**Scheme 9**);[26] stereodefined trisubstituted alkenes can be prepared using a 1,2-metalate rearrangement starting with phenylthioacetylene (**Scheme 10**);[27] and di- and tri-substituted alkenes are obtained in moderate yields using the reactions of vinyl radicals with electron deficient alkenes (**Scheme 11**).[28]



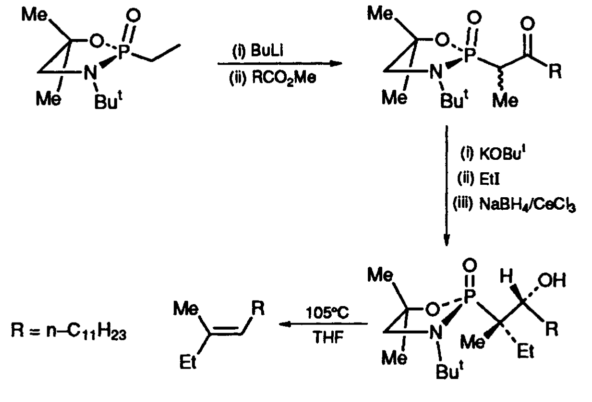
Scheme 9



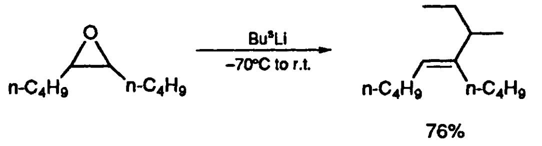
Scheme 10



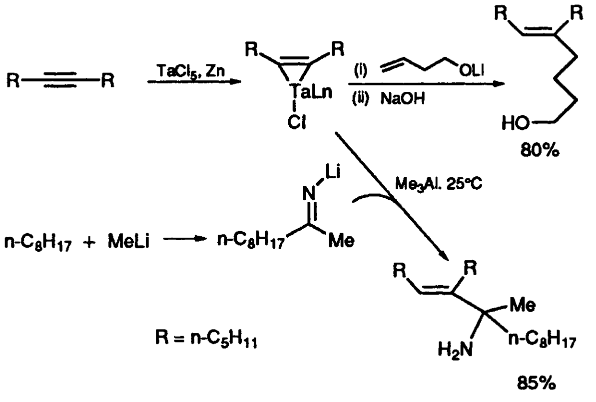
Scheme 11



Scheme 12



Scheme 13

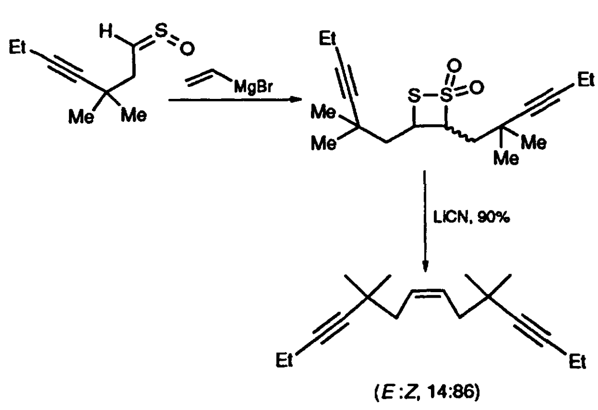


Scheme 14

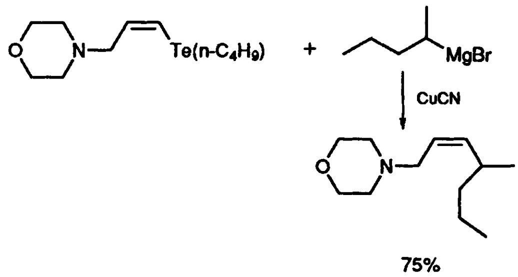
In a new, and general, stereoselective, high yielding protocol, easily prepared phosphorus heterocycles have been used to synthesize β-keto phosphonoamidates, which after keto group reduction to the corresponding alcohol and cycloelimination generate trisubstituted olefins in high stereopurity (**Scheme 12**).[29] Stereoselectively alkylated olefins can be prepared by the reaction of organolithium reagents with epoxides at low temperature followed by elimination (**Scheme 13**).[30] Treatment of tantalum–alkyne complexes with lithium alkoxy olefins or lithioimines afforded trisubstituted olefins and (*E*)-allylic amines respectively, via the stereoselective addition to the terminal olefinic group of these lithiated species (**Scheme 14**).[31,32]

Reported procedures for the synthesis of (*Z*)-alkenes include the simple use of atmospheric hydrogenations of alkynes in the presence of a metallic nickel catalyst and modifiers;[33] treatment of substituted 1,2-dithietane-1,1-dioxides, prepared from the reaction of allenic sulfinates with vinyl magnesium bromide, with lithium cyanide (**Scheme 15**);[34] and the cross-coupling reaction of (*Z*)-vinylic tellurides with Grignard reagents mediated by lower order cyano cuprates (**Scheme 16**).[35]

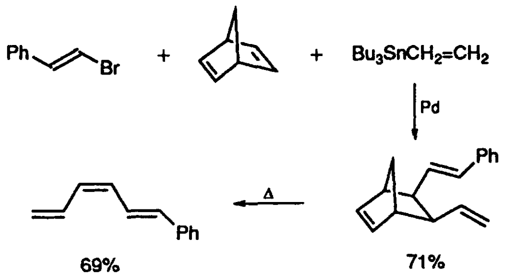
5,6-Disubstituted norbornenes have been prepared from palladium-catalysed cross-coupling reactions, and shown to undergo a retro Diels–Alder reaction to generate (*Z*)-olefins in good yield (**Scheme 17**).[36] Polyfunctional di-substituted alkenes can be readily obtained by a cross-coupling reaction between (*E*)- or (*Z*)-alkenyl iodides and alkyl copper zinc reagents (RCu(CN)ZnI) with complete



Scheme 15

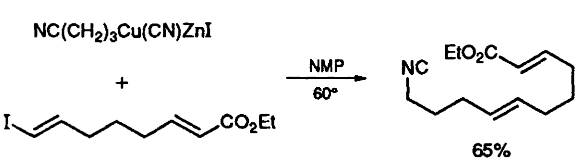


Scheme 16



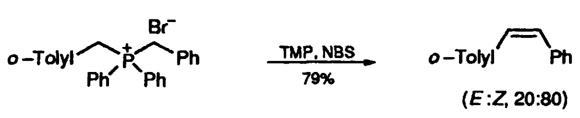
Scheme 17

retention of the configuration (**Scheme 18**).[37] Styrenes have been smoothly prepared at room temperature from the highly selective cross-metathesis of terminal olefins using molybdenum catalysis.[38]

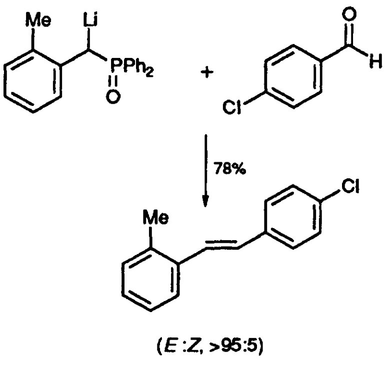


Scheme 18

(*E*)- and (*Z*)-Stilbenes were prepared using a Ramberg–Bäcklund type reaction of phosphonium salts with *N*-bromosuccinimide and 2,2,6,6-tetramethylpiperidine with moderate selectivity (**Scheme 19**),[39] whilst (*E*)-stilbenes were obtained with a high degree of stereoselectivity from the reaction of (α-lithiobenzyl)phosphine oxides with aldehydes (**Scheme 20**).[40]

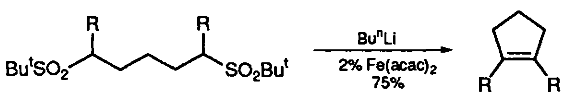


Scheme 19



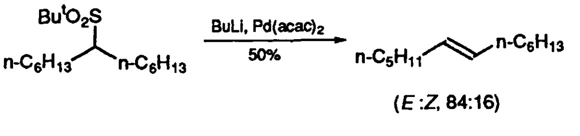
Scheme 20

A modification of the Julia olefination procedure whereby β-hydroxy or acetoxy sulfones are treated with SmI_2–HMPA has been reported, but only with moderate stereocontrol.[41] Symmetrical alkenes have been obtained from lithiated sulfones in the presence of catalytic amount of an iron salt with moderate stereocontrol, whilst disulfones give rise to cyclic alkenes (**Scheme 21**).[42] Lithiated tertiary-butyl alkyl sulfones eliminate easily in the presence of $Pd(acac)_2$ to generate the corresponding olefin (**Scheme 22**).[43]



$R = C_{10}H_{21}$

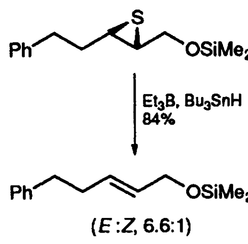
Scheme 21



Scheme 22

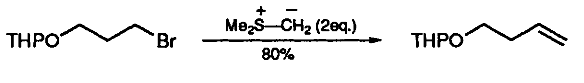
Vicinal dibromides have been debrominated reductively with SmI_2 to afford (*E*)-alkenes[44] and the application of microwave irradiation to vicinal sulfonyloxy groups in pyranosides has been found to considerably increase the rate of reaction for generating unsaturated products.[45] Desulfurizations of thiiranes with triethylborane and tributyl tin hydride at low temperature afford alkenes in good yield (**Scheme 23**).[46]

Terminal olefins can be obtained in good yield from the simple reactions of benzylic, allylic, propargylic, and primary halides or mesylates with

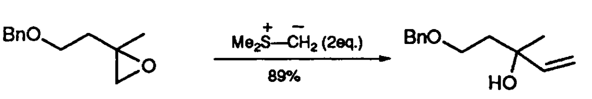


Scheme 23

dimethylsulfonium methylide, whilst unactivated secondary halides/mesylates proved unreactive (**Scheme 24**).[47] The reactions of excess dimethylsulfonium methylide with terminal, allylic, or benzylic epoxides was found to lead to the corresponding one-carbon homologated allylic alcohols in good yields (**Scheme 25**).[48]



Scheme 24



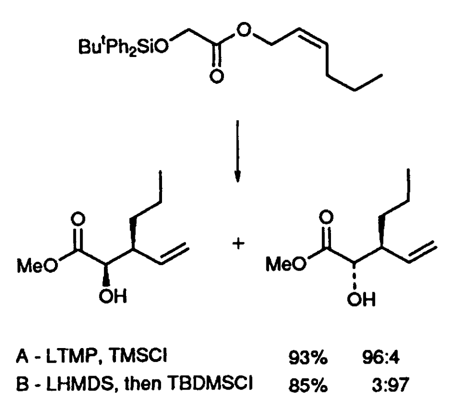
Scheme 25

Procedures for the preparation of functionalized olefins which have been reported include protocols for the dichloromethylenation of lactones,[49] the conversion of carbonyl compounds into vinyl iodides, 1,1-diiodoalkenes, and 3,3-difluoropropene derivatives,[50-52] a simple preparation of conjugated nitro olefins from β-nitro alcohols,[53] the generation of vinyl triflates from terminal alkynes,[54] and the synthesis of vinyl triflones from aldehydes using a Peterson olefination procedure.[55] The preparations of synthetically useful vinyl stannanes can be achieved: (i) using chromium-mediated additions of $Bu_3SnCHBr_2$ to aldehydes to afford (*E*)-alkenyl stannanes;[56] (ii) through the use of organocopper coupling chemistry to furnish 2-tributylstannyl-1-alkenes;[57] (iii) via the Pd^0-catalysed *syn*-stannylstannylations and *syn*-silylstannations of 1-alkoxy-1-alkynes and phenylthio-1-alkynes;[58] (iv) via the Pd^0-catalysed hydrostannation of disubstituted propargyl alcohols;[59] and finally (v) in the preparation of (*E*)-2-methyl-1-alkenyltrimethylstannanes from terminal acetylenes.[60] Procedures for the synthesis of vinyl silanes include the hydrosilylations of alk-1-ynes, to afford selectively either (*E*)- or (*Z*)-vinyl silanes using rhodium catalysis,[61] the conversion of a molybdenum carbene complex into (*E*)- or (*Z*)-vinyl silanes by the addition of organolithiums or Grignard reagents,[62] and the preparation of 1,1-bis(trimethylsilyl)alkenes from the addition of $(trimethylsilyl)_2CBr_2$ to aldehydes using chromium chemistry.[63]

4 Stereoselective simultaneous formation of *sp*^{3} and *sp*^{2} centres

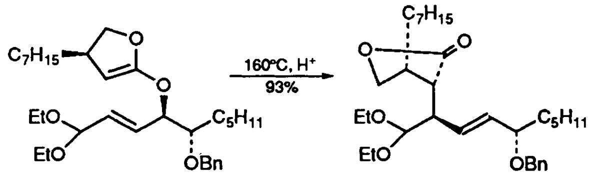
4.1 Claisen rearrangements

A useful protocol for preventing abnormal aromatic Claisen rearrangement products from forming has been reported and uses 1,1,1,3,3,3,-hexamethyldisilazane or N,O-bis(trimethylsilyl)acetamide to efficiently trap the normal products as their silyl ethers.[64] Methodologies for the stereoselective preparation of silyl ketene acetals of α-siloxy esters, β-hydroxy esters, and α-amino esters have been reported and applied to the Ireland ester enolate Claisen rearrangement of allyl glycolates (**Scheme 26**).[65]



Scheme 26

The utility of the [3,3]-Claisen sigmatropic rearrangement has been demonstrated with a number of different substrates, including the rearrangement of the cyclic keteneacetal **4** in the synthesis of carbacyclin (**Scheme 27**),[66] in the conversion of allyl *N*-phenylimidates, via *N*-silyl ketene *N*,*O*-acetals, into γ,δ-unsaturated anilides (**Scheme 28**),[67] in the preparation of (*E*)-olefin



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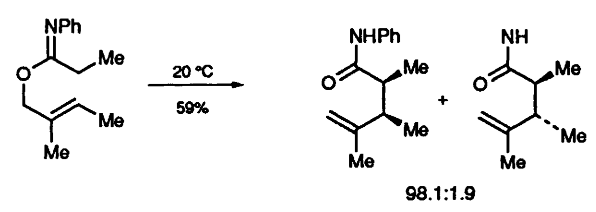
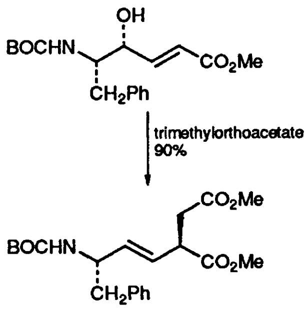
Scheme 27

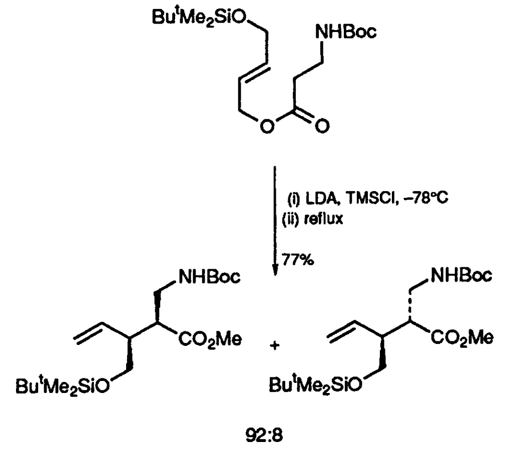


Scheme 28

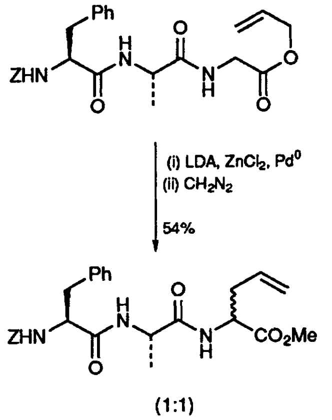
dipeptide isosteres with high stereoselectivity (**Scheme 29**),[68] in the synthesis of α-allyl-β-amino acids in good yields (**Scheme 30**),[69] for the introduction of allylic side-chains onto peptides using Pd^0 catalysis and $ZnCl_2$ (**Scheme 31**),[70] and as the key sequential steps in the preparation of the antiviral (−)-reiswigin.[71]



Scheme 29

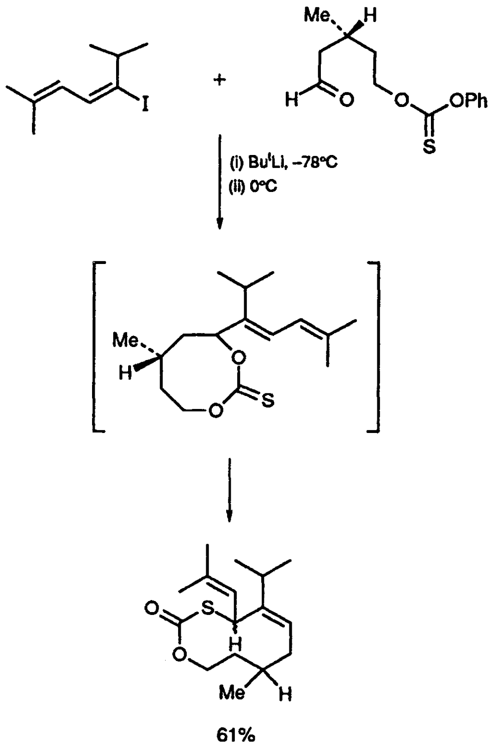


Scheme 30

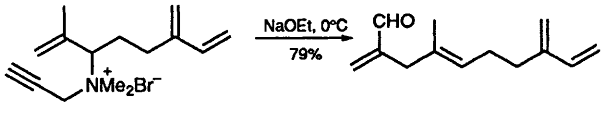


Scheme 31

The Claisen rearrangement has also found application in the regioselective and stereocontrolled 2-C and 3-C allylation of L-ascorbic acid,[72] in the preparation of the (−)-yellow-scale-pheromone via a ring expansion of an eight-membered cyclic thionocarbonate prepared in a one-pot, four step reaction sequence (**Scheme 32**),[73] as the key part of the stereoselective synthesis of the trisubstituted (*E*)-olefins from *N*-disubstituted dimethylammonium salts (**Scheme 33**),[74] and finally in the synthesis γ,δ-unsaturated perfluoroketones.[75]



Scheme 32

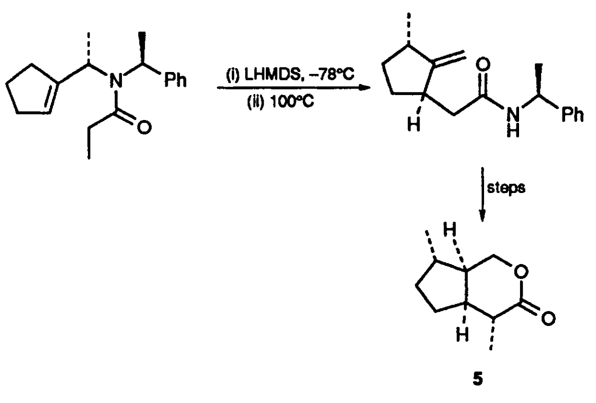


Scheme 33

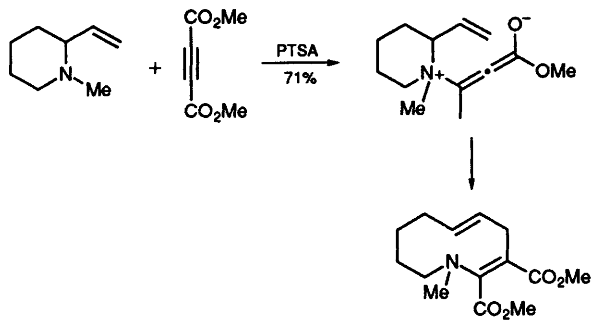
Aza-Claisen rearrangements have been applied in the synthesis of (−)-isoiridomyrmecin **5** with very high stereoselectivity (**Scheme 34**).[76] They have also been used on carboxamides of isomerically pure (*E*)- and (*Z*)-crotylamines (with unfortunately little stereocontrol),[77] and on substrates generated from the acid-catalysed Michael additions of allylamines to acetylene carboxylates, where Lewis acids are also found to give satisfactory results, and the overall strategy can be applied to ring expansion reactions (**Scheme 35**).[78]

4.2 Wittig rearrangements

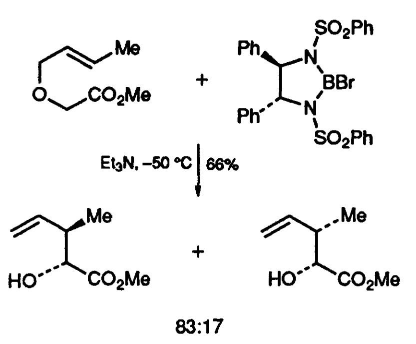
An enantioselective ester enolate [2,3]-Wittig rearrangement has been realized using chiral boron bis-sulfonamides to control stereoselectivity (e.e. up to 96%) with high *threo* preference but in only moderate yields (**Scheme 36**).[79] Good asymmetric



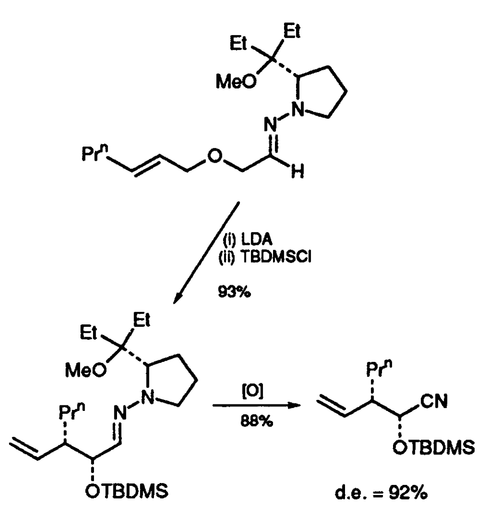
Scheme 34



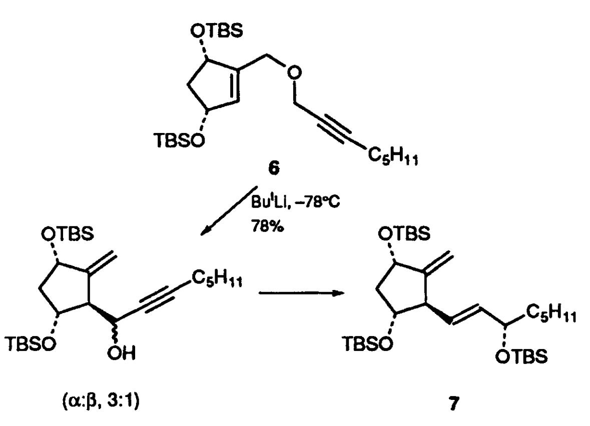
Scheme 35



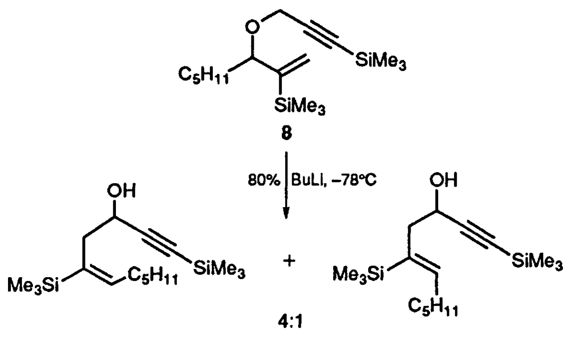
Scheme 36



Scheme 37



Scheme 38

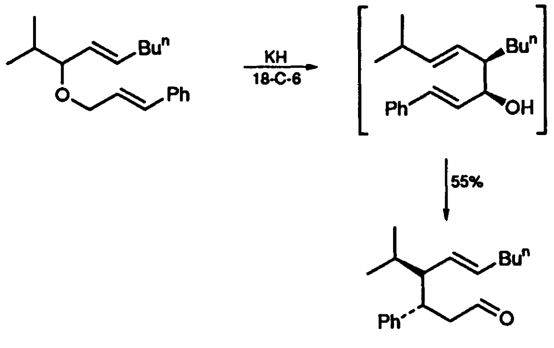


Scheme 39

control has also been obtained in the [2,3]-Wittig rearrangement of chiral allyloxy-acetaldehyde hydrazones undertaken in the synthesis of γ,δ-unsaturated-α-hydroxyaldehydes and cyanohydrins (**Scheme 37**).[80]

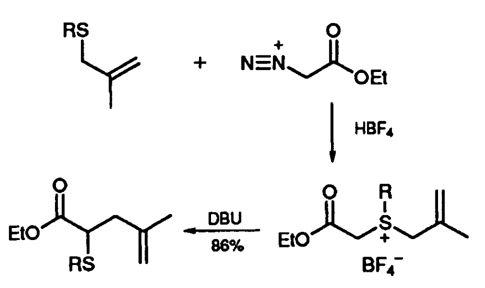
The [2,3]-Wittig rearrangement has been applied with a number of different substrates, such as the propargylic ether **6** with good stereocontrol in an asymmetric synthesis of Stork's prostaglandin intermediate **7** (**Scheme 38**),[81] and on prop-2-ynyl ethers **8**, where stereocontrol is realized by the use of the silicon groups favouring the required transition state in a general approach to leukotrienes (**Scheme 39**).[82]

A one-pot tandem [2,3]-Wittig anionic oxy-Cope rearrangement reaction has been shown to transform very rapidly (45 minutes at room temperature) bis-allylic ethers to δ,ε-unsaturated aldehydes with good selectivity (**Scheme 40**).[83] The [2,3]-sigmatropic rearrangement of β-phenylsulfonylpropargylic sulfenates provides a method for preparing 1,4-bis(phenylsulfonyl)1,3-butadienes,[84] whilst repeated alternate additions of a diazonium salt and tetrafluoroboric acid at low temperature enables the conversion of allyl 4-methoxyphenylsulfides into sulfonium ylides which



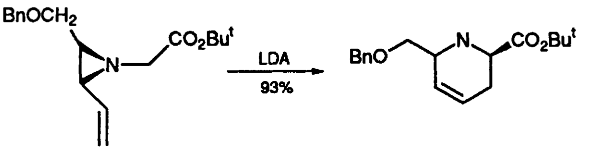
Scheme 40

then undergo [2,3]-Wittig rearrangement in high yield and good stereoselectivity (**Scheme 41**).[85] A study of the aza-Wittig rearrangement of vinylaziridines has provided an interesting approach to tetrahydropyridines (**Scheme 42**).[86]



R = 4-MeOC$_6$H$_4$

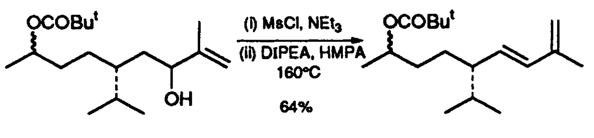
Scheme 41



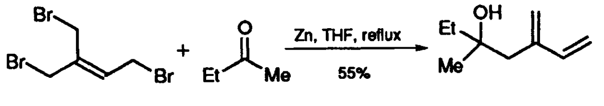
Scheme 42

5 Conjugated dienes

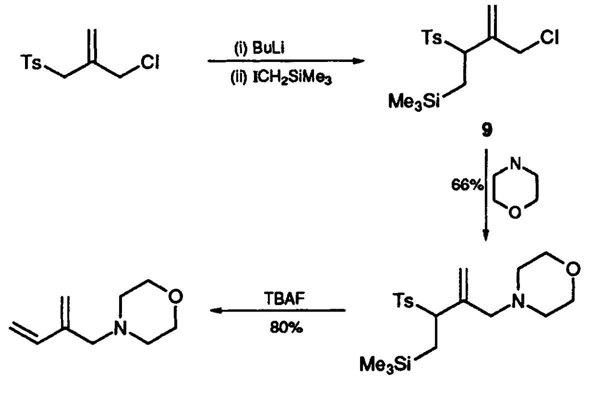
A facile elimination of allylic alcohols via the corresponding mesylates has been reported to provide a two step method for the preparation of terminal 1,3-dienes (**Scheme 43**).[87] The coupling of 2-bromomethyl-1,4-dibromo-2-butene with various aldehydes and ketones allows a simple entry to isoprenylated alcohols (**Scheme 44**),[88] and 2-(chloromethyl)-3-tosylpropene can be used via its β-silyl sulfone derivative **9** to generate 2-alkyl substituted 1,3-dienes in a straightforward coupling reaction, with either a nucleophile or an aldehyde, followed by an elimination procedure (**Scheme 45**).[89]



Scheme 43

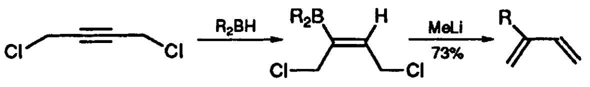


Scheme 44



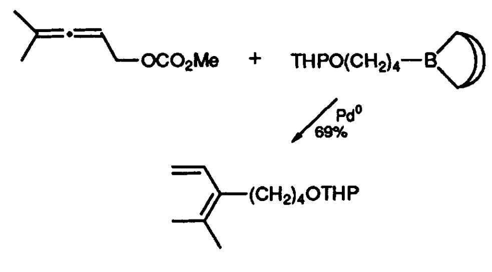
Scheme 45

A range of substituted buta-1,3-dienes can be prepared from 1,4-dichlorobut-2-yne via a hydroboration strategy (**Scheme 46**),[90] or by the regioselective palladium-catalysed cross-coupling of 2,3-butadienyl carbonates with 9-alkyl-9-borobicyclo[3.3.1]nonanes, 1-alkenylboronic acids, or arylboronic acids (**Scheme 47**).[91]



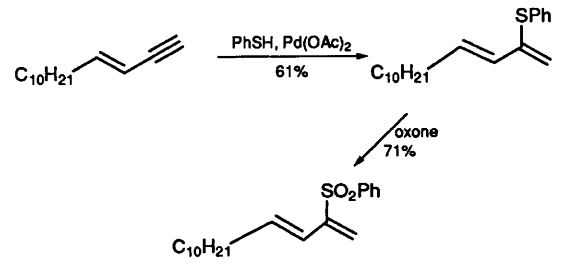
R = Me$_2$CHCHMe

Scheme 46

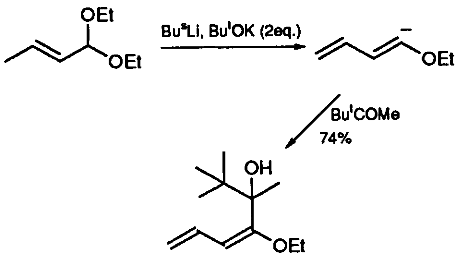


Scheme 47

2-Phenylsulfinyl or 2-phenylsulfonyl 1,3-dienes can be prepared stereoselectively in good yields using a Pd-catalysed addition reaction of thiophenol to conjugated enynes with a terminal alkyne followed by oxidation (**Scheme 48**)[92] and 1-substituted-1-ethoxy dienes are obtained from the coupling reaction of 1,1-diethoxybut-2-ene with a range of carbonyl electrophiles using the mixed metal base LICKOR (**Scheme 49**).[93]

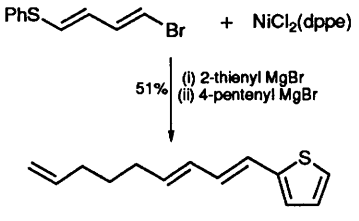


Scheme 48

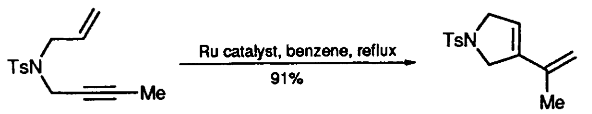


Scheme 49

The selective preparation of protected (E,E)- and (E,Z)-hepta-2,4-dien-1-ol has been reported using a Horner–Wittig elimination of easily separated *syn*- and *anti*-β-acetoxy triphenylphosphine oxides.[94] A simple methodology for the preparation of conjugated (E,E)-dienes has been reported and uses a sequential coupling reaction between Grignard reagents in the presence of $NiCl_2$(dppe) and readily available (E,E)-1-bromo-4-phenylthio-1,3-butadiene (**Scheme 50**).[95] An enyne metathesis reaction involving the use of a ruthenium catalyst allowed the preparation of five-, six-, and seven-membered heterocycles containing the 1,3-diene moiety in good yields (**Scheme 51**).[96]



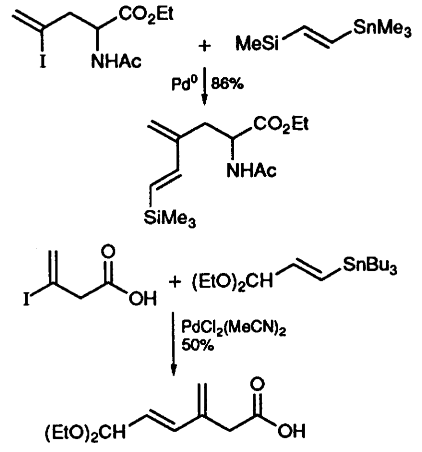
Scheme 50



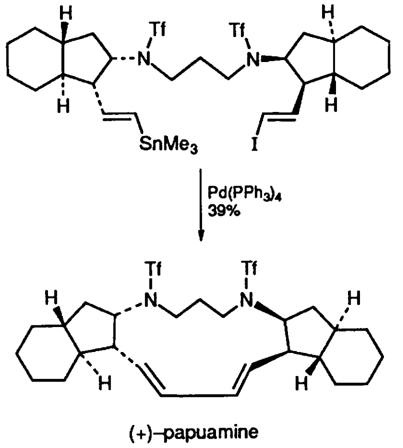
Scheme 51

Palladium-catalysed Stille cross-coupling procedures using vinyl stannanes leading to 1,3-dienes on the side-chains of α-amino acids, and 1,3-diene derivatives of 3-iodobut-3-enoic acid have been reported (**Scheme 52**).[97,98] The utility of the Stille cross-coupling has been demonstrated in a total synthesis of (+)-papuamine (**Scheme 53**).[99]

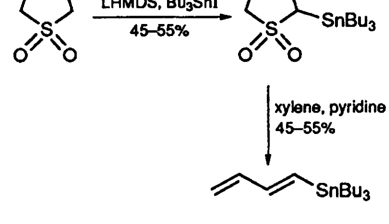
A number of reports have dealt with the synthesis of dienyltrialkylstannanes, such as the simple, two-step preparation of (E)-1,3-butadienyl(tributyl)stannane from 3-sulfolene (**Scheme 54**),[100] the use of 1,2-metalate rearrangements of 5-lithio-2,3-dihydrofurans with a suitable cyanocuprate (**Scheme 55**),[101] the high yielding direct stereoselective stannylcupration of enynes with terminal alkynes (**Scheme 56**),[102] and the stereo- and regio-controlled Pd-catalysed hydrostannylation of enynes (**Scheme 57**).[103]



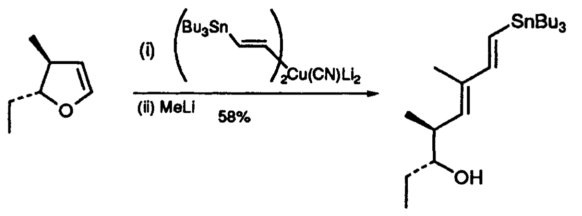
Scheme 52



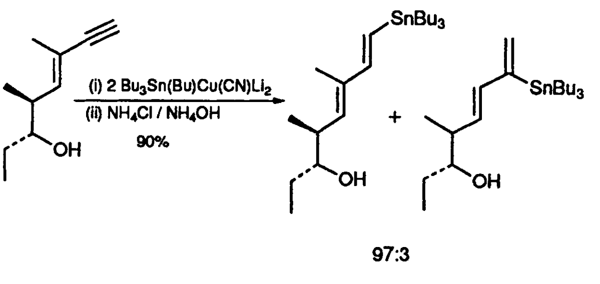
Scheme 53



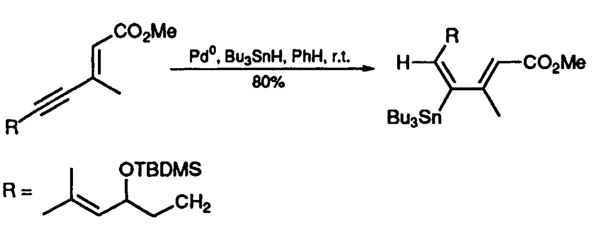
Scheme 54



Scheme 55

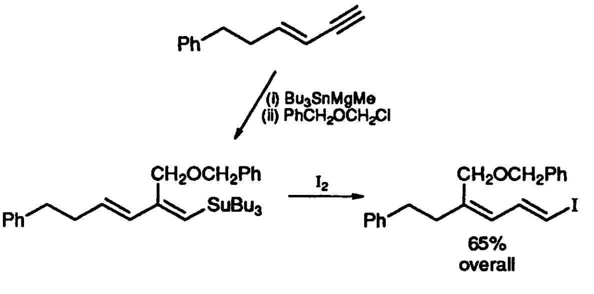


Scheme 56



Scheme 57

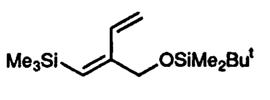
The stereocontrolled preparation of 2-substituted 1-iodo-1,3-dienes has been achieved by the addition of methylmagnesium tributyltin to 6-phenylhex-3-enyne, followed by alkylation with an appropriate electrophile and conversion of the resulting stannyldiene by reaction with iodine (**Scheme 58**).[104]



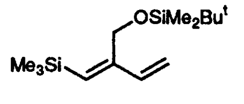
Scheme 58

A general stereoselective synthesis of the novel silyl-1,3-butadienes, **10** and **11**, has been reported, and these compounds will no doubt find use in a number of applications such as intra- and intermolecular cycloadditions.[105]

Finally, vinyl bromides have been shown to couple with the organoborane **12** with retention of stereochemistry in a palladium-catalysed reaction under basic conditions to generate *trans*-dienyl silanes (**Scheme 59**).[106]



10



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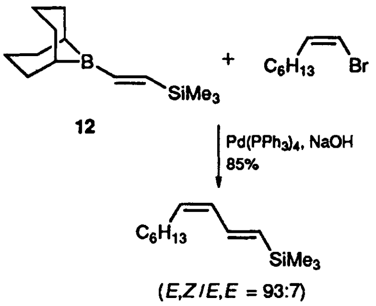
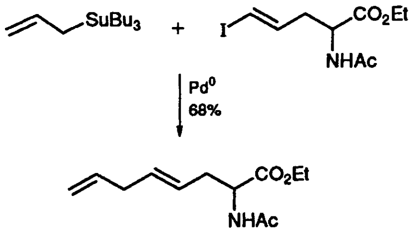


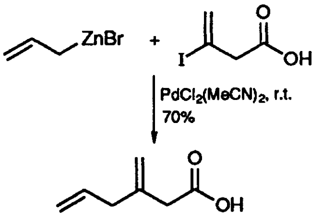
Scheme 59

6 Non-conjugated dienes

The application of the Stille cross-coupling reaction has been reported to allow the easy introduction of 1,4-diene systems into the side-chains of α-amino acids containing a vinyl iodide (**Scheme 60**),[97] whilst the Pd-catalysed cross-coupling of an allyl organozinc with 3-iodobut-2-enoic acid allows facile generation of a 1,4-diene moiety (**Scheme 61**).[98]

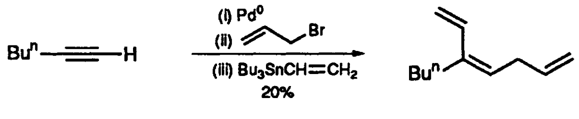


Scheme 60



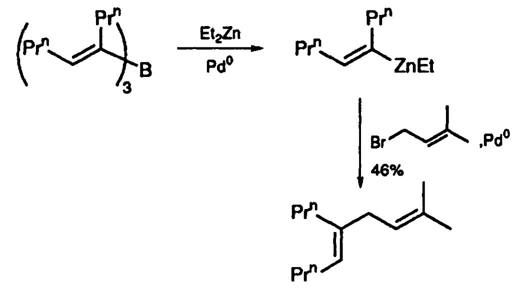
Scheme 61

A one-pot palladium-catalysed reaction between terminal acetylenes, allyl bromide, and organostannanes has allowed elaboration of 1-substituted 1,4-pentadienes in moderate yields, but better overall yields can be realized in two separate steps (**Scheme 62**).[107]



Scheme 62

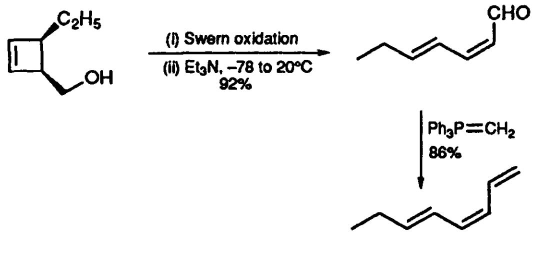
Preparations of (*E*-1-alkenyl)ethylzinc reagents from the corresponding (*Z*)-trialkenylboranes have been utilized in the cross-coupling reactions of zinc reagents with allylic halides to provide 1,4-dienes, regio- and stereo-selectively in the absence of a transition metal catalyst (**Scheme 63**).[108]



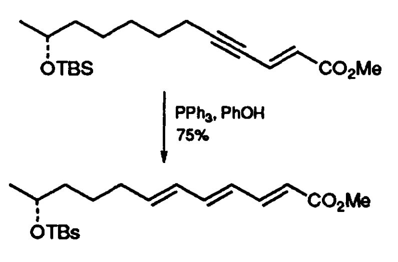
Scheme 63

7 Polyenes

Methodology for controlling the thermal electrocyclic ring-opening reactions of 4-alkyl-2-cyclobutene-1-carbaldehydes have been reported and allows the easy stereoselective preparation of (*Z*,*E*)- or (*E*,*E*)-dienals at low temperature which can then be further elaborated to stereodefined trienes (**Scheme 64**).[109] The isomerizations of enyne esters to (*E*,*E*,*E*)-trienes in good yields using a simple triphenylphosphine–phenol catalysed protocol have been reported (**Scheme 65**).[110]

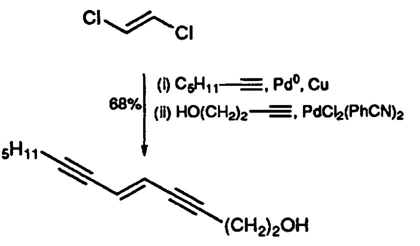


Scheme 64

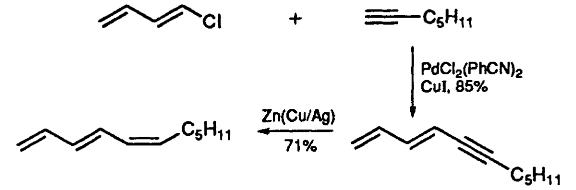


Scheme 65

A simple one-pot stereospecific preparation of unsymmetrical (*Z*)- or (*E*)-enediynes from (*Z*)- or (*E*)-1,2-dichloroethylene and 1-alkynes has been reported, using sequential palladium-catalysed coupling reactions (**Scheme 66**);[111] pure (*Z*,*Z*,*Z*)- or (*Z*,*E*,*Z*)-conjugated trienes may then be subsequently produced through the use of zinc reduction. In a similar approach the palladium–copper coupling reaction between (*E*)-1-chloro-1,3-butadiene and 1-alkynes, followed by stereoselective zinc reduction, furnishes trienes with high stereo purity (**Scheme 67**).[112]

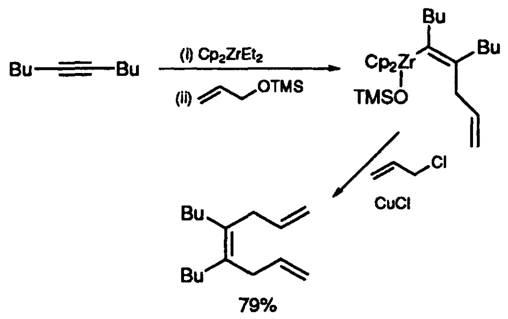


Scheme 66

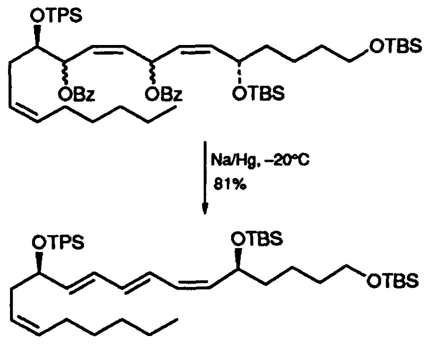


Scheme 67

The allylzirconations of alkynes has afforded intermediates which can be reacted with allyl chloride in the presence of copper salts to give stereodefined nonconjugated 1,4,7-trienes in good yield (**Scheme 68**).[113] The use of sodium amalgam induced reductive eliminations of allylic dibenzoates has been exemplified in a synthesis of leukotriene B4 (**Scheme 69**).[114]

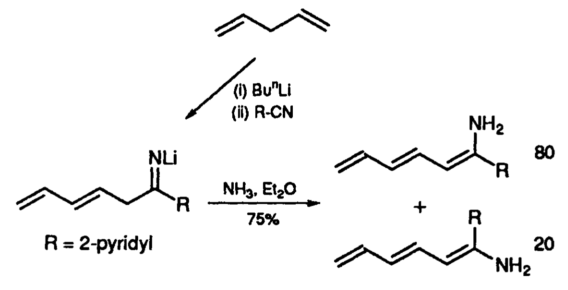


Scheme 68



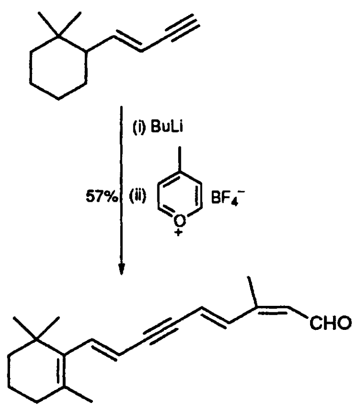
Scheme 69

Nitriles have been reacted with pentadienyl lithium to yield metalated 1-substituted trienamines which upon careful workup produce 1-aminohexa-1,3,5-trienes with fairly good stereocontrol (**Scheme 70**).[115]

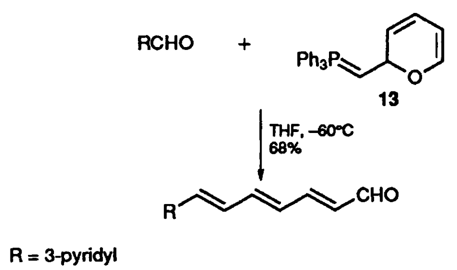


Scheme 70

A new approach to retinoids involving the addition of organometallic reagents to a variety of pyrylium tetrafluroborate salts has allowed the preparation of (*Z*,*E*)- or (*E*,*E*)-dienals in a stereocontrolled manner (**Scheme 71**),[116] and in an extension of this approach to polyenes a direct route to trienals has been described whereby aldehydes are homologated by six carbon atoms by reaction with the 2-substituted 2*H*-pyran-based Wittig reagent **13** in good yields (**Scheme 72**).[117]

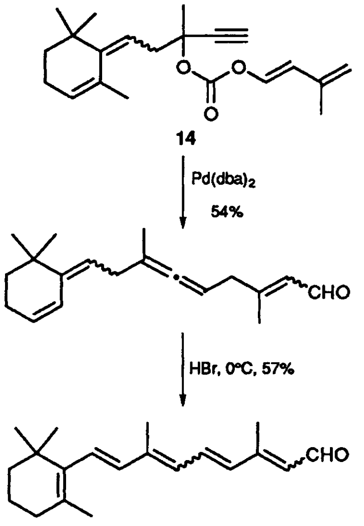


Scheme 71



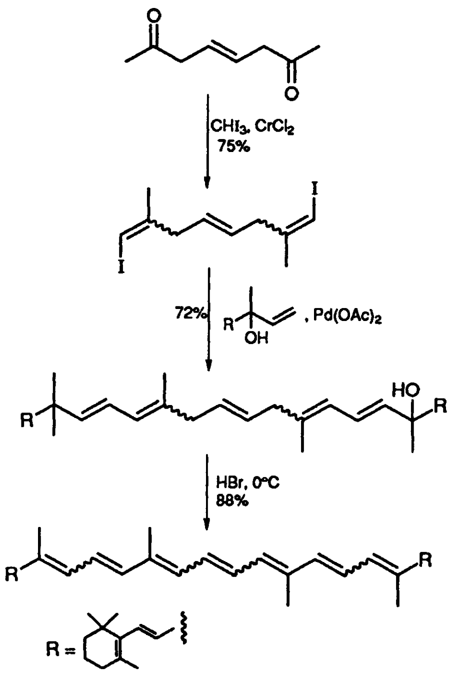
Scheme 72

In an alternative synthesis of retinal the key step involved a Pd-catalysed rearrangement of the mixed propargylic-dienyl carbonate **14** to an allenyl aldehyde followed by subsequent reconjugation (**Scheme 73**).[118]



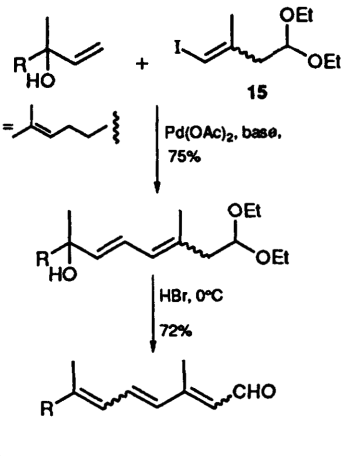
Scheme 73

A variety of symmetrical carotenoids have been synthesized by first using a chromium assisted iodomethylenation of a diketone followed by a silver-assisted Heck reaction with good stereocontrol (**Scheme 74**).[119] The iodoacetal **15** can be coupled to tertiary allylic alcohols using Heck chemistry, and subsequently hydrolysed and dehydrated to provide substituted trienals regioselectively (**Scheme 75**).[120]

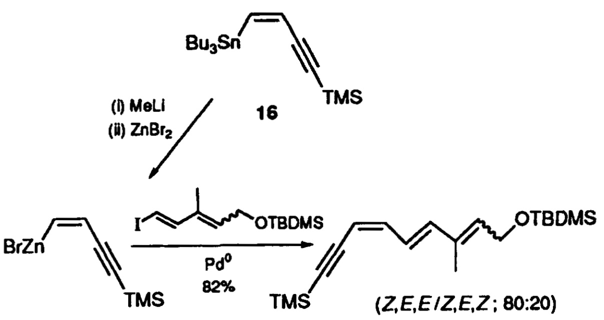


Scheme 74

Palladium-mediated coupling reactions of zinc bromide derivatives (generated from the enyne **16**) with unactivated vinyl iodides have allowed facile preparations of polyenes with high stereocontrol (**Scheme 76**).[121]

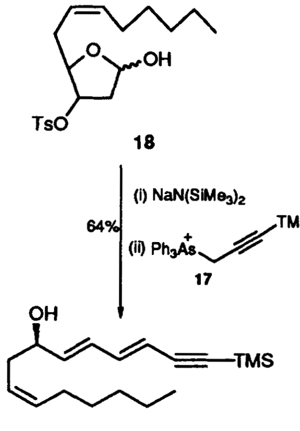


Scheme 75



Scheme 76

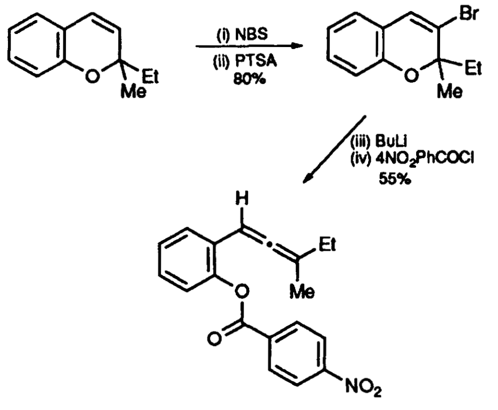
In a new triply convergent synthesis of leukotriene B4, a stereocontrolled coupling reaction, ring-opening process, and elimination reaction involving the propargylic arsonium salt **17** and the furanose **18** affords an intermediate polyene in good yield, which is then further elaborated to the final product (**Scheme 77**).[122]



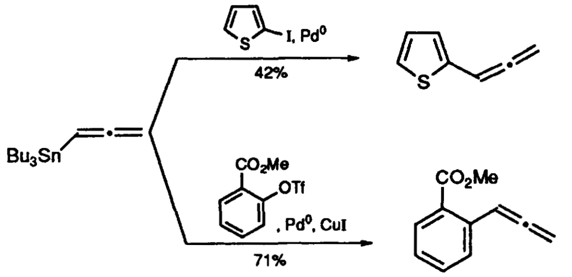
Scheme 77

8 Allenes

A number of new approaches to aryl allenes have been published, including a simple conversion from benzopyrans using an anionic cleavage reaction (**Scheme 78**),[123] and the palladium-catalysed coupling reactions of stannyl allenes with either aryl iodides or aryl triflates in the presence of a copper co-catalyst (**Scheme 79**).[124,125]

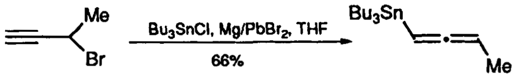


Scheme 78



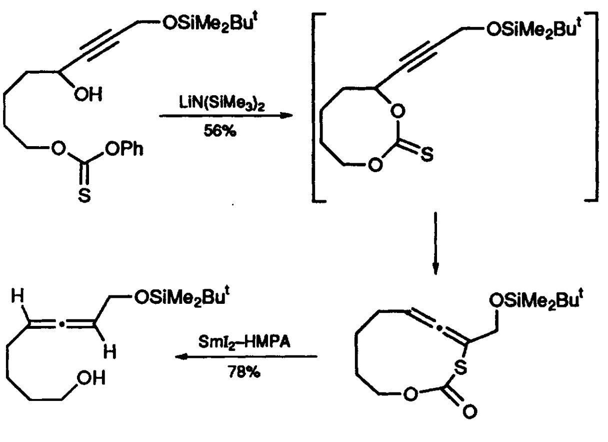
Scheme 79

The regioselective preparation of allenyl stannanes has been achieved using a reductive coupling reaction of propargylic bromides with tributylstannyl chloride in the presence of magnesium metal and lead bromide (**Scheme 80**).[126] A novel [3,3]-sigmatropic rearrangement of cyclic thionocarbonates has been used to prepare medium-ring heterocyclic allenes in moderate yield (**Scheme 81**).[127]

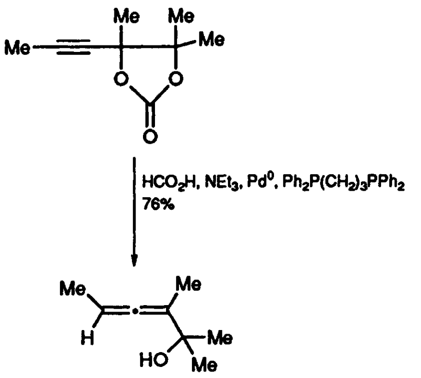


Scheme 80

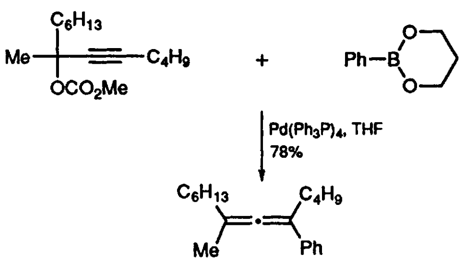
A number of approaches towards allenes have utilized functionalized alkynes and these include: the 1,6-addition of organocuprates to chiral eneynes, leading to allenes with moderate diastereoselectivity;[128] the hydrogenolysis of alkynyl cyclic carbonates to α-allenyl alcohols with triethylammonium formate and a palladium(o) catalyst in the presence of chelating diphosphines (**Scheme 82**);[129] and the cross-coupling reactions of organoboranes with propargylic carbonates with palladium catalysis to afford tetrasubstituted allenes (**Scheme 83**).[130]



Scheme 81

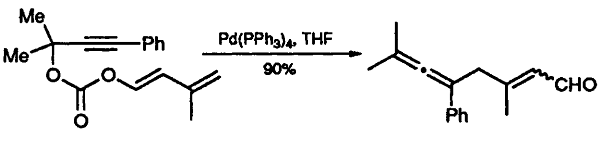


Scheme 82

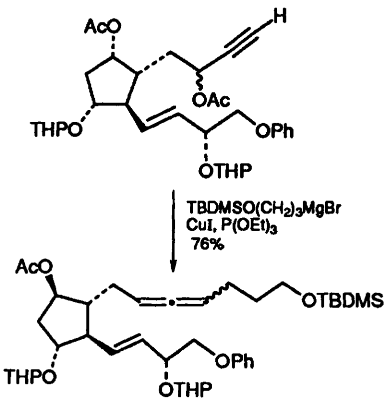


Scheme 83

Propargylic mixed carbonates have been rearranged into allenic carbonyls compounds using palladium catalysis (**Scheme 84**),[131] and the allenic moiety of enprostil has been introduced via a propargylic acetate using a Grignard reagent in the presence of a copper catalyst (**Scheme 85**).[132]



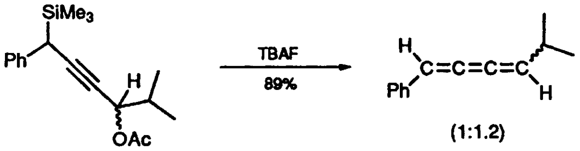
Scheme 84



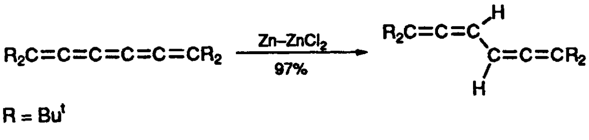
Scheme 85

A range of chiral alcohols have been converted into propargylic ethers which were then isomerized under base catalysis to generate optically active allenic ethers.[133]

A simple procedure involving 1,4-elimination from 1-acetoxy-4-trimethylsilylbut-2-ynes using tetrabutylammonium fluoride has enabled the preparation of alkyl and aryl substituted 1,2,3-butatrienes (**Scheme 86**),[134] whilst the reduction of tetraalkylhexapentaenes with Zn–ZnCl$_2$ affords 1,2,4,5-diallenyl systems efficiently (**Scheme 87**).[135]



Scheme 86

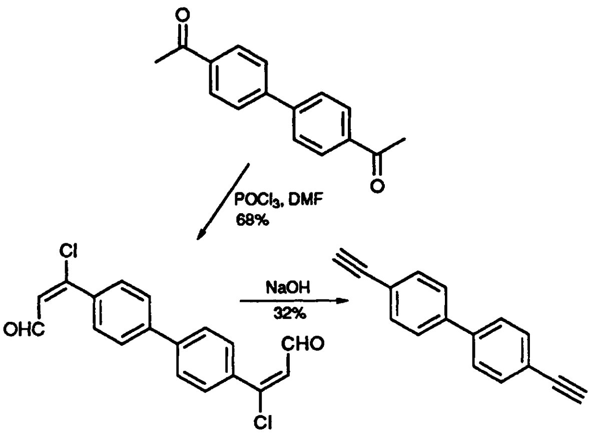


Scheme 87

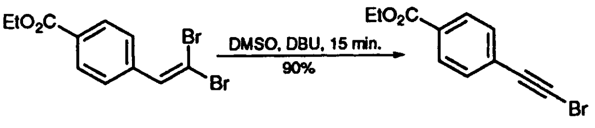
9 Alkynes

The procedure for converting aryl methyl ketones into aryl ethynyl products using phosphoryl chloride and DMF has been extended to diphenyldiynes (**Scheme 88**),[136] and the dehydrobromination of 1,1-dibromoethylenes under mild conditions using DMSO and DBU has allowed the preparation of 1-bromoarylalkynes in excellent yields (**Scheme 89**).[137]

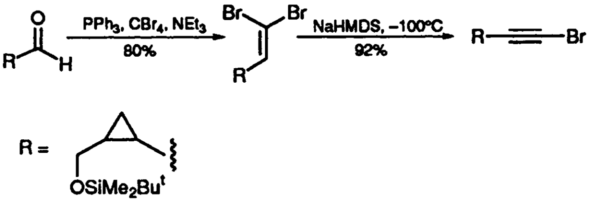
A modification of the McKelvie–Corey procedure for converting 1,1-dibromoalkenes into 1-bromoalkynes using NaHMDS for the elimination reaction, has led to a series of epoxy, cyclopropyl, and alkyl derivatives in good yields (**Scheme 90**).[138]



Scheme 88



Scheme 89

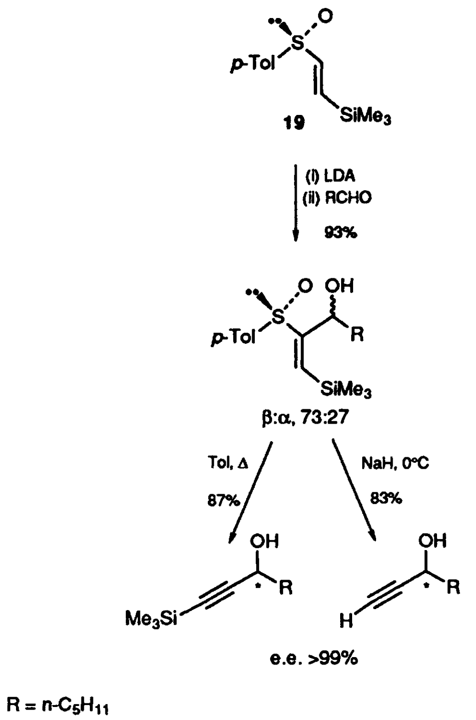


Scheme 90

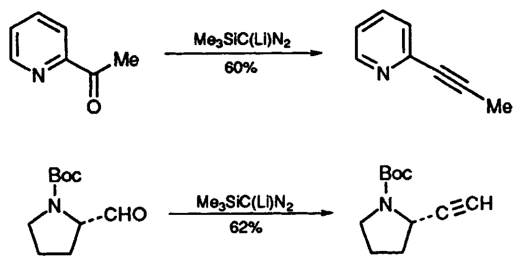
The chiral synthon **19** has been used to prepare a series of optically active propargylic alcohols from the reaction of the derived α-vinyl anion with aldehydes followed by the β-elimination of the sulfinyl and trimethylsilyl groups or by the thermal elimination of the sulfinyl group (**Scheme 91**).[139]

The (Colvin) rearrangement of aryl alkyl ketones and aldehydes by reaction with lithium trimethylsilyldiazomethane generates the corresponding homologous disubstituted and terminal alkynes respectively in moderate to good yields (**Scheme 92**).[140]

Both cyclic and acyclic 1,5-diynes have been prepared using intra- and inter-molecular coupling reactions of $Co_2(CO)_6$-complexed propargyl radicals, in reasonable yields and with moderate diastereoselectivity.[141] The preparation of a nine-membered cyclic 1,5-diene has been achieved through the cerium-assisted coupling reaction of a lithium acetylide with an aldehyde, affording a single diastereoisomer.[142]



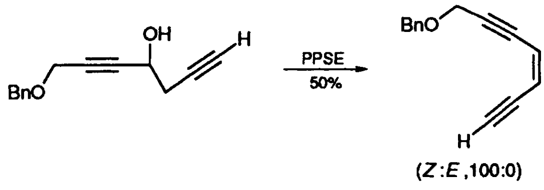
Scheme 91



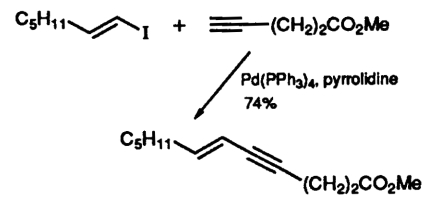
Scheme 92

10 Enynes

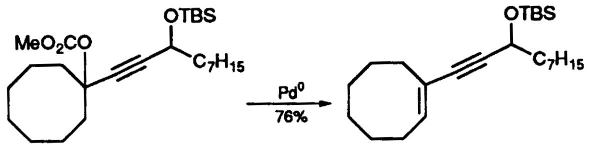
(Z)-Enynes and (Z)-enediynes are reported to be easily generated by the dehydration of propargylic alcohols with polyphosphoric acid trimethylsilyl ester (PPSE) (**Scheme 93**).[143] A straightforward procedure for coupling terminal alkynes to vinyl halides using Pd^0 catalysis in the presence of piperidine or pyrrolidine has furnished enynes in good yield (**Scheme 94**),[144] whilst a palladium-catalysed elimination from propargylic carbonates produced conjugated enynes using mild and neutral conditions (**Scheme 95**).[145]



Scheme 93

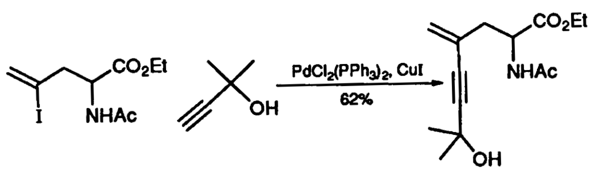


Scheme 94

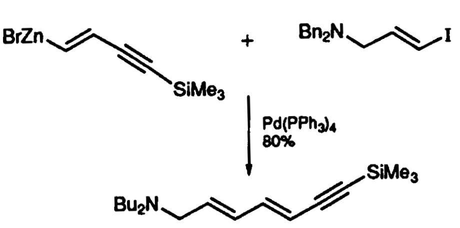


Scheme 95

The palladium–copper catalysed coupling reaction of terminal acetylenes with α-amino acids containing vinyl iodide side-chains has been shown to readily introduce enyne groups (**Scheme 96**).[97] The zinc bromide derivatives of preformed (*Z*)- or (*E*)-1-stannyl-4-trimethylsilyl-1-buten-3-ynes have been used in palladium-catalysed coupling reactions with a range of unactivated vinyl iodides and proceed in good yield with stereoretention, to afford terminal conjugated dienyne systems (**Scheme 97**).[121]



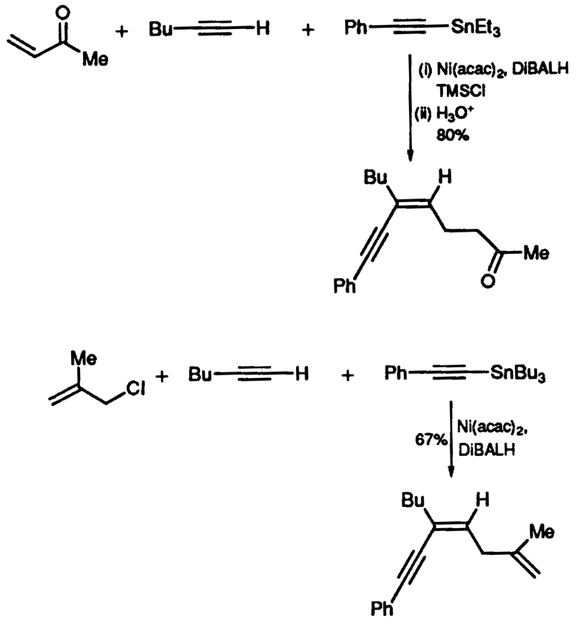
Scheme 96



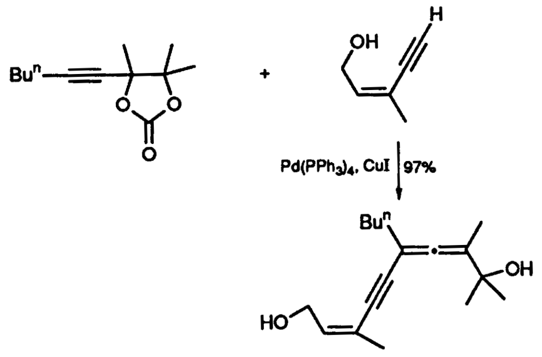
Scheme 97

A three-component one-pot reaction involving a terminal acetylene, a 1-alkynyl stannane, and either an enone or an allyl chloride, using a nickel catalyst generated from Ni(acac)$_2$, afforded regio- and stereo-defined enynes and 3,6-dien-1-ynes respectively in good yields (**Scheme 98**).[146,147]

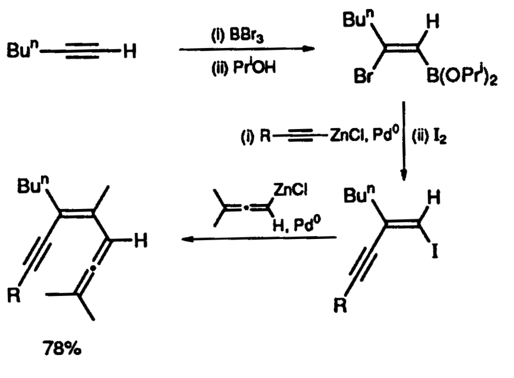
Conjugated alkynyl α-allenols have been obtained readily in good yields from the palladium–copper catalysed coupling reaction of alkynyl cyclic carbonates with terminal alkynes (**Scheme 99**).[148] A straightforward sequence of reactions starting with bromoboration of a terminal alkyne and subsequent Pd^0 coupling with acetylenic zinc chlorides and allenic zinc chlorides has led to acyclic enyne-allenes or enediynes with tri- or tetra-substituted double bonds with a high degree of stereocontrol (**Scheme 100**).[149,150]



Scheme 98

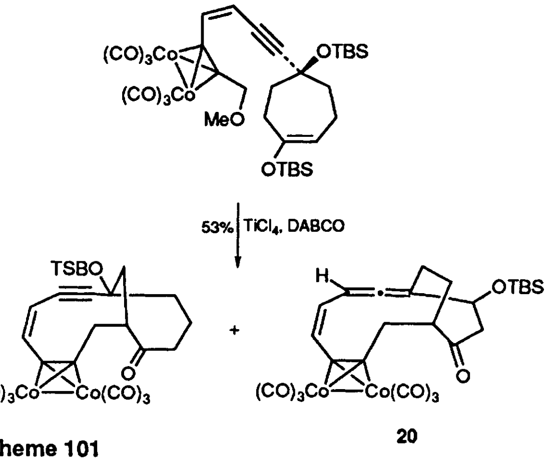


Scheme 99



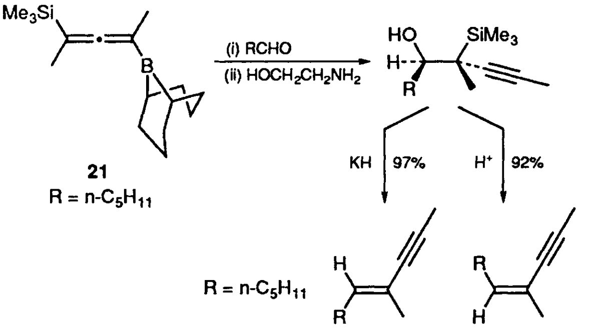
Scheme 100

An intramolecular Nicholas reaction on a dicobaltohexacarbonyl-complexed propargylic silylenol ether has enabled the preparation of the reactive bicyclic [7.4.1]enediyne, and the surprisingly stable bicyclic enyne-allene **20** (**Scheme 101**).[151]



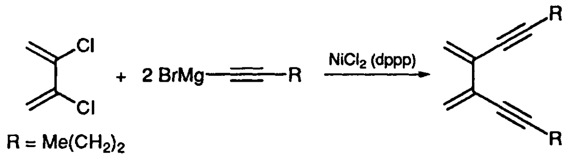
Scheme 101

The isomerization of (*Z*)- to (*E*)-enynes using trifluoromethane sulfonic acid at room temperature was found to be more readily accomplished when the acetylene group is protected as the dicobaltohexacarbonyl complex.[152] The readily prepared γ-silylallenylborane **21** can be used to prepare enynes and enediynes with high geometric purity by reaction with simple alkyl and acetylenic aldehydes respectively, followed by an elimination step using Peterson olefination procedures to define the stereochemistries of the alkene bonds (**Scheme 102**).[153]

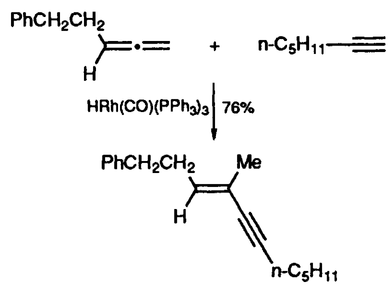


Scheme 102

Symmetric dienediynes have been prepared using a nickel-catalysed coupling reaction of 2,3-dichloro-1,3-butadiene with terminal acetylenes (**Scheme 103**)[154] and conjugated dienynes are obtained with good regioselectivity from the monocoupling of (*Z*)-conjugated bis(enoltriflates) and trimethylsilylacetylene using palladium catalysis.[155] The coupling of unactivated allenes and 1-alkynes can be achieved using a rhodium-based catalyst with a high regio- and stereo-selectivity, leading to *endo*-(*E*)-enynes in good yields (**Scheme 104**).[156]

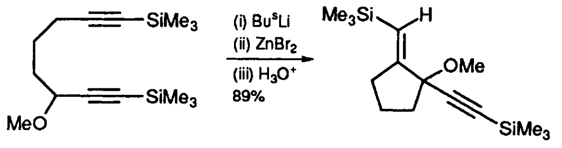


Scheme 103

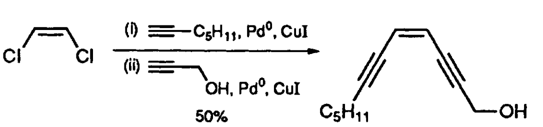


Scheme 104

Carbocyclization of 1,8-bis-trimethylsilyloctadiyne has been accomplished using a propargylic organozinc derivative to provide stereocontrolled 1,4-enyne cyclopentanes with an exocyclic double bond ready for further elaboration (**Scheme 105**).[157] Palladium-catalysed sequential coupling reactions of (*E*)- and (*Z*)-dichloroethenes with 1-alkynes afford (*Z*)- and (*E*)-enediynes bearing different substituents on the alkyne groups (**Scheme 106**).[158]

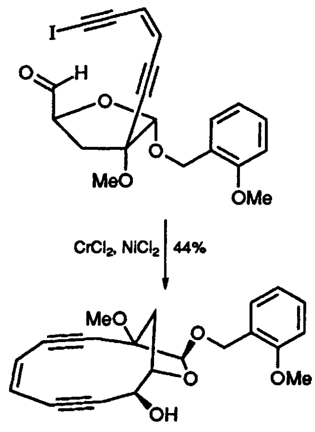


Scheme 105

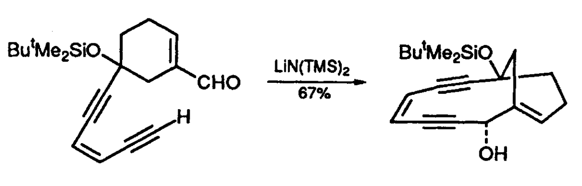


Scheme 106

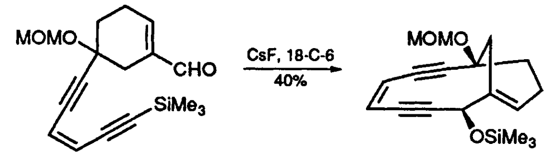
A large number of biologically active molecules containing the enediyne group have been isolated and a number of different synthetic strategies have been developed to prepare these interesting molecules. A convergent total synthesis of calicheamicin $\gamma^1{}_1$ has been reported,[159] and studies directed at calicheamicin and esperamicin type chromophores and aglycones include: the synthesis of an oxabicyclo[7.2.1]enediyne via a Nozaki reaction using $CrCl_2$ and catalytic $NiCl_2$ to generate a single diastereoisomer (**Scheme 107**),[160] the use of a [2,3]-Wittig rearrangement to generate 1,5-diynes which are further elaborated to generate enediyne systems;[161] the use of straightforward cyclizations mediated by $LiN(TMS)_2$ (**Scheme 108**),[162] or initiated by caesium fluoride (**Scheme 109**);[163] and



Scheme 107

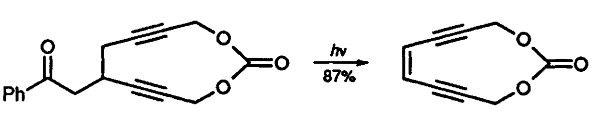


Scheme 108



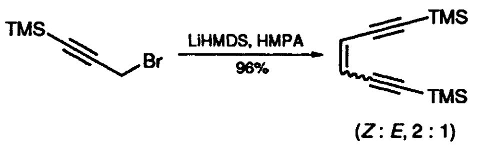
Scheme 109

the utilization of the Norrish Type II photochemical reaction in the highly efficient preparation of acyclic and cyclic enediynes (**Scheme 110**).[164]



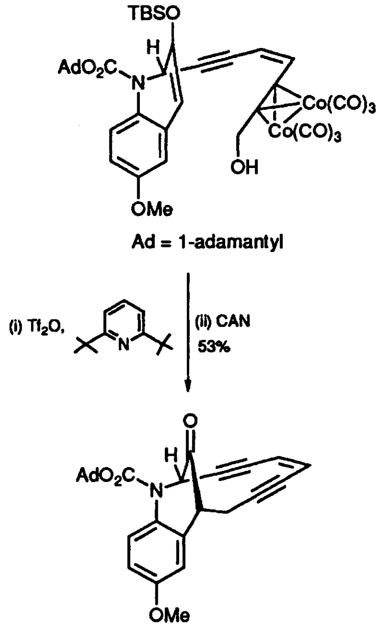
Scheme 110

In an attempt to circumvent the use of the expensive (*Z*)-dichloroethene and palladium catalysts, the direct self-coupling of trimethylsilyl propargylic bromide has been achieved using strong lithium bases with concommitant elimination to prepare acyclic (*Z*)-enediynes (**Scheme 111**).[165]

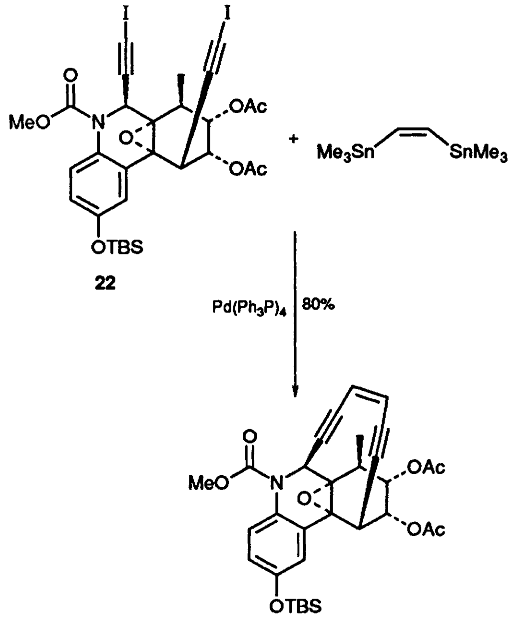


Scheme 111

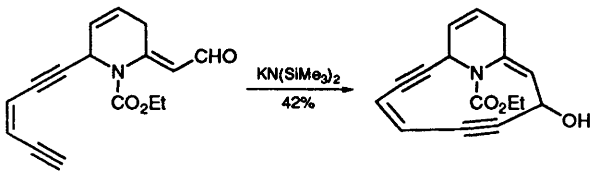
Studies directed towards the synthesis of dynemicin-type compounds include: constructing the enediyne unit from a terminal acetylene derivative, generated from the addition of a magnesium acetylide in a 1,4-asymmetric induction and subsequently elaborated for a caesium fluoride mediated cyclization;[166] the use of a dicobaltohexacarbonyl propargylic alcohol in a cyclization reaction with a bridgehead enolate mediated by trifluoromethylsulfonic anhydride (**Scheme 112**);[167] palladium-mediated cross-coupling of the diiodoacetylene derivative **22** with (*Z*)-distannylethylenes (**Scheme 113**),[168,169] and acetylene anion addition to a conjugated aldehyde (**Scheme 114**).[170]



Scheme 112

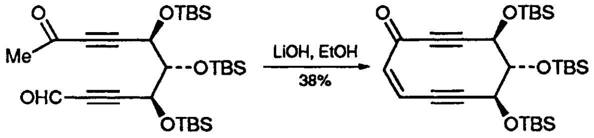


Scheme 113



Scheme 114

Other studies published in this area have included the preparation of monocyclic dienediyne systems related to the neocarzinostatin chromophore starting from D-xylitol and using an aldol cyclization as the key step (**Scheme 115**);[171] a description of the general strategies using dicobaltohexacarbonyl complexed acetylenes for the synthesis of enediyne antitumour agents;[172] and the synthesis of enetetraynes using palladium-mediated coupling reactions starting with (*Z*)-dichloroethylenes.[173]



Scheme 115

11 References

1 D.H.R. Barton, D.O. Jang and J.Cs. Jaszberenyi, *J. Org. Chem.*, 1993, **58**, 6838.
2 M. Oba and K. Nishiyama, *Synthesis*, 1994, 624.
3 M. Oba and K. Nishiyama, *Tetrahedron*, 1994, **50**, 624.
4 J.B. Hendrickson, M. Singer and Md.S. Hussoin, *J. Org. Chem.*, 1993, **58**, 6913.
5 D.J. Wustrow, W.J. Smith III and L.D. Wise, *Tetrahedron Lett.*, 1994, **35**, 61.
6 H. Maeda, T. Maki, K. Eguchi, T. Koide and H. Ohmori, *Tetrahedron Lett.*, 1994, **35**, 4129.
7 S. Hannesian and C. Girard, *Synlett*, 1994, 861.
8 G. Georg and Z.S. Cheruvallath, *J. Org. Chem.*, 1994, **59**, 4015.
9 R.A. Holton, C. Somoza and K.-B. Chai, *Tetrahedron Lett.*, 1994, **35**, 1665.
10 A. Ogawa, T. Nanke, N. Takami, Y. Sumino, I. Ryu and N. Sonoda, *Chem. Lett.*, 1994, 379.
11 N.M. Yoon, H.J. Lee, J.H. Ahn and J. Choi, *J. Org. Chem.*, 1994, **59**, 4687.
12 U. Maitra and K.D. Sarma, *Tetrahedron Lett.*, 1994, **35**, 7861.
13 Y. Zhang, S. Liao and Y. Xu, *Tetrahedron Lett.*, 1994, **35**, 4599.
14 G.B. Fisher, J.C. Fuller, J. Harrison, S.G. Alvarez, E.R. Burkhardt, C.T. Goralski and B. Singaram, *J. Org. Chem.*, 1994, **59**, 6378.
15 C.M. Belisle, Y.M. Young and B. Singaram, *Tetrahedron Lett.*, 1994, **35**, 5595.
16 M. Yamashita, Y. Tanaka, A. Arita and M. Nishida, *J. Org. Chem.*, 1994, **59**, 3500.
17 I.S. Cho and H. Alper, *J. Org. Chem.*, 1994, **59**, 4028.
18 R.D. Broene and S.L. Buchwald, *J. Am. Chem. Soc.*, 1993, **115**, 12569.
19 A.G. Martinez, A.H. Fernandez, R.M. Alvarez, J.O. Barcina, C.G. Gomez and L.R. Subramanian, *Synthesis*, 1993, 1063.
20 F. Chemla, I. Marek and J.-F. Normant, *Synlett*, 1993, 665.
21 E. Vedejs, J. Cabaj and M.J. Peterson, *J. Org. Chem.*, 1993, **58**, 6509.
22 M. Knecht and W. Boland, *Synlett*, 1993, 837.
23 D. Bell, E.A. Crowe, N.J. Dixon, G.R. Geen, I.S. Mann and M.R. Shipton, *Tetrahedron*, 1994, **50**, 6643.
24 K. Takai, T. Kakiuchi, Y. Kataoka and K. Utimoto, *J. Org. Chem.*, 1994, **59**, 2668.
25 S. Kusuda, Y. Ueno and T. Toru, *Tetrahedron*, 1994, **50**, 1045.
26 T. Fujiwara, T. Iwasaki, J. Miyagawa and T. Takeda, *Chem. Lett.*, 1994, 343.
27 I. Creton, I. Marek, D. Brasseur, J-L. Jestin and J-F. Normant, *Tetrahedron Lett.*, 1994, **35**, 6873.
28 K. Miura, D. Itoh, K. Hondo and A. Hosomi, *Tetrahedron Lett.*, 1994, **35**, 9605.
29 S.E. Denmark and J. Amburgey, *J. Am. Chem. Soc.*, 1993, **115**, 10386.
30 E. Doris, L. Dechoux and C. Miroskowski, *Tetrahedron Lett.*, 1994, **35**, 7943.
31 K. Takai, M. Yamada, H. Odaka and K. Utimoto, *J. Org. Chem.*, 1994, **59**, 5852.
32 K. Takai, H. Odaka, Y. Kataoka and K. Utimoto, *Tetrahedron Lett.*, 1994, **35**, 1893.
33 M. Sakai, Y. Takai, H. Mochizuki, K. Sasaki and Y. Sakakibara, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 1984.
34 J-B. Baudin, M-G. Commenil, S.A. Julia, L. Toupet and Y. Wang, *Synlett*, 1993, 839.
35 A. Chieffi and J.V. Comasseto, *Tetrahedron Lett.*, 1994, **35**, 4063.
36 M. Kosugi, T. Kimura, H. Oda and T. Migita, *Bull. Chem. Soc. Jpn*, 1993, **66**, 3522.
37 S. Marquais, G. Cahiez and P. Knochel, *Synlett*, 1994, 849.
38 W.E. Crowe and Z.J. Zhang, *J. Am. Chem. Soc.*, 1993, **115**, 10998.
39 N.J. Lawrence and F. Muhammad, *Tetrahedron Lett.*, 1994, **35**, 5903.
40 K.M. Brown, N.J. Lawrence, J. Liddle, F. Muhammad and D.A. Jackson, *Tetrahedron Lett.*, 1994, **35**, 6733.
41 M. Ihara, S. Suzuki, T. Taniguchi, Y. Tokunaga and K. Fukumoto, *Synlett*, 1994, 859.
42 L. Jin, M. Julia and J.N. Verpeaux, *Synlett*, 1994, 215.
43 Y. Gai, L. Jin, M. Julia and J.N. Verpeaux, *J. Chem. Soc., Chem. Commun.*, 1993, 1625.
44 R. Yanada, K. Bessho and K. Yanada, *Chem. Lett.*, 1994, 1279.
45 L.H.B. Baptistella, A.Z. Neto, H. Onaga and E.A.M. Godoi, *Tetrahedron Lett.*, 1993, **34**, 8407.
46 J. Uenishi and Y. Kubo, *Tetrahedron Lett.*, 1994, **35**, 6697.
47 L. Alcaraz, J.J. Harnett, C. Mioskowski, J.P. Martel, T. Le Gall, D-S. Shin and J.R. Falck, *Tetrahedron Lett.*, 1994, **35**, 5443.
48 L. Alcaraz, J.J. Harnett, C. Mioskowski, J.P. Martel, T. Le Gall, D-S. Shin and J.R. Falck, *Tetrahedron Lett.*, 1994, **35**, 5449.
49 M. Lakhrissi and Y. Chapleur, *J. Org. Chem.*, 1994, **59**, 5752.
50 J. Chen, T. Wang and K. Zhao, *Tetrahedron Lett.*, 1994, **35**, 2827.
51 B. Bonnet, Y. Le Gallic, G. Plé and L. Duhamel, *Synthesis*, 1993, 1071.
52 F. Tellier and R. Sauvêtre, *Tetrahedron Lett.*, 1994, **35**, 7565.
53 A.K. Saikia, N.C. Barua, R.P. Sharma and A.C. Ghosh, *Synthesis*, 1993, 685.
54 G.T. Crisp and A.G. Meyer, *Synthesis*, 1994, 667.
55 A. Mahadevan and P.L. Fuchs, *Tetrahedron Lett.*,

1994, **35**, 6025.
56 D.M. Hodgson, L.T. Boulton and G.N. Maw, *Tetrahedron Lett.*, 1994, **35**, 2231.
57 F.B. Bellina, A. Carpita, M. De Santis and R. Rossi, *Tetrahedron*, 1994, **50**, 4853.
58 S. Casson, P.J. Kocienski, G. Reid, N. Smith, J.M. Street and M. Webster, *Synthesis*, 1994, 1301.
59 N. Greeves and J.S. Torode, *Synlett*, 1994, 537.
60 F.B. Bellina, A. Carpita, E.A. Fontana and R. Rossi, *Tetrahedron*, 1994, **50**, 5189.
61 R. Takeuchi and N. Tanouchi, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2909.
62 N. Iwasawa and M. Saitou, *Chem. Lett.*, 1994, 231.
63 D.M. Hodgson and P.J. Comina, *Tetrahedron Lett.*, 1994, **35**, 9469.
64 T. Fukuyama, T. Li and G. Peng, *Tetrahedron Lett.*, 1994, **35**, 2145.
65 K. Hattori and H. Yamamoto, *Tetrahedron*, 1994, **50**, 3099.
66 T. Takahashi, M. Miyazawa, Y. Sakamoto and H. Yamada, *Synlett*, 1994, 902.
67 P. Metz and C. Linz, *Tetrahedron*, 1994, **50**, 3951.
68 J.A. McKinney, D.F. Eppley and R.M. Keenan, *Tetrahedron Lett.*, 1994, **35**, 5985.
69 C.P. Dell, K.M. Khan and D.W. Knight, *J. Chem. Soc., Perkin Trans. 1*, 1994, 341.
70 U. Kazmaier, *J. Org. Chem.*, 1994, **59**, 6667.
71 D. Kim, K.J. Shin, I.Y. Kim and S.W. Park, *Tetrahedron Lett.*, 1994, **35**, 7957.
72 K. Wimalasena and M.P.D. Mahindaratne, *J. Org. Chem.*, 1994, **59**, 3427.
73 S. Harusawa, S. Takemura, R. Yoneda and T. Kurihara, *Tetrahedron*, 1993, **49**, 10577.
74 K. Honda and S. Inoue, *Synlett*, 1994, 739.
75 J.-P. Bégué, D. Bonnet-Delpon, S.-W. Wu, A. M'Bida, T. Shintani and T. Nakai, *Tetrahedron Lett.*, 1994, **35**, 2907.
76 T. Tsunoda, S. Tatsuki, K. Kataoka and S. Itô, *Chem. Lett.*, 1994, 543.
77 M.A. Walters and H.B. Hoem, *J. Org. Chem.*, 1994, **59**, 2645.
78 E. Vedejs and M. Gingras, *J. Am. Chem. Soc.*, 1994, **116**, 579.
79 K. Fujimoto and T. Nakai, *Tetrahedron Lett.*, 1994, **35**, 5019.
80 D. Enders, D. Backhaus and J. Runsink, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2098.
81 M. Nakazawa, Y. Sakamoto, T. Takahashi, K. Tomooka, K. Ishikawa and T. Nakai, *Tetrahedron Lett.*, 1993, **34**, 5923.
82 J.E. Crawley, A.D. Kaye, G. Pattenden and S.M. Roberts, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2001.
83 N. Greeves and K.J. Vines, *Tetrahedron Lett.*, 1994, **35**, 7077.
84 X. Wang, Z. Ni, X. Lu, A. Hollis, H. Banks, A. Rodriguez and A. Padwa, *J. Org. Chem.*, 1993, **58**, 5377.
85 R.C. Hartley, S. Warren and I.C. Richards, *J. Chem. Soc., Perkin Trans. 1*, 1993, 507.
86 J. Ahman and P. Somfai, *J. Am. Chem. Soc.*, 1994, **116**, 9781.
87 T. Kitahara, T. Matsuoka, H. Hiyota, Y. Warita, H. Kurata, A. Horiguchi and K. Mori, *Synthesis*, 1994, 692.
88 M. Tokuda, N. Mimura, K. Yoshioka, T. Karasawa, H. Fujita and H. Suginome, *Synthesis*, 1993, 1086.
89 C. Nájera and J.M. Sansano, *Tetrahedron*, 1994, **50**, 5829.
90 M. Hoshi and A. Arase, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2693.
91 T. Moriya, T. Furuuchi, N. Miyaura and A. Suzuki, *Tetrahedron*, 1994, **50**, 7961.
92 J-E. Bäckvall and A. Ericsson, *J. Org. Chem.*, 1994, **59**, 5850.
93 C. Prandi and P. Venturello, *Tetrahedron*, 1994, **50**, 12463.
94 J. Clayden and S. Warren, *J. Chem. Soc., Perkin Trans 1*, 1993, 1529.
95 F. Babudri, V. Fiandanese, L. Mazzone and F. Naso, *Tetrahedron Lett.*, 1994, **35**, 8847.
96 A. Kinoshita and M. Mori, *Synlett*, 1994, 1020.
97 G.T. Crisp and P.T. Glink, *Tetrahedron*, 1994, **35**, 2623.
98 A. Duchêne, M. Abarbri, J.-L. Parrain, M. Kitamura and R. Noyori, *Synlett*, 1994, 524.
99 A.G.M. Barrett, M.L. Boys and T.L. Boehm, *J. Chem. Soc., Chem. Commun.*, 1994, 1881.
100 A.M. Gómez, J.C. López and B. Fraser-Reid, *Synthesis*, 1993, 943.
101 P. Lé Menez, N. Firmo, V. Fargeas, J. Ardisson and A. Pancrazi, *Synlett*, 1994, 995.
102 P. Lé Menez, I. Berque, V. Fargeas, J. Ardisson and A. Pancrazi, *Synlett*, 1994, 998.
103 B.M. Trost and C.-J. Li, *Synthesis*, 1994, 1267.
104 J. Uenishi, R. Kawahama, A. Tanio and S. Wakabayashi, *J. Chem. Soc., Chem. Commun.*, 1993, 1438.
105 T. Wong, M.A. Romero and A.G. Fallis, *J. Org. Chem.*, 1994, **59**, 5527.
106 J.A. Soderquist and J.C. Colberg, *Tetrahedron Lett.*, 1994, **35**, 27.
107 M. Kosugi, T. Sakaya, S. Ogawa and T. Migita, *Bull. Chem. Soc. Jpn.*, 1993, **66**, 3058.
108 K.A. Agrios and M. Srebnik, *J. Org. Chem.*, 1994, **59**, 5468.
109 K.J. Hodgetts, S.T. Saengchantara, C.J. Wallis, T.W. Wallace, *Tetrahedron Lett.*, 1993, **34**, 6321.
110 S.D. Rychnovsky and J. Kim, *J. Org. Chem.*, 1994, **59**, 2659.
111 M. Alami, B. Crousse and G. Linstrumelle, *Tetrahedron Lett.*, 1994, **35**, 3543.
112 C. Huynh, M. Alami and G. Linstrumelle, *Synth. Commun.*, 1994, **24**, 2273.
113 T. Takahashi, M. Kotora, K. Kasai and N. Suzuki, *Tetrahedron Lett.*, 1994, **35**, 5685.
114 G. Solladié, A. Urbano and G.B. Stone, *Tetrahedron Lett.*, 1993, **34**, 6489.
115 M. Riedel and G. Erker, *Synthesis*, 1994, 1039.
116 K. Hemming, E. Faria De Medeiros and R.J.K. Taylor, *J. Chem. Soc., Chem. Commun.*, 1994, 2623.
117 K. Hemming and R.J. K. Taylor, *J. Chem. Soc., Chem. Commun.*, 1993, 1409.
118 H. Bienaymé, *Tetrahedron Lett.*, 1994, **35**, 7383.
119 H. Bienaymé, *Tetrahedron Lett.*, 1994, **35**, 6867.
120 H. Bienaymé and C. Yezeguelian, *Tetrahedron Lett.*, 1994, **35**, 3389.
121 B.H. Lipshutz, M. Alami and R.B. Susfalk, *Synlett*, 1993, 693.
122 R.K. Bhatt, K. Chauhan, P. Wheelan, R.C. Murphy and J.R. Falck, *J. Am. Chem. Soc.*, 1994, **116**, 5050.
123 C.D. Gabbutt, J.D. Hepworth, B.M. Heron and M.M. Rahman, *J. Chem. Soc., Perkin Trans. 1*, 1994, 1733.
124 I.S. Aidhen and R. Braslau, *Synth. Commun.*, 1994, **24**, 789.
125 D. Badone, R. Cardamone and U. Guzzi, *Tetrahedron Lett.*, 1994, **35**, 5477.
126 H. Tanaka, A.K.M.A. Hai, H. Ogawa and S. Torii, *Synlett*, 1993, 835.
127 S. Harusawa, N. Kase, R. Yoneda and T. Kurihara, *Tetrahedron Lett.*, 1994, **35**, 1255.

128 G. Handke and N. Krause, *Tetrahedron Lett.*, 1993, **34**, 6037.
129 C. Darcel, S. Bartsch, C. Bruneau and P.H. Dixeuf, *Synlett*, 1994, 457.
130 T. Moriya, N. Miyaura and A. Suzuki, *Synlett*, 1994, 149.
131 H. Bienaymé, *Tetrahedron Lett.*, 1994, **35**, 7387.
132 Y.S. Lee, K.H. Nam, S.H. Jung and H. Park, *Synthesis*, 1994, 792.
133 P. Rochet, J-M. Vatèle and J. Gorè, *Synthesis*, 1994, 795.
134 H-F. Chow, X-P. Cao and M. Leung, *J. Chem. Soc., Chem. Commun.*, 1994, 2121.
135 F. Toda, K. Tanaka and H. Nawata, *J. Chem. Soc., Perkin Trans. 1*, 1994, 2043.
136 B.J.L. Royles and D.M. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1994, 355.
137 V. Ratovelomanana, Y. Rollin, C. Gébéhenne, C. Gosmini and J. Périchon, *Tetrahedron Lett.*, 1994, **35**, 4777.
138 D. Grandjean, P. Pale and J. Chuche, *Tetrahedron Lett.*, 1994, **35**, 3529.
139 K. Kusuda, K. Kawamura, Y. Ueno and T. Toru, *Tetrahedron Lett.*, 1993, **34**, 6587.
140 K. Miwa, T. Aoyama and T. Shioiri, *Synlett*, 1994, 107.
141 G.G. Melikyan, R.C. Combs, J. Lamirand, M. Khan and K.M. Nicholas, *Tetrahedron Lett.*, 1994, **35**, 363.
142 K. Iida and M. Hirama, *J. Am. Chem. Soc.*, 1994, **116**, 10310.
143 M. Yoshimatsu, H. Yamada, H. Shimizu and T. Kataoka, *J. Chem. Soc., Chem. Commun.*, 1994, 2107.
144 M. Alami, F. Ferri and G. Linstrumelle, *Tetrahedron Lett.*, 1993, **34**, 5403.
145 T. Mandai, Y. Tsujiguchi, S. Matsuoka and J. Tsuji, *Tetrahedron Lett.*, 1994, **35**, 7615.
146 S. Ikeda and Y. Sato, *J. Am. Chem. Soc.*, 1994, **116**, 5975.
147 S. Ikeda, D.-M. Cui and Y. Sato, *J. Org. Chem.*, 1994, **59**, 6877.
148 C. Darcel, C. Bruneau and P.H. Dixeuf, *J. Chem. Soc., Chem. Commun.*, 1994, 1845.
149 K.K. Wang and Z. Wang, *Tetrahedron Lett.*, 1994, **35**, 1829.
150 Z. Wang and K.K. Wang, *J. Org. Chem.*, 1994, **59**, 4738.
151 M.E. Maier and D. Langenbacher, *Synlett*, 1994, 713.
152 J. Isihara, N. Kanoh, A. Fukuzawa and A. Murai, *Chem. Lett.*, 1994, 1563.
153 K.K. Wang, Z. Wang and Y.G. Gu, *Tetrahedron Lett.*, 1993, **34**, 8391.
154 H. Hopf and M. Theurig, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1099.
155 M. Moniatte, M. Eckhardt, K. Brickmann, R. Brückner and J. Suffert, *Tetrahedron Lett.*, 1994, **35**, 1965.
156 M. Yamaguchi, K. Omata and M. Hirama, *Tetrahedron Lett.*, 1994, **35**, 5689.
157 C. Meyer, I. Marek, J-F. Normant and N. Platzer, *Tetrahedron Lett.*, 1994, **35**, 5645.
158 D. Chemin and G. Linstrumelle, *Tetrahedron*, 1994, **50**, 5335.
159 S.A. Hitchcock, S.H. Boyer, M.Y. Chu-Moyer, S.H. Olson and S.J. Danishefsky, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 858.
160 T. Brandstetter and M.E. Maier, *Tetrahedron*, 1994, **50**, 1435.
161 H. Audrain, T. Skrydstrup, G. Ulibarri, C. Riche, A. Chiaroni and D.S. Grierson, *Tetrahedron*, 1994, **50**, 1469.
162 J.F. Kadow, D.J. Cook, T.W. Doyle, D.R. Langley, K.M. Pham, D.M. Vyas and M.D. Wittman, *Tetrahedron*, 1994, **50**, 1519.
163 T. Nishikawa, S. Shibuya and M. Isobe, *Synlett*, 1994, 482.
164 J.M. Nuss and M.M. Murphy, *Tetrahedron Lett.*, 1994, **35**, 37.
165 R.S. Huber and G.B. Jones, *Tetrahedron Lett.*, 1994, **35**, 2655.
166 T. Nishikawa, M. Yoshikai, K. Obi and M. Isobe, *Tetrahedron Lett.*, 1994, **35**, 7997.
167 P. Magnus, D. Parry, T. Iliadis, S.A. Eisenbeis and R.A. Fairhurst, *J. Chem. Soc., Chem. Commun.*, 1994, 1543.
168 M.D. Shair, T. Yoon, T-C. Chou and S.J. Danishefsky, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2477.
169 M.D. Shair, T. Yoon and S.J. Danishefsky, *J. Org. Chem.*, 1994, **59**, 3755.
170 M.F. Braña, M. Morán, M.J.P. de Vega and I. Pita-Romero, *Tetrahedron Lett.*, 1994, **35**, 8655.
171 K. Toshima, K. Yanagawa, K. Ohta, T. Kano and M. Nakata, *Tetrahedron Lett.*, 1994, **35**, 1573.
172 P. Magnus, *Tetrahedron*, 1994, **50**, 1397.
173 D. Elbaum, T.B. Nguyen, W.L. Jorgensen and S.L. Schreiber, *Tetrahedron*, 1994, **50**, 1503.