Synthesis of thiols, selenols, sulfides, selenides, sulfoxides, selenoxides, sulfones and selenones

Charlotte P. Baird and Christopher M. Rayner *

School of Chemistry, University of Leeds, Leeds, UK LS2 9JT

Covering: June 1996 to June 1997
Previous review: *Contemp. Org. Synth.*, 1996, 3, 499

1 Introduction

This review continues from the previous ones published in 1994,[1] 1995[2] and 1996.[3] It covers new methods for the synthesis of acyclic thiols and selenols, disulfides and diselenides, sulfides and selenides, sulfoxides and selenoxides, and sulfones and selenones. Cyclic systems will be covered elsewhere. A similar format has been adopted to that of the previous review in that it is divided into three sections: thiols, selenols, disulfides, diselenides, sulfides and selenides; sulfoxides and selenoxides; and sulfones and selenones. Each section begins with synthetic routes to simple systems, and then goes on to consider methods leading to more complex, polyfunctional molecules. Considerable emphasis has been placed on stereo- and enantio-selective reactions, reflecting the current interest in this area.

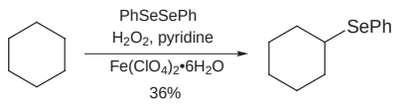
A new general introductory text to organosulfur chemistry has been published,[4] as has a monograph containing chapters on asymmetric sulfoxidation, synthesis of chiral sulfoxides, conformational studies of cyclic sulfoxides, chiral sulfoxides as stereocontrolling elements in organic synthesis, the chemistry of α,β-unsaturated sulfoxides, and the preparation of 3-sulfolenes.[5] A number of general reviews on organosulfur and organoselenium chemistry have also been published. These include a discussion of the distribution and properties of selenocysteine containing enzymes and proteins that have been discovered to date;[6] and *Allium* chemistry—the natural abundance of organoselenium compounds from garlic, onion and related plants and in human garlic breath.[7]

2 Synthesis of thiols and disulfides, selenols and diselenides, sulfides and selenides

An excellent review on electrophile mediated heteroatom cyclisation onto carbon–carbon π-bonds includes a section on organoselenium induced reactions.[8] The production and reactivity of new organoselenium intermediates leading to the formation of C–O and C–N bonds has also been reviewed[9] as has the use of sulfenyl chlorides in organic synthesis[10] and recent progress in electrophilic aromatic substitution with α-thiocarbocations such as those derived from α-chloro sulfides or sulfoxides.[11] A review of arene catalysed lithiation reactions also includes some examples of sulfide synthesis.[12]

2.1 Simple alkyl thiols, disulfides, selenols, diselenides, dialkyl sulfides and selenides

The selective functionalisation of saturated hydrocarbons is generally very difficult to achieve, however using Gif (IV) oxidation conditions, moderate yields of alkyl phenyl sulfides or selenides can be obtained when used in conjunction with thiols and disulfides or selenols and diselenides (**Scheme 1**).[13]



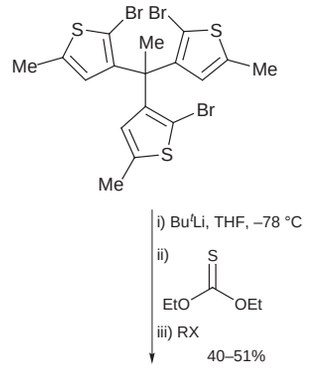
Scheme 1

A much more established method for sulfide and selenide synthesis is the reaction of metal thiolates or selenolates with alkyl halides, and these have been discussed extensively in previous reviews.[1–3] A recent X-ray crystal structure of a lithium thiolate tetrahydrofuran complex has been reported and reveals a trimeric structure at least in the solid state.[14] Such intermediates have been used in the synthesis of interesting thiophene-triptycene 8-thioethers and the corresponding thiol by sequential addition of organolithium species to diethyl thiocarbamate, and quenching the resultant thiolate with either an alkyl halide or acid respectively (**Scheme 2**).[15]

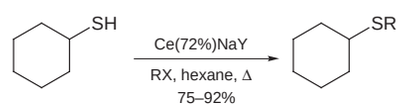
These reactions can be quite basic, so conditions have been developed which help avoid this such as using weakly basic cerium-exchanged NaY zeolites as catalysts (**Scheme 3**)[16] or a base free method using an organocobalt(III) intermediate, generated from $CoCl_2$ which is reduced *in situ* using zinc to the Co^I species which undergoes oxidative addition with an alkyl halide. This species then reacts with a disulfide to give alkyl aryl thioethers (**Scheme 4**).[17]

Another mild procedure involves the use of zinc dimethyldithiocarbamate under Mitsunobu conditions (**Scheme 5**).[18]

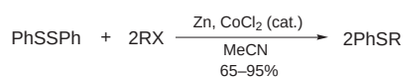
An approach to the stereoselective synthesis of 1,2-dialkyl-1-phenylcyclopentanes involving an intramolecular carbolithiation of an α-thioalkene, can give thioethers in good yields and with moderate stereoselectivities (**Scheme 6**).[19] The initial organolithium intermediate is generated by lithium–selenium exchange of the appropriate selenide precursor.



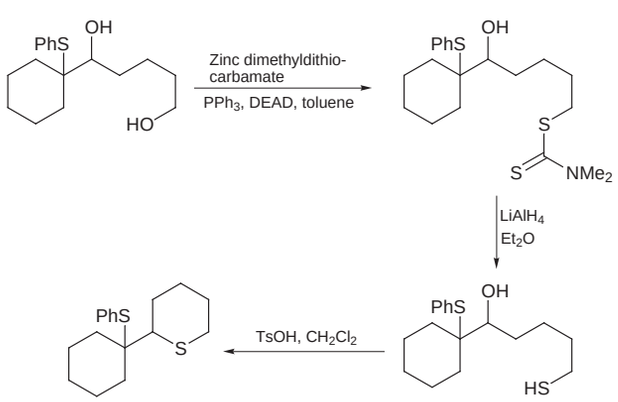
Scheme 2



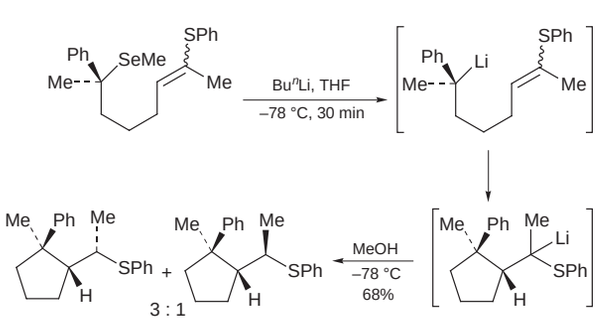
Scheme 3



Scheme 4

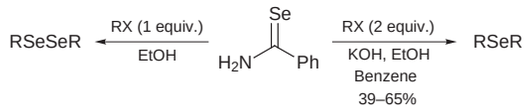


Scheme 5



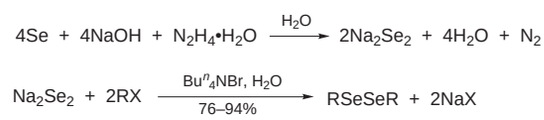
Scheme 6

The synthesis of selenides using selenobenzamide and two equivalents of alkyl halides proceeds in moderate yield (**Scheme 7**).[20] If however just one equivalent of alkyl halide is used then the corresponding diselenide is the major product. An alternative approach for diselenide synthesis utilises hydrazine hydrate as reductant for elemental selenium to generate the diselenide dianion as a dark red solution in water. Subsequent



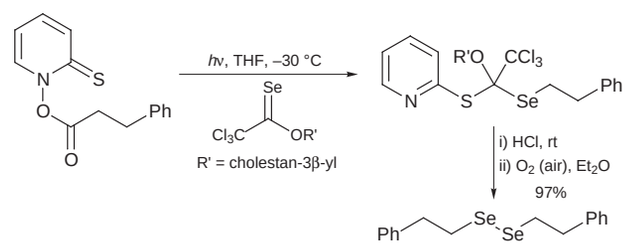
Scheme 7

reaction with alkyl halides under phase transfer conditions (PTC) gives the diselenides in good to excellent yields (**Scheme 8**).[21] Note that no organic solvents are required for this process.



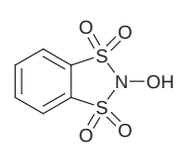
Scheme 8

Radical reactions can also be used for diselenide synthesis. Thus *N*-hydroxythiopyridone derivatives undergo photolysis in the presence of a selenoester to form an O,Se acetal. Acid hydrolysis gives the selenol which then undergoes oxidation by atmospheric oxygen to give the diselenide (**Scheme 9**).[22]

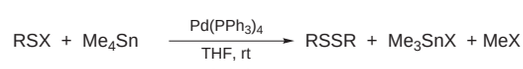


Scheme 9

New reagent systems have been reported for the oxidation of thiols to disulfides. These include iodine and morpholine in THF;[23] methyltrichlorosilane, trifluoroacetic acid and diphenyl sulfoxide;[24] and *N*-hydroxy-*O*-benzenedisulfonimide **1**.[25] Alternatively the palladium catalysed reaction of organostannanes and sulfenyl halides also leads to efficient disulfide formation (**Scheme 10**).[26] This paper also describes the synthesis of some unusual arenesulfenyl chlorides using the corresponding disulfide and Cl_2.



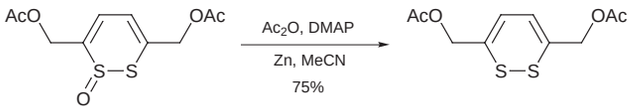
1



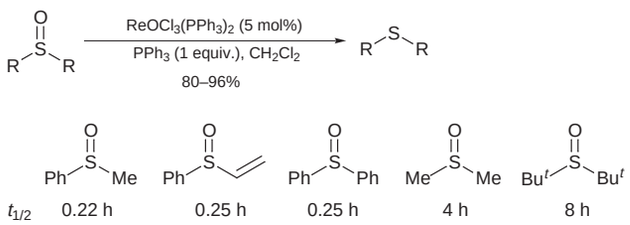
Scheme 10

The reduction of sulfoxides can be used as a method for sulfide synthesis. New methods for this include acetic anhydride, 4-*N*,*N*-dimethylaminopyridine, activated zinc (**Scheme 11**);[27] and a rhenium catalysed reduction using $ReOCl_3(PPh_3)_2$ and PPh_3 (**Scheme 12**).[28] In the latter case, the order of reactivity is the opposite of that observed for the high temperature reduction of sulfoxides using PPh_3, or when activated by other reagent combinations, and does not follow sulfoxide bond strengths as aryl sulfoxides typically possess sulfoxide bonds 1–3 kcal mol^{-1} stronger than alkyl sulfoxides.

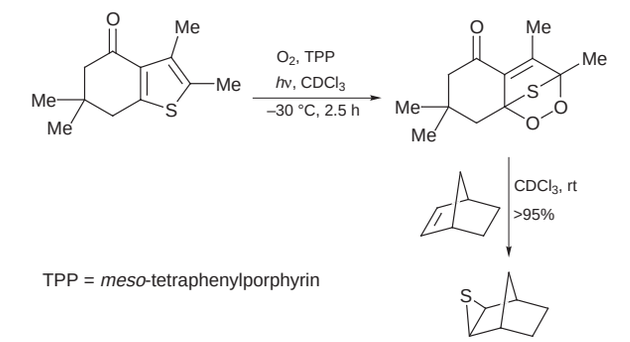
Finally, an interesting reaction, effectively the sulfur equivalent of epoxidation, by direct transfer of sulfur to cycloalkenes during the thermolysis of a thiophene endoperoxide has been reported. Yields can be as high as 95% but are generally much lower (**Scheme 13**).[29]



Scheme 11



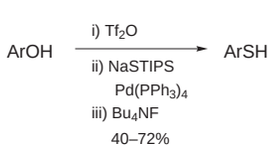
Scheme 12



Scheme 13

2.2 Unsaturated thiols, disulfides, selenols, diselenides, sulfides and selenides

A review on the synthesis of unsaturated organoselenium compounds has been published.[30] New methods for the synthesis of aromatic thiols have been reported. Phenols are converted into the corresponding trifluoromethanesulfonates, which then undergo palladium catalysed displacement with triisopropylsilylthiolate to give the silyl thioether which can be deprotected using fluoride (**Scheme 14**).[31]



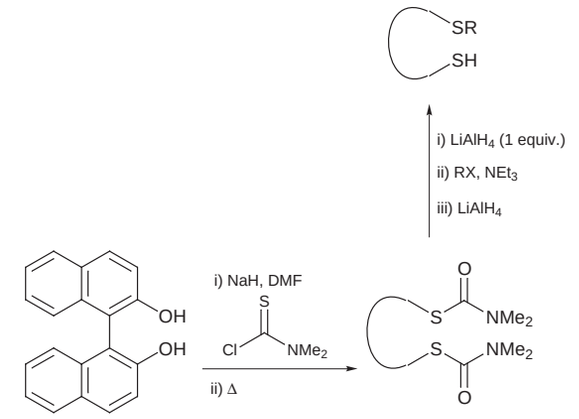
Scheme 14

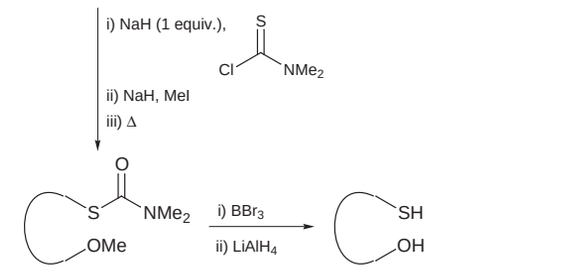
The Newman–Kwart rearrangement has been previously used in the conversion of phenols into aromatic thiols.[2,3] Related chemistry has now been used to synthesise unsymmetrical 2,2′-disubstituted 1,1′-binaphthalene derivatives based on either the dithiol or naphthalenol thiol (**Scheme 15**).[32] The reaction of electron rich arenes with phthalimidosulfenyl chloride leads to monosubstituted phthalimidosulfenyl derivatives which can then readily be converted into the corresponding disulfides, thiols or masked thiols (**Scheme 16**).[33]

Chiral 2-aryloxazolines containing thiols, thioethers and selenoethers have been prepared (**Scheme 17**).[34] In the case of the thiol, the reaction work-up and chromatography is best performed in an inert atmosphere to prevent oxidation to the disulfide, but when pure the thiol is only slightly sensitive towards oxidation.

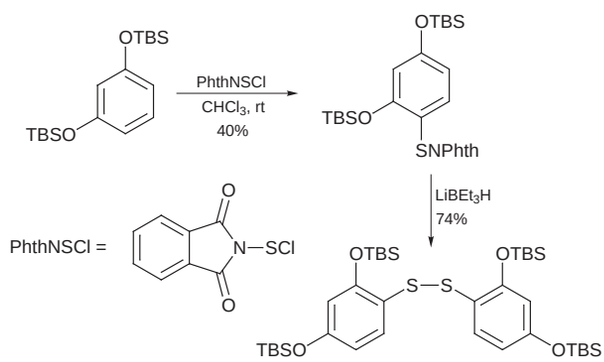
The palladium catalysed cross coupling reaction of 9-organothio-9-borabicyclo[3.3.1]nonanes with organic electrophiles (aryl and vinyl iodides) provides access to a range of aryl alkyl and aryl vinyl sulfides (**Scheme 18**).[35]

Hypervalent iodine reagents facilitate the nucleophilic substitution reaction of *para*-substituted phenolic ethers by introduction of a phenylthio group using either *S*-trimethylsilylthio-

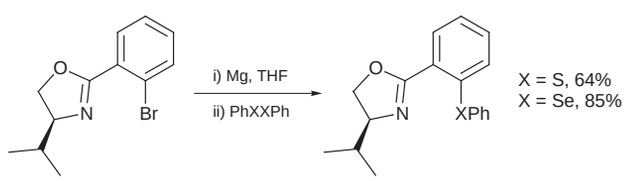


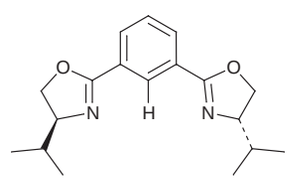


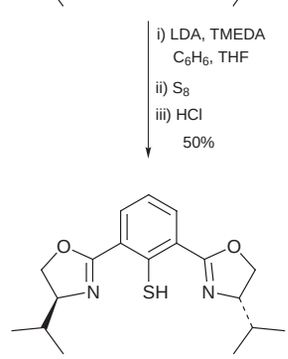
Scheme 15



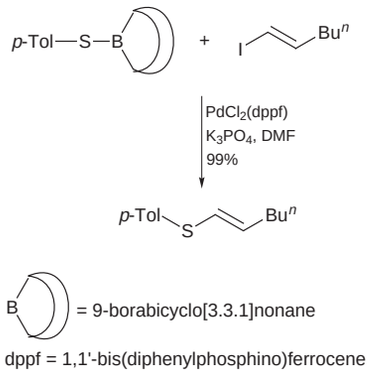
Scheme 16





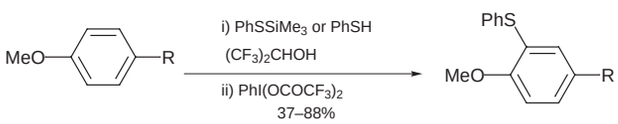


Scheme 17

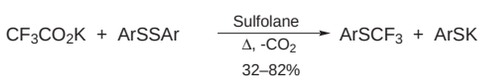


Scheme 18

phenol or thiophenol itself as nucleophiles (**Scheme 19**).[36] A convenient synthesis of trifluoromethyl aryl sulfides utilises the potassium salt of trifluoroacetic acid as a nucleophilic CF_3 equivalent, which after decarboxylation reacts with diaryl disulfides in low to good yield (**Scheme 20**).[37]

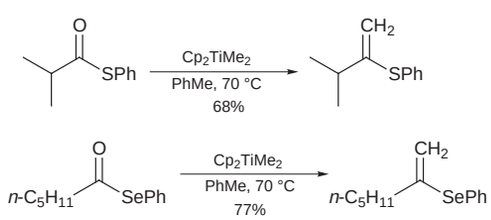


Scheme 19



Scheme 20

Many new procedures have been reported for the synthesis of vinyl sulfides. A recent review describes the synthesis of vinyl sulfides and selenides using Tebbe's reagent on the corresponding thio- and seleno-esters (**Scheme 21**).[38]



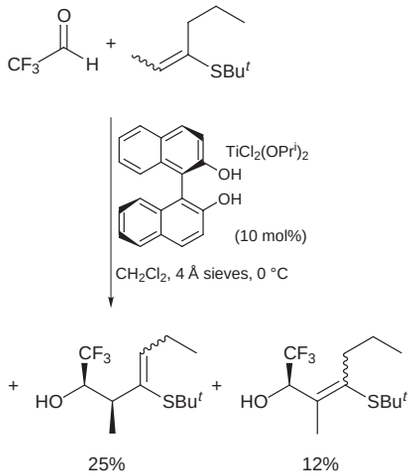
Scheme 21

The fluoral-ene reaction with vinyl sulfides can be catalysed by chiral Lewis acids such as the complex between binaphthol and $TiCl_2(OPr^i)_2$ to give α-trifluoromethyl-β-methyl alcohols containing an adjacent vinyl sulfide group (**Scheme 22**).[39] Good diastereoselectivities can be achieved with excellent enantiomeric purity of the major product. In related chemistry, *N*-acyliminium ions react with vinyl sulfides in an ene-type process to give substituted pyrrolidone derivatives with high diastereoselectivity (**Scheme 23**).[40]

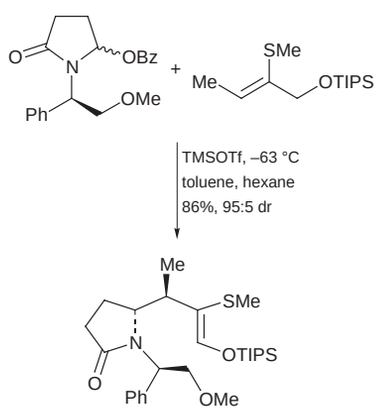
Thionium ions, generated from α-thiostannanes and related compounds, add to electron rich aromatic rings to give α-thiostyrene derivatives in good yield (**Scheme 24**).[41]

The addition of benzenesulfenyl chloride to alkenes followed by elimination provides a facile route to vinyl sulfides, and has recently been applied to the synthesis of fluorinated vinyl sulfides (**Scheme 25**).[42] Alkyl aryl sulfides can be effectively dehydrogenated to aryl vinyl sulfides by chlorination and elimination (**Scheme 26**).[43] The presence of an adjacent carbonyl group facilitates this process.

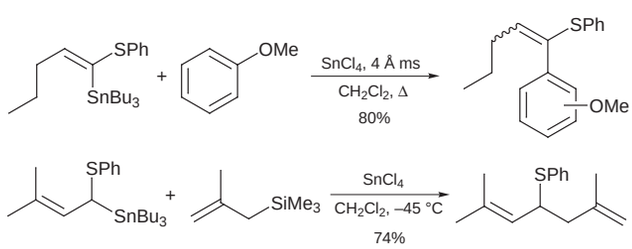
More basic conditions are required for elimination in less activated systems. Thus use of one equivalent of organolithium reagent induces elimination of an allylic acetal, whereas two



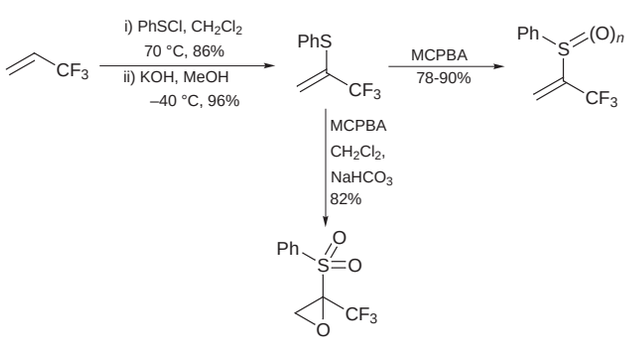
Scheme 22



Scheme 23



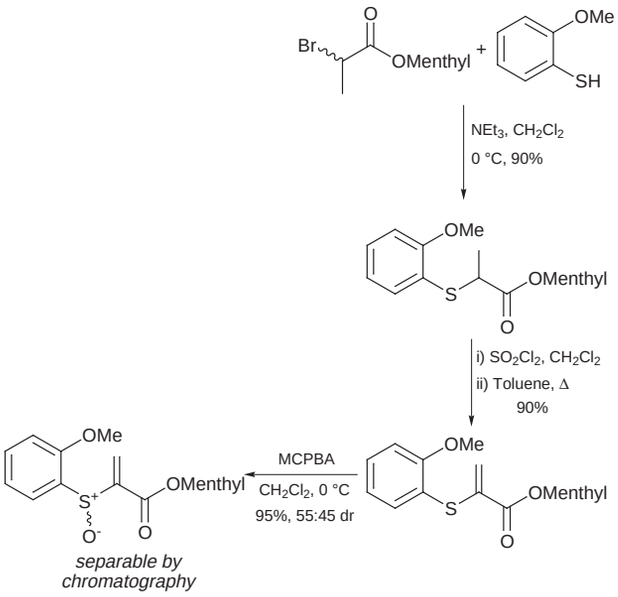
Scheme 24



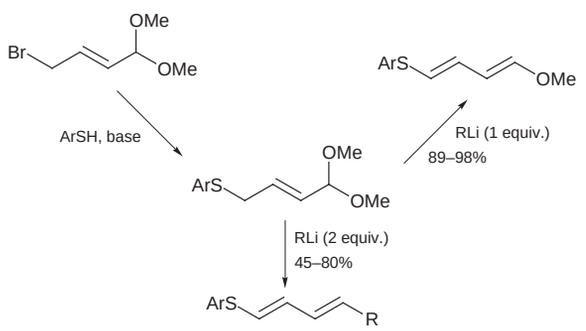
Scheme 25

equivalents leads to further substitution of the remaining alkoxy group with the organolithium reagent (**Scheme 27**).[44]

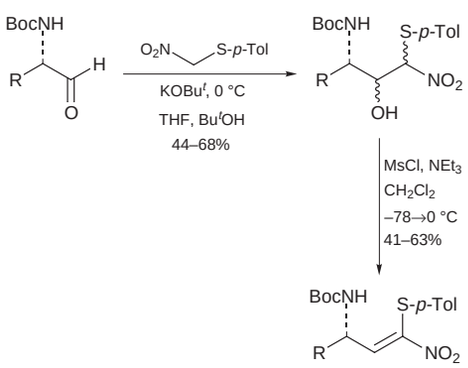
The synthesis of 1-arylthio-1-nitroalkenes can be readily accomplished by condensation between an aldehyde and an arylthionitromethane. The intermediate alcohol is best dehydrated *via* the derived mesylate (**Scheme 28**).[45] The sulfenylation of α-phosphoryl sulfoxides allows access to reagents which, after condensation with aldehydes, lead to formation of unsaturated dithioacetal mono-*S*-oxides (**Scheme 29**).[46] Good



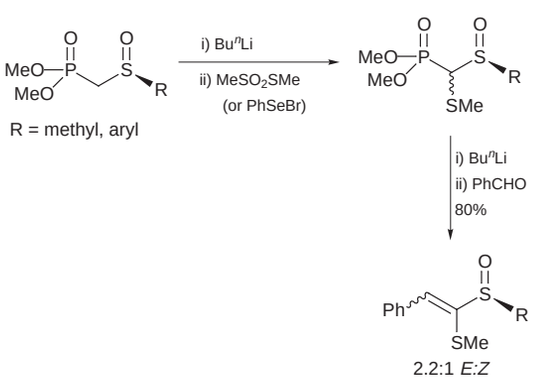
Scheme 26



Scheme 27



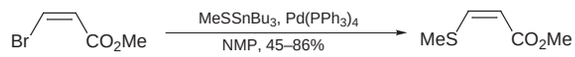
Scheme 28



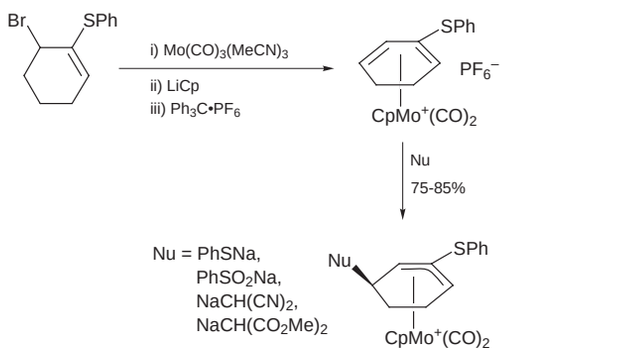
Scheme 29

yields are obtained but control of double bond geometry is modest.

The palladium mediated coupling of aryl- or alkyl-thiotributylstannanes with 3-halopropenoates allows access to vinyl sulfides with retention of double bond geometry (**Scheme 30**).[47] Regio- and stereo-controlled nucleophilic addition reactions to a phenylthio-substituted cationic cyclohexadiene molybdenum complex also provide access to a variety of vinyl sulfides (**Scheme 31**).[48] Complexation and hydride abstraction give an η^4 cationic complex which undergoes nucleophilic addition with thiolate, sulfinate and various malonate equivalents. Subsequent transformations allow the synthesis of some highly functionalised vinyl sulfides.

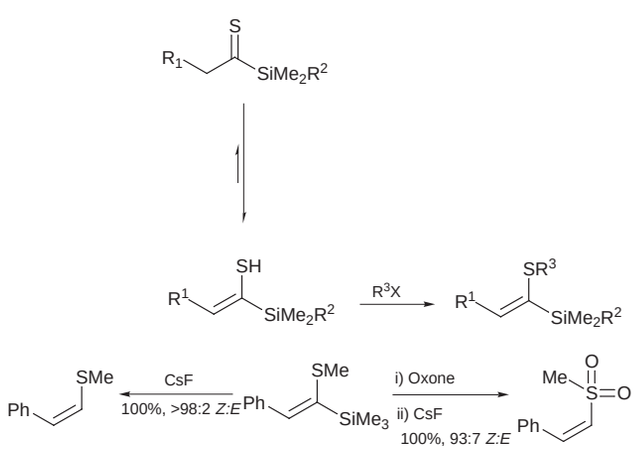


Scheme 30



Scheme 31

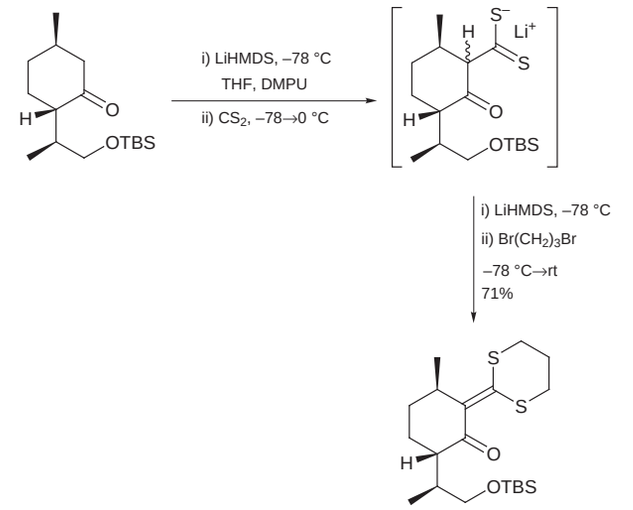
Silyl thioketones exist in tautomeric equilibrium with the corresponding enethiol form which can undergo alkylation with a variety of reactive electrophiles (**Scheme 32**).[49] Desilylation then gives the (*Z*)-vinyl sulfide in excellent yield and with full control of double bond geometry. Related chemistry can also provide an attractive alternative approach to the synthesis of unsaturated 1,3-dithianes (**Scheme 33**).[50]



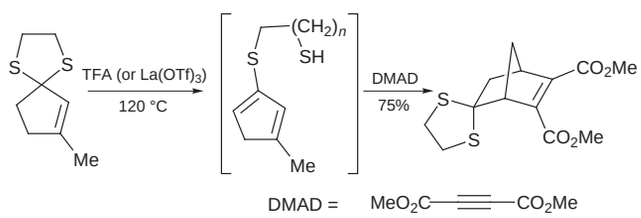
Scheme 32

The interconversion between cyclic dithioacetals and their ring opened vinyl sulfide forms can be accomplished at elevated temperatures in the presence of a catalyst, either trifluoroacetic acid, or $La(OTf)_3$. This can be used to reveal a diene system which can undergo cycloaddition. Subsequent reclosure of the vinyl sulfide reforms the cyclic dithioacetal in good overall yield (**Scheme 34**).[51]

The stereoselective synthesis of (*E*)-vinyl selenides can be

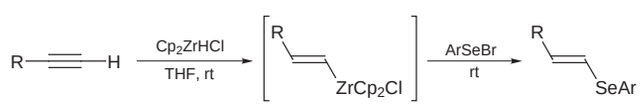


Scheme 33

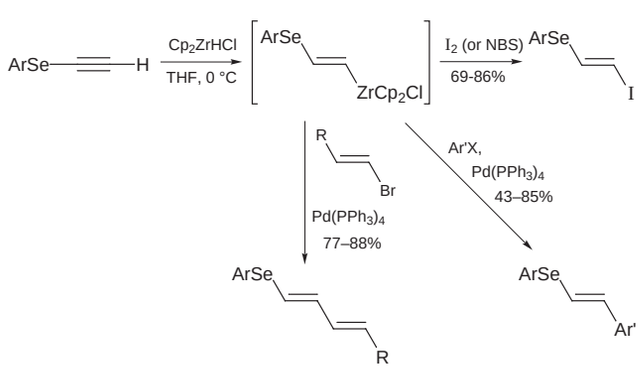


Scheme 34

achieved *via* hydrozirconation of terminal alkynes, and quenching the intermediate organozirconium species with an aryl selenyl bromide (**Scheme 35**).[52] Similarly, selenoalkynes, which can be prepared from ethynylmagnesium bromide and a selenyl bromide[53] undergo hydrozirconation, and the intermediate organometallic can be converted into halide functionality (**Scheme 36**),[54] or can be cross-coupled directly with aryl or vinyl halides using palladium catalysis to give β-selenostyrenes or (*E*,*E*)-1-aryl selenobutadienes respectively with full control of double bond geometry (Scheme 36).[55,56]



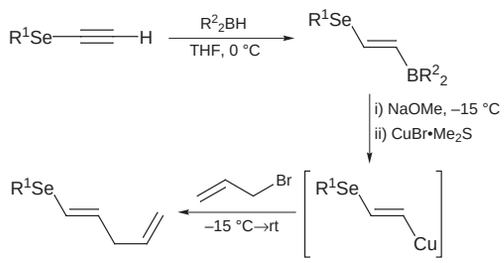
Scheme 35



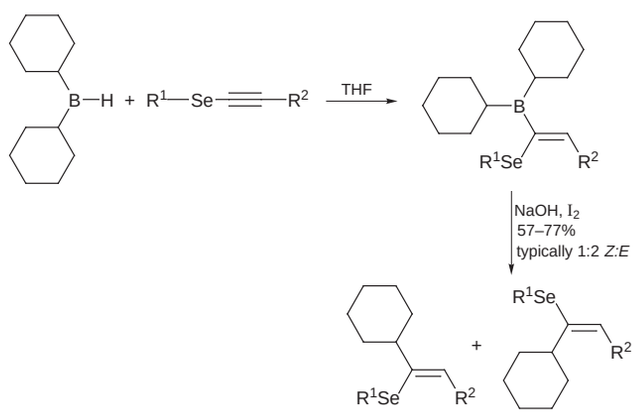
Scheme 36

Selenoalkynes also undergo stereoselective hydroboration. The intermediate boranes can then be either transmetallated and alkylated (**Scheme 37**)[57] or undergo rearrangement (**Scheme 38**),[58] although in the latter case, a mixture of double bond isomers is usually formed.

Other additions to selenoalkynes have also been reported,

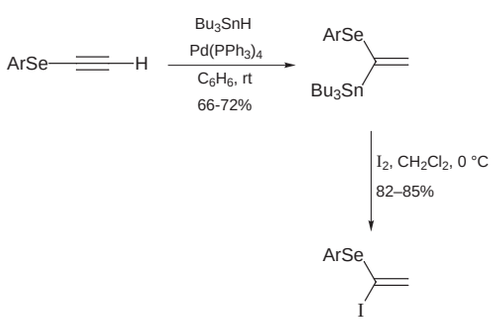


Scheme 37



Scheme 38

including palladium catalysed hydrostannylation and subsequent iodination (**Scheme 39**),[59] hydrosilylation (**Scheme 40**),[60] or direct addition of hydrogen halides (**Scheme 41**).[61] The product vinyl halides are useful precursors to organometallic reagents which allow further functionalisation of the vinyl selenide.



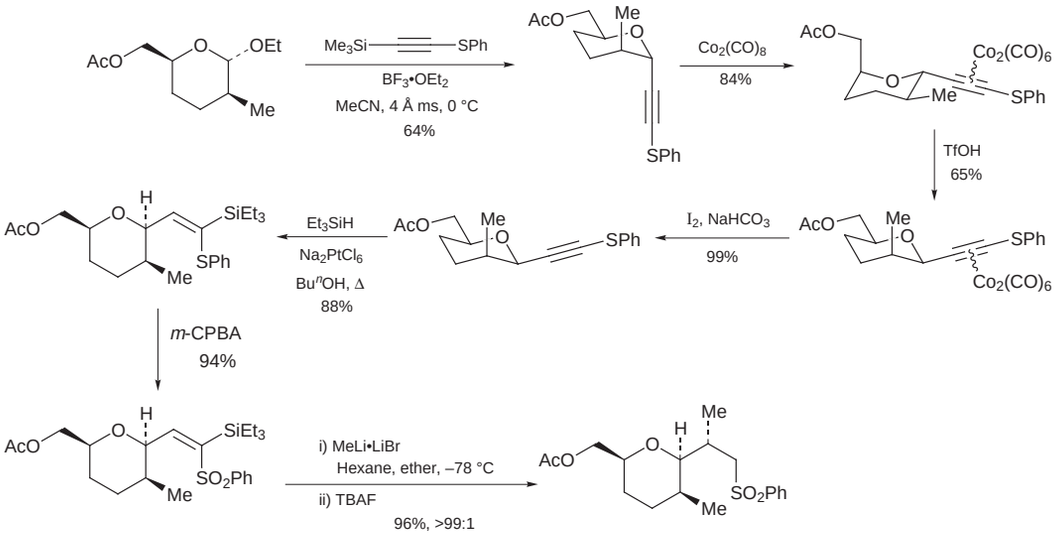
Scheme 39

The photochemically induced selenosulfonation of alkynes provides a versatile route to the synthesis of sulfone-substituted vinyl selenides, usually with good stereocontrol (**Scheme 42**).[62] Further structural elaboration is also possible allowing access to quite complex dienyl selenides (**Scheme 43**).[63]

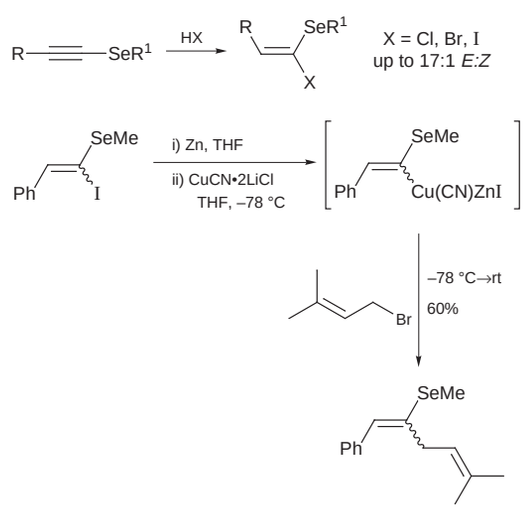
Alternatively, nucleophilic addition of sodium selenides to conjugated enyne sulfones also provides access to dienyl selenides with good stereocontrol and excellent yields (**Scheme 44**).[64]

Vinyl selenides substituted with other heteroatoms have also been prepared. Condensation of an α-seleno aldehyde with a primary amine equivalent gives an enamino selenide, which in this case is not isolated but undergoes intramolecular Diels–Alder cycloaddition with an adjacent diene (**Scheme 45**).[65] Intramolecular addition of alkoxides to alkynyl selenides gives the vinyl selenide (**Scheme 46**).[66] Related chemistry can also be achieved using alkynyl sulfides.

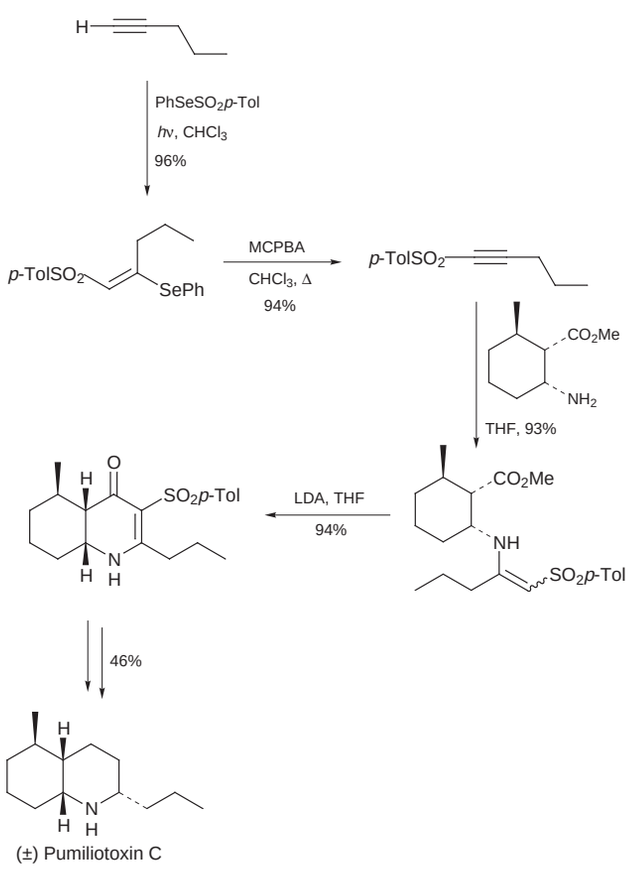
A variety of benzyl selenides can be prepared from benzyl alcohol using a combination of the selenolate anion and aluminium chloride (**Scheme 47**).[67] Good yields can be achieved but a large excess of $AlCl_3$ and $NaBH_4$ are usually required.



Scheme 40



Scheme 41



Scheme 42

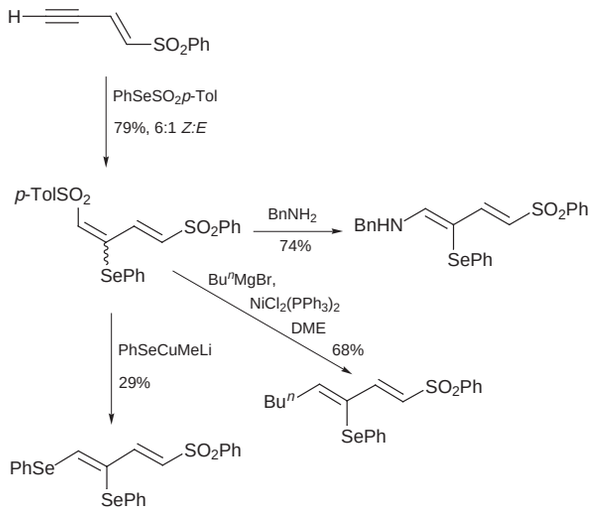
Organometallic routes have also been developed to allyl selenides using an allyl (or prop-2-ynyl) bromide and samarium (**Scheme 48**),[68] or indium (**Scheme 49**).[69,70] Some of the reactions can be carried out in aqueous media with no need for an inert atmosphere[70] and in all cases, diselenides are used as electrophiles.

In an extension to previous organometallic chemistry based on rhenium, diallyl sulfide complexes of chiral iron and ruthenium Lewis acids have been used to promote ylide generation and diastereoselective [2,3]-sigmatropic rearrangement to give thiolate complexes with new carbon stereocentres which can be converted into free allyl thioethers (**Scheme 50**).[71,72] The [3,3]-sigmatropic rearrangement of allyl xanthates to dithiocarbonates provides another stereoselective route to allyl thioethers (**Scheme 51**).[73]

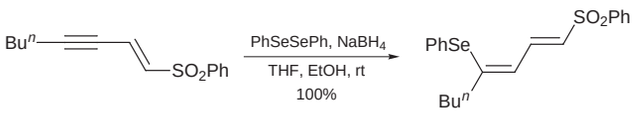
An alternative route is the metal catalysed substitution of allylic cyclic carbonates. Interestingly the regioselectivity of this process is metal dependent. Using $Pd(PPh_3)_4$ and PhSNa internal substitution is favoured, and proceeds with inversion of stereochemistry (**Scheme 52**).[74] However using $CpRu(PPh_3)_2Cl$ and PhSH, introduction of the thioether occurs at the least hindered terminal position.

Thionium ions, generated from α-thiostannanes under Lewis acidic conditions, react efficiently with allyl silanes to give allylic sulfides, as described earlier (Scheme 24).[41] Homoallylic sulfides and selenides can be accessed using tris(phenylchalcogeno)methanes which undergo Lewis acid mediated cleavage in the presence of allyl trimethylsilane (**Scheme 53**).[75] Alternatively, zinc mediated coupling of chloro(phenylthio)methane and allyl bromides also provides a route to substituted homoallylic sulfides (**Scheme 54**).[76]

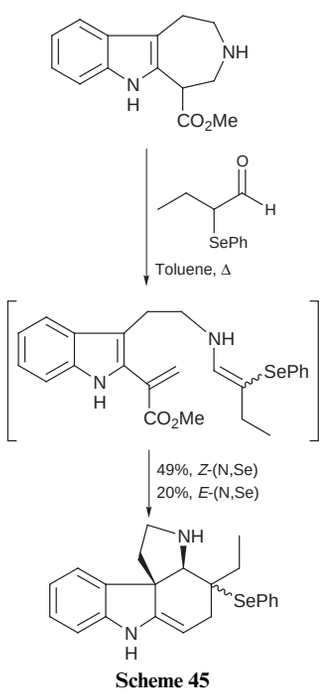
Finally, an interesting paper describes a method for stereochemical control during the preparation of alkynyl sulfides (Scheme 40).[60] Unfortunately, after introduction of the alkynyl sulfide moiety, the unwanted isomer predominated, with the relatively sterically undemanding alkyne group introduced axial, rather than in the desired equatorial position. Formation of the $Co_2(CO)_6$ alkyne complex and acid catalysed equilibration gave a much more favourable stereoisomeric ratio due to the increased steric demand of the alkyne complex, which was subsequently deprotected in excellent yield.



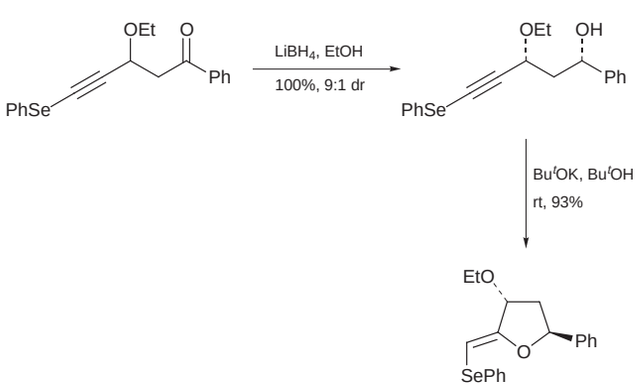
Scheme 43



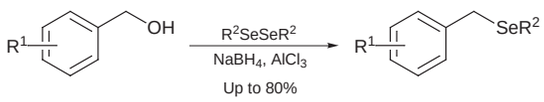
Scheme 44



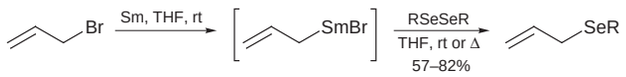
Scheme 45



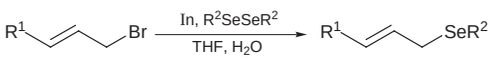
Scheme 46



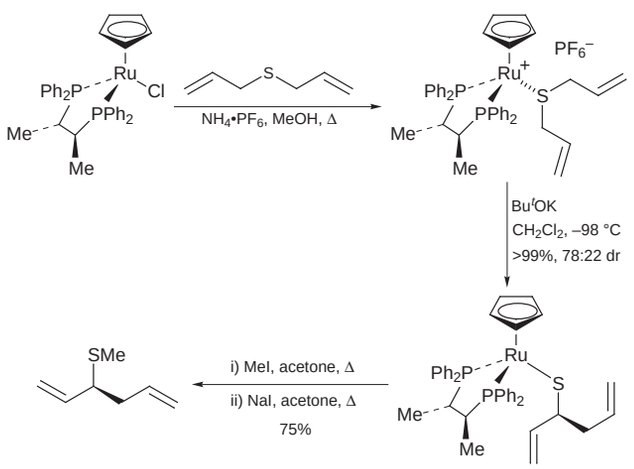
Scheme 47



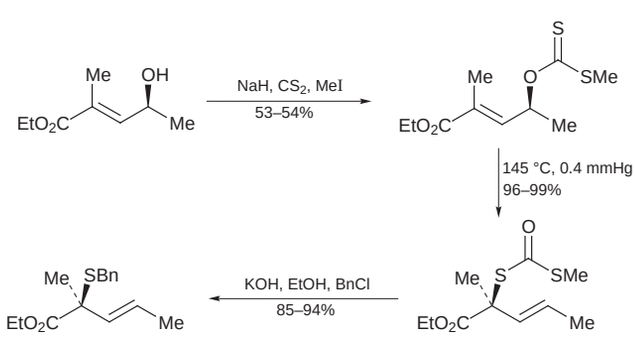
Scheme 48



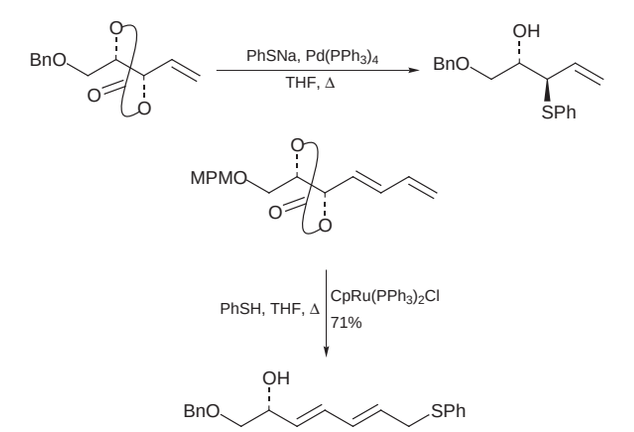
Scheme 49



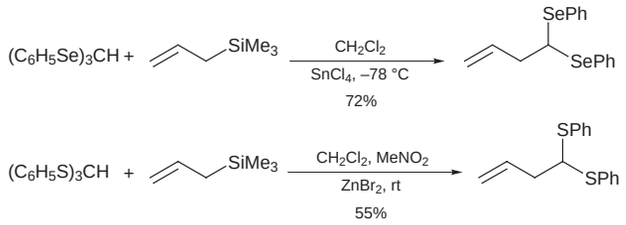
Scheme 50



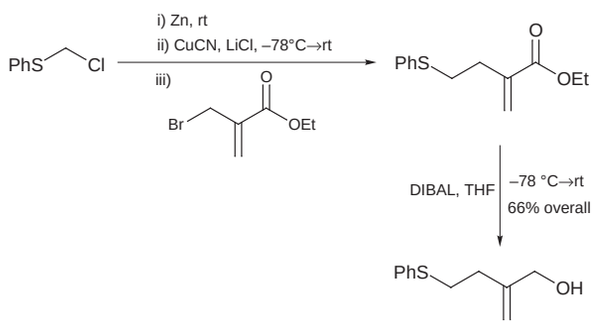
Scheme 51



Scheme 52



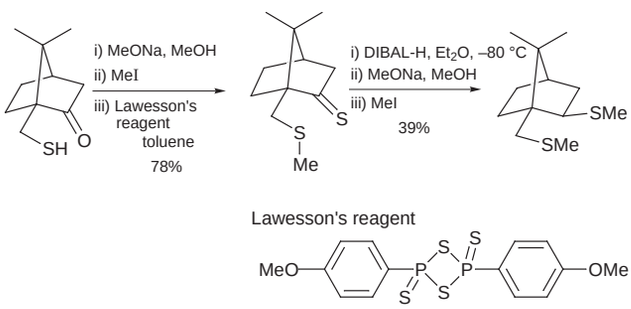
Scheme 53



Scheme 54

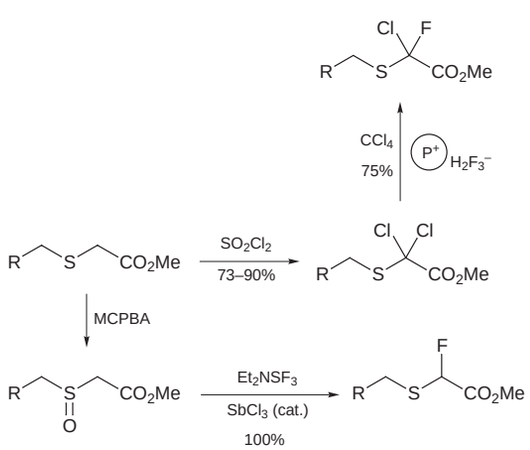
2.3 Substituted thiols and disulfides, selenols and diselenides, sulfides and selenides

The synthesis of a series of camphor-derived bis-sulfides has been reported which may have application as ligands in asymmetric metal catalysed processes (**Scheme 55**).[77]



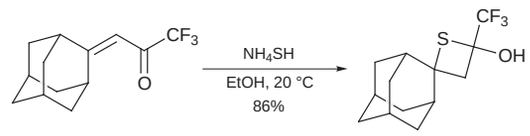
Scheme 55

New methods for the α-fluorination of sulfides have been reported. Sulfoxide formation and treatment with diethylaminosulfur trifluoride (DAST) allows access to the mono α-fluoro sulfide (**Scheme 56**).[78] Alternatively, bis-α-chlorination of a sulfide and treatment with fluoride leads to selective exchange of one chlorine atom for fluorine. The use of polymer supported dihydrogen trifluoride in CCl_4 gives best yields.

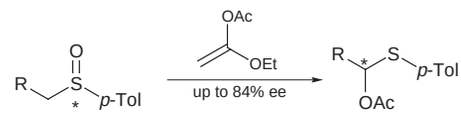


Scheme 56

The addition of ammonium hydrosulfide to α,β-unsaturated trifluoromethyl ketones leads to the formation of unusual strained hemithioacetals (**Scheme 57**).[79] Further work on the asymmetric Pummerer rearrangement [1–3] as a route to optically active acyclic O,S-acetals has been reported. A series of ethoxyvinyl esters were investigated to induce reaction, with ethoxyvinyl acetate generally working best (**Scheme 58**).[80]

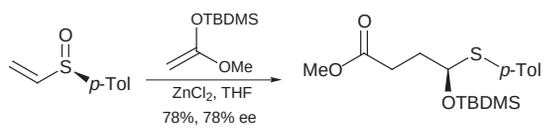


Scheme 57



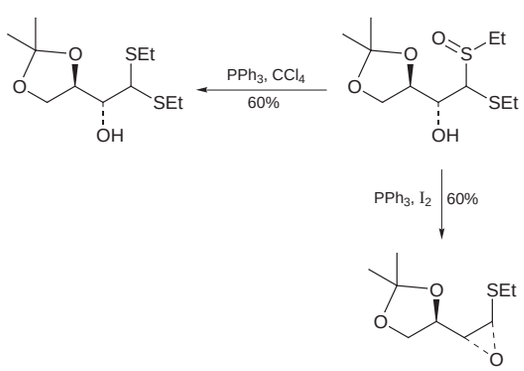
Scheme 58

In an interesting extension of this reaction, the additive Pummerer-type reaction of chiral non-racemic vinyl sulfoxides initiated by silyl ketene acetals also results in overall addition of the enolate equivalent to the vinyl sulfoxide (**Scheme 59**).[81] Aspects of the sila-Pummerer rearrangement are also included in a review on novel strategies for natural product elaboration and the development of new synthetic methodology.[82]

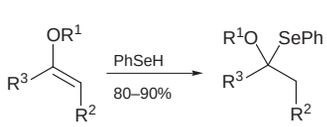


Scheme 59

During the attempted reduction of a dithioacetal mono-*S*-oxide, an interesting α-thioepoxide was formed as the major product (**Scheme 60**).[83] A method for the synthesis of O,Se-acetals has been reported which relies on the addition of selenols to enol ethers (**Scheme 61**).[84] Good yields are obtained for a variety of substrates.

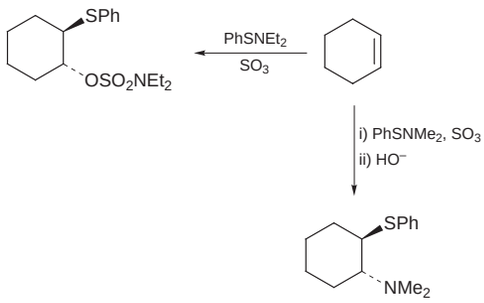


Scheme 60



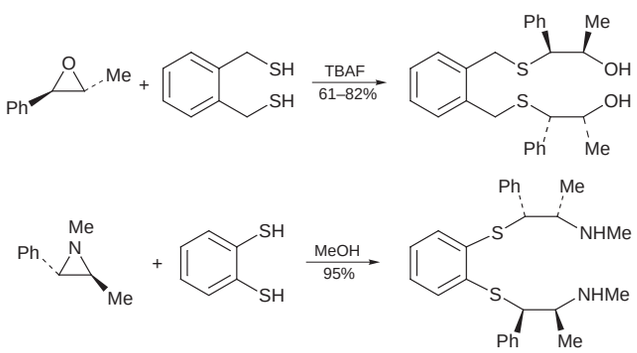
Scheme 61

The synthesis of β-hydroxy sulfides can be carried out by a number of methods. A recent review includes the sulfur trioxide mediated addition of sulfenamides to alkenes. Initial insertion of SO_3 into the S–N bond is followed by addition of this reactive species to an alkene leading to formation of a β-hydroxy sulfide derivative (**Scheme 62**).[85]

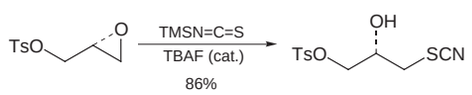


Scheme 62

One of the most established methods for the synthesis of β-hydroxy sulfides is the opening of an epoxide by thiolate. This has been used in the preparation of enantiomerically pure C_2-symmetric β-hydroxy sulfides using a dithiol, two equivalents of an enantiomerically pure epoxide, and tetra-*n*-butylammonium fluoride as catalyst (**Scheme 63**).[86] Similar conditions have been developed for the ring opening of epoxides using isothiocyanate, thiocarbonyl and trimethylsilylthioether nucleophiles (**Scheme 64**).[87]

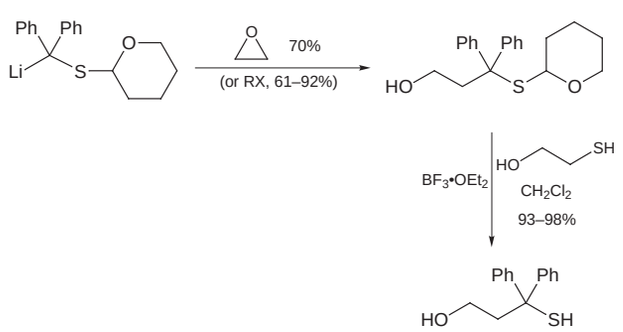


Scheme 63



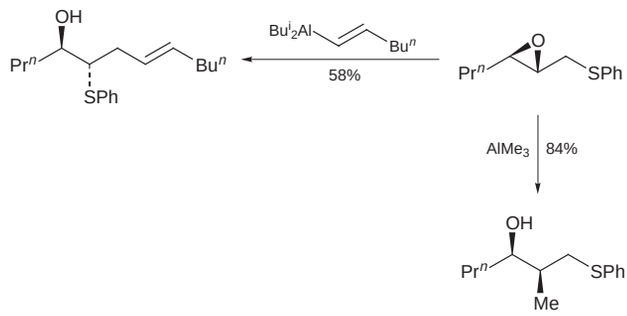
Scheme 64

In an alternative approach, carbanions stabilised by sulfur and other adjacent substituents react with epoxides to form γ-hydroxy sulfides (**Scheme 65**).[88] Subsequent deprotection liberates the corresponding γ-hydroxy thiol.



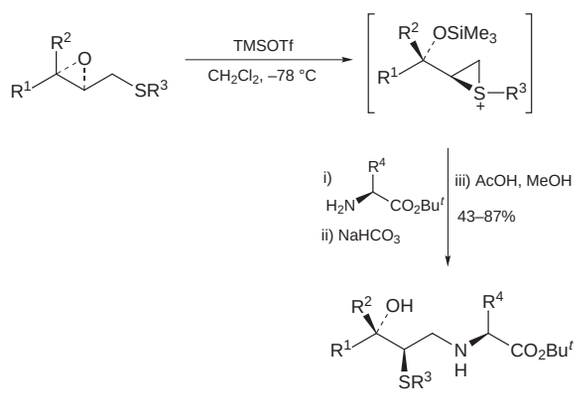
Scheme 65

In an interesting extension of previous work based on the Lewis acid induced rearrangement of 2,3-epoxy sulfides to the corresponding 3-alkoxy-1,2-thiiranium ion, the reactive intermediates have been trapped using alkyl- or vinyl-aluminium reagents to give the corresponding β- or γ-hydroxy sulfide depending on regioselectivity (**Scheme 66**).[89] In the case of trimethylaluminium, the reaction probably proceeds *via* an alkoxyaluminium ate complex. This delivers a methyl group



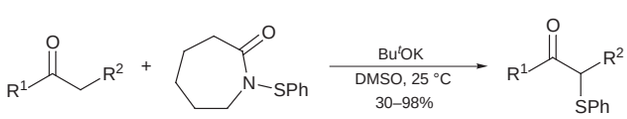
Scheme 66

intramolecularly resulting in ring opening of the thiiranium ion at the more substituted centre. Note that overall retention of stereochemistry is observed at the reacting centre, indicative of the intermediacy of a thiiranium ion. Further work on the addition of nucleophiles to 3-trimethylsilyloxy-1,2-thiiranium ions, including precursors to amino acids and nucleic acids, has also been published (**Scheme 67**).[90,91]

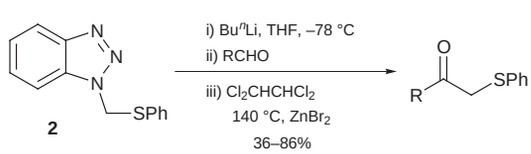


Scheme 67

A new approach to the synthesis of α-thiocarbonyl compounds utilises *N*-phenylthiocaprolactam as an electrophilic sulfenylating agent for reaction with ketone enolates (**Scheme 68**).[92] Similar compounds can also be accessed using the reaction between phenylthiomethylbenzotriazole derivative **2** and an aldehyde (**Scheme 69**).[93–96] An initially formed epoxide undergoes rearrangement on thermolysis in the presence of zinc bromide to give α-thio ketones in moderate to good yield.



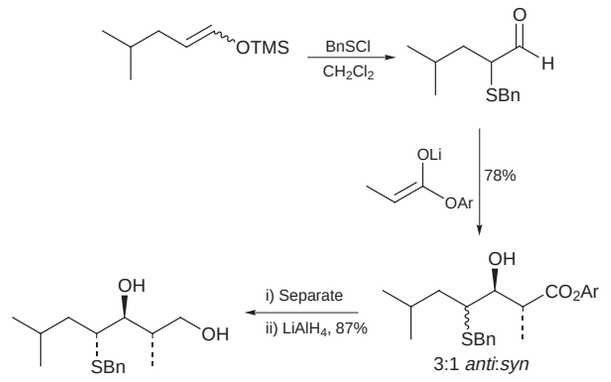
Scheme 68



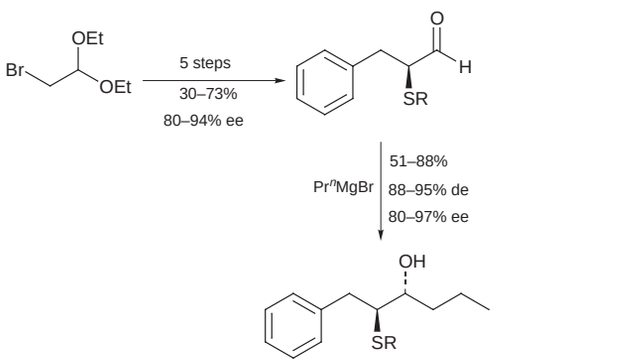
Scheme 69

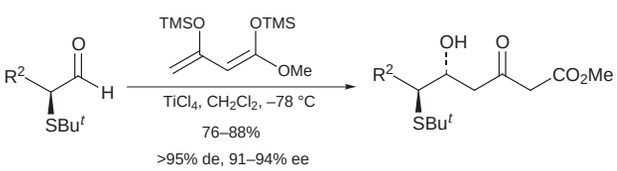
α-Thio carbonyl compounds can also be prepared by the addition of sulfenyl chlorides to silyl enol ethers (**Schemes 70** and **71**).[97,98] Subsequent addition of enolate anions, Grignard reagents, or trimethylsilylketene acetals with Lewis acid catalysis, leads to β-hydroxy sulfide formation with excellent stereocontrol in some cases.

A related protocol using an α-seleno aldehyde intermediate has also been applied to the synthesis of peptide-derived β-hydroxy selenides (**Scheme 72**).[99] In an interesting extension to this work, synthesis of a 4-C′-selenated deoxyribonucleoside

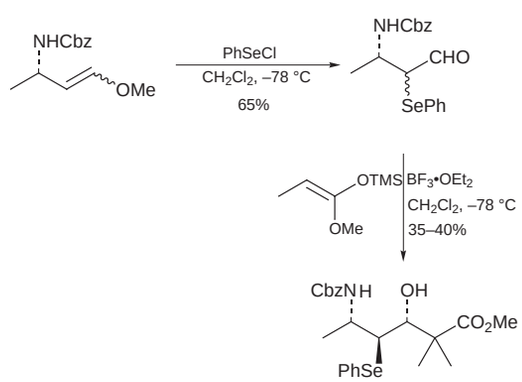


Scheme 70





Scheme 71

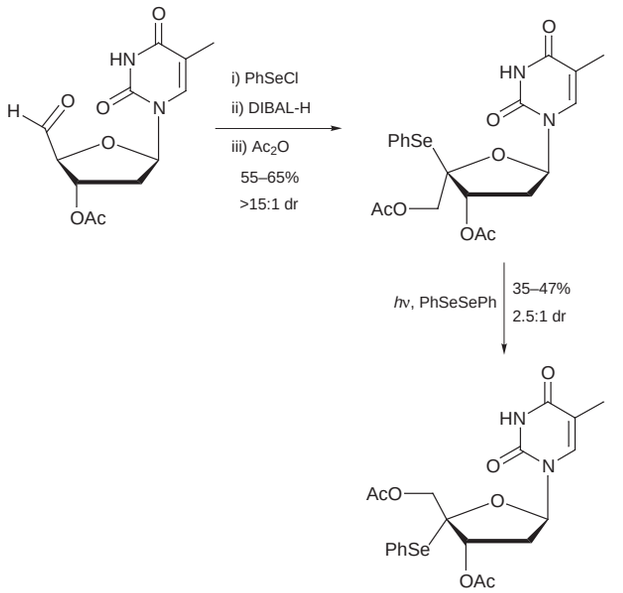


Scheme 72

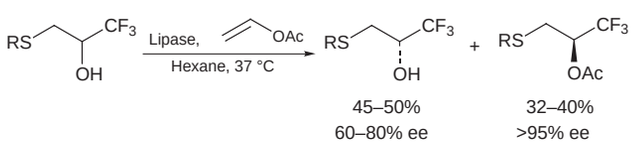
was achieved with high stereoselection by addition of benzeneselenenyl chloride to an aldehyde (**Scheme 73**).[100] Unfortunately the major product was the undesired stereoisomer. Reduction of the aldehyde and protection gave a β-acetoxy selenide, which underwent photolytically induced radical epimerisation in the presence of diphenyl diselenide to give the desired stereoisomer as the major component at equilibrium.

Chiral β-hydroxy sulfides have been resolved using enzymatic procedures. β-Thiotrifluoromethyl alcohols have been resolved by enantioselective acylation using a lipase and vinyl acetate (**Scheme 74**).[101]

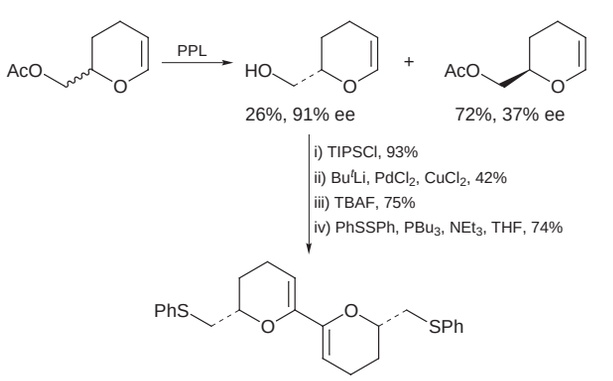
Good yields and optical purities of either enantiomeric series could be obtained. Lipases have also been used to resolve precursors to chiral 2,2′-bis(phenylthiomethyl)dihydropyrans, which themselves are useful protecting and resolving agents for 1,2-diols (**Scheme 75**),[102,103] and chiral ferrocenyl sulfides, which can act as precursors to chiral sulfoxides (**Scheme 76**).[104]



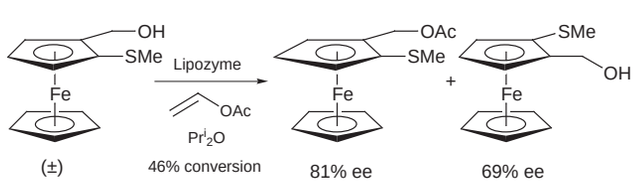
Scheme 73



Scheme 74

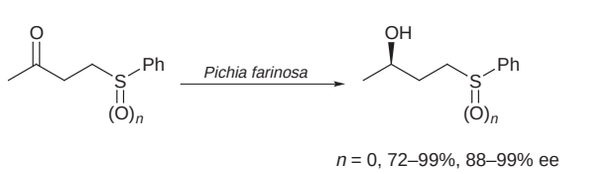


Scheme 75



Scheme 76

Optically active sulfur-containing secondary alcohols have been prepared by *Pichia farinosa* catalysed reduction of suitable carbonyl precursors (**Scheme 77**).[105] High enantioselectivities and chemical yields can be achieved.

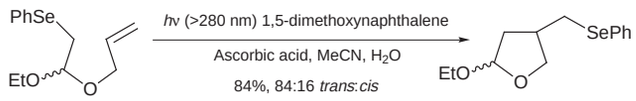


Scheme 77

Benzeneselenenyl sulfate has been reported to be a useful electrophilic selenenylating agent (**Scheme 78**).[106,107] The use of organoselenium derived radical translocation reactions has

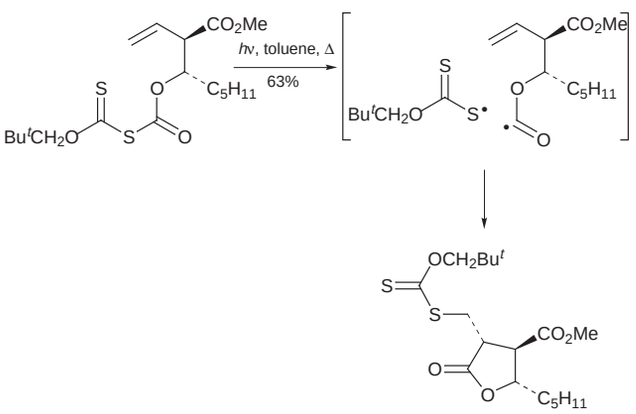
Scheme 78

also been reported. Selenides undergo homolytic cleavage on photolysis to generate a carbon radical. This adds to an adjacent double bond to generate a new radical which is trapped by the selenium species generated in the first step (**Scheme 79**).[108,109]



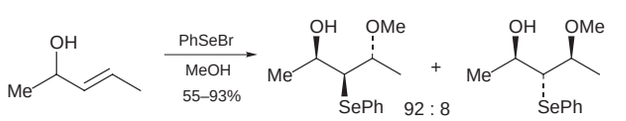
Scheme 79

In a related process, alkoxycarbonyl radicals, generated by photolysis of a xanthate ester, add to an adjacent alkene. The resulting radical then recombines with the xanthate radical generated in the first step to give the product as a single diastereoisomer (**Scheme 80**).[110]



Scheme 80

The stereoselective methoxyselenation of allylic alcohol derivatives provides a route to 2-seleno-1,3-diols with good stereocontrol (**Scheme 81**).[111] A similar degree of stereoselectivity is obtained with a variety of protected alcohol derivatives, and this can be rationalised by a stabilising interaction between the positive selenium and allylic oxygen atoms in the intermediate episelenonium ion, and non-bonding steric interactions.

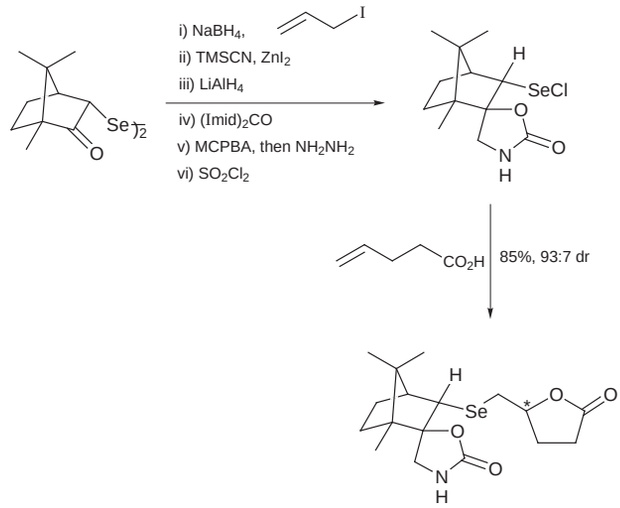


Scheme 81

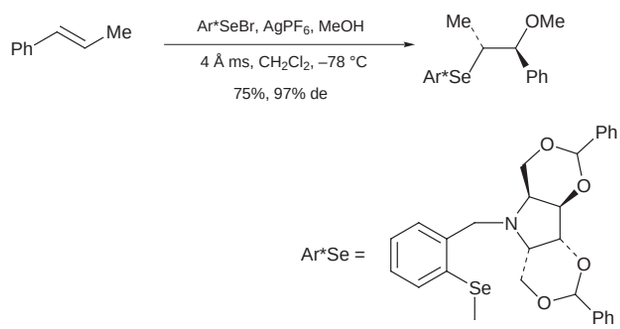
New camphor based electrophilic asymmetric organoselenium reagents have been reported, and in some cases give excellent stereocontrol in oxyselenenylation reactions (**Scheme 82**).[112] Further details on related asymmetric oxyselenenylations using optically active selenium reagents containing a tertiary amino group have also been published (**Scheme 83**).[113] Very variable selectivities are obtained depending on substrate structure, additives and selenenylating agent.

New methods for the synthesis of β-thio- and β-selenocarbonyl derivatives have been reported. Nucleophilic ring opening of resolved (90% ee) β-butyrolactone by a lithium thiolate gives the carboxylic acid with clean inversion of stereochemistry (**Scheme 84**).[114] Reaction of α-chloro-α-phenylseleno esters with a variety of silyl enol ethers under Lewis acidic conditions gives β-seleno ketones (**Scheme 85**).[115]

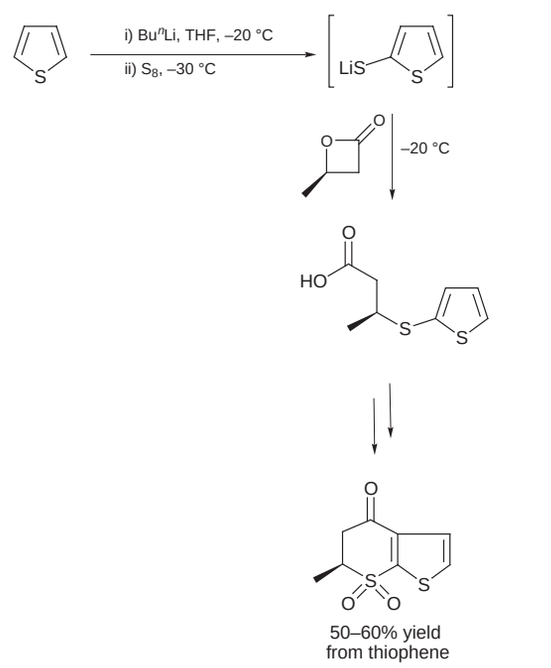
A more conventional approach to these types of molecule is the conjugate addition of thiolate or selenolate to α,β-unsaturated carbonyl compounds. This has recently been



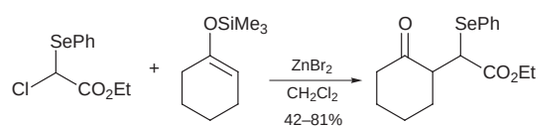
Scheme 82



Scheme 83

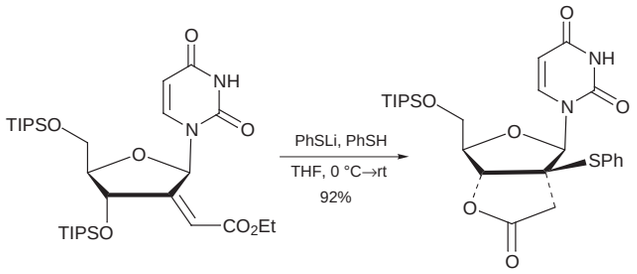


Scheme 84



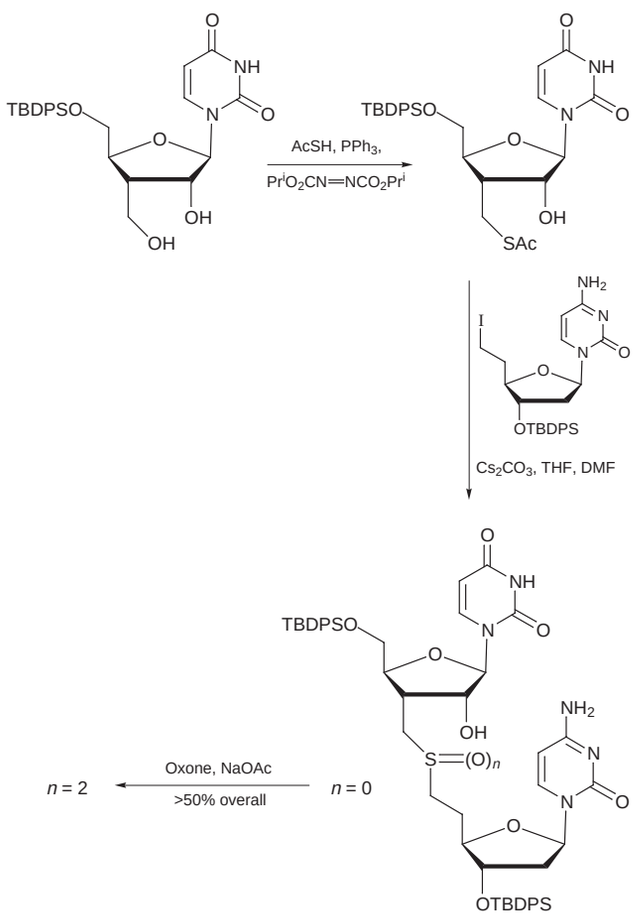
Scheme 85

applied to the synthesis of nucleoside derivatives (**Scheme 86**).[116] High stereoselectivity is observed, and in the case of the lithium thiolate, the involvement of a coordinated intermediate helps explain delivery of thiolate to the most sterically hindered



Scheme 86

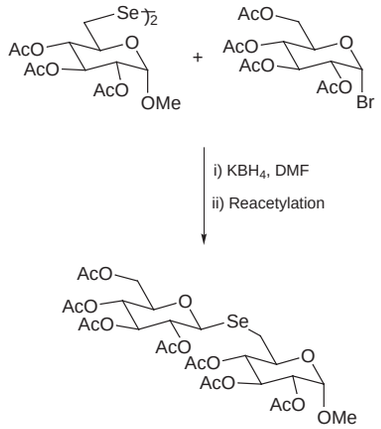
β-face. Interestingly, a reversal of stereoselectivity is observed when using the potassium thiolate. Other sulfur containing nucleoside analogues have been synthesised for the preparation of non-ionic analogues of RNA and DNA. A variety of methods for sulfide synthesis have been used based on conventional procedures (**Scheme 87**).[117–120] The synthesis of selenium containing sugars as potential glucosidase inhibitors has also been described (**Scheme 88**).[121]



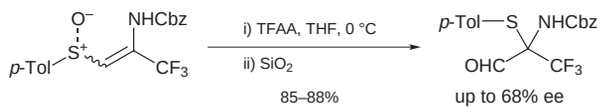
Scheme 87

New methods for the synthesis of N,S-acetals have been reported. The enantioselective Pummerer-type rearrangement of β-enamino sulfoxides gives chiral non-racemic α,α-*N*,*S*-disubstituted ketals of β-fluoropyruvaldehydes (**Scheme 89**).[122] Alternatively, an unusual cleavage of β-lactam rings induced by Lewis acids in the presence of a nitrile also allows access to acyclic N,S-acetals with moderate diastereoselectivity (**Scheme 90**).[123] Similar cleavage can be achieved using trimethylsilyl azide and a Lewis acid giving related products.

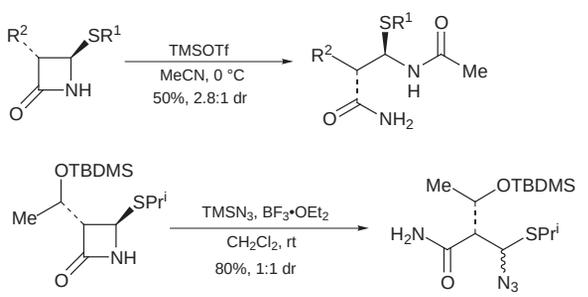
The synthesis of β-amino sulfide derivatives can be accomplished by the ring opening of aziridines by thiolate nucleophiles. For example, the preparation of enantiomerically pure C_2-symmetric β-amino sulfides by reacting a dithiol with an *N*-methylaziridine has been reported (Scheme 63).[86,124] An alternative approach to the asymmetric synthesis of β-amino sulfides



Scheme 88

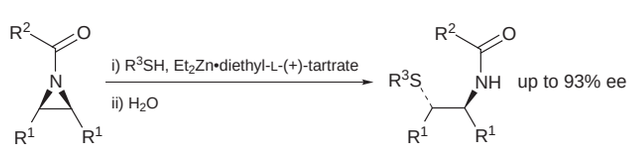


Scheme 89



Scheme 90

is by the nucleophilic ring opening of prochiral *N*-acylaziridines by thiols, catalysed by chiral dialkyl tartrate–diethylzinc complexes (**Scheme 91**).[125] Only low enantioselectivities are observed with alkylthiol nucleophiles, however thiophenols give up to 93% ee.

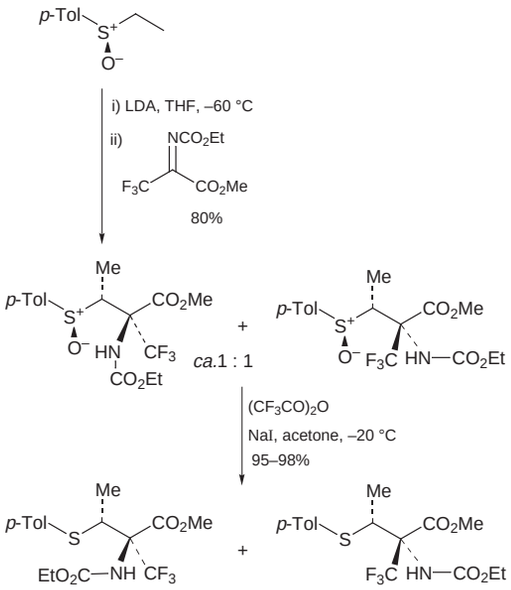


Scheme 91

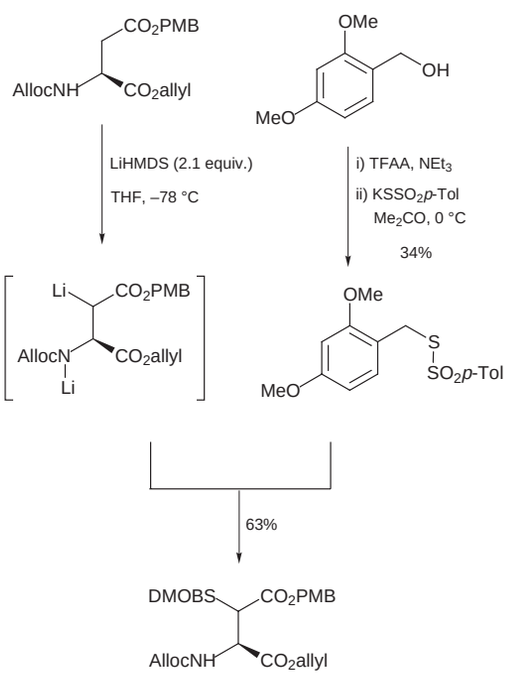
Addition of a sulfenamide to alkenes mediated by SO_3 has also been reported to lead to β-amino sulfide formation after aqueous base hydrolysis (Scheme 62).[85] The addition of α-lithiosulfoxides to electron deficient *N*-acylimines and subsequent sulfoxide reduction provides a route to β-amino sulfides. Good yields can be obtained; however stereoselectivity is poor (**Scheme 92**).[126]

The stereoselective synthesis of protected mercaptoaspartic acid derivatives by sulfenylation of a β-aspartyl enolate has been reported (**Scheme 93**).[127,128] Note the use of the sulfenylating agent derived from 2,4-dimethoxyphenylmethanethiol to allow ready deprotection to the thiol at a later stage in the synthesis. The preparation of novel selenocysteine derivatives by reaction of a β-chloro-α-amino acid with alkane- or arene-selenolate nucleophiles has been reported (**Scheme 94**).[129] Moderate yields are obtained in most cases. The synthesis of related cysteine-derived thioethers under mild, base free conditions, has been reported using chemistry previously used to synthesise simpler thioethers (Scheme 4).[17]

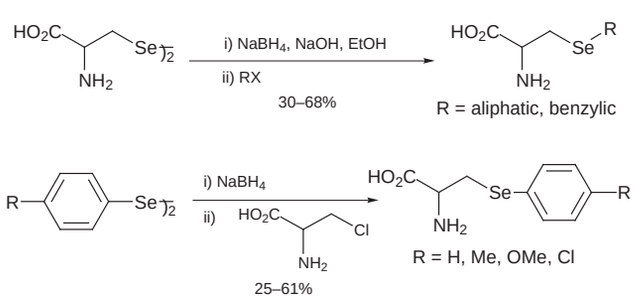
The free radical azidoselenenylation of alkenes induced by hypervalent iodine (**Scheme 95**)[130] is an interesting alternative to previously reported aminoselenenylation reactions. The latter has recently been applied to the synthesis of selenoaze-



Scheme 92



Scheme 93

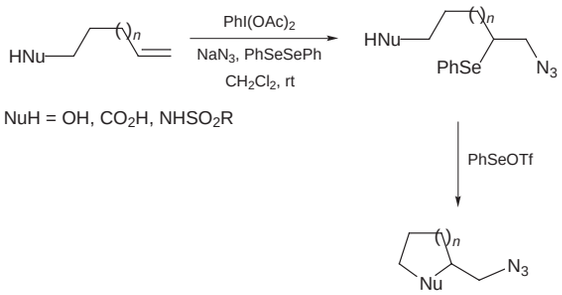


Scheme 94

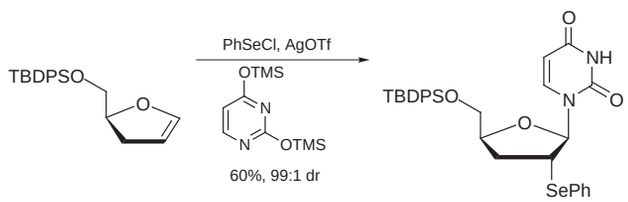
tidines and other cyclic amines,[131,132] and to the stereocontrolled synthesis of nucleoside analogues (**Scheme 96**)[133] and azidosugars (**Scheme 97**).[134]

2.4 Thiols, disulfides, selenols, diselenides, sulfides and selenides as mediators of asymmetric transformations

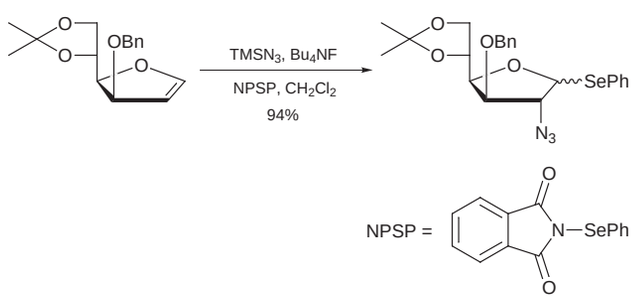
There have been a number of reports of the use of organosulfur and -selenium compounds for asymmetric induction,



Scheme 95



Scheme 96



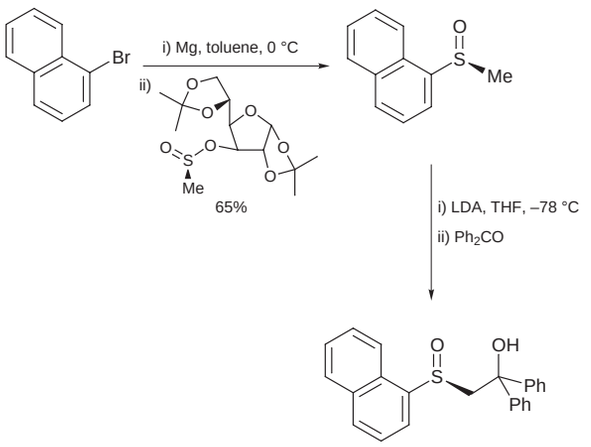
Scheme 97

including reviews on high symmetry chiral auxiliaries containing heteroatoms,[135] transition metal Lewis acid catalysed asymmetric reactions with chiral organosulfur functionality,[136] chiral ferrocenyl dichalcogenides and their applications to asymmetric reactions,[137] and synthetic and mechanistic aspects of asymmetric reactions of organoselenium compounds.[138] Further reports on chiral optically active selenium reagents for asymmetric selenylation reactions have appeared (Schemes 82 and 83).[112,113] Routes to new chiral sulfur and selenium containing compounds with possible applications in asymmetric metal catalysed processes have been described, including camphor-derived bis-thiols and -thioethers (Scheme 55),[77] 2-aryloxazolines (Scheme 17),[34] 2,2′-disubstituted 1,1′-binaphthalene derivatives (Scheme 15),[32] and β-hydroxy sulfides and β-amino sulfides (Scheme 63).[86] The enantioselective catalytic reduction of dihydroisoquinoline derivatives using borane with a zinc β-amino thiol catalyst gives low to good enantioselectivities,[124] and magnesium based Lewis acids modified by chiral β-hydroxy sulfoxides catalyse Diels–Alder cycloadditions with excellent enantio- and diastereo-selectivities (**Scheme 98**).[139] Further progress on the enantioselective synthesis of epoxides using chiral sulfur ylides has been reported[140,141] as has the use of chiral 2,2′-bis(phenylthiomethyl)dihydropyrans as new protecting and resolving agent for 1,2-diols (Scheme 75).[102]

3 Synthesis of sulfoxides and selenoxides

3.1 Oxidation of sulfides and selenides

The preparation of sulfoxides and selenoxides by oxidation of the corresponding sulfides and selenides, respectively, continues to be an important area of research and has been reviewed.[142] This section is divided into three parts. The first is concerned with new methods of oxidation where chirality at sulfur is not addressed. The second part is concerned with diastereoselective



Scheme 98

processes, whereas the final part concentrates on new methods for enantioselective oxidation.

3.1.1 Non-stereoselective oxidation

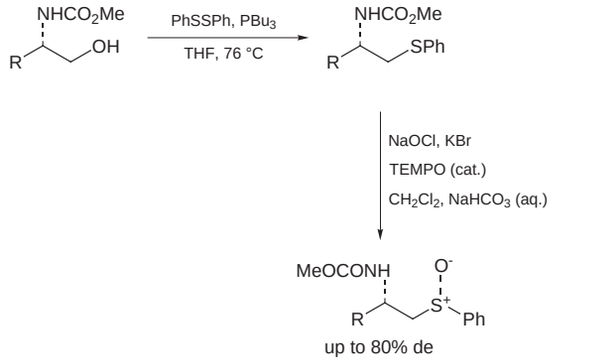
A review of oxidation reactions using peroxyacetals includes a section on sulfur oxidation.[143] The synthesis and reactivity of polyfluorinated oxaziridines has also been reviewed,[144] as has the use of hydrogen peroxide in catalytic oxidations.[145] New methods for the oxidation of simple sulfides and selenides to sulfoxides and selenoxides respectively have been reported. These include *N*-hydroxy-*O*-benzenedisulfonimide **1** in the presence of acetic acid;[25] tetrabutylammonium peroxydisulfate;[146] *tert*-butyl hydroperoxide, catalysed by camphorsulfonic acid;[147] salts between selenoxides and sulfonic acids;[148] hydrogen peroxide with either sodium tungstate under phase transfer conditions;[149] a zeolite catalyst,[150] methyltrioxorhenium,[151,152] or ammonium molybdate supported on a strongly basic anion exchange resin;[153] peroxynitrite;[154–156] sodium chlorite catalysed by $Mn(acac)_3$ and moist alumina;[157] 2-methylpropanal and oxygen;[158] and trifluoromethanesulfonic anhydride, although more sensitive substrates can give side reactions.[159] Mechanistic studies have also been published on oxidation using vanadium catalysis,[160] bis(2-ethyl-2-hydroxybutyrato)oxochromate(v),[161] pyridinium fluorochromate,[162] pyridinium bromide perbromide[163] and singlet oxygen.[164]

3.1.2 Stereoselective oxidation

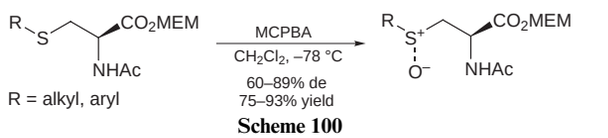
There have been a limited number of studies on the diastereoselective oxidation of sulfides to sulfoxides. Oxidation of β-amino sulfides using sodium hypochlorite with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) catalyst gives up to 80% de of the *syn* β-amino sulfoxide diastereoisomer (**Scheme 99**).[165] Use of MCPBA or $NaIO_4$ as oxidants gave almost no diastereoselectivity with the same substrates.

The diastereoselective oxidation of esters of protected cysteine derived α-amino acids has been studied. Use of MEM esters and the acetamide group for N-protection gave highest selectivities (**Scheme 100**).[166] Attempted oxidations of related methionine derivatives[167] or unsaturated sulfides[168] gave little or no significant diastereoselectivities. The chemoselective oxidation of penicillins and cephalosporins using a cobalt(III) catalyst, oxygen and an aldehyde has also been reported (**Scheme 101**).[169] High yields and excellent stereoselectivities are observed.

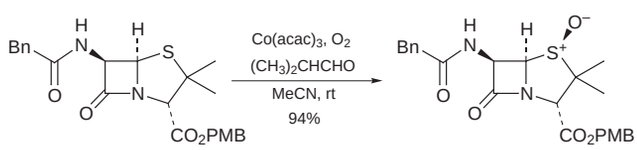
Finally, the oxidation of homochiral sulfides using asymmetric oxidising agents provides considerable potential for stereochemical control and the formation of diastereomerically enriched products. In an approach to the synthesis of Ustilotoxins A and B (**Scheme 102**), use of TBHP–$Ti(OPr^i)_4$ with (*R*)-BINOL as the chiral ligand gives the sulfoxide product with >50:1 diastereomeric ratio. Using (*S*)-BINOL instead gave the opposite diastereomer as the major product, but with



Scheme 99

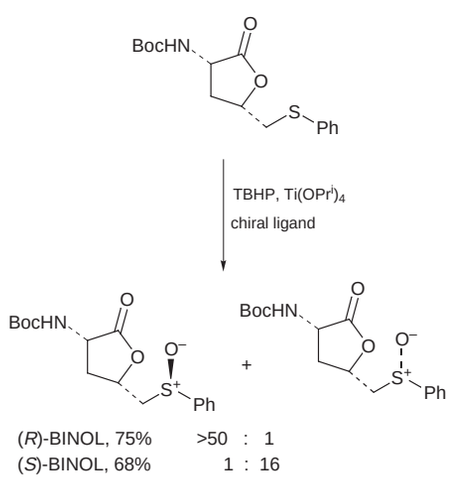


Scheme 100



Scheme 101

reduced diastereomer selectivity (16:1) indicative of matched/mismatched pairings.[170] Use of either enantiomer of diethyl tartrate as the chiral ligand gave only very poor diastereoselectivities (up to 1.2:1).

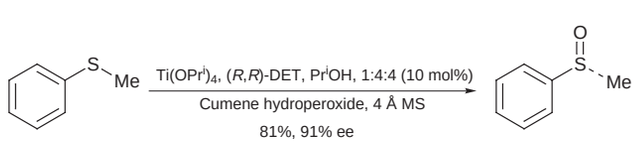


Scheme 102

3.1.3 Enantioselective oxidation

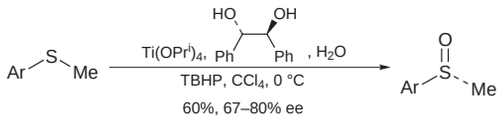
The enantioselective oxidation of sulfides to sulfoxides continues to be a popular and important area of organosulfur chemistry, and has been included in a recent review.[142] The two main approaches are using chemical and biochemical processes which are best considered separately.

Further developments in the area of titanium catalysed asymmetric sulfur oxidation have been reported. The use of 10 mol% of a catalyst prepared from $Ti(OPr^i)_4$, diethyl tartrate and propan-2-ol in the ratio 1:4:4, gives enantioselectivities up to 96% ee for the oxidation of dialkyl and alkyl aryl sulfides using cumene hydroperoxide as stoichiometric oxidant (**Scheme 103**).[171,172] Oxidation of methyl aryl sulfides using



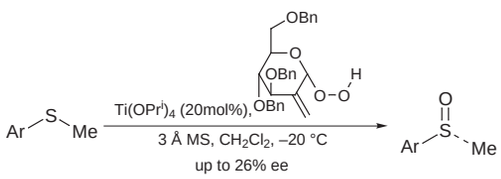
Scheme 103

TBHP and 5 mol% of a catalyst derived from $Ti(OPr^i)_4$, (*S*,*S*)-1,2-diphenylethane-1,2-diol and water, gives sulfoxides of up to 80% ee (**Scheme 104**).[173]

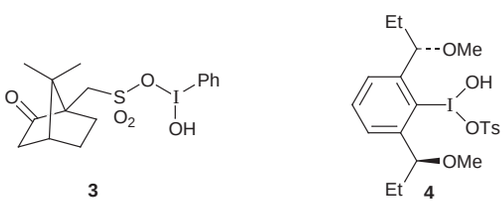


Scheme 104

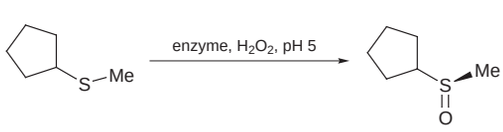
Optically pure sugar hydroperoxides have been shown to oxidise methyl aryl sulfides in the presence of $Ti(OPr^i)_4$ with up to 26% ee (**Scheme 105**).[174] Chiral hypervalent iodine reagents **3** and **4** also have been shown to oxidise sulfides to sulfoxides although enantioselectivities are low (up to 13%).[175,176] Poor enantioselectivities have also been observed using sodium chlorite as oxidant with chiral Mn^{III} catalysts in the presence of alumina.[177]



Scheme 105

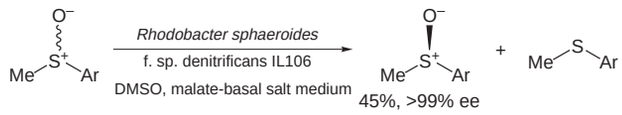


The use of biocatalysts for asymmetric sulfur oxidation continues to be an active area of research. A recent review on the structural studies and synthetic applications of Baeyer–Villiger monooxygenases includes a section on sulfur oxidation.[178] The use of bacterial cyclohexanone monooxygenases for the oxidation of a variety of sulfur-containing functionality has also been reviewed.[179] An active site model for oxidation using cyclohexanone monooxygenase from *Acinetobacter* NCIMB9871 has been published,[180] and this and related enzymes have been shown to give moderate to excellent enantioselectivities for the oxidation of dialkyl sulfides (**Scheme 106**)[181] and alkyl aryl sulfides.[182,183] Use of a *tert*-butanol–water (1 : 1) mixed solvent system prevents background racemic oxidation which can be observed when water alone is used.[182] Enantioselective oxidations by the diketocamphane monooxygenase isozymes from *Pseudomonas putida* gave >55% ee for the oxidation of aryl alkyl sulfides,[184] and a series of (*S*)-*para*-substituted phenyl methyl sulfoxides have been prepared by sulfide oxidation using *Helminthosporium* sp. NRRL4671.[185] Whole cell cultures of *Acinetobacter calcoaceticus* NCIMB9871 have been used in a preparative scale synthesis of 1,3-dithiane 1-oxide, giving the (*R*)-enantiomer with 98% ee in 76% yield. The stereoselectivity observed is in agreement with a previously published active site model of the cyclohexanone monooxygenase enzyme isolated from such cells. The opposite enantiomer can be accessed using *Pseudomonas* sp. NCIMB9872, however lower enantioselectivity is observed (57% ee).[186]



Scheme 106

Finally, asymmetric deoxygenation of racemic alkyl aryl sulfoxides by *Rhodobacter sphaeroides* f. sp. denitrificans IL106 gives resolved sulfoxides in excellent enantiomeric excess, along with the reduced sulfide by-product (**Scheme 107**).[187]

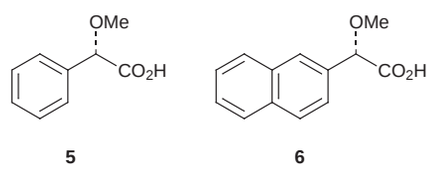


Scheme 107

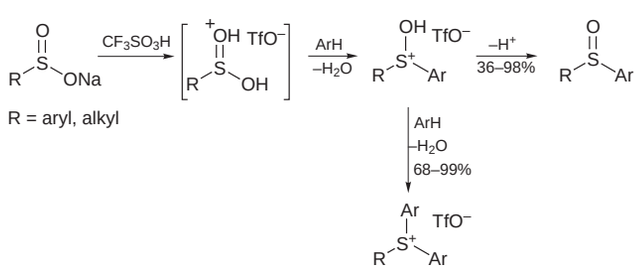
3.2 Non-oxidative sulfoxide and selenoxide synthesis

3.2.1 General methods for sulfoxide and selenoxide synthesis

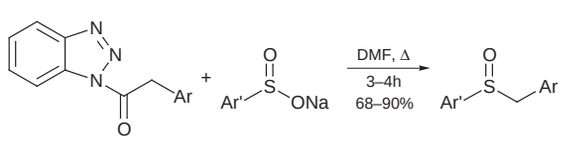
Several recent reviews in this area have been published including one on the use of the diarylhydroxymethyl group in synthesis, which includes a section on the asymmetric synthesis of sulfoxides from cyclic sulfites;[188] the use of oxiranyl and aziridinyl anions which includes sections on sulfinyl stabilised anions;[189] and reactions of hypervalent species, including ligand coupling reactions of sulfoxides.[190,191] α-Methoxyarylacetic acids **5** and **6** have been reported to be effective chiral shift reagents for enantiomeric excess determination of sulfoxides.[192] Best resolution was observed in C_6D_6 solvent.



A one pot synthesis of aryl sulfoxides utilises a sulfinic acid as an electrophilic sulfurising agent, adding to aromatic rings to give the sulfoxides in modest to excellent yields (**Scheme 108**).[193] Sulfonium salts are formed under more forcing conditions. Arenesulfinates can also be converted into aryl benzyl sulfoxides by reaction with *N*-(arylacetyl)benzotriazoles, the reaction proceeding *via* an aryl ketene intermediate (**Scheme 109**).[194]

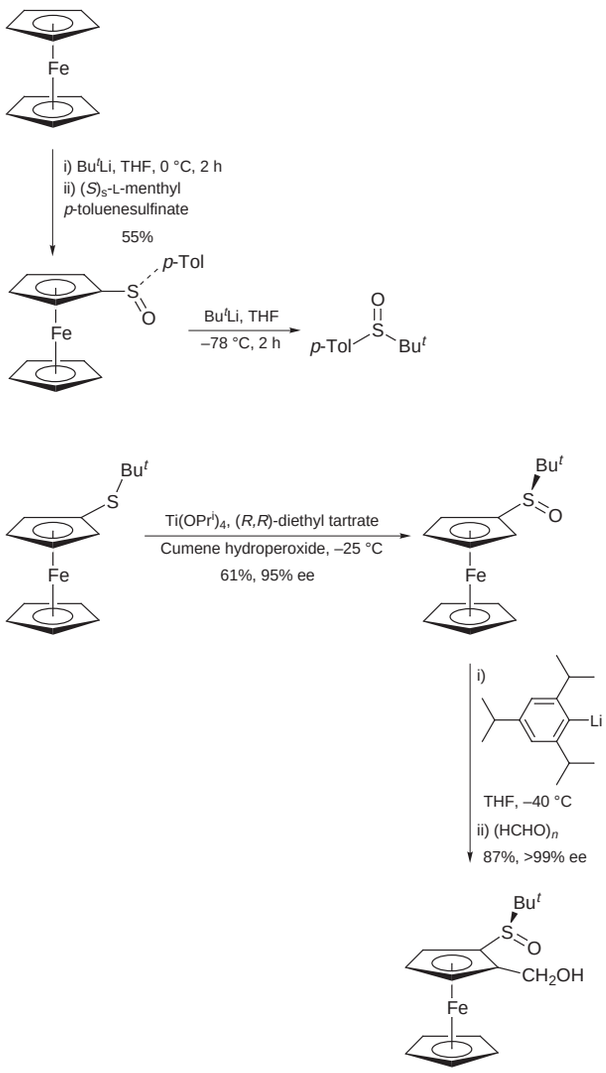


Scheme 108



Scheme 109

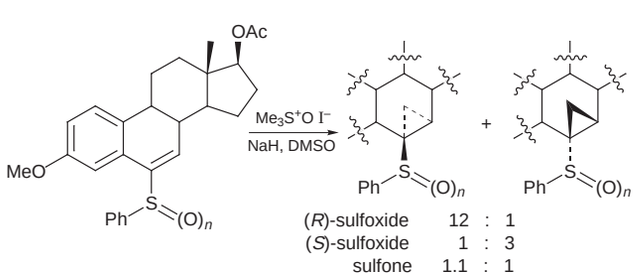
The enantioselective synthesis of sulfur-containing ferrocenes has been reported. Lithiation of ferrocene and reaction with a menthyl toluene-*p*-sulfinate (the Andersen procedure) gives moderate yields of the optically active sulfinyl ferrocenes (**Scheme 110**).[195] Subsequent attemps at lithiation using *tert*-butyllithium were unsuccessful and led to formation of *tert*-butyl *p*-tolyl sulfoxide and some racemisation. In an alternative approach *tert*-butylsulfinylferrocene was prepared in high enantiomeric excess by asymmetric oxidation. This allowed for lithiation of the ferrocene (rather than the cleavage reaction



Scheme 110

observed previously) and subsequent quenching with paraformaldehyde gave the desired optically pure disubstituted sulfinyl ferrocene.

Methylene bridged derivatives of estradiol have been prepared by methylenation of unsaturated sulfoxides using trimethylsulfoxonium iodide and base. Good stereoselectivity can be observed and is dependent on the chirality of the sulfoxide moiety (**Scheme 111**).[196]

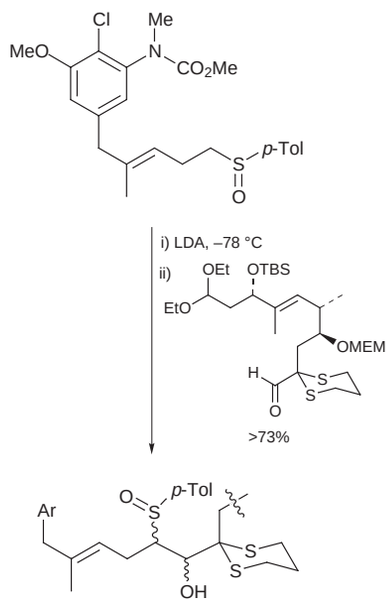


Scheme 111

Finally, whilst strictly outside the scope of this chapter, it is of interest to note that the well known β-elimination reactions of sulfoxides and selenoxides have been promoted by either microwave irradiation[197] or catalytic antibodies[198] respectively.

3.2.2 Functionalised sulfoxides

Applications of sulfoxides in the synthesis of biologically active compounds have been reviewed.[199] The condensation between an α-metallo sulfoxide and a carbonyl compound is a well established route to β-hydroxy sulfoxides. This reaction has recently been exploited for formation of a crucial C–C bond in a synthesis of (−)-maytansinol, although a mixture of diastereomeric products was formed (**Scheme 112**).[200] A similar reaction has been used to prepare optically active β-hydroxy sulfoxides which, when complexed with MgI_2, form Lewis acid complexes which are efficient and highly selective asymmetric Diels–Alder catalysts (Scheme 98).[139] Sulfoxide anions can also undergo conjugate addition reactions. In the example shown (**Scheme 113**), which is the key step in an asymmetric synthesis of (−)-podophyllotoxin, the enolate intermediate initially formed after conjugate addition, is reacted with an aldehyde to further increase the complexity of the product.[201]



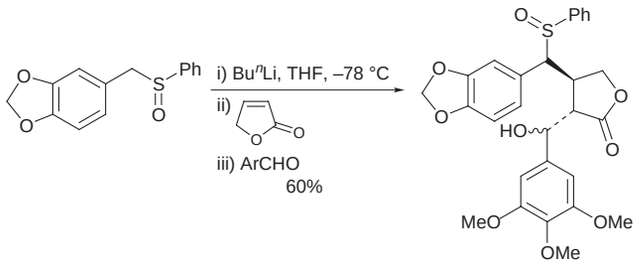
Scheme 112

β-Keto sulfoxides have been prepared by the addition of vinylogous ester enolates to sulfinate esters or their equivalent. The original menthyl sulfinate esters can suffer from low reactivity, and recently developed sulfinamide derivatives give greatly increased yields and products of high enantiomeric purity (**Scheme 114**).[202] Higher yields of β-keto esters and reduced racemisation can be obtained if anions derived from *N*,*N*-dimethylhydrazones are reacted with sulfinate esters, rather than enolates of the parent ketone (**Scheme 115**).[203]

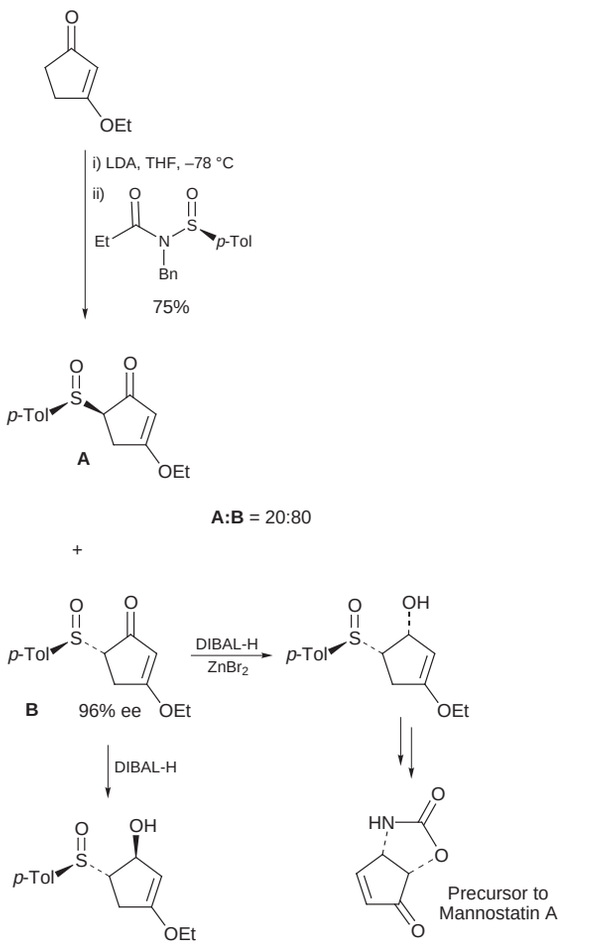
The stereoselective reduction of β-keto sulfoxides is a well established method for the synthesis of optically active alcohols, and has recently been exploited in the synthesis of a precursor to mannostatin A (Scheme 114),[202] haminol-1, an alarm pheromone (**Scheme 116**),[204] (−)-(5*S*,7*R*)-tarchonanthus lactone (**Scheme 117**),[205] (+)-monomorine (**Scheme 118**)[206] and (+)-isobretonin-A (**Scheme 119**).[207] A similar approach has also been used for the stereoselective synthesis of thienyl carbinols.[208]

The addition of lithium ester enolates to cyclic β-keto sulfoxides has been shown to proceed with remarkably high stereoselectivity (**Scheme 120**).[209] A tricoordinate lithium species, which involves the enolate, sulfinyl and carbonyl oxygens was invoked to explain the stereoselectivity.

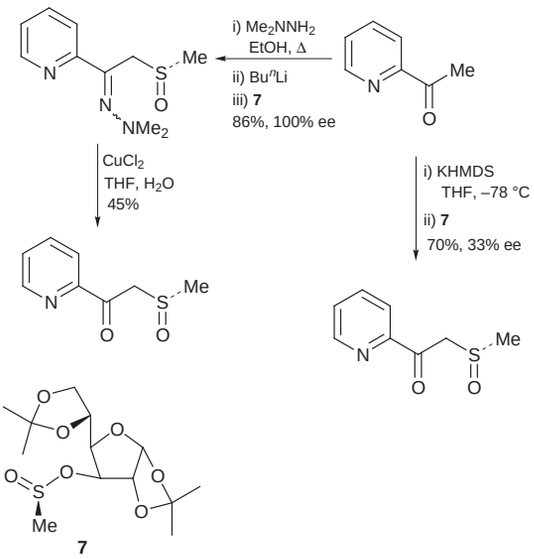
Good levels of selectivity are reported for the addition of diazomethane to β-keto sulfoxides (**Scheme 121**).[210] Modest yields of epoxides are obtained, but they can be improved at the expense of stereoselectivity by using other solvents. The products can be further converted into useful synthetic intermediates by a range of subsequent transformations. Related chemistry has been used for the synthesis of arylsulfinyl epoxides as their $Cr(CO)_3$ complexes, by addition of dimethyl-



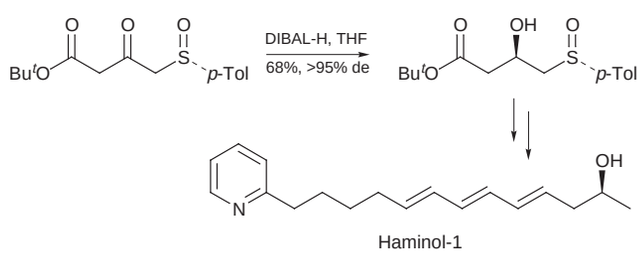
Scheme 113



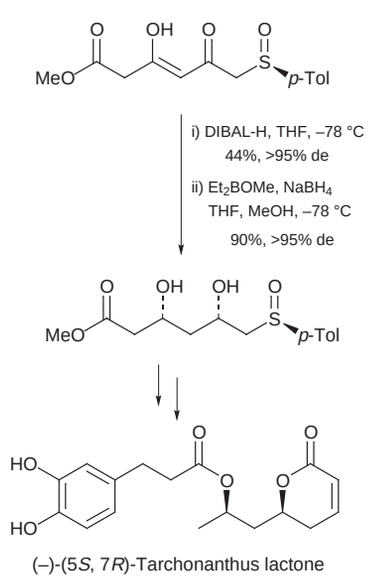
Scheme 114



Scheme 115



Scheme 116



Scheme 117

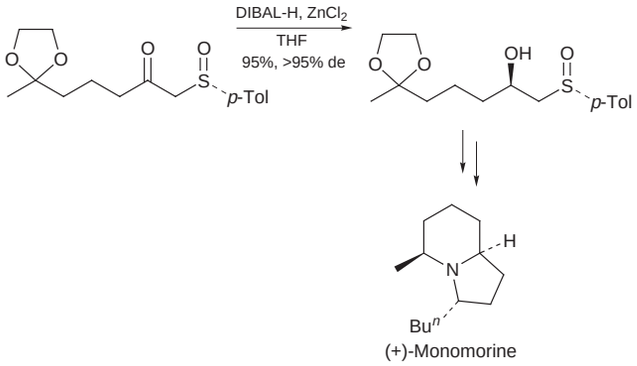
sulfonium methylide to a ketone, with high levels of stereocontrol (**Scheme 122**).[211]

In an approach to the synthesis of enantiomerically pure 3-fluoromethylthreonines, (*S*)-1-fluoro-3-*p*-tolylsulfinylacetone undergoes an aldol reaction with methyl isocyanoacetate to give a mixture of oxazoline products, which can be separated and hydrolysed to the desired 3-fluoromethylthreonine analogues in near quantitative yield (**Scheme 123**).[212] Difluoroallylic alcohols react with benzenesulfenyl chloride to give a sulfenate ester which undergoes rapid [2,3]-rearrangement to give the α,α-difluoro sulfoxide in good yield (**Scheme 124**).[213] It would appear that there is a strong preference for the CF_2 centre to be in the sp^3 hybridisation state as attempts to reverse the reaction using triethyl phosphite were unsuccessful.

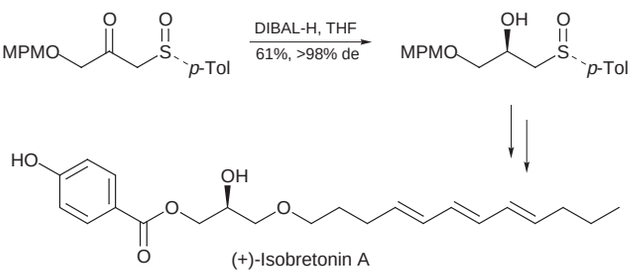
The synthesis of β-amino sulfoxides can be achieved by a number of methods. Addition of an α-lithio sulfoxide to an imine proceeds in good yield but with low stereoselectivity (Scheme 92).[126] α-Lithio sulfoxides react with oxaziridines to form β-amino sulfoxide derivatives, although again, only moderate stereoselectivity is observed (**Scheme 125**).[214]

Hydrocyanation of α-trifluoromethyl-β-sulfinylenamines proceeds mainly to give the *syn* diastereoisomer in high yield but modest stereoselectivity (**Scheme 126**),[215] and condensation of α-lithio sulfoxides with acetimidoyl chlorides gives a β-imino sulfoxide which can undergo subsequent stereoselective reduction to the β-amino sulfoxide (**Scheme 127**).[216] The β-imino sulfoxide intermediates can also be prepared using an aza-Wittig reaction between a β-keto sulfoxide and an iminophosphorane.

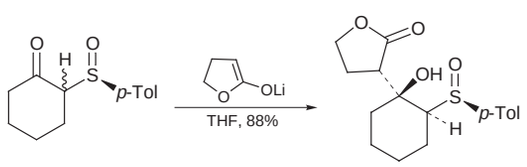
Finally, an interesting extension to the Swern oxidation procedure has been developed which allows the use of solid supported sulfoxides in place of dimethyl sulfoxide. The sulfoxide is attached to a Merrifield resin *via* an ester linkage (**Scheme 128**),[217] and when used in conjunction with oxalyl chloride, gives yields typically >90% in Swern oxidations of alcohols. Work-up is particularly easy, and no foul smelling by-products (*cf.* Me_2S) are formed. The sulfoxide can be regenerated using $NaIO_4$.



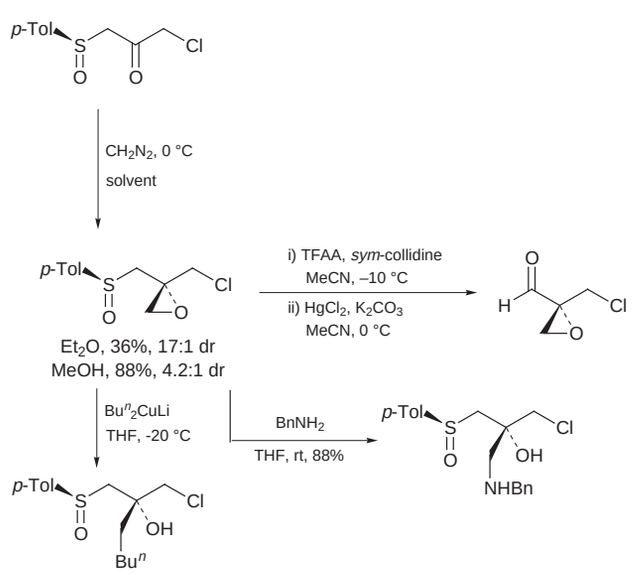
Scheme 118



Scheme 119



Scheme 120

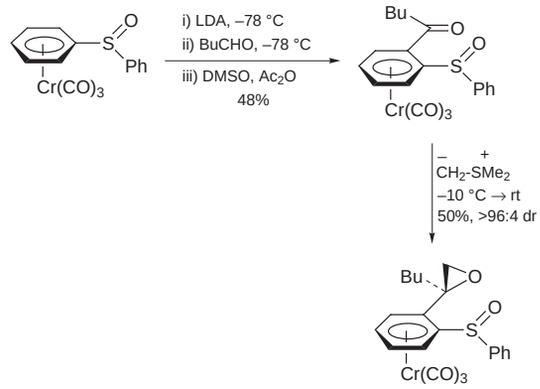


Scheme 121

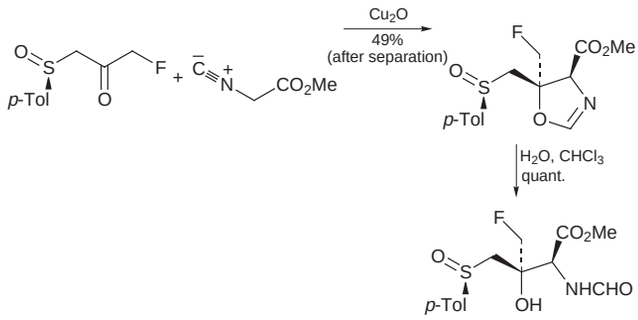
3.2.3 Unsaturated sulfoxides and selenoxides

New methods for the synthesis of unsaturated sulfoxides have been reported. Condensation of the anion derived from an optically active 1,1-bis-sulfoxide with a carbonyl compound generates a β-hydroxy bis-sulfoxide which readily undergoes dehydration (**Scheme 129**).[218] Similarly, anions of β-keto sulfoxides react with aldehydes to give the corresponding unsaturated sulfoxide, which can be used as a precursor to 1,4-dihydropyridines containing a chiral sulfinyl group (**Scheme 130**).[219]

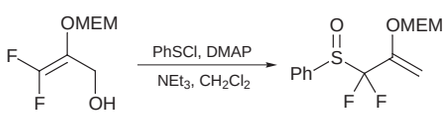
An alternative route to similar dihydropyridines utilises Andersen sulfinate methodology on the Grignard reagent



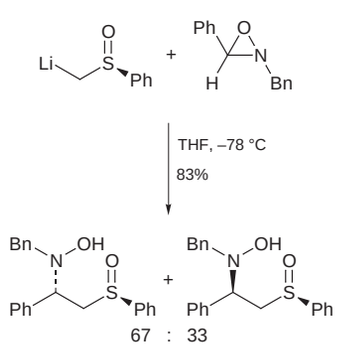
Scheme 122



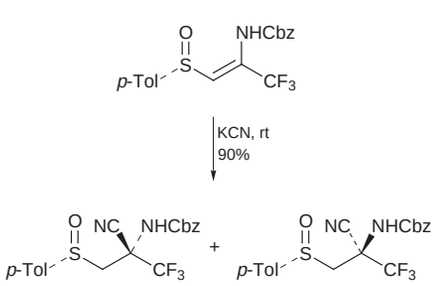
Scheme 123



Scheme 124



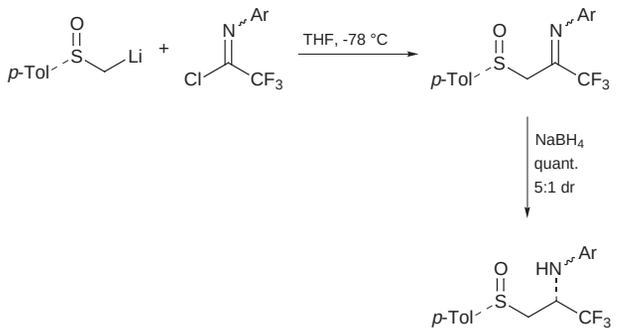
Scheme 125



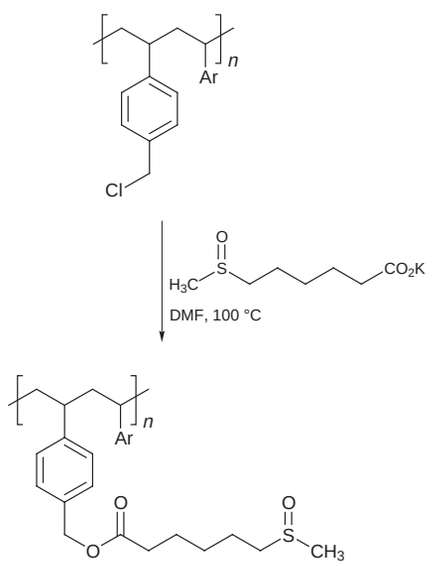
Scheme 126

derived from 3-bromopyridine (**Scheme 131**).[220] Sulfinyl-substituted benzoquinone imines have also been prepared using related methodology although yields were low, and a synthesis of the racemate proved to be much more efficient (**Scheme 132**).[221]

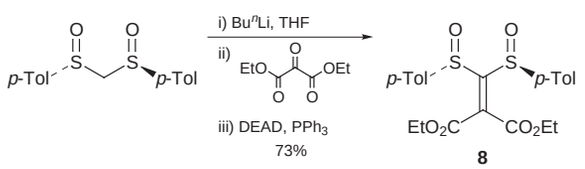
The synthesis of α,β-unsaturated sulfoxides has been



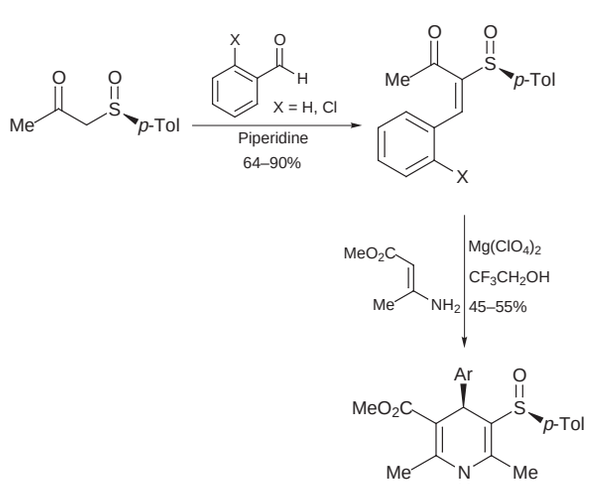
Scheme 127



Scheme 128

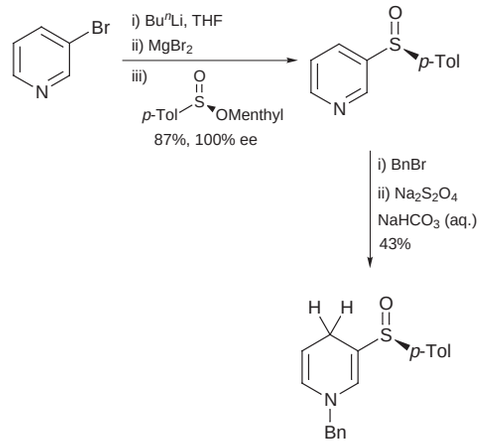


Scheme 129

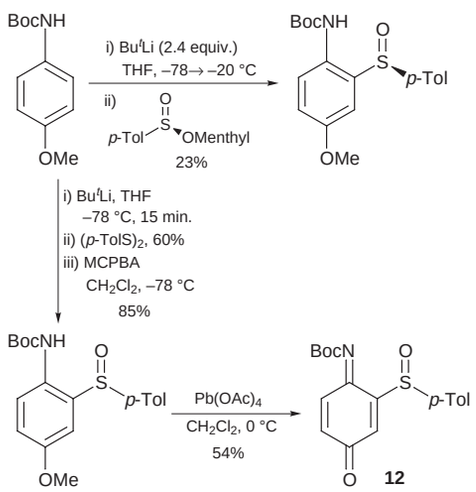


Scheme 130

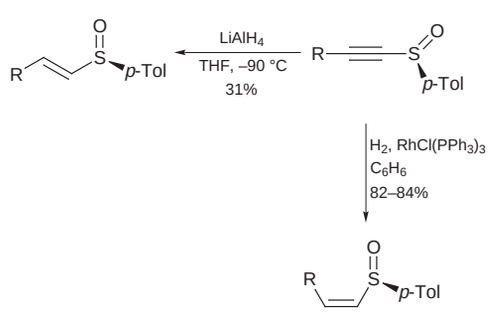
achieved using a vinyl Grignard reagent and a menthyl sulfinate[222] however mixtures of geometrical isomers can result. Alternatively, reduction of alkynyl sulfoxides using $LiAlH_4$ or H_2–$RhCl(PPh_3)_3$ gives either the (*E*)- or (*Z*)-α,β-unsaturated sulfoxides respectively with high stereoselectivity (**Scheme 133**).[222]



Scheme 131

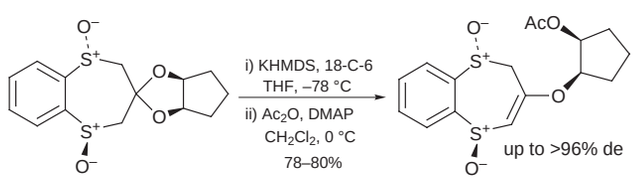


Scheme 132

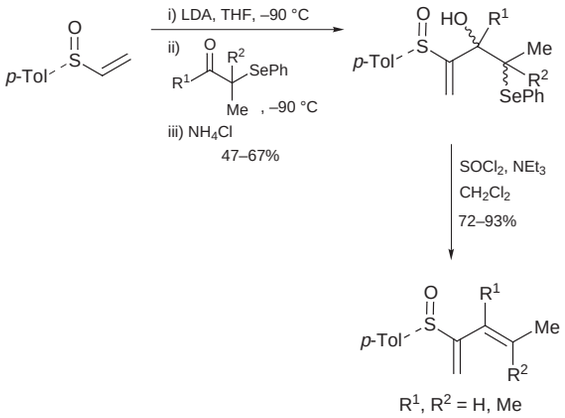


Scheme 133

1,5-Benzodithiepan-3-one 1,5-dioxide has been reported to be a novel chiral auxiliary for asymmetric desymmetrisation of *meso*-1,2-diols by base induced elimination to the α,β-unsaturated sulfoxide (**Scheme 134**).[223] Further work on related systems has also been reported, although lower diastereoselectivities are observed.[224] Elimination of β-hydroxy selenides has been used in the synthesis of unsaturated sulfoxides (**Scheme 135**).[225]

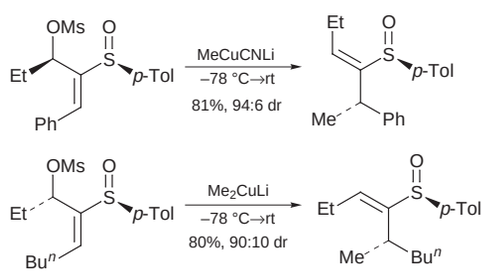


Scheme 134

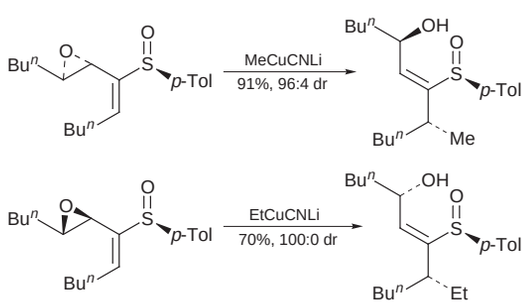


Scheme 135

The S_N2' displacement of allylic mesylates or epoxides allows for the stereoselective synthesis of α,β-unsaturated sulfoxides (**Schemes 136** and **137**).[226,227] In the case of allylic mesylates, the stereochemical outcome of the reaction appears to be controlled by the configuration of the mesylate group, whereas in the case of the allylic epoxides, the effect of the sulfinyl group is predominant.

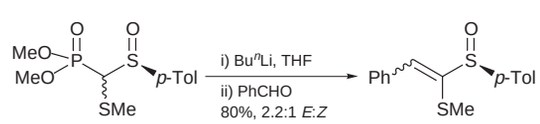


Scheme 136

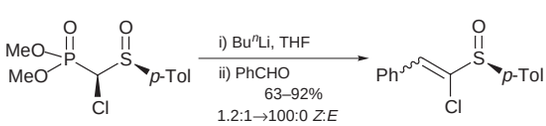


Scheme 137

α-Phosphoryl sulfoxides have also been used as precursors to a variety of substituted unsaturated sulfoxides, including optically active ketene dithioacetal mono-*S*-oxides (**Scheme 138**),[228] and optically active α-chlorovinyl sulfoxides (**Scheme 139**).[229] These kinds of reaction are also reported to be accelerated by sonication.[230]



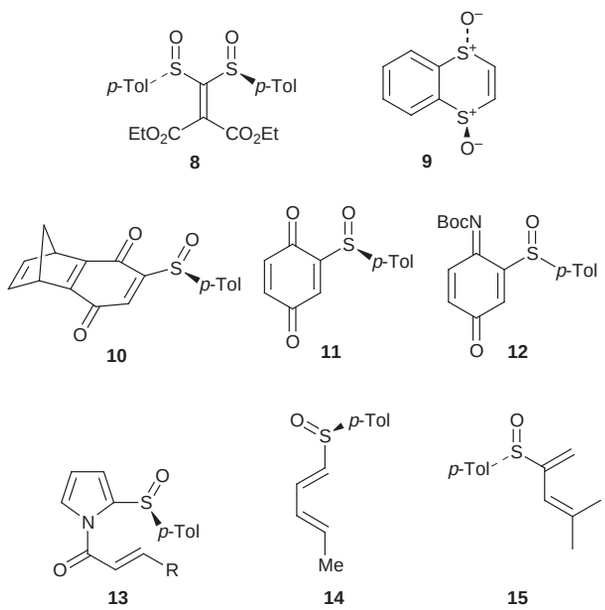
Scheme 138



Scheme 139

The use of unsaturated sulfoxides as dienophiles, dienes and dipolarophiles in cycloaddition reactions has continued to be an important area of research, and the use of the sulfinyl group as a chiral inductor in asymmetric Diels–Alder reactions has been reviewed.[231] Whilst it is beyond the scope of this review to give a detailed account of this area of chemistry, a brief discussion of the kinds of systems which have been investigated will be included. Syntheses of many of these compounds have been reported previously; any important new synthetic routes have been discussed above.

(−)-*E*-1,4-Benzodithiine-*S*,*S*′-dioxide **9**, obtained in an almost enantiomerically pure form by asymmetric Modena oxidation gives high *endo*/*exo* ratios and yields for cycloaddition with cyclopentadiene with $AlEt_2Cl$ catalysis.[232] Optically active 1,1-bis(ethoxycarbonyl)-2,2-bis(*p*-tolylsulfinyl) ethene **8**[218] has also been synthesised and investigated as a Diels–Alder dienophile, but was found to be unexpectedly unreactive requiring high pressures (13 kbar) for reaction with cyclopentadiene. Sulfinyl-substituted quinones **10**[233] and **11**[234] and benzoquinone-4-imines **12** (Scheme 132)[221] also undergo efficient selective cycloaddition reactions. Sulfinyl groups have been used to induce diastereoselectivity in cycloadditions of substrates containing remote double bonds, such as **13**.[235]



Dienes containing sulfinyl groups at either positions 1 (**14**)[236] or 2 (**15**),[237] undergo efficient Diels–Alder reactions, in some cases with good levels of stereoselectivity. 1-Sulfinyl dienes show high facial selectivity for complexation with $Fe(CO)_5$ (**Scheme 140**).[238] The complexes thus formed can undergo highly diastereoselective reactions prior to decomplexation.

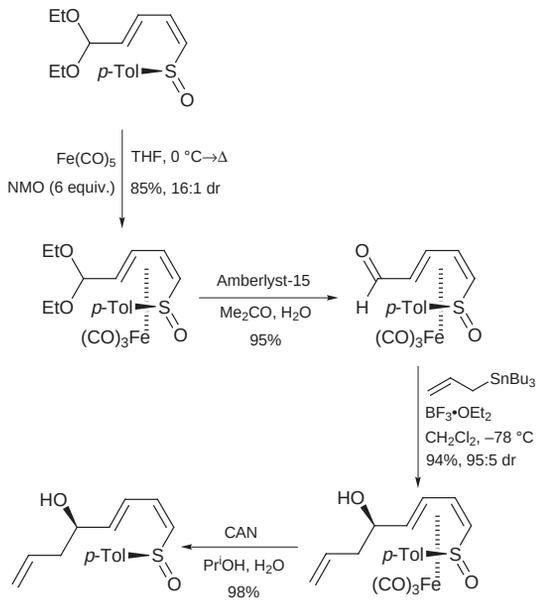
The synthesis of γ,δ-unsaturated sulfoxides using α-sulfinyl radicals is included in a review.[239] Alternatively, similar products can be obtained by Claisen rearrangement with a high degree of stereochemical control induced by an adjacent sulfinyl group (**Scheme 141**).[240]

4 Synthesis of sulfones and selenones

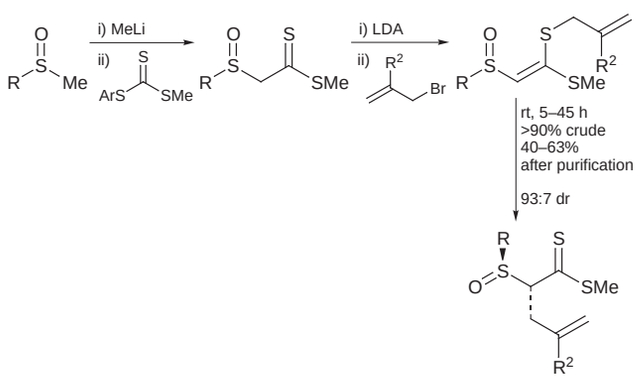
Although this section in principle includes methods for the synthesis of selenones as well as sulfones, very little literature has been published on them, and they have found only limited synthetic utility and so will not be discussed in any detail here.

4.1 Oxidation of sulfides and sulfoxides

The formation of sulfones by oxidation of sulfides and sulfoxides is now well established and relatively little new work in the area has been published. Oxone efficiently oxidises methionine

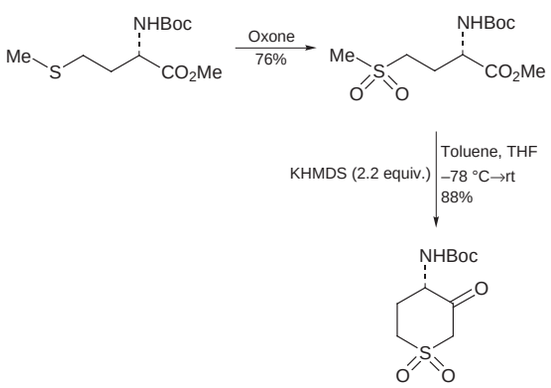


Scheme 140



Scheme 141

derivatives to the corresponding sulfones, which on treatment with base undergo cyclisation to give thiopyran *S*,*S*-dioxides (**Scheme 142**).[167] Interestingly, cyclisation of the corresponding sulfoxide causes racemisation.



Scheme 142

Interesting new nucleotide derivatives where the phosphate linkage has been replaced by a sulfone or other sulfur functionality have been synthesised. Again Oxone is the reagent of choice for oxidation of the thioether precursors (Scheme 87).[118–120]

Mechanistic studies have been published on the formation of sulfones by singlet oxygen oxidation of sulfides,[241] and by oxidation using tetramethylammonium peroxynitrite.[242]

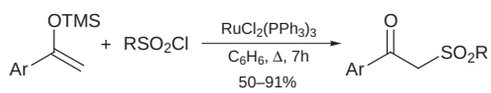
4.2 Non-oxidative sulfone synthesis

4.2.1 General methods for sulfone synthesis

Little new work has been published on the synthesis of simple sulfones. A review of the chemistry of oxiranyl and aziridinyl anions includes a section on sulfonyl stabilised anions.[189] Methylene bridged derivatives of estradiol have been prepared by methylenation of unsaturated sulfones using trimethylsulfoxonium iodide and base, although poor stereoselectivity is observed compared with unsaturated sulfoxides (Scheme 111).[196]

4.2.2 Functionalised sulfones

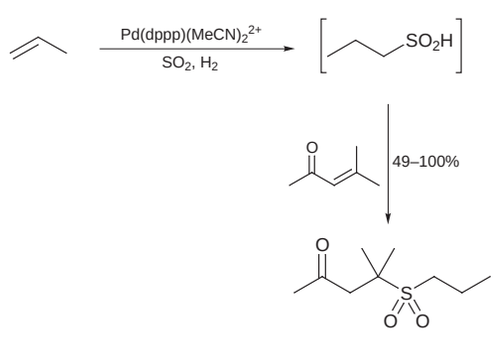
An interesting new route to β-keto sulfones utilises the ruthenium catalysed addition of silyl enol ethers to sulfonyl chlorides (**Scheme 143**).[243] Good yields are obtained using a variety of aromatic enol ethers and alkyl and aryl sulfonyl chlorides.



Scheme 143

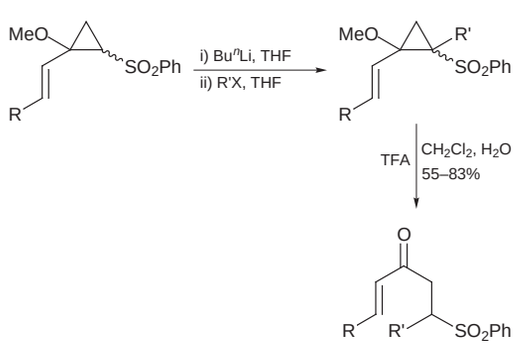
The palladium or platinum catalysed hydrosulfination of α,β-unsaturated ketones leads to formation of γ-keto sulfones in moderate to excellent yield (**Scheme 144**).[244] Initial hydrosulfination of the more electron rich olefin yields a sulfinic acid intermediate which then undergoes subsequent conjugate addition to an electron deficient alkene to give the product. Palladium catalysis usually gives better yields than platinum. γ-Keto sulfones can also be prepared by rearrangement of 2-alkenyl-2-methoxycyclopropyl phenyl sulfones (**Scheme 145**).[245]

An asymmetric synthesis of β-hydroxy sulfones utilises the diastereoselective reduction of β-keto sulfones derived from optically pure α-methylbenzylamine (**Scheme 146**).[246]



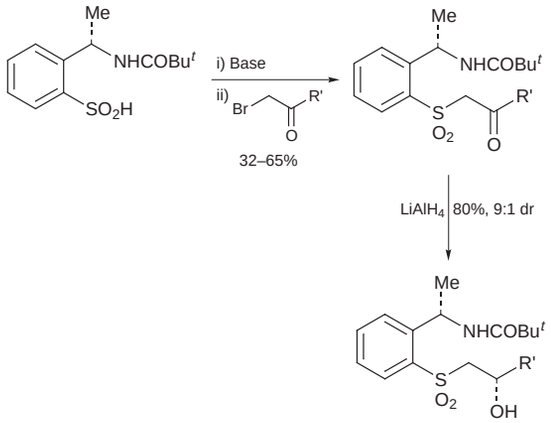
dppp = 1,3-bis(diphenylphosphino)propane

Scheme 144



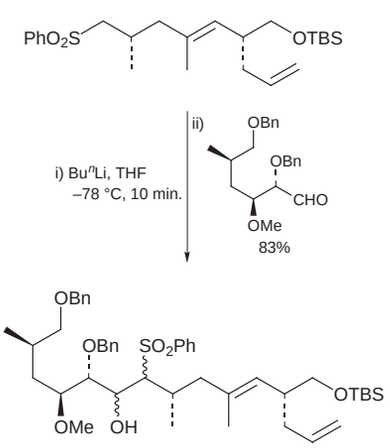
Scheme 145

The other main route to β-hydroxy sulfones is by addition of an α-sulfonyl anion to a carbonyl compound. This has been exploited in one of the key C–C bond forming reactions in a

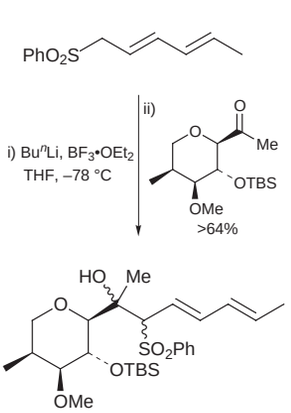


Scheme 146

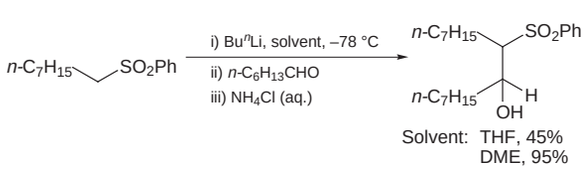
synthesis of the C10–C22 fragment of FK-506 (**Scheme 147**),[247] and (+)-lanomycin (**Scheme 148**).[248] In the second example, $BF_3{\cdot}Et_2O$ is required for efficient condensation, presumably due to the lower reactivity of the ketone. The initial products formed in this reaction are usually converted to alkenes as part of a Julia–Lythgoe alkene synthesis. Increased yields of β-hydroxy sulfones can be achieved if DME is used as solvent rather than THF (**Scheme 149**), although this increase can be marginal in some cases.[249] An alternative to the Julia–Lythgoe reaction has been recently introduced which does not involve isolation of an intermediate β-hydroxy sulfone.[250–252]



Scheme 147

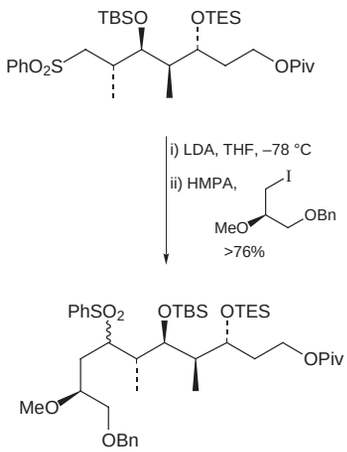


Scheme 148

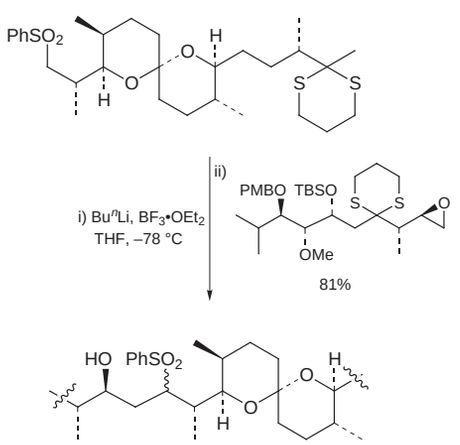


Scheme 149

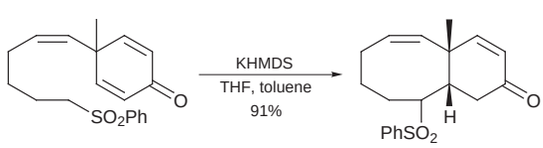
α-Lithiated sulfones have also been alkylated with other electrophiles as key steps in the synthesis of natural products, including the use of alkyl halides (**Scheme 150**),[253] epoxides (**Scheme 151**)[254] and α,β-unsaturated ketones (**Scheme 152**).[255]



Scheme 150

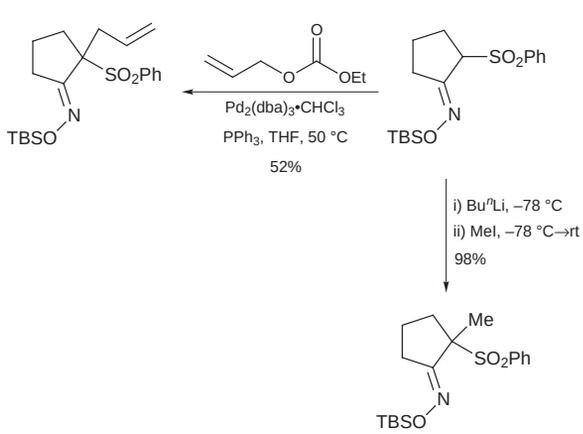


Scheme 151



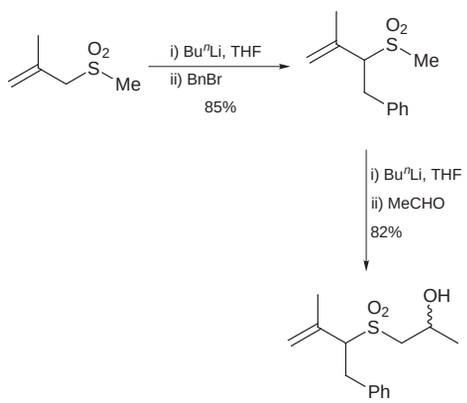
Scheme 152

Lithiated cyclopentane β-ketoxime sulfones also undergo conventional alkylation reactions with alkyl halides, and palladium catalysed allylations with allylic carbonates (**Scheme 153**).[256]

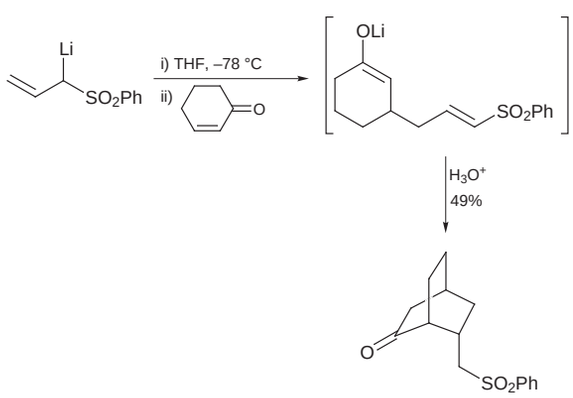


Scheme 153

2-Methylprop-2-enyl methyl sulfones can be regioselectively alkylated at the more acidic allylic position on treatment with base and an alkyl halide. Addition of a further equivalent of base allows regioselective deprotonation of the methyl group which can also undergo alkylation (**Scheme 154**).[257] Conjugate addition of a lithiated allyl sulfone to an α,β-unsaturated ketone and subsequent cyclisation of the initial enolate intermediate onto the vinyl sulfone provides an efficient route to bicyclo[2.2.2]-octan-2-one derivatives (**Scheme 155**).[258,259] In some cases the reaction is best carried out in one pot. Other stereoselective additions of carbon nucleophiles to functionalised α,β-unsaturated sulfones have been reported (Scheme 40).[60]

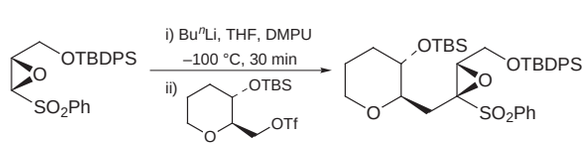


Scheme 154



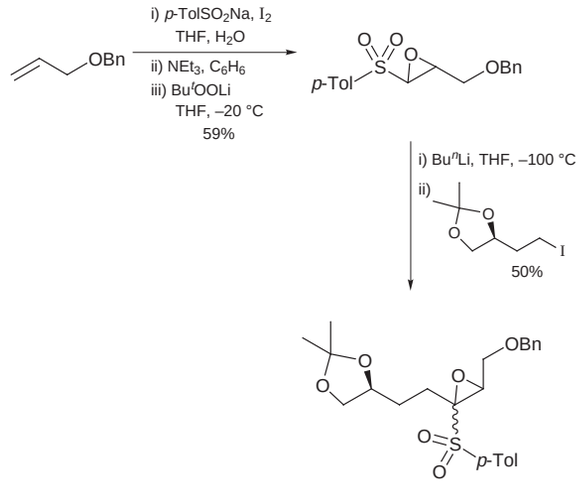
Scheme 155

Epoxidation of α,β-unsaturated sulfones has been reported using either MCPBA/$NaHCO_3$ (Scheme 25),[42] TBHP with KF/Al_2O_3 catalysis,[260] or the lithium salt of TBHP (**Schemes 156**, **157** and **158**), in some cases with excellent stereocontrol.[261–263] The products of these reactions can undergo deprotonation to form sulfone stabilised oxiranyl anions which undergo efficient alkylation with alkyl triflates (Scheme 156)[261] and iodides (Scheme 157).[262]

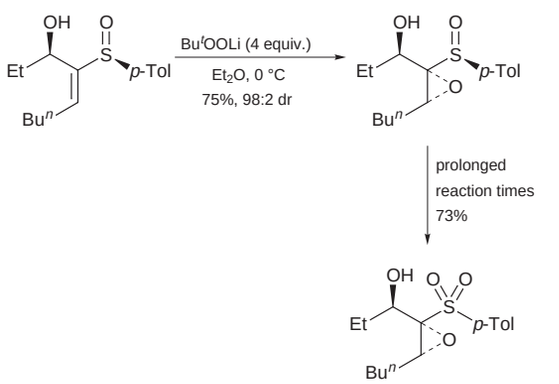


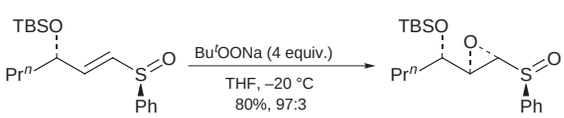
Scheme 156

β-Aminoalkyl sulfones can be prepared by addition of amines to α,β-unsaturated sulfones (**Scheme 159**).[264] They can then undergo subsequent deprotonation α to the sulfonyl group and the anions thus formed, alkylated with a variety of electrophiles to give mainly the *anti*-diastereoisomers. In a related reaction, primary or secondary amines add to α,β-unsaturated sulfones in the presence of base and CCl_4 to give β-amino-α,α-dichloro sulfones directly (**Scheme 160**).[265]

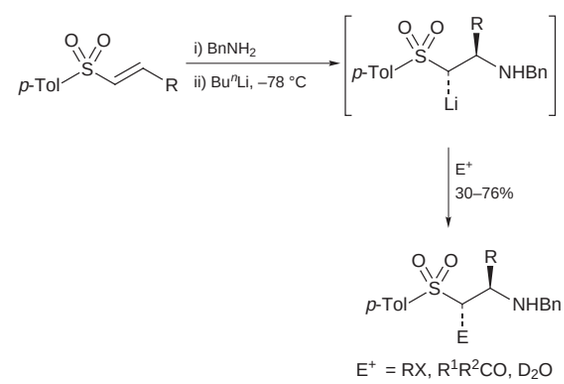


Scheme 157

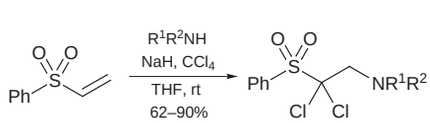




Scheme 158



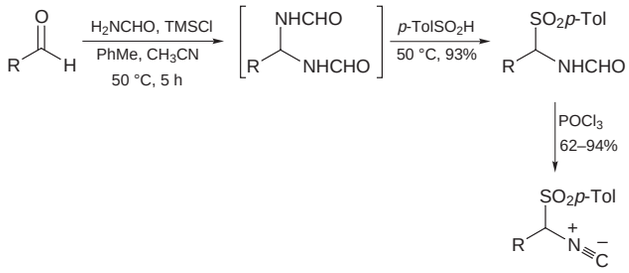
Scheme 159



Scheme 160

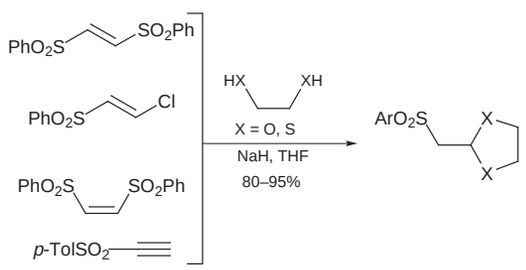
Tosyl methyl isocyanate (TosMIC) derivatives are valuable reagents but substituted derivatives can be difficult to prepare. Sequential treatment of an alkyl or aryl aldehyde with formamide, a sulfinic acid and $POCl_3$ gives good overall yields for a variety of substitution patterns (**Scheme 161**).[266]

A Michael route to acetal and dithioacetal derivatives of



Scheme 161

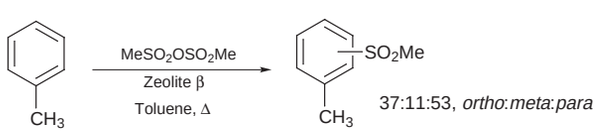
2-sulfonylacetaldehyde has been developed (**Scheme 162**).[267] Treatment of a 1,2-bis(sulfonyl)ethene or a 1-chloro-2-sulfonylethene with a 1,2-diol or -dithiol and base gives the corresponding acetal or dithioacetal with loss of a sulfonyl or chloride group respectively. The same products can also be obtained by a double Michael addition of a 1,2-diol or -dithiol to an acetylenic sulfone.



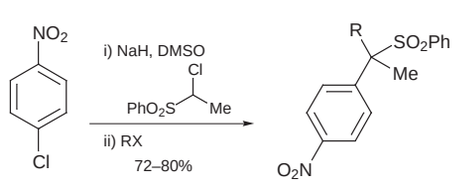
Scheme 162

4.2.3 Unsaturated sulfones

The regioselective methanesulfonylation of toluene by methanesulfonic anhydride has been reported to give high *para*-selectivity when catalysed by cation exchanged zeolite β (**Scheme 163**).[268] A one pot vicarious nucleophilic substitution of hydrogen using phenylsulfonyl stabilised anions provides a route to substituted benzyl sulfones (**Scheme 164**).[269,270]



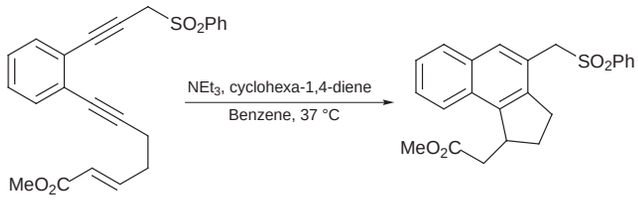
Scheme 163



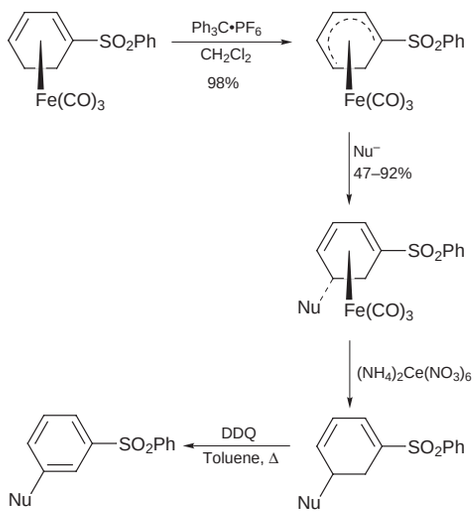
Scheme 164

Tandem enyne allene radical cyclisations also provide a route to various benzylic sulfones. The initial propynyl sulfones undergo base induced conversion to the allene which subsequently undergo the radical cyclisation (**Scheme 165**).[271] Related reactions have also been exploited by sulfone-containing DNA cleaving agents based on enediynes.[272–276]

Iron tricarbonyl complexes of butadienyl sulfones undergo hydride abstraction to give a dienylium iron complex which can be reacted with a wide variety of carbon and heteroatom-based nucleophiles (**Scheme 166**).[277] Decomplexation of the metal regenerates the substituted dienyl sulfone, which in some cases can be aromatised using DDQ to give a substituted aromatic sulfone.

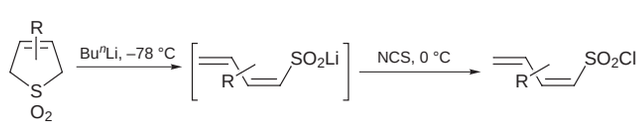


Scheme 165

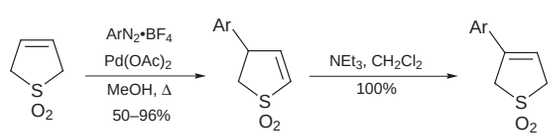


Scheme 166

A novel one pot synthesis of substituted buta-1,3-diene-1-sulfonyl chlorides from 3-sulfolenes relies on ring opening of a lithiated sulfolene and quenching the intermediate sulfinate anion with *N*-chlorosuccinimide (**Scheme 167**).[278] Sulfolene, when treated with an aromatic diazonium salt in the presence of a palladium catalyst also provides access to either vinyl or allyl sulfones *via* a Heck-like coupling reaction (**Scheme 168**).[279] A variety of substituted aromatic diazonium salts can be used with moderate to excellent efficiency.

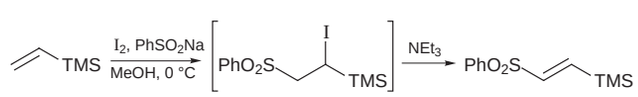


Scheme 167



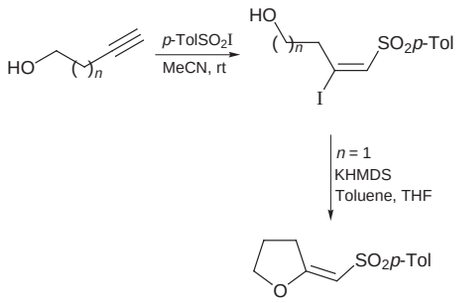
Scheme 168

A simple and efficient synthesis of (*E*)-1-phenylsulfonyl-2-(trimethylsilyl)ethylene utilises the iodosulfonation of trimethylsilylethene followed by base induced elimination (**Scheme 169**).[280] Quantitative yields of the product as an 8 : 1 mixture of (*E*)- and (*Z*)-isomers can be obtained, or alternatively, the pure (*E*)-isomer can be obtained in 72% overall yield. Oxidation of silicon-substituted vinyl sulfides followed by desilylation also provides access to unsaturated sulfones with excellent control over double bond geometry (Scheme 32).[49]

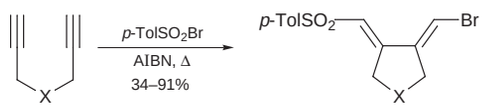


Scheme 169

Iodosulfonations of alkynes lead to formation of 1-*p*-tolylsulfonyl-2-iodoalkenes which can undergo further reaction to form sulfone-containing cyclic enol ethers (**Scheme 170**).[281] Bromosulfonation (**Scheme 171**)[282] and selenosulfonation (Schemes 43 and 44)[63,64] have also both been used as routes to substituted unsaturated sulfones.

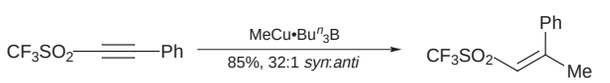


Scheme 170

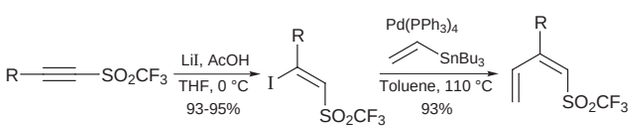


Scheme 171

Nucleophilic addition of organocopper reagents to acetylenic sulfones gives good yields of the corresponding vinylic sulfones with excellent control of double bond geometry (**Scheme 172**).[283] Addition of hydrogen iodide to acetylenic sulfones also proceeds with high stereoselectivity (**Scheme 173**).[284] The vinyl iodide products can undergo subsequent palladium catalysed coupling with vinyl stannanes to give dienyl sulfones again with good stereocontrol.

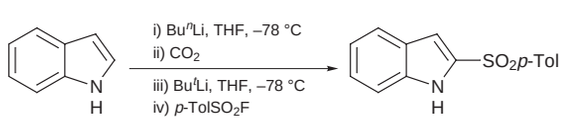


Scheme 172

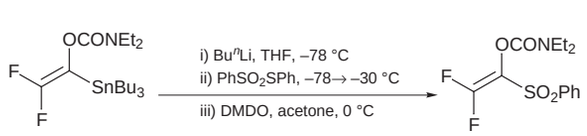


Scheme 173

Toluene-*p*-sulfonyl fluoride has been reported as an electrophile for sulfonation of organometallic anions (**Scheme 174**).[285] In this case the initial lithiation reaction is aided by N-carboxylation of an indole moiety. Transmetallation of a vinyl tin reagent with Bu″Li, quenching with phenyl thiophenylsulfonate, and oxidation with dimethyldioxirane (DMDO) has also been used for vinyl sulfone formation (**Scheme 175**).[286,287]

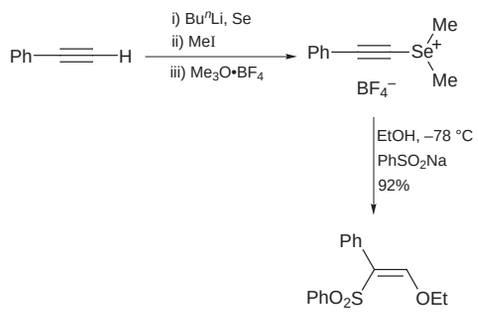


Scheme 174

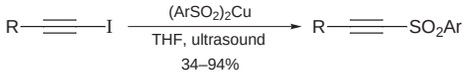


Scheme 175

Addition of sodium benzene sulfinate to alkynylselenonium salts gives vinyl sulfones (**Scheme 176**)[288] whereas copper sulfinates and alkynyl halides react under sonochemical initiation to form alkynyl sulfones (**Scheme 177**).[289–291]

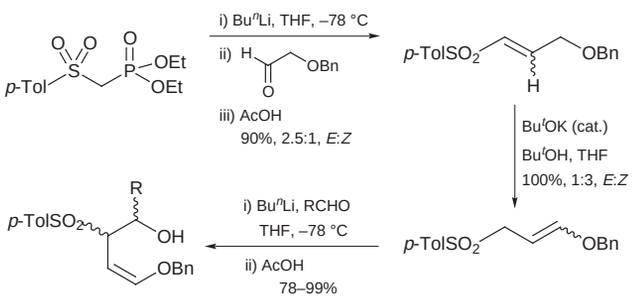


Scheme 176



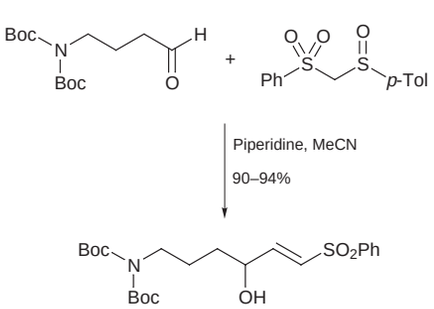
Scheme 177

Reaction of sulfonyl phosphonates with aldehydes allows formation of α,β-unsaturated sulfones, which can undergo base catalysed isomerisation to the corresponding β,γ-unsaturated sulfones (**Scheme 178**).[292] Subsequent lithiation and quenching with electrophiles allows further functionalisation of the allyl sulfone moiety.

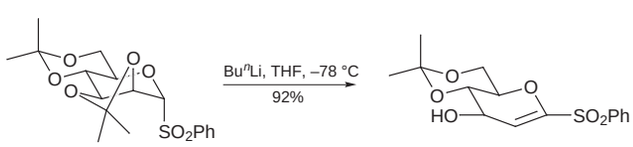


Scheme 178

The synthesis of γ-oxygenated α,β-unsaturated sulfones can be carried out directly by condensation of an aldehyde with a sulfinyl sulfone (**Scheme 179**).[293] The reaction proceeds by initial addition of the sulfur stabilised anion to an aldehyde. Subsequent 2,3-sigmatropic sulfoxide–sulfenate rearrangement then gives the γ-hydroxy α,β-unsaturated sulfone in excellent overall yield. Related sugar-derived α,β-unsaturated sulfones have also been synthesised by elimination of a glycosyl sulfone (**Scheme 180**).[294]

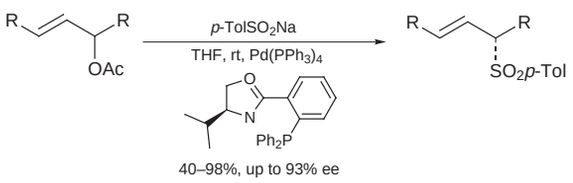


Scheme 179

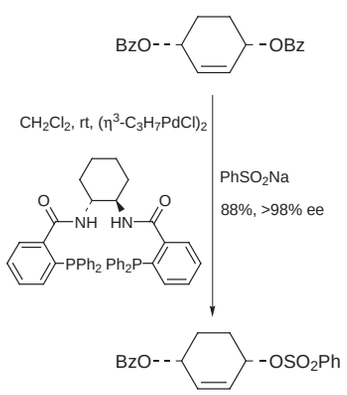


Scheme 180

The palladium catalysed allylic sulfonation of allylic acetates gives allyl sulfones in good yield and with up to 93% enantiomeric excess (**Scheme 181**).[295] Related chemistry has also been used for the desymmetrisation of allylic dibenzoates to give allyl sulfones of high enantiomeric excess (**Scheme 182**).[296]

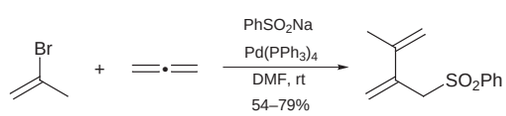


Scheme 181

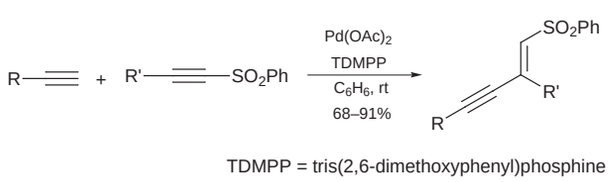


Scheme 182

Palladium catalysis has also been used for the carbopalladation–sulfonylation of allene for the preparation of 2-vinyl or 2-aryl allyl sulfones (**Scheme 183**);[297] the addition of terminal alkynes to electron deficient alkynes, to give sulfone-substituted enynes (**Scheme 184**);[298] and [3 + 2]-cycloaddition reactions of sulfonyl activated carbohydrate derivatives (**Scheme 185**).[299]



Scheme 183



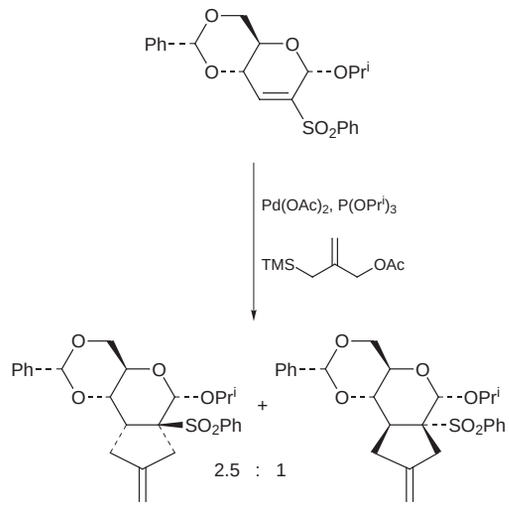
TDMPP = tris(2,6-dimethoxyphenyl)phosphine

Scheme 184

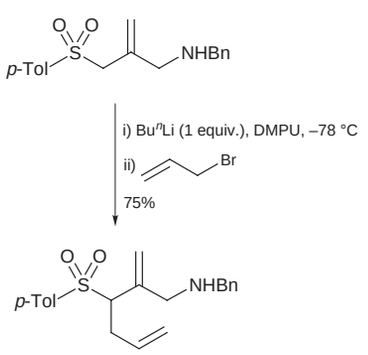
The alkylation of sulfonyl stabilised anions with electrophiles provides a powerful protocol for the further functionalisation of unsaturated sulfones (**Schemes 186** and **187**).[300–302] With delocalised allyl anions, alkylation occurs exclusively adjacent to the sulfone moiety.

Lewis acid induced rearrangement of sulfonyl cyclopropanes gives α,β-unsaturated sulfones in moderate yield (**Scheme 188**),[303] whereas lithiated episulfones undergo ring opening to give sulfinate anions which can be trapped with a variety of electrophiles leading to the formation of vinyl sulfones in moderate to good yields and with excellent control of double bond geometry (**Scheme 189**).[304]

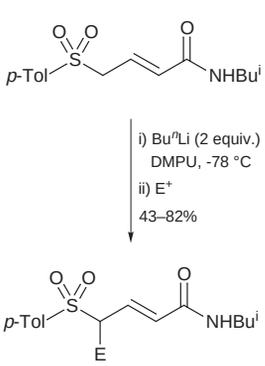
The use of unsaturated sulfones in Diels–Alder reactions continues to be investigated and has been reviewed.[305,306]



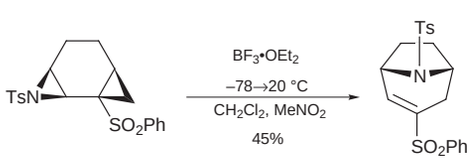
Scheme 185



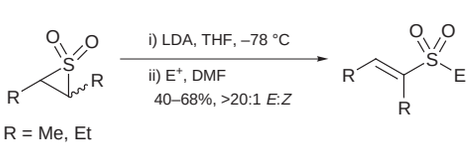
Scheme 186



Scheme 187



Scheme 188



R = Me, Et

Scheme 189

5 Conclusion

Organo-sulfur and -selenium chemistry continues to play a crucial role in organic synthesis, particularly with new stereoselective and asymmetric processes being developed. We hope

this review will encourage the further development and exploitation of these methods in the future.

6 References

1 C. M. Rayner, *Contemp. Org. Synth.*, 1994, **1**, 191.
2 C. M. Rayner, *Contemp. Org. Synth.*, 1995, **2**, 409.
3 C. M. Rayner, *Contemp. Org. Synth.*, 1996, **3**, 499.
4 R. J. Cremlyn, *An Introduction to Organosulfur Chemistry*, J. Wiley, Chichester, 1996.
5 *Organosulfur Chemistry: Synthetic and Stereochemical Aspects*, ed. P. C. B. Page, Academic Press, San Diego, 1998.
6 T. C. Stadtman, *Ann. Rev. Biochem.*, 1996, **65**, 83.
7 E. Block, X. J. Cai, P. C. Uden, X. Zhang, B. D. Quimby and J. J. Sullivan, *Pure Appl. Chem.*, 1996, **68**, 937.
8 M. Frederickson and R. Grigg, *Org. Prep. Proced. Int.*, 1997, **29**, 33.
9 M. Tiecco, L. Testaferri, M. Tingoli, L. Bagnoli, F. Marini, C. Sanit and A. Temperini, *Gazz. Chim. Ital.*, 1996, **126**, 635.
10 I. Koval, *Russ. Chem. Rev.*, 1995, **64**, 731.
11 H. Ishibashi and M. Ikeda, *Rev. Heteroatom. Chem.*, 1996, **14**, 59.
12 M. Yus, *Chem. Soc. Rev.*, 1996, **25**, 155.
13 D. H. R. Barton and B. M. Chabot, *Tetrahedron*, 1996, **52**, 10 287.
14 K. Ruhlandtsenge, U. Englich, M. O. Senge and S. Chadwick, *Inorg. Chem.*, 1996, **35**, 5820.
15 A. Ishii, K. Komiya and J. Nakayama, *J. Am. Chem. Soc.*, 1996, **118**, 12 836.
16 T. I. Reddy and R. S. Varma, *Chem. Commun.*, 1997, 621.
17 S. Chowdhury and S. Roy, *Tetrahedron Lett.*, 1997, **38**, 2149.
18 J. Eames, R. V. H. Jones and S. Warren, *Tetrahedron Lett.*, 1996, **37**, 707.
19 A. Krief, B. Kenda and B. Remacle, *Tetrahedron*, 1996, **52**, 7435.
20 X. B. Zhang, M. D. Ruan and W. Q. Fan, *Synth. Commun.*, 1996, **26**, 4665.
21 X. B. Hu, Z. J. Tian, X. R. Lu and Y. Y. Chen, *Synth. Commun.*, 1997, **27**, 553.
22 D. H. R. Barton and G. Fontana, *Tetrahedron*, 1996, **52**, 11 163.
23 K. Ramadas and N. Srinivasan, *Synth. Commun.*, 1996, **26**, 4179.
24 K. Akaji, *Yakugaku Zasshi—J. Pharm. Soc. Japan*, 1996, **116**, 441.
25 M. Barbero, I. Degani, R. Fochi and P. Perracino, *J. Org. Chem.*, 1996, **61**, 8762.
26 J. C. Cochran, S. R. Friedman and J. P. Frazier, *J. Org. Chem.*, 1996, **61**, 1533.
27 Y. Wang and M. Koreeda, *Synlett*, 1996, 885.
28 J. B. Arterburn and M. C. Perry, *Tetrahedron Lett.*, 1996, **37**, 7941.
29 W. Adam and S. Weinkotz, *Chem. Commun.*, 1996, 177.
30 V. A. Potapov and S. V. Amosova, *Zh. Org. Khim.* (*Chem. Abstr.*, 1997, 126, 305595h), 1996, **32**, 1142.
31 J. C. Arnould, M. Didelot, C. Cadilhac and M. J. Pasquet, *Tetrahedron Lett.*, 1996, **37**, 4523.
32 D. Fabbri, S. Pulacchini and S. Gladiali, *Synlett*, 1996, 1054.
33 G. Capozzi, C. Falciani, S. Menichetti and C. Nativi, *Gazz. Chim. Ital.*, 1996, **126**, 227.
34 M. Peer, J. C. Dejong, M. Kiefer, T. Langer, H. Rieck, H. Schell, P. Sennhenn, J. Sprinz, H. Steinhagen, B. Wiese and G. Helmchen, *Tetrahedron*, 1996, **52**, 7547.
35 T. Ishiyama, M. Mori, A. Suzuki and N. Miyaura, *J. Organomet. Chem.*, 1996, **525**, 225.
36 Y. Kita, T. Takada and T. Tohma, *Pure Appl. Chem.*, 1996, **68**, 627.
37 B. Quicletsire, R. N. Saicic and S. Z. Zard, *Tetrahedron Lett.*, 1996, **37**, 9057.
38 N. A. Petasis, S. P. Lu, E. I. Bzowej, D. K. Fu, J. P. Staszewski, I. Akritopoulouzanze, M. A. Patane and Y. H. Hu, *Pure Appl. Chem.*, 1996, **68**, 667.
39 K. Mikami, T. Yajima, N. Siree, M. Terada, Y. Suzuki and I. Kobayashi, *Synlett*, 1996, 837.
40 K. Sato, T. Koga, K. Masuya, K. Tanino and I. Kuwajima, *Synlett*, 1996, 751.
41 T. Takeda and T. Fujiwara, *Synlett*, 1996, 481.
42 M. A. Plancquaert, M. Redon, Z. Janousek and H. G. Viehe, *Tetrahedron*, 1996, **52**, 4383.
43 T. Y. Chau, H. C. Lin and W. Hu, *Synth. Commun.*, 1996, **26**, 1867.
44 J. Maddaluno, O. Gaonach, A. Marcual, L. Toupet and C. Giessner-prettre, *J. Org. Chem.*, 1996, **61**, 5290.
45 L. Ambroise and R. F. W. Jackson, *Tetrahedron Lett.*, 1996, **37**, 2311.
46 M. Mikolajczyk, W. H. Midura, B. Wladislaw, F. C. Biaggio, L. Marzorati, M. W. Wieczorek and J. Blaszczyk, *Tetrahedron*, 1997, **53**, 2959.
47 R. Rossi, F. Bellina and L. Mannina, *Tetrahedron*, 1997, **53**, 1025.
48 S. S. P. Chou and H. T. Sheng, *Organometallics*, 1996, **15**, 4113.
49 B. F. Bonini, M. Comes-Franchini, M. Fochi, G. Mazzanti, F. Peri and A. Ricci, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2803.
50 S. Gill, P. Kocienski, A. Kohler, A. Pontiroli and L. Qun, *Chem. Commun.*, 1996, 1743.
51 M. Ohkita, O. Nishizawa, T. Imai, S. Nishida and T. Tsuji, *Tetrahedron*, 1996, **52**, 9979.
52 X. Huang and L. S. Zhu, *J. Chem. Soc., Perkin Trans. 1*, 1996, 767.
53 D. Y. Yang, X. Huang and P. Li, *Chin. Chem. Lett.*, 1996, **7**, 1085.
54 L. S. Zhu, Z. Z. Huang and X. Huang, *J. Chem. Res.* (*S*), 1996, **2**, 112.
55 L. S. Zhu, Z. Z. Huang and X. Huang, *Tetrahedron*, 1996, **52**, 9819.
56 X. Huang and L. S. Zhu, *J. Organomet. Chem.*, 1996, **523**, 9.
57 D. Y. Yang and X. Huang, *Synth. Commun.*, 1996, **26**, 4369.
58 D. Y. Yang and X. Huang, *J. Organomet. Chem.*, 1996, **523**, 139.
59 Y. Ma and X. Huang, *Synth. Commun.*, 1997, **27**, 225.
60 Y. M. Jiang, Y. Ichikawa and M. Isobe, *Tetrahedron*, 1997, **53**, 5103.
61 J. V. Comasseto, P. H. Menezes, H. A. Stefani, G. Zeni and A. L. Braga, *Tetrahedron*, 1996, **52**, 9687.
62 T. G. Back and K. Nakajima, *Tetrahedron Lett.*, 1997, **38**, 989.
63 M. Yoshimatsu, M. Hayashi, G. Tanabe and O. Muraoka, *Tetrahedron Lett.*, 1996, **37**, 4161.
64 M. Yoshimatsu and J. Hasegawa, *J. Chem. Soc., Perkin Trans. 1*, 1997, 211.
65 M. E. Kuehne, T. S. Wang and P. J. Seaton, *J. Org. Chem.*, 1996, **61**, 6001.
66 M. Yoshimatsu, M. Naito, H. Shimizu, O. Muraoka, G. Tanabe and T. Kataoka, *J. Org. Chem.*, 1996, **61**, 8200.
67 H. Abe, A. Yamasaki, H. Fujii and T. Harayama, *Chem. Pharm. Bull.*, 1996, **44**, 2223.
68 M. X. Yu, Y. M. Zhang and W. L. Bao, *Synth. Commun.*, 1997, **27**, 609.
69 Y. F. Zheng, W. L. Bao and Y. M. Zhang, *Synth. Commun.*, 1997, **27**, 79.
70 W. L. Bao, Y. F. Zheng, Y. M. Zhang and J. Q. Zhou, *Tetrahedron Lett.*, 1996, **37**, 9333.
71 P. C. Cagle, O. Meyer, D. Vichard, K. Weickhardt, A. M. Arif and J. A. Gladysz, *Organometallics*, 1996, **15**, 194.
72 P. T. Bell, P. C. Cagle, D. Vichard and J. A. Gladysz, *Organometallics*, 1996, **15**, 4695.
73 M. S. Chambers and E. J. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1997, 417.
74 S. K. Kang, D. Y. Kim, R. K. Hong and P. S. Ho, *Synth. Commun.*, 1996, **26**, 3225.
75 C. C. Silveira, G. L. Fiorin and A. L. Braga, *Tetrahedron Lett.*, 1996, **37**, 6085.
76 S. Weigand and R. Bruckner, *Synthesis*, 1996, 475.
77 E. Montenegro, R. Echarri, C. Claver, S. Castillon, A. Moyano, M. A. Pericas and A. Riera, *Tetrahedron: Asymmetry*, 1996, **7**, 3553.
78 C. Jouen, M. C. Lasne and J. C. Pommelet, *Tetrahedron Lett.*, 1996, **37**, 2413.
79 A. V. Sanin, V. G. Nenajdenko, V. S. Kuzmin and E. S. Balenkova, *J. Org. Chem.*, 1996, **61**, 1986.
80 N. Shibata, M. Matsugi, N. Kawano, S. Fukui, C. Fujimori, K. Gotanda, K. Murata and Y. Kita, *Tetrahedron: Asymmetry*, 1997, **8**, 303.
81 N. Shibata, C. Fujimori, S. Fujita and Y. Kita, *Chem. Pharm. Bull.*, 1996, **44**, 892.
82 P. J. Parsons, C. S. Penkett and A. J. Shell, *Chem. Rev.*, 1996, **96**, 195.
83 Y. Arroyo-Gómez, J. A. López-Sastre, J. F. Rodríguez-Amo and M. A. Sanz-Tejedor, *J. Chem. Soc., Perkin Trans. 1*, 1996, 2933.
84 A. L. Braga, C. C. Silveira, G. Zeni, W. A. Severo and H. A. Stefani, *J. Chem. Res.* (*S*), 1996, 206.
85 N. S. Zefirov, *Pure Appl. Chem.*, 1996, **68**, 881.
86 B. Koning, R. Hulst and R. M. Kellogg, *Recl. Trav. Chim. Pays-Bas.*, 1996, **115**, 49.
87 Y. Tanabe, K. Mori and Y. Yoshida, *J. Chem. Soc., Perkin Trans. 1*, 1997, 671.
88 H. Watanabe, S. Ogo and T. Yamamura, *Chem. Lett.*, 1996, **11**, 999.
89 C. Q. Liu, Y. Hashimoto, K. Kudo and K. Saigo, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2095.
90 D. M. Gill, N. A. Pegg and C. M. Rayner, *Tetrahedron*, 1996, **52**, 3609.
91 D. M. Gill, N. A. Pegg and C. M. Rayner, *Tetrahedron*, 1997, **53**, 3383.
92 G. Foray, A. B. Penenory and R. A. Rossi, *Tetrahedron Lett.*, 1997, **38**, 2035.
93 A. R. Katritzky, L. H. Xie and L. Serdyuk, *J. Org. Chem.*, 1996, **61**, 7564.

94 A. R. Katritzky, D. Toader and L. H. Xie, *J. Org. Chem.*, 1996, **61**, 7571.
95 W. L. Bao, Y. M. Zhang, J. Q. Zhou and Y. F. Zheng, *Synth. Commun.*, 1996, **26**, 3277.
96 J. Q. Zhou, W. L. Bao, Y. M. Zhang and J. Q. Wang, *Synth. Commun.*, 1996, **26**, 3283.
97 D. Enders, O. Piva and F. Burkamp, *Tetrahedron*, 1996, **52**, 2893.
98 J. Eames, R. V. H. Jones and S. Warren, *Tetrahedron Lett.*, 1996, **37**, 4823.
99 A. Mann, L. Quaranta, G. Reginato and M. Taddei, *Tetrahedron Lett.*, 1996, **37**, 2651.
100 F. Wackernagel, U. Schwitter and B. Giese, *Tetrahedron Lett.*, 1997, **38**, 2657.
101 I. Petschen, E. A. Malo, M. P. Bosch and A. Guerrero, *Tetrahedron: Asymmetry*, 1996, **7**, 2135.
102 S. V. Ley, S. Mio and B. Meseguer, *Synlett*, 1996, 791.
103 S. V. Ley, S. Mio and B. Meseguer, *Synlett*, 1996, 787.
104 A. Patti, D. Lambusta, M. Piattelli, G. Nicolosi, P. McArdle, D. Cunningham and M. Walsh, *Tetrahedron*, 1997, **53**, 1361.
105 Y. Ohtsuka, O. Katoh, T. Sugai and H. Ohta, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 483.
106 M. Tiecco, L. Testaferri, F. Marini, L. Bagnoli, C. Santi and A. Temperini, *Tetrahedron*, 1997, **53**, 4441.
107 M. Tiecco, L. Testaferri and F. Marini, *Tetrahedron*, 1996, **52**, 11 841.
108 G. Pandey, K. S. S. P. Rao and K. V. N. Rao, *J. Org. Chem.*, 1996, **61**, 6799.
109 T. G. Back, P. L. Gladstone and M. Parvez, *J. Org. Chem.*, 1996, **61**, 3806.
110 R. N. Saicic and S. Z. Zard, *Chem. Commun.*, 1996, 1631.
111 K. S. Kim, H. B. Park, J. Y. Kim, Y. H. Ahn and I. H. Jeong, *Tetrahedron Lett.*, 1996, **37**, 1249.
112 T. G. Back and B. P. Dyck, *Chem. Commun.*, 1996, 2567.
113 K. Fujita, K. Murata, M. Iwaoka and S. Tomoda, *Tetrahedron*, 1997, **53**, 2029.
114 O. Tempkin, T. J. Blacklock, J. A. Burke and M. Anastasia, *Tetrahedron: Asymmetry*, 1996, **7**, 2721.
115 C. C. Silveira, A. L. Braga, A. Machado, G. L. Fiorin and M. J. Dabdoub, *Tetrahedron Lett.*, 1996, **37**, 9173.
116 A. E. A. Hassan, S. Shuto and A. Matsuda, *J. Org. Chem.*, 1997, **62**, 11.
117 C. Richert, A. L. Roughton and S. A. Benner, *J. Am. Chem. Soc.*, 1996, **118**, 4518.
118 D. K. Baeschlin, B. Hyrup, S. A. Benner and C. Richert, *J. Org. Chem.*, 1996, **61**, 7620.
119 D. G. Wang, B. Meng, M. J. Damha and G. Just, *Nucleosides, Nucleotides*, 1995, **14**, 1961.
120 S. Wendeborn, C. Jouanno, R. M. Wolf and A. Demesmaeker, *Tetrahedron Lett.*, 1996, **37**, 5511.
121 S. Czernecki and D. Randriamandimby, *J. Carbohydr. Chem.*, 1996, **15**, 183.
122 P. Bravo, M. Crucianelli, G. Fronza and M. Zanda, *Synlett*, 1996, 249.
123 Y. Kita, N. Shibata, N. Kawano, N. Yoshida, K. Matsumoto and Y. Takebe, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, 2321.
124 J. Kang, J. B. Kim, K. H. Cho and B. T. Cho, *Tetrahedron: Asymmetry*, 1997, **8**, 657.
125 M. Hayashi, K. Ono, H. Hoshimi and N. Oguni, *Tetrahedron*, 1996, **52**, 7817.
126 P. Bravo, F. Viani, M. Zanda, V. P. Kukhar, V. A. Soloshonok, N. Fokina, O. V. Shishkin and Y. T. Struchkov, *Gazz. Chim. Ital.*, 1996, **126**, 645.
127 N. Shibata, J. E. Baldwin, A. Jacobs and M. E. Wood, *Synlett*, 1996, 519.
128 N. Shibata, J. E. Baldwin, A. Jacobs and M. E. Wood, *Tetrahedron*, 1996, **52**, 12 839.
129 I. Andreadou, W. M. P. B. Menge, J. N. M. Commandeur, E. A. Worthington and N. P. E. Vermeulen, *J. Med. Chem.*, 1996, **39**, 2040.
130 M. Tingoli, L. Testaferri, A. Temperini and M. Tiecco, *J. Org. Chem.*, 1996, **61**, 7085.
131 B. Berthe, F. Outurquin and C. Paulmier, *Tetrahedron Lett.*, 1997, **38**, 1393.
132 M. Tiecco, L. Testaferri and L. Bagnoli, *Tetrahedron*, 1996, **52**, 6811.
133 Y. Diaz, A. Ellaghdach, M. I. Matheu and S. Castillon, *J. Org. Chem.*, 1997, **62**, 1501.
134 E. Chelain, S. Czernecki, M. Chmielewski and Z. Kaluza, *J. Carbohydr. Chem.*, 1996, **15**, 571.
135 O. De Lucchi, *Pure Appl. Chem.*, 1996, **68**, 945.
136 K. Hiroi, *Rev. Heteroatom. Chem.*, 1996, **14**, 21.
137 Y. Nishibayashi and S. Uemura, *Rev. Heteroatom. Chem.*, 1996, **14**, 83.
138 N. Komatsu and S. Uemura, *Advances in Detailed Reaction Mechanisms*, *vol. 4: Synthetically Useful Reactions*, ed. J. M. Coxon, JAI Press, Greenwich, CT, 1995.
139 M. Ordonez, V. Guerrerodelarosa, V. Labastida and J. M. Llera, *Tetrahedron: Asymmetry*, 1996, **7**, 2675.
140 A. Solladie-Cavallo, A. Diepvohuule, V. Sunjic and V. Vinkovic, *Tetrahedron: Asymmetry*, 1996, **7**, 1783.
141 V. K. Aggarwal, H. Abdel-Rahman, L. Fan, R. V. H. Jones and M. C. H. Standen, *Chem. Eur. J.*, 1996, **2**, 1024.
142 E. G. Mata, *Phosphorous*, *Sulfur*, *Silicon Relat. Elem.*, 1996, **117**, 231.
143 P. A. Ganeshpure and W. Adam, *Synthesis*, 1996, 179.
144 V. A. Petrov and G. Resnati, *Chem. Rev.*, 1996, **96**, 1809.
145 J. Mlochowski and S. B. Said, *Pol. J. Chem.*, 1997, **71**, 149.
146 F. Chen, J. L. Wan, C. S. Guan, J. S. Yang and H. Zhang, *Synth. Commun.*, 1996, **26**, 253.
147 F. Bonadies, F. Deangelis, L. Locati and A. Scettri, *Tetrahedron Lett.*, 1996, **37**, 7129.
148 D. J. Procter, M. Thornton Pett and C. M. Rayner, *Tetrahedron*, 1996, **52**, 1841.
149 Z. Stec, J. Zawadiak, A. Skibinski and G. Pastuch, *Pol. J. Chem.*, 1996, **70**, 1121.
150 V. Hulea and P. Moreau, *J. Mol. Catal. A*, 1996, **113**, 499.
151 S. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2955.
152 K. N. Brown and J. H. Espenson, *Inorg. Chem.*, 1996, **35**, 7211.
153 S. W. Brown, A. Johnstone, C. W. Jones, A. M. Lee, S. C. Oakes and S. L. Wilson, *Recl. Trav. Chim. Pays-Bas.*, 1996, **115**, 244.
154 S. Padmaja, G. L. Squadrito, J. N. Lemercier, R. Cueto and W. A. Pryor, *Free Radicals Biol. Med.*, 1996, **21**, 317.
155 H. Masumoto and H. Sies, *Chem. Res. Toxicol.*, 1996, **9**, 262.
156 E. Bosch and J. K. Kochi, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, **22**, 2731.
157 M. Hirano, S. Yakabe, J. H. Clark and T. Morimoto, *J. Chem. Soc.*, *Perkin Trans. 1*, 1996, 2693.
158 V. Khanna, G. C. Maikap and J. Iqbal, *Tetrahedron Lett.*, 1996, **37**, 3367.
159 V. G. Nenajdenko, P. V. Vertelezkij, A. B. Koldobskij, I. V. Alabugin and E. S. Balenkova, *J. Org. Chem.*, 1997, **62**, 2483.
160 H. Schmidt, M. Bashirpoor and D. Rehder, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3865.
161 J. B. Bharathy, T. K. Ganesan, A. I. A. M. Sheriff and S. Rajagopal, *Tetrahedron*, 1997, **53**, 1131.
162 V. Sharma, P. K. Sharma and K. K. Banerji, *J. Chem. Res.* (*S*), 1996, 290.
163 V. K. Vyas, N. Jalani, S. Kothari and K. K. Banerji, *J. Chem. Res.* (*S*), 1996, 370.
164 E. L. Clennan and A. Greer, *J. Org. Chem.*, 1996, **61**, 4793.
165 R. Siedlecka and J. Skarzewski, *Synlett*, 1996, 757.
166 S. Nakamura, K. Goto, M. Kondo, S. Naito, M. Bando, M. Kido and K. Shishido, *Bioorg. Med. Chem. Lett.*, 1996, **6**, 937.
167 M. P. Gamble, G. M. P. Giblin, J. G. Montana, P. O'Brien, T. P. Ockendon and R. J. K. Taylor, *Tetrahedron Lett.*, 1996, **37**, 7457.
168 T. Y. Chau, H. C. Lin and W. Hu, *Synth. Commun.*, 1996, **26**, 1867.
169 H. Tanaka, R. Kikuchi and S. Torii, *Tetrahedron*, 1996, **52**, 2343.
170 C. A. Hutton and J. M. White, *Tetrahedron Lett.*, 1997, **38**, 1643.
171 J. M. Brunel and H. B. Kagan, *Bull. Soc. Chim. Fr.*, 1996, **133**, 1109.
172 J. M. Brunel and H. B. Kagan, *Synlett*, 1996, 404.
173 S. Superchi and C. Rosini, *Tetrahedron: Asymmetry*, 1997, **8**, 349.
174 H. J. Hamann, E. Hoft, D. Mostowicz, A. Mishnev, Z. Urbanczyk-lipkowska and M. Chmielewski, *Tetrahedron*, 1997, **53**, 185.
175 X. Min and Z. C. Chen, *Synth. Commun.*, 1997, **27**, 1315.
176 T. Wirth and U. H. Hirt, *Tetrahedron: Asymmetry*, 1997, **8**, 23.
177 M. Hirano, S. Yakabe, S. J. H. Clark, H. Kudo and T. Morimoto, *Synth. Commun.*, 1996, **26**, 1875.
178 A. Willetts, *Trends Biotech.*, 1997, **15**, 55.
179 S. Colonna, N. Gaggero, P. Pasta and G. Ottolina, *Chem. Commun.*, 1996, 2303.
180 G. Ottolina, G. Carrea, S. Colonna and A. Ruckemann, *Tetrahedron: Asymmetry*, 1996, **7**, 1123.
181 S. Colonna, N. Gaggero, G. Carrea and P. Pasta, *Chem. Commun.*, 1997, 439.
182 M. P. J. Vandeurzen, I. J. Remkes, F. Vanrantwijk and R. A. Sheldon, *J. Mol. Catal. A*, 1997, **117**, 329.
183 M. B. Fisher and A. E. Rettie, *Tetrahedron: Asymmetry*, 1997, **8**, 613.
184 J. Beecher, G. Grogan, S. Roberts and A. Willetts, *Biotech. Lett.*, 1996, **18**, 571.

185 H. L. Holland, M. J. Bornmann and G. Lakshmaiah, *J. Mol. Catal. B*, 1996, **1**, 97.
186 V. Alphand, N. Gaggero, S. Colonna and R. Furstoss, *Tetrahedron Lett.*, 1996, **37**, 6117.
187 M. Abo, A. Okubo and S. Yamazaki, *Tetrahedron: Asymmetry*, 1997, **8**, 345.
188 M. Braun, *Angew. Chem.*, *Int. Ed. Engl.*, 1996, **35**, 519.
189 T. Satoh, *Chem. Rev.*, 1996, **96**, 3303.
190 S. Oae, *Pure Appl. Chem.*, 1996, **68**, 805.
191 T. Satoh, *J. Synth. Org. Chem. Jpn.*, 1996, **54**, 481.
192 N. Gautier, N. Noiret, C. Nugierchauvin and H. Patin, *Tetrahedron: Asymmetry*, 1997, **8**, 501.
193 K. Yamamoto, K. Miyatake, Y. Nishimura and E. Tsuchida, *Chem. Commun.*, 1996, 2099.
194 A. R. Katritzky, B. Z. Yang and Y. F. Qian, *Synlett*, 1996, 701.
195 D. H. Hua, N. M. Lagneau, Y. Chen, P. M. Robben, G. Clapham and P. D. Robinson, *J. Org. Chem.*, 1996, **61**, 4508.
196 H. Kunzer, M. Thiel and B. Peschke, *Tetrahedron Lett.*, 1996, **37**, 1771.
197 F. M. Moghaddam and M. Ghaffarzadeh, *Tetrahedron Lett.*, 1996, **37**, 1855.
198 Z. S. Zhou, N. Jiang and D. Hilvert, *J. Am. Chem. Soc.*, 1997, **119**, 3623.
199 M. C. Carreno, *Chem. Rev.*, 1995, **95**, 1717.
200 M. Benechie and F. Khuonghuu, *J. Org. Chem.*, 1996, **61**, 7133.
201 S. B. Hadimani, R. P. Tanpure and S. V. Bhat, *Tetrahedron Lett.*, 1996, **37**, 4791.
202 A. B. Bueno, M. C. Carreno, J. L. G. Ruano, R. G. Arrayas and M. M. Zarzuelo, *J. Org. Chem.*, 1997, **62**, 2139.
203 H. Elouazzani, N. Khiar, I. Fernandez and F. Alcudia, *J. Org. Chem.*, 1997, **62**, 287.
204 G. Solladie, F. Somny and F. Colobert, *Tetrahedron: Asymmetry*, 1997, **8**, 801.
205 G. Solladie and L. Gressotkempf, *Tetrahedron: Asymmetry*, 1996, **7**, 2371.
206 G. Solladie and G. H. Chu, *Tetrahedron Lett.*, 1996, **37**, 111.
207 G. Solladie, M. Adamy and F. Colobert, *J. Org. Chem.*, 1996, **61**, 4369.
208 Y. Arai, A. Suzuki, T. Masuda, Y. Masaki and M. Shiro, *Chem. Pharm. Bull.*, 1996, **44**, 1765.
209 J. L. G. Ruano, D. Barros, M. C. Maestro, R. Arayamaturana and J. Fischer, *J. Org. Chem.*, 1996, **61**, 9462.
210 F. Abrate, P. Bravo, M. Frigerio, F. Viani and M. Zanda, *Tetrahedron: Asymmetry*, 1996, **7**, 581.
211 S. G. Davies, T. Loveridge and J. M. Clough, *Synlett*, 1997, 66.
212 A. Arnone, D. Gestmann, S. V. Meille, G. Resnati and G. Sidoti, *Chem. Commun.*, 1996, 2569.
213 K. Blades, S. T. Patel, J. M. Percy and R. D. Wilkes, *Tetrahedron Lett.*, 1996, **37**, 6403.
214 A. R. Hajipour, *Synth. Commun.*, 1996, **26**, 3627.
215 P. Bravo, S. Capelli, S. V. Meille, P. Seresini, A. Volonterio and M. Zanda, *Tetrahedron: Asymmetry*, 1996, **7**, 2321.
216 P. Bravo, G. Cavicchio, M. Crucianelli, A. L. Markovsky, A. Volonterio and M. Zanda, *Synlett*, 1996, 887.
217 Y. Q. Liu and J. C. Vederas, *J. Org. Chem.*, 1996, **61**, 7856.
218 J. C. Carretero, J. L. G. Ruano and L. M. M. Cabrejas, *Tetrahedron: Asymmetry*, 1997, **8**, 409.
219 K. Miyashita, M. Nishimoto, T. Ishino, H. Murafuji, S. Obika, O. Muraoka and T. Imanishi, *Tetrahedron*, 1997, **53**, 4279.
220 T. Imanishi, S. Obika, T. Nishiyama, M. Nishimoto, Y. Hamano, K. Miyashita and C. Iwata, *Chem. Pharm. Bull.*, 1996, **44**, 267.
221 J. M. Bartolome, M. C. Carreno and A. Urbano, *Tetrahedron Lett.*, 1996, **37**, 3187.
222 C. Louis and C. Hootele, *Tetrahedron: Asymmetry*, 1997, **8**, 109.
223 N. Maezaki, A. Sakamoto, M. Soejima, I. Sakamoto, L. Y. Xia, T. Tanaka, H. Ohishi, K. Sakaguchi and C. Iwata, *Tetrahedron: Asymmetry*, 1996, **7**, 2787.
224 N. Maezaki, M. Murakami, M. Soejima, T. Tanaka, T. Iwanishi and C. Iwata, *Chem. Pharm. Bull.*, 1996, **44**, 1146.
225 P. Gosselin, E. Bonfand and C. Maignan, *Synthesis*, 1996, 1079.
226 J. P. Marino, A. Viso and J. D. Lee, *J. Org. Chem.*, 1997, **62**, 645.
227 J. P. Marino, L. J. Anna, R. F. de la Pradilla, M. V. Martinez, C. Montero and A. Viso, *Tetrahedron Lett.*, 1996, **37**, 8031.
228 M. Mikolajczyk, W. H. Midura, B. Wladislaw, F. C. Biaggio, L. Marzorati, M. W. Wieczorek and J. Blaszczyk, *Tetrahedron*, 1997, **53**, 2959.
229 M. Mikolajczyk, J. A. Krysiak, W. H. Midura, M. W. Wieczorek and J. Blaszczyk, *Tetrahedron: Asymmetry*, 1996, **7**, 3513.
230 H. Elfakih, F. Pautet, D. Peters, H. Fillion, M. Soufiaoui and J. L. Luche, *J. Prakt. Chem./Chem.–Ztg.*, 1997, **339**, 176.
231 J. L. G. Ruano, J. C. Carretero, M. C. Carreno, L. M. M. Cabrejas and A. Urbano, *Pure Appl. Chem.*, 1996, **68**, 925.
232 E. Cecchet, F. Difuria, G. Licini, and G. Modena, *Tetrahedron: Asymmetry*, 1996, **7**, 369.
233 M. C. Carreno, J. L. G. Ruano, A. Urbano and M. I. Lopez-Solera, *J. Org. Chem.*, 1997, **62**, 976.
234 M. C. Carreno, J. L. G. Ruano, A. Urbano and M. A. Hoyos, *J. Org. Chem.*, 1996, **61**, 2980.
235 Y. Arai, T. Masuda and Y. Masaki, *Chem. Lett.*, 1997, 145.
236 M. C. Carreno, M. B. Cid and J. L. G. Ruano, *Tetrahedron: Asymmetry*, 1996, **7**, 2151.
237 P. Gosselin, E. Bonfand and C. Maignan, *J. Org. Chem.*, 1996, **61**, 9049.
238 R. S. Paley, M. B. Rubio, R. F. de la Pradilla, R. Dorado, G. H. Sood and M. Martinez-Ripoll, *Organometallics*, 1996, **15**, 4672.
239 P. Renaud, *Chimia*, 1996, **50**, 135.
240 C. Alayrac, C. Fromont, P. Metzner and N. T. Anh, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, **36**, 371.
241 K. Ishiguro, M. Hayashi and Y. Sawaki, *J. Am. Chem. Soc.*, 1996, **118**, 7265.
242 D. C. Bohle, P. A. Glassbrenner and B. Hansert, *Tetrahedron Lett.*, 1997, **38**, 2425.
243 N. Kamigata, K. Udodaira and T. Shimizu, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 783.
244 W. Keim, J. Herwig and G. Pelzer, *J. Org. Chem.*, 1997, **62**, 422.
245 J. Lee and P. H. Lee, *Tetrahedron Lett.*, 1996, **37**, 9305.
246 M. C. Bernabeu, P. Bonete, F. Caturla, R. Chinchilla and C. Najera, *Tetrahedron: Asymmetry*, 1996, **7**, 2475.
247 Y. Morimoto, A. Mikami, S. Kuwabe and H. Shirahama, *Tetrahedron: Asymmetry*, 1996, **7**, 3371.
248 S. H. Kang and C. M. Kim, *Synlett*, 1996, 515.
249 D. J. Hart and W. L. Wu, *Tetrahedron Lett.*, 1996, **37**, 5283.
250 R. Bellingham, K. Jarowicki, P. J. Kocienski and V. Martin, *Synthesis*, 1996, 285.
251 A. B. Charette and H. Lebel, *J. Am. Chem. Soc.*, 1996, **118**, 10 327.
252 N. D. Smith, P. J. Kocienski and S. D. A. Street, *Synthesis*, 1996, 652.
253 H. Kigoshi, K. Suenaga, T. Mutou, T. Ishigaki, T. Atsumi, H. Ishiwata, A. Sakakura, T. Ogawa, M. Ojika and K. Yamada, *J. Org. Chem.*, 1996, **61**, 5326.
254 K. Tsuboi, Y. Ichikawa, Y. M. Jiang, A. Naganawa and M. Isobe, *Tetrahedron*, 1997, **53**, 5123.
255 M. Ihara, S. Suzuki, Y. Tokunaga, H. Takeshita and K. Fukumoto, *Chem. Commun.*, 1996, 1801.
256 B. M. Trost and D. Barrett, *Tetrahedron*, 1996, **52**, 6903.
257 E. D. Phillips, S. Warren and G. H. Whitham, *Tetrahedron*, 1997, **53**, 307.
258 Z. M. Dong, S. G. Pyne, B. W. Skelton and A. H. White, *Synlett*, 1997, 103.
259 M. A. Collins and D. N. Jones, *Tetrahedron*, 1996, **52**, 8795.
260 V. K. Yadav and K. K. Kapoor, *Tetrahedron*, 1996, **52**, 3659.
261 Y. Mori, K. Yaegashi and H. Furukawa, *J. Am. Chem. Soc.*, 1996, **118**, 8158.
262 Y. Mori, K. Yaegashi, K. Iwase, Y. Yamamori and H. Furukawa, *Tetrahedron Lett.*, 1996, **37**, 2605.
263 R. F. de la Pradilla, P. Manzano, J. Priego, A. Viso, M. Martinez-Ripoll and A. Rodriguez, *Tetrahedron Lett.*, 1996, **37**, 6793.
264 D. A. Alonso, A. Costa, B. Mancheno and C. Najera, *Tetrahedron*, 1997, **53**, 4791.
265 J. H. Jung, J. W. Lee, C. W. Lee and D. Y. Oh, *Synth. Commun.*, 1996, **26**, 3715.
266 J. Sisko, M. Mellinger, P. W. Sheldrake and N. H. Baine, *Tetrahedron Lett.*, 1996, **37**, 8113.
267 S. Cossu, O. De Lucchi, F. Fabris, R. Ballini and G. Bosica, *Synthesis*, 1996, 1481.
268 K. Smith, G. M. Ewart and K. R. Randles, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 1085.
269 N. J. Lawrence, J. Liddle and D. A. Jackson, *Synlett*, 1996, 55.
270 M. Makosza, *Pure Appl. Chem.*, 1997, **69**, 559.
271 J. W. Grissom, D. Klingberg, D. H. Huang and B. J. Slattery, *J. Org. Chem.*, 1997, **62**, 603.
272 M. J. Wu, C. F. Lin and C. W. Ong, *Bioorg. Med. Chem. Lett.*, 1996, **6**, 675.
273 W. M. Dai, K. C. Fong, H. Danjo, S. Nishimoto, M. Solow, W. L. Mak and M. L. Yeung, *Bioorg. Med. Chem. Lett.*, 1996, **6**, 1093.
274 H. Lhermitte and D. S. Grierson, *Contemp. Org. Synth.*, 1996, **3**, 93.
275 M. J. Wu, C. F. Lin, H. T. Chen, T. H. Duh, S. S. Wang and S. C. Hsu, *Bioorg. Med. Chem. Lett.*, 1996, **6**, 2183.

276 W. M. Dai, K. C. Fong, H. Danjo and S. Nishimoto, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 779.
277 S. S. P. Chou and C. H. Hsu, *Tetrahedron Lett.*, 1996, **37**, 5373.
278 Y. S. Lee, E. K. Ryu, K. Y. Yun and Y. H. Kim, *Synlett*, 1996, 247.
279 S. Sengupta and S. Bhattacharyya, *Synth. Commun.*, 1996, **26**, 231.
280 R. Grigg, C. Najera, J. M. Sansano and M. Yus, *Synth.Commun.*, 1997, **27**, 1111.
281 G. L. Edwards, C. A. Muldoon and D. J. Sinclair, *Tetrahedron*, 1996, **52**, 7779.
282 S. Caddick, C. L. Shering and S. N. Wadman, *Chem. Commun.*, 1997, 171.
283 J. Xiang and P. L. Fuchs, *J. Am. Chem. Soc.*, 1996, **118**, 11 986.
284 J. S. Xiang, A. Mahadevan and P. L. Fuchs, *J. Am. Chem. Soc.*, 1996, **118**, 4284.
285 K. Aboutayab, S. Caddick, K. Jenkins, S. Joshi and S. Khan, *Tetrahedron*, 1996, **52**, 11 329.
286 P. J. Crowley, J. M. Percy and K. Stansfield, *Tetrahedron Lett.*, 1996, **37**, 8233.
287 P. J. Crowley, J. M. Percy and K. Stansfield, *Tetrahedron Lett.*, 1996, **37**, 8237.
288 T. Kataoka, Y. Banno, S. Watanabe, T. Iwamura and H. Shimizu, *Tetrahedron Lett.*, 1997, **38**, 1809.
289 H. Suzuki and H. Abe, *Tetrahedron Lett.*, 1996, **37**, 3717.
290 J. L. Luche, *C. R. Acad. Sci., Ser. 2*, 1996, **323**, 203.
291 J. L. Luche, *Ultrasonics Sonochemistry*, 1996, S215.
292 D. Craig, C. J. Etheridge and A. M. Smith, *Tetrahedron*, 1996, **52**, 15 267.
293 J. C. Carretero, R. G. Arrayas and I. S. Degracia, *Tetrahedron Lett.*, 1996, **37**, 3379.
294 M. Casillas, A. M. Gomez, J. C. Lopez and S. Valverde, *Synlett*, 1996, 628.
295 H. Eichelmann and H. J. Gais, *Tetrahedron: Asymmetry*, 1995, **6**, 643.
296 B. M. Trost, *Pure Appl. Chem.*, 1996, **68**, 779.
297 N. Vicart, B. Cazes and J. Gore, *Tetrahedron*, 1996, **52**, 9101.
298 B. M. Trost, M. T. Sorum, C. Chan, A. E. Harms and G. Ruhter, *J. Am. Chem. Soc.*, 1997, **119**, 4, 698.
299 C. W. Holzapfel and T. L. Vandermerwe, *Tetrahedron Lett.*, 1996, **37**, 2303.
300 D. A. Alonso, L. R. Falvello, B. Mancheno, C. Najera and M. Tomas, *J. Org. Chem.*, 1996, **61**, 5004.
301 F. Caturla and C. Najera, *Tetrahedron Lett.*, 1996, **37**, 4787.
302 E. Ghera, T. Yechezkel and A. Hassner, *J. Org. Chem.*, 1996, **61**, 4959.
303 C. M. G. Lofstrom and J. E. Backvall, *Tetrahedron Lett.*, 1996, **37**, 3371.
304 A. P. Dishington, R. E. Douthwaite, A. Mortlock, A. B. Muccioli and N. S. Simpkins, *J. Chem. Soc., Perkin Trans. 1*, 1997, 323.
305 A. Padwa, Z. Ni and S. H. Watterson, *Pure Appl. Chem.*, 1996, **68**, 831.
306 J. F. King, M. S. Gill and D. F. Klassen, *Pure Appl. Chem.*, 1996, **68**, 825.