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RECENT ADVANCES IN THE SYNTHESIS AND TRANSFORMATIONS OF HETEROCYCLES MEDIATED BY FLUORIDE ION ACTIVATED ORGANOSILICON COMPOUNDS

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Abstract – Modern methodologies of preparation and transformation of three-, four-, five- and six-membered heterocycles and their functional groups using silanes in the presence of fluoride ion have been reviewed. Syntheses of large sized heterocyclic compounds are also included.

INTRODUCTION

Reactions of organosilicon compounds catalyzed by nucleophiles are under extensive study more than twenty five years. In this field two excellent reviews are published.[1] Fluoride ion as activator of silicon bonds is widely described in these works. Some reactions of silyl derivatives of furans mediated by fluoride ion were described in reviews.[2] Recently we have published two reviews dedicated to fluoride ion activation of silicon bonds in organic synthesis [3] and transition metal catalysed coupling reactions of silanes activated by fluoride ion.[4] However, synthesis and transformations of heterocyclic compounds mediated by fluoride ion activation of silicon bonds were not included in these reviews.

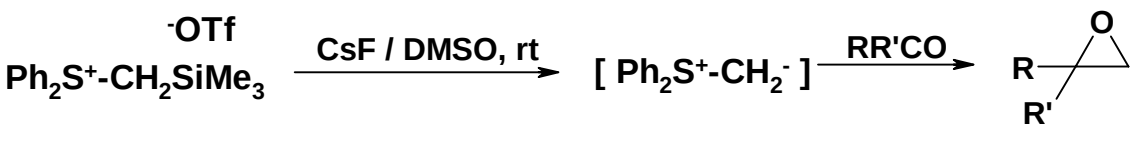
The aim is to describe modern methodologies in the synthesis of different classes of heterocyclic compounds mediated by fluoride ion activated organosilicon compounds. The influence of different sources of fluoride ion on processes and mechanisms of reactions will be discussed. Characteristic reactions in side chains of heterocyclic compounds are also presented.

The literature data published between January 1994 and July 2001 are included in this review.

THREE-MEMBERED RINGS

1.1. Oxiranes

The reaction of diphenylsulfonium methylide with carbonyl compounds is an excellent route to oxiranes. The necessary methylide (**2**) was successfully obtained by treatment of diphenyl(trimethyl-silylmethyl)sulfonium triflate (**1**) with CsF in DMSO. The ylide formed reacted with carbonyl compounds to afford oxiranes (**3**) in yields up to 94% (Scheme 1).[5]

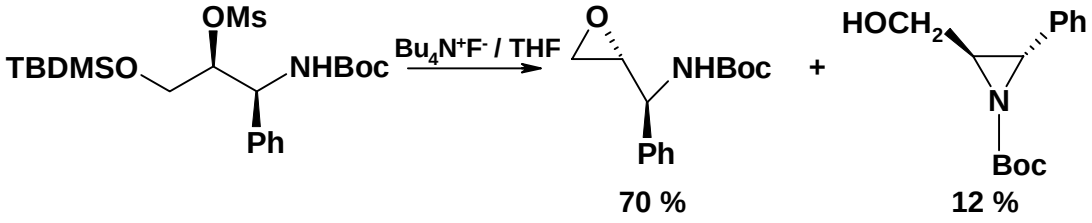


1 **2** **3**

R, R' = H, alkyl, aryl

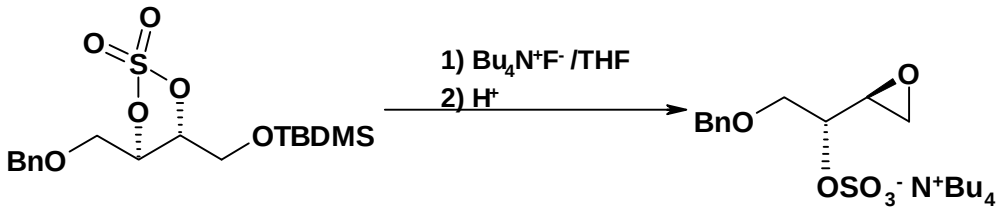
Scheme 1

Stereoselective synthesis of (*1S,2R*)-*N*-*tert*-butoxycarbonyl-1-phenyl-2,3-epoxy-1-propylamine (**5**) from (*1S,2S*)-*N*-*tert*-butoxycarbonylamino-3-*tert*-butyldimethylsiloxy-2-mesyloxy-1-phenyl-1-propylamine (**4**) in the presence $Bu_4N^+F^-$ / THF was carried out. However, reaction mixture after reaction completion contained also 12% of aziridine (**6**) (Scheme 2).[6]



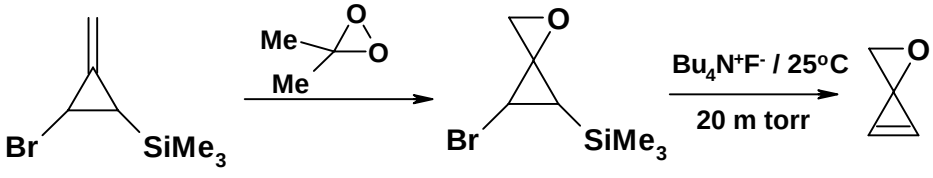
Scheme 2

Interaction of silylated cyclic sulfates with fluoride ion afforded anions of epoxy substituted sulfonic acids. For example, sulfate (**7**) in the presence of $Bu_4N^+F^- \cdot 3\ H_2O$ / THF gave epoxide (**8**) as the main product (Scheme 3). Nucleophilic epoxide ring opening provides an excellent route to *erythro*-2,3-diols.[7,8]



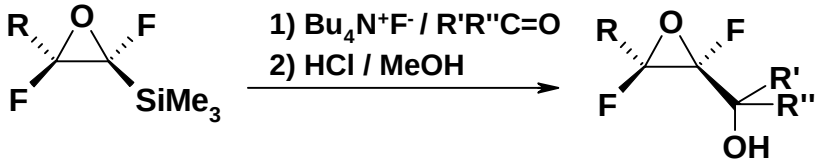
Scheme 3

Synthesis of oxaspiropentene (**11**) was recently described. Thus, epoxidation of *cis*- or *trans*-1-methylene-2-bromo-3-(trimethylsilyl)cyclopropane (**9**) by dimethyldioxirane followed by interaction of intermediate (**10**) with $Bu_4N^+F^-$ using the vacuum gas-solid reaction procedure led to oxirane (**11**) (Scheme 4).[9]



Scheme 4

Difluorinated epoxides (**12**) and carbonyl compounds in the presence of fluoride ion source afforded epoxy alcohols (**13**) in 48-85 % yields (Scheme 5). The resulting epoxides are valuable fluorinated building blocks.[10]

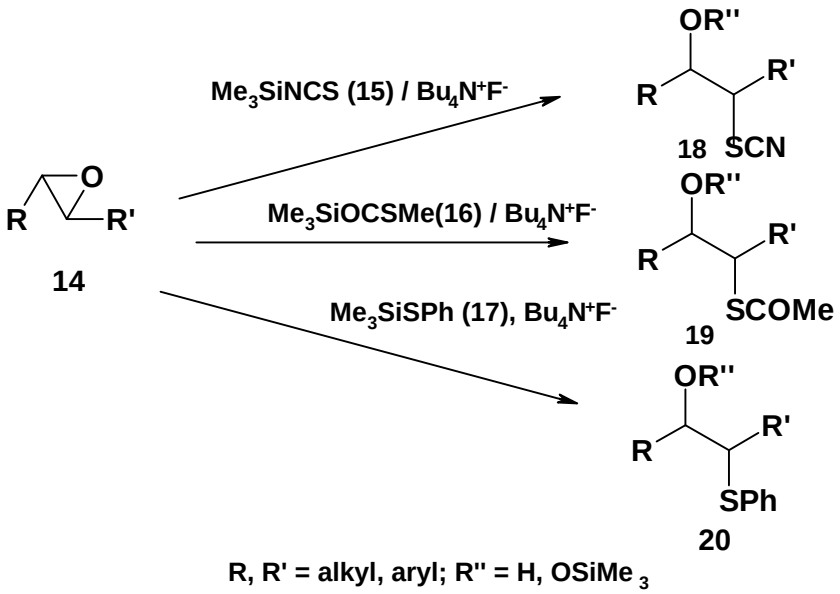


12 **13**

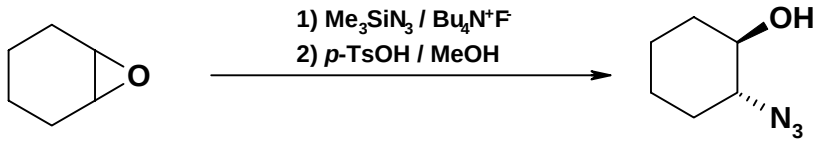
R, R', R'' = H, alkyl, aryl

Scheme 5

Regioselective oxirane ring opening by interaction with silylated nucleophiles in the presence of fluoride ion source was reported in some articles. Thus, oxiranes (**14**) and isothiocyanatotrimethylsilane (**15**), *O*-trimethylsilyl thioacetate (**16**) or phenylthiotrimethylsilane (**17**) in the presence of catalytic amounts of $Bu_4N^+F^-$ afforded corresponding alcohols or their silyl ethers (**18**-**20**) in overall yields up to 99% (Scheme 6).[11] Cyclohexene oxide (**21**) and azidotrimethylsilane in the presence of $Bu_4N^+F^-$ at room temperature gave alcohol (**22**) in 93 % yield.[12]



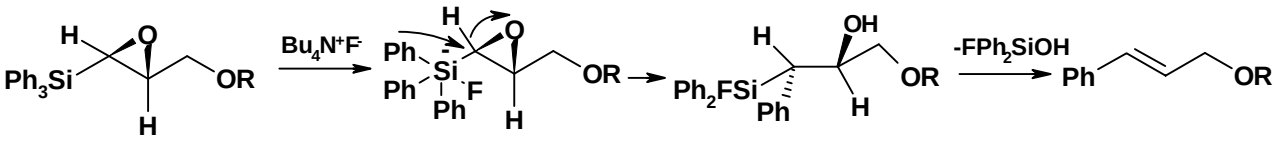
R, R' = alkyl, aryl; R'' = H, OSiMe 3



21 **22**

Scheme 6

Migration of aryl groups from silicon to carbon in α,β-epoxysilanes (**23**) in the presence of $Bu_4N^+F^-$ was explained by formation of hypervalent silicon intermediate (**24**). Pentacoordinate silicon derivative (**24**) rearranges with simultaneous epoxide ring opening to give β-hydroxysilane (**25**). The last step of rearrangement involves the fluorodiphenylsilanolate elimination and formation of alkenes (**26**) as main products (Scheme 7).[13]



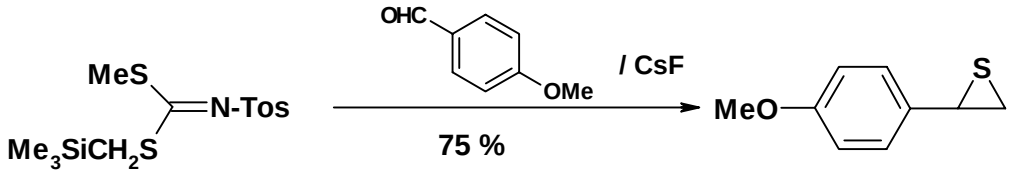
23 **24** **25** **26**

R = H,*p*-$O_2NC_6H_4CO$

Scheme 7

1.2. Thiiranes

The reaction of *S*-methyl-*S*'-trimethylsilylmethyl *N*-*p*-toluenesulfonylcarboimidodithiate (**27**) with *p*-methoxybenzaldehyde was carried out in the presence of different sources of fluoride ion. Using CsF in MeCN at room temperature the desired 2-(3-methoxyphenyl)thiirane (**28**) was obtained in 75 % yield (Scheme 8).[14] Similarly 2-arylthiiranes can be prepared. Formation of thiiranes proceeds *via* ring construction of intermediates 1,3-oxathiolanes.

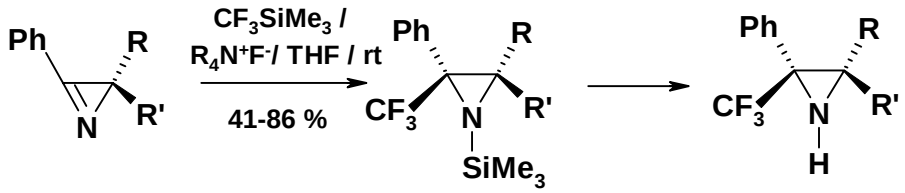


27 **28**

Scheme 8

1.3. Aziridines

Novel stereoselective synthesis of *E*-aziridines (**30**) by addition of CF_3SiMe_3 to azirines (**29**) in the presence of $R_4N^+F^-$ (R = Et, *n*-Bu) / THF was described (Scheme 9).[15]

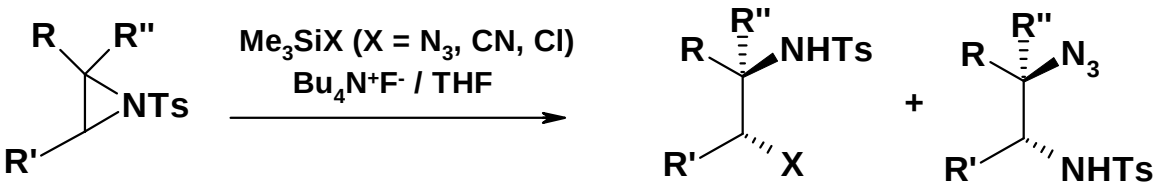


29 **30**

R, R' = H, Me, Ph, CO_2Me

Scheme 9

Ring-opening reactions of aziridines with different silylated compounds proceed regioselectively in the presence of $Bu_4N^+F^-$ to give corresponding products in excellent yields. Thus, *N*-tosylaziridines (**31**) in the system Me_3SiX (X = N_3, CN, Cl) / $Bu_4N^+F^-$ / THF at room temperature afforded N-tosylamines (**32-34)** in 60-99 % yields (Scheme 10). Only in the case of azidotrimethylsilane as silicon nucleophile the formation of isomeric amines (**35**) was detected in yields up to 58%.[16]



31

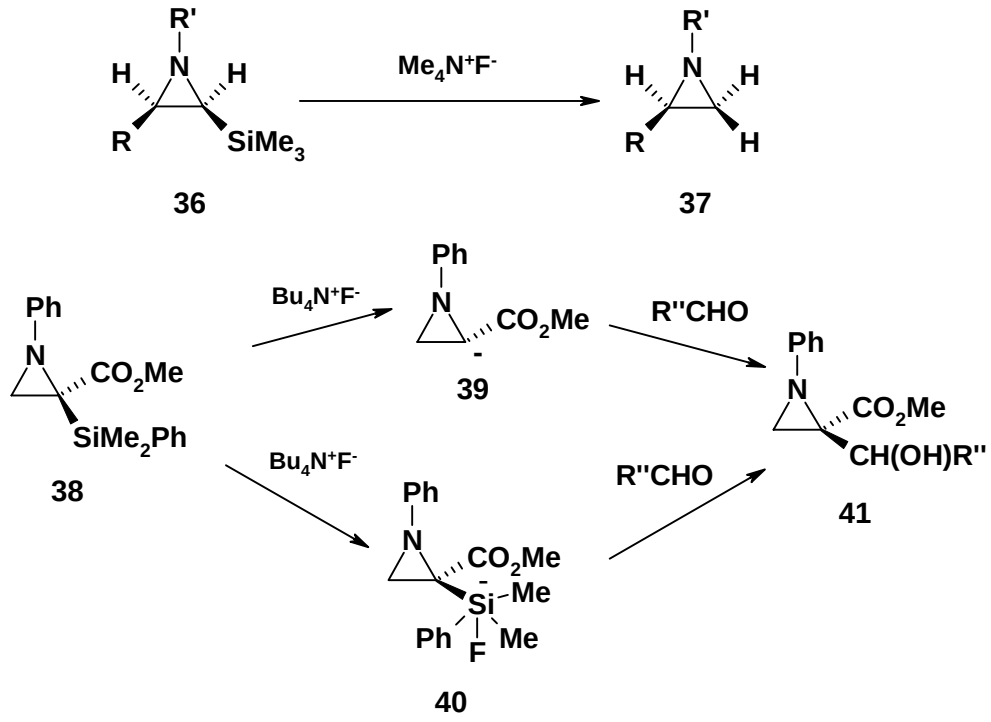
32; X = N_3
33; X =CN
34; X = Cl

35

R, R', R'' = H, alkyl, aryl

Scheme 10

trans-1,3-Diphenyl-2-trimethylsilylaziridine (**36**) reacts with $Me_4N^+F^-$ to give the desilylated product (**37**) rather than a ring opened product (Scheme 11). The interaction of aziridine (**38**) with fluoride ion in the presence of aldehydes affords addition products (**41**) in yields up to 56 %. Two mechanisms can be proposed for the desilylation and concomitant reaction with the aldehyde or proton. Firstly fluoride ion attacks the silicon to form trialkylsilyl fluoride and a free aziridinyl carbanion (**39**). Intermediate (**39**) then reacts with carbonyl compound to form aziridine (**41**). Alternatively, fluoride ion could attack the silicon to generate pentacoordinate silicon species (**40**) which subsequently attacks the carbonyl compound.[17]



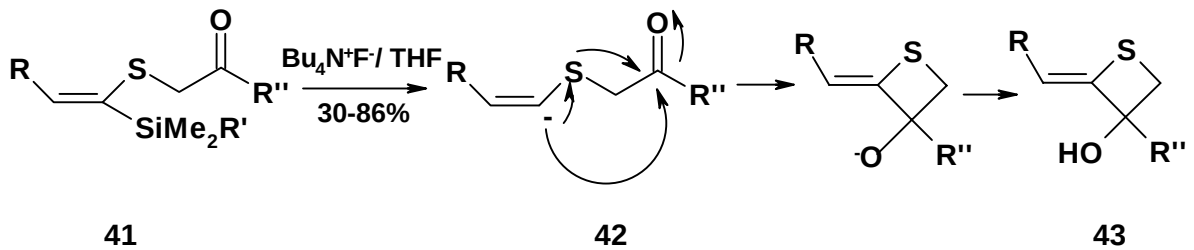
R, R' = H, alkyl, aryl; R'' = alkyl, aryl

Scheme 11

Similar addition of aldehydes to 2-trimethylsilylaziridines can be carried out in the presence of tetrabutylammonium triphenyldifluorosilicate as fluoride ion source.[18]

2. FOUR- MEMBERED RINGS

Fluoride mediated synthesis of thietanols (**43**) from *Z*-α-silyl vinyl sulfides (**41**) was described. The formation of products (**43**) occurs *via* desilylated intermediates (**42**), which easily undergo cyclization to thietanol derivatives (Scheme 12).[19]

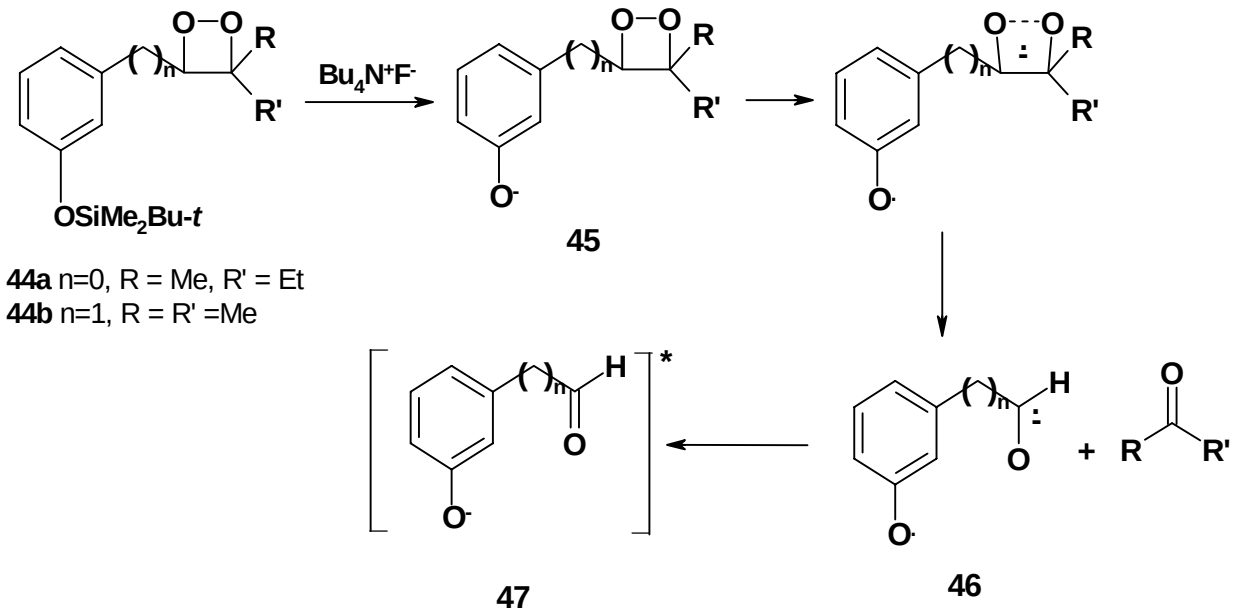


41 **42** **43**

R, R', R'' = alkyl, aryl

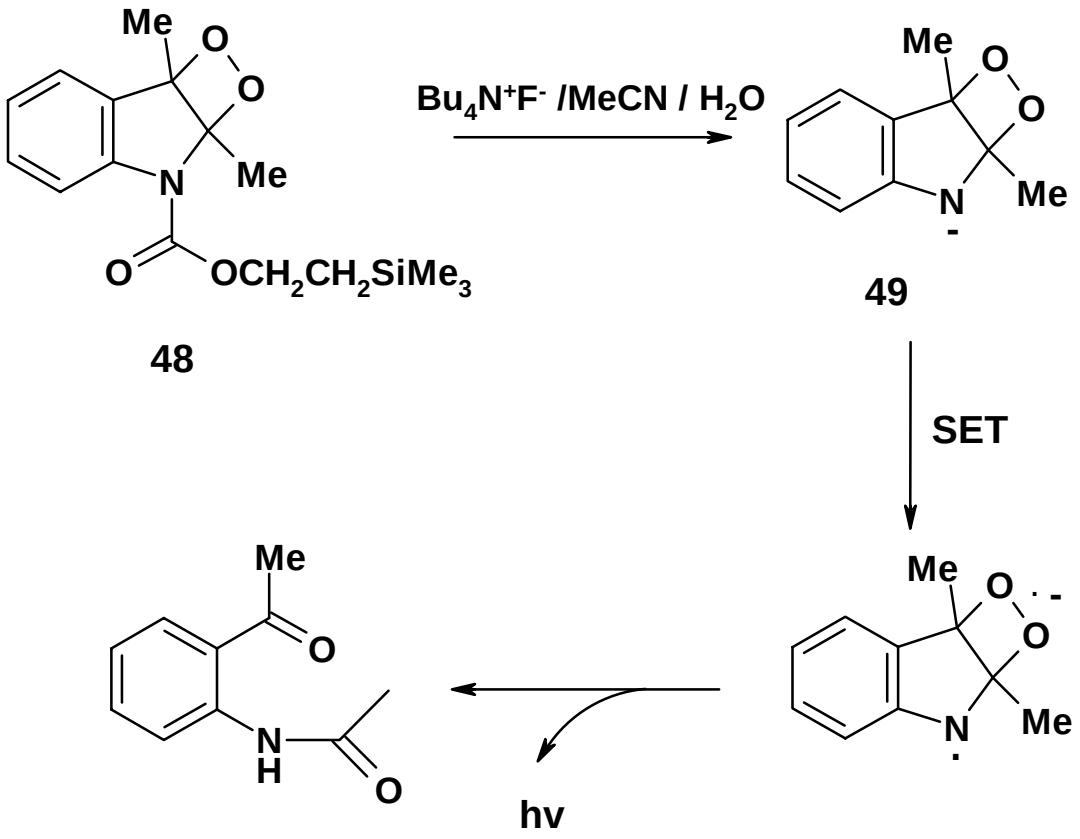
Scheme 12

Fluoride-mediated decomposition of silicon containing dioxetanes by an intramolecular electron transfer mechanism was described in some articles. Thus, interaction of dioxetanes (**44**) with $Bu_4N^+F^-$ leads to formation of phenoxide ions (**45**). The first electron transfer from the phenoxide to the peroxide ring, which is supposed to be accompanied by the peroxide cleavage, occurs with similar rate constants in both cases. In the case of **44a**, the carbonyl radical anion (**46**) (n = 0), generated after the peroxide cleavage, represents directly the excited state (**47**) (n = 0). In the case of **44b** this stabilization is not possible, turning excited state formation by back electron transfer less efficient (Scheme 13).[20]



Scheme 13

Similar CIEEF (chemically initiated electron exchange fluorescence) emission was detected by fluoride ion mediated decomposition of 2a,7b-dimethyl-3-[2-(trimethylsilyl)ethoxycarbonyl]-2a,7b-dihydro-1,2-dioxeto[3,4-*b*]indole (**48**). The proposed mechanism involves removal of *N*-silyl protecting through fluoride ion promoted *E*-2 type elimination to generate the free indolyl anion (**49**), which subsequently acts as intramolecular electron donor to dioxetane moiety. After single electron transfer (SET), breakage of O-C bond with formation of ketyl radical, and electron back-transfer, an electronically excited state is generated, which emits fluorescence (Scheme 14).[21]

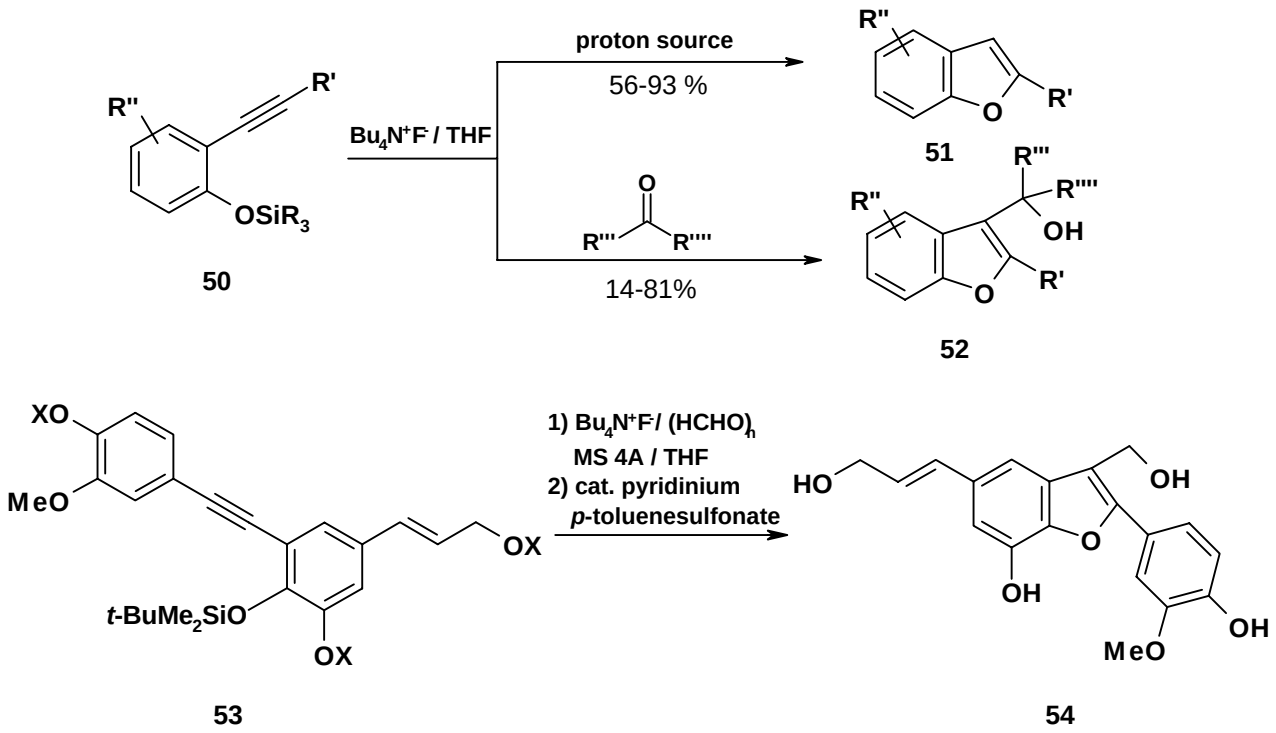


Scheme 14

3. FIVE-MEMBERED RINGS

3.1. Furan, tetrahydrofuran, tetrahydrothiophenes, tetrahydroselenophenes

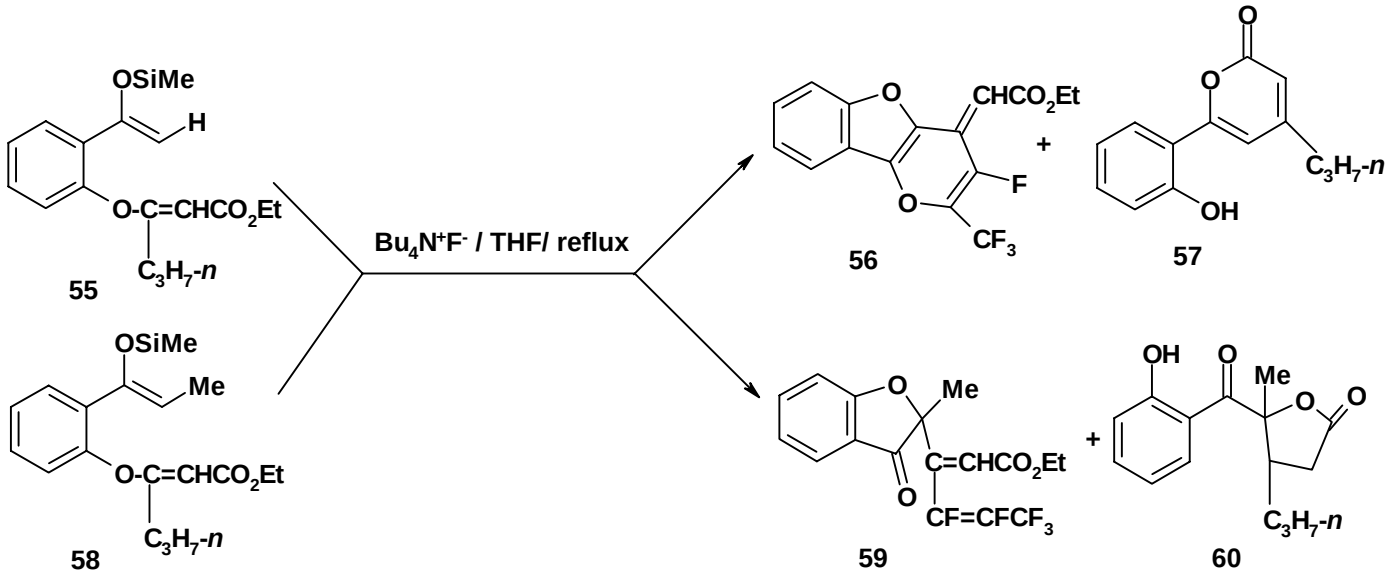
A general fluoride mediated method of synthesis of substitituted benzofurans was developed. Thus, *o*-triisopropylsiloxyarylacetylenes (**50**) were easily converted to benzofurans (**51**) or (**52**) by treatment with proton source or carbonyl compound in the $Bu_4N^+F^-$ / molecular sieves 4A / THF /system.[22] The above method was successfully used in the synthesis of benzofuran-type lignan vibsanol (**54**) from silyl ether (**55**) (Scheme 15).[23,24]



R = i-Pr; R', R'' = H, alkyl, methoxy; R''', R'''' = H, alkyl, aryl, hetaryl; X = $EtOCH_2CH_2$

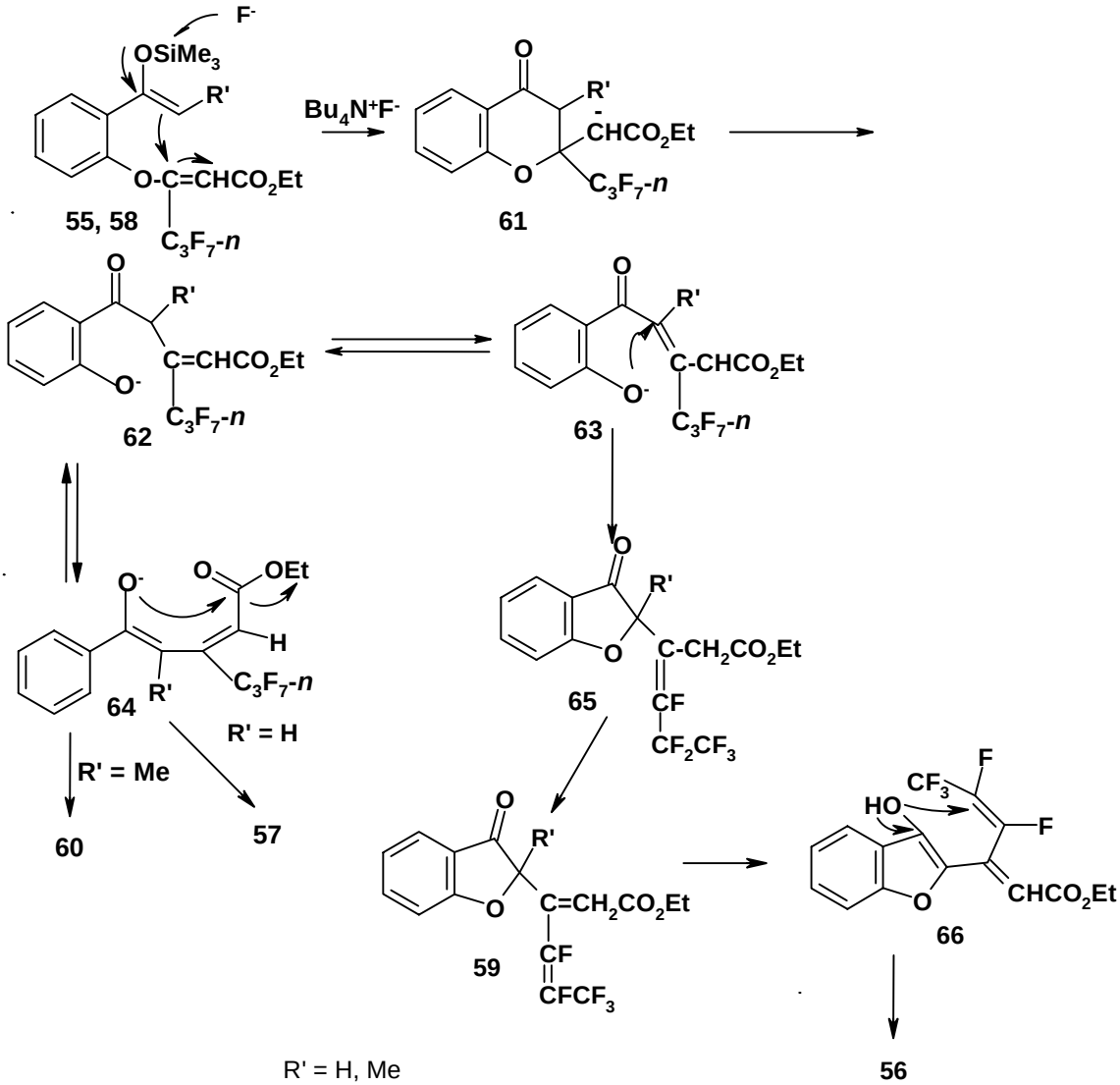
Scheme 15

Synthesis of fluorinated derivatives of benzofurans from silyl enol ethers was reported. For example, acetophenone derivative (**55**) in the presence $Bu_4N^+F^-$ / MeCN afforded a mixture of benzofuran (**56**) (41 %) and lactone (**57**) (22 %). Propiophenone derivative (**58**) in the similar conditions afforded mixture of 3(2*H*)-benzofuranone (**59**) (28 %) and lactone (**60**) (43%) (Scheme 16).[25]



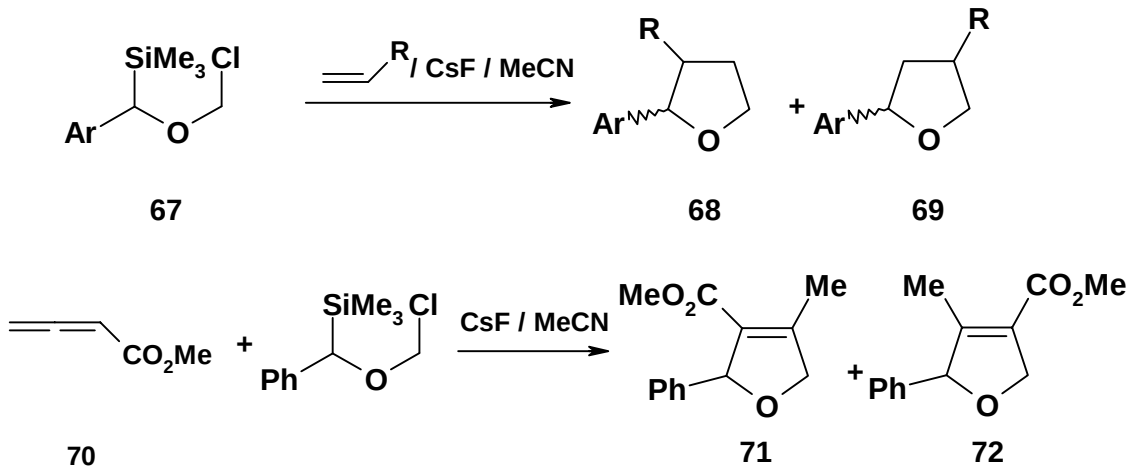
Scheme 16

The proposed mechanism of formation of compounds (**56, 57, 59** and **60**) from silyl enol ethers (**55** and **58**) is illustrated in Scheme 18. Upon treatment of compounds (**55**, **58)** with $Bu_4N^+F^-$, the O-Si bond of silyl enol ethers is cleaved with the formation of an enolate ion, which undergoes intramolecular Michael addition reaction to the α,β-unsaturated carbonyl group. The resulting intermediate (**61**) then opens the ring with the aryloxy anion as a leaving group, and the formation of intermediate (**62**), which can isomerize to **63** or enolize to **64**. In intermediate (**63**), the aryloxy anion acts as a nucleophile to attack the double bond to give benzofuranone (**65**)**,** which dehydrofluorinates further and gives **59**. Starting with propiophenone derivative (**58**) (R' = Me) benzofuranone (**59**) is final product. With the acetophenone derivative (**55**) (R = H), **59** tautomerizes to **66**. In benzofuran (**66**), the enol acts as a nucleophile and adds intramolecularly in a 1,6-conjugate manner followed by elimination of fluoride to give **56** as final product (Scheme 17).



Scheme 17

Reaction of carbonyl ylides, generated from chloromethyl silylmethyl ethers, with alkenes provides a good route to di- or trisubstituted tetrahydrofurans. Thus, reaction of ethers (**67**) with alkenes in the presence of CsF / MeCN leads to tetrahydrofurans (**68** and **69**) in overall yield 55-93 % (Scheme 18). Allene (**70**) in the similar reaction afforded a mixture of two dihydrofurans (**71**) and (**72**) (ratio 68: 32) in overall yield 72 %. [26]



R = alkyl, aryl; Ar = aryl

Scheme 18

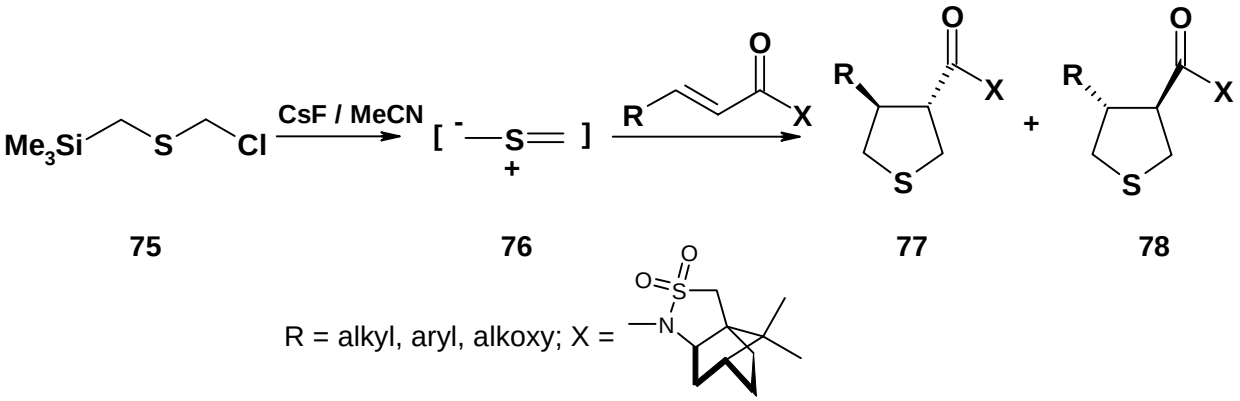
A variety of α-trimethylsilylmethyl-substituted butyrolactones are easily obtained by tandem ene-reaction / oxidative desilylation reaction. Reaction of silyl enol ether (**73**) with $Bu_4N^+F^-$ / THF and then with tetra(*n*-propyl)ammonium perruthenate (TPAP) and *N*-methylmorpholine *N*-oxide (NMO) afforded lactones (**74**) in 55-80 % yields with *de* up to 70% (Scheme 19).[27,28]

R = alkyl

Scheme 19

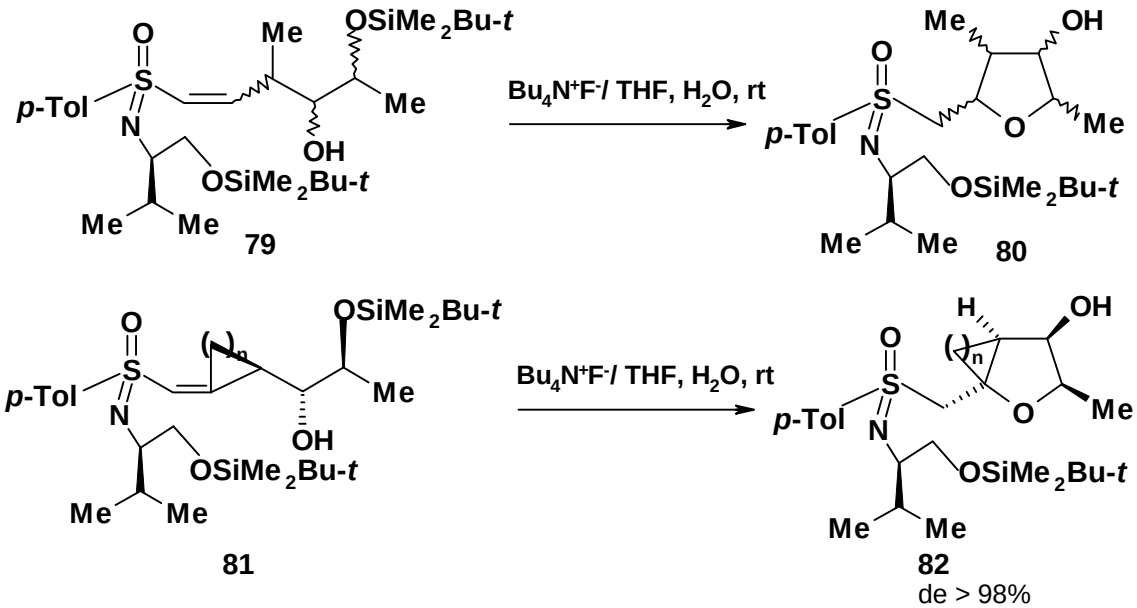
Asymmetric 1,3-dipolar cycloaddition of sulfur-containing 1,3-dipole and α,β-unsaturated camphorsultam amides as dipolarophiles was described. Thus, interaction of chloromethyl trimethylsilylmethyl sulfide (**75**) with CsF / MeCN furnishes thiocarbonyl ylide (**76**), which further reacts

with chiral α,β-unsaturated amides to afforded tetrahydrothiophenes (**77**) and (**78**) (ratio up to 90 : 10) in 90-95 % yields (Scheme 20).[29]



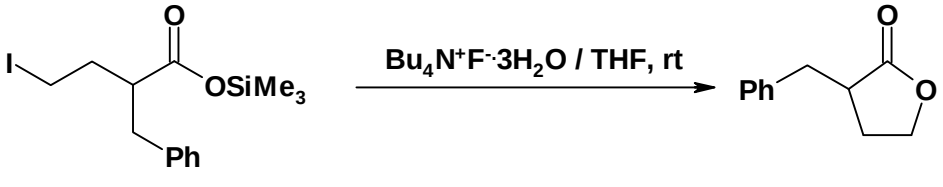
Scheme 20

5-Siloxy substituted vinyl sulfoximines (**79**) in the presence of fluoride ion undergo deprotection followed by cyclization reaction to form tetrahydrofuran derivatives (**80**) as main products. Similarly, silyl ethers (**81**) in the system $Bu_4N^+F^-$ / THF / H_2O were transformed to bicyclic tetrahydrofurans (**82**) (Scheme 21).[30,31]



Scheme 21

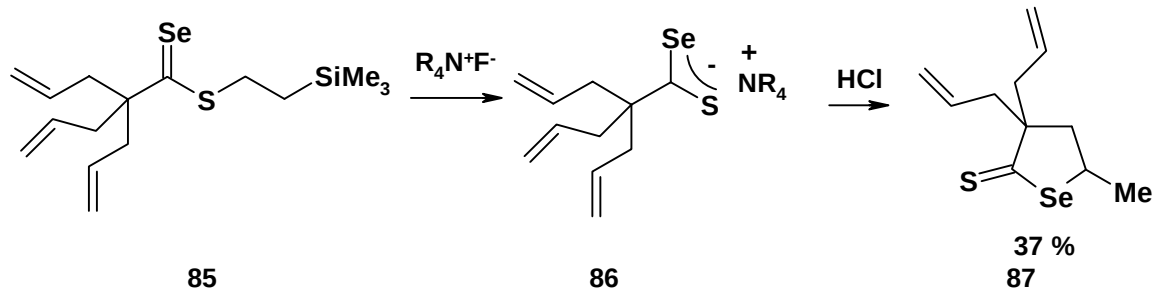
Treatment of trimethylsilyl 4-iodo-2-benzylbutanoate (**83**) with $Bu_4NF{\cdot}3H_2O$ / THF at room temperature



83 **Scheme 22** **84**

afforded lactone (**84**) in 98 % yield (Scheme 22).[32]

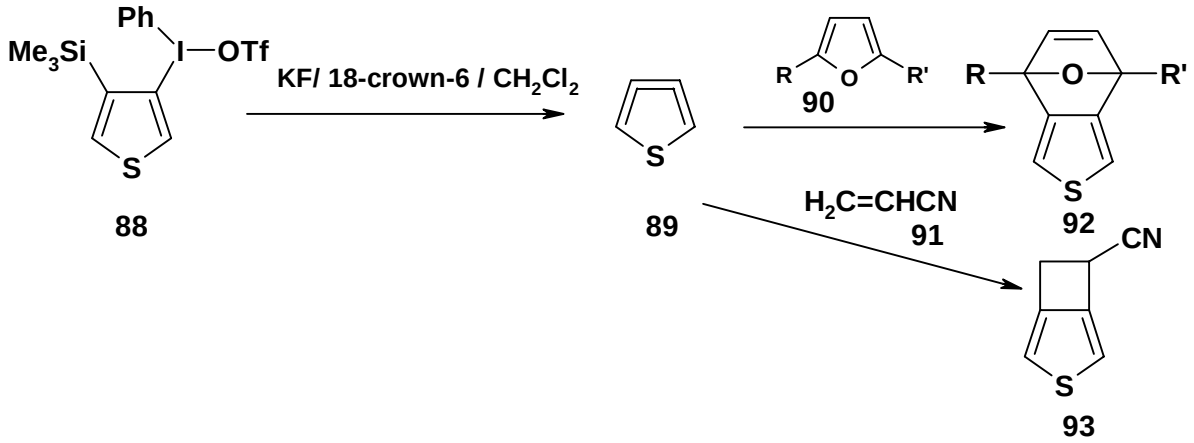
Selenothiolactone (**87**) was successfully obtained from selenothioic acid *S*-2-trimethylsilylethyl ester (**85**) by treatment with $R_4N^+F^-$ (R = Me, Bu) / THF and then with HCl / Et_2O. The formation of product (**87**) occurs *via* intermediate ammonium selenothioates (**86**) (Scheme 23).[33]



R = Me, Bu

Scheme 23

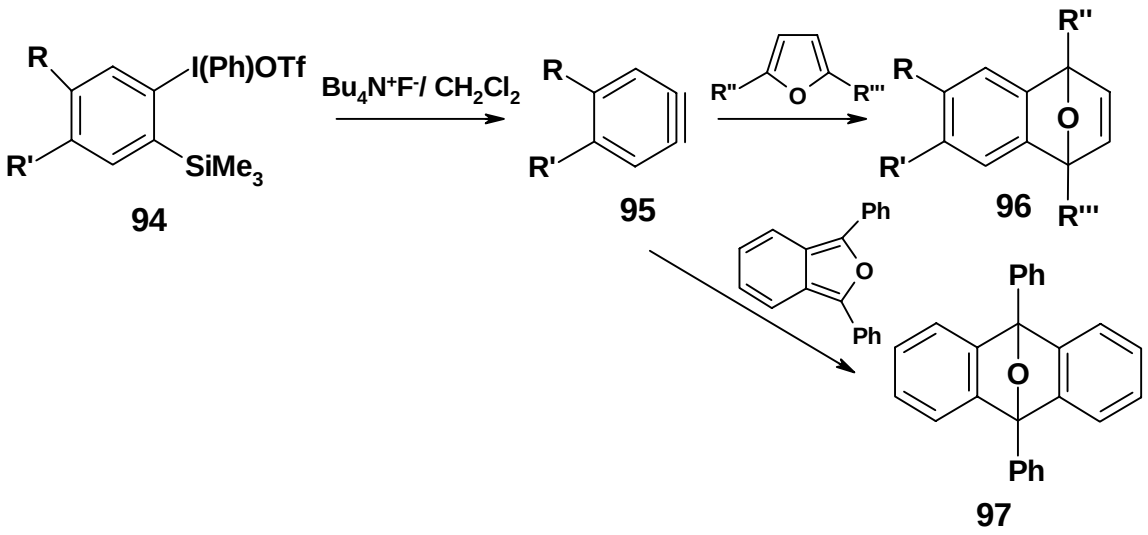
Phenyl[4-(trimethylsilyl)thien-3-yl]iodonium triflate (**88**) was found to be an excellent precursor of 3,4-didehydrothiophene. Thus, treatment of thiophene (**88**) with KF / 18-crown-6 / CH_2Cl_2 system afforded intermediate (**89**)**,** which can be trapped with various alkenes (for example, furan derivatives (**90**) or acrylonitrile (**91**)) to obtain addition products (**92)** or (**93)** in 13-31% yields (Scheme 24).[34,35]



R, R' = H, Me

Scheme 24

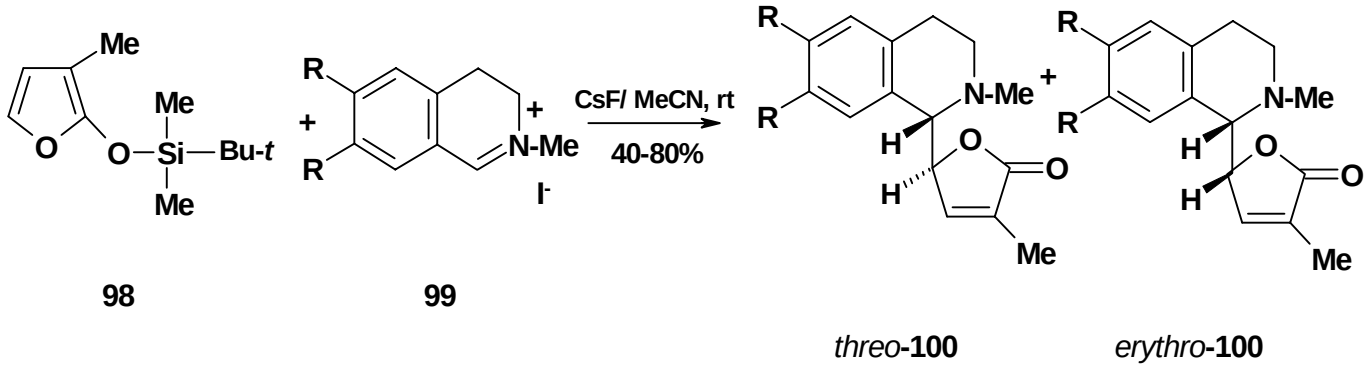
Similarly, the interaction of benzynes (**95**)**,** generated from corresponding iodonium triflates (**94**) in the presence of $Bu_4N^+F^-$ / CH_2Cl_2, with furans led to corresponding addition products (**96**) or (**97**) in 82-100 % yields (Scheme 25).[36-40]



R, R' = H, CO_2Me, R,R' = C_6H_4; R'', R''' = H, CO_2Me

Scheme 25

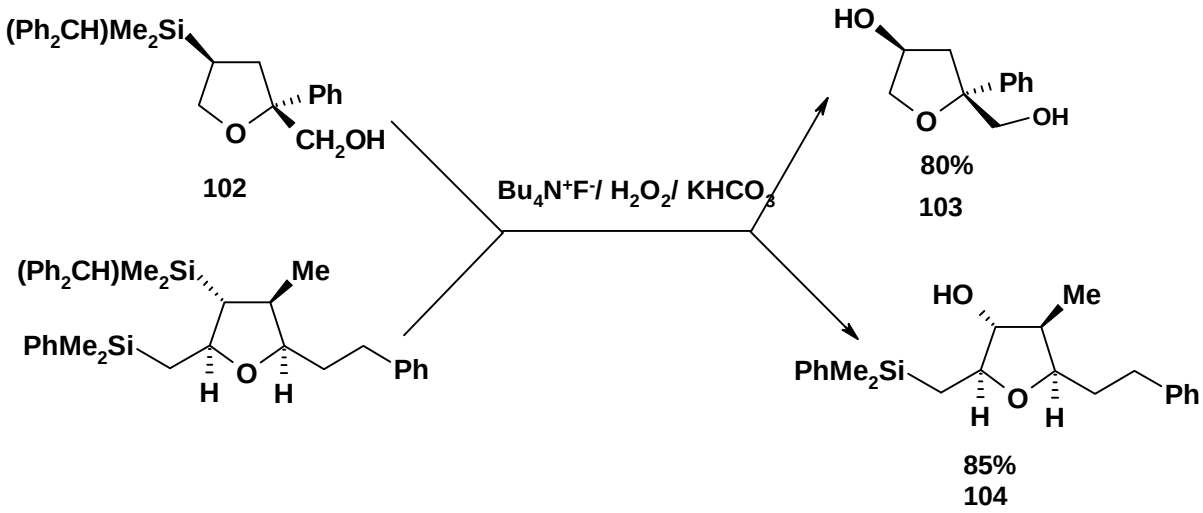
2-(*tert*-Butyldimethylsiloxy)-3-methylfuran (**98**) on treatment with dihydroisoquinolinium salts (**99**) in the presence of CsF in MeCN at room temperature afforded a mixture of addition products (**100**) with *threo* isomer predominating over *erythro* isomer (Scheme 26).[41]



R = alkyl, alkoxy

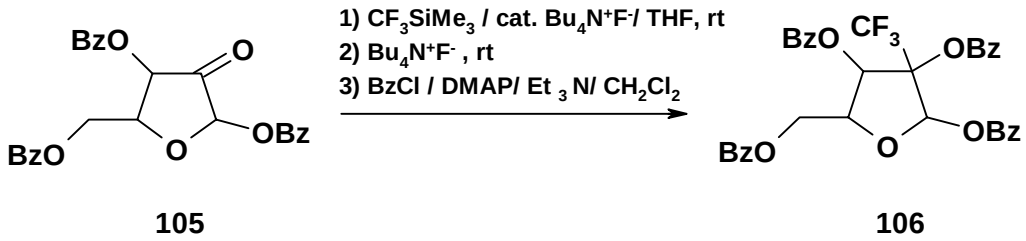
Scheme 26

Silylated tetrahydrofuran derivatives (**101, 102**) were successfully converted to corresponding alcohols (**103, 104**) in the presence of $Bu_4N^+F^-$ / H_2O_2 / $KHCO_3$ system (Scheme 27).[42]



Scheme 27

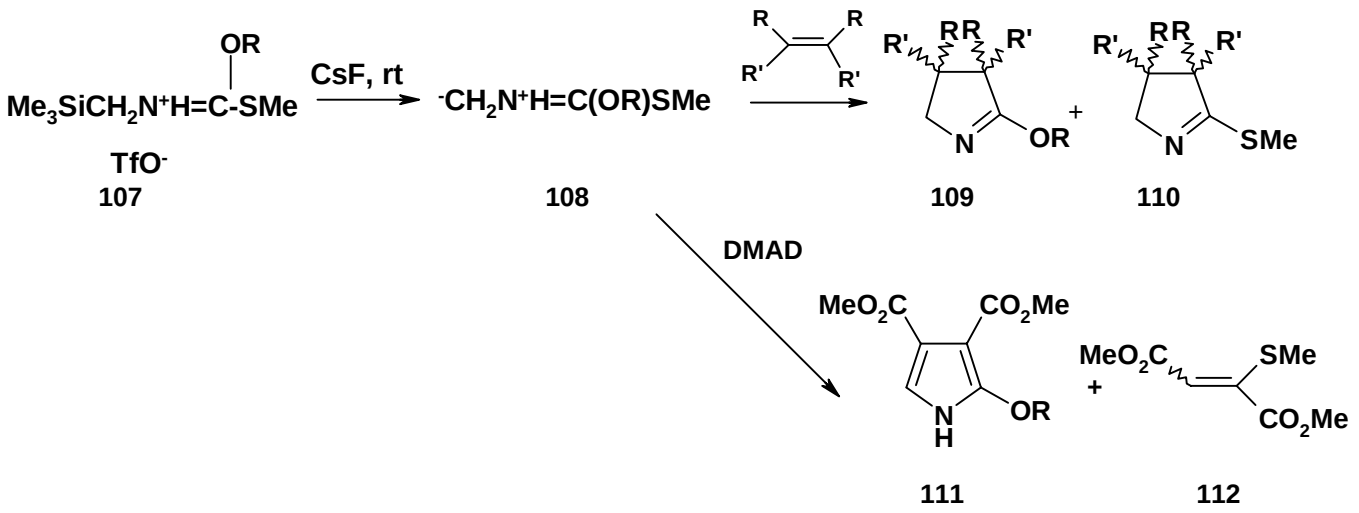
Synthesis of perbenzoylated 2'-*C*-β-trifluoromethyl-α-D-ribofuranose (**106)** from 1,3,5-tri-*O*-benzoyl-α-D-2-ketoribofuranose (**105)** was carried out in three-step process. Thus, nucleophilic trifluoromethylation of tetrahydrofuran (**105**) with CF_3SiMe_3 / $Bu_4N^+F^-$ (5 mol%) / THF, followed by desilylation with stoichiometric amount of $Bu_4N^+F^-$ and treatment with benzoyl chloride / DMAP / Et_3N afforded the desired product (**106**) in overall yield 73 % (Scheme 28).[43]



Scheme 28

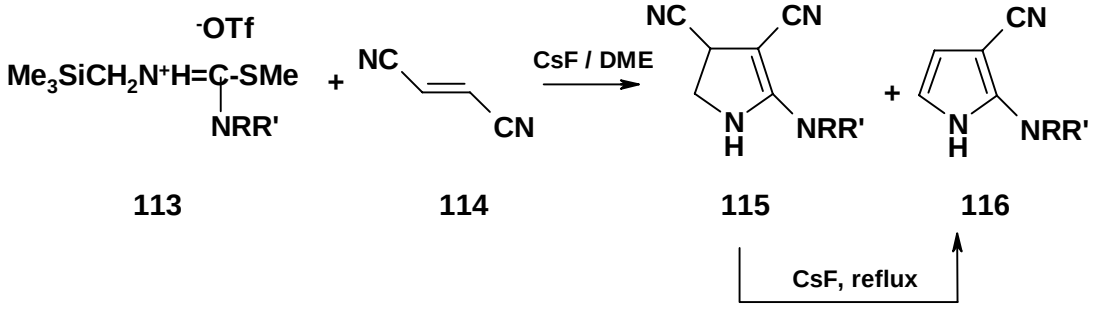
3.2. Pyrroles, pyrrolidines and indoles

Addition of azomethine ylides (**108**), generated from *N*-silylmethyliminium triflates in the presence of fluoride ion source, to electron-deficient olefins provide a good route to pyrrole or dihydropyrrole derivative. For example, interaction of silane (**107**) with CsF / MeCN or DME and then with olefin afforded a mixture of 2-alkoxy- (**109**) (27-68%) and 2-methylthiopyrrolines (**110**) (5-28%). The reaction of **107** with dimethyl acetylenedicarboxylate (DMAD) in the presence of CsF afforded the corresponding 2-alkoxypyrroles (**111**) (49-61 %) together with 1,2-*bis*(methoxycarbonyl)-1-methylthioethylene (**112**) (32-46%) (Scheme 29).[44]



Scheme 29

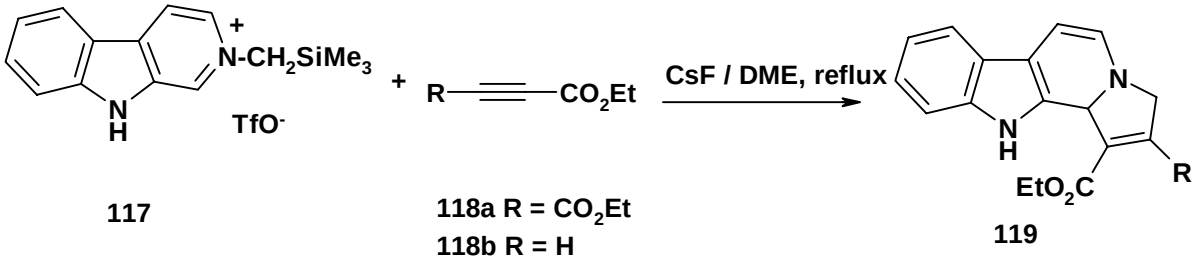
Similarly, cycloaddition of azomethyne ylides, generated from *N*-(trimethylsilylmethyl)thioureas (**113**) and CsF, to alkenes (for example, (**114**)) led to 2-amino derivatives of pyrrolines (**115**) (24-61%) or 3-cyanopyrroles (**116**) (0-46%)**.** The relative yields of products (**115**) and (**116**) depended upon reaction conditions: when **115** was heated with CsF in DME for 24 h pyrroles (**116**) were obtained as main products in yields up to 46 % (Scheme 30).[45]



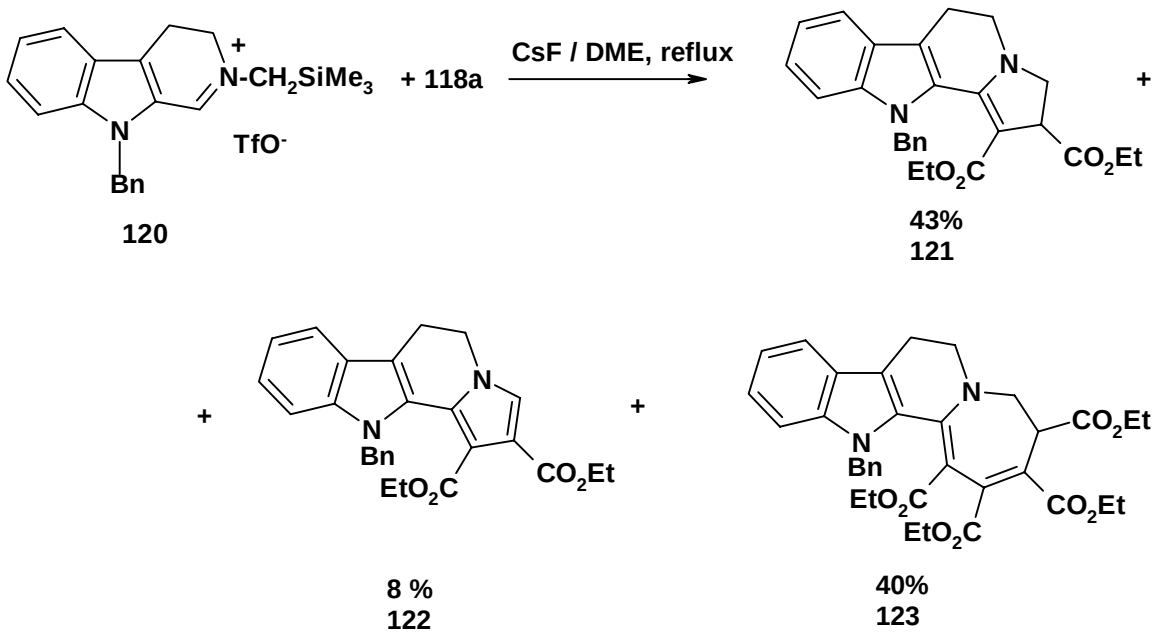
R, R' = H, alkyl, aryl

Scheme 30

Preparation of C-1 and/or C-2 functionalized indolizino[8,7-*b*]indole derivative by 1,3-dipolar cycloaddition reaction of β-carboline ylides was described. Thus, 2-*N*-(trimethylsilylmethyl)-β-carboline triflate (**117**) reacted with diethyl acetylenedicarboxylate (**118a**) or ethyl propiolate (**118**) in the presence of CsF to afford cycloaddition products (**119**) in 8-35% yields. Similarly, *N*-benzyl derivative (**120**) reacted with acetylene (**118a**) to give cycloaddition products (**121**) and (**122**) and novel azepine derivative (**123**) (Scheme 31).[46]



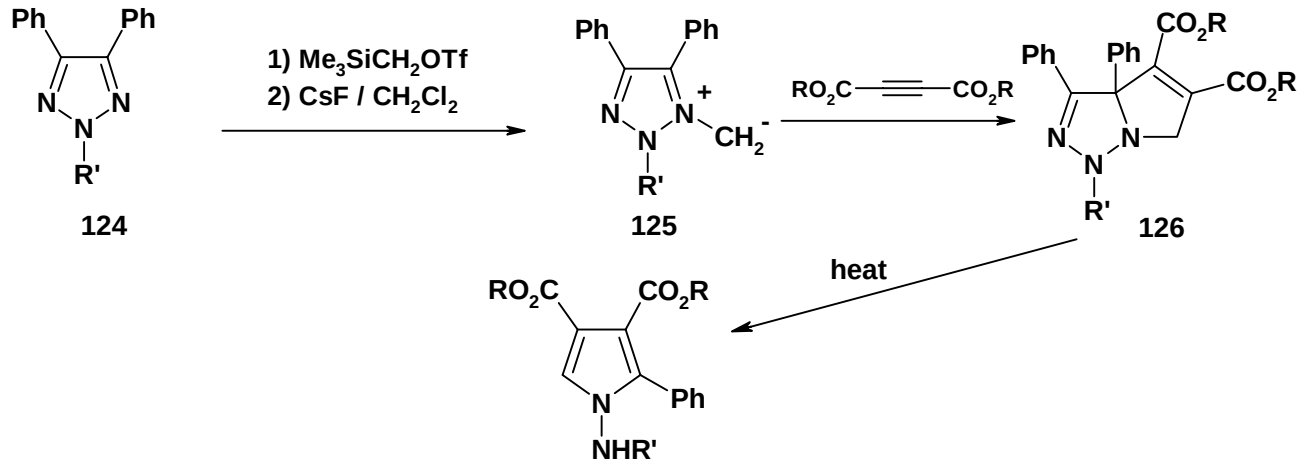
117 **118a R = CO_2Et** **118b R = H** **119**



120 **43%** **121** **8 %** **122** **40%** **123**

Scheme 31

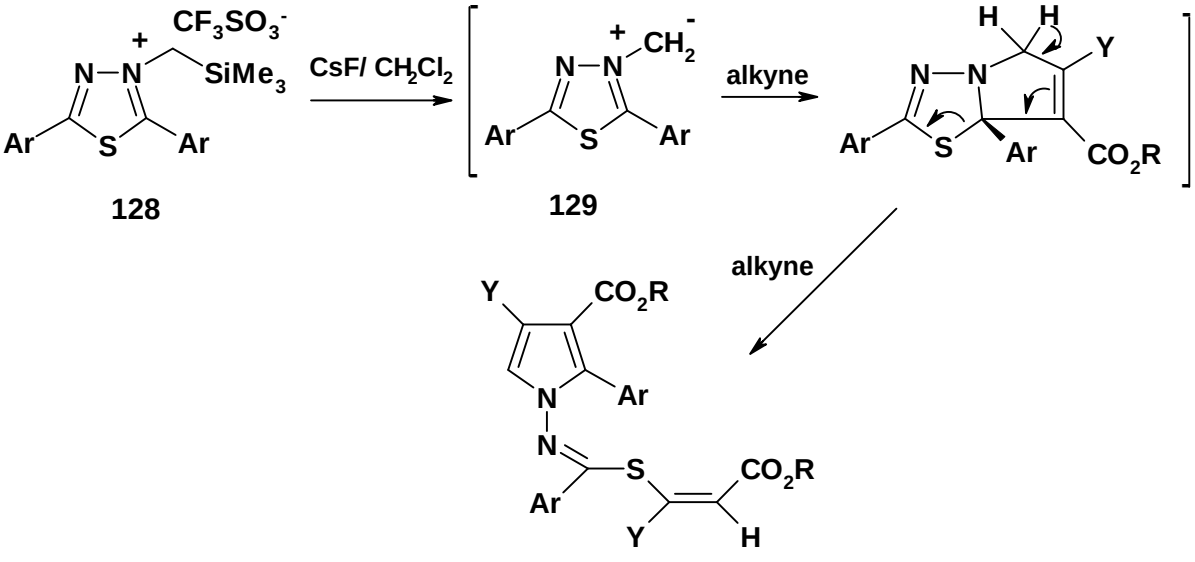
The possibilities of generation and trapping of a 1,2,3-triazolium 1-unsubstituted methanide (**125**) was investigated. Thus, interaction of 1,2,3-triazole (**124**) with trimethylsilylmethyl trifluoromethanesulfonate and then with CsF / CH_2Cl_2 led to methanide (**125**), which in the presence dialkyl acetylenedicarboxylate afforded pyrrolo[1,2-*c*][1,2,3]triazoles (**126**)**.** The compounds (**126**) underwent thermal rearrangement giving 1-aminopyrroles (**127**) in 85-90% yields (Scheme 32).[47]



R = alkyl; R' = aryl

Scheme 32

1,3,4-Thiadiazolium-3-methanides (**129**), generated from 2,5-diaryl-3-trimethysilylmethyl-1,3,4-thiadiazolium triflate (**128**) and CsF, in the presence of alkyne dipolarophiles (dimethyl and diethylacetylenedicarboxylates, methyl propiolate) afforded 2,3-di- or 2,3,4-trisubstituted 1-[(1-vinylthio-1-phenylmethylidene)amino]pyrroles (**130**) in 73-93 % yields (Scheme 33).[48]

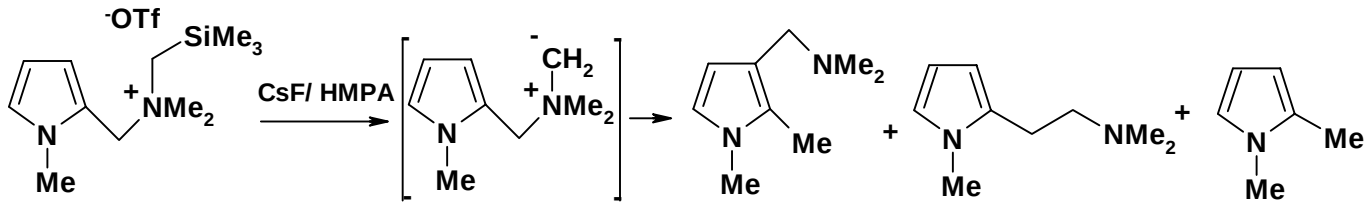


R = Me, Et; Ar = aryl; Y = H, CO_2R

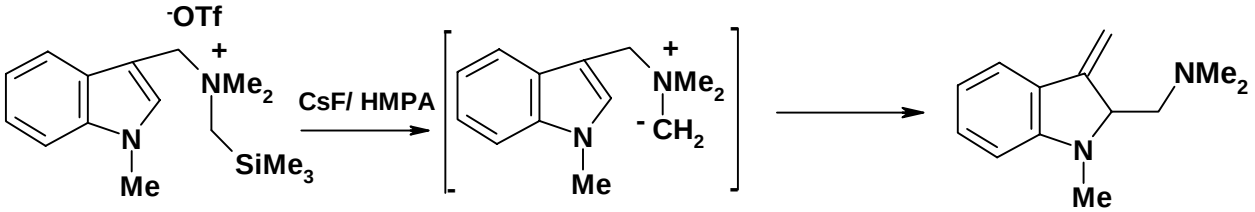
Scheme 33

Generation and reactions of *N*,*N*-dimethyl(1-methylpyrrolyl(or indolyl)methyl)ammonium *N*-methylides in the presence of fluoride were investigated in details by Y. Sato *et al.*[49,50] For example, interaction of *N*,*N*-dimethyl-*N*-(trimethylsilylmethyl)(1-methyl-2-pyrrolylmethyl)ammonium triflate (**131**) with CsF in

HMPA afforded a mixture of 3-dimethylaminomethyl-1,2-dimethylpyrrole (Sommelet-Houser rearragement product) (**132**), 2-[2-(dimethylamino)ethyl]-1-methylpyrrole (Stevens rearrangement product) (**133**) and 1,2-dimethylpyrrole (**134**) in a ratio 45 : 25 : 30 in overall yield 38 %. Reaction of *N*,*N*-dimethyl-*N*-(trimethylsilylmethyl)(1-methyl-2-indolylmethyl)ammonium triflate with CsF led to similar mixture of three products. However, 3-substituted triflate (**135**) and CsF afforded 2-(dimethylamino)methyl-1-methyl-3-methylene-2,3-dihydroindole (**136**) as single product in 81 % yield (Scheme 34).[49, 50]



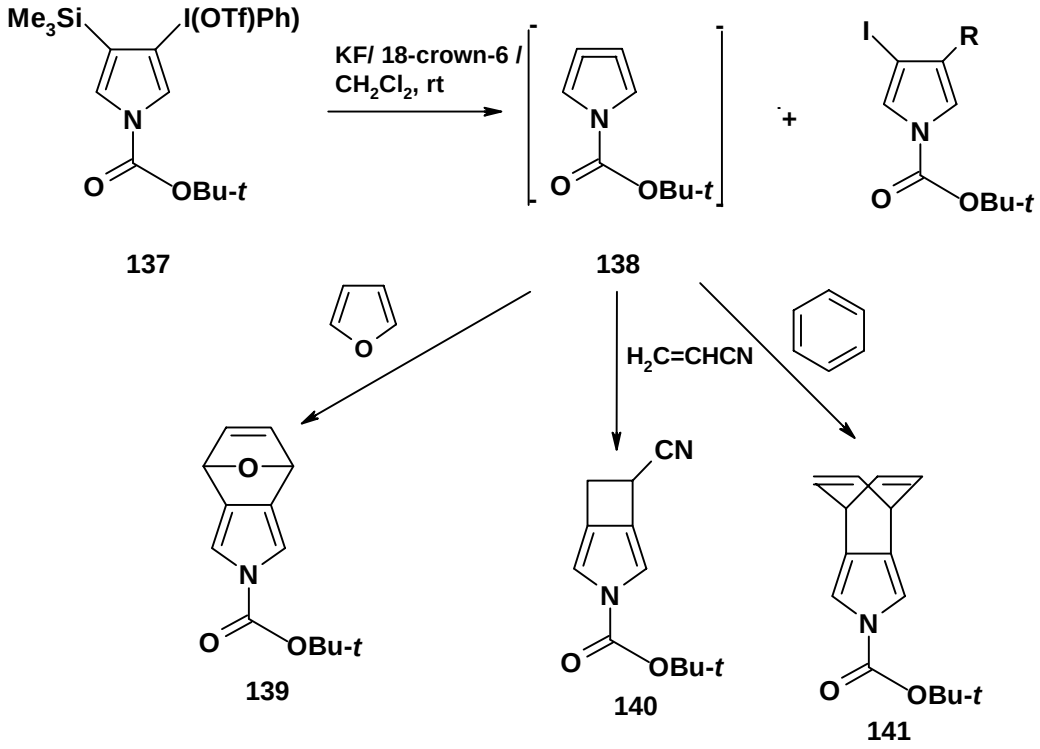
131 **132** **133** **134**



135 **136**

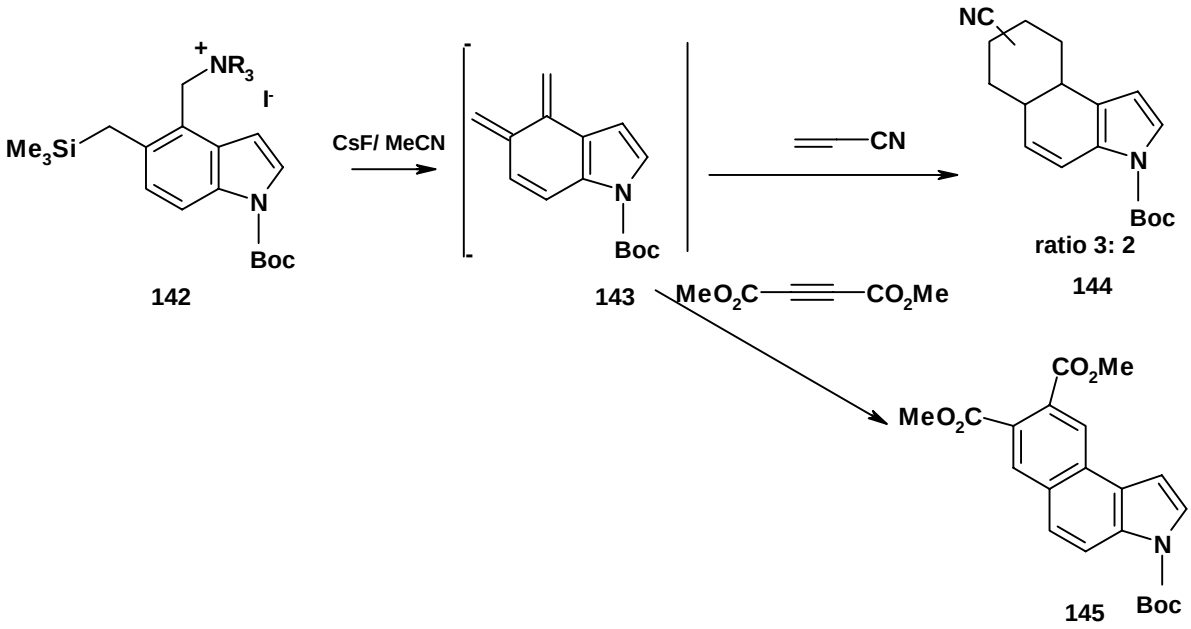
Scheme 34

Pyrrole containing monoiodonium triflate (**137**) was found to be a source of 1-*tert*-butoxycarbonyl-3,4-didehydro-1*H*-pyrrole (**138**). The intermediate (**138**) can be trapped with furan, acrylonitrile and benzene affording cycloadducts (**139-141**) in low yields (Scheme 35).[51]



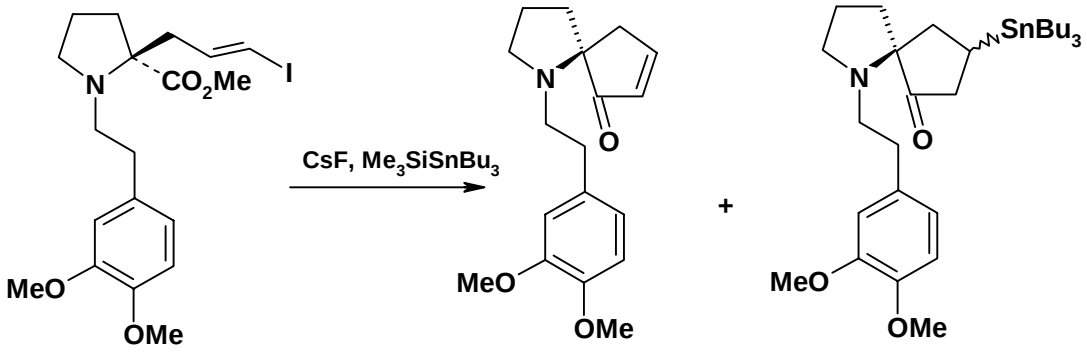
Scheme 35

Cycloaddition reaction of indolo-4,5-quinodimethanes (**143**), generated from *N*-Boc protected indoles (**142**) by CsF / MeCN at room temperature, and dienophiles (for example, acrylonitrile and dimethyl acetylenedicarboxylate) afforded 4,5-fused indoles (**144**) and (**145**) in 68-95 % yields (Scheme 36).[52]



Scheme 36

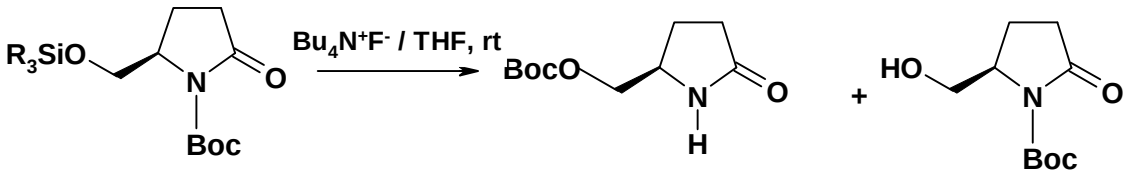
Synthesis of 1-azaspiro[4.4]nonane system by stannyl anion mediated cyclization of pyrrolidine derivatives **146** in the system $Me_3SiSnBu_3$ / CsF / DMF system was described. Depending on reaction conditions two spirocompounds were isolated. Using 1.2 equiv. of $Me_3SiSnBu_3$ the desired products (**147**) and **(148**) were obtained in 51% and 3% yields, correspondingly. In the presence of 4 equiv. of silane spiro compound (**148**) was obtained as a single product in 63% yield (Scheme 37).[53, 54]



146 **147** **148**

Scheme 37

Finally, cleavage of *O*-silyl ether in an *N*-Boc-protected pyrroglutaminol (**149**) using $Bu_4N^+F^-$ / THF at room temperature led to lactam derivative (**150**)**.** Product (**150**) of the Boc group migration was isolated in yields up to 100% along with hydroxy derivative (**151**) (Scheme 38).[55]



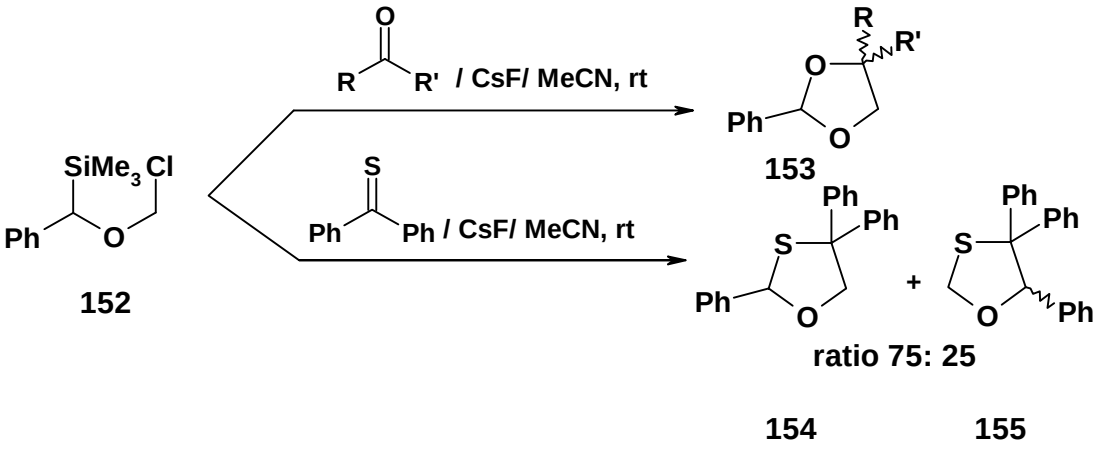
149 **150** **151**

R_3Si = *t*-$BuMe_2Si$, *t*-$BuPr_2Si$

Scheme 38

3.3. Dioxolanes and oxathiolanes

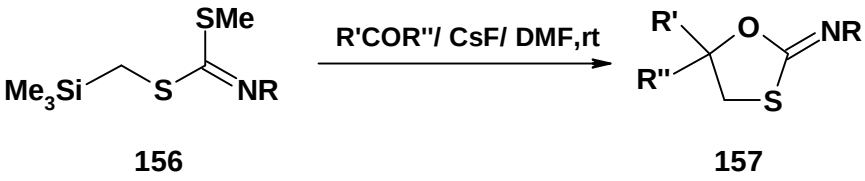
Reaction of carbonyl ylide, generated from chloromethyl silylmethyl ethers (**152**), with ketones or thioketones provides a good route to dioxolanes or oxathiolanes. The reaction products (**153-155**) were isolated in 57-82 % yields (Scheme 39).[26]



R, R' = alkyl, aryl

Scheme 39

S-Trimethylsilylmethyl carbonimidoditioate derivates (**156**) can be used as a synthetic equivalent of thiocarbonyl ylide ($^{-}CH_2S^{+}$=C=NR). Thus, reaction of silane (**156**) with carbonyl compounds in the presence of CsF and DMF at room temperature afforded oxathiolanes (**157**) in yields up to 68 % (Scheme 40).[56]

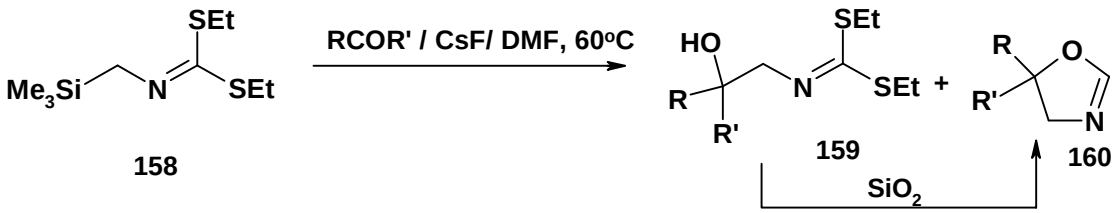


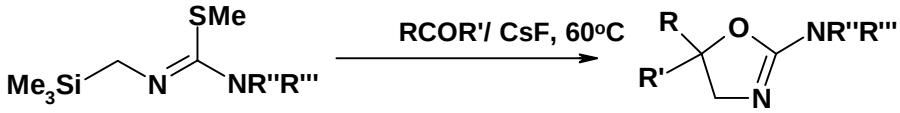
R = alkyl, aryl; R' = aryl; R'' = H, alkyl

Scheme 40

3.4. Oxazoles, oxazolines and isoxazoles

General method of synthesis of oxazoline derivatives by addition of alkylthionitrile ylides and related compounds to carbonyl compounds was described in some articles. Thus, interaction of diethyl *N*-trimethylsilylmethyl isothiocyanate (**158**) with carbonyl compounds in the presence of CsF / DMF led to mixture of products (**159**) and (**160**). The aldol-type adducts (**159**) were readily converted to oxazolines (**160**) by treatment with silica gel.[57] Similarly, *N*-trimethylsilylmethylisothiourea (**161**) underwent cycloaddition with carbonyl compounds in the presence of fluoride ion source to afford 2-aminooxazolines (**162**) in yields up to 84 % (Scheme 41).[58]

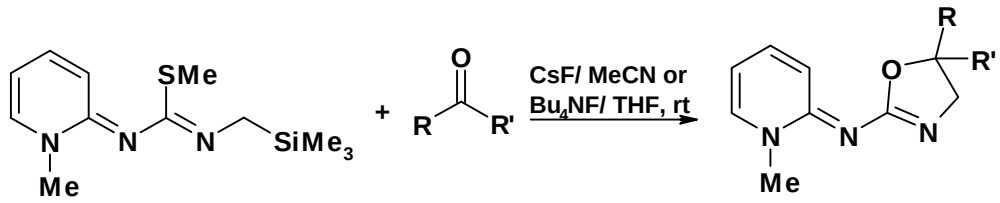




R, R' = H, alkyl, aryl; R'', R''' = alkyl; cycloalkyl

Scheme 41

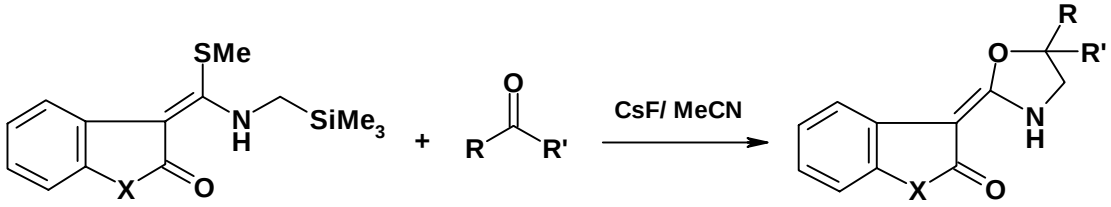
Reaction of 1,2-dihydropyridine (**163**) with carbonyl compounds in the presence of CsF in MeCN or $Bu_4N^+F^-$ in THF afforded aminooxazoline derivatives (**164**) in 38-77 % yields (Scheme 42).[59,60]



R, R' = H, alkyl, aryl, hetaryl

Scheme 42

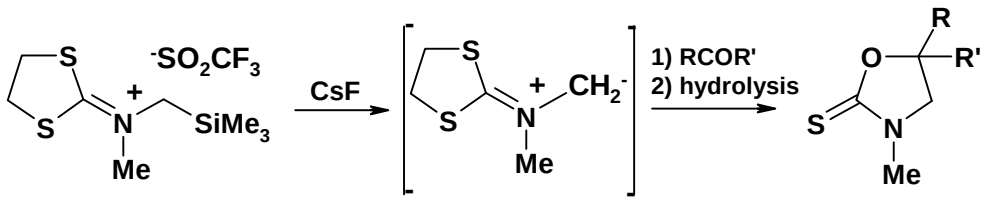
Treatment of cumarone (**165**) and indole (**166**) with aldehydes and ketones gave 1,3-dipolar cycloadducts, 2-oxazolidinylidines (**167**) and (**168**) in 11-69% yields (Scheme 43).[61]



R, R' = H, aryl

Scheme 43

Dithiolane methylide, generated from iminodithiolane salt (**169**) and CsF, underwent efficient cycloaddition to carbonyl compounds to afford after hydrolysis 1,3-oxazolidine-2-thiones (**170**) in 28-63 % yields (Scheme 44).[62]

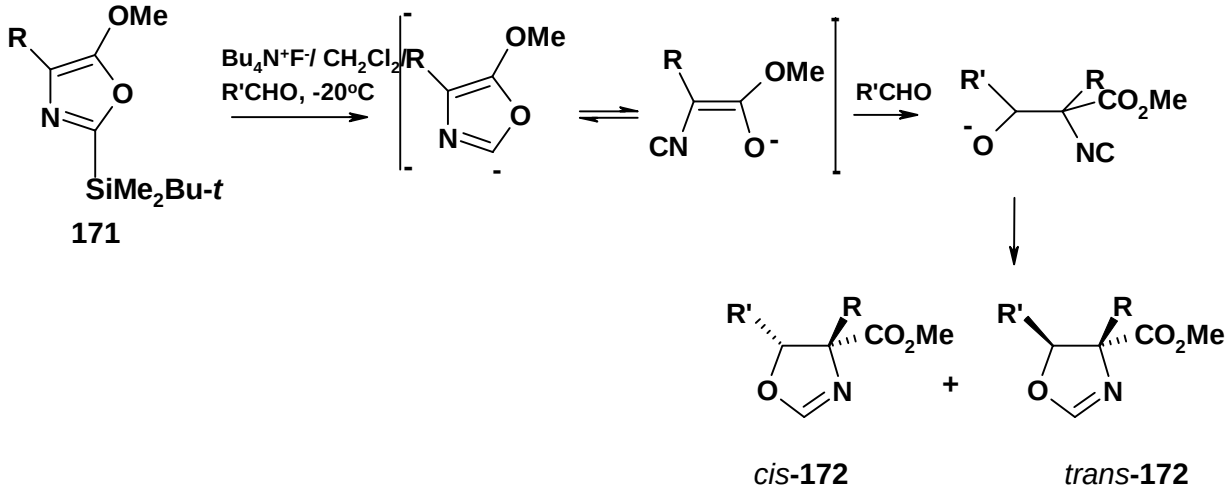


169 **170**

R, R' = H, aryl, vinyl

Scheme 44

Fluoride-induced aldol-type reaction of 2-silyl derivatives (**171**) of oxazoles with aldehydes was described. Products (**172**) of reaction oxazolines were isolated in 77-80% overall yield with excellent *cis*-selectivity. The proposed mechanism of reaction included formation of C-Si bond cleavage products, which were in equilibrium with ring-opened enolate anion. Addition of the enolate anion to aldehydes was followed by cyclization forming the oxazoline (**172**) ring (Scheme 45).[63]

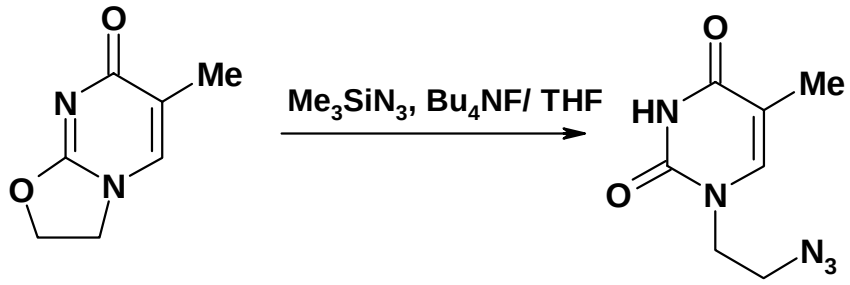


171

R = alkyl; R' = alkyl, aryl,hetaryl

Scheme 45

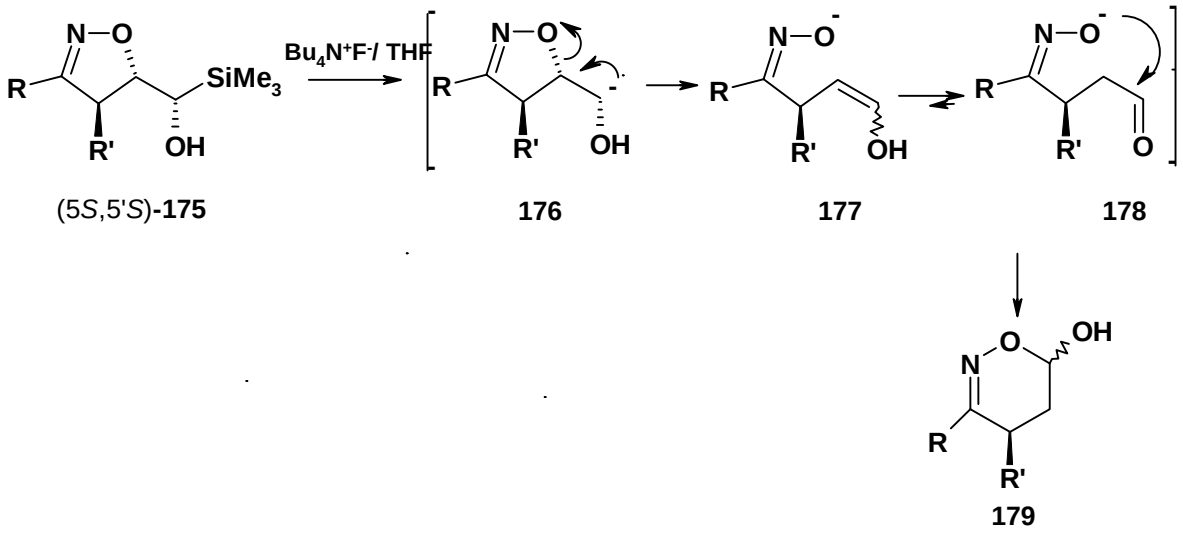
Reaction of 2,3-dihydro-6-methyl-7*H*-oxazolo[3,2-*a*]pyrimidin-7-one (**173**) in the presence of Me_3SiN_3, Bu_4NF/ THF gave a good yield of oxazole ring opening product (**174**) (Scheme 46).[64]



173 174

Scheme 46

Isoxazole derivatives also undergo some transformations mediated by fluoride ion activation of silicon bonds. Thus, optically active 3,4,5-trisubstituted 4,5-dihydroisoxazoles (**175**) were easily converted into chiral 4-substituted 5,6-dihydro-4*H*-[1,2]oxazines (**179**) in 73-100% yields. The mechanism of reaction included fluoride ion generation of desilylated intermediate (**176**)**,** from which an oximate anion was generated to give enol intermediate (**177**). Through the keto-enol tautomerism, intermediate (**177**) isomerized to aldehyde (**178**), which was then intramolecularly attacked by the oximate anion to give oxazine (**179**) (Scheme 47).[65]

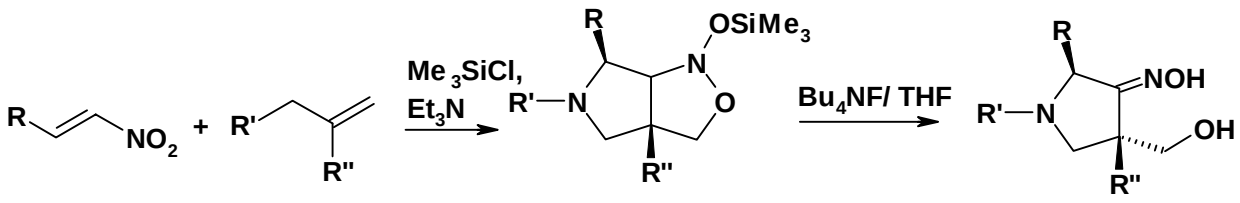


(5*S*,5'*S*)-**175** **176** **177** **178** **179**

R =benzyl, aryl; R' = alkyl

Scheme 47

Bicyclic isoxazole derivatives (**180**), easily prepared from nitroolefin and secondary allylic amine in the presence of Me_3SiCl, Et_3N, underwent ring opening in the presence of $Bu_4N^+F^-$ to provide oximes (**181**) in 60-66% yields (Scheme 48).[66]



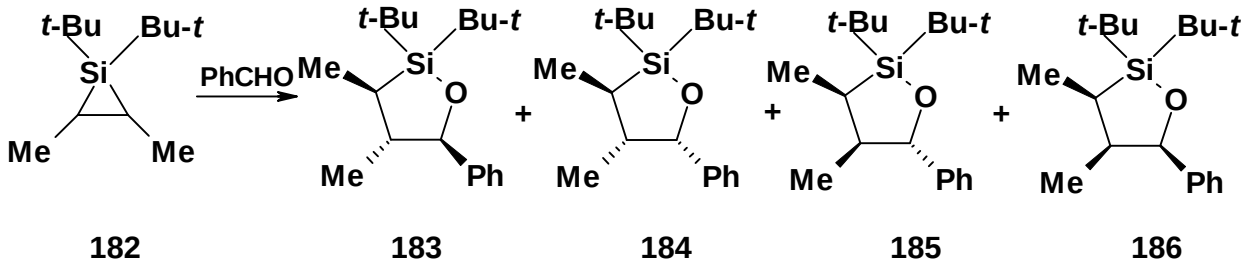
180 **181**

R = aryl; R' = alkyl; R'' = H, Me

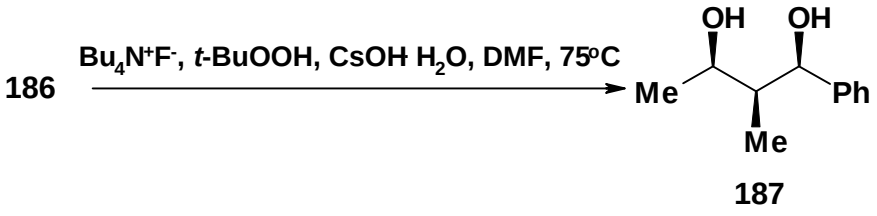
Scheme 48

3.5. Oxasilacyclopentanes

Oxasilacyclopentanes (**183-186**), which can be readily obtained by insertion of carbonyl compounds into silacyclopropanes (**182**), undergo ring opening in the presence of $Bu_4N^+F^-$, t-BuOOH, $CsOH{\cdot}H_2O$ [67], CsF, t-BuOOH, $CsOH{\cdot}H_2O$, KH, DMF [68] or KF, 30% H_2O_2, $KHCO_3$, MeOH, THF [69, 70] systems to afford 1,3-diols. For example, interaction of oxasilacyclopentane (**186**) with $Bu_4N^+F^-$, *t*-BuOOH, $CsOH{\cdot}H_2O$ in DMF led stereospecifically to diol (**187**) in 64 % yield (Scheme 49).



182 **183** **184** **185** **186**



187

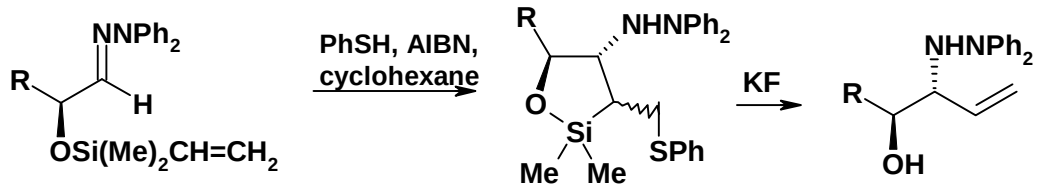
Scheme 49

In the absence of the oxidant oxasilacyclopentanes in the presence of fluoride ion source gave the corresponding alcohols. Thus, protodesilylation of allene (**188**) in the presence of Bu_4NF / 1-methyl-2-pyrrolidinone (NMP) at room temperature led to alcohol (**189**) (Scheme 50).[71]

188 **189**

Scheme 50

Diastereoselective vinyl addition to chiral hydrazones *via* tandem thiyl radical addition and silicon tethered cyclization to oxasilacyclopentane (**190**) was described. The interaction of heterocycles (**190**) with KF led to alcohols (**191**) in 45-89 % yields with *anti: syn* ratio up to 98:2 (Scheme 51).[72]



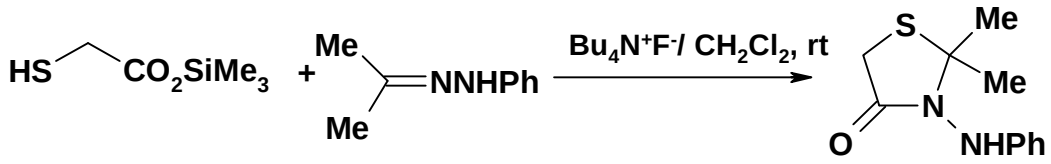
190 **191**

R = H, alkyl, aryl

Scheme 51

3.6. Thiazoles and thiazolines

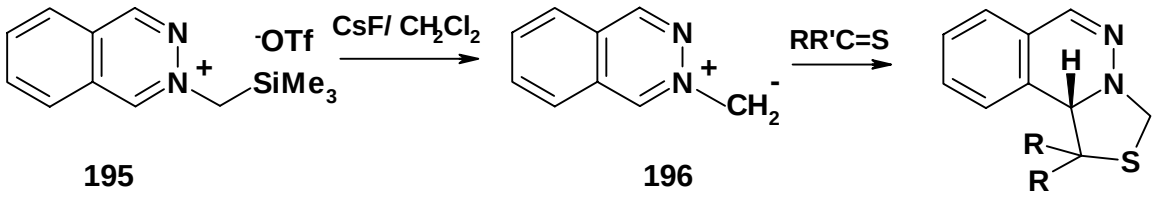
The cyclocondensation reactions were succesfully used in the preparation of thiazole derivatives. For example, interaction of trimethylsilyl mercaptoalkanoate (**192**) with hydrazine (**193**) in the presence of $Bu_4N^+F^-$ in CH_2Cl_2 leads to 2,2-dimethyl-3-anilinothiazolidin-4-one (**194**) in 21% yield (Scheme 52).[73]



192 **193** **194**

Scheme 52

Cycloaddition reaction of phthalizinium-2-methanide (**196**), prepared from triflate (**195**) and CsF, with C=S dipolarophiles (thiobenzophenone, phenyl dithioacetate and methyl cyanodithioformate) led to thiazolo[4,3-*a*]phthalazines (**197**) in yields up to 51% (Scheme 53).[74,75]



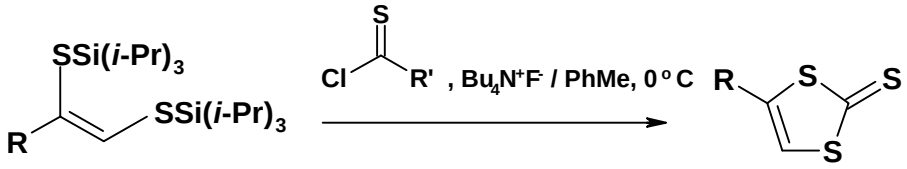
195 **196** **197**

R, R' = alkyl

Scheme 53

3.7. Dithiolanes and dithiolones

Preparation of 1,3-dithiol-2-thiones (**199**) from *Z*-1,2-bis-triisopropylsilylthioalkenes (**198**) and thiophosgene or phenyl chlorothionoformate in the presence of $Bu_4N^+F^-$ / toluene at 0°C was described. The reaction products (**199**) were isolated in 35-89% yields (Scheme 54).[76]

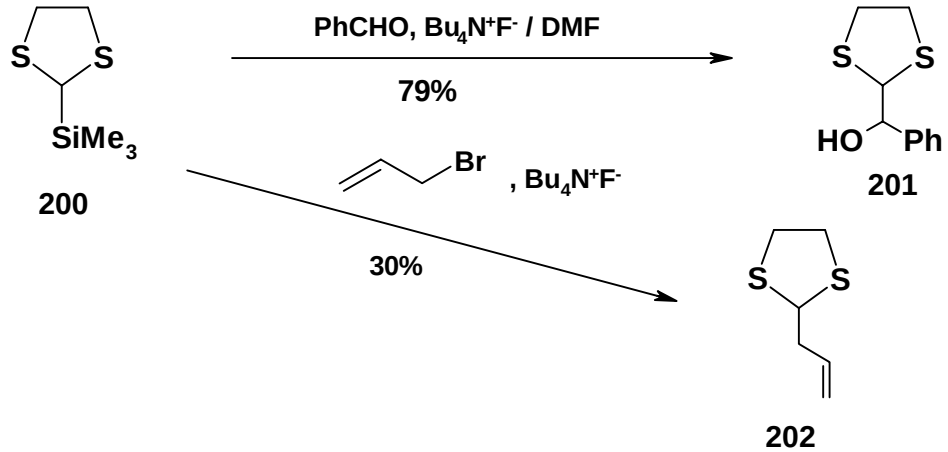


198 **199**

R = alkyl; R' = Cl, OPh

Scheme 54

It has been found that 2-trimethylsilyl-1,3-dithiolane (**200**) can serve as a source of dithiolane anion. Thus, interaction of dithiolane (**200**) with benzaldehyde or allyl bromide in the presence of fluoride ion led to corresponding 2-substituted 1,3-dithiolanes (**201**) or (**202**) (Scheme 55).[77]

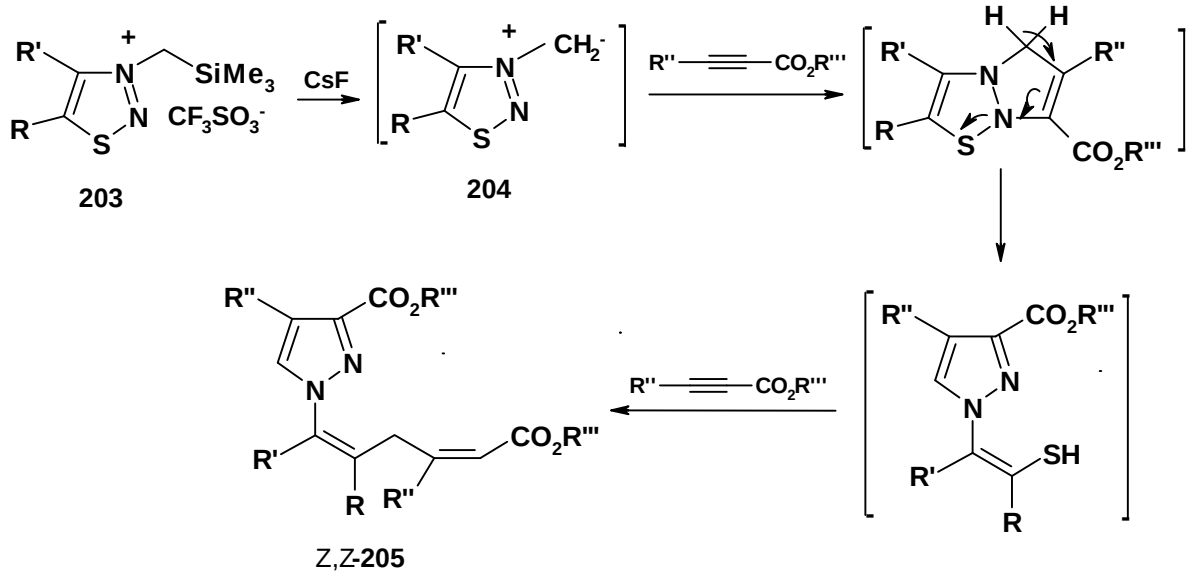


200 **201** **202**

Scheme 55

3.8 Pyrazoles and imidazoles

1,2,3-Thiadiazol-3-ium-3-methanide 1,3-dipoles (**204**), generated from trimethylsilylmethyl trifluoromethanesulfonate salts of 1,2,3-thiadiazoles (**203**) and CsF / CH_2Cl_2, underwent interaction with alkynes to afford 1-(2-vinylthioethenyl)pyrazoles (**205**) in 58-90 % yields (Scheme 56).[78]

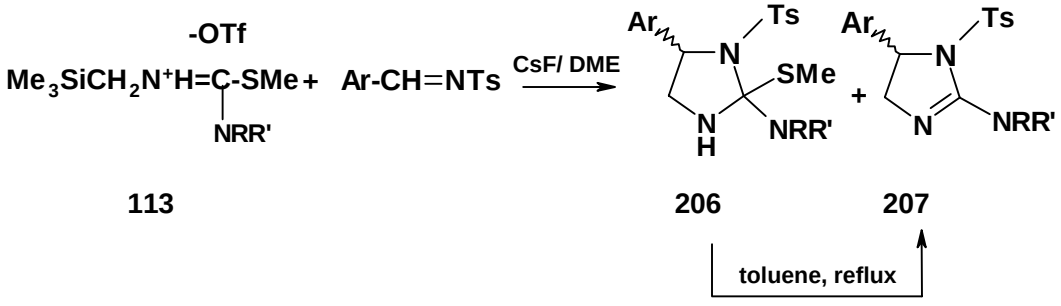


R, R' = aryl; R'' = H, CO_2Et; R''' = Me, Et

Scheme 56

Similar reactions of 1,2,3-triazolium ylides in the synthesis of various azoles were reviewed by R. N Butler and D. F. O'Shea in 1994.[79]

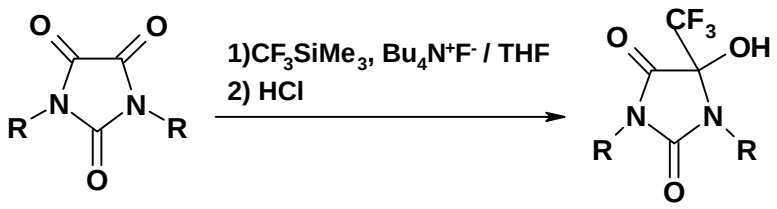
N-Unsubstituted nonstabilized azomethine ylides, generated from *N*-(trimethylsilylmethyl)iminium triflates (**113**) and CsF in DME, underwent cycloaddition to strongly polarized sulfonylimines giving imidazolines (**206**) and/or (**207**) in yields up to 70%. The initial cycloadducts (**206**) were quantitatively transformed to imidazolines (**207**) in refluxing toluene (Scheme 57).[80]



R, R' = H, alkyl, aryl

Scheme 57

Finally, imidazolidine triones (**208**) were easily trifluoromethylated by CF_3SiMe_3 in the presence of $Bu_4N^+F^-$ in THF to afford alcohols (**209**) in 25-58% yields (Scheme 58).[81]



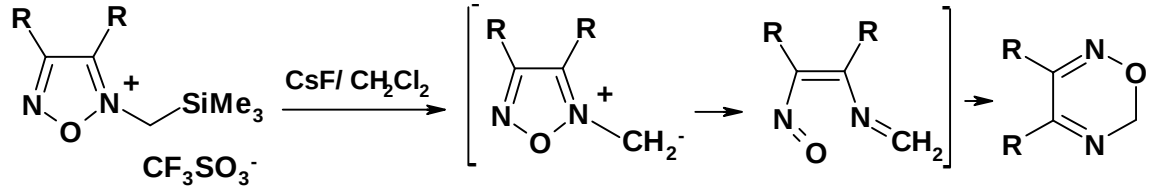
208 **209**

R = alkyl, aryl

Scheme 58

3.9. Oxadiazoles and triazoles

Desilylation of *N*-trimethylsilylmethyl-1,2,5-oxadiazolium (furazan) salts (**210**) in the presence of CsF led to 6*H*-1,2,5-oxadiazines (**211**) in 80-93% yields. The formation of products (**211**) proceeds *via* intermediates - furazan-*N*-methanides (Scheme 59).[82]

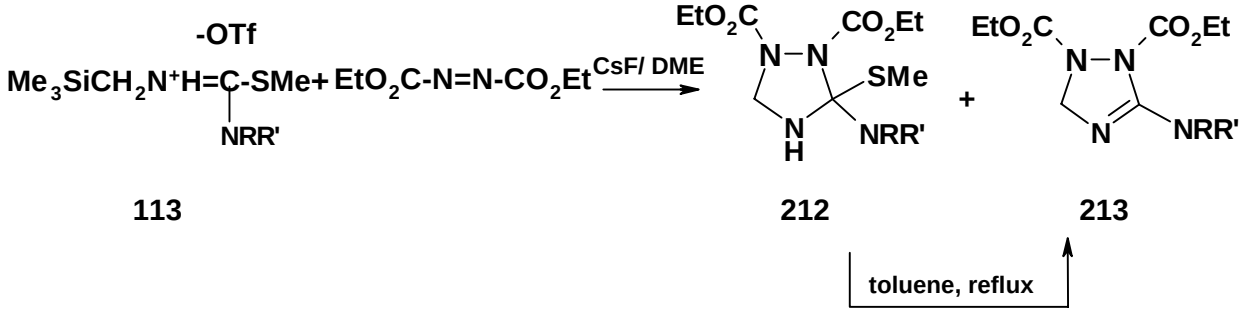


210 **211**

R = aryl

Scheme 59

Reaction of *N*-(trimethylsilylmethyl)iminium triflates (**113**) with diethyl azodicarboxylate in the presence of CsF in DME led to cycloaddition products (**212**) and/or (**213**) in yields up to 74%. The 1,2,3-triazolidines (**212**) were quantitatively transformed to triazolines (**213**) in refluxing toluene (Scheme 60).[80]



113 **212** **213**

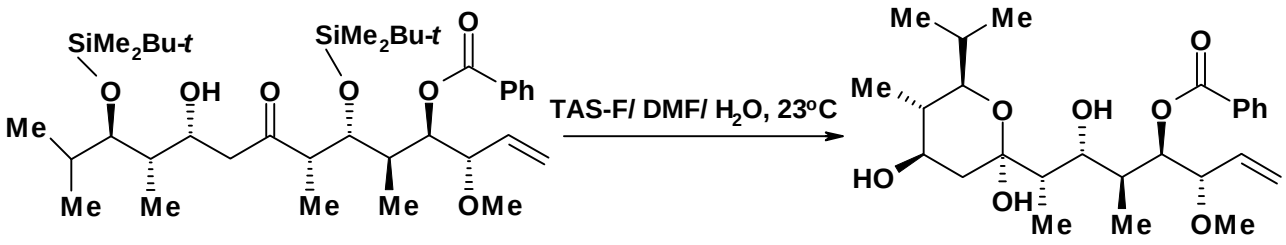
R, R' = H, aryl

Scheme 60

4. SIX-MEMBERED RINGS

4.1. Pyrones and thiopyrones

Synthesis of pyrone (**215**) by treatment of silyl ether (**214**) with TAS-F [tris(dimethylamino)sulfonium difluorotrimethylsilicate] as fluoride ion source was successfully carried out. The product **215** of reaction was isolated in 75 % yield (Scheme 61). Using $Bu_4N^+F^-$ as fluoride ion source the disilylated product was

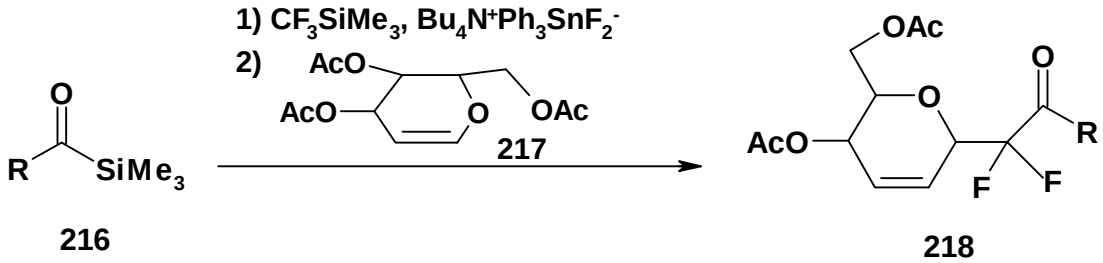


214 **215**

Scheme 61

obtained.[83]

Synthesis of *gem*-difluoro-C-glucosides and C-disaccharides in the presence of $Bu_4N^+Ph_3SnF_2^-$ (TBAT) as fluoride ion souce was described. Thus, difluoroenoxysilanes, prepared from acylsilanes (**216**) and CF_3SiMe_3 under fluoride ion action were glucosylated by glucal (**217**) to yield C-difluoroglucosides (**218**) (α / β ratio up to 80 :20) in 60-63 % yields (Scheme 62).[84]

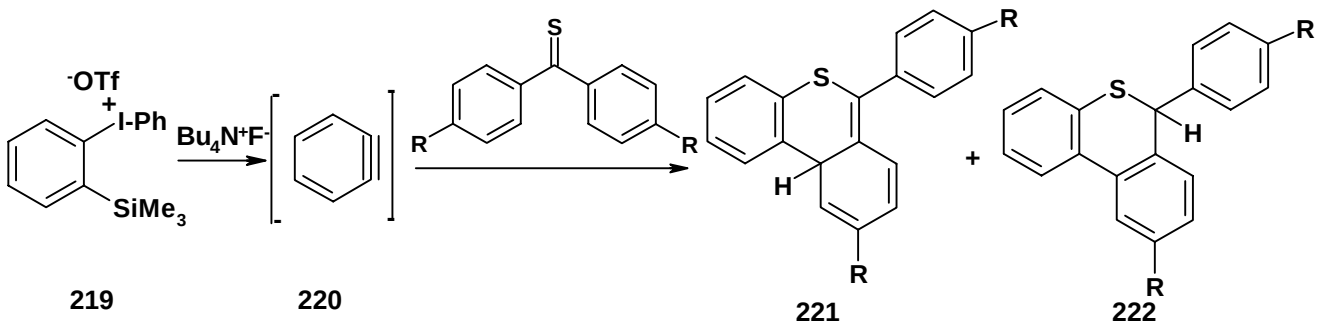


216 **218**

R = alkyl, aryl

Scheme 62

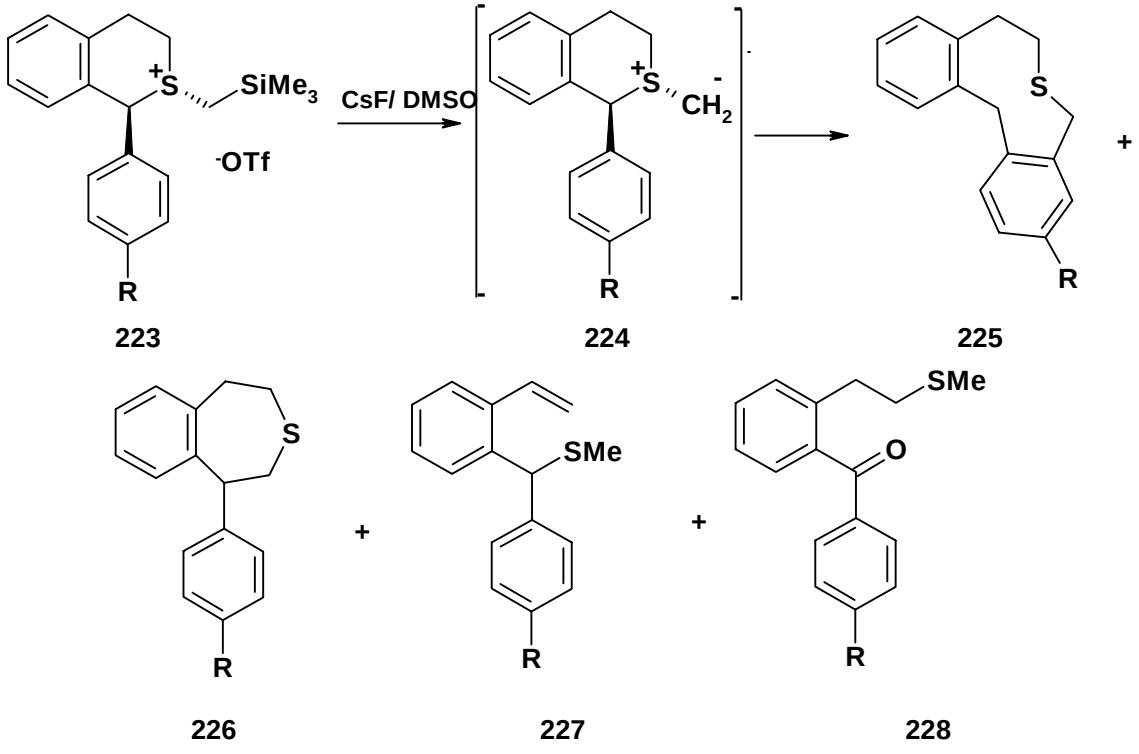
Reaction of benzyne (**220**), generated from phenyl(2-trimethylsilylphenyl)iodonium trifluoromethane-sulfonate (**219**) in the presence of $Bu_4N^+F^-$ in CH_2Cl_2, with thiobenzophenones led to formation of cycloadducts (**221**) and (**222**) (Scheme 63).[85, 86]



R = H, Me, OMe

Scheme 63

Finally, *trans*-1-phenyl-2-benzothiopyranium 2-methylides (**224**), generated by fluoride ion-induced desilylation of triflates (**223**) in DMSO, rearranged to 3-substituted 7,8-dihydro-5*H*,13*H*-dibenzo[*c*,*f*]thionines (**225**) (9-97% yields) (Sommelet-Houser rearrangement products), 1-(4-substituted phenyl)-1,2,3,4-tetrahydro-3-benzothiepines (**226**) (2-27%) (Stevens rearrangement products) and (4-substituted phenyl)(2-vinylphenyl)methyl methyl sulfides (**227**) (0-15%) (Hofmann degradation products). Above reaction in the presence of oxygen led to ketones (**228**) as main products in 57-86% yields (Scheme 64). [87]

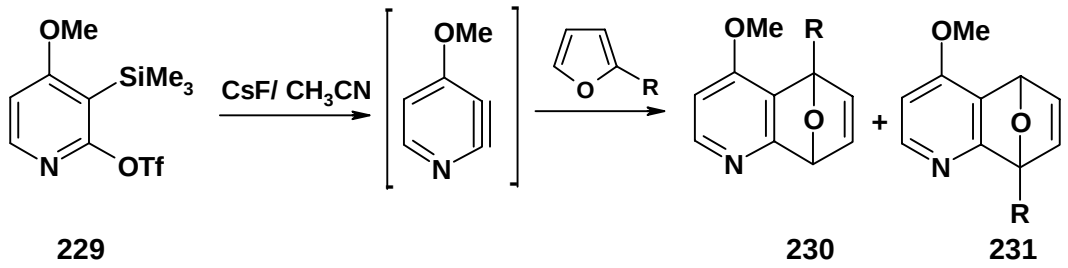


R = H, Cl, OMe, CF_3

Scheme 64

4.2. Pyridines and quinolines

The 2,3-pyridyne, which can be easily obtained from 4-methoxy-2-trifluoromethanesulfonyloxy-3-trimethylsilylpyridine (**229**) in the presence of fluoride ion source, was trapped with furan, 2-methylfuran and 2-methoxyfuran to afford addition products (**230**) and (**231**) in good yields. (Scheme 65).

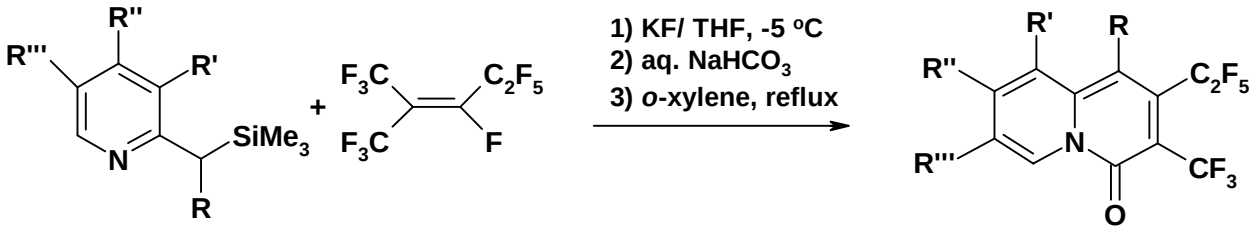


229 **230** **231**

R = H, Me, OMe

Scheme 65

A convenient method of preparation of 2-pentafluoroethyl-3-trifluoromethyl-4*H*-quinolizin-4-ones (**234**) by reaction of 2-trimethylsilylmethylpyridines (**232**) with perfluoro(2-methyl-2-pentene) (**233**) in the presence of KF was developed. Reaction products were isolated in 53-98% yields (Scheme 66).[89]

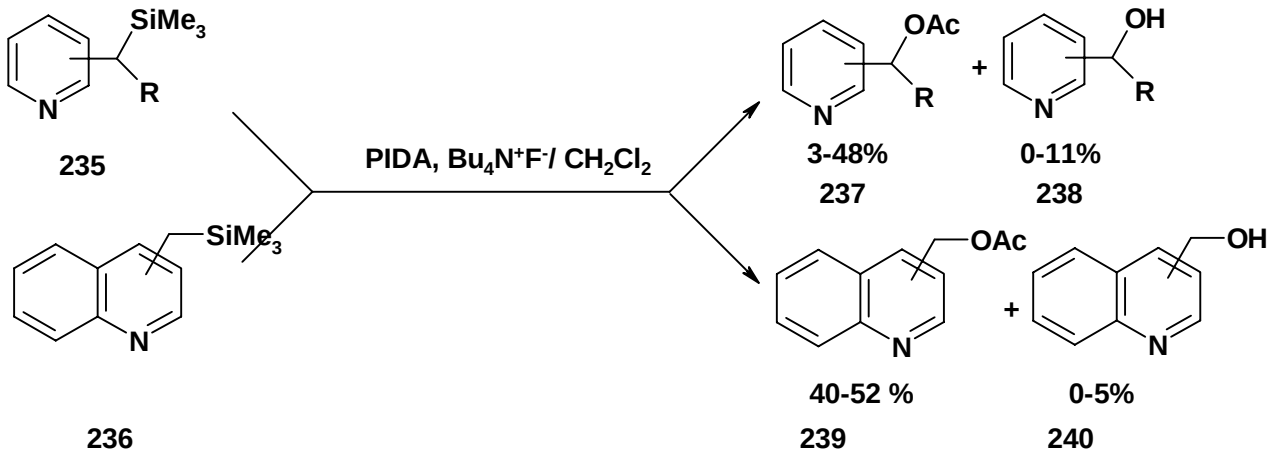


232 **233** **234**

R'-R''' = H, alkyl

Scheme 66

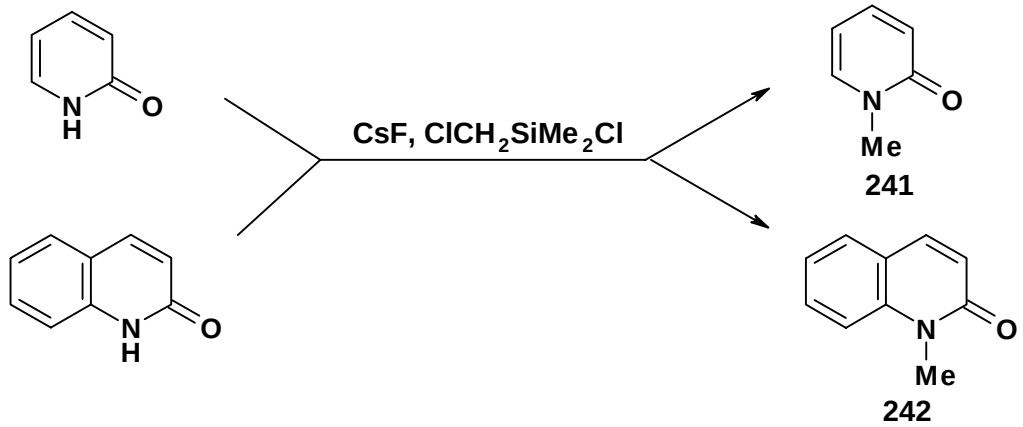
2-, 3- And 4-trimethylsilylmethylpyridines (**235**) and similar quinolines (**236**) can be transformed to corresponding acetates (**237**) and (**239**) or alcohols (**238**) and (**240**) by treatment with $PhI(OAc)_2$ (PIDA) / $Bu_4N^+F^-$ in CH_2Cl_2 (Scheme 67).[90]



R = H, Me, Ph

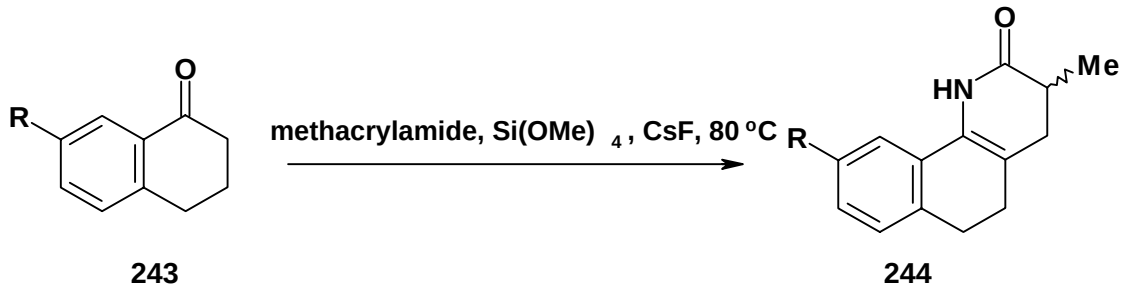
Scheme 67

Chemoselective methylation of heterocycles (for example, 2-pyridone or 2-quinolone) in the presence CsF / $ClCH_2SiMe_2Cl$ / MeCN system was described. *N*-Methylated heterocycles (**241**) and (**242**) were isolated in 75 and 77% yields, correspondingly (Scheme 68).[91]



Scheme 68

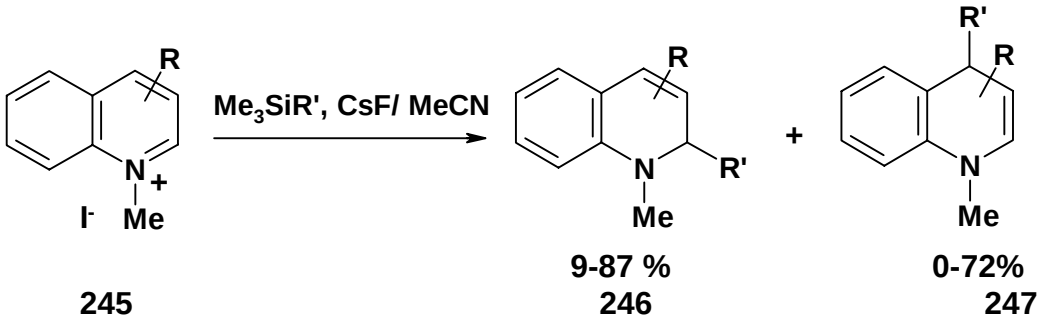
Derivatives of benzo[*h*]quinolines (**244**) can be easily obtained by Corriu method from tetralones (**243**) in the presence of methacrylamide / $Si(OMe)_4$ / CsF system at 80°C (Scheme 69).[92]

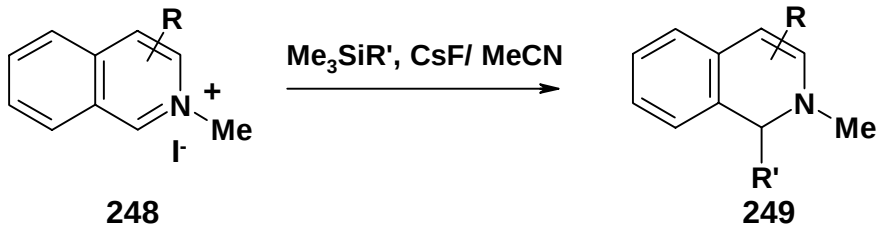


R = H, Br, OMe

Scheme 69

N-Methylquinolinium and isoquinolinium iodides reacted with silicon nucleophiles in the presence of fluoride ion source to provide a good route to substituted dihydroquinolines and dihydroisoquinolines. Thus, interaction of quinoline salts (**245**) with trimethylsilylacetonitrile or ethyl trimethylsilylacetate in the presence CsF in MeCN led to a mixture of 2- and 4-substituted quinolines (**246, 247**). Similar reaction of isoquinolines (**248**) proceeded regioselectively and afforded 1-substituted 1,2-dihydroisoquinolines (**249**) in yields up to 77 % (Scheme 70).[92,93]

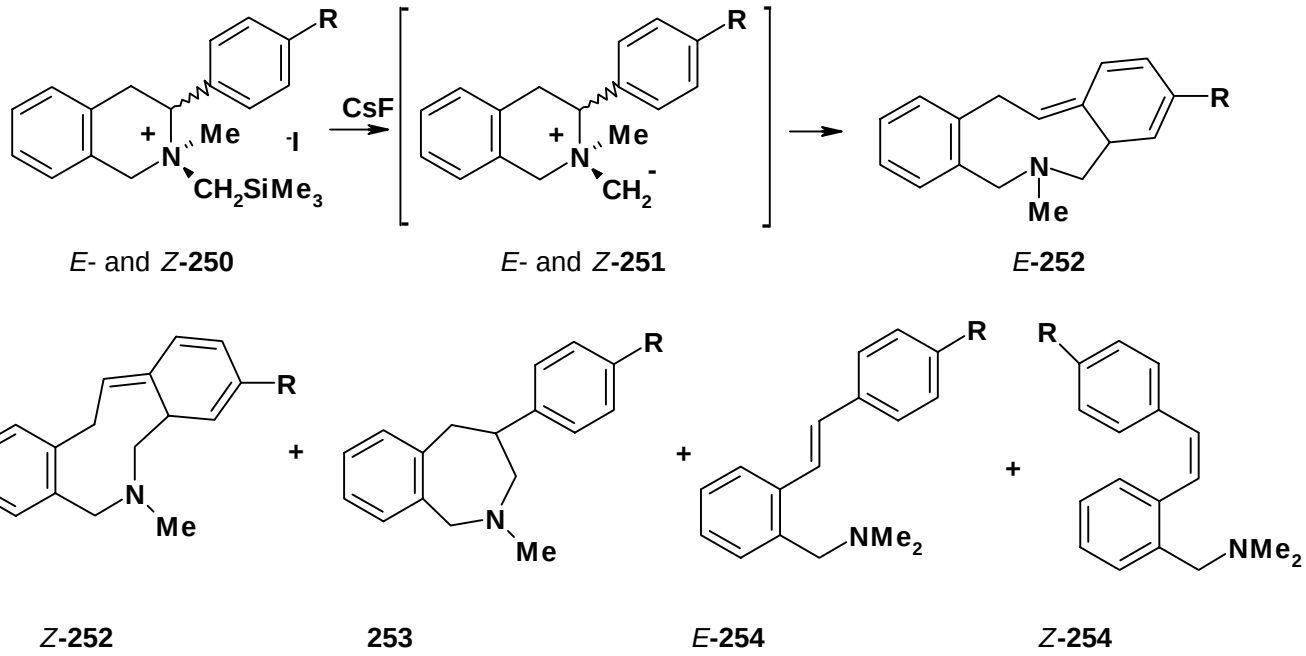




R = H, alkyl, aryl; R' = CH_2CN, CH_2CO_2Et

Scheme 70

Rearrangement of *cis*- and *trans*-2-methyl-3-(substituted phenyl)-1,2,3,4-tetrahydroisoquinolinium 2-methylides (**251**), generated from iodides (**250**) in the presence of CsF, led to a mixture of *E*- and *Z*-6-methyl-4a,5,6,7-tetrahydro-12*H*-dibenzo[*c*,*g*]azonines (**252**) (0-77%) ([2,3] sigmatropic rearrangement products), 4-(4-substituted phenyl)-2-methyl-2,3,4,5-tetrahydro-1*H*-2-benzazepines (**253**) (0-10%) (Stevens rearrangement products) and Hofmann degradation products *E*- and *Z*-**254** (0-100%) (Scheme 71).[95]

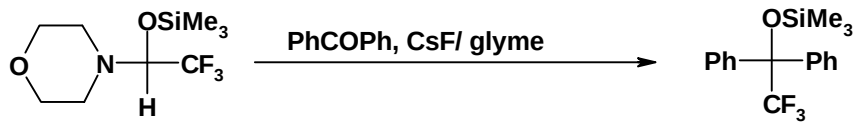


R = H, Me, OMe

Scheme 71

4.3. Morpholines and piperazines

1-(2,2,2-Trifluoro-1-trimethylsiloxyethyl)morpholine and related compounds can serve as new reagents for trifluoromethylation of non-enolizable carbonyl compounds. For example, silyl ether (**255**) and benzophenone in the presence of CsF in glyme afforded addition product (**256**) in 80 % yield (Scheme 72).[96, 97]



255 **256**

Scheme 72

Reaction of silyl ethers of morpholines and piperazines (**257**) with disulfides or diselenides in the presence of TBAT as a fluoride ion source led to trifluoromethylsulfides or selenides (**258**) in yields up to 95% (Scheme 73).[98]

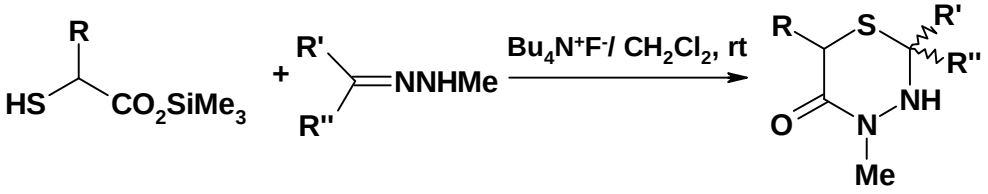
257 **258**

X = O, NCH_2Ph, Y = S, Se; R = alkyl, aryl

Scheme 73

4.4. Thiadiazones

Reaction of substituted trimethylsilyl mercaptoalkanoate (**259**) with hydrazines (**260**) in the presence of $Bu_4N^+F^-$ in CH_2Cl_2 gave perhydro-1,2,4-thiadiazin-5-ones (**261**) in 23- 67 % yield (Scheme 74).[73]



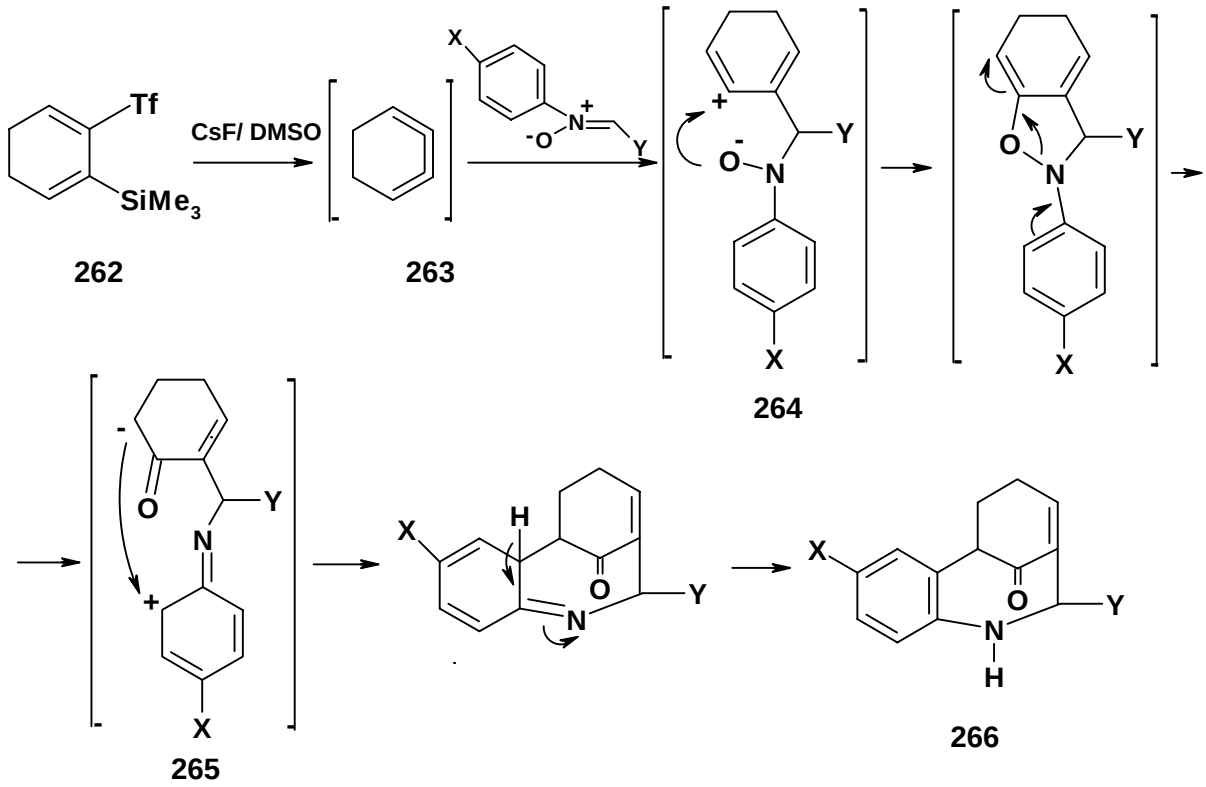
259 **260** **261**

R = H, Me; R', R'' = H, alkyl, cycloalkyl

Scheme 74

5. LARGE-MEMBERED RING SYSTEMS

[4+2] Cycloaddition of cyclohexa-1,2,3-triene (**263**), generated from triflate (**262**) and CsF, with *N*,α-diphenylnitrones afforded seven-membered cyclic amines (**266**) in 6-54 % yields. The formation of heterocycles proceeded *via* (**264**), which generated ionic intermediates (**265**) by cleavage of N-O bond. The last step was the formation of C-C bond in **265**, followed by an appropriate hydrogen shift to afford the cycloadduct (**266**) (Scheme 75).[99]

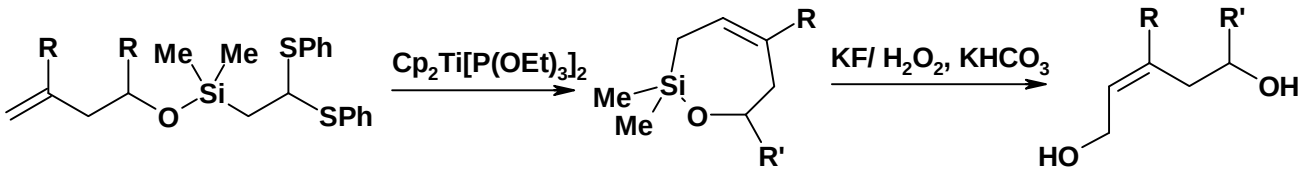


262 **263** **264** **265** **266**

X = H, Me, Cl; Y = aryl

Scheme 75

Oxidative cleavage of carbon-silicon bonds in 1,2-oxasilepin in the presence of oxidant and fluoride ion source provides a good route to diols.[100] For example, oxasilepin (**268**), prepared from silyl ethers (**267**) and $CpTi[P(OEt)_3]_2$ catalyst, underwent ring opening in the presence of KF / H_2O_2 / $KHCO_3$ system to afford olefinic diols (**269**) in 50-68 % yields with high *Z* stereoselectivity (Scheme 76).[101]

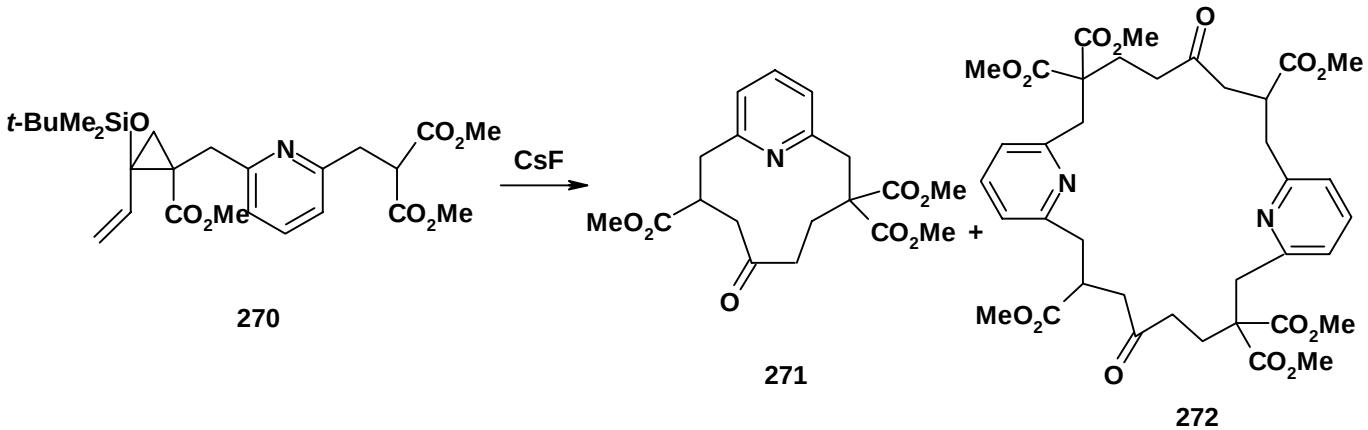


267 **268** **269**

R = H, Me; R' = alkyl, aryl

Scheme 76

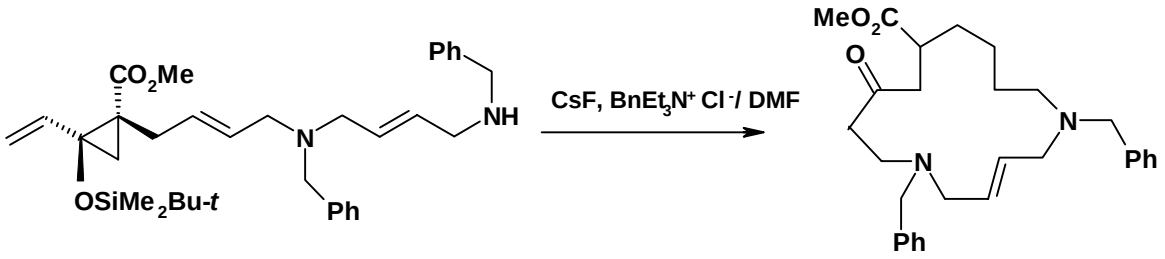
Synthesis of large-membered heterocycles by rearrangements of ammonium ylides was shorthly reviewed by Y. Sato and N. Shirai in 1994.[50] Some of more recent examples were described in Chapters 4.1 and 4.2. Synthesis of functionalized cyclophanes by ring-opening / ring-closure cascade reactions of siloxycyclopropanes was described. Thus, cyclopropane (**270**) in the presence of system CsF / $BnEt_3N^+Cl^-$ / DMF at 90°C afforded a mixture of 5-oxo-2,2,7-trimethoxycarbonyl-[8](2,6)pyridinophane (**271**) (36%) and 5,19-oxo-2,2,7,16,16,21-hexa(methoxycarbonyl)-[8_2](2,6)pyridinophane (**272**) (19%) as mixture of two diastereomers (Scheme 77).[102]



270 **271** **272**

Scheme 77

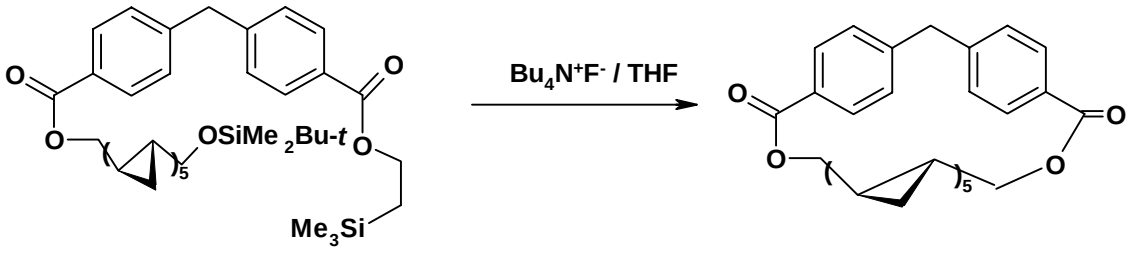
Recently synthesis of azamacrocycles from methyl 2-siloxy-2-vinylcyclopropanecarboxylates was also described. For example, silyl ether (**273**) in the presence of CsF / $BnEt_3N^+Cl^-$ / DMF system afforded azacycle (**274**) in 31 % yield (Scheme 78).[103]



273 **274**

Scheme 78

Finally, macrocyclization of silyl ether (**275**) in the presence of $Bu_4N^+F^-$ in THF afforded coronane (**276**) in 90% yield (Scheme 79).[104]



275 **276**

Scheme 79

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