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Functionalized fluoroalkyl and alkenyl silanes: Preparations, reactions, and synthetic applications

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Trifluoroacetylsilane
C–F bond activation
Desilylation
Defluorination

ABSTRACT

Preparations, reactions, and synthetic applications of functionalized fluoroalkyl and alkenyl silanes have been summarized. This review focuses mainly on the chemistries of (1) 1-substituted difluoromethylsilanes (XCF_2SiR_3), (2) 1-substituted 2,2-difluorovinylsilanes ($CF_2{=}CX{-}SiR_3$), (3) trifluoroisopropenyl, trifluoroacetimidoyl, and trifluoroacetyl silanes [$CF_3C(SiR_3){=}X$, $X{=}CH_2$, NAr, O] and (4) other fluorinated alicyclic silanes.

Contents

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1. Introduction

Silicon plays an important role in modern synthetic organic chemistry. Protection–deprotection chemistry of hydroxyl group *via* the formation of silicon–oxygen bond and its breaking has been employed most frequently in natural product syntheses. And also many useful silicon-based C–C and C–O bond formations such as the fluoride ion-mediated oxygen–silicon bond activation and C–C bond formation (Mukaiyama reaction), carbon–silicon bond activation followed by C–C bond formation (Hiyama coupling) and carbon–oxygen bond formation (Tamao alcohol synthesis), respectively have been used for organic syntheses [1]. Advantages of organic silicon compounds such as high availability, reliable stability and versatile reactivity along with sufficient information through the well-documented reviews and reference books on silicon chemistry [1] have accelerated utilization of the silicon-based chemistry in modern synthetic organofluorine chemistry. One of the most successful outcomes in the fluorine-related silicon chemistry is nucleophilic trifluoromethylation with Ruppert–Prakash reagent, of which chemistry was summarized in excellent reviews [2]. Stimulated by the successful achievement of Ruppert–Prakash reagents, a number of the functionalized fluoroalkyl and alkenylsilanes have been synthesized and employed for the syntheses of the useful organofluorine compounds over the last decade. The present review summarizes the recent development of the syntheses and reactions of the functionalized fluoroalkyl and alkenylsilanes, which include a carbon–silicon bond. However, the chemistry of trifluoromethyl and perfluoroalkyltrialkylsilanes is not included in this review since the key chemistry of these silanes was well documented in the reviews [2]. And also syntheses and reactions of fluoroaromatic silanes and silanes with X–Si bond (X = O, S, N etc.) such as fluoroalkenyl trialkylsilyl ethers are excluded, which will be described elsewhere.

Advantages of fluoroalkylsilanes for nucleophilic fluoroalkylation involve:

(1) Fluoroalkylsilanes are in general readily prepared by the deprotonative lithiation–silylation of a C–H bond, halogen–lithium exchange followed by silylation of a C–X bond, and Mg-promoted C–X bond activation–silylation (X = halogen, sulfur).
(2) Fluoroalkylsilanes are stable and storable.
(3) Pentavalent fluorosilicate, a metal-free fluoroalkyl carbanion equivalent is much more stable than the corresponding fluoroalkyl alkaline metals so as to be handled even at room temperature.
(4) Fluoroalkylation with fluoroalkylsilanes proceeds under mild conditions.

Functionalized fluoroalkyl and alkenylsilanes discussed in this review are summarized in Fig. 1. This review includes five sections; preparations and reactions of substituted difluoromethylsilanes are described in Section 2. 1-Substituted 2,2-difluoroethenylsilanes-related chemistry is discussed in Section 3. In particular, synthetic applications of trifluoroisopropenyl, trifluoroacetimidoyl, and trifluoroacetyl silanes are described in details in

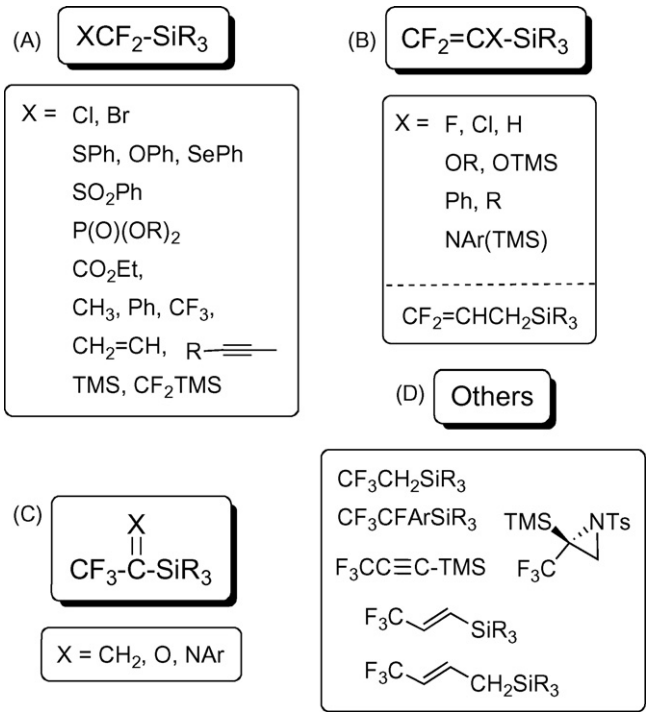


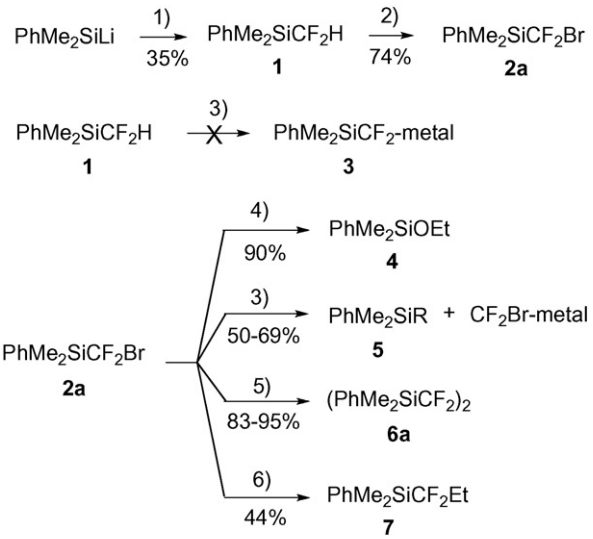
Fig. 1. Functionalized fluoroalkyl and alkenyl silanes.

Section 4. In Section 5, some functionalized cyclic fluoroalkylsilanes are summarized.

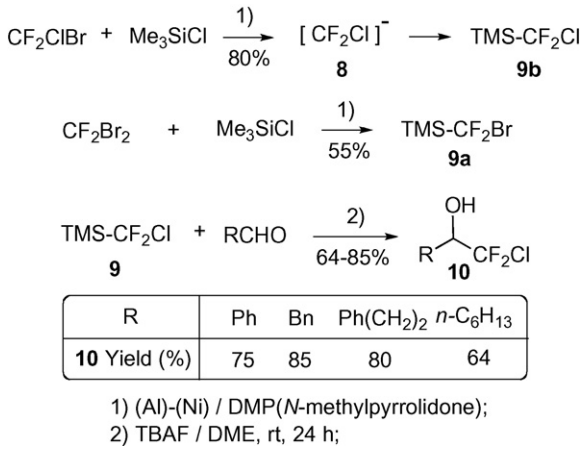
2. 1-Substituted difluoromethyltrialkylsilanes

2.1. Halodifluoromethyltrialkylsilanes

Bromodifluoromethyl(dimethylphenyl)silane **2a** was prepared by the radical bromination of difluoromethylsilane **1** with NBS, which was supplied by nucleophilic substitution of chlorodifluoromethane with dimethylphenylsilyllithium [3]. Bromodifluoromethylsilane **2a** undergoes three types of reactions with nucleophiles; the first is the nucleophilic substitution on silicon atom followed by cleavage of C–Si bond and leaving of bromodifluoromethyl group, and the second is Group VIII transition metal-catalyzed cleavage of C–Br bond and dimerization of difluoro(dimethylphenyl)silylmethyl unit, and the third is silver ion-catalyzed substitution of bromine with an alkyl group of Grignard reagent (Scheme 1) [3]. Therefore, the reactions of **2a** with sodium ethoxide in ethanol, ethyl Grignard reagent in ether, and phenyllithium in THF provided **4** and **5** as observed in the reaction of perfluoroalkyl(dimethyl)silanes with alkylmetals [4]. However, the halogen–metal exchange reaction did not occur even though it is common reaction for perfluoroalkyl bromides and iodides [2]. In connection with this fact, it is interesting that difluoromethylsilane **1** undergoes neither deprotonation nor nucelophilic attack to the silicon atom on treating with butyl lithium. In contrast, the reaction of **2a** with ethylmagnesium bromide in the presence of a catalytic amount of Group VIII metal salts such as $NiCl_2$, $PdCl_2$, $PtCl_2$, and $FeCl_3$ induced chemoselective C–Br bond cleavage, providing 1,2-bis(dimethylphenylsilyl)-1,1,2,2-tetrafluoroethane **6a** in excellent yields [3]. It was proposed that the reaction is initiated by reduction of the Group VIII metal salts to the low valent metals by Grignard reagent, to which oxidative addition of bromodifluoromethylsilane **2a** takes place. The silver ion catalysis enables replacement



Scheme 1.



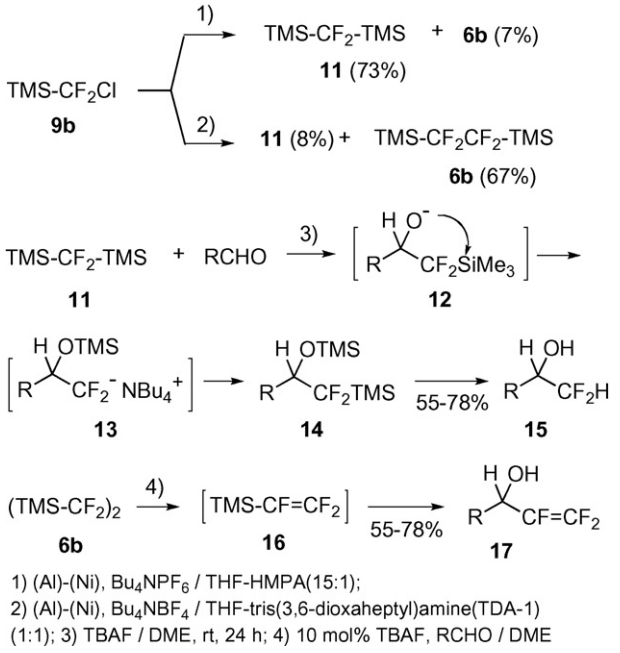
Scheme 2.

of bromine of **2a** with an alkyl group of Grignard reagent to produce **7**.

Another preparation method for halodifluoromethylsilane is electroreduction of bromohalomethanes in the presence of chlorotrimethylsilane. Bromochlorodifluoromethane was transformed to chlorodifluoromethyltrimethylsilane **9b** in 80% yield on reducing with a nickel cathode and an aluminum anode. Likewise, the bromide **9a** was prepared in 55% yield [5]. The intermediate chlorodifluoromethyl anion **8** does not undergo α-elimination, but can trap chlorotrimethylsilane effectively. No α-elimination leading to difluorocarbene suggests the chlorodifluoromethyl anion **8** must be effectively stabilized by the cationic aluminum species. The silane **9b** is a useful nucleophilic chlorodifluoromethylating agent so that the fluoride ion-catalyzed chlorodifluoromethylation of aldehydes proceeds smoothly to provide alcohols **10** in good to excellent yields (Scheme 2). However, the silane **9b** is less reactive than CF_3TMS (TMS: represents trimethylsilyl group hereafter) [6] and requires more amount of TBAT (10 mol%) in comparison with 2–3 mol% for CF_3TMS.

The further electroreduction of **9b** proceeds successfully, affording bis(trimethylsilyl)difluoromethane **11** in a mixed solvent of THF–HMPA (15:1) and 1,2-bis (trimethylsilyl)tetrafluoroethane **6b** in a mixed solvent of THF–tris(3,6-dioxaheptyl)amine (TDA-1) although aluminum and magnesium metals themselves cannot reduce **9b**. The solvent (TDA-1) may increase the life time of the radical cage and would promote the radical homo-coupling to produce the dimer **6** preferentially. Bissilane **11** is less volatile (bp = 130 °C) than TMS–CHF_2 (bp = 50 °C) and stable against hydrolysis.

The reactions of bissilanes **11** and **6** are somewhat different from those of CF_3TMS and CF_2Cl–TMS since the former silanes are not alkylated with aldehydes on *gem*-difluoromethylene carbon, while the latter silanes are alkylated. Fluoride ion-catalyzed reaction of bissilane **11** with aldehydes provides difluoromethyl alcohols **15** as a final product. The initially formed intermediate **12** rearranges to **13** *via* Brook rearrangement (Scheme 3). Meanwhile, the tetravalent fluorosilicate intermediate formed from **6** does not react with aldehyde at the *gem*-difluorinated carbon, but it undergoes defluorination from C-2 to form trifluorovinylsilane **16**. Then, the second Si–C activation of **16** by fluoride ion generates trifluorovinyl anion equivalent which adds to aldehydes, providing trifluorovinyl alcohols **17** as final products (Scheme 3) [5].



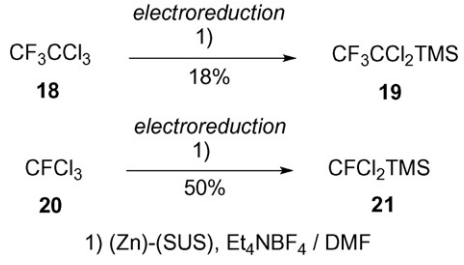
Scheme 3.

Electroreduction of 1,1,1-trichloro-2,2,2-trifluoroethane **18** and trichlorofluoromethane **20** produces dechlorinative silylation products **19** and **21**, respectively (Scheme 4) [7].

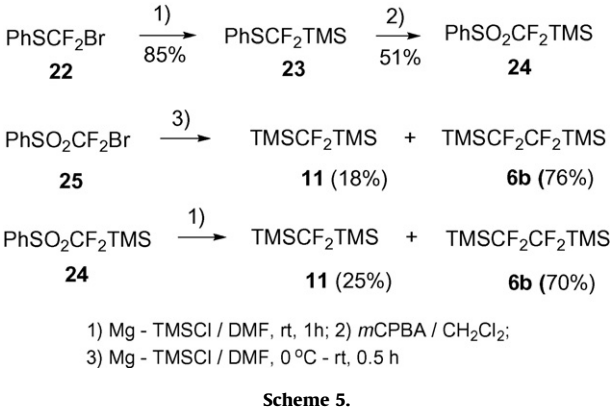
2.2. Difluoro(phenylthio)methyltrimethylsilane

The chemistry of difluoromethylated compounds has been accepting a great attention because they have interesting biological activities which arise from the strong electronic effect and the moderate steric bulkiness of difluoromethyl group [8]. However, chemistry of these compounds has not been well explored since they are less commercially available and their syntheses are not straightforward. Difluoro(phenylthio)methyl and difluoro(phenylsulfonyl)methylsilanes and the corresponding selenides have been recognized as useful building units for difluoromethyl group since sulfur and seleno moieties can be replaced with hydrogen reductively [9].

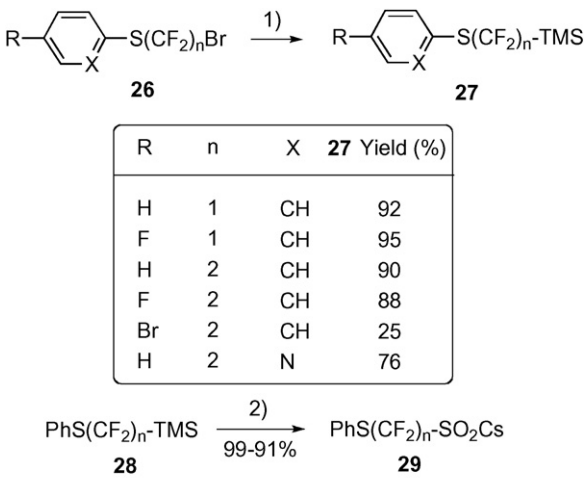
Fluoroalkylation with difluoro(trimethylsilyl)methylsulfides, sulfones, and sulfoxides is summarized. Difluoro(trimethylsilyl)-methyl phenyl sulfide **23** was prepared in 85% yield by Barbier type reaction of the bromide **22** in an Mg–TMSCl–DMF system [10]. The oxidation of sulfide **23** with *m*CPBA provides the sulfone **24**. In contrast to the selective cleavage of the carbon–bromine bond of the sulfide **22**, the reduction of the sulfone **25** under the same conditions resulted in the formation of the products **6** and **11**



Scheme 4.



Scheme 5.

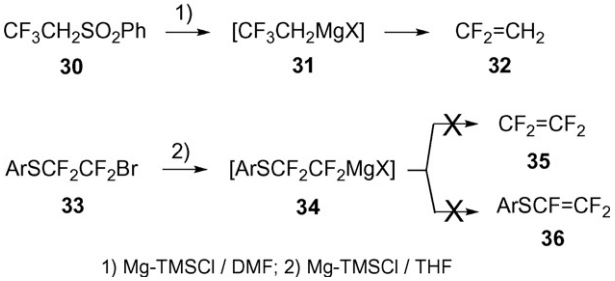


R	n	X	**27** Yield (%)
H	1	CH	92
F	1	CH	95
H	2	CH	90
F	2	CH	88
Br	2	CH	25
H	2	N	76

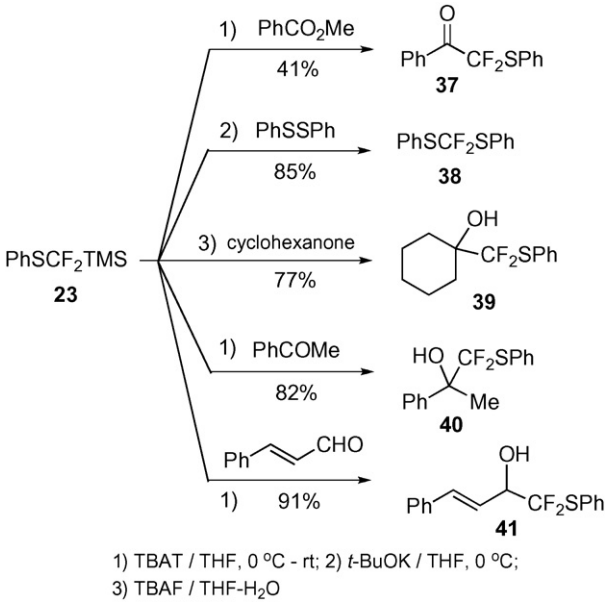
Scheme 6.

which would arise from the further cleavage of the sulfonyl sulfur–carbon bond. The difluoro(trimethylsilyl)methyl sulfone **24** was proposed as an intermediate, which then underwent further reductive cleavage of the S–C bond (Scheme 5). In fact, the sulfone **24** was transformed to **6b** and **11** under the same reaction conditions. These results suggest LUMO of the sulfide **23** is not low enough to accept an electron from metal magnesium, meanwhile the sulfone **24** accepts an electron.

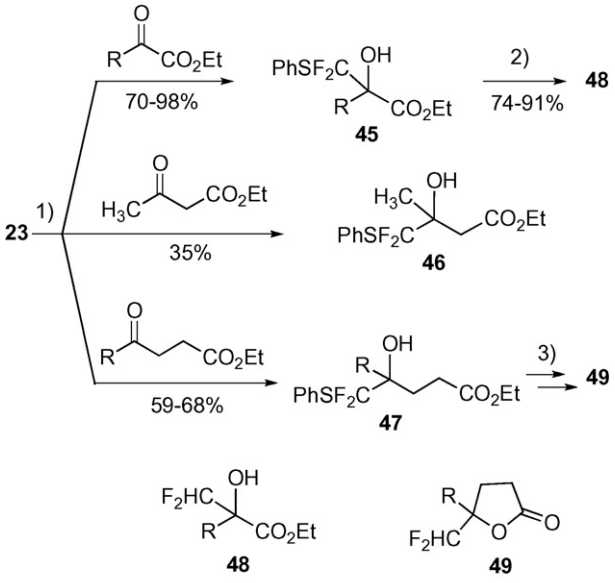
Not only bromodifluoromethyl sulfide **22** but also 2-bromo-1,1,2,2-tetrafluoroethyl sulfide **26** undergoes silylation in an Mg–TMSCl–THF system to give tetrafluorosilane **27** in excellent yields (Scheme 6) [11]. It is noticeable that 1,1,2,2-tetrafluoro-2-phenylthioethyl magnesium intermediate **34** does not defluorinate



Scheme 7.



Scheme 8.

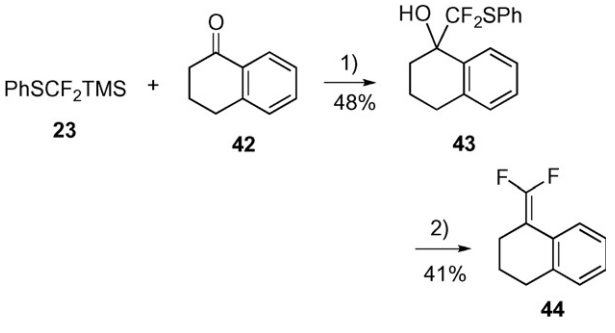


Scheme 10.

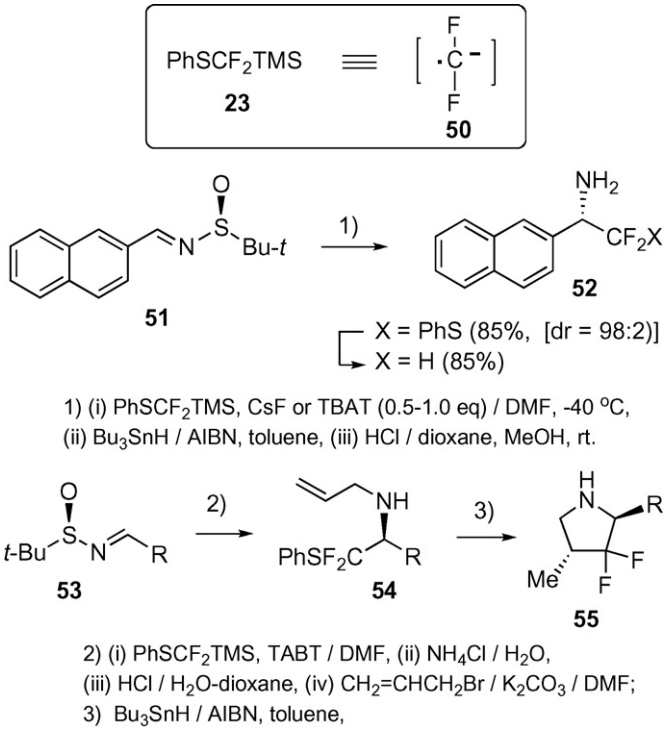
and it reacts effectively with TMSCl. In contrast, 2,2,2-trifluoroethyl magnesium intermediate **31** generated from 2,2,2-trifluoroethyl phenyl sulfone **30** does eliminate fluoride to provide 1,1-difluoroethylene quantitatively (Scheme 7) [10]. This chemical fate of the tetrafluoroethylmagnesium **34** is as similar as those of pentafluoroethyl lithium and magnesium, which are more stable in general than trifluoromethyl and 2,2,2-trifluoroethyl metals. Fluoride ion-catalyzed desilylation of **28** followed by sulfinylation with sulfur dioxide provided cesium sulfinate **29** in excellent yields [11].

Nucleophilic addition of difluoro(phenylthio)methyl carbanion equivalent generated by fluoride ion-catalyzed desilylation of **23** to carbonyl compounds and the subsequent desulfurization are an excellent approach to the introduction of difluoromethyl group to a target molecule. Schemes 8–12 show examples of the recent development in this field. Desilylative alkylations of **23** demonstrate successful benzoylation (**37**), sulfenylation (**38**), and alkylation with ketones (**39** and **40**) and α,β-unsaturated aldehyde (**41**) (Scheme 8) [12]. Difluoro(phenylthio)methylsilane **23** can be used for difluoromethylenation of ketones although thermal elimination of benzene sulfinic acid from the sulfoxide of **43** requires high temperature (Scheme 9) [13]. α-, β-, and γ-Ketoesters react with the silane **23** to provide hydroxyesters **45**, **46**, and **47**, respectively (Scheme 10) [14]. β-Ketoester was found to be less reactive presumably due to either the enolization of the ester under the reaction conditions or deprotonation from the active methylene by fluoride ion.

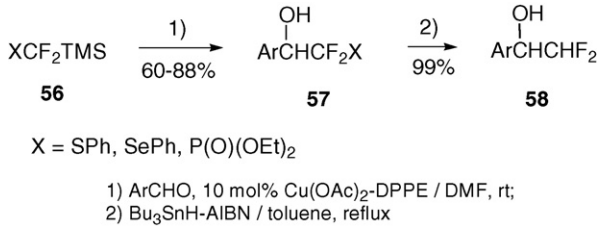
Difluoro(phenylthio)methylsilane **23** behaves as a bidentate anion and radical species **50** (Scheme 11) at the difluoromethylene carbon. Thus, γ-hydroxyester **47** was transformed into 4-substituted-4-difluoromethyl-γ-lactone **49** by acid-catalyzed



Scheme 9.



Scheme 11.



Scheme 12.

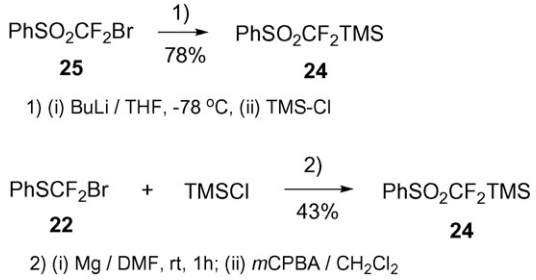
cyclization followed by desulfurization *via* the radical pathway with tin hydride [14]. The same protocol is applicable for the highly diastereoselective syntheses of enantiomerically enriched 1-(2′-naphthyl)-2,2-difluoroethyl amine **52** and 3,3-difluoropyrrolidine **55** *via* difluoro(phenylthio)methylation of optically active *N*-*t*-butylsulfinylaldimines **51** and **53**, respectively (Scheme 11) [15].

The first Lewis acid-catalyzed trifluoromethylation reactions of aldehydes with CF_3TMS under TiF_4/DMF, $Ti(OiPr)_4$/DMF and $Cu(OAc)_2$/dppp/toluene conditions have been reported [16]. This method was applied to the difluoromethylation of aldehydes using Me_3SiCF_2SePh, $Me_3SiCF_2P(O)(OEt)_2$ and Me_3SiCF_2SPh in the presence of 10 mol% of the catalyst, $Cu(OAc)_2$-DPPE (Scheme 12). The deselenation of **57** *via* a radical pathway provided **58** quantitatively.

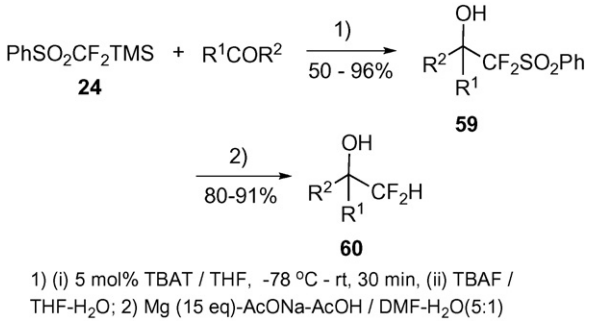
2.3. Difluoro(trimethylsilyl)methyl phenyl sulfone

Both (difluoromethyl)trialkylsilanes (R3SiCF2H) [17] and bis(trimethylsilyl)difluoromethane [5] were found not to be general reagents for difluoromethylation. Meanwhile, difluoromethylation with difluoromethyl phenyl sulfone ($PhSO_2CHF_2$) [18] is less effective for enolizable aldehydes and ketones. On the basis of these drawbacks, difluoro(trimethylsilyl)methyl phenyl sulfone **24** has been developed for the more effective difluoromethylation of carbonyl compounds. The sulfone **24** was firstly prepared by *m*CPBA oxidation of sulfide **23** [10] and later on was synthesized more effectively by sequential lithiation and silylation of bromodifluoromethyl phenyl sulfone **25** (Scheme 13) [19].

Difluoro(phenylsulfonyl)methylation with the silane **24** was conducted at −78 °C to room temperature by the use of TBAT for aldehydes and CsF for ketones. Even enolizable aldehydes are allowed to react well with the silane reagent **24** due to the milder basic conditions [19]. The corresponding lithium reagent from $PhSO_2CF_2H$ is usable for normal aldehydes and ketones, but less effective for the enolizable aldehydes [19]. The selective 1,2-addition to α,β-unsaturated aldehydes and ketones was observed



Scheme 13.



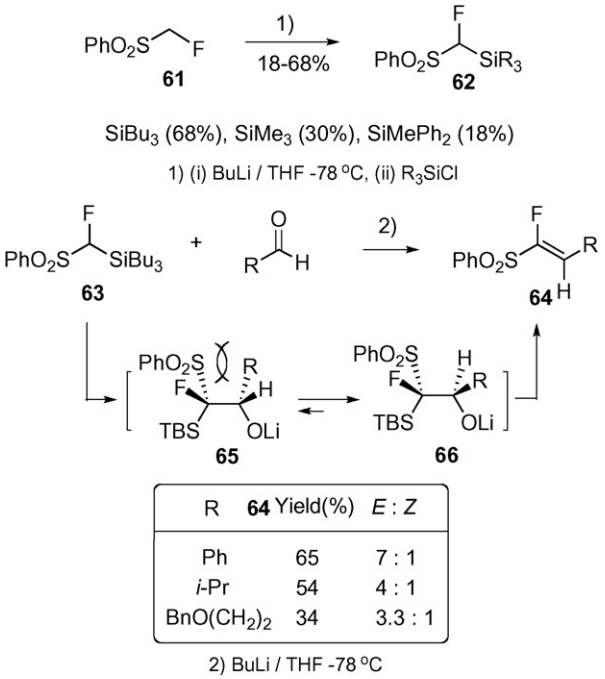
Scheme 14.

(Scheme 14) [19]. The environmentally friendly desulfonylation of **59** was also achieved by the use of metallic magnesium in aqueous DMF.

Deprotonation–silylation of **61** produces fluoro(trialkylsilyl)-methyl phenyl sulfones **62** in 18–68% yields. Peterson olefination of **62** with aldehydes provides (*E*)-1-fluoroalkenyl phenyl sulfones **64** as major products [20]. The intermediate **66** is thermodynamically more favorable than **65** due to the less steric repulsion in the *syn*-elimination transition state (Scheme 15).

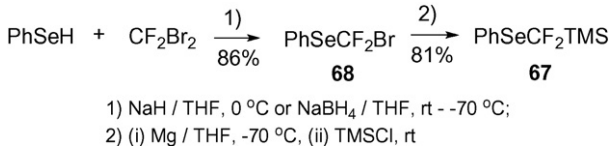
2.4. Difluoro(phenylseleno)methyl(trimethyl)silane

The selenosilane **67** is prepared and is allowed to react with electrophiles in a similar manner as the corresponding thiosilane **23**. The SET reaction of sodium benzeneselenolate with CF_2Br_2 in THF and the subsequent Grignard reaction of bromodifluoromethyl selenide **68** followed by trapping with TMSCl give difluoro(trimethylsilyl)methyl phenyl selenide **67** in excellent yields (Scheme 16) [21]. Upon treating **67** with TBAF in THF at



R	**64** Yield(%)	*E* : *Z*
Ph	65	7 : 1
i-Pr	54	4 : 1
$BnO(CH_2)_2$	34	3.3 : 1

Scheme 15.



Scheme 16.

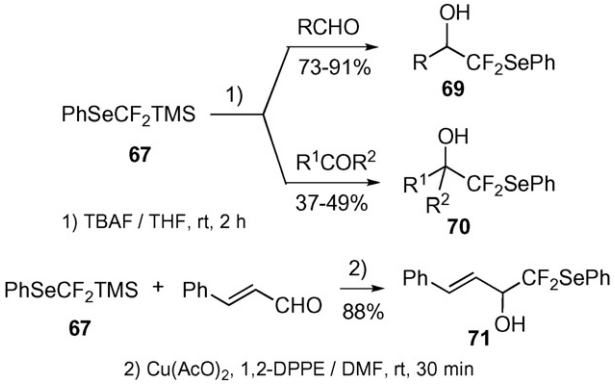
room temperature and trapping difluoro(phenylseleno)methyl anion equivalent with aldehydes and ketones, alcohols **69** and **70** are produced in reasonable yields, although the anion equivalent from **67** is less reactive with ketones (Scheme 17) [22]. The deselenative transformation of CF_2SePh involved in alcohol **69** to CHF_2 is easily carried out in the AIBN–Bu_3SnH–toluene system at 100 °C [21]. The TBAF-catalyzed difluoro(phenylseleno)methylation with **67** is conducted favorably in the presence of MS-4A so as to avoid protonation of the anion equivalent and to suppress the formation of difluoromethyl selenide. The reaction of **67** with optically active aldehyde **74** bearing chiral sulfinyl group proceeds diastereoselectively [22]. The reaction mode of the selenide **67** is as same as that of the corresponding sulfide **23**. However, Cu(II)-catalyzed addition of **67** to aryl aldehydes proceeds much faster than that of the sulfide **23** and gives the adducts **73** (X = SePh) in higher yield (94% in 0.5 h) than that of **73** (60% in 12 h, X = SPh) (Scheme 18, Table) [16].

2.5. Difluoro(phenoxy)methyltrimethylsilane

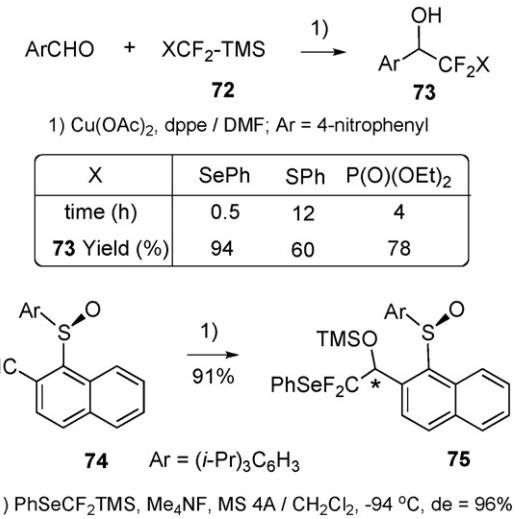
Difluoro(phenoxy)methyltrimethylsilane **77** and difluoro(1-*N*-imidazolyl)methyltrimethylsilane **79** can be prepared by Grignard type reaction of chlorodifluoromethyl phenyl ether **76** in DMF and SET type reductive silylation of **78**, respectively [23]. The corresponding pentafluorophenoxy silane was also prepared [24]. The fluoride ion-catalyzed C–Si bond activation of the phenoxy silane **77** followed by alkylation with isocyanate and aldehydes provide the difluoro(phenoxy)acetamide **81** and 1-substituted 2,2-difluoro-2-phenoxyethanols **82** and **83** (Scheme 19) [24].

2.6. Diethyl difluoro(trimethylsilyl)methylphosphonate

Diethyl difluoro(trimethylsilyl)methylphosphonate **84a** was prepared by the reaction of bromide **85** with metal cadmium in DMF [25]. Later on deprotonation and silylation of difluoromethylphosphonate **86** [26], bromine–lithium [27] and bromine–magnesium [28] exchange reactions of bromodifluoromethylphosphonate



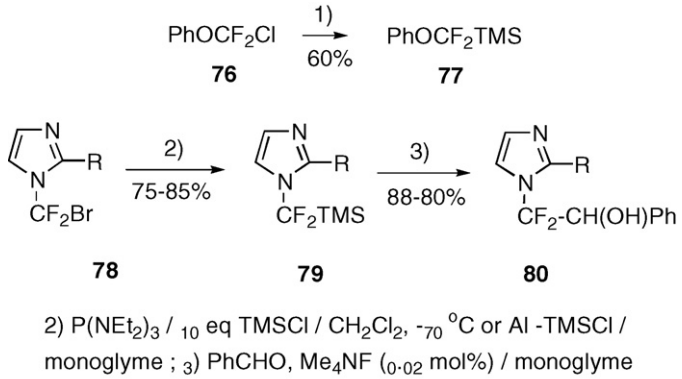
Scheme 17.

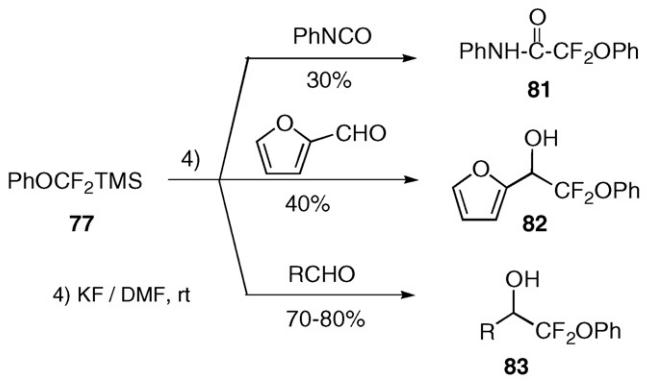


Scheme 18.

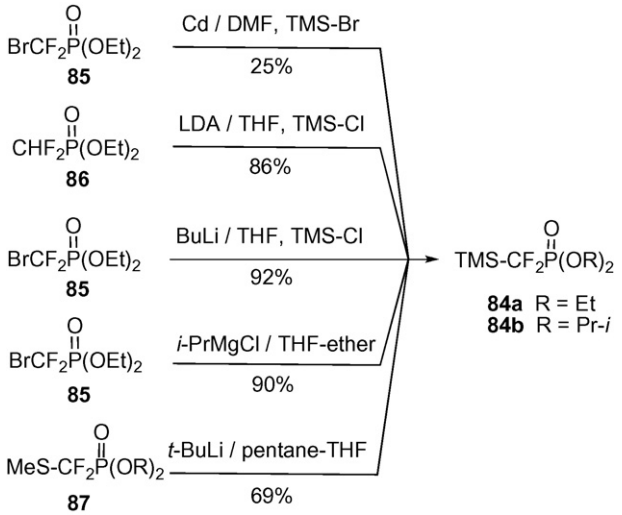
85 followed by silylation with TMSCl, and sulfur–lithium [29] exchange and silylation of difluoro(methylthio)methylphosphonate **87** were employed for the purpose (Scheme 20). Most favorably in laboratory scale preparation, the reaction of easily available bromide **85** with either butyl lithium or Grignard reagent followed by silylation with TMSCl provides **84a** in over 90% yield.

The silyl reagent **84a** provides the desired adducts of even very reactive *p*-nitrophenyl and 4-pyridyl ketones. In contrast, the corresponding lithium species generated from **86** is too basic to provide a complex mixture with these reactive aldehydes





Scheme 19.



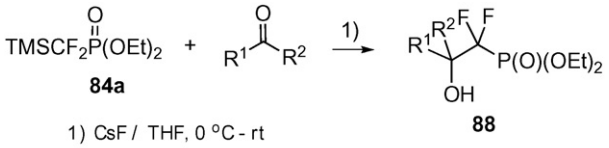
Scheme 20.

(Scheme 21) [30]. The same coupling reaction of **84** with aldehydes under the non-fluoride catalysis ($Cu(AcO)_2$, 1,2-DPPE/DMF, rt, 30 min) has been also reported [16].

Diastereoselective reactions of **84a** with functionalized aldehydes **74**, **90**, **92** are summarized in Scheme 22. The reaction of **84a** with naphthyl aryl sulfoxide **74** provided difluoroethylphosphate **89** in high diastereoselectivity (de > 96%) *via* rearrangement of the phosphonate group from carbon to oxygen in which intramolecular nucleophilic attack of alkoxide anion of the intermediate to the phosphorus atom of the difluorophosphonate moiety may take place (Scheme 22) [22]. The reaction of **84a** with cyclopropyl aldehyde **90** (*trans–cis* = 90:10) followed by Dess–Martin oxidation provided *trans*-**91** as a sole product [29]. Optically active glyceraldehyde derivative **92** was transformed to **93** [27].

The difluoromethylene analogue **96** of aspartyl phosphate has been prepared by the fluoride-catalyzed coupling of **84a** with aldehyde **94** followed by Dess–Martin oxidation and deprotection; the compound **96** inhibited (KI 95 mM) aspartate semi-aldehyde dehydrogenase, a key enzyme involved in bacterial amino acid and peptidoglycan biosynthesis (Scheme 23) [31].

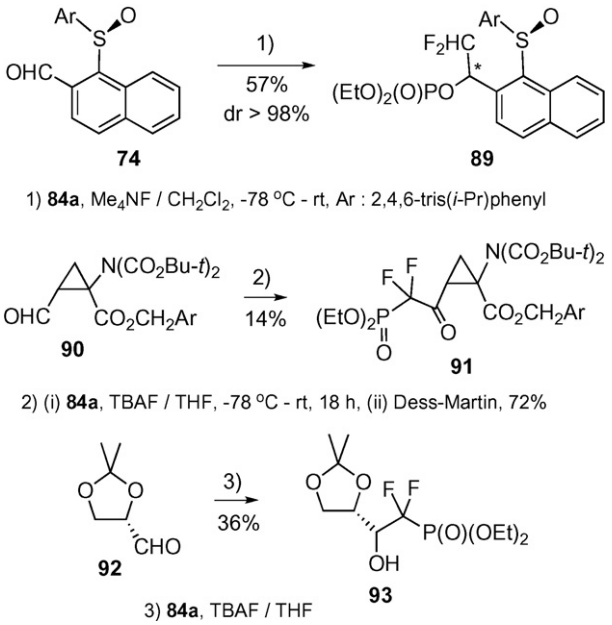
The phosphonic acid **97** was prepared (Scheme 24) and developed as a novel chemical shift-sensitive reagent for *in situ* pH measurement in NMR experiments conducted at near-neutral pH. It is highly stable and has a chemical shift that (1) does not overlap with analyte components, (2) is sensitive to pH (>0.005 ppm/pH unit) in the pH range 6–8, and (3) is insensitive



R^1	H	H	H	H	H	Me
R^2	*p*-BuOAr	Ph	*p*-NO_2Ar	4-Py	2-C_4H_3S	*p*-NO_2Ar
Yield (%)	66	58	87	57	84	38

Ar: C_6H_4, 2-C_4H_3S: 2-thiophenyl

Scheme 21.

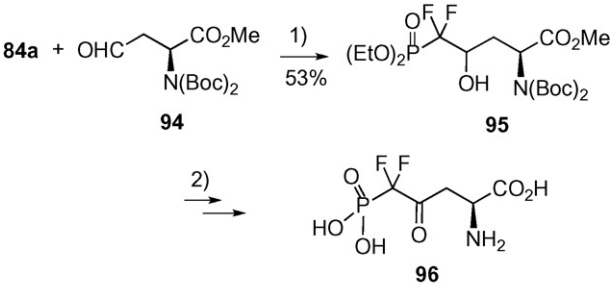


Scheme 22.

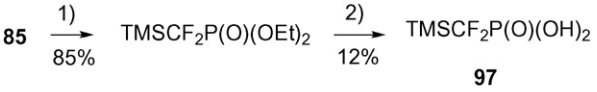
to Ca^{2+} and Mg^{2+} concentrations often found in biological samples [32].

2.7. Difluoro(trimethylsilyl)acetate

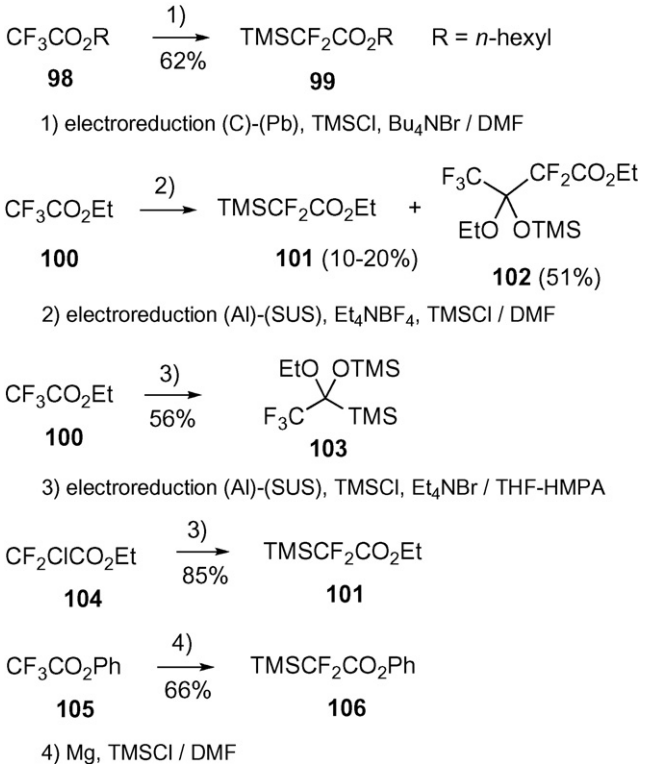
Difluoro(trimethylsilyl)acetates **99**, **101**, and **106** are excellent nucleophilic difluoro(alkoxycarbonyl)methyl transfer reagents. They are prepared by dehalogenative–silylation of either trifluoro **98**, **100**, and **105** or halodifluoroacetates **104** (Scheme 25). Reductive dehalogenation can be conducted by either electroreduction or magnesium metal-promoted reaction. Electroreduc-



Scheme 23.



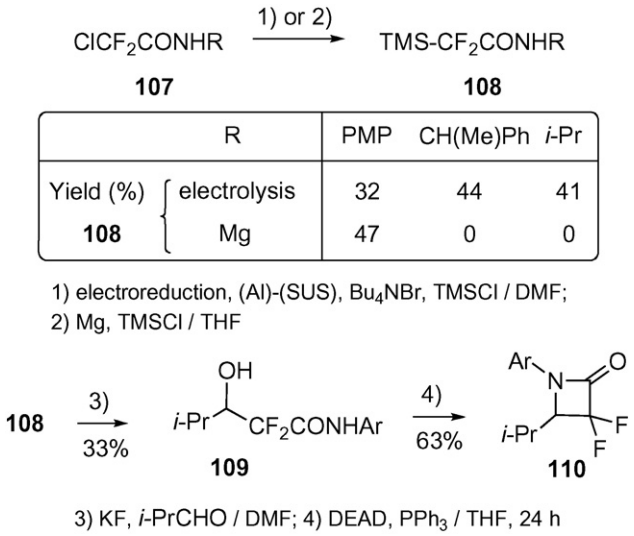
Scheme 24.



Scheme 25.

tion of **98** using carbon rod as an anode and lead as a cathode in DMF provided difluorotrimethylsilyl acetate **99** as a major product [33]. Meanwhile, electrolysis of **100** using aluminum as an anode and stainless steel as a cathode in DMF gave the Claisen product **102** preferentially [34]. In contrast to these results, electroreduction of **100** using aluminum as an anode and stainless steel as a cathode in the presence of large excess amount (15 eq.) of TMSCl in THF–HMPA at −25 °C produced ketal **103** of trifluoroacetyltrimethylsilane [35]. It is unclear at this moment that electroreduction conditions employed in these three experiments affect products so dramatically. Alternative method useful for the selective preparation of **101** is electroreduction of chlorodifluoroacetate **104** which provides **101** in 85% yield [36]. Instead, magnesium-promoted defluorinative silylation of phenyl trifluoroacetate **105** is also usable to give **106** in a reasonable yield [37]. However, the magnesium protocol is not successful for the silylation of ethyl trifluoroacetate **100** due to its higher LUMO than that of phenyl trifluoroacetate. Metal magnesium has its proper potential which must fit with the reduction potential of applicable substrates, otherwise no reduction occurs. Meanwhile, electrochemical reduction potential is variable so as to reduce the target substrates.

Dechlorinative silylation of chlorodifluoroacetamide **107** was tried by both electroreduction and magnesium-promoted dechlorination. The electroreduction provided 1-trimethylsilyldifluoroacetamides **108** in moderate yields, having nothing to do with *N*-substituents. Meanwhile, only *N*-(*p*-methoxyphenyl) acetamide **107** was reduced by metal magnesium in THF (Scheme 26) [38]. The acetamides **108** could transfer difluoro(amidocarbonyl) moiety to formyl group of isobutenal on treating with potassium fluoride to give **109**. Then, lactamization of **109** under Mitsunobu conditions provided β-lactam **110** (Scheme 26).

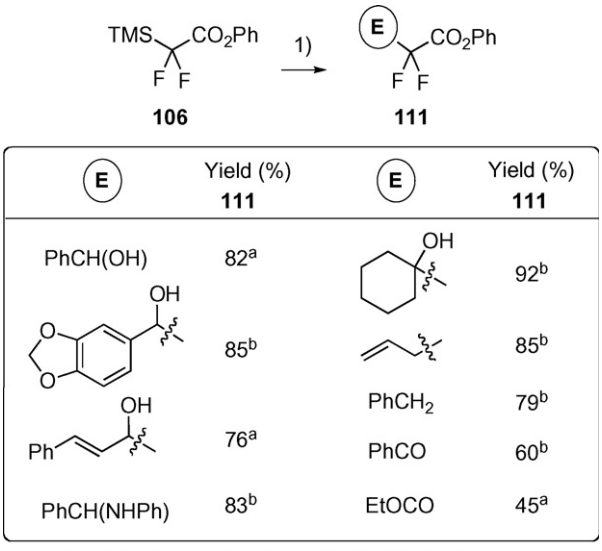


Scheme 26.

The syntheses of α-substituted difluoroacetate **111** by the fluoride ion-catalyzed Si–C bond activation of **106** followed by difluoro(carbophenoxy)methyl group transfer to a variety of electrophiles are summarized in Scheme 27 [39]. The reaction with aromatic and α,β-unsaturated aldehydes, ketone, imine, acyl chloride and chloroformate gave the desired adducts in good to excellent yields. In particular, it is noteworthy that benzylation and allylation are also successful with benzyl and allyl bromides.

2.8. α,α-Difluorobenzyltrimethylsilane

α,α-Difluorobenzyltrimethylsilane **112** is a stable silyl-protected difluorobenzyl carbanion equivalent. It is prepared by dehalogenative silylation of either chlorodifluorotoluene **113** or benzotrifluoride **114**. Metal magnesium in DMF [23,24] and samarium diiodide [40] in a mixture of benzene–HMPA are excellent reductive silylation systems for **113**, both of which

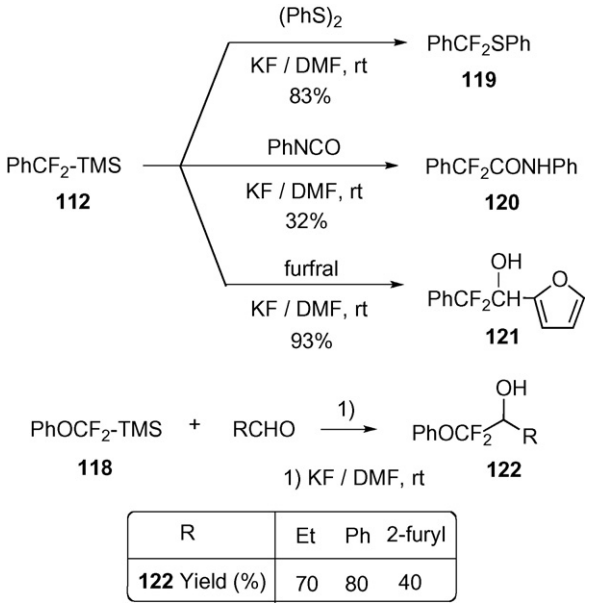


Scheme 27.

provide α,α-difluorobenzyltrimethylsilane **112** quantitatively. Benzotrifluoride **114** is more easily available than the chloride **113** so that a selective defluorinative monosilylation of **114** is valuable. Electroreduction could achieve selective monosilylation [41]. The desired silane **112** was prepared in 92% yield by electroreduction of **114** in a mixture of THF and HMPA using a sacrificial aluminum anode and stainless steel grid as a cathode in an undivided cell. Benzylic fluorines were successively replaced with trimethylsilyl group depending on the amount of electricity; monosilyl **112**, disilyl **115**, and trisilyl **116** were obtained in 92%, 83%, and 65% yields when 2.1, 4.3, and 6.3 F/mol of electricity were passed, respectively (Scheme 28) [41]. A mixed solvent of THF–DMPU is usable instead of THF–HMPA for the purpose although the yield is low (76% of **112**). In contrast, reduction with metals was less effective since no reduction of **114** occurred with magnesium, while over reduction of **114** to α,α,α-trisilyl toluene **116** (67%) was predominant with metal lithium in THF [41]. Likewise, chlorodifluoromethyl ether **117** was transformed to difluorosilane **118** by magnesium reduction in DMF [24].

The silane **112** is a nucleophilic difluorobenzylation reagent. The treatment of **112** with KF in DMF at room temperature leads to difluorobenzylation of disulfide, isocyanate, and aldehydes (Scheme 29) [24]. Fluorodifluorobenzyl(trimethyl)silicate is stable and can be handled at room temperature in contrast to the instability of difluorobenzyl lithium. In connection with this, difluoro(phenoxy)methyl(trimethyl)silane **118** is also a good nucleophilic difluoro(phenoxy)methyl transfer reagent (Scheme 29), which provides alcohols **122** in reasonable yields upon reacting with aldehydes under the fluoride ion catalysis [24].

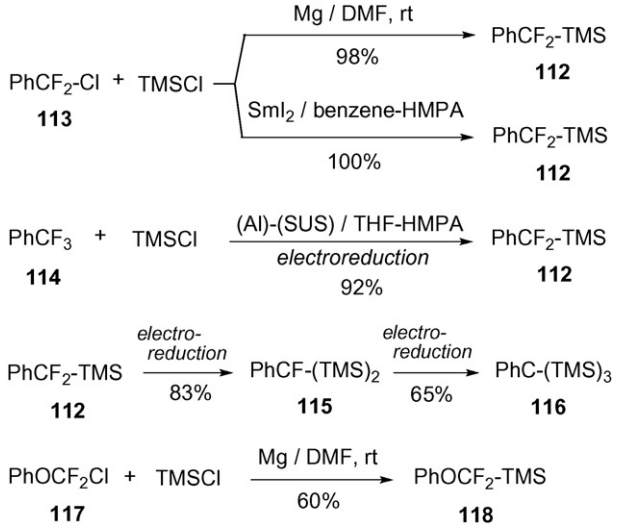
The electrochemical method is usable for silylation of trifluoromethyl group involved in the functionalized benzotrifluorides **123** and **125** even though the electron-donating amino and hydroxyl groups are unfavorable against the reduction. The electrochemical defluorinative silylation under the same conditions used for benzotrifluoride **114** was applied for **123** and **125** to give monosilanes **124** and **126** in excellent yields, respectively (Scheme 30) [42]. The more reactive *m*-hexafluoroxylene **127** was silylated in a same manner. Photochemical silylation of *meta* and *para*-hexafluoroxylenes **129** ($n = 1$) and nonafluoromesitylene **129** ($n = 2$) with disilane $(Me_3Si)_2$ resulted in poor yields of the desired difluoro(trimethylsilyl) compounds **130**, **131**, and **132** (Scheme 31) [43].



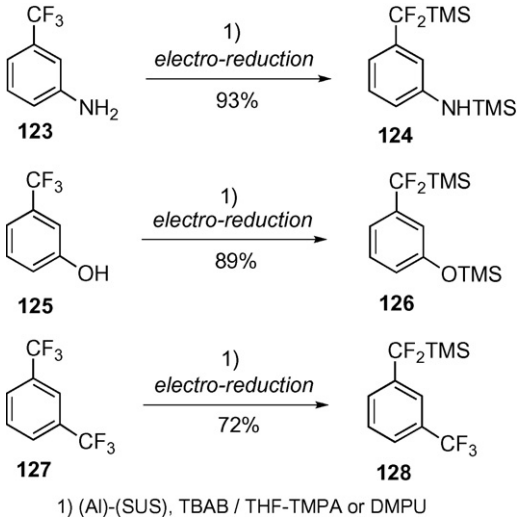
R	Et	Ph	2-furyl
122 Yield (%)	70	80	40

Scheme 29.

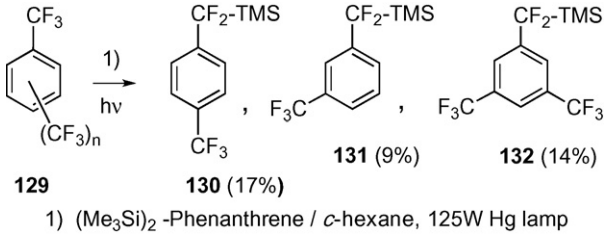
The C–F bond on benzylic carbon is cleaved and silylated by the magnesium-promoted defluorinative silylation when the substrates have their LUMO low enough to accept electrons from magnesium. Hexafluoro-*p*-xylene **133** is allowed to react with magnesium in DMF in the presence of TMSCl, affording **134** in 48% yield. Then, the difluorosilane **134** undergoes the fluoride ion-catalyzed desilylative defluorination (1,6-elimination) on heating in anisole in the presence of 5 mol% of CsF at 160 °C to be transformed into *p*-xylylene intermediate **135** (Scheme 32) [44]. The tetrafluoro-*p*-xylylene **135** dimerizes to octafluoro[2.2]paracyclophane **136** (AF4) (53% isolated yield), which is an excellent precursor of the insulating parylene polymer [45]. A rather high reaction temperature is required for the 1,6-desilylative defluorination leading to the thermodynamically unfavorable tetrafluoroquinodimethane **135**. Not only fluoride ion but also lithium acetate induces the transfer of difluorobenzyl moiety of **134** to aldimine to give **137** (Scheme 32) [46].



Scheme 28.



Scheme 30.



Scheme 31.

2.9. 1,1-Difluoroalkylsilanes and 1,1-difluoroethylsilane

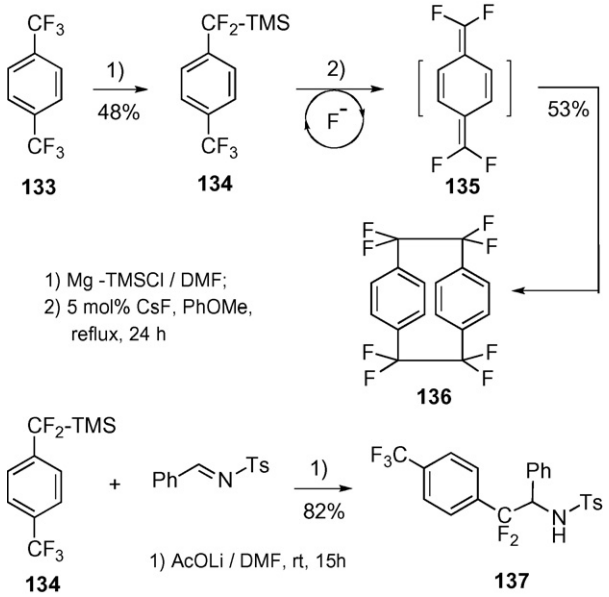
As discussed in Section 2.1, bromodifluoromethylsilane **2a** undergoes three types of reaction with nucleophiles [3]. Under the silver ion catalysis, replacement of bromine with alkyl group occurs to provide difluoroalkylsilanes **138**, which react with aldehydes (43–82%) and ketones (20–35%), respectively (Scheme 33) [17].

The sulfone **140** is prepared by methylation of difluoro(phenylsulfonyl)methyl potassium with methyl iodide. Desulfonylative silylation of **140** with magnesium and TMSCl in DMF provides **141** (Scheme 34) [47]. The corresponding TESCl is less reactive than TMSCl in the silylation of 1,1-difluoroethyl anion equivalent. In contrast to the highly reactive CF_3TMS, the silane **141** reacts much more slowly with aromatic aldehydes, affording 1,1-difluoroethyl alcohols **142**, but not with ketones and aliphatic aldehydes. In connection to the successful silylation of the sulfone **140**, it attracts a considerable attention that 2,2,2-trifluoroethyl phenyl sulfone **30** undergoes defluorination predominantly under the same reaction conditions, and never provides **143** [10].

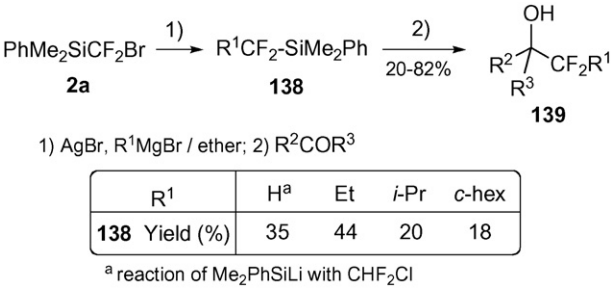
The mercury-photosensitized photolysis of a gas-phase mixture of trimethylsilane and 1,1-difluoroethylene at 30–80 °C produces **141** along with a dimeric mixture [48].

2.10. Pentafluoroethyl(trimethyl)silane

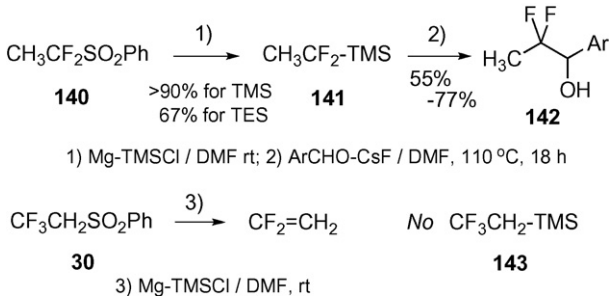
2,2,2-Trifluoroethyl lithium and magnesium have never been used for trifluoroethylation due to their instability. In contrast,



Scheme 32.



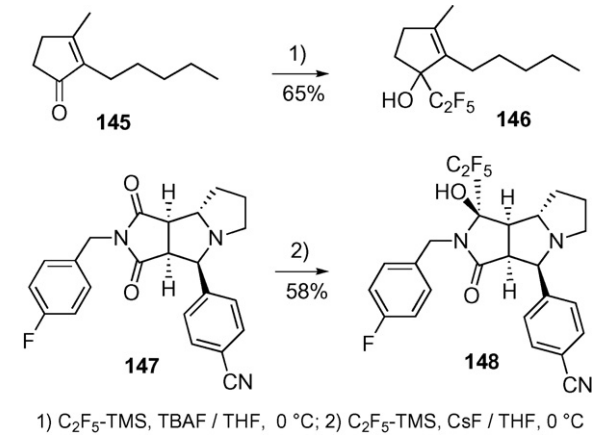
Scheme 33.



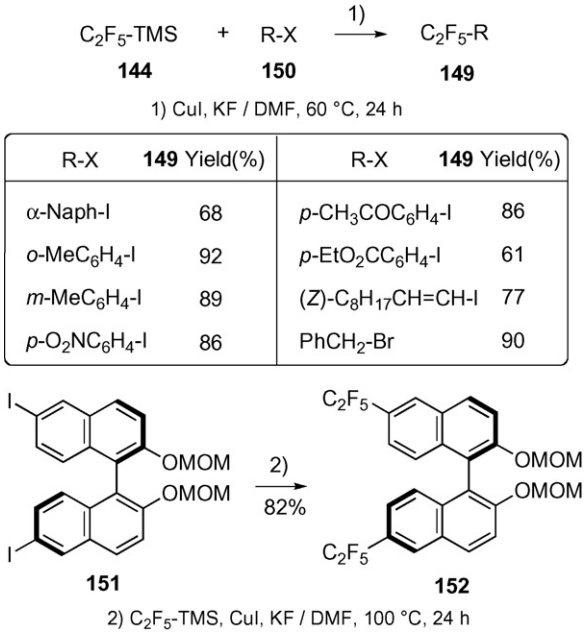
Scheme 34.

pentafluoroethyl lithium is an excellent agent although it has to be handled at low temperature, at least −40 °C [49,50]. In relation to this, pentafluoroethyl(trimethyl)silane **144** is stable and storable nucleophilic pentafluoroethylating reagent which is usable mostly at room temperature and even at 100 °C [51]. However, surprisingly there has been no report on the synthetic use of 2,2,2-trifluoroethyl(trialkyl)silane [52].

There have been many reports on the applications of pentafluoroethyl(trimethyl)silane **144** for not only C–C bond formation with ketones **145** [53], amide **147** (Scheme 35) [54], and aryl and alkenyl iodides **150** (Scheme 36) [55], but also carbon–heteroatom bond formations with sulfur and nitrogen reagents [56] (Scheme 37), and phosphorus [57] and boron derivatives [58] (Scheme 38). The pentavalent fluorosilicate of **144** is stable enough to react with the less reactive naphthyl iodide **151** at 100 °C (Scheme 36). The silane **144** reacts with NOCl, CO_2, SO_2. PhNSO, and SO_2 to produce a variety of pentafluoroethyl compounds bearing sulfur and nitrogen functional groups [56]. Substitutions of phenoxy group on



Scheme 35.

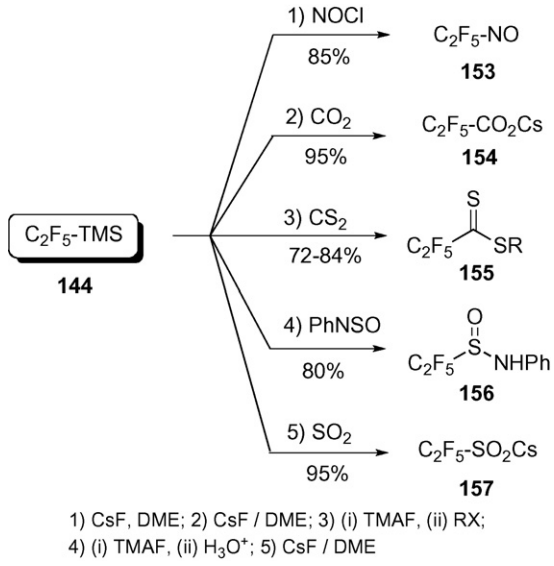


Scheme 36.

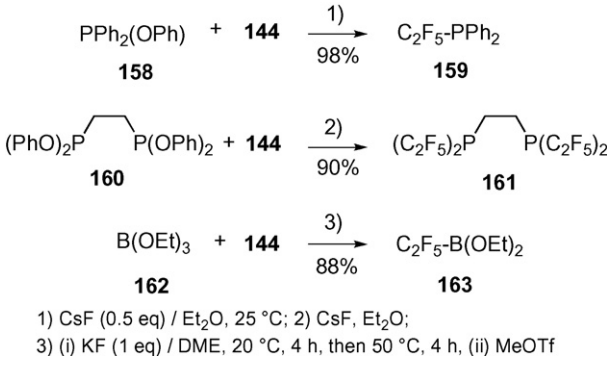
phosphorus and ethoxyl group on boron with pentafluoroethyl group are also successful (Scheme 38).

2.11. 1,1-Difluoroallyltrimethylsilane

Lithium–bromine exchange of **164** with BuLi proceeds faster than the addition of BuLi to carbonyl group so that a simple mixing of BuLi to a solution of 3-bromo-3,3-difluoropropene and aldehydes and ketones provides the desired difluorinated homoallyl alcohols in reasonable yields [59]. The lithium species of **164** reacts with trialkylsilanes to give 1,1-difluoroallyltrialkylsilanes **165** where trimethylsilane **165** (R = Me) forms in 89% yield (Scheme 39) [59]. Likewise, bis(difluoroallyl)dimethylsilane **166** is prepared. The fluoride ion-catalyzed difluoroallylation of benzaldehyde with **167** occurs regioselectively at difluoromethylene carbon, affording **168** (Scheme 40) [60].



Scheme 37.



Scheme 38.

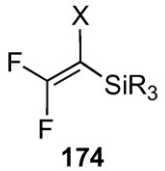
Electroreduction of **169** in DMF using Mg as an anode and SUS as a cathode produces **170** in an excellent yield (Scheme 41) [61].

2.12. 1,1-Difluoropropargyl silanes

Grignard reaction of difluoropropargyl bromide **171** with TMSCl provides difluoropropargyl silanes **172**, which are then alkylated with benzaldehyde and with alkyl and allyl halides by TBAF-catalyzed desilylative alkylation to give **173** (Scheme 42) [62].

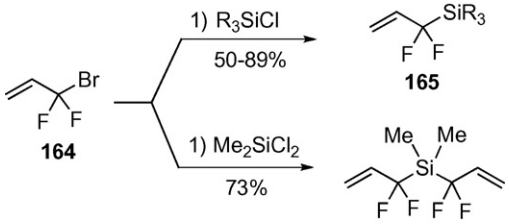
3. 1-Substituted 2,2-difluoroethenylsilanes

1-Substituted 2,2-difluoroethenylsilanes **174** are potentially multifunctional and usable for the syntheses of various fluoroorganic compounds (Fig. 2). The difluoromethylene carbon of **174** is



X = F, Cl, OTMS, OR, H, Ph, R

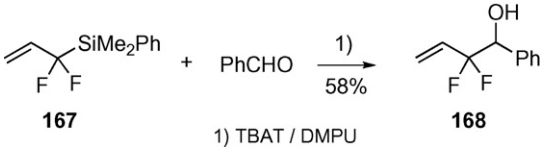
Fig. 2. 1-Substituted 2,2-difluoroethenylsilanes.



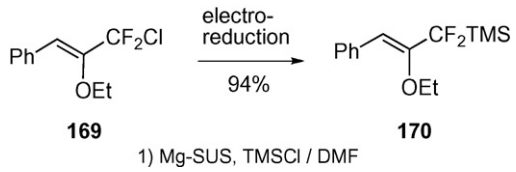
SiR_3	$SiMe_3$	$SiEt_3$	$Si(n\text{-}Pr)_3$	$SiMe_2Ph$
165 Yield	89%	51%	50%	71%

1) BuLi / THF-ether-pentane, -95 °C

Scheme 39.



Scheme 40.



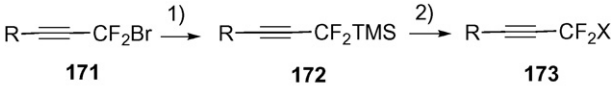
Scheme 41.

highly electrophilic so as to react nucleophiles under mild conditions *via* addition–elimination and addition–protonation pathways. It is reactive even with electrophiles when substituents X are electron-donating silyloxyl groups. The fluoride ion-catalyzed activation of the C–Si bond enables alkylation on C-1 with electrophiles. Moreover, chlorine–lithium exchange (X = Cl) and deprotonation–lithiation (X = H) of **174** provide another opportunity for the functionalization on C-1. This section summarizes preparations and reactions of 1-substituted 2,2-difluoroethenylsilanes **174** and the related fluoroalkenyl silanes.

3.1. Trifluorovinyltrimethylsilane

Trifluorovinyltrimethylsilane **174a** is prepared by the carbon-halogen bond activation of halotrifluoroethenes either by low valent metals or electroreduction followed by silylation. Thus, lithiation of chlorotrifluoroethene **175** with butyl lithium [63] or zincation [64] of bromotrifluoroethene **176** with metal zinc followed by treatment with chlorotrimethylsilane affords trifluorovinyltrimethylsilane **174a** in 90% or 65% yield, respectively (Scheme 43). Electroreduction of the bromide **176** and subsequent trapping the trifluorovinyl carbanion generated *in situ* is also successful for the preparation of **174a** [65]. The same electrochemical reaction is applicable for the preparation of 2-chloro-1,2-difluorovinyltrimethylsilane from 1,2-dichloro-1,2-difluoroethene [65]. Fluoride ion-catalyzed desilylative defluorination [66] of bis(trimethylsilyl)tetrafluoroethane **6b** is an alternative method for the preparation of **174a** where the vinylsilane **174a** is subjected to alkylation with aldehydes *in situ* without isolation [5].

Trifluorovinyltrimethylsilane **174a** is a stable and storable compound which is the synthetic equivalent of the metal-free trifluorovinyl anion. Fluoride ion-catalyzed carbon–silicon bond activation of **174b** enables the generation of trifluorovinyl anion equivalent and its alkylation with aldehydes at room temperature (Scheme 44) [60,67]. The trifluorovinyl synthetic intermediate **178** was transformed to the trifluoromethylated pyrethroids **179** by S_N2' type dehydroxylative fluorination with DAST [67]. This successful alkylation with **174** at room temperature contrasts sharply to the

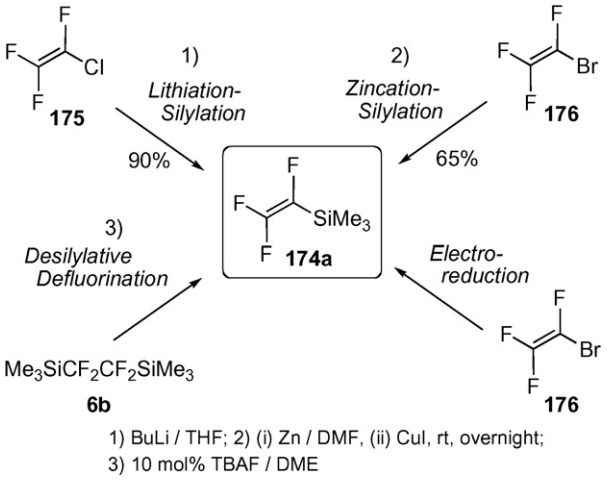


R	*p*-MeC_6H_4	*p*-$MeOC_6H_4$	Ph	Hex	TIPS	TES
172 Yield (%)	81	90	51	63	82	93

X	PhCH(OH)	CH_2=$CHCH_2$	$PhCH_2$	Me
173[a] Yield (%)	90 (i)	65 (ii)	36 (ii)	26 (iii)

[a] R in **173** = Ph

Scheme 42.



Scheme 43.

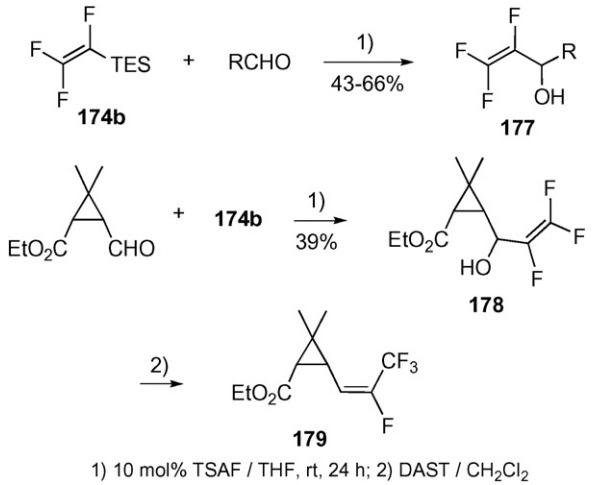
reaction of trifluorovinyl lithium, which is thermally unstable and must be handled at the temperature below −78 °C [68].

The reactions of the trifluorovinylsilane **174a** with electrophiles occur at the α-silylated carbon, meanwhile the nucleophilic substitution to **174a** does exclusively at the difluoromethylene carbon, affording β-substituted-α,β-difluorovinylsilanes. Thus, the reactions of **174a** and **174c** with $LiAlH_4$ provide (*Z*)-1,2-difluorovinylsilanes **180** [69] and **183** [70], respectively (Scheme 45). The silyl group of **180** and **183** can be replaced with stannyl group [69] and iodine, respectively [70] so that the silylated vinyl carbon in **174** offers the reaction site not only for the reaction with electrophiles but also for the transition metal-catalyzed cross-coupling reactions *via* the corresponding stannanes **181** and **182**, and iodide **184**.

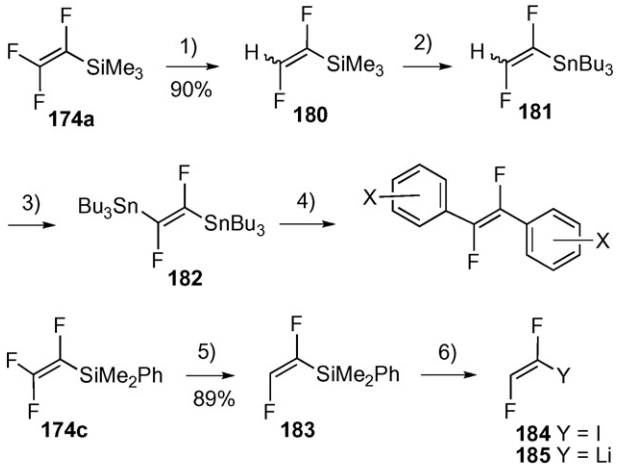
The Pd-catalyzed cross-coupling reaction of the related stannane **186** with alkenyl iodide **187** is shown in Scheme 46 [71].

The α-fluoro-β-substituted γ-unsaturated carboxylic acids **190** were synthesized *via* a diastereoselective Claisen rearrangement of allyl difluorovinyl ethers **189** which were prepared *in situ* from allyl alcohols **188** and trifluorovinylsilane **174d** (Scheme 47) [72].

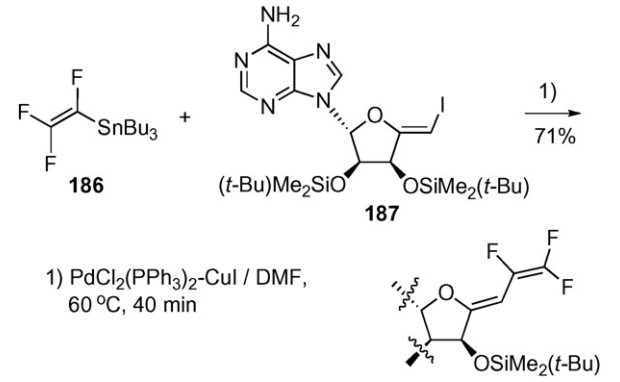
Trifluorovinylsilane **174a** undergoes cycloaddition with sulfur trioxide, providing **191** which is transformed to either trimethylsilyl ester **192** [73] or ethyl ester **193** [74] of 1,2,2-trifluorovinylsulfonic acid (Scheme 48).



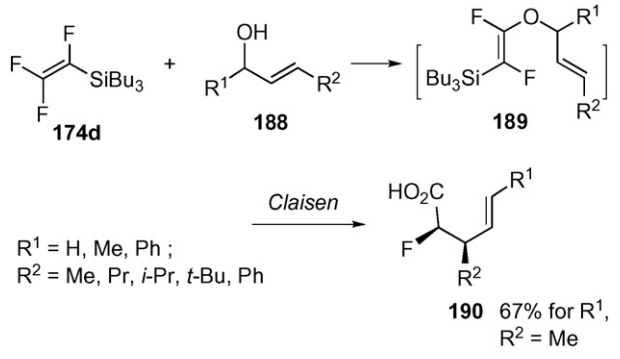
Scheme 44.



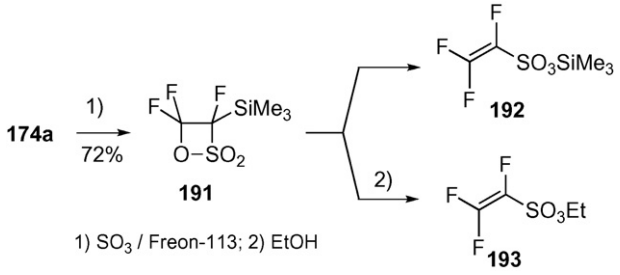
Scheme 45.



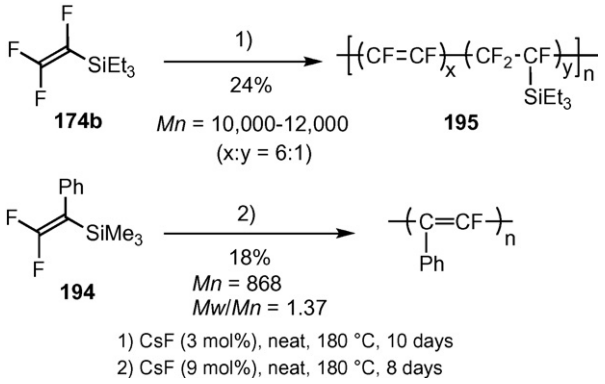
Scheme 46.



Scheme 47.



Scheme 48.



Scheme 49.

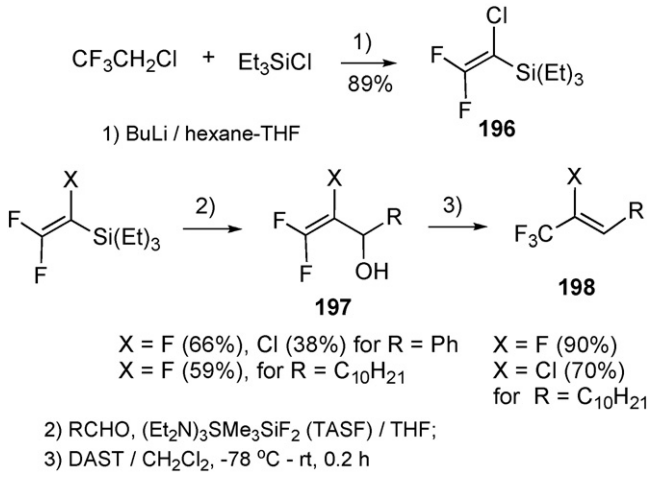
The CsF-catalyzed desilyl-defluorination of trifluorovinylsilane**174b** [75] and difluorovinyl silane **194** [76] is applicable to the polymerization, which is proposed to undergo *via* the very reactive fluoroalkyne intermediates. The vinyl silane **174b** gives semiconductor fluoropolyacetylene polymer **195**, which shows conductivity of 10^{-9} to $10^{-10}\ \Omega^{-1}\ cm^{-1}$ [75] (Scheme 49).

3.2. 1-Chloro-2,2-difluoroethenyltrialkylsilane

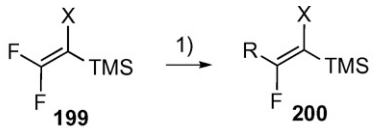
1-Chloro-2,2-difluoroethenyltriethylsilane **196** is prepared from 1-chloro-2,2,2-trifluoroethane by a sequence of the base-catalyzed dehydrofluorination, deprotonation and silylation in an excellent yield (Scheme 50) [77]. Likewise the chemistry of trifluorovinylsilane, the chloride **196** also undergoes the fluoride ion-catalyzed C–C bond formation with aldehydes to provide **197**. The subsequent fluorination of **197** with DAST *via* the dehydroxylative S_N2' type reaction proceeds smoothly to give 1-chloro- and 1-fluoro-1-trifluoromethylalkenes **198** in good yields (Scheme 50). The same transformation of **197** to **198** can be applied for the synthesis of trifluoromethylated pyrethroids **179** (Scheme 44) [67,78].

3.3. 1,2-Difluoroethenyl and 1-chloro-2-fluoroethenyltrialkylsilanes

Nucleophilic alkylation of **199** with alkyl lithiums occurs regio- and stereoselectively at the difluoromethylene carbon *via* addition–elimination pathway, affording *Z*-difluoro [63] and chlorofluoroalkenes [79] **200** in good to excellent yields (Scheme 51). The *Z*-preference in the stereochemistry can be explained on the basis



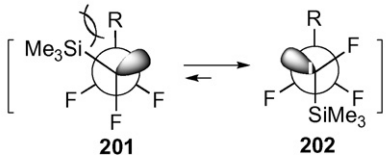
Scheme 50.



1) RLi / THF-ether, -100 °C

Yield of **200** (%)

R	*n*-Bu	*n*-Pn	*t*-Bu	Ph	CH=CMe$_2$
X = F	80	–	74	50	72
X = Cl	–	85	–	84	–



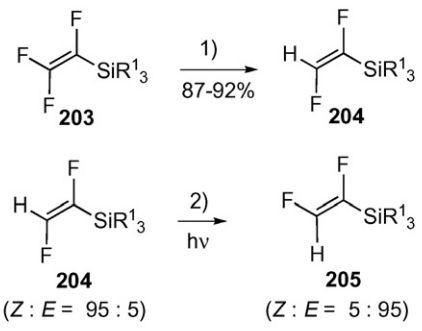
Scheme 51.

of the preferred defluorination from the thermodynamically more stable carbanion intermediate **202**. Stereoselective replacement of one of the *gem*-fluorines of **203** is achieved by reduction with $LiAlH_4$. *Z*-1,2-Difluoroethenylsilane **204** was prepared in excellent yields and only minor contamination of the *E*-isomer is observed [67,80]. Meanwhile, (*E*)-rich 1,2-difluoroethenylsilane **205** (>95% de) is obtained by photolytic isomerization of (*Z*)-rich isomer **204** in the presence of a trace amount of diphenyl disulfide (Scheme 52) [81].

The fluoride ion-catalyzed desilylative functionalizations of alkene **200** and epoxide **206** proceed stereospecifically, providing **207**, **208**, and **209**, respectively where the pentavalent fluorosilicate intermediates from **200** and **206** retain their stereochemistry in the protonation and alkylation reactions (Scheme 53) [63].

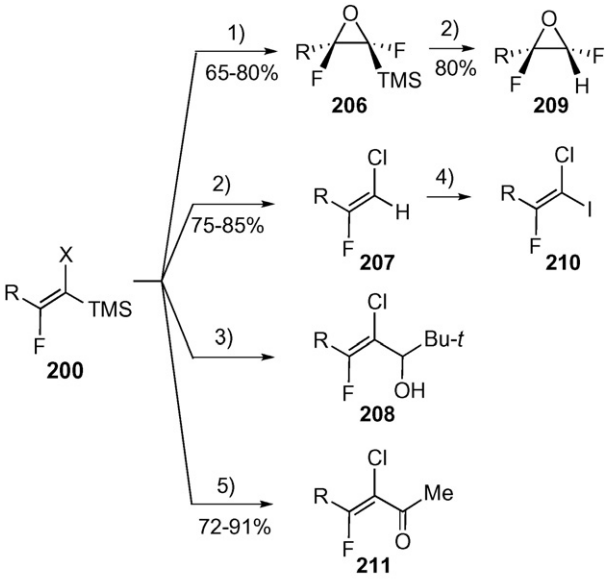
The same stereochemical outcome was also observed even in the carbocation chemistry as shown in the Friedel–Crafts type acetylation of **200** to **211**. The *E*-preference in the Friedel-Crafts type *tert*-butylation of **200** is shown in Scheme 54 where desilylation occurs from the more stable conformational intermediate **212** [63].

Lithiation of *Z*-1,2-difluorotrialkylsilane **204** (R^1 = Me) followed by reactions of **214a** with electrophiles are useful for the preparations of a variety of functionalized 1,2-difluoroalkenes **215**-**219** as shown in Scheme 55 [80]. The corresponding zinc species **214b** are usable for the palladium-catalyzed cross-coupling with organic zinc species (Scheme 56) [80]. A combination of a series of the stereochemically preserved



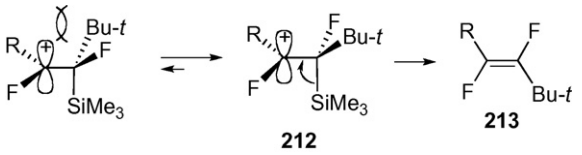
1) $LiAlH_4$ / THF, reflux, 7 h; $SiEt_3$ (87%, *Z*/*E* = 97/3), $SiMe_2Ph$ (92%, *Z*/*E* = 93/7); 2) $(PhS)_2$ 254 nm, hν, 72 h

Scheme 52.



1) m-CPBA / CH_2Cl_2, 20 °C, 1 h; 2) KF / H_2O-DMSO; 3) KF-*t*-BuCHO / DMSO; 4) (i) *s*-BuLi / THF, (ii) I_2; 5) AcCl / CH_2Cl_2

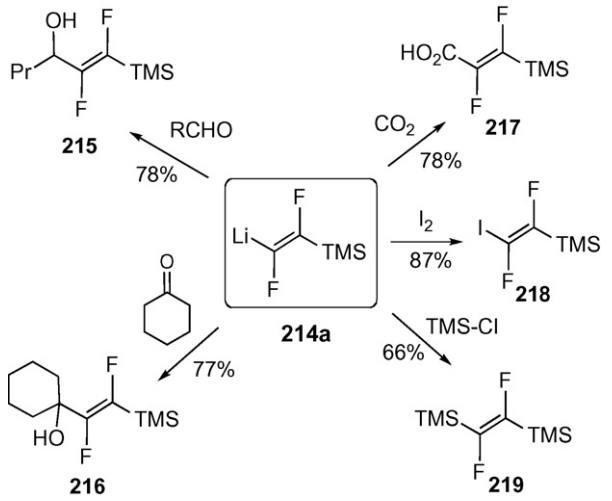
Scheme 53.



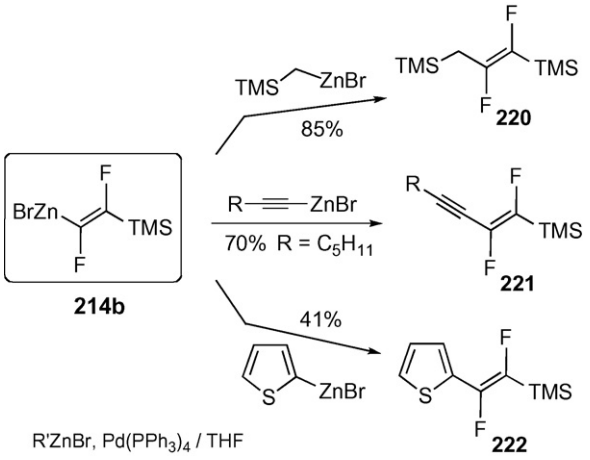
Scheme 54.

desilylation-protonation, lithiation–iodination and the palladium-catalyzed cross-coupling of the vinyl iodide with organic zinc species at the final stage leads to the efficient synthesis of oligoperfluoroalkenes **224** *via* **223** in reasonable yields (Scheme 57) [80]. Chemistry of the related fluoroalkenyl metals was well reviewed by Burton and Lu [82].

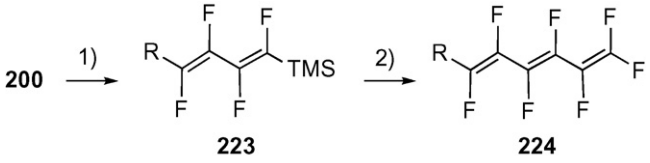
Lithiation and stereospecific carboxylation of **225** followed by fluoride ion-catalyzed desilylative stannylation of **226** and palladium-catalyzed cross-coupling of **227** with aryl iodides at



Scheme 55.

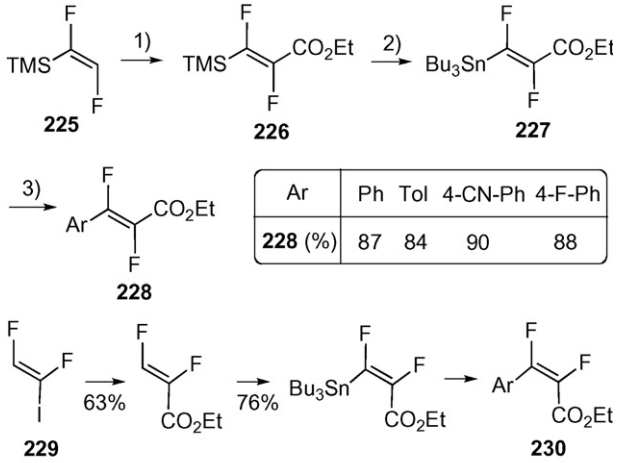


Scheme 56.



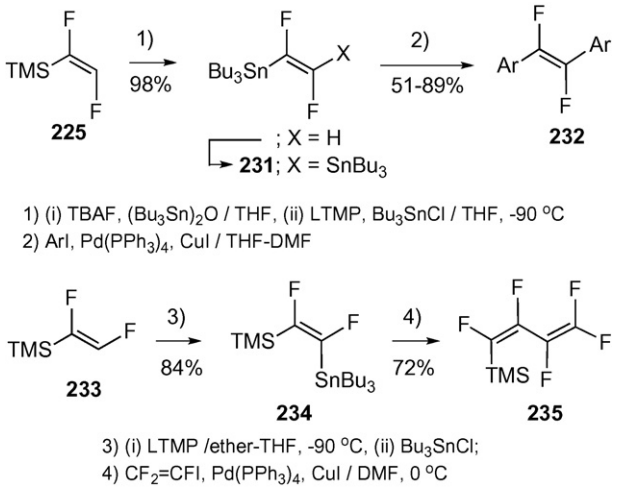
Scheme 57.

the final step accomplish the synthesis of (*E*)-1,2-difluorocinnamates **228** (Scheme 58) [83]. Starting from (*E*)-iodide **229**, the (*Z*)-isomer **230** also can be synthesized. (*E*)-1,2-difluoro-1,2-bis(stannyl)ethene **231** is prepared from **225** and then transformed to (*E*)-1,2-difluorostilbene **232** by Pd-catalyzed cross-coupling with aryl iodide (Scheme 59) [69]. Deprotonation of (*E*)-1,2-difluoroethenylsilane **233** with lithium amide followed by stannylation gives (*Z*)-(1,2-difluoro-2-trimethylsilyl)ethenyl(tributyl)stannane **234**. Pd-catalyzed cross-coupling of **234** with trifluoroiodoethene synthesizes perfluorobutadienylsilane **235** (Scheme 59) [84].



Ar	Ph	Tol	4-CN-Ph	4-F-Ph
228 (%)	87	84	90	88

Scheme 58.



Scheme 59.

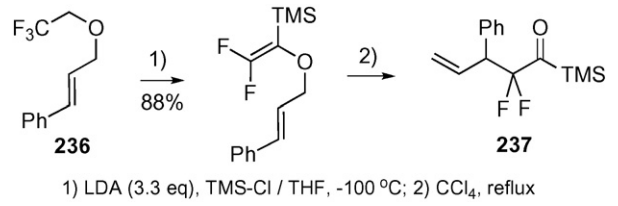
3.4. 2,2-Difluoro-1-trialkylsilylethenyl trimethylsilyl ethers

2,2,2-Trifluoroethanol is an excellent source for the 1-functionalized 2,2-difluoroethenyl ethers, carbamates and tosylates. The synthetic applications of these difluoroethenyl derivatives have been well documented by Percy [85] and Ichikawa [86]. 2,2,2-Trifluoroethanol derivatives have been transformed to the 2,2-difluoroethenyl derivatives by a sequence of reactions; base-catalyzed dehydrofluorination, deprotonation–metalation, and trapping of the vinylic metal species with electrophiles. This protocol provides us a straightforward synthesis of 1-alkoxy-2,2-difluoroethenylsilanes. The first example is shown in Scheme 60 [87], which suggests a possible synthesis of 2,2-difluoroacylsilane **237** from **236**. A series of the functionalized 2,2-difluoroacylsilanes **240** were effectively synthesized by Claisen rearrangement of 2,2-difluoro-1-trimethylsilylethenyl ethers **239** (Scheme 61) [88].

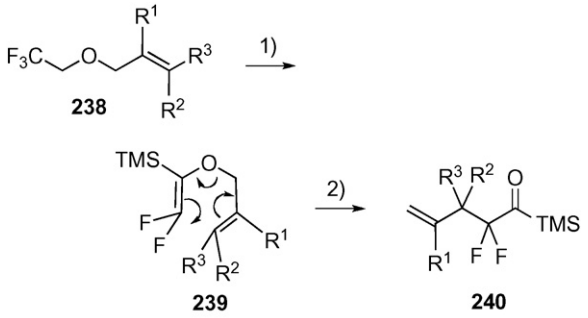
The application of this protocol to 2,2,2-trifluoroethyl trialkylsilyl ethers enables the synthesis of a variety of 2,2-difluoro-1-trialkylsilylethenyl trimethylsilyl ethers **242**. The intermediate **241** undergoes retro-Brook rearrangement to difluoroenolates which are then trapped with chlorotrimethylsilane. The acid-catalyzed hydrolysis of **242** provides difluoroacetyltrialkylsilanes **243** (Scheme 62) [89]. The reactions of **244** with the electrophilic halogenating reagents such as Selectflour™ [90], NCS, NBS and iodine [89] provide trifluoro and halodifluoroacetylsilanes **245** in reasonable yields, respectively (Scheme 63).

Aldol reaction of **242** with aldehydes provides 2,2,-difluoro-3-hydroxyacylsilanes **246** in good yields (Scheme 63) [91].

Mg-promoted defluorination [92] of difluoroacetylsilane **243** followed by trimethylsilylation of the enolate and acid-catalyzed hydrolysis of **247** result in the preparation of fluoroacetylsilanes **248** (Scheme 64) [91]. Nucleophilic addition of dimethylsulfoxoniummethylide **250** to mono- and difluoroacetylsilanes **249** and subsequent Brook rearrangement *via* **251** produce enol silyl ethers **252**. The enolsilanes **252** are transformed to a mixture of keto-



Scheme 60.



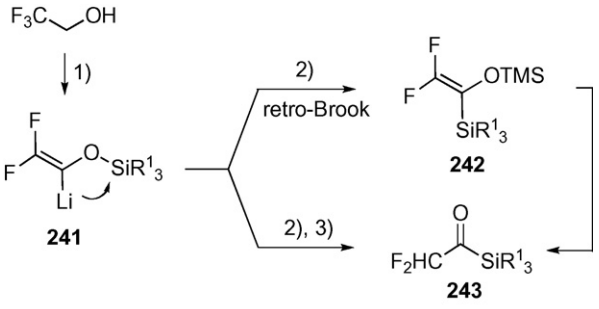
1) LDA or BuLi, TMS-Cl / THF, -78 °C or -100 °C;
2) thermolysis at 80-150 °C

R^1	R^2	R^3	**239** Yield(%)	**240** Yield(%)
H	H	H	94	79
Me	H	H	90	100
H	H	Me	94	75
H	Me	Me	85	85
H	CH_2OBn	H	78	100
H	H	$CH{=}CH_2$	91	68

Scheme 61.

alcohol **253** and α,β-unsaturated ketones **254** (Scheme 65) [93]. The reaction of difluoroacetylsilane **243** with Wittig reagents proceeds *via* two different reaction pathways depending on the structure of Wittig reagents and trialkylsilyl groups as shown in Scheme 65. The reaction of difluoroacetyltriethylsilane **243** (R^1 = Et) with methylenetriphenylphosphorane forms enol silyl ether **255** *via* Brook rearrangement. Meanwhile, the same reaction of difluoroacetyldiphenyl(*t*-butyl)silane with benzylidenetriphenylphosphorane produces normal Wittig product **256** in 75% yield [93].

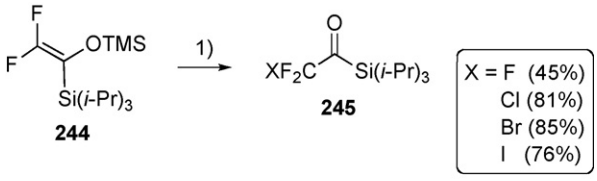
Mannich reaction of 2,2-difluoro-1-trialkylsilyl-1-trimethylsilyloxyethenes **238** with *N*-(4-methoxy, 4-methyl, and 4-nitrophenylsulfonyl)aldimines **257** proceeds smoothly under Lewis acid-catalyzed conditions, providing 3-amino-2,2-difluoroacylsilanes



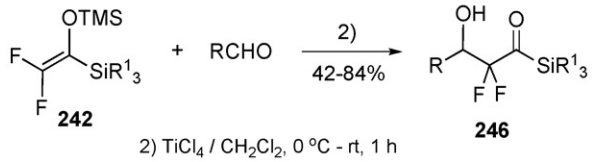
$R^1{}_3Si$	Yield % **242**	**243**
TES	80	60
TIPS	69	63
TBDPS	71	74
TBDMS	65	13
TMS	62	0

1) 3LDA, $R^1{}_3Si$-Cl (1 eq) /THF; 2) TMSCl (1.5 eq); 3) HF - H_2O

Scheme 62.

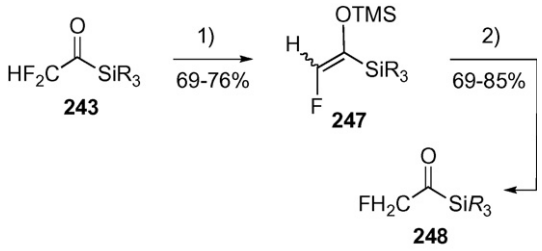


1) Selectfluor™, NCS, NBS, I_2 / MeCN-CH_2Cl_2 (4:1)



2) $TiCl_4$ / CH_2Cl_2, 0 °C - rt, 1 h

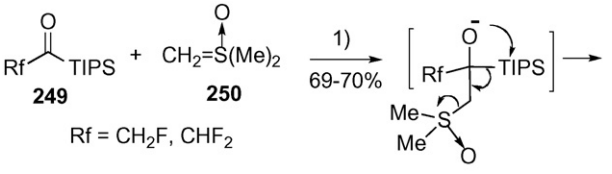
Scheme 63.

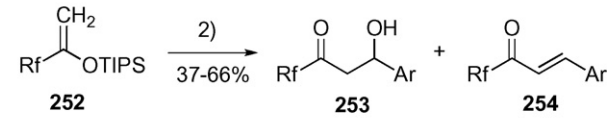


1) Mg - TMSCl / THF-HMPA, 0 °C - rt; 2) 2M HCl

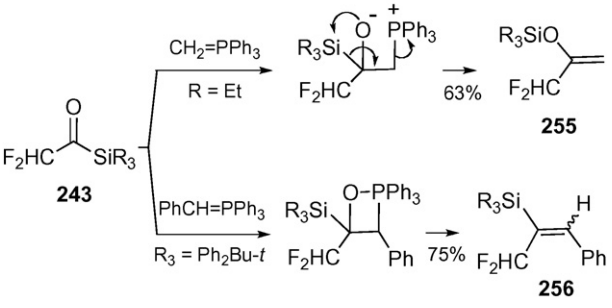
Scheme 64.

258 in 75–85% yields (Scheme 66) [94]. Aldimines of aliphatic aldehydes react with **238** under the same conditions, affording **258** in slightly lower yields (49–63%) as compared with those (62–91%) of the aromatic aldimines. The silanes **238** are not only synthetic equivalents of difluoroacylsilanes but also those of difluorocarbonyl compounds such as aldehyde, carboxylic acid and carbamide

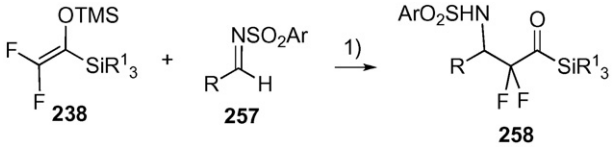




1) BuLi / THF, 0 °C ; 2) ArCHO, BCl_3 / CH_2Cl_2, 0 °C-rt, 3 h



Scheme 65.

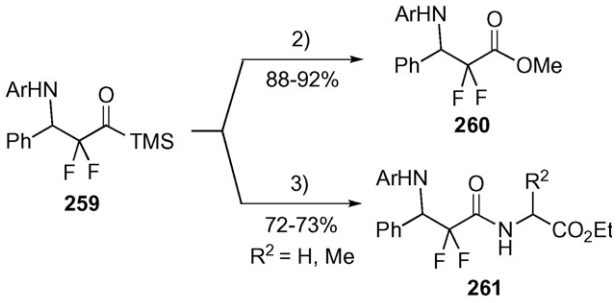


1) (i) TfOTMS or $Sc(OTf)_3$ / CH_2Cl_2, 0 °C or (ii) $Cu(OTf)_2$ / CH_2Cl_2

Yield of **258** (%) with 10 mol% of Lewis acid[a]

$SiR^1{}_3$	Me_3	Et_3	Me_2Bu-*t*	Ph_2Bu-*t*	Ph_3	(Pr-*i*)$_3$
$Sc(OTf)_3$	91	77	80	82	86	62[b]
TMSOTf	76	85	74	84	88	68[b]

[a]; R = Ph, [b]; 125 mol% of Lewis acid

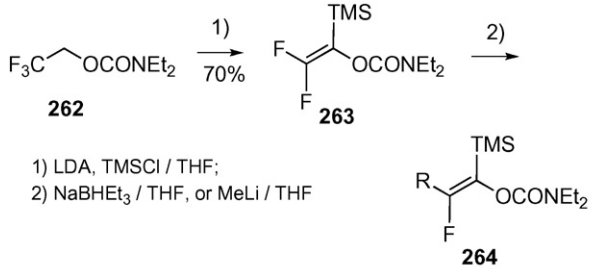


2) (i) H_2O_2, TBAF / THF, (ii) TMSCl / MeOH;
3) $[R^2CH(NH_3)CO_2Et]^+Cl^-$, NEt_3 / CH_2Cl_2, reflux

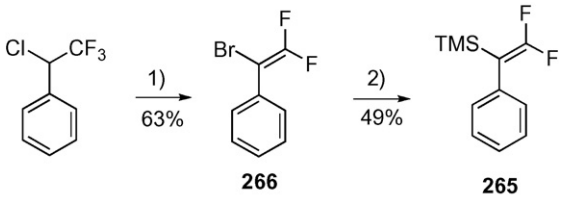
Scheme 66.

derivatives. Thus, the reaction of **259** with hydrogen peroxide in the presence of TBAF followed by esterification in methanol provides methyl esters **260** in excellent yields. Meanwhile, the reaction of **259** with glycine ethyl ester leads to the effective synthesis of dipeptide **261** in 72% yield. However, the reaction with L-alanine proceeds more slowly to give **261** (R^2 = Me) in 73% yield with no diastereoselectivity (dr = 1:1) [94].

2,2-Difluoro-1-trimethylsilylethenylcarbamate **263** was prepared from **262** by the same dehydrofluorination, metalation and silylation sequence in good yield [95]. Nucleophilic substitution of one of the *gem*-fluorines with hydride and methyl anion forms 2-fluoro-1-trimethylsilylethenyl and propenyl carbamates **264** (Scheme 67) [96]. The stereochemistry in the addition–elimination reaction of alkyl lithiums with **263** was found to be remarkably solvent-dependent; *E*:*Z* = 90:10 in THF, while *E*:*Z* = 10:90 in ether for *sec*-BuLi [96].



Scheme 67.

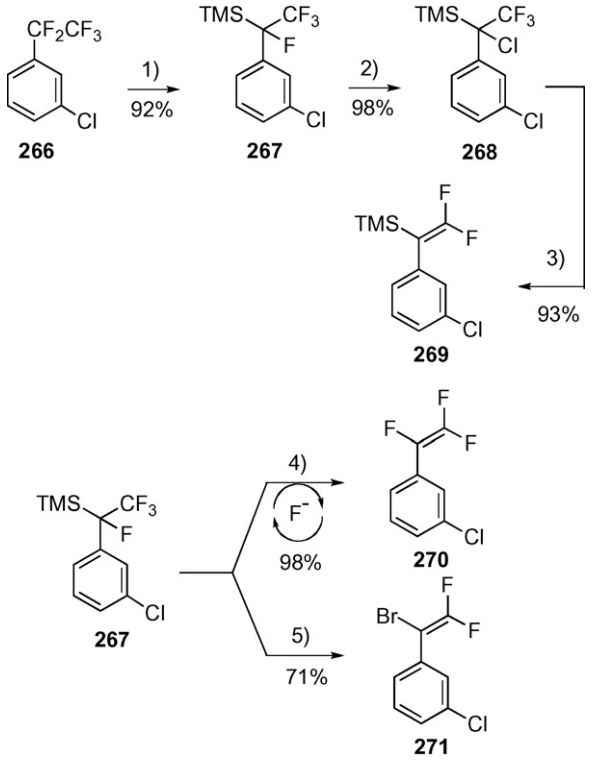


1) (i) Zn / EtOH, (ii) Br_2 / hexane, (iii) Li_2CO_3 / DMF;
2) BuLi - TMSCl / THF

Scheme 68.

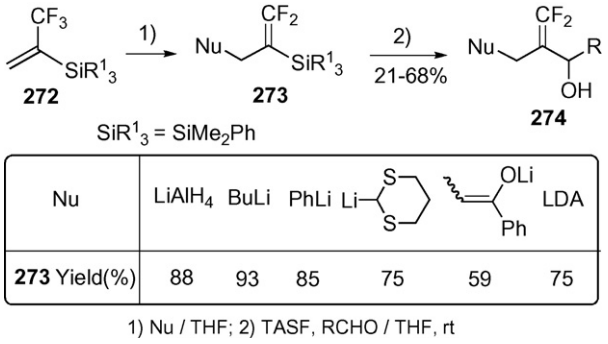
3.5. 2,2-Difluoro-1-phenylethenyl(trimethyl)silane

2,2-Difluoro-1-phenylethenyl(trimethyl)silane **265** is prepared by lithiation of the bromide **266** followed by silylation with TMSCl, where 2,2-difluoro-1-phenylethenyl lithium is rather unstable to eliminate fluoride ion and to provide 1-phenylhexyne as a byproduct *via* a possible intermediate of 2-fluorophenylacetylene (Scheme 68) [76]. The more straightforward synthesis was reported recently as shown in Scheme 69 [97]. A series of reactions, magnesium-promoted defluorinative silylation of **266**, replacement of benzylic fluorine of **267** with chlorine using Et_2AlCl, and then reductive dechloro-defluorination of **268** at the final step provided 2,2-difluoro-1-trimethylsilyl(3′-chloro)styrene **269** in an excellent overall yield. Fluoride ion-catalyzed desilylative defluorination of **267** with 0.2 mole % of TBAT in hexane yielded 1,2,2-trifluoro(3′-chloro)styrene **270** quantitatively. Reaction of **267** with aluminum bromide produced 1-bromo-2,2-difluoro-3′-chlorostyrene **271** in one pot reaction *via* replacement of benzylic fluorine with bromine followed by the fluoride ion-catalyzed

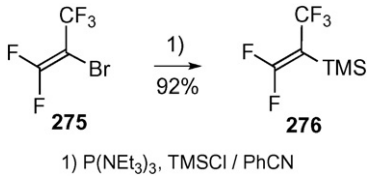


1) Mg-TMSCl / DMF; 2) Et_2AlCl / hexane, rt, 30 min ;
3) Zn / THF; 4) (0.5 mol%)TBAT, hexane, 60 °C ;
5) $AlBr_3$ / hexane, rt, 30 min.

Scheme 69.



Scheme 70.



Scheme 71.

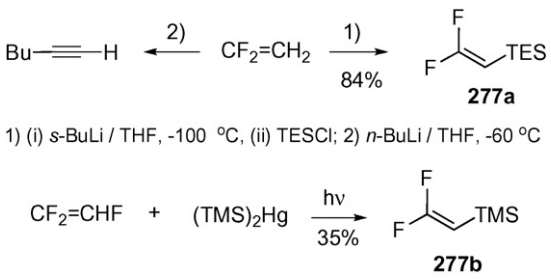
desilyl-defluorination of 1-bromo-2,2,2-trifluoro-1-(3′-chlorophenyl)ethyltrimethylsilane.

3.6. 1-Substituted 2,2-difluorovinylsilanes

1-Substituted 2,2-difluorovinylsilanes **273** are prepared by either S_N2' reaction of 3,3,3-trifluoroisopropenylsilane **272** with applicable nucleophiles (Scheme 70) or lithiation of difluoroethenylbromide **275** followed by silylation (Scheme 71). The terminal sp^2-carbon of 3,3,3-trifluoroisopropenyl moiety is highly electrophilic and thus very reactive toward nucleophiles due to the strong electron withdrawing effect of trifluoromethyl group based on its negative hyperconjugation [8]. Therefore, 3,3,3-trifluoroisopropenyl(dimethylphenyl)silane **272** reacts with a variety of carbon nucleophiles along with hydride and metal amide, affording S_N2' products **273** as shown in Scheme 70. The silyl group can be replaced further with electrophiles by the fluoride ion-promoted carbon–silicon bond activation [98]. The reductive debromosilylation of **275** with $P(NMe_2)_3$ provides perfluoroisopropenyl(trimethyl)silane **276** (Scheme 71) [99].

3.7. 2,2-Difluorovinylsilane

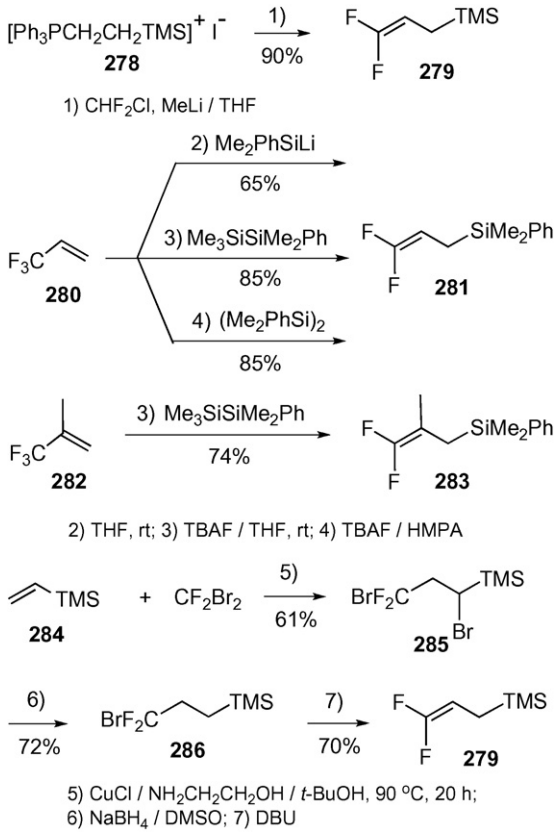
Lithiation of 1,1-difluoroethene with *sec*-butyl lithium proceeds quantitatively at −100 °C and the subsequent silylation with chlorotriethylsilane provides 2,2-difluorovinyl(triethyl)silane **277a** in 84% yield (Scheme 72) [100]. The stability of the difluorovinyl lithium is dependent on the reaction temperature. Thus, dehydrofluorination and alkylation with *n*-BuLi at −60 °C results in the formation of 1-hexyne rather than difluorovinylsilane **277a** [100]. Photochemical reaction of trifluoroethene with bis(trimethylsilyl)-mercury forms 2,2-difluorovinyl(trimethyl)silane **277b** [101].



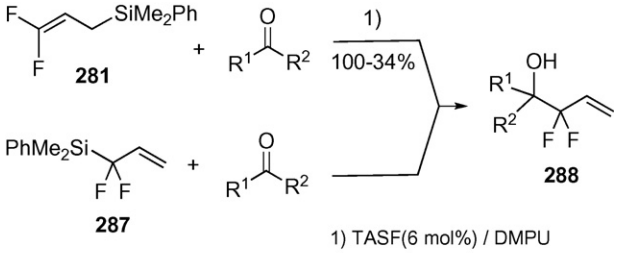
Scheme 72.

3.8. 3,3-Difluoroallylsilanes

3,3-Difluoroallylsilanes are useful nucleophilic 1,1-difluoroallylating agents for aldehydes and ketones. The silanes were firstly prepared by the thermolysis of chloro(difluorocyclopropyl)dimethylsilane and dichloro(difluorocyclopropyl)methylsilane at 600 °C [102]. The result suggests the apparent high thermal stability of the difluoroallylsilanes. Three types of preparations of 3,3-difluoroallylsilane derivatives are shown in Scheme 73. The first one is initiated by trapping difluorocarbene with (2-TMS-ethylidene)triphenylsulfonium ylide [103]. The phosphonium iodide **278** was subjected to deprotonation with methyl lithium and nucleophilic trapping difluorocarbene generated *in situ*, yielding **279** in 90% yield [104]. Two moles of ylide are needed, but each one mole of phosphonium salt and triphenylphosphine are recycled in principle. The second is S_N2' addition of either dimethylphenylsilyl lithium or the fluorosilicate from either trimethyl(dimethylphenyl)disilane or bis(dimethylphenyl)disilane to 3,3,3-trifluoropropene **280** [67]. The desired silanes **281** and **283** are prepared in high yields. The silyl anion equivalent bearing a phenyl group is generated exclusively by the fluoride ion-catalyzed Si–Si bond cleavage of the dissymmetrical trimethyl(dimethylphenyl)disilane. The third method involves radical bromo-bromodifluoromethylation of vinylsilane **284** as a key step [105]. The subsequent reductive debromination on C-1 of **285** with $NaBH_4$ followed by DBU-catalyzed dehydrobromination produces **279**.

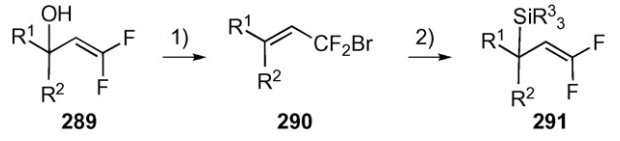


Scheme 73.

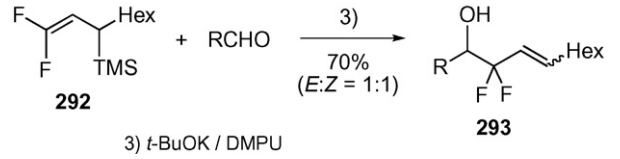


R^1	Ph	4-ClC_6H_4	PhCH=CH	$C_{10}H_{21}$	Ph
R^2	H	H	H	H	Ph
288 (yield %)	93	100	52	44	34

Scheme 74.



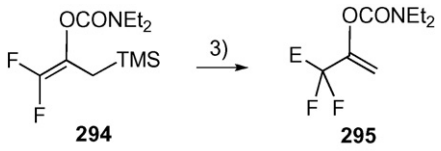
1) $SOBr_2$; 2) (i) $(R_3Si)_2$, MeLi / ether-HMPA, (ii) CuCN, difluoroallyl bromide $R^3{}_3$: Me_3, Me_2Ph



Scheme 75.

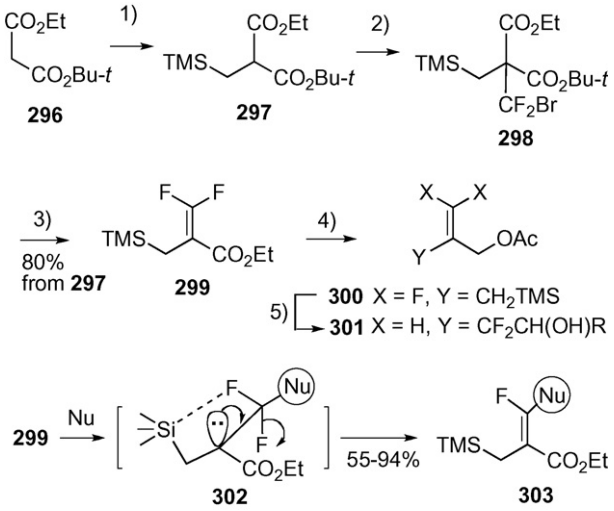
The difluoroallylation of aldehydes and ketones by the TASF-catalyzed reaction of **281** in DMPU provides **288** in reasonable yields [67] (Scheme 74). Noteworthy is the fact that either 3,3-difluoroallylsilane **281** or 1,1-difluoroallylsilane **287** gives the same 2,2-difluorohomoallyl alcohol **288**. The similar S_N2' reaction of silyl lithium to difluorobromide **290** provides **291** [106,107]. *tert*-Butoxide also catalyzes the difluoroallylation of **292** (Scheme 75) [107]. The carbamates **294** undergo difluoroallylation in a similar manner (Scheme 76) [96].

Scheme 77 shows another synthesis of 3,3-difluoroallylsilane **299** and its stereoselective nucleophilic substitution of one of the *gem*-fluorines with nucleophiles. Trimethylsilylmethylation of malonate **296** with $TMSCH_2Cl$, bromodifluoromethylation of **297** with CF_2Br_2, and TFA-catalyzed decarboxylative debromination of **298** produce **299** in 65% overall yield [108]. The acetate **300** was



electrophile	E	Yield %
H_2O	H	79
PhCHO	PhCH(OH)	64
i-PrCHO	*i*-PrCH(OH)	38

Scheme 76.



Scheme 77.

subjected to the TBAF-catalyzed alkylation with aromatic aldehydes to give the alcohols **301** in 75–85% yields. Here again, alkylation takes place chemoselectively at the difluoromethylene carbon. The highly stereoselective nucleophilic substitution proceeds at the difluoromethylene carbon with the aid of the through-space Si–F interaction which would fix the conformation favorable for the transition state as shown in **302**. Carbon, oxygen, and nitrogen nucleophiles along with hydride can be introduced into the double bond of **299** in *anti* position to the Me_3SiCH_2 group [109]. In contrast, the reduction of 2-alkyl-3,3-difluoropropenoate with $LiAlH_4$ in THF produces 1:1 mixture of the stereoisomers of 2-alkyl-3-fluoropropenoate.

4. Trifluoroisopropenylsilane and its related silanes

The silanes of trifluoroisopropenyl **304**, trifluoroacetimidoyl **305**, and trifluoroacetyl **306** silanes involve a common structure which contains a double bond C=X (X = C, N, O) bearing CF_3 and TMS groups at *geminal* position (Fig. 3). They are stable and storable, and possible alternatives for the corresponding lithium species which are extremely unstable. Preparations and reactions of these useful silanes are described in this section.

4.1. 3,3,3-Trifluoroisopropenylsilane

3,3,3-Trifluoroisopropenyl lithium is generated by the bromine–lithium exchange of 2-bromo-3,3,3-trifluoropropene **307** with *n*-BuLi in hexane at the temperature below −90 °C and can be trapped with carbonyl compounds (32–51% yield) [110]. However, the lithium species is extremely unstable even at around at −90 °C and thus it undergoes defluorination rapidly resulting in the

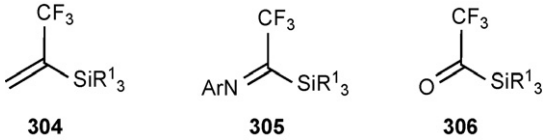
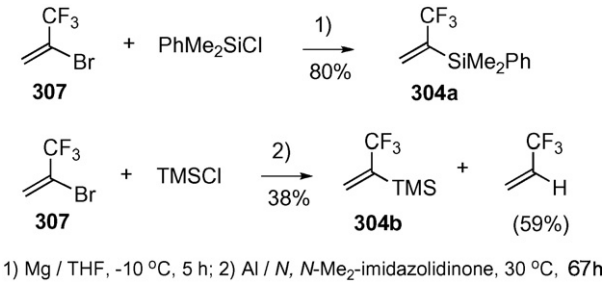
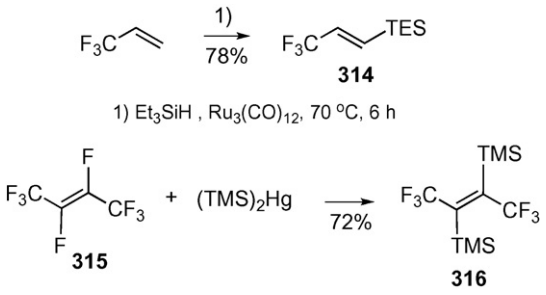


Fig. 3. Trifluoroisopropenylsilane and its relatives.



Scheme 78.



Scheme 80.

formation of 1,1-difluoropropadiene in quantitatively [111]. The corresponding magnesium species is more stable and can be handled at −10 °C. In contrast, 3,3,3-trifluoroisopropenylsilane **304** is a stable and storable 3,3,3-trifluoroisopropenyl carbanion equivalent and can be handled even at 50 °C.

The reaction of 2-bromo-3,3,3-trifluoropropene **307** with magnesium [112] in the presence of chloro(dimethyl)phenylsilane in THF at −10 °C provides 3,3,3-trifluoroisopropenyl(dimethylphenyl)silane **304a** in 80% yield (Scheme 78) [98]. The reductive trimethylsilylation of **307** with metal aluminum in *N*,*N*-dimethylimidazolidinone was patented [113].

The fluoride ion-catalyzed generation of trifluoroisopropenyl carbanion equivalent from **304b** and its reaction of benzaldehyde were conducted at 50 °C to give the alcohol **308** in 62% yield (Scheme 79) [114]. On the other hand, the reaction of **304a** with nucleophiles proceeds in an S_N2' manner to give 3-substituted 1,1-difluoro-2-silyl-1-alkenes **309** in excellent yields. The silyl group on C-2 is activated by TASF in THF and the carbon-2 is alkylated with aryl aldehydes to give **274** in good yields (Scheme 70) [98]. However, aliphatic aldehyde is less reactive with the silane **309**. The one pot synthesis of 3-substituted 1,1-difluoro-1-alkene **310** from **304a** is successful. Bromination of **309** and the subsequent fluoride ion-catalyzed desilylative debromination of **312** results in one pot synthesis of 3-substituted 2-bromo-1,1-difluoro-1-alkene **313** [98].

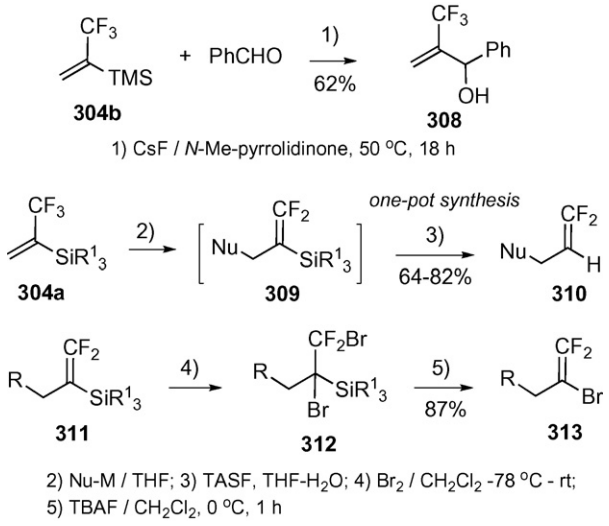
4.2. 3,3,3-Trifluoro-1-propenylsilane

(*E*)-3,3,3-Trifluoropropenyl(triethyl)silane **314** is directly prepared by Ru-catalyzed silylation of 3,3,3-trifluoropropene (Scheme 80) [115]. The silylation is highly dependent on the nature of the hydrosilanes. Only triethylsilane provides **314** exclusively, and other hydrosilanes lead to a mixture of propenyl and propylsilanes. In particular, the use of $(EtO)_3SiH$ induces overhydrogenation leading to 3,3,3-trifluoropropylsilane. The reaction of (*E*)-perfluoro-2-butene **315** with bis(trimethylsilyl) mercury provides (*E*)-2,3-bis(trimethylsilyl)-1,1,1,4,4,4-hexafluoro-2-butene **316** [101].

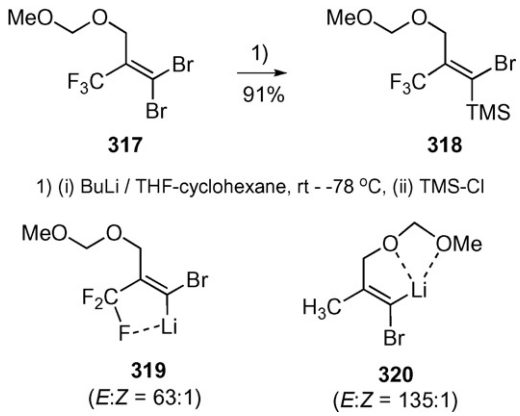
One of the methods for the preparation of substituted 3,3,3-trifluoropropenylsilanes is a lithiation–silylation sequence of either substituted 1-bromo-3,3,3-trifluoropropenes or substituted 3,3,3-trifluoropropenes as shown in Schemes 81 and 82. Lithium–bromine exchange of dibromide **317** in THF followed by silylation with TMSCl provides **318** stereoselectively [116]. (*E*)-Stereochemistry (Li is *syn* to CF_3 group) of **319** is thermodynamically favorable due to the interaction of lithium with fluorine of the trifluoromethyl group. In contrast, the *anti*-stereochemistry (Li is *anti* to CH_3 group) is more stable for the non-fluorinated analogue **320** [117] (Scheme 81).

Deprotonation of (*E*)-3,3,3-trifluoro-1-propenyl phenyl sulfide **321** takes place regio- and stereoselectively at C-1, affording (*E*)-silane **322** in 90% yield (Scheme 82) [118]. Here again, *syn*-lithiation to the CF_3 group of **321** is suggested. Deprotonation of **324** with *n*-BuLi and trimethylsilylation with TMSCl proceeds in a manner of retention of its configuration to give **325** [119]. The retention of the configuration was observed in the deprotonation–silylation sequence of **326** [120].

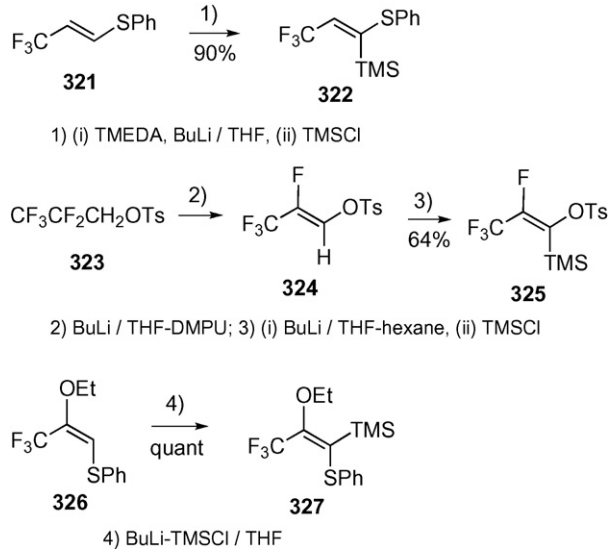
The reaction of trifluoroacetylamide **328**, ester **329**, ketone **330** and thioester **331** with 1.3 eq. of cyclopentadienyl tris(trimethylsilylmethyl)titanium (IV) **332** in toluene at 110 °C leads to trimethylsilylmethylenation of the carbonyl group. This method provides us one step preparation of 2-heteroatom-substituted 3,3,3-trifluoropropenyl(trimethyl)silanes **333**, **334**, **335**, and **336** from readily available trifluoroacetic acid derivatives although



Scheme 79.



Scheme 81.

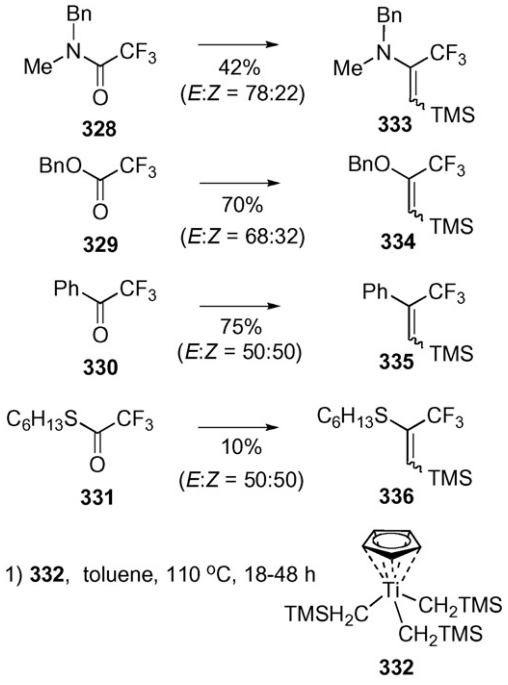


Scheme 82.

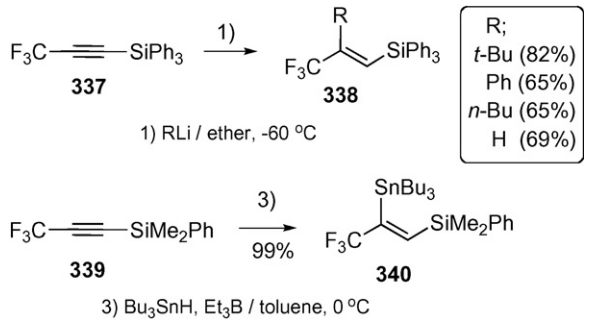
heating at 110 °C for a long time results in an unsatisfactory stereoselectivity (Scheme 83) [121].

The regio- and stereoselective addition of alkyl lithium to 3,3,3-trifluoropropynyl(triphenyl)silane **337** is useful for the synthesis of 2-substituted 3,3,3-trifluoropropenylsilanes **338**. Here again, location of lithium on C-1 in the intermediate 3,3,3-trifluoropropenyllithium is *syn* to the CF_3 group (Scheme 84) [122]. Hydrostannylation by the addition of stannyl radical to a triple bond of **339** enables a regio- and stereoselective synthesis of (*Z*)-2-stannyl-3,3,3-trifluoropropenyl(dimethylphenyl)silane **340** [123].

The related 4,4,4-trifluoro-2-butenyl(trimethyl)silanes **341** [118] and **343** [124] have been prepared (Scheme 85).



Scheme 83.



Scheme 84.

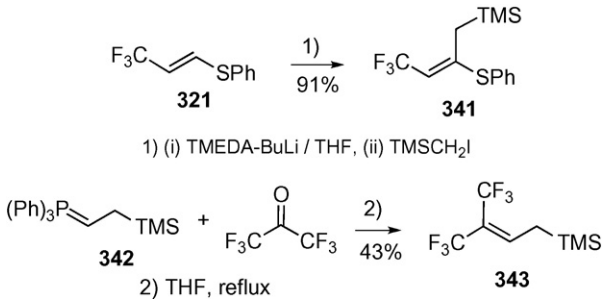
4.3. 3,3,3-Trifluoropropynylsilane

The *in situ* generation of 3,3,3-propynyl lithium and its trapping with triphenylsilane is a reliable method for the straightforward synthesis of 3,3,3-trifluoropropynyl(triphenyl)silane **337** (Scheme 86). The first dehydrofluorination from **344** occurs from the less fluorine-substituted CHF_2 group rather than the CF_3 group [122]. Deprotonation of trifluoropropyne **345** with methyl magnesium iodide followed by trimethylsilylation with TMSCl is less effective [125]. The synthesis of **346** by stannyl-silyl exchange reaction was also reported [126].

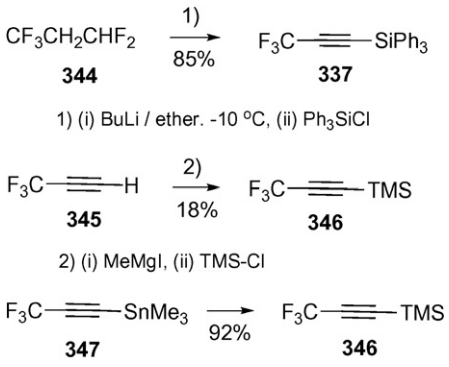
4.4. Trifluoroacetimidoyl silanes

A variety of trifluoroacetimidoyl metals have been prepared and demonstrated their utilization for the syntheses of trifluoromethylated amino acids and heterocycles [127]. For instance, trifluoroacetimidoyl lithium species **348a**, a typical trifluoroacetimidoyl carbanion equivalent is generated readily by the lithium–iodine exchange reaction of iodide **347b** at −70 °C in THF and can be trapped with electrophiles, providing **349** [128]. However, the lithium species is very unstable so that it must be handled at least below −60 °C otherwise it undergoes migration of lithium to imino-nitrogen from imino-carbon to generate carbene-type intermediate **350** which readily dimerizes (**348a** → **350** → dimer, Scheme 87). The order of the stability of the trifluoroacetimidoyl metals **348b** is strongly dependent on the degree of covalency of the bond between the imino-carbon and the metal. The order of the stability was estimated from the some reactions: Li < Mg < Zn < Pd ≦ Rh ∼ Si [127].

The corresponding imidoyl silane **351** is an excellent alternative for the lithium species **348a** and is prepared easily by the Grignard type reaction of the imidoyl chloride **347a** with TMSCl at around −73 °C in 73% yields [129]. In contrast to the instability of the lithium species **348a**, the silicate intermediate **352** is stable enough even at 50 °C to give **349** so that the silane **351** is useful for the alkylation of the less reactive electrophiles [130]. The imidoyl



Scheme 85.

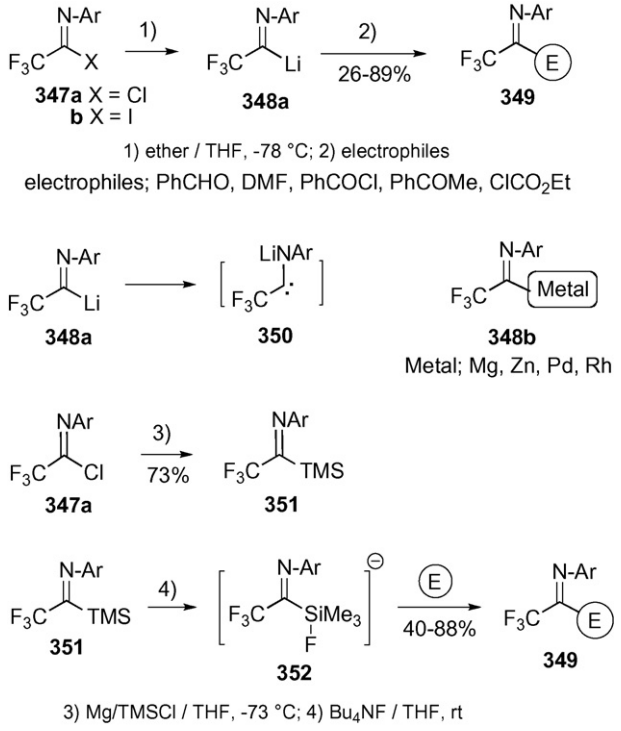


Scheme 86.

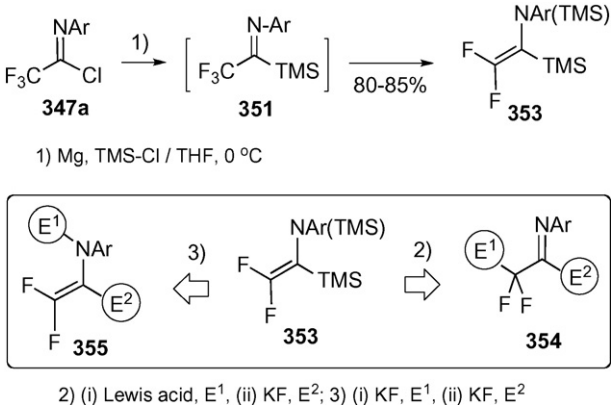
chloride **347a** is transformed into a bis-silylated difluoroenamine **353** on treating **347a** with metal magnesium in THF at 0 °C [131]. The Mg-promoted defluorination of the initially formed imidoyl silane **351** takes place under the conditions in a similar manner as the defluorination of trifluoromethylimines [132]. Both the N–Si and C–Si bonds involved in **353** are activated under either Lewis acid- or KF-catalyzed conditions. Therefore, **353** is a synthetic equivalent of either **354** or **355** (Scheme 88). Scheme 89 shows a synthesis of 3,3-difluoro-4-hydroxy-2-amino acid precursors **359** by the BF_3 etherate-catalyzed alkylation with benzaldehyde, and the subsequent KF-catalyzed iodination followed by Pd-catalyzed carboalkoxylation. Scheme 90 summarizes syntheses of difluorinated nitrogen compounds **361**, **362**, and **363** by the KF-catalyzed desilylative *N*-allylation of **356** followed by thermal rearrangements of **360** (Scheme 90) [133].

4.5. Trifluoroacetyl silanes

Trifluoroacetyl silanes are masked trifluoroacetyl carbanion equivalents and potential synthetic blocks for trifluoromethyl



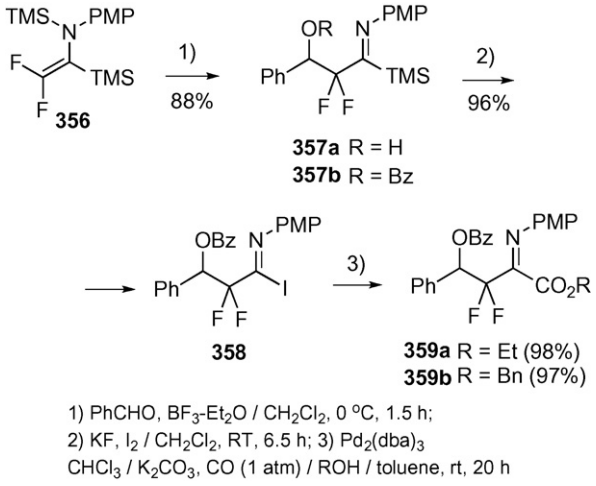
Scheme 87.



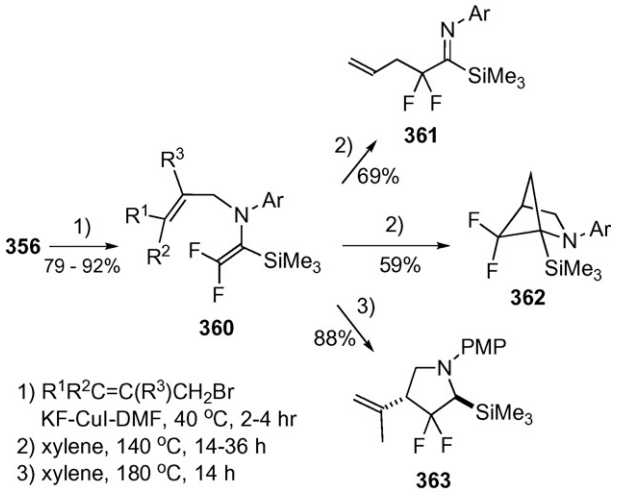
Scheme 88.

ketones, alcohols and alkenes, and also 2,2-difluoroenol silyl ethers. They are prepared by three different methods as shown in Scheme 91. The Cu(I)-catalyzed nucleophilic replacement of either chloride or acetoxyl group in trifluoroacetyl chloride or anhydride **364**, respectively with trialkyl and triarylsilyl lithiums gives trifluoroacetyl(trialkyl) and (triaryl)silanes. Trifluoroacetyl triphenylsilane **365** is obtained in 75% yield [134]. The synthetic method is useful for aryl-substituted silanes due to the favorable stability of aryl-substituted silyl lithiums in comparison with the less stable trialkylsilyl lithiums. Bordeau [35] proposed a new method based on electrosynthesis as a key reaction. Electroreduction of ethyl trifluoroacetate in THF–HMPA or DMPU using an aluminum sacrificial anode and an SUS cathode provides *O*-ethyl,*O*-trimethylsilyl acetal **103** of trifluoroacetyl silane in reasonable yields, which is then transformed into trifluoroacetyl(trimethyl)silane **366** by treating with conc. sulfuric acid [35]. Meanwhile, Welch developed a new method usable for the syntheses of not only trifluoroacetyl, but also difluoro, monofluoro, and halodifluoroacetyl silanes *via* 2,2-difluoro-1-silylethenyl trimethylsilyl ethers **242** of which details are described in Section 3.4, Schemes 62–64 [90]. Electrophilic fluorination of **242** with Selectfluor provides a variety of trifluoroacetylsilanes **367** [90].

Three types of reactions of trifluoroacetyl silanes with nucleophiles are known. The reaction intermediates **368**, **369**, and **370** are affected by the structure of the nucleophiles and the reaction conditions. The reactions with alkyl lithiums and Grignard reagents in aprotic solvents induce mostly defluorination initiated by Brook rearrangement [135] to give difluoroenol silyl ethers *via*



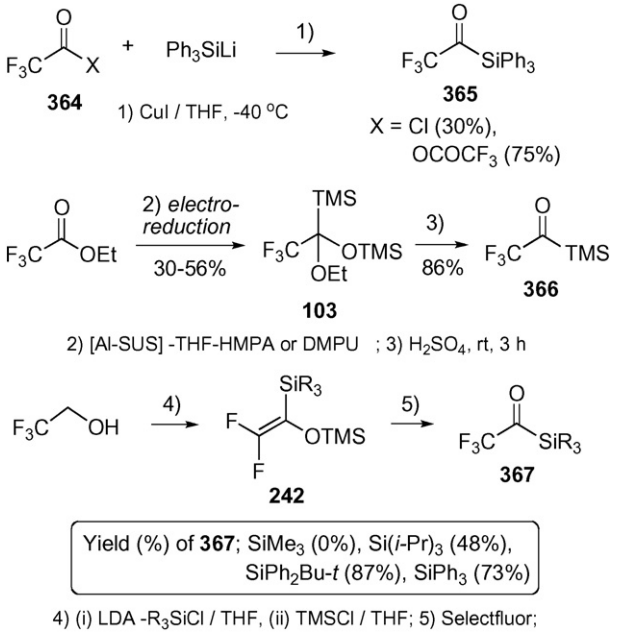
Scheme 89.



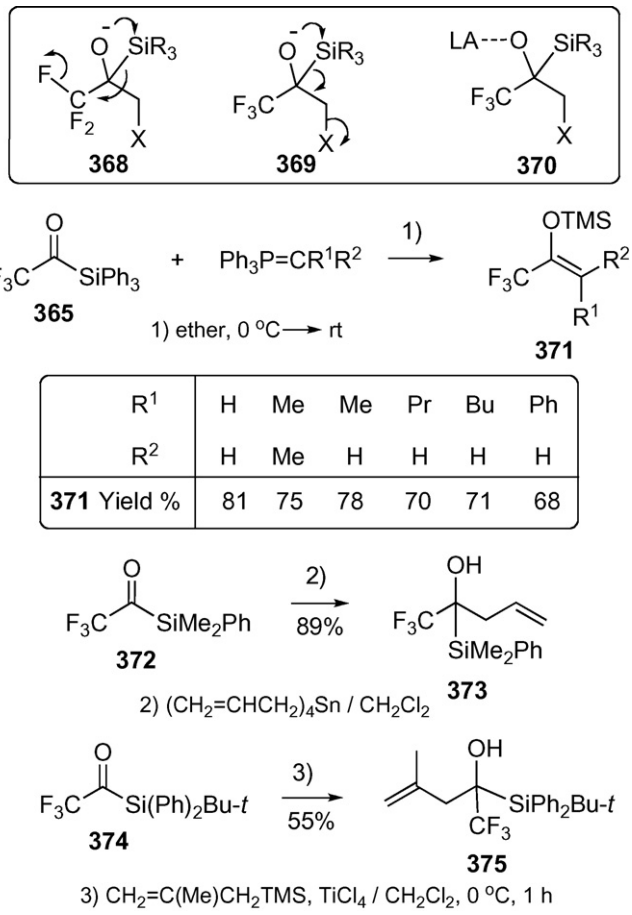
Scheme 90.

368. On the other hand, when the nucleophiles like Wittig reagents bear a potential leaving group, the intermediate carbanions generated *via* Brook rearrangement of **369** undergo another elimination rather than defluorination, affording trifluoromethylalkenyl silyl ether such as **371** [136]. Meanwhile, the Lewis acid-catalyzed reactions result in the formation of *tert*-alcohols **373** [137] and **375** [90], where oxygen anion of alkoxide in the intermediate **370** is blocked with Lewis acid so as to prevent its intramolecular nucleophilic attack to the silyl group (Scheme 92).

The defluorination products, 2,2-difluoroenol silyl ethers **376**, **378**, **379**, and **380** formed *via* Brook rearrangement of **368** are summarized in Scheme 93. The reaction of **365** with vinyl magnesium bromide provides 1,1-difluorobutadiene **376** which undergoes Diels–Alder reaction to give **377** [138]. Likewise, the reactions of **365** with Grignard reagents, and silyl and alkyl lithiums afford **378** [139], **379**, and **380** [134,137] in excellent yields, respectively. The enol silyl ether **379** is an analogue of the

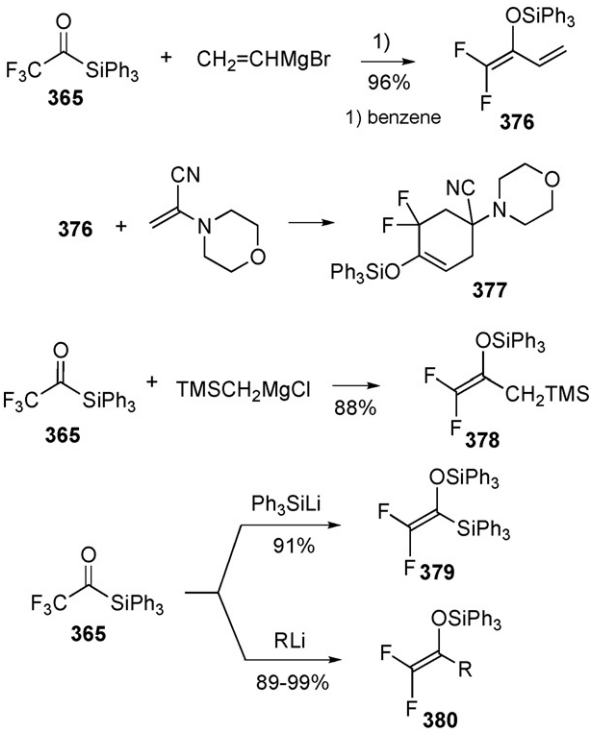


Scheme 91.



	R^1	H	Me	Me	Pr	Bu	Ph
	R^2	H	Me	H	H	H	H
371 Yield %		81	75	78	70	71	68

Scheme 92.



Scheme 93.

silanes **242** prepared from trifluoroethanol by Chung and Welch [90].

5. Others

5.1. Difluorocyclopropylsilane

In many cases, pentavalent fluorosilicates, metal-free carbanion equivalents are thermally stable as compared with the corresponding lithium species and thus survive at higher temperature. In fact, deprotonation of difluorocyclopropanes **381** with alkyl lithium (RLi) proceeds rapidly at −70 °C, and the resultant cyclopropyl lithiums **382** are so unstable even at the very low temperature to eliminate LiF. The addition of RLi to cyclopropenyl fluoride **383** followed by elimination of fluoride ion results in the formation of **384** as final products [140]. On the contrary, silyl-substituted difluorocyclopropane **385** reacts successfully with a variety of aldehydes without undesirable defluorination. In the presence of a catalytic amount of TBAF, the reaction proceeds smoothly at room temperature to yield the corresponding cyclopropylcarbinol **386** (Scheme 94) [141].

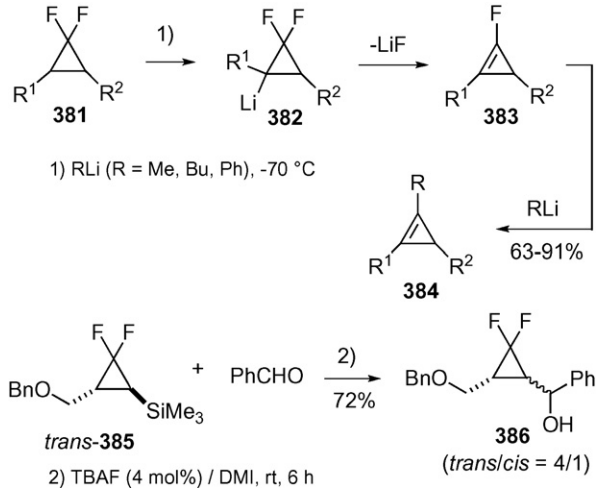
5.2. Difluorocyclopropenylsilane

The method, generating 3,3,3-propynyl lithium from 1,1,1,3,3-pentafluoropropane (HFC245fa) and its trapping *in situ* with chlorotriphenylsilane, is reliable for the straightforward synthesis of 3,3,3-trifluoropropynyl(triphenyl)silane **337** (Scheme 95) [122]. This method is also useful for the preparation of the corresponding trifluoropropynyl compounds of the group IVA elements such as C, Ge, Sn, and Pb.

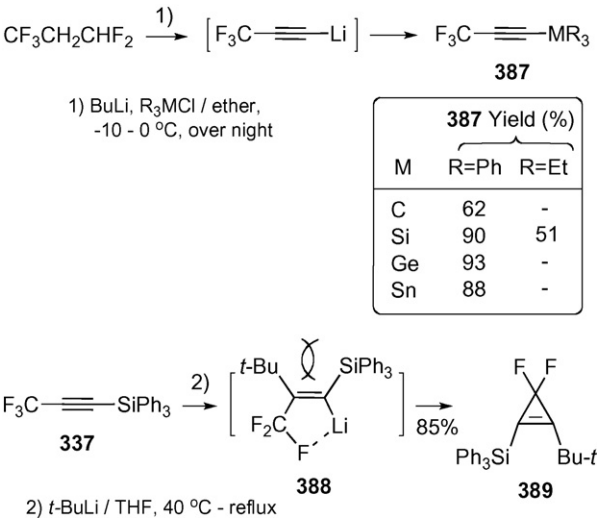
The reaction of trifluoropropynyl triphenylsilane **337** with a bulky alkyl lithium such as *t*-BuLi at the refluxing temperature of THF induces a unique difluorocyclopropanation (Scheme 95) [122] although only 1,2-addition products are formed at the low temperature around −60 °C. This remarkably facile cyclization presumably occurs by elimination of LiF from the lithiated intermediate **388**, driven by the steric strain associated with the introduction of a bulky *t*-Bu group *cis* to the Ph_3Si fragment.

5.3. 1-Trifluoromethyloxiranyl- and 1-trifluoromethylaziridinylsilanes

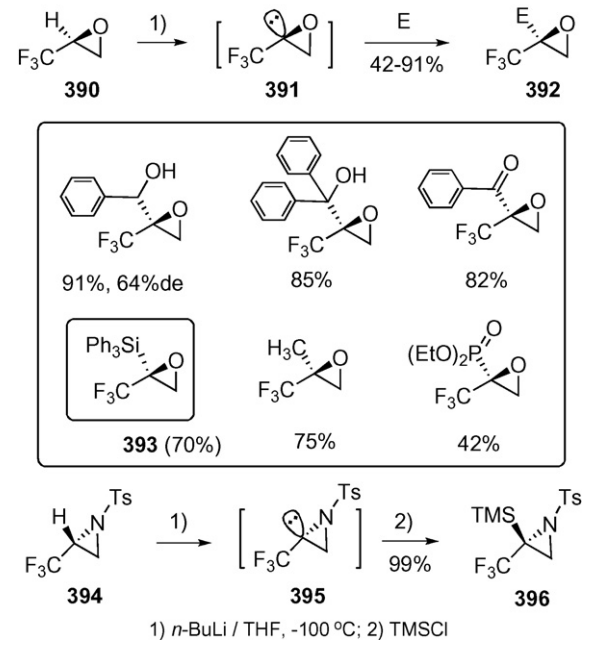
1-Trifluoromethyloxirany- and 1-trifluoromethylaziridinylsilanes **393** and **396** are potent precursors for optically active



Scheme 94.



Scheme 95.



Scheme 96.

trifluoromethyl alcohols and amines, which arise from the nucleophilic ring opening of **393** and **396** at the methylene carbon, respectively. The oxiranyl anion **391** generated from the optically active 2,3-epoxy-1,1,1-trifluoropropane **390** with *n*-BuLi was found thermally unstable. Its generation and reaction should be undertaken below −100 °C. Application of a higher temperature condition (−40 °C) resulted in decomposition. However, the anion **391** reacts at −100 °C with a variety of electrophiles to give optically active 2-substituted-2-trifluoromethyl oxiranes **392** with retention of its configuration in good yields [142]. Enantiomerically enriched trifluoromethyloxiranylsilane **393** is obtained in 70% yield. Likewise, the corresponding aziridinyl silane **396** can be prepared in a quantitative yield (Scheme 96) [143].

6. Conclusion

This review summarizes recent advances in the preparations, reactions, and synthetic applications of the functionalized

fluoroalkyl and alkenylsilanes. High availability, stable and storable property, unique reactivity, and reaction under mild conditions, all of these properties of fluoroalkyl and alkenyl silanes provide us a great number of successful outcomes for synthetic organofluorine chemistry. Moreover, silicon is the second largest element in weight percent among elements which consist of the earth's crust, and the weight percent of silicon is much larger than that of carbon. Therefore, silicon-based material science and reaction chemistry related to the fluorine science and technology have been growing year by year. Meanwhile, silicon has a strong affinity with fluorine so that a combination of silicon and fluorine creates a unique reaction chemistry otherwise impossible. Judging from these backgrounds, silicon would provide an increasing contribution in synthetic and reaction organofluorine chemistry.

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