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Recent advances in fluorinated vinylstannanes and their synthetic utility

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Abstract

Fluorinated vinylstannanes have attracted much interest in recent years because they provided a useful and convenient methodology for the introduction of monofluoro, difluoro, trifluoro or polyfluoro functionality into organic molecules with retention of configuration, particularly in the synthesis of fluorine-containing naturally occurring compounds. The new methodologies discussed in this review are, therefore, potentially useful in organic synthesis particularly in the medicinal and agricultural chemistry for the synthesis of fluorine-containing biologically active compounds.

Keywords: Fluorinated vinylstannanes; Synthetic utility; Monofluoro, difluoro, trifluoro or polyfluoro functionality; Fluorine-containing biologically active compounds; Medicinal and agricultural chemistry

1. Introduction

In the past several decades, much effort has been devoted to introducing a fluorine atom or trifluoromethyl group into organic molecules, since the resulting compounds often lead to pronounced activity enhancement, and organofluorine compounds are increasingly being applied in pharmaceuticals, agrochemicals and other field [1]. For example, 2′,3′-dideoxy-3-(trifluoromethyl)-pentafuranosyl nucleosides which have been used as antitumor and antiviral agents [2a]. Organometallic chemistry is one of the most rapidly developing areas in all of chemistry. Every day useful new reagents and reactions, including organometallic compounds, are reported worldwide in the chemical literature. Many useful synthetic transformation, which seemed to be impossible by conventional methods have been realized and applied to the synthesis of natural products. Fluorinated organometallic reagents provide a useful and convenient methodology for the introduction of fluorine or trifluoromethyl functionality into organic molecules [2b,2c]. Among them, organotin compounds are versatile reagents in synthetic organic chemistry, and vinylstannanes have attracted much attention and emerged recently as highly valuable intermediates in organic synthesis, particularly in the synthesis of naturally occurring compounds [3]. Thus, this paper reviews recent progress in the synthesis of fluorinated vinylstannanes, and their application in organic synthesis.

2. Monofluorovinylstannanes

2.1. Synthesis of 1-fluorovinylstannane and its application in Stille reaction

1-Fluorovinylstannane **1** was prepared according to the following reaction sequences.

The starting material ethyl phenyl sulfide **2** was converted to α-fluorosulfoxide **3** with diethylaminosulfur trifluoride (DAST), followed by oxidation with *m*-chloroperoxybenzoic acid (*m*-CPBA) affording **3** in 60% overall yield. The optimum conditions for the conversion of sulfoxide **3** to **4** were addition of a solution of sulfoxide **3** and 1.1 equiv. of Bu_3SnI in THF to a −70 °C solution of

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LDA (1.5–2.0 eq.) in 10% TMEDA-THF with a reaction time of 15 min, work-up and flash chromatography gave α-stannyl sulfoxide **4** in 35% yield. Pyrolysis of sulfoxide **4** in refluxing toluene in the presence of base gave **1** in 50% yield (Scheme 1) [4].

The palladium-catalyzed coupling of **1** with substrates examined was succeeded in yields ranging from 45% to 85% (Scheme 2) [4].

It is remarkable that the preparation of uracil derivative **7** was also succeeded in 45% yields (Scheme 3).

2.2. Synthesis of functionalized fluorovinylstannane and its synthetic utility

Functionalized fluorovinyl stannane **8** can be prepared via the following reaction sequences.

The hemiketal **9**, generated from ethyl trifluoropyruvate and methanol, was treated with $SOCl_2$ and pyridine to give α-chloroether **10** in 75% yield. Subsequent reductive dehalogenation of **10** with Zn powder in DMF afforded **11** in 85% yield, which reacted with $(Bu_3Sn)_2CuLi$ producing functionalized fluorovinyl stannane **8** in 81% yield (Scheme 4) [5].

Interestingly the coupling reaction of **8** with a variety of substrates was succeeded at room temperature giving the desired coupling products in yields ranging from 50% to 95% (Scheme 5) [5].

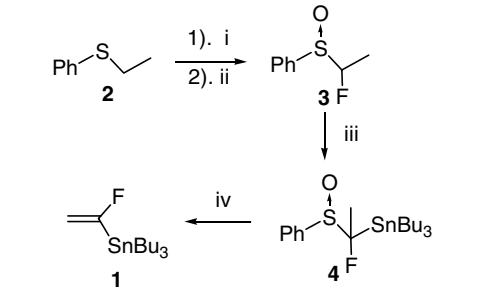
It has been found that in the absence of CuI, no reaction occurred at room temperature, while in the elevated temperature the reaction led to the formation of a substantial amount of homocoupling product [5].

2.3. Synthesis of substituted fluorovinylstannane and its synthetic utility

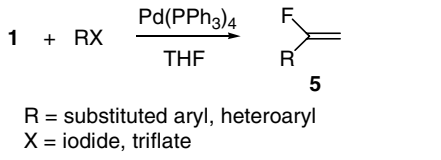
Substituted 1-fluorovinylstannanes **16** are readily prepared via the reaction sequences shown in Scheme 6.

The condensation of fluoromethyl phenyl sulfone **14** with carbonyl compounds gave 1-fluorovinyl phenyl sulfones **15** which reacted with tributyltin hydride affording substituted 1-fluorovinylstannanes **16** in 55–80% yields (Scheme 6) [6]. Two stereoisomers were separable by silica gel chromatography.

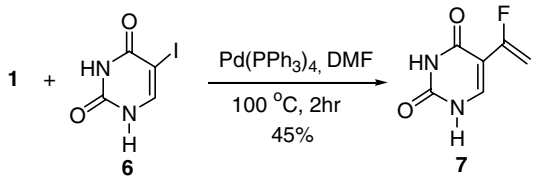
The palladium–CuI cocatalyzed coupling reaction of **16** with organic halides or acyl chloride also successfully proceeded giving the desired product **17** or **18** in 42–91% or 48–92% yields, respectively (Scheme 7) [6].



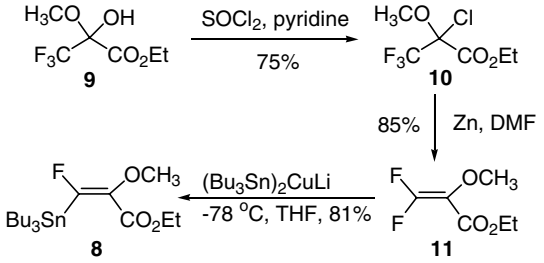
Scheme 1.



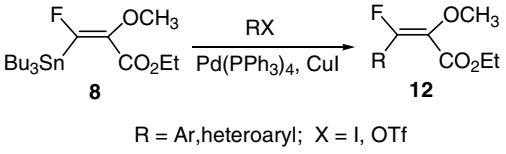
Scheme 2.



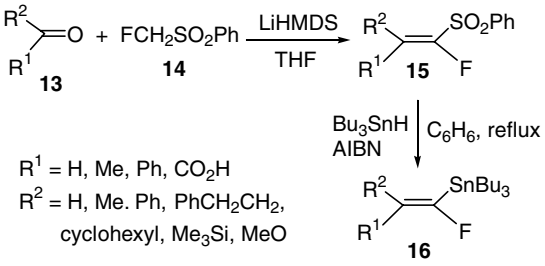
Scheme 3.



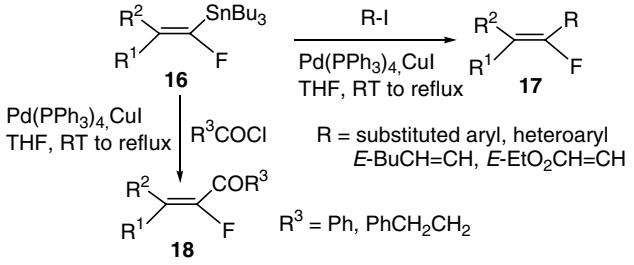
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

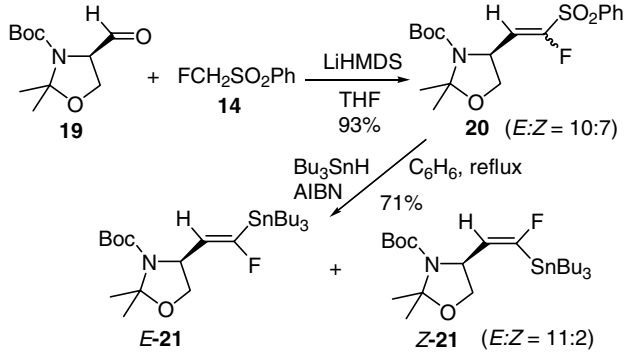
The reaction takes place with CuI as cocatalyst at ambient temperature or in refluxing tetrahydrofuran producing stereoisomerically pure highly functionalized monofluoroolefins. Many functional groups are tolerated on the substrates.

2.4. Synthesis of monofluoro amino acids

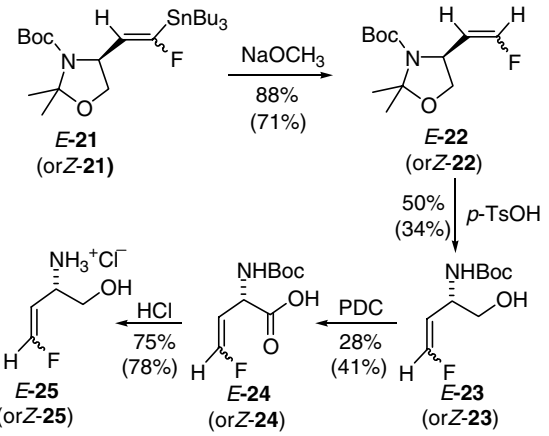
Much attention has been paid to the monofluoro amino acids because of their antibacterial activity as alanine racemase inhibitors [7].

The condensation of fluoromethyl phenyl sulfone **14** with aldehyde **19** gave 1-fluorovinyl phenyl sulfones **20** in 93% yield which reacted with tributyltin hydride affording substituted 1-fluorovinylstannanes **21** in 71% yield (Scheme 8) [8]. Two stereoisomers were separable by silica gel chromatography.

Treatment of *E*- or *Z*-**21** with one equivalent of sodium methoxide in methanol gave destannylated products *E*- or *Z*-**22** in 88% and 71% yields, respectively. The isopropylidene group was removed with *p*-toluenesulfonic acid monohydrate in methnol to afford *E*- or *Z*-**23** in 50% and 34% yields. Oxidation of the alcohol to the carboxylic acid *E*- or *Z*-**24** was accomplished with pyridium dichromate in acetic acid at room temperature in 28% and 41% yields. The protecting group was removed with HCl-dioxane to produce amino acid *E*- or *Z*-**25** in 75% and 78% yields, respectively (Scheme 9) [8].



Scheme 8.



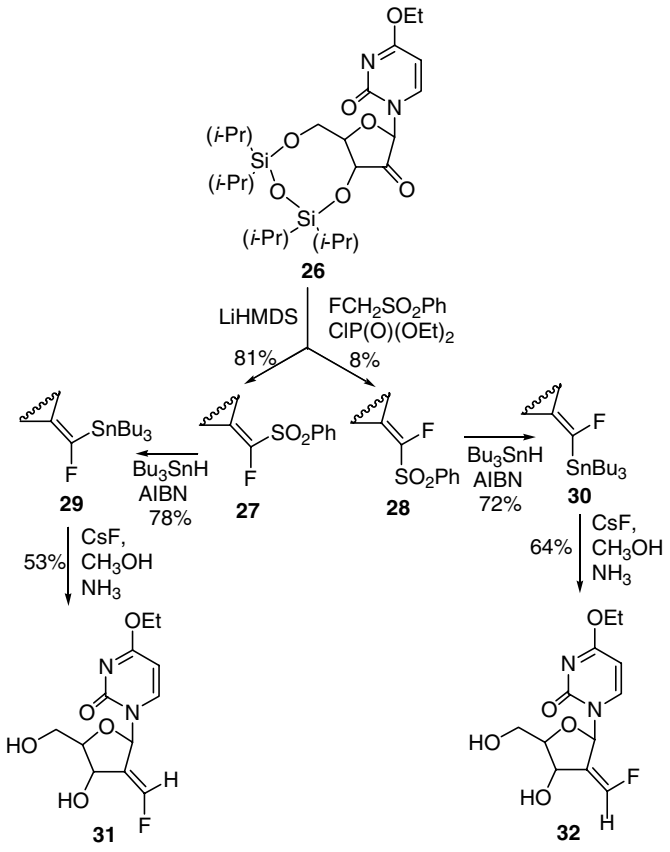
Scheme 9.

2.5. Synthesis of 2′-deoxy-2′-fluoromethylene nucleosides

The reaction sequences for the preparation of fluoroolefin nucleosides **31** and **32** are showed in Scheme 10.

2′-Ketonucleoside **26** was transformed to a mixture of readily separable fluorovinyl sulfones **27** and **28** using the Horner–Wittig reaction in 81% and 8% yields, respectively [9].

Treatment of fluorovinyl sulfones **27** and **28** with 2 equiv. of tributyltin hydride and catalytic amount of



Scheme 10.

AIBN afforded fluorovinylsatnnanes **29** and **30** in 72% and 78% yields, respectively. (*E*)-2′-deoxy-2′-(fluoromethylene)cytidine **31** and (*Z*)-2′-deoxy-2′-(fluoromethylene)cytidine **32** were obtained in 64% and 53% yields by "one-pot" stereospecific destannylation procedure with CsF, NH_3 and CH_3OH (Scheme 10) [10].

Fluoroolefin **31** is a potent cytotoxic agent, while the geometric isomer **32** is less active indicating that the geometry is important for the biological activity of fluoroolefins [10].

3. Difluorovinylstannanes

3.1. Stereospecific conversion of vinylsilanes to vinylstannanes

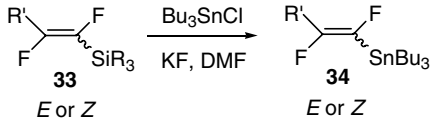
Difluorovinylstannanes **34** can be readily prepared by reaction of difluorovinylsilanes **33** with tributyltin chloride in the presence of potassium fluoride in yields ranging from 70% to 92% (Scheme 11) [11].

When *R′* was hydrogen, the reaction proceeded slowly at room temperature, no reaction was found at the same temperature when *R′* was an alkyl group. However, at the elevated temperature (70–80 °C) the reaction occurred readily regardless of the nature of the R group. In all cases, retention of the configuration of the products was found.

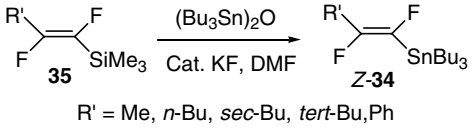
Further investigation revealed that when bis(tributyltin) oxide was instead of tributyltin chloride, only catalytic amount of KF (5–10 mol%) was necessary to complete the reaction under similar conditions giving the desired products *Z*-**34** in 79–90% yields (Scheme 12) [11].

3.2. Stereospecific conversion of vinyl zinc compounds to vinylstannanes

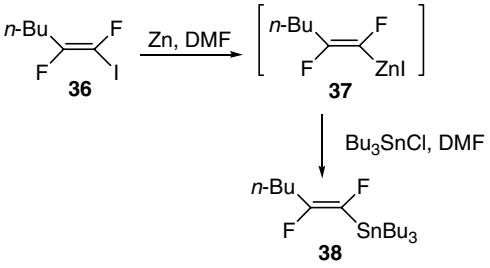
The zinc compound of (*Z*)-1-iodo-2,2-difluoro-2-butylpropene **36** reacted readily with tri-*n*-butyltin chloride to produce the corresponding stannane **38** in 49% yield (Scheme 13) [12].



Scheme 11.



Scheme 12.



Scheme 13.

This transformation was found to be stereospecific giving (*Z*)-isomer exclusively.

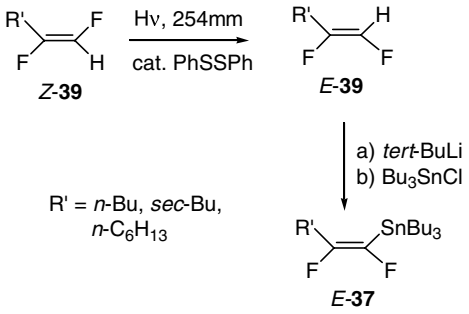
3.3. Synthesis of (*E*)- and (*Z*)-1,2-difluorovinylstannanes

The (*Z*)-isomer of 1,2-difluorovinylstannanes can be prepared according the method described in Sections 3.1 and 3.2.

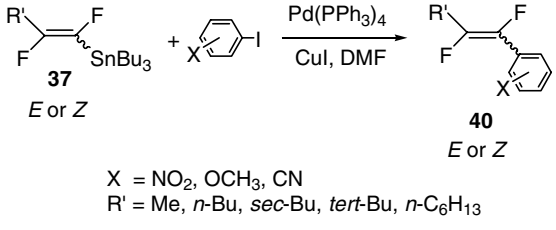
The corresponding (*E*)-1,2-difluorovinylethenes *E*-**39** were prepared by photochemical isomerization of *Z*-**39** [13]. Two isomers were separable by fractional distillation. Then *E*-**39** was treated with *tert*-BuLi and trapped with chlorotributylstannane producing the (*E*)-1,2-difluorovinylstannanes *E*-**37** (Scheme 14) [14].

3.4. Stille coupling reaction of (*E*)- and (*Z*)-1,2-difluorovinylstannanes

The cross coupling reaction of *E*- or *Z*-**37** with aryl iodides in the presence of a catalytic amount of $Pd(PPh_3)_4$ and CuI provided 1,2-disubstituted-1,2-difluoroolefins *E*- or *Z*-**40** in yields ranging from 81% to 92% (Scheme 15) [14].



Scheme 14.



Scheme 15.

In addition, the palladium/CuI catalyzed cross-coupling of the 2-substiuted-1,2-difluorovinylstannane **41** with vinyl halide was also succeeded under similar conditions to provide the corresponding conjugated diene **42** in 92% yield (Scheme 16) [14].

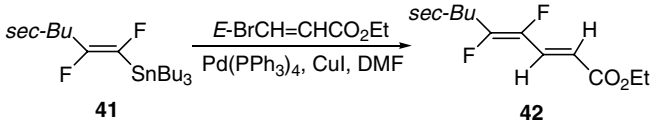
3.5. Synthesis of 2,2-difluoroenolstannanes

The phase transfer-catalyzed allylation of trifluoroethanol **43** was very successfully giving allyl trifluoroethyl ether **44** in quantitative yield [15]. The dehydrofluorination/metallation of **44** could be achieved at −78 °C with *n*-BuLi and Bu_3SnCl affording 2,2-difluoroenolstannane **45** in 85% yield (Scheme 17) [16].

Attempt to carry out the palladium/CuI catalyzed cross-coupling of the 2,2-difluoroenolstannane **45** with aryl iodides was succeeded producing the coupling products **46** in 60% and 72% yields (Scheme 18) [16].

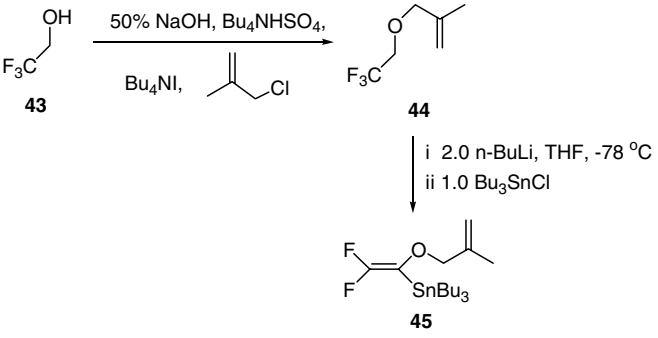
3.6. Palladium-catalyzed coupling of 2,2-difluorovinylstannane with carbamate moiety

It was found that Stille couplings of stannane **47** [17] with aryl, heteroaryl, allyl and vinyl iodides was achieved affording the products **48** in 44–87% yields (Scheme 19) [18].



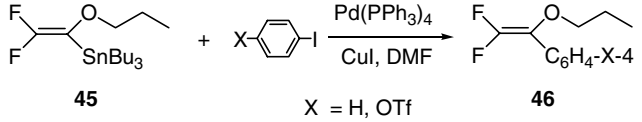
41 42

Scheme 16.



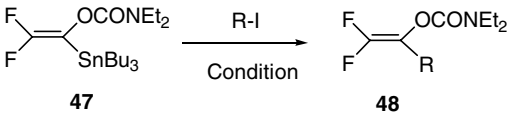
43 44 45

Scheme 17.



45 X = H, OTf 46

Scheme 18.



47 48

R = Aryl, heteroaryl, allyl, vinyl

Conditions: 5% $Pd_2dba_3 \cdot CHCl_3$, PPh_3, CuI, DMF, 50°C, 16 hr.

Scheme 19.

4. Trifluorovinylstanannes

4.1. Synthesis of 1-trifluoromethylvinylstannane and its synthetic utility

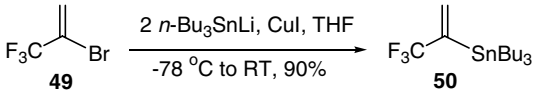
Trifluoromethylvinylstannane **50** was prepared in 90% yield from 2-bromotrifluoroisopropene **49** and lithium tributylstannate in the presence of CuI (Scheme 20) [19].

Interestingly, **50** underwent the coupling reaction with a variety of acyl halides catalyzed by palladium producing α-(trifluoromethyl)vinyl ketones in 78–97% yields (Scheme 21) [19].

It is remarkable that this reaction can be applied to the introduction of CF_3-containing side chain to a steroidal compound in which further elaboration would provide some interesting CF_3 analogues of biological activity (Scheme 22) [19].

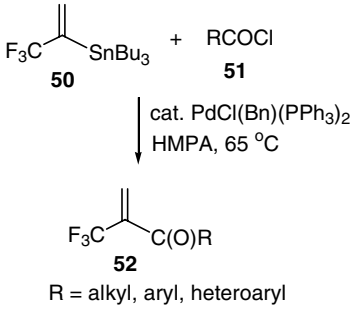
4.2. Synthesis of 5-trifluoromethyl-2-cyclopentenones

1-Trifluoromethylvinyl vinyl ketones **56** were prepared by the Stille cross coupling of trifluoromethylvinylstannane **50** with α,β-unsaturated acyl chlorides **55** affording **56** in yields ranging from 37% to 75%. The cyclization of substrates **56** produced the corresponding cyclopentenones **57** in 55–95% yields (Scheme 23) [20].



49 50

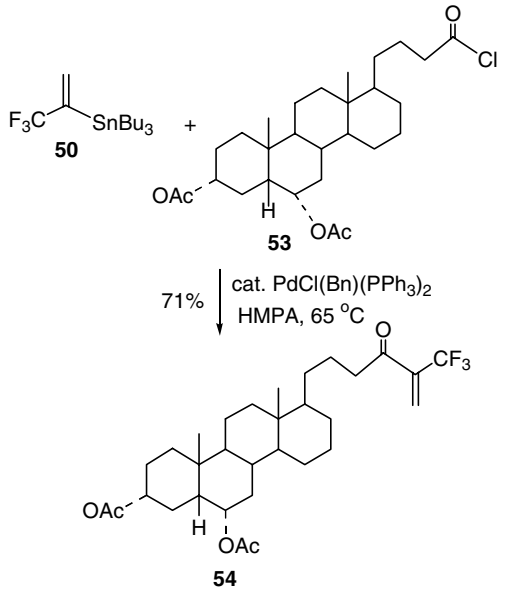
Scheme 20.



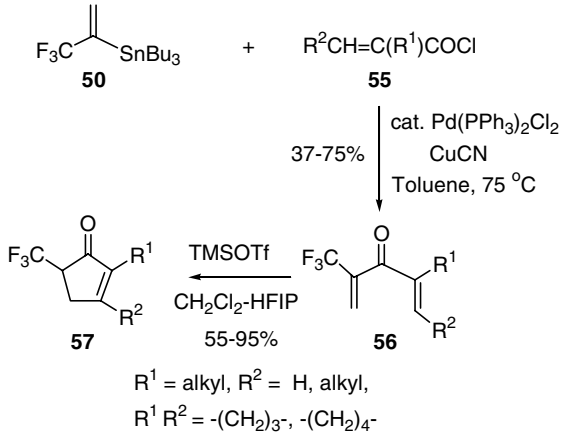
50 51 52

R = alkyl, aryl, heteroaryl

Scheme 21.



Scheme 22.

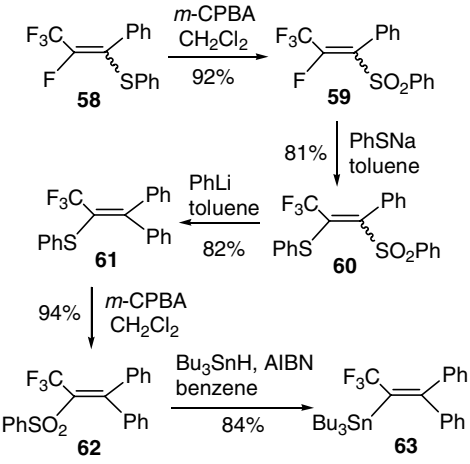


Scheme 23.

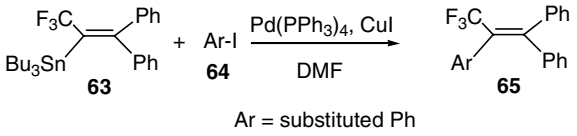
Thus this method provides a regioselective preparation of trifluoromethylated 2-cyclopentenones.

4.3. Synthesis of 2,2-diphenyl-1-(trifluoromethyl)-vinylstannane and its application in organic synthesis

2,2-diphenyl-1-(trifluoromethyl)vinylstannane **63** was prepared starting from 2,3,3,3-tetrafluoro-1-phenyl-1-phenylthiopropene **58** via the reaction sequences shown in Scheme 24. Starting material **58** was oxidized with *m*-chloroperbenzonic acid (*m*-CPBA) in dichloromethane at reflux temperature for 24 h giving 2,3,3,3-tetrafluoro-1-phenyl-1-phenylsulfonylpropene **59** in 92% yields. Treatment of **59** with sodium thioperoxide in benzene at 0 °C for 24 h afforded 3,3,3-trifluoro-1-phenyl-1-phenylsulfonyl-2-phenylthiopropene **60** in 81% yields. **60** was treated with phenyllithium in toluene at −78 °C for 24 h producing 3,3,3-trifluoro-1,1-diphenyl-2-phenylthiopropene **61** in 82% yields. Oxidation of **61** with *m*-CPBA in dichloromethane at reflux temperature for 24 h gave 3,3,3-trifluoro-1,1-diphenyl-2-phenylsulfonylpropene **62** in 94% yield. Treatment of **62** with Bu_3SnH, AIBN in benzene at reflux temperature for 24 h resulted in the formation of **63** in 84% yield [21].



Scheme 24.



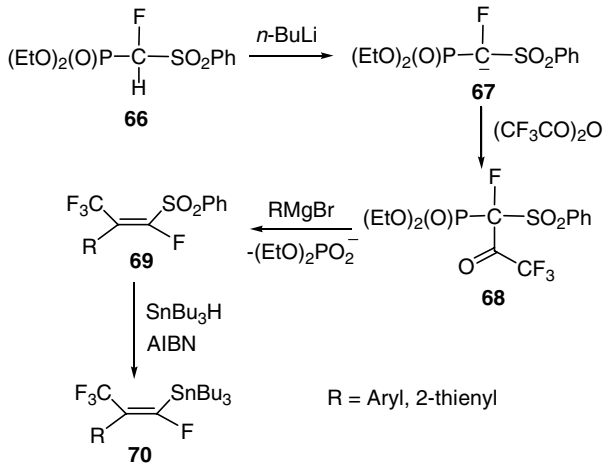
Scheme 25.

The palladium/CuI catalyzed cross-coupling of the 2,2-diphenyl-1-(trifluoromethyl)vinylstannane **63** with aryl iodides was also succeeded by using a mixture of 10 mol% of $Pd(PPh_3)_4$ and 10 mol% CuI in DMF to provide the products **65** in yields ranging from 80% to 93% (Scheme 25) [21].

5. Polyfluorovinyl stannanes

5.1. Synthesis of (Z)-α-fluoro-β-trifluoromethylvinylstannanes

Diethyl (1-fluoro-1-phenylsulfonyl)methylphosphonate **66** was treated with *n*-butyl lithium affording carbanion **67**, which reacted with trifluoroacetic anhydride to form the trifluoromethylated phosphonate **68**. Without isolation, **68** was attacked by Grignard reagents followed by elimination of phosphonic acid anion to give the polyfluorinated sulfones **69** in 77–98% yield (in three steps) with the *Z*-isomer being formed exclusively. The polyfluorinated sulfones **69** were readily converted to polyfluorinated stannanes **70** by treatment of **69** with tributyltin hydride and 2,2′-azobisisobutyronitrile (AIBN) in yields ranging from 77% to 98% with retention of configuration (Scheme 26) [22].



Scheme 26.

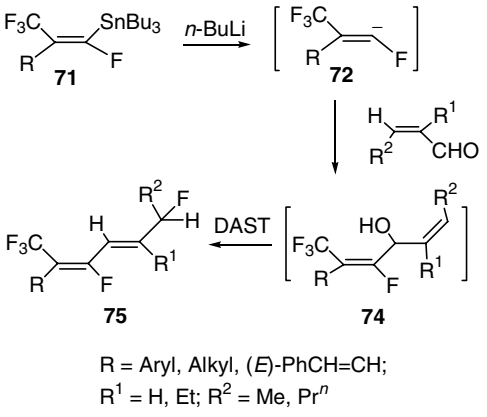
5.2. "One-pot" conversion of aldehydes to (*E*)-α-fluoro-β-trifluoromethyl allylic alcohols

It was found that the (*Z*)-α-fluoro-β-trifluoromethylvinylstannanes **71** were efficient synthetic reagents for the generation of tetrafluoropropenyl anions **72**. Such carbanions reacted with aldehydes to produce α-fluoro-β-trifluoromethyl allylic alcohols **73** exclusively with (*E*)-configuration in yields ranging from 65% to 99% (Scheme 27) [23].

5.3. Stereoselective synthesis of polyfluorinated alka-2*E*,4*E*-dienes

Treatment of (*Z*)-α-fluoro-β-trifluoromethylvinylstannanes **71** with *n*-butyl lithium afforded a new synthetic intermediate, tetrafluoropropene anions **72**, which reacted with α,β-unsaturated aldehydes producing intermediates **74**. Subsequent addition of (diethylamino)sulfur trifluoride (DAST) to **74** (with or without isolation) resulted in the formation of polyfluorinated alka-(2*E*,4*E*)-dienes **75** in yields ranging from 58% to 71% ("one-pot" method) (Scheme 28) [24].

It is remarkable that the reaction of DAST with polyfluorinated diallylic alcohols produced polyfluorinated alka-(2*E*,4*E*) isomers exclusively. No other isomers were isolated and were detectable, and the migration of double bond occurred only at the non-fluorine-containing one.



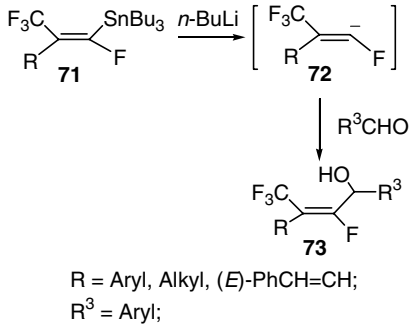
Scheme 28.

5.4. Stereospecific synthesis of polyfluoro-alkenes and α,β-unsaturated ketones

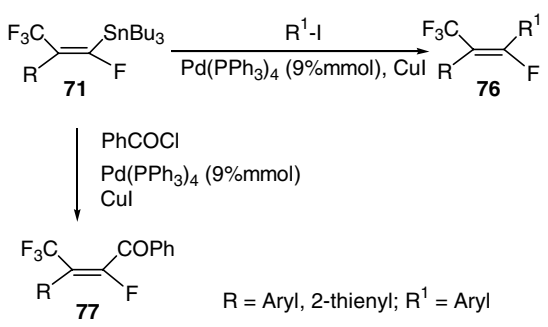
The cross coupling reaction of (*Z*)-α-fluoro-β-trifluoromethylvinylstannanes **71** with aryl iodides in the presence of palladium/copper (I) iodide gave substituted (*E*)-α-fluoro-β-trifluoromethylethenes **76** stereospecifically in yields ranging from 50% to 98% (Scheme 29) [25]. The reaction proceeds best in THF as solvent with $Pd(PPh_3)_4$ as catalyst (9% mmol), CuI as cocatalyst at refluxing temperature for 24 h. Similarly the palladium/copper (I) iodide catalyzed coupling reaction of (*Z*)-α-fluoro-β-trifluoromethylvinylstannanes **71** with acid chloride proceeded smoothly under the same condition producing substituted (*E*)-α-fluoro-β-trifluoromethyl-α,β-unsaturated ketones **77** in 68-87% yield stereospecifically (Scheme 29) [25].

5.5. Stereospecific synthesis of polyfluorinated alka-2,4-dienes

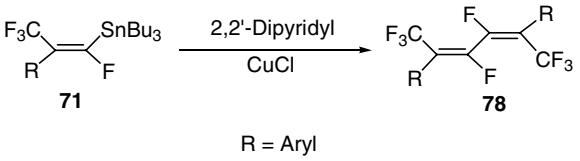
The lower reactivity of fluorinated vinylstannanes in coupling reaction than that of the corresponding nonfluorinated vinylstannanes is obviously due to its strong electron-withdrawing effect of fluorine [6a,14,21].



Scheme 27.



Scheme 29.



Scheme 30.

The copper (I) chloride mediated homocoupling reaction of (*Z*)-α-fluoro-β-trifluoromethylvinylstannanes **71** in the absence of 2,2′-bipyridyl has been tried and was found to be sluggish. After the reaction mixture was stirring at 20 °C in DMF as solvent for 24 h, TLC showed that much of the starting material was unreacted. The reaction proceeded best in DMF as solvent and 2,2′-bipyridyl as ligand, giving substituted polyfluorinated alka-2,4-dienes **78** in 60–82% yield stereospecifically (Scheme 30) [26].

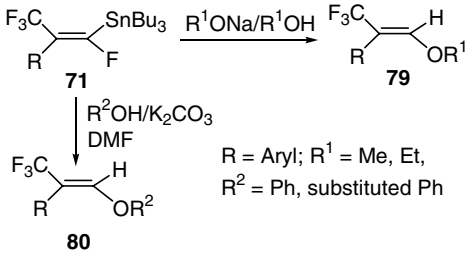
5.6. Stereospecific synthesis of substituted trifluoromethyl vinyl ethers

Recently much interest has been attracted to the synthesis of vinyl ethers since they emerged as highly valuable intermediates in a variety of synthetic applications [27], especially in the synthesis of biologically active compounds [28].

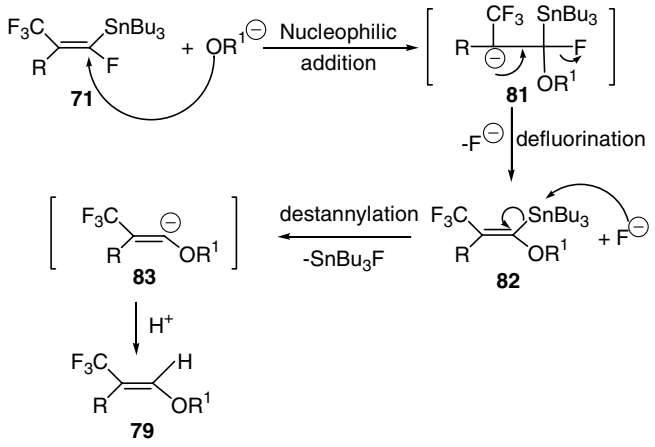
(*Z*)-α-Fluoro-β-trifluoromethylvinylstannanes **71** were treated with sodium methoxide (or ethoxide) in refluxing methanol (or ethanol) giving trifluoromethylated alkyl vinyl ethers **79** stereospecifically in yields ranging from 73% to 95%. Similarly, **71** reacted with phenol in the presence of potassium carbonate in *N*,*N*-dimethylformamide (DMF) to afford trifluoromethylated aryl vinyl ethers **80** in 82–96% yield exclusively as the *E*-isomer (Scheme 31) [29].

It is remarkable that a novel tandem reaction including nucleophilic addition, defluorination and destannylation reaction has been found. The Ad_N–*E* mechanism shown in Scheme 32 was proposed.

The reaction is initiated from the nucleophilic attack of sodium alkoxide ion forming intermediate **81**. After simultaneous movement of two pairs of electrons, the defluorination occurred and the intermediate **82** and fluoride ion were formed. Finally, the destannylation takes place when the fluoride ion attacks tributylstannyl group to afford **83**,



Scheme 31.



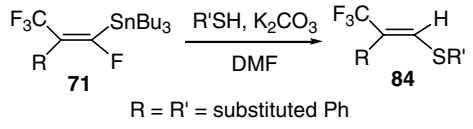
Scheme 32.

followed by abstraction of a proton giving **79**. In this studies, the retention of configuration was observed for the tandem nucleophilic addition, defluorination and destannylation reaction in polyfluorovinylstannane.

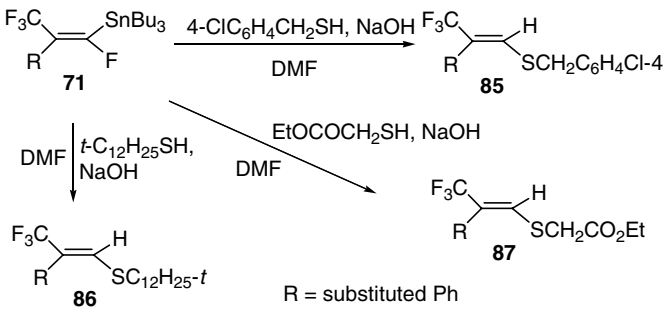
5.7. Stereospecific synthesis of trifluoromethylated vinyl sulfides

Treatment of (*Z*)-α-fluoro-β-trifluoromethylvinylstannanes **71** with aryl thiols in the presence of K_2CO_3 in DMF at 25 °C for 6 h afforded trifluoromethylated vinyl sulfides **84** in yields ranging from 68% to 97%. The reaction was stereospecific and produced *E*-isomer exclusively (Scheme 33) [30].

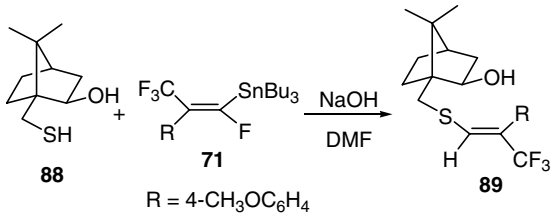
With the best conditions in hand, the present protocol was applied to various types of thiols, such as benzyl thiol (66%, 86% yields), alkyl thiol (70% yield) and a thiol with an ethoxycarbonyl moiety (70%, 71% yields), giving **85**, **86** and **87**, respectively (Scheme 34) [30].



Scheme 33.



Scheme 34.



Scheme 35.

The nucleophilic substitution reaction of 10-sulfanylisoborneol **88** with (*Z*)-α-fluoro-β-trifluoromethylvinylstannane **71** was also examined affording **89** stereospecifically in excellent yield (94%) with an *E*-configuration (Scheme 35) [30].

6. Conclusion

Fluorinated vinylstannanes have attracted much interest in recent years because they provided a useful and convenient methodology for the introduction of monofluoro, difluoro, trifluoro or polyfluoro functionality into organic molecules and emerged as highly valuable intermediates in organic synthesis, particularly in the synthesis of fluorine-containing naturally occurring compounds. In addition, the new methodologies discussed in this review possess high stereoselectivity. They are, therefore, potentially useful in organic synthesis, particularly in the medicinal and agricultural chemistry for the synthesis of fluorine-containing biologically active compounds.

Acknowledgements

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