A Novel Stereospecific Route to (*E*)- and (*Z*)-(2-Substituted-1,2-difluoroethenyl)stannanes

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In the presence of 1.2−1.5 equiv of potassium fluoride, a variety of (*E*)- and (*Z*)-(2-substituted-1,2-difluoroethenyl)silanes reacted with tributyltin chloride in DMF at room temperature to 80 °C to afford the corresponding stannanes in good yields with overall retention of configuration. These stannanes are useful intermediates for the introduction of the (*E*)- and (*Z*)-1,2-difluoroethylene unit into organic molecules. Under similar reaction conditions, only catalytic potassium fluoride (5−10%) was needed for these conversions when tributyltin chloride was replaced by tributyltin oxide. The mechanism and scope of this transformation is discussed.

Introduction

Introduction of fluorine into an organic molecule often leads to dramatic changes in biological activities due to the unique properties of fluorine, and fluorine-containing compounds have been utilized in pharmaceuticals, agrochemicals, and other bioactive products.[1−3] The role of fluorine-containing organometallics in the preparation of fluorinated organic molecules has been well reviewed.[4] However, fluorine-containing organostannanes have received little attention in part due to the limited methodology in the preparation of fluorine-containing organostannanes. Since non-fluorinated alkenylstannanes have been widely utilized in the formation of carbon−carbon bonds *via* palladium-catalyzed cross-coupling with organic halides and sulfonates (Stille reaction),[5] fluorine-containing alkenylstannanes would be particularly invaluable synthetic building blocks for incorporation of fluorine into organic molecules. (Trifluorovinyl)stannanes (CF_2=$CFSnR_3$) have been prepared from the corresponding (trifluorovinyl)magnesium[6] or (trifluorovinyl)lithium[7] reagents and trialkylstannyl halides and have been successfully employed in the Stille reaction.[8,9] The stereospecific preparation of (*E*)- and (*Z*)-(α-fluorovinyl)stannanes *via* the radical reaction of the corresponding α-fluorovinyl sulfones with tributyltin hydride has been reported by McCarthy.[10] Recently, ethyl 3-(tributylstannyl)-2-methoxyacrylate was prepared from ethyl trifluoropyruvate in several steps and used in the Stille reaction for the synthesis of *β*-fluoro-α-keto acid derivatives.[11] In a recent communication,[12] we have described a novel, general, and convenient method for the preparation of a variety of fluorinated alkenylstannanes from the corresponding alkenylsilanes. Here we wish to discuss our detailed results including the scope, mechanism, and a new improved modification of this transformation.

Results and Discussion

Preparation of a Variety of (*E*)- and (*Z*)-(2-Substituted-1,2-difluoroethenyl)silanes. The methodology for preparation of (*E*)- and (*Z*)-(2-substituted-1,2-difluoroethenyl)silanes, R′CF=$CFSiR_3$ (where R′ = alkyl, aryl, H, I, etc.), has been well established (Scheme 1).[13−18] The key intermediate, (trifluorovinyl)triethylsilane (CF_2=$CFSiEt_3$), was prepared utilizing MeLi (ether solution), bromotrifluoroethylene, and chlorotriethylsilane in ether [13] or *n*-BuLi (hexane solution), chlorotrifluoroethylene, and chlorotriethylsilane in THF.[14] Treatment of CF_2=$CFSiEt_3$ with $LiAlH_4$ in tetrahydrofuran resulted in the (*Z*)-(1,2-difluorovinyl)triethylsilane (*trans*-HCF=$CFSiEt_3$) as the predominant isomer (*Z*:*E* = 95:5 by ^{19}F NMR analysis),[15,16] which underwent isomerization easily with ultraviolet light (254 nm) and catalytic phenyl disulfide to afford the corresponding (*E*) isomer (*Z*:*E* = 5:95) in

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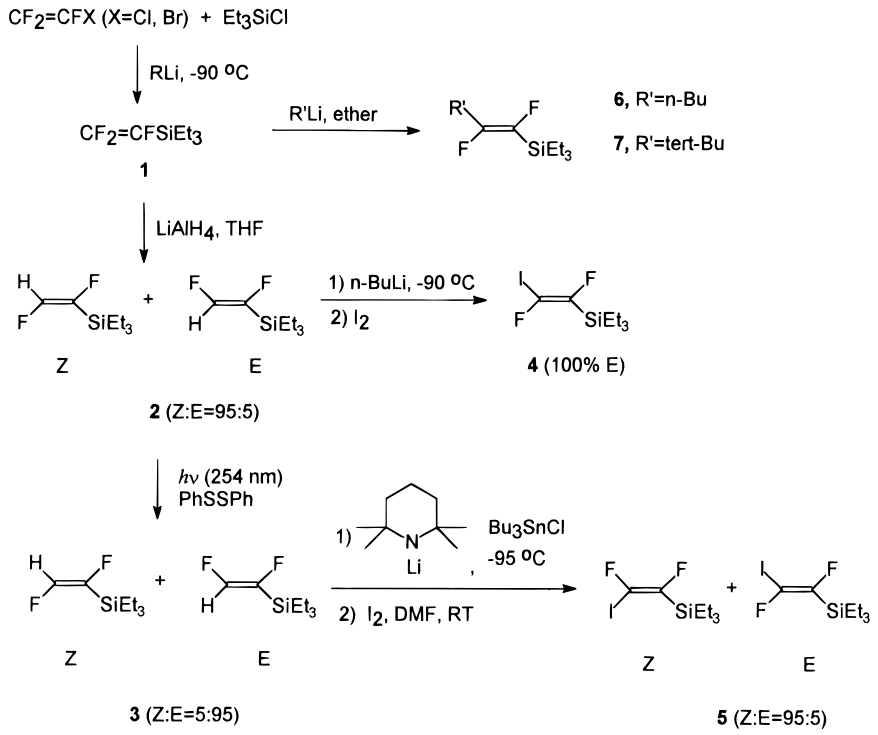
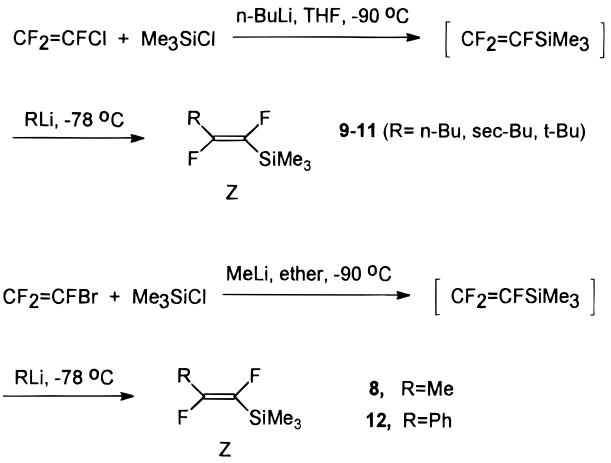
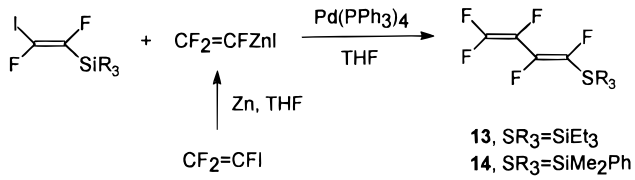
Scheme 1



Scheme 2



Scheme 3



high yield.[13] (*E*)-(1,2-Difluoro-2-iodovinyl)triethylsilane (*trans*-ICF=CFSiEt$_3$) was readily prepared *via* low temperature iodination of the pregenerated *trans*-vinyllithium intermediate.[16] In contrast, the (*Z*) isomer (*cis*-ICF=CFSiEt$_3$) was obtained from the corresponding vinyl stannane due to the instability of *cis*-vinyllithium intermediate.[13]

(*Z*)-(2-Alkyl- or (2-aryl-1,2-difluoroethenyl)silanes (*trans*) were prepared through an addition−elimination reaction of (trifluorovinyl)silane with alkyl or aryl lithium reagents *via* a modified literature procedure (Scheme 2).[17,18] Chlorotrimethylsilane was used *in situ* to trap the unstable CF$_2$=CFLi. It should be noted that compound **12** was obtained in better yield (75%) in ethyl ether than THF (41%), and ether could only be used for preparation of the volatile compound **8** (bp 95 °C).

(*Z*)-1-(Triethylsilyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (*trans*-CF$_2$=CFCF=CFSiEt$_3$, **13**) and (*Z*)-1-(dimethylphenylsilyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (*trans*-CF$_2$=CFCF=CFSiMe$_2$Ph, **14**) can be easily synthesized in high yields from the corresponding (*E*)-(2-iodo-1,2-difluorovinyl)silane and (trifluorovinyl)zinc iodide[19] *via* a palladium(0)-catalyzed cross-coupling reaction in THF (Scheme 3).

Preparation of (*E*)- and (*Z*)-(2-Substituted-1,2-difluoroethenyl)stannanes. Palladium-catalyzed cross-coupling reactions of vinyltrimethylsilane and alkenylfluorosilanes with aryl and vinyl halides in the presence of fluoride for the formation of the carbon−carbon bond has been reported by Hiyama *et al.*[20] But the low reactivity of alkenyltrimethylsilane and the lack of availability of alkenylfluorosilanes limited further applications of this reaction. Recently, new efforts have been made through the conversion of the vinylsilanes to the corresponding vinylboronates followed by the Suzuki−Miyaura cross-coupling reaction without isolation of the intermediate.[21] Our recent interest in the development of (*E*)- and (*Z*)-1,2-difluoroethenyl synthon[13] prompted our attention to the preparation of (*E*)- and (*Z*)-(2-substituted-1,2-difluoroethenyl)stannanes, R′CF=CFSnR$_3$ (where R′ = alkyl, aryl, H, I, etc.) for potential utilization in the Stille cross-coupling reaction.[5] As noted above (trifluorovinyl)stannanes (CF$_2$=CFSnR$_3$) have been prepared from the corresponding (trifluorovinyl)magnesium[6] or (trifluorovinyl)-lithium[7] reagents and trialkyltin chlorides. In contrast to analogous fluorinated vinylsilane, reaction of CF$_2$=CFSnR$_3$ with R′Li (R′ = alkyl, aryl) only gave the

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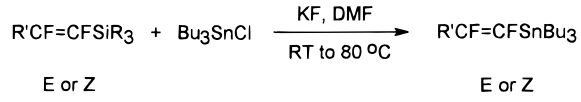
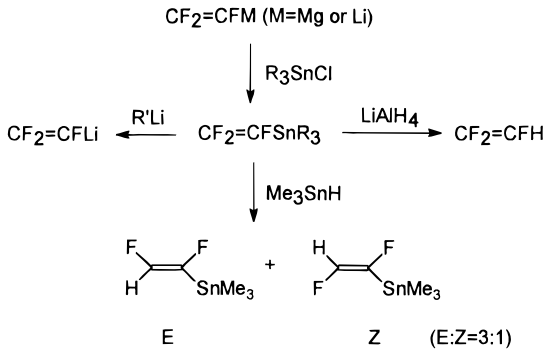
Table 1. Reaction of Vinylsilanes with Tributyltin Chloride in the Presence of Potassium Fluoride



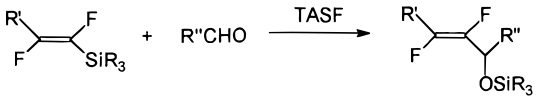
Entry	R′CF=CFSiR$_3$	reaction conditions	products	yield (%)[a]
1	CF_2=CFSiEt$_3$, **1**	rt, overnight	**1a**	92
2[b]	(*Z*)-HCF=CFSiEt$_3$, **2**	70 °C, overnight	**2a**[b]	80
3[c]	(*E*)-HCF=CFSiEt$_3$, **3**	70 °C, overnight	**3a**[c]	74
4	(*E*)-ICF=CFSiEt$_3$, **4**	rt, overnight	**4a**	83
5[d]	(*Z*)-ICF=CFSiEt$_3$, **5**	rt, overnight	**5a**[d]	82
6	(*Z*)-*n*-BuCF=CFSiEt$_3$, **6**	80 °C, 24 h	**6a**	72
7	(*Z*)-*tert*-BuCF=CFSiEt$_3$, **7**	80 °C, 24 h	**7a**	71
8	(*Z*)-MeCF=CFSiMe$_3$, **8**	80 °C, 10 h	**8a**	74
9	(*Z*)-*n*-BuCF=CFSiMe$_3$, **9**	rt, overnight	−	NR
10	(*Z*)-*n*-BuCF=CFSiMe$_3$, **9**	80 °C, 10 h	**6a**	78
11	(*Z*)-*sec*-BuCF=CFSiMe$_3$, **10**	80 °C, 10 h	**10a**	87
12	(*Z*)-*tert*-BuCF=CFSiMe$_3$, **11**	80 °C, 10 h	**7a**	79
13	(*Z*)-PhCF=CFSiMe$_3$, **12**	rt, 12 h	**12a**	70
14	(*Z*)-CF_2=CFCF=CFSiEt$_3$, **13**	rt, 24 h	**13a**	82
15	(*Z*)-CF_2=CFCF=CFSiMe$_2$Ph, **14**	rt, 24 h	**13a**	69

[a] Isolated yields based on vinylsilanes. [b] *Z*:*E* = 95:5; [c] *E*:*Z* = 95:5; [d] *Z*:*E* = 95:5.

Scheme 4



Scheme 5



exchange product, (trifluorovinyl)lithium (CF_2=CFLi)[7,22] and none of the addition−elimination product. Similarly, reduction of (trifluorovinyl)stannane with $LiAlH_4$ yielded only trifluoroethylene (CF_2=CFH) rather than HCF=CFSnR$_3$.[23] A mixture of (*E*)- and (*Z*)-HCF=CFSnMe$_3$ (*E*:*Z* = 3:1) was obtained in about 50% yield through the radical reduction of (trifluorovinyl)trimethylstannane with trimethyltin hydride (Scheme 4). Consequently, if these stannanes were to be utilized in Stille coupling processes it was necessary to develop a novel, convenient, and stereospecific route to these (*E*)- and (*Z*)-(2-substituted-1,2-difluoroethenyl)stannanes.

Hiyama reported the fluoride ion-catalyzed generation and carbonyl addition of *trans*-2-substituted-1,2-difluoroethenyl carbanions from the corresponding *trans*-(2-substituted-1,2-difluoroethenyl)silanes (Scheme 5).[15] In place of aldehydes, tributyltin chloride, a well-known good electrophile, was employed to react with *trans*-(2-substituted-1,2-difluoroethenyl)silanes in DMF in the presence of dry potassium fluoride (1.5−2.0 equiv) at room temperature to 80 °C to stereospecifically afford the corresponding stannanes in good yields. To our knowledge, this is the first report of the stereospecific conversion of a vinylsilane to the corresponding vinylstannane, although recently Buchwald reported the conversion of alkynyltrimethylsilanes as well as allyl- and benzyltrimethylsilane to the corresponding stannanes utilizing TBAF and tributyltin oxide.[24] Also Olah recently synthesized (trifluoromethyl)tributylstannane from the corresponding (trifluoromethyl)trimethylsilane *via* Buchwald's method (Scheme 6).[25]

Scheme 6

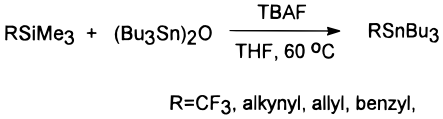


Table 1 summarizes our detailed results. In all cases, the configuration of the double bond was unchanged. When R was iodine, phenyl, fluorine, or trifluorovinyl, the conversion occurred readily at room temperature (entries 1, 4, 5, 13−15). The conversion proceeded slowly at room temperature when R was hydrogen, and no reaction was observed at room temperature when R was an alkyl group. However, at 70−80 °C the conversion of the vinylsilane to the vinyl stannane occurred readily regardless of the nature of the R group. The triethylsilyl derivatives were less reactive than the corresponding trimethylsilyl derivatives, and longer reaction time was needed (entries 6, 7), presumably due to more facile attack by fluoride ion on the smaller trimethylsilyl group. A possible reaction mechanism is described below. Fluoride ion attacks the silyl group to generate the vinyl carbanion and trialkylsilyl fluoride. The vinyl carbanion reacted with tributyltin chloride to yield the desired vinylstannane (Scheme 7). Therefore, theoretically at least 1 equiv of potassium fluoride was needed for complete conversion, and 1 equiv of trialkylsilyl fluoride was formed as a major byproduct.

Further studies indicated that when tributyltin chloride was replaced with bis(tributyltin) oxide (0.5 equiv), only catalytic potassium fluoride (5−10%) was needed to complete the conversion under similar reaction conditions

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Scheme 7

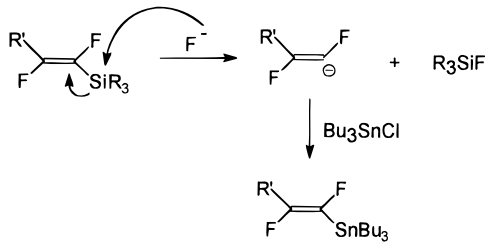
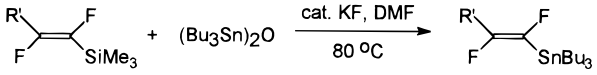


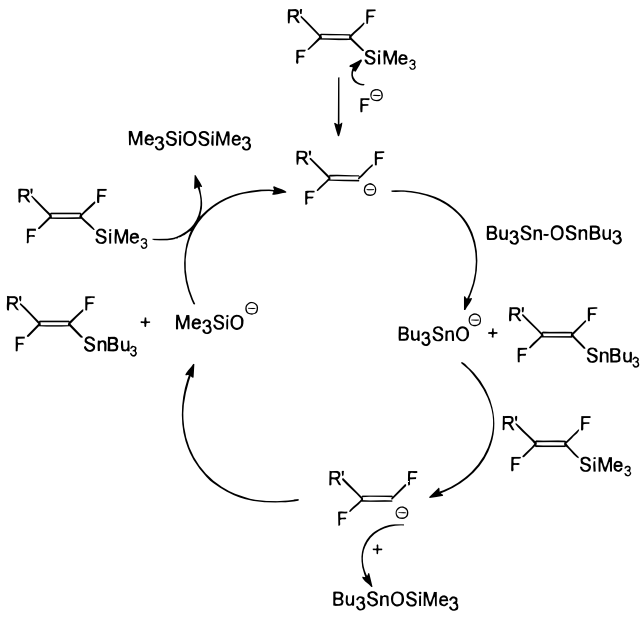
Table 2. Reaction of Vinylsilanes with Bis(tributyltin) Oxide in the Presence of Catalytic Potassium Fluoride



entry	R′	reaction conditions	products	yield (%)[a]
1	Me, **8**	80 °C, 10 h	**8a**	85
2	*n*-Bu, **9**	80 °C, 10 h	**6a**	90
3	*sec*-Bu, **10**	80 °C, 10 h	**10a**	87
4	*tert*-Bu, **11**	80 °C, 10 h	**7a**	88
5	Ph, **12**	80 °C, 10 h	**12a**	79

[a] Isolated yields based on vinylsilanes.

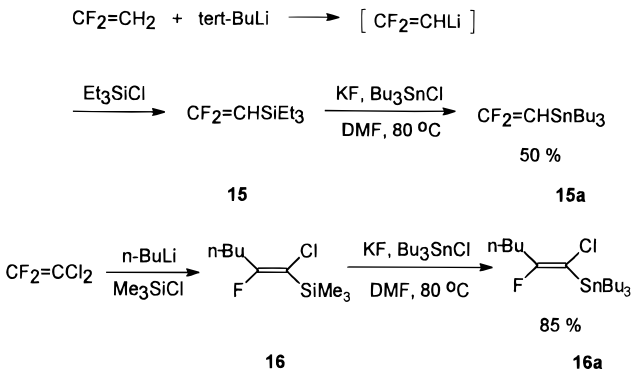
Scheme 8



(Table 2). This modified procedure provided better yields, probably due to minimizing the formation of the reduced product (R′CF=CFH), which is usually formed in about 10% yield. It should be noted that this modified procedure is best employed in the conversion of fluorinated vinyltrimethylsilanes to the corresponding stannanes, since in these cases the volatile trimethylsiloxane ($Me_3SiOSiMe_3$) was formed as the major byproduct, which can be easily seperated from the product. The catalytic cycle is shown below (Scheme 8).

Several other fluorinated vinylsilanes can also be converted to the corresponding stannanes under the same reaction conditions. 2,2-(Difluorovinyl)triethylsilane (**15**, CF_2=$CHSiEt_3$) which was prepared from (2,2-difluorovinyl)lithium reagent[26] and chlorotriethylsilane reacted with tributyltin chloride in the presence of KF at 80 °C to afford the the corresponding stannane (**15a**, CF_2=$CHSnBu_3$) in 50% yield. Similarly, (*Z*)-(1-chloro-2-fluoro-1-hexenyl)tributylstannane ((*Z*)-*n*-BuCF=$CClSnBu_3$, **16a**) was obtained in 85% yield from the corresponding silane-((*Z*)-*n*-BuCF=$CClSiMe_3$, **16**) (Scheme 9). However, no conversion of silane to stannane was observed when a vinylsilane without vinyl fluorine was employed, such as CH_2=$CHSiMe_3$ or (*E*)-R_FCH=$CHSiMe_3$, presumably due to the low polarity of the carbon−silicon bond when no fluorine is present on the double bond.

Scheme 9



In conclusion, we have described a novel, efficient, and stereospecific method for the synthesis of a variety of (*E*)- and (*Z*)-(2-substituted-1,2-difluoroethenyl)stannanes and related fluorinated stannanes from the corresponding silanes. These fluorinated alkenylstannanes are potentially valuable synthons for the stereospecific introduction of the 1,2-difluoroethylene unit into organic molecules. The detailed results of the palladium-catalyzed cross-coupling reaction (Stille reaction) of these stannanes with aryl and vinyl halides will be described in future reports.

Experimental Section

General. All boiling points are uncorrected. ^{19}F NMR (282.44 MHz), ^1H NMR (300.17 MHz), and ^{13}C NMR (75.48 MHz) spectra were recorded in $CDCl_3$ solvent. All chemical shifts are reported in parts per million downfield (positive) of the standards. ^{19}F NMR spectra are referenced against internal $CFCl_3$, and ^1H NMR and ^{13}C NMR spectra against internal tetramethylsilane (TMS). FT-IR spectra were recorded as CCl_4 solutions using a solution cell with a 0.1-cm path length and absorbance frequencies reported in cm^{-1}. GC-MS spectra were obtained at 70 eV in the electron-impact mode. High resolution mass spectral determinations were made at the University of Iowa High Resolution Mass Spectrometry Facility. GLPC analysis were performed on a 5% OV-101 column with a thermal conductivity detector. Photochemical reactions were carried out in a quartz Rotoflo tube in a photoreactor equipped with 254 nm bulbs.

Materials. MeLi (1.4 M in ethyl ether), *n*-BuLi (2.5 M in hexane), *sec*-BuLi (1.3 M in cyclohexane), *tert*-BuLi (1.7 M in pentane), and PhLi (18 M in pentane/ethyl ether) were obtained from Aldrich Chemical Co. Chlorotriethylsilane, bromotrifluoroethylene, chlorotrifluoroethylene, 1,1-dichloro-2,2-difluoroethylene, and 1,1-difluoroethylene were obtained from PCR Specialty Chemicals. Tributyltin chloride, chlorotrimethylsilane, tributyltin oxide, lithium aluminum hydride, and potassium fluoride were obtained from Aldrich Chemical Co. without further purification. Potassium fluoride was dried by refluxing with benzene prior to use. DMF was dried by distillation from CaH_2 and stored under nitrogen. (Trifluorovinyl)triethylsilane (CF_2=$CFSiEt_3$, **1**), (*Z*)-(1,2-difluorovinyl)-triethylsilane (*trans*-HCF=$CFSiEt_3$, **2**), (*E*)-(1,2-difluorovinyl)-triethylsilane (*cis*-HCF=$CFSiEt_3$, **3**), (*E*)-(1,2-difluoro-2-iodovinyl)triethylsilane (*trans*-ICF=$CFSiEt_3$, **4**), (*Z*)-(1,2-di-

(26) Sauvetre, R.; Normant, J. F. *Tetrahedron Lett.* **1981**, *22*, 957.

fluoro-2-iodovinyl)triethylsilane (*cis*-ICF=CFSiEt$_3$, **5**) were prepared according to the literature procedure.[13]

Preparation of (*Z*)-(1,2-Difluoro-1-alkenyl)trialkylsilanes (*trans*-R′CF=CFSiR$_3$). Preparation of (*Z*)-1,2-Difluoro-1-(trimethylsilyl)-1-hexene (*trans*-*n*-BuCF=CFSiMe$_3$, 9). A 1000 mL three-necked flask equipped with a low temperature thermometer, a magnetic stir bar, a N_2 tee, and a dry ice/acetone condenser was charged with 150 mL of tetrahydrofuran, 21.7 g (0.2 mol) of trimethylsilyl chloride, and cooled to −85 °C with a pentane/liquid nitrogen bath. Then, chlorotrifluoroethylene (25.6 g, 0.22 mol) was condensed into the cooled solution. *n*-BuLi (88 mL, 2.5 M in hexane, 0.22 mol) was slowly added over three hours *via* syringe. During addition, the solution was maintained below −80 °C. After the addition was completed, the solution was stirred at −78 °C for 2 h and then allowed to warm to room temperature over 3 h. Then the reaction mixture was recooled to −78 °C with a dry ice/acetone bath, and *n*-BuLi (80 mL, 2.5 M in hexane, 0.2 mol) was added slowly into the mixture *via* syringe. After the addition was completed, the reaction mixture was warmed to room temperature and stirred overnight. Aqueous HCl solution (0.1 N, 300 mL) was added slowly, and the reaction mixture was extracted with ether (200 mL × 2). The combined organic layers were washed with brine and dried over $MgSO_4$. After evaporation of ether, the residue was distilled under reduced pressure to afford (*Z*)-1,2-difluoro-1-(trimethylsilyl)-1-hexene (32.6 g) in 85% yield, bp 95 °C/100 mmHg. (lit.[18b] 50−52 °C/11 mmHg). ^{1}H NMR ($CDCl_3$): 2.40 (m, 2H), 1.50 (m, 2H), 1.35 (m, 2H), 0.92 (t, 3H), 0.2 (q, $^4J_{HF}$ = 0.7 Hz, 9H) ppm. ^{19}F NMR ($CDCl_3$): −146.1 (dt, $^3J_{FF}$ = 125.9 Hz, $^3J_{HF}$ = 23.5 Hz, 1F), −174.3 (dt, $^3J_{FF}$ = 125.9 Hz, $^4J_{FH}$ = 6.4 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 165.5 (dd, *J* = 237.8 Hz, *J* = 41.9 Hz), 155.5 (dd, *J* = 254.5 Hz, *J* = 74.4 Hz), 27.81 (dd, *J* = 2.2 Hz, *J* = 0.9 Hz), 26.36 (dd, *J* = 25.3 Hz, *J* = 1.5 Hz), 22.05 (s), 13.70 (s), −2.37 (s) ppm. GC-MS: 192 (M^+, 6.69), 149 ($M^+ - C_3H_7$, 0.14). FTIR: 1675.21 (C=C) cm^{-1}.

Preparation of (*Z*)-1,2-Difluoro-1-(trimethylsilyl)-1-propene (*trans*-MeCF=CFSiMe$_3$, 8). Similarly, (trifluorovinyl)trimethylsilane (CF_2=CFSiMe$_3$), prepared *in situ* from bromotrifluoroethylene (72.5 g, 0.45 mol), MeLi (325 mL, 1.4 M in Et_2O, 0.45 mol), and chlorotrimethylsilane (43.4 g, 0.4 mol) in ethyl ether was reacted with MeLi (300 mL, 1.4 M in Et_2O, 0.42 mol) followed by fractional distillation through a 25 cm long spinning band column to afford (*Z*)-1,2-difluoro-1-(trimethylsilyl)-1-propene (37.1 g) in 62% yield, bp 95 °C. ^{1}H NMR ($CDCl_3$): 2.00 (dd, $^3J_{HF}$ = 17.6 Hz, $^4J_{HF}$ = 6.2 Hz, 3H), 0.20 (s, 9H) ppm. ^{19}F NMR ($CDCl_3$): −138.3 (dq, $^3J_{FF}$ = 126.5 Hz, $^3J_{HF}$ = 17.6 Hz, 1F), −173.4 (dq, $^3J_{FF}$ = 126.5 Hz, $^4J_{HF}$ = 5.7 Hz ,1F) ppm. ^{13}C NMR ($CDCl_3$): 162.3 (dd, *J* = 235.2 Hz, *J* = 43.0 Hz), 155.9 (dd, *J* = 254.2 Hz, *J* = 73.2 Hz), 12.75 (dd, *J* = 27.2 Hz, *J* = 2.4 Hz) ppm. GC-MS: 150 (M^+), 135 ($M^+ - CH_3$). FTIR: 1683.90 (C=C) cm^{-1}.

Preparation of (*Z*)-1,2-Difluoro-3-methyl-1-(trimethylsilyl)-1-pentene (*trans*-*sec*-BuCF=CFSiMe$_3$, 10). Similarly, (trifluorovinyl)trimethylsilane, prepared *in situ* from chlorotrifluoroethylene (25.6 g, 0.22 mol), *n*-BuLi (88 mL, 2.5 M in hexane, 0.22 mol), and chlorotrimethylsilane (21.7 g, 0.2 mol) in THF, was reacted with *sec*-BuLi (170 mL, 1.3 M in cyclohexane, 0.22 mol) to give 28.0 g of (*Z*)-1,2-difluoro-3-methyl-1-(trimethylsilyl)-1-pentene in 73% yield, bp 85 °C/100 mmHg. (lit.[18b] 40 °C/11 mmHg). ^{1}H NMR ($CDCl_3$): 2.80 (m, 1H), 1.43 (m, 2H), 1.09 (d, *J* = 7.9 Hz, 3H), 0.89 (t, *J* = 8.0 Hz, 3H), 0.21 (m, 9H) ppm. ^{19}F NMR ($CDCl_3$): −159.4 (dd, $^3J_{FF}$ = 125.9 Hz, $^3J_{HF}$ = 33.1 Hz, 1F), −175.6 (dd, $^3J_{FF}$ = 125.9 Hz, $^4J_{HF}$ = 5.1 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 167.7 (dd, *J* = 240.8, 40.3 Hz), 154.9 (dd, *J* = 254.9, 75.7 Hz), 32.99 (dd, *J* = 24.4, 1.2 Hz), 26.12 (d, *J* = 2.4 Hz), 16.86 (d, *J* = 1.5 Hz), 11.81 (s), −2.32 (m) ppm. GC-MS: 192 (M^+, 16.99), 163 ($M^+ - C_2H_5$, 1.02). FTIR: 1668.61 (C=C) cm^{-1}.

Preparation of (*Z*)-1,2-Difluoro-3,3-dimethyl-1-(trimethylsilyl)-1-butene (*trans*-tert-BuCF=CFSiMe$_3$, 11). Similarly, (trifluorovinyl)trimethylsilane, prepared *in situ* from chlorotrifluoroethylene (25.6 g, 0.22 mol), *n*-BuLi (88 mL, 2.5 M in hexane, 0.22 mol), and chlorotrimethylsilane (21.7 g, 0.2 mol) in THF, was reacted with *tert*-BuLi (130 mL, 1.7 M in pentane, 0.22 mol) to give 28.8 g of (*Z*)-1,2-difluoro-3,3-dimethyl-1-(trimethylsilyl)-1-butene in 75% yield, bp 75 °C/100 mmHg (lit.[18b] 35 °C/10 mmHg). ^{1}H NMR ($CDCl_3$): 1.21(m, 9H), 0.18 (m, 9H) ppm. ^{19}F NMR ($CDCl_3$): −149.4 (d, $^3J_{FF}$ = 125.2 Hz, 1F), −172.9 (d, $^3J_{FF}$ = 125.2 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 169.1 (dd, *J* = 236.9, 34.5 Hz), 154.9 (dd, *J* = 260.7, 87.0 Hz), 35.60 (dd, *J* = 24.1, 2.7 Hz), 27.51 (dd, *J* = 4.9, 3.9 Hz), −2.21 (dd, *J* = 2.8, 2.4 Hz) ppm. GC-MS: 192 (M^+, 9.29), 177 ($M^+ - CH_3$, 0.75). FTIR: 1728.05 (C=C) cm^{-1}.

Preparation of (*Z*)-1,2-Difluoro-1-(trimethylsilyl)styrene (*trans*-PhCF=CFSiMe$_3$, 12). Similarly, (trifluorovinyl)trimethylsilane, prepared *in situ* from bromotrifluoroethylene (81 g, 0.5 mol) and MeLi (360 mL, 1.4 M in Et_2O, 0.5 mol) in ethyl ether, was reacted with PhLi (250 mL, 1.8 M in pentane/ether, 0.45 mol) to give (*Z*)-1,2-difluoro-1-(trimethylsilyl)styrene (64.0 g) in 75% yield, bp 78−81 °C/1.0 mmHg (lit.[18b] 50 °C/0.01 mmHg). ^{1}H NMR ($CDCl_3$): 7.30−7.70 (m, 5H, Ph), 0.30 (dd, $^4J_{HF}$ = 1.3 Hz, $^5J_{HF}$ = 0.8 Hz, 3 × CH_3) ppm. ^{19}F NMR ($CDCl_3$): −152.9 (d, $^3J_{FF}$ = -152.2 Hz, 1F), −164.6 (d, $^3J_{FF}$ = 125.2 Hz ,1F) ppm. ^{13}C NMR ($CDCl_3$): 157.9 (dd, *J* = 224.6 Hz, *J* = 33.3 Hz), 156.7 (dd, *J* = 271.0 Hz, *J* = 82.4 Hz), 130.1 (dd, *J* = 26.8 Hz, *J* = 3.9 Hz), 129.0 (d, *J* = 2.1 Hz), 128.7 (s), 128.4 (d, *J* = 2.1 Hz), 127.2 (d, *J* = 4.2 Hz), 125.7 (dd, *J* = 9.8 Hz, *J* = 7.6 Hz) ppm. GC-MS: 212 (M^+, 20.36), 197 ($M^+ - CH_3$, 0.51), 77 (Ph^+, 100). FTIR: 1640.25 (C=C) cm^{-1}.

Preparation of (*Z*)-1,2-Difluoro-1-(triethylsilyl)-1-hexene (*trans*-*n*-BuCF=CFSiEt$_3$, 6). A 250 mL three-necked flask equipped with a low temperature thermometer, magnetic stir bar, and N_2 tee was charged with CF_2=CFSiEt$_3$ (19.6 g, 0.1 mol) and dry ether (100 mL) and cooled to −78 °C with dry ice/acetone bath. *n*-BuLi (2.5 M in hexane, 48 mL, 0.12 mol) was added slowly *via* syringe. The reaction mixture was stirred at −78 °C for 1 h and then warmed to room temperature for 2 h. The reaction mixture was recooled with an ice−water bath, and dilute HCl solution (0.1 N, 80 mL) was added to decompose the excess lithium reagent. The organic layer was separated, and the aqueous layer was extracted with ethyl ether (30 mL × 2). The combined organic layers were washed with saturated brine solution and dried over anhydrous $MgSO_4$. Evaporation of solvents on a rotary evaporator, followed by distillation under vaccum, gave the addition−elimination product (21.0 g, 90% yield), bp 73−77 °C/2 mmHg (lit.[17] 53 °C/ 0.4 mmHg). GLPC 95.5%. ^{1}H NMR ($CDCl_3$): 2.40 (m, 2H), 1.51 (m, 2H), 1.36 (m, 2H), 0.97 (m, 12H), 0.72 (q, 6H) ppm. ^{19}F NMR ($CDCl_3$): −146.2 (dt, $^3J_{FF}$ = 124.6 Hz, $^3J_{HF}$ = 23.6 Hz, 1F), −173.8 (dt, $^2J_{FF}$ = 124.6 Hz, $^4J_{HF}$ = 6.4 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 166.5 (dd, *J* = 238.1 Hz, *J* = 41.8 Hz), 154.2 (dd, *J* = 255.5 Hz, *J* = 76.0 Hz), 27.9 (dd, *J* = 2.5 Hz, *J* = 1.2 Hz), 26.3 (dd, *J* = 25.6 Hz, *J* = 1.8 Hz), 22.0 (s), 13.7 (s), 7.1 (s), 2.5 (dd, *J* = 2.2 Hz, *J* = 2.1 Hz) ppm. FTIR: 1672.9 (C=C) cm^{-1}. GC-MS: 234 (M^+, 5.69), 177 (M^+ − Bu, 0.23), 119 ($M^+ - Et_3Si$, 1.10).

Preparation of (*Z*)-1,2-Difluoro-3,3-dimethyl-1-(triethylsilyl)-1-butene (*trans*-*tert*-BuCF=CFSiEt$_3$, 7). Similarly, CF_2=CFSiEt$_3$ (9.8 g, 0.05 mol) reacted with *tert*-BuLi (1.7 M in pentane, 35 mL, 0.06 mol) in 100 mL of dry ether to afford the (*Z*)-1,2-difluoro-3,3-dimethyl-1-(triethylsilyl)-1-butene (10.7 g, 91% yield), bp 64−65 °C/2 mmHg, GLPC 98.7%. ^{1}H NMR ($CDCl_3$): 1.21 (dd, $^4J_{HF}$ = 2.0 Hz, $^5J_{HF}$ = 1.9 Hz, 9H), 0.97 (t, $^3J_{HH}$ = 7.9 Hz, 9H), 0.68 (q, $^3J_{HH}$ = 7.9 Hz, 6H) ppm. ^{19}F NMR ($CDCl_3$): −149.5 (d, $^3J_{FF}$ = 124.0 Hz), −172.6 (d, $^3J_{FF}$ = 124.0 Hz) ppm. ^{13}C NMR ($CDCl_3$): 170.0 (dd, *J* = 236.8 Hz, *J* = 34.5 Hz), 153.6 (dd, *J* = 260.9 Hz, *J* = 88.5 Hz), 35.7 (dd, *J* = 24.1 Hz, *J* = 2.5 Hz), 27.6 (dd, *J* = 4.9 Hz, *J* = 4.0 Hz), 7.1 (s), 2.6 (dd, *J* = 2.5 Hz, *J* = 2.4 Hz) ppm. FTIR: 1649.6 (C=C) cm^{-1}. GC-MS: 234 (M^+, 3.22), 205 ($M^+ - C_2H_5$, 0.16), 177 (M^+ − Bu, 0.21). HRMS: Calcd for $C_{12}H_{24}F_2Si$: 234.1615. Found: 234.1611.

Preparation of (2,2-Difluorovinyl)triethylsilane (CF_2=CHSiEt$_3$, 15). A 250 mL three-necked flask equipped with a low temperature thermometer, a magnetic stir bar, a N_2 tee, and a dry ice/acetone condenser, was charged with anhydrous ether (8 mL), anhydrous tetrahydrofuran (30 mL), chlorotriethylsilane (15.1 g, 0.10 mol), and vinylidene fluoride (8.0 g, 0.125 mol) and cooled to −110 °C with a pentane/liquid nitrogen bath. *tert*-BuLi (70 mL, 1.7 M in pentane, 0.119 mol)

was slowly added over 3 h *via* syringe with stirring. During addition, the solution was maintained between −100 to −110 °C. After the addition was completed, the solution was stirred at −100 °C for 1 h, −78 °C for 2 h, and then allowed to warm to room temperature and stirred overnight. The reaction mixture was treated with 0.1 N aqueous hydrogen chloride (20 mL) and extracted with ether (100 mL × 2). The combined organic layers were washed with brine and dried over $MgSO_4$. After evaporation of ether, the residue was fractionally distilled through a 25 cm long spinning band column to give the (2,2-difluorovinyl)triethylsilane (10.7 g) in 60% yield, bp 140 °C. ^{1}H NMR ($CDCl_3$): 3.74 [dd, $^3J_{HF}$(trans) = 42.1 Hz, $^3J_{HF}$(cis) = 9.9 Hz, 1H], 0.95 (t, J = 8.0 Hz, 9H), 0.62 (q, J = 8.0 Hz, 6H) ppm. ^{19}F NMR ($CDCl_3$): −62.09 [dd, $^2J_{FF}$ = 24.2 Hz, $^3J_{HF}$(cis) = 9.9 Hz, 1F], −72.48 (dd, $^3J_{HF}$ = 42.1 Hz, $^2J_{FF}$ = 24.2 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 159.4 (dd, J = 306.4, 287.5 Hz), 65.24 (dd, J = 34.2, 4.3 Hz), 7.02 (s), 3.82 (s) ppm. GC-MS: 178 (M^+, 2.05), 149 ($M^+ - C_2H_5$, 14.46). FTIR (CCl_4): 1689.89 (C=C) cm^{-1}. HRMS: Calcd for $C_8H_{16}F_2Si$: 178.0989. Found: 178.1011.

Preparation of (*Z*)-1-Chloro-2-fluoro-1-(trimethylsilyl)-1-hexene ((*Z*)-*n*-BuCF=CClSiMe$_3$, 16). (*Z*)-1-Chloro-2-fluoro-1-(trimethylsilyl)-1-hexene was prepared according to the literature procedure[27] in 80% yield, bp 60−61 °C/1.5 mmHg (lit.[27] 82−84 °C/20 mmHg). ^{1}H NMR ($CDCl_3$): 2.50 (dt, $^3J_{HF}$ = 22.7 Hz, $^3J_{HH}$ = 7.3 Hz, 2H), 1.53 (m, 2H), 1.37 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H), 0.21 (d, J = 1.3 Hz, 9H) ppm. ^{19}F NMR ($CDCl_3$): −95.32 (t, $^3J_{HF}$ = 22.7 Hz, 1F) ppm. GC-MS: 208 (M^+, 10.04), 151 ($M^+ - C_4H_9$, 2.15). FTIR: 1640.75 (C=C) cm^{-1}.

Preparation of (*Z*)-1-(Triethylsilyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (*trans*-CF$_2$=CFCF=CFSiEt$_3$, 13). A 250 mL three-necked, round-bottomed flask equipped with a water condenser, a rubber septum, a thermometer, a Teflon-coated magnetic stir bar, and a nitrogen gas inlet was charged with tetrakis(triphenylphosphine)palladium (0.3 g), (*E*)-(1,2-difluoro-2-iodovinyl)triethylsilane (*trans*-ICF=CFSiEt$_3$, 15.2 g, 50 mmol) and 20 mL of dry tetrahydrofuran. To the stirred solution, (trifluorovinyl)zinc iodide[19] in THF (72 mL, 0.76 M, 55 mmol) was added *via* syringe. The reaction mixture was heated at 60 °C until ^{19}F NMR analysis showed no silyl iodide remained (about 12−24 h), and it was extracted with ether (200 mL × 3). The combined ethereal layers were washed with saturated brine solution and dried over $MgSO_4$. After evaporation of solvents, the residue was fractionally distilled to afford (*Z*)-1-(triethylsilyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (10.1 g) in 81% yield, bp 83−85 °C/20 mmHg. GLPC 100%. ^{1}H NMR ($CDCl_3$): 1.02 (t, J = 7.7 Hz, 9H), 0.80 (q, J = 7.7 Hz, 6H) ppm. ^{19}F NMR ($CDCl_3$): −96.5 (dd, J = 52.0, 32.0 Hz, 1F), −107.6 (dddd, J = 115.0, 52.0, 22.5, 12.4 Hz, 1F), −151.0 (ddt, J = 138.0, 19.9, 8.3 Hz), −158.9 (ddd, J = 138.0, 32.0, 11.5 Hz, 1F), −182.6 (dtd, J = 115.0, 32.0, 10.4 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 161.7 (dd, J = 281.2, 70.8 Hz), 154.2 (tdm, J = 291.6, 52.4 Hz), 150.2 (dddm, J = 227.2, 22.2, 10.4 Hz), 119.5 (dddd, J = 232.2, 57.9, 33.7, 24.1 Hz), 7.07 (s), 2.55 (s) ppm. GC-MS: 258 (M^+, 1.34), 105 (100). FTIR: 1773 (C=C) cm^{-1}.

Preparation of (*Z*)-1-(Dimethylphenylsilyl)-1,2,3,4,4-pentafluorobutadiene (*trans*-CF$_2$=CFCF=CFSiMe$_2$Ph, 14). Similarly, the reaction of (*E*)-1,2-difluoro-1-iodo-2-(dimethylphenylsilyl)ethylene (*trans*-ICF=CFSiMe$_2$Ph, 23.4 g, 72 mmol) and CF$_2$=CFZnI in THF (approximately 100 mmol) in the presence of tetrakis(triphenylphosphine)palladium (1.0 g) yielded (*Z*)-1-(dimethylphenylsilyl)-1,2,3,4,4-pentafluorobutadiene (16.4 g) in 82% yield, bp 98−102 °C/20 mmHg. GLPC 97%. ^{1}H NMR ($CDCl_3$): 7.5 (m, 2H), 7.3 (m, 3H), 0.5 (s, 6H) ppm. ^{19}F NMR ($CDCl_3$): −95.8 (ddm, J = 50.5, 31.8 Hz, 1F), −106.9 (dddd, J = 114.6, 50.5, 22.8, 12.9 Hz, 1F), −151.2 (dm, J = 139.9 Hz, 1F), −157.4 (ddd, J = 139.9, 33.2, 12.9 Hz, 1F), −183.2 (dddd, J = 114.6, 32.8, 31.8, 10.8 Hz) ppm. ^{13}C NMR ($CDCl_3$): 160.7 (ddm, J = 280.7, 69.5 Hz), 153.7 (tdm, J = 287.0, 46.3 Hz), 149.4 (ddm, J = 229.3, 39.2 Hz), 133.9 (s), 133.8 (s), 130.3 (s), 128.3 (s), 119.4 (dddd, J = 231.9, 59.0, 34.6, 24.4 Hz), −4.3 (s) ppm. GC-MS: 277 ($M^+ - 1$, 1.63), 182 (100). FTIR: 1770 (C=C), 1751 (C = C) cm^{-1}.

Preparation of (*E*) and (*Z*)-1,2-Difluoro-1-(tributylstannyl)-1-alkenes Using Tributyltin Chloride. Preparation of (Trifluorovinyl)tributylstannane (CF$_2$=CFSnBu$_3$, 1a). A round-bottom flask equipped with a Teflon-coated magnetic stir bar, a nitrogen tee, and rubber septum was charged with anhydrous potassium fluoride (0.22 g, 3.8 mmol), CF$_2$=CFSiEt$_3$ (0.48 g, 2.4 mmol), and dry DMF (2 mL). Tributyltin chloride (0.57 g, 1.8 mmol) was added *via* syringe, and the reaction mixture was stirred at room temperature overnight. Analysis by ^{19}F NMR indicated the absence of the vinylsilane. The reaction mixture was extracted with ether and washed with water. Evaporation of solvent followed by chromatography on silica gel using hexane as eluant gave 0.6 g of (trifluorovinyl)tributylstannane in 92% yield. ^{19}F NMR ($CDCl_3$): −88.5 (dd, J = 79.5, 33.7 Hz, 1F), −123.1 (dd, J = 113.8, 79.5 Hz, 1F), −193.1 (dd, J = 113.8, 34.4 Hz, 1F) ppm. ^{1}H NMR ($CDCl_3$): 1.55 (m, 2H), 1.33 (m, 2H), 1.10 (m, 2H), 0.91 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$): 161.7 (ddd, J = 315.6, 265.5, 34.1 Hz), 133.3 (ddd, J = 291.1, 86.1, 9.7 Hz), 28.8 (s), 27.2 (s), 13.6 (s), 10.0 (s) ppm.

Preparation of (*Z*)-(1,2-Difluorovinyl)tributylstannane (*trans*-HCF=CFSnBu$_3$, 2a). Similarly, the reaction of (*Z*)-(1,2-difluorovinyl)triethylsilane (5.0 g, 28.1 mmol) with tributyltin chloride (9.22 g , 28.3 mmol) in the presence of anhydrous potassium fluoride (2.66 g, 45.9 mmol) in dry DMF (20 mL) gave 8.26 g of (*Z*)-(1,2-difluorovinyl)tributylstannane in 83% yield. GLPC 97.8%. ^{19}F NMR ($CDCl_3$): −173.0 (dd, J = 119.2, 11.1 Hz, 1F), −177.7 (dd, J = 119.6, 83.0 Hz, 1F) ppm. ^{1}H NMR ($CDCl_3$): 7.68 (dd, J = 83.1, 11.1 Hz, 1H), 1.55 (m, 6H), 1.33 (m, 6H), 1.09 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H) ppm. ^{13}C NMR ($CDCl_3$): 165.8 (dd, J = 297.9, 78.7 Hz), 153.8 (dd, J = 229.5, 47.0 Hz), 28.8 (s), 28.8 (d, J = 21.4 Hz), 27.1 (s), 27.1 (d, J = 59.9 Hz), 13.6 (s), 9.8 (s) ppm. GC-MS: 297 (M^+-C_4H_9, 91.6), 295 (76.7), 293 (44.1), 253 (70.3), 241 (88.6), 195 (33.2), 181 (37.1), 177 (64.9), 139 (71.8), 121 (36.6), 57 (66.3). HRMS: Calcd for $C_{10}H_{19}F_2Sn$ (M^+ − Bu): 297.0477. Found: 297.0476.

Preparation of (*E*)-(1,2-Difluorovinyl)tributylstannane (*cis*-HCF=CFSnBu$_3$, 3a). Similarly, the reaction of (*E*)-(1,2-difluorovinyl)triethylsilane (2.1 g, 11.8 mmol) with tributyltin chloride (3.2 g, 9.8 mmol) in the presence of anhydrous potassium fluoride (0.8 g, 13.8 mmol) in dry DMF (5 mL) gave 2.6 g of (*E*)-(1,2-difluorovinyl)tributylstannane in 74% yield. Bp 87−90 °C/0.2 mmHg, GLPC 99%. ^{19}F NMR ($CDCl_3$): −143.0 (dd, J = 77.3, 9.2 Hz, 1F), −147.0 (dd, J = 25.7, 9.2 Hz, 1F) ppm; ^{1}H NMR ($CDCl_3$): 5.95 (dd, J = 77.3, 25.5 Hz, 1H), 5.96 (ddd, J = 77.3, 25.5, 4.8 Hz, 1H), 1.53 (m, 6H), 1.33 (m, 6H), 1.03 (tm, J = 8.3 Hz, 6H), 0.91 (t, J = 7.2 Hz, 9H) ppm. ^{13}C NMR ($CDCl_3$): 154.9 (dd, J = 313.1, 7.3 Hz), 141.5 (dd, J = 282.3, 7.1 Hz), 28.8 (s), 28.8 (d, J = 21.9 Hz), 27.2 (s), 27.2 (d, J = 59.2 Hz), 13.6 (s), 10.0 (s) ppm. GC-MS: 297 ($M^+ - C_4H_9$, 95.0), 295 (75.3), 293 (44.0), 253 (9.6), 241 (100.0). HRMS: Calcd for $C_{10}H_{19}F_2Sn$ (M^+ − Bu): 297.0477. Found: 297.0472.

Preparation of (*E*)-1-Iodo-(1,2-difluorovinyl)tributylstannane (*trans*-ICF=CFSnBu$_3$, 4a). Similarly, the reaction of (*E*)-2-iodo-(1,2-difluorovinyl)triethylsilane (4.95 g, 16.3 mmol) with tributyltin chloride (5.21 g , 16.0 mmol) in the presence of anhydrous potassium fluoride (1.33 g, 22.9 mmol) in dry DMF (60 mL) gave 6.5 g of (*E*)-2-iodo-(1,2-difluorovinyl)-tributylstannane in 85% yield. ^{19}F NMR ($CDCl_3$): −122.8 (d, J = 137.3 Hz, 1F), −133.7 (d, J = 137.3 Hz, 1F) ppm. ^{1}H NMR ($CDCl_3$): 1.55 (m, 2H), 1.34 (m, 2H), 1.23 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$): 166.9 (dd, J = 313.1, 84.2 Hz), 108.0 (dd, J = 300.9, 55.9 Hz), 28.7 (s), 28.6 (d, J = 22.3 Hz), 27.5 (s), 13.6 (s), 10.6 (t, J = 1.5 Hz) ppm. GC-MS: 423 ($M^+ - C_4H_9$, 22.66), 253 (100). FTIR: 1606.0 (C=C) cm^{-1}.

Preparation of (*Z*)-2-Iodo-(1,2-difluorovinyl)tributylstannane (*cis*-ICF=CFSnBu$_3$, 5a). Similarly, the reaction of (*Z*)-2-iodo-(1,2-difluorovinyl)triethylsilane (1.53 g, 5.0 mmol) with tributyltin chloride (2.6 g, 8.0 mmol) at 50 °C in the presence of anhydrous potassium fluoride (0.48 g, 8.0 mmol) in dry DMF (5 mL) gave (*Z*)-1-iodo-(1,2-difluorovinyl)tributylstannane in 82% yield. ^{1}H NMR ($CDCl_3$): 1.55 (m, 6H), 1.35

(27) Martin, S.; Sauvetre, R.; Normant, J. F. *J. Organomet. Chem.* **1986**, *303*, 317.

(m, 6H), 1.16 (m, 6H), 0.91 (t, J = 7.3 Hz, 9H) ppm. ^{19}F NMR ($CDCl_3$): −83.32 (d, J = 4.8 Hz, 1F), −108.1 (d, J = 4.8 Hz, 1F) ppm.

Preparation of (*Z*)-1,2-Difluoro-1-(tributylstannyl)-1-propene (*trans*-MeCF=CFSnBu$_3$, 8a). General Procedure. A 100 mL, round-bottom flask equipped with a nitrogen tee, a condenser, and Teflon-coated magnetic stir bar was charged with dry DMF (15 mL), fresh dried potassium fluoride (3.5 g, 60 mmol), tributyltin chloride (10.0 g, 30.7 mmol), and (*Z*)-1,2-difluoro-1-(trimethylsilyl)-1-propene (4.5 g, 30 mmol). The mixture was stirred at 80 °C for about 10 h, and the starting silane had disappeared by ^{19}F NMR analysis. The reaction mixture was treated with water (50 mL) and extracted with ethyl ether (50 mL × 2). The ethereal phase was dried and concentrated. The residue was purified on a silica gel column using hexane as eluant to afford 8.2 g of (*Z*)-1,2-difluoro-1-(tributylstannyl)-1-propene in 74% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): 2.03 (dd, $^3J_{HF}$ = 17.1 Hz, J = 6.2 Hz, 3H), 1.53 (m, 6H), 1.32 (m, 6H), 1.15 (m, 6H), 0.90 (t, J = 7.2 Hz, 9H) ppm. ^{19}F NMR ($CDCl_3$): −141.5 (dq, $^3J_{FF}$ = 116.3 Hz, $^3J_{HF}$ = 17.1 Hz, 1F), −165.3 (dm, $^3J_{FF}$ = 116.3 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 162.2 (dd, J = 225.0, 35.7 Hz), 158.9 (dd, J = 293.3, 97.6 Hz), 28.88 (s), 27.18 (s), 13.62 (s), 12.3 (dm, J = 31.5 Hz), 9.80 (t, J = 1.7 Hz) ppm. GC-MS: 311 (M^+ − C_4H_9, 29.70), 253 (100). FTIR: 1675.76 (C=C) cm^{-1}. HRMS: Calcd for $C_{11}H_{21}F_2Sn$ (M^+ − Bu): 311.0633. Found: 311.0623.

Preparation of (*Z*)-1,2-Difluoro-1-(tributylstannyl)-1-hexene (*trans*-*n*-BuCF=CFSnBu$_3$, 6a). Similarly, the reaction of (*Z*)-1,2-difluoro-1-(trimethylsilyl)-1-hexene (9.6 g, 50 mmol), potassium fluoride (5.8 g, 100 mmol), and tributyltin chloride (16.3 g, 50.1 mmol) in DMF (30 mL) at 80 °C for 10 h afforded (*Z*)-1,2-difluoro-1-(tributylstannyl)-1-hexene (16.0 g) as a colorless oil in 78% yield. ^{1}H NMR ($CDCl_3$): 2.42 (m, 2H), 1.52 (m, 8H), 1.32 (m, 8H), 1.15 (m, 6H), 0.89 (m, 12H) ppm. ^{19}F NMR ($CDCl_3$): −149.1 (dt, $^3J_{FF}$ = 115.7 Hz, $^3J_{HF}$ = 22.9 Hz, 1F), −166.3 (dt, $^3J_{FF}$ = 115.7 Hz, $^4J_{HF}$ = 5.7 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 165.6 (dd, J = 227.4, 34.8 Hz), 158.4 (dd, J = 293.9, 98.6 Hz), 28.95 (s), 28.11 (m), 27.19 (s), 26.01 (dd, J = 26.8, 2.1 Hz), 22.01 (s), 13.69 (s), 13.63 (s), 9.87 (s) ppm. GC-MS: 353 (M^+ − C_4H_9, 18.48), 253 (100). FTIR: 1667.56 (C=C) cm^{-1}. HRMS: Calcd for $C_{14}H_{27}F_2Sn$ (M^+ − Bu): 353.1103. Found: 353.1101.

Preparation of (*Z*)-1,2-Difluoro-1-(tributylstannyl)-1-hexene (*trans*-*n*-BuCF=CFSnBu$_3$, 6a) from the Corresponding Triethylsilane (6). Similarly, the reaction of (*Z*)-1,2-difluoro-1-(triethylsilyl)-1-hexene (11.7 g, 50 mmol), potassium fluoride (5.8 g, 100 mmol), and tributyltin chloride (16.3 g, 50.1 mmol) in DMF (30 mL) at 80 °C for 24 h afforded (*Z*)-1,2-difluoro-1-(tributylstannyl)-1-hexene (14.7 g) as a colorless oil in 72% yield.

Preparation of (*Z*)-1,2-Difluoro-3-methyl-1-(tributylstannyl)-1-pentene (*trans*-*sec*-BuCF=CFSnBu$_3$, 9a). Similarly, reaction of (*Z*)-1,2-difluoro-3-methyl-1-(trimethylsilyl)-1-pentene (9.6 g, 50 mmol), potassium fluoride (5.8 g, 100 mmol), and tributyltin chloride (16.5 g, 50.7 mmol) in DMF (50 mL) at 80 °C for 10 h afforded 17.8 g (87% yield) of (*Z*)-1,2-difluoro-3-methyl-1-(tributylstannyl)-1-pentene as a colorless oil. ^{1}H NMR ($CDCl_3$): 2.85 (m, 1H), 1.25−1.70 (m, 15H), 0.85−1.12 (m, 20H) ppm. ^{19}F NMR ($CDCl_3$): −162.3 (dd, $^3J_{FF}$ = 115.1 Hz, $^3J_{HF}$ = 33.1 Hz, 1F), −167.7 (dd, $^3J_{FF}$ = 115.1 Hz, $^4J_{HF}$ = 5.7 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 167.8 (dd, J = 230.1, 32.7 Hz), 157.8 (dd, J = 293.6, 99.8 Hz), 32.91 (dd, J = 25.6, 2.1 Hz), 28.89 (s), 27.11 (s), 26.22 (d, J = 2.7 Hz), 17.33 (d, J = 2.4 Hz), 13.65 (s), 11.9 (s), 9.86 (t, J = 2.0 Hz) ppm. GC-MS: 353 (M^+-C_4H_9, 5.51), 253 (100). FTIR: 1665.19 (C=C) cm^{-1}. HRMS: Calcd for $C_{14}H_{27}F_2Sn$ (M^+-Bu): 353.1103. Found: 353.1086.

Preparation of (*Z*)-1,2-Difluoro-3,3-dimethyl-1-(tributylstannyl)-1-butene (*trans*-tert-BuCF=CFSnBu$_3$, 7a). Similarly, the reaction of (*Z*)-1,2-difluoro-3,3-dimethyl-1-(trimethylsilyl)-1-butene (9.6 g, 50 mmol), potassium fluoride (5.8 g, 100 mmol), and tributyltin chloride (16.3 g, 50.1 mmol) in DMF (30 mL) at 80 °C for 10 h afforded (*Z*)-1,2-difluoro-3,3-dimethyl-1-(tributylstannyl)-1-butene (16.2 g) as a colorless oil in 79% yield. ^{1}H NMR ($CDCl_3$): 1.53 (m, 6H), 1.32 (m, 6H), 1.21 (dd, J = 2.4, 1.6 Hz, 9H), 1.02 (m, 6H), 0.91 (t, J = 7.2 Hz, 9H) ppm. ^{19}F NMR ($CDCl_3$): −151.1 (d, $^3J_{FF}$ = 112.6 Hz, 1F), 164.0 (dd, $^3J_{FF}$ = 112.6 Hz, $^4J_{HF}$ = 2.0 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 168.5 (dd, J = 225.2, 26.5 Hz), 157.9 (dd, J = 299.7, 113.9 Hz), 35.54 (dd, J = 26.0, 1.9 Hz), 28.93 (s), 27.67 (dd, J = 4.8, 1.2 Hz), 27.18 (s), 13.68 (s), 9.93 (t, J = 2.2 Hz) ppm. GC-MS: 353 (M^+-C_4H_9, 8.43), 253 (100). FTIR: 1650.23 (C=C) cm^{-1}. HRMS: Calcd for $C_{14}H_{27}F_2Sn$ (M^+-Bu): 353.1103. Found: 353.1112.

Preparation of (*Z*)-1,2-Difluoro-3,3-dimethyl-1-(tributylstannyl)-1-butene (*trans*-*tert*-BuCF=CFSnBu$_3$, 7a) from the Corresponding Triethylsilane (7). Similarly, the reaction of (*Z*)-1,2-difluoro-3,3-dimethyl-1-(triethylsilyl)-1-butene (11.7 g, 50 mmol), potassium fluoride (5.8 g, 100 mmol), and tributyltin chloride (16.3 g, 50.1 mmol) in DMF (30 mL) at 80 °C for 24 h afforded (*Z*)-1,2-difluoro-3,3-dimethyl-1-(tributylstannyl)-1-butene (14.4 g) as a colorless oil in 71% yield.

Preparation of (*Z*)-1,2-Difluoro-1-(tributylstannyl)styrene (*trans*-PhCF=CFSnBu$_3$, 12a). Similarly, the reaction of (*Z*)-1,2-difluoro-1-(trimethylsilyl)styrene (4.24 g, 20 mmol), potassium fluoride (2.3 g, 40 mmol), and tributyltin chloride (7.8 g, 24 mmol) in DMF (15 mL) at room temperature for 24 h afforded (*Z*)-1,2-difluoro-1-(tributylstannyl)styrene (6.0 g) as a colorless oil in 70% yield. ^{1}H NMR ($CDCl_3$): 7.67(m, 2H), 7.34 (m, 3H), 1.58 (m, 6H), 1.35 (m, 6H), 1.14 (m, 6H), 0.91 (t, J = 7.2 Hz, 9H) ppm. ^{19}F NMR ($CDCl_3$): −154.2 (d, $^3J_{FF}$ = 113.1 Hz, 1F), −155.0 (d, $^3J_{FF}$ = 113.1 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 163.7 (d, J = 202.0 Hz), 159.5 (d, J = 187.4 Hz), 129.9 (d, J = 25.7 Hz), 128.5 (d, J = 1.8 Hz), 128.3 (d, J = 1.8Hz), 125.2 (dd, J = 9.5 Hz, J = 7.7 Hz), 28.88 (s), 27.17 (s), 13.65 (s), 10.14 (s) ppm. GC-MS: 373 (M^+-C_4H_9, 6.66), 253 (100). FTIR: 1628.61 (C=C), 1600.89 (Ar) cm^{-1}. HRMS: Calcd for $C_{16}H_{23}F_2Sn$ (M^+ − Bu): 373.0790. Found: 373.0790.

Preparation of (2,2-Difluorovinyl)tributylstannane (CF_2=CHSnBu$_3$, 15a). Similarly, the reaction of (2,2-difluorovinyl)triethylsilane (1.78 g, 10.0 mmol) with tributyltin chloride (3.3 g, 10.2 mmol) in the presence of anhydrous potassium fluoride (1.0 g, 17.3 mmol) in dry DMF (10 mL) gave 1.76 g of (2,2-difluorovinyl)tributylstannane in 50% yield. ^{1}H NMR ($CDCl_3$): 3.87 [dd, $^3J_{HF}$(trans) = 47.6 Hz, $^3J_{HF}$(cis) = 9.9 Hz, 1H], 1.49 (m, 6H), 1.32 (m, 6H), 0.97 (m, 6H), 0.89 (t, J = 8.0 Hz, 9H) ppm. ^{19}F NMR ($CDCl_3$): −61.23 [dd, $^2J_{FF}$ = 36.9 Hz, $^3J_{HF}$(cis) = 9.9 Hz, 1F], −73.40 [dd, $^3J_{HF}$(trans) = 47.6 Hz, $^2J_{FF}$ = 36.9 Hz, 1F] ppm. ^{13}C NMR ($CDCl_3$): 157.8 (dd, J = 311.6, 277.1 Hz), 63.74 (dd, J = 48.3, 14.4 Hz), 28.88 (s), 27.16 (s), 13.62 (s), 9.99 (s) ppm. GC-MS: 297 (M^+-C_4H_9, 48.44), 253 (100). FTIR: 1678.58 (C=C) cm^{-1}. HRMS: Calcd for $C_{10}H_{19}F_2$-Sn (M^+-Bu): 297.0477. Found: 297.0474.

Preparation of (*Z*)-1-Chloro-2-fluoro-1-(tributylstannyl)-1-hexene ((*Z*)-*n*-BuCF=CClSnBu$_3$, 16a). Similarly, reaction of (*Z*)-*n*-BuCF=CClSiMe$_3$ (4.2 g, 20 mmol) with tributyltin chloride (6.6 g, 20.3 mmol) in the presence of potassium fluoride (2.3 g, 40 mmol) in DMF (20 mL) at 80 °C for 12 h afforded the corresponding stannane (7.2 g) in 85% yield as a colorless liquid. ^{1}H NMR ($CDCl_3$): 2.51 (dt, $^3J_{HF}$ = 22.1 Hz, $^3J_{HH}$ = 7.2 Hz, 2H), 1.52 (m, 8H), 1.33 (m, 8H), 1.06 (m, 6H), 0.93 (t, J = 7.2 Hz, 3H), 0.90 (t, J = 7.3 Hz, 9H) ppm. ^{19}F NMR ($CDCl_3$): −94.29 (t, $^3J_{HF}$ = 22.1 Hz, 1F) ppm. ^{13}C NMR ($CDCl_3$): 168.3 (d, J = 240.4 Hz), 114.1 (d, J = 94.6 Hz), 28.80 (s), 28.46 (s), 28.08 (m), 27.18 (s), 22.00 (s), 13.78 (s), 13.66 (s), 10.67 (d, J = 1.2 Hz) ppm. GC-MS: 369 (M^+-C_4H_9, 4.70), 251 (100). FTIR: 1635.53 (C=C) cm^{-1}. HRMS: Calcd for $C_{14}H_{27}ClFSn$ (M^+-Bu): 369.0807. Found: 369.0772.

Preparation of (*Z*)-1-(Tributylstannyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (*trans*-CF_2=CFCF=CFSnBu$_3$, 13a) from (*Z*)-1-(Triethylsilyl)-1,2,3,4,4-pentafluorobutadiene (*trans*-CF_2=CFCF=CFSiEt$_3$, 13). Similarly, reaction of (*Z*)-1-(triethylsilyl)-1,2,3,4,4-pentafluorobutadiene (*trans*-CF_2=CFCF=CFSiEt$_3$, 19.5 g, 75.5 mmol) with tributyltin chloride (27.7 g, 85.0 mmol) in the presence of potassium fluoride (4.93 g, 85.0 mmol) in DMF (120 mL) at room temperature for 30 h afforded the corresponding stannane (24.5 g) in 75% yield. ^{1}H NMR ($CDCl_3$): 1.55 (m, 6H), 1.35 (m, 6H), 1.1 (m, 6H), 0.9 (t, J = 7.3 Hz, 9H) ppm. ^{19}F NMR ($CDCl_3$): −97.2 (dd, J = 53.3, 29.1 Hz, 1F), −108.6 (dddd, J = 115.0, 53.3, 19.3, 12.3 Hz, 1F), −142.2 (dm, J = 129.8 Hz, 1F), −160.9 (ddd, J = 129.8,

34.7, 12.3 Hz), −181.4 (dddd, J = 115.0, 34.7, 30.0, 10.7 Hz) ppm. ^{13}C NMR ($CDCl_3$): 167.7 (ddm, J = 323.0, 98.3 Hz), 153.4 (tdm, J = 288.2, 44.0 Hz), 149.3 (dm, J = 215.9 Hz), 118.8 (dm, J = 233.2 Hz), 28.8 (s), 27.2 (s), 13.5 (s), 10.3 (s) ppm. GC-MS: 377 (M^+-Bu, 4.12), 257 (15.53), 251 (100). FTIR: 2972 (s), 2907 (s), 1418 (w), 1359 (w) cm^{-1}.

Preparation of (*Z*)-1-(Tributylstannyl)-1,2,3,4,4-pentafluoro-1,3-butadiene (*trans*-CF_2=CFCF=$CFSnBu_3$, 13a) from (*Z*)-1-(Dimethylphenylsilyl)-1,2,3,4,4-pentafluorobutadiene (*trans*-CF_2=CFCF=$CFSiMe_2Ph$, 14). Similarly, reaction of (*Z*)-1-(dimethylphenylsilyl)-1,2,3,4,4-pentafluorobutadiene (*trans*-CF_2=CFCF=$CFSiMe_2Ph$, 21.0 g, 75.5 mmol) with tributyltin chloride (27.7 g, 85.0 mmol) in the presence of potassium fluoride (4.93 g, 85.0 mmol) in DMF (120 mL) at room temperature for 30 h afforded the corresponding stannane (22.6 g) in 69% yield.

Preparation of (*Z*)-1,2-Difluoro-1-(tributylstannyl)-1-alkenes Using Bis(tributyltin)oxide. Preparation of (*Z*)-1,2-Difluoro-1-(tributylstannyl)-1-propene (8a). General Procedure. A 100 mL, round-bottom flask equipped with a nitrogen tee, a condenser, and Teflon-coated magnetic stir bar was charged with dry DMF (25 mL), fresh dried potassium fluoride (0.18 g, 3.1 mmol), bis(tributyltin) oxide (9.0 g, 15.1 mmol), and (*Z*)-1,2-difluoro-1-(trimethylsilyl)-1-propene (4.5 g, 30 mmol). The mixture was stirred at 80 °C for about 12 h, and the starting silane had disappeared by ^{19}F NMR analysis. The reaction mixture was treated with water (50 mL) and extracted with ethyl ether (50 mL × 2). The ethereal phase was washed with water, dried, and concentrated. The residue was purified on silica gel column using hexane as eluant to afford (*Z*)-1,2-difluoro-1-(tributylstannyl)-1-propene as a colorless oil in 85% yield.

Preparation of (*Z*)-1,2-Difluoro-1-(tributylstannyl)-1-hexene (6a). Similarly, the reaction of (*Z*)-1,2-difluoro-1-(trimethylsilyl)-1-hexene (5.76 g, 30 mmol), potassium fluoride (0.26 g, 4.5 mmol), and bis(tributyltin) oxide (10.0 g, 16.8 mmol) in DMF (20 mL) at 80 °C for 20 h afforded (*Z*)-1,2-difluoro-1-(tributylstannyl)-1-hexene (11.0 g) as a colorless oil in 90% yield.

Preparation of (*Z*)-1,2-Difluoro-3-methyl-1-(tributylstannyl)-1-pentene (9a). Similarly, the reaction of (*Z*)-1,2-difluoro-3-methyl-1-(trimethylsilyl)-1-pentene (5.76 g, 30 mmol), potassium fluoride (0.18 g, 3.1 mmol), and bis(tributyltin) oxide (9.0 g, 15.1 mmol) in DMF (30 mL) at 80 °C for 10 h afforded 10.7 g (87% yield) of (*Z*)-1,2-difluoro-3-methyl-1-(tributylstannyl)-1-pentene as a colorless oil.

Preparation of (*Z*)-1,2-Difluoro-3,3-dimethyl-1-(tributylstannyl)-1-butene (7a). Similarly, the reaction of (*Z*)-1,2-difluoro-3,3-dimethyl-1-(trimethylsilyl)-1-butene (5.76 g, 30 mmol), potassium fluoride (0.18 g, 3.1 mmol), and tributyltin oxide (9.0 g, 15.1 mmol) in DMF (30 mL) at 80 °C for 10 h afforded (*Z*)-1,2-difluoro-3,3-dimethyl-1-(tributylstannyl)-1-butene (10.8 g) as a colorless oil in 88% yield.

Preparation of (*Z*)-1,2-Difluoro-1-(tributylstannyl)styrene (12a). Similarly, the reaction of (*Z*)-1,2-difluoro-1-(trimethylsilyl)styrene (4.24 g, 20 mmol), potassium fluoride (0.12 g, 2.1 mmol), and tributyltin oxide (6.0 g, 10.1 mmol) in DMF (20 mL) at 80 °C for 10 h afforded (*Z*)-1,2-difluoro-1-(tributylstannyl)styrene (6.78 g) as a colorless oil in 79% yield.

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