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The stereoselective synthesis of (*Z*)-HFC=CFZnI and stereospecific preparation of (*E*)-1,2-difluorostyrenes from (*Z*)-HFC=CFZnI *via* an unusual $Pd(PPh_3)_4$–Cu(I)Br co-catalysis approach or (*Z*)-HFC=$CFSnBu_3$

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(*E*)-1,2-Difluorostyrenes

ABSTRACT

(*Z*)-HFC=CFZnI was stereoselectively synthesized from activated zinc dust and (*Z*)-HFC=CFI that was synthesized from chlorotrifluoroethene in a sequential manner. Compared to (*E*)-HFC=CFZnI, (*Z*)-HFC=CFZnI was more challenging to prepare in terms of sluggish metallation and formation of by-products, and underwent slower and incomplete Negishi coupling with aryl iodides. In a modification of Negishi coupling, (*E*)-α,β-difluorostyrenes were stereospecifically prepared in good to excellent yields under mild conditions from aryl iodides and (*Z*)-HFC=CFZnI with the co-catalysis of $Pd(PPh_3)_4$/Cu(I)Br. Experimental investigation and mechanistic rationalization suggested that Cu(I)Br would be a scavenger of free ligands for the facilitation of $Pd(PPh_3)_2$ formation, and a supplier of ligand for the metathesis process. Alternatively, (*Z*)-HFC=$CFSnBu_3$ and aryl iodides with an electron-withdrawing group underwent Stille–Liebiskind coupling to afford (*E*)-α,β-difluorostyrenes.

1. Introduction

Fluorinated styrenes are useful building blocks in organofluorine chemistry and have found application as monomers [1], as precursors for anti-inflammatory [2] and antifertility [3] compounds, and as precursors for 1,4-diaryl-perfluoro-1,3-butadienes [4]. Several strategies have been utilized in the preparation of α,β-difluorostyrenes. α,β-Difluorostyrene has been prepared in low yield by dehalogenation of 1-chloro-1-phenyl-1,2,2-trifluoroethane [5]. The stereochemistry of the resultant styrene was not reported. Dehydrofluorination of 1-phenyl-1,1,2-trifluoroethane resulted in a low yield of α,β-difluorostyrene; this dehydrofluorination was not extended to other 1-aryl-1,1,2-trifluoroethanes [6]. Low temperature metallation of several isomeric α,β-difluoro-β-chlorostyrenes with an alkyllithium reagent, followed by hydrolysis, has been reported to give predominantly (*E*)-α,β-difluorostyrenes [7]. Protodesilylation of (*Z*)-1,2-difluoro-2-arylvinylsilanes by potassium fluoride in aqueous DMSO gave (*E*)-α,β-difluorostyrenes [8,9]. However, a general, stereoselective preparation of (*E*)-α,β-difluorostyrenes has not been reported.

Cuprous halide is well known as a co-catalyst in Stille–Liebiskind coupling with stannanes [10–12]. However, in the chemical literature, only one paper has been found that employs a cuprous salt to assist sluggish Negishi coupling with an organozinc reagent [13].

Previous reports from our laboratories have described a facile preparation of (*Z*)-α,β-difluorostyrenes *via* a $Pd(PPh_3)_4$ catalyzed cross-coupling of (*E*)-1,2-difluoroethenylzinc iodide with aryl iodides [14]. We now report in detail the stereoselective preparation of (*Z*)-HFC=CFZnI and the stereospecific synthesis of (*E*)-α,β-difluorostyrenes with (*Z*)-HFC=CFZnI under the co-catalysis of $Pd(PPh_3)_4$/Cu(I)Br in dry DMAC [15], and with (*Z*)-HFC=$CFSnBu_3$ under the co-catalysis of $Pd(PPh_3)_4$/Cu(I)I in DMF.

2. Results and discussion

2.1. Synthesis of isomerically pure (*Z*)-HFC=CFZnI (**2(Z)**) and a mixture of 94:6 (*Z*)/(*E*)-HFC=CFZnI (**2(Z)** and **2(E)**)

Isomerically pure (*Z*)-HFC=CFZnI (**2(Z)**) can be prepared by metallation of (*Z*)-HFC=CFI (**1(Z)**) with activated zinc dust in anhydrous dry DMAC (76% NMR yield) or DMF (<50% NMR yield), as illustrated in Fig. 1. Likewise, a 94:6 mixture of **2(Z)**/**2(E)** can be prepared from a 95:5 mixture of **1(Z)**/**1(E)**. Noticeably, the *Z*/*E* ratio of **2(Z)**/**2(E)** can decrease to as low as 85/15 when the solution was stored for extended time periods at ambient temperature.

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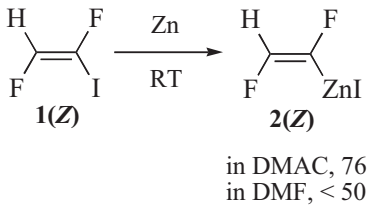


Fig. 1.

Unlike the facile conversion of **1(E)** to **2(E)** [14], the zinc metallation of **1(Z)** requires effectively activated zinc dust to secure initiation of the reaction and avoid incomplete reaction, suggesting the C–I bond in **1(Z)** is stronger than in **1(E)**. When DMF was employed as solvent, the zinc metallation of **1(Z)** afforded no more than 50% NMR yield of **2(Z)**, in addition to an unidentified by-product and the reduction product, (*E*)-HFC=CFH. A higher yield was obtained in dry DMAC (*N*,*N*-dimethylacetamide) solvent; however an unidentified by-product and the reduction product also accompanied the metallation. Although the by-product was not isolated and identified, it was believed to be generated from the addition reaction of a (*Z*)-1,2-difluoroethenyl intermediate and DMF or dry DMAC based on a report of a related case carried out in DMF solvent [16]. A lower amount of the by-product was generated in dry DMAC, presumably because the carbonyl carbon is less susceptible to nucleophilic attack in DMAC than in DMF.

As illustrated in Scheme 1, the fluorinated vinyl iodide, **1(Z)** can be stereoselectively prepared from chlorotrifluoroethene *via* the silyliodoethene, **5**, using Normant's method [17]. Treatment of a mixture of chlorotrifluoroethene and triethylsilyl chloride with butyllithium reagent and *in situ* trapping of trifluorovinyl lithium with triethylsilyl chloride gave the trifluorovinylsilane, **3**. Reduction of **3** with lithium aluminum hydride gave predominantly the *Z*-isomer of the 1,2-difluoroethenylsilane, **4**. Further deprotonation/iodination of **4** at −100 °C gave the silyliodoethene, **5** in an excellent isolated yield. **4(E)** decomposed upon lithiation, presumably *via* LiF elimination. **5** Was converted to the vinyl iodide **1(Z)** *via* protodesilylation in DMF at ambient temperature.

In a shorter route, a 95:5 isomeric mixture of **1(Z)**/**1(E)** was prepared from **4**, KF and iodine in DMF (Scheme 1).

In an exploratory reaction, as outlined in Fig. 2, we demonstrated that **2(Z)** was capable of undergoing an S_N2 reaction with allyl chloride in DMF to form the pentadiene, **7**. The reaction could be effectively accelerated by the mediation of Cu(I)Br.

2.2. Attempted preparation of (*E*)-1,2-difluorostyrenes (8(E)) from a 94:6 isomeric mixture of 2(Z)/2(E)

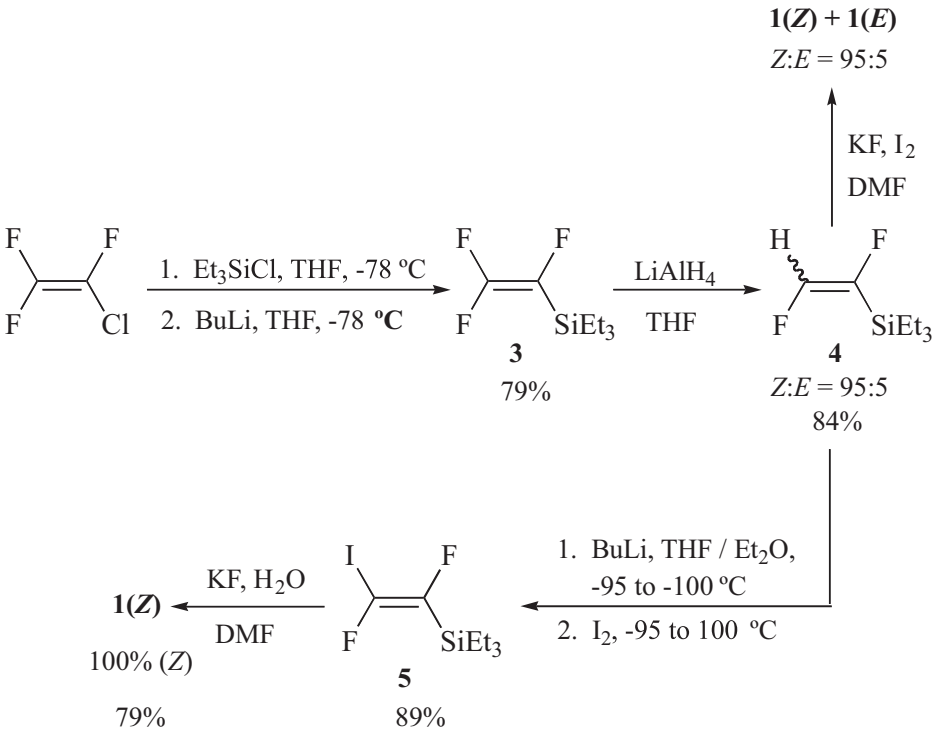
Previous work from our laboratory had established a facile approach to the stereoselective synthesis of (*Z*)-1,2-difluorostyrenes, **8(Z)**, using a 95:5 isomeric mixture of **2(E)** and **2(Z)** (Fig. 3) [14]. When we attempted to employ a 94:6 mixture of **2(Z)**/**2(E)** in a similar fashion to prepare an **8(E)**/**8(Z)** mixture, we discovered an interesting difference.

Unlike the facile preparation of **8(Z)** from a 95:5 mixture of **2(E)**/**2(Z)** (Fig. 3), the coupling reaction of 94:6 **2(Z)**/**2(E)** with aryl iodides (Fig. 4) resulted in a dilemma of incomplete reaction and shift of stereochemistry to a lower (*E*)/(*Z*) ratio in the coupling product even at elevated temperatures and after prolonged reaction time. Technically, the synthesis was challenging because **8(E)** could not be separated from the unreacted aryl iodide due to their similarity in affinity to chromatographic silica gel, and boiling points.

It is not clear why the (*E*)-isomer isomerizes so rapidly to the (*Z*)-isomer in this case. When we attempted to equilibrate the (*E*)/(*Z*) styrenes with Ph_2S_2 [18], we only obtained polymerization of the styrenes [19]; thus we could not determine the relative stabilities of the styrene isomers. Leroy obtained similar results [6].

2.3. Stereospecific preparation of 8(E) from 2(Z)

Concerning the isomerization of **8(E)** to **8(Z)**, we attempted a stereospecific preparation **8(E)** using Negishi cross-coupling of



Scheme 1. Preparation of **1(Z)** and 95:5 **1(Z)**/**1(E)** mixture from CF_2=CFC1.

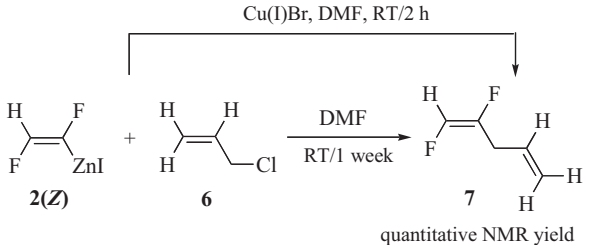


Fig. 2.

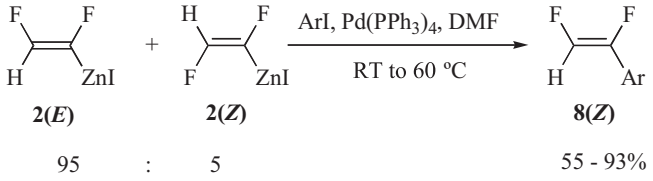
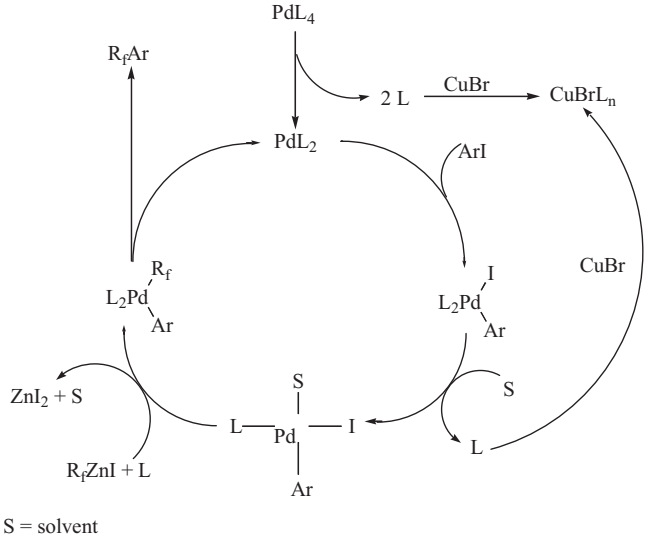


Fig. 3.



Scheme 2. Proposed mechanism of Pd–Cu(I)Br co-catalyzed coupling of **2(Z)** with ArI.

2(Z) with aryl iodides under the catalysis of $Pd(PPh_3)_4$ in DMF; however, an incomplete reaction mixture was obtained. To overcome the sluggish metathesis process as mentioned in the mechanism discussion (Scheme 2), we introduced Cu(I)Br to the reaction system. We were delighted with the results: a series of **8(E)** compounds were readily synthesized in excellent isolated yields in less than 6 h, at ambient temperature to 40 °C, under $Pd(PPh_3)_4$ catalysis and Cu(I)Br mediation (Table 1) in DMAC as the solvent.

The rate of the Cu(I)Br-mediated Negishi coupling depends on the type and position of the substituent on the aromatic ring. In general, an aryl iodide with an electron-withdrawing group underwent faster reaction than an aryl iodide with an electron-releasing group.

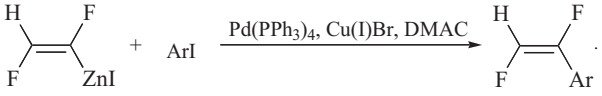
2.4. Analysis of the role of Cu(I)Br in the formation of 8(E)

To determine if Cu(I)Br would convert **2(Z)** to (*Z*)-HFC=CFCu and thus accelerate the sluggish coupling reaction with a more nucleophilic organocopper(I) reagent, we attempted to perform the cross-coupling reaction stepwise, (1) react **2(Z)** with Cu(I)Br in solventand (2) conduct the reaction using the mixture, aryl iodide and $Pd(PPh_3)_4$. Unfortunately, the reaction mixture for the first step showed faint ^{19}F NMR signals, suggesting decomposition or side reactions from the fluorinated organometallic upon treatment with Cu(I)Br.

As outlined in Fig. 5, the role of Cu(I)Br in Negishi coupling was alternatively investigated with a similar organozinc reagent, CF_2=CFZnBr, **9**; CF_2=CFCu is known to be stable. Surprisingly, in the presence of Cu(I)Br, the Pd-catalyzed cross-coupling of **9** with PhI yielded a reaction mixture containing the styrene **10** in only 33% NMR yield along with 30% NMR yield of the vinylcopper reagent, **11**. After an elongated reaction time of 10 h, the vinylcopper reagent, **11**, showed no reaction with the unreacted PhI. On the other hand, without Cu(I)Br, **9** coupled with iodobenzene in the presence of $Pd(PPh_3)_4$ to give **10** in an excellent isolated yield (Fig. 6). These observations encouraged us to look into an alternative mechanistic possibility for the Cu(I)Br effect.

The role of the cuprous salt is suggested to be a scavenger of free ligands, similar to the proposal by Farina et al. [10]. Scheme 2 illustrates the suggested mechanistic proposal for this rare cuprous salt modified Negishi coupling. $Pd(PPh_3)_4$ undergoes ligand dissociation to give the active Pd(0) complex, $Pd(PPh_3)_2$. This step may be accelerated with the removal of free ligands from the

Table 1
Preparation of (*E*)-l,2-difluorostyrenes (**8(E)**).



Entry	ArI	Product	Yield[a] (%)
1	*p*-FC_6H_4–I	*p*-FC_6H_4CF=CFH (**8(E)-1**)	89
2	*p*-ClC_6H_4–I	*p*-ClC_6H_4CF=CFH (**8(E)-2**)	95
3	*p*-BrC_6H_4–I	*p*-BrC_6H_4CF=CFH (**8(E)-3**)	94
4	*p*-IC_6H_4–I	*p*-$C_6H_4(CF=CFH)_2$ (**8(E)-4**)	92
5	C_6H_5–I	C_6H_5CF=CFH (**8(E)-5**)	74[b]
6	*p*-$MeOC_6H_4$–I	*p*-$MeOC_6H_4CF$=CFH (**8(E)-6**)	94
7	*m*-$CF_3C_6H_4$–I	*m*-$CF_3C_6H_4CF$=CFH (**8(E)-7**)	84
8	1-$C_{10}H_7$–I	l-NaphthylCF=CFH (**8(E)-8**)	87
9	*m*-$NO_2C_6H_4$–I	*m*-$NO_2C_6H_4CF$=CFH (**8(E)-9**)	93
10	*p*-$NO_2C_6H_4$–I	*p*-$NO_2C_6H_4CF$=CFH (**8(E)-10**	87
11	2-Thiophenyl-I	2-ThiopheneCF=CFH (**8(E)-11**)	73

[a] Isolated yield of (*E*)-isomer only.
[b] Without Cu(I)Br, the reaction took 6 h at 50 °C, the product was isolated in a yield of 41%, GLPC purity = 95%.

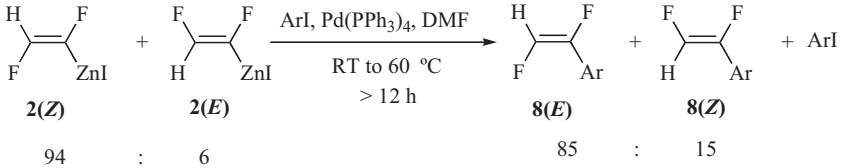


Fig. 4.

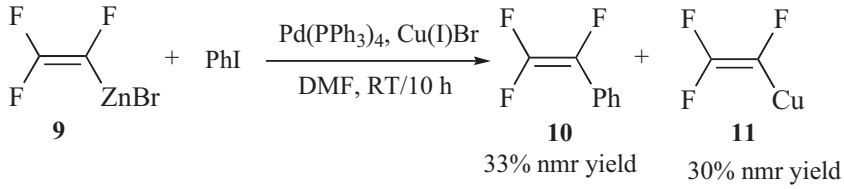


Fig. 5.

Fig. 6.

reaction mixture *via* the formation of Cu(I)BrL_n complex. Oxidative addition of ArI to $Pd(PPh_3)_2$ gives $ArIPd(PPh_3)_2$. One of the two PPh_3 ligands in $ArIPd(PPh_3)_2$ may be replaced by a solvent molecule to create a susceptible site for a nucleophilic displacement with the presumably weaker nucleophile, **2(Z)**. The free ligand generated here may again be scavenged by Cu(I)Br. Further transmetallation of $ArIPd(S)(PPh_3)$ (*note*: S = solvent) with **2(Z)** followed by ligand displacement gives $ArR_fPd(PPh_3)_2$. Eventual reductive elimination in $ArR_fPd(PPh_3)_2$ affords the cross-coupling product, **8(E)**, and regenerates the active Pd(0) complex, $Pd(PPh_3)_2$ for the next catalytic coupling cycle.

2.5. Stereoselective synthesis of (Z)-HFC=CFSnBu$_3$ (12(Z)) from CF_2=CFCl

(*Z*)-HFC=CFSnBu_3 (**12(Z)**) has been stereoselectively synthesized sequentially from CF_2=CFCl [20]. As illustrated in Scheme 3, butyl lithium underwent chlorine–lithium exchange to generate [CF_2=CFLi] at low temperature, which was *in situ* trapped with Me_3SiCl to give **13**. Me_3SiCl was used as the limiting reagent to avoid contaminants with close boiling points in the product, while CF_2=CFCl and the by-product CF_2=CFH are gases at room temperature. The vinylsilane **13** was isolated with THF by flash distillation, and used in the next step without further purification.

Reduction of **13** in THF with $LiAlH_4$ afforded the vinylsilanes **14(Z)** and **14(E)** in the ratio of 91:9, hence sets a foundation for further introduction of the *trans*-1,2-difluoroethenyl unit into organic molecules.

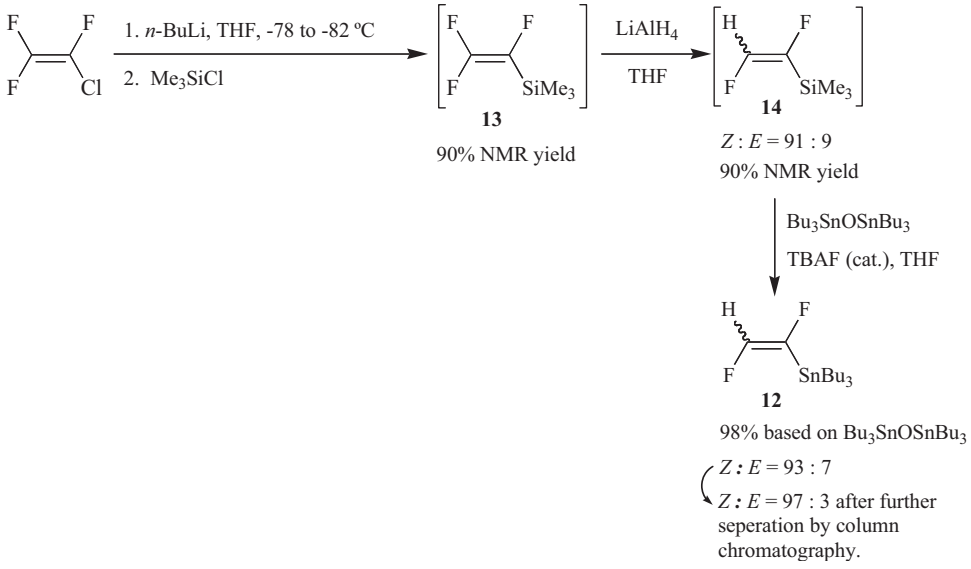
The mono-stannane **12** was synthesized from **14** and bis(-tributyltin) oxide under the catalysis of TBAF in nearly quantitative isolated yield. A flash chromatographic purification increased the ratio of *Z/E* isomers possibly due to decomposition of **12(E)**.

The mono-stannane **12(Z)** could be alternatively prepared using tributyltin chloride (Fig. 7).

2.6. Pd-catalyzed couplings of (Z)-HFC=CFSnBu$_3$ (12(Z)) with aryl iodides

As summarized in Table 2, **12(Z)** has also been utilized for the preparation of **8(E)**. In general, the cross-coupling of aryl iodides with **12(Z)** are slower than those with **2(Z)**; **12(Z)** behaved as a less nucleophilic reagent for transmetallation than **2(Z)**. For example, *para*-bromoiodobenzene underwent cross-coupling at RT with **2(Z)** in 1 h, whereas **12(Z)** required 3 h at 70 °C for cross-coupling of the same aryl iodide. In the Stille–Liebeskind coupling reaction between **12(Z)** and aryl iodides, those aryl iodides with electron-releasing groups (e.g., methyl or methoxy) were not completely consumed, even under forced conditions. As a consequence, the cross-coupling product could not be obtained pure due to the lack of inefficient separation from the un-reacted aryl iodide. On the other hand, aryl iodides containing electron-withdrawing groups coupled readily with **12(Z)**.

The advantages of **12(Z)** over **2(Z)** are two-fold. (1) **12(Z)** is far more stable due to its greater moisture stability than **2(Z)**. Thus, **12(Z)** does not need to be used in excess; whereas **2(Z)**



Scheme 3. Stereoselective synthesis of **12(Z)** from CF_2=CFC1.

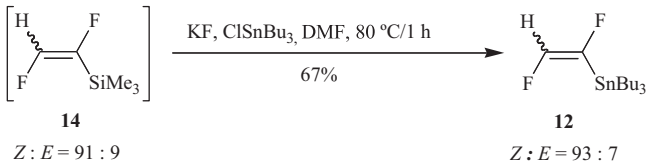
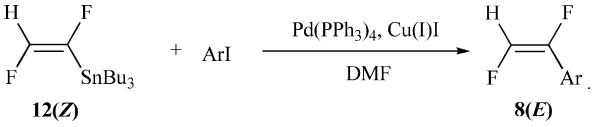


Fig. 7.

Table 2
$Pd(PPh_3)_4$-catalyzed cross-couplings of (*Z*)-l,2-difluoroethenyltributylstannane with aryl iodides.



Entry	ArI	Conditions	Products	Isolated yield
1	3-ClC_6H_4I	RT/1 h	**8(E)-12**	82%
2	4-CNC_6H_4I	RT/1 h	**8(E)-13**	83%
3	4-BrC_6H_4I	70 °C/3 h	**8(E)-3**	92%
4	2-Pyridyl-I	RT/1 h	**8(E)-14**	21%[a]
5	3-MeC_6H_4I	RT/3 days	**8(E)-15**	N.A[b]
6	4-$MeOC_6H_4I$	60 °C/18 h	**8(E)-6**	N.A[b]

[a] Unstable product quickly decomposed at room temperature.
[b] Incomplete reaction (NMR yield was less than 60%), product was isolated together with the unreacted aryl iodide.

was used in excess. (2) **12(Z)** is easier to prepare in terms of a shorter synthetic route, and easier to store, due to its moisture stability than **2(Z)**.

Except for the relatively low reactivity, the most awkward drawback of the tin reagent, **12(Z)** is the toxicity of both **12(Z)** and its by-product, Bu_3SnI. It can be difficult to remove Bu_3SnI from the coupling product. On the other hand, the zinc reagent, **2(Z)** is not toxic, and its by-product, ZnI_2 is easy to separate from the styrene product.

2.7. NMR characteristics of 8(E)

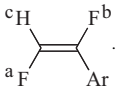
Selective ^{19}F NMR chemical shifts and coupling constants data of **8(E)** are summarized in Table 3. Generally, the chemical shift of the vinyl fluorine varies in a narrow range, with the exception of the naphthyl (entry 8), 4-nitrophenyl (entry 10), 2-thiophenyl (entry 11), 4-cyanophenyl (entry 13), and 2-pyridyl derivatives (entry 14). The variation in chemical shift is affected by the anisotropic effect from the aromatic ring.

In general, F_a shifts downfield relative to the $CFCl_3$ internal reference when an electron-withdrawing group is attached to the aromatic ring; upfield when the aromatic ring is substituted with an electron-releasing group. Interestingly, except for **8(E)-8**, **8(E)-10**, **8(E)-11**, **8(E)-13**, **8(E)-14**, the chemical shift of F_b is nearly independent of the substituent group. On the other hand, coupling constants between the vinyl fluorines or between the vinyl proton and the vinyl fluorine showed almost no variation with the exception of **8(E)-8**, **8(E)-10**, **8(E)-11**, **8(E)-13**, **8(E)-14**.

The ^{19}F NMR of **8(E)-10** (entry 10) and **8(E)-13** (entry 13) appeared as second-order spectra. The $\{^1H\}^{19}F$ NMR of **8(E)-10** revealed a singlet peak at −167.1 ppm, indicating the two fluorines occurred to have identical chemical shift owing to the electron-withdrawing effect from the *para*-nitro group. The $\{^1H\}^{19}F$ NMR of **8(E)-13** showed two adjacent singlet peaks at −167.8 ppm and −168.2 ppm. Thus, instead of AXY spin systems like the other examples (entries 1–9, 11, and 12), **8(E)-10** and **8(E)-13** behaved like an AXX' spin system.

Table 4 summarizes the carbon/fluorine coupling constants on the vinyl carbons and the most adjacent aromatic carbon. Generally, the magnitude of $^1J_{FC}$ are consistent with slight variation among the benzene-based derivatives, between 248 Hz and 254 Hz for $^1J_{FCa}$; 228 Hz and 229 Hz for $^1J_{FCb}$. Except for **8(E)-8** and **8(E)-11** of different aromatic systems, and **8(E)-9** and **8(E)-10** with nitro substituents, the $^2J_{FC}$ fall into a narrow range, $^2J_{FCa}$ = 71–74 Hz; $^2J_{FCb}$ = 30–32 Hz. The values of $^3J_{FCc}$ and $^2J_{FCc}$ are stabilized in a narrow range. Both **8(E)-10** and **8(E)-13** have second-order spectrum coupling patterns in the vinyl carbon. **8(E)-14**, a 2-pyridyl system showed substantial differences in both chemical shift and coupling constant. In general, $^1J_{FCa} \sim 250$ Hz, $^2J_{FCa} \sim 70$ Hz, $^2J_{FCb} \sim 31$ Hz, $^1J_{FCb} \sim 230$ Hz, $^3J_{FCc} \sim 6$ Hz, $^2J_{FCc} \sim 25$ Hz.

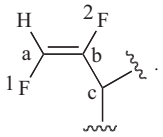
Table 3
^{19}F NMR data of (*E*)-l,2-difluorostyrenes (**8(E)**).



Entry	8(E)	δ_{F_a} (ppm)	δ_{F_b} (ppm)	$^3J_{F_aF_b}$	$^2J_{HcF_b}$	$^3J_{F_bHc}$
1	*p*7FC_6H_4CF=CFH (**8(E)-1**)	−175.0	−166.3	125	75	5
2	*p*-ClC_6H_4CF=CFH **8(E)-2**)	−172.7	−167.0	126	75	5
3	*p*BrC_6H_4CF=CFH **8(E)-3**)	−172.46	−167.1	125	75	5
4	*p*$C_6H_4(CF{=}CFH)_2$ (**8(E)-4**)	−172.0	−167.8	125	75	5
5	C_6H_5CF=CFH (**8(E)-5**)	−174.1	−166.9	125	76	5
6	*p*-$MeOC_6H_4CF$=CFH (**8(E)-6**)	−177.3	−166.3	125	76	5
7	m$CF_3C_6H_4CF$=CFH (**8(E)-7**)	−171.6	−167.6	125	75	5
8	1-NaphthylCF=CFH (**8(E)-8**)	−174.2	−147.8	137	76	0
9	*m*-$NO_2C_6H_4CF$=CFH (**8(E)-9**)	−169.6	−167.1	126	74	5
10	*p*-$NO_2C_6H_4CF$=CFH (**8(E)-10**)	ND	ND	ND	ND	ND
11	2-ThiophenylCF=CFH (**8(E)-11**)	−172.3	−161.1	125	75	0
12	*m*-$C_1C_6H_4CF$=CFH (**8(E)-12**)	−171.9	−167.2	125	75	5
13	*p*-CNC_6H_4CF=CFH (**8(E)-13**)	−168.2 or −167.8	−168.2 or −167.8	125	ND[a]	ND[a]
14	2-PyridylCF=CFH (**8(E)-14**)	−169.2	−169.9	127	67	13

[a] ND, not determined, because the spectrum is second-order.

Table 4
J_{CF} (Hz) in the $\{^1H\}^{13}C$ NMR spectra of (*E*)-l,2-difluorostyrenes (**8(E)**).



Entry	8(E)	$^1J_{CaF1}$	$^2J_{CaF2}$	$^2J_{CbF1}$	$^1J_{CbF2}$	$^3J_{CcF1}$	$^2J_{CcF2}$
1	*p*-FC_6H4CF=CFH (**8(E)-1**)	250	73	32	229	6	25
2	*p*-ClC_6H_4CF=CFH (**8(E)-2**)	252	72	31	228	6	25
3	*p*-BrC_6H_4CF=CFH (**8(E-2**)	252	72	31	229	6	25
4	*p*-$C_6H_4(CF=CFH)_2$ (**8(E)-4**)	253	72	30	229	7	25
5	C_6H_5CF=CFH (8(**E**)-5)	251	73	31	229	6	24
6	*p*-$MeOC_6H4CF$=CFH (**8(E)-6**)	248	74	32	228	6	25
7	*m*-$CF_3C_6H_4CF$=CFH (**8(E)-7**)	253	71	30	229	6	25
8	1-NaphthaleneCF=CFH (**8(E)-8**)	246	71	37	237	4	22
9	*m*-$NO_2C_6H_4CF$=CFH (**8(E)-9**)	254	69	29	228	6	26
10	*p*-NO_2C_6H4CF=CFH (**8(E)-10**)	ND	ND	ND	ND	6	11
11	2-ThiopheneCF=CFH (**8(E)-11**)	250	68	37	228	8	29
12	*m*-ClC_6H_4CF=CFH (**8(E)-12**)	253	72	31	228	6	25
13	*p*-CNC_4H_4CF=CFH (**8(E)-13**)	ND	ND	ND	ND	ND	ND
14	2-PyridylCF=CFH (**8(E)-14**)	196 or ND	5 or ND	5 or ND	196 or ND	3	20

ND: not determined, because the spectrum is second-order (a novel virtual coupling pattern). This unique virtual coupling will be presented elsewhere.

3. Conclusion

(*Z*)-HFC=CFZnI was sequentially synthesized from CF_2=CFCl *via* (*Z*)-HFC=CFI. (*Z*)-HFC=CFZnI showed substantially lower reactivity than (*E*)-HFC=CFZnI in cross-coupling reactions with aryl iodides under catalysis of $Pd(PPh_3)_4$; and the slow cross-coupling resulted in isomerization in the styrene product. Consequently, we required Cu(I)Br co-catalysis to facilitate the reaction and avoid E/Z isomerization of the difluorostyrene. The role of Cu(I)Br in the unusual Cu(I)Br/Pd(0) co-catalysis in organozinc cross-coupling reaction was suggested as a ligand scavenger to accelerate ligand dissociation, as well as to compensate free ligands in metathesis where free ligands were needed. A series of (*E*)-α,β-difluorostyrenes were stereospecifically prepared in excellent isolated yields from isomerically pure (*Z*)-HFC=CFZnI under the co-catalysis of $Pd(PPh_3)_4$/Cu(I)Br. (*Z*)-HFC=$CFSnBu_3$ also coupled with aryl iodides containing an electron-withdrawing group under the co-catalysis of $Pd(PPh_3)_4$/Cu(I)I to afford (*E*)-α,β-difluorostyrenes in good yields.

4. Experimental

4.1. General experimental procedures

All glassware was oven-dried prior to use. ^{19}F NMR (282.44 MHz), ^1H NMR (300.17 MHz) and $\{^1H\}^{13}C$ NMR (75.48 MHz) spectra were recorded on an AC-300 spectrometer in $CDCl_3$ solvent. The chemical shifts are reported in parts per million downfield to the TMS internal standard for ^1H NMR and $\{^1H\}^{13}C$ NMR. The chemical shifts are reported in parts per million upfield to the $CFCl_3$ internal standard for ^{19}F NMR. FTIR spectra were recorded as CCl_4 solutions and reported in wavenumbers (cm^{-1}). Low resolution GC–MS spectra were obtained at 70 eV in the electron-impact mode on a TRIO-1-GC–MS instrument. GLPC analysis were performed on a 5% OV-101 on Chromosorb P column with a thermal conductivity detector. High-resolution mass spectral determinations were made at the University of Iowa High Resolution Mass Spectrometry Facility. All reactions were carried out under an atmosphere of nitrogen. DMAC (CaH_2) and DMF (CaH_2) were distilled at reduced pressure. THF was dried by distillation from sodium benzophenone ketyl at ambient pressure. Zinc (325 mesh, Aldrich) was activated by washing with dilute HCl and then dried *in vacuo* at room temperature. Cu(I)Br was treated with aqueous HBr (48%), precipitated with excess cold water, washed with water, acetone, and ether, and then dried *in vacuo*. Cu(I)I was purified by dissolution–precipitation process in water using NaI or KI [21]. $Pd(PPh_3)_4$ was prepared by Coulson's procedure [22]. CF_2=$CFSiEt_3$ [23] was prepared by a modification of the literature procedure from CF_2=CFCl, BuLi, Et_3SiCl in THF. CHF=$CFSiEt_3$ (*Z*:*E* = 95:5) [18] and (*E*)-IFC=$CFSiEt_3$ [17] were prepared by the literature procedures. All reagents were obtained from common commercial sources.

4.2. Preparation of (Z)-HFC=CFI (1(Z))

A two-neck 1-l round bottom flask equipped with a Teflon-coated stir bar, dry ice/isopropanol condenser and rubber septum, was charged with dry DMF (300 ml), (*E*)-1,2-difluoro-2-iodo-1-triethylsilylethene (92.1 g, purity 95%, 288 mmol), and KF (18.2 g, 314 mmol). Water (5.2 g, 289 mmol) was then gradually introduced into the solution *via* a syringe over 5 min. A mild exothermic reaction was observed. The reaction mixture was stirred at room temperature for 0.5 h, then subjected to flash distillation at RT/1 mmHg, and the distillate was trapped in a liquid nitrogen cooled flask. The resultant colorless distillate was dried over 5 g of P_2O_5 and distilled by flash distillation RT/1 mmHg. Further fractional distillation of the distillate through a 10 cm Vigreux column yielded 42.7 g (79%) of a colorless liquid, GLPC purity = 100%, bp = 44–45 °C. ^{19}F NMR: δ −132.1 (d, $^3J_{FF}$ = 145 Hz), −158.8 (dd, $^3J_{FF}$ = 145 Hz, $^2J_{HF}$ = 76 Hz). ^1H NMR: δ 7.5 (dd, $^2J_{HF}$ = 76 Hz, 1 Hz). ^{13}C NMR: δ 146.3 (dd, $^1J_{CF}$ = 248 Hz, $^2J_{CF}$ = 56 Hz), 104.2 (dd, $^1J_{CF}$ = 315 Hz, $^2J_{CF}$ = 57 Hz). GC–MS, *m*/*z* (relative intensity): 190 (M^+, 100), 127 (49), 63 (76). HRMS calcd for C_2HF_2I 189.9090, obsd. 189.9106.

Literature data [17]: ^{19}F NMR (d, $CDCl_3$ as solvent, $C_6H_5CF_3$ as internal standard): δ −68.9 (d, *J* = 145 Hz), −95.7 (dd, *J* = 145, 76.3 Hz); ^1H NMR: δ 7.45 (dd, *J* = 76.4, 0.9 Hz); ^{13}C NMR: δ 104.1 (dd, *J* = 314.9, 56.4 Hz), 146.3 (dd, *J* = 247, 56.4 Hz).

4.3. Preparation of (Z)-HFC=CFZnI (2(Z))

A two-neck 500-ml round bottom flask equipped with a Teflon-coated stir bar, a dry ice/isopropanol condenser attached to a nitrogen source and a rubber septum, was charged with 190 ml of

dry DMAC, 30 g (461 mmol) of acid-washed zinc dust and 39.9 g (209.8 mmol) of (*Z*)-1,2-difluoroiodoethene (**1(Z)**). After the reaction mixture had been stirred for 0.5 h, a strong exothermic reaction was observed. The solution was then stirred for an additional 1.5 h. Analysis of the ^{19}F NMR spectrum of the reaction mixture indicated complete consumption of **1(Z)**. The ^{19}F NMR yield ($C_6H_5CF_3$ as the internal standard) of **2(Z)** was 76%. ^{19}F NMR: δ (DMAC) −172.3 (dd, $^3J_{FF}$ = 104 Hz, $^3J_{HF}$ = 12 Hz, 1 F), −184.5 (dd, $^3J_{FF}$ = 104 Hz, $^2J_{HF}$ = 87 Hz, 1 F).

If the reaction could not be initiated after stirring the reaction mixture for a number of hours, it is our experience that the initiation may be accomplished by following the next two steps: (1) Stop stirring until a brown material appears on the surface of the zinc metal, and then (2) restart stirring. This process can normally help initiate the metallation.

4.4. General procedure for the preparation of (*E*)-α,β-difluorostyrenes (8(E)) from (*Z*)-HFC=CFZnI (2(Z))

A two-neck 50-ml round bottom flask equipped with a Teflon-coated stir bar, a cold water condenser attached to a nitrogen source and a septum, was charged with the aryl iodide (7.4 mmol, 99% purity), $Pd(PPh_3)_4$ (0.5 g, 0.4 mmol, 6 mol%), Cu(I)Br (1 g, 7 mmol) and **2(Z)** (19 ml, 11.4 mmol, 0.60 M) in dry DMAC. The reaction mixture was stirred at room temperature for 1 h. ^{19}F NMR analysis of the reaction mixture showed the formation of **8(E)**; GC–MS of a pre-chromatographed reaction mixture showed the complete disappearance of the aryl iodide. The dark reaction mixture was poured directly onto a silica gel column and eluted with pentane. Eluents with similar UV-active TLC spots were combined and the majority of the pentane was removed by simple distillation. Removal of the remaining trace amount of solvent at −35 °C/1 mmHg yielded **8(E)**.

4.4.1. (*E*)-*p*-FC_6H_4CF=CFH (8(E)-1)

Similarly, a mixture of 4-fluoroiodobenzene (2.12 g, 9.54 mmol), 10 ml of dry DMAC, $Pd(PPh_3)_4$ (0.5 g, 0.4 mmol, 5 mol%), **2(Z)** (6.25 ml, 15 mmol, 2.4 M, 1.5 eq.) in dry DMAC, and Cu(I)Br (1.4 g, 9.8 mmol) was stirred at 45 °C for 3 h. After silica gel column chromatography (pentane, R_f = 0.46), removal of the solvent gave 1.39 g (89%) of a colorless liquid, GLPC purity: 96%. ^{19}F NMR: δ −111.1 (t, $^3J_{HF}$ = 5 Hz, 1 F), −166.3 (dd, $^3J_{FF}$ = 125 Hz, $^3J_{HF}$ = 5 Hz, 1 F), −175.0 (dd, $^3J_{FF}$ = 125 Hz, $^2J_{HF}$ = 75 Hz, 1 F). ^{1}H NMR: δ 7.6 (ddm, $^3J_{HH}$ = 9 Hz, $^3J_{HF}$ = 5 Hz, 2 H), 7.3 (dd, $^2J_{HF}$ = 75 Hz, $^3J_{HF}$ = 5 Hz, 1 H), 7.0 (dm, $^3J_{HH}$ = 9 Hz, 2 H). ^{13}C NMR: δ 163.3 (dd, $^1J_{CF}$ = 250 Hz, $^5J_{CF}$ = 3 Hz), 151.4 (ddd, $^1J_{CF}$ = 229 Hz, $^2J_{CF}$ = 32 Hz, $^5J_{CF}$ = 1 Hz), 140.8 (ddd, $^1J_{CF}$ = 250 Hz, $^2J_{CF}$ = 73 Hz, $^6J_{CF}$ = 2 Hz), 127.6 (dd, $^3J_{CF}$ = 16 Hz, $^3J_{CF}$ = 8 Hz), 125.5 (ddd, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 6 Hz, $^4J_{CF}$ = 3 Hz), 115.9 (dd, $^2J_{CF}$ = 22 Hz, $^4J_{CF}$ = 2 Hz). GC–MS, *m*/*z* (relative intensity): 158 (M^+, 93), 157 (100), 138 (28), 127 (25), 107 (47). FTIR (CCl_4, cm^{-1}): 1607 (m), 1512 (s), 1370 (m), 1352 (m), 1240 (s), 1160 (m), 1148 (vs), 1102 (m). HRMS calcd for $C_8H_5F_3$ 158.0343, obsd. 158.0345.

4.4.2. (*E*)-*p*-ClC_6H_4CF=CFH (8(E)-2)

Similarly, a mixture of 4-chloroiodobenzene (1.79 g, 7.43 mmol, 99%), $Pd(PPh_3)_4$ (0.5 g, 0.5 mmol, 6 mol%), **2(Z)** (19 ml, 11.4 mmol, 0.60 M, 1.5 eq.) in dry DMAC, and Cu(I)Br (1 g, 7 mmol) was stirred at room temperature for 1 h. After silica gel column chromatography (pentane, R_f = 0.57), removal of the solvent gave 1.23 g (95%) of a colorless liquid, GLPC purity > 99%. ^{19}F NMR: δ −167.0 (dd, $^3J_{FF}$ = 126 Hz, $^3J_{HF}$ = 5 Hz, 1 F), −172.7 (dd, $^3J_{FF}$ = 126 Hz, $^2J_{HF}$ = 75 Hz, 1 F). ^{1}H NMR: δ 7.5–7.1 (m, 5 H). ^{13}C NMR: δ 151.4 (dd, $^1J_{CF}$ = 228 Hz, $^2J_{CF}$ = 31 Hz), 141.3 (dd, $^1J_{CF}$ = 252 Hz, $^2J_{CF}$ = 72 Hz), 135.6 (d, $^5J_{CF}$ = 3 Hz), 129.1 (s), 127.7 (dd, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 6 Hz), 126.7 (dd as t, $^3J_{CF}$ and $^4J_{CF}$ = 8 Hz). GC–MS, *m*/*z* (relative intensity): 174 (M^+, 100), 139 (27), 119 (40). FTIR (CCl_4, cm^{-1}): 1598 (m), 1494 (s), 1399 (m), 1354 (m), 1151 (vs), 1121 (m), 1107 (s), 1098 (m). HRMS calcd for $C_8H_5{}^{35}ClF_2$ 174.0048, obsd. 174.0049.

4.4.3. (*E*)-*p*-BrC_6H_4CF=CFH (8(E)-3)

Similarly, a mixture of 4-bromoiodobenzene (1.72 g, 5.96 mmol, 98%), $Pd(PPhh_3)_4$ (0.3 g, 0.3 mmol, 4 mol%), **2(Z)** (60 ml, 9 mmol, 0.15 M, 1.5 eq.) in dry DMAC, and Cu(I)Br (1 g, 7 mmol) was stirred at room temperature for 1 h. After silica gel column chromatography (pentane, R_f = 0.56), removal of the solvent gave 1.22 g (94%) of a colorless liquid, GLPC purity > 99%. ^{19}F NMR: δ −167.1 (dd, $^3J_{FF}$ = 125 Hz, $^3J_{HF}$ = 5 Hz, 1 F), −172.4 (dd, $^3J_{FF}$ = 125 Hz, $^2J_{HF}$ = 75 Hz, 1 F). ^{1}H NMR: δ 7.5 (d, distorted, $^3J_{HH}$ = 9 Hz, 2 H), 7.4 (d, distorted, partially overlapping with peak at 7.3 ppm, $^3J_{HH}$ = 9 Hz, 2 H), 7.3 (dd, partially overlapping with peak at δ = 7.4 ppm, $^2J_{HF}$ = 75 Hz, $^3J_{HF}$ = 5 Hz, 1 H). ^{13}C NMR: δ 151.0 (dd, $^1J_{CF}$ = 229 Hz, $^2J_{CF}$ = 31 Hz), 141.2 (dd, $^1J_{CF}$ = 252 Hz, $^2J_{CF}$ = 72 Hz), 131.8 (d, $^4J_{CF}$ = 2 Hz), 127.9 (dd, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 6 Hz), 126.7 (dd, $^3J_{CF}$ = 9 Hz, $^4J_{CF}$ = 7 Hz), 123.6 (d, $^5J_{CF}$ = 3 Hz). GC–MS, *m*/*z* (relative intensity): 220 (M^+, 97), 218 (M^+, 100), 139 (33), 119 (98). FTIR (CCl_4, cm^{-1}): 1489 (m), 1151 (s), 1118 (m), 1106 (m), 1083 (m), 1010 (m). HRMS calcd for $C_8H_5F_{27}{}^9Br$ 217.9543, obsd. 217.9557.

4.4.4. (*E,E*)-*p*-(HFC=CF)C_6H_4(CF=CFH) (8(E)-4)

Similarly, a mixture of 1,4-diiodobenzene (2.02 g, 6.06 mmol, 99%), $Pd(PPh_3)_4$ (0.65 g, 0.6 mmol, 5 mol%), **2(Z)** (30 ml, 18 mmol, 0.60 M, 1.48 eq.) in dry DMAC, and Cu(I)Br (1.8 g, 13 mmol) was stirred at room temperature for 2 h. After silica gel column chromatography (pentane, R_f = 0.56), removal of the solvent gave 1.12 g (92%) of a white crystalline solid, mp 49.5–50.5 °C. ^{19}F NMR: δ −167.8 (dd, $^3J_{FF}$ = 125 Hz, $^3J_{HF}$ = 5 Hz, 2 F), −172.0 (dd, $^3J_{FF}$ = 125 Hz, $^2J_{HF}$ = 75 Hz, 2 F). ^{1}H NMR: δ 7.7 (s, 4 H), 7.4 (dd, $^2J_{HF}$ = 75 Hz, $^3J_{HF}$ = 5 Hz, 2 H). ^{13}C NMR: δ 151.1 (dd, $^1J_{CF}$ = 229 Hz, $^2J_{CF}$ = 30 Hz), 141.6 (dd, $^1J_{CF}$ = 253 Hz, $^2J_{CF}$ = 72 Hz), 129.6 (ddd, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 7 Hz, $^5J_{CF}$ = 3 Hz), 125.3 (ddd, $^3J_{CF}$ = 9 Hz, $^4J_{CF}$ = 7 Hz, $^4J_{CF}$ = 2 Hz). GC–MS, *m*/*z* (relative intensity): 202 (M^+, 100), 151 (31). FTIR (CCl_4, cm^{-1}): 1685 (m), 1410 (m), 1361 (m), 1227 (m), 1158 (vs), 1120 (s), 1089 (m). HRMS calcd for $C_{10}H_6F_4$ 202.0406, obsd. 202.0406.

4.4.5. (*E*)-C_6H_5CF=CFH (8(E)-5)

Similarly, a mixture of iodobenzene (1.94 g, 9.51 mmol), $Pd(PPh_3)_4$ (0.34 g, 0.29 mmol, 5 mol%), **2(Z)** (16 ml, 10.4 mmol, 0.65 M, 1.1 eq.) in dry DMAC, and Cu(I)Br (1.4 g, 9.8 mmol) was stirred at 40 °C for 4 h. After silica gel column chromatography (pentane), removal of the solvent gave 0.98 g (74%) of a colorless liquid, GLPC purity > 99%. ^{19}F NMR: δ −166.9 (dd, $^3J_{FF}$ = 125 Hz, $^3J_{HF}$ = 5 Hz, 1 F), −174.1 (dd, $^3J_{FF}$ = 125 Hz, $^2J_{HF}$ = 76 Hz, 1 F). ^{1}H NMR: δ 7.6 (d, $^3J_{HH}$ = 8 Hz, 2 H), 7.3–7.2 (m, partially overlapping with peak at 7.19 ppm, 3 H), 7.2 (dd, $^2J_{HF}$ = 76 Hz, $^3J_{HF}$ = 5 Hz, 1 H). ^{13}C NMR: δ 152.1 (dd, $^1J_{CF}$ = 229 Hz, $^2J_{CF}$ = 31 Hz), 141.1 (dd, $^1J_{CF}$ = 251 Hz, $^2J_{CF}$ = 73 Hz), 129.5 (d, $^5J_{CF}$ = 2 Hz), 129.4 (dd, $^2J_{CF}$ = 24 Hz, $^3J_{CF}$ = 6 Hz), 128.8 (d, $^4J_{CF}$ = 2 Hz), 125.5 (dd, $^3J_{CF}$ = 8 Hz, $^4J_{CF}$ = 7 Hz). GC–MS, *m*/*z* (relative intensity): 140 (M^+, 100), 139 (35), 114 (27). FTIR (CCl_4, cm^{-1}): 3109 (m), 3064 (m), 1688 (m), 1497 (m), 1447 (m), 1358 (s), 1226 (m), 1149 (vs), 1101 (s). The spectroscopic data is in agreement with the reported literature data [7].

4.4.6. (*E*)-*p*-$CH_3OC_6H_4CF$=CFH (8(E)-6)

Similarly, a mixture of 4-iodoanisole (1.17 g, 7.23 mmol, 99%), $Pd(PPh_3)_4$ (0.6 g, 0.5 mmol, 7 mol%), **2(Z)** (18 ml, 10.8 mmol, 0.60 M, 1.5 eq.) in dry DMAC, and Cu(I)Br (1.1 g, 7.7 mmol) was stirred at 40 °C for 6 h. After silica gel column chromatography

(pentane/CH_2Cl_2 (9:2, v/v), R_f = 0.48), removal of the solvent gave 1.16 g (94%) of a slightly yellow liquid, GLPC purity: 100%. ^{19}F NMR: δ −166.2 (dd, $^3J_{FF}$ = 125 Hz, $^3J_{HF}$ = 5 Hz, 1 F), −177.3 (dd, $^3J_{FF}$ = 125 Hz, $^2J_{HF}$ = 76 Hz, 1 F). ^1H NMR: δ 7.5 (dm, $^3J_{HH}$ = 9 Hz, 2 H), 7.2 (dd, $^2J_{HF}$ = 76 Hz, $^3J_{HF}$ = 5 Hz, 1 H), 6.8 (dm, $^3J_{HH}$ = 9 Hz, 2 H), 3.7 (s, 3H). ^{13}C NMR: δ 160.5 (d, $^5J_{CF}$ = 2 Hz), 152.1 (dd, $^1J_{CF}$ = 228 Hz, $^2J_{CF}$ = 32 Hz), 139.9 (dd, $^1J_{CF}$ = 248 Hz, $^2J_{CF}$ = 74 Hz), 127.0 (dd as t, $^3J_{CF}$ and $^4J_{CF}$ = 8 Hz), 121.8 (dd, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 6 Hz), 114.1 (d, $^4J_{CF}$ = 2 Hz), 55.1 (s). GC–MS, *m/z* (relative intensity): 170 (M^+, 100), 155 (34). FTIR (CCl_4, cm^{-1}): 3007 (m), 2959 (m), 2936 (m), 2911 (m), 2838 (m), 1610 (s), 1577 (m), 1515 (s), 1464 (m), 1364 (m), 1303 (m), 1255 (s), 1225 (m), 1181 (s), 1145(vs), 1114 (s), 1036 (s). HRMS calcd for $C_9H_8F_2O$ 170.0543, obsd. 170.0527.

4.4.7. (E)-m-$CF_3C_6H_4CF$=CFH (8(E)-7)

Similarly, a mixture of 3-iodobenzotrifluoride (1.94 g, 7.13 mmol), $Pd(PPh_3)_4$ (0.4 g, 0.34 mmol, 5 mol%), **2(Z)** (17 ml, 10.4 mmol, 0.61 M, 1.45 eq.) in dry DMAC, and Cu(I)Br (1 g, 7 mmol) was stirred at 40 °C for 2 h. After silica gel column chromatography (pentane), removal of the solvent gave 1.24 g (84%) of a colorless liquid, GLPC purity: 100%. ^{19}F NMR: δ −63.4 (s, 3 F), −167.6 (dd, $^3J_{FF}$ = 125 Hz, $^3J_{HF}$ = 5 Hz, 1 F), −171.6 (dd, $^3J_{FF}$ = 125 Hz, $^2J_{HF}$ = 75 Hz, 1 F). ^1H NMR: δ 7.9 (s, 1 H), 7.7 (d, $^3J_{HH}$ = 8 Hz, 1 H), 7.5 (d, $^3J_{HH}$ = 7.8 Hz, 1 H), 7.4 (dd as t, partially overlapping with peak at 7.3 ppm, $^3J_{HH}$ = 8 Hz, 1 H), 7.3 (dd, partially overlapping with peak at 7.4 ppm, $^2J_{HF}$ = 75 Hz, $^3J_{HF}$ = 5 Hz, 1 H). ^{13}C NMR: δ 151.1 (dd, $^1J_{CF}$ = 229 Hz, $^2J_{CF}$ = 30 Hz), 142.3 (dd, $^1J_{CF}$ = 253 Hz, $^2J_{CF}$ = 71 Hz), 131.9 (qd, $^2J_{CF}$ = 33 Hz, $^4J_{CF}$ = 2 Hz), 130.5 (dd, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 6 Hz), 129.6 (d, $^3J_{CF}$ = 2 Hz), 128.8 (m), 126.3 (m), 124.6 (q, $^1J_{CF}$ = 272 Hz), 122.5 (qd, $^3J_{CF}$ = 8 Hz, $^3J_{CF}$ = 4 Hz). GC–MS, *m/z* (relative intensity): 208 (M^+, 100), 189 (21), 158 (16). FTIR (CCl_4, cm^{-1}): 1316 (s), 1173 (s), 1153 (s), 1140 (s), 1075 (m). HRMS calcd for $C_9H_5F_5$ 208.0311, obsd. 208.0294.

4.4.8. (E)-1-$C_{10}H_7CF$=CFH (8(E)-8)

Similarly, a mixture of 1-iodonaphthalene (1.27 g, 5.00 mmol), $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol, 3 mol%), **2(Z)** (15 ml, 8 mmol, 0.53 M, 1.6 eq.) in dry DMAC, and Cu(I)Br (0.7 g, 4.9 mmol) was stirred at 40 °C for 2.5 h. After silica gel column chromatography (pentane/CH_2Cl_2 (4:1, v/v), R_f = 0.49), removal of the solvent gave 0.83 g (87%) of a slightly yellow liquid, GLPC purity > 99%. ^{19}F NMR: δ −147.8 (d, $^3J_{FF}$ = 137 Hz, 1 F), −174.2 (dd, $^3J_{FF}$ = 137 Hz, $^2J_{HF}$ = 76 Hz, 1 F). ^1H NMR: δ 7.2–8.0 (m). ^{13}C NMR: δ 153.0 (dd, $^1J_{CF}$ = 237 Hz, $^2J_{CF}$ = 37 Hz), 140.8 (dd, $^1J_{CF}$ = 246 Hz, $^2J_{CF}$ = 71 Hz), 133.8 (d, $^3J_{CF}$ = 1 Hz), 131.1 (s), 130.9 (s), 128.6 (s), 128.5 (s), 127.1 (s), 126.4 (s), 125.7 (dd, $^2J_{CF}$ = 22 Hz, $^3J_{CF}$ = 4 Hz), 125.3 (d, $^3J_{CF}$ = 2 Hz), 125.0 (s). GC–MS, *m/z* (relative intensity): 190 (M^+, 93), 189 (53), 188 (56), 170 (100). FTIR (CCl_4, cm^{-1}): 3053 (m), 1509 (m), 1348 (m), 1185 (m), 1165 (m), 1140 (vs). HRMS calcd for $C_{12}H_8F_2$ 190.0594, obsd. 190.0585.

4.4.9. (E)-m-$NO_2C_6H_4CF$=CFH (8(E)-9)

Similarly, a mixture of 3-nitroiodobenzene (1.83 g, 7.27 mmol, 99%), $Pd(PPh_3)_4$ (0.3 g, 0.3 mmol, 4 mol%), **2(Z)** (18 ml, 10.8 mmol, 0.60 M, 1.5 eq.) in dry DMAC, and Cu(I)Br (1 g, 7 mmol) was stirred at room temperature for 1 h. After silica gel column chromatography (CH_2Cl_2, R_f = 0.76), removal of the solvent gave 1.24 g (93%) of a slightly yellow semi-solid. ^{19}F NMR: δ −167.1 (dd, $^3J_{FF}$ = 126 Hz, $^3J_{HF}$ = 5 Hz, 1 F), −169.6 (dd, $^3J_{FF}$ = 126 Hz, $^2J_{HF}$ = 74 Hz, 1 F). ^1H NMR: δ 8.4 (s, 1 H), 8.2 (d, $^3J_{HH}$ = 8 Hz, 1 H), 7.9 (d, $^3J_{HH}$ = 8 Hz, 1 H), 7.6 (dd as t, partially overlapping with 7.5 ppm peak, $^3J_{HH}$ = 8 Hz, 1 H), 7.5 (dd, $^2J_{HF}$ = 74 Hz, $^3J_{HF}$ = 5 Hz, 1 H). ^{13}C NMR: δ 149.9 (dd, $^1J_{CF}$ = 228 Hz, $^2J_{CF}$ = 29 Hz), 148.5 (s), 142.5 (dd, $^1J_{CF}$ = 254 Hz, $^2J_{CF}$ = 69 Hz), 130.9 (dd, $^3J_{CF}$ = 10 Hz, $^4J_{CF}$ = 7 Hz), 130.6 (dd, $^2J_{CF}$ = 26 Hz, $^3J_{CF}$ = 6 Hz), 129.9 (d, $^4J_{CF}$ = 2 Hz), 124.0 (d, $^5J_{CF}$ = 1 Hz), 120.2 (dd as t, $^3J_{CF}$ and $^4J_{CF}$ = 9 Hz). GC–MS, *m/z* (relative intensity): 185 (M^+, 100), 139 (44), 119 (80). FTIR (CCl_4, cm^{-1}): 1537 (s), 1351 (s), 1155 (vs). HRMS calcd for $C_8H_5F_2NO_2$ 185.0288, obsd. 185.0274.

4.4.10. (E)-p-$NO_2C_6H_4CF$=CFH (8(E)-10)

Similarly, a mixture of 4-nitroiodobenzene (1.28 g, 5.04 mmol, 98%), $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol, 3 mol%), **2(Z)** (50 ml, 7.5 mmol, 0.15 M, 1.5 eq.) in dry DMAC, and Cu(I)Br (0.7 g, 4.9 mmol) was stirred at room temperature for 20 min. After silica gel column chromatography (pentane/CH_2Cl_2 (4:1, v/v)), removal of the solvent gave 0.81 g (87%) of a white solid, mp 83–84 °C. ^{19}F NMR: δ −166.9to −167.1 (2nd order NMR spectrum, 2F). $\{^1H\}^{19}F$ NMR (δ) −167.1 (s, 2F). ^1H NMR: δ 8.3 (dm, $^3J_{HH}$ = 9 Hz, 2 H), 7.8 (dm, $^3J_{HH}$ = 9 Hz, 2 H), 7.5 (dd, $^2J_{HF}$ = 44 Hz, $^3J_{HF}$ = 35 Hz, 1 H). ^{13}C NMR: δ 150.0 (2nd order NMR spectrum), 147.9 (s), 143.1 (2nd order NMR spectrum), 134.8 (dd, $^2J_{CF}$ = 11 Hz, $^3J_{CF}$ = 6 Hz), 126.0 (dd as t, $^3J_{CF}$ and $^4J_{CF}$ = 9 Hz), 123.9 (s). GC–MS, *m/z* (relative intensity): 185 (M^+, 100), 127 (47), 119 (95). FTIR (CCl_4, cm^{-1}): 1683 (m), 1602 (m), 1528 (s), 1347 (vs), 1320 (m), 1156 (s), 1114 (m). HRMS calcd for $C_8H_5F_2NO_2$ 185.0288, obsd. 185.0287.

4.4.11. (E)-2-C_4H_3SCF=CFH (8(E)-11)

Similarly, a mixture of 2-iodothiophene (1.80 g, 8.48 mmol, 99%), $Pd(PPh_3)_4$ (0.3 g, 0.3 mmol, 3 mol%), **2(Z)** (20 ml, 12 mmol, 0.60 M, 1.4 eq.) in dry DMAC, and Cu(I)Br (0.7 g, 4.9 mmol) was stirred at room temperature for 1 h. After silica gel column chromatography (pentane), removal of the solvent gave 0.90 g (73%) of a colorless liquid, GLPC purity > 99%. The product quickly decomposed to a dark residue at room temperature. ^{19}F NMR: δ −161.1 (d, $^3J_{FF}$ = 125 Hz, 1 F), −172.3 (dd, $^3J_{FF}$ = 125 Hz, $^2J_{HF}$ = 75 Hz, 1 F). ^1H NMR: δ 7.3 (m, 2 H), 7.2 (dd, $^2J_{HF}$ = 75 Hz, $^3J_{HF}$ = 3 Hz, 1 H), 7.0–6.9 (m, 1 H). ^{13}C NMR: δ 149.8 (dd, $^1J_{CF}$ = 228 Hz, $^2J_{CF}$ = 37 Hz), 139.1 (dd, $^1J_{CF}$ = 250 Hz, $^2J_{CF}$ = 68 Hz), 130.5 (dd, $^2J_{CF}$ = 29 Hz, $^3J_{CF}$ = 8 Hz), 127.5–127.4 (m), 125.9 (dd, $^3J_{CF}$ = 6 Hz, $^4J_{CF}$ = 4 Hz). GC–MS, *m/z* (relative intensity): 146 (M^+, 100). HRMS calcd for $C_6H_4F_2S$ 146.0002, obsd. 146.0004.

4.5. (E)-C_6H_4CF=CFH (8(E)-5) from a 94:6 isomeric mixture of (Z)- and (E)-HFC=CFZnI (2(Z) and 2(E)) in the absence of Cu(I)Br

A two-neck 25-ml round bottom flask equipped with a Teflon-coated stir bar, a cold water condenser attached to a nitrogen source and a septum, was charged with (*Z*)- and (*E*)-1,2-difluoroethenylzinc iodide (*Z*:*E* = 94:6, 28.5 mmol, 15 ml, 1.9 M, 2.9 eq.) in dry DMAC, iodobenzene (2.00 g, 9.61 mmol), and $Pd(PPh_3)_4$ (0.3 g, 0.26 mmol, 3 mol%). The reaction mixture was stirred at 50 °C for 6 h. Only 60–65% ^{19}F NMR yield of the product was estimated. Additional reaction time (50 °C/2 h) did not improve the conversion. Then the dark mixture was poured onto a silica gel column and washed with pentane. Eluents with similar UV-active TLC spots were combined and the majority of the pentane was removed by simple distillation. Removal of the remaining trace amount of solvent at −30 °C/1 mmHg yielded 0.59 g (41%) of a colorless liquid, GLPC purity = 95%. This product exhibited ^{19}F, ^1H and ^{13}C NMR spectra similar to the previously prepared sample (4.4.5).

4.6. Preparation of (Z)-1,2-difluoroethenyltributylstannane (12(Z))

A one-neck 1-l round bottom flask equipped with a Teflon-coated stir bar, cold-water condenser and nitrogen tee, was charged with a 91:9 isomeric mixture of (*Z*) and (*E*)-1,2-difluorotrimethylsilylethylenes (404 mmol, in hexanes), tributyltin chloride (144 g, 424 mmol, 96%, 1.05 eq.), KF (27.0 g, 465 mmol, 1.15 eq.) and 700 ml of DMF. The solution was stirred at 80 °C for 1 h. Most of the low boiling point materials in the reaction mixture

was removed by rotary evaporation. The resultant residue was extracted with ether (5 × 150 ml) and washed with 1 l (5 × 200 ml) of cold water. The organic layer was separated with a separatory funnel and dried over anhydrous $MgSO_4$. Most of the solvent was removed by rotary evaporation. The resultant residue was eluted with hexanes through a silica gel column. Fractions with similar R_f values were combined. The solvent was removed at RT/1 mmHg. Vacuum distillation of the residue yielded 94.68 g (67%) of a colorless liquid, GLPC purity = 99% (*Z*:*E* = 93:7), bp 76–78 °C/0.1 mmHg. The colorless liquid was further eluted with hexanes through a silica gel column. Fractions with similar R_f values were collected. Most of the solvent was removed by rotary evaporation. Removal of the remaining solvent at 20 °C/0.1 mmHg yielded a colorless liquid, GLPC purity > 99% (*Z*: 97%, *E*: 3%). This product has ^{19}F, ^{1}H and $\{^{1}H\}^{13}C$ NMR spectra similar to the alternatively prepared sample [20].

4.7. General procedure for the preparation of (*E*)-α,β-difluorostyrenes 8(E) from (*Z*)-HFC=CFSn($CH_2CH_2CH_2CH_3$)$_3$ (12(Z))

A one-neck 25-ml round bottom flask equipped with a Teflon-coated stir bar and a nitrogen tee, was charged with 15 ml of dry DMF, aryl iodide (7.07 mmol, 99% purity), **12(Z)** (3.97 g, 11.3 mmol, 1.5 eq.), $Pd(PPh_3)_4$ (0.3 g, 0.3 mmol, 5 mol%), and Cu(I)I (1.0 g, 5.2 mmol). The reaction mixture was stirred at room temperature to 70 °C for 1–3 h. ^{19}F NMR analysis of the reaction mixture showed the formation of **8(E)**; GC–MS of a pre-chromatographed reaction mixture showed the complete disappearance of the aryl iodide. The dark reaction mixture was poured directly onto a silica gel column and eluted with pentane. Eluents with similar UV-active TLC spots were combined and the majority of the pentane was removed by simple distillation. Removal of the remaining trace amount of solvent at −35 °C/1 mmHg yielded **8(E)**.

4.7.1. (*E*)-*p*-BrC_6H_4CF=CFH (8(E)-3)

Similarly, a mixture of DMF (15 ml), 4-bromoiodobenzene (2.05 g, 7.1 mmol, 99%), (*Z*)-1,2-difluoroethenyltributylstannane (3.97 g, 11.3 mmol, 1.5 eq.), $Pd(PPh_3)_4$ (0.3 g, 0.3 mmol, 5 mol%), and Cu(I)I (1.0 g, 5.2 mmol) was stirred at 70 °C for 3 h. After silica gel column chromatography (pentane, R_f = 0.6), removal of the solvent at −10 °C/1 mmHg gave 1.41 g (92%) of a colorless liquid, GLPC purity = 100%. The product exhibited ^{19}F, ^{1}H and ^{13}C NMR spectra similar to the previously prepared sample (Section 4.4.3).

4.7.2. (*E*)-*m*-ClC_6H_4CF=CFH (8(E)-12)

Similarly, a mixture of DMF (10 ml), 3-chloroiodobenzene (1.38 g, 5.7 mmol, 98%), (*Z*)-1,2-difluoroethenyltributylstannane (2.17 g, 5.95 mmol, 96.5%, 1.05 eq.), $Pd(PPh_3)_4$ (0.3 g, 0.26 mmol, 5 mol%), and Cu(I)I (1.0 g, 5.2 mmol) was stirred at room temperature for 1 h. After silica gel column chromatography (pentane), removal of the solvent at −10 °C/1 mmHg gave 0.83 g (82%) of a colorless liquid, GLPC purity = 97%. ^{19}F NMR: δ −167.2 (dd, $^{3}J_{FF}$ = 125 Hz, $^{3}J_{HF}$ = 5 Hz, 1 F), −171.9 (dd, $^{3}J_{FF}$ = 125 Hz, $^{2}J_{HF}$ = 75 Hz, 1 F); ^{1}H NMR: δ 7.6 (s, broad, 1 H), 7.5 (m, 1 H), 7.3 (dd, partially overlapping, $^{2}J_{HF}$ = 75 Hz, $^{3}J_{HF}$ = 5 Hz, 1 H), 7.3 (m, 2 H); ^{13}C NMR: δ 150.5 (dd, $^{1}J_{CF}$ = 229 Hz, $^{2}J_{CF}$ = 31 Hz), 141.5 (dd, $^{1}J_{CF}$ = 253 Hz, $^{2}J_{CF}$ = 72 Hz), 134.6 (d, $^{4}J_{CF}$ = 2 Hz), 130. 7 (dd, $^{2}J_{CF}$ = 25 Hz, $^{3}J_{CF}$ = 6 Hz), 129.9 (d, $^{4}J_{CF}$ or $^{5}J_{CF}$ = 2 Hz), 129.4 (d, $^{4}J_{CF}$ or $^{5}J_{CF}$ = 2 Hz), 125.3 (dd as t, $^{3}J_{CF}$ = 9 Hz, $^{4}J_{CF}$ = 8 Hz), 123.3 (dd as t, $^{3}J_{CF}$ = 9 Hz, $^{4}J_{CF}$ = 8 Hz); GC–MS, *m*/*z* (relative intensity): 176(27), 174 (M^+, 100), 139 (65); HRMS calcd for $C_8H_5{}^{35}ClF_2$ 174.0048, obsd 174.0060.

4.7.3. (*E*)-*p*-CNC_6H_4CF=CFH (8(E)-13)

Similarly, a mixture of dry DMF (5 ml), 4-cyanoiodobenzene (0.42 g, 1.8 mmol), (*Z*)-1,2-difluoroethenyltributylstannane (0.70 g, 1.9 mmol, 96%, 1.1 eq.), $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol, 2 mol%), and Cu(I)I (0.12 g, 0.63 mmol) was stirred at room temperature for 1 h. The reaction mixture was washed with aqueous KF (4 × 50 ml) and water (5 × 25 ml), then was extracted with ether (4 × 30 ml). The combined ether layers were dried over anhydrous $MgSO_4$. $MgSO_4$ was then filtered *via* gravity filtration. Removal of the solvent *via* rotary evaporation yielded a solid, which was eluted with CH_2Cl_2 through a silica gel column; R_f = 0.6. Most of the solvent was removed *via* rotary evaporation. Removal of the remaining solvent at −10 °C/1 mmHg yielded 0.25 g (83%) of a light yellow solid. ^{19}F NMR: δ −167.5 to −168.5 ppm (2nd order NMR spectrum); $\{^{1}H\}^{19}F$ NMR: δ −167.8 (d, AB pattern, $^{3}J_{FF}$ = 125 Hz, 1 F), −168.2 (d, AB pattern, $^{3}J_{FF}$ = 125 Hz, 1 F); ^{1}H NMR: δ 7.8 (distorted d, $^{4}J_{HF}$ or $^{5}J_{HF}$ = 9 Hz, 2 H), 7.7 (d, $^{4}J_{HF}$ or $^{5}J_{HF}$ = 9 Hz, 2 H), 7.4 (dd, $^{2}J_{HF}$ = 50 Hz, $^{3}J_{HF}$ = 30 Hz, 1 H); ^{13}C NMR: δ 150.0 (2nd order NMR spectrum), 142.7 (2nd order NMR spectrum), 133.1 (dd, $^{2}J_{CF}$ = 16 Hz, $^{3}J_{CF}$ = 2 Hz), 132.6 (d, $^{4}J_{CF}$ = 2 Hz), 125.6 (dd as t, $^{3}J_{CF}$ = 9 Hz, $^{4}J_{CF}$ = 9 Hz), 118.3 (s), 112.8 (d, $^{5}J_{CF}$ = 1 Hz); GC–MS, *m*/*z* (relative intensity): 166 (8), 165 (M^+, 100); FTIR (CCl_4, cm^{-1}): 2232 (m), 1683 (m), 1509 (m), 1407 (m), 1361 (m), 1156 (vs); HRMS calcd for $C_9H_5F_2N$ 165.0390, obsd 165.0394.

4.7.4. (*E*)-2-C_5H_4NCF=CFH (8(E)-14)

Similarly, a mixture of dry DMF (10 ml), 2-iodopyridine (1.58 g, 99%, 7.6 mmol), (*Z*)-1,2-difluoroethenyltributylstannane (3.10 g, 8.4 mmol, 96.5%, 1.1 eq.), $Pd(PPh_3)_4$ (0.44 g, 0.38 mmol, 5 mol%), and Cu(I)I (1.5 g, 7.9 mmol, 1 eq.) was stirred at room temperature for 1 h. The reaction mixture was poured directly onto a silica gel column and eluted with CH_2Cl_2; R_f = 0.2. Most of the solvent was removed *via* rotary evaporation. Removal of the remaining solvent at −10 °C/1 mmHg yielded 0.23 g (21%) of a colorless liquid. The product quickly decomposed to a dark residue at room temperature. ^{19}F NMR: δ −169.2 (dd, $^{3}J_{FF}$ = 127 Hz, $^{2}J_{HF}$ = 67 Hz, 1 F), −169.9 (dd, $^{3}J_{FF}$ = 127 Hz, $^{3}J_{HF}$ = 13 Hz, 1 F); ^{1}H NMR: δ 8.7 (d, $^{3}J_{HH}$ = 5 Hz, 1 H), 7.7 (ddd as dt, $^{3}J_{HH}$ = 8 Hz, $^{5}J_{HF}$ = 1 Hz, 1 H), 7.6 (d, $^{3}J_{HH}$ = 8 Hz, 1 H), 7.5 (dd, partially overlapping with the peak at 7.6 ppm, $^{2}J_{HF}$ = 67 Hz, $^{3}J_{HF}$ = 13 Hz, 1 H), 7.2 (ddd, $^{3}J_{HH}$ = 8 Hz, $^{3}J_{HH}$ = 5 Hz, $^{6}J_{HF}$ = 1 Hz, 1 H); ^{13}C NMR: δ 150.6 (dd, $^{1}J_{CF}$ = 196 Hz, $^{2}J_{CF}$ = 5 Hz), 149.8(d, $^{4}J_{CF}$ = 1 Hz), 148.3 (dd, $^{2}J_{CF}$ = 20 Hz, $^{3}J_{CF}$ = 3 Hz), 142.9 (2nd order NMR spectrum), 136.6 (d, $^{4}J_{CF}$ = 2 Hz), 123.8 (d, $^{5}J_{CF}$ = 1 Hz), 121.7 (dd, $^{3}J_{CF}$ = 9 Hz, $^{4}J_{CF}$ = 4 Hz); GC–MS, *m*/*z* (relative intensity): 142(8), 141 (M^+, 100), 140 (16), 122 (30), 114(14).

4.8. Attempted preparation of 8(E)-6 from 12(Z)

A one-neck 25-ml round bottom flask equipped with a Teflon-coated stir bar and a nitrogen tee, was charged with 10 ml of dry DMF, 4-iodoanisole (1.70 g, 7.3 mmol), **12(Z)** (2.93 g, 8 mmol, 1.1 eq.), $Pd(PPh_3)_4$ (0.4 g, 0.3 mmol, 5 mol%) and Cu(I)I (1.5 g, 7.9 mmol, 1 eq.). The reaction mixture was stirred at 60 °C for 6 h. ^{19}F NMR analysis of the reaction mixture showed the formation of the **8(E)-6** (60% NMR yield) and about 30% of unreacted **12(Z)**; GC–MS analysis of a pre-chromatographed reaction mixture also showed a significant amount of unreacted 4-iodoanisole.

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