Stereoselective Preparation of (*Z*)-α,*β*-Difluorostyrenes and Stereospecific Conversion to (*E*)-α,*β*-Difluoro-*β*-iodostyrenes[1]

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Substituted aromatic iodides coupled with (*E*)-HFC=CFZnI (E:Z 95:5) under mild conditions, in the presence of catalytic $Pd(PPh_3)_4$, in DMF to give (*Z*)-α,*β*-difluorostyrenes in good yields. The coupling reaction was tolerant of a variety of functionalities. Isomerically pure (*Z*)-α,*β*-difluorostyrenes were readily converted to the corresponding (*E*)-α,*β*-difluoro-*β*-iodostyrenes in good yields by two methods; in one method, treatment of the (*Z*)-α,*β*-difluorostyrenes with LTMP at low-temperature gave vinyllithium reagents which were captured in situ with Bu_3SnCl to form vinylstannanes. The intermediate vinylstannanes could be isolated or treated directly with I_2 to give (*E*)-α,*β*-difluoro-*β*-iodostyrenes in a one-flask procedure. In a second approach, *n*-BuLi was utilized to pregenerate vinyllithium reagents which were quenched with I_2 to afford (*E*)-α,*β*-difluoro-*β*-iodostyrenes.

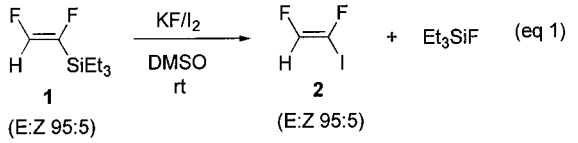
Introduction

Fluorinated styrenes are useful building blocks in organofluorine chemistry and have found application as monomers,[3] as precursors for antiinflammatory[4] and antifertility[5] compounds, and as precursors for 1,4-diaryl-perfluoro-1,3-butadienes.[6]

Several strategies have been applied 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.[7] 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.[8] Low-temperature metalation 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.[9] Protodesilylation of (*Z*)-1,2-difluoro-2-arylvinylsilanes by potassium fluoride in aqueous DMSO gave (*E*)-α,*β*-difluorostyrenes.[10,11] In a recent preliminary communication,[12] we briefly described a procedure for the preparation of (*Z*)-α,*β*-difluorostyrenes. However, a general, stereoselective preparation of (*E*)-α,*β*-difluoro-*β*-iodostyrenes has not been reported. Several α,*β*-difluoro-*β*-iodostyrenes have been obtained by a Hunsdiecker reaction of α,*β*-difluorocinnamic acid salts, but this method is applicable to the preparation of only the (*Z*)-isomers.[6] (*Z*)-PhCF=CFI has been prepared *via* iodination of (*E*)-PhCF=CFLi.[11] More recently, a series of the (*Z*)-isomers has been prepared by iodination of (*Z*)-2-aryl-1,2-difluorovinylphosphoranes.[13] The paucity of methodology for the preparation of (*E*)-*β*-iodostyrenes analogues has impeded their utility as synthetic intermediates and has been due, in part, to the lack of suitable stereodefined precursors. Here we describe in detail the stereoselective preparation of (*Z*)-α,*β*-difluorostyrenes and their subsequent conversion to (*E*)-α,*β*-difluoro-*β*-iodostyrenes.

Results and Discussion

Our recent development of (*E*) and (*Z*)-difluoroethene synthons[14] and our prior studies with fluorinated zinc reagents[15] prompted us to investigate a route to (*Z*)-α,*β*-difluorostyrenes via the $Pd(PPh_3)_4$-catalyzed arylation of (*E*)-HFC=CFZnI, **3**. Vinylzinc reagent **3** was prepared in two steps from **1**, which is readily prepared from bromotrifluoroethylene[14] or chlorotrifluoroethylene.[16] Iododesilylation[17] of **1** with KF/I_2 gave a mixture of (*E*)-HFC=CFI, **2**, and Et_3SiF (eq 1).



The mixture of Et_3SiF and **2**, after removal from the reaction mixture under vacuum, was treated with activated zinc metal in DMF to give **3** (55−63%, based on **1**, as determined by internal $PhCF_3$ standard) and 1,2-difluoroethylene, **4** (eq 2). Zinc reagent **3** exhibits excel-

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(17) Iododesilylation has been used extensively in our group to prepare (*E*)- and (*Z*)-RCF=CFI from (*E*)- and (*Z*)-RCF=$CFSiR_3$, unpublished results, University of Iowa.

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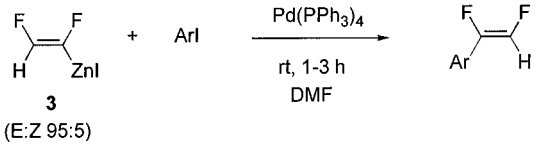
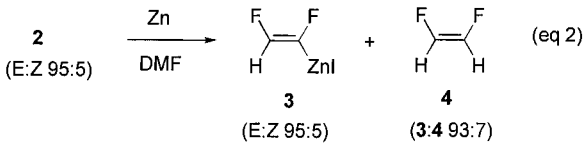
Table 1. $Pd(PPh_3)_4$ Catalyzed Arylation of (*E*)-HFC=CFZnI



ArI	product	no.	yield (%)[a]
C_6H_5I	$C_6H_5CF{=}CFH$	**5**	65
p-$CH_3OC_6H_4I$	*p*-$CH_3OC_6H_4CF{=}CFH$	**6**	85
p-$NO_2C_6H_4I$	*p*-$NO_2C_6H_4CF{=}CFH$	**7**	66[b]
o-$NO_2C_6H_4I$	*o*-$NO_2C_6H_4CF{=}CFH$	**8**	78
p-$CH_3C_6H_4I$	*p*-$CH_3C_6H_4CF{=}CFH$	**9**	72
p-$EtO_2CC_6H_4I$	*p*-$EtO_2CC_6H_4CF{=}CFH$	**10**	93
p-$CH_3C(O)C_6H_4I$	*p*-$CH_3C(O)C_6H_4CF{=}CFH$	**11**	71
m-ClC_6H_4I	*m*-$ClC_6H_4CF{=}CFH$	**12**	60
1,4-$C_6H_4I_2$	*p*-$HFC{=}CFC_6H_4CF{=}CFH$	**13**	80
p-$CF_3C_6H_4I$	*p*-$CF_3C_6H_4CF{=}CFH$	**14**	70
o-$(CH_3)_2CHC_6H_4I$	*o*-$(CH_3)_2CHC_6H_4CF{=}CFH$	**15**	55[c]

[a] Isolated yield of (*Z*)-isomer only. [b] Isolated as a 95:5 (*Z*:*E*) mixture; reaction was carried out at 0 °C. [c] Reaction conditions: 60 °C, 8 h.

lent thermal stability. Significant loss of molarity, with concomitant formation of **4**, occurred only after extended heating (12 h) at temperatures at or above 100 °C. Treatment of **3** with HCl resulted in quantitative formation of **4** by ^{19}F NMR analysis.



Substituted aromatic iodides coupled smoothly under mild conditions with **3**, in the presence of catalytic $Pd(PPh_3)_4$, to give (*Z*)-α,*β*-difluorostyrenes in good to excellent yields (eq 3).

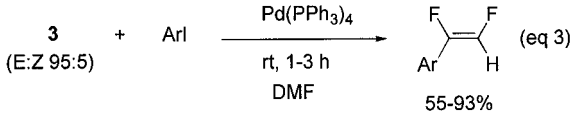
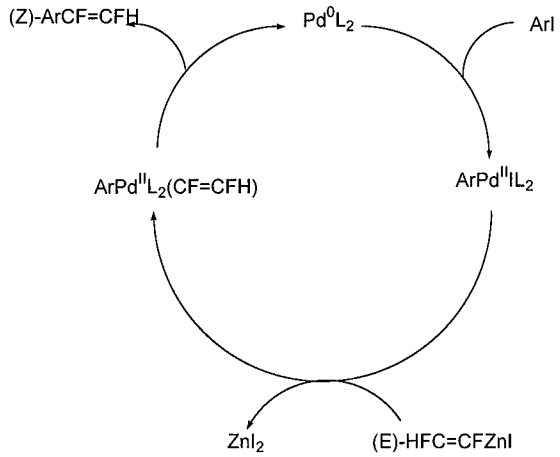


Table 1 summarizes our results. The coupling reaction was tolerant of a variety of functionalities; significant differences in reaction time or yield were not observed between electron-releasing and electron-withdrawing groups. One exception was the reaction of *p*-$NO_2C_6H_4I$ with **3** which gave **7** in reasonable yield when carried out at 0 °C. Arylation of **3** with the sterically hindered *o*-$(CH_3)_2CHC_6H_4I$ substrate was optimized on heating. *p*-Diiodobenzene coupled with 2 equivalents of **3** to give the 1,4-disubstituted product **13**. In each case, an excess of **3** (1.3−1.5 equiv) was utilized to completely consume the aryl iodide, thus avoiding a separation problem. In no case was the minor (*E*)-α,*β*-difluorostyrene isomer detected at a level above 5% of the product mixture. Except for **7**, the major (*Z*)-isomer was separated from the (*E*)-isomer impurity by silica gel column chromatography. The coupling reaction is proposed to proceed via the following catalytic cycle (Scheme 1). Oxidative addition of ArI to Pd^0L_2 is followed by metathesis with vinylzinc reagent **3**; subsequent reductive elimination of

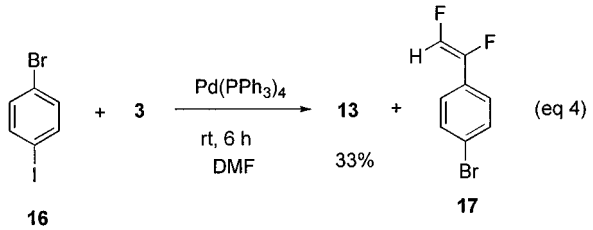
Scheme 1



$ArPdL_2(CF{=}CFH)$ affords the styrene product and regenerates Pd^0L_2.[18,19]

Although reaction of **3** with aryl iodides proceeds under mild conditions, **3** did not undergo arylation with *p*-$CH_3C_6H_4Br$ under similar conditions (12 h, room temperature).

Reaction of **16** with 1.5 equiv of **3**, however, gave a mixture from which **13** was isolated, strongly suggesting that aryl bromides containing electron-withdrawing groups will undergo similar coupling (eq 4).



(*Z*)-α,*β*-Difluorostyrenes were readily converted to (*E*)-α,*β*-difluoro-*β*-iodostyrenes in good yields. In one approach (method A), (*Z*)-α,*β*-difluorostyrenes, **18**, were treated with Li-2,2,6,6-tetramethylpiperidide (LTMP) at −78 °C, and the resultant vinyllithium reagents were trapped in situ with Bu_3SnCl to form the vinylstannanes, **19** (Scheme 2). Subsequent cleavage of the tin moiety with I_2 gave the iodostyrenes, **20**. Although vinylstannanes **19a** and **19b** were isolated, the transformation was amenable to a one-flask procedure. Reaction mixtures containing the intermediate vinylstannanes **19c** and **19d** were treated directly with I_2 (entries 9 and 10, Table 2) to give **27** and **28**, respectively. The hindered LTMP base was employed to hinder side reaction of the base with Bu_3SnCl. In a second approach (method B), the iodostyrenes were directly prepared by low-temperature iodination of pregenerated vinyllithium reagents, **21** (Scheme 2). Method B is particularly convenient for preparation of iodostyrenes containing functionalities compatible with *n*-BuLi, as preparation of LTMP is not required and separation of Bu_3SnI is avoided. Our results utilizing both approaches are summarized in Table 2.

Although the vinyllithium reagents were successfully trapped in situ with Bu_3SnCl at −78 °C in method A, method B was not attempted at −78 °C. As a minor component of a (*E*/*Z*) mixture, (*Z*)-PhCF=CFLi has been

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Scheme 2

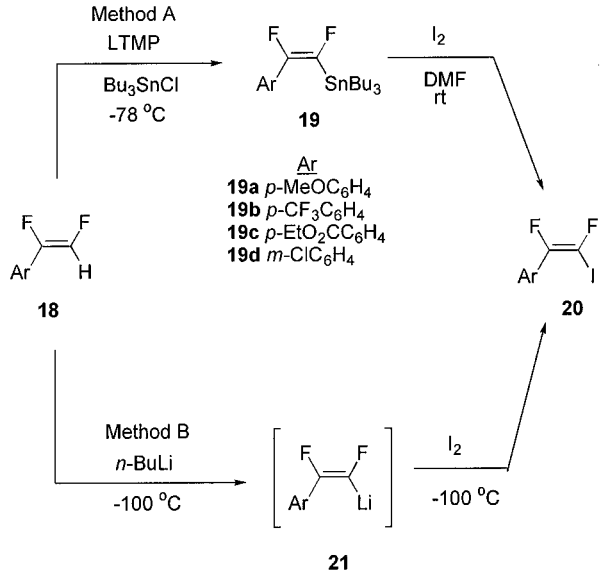
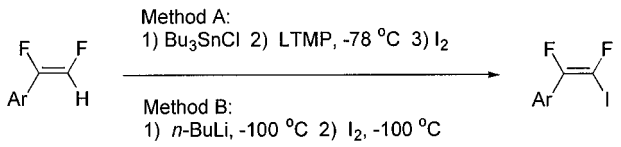


Table 2. Conversion of (*Z*)-α,*β*-Difluorostyrenes to (*E*)-α,*β*-Difluoro-*β*-iodostyrenes



entry	product	no.	method	yield[a]
1	*p*-$CH_3OC_6H_4CF{=}CFI$	**22**	A	87
2	*p*-$CH_3OC_6H_4CF{=}CFI$	**22**	B	85
3	$C_6H_5CF{=}CFI$	**23**	B	83
4	*p*-$CH_3C_6H_4CF{=}CFI$	**24**	B	65
5	*o*-$(CH_3)_2CHC_6H_4CF{=}CFI$	**25**	B	54
6	*p*-$CF_3C_6H_4CF{=}CFI$	**26**	A	92[b]
7	*p*-$CF_3C_6H_4CF{=}CFI$	**26**	B	81
8	*p*-$EtO_2CC_6H_4CF{=}CFI$	**27**	B	39[c]
9	*p*-$EtO_2CC_6H_4CF{=}CFI$	**27**	A	77[d]
10	*m*-$ClC_6H_4CF{=}CFI$	**28**	A	85[d]

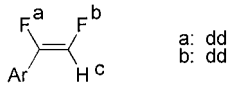
[a] Isolated yields, based on ArCF=CFH. [b] Product obtained as a mixture containing Bu_3SnI; an analytical sample of **26** (30%) was obtained by chromatography. [c] LTMP substituted for *n*-BuLi. [d] One-flask procedure: the vinylstannane intermediate was treated directly with I_2.

reported to undergo decomposition at temperatures above −85 °C whereas the major (*E*)-isomer exhibited thermal stability up to −5 °C.[9,20] The difference in stability is presumably due to facile decomposition of (*Z*)-PhCF=CFLi via an anti *β*-elimination pathway, unavailable to the (*E*)-isomer, to give PhC≡CF and LiF.[9]

The stereochemistry of both the (*Z*)-α,*β*-difluorostyrenes and the (*E*)-α,*β*-difluoro-*β*-iodostyrenes was unambiguously assigned on the basis of ^{19}F NMR coupling constants. All products exhibited vicinal couplings ($^3J_{F,F}$ = 0−22 Hz) consistent with the *cis*-CF=CF stereochemistry vs the corresponding *trans*-CF=CF analogues ($^3J_{F,F}$ = 100−140 Hz).[9,11] ^{19}F data for the (*Z*)-α,*β*-difluorostyrenes is presented in Table 3. The (*Z*)-α,*β*-difluorostyrenes and the (*E*)-α,*β*-difluoro-*β*-iodostyrenes, once purified, were stored for extended periods at 0−10 °C without significant decomposition or detectable isomerization.

In conclusion, we have described a general method for the stereoselective preparation of (*Z*)-α,*β*-difluorostyrenes and for their subsequent stereospecific conversion to (*E*)-α,*β*-difluoro-*β*-iodostyrenes. Work aimed at utilizing the resultant styrenes in the stereospecific construction of functionalized fluorinated alkenes is in progress.

Table 3. ^{19}F NMR Data of (*Z*)-α,*β*-Difluorostyrenes[a]



no.	subst	a	b	J_{ab}	J_{ac}	J_{bc}
5	H	−142.6	−164.8	11.8	17.0	73.2
6	*p*-CH_3O	−140.9	−167.1	12.8	14.9	73.4
7	*p*-NO_2	−143.7	−157.3	9.8	16.0	71.2
8	*o*-NO_2	−145.8	−156.4	15.8	12.9	71.9
9	*p*-CH_3	−142.1	−166.1	12.0	15.9	73.2
10	*p*-EtO_2C	−143.7	−161.2	10.2	15.7	71.9
11	*p*-$CH_3C(O)$	−143.9	−160.6	10.1	16.9	72.0
12	*m*-Cl	−142.9	−162.5	10.5	16.9	71.9
13	*p*-HFC=CF	−143.6	−162.9	11.4	16.7	72.3
14	*p*-CF_3[b]	−143.7	−161.0	10.3	16.9	71.8
15	*o*-$(CH_3)_2CH$	−121.2	−159.4	19.1	17.8	74.3

[a] All spectra were recorded in $CDCl_3$ and chemical shifts are reported in ppm *vs* internal $CFCl_3$ standard. [b] *p*-CF_3 appears at −63.6 (s, 3F).

Experimental Section

General. All glassware was oven-dried prior to use. ^1H NMR and $\{^1H\}^{13}C$ NMR spectra were recorded at 300 MHz and referenced against internal tetramethylsilane (TMS). ^{19}F NMR spectra were recorded at 300 or 90 MHz and referenced vs internal $CFCl_3$. GC-MS spectra were obtained at 70 eV in the electron impact mode and reported as *m*/*z* (rel intens). High-resolution mass spectral determinations were made at the University of Iowa High-Resolution Mass Spectrometry Facility. GLPC analyses were carried out on a 5% OV-101 column with a thermal conductivity detector.

Materials. DMF and DMSO were distilled from CaH_2. THF and Et_2O were distilled from sodium benzophenone ketyl. KF was dried by azeotropic distillation with benzene. $Pd(PPh_3)_4$ was prepared according to Coulson's procedure.[21] *n*-BuLi, 2,2,6,6-tetramethylpiperidine, and all aryl iodides were obtained from commercial sources and used without further purification.

Preparation of (*E*)-HFC=CFZnI (3). A 250 mL, three-necked flask equipped with a magnetic stir bar, thermometer adapter, coldfinger condenser set to −20 °C, and N_2 source, was charged with anhydrous KF (12.7 g, 219 mmol), I_2 (38 g, 150 mmol), and 90 mL of DMSO. To the stirred mixture was added (*E*)-HFC=CFSiEt_3, **1** (13.0 g, 73 mmol, *E*:*Z* 95:5), via syringe, in one portion. An exotherm resulted (60−70 °C) followed by cooling to rt. The reaction mixture was stirred at rt for an additional 36 h or until no starting material was detected by ^{19}F NMR analysis. The reaction flask was connected to a liquid N_2 cooled receiver and flash distilled (ca. 60 °C bath temperature, 10 mmHg). The contents of the reaction flask were periodically analyzed by ^{19}F NMR to determine when all product had been removed from the reaction mixture. The cooled receiver contained **2**, Et_3SiF, and DMSO. The distillate was then redistilled through a short path apparatus at atmospheric pressure, and a mixture of **2** and Et_3SiF was collected and used without further purification (bp 50−105 °C). ^{19}F NMR for **2** ($CDCl_3$) −106.5 (d, $^3J_{F,H}$ = 15.2 Hz, 1 F), −130.7 (d, $^2J_{F,H}$ = 75.2 Hz, 1 F).

A 50 mL flask equipped with a cold-water condenser, magnetic stir bar, N_2 source, and septum port, was charged with acid-washed Zn metal (4.9 g, 75 mmol) and 30 mL of DMF. A volume of **2**/Et_3SiF mixture (ca. 25 mmol) was added *via* syringe in one portion. Induction occurred in 20−30 min and an exotherm was observed. The remainder of the starting material (25 mmol) was added dropwise, with the temperature maintained at ≤60 °C. The dark-colored mixture was stirred

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(21) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121−124.

an additional 45 min, and formation of **3** was confirmed by ^{19}F NMR analysis of the reaction mixture (**3**:**4** 93:7). The molarity of the vinylzinc reagent was determined by internal $PhCF_3$ standard. The excess Zn was allowed to settle, and the solution was filtered through a coarse-fritted funnel and the vinylzinc reagent was stored under N_2 at rt. ^{19}F NMR for **3** (DMF solution) −149.2 (d, $^2J_{F,H}$ = 83 Hz, 1 F), −146.8 (d, $^3J_{F,H}$ = 29 Hz, 1 F); ^{19}F NMR for (*Z*)-HFC=CFH, **4** (DMF solution) −164.2 (dd, $^2J_{F,H}$ = 66 Hz, $^3J_{F,H}$ = 32 Hz).

General Procedure for the Preparation of (*Z*)-α,β-Difluorostyrenes. Preparation of (*Z*)-*p*-$CO_2EtC_6H_4$-CF=CFH (10). A two-necked, 25 mL flask equipped with a N_2 source, magnetic stir bar, and rubber septum was charged with $Pd(PPh_3)_4$ (0.29 g, 0.25 mmol, 3 mol %) and *p*-$CO_2EtC_6H_4I$ (2.3 g, 8.3 mmol). A DMF solution of **3** (12 mmol) was added via syringe, and the resultant mixture was stirred 2 h at rt. The reaction mixture was diluted with cold water (75 mL) and extracted with 1:1 pentane:Et_2O (4 × 50 mL). The combined extracts were dried ($MgSO_4$) and concentrated by rotary evaporation. Chromatography on SiO_2 (80% pentane-EtOAc, R_f 0.5) gave 1.63 g (93%) of **10** as a pale-yellow solid: mp 52−53 °C; ^1H NMR ($CDCl_3$) δ 1.4 (t, 7.1 Hz, 3 H), 4.4 (q, 7.1 Hz, 2 H), 7.1 (dd, 72.5, 16.9 Hz, 1 H), 7.5 (d, 8.4 Hz, 2 H), 8.0 (d, 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 61.3, 123.2, (t, 4.2 Hz), 130.0, 131.2, 133.1 (d, 23.5 Hz), 135.4 (dd, 260.6, 15.1 Hz), 145.7 (dd, 247.5, 10.9 Hz), 165.8; FTIR (CCl_4) 3122 (w), 2984 (w), 1724 (s), 1694 (s), 1411 (m), 1275 (s), 1146 (s), 1108 (s), 1013 (m) cm^{-1}; HRMS calcd for $C_{11}H_{10}F_2O_2$ 212.0649, obsd 212.0641.

(*Z*)-C_6H_5CF=CFH (5). According to the general procedure, C_6H_5I (1.63 g, 8.0 mmol), $Pd(PPh_3)_4$, and **3** (12 mmol) were stirred 2 h at rt. Following the standard workup, the solvent was removed at atmospheric pressure. Chromatography on SiO_2 (pentane, R_f 0.4) gave 0.73 g (65%) of **5** as an oil: GLPC > 99%; ^1H NMR ($CDCl_3$) δ 6.9 (dd, *J* = 72.9, 17.1 Hz, 1 H), 7.4 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 148.5 (dd, 247.0, 10.2 Hz), 134.1 (dd, *J* = 256.7, 15.6 Hz), 129.3, 129.0, 128.7, 123.6 (*J* = t, 5.5 Hz); GC-MS 140 (M^+, 100), 139 (26), 120 (17), 119 (18), 114 (26), 101 (13), 89 (13), 63 (18), 51 (17); HRMS calcd for $C_8H_6F_2$ 140.0438, obsd 140.0430; FTIR (CCl_4) 3120 (w), 3066 (w), 1697 (s), 1335 (s), 1292 (m), 1142 (s), 1041 (s), 837 (s) cm^{-1}.

(*Z*)-*p*-$CH_3OC_6H_4CF$=CFH (6). According to the general procedure, *p*-$CH_3OC_6H_4I$ (4.2 g, 18.0 mmol), $Pd(PPh_3)_4$, and **3** (25 mmol) were stirred 2 h at rt. Following the standard workup, chromatography on SiO_2 (85% pentane−EtOAc, R_f 0.6) gave 2.6 g (85%) of **6** as a low-melting solid: GLPC 96%; ^1H NMR ($CDCl_3$) δ 3.8 (s, 3 H), 6.8 (dd, *J* = 73.4, 17.3 Hz, 1 H), 6.9 (d, *J* = 8.7 Hz, 2 H), 7.3 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 160.7, 148.7 (dd, *J* = 246.3, 10.0 Hz), 133.2 (dd, *J* = 254.3, 16.3 Hz), 125.6 (t, *J* = 4.5 Hz), 121.3 (d, *J* = 24.4 Hz), 114.3, 55.3; GC-MS 170 (M^+, 100) 171 (10), 155 (55), 127 (67), 101 (15); HRMS calcd for $C_9H_8F_2O$ 170.0543, obsd 170.0543; FTIR (CCl_4) 2959 (w), 2839 (w), 1699 (m), 1610 (s), 1252 (s), 1138 (s), 1023 (s), 820 (m) cm^{-1}.

(*Z*)-*p*-$NO_2C_6H_4CF$=CFH (7). According to the general procedure, *p*-$NO_2C_6H_4I$ (1.25 g, 5.0 mmol), $Pd(PPh_3)_4$, and **3** (7.5 mmol) were stirred 1 h at 0 °C and 3 h at rt. Following the standard workup, chromatography on SiO_2 (85% hexanes−EtOAc, R_f 0.4) gave 0.62 g (66%) of **7** as a yellow solid: mp 78−79 °C; ^1H NMR ($CDCl_3$) δ 7.2 (dd, *J* = 71.2, 16.7 Hz, 1 H), 7.6 (d, *J* = 8.9 Hz, 2 H), 8.3 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 148.2, 147.0 (dd, *J* = 248.0, 11.9 Hz), 136.4 (dd, *J* = 264.3, 14.9 Hz), 135.2 (d, *J* = 23.9 Hz), 124.2, 124.1 (t, *J* = 4.5 Hz); GC-MS 185 (M^+, 100), 155 (36), 139 (13), 138 (17), 127 (37), 119 (77), 99 (44), 88 (16), 63 (31); HRMS calcd for $C_8H_5F_2NO_2$ 185.0288, obsd 185.0295; FTIR (CCl_4) 3122 (w), 2927 (w), 2856 (w), 1693 (m), 1528 (s), 1337 (s), 1151 (s), 1020 (m), 870 (m) cm^{-1}.

(*Z*)-*o*-$NO_2C_6H_4CF$=CFH (8). According to the general procedure, *o*-$NO_2C_6H_4I$ (1.25 g, 5.0 mmol), $Pd(PPh_3)_4$, and **3** (7.5 mmol) were stirred 2 h at rt. Following the standard workup, chromatography on SiO_2 (CH_2Cl_2, R_f 0.75) gave 0.72 g (78%) of **8** as a yellow-orange solid: mp 69−70 °C; ^1H NMR ($CDCl_3$) δ 6.8 (dd, *J* = 71.9, 15.8 Hz, 1 H), 7.5 (d, *J* = 7.0 Hz, 1 H), 7.7 (m, 2 H), 8.0 (dd, *J* = 7.3, 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 147.9, 145.8 (dd, *J* = 251.5, 12.9 Hz), 135.4 (dd, *J* = 261.5, 15.2 Hz), 133.4, 131.5, 131.3, 125.0, 123.0 (dd, *J* = 21.8, 3.8 Hz); GC-MS 185 (M^+, 10), 138 (14), 127 (50), 119 (29), 109 (100), 107 (24), 101 (27), 99 (36), 89 (22), 63 (34); HRMS calcd for $C_8H_5F_2NO_2$ 185.0288, obsd 185.0272; FTIR (CCl_4) 3117 (w), 1541 (s), 1338 (s), 1258 (w), 1142 (s), 1017 (m), 861 (w) cm^{-1}.

(*Z*)-*p*-$CH_3C_6H_4CF$=CFH (9). According to the general procedure, *p*-$CH_3C_6H_4I$ (1.75 g, 8.0 mmol), $Pd(PPh_3)_4$, and **3** (12 mmol) were stirred 2 h at rt. Following the standard workup, the solvent was removed at atmospheric pressure. Chromatography on SiO_2 (pentane, R_f 0.4) gave 0.89 g (72%) of **9** as an oil: GLPC > 99%; ^1H NMR ($CDCl_3$) δ 2.3 (s, 3 H), 6.9 (dd, *J* = 73.2, 17.2 Hz, 1 H), 7.1 (d, *J* = 8.2 Hz, 2 H), 7.2 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 148.7 (dd, *J* = 246.7, 10.8 Hz), 139.5 (d, *J* = 3.8 Hz), 133.6 (dd, *J* = 255.7, 15.9 Hz), 129.4, 127.0 (d, *J* = 24.2 Hz), 123.6 (t, *J* = 5.2 Hz), 21.1; GC-MS 154 (M^+, 100), 153 (65), 134 (17), 133 (59), 127 (14), 115 (6), 104 (10), 91 (6), 63 (11); HRMS calcd for $C_9H_8F_2$ 154.0594, obsd 154.0585; FTIR (CCl_4) 3122 (w), 3036 (w), 2924 (w), 1698 (s), 1542 (s), 1331 (s), 1291 (m), 1137 (s), 1012 (s) cm^{-1}

(*Z*)-*p*-$CH_3(CO)C_6H_4CF$=CFH (11). According to the general procedure, *p*-$CH_3C(O)C_6H_4I$ (1.85 g, 7.5 mmol), $Pd(PPh_3)_4$, and **3** (11 mmol) were stirred 3 h at rt. Following the standard workup, chromatography on SiO_2 (90% pentane-EtOAc, R_f 0.2) gave 0.97 g (71%) of **11** as a pale-yellow solid: mp 48−49 °C; ^1H NMR ($CDCl_3$) δ 2.6 (s, 3 H), 7.1 (dd, *J* = 72.5, 16.9 Hz, 1 H), 7.5 (d, *J* = 8.4 Hz, 2 H), 7.9 (d, 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 197.0, 147.5 (dd, *J* = 247.6, 11.0 Hz), 137.4 (d, *J* = 2.3 Hz), 135.5 (dd, *J* = 261.2, 15.1 Hz), 133.2 (d, *J* = 23.4 Hz), 123.3 (t, *J* = 5.5 Hz), 128.7, 26.4; GC-MS 182 (M^+, 35), 167 (100), 139 (36), 119 (52), 99 (14), 63 (9), 43 (28); HRMS calcd for $C_{10}H_8F_2O$ 182.0543, obsd 182.0545; FTIR (CCl_4) 3122 (w), 1691 (s), 1609 (m), 1359 (m), 1267 (s), 1148 (s), 1011 (m) cm^{-1}.

(*Z*)-*m*-ClC_6H_4CF=CFH (12). According to the general procedure, *m*-ClC_6H_4I (1.55 g, 6.5 mmol), $Pd(PPh_3)_4$, and **3** (9 mmol) were stirred 2 h at rt. Following the standard workup, the solvent was removed at atmospheric pressure. Chromatography on SiO_2 (pentane, R_f 0.4) gave 0.68 g (60%) of **12** as an oil: GLPC > 99%; ^1H NMR ($CDCl_3$) δ 7.0 (dd, *J* = 71.9, 16.9 Hz, 1 H), 7.2−7.4 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 147.5 (dd, *J* = 247.8, 11.0 Hz), 134.8 (dd, *J* = 259.3, 15.1 Hz), 135.0, 130.8 (d, *J* = 23.9 Hz), 130.2, 123.8 (t, *J* = 4.7 Hz), 129.5, 121.7 (t, *J* = 4.2 Hz); GC-MS 174 (M^+, 100) 176 (M^+, 32) 139 (56), 138 (16), 120 (10), 119 (48), 99 (11), 63 (7); HRMS calcd for $C_8H_5{}^{35}ClF_2$ 174.0048, obsd 174.0063; FTIR (CCl_4) 3126 (w), 1698 (m), 1566 (s), 1327 (w), 1148 (m), 1038 (m) cm^{-1}.

(*Z*,*Z*)-*p*-(HFC=CF)C_6H_4(CF=CFH) (13). According to the general procedure, *p*-$C_6H_4I_2$ (1.65 g, 5.0 mmol), $Pd(PPh_3)_4$, and **3** (15 mmol) were stirred 2 h at rt. Following the standard workup, chromatography on SiO_2 (95% pentane−EtOAc, R_f 0.4) gave 0.81 g (80%) of **13** as a yellow solid: mp 41−42 °C; ^1H NMR ($CDCl_3$) δ 7.0 (dd, *J* = 72.3, 17.1 Hz, 2 H), 7.4 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 147.9 (dd, *J* = 246.9, 11.0 Hz), 134.6 (dd, *J* = 259.2, 15.4 Hz), 129.7 (d, 24.0 Hz), 123.8 (t, *J* = 3.8 Hz); GC-MS 202 (M^+, 100), 200 (7), 183 (5), 182 (20), 151 (36), 133 (9), 114 (3); HRMS calcd for $C_{10}H_6F_4$ 202.0406, obsd 202.0408; FTIR (CCl_4) 3122 (w), 1696 (s), 1413 (w), 1339 (m), 1296 (w), 1146 (s), 1040 (s), 1009 (m), 840 (m) cm^{-1}.

Preparation of 13 by Reaction of 3 and *p*-BrC_6H_4I, 16. According to the general procedure, **16** (1.43 g, 5.0 mmol), $Pd(PPh_3)_4$, and **3** (10 mmol) were stirred 8 h at rt. Following the standard workup, chromatography on SiO_2 (85% pentane−EtOAc, R_f **13** 0.6, R_f **17** 0.7) gave 0.33 g (33%) of **13** (mp 41−42 °C) and 0.17 g of a mixture containing **17** and **13** (**17**:**13** 1:1). Data for **17**: ^{19}F NMR ($CDCl_3$) δ −143.1 (dd, 17.6, 10.6 Hz, 1 F), −163.4 (dd, 72.4, 11.9 Hz, 1 F); ^1H NMR ($CDCl_3$) δ 6.9 (dd, 72.4, 17.0 Hz, 1 H), 7.2 (d, 8.6 Hz, 2 H), 7.5 (d, 8.4 Hz, 2 H); GC-MS 220 (M^+, 95.4), 218 (M^+, 100), 139 (38.4), 138 (18.6), 120 (16.6), 119 (84.7), 99 (26.5), 88 (11.0), 63 (10.1), 50 (11.9).

(*Z*)-*p*-$CF_3C_6H_4CF$=CFH (14). According to the general procedure, *p*-$CF_3C_6H_4I$ (3.2 g, 11.7 mmol), $Pd(PPh_3)_4$, and **3** (17 mmol) were stirred 2 h at rt. Following the standard workup, the solvent was removed at atmospheric pressure. Chromatography on SiO_2 (95% pentane−CH_2Cl_2, R_f 0.6) gave 1.7 g (70%) of **14** as an oil: GLPC 99%; ^1H NMR ($CDCl_3$) δ 7.1 (dd, *J* = 71.8, 16.9 Hz, 1 H), 7.5 (d, *J* = 8.4 Hz, 2 H), 7.6 (d, *J*

= 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 147.5 (dd, J = 247.7, 11.1 Hz), 135.3 (dd, J = 260.8, 15.0 Hz), 132.5 (d, J = 24.1 Hz), 131.3 (q, J = 33.5 Hz), 125.8, 123.5 (q, J = 272.2 Hz), 123.7 (t, J = 5.5 Hz); GC-MS 208 (M^+, 100), 189 (27), 187 (11), 169 (13), 158 (28), 139 (34), 138 (15), 119 (22), 63 (6); HRMS calcd for $C_9H_5F_5$ 208.0311, obsd 208.0289; FTIR (CCl_4) 3123 (w), 1696 (m), 1622 (w), 1334 (s), 1163 (s), 1070 (w), 1020 (m) cm^{-1}.

(*Z*)-*o*-$(CH_3)_2CHC_6H_4CF$=CFH (15). According to the general procedure, *o*-$(CH_3)_2CHC_6H_4I$ (2.46 g, 10.0 mmol), $Pd(PPh_3)_4$, and **3** (15 mmol) were stirred 8 h at 60 °C. Following the standard workup, chromatography on SiO_2 (pentane, R_f 0.5) gave 1.0 g (55%) of **15** as an oil: GLPC > 99%; ^{1}H NMR ($CDCl_3$) δ 3.2 (septet of doublets, J = 6.8, 2.8 Hz, 1 H), 1.2 (d, J = 6.8 Hz, 6 H), 6.5 (dd, J = 74.3, 16.2 Hz, 1 H), 7.1−7.3 (m, 2 H), 7.3−7.4 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 149.8 (d, J = 4.2 Hz), 148.0 (dd, J = 253.2, 9.4 H), 135.0 (dd, J = 258.5, 17.0 Hz), 131.0 (d, J = 1.8 Hz), 130.6 (t, J = 2.4 Hz), 126.7 (dd, J = 20.7, 1.8 Hz), 126.0 (d, J = 1.5 Hz), 125.7, 30.5 (d, J = 2.3 Hz), 24.0; FTIR (CCl_4) 2967 (m), 1709 (m), 1559 (s), 1449 (w), 1320 (m), 1131 (m), 1011 (m), 826 (w) cm^{-1}; GC-MS 182 (M^+, 12), 167 (100), 149 (13), 147 (85), 146 (48), 133 (23), 129 (34), 128 (13), 127 (37), 115 (18); HRMS calcd for $C_{11}H_{12}F_2$ 182.0907, obsd 182.0893.

General Procedure for Conversion of (*Z*)-α,*β*-Difluorostyrenes to (*E*)-α,*β*-Difluoro-*β*-iodostyrenes. Preparation of (*E*)-*p*-$MeOC_6H_4CF$=CFI (22). Method A. A three-necked, 50 mL flask equipped with a magnetic stir bar, N_2 source, low-temperature thermometer adapter, and septum port was charged with THF (20 mL) and 2,2,6,6-tetramethylpiperidine (1.2 g, 8.1 mmol). The solution was cooled to −20 °C via dry ice/IPA bath. *n*-BuLi (8.1 mmol, 2.5 M in hexanes) was added dropwise at ≤0 °C. The resultant LTMP solution was stirred an additional 5 min at 0 °C. A 50 mL, three-necked flask equipped with a low-temperature thermometer adapter, N_2 source, magnetic stir bar, and septum port was charged with **6** (1.05 g, 6.27 mmol), THF (20 mL), and Bu_3SnCl (2.6 g, 7.9 mmol). The solution was cooled to −78 °C via dry ice/IPA bath. The LTMP base solution was added dropwise via syringe at −78 °C. After addition was complete, the solution was stirred at −78 °C for 1 h and allowed to warm to rt. The mixture was poured into water (75 mL) and extracted with Et_2O (3 × 75 mL). The Et_2O fractions were dried ($MgSO_4$) and concentrated by rotary evaporation. Chromatography on SiO_2 (85% hexanes−EtOAc, R_f 0.6) gave 2.77 g (95%) of (*E*)-*p*-$MeOC_6H_4CF$=CF$SnBu_3$, **19a**, as an oil: ^{19}F NMR ($CDCl_3$) δ −109.7 (d, J = 5.6 Hz, 1 F), −140.6 (d, J = 5.6 Hz, 1 F), −140.6 (dd J_{FSn} = 168.5 Hz, J_{FF} = 5.6 Hz; ^{1}H NMR ($CDCl_3$) δ 0.9−1.5 (m, 27 H), 3.8 (s, 3 H), 6.9 (d, J = 9.0 Hz, 2 H), 7.3 (d, J = 9.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 160.9, 155.4 (dd, J = 258.9, 11.1 Hz), 153.2 (d, J = 308.0 Hz), 129.9, 123.3 (dd, J = 26.1, 3.2 Hz), 113.9, 55.3, 28.8, 28.8 (d, J_{CSn} = 23 Hz), 27.2, 27.2 (d, J_{CSn} = 64 Hz), 13.6, 10.8, 10.8 (d, J_{CSn} = 362 Hz); FTIR (CCl_4) 2958 (s), 2926 (s), 2873 (m), 1643 (w), 1609 (m), 1512 (s), 1458 (m), 1250 (s), 1030 (s) cm^{-1}; GC-MS 403 ($M^+ - C_4H_8$, 35), 401 (27), 399 (16), 253 (67), 251 (54), 249 (33), 177 (60), 159 (83), 150 (100), 135 (70), 107 (57), 57 (60). A two-necked, 25 mL flask equipped with a magnetic stir bar, N_2 source, and septum port was charged with I_2 (2.1 g, 8.0 mmol) and DMF (15 mL). A solution of vinylstannane **19a** (2.3 g, 5.0 mmol, in 5 mL DMF) was added in one portion via syringe, and the mixture was stirred 1 h at rt. The mixture was diluted with hexane (250 mL) and washed with saturated aq $NaHSO_3$ (75 mL). The hexane fraction was dried ($MgSO_4$) and concentrated by rotary evaporation. Chromatography on SiO_2 (85% hexanes−EtOAc, R_f 0.4) gave 1.35 g (87%, based on **6**) of **22** as a clear oil: GLPC ≥ 99%; ^{19}F NMR ($CDCl_3$) δ −102.9 (bs, 1 F), −107.6 (bs, 1 F); ^{1}H NMR ($CDCl_3$) δ 3.8 (s, 3 H), 6.9 (d, J = 8.9 Hz, 2 H), 7.5 (d, J = 8.9 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 160.9, 147.8 (dd, J = 256.7, 13.0 Hz), 130.4, 120.5 (d, J = 24.5 Hz), 113.7, 95.2 (dd, J = 325.8, 34.4 Hz), 55.3; GC-MS 296 (M^+, 77), 281 (18), 169 (12), 154 (54), 126 (100), 107 (20), 101 (16), 75 (21), 62 (17); HRMS calcd for $C_9H_7OF_2I$ 295.9510, obsd 295.9505; FTIR (CCl_4) 2960 (w), 2841 (w), 1610 (s), 1513 (s), 1255 (s), 1033 (s), 766 (s) cm^{-1}.

Method B. A three-necked, 50 mL flask equipped with a magnetic stir bar, N_2 source, and septum port was charged with 3:2 THF:Et_2O (30 mL) and **6** (1.25 g, 7.35 mmol) and cooled to −100 °C via liquid N_2/pentane bath. *n*-BuLi (9.6 mmol, 2.5 M in hexanes) was added dropwise via syringe at −95 to −100 °C. After addition was complete, the solution was stirred 30 min at −100 °C. A solution of I_2 (2.8 g, 11 mmol, in 15 mL THF) was added dropwise at −100 °C. The resultant solution was stirred an additional 30 min at −100 °C and allowed to warm to −20 °C. Dilute HCl (2 mL) was added dropwise and the solution was allowed to warm to rt. The mixture was poured into saturated aq $NaHSO_3$ (50 mL) and extracted with Et_2O (3 × 75 mL). The Et_2O fractions were dried ($MgSO_4$) and concentrated by rotary evaporation. Chromatography on SiO_2 (80% hexanes−EtOAc, R_f 0.4) gave 1.75 g (85%) of **22**: GLPC > 99%.

(*E*)-C_6H_5CF=CFI (23). Method B. Preparation of **23** was carried out according to the general procedure using **5** (0.55 g, 3.9 mmol), 1:1 THF:Et_2O (30 mL), *n*-BuLi (5.1 mmol), and I_2 (1.6 g, 6.2 mmol). Following the standard workup, chromatography on SiO_2 (pentane, R_f 0.4) gave 0.86 g (83%) of **23** as an oil: GLPC > 98%; ^{19}F NMR ($CDCl_3$) δ −101.1 (d, J = 5.1 Hz, 1 F), −109.0 (d, J = 5.1 Hz, 1 F); ^{1}H NMR ($CDCl_3$) δ 7.4 (m, 3 H), 7.6 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 147.9 (dd, J = 257.0, 12.8 Hz), 130.3, 128.8 (d, J = 7.0 Hz), 128.7, 128.3, 96.1 (dd, J = 362.2, 33.6 Hz); GC-MS 266 (M^+, 100.0), 140 (3.3), 139 (33.3), 138 (11.3), 127 (5.1), 119 (35.8), 99 (14.4), 75 (3.7), 63 (7.1); FTIR (CCl_4) 3063 (w), 1653 (m), 1495 (w), 1446 (w), 1302 (m), 1280 (m), 1130 (s), 1057 (s), 1025 (m), 884 (s) cm^{-1}; HRMS calcd for $C_8H_5F_2I$ 265.9404, obsd 265.9391.

(*E*)-*p*-$CH_3C_6H_4CF$=CFI (24). Method B. Preparation of **24** was carried out according to the general procedure using **9** (2.3 g, 14.9 mmol), 3:2 THF:Et_2O (50 mL), *n*-BuLi (19.5 mmol), and I_2 (6.1 g, 24 mmol). Following the standard workup, chromatography on SiO_2 (pentane, R_f 0.4) gave 2.7 g (65%) of **24** as an oil: GLPC > 98%; ^{19}F NMR ($CDCl_3$) δ −102.2 (d, J = 4.2 Hz, 1 F), −108.6 (d, J = 4.2 Hz, 1 F); ^{1}H NMR $CDCl_3$) δ 2.4 (s, 3 H), 7.2 (d, J = 8.0 Hz, 2 H), 7.5 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 148.0 (dd, J = 256.6, 12.8 Hz), 140.6, 129.0, 128.7 (t, J = 3.4 Hz), 125.7 (d, J = 24.0 Hz), 95.7 (dd, J = 325.9, 34.2 Hz), 21.4; FTIR (CCl_4) 3036 (w), 2925 (w), 1657 (m), 1612 (m), 1514 (m), 1300 (s), 1130 (s), 1052 (s), 886 (s) cm^{-1}; GC-MS 280 (M^+, 100.0), 153 (20.6), 151 (35.9), 138 (13.1), 133 (79.4), 127 (31.9), 125 (52.2), 107 (9.1), 101 (7.5), 75 (10.3); HRMS calcd for $C_9H_7F_2I$ 279.9561, obsd 279.9587.

(*E*)-*o*-$(CH_3)_2CHC_6H_4CF$=CFI (25). Method B. Preparation of **25** was carried out according to the general procedure using **15** (0.75 g, 4.1 mmol), 1:1 THF:Et_2O (20 mL), *n*-BuLi (5.3 mmol), and I_2 (1.7 g, 6.6 mmol). Following the standard workup, chromatography on SiO_2 (pentane, R_f 0.5) gave 0.67 g (54%) of **25** as an oil: GLPC 98%; ^{19}F NMR ($CDCl_3$) δ −98.1 (bs, 1 F), −103.5 (bs, 1 F); ^{1}H NMR ($CDCl_3$) 1.2 (d, J = 7.0 Hz, 6 H), 3.1 (septet of doublets, J = 2.5 Hz, 1 H), 7.1−7.5 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 149.8 (d, J = 3.4 Hz), 147.5 (dd, J = 263.0, 11.0 Hz), 132.0 (dd, J = 3.4, 1.2 Hz), 131.5 (d, J = 3.0 Hz), 98.6 (dd, J = 329.6, 33.6 Hz), 127.5 (d, J = 21.0 Hz), 126.5 (d, J = 12.5 Hz), 126.0 (dd, J = 4.5, 2.1 Hz), 30.9, 24.0; FTIR (CCl_4) 2967 (s), 2871 (w), 1676 (m), 1457 (m), 1295 (s), 1267 (m) 1128 (s), 1026 (s), 872 (s) cm^{-1}; GC-MS 308 (M^+, 8.7), 181 (44.1), 166 (19.5), 165 (23.3), 164 (19.5), 151 (49.3), 146 (100.0), 133 (28.7), 115 (29.2); HRMS calcd for $C_{11}H_{11}F_2I$ 307.9874, obsd 307.9862.

(*E*)-*p*-$CF_3C_6H_4CF$=CFI (26). Method A. Preparation of **26** was carried out according to the general procedure using **14** (1.7 g, 8.2 mmol), Bu_3SnCl (3.25 g, 10.0 mmol), THF (25 mL), and a solution of LTMP prepared from 2,2,6,6-tetramethylpiperidine (1.50 g, 10.4 mmol), *n*-BuLi (10.4 mmol), and THF (20 mL). Following the standard workup, chromatography on SiO_2 (85% hexanes−EtOAc, R_f 0.7) gave 3.9 g (96%) of (*E*)-*p*-$CF_3C_6H_4CF$=CF$SnBu_3$, **19b**, as an oil: ^{19}F NMR ($CDCl_3$) δ −135.0 (bs, 1 F), −135.0 (d, J_{FSn} = 192 Hz), −115.5 (bs, 1 F), −64.6 (s, 3 F); ^{1}H NMR ($CDCl_3$) δ 0.8−1.5 (m, 27 H), 7.5 (d, J = 8.2 Hz, 2 H), 7.6 (d, J = 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 156.4 (d, J = 312.0 Hz), 154.6 (dd, J = 269.0, 12.3 Hz), 134.7 (d, J = 26.9 Hz), 131.6 (q, J = 32.9 Hz), 127.8 (t, J = 3.2 Hz), 125.5 (q, J = 3.6 Hz), 123.9 (q, J = 271.7 Hz), 28.9 (d, J_{CSn} = 22 Hz), 27.2 (d, J_{CSn} = 54 Hz), 13.6, 11.0 (d, J_{CSn} = 366 Hz); FTIR (CCl_4) 2960 (s), 2926 (s), 2855 (m), 1326 (s), 1173 (m),

1137 (m), 1070 (s), 847 (m) cm^{-1}. Conversion of **19b** to **26** was carried out using **19b** (3.9 g, 7.85 mmol), I_2 (3.20 g, 12.6 mmol), and DMF (20 mL). Following analogous workup, the residue was twice chromatographed on SiO_2 (pentane, R_f 0.5) to give 3.0 g of an oil containing **26** and Bu_3SnI (**26**:Bu_3SnI 1.6:1.0) and an additional 0.83 g (30%) of **26** as an analytically pure sample: GLPC > 99%; ^{19}F NMR ($CDCl_3$) δ −63.6 (s, 3 F), −97.5 (d, J = 4.2 Hz, 1 F), −111.0 (d, J = 4.2 Hz, 1 F); ^1H NMR ($CDCl_3$) δ 7.7 (d, J = 8.3 Hz, 2 H), 7.8 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 146.9 (dd, J = 257, 14 Hz), 132.4 (d, J = 23 Hz), 132.3 (q, J = 32.8 Hz), 129.0 (t, J = 3.5 Hz), 125.5 (q, J = 1.9 Hz), 123.7 (q, J = 272 Hz), 97.4 (dd, J = 328, 32 Hz); GC-MS 334 (M^+, 58), 315 (6), 207 (35), 133 (13), 187 (67), 156 (11), 142 (17), 138 (100), 69 (13); HRMS calcd for $C_9H_4F_5I$ 333.9278, obsd 333.9283; FTIR (CCl_4) 2959 (m), 2928 (m), 2860 (w), 1326 (s) 1175 (s), 1138 (s), 1074 (s), 886 (m) cm^{-1}.

Method B. Preparation of **26** was carried out according to the general procedure using **14** (1.37 g, 6.6 mmol), 1:1 THF:Et_2O (50 mL), *n*-BuLi (8.6 mmol), and I_2 (2.7 g, 10.6 mmol). Following the standard workup, chromatography on SiO_2 (pentane, R_f 0.5) gave 1.78 g (81%) of **26**: GLPC > 99%.

(*E*)-*p*-$CO_2EtC_6H_4CF$═CFI (27). Method A. Preparation of **27** was carried out according to the general procedure using **10** (1.21 g, 5.7 mmol), THF (25 mL), Bu_3SnCl (2.3 g, 7.1 mmol), and a solution of LTMP prepared from 2,2,6,6-tetramethylpiperidine (1.05 g, 7.4 mmol) and *n*-BuLi (7.5 mmol) in 10 mL of THF. The reaction mixture containing the intermediate (*E*)-*p*-$CO_2EtC_6H_4CF$═CF$SnBu_3$, **19c**, was treated directly with I_2 (2.3 g, 9.1 mmol) at rt and stirred overnight. Following the standard workup, chromatography on SiO_2 (80% hexanes−EtOAc, R_f 0.45) gave 1.49 g (77%) of **27** as yellow-orange solid: mp 44 °C; ^{19}F NMR ($CDCl_3$) δ −97.7 (d, J = 5.7 Hz, 1 F), −111.1 (d, J = 5.7 Hz, 1 F); ^1H NMR ($CDCl_3$) δ 8.1 (d, J = 8.1 Hz, 2 H), 7.7 (d, J = 8.3 Hz, 2 H), 4.4 (q, J = 7.0 Hz, 2 H), 1.4 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.5, 147.2 (dd, J = 256.3, 13.8 Hz), 132.5 (d, J = 23.8 Hz), 131.8, 129.4, 128.4 (t, J = 3.3 Hz), 97.1 (dd, J = 328.1, 32.4 Hz), 61.3, 14.2; GC-MS 338 (M^+, 47.4), 310 (31.9), 293 (100.0), 265 (9.9), 183 (3.2), 138 (81.0), 119 (14.0), 112 (10.5), 88 (17.5), 87 (14.3); FTIR (CCl_4) 2983 (m), 2961 (m), 2931 (m), 1726 (s), 1408 (w), 1276 (s), 1108 (s), 1054 (s), 888 (m) cm^{-1}; HRMS calcd for $C_{11}H_9F_2IO_2$ 337.9615, obsd 337.9611.

Method B. Preparation of **27** was carried out according to the general procedure using **10** (1.04 g, 4.95 mmol), 3:2 THF:Et_2O (30 mL), a solution of LTMP prepared from 2,2,6,6-tetramethylpiperidine (0.88 g, 6.2 mmol) and *n*-BuLi (6.2 mmol) in 10 mL of THF, and I_2 (2.0 g, 8.0 mmol). Following the standard workup, chromatography on SiO_2 (75% hexanes−EtOAc, R_f 0.5) gave 0.56 g (39%) of **27**.

(*E*)-*m*-ClC_6H_4CF═CFI (28). Method A. Preparation of **28** was carried out according to the general procedure using **12** (0.39 g, 2.24 mmol), 3:2 THF:Et_2O (30 mL), Bu_3SnCl (0.93 g, 2.86 mmol), and a solution of LTMP prepared from 2,2,6,6-tetramethylpiperidine (0.41 g, 2.9 mmol) and *n*-BuLi (2.9 mmol) in 10 mL of THF. The reaction mixture containing the intermediate (*E*)-*m*-ClC_6H_4CF═CF$SnBu_3$, **19d**, was treated directly with I_2 (1.4 g, 5.5 mmol) at rt and stirred overnight. Following the standard workup, chromatography on SiO_2 (hexane, R_f 0.5) gave 0.56 g (85%) of **28** as an oil: GLPC 93%; ^{19}F NMR ($CDCl_3$) δ −98.7 (d, J = 5.1 Hz, 1 F), −110.1 (d, J = 5.1 Hz, 1 F); ^1H NMR ($CDCl_3$) δ 7.3−7.4 (m, 2 H), 7.5 (m, 1 H), 7.6 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 146.7 (dd, J = 256.9, 13.7 Hz), 140.2, 134.4, 130.3, 129.6, 128.6 (t, J = 3.6 Hz), 126.8 (t, J = 3.4 Hz), 96.8 (dd, J = 328.1, 33.0 Hz); FTIR (CCl_4) 3072 (w), 1653 (w), 1558 (s), 1479 (w), 1415 (w), 1286 (m), 1134 (s), 1062 (s), 906 (s) cm^{-1}; GC-MS 300 (M^+, 64.4), 302 (M^+, 21.5), 173 (31.3), 175 (10.5), 139 (9.4), 138 (100.0), 127 (9.1), 118 (6.3), 88 (7.8), 87 (15.1).

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Supporting Information Available: Copies of NMR spectra for compounds **5**−**15**, **17**, and **22**−**28** (42 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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