Coupling of 2-Substituted 1-Fluorovinylstannanes with Organic Halides Catalyzed by Palladium(0)/Copper(I) Iodide. A Mild and Stereospecific Method to Monofluoroolefins

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The palladium-catalyzed cross-coupling reactions of (*E*)- or (*Z*)-1-fluorovinylstannanes with aryl iodides and vinyl iodides provide good yields of stereoisomerically pure substituted fluoroolefins with retention of the double bond geometry. The reaction takes place with copper(I) iodide present as a cocatalyst at ambient temperature or in refluxing tetrahydrofuran and is tolerant of a variety of functional groups. Highly functionalized and stereoisomerically pure monofluorovinyl ketones also were obtained under mild conditions by the coupling of 1-fluorovinylstannanes with acid chlorides. ^{1}H-{^{19}F} NOE NMR experiments unequivocally established the stereochemistry of the coupling products *E*-**14** and *Z*-**14**.

Introduction

There has been considerable interest in fluoroorganic compounds as agrochemical and pharmaceutical agents.[1] It is believed that fluorine alters the physiochemical properties of organic compounds, thereby modifying biological activity.[2] This has been particularly true for olefins, and new methods for the synthesis of fluoroolefins have received considerable attention.[3] The use of 1-fluorovinylstannanes has provided an entry to monosubstituted 2-fluoro-1-olefins. The palladium-catalyzed cross-coupling of 2-trimethylsilyl-1-fluorovinylstannane (**1b**) with aryl iodides or acid chlorides[4] under Stille coupling conditions[5] has been demonstrated to be useful for the design and synthesis of mechanism-based enzyme inhibitors containing 2-fluorinated terminal olefins.[6] A similar coupling reaction of an unsubstituted 1-fluorovinylstannane (**1a**) with an acid chloride, aryl iodide, or aryl triflate was subsequently developed to avoid the removal of the somewhat capricious trimethylsilyl group.[7] It should be noted that 1-fluorovinylstannane enol ethers have proved useful for the synthesis of monoofluorovinyl ethers as well. Shi and co-workers[8] reported the synthesis of β-fluorophenylalanine via palladium-catalyzed cross-coupling of ethyl 3-fluoro-3-tributylstannyl-2-methoxyacrylate (**1c**) with aryl iodides or triflates. Percy and Wilkes[9] demonstrated in an informative paper the utility of 1-lithio-1-fluorovinyl enol ethers, derived from trifluoroethanol, for the synthesis of substituted analogues. Interestingly, the corresponding fluorovinylstannane ether obtained by reacting the 1-lithio-1-fluorovinyl enol ether with tributyltin chloride provided only moderate yields of coupling products with aryl iodides. However, it was felt that 2-substituted-1-fluorovinylstannanes would be an efficient synthetically equivalent 1-fluoroalkene anion for the synthesis of di- and trisubstituted fluoroolefins based on the successful synthesis of terminal 1-fluoro-2-substituted olefins.[4,6,7] Such fluorovinylstannanes would be an alternative for labile 1-fluoro-1-lithioalkenes.[3b,3c] Herein, we report the scope of the stereospecific palladium-catalyzed cross-coupling reactions of 2-monosubstituted- and 2,2-disubstituted-1-fluorovinylstannnanes with aryl iodides and acid chlorides to form multisubstituted monofluoroolefins. A portion of this work was published as a communication.[10]

Results and Discussion

The condensations of carbonyl compounds with the in situ generated Horner−Wittig reagent formed between fluoromethyl phenyl sulfone[11] and diethyl chlorophosphate in the presence of lithium hexamethyldisilazane

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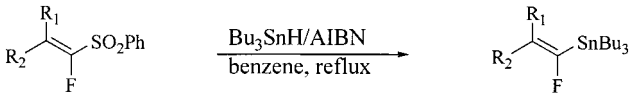
Scheme 1



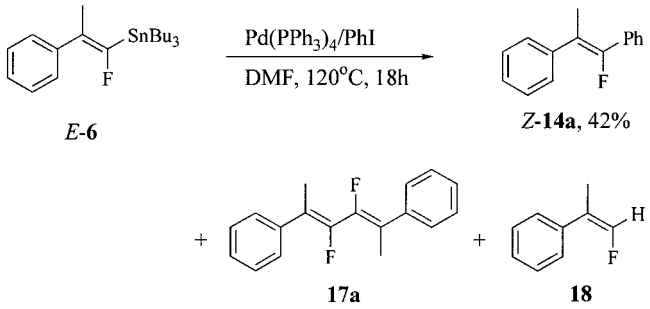
2a-f **1, 3-8**

		R^1	R^2
	1a	H	H
	1b	H	Me_3Si
	1c	COOEt	MeO
2a	**3**	H	Ph
2b	**4**	H	6,8-Dichlorochrom-4-on-3-yl
2c	**5**	H	Cyclohexyl
E-**2d**	*E*-**6**	Me	Ph
Z-**2d**	*Z*-**6**	Ph	Me
2e	**7**	Me	$PhCH_2CH_2$-
2f	**8**	Ph	Ph

proceeded readily to give 1-fluorovinyl sulfones **2a**−**f**.[12,18a] The *E*- and *Z*-isomers were easily separated on a silica gel column. Reaction of the 1-fluorovinyl sulfones with 2 equiv of tributyltin hydride in refluxing benzene[13] afforded the required 1-fluorovinylstannanes **3**−**8** in good to excellent yields (Scheme 1).[3a] This transformation is stereoselective when the 1-fluorovinyl sulfone is 2,2-disubstituted. The two stereoisomers of 2-monosubstituted-1-fluorovinylstannanes were separable by silica gel chromatography. The *E* configuration of the fluorovinylstannanes **3**−**5** were established on the basis of the $^3J_{H-F}$ coupling constant (about 60 Hz).[14] The stereochemistry of **6** was determined by ^1H-{^{19}F} NOE NMR experiments, which were reported earlier for compound **7**.[3a]

The palladium-catalyzed coupling reaction of organostannanes with organic halides and sulfonates,[5,15] known as Stille coupling, has already been established as an efficient stereospecific method for the formation of carbon−carbon bonds under mild conditions. In an effort to arrive at the optimum conditions for the coupling of **3**−**8**, a variety of reaction conditions (catalyst, solvent, and temperature) were tried using (*E*)-1-fluoro-2-phenylpropenyltributylstannane (*E*-**6**) and iodobenzene (**9a**) or 4′-iodoacetophenone (**9b**) (Table 1). Initial attempts at coupling 1-fluorovinylstannane *E*-**6** with iodobenzene under standard Stille conditions [$Pd(PPh_3)_4$ (5 mol %), THF, reflux] only gave the expected cross-coupling product, (*Z*)-1,2-diphenyl-1-fluoropropene (*Z*-**14a**), in 10% yield after 18 h, while most of the starting material remained unchanged (entry 13). The lower reactivity of 1-fluorovinylstannane *E*-**6**, compared with the corresponding nonfluorinated vinylstannanes, apparently is due to the electronic effects of fluorine. Also, *E*-**6** is less reactive than the unsubstituted 1-fluorovinylstannane (**1a**), as would be expected on the basis of steric effects.[7] The coupling reaction of *E*-**6** with iodobenzene proceeded in 42% isolated yield when carried out in DMF at 120 °C for 18 h to give *Z*-**14a** (entry 14). 1,4-Dimethyl-1,4-diphenyl-2,3-difluorobutadiene (**17a**) was also isolated as the result of homocoupling of the starting tin compound,

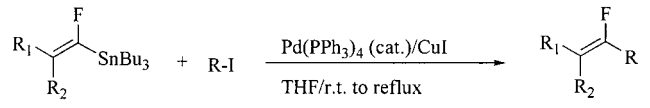
Scheme 2



E-**6** *Z*-**14a**, 42%

17a **18**

Scheme 3



3-8 **9a-g** **11-16**

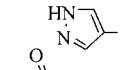
9a: R = Ph-

9b: R = 4-AcC_6H_4-

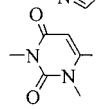
9c: R = 4-ClC_6H_4-

9d: R = 4-$MeOC_6H_4$-

9e: R =



9f: R =



9g: R = *trans*-BuCH=CH-

9h: R = *trans*-EtOOCCH=CH-

along with the reduced product, 1-methyl-2-fluorostyrene (**18**) (Scheme 2). The modest yields and sluggish nature of the coupling are consistent with results reported by Percy[9] for the condensation of monofluorovinylstannane enol ethers with aryl iodides.

It has been reported that copper(I) iodide cocatalyst accelerates sluggish or otherwise unsuccessful Stille coupling reactions.[16] When 1-fluorovinylstannane *E*-**6** was coupled with 4′-iodoacetophenone (**9b**) in refluxing THF under nitrogen for 30 min, using 5 mol % of $Pd(PPh_3)_4$ and 1 equiv of CuI as the cocatalyst, the desired coupling product *Z*-**14b** was isolated in 83% yield (entry 15). The effect of CuI cocatalyst was demonstrated by the following coupling results. CuI alone as the catalyst did not yield *Z*-**14b** from *E*-**6** and 4′-iodoacetophenone (**9b**) (entry 16), and $Pd(PPh_3)_4$ alone only gave 10% of the coupling product in refluxing THF (entry 13). The Pd(0)/CuI-cocatalyzed coupling reaction also proceeded at ambient temperature with a longer reaction time (entry 17). The results obtained from the coupling reaction of 1-fluorovinylstannanes **3**−**8** with a variety of halides (Scheme 3) are summarized in Table 1. The cross-coupling reaction of (*E*)-1-fluoro-2-phenylvinyltributylstannane (**3**) with a variety of aryl iodides (entries 1−6) proceeded smoothly to give the substituted fluoroolefins **11a**−**f** as single geometric isomers in good to excellent yields. With electron-rich aryl iodides, the reaction was slower and yields were slightly lower (see entries 4 and 6). It should be noted that coupling reactions with 4-iodoanisole (entries 4 and 18) yielded homocoupling product **17b** or **17a** in addition to the desired product. More homocoupling was observed when both an electron rich aromatic iodide and sterically hindered vinylstannane were used (entry 18). In addition to aryl iodides, compound **3** was coupled with (*E*)-1-iodo-1-hexene (**9g**)

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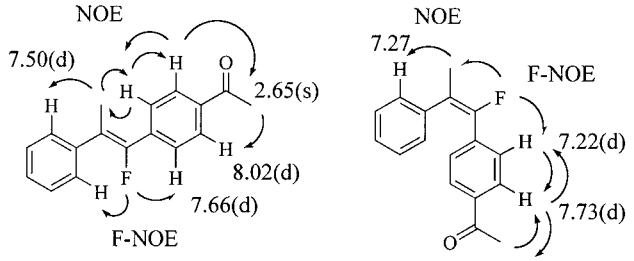
Table 1. Palladium(0)/CuI-Catalyzed Coupling Reactions of 1-Fluorovinylstannanes with Organic Halides

entry	vinylstannanes **3**−**7**	RI or RCOCl	catalyst	solv/T (°C)	hours	product	yield (%)[d]	dimer **17** (%)
1	(*E*)-PhCH=CFSnBu$_3$ (**3**)	PhI (**9a**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	1	(*Z*)-PhCH=CFPh (**11a**)	86	
2		*p*-CH$_3$COC$_6$H$_4$I (**9b**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	0.5	(*Z*)-PhCH=CFC$_6$H$_4$COCH$_3$-*p* (**11b**)	90	
3		*p*-ClC$_6$H$_4$I (**9c**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	1	(*Z*)-PhCH=CFC$_6$H$_4$Cl-*p* (**11c**)	91	
4		*p*-CH$_3$OC$_6$H$_4$I (**9d**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	3	(*Z*)-PhCH=CFC$_6$H$_4$OCH$_3$-*p* (**11d**)	71	12 (**17b**)
5		5-iodo-1,3-dimethylpyrimidone (**9e**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	2	(*Z*)-PhCH=CFAr^2 (**11e**)[b]	89	
6		3-iodopyrazole (**9f**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	4	(*Z*)-PhCH=CFAr^3 (**11f**)[c]	67	
7		*trans*-ICH=CHBu (**9g**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	2	(*Z*,*E*)-PhCH=CFCH=CHBu (**11g**)	83	
8		PhCOCl (**10a**)	Pd(PPh$_3$)$_4$/CuI	THF/rt	1	(*Z*)-PhCH=CFCOPh (**11h**)	92	
9		EtOCOCl (**10c**)	Pd(PPh$_3$)$_4$/CuI	THF/rt	16	(*Z*)-PhCH=CFCOOEt (**11i**)	0	89 (**17b**)
10	(*E*)-Ar^{1}CH=CFSnBu$_3$ (**4**)a	*trans*-ICH=CHCOOEt (**9h**)	Pd(PPh$_3$)$_4$/CuI	THF/rt	16	(*Z*,*E*)-Ar^{1}CH=CFCH=CHCOOEt (**12a**)[a]	68	
11		PhCOCl (**10a**)	Pd(PPh$_3$)$_4$	THF/rt	6	(*Z*)-Ar^{1}CH=CFCOPh (**12b**)[a]	48	
12	(*E*)-*c*-HexylCH=CFSnBu$_3$ (**5**)	*p*-CH$_3$COC$_6$H$_4$I (**9b**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	4	(*Z*)-*c*-HexylCH=CFC$_6$H$_4$COCH$_3$-*p* (**13**)	72	
13	(*E*)-PhMeC=CFSnBu$_3$ (*E*-**6**)	PhI (**9a**)	Pd(PPh$_3$)$_4$	THF/reflux	18	(*Z*)-PhCMe=CFC$_6$H$_5$ (*Z*-**14a**)	10	
14			Pd(PPh$_3$)$_4$	DMF/120	18	*Z*-**14a**	42	
15		*p*-CH$_3$COC$_6$H$_4$I (**9b**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	0.5	(*Z*)-PhCMe=CFC$_6$H$_4$COCH$_3$-*p* (*Z*-**14b**)	83	
16			CuI	THF/reflux	1	*Z*-**14b**	0	0
17			Pd(PPh$_3$)$_4$/CuI	THF/rt	16	*Z*-**14b**	90[e]	
18		*p*-CH$_3$OC$_6$H$_4$I (**9d**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	1	(*Z*)-PhCMe=CFC$_6$H$_4$OCH$_3$-*p* (*Z*-**14c**)	50	37 (**17a**)
19		PhCOCl (**10a**)	Pd(PPh$_3$)$_4$	THF/reflux	5	(*Z*)-PhCMe=CFCOPh (*Z*-**14d**)	50	
20		PhCH$_2$CH$_2$COCl (**10b**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	0.25	(*Z*)-PhCMe=CFCOCH$_2$CH$_2$Ph (*Z*-**14e**)	82	
21		EtOCOCOCl (**10d**)	Pd(PPh$_3$)$_4$/CuI	THF/rt	3	(*Z*)-PhCMe=CFCOCOOEt (*Z*-**14f**)	0	54% (**17a**)[f]
22	(*Z*)-PhMeC=CFSnBu$_3$ (*Z*-**6**)	*p*-CH$_3$COC$_6$H$_4$I (**9b**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	12	(*E*)-PhCMe=CFC$_6$H$_4$COCH$_3$-*p* (*E*-**14b**)	75	
23		PhCH$_2$CH$_2$COCl (**10b**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	1	(*E*)-PhCMe=CFCOCH$_2$CH$_2$Ph (*E*-**14e**)	78	
24	(*Z*)-PhCH$_2$CH$_2$CMe=CFSnBu$_3$ (**7**)	PhI (**9a**)	Pd(PPh$_3$)$_4$	DMF/120	18	(*E*)-PhCH$_2$CH$_2$CMe=CFPh (**15**)	45	
25	Ph$_2$C=CFSnBu$_3$ (**8**)	*p*-CH$_3$COC$_6$H$_4$I (**9b**)	Pd(PPh$_3$)$_4$/CuI	THF/reflux	6	Ph$_2$C=CFC$_6$H$_4$COCH$_3$-*p* (**16**)	87	

[a] Ar^1 = 6,8-dichlorochrom-4-on-3-yl. [b] Ar^2 = 1,3-dimethylpyrimidon-5-yl. [c] Ar^3 = pyrazol-4-yl. [d] Isolated yield. [e] Yield was estimated on the basis or ^{19}F NMR. [f] (*E*)-1-Methyl-2-fluorostyrene (**18**, 28% yield) was also isolated.



Z-14b δ: 2.19 ppm (d, J = 3.0Hz, Me) ^{19}F: -104.8 ppm

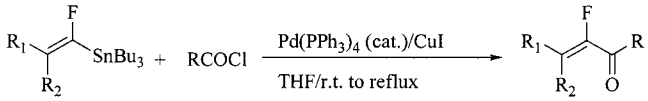
E-14b δ: 2.20 ppm (d, J = 4.0Hz, Me) ^{19}F: -107.4 ppm

Figure 1. Summary of proton NOE and ^{1}H-{^{19}F} NOE NMR experiments. Normal NOE:→ Fluorine NOE:⇀.

to afford the diene **11g** in 83% yield (entry 7) with retention of double bond geometry present for both coupling partners, and with benzoyl chloride to afford ketone **11h** in 92% yield (entry 8). Attempts to couple **3** with ethyl chloroformate gave only the dimerized product **17b** in 89% yield (entry 9). (*E*)-1-Fluoro-2-cyclohexylvinyltributylstannane (**5**) demonstrated similar reactivity as **3** and coupled with 4′-iodoacetophenone (**9b**) to afford compound **13** in 72% yield (entry 12). In all cases, only a single isomer was isolated from the coupling reaction. The *Z* stereochemistry of products **11**−**13** was readily assigned on the basis of the $J_{H,F}$ coupling constant between 39 and 46 Hz and by comparison with model compounds.[14]

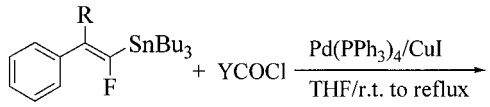
The palladium/copper(I) iodide cocatalyzed coupling reaction of 2,2-disubstituted-1-fluorovinylstannanes **6**−**8** with a variety of aryl iodides **9** in THF at room temperature or reflux gave the corresponding fluoroolefins as single geometric isomers in good yields (entries 15, 18, 22, and 25). Thus, coupling of *E*-**6** with 4′-iodoacetophenone (**9b**) gave *Z*-**14b** in 83% yield (entry 15). Similarly, reaction of *Z*-**6** with **9b** gave the corresponding *E*-**14b** in 75% yield (entry 22), although the reaction of *E*-**6** proceeded much faster than that of *Z*-**6**, which is consistent with increased steric hindrance for *Z*-**6**. Without copper(I) iodide, the coupling reactions required higher temperatures (DMF/120 °C) and gave lower yields (entries 14 and 24). The assignments for the geometric isomers of **14** and **15** were not straightforward. On the basis of the uniformity of the Stille coupling mechanism[5] and the well-established stereochemistry[3a] for the 1-fluorovinylstannanes, the *E* and *Z* configurations initially were assumed for compounds **14** and **15**. Proton NMR experiments show a NOE between the vinyl methyl group and the *ortho*-proton on the acetylphenyl group of *Z*-**14b** but not *E*-**14b** (Figure 1). Thus, for *Z*-**14b** when the vinyl methyl (δ 2.19 ppm) was irradiated, NOEs were observed for *ortho*-protons on both phenyl rings (at 7.50 and 7.66 ppm, respectively). However, for *E*-**14b**, only one NOE was observed for *ortho*-protons (at 7.27 ppm) on the unsubstituted phenyl ring. The results of proton NOE NMR experiments are summarized in Figure 1. We applied the ^{1}H-{^{19}F} NOE NMR technique to confirm the retention of configuration for the conversion of tin compounds *E*-**6** and *Z*-**6**[3a] to *Z*-**14b** and *E*-**14b.** Thus, by irradiation of the fluorine (at −104.8 ppm) on *Z*-**14b**, a strong NOE was observed on the *ortho*-protons of both phenyl groups (at 7.50 and 7.66 ppm) but not the vinyl methyl group (δ 2.19 ppm). Alternatively, by irradiation of the fluorine (at −107.4 ppm) on *E*-**14b**, a strong NOE

Scheme 4



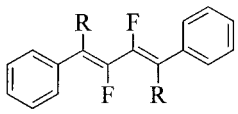
3, 4, 6 **10a**: R = Ph **10b**: R = $PhCH_2CH_2$ **11h, 12b, 14d, 14e**

Scheme 5



***E*-6**, R = Me **10c**: Y = EtOCO

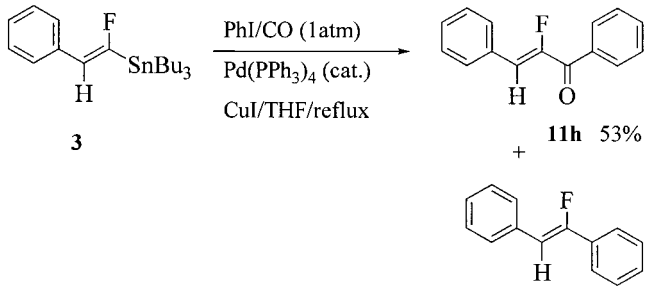
3, R = H **10d**: Y = EtO



17a, R = Me, 54%

17b, R = H, 89%

Scheme 6



3

11h 53%

+

11a 36%

was observed on the vinyl methyl group (δ 2.20 ppm) and the *ortho*-protons of acetylphenyl group (δ 7.22 ppm) but not the unsubstituted phenyl group.

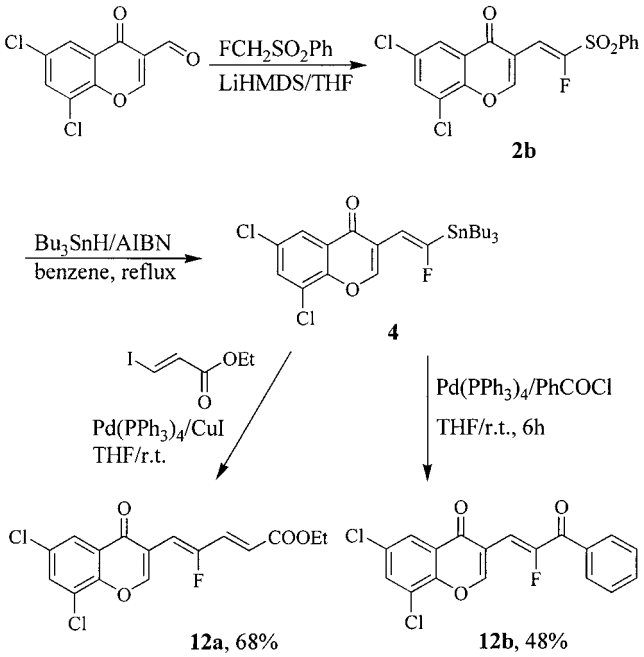
The palladium-catalyzed cross-coupling reactions of 1-fluorovinylstannanes *E*-**6** and *Z*-**6** with acid chlorides **10a** and **10b** were carried out under the same conditions[17] to afford α-fluoro-α,β-unsaturated ketones **14** in good yields (entries 19, 20, and 23) (Scheme 4). Attempts to couple *E*-**6** with ethyl oxalyl chloride or ethyl chloroformate provided only the homocoupling product 1,4-dimethyl-1,4-diphenyl-2,3-difluorobutadiene (**17a**) (Scheme 5).

Coupling of 1-fluorovinylstannane **3** with iodobenzene (**9a**) under a carbon monoxide atmosphere gave the direct coupling product **11a** and CO insertion product **11h** in 36% and 53% yield, respectively (Scheme 6). Although 1-fluorovinyltributylstannanes **1a** and **1c** also are reported to couple with 4-acetylphenyl triflate,[7,8] reaction of **3** with phenyl triflate failed under similar conditions (with or without CuI) even in the presence of 2 equiv of LiCl, and the only isolated product was (*E*,*E*)-1,4-diphenyl-2,3-difluorobutadiene (**17b**).

Chromones are present in a variety of biologically active molecules. 3-Formylchromones are readily available and useful intermediates for various derivatives. Condensation of 6,8-dichloro-3-formylchromone with flu-

(17) For the palladium-catalyzed coupling reaction of organotins with acid chlorides, see: (a) Milstein, D.; Stille, J. K. *J. Org. Chem.* **1979**, *44*, 1614. (b) Labadie, J.; Tueting, D.; Stille, J. K. *J. Org. Chem.* **1983**, *48*, 4634.

Scheme 7



oromethyl phenyl sulfone under the reaction conditions described above afforded the vinyl sulfone **2b**, which was converted to the corresponding fluorovinylstannane **4**. Palladium(0)/copper iodide catalyzed cross-coupling reaction of **4** with ethyl 3-iodoacrylate (**9h**) gave the diene derivative **12a** in 68% isolated yield (Scheme 7). Similarly, coupling of **4** with benzoyl chloride afforded the ketone derivative **12b** in 48% yield. It should be noted that these highly functionalized chromones are potentially useful intermediates for the synthesis of biologically active fluorinated molecules.

Conclusion

A palladium/copper-cocatalyzed cross-coupling reaction of 1-fluorovinylstannanes (**3**−**8**) with a variety of aryl iodides has been developed that affords substituted monofluoroolefins **11**−**16** with the same double bond geometry present in the coupling partners. The reaction takes place with CuI present as a cocatalyst at ambient temperature or in refluxing tetrahydrofuran. Many functional groups are tolerated on the substrates. Highly functionalized and stereoisomerically pure monofluoroolefins were obtained under mild conditions by the cross-coupling of the appropriate organic halides with the 1-fluorovinylstannanes. When the coupling reaction was carried out under a carbon monoxide atmosphere or with an acid chloride as the substrate, α-fluoro-α,β-unsaturated ketones were obtained stereospecifically in good yield. This mild, selective, and general method will be useful for the synthesis of a wide variety of new monofluoroolefins.

Experimental Section

General. (*E*)-1-Fluoro-1-phenylsulfonyl-2-(phenethyl)propene (**2e**), (*E*)-1-fluoro-1-tributylstanyl-2-(phenethyl)propene (**7**), and 1-fluoro-1-tributylstanyl-2,2-diphenylethene (**8**) were synthesized by literature procedures.[3,12,18]

1-Fluorovinyl Sulfone 2a−**d.** The following 1-fluorovinyl sulfones were synthesized from fluoromethylphenyl sulfone and aldehydes or ketones as reported.[12,18]

(*E*)-1-Fluoro-1-phenylsulfonyl-2-phenylethene (2a). White solid (lit. mp 77.5−78.5 °C[12,18]), 80% yield. ^{1}H NMR: 7.05 (d, $J_{H,F}$ = 30 Hz, 1H), 7.38 (m, 3H), 7.58 (m, 5H), 8.01 (d, J = 7.8 Hz, 2H). Anal. Calcd for $C_{14}H_{11}FO_2S$ (262.3): C, 64.11; H, 4.23. Found: C, 63.85; H, 4.50.

(*E*)-6,8-Dichloro-3-(2-fluoro-2-phenylsulfonylvinyl)-4-chromone (2b). Yellow solid, mp 212−214 °C, 49% yield. ^{1}H NMR: 7.50 (d, J = 36 Hz, 1H), 7.62 (t, J = 7.8 Hz, 2H), 7.73 (t, J = 7.8 Hz, 1H), 7.76 (d, J = 2.4 Hz, 1H), 8.03 (d, J = 7.8 Hz, 2H), 8.12 (d, J = 2.4 Hz, 1H), 8.55 (s, 1H). ^{19}F NMR: −117.9 (d, J = 36.7 Hz). CIMS: *m/e* 399 (M + H). Anal. Calcd for $C_{17}H_9Cl_2FO_4S$ (399.22): C, 51.15; H, 2.27. Found: C, 50.91; H, 2.34.

(*E*)-1-Fluoro-1-phenylsulfonyl-2-cyclohexylethene (2c). Colorless oil, 76% yield. ^{1}H NMR: 1.10−1.70 (m, 10 H), 2.42 (m, 1H), 6.11 (dd, J = 9.7 Hz, 33.5 Hz, 1H), 7.53 (m, 2H), 7.62 (m, 1H), 7.90 (m, 2H). ^{19}F NMR: −128.3 (d, J = 33.4 Hz). MS (EI): *m/e* 268 (M^+). Anal. Calcd for $C_{14}H_{17}FO_2S$ (268.35): C, 62.66; H, 6.39. Found: C, 62.60; H, 6.52.

(*E*)-1-Fluoro-1-phenylsulfonyl-2-phenylpropene (*E*-2d). Brownish oil,[11] 1.2 g (68% yield); ^{1}H NMR: 2.52 (d, J = 3.6 Hz, 3H), 7.33 (m, 5H), 7.59 (t, J = 7.8 Hz, 2H), 7.69 (t, J = 7.8 Hz, 1H), 8.01 (d, J = 7.8 Hz, 2H). ^{19}F NMR: −119.9 (s). HRMS (FAB): calcd. for $C_{15}H_{14}FO_2S$ $[M + H]^+$ 277.0699; found 277.0689.

(*Z*)-1-Fluoro-1-phenylsulfonyl-2-phenylpropene (*Z*-2d). White solid,[11] mp 57−59 °C (from ether−hexanes), 0.16 g (9% yield); ^{1}H NMR: 2.10 (d, J = 4.5 Hz, 3H), 7.18−8.00 (m, 10H). ^{19}F NMR: −119.8 (s). MS (EI): *m/e* 276 (M+). Anal. Calcd for $C_{15}H_{13}FO_2S$ (276.33): C, 65.20; H, 4.74. Found: C, 64.89; H, 4.86.

1-Fluorovinylstannanes 3−**6.** The following 1-fluorovinylstannanes were synthesized from 1-fluorovinyl sulfones and tributyltin hydride as reported.[3a,18]

(*E*)-1-Fluoro-1-tributylstanyl-2-phenylethene (3). Colorless oil, 74% yield. ^{1}H NMR: 0.95−1.85 (m, 27H), 5.77 (d, $J_{H,F}$ = 57.3 Hz, 0.84H), 5.77 (dd, $J_{H,F}$ = 57.3 Hz, $J_{H,Sn}$ = 15.6 Hz, 0.16H); 7.29 (t, J = 7.5 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.64 (d, J = 7.5 Hz, 2H). ^{19}F NMR: −91.4 (d, $J_{F,H}$ = 57.3 Hz, 0.84F), −91.4 (dd, $J_{F,H}$ = 57.3 Hz, $J_{F,Sn}$ = 238.6 Hz, 0.16F). ^{13}C NMR: 11.5 (d, $J_{C,F}$ = 2.0 Hz), 15.1, 28.6 (s), 28.6 (d, $J_{C,Sn}$ = 57.0 Hz), 30.3 (s), 30.3 (d, $J_{C,Sn}$ = 21.4 Hz), 124.4 (d, $J_{C,F}$ = 6.9 Hz), 124.4 (dd, $J_{C,F}$ = 6.9 Hz, $J_{C,Sn}$ = 67.5 Hz), 128.3, 129.8, 130.2 (d, $J_{C,F}$ = 7.5 Hz), 135.2 (d, $J_{C,F}$ = 5.3 Hz), 135.2 (dd, $J_{C,F}$ = 5.3 Hz, $J_{C,Sn}$ = 31.5 Hz), 175.8 (d, $J_{C,F}$ = 330 Hz). MS (EI): *m/e* 353 and 355 (M^+ − Bu). Anal. Calcd for $C_{20}H_{33}FSn$ (411.18): C, 58.42; H, 8.09; F, 4.62. Found: C, 58.15; H, 8.45; F, 4.40.

(*E*)-6,8-Dichloro-3-(2-fluoro-2-tributylstanylvinyl)-4-chromone (4). Colorless oil, 55% yield. ^{1}H NMR: 0.85−1.65 (m, 27H), 6.07 (d, J = 60 Hz, 0.84H), 6.07 (dd, $^2J_{H,F}$ = 60 Hz, $^3J_{Sn,H}$ = 14.7 Hz, 0.16H), 7.70 (d, J = 2.6 Hz, 1H), 8.11 (d, J = 2.6 Hz, 1H), 8.75 (d, J = 3.0 Hz, 1H). ^{19}F NMR: −84.4 (d, J = 56.4 Hz, 0.84F), −84.4 (dd, $^2J_{F,Sn}$ = 210.7, $^3J_{F,H}$ = 56.4 Hz, 0.16F). MS (EI): calcd for $C_{23}H_{31}Cl_2FO_2Sn$: 546; found: *m/e* 489, 491 (M^+ − Bu).

(*E*)-1-Fluoro-1-tributylstanyl-2-cyclohexylethene (5). Colorless oil, 80% yield. ^{1}H NMR: 0.85−1.75 (m, 37H), 2.65 (m, 1H), 4.70 (dd, $J_{H,H}$ = 8.5 Hz, $J_{H,F}$ = 56.4, 0.84H), 4.70 (ddd, $J_{H,H}$ = 8.5 Hz, $J_{H,Sn}$ = 10.0 Hz, $J_{H,F}$ = 56.4 Hz, 0.16H). ^{19}F NMR: −103.3 (d, $J_{F,H}$ = 54.9 Hz, 0.84F), −103.3 (dd, $J_{F,H}$ = 54.9 Hz, $J_{F,Sn}$ = 274.5 Hz, 0.16F). ^{13}C NMR: 11.2, 15.0, 27.5 (s), 27.5 (d, $J_{C,Sn}$ = 37.3 Hz, 16%), 28.5, 28.8, 30.2 (s), 30.2 (d, $J_{C,Sn}$ = 20.0 Hz, 16%), 32.0 (s), 32.0 (d, $J_{C,Sn}$ = 10.0 Hz, 16%), 34.8, 132.0 (s), 132.0 (d, $J_{C,Sn}$ = 61.5 Hz, 16%), 169.4 (d, $J_{C,F}$ = 314.8 Hz). MS (EI): *m/e* 359 and 361 (M^+ − Bu). Anal. Calcd for $C_{20}H_{39}FSn$ (417.23): C, 57.57; H, 9.42; F, 4.55. Found: C, 57.14; H, 9.78; F, 4.32.

(*E*)-1-Fluoro-1-tributylstanyl-2-phenylpropene (*E*-6). Colorless oil, 65% yield. ^{1}H NMR: 0.91 (t, J = 7 Hz, 9H), 1.10 (dt, J = 7.0, 7.0 Hz, 6H), 1.35 (m, 6H), 1.66 (m, 6H), 1.92 (d, J = 4.2 Hz, 3H), 7.21 (t, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz,

(18) McCarthy, J. R.; Matthew, D. P.; Paolini, J. P. *Org. Synth.* **1995**, *72*, 216. (b) Koizumi, T.; Hagi, T.; Horie, Y.; Takeuchi, Y. *Chem Pharm. Bull.* **1987**, *35*, 3959. (c) Appell, R. A. *Synth. Commun.* **1995**, *25*, 3583.

2H), 7.38 (d, J = 7.5 Hz, 2H). ^{19}F NMR: −110.2 (s, 0.84F), −100.2 (d, $^{2}J_{F,Sn}$ = 271.3 Hz, 0.16F). ^{13}C NMR: 11.9 (d, $J_{C,F}$ = 2.6 Hz), 15.1 (s), 19.8 (d, $J_{C,F}$ = 11.2 Hz, 84%), 19.8 (dd, $J_{C,F}$ = 11.2 Hz, $J_{C,Sn}$ = 22.0 Hz, 16%), 28.6 (s), 28.6 (d, $J_{C,Sn}$ = 58.1 Hz, 16%), 30.4 (s), 30.4 (d, $J_{C,Sn}$ = 21.8 Hz, 16%), 128.2, 129.4, 129.5, 130.7, 139.2 (d, $J_{C,F}$ = 7.7 Hz), 168.6 (d, $J_{C,F}$ = 312.0 Hz). MS (EI): *m/e* 367 and 369 (M^+ − Bu), 310 and 312, 251 and 253; Anal. Calcd. for $C_{21}H_{35}FSn$ (425.21): C, 59.32; H, 8.30; F, 4.47. Found: C, 58.94; H, 8.71; F, 4.19.

(*Z*)-1-Fluoro-1-tributylstanyl-2-phenylpropene (*Z*-6). Colorless oil, 10% yield. ^{1}H NMR: 0.74 (m, 6H), 0.89 (m, 9H), 1.25 (m, 6H), 1.39 (m, 6H), 2.10 (d, J = 5.2 Hz, 3H), 7.22 (m, 2H), 7.32 (m, 3H). ^{19}F NMR: −96.7 (s, 0.84F), −96.7 (d, $J_{F,Sn}$ = 259.4 Hz, 0.16F). ^{13}C NMR: 11.9, 15.0, 16.1 (d, $^{3}J_{C,F}$ = 14.1 Hz), 16.1 (dd, $^{3}J_{C,F}$ = 14.1 Hz, $^{3}J_{C,Sn}$ = 17.9 Hz, 16%), 28.5 (s), 28.5 (d, $^{2}J_{C,Sn}$ = 61.2 Hz, 16%), 30.1 (s) 30.1 (d, $^{3}J_{C,Sn}$ = 20.3 Hz, 16%), 128.6, 129.6, 129.9, 135.2 (d, $^{2}J_{C,F}$ = 4.2 Hz), 142.0 (d, $^{3}J_{C,F}$ = 14.8 Hz), 169.7 (d, $^{1}J_{C,F}$ = 312.6 Hz). HRMS (FAB): calcd. for $C_{21}H_{35}FSn$ (M^+ − Bu) 367.1041; found 367.1024.

Cross-Coupling Reaction of 1-Fluorovinylstannanes (3−8) with Organic Halides: Typical Procedure. Method A. Under argon in a three-neck 10 mL flask, iodobenzene (204 mg, 1 mmol) was added to a stirred DMF (3 mL) solution of $Pd(PPh_3)_4$ (400 mg, 0.35 mmol), anhydrous LiCl (42 mg, 1 mmol), and (*E*)-1-fluoro-1-tributylstanyl-2-phenylpropene (*E*-**6**, 453 mg, 1 mmol) at room temperature. After 18 h of stirring at 120 °C, the reaction was quenched with water, and the product was extracted into ether. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Chromatography on silica gel (hexanes) afforded (*Z*)-1-fluoro-1,2-diphenylpropene (*Z*-**14a**) as a colorless oil (90 mg, 42%).

Method B. A mixture of (*E*)-1-fluoro-1-tributylstanyl-2-phenylpropene (*E*-**6**, 215 mg, 0.5 mmol), 4′-iodoacetophenone (130 mg, 0.5 mmol), tetrakis(triphenylphosphine)palladium-(0) (30 mg, 0.026 mmol), and CuI (90 mg, 0.47 mmol) in THF (8 mL) was heated at reflux for 30 min. The black deposit indicated the completion of the reaction. The mixture was concentrated in vacuo and chromatographed on silica gel with 1:5 ethyl acetate−hexanes to give (*Z*)-1-fluoro-1-(4-acetylphenyl)-2-phenylpropene (*Z*-**14b**) as a white solid (105 mg, 83% yield).

Method C. Under argon in a three-neck 10 mL flask, benzoyl chloride (140 mg, 1 mmol) was added to a stirred THF (3 mL) solution of $Pd(PPh_3)_4$ (400 mg, 0.35 mmol) and (*E*)-1-fluoro-1-tributylstanyl-2-phenylpropene (*E*-**6**, 425 mg, 1 mmol) at room temperature. After 5 h of stirring at 65 °C, the reaction was quenched with water, and the product was extracted into ether. The organic layer was dried ($MgSO_4$) and concentrated in vacuo. Chromatography on silica gel (methylene dichloride−hexanes, 1:1) afforded (*Z*)-2-fluoro-1,4-diphenylbut-2-en-1-one (*Z*-**14d**) as a colorless oil (120 mg, 50% yield).

Method D. A mixture of (*E*)-1-fluoro-1-tributylstanyl-2-phenylpropene (*E*-**6**, 215 mg, 0.5 mmol), hydrocinnamoyl chloride (100 mg, 0.6 mmol), tetrakis(triphenylphosphine)-palladium(0) (60 mg, 0.05 mmol), and CuI (95 mg, 0.5 mmol) in THF (8 mL) was heated to reflux for 20 min. Chromatography on silica gel with 1:5 ethyl acetate−hexanes gave (*Z*)-1,5-diphenyl-4-fluoro-5-methyl-4-buten-3-one (*Z*-**14e**) as a colorless oil (110 mg, 82% yield).

Method E. A mixture of (E)-1-fluoro-1-tributylstanyl-2-phenylethene (**3**, 205 mg, 0.5 mmol), iodobenzene (120 mg, 0.59 mmol), tetrakis(triphenylphosphine)palladium(0) (60 mg, 0.05 mmol), and CuI (95 mg, 0.5 mmol) in THF (8 mL) was heated to reflux under a carbon monoxide atmosphere (CO balloon) for 1 h. Chromatography on silica gel with 1:5 ethyl acetate−hexanes gave (*Z*)-1,3-diphenyl-2-fluoro-2-propen-1-one (**11h**) as a colorless oil (61 mg, 53% yield). A byproduct, compound **11a**, was also isolated as 36 mg of a white solid (36%).

(*Z*)-1-Fluoro-1,2-diphenylethene (11a). From Method B, 1 h; white solid, mp 93−94 °C (from hexanes) (lit. mp 93.5−94 °C[20]), 86% yield. ^{1}H NMR: 6.31 (d, J = 39.6 Hz, 1H), 7.26 (m, 1H), 7.40 (m, 5H), 7.62 (m, 4H). ^{19}F NMR: −113.3 (d, J = 40 Hz). ^{13}C NMR: 105.7 (d, $J_{C,F}$ = 10.6 Hz), 124.1 (d, $J_{C,F}$ = 7.5 Hz), 127.1 (d, $J_{C,F}$ = 2.6 Hz), 128.4, 128.5, 128.7, 132.7 (d, $J_{C,F}$ = 27.8 Hz), 133.5 (d, $J_{C,F}$ = 3.2 Hz), 157.0 (d, $J_{C,F}$ = 257.9 Hz). MS (EI) *m/e* 198 (M^+). Anal. Calcd for $C_{14}H_{11}F$ (198.24): C, 84.82; H, 5.59. Found: C, 84.68; H, 5.54.

(*Z*)-1-Fluoro-1-(4-acetylphenyl)-2-phenylethene (11b). From Method B, 0.5 h; white solid, mp 139−141 °C (from ether−hexanes), 90% yield. ^{1}H NMR: 2.63 (s, 3H), 6.46 (d, J = 39.3 Hz, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.4 Hz, 2H), 7.67 (d, J = 7.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H). ^{19}F NMR: −114.3 (d, J = 39.2 Hz). ^{13}C NMR: 26.7, 108.2 (d, $J_{C,F}$ = 10.0 Hz), 124.1 (d, J = 7.7 Hz), 127.8 (d, $J_{C,F}$ = 2.6 Hz), 128.5, 128.6, 129.0, 129.2, 132.9 (d, $J_{C,F}$ = 3.2 Hz) 136.7 (d, $J_{C,F}$ = 3.7 Hz), 155.1 (d, $J_{C,F}$ = 244.0 Hz), 197.1. MS (EI): *m/e* 240 (M^+). Anal. Calcd for $C_{16}H_{13}FO$ (240.28): C% 79.98; H, 5.45. Found: C, 79.78; H, 5.67.

(*Z*)-1-(4-Chlorophenyl)-1-fuoro-2-phenylethene (11c). From Method B, 1 h; white solid, mp 114−116 °C (from ether−hexanes), 91% yeild; ^{1}H NMR: 6.35 (d, J = 39.6 Hz, 1H), 7.27 (m, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.56 (d, J = 7.4 Hz, 2H), 7.62 (d, J = 8.1 Hz, 2H). ^{19}F NMR: −115.1 (d, J = 39.8 Hz). ^{13}C NMR: 106.2 (d, J = 10.3 Hz), 125.4 (d, J = 7.5 Hz), 127.4 (d, J = 2.3 Hz), 128.5 (s), 128.7 (d, J = 2.3 Hz), 128.9 (d, J = 8.0 Hz), 131.2 (d, J = 28.6 Hz), 133.2 (d, J = 3.2 Hz), 134.7 (s), 156.0 (d, J = 257.7 Hz). MS (EI): *m/e* 232 (M^+). Anal. Calcd for $C_{14}H_{10}ClF$ (232.68): C, 72.27; H, 4.33. Found: C, 72.04; H, 4.54.

(*Z*)-1-(4-Methoxyphenyl)-1-fuoro-2-phenylethene (11d). From Method B, 3 h; white solid, mp 88−89 °C (from ether−hexanes), 71% yeild; ^{1}H NMR: 3.80 (s, 3H), 6.11 (d, J = 39.3 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.35 (dd, J = 7.4, 7.8 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 7.8 Hz, 2H). ^{19}F NMR: −114.0 (d, J = 39.5 Hz). ^{13}C NMR: 55.3 (s), 104.0 (d, J = 10.9 Hz, 125.3 (d, J = 28.1 Hz), 125.7 (d, J = 7.6 Hz), 126.8 (d, J = 2.1 Hz), 128.4 (s), 128.5 (s), 128.6 (s), 133.8 (d, J = 3.2 Hz), 157.1 (d, J = 257.6 Hz), 160.1 (s). MS (EI): *m/e* 228 (M^+). Anal. Calcd for $C_{15}H_{13}FO$ (228.26): C, 78.93; H, 4.74. Found: C, 78.87; H, 4.87.

(*Z*)-5-(1-Fluoro-2-phenylvinyl)-1,4-dimethyluracil (11e). From Method B, 2 h; white solid (from ether−hexanes), mp 175−177 °C (from CH_2Cl_2−ether−hexanes), 89% yield. ^{1}H NMR: 3.39 (s, 3H), 3.42 (s, 3H), 7.17 (d, J = 46.0 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 3.5 Hz, 2H), 7.53 (s, 1H), 7.56 (d, J = 7.5 Hz, 2H). ^{19}F NMR: −115.9 (d, J = 46.0 Hz). ^{13}C NMR: 29.6, 38.9, 110.2 (d, ^{2}J = 5.3 Hz), 128.7, 129.8, 130.6 (d, ^{3}J = 7.6 Hz), 135.1 (d, ^{1}J = 250.9 Hz), 151.9, 161.2 (d, ^{3}J = 10.5 Hz). MS (ion spray): *m/e* 261 (M^+ + H). Anal. Calcd for $C_{14}H_{13}FN_2O_2$ (260.27): C, 64.61; H, 5.03; N, 10.76. Found: C, 64.66; H, 5.41; N, 10.51.

(*Z*)-4-(1-Fluoro-2-phenylvinyl)pyrrole (11f). From Method B, 4 h; tan solid (from CH_2Cl_2−hexanes), mp >200 °C (from ether−hexanes); 67% yield. ^{1}H NMR: 3.90 (brs, 1H), 6.03 (d, J = 40.1 Hz, 1H), 7.26 (t, J = 7.4 Hz, 1H), 7.38 (dd, J = 7.4, 7.6 Hz, 2H), 7.59 (d, J = 7.6 Hz, 2H), 7.90 (brs, 2H). ^{19}F NMR: −115.9 (d, J = 40 Hz). MS (ion spray): *m/e* 189 (M^+ + H). Anal. Calcd for $C_{11}H_9FN_2$ (188.21): C, 70.20; H, 4.82; N, 14.88. Found: C, 69.97; H, 5.06; N, 14.46.

2-Fluoro-1-phenyl-octa-(1*Z*,3*E*)-diene (11g). From Method B, 2 h; colorless oil, 83% yield. ^{1}H NMR: 0.92 (t, J = 7.2 Hz, 3H), 1.36 (m, 4H), 2.16 (m, 2H), 5.53 (d, J = 39.4 Hz, 1H), 5.90 (ddt, J = 1.2, 15.9, 25.8 Hz, 1H), 6.12 (dt, J = 7.2, 15.9 Hz, 1H), 7.19 (m, 1H), 7.31 (m, 2H), 7.52 (m, 2H). ^{19}F NMR: −117.2 (dd, J = 27.4, 39.5 Hz). ^{13}C NMR: 9.7, 18.0, 26.9, 28.0, 103.4 (d, $J_{C,F}$ = 9.5 Hz), 118.2, $J_{C,F}$ = 22.9 Hz), 122.5 (d, $J_{C,F}$ = 2.6 Hz), 124.1, 124.2, 124.3, 128.7 (d, $J_{C,F}$ = 3.7 Hz), 152.5 (d, $J_{C,F}$ = 256.5 Hz). MS (EI): *m/e* 204 (M^+). Anal. Calcd for $C_{14}H_{17}F$ (204.28): C, 82.31; H, 8.39; F, 9.30. Found: C, 81.89; H, 8.56; F, 9.04.

(*Z*)-1,3-Diphenyl-2-fluoro-2-propen-1-one (11h). From Method C; colorless oil, (lit. bp 119−120 °C/0.01 Torr[21]), 92%

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yield. ^{1}H NMR: 6.83 (d, J = 36.6 Hz, 1H), 7.40 (m, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.67 (dd, J = 7.5, 1.8 Hz, 2H), 7.85 (d, J = 8.7 Hz, 2H). ^{19}F NMR: −118.4 (d, J = 36.6 Hz). ^{13}C NMR: 121.6 (d, J = 5.8 Hz), 129.8, 130.2, 130.6, 130.7, 131.4 (d, J = 2.6 Hz), 131.9, 132.0, 134.3, 155.7 (d, J = 271.3 Hz), 189.3 (d, J = 28.2 Hz). HRMS (FAB): calcd. for $C_{15}H_{11}FO$ 226.0794; found 226.0781.

6,8-Dichloro-3-[2-fluoro-2-(4-ethoxycarbonyl-(1*Z*,3*E*)-butadien-yl)]-4-chromone (12a). From Method B, room temperature,16 h; white solid, mp 196−198 °C (from CH_2Cl_2−ether−hexanes), 68% yield. ^{1}H NMR: 1.34 (t, J = 7.5 Hz, 3H), 4.26 (q, J = 7.5 Hz, 2H), 6.27 (d, J = 15.6 Hz, 1H), 6.43 (d, J = 39.3 Hz, 1H), 7.18 (dd, J = 15.6, 27.0 Hz, 1H), 7.75 (d, J = 2.4 Hz, 1H), 8.13 (d, J = 2.4 Hz, 1H), 8.72 (d, J = 2.4 Hz, 1H). ^{19}F NMR: −112.3 (dd, J = 27.4, 39.5 Hz). MS (EI): *m/e* 356 (M^+). Anal. Calcd for $C_{16}H_{11}Cl_2FO_4$ (357.16): C, 53.81; H, 3.10; Cl, 19.85; F, 5.32. Found: C, 53.54; H, 3.43; Cl, 19.67; F, 4.99.

(*Z*)-6,8-Dichloro-3-(2-fluoro-2-benzoylvinyl)-4-chromone (12b). From Method C, room temperature, 6 h; colorless oil, 48% yield. ^{1}H NMR: 7.21 (d, J = 39.0 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.64 (t, J = 7.6 Hz, 1H), 7.77 (d, J = 2.8 Hz, 1H), 7.86 (d, J = 7.6 Hz, 2H), 8.18 (d, J = 2.8 Hz, 1H), 8.83 (d, J = 2.7 Hz, 1H). ^{19}F NMR: −112.7 (d, J = 38.9 Hz). GC−MS: *m/e* 257 (M^+ − PhCO). Anal. Calcd for $C_{18}H_9Cl_2FO_3$ (363.17): C, 59.53; H, 2.50. Found: C, 59.26; H, 2.72. **(*Z*)-6,8-Dichloro-3-(2-fluorovinyl)-4-chromone** was also isolated as a byproduct. ^{1}H NMR: 6.10 (dd, J = 46.5, 5.1 Hz, 1H), 6.82 (dd, J = 84.0, 5.1 Hz, 1H), 7.73 (d, J = 2.5 Hz, 1H), 8.12 (d, J = 2.5 Hz, 1H), 8.60 (d, J = 1.8 Hz, 1H). ^{19}F NMR: −116.1 (dd, J = 46.5, 82.9 Hz). MS (EI): calcd. for $C_{11}H_5Cl_2FO_2$ *m/e* 258, found 258 (M^+).

(*Z*)-1-Fluoro-1-(4-acetylphenyl)-2-cyclohexylethene (13). From Method B, 4 h; colorless oil, 72% yield. ^{1}H NMR: 1.10−1.85 (m, 10H), 2.59 (s, 3H), 2.65 (m, 1H), 5.43 (dd, J = 9.3, 37.8 Hz, 1H), 7.56 (d, J = 8.1 Hz, 2H), 7.91 (d, J = 8.1 Hz, 2H). ^{19}F NMR: −102.7 (d, J = 37.4 Hz). HRMS (FAB): calcd. for $C_{16}H_{19}FO$ M^+ 246.1420, found 246.1403.

(*Z*)-1-Fluoro-1,2-diphenylpropene (*Z*-14a). From Method A, colorless oil (lit. mp 78.6−79.6 °C[22]), 90 mg (42% yield); ^{1}H NMR: 2.14 (d, J = 3.0 Hz, 3H), 7.28−7.56 (m, 10H). ^{19}F NMR: −102.7 (s). GC−MS (EI): *m/e* 212 (M^+). HRMS (FAB): calcd. for $C_{15}H_{13}F$ M^+ 212.1001, found 212.1006.

(*Z*)-1-Fluoro-1-(4-acetylphenyl)-2-phenylpropene (*Z*-14b). From Method B; white solid (105 mg, 83% yield). Analytical sample was obtained by recrystallization from ether−hexanes, mp 96−8 °C; ^{1}H NMR: 2.19 (d, J = 3.0 Hz, 3H), 2.65 (s, 3H), 7.32 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.4 Hz, 2H), 7.50 (d, J = 7.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H). ^{19}F NMR: −104.8; ^{13}C NMR: 20.0 (d, J = 3.0 Hz), 28.0, 118.5 (d, J = 15.0 Hz), 128.8, 129.5, 129.6, 129.9, 130.0, 138.2, 138.9 (d, J = 29.0 Hz), 139.6, 152.9 (d, $J_{C,F}$ = 243.5 Hz), 198.8. MS (EI): *m/e* 254 (M^+). Anal. Calcd for $C_{17}H_{15}FO$ (254.31): C, 80.29; H, 5.95. Found: C, 80.12; H, 6.04.

(*E*)-1-Fluoro-1-(4-acetylphenyl)-2-phenylpropene (*E*-14b). From Method B, 12 h; colorless oil, 75% yield: ^{1}H NMR: 2.20 (d, $^4J_{H,F}$ = 4.0 Hz, 3H), 2.53 (s, 3H), 7.15−7.30 (m, 7H), 7.73 (d, J = 8.4 Hz, 2H). ^{19}F NMR: −107.4; ^{13}C NMR: 19.4 (d, $^3J_{C,F}$ = 7.5 Hz), 27.9, 121.2, 128.9, 129.1, 129.3, 129.4, 130.1, 137.5, 138.6 (d, $^2J_{C,F}$ = 29.2 Hz), 140.5 (d, J = 6.0 Hz, 153.7 (d, $^1J_{C,F}$ = 232.5 Hz), 198.7. HRMS (FAB): calcd. for $C_{17}H_{15}FO$ $[M + H]^+$ 254.1107, found 254.1126.

(*Z*)-1-Fluoro-1-(4-methoxyphenyl)-2-phenylpropene (*Z*-14c). From Method B, 5 h; colorless oil, 50% yield. ^{1}H NMR: 2.14 (d, J = 3.0 Hz, 3H), 3.87 (s, 3H), 6.98 (d, J = 8.6 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.4 Hz, 2H), 7.49 (m, 4H). MS (EI): *m/e* 242 (M^+). Anal. Calcd for $C_{16}H_{15}FO$ (242.30): C, 79.32; H, 6.24. Found: C, 79.00; H, 6.34. **2,3-Difluoro-1,4-diphenylhexa-2,4-diene** (**17a**, 26 mg, 37% yield) was also isolated.

(*Z*)-2-Fluoro-1,4-diphenylbut-2-en-1-one (*Z*-14d). From Method C; colorless oil, 120 mg, 50% yield. ^{1}H NMR: 2.34 (d, J = 3.7 Hz, 3H), 7.35−7.60 (m, 8H), 7.90 (d, J = 6.5 Hz, 2H). ^{19}F NMR: −116.0 (s). GC−MS: 240 (M^+). HRMS (EI): calcd. for $C_{16}H_{13}FO$ $[M + H]^+$ 241.1029, found 241.1024.

(*Z*)-1,5-Diphenyl-4-fluoro-5-methyl-4-buten-3-one (*Z*-14e). From Method D; colorless oil, 110 mg, 82% yield. ^{1}H NMR: 2.44 (d, J = 3.6 Hz, 3H), 3.02 (m, 4H), 7.20−7.40 (m, 10H). ^{19}F NMR: −114.9. MS (EI): *m/e* 267 (M^+). Anal. Calcd for $C_{18}H_{17}FO$ (268.33): C, 80.57; H, 6.39. Found: C, 80.31; H, 6.24.

(*E*)-1,5-Diphenyl-4-fluoro-5-methyl-4-buten-3-one (*E*-14e). From Method D, 1 h; colorless oil, 78% yield. ^{1}H NMR: 2.15 (d, J = 4.5 Hz, 3H), 2.84 (m, 4H), 7.10−7.34 (m, 10H). ^{19}F NMR: −121.2. HRMS: Calcd. for $C_{18}H_{17}FO$ $[M + H]^+$ 268.1263, found 268.1268.

(1*E*)-1-Fluoro-2-methyl-1, 4-diphenylbutene (15). From Method A; colorless oil, R_f = 0.25 (hexanes), 45% yield. ^{1}H NMR: 1.89 (d, J = 3.3 Hz, 3H), 2.38 (t, J = 7.0 Hz, 2H), 2.78 (t, J = 7.0 Hz, 2H), 7.08−7.35 (m, 10H). ^{19}F NMR: −102.5. HRMS (FAB): Calcd. for $C_{17}H_{17}F$ M^+ 240.1314, found 240.1319.

1-Fluoro-1-(4-acetylphenyl)-2,2-diphenylethene (16). From Method B, 6 h; colorless oil, 87% yield. ^{1}H NMR: 2.54 (s, 3H), 7.14 (m, 2H), 7.23−7.37 (m, 10H), 7.75 (d, J = 8.1 Hz, 2H). ^{19}F NMR: −105.7; HRMS (FAB): calcd. for $C_{22}H_{17}FO$ M^+ 316.1263, found 316.1251.

1,4-Dimethyl-1,4-diphenyl-2,3-difluorobutadiene (17a) and (*E*)-1-Methyl-2-fluorostyrene (18). Dimerization of (*E*)-1-Fluoro-1-tributylstanyl-2-phenylpropene. A mixture of the tin compound *E*-**6** (300 mg, 0.7 mmol), ethyl oxalyl chloride (136 mg, 1.0 mmol), tetrakis(triphenylphosphine)-palladium(0) (80 mg, 0.065 mmol), and CuI (190 mg, 1.0 mmol) in THF (10 mL) was stirred at rt for 3 h. Chromatography on silica gel with 1:10 ethyl acetate−hexanes gave the reduced product **18** and the dimeric compound **17a**. Data for **18**: colorless oil (82 mg, 28%).[23] ^{1}H NMR: 1.93 (d, J = 4.8 Hz, 3H), 6.67 (d, J = 84.5 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.38 (t, J = 7.2 Hz, 2H), 7.51 (d, J = 7.2 Hz, 2H). ^{19}F NMR: −128.8 (d, $^2J_{F,H}$ = 84.3 Hz). MS (EI): calcd. for C_9H_9F *m/e* 136, found 136 (M^+). Data for **17a**: colorless oil (160 mg, 54%). ^{1}H NMR: 2.14 (t, J = 3.6 Hz, 3H), 7.35 (t, J = 7.0 Hz, 2H), 7.43 (t, J = 7.0 Hz, 4H), 7.52 (d, J = 4H). ^{19}F NMR: −113.0 (s). MS (EI): calcd. for $C_{18}H_{16}F_2$ *m/e* 270, found 270 (M^+).

1,4-Diphenyl-2,3-difluoro-butadiene (17b). Dimerization of (*E*)-1-Fluoro-1-tributylstanyl-2-phenylethene. A mixture of the tin compound **3** (215 mg, 0.5 mmol), ethyl chloroformate (126 mg, 1.0 mmol), tetrakis(triphenylphosphine)palladium(0) (45 mg, 0.04 mmol), and CuI (95 mg, 0.5 mmol) in THF (8 mL) was stirred at rt overnight. Chromatography on silica gel with 1:5 ethyl acetate−hexanes gave the dimeric product 1,4-diphenyl-2,3-difluoro-butadiene **(17b)** as a white solid (60 mg, 89% yield), which solidified on standing, mp 102−4 °C; ^{1}H NMR: 6.28 (six peaks, $^3J_{H,F}$ = 39.1 Hz, $^4J_{H,F}$ = 4.0 Hz, $^3J_{F,F}$ = 36.4 Hz, $^5J_{H,H}$ = 0 Hz, 2H),[19] 7.73 (t, J = 7.1 Hz, 2H), 7.81 (dd, J = 7.1, 7.9 Hz, 4H), 8.03 (d, J = 7.9 Hz, 4H). ^{19}F NMR: −127.0 (six peaks, $^3J_{H,F}$ = 39.1 Hz, $^4J_{H,F}$ = 4.0 Hz, $^3J_{H,H}$ = 36.4 Hz, $^5J_{H,H}$ = 0 Hz, 2H). MS (EI): calcd. for $C_{16}H_{12}F_2$ *m/e* 242, found 242 (M^+).

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Supporting Information Available: Copies of the ^{1}H-{^{19}F} NOE NMR spectra of *E*-**14b** and *Z*-**14b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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