Preparation of β,β-Difluoro-α-(trifluoromethyl)styrenes by Palladium-Catalyzed Coupling of Aryl Iodides with Pentafluoropropen-2-ylzinc Reagent

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Substituted aromatic iodides are functionalized by pentafluoropropen-2-ylzinc, $CF_3C(ZnX){=}CF_2$ (X = Br, I, or $CF_2{=}CCF_3$–), in the presence of $Pd(PPh_3)_4$ to give the corresponding arenes in good yields. This is particularly attractive for preparation of title styrenes substituted with groups such as $-NO_2$ or CO_2R, which are incompatible with organomagnesium reagents. The best yields of the title styrenes with electron-donating substituents were obtained in DMF. For electron-withdrawing substituents, the best results were achieved in triglyme. A correlation was observed between Hammett σ constants and ^{19}F NMR chemical shifts (R = 0.93–0.99, n = 8) and $^2J_{F-F}$ coupling constants (R = 0.94, n = 8).

Introduction

β,β-Difluoro-α-(trifluoromethyl)styrenes (DFT styrenes) are useful building blocks in organofluorine chemistry. The unique biological properties[1] that fluorine imparts to organic molecules are well-known, and the title compounds have been utilized as precursors for the preparation of antiinflammatory[2] and antifertility[3] compounds. DFT styrenes also find useful application as monomers,[4] since fluorine enhances the thermal and chemical stability of polymers.[5]

Two synthetic strategies have been previously reported for the preparation of DFT styrenes. One involved the reaction of chloropentafluoroacetone with an aryl Grignard reagent to give an alcohol. The alcohol has also been prepared by treatment of C_6H_5Y (Y = H, alkyl) with $CF_3COCF_2Cl/AlCl_3$.[2] These alcohols were chlorinated with PCl_5[6] or $SOCl_2$[3] and then dechlorinated with zinc to give the DFT styrenes. The alcohol has also been treated with dibromotriphenylphosphorane[7] at 200 °C to give the DFT styrene. Alternatively, the DFT styrenes have been prepared by the Wittig reaction of α,α,α-trifluoroacetophenones with difluoromethylenetriphenylphosphorane.[8] Trifluoroacetophenones[9] are readily prepared by either the reaction of an aryl Grignard reagent with CF_3COX (X = OH, Cl, Li, Et) or by the electrophilic acylation of C_6H_5Y where Y = H, R, or OR. These methods, however, are not amenable for the preparation of α,α,α-trifluoroacetophenones with electron-withdrawing groups, such as $-NO_2$ or $-CO_2R$. They must be introduced by a tedious process[10] after the trifluoroacetyl moiety has been prepared.

Recent reports from our laboratory have detailed the synthetic applications of polyfluorinated vinyl organozinc,[11] cadmium,[12] and copper[13] reagents. The exceptional thermal stability of these reagents, in contrast to their lithium and magnesium counterparts, enables us to access a wide range of applications with these carbanion equivalents.[14] The terminal vinyl zinc reagents $CF_2{=}CFZnX$ (1), (Z)-$CF_3CF{=}CFZnX$ (2), and (E)-$CF_3CF{=}CFZnX$ (3) have provided the best synthetic routes to α,β,β-trifluorostyrenes and 1-arylperfluoropropenes.[15]

Previous studies of fluorinated vinyl zinc reagents have focused on the terminal examples. We recently reported the preparation of the first *per*fluorinated *internal* vinyl zinc reagent, $CF_3(ZnX)C{=}CF_2$ **7a–c**, from the readily accessible precursor $CF_3CBr_2CF_3$ (**6**).[18] Xu later reported the synthesis and palladium-catalyzed coupling reactions of the partially fluorinated internal zinc reagent $CF_3(ZnX)C{=}CH_2$ (4) with aryl[16] and vinyl[17] halides. We now describe the facile preparation of DFT styrenes by the palladium-catalyzed coupling reaction of readily available aromatic iodides with pentafluoropropen-2-ylzinc, **7a–c**.

Results and Discussion

Pentafluoropropen-2-ylzinc, **7a**, is prepared by dehalogenation/metalation of **6** by zinc,[18] which is obtained by the $AlCl_3$-catalyzed rearrangement of **5**.[19] Both reactions can be readily performed on a molar scale. The zinc reagent is also prepared by the treatment of $CF_3CX{=}CF_2$ (X =

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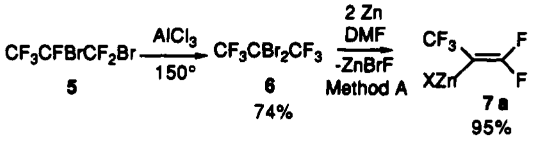
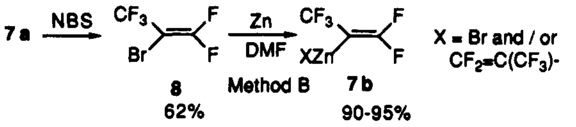
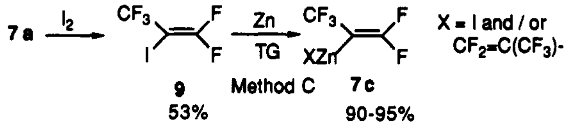
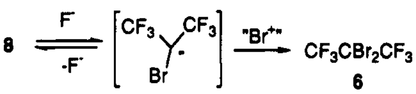


Br, I) with Zn in DMF or triglyme (TG). These exothermic reactions are complete in 1 h with ^{19}F NMR yields (vs internal hexafluorobenzene standard) of 90–95%.



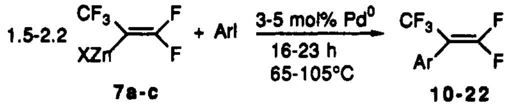


Bromination of **7a** in DMF is complicated by formation of 10% **6** in the reaction mixture. The formation of **6** can be rationalized by attack[20] of fluoride ion on **8** to give a carbanion, $(CF_3)_2CBr^-$, which may eliminate fluoride ion reversibly or react with an electrophilic halogen, either from the halogenating agent or the bromoalkene product.[21]



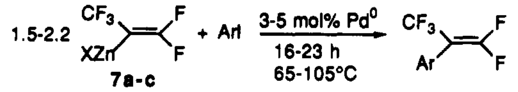
We were able to circumvent this problem by removal of **8** (bp 25–26 °C) from the reaction mixture at reduced pressure as it was formed. Since it was necessary to generate **8** in a vacuum, we employed NBS rather than bromine (bp 59.5 °C) as a source of electrophilic bromine. 2-Iodopentafluoropropene (bp 51–52 °C), **9**, was prepared by a similar procedure from **7a** and iodine.

Zinc reagent **7a–c** reacted smoothly with aryl iodides in DMF in the presence of 3–5 mol % $Pd(PPh_3)_4$ to give styrenes **10–22** (Table I). Typical conditions for complete



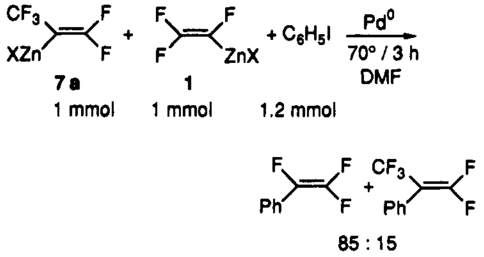
consumption of ArI involved stirring a 2.2:1 ratio of **7a–c** to ArI at 65–105 °C for 16–23 h with 3–5 mol % Pd(0) catalyst. These conditions are more vigorous than those reported for $CF_2{=}CFZnX$, **1**, (65–75 °C/3 h)[15] in a similar Pd(0) coupling reaction. Zinc reagent **7** is more sterically demanding than analogues **1–3** and has less carbanion character than its dihydro counterpart, **4**, due to the additional vinyl fluorines. Indeed, in a competition experiment, **7a** was found to react slower than **1** with iodobenzene. This coupling reaction worked well for a variety of functionalized aryl iodides (Table I). 1,3- and 1,4-diiodobenzene gave disubstituted products in good yields.

Table I. Isolated Yields of β,β-Difluoro-α-(trifluoromethyl)styrenes

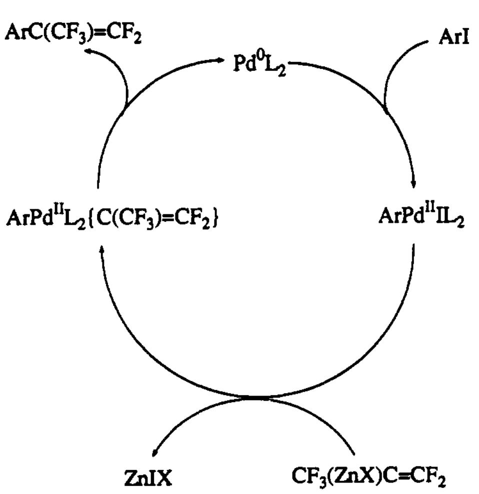


no.	β,β-difluoro-α-(trifluoromethyl)styrene	condns[a]	isolated yield, %
10	$C_6H_5C(CF_3){=}CF_2$	DMF (A)	62
11	p-$NO_2C_6H_4C(CF_3){=}CF_3$	TG (C)	75
12	m-$NO_2C_6H_4C(CF_3){=}CF_2$	TG (C)	72
13	o-$NO_2C_6H_4C(CF_3){=}CF_2$	TG (C)[b]	38[c]
14	p-$MeOC_6H_4C(CF_3){=}CF_2$	DMF (B)	68
15	p-$BrC_6H_4C(CF_3){=}CF_2$	TG (C)	64
16	3,5-$(CF_3)_2C_6H_3C(CF_3){=}CF_2$	TG (C)	66
17	m-$ClC_6H_4C(CF_3){=}CF_2$	TG (C)	45
18	p-$EtO_2CC_6H_4C(CF_3){=}CF_2$	TG (C)	73
19	p-$CH_3C_6H_4C(CF_3){=}CF_2$	DMF (B)	66
20	o-$FC_6H_4C(CF_3){=}CF_2$	DMF (B)	64
21	p-$CF_2{=}C(CF_3)C_6H_4C(CF_3){=}CF_2$	DMF (B)	63
22	m-$CF_2{=}C(CF_3)C_6H_4C(CF_3){=}CF_2$	DMF (B)	66
23	o-$CH_3C_6H_4C(CF_3){=}CF_2$	DMF (B)[d]	
24	o-$ClC_6H_4C(CF_3){=}CF_2$	TG (C)[e]	

[a] Solvent and method of generation of **7a–c** (see text). [b] 102 h/70–105 °C. [c] Based on 60% conversion of o-$NO_2C_6H_4I$. [d] 72 h/70–95 °C, 74% conversion of o-$CH_3C_6H_4I$. [e] 66 h/90–105 °C, <2% conversion of o-ClC_6H_4I.



Hindered zinc reagents such as $(CF_3)_2C{=}C(CF_3)ZnX$ have proven to be either unreactive or to undergo side reactions such as halogen exchange or self-coupling when submitted to Pd-catalyzed coupling reactions with vinyl iodides.[22] However, zinc reagents **7a–c** reacted smoothly with aryl iodides under the Pd-catalysis conditions, and no exchange products were detected. The palladium coupling reactions are generally believed to proceed by the following route, with key steps involving metathesis of **7a–c** with $ArPd^{II}IL_2$ to afford $ArPd^{II}L_2\{(CF_3)C{=}CF_2\}$, which subsequently undergoes reductive elimination to yield styrene and regenerate Pd^0L_2.[15,23]



The zinc reagent in DMF reacted smoothly with IC_6H_4Y when Y = H, p-OCH_3, p-CH_3, or o-F. However, reaction

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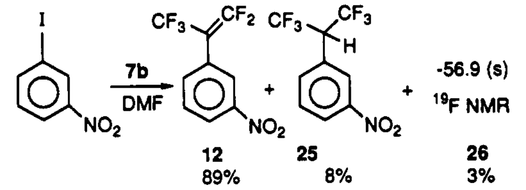
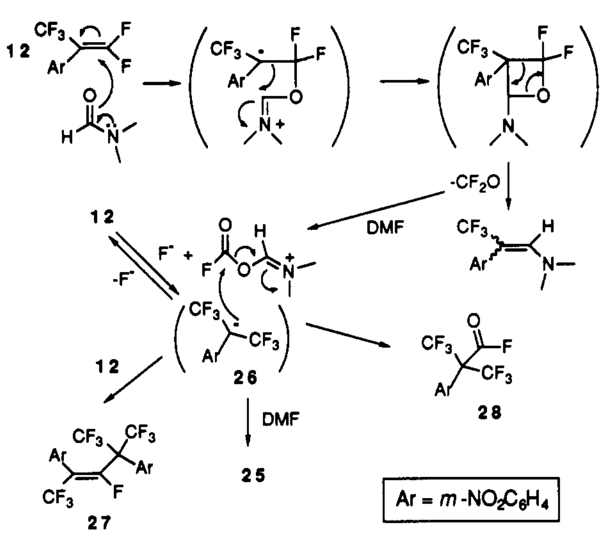
of **7b** in DMF with m-$NO_2C_6H_4I$[24] was complicated by side reactions. ^{19}F NMR analysis of the reaction mixture revealed 89% styrene **12**, 8% **25**, and a singlet at −56.9 ppm (3%). Addition of HCl/H_2O to this reaction mixture resulted in the complete disappearance of the singlet and a concomitant increase in the amount of **25**. The ^{19}F NMR multiplicity and the chemical reactivity prompts us to assign the structure of the singlet as carbanion **26**.



Carbanion **26** is formed by reaction of **12** with fluoride anion. There are two sources of fluoride ion in the reaction mixture. The first source is ZnBrF which is always produced during the preparation of **1a** in DMF. The second source of fluoride, which is less obvious, is generated by nucleophilic attack of DMF on the product styrene. To test the role of DMF in the decomposition of **12**, a sample of pure **12** and DMF was heated to 75–80 °C for 18 h. Indeed, ^{19}F NMR analysis of the solution revealed 78% **12**, 11% **25**, 1% **26**, and 10% of $Ar(CF_3)_2CCF{=}C(CF_3)Ar$ ($Ar = m$-$NO_2C_6H_4$)[25] **27**. After prolonged heating (5 days/75–80 °C) of **12** in DMF, ^{19}F NMR signals (12%) consistent with the formation of m-$NO_2C_6H_4C(CF_3)_2COF$,[26] **28**, were also observed.

DMF has been reported to react with fluorinated alkenes and alkene derivatives.[27] For example, perfluoroisobutylene reacts with 1-equiv of DMF in 2 days at room temperature to give $(CF_3)_2C{=}CHNMe_2$ and $(CF_3)_3CCOF$.[28] The mechanism for this unusual transformation has been proposed[28] to involve nucleophilic attack of DMF on the terminal difluoromethylene carbon of perfluoroisobutylene to give an anion, which decomposes by loss of carbonyl fluoride. Reaction of carbonyl fluoride with DMF gives fluoride anion and $FCOOCH{=}NMe_2^+$. A similar mechanistic interpretation for the reaction of **12** with DMF can ultimately afford **26**, which can capture a proton from the solvent or undergo an addition/elimination reaction with **12** to give **27**.[29]

Utilization of TG for the reaction of m-$NO_2C_6H_4I$ with **7c** gave styrene **12** in 72% isolated yield, and **25** was not detected in the reaction mixture. Zinc reagent **7c** also reacted smoothly with IC_6H_4Y (Y = p-NO_2, p-Br, m-Cl, and p-EtO_2C) and 3,5-$(CF_3)_2C_6H_3I$. TG was not the best solvent in all instances. We found that the reaction with electron-rich aryl iodides was much more facile in DMF than TG. Prolonged reaction time and elevated temperature (73 h/95–110 °C) were necessary for the complete consumption of p-$CH_3C_6H_4I$ when reacted with **7c** in TG (32% isolated yield of **19**). The reaction with **7b** in DMF however, afforded a better yield (66%) under milder conditions (17 h/85 °C). The effect of solvents in organometallic reactions is not uniform, and there are no universal correlations between the solvent donor number and the reaction rate.[30] It is not unreasonable to propose, however, that DMF, the better donor solvent in the **7**·solvent complex, imparts more electron density to the nucleophilic carbon. Also, the **7**·DMF complex should be less sterically demanding than **7**·TG.[31]



The coupling reaction fails with most ortho substituents, presumably due to steric hindrance. o-FC_6H_4I was the only ortho-substituted substrate to give a reasonable yield of DFT styrene. o-$NO_2C_6H_4I$ reacted with **7c** in TG to 60% conversion: 23% of styrene **13** and 40% o-$NO_2C_6H_4I$ were isolated after 72 h at 70–95 °C. Reaction of **7c** with o-ClC_6H_4I (90–105 °C/66 h) gave less than 2% styrene, and **7b** with o-$CH_3C_6H_4I$ (85–115 °C/49 h) gave 74:26 DFT styrene/o-$CH_3C_6H_4I$.

A correlation was observed when Hammett σ values were plotted vs ^{19}F NMR chemical shifts and geminal fluorine coupling constants: σ vs δ CF_3 ($y = 1.2x + 74$, $R = 0.93$), Fb ($y = 0.27x + 21$, $R = 0.98$), Fc ($y = 0.31x + 24$, $R = 0.99$), and $^2J_{Fa-Fb}$ ($y = -0.13x + 1.6$, $R = 0.94$). No correlation with σ was observed for either of the CF_3-F coupling constants, any ^{13}C NMR signals, or any IR data. Use of σ^+ or σ^- values worsened the correlations. Other workers have correlated substituent effects with ^{19}F NMR in para-substituted β,β-difluorostyrenes[32] and α,β,β-trifluorostyrenes.[33]

In conclusion, we have demonstrated a new and useful route to substituted β,β-difluoro-α-(trifluoromethyl)styrenes in good yields under mild conditions. The Pd-catalyzed coupling reaction has the advantage of tolerating a variety of functional groups such as NO_2 and CO_2R that are difficult to incorporate via previously reported methods. Styrenes with electron-donating substituents were best prepared in DMF while TG gave the best results with

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(24) Treatment of p-$NO_2C_6H_4I$ with **7b** in DMF revealed 63% **11**, 25% p-$NO_2C_6H_4CH(CF_3)_2$, and 12% p-$NO_2C_6H_4C(CF_3)_2^-$ as determined by ^{19}F NMR.

(25) ^{19}F NMR: δ −58.7 (d, $J \approx 24$ Hz, 3 F), −62.4 (d, $J = 12$ Hz, 6 F), −90.5 (m, 1 F).

(26) δ +33.2 (sept, $J = 10$ Hz, 1 F), −64.5 (d, $J = 10$ Hz, 6 F).

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(29) No effort was made to isolate the compounds in the reaction mixture, and it could not be determined if the ^{19}F NMR singlet expected for p-$NO_2C_6H_4C(CF_3){=}CHNMe_2$ was absent or present and overlapping with other multiplets in the CF_3 region.

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styrenes containing electron-withdrawing groups. *o*-FC_6H_4I was the only ortho-substituted aryl iodide to react to completion with the zinc reagent **7a–c**. We are currently examining the structure and properties of carbanion **26** and its analogs.

Experimental Section

General. All boiling points are uncorrected. All glassware was oven-dried. ^{19}F and ^1H NMR were recorded on a 90- or 300-MHz spectrometer, and $\{^1H\}^{13}C$ NMR spectra were recorded on a 300-MHz spectrometer. All samples were taken in $CDCl_3$ solvent unless noted otherwise. No attempt was made to control the concentration of the samples or, ideally, extrapolate the values to infinite dilution. However, the broad chemical shift region of ^{19}F NMR does minimize this experimental uncertainty. All chemical shifts are reported in parts per million downfield (positive) of the standard: TMS for ^1H and ^{13}C; $CFCl_3$ for ^{19}F NMR. FT-IR spectra were recorded as CCl_4 solutions and reported in wavenumbers (cm^{-1}). GC–MS spectra were obtained at 70 eV in the electron impact mode. GLPC analyses were performed on a 5% OV-101 column with thermal conductivity detector. High-resolution mass spectral determinations were made at the Midwest Center for Mass Spectrometry with partial support by the National Science Foundation, Biology Division (Grant No. DIR9017262). The elemental analysis was performed by Schwarzkopf Microanalytical Lab., Inc., Woodside, NY.

Materials. Dimethylformamide (DMF) was distilled at reduced pressure from CaH_2. Triglyme (TG, Grant Chemical) was distilled twice at reduced pressure from sodium benzophenone ketyl. $Pd(PPh_3)_4$ was prepared by Coulson's procedure.[34] Zinc (325 mesh, Aldrich) was activated by washing with dilute HCl and then dried in vacuo at room temperature. Molecular sieves (4 Å, Fisher) were activated by heating at 300 °C for 16 h at 0.5 mmHg. All other materials were used without further purification. All reagents and aryl iodides were obtained from Aldrich, with the exceptions of compound **5** (Du Pont), 3,5-$(CF_3)_2C_6H_3I$ (Fairfield Chemical Co.), *m*-IC_6H_4I (Eastman Kodak), *p*-$EtO_2CC_6H_4I$ (Lancaster), and *o*-ClC_6H_4I (Alfa).

2,2-Dibromo-1,1,1,3,3,3-hexafluoropropane (6).[19] This isomerization reaction was carried out at 150 °C in a Parr Hastelloy-C pressure reactor equipped with a 2000 psi Inconel rupture disk.[35] The reaction was complete in 3 days when a pressure reactor head with a mechanical stirring apparatus was utilized. The reaction required 9 days to achieve 100% conversion in a sealed pressure reactor without stirring. We recommend using an *unstirred* vessel as the corrosive nature of the reaction mixture ($AlCl_3$, Br_2) and the high temperature destroy the seals and bearings of the stirrer. 1,2-Dibromo-1,1,2,3,3,3-hexafluoropropane (1170 g, 3.78 mol) and aluminum chloride (140 g, 1.05 mol) were placed in a sealed 1-L Hastelloy-C pressure reactor equipped with a blow-out seal (2000 psi) and heated to 150 °C for 9 days. After cooling to room temperature, ^{19}F NMR analysis of the reaction mixture revealed a singlet at −72.5 ppm (CCl_4). The reaction mixture was washed with H_2O (2 × 1 L) and 5% $Na_2S_2O_3$ (2 × 1 L), and then the chunky, dark, organic residue was steam distilled. The organic layer of the distillate was separated and melted on a hot plate and the upper aqueous layer removed by pipet. The 860 g (74%) solid/liquid $CF_3CBr_2CF_3$ which remains after cooling is adequate for preparation of the zinc reagent, but better yields are obtained if the remaining water is removed. The best method we have found for final drying was to distill (bp 75 °C) the solid from activated 4-Å molecular sieves, yielding 776 g (67%) of colorless, solid $CF_3CBr_2CF_3$: mp 53 °C (lit.[36] mp 52 °C); ^{19}F NMR δ −72.2 (s); FTIR 1238.1 (m), 1222.9 (m), 793.6 (vs), 778.3 (vs); GC–MS 312 ($M^{\cdot+}$, 13), 310 ($M^{\cdot+}$, 28), 308 ($M^{\cdot+}$, 16), 231 (33), 229 (35), 131 (49), 129 (35), 69 (100).

Pentafluoropropen-2-ylzinc (7a): Method A. A 4-neck 2-L round-bottom flask was equipped with a pressure-equalizing dropping funnel, immersion thermometer, Teflon-coated magnetic stir bar, and a dry ice/isopropyl alcohol (IPA) condenser attached to a nitrogen source. The apparatus was purged with nitrogen and then charged with zinc dust (155 g, 2.37 mol) and 600 mL of DMF. A solution of **6** (300 g, 0.968 mol) in DMF (300 mL) was transferred to the dropping funnel and added dropwise to the well-stirred reaction mixture over a 3–4-h period at a rate that maintained the internal temperature at 70–80 °C.[37] The induction period was approximately 1 min if pure reagents were employed and was realized when the solution became warm and turned light green then black. The excess zinc was removed by filtration through a medium-frit Schlenk funnel under positive nitrogen pressure. The yield of the zinc reagent was determined by ^{19}F NMR integration vs internal hexafluorobenzene standard. Yields ranged from 90 to 95%: ^{19}F NMR (DMF) δ −49.0 (dd, *J* = 18, 13 Hz, 3 F), −60.9 (dq, *J* = 37, 18 Hz, 1 F), −72.5 (dq, *J* = 37, 13 Hz, 1 F).

2-Bromopentafluoropropene (8). A 3-neck 1-L round-bottom flask was equipped with a Teflon-coated magnetic stir bar, rubber septum, and a pressure-equalizing dropping funnel. Two −196 °C traps were linked in series between the apparatus and a vacuum source. The flask was charged with a solution of **7a** (2.13 M, 200 mL, 425 mmol) in DMF and cooled to −10 °C with a dry ice/IPA bath. The dropping funnel was charged with a solution of *N*-bromosuccinimide (NBS, 90.1 g, 506 mmol) dissolved in 250 mL of DMF. The apparatus was evacuated to 1–2 mmHg, and then the NBS/DMF solution was added at a rate to keep the rapidly evolving $CF_3CBr{=}CF_2$ from bubbling the reaction mixture into the −196 °C trap. After the addition of NBS was complete, the reaction mixture was allowed to warm to room temperature for 1 h under vacuum. Most of the volatiles, including some DMF, were collected in the first trap, and then this trap was warmed to 50 °C at atmospheric pressure to transfer $CF_3CBr{=}CF_2$ to the second trap, affording 55.2 g (62%) of **8**, GLPC purity 100%: bp 25–26 °C (lit.[38] bp 26–28 °C); ^{19}F NMR (DMF) δ −62.6 (dd, *J* = 20, 15 Hz, 3 F), −68.8 (m, 1 F), −69.1 (m, 1 F); ^{13}C NMR ($CDCl_3$) δ 156.8 (ddq, *J* = 310, 294, 6 Hz), 121.1 (qdd, *J* = 270, 9, 5 Hz), 72.3 (qdd, *J* = 43, 32, 28 Hz); FTIR 1730.6 (vs), 1341.8 (vs), 1291.8 (vs), 1150.9 (vs), 1026.5 (vs), 648.3 (m); GC–MS 212 ($M^{\cdot+}$, 56), 210 ($M^{\cdot+}$, 65), 193 (32), 191 (36), 131 (54), 112 (42), 93 (100), 69 (98).

A similar reaction was carried out at atmospheric pressure. After treatment of **7a** (0.96 M, 4.0 mL, 3.8 mmol) in DMF with NBS (0.70 g, 3.9 mmol) at 25 °C, ^{19}F NMR analysis revealed that the reaction mixture contained 90% **8** and 10% $CF_3CBr_2CF_3$, **6**: ^{19}F NMR (DMF) δ −70.9 (s) for **6**.

2-Iodopentafluoropropene (9). Zinc reagent **7a** was prepared from 300 g (0.968 mol) of **6** and 155 g (2.37 mol) of Zn in 900 mL of DMF. The solution of **7a** was passed through a Schlenk funnel with a coarse frit under positive nitrogen pressure. This solution was added to a 3-neck 2-L round-bottom flask equipped with a Teflon-coated magnetic stir bar and a solid addition funnel charged with 435 g (1.71 mol) of iodine. Two −196 °C traps were linked in series between the apparatus and a vacuum source. The flask was cooled in an ice–water bath and then evacuated to 1–2 mmHg. Iodine was added at a rate to keep the rapidly evolving $CF_3CI{=}CF_2$ from bubbling the reaction mixture into the −196 °C trap. After the addition of I_2 was complete, the reaction mixture was allowed to warm to room temperature for 1 h under vacuum. The volatile materials (179 g) from both traps were collected and washed with 5% $Na_2S_2O_3$ (2 × 200 mL), dried over $MgSO_4$, and then distilled through a short-path distillation apparatus to give 132 g (53%) of **9**: bp 51–52 °C (lit.[39] bp 51–53 °C); GLPC purity 99%; ^{19}F NMR δ −58.8 (dd, *J* = 22, 11 Hz, 3 F), −61.6 (qd, *J* = 22, 3 Hz, 1 F), −62.0 (qd, *J* = 11, 3 Hz, 1 F); FTIR 1719.2 (vs), 1323.0 (vs), 1277.1 (s), 1154.8 (vs); GC–MS 258 ($M^{\cdot+}$, 100), 239 (35), 131 (14), 127 (76), 112 (72), 93 (50), 69 (29).

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(34) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121–124.

(35) NOTE: The blow-out seal should be examined after each reaction as the corrosive reaction mixture will pit and eventually compromise the seal. This has happened to us on one occasion, with subsequent escape of the vessel's contents at high pressure and temperature. For this reason, the reaction should only be carried out in a well ventilated hood behind a blast shield.

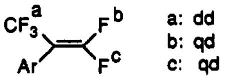
(36) Weigert, F. J.; Mahler, W. *J. Am. Chem. Soc.* **1972**, *94*, 5314–5318.

(37) When the exotherm was quenched with an ice bath, incomplete conversion and side reactions were observed by ^{19}F NMR analysis.

(38) Zeifman, Y. V.; Lantseva, L. T.; Postovoi, S. A. *Izv. Akad. Nauk Ser. Khim.* **1981**, 1350–1352 (Eng. Transl.).

(39) Knunyants, I. L.; Sterlin, R. N.; Bogachev, V. E. *Izv. Akad. Nauk. Ser. Khim.* **1958**, *22*, 407–409 (Eng. Transl.).

Table II. ^{19}F NMR Data of β,β-Difluoro-α-(trifluoromethyl)styrenes[a]



no.	subst	*a*	*b*	*c*	J_{ab}	J_{ac}	J_{bc}
10	H	−59.8	−76.4	−78.1[b]	23	10	13
11	*p*-NO_2	−59.2	−73.1	−75.3	23	10	6.1
12	*m*-NO_2	−59.5	−73.4	−75.6	24	11	6.4
13	*o*-NO_2	−60.1	−74.9	−75.5	18	10	8.9
14	*p*-MeO[c]	−60.1	−76.7	−78.5[b]	24	12	12
15	*p*-Br	−59.8	−75.2	−77.1[b]	24	11	10
16	3,5-$(CF_3)_2$[d]	−59.5	−72.7	−75.1	24	11	5
17	*m*-Cl	−59.7	−75.1	−76.7[b]	24	11	9
18	*p*-EtO_2C	−59.4	−75.0	−76.9[b]	23	10	10
19	*p*-CH_3[e]	−59.9	−76.7	−78.5[b]	25	11	13
20	*o*-F	−60.1[f]	−74.2[g]	−74.8[f]	21		5.8
21	*p*-$CF_2{=}C(CF_3)$	−59.6	−75.2	−77.2[b]	23	10	10
22	*m*-$CF_2{=}C(CF_3)$	−59.8	−75.4	−77.3[b]	24	11	10

[a] All spectra recorded in $CDCl_3$, chemical shifts are reported in ppm vs internal $CFCl_3$ standard. [b] $J_{ac} \approx J_{bc}$, appears as a pentet. [c] Reference 3 data: δ −60.2 (dd, J = 24, 11 Hz, 3 F), −77.4 (qd, J = 24, 15 Hz, 1 F), −79.2 (dq, J = 15, 11 Hz, 1 F). [d] Aromatic CF_3's appear at −63.7 ppm (s). [e] Reference 8c data: δ −60.8 (dd, J = 24.5, 11.5 Hz, 3 F), −78.4 (qd, J = 24.5, 10.8 Hz, 1 F), −76.7 (qd, J = 11.5, 10.8 Hz, 1 F). [f] Multiplet. [g] qdd, $J_{o\text{-}F,Fb}$ = 2 Hz, *o*-F appears at −113.3 ppm (m).

Pentafluoropropen-2-ylzinc (7b): Method B. To zinc (0.84 g, 13 mmol) and 8 mL of DMF was added a quantity of **8** under positive nitrogen pressure via cannula to the reaction mixture. The reaction initiated in 1 min, and a similar exotherm and color change was observed as described for **7a**. The reaction mixture was stirred for 1 h at room temperature and then filtered under positive nitrogen pressure through a medium-frit Schlenk funnel. The ^{19}F NMR spectrum was identical to **7a**, and the NMR yield was 90–95%. For larger scale preparations of this zinc reagent it is necessary to add **8** at a slower rate to control the exotherm.

Pentafluoropropen-2-ylzinc (7c): Method C. To zinc (1.4 g, 21 mmol) and 10 mL of TG was added **9** (3.6 g, 14 mmol) slowly via syringe over a 5-min period. The reaction initiated in 1 min, and a similar exotherm and color change was observed as described for **7a**. After being stirred at room temperature for 1 h, the reaction mixture was filtered under positive nitrogen pressure through a medium-frit Schlenk funnel. The ^{19}F NMR yield was 90–95%.

The molarity of **7b** and **7c** were estimated in several instances by integration vs internal hexafluorobenzene standard, and the ^{19}F NMR yields were in the 90–95% range. Thereafter, the yield was assumed to be 100%, and the molarity was determined by dividing the mmol of $CF_3CX{=}CF_2$ (X = Br, I) by the total volume of filtered solution in mL.

General Procedure for the Coupling of 7a–c with Aryl Halides. To 3–5 mol % $Pd(PPh_3)_4$ and the aryl iodide was added **7a–c** via syringe, and the mixture was stirred and heated in an oil bath to the indicated temperature. The progress of the reactions was monitored by ^{19}F NMR analysis. After workup, the styrenes were isolated by distillation or chromatography. The fractions collected from silica gel chromatography were analyzed by TLC, and fractions that contained similar spots were combined and the solvent evaporated under vacuum. See Table II for ^{19}F NMR data. The purity of most compounds was determined by GLPC analysis. For **11** and **12**, no impurities in greater than 3% concentration were observed by GC–MS or ^{19}F, ^1H, or ^{13}C NMR spectroscopy.

β,β-Difluoro-α-(trifluoromethyl)styrene (10). C_6H_5I (5.10 g, 25.0 mmol) and **7a** (0.71 M, 70 mL, 50 mmol) in DMF were stirred for 18 h at 80 °C. The reaction mixture was extracted with pentane (5 × 75 mL), and the pentane extracts were washed with 5% HCl (1 × 100 mL). The pentane was removed at atmospheric pressure, and the residue was passed through a 60-g silica gel column with pentane eluent. The solvent was removed at atmospheric pressure, and then the residue was distilled at reduced pressure, collecting 3.22 g (62%) **10**: bp 68–69 °C/80 mmHg; 99% GLPC purity; ^1H NMR showed an asymmetric signal between 7.31 and 8.78 ppm; ^{13}C NMR δ 157.1 (ddq, J = 306, 296, 3.6 Hz), 130.5, 129.9, 129.2, 126.7, 123.3 (qdd, J = 271, 12, 6.1 Hz), 90.6 (qdd, J = 34, 28, 13 Hz); GC–MS 208 (100, $M^{\bullet+}$), 189 (15), 169 (11), 139 (26), 138 (10), 119 (28), 99 (14), 96 (46), 69 (8); FTIR 3068.1 (vw), 1736.6 (vs), 1500.9 (m), 1345.3 (vs), 1281.3 (vs), 1170.7 (vs) (lit.[8c] 1740 for $C{=}CF_2$).

4-Nitro-β,β-difluoro-α-(trifluoromethyl)styrene (11). *p*-$NO_2C_6H_4I$ (0.99 g, 4.0 mmol) and **7c** (1.2 M, 8 mL, 9.8 mmol) in TG were stirred for 18 h at 70–75 °C. The reaction mixture was extracted with pentane (4 × 25 mL), and then the combined pentane extracts were washed with H_2O (5 × 25 mL). The extracts were combined with 1.5 g of silica gel, and then the solvent was removed at reduced pressure. The silica gel sample was loaded onto a 75-g silica gel column and eluted with 8:2 pentane/CH_2Cl_2. Compound **11**, 0.77 g (75%), was isolated as a yellow oil: ^1H NMR δ 8.31 (d, J = 8.6 Hz, 2 H), 7.59 (d, J = 8.6 Hz, 2 H); ^{13}C NMR δ 157.2 (ddq, J = 308, 295, 3.7 Hz), 149.0, 133.1, 131.7, 124.4, 122.9 (qdd, J = 272, 12, 6 Hz), 89.6 (qdd, J = 36, 27, 14 Hz); GC–MS 253 ($M^{\bullet+}$, 100), 234 (20), 223 (29), 207 (40), 187 (86), 157 (47), 145 (33), 138 (60), 137 (33), 99 (16), 69 (14); FTIR 3087.3 (vw), 1733.2 (vs), 1529.8 (s), 1352.1 (s), 1255.3 (vs), 1181.3 (vs); HRMS calcd for $C_9H_4F_5NO_2$ 253.0162, obsd 253.0159.

3-Nitro-β,β-difluoro-α-(trifluoromethyl)styrene (12). *m*-$NO_2C_6H_4I$ (0.97 g, 3.9 mmol) and **7c** (1.2 M, 10 mL, 12 mmol) in TG were stirred for 19 h at 90–100 °C. Styrene **12**, 0.72 g (72%), was isolated as a yellow oil by the procedure described for **11**: ^1H NMR δ 8.33 (dm, J = 7.8 Hz, 1 H), 8.26 (bs, 1 H), 7.65–7.80 (m, 2 H); ^{13}C NMR δ 157.3 (ddq, J = 308, 295, 3.5 Hz), 149.0, 136.5, 130.6, 128.2, 125.6, 124.9, 122.6 (qdd, J = 272, 12, 6.0 Hz), 89.3 (qdd, J = 35.4, 26.9, 13.4 Hz); GC–MS 253 ($M^{\bullet+}$, 100), 234 (17), 207 (68), 187 (92), 157 (45), 138 (67), 137 (37), 99 (17), 69 (19); FTIR 3087.8 (vw), 1736.9 (vs), 1536.2 (s), 1353.8 (vs), 1182.1 (vs), 1143.2 (vs); HRMS calcd for $C_9H_4F_5NO_2$ 253.0162, obsd 253.0165.

Using DMF as the solvent: *m*-$NO_2C_6H_4I$ (0.61 g, 2.4 mmol) and **7b** (1.0 M, 3.2 mL, 3.2 mmol) in DMF were stirred for 17 h at 90–95 °C. ^{19}F NMR analysis of the reaction mixture indicated 89% **12**; 8% **25**; and 3% δ −56.9 (s, assigned as structure **26**). After the addition of several drops of 50% HCl/H_2O to the NMR tube, the ^{19}F NMR spectrum revealed 89% **12** and 11% **25** (no singlet at δ −56.9 was observed). In a separate experiment, *m*-$NO_2C_6H_4I$ (0.57 g, 2.3 mmol) and **7b** (1.0 M, 3.3 mL, 3.3 mmol) in DMF were stirred for 5 days at 50 °C. ^{19}F NMR analysis revealed similar formation of **12**, **25**, and **26**. The reaction mixture was loaded directly onto a column with 60 g of silica gel and eluted with 8.5:1.5 pentane/CH_2Cl_2. Compounds **12** and **25** eluted simultaneously, and 0.41 g (≈70%) of a mixture of **12** and **25** were isolated as a yellow oil: ^{19}F NMR 87% **12**, 13% **25** δ −65.7 (d, J_{HF} = 7.8 Hz); ^1H NMR for **25** δ 4.25 (sept, J_{HF} = 8 Hz); GC–MS for **25** 273 ($M^{\bullet+}$, 60), 254 (12), 227 (37), 207 (55), 177 (66), 158 (80), 145 (33), 127 (100), 83 (34), 69 (46).

2-Nitro-β,β-difluoro-α-(trifluoromethyl)styrene (13). When *o*-$NO_2C_6H_4I$ (0.99 g, 4.0 mmol) and **7c** (1.2 M, 8 mL, 9.8 mmol) in TG were stirred for 102 h at 70–105 °C, 95% of **7c** was consumed (^{19}F NMR). The reaction mixture was worked up as described for **11**, and 0.40 g (40%) *o*-$NO_2C_6H_4I$ and 0.23 g (23%) **13** were isolated. Data for **13**: ^1H NMR (~90% pure) δ 8.18 (dd, J = 7.8, 1.5 Hz, 1 H), 7.70 (m, 2 H), 7.48 (dd, J = 7.3, 1.4 Hz, 1 H); ^{13}C NMR δ 156.3 (ddq, J = 306, 293, 3.5 Hz), 149.1, 134.0, 133.7, 131.6, 125.6, 122.2 (qdd, J = 272, 12, 6 Hz), 120.7, 87.6 (qdd, J = 37, 28, 18 Hz); GC–MS 253 ($M^{\bullet+}$, 22), 187 (49), 157 (54), 145 (79), 138 (38), 137 (100), 123 (33), 107 (21), 69 (20); FTIR 2929.0 (vw), 1746.8 (vs), 1537.8 (s), 1357.9 (vs), 1245.7 (s), 1186.5 (vs).

4-Methoxy-β,β-difluoro-α-(trifluoromethyl)styrene (14). p-$MeOC_6H_4I$ (0.58 g, 2.5 mmol) and **7b** (1.0 M, 3.2 mL, 3.2 mmol) in DMF were stirred for 17 h at 90–95 °C. The reaction mixture was poured in 50 mL of 5% HCl/H_2O and extracted with CH_2Cl_2 (4 × 50 mL). The combined organic extracts were washed with 5% HCl/H_2O (1 × 100 mL), and then the solvent was evaporated under vacuum. The residue was loaded onto a silica gel column (50 g) and eluted with 9:1 hexane/CH_2Cl_2 to afford 0.41 g (68%) of a yellow liquid, 14: 98% GLPC purity; ^1H NMR δ 7.2 (d, J = 7 Hz, 2 H), 6.9 (d, J = 7 Hz, 2 H), 3.8 (s, 3 H); ^{13}C NMR δ 160.5, 156.2 (ddq, J = 306, 292, 3.5 Hz), 131.4, 122.8 (qdd, J = 272, 12, 6.3 Hz), 118.0, 114.3, 89.5 (qdd, J = 34, 28, 13 Hz), 55.3; GC–MS 238 ($M^{\bullet+}$, 100), 223 (19), 219 (13), 195 (34), 145 (80), 99 (19), 69 (12); FTIR 2959.1 (vw), 1732.7 (vs), 1515.7 (s), 1356.3 (vs), 1294.9 (vs), 1250.7 (s), 1174.7 (vs) (lit.[3] 1740 for $C{=}CF_2$).

4-Bromo-β,β-difluoro-α-(trifluoromethyl)styrene (15). p-BrC_6H_4I (1.07 g, 3.78 mmol) and **7c** (1.0 M, 6 mL, 6 mmol) in TG were stirred for 23 h at 80 °C. The isolation procedure described for **11** gave 0.69 g (64%) of **15**, 100% GLPC purity, as a yellow oil: ^1H NMR δ 7.56 (dm, J = 8 Hz, 1 H), 7.20 (d, J = 8 Hz, 1 H); ^{13}C NMR δ 156.7 (ddq, J = 307, 293, 3.6 Hz), 132.4, 131.9, 125.2, 123.3, 122.7 (qdd, J = 271, 12, 6 Hz), 89.6 (qdd, J = 35.4, 28.1, 13.4 Hz); GC–MS 288 ($M^{\bullet+}$, 63), 286 ($M^{\bullet+}$, 67), 219 (7), 217 (7), 207 (23), 187 (52), 157 (24), 138 (100), 99 (18), 87 (22), 69 (29); FTIR 3057.2 (vw), 1734.5 (vs), 1354.8 (vs), 1253.6 (s), 1140.5 (vs); HRMS calcd for $C_9H_4F_5{}^{79}Br$ 285.9417, obsd 285.9418; HRMS calcd for $C_9H_4F_5{}^{81}Br$ 287.9396, obsd 287.9397.

3,5-Bis(trifluoromethyl)-β,β-difluoro-α-(trifluoromethyl)styrene (16). 3,5-$(CF_3)_2C_6H_3I$ (3.09 g, 9.09 mmol) and **7c** (1.2 M, 15 mL, 18 mmol) in TG were stirred for 20 h at 90–95 °C. The reaction mixture was triturated with pentane (6 × 20 mL), and the combined pentane extracts were washed with water (6 × 15 mL), dried over $MgSO_4$, and filtered. The pentane was removed by distillation at atmospheric pressure, and the residue was distilled to give 2.06 g (66%) of clear liquid: bp 144–145 °C; 98% GLPC purity; ^1H NMR δ 7.97 (s, 1 H), 7.81 (s, 2 H); ^{13}C NMR δ 157.4 (ddq, J = 309, 295, 3.3 Hz), 133.2 (q, J = 34.0 Hz), 130.7, 128.8, 124.0 (sept, J = 3.4 Hz), 123.3 (q, J = 273 Hz), 122.5 (qdd, J = 271, 11, 6 Hz), 89.1 (qdd, J = 36, 27, 15 Hz); GC–MS 344 ($M^{\bullet+}$, 100), 325 (64), 294 (14), 275 (47), 255 (24), 232 (21), 205 (28), 187 (33), 69 (42); FTIR 3090.5 (vw), 1743.4 (m), 1389.1 (s), 1350.3 (s), 1279.7 (vs), 1236.4 (s), 1180.5 (vs). Anal. Calcd for $C_{11}H_3F_{11}$: C, 38.39; H, 0.88. Found: C, 37.71; H, 0.91.

3-Chloro-β,β-difluoro-α-(trifluoromethyl)styrene (17). m-ClC_6H_4I (3.56 g, 14.9 mmol) and **7c** (1.3 M, 23 mL, 30 mmol) in TG were stirred for 17 h at 90–95 °C. The isolation procedure described for **16** gave 1.63 g (45%) of clear liquid: bp 143–145 °C; 99% GLPC purity; ^1H NMR an asymmetric multiplet was observed between 7.19 and 7.40 ppm; ^{13}C NMR δ 156.8 (ddq, J = 307, 293, 3.5 Hz), 135.1, 130.4, 130.3, 130.0, 128.5, 128.0, 122.7 (qdd, J = 272, 12, 6 Hz), 89.5 (qdd, J = 35.4, 28.1, 13.4 Hz); GC–MS 244 ($M^{\bullet+}$, 29), 242 ($M^{\bullet+}$, 100), 223 (15), 207 (35), 187 (32), 138 (72), 130 (34), 132 (11), 99 (14), 69 (30); FTIR 3047.8 (vw), 1731.2 (s), 1353.3 (s), 1285.0 (m), 1176.6 (s), 1143.4 (s); HRMS calcd for $C_9H_4F_5{}^{35}Cl$ 241.9922, obsd 241.9920.

***p*-(Ethoxycarbonyl)-β,β-difluoro-α-(trifluoromethyl)styrene (18).** p-$EtO_2CC_6H_4I$ (1.37 g, 4.96 mmol) and **7c** (1.0 M, 12 mL, 12 mmol) in TG were stirred for 17 h at 65 °C. The isolation procedure described for 11 gave 1.01 g (73%) 18, 100% GLPC purity, as a yellow oil: ^1H NMR δ 8.11 (d, J = 8.4 Hz, 2 H), 7.42 (d, J = 8.2 Hz, 2 H), 4.34 (q, J = 7.1 Hz, 2 H), 1.37 (t, J = 7.1 Hz, 3 H); ^{13}C δ 165.2, 156.3 (ddq, J = 307, 294, 3.5 Hz), 131.5, 130.1, 129.7, 129.6, 122.3 (qdd, J = 272, 12, 6 Hz), 89.4 (qdd, J = 35.4, 28.1, 13.4 Hz), 60.8, 13.6; GC–MS 280 ($M^{\bullet+}$, 12), 252 (27), 235 (100), 207 (32), 187 (37), 157 (19), 138 (32), 69 (8); FTIR 3430.9 (vw), 2985.2 (w), 1741–1711 (m, broad), 1344.4 (s), 1257.7 (vs), 1134.0 (s); HRMS calcd for $C_{12}H_9F_5O_2$ 280.0523, obsd 280.0530.

4-Methyl-β,β-difluoro-α-(trifluoromethyl)styrene (19). p-$CH_3C_6H_4I$ (2.45 g, 11.2 mmol) and **7b** (0.89 M, 24 mL, 21 mmol) in DMF were stirred for 17 h at 85 °C. The reaction mixture was extracted with pentane (6 × 20 mL), and the combined pentane extracts were washed with 10% HCl/H_2O (2 × 50 mL), dried over $MgSO_4$, and filtered. The pentane was removed by distillation at atmospheric pressure, and the residue was distilled at reduced pressure to give 1.64 g (66%) of **19**: bp 83–85 °C/65 mmHg; GLPC purity 98%; ^1H NMR δ 7.20 (bs, 4 H), 2.35 (s, 3 H); ^{13}C NMR δ 156.7 (ddq, J = 306, 292, 3.6 Hz), 139.8, 130.1, 129.8, 123.3, 123.1 (qdd, J = 272, 11, 6 Hz), 90.2 (qdd, J = 34, 28, 12 Hz), 21.3; GC–MS 222 ($M^{\bullet+}$, 62), 221 (100), 203 (21), 153 (55), 151 (52), 133 (96), 101 (16), 91 (12), 75 (16), 69 (19); FTIR 2925.5 (vw), 1732.9 (vs), 1516.2 (m), 1354.9 (vs), 1256.1 (s), 1174.8 (vs), 1137.1 (vs); (lit.[8c] 1740 for $C{=}CF_2$).

2-Fluoro-β,β-difluoro-α-(trifluoromethyl)styrene (20). o-FC_6H_4I (2.14 g, 9.64 mmol) and **7b** (1.0 M, 20 mL, 20 mmol) in DMF were stirred for 18 h at 65 °C. The isolation was carried out as described for **19** to give 1.40 g (64%) yellow liquid **20**: bp 125–126 °C at ambient pressure (lit.[3] bp 130–132 °C); GLPC purity 96%; ^1H NMR asymmetric multiplet between 7.1–7.5 ppm; ^{13}C NMR δ 161.5 (d, J = 250 Hz), 157.5 (ddq, J = 307, 294, 3.5 Hz), 132.7 (bs), 132.5 (d, J = 8.4 Hz), 125.0 (d, J = 3.6 Hz), 123.0 (qdd, J = 271, 12, 6 Hz), 116.7 (d, J = 22 Hz), 114.5 (d, J = 16 Hz), 85.1 (qdd, J = 37, 29, 16 Hz); GC–MS 226 ($M^{\bullet+}$, 100), 207 (20), 157 (56), 137 (38), 114 (44), 107 (26), 69 (27); FTIR 2959.9 (vw), 1738.4 (vs), 1496.8 (s), 1359.1 (vs), 1179.5 (vs), 1140.8 (vs).

p-$CF_2{=}C(CF_3)C_6H_4C(CF_3){=}CF_2$ (21). 1,4-Diiodobenzene (1.70 g, 5.15 mmol) and **7b** (1.10 M, 20 mL, 22 mmol) in DMF were stirred for 16 h at 95 °C. The isolation procedure described for **14** gave 1.10 g (63%) of a colorless liquid, **21**: GLPC purity 100%; ^1H NMR δ 7.40 (s); ^{13}C NMR δ 157.7 (ddq, J = 303, 293, 3.7 Hz), 131.3, 128.4, 123.6 (qdd, J = 271, 12, 6 Hz), 90.5 (qdd, J = 35.4, 26.9, 13.4 Hz); GC–MS 338 ($M^{\bullet+}$, 100), 319 (27), 269 (28), 249 (27), 226 (47), 219 (30), 200 (63), 169 (35), 99 (20), 69 (35); FTIR 3047.8 (vw), 1742.5 (vs), 1726.3 (vs), 1356.2 (vs), 1322.6 (s), 1284.4 (vs), 1255.7 (vs); HRMS calcd for $C_{12}H_4F_{10}$ 338.0153, obsd 338.0137.

m-$CF_2{=}C(CF_3)C_6H_4C(CF_3){=}CF_2$ (22). 1,3-Diiodobenzene (1.70 g, 5.15 mmol) and **7b** (0.89 M, 24 mL, 21 mmol) in DMF were stirred for 17 h at 85 °C. The isolation procedure described for **14** gave 1.15 g (66%) of a light yellow liquid, **22**: GLPC purity 98%; ^1H NMR δ asymmetric multiple centered at 7.40 ppm; ^{13}C NMR δ 157.3 (ddq, J = 307, 293, 3.6 Hz), 132.2, 131.6, 129.8, 127.5, 123.1 (qdd, J = 271, 12.2, 6.1 Hz), 90.1 (qdd, J = 35.4, 26.9, 13.4 Hz); GC–MS 338 ($M^{\bullet+}$, 100), 319 (31), 269 (25), 249 (32), 226 (65), 219 (39), 200 (81), 169 (48), 99 (24), 69 (59); FTIR 3071.1 (vw), 1728.2 (s), 1340.4 (s), 1274.0 (s), 1147.8 (vs), 1134.0 (s); HRMS calcd for $C_{12}H_4F_{10}$ 338.0153, obsd 338.0152.

Competition Reaction between 1 and 7a with C_6H_5I. Zinc reagents **1** (0.58 M, 1.7 mL, 1.0 mmol) and **7a** (0.71 M, 1.4 mL, 1.0 mmol) in DMF and C_6H_5I (0.24 g, 1.2 mmol) were stirred for 3 h at 70 °C. ^{19}F NMR analysis of the reaction mixture revealed an 85:15 ratio of $C_6H_5CF{=}CF_2$ to **10**, as well as unreacted **7a** (no zinc reagent **1** was observed).

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Supplementary Material Available: ^{13}C NMR spectra of compounds **8**, **10–21**, and **22**, plots of σ vs ^{19}F NMR chemical shifts, and $^2J_{F_b-F_c}$ coupling constants (16 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.