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A New Route for the Preparation of Substituted 2,2-Difluorostyrenes and a Convenient Route to Substituted (2,2,2-Trifluoroethyl)benzenes

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The (2,2-difluoroethenyl)zinc reagent **II** is coupled with aryl iodides or bromides in the presence of $Pd(PPh_3)_4$ in DMF to give the corresponding 2,2-difluorostyrenes **IV**. The 4-substituted (tetrafluoroaryl)copper reagents are coupled with 2,2-difluoro-1-iodoethylene (**I**) to produce the corresponding styrene derivatives **VII**. Both methods provide good yields of the coupled products. These products react with wet KF in DMF or DMSO to form the (2,2,2-trifluoroethyl)benzene derivatives **VIII** in good yields.

Introduction

In recent years, 2,2-difluorostyrenes have been shown to be important substances in organic synthesis and material science.[1] However, few methods for the preparation of 2,2-difluorostyrenes have been reported. One involved the reaction of difluoromethylene ylide[2] with aldehydes.[3] This Wittig reaction has limited application because of the lack of tolerance for groups substituted on the benzaldehyde and gives moderate yields.

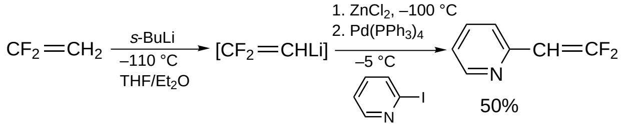
$$2Ph_3P + CF_2Br_2 + RCHO \xrightarrow[70\ °C]{TG}$$

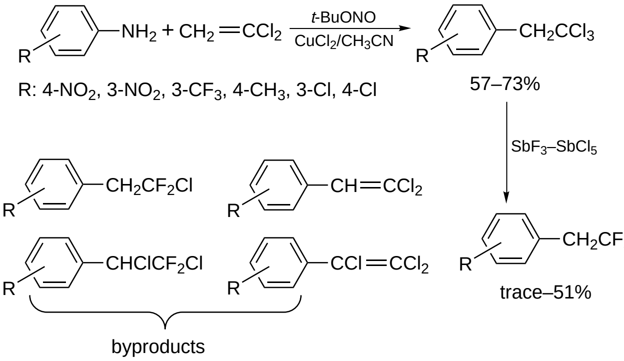
$$RCH{=}CF_2 + Ph_3PO + Ph_3PBr_2$$

$$\begin{array}{lll} R: & C_6H_5 & 65\% \\ & C_6F_5 & 20\% \end{array}$$

An alternative method to 2,2-difluorostyrenes is *via* metalation of 1,1-difluoroethylene with *s*-BuLi at −110 °C to form the lithium reagent,[4] which undergoes exchange with $ZnCl_2$ at low temperature to yield the zinc reagent **II**.[5] This zinc reagent is stable and readily couples with 2-iodopyridine in the presence of a catalytic amount of $Pd(PPh_3)_4$.[6] This is the only reported reaction with zinc reagent **II** for the preparation of a 2,2-difluorostyrenes. Zinc reagents **II** prepared by this method have some drawbacks, since 1,1-difluoroethylene has a low boiling point (−83 °C) and the reaction sequences at low temperature are difficult to monitor.

In 1988, Kumadaki and co-workers[7] reported the synthesis of (2,2,2-trifluoroethyl)aryls. In this method, aromatic amines were treated with 1,1-dichloroethene, *t*-BuONO, and $CuCl_2$ in acetonitrile to form the trichloroethyl compounds, which on treatment with $SbF_3{-}SbCl_5$ form the trifluoroethyl compounds. This type of reaction produces many byproducts, and the yields of the trifluoroethyl compounds are often low.





Recently, we reported the synthetic applications of polyfluorinated vinyl zinc, cadmium, and copper reagents.[8] We now describe two facile methods for the preparation of 2,2-difluorostyrenes. For simple aryl derivatives, the palladium catalyzed coupling reaction of aromatic iodides with (2,2-difluoroethenyl)zinc (**II**) worked well. For perfluoroaryl halides, (perfluoroaryl)copper reagents were coupled with 2,2-difluoroiodoethylene (**I**). A convenient route to {2,2,2-trifluoroethyl}benzenes was developed by treatment of the 2,2-difluorostyrene derivatives with wet KF in DMF or DMSO.

Results and Discussion

Coupling of (2,2-Difluoroethenyl)zinc Reagent II with Aryl Iodides III. Mono- and bis(2,2-difluoroethenyl)zinc reagent **II** was prepared by treatment of 2,2-difluoroiodoethylene with acid-washed zinc in dry DMF.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

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[6] Gillet, J. P.; Sauvetre, R.; Normant, J. F. *Synthesis* **1986**, 538. Recently, Ichikawa has proposed a zinc intermediate in the coupling of aryl iodides with a vinylzirconium intermediate in the presence of zinc iodide: Ichikawa, J., Fujiwara, M., Nawata, T., Okauchi, T., Minami, T. *Tetrahedron Lett.* **1996**, *37*, 8799.

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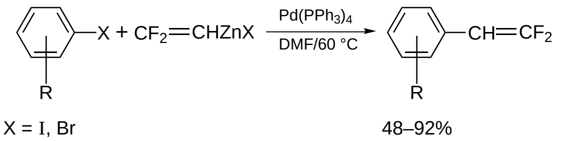
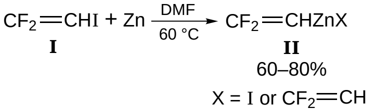
Table 1. Reaction of Aryl Halides with (2,2-Difluoroethenyl)zinc Reagent



entry[a]	R	product	yield, %[b]
1	*o*-CH_3	*o*-$CH_3C_6H_4CH{=}CF_2$	71
2	*m*-CH_3	*m*-$CH_3C_6H_4CH{=}CF_2$	78
3	*p*-CH_3	*p*-$CH_3C_6H_4CH{=}CF_2$	75
4	*m*-CH_3O	*m*-$CH_3OC_6H_4CH{=}CF_2$	88
5	*p*-$CH_3C(O)$	*p*-$CH_3C(O)C_6H_4CH{=}CF_2$	78
6	*m*-NO_2	*m*-$NO_2C_6H_4CH{=}CF_2$	92
7	*p*-NO_2	*p*-$NO_2C_6H_4CH{=}CF_2$	86
8	*o*-F	*o*-$FC_6H_4CH{=}CF_2$	69
9	*m*-CF_3	*m*-$CF_3C_6H_4CH{=}CF_2$	62
10	*p*-CF_3	*p*-$CF_3C_6H_4CH{=}CF_2$	80
11	1,4-diiodo	1,4-$CF_2{=}CHC_6H_4CH{=}CF_2$	69
12	C_6H_5	$C_6H_5CBr{=}CF_2$	48
13	C_6H_5	$C_6H_5CH{=}CF_2$	81[c]
14	C_6H_5	$C_6H_5CH{=}CF_2$	71[d]

[a] The entry number is the product number. [b] Isolated yield is based on aryl halides. [c] Isolated yield is based on iodobenzene. [d] Isolated yield is based on bromobenzene.

The reaction mixture was heated to 60 °C to initiate the reaction. When the reaction started, the heating was discontinued. The reaction gave a 60−80% yield of **II** in 1 h on the basis of ^{19}F NMR (*vs* internal α,α,α-trifluorotoluene). The reaction gave the best yield of the zinc reagent **II** when the temperature was maintained between 50 and 60 °C: ^{19}F NMR (internal standard $CFCl_3$) -63.0 (dd, $J = 56.2$, 14.0 Hz), -76.4 (dd, $J = 56.8$, 56.8 Hz), -63.1 (dd, $J = 55.6$, 13.3 Hz), -76.4 (dd, $J = 55.7$, 55.7 Hz).

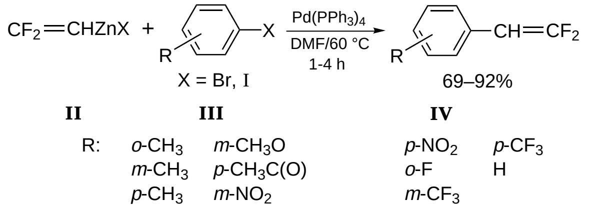


$$\underset{\textbf{I}}{CF_2{=}CHI} + Zn \xrightarrow[60\ °C]{DMF} \underset{\textbf{II}}{CF_2{=}CHZnX}$$

60–80%

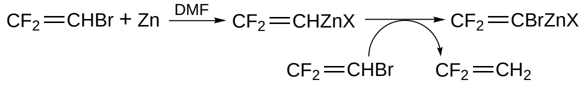
X = I or $CF_2{=}CH$

The zinc reagent **II** reacted smoothly with aryl iodides or bromides **III** in DMF in the presence of 5 mol % of $Pd(PPh_3)_4$ at 60 °C to give 2,2-difluorostyrenes **IV** (Table 1). In cases where the aryl iodides were substituted with electron-donating groups, such as methyl and methoxy, the reaction required 4 h. When the aryl iodides were substituted with electron-withdrawing groups, such as fluorine and trifluoromethyl, the reaction was completed in 2 h. Typical conditions for complete consumption of **III** involved stirring a 1.4:1 ratio of **II** to **III** at 60 °C for 1−6 h with 5 mol % of the $Pd(PPh_3)_4$ catalyst. The reaction of 1,4-diiodobenzene with 2.5 equiv of **II** in DMF and a catalytic amount of $Pd(PPh_3)_4$ at 60 °C for 2 h gave a 69% yield of 1,4-bis(2,2-difluoroethenyl)benzene (entry 11). In the presence of $Pd(PPh_3)_4$ the reaction of 4′-iodoacetophenone can be accomplished at 60 °C in 3 h to give a 78% isolated yield. The aceto group on the benzene ring is preserved under these conditions, and the product is readily isolated by chromatography (entry 5, Table 1).

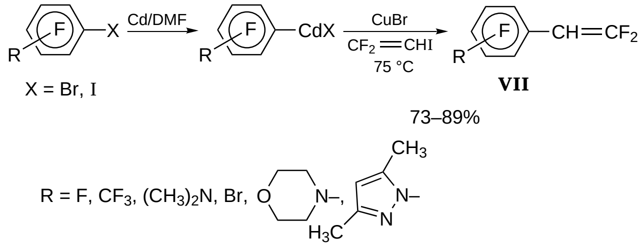


When $F_2C{=}CHBr$ (**V**) was utilized as a precursor to the vinylzinc reagent, less satisfactory results were obtained, and a novel acid−base reaction was observed. Thus, when **V** in DMF was heated at 90 °C for 1 h with zinc previously activated with $ClSiMe_3$ and CH_2I_2,[9] a 60% average yield of two different zinc reagents, **VI**, was observed by ^{19}F NMR analysis of the reaction mixture and a continuous evolution of gas was noted. The ^{19}F NMR spectrum of the reaction mixture indicated the presence of $F_2C{=}CHZnX$ [-63.0 (dd, $J = 56.8$, 14.0 Hz), -76.1 (dd, $J = 57.2$, 57.2 Hz)] and $F_2C{=}CBrZnX$ [-69.8 (d, $J = 56.6$ Hz), -85.0 (d, $J = 56.6$ Hz)];[10] the average ratio of these zinc reagent signals was 40/60, respectively. Confirmation of these assignments was obtained by treatment of this mixture with I_2 to give $F_2C{=}CHI$ and $F_2C{=}CBrI$, confirmed by comparison to authentic samples. In addition, when **VI** was treated with iodobenzene and a catalytic amount of $Pd(PPh_3)_4$ in DMF at 60 °C, a mixture of $F_2C{=}CHC_6H_5$ and $F_2C{=}CBrC_6H_5$ was formed. These two products were not easily separated by column chromatography, but $F_2C{=}CHC_6H_5$ could be selectively removed under full vacuum at 60 °C to give pure $F_2C{=}CBrC_6H_5$.

The formation of $F_2C{=}CBrZnX$ can be rationalized as shown below. The initially formed $F_2C{=}CHZnX$ undergoes an acid−base exchange reaction with $F_2C{=}CHBr$ to form $F_2C{=}CBrZnX$. Similar exchange did not occur with $F_2C{=}CHI$ (no $F_2C{=}CIZnX$ detected), and we have no explanation for this unusual result.



When this reaction was repeated and the low-boiling gas condensed (at −110 °C) into Br_2, we obtained a 29% yield of CF_2BrCH_2Br, confirmed by comparison to an authentic sample. Subsequent quenching of the zinc reagents formed in this reaction gave $F_2C{=}CHI$ and $F_2C{=}CBrI$[11] in 21% and 30% isolated yields, respectively.



Reaction of (Perfluoroaryl)copper Reagent with I. The 4-substituted (tetrafluoroaryl)copper reagent was prepared by treatment of the 4-substituted tetrafluoroaryl iodide (or bromide) with acid-washed cadmium (or zinc powder) in DMF at room temperature under a nitrogen atmosphere to form the (perfluoroaryl)cadmium or zinc reagents in quantitative yield.[12] The cadmium or zinc reagents undergo metathesis with CuBr at room temperature to give the corresponding copper reagent.

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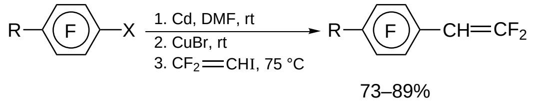
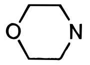
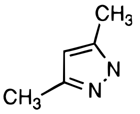
(10) Prepared independently from $F_2C{=}CBr_2$ and Zn.

(11) Prepared independently by quenching the zinc reagent from $F_2C{=}CBr_2$[10] with I_2.

(12) Nguyen, B. V.; Burton. D. J. *J. Fluorine Chem.* **1994**, *67*, 205.

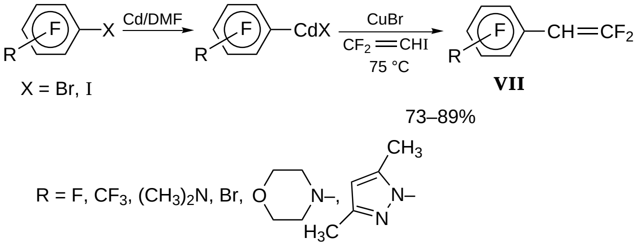
Table 2. Coupling between the Substituted (4-Tetrafluoroaryl)copper Reagent with 2,2-Difluoro-1-iodoethene



Entry[a]	X	R	Yield %[b]
15	I	F	84
16	Br	CF_3	73
17	I	$(CH_3)_2N$	73
18	I		86
19	I		89
20	Br	Br	89

[a] The entry number is the product number. [b] Isolated yield is based on the substituted (4-tetrafluoroaryl)copper reagent.

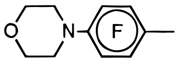
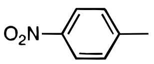
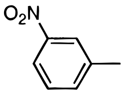
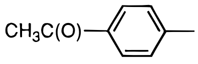
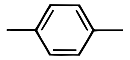
The copper reagent readily undergoes coupling with **I** at 75 °C to give high yields of the expected coupled products **VII**. The results of this study are summarized in Table 2. The coupling reaction proceeded without metal–halogen exchange as determined by ^{19}F NMR analysis of the reaction mixture. For example, treatment of 1,4-dibromotetrafluorobenzene with excess acid-washed cadmium in DMF at 80 °C for 2 h produced the (4-bromotetrafluorophenyl)cadmium reagent,[13] which subsequently undergoes a quantitative metathesis reaction with cuprous bromide at room temperature. The copper reagent coupled with **I** at 75 °C in 3 h to afford an 89% isolated yield of 1-bromo-4-(2,2-difluoroethenyl)tetrafluorobenzene (entry 20).



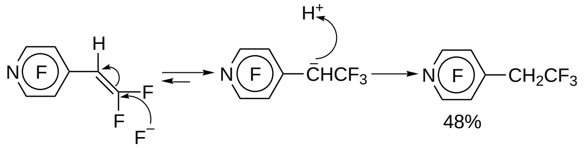
Under the same conditions, (4-tetrafluoropyridyl)copper reagent reacts with **I** at 75 °C in 4 h to give only 4-(2,2,2-trifluoroethyl)tetrafluoropyridine in 48% isolated yield. This product may be explained by attack of fluoride ion in the reaction mixture on the vinyl group of the initially formed coupled product to form an anion which abstracts a proton from solvent to produce the 4-(2,2,2-trifluoroethyl)tetrafluoropyridine.

Table 3. Reaction of 1,1-Difluorostyrenes with KF

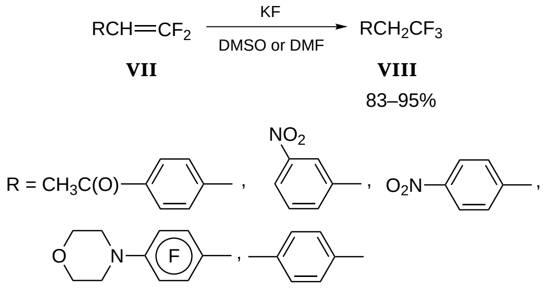
$$RCH{=}CF_2 \xrightarrow[\text{DMSO or DMF}]{\text{KF (wet)}} \underset{83-95\%}{RCH_2CF_3}$$

Entry[a]	R	Temp.	Time (h)	Yield %[b]
22		60	3	94
23		rt	10	92
24		70	5	95
25		60	2	90
26		100	12	83

[a] The entry number is the product number. [b] Isolated yield is based on 1,1-difluoroalkene.



Reaction of Styrene Derivatives with Wet KF. 2,2-Difluorostyrenes react with wet KF in DMF or DMSO to give (2,2,2-trifluoroethyl)benzene in good yield. This method can be used as an alternative route to introduce the 2,2,2-trifluoroethyl group into organic molecules.[7] In entry 25 (Table 3), 4-(2,2-difluoroethenyl)-1-acetophenone added HF across the 2,2-difluoroethenyl group when it was treated with wet KF in DMF at 60 °C for 2 h to give a 90% isolated yield of the addition product. 1,4-Bis(2,2-difluoroethenyl)benzene reacted with excess wet KF in DMSO at 100 °C for 12 h and gave complete addition of HF to both 2,2-difluoroethenyl groups in 83% yield (entry 26).



In conclusion, we have presented a new method for the preparation of 2,2-difluorostyrenes *via* the $Pd(PPh_3)_4$-catalyzed coupling reaction with the (2,2-difluoroethenyl)zinc reagent, or the coupling of tetrafluoroaryl copper reagents with iododifluoroethylene. The availability of the catalysts and substituted aryl halide precursors, the simplicity of the experimental procedure, and the high yields obtained make this approach a facile method to (2,2-difluoroethenyl)benzenes and should provide a convenient entry for the introduction of the CF_3CH_2 group into organic molecules.

Experimental Section

General. All reactions were monitored by ^{19}F NMR analysis of the reaction mixtures on a 90-MHz spectrometer. The ^1H, ^{19}F, and ^{13}C NMR spectra of final products were obtained on a 300-MHz spectrometer ($CDCl_3$, $CFCl_3$, or TMS internal

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[13] Burton, D. J.; Yang, Z. Y.; MacNeil, K. J. *J. Fluorine Chem.* **1991**, *52*, 251.

references). FT-IR spectra were recorded as CCl_4 solutions in a 0.1 cm path length cell. Low-resolution mass spectra analyses were performed at 70 eV in the electron-impact mode on a single quadrapole instrument interfaced to a gas chromatograph fitted with an OV-101 column. High-resolution mass spectral analyses were performed by the University of Iowa High Resolution Mass Spectroscopy Facility at 70 eV in the electron impact mode. GLPC analyses were performed on a 5% OV-101 column and thermal conductivity detector, except for the viscous liquids. Melting points were obtained on a capillary melting point apparatus in open-ended capillaries and are uncorrected. $F_2C{=}CHBr$ is available commercially,[14] and $F_2C{=}CHI$ can be prepared by the method of Park.[15] All aromatic iodides were obtained from commercial sources and used directly.

Preparation of $CF_2{=}CHZnX$. A 100 mL two-necked, round-bottomed flask equipped with a septum, a Teflon-coated magnetic stir bar, and a dry ice condenser which was connected to N_2 and a mineral oil bubbler was charged with 1.9 g (30 mmol) of acid-washed zinc, 20 mL of dry DMF, and 0.8 g of $CF_2{=}CHI$. The reaction mixture was heated to 60 °C to initiate the reaction. When the reaction started, the heating was stopped, 2 g of $CF_2{=}CHI$ was added slowly, and the temperature was maintained at 50−60 °C. ^{19}F NMR (internal standard $CFCl_3$): δ −63.0 (dd, J = 56.2, 14.0 Hz), −76.4 (dd, J = 56.8, 56.8 Hz), −63.1 (dd, J = 55.6, 13.3 Hz), −76.4 (dd, J = 55.7, 55.7 Hz). The yield of the mono- and biszinc reagents was 80% and the ratio of mono-/biszinc was 90/10.

Preparation of 2-(2,2-Difluoroethenyl)toluene (1). In a typical experimental procedure, a 50 mL two-necked, round-bottomed flask equipped with a septum, a Teflon-coated magnetic stir-bar, and an N_2 inlet which was connected to a mineral oil bubbler was charged with 2.2 g (10 mmol) of 2-iodotoluene, 14.2 mmol (7.5 mL × 1.9 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$. The reaction mixture was stirred at 60 °C under an N_2 atmosphere for 4 h. ^{19}F NMR analysis showed the reaction was completed. The reaction mixture was introduced onto a silica gel column and eluted with hexane to give 1.1 g (71%) of clear liquid **1**: GLPC purity 100.0%; ^{19}F NMR δ −84.8 (d, J = 31.6 Hz, 1F), −85.7 (dd, J = 31.4, 25.9 Hz, 1F); ^{1}H NMR δ 7.4 (m, 1H), 7.1 (m, 3H), 5.3 (dd, J = 25.4, J = 3.9 Hz, 1H), 2.3 (s, 3H); ^{13}C NMR δ 156.8 (dd, J = 296.6, 287.4 Hz), 136.5 (d, J = 4.3 Hz), 130.5 (s), 129.3 (t, J = 5.7 Hz), 128.6 (d, J = 7.7 Hz), 127.7 (s), 126.5 (s), 79.7 (dd, J = 28.8, 14.9 Hz), 19.5 (s); FT-IR (cm^{-1}) 3080.5 (w), 3036.1 (w), 2958.9 (w), 2935.8 (w), 2864.5 (w), 2669.6 (w), 1736.0 (s), 1498.7 (w), 1460.2 (m), 1354.1 (s), 1294.3 (w), 1249.9 (s), 1226.8 (s), 1176.6 (s), 1111.1 (w); GCMS 155 (M^+ + 1, 10.0), 154 (100.0), 139 (1.5), 135 (5.8), 134 (28.3), 133 (53.3), 127 (11.1), 119 (2.1), 104 (15.7), 91 (3.5), 77 (13.9), 76 (5.3), 75 (7.2), 63 (10.6); HRMS calcd for $C_9H_8F_2$ 154.0594, found 154.0601.

Preparation of 3-(2,2-Difluoroethenyl)toluene (2). Similarly, **2** was prepared from 2.2 g (10 mmol) of 3-iodotoluene, 14.2 mmol (7.5 mL × 1.9 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 4 h. Usual workup with hexane as eluent gave 1.2 g (78%) of clear liquid **2**: GLPC purity 97.5%; ^{19}F NMR δ −83.1 (dd, J = 31.9, 26.9 Hz, 1F), −85.3 (d, J = 32.8 Hz, 1F); ^{1}H NMR δ 7.2 (m, 1H), 7.1 (m, 2H), 7.0 (t, J = 7.4 Hz, 1H), 5.2 (dd, J = 26.3, 3.9 Hz, 1H), 2.3 (s, 2H); ^{13}C NMR δ 156.8 (dd, J = 297.7, 287.3 Hz), 138.6 (s), 130.7 (t, J = 5.9 Hz), 128.9 (s), 128.8 (s), 128.2 (s), 125.2 (s), 82.5 (dd, J = 28.8, 13.6 Hz), 21.3 (s); FT-IR (cm^{-1}) 3041.9 (w), 2922.3 (w), 2870.2 (w), 1734.1 (s), 1604.9 (w), 1489.1 (w), 1338.7 (m), 1265.4 (m), 1188.2 (m), 1167.0 (w); GCMS 155 (M^+ + 1, 18.1), 154 (100.0), 153 (93.9), 139 (3.2), 135 (12.5), 134 (60.2), 133 (96.9), 127 (26.4), 119 (4.0), 104 (31.7), 103 (20.8), 102 (10.9), 101 (10.8), 89 (12.4), 77 (32.6), 76 (13.5), 75 (18.4), 63 (28.3), 62 (13.1); HRMS calcd for $C_9H_8F_2$ 154.0594, found 154.0588.

Preparation of 4-(2,2-Difluoroethenyl)toluene (3). Similarly, **3** was prepared from 2.2 g (10 mmol) of 4-iodotoluene, 14.2 mmol (7.5 mL × 1.9 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 4 h. Usual workup with hexane as eluent gave 1.15g (75%) of clear liquid **3**: GLPC purity 97.2%; ^{19}F NMR δ −83.8 (dd, J = 34.1, 26.3 Hz, 1F), −85.4 (d, J = 33.5 Hz, 1F); ^{1}H NMR δ 7.2 (dm, J = 8.2 Hz, 2H), 7.1 (dm, J = 8.1 Hz, 2H), 5.2 (dd, J = 26.4, 3.9 Hz, 1H), 2.3 (s, 3H); ^{13}C NMR δ 156.7 (dd, J = 297.5, 286.9 Hz), 137.1 (m), 129.7 (s), 127.9 (m), 82.3 (dd, J = 29.1, 14.2 Hz), 21.1 (s); FT-IR (cm^{-1}) 3099.8 (w), 3030.4 (w), 2920.4 (w), 2862.5 (w), 1722.5 (s), 1512.3 (w), 1344.5 (w), 1244.2 (m), 1165.1 (m), 949.0 (m); GCMS 155 (M^+ + 1, 9.5), 154 (100.0), 153 (55.6), 151 (7.6), 135 (5.8), 134 (26.9), 133 (48.1), 127 (10.8), 115 (2.7), 104 (17.5), 103 (9.2), 89 (5.6), 78 (6.2), 77 (18.6), 76 (6.7), 75 (9.8), 63 (12.0); HRMS calcd for $C_9H_8F_2$ 154.0594, found 154.0593.

Preparation of 3-(2,2-Difluoroethenyl)anisole (4). Similarly, **4** was prepared from 2.3 g (10 mmol) of 3-iodoanisole, 14.2 mmol (7.5 mL × 1.9 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 4 h. Usual workup with hexane as eluent gave 1.5 g (88%) of clear liquid **4**: GLPC purity 98%; ^{19}F NMR δ −82.4 (dd, J = 30.0, 26.7 Hz, 1F), −84.7 (d, J = 31.5 Hz, 1F); ^{1}H NMR δ 7.2 (t, J = 7.9 Hz, 1H), 6.9 (m, 2H), 6.8 (dd, J = 8.2, 2.4 Hz, 1H), 5.2 (dd, J = 26.0, 3.9 Hz, 1H), 3.8 (s, 3H); ^{13}C NMR δ 160.4 (s), 156.8 (dd, J = 297.9, 288.0 Hz), 132.0 (t, J = 6.5 Hz), 129.9 (s), 120.5 (dd, J = 6.0, 3.6 Hz), 113.7 (dd, J = 6.1, 3.6 Hz), 112.9 (m), 82.5 (dd, J = 29.3, 13.3 Hz), 55.1 (s); FT-IR (cm^{-1}) 3036.1 (w), 3005.3 (w), 2955.1 (w), 2827.8 (w), 1739.9 (s), 1599.1 (m), 1583.6 (m), 1489.1 (m), 1458.3 (m), 1427.4 (m), 1348.3 (m), 1292.4 (m), 1267.3 (s), 1211.4 (m), 1151.6 (m), 1045.5 (m); GCMS 171 (M^+ + 1, 10.2), 170 (100.0), 141 (8.8), 140 (36.2), 139 (11.8), 127 (44.7), 119 (6.6), 107 (6.4), 101 (11.6), 99 (4.9), 91 (6.9), 77 (14.1), 75 (5.2), 63 (5.5); HRMS calcd for $C_9H_8F_2O$ 170.0543, found 170.0518.

Preparation of 4′-(2,2-Difluoroethenyl)acetophenone (5). Similarly, **5** was prepared from 2.5 g (10 mmol) of 4′-iodoacetophenone, 13.2 mmol (15 mL × 0.88 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 3 h. Usual workup with a mixture of hexane/ether (10/2) as eluent gave 1.4 g (78%) of white solid **5**, mp 38−39 °C: ^{19}F NMR δ −79.6 (td, J = 25.3, 5.9 Hz, 1F), −81.3 (d, J = 24.2 Hz, 1F); ^{1}H NMR δ 7.9 (dd, J = 8.6, 2.1 Hz, 2H), 7.4 (dd, J = 8.4, 2.1 Hz, 2H), 5.3 (dm, J = 26.0 Hz, 1H), 2.5 (d, J = 2.6 Hz, 3H); ^{13}C NMR δ 197.0 (s), 157.3 (dd, J = 300.3, 290.5 Hz), 136 (m), 135.5 (t, J = 12.3 Hz), 129 (s), 127.9 (dd, J = 6.7, 3.6 Hz), 82.7 (dd, J = 29.5, 12.4 Hz), 26.4 (s); FT-IR (cm^{-1}) 3352.5 (w), 3094.0 (w), 3030.4 (w), 2999.5 (w), 2958.9 (w), 1730.2 (s), 1689.7 (s), 1606.0 (m), 1413.9 (w), 1357.9 (m), 1275.0 (s), 1180.5 (m), 958.6 (m); GCMS 183 (M^+ + 1, 4.1), 182 (39.4), 168 (10.0), 167 (100.0), 140 (4.0), 139 (45.9), 138 (7.0), 120 (5.4), 119 (41.6), 99 (13.1), 89 (6.8), 88 (6.4), 75 (5.2), 63 (15.1), 62 (6.8); HRMS calcd for $C_{10}H_8F_2O$ 182.0543, found 182.0554.

Preparation of 3-(2,2-Difluoroethenyl)nitrobenzene (6). Similarly, **6** was prepared from 2.5 g (10 mmol) of 3-iodonitrobenzene, 12.2 mmol (17 mL × 0.72 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 4 h. Usual workup with a mixture of hexane/ether (9.5/0.5) as eluent gave 1.7 g (92%) of white solid **6**: mp 32−33 °C; ^{19}F NMR δ −79.5 (dd, J = 24.6, 5.9 Hz, 1F), −81.2 (d, J = 23.7 Hz, 1F); ^{1}H NMR δ 8.2 (t, J = 1.7 Hz, 1H), 8.1 (dm, J = 8.1 Hz, 1H), 7.7 (dm, J = 7.8 Hz, 1H), 7.5 (t, J = 8.0 Hz, 1H), 5.4 (dd, J = 25.2, 3.2 Hz, 1H); ^{13}C NMR δ 157.1 (dd, J = 299.1, 290.6 Hz), 148.7 (s), 133.5 (dd, J = 6.1, 3.6 Hz), 132.4 (dd, J = 6.7, 6.7 Hz), 129.8 (s), 122.4 (dd, J = 7.0, 3.6 Hz), 121.9 (m), 81.3 (dd, J = 31.3, 13.1 Hz); FT-IR (cm^{-1}) 3076.6 (w), 2972.5 (w), 2945.5 (w), 2866.4 (w), 1563.4 (m), 1479.5 (w), 1442.8 (w), 1348.3 (s), 1315.5 (w), 1253.8 (m), 1201.7 (w), 1138.1 (s), 1095.6 (m); GCMS 186 (M^+ + 1, 8.4), 185 (94.3), 169 (7.3), 155 (33.2), 139 (78.7), 127 (19.7), 119 (100.0), 113 (5.4), 99 (24.8), 89 (9.5), 77 (5.5), 75 (6.0), 63 (17.1); HRMS calcd for $C_8H_5F_2NO_2$ 185.0288, found 185.0294.

Preparation of 4-(2,2-Difluoroethenyl)nitrobenzene (7). Similarly, **7** was prepared from 2.5 g (10 mmol) of 4-iodonitrobenzene, 13.2 mmol (15 mL × 0.88 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 1 h. Usual workup with a mixture of hexane/ether (10/2) as eluent gave 1.6 g (86%) of white solid **7**; mp 35−36 °C; ^{19}F NMR δ −77.9 (dd, J = 25.1, 18.7 Hz, 1F), −79.2 (d, J = 18.2

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[14] PCR, Gainesville, FL.

[15] Park, J. D.; Abramo, J.; Hein, M.; Gray, D. N.; Lacher, J. R. *J. Org. Chem.* **1958**, *23*, 1661.

Hz, 1F); ^{1}H NMR δ 8.2 (dm, J = 8.9 Hz, 2H), 7.5 (dm, J = 8.9 Hz, 2H), 5.4 (dd, J = 25.5, 3.3 Hz, 1H); ^{13}C NMR δ 157.3 (dd, J = 301.6, 292.9 Hz), 146.6 (s), 137.5 (t, J = 7.2 Hz), 128.2 (dd, J = 6.5, 3.4 Hz), 124.1 (s), 81.8 (dd, J = 30.6, 13.1 Hz); FT-IR (cm^{-1}) 3078.6 (w), 3040.0 (w), 2945.5 (w), 2856.7 (w), 2654.2 (w), 1734.1 (s), 1602.9 (m), 1514.2 (s), 1350.2 (s), 1305.9 (w), 1255.7 (m), 1172.8 (m), 1107.2 (w), 941.3 (m), 860.3 (m); GCMS 186 (M$^+$ + 1, 6.1), 185 (80.5), 169 (2.2), 156 (3.3), 155 (47.7), 139 (25.8), 138 (19.5), 128 (3.0), 127 (47.1), 120 (10.8), 119 (100.0), 101 (7.8), 99 (37.6), 89 (15.9), 88 (17.9), 77 (10.9), 76 (3.3), 75 (12.4), 74 (8.6), 69 (2.5), 63 (37.4), 62 (16.9), 51 (18.4), 50 (17.9); HRMS calcd for $C_8H_5F_2NO_2$ 185.0288, found 185.0287.

Preparation of 1-(2,2-Difluoroethenyl)-2-fluorobenzene (8). Similarly, **8** was prepared from 2.2 g (10 mmol) of 2-fluoro-1-iodobenzene, 12.5 mmol (10 mL × 1.25 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 2 h. Usual workup with pentane as eluent gave 1.1 g (69%) of clear liquid **8**: GLPC purity >99%; ^{19}F NMR δ −81.8 (dd, J = 26.2, 26.2 Hz, 1F), −82.3 (d, J = 26.9 Hz, 1F), −117.8 (s, 1F); ^{1}H NMR δ 7.5 (m, 1H), 7.2 (m, 1H), 7.1 (m, 1H), 7.0 (m, 1H), 5.4 (dd, J = 25.9, 3.7 Hz, 1H); ^{13}C NMR δ 159.9 (dd, J = 248.6, 3.8 Hz), 157.0 (dd, J = 298.1, 288.7 Hz), 128.9 (d, J = 7.8 Hz), 124.5 (d, J = 3.5 Hz), 118.6 (dt, J = 12.8, 6.4 Hz), 115.7 (d, J = 21.8 Hz), 74.9 (ddd, J = 32.3, 13.5, 7.4 Hz); FT-IR (cm^{-1}) 3103.7 (w), 3047.7 (w), 2951.3 (w), 2667.7 (w), 1734.1 (s), 1574.0 (w), 1487.2 (m), 1462.1 (m), 1354.1 (m), 1246.1 (m), 1224.9 (m), 1168.9 (w), 949.0 (m); GCMS 159 (M$^+$ + 1, 8.2), 158 (100.0), 157 (10.7), 139 (6.2), 138 (15.1), 137 (6.2), 132 (8.4), 119 (4.4), 114 (3.4), 108 (14.5), 107 (25.0), 106 (2.1), 99 (3.2), 89 (11.9), 81 (6.9), 75 (4.6), 69 (3.7), 63 (8.8), 57 (8.8); HRMS calcd for $C_8H_5F_3$ 158.0343, found 158.0350.

Preparation of 3-(2,2-Difluoroethenyl)benzotrifluoride (9). Similarly, **9** was prepared from 2.7 g (10 mmol) of 3-iodobenzotrifluoride, 12.5 mmol (10 mL × 1.25 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 2 h. Usual workup with hexane as eluent gave 1.3 g (62%) of clear liquid **9**: GLPC purity >99%; ^{19}F NMR δ −63.5 (s, 3F), −81.0 (dd, J = 26.5, 26.5 Hz, 1F), −82.7 (d, 26.5 Hz, 1F); ^{1}H NMR δ 7.6 (s, 1H), 7.5−7.4 (m, 3H), 5.3 (dd, J = 25.6, 3.4 Hz, 1H); ^{13}C NMR δ 157.5 (dd, J = 298.9, 290.5 Hz), 132.0 (t, J = 6.7 Hz), 131.2 (m), 130.0 (q, J = 32.3 Hz), 129.6 (s), 124.8 (m), 124.7 (q, J = 272.2 Hz), 124.2 (m), 81.9 (dd, J = 30.5, 13.5 Hz); FT-IR (cm^{-1}) 3068.9 (w), 3036.1 (w), 2859.5 (w), 1730.2 (m), 1438.9 (w), 1352.2 (m), 1330.9 (m), 1234.5 (m), 1180.5 (s), 1141.9 (s), 1099.5 (m), 1078.3 (m); GCMS 209 (M$^+$ + 1, 9.3), 208 (100.0), 207 (9.1), 189 (22.3), 187 (9.1), 169 (9.3), 158 (30.8), 145 (2.7), 139 (14.7), 138 (12.0), 119 (15.5), 107 (4.5), 99 (8.5), 94 (2.5), 89 (4.9), 88 (7.0), 75 (7.8), 69 (7.4), 63 (9.1); HRMS calcd for $C_9H_5F_5$ 208.0311, found 208.0302.

Preparation of 4-(2,2-Difluoroethenyl)benzotrifluoride (10). Similarly, **10** was prepared from 2.0 g (7.3 mmol) of 4-iodobenzotrifluoride, 10 mmol (8 mL × 1.25 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 2 h. Usual workup with pentane as eluent gave 1.2 g (80%) of clear liquid **10**: GLPC purity >99%; ^{19}F NMR δ −63.2 (s, 3F), −80.4 (dd, J = 25.4, 25.4 Hz, 1F), −82.0 (d, J 25.3 Hz, 1F); ^{1}H NMR δ 7.5 (d, J = 8.3 Hz, 2H), 7.4 (d, J = 8.3 Hz, 2H), 5.3 (dd, J = 25.7, 3.5 Hz, 1H); ^{13}C NMR δ 157.7 (dd, J = 299.8, 290.4 Hz), 134.9 (t, J = 6.6 Hz), 129.8 (qm, J = 32.7 Hz), 128.3 (dd, J = 6.9, 3.5 Hz), 126.1 (m), 124.8 (q, J = 271.8 Hz), 82.0 (dd, J = 30.2, 13.4 Hz); FT-IR (cm^{-1}) 3047.7 (w), 2665.8 (w), 1736.0 (s), 1608.7 (w), 1411.9 (w), 1354.1 (w), 1327.1 (s), 1248.0 (m), 1174.7 (s), 1141.9 (s), 1062.8 (m), 1020.4 (w), 935.5 (m); GCMS 209 (M$^+$ + 1, 9.9), 208 (100.0), 207 (8.9), 189 (35.7), 187 (9.9), 169 (12.9), 158 (46.1), 139 (18.4), 138 (14.1), 119 (14.9), 107 (5.7), 99 (10,0), 88 (8.0), 87 (6.4), 79 (7.0), 75 (7.5), 63 (10.4); HRMS calcd for $C_9H_5F_5$ 208.0311, found 208.0316.

Preparation of 1,4-Bis(2,2-difluoroethenyl)benzene (11). Similarly, **11** was prepared from 3.3 g (10 mmol) of 1,4-diiodobenzene, 25 mmol (20 mL × 1.25 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 2 h. Usual workup with pentane as eluent gave 1.1 g (69%) of clear liquid **11**: GLPC purity >99%; ^{19}F NMR δ −82.2 (dd, J = 28.4, 28.4 Hz, 1F), −84.3 (d, J = 30.3 Hz, 1F); ^{1}H NMR δ 7.3 (s, 4H), 5.2 (dd, J = 26.1, 3.6 Hz, 2H); ^{13}C NMR δ 157.2 (dd, J = 298.1, 288.7 Hz), 129.8 (m), 128.4 (m), 82.4 (dd, J = 29.6, 13.6 Hz); FT-IR (cm^{-1}) 3099.8 (w), 3040.0 (w), 2669.6 (w), 1865.3 (w), 1743.7 (s), 1512.3 (w), 1423.5 (w), 1357.9 (m), 1292.4 (w), 1269.2 (m), 1192.1 (s), 1093.7 (w), 949.0 (m), 868.0 (m); GCMS 203 (M$^+$ + 1, 11.0), 202 (100.0), 201 (5.2), 182 (14.6), 163 (3.2), 152 (10.9), 151 (62.0), 133 (28.6), 125 (4.7), 114 (5.9), 101 (17.3), 99 (5.5), 88 (7.2), 75 (8.2), 63 (9.5); HRMS calcd for $C_{10}H_6F_4$ 202.0406, found 202.0419.

Preparation of α-Bromo-*β*,*β*-difluorostyrene (12). A 100 mL two-necked, round-bottomed flask equipped with a septum, a Teflon-coated magnetic stir bar, and a dry ice condenser which was connected to N_2 and a mineral oil bubbler was charged with 1.9 g (30 mmol) of acid-washed zinc, 0.3 g (1.1 mmol) of diiodomethane, 0.12 mL (1.2 mmol) of $ClSiMe_3$ and 10 mL of dry THF. The reaction mixture was heated to reflux and then cooled to room temperature. The THF was removed *via* syringe, and full vacuum was applied to remove the remaining liquid. Then 20 mL of dry DMF and 2.9 g (20 mmol) of $CF_2{=}CHBr$ were added to the reaction flask. The reaction mixture was heated to 60−90 °C for 30 min. ^{19}F NMR analysis showed two types of zinc reagents, which were $CF_2{=}CHZnX$ [−63.0 (dd, J = 56.8, 14.0 Hz), −76.1 (dd, J = 57.2, 57.2 Hz)] and $CF_2{=}CBrZnX$ [−69.8 (d, J = 56.6 Hz), −85.0 (d, J = 56.6 Hz)]. The average ratio of these zinc reagents was 40/60, respectively. The total yield of both zinc reagents was 60%. The zinc reagent was syringed into a flask which contained 5 mol % of $Pd(PPh_3)_4$ and 2 g (20 mmol) of iodobenzene. The reaction mixture was heated at 60 °C for 4 h to give (2,2-difluoroethenyl)benzene and (1-bromo-2,2-difluoroethenyl)benzene in a 40/60 ratio based on ^{19}F NMR. The reaction mixture was introduced onto a silica gel column and eluted with hexane to give a mixture of the two products. *β*,*β*-Difluorostyrene was removed under full vacuum at 60 °C, and the α-bromo-*β*,*β*-difluorostyrene, 1.8 g (48%), remained in the flask: ^{19}F NMR δ −78.9 (d, J = 31.2 Hz, 1F), −85.2 (d, J = 31.2 Hz, 1F); ^{1}H NMR δ 7.4 (m, 2H), 7.3−7.2 (m, 3H); ^{13}C NMR δ 153.4 (dd, J = 294.2, 285.9 Hz), 131.8 (d, J = 3.6 Hz), 129.0 (m), 128.6 (s), 80.2 (dd, J = 34.3, 25.8 Hz); FT-IR (cm^{-1}) 3084.4 (w), 3061.2 (w), 3038.1 (w), 1728.3 (s), 1435.1 (w), 1282.7 (m), 1259.6 (m), 995.3 (s), 910.5 (w); GCMS 221 (M$^+$ + 1, 5.2), 220 (64.0), 219 (5.8), 218 (71.0), 140 (8.5), 139 (100.0), 138 (12.5), 120 (10.5), 119 (78.5), 112 (4.7), 99 (21.0), 89 (12.4), 87 (10.1), 75 (4.8), 69 (10.6), 63 (18.0); HRMS calcd for $C_8H_5F_2Br$ 218.9532, found 218.9738.

Preparation of *β*,*β*-Difluorostyrene from Iodobenzene (13). Similarly, **13** was prepared from 1.02 g (5 mmol) of iodobenzene, 7 mmol (10 mL × 0.7 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 4 h. Usual workup with pentane as eluent gave 0.57 g (81%) of clear liquid **13**: GLPC purity 97%; ^{19}F NMR δ −82.9 (dd, J = 30.8, 26.4 Hz, 1F), −84.8 (d, J = 33.9 Hz, 1F); ^{1}H NMR δ 7.3−7.2 (m, 5H), 5.3 (dd, J = 26.3, 3.9 Hz, 1H); ^{13}C NMR δ 156.6 (dd, J = 297.9, 288.4 Hz), 130.6 (t, J = 6.1 Hz), 128.9 (s), 127.8 (dd, J = 5.9, 3.7 Hz), 127.2 (s), 82.4 (dd, J = 29.2, 13.5 Hz); FT-IR (cm^{-1}) 3088.2 (w), 3063.1 (w), 3032.3 (w), 2660.0 (w), 1716.7 (s), 1491.1 (w), 1438.9 (w), 1346.4 (m), 1238.4 (m), 1161.2 (m), 939.4 (m), 902.7 (m); GCMS 142 (M$^+$ + 2, 0.2), 141 (5.4), 140 (100.0), 121 (3.2), 120 (8.9), 119 (9.0), 114 (13.9), 101 (4.5), 100 (1.5), 99 (4.3), 90 (56.4), 89 (12.9), 88 (5.9), 77 (1.1).

Preparation of *β*,*β*-Difluorostyrene from Bromobenzene (14). Similarly, **14** was prepared from 0.78 g (5 mmol) of bromobenzene, 7 mmol (10 mL × 0.7 M) of $CF_2{=}CHZnX$ reagent in DMF, and 5 mol % of $Pd(PPh_3)_4$ at 60 °C for 6 h. Usual workup with pentane as eluent gave 0.5 g (71%) of clear liquid **14**: GLPC purity >98%; ^{19}F NMR δ −82.9 (dd, J = 30.8, 26.3 Hz, 1F), −84.8 (d, J = 33.8 Hz, 1F); ^{1}H NMR δ 7.3−7.2 (m, 5H), 5.3 (dd, J = 26.3, 3.9 Hz, 1H); ^{13}C NMR δ 156.6 (dd, J = 297.9, 288.1 Hz), 130.6 (t, J = 6.1 Hz), 128.9 (s), 127.8 (dd, J = 5.9, 3.7 Hz), 127.2 (s), 82.4 (dd, J = 29.3, 13.5 Hz); FT-IR (cm^{-1}) 3082.4 (w), 3065.1 (w), 3028.4 (w), 2660.0 (w), 1734.1 (s), 1494.9 (w), 1440.9 (w), 1350.2 (m), 1242.2 (m), 1168.9 (m), 943.2 (m), 906.6 (w); GCMS 142 (M$^+$ + 2, 0.1), 141 (5.3), 140 (100.0), 121 (2.8), 120 (8.0), 119 (7.9), 114 (12.4), 101 (4.1), 100 (1.4), 99 (3.9), 90 (5.2), 89 (10.6), 88 (5.0), 77 (0.8).

Preparation of (2,2-Difluoroethenyl)pentafluorobenzene (15). A 50 mL, two-necked, round-bottomed flask equipped with a septum, a Teflon-coated magnetic stir bar, and an N_2 inlet which was connected to a mineral oil bubbler was charged with 2.9 g (10 mmol) of iodopentafluorobenzene, 1.7 g (15 mmol) of cadmium, and 10 mL of DMF. Then the reaction mixture was stirred at room temperature under an N_2 atmosphere for 30 min. The reaction mixture was transferred *via* syringe to a 100 mL, two-necked, round-bottomed flask equipped with a septum, a Teflon-coated magnetic stir bar, and a dry ice condenser connected to a nitrogen inlet, and the flask was charged with 1.4 g (10 mmol) of CuBr. The reaction mixture was stirred at room temperature under an N_2 atmosphere for 5 min, then 2.8 g (15 mmol) of $CF_2{=}CHI$ was added *via* syringe, and the reaction mixture was stirred for 3 h at 75 °C. The product was flash distilled, washed with water, and then extracted with ether. The organic layer was dried over $MgSO_4$, filtered, and distilled to give 1.9 g (84%) of **15**: bp 90 °C; GLPC purity >97%; ^{19}F NMR δ −74.6 (m, 1F), −78.7 (s, 1F), −139.5 (t, J = 19.9 Hz, 2F), −155.0 (t, J = 20.6 Hz, 1F), −162.6 (m, 2F); ^{1}H NMR δ 5.2 (d, J = 25.1 Hz); ^{13}C NMR δ 157.8 (dd, J = 300.1, 291.4 Hz), 145.2 (d, J = 252.4 Hz), 141.7 (dm, J = 259.9 Hz), 138.7 (dm, J = 224.6 Hz), 106.1 (m), 68.5 (dd, J = 38.9, 18.3 Hz); FT-IR (cm^{-1}) 3101.7 (w), 3051.6 (w), 2634.9 (w), 1726.4 (s), 1516.1 (s), 1487.2 (s), 1421.6 (w), 1336.7 (w), 1298.2 (m), 1209.4 (m), 1126.5 (w), 1003.0 (m), 981.8 (m), 902.7 (m); GCMS 230 (M$^+$, 100.0), 211 (10.5), 199 (4.0), 180 (24.8), 161 (84.9), 141 (8.1), 130 (10.6), 117 (6.2), 111 (5.0), 99 (4.6), 93 (8.6); HRMS calcd for $C_8H_5F_7$ 229.9966, found 229.9963.

Preparation of 1-(2,2-Difluoroethenyl)-4-(trifluoromethyl)tetrafluorobenzene (16). Similarly, **16** was prepared from 3.0 g (10 mmol) of 4-bromoheptafluorotoluene and 1.7 g (15 mmol) of cadmium, 10 mL of DMF, 1.4 g (10 mmol) CuBr, and 1.9 g (10 mmol) of $CF_2{=}CHI$ at 75 °C for 3 h. Usual workup gave 2.1 g (73%) of **16**: bp 90 °C; GLPC purity >99%; ^{19}F NMR δ −56.9 (t, J = 21.7 Hz, 3F), −71.1 (qm, J = 24.1 Hz, 1F), −76.0 (s, 1F), −137.9 (m, 2F), −141.3 (m, 2F); ^{1}H NMR δ 5.3 (d, J = 25.1 Hz); ^{13}C NMR δ 157.6 (dd, J = 302.6, 293.1 Hz), 144.6 (dm, J = 247.9 Hz), 144.4 (dm, J = 258.9 Hz), 121.1 (q, J = 274.5 Hz), 114.9 (m), 109.2 (qt, J = 35.2, 13.1 Hz), 68.5 (dd, J = 39.8, 17.8 Hz); FT-IR (cm^{-1}) 3107.5 (w), 3061.2 (w), 1739.9 (s), 1666.6 (m), 1489.1 (s), 1321.3 (s), 1253.8 (m), 1207.5 (s), 1159.3 (s), 1070.5 (m), 981.8 (m), 925.9 (m), 871.9 (m); GCMS 281 (M$^+$ + 1, 9.3), 280 (100.0), 261 (69.9), 241 (6.6), 230 (85.5), 211 (26.4), 192 (27.8), 180 (16.9), 161 (76.2), 142 (14.1), 141 (20.8), 123 (20.9), 117 (14.9), 93 (15.0), 69 (32.4); HRMS calcd for C_9HF_9 279.9934, found 279.9920.

Preparation of 1-(2,2-Difluoroethenyl)-4-(*N*,*N*-dimethylamino)tetrafluorobenzene (17). Similarly, **17** was prepared from 3.2 g (10 mmol) of 4-(*N*,*N*-dimethylamino)-1-iodotetrafluorobenzene and 1.7 g (15 mmol) of cadmium, 10 mL of DMF, 1.4 g (10 mmol) CuBr, and 2.3 g (12 mmol) of $CF_2{=}CHI$ at 75 °C for 5 h. The reaction mixture was filtered through a short silica gel column. The filtrate was concentrated *via* rotary evaporation, then introduced onto a silica gel column, and eluted with hexane to give 1.8 g (73%) of clear liquid **17**: GLPC purity >99%; ^{19}F NMR δ −76.6 (m, 1F), −81.2 (d, J = 16.3 Hz, 1F), −142.6 (tm, J = 20.3 Hz, 2F), −152.6 (dm, J = 13.7 Hz, 2F); ^{1}H NMR δ 5.2 (dm, J = 25.6 Hz, 1H), 3.0 (t, J = 2.1 Hz, 6H); ^{13}C NMR δ 157.2 (dd, J = 299.4, 289.2 Hz), 144.8 (dm, J = 244.6 Hz), 142.7 (dddd, J = 244.1, 14.6, 5.7, 3.8 Hz), 131.6 (tm, J = 10.9 Hz), 101.7 (tdd, J = 18.0, 8.2, 4.5 Hz), 69.1 (ddm, J = 38.7, 18.5 Hz), 43.4 (t, J = 4.1 Hz); FT-IR (cm^{-1}) 3045.8 (w), 2982.1 (w), 2933.9 (w), 2881.8 (w), 2791.1 (w), 1736.0 (s), 1639.6 (w), 1506.5 (w), 1475.6 (s), 1421.6 (w), 1346.4 (w), 1255.7 (m), 1197.8 (m), 1097.5 (w), 1010.7 (w), 974.1 (m), 910.5 (m); GCMS 256 (M$^+$ + 1, 6.9), 255 (71.0), 254 (100.0), 239 (18.4), 238 (28.4), 226 (3.5), 225 (5.3), 218 (3.8), 211 (2.6), 207 (3.1), 184 (3.9), 170 (3.7), 168 (4.7), 161 (23.6), 143 (9.7), 127 (11.9), 119 (7.4), 99 (4.6), 93 (4.6), 75 (4.8), 69 (5.1); HRMS calcd for $C_{10}H_7F_6N$ 255.0482, found 255.0459.

Preparation of 1-(2,2-Difluoroethenyl)-4-morpholinotetrafluorobenzene (18). Similarly, **18** was prepared from 1.8 g (5 mmol) of 4-morpholino-1-iodotetrafluorobenzene and 0.9 g (8 mmol) of cadmium, 10 mL of DMF, 0.8 g (5 mmol) CuBr, and 1.1 g (6 mmol) of $CF_2{=}CHI$ at 75 °C for 5 h. The reaction mixture was filtered through a short silica gel column. The filtrate was concentrated *via* rotary evaporation, then introduced onto a silica gel column, and eluted with hexane to give 1.3 g (86%) of clear solid **18**: ^{19}F NMR δ −76.0 (m, 1F), −80.5 (d, J = 15.0 Hz, 1F), −141.9 (tm, J = 32.4 Hz, 2F), −152.0 (dd, J = 19.7, 8.2 Hz, 2F); ^{1}H NMR δ 5.2 (dm, J = 25.5 Hz, 1H), 3.8 (t, J = 4.8 Hz, 4H), 3.3 (m, 4H); ^{13}C NMR δ 156.9 (dd, J = 299.8, 289.7 Hz), 144.9 (dm, J = 248.3 Hz), 142.8 (ddt, J = 245.1, 13.8, 4.8 Hz), 129.9 (tm, J = 10.7 Hz), 103.1 (tdd, J = 17.9, 8.0, 3.9 Hz), 68.9 (dd, J = 38.3, 18.1 Hz), 67.7 (s), 51.6 (t, J = 3.1 Hz); FT-IR (cm^{-1}) 3101.7 (w), 3047.7 (w), 2953.2 (w), 2901.1 (w), 2891.5 (w), 2843.2 (w), 1734.1 (m), 1633.8 (w), 1492.9 (s), 1444.7 (w), 1346.4 (w), 1325.2 (w), 1267.3 (m), 1213.3 (m), 1155.4 (w), 1114.9 (m), 987.6 (m), 908.5 (m); GCMS 298 (M$^+$ + 1, 5.7), 297 (45.5), 296 (5.2), 240 (11.4), 239 (100.0), 238 (69.1), 225 (5.9), 218 (4.8), 168 (4.2), 161 (22.6), 143 (4.4), 141 (2.9), 123 (2.9), 119 (2.5), 117 (2.4); HRMS calcd for $C_{12}H_9F_6NO$ 297.0588, found 297.0567.

Preparation of 1-(2,2-Difluoroethenyl)-4-(3,5-dimethylpyrazoyl)tetrafluorobenzene (19). Similarly, **19** was prepared from 1.1 g (2.9 mmol) of 4-(3,5-dimethylpyrazoyl)-1-iodotetrafluorobenzene and 0.7 g (6 mmol) of cadmium, 10 mL of DMF, 0.7 g (5 mmol) CuBr, and 0.7 g (4 mmol) of $CF_2{=}CHI$ at 75 °C for 4 h. The reaction mixture was filtered through a short silica gel column. The filtrate was concentrated *via* rotary evaporation, then introduced onto a silica gel column, and eluted with hexane to give 0.8 g (89%) of clear liquid **19**: GLPC purity >99%; ^{19}F NMR δ −73.1 (m, 1F), −77.7 (s, 2F), −139.4 (s, 2F), −146.9 (dd, J = 20.3, 9.7 Hz, 2F); ^{1}H NMR δ 6.1 (s, 1H), 5.3 (d, J = 25.2 Hz, 1H), 2.3 (s, 3H), 2.2 (s, 3H); ^{13}C NMR δ 157.4 (dd, J = 301.5, 292.0 Hz), 152.1 (s), 144.5 (dm, J = 252.5 Hz), 143.9 (ddm, J = 254.9, 11.9 Hz), 142.7 (s), 119.2 (tm, J = 13.7 Hz), 111.2 (tdd, J = 17.2, 8.2, 3.8 Hz), 107.3 (s), 69.0 (ddm, J = 38.9, 17.4 Hz), 13.7 (s), 10.8 (s); FT-IR (cm^{-1}) 3119.1 (w), 3057.4 (w), 2997.6 (w), 2931.9 (w), 1736.0 (s), 1566.3 (w), 1527.7 (m), 1494.9 (s), 1435.1 (w), 1406.2 (w), 1352.2 (w), 1302.0 (m), 1242.2 (m), 1120.7 (w), 1064.8 (w), 993.4 (m), 922.0 (m); GCMS 307 (M$^+$ + 1, 15.0), 306 (100.0), 305 (33.8), 291 (7.0), 287 (11.6), 264 (20.9), 252 (29.2), 250 (10.6), 246 (6.6), 238 (16.5), 237 (18.8), 225 (5.1), 215 (4.9), 211 (4.7), 205 (4.8), 199 (5.1), 187 (4.1), 175 (5.2), 168 (7.9), 161 (34.3), 69 (5.2), 65 (4.4); HRMS calcd for $C_{13}H_8F_6N_2$ 306.0592, found 306.0582.

Preparation of 1-Bromo-4-(2,2-difluoroethenyl)tetrafluorobenzene (20). A 50 mL, two-necked, round-bottomed flask equipped with a septum, a Teflon-coated magnetic stir bar, and an N_2 inlet which was connected to a mineral oil bubbler was charged with 3.1 g (10 mmol) of 1,4-dibromotetrafluorobenzene, 2.8 g (25 mmol) of cadmium, and 10 mL of DMF. The reaction mixture was stirred at 80 °C under an N_2 atmosphere for 2 h. The ^{19}F NMR showed that only the monocadmium reagent was formed. The reaction mixture was transferred *via* syringe to a 100 mL, two-necked, round-bottomed flask equipped with a septum, a Teflon-coated magnetic stir bar, and a dry ice condenser connected to a nitrogen inlet, and the flask was charged with 1.4 g (10 mmol) of CuBr. The reaction mixture was stirred at room temperature under an N_2 atmosphere for 5 min, then 2.3 g (12 mmol) of $CF_2{=}CHI$ was added *via* syringe, and the reaction mixture was stirred for 3 h at 70 °C. The reaction mixture was filtered through a short silica gel column. The filtrate was concentrated *via* rotary evaporation, then introduced onto a silica gel column, and eluted with hexane to give 2.6 g (89%) of **20**: GLPC purity 98%; ^{19}F NMR δ −77.5 (m, 1F), −78.1 (m, 1F), −133.9 (m, 2F), −138.5 (m, 2F); ^{1}H NMR δ 5.3 (d, J = 25.1 Hz); ^{13}C NMR δ 157.9 (dd, J = 301.5, 291.7 Hz), 145.9 (ddm, J = 250.9, 20.1 Hz), 144.9 (dm, J = 253.1 Hz), 110.6 (tdd, J = 17.0, 8.5, 3.7 Hz), 100.0 (t, J = 22.5 Hz), 69.3 (ddm, J = 39.2, 18.1 Hz); FT-IR (cm^{-1}) 3107.5 (w), 3059.3 (w), 2654.2 (w), 1730.3 (s), 1487.2 (s), 1396.5 (w), 1338.7 (w), 1275.0 (s), 1201.7 (m), 1074.4 (w), 974.1 (m), 916.2 (m), 831.4 (m); GCMS 293 (M$^+$ + 2, 3.1), 292 (43.2), 291 (5.3), 290 (47.1), 223 (13.1), 221 (14.3), 211 (18.4), 192 (13.5), 161 (100.0), 142 (16.2), 141 (19.4), 123 (15.8), 117 (10.4), 98 (8.6), 93 (13.1), 92 (14.5), 75 (10.0), 69 (12.1); HRMS calcd for $C_8H^{79}BrF_6$ 290.9155, found 290.9209.

Preparation of 4-(2,2,2-Trifluoroethyl)tetrafluoropyridine (21). A 50 mL, two-necked, round-bottomed flask equipped with a septum, a Teflon-coated magnetic stir bar, and an N_2 inlet which was connected to a mineral oil bubbler was charged with 7.7 mL of a 1.3 M solution in DMF (10 mmol) of 4-iodotetrafluoropyridine and 1.7 g (15 mmol) of cadmium. The reaction mixture was stirred at room temperature under an N_2 atmosphere for 30 min. The reaction mixture was transferred to a 100 mL, two-necked, round-bottomed flask equipped with a septum, a Teflon-coated magnetic stir-bar, and a dry-ice condenser connected with a nitrogen inlet, and the flask was charged with 1.4 g (10 mmol) of CuBr. The reaction mixture was stirred at room temperature under an N_2 atmosphere for 5 min, then 1.9 g (10 mmol) of $CF_2{=}CHI$ was added *via* syringe, and the reaction mixture was stirred for 4 h at 75 °C. The reaction mixture was poured into 100 mL of water, and product was extracted with 3 × 50 mL of diethyl ether. The organic layer was collected, dried over $MgSO_4$, filtered, and distilled to give 1.1 g (48%) of **21**: bp 120 °C; GLPC purity 99%; ^{19}F NMR δ −65.4 (m, 3F), −89.8 (m, 2F), −142.9 (m, 2F); ^{1}H NMR δ 3.7 (qm, J = 9.7 Hz); ^{13}C NMR δ 144.1 (dm, J = 245.7 Hz), 141.8 (dm, J = 261.5 Hz), 124.6 (q, J = 277.7 Hz), 123.8 (tm, J = 15.9 Hz), 29.2 (q, J = 33.9 Hz); FT-IR (cm^{-1}) 1730.2 (w), 1687.8 (w), 1647.3 (w), 1547.0 (w), 1491.0 (m), 1469.8 (s), 1356.0 (m), 1267.3 (m), 1236.4 (m), 1153.5 (m), 1095.6 (m), 1018.5 (w), 967.0 (w); GCMS 234 (M^{+} + 1, 4.0), 233 (57.9), 214 (19.3), 194 (6.8), 182 (5.4), 165 (5.9), 164 (100.0), 144 (8.8), 138 (8.2), 137 (7.2), 133 (3.3), 119 (11.4), 114 (8.1), 99 (10.5), 93 (7.1), 75 (5.0), 69 (34.1); HRMS calcd for $C_7H_2F_7N$ 233.0075, found 233.0061.

Preparation of 1-(2,2,2-Trifluoroethyl)-4-morpholinotetrafluorobenzene (22). A 50 mL, two-necked, round-bottomed flask equipped with a septum, a Teflon-coated magnetic stir bar, and an N_2 inlet which was connected to a mineral oil bubbler was charged with 1.0 g (3.36 mmol) of 1-(2,2-difluoroethenyl)-4-morpholino-2,3,5,6-tetrafluorobenzene, 0.6 g (10 mmol) of potassium fluoride, 10 mL of DMSO, and 0.5 mL of H_2O. The reaction was stirred at 60 °C for 2 h, and the NMR showed that the reaction was finished. The reaction mixture was filtered through a short silica gel column. The filtrate was concentrated *via* rotary evaporation with some silica gel; then the dry silica gel and product were introduced onto a silica gel column and eluted with hexane/ether (9/1) to give 1.0 g (94%) of white solid: mp 48−49 °C; ^{19}F NMR δ −66.7 (m, 3F), −144.1 (m, 2F), −151.5 (m, 2F); ^{1}H NMR δ 3.8 (m, 4H), 3.5 (qm, J = 10.1 Hz, 2H), 3.3 (m, 4H); ^{13}C NMR δ 146.6 (dddd, J = 246.9, 14.4, 8.4, 3.7 Hz), 142.6 (dddd, J = 245.4, 14.2, 4.6, 4.6 Hz), 131.0 (tm, J = 10.4 Hz), 125.2 (q, J = 277.4 Hz), 102.0 (tm, J = 18.4 Hz), 67.6 (s), 51.6 (t, J = 3.3 Hz), 27.7 (q, J = 33.2 Hz); FT-IR (cm^{-1}) 2968.6 (w), 2910.7 (w), 2895.3 (w), 2856.7 (w), 1668.5 (w), 1502.6 (s), 1438.9 (w), 1365.7 (w), 1269.2 (m), 1257.7 (m), 1163.1 (s), 1118.8 (m), 1103.3 (m), 985.7 (m); GCMS 318 (M^{+} + 1, 4.4), 317 (52.3), 298 (6.7), 260 (10.0), 259 (100.0), 245 (2.3), 208 (2.8), 191 (7.9), 190 (78.9), 189 (31.9), 181 (8.7), 162 (10.0), 143 (4.6), 117 (2.5), 69 (5.7); HRMS calcd for $C_{12}H_{10}F_7NO$ 317.0651, found 317.0672.

Preparation of 4-(2,2,2-Trifluoroethyl)nitrobenzene (23). Similarly, **23** was prepared from 1.1 g (6 mmol) of 4-(2,2-difluoroethenyl)nitrobenzene, 0.6 g (10 mmol) of potassium fluoride, 10 mL of DMF, and 0.5 mL of H_2O at room temperature for 10 h. Usual workup with a mixture of hexane/dichloromethane (10/2) as eluent gave 1.1 g (92%) of white solid **23**: mp 67−68 °C; ^{19}F NMR δ −65.9 (t, J = 10.2 Hz); ^{1}H NMR δ 8.2 (dm, J = 8.8 Hz, 2H), 7.5 (d, J = 8.5 Hz, 2H), 3.5 (q, J = 10.5 Hz, 2H); ^{13}C NMR δ 148.2 (s), 137.8 (m), 131.6 (s), 125.6 (q, J = 277.0 Hz), 124.0 (s), 40.1 (q, J = 30.3 Hz); FT-IR (cm^{-1}) 3078.6 (w), 2949.3 (w), 2862.5 (w), 1923.1 (w), 1604.8 (w), 1523.8 (m), 1498.8 (w), 1421.6 (w), 1359.9 (s), 1267.3 (m), 1199.8 (w), 1149.6 (s), 1118.8 (m), 1076.3 (m); GCMS 206 (M^{+} + 1, 2.6), 205 (32.3), 186 (4.1), 175 (11.2), 159 (17.2), 147 (3.5), 139 (10.6), 127 (13.8), 119 (16.1), 110 (6.7), 109 (100.0), 99 (4.4), 90 (6.6), 89 (21.6), 83 (18.7), 69 (7.5), 63 (22.0); HRMS calcd for $C_8H_6F_3NO_2$ 205.0351, found 205.0340.

Preparation of 3-(2,2,2-Trifluoroethyl)nitrobenzene (24). Similarly, **24** was prepared from 0.92 g (5 mmol) of 3-(2,2-difluoroethenyl)nitrobenzene, 0.6 g (6 mmol) of potassium fluoride, 10 mL of DMF, and 0.5 mL of H_2O at 70 °C for 5 h. Usual workup with a mixture of hexane/ether (9.5/0.5) as eluent gave 0.98 g (95%) of white solid **24**: mp 45−46 °C; ^{19}F NMR δ −66.3 (t, J = 10.5 Hz); ^{1}H NMR δ 8.2 (s, 1H), 8.1 (dm, J = 8.1 Hz, 1H), 7.7 (d, J = 7.6 Hz, 1H), 7.6 (t, J = 7.9 Hz, 1H), 3.6 (q, J = 10.7 Hz, 2H); ^{13}C NMR δ 148.9 (s), 137.0 (s), 132.8 (q, J = 3.2 Hz), 130.3 (s), 126.1 (q, J = 276.9 Hz), 125.5 (s), 123.6 (s), 39.9 (q, J = 30.4 Hz); FT-IR (cm^{-1}) 3097.9 (w), 3051.6 (w), 2879.9 (w), 1745.7 (s), 1537.4 (m), 1359.9 (s), 1292.4 (w), 1255.7 (m), 1182.4 (w), 1095.6 (w), 970.2 (w), 918.2 (w); GCMS 206 (M^{+} + 1, 4.5), 205 (51.8), 189 (4.5), 175 (11.1), 159 (50.4), 139 (19.4), 127 (8.3), 119 (17.0), 109 (100.0), 89 (12.2), 83 (9.4), 75 (4.4), 69 (2.9), 63 (9.9); HRMS calcd for $C_8H_6F_3NO_2$ 205.035, found 205.0344.

Preparation of 4′-(2,2,2-Trifluoroethyl)acetophenone (25). Similarly, **25** was prepared from 1.1 g (6 mmol) of 4′-(2,2-difluoroethenyl)-1-acetophenone, 0.6 g (10 mmol) of potassium fluoride, 10 mL of DMF, and 0.5 mL of H_2O at 60 °C for 2 h. Usual workup with a mixture of hexane/dichloromethane (10/2) as eluent gave 1.1 g (90%) of white solid **25**: mp 37−38 °C; ^{19}F NMR δ −66.0 (t, J = 10.6 Hz); ^{1}H NMR δ 7.9 (dm, J = 8.3 Hz, 2H), 7.4 (d, J = 8.0 Hz, 2H), 3.4 (q, J = 10.7 Hz, 2H), 2.6 (s, 3H); ^{13}C NMR δ 197.6 (s), 137.2 (s), 135.7 (m), 130.8 (s), 128.9 (s), 126.0 (q, J = 276.9 Hz), 40.1 (q, J = 29.8 Hz); FT-IR (cm^{-1}) 3354.4 (w), 3088.2 (w), 3045.8 (w), 2993.7 (w), 2931.9 (w), 1685.9 (s), 1602.9 (w), 1419.7 (w), 1352.2 (s), 1263.4 (s), 1199.8 (w), 1170.6 (w), 1138.1 (s), 1080.2 (m), 1012.7 (w), 960.6 (w), 902.7 (w); GCMS 202 (M^{+}, 16.3), 188 (9.7), 187 (100.0), 159 (29.0), 139 (16.4), 119 (14.4), 109 (100.0), 99 (4.6), 91 (6.0), 90 (16.8), 89 (31.6), 83 (12.7), 75 (9.8), 69 (16.6), 63 (36.5); HRMS calcd for $C_{10}H_9F_3O$ 202.0605, found 202.0595.

Preparation of 1,4-Bis(2,2,2-trifluoroethyl)benzene (26). Similarly, **26** was prepared from 0.5 g (2.5 mmol) of 1,4-bis-(2,2-difluoroethenyl)benzene, 0.6 g (10 mmol) of potassium fluoride, 10 mL of DMSO, and 0.5 mL of H_2O at 100 °C for 12 h. Usual workup with hexane as eluent gave 0.5 g (83%) of white solid **25**: ^{19}F NMR δ −66.4 (t, J = 10.4 Hz); ^{1}H NMR δ 7.3 (s, 4H), 3.3 (q, J = 10.8 Hz, 4H); ^{13}C NMR δ 131.5 (m), 127.2 (q, J = 375.9 Hz), 39.9 (q, J = 29.4 Hz); FT-IR (cm^{-1}) 3061.2 (w), 3040.0 (w), 2943.5 (w), 1520.0 (w), 1425.5 (w), 1356.0 (m), 1292.4 (w), 1261.5 (s), 1209.4 (w), 1145.8 (s), 1076.3 (m); GCMS 243 (M^{+} + 1, 4.2), 242 (38.6), 223 (7.0), 203 (2.7), 191 (3.4), 174 (12.5), 173 (100.0), 153 (10.4), 133 (12.5), 122 (5.9), 109 (12.3), 104 (16.6), 103 (6.9), 89 (2.3), 77 (6.7), 69 (5.3); HRMS calcd for $C_{10}H_8F_6$ 242.0530, found 242.0521.

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Supporting Information Available: ^{13}C NMR spectra of all compounds (26 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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