

## Experimental Section

All moisture sensitive reactions were done using flame-dried glassware flushed with argon, magnetic stirring, and dry, freshly distilled solvents. THF was distilled from Na/benzophenone. Toluene was distilled from calcium hydride. Other solvents were HPLC grade and were used without purification.  $\text{CH}_2\text{Cl}_2$  (HCFC-21, 97%) and  $\text{CH}_2\text{Br}_2$  (Halon 1102, 98%) were purchased from SynQuest Laboratories, Inc. (Alachua, FL) and used without further purification. Other commercial reagents were purchased from Aldrich and used as received. TIPS-acetylene was purchased from GFS Chemicals, Inc. (Columbus, OH). Standard work-up involves washing ether extraction layer with sat.  $\text{NH}_4\text{Cl}$ , then brine; drying over  $\text{MgSO}_4$ ; and concentration *in vacuo*. All reactions were monitored using one of the following techniques: TLC, GC-MS, and/or  $^{19}\text{F}$  NMR. Analytical TLC was performed using Macherey-Nagel Polygram Sil G/UV<sub>254</sub> precoated plastic plates and visualized using phosphomolybdic acid (5% in methanol). Flash chromatography was performed using silica gel 230-400 mesh, 40-63 microns (Lagand Chemicals).  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  at 300, 282, and 75 MHz respectively.  $^{19}\text{F}$  NMR spectra was referenced against external  $\text{CFCl}_3$ .  $^{19}\text{F}$  NMR spectra was broadband decoupled from hydrogen nuclei. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

### General procedure for the synthesis of 1-trialkylsilyl-3-halo-3-fluoropropyne.

**1-Tri(isopropyl)silyl-3-chloro-3-fluoropropyne.** To a solution of tri(isopropyl)silylacetylene (8.480 g, 46.6 mmol) in THF (35 mL) at  $-80^\circ\text{C}$  was added *n*-BuLi (1.6M in hexane, 32 mL, 51.2 mmol), then warmed to room temperature and stirred for 30 min. At  $-80^\circ\text{C}$ , dichlorofluoromethane ( $d^{23} = 1.366$ , 5mL, 6.83 g, 66.4 mmol) was added dropwise by *cannula*. The dark brown solution was stirred at  $0^\circ\text{C}$  for 1 h and quenched with saturated  $\text{NH}_4\text{Cl}$ . THF was removed *in vacuo*, and the residue was extracted by diethyl ether, washed with saturated  $\text{NH}_4\text{Cl}$  and brine. The combined organic layers were dried ( $\text{MgSO}_4$ ) and concentrated. Vacuum distillation afforded **3a** (50-52°C/0.1 mmHg, 8.806 g, 76%).  $^1\text{H}$  NMR:  $\delta$  1.11 (s, 21H), 6.56 (d, 1H,  $^1J_{\text{CF}} = 50.6$  Hz);  $^{13}\text{C}$  NMR:  $\delta$  11.2, 18.2, 85.8 (d,  $^1J_{\text{CF}} = 236$  Hz), 94.4 (d,  $^3J_{\text{CF}} = 4$  Hz), 99.0 (d,  $^2J_{\text{CF}} = 27$  Hz);  $^{19}\text{F}$  NMR:  $\delta$  -121; Anal.Calcd for  $\text{C}_{12}\text{H}_{22}\text{ClFSi}$ : C, 57.92; H, 8.91; Found C, 57.70; H, 8.83.

**1-Tri(isopropyl)silyl-3-bromo-3-fluoropropyne (1a).** Dibromofluoromethane (5.230 g, 27.26 mmol) was added to TIPS-acetylene (4.536 g, 24.92 mmol) in THF according to the above general procedure. The ratio of the reagents was as follows: TIPS-acetylene : *n*-BuLi :  $\text{CH}_2\text{Br}_2\text{F} = 1 : 1.1 : 1.1$ . Vacuum distillation provided **3b** (b.p.  $67^\circ\text{C}/0.1$  mmHg, 4.661 g, 64%).  $^1\text{H}$  NMR  $\delta$  1.11 (s, 21H), 6.79 (d, 1H,  $^2J_{\text{HF}} = 51.5$  Hz);  $^{13}\text{C}$  NMR  $\delta$  11.0, 18.4, 73.5 (d,  $^1J_{\text{CF}} = 246$  Hz), 96.7 (d,  $^3J_{\text{C}} = 6$  Hz), 99.5 (d,  $^2J_{\text{CF}} = 26$  Hz);  $^{19}\text{F}$  NMR  $\delta$  -125; Anal.Calcd for  $\text{C}_{12}\text{H}_{22}\text{BrFSi}$ : C, 49.14; H, 7.56; Found C, 48.64; H, 7.42.

**1-Trimethylsilyl-3-bromo-3-fluoropropyne.** To a solution of trimethylsilylacetylene (5.014g, 98%, 50 mmol) in THF (50mL) at  $-80^\circ\text{C}$  was added *n*-BuLi (1.6M in hexane, 32 mL, 51.2 mmol), and the resulting mixture stirred for 0.5 hour. At  $-80^\circ\text{C}$ , dibromofluoromethane ( $d^{18.5} = 2.4256$ , 6mL, 75 mmol) was added dropwise *via cannula*. The dark brown solution was stirred for 1 h and quenched with saturated  $\text{NH}_4\text{Cl}$ . THF was removed *in vacuo*, and the residue was extracted with diethyl ether. Standard work-up followed by vacuum distillation afforded a colorless oil (50-52°C/20 mmHg, 1.4597 g,

14%).  $^1\text{H}$  NMR  $\delta$  0.23 (s, 9H, TMS), 6.75 (d, 1H, CFB<sub>r</sub>H,  $J_{\text{HF}} = 51.5$  Hz);  $^{13}\text{C}$  NMR  $\delta$  0.7, 74.4 (d,  $^1J_{\text{CF}} = 247$  Hz), 98.1 (d,  $^2J_{\text{CF}} = 26$  Hz), 100;  $^{19}\text{F}$  NMR  $\delta$  -126.

**General procedure for the preparation of fluoroallenol (3a) and 4-triisopropylsilyl-2-fluoro-3-butyn-1-ol (5a).** Indium powder (1eq.) was added to 1-triisopropylsilyl-3-bromo-3-fluoropropyne **1a** (1eq.) in THF mixed with formaldehyde (37% w/w, 5 eq.). The mixture was stirred at room temperature until the disappearance of the signal at  $^{19}\text{F}$  NMR  $\delta$  -125 was observed. Standard work-up and purification by flash chromatography (hexane : EtOAc = 9 : 1) afforded fluoroallenol **3a** and **5a** in 66% overall yield as the ratio of 7:1.

**1-Fluoro-3-triisopropylsilyl-1,2-butadiene-4-ol (3a).**  $^1\text{H}$  NMR  $\delta$  7.36 (dt, 1H, C=C=CHF,  $^2J_{\text{HF}} = 88$  Hz,  $^5J_{\text{HH}} = 2.4$  Hz), 4.27 (m, 2H, CH<sub>2</sub>C=C=C,  $^5J_{\text{HF}} = 11.5$  Hz,  $^5J_{\text{HH}} = 2.3$  Hz), 1.1 (s, 21H, TIPS);  $^{19}\text{F}$  NMR  $\delta$  -172.6;  $^{13}\text{C}$  NMR  $\delta$  11.1, 18.3, 62.3 (d,  $^4J_{\text{CF}} = 2$  Hz), 122 (d,  $^3J_{\text{CF}} = 14$  Hz), 133 (d,  $^1J_{\text{CF}} = 239$  Hz), 194 (d,  $^2J_{\text{CF}} = 14$  Hz); MS (m/e) 201 ( $\text{M}^+ - 43$ , 12), 151 (19), 131 (43), 103 (62), 75 (100), 59 (64). Attempts to get a correct elemental analysis failed each one of the three times a sample was sent to Norcross, Georgia.

**4-Triisopropylsilyl-2-fluoro-3-butyn-1-ol. (5a)**  $^1\text{H}$  NMR  $\delta$  5.18 (dq, 1H, C $\equiv$ CCHF,  $^2J_{\text{HF}} = 50$  Hz,  $^3J_{\text{HH}} = 3.7$  Hz), 3.84 (m, 2H, CHOH), 1.08 (s, 21H, TIPS);  $^{19}\text{F}$  NMR  $\delta$  -182;  $^{13}\text{C}$  NMR  $\delta$  11.1, 18.4, 65.5 (d,  $^2J_{\text{CF}} = 24$  Hz), 83.5 (d,  $^1J_{\text{CF}} = 169$  Hz), 92.3 (d,  $^3J_{\text{CF}} = 8$  Hz), 99.9 (d,  $^2J_{\text{CF}} = 23$  Hz); MS (m/e) 201 ( $\text{M}^+ - 43$ , 38), 79 (39), 77 (100), 63 (31)

**2-Fluoro-4-triisopropylsilyl-2, 5-dihydrofuran 4.** To a solution of NaH (40 mg, 60% in mineral oil, 1 mmol) in THF (3mL) was added a mixture of **3a** and **5a** (244 mg, 1mmol). The resulting solution was stirred at room temperature until the disappearance of the signal at  $^{19}\text{F}$  NMR  $\delta$  -173 was observed after approximately 2 hours, then quenched with NH<sub>4</sub>Cl. Standard work-up gave the crude product which was further purified by flash chromatography (hexane: CH<sub>2</sub>Cl<sub>2</sub> = 95:5) yielding **4** (160 mg, 75%, 30 mg of **5a** were recovered) as a colorless oil.  $^1\text{H}$  NMR  $\delta$  7.15 (ddt,  $^2J_{\text{HF}} = 87$  Hz,  $^3J_{\text{HH}} = 5.4$  Hz,  $^4J_{\text{HH}} = 2.0$  Hz, 1H), 6.06 (ddd,  $^3J_{\text{HF}} = 10.5$  Hz,  $^3J_{\text{HH}} = 5.1$  Hz,  $^4J_{\text{HH}} = 2.1$  Hz, 1H), 4.36 (ddq,  $^4J_{\text{HF}} = 10.3$  Hz,  $^4J_{\text{HH}} = 5.1$  Hz,  $^5J_{\text{HH}} = 1.0$  Hz, 2H), 1.10 (s, 21H);  $^{19}\text{F}$  NMR  $\delta$  -163.4;  $^{13}\text{C}$  NMR  $\delta$  192 (d,  $^2J_{\text{CF}} = 14$  Hz), 130 (d,  $^1J_{\text{CF}} = 242$  Hz), 111 (d,  $^3J_{\text{CF}} = 12$  Hz), 61.8 (d,  $^3J_{\text{CF}} = 7.4$  Hz), 17.9, 12.0

**4-Fluoro-2-triisopropylsilyl-2,3-diene-butyraldehyde (6a).** Dess-Martin periodinane solid (0.73 g, 1.72 mmol) was added to the stirred solution of **3a** (0.417 g, 1.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) at room temperature. When the absence of the starting material was observed ( $^{19}\text{F}$  NMR  $\delta$  -173), the mixture was diluted with 10 ml of ether and poured into 30 ml of a 0.26 M solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in saturated aqueous NaHCO<sub>3</sub>. The organic layer was separated, washed sequentially with NaHCO<sub>3</sub> and water. The aqueous layers were back extracted with ether, and the combined ether layer was dried (MgSO<sub>4</sub>) and concentrated *in vacuo*. The residue was purified by flash chromatography (hexane: EtOAc = 95: 5) affording a colorless oil of **6a** (0.34 g, 83%).  $^1\text{H}$  NMR  $\delta$  9.65 (s, 1H), 7.61 (d,  $^2J_{\text{HF}} = 82$  Hz), 1.06 (s, 21H);  $^{13}\text{C}$  NMR  $\delta$  220 (d,  $^2J_{\text{CF}} = 20$  Hz), 192, 131 (d,  $^1J_{\text{CF}} = 242$  Hz), 122 (d,  $^3J_{\text{CF}} = 12$  Hz), 18.4, 11.2;  $^{19}\text{F}$  NMR  $\delta$  -180.5; GC-MS m/z 199 ( $\text{M}^+ - 43$ , 16), 129 (11), 105 (29), 77 (100), 59 (30). Anal. Calcd for C<sub>13</sub>H<sub>23</sub>OSiF: C, 64.41; H, 9.56. Found: C, 64.29; H, 9.79.

**N-tert-Butoxycarbonyl-N-p-toluenesulfonyl-(4-fluoro-2-triisopropylsilyl-1,2-butadienyl)amine (6b).** To a solution of **3a** (448 mg, 1.8 mmol) in THF was added triphenylphosphine (483 mg, 1.8 mmol), *N*-(*tert*-butoxycarbonyl)-*p*-toluenesulfonamide

(488 mg, 1.8 mmol), diethyl azodicarboxylate (313 mg, 1.8 mmol). The resulting solution was stirred at room temperature until the disappearance of signal at  $^{19}\text{F}$  NMR  $\delta$  -173 was observed. The reaction mixture was concentrated to a small volume and was directly purified by flash chromatography (hexane: ethyl acetate = 9:1) to give **6b** (528 mg, 83%) as a solid after evaporation.  $^1\text{H}$  NMR  $\delta$  7.82 (d, 2H), 7.28 (d, 2H), 6.83 (d, C=C=CHF,  $^2J_{\text{HF}}$  = 88 Hz, 1H), 4.66 (m,  $\text{CH}_2\text{C}=\text{C}=\text{C}$ , 2H), 2.44 (s, 3H), 1.38 (s, 9H), 1.14 (s, 21H);  $^{19}\text{F}$  NMR  $\delta$  -173.1;  $^{13}\text{C}$  NMR  $\delta$  11.2, 18.3, 18.4, 21.6, 48.6, 84.0, 116.2 (d,  $^3J_{\text{CF}}$  = 14 Hz), 128.5, 129.0, 132.1 (d,  $J_{\text{CF}}$  = 239 Hz), 137.1, 144.1, 150.4, 196.3 (d,  $^2J_{\text{CF}}$  = 15 Hz); MS (m/e) 334 ( $\text{M}^+$  -163, 100), 292 (56), 264 (57), 149 (48), 135 (74), 91 (76).

**N-*p*-Toluenesulfonyl-(4-fluoro-2-triisopropylsilyl-1,2-butadienyl)amine (6c).** Tri-fluoroacetic acid (40 mg, 3 eq.) was added to **6b** (43 mg, 0.086 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL). The solution was stirred at room temperature for 2 hours and then quenched with saturated  $\text{Na}_2\text{CO}_3$ . Diethyl ether was added to extract organics. After separation, the ether layer was washed by water, dried over  $\text{MgSO}_4$  and concentrated *in vacuo*. The crude was recrystallised from hexane to give **6c** (26 mg, 76%).  $^1\text{H}$  NMR  $\delta$  7.74 (d, 2H), 7.29 (d, 2H), 7.14 (dt,  $^2J_{\text{HF}}$  = 84 Hz,  $^5J_{\text{HH}}$  = 2.1 Hz, 1H), 4.77 (t,  $^3J_{\text{HH}}$  = 5.1 Hz, 1H), 3.74 (ddd,  $^5J_{\text{HF}}$  = 12 Hz,  $^3J_{\text{HH}}$  = 5.4 Hz,  $^5J_{\text{HH}}$  = 2.3 Hz, 2H), 2.41 (s, 3H), 0.98 (s, 21H);  $^{19}\text{F}$  NMR  $\delta$  -171.8;  $^{13}\text{C}$  NMR  $\delta$  11.0, 18.2, 43.9 (d,  $^4J$  = 2 Hz), 116.2 (d,  $^3J_{\text{CF}}$  = 13 Hz), 127.3, 129.7, 132.4 (d,  $J_{\text{CF}}$  = 242 Hz), 136.7, 143.6, 195.3 (d,  $^2J_{\text{CF}}$  = 14 Hz). In lieu of elemental analysis, the CIF data corresponding to the crystal structure of **6c** is provided in the supplemental material. The ORTEP view is shown in reference 10 in the manuscript.

**1-Fluoro-3-triisopropylsilyl-4-bromo-1,2-butadiene (6d).** Diethyl azodicarboxylate (103 mg, 0.59 mmol) was added to the solution of **3a** (143 mg, 0.59 mmol), *n*-propyl bromide (72 mg, 0.59 mmol), and triphenylphosphine (157 mg, 0.59 mmol) in THF. The mixture was stirred at room temperature for 3 hours, then concentrated to a small volume, and purified by flash chromatography (hexane = 100%) to yield **6c** (75 mg, 42%) as a colorless oil.  $^1\text{H}$  NMR  $\delta$  7.33 (dt,  $^2J_{\text{HF}}$  = 86 Hz,  $^5J_{\text{HH}}$  = 2 Hz, 1H), 4.08 (m, 2H), 1.11 (s, 21H);  $^{13}\text{C}$  NMR  $\delta$  11.3, 18.4, 31.6, 116.6 (d,  $^3J_{\text{CF}}$  = 14 Hz), 131.3 (d,  $J_{\text{CF}}$  = 238 Hz), 201.9 (d,  $^2J_{\text{CF}}$  = 16 Hz);  $^{19}\text{F}$  NMR  $\delta$  -175.6; MS (m/e) 265 ( $\text{M}^+$  - 43, 7), 263 (9), 195 (22), 193 (22), 157 (25), 137 (44), 115 (64), 87 (86), 77 (97), 59 (100).

**1-Fluoro-2-iodo-3-triisopropylsilyl-1, 3-butadiene (7a).** Diethyl azodicarboxylate (61 mg, 0.35 mmol) was added to the solution of **3a** (86 mg, 0.35 mmol) triphenylphosphine (93 mg, 0.35 mmol), and methyl iodide (50 mg, 0.35 mmol) in THF. The mixture was stirred at 60°C for 3 hours, then concentrated to a small volume, and purified by flash chromatography (hexane = 100%) to yield **7a** (92 mg, 74%) as a pale yellowish oil. *Z/E*  $^1\text{H}$  NMR  $\delta$  6.69 (d,  $^2J_{\text{HF}}$  = 85 Hz, 1H), 5.99 (d,  $^2J_{\text{HH}}$  = 2.5 Hz, 1H), 5.60 (d,  $^2J_{\text{HH}}$  = 2.5 Hz, 1H), 1.12 (s, 21H);  $^{13}\text{C}$  NMR  $\delta$  11.7, 18.7, 87.1 (d,  $^2J_{\text{CF}}$  = 19 Hz), 135.0 (d,  $^4J_{\text{CF}}$  = 2.4 Hz), 144.5, 145.2 (d,  $J_{\text{CF}}$  = 276 Hz);  $^{19}\text{F}$  NMR  $\delta$  -95.1; MS (m/e) 269 ( $\text{M}^+$  - 85, 8), 227 (15), 189 (12), 133 (11), 105 (50), 77 (100). *E/Z*  $^1\text{H}$  NMR  $\delta$  6.70 (d,  $^2J_{\text{HF}}$  = 86 Hz, 1H), 6.10 (d,  $^2J_{\text{HH}}$  = 2.0 Hz, 1H), 5.62 (dt,  $^2J_{\text{HH}}$  = 2.0 Hz, 1H), 1.11 (s, 21H);  $^{19}\text{F}$  NMR  $\delta$  -96.6; MS (m/e) 311 ( $\text{M}^+$  - 43, 81), 241 (15), 213 (27), 185 (24), 105 (65), 77 (100).

**1-Fluoro-2-bromo-3-triisopropylsilyl-1, 3-butadiene (7b).** To a solution of **3a** (250 mg, 1.02 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) at 0°C, was added methanesulfonyl chloride (130 mg, 1.13 mmol) followed by triethylamine (114 mg, 1.13 mmol). The resulting mixture was stirred at 0°C, until the disappearance of the signal of **3a** ( $^{19}\text{F}$  NMR  $\delta$  -173), was observed. Standard work-up gave the corresponding mesylate **6e** (193 mg, 60% crude yield) ( $^{19}\text{F}$  NMR  $\delta$  -176), which was used without further purification in the next step. To the

acetone solution of the mesylate (193 mg, 0.6 mmol) obtained from the previous step was added lithium bromide (155 mg, 1.8 mmol) at room temperature. The resulting mixture was stirred for about 5 hours. Standard work-up followed by flash chromatography (hexane : CH<sub>2</sub>Cl<sub>2</sub> = 99 : 1) afforded **7b** (109 mg, 60%) as a colorless oil. *Z/E* <sup>1</sup>H NMR δ 6.76 (d, <sup>2</sup>J<sub>HF</sub> = 83 Hz, 1H), 6.06 (d, <sup>2</sup>J<sub>HH</sub> = 2.6 Hz, 1H), 5.72 (d, <sup>2</sup>J<sub>HH</sub> = 2.6 Hz, 1H), 1.12 (s, 21H); <sup>19</sup>F NMR δ -115.2. *E/Z* <sup>1</sup>H NMR δ 6.96 (d, <sup>2</sup>J<sub>HF</sub> = 83 Hz, 1H), 6.19 (d, <sup>2</sup>J<sub>HH</sub> = 2.4 Hz, 1H), 5.64 (dt, <sup>2</sup>J<sub>HH</sub> = 2.4 Hz, 1H), 1.11 (s, 21H); <sup>19</sup>F NMR δ -114.6.

**Author's Note:** the halides **6d**, **7a** and **7b** needed to be kept refrigerated, hence, their lack of elemental analysis data. However, the aryl-substituted derivatives of **7a**, namely **8a-d**, all of which are room temperature stable, had correct elemental analysis, as shown below.

**General procedure for palladium catalyzed cross-coupling of 7a with arylboronic acids:** To a solution of **7a** in toluene (2 mL) was added Pd<sub>2</sub>(dba)<sub>3</sub> (9.6 mg), triphenylphosphine (26 mg), arylboronic acid and Na<sub>2</sub>CO<sub>3</sub> 2M (1 mL). The resulting mixture was stirred under argon at 100°C for 8 hours. Diluted with ether and water, separated organic layer was dried over MgSO<sub>4</sub>. After concentration, the crude was purified by flash chromatography using hexane.

**1-Fluoro-2-phenyl-3-triisopropylsilyl-1, 3-butadiene (8a).** **7a** (102 mg, 0.3 mmol) and phenylboronic acid (37.5 mg, 0.3 mmol) yielded **8a** (75 mg, 85%). <sup>1</sup>H NMR δ 7.34 (m, 5H), 6.64 (d, <sup>2</sup>J<sub>HF</sub> = 86 Hz, 1H), 5.92 (d, <sup>2</sup>J<sub>HH</sub> = 3.3 Hz, 1H), 5.65 (d, <sup>2</sup>J<sub>HH</sub> = 3.3 Hz, 1H), 0.98 (s, 21H); <sup>19</sup>F NMR δ -131.9; <sup>13</sup>C NMR δ 11.5, 18.6, 127.6, 127.9, 129.3 (d, <sup>4</sup>J<sub>CF</sub> = 4.5 Hz), 130.4, 133.0 (d, <sup>4</sup>J<sub>CF</sub> = 4.2 Hz), 134.3, 143.0, 143.3 (d, <sup>4</sup>J<sub>CF</sub> = 269 Hz); MS (m/e) 261 (M<sup>+</sup> - 43, 7), 128 (10), 105 (27), 77 (100). Anal. Calcd for C<sub>19</sub>H<sub>29</sub>FSi: C, 74.94; H, 9.60. Found: C, 74.98; H, 9.58.

**1-Fluoro-2-(4'-fluorophenyl)-3-triisopropylsilyl-1, 3-butadiene (8b).** **7a** (106 mg, 0.3 mmol) and 4-fluorophenylboronic acid (43.6 mg, 0.3 mmol) yielded **8b** (67 mg, 70%). <sup>1</sup>H NMR δ 7.33 (dd, *J* = 8.1 Hz, *J* = 5.2 Hz, 2H), 7.02 (t, *J* = 8.8 Hz, 2H), 6.62 (d, <sup>2</sup>J<sub>HF</sub> = 85 Hz, 1H), 5.91 (d, <sup>2</sup>J<sub>HH</sub> = 3.3 Hz, 1H), 5.66 (d, <sup>2</sup>J<sub>HH</sub> = 3.3 Hz, 1H), 0.98 (s, 21H); <sup>19</sup>F NMR δ -114.4, -132.0; <sup>13</sup>C NMR δ 11.5, 18.6, 114.9 (d, <sup>2</sup>J<sub>CF</sub> = 21 Hz), 129.5 (d, <sup>2</sup>J<sub>CF</sub> = 2.3 Hz), 130.3 (d, <sup>4</sup>J<sub>CF</sub> = 3.2 Hz), 130.9 (dd, <sup>3</sup>J<sub>CF</sub> = 8.2 Hz, <sup>4</sup>J<sub>CF</sub> = 4.8 Hz), 133.1 (d, <sup>4</sup>J<sub>CF</sub> = 4.3 Hz), 142.9 (d, <sup>4</sup>J<sub>CF</sub> = 2 Hz), 143.2 (d, <sup>4</sup>J<sub>CF</sub> = 269 Hz), 162.2 (d, <sup>4</sup>J<sub>CF</sub> = 247 Hz); MS (m/e) 322 (M<sup>+</sup>, 1), 279 (6), 127 (28), 105 (20), 77 (100). Anal. Calcd for C<sub>19</sub>H<sub>28</sub>F<sub>2</sub>Si: C, 70.76; H, 8.75. Found: C, 70.50; H, 8.82.

**1-Fluoro-2-(4'-ethoxyphenyl)-3-triisopropylsilyl-1, 3-butadiene (8c).** **7a** (103 mg, 0.3 mmol) and 4-ethoxyphenylboronic acid (51.8 mg, 0.3 mmol) yielded **8c** (79 mg, 77%). <sup>1</sup>H NMR δ 7.27 (d, *J* = 9.3 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 6.59 (d, <sup>2</sup>J<sub>HF</sub> = 86 Hz, 1H), 5.90 (d, <sup>2</sup>J<sub>HH</sub> = 3.3 Hz, 1H), 5.63 (d, <sup>2</sup>J<sub>HH</sub> = 3.5 Hz, 1H), 4.04 (q, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 2H), 1.41 (t, <sup>3</sup>J<sub>HH</sub> = 7 Hz, 3H), 0.98 (s, 21H); <sup>19</sup>F NMR δ -133.4; <sup>13</sup>C NMR δ 11.5, 14.8, 18.6, 63.4, 113.9, 126.6, 128.4 (d, <sup>2</sup>J<sub>CF</sub> = 3.5 Hz), 130.4 (d, <sup>2</sup>J<sub>CF</sub> = 3.4 Hz), 132.6 (d, <sup>4</sup>J<sub>CF</sub> = 4.6 Hz), 142.7 (d, <sup>4</sup>J<sub>CF</sub> = 264 Hz), 143.2 (d, <sup>4</sup>J<sub>CF</sub> = 3 Hz), 158.4; MS (m/e) 348 (M<sup>+</sup>, 5), 277 (31), 276 (21), 105 (11), 77 (100). Anal. Calcd for C<sub>21</sub>H<sub>33</sub>FSiO: C, 72.36; H, 9.54. Found: C, 72.13; H, 9.58.

**1-Fluoro-2-(3'-nitrophenyl)-3-triisopropylsilyl-1, 3-butadiene (8d).** **7a** (224 mg, 0.6 mmol) and 3-nitrophenylboronic acid (100 mg, 0.6 mmol) yielded **8d** (120 mg, 54%). <sup>1</sup>H NMR δ 8.20 (t, *J* = 2 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.53 (t,

$J = 7.8$  Hz, 1H), 6.72 (d,  $^2J_{\text{HF}} = 84$  Hz, 1H), 5.98 (d,  $^2J_{\text{HH}} = 3.1$  Hz, 1H), 5.77 (d,  $^2J_{\text{HH}} = 3.0$  Hz, 1H), 0.99 (s, 21H);  $^{19}\text{F}$  NMR  $\delta$  -128.8;  $^{13}\text{C}$  NMR  $\delta$  11.5, 18.5, 122.5, 124.0 (d,  $J_{\text{CF}} = 4.8$  Hz), 128.6 (d,  $J_{\text{CF}} = 2.5$  Hz), 128.9, 134.6 (d,  $J_{\text{CF}} = 4.5$  Hz), 135.2 (d,  $J_{\text{CF}} = 5.9$  Hz), 136.2, 142.1 (t,  $J_{\text{CF}} = 2.3$  Hz), 144.6 (d,  $J_{\text{CF}} = 273$  Hz), 148.0; MS (m/e) 306 ( $\text{M}^+$ - 43, 13), 262 (19), 190 (21), 128 (11), 105 (27), 77 (100). Anal. Calcd for  $\text{C}_{19}\text{H}_{28}\text{O}_2\text{NFSi}$ : C, 65.29; H, 8.07. Found: C, 65.93; H, 8.29 .