Experimental Section

The solvents are reagent grade and used without purification. The indium metal powder (100 mesh) and all other commercial reagents were purchased from Aldrich and used as received. All palladium catalyst cross-coupling reaction were done under argon atmosphere and the reaction progress were monitored using one of the following techniques: ^{19}F NMR, TLC and GC-MS. Analytical TLC was performed using Macherey-Nagel Polygram Sil G/UV$_{254}$ precoated plastic plates and visualized using phosphomolybdic acid (5% in methanol). Flash chromatography (eluent: hexane/ethyl acetate) was performed using silica gel 230-400 mesh, 40-63μm (Lagand Chemicals). IR spectra were recorded on a Bruker Vector –22 FT-IR spectrophotometer. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded in CDCl$_3$ at 300, 282 and 75 MHz, respectively. ^{19}F NMR spectra were referenced against external CFCl$_3$ and were broadband decoupled from hydrogen nuclei. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Synthesis of difluoroallenyl alcohol 2a : To a vigorously stirred suspension of 1 (12.44g, 40mmol) in 100mL H$_2$O/THF(80/20, v/v) was added indium powder(5.00g, 1.1eq) and the resulting mixture was stirred at room temperature for 2h. ^{19}F showed the disappearance of the starting material. Then formadehyde (37% wt solution in water, 9.26g, 5eq) was added. The mixture was sonicated at room temperature for 24hs. And worked up by adding brine and extracting with diethyl ether, dried over MgSO$_4$ and concentrated to yield a pale yellow oil. Further purification by flash chromatography afforded **2a** (6.19g, 59 %) as a colorless oil.

Typical procedure for synthesis of 1,1-Difluoro-3-(triisopropylsilyl)-4-bromo-1,2-butadiene 2b: To a solution of **2a** (0.262g, 1mmol) and MsCl (0.126g, 1.1mmol) in 2mL CH$_2$Cl$_2$ at ice-water bath was added Et$_3$N (0.202g, 2mmol). The resulting mixture was stirred at this temperature for about 5hs. ^{19}F NMR showed the disappearance of the starting material. Standard work-up gave a red crude product which was used without purification in the next step. To the solution of the mesylate obtained from the previous step in acetone was added lithium bromide (0.086g, 1mmol) at room temperature. The resulting mixture was stirred for about 5hs. ^{19}F NMR showed the disappearance of the starting material. Standard work-up gave a red crude product which was purified by flash chromatography to give **2b** (0.303g, yield 93% for two steps) as a colorless oil. ^{1}H NMR (CDCl$_3$, 300MHz) δ 4.2 (t, $^{4}J_{HF}$ = 5.2Hz, 2H), 1.22 (m, 3H), 1.08 (s, 18H) ppm; ^{19}F NMR (CDCl$_3$, 282MHz) δ -107.36 (s, 1F) ppm; MS m/z (relative intensity) 115 (98.1), 157 (100), 281 (5.2, M$^+$-43), 283 (4.9, M$^+$-Isopropyl+2). Anal. Calcd for C13H23BrF2Si: C, 48.00; H, 7.13. Found: C, 47.92; H, 6.97.

1,1-Difluoro-2-bromo-3-(triisopropylsilyl)-1,3-butadiene (3, R' = Br): ^{1}H NMR (CDCl$_3$, 300MHz) δ 6.09(m, 1H), 5.74 (m,1H), 1.24 (m, 3H), 1.12 (m, 18H) ppm; ^{19}F NMR (CDCl$_3$, 282MHz) δ -84.60 (d, $^{2}J_{FF}$ = 39.8Hz, 1F), -87.41 (d, $^{2}J_{FF}$ = 39.5Hz, 1F) ppm; MS m/z (relative intensity) 128 (100), 130 (99.7), 281 (1.3, M$^+$-43), 283 (1.3, M$^+$-Isopropyl+2). Anal. Calcd for C$_{13}$H$_{23}$BrF$_2$Si: C, 48.00; H, 7.13. Found: C, 8.03; H, 6.99.

Typical procedure for Palladium catalyst cross-coupling of TIPS-α-bromo difluoroallene with aryl halides: To a solution of α-bromo difluoroallene (0.326g, 1mmol) in 3mL DMF was added Zinc powder (71mg, 1.1mmol). The resulting mixture was stirred for about 2h at 60°C. ^{19}F NMR showed the disappearance of the starting material. To this solution was added Pd(PPh$_3$)$_4$ (25mg, 2mmol%) and phenyl iodide (0.224g, 1.1mmol). The resulting mixture was stirred for another 3h at 60°C. Standard work-up gave a yellow crude product which was purified by flash chromatography.

1,1-difluoro-2-Phenyl-3-(triisopropylsilyl)-1,3-butadiene (3a): ^{1}H NMR (CDCl$_3$, 300MHz) δ 7.32 (m, 5H), 6.05 (d, $^{2}J_{HH}$ = 3.0Hz, 1H), 5.85 (d, $^{2}J_{HH}$ = 2.8Hz, 1H), 0.97 (s, 21H) ppm; ^{19}F NMR (CDCl$_3$, 282MHz) δ -88.50 (d, $^{2}J_{FF}$ = 39.0Hz, 1F), -93.47 (d, $^{2}J_{FF}$ = 39.5Hz, 1F) ppm; ^{13}C NMR (CDCl$_3$, 75Hz) δ 152.04 (dd, $^{1}J_{CF}$ = 286.3, $^{1}J_{CF}$ = 286.2Hz), 140.23, 134.77 (t, $^{4}J_{CF}$ = 2.9Hz), 133.06 (t, $^{3}J_{CF}$ = 4.2Hz), 128.92 (t, $^{3}J_{CF}$ = 3.3Hz), 128.08, 127.35, 99.11 (dd, $^{2}J_{CF}$ = 22.0, $^{2}J_{CF}$ = 21.2Hz), 18.40, 7.36; MS m/z (relative intensity) 77 (96.3), 127 (100), 279 (6.1, M$^+$-43). Anal. Calcd for C$_{19}$H$_{28}$F$_2$Si: C, 70.76; H, 8.75. Found: C, 70.95; H, 8.84.

1,1-difluoro-2-(4'-aminophenyl)-3-(triisopropylsilyl)-1,3-butadiene (3b): ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.09 (m, 2H), 6.62 (m, 2H), 5.99 (d, $^{2}J_{HH}$ = 1.3Hz, 1H), 5.79 (d, $^{2}J_{HH}$ = 2.8Hz, 1H), 0.97 (s, 21H) ppm; ^{19}F NMR (CDCl$_3$, 282MHz) δ -90.35 (d, $^{2}J_{FF}$ = 43.4Hz, 1F), -94.96 (d, $^{2}J_{FF}$ = 46.5Hz, 1F) ppm; ^{13}C NMR (CDCl$_3$, 75Hz) δ 152.06 (dd, $^{1}J_{CF}$ = 285.1, $^{1}J_{CF}$ = 285.2Hz), 145.79, 140.67, 134.30 (t, $^{4}J_{CF}$ = 3.0Hz), 130.09 (t, $^{3}J_{CF}$ = 3.4Hz), 123.13 (t, $^{3}J_{CF}$ = 3.4Hz), 114.91, 98.99 (dd, $^{2}J_{CF}$ = 21.4, $^{2}J_{CF}$ = 21.4Hz), 18.65, 11.53; MS m/z (relative intensity) 77 (91.0), 142 (100), 337 (3.4, M$^+$). Anal. Calcd for $C_{19}H_{29}F_2NSi$: C, 67.61; H, 8.66. Found: C, 67.98; H, 8.83.

1,1-difluoro-2-(4'-acetyl)-3-(triisopropylsilyl)-1,3-butadiene (3c): ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.92 (m, 2H), 7.44 (m, 2H), 6.09 (d, $^2J_{HH}$ = 2.7Hz, 1H), 5.91 (d, $^2J_{HH}$ = 2.7Hz, 1H), 2.62 (s, 3H), 0.97 (s, 21H) ppm; ^{19}F NMR ($CDCl_3$, 282MHz) δ -85.61 (d, $^2J_{FF}$ = 34.4Hz, 1F), -90.90 (d, $^2J_{FF}$ = 34.7Hz, 1F) ppm; ^{13}C NMR ($CDCl_3$, 75Hz) δ 197.63, 152.24 (dd, $^1J_{CF}$ = 287.7, $^1J_{CF}$ = 287.7Hz), 139.71, 138.19(t, $^3J_{CF}$ = 4.3Hz), 135.70 (t, $^3J_{CF}$ = 3.8Hz), 130.87, 128.90 (t, $^4J_{CF}$ = 3.5Hz), 128.14, 98.72 (dd, $^2J_{CF}$ = 22.6, $^2J_{CF}$ = 12.1Hz), 26.61, 18.65, 11.53; MS m/z (relative intensity) 169 (100), 321(90.5, M$^+$-43), 364 (5.0, M$^+$). Anal. Calcd for $C_{21}H_{30}F_2OSi$: C, 69.19; H, 8.29. Found: C, 69.29; H, 8.39.

1,1-difluoro-2-(4'-methoxyphenyl)-3-(triisopropylsilyl)-1,3-butadiene (3d): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.25 (m, 2H), 6.86 (m, 2H), 6.01 (m 1H), 5.82 (m, 1H), 0.97 (s, 21H) ppm; ^{19}F NMR ($CDCl_3$, 282MHz) δ -89.67 (d, $^2J_{FF}$ = 43.7Hz, 1F), -94.48 (d, $^2J_{FF}$ = 43.3Hz, 1F) ppm; ^{13}C NMR ($CDCl_3$, 75Hz) δ 159.05, 152.15 (dd, $^1J_{CF}$ = 285.9, $^1J_{CF}$ = 285.7Hz), 145.79, 140.64, 134.65 (t, $^4J_{CF}$ = 3.3Hz), 130.28 (t, $^3J_{CF}$ = 3.4Hz), 125.51 (t, $^3J_{CF}$ = 3.5Hz), 113.76, 98.83 (dd, $^2J_{CF}$ = 21.4, $^2J_{CF}$ = 21.4Hz), 18.65, 11.53; MS m/z (relative intensity) 157 (100), 309 (31.5, M$^+$-43), 352 (27.6, M$^+$). Anal. Calcd for $C_{20}H_{30}F_2OSi$: C, 68.14; H, 8.58. Found: C, 68.24; H, 8.64.

1,1-difluoro-2-(2'-thienyl)-3-(triisopropylsilyl)-1,3-butadiene (3e): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26 (m, 2H), 6.99 (m, 1H), 6.05 (d, $^2J_{HH}$ = 1.4Hz, 1H), 5.83 (d, $^2J_{HH}$ = 2.5Hz, 1H), 1.05 (s, 21H) ppm; ^{19}F NMR ($CDCl_3$, 282MHz) δ -87.99 (d, $^2J_{FF}$ = 34.8Hz, 1F), -88.51(d, $^2J_{FF}$ = 34.9Hz, 1F) ppm; ^{13}C NMR ($CDCl_3$, 75Hz) δ 151.65 (dd, $^1J_{CF}$ = 286.7, $^1J_{CF}$ = 286.8Hz), 145.79, 140.15, 135.47, 128.31 (t, $^3J_{CF}$ = 3.4Hz), 127.26, 126.61(t, $^3J_{CF}$ = 5.21Hz), 125.69 (t, $^4J_{CF}$ = 2.0Hz), 94.69 (dd, $^2J_{CF}$ = 14.2, $^2J_{CF}$ = 13.3Hz), 18.65, 11.53; MS m/z (relative intensity) 77(99.2), 133 (100), 285 (46.8, M$^+$-43), 328 (2.8, M$^+$).

Typical procedure for Palladium catalyst cross-coupling of TIPS- α-bromo difluoroallene with Arylboronic acids: To a solution of α-bromo difluoroallene (0.324g, 1mmol) in 2mL toluene was added $Pd_2(dba)_3$ (14mg, 2mmol%), triphenylphosphine (10mg, 4mmol%), phenylboronic acid (0.122g, 1mmol) and 2M Na_2CO_3 (1.0mL, 2.0mmol). The resulting mixture was stirred under Argon for about 8h at 100°C. ^{19}F NMR showed the disappearance of the starting material. Standard work-up gave a red crude product which was purified by flash chromatography.

1,1-difluoro-2-(3'-nitrophenyl)-3-(triisopropylsilyl)-1,3-butadiene (3f): ^{1}H NMR ($CDCl_3$, 300MHz) δ 8.20 (s, 18.14H), 8.14 (d, $^2J_{HH}$ = 8.1Hz, 1H), 7.71 (d, $^2J_{HH}$ = 7.8Hz, 1H), 7.53 (t, $^2J_{HH}$ = 8.0Hz, 1H), 6.14 (d, $^2J_{HH}$ = 2.6Hz, 1H),), 5.98 (d, $^2J_{HH}$ = 2.6Hz, 1H), 0.97 (s, 21H) ppm; ^{19}F NMR ($CDCl_3$, 282MHz) δ -85.35 (d, $^2J_{FF}$ = 34.2Hz, 1F), -90.90 (d, $^2J_{FF}$ = 33.8Hz, 1F) ppm; ^{13}C NMR ($CDCl_3$, 75Hz) δ 152.46 (dd, $^1J_{CF}$ = 287.6, $^1J_{CF}$ = 287.5Hz), 148.34, 139.65, 136.76 (t, $^4J_{CF}$ = 2.6Hz), 135.48, 134.82 (t, $^3J_{CF}$ = 3.6Hz), 129.40, 123.88 (t, $^4J_{CF}$ = 3.3Hz), 122.49, 98.15 (dd, $^2J_{CF}$ = 22.0, $^2J_{CF}$ = 21.2Hz), 18.58, 11.53; MS m/z (relative intensity) 172 (100), 324 (26.1, M$^+$-43), 367 (0.04, M$^+$). Anal. Calcd for $C_{19}H_{27}F_2NO_2Si$: C, 62.10; H, 7.41. Found: C, 62.92; H, 7.57.

1,1-difluoro-2-(4'-fluorophenyl)-3-(triisopropylsilyl)-1,3-butadiene (3h): ^{1}H NMR ($CDCl_3$, 300MHz) δ 7.28 (m, 2H), 7.01 (m, 2H), 6.04 (dd, $^5J_{HF}$ = 2.7Hz, $^5J_{HF}$ = 1.4Hz, 1H), 5.83 (dd, $^5J_{HF}$ = 2.7Hz, $^5J_{HF}$ = 2.5Hz, 1H), 1.05 (s, 21H) ppm; ^{19}F NMR ($CDCl_3$, 282MHz) δ -128.60 (s, 1F), -102.44 (d, $^2J_{FF}$ = 40.1Hz, 1F), -107.40 (d, $^2J_{FF}$ = 39.3Hz, 1F) ppm; ^{13}C NMR ($CDCl_3$, 75Hz) δ 158.39 (d, $^1J_{CF}$ = 247.1Hz), 152.27 ($^1J_{CF}$ = 286.3, $^1J_{CF}$ = 286.3Hz), 148.42, 140.46, 135.19 (t, $^4J_{CF}$ = 3.3Hz), , 130.80 (dd, $^3J_{CF}$ = 3.5Hz, $^3J_{CF}$ = 3.5Hz), 129.26 (dd, $^2J_{CF}$ = 7.3, $^2J_{CF}$ = 7.3Hz), 115.33 (d, $^2J_{CF}$ = 21.4Hz), 98.56 (dd, $^2J_{CF}$ = 13.6, $^2J_{CF}$ = 13.6Hz), 18.58, 11.53;; MS m/z (relative intensity) 145 (100), 297 (12.8, M$^+$-43), 340 (3.1, M$^+$). ^{13}C NMR spectrum has been supplied as indication of purity.

1,1-difluoro-2-(4'-bromophenyl)-3-(triisopropylsilyl)-1,3-butadiene (3i): ^{1} H NMR ($CDCl_3$, 300MHz) δ 7.45 (d, $^2J_{HH}$ = 8.5Hz, 2H), 7.18 (d, $^2J_{HH}$ = 8.3Hz, 2H), 6.04 (dd, $^5J_{HF}$ = 2.7Hz, $^5J_{HF}$ = 1.4Hz, 1H), 5.86 (dd, $^5J_{HF}$ = 2.7Hz, $^5J_{HF}$ = 2.5Hz, 1H), 0.97 (s, 21H) ppm; ^{19}F NMR ($CDCl_3$, 282MHz) δ -87.51 (d, $^2J_{FF}$ = 39.2Hz, 1F), -92.63 (d, $^2J_{FF}$ = 39.2Hz, 1F) ppm; ^{13}C NMR ($CDCl_3$, 75Hz) δ 152.20 ($^1J_{CF}$ = 286.3, $^1J_{CF}$ = 286.3Hz), 140.18, 135.56 (t, $^4J_{CF}$ = 3.2Hz), , 132.36 (dd, $^3J_{CF}$ = 3.5Hz, $^3J_{CF}$ = 3.5Hz), 131.53 (t, $^3J_{CF}$ = 3.8Hz), 130.67 (t, $^4J_{CF}$ = 3.4Hz), 121.62, 98.58(dd, $^2J_{CF}$ = 23.6, $^2J_{CF}$ = 12.9Hz), 18.58, 11.53; MS m/z (relative intensity) 126 (100), 193 (70.1) 357 (0.08, M$^+$-43), 400 (0.82, M$^+$), 402 (0.82, M$^+$+2). ^{13}C NMR spectrum has been supplied as indication of purity.

Typical procedure for Palladium catalyst cross-coupling of TIPS-α-bromo difluoroallene with acetylene: To a solution of α-bromo difluoroallene (0.324g, 1mmol) in 2mL THF was added $Pd(PPh_3)_2Cl_2$

(25mg, 2mmol%), CuI (200mg, 1mmol), triethylamine (0.202g, 2mmol) and acetylene (1.2mmol). The resulting mixture was stirred with refluxing under Argon for about 3h . ^{19}F NMR showed no change of the starting material. The mixture was warmed up to reflux for another 2hs. ^{19}F NMR showed the disappearance of the starting material. Standard work-up gave a red crude product which was purified by flash chromatography.

1,1-difluoro-2-(1-triisopropylsilylethylidene)-4-phenyl-but-1-ene-3-yne (4a): ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.42 (m, 2H), 7.27 (m, 3H), 6.04 (dd, $^{5}J_{HF}$ = 2.7Hz, $^{5}J_{HF}$ = 1.4Hz, 1H), 5.83 (dd, $^{5}J_{HF}$ = 2.7Hz, $^{5}J_{HF}$ = 2.5Hz, 1H), 1.35 (m, 3H), 1.05 (s, 18H) ppm; ^{19}F NMR (CDCl$_3$, 282MHz) δ -80.36 (d, $^{2}J_{FF}$ = 9.1Hz, 1F), -83.83 (d, $^{2}J_{FF}$ = 9.4Hz, 1F) ppm; ^{13}C NMR (CDCl$_3$, 75Hz) δ 158.12 (dd, $^{1}J_{CF}$ = 299.2, $^{1}J_{CF}$ = 295.8Hz), 137.66 (t, $^{4}J_{CF}$ = 2.1Hz), 134.42 (t, $^{4}J_{CF}$ = 3.1Hz), 131.41, 128.52, 123.34, 94.17 (t, $^{3}J_{CF}$ = 5.7Hz), 85.43 (t, $^{2}J_{CF}$ = 16.1Hz), 81.835 (t, $^{3}J_{CF}$ = 4.6Hz), 66.08, 18.84, 11.46; MS m/z (relative intensity) 151 (100), 303 (35.4, M^{+}-43), 346 (3.1, M^{+}). ^{13}C NMR spectrum has been supplied as indication of purity.

1,1-difluoro-2-(1-triisopropylsilylethylidene)-4-(trimethylsilyl)-but-1-ene-3-yne (4b): ^{1}H NMR (CDCl$_3$, 300 MHz) δ 5.96 (dd, $^{5}J_{HF}$ = 2.5Hz, $^{5}J_{HF}$ = 1.3Hz, 1H), 5.69 (dd, $^{5}J_{HF}$ = 1.7Hz, $^{5}J_{HF}$ = 2.2Hz, 1H), 1.27 (m, 3H), 1.12 (s, 18H), 0.18 (s, 9H) ppm; ^{19}F NMR (CDCl$_3$, 282MHz) δ -79.61 (d, $^{2}J_{FF}$ = 9.9Hz, 1F), -83.51 (d, $^{2}J_{FF}$ = 8.7Hz, 1F) ppm; ^{13}C NMR (CDCl$_3$, 75Hz) δ 158.98 (dd, $^{1}J_{CF}$ = 294.4, $^{1}J_{CF}$ = 295.9Hz), 137.51 (t, $^{4}J_{CF}$ = 2.5Hz), 134.26 (t, $^{4}J_{CF}$ = 3.5Hz), 100.20 (t, $^{3}J_{CF}$ = 4.6Hz), 96.90, 88.25, 85.60 (dd, $^{2}J_{CF}$ = 24.5, $^{2}J_{CF}$ = 21.2Hz), 85.18, 32.19, 29.93, 22.95, 18.75, 14.35, 11.68, 0.23; MS m/z (relative intensity) 121 (100), 299 (3.9, M^{+}-43), 342 (0.1, M^{+}). ^{13}C NMR spectrum has been supplied as indication of purity.

1,1-difluoro-2-(1-triisopropylsilylethylidene)-oct-1-ene-3-yne (4c): ^{1}H NMR (CDCl$_3$, 300 MHz) δ 5.93 (dd, $^{5}J_{HF}$ = 2.5Hz, $^{5}J_{HF}$ = 1.3Hz, 1H), 5.64 (dd, $^{5}J_{HF}$ = 2.4Hz, $^{5}J_{HF}$ = 1.7Hz, 1H), 2.30 (t, $^{2}J_{HH}$ = 1.2Hz, 2H), 1.44 (m, 4H), 1.27 (m, 3H), 1.10 (s, 18H), 0.90 (t, $^{2}J_{HH}$ = 7.3Hz, 3H) ppm; ^{19}F NMR (CDCl$_3$, 282MHz) δ -83.26 (d, $^{2}J_{FF}$ = 17.5Hz, 1F), -86.24 (d, $^{2}J_{FF}$ = 17.8Hz, 1F) ppm; ^{13}C NMR (CDCl$_3$, 75Hz) δ 158.25 (dd, $^{1}J_{CF}$ = 293.3, $^{1}J_{CF}$ = 293.3Hz), 138.24 (t, $^{4}J_{CF}$ = 2.2Hz), 133.70 (t, $^{4}J_{CF}$ = 3.5Hz), 95.52 (t, $^{3}J_{CF}$ = 5.9Hz), 85.53 (dd, $^{2}J_{CF}$ = 16.6, $^{2}J_{CF}$ = 16.3Hz), 72.70, 32.17, 29.90, 22.19, 18.75, 3.79, 11.69; MS m/z (relative intensity) 115 (100), 199 (62.1), 241 (19.5), 283 (4.5, M^{+}-43), 326 (0.1, M^{+}). ^{13}C NMR spectrum has been supplied as indication of purity.