Supporting information

Effect of fluorine on Palladium-catalyzed Cross-coupling Reactions of Aryl Bromides with Trifluoromethyl Aryl Ketones Via Difluoroenol Silyl or Monofluoroenol Silyl Ethers

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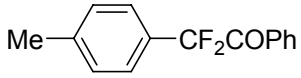
General Methods. Difluoroenol silyl ethers[1] **2a-2e** and monofluoro silyl enol ether[2] **4** were prepared as described previously. Tri-n-butyltin fluoride and a 1M toluene solution of P(*t*-Bu)$_3$, were purchased from Aldrich Chemical Co. and used as received. Toluene was distilled under nitrogen over sodium prior to use. All other chemicals were used as received from commercial sources. ^{1}H NMR spectra were obtained on a 300- or 500-MHz spectrometer, and chemical shifts were recorded relative to a residual protonated solvent. ^{13}C NMR spectra were obtained at 75.5 MHz on a 300-MHz instrument, and chemical shifts were recorded relative to the solvent resonance. Both ^{1}H NMR and ^{13}C NMR chemical shifts are reported in parts per million relative to tetramethylsilane. ^{19}F NMR chemical shifts are reported in parts per million from $CFCl_3$. The solvent was $CDCl_3$ unless otherwise stated. The purity of products was determined by CH&N elemental analyses. Column chromatography was carried out using ACROS silicagel (0.060-0.200 mm). Thin layer chromatography (TLC) was carried out on commercially available pre-coated plates (Whatman UV_{254} silica).

General procedure for Pd-catalyzed arylation: A mixture containing a TMS enol ether (2 mmol), aryl halide (1 mmol), 5 mol % of $Pd(OAc)_2$ (11.2 mg), and Bu_3SnF (927 mg, 3 mmol) in toluene (1.5 mL) under a nitrogen atmosphere was treated with a solution of $^tBu_3P$ (0.1 mL, 1M solution in toluene) at room temperature. The resulting mixture was heated to 85 ^oC and was stirred for 8 hours. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (20 mL) (when the precipitate of tin residue was formed, it was removed by decantation with ethyl acetate). The solution was concentrated and 5 mL of saturated KF solution and 5 mL ethyl acetate were added. The mixture was stirred for 1 hour. The resulting precipitate was removed by filtration. The organic layer of the filtrate was separated. The aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$. After filtration and evaporation, the residue was purified by column chromatography on silica gel.

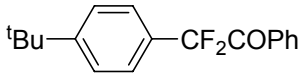
$PhCF_2COPh$
3a

2,2-Difluoro-1,2-diphenylethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (100:1); R_F [hexanes / ethyl acetate, 10:1] = 0.43. IR (film) 1704, 1254, 1130 cm^{-1}; ^1H NMR δ 7.42-7.48 (m, 5H), 7.56-7.63(m, 3H), 8.03(d, J = 8.1Hz, 2H); ^{19}F NMR δ -97.5 (s); ^{13}C NMR δ 117.0 (t, J = 253 Hz), 125.6 (t, J = 6.0 Hz), 128.6, 128.8, 130.3 (t, J = 3.0 Hz), 130.9 (t, J = 1.8 Hz), 132.2 (t, J = 1.4 Hz), 133.2 (t, J = 25.0 Hz), 134.2, 189.0 (t, J = 31.0 Hz); EI-MS (m/z, relative intensity) 232 (M^+, 0.23), 105 (100), 77 (52). Anal. Calcd for $C_{14}H_{10}F_2O$: C, 72.41; H, 4.34. Found: C, 72.18; H, 4.34.



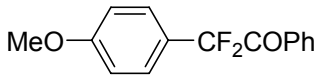
3b

2,2-Difluoro-2-(4-methylphenyl)-1-phenylethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (100:1); R_F [hexanes / ethyl acetate, 10:1] = 0.47. IR (film) 1704, 1260 cm^{-1}; ^1H NMR δ 2.39 (s, 3H), 7.26 (d, J = 7.4 2H), 7.41-7.60 (m, 5H), 8.02 (d, J = 7.9 Hz, 2H); ^{19}F NMR δ -97.1 (s); ^{13}C NMR δ 21.3, 117.1 (t, J = 253 Hz), 125.6 (t, J = 5.9 Hz), 128.6, 129.5, 130.3 (t, J = 2.9 Hz), 130.4 (t, J = 25.2 Hz), 132.3, 134.1, 141.2 (t, J = 1.8 Hz), 189.1 (t, J = 31.2 Hz); EI-MS (*m*/*z*, relative intensity) 246 (M^+, 1.49), 141 (12), 105 (100), 77 (27). Anal. Calcd for $C_{15}H_{12}F_2O$: C, 73.16; H, 4.91. Found: C, 72.83; H, 4.95.



3c

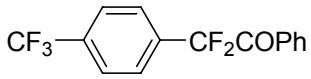
2-(4-*tert*-Butylphenyl)-2,2-difluoro-1-phenylethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (100:1); R_F [hexanes / ethyl acetate, 10:1] = 0.52. IR (film) 2964, 1705, 1263 cm^{-1}; ^1H NMR δ 1.34 (s, 9H), 7.46-7.58 (m, 7H), 8.06 (d, J = 7.4 Hz, 2H); ^{19}F NMR δ -96.9 (s); ^{13}C NMR δ 31.1, 34.8, 117.1 (t, J = 253 Hz), 125.4 (t, J = 5.9 Hz), 125.7, 128.6, 129.9, 130.3 (t, J = 2.9 Hz), 132.3, 134.1, 154.2 (t, J = 1.8 Hz), 189.1 (t, J = 31.2 Hz); EI-MS (*m*/*z*, relative intensity) 288 (M^+, 1.15), 183 (14), 153 (11), 105 (100), 77 (31). Anal. Calcd for $C_{18}H_{18}F_2O$: C, 74.98; H, 6.29. Found: C, 74.99; H, 6.34.



3d

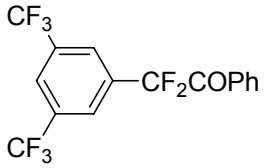
2,2-Difluoro-2-(4-methoxyphenyl)-1-phenylethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (40:1); R_F [hexanes / ethyl acetate, 10:1] = 0.30. IR (film) 1703, 1608, 1514, 1250 cm^{-1}; ^1H NMR δ 3.82 (s, 3H), 6.96 (d, J =

8.5 Hz, 2H), 7.41-7.46 (m, 2H), 7.53-7.60 (m, 3H), 8.03 (d, J = 8.5 Hz, 2H); ^{19}F NMR δ -96.2 (s); ^{13}C NMR δ 55.3, 114.2, 117.1 (t, J = 253 Hz), 125.2 (t, J = 25.7 Hz), 127.3 (t, J = 5.9 Hz), 128.6, 130.2 (t, J = 2.9 Hz), 132.3 (t, J = 1.4 Hz), 134.1, 161.5 (t, J = 1.7 Hz), 189.2 (t, J = 31.4 Hz); EI-MS (m/z, relative intensity) (M^+,), Anal. Calcd for $C_{15}H_{12}F_2O_2$: C, 68.70; H, 4.61. Found: C, 69.01; H, 4.55.



3e

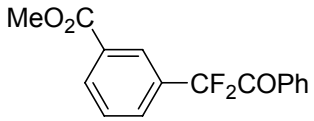
2,2-Difluoro-1-phenyl-2-(4-trifluoromethylphenyl)ethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (100:1); R_F [hexanes / ethyl acetate, 10:1] = 0.48. White solid; mp 46-48 ^{o}C ; IR (KBr) 1701, 1326, 1068 cm^{-1}; ^{1}H NMR δ 7.48 (m, 2H), 7.63 (m, 1H), 7.74 (s, 4H), 8.06 (d, J = 8.2 Hz, 2H); ^{19}F NMR δ -63.0 (s, 3F), -97.9 (s, 2F); ^{13}C NMR δ 116.5 (t, J = 255 Hz), 123.6 (q, J = 273 Hz), 125.8 (q, J = 3.7 Hz), 126.4 (t, J = 6.2 Hz), 128.8, 130.2 (t, J = 3.1 Hz), 131.9 (t, J = 2.0 Hz), 133.0 (q, J = 32.9 Hz), 134.5, 136.8 (t, J = 30.4 Hz), 137.2, 188.3 (t, J = 31.2 Hz); EI-MS (m/z, relative intensity) 300 (M^+, 0.02), 105 (100), 77 (68). Anal. Calcd for $C_{15}H_9F_5O$: C, 60.01; H, 3.02. Found: C, 59.98; H, 2.90.



3f

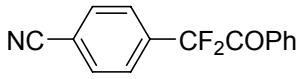
2-[3,5-Bis(trifluoromethyl)phenyl]-2,2-difluoro-1-phenylethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (100:1); R_F [hexanes / ethyl acetate, 10:1] = 0.52. IR (film) 1704, 1281, 1231, 1184, 1139 cm^{-1}; ^{1}H NMR δ 7.51-7.56 (m 2H), 7.66-7.71(m, 1H), 8.04 (s, 3H), 8.12 (d, J = 8.2, 2H); ^{19}F NMR δ -63.0 (s, 6F), -

97.2 (s, 2F); ^{13}C NMR δ 116.1 (t, *J* = 257 Hz), 122.8 (q, *J* = 273 Hz), 124.8 (m), 126.6 (m), 128.9, 130.3 (t, *J* = 3.2 Hz), 131.4 (t, *J* = 2.7 Hz), 132.3 (q, *J* = 34.6 Hz), 134.9, 135.6 (t, *J* = 26.0 Hz), 187.7 (t, *J* = 32.1 Hz); EI-MS (*m*/*z*, relative intensity) 367(M^+-1, 0.06), 349 (5), 105 (100), 77 (61). Anal. Calcd for $C_{16}H_8F_8O$: C, 52.19; H, 2.19. Found: C, 51.97; H, 2.04.



3g

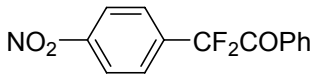
Methyl 3-(1,1-difluoro-2-oxo-2-phenylethyl)benzonate: Isolated by column chromatography eluting with hexane/ethyl acetate (40:1 to 30:1); R_F [hexanes / ethyl acetate, 10:1] = 0.25. IR (film) 1727, 1704, 1229 cm^{-1}; ^{1}H NMR δ 3.94 (s, 3H), 7.44-7.61 (m, 4H), 7.77-7.80 (m, 1H), 8.03-8.07 (m, 2H), 8.17 (d, *J* = 7.7 Hz, 1H), 8.30 (s, br., 1H); ^{19}F NMR δ -97.4 (s); ^{13}C NMR δ 52.3, 116.6 (t, *J* = 255 Hz), 128.7, 128.9, 129.0, 130.1 (t, *J* = 5.9 Hz), 130.2 (t, *J* = 3.1 Hz), 131.0, 131.9 (t, *J* = 1.4 Hz), 133.7 (t, *J* = 25.5 Hz), 134.3, 134.4, 166.0, 188.5 (t, *J* = 31.3 Hz); EI-MS (*m*/*z*, relative intensity) 290 (M^+, 0.02), 259 (9), 105 (100), 77 (40). Anal. Calcd for $C_{16}H_{12}F_2O_3$: C, 66.21; H, 4.17. Found: C, 66.12; H, 4.13.



3h

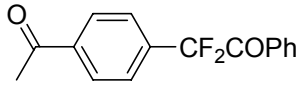
2-(4-Cyanophenyl)-2,2-difluoro-1-phenylethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (40:1 to 30:1); R_F [hexanes / ethyl acetate, 10:1] = 0.23. White solid; mp 78-80.5 ^{o}C; IR (KBr) 2230, 1703, 1240 cm^{-1}; ^{1}H NMR δ 7.49 (t, *J* = 7.7 Hz, 2H), 7.62-7.99 (m, 5H), 8.05 (d, *J* = 7.4 Hz, 2H); ^{19}F NMR δ -98.2 (s); ^{13}C NMR δ 115.0 (t, *J* = 1.8 Hz), 116.3 (t, *J* = 256 Hz), 117.7, 126.8 (t, *J* = 6.2

Hz), 128.9, 130.2 (t, J =3.1 Hz), 131.6 (t, J = 2.0 Hz), 132.5, 134.7, 137.5 (t, J =25.4 Hz), 188.0 (t, J = 31.3 Hz); EI-MS (m/z, relative intensity) 238 (M^+-F, 0.16), 105 (100), 77 (53). Anal. Calcd for $C_{15}H_9F_2NO$: C, 70.04; H, 3.53; N, 5.45. Found: C, 69.76; H, 3.41, N, 5.47.



3i

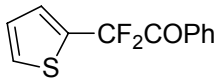
2,2-Difluoro-2-(4-nitrophenyl)-1-phenylethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (40:1); R_F [hexanes / ethyl acetate, 10:1] = 0.33. White solid; mp 89.5-91.5 ^oC; IR (KBr) 1700, 1524, 1349, 1240 cm^{-1}; ^1H NMR δ 7.48-7.54 (m, 2H), 7.63-7.69 (m, 1H), 7.78-7.81 (m, 2H), 8.06-8.09 (m, 2H), 8.33 (d, J = 9.1 Hz, 2H); ^{19}F NMR δ -97.8 (s); ^{13}C NMR δ 116.3 (t, J = 256 Hz), 123.8, 127.3 (t, J = 6.1 Hz), 128.9, 130.2 (t, J = 3.2 Hz), 131.6 (t, J = 2.3 Hz), 134.8, 139.2 (t, J = 25.3 Hz), 149.4, 187.9 (t, J = 31.3 Hz); EI-MS (m/z, relative intensity) 276 (M^+-1, 0.01), 105 (100), 77 (60). Anal. Calcd for $C_{14}H_9F_2NO_3$: C, 60.66; H, 3.27; N, 5.05. Found: C, 60.54; H, 3.08, N 5.08.



3j

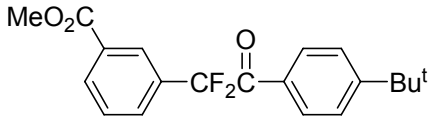
2-(4-Acetylphenyl)-2,2-difluoro-1-phenylethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (40:1 to 30:1 to 20:1); R_F [hexanes / ethyl acetate, 10:1] = 0.15. White solid; mp 76.5-78 ^oC; IR (KBr) 1686, 1236 cm^{-1}; ^1H NMR δ 2.62 (s, 3H), 7.44-7.49 (m, 2H), 7.59-7.64 (m, 1H), 7.72 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.4, 4H); ^{19}F NMR δ -98.0 (s); ^{13}C NMR δ 26.7, 116.6 (t, J = 255 Hz), 126.1 (t, J = 6.0 Hz), 128.6, 128.7, 130.2 (t, J = 3.0 Hz), 131.9 (t, J = 1.7 Hz), 134.4, 137.3 (t, J

= 25.0 Hz), 138.9 (t, *J* = 1.6 Hz), 188.4 (t, *J* = 31.0 Hz), 197.1; EI-MS (*m*/*z*, relative intensity) 274 (M^+, 0.16), 105 (100), 77 (60). Anal. Calcd for $C_{16}H_{12}F_2O_2$: C, 70.07; H, 4.41. Found: C, 70.04; H, 4.17.



3k

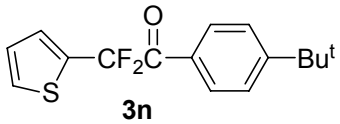
2,2-Difluoro-1-phenyl-2-(2-thienyl)ethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (100:1); R_F [hexanes / ethyl acetate, 10:1] = 0.38. IR (film) 1704, 1240 cm^{-1}; ^1H NMR δ 7.03-7.07 (m, 1H), 7.30-7.33 (m, 1H), 7.45-7.52 (m, 3H), 7.59-7.64 (m, 1H), 8.07 (d, *J* = 7.9 Hz, 2H); ^{19}F NMR δ -86.9 (s); ^{13}C NMR δ 115.2 (t, *J* = 251 Hz), 127.3, 128.7, 128.9 (t, *J* = 5.8 Hz), 129.2 (t, *J* = 1.6 Hz), 130.4 (t, *J* = 3.0 Hz), 132.0 (t, *J* = 1.4 Hz) 134.4, 134.7 (t, *J* = 29.5 Hz), 187.9 (t, *J* = 30.8 Hz); EI-MS (*m*/*z*, relative intensity) 238 (M^+, 1.03), 105 (100), 77 (54). Anal. Calcd for $C_{12}H_8F_2OS$: C, 60.49; H, 3.38. Found: C, 60.70; H, 3.32.



3m

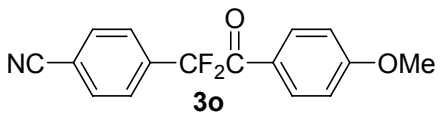
Methyl 3-[2-(4-tert-butylphenyl)-1,1-difluoro-2-oxo]benzoate: Isolated by column chromatography eluting with hexane/ethyl acetate (40:1); R_F [hexanes / ethyl acetate, 50:1] = 0.32. IR (film) 2963, 1728, 1700, 1230 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.33 (s, 9H), 3.94 (s, 3H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.1 Hz, 1H), 7.99 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 7.7 Hz, 1H), 8.31 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ -97.4 (s); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 30.9, 35.2, 52.3, 116.6 (t, *J* = 264 Hz), 125.3, 125.5, 125.7, 126.9 (t, *J* =6.2 Hz), 129.0, 130.1 (t, *J* = 5.9 Hz), 130.3 (t, *J* = 3.0 Hz), 130.9, 131.9 (t, *J* = 1.6 Hz), 158.5, 166.0, 188.0 (t, *J* = 31.0 Hz); EI-MS (*m*/*z*,

relative intensity) 345 (M^+-1, 0.01), 161 (100). Anal. Calcd for $C_{20}H_{20}F_2O_3$: C, 69.35; H, 8.32. Found: C, 69.01; H, 5.71.



3n

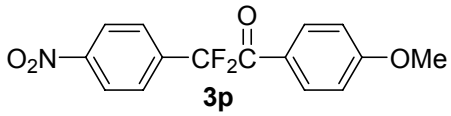
1-(4-*tert*-Butylpheyl)-2,2-difluoro-2-(2-thienyl)ethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (100:1); R_F [hexanes / ethyl acetate, 10:1] = 0.44. IR (film) 2964, 1699, 1604, 1240, 1103 cm^{-1}; ^1H NMR δ 1.34 (s, 9H), 7.03-7.07 (m, 1H), 7.30-7.32 (m, 1H), 7.46-7.56 (m, 3H), 8.02 (d, J = 8.4 Hz, 2H); ^{19}F NMR δ -86.8 (s); ^{13}C NMR δ 30.9, 35.3, 115.1 (t, J = 251 Hz), 125.7, 127.2, 128.8 (t, J = 5.8 Hz), 129.0 (t, J = 1.7 Hz), 129.3 (t, J = 1.5 Hz), 129.6 (t, J = 2.3 Hz), 130.4 (t, J = 3.0 Hz), 135.0 (t, J = 29.5 Hz), 158.5, 187.4 (t, J = 30.5 Hz); EI-MS (*m*/*z*, relative intensity) 294 (M^+, 0.02), 161 (100). Anal. Calcd for $C_{16}H_{16}F_2OS$: C, 65.28; H, 5.48. Found: C, 64.97; H, 5.39.



3o

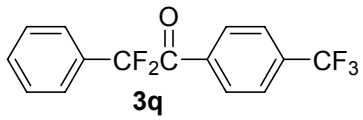
2-(4-Cyanophenyl)-2,2-difluoro-1-(4-methoxylphenyl)ethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (20:1); R_F [hexanes / ethyl acetate, 10:1] = 0.15. White solid; mp 97.5-99.5 ^oC; IR (KBr) 2231, 1597, 1247 cm^{-1}; ^1H NMR δ3.89 (s, 3H), 6.96 (d, J = 7.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 8.06 (d, J =7.0 Hz, 2H); ^{19}F NMR δ -98.2 (s); ^{13}C NMR δ 55.6, 114.2, 114.8 (t, J = 1.9 Hz), 116.4 (t, J = 256 Hz), 117.8, 124.4 (t, J = 2.2 Hz), 126.7 (t, J = 6.2 Hz), 132.4, 132.8 (t, J = 3.3 Hz), 137.9 (t, J = 25.4), 164.8, 186.2 (t, J = 30.7); EI-MS (*m*/*z*, relative

intensity) 287 (M^+, 0.14), 135 (100), 77 (15). Anal. Calcd for $C_{16}H_{11}F_2NO_2$: C, 66.90; H, 3.86; N, 4.88. Found: C, 66.70; H, 3.75, N, 4.89.



3p

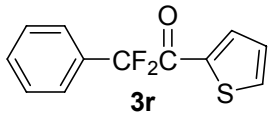
2,2-Difluoro-1-(4-methoxyphenyl)-2-(4-nitrophenyl)ethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (20:1); R_F [hexanes / ethyl acetate, 10:1] = 0.17. Pale yellow solid; mp 85-87°C; IR (film) 1688, 1600, 1261cm^{-1}; ^{1}H NMR (500 MHz) δ 3.90 (s, 3H), 6.96 (d, J = 9 Hz, 2H), 7.79 (d, J = 9 Hz, 2H), 8.08 (d, J = 9 Hz, 2H), 8.32 (d, J = 9 Hz, 2H); ^{19}F NMR (470 MHz) δ -97.8 (s); ^{13}C NMR δ 55.6, 114.2, 116.4 (t, J = 256 Hz), 123.8, 124.3 (t, J = 2.2 Hz), 127.2 (t, J = 6.1 Hz), 132.8 (t, J = 3.3 Hz), 139.6 (t, J = 25.4 Hz), 149.3, 164.8, 186.2 (t, J = 30.7 Hz); EI-MS (*m*/*z*, relative intensity) 307(M^+, 0.18), 135 (100), 77 (14). Anal. Calcd for $C_{15}H_{11}F_2NO_4$: C, 58.64; H, 3.61; N, 4.56. Found: C, 58.34; H, 3.66, N, 4.56.



3q

2,2-Difluoro-2-phenyl-1-(4-trifluoromethylphenyl)ethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (100:1); R_F [hexanes / ethyl acetate, 10:1] = 0.51. IR (film) 1715, 1325, 1134, 1167 cm^{-1}; ^{1}H NMR) δ 7.46-7.52 (m, 3H), 7.59-7.62 (m, 2H), 7.72 (d, J = 8.4 Hz, 2H), 8.14 (d, J = 8.2 Hz, 2H); ^{19}F NMR δ -63.5 (s, 3F), -98.0 (2F); ^{13}C NMR δ 116.8 (t, J = 254 Hz), 123.3 (q, J = 273 Hz), 125-127 (m), 128.9, 130.5 (t, J = 3.1 Hz), 131.2 (t, J = 1.8 Hz), 132.4 (t, J = 24.8 Hz), 135.0(m), 135.3 (q, J = 32.9 Hz), 137.2, 188.2 (t, J = 32.2); EI-MS (*m*/*z*, relative intensity) 300 (M^+, 0.50),

173 (100), 145 (45), 127 (31). Anal. Calcd for $C_{15}H_9F_5O$: C, 60.01; H, 3.02. Found: C, 59.64; H, 2.97.



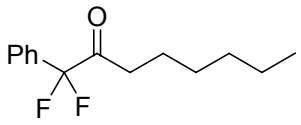
3r

2,2-Difluoro-2-phenyl-1-(2-thienyl)ethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (100:1); R_F [hexanes / ethyl acetate, 10:1] = 0.34. IR (film) 1678, 1410, 1258, 1128, 1061 cm^{-1}; ^1H NMR δ 7.16 (t, J = 4.4 Hz, 1H), 7.42-7.55 (m, 3H), 7.60-7.70 (m, 2H), 7.76 (d, J = 4.9 Hz, 1H), 7.96-7.98 (m, 1H); ^{19}F NMR δ -99.3 (s); ^{13}C NMR δ 116.6 (t, J = 254 Hz), 125.7 (t, J = 6.1 Hz), 128.7, 128.8, 131.0 (t, J = 1.8 Hz), 132.9 (t, J = 25.3 Hz), 135.9 (t, J = 4.8 Hz), 136.4 (t, J =1.1 Hz), 138.1, 182.3 (t, J =32.7); EI-MS (m/z, relative intensity) 238 (M+, 3.24), 127 (20), 111 (100), 39 (45). Anal. Calcd for $C_{12}H_8F_2OS$: C, 60.49; H, 3.38. Found: C, 60.57; H, 3.25.

PhCHFCOPh

5a

1,2-Diphenyl-2-fluoroethanone: Isolated by column chromatography eluting with hexane/ethyl acetate (40:1); R_F [hexanes / ethyl acetate, 10:1] = 0.32. White solid; mp 59.5-61.5°C; IR (KBr) 1693 cm^{-1}; ^1H NMR δ 6.51 (d, J = 48.7 Hz), 7.38-7.55 (m, 8H), 7.93-7.96 (m, 2H); ^{19}F NMR (470 MHz) δ -176.5 (d, J = 48.4 Hz); ^{13}C NMR δ 93.9 (d, J = 186 Hz), 127.4 (d, J = 5.5 Hz), 128.7, 129.0 (d, J = 2.8 Hz), 129.1, 129.6 (d, J = 2.6 Hz), 133.8, 134.1, 134.3 (d, J = 19.9 Hz), 194.3 (d, J = 21.4 Hz); EI-MS (m/z, relative intensity) 214 (M^+, 0.20), 105 (100), 77 (41). Anal. Calcd for $C_{14}H_{11}FO$: C, 78.49; H, 5.18. Found: C, 78.44; H, 5.06.



3s

To TMSCl (2.2 g, 20 mmol) in DMF (24 ml) and Mg (972 mg, 40 mmol) cooled down to 0 °C under an nitrogen atmosphere, 1,1,1-trifluoro-2-octanone (910 mg, 5.0 mmol) was added dropwise and then stirred for an additional 3 hours. Hexane (20 ml) was added to the solution. The hexane layer was separated and hexane was removed under vacuum. The residue was diluted in toluene. The crude product in toluene was added to a mixture containing monobromobenzene (157 mg, 1 mmol), 5 mol % of $Pd(OAc)_2$ (11.2 mg), and Bu_3SnF (927 mg, 3 mmol) in toluene (1.5 mL) and a solution of $^tBu_3P$ (0.1 mL, 1M solution in toluene) under a nitrogen atmosphere. The resulting mixture was heated to 85 ^oC and was stirred for 8 hours. The isolation was as in general procedure. Because of much impurity generated in reaction process, pure **3s** was hard to obtain. The yield of **3s** was 6% based on ^{19}F NMR analysis. The yield of 1,1-difluoro-2-octanone was 70%.

1,1-difluoro-1-phenyl-octanone: ^{19}F NMR ($CDCl_3$) δ -106.6; GC-MS (*m*/*z*, relative intensity) 240 (M^+, 0.03), 221(M^+-F, 0.07), 163(M^+-Ph, 0.12), 127($PhCF_2^+$, 24), 113 ($C_6H_{13}CO^+$, 44), 85($C_6H_{13}^+$, 15), 77(Ph^+, 7), 43 ($C_3H_7^+$, 100).

Comparison experiment: A mixture containing a nonfluorinated TMS enol ether (1 mmol), difluoro enol ether **2a** (228 mg, 1 mmol), monobromobenzene (157 mg, 1 mmol), 5 mol % of $Pd(OAc)_2$ (11.2 mg), and Bu_3SnF (927 mg, 3 mmol) in toluene (1.5 mL) under a nitrogen atmosphere was treated with a solution of $^tBu_3P$ (0.1 mL, 1M solution in toluene) at room temperature. The resulting mixture was heated to 85 ^oC and was stirred for 1 hours. After cooling to room temperature, the reaction mixture was diluted with

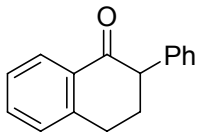
ethyl acetate (20 mL) (when the precipitate of tin residue was formed, it was removed by decantation with ethyl acetate). The solution was concentrated. The residue was added internal standard benzotrifluoride and 1,2-dichloroethane. The yields were reported based on NMR or GC-MS analysis.

Table S1: relative rate of silyl enol ethers

Strating materials	Yield (%) [a]	relative rate
2a and **2g**	**3a** (14) **3t** (27)	**3a/3t** = 0.52
2a and **2h**	**3a** (28) **3u** (14)	**3a/3u** = 2.0
2a and **2i**	**3a** (20) **3v** (4)	**3a/3v** = 5.0
2a and **2j**	**3a** (24) **3w** (<1) [b]	**3a/3w** = >20

[a]yield based on NMR analysis, [b]yield based on GC-MS

$PhCH_2COPh$
3t



3u

PhCH(Me)COPh
3v

$PhC(Me)_2COPh$
3w

References

1 H. Amii, T. Kobayashi, Y. Hatamoto, K. Uneyama, *Chem. Commun.* 1999, 1323.

2 G. K. S. Prakash, J. Hu, G. A. Olah, *J. Fluorine Chem.* 2001, **112**, 357.