Supplementary Material (ESI) for Organic & Biomolecular Chemistry


# Supplementary Information

## Remarkable Access to Fluoroalkylated Trisubstituted Alkenes *via* Highly Stereoselective Cobalt-catalyzed Hydrosilylation Reaction of Fluoroalkylated Alkynes

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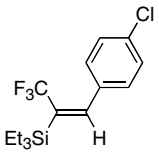
## Experimental

$^1$H NMR spectra were measured with a Bruker DRX (500.13 MHz) spectrometer in a chloroform-*d* ($CDCl_3$) solution with tetramethylsilane ($Me_4Si$) as an internal reference. $^{13}$C NMR spectra were recorded on a Bruker DRX (125.77 MHz). A JEOL JNM-EX90 (84.21 MHz, FT) spectrometer was used for determining $^{19}$F NMR yield with internal $C_6F_6$. It was also used for determining regioselectivity and stereoselectivity and for taking $^{19}$F NMR spectra in a $CDCl_3$ solution with internal $CFCl_3$. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8200A (PC) spectrophotometer. Mass spectra (MS) were taken on a JEOL JMS-700. Dichloromethane and 1,2-dichloroethane were freshly distilled from calsium hydride under argon. All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use. Thin layer chromatography (TLC) was done with Merck silica gel 60 $F_{254}$ plates and column chromatography was carried out with Wako gel C-200. All acetylenes were prepared according to the literature procedure.[1]

**General procedure for the hydrosilylation**

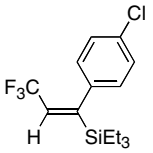
To a solution of fluoroalkylated acetylene (0.25 mmol) in $ClCH_2CH_2Cl$ (2 mL) was added $Co_2(CO)_8$ (4.3 mg, 5 mol%) and $Et_3SiH$ (35 mg, 1.2 mmol) at room temperature. The whole was stirred for 3 h at the reflux temperture. The reaction mixture was cooled and filtrated. The resulting filtrate was concentrated in *vacuo*. The residue was chromatographed on silica gel to afford fluoroalkylated vinylsilanes (45-97% yield).

**(*E*)-3-(4-Chlorophenyl)-1,1,1-trifluoro-2-triethylsilylpropene (2a)**




$^1$H NMR ($CDCl_3$) δ = 0.79 (q, *J* = 7.9 Hz, 6H), 1.02 (t, *J* = 7.9 Hz, 9H), 7.28 ~ 7.34 (m, 4H); $^{13}$C NMR ($CDCl_3$) δ = 3.2, 7.1, 125.7 (q, *J* = 275.9 Hz), 131.7 (q, *J* = 30.6 Hz), 147.4 (q, *J* = 7.0 Hz), 128.3, 134.4, 134.8, 147.5; $^{19}$F NMR ($CDCl_3$) δ = -53.1 (s, 3F).

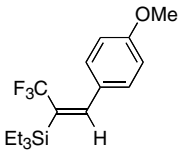
**(*E*)-1-(4-Chlorophenyl)-1-triethylsilyl-3,3,3-trifluoropropene (3a)**




$^1$H NMR ($CDCl_3$) δ = 0.62 (q, *J* = 7.9 Hz, 6H), 0.93 (t, *J* = 7.9 Hz, 9H), 6.00 (q, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 2.1, 6.9, 127.5 (q, *J* = 32.2 Hz), 128.2; $^{19}$F NMR ($CDCl_3$) δ = -57.6 (d, *J* = 8.5 Hz, 3F).

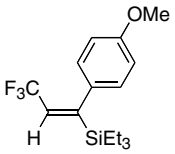
Combined yield: 95%; IR (neat) 2959, 2939, 2914, 2878, 1610, 1489, 1458, 1418, 1362, 1279, 1223, 1196, 1148, 1119, 1103, 1016, 1007, 982, $cm^{-1}$; HRMS calcd for $C_{15}H_{20}{}^{35}ClF_3{}^{28}Si$ ($M^+$) 320.0975 found 320.0980; Anal. Calcd for $C_{15}H_{20}ClF_3Si$: C, 56.15; H, 6.28. Found: C, 55.81; H, 6.65.

**(*E*)-1,1,1-Trifluoro-3-(4-methoxyphenyl)-2-triethylsilyl-propene (2b)**




$^1$H NMR ($CDCl_3$) δ = 0.70 (q, *J* = 7.8 Hz, 6H), 0.96 (t, *J* = 7.9 Hz, 9H), 3.81 (s, 3H), 6.28 (t, *J* = 7.4 Hz, 1H), 6.83 ~ 7.13 (m, 4H); $^{13}$C NMR ($CDCl_3$) δ = 3.1, 7.0, 55.2, 126.3 (q, *J* = 276.6 Hz), 127.8 (q, *J* = 30.4 Hz), 152.0 (q, *J* = 6.4 Hz), 113.5, 114.1, 129.5, 158.3; $^{19}$F NMR ($CDCl_3$) δ = -53.3 (s, 3F).

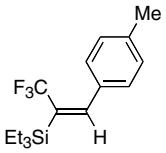
**(*E*)-1-(4-Methoxyphenyl)-1-triethylsilyl-3,3,3-trifluoropropene (3b)**




$^1$H NMR ($CDCl_3$) δ = 0.79 (q, *J* = 7.8 Hz, 6H), 1.03 (t, *J* = 7.9 Hz, 9H), 3.84 (s, 3H), 5.97 ~ 6.02 (m, 1H), 7.40 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 3.3, 7.1, 36.3, 148.5 (q, *J* = 6.9 Hz), 160.0; $^{19}$F NMR ($CDCl_3$) δ = -57.4 (d, *J* = 7.1 Hz, 3F).

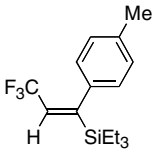
Combined yield: 64%; IR (neat) 2957, 2878, 2837, 1614, 1512, 1466, 1443, 1420, 1366, 1302, 1250, 1178, 1140, 1115, 1038, 1005, 829, 735, 698 cm$^{-1}$; HRMS calcd for $C_{16}H_{23}F_3O^{28}Si$ ($M^+$) 316.1470 found 316.1465.

**(*E*)-1,1,1-Trifluoro-3-(4-methylphenyl)-2-triethylsilylpropene (2c)**




$^1$H NMR ($CDCl_3$) δ = 0.76 (q, *J* = 7.9 Hz, 6H), 0.99 (t, *J* = 7.8 Hz, 9H), 2.35 (s, 3H), 7.06 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 3.3, 7.1, 21.3, 125.8, 125.9 (q, *J* = 275.7 Hz), 126.7 (q, *J* = 31.8 Hz), 128.6, 128.8, 138.6, 149.0 (q, *J* = 6.7 Hz); $^{19}$F NMR ($CDCl_3$) δ = -53.1 (s, 3F).

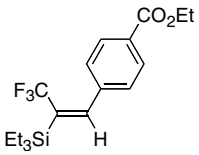
**(*E*)-1-(4-Methylphenyl)-1-triethylsilyl-3,3,3-trifluoropropene (3c)**




$^1$H NMR ($CDCl_3$) δ = 0.60 (q, *J* = 7.9 Hz, 6H), 0.92 (t, *J* = 7.9 Hz, 9H), 2.33 (s, 3H), 5.95 (q, *J* = 7.9 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 2.2, 7.0, 21.1, 128.7 (q, *J* = 2.8 Hz), 129.5 (q, *J* = 30.4 Hz); $^{19}$F NMR ($CDCl_3$) δ = -57.4 (d, *J* = 7.1 Hz, 3F).

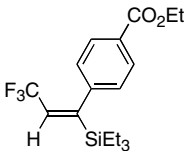
Combined yield: 45%; IR (neat) 2957, 2909, 2877, 1607, 1509, 1458, 1357, 1281, 1224, 1178, 1143, 1109, 1005, 812, 735, 698, cm$^{-1}$; HRMS calcd for $C_{16}H_{23}F_3{}^{28}Si$ ($M^+$) 300.1521 found 300.1521.

**(*E*)-Ethyl 4-(2-triethylsilyl-3,3,3-trifluoropropenyl)-benzoate (2d)**




$^1$H NMR ($CDCl_3$) δ = 0.78 (q, *J* = 7.9 Hz, 6H), 1.01 (t, *J* = 7.9 Hz, 9H), 1.39 (t, *J* = 7.1 Hz, 3H), 4.38 (q, *J* = 7.1 Hz, 2H), 7.13 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 3.2, 7.0, 14.3, 61.0, 125.5 (q, *J* = 275.9 Hz), 128.2, 129.3, 130.2, 133.0 (q, *J* = 30.2 Hz), 141.0, 147.7 (q, *J* = 6.9 Hz), 166.2; $^{19}$F NMR ($CDCl_3$) δ = -53.01 (s, 3F).

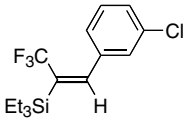
**(*E*)-Ethyl 4-(1-triethylsilyl-3,3,3-trifluoropropenyl)-benzoate (3d)**



$^1$H NMR ($CDCl_3$) δ = 0.61 (q, *J* = 7.9 Hz, 6H), 0.92 (t, *J* = 8.0 Hz, 9H), 1.39 (t, *J* = 6.9 Hz, 3H), 4.37 (q, *J* = 7.0 Hz, 2H), 5.99 (q, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.2 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 2.2, 6.9, 60.9, 128.2 (q, *J* = 9.5 Hz), 144.6; $^{19}$F NMR ($CDCl_3$) δ = -57.7 (d, *J* = 7.1 Hz, 3F).

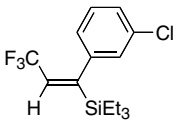
Combined yield: 61%; IR (neat) 2958, 2912, 2878, 1720, 1604, 1465, 1411, 1367, 1276, 1223, 1182, 1109, 1021, 853, 777, 736 cm$^{-1}$; HRMS calcd for $C_{18}H_{26}F_3O_2{}^{28}Si$ (M+H) 359.4786 found 359.1643.

**(*E*)-3-(3-Chlorophenyl)-1,1,1-trifluoro-2-triethylsilylpropene (2e)**




$^1$H NMR ($CDCl_3$) δ = 0.77 (q, *J* = 7.9 Hz, 6H), 1.00 (t, *J* = 7.9 Hz, 9H), 7.04 (s, 1H), 7.19 ~ 7.30 (m, 4H); $^{13}$C NMR ($CDCl_3$) δ = 3.2, 7.0, 124.2, 124.2, 125.5 (q, *J* = 275.9 Hz), 125.8, 125.8, 127.4 (q, *J* = 32.1 Hz), 128.4, 129.3, 147.1 (q, *J* = 7.0 Hz); $^{19}$F NMR ($CDCl_3$) δ = -53.1 (s, 3F).

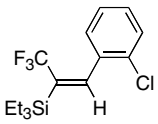
**(*E*)-1-(3-Chlorophenyl)-1-triethylsilyl-3,3,3-trifluoropropene (3e)**




$^1$H NMR ($CDCl_3$) δ = 0.61 (q, *J* = 7.9 Hz, 6H), 0.93 (t, *J* = 8.0 Hz, 9H), 5.98 (q, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 7.2 Hz, 1H), 6.95 (s, 1H); $^{13}$C NMR ($CDCl_3$) δ = 2.1, 6.9, 126.5 (q, *J* = 2.8 Hz), 129.2, 132.5 (q, *J* = 30.3 Hz); $^{19}$F NMR ($CDCl_3$) δ = -57.7 (d, *J* = 9.8 Hz, 3F).

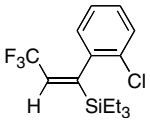
Combined yield: 67%; IR (neat) 2958, 2913, 2878, 1614, 1592, 1567, 1471, 1417, 1356, 1276, 1221, 1147, 1117, 1080, 1005, 737 cm$^{-1}$; HRMS calcd for $C_{15}H_{20}{}^{35}ClF_3Na^{28}Si$ (M+Na) 343.0872 found 343.0878; Anal. Calcd for $C_{15}H_{20}{}^{35}ClF_3Si$: C, 56.15; H, 6.28. Found: C, 55.98; H, 6.53.

**(*E*)-1,1,1-Trifluoro-3-(2-chlorophenyl)-2-triethylsilylpropene (2f)**




$^1$H NMR ($CDCl_3$) δ = 0.79 (q, *J* = 7.9 Hz, 6H), 1.02 (t, *J* = 8.0 Hz, 9H), 7.15 (s, 1H), 7.16 ~ 7.39 (m, 4H); $^{13}$C NMR ($CDCl_3$) δ = 3.2, 7.0, 125.6 (q, *J* = 276.1 Hz), 126.2, 126.3, 127.8, 128.9, 129.3, 129.4, 132.9 (q, *J* = 30.2 Hz), 145.8 (q, *J* = 6.9 Hz); $^{19}$F NMR ($CDCl_3$) δ = -53.5 (s, 3F).

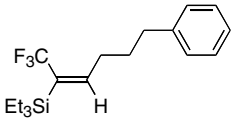
**(*E*)-1-(2-Chlorophenyl)-1-triethylsilyl-3,3,3-trifluoropropene (3f)**




$^1$H NMR ($CDCl_3$) δ = 0.59 ~ 0.72 (m, 6H), 0.92 (t, *J* = 7.9 Hz, 9H), 6.04 (q, *J* = 7.7 Hz, 1H), 6.91 (dd, *J* = 7.4, 1.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ = 2.8, 6.9, 129.8 (q, *J* = 3.5 Hz); $^{19}$F NMR ($CDCl_3$) δ = -60.1 (d, *J* = 7.1 Hz, 3F).

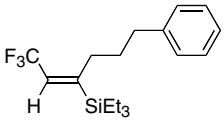
Combined yield: 83%; IR (neat) 2957, 2913, 2878, 1617, 1467, 1354, 1280, 1221, 1201, 1149, 1130, 1114, 1054, 1005, 773, 747 $cm^{-1}$; HRMS calcd for $C_{15}H_{20}{}^{35}ClF_3Na^{28}Si$ (M+Na) 343.0875 found 343.0862; Anal. Calcd for $C_{15}H_{20}ClF_3Si$: C, 56.15; H, 6.28. Found: C, 55.83; H, 6.48.

**(*E*)-1,1,1-Trifluoro-6-phenyl-2-triethylsilyl-2-hexene (2g)**




$^1H$ NMR ($CDCl_3$) δ = 0.69 (q, *J* = 7.9 Hz, 6H), 0.96 (t, *J* = 8.0 Hz, 9H), 1.80 (quint., *J* = 7.8 Hz, 2H), 2.37 ~ 2.46 (m, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 6.19 (t, *J* = 7.4 Hz, 1H), 7.21 (m, 3H), 7.31 (t, *J* = 7.5 Hz, 2H); $^{13}C$ NMR ($CDCl_3$) δ = 3.1, 7.1, 30.6, 30.9, 35.5, 126.3 (q, *J* = 276.7 Hz), 129.7 (q, *J* = 29.2 Hz), 153.5 (q, *J* = 6.4 Hz), 125.9, 128.3, 128.3, 141.9; $^{19}F$ NMR ($CDCl_3$) δ = -54.3 (s, 3F).

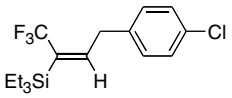
**(*E*)-1,1,1-Trifluoro-6-phenyl-3-triethylsilyl-2-hexene (3g)**




$^1H$ NMR ($CDCl_3$) δ = 0.64 (q, *J* = 7.9 Hz, 6H), 5.78 0.96 (q, *J* = 8.8 Hz, 1H), 7.19 ~ 7.23 (m, 3H), 7.29 ~ 7.32 (m, 2H); $^{13}C$ NMR ($CDCl_3$) δ = 2.7, 7.1, 126.4 (q, *J* = 32.2 Hz), 141.8; $^{19}F$ NMR ($CDCl_3$) δ = -58.2 (s, 3F).

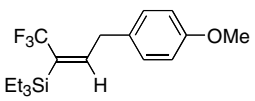
Combined yield 75%; IR (neat) 3028, 2957, 2914, 2878, 1618, 1497, 1456, 1420, 1369, 1242, 1173, 1115, 1005, 843, 735, 698, 663 $cm^{-1}$; HRMS calcd for $C_{18}H_{27}F_3{}^{28}Si$ ($M^+$) 328.1834 found 328.1829.

**(*E*)-4-(4-Chlorophenyl)-1,1,1-trifluoro-2-triethylsilyl-2-butene (2h)**



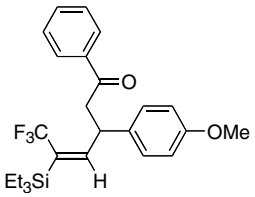

Yield 83%; $^1H$ NMR ($CDCl_3$) δ = 0.67 (q, *J* = 7.9 Hz, 6H), 0.93 (t, *J* = 7.9 Hz, 9H), 3.67 (dd, *J* = 7.4, 1.8 Hz, 2H), 6.21 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H); $^{13}C$ NMR ($CDCl_3$) δ = 3.0, 7.0, 36.5, 126.1 (q, *J* = 276.6 Hz), 128.8, 129.8, 130.7 (q, *J* = 29.7 Hz), 132.3, 137.3, 150.7 (q, *J* = 6.4 Hz); $^{19}F$ NMR ($CDCl_3$) δ = -53.9 (s, 3F); IR (neat) 2957, 2909, 2877, 1618, 1492, 1458, 1366, 1236, 1139, 1115, 1016, 794, 736, 699 $cm^{-1}$; HRMS calcd for $C_{16}H_{22}{}^{35}ClF_3{}^{28}Si$ ($M^+$) 334.1131 found 334.1129.

**(*E*)-1,1,1-Trifluoro-4-(4-methoxyphenyl)-2-triethylsilyl-2-butene (2i)**



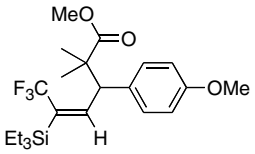

Yield 84%; $^1H$ NMR ($CDCl_3$) δ = 0.66 (q, *J* = 7.9 Hz, 6H), 0.92 (t, *J* = 7.9 Hz, 9H), 3.63 (dd, *J* = 2.0, 7.4 Hz, 2H), 3.79 (s, 3H), 6.24 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H); $^{13}C$ NMR ($CDCl_3$) δ = 3.1, 7.0, 36.3, 55.2, 126.3 (q, *J* = 276.3 Hz), 129.8 (q, *J* = 29.2 Hz), 152.0 (q, *J* = 6.4 Hz), 114.1, 129.5, 130.9, 158.3; $^{19}F$ NMR ($CDCl_3$) δ = -53.7 (s, 3F); IR (neat) 2957, 2878, 2837, 1616, 1585, 1512, 1464, 1441, 1420, 1366, 1302, 1250, 1178 (s) 1113, 1040, 1005, 827, 733, 698, 474, 455, 409 $cm^{-1}$; HRMS calcd for $C_{17}H_{25}F_3O^{28}Si$ ($M^+$) 330.1618 found 330.1627; Anal. Calcd for $C_{17}H_{25}F_3OSi$: C, 61.79; H, 7.63. Found: C, 61.74; H, 7.71.

**(*E*)-6,6,6-Trifluoro-3-(4-methoxyphenyl)-1-phenyl-5-triethylsilyl-4-buten-1-one (2j)**



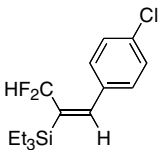

Yield 86%; $^{1}$H NMR ($CDCl_3$) δ = 0.64 (q, *J* = 7.9 Hz, 6H), 0.88 (t, *J* = 7.7 Hz, 9H), 3.23 (dd, *J* = 6.4, 15.8 Hz, 1H), 3.50 (dd, *J* = 7.8, 15.8 Hz, 1H), 3.75 (s, 3H), 4.61 (br, 1H), 6.28 (d, *J* = 10.8 Hz, 1H), 6.82 ~ 7.96 (m, 9H) $^{13}$C NMR ($CDCl_3$) δ = 3.0, 7.0, 22.6, 44.7, 55.1, 114.2, 126.1 (q, *J* = 276.6 Hz), 128.3 (q, *J* = 30.1 Hz), 128.09, 128.13, 128.6, 133.1, 133.7, 136.9, 154.3 (q, *J* = 6.3 Hz), 158.4, 197.3; $^{19}$F NMR ($CDCl_3$) δ = -53.6 (s, 3F); IR (neat) 2957, 2878, 1688, 1614, 1582, 1512, 1448, 1418, 1366, 1250, 1207, 1180, 1138, 1113, 1036, 1003, 829, 725, 690, 411 cm$^{-1}$; HRMS calcd for $C_{25}H_{31}F_3O_2{}^{28}Si$ ($M^+$) 448.2045 found 448.2039.

**(*E*)-6,6,6-Trifluoro-3-(4-methoxyphenyl)-2,2-dimethyl-5-triethylsilyl-4-hexenoate (2k)**



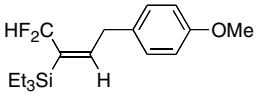

Yield 74%; $^{1}$H NMR ($CDCl_3$) δ = 0.69 (q, *J* = 7.9 Hz, 6H), 0.93 (t, *J* = 7.9 Hz, 9H), 1.16 (s, 3H), 1.18 (s, 1H), 3.61 (s, 3H), 3.77 (s, 3H), 4.05 (d, *J* = 11.4 Hz, 1H), 6.77 (d, *J* = 11.6 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 3.2, 7.0, 22.9, 23.4, 46.4, 51.6, 52.5, 55.1, 113.5, 126.0 (q, *J* = 276.9 Hz), 129.6, 130.2 (q, *J* = 29.9 Hz), 131.7, 151.2 (q, *J* = 6.0 Hz), 158.5, 176.6; $^{19}$F NMR ($CDCl_3$) δ = -53.5 (s, 3F); IR (neat) 2957, 2878, 1736, 1612, 1512, 1464, 1420, 1375, 1327, 1306, 1225, 1180, 1115, 1074, 1038, 1007, 833, 723, 698, 446, 422, 407 cm$^{-1}$; HRMS (EI) calcd for $C_{22}H_{33}F_3O_3{}^{28}Si$ ($M^+$) 430.2151 found 430.2157.

**(*E*)-3-(4-Chlorophenyl)-1,1-difluoro-2-triethylsilylpropene (2l)**



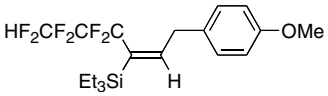

Yield: 87%; $^{1}$H NMR ($CDCl_3$) δ = 0.78 (q, *J* = 7.9 Hz, 6H), 0.99 (t, *J* = 8.0 Hz, 9H), 6.33 (t, *J* = 57.4 Hz, 1H), 7.05 (s, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 3.4, 7.2, 115.8 (t, *J* = 231.0 Hz), 128.7, 130.1, 134.2, 134.4, 136.5 (t, *J* = 30.8 Hz), 145.6 (t, *J* = 14.6 Hz); $^{19}$F NMR ($CDCl_3$) δ = -104.2 (d, *J* = 56.4 Hz, 2F); IR (neat) 2955, 2909, 2876, 1605, 1488, 1457, 1416, 1376, 1235, 1129, 1081, 1015, 893, 811, 716 cm$^{-1}$; HRMS calcd for $C_{15}H_{21}{}^{35}ClF_2Si$ ($M^+$) 302.1069 found 302.1067; Anal. Calcd for $C_{15}H_{21}{}^{35}ClF_2Si$: C, 59.49; H, 6.99. Found: C, 59.09; H, 7.05.

**(*E*)-1,1-Difluoro-4-(4-methoxyphenyl)-2-triethylsilyl-2-butene (2m)**



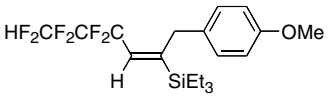

Yield 66%; $^{1}$H NMR ($CDCl_3$) δ = 0.69 (q, *J* = 7.7 Hz, 6H), 0.94 (t, *J* = 7.6 Hz, 9H), 3.53 (d, *J* = 6.2 Hz, 2H), 3.87 (s, 3H), 6.18 (t, *J* = 7.1 Hz, 1H), 6.62 (t, *J* = 57.8 Hz, 1H), 6.86 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 3.3, 7.2, 34.5, 55.3, 115.6 (t, *J* = 233.0 Hz), 133.8 (t, *J* = 28.7 Hz), 148.3 (q, *J* = 13.7 Hz), 114.1, 129.4, 130.8, 158.3; $^{19}$F NMR ($CDCl_3$) δ = -107.3 (2F, d, *J* = 56.5 Hz); IR (neat) 2876, 2837, 1614, 1585, 1512, 1464, 1443, 1418, 1381, 1302, 1248, 1176, 1080, 1018, 976, 910, 827, 735, 650, 413 cm$^{-1}$; HRMS calcd for $C_{17}H_{26}F_2O^{28}Si$ ($M^+$) 312.1721 found 312.1716.

**(*E*)-4,4,5,5,6,6-Hexafluoro-1-(4-methoxyphenyl)-3-triethylsilyl-2-hexene (2n)**



$^1$H NMR ($CDCl_3$) δ = 0.45 (q, *J* = 7.6 Hz, 6H), 0.82 (t, *J* = 7.3 Hz, 9H), 3.71 (s, 2H), 3.79 (s, 3H), 5.87 (t, *J* = 15.8 Hz, 1H), 6.04 (t, *J* = 52.4 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 2.8, 6.9, 36.2, 55.2, 108.1 (tt, *J* = 31.8, 252.5 Hz), 125.0 (t, *J* = 21.9 Hz), 155.5 (t, *J* = 4.8 Hz), 113.7, 114.1, 129.5, 129.9, 130.0, 158.2; $^{19}$F NMR ($CDCl_3$) δ = -105.9 (t, *J* = 5.7 Hz, 2F), -131.7 (t, *J* = 5.7 Hz, 2F), -137.3 (dquint., *J* = 8.5, 45.2 Hz, 2F).

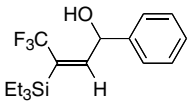
**(*E*)-4,4,5,5,6,6-Hexafluoro-1-(4-methoxyphenyl)-2-triethylsilyl-2-hexene (3n)**



$^1$H NMR ($CDCl_3$) δ = 0.67 (q, *J* = 7.5 Hz, 6H), 0.91 (t, *J* = 7.2 Hz, 9H), 3.71 (s, 3H), 6.38 (t, *J* = 6.3 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ = 3.6, 7.0, 65.9, 130.1, 158.3; $^{19}$F NMR ($CDCl_3$) δ = -99.1 (t, *J* = 5.7 Hz, 2F), -129.0 (t, *J* = 5.7 Hz, 2F), -137.3 (dquint., *J* = 45.2, 8.5 Hz, 2F).

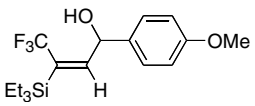
Combined yield 71%; IR (neat) 2957, 2939, 2914, 2878, 1612, 1512, 1466, 1302, 1250, 1200, 1178, 1151, 1132, 1038, 1005, 978, 818, 735, 413 cm$^{-1}$; HRMS calcd for $C_{19}H_{26}F_6O^{28}Si$ ($M^+$) 412.1657 found 412.1653.

**(*E*)-1,1,1-Trifluoro-4-hydroxy-4-phenyl-2-triethylsilyl-2-butene (5a)**



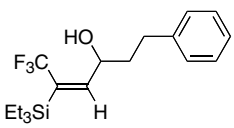
Yield: 79%; $^1$H NMR ($CDCl_3$) δ = 0.70 (q, *J* = 7.9 Hz, 6H), 0.92 (t, *J* = 7.9 Hz, 9H), 2.21 (s, 1H), 5.75 (d, *J* = 8.4 Hz, 1H), 6.29 (d, *J* = 9.3 Hz, 1H), 7.28 ~ 7.32 (m, 1H), 7.35 ~ 7.40 (m, 4H); $^{13}$C NMR ($CDCl_3$) δ = 2.9, 7.0, 70.8, 125.9 (q, *J* = 276.8 Hz), 126.0, 128.0, 128.7, 129.7 (q, *J* = 30.2 Hz), 141.4, 152.6 (q, *J* = 6.0 Hz); $^{19}$F NMR ($CDCl_3$) δ = -52.9 (s, 3F); IR (neat) 3367, 2957, 2913, 2878, 1621, 1490, 1455, 1416, 1359, 1216, 1144, 1116, 1018, 763, 737, 698 cm$^{-1}$; HRMS calcd for $C_{16}H_{22}F_3O^{28}Si$ (M-H) 315.1390 found 315.1381.

**(*E*)-1,1,1-Trifluoro-4-hydroxy-4-(4-methoxyphenyl)-2-triethylsilyl-2-butene (5b)**



Yield 97%; $^1$H NMR ($CDCl_3$) δ = 0.68 (q, *J* = 7.9 Hz, 6H), 0.91 (t, *J* = 8.0 Hz, 9H), 2.17 (br, 1H), 3.79 (s, 3H), 5.68 (d, *J* = 9.1 Hz, 1H), 6.28 (d, *J* = 9.2 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 3.0, 7.0, 55.2, 70.5, 114.1, 126.0 (q, *J* = 276.7 Hz), 127.3, 129.3 (q, *J* = 29.8 Hz), 133.8, 152.9 (q, *J* = 5.9 Hz), 159.3; $^{19}$F NMR ($CDCl_3$) δ = -53.0 (s, 3F); IR (neat) 3420, 2957, 2878, 2837, 1612, 1587, 1512, 1464, 1443, 1418, 1358, 1304, 1217, 1175, 1117, 1007, 964, 934, 831, 725, 698, 413 cm$^{-1}$; HRMS calcd for $C_{17}H_{25}F_3O_2{}^{28}Si$ ($M^+$) 346.1578 found 346.1569.

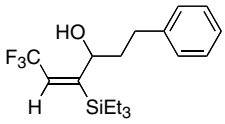
**(*E*)-1,1,1-Trifluoro-4-hydroxy-6-phenyl-2-triethylsilyl-2-hexene (5c)**



Yield: 62%; $^1$H NMR ($CDCl_3$) δ = 0.70 (q, *J* = 7.9 Hz, 6H), 0.95 (t, *J* = 8.0 Hz, 9H), 1.78 ~ 1.85 (m, 1H), 1.88 ~ 1.96 (m, 2H), 2.63 ~ 2.69 (m, 1H), 2.78 ~ 2.84 (m, 1H), 4.71 (s, 1H), 6.14 (d, *J* = 8.8 Hz, 1H), 7.19 ~ 7.22 (m, 3H), 7.30 (m, 2H); $^{13}$C NMR ($CDCl_3$) δ = 2.9, 7.0, 31.5, 38.3, 68.9, 125.9 (q, *J* = 276.7 Hz), 126.0, 128.4, 128.4, 130.0 (q, *J* = 30.2 Hz), 141.4, 154.4 (q, *J* = 6.2 Hz); $^{19}$F NMR ($CDCl_3$)

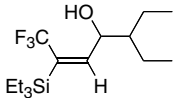
δ = -53.5 (s, 3F); IR (neat) 3357, 3028, 2956, 2877, 1621, 1496, 1455, 1418, 1365, 1218, 1143, 1116, 1042, 1006, 738, 698 $cm^{-1}$; HRMS calcd for $C_{18}H_{27}F_3NaO^{28}Si$ (M+Na) 367.1683 found 367.1705.

**(*E*)-1,1,1-Trifluoro-4-hydroxy-6-phenyl-3-triethylsilyl-2-hexene (6c)**



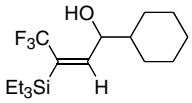

Yield: 18%; $^1$H NMR ($CDCl_3$) δ = 0.72 ~ 0.76 (m, 6H), 0.94 (t, *J* = 7.9 Hz, 9H), 1.72 ~ 1.79 (m, 1H), 1.76 (d, *J* = 4.0 Hz, 1H), 1,89 ~ 1.96 (m, 1H), 2.63 ~ 2.70 (m, 1H), 2.84 ~ 2.90 (m, 1H), 4.87 (d, *J* = 9.9 Hz, 1H), 5.69 (qd, *J* = 9.2, 1.2 Hz, 1H), 7.19 ~ 7.22 (m, 3H), 7.28 ~ 7.31 (m, 2H); $^{13}$C NMR ($CDCl_3$) δ = 3.9, 7.3, 32.6, 38.9, 72.1, 122.4 (q, *J* = 275.3 Hz), 124.8 (q, *J* = 33.0 Hz), 126.0, 128.4, 128.5, 141.4, 158.8 (q, *J* = 4.3 Hz); $^{19}$F NMR ($CDCl_3$) δ = -57.6 (d, *J* = 9.8 Hz, 3F); IR (neat) 3584, 3477, 3028, 2956, 2876, 1601, 1496, 1455, 1343, 1265, 1149, 1119, 1050, 1013, 735, 699 $cm^{-1}$; HRMS calcd for $C_{18}H_{27}F_3NaO^{28}Si$ (M+Na) 367.1683 found 367.1686.

**(*E*)-5-Ethyl-1,1,1-trifluoro-4-hydroxy-2-triethylsilyl-2-heptene (5d)**



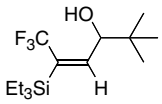

Yield: 79%; $^1$H NMR ($CDCl_3$) δ = 0.69 (q, *J* = 7.9 Hz, 6H), 0.88 ~ 0.95 (m, 15H), 1.23 ~ 1.54 (m, 5H), 1.69 (s, 1H), 4.57 ~ 4.60 (m, 1H), 6.18 (d, *J* = 9.2 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ = 3.0, 7.0, 11.0, 11.4, 20.7, 21.7, 46.7, 70.0, 125.9 (q, *J* = 276.6 Hz), 130.1 (q, *J* = 30.1 Hz), 154.2 (q, *J* = 6.2 Hz); $^{19}$F NMR ($CDCl_3$) δ = -53.1 (s, 3F); IR (neat) 3621, 3387, 2961, 2878, 1620, 1460, 1418, 1379, 1260, 1216, 1146, 1116, 1005, 805, 737, 699 $cm^{-1}$; Anal. Calcd for $C_{15}H_{29}F_3OSi$: C, 58.03; H, 9.41. Found: C, 57.81; H, 9.23.

**(*E*)-4-Cyclohexyl-1,1,1-trifluoro-4-hydroxy-2-triethylsilyl-2-butene (5e)**



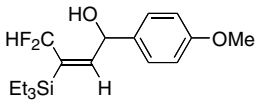

Yield: 97%; $^1$H NMR ($CDCl_3$) δ = 0.69 (q, *J* = 7.9 Hz, 6H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.97 ~ 1.06 (m, 2H), 1.10 ~ 1.27 (m, 3H), 1.37 ~ 1.43 (m, 1H), 1.53 ~ 1.56 (m, 1H), 1.64 ~ 1.77 (m, 4H), 1.92 ~ 1.95 (m, 1H), 4.33 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.09 (d, *J* = 9.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ = 3.0, 7.0, 25.9, 26.1, 26.4, 28.3, 28.7, 43.4, 72.9, 125.9 (q, *J* = 276.3 Hz), 130.6 (q, *J* = 29.8 Hz), 153.6 (q, *J* = 6.0 Hz); $^{19}$F NMR ($CDCl_3$) δ = -52.8 (s, 3F); IR (neat) 3364, 2929, 2878, 2855, 1622, 1451, 1417, 1365, 1260, 1220, 1147, 1116, 1016, 804, 737, 700 $cm^{-1}$; HRMS calcd for $C_{16}H_{29}F_3NaO^{28}Si$ (M+Na) 345.1840 found 345.1843.

**(*E*)-1,1,1-Trifluoro-4-hydroxy-5,5-dimethyl-2-triethylsilyl-2-hexene (5f)**



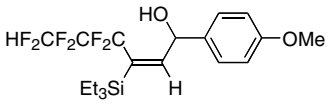

Yield: 80%; $^1$H NMR ($CDCl_3$) δ = 0.70 (q, *J* = 7.9 Hz, 6H), 0.93 (s, 9H), 0.94 (t, *J* = 8.0 Hz, 9H), 1.68 (s, 1H), 4.29 (d, *J* = 10.2 Hz, 1H), 6.19 (d, *J* = 10.2 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ = 3.0, 7.0, 25.5, 34.5, 75.2, 125.9 (q, *J* = 276.7 Hz), 131.6 (q, *J* = 30.1 Hz), 151.2 (q, *J* = 5.9 Hz); $^{19}$F NMR ($CDCl_3$) δ = -52.5 (s, 3F); IR (neat) 3625, 3459, 2959, 2878, 1621, 1466, 1417, 1365, 1327, 1261, 1225, 1142, 1117, 1003, 804, 738 $cm^{-1}$.

**(*E*)-1,1-Difluoro-4-hydroxy-4-(4-methoxyphenyl)-2-triethylsilyl-2-butene (5g)**




Yield: 78%; $^{1}$H NMR ($CDCl_3$) δ = 0.69 (q, *J* = 7.9 Hz, 6H), 0.93 (t, *J* = 7.9 Hz, 9H), 2.38 (s, 1H), 5.52 (d, *J* = 7.9 Hz, 1H), 6.18 (d, *J* = 7.9 Hz, 1H), 6.68 (t, *J* = 57.7 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 3.2, 7.1, 55.2, 70.5, 114.1, 115.2 (t, *J* = 233.7 Hz), 127.4, 128.6, 133.9 (t, *J* = 29.7 Hz), 149.9 (t, *J* = 13.0 Hz), 159.3; $^{19}$F NMR ($CDCl_3$) δ = -106.5 (dd, *J* = 57.3, 37.8 Hz, 2F); IR (neat) 3404, 2955, 2911, 2876, 2835, 1611, 1512, 1463, 1417, 1377, 1304 1251, 1174, 1144, 1085, 1020 cm$^{-1}$; HRMS calcd for $C_{17}H_{28}F_2O_2{}^{28}Si$ ($M^+$) 328.1670, found 328.1667.

**(*E*)-4,4,5,5,6,6-Hexafluoro-1-hydroxy-1-(4-methoxyphenyl)-3-triethylsilyl-2-hexene (5h)**

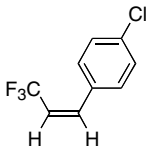



Yield: 62%; $^{1}$H NMR ($CDCl_3$) δ = 0.67 (q, *J* = 8.0 Hz, 6H), 0.98 (t, *J* = 8.0 Hz, 9H), 3.83 (s, 3H), 4.69 (m, 1H), 6.05 (dd, *J* = 15.5, 7.2 Hz, 1H), 6.16 (tt, *J* = 52.6, 6.0 Hz, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 4.7, 6.4, 29.7, 30.3, 55.3, 73.4 (dd, *J* = 29.5, 25.5 Hz), 108.3 (tt, *J* = 252.8, 29.9 Hz), 113.4 (tt, *J* = 285.9, 32.2 Hz), 114.1, 115.2 (tt, *J* = 257.4, 28.2 Hz), 115.9 (t, *J* = 4.7 Hz), 120.0, 128.1, 135.3, 160.0; $^{19}$F NMR ($CDCl_3$) δ = -118.9 (dq, *J* = 278.1, 7.3 Hz, 1F), -126.3 (dq, *J* = 276.2, 10.5 Hz, 1F), -130.9 (dq, *J* = 284.5, 6.8 Hz, 1F), -131.8 (dq, *J* = 284.7, 6.5 Hz, 1F), -137.5 ~ -137.8 (m, 2F); IR (neat) 2959, 2914, 2880, 2831, 1608, 1513, 1465, 1302, 1255, 1175, 1143, 1035, 1015, 972, 830, 802 cm$^{-1}$; HRMS calcd for $C_{19}H_{26}F_6O_2{}^{28}Si$ ($M^+$) 428.1606 found 428.1617.

**Protodesilylation for the determination of the stereochemistry**

To **2a** and **3a** (160 mg, 0.50 mmol) in THF (1.9 mL) and MeOH (0.25 mL) was dropwise added a solution of TBAF (1 M in THF, 0.60 mL, 0.60 mmol) at room temperature. The mixture was stirred at room temperature for 6 h, and then water (2.5 mL) was added. The resulting mixture was extracted with $Et_2O$ (three times) and the ethereal layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was chromatographed on silica gel to afford (*Z*)-1-(4-chlorophenyl)-2-trifluoromethylethene **7** (82% yield).

**(*Z*)-1-(4-Chlorophenyl)-2-trifluoromethylethane (7)**

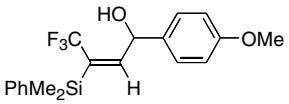



Yield: 82%; $^{1}$H NMR ($CDCl_3$) δ = 5.78 (dq, *J* = 12.5, 8.99 Hz, 1H), 6.86 (d, *J* = 12.5 Hz, 1H), 7.33 (d, *J* = 2.0 Hz, 4H); $^{13}$C NMR ($CDCl_3$) δ = 116.1 (q, *J* = 34.0 Hz), 123.4 (q, *J* = 268.9 Hz), 128.7, 129.1, 131.8, 135.9, 136.3 (q, *J* = 6.5 Hz); $^{19}$F NMR ($CDCl_3$) δ = -58.1 (d, *J* = 8.8 Hz, 3F); IR (neat) 1666, 1596, 1492, 1407, 1315, 1276, 1203, 1126, 1014, 972, 945, 837, 810, 705, cm$^{-1}$; HRMS calcd for $C_9H_6{}^{35}ClF_3$ ($M^+$) 206.0110 found 206.0108.

**Hydrosilylation of 4b**

To a solution of **4b** (0.0 mmol) in $ClCH_2CH_2Cl$ (0 mL) was added $Co_2(CO)_8$ (4.3 mg, 5 mol%) and $Me_2PhSiH$ (00 mg, 0.0 mmol) at room temperature. The whole was stirred for 3 h at the reflux temperture. The reaction mixture was cooled and filtrated. The resulting filtrate was concentrated in *vacuo*. The residue was chromatographed on silica gel to afford the corresponding vinylsilanes **5i** (93% yield).

**(*E*)-4,4,4-Trifluoro-1-(4-methoxyphenyl)-3-dimethylphenylsilyl-2-buten-1-ol (5i)**

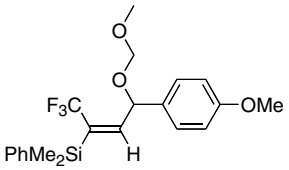



Yield: 86%; $^{1}$H NMR ($CDCl_3$) δ = 0.45 (s, 3H), 0.47 (s, 3H), 1.98 ~ 2.00 (m, 1H), 3.81 (s, 3H), 5.68 (br d, *J* = 8.79 Hz, 1H), 6.29 (d, *J* = 9.19 Hz, 1H), 6.89 (d, *J* = 8.39 Hz, 2H), 7.25 ~ 7.28 (d, *J* = 8.39 Hz, 2H), 7.32 ~ 7.40 (m, 3H), 7.46 ~ 7.49 (m, 2H),; $^{13}$C NMR ($CDCl_3$) δ = -2.8, -2.7, 55.2, 70.5, 114.1, 125.8 (q, *J* = 279.9 Hz), 127.4, 128.0, 129.6, 130.6 (q, *J* = 26.7 Hz), 133.5, 133.9, 135.7, 153.2 (q, *J* = 5.7 Hz), 159.4; $^{19}$F NMR ($CDCl_3$) δ = -52.4 (s, 3F); IR (neat) 3408, 290, 1613, 1512, 1428, 1359, 1175, 1033 cm$^{-1}$; HRMS (FAB) calcd for ($M^+$) $C_{19}H_{21}F_3O_2{}^{28}Si$: 366.1263, found 366.1262; Anal. Calcd for $C_{19}H_{21}F_3O_2{}^{28}Si$: C, 62.27; H, 5.78. Found: C, 62.06; H, 5.69.

**Procedure for the preparation of (*E*)-4,4,4-trifluoro-3-(dimethylphenylsilyl)-1-(4-methoxyphenyl)-2-buten-1-yl methoxymethyl ether**

A 50 mL three-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum and an inlet tube for argon was charged with (*E*)-4,4,4-trifluoro-3-(dimethylphenylsilyl)-1-(4-methoxyphenyl)-2-buten-1-ol (**5i**) (1.10 g, 3.0 mmol) in $CH_2Cl_2$ (5 mL). To this solution was added *N,N'*-diisopropylethylamine (1.16 g, 9.0 mmol) and chloromethyl methyl ether (0.72 g, 9.0 mmol) at 0 °C, and the whole was stirred at room temperature. After being stirred for 15 h, the reaction mixture was poured into ice-cooled saturated aqueous $NH_4Cl$ (30 mL), followed by extraction with $Et_2O$ (30 mL x 3). The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. Column chromatography on silica gel of the residue using hexane/AcOEt (5 : 1) as an eluent yielded pure (*E*)-4,4,4-trifluoro-3-(dimethylphenylsilyl)-1-(4-methoxyphenyl)-2-buten-1-yl methoxymethyl ether **8i** (1.05 g, 85%).

**(*E*)-4,4,4-trifluoro-3-(dimethylphenylsilyl)-1-(4-methoxyphenyl)-2-buten-1-yl methoxymethyl ether (8i)**

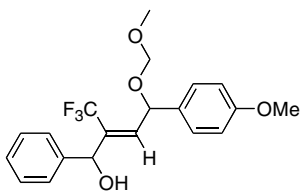



Yield: 85%; $^{1}$H NMR ($CDCl_3$) δ = 0.44 (s, 3H), 0.47 (s, 3H), 3.33 (s, 3H), 3.81 (s, 3H), 4.59 (d, *J* = 6.5 Hz, 1H), 4.61 (d, *J* = 6.5 Hz, 1H), 5.57 (dd, *J* = 9.5, 1.5 Hz, 1H), 6.28 (d, *J* = 9.5 Hz, 1H), 6.88 (ABq, *J* = 8.5 Hz, 2H), 7.24 (ABq, *J* = 8.5 Hz, 2H), 7.3 ~ 7.4 (m, 3H), 7.4 ~ 7.5 (m, 2H); $^{13}$C NMR ($CDCl_3$) δ -2.8, -2.6, 55.2, 55.4, 74.0, 93.9, 114.1, 125.8 (q, *J* = 275.9 Hz), 127.9, 128.2, 129.6, 131.0 (q, *J* = 30.3 Hz), 131.2, 133.9, 135.8, 151.9 (q, *J* = 5.5 Hz), 159.5; $^{19}$F NMR ($CDCl_3$) δ -52.5 (s, 3F); IR (neat) 2955, 2898, 1611, 1513, 1250, 1225, 1146, 1119, 1029 cm$^{-1}$; HRMS (FAB) calcd for ($M^+$) $C_{21}H_{25}F_3O_3{}^{28}Si$: 410.1525, found 410.1521.

**Typical procedure for the coupling reaction of (*E*)-4,4,4-trifluoro-3-(dimethylphenylsilyl)-1-(4-methoxyphenyl)-2-buten-1-yl methoxymethyl ether with benzaldehyde in the presence of TBAF**

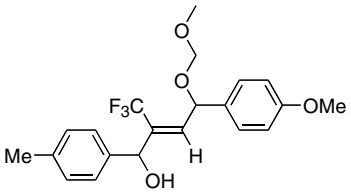
A 30 mL two-necked round-bottomed flask equipped with a magnetic stirrer bar, a rubber septum and an inlet tube for argon was charged with a solution of vinylsilane compound (82 mg, 0.2 mmol), benzaldehyde (32 mg, 0.3 mmol), tetrabutyl-ammonium fluoride (TBAF) (0.02 mL, 0.02 mmol) and zinc triflate (0.11 g, 0.3 mmol) in *N*-methyl-2-pyrrolidone (NMP) (1.0 mL). After the whole was stirred at 80 °C (bath temperature) for 20 h, the reaction mixture was poured into ice-cooled saturated aqueous $NH_4Cl$ (20 mL) and a small amount of hydrochloric acid, followed by extraction with $Et_2O$ (20 mL x 5). The organic layers were dried over anhydrous $Na_2SO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography using (hexane/AcOEt = 5 : 1) to give 2-(trifluoromethyl)-4-(methoxymethyl)oxy-4-(4-methoxyphenyl)-1-phenyl-2-buten-1-ol (**9a**) as a diastereomeric mixture (44 mg, 59%).

**2-(Trifluoromethyl)-4-(methoxymethyl)oxy-4-(4-methoxyphenyl)-1-phenyl-2-buten-1-ol (9a)**



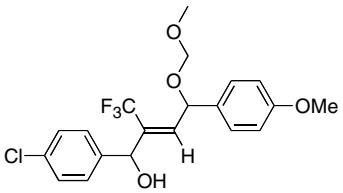
Yield: 59%; Mp: 95 ~ 98 °C; $^1$H NMR ($CDCl_3$) δ = 2.33 (brs, 1H), 2.42 (brs, 1H), 3.34 (s, 3H), 3.36 (s, 3H), 3.80 (s, 3H), 3.81 (s, 3H), 4.60 ~ 4.66 (m, 4H), 5.37 (s, 1H), 5.41 (s, 1H), 5.62 (d, *J* = 10.2 Hz, 1H), 5.63 (d, *J* = 10.2 Hz, 1H), 6.46 (d, *J* = 10.2 Hz, 1H), 6.49 (d, *J* = 10.2 Hz, 1H), 6.88 ~ 6.92 (m, 4H), 7.20 ~ 7.24 (m, 2H), 7.27 ~ 7.38 (m, 12H); $^{13}$C NMR ($CDCl_3$) δ = 55.2, 55.4, 55.5, 72.0 ~ 72.2 (m), 72.6 ~ 72.8 (m), 93.8, 93.9, 114.1, 114.1, 123.4 (q, *J* = 276.4 Hz), 126.8, 126.9, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 131.4, 131.9 (q, *J* = 27.8 Hz), 137.4 (q, *J* = 2.9 Hz), 137.6 (q, *J* = 3.1 Hz), 140.3, 140.3, 159.5, 159.5; $^{19}$F NMR ($CDCl_3$) δ -57.5 (s, 3F); -57.7 (s, 3F); IR (KBr) 3397, 2947, 2890, 1610, 1512, 1456, 1381, 1275, 1210, 1096 cm$^{-1}$; HRMS (FAB) calcd for ($M^+$) $C_{20}H_{21}F_3O_4$: 382.1392, found 382.1389; Anal. Calcd for $C_{20}H_{21}F_3O_4$: C, 62.82; H, 5.54. Found: C, 62.51; H, 5.68.

**2-(Trifluoromethyl)-4-(methoxymethyl)oxy-4-(4-methoxyphenyl)-1-(4-methylphenyl)-2-buten-1-ol (9b)**



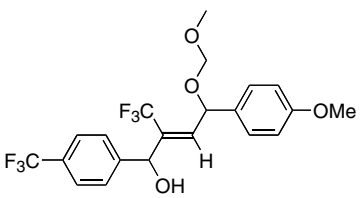

Yield: 44%; Mp: 78 ~ 80 °C; $^1$H NMR ($CDCl_3$) δ 2.30 (s, 3H), 2.34 (s, 3H), 3.33 (s, 3H), 3.35 (s, 3H), 3.78 (s, 3H), 3.80 (s, 3H), 4.58 ~ 4.65 (m, 4H), 5.31 (s, 1H), 5.34 (s, 1H), 5.60 (d, *J* = 10.3 Hz, 1H), 5.62 (d, *J* = 10.3 Hz, 1H), 6.46 (d, *J* = 10.3 Hz, 1H), 6.48 (d, *J* = 10.3 Hz, 1H), 6.89 (ABq, *J* = 8.7 Hz, 4H), 7.05 ~ 7.11 (m, 4H), 7.16 (ABq, *J* = 8.0 Hz, 2H), 7.23 (ABq, *J* = 8.0 Hz, 2H), 7.28 ~ 7.33 (m, 4H); $^{13}$C NMR ($CDCl_3$) δ 21.07, 21.11, 55.2, 55.4, 71.7 ~ 71.9 (m), 72.5 ~ 72.7 (m), 93.8, 93.9, 114.08, 114.10, 123.4 (q, *J* = 275.9 Hz), 126.8, 126.9, 128.2, 128.3, 129.3, 129.4, 131.47, 131.50, 132.0 (q, *J* = 27.8 Hz), 137.0 (q, *J* = 2.8 Hz), 137.2 (q, *J* = 2.8 Hz), 137.4, 138.2, 138.3, 159.4, 159.5; $^{19}$F NMR ($CDCl_3$) δ -57.5 (s, 3F); -57.7 (s, 3F); IR (KBr) 3429, 2953, 1611, 1513, 1251, 1212, 1164, 1126, 1030 cm$^{-1}$; HRMS (FAB) calcd for ($M^+$) $C_{21}H_{23}F_3O_4$: 396.1548, Found 396.1551; Anal. Calcd for $C_{21}H_{23}F_3O_4$: C, 63.63; H, 5.85. Found: C, 63.54; H, 5.98.

**1-(4-Chlorophenyl)-2-(trifluoromethyl)-4-(methoxymethyl)oxy-4-(4-methoxyphenyl)-2-buten-1-ol (9c)**




Yield: 59%; Mp: 90 ~ 93 °C; $^1$H NMR ($CDCl_3$) δ 2.2 ~ 3.0 (m, 2H), 3.316 (s, 3H), 3.318 (s, 3H), 3.78 (s, 3H), 3.80 (s, 3H), 4.5~4.6 (m, 4H), 5.31 (s, 1H), 5.34 (s, 1H), 5.58 (d, *J* = 9.8 Hz, 1H), 5.60 (d, *J* = 9.8 Hz, 1H), 6.42 (d, *J* = 10.5 Hz, 1H), 6.44 (d, *J* = 10.5 Hz, 1H), 6.88 (ABq, *J* = 8.6 Hz, 4H), 7.12 (ABq, *J* = 8.4 Hz, 2H), 7.2 ~ 7.3 (m, 10H); $^{13}$C NMR ($CDCl_3$) δ 55.2, 55.4, 55.5, 71.4 ~ 71.5 (m), 72.7, 93.8, 93.9, 114.2, 123.3 (q, *J* = 276.6 Hz), 128.1, 128.17, 128.21, 128.3, 131.6 (q, *J* = 28.0 Hz), 134.1, 134.2, 137.8 (q, *J* = 3.1 Hz), 138.0 (q, *J* = 3.0 Hz), 138.77, 138.83, 159.51, 159.54; $^{19}$F NMR ($CDCl_3$, $CFCl_3$) δ -57.4 (s, 3F); -57.6 (s, 3F); IR (KBr) 3411, 2947, 1610, 1512, 1379, 1251, 1166, 1123, 1035 cm$^{-1}$; HRMS (FAB) calcd for (M+H) $C_{20}H_{20}ClF_3O_4$: 416.1002, Found 416.1012; Anal. Calcd for $C_{20}H_{20}ClF_3O_4$: C, 57.63; H, 4.84. Found: C, 57.19; H, 5.27.

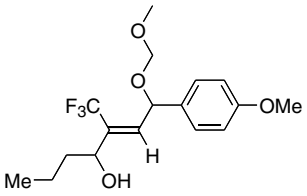
**2-(Trifluoromethyl)-1-{4-(trifluoromethyl)phenyl}-4-(methoxymethyl)oxy-4-(4-methoxyphenyl)-2-buten-1-ol (9d)**




Yield: 72%; $^1$H NMR ($CDCl_3$) δ = 2.31 (brs, 1H), 2.38 (brs, 1H), 3.34 (d, *J* = 1.0 Hz, 3H), 3.37 (d, *J* = 1.0 Hz, 3H), 3.81 (d, *J* = 1.0 Hz, 3H), 3.82 (d, *J* = 1.0 Hz, 3H), 4.6 ~ 4.7 (m, 4H), 5.44 (s, 1H), 5.47 (s, 1H), 5.60 (d, *J* = 10.0 Hz, 1H), 5.62 (d, *J* = 10.0 Hz, 1H), 6.45 (d, *J* = 9.5 Hz, 1H), 6.46 (d, *J* = 9.5 Hz), 6.88 ~ 6.93 (m, 4H), 7.24 ~ 7.29 (m, 2H), 7.31 (ABq, *J* = 8.5 Hz, 2H), 7.36 (ABq, *J* = 8.0 Hz, 2H),

7.48 (ABq, $J$ = 8.0 Hz, 2H), 7.57 (ABq, $J$ = 8.0 Hz, 2H), 7.63 (ABq, $J$ = 8.0 Hz, 2H); $^{19}$F NMR ($CDCl_3$) δ -57.3 (s, 3F), -57.5 (s, 3F), -63.1 (s, 6F); IR (neat) 3422, 2954, 1611, 1514, 1327, 1251, 1127, 1068, 1030 $cm^{-1}$; HRMS (FAB) calcd for ($M^+$) $C_{21}H_{20}F_6O_4$: 450.1266, found 450.1265.

**3-(Trifluoromethyl)-1-(methoxymethyl)oxy-1-(4-methoxyphenyl)-2-hepten-4-ol (9e)**




Yield: 54%; $^1$H NMR ($CDCl_3$) δ = 0.89 (t, $J$ = 7.2 Hz, 3H), 0.93 (t, $J$ = 7.4 Hz, 3H), 1.3 ~ 1.7 (m, 8H), 1.84 (brs, 1H), 1.94 (brs, 1H), 3.348 (s, 3H), 3.351 (s, 3H), 3.79 (s, 3H), 3.80 (s, 3H), 4.31 (t, $J$ = 7.7 Hz, 1H), 4.32 (t, $J$ = 7.7 Hz, 1H), 4.56 ~ 4.64 (m, 4H), 5.56 (s, 3H), 5.58 (s, 3H), 6.27 (d, $J$ = 9.9 Hz, 1H), 6.28 (d, $J$ = 9.9 Hz, 1H), 6.88 (ABq, $J$ = 6.7 Hz, 2H), 6.89 (ABq, $J$ = 6.7 Hz, 2H), 7.29 (ABq, $J$ = 8.6 Hz, 2H), 7.30 (ABq, $J$ = 8.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ = 13.69, 13.73, 18.7, 18.8, 38.6, 38.7, 55.2, 55.4, 55.5, 69.9 (q, $J$ = 2.6 Hz), 70.1 (q, $J$ = 1.9 Hz), 72.3 (q, $J$ = 1.8 Hz), 72.6 (q, $J$ = 1.8 Hz), 93.68, 93.71, 114.08, 114.10, 123.7 (q, $J$ = 276.7 Hz), 123.8 (q, $J$ = 276.8 Hz), 128.2, 131.4, 131.6, 133.2 (q, $J$ = 27.5 Hz), 133.3 (q, $J$ = 27.5 Hz), 136.4 (q, $J$ = 3.6 Hz), 136.5 (q, $J$ = 2.8 Hz), 159.5; $^{19}$F NMR ($CDCl_3$) δ -58.0 (s, 3F); -58.1 (s, 3F); IR (neat) 3446, 2961, 1611, 1513, 1251, 1163, 1125, 1031, 910 $cm^{-1}$; HRMS (FAB) calcd for ($M^+$) $C_{17}H_{23}F_3O_4$: 348.1548, Found 348.1552; Anal. Calcd for $C_{17}H_{23}F_3O_4$: C, 58.61; H, 6.65. Found: C, 58.30; H, 7.03.

## Reference

1. (a) Konno, T.; Morigaki, A.; Ninomiya, K.; Miyabe, T.; Ishihara, T. *Synthesis*, **2008**, 564-572. (b) Konno, T.; Nagai, G.; Ishihara, T. *J. Fluorine Chem*. **2006**, *127*, 510-518. (c) Konno, T.; Chae, J.; Kanda, M.; Nagai, G.; Tamura, K.; Ishihara, T.; Yamanaka, H. *Tetrahedron*, **2003**, *59*, 7571-7580. (d) Yamazaki, T.; Mizutani, K.; Kitazume, T. *J. Org. Chem*. **1995**, *60*, 6046-6056. (e) Hamper, B. C. *Org. Synth*. **1991**, *70*, 246-253. (f) Hiyama, T.; Sato, K.; Fujita, M. Bull. *Chem. Soc. Jpn*. **1989**, *62*, 1352-1354.