# Synthesis of (Z)-Vinylsilanes with High Diastereoselectivity by using Samarium Diiodide

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## Supporting information

**1-Chloro-1-(trimethyl)silylhexan-2-yl acetate (1a):** Isomeric composition 71/ 29. Yield: 71%. R*f* = 0.1, 0.4 (hexane/ethyl acetate 10/1); $^{1}$H NMR ($CDCl_3$, 200MHz) δ 5.11 (2 H, td, J = 6.9, J = 3.1), 3.48 (1 H, d, J = 3.1), 3.36 (1 H, d, J = 3.1), 2.12 (3 H, s), 2.03 (3 H, s), 1.63-1.77 (4 H, m), 1.10-1.42 (8 H, m), 0.87 (6 H, t, J = 6.8), 0.13 (9 H, s), 0.10 (9 H, s); $^{13}$C NMR ($CDCl_3$, 50MHz) δ 170, 169.9, 75.2, 74.0, 52.7, 52.2, 31.9, 31.2, 27.5, 27.4, 22.3, 21.0, 13.8, -2.9, -2.5; IR (neat) 1732; MS, *m/z* 117 (21), 73 (63), 59 (11), 43 (100).

**1-Chloro-1-[(dimethyl)phenylsilyl]hexan-2-yl acetate (1b):** Isomeric composition 75/25. Yield: 69%. R*f* = 0.3, 0.5 (hexane/ethyl acetate 5/1); $^{1}$H NMR ($CDCl_3$, 200MHz) δ 7.40-7.60 (5 H, m), 7.39-7.28 (5 H, m), 5.09 (2 H, td, J = 6.9, J = 3.1), 3.75 (1 H, d, J = 4.1), 3.60 (1 H, d, J = 3.1), 1.94 (3 H, s), 1.85 (3 H, s), 1.65-1.72 (4 H, m), 1.16-1.35 (8 H, m), 0.87 (6 H, t, J = 6.8), 0.32-0.51 (12 H, m); $^{13}$C NMR ($CDCl_3$, 50MHz) δ 170.4, 169.9, 135.5, 135.4, 134.0, 133.8, 129.6, 128.7, 127.8, 127.6, 75.2, 73.8, 51.0, 51.7, 31.8, 31.2, 27.4, 27.3, 22.3, 22.1, 20.8, 13.8, -3.6, -4.1, -4.5, -4.7; IR (neat) 1740; MS, *m/z* 135 (57), 129 (5), 77 (14), 59 (10), 43 (46).

**1-Chloro-4-methyl-1-(trimethylsilyl)pentan-2-yl acetate (1c):** Isomeric composition 68/32. Yield: 70%. R*f* = 0.3, 0.5 (hexane/ethyl acetate 10/1); $^{1}$H NMR ($CDCl_3$, 200MHz) δ 5.17-5.23 (2 H, m), 3.50 (1 H, d, J = 3.1), 3.31 (1 H, d, J = 3.5), 2.00 (3 H, s), 1.99 (3 H, s), 1.47-1.58 (4 H, m), 0.70-1.11 (14 H, m), 0.11 (9 H, s), 0.09 (9 H, s); $^{13}$C NMR ($CDCl_3$, 50MHz) δ 169.3, 168.7, 72.1, 71.1, 40.1, 39.2, 22.3, 22.2, 21.4, 21.2, 20.3, 19.9, -3.7, -3.9; IR (neat) 1732.

**2-Chloro-1-phenyl-2-(trimethylsilyl)ethyl acetate (1d):** Isomeric composition 67/33. Yield: 66%. R*f* = 0.4 (hexane/ethyl acetate 5/1); $^{1}$H NMR ($CDCl_3$, 200MHz) δ 7.36-7.50 (10 H, m), 6.00-6.07 (2 H, m), 3.74 (1 H, d, J = 6.7), 3.66 (1 H, d, J = 8.3), 2.12 (3 H, s), 2.11 (3 H, s), 0.09 (9 H, s), -0.01 (9 H, s); $^{13}$C NMR ($CDCl_3$, 50MHz) δ 169.7, 169.3, 138.0, 128.3, 128.0, 127.2, 127.1, 70.0, 53.1, 52.2, 20.9, -2.6, -3.0; IR (neat) 1756; MS, *m/z* 138 (100), 149 (22), 77 (58), 73 (79), 43 (72).

**2-Chloro-1-(4-chlorophenyl)-2-(trimethylsilyl)ethyl acetate (1e):** Isomeric composition 71/29. Yield: 75%. R*f* = 0.3, 0.5 (hexane/ethyl acetate 5/1); $^{1}$H NMR ($CDCl_3$, 300MHz) δ 7.27-7.38 (8 H, m), 5.94 (1 H, d, J = 7.4), 5.93 (1 H, d, J = 7.0), 3.65 (1 H, d, J = 7.0), 3.56 (1 H, d, J = 7.4), 2.10 (3 H, s), 2.01 (3 H, s), 0.07 (9 H, s), 0.01 (9 H, s); $^{13}$C NMR ($CDCl_3$, 75MHz) δ 169.6, 169.3, 136.7, 134.3, 134.1, 128.6, 128.4, 128.3, 127.9, 76.1, 74.0, 53.0, 51.8, 21.0, 20.9, -2.6, -2.9; IR (neat) 1756; MS, *m/z* 172 (100), 145 (2), 79 (73), 59 (12), 43 (72).

**2-Chloro-1-(4-methoxyphenyl)-2-(trimethylsilyl)ethyl acetate (1f):** Isomeric composition 74/26. Yield: 66%. R*f* = 0.3, 0.5 (hexane/ethyl acetate 10/1); $^{1}$H NMR ($CDCl_3$, 300MHz) δ 7.38 (2 H, d, J = 8.7), 7.29 (2 H, d, J = 8.7), 6.89 (4 H, d, J = 8.7), 5.97 (1 H, d, J = 6.8), 5.94 (1 H, d, J = 9.0), 3.81 (6 H, s), 3.71 (1 H, d, J = 6.8), 3.63 (1 H, d, J = 9.0), 2.10 (6 H, s), 0.07 (9 H, s), -0.05 (9 H, s); $^{13}$C NMR ($CDCl_3$, 75MHz) δ 169.6, 169.2, 159.7, 159.4, 129.9, 128.4, 113.7, 113.3, 76.8, 76.3, 54.9, 52.9, 52.9, 52.1, 20.8, -2.8, -3.1; IR (neat) 1732; MS, *m/z* 137 (100), 179 (26), 73 (81), 59 (8), 43 (75).

**2-Chloro-1-cyc1ohexyl-2-(trimethylsilyl)ethyl acetate (1g):** Isomeric composition 85/15. Yield: 65%. R*f* = 0.3, 0.6 (hexane/ethyl acetate 10/1); $^{1}$H NMR ($CDCl_3$, 200MHz) δ 5.01 (1 H, d, J = 2.6), 4.96 (1 H, d, J = 2.6), 3.50 (2 H, d, J = 2.6), 2.07 (3 H, s), 2.06 (3 H, s), 0.70-1.91 (22 H, m), 0.07- -0.09 (18 H, m); $^{13}$C NMR ($CDCl_3$, 50MHz) δ 170.1, 77.1, 51.0, 39.3, 28.9, 28.5, 25.9, 25.6, 25.5, 21.0, -0.1, -2.5; IR (neat) 1724.

**1-Chloro-1-(trimethylsilyl)nonan-2-yl acetate (1h):** Isomeric composition 69/31. Yield: 73%. R*f* = 0.4, 0.5 (hexane/ethyl acetate 5/1); $^{1}$H NMR ($CDCl_3$, 200MHz) δ 5.12 (2 H, m), 3.49 (1 H, d, J = 3.8), 3.37 (1 H, d, J = 2.8), 2.04 (3 H, s), 2.03 (3 H, s), 1.11-1.42 (24 H, m), 0.81-0.88 (6 H, m), 0.15 (9 H, s), 0.11 (9 H, s); $^{13}$C NMR ($CDCl_3$, 50MHz) δ 170.0, 75.3, 74.1, 52.3, 52.2, 32.2, 31.6, 29.1, 29.0, 25.2, 22.5, 21.0, 13.9, -2.5, -2.8; IR (neat) 1732; MS, *m/z* 171 (2), 117 (100), 73 (93), 43 (78).

**1-Chloro-3-phenyl-1-(trimethylsilyl)butan-2-yl acetate (1i):** Isomeric composition 80/20. Yield: 70%. R*f* = 0.4 (hexane/ethyl acetate 5/1); $^{1}$H NMR ($CDCl_3$, 200MHz) δ 7.24-7.36 (10 H, m), 5.47-5.64 (2 H, m), 3.33-3.79 (4 H, m), 2.17 (3 H, s), 2.06 (3 H, s), 1.30 (3 H, d, J = 6.9), 1.24 (3 H, d, J = 6.9), 0.02-0.20 (18 H, m); $^{13}$C NMR ($CDCl_3$, 75MHz) δ 170.2, 169.5, 142.8, 142.7, 128.7, 127.5,127.4, 126.8, 80.5, 76.6, 51.4, 49.7, 43.2, 42.0, 18.1, 17.5, 1.91, -3.3; IR (neat) 1740.

**1-Chloro-4,8-dimethyl-1-(trimethylsilyl)non-7-en-2-yl acetate (1j):** Isomeric composition 37/36/14/15. Yield: 73%. R*f* = 0.4, 0.3, 0.2, 0.1 (hexane/ethyl acetate 10/1); $^{13}$C NMR ($CDCl_3$, 50MHz) δ 169.9, 169.8, 131.2, 131.1, 124.3, 73.5, 72.9, 72.3, 72.1, 53.6, 53.0, 52.0, 39.8, 38.9, 38.7, 38.5, 37.6, 37.0, 36.7, 35.7, 28.9, 28.6, 25.3, 25.2, 24.9, 21.0, 20.9, 19.5, 19.4, 19.0,17.5, -0.9, -2.5, -2.7, -2.8; IR (neat) 1732; MS, *m/z* 171 (2), 121 (11), 73 (100), 59 (8), 43 (76).

**(*Z*)-Hex-1-enyl(trimethyl)silane (3a)**: $^{1}$H NMR ($CDCl_3$, 200 MHz) δ 6.30 (1 H, dt, J = 13.9, 7.4), 5.46 (1 H, d, *J* = 13.9), 2.07-2.17 (2 H, m), 1.25-1.50 (4 H, m), 0.91 (3 H, t, J = 5.9), 0.04-0.14 (9 H, m); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 149.2, 128.6, 33.2, 31.9, 22.3, 13.9, 0.1; IR (neat) 1620; MS, *m/z* 117 (72), 73 (69), 45 (16), 43 (100).

**(*Z*)-Hex-1-enyl(dimethyl)phenylsilane (3b)**: $^{1}$H NMR ($CDCl_3$, 200 MHz) δ 7.66–7.40 (5 H, m), 6.52 (1 H, dt, J =13.8, 7.5), 5.68 (1 H, dt, *J* = 13.8, 1.0), 2.09-2.19 (2 H, m), 1.20-1.53 (4 H, m), 0.87-1.12 (3 H, m), 0.47 (6 H, s); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 150.9, 139.6, 128.6, 127.8, 127.6, 126.3, 33.4, 31.6, 22.3, 13.9, -0.8; IR (neat) 1611; MS, *m/z* 203 (4), 135 (11), 77 (7), 43 (74); HRMS Calcd for $C_9H_{20}Si$: 218.1491, found: 218.1493.

**(*Z*)-4-Methylpent-1-enyl(trimethyl)silane (3c)**: $^{1}$H NMR ($CDCl_3$, 200 MHz) δ 6.31 (1 H, dt, J =14.1, 7.2), 5.51 (1 H, d, *J* = 14.1), 1.97-2.06 (2 H, m), 1.56-1.86 (1 H, m), 0.91 (6 H, d, J = 6.7), 0.04-0.14 (9 H, m); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 148.0, 129.3, 42.3, 28.6, 22.3, 0.2; IR (neat) 1643; MS, *m/z* 117 (32), 73 (56), 57 (4), 43 (100).

**(*Z*)-2-(Phenylethenyl)trimethylsilane (3d)**: $^{1}$H NMR ($CDCl_3$, 300 MHz) δ 7.27–7.52 (6 H, m), 5.91 (1 H, d, *J* = 14.8), 0.12-0.15 (9 H, m); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 146.5, 140.0, 132.7, 128.0, 127.8, 126.2, 0.1; IR (neat) 1603; MS, *m/z* 176 ($M^+$, 21), 161 (100), 103 (14), 77 (9), 73 (19).

**(*Z*)-[2-(4-Chlorophenyl)ethenyl]trimethylsilane (3e)**: $^{1}$H NMR ($CDCl_3$, 300 MHz) δ 7.20–7.41 (4 H, m), 7.32 (1 H, d, *J* = 15.1), 5.90 (1 H, d, J = 15.1), 0.09-0.19 (9H, m); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 145.1, 138.4, 133.7, 133.0, 129.3, 128.0, 0.0; IR (neat) 1604; MS, *m/z* 210 ($M^+$, 4), 195 (7), 73 (65), 43 (100); HRMS Calcd for $C_{11}H_{15}ClSi$: 210.0632, found: 210.0631.

**(*Z*)-[2-(4-Methoxyphenyl)ethenyl]trimethylsilane (3f)**: $^{1}$H NMR ($CDCl_3$, 200 MHz) δ 6.91–7.45 (5 H, m), 5.77 (1 H, d, *J* = 15.3), 3.85 (3 H, s), 0.14 (9H, s); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 158.8, 146.0, 131.2, 129.3, 126.9, 113.2, 55.1, 0.1; IR (neat) 1619; MS, *m/z* 206 ($M^+$, 56), 191 (100), 175 (40), 73 (4); HRMS Calcd for $C_{12}H_{18}0Si$: 206.1127, found: 206.1122.

**(*E*)-[2-(4-Methoxyphenyl)ethenyl]trimethylsilane**: $^{1}$H NMR ($CDCl_3$, 200 MHz) δ 6.91–7.45 (5 H, m), 6.37 (1 H, d, *J* = 19.3), 3.84 (3 H, s), 0.20 (9H, s); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 159.3, 142.9, 130.6, 127.4, 126.4, 113.7, 55.1, -1.2; IR (neat) 1619; MS, *m/z* 206 ($M^+$, 41), 191 (100), 175 (36), 73 (5); HRMS Calcd for $C_{12}H_{18}0Si$: 206.1127, found: 206.1122.

**(*Z*)-(2-Cyclohexylethenyl)trimethylsilane (3g)**: $^{1}$H NMR ($CDCl_3$, 200 MHz) δ 6.11 (1 H, dd, J =13.9, 10.0), 5.37 (1 H, d, *J* = 13.9), 1.78-2.30 (11 H, m), 0.11 (9 H, s); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 154.9, 126.4, 44.7, 33.0, 25.8, 25.7, 0.3; IR (neat) 1606; MS, *m/z* 182 ($M^+$, 2), 167 (4), 109 (6), 73 (100); HRMS Calcd for $C_{11}H_{22}Si$: 182.1491, found: 182.1480.

**(*Z*)-Non-1-enyl(trimethyl)silane (3h)**: $^{1}$H NMR ($CDCl_3$, 200 MHz) δ 6.31 (1 H, dt, J =14.1, 7.2), 5.47 (1 H, d, *J* = 14.1), 2.08-2.14 (2 H, m), 1.18-1.50 (10 H, m), 0.90 (3 H, t, J = 6.4), 0.12-0.15 (9 H, m); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 149.2, 128.6, 33.5, 31.8, 29.7, 29.3, 29.2, 22.5, 14.0, 0.2; IR (neat) 1615; MS, *m/z* 198 ($M^+$, 1), 183 (45), 99 (30), 73 (100), 43 (22); HRMS Calcd for $C_{11}H_{26}Si$: 198.1804, found: 198.1802.

**(*Z*)-(3-phenylbut-1-enyl)trimethylsilane (3i)**: $^{1}$H NMR ($CDCl_3$, 200 MHz) δ 7.23–7.40 (5 H, m), 6.43 (1 H, dd, J =13.9, 10.3), 5.54 (1 H, d, *J* = 13.9), 3.65-3.85 (1 H, m), 1.48 (3 H, d, J = 6.9), 1.24 (9 H, s); $^{13}$C NMR ($CDCl_3$, 50 MHz) δ 153.1, 145.4, 128.4, 127.2, 126.7, 125.9, 43.0, 21.8, 0.4; IR (neat) 1601; MS, *m/z* 204 ($M^+$, 27), 189 (12), 105 (19), 73 (100).

**(*Z*)-(4,8-Dimethylnonan-1,7-dienyl)trimethylsilane (3j)**: $^{1}$H NMR ($CDCl_3$, 200 MHz) δ 6.31 (1 H, dt, J = 14.1, 7.2), 5.52 (1 H, d, J = 14.1), 5.11 (1 H, t, J = 7.1), 1.69 (3 H, s), 1.61 (3 H, s), 1.05-2.23 (7 H, m), 0.90 (3 H, d, J = 6.7), 0.04-0.18 (9 H, m); $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 148.0 , 131.0, 129.4, 124.7, 40.6, 36.9, 32.9, 25.6, 25.5, 19.3, 17.6, 0.2; IR (neat) 1611; MS, *m/z* 224 ($M^+$, 2), 209 (6), 125 (11), 73 (100); HRMS Calcd for $C_{14}H_{28}Si$: 224.1960, found: 224.1962.

**REPRESENTATIVE PROCEDURE FOR THE SYNTHESIS OF (*Z*)-VINYLSILANES 3**

A solution of $SmI_2$ (5 mmol) in THF (60 mL) was added, under nitrogen atmosphere, to a solution of the corresponding *O*-acetyl 1-chloro-1-trimethylsilylalkan-2-ol **1** (1 mmol) in THF (10 mL). After stirring at reflux for 3.5 h, the mixture was treated with aqueous HCl (0.1M, 25 mL) and after usual work-up, the corresponding crude vinylsilane was obtained. Distillation at reduced pressure provided pure (*Z*)-vinylsilane **3**.