

Supporting Information for
Highly Stereoselective and Efficient Hydrosilylation of Terminal Alkynes
Catalyzed by [RuCl₂(*p*-cymene)]₂

Youngim Na and Sukbok Chang*

Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea

(Z)-1-Triphenylsilyl-2-phenylethene (entry 1 in Table 1): ¹H-NMR (CDCl₃, 250 MHz) δ 7.82 (1H, d, *J* = 15.3 Hz), 7.66-7.33 (15H, m), 7.26-6.99 (5H, m), 6.43 (1H, d, *J* = 15.3 Hz); ¹³C-NMR (CDCl₃, 62.5 MHz) δ 150.8, 138.4, 136.2, 135.5, 129.8, 129.1, 128.3, 128.1, 127.9, 125.7; HRMS (EI) calcd for C₂₆H₂₂Si 362.1492 (M⁺), found 362.1490.

(Z)-1-Triethylsilyl-2-phenylethene^{11(b)} (entry 2 in Table 1): ¹H-NMR (CDCl₃, 250 MHz) δ 7.53 (1H, d, *J* = 15.2 Hz), 7.38-7.34 (5H, m), 5.84 (1H, d, *J* = 15.2 Hz), 0.94 (9H, t, *J* = 7.9 Hz), 0.62 (6H, q, *J* = 7.9 Hz); ¹³C-NMR (CDCl₃, 62.5 MHz) δ 148.2, 140.9, 129.9, 128.3, 127.8, 7.9, 5.2.

(Z)-1-Triphenylsilyl-1-hexene (entry 3 in Table 1): ¹H-NMR (CDCl₃, 250 MHz) δ 7.74 (m, 6H), 7.45 (m, 9H), 6.85 (1H, dt, *J* = 13.9, 7.5 Hz), 6.18 (1H, d, *J* = 14.0 Hz), 2.07 (2H, q, *J* = 7.5 Hz), 1.33-1.06 (4H, m), 0.79 (3H, t, *J* = 7.2 Hz); ¹³C-NMR (CDCl₃, 62.5 MHz) δ 154.5, 136.3, 136.1, 130.3, 128.4, 123.2, 34.8, 31.7, 22.8, 14.4; HRMS (EI) calcd for C₂₄H₂₆Si 342.1805 (M⁺), found 342.1803.

(Z)-1-Triethylsilyl-1-hexene^{11(b)} (entry 4 in Table 1): ¹H-NMR (CDCl₃, 250 MHz) δ 6.42 (1H, dt, *J* = 14.1, 7.3 Hz), 5.43 (1H, d, *J* = 14.1 Hz), 2.14 (2H, m), 1.40 (4H, m), 0.99 (12H, m), 0.65 (6H, q, *J* = 7.8 Hz); ¹³C-NMR (CDCl₃, 62.5 MHz) δ 150.8, 125.3, 34.2, 32.4, 22.9, 14.5, 8.0, 5.1.

(Z)-2-(4-Methylphenyl)-1-triphenylsilylethene (entry 5 in Table 1): ¹H-NMR (CDCl₃, 250 MHz) δ 7.76 (1H, d, *J* = 15.4 Hz), 7.65-7.33 (15H, m), 7.14 (2H, d, *J* = 7.9 Hz), 7.0 (2H, d, *J* = 7.9 Hz), 6.30 (1H, d, *J* = 15.4 Hz), 2.23 (3H, s); ¹³C-NMR (CDCl₃, 62.5 MHz) δ 150.8, 138.1, 136.2, 135.7, 129.7, 129.2, 128.7, 128.3, 124.4, 21.6; HRMS (EI) calcd for C₂₇H₂₄Si 376.1648 (M⁺), found 376.1652.

(Z)-5-Chloro-1-triphenylsilyl-1-pentene (entry 6 in Table 1): ¹H-NMR (CDCl₃, 250 MHz) 7.63 (6H, m), 7.37 (9H, m), 6.71 (1H, dt, *J* = 13.9, 7.5 Hz), 6.17 (1H, d, *J* = 13.9 Hz), 3.13 (2H, t, *J* = 6.9 Hz), 2.06 (2H, m), 1.60 (2H, m); ¹³C-NMR (CDCl₃, 62.5 MHz) δ 151.9, 136.2, 135.7, 129.9, 128.4, 125.1, 44.6, 32.5, 32.3; IR (neat) cm⁻¹ 3069, 2999, 1603, 1429, 1109, 701; HRMS (CI) calcd for C₂₃H₂₃Si 327.1570 ([M-Cl]⁺), found 327.1578.

(Z)-4-Benzyloxy-1-triphenylsilyl-1-pentene (entry 7 in Table 1): ¹H-NMR (CDCl₃, 250 MHz) δ 7.68 (6H, m), 7.26 (9H, m), 7.15 (5H, m), 6.92 (1H, dt, *J* = 14.2, 7.3 Hz), 6.28 (1H, d, *J* = 14.2 Hz), 4.34 (2H, m), 3.40 (1H, m), 2.39-2.16 (2H, m), 1.0 (3H, d, *J* = 6.1 Hz); ¹³C-NMR (CDCl₃, 62.5 MHz) δ 150.2, 139.3, 136.3, 135.8, 129.9, 128.7, 128.4, 127.9, 127.8, 125.6, 74.9,

70.6, 41.0, 19.9; HRMS (EI) calcd for $C_{30}H_{30}OSi$ 434.2067 (M^+), found 434.2054.

(Z)-3-Benzoyloxy-1-triphenylsilyl-1-propene (entry 8 in Table 1): 1H -NMR ($CDCl_3$, 250 MHz) δ 7.64-7.41 (15H, m), 7.33-7.19 (5H, m), 6.93 (1H, dt, $J = 14.5, 7.4$ Hz), 6.36 (1H, d, $J = 14.5$ Hz), 4.16 (2H, s), 3.88 (2H, d, $J = 6.2$ Hz); ^{13}C -NMR ($CDCl_3$, 62.5 MHz) δ 149.4, 138.5, 136.4, 135.9, 130.0, 128.7, 128.3, 128.4, 128.0, 126.8, 72.9, 71.3; HRMS (EI) calcd for $C_{28}H_{26}OSi$ 406.1754, found 406.1750.

(Z)-Benzyl-5-triphenylsilyl-4-pentenoate (entry 9 in Table 1): 1H -NMR ($CDCl_3$, 250 MHz) 7.70-7.38 (20H, m), 6.79 (1H, dt, $J = 13.9, 7.3$ Hz), 6.26 (1H, d, $J = 13.9$ Hz), 5.12 (2H, s), 2.42-2.20 (4H, m); ^{13}C -NMR ($CDCl_3$, 62.5 MHz) δ 172.9, 151.3, 136.2, 135.6, 130.0, 129.0, 128.7, 128.6, 128.5, 125.5, 66.6, 33.7, 29.9; IR (neat) cm^{-1} 3068, 1737, 1604, 1428, 1151, 1110; HRMS (CI) calcd for $C_{30}H_{29}O_2Si$ 449.1937 ($[M+H]^+$), found 449.1930.

(Z)-3-Butenyl-5-triphenylsilyl-4-pentenoate (entry 10 in Table 1): 1H -NMR ($CDCl_3$, 250 MHz) δ 7.70-7.43 (15H, m), 6.79 (1H, dt, $J = 14.0, 7.4$ Hz), 6.25 (1H, d, $J = 14.0$ Hz), 5.8 (1H, m), 5.16 (2H, m), 4.13 (2H, t, $J = 6.7$ Hz), 2.44-2.16 (6H, m); ^{13}C -NMR ($CDCl_3$, 62.5 MHz) δ 173.1, 151.4, 136.7, 136.2, 135.6, 134.5, 129.9, 128.5, 125.4, 117.7, 63.8, 33.7, 29.9; IR (neat) cm^{-1} 3069, 1735, 1604, 1429, 1154, 1110; HRMS (EI) calcd for $C_{27}H_{28}O_2Si$ 412.1862 (M^+), found 412.1851.

3-Triphenylsilyl-3-buten-1-ol (entry 1 in Table 2): m.p 105-106 °C; 1H -NMR ($CDCl_3$, 250 MHz) δ 7.62-7.28 (15H, m), 6.12 (1H, d, $J = 2.2$ Hz), 5.72 (1H, d, $J = 2.2$ Hz), 3.57 (2H, t, $J = 6.5$ Hz), 2.58 (2H, t, $J = 6.5$ Hz), 1.35 (1H, bs); ^{13}C -NMR ($CDCl_3$, 62.5 MHz) δ 143.6, 136.6, 134.0, 133.4, 130.1, 128.4, 61.9, 39.9; IR (neat) cm^{-1} 3309, 3067, 2911, 1427, 1109; MS (EI) m/z 330 (M^+ , $C_{22}H_{22}OSi$), 330 (38), 300 (6), 259 (100), 217 (26), 181 (14), 130 (30).

(Z)-4-Benzoyloxy-1-triphenylsilyl-1-butene (entry 2 in Table 2): 1H -NMR ($CDCl_3$, 250 MHz) 7.63-7.26 (20H, m), 6.81 (1H, dt, $J = 14.1, 7.2$ Hz), 6.21 (1H, d, $J = 14.1$ Hz), 4.33 (2H, s), 3.32 (2H, t, $J = 6.7$ Hz), 2.30 (2H, q, $J = 6.8$ Hz); ^{13}C -NMR ($CDCl_3$, 62.5 MHz) δ 150.4, 139.1, 136.4, 135.9, 130.1, 128.9, 128.6, 128.2, 126.0, 73.3, 69.8, 35.4; HRMS (EI) calcd for $C_{29}H_{28}OSi$ 420.1910 (M^+), found 420.1907.

1-Phenyl-2-triphenylsilyl-2-propen-1-ol (major product of entry 4 in Table 2): 1H -NMR ($CDCl_3$, 250 MHz) δ 7.60-7.37 (15H, m), 7.23-7.11 (5H, m), 6.21 (1H, d, $J = 2.0$ Hz), 5.81 (1H, d, $J = 2.0$ Hz), 5.48 (1H, s), 1.93 (1H, bs); ^{13}C -NMR ($CDCl_3$, 62.5 MHz) δ 149.6, 142.5, 136.8, 135.4, 134.3, 132.2, 129.9, 128.5, 128.2, 127.8, 127.6; HRMS (EI) calcd for $C_{27}H_{24}OSi$ ($[M^+]$) 392.1597, found 392.1566.

(Z)-3-Triphenylsilyl-1-phenyl-2-propen-1-ol (minor isomer of entry 4 in Table 2): 1H -NMR ($CDCl_3$, 250 MHz) δ 7.74-7.44 (15H, m), 7.32-7.11 (5H, m), 6.93 (1H, dd, $J = 14.0, 9.1$ Hz), 6.39 (1H, d, $J = 14.0$ Hz), 5.13 (1H, d, $J = 9.1$ Hz), 1.78 (1H, bs); ^{13}C -NMR ($CDCl_3$, 62.5 MHz) δ 153.3, 142.7, 136.3, 135.5, 130.2, 128.9, 128.6, 128.4, 128.1, 126.8, 126.1, 74.3; IR (neat) cm^{-1} 3559, 3395, 3050, 1602, 1428, 1109, 1429. HRMS (CI) calcd for $C_{27}H_{23}OSi$ 391.1488 ($[M-H]^+$), found 391.1503.

4-Triphenylsilyl-4-penten-2-ol (entry 4 in Table 2): $^1\text{H-NMR}$ (CDCl_3 , 250 MHz) δ 7.63-7.29 (15H, m), 6.15 (1H, d, J = 1.2 Hz), 5.77 (1H, d, J = 2.6 Hz), 3.63 (1H, m), 2.57-2.33 (2H, m), 1.64 (1H, bs), 1.64 (3H, d, J = 6.1 Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 62.5 MHz) δ 144.4, 136.7, 134.0, 130.1, 128.4, 66.5, 47.2, 23.2; IR (neat) cm^{-1} 3578, 3398, 3050, 2969, 1428, 1109; HRMS (CI) calcd for $\text{C}_{23}\text{H}_{25}\text{OSi}$ 345.1676 ($[\text{M}+\text{H}]^+$), found 345.1664.

(Z)-7-Triphenylsilyl-6-hepten-3-ol (entry 5 in Table 2): $^1\text{H-NMR}$ (CDCl_3 , 250 MHz) m), 6.74 (1H, dt, J = 13.9, 7.2 Hz), 6.12 (1H, d, J = 13.9 Hz), 3.12 (1H, m), 2.10 (2H, m), 1.21 (3H, m), 0.91 (2H, m), 0.79 (3H, t, J = 7.4 Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 62.5 MHz) δ 153.6, 136.2, 136.0, 129.8, 128.3, 123.9, 73.1, 36.5, 30.2, 23.1, 10.2; IR (neat) cm^{-1} 3588, 3382, 3069, 2969, 1603, 1429, 1110.

(Z)-8-Triphenylsilyl-7-octen-3-ol (entry 6 in Table 2): $^1\text{H-NMR}$ (CDCl_3 , 250 MHz) 7.65-7.37 (15H, m), 6.75 (1H, dt, J = 14.0, 7.5 Hz), 6.12 (1H, d, J = 14.0 Hz), 3.26 (1H, m), 2.03 (2H, m), 1.39 (4H, m), 1.09 (3H, m), 0.89 (3H, t, J = 7.4 Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 62.5 MHz) δ 153.9, 136.2, 136.0, 129.8, 128.3, 123.6, 73.3, 36.8, 34.9, 30.4, 25.5, 10.3; IR (neat) cm^{-1} 3375, 1603, 1428, 1109; HRMS (CI) calcd for $\text{C}_{26}\text{H}_{29}\text{OSi}$ 385.1989 ($[\text{M}-\text{H}]^+$), found 385.1981.

(Z)-13-Triphenylsilyl-12-tridecen-3-ol (entry 7 in Table 2): $^1\text{H-NMR}$ (CDCl_3 , 250 MHz) 7.63-7.29 (15H, m), 6.73 (1H, dt, J = 14.0, 7.4 Hz), 6.07 (1H, d, J = 14.0 Hz), 3.56 (1H, bs), 1.95 (2H, m), 1.67-0.96 (20H, m); $^{13}\text{C-NMR}$ (CDCl_3 , 62.5 MHz) δ 152.9, 134.6, 128.3, 126.8, 121.6, 72.3, 35.9, 33.5, 29.1, 28.6, 28.4, 28.3, 28.1, 28.0, 24.6, 8.9; IR (neat) cm^{-1} 3356, 3049, 2927, 1603, 1428, 1109; HRMS (CI) calcd for $\text{C}_{31}\text{H}_{39}\text{OSi}$ 455.2772 ($[\text{M}-\text{H}]^+$), found 455.2766.

(Z)-3-Ethyl-7-triphenylsilyl-6-hepten-3-ol (entry 8 in Table 2): $^1\text{H-NMR}$ (CDCl_3 , 250 MHz) 7.67-7.42 (15H, m), 6.76 (1H, dt, J = 13.9, 7.3 Hz), 6.14 (1H, d, J = 13.9 Hz), 2.04 (2H, m), 1.35-1.15 (7H, m), 0.70 (6H, t, J = 7.4 Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 62.5 MHz) δ 153.9, 136.2, 135.9, 135.5, 129.9, 128.4, 123.6, 74.5, 37.7, 30.9, 29.0, 8.1; IR (neat) cm^{-1} 3579, 3461, 2969, 1604, 1429, 1110; MS (CI) m/z 399 ($[\text{M}-\text{H}]^+$, $\text{C}_{27}\text{H}_{31}\text{OSi}$), 399 (3), 383 (44), 305 (100), 259 (89), 199 (67).