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Supporting Information

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γ-Silyl Group Effect in Hydroalumination and Carbolithiation of Propargylic Alcohols

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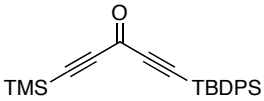
General Experimental.

All reactions were carried out with dry glassware under atmosphere of argon otherwise noted. Dry Et_2O, THF, CH_2Cl_2, hexane and toluene were purchased from Kanto Chemical Co., Inc. ^{1}H-NMR spectra were recorded on a Varian Gemini-2000 (300 MHz) or a Varian Mercury (300 MHz) spectrometer using $CDCl_3$ as solvent: $CHCl_3$ (^{1}H, δ 7.26) was used as an internal reference. ^{13}C-NMR spectra were recorded on a Varian Gemini-2000 (75 MHz) or a Varian Mercury (75 MHz) spectrometer using $CDCl_3$ as solvent: $CDCl_3$ (^{13}C, δ 77.1) was used as an internal reference. Peak multiplicities were given as followed: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Infrared spectra were recorded on a Fourier transfer infrared spectrophotometer (JASCO FT/IR-5000 or Perkin Elmer SpectrumOne) as neat liquid on NaCl plates. Mass spectra were recorded on a JEOL JMS-T100CS. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} (Merck 5715) plates. Developed plates were visualized by ultraviolet illumination at 254 nm and by heating on a hot plate after staining with 4% solution of phosphomolybdic acid in ethanol, a 2.5% solution of *p*-anisaldehyde in ethanol, or an aqeous solution of pottassium permanganate. Column chromatography was performed on Fuji Silysia FL100D or Kanto 60N (100~210 μm). Elemental analyses were performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology. Red-Al was purchased from Aldrich and diluted by toluene to 1.5~1.7 M, the concentration was titrated by using 9*H*-fluoren-9-one.[1] Theoretical calculations were performed by using Gaussian 98, Revision A.7.[2]

1-(*tert*-butyl-diphenyl-silyl)-5-trimethylsilyl-pent-1,4-diyn-3-on (i)

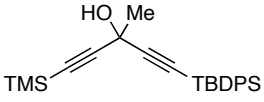


To a solution of **3a** (1.039 g, 2.66 mmol)[3] in hexane (30 mL) at room temperature was added MnO_2 (2.5 g, 28.8 mmol) and stirred for 1 h at that temperature. The reaction mixture was filtered by a pad of celite and the solvent was removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane:Et_2O = 50:1) to afford 854 mg of **i** (83%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84-7.75 (m, 4H), 7.47-7.37 (m, 6H), 1.14 (s, 9H), 0.29 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.02, 135.64, 131.26, 130.23, 128.11, 105.99, 102.76, 100.52, 95.75, 27.03, 19.04, 0.82.

1-(*tert*-butyl-diphenyl-silyl)-3-methyl-5-trimethylsilyl-pent-1,4-diyn-3-ol (3b)



To a solution of **i** (388 mg, 1 mmol) in THF (10 mL) at –78 °C was added MeMgBr (1.18 mL of 0.93 M solution in THF, 1.1mmol) and stirred for 1 h at that temperature. The reaction was quenched by sat. aq. NH_4Cl. The aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and the solvent was removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane:Et_2O = 20:1) to afford 278 mg of **3b** (69%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.79 (m, 4H), 7.45-7.36 (m, 6H), 2.63 (s, 1H), 1.88 (s, 3H), 1.11 (s, 9H), 0.28 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.64, 132.93, 129.69, 127.83, 110.49, 105.88, 87.62, 82.84, 60.62, 31.53, 27.08, 18.83, -0.18.

IR (neat, cm^{-1}) 3547, 3436, 2959, 2174, 1589, 1429, 1251, 1182, 1111, 1058, 844, 699.

Anal. Calcd for $C_{25}H_{52}OSi_2$: C, 74.20; H, 7.97. Found: C, 74.26; H, 8.12.

Typical procedures for hydroalumination reaction of propargylic alcohols

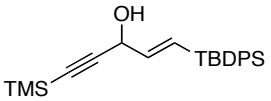
Hydroalumination reaction of alcohol 3a by using $LiAlH_4$:

To a solution of **3a** (51.5 mg, 0.132 mmol) in THF (7 mL) at –78 °C was added $LiAlH_4$ (0.33 mL of 1.0 M solution in THF, 0.33 mmol) and stirred at that temperature. After 20 min the reaction mixture was warmed up to -10 °C and stirred for 20 min at that temperature. The reaction was quenched by $Na_2SO_4 \cdot 10H_2O$, diluted with hexane (10 mL) and added Na_2SO_4. After the organic layer changed to clear solution, the slurry was filtered and the solvent was removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane:Et_2O = 20:1) to afford 28.9 mg of mixture of **4a** and **5a** (**4a**: 49%, **5a**: 6%) and 3.2 mg of **4a'** (9%). To a solution of **4a** and **5a** in MeOH (4 mL) was added MeONa (5.0 mg, 0.092 mmol) and stirred for 1.5 h at room temperature. The reaction was quenched by sat. aq. NH_4Cl. The aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine, dried over with Na_2SO_4, filtered and the solvent was removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane:Et_2O = 20:1) to afford 14.5 mg of **4a'** (34%) and 8.0 mg of the mixture (**4a**: 9%, **5a**: 6%).

Hydroalumination reaction of alcohol 3a by using Red-Al:

To a solution of **3a** (77.7 mg, 0.199 mmol) in toluene (7 mL) at 0 °C was added Red-Al (0.130 mL of 1.69 M solution in toluene, 0.219 mmol) and stirred for 1 h at that temperature. The reaction was quenched by $Na_2SO_4 \cdot 10H_2O$, diluted with hexane (10 mL) and added Na_2SO_4. After the organic layer changed to clear solution, the slurry was filtered and the solvent was removed *in vacuo*. The crude product was purified by silica gel chromatography (hexane:Et_2O = 20:1) to afford 71.2 mg of the mixture of **4a** and **5a** (**4a**: 88%, **5a**: 3%) and 3.2 mg of **4a'** (7%).

***E*-1-(*tert*-butyl-diphenyl-silyl)-5-trimethylsilyl-pent-1-en-4-yn-3-ol (4a)**



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.59 (m, 4H), 7.41-7.32 (m, 6H),6.55 (dd, *J* = 18.6, 1.8 Hz, 1H), 6.15 (dd, *J*

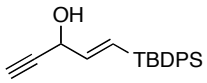
= 18.6, 4.5 Hz, 1H), 4.95 (ddd, *J* = 6.9, 4.5, 1.8 Hz, 1H), 1.96, (d, *J* = 6.9 Hz, 1H), 1.09 (s, 9H), 0.20 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.70, 136.29, 134.22, 129.34, 127.72, 124.97, 104.21, 91.79, 65.24, 27.73, 18.33, -0.10.

IR (neat, cm^{-1}) 3401, 2959, 2172, 1622, 1427, 1250, 1194, 1107, 1028, 844, 701.

MS (ESI, pos.) Calcd for $C_{24}H_{32}OSi_2Na$ ($[M+Na]^+$): 415.19. Found: 415.09.

***E*-1-(*tert*-butyl-diphenyl-silyl)-pent-1-en-4-yn-3-ol (4a')**



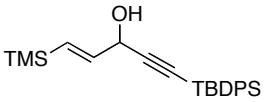
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.59 (m, 4H), 7.41-7.34 (m, 6H), 6.57 (dd, *J* = 18.3, 1.5 Hz, 1H), 6.13 (dd, *J* = 18.3, 4.5 Hz, 1H), 4.96 (dddd, *J* = 6.6, 4.5, 2.1, 1.5 Hz, 1H), 2.60 (d, *J* = 2.1 Hz, 1H), 1.95, (d, *J* = 6.6 Hz, 1H), 1.10 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.18, 136.29, 134.08, 129.38, 127.75, 125.44, 82.62, 74.87, 64.60, 27.79, 18.33.

IR (neat, cm^{-1}) 3543, 3296, 2959, 1959, 2888, 1824, 1621, 1195, 1106, 1074, 991, 700.

Anal. Calcd for $C_{21}H_{24}OSi$: C, 78.70; H, 7.55. Found: C, 78.38; H, 7.70.

***E*-1-(*tert*-butyl-diphenyl-silyl)-5-trimethylsilyl-pent-4-en-1-yn-3-ol (5a)**



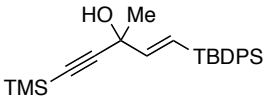
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.78 (m, 4H), 7.41-7.32 (m, 6H), 6.27 (d, *J* = 18.9 Hz, 1H), 6.16 (dd, *J* = 18.9, 3.9, 1H), 5.03 (dd, *J* = 6.6, 3.9 Hz, 1H), 2.04, (d, *J* = 6.6 Hz, 1H), 1.10 (s, 9H), 0.122 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.23, 135.86, 133.06, 132.30, 129.68, 127.83, 108.73, 86.94, 65.39, 27.11, 18.64, -1.36.

IR (neat, cm^{-1}) 3373, 2957, 2858, 2173, 1616, 1428, 1248, 1111, 866, 839, 844, 699.

MS (ESI, pos.) Calcd for $C_{24}H_{32}OSi_2Na$ ($[M+Na]^+$): 415.19. Found: 415.11.

***E*-1-(*tert*-butyl-diphenyl-silyl)-5-trimethylsilyl-3-methyl-pent-1-en-4-yn-3-ol (4b)**



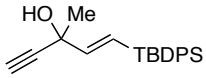
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64-7.60 (m, 4H), 7.42-7.31 (m, 6H),6.87 (d, *J* = 18.6 Hz, 1H), 6.46 (d, *J* = 18.6 Hz, 1H), 2.20, (s, 1H), 1.56 (s, 3H), 1.11 (s, 9H), 0.22 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.84, 136.26, 134.38, 129.29, 127.70, 121.64, 107.64, 89.70, 70.02, 29.75, 27.73, 18.36, 0.01.

IR (neat, cm^{-1}) 3437, 2959, 2857, 2166, 1618, 1428, 1251, 1194, 1108, 843, 701.

MS (ESI, pos.) Calcd for $C_{25}H_{34}OSi_2Na$ ($[M+Na]^+$): 429.20. Found: 429.10.

***E*-1-(*tert*-butyl-diphenyl-silyl)-3-methyl-pent-1-en-4-yn-3-ol (4b')**, derived from **4b**, **8c** or **9d**.



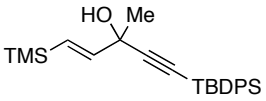
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.60 (m, 4H), 7.42-7.34 (m, 6H), 6.61 (d, *J* = 18.6 Hz, 1H), 6.17 (d, *J* = 18.6 Hz, 1H), 2.61 (s, 1H), 2.26 (s, 1H), 1.58 (s, 3H), 1.12 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.33, 136.28, 134.24, 129.34, 127.73, 121.94, 85.97, 73.33, 69.59, 27.78, 27.78, 18.35.

IR (neat, cm^{-1}) 3412, 3303, 2930, 2857, 1620, 1470, 1428, 1108, 998, 701.

Anal. Calcd for $C_{22}H_{26}OSi$: C, 78.99; H, 7.83. Found: C, 79.26; H, 7.73.

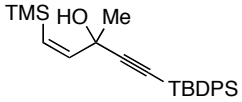
_E_-1-(*tert*-butyl-diphenyl-silyl)-5-trimethylsilyl-3-methyl-pent-4-en-1-yn-3-ol (_E_-5b)



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.77 (m, 4H), 7.41-7.34 (m, 6H), 6.29 (d, *J* = 18.6 Hz, 1H), 6.16 (d, *J* = 18.6 Hz, 1H), 2.20 (s, 1H), 1.67 (s, 3H), 1.10 (s, 9H), 0.12 (s, 9H).

MS (ESI, pos.) Calcd for $C_{25}H_{34}OSi_2Na$ ($[M+Na]^+$): 429.20. Found: 429.19.

_Z_-1-(*tert*-butyl-diphenyl-silyl)-5-trimethylsilyl-3-methyl-pent-4-en-1-yn-3-ol (_Z_-5b)



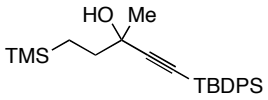
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.75 (m, 4H), 7.40-7.33 (m, 6H), 6.49 (d, *J* = 14.7 Hz, 1H), 5.63 (d, *J* = 14.7 Hz, 1H), 2.05 (s, 1H), 1.67 (s, 3H), 1.08 (s, 9H), 0.18 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.90, 135.54, 133.05, 129.53, 129.03, 127.71, 113.04, 83.38, 69.62, 31.42, 27.20, 18.77, 1.60.

IR (neat, cm^{-1}) 3461, 2959, 2858, 2167, 1607, 1429, 1260, 1110, 841, 699.

MS (ESI, pos.) Calcd for $C_{25}H_{34}OSi_2Na$ ($[M+Na]^+$): 429.20. Found: 479.18.

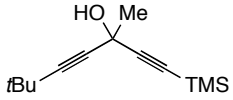
1-(*tert*-butyl-diphenyl-silyl)-5-trimethylsilyl-pent-1-yn-3-ol (6b)



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.77 (m, 4H), 7.41-7.34 (m, 6H), 2.14 (s, 1H), 1.78-1.70 (m, 2H), 1.60 (s, 3H), 0.84-0.78 (m, 2H), 1.09 (s, 9H), 0.04 (s, 9H).

MS (ESI, pos.) Calcd for $C_{25}H_{36}OSi_2Na$ ($[M+Na]^+$): 431.22. Found: 431.20.

1-trimethylsilyl-3,6,6-trimethyl-hept-1,4-diyn-3-ol (7a)



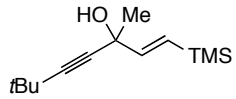
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 1H), 1.71 (s, 3H), 1.22 (s, 9H), 0.17 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 107.01, 91.50, 86.22, 80.19, 60.34, 32.34, 30.79, 27.32, -0.14.

IR (neat, cm^{-1}) 3413, 2969, 2228, 2174, 1363, 1251, 1060, 938, 844, 761.

Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 70.28; H, 9.89.

***E*-1-trimethylsilyl-3,6,6-trimethyl-hept-1-en-4-yn-3-ol (8a)**



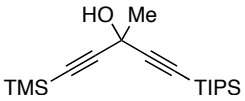
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.07 (s, 2H), 1.98 (s, 1H), 1.48 (s, 3H), 1.22 (s, 9H), 0.08 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.59, 127.49, 94.20, 80.85, 69.45, 30.96, 30.20, 27.26, -1.49.

IR (neat, cm^{-1}) 3400, 2969, 1614, 1363, 1249, 1067, 989, 867, 839.

MS (ESI, pos.) Calcd for $C_{13}H_{24}OSiNa$ ($[M+Na]^+$): 247.15. Found: 247.08.

1-triisopropylsilyl-5-trimethylsilyl-3-methyl-pent-1,4-diyn-3-ol (7b)



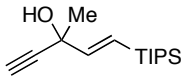
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.49 (s, 1H), 1.75 (s, 3H), 1.07 (m, 21H), 0.17 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 108.56, 106.36, 86.94, 83.83, 60.49, 31.72, 18.62, 11.26, -0.21.

IR (neat, cm^{-1}) 3412, 2944, 2867, 2173, 1464, 1251, 1182, 1137, 1070, 804, 677.

Anal. Calcd for $C_{18}H_{34}OSi_2$: C, 67.01; H, 10.62. Found: C, 66.85; H, 10.56.

***E*-1-triisopropylsilyl-3-methyl-pent-1-en-4-yn-3-ol (8b')**, derived from **8b**.

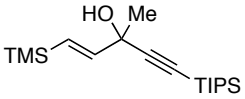


^{1}H NMR (300 MHz, $CDCl_3$) δ 6.17 (d, J = 18.9, 1H), 6.04 (d, J = 18.9, 1H), 2.58 (s, 1H), 2.11 (s, 1H), 1.57 (s, 3H), 1.17-1.01 (m, 21H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.10, 122.14, 86.11, 73.08, 69.64, 30.13, 18.77, 11.03.

IR (neat, cm^{-1}) 3400, 3312, 2942, 2866, 1619, 1464, 1069, 994, 883, 794, 778.

***E*-1-triisopropylsilyl-5-trimethylsilyl-3-methyl-pent-4-en-1-yn-3-ol (9b)**



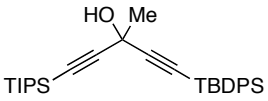
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.19 (d, J = 18.6, 1H), 6.07 (d, J = 18.6, 1H), 2.08 (s, 1H), 1.54 (s, 3H), 1.07 (m, 21H), 0.79 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.53, 128.28, 109.94, 85.70, 70.07, 30.13, 18.77, 11.39, –1.17.

IR (neat, cm^{-1}) 3380, 2866, 22944, 2166, 1615, 1463, 1248, 989, 868, 841, 677.

MS (ESI, pos.) Calcd for $C_{18}H_{36}OSi_2Na$ ($[M+Na]^+$): 347.22. Found: 347.14.

1-(*tert*-butyl-diphenyl-silyl)-5-triisopropylsilyl-3-methyl-pent-1,4-diyn-3-ol (**7c**)



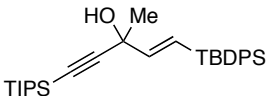
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.77 (m, 4H), 7.43-7.33 (m, 6H), 2.63 (s, 1H), 1.88 (s, 3H), 1.10 (m, 21H), 1.08 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.63, 132.94, 129.66, 127.81, 110.59, 108.14, 83.98, 82.41, 60.60, 31.84, 27.07, 18.73, 18.65, 11.20.

IR (neat, cm^{-1}) 3452, 2943, 2865, 2173, 1463, 1428, 1181, 1111, 935, 882, 819, 699.

Anal. Calcd for $C_{31}H_{44}OSi_2$: C, 76.16; H, 9.07. Found: C, 76.38; H, 9.16.

***E*-1-(*tert*-butyl-diphenyl-silyl)-5- triisopropylsilyl -3-methyl-pent-1-en-4-yn-3-ol** (**8c**)



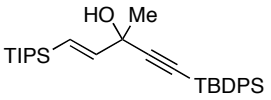
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.59 (m, 4H), 7.41-7.30 (m, 6H), 6.65 (d, *J* = 18.3 Hz, 1H), 6.16 (d, *J* = 18.3 Hz, 1H), 2.18, (s, 1H), 1.57 (s, 3H), 1.10 (m, 21H), 1.09 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.88, 136.18, 134.30, 129.19, 127.62, 121.67, 109.62, 85.93, 70.32, 30.16, 27.84, 18.83, 18.42, 11.37.

IR (neat, cm^{-1}) 3446, 2942, 2864, 2165, 1615, 1463, 1428, 1108, 996, 820, 701.

MS (ESI, pos.) Calcd for $C_{31}H_{46}OSi2Na$ ($[M+Na]^+$): 513.30. Found: 313.20.

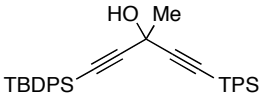
***E*-1-(*tert*-butyl-diphenyl-silyl)-5- triisopropylsilyl -3-methyl-pent-1-yn-4-en-3-ol** (**9c**)



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.78 (m, 4H), 7.40-7.31 (m, 6H), 6.27 (d, *J* = 18.0 Hz, 1H), 6.19 (d, *J* = 18.0 Hz, 1H), 2.21, (s, 1H), 1.66 (s, 3H), 1.06 (m, 21H), 1.05 (s, 9H).

MS (ESI, pos.) Calcd for $C_{31}H_{46}OSi_2Na$ ($[M+Na]^+$): 513.30. Found: 313.20.

1-triphenylsilyl-5-(*tert*-butyl-diphenyl-silyl)-3-methyl-pent-1,4-diyn-3-ol (**7d**)



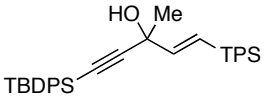
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.80 (m, 4H), 7.70-7.67 (m, 6H), 7.47-7.31 (m, 15H), 2.74 (s, 1H), 1.98 (s, 3H), 1.11 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.85, 133.27, 133.01, 130.34, 129.90, 128.32, 128.07, 110.44, 110.04, 83.44, 82.94, 60.73, 31.35, 26.90, 18.54.

IR (neat, cm^{-1}) 3543, 3445, 3071, 2932, 2173, 1960, 1889, 1823, 1428, 1187, 1112, 936, 819, 697.

Anal. Calcd for $C_{40}H_{38}OSi_2$: C, 81.30; H, 6.48. Found: C, 81.71; H, 6.89.

***E*-1-triphenylsilyl-5-(*tert*-butyl-diphenyl-silyl)-3-methyl-pent-1-en-4-yn-3-ol (8d)**



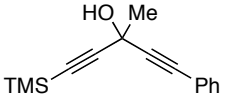
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.76 (m, 4H), 7.54-7.51 (m, 6H), 7.45-7.30 (m, 15H), 6.83 (d, *J* = 18.3 Hz, 1H), 6.33 (d, *J* = 18.3 Hz, 1H), 2.25 (s, 1H), 1.70 (s, 3H), 1.10 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.69, 135.90, 135.51, 134.05, 132.98, 129.65, 129.55, 127.94, 127.76, 122.64, 111.66, 85.31, 70.29, 29.97, 27.25, 18.77.

IR (neat, cm^{-1}) 3445, 3069, 2930, 2858, 2169, 1615, 1428, 1111, 998, 821, 699.

MS (ESI, pos.) Calcd for $C_{40}H_{40}OSi_2Na$ ($[M+Na]^+$): 615.25. Found: 615.15.

1-trimethylsilyl-3-methyl-5-phenyl-pent-1,4-diyn-3-ol (7e)



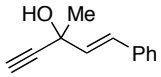
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2H), 7.33-7.30 (m, 3H), 2.75 (s, 1H), 1.86 (s, 3H), 0.21 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 131.86, 128.70, 128.30, 122.23, 106.04, 90.11, 87.26, 82.55, 60.66, 32.02, 0.16.

IR (neat, cm^{-1}) 3369, 2961, 1490, 1165, 1127, 861, 844, 757, 691.

Anal. Calcd for $C_{15}H_{18}OSi$: C, 74.33; H, 7.49. Found: C, 74.46; H, 7.54.

***E*-3-methyl-1-phenyl-pent-1-en-4-yn-3-ol (8e')**, derived from **8e**, **8f** and **9g**.



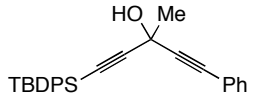
^{1}H NMR (300 MHz, $CDCl_3$) δ7.43-7.39 (m, 2H), 7.60-7.24 (m, 3H), 6.90 (d, *J* = 15.9 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 2.65 (s, 1H), 2.27 (s, 1H), 1.67 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 136.40, 133.01, 129.71, 128.90, 128.28, 127.07, 86.03, 73.23, 68.06, 30.28.

IR (neat, cm^{-1}) 3401, 3069, 2237, 2174, 14901, 1429, 1264, 1162, 1114, 931, 829, 710, 698.

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.44; H, 7.18.

1-(*tert*-butyl-diphenyl-silyl)-3-methyl-5-phenyl-pent-1,4-diyn-3-ol (7f)



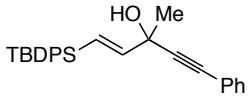
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.81 (m, 4H), 7.50-7.47 (m, 2H), 7.40-7.34 (m, 9H), 2.73 (s, 1H), 1.99 (s, 3H), 1.13 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.54, 132.79, 131.81, 129.62, 128.74, 128.31, 127.77, 122.07, 110.38, 89.89, 83.00, 82.94, 60.90, 31.83, 27.20, 18.87.

IR (neat, cm^{-1}) 3401, 2956, 2930, 2858, 2237, 2173, 1428, 1162, 1111, 931, 820, 756, 700.

Anal. Calcd for $C_{28}H_{28}OSi$: C, 82.30; H, 6.91. Found: C, 82.13; H, 7.14.

***E*-1-(*tert*-butyl-diphenyl-silyl)-3-methyl-5-phenyl-pent-1-en-4-yn-3-ol (9f)**



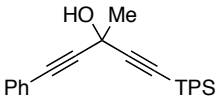
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.46 (m, 4H), 7.46-7.31 (m, 11H), 6.64 (d, *J* = 18.6 Hz, 1H), 6.26 (d, *J* = 18.6 Hz, 1H), 2.21 (s, 1H), 1.66 (s, 3H), 1.12 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.87, 136.20, 134.29, 134.26, 131.71, 129.24, 128.44, 128.30, 127.65, 122.63, 121.44, 91.15, 85.25, 70.12, 30.11, 27.91, 18.48.

IR (neat, cm^{-1}) 3418, 3070, 2928, 2857, 2229, 1599, 1488, 1428, 1107, 998, 921, 820, 701.

MS (ESI, pos.) Calcd for $C_{28}H_{30}OSiNa$ ($[M+Na]^+$): 433.20. Found: 433.12.

1-triphenylsilyl-3-methyl-5-phenyl-pent-1,4-diyn-3-ol (7g)



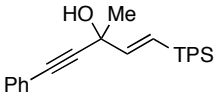
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72-7.69 (m, 6H), 7.51-7.34 (m, 14H), 2.94 (s, 1H), 1.98 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.87, 133.33, 132.10, 130.32, 129.01, 128.56, 128.28. 122.31, 110.94, 89.90, 83.07, 82.68, 60.81, 31.55.

IR (neat, cm^{-1}) 3369, 3294, 2984, 1492, 1448, 1273, 968, 918, 749, 692.

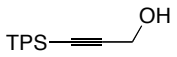
Anal. Calcd for $C_{30}H_{24}OSi$: C, 84.07; H, 5.64. Found: C, 83.92; H, 5.99.

***E*-1-triphenylsilyl-3-methyl-5-phenyl-pent-1-en-4-yn-3-ol (8g)**



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.55 (m, 6H), 7.55-7.29 (m, 14H), 6.77 (d, *J* = 18.3 Hz, 1H), 6.36 (d, *J* = 18.3 Hz, 1H), 2.28 (s, 1H), 1.68 (s, 3H).

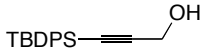
3-(triphenyl-silyl)-propargylalcohol (10)[4]



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.63 (m, 6H), 7.46-7.35 (m, 9H), 4.43 (d, *J* = 6.3 Hz, 2H), 1.70 (t, *J* = 6.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.50, 132.99, 130.04, 128.00, 108.37, 85.95, 52.03.

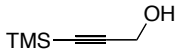
3-(*tert*-butyl-diphenyl-silyl)-propargylalcohol (11)[3]



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.78 (m, 4H), 7.42-7.35 (m, 6H), 4.44 (br, 2H), 1.70 (br, 1H), 1.12 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.52, 132.89, 129.59, 127.74, 107.84, 86.06, 52.00, 27.20, 18.67.

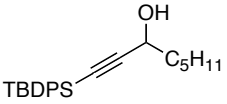
3-(trimethyl-silyl)-propargylalcohol (12)[5]



^{1}H NMR (300 MHz, $CDCl_3$) δ 4.27 (d, *J* = 5.4 Hz, 2H), 1.75 (br, 1H), 0.19 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 103.81, 90.75, 51.78, 0.00.

1-(*tert*-butyl-diphenyl-silyl)-oct-1-yn-3-ol (13)



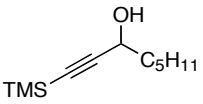
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.78 (m, 4H), 7.42-7.37 (m, 6H), 4.53 (dt, *J* = 6.6, 6.6 Hz, 1H), 1.91 (d, *J* = 6.6 Hz, 1H), 1.87-1.79 (m, 2H), 1.63-1.52 (m, 2H), 1.40-1.31 (m, 4H), 1.10 (s, 9H), 0.92 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.63, 133.17, 129.63, 127.80, 111.22, 84.75, 63.24, 37.87, 31.53, 27.11, 24.96, 22.68, 18.57, 14.06.

IR (neat, cm^{-1}) 3336, 2956, 2930, 2858, 2172, 1470, 1428, 1110, 1028, 699.

Anal. Calcd for $C_{24}H_{32}OSi$: C, 79.06; H, 8.95. Found: C, 79.34; H, 9.05.

1-trimethylsilyl -oct-1-yn-3-ol (14)



^{1}H NMR (300 MHz, $CDCl_3$) δ 4.35 (dt, *J* = 6.6, 6.6 Hz, 1H), 1.73-1.65 (m, 3H), 1.50-1.38 (m, 2H), 1.38-1.27 (m, 4H), 0.90 (t, *J* = 6.6 Hz, 3H), 0.17 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 107.03, 89.36, 63.01, 37.76, 31.47, 24.85, 22.60, 14.03, 0.05.

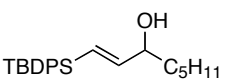
IR (neat, cm^{-1}) 3339, 2959, 2934, 2862, 2173, 1463, 1250, 1032, 843, 760.

Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.66; H, 11.18.

Competitive Experiment of hydroalumination reaction between 13 and 14:

To a solution of **13** and **14** (53.7 mg, 0.192 mmol, **13**:**14** = 50:50) in toluene (7 mL) at 0 °C was added Red-Al (0.110 mL of 1.75 M solution in toluene, 0.192 mmol) and stirred for 5 min at that temperature. The reaction was quenched by $Na_2SO_4 \cdot 10H_2O$, diluted with hexane (10 mL) and added Na_2SO_4. After the organic layer changed to clear, the slurry was filtered and the solvent was removed *in vacuo*. The crude product was analyzed by ^{1}H-NMR and determined the yields (**13**: 40%, **14**: 95%, **15**: 60%, **16**: 5%).

***E*-1-(*tert*-butyl-diphenyl-silyl) -oct-1-en-3-ol (15)**



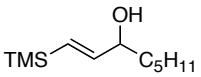
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.58 (m, 4H), 7.41-7.30 (m, 6H), 6.28 (dd, *J* = 18.9, 1.2 Hz, 1H), 6.10 (dd, *J* = 18.9, 4.8 Hz, 1H), 4.21 (m, 1H), 1.58-1.26 (m, 9H), 1.09 (s, 9H), 0.89 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 154.41, 136.31, 134.63, 129.22, 127.65, 122.23, 74.84, 37.00, 31.82, 27.81, 25.08, 22.70, 18.23, 14.08.

IR (neat, cm^{-1}) 3351, 2929, 2857, 1621, 1470, 1427, 1107, 999, 701.

Anal. Calcd for $C_{24}H_{34}OSi$: C, 78.63; H, 9.35. Found: C, 78.50; H, 9.35.

***E*-1-trimethylsilyl -oct-1-en-3-ol (16)**



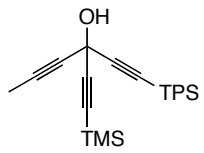
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.04 (dd, *J* = 18.6, 5.1 Hz, 1H), 6.10 (dd, *J* = 18.6, 1.2 Hz, 1H), 4.07 (m, 1H), 1.59-1.22 (m, 9H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.06 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.05, 129.42, 74.79, 36.84, 31.68, 24.93, 22.46, 13.85, –1.52.

IR (neat, cm^{-1}) 3342, 2955, 1620, 1467, 1247, 989, 838.

Anal. Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07. Found: C, 65.70; H, 11.81.

1-triphenylsilyl-5-trimethylsilyl-3-(1-propyn)-pent-1,4-diyn-3-ol (17)



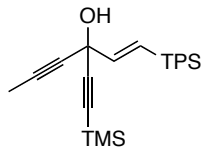
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.65 (m, 6H), 7.47-7.36 (m, 9H), 2.95 (s, 1H), 1.93 (s, 3H), 0.24 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.61, 132.77, 130.07, 127.99, 106.79, 101.80, 88.02, 82.80, 80.77, 76.80, 54.96, 4.05, –0.19.

IR (neat, cm^{-1}) 3522, 3069, 2960, 2243, 2179, 1429, 1251, 1113, 1083, 1018, 845, 710, 699.

MS (ESI, pos.) Calcd for $C_{29}H_{28}OSi_2Na$ ([M+Na]$^+$): 471.16. Found: 471.10.

1-triphenylsilyl-5-trimethylsilyl-3-(1-propyn)-pent-1-en-4-yn-3-ol (18)



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.53 (m, 6H), 7.44-7.35 (m, 9H), 2.55 (s, 1H), 1.92 (s, 3H), 0.23 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.90, 136.17, 134.14, 129.88, 128.12, 123.81, 103.91, 90.12, 82.62, 78.20, 65.44, 4.29, 0.19.

IR (neat, cm^{-1}) 3536, 3068, 2959, 2243, 2171, 1613, 1428, 1250, 1112, 997, 860, 844, 700.

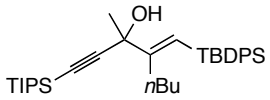
MS (ESI, pos.) Calcd for $C_{29}H_{28}OSi_2Na$ ([M+Na]$^+$): 473.17. Found: 473.13.

Carbolithiation reaction of alcohol 7c:

To a solution of **7c** (43.3 mg, 0.0886 mmol) in toluene (5 mL) was added *n*BuLi (0.409 mL of 1.08 M solution in

hexane, 0.443 mmol) and TMEDA (13.4 μL, 0.0886 mmol) at 0 °C and the mixture was warmed up to room temperature. After 22h, the reaction was quenched by sat. aq. NH_4Cl and the aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated in *vacuo* and the residue was purified by silica gel chromatography (hexane:AcOEt = 20:1) to afford 34.8 mg of **19** (80%). To a solution of **19** in THF (5 mL) was added TBAF (0.3 ml of 1.0 M solution in THF, 0.3 mmol) at room temperature. After 15 min, the reaction was quenched by sat. aq. $NaHCO_3$ and the aqueous layer was extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4 and filtered. The filtrate was concentrated in *vacuo* and the residue was purified by silica gel chromatography (hexane:AcOEt = 20:1) to afford 27.6 mg of **19'** (100%).

***E*-1-(*tert*-butyl-diphenyl-silyl)-5- triisopropylsilyl -2-*n*-butyl-3-methyl-pent-1-en-4-yn-3-ol (19)**



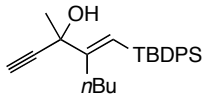
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.67 (m, 4H), 7.40-7.30 (m, 6H), 6.40 (s, 1H), 2.11 (s, 1H), 2.05-1.85 (m, 2H), 1.70 (s, 3H), 1.18-0.80 (m, 23H), 1.03 (s, 9H), 0.60-0.40 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 165.31, 136.13, 136.10, 135.04, 129.02, 129.00, 127.50, 127.47, 116.44, 111.45, 84.86, 72.99, 33.95, 32.76, 31.70, 27.73, 23.28, 18.83, 18.52, 13.71, 11.40.

IR (neat, cm^{-1}) 3454, 2958, 2864, 1603, 1464, 1428, 1362, 1106, 883, 701.

MS (ESI, pos.) Calcd for $C_{35}H_{54}OSi_2Na$ ($[M+Na]^+$): 569.36. Found: 569.32.

***E*-1-(*tert*-butyl-diphenyl-silyl)-2-*n*-butyl-3-methyl-pent-1-en-4-yn-3-ol (19')**



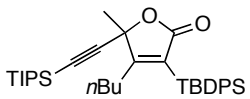
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.66 (m, 4H), 7.40-7.32 (m, 6H), 6.40 (s, 1H), 2.58, (s, 1H), 2.15 (s, 1H), 2.02-1.84 (m, 2H), 1.70 (s, 3H), 1.08-0.86 (m, 2H), 1.03 (s, 9H), 0.60-0.52 (m, 2H), 0.50-40 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 164.73, 136.11, 136.08, 134.88, 134.71, 129.07, 127.55, 127.52, 116.79, 87.50, 72.61, 72.57, 33.55, 32.65, 31.42, 27.75, 23.17, 18.58, 13.68.

IR (neat, cm^{-1}) 3445, 3306, 2957, 2930, 2857, 1603, 1470, 1427, 1363, 1105, 819, 740, 701.

MS (ESI, pos.) Calcd for $C_{26}H_{34}OSiNa$ ($[M+Na]^+$): 413.23. Found: 413.12.

3-(tert-butyl-diphenyl-silyl)-5-methyl-5-[(triisopropyl)-ethynyl]-5*H*-furan-2-one (20)



This compound was prepared from alcohol **7c** by the same reaction condition of the preparation of alcohol **19** then quenched with CO_2 gas (supplied from CO_2 cylinder and dried with $SiO_2/CaCl_2$ column) instead of sat. aq. NH_4Cl.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.58 (m, 4H), 7.44-7.32 (m, 6H), 1.93(ddd, *J* = 13.2, 12.3, 5.1, 1H), 1.81

(ddd, J = 13.2, 12.3, 4.8, 1H), 1.73 (s, 3H), 1.18 (s, 9H), 1.06-0.85 (m, 23H), 0.70-0.47 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 185.50, 174.74, 135.93. 135.80, 133.96. 133.67, 129.56, 127.84, 122.14, 103.37, 88.72, 82.70, 31.58, 29.89, 29.28, 28.78, 27.13, 23.36, 18.71, 13.44, 11.26.

IR (neat, cm^{-1}) 2941, 1757, 1589, 1463, 1220, 1107, 987, 883, 701.

MS (ESI, pos.) Calcd for $C_{36}H_{52}O_2Si_2Na$ ($[M+Na]^+$): 595.34. Found: 595.20.

References and Notes

[1] E, Brown, A. Lézé, J. Touet, *Tetrahedron Lett.* **1991**, *32*, 4309-4310.

[2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

[3] Alcohol **3a** and **11** were prepared in the total synthesis of zaragozic acid A: see ref. [3] in the main article.

[4] Alcohol **12** is reported compound: J. M. Schwab, T. Ray, C. -K. Ho, *J. Am. Chem. Soc.* **1989**, *111*, 1057-1063.

[5] Alcohol **10** is available from Aldrich.