Supporting Information

Trialkylsilyl group-directed regioselective transformations of 2-(alk-1-yn-1-yl)-2-(trialkylsilyl)-1,3-dithianes to alkynylcyclopropanes and enynes

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Experimental procedures and characterization data for compounds **5a-i**, **10a-j**, **11a**, **11b**, **11f**, and **12a-f**.

A typical experimental procedure for cyclopropanation: Cp_2TiCl_2 (149 mg, 0.6 mmol), magnesium turnings (17 mg, 0.7 mmol; purchased from Nacalai Tesque Inc. Kyoto, Japan), and finely powdered molecular sieves 4 A (60 mg) were placed in a flask and dried with heating in vacuo. After cooling, THF (1.2 ml), $\text{P}(\text{OEt})_3$ (0.21 ml, 1.2 mmol), and **2c** (0.36 ml, 2.4 mmol) were added successively with stirring at 25 °C under argon. After 3 h, **6a** (100 mg, 0.3 mmol) in THF (0.9 ml) was added to the mixture, and stirring was continued for 1 h. The reaction was quenched by addition of 1 M NaOH, and the resulting insoluble materials were filtered off through Celite and washed with ether. The organic materials were extracted with ether and dried. After removal of the solvent, the residue was purified by PTLC (hexane : AcOEt = 98 : 2) to give **5c** (73 mg, 67%).

A typical experimental procedure for carbonyl olefination: To a THF (1.8 ml) solution of **4**, prepared from Cp_2TiCl_2 (224 mg, 0.9 mmol), magnesium turnings (26 mg, 1.1 mmol), molecular sieves 4 A (90 mg), and $\text{P}(\text{OEt})_3$ (0.31 ml, 1.8 mmol), was added a THF (0.9 ml) solution of **6d** (82 mg, 0.3 mmol) at 25 °C. After 10 min, **9e** (86 mg, 0.36 mmol) in THF (0.9 ml) was added dropwise over 5 min and the mixture was stirred for 1 h. The usual work-up and purification gave **10i** (83 mg, 71%).

Spectral data and elemental analyses

2-Butyl-1-(3-phenylpropyl)-1-[(trimethylsilyl)ethynyl]cyclopropane (5a): IR (neat) 3064, 3026, 2956, 2930, 2858, 2158, 1604, 1496, 1454, 1249, 1031, 841, 759, 698, 634 cm^{-1} ; ^1H NMR δ 0.12 (s, 5.1H), 0.13 (s, 3.9H), 0.22 (dd, J = 6.1, 4.1 Hz, 0.57H), 0.53 (dd, J = 2.2, 4.3 Hz, 0.43H), 0.63-0.74 (m, 0.86H), 0.86-0.92 (m, 3.57H), 1.02 (dd, J = 4.0, 8.6 Hz, 0.57H), 1.06-1.53 (m, 8H), 1.80-1.96 (m, 2H), 2.57-2.75 (m, 2H), 7.14-7.20

(m, 3H), 7.24-7.30 (m, 2H); ^{13}C NMR δ -0.03, 0.00, 13.7, 13.8, 16.1, 18.0, 21.6, 21.7, 22.2, 22.3, 26.1, 27.1, 27.9, 29.0, 29.2, 30.3, 31.1, 31.2, 31.4, 35.2, 35.3, 37.8, 79.3, 82.3, 109.7, 113.3, 124.9, 125.3, 127.88, 127.89, 128.03, 128.04, 142.3. Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{Si}$: C, 80.70; H, 10.32. Found: C, 80.97; H, 10.57.

1-(3-Phenylpropyl)-1-[(trimethylsilyl)ethynyl]cyclopropane (5b): IR (neat) 3086, 3026, 2937, 2859, 2160, 1604, 1496, 1454, 1250, 841, 759, 698 cm^{-1} ; ^1H NMR δ 0.20 (s, 9H), 0.61 (dd, $J = 4.1, 6.5$ Hz, 2H), 0.96 (dd, $J = 4.1, 6.5$ Hz, 2H), 1.40-1.45 (m, 2H), 1.90-2.02 (m, 2H), 2.73 (t, $J = 7.8$ Hz, 2H), 7.21-7.27 (m, 3H), 7.32-7.37 (m, 2H); ^{13}C NMR δ 0.00, 12.2, 15.5, 29.1, 35.2, 37.1, 80.2, 111.7, 125.3, 128.0, 128.1, 142.3. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{Si}$: C, 79.62; H, 9.43. Found: C, 79.32; H, 9.84.

2-Phenethyl-1-(3-phenylpropyl)-1-[(trimethylsilyl)ethynyl]cyclopropane (5c): IR (neat) 3063, 3025, 2938, 2858, 2156, 1603, 1495, 1454, 1248, 1031, 840, 758, 698, 635 cm^{-1} ; ^1H NMR δ 0.13 (s, 5.49H), 0.16 (s, 3.51H), 0.24 (dd, $J = 4.3, 6.5$ Hz, 0.61H), 0.58 (dd, $J = 3.8, 5.4$ Hz, 0.39H), 0.67-0.76 (m, 0.78H), 1.04 (dd, $J = 4.2, 8.8$ Hz, 0.61H), 1.14-1.53 (m, 3.61H), 1.66-1.95 (m, 3H), 2.56-2.86 (m, 4H), 7.15-7.30 (m, 10H); ^{13}C NMR δ -0.03, 0.00, 16.4, 18.2, 21.4, 21.6, 25.5, 26.7, 29.0, 29.2, 30.4, 31.2, 32.6, 35.1, 35.2, 35.3, 35.5, 37.7, 79.6, 82.7, 109.3, 112.9, 125.3, 125.4, 127.86, 127.88, 127.90, 127.94, 128.01, 128.07, 128.12, 141.7, 142.1, 142.18, 142.23. Anal. Calcd for $\text{C}_{25}\text{H}_{32}\text{Si}$: C, 83.27; H, 8.94. Found: C, 83.57; H, 9.21.

2-Benzyl-1-(3-phenylpropyl)-1-[(trimethylsilyl)ethynyl]cyclopropane (5d): IR (neat) 3027, 2937, 2157, 1604, 1496, 1454, 1248, 840, 758 cm^{-1} ; ^1H NMR δ 0.13 (s, 5.58H), 0.16 (s, 3.42H), 0.44 (dd, $J = 4.4, 6.6$ Hz, 0.62H), 0.73 (dd, $J = 4.6, 6.1$ Hz, 0.38H), 0.78 (dd, $J = 4.3, 8.2$ Hz, 0.38H), 0.98-1.04 (m, 0.38H), 1.14 (dd, $J = 4.6, 8.9$ Hz, 0.62H), 1.27-1.32 (m, 0.62H), 1.40-1.60 (m, 2H), 1.79-1.97 (m, 2H), 2.39 (dd, $J = 8.9, 15.3$ Hz, 0.62H), 2.57-2.74 (m, 2.38H), 2.85-2.90 (m, 1H), 7.11-7.33 (m, 10H); ^{13}C NMR δ 0.00, 16.8, 18.8, 21.7, 21.8, 27.4, 27.5, 28.8, 29.2, 31.5, 34.1, 35.0, 35.3, 36.4, 37.6, 80.0, 83.7, 109.5, 112.5, 125.3, 125.4, 125.6, 125.7, 127.9, 128.0, 128.1, 128.3, 140.8, 141.5, 142.2. Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{Si}$: C, 83.17; H, 8.72. Found: C, 83.46; H, 8.81.

1-[(*tert*-Butyldimethylsilyl)ethynyl]-2-phenyl-1-(3-phenylpropyl)cyclopropane (5e): IR (neat) 3026, 2928, 2155, 1603, 1496, 1454, 1249, 835, 774, 697 cm^{-1} ; ^1H NMR δ 0.16 (s, 6H), 0.98-1.04 (m, 10H), 1.06-1.34 (m, 3H), 1.44 (dd, $J = 5.1, 8.7$ Hz, 1H), 1.71-1.98 (m, 2H), 2.41-2.65 (m, 2H), 7.07-7.09 (m, 2H), 7.20-7.34 (m, 8H); ^{13}C NMR

δ -4.4, 16.7, 19.5, 19.7, 26.2, 28.8, 31.7, 31.8, 35.4, 78.8, 113.0, 125.5, 126.4, 128.0, 128.1, 128.2, 129.0, 137.0, 142.4. Anal. Calcd for C₂₆H₃₄Si: C, 83.36; H, 9.15. Found: C, 83.56; H, 8.85.

1-Butyl-1-[(*tert*-butyldimethylsilyl)]ethynyl-2-phenylcyclopropane (5f): IR (neat) 2954, 2158, 1603, 1497, 1462, 1249, 825, 775, 697 cm⁻¹; ¹H NMR δ 0.09 (s, 6H), 0.73 (t, J = 7.2 Hz, 3H), 0.87-0.98 (m, 10H), 1.06-1.25 (m, 4H), 1.33-1.45 (m, 3H), 2.53 (dd, J = 7.9, 7.9 Hz, 1H), 7.19-7.30 (m, 5H); ¹³C NMR δ -4.4, 13.9, 16.7, 19.5, 19.8, 22.3, 26.1, 29.5, 31.7, 31.8, 78.5, 113.3, 126.3, 128.0, 129.1, 137.2; Anal. Calcd for C₂₁H₃₂Si: C, 80.21; H, 9.92. Found: C, 80.27; H, 10.17.

1-Butyl-2-phenethyl-1-[(trimethylsilyl)ethynyl]cyclopropane (5g): IR (neat) 3064, 2957, 2158, 1604, 1496, 1454, 1248, 841, 635 cm⁻¹; ¹H NMR δ 0.12 (s, 7.29H), 0.15 (s, 1.71H), 0.25 (dd, J = 4.2, 6.4 Hz, 0.81H), 0.56 (dd, J = 3.6, 6.6 Hz, 0.19H), 0.68-0.78 (m, 0.38H), 0.90 (t, J = 7.2 Hz, 3H), 1.03 (dd, J = 4.0, 8.8 Hz, 0.81H), 1.13-1.56 (m, 7.81H), 1.79-1.91 (m, 1H), 2.71 (t, J = 7.7 Hz, 2H), 7.18-7.30 (m, 5H); ¹³C NMR (major isomer) δ 0.00, 13.8, 16.6, 21.4, 22.3, 26.8, 29.8, 30.5, 31.5, 35.6, 79.3, 113.2, 125.5, 128.0, 128.1, 141.8. Anal. Calcd for C₂₀H₃₀Si: C, 80.46; H, 10.13. Found: C, 80.27; H, 10.01.

2-Benzyl-1-butyl-1-[(trimethylsilyl)ethynyl]cyclopropane (5h): IR (neat) 3064, 2957, 2159, 1249, 1603, 1496, 1454, 1249, 841, 758, 697 cm⁻¹; ¹H NMR δ 0.12 (s, 6.21H), 0.15 (s, 2.79H), 0.45 (dd, J = 4.4, 6.4 Hz, 0.69H), 0.73 (dd, J = 4.6, 5.9 Hz, 0.31H), 0.77-1.04 (m, 0.62H), 0.86 (t, J = 7.2 Hz, 0.93H), 0.92 (t, J = 7.3 Hz, 2.07H), 1.13 (dd, J = 4.4, 8.8 Hz, 0.69H), 1.22-1.60 (m, 6.69H), 2.44 (dd, J = 8.9, 14.9 Hz, 0.69H), 2.72 (dd, J = 6.2, 14.7 Hz, 0.31H), 2.85-2.96 (m, 1H), 7.17-7.33 (m, 5H); ¹³C NMR δ 0.00, 13.7, 13.8, 17.0, 18.9, 21.6, 21.7, 22.1, 22.4, 27.3, 27.6, 29.4, 29.8, 31.7, 34.2, 36.4, 37.9, 79.7, 83.4, 109.9, 112.8, 125.5, 125.7, 127.90, 127.94, 128.1, 128.3, 140.9, 141.5. Anal. Calcd for C₁₉H₂₈Si: C, 80.21; H, 9.92. Found: C, 80.27; H, 10.17.

1-Methyl-1-[(trimethylsilyl)ethynyl]-2-phenethylcyclopropane (5i): IR (neat) 3064, 2959, 2157, 1603, 1496, 1454, 1249, 840, 698, 631 cm⁻¹; ¹H NMR δ 0.13 (s, 7.29H), 0.14 (s, 1.71H), 0.25 (dd, J = 4.2, 6.2 Hz, 0.81H), 0.57 (dd, J = 3.8, 5.7 Hz, 0.19H), 0.67-0.78 (m, 0.38H), 1.05 (dd, J = 4.1, 8.9 Hz, 0.81H), 1.12-1.23 (m, 0.81H), 1.21 (s, 2.43H), 1.25 (s, 0.57H), 1.46-1.69 (m, 1H), 1.67-1.84 (m, 1H), 2.70-2.81 (m, 2H), 7.16-7.30 (m, 5H); ¹³C NMR (major isomer) δ 0.0, 11.1, 18.0, 22.3, 26.5, 30.7, 35.6,

78.1, 114.3, 125.5, 128.0, 128.2, 141.8. Anal. Calcd for C₁₇H₂₄Si: C, 79.62; H, 9.43. Found: C, 79.98; H, 9.82.

A mixture of 4-ethyl-3-(3-phenylpropyl)-1-(trimethylsilyl)hex-3-en-1-yne (10a) and 3-ethyl-9-phenyl-4-(trimethylsilyl)non-3-en-5-yne (11a): IR (neat) 2964, 2133, 1454, 1249, 841, 758, 698 cm⁻¹; ¹H NMR δ 0.19 (s, 7.20H), 0.21 (s, 1.80H), 0.94 (t, *J* = 7.6 Hz, 2.40H), 0.99-1.09 (m, 3.6H), 1.85 (quint, *J* = 7.7 Hz, 2H), 2.07 (q, *J* = 7.5 Hz, 1.60H), 2.16 (q, *J* = 7.6 Hz, 1.60H), 2.22 (q, *J* = 8.1 Hz, 0.40H), 2.36 (q, *J* = 7.8 Hz, 2H), 2.45 (q, *J* = 7.5 Hz, 0.40H), 2.63 (t, *J* = 7.8 Hz, 1.60H), 2.75 (t, *J* = 7.7 Hz, 0.40H), 7.13-7.31 (m, 5H); ¹³C NMR δ 0.0, 0.3, 12.5, 12.6, 12.8, 13.3, 19.2, 23.8, 27.75, 27.78, 28.1, 30.2, 30.5, 30.9, 34.9, 35.1, 94.9, 95.7, 106.0, 116.4, 125.4, 125.6, 128.0, 128.1, 128.2, 128.3, 141.8, 142.4, 153.0, 167.1. Anal. Calcd for C₂₀H₃₀Si: C, 80.46; H, 10.13. Found: C, 80.39; H, 10.12.

A mixture of 1-(*tert*-butyldimethylsilyl)-4-ethyl-3-(3-phenylpropyl)hex-3-en-1-yne (10b) and 4-(*tert*-butyldimethylsilyl)-3-ethyl-9-phenylnon-3-en-5-yne (11b): IR (neat) 2932, 2134, 1604, 1496, 1454, 1361, 1248, 1007, 832 cm⁻¹; ¹H NMR δ 0.12 (s, 5.64H), 0.22 (s, 0.36H), 0.91-1.05 (m, 15H), 1.86 (tt, *J* = 7.7, 7.7 Hz, 2H), 2.03-2.24 (m, 4H), 2.36 (q, *J* = 7.5 Hz, 1.88H), 2.46 (q, *J* = 7.5 Hz, 0.12H), 2.62 (t, *J* = 7.8 Hz, 1.88H), 2.74 (t, *J* = 7.8 Hz, 0.12H), 7.14-7.31 (m, 5H); ¹³C NMR (major isomer) δ -4.4, 12.8, 13.0, 16.7, 24.1, 26.1, 26.2, 28.0, 30.4, 30.7, 34.2, 35.3, 94.1, 106.6, 116.7, 125.6, 128.2, 128.4, 142.6, 153.0. Anal. Calcd for C₂₃H₃₆Si: C, 81.10; H, 10.65. Found: C, 81.39; H, 11.05.

1-(*tert*-Butyldimethylsilyl)-4-methyl-3-(3-phenylpropyl)pent-3-en-1-yne (10c): IR (neat) 2928, 2136, 1604, 1496, 1454, 1249, 1008, 826, 774 cm⁻¹; ¹H NMR δ 0.12 (s, 6H), 0.95 (s, 9H), 1.70 (s, 3H), 1.85 (tt, *J* = 7.6, 7.7 Hz, 2H), 1.97 (s, 3H), 2.17 (t, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 7.13-7.20 (m, 3H), 7.23-7.29 (m, 2H); ¹³C NMR δ -4.4, 16.7, 19.8, 23.9, 26.2, 30.0, 31.2, 35.2, 94.1, 106.8, 117.3, 125.6, 128.2, 128.4, 141.5, 142.5. Anal. Calcd for C₂₁H₃₂Si: C, 80.70; H, 10.32. Found: C, 80.96; H, 10.70.

[1-(*tert*-Butyldimethylsilyl)-6-phenylhex-1-yn-3-yliden]cyclohexane (10d): IR (neat) 2928, 2855, 2136, 1453, 1496, 1249, 836, 774, 698 cm⁻¹; ¹H NMR δ 0.12 (s, 6H), 0.94 (s, 9H), 1.45-1.63 (m, 6H), 1.84 (tt, *J* = 7.6, 7.6 Hz, 2H), 2.16 (t, *J* = 5.6 Hz, 2H), 2.20 (t, *J* = 7.4 Hz, 2H), 2.49 (t, *J* = 5.4 Hz, 2H), 2.62 (t, *J* = 7.8 Hz, 2H), 7.14-7.20 (m, 3H),

7.23-7.30 (m, 2H); ^{13}C NMR δ -4.4, 16.7, 26.2, 26.6, 27.86, 27.95, 30.1, 30.5, 30.8, 34.1, 35.3, 94.0, 106.8, 114.1, 125.6, 128.2, 128.4, 142.6, 149.2. Anal. Calcd for $\text{C}_{24}\text{H}_{36}\text{Si}$: C, 81.75; H, 10.29. Found: C, 82.08; H, 10.61.

1-(*tert*-Butyldimethylsilyl)-4-methyl-3-(3-phenylpropyl)hex-3-en-1-yne (10e): IR (neat) 3305, 3026, 2927, 2854, 2087, 1496, 1452, 1350, 669 cm^{-1} ; ^1H NMR δ 0.12 (s, 6H), 0.92-1.04 (m, 3H), 0.95 (s, 9H), 1.67 (s, 2.49H), 1.85 (tt, $J = 7.6$, 7.6 Hz, 2H), 1.96 (s, 0.51H), 2.07 (q, $J = 7.6$ Hz, 0.34H), 2.15 (t, $J = 7.2$ Hz, 2H), 2.37 (q, $J = 7.6$ Hz, 1.66H), 2.62 (t, $J = 7.6$ Hz, 2H), 7.14-7.29 (m, 5H); ^{13}C NMR (major isomer) δ -4.4, 12.4, 16.7, 17.3, 26.2, 30.0, 30.7, 31.2, 35.2, 93.89, 106.5, 116.7, 125.6, 128.2, 128.4, 136.3, 142.6, 147.3. Anal. Calcd for $\text{C}_{22}\text{H}_{34}\text{Si}$: C, 80.91; H, 10.49. Found: C, 81.24; H, 10.57.

A mixture of

3-butyl-1-(*tert*-butyldimethylsilyl)-4-phenethyl-6-phenylhex-3-en-1-yne (10f) and 4-(*tert*-butyldimethylsilyl)-3-phenethyldec-3-en-5-yne (11f): IR (neat) 3027, 2953, 2135, 1454, 1249, 836, 774, 698 cm^{-1} ; ^1H NMR δ 0.14 (s, 2.61H), 0.15 (s, 2.61H), 0.229 (s, 0.39H), 0.234 (s, 0.39H), 0.87-0.96 (m, 12H), 1.29 (tt, $J = 7.3$, 7.3 Hz, 1.74H), 1.42-1.54 (m, 2.26H), 2.11 (t, $J = 7.5$ Hz, 1.74H), 2.36-2.47 (m, 2.26H), 2.62-2.82 (m, 6H), 7.15-7.31 (m, 10H); ^{13}C NMR δ -4.4, -3.0, 13.6, 14.1, 16.7, 18.4, 19.6, 22.1, 22.3, 26.2, 27.0, 30.9, 31.2, 31.3, 34.0, 34.77, 34.82, 35.5, 37.5, 37.9, 38.5, 95.0, 97.2, 106.5, 119.9, 125.7, 125.8, 125.9, 126.0, 128.18, 128.24, 128.3, 128.4, 128.5, 141.78, 141.84, 142.1, 142.2, 147.4, 162.8. Anal. Calcd for $\text{C}_{30}\text{H}_{42}\text{Si}$: C, 83.65; H, 9.83. Found: C, 83.86; H, 10.21.

1-[1-(*tert*-butyldimethylsilyl)hept-1-yn-3-yliden]-4-phenylcyclohexane (10g): IR (neat) 2927, 2134, 1492, 1462, 1250, 1006, 826, 774, 698 cm^{-1} ; ^1H NMR δ 0.20 (s, 6H), 1.00 (t, $J = 7.3$ Hz, 3H), 1.03 (s, 9H), 1.36-1.73 (m, 6H), 2.00-2.19 (m, 4H), 2.27 (t, $J = 7.3$ Hz, 2H), 2.71-2.93 (m, 2H), 3.32 (bd, $J = 13.8$ Hz, 1H), 7.23-7.38 (m, 5H); ^{13}C NMR δ -4.4, 14.0, 16.7, 22.3, 26.2, 29.8, 31.19, 31.21, 33.8, 35.0, 35.2, 44.5, 94.1, 106.8, 115.4, 126.0, 126.8, 128.4, 146.6, 147.0. Anal. Calcd for $\text{C}_{25}\text{H}_{38}\text{Si}$: C, 81.89; H, 10.45. Found: C, 81.88; H, 10.52.

1-[1-(*tert*-Butyldimethylsilyl)but-1-yn-3-ylidene]-4-phenylcyclohexane (10h): IR (neat) 2927, 2855, 2141, 1470, 1249, 824, 774, 698 cm^{-1} ; ^1H NMR δ 0.13 (s, 6H), 0.96 (s, 9H), 1.41-1.64 (m, 2H), 1.86 (s, 3H), 1.88-2.11 (m, 4H), 2.61-2.85 (m, 2H), 3.25 (brd,

$J = 13.2$ Hz, 1H), 7.16-7.31 (m, 5H); ^{13}C NMR δ -4.4, 16.7, 18.0, 26.2, 29.8, 33.5, 34.7, 34.8, 44.4, 93.4, 107.5, 109.5, 126.0, 126.8, 128.3, 146.6, 147.4. Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{Si}$: C, 81.41; H, 9.94. Found: C, 81.83; H, 10.34.

1-(*tert*-Butyldimethylsilyl)-3-methyl-4-phenethylhex-3-en-1-yne (10i): IR (neat) 2928, 2137, 1604, 1496, 1454, 1249, 697 cm^{-1} ; ^1H NMR δ 0.14 (s, 6H), 0.96 (s, 9H), 1.79 (s, 3H), 2.40 (dd, $J = 6.1, 10.4$ Hz, 2H), 2.63-2.81 (m, 6H), 7.16-7.32 (m, 10H); ^{13}C NMR δ -4.4, 16.7, 18.4, 26.2, 34.1, 34.2, 34.7, 37.5, 94.0, 107.4, 114.1, 125.8, 126.0, 128.3, 128.36, 128.41, 141.7, 142.1, 147.9. Anal. Calcd for $\text{C}_{27}\text{H}_{36}\text{Si}$: C, 83.44; H, 9.34. Found: C, 83.74; H, 9.24.

1-(*tert*-Butyldimethylsilyl)-3-methyl-4-phenylpent-1-yn-3-ene (10j: major isomer): IR (neat) 2927, 2136, 1470, 1249, 1008, 860, 774, 697 cm^{-1} ; ^1H NMR δ -0.04 (s, 6H), 0.77 (s, 9H), 1.97 (q, $J = 1.1$ Hz, 3H), 2.06 (q, $J = 1.1$ Hz, 3H), 7.16-7.30 (m, 3H), 7.37-7.45 (m, 2H); ^{13}C NMR δ -4.7, 16.6, 20.1, 20.4, 26.0, 93.1, 108.4, 114.4, 126.8, 127.6, 128.1, 143.4, 144.0.

1-(*tert*-Butyldimethylsilyl)-3-methyl-4-phenylpent-1-yn-3-ene (10j: minor isomer): IR (neat) 2928, 2139, 1470, 1250, 1069, 774, 700 cm^{-1} ; ^1H NMR δ 0.17 (s, 6H), 1.00 (s, 9H), 1.78 (q, $J = 1.5$ Hz, 3H), 2.27 (q, $J = 1.5$ Hz, 3H), 7.12-7.17 (m, 2H), 7.20-7.27 (m, 1H), 7.29-7.36 (m, 2H); ^{13}C NMR δ -4.4, 16.7, 20.1, 24.0, 26.2, 95.8, 107.5, 114.7, 126.8, 127.7, 128.1, 142.2, 144.8. Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{Si}$: C, 79.93; H, 9.69. Found: C, 80.13; H, 10.01.

4-Ethyl-3-(3-phenylpropyl)hex-3-en-1-yne (12a): IR (neat) 3307, 3062, 3027, 2966, 2087, 1603, 1496, 1454, 1374, 1076, 1031, 754, 699 cm^{-1} ; ^1H NMR δ 0.95 (t, $J = 7.6$ Hz, 3H), 1.02 (t, $J = 7.5$ Hz, 3H), 1.85 (tt, $J = 7.1, 8.8$ Hz, 2H), 2.08 (q, $J = 7.6$ Hz, 2H), 2.18 (t, $J = 7.6$ Hz, 2H), 2.36 (q, $J = 7.6$ Hz, 2H), 2.63 (t, $J = 7.8$ Hz, 2H), 3.02 (s, 1H), 7.15-7.20 (m, 3H), 7.25-7.30 (m, 2H); ^{13}C NMR δ 12.8, 12.9, 23.9, 27.8, 30.4, 31.0, 35.4, 79.1, 115.4, 125.6, 128.2, 128.4, 142.5, 153.4. Anal. Calcd for $\text{C}_{17}\text{H}_{22}$: C, 90.20; H, 9.80. Found: C, 90.05; H, 9.77.

4-Methyl-3-(3-phenylpropyl)pent-3-en-1-yne (12b): IR (neat) 3304, 3062, 3027, 2929, 2088, 1604, 1496, 1453, 1374, 745, 669 cm^{-1} ; ^1H NMR δ 1.71 (s, 3H), 1.81-1.90 (m, 2H), 1.97 (s, 3H), 2.19 (t, $J = 7.6$ Hz, 2H), 2.62 (t, $J = 7.8$ Hz, 2H), 3.04 (s, 1H), 7.14-7.20 (m, 3H), 7.25-7.30 (m, 2H); ^{13}C NMR δ 19.8, 23.7, 30.0, 31.4, 35.3, 79.1,

84.5, 116.0, 125.6, 128.2, 128.4, 141.9, 142.4. Anal. Calcd for C₁₅H₁₈: C, 90.85; H, 9.15. Found: C, 90.68; H, 9.40.

(6-Phenylhex-1-yn-3-yliden)cyclohexane (12c): IR (neat) 3305, 3026, 2927, 2854, 2087, 1604, 1496, 1452, 1030, 745, 699 cm⁻¹; ¹H NMR δ 1.45-1.66 (m, 6H), 1.83 (tt, *J* = 7.7, 7.7 Hz, 2H), 2.16-2.24 (m, 4H), 2.43-2.54 (m, 2H), 2.62 (t, *J* = 7.9 Hz, 2H), 3.01 (s, 1H), 7.14-7.30 (m, 5H); ¹³C NMR δ 26.5, 27.9, 30.0, 30.5, 30.9, 34.0, 35.3, 79.0, 84.5, 112.8, 125.6, 128.2, 128.4, 142.5, 149.7. Anal. Calcd for C₁₈H₂₂: C, 90.70; H, 9.30. Found: C, 90.49; H, 9.34.

4-Methyl-3-(3-phenylpropyl)hex-3-en-1-yne (12d): IR (neat) 3306, 3027, 2967, 2933, 2859, 2087, 1496, 1454, 699, 633 cm⁻¹; ¹H NMR δ 0.96 (t, *J* = 7.9 Hz, 0.54H), 1.01 (t, *J* = 7.5 Hz, 2.46H), 1.69 (s, 2.46H), 1.84 (tt, *J* = 7.6, 7.6 Hz, 2H), 1.95 (s, 0.54H), 2.09 (q, *J* = 7.6 Hz, 0.36H), 2.18 (t, *J* = 7.4 Hz, 2H), 2.36 (q, *J* = 7.5 Hz, 1.64H), 2.62 (t, *J* = 7.8 Hz, 2H), 3.01 (s, 0.82H), 3.04 (s, 0.18H), 7.14-7.30 (m, 5H); ¹³C NMR (major isomer) δ 12.4, 17.2, 30.0, 30.5, 31.4, 35.3, 78.9, 84.2, 115.4, 125.6, 128.2, 128.4, 142.4, 147.6. Anal. Calcd for C₁₆H₂₀: C, 90.51; H, 9.49. Found: C, 90.64; H, 9.54.

1-(Hept-1-yn-3-ylidene)-4-phenylcyclohexane (12e): IR (neat) 3306, 2925, 2088, 1602, 1493, 1452, 756, 699 cm⁻¹; ¹H NMR δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.26-1.65 (m, 6H), 1.93-2.14 (m, 4H), 2.21 (t, *J* = 7.5 Hz, 2H), 2.67-2.83 (m, 2H), 3.03 (s, 1H), 3.16-3.27 (m, 1H), 7.16-7.32 (m, 5H); ¹³C NMR δ 14.0, 22.3, 29.8, 31.2, 31.3, 33.6, 34.9, 35.2, 44.4, 79.0, 84.6, 114.1, 126.1, 126.8, 128.4, 146.5, 147.6. Anal. Calcd for C₁₉H₂₄: C, 90.42; H, 9.58. Found: C, 90.11; H, 9.73.

3-Methyl-4-phenethyl-6-phenylhex-1-yn-3-en (12f): IR (neat): 3285, 3026, 2928, 2088, 1496, 1454, 750, 699 cm⁻¹; ¹H NMR δ 1.76 (s, 3H), 2.41 (dd, *J* = 6.3, 9.8 Hz, 2H), 2.62-2.79 (m, 6H), 3.09 (s, 1H), 7.16-7.32 (m, 10H); ¹³C NMR δ 18.2, 34.0, 34.2, 34.7, 37.3, 79.2, 85.1, 113.0, 125.8, 126.0, 128.30, 128.32, 128.34, 128.4, 141.6, 142.1, 148.3. Anal. Calcd for C₂₁H₂₂: C, 91.92; H, 8.08. Found: C, 91.62; H, 8.29.