Supporting Information

W(CO)₅(L)-Catalyzed Endo-Selective Cyclization of Allenyl Silyl Enol Ethers : An Efficient Method for the Cyclopentene Annulation onto α,β -Unsaturated Ketones

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General. All operations were performed under an argon atmosphere. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX500, a JEOL AL-400, or a JEOL Lambda-400 spectrometer using CHCl₃ (¹H, δ = 7.24), benzene (¹H, δ = 7.15) and CDCl₃ (¹³C, δ = 77.0) as an internal standard. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. Mass spectra were recorded on a JEOL JMS-700 spectrometer. Photochemical reactions were performed with an USHIO INC. super high-pressure mercury lamp (250 W). Flash column chromatography was conducted on silica gel (Kanto 60N) and preparative thin-layer chromatography (PTLC) was carried out on silica gel (Wako gel B-5F). Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl, and all other solvents were distilled according to the usual procedures and stored over molecular sieves. Indium powder and tungsten hexacarbonyl were purchased from Nacalai Tesque, Inc. and Soekawa Chemical Co., Ltd., respectively, and used without further purification.

Synthesis of cyclic 6-siloxy-1,2,5-triene (2a–2e)

1-(*tert*-Butyldimethylsiloxy)-2-methyl-3-(1-methylpropa-1,2-dienyl)cyclohexene (2a)

A typical procedure is described for the preparation of **2a**.

To a THF (2 mL) solution of 2-methylcyclohex-2-en-1-one **1a** (222 mg, 2.0 mmol) were added dimethylsulfide (1.9 mL, 2.6 mmol) and TBSOTf (0.50 mL, 2.2 mmol) successively at -78°C . After 10 minutes, a THF (2 mL) suspension of organoindium reagent, prepared from 1-bromobut-2-

yne (0.55 mL, 6.2 mmol) and indium (460 mg, 4 mmol) at room temperature for 30 minutes, was added at -78°C . The mixture was slowly warmed to room temperature overnight, and then poured into sat. NaHCO_3 aq. After filtration through a short pad of Celite[®], the aqueous layer was extracted with ether three times. The combined extracts were dried over MgSO_4 and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane:ethyl acetate = 50:1) to give the title compound **2a** (430 mg, 15 mmol) in 77% yield as colorless oil.

IR (neat) 2931, 2858, 1957, 1682, 1255, 1195 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 0.09 (6H, s), 0.93 (9H, s), 1.47–1.75 (4H, m), 1.52 (3H, s), 1.61 (3H, t, J = 3.1 Hz), 1.93–2.05 (2H, m), 2.55–2.63 (1H, m), 4.47–4.58 (2H, m);

^{13}C NMR (CDCl_3) (100 MHz): δ = -3.9 , -3.7 , 15.1, 16.7, 18.2, 20.7, 25.9, 27.5, 30.5, 45.1, 73.6, 100.9, 112.9, 145.2, 207.4;

Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{OSi}$: C 73.31, H 10.86. Found: C 73.09, H 10.99.

1-(*tert*-Butyldimethylsiloxy)-2-methyl-3-(1-methylpropa-1,2-dienyl)cyclopentene (2b)

IR (neat) 2930, 1956, 1687, 1254, 840 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 0.10 (6H, s), 0.92 (9H, s), 1.46 (3H, s), 1.55 (3H, t, J = 2.9 Hz), 1.60–1.72 (1H, m), 1.98–2.10 (1H, m), 2.14–2.36 (2H, m), 3.02–3.10 (1H, m), 4.53 (2H, q, J = 2.9 Hz);

^{13}C NMR (CDCl_3) (100 MHz): δ = -4.1 , -4.0 , 10.6, 14.9, 18.1, 25.6, 25.7, 33.0, 50.0, 73.1, 101.0, 114.1, 148.2, 206.3;

Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{OSi}$: C 72.66, H 10.67. Found: C 72.62, H 10.51.

1-(*tert*-Butyldimethylsiloxy)-5-isopropenyl-2-methyl-3-(1-methylpropa-1,2-dienyl)cyclohexene (2c)

The product **2c** was obtained as a single stereoisomer. The relative stereochemistry between the isopropenyl substituent and prop-2-ynyl substituent was assigned as *trans* on the basis of the relative stereochemistry of **3c**.

IR (neat) 3083, 2929, 1957, 1685, 1192, 835 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 0.10 (6H, s), 0.93 (9H, s), 1.45–1.60 (4H, m), 1.65–1.80 (7H, m), 1.90–2.07 (2H, m), 2.32–2.43 (1H, m), 2.50–2.57 (1H, m), 4.47–4.52 (2H, m), 4.69–4.74 (2H, m);

^{13}C NMR (CDCl_3) (100 MHz): δ = -3.74 , -3.66 , 15.7, 18.2, 18.3, 20.8, 25.9, 31.7, 35.6, 37.6, 44.8, 74.4, 101.1, 108.8, 112.4, 144.3, 149.3, 207.4;

Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{OSi}$: C 75.40, H 10.76. Found: C 75.20, H 10.84.

1-(*tert*-Butyldimethylsiloxy)-3-(1-butylpropa-1,2-dienyl)-5-isopropenyl-2-methylcyclohexene (2d)

The product **2d** was obtained as a single stereoisomer. The relative stereochemistry between the isopropenyl substituent and prop-2-ynyl substituent was assigned as *trans* on the basis of the

relative stereochemistry of **3d**.

IR (neat) 2929, 1954, 1686, 1179, 835 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 0.10 (6H, s), 0.89 (3H, t, J = 7.0 Hz), 0.93 (9H, s), 1.22–1.62 (9H, m), 1.67–1.80 (4H, m), 1.82–2.07 (3H, m), 2.34–2.43 (1H, m), 2.50–2.56 (1H, m), 4.54–4.76 (4H, m);

^{13}C NMR (CDCl_3) (100 MHz): δ = –3.7, –3.6, 14.0, 15.6, 18.2, 20.8, 22.4, 25.9, 30.1, 31.1, 32.0, 35.6, 37.5, 43.9, 76.1, 106.2, 108.7, 112.5, 144.2, 149.4, 207.1;

Anal. Calcd for $\text{C}_{23}\text{H}_{40}\text{OSi}$: C 76.60, H 11.18. Found: C 76.55, H 11.20.

1-(*tert*-Butyldimethylsiloxy)-5-isopropenyl-2-methyl-3-(1-phenylpropa-1,2-dienyl)cyclohexene (2e)

The product **2e** was obtained as a single stereoisomer. The relative stereochemistry between the isopropenyl substituent and prop-2-ynyl substituent was assigned as *trans* on the basis of the relative stereochemistry of **3e**.

IR (neat) 2928, 1938, 1686, 1179, 836 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 1.14 (6H, s), 0.95 (9H, s), 1.57–1.68 (7H, m), 1.73–1.82 (1H, m), 1.96–2.12 (2H, m), 2.38–2.46 (1H, m), 3.29–3.33 (1H, m), 4.62–4.68 (2H, m), 4.97 (1H, dd, J = 11.6, 2.1 Hz), 5.06 (1H, dd, J = 11.4, 2.5 Hz), 7.18 (1H, t, J = 7.5 Hz), 7.30 (2H, t, J = 7.5 Hz), 7.42 (2H, t, J = 7.5 Hz);

^{13}C NMR (CDCl_3) (100 MHz): δ = –3.7, –3.6, 15.7, 18.2, 20.8, 25.9, 32.3, 35.7, 37.5, 41.2, 78.4, 108.4, 108.9, 112.1, 126.5, 126.6, 128.4, 136.5, 145.0, 149.0, 209.7;

Anal. Calcd for $\text{C}_{25}\text{H}_{36}\text{OSi}$: C 78.89, H 9.53. Found: C 79.17, H 9.54.

Synthesis of cyclic 5-siloxy-1,2,5-triene (6a)

1-*tert*-Butyldimethylsiloxy-1-(2-vinylidenecyclohexyl)ethene (6a)

To a CH_2Cl_2 (4 mL) solution of 1-acetyl-2-vinylidenecyclohexane¹ (200 mg, 1.33 mmol) were added *i*-Pr₂NEt (0.47 mL, 2.7 mmol) and TBSOTf (0.46 mL, 2.0 mmol) at –78 °C. The reaction mixture was further stirred at –78 °C. After 1 hour, the reaction was quenched with pH7 phosphate buffer. The aqueous layer was extracted with ether three times, and the combined extracts were washed with brine and dried over MgSO_4 . The solvent was removed under reduced pressure and the residue was purified by deactivated alumina-gel column chromatography (hexane:ethyl acetate=50:1) to give **6a** (251 mg, 0.95 mmol) in 72 % yield as colorless oil.

IR (neat) 2930, 1962, 1618, 1253 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 0.15 (6H, s), 0.90 (9H, s), 1.20–1.43 (2H, m), 1.47–1.78 (4H, m), 1.95–2.07 (1H, m), 2.22–2.32 (1H, m), 2.66–2.74 (1H, m), 4.03 (1H, s), 4.06 (1H, s), 4.56 (2H, s);

^{13}C NMR (CDCl_3) (100 MHz): δ = –4.8, –4.7, 18.1, 24.5, 25.7, 27.0, 30.2, 30.6, 46.8, 74.0, 89.0, 102.4, 159.9, 203.8;

Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{OSi}$: C 72.66, H 10.67. Found: C 72.37, H 10.59.

Synthesis of acyclic 5-siloxy-1,2,5-triene (6b and 6c)

3,3-Dimethyl-4-phenylhexa-4,5-dien-2-ol (9b)

To a THF (10 mL) solution of 2,2-dimethyl-3-phenylpenta-3,4-dienal **8**² (2.0 g, 11 mmol) was added a 0.93 M THF solution of methylmagnesium bromide (13.7 mL, 13 mmol) at 0 °C. After 10 minutes, the reaction was quenched with pH7 phosphate buffer. The aqueous layer was extracted with ethyl acetate three times, and the combined extracts were washed with brine and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (hexane:ethyl acetate=10:1) to give **9b** (1.9 g, 9.5 mmol) in 89% yield as colorless oil.

IR (neat) 3428, 3054, 2973, 1948, 1069 cm⁻¹;

¹H NMR (CDCl₃) (400 MHz): δ = 1.03 (3H, s), 1.11 (3H, s), 1.16 (3H, d, *J* = 6.5 Hz), 1.86 (1H, br s), 3.79 (1H, q, *J* = 6.5 Hz), 4.82 (2H, s), 7.20–7.32 (5H, m);

¹³C NMR (CDCl₃) (100 MHz): δ = 17.1, 21.6, 23.7, 42.0, 71.9, 75.8, 112.0, 127.0, 128.0, 129.4, 136.7, 207.2;

Anal. Calcd for C₁₄H₁₈O: C 83.12, H 8.97. Found: C 82.84, H 8.97.

4,4-Dimethyl-5-phenylhepta-5,6-dien-3-ol (9c)

Alkylation of 2,2-dimethyl-3-phenylpenta-3,4-dienal using a THF solution of EtMgCl was carried out as above to give **9c** in 57% yield as colorless oil.

IR (neat) 3434, 3054, 2970, 1948, 1465 cm⁻¹;

¹H NMR (CDCl₃) (400 MHz): δ = 0.99 (3H, t, *J* = 7.5 Hz), 1.04 (3H, s), 1.11 (3H, s), 1.26–1.40 (1H, m), 1.58–1.70 (1H, m), 1.79 (1H, br s), 3.41 (1H, dd, *J* = 10.4, 1.7 Hz), 4.81 (2H, s), 7.15–7.35 (5H, m);

¹³C NMR (CDCl₃) (100 MHz): δ = 11.6, 22.6, 23.3, 24.2, 42.1, 75.7, 77.9, 112.1, 126.9, 128.0, 129.4, 136.7, 207.3;

Anal. Calcd for C₁₅H₂₀O: C 83.28, H 9.32. Found: C 83.14, H 9.53.

3,3-Dimethyl-4-phenylhexa-4,5-dien-2-one (10b)

To a CH₂Cl₂ (15 mL) solution of **9b** (1.9 g, 9.5 mmol) were added TPAP (125 mg, 0.35 mmol), NMO (1.75 g, 15 mmol), and MS 4A (48 g) at room temperature. After 1 hour, the reaction mixture was filtered through a short pad of neutral alumina-gel, and concentrated under reduced

pressure. The residue was purified by silica-gel column chromatography (hexane:ethyl acetate=10:1) to give **10b** (1.8 g, 9.0 mmol) in 95% yield as yellowish oil.

IR (neat) 3056, 2978, 1939, 1708, 1120 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 1.32 (6H, s), 2.16 (3H, s), 5.17 (2H, s), 7.11–7.30 (5H, m);

^{13}C NMR (CDCl_3) (100 MHz): δ = 25.0, 25.2, 49.8, 78.9, 111.0, 126.9, 127.2, 128.4, 134.9, 209.0, 212.8;

Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: C 83.96, H 8.05. Found: C 83.70, H 8.24.

4,4-Dimethyl-5-phenylhexa-5,6-dien-3-one (**10c**)

Oxidation of **10c** was carried out according to the same procedure as that of the synthesis of **10b** to give **10c** in 79% yield as colorless oil.

IR (neat) 3056, 2978, 1939, 1709 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 0.98 (3H, t, J = 7.2 Hz), 1.32 (6H, s), 2.54 (2H, q, J = 7.2 Hz), 5.16 (2H, s), 7.21–7.36 (5H, m);

^{13}C NMR (CDCl_3) (100 MHz): δ = 8.4, 25.3, 30.1, 49.5, 78.9, 111.1, 126.9, 127.2, 128.4, 135.0, 209.2, 215.5;

Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$: C 84.07, H 8.47. Found: C 83.77, H 8.57.

2-Triethylsiloxy-3,3-dimethyl-4-phenylhexa-1,4,5-triene (**6b**)

Silylation of **10b** using TESOTf was carried out according to the same procedure as that of the synthesis of **6a** to give **6b** in 99% yield as colorless oil.

IR (neat) 3056, 2956, 1945, 1612 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 0.69 (6H, q, J = 8.1 Hz), 0.97 (9H, t, J = 8.1 Hz), 1.27 (6H, s), 4.06–4.08 (1H, m), 4.17–4.19 (1H, m), 4.90 (2H, s), 7.14–7.28 (3H, m), 7.38–7.42 (2H, m);

^{13}C NMR (CDCl_3) (100 MHz): δ = 5.0, 6.7, 27.3, 42.6, 76.5, 87.3, 112.0, 126.4, 127.6, 128.6, 137.1, 164.0, 209.0;

Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{OSi}$: C 76.37, H 9.61. Found: C 76.26, H 9.80.

3-Triethylsiloxy-4,4-dimethyl-5-phenylhepta-2,5,6-triene (**6c**)

Silylation of **10c** by the use of TESOTf was carried out according to the same procedure as that of the synthesis of **6a** to give **6c** in 64% yield as colorless oil. This compound **6c** was obtained as a 96:4 mixture of two geometrical isomers. The geometry was not determined.

IR (neat) 3057, 2957, 1943, 1661, 1320 cm^{-1} ;

Major isomer: ^1H NMR (CDCl_3) (400 MHz): δ = 0.70 (6H, q, J = 8.0 Hz), 0.97 (9H, t, J = 8.0 Hz), 1.20 (6H, s), 1.52 (3H, d, J = 6.8 Hz), 4.62 (1H, q, J = 6.8 Hz), 4.90 (2H, s), 7.13–7.24 (3H, m), 7.32–7.38 (2H, m);

^{13}C NMR (CDCl_3) (100 MHz): δ = 6.2, 7.0, 11.5, 27.5, 42.5, 76.6, 99.8, 112.8, 126.4, 127.6, 128.8, 136.9, 155.8, 208.6;

Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{OSi}$: C 76.77, H 9.82. Found: C 76.48, H 9.78.

General procedure for the endo cyclization of 2 and 6 in the presence of H₂O (3a-3e, 7a-7c)

To a degassed THF (5 mL) solution of a cyclization precursor (0.2 mmol) were added W(CO)₆ (70 mg, 0.2 mmol) and H₂O (10.8 μ L, 0.6 mmol) at room temperature. The mixture was irradiated using high-pressure 250W mercury lamp at ambient temperature (rt~40 °C) until the starting material disappeared (8~10 hours), and then the resulting mixture was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate=20:3) to give the cyclized product.

Catalytic Reaction: to a degassed THF (2 mL) solution of a cyclization precursor (0.2 mmol) was added W(CO)₆ (7 mg, 0.02 mmol) and H₂O (10.8 μ L, 0.6 mmol) at room temperature. The mixture was irradiated using high-pressure 250W mercury lamp at ambient temperature (rt~40 °C) until the starting material disappeared (8~10 hours). The purification was carried out by the same procedure as mentioned above.

1,7-Dimethylbicyclo[4.3.0]non-7-en-2-one (3a)

The stereochemistry of the ring junction of **3a** was assigned as *cis* on the basis of differential NOE spectra.

IR (neat) 3040, 2930, 1704, 1452 cm⁻¹;

¹H NMR (CDCl₃) (400 MHz): δ = 1.17 (3H, s), 1.49–1.58 (1H, m), 1.64 (3H, s), 1.64–1.74 (2H, m), 1.76–1.87 (1H, m), 1.92–1.99 (1H, m), 2.30–2.38 (2H, m), 2.42–2.50 (1H, m), 2.71–2.80 (1H, m), 5.29 (1H, s);

¹³C NMR (CDCl₃) (100 MHz): δ = 14.7, 21.4, 24.4, 25.7, 38.5, 42.4, 54.8, 56.8, 123.4, 141.5, 216.6;

HRMS (EI⁺): Calcd for C₁₁H₁₆O, M 164.1201. Found m/z 164.1222.

2,5-Dimethylbicyclo[3.3.0]oct-2-en-6-one (3b)

IR (neat) 3039, 2928, 1737, 1448, 1121 cm⁻¹;

¹H NMR (CDCl₃) (400 MHz): δ = 1.14 (3H, s), 1.67 (3H, s), 1.87–2.30 (5H, m), 2.45–2.55 (1H, m), 2.83–2.90 (1H, m), 5.23 (1H, s);

¹³C NMR (CDCl₃) (100 MHz): δ = 14.6, 20.9, 21.8, 36.1, 43.6, 55.0, 57.2, 124.8, 140.7, 225.4;

HRMS (EI⁺): Calcd for C₁₀H₁₄O, M 150.1045. Found m/z 150.1045.

4-Isopropenyl-1,7-dimethylbicyclo[4.3.0]non-7-en-2-one (3c)

The relative stereochemistry between the angular methyl group (H_a) and H_b , H_d , and H_e was assigned as *cis* to each other on the basis of the observed NOEs shown below. The large coupling constants ($J_{H_c-H_d} = J_{H_c-H_e} = 11.9$ Hz) in the ^1H -NMR spectrum (C_6D_6) clearly indicated that all the three protons (H_c , H_d , and H_e) were situated on axial position. Therefore, the stereochemistry of **3c** was unambiguously determined as shown below.

IR (neat) 3041, 2929, 1705, 1645, 1442, 891 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 1.21 (3H, s), 1.64 (3H, s), 1.64–1.73 (1H, m), 1.72 (3H, s), 1.89–1.99 (2H, m), 2.20–2.48 (3H, m), 2.59–2.66 (1H, m), 2.88 (1H, dq, $J = 15.9, 1.9$ Hz), 4.69 (1H, s), 4.75 (1H, s), 5.35–5.40 (1H, m);

^1H NMR (C_6D_6) (500 MHz): δ = 1.12 (3H, s), 1.38–1.44 (4H, m), 1.49 (3H, s), 1.67 (1H, dq, $J = 13.9, 2.8$ Hz), 1.86 (1H, dq, $J = 15.8, 2.4$ Hz), 2.07 (1H, tt, $J = 11.9, 3.2$ Hz), 2.16 (1H, dd, $J = 15.1, 11.9$ Hz), 2.31–2.35 (1H, m), 2.40 (1H, ddd, $J = 15.1, 3.9, 2.3$ Hz), 3.10 (1H, dd, $J = 15.8, 1.9$ Hz), 4.63 (1H, br s), 4.69–4.71 (1H, m), 5.25 (1H, br s);

^{13}C NMR (CDCl_3) (100 MHz): δ = 14.6, 20.7, 23.6, 29.3, 39.5, 41.9, 43.6, 54.8, 54.9, 109.7, 125.2, 140.7, 147.6, 216.0;

Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}$: C 82.30, H 9.87. Found: C 82.00, H 9.80.

7-Butyl-4-isopropeny-1-methylbicyclo[4.3.0]non-7-en-2-one (3d)

The relative stereochemistry between the angular methyl group (H_a) and H_b , H_d , and H_e was assigned as *cis* to each other on the basis of the observed NOEs shown below. The large coupling constants ($J_{H_c-H_d} = J_{H_c-H_e} = 11.5$ Hz) in the ^1H -NMR spectrum (C_6D_6) clearly indicated that all the three protons (H_c , H_d , and H_e) were situated on axial position. Therefore, the stereochemistry of **3d** was unambiguously determined as shown below.

IR (neat) 3047, 2927, 1707, 1645, 1456, 891 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 0.88 (3H, t, $J = 7.1$ Hz), 1.12 (3H, s), 1.20–1.48 (4H, m), 1.62–1.78 (1H, m), 1.71 (3H, s), 1.82–2.10 (4H, m), 2.22–2.35 (2H, m), 2.38–2.50 (1H, m), 2.62–2.69 (1H, m), 2.82–2.91 (1H, m), 4.67 (1H, s), 4.75 (1H, s), 5.35 (1H, s);

^{13}C NMR (CDCl_3) (100 MHz): δ = 13.9, 20.7, 22.5, 23.6, 28.5, 29.4, 29.6, 39.5, 41.9, 43.6, 53.7, 54.5, 109.7, 123.6, 145.2, 147.6, 216.1;

Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}$: C 82.87, H 10.64. Found: C 82.71, H 10.75.

4-Isopropenyl-1-methyl-7-phenylbicyclo[4.3.0]non-7-en-2-one (3e)

The relative stereochemistry between the angular methyl group (H_a) and H_b , H_d , and H_e was assigned as *cis* to each other on the basis of the observed NOEs shown below. The large coupling constants ($J_{\text{H}_c-\text{H}_d} = J_{\text{H}_c-\text{H}_e} = 9.7$ Hz) in the ^1H -NMR spectrum (C_6D_6) clearly indicated that all the three protons (H_c , H_d , and H_e) were situated on axial position. Therefore, the stereochemistry of **3e** was unambiguously determined as shown below.

IR (KBr) 3045, 2961, 1699, 1457, 760 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 1.27 (3H, s), 1.59 (3H, s), 1.75–1.92 (2H, m), 2.23 (1H, d, $J = 17.7$ Hz), 2.30–2.45 (2H, m), 2.50–2.62 (1H, m), 2.93 (1H, d, $J = 17.1$ Hz), 3.17–3.22 (1H, m), 4.58 (1H, s), 4.71 (1H, s), 6.00 (1H, s), 7.27–7.38 (5H, m);

^1H NMR (C_6D_6) (500 MHz): δ = 1.25 (3H, s), 1.37 (3H, s), 1.55 (1H, ddd, $J = 13.9, 9.7, 5.5$ Hz), 1.69–1.75 (1H, m), 2.03 (1H, ddd, $J = 17.0, 2.5, 1.5$ Hz), 2.14–2.21 (1H, m), 2.30 (1H, dd, $J = 16.2, 9.7$ Hz), 2.42 (1H, ddd, $J = 16.2, 5.0, 1.6$ Hz), 2.89 (1H, dt, $J = 17.0, 1.5$ Hz), 2.96–3.00 (1H, m), 4.59 (1H, s), 4.64 (1H, s), 5.71–5.73 (1H, m), 7.03–7.20 (5H, m);

^{13}C NMR (CDCl_3) (100 MHz): δ = 21.0, 24.0, 30.5, 38.8, 43.36, 43.41, 52.1, 53.9, 110.1, 125.4, 126.2, 127.3, 128.5, 135.8, 145.3, 147.2, 215.7;

Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}$: C 85.67, H 8.32. Found: C 85.77, H 8.54.

Bicyclo[4.4.0]dec-1-en-5-one (7a)

Bicyclo[4.4.0]dec-1-en-5-one is a known compound.³ Only NMR data are shown below.

^1H NMR (CDCl_3) (400 MHz): δ = 1.10–1.42 (3H, m), 1.45–1.54 (1H, m), 1.70–2.21 (4H, m), 2.22–2.50 (4H, m), 2.57–2.67 (1H, m), 5.50 (1H, br s).

^{13}C NMR (CDCl_3) (100 MHz): δ = 25.3, 25.9, 27.4, 30.1, 34.6, 37.8, 50.2, 118.1, 139.8, 212.9.

2,2-Dimethyl-3-phenylcyclohex-3-en-1-one (7b)

IR (neat) 3022, 2971, 1713, 1463 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 1.17 (6H, s), 2.48–2.55 (2H, m), 2.62–2.67 (2H, m), 5.64 (1H, t, $J = 4.1$ Hz), 7.11–7.16 (2H, m), 7.25–7.31 (3H, m);

^{13}C NMR (CDCl_3) (100 MHz): δ = 24.8, 25.3, 35.6, 47.9, 125.2, 126.8, 127.6, 129.2, 140.9, 146.8, 214.6;

Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}$: C 83.96, H 8.05. Found: C 83.70, H 8.10.

2,2,6-Trimethyl-3-phenylcyclohex-3-en-1-one (7c)

IR (neat) 3021, 2971, 2929, 1712, 1462 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): δ = 1.07 (3H, s), 1.13 (3H, d, J = 6.3 Hz), 1.25 (3H, s), 2.14 (1H, ddd, J = 17.0, 11.9, 2.4 Hz), 2.59 (1H, ddd, J = 17.4, 6.3, 5.9 Hz), 2.93–3.05 (1H, m), 5.59 (1H, dd, J = 5.9, 2.0 Hz), 7.10–7.17 (2H, m), 7.22–7.35 (3H, m);

^{13}C NMR (CDCl_3) (100 MHz): δ = 14.4, 22.7, 27.7, 34.2, 38.8, 48.3, 124.6, 126.7, 127.5, 129.3, 140.8, 146.8, 215.7;

Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$: C 84.07, H 8.47. Found: C 84.04, H 8.68.

1-(tert-Butyldimethylsiloxy)-2-methyl-3-(1-methylprop-2-ynyl)cyclohexene (4)

This compound was obtained as a 1:1 mixture of *syn* and *anti* isomers.

IR (neat): 3311, 2931, 2859, 1674 cm^{-1} ;

^1H NMR (CDCl_3) (400 MHz): (*syn*, *anti* mixture) δ = 0.07 (1.5H, s), 0.08 (1.5H, s), 0.09 (1.5H, s), 0.10 (1.5H, s), 0.92 (4.5H, s), 0.93 (4.5H, s), 0.97 (1.5H, d, J = 7.0 Hz), 1.17 (1.5H, d, J = 7.3 Hz), 1.33–1.62 (2H, m), 1.53 (1.5H, s), 1.60 (1.5H, s), 1.66–1.89 (2H, m), 1.90 (0.5H, d, J = 2.4 Hz), 1.91–2.00 (1H, m), 2.01 (0.5H, d, J = 2.4 Hz), 2.02–2.12 (1.5H, m), 2.34–2.41 (0.5H, m), 2.79–2.92 (1H, m);

^{13}C NMR (CDCl_3) (100 MHz): (*syn*, *anti* mixture) δ = -4.1, -4.0, -3.8, -3.7, 13.7, 14.0, 14.8, 18.2, 18.9, 21.8, 22.0, 23.8, 24.1, 25.8, 25.9, 27.1, 28.4, 30.8, 30.9, 43.1, 44.1, 68.5, 69.2, 87.2, 89.1, 112.2, 113.4, 145.9, 146.7;

Anal. Calcd for $\text{C}_{17}\text{H}_{30}\text{OSi}$: C, 73.31; H, 10.86. Found: C, 73.02; H, 11.13.

6,9-Dimethylbicyclo[4.3.0]non-7-en-5-one (5)

A 0.1 M THF solution of $\text{W}(\text{CO})_5(\text{thf})$ was prepared by irradiation of a slurry of $\text{W}(\text{CO})_6$ (176 mg, 0.5 mmol) in THF (5.0 mL) for 2 hours. To a 6-siloxy-5-ene-1-yne (0.3 mmol) were added a yellow solution of $\text{W}(\text{CO})_5(\text{thf})$ in THF (0.15 mL, 0.015 mmol) and H_2O (16.2 mL, 0.9 mmol) at room temperature. The mixture was stirred at room temperature until the starting material disappeared (5 days), and then the resulting mixture was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (pentane:ether = 10:1) to give the *endo*-cyclized cyclopentene derivatives.

This compound was obtained as a 1:1 mixture of stereoisomers concerning the methyl group at C-9. The product was obtained as a 90:10 mixture of 6,9-dimethylbicyclo[4.3.0]non-7-en-5-one **5** and 1,7-dimethylbicyclo[4.3.0]non-7-en-2-one **3a**. The stereochemistry of the ring junction was assigned as *cis* on the basis of differential NOE spectra of **5**.

IR (neat): 3044, 2927, 1704, 1455 cm^{-1} ;

^1H NMR (CDCl_3) (500 MHz): (*cis*, *trans* mixture) δ = 0.98 (1.5H, d, J = 7.3 Hz), 1.03 (1.5H, d, J = 6.8 Hz), 1.19 (1.5H, s), 1.29 (1.5H, s), 1.35–1.45 (0.5H, m), 1.61–1.95 (3.5H, m), 2.16–2.27 (1.5H, m), 2.32–2.52 (2H, m), 2.97–3.04s (0.5H, m), 5.55–5.60 (1H, m), 5.63–5.68 (1H, m);

^{13}C NMR (CDCl_3) (125 MHz): (*cis*, *trans* mixture) δ = 14.4, 19.6, 22.0, 22.87, 22.89, 23.5, 24.3, 25.5, 38.4, 38.6, 42.1, 43.9, 51.0, 56.9, 60.8, 61.2, 134.6, 134.8, 136.2, 136.7, 215.7, 217.0;

HRMS (EI^+): Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$, M 164.1201. Found m/z 164.1173.

1. Dulcere, J.-P.; Santelli, M. *Israel J. Chem.* **1985**, 26, 152.
2. Jean, C.; Pierre, C. *C. R. Acad. Sci., Ser. C* **1970**, 270, 2077.
3. Wharton, P. S.; Johnson, D. W. *J. Org. Chem.* **1973**, 38, 4117.

¹H and ¹³C NMR chart for compounds 2a and 3a