Supporting Information

$W(CO)_5(L)$-Catalyzed Formal Cope Rearrangement of Allenyl Silyl Enol Ethers

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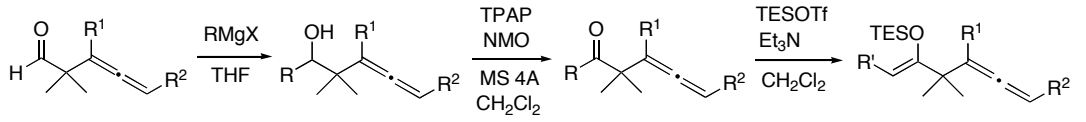
General. All operations were performed under an argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX500, a JEOL AL-400, or a JEOL Lambda-400 spectrometer using $CHCl_3$ (^1H, δ = 7.24), C_6H_6 (^1H, δ = 7.15) and $CDCl_3$ (^{13}C, δ = 77.0) as internal standards. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. Photochemical reactions were performed with an USHIO INC. super high-pressure mercury lamp. Flash column chromatography was conducted on silica gel (Kanto 60N) and preparative thin-layer chromatography (PTLC) was carried out on silica gel (Wakogel B-5F). Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl, and all other solvents were distilled according to the standard procedures and stored over molecular sieves or KOH. $W(CO)_6$ was purchased from Soekawa Chemical Co., Ltd and used without further purification.

Synthesis of acyclic 5-siloxyhexa-1,2,5-triene (1a–1e)



I(a,b) (R^1=Ph, R^2=H)
Ic (R^1=Me, R^2=H)
I(d,e) (R^1=Ph, R^2=Me)

IIa (R^1=Ph, R^2=H, R=Me)
IIb (R^1=Ph, R^2=H, R=Et)
IIc (R^1=Me, R^2=H, R=Et)
IId (R^1=Ph, R^2=Me, R=Me)
IIe (R^1=Ph, R^2=Me, R=Et)

IIIa (R^1=Ph, R^2=H, R=Me)
IIIb (R^1=Ph, R^2=H, R=Et)
IIIc (R^1=Me, R^2=H, R=Et)
IIId (R^1=Ph, R^2=Me, R=Me)
IIIe (R^1=Ph, R^2=Me, R=Et)

1a (R^1=Ph, R^2=H, R'=H)
1b (R^1=Ph, R^2=H, R'=Me)
1c (R^1=Me, R^2=H, R'=Me)
1d (R^1=Ph, R^2=Me, R'=H)
1e (R^1=Ph, R^2=Me, R'=Me)

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

To a THF (10 mL) solution of 2,2-dimethyl-3-phenylpenta-3,4-dienal **I(a,b)**[1] (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 pH 7 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 silica-gel column chromatography (hexane:ethyl acetate=10:1) to give **IIa** (1.9 g, 9.5 mmol) in 89%

(1) Jean, C.; Pierre, C. *C. R. Acad. Sci., Ser. C* **1970**, *270*, 2077.

yield as colorless oil.
IR (neat): 3428, 3054, 2973, 1948, 1069 cm^{-1}; ^1H NMR ($CDCl_3$) (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); ^{13}C NMR ($CDCl_3$) (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 $C_{14}H_{18}O$: C 83.12, H 8.97. Found: C 82.84, H 8.97.

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

Alkylation of 2,2-dimethyl-3-phenylpenta-3,4-dienal **I(a,b)**[1] using a THF solution of EtMgBr was carried out according to the same procedure as described above to give **IIb** in 57% yield as colorless oil.
IR (neat): 3434, 3054, 2970, 1948, 1465 cm^{-1}; ^1H NMR ($CDCl_3$) (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); ^{13}C NMR ($CDCl_3$) (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 $C_{15}H_{20}O$: C 83.28, H 9.32. Found: C 83.14, H 9.53.

3,3-Dimethyl-4-phenylhepta-4,5-dien-2-ol (IId)

Alkylation of 2,2-dimethyl-3-phenylhexa-3,4-dienal **I(d,e)**[1], which was prepared from 4-phenylbut-3-yn-2-ol and isobutyraldehyde, using a THF solution of MeMgBr was carried out according to the same procedure as described above to give **IId** in 42% yield. This compound was obtained as a diastereomeric mixture in a ratio of 1:1. The stereochemistry was not determined.
IR (neat): 3434, 3056, 2973, 1953, 1071 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz):(diastereomer mixture) δ = 1.02 (3.0H, s), 1.08 (1.5H, s), 1.09 (1.5H, s), 1.17 (3.0H, d, *J* = 6.4 Hz), 1.70 (3.0H, d, *J* = 6.8 Hz), 1.82 (0.5H, d, *J* = 3.6 Hz), 1.85 (0.5H, d, *J* = 3.6 Hz), 3.77–3.83 (1.0H, m), 5.20–5.26 (1.0H, m), 7.16–7.31 (5.0H, m); ^{13}C NMR ($CDCl_3$) (100 MHz):(diastereomer mixture) δ = 14.8, 14.9, 17.0, 17.1, 21.6, 21.7, 23.98, 24.01, 42.6, 42.7, 71.9, 72.0, 86.65, 86.70, 112.05, 112.10, 125.2, 126.7, 129.3, 137.48, 137.49, 203.7, 203.8; Anal. Calcd for $C_{15}H_{20}O$: C 83.28, H 9.32. Found: C 83.00, H 9.48.

4,4-Dimethyl-5-phenylocta-5,6-dien-3-ol (IIe)

Alkylation of 2,2-dimethyl-3-phenylhexa-3,4-dienal **I(d,e)**[1] using a THF solution of EtMgBr was carried out according to the same procedure as described above to give **IIe** in 20% yield. This compound was obtained as a diastereomeric mixture in a ratio of 1:1. The stereochemistry was not determined.
IR (neat): 3434, 3056, 2970, 1953, 1465 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz):(diastereomer mixture) δ = 0.99–1.03 (3.0H, m), 1.028 (1.5H, s), 1.031 (1.5H, s), 1.095 (1.5H, s), 1.101 (1.5H, s), 1.29–1.40 (1.0H, m), 1.62–1.68 (1.0H, m), 1.699 (1.5H, d, *J* = 6.8 Hz), 1.700 (1.5H, d, *J* = 6.8 Hz),

1.73–1.74 (0.5H, m), 1.76–1.77 (0.5H, m), 3.40–3.44 (1.0H, m), 5.19–5.25 (1.0H, m), 7.21–7.32 (5.0H, m); ^{13}C NMR ($CDCl_3$) (100 MHz):(diastereomer mixture) δ = 11.8, 14.7, 14.9, 22.8, 22.9, 23.5, 23.6, 24.22, 24.25, 42.6, 42.7, 77.97, 78.02, 86.55, 86.61, 112.2, 112.3, 126.7, 127.9, 129.3, 137.55, 137.57, 203.8, 203.9; Anal. Calcd for $C_{16}H_{22}O$: C 83.43, H 9.63. Found: C 83.46, H 9.63.

3,3-Dimethyl-4-phenylhepta-4,5-dien-2-one (IIIa)

To a CH_2Cl_2 (15 mL) solution of **IIa** (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 Celite®, and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane:ethyl acetate=10:1) to give **IIIa** (1.8 g, 9.0 mmol) in 95% yield as yellowish oil.

IR (neat): 3056, 2978, 1939, 1708, 1120 cm^{-1}; ^{1}H 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 $C_{14}H_{16}O$: C 83.96, H 8.05. Found: C 83.70, H 8.24.

4,4-Dimethyl-5-phenylhexa-5,6-dien-3-one (IIIb)

Oxidation of **IIb** was carried out according to the same procedure as that of the synthesis of **IIIa** to give **IIIb** in 95% yield as colorless oil.

IR (neat): 3056, 2978, 1939, 1709 cm^{-1}; ^{1}H 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), 7.15–7.19 (3H, m), 7.23–7.27 (2H, 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 $C_{15}H_{18}O$: C 84.07, H 8.47. Found: C 83.77, H 8.57.

3,3-Dimethyl-4-phenylhepta-4,5-dien-2-one (IIId)

Oxidation of **IId** was carried out according to the same procedure as that of the synthesis of **IIIa** to give **IIId** in 93% yield.

IR (neat): 3058, 2977, 1946, 1708, 1120 cm^{-1}; ^{1}H NMR ($CDCl_3$) (400 MHz): δ = 1.29 (3H, s), 1.30 (3H, s), 1.80 (3H, d, *J* = 6.8 Hz), 2.17 (3H, s), 5.57 (1H, q, *J* = 6.8 Hz), 7.15–7.18 (3H, m), 7.22–7.27 (2H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 14.2, 25.0, 25.2, 25.3, 50.6, 89.7, 111.1, 126.6, 127.2, 128.3, 135.9, 205.4, 213.0; Anal. Calcd for $C_{15}H_{18}O$: C 84.07, H 8.47. Found: C 83.77, H 8.35.

4,4-Dimethyl-5-phenylocta-5,6-dien-3-one (IIIe)

Oxidation of **IIe** was carried out according to the same procedure as that of the synthesis of **IIIa** to give **IIIe** in 91% yield.

IR (neat): 3057, 2977, 1946, 1709, 1461 cm^{-1}; ^{1}H NMR ($CDCl_3$) (400 MHz): δ = 1.07 (3H, t, *J* = 7.6

Hz), 1.38 (3H, s), 1.39 (3H, s), 1.89 (3H, d, J = 7.2 Hz), 2.64 (2H, q, J = 7.6 Hz), 5.65 (1H, q, J = 7.2 Hz), 7.22–7.26 (3H, m), 7.31–7.34 (2H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 8.6, 14.2, 25.3, 25.6, 30.1, 50.2, 89.7, 111.1, 126.6, 127.2, 128.2, 135.9, 205.5, 215.6; Anal. Calcd for $C_{16}H_{20}O$: C 84.16, H 8.83. Found: C 83.90, H 8.81.

4,4-Dimethyl-3-phenyl-5-(triethylsiloxy)hexa-1,2,5-triene (1a)

To a CH_2Cl_2 (1.2 mL) solution of **IIIa** (49.1 mg, 0.25 mmol) were added Et_3N (59.8 mL, 0.43 mmol) and TESOTf (83.2 mL, 0.37 mmol) at 0 ˚C. The reaction mixture was stirred at room temperature. After 20 hours, the reaction was quenched with pH 7 phosphate buffer. The aqueous layer was extracted with CH_2Cl_2 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 silica-gel column chromatography (hexane only) to give **1a** in 90% yield as colorless oil.

IR (neat): 3056, 2956, 1945, 1612 cm^{-1}; ^{1}H 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 $C_{20}H_{30}OSi$: C 76.37, H 9.61. Found: C 76.26, H 9.80.

4,4-Dimethyl-3-phenyl-5-(triethylsiloxy)hepta-1,2,5-triene (1b)

Silylation of **IIIb** by the use of TESOTf was carried out according to the same procedure as that of the synthesis of **1a** to give **1b** in 84% yield as colorless oil. This compound **1b** was obtained as a 4:96 mixture of *E* and *Z* isomers.

IR (neat): 3057, 2957, 1661, 1320 cm^{-1}; *Z* isomer: ^{1}H 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 $C_{21}H_{32}OSi$: C 76.77, H 9.82. Found: C 76.48, H 9.78.

(*Z*)-5-Triethylsiloxy-3,4,4-trimethylhepta-1,2,5-triene (1c)

Silylation of **IIIc**[2] by the use of TESOTf was carried out according to the same procedure as that of the synthesis of **1a** to give **1c** in 17% yield. The geometry was assigned to be *Z*.

IR (neat): 3047, 2955, 1956, 1661 cm^{-1}; ^{1}H NMR ($CDCl_3$) (400 MHz): δ = 0.68 (6H, q, J = 7.6 Hz), 0.97 (9H, t, J = 7.6 Hz), 1.13 (6H, s), 1.51 (3H, d, J = 6.8 Hz), 1.59 (3H, t, J = 3.2 Hz), 4.55–4.61 (3H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 6.1, 7.0, 11.5, 15.4, 26.3, 42.4, 74.8, 99.4, 105.2, 155.7,

(2) Bly, R. S.; Koock, S. U. *J. Am. Chem. Soc.* **1969**, *91*, 3292.

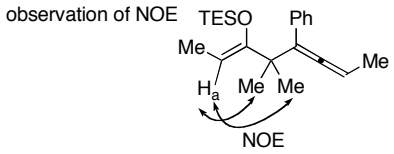
206.4; Anal. Calcd for $C_{16}H_{30}OSi$: C 72.11, H 11.35. Found: C 71.83, H11.48.

5,5-dimethyl-4-phenyl-6-(triethylsiloxy)hepta-2,3,6-triene (1d)

Silylation of **IIId** by the use of TESOTf was carried out according to the same procedure as that of the synthesis of **1a** to give **1d** in 76% yield as colorless oil.
IR (neat): 3057, 2958, 1951, 1611 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 0.67 (6H, q, *J* = 7.6 Hz), 0.95 (9H, t, *J* = 7.6 Hz), 1.24 (6H, s), 1.72 (3H, d, *J* = 6.8 Hz), 4.04 (1H, d, *J* = 1.2 Hz), 4.17 (1H, d, *J* = 1.6 Hz), 5.29 (1H, q, *J* = 6.8 Hz), 7.12–7.16 (1H, m), 7.18–7.23 (2H, m), 7.36–7.39 (2H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 5.0, 6.8, 14.6, 27.5, 27.6, 43.2, 87.1, 87.3, 112.2, 126.1, 127.4, 128.5, 137.9, 164.2, 205.2; Anal. Calcd for $C_{21}H_{32}OSi$: C 76.77, H 9.82. Found: C 76.49, H 9.79.

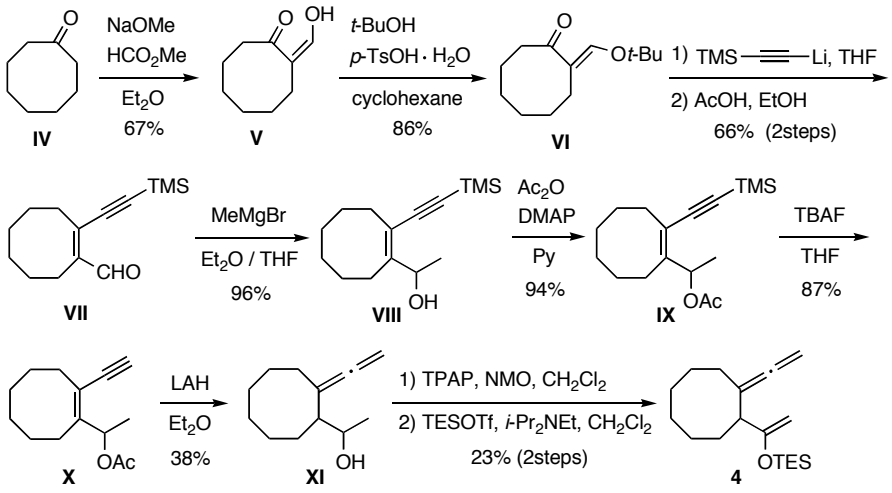
5,5-Dimethyl-4-phenyl-6-(triethylsiloxy)octa-2,3,6-triene (1e)

Silylation of **IIIe** by the use of TESOTf was carried out according to the same procedure as that of the synthesis of **1a** to give **1e** in 91% yield as colorless oil. This compound **1e** was obtained as a 5:95 mixture of *E* and *Z* isomers.



IR (neat): 3057, 2958, 1661, 1319 cm^{-1}; *Z* isomer: ^1H NMR ($CDCl_3$) (400 MHz): δ = 0.74 (6H, q, *J* = 8.0 Hz), 1.01 (9H, t, *J* = 8.0 Hz), 1.23 (3H, s), 1.25 (3H, s), 1.56 (3H, d, *J* = 6.8 Hz), 1.77 (3H, d, *J* = 7.2 Hz), 4.68 (1H, q, *J* = 6.8 Hz), 5.33 (1H, q, *J* = 7.2 Hz), 7.16–7.28 (3H, m), 7.36–7.39 (2H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 6.2, 7.1, 11.6, 14.6, 27.5, 28.0, 43.2, 87.3, 99.7, 113.1, 126.1, 127.4, 128.7, 137.8, 155.9, 204.9; Anal. Calcd for $C_{22}H_{34}OSi$: C 77.13, H 10.00. Found: C 77.02, H 10.15.

Synthesis of cyclic 5-siloxyhexa-1,2,5-triene (4)



2-(Hydroxymethylene)cyclooctanone (V)

NaOMe was prepared from Na (8.6 g, 374 mmol) in 100 mL of MeOH. Excess MeOH was removed under reduced pressure. To an ether suspension of the prepared NaOMe was added methyl formate (21.0 mL, 340 mmol) followed by the dropwise addition of cyclooctanone **IV** (22.4 mL, 170 mmol). The slurry was stirred at 0 °C for 1 hour and then warmed to room temperature over 15 hours. The yellowish mixture was quenched with water, and the organic layer was extracted with cold, dilute NaOH three times. The combined aqueous layer was washed twice with Et_2O (to remove any starting material) and was then acidified with conc. HCl. The aqueous layer was extracted with Et_2O three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (hexane:ethyl acetate=6:1) to give **V** in 67% yield.

IR (neat): 2926, 2856, 1635, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.43–1.56 (6H, m), 1.70–1.76 (2H, m), 2.28–2.36 (2H, m), 2.43–2.49 (2H, m), 8.14 (1H, d, *J* = 5.0 Hz), 15.1 (1H, d, *J* = 5.0 Hz); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 25.8, 25.9, 26.2, 28.3, 32.5, 35.4, 112.7, 180.1, 195.8.

2-(*t*-Butoxymethylene)cyclooctanone (VI)

t-Butyl alcohol (11.0 mL, 114.82 mmol) and *p*-toluenesulfonic acid monohydrate (86.4 mg, 0.454 mmol) were added to a cyclohexane solution (36 mL) of **V** (2.4 g, 15.6 mmol). The flask was equipped with a Dean-Stark trap and a reflux condenser. The solution was stirred at 85 °C for 3 hours. The solution was then cooled to room temperature, extracted with Et_2O 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 silica-gel column chromatography (hexane:ethyl acetate=9:1) to give **VI** in 86% yield.

IR (neat): 2978, 2927, 2855, 1672, 1585, 1154 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.30 (9H, s), 1.39–1.53 (6H, m), 1.69 (2H, quint, *J* = 6.4 Hz), 2.46 (2H, t, *J* = 6.4 Hz), 2.54 (2H, t, *J* = 6.4 Hz),

7.57 (1H, s); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 22.9, 26.2, 26.3, 28.3, 29.2, 29.5, 39.2, 79.2, 118.9, 151.3, 205.2; Anal. Calcd for $C_{13}H_{22}O_2$: C 74.24, H 10.54. Found: C 74.13, H 10.71.

2-(2-Trimethylsilylethynyl)cyclooct-1-enecarbaldehyde (VII)

n-Butyllithium (41.3 mL, 1.6 M, 65.2 mmol) was added dropwise to a solution of (trimethylsilyl)acetylene (9.2 mL, 65.2 mmol) in THF (100 mL) at –78 ˚C. The mixture was stirred at –78 ˚C for 1.5 hours and then a solution of **VI** (6.86 g, 32.6 mmol) in THF (50 mL) was added slowly at –78 ˚C. The reaction mixture was stirred at –78 ˚C for 4 hours. The reaction was quenched with sat. $NaHCO_3$ solution and brine. The separated aqueous layer was extracted with Et_2O three times. The combined organic layers were washed with brine and concentrated to a cloudy yellow oil. To the oil was added 1:1 EtOH/0.1 M CH_3CO_2H (500 mL), and the mixture was stirred at room temperature for 1 hour and then quenched with sat. $NaHCO_3$ and brine. The mixture was diluted with Et_2O and the organic layer was washed with brine, dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (hexane:ethyl acetate=20:1) to give **VII** in 66% yield.
IR (neat): 2927, 2854, 2140, 1675, 1251, 844 cm^{-1}; ^{1}H NMR ($CDCl_3$) (400 MHz): δ = 0.20 (9H, s), 1.39–1.51 (6H, m), 1.73 (2H, quint, *J* = 6.8 Hz), 2.41 (2H, t, *J* = 6.4 Hz), 2.53 (2H, t, *J* = 6.4 Hz), 10.2 (1H, s); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = –0.1, 23.5, 26.0, 26.5, 28.9, 29.8, 34.0, 101.8, 105.1, 142.8, 146.8, 192.6; HRMS (FAB$^+$/NBA): Calcd for $C_{14}H_{22}OSi$, M^+ 234.1440. Found m/z 234.1415.

1-[2-(2-Trimethylsilylethynyl)cyclooct-1-enyl]ethanol (VIII)

To a THF (30 mL) solution of **VII** (4.8 g, 20.5 mmol) was added a 3.0 M Et_2O solution of methylmagnesium bromide (8.47 mL, 25.4 mmol) at 0 ˚C. After 30 minutes, the reaction was quenched with pH 7 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 silica-gel column chromatography (hexane:ethyl acetate=10:1) to give **VIII** in 96% yield.
IR (neat): 3347, 2926, 2139, 1249 cm^{-1}; ^{1}H NMR ($CDCl_3$) (400 MHz): δ = 0.15 (9H, s), 1.26 (3H, d, *J* = 6.4 Hz), 1.39–1.60 (8H, m), 2.01 (1H, s), 2.19–2.34 (4H, m), 5.01 (1H, q, *J* = 6.4 Hz);
^{13}C NMR ($CDCl_3$) (100 MHz): δ = 0.16, 21.3, 26.0, 26.1, 26.5, 28.4, 31.2, 31.5, 70.4, 97.8, 105.1, 118.2, 151.8; Anal. Calcd for $C_{15}H_{26}OSi$: C 71.93, H 10.46. Found: C 71.94, H 10.71.

1-[2-(2-Trimethylsilylethynyl)cyclooct-1-enyl]ethyl acetate (IX)

A pyridine solution (39 mL) of **VIII** (4.92 g, 19.6 mmol) and DMAP (239.5 mg, 1.96 mmol) was treated with acetic anhydride (2.4 mL, 25.5 mmol) at room temperature. After 6 hours, the mixture was treated with saturated $NaHCO_3$. The aqueous layer was extracted with ethyl acetate,

and the combined extracts were washed with 1 N HCl, sat. $CuSO_4$, sat. NH_4Cl, water and brine, dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (hexane:ethyl acetate=10:1) to give **IX** in 94% yield.
IR (neat): 2928, 2142, 1745, 1239, 843 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 0.17 (9H, s), 1.30 (3H, d, *J* = 6.4 Hz), 1.40–1.63 (8H, m), 2.01 (3H, s), 2.27 (4H, t, *J* = 6.4 Hz), 6.06 (1H, q, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 0.16, 19.0, 21.4, 26.0, 26.1, 26.4, 28.4, 30.9, 31.3, 73.1, 98.3, 104.6, 120.0, 147.2, 169.9; Anal. Calcd for $C_{17}H_{28}O_2Si$: C 69.81, H 9.65. Found: C 69.55, H 9.42.

1-(2-Ethynycyclooct-1-enyl)ethyl acetate (X)

A solution of **IX** (5.34 g, 18.3 mmol) in 55 mL of THF at room temperature was treated with TBAF (1.0 M solution in THF, 36.5 mL, 36.5 mmol). After 2.5 hours, the mixture was treated with saturated NH_4Cl and then extracted with ethyl acetate three times and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (hexane:ethyl acetate=20:1) to give **X** in 87% yield.
IR (neat): 2928, 1737, 1370, 1240, 1052 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.30 (3H, d, *J* = 6.4 Hz), 1.40–1.65 (8H, m), 2.00 (3H, s), 2.26–2.31 (4H, m), 3.14 (1H, s), 6.06 (1H, q, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 19.2, 21.3, 25.9, 26.0, 26.5, 28.2, 30.9, 31.3, 73.1, 81.4, 82.9, 119.0, 147.5, 170.0; Anal. Calcd for $C_{14}H_{20}O_2$: C 76.33, H 9.15. Found: C 76.12, H 8.92.

1-(2-Vinylidenecyclooctyl)ethanol (XI)

To a solution of **X** (3.47 g, 15.8 mmol) in 23 mL of THF at room temperature was slowly added a solution of $LiAlH_4$ (1.07 M solution in Et_2O, 23.1 mL, 24.7 mmol). The reaction mixture was heated under reflux, then cooled in an ice-bath and quenched with a sequential slow addition of water and 1 N HCl. The organic layer was extracted with ethyl acetate three times and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (pentane:ether=10:1) to give **XI** in 38% yield.
IR (neat): 3410, 2925, 1948, 1444, 842 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 1.18 (3H, d, *J* = 6.0 Hz), 1.28–1.64 (10H, m), 1.92–1.97 (1H, m), 2.06–2.19 (3H, m), 3.52–3.59 (1H, m), 4.64 (1H, s), 4.65 (1H, s); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 20.5, 25.8, 26.5, 26.8, 27.0, 29.4, 32.0, 49.8, 70.9, 74.8, 103.9, 206.1; HRMS (EI^+): Calcd for $C_{12}H_{20}O$, M 180.1514. Found m/z 180.1521.

1-[1-(Triethylsiloxy)ethenyl]-2-vinylidenecyclooctane (4)

To a CH_2Cl_2 (10.1 mL) solution of **XI** (364.0 mg, 2.0 mmol) were added TPAP (70.3 mg, 0.20 mmol), NMO (355.0 mg, 3.0 mmol), and MS 4A (1.5 g) at room temperature. After 28 hours, the reaction mixture was filtered through a short pad of neutral alumina, and the filtrate was concentrated under reduced pressure. The residue was purified by silica-gel column

chromatography (hexane:ethyl acetate=20:1) to give a mixture of the desired ketone and its regioisomer**.** Then to a CH_2Cl_2 (3.8 mL) solution of the obtained mixture (222.0 mg, 1.3 mmol) were added *i*-Pr_2NEt (0.44 mL, 2.54 mmol) and TESOTf (0.43 mL, 1.88 mmol) at –78 ˚C. The reaction mixture was further stirred at room temperature. After 24 hours, the reaction was quenched with pH 7 phosphate buffer. The aqueous layer was extracted with CH_2Cl_2 three times and the combined extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by deactivated alumina column chromatography at –78 ˚C (hexane) to give **4** in 23% yield.
IR (neat): 2925, 1953, 1615, 1017 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 0.66 (6H, q, *J* = 8.0 Hz), 0.95 (9H, t, *J* = 8.0 Hz), 1.34–1.74 (10H, m), 2.02 (1H, dt, *J* = 11.6, 3.2 Hz), 2.23–2.26 (1H, m), 2.69 (1H, dd, *J* = 10.8, 5.2 Hz), 3.96 (1H, s), 4.01 (1H, s), 4.55 (1H, s), 4.56 (1H, s);
^{13}C NMR ($CDCl_3$) (100 MHz): δ = 5.0, 6.8, 26.0, 26.4, 27.0, 28.3, 28.7, 29.2, 48.7, 73.5, 87.5, 104.2, 162.1, 207.7; HRMS (FAB^+/Nitrophenyloctylether): Calcd for $C_{18}H_{32}OSi$, M 292.2222. Found m/z 292.2220.

General procedure for the formal Cope rearrangement of 5-siloxyhexa-1,2,5-triene (3a–3e, 5)

To a degassed toluene (2.0 mL) solution of 5-siloxy-hexa-1,2,5-trienes (0.2 mmol) was added $W(CO)_6$ (14.1 mg, 0.04 mmol) and DABCO (2.2 mg, 0.02 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, and then the resulting mixture was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane) to give the formal Cope rearrangement products, 2-siloxyhex-1-en-5-ynes as colorless oil.

1-Phenyl-6-methyl-5-triethylsiloxyhept-5-en-1-yne (3a)
90% yield (20 mol% $W(CO)_6$).
IR (neat): 2955, 2914, 1680, 1258, 1198 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 0.67 (6H, q, *J* = 8.0 Hz), 0.98 (9H, t, *J* = 8.0 Hz), 1.62 (3H, s), 1.65 (3H, s), 2.41–2.44 (2H, m), 2.52–2.56 (2H, m), 7.23–7.28 (3H, m), 7.35–7.39 (2H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 5.6, 6.9, 17.9, 18.0, 18.9, 32.1, 80.6, 90.0, 110.8, 124.0, 127.4, 128.1, 131.4, 142.7; Anal. Calcd for $C_{20}H_{30}OSi$: C 76.37, H 9.61. Found: C 76.17, H 9.87.

4,6-Dimethyl-1-Phenyl-5-triethylsiloxy-hept-5-en-1-yne (3b)
68% yield (20 mol% $W(CO)_6$).
IR (neat): 2957, 1672, 1262, 1189 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): δ = 0.72 (6H, q, *J* = 8.0 Hz), 0.99 (9H, t, *J* = 8.0 Hz), 1.12 (3H, d, *J* = 6.8 Hz), 1.60 (3H, s), 1.66 (3H, s), 2.36 (1H, dd, *J* = 8.0 Hz, 16.8 Hz), 2.46 (1H, dd, *J* = 6.8 Hz, 16.8 Hz), 2.98 (1H, sext, *J* = 6.8 Hz), 7.22–7.27 (3H, m),

7.35–7.37 (2H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 6.1, 7.1, 17.8, 18.9, 19.0, 24.8, 35.0, 81.2, 89.7, 108.4, 124.1, 127.3, 128.1, 131.4, 146.6; Anal. Calcd for $C_{21}H_{32}OSi$: C 76.77, H 9.82. Found: C 76.57, H 10.09.

2,4-Dimethyl-3-triethylsiloxyoct-2-en-6-yne (3c)

61% yield (20 mol% $W(CO)_6$).

IR (neat): 2957, 2917, 2877, 1671, 1261, 1190 cm^{-1}; ^{1}H NMR ($CDCl_3$) (400 MHz): δ = 0.68 (6H, q, *J* = 8.0 Hz), 0.96 (9H, t, *J* = 8.0 Hz), 1.04 (3H, d, *J* = 6.8 Hz), 1.56 (3H, s), 1.60 (3H, s), 1.75–1.77 (3H, m), 2.02–2.11 (1H, m), 2.14–2.20 (1H, m), 2.80 (1H, sext, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 3.6, 6.0, 7.1, 17.6, 18.87, 18.89, 24.1, 35.1, 76.1, 78.6, 108.0, 147.0; Anal. Calcd for $C_{16}H_{30}OSi$: C 72.11, H 11.35. Found: C 71.84, H 11.13.

3,6-Dimethyl-1-phenyl-5-triethylsiloxyhept-5-en-1-yne (3d)

86% yield (20 mol% $W(CO)_6$).

IR (neat): 2958, 1680, 1250, 1174 cm^{-1}; ^{1}H NMR ($CDCl_3$) (400 MHz): δ = 0.67 (6H, q, *J* = 7.6 Hz), 0.98 (9H, t, *J* = 7.6 Hz), 1.22 (3H, d, *J* = 7.2 Hz), 1.64 (3H, s), 1.66 (3H, s), 2.26 (1H, dd, *J* = 8.0 Hz, 14.0 Hz), 2.47 (1H, dd, *J* = 6.4 Hz, 14.0 Hz), 2.92 (1H, sext, *J* = 7.2 Hz), 7.21–7.28 (3H, m), 7.33–7.37 (2H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 5.6, 6.9, 18.0, 19.3, 20.4, 25.0, 39.7, 80.4, 94.7, 111.7, 124.1, 127.3, 128.0, 131.5, 141.9; Anal. Calcd for $C_{21}H_{32}OSi$: C 76.77, H 9.82. Found: C 76.50, H 9.59.

1-Phenyl-5-triethylsiloxy-3,4,6-trimethylhept-5-en-1-yne (3e)

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

47% yield (20 mol% $W(CO)_6$).

IR (neat): 2957, 1672, 1261, 1197 cm^{-1}; ^{1}H NMR ($CDCl_3$) (400 MHz):(*syn*, *anti* mixture) δ = 0.61–0.70 (6.0H, m), 0.90–0.95 (9.0H, m), 0.97 (1.5H, d, *J* = 6.8 Hz), 1.10 (1.5H, d, *J* = 6.0 Hz), 1.15 (1.5H, d, *J* = 6.4 Hz), 1.19 (1.5H, d, *J* = 6.8 Hz), 1.53 (1.5H, s), 1.55 (1.5H, s), 1.56 (1.5H, s), 1.62 (1.5 H, s), 2.52–2.61 (1.5H, m), 2.66–2.73 (0.5H, m), 7.16–7.26 (4H, m), 7.33–7.35 (1H, m); ^{13}C NMR ($CDCl_3$) (100 MHz):(*syn*, *anti* mixture) δ = 6.1, 6.2, 7.1, 7.2, 15.4, 17.7, 18.7, 18.8, 19.0, 19.1, 19.4, 19.5, 30.2, 30.3, 40.4, 40.9, 80.8, 81.3, 94.7, 94.8, 108.4, 109.0, 124.1, 124.4, 127.1, 127.3, 128.0, 128.1, 131.3, 131.4, 145.6, 147.0; Anal. Calcd for $C_{22}H_{34}OSi$: C 77.13, H 10.00. Found: C 77.22, H 9.82.

2-Triethylsiloxycyclododec-1-en-5-yne (5)

This compound was obtained as a 86:14 mixture of geometrical isomers. The geometry was not determined. NMR data were described for the major product.

53% yield (100 mol% $W(CO)_6$).

IR (neat): 2917, 1672, 1148, 1005, 729 cm^{-1}; ^1H NMR (C_6D_6) (400 MHz): δ = 0.60 (6H, q, *J* = 8.0 Hz), 0.98 (9H, t, *J* = 8.0 Hz), 1.37 (2H, quint, *J* = 6.4 Hz), 1.44–1.63 (6H, m), 2.03 (2H, t, *J* = 6.0 Hz), 2.11–2.14 (2H, m), 2.25 (2H, q, *J* = 6.8 Hz), 2.32–2.36 (2H, m), 4.51 (1H, t, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$) (100 MHz): δ = 5.5, 6.9, 16.8, 17.4, 23.5, 24.5, 25.2, 26.1, 26.3, 36.3, 80.1, 81.8, 110.9, 148.0; Anal. Calcd for $C_{18}H_{32}OSi$: C 73.90, H 11.03. Found: C 73.80, H 10.77.

Typical procedure for the 6-endo cyclization in the presence of H_2O

To a degassed THF (0.21 mL) solution of a silyl enol ether **1a** (64.5 mg, 0.21 mmol) was added $W(CO)_6$ (14.4 mg, 0.041 mmol) and H_2O (11.1 μL, 0.62 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, and then the resulting mixture was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane: ethyl acetate=10:1) to give 2,2-dimethyl-3-phenylcyclohex-3-en-1-one **2a** (28.1 mg, 0.14 mmol) in 68% yield as colorless oil.

2,2-Dimethyl-3-phenylcyclohex-3-en-1-one (2a)

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, 125.1, 126.8, 127.6, 129.2, 140.9, 146.8, 214.6;

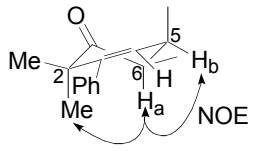
Anal. Calcd for $C_{14}H_{16}O$: C 83.96, H 8.05. Found: C 83.70, H 8.10.

2,2,5,6-Tetramethyl-3-phenylcyclohex-3-en-1-one(2e)

71% yield (20 mol% $W(CO)_6$)

The relative stereochemistry of the two methyl groups at C_5 and C_6 was assigned as *syn* on the basis of the measurement of differential NOE spectra and the coupling constant between Ha and Hb (6.8 Hz).

observation of NOE



IR (neat): 2970, 2931, 1713, 1460 cm^{-1};

^1H NMR ($CDCl_3$) (400 MHz): δ = 0.86 (3H, d, *J* = 7.2Hz), 1.08 (3H, d, *J* = 6.8 Hz), 1.08 (3H, s), 1.20 (3H, s), 2.63 (1H, sext, *J* = 6.8 Hz), 3.20 (1H, quint, *J* = 6.8 Hz), 5.70 (1H, d, *J* = 6.0 Hz), 7.13–7.15 (2H, m), 7.26–7.31 (3H, m);

^{13}C NMR ($CDCl_3$) (100 MHz): δ = 11.6, 15.8, 23.0, 27.2, 37.2, 43.3, 48.4, 126.7, 127.5, 129.4,

131.8, 140.7, 145.3, 215.8;

HRMS (EI^+): Calcd for $C_{16}H_{20}O$, M 228.1514. Found m/z 228.1493.