Facile Construction of a Tricyclo[5.3.0.0^{1,4}]decenone Ring System by the Brook Rearrangement-Mediated [3 + 4] Annulation

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Supporting Information

General: IR spectra were recorded on a Perkin-Elmer FT1640 spectrometer. ^{1}H NMR spectra were taken on Varian UnityPlus 500 (500 MHz) in $CDCl_3$ with reference to $CHCl_3$ (δ 7.26) unless otherwise noted. ^{13}C NMR spectra were measured with Varian UnityPlus 500 (125 MHz) in $CDCl_3$ with reference to the $CDCl_3$ triplet (δ 77.2) unless otherwise noted. Resonance patterns were described as s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. The assignment of ^{1}H and ^{13}C NMR spectra is based on H-H decoupling and HMQC experiments. Low- and high-resolution mass spectra (EI-MS) were obtained with a JEOL JMS-D-300 spectrometer combined with a JEOL JMA-2000 data processing system. For routine chromatography, the following adsorbents were used: Fuji-Davison silica gel BW-200 (150-325 mesh) for column chromatography; Merck precoated silica gel 60 F-254 plates for analytical thin-layer chromatography. All moisture sensitive reactions were performed under a positive pressure of nitrogen. Anhydrous $MgSO_4$ was used for drying all organic solvent extracts in workup, and the removal of the solvents was performed with a rotary evaporator. Dry solvents and reagents were obtained by using standard procedures. Melting points (uncorrected) were determined by using a Yanagimoto micro-melting point apparatus. Elemental combustion analysis was performed at the Microanalysis Laboratory of this University.

1-(*tert*-Butyldimethylsilyl)-3-alkyl-3-chloro-2-propen-1-one (1). The following procedure for **1a** (R = Me) is representative: These compounds were prepared by a modified procedure of Cunico as described for the the corresponding trimethylsilyl derivative. A solution of (1-(ethoxy)ethenyl)-*tert*-butyldimethylsilane (6.00 g, 32.2 mmol), $BrCCl_3$ (6.30 mL, 64.4 mmol), and DBU (4.80 mL, 32.2 mmol) in CCl_4 (21 mL) was irradiated with a sunlamp for 4 h before addition of H_2O (20 mL). The mixtue was extracted with pentane (20 mL x 3). The combined organic phases were successively washed with hydrochloric acid (0.1N) and saturated brine, and concentrated. The residual oil was filtered through a pad of Florisil (pentane), and then subjected to column chromatography (silica gel, 200 g; elution with 5:1 pentane-CH_2Cl_2) to give **1** (R = Cl) (6.56 g, 85%). a red oil. R_f = 0.23 (hexane : CH_2Cl_2 = 5 : 1). IR (film) 1630 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.21 (6H, s, Si*Me*$_2$), 0.94 (9H, s, Si*tBu*), 7.01 (1H, s, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ -7.14 (Si*Me*$_2$), 17.1 (Si*C*), 26.6 (Si-*tBu*), 128.7 (C-2), 130.0 (C-3), 231.9 (C-1). HRMS calcd for $C_9H_{16}OCl_2Si$ 238.0347, found 238.0336.

To a cooled (-80 °C) suspension of anhydrous CuCN (1.34 g, 14.7 mmol) in THF (120 mL) was added dropwise a solution of MeLi (1.0 M in Et_2O, 14.7 mL, 14.7 mmol). The reaction mixture was allowed to warm to –20 °C. After the mixture became a clear solution, the solution was cooled to –80 °C. To this solution was added dropwise a solution of **1** (R = Cl) (2.50 g, 10.5 mmol) in THF (175 mL). The reaction mixture was allowed to warm to –30 °C before addition of AcOH (0.86 mL, 14.7 mmol) in THF (5 mL). The mixture was diluted with H_2O (200 mL), and then extracted with pentane (150 mL x 3). The combined organic phases were washed with saturated brine, dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 120 g; elution with 19:1 hexane-Et_2O) to give **1a** (R = Me) (1.84 g, 80%).

1a (R = Me): a yellow oil. R_f = 0.42 (hexane : CH_2Cl_2 = 5 : 1). IR (film) 1635 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.19 (3H, s, Si*Me*), 0.19 (3H, s, Si*Me*), 0.93 (9H, s, Si*tBu*), 2.47 (3H, s, H-4), 6.88 (1H, q, J = 0.4 Hz, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-7.1 (Si*Me*$_2$), 17.1 (Si*C*), 24.6 (C-4), 26.7 (Si*tBu*), 129.4 (C-2), 147.7 (C-3), 234.8 (C-1). HRMS calcd for $C_{10}H_{19}OClSi$, 218.0894, found 218.0925.

1b (R = *n*-Bu): an orange oil. R_f = 0.48 (hexane : CH_2Cl_2 = 6 : 1). IR (film) 1630 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.18 (6H, s, Si*Me*$_2$), 0.90 (3H, t, J = 7.5 Hz, H-7), 0.92 (9H, s, Si*tBu*), 1.34 (2H, m, H-5), 1.56 (2H, m, H-6), 2.81 (2H, t, J = 7.7 Hz, H-4), 6.86 (1H, s, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-7.1 (Si*Me*$_2$), 14.0 (C-7), 17.0 (SiC), 22.2 (C-6), 26.7 (Si*tBu*), 30.2 (C-5), 36.4 (C-4), 129.4 (C-2), 152.7 (C-3), 234.5 (C-1). HRMS calcd for $C_{13}H_{25}ClOSi$ 260.1363, found 260.1368.

1c (R = *n*-hexyl): a yellow oil. R_f = 0.38 (hexane : CH_2Cl_2 = 9 : 1). IR (film) 1640 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.19 (6H, s, Si*Me*$_2$), 0.87 (3H, t, *J* = 7.5, H-9), 0.93 (9H, s, Si*tBu*), 1.25-1.35 (6H, m), 1.54-1.59 (2H, m), 2.81 (2H, t, *J* = 7.5 Hz, H-4), 6.86 (1H, s, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-7.0 (Si*Me*$_2$), 14.2 (C-9),17.1 (Si*C*), 22.7, 26.7 (Si*tBu*), 28.1, 28.7, 31.7, 36.6 (C-4), 129.5 (C-2), 152.7 (C-3), 234.5 (C-1). HRMS calcd for $C_{15}H_{29}ClOSi$ 288.1676, found 288.1673.

1d (R = *t*-Bu): a yellow oil. R_f = 0.38 (hexane : CH_2Cl_2 = 9 : 1). IR (film) 1630 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.20 (6H, s, Si*Me*$_2$), 0.94 (9H, s, Si*tBu*), 1.19 (9H, s, *t*-Bu), 6.43 (1H, s, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-6.6 (Si*Me*$_2$), 17.0 (Si*C*), 26.6 (Si*tBu*), 30.1 (*t*-Bu), 40.4 (C-4), 133.4 (C-2), 151.1 (C-3), 238.8 (C-1). HRMS calcd for $C_9H_{16}OClSi$ (M^+ - C_4H_9), 203.0659, found 203.0629.

General Procedure for the [3 + 4] Annulation Leading to Cycloheptenediones 2: Reaction of 1a with Lithium Enolate of 3-Nonen-2-one. To a cooled (-80°C) solution of lithium diisopropylamide (LDA), prepared from diisopropylamine (0.100 mL, 80 mg, 0.789 mmol) and *n*-BuLi (1.41 M in hexane, 0.55 mL, 0.775 mmol) in THF (0.8 mL) was added dropwise a solution of 3-nonen-2-one (130 μL, 109 mg, 0.775 mmol) in THF (0.8 mL). After stirring at -80 °C for 30 min, the solution was added dropwise via a cannula to a cooled (-80 °C) solution of **1a** (150 mg, 0.686 mmol) in THF (31 mL). The reaction mixture was allowed to warm to 0 °C, and then quenched by addition of AcOH (46 μL, 0.789 mmol). The mixture was diluted with saturated aqueous NH_4Cl solution, and extracted with Et_2O (50 mL x 3). The combined organic phases were washed with saturated brine, dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 40 g; elution with 1:2 hexane-Et_2O) to give **2a** (106 mg, 75%).

2a (R = Me): a pale yellow oil. R_f = 0.16 (hexane : Et_2O = 5 : 1). IR (film) 1655 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.85 (3H, t, *J* = 6.8 Hz, H-5'), 1.21-1.31 (5H, br m), 1.42-1.47 (2H, br m), 1.67-1.72 (1H, br m), 2.00 (3H, d, *J* = 1.3 Hz, CH_3), 2.57-2.62 (1H, br m, H-6), 2.67 (1H, dd, *J* = 15.3, 6.6 Hz, H-7), 2.78 (1H, dd, *J* = 15.3, 3.2 Hz, H-7), 3.62 (1H, d, *J* = 16.7, H-2), 3.71 (1H, d, *J* = 16.7, H-2), 5.96 (1H, s, H-4). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.1 (C-5'), 22.5, 25.9 (CH_3), 27.5, 31.6, 32.0, 41.0 (C-6), 46.1 (C-7), 60.7 (C-2), 129.0 (C-4), 161.5 (C-5), 193.4 (C-3), 203.6 (C-1). HRMS calcd for $C_{13}H_{20}O_2$, 208.1463, found 208.1494.

2b (R = *n*-Bu): a colorless oil. R_f = 0.23 (hexane : Et_2O = 1 : 2). IR (film) 1650, 1575 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.85 (3H, t, *J* = 6.8, H-5"), 0.89 (3H, t, *J* = 7.3, H-4'), 1.21-1.38 (7H, br m), 1.39-1.49 (4H, m), 1.67 (1H, m), 2.20 (2H, t, *J* = 8.1 Hz), 2.53 (1H, m, H-6), 2.74 (2H, app d, *J* = 4.7 Hz, H-7), 3.58 (1H, dd, *J* = 16.8, 0.9 Hz, H-2), 3.76 (1H, d, *J* = 16.8 Hz, H-2), 5.94 (1H, d, *J* = 0.9, H-4). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.0 (C-5"), 14.1 (C-4'), 22.5, 27.6, 30.4, 30.5, 31.6, 32.4, 38.7, 40.0 (C-6), 46.3 (C-7), 60.9 (C-2), 127.9 (C-4), 165.6 (C-5), 193.7 (C-3), 203.6 (C-1). HRMS calcd for $C_{16}H_{26}O_2$ 250.1933, found 250.1929.

2c (R = *n*-hexyl): a colorless oil. R_f = 0.21 (hexane : Et_2O = 1 : 1). IR (film) 1650, 1575 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.89 (6H,m, H-6'and H-5"), 1.23-1.36 (11H, m), 1.43-1.55 (4H, m), 1.67-1.71 (1H, m), 2.23 (2H, t, *J* = 7.0 Hz, H-1'), 2.54-2.59 (1H, m, H-6), 2.78 (2H, app d, *J* = 7.1 Hz, H-7), 3.62 (1H, dd, *J* = 16.9, 1.0 Hz, H-2), 3.80 (d, *J* = 16.9 Hz, 1H, H-2), 5.98 (1H, d, *J* = 1.0 Hz, H-4). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.1 (C-5"), 14.2 (C-6'), 22.6, 22.7, 27.7, 28.4, 29.2, 31.7, 32.5, 39.1 (C-1'), 40.1 (C-6), 46.4 (C-7), 61.0 (C-2), 128.0 (C-4), 165.7 (C-5), 193.9 (C-3), 203.7 (C-1). HRMS calcd for $C_{18}H_{30}O_2$ 278.2246, found 278.2232.

2d (R = *t*-Bu): an amorphous solid, R_f = 0.21 (hexane : Et_2O = 1 : 2). IR (film) 1640, 1575 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.86 (3H, t, *J* = 7.1 Hz, H-5'), 1.15 (9H, s, tBu), 1.19-1.29 (5H, m, H-2', H-3', and H-4'), 1.46-1.53 (2H, m, H-1' and H-2'), 1.59-1.63 (1H, m, H-1'), 2.65-2.72 (2H, m, H-6 and H-7), 2.90 (1H, dd, *J* = 15.6, 4.3 Hz, H-7), 3.62 (1H, d, *J* = 16.6 Hz, H-2), 3.89 (1H, d, *J* = 16.6 Hz, H-2), 6.03 (1H, s, H-4). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.1 (C-5'), 22.6 (C-2'), 27.9 (C-3'), 28.6 (tBu), 31.6 (C-4'), 35.2 (C-1'), 35.3 (C-6), 38.9 (*C*Me$_3$), 45.6 (C-7), 61.3 (C-2), 125.3 (C-4), 171.6 (C-5), 194.9 (C-3), 203.4 (C-1). HRMS calcd for $C_{16}H_{26}O_2$ 250.1933 found 250.1936

Reaction of 1 with Lithium Enolate of 1-Acetyl-1-cyclopentene. Reaction was carried out in the same way as described for the [3 + 4] annulation leading to cycloheptenediones **2**.

5a (R = CH_3): a pale yellow oil, R_f = 0.41 (hexane : Et_2O = 12 : 1). IR (film) 1775 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.09 (3H, s, Si*Me*), 0.10 (3H, s, Si*Me*), 0.89 (9H, s, Si*tBu*), 1.43-1.53 (2H, br m, H-8 and H-10), 1.64-1.71 (3H, br m, H-8, H-9, and H-10), 1.72 (3H, d, *J* = 0.9 Hz, CH_3), 2.18-2.22 (m, 1H, H-9), 2.98 (1H, br d, H-7), 3.02 (1H, d, *J* = 17.7 Hz, H-3), 3.08 (1H, d, *J* = 17.7 Hz, H-3), 5.50 (1H, s, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ -3.0 (Si*Me*), -2.6 (Si*Me*), 15.7 (6-CH_3), 18.2 (Si*C*), 25.9 (Si*tBu*), 26.5 (C-8), 28.8 (C-9), 30.4 (C-10),

57.9 (C-7), 60.2 (C-3), 81.0 (C-4), 82.3 (C-1), 129.2 (C-5), 145.7 (C-6), 215.9 (C-2). In order to obtain a crystaline derivative for an X-ray analysis, this compound was transformed into 4-(*tert*-butyldimethylsiloxy)-6-methyltricyclo[5.4.0.0^{1,4}]undec-5-en-2-yl 3,5-dinitrobenzoate by the following sequence: (1) DIBAL, Et_2O (2) 3,5-dinitrobenzoyl chloride, pyridine (3) 5% HF-MeCN (4) separation of the diastereomers (5) Ac_2O, NEt_3, CH_2Cl_2. X ray; monoclinic $P2_1/a$(#14), a = 10.629(1), b = 10.277(1), c = 18.411(1) Å, δ = 96.535(7)°, V = 1998.0(3) Å^3, Z = 4, D_{calc} = 1.384 g/cm^3, R = 3.9 for 2996 reflections. Diffraction data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Ka radiation and rotating anode generator. The structure was solved by the direct methods and expanded using Fourier techniques.

5b (R = *n*-Bu): a colorless oil. R_f = 0.44 (hexane : Et_2O = 19 : 1). IR (film) 1775 cm^{-1}. ^{1}H-NMR (500 MHz , $CDCl_3$) δ0.09 (3H, s, Si*Me*), 0.11 (3H, s, Si*Me*), 0.89 (9H, s, Si*tBu*), 0.90 (3H, t, *J* = 7.5 Hz, H-4'), 1.25-1.43 (4H, m, H-2' and H-3'), 1.43-1.52 (2H, m, H-9, and H-10), 1.63-1.72 (3H, m, H-8, H-9, and H-10), 1.96-2.02 (1H, m, H-1'), 2.06-2.13 (1H, m, H-1'), 2.16-2.21 (1H, m, H-8), 3.03 (1H, br m, H-7), 3.03 (1H, d, *J* = 18.0 Hz, H-3), 3.07 (1H, d, J = 18.0 Hz, H-3), 5.50 (1H, d, J = 0.8 Hz, H-5). 13C-NMR (125 MHz, CDCl3) ; -3.0 (SiMe), -2.6 (SiMe), 14.1 (C-4'), 18.2 (SiC), 22.7 (C-3'), 25.9 (SitBu), 26.6 (C-10), 28.6 (C-8), 29.6 (C-1'), 30.1 (C-2'), 30.8 (C-9), 56.7 (C-7), 60.3 (C-3), 80.8 (C-4), 81.8 (C-1), 127.7 (C-5), 150.4 (C-6), 216.0 (C-2). HRMS calcd for C20H34O2Si 334.2328, found 334.2306

5c (R = n-hexyl): a yellow oil. Rf = 0.43 (hexane : Et2O = 15 : 1). IR (film) 1775 cm-1. 1H-NMR (500 MHz, $CDCl_3$) δ0.09 (3H, s, Si*Me*), 0.11 (3H, s, Si*Me*), 0.87 (3H, t, *J* = 6.4 Hz, H-6'), 0.89 (9H, s, Si*tBu*), 1.24-1.34 (8H, m, H-2', H-3', H-4', and H-5'), 1.44-1.52 (2H, m, H-9 and H-10), 1.64-1.72 (3H, m, H-8, H-9, and H-10), 1.96-2.01 (1H, m, H-1'), 2.04-2.11 (1H, m, H-1'), 2.14-2.21 (1H, m, H-8), 3.03 (1H, br s, H-7), 3.03 (1H, d, *J* = 17.8 Hz, H-3), 3.07 (1H, d, *J* = 17.8 Hz, H-3), 5.50 (1H, d, *J* = 1.1 Hz, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-3.0 (Si*Me*), -2.6 (Si*Me*), 14.3 (C-6'), 18.2 (Si*C*), 22.8 (C-5'), 25.9 (Si*tBu*), 26.6 (C-10), 26.7 (C-8), 27.8 (C-1'), 28.6 (C-9), 29.3, 29.9, 30.8, 56.7 (C-7), 60.3 (C-3), 80.8 (C-4), 81.8 (C-1), 127.7 (C-5), 150.4 (C-6), 216.0 (C-2). HRMS calcd for $C_{22}H_{38}O_2Si$ 362.2641, found 362.2651.

5d (R = *t*-Bu): colorless oil, R_f = 0.38 (hexane : Et_2O = 19 : 1). IR (film) 1775 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 0.09 (3H, s, Si*Me*), 0.11 (3H, s, Si*Me*), 0.90 (9H, s, Si*tBu*), 1.08 (9H, s, tBu), 1.37-1.44 (1H, m, H-8), 1.64-1.77 (3H, m, H-9 and H-10), 1.91 (1H, m, H-8), 2.11 (1H, m, *J* = 6.4 Hz, H-10), 3.06 (1H, d, *J* = 7.5 Hz, H-3), 3.09 (1H, d, *J* = 7.5 Hz, H-3), 3.12 (1H, t, *J* = 8.3, H-7), 5.54 (1H, s, H-5). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ-2.8 (Si*Me*), -2.5 (Si*Me*), 18.2 (Si*C*), 25.9 (Si*tBu*), 27.4 (C-10), 28.2 (C-9), 30.5 (C*Me$_3$*), 34.4 (C-8), 55.6 (C-7), 60.8 (C-3), 79.3 (C-4), 81.3 (C-1), 126.1 (C-5), 159.2 (C-6), 216.2 (C-2). HRMS calcd for $C_{20}H_{34}O_2Si$ 334.2328, found 334.2299

6a (R = CH_3): a colorless prism, mp 105-107 °C. R_f = 0.12 (hexane : Et_2O = 2 : 1). IR (KBr) 1715, 1655 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ1.48-1.65 (2H, m, H-8 and H-9), 1.74-1.88 (2H, m, H-9 and H-10), 2.04 (3H, s, CH_3), 2.20-2.26 (2H, m, H-8 and H-10), 2.72-2.78 (1H, ddd, *J* = 13.8, 10.0, 10.0 Hz, H-1), 2.89-2.95 (1H, m, H-7), 3.53 (1H, dd, *J* = 16.0, 1.5 Hz, H-3), 3.90 (1H, d, *J* = 16.0 Hz, H-3), 6.06 (1H, m, H-3). ^{13}C-NMR (125 MHz, $CDCl_3$) δ23.2 (C-9), 24.4 (CH_3), 25.3 (C-8), 32.2 (C-10), 48.0 (C-7), 57.3 (C-1), 60.0 (C-3), 129.8 (C-5), 160.3 (C-6), 194.4 (C-4), 204.3 (C-2). Anal. calcd for $C_{11}H_{14}O_2$ C 74.33, H 7.92. found C 74.13, H 7.92.

6b (R = *n*-Bu): a colorless oil. R_f = 0.20 (hexane : Et_2O = 3 : 1). IR (film) 1715, 1655 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ0.93 (3H, t, *J* =7.3 Hz, H-4'), 1.31-1.42 (2H, m, H-3'), 1.43-1.64 (4H, br m, H-2', H-9, and H-10), 1.72-1.87 (2H, m, H-8 and H-9), 2.21-2.29 (3H, m, H-1', H-8, and H-10), 2.34-2.40 (1H, m, H-1'), 2.75-2.81 (1H, m, H-7), 2.90-2.96 (1H, m, H-1), 3.55 (1H, dd, *J* = 16.2, 1.5 Hz, H-3), 3.88 (1H, d, *J* = 16.2 Hz, H-3), 6.05 (1H, s, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ14.1 (C-4'), 22.7 (C-3'), 23.2 (C-9), 25.3 (C-10), 30.6 (C-2'), 32.0 (C-8), 37.2 (C-1'), 47.6 (C-7), 57.5 (C-1), 59.9 (C-3), 128.6 (C-5), 164.0 (C-6), 195.1 (C-4), 204.4 (C-2). HRMS calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1450.

6c (R = *n*-hexyl): a colorless oil. R_f = 0.21 (hexane : Et_2O = 2 : 1). IR (film) 1715, 1655 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ0.89 (3H, t, *J* = 6.8 Hz, H-6'), 1.25-1.40 (7H, m), 1.40-1.67 (3H, m), 1.75-1.87 (2H, m, H-8 and H-10), 2.20-2.30 (3H, m, H-8, H-10, and H-1'), 2.32-2.40 (1H, m, H-1'), 2.74-2.81 (1H, m, H-1), 2.89-2.96 (1H, m, H-7), 3.36 (1H, dd, *J* = 16.2, 1.5 Hz, H-3), 3.99 (1H, d, *J* = 16.2 Hz, H-3), 6.05 (1H, app q, *J* = 1.3 Hz, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ14.2 (C-6'), 22.7, 23.2, 25.3 (C-8), 28.5, 29.3, 31.8 (C-10), 32.0, 37.5 (C-1'), 47.7 (C-1), 57.5 (C-7), 59.9 (C-3), 128.6 (C-5), 163.9 (C-6), 195.0 (C-4), 204.4 (C-2). HRMS calcd for $C_{16}H_{24}O_2$ 248.1776, found 248.1797.

6d (R = *t*-Bu): colorless oil, R_f = 0.11 (hexane : CH_2Cl_2 = 1 : 1). IR (film) 1710, 1655 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ1.11 (9H, s, C*Me*$_3$), 1.74-1.85 (2H, m, H-8 and H-10), 1.91-1.97 (1H, m, H-9), 2.00-2.04 (1H, m, H-10), 2.18-2.27 (2H, m, H-8 and H-9), 2.91-2.99 (2H, m, H-1 and H-7), 3.32 (1H, dt, *J* = 15.8, 1.7 Hz, H-3), 4.05 (1H, d, *J* = 15.8 Hz, H-3), 5.97 (1H, s, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ25.8 (C-10), 28.4 (C*Me*$_3$), 30.3 (C-9), 37.4 (C-8), 43.2 (C-7), 54.9 (C-1), 56.5 (C-3), 125.1 (C-5), 170.2 (C-6), 194.2 (C-4), 206.1 (C-2). HRMS calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1461

Reaction of 1 with Lithium Enolate of 1-Acetyl-1-cyclohexene. Reaction was carried out in the same way as described for the [3 + 4] annulation leading to cycloheptenediones **2**.

8d (R = *t*-Bu): a pale yellow oil, R_f = 0.41 (hexane : Et_2O = 19 : 1). IR (film) 1775 cm^{-1}. ^{1}H-NMR (500 MHz, C_6D_6) δ 0.08 (3H, s, Si*Me*), 0.10 (3H, s, Si*Me*), 1.01 (9H, m, Si*tBu*), 1.03 (9H, s, tBu), 1.10-1.17 (1H, m, H-10), 1.50-1.65 (2H, m, 2H, H-9 and H-11), 1.80-1.83 (1H, m, H-10), 1.85-1.89 (1H, m, H-11), 1.90-1.94 (2H, m, H-8 and H-9), 2.27 (1H, dddd, *J* = 12.4, 12.4, 12.4, 3.4 Hz, H-8), 2.63 (1H, ddd, *J* = 12.4, 3.0, 3.0 Hz, H-7), 2.87 (1H, d, *J* = 15.8 Hz, H-3), 3.28 (1H, d, *J* = 15.8 Hz, H-3), 5.46 (1H, d, *J* = 3.0 Hz, H-5). ^{13}C-NMR (C_6D_6, 125 MHz) δ -2.8 (Si*Me*), -2.7 (Si*Me*), 18.2 (Si*C*), 22.7 (C-11), 26.0 (Si*tBu*), 26.9 (C-9), 27.0 (C-8), 27.2 (C-10), 28.7 (C*Me*$_3$), 33.9 (*C*Me$_3$), 53.9 (C-7), 59.9 (C-3), 73.8 (C-4), 77.9 (C-1), 125.3 (C-5), 159.7 (C-6), 210.7 (C-2). HRMS calcd for $C_{21}H_{36}O_2Si$ 348.2485 found 348.2475.

7a (R = CH_3): a colorless prism, mp 96-98 °C, R_f = 0.27 (hexane : Et_2O = 1 : 1). IR (KBr): 1655, 1570 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ1.39-1.46 (3H, m, H-9 and H-10), 1.50-1.58 (2H, m, H-8 and H-11), 1.79-1.84 (1H, m, H-9), 1.93-1.97 (1H, br d, *J* = 12.9 Hz, H-11), 2.03 (3H, d, *J* = 1.3 Hz, CH_3), 2.24-2.27 (1H, br m, H-8), 2.57 (1H, ddd, *J* = 11.8, 7.1, 7.1 Hz, H-1), 2.73-2.74 (1H, m, H-7), 3.63 (1H, dd, *J* = 14.9, 1.5 Hz, H-3), 3.90 (1H, dd, *J* = 14.9, 0.6 Hz, H-3), 6.03 (1H, dq, *J* = 1.3 Hz, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 22.4 (C-11), 26.6 (C-10), 26.6 (CH_3), 27.8 (C-9), 28.4 (C-8), 46.6 (C-1), 50.6 (C-7), 62.1 (C-3), 129.3 (C-5), 161.1 (C-6), 192.6 (C-4), 204.7 (C-2). Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39, found C, 75.28; H, 8.30.

7b (R =*n*-Bu): a colorless oil. R_f = 0.20 (hexane : Et_2O = 2 : 1). IR (film) 1705, 1660 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.92 (3H, t, *J* = 7.3 Hz, H-4'), 1.29-1.60 (9H, m), 1.84-1.86 (1H, m), 1.94 (1H, br d, *J* = 13.4 Hz), 2.23 (2H, t, *J* = 8.3 Hz, H-1'), 2.35 (1H, br d, *J* = 13.4 Hz), 2.52 (1H, dt, *J* = 12.1, 3.2 Hz, H-1), 2.70 (1H, br s, H-7), 3.63 (1H, dd, *J* = 15.0, 1.7 Hz, H-3), 4.00 (1H, d, *J* = 15.0 Hz, H-3), 6.02 (1H, s, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.0 (C-4'), 22.2, 22.6, 26.9, 28.1, 29.2, 30.7, 39.1, 45.9 (C-1), 50.4 (C-7), 62.5 (C-3), 128.2 (C-5), 165.6 (C-6), 192.8 (C-4), 205.0 (C-2). HRMS calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1611.

7c (R =*n*-hexyl): a colorless oil. R_f = 0.16 (hexane : Et_2O = 3 : 1). IR (film) 1705, 1660 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* = 4.0 Hz, H-6'), 1.27-1.60 (13H, m), 1.84-1.87 (1H, br m), 1.92-1.95 (H-1, br d, *J* = 13.3 Hz), 2.23 (2H, m, H-1'), 2.35 (1H, br d, *J* = 11.3 Hz), 2.50-2.54 (1H, dt, *J* = 12.4, 3.9 Hz, H-1), 2.69 (1H, br s, H-7), 3.63 (1H, dd, *J* = 14.9, 1.5 Hz, H-3), 3.99 (1H, d, *J* = 14.9 Hz, H-3), 6.01 (1H, d, *J* = 0.9 Hz, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.2 (C-6'), 22.2, 22.7, 26.9, 28.1, 28.5, 29.1, 29.2, 31.7, 39.4 (C-1'), 45.9 (C-1), 50.4 (C-7), 62.5 (C-3), 128.2 (C-5), 165.6 (C-6), 192.7 (C-4), 205.0 (C-2).

7d (R =*t*-Bu): colorless prism, mp 152-155 °C, R_f = 0.08 (hexane : CH_2Cl_2 = 1 : 1). IR (KBr) 1650, 1575 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) δ 1.15 (9H, s, tBu), 1.24-1.34 (1H, m, H-9), 1.39-1.48 (1H, m, H-10), 1.61-1.68 (2H, m, H-8 and H-9), 1.77 (1H, ddd, *J* = 12.7, 4.1, 4.1 Hz, H-11), 1.89 (2H, br m, H-10 and H-11), 2.30 (1H, br d, *J* = 11.6 Hz, H-8), 2.64 (1H, br s, H-7), 2.71 (1H, ddd, *J* = 12.4, 4.3, 4.3, H-1), 3.68 (1H, dd, *J* = 16.4, 1.1 Hz, H-3), 4.23 (1H, d, *J* = 16.5 Hz, H-3), 6.08 (1H, s, H-5). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 21.8 (C-9), 26.4 (C-10), 28.5 (CH_3), 30.3 (C-11), 31.5 (C-8), 39.2 (*C*Me$_3$), 39.9 (C-7), 50.2 (C-1), 62.5 (C-3), 126.2 (C-5), 172.2 (C-6), 193.7 (C-4), 207.4 (C-2). Anal. $C_{15}H_{22}O_2$ calcd for C 76.88, H 9.46, found C 77.02, H 9.80.

7e (R = *c*-C_3H_5): a pale yellow needle. mp = 92-94 °C, R_f = 28 (hexane : Et_2O = 1 : 1). IR (KBr) 1655, 1555 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.59-0.64 (1H, m, H-2'), 0.69-0.75 (1H, m, H-3'), 0.88-1.00 (2H, m, H-2' and H-3'), 1.34-1.51 (4H, m, H-1', H-8, H-9, and H-10), 1.54-1.64 (2H, m, H-9, 11), 1.83-1.88 (1H, m, H-10), 2.04-2.09 (1H, br d, *J* = 13.7 Hz, H-11), 2.30-2.33 (1H, br d, *J* = 13.7, H-8), 2.62-2.66 (1H, dt, *J* = 12.0, 3.4 Hz, H-1), 2.70-2.71 (1H, br m, H-7), 3.61 (1H, dd, *J* = 15.2, 1.7 Hz, H-3), 3.94 (1H, d, *J* = 15.2, H-3), 5.74 (1H, d, *J* = 1.7 Hz, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 8.69 (C-2'), 10.8 (C-3'), 19.3 (C-1'), 22.2 (C-9), 26.7 (C-10), 28.5 (C-8), 28.9 (C-11), 46.5 (C-1), 50.5 (C-7), 62.2 (C-3), 123.5 (C-5), 167.7 (C-6), 192.4 (C-4), 204.9 (C-2). Anal. calcd for $C_{14}H_{18}O_2$ C 77.03, H 8.31, found C 77.23, H 8.60.

1-(*tert*-Butyldimethylsilyl)-3-alkyl-3-bromo-2-propen-1-one (9). The following procedure for **9a** (R = Me) is representative: These compounds were prepared by a modified procedure of Cunico as described for the corresponding trimethylsilyl derivative. A solution of (1-(ethoxy)ethenyl)-*tert*-butyldimethylsilane (10.00 g, 53.7 mmol), CBr_4 (35.5 g, 107 mmol), and pyridine (1.7 mL, 21.5 mmol) in CCl_4 (45 mL) was irradiated with a sunlamp for 8 h before addition of H_2O (40 mL). The mixtue was extracted with pentane (50 mL x 3). The combined organic phases were washed with H_2O, and concentrated. The residual oil was subjected to column chromatography (silica gel, 240 g; elution with 6:1 pentane-CH_2Cl_2) to give **9** (R = Br) (9.03 g, 51%). red oil. R_f = 0.31 (hexane:CH_2Cl_2 = 5 : 1). IR (film) 1630 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.20 (6H, s, Si*Me*$_2$), 0.94 (9H, s, Si*tBu*), 7.62 (1H, s, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ -7.2 (Si*Me*$_2$), 17.2 (Si*C*), 26.6 (Si*tBu*), 97.9 (C-2), 136.7 (C-3), 232.6 (C-1). HRMS calcd for $C_9H_{16}OBr_2Si$ 329.9337, found 329.9298.

To a cooled (-80 °C) suspension of anhydrous CuCN (455 mg, 4.98 mmol) in THF (42 mL) was added dropwise a solution of MeLi (1.25 M in Et_2O, 4.0 mL, 4.98 mmol). The reaction mixture was allowed to warm to –20 °C. After the mixture became a clear solution, the solution was cooled to –80 °C. To this solution was added dropwise a solution of **9** (R = Br) (1.50 g, 3.32 mmol) in THF (66 mL). The reaction mixture was stirred at the same temperature for 1 h, and then allowed warm to –30 °C before addition of AcOH (0.29 mL, 4.98 mmol) in THF (8 mL). The mixture was diluted with H_2O (100 mL), and then extracted with pentane (100 mL x 3). The combined organic phases were washed with saturated brine, dried, and concentrated. The residual oil was filtered through a pad of Florisil (pentane), and then subjected to column chromatography (silica gel, 100 g; elution with 19:1 hexane-Et_2O) to give **9a** (R = Me) (730 mg, 57%).

9a (R = Me): a yellow oil, R_f = 0.32 (hexane : CH_2Cl_2 = 5 : 1). IR (film) 1640, 1560 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.19 (6H, s, Si*Me*$_2$), 0.93 (9H, s, Si*tBu*), 2.67 (3H, t, *J* = 1.1 Hz, H-4), 7.11 (1H, q, *J* = 1.1, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-7.1 (Si*Me*$_2$), 17.1 (Si*C*), 26.6 (Si*tBu*), 27.3 (C-4), 133.6 (C-2), 139.8 (C-3), 234.7 (C-1). Anal. Calcd. for $C_{10}H_{19}OBrSi$,: C, 45.63; H, 7.27, found C, 45.44; H, 7.52.

9b (R = *n*-Bu): a yellow oil. R_f = 0.38 (hexane : CH_2Cl_2 = 7 : 1). IR (film) 1645, 1555 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ0.18 (3H, s, Si*Me*$_2$), 0.18 (3H, s, Si*Me*$_2$), 0.90 (3H, t, *J* = 10.5, H-7), 1.33 (2H, sex, *J* = 7.7 Hz, H-6), 1.55 (2H, m, H-5), 2.92 (2H, t, *J* = 7.7 Hz, H-4), 7.11 (1H, t, *J* = 0.4 Hz, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-6.8 (Si*Me*$_2$), 14.3 (C-7), 17.3 (SiC), 22.3 (C-6), 26.9 (Si*tBu*), 31.3 (C-5), 38.8 (C-4), 133.9 (C-2), 146.8 (C-3), 234.5 (C-1). HRMS calcd for $C_{13}H_{25}O^{81}BrSi$ 306.0837, found 306.0833.

9c (R = *n*-hexyl): a yellow oil. R_f = 0.50 (hexane : CH_2Cl_2 = 6 : 1). IR (film) 1645, 1550 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.18 (6H, s, Si*Me*$_2$), 0.87 (3H, t, *J* = 7.5, H-9), 0.92 (9H, s, Si*tBu*), 1.25-1.32 (6H, m, H-5), 1.54-1.58 (2H, m), 2.92 (2H, t, *J* = 7.5, H-4), 7.11 (1H, s, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-7.1 (Si*Me*$_2$), 14.2 (C-9),17.1 (Si*C*), 22.7, 26.7 (Si*tBu*), 28.6, 28.9, 31.7, 38.7 (C-4), 133.7 (C-2), 146.5 (C-3), 234.3 (C-1). HRMS calcd for $C_{15}H_{29}OBrSi$, 332.1171, found 332.1211.

9d (R = *t*-Bu): a yellow oil. R_f = 0.37 (hexane : CH_2Cl_2 = 6 : 1). IR (film) 1640, 1620 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ0.20 (6H, s, Si*Me*$_2$), 0.94 (9H, s, Si*tBu*), 1.19 (9H, s, *t*-Bu), 6.62 (1H, s, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-6.6 (Si*Me*$_2$), 17.0 (SiC), 26.6 (SitBu), 30.8 (t-Bu), 41.3 (C-4), 138.1 (^{C}-2), 144.8 (C-), 239.4 (C-1). $_H$RMS calcd f$_o$r C13H25O81BrS^i 306.0837, $_f$ound 306.0848.

9e (R = c-C3H5): a yellow oil. Rf = 0.33 (hexane : CH2Cl2 = 5 : 1). IR (film) 1535 cm-1. 1H-NMR (500 MHz, CDCl3) δ0.20 (6H, s, Si*Me*$_2$), 0.84 (2H, m), 0.87 (9H, s, Si*tBu*), 1.10 (2H, m), 3.21 (m, 1H), 7.18 (1H, s, H-2). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-6.8 (Si*Me*$_2$), 10.9, 17.4, 17.9, 26.9 (Si*tBu*), 133.2 (C-2), 151.8 (C-3), 234.0 (C-1). HRMS calcd for $C_{13}H_{21}BrO$ 272.0776, found $C_{13}H_{22}{}^{79}BrO$ 273.0857.

Reaction of 9 with Lithium Enolate of 1-Acetyl-1-cyclopentene. Reaction was carried out in the same way as described for the reaction of the corresponding derivative **2**.

5e (R = *c*-C_3H_5): a yellow oil. R_f = 0.33 (hexane : Et_2O = 16 : 1). IR (film) 1775 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.06 (s, 3H, Si*Me*), 0.08 (3H, s, Si*Me*), 0.42-0.49 (2H, m, H-2' and H-3'), 0.66-0.74 (1H, m, H-2'), 0.74-0.78 (1H, m, H-3'), 0.87 (9H, s, Si*tBu*), 1.23-1.28 (1H, m, H-1'), 1.48-1.52 (1H, m, H-10), 1.58-1.73 (4H, m, H-8, H-9, and H-10), 2.15-2.19 (1H, m, H-9), 3.00 (1H, d, *J* = 17.6 Hz, H-3), 3.04 (1H, d, J = 17.6 Hz, H-3), 3.04 (1H, m, H-7), 5.33 (1H, s, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ -3.0 (Si*Me*), -2.6 (Si*Me*), 7.0 (C-2'), 7.9 (C-3'), 10.8 (C-1'), 18.1 (Si*C*), 25.8 (Si*tBu*), 26.6 (C-8), 28.5 (C-9), 31.4 (C-10), 56.5 (C-7), 60.3 (C-3), 80.4 (C-4), 81.9 (C-1), 124.8 (C-5), 152.4 (C-6), 215.6 (C-2). HRMS calcd for $C_{19}H_{30}O_2Si$ 318.2015, found 318.2036.

Reaction of 9 with Lithium Enolate of 1-Acetyl-1-cyclohexene. Reaction was carried out in the same way as described for the reaction of the chloro derivative **2**.

8a (R = Me): colorless oil, R_f = 0.31 (hexane : Et_2O = 12 : 1). IR (film) 1780 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.09 (3H, s, Si*Me*), 0.11 (3H, s, Si*Me*), 0.89 (9H, s, Si*tBu*), 0.86-0.95 (1H, m, H-8), 1.12-1.20 (1H, m, H-9), 1.30-1.38 (1H, m, H-10), 1.46-1.52 (1H, ddd, *J* = 13.7, 13.7, 4.7 Hz, H-11), 1.62-1.65 (2H, br d, *J* = 10.7, H-9 and H-10), 1.69 (3H, s, CH_3), 1.99-2.05 (1H, m, H-8), 2.18-2.22 (1H, br d, *J* = 13.7 Hz, H-11), 2.34 (1H, dd, *J* = 11.1, 6.6 Hz, H-7), 2.93 (1H, d, *J* = 16.4 Hz, H-3), 3.28 (1H, d, *J* = 16.4 Hz, H-3), 5.43 (1H, s, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-2.8 (Si*Me*), -2.5 (Si*Me*), 15.6 (CH_3), 18.3 (SiC), 26.1 (Si*tBu*), 23.1 (C-10), 23.9 (C-9), 24.7 (C-11), 26.1 (CH_3), 30.6 (C-8), 47.7 (C-7), 59.0 (C-3), 73.1 (C-4), 81.0 (C-1), 127.6 (C-5), 150.2 (C-6), 215.5 (C-2). HRMS : calcd for $C_{18}H_{30}O_2Si$ 306.5151, found 306.2007.

8b (R = *n*-Bu): a colorless oil. R_f = 0.40 (hexane : Et_2O = 19 : 1). IR (film) 1780 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.11 (3H, s, Si*Me*), 0.13 (3H, s, Si*Me*), 0.89 (3H, t, *J* = 7.0, C-4'), 0.90 (9H, s, Si*tBu*), 1.14-1.48 (7H, m), 1.49-1.55 (1H, m, H-11), 1.63-1.65 (2H, m), 1.96-2.10 (3H, m, H-3'and H-8), 2.21 (1H, d, *J* = 13.7 Hz, H-11), 2.42 (1H, dd, *J* = 11.4, 6.6 Hz, H-7), 2.93 (1H, d, *J* = 16.4 Hz, H-3), 3.30 (1H, d, *J* = 16.4 Hz, H-3), 5.44 (1H, s, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ -3.1 (Si*Me*), -2.7 (Si*Me*), 14.1 (C-4'), 18.1 (Si*C*), 22.6, 22.9, 23.9, 24.6, 25.9 (Si*tBu*), 26.7, 29.1, 29.8, 30.7, 46.1 (C-7), 58.9 (C-3), 72.5 (C-4), 80.5 (C-1), 126.0 (C-5), 154.7 (C-6), 215.7 (C-2). HRMS calcd for $C_{21}H_{36}O_2Si$ 348.2485, found 348.2470.

8c (R = *n*-hexyl): a pale yellow oil. R_f = 0.35 (hexane : CH_2Cl_2 = 3 : 1). IR (film) 1780 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.09 (3H, s, Si*Me*), 0.11 (3H, s, Si*Me*), 0.87 (3H, t, *J* = 7.0 Hz, H-6'), 0.90 (9H, s, Si*tBu*), 1.11-1.21 (1H, m, H-11), 1.22-1.32 (8H, br m, H-2', H-3', H-4', and H-5'), 1.33-1.41 (2H, m), 1.46-1.53 (1H, ddd, *J* = 15.3, 13.2, 4.2 Hz), 1.63-1.66 (2H, m), 1.95-2.08 (3H, m, H-8 and H-1'), 2.20 (1H, d, *J* = 3.7 Hz), 2.40 (1H, dd, *J* = 11.1, 6.6 Hz, H-7), 2.92 (1H, d, *J* = 6.6 Hz, H-3), 3.29 (1H, d, *J* = 6.6 Hz, H-3), 5.43 (1H, s, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ -3.1 (Si*Me*), -2.7 (Si*Me*), 14.3 (C-6'), 18.0 (Si*C*), 22.9, 23.8, 24.5, 25.8 (Si*tBu*), 29.2, 29.4, 30.7, 31.8, 46.1 (C-7), 58.9 (C-3), 72.5 (C-4), 80.5 (C-1), 126.0 (C-5), 154.7 (C-6), 215.2 (C-2). HRMS calcd for $C_{19}H_{31}O_2Si$ (M^+ - C_4H_9) 319.2093, found 319.2084.

8e (R = *c*-C_3H_5): a yellow oil. R_f = 0.35 (hexane : Et_2O = 16 : 1). IR (film) 1780 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.06 (3H, s, Si*Me*), 0.09 (3H, s, Si*Me*), 0.43-0.45 (2H, m, H-2' and H-3'), 0.65-0.68 (1H, m, H-2'), 0.72-0.76 (1H, m, H-3'), 0.88 (9H, s, Si*tBu*), 0.98-1.03 (1H, dddd, *J* = 11.1, 11.1, 11.1, 3.4 Hz, H-8), 1.15-1.26 (2H, m, H-9 and H-1'), 1.31-1.39 (1H, m, H-10), 1.46-1.53 (1H, ddd, *J* = 13.0, 13.0, 4.1 Hz, H-11), 1.60-1.66 (2H, m, H-9 and H-10), 2.06-2.12 (1H, br d, H-8), 2.18-2.23 (1H, br d, *J* = 13.7 Hz, H-11), 2.46 (1H, dd, *J* = 11.1, 6.4 Hz, H-7), 2.89 (1H, d, *J* = 16.3 Hz, H-3), 3.27 (1H, d, *J* = 16.3 Hz, H-3), 5.24 (1H, d, *J* = 0.7 Hz, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ -3.1 (Si*Me*), -2.7 (Si*Me*), 6.9 (C-3'), 8.3 (C-2'), 10.6 (C-1'), 18.0 (Si*C*), 22.9 (C-10), 23.8 (C-9), 24.5 (C-11), 25.8 (Si*tBu*), 31.3 (C-8), 47.0 (C-7), 58.9 (C-3), 72.6 (C-4), 80.2 (C-1), 122.9 (C-5), 156.7 (C-6), 214.9 (C-2). HRMS calcd for $C_{20}H_{32}O_2Si$ 332.2172, found 332.2143.

Low-temperature Quenching of the raction of 1a with 3. Reaction was carried out in the same way as described for the above reaction of **1** with **3** except the quenching temperature.

10: a pale yellow oil, R_f = 0.17 (hexane : Et_2O = 19 : 1). IR (film) 1685 cm^{-1}. ^{1}H-NMR (500 MHz, C_6D_6) δ0.08 (6H, s, $SiMe_2$), 0.95 (9H, s, Si*tBu*), 0.96 (3H, s, CH_3), 1.24-1.32 (1H, m, H-10), 1.43-1.57 (2H, m, H-10 and H-10), 1.62-1.74 (2H, m, H-7), 1.75 (1H, d, *J* = 5.6 Hz, H-7), 2.88 (1H, dd, *J* = 21.4, 2.4 Hz, H-3), 2.97 (1H, d, *J* = 21.4 Hz, H-3), 3.04-3.12 (1H, m, H-10), 5.13 (1H, d, *J* = 2.4 Hz, H-5). ^{13}C-NMR (125 MHz, C_6D_6) δ-4.5 (Si*Me*), -4.5 (Si*Me*), 14.7 (CH_3), 18.1 (Si*C*), 24.1 (C-10), 25.7 (Si*tBu*), 26.2 (C-9), 27.0 (C-8), 34.2 (C-6), 42.5 (C-3), 48.1 (C-7), 49.7 (C-1), 111.8 (C-5), 144.7 (C-4), 203.4 (C-2). HRMS calcd for $C_{17}H_{28}O_2Si$ 292.1859, found 292.1859.

11: a pale yellow oil, R_f = 0.24 (hexane : Et_2O = 15 : 1). IR (film) 1655 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 0.12 (6H, s, $SiMe_2$), 0.91 (9H, s, Si*tBu*), 1.27 (3H, d, *J* = 7.5 Hz, CH_3), 1.70-1.82 (2H, m, H-10), 2.50-2.68 (3H, m, H-8 and H-9), 2.71-2.80 (1H, m, H-9), 3.14-3.22 (1H, m, H-6), 3.35 (1H, dd, *J* = 15.1, 1.1 Hz, H-3), 3.43 (1H, d, *J* = 15.1 Hz, H-3), 5.02 (1H, d, *J* = 6.0 Hz, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-4.4 (Si*Me*), -4.4 (Si*Me*), 18.1 (Si*C*), 18.5 (CH_3), 20.8 (C-10), 25.8 (Si*tBu*), 33.2 (C-8), 39.2 (C-10), 51.0 (C-3), 112.5 (C-5), 136.7 (C-7), 148.0 (C-1), 164.9 (C-4), 192.9 (C-2). HRMS calcd for $C_{17}H_{28}O_2Si$ 292.1859, found 292.1850.

12: pale yellow oil, R_f = 0.45 (hexane : Et_2O = 15 : 1). IR (film) 1715 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ0.16 (3H, s, Si*Me*), 0.18 (3H, s, Si*Me*), 0.93 (9H, s, Si*tBu*), 1.65-1.75 (3H, m, H-9 and H-10), 1.76 (3H, d, *J* = 1.2 Hz,

CH_3), 2.25-2.29 (1H, m, H-8), 2.32-2.38 (2H, m, H-8 and H-10), 3.03 (1H, dd, *J* = 18.6, 0.9 Hz, H-3), 3.17-3.22 (2H, m, H-3 and H-1), 5.49 (1H, s, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-4.5 (Si*Me*), -4.2 (Si*Me*), 18.2 (Si*C*), 20.0 (CH_3), 25.8 (Si*tBu*), 26.6 (C-9 and C-10), 31.2 (C-8), 50.3 (C-3), 57.0 (C-1), 114.2 (C-5), 125.4 (C-4), 133.9, 146.8, 208.3 (C-2). HRMS: calcd for $C_{17}H_{28}O_2Si$ 292.1859, found 292.1866.

13: a pale yellow oil, R_f = 0.14 (hexane : Et_2O = 15 : 1). IR (film) 1640 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ0.21 (6H, s, SiMe_2), 0.94 (9H, s, Si*tBu*), 1.43-1.45 (1H, m, H-9), 1.60-1.68 (1H, m, H-8), 1.70-1.77 (2H, m, H-10 and H-9), 1.96-2.02 (1H, m, H-8), 2.02 (3H, dd, *J* = 1.3, 1.1 Hz, CH_3), 2.25-2.33 (1H, m, H-10), 2.52-2.58 (1H, m, H-1), 2.64-2.72 (1H, m, H-7), 5.63 (1H, d, *J* = 1.7 Hz, H-3), 5.75 (1H, dq, *J* = 1.7 Hz, H-5). ^{13}C-NMR (125 MHz, $CDCl_3$) δ-4.4 (Si*Me*), -4.2 (Si*Me*), 18.3 (Si*C*), 24.9 (CH_3), 25.5 (C-9), 25.7 (C-10), 25.7 (Si*tBu*), 30.8 (C-8), 44.8 (C-7), 53.5 (C-1), 113.6 (C-3), 124.3 (C-5), 154.7 (C-6), 163.9 (C-4), 200.2 (C-2). HRMS calcd for $C_{17}H_{28}O_2Si$ 292.1859, found 292.1858.