Supporting Information

Stereoselective Construction of Eight-Membered Oxygen Heterocycles by Brook Rearrangement-Mediated [3 + 4] Annulation

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General. IR spectra were recorded on a Horiba FT-710 spectrometer. ^1H NMR spectra were taken on JEOL Delta-500 (500 MHz) spectrometer in CDCl_3 with reference to CHCl_3 (δ 7.26) or in C_6D_6 with reference to C_6H_6 (δ 7.20). ^{13}C NMR spectra were measured with JEOL Delta-500 (125 MHz) spectrometer in CDCl_3 with reference to the CDCl_3 triplet (δ 77.2) or in C_6D_6 with reference to C_6H_6 triplet (δ 128.0). Resonance patterns were described as s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. The assignment of ^1H 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-SX102 spectrometers. For routine chromatography, the following adsorbents were used: Kanto Kagaku silica gel 60N 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.

General Procedure for the [3 + 4] Annulation leading to 8: Preparation of 8-(*tert*-Butyldimethylsiloxy)-6-trimethylsilyl-2-oxabicyclo[3.3.2]dec-7-en-9-one (8a).

To a cooled ($-98\text{ }^\circ\text{C}$) solution of NHMDS (1.0 M in THF, 2.16 mL, 2.16 mmol) in CPME (15.4 mL) was added dropwise a solution of 6-oxacyclohept-2-en-1-one (**5**) (222 mg, 1.98 mmol) in CPME (3.3 mL) over a period of 6 min, and then the solution was stirred at the same temperature for 10 min. To this solution was added dropwise a cooled ($-80\text{ }^\circ\text{C}$) solution of **7** ($\text{R} = \text{SiMe}_3$) (437 mg, 1.80 mmol) in CPME (7.0 mL) over a period of 4 min, and then the solution was warmed to $-50\text{ }^\circ\text{C}$ over a period of 70 min before addition of AcOH (1.0 M in THF, 2.16 mL, 2.16 mmol). The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residual oil was subjected to column chromatography (silica gel, 45 g, elution with hexane: Et_2O = 5:1) to give **8a** ($\text{R} = \text{SiMe}_3$) (533 mg, 83%).

8a ($\text{R} = \text{SiMe}_3$): mp $59\text{--}61\text{ }^\circ\text{C}$, colorless plates (petroleum ether). R_f = 0.34 (hexane: Et_2O = 3:1). IR (KBr) 1706 cm^{-1} . ^1H NMR (CDCl_3) δ 0.04 (9H, s, SiMe_3), 0.12 (6H, s, SiMe_2), 0.90 (9H, s, *t*-Bu), 1.74 (1H, br dm, J = 13.6 Hz, H-4), 1.80–1.82 (1H, m, H-6), 2.12 (1H, dddd, J = 13.6, 13.6, 6.0, 2.9 Hz, H-4), 2.33–2.36 (1H, m, H-5), 2.59 (1H, ddd, J = 18.5, 5.5, 1.6 Hz, H-10), 2.84 (1H, br d, J = 18.5 Hz, H-10), 3.90 (1H, dd, J = 12.8, 6.0 Hz, H-3), 4.21 (1H, ddd, J = 12.8, 12.8, 2.9 Hz, H-3), 4.46 (1H, d, J = 2.0, H-1), 5.56 (1H, dd, J = 5.0, 2.0 Hz, H-7). ^{13}C NMR δ -4.1 and -4.0 (SiMe_2), -1.5 (SiMe_3), 18.1 (CMe_3), 25.8 (CMe_3), 30.2 (C-5), 34.6 (C-6), 41.8 (C-4), 46.7 (C-10), 62.7 (C-3), 89.3 (C-1), 119.1 (C-7), 139.2 (C-8), 206.6 (C=O). MS 354(M^+).

8b ($\text{R} = \text{SiMe}_2\text{Ph}$): mp $95\text{--}96\text{ }^\circ\text{C}$, colorless plates (petroleum ether). R_f = 0.39 (hexane: Et_2O = 3:1). IR (KBr) 1702 cm^{-1} . ^1H NMR (C_6D_6) δ 0.13, 0.16, 0.22 and 0.25 (each 3H, s, SiMe_2), 0.90 (9H, s, *t*-Bu), 1.18 (1H, br dm, J = 13.7 Hz, H-4), 1.64 (1H, dddd, J = 13.7, 13.7, 6.1, 3.0 Hz, H-4), 1.78 (1H, dd, J =

5.5, 2.8 Hz, H-6), 1.89 (1H, br s, H-5), 2.53 (2H, d, $J = 3.9$ Hz, H-10), 3.73 (1H, dd, $J = 13.7$, 6.1 Hz, H-3), 4.11 (1H, ddd, $J = 13.7$, 13.7, 3.0 Hz, H-3), 4.89 (1H, d, $J = 2.1$ Hz, H-1), 5.53 (1H, dd, $J = 5.5$, 2.1 Hz, H-7), 7.17-7.20 (3H, m, ArH), 7.33-7.36 (2H, m, ArH). ^{13}C NMR (C_6D_6) δ -5.8, -5.6, -4.3 and -4.2 (SiMe_2), 17.3 and 17.8 (CMe_3), 25.6 and 27.1 (CMe_3), 30.9 (C-5, C-6), 41.5 (C-4), 46.4 (C-10), 62.4 (C-3), 89.3 (C-1), 120.0 (C-7), 139.7 (C-8), 205.1 (C=O). MS 416 (M^+), Anal. Calcd for $\text{C}_{23}\text{H}_{36}\text{O}_4\text{Si}_2$: C, 66.29; H, 8.71. found: C, 66.33; H, 8.56.

8c (**R** = **SiMe₂Bu^t**): mp 60 °C, colorless plates (petroleum ether). $R_f = 0.47$ (hexane:Et₂O = 3:1). IR (KBr) 1705 cm^{-1} . ^1H NMR (CDCl_3) δ -0.03 and 0.02 (each 3H, s, SiMe_2), 0.12 (6H, s, SiMe_2), 0.90 and 0.92 (9H, s, *t*-Bu), 1.76 (1H, br d, $J = 13.9$ Hz, H-4), 2.03-2.04 (1H, br s, H-6), 2.11 (1H, dddd, $J = 13.9$, 13.9, 6.0, 2.9 Hz, H-4), 2.35-2.37 (1H, m, H-5), 2.61 (1H, ddd, $J = 18.4$, 3.8, 1.6 Hz, H-10), 2.83 (1H, br d, $J = 18.4$ Hz, H-10), 3.90 (1H, dd, $J = 13.9$, 6.0 Hz, H-3), 4.19 (1H, ddd, $J = 13.9$, 13.9, 2.9 Hz, H-3), 4.46 (1H, d, $J = 1.7$ Hz, H-1), 5.53 (1H, dd, $J = 5.5$, 1.7 Hz, H-7). ^{13}C NMR (C_6D_6) δ -4.2, -4.1, -3.5 and -3.2 (SiMe_2), 18.0 (CMe_3), 25.8 (CMe_3), 30.0 (C-5), 34.4 (C-6), 41.7 (C-4), 46.6 (C-10), 62.6 (C-3), 89.2 (C-1), 118.4 (C-7), 139.7 (C-8), 206.5 (C=O). MS 396 (M^+), Anal. Calcd for $\text{C}_{21}\text{H}_{40}\text{O}_3\text{Si}_2$: C, 63.58; H, 10.16. found: C, 63.63; H, 10.00.

8d (**R** = ***i*-Pr**): a colorless oil. $R_f = 0.36$ (hexane:Et₂O = 3:1). IR (film) 1715 cm^{-1} . ^1H NMR (CDCl_3) δ 0.10 and 0.11 (each 3H, s, SiMe_2), 0.87 (9H, s, *t*-Bu), 0.89 and 0.93 (each 3H, d, $J = 6.8$ Hz, CHMe_2), 1.52-1.62 (1H, m, CHMe_2), 1.69-1.73 (1H, br d, $J = 13.9$ Hz, H-4), 1.97-2.00 (1H, m, H-6), 2.05 (1H, dddd, $J = 13.9$, 13.9, 6.5, 3.4 Hz, H-4), 2.30-2.34 (1H, m, H-5), 2.66 (1H, ddd, $J = 18.0$, 5.5, 1.4 Hz, H-10), 2.75 (1H, d, $J = 18.0$, 2.7 Hz, H-10), 3.84 (1H, dd, $J = 13.9$, 6.5 Hz, H-3), 4.12 (1H, ddd, $J = 13.9$, 13.9, 3.4 Hz, H-3), 4.36 (1H, d, $J = 2.1$ Hz, H-1), 5.53 (1H, br d, $J = 5.7$ Hz, H-7). ^{13}C NMR (CDCl_3) δ -4.3 and -4.2 (SiMe_2), 18.0 (CMe_3), 21.6 and 22.0 (CHMe_2), 25.7 (CMe_3), 31.0 (C-5), 32.1 (CHMe_2), 39.1 (C-4), 43.7 (C-10), 48.1 (C-6), 62.8 (C-3), 88.6 (C-1), 119.8 (C-7), 141.3 (C-8), 207.5 (C=O). HRMS calcd for $\text{C}_{18}\text{H}_{32}\text{O}_3\text{Si}$, (M^+), 324.2121, found 324.2159.

8e (**R** = ***t*-Bu**): mp 72 °C, colorless plates (*i*-Pr₂O). $R_f = 0.38$ (hexane:Et₂O = 3:1). IR (KBr) 1711 cm^{-1} . ^1H NMR (CDCl_3) δ 0.13 and 0.14 (each 3H, s, SiMe_2), 0.89 (9H, s, *t*-Bu), 0.94 (9H, s, *t*-Bu), 1.68-1.71 (1H, br d, $J = 13.7$ Hz, H-4), 2.03 (1H, dddd, $J = 13.7$, 13.7, 6.3, 3.1 Hz, H-4), 2.13 (1H, dd, $J = 5.0$, 2.3 Hz, H-6), 2.50 (1H, br s, H-5), 2.75 (1H, dd, $J = 18.6$, 4.6 Hz, H-10), 2.79 (1H, dd, $J = 18.6$, 3.4 Hz, H-10), 3.86 (1H, dd, $J = 13.7$, 6.3 Hz, H-3), 4.12 (1H, ddd, $J = 13.7$, 13.7, 3.1 Hz, H-3), 4.39 (1H, s, H-1), 5.63 (1H, d, $J = 5.0$ Hz, H-7). ^{13}C NMR (CDCl_3) δ -4.1 and -4.0 (SiMe_2), 18.0 (SiCMe_3), 25.8 (SiCMe_3), 29.4 (CMe_3), 29.8 (C-5), 35.7 (CMe_3), 40.7 (C-4), 45.1 (C-10), 51.9 (C-6), 62.9 (C-3), 88.8 (C-1), 118.7 (C-7), 142.2 (C-8), 207.0 (C=O). MS 338 (M^+), Anal. Calcd for $\text{C}_{19}\text{H}_{34}\text{O}_3\text{Si}$: C, 67.40; H, 10.12. found: C, 67.56; H, 10.03.

General Procedure for α -Hydroxylation of **8**: Preparation of **8-(tert-Butyldimethylsiloxy)-6-trimethylsilyl-10-hydroxy-2-oxabicyclo[3.3.2]dec-7-en-9-one (10b)** (**R** = **SiMe₂Ph**)

To a cooled (-80 °C) solution of NHMDS (0.98 M in THF, 0.38 mL, 0.34 mmol) and 18-crown-6 (99 mg, 0.34 mmol) in THF (3.1 mL) was added dropwise a solution of **8b** (**R** = **SiMe₂Ph**) (74 mg, 0.18 mmol) in THF (0.8 mL) over a period of 1 min., and then the solution was stirred at the same temperature for 30 min before addition of a solution of 2-benzenesulfonyl-3-(3-nitrophenyl)oxiziridine (114 mg, 0.37 mmol) in THF (0.8 mL) was added to the above solution, and then the mixture was stirred at the same temperature for 30 min. The reaction mixture was diluted with saturated aqueous NH_4Cl solution (20 mL), phases were separated, and the aqueous phase was extracted with Et₂O (15 mL x 3). Combined organic phases were washed with saturated brine (20 mL), dried (MgSO_4), and concentrated under reduced pressure. The residual oil was subjected to column chromatography (silica gel, 35 g, elution with hexane:AcOEt = 6:1) to give **10b** (**R** = **SiMe₂Ph**) (66 mg, 86%).

10a (**R** = **SiMe₃**): mp 85-86 °C, colorless needles (*i*-Pr₂O). $R_f = 0.31$ (hexane:AcOEt = 5:1). IR (KBr) 3410, 1713 cm^{-1} . ^1H NMR (CDCl_3) δ 0.09 and 0.13 (each 3H, s, SiMe_2), 0.14 (9H, s, SiMe_3), 0.90 (9H, s, *t*-Bu), 1.48 (1H, br dd, $J = 12.8$, 7.1 Hz, H-4), 1.75 (1H, br d, $J = 3.4$ Hz, H-6), 1.97 (1H, ddd, $J =$

12.8, 12.8, 3.9 Hz, H-4), 2.50 (1H, br d, $J = 7.1$ Hz, H-5), 3.47 (1H, s, OH), 3.78 (1H, ddd, $J = 12.8, 3.4, 3.4$ Hz, H-3), 3.97 (1H, br dd, $J = 12.8, 12.8$ Hz, H-3), 4.18 (1H, br s, H-10), 4.43 (1H, d, $J = 1.6$ Hz, H-1), 5.53 (1H, br s, H-7). ^{13}C NMR (CDCl_3) δ -4.3 and -4.2 (SiMe_2), -1.7 (SiMe_3), 18.1 (CMe_3), 25.8 (CMe_3), 31.6 (C-6), 33.3 (C-4), 34.3 (C-5), 61.8 (C-3), 77.1 (C-10), 83.4 (C-1), 116.7 (C-7), 140.8 (C-8), 205.9 (C=O). MS 370 (M^+), Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{O}_4\text{Si}_2$: C, 58.33; H, 9.25. found: C, 58.26; H, 9.03.

10b (R = SiMe₂Ph): mp 86 °C, colorless plates (*i*-Pr₂O). $R_f = 0.26$ (hexane:AcOEt = 5:1). IR (KBr) 3410, 1717 cm^{-1} . ^1H NMR (CDCl_3) δ 0.01, 0.06, 0.43 and 0.44 (each 3H, s, SiMe_2), 0.87 (9H, s, *t*-Bu), 1.42-1.46 (1H, br dm, H-4), 1.92 (1H, ddm, $J = 12.8, 12.8$ Hz, H-4), 1.97 (1H, dd, $J = 3.3, 1.4$ Hz, H-6), 2.51 (1H, br d, $J = 7.1$ Hz, H-5), 3.33 (1H, br s, OH), 3.76 (1H, ddd, $J = 12.8, 3.3, 3.3$ Hz, H-3), 3.94 (1H, ddd, $J = 12.8, 12.8, 1.4$ Hz, H-3), 4.09 (1H, br s, H-10), 4.39 (1H, d, $J = 1.6$ Hz, H-1), 5.47 (1H, br s, H-7), 7.35-7.39 (3H, m, Ph), 7.52-7.54 (2H, m, Ph). ^{13}C NMR (CDCl_3) δ -4.4, -4.3 -3.7 and -3.4 (SiMe_2), 18.0 (CMe_3), 25.8 (CMe_3), 31.4 (C-6), 33.3 (C-4), 34.1 (C-5), 61.8 (C-3), 77.0 (C-10), 83.3 (C-1), 116.0 (C-7), 128.3, 129.9, 133.9 and 136.6 (Ph), 141.3 (C-8), 205.8 (C=O). MS 432 (M^+), Anal. Calcd for $\text{C}_{23}\text{H}_{36}\text{O}_4\text{Si}_2$: C, 63.84; H, 8.39. found: C, 63.75; H, 8.19.

10c (R = SiMe₂Bu^t): mp 67 °C, colorless plates (*i*-Pr₂O). $R_f = 0.44$ (hexane:AcOEt = 5:1). IR (KBr) 3507, 1707 cm^{-1} . ^1H NMR (C_6D_6) δ -0.05, 0.03, 0.07 and 0.11 (each 3H, s, SiMe_2), 0.84 and 0.90 (each 9H, s, *t*-Bu), 1.02-1.09 (1H, m, H-4), 1.74 (1H, dd, $J = 2.1, 1.6$ Hz, H-6), 1.95 (1H, dddd, $J = 12.8, 12.8, 4.1, 1.4$ Hz, H-4), 2.49 (1H, br d, $J = 7.1$ Hz, H-5), 3.53 (1H, br s, OH), 3.59 (1H, dd, $J = 12.8, 3.3, 3.3$ Hz, H-3), 3.84 (1H, ddd, $J = 12.8, 12.8, 1.5$ Hz, H-3), 4.13 (1H, br s, H-10), 4.82 (1H, d, $J = 1.8$ Hz, H-1), 5.56 (1H, br s, H-7). ^{13}C NMR δ -5.7, -5.2 and -4.3 (SiMe_2), 17.7 and 18.0 (*t*-Bu-C), 25.8 and 27.1 (*t*-Bu-Me), 27.7 (C-6), 33.0 (C-4), 35.1 (C-5), 61.7 (C-3), 77.3 (C-10), 83.3 (C-1), 118.0 (C-7), 140.1 (C-8), 205.9 (C=O). MS 412 (M^+), Anal. Calcd for $\text{C}_{21}\text{H}_{40}\text{O}_4\text{Si}_2$: C, 61.11; H, 9.77. found: C, 61.24; H, 9.77.

10d (R = *i*-Pr): a colorless oil. $R_f = 0.29$ (hexane:AcOEt = 5:1). IR (film) 3441, 1734 cm^{-1} . ^1H NMR (CDCl_3) δ 0.13 and 0.16 (each 3H, s, SiMe_2), 0.92 (9H, s, *t*-Bu), 1.07 and 1.08 (each 3H, d, $J = 7.3$ Hz, CHMe_2), 1.52-1.58 (1H, m, H-4), 1.83-1.94 (2H, m, H-4 and CHMe_2), 2.14-2.17 (1H, m, H-6), 2.45 (1H, br d, $J = 7.1$ Hz, H-5), 3.42 (1H, br s, OH), 3.79 (1H, ddd, $J = 12.6, 3.4, 3.4$ Hz, H-3), 3.92 (1H, ddd, $J = 12.6, 12.6, 1.6$ Hz, H-3), 4.40 (2H, br s, H-1 and H-10), 5.52 (1H, br s, H-7). ^{13}C NMR (CDCl_3) δ -4.3 (SiMe_2), 18.1 (CMe_3), 21.3 and 21.6 (CHMe_2), 25.8 (CMe_3), 32.1 (C-4), 32.8 (CHMe_2), 35.3 (C-5), 45.5 (C-6), 62.3 (C-3), 75.7 (C-10), 82.9 (C-1), 118.0 (C-7), 142.6 (C-8), 206.2 (C=O). HRMS calcd for $\text{C}_{18}\text{H}_{32}\text{O}_4\text{Si}$, (M^+), 340.2070, found 340.2106.

10e (R = *t*-Bu): a colorless oil. $R_f = 0.32$ (hexane:AcOEt = 5:1). IR (film) 3505, 1720 cm^{-1} . ^1H NMR (CDCl_3) δ 0.10 and 0.13 (each 3H, s, SiMe_2), 0.89 (9H, s, *t*-Bu), 1.05 (9H, s, *t*-Bu), 1.46-1.50 (1H, m, H-4), 1.84 (1H, br dm, $J = 12.6, 12.6$ Hz, H-4), 2.10 (1H, br d, $J = 2.5$ Hz, H-6), 2.59 (1H, br d, $J = 7.1$ Hz, H-5), 3.41 (1H, br s, OH), 3.77 (1H, dm, $J = 12.6$ Hz, H-3), 3.84 (1H, br dd, $J = 12.6, 12.6$ Hz, H-3), 4.33 (1H, br s, H-1), 4.47 (1H, br s, H-10), 5.62 (1H, br s, H-7). ^{13}C NMR (CDCl_3) δ -4.3 (SiMe_2), 18.1 (SiCMe_3), 25.8 (SiCMe_3), 28.9 (CMe_3), 32.8 (C-4), 33.5 (C-5), 35.5 (CMe_3), 49.2 (C-6), 62.5 (C-3), 76.4 (C-10), 82.5 (C-1), 116.4 (C-7), 144.4 (C-8), 206.2 (C=O). HRMS calcd for $\text{C}_{19}\text{H}_{34}\text{O}_4\text{Si}$, (M^+), 354.2226, found 354.2227.

General Procedure for the oxidative cleavage of 10: (2*R,5*R**,6*R**)-3-(*tert*-Butyldimethylsiloxy)-5-(trimethylsilyl)-6-formyl-5,6,7,8-tetrahydro-2*H*-oxocine-2-carboxylic acid methyl ester (11a)(R = SiMe₃)**

To a cooled (by ice-water) solution of **10a** (R = SiMe₃) (22 mg, 0.059 mmol) in MeOH-benzene (1:1, 3.0 mL) was added Pb(OAc)₄ (58 mg, 0.118 mmol). The bath was then removed, and the mixture was stirred at room temperature for 15 min. The mixture was passed through a pad of Celite, and the filtrate was concentrated. The residual oil was subjected to column chromatography (silica gel, 10 g; elution with hexane:AcOEt = 2:1) to give **11a** (R = SiMe₃) (22 mg, 93%).

11a (R = SiMe₃): a colorless oil. R_f = 0.46 (hexane:AcOEt = 4:1). IR (film) 1749, 1726 cm⁻¹. ¹H NMR δ 0.11 (9H, s, SiMe₃) 0.15 and 0.16 (each 3H, s, SiMe₂), 0.83 (9H, s, *t*-Bu), 1.79 (1H, ddd, J = 15.8, 8.6, 5.3 Hz, H-7), 2.19 (1H, dd, J = 11.0, 3.0 Hz, H-5), 2.30 (1H, br dt, J = 15.8, 6.6 Hz, H-7), 2.77 (1H, br s, H-6), 3.74 (3H, s, COMe), 3.89 (1H, dd, J = 12.9, 6.6 Hz, H-8), 4.13 (1H, dd, J = 12.9, 8.6 Hz, H-8), 4.94 (1H, d, J = 11.0 Hz, H-4), 4.95 (1H, br s, H-2), 9.66 (1H, d, J = 0.7 Hz, CHO). ¹³C NMR δ -4.4 and -4.3 (SiMe₂), -1.8 (SiMe₃), 18.1 (CMe₃), 25.4 (C-5), 25.7 (CMe₃), 30.0 (C-7), 52.0 (OMe), 53.1 (C-6), 66.5 (C-8), 76.9 (C-2), 106.5 (C-4), 150.2 (C-3), 169.9 (COOMe), 203.4 (CHO). HRMS calcd for C₁₉H₃₆O₅Si₂, (M⁺), 400.2101, found 400.2099.

11b (R = SiMe₂Ph): a colorless oil. R_f = 0.46 (hexane:AcOEt = 4:1). IR (film) 1748, 1724 cm⁻¹. ¹H NMR (C₆D₆) δ 0.12, 0.14, 0.31 and 0.33 (each 3H, s, SiMe₂), 0.89 (9H, s, *t*-Bu), 1.33-1.40 (1H, m, H-7), 1.99 (1H, br dt, J = 15.6, 6.6 Hz, H-7), 2.36 (1H, td, J = 5.5, 2.4 Hz, H-6), 2.59 (1H, dd, J = 11.0, 2.4 Hz, H-5), 3.41 (3H, s, OMe), 3.71 (1H, ddd, J = 12.7, 6.6, 1.8 Hz, H-8), 4.16 (1H, dd, J = 12.7, 8.4 Hz, H-8), 5.04 (1H, d, J = 1.6 Hz, H-2), 5.16 (1H, dd, J = 11.0, 1.6 Hz, H-4), 7.17-7.22 (3H, m, Ph), 7.44-4.46 (2H, m, Ph), 9.27 (1H, s, CHO). ¹³C NMR (C₆D₆) δ -4.7, -4.5, -3.9 and -3.2 (SiMe₂), 17.9 (CMe₃), 24.2 (C-5), 25.5 (CMe₃), 29.5 (C-7), 51.0 (OMe), 52.1 (C-6), 66.0 (C-8), 77.6 (C-2), 106.2 (C-4), 128.1, 129.4 and 134.1 (Ph), 150.2 (C-3), 169.3 (CO), 202.1 (CHO). HRMS calcd for C₂₄H₃₈O₈Si₂, (M⁺), 462.2258, found 462.2249.

11c (R = SiMe₂Bu^t): a colorless oil. R_f = 0.47 (hexane:AcOEt = 4:1). IR (film) 1748, 1725 cm⁻¹. ¹H NMR (C₆D₆) δ -0.09, 0.17, 0.18 and 0.21 (each 3H, s, SiMe₂), 0.88 and 0.90 (each 9H, s, *t*-Bu), 1.43 (1H, dddd, J = 15.7, 8.9, 5.6, 1.8 Hz, H-7), 2.05 (1H, dtd, J = 15.7, 7.2, 1.2 Hz, H-7), 2.32-2.35 (1H, m, H-6), 2.44 (1H, dd, J = 11.0, 2.7 Hz, H-5), 3.42 (3H, s, OMe), 3.67 (1H, ddd, J = 12.8, 7.2, 1.8 Hz, H-8), 4.08 (1H, ddd, J = 12.8, 8.9, 1.2 Hz, H-8), 5.02 (1H, dd, J = 1.5 Hz, H-2), 5.12 (1H, dd, J = 11.0, 1.5 Hz, H-4), 9.33 (1H, s, CHO). ¹³C NMR (C₆D₆) δ -6.5, -6.4, -4.6 and -4.5 (SiMe₂), 17.4 and 17.9 (CMe₃), 20.4 (C-5), 25.5 and 26.9 (CMe₃), 29.3 (C-7), 51.0 (OMe), 53.4 (C-6), 66.4 (C-8), 77.4 (C-2), 107.6 (C-4), 149.3 (C-3), 169.1 (CO), 202.1 (CHO). HRMS calcd for C₂₂H₄₂O₅Si₂, (M⁺), 442.2571, found 442.2534.

11d (R = *i*-Pr): a colorless oil. R_f = 0.43 (hexane:AcOEt = 4:1). IR (film) 1748, 1723 cm⁻¹. ¹H NMR (C₆D₆) δ 0.16 and 0.20 (each 3H, s, SiMe₂), 0.78 and 0.86 (each 3H, d, J = 6.6 Hz, *i*-Pr), 0.91 (9H, s, *t*-Bu), 1.27-1.33 (1H, m, H-7), 1.57-1.64 (1H, dq, J = 9.9, 6.6 Hz, CHMe₂), 2.13 (1H, dtd, J = 15.6, 8.0, 1.6 Hz, H-7), 2.36-2.40 (1H, m, H-6), 2.53 (1H, td, J = 9.9, 3.3 Hz, H-5), 3.40 (3H, s, OMe), 3.63 (1H, ddd, J = 12.8, 8.0, 1.9 Hz, H-8), 4.07 (1H, ddd, J = 12.8, 8.0, 1.6 Hz, H-8), 4.84 (1H, dd, J = 9.9, 1.5 Hz, H-4), 4.90 (1H, d, J = 1.5 Hz, H-2), 9.42 (1H, d, J = 2.1 Hz, CHO). ¹³C NMR (C₆D₆) δ -4.6 and -4.5 (SiMe₂), 17.9 (CMe₃), 20.6 and 22.2 (*i*-Pr), 25.5 (CMe₃), 28.4 (C-7), 31.4 (CHMe₂), 43.7 (C-5), 51.0 (OMe), 52.4 (C-6), 66.4 (C-8), 77.7 (C-2), 110.5 (C-4), 148.7 (C-3), 168.9 (CO), 202.0 (CHO). HRMS calcd for C₁₉H₃₄O₅Si, (M⁺), 370.2176, found 370.2186.

11e (R = *t*-Bu): a colorless oil. R_f = 0.45 (hexane:AcOEt = 4:1). IR (film) 1750, 1719 cm⁻¹. ¹H NMR (C₆D₆) δ 0.15 and 0.18 (each 3H, s, SiMe₂), 0.79 (9H, s, *t*-Bu), 0.89 (9H, s, *t*-Bu), 1.38-1.44 (1H, m, H-7), 2.04 (1H, br d, J = 15.1 Hz, H-7), 2.43-2.46 (1H, m, H-6), 2.92 (1H, dd, J = 10.7, 1.4 Hz, H-5), 3.39 (3H, s, OMe), 3.92 (1H, ddd, J = 12.8, 5.3, 2.1 Hz, H-8), 4.35 (1H, br dd, J = 12.8, 10.8 Hz, H-8), 5.04 (1H, d, J = 1.8 Hz, H-2), 5.13 (1H, dd, J = 10.7, 1.7 Hz, H-4), 9.65 (1H, d, J = 1.7 Hz, CHO). ¹³C NMR (C₆D₆) δ -4.5 (SiMe₂), 17.9 (SiCMe₃), 25.5 (SiCMe₃), 27.9 (CMe₃), 30.4 (C-7), 33.5 (CMe₃), 46.0 (C-5), 50.7 (C-6), 51.0 (OMe), 65.4 (C-8), 78.0 (C-2), 107.5 (C-4), 148.4 (C-3), 169.6 (CO), 202.0 (CHO). HRMS calcd for C₂₀H₃₆O₅Si, (M⁺), 384.2332, found 384.2311.

(1R*,2S*)-1-(2-Ethenylcyclohexyloxy)-but-3-en-2-one (14)

To a suspension of NaH (60%, 1.82 g, 45.6 mmol) (washed with hexane) in DMF (27 mL) was added dropwise a solution of 2-ethenylcyclohexanol (**12**) (2.88 g, 22.8 mmol) in DMF (5 mL) over a period of 10 min, and the reaction mixture was stirred at room temperature for 5 min. To the solution was added 1-chloro-3-triphenylphosphoranylidene)-2-propanone (8.44 g, 24.0 mmol) in DMF (12 mL) in one

portion, and the mixture was stirred at room temperature for 1 h before addition of water (50 mL). The mixture was extracted with Et₂O (50 mL x 3), and combined organic phases were washed with saturated brine (30 mL), dried, and concentrated. The residual oil was passed through a short pad of silica gel (20 g, elution with CH₂Cl₂:MeOH = 20:1), and the filtrate was concentrated. To the solution of the residue in Et₂O (120 mL) was added a 35% aqueous solution of HCHO (12 mL, ca. 140 mmol) was added, and the solution was stirred at room temperature for 15 min before addition of H₂O (50 mL). The phases were separated, and the aqueous phase was extracted with Et₂O (30 mL x 2). Combined organic phases were washed with saturated brine (30 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 45 g, elution with hexane:Et₂O = 4:1) to give **14** (2.31 g, 52%). a colorless oil. *R_f* = 0.31 (hexane:Et₂O = 5:2). IR (film) 1701, 1615 cm⁻¹. ¹H NMR (C₆D₆) δ 0.87-1.11 (4H, m, H-3, H-4, H-5, and H-6), 1.35-1.42 (1H, m, H-4), 1.45-1.51 (1H, m, H-5), 1.57-1.65 (1H, m, H-3), 1.77-1.83 (1H, m, H-6), 2.00-2.07 (1H, m, H-2), 2.75 (1H, td, *J* = 9.9, 3.9 Hz, H-1), 3.85 (1H, d, *J* = 16.3 Hz, H-1'), 3.95 (1H, d, *J* = 16.3 Hz, H-1'), 5.02 (1H, br d, *J* = 10.5 Hz, H-2''), 5.06 (1H, br d, *J* = 17.3 Hz, H-2''), 5.25 (1H, dd, *J* = 10.7, 1.8 Hz), 5.86 (1H, ddd, *J* = 17.3, 10.5, 7.3 Hz, H-1''), 6.23 (1H, dd, *J* = 17.4, 1.8 Hz), 6.57 (1H, dd, *J* = 17.4, 10.7 Hz). ¹³C NMR (CDCl₃) δ 24.7, 25.1, 31.2, 48.0 (C-2), 73.6 (C-1'), 83.0 (C-1), 114.7 (C-2''), 129.1 (C-4'), 132.7 (C-3'), 141.5 (C-1''), 198.3 (C=O). HRMS calcd for C₁₂H₁₈O₂, (*M*⁺), 194.1307, found 194.1332.

(1R*,7S*)-2-Oxabicyclo[5.4.0]undec-5-en-4-one (15)

A solution of **14** (2.21 g, 11.4 mmol) and the second generation Grubbs' catalyst (96 mg, 0.11 mol) in CH₂Cl₂ (380 mL) was refluxed for 18 h, and the reaction mixture was concentrated. The residue was subjected to column chromatography (silica gel, 30 g, elution with hexane:CH₂Cl₂ = 1:3 to AcOEt) followed by distillation under reduced pressure to give **15** (1.14 g, 60%). a colorless oil. *R_f* = 0.33 (hexane:AcOEt = 4:1). IR (film) 1665 cm⁻¹. ¹H NMR (C₆D₆) δ 0.63-0.73 (1H, m), 0.78-0.93 (2H, m), 1.15-1.25 (1H, m), 1.28-1.40 (2H, m), 1.40-1.50 (1H, m), 1.70-1.78 (1H, m), 1.92-2.00 (1H, m), 2.77 (1H, ddd, *J* = 11.0, 11.0, 4.4 Hz, H-1), 4.05 and 4.30 (each 1H, d, *J* = 18.1 Hz, H-3), 5.68 (1H, dd, *J* = 12.6, 2.5 Hz, H-5), 5.91 (1H, dd, *J* = 12.6, 2.5 Hz, H-6). ¹³C NMR (C₆D₆) δ 24.8, 25.5, 31.0, 33.1, 49.6, 77.7 (C-3), 83.0 (C-1), 128.3 (C-6), 149.3 (C-5), 202.5 (C=O). HRMS calcd for C₁₀H₁₄O₂, (*M*⁺), 166.0994, found 166.0994.

General Procedure for the [3 + 4] Annulation leading to 16: Preparation of 10-(*tert*-Butyldimethylsiloxy)-12-(dimethylphenylsilyl)-8-oxa-tricyclo[7.3.2.0^{7,2}]tetradec-10-en-14-one (16b) (R = SiMe₂Ph)

To a cooled (-98 °C) solution of NHMDS (1.0 M in THF, 0.54 mL, 0.54 mmol) in CPME (5.2 mL) was added dropwise a solution of **15** (82 mg, 0.49 mmol) in CPME (1.2 mL) over a period of 3 min, and the solution was stirred at the same temperature for 10 min before addition of a cooled (-80 °C) solution of **7** (R = SiMe₂Ph) (136 mg, 0.445 mmol) in CPME (2.2 mL) in one portion. The mixture was allowed to warm to -50 °C before addition AcOH (1.0 M in THF, 0.54 mL, 0.54 mmol), and concentrated. The residue was subjected to column chromatography (silica gel, 25g, elution with hexane:Et₂O = 10:1) to give **16b** (R = SiMe₂Ph) (179 mg, 85%).

16a (R = SiMe₃): mp 129 °C, a colorless prisms (petroleum ether). *R_f* = 0.38 (hexane:Et₂O = 5:1). IR (KBr) 1703 cm⁻¹. ¹H NMR (C₆D₆) δ -0.04 (9H, s, SiMe₃), 0.20 and 0.20 (each 3H, s, SiMe₂), 0.71-0.85 (1H, m), 0.96 (9H, s, *t*-Bu), 1.21-1.32 (1H, m, H-6), 1.33-1.43 (3H, m), 1.46-1.52 (1H, m), 1.55-1.59 (1H, m, H-1), 1.61-1.65 (1H, m, H-12), 2.06 (1H, br d, *J* = 14.4 Hz, H-6), 2.39 (1H, dd, *J* = 19.5, 3.9 Hz, H-13), 2.52 (1H, dd, *J* = 19.5, 3.9 Hz, H-13), 3.08 (1H, ddd, *J* = 10.3, 10.3, 3.9 Hz, H-7), 4.96 (1H, d, *J* = 1.8 Hz, H-9), 5.22 (1H, dd, *J* = 5.3, 1.8 Hz, H-11). ¹³C NMR (CDCl₃) δ -4.5 and -4.3 (SiMe₂), -2.0 (SiMe₃), 18.0 (CMe₃), 24.7, 25.7 (CMe₃), 26.1, 34.1, 34.3, 36.7, 37.3, 42.2 (C-13), 51.4, 75.7 (C-7), 88.6 (C-9), 112.0 (C-11), 147.0 (C-10), 202.8 (C=O). MS 408 (*M*⁺), Anal. Calcd for C₂₂H₄₀O₃Si₂: C, 64.65; H, 9.86. found: C, 64.65; H, 9.68.

16b (R = SiMe₂Ph): mp 138 °C, a colorless needles (petroleum ether). *R_f* = 0.36 (hexane:Et₂O = 5:1).

IR (KBr) 1701 cm^{-1} . ^1H NMR (C_6D_6) δ 0.16 and 0.17 (each 3H, s, SiMe_2), 0.23 and 0.24 (each 3H, s, SiMe_2), 0.63-0.67 (1H, m), 0.85-0.95 (2H, m), 0.93 (9H, s, *t*-Bu), 1.20-1.50 (5H, m), 1.56 (1H, br m, H-1), 1.95-2.00 (1H, m, H-12) 2.02 (1H, br d, J = 10.3 Hz, H-6), 2.31 (1H, dd, J = 19.5, 4.1 Hz, H-13), 2.52 (1H, dd, J = 19.5, 3.7 Hz, H-13), 3.01 (1H, ddd, J = 10.3, 10.3, 4.1 Hz, H-7), 4.94 (1H, d, J = 1.8 Hz, H-9). ^{13}C NMR (C_6D_6) δ -4.5 and -4.3 (SiMe_2), -3.9 and -3.3 (SiMe_2), 18.0 (CMe_3), 24.7, 25.7 (CMe_3), 26.0, 33.9, 34.0, 36.4, 36.9, 42.0 (C-13), 51.8, 75.8 (C-7), 88.7 (C-9), 111.4 (C-11), 128.1 (Ar), 129.4 (Ar), 133.7 (Ar), 137.4 (Ar), 147.5 (C-10), 202.8 (C=O). MS 470 (M^+), Anal. Calcd for $\text{C}_{27}\text{H}_{42}\text{O}_3\text{Si}_2$: C, 68.88; H, 8.99. found: C, 68.63; H, 8.87.

16c (**R** = SiMe_2Bu^t): mp 109 $^\circ\text{C}$, a colorless needles (petroleum ether). R_f = 0.36 (hexane: Et_2O = 5:1). IR (KBr) 1703 cm^{-1} . ^1H NMR (C_6D_6) δ -0.05 and -0.01 (each 3H, s, SiMe_2), 0.20 and 0.21 (each 3H, s, SiMe_2), 0.70-1.00 (3H, m), 0.92 (9H, s, *t*-Bu), 1.22-1.34 (1H, m, H-6), 1.34-1.52 (4H, m), 1.67-1.72 (1H, br m, H-1), 1.95-1.99 (1H, m, H-12), 2.07 (1H, br d, J = 11.2 Hz, H-6), 2.41 (1H, dd, J = 19.5, 3.7 Hz, H-13), 2.58 (1H, dd, J = 19.5, 3.7 Hz, H-13), 3.10 (1H, ddd, J = 10.1, 10.1, 4.1 Hz, H-7), 4.94 (1H, d, J = 1.8 Hz, H-9), 5.27 (1H, dd, J = 5.5, 1.1 Hz, H-11). ^{13}C NMR (C_6D_6) δ -5.9 and -5.3 (SiMe_2), -4.4 and -4.3 (SiMe_2), 17.4 (CMe_3), 18.0 (CMe_3), 24.7, 25.7 (CMe_3), 26.1, 27.2 (CMe_3), 33.7, 34.1, 34.6, 38.0, 42.5 (C-13), 50.9, 75.7 (C-7), 88.2 (C-9), 113.1 (C-11), 146.8 (C-10), 202.8 (C=O). MS 450 (M^+), Anal. Calcd for $\text{C}_{27}\text{H}_{42}\text{O}_3\text{Si}_2$: C, 68.88; H, 8.99. found: C, 68.63; H, 8.87.

16d (**R** = *i*-Pr): a colorless oil, R_f = 0.41 (hexane: Et_2O = 5:1). IR (KBr) 1710 cm^{-1} . ^1H NMR (CDCl_3) δ 0.09 and 0.12 (each 3H, s, SiMe_2), 0.89 (9H, s, *t*-Bu), 0.91 and 0.95 (each 3H, d, J = 6.6 Hz, CHMe_2) 1.12-1.37 (4H, m), 1.52-1.80 (6H, m), 1.98 (1H, br d, J = 9.9 Hz, H-6), 2.18-2.22 (1H, m, H-12), 2.53 (1H, d, J = 19.5, 4.1 Hz, H-13), 2.72 (1H, dd, J = 19.5, 3.9 Hz, H-13), 3.33 (1H, ddd, J = 10, 10, 3.9 Hz, H-7), 4.40 (1H, d, J = 1.6 Hz, H-9), 5.05 (1H, d, J = 4.4 Hz, H-11). ^{13}C NMR (CDCl_3) δ -4.5 and -4.3 (SiMe_2), 18.0 (CMe_3), 21.1, 25.0, 25.8 (CMe_3), 26.1, 33.2, 34.1, 37.7, 39.4 (C-13), 50.5 (C-12), 50.9, 78.1 (C-7), 88.3 (C-9), 113.3 (C-11), 148.5 (C-10), 205.1 (C=O). HRMS calcd for $\text{C}_{22}\text{H}_{38}\text{O}_3\text{Si}$, (M^+), 378.2590, found 378.2600.

16e (**R** = *t*-Bu): mp 41-42 $^\circ\text{C}$, a colorless plates (*i*-Pr₂O), R_f = 0.41 (hexane: Et_2O = 5:1). IR (film) 1710 cm^{-1} . ^1H NMR (C_6D_6) δ 0.17 and 0.17 (each 3H, s, SiMe_3), 0.82 (9H, s, *t*-Bu), 1.24-1.50 (5H, m), 1.64 (br s, H-1), 1.93 (1H, br d, J = 9.2 Hz, H-6), 2.27-2.31 (1H, m, H-12), 2.35 (1H, dd, J = 19.5, 4.1 Hz, H-13), 2.74 (1H, dd, J = 19.5, 3.9 Hz, H-13), 3.14 (1H, ddd, J = 10.3, 10.3, 3.9 Hz, H-7), 4.86 (1H, d, J = 0.9 Hz, H-9), 5.28 (1H, ddd, J = 3.7, 1.8, 0.9 Hz, H-11). ^{13}C NMR (C_6D_6) δ -4.7 and -4.4 (SiMe_2), 18.0 (CMe_3), 25.0, 25.6 (CMe_3), 26.2, 28.2, 32.8, 34.1, 34.9, 36.1, 39.8 (C-13), 53.5, 54.7 (C-12), 78.7 (C-7), 89.5 (C-9), 111.2 (C-11), 149.6 (C-10), 203.1 (C=O). MS 392 (M^+), Anal. Calcd for $\text{C}_{23}\text{H}_{40}\text{O}_3\text{Si}$: C, 70.35; H, 10.27. found: C, 70.33; H, 10.47.

General Procedure for α -Hydroxylation of 16: Preparation of 10-(*tert*-Butyldimethylsiloxy)-12-(dimethylphenylsilyl)-13-hydroxy-8-oxa-tricyclo[7.3.2.0^{7,2}]tetradec-10-en-14-one (17b) (R** = SiMe_2Ph)**

To a cooled (-80 $^\circ\text{C}$) solution of NHMDS (1.0 M in THF, 0.39 mL, 0.39 mmol) and 18-crown-6 (15 mg, 0.06 mol) in THF (1.8 mL) was added a solution of **16b** (**R** = SiMe_2Ph) (80 mg, 0.20 mmol) in THF (0.8 mL), and the solution was stirred at the same temperature for 30 min. To the mixture was added a solution of Davis' reagent (119 mg, 0.39 mmol) in THF (1.3 mL) in one portion, and the reaction mixture was stirred at the same temperature for 30 min before addition of saturated aqueous NH_4Cl solution (20 mL). The mixture was extracted with Et_2O (20 mL x 3), washed with saturated brine (15 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 20 g, elution with hexane:AcOEt = 15:1) to give **17b** (**R** = SiMe_2Ph) (43 mg, 52 %)

17a (**R** = SiMe_3): a colorless oil R_f = 0.49 (hexane:AcOEt = 5:1). IR (film) 3472, 1711 cm^{-1} . ^1H NMR (CDCl_3) δ 0.03 and 0.09 (each 3H, s, SiMe_2), 0.09 (9H, s, SiMe_3), 0.88 (9H, s, *t*-Bu), 1.00-1.30 (3H, m, H-4, H-5 and H-6), 1.38-1.48 (1H, m, H-2), 1.48-1.62 (2H, m, H-4 and H-5), 1.65-1.83 (2H, m, H-3),

1.89 (1H, dd, $J = 3.4, 1.6$ Hz, H-12), 1.92-1.97 (1H, m, H-6), 2.24 (1H, br s, H-1), 3.00 (1H, br s, OH), 3.10-3.18 (1H, m, H-7), 4.02 (1H, d, $J = 2.7$ Hz, H-13), 4.60 (1H, d, $J = 1.8$ Hz, H-9), 5.11 (1H, dd, $J = 3.4, 1.8$ Hz, H-11). ^{13}C NMR (CDCl_3) δ -4.5 and -4.1 (SiMe_3), -1.8 (SiMe_3), 18.1 (CMe_3), 25.3, 25.8 (CMe_3), 26.6, 34.0, 35.0, 36.2 (C-12), 41.7 (C-1), 55.0, 75.2 (C-7), 76.6 (C-13), 85.6 (C-9), 110.9 (C-11), 146.2 (C-10), 208.6 (C=O). HRMS calcd for $\text{C}_{22}\text{H}_{40}\text{O}_4\text{Si}_2$, (M^+), 424.2465, found 424.2426.

17b (R = SiMe₂Ph): a colorless oil $R_f = 0.46$ (hexane:AcOEt = 5:1). IR (film) 3421, 1712 cm^{-1} . ^1H NMR (CDCl_3) δ 0.06 and 0.09 (each 3H, s, SiMe_2), 0.24 and 0.25 (each 3H, s, SiMe_2), 0.90 (9H, s, *t*-Bu), 0.88-1.03 (2H, m), 1.22-1.32 (1H, m), 1.35-1.65 (5H, m), 1.98 (1H, br d, $J = 9.4$ Hz, H-6), 2.08 (1H, dd, $J = 3.2, 1.6$ Hz, H-12), 2.34 (1H, br s, H-1), 2.81 (1H, br s, OH), 3.34 (1H, ddd, $J = 10.1, 10.1, 4.1$ Hz, H-7), 4.07 (1H, d, $J = 1.8$ Hz, H-13), 5.03 (1H, d, $J = 1.8$ Hz, H-9), 5.21 (1H, dd, $J = 3.4, 1.8$ Hz, H-11), 7.12-7.22 (3H, m, ArH), 7.40-7.45 (2H, m, ArH). ^{13}C NMR (CDCl_3) δ -4.7 and -4.4 (SiMe_3), -4.1 and -3.9 (SiMe_2), 17.9 (CMe_3), 25.1, 25.6 (CMe_3), 26.6, 34.2, 34.8, 35.6 (C-12), 41.6 (C-1), 55.3, 75.2 (C-7), 76.4 (C-13), 86.1 (C-9), 110.2 (C-11), 128.1 (Ar), 129.6 (Ar), 133.9 (Ar), 136.9 (Ar), 147.0 (C-10), 207.9 (C=O). HRMS calcd for $\text{C}_{27}\text{H}_{42}\text{O}_4\text{Si}_2$, (M^+), 486.2622, found 486.2641.

17c (R = SiMe₂Bu^t): a colorless oil $R_f = 0.51$ (hexane:AcOEt = 5:1). IR (film) 3493, 1712 cm^{-1} . ^1H NMR (CDCl_3) δ 0.02 and 0.05 (each 3H, s, SiMe_2), 0.09 and 0.10 (each 3H, s, SiMe_2), 0.89 (9H, s, *t*-Bu), 0.96 (9H, s, *t*-Bu), 1.05-1.15 (1H, m), 1.15-1.27 (2H, m), 1.45-1.55 (2H, m), 1.60 (1H, br d, $J = 12.6$ Hz, H-6), 1.63-1.80 (2H, m), 1.92-2.00 (1H, br m), 2.11 (1H, dd, $J = 3.9, 2.1$ Hz, H-12), 2.29 (1H, br s, H-1), 2.96 (1H, br s, OH), 3.12-3.20 (1H, m, H-7), 4.00 (1H, d, $J = 2.5$ Hz, H-13), 4.58 (1H, d, $J = 1.8$ Hz, H-9), 5.14 (1H, ddd, $J = 1.8, 1.8, 1.1$ Hz, H-11). ^{13}C NMR (CDCl_3) δ -5.6 and -5.0 (SiMe_2), -4.4 and -4.1 (SiMe_2), 17.9 (CMe_3), 18.1 (CMe_3), 25.2, 25.8 (CMe_3), 26.6, 27.3 (CMe_3), 32.8 (C-12), 34.0, 35.4, 42.5 (C-1), 54.1, 75.0 (C-13), 85.2 (C-9), 112.3 (C-11), 145.5 (C-10), 208.8 (C=O). HRMS calcd for $\text{C}_{25}\text{H}_{46}\text{O}_4\text{Si}_2$, (M^+), 466.2935, found 466.2953.

17d (R = *i*-Pr): a colorless oil $R_f = 0.49$ (hexane:AcOEt = 5:1). IR (film) 3447, 1713 cm^{-1} . ^1H NMR (CDCl_3) δ 0.06 and 0.12 (SiMe_2), 0.88 (*t*-Bu), 0.97 and 1.00 (each 3H, d, $J = 6.9$ Hz, CHMe_2), 1.05-1.33 (3H, m), 1.50-1.65 (3H, m), 1.68-1.85 (3H, m), 1.93 (1H, br d, $J = 11.9$ Hz, H-6), 2.10 (1H, br s, H-12), 2.48-2.52 (1H, m, H-1), 2.96 (1H, s, OH), 3.18-3.25 (1H, m, H-7), 4.33 (1H, d, $J = 3.0$ Hz, H-13), 4.53 (1H, d, $J = 1.6$ Hz, H-9), 4.99 (1H, br s, H-11). ^{13}C NMR (CDCl_3) δ -4.6 and -4.2 (SiMe_2), 18.1 (CMe_3), 20.4, 20.4, 25.4, 25.8, 26.8 (CMe_3), 34.2, 34.4, 34.9, 42.4, 50.3 (C-1), 54.7, 75.3 (C-13), 77.7 (C-7), 85.9 (C-9), 112.5 (C-11), 148.1 (C-10), 208.9 (C=O). HRMS calcd for $\text{C}_{22}\text{H}_{38}\text{O}_4\text{Si}$, (M^+), 394.2539 found 394.2558.

17e (R = *t*-Bu): a colorless oil $R_f = 0.49$ (hexane:AcOEt = 5:1). IR (film) 3449, 1713 cm^{-1} . ^1H NMR (CDCl_3) δ 0.05 and 0.12 (SiMe_2), 0.88 (9H, s, *t*-Bu), 0.98 (9H, s, *t*-Bu), 1.05-1.37 (3H, m), 1.52-1.66 (3H, m), 1.68-1.77 (2H, m), 1.93 (1H, br d, $J = 11.9$ Hz, H-6), 2.27 (1H, br s, H-12), 2.56 (1H, br s, H-1), 2.97 (1H, br s, OH), 3.13-3.22 (1H, m, H-7), 4.41 (1H, d, $J = 3.4$ Hz, H-13), 4.53 (1H, d, $J = 1.4$ Hz, H-9), 5.15 (1H, br s, H-11). ^{13}C NMR (CDCl_3) δ -4.6 and -4.1 (SiMe_2), 18.1 (CMe_3), 25.6, 25.8 (SiCMe_3), 27.0, 27.9 (CMe_3), 33.5, 34.3, 35.7, 40.2, 54.6 (C-1), 56.7, 75.5 (C-13), 79.0 (C-7), 86.6 (C-9), 110.4 (C-11), 148.6 (C-10), 208.8 (C=O). HRMS calcd for $\text{C}_{23}\text{H}_{40}\text{O}_4\text{Si}$, (M^+), 408.2696 found 408.2664.

General Procedure for the oxidative cleavage of 17: (1R*,3R*,6R*,7R*,8R*)-3-(*tert*-Butyldimethylsiloxy)-5-(dimethylphenylsilyl)-6-formyl-2-oxa-bicyclo[6.4.0]dodec-4-ene-3-carboxylic acid Methyl Ester (18b)

To a cooled (ice-water) solution of **17b** (R = SiMe₂Ph) (84.2 mg, 0.173 mmol) in MeOH-PhH (1:1, 8.6 mL) was added Pb(OAc)₄ (167 mg, 0.346 mmol), and the mixture was stirred at the same temperature for a period of 15 min before dilution with hexane (80 mL). The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residual oil was subjected to column chromatography (silica gel, 15 g, elution with hexane:Et₂O = 5:1) to give **18b** (R = SiMe₂Ph) (89.3 mg, 100%).

18a (R = SiMe₃): a colorless oil $R_f = 0.35$ (hexane:AcOEt = 10:1). IR (film) 1750, 1719 cm⁻¹. ¹H NMR (C₆D₆) δ 0.07 (9H, SiMe₃), 0.14 and 0.18 (each 3H, s, SiMe₂), 0.85-1.10 (3H, m), 0.89 (9H, s, *t*-Bu), 1.30-1.60 (5H, m), 2.33 (1H, br dm, $J = 12.6$ Hz, H-12), 2.50 (1H, dd, $J = 4.8, 4.8$ Hz, H-7), 2.74 (1H, d, $J = 11.0$ Hz, H-6), 3.41 (3H, s, CO₂Me), 4.85 (1H, ddd, $J = 10.3, 10.3, 5.0$ Hz, H-1), 5.00 (1H, dd, $J = 11.0, 2.3$ Hz, H-5), 5.20 (1H, d, $J = 2.3$ Hz, H-3), 9.90 (1H, d, $J = 4.8$ Hz, CHO). ¹³C NMR (C₆D₆) δ -4.9 and -4.3 (SiMe₂), -2.9 (SiMe₃), 17.9 (CMe₃), 24.8, 25.1, 25.5 (CMe₃), 26.0, 30.6, 35.5, 46.6, 51.1 (CO₂Me), 55.6 (C-7), 75.7 (C-1), 77.5 (C-3), 105.4 (C-5), 149.7 (C-4), 169.8 (CO₂Me), 205.1 (CHO). HRMS calcd for C₂₃H₄₂O₅Si₂, (M⁺), 454.2571 found 454.2581.

18b (R = SiMe₂Ph): a colorless oil. $R_f = 0.35$ (hexane:AcOEt = 10:1). IR (film) 1749, 1718 cm⁻¹. ¹H NMR (C₆D₆) δ 0.04 and 0.11 (each 3H, s, SiMe₂), 0.33 and 0.38 (each 3H, s, SiMe₂), 0.80-0.95 (1H, m), 0.87 (3H, s, *t*-Bu), 1.15-1.60 (7H, m), 2.30 (1H, br dm, $J = 12.8$ Hz, H-12), 2.57 (1H, dd, $J = 4.8, 4.8$ Hz, H-7), 3.12 (1H, d, $J = 11.2$ Hz, H-6), 3.40 (CO₂Me), 4.84 (1H, ddd, $J = 10.3, 10.3, 5.0$ Hz, H-1), 5.03 (1H, dd, $J = 11.2, 2.3$ Hz, H-5), 5.21 (1H, d, $J = 2.3$ Hz, H-3), 7.12-7.20 (3H, m, ArH), 7.48-7.52 (2H, m, ArH), 9.84 (1H, d, $J = 4.8$ Hz, CHO). ¹³C NMR (C₆D₆) δ -5.1 and -4.8 (SiMe₂), -4.3 and -4.2 (SiMe₂), 17.8 (CMe₃), 24.5, 24.8, 25.5 (CMe₃), 25.9, 30.4, 35.5, 46.5, 51.1 (CO₂Me), 55.4 (C-7), 75.8 (C-1), 77.5 (C-3), 105.4 (C-5), 128.1 (Ar), 129.4 (Ar), 134.2 (Ar), 137.3 (Ar), 149.8 (C-4), 169.7 (CO₂Me), 205.1 (CHO). HRMS calcd for C₂₈H₄₄O₅Si₂, (M⁺), 516.2727 found 516.2747.

18c (R = SiMe₂Bu^t): a colorless oil. $R_f = 0.39$ (hexane:AcOEt = 10:1). IR (film) 1751, 1719 cm⁻¹. ¹H NMR (C₆D₆) δ 0.11 and 0.12 (SiMe₂), 0.17 and 0.21 (each 3H, s, SiMe₂), 0.89 (9H, s, *t*-Bu), 0.95-1.05 (3H, m), 0.91 (9H, s, *t*-Bu), 1.20-1.65 (5H, m), 2.38 (1H, br dm, $J = 12.8$ Hz, H-12), 2.59 (1H, dd, $J = 4.6, 4.6$ Hz, H-7), 3.07 (1H, d, $J = 11.5$ Hz, H-6), 3.40 (3H, s, CO₂Me), 4.87 (1H, ddd, $J = 10.3, 10.3, 5.0$ Hz, H-1), 5.04 (1H, dd, $J = 11.4, 2.5$ Hz, H-5), 5.25 (1H, d, $J = 2.5$ Hz, H-3), 9.95 (1H, d, $J = 4.4$ Hz, CHO). ¹³C NMR (C₆D₆) δ -7.2 and -6.5 (SiMe₂), -4.4 (SiMe₂), 17.3 (CMe₃), 17.8 (CMe₃), 21.9, 24.8, 25.5 (CMe₃), 26.0 (CMe₃), 27.1, 30.5, 35.5, 46.4, 51.1 (CO₂Me), 55.8 (C-7), 75.7 (C-1), 77.7 (C-3), 106.6 (C-5), 148.6 (C-4), 169.9 (CO₂Me), 205.2 (CHO). HRMS calcd for C₂₆H₄₈O₅Si₂, (M⁺), 496.3040 found 496.3026.

18d (R = *i*-Pr): a colorless oil. $R_f = 0.41$ (hexane:AcOEt = 10:1). IR (film) 1750, 1718 cm⁻¹. ¹H NMR (CDCl₃) δ 0.13 and 0.14 (SiMe₂), 0.84 and 0.93 (each 3H, d, $J = 6.6$ Hz, CHMe₂), 0.86 (9H, s, *t*-Bu), 1.00-1.32 (3H, m), 1.50-1.70 (5H, m), 2.00-2.11 (1H, br m, H-8), 2.43 (1H, dd, $J = 4.8, 4.8$ Hz, H-7), 2.93 (1H, dd, $J = 9.2, 9.2$ Hz, H-6), 3.72 (3H, s, CO₂Me), 4.52-4.60 (1H, br m, H-1), 4.60 (1H, dd, $J = 9.8, 2.1$ Hz, H-5), 4.94 (1H, d, $J = 2.1$ Hz, H-3), 9.82 (1H, d, $J = 5.0$ Hz, CHO). ¹³C NMR (CDCl₃) δ -4.5 and -4.1 (SiMe₂), -4.4 (SiMe₂), 18.0 (CMe₃), 20.5, 21.1, 25.0, 25.7 (CMe₃), 26.0, 31.0, 32.9, 35.3, 43.6, 45.9, 51.9 (CO₂Me), 57.5 (C-7), 75.9 (C-1), 77.3 (C-3), 109.1 (C-5), 147.6 (C-4), 170.1 (CO₂Me), 207.5 (CHO). HRMS calcd for C₂₃H₄₀O₅Si, (M⁺), 424.2645 found 424.2605.

18e (R = *t*-Bu): mp 110 °C, a colorless plates (*i*-Pr₂O). $R_f = 0.41$ (hexane:AcOEt = 10:1). IR (film) 1758, 1717 cm⁻¹. ¹H NMR (C₆D₆) δ 0.13 and 0.18 (SiMe₂), 0.89 (9H, s, *t*-Bu), 0.89 (9H, s, *t*-Bu), 0.80-1.10 (3H, m), 1.25-1.62 (5H, m), 2.26 (1H, dm, $J = 12.8$ Hz, H-12), 2.52 (1H, dd, $J = 4.8, 4.8$ Hz, H-7), 3.34 (1H, d, $J = 10.3$ Hz, H-6), 3.40 (3H, s, CO₂Me), 4.85 (1H, ddd, $J = 10.3, 10.3, 5.0$ Hz, H-1), 4.98 (1H, dd, $J = 10.3, 2.3$ Hz, H-5), 5.18 (1H, d, $J = 2.3$ Hz, H-3), 10.00 (1H, d, $J = 4.8$ Hz, CHO). ¹³C NMR (C₆D₆) δ -4.7 and -4.4 (SiMe₂), 17.8 (CMe₃), 24.8, 25.5 (CMe₃), 25.9, 27.3 (CMe₃), 30.9, 34.1, 35.6, 46.1, 46.7, 51.1 (CO₂Me), 56.1 (C-7), 75.8 (C-1), 77.5 (C-3), 107.3 (C-5), 148.0 (C-4), 169.6 (CO₂Me), 205.5 (CHO). MS 438 (M⁺), Anal. Calcd for C₂₄H₄₂O₅Si: C, 65.71; H, 9.65. found: C, 65.71; H, 9.53.

8a ($R = \text{SiMe}_3$)

8d (R = *i*Pr)

10d ($R = iPr$)

10e (R = tBu)

11a (R = SiMe₃)

X : parts per Million : 13C

11e (R = *t*Bu)

¹H NMR spectrum (CDCl₃) of compound 6. The x-axis represents the chemical shift in ppm, ranging from 0 to 10. The spectrum shows several distinct signals:

- Aromatic region (7.0-8.0 ppm): Multiple sharp singlets.
- Vinyl region (6.0-7.0 ppm): Two multiplets.
- Olefinic/methine region (4.0-6.0 ppm): Several multiplets.
- Methyl region (0.5-2.0 ppm): A complex set of signals including doublets, triplets, and smaller peaks.

Integration values (area under the curve) are provided for specific regions of the spectrum:

Chemical Shift Range (ppm)	Integration Value
~9.0	1.00000
~7.5	0.98099
~4.5	1.00946
~3.5	2.6301
~2.5	1.00191
~1.5	3.17333
~0.5	7.42654
~0.1	9.77519

17b (R = SiMe₂Ph)

17c (R = SiMe₂tBu)

17d (R = *i*Pr)

17e (R = tBu)

18a (R = SiMe₃)

18b ($R = \text{SiMe}_2\text{Ph}$)

18c (R = SiMe₂tBu)