Supporting Information

A New Strategy for Construction of Eight-Membered Carbocycles by Brook Rearrangement-Mediated [6 + 2] Annulation

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General. IR spectra were recorded on a Perkin-Elmer FT1640 spectrometer or Horiba FT-710 spectrometer. ¹H NMR spectra were taken on Varian UnityPlus 500 (500 MHz) spectrometer or JEOL Delta-500 (500 MHz) spectrometer in CDCl₃ with reference to CHCl₃ (δ 7.26) unless otherwise noted. ¹³C NMR spectra were measured with Varian UnityPlus 500 (125 MHz) spectrometer or JEOL Delta-500 (125 MHz) spectrometer in CDCl₃ with reference to the CDCl₃ triplet (δ 77.2). Resonance patterns were described as s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, and br = broad. The assignment of ¹H and ¹³C 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 or a JEOL JMS-SX102 spectrometers. For routine chromatography, the following adsorbents were used: Fuji-Silycia 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 MgSO₄ 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 Preparation of 11a-d [Specific for 11a]. To a solution of 1,3-dithiane (20.0 g, 64.0 mmol) in THF (120 mL) was added *n*-BuLi (1.37 M in hexane, 49.0 mL, 97.0 mmol) at -20 °C over 35 min, and the solution was stirred at the same temperature for 1 h before addition of 3-bromopropoxy(trimethyl)silane (13.5 g, 67.2 mmol) in THF (10 mL). After being stirred at -20 °C for 90 min, the mixture was allowed to warm to room temperature. The reaction mixture was poured into aqueous NH₄Cl solution (100 mL), and extracted with Et₂O (50 mL x 3). Combined organic phases were shaken in a separatory funnel with 2N HCl (100 mL) for several minutes. The organic phase was subsequently washed with aqueous NaHCO₃ (150 mL) and saturated brine (150 mL), dried, and concentrated to give essentially pure alcohol (23.0 g, 93%).

To a suspension of PCC (2.50 g, 11.4 mmol), molecular sieves (4A, powder, 2.50 g), and Celite® (2.50 g) in CH₂Cl₂ (7.0 mL) was added solution of the above alcohol (2.20 g, 7.60 mmol) in CH₂Cl₂ (7.0 mL). After being stirred at room temperature for 1 h, the mixture was diluted with Et₂O (10 mL) and filtered through Florisil. The filtrate was concentrated, and subjected to column chromatography (silica gel, 100 g, elution with hexane:AcOEt = 15:1) to give **9a** (942 mg, 43 %).

9a: a pale yellow oil, *R*_f = 0.50 (hexane:AcOEt = 5:1). ¹H NMR (500 MHz) δ 0.23 (6H, s), 1.04 (9H, s), 1.86-2.08 (2H, m), 2.36-2.44 (2H, m), 2.67-2.73 (4H, m), 2.96-3.06 (2H, m), 9.87 (1H, s). ¹³C NMR δ -5.4, 23.3, 24.5, 28.1, 28.1, 29.9, 42.6, 200.9.

9b: a pale yellow oil, $R_f = 0.71$ (hexane:AcOEt = 5:2). ^1H NMR (500 MHz) δ 0.22 and 0.22 (each 3H, s), 1.04 (9H, s), 1.82-2.07 (4H, m), 2.31-2.36 (2H, m), 2.41 (2H, dt, $J = 13.7, 3.3$ Hz), 2.51 (2H, t, $J = 7.1$ Hz), 3.01-3.49 (2H, m), 9.81 (1H, s, s).

9c: a pale yellow oil, $R_f = 0.82$ (hexane:AcOEt = 5:2). ^1H NMR (500 MHz) δ 0.18 (6H, s), 1.02 (9H, s), 1.52-1.73 (4H, m), 1.79-2.05 (2H, m), 2.29-2.37 (2H, m), 2.40 (2H, dt, $J = 14.8, 4.8$ Hz), 2.48 (2H, td, $J = 7.1, 1.6$ Hz, H-2), 2.96-3.06 (2H, m, H-4'), 9.77 (1H, s, H-1). ^{13}C NMR δ -5.0, 20.0, 22.7, 23.8, 25.2, 27.8, 28.5, 38.0, 40.9, 44.1, 202.3.

9d: a yellow oil, $R_f = 0.82$ (hexane:AcOEt = 5:2). ^1H NMR (500 MHz) δ 0.18 (6H, s), 1.02 (9H, s), 1.52-1.73 (4H, m), 1.79-2.05 (2H, m), 2.29-2.37 (2H, m), 2.40 (2H, dt, $J = 14.8, 4.8$ Hz), 2.48 (2H, td, $J = 7.1, 1.6$ Hz), 2.96-3.06 (2H, m), 9.77 (1H, s). ^{13}C NMR δ -4.9, 20.0, 22.3, 28.1, 28.5, 29.9, 38.1, 41.1, 44.4, 202.5.

To a solution of **9a** (6.8 g, 23.4 mmol) in Et_2O (67 mL) was added *i*-PrMgBr (1.0 M in THF, 23.4 mL, 23.4 mmol) at 0 °C over 20 min, and the solution was stirred at room temperature for 40 min. The mixture was poured into aqueous NH_4Cl solution (100 mL), extracted with Et_2O (70 mL x 3). Combined organic phases were washed with saturated brine (120 mL), dried, and concentrated. The residual oil was used for the next reaction without further purification.

To a suspension of PCC (3.30 g, 15.5 mmol), molecular sieves (4A, powder, 3.30 g), and Celite® (3.30 g) in CH_2Cl_2 (45 mL) was added the above compound (4.69 g, 14.1 mmol) in CH_2Cl_2 (10 mL). After being stirred at room temperature for 1 h, the mixture was diluted with Et_2O (40 mL), and filtered through Florisil. The filtrate was concentrated, and subjected to column chromatography (silica gel, 200 g, elution with hexane:AcOEt = 12:1) to give **10a** (2.32 g, 50%).

10a: a pale yellow, $R_f = 0.70$ (hexane:AcOEt = 10:1). ^1H NMR (500 MHz) δ 0.22 (6H, s), 1.02 (9H, s), 1.11 (6H, d, $J = 6.6$ Hz), 1.84-2.04 (2H, m), 2.37 (2H, dt, $J = 14.3, 3.8$ Hz), 2.60-2.74 (5H, m, H-2), 3.00-3.10 (2H, m). ^{13}C NMR δ -4.9, 18.6, 20.0, 23.6, 25.1, 28.5, 31.3, 39.1, 40.7, 41.6, 214.1.

10b: a pale yellow oil, $R_f = 0.55$ (hexane:AcOEt = 10:1). ^1H NMR (500 MHz) δ 0.22 (6H, s), 1.04 (9H, s), 1.11 (6H, d, $J = 7.1$ Hz), 1.81-2.06 (4H, m), 2.27-2.31 (2H, m), 2.42 (2H, dt, $J = 7.7, 3.3$ Hz), 2.52 (2H, t, $J = 7.1$ Hz), 2.49-2.54 (1H, m), 3.04-3.49 (2H, m).

10c: a pale yellow oil, $R_f = 0.75$ (hexane:AcOEt = 5:1). ^1H NMR (500 MHz) δ 0.19 (6H, s), 1.03 (9H, s), 1.10 (6H, d, $J = 7.1$ Hz), 1.52-1.62 (4H, m), 1.70-2.10 (2H, m), 2.30-2.36 (2H, m), 2.42 (2H, dt, $J = 7.7, 3.3$ Hz), 2.50 (2H, t, $J = 7.1$ Hz), 2.58-2.63 (1H, m), 2.99-3.06 (2H, m). ^{13}C NMR δ -5.0, 20.0, 22.7, 23.8, 25.2, 27.8, 28.5, 38.0, 40.9, 44.1, 202.3.

10d: a pale yellow oil, $R_f = 0.70$ (hexane:AcOEt = 5:1). ^1H NMR (500 MHz) δ 0.18 (6H, s), 1.01 (9H, s), 1.08 (6H, d, $J = 7.1$ Hz), 1.29-1.36 (2H, m), 1.50-1.67 (4H, m), 1.84-2.03 (2H, m), 2.26-2.32 (2H, m), 2.38 (2H, dt, $J = 14.3, 3.8$ Hz), 2.45 (2H, t, $J = 7.1$ Hz), 2.54-2.63 (1H, m), 2.97-3.07 (2H, m). ^{13}C NMR δ -4.9, 18.5, 20.0, 23.7, 24.0, 25.3, 28.1, 28.5, 30.4, 38.1, 40.5, 41.0, 41.2, 214.7.

To an ice-cooled solution of NBS (6.57 g, 36.9 mmol) in MeCN (150 mL) and H_2O (40 mL) was added **10a** (3.05 g, 9.23 mmol) in one portion. The reaction mixture was stirred at room temperature for 10 min before pouring into 10% aqueous Na_2SO_3 solution (200 mL). The mixture was extracted with Et_2O (200 mL x 3). Combined organic phases were subsequently washed with saturated aqueous NaHCO_3 solution, H_2O (200 mL), and saturated brine, and concentrated. The residual oil was subjected to column chromatography (silica gel, 100 g, elution with hexane:AcOEt = 20:1) to give **11a** (1.96 g, 84%).

11a: a pale yellow oil, $R_f = 0.39$ (hexane:AcOEt = 10:1). IR (film) 1715 and 1640 cm^{-1} . ^1H NMR (500 MHz) δ 0.18 (6H, s, SiMe_2), 0.92 (9H, s, SiBu), 1.09 (6H, d, $J = 6.8$ Hz, CHMe_2), 2.61-2.68 (1H, m, H-5), 2.66 (2H, t, $J = 6.4$ Hz, H-3), 2.86 (2H, t, $J = 6.4$ Hz, H-2). ^{13}C NMR δ -6.9 (SiMe_3), 16.6 (CMe_3), 18.5 (CHMe_2), 26.6 (CMe_3), 32.5 (C-3), 41.0 (C-5), 43.8 (C-2), 213.4 (C-4), 245.0 (C-1). HRMS calcd for $\text{C}_{13}\text{H}_{26}\text{O}_2\text{Si}$ 242.1704, found 242.1700.

11b: a pale yellow oil, $R_f = 0.39$ (hexane:AcOEt = 10:1). IR (film) 1720 and 1640 cm^{-1} . ^1H NMR (500 MHz)

δ 0.14 (6H, s, SiMe₂), 0.89 (9H, s, SiBu), 1.04 (6H, d, J = 6.8 Hz, CHMe₂), 1.74 (2H, tt, J = 7.1, 7.1 Hz, H-3), 2.41 (2H, t, J = 7.1 Hz, H-4), 2.51-2.57 (1H, m, H-6), 2.60 (2H, t, J = 7.1 Hz, H-2). ¹³C NMR δ -6.6 (SiMe₂), 16.5 (C-3), 16.9 (CMe₃), 18.6 (C-7), 26.8 (CMe₃), 39.7 (C-4), 41.1 (C-6), 49.6 (C-2), 214.8 (C-5), 247.5 (C-1). HRMS calcd for 256.1859, found 256.1851

11c: a pale yellow oil, R_f = 0.30 (hexane:AcOEt = 15:1). IR (film) 1710 and 1640 cm⁻¹. ¹H NMR (500 MHz) δ 0.14 (6H, s, SiMe₂), 0.89 (9H, s, SiBu), 1.05 (6H, d, J = 6.8 Hz, CHMe₂), 1.45-1.49 (4H, m, H-3 and H-4), 2.41 (2H, t, J = 7.1 Hz, H-5), 2.50-2.58 (1H, m, H-7), 2.58 (2H, t, J = 6.6 Hz, H-2). ¹³C NMR δ -6.8 (SiMe₂), 16.6 (CMe₃), 18.4 (C-8), 21.6 (C-4), 23.6 (C-3), 26.6 (CMe₃), 40.4 (C-5), 41.0 (C-7), 50.2 (C-2), 214.7 (C-6), 247.4 (C-1). HRMS calcd for C₁₅H₃₀O₂Si 270.2015, found 270.1973.

11d: a pale yellow oil, R_f = 0.50 (hexane:AcOEt = 10:1). IR (film) 1710 and 1640 cm⁻¹. ¹H NMR (500 MHz) δ 0.13 (6H, s, SiMe₂), 0.88 (9H, s, SiBu), 1.04 (6H, d, J = 7.1 Hz, CHMe₂), 1.16-1.23 (2H, m, H-4), 1.44-1.54 (4H, m, H-3 and H-5), 2.40 (2H, t, J = 7.5 Hz, H-4), 2.53-2.57 (1H, m, H-8), 2.55 (2H, t, J = 7.5 Hz, H-2). ¹³C NMR δ -6.8 (SiMe₂), 16.6 (CMe₃), 18.4 (C-9), 21.7 (C-5), 23.7 (C-3), 26.6 (CMe₃), 29.0 (C-4), 40.2 (C-6), 40.9 (C-8), 50.1 (C-2), 215.0 (C-7), 247.7 (C-1). HRMS calcd for C₁₆H₂₂O₂Si 284.2172, found 284.2195.

General Procedure for the Reaction of 11 with Phenyllithium [Specific for 11a] To a cooled (-80 °C) solution of **11a** (184 mg, 0.759 mmol) in THF (15 mL) was added PhLi (1.07 M in THF, 0.710 mL, 0.759 mmol) over 7 min, and the solution was allowed to warm to -30 °C. After being stirred at the same temperature for 30 min, the mixture was diluted with aqueous NH₄Cl solution (20 mL) and extracted with Et₂O (20 mL x 3). Combined organic phases were washed with saturated brine (30 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 30 g, elution with hexane:AcOEt = 15:1) and then MPLC (hexane:AcOEt = 30:1) to give **12a** (164 mg, 67%), **13a** (28 mg, 10%), and **14a** (21 mg, 9%).

12a: a colorless oil, R_f = 0.31 (hexane:AcOEt = 30:1). IR (film) 3470 cm⁻¹. ¹H NMR (500 MHz) δ -0.24 and -0.05 (each 3H, s, SiMe₂), 0.68 and 0.71 (each 3H, d, J = 6.8 Hz, CHMe₂), 0.97 (9H, s, SiBu), 1.20-1.25 (1H, m, CHMe₂), 1.87-1.99 (2H, m, H-4), 2.35-2.41 (1H, m, H-3), 2.45-2.50 (1H, m, H-3) 3.86 (1H, s, OH), 7.23-7.37 (2H, m, Ar-H), 7.42-7.50 (2H, m, Ar-H), 7.61 (1H, m, Ar-H). ¹³C NMR δ -3.0 and -2.7 (SiMe₂), 16.1 and 16.9 (CHMe₂), 18.4 (CMe₃), 26.2 (CMe₃), 28.7 (C-4), 30.3 (C-3), 32.4 (CHMe₂), 82.7 (C-1), 83.0 (C-2), 126.9, 127.4, 128.9, and 142.3 (Ar). HRMS calcd for C₁₉H₃₃O₂Si 321.2250, found 321.2151.

13a: a colorless oil, R_f = 0.15 (hexane:AcOEt = 30:1). IR (film) 3470 cm⁻¹. ¹H NMR (500 MHz) δ -0.37 and -0.05 (each 3H, s, SiMe₂), 0.89 (9H, s, SiBu), 0.96 and 1.14 (each 3H, d, J = 6.8 Hz, CHMe₂), 1.43 (1H, dt, J = 12.2 Hz, H-4), 1.97 (1H, ddd, J = 12.2, 12.2, 10.4 Hz, H-3), 2.13 (1H, ddd, J = 12.2, 9.6, 3.4 Hz, H-4), 2.30 (1H, sep, CHMe₂), 2.65 (1H, ddd, J = 12.2, 9.6, 3.4 Hz, H-3), 7.26-7.31 (1H, m, Ar-H), 7.37-7.47 (2H, m, Ar-H), 7.47-7.49 (2H, m, Ar-H). ¹³C NMR δ -3.1 and -2.6 (SiMe₂), 17.7 and 17.7 (CHMe₂), 18.3 (CMe₃), 26.1 (C-3), 26.1 (CMe₃), 29.3 (C-4), 31.0 (CHMe₂), 83.0 (C-2), 85.0 (C-1), 127.7, 127.7, 128.3, and 141.1 (Ar). HRMS calcd for C₁₉H₃₃O₂Si 321.2250, found 321.2228.

14a: a pale yellow oil, R_f = 0.65 (hexane:AcOEt = 30:1). IR (film) 3450 cm⁻¹. ¹H NMR (500 MHz) δ 0.11 and 0.15 (each 3H, s, SiMe₂), 0.75 and 0.92 (each 3H, d, J = 6.8 Hz, CHMe₂), 0.99 (9H, s, SiBu), 2.05 (1H, sep, CHMe₂), 2.77 (1H, dd, J = 15.8, 2.6 Hz, H-3), 2.98 (1H, dd, J = 15.8, 2.6 Hz, H-3), 5.03 (1H, dd, J = 2.6, 2.6 Hz, H-2), 7.19-7.22 (1H, m, Ar-H), 7.26-7.32 (2H, m, Ar-H), 7.35-7.37 (2H, m, Ar-H). ¹³C NMR δ -6.4 and -6.3 (SiMe₂), 16.6 (CMe₃), 17.1 and 17.9 (CHMe₂), 26.7 (CMe₃), 38.6 (CHMe₂), 42.2 (C-3), 93.2 (C-4), 111.1 (C-2), 125.8, 126.4, 127.8, and 147.7 (Ar), 160.3 (C-1). HRMS calcd for C₁₉H₃₀OSi 302.2066, found 302.2049.

12b: a colorless oil, R_f = 0.46 (hexane:AcOEt = 20:1). IR (film) 3430 cm⁻¹. ¹H NMR (500 MHz) δ -0.23 and 0.04 (each 3H, s, SiMe₂), 0.68 and 0.99 (each 3H, d, J = 6.6 Hz, CHMe₂), 0.97 (9H, s, SiBu), 1.28 (1H, sep, CHMe₂), 1.63-1.70 (1H, m, H-5), 1.72-1.83 (2H, m, H-4 and H-5), 2.06-2.16 (1H, m, H-4), 2.28-2.33 (1H,

m, H-3), 2.40-2.46 (1H, m, H-3), 3.20 (1H, d, $J = 1.7$ Hz, OH), 7.24-7.28 (1H, m, Ar-H), 7.29-7.33 (2H, m, Ar-H), 7.45-7.49 (2H, m, Ar-H). ^{13}C NMR δ -3.0 and -1.9 (SiMe₂), 17.2 and 20.4 (CHMe₂), 18.8 (CMe₃), 19.2 (C-4), 26.4 (CMe₃), 32.2 (CHMe₂), 33.0 (C-5), 38.6 (C-3), 86.2 (C-1), 89.7 (C-2), 126.9, 127.3, 127.7, and 144.6 (Ar-H). HRMS calcd for C₂₀H₃₄O₂Si 334.2328, found 224.2344.

12c: a colorless oil, $R_f = 0.53$ (hexane:AcOEt = 10:1). IR (film) 3420 cm⁻¹. ^1H NMR (500 MHz) δ -0.27 and 0.05 (each 3H, s, SiMe₂), 0.60 and 1.16 (each 3H, d, $J = 6.8$ Hz, CHMe₂), 1.00 (9H, s, Bu), 1.53-1.91 (8H, m, H-3, H-4, H-5, H-6, and CHMe₂), 2.80 (1H, ddd, $J = 13.7, 13.7, 4.1$ Hz, H-3), 7.25-7.28 (1H, m, Ar-H), 7.31-7.34 (2H, m, Ar-H), 7.53-7.55 (2H, m, Ar-H). ^{13}C NMR δ -1.6 and -0.7 (SiMe₂), 18.5 and 20.6 (CHMe₂), 19.5 (CMe₂), 20.7, 21.6, 26.1, 27.0, and 33.3 (C-4, C-5, C-6, and CHMe₂), 34.0 (C-3), 76.4 (C-1), 83.6 (C-2), 127.3, 127.4, 128.8, and 143.7 (Ar). HRMS calcd for C₂₁H₃₆O₂Si 348.2485, found 348.2495.

12d: a colorless oil, $R_f = 0.53$ (hexane:AcOEt = 10:1). IR (film) 3360 cm⁻¹. ^1H NMR (500 MHz) δ -0.41 and 0.01 (each 3H, s, SiMe₂), 0.90 and 1.03 (each 3H, d, $J = 6.6$ Hz, CHMe₂), 0.91 (9H, s, SiBu), 1.38-1.93 (8H, m, H-4, H-5, H-6 and H-7), 1.78 (1H, sep, CHMe₂), 1.99 (1H, s, OH), 2.04 (1H, ddd, $J = 14.7, 6.2, 6.2$ Hz, H-3), 2.62 (1H, ddd, $J = 14.7, 8.5, 6.2$ Hz, H-3), 7.22-7.46 (3H, m, Ar-H), 7.64-7.68 (2H, m, Ar-Hs). ^{13}C NMR δ -2.5 and -1.1 (SiMe₂), 19.0 and 19.2 (CHMe₂), 19.2 (CMe₃), 22.8, 23.7, 27.0, and 28.1 (C-4, C-5, C-6, and C-7), 34.5 (CHMe₂), 37.7 (C-3), 80.0 (C-1), 86.7 (C-2), 127.1, 127.3, 129.1, and 146.0 (Ar). HRMS calcd for C₂₂H₃₈O₂Si 362.2641, found 362.2633.

General Procedure for Preparation of 2-(1-Ethoxyethoxy)alk-3-enenitrile 17a-d [Specific for 17b]

To *trans*-hexanal (5.91 mL, 50.9 mmol) was added ZnI₂ (16 mg, 0.051 mmol) at room temperature and the mixture was stirred at the same temperature for 10 min before dropwise addition of TMSCN (7.0 mL, 56.0 mmol). The solution was stirred at room temperature for 30 min, and HF solution (5% in MeCN, 20 mL) was added. After being stirred at the same temperature for 1 h, the reaction mixture was diluted with aqueous NaHCO₃ solution (50 mL) and extracted with Et₂O (50 mL x 3). Combined organic phases were washed with saturated brine (50 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 250 g, elution with hexane:Et₂O = 1:1) to give cyanohydrin (5.32 g, 83%).

To a solution of this material in ethyl vinyl ether (7.9 mL, 83 mmol) was added trifluoroacetic acid (4 drops). After being stirred at room temperature for 1h, the reaction mixture was concentrated. The residual oil was subjected to column chromatography (silica gel, 150 g, elution with hexane:Et₂O = 3:1) to give **17b** (4.95 g, 60%) as a mixture of diastereomers about the C-2 carbon atom and the ethoxyethoxy group.

17b: a yellow oil, $R_f = 0.68$ (hexane:Et₂O = 2:1). IR (film) 2964, 1458, 1444, and 1387 cm⁻¹. ^1H NMR (500 MHz) δ 0.91 (3H x 2, t, $J = 7.4$ Hz, H-9), 1.20-1.23 (3H x 2, m, H-4'), 1.35-1.47 (3H x 2, m, H-2' and H-8), 2.06-2.10 (2H, m, H-7), 3.49-3.57 (1H x 2, m, H-3'), 3.61-3.70 (1H x 2, m, H-3'), 4.85 (1H x 2, q, $J = 5.0$ Hz, H-1'), 4.95 (1H x 2, q, $J = 5.0$ Hz, H-1'), 5.48-5.55 (1H x 2 m, H-5'), 5.98-6.07 (1H x 2, m, H-6'). ^{13}C NMR δ 13.6, 15.0, 15.2, 19.9, 21.8, 34.0, 61.1, 62.9, 63.4, 98.8, 99.4, 117.5, 118.2, 122.6, 122.8, 137.7, 137.8. HRMS calcd for C₁₁H₁₉NO₂ 197.1416, found 197.1411.

17c: a pale yellow oil, $R_f = 0.39$ (hexane: Et₂O = 10:1). IR (film) 2928, 1464, 1445, and 1387 cm⁻¹. ^1H NMR (500 MHz) δ 0.87 (3H x 2, t, $J = 6.9$ Hz, H-13), 1.19-1.39 (3H x 2, 3H x 2 10H x 2, m, H-4'), 2.09 (2H x 2, m, H-7), 3.46-3.56 (1H x 2, m, H-3'), 3.60-3.69 (1H x 2, m, H-3'), 4.82-4.87 (1H x 2, m, H-1'), 4.93-4.96 (1H, m, H-1'), 5.46-5.53 (1H x 2 m, H-5'), 5.97-6.07 (1H x 2, m, H-6'). ^{13}C NMR δ 14.1, 15.0, 15.2, 19.7, 22.7, 28.6, 29.1, 31.8, 32.1, 61.0, 61.1, 62.9, 63.5, 98.8, 99.4, 117.5, 118.3, 122.3, 122.5, 138.1, 138.2. HRMS calcd for C₁₅H₂₇NO₂ 253.2042, found 253.1993.

17d: a pale yellow oil, $R_f = 0.38$ (hexane:AcOEt = 10:1). IR (film) 2928, 1449, and 1387 cm⁻¹. ^1H NMR (500 MHz) δ 1.06-1.35 (18H, m), 1.36 (3H, d, $J = 5.3$ Hz, H-2'), 1.40 (3H, d, $J = 5.3$ Hz, H-2'), 1.72-1.74 (2H x 4, br d, H-2''), 2.02-2.04 (2H x 2, m, H-1''), 3.45-3.56 (1H x 2, m, H-3'), 3.61-3.70 (1H x 2, m, H-3'), 4.85 (1H x 2, q, $J = 5.3$ Hz, H-1'), 4.95 (1H x 2, q, $J = 5.3$ Hz, H-1'), 5.38-5.48 (1H x 2 m, H-5'), 5.92-6.01 (1H x 2, m, H-6'). ^{13}C NMR δ 15.0, 15.2, 19.7, 25.9, 26.0, 30.3, 32.2, 32.3, 38.2, 61.0, 61.1, 63.1, 63.7, 98.8, 99.4, 117.6, 118.3, 120.2, 120.3, 143.2, 143.4 (C-6).HRMS calcd for C₁₄H₂₃NO₂ 237.1729, found 237.1720.

General Procedure for Preparation of 20a-d [Specific for 20d] To a cooled (-80 °C) solution of LDA, generated from *i*-Pr₂NH (296 µL, 2.11 mmol) and *n*-BuLi (2.05 M in hexane, 1.1 mL, 2.11 mmol) in THF (7 mL), was added 4-cyclohexyl-2-(1-ethoxyethoxy)but-3-enenitrile (500 mg, 2.11 mmol) and HMPA (367 µL, 2.11 mmol) in THF (2.1 mL), and the solution was stirred at the same temperature for 10 min before addition of 1-(*tert*-butyldimethylsilyl)propenone (395 mg, 2.32 mmol) in THF (2.3 mL). After being stirred at the same temperature for 10 min, the reaction mixture was poured into sat.NH₄Cl solution (20mL), extracted with Et₂O (10 mL x 2). Combined organic phases were washed with H₂O (20 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 30g, elution with hexane:Et₂O = 10:1) to give **19d** (573 mg, 67%).

19a: a pale yellow oil, *R_f* = 0.42 (hexane:AcOEt = 15:1). IR (film) 2931, 2851 and 1641 cm⁻¹. ¹H NMR (500 MHz) δ 0.16 (6H x 2, s, SiMe₂), 0.90 (9H x 2, s, SiBu), 1.16-1.22 (3H x 2, m), 1.29-1.38 (3H x 2, m), 1.75-1.76 (2H x 2, m, H-7), 1.97-2.03 (2H, m), 2.05-2.11 (2H, m), 2.66-2.77 (2H, m), 2.78-2.92 (2H, m), 3.30-3.36 (1H, m, H-3'), 3.46-3.56 (2H, m, H-3'), 3.58-3.67 (1H, m, H-3'), 4.81 (1H, q, *J* = 5.3 Hz, H-1'), 4.85 (1H, q, *J* = 5.3 Hz, H-1'), 5.23 (1H, d, *J* = 15.6 Hz, H-5'), 5.37 (1H, d, *J* = 15.6 Hz, H-5'), 5.97-6.17 (1H x 2, m, H-6'). ¹³C NMR δ -7.0, 15.0, 15.1, 16.5, 17.5, 19.6, 21.1, 21.2, 26.4, 32.7, 33.2, 44.5, 44.6, 60.8, 61.2, 97.3, 98.0, 118.3, 118.8, 127.1, 128.3, 129.2, 130.5, 244.3, 244.4. HRMS calcd for C₁₈H₃₃NO₃Si 339.2230, found 339.2237.

19b: a pale yellow oil, *R_f* = 0.47 (hexane:Et₂O = 6:1). IR (film) 2932, 2860 and 1643 cm⁻¹. ¹H NMR (400 MHz) δ 0.19 (6H x 2, s, SiMe₂), 0.89-0.93 (9H x 2 and 6H x 2, m, SiBu and H-9), 1.15 (3H, t, *J* = 7.1 Hz, H-4'), 1.16-1.28 (3H x 2, m), 1.34-1.48 (7H, m), 1.98-2.16 (8H, m), 2.68-2.79 (2H, m), 2.84-2.95 (2H, m), 3.32-3.38 (1H, m, H-3'), 3.52-3.58 (2H, m, H-3'), 3.64-3.70 (1H, m, H-3'), 4.82-4.89 (1H x 2, m, H-1'), 5.23 (1H, d, *J* = 14.2 Hz, H-5'), 5.38 (1H, d, *J* = 14.2 Hz, H-5'), 6.04-6.16 (1H x 2, m, H-6'). ¹³C NMR δ -7.0, 13.7, 13.8, 15.0, 15.2, 16.6, 21.1, 21.4, 26.5, 33.0, 33.4, 34.1, 44.7, 60.9, 61.9, 97.4, 98.1, 126.7, 127.6, 128.0, 135.8, 137.0, 244.5. HRMS calcd for C₂₀H₃₇NO₃Si 367.2543, found 367.2527.

19c: a pale yellow oil, *R_f* = 0.47 (hexane:Et₂O = 10:1). IR (film) 2930, 2858 and 1642 cm⁻¹. ¹H NMR (500 MHz) δ 0.17 (6H x 2, s, SiMe₂), 0.86 (3H x 2, t, *J* = 6.9 Hz, H-13), 0.87 (9H x 2, s, SiBu), 1.13 (3H, t, *J* = 6.9 Hz, H-4'), 1.17-1.29 (18H, m), 1.35-1.39 (5H, m), 1.96-2.02 (1H, m), 2.07-2.14 (8H, m), 2.67-2.78 (2H, m), 2.83-2.93 (2H, m), 3.30-3.36 (1H, m, H-3'), 3.50-3.58 (2H, m, H-3'), 3.61-3.68 (1H, m, H-3'), 4.82 (1H, q, *J* = 5.1 Hz, H-1'), 4.86 (1H, q, *J* = 5.1 Hz, H-1'), 5.20 (1H, d, *J* = 15.6 Hz, H-6'), 5.36 (1H, d, *J* = 15.6 Hz, H-6'), 6.03-6.15 (1H x 2, m, H-5'). ¹³C NMR δ -7.0, 14.1, 15.0, 15.2, 16.5, 21.1, 21.3, 22.7, 26.4, 26.7, 28.8, 29.1, 29.2, 31.8, 32.0, 32.9, 33.3, 44.6, 44.7, 61.0, 61.7, 97.4, 98.0, 118.4, 118.8, 127.1, 127.8, 136.0, 137.3, 244.3, 244.4. HRMS calcd for C₂₄H₄₅NO₃Si 423.3169, found 423.3199.

19d: a pale yellow oil, *R_f* = 0.25 (hexane:Et₂O = 10:1). IR (film) 2929, 2857 and 1640 cm⁻¹. ¹H NMR (500 MHz) δ 0.16 (6H x 2, s, SiMe₂), 0.90 (9H x 2, s, SiBu), 1.02-1.37 (20H, m), 1.62-1.72 (6H x 2, m), 1.94-2.12 (6H, m), 2.65-2.75 (2H, m), 2.82-2.92 (2H, m), 3.29-3.41 (1H, m, H-3'), 3.42-3.60 (2H, m, H-3'), 3.60-3.68 (1H, m, H-3'), 4.74-4.84 (2H, m, H-1'), 5.15 (1H, d, *J* = 15.8 Hz, H-5'), 5.30 (1H, d, *J* = 15.8 Hz, H-5'), 6.00 and 6.06 (1H x 2, dd, *J* = 15.8, 6.6 Hz, H-6'). ¹³C NMR δ -7.0, 15.0, 15.2, 16.5, 21.1, 21.5, 25.9, 26.0, 26.4, 26.7, 32.5, 32.9, 33.3, 40.2, 44.6, 44.7, 61.2, 61.9, 97.5, 98.0, 118.4, 118.8, 124.9, 125.5, 141.4, 142.5, 244.3, 244.4. HRMS calcd for C₂₃H₄₁NO₃Si 407.2856, found 407.2828.

To a solution of **19d** (100 mg, 0.245 mmol) in THF (5 mL)-H₂O (5 mL) was added H₂SO₄ (98%, 0.25 mL), and the reaction mixture was refluxed for 1h. The reaction mixture was poured into a separatory funnel containing aqueous NaOH solution (10%, 10 mL). After being shaken for a few minutes, the mixture was neutralized with saturated aqueous NH₄Cl solution (40 mL), extracted with Et₂O (10 mL x 3). Combined organic phases were dried, and concentrated to give essentially pure **20d** (74 mg, 98%).

20a: a pale yellow oil, *R_f* = 0.33 (hexane:AcOEt = 10:1). IR (film) 1680 and 1640 cm⁻¹. ¹H NMR (500 MHz) δ 0.18 (6H, s, SiMe₂), 0.91 (9H, SiBu), 1.87 (3H, dd, *J* = 6.8, 1.5 Hz, H-7), 2.74 (2H, t, *J* = 6.2 Hz, H-3), 2.89

(2H, t, $J = 6.2$ Hz, H-2), 6.11 (1H, dq, $J = 15.8, 1.5$ Hz, H-7), 6.85 (1H, dq, $J = 15.8, 6.8$ Hz, H-5). ^{13}C NMR δ -6.9 (SiMe₃), 16.6 (C-7), 18.4 (CMe₃), 26.5 (CMe₃), 32.0 (C-3), 48.2 (C-2), 131.9 (C-5), 142.7 (C-6), 198.9 (C-4), 245.2 (C-1). HRMS calcd for C₁₃H₂₄O₂Si 240.1546, found 240.1520.

20b: a pale yellow oil, $R_f = 0.39$ (hexane:Et₂O = 5:1). IR (film) 1675 and 1640 cm⁻¹. ^1H NMR (500 MHz) δ 0.20 (6H, s, SiMe₂), 0.93 (9H, m, SiBu), 0.94 (3H, t, $J = 6.9$ Hz, H-9), 1.49 (2H, tq, $J = 7.1, 7.1$ Hz, H-8), 2.18 (2H, dt, $J = 7.1, 7.1$, H-7), 2.78 (2H, t, $J = 6.4$ Hz, H-3) 2.91 (2H, t, $J = 6.4$ Hz, H-3), 6.09 (1H, dt, $J = 15.8, 1.4$ Hz, H-5), 6.85 (1H, dt, $J = 15.8, 6.9$ Hz, H-6). ^{13}C NMR δ -7.0 (SiMe₃), 13.8 (C-9), 16.6 (CMe₃), 21.4 (C-8), 26.5 (CMe₃), 32.1 (C-3), 34.6 (C-7), 130.4 (C-5), 147.4 (C-6), 199.1 (C-4), 245.2 (C-1). HRMS calcd for C₁₃H₂₄O₂Si 268.1859, found 268.1901.

20c: a pale yellow oil, $R_f = 0.31$ (hexane:AcOEt = 16:1). IR (film) 1676 and 1638 cm⁻¹. ^1H NMR (500 MHz) δ 0.20 (6H, s, SiMe₂), 0.88 (3H, t, $J = 7.1$ Hz, H-13), 0.94 (9H, SiBu), 1.20-1.34 (8H, m, H-9, H-10, H-11, and H-12), 1.42-1.48 (2H, m, H-8), 2.20 (2H, dt, $J = 6.9$ Hz, H-7), 2.78 (2H, t, $J = 6.2$ Hz, H-3) 2.91 (2H, t, $J = 6.2$ Hz, H-2), 6.04 (1H, dq, $J = 15.8, 1.6$ Hz, H-5), 6.78 (1H, dq, $J = 15.8, 6.9$ Hz, H-6). ^{13}C NMR δ -7.0 (SiMe₃), 14.1 (C-13), 16.6 (CMe₃), 22.7 (C-6'), 26.5 (CMe₃), 28.1, 29.1, 29.2, 31.8 (C-8, C-9, C-10, C-11, and C-12), 32.1 (C-3), 32.6 (C-7), 43.8 (C-2), 130.2 (C-5), 147.7 (C-6), 198.9 (C-4), 245.0 (C-1). HRMS calcd for C₁₃H₂₄O₂Si 324.2485, found 324.2475.

20d: a yellow oil, $R_f = 0.46$ (hexane:Et₂O = 7:1). IR (film) 1675 and 1640 cm⁻¹. ^1H NMR (500 MHz) δ 0.20 (6H, s, SiMe₂), 0.94 (9H, SiBu), 1.06-1.33 (5H, m), 1.50-1.80 (5H, m) 2.08-2.17 (1H, m, H-1'), 2.79 (2H, t, $J = 6.2$ Hz, H-3), 2.90 (2H, t, $J = 6.2$ Hz, H-2), 6.04 (1H, d, $J = 16.0$ Hz, H-5), 6.78 (1H, dq, $J = 16.0, 6.9$ Hz, H-6). ^{13}C NMR δ -6.9 (SiMe₃), 16.1 (CMe₃), 25.8, 26.0, 31.8 (C-2', C-3', C-4'), 26.5 (CMe₃) 32.2 (C-3), 40.7 (C-1'), 43.7 (C-2), 127.8 (C-5), 152.4 (C-6), 199.6 (C-4), 245.2 (C-1). HRMS calcd for C₁₃H₂₄O₂Si 308.2172, found 308.2196.

General Procedure for the reaction of 20a-d with (2-trimethylsilylvinyl)lithium 21 [Specific for 21a]

To a cooled (-80 °C) solution of **20a** (80 mg, 0.333mmol) in THF (5.5 mL) was added in one portion **21**, generated from 2-bromovinyltrimethylsilane (54 μL , 65 mg, 0.350 mmol) and *t*-BuLi (1.12M in pentane, 625 μL , 0.70 mmol) in THF (1.2 mL). After being stirred at the same temperature for 10 min, the solution was allowed to warm to -10 °C over 70 min before addition of AcOH (1M in THF, 0.5 mL). The reaction mixture was filtered through a 5 g plug of basic alumina with Et₂O as solvent, and the filtrate was concentrated. The residual oil was subjected to column chromatography (silica gel, 15 g, elution with hexane:Et₂O = 6:1) to give **22a** (51 mg, 45%)

22a: a colorless oil, $R_f = 0.60$ (hexane:AcOEt = 10:1). IR (film) 1700 cm⁻¹. ^1H NMR (500 MHz) δ -0.01 (9H, s, SiMe₃), 0.15 and 0.17 (each 3H, s, SiMe₂), 0.87 (3H, d, $J = 7.1$ Hz, 7-Me), 0.93 (9H, s, SiBu), 1.39 (1H, dd, $J = 11.5, 3.6$ Hz, H-6), 1.99-2.03 (1H, m, H-3), 2.14-2.19 (1H, m, H-7), 2.28 (1H, ddd, $J = 10.9, 4.9, 1.5$ Hz, H-8), 2.36-2.39 (1H, m, H-2), 2.57 (1H, dd, $J = 10.9, 10.3$ Hz, H-8), 2.68-2.77 (2H, m, H-2 and H-3), 4.64 (1H, d, $J = 11.5$ Hz, H-5). ^{13}C NMR δ -4.2 and -4.1 (SiMe₂), -1.8 (SiMe₃), 17.9 (7-Me), 18.2 (CMe₃), 25.9 (CMe₃), 29.3 (C-3), 31.2 (C-6), 32.3 (C-7), 46.2 (C-2), 49.8 (C-8), 102.7 (C-5), 153.4 (C-4), 214.7 (C-1). HRMS calcd for C₁₈H₃₆O₂Si₂ 340.2254, found 340.2229.

22b: a colorless oil, $R_f = 0.45$ (hexane:Et₂O = 7:1). IR (film) 1703, 1642 cm⁻¹. ^1H NMR (500 MHz, C₆D₆) δ 0.00 (9H, s, SiMe₃), 0.15 and 0.17 (each 3H, s, SiMe₂), 0.88 (3H, t, $J = 6.9$ Hz, H-3'), 0.93 (9H, s, SiBu) 1.13-1.37 (4H, m, H-1' and H-2'), 1.55 (1H, dd, $J = 11.5, 3.4$ Hz, H-6), 1.86 (1H, ddd, $J = 14.0, 3.0, 3.0$ Hz, H-3), 2.05-2.15 (1H, m, H-7), 2.20-2.28 (2H, m, H-2 and H-3), 2.35 (1H, dd, $J = 11.5, 9.4$ Hz, H-8), 2.59 (1H, ddd, $J = 11.5, 11.5, 3.4$ Hz, H-8), 2.68 (1H, ddd, $J = 14.0, 14.0, 3.0$ Hz, H-2), 4.75 (1H, d, $J = 11.5$ Hz, H-5). ^{13}C (500 MHz) NMR δ -4.3 and -4.2 (SiMe₂), -1.7 (SiMe₃), 14.1 (C-3'), 18.1 (CMe₃), 20.7 (C-2'), 25.8 (CMe₃), 29.4 (C-1'), 31.8 (C-7), 34.6 (C-6), 36.7 (C-3), 46.1 (C-8), 46.3 (C-2), 103.5 (C-5), 152.9 (C-4), 215.6 (C-1). HRMS calcd for C₂₀H₄₀O₂Si₂ 368.2567, found 368.2577.

22c: a colorless oil, $R_f = 0.45$ (hexane:Et₂O = 7:1). IR (film) 1702 and 1642 cm⁻¹. ^1H NMR (500 MHz) δ -0.05

(9H, s, SiMe₃), 0.10 and 0.12 (each 3H, s, SiMe₂), 0.82 (3H, *J* = 7.1 Hz, H-7'), 0.89 (9H, s, SiBu) 1.10-1.35 (12H, m, H-1', H-2', H-3', H-4', H-5' and H-6'), 1.36 (1H, dd, *J* = 11.9, 3.7 Hz, H-6), 1.94-2.06 (2H, m, H-3 and H-7), 2.34-2.40 (2H, m, H-2 and H-8), 2.53 (1H, dd, *J* = 10.8, 10.8 Hz, H-8), 2.70-2.71 (2H, m, H-2 and H-3), 4.63 (1H, d, *J* = 11.9 Hz, H-5). ¹³C NMR (125 MHz) δ -4.3 and -4.2 (SiMe₂), -1.7 (SiMe₃), 14.1 (C-7'), 18.1 (CMe₃), 22.7, 27.6, 29.3, 29.4, and 31.8 (C-1', C-2', C-3', C-4', C-5', and C-6'), 25.8 (CMe₃), 29.6 (C-3), 32.4 (C-6), 37.1 (C-7), 46.1 (C-8), 46.3 (C-2), 103.5 (C-5), 152.8 (C-4), 215.5 (C-1). HRMS calcd for C₂₄H₄₈O₂Si₂ 424.3193, found 424.3200.

22d: a colorless oil, *R_f* = 0.55 (hexane:Et₂O = 14:1). IR (film) 1704 and 1640 cm⁻¹. ¹H NMR δ 0.00 (9H, s, SiMe₃), 0.15 and 0.18 (each 3H, s, SiMe₂), 0.80-1.30 (4H, m), 0.97 (9H, s, SiBu), 1.35 (1H, dd, *J* = 12.4, 5.7 Hz, H-6), 1.44-1.69 (7H, m), 1.85-1.87 (1H, m, H-7), 2.00-2.14 (2H, m, H-3 and H-8), 2.33-2.40 (1H, m, H-2), 2.48-2.58 (1H, m, H-3), 2.70-2.84 (2H, m, H-2 and H-8), 4.69 (1H, d, *J* = 11.9 Hz, H-5). ¹³C NMR (125 MHz) δ -4.3 and -4.1 (SiMe₂), -1.9 (SiMe₃), 18.1 (CMe₃), 25.8 (CMe₃), 26.4, 26.8, 27.2, 29.7, and 33.1 (*c*-Hex), 30.1 (C-3), 31.8 (C-6), 41.5 (C-8), 42.7 (C-7), 46.2 (C-2), 105.2 (C-5), 152.2 (C-4), 216.9 (C-1). HRMS calcd for C₂₃H₄₄O₂Si₂ 408.2880, found 408.2885.