Supporting Information

Nitrile Anion Cyclization with Epoxysilanes Followed by Brook Rearrangement/Ring-Opening of Cyclopropane Nitriles/Alkylation

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General. IR spectra were recorded on an FT spectrometer. ^1H NMR spectra were taken on either 500 MHz or 400 MHz spectrometers in CDCl_3 with reference to CHCl_3 (δ 7.26). ^{13}C NMR spectra were measured with either 125 MHz or 100 MHz spectrometers in CDCl_3 with reference to the CDCl_3 triplet (δ 77.2). Resonance patterns were described as s = singlet, d = doublet, t = triplet, sep = septet, and m = multiplet. The assignment of ^1H and ^{13}C NMR spectra is based on H-H decoupling and HMQC experiments. Mass spectrometry was electron impact mass spectra. Liquid chromatography under medium pressures (MPLC) was carried out using prepacked columns (22 mm x 300 mm, 10 μ silica gel). For routine chromatography, the following adsorbents were used: silica gel 60 of particle size 63-210 μm for column chromatography; 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. We were unable to obtain a consistent HRMS or elemental analysis for (*E*)-(3-bromoprop-1-enyl)-*tert*-butyldimethylsilane, (*Z*)-(3-bromoprop-1-enyl)-*tert*-butyldimethylsilane, and **23** because of their volatility.

(*E*)-(3-Bromoprop-1-enyl)-*tert*-butyldimethylsilane.

To a cooled (0 $^{\circ}\text{C}$) solution of NBS (13.6 g, 76.5 mmol) in CH_2Cl_2 (200 mL) was added dropwise Me_2S (6.70 mL, 91.8 mmol). The solution was stirred at the same temperature for 20 min and recooled to -15 $^{\circ}\text{C}$ before addition of a solution of 3-(*tert*-butyldimethylsilyl)prop-2-en-1-ol (**8**) (8.80 g, 51.0 mmol) in CH_2Cl_2 (50 mL). The mixture was warmed to room temperature and stirred for 3 h. The reaction mixture was poured into hexane- Et_2O (1:1, 100 mL) and ice-water (100 mL). Phases were separated and the aqueous phase was extracted with Et_2O . Combined organic phases were washed with saturated brine (100 mL), dried, and concentrated. The residual oil was filtered through a short pad of silica gel to give the title compound (6.18 g, 54%). Colorless oil, R_f = 0.80 (hexane:AcOEt = 3:1). IR (film) 1610, 833 cm^{-1} . ^1H NMR (400 MHz) δ 0.05 (6H, s, SiMe_2), 0.88 (9H, s, *t*-Bu), 3.95 (2H, d, J = 6.8 Hz, H-3), 5.94 (1H, d, J = 18.4 Hz, H-1), 6.17 (1H, dt, J = 18.4, 6.8 Hz, H-2). ^{13}C NMR (100 MHz) δ -6.1 (SiMe_2), 16.7 (CMe_3), 26.5 (CMe_3), 35.2 (C-3), 133.1 (C-2), 142.3 (C-1). MS 177 (M^+ - *t*-Bu).

(2*R,3*R**)-3-(3-(*tert*-Butyldimethylsilyl)oxiran-2-yl)propanenitrile (*trans*-9).**

To a cooled (-80 $^{\circ}\text{C}$) solution of MeCN (806 μL , 15.4 mmol) in THF (80 mL) was added dropwise *n*-BuLi (2.25 M in hexane, 6.80 mL, 15.3 mmol) and the solution was stirred at the same temperature for 10 min. This mixture was added to a solution of (*E*)-(3-bromoprop-1-enyl)-*tert*-butyldimethylsilane (3.00g, 12.8 mmol) in THF (48 mL) via cannula over a period of 30 min. The reaction mixture was stirred at the same temperature for 5 min and diluted with 10% aqueous NH_4Cl solution (50 mL). Phases were separated and the aqueous phase was extracted with Et_2O (20 mL x 3). Combined organic phases were washed with saturated brine (50 mL), dried, and concentrated to give crude (*E*)-4-(*tert*-butyldimethylsilyl)but-3-enenitrile (3.00 g).

This compound was dissolved in CHCl_3 (26 mL) and mCPBA (70%, 4.40 g, 17.8 mmol) was added. The reaction mixture was stirred at room temperature for 12 h, and diluted with Et_2O (50 mL) and saturated aqueous K_2CO_3 solution (50 mL). Phases were separated and the aqueous phase was extracted with Et_2O (20 mL x 2). Combined organic phases were washed with saturated brine (50 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 60 g, elution with hexane:AcOEt = 3:1) to give *trans*-9 (2.16 g, 80%). Colorless oil, R_f = 0.41 (hexane:AcOEt = 2:1). IR (film) 2361 cm^{-1} . ^1H NMR (400 MHz) δ -0.05 and -0.02 (each 3H, s, SiMe_2), 0.95 (9H, s, *t*-Bu), 1.76-1.88 and 1.98-2.08 (each 1H, m, H-3), 2.14 (1H, d, J = 3.2 Hz, H-3'), 2.49 (2H, t, J = 7.2 Hz, H-2), 2.83-2.89 (1H, m, H-2'). ^{13}C NMR (100 MHz) δ -8.3 (SiMe_2), 14.3 (C-2), 16.8 (CMe_3), 26.6 (CMe_3), 30.1 (C-3), 50.2 and 50.6 (C-2' and C-3'), 119.2 (CN). HRMS calcd for $\text{C}_7\text{H}_{12}\text{NOSi}$, 154.0688 (M^+ - *t*-Bu), found 154.0702.

(2*R,3*R**)-2-((3-(*tert*-Butyldimethylsilyl)oxiran-2-yl)methyl)malononitrile (10).**

To a cooled (-80 °C) solution of malononitrile (284 μ L, 5.12 mmol) in THF (35 mL) was added *n*-BuLi (2.25 M in *n*-hexane, 2.28 mL, 5.12 mmol) and the mixture was stirred at the same temperature for 10 min before addition of a solution of (*E*)-(3-bromoprop-1-enyl)-*tert*-butyldimethylsilane (1.00g, 4.27 mmol) in THF (5 mL). After warming to room temperature, the reaction mixture was poured into 10% aqueous NH_4Cl solution (20 mL), and extracted with Et_2O (10 mL x 3). Combined organic phases were washed with saturated brine (20 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 30 g, elution with hexane:AcOEt = 5:1) to give 2-((*E*)-3-(*tert*-butyldimethylsilyl)allyl)malononitrile (265 mg, 28%) and bis(3-(*tert*-butyldimethylsilyl)allyl)malononitrile (481 mg, 30%).

The monoalkylated product was dissolved in CHCl_3 (2.4 mL) and mCPBA (70%, 228 mg, 1.32 mmol) was added. The reaction mixture was stirred at room temperature for 12 h, and diluted with Et_2O (5 mL) and saturated aqueous K_2CO_3 solution (10 mL). Phases were separated and the aqueous phase was extracted with Et_2O (5 mL x 3). Combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 10 g, elution with hexane:AcOEt = 4:1) to give **10** (194 mg, 64%). Colorless oil, R_f = 0.28 (hexane:AcOEt = 3:1). IR (film) 2258 cm^{-1} . ^1H NMR (500 MHz) δ -0.02 and -0.08 (each 3H, s, SiMe_2), 0.95 (9H, s, *t*-Bu), 2.15 (1H, ddd, J = 14.0, 7.1, 5.5 Hz, H-2), 2.24 (1H, d, J = 3.5 Hz, H-3'), 2.41 (1H, ddd, J = 14.0, 8.5, 3.5 Hz, H-2), 2.98 (1H, ddd, J = 7.1, 3.5, 3.5 Hz, H-2'), 3.93 (1H, dd, J = 6.8, 4.4, H-1). ^{13}C NMR (125 MHz) δ -8.4 and -8.2 (SiMe_2), 16.7 (CMe_3), 20.2 (C-1), 26.5 (*t*-Bu), 35.6 (C-2), 50.9 and 51.2 (C-2' and C-3'), 112.2 and 112.4 (CN). HRMS calcd for $\text{C}_8\text{H}_{11}\text{N}_2\text{OSi}$, 179.0641 (M^+ - *t*-Bu), found 179.0620.

(2*R,3*R**)-3-(3-(*tert*-Butyldimethylsilyl)oxiran-2-yl)-2-phenylpropanenitrile (11).**

To a cooled (-80 °C) solution of benzyl cyanide (1.76 mL, 15.4 mmol) in THF (30 mL) was added *n*-BuLi (2.25 M in *n*-hexane, 6.80 mL, 15.4 mmol) and the mixture was stirred at the same temperature for 10 min. This mixture was added to a cooled (-80 °C) solution of (*E*)-(3-bromoprop-1-enyl)-*tert*-butyldimethylsilane (3.00 g, 12.8 mmol) in THF (55 mL) via cannula over a period of 30 min and stirred at the same temperature for 5 min. The solution was diluted with 10% NH_4Cl solution (50 mL), and extracted with Et_2O (20 mL x 3). Combined organic phases were washed with saturated brine (50 mL), dried, and concentrated to give crude (*E*)-5-(*tert*-butyldimethylsilyl)-2-phenylpent-4-enenitrile.

This compound was dissolved in CHCl_3 (26 mL) and mCPBA (70%, 4.40 g, 17.8 mmol) was added. The reaction mixture was stirred at room temperature for 12 h, and diluted with Et_2O (50 mL) and saturated aqueous K_2CO_3 solution (50 mL). Phases were separated and the aqueous phase was extracted with Et_2O (20 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, 60 g, elution with hexane:AcOEt = 3:1) to give **11** (2.56 g, 70%) as a 1:1 mixture of diastereomers. This mixture was separated by MPLC (elution with hexane:AcOEt = 1:2) to give **11a** (more polar) and **11b** (less polar). **11a**: Colorless oil, R_f = 0.32 (hexane:AcOEt = 5:1). IR (film) 2245, 1601 cm^{-1} . ^1H NMR (400 MHz) δ -0.10 and -0.07 (each 3H, s, SiMe_2), 0.94 (9H, s, *t*-Bu), 2.08-2.13 (1H, m, H-3), 2.17 (1H, d, J = 3.6 Hz, H-3'), 2.24-2.32 (1H, m, H-3), 2.71-2.76 (1H, m, H-2'), 3.96 (1H, dd, J = 7.2, 7.2 Hz, H-2), 7.25-7.42 (5H, m, Ph). ^{13}C NMR (100 MHz) δ -8.4 and -8.2 (SiMe_2), 16.7 (CMe_3), 26.6 (CMe_3), 34.6 (C-2), 39.9 (C-3), 50.4 and 52.3 (C-2' and C-3'), 120.5 (CN), 127.5, 128.5, 129.4, and 134.9 (Ar). HRMS calcd for $\text{C}_{13}\text{H}_{16}\text{NOSi}$, 230.1001 (M^+ - *t*-Bu), found 230.0997. **11b**: Colorless oil, R_f = 0.32 (hexane:AcOH = 5:1). IR (film) 2245, 1601 cm^{-1} . ^1H NMR (400 MHz) -0.03 and -0.01 (each 3H, s, SiMe_2), 0.95 (9H, s, *t*-Bu), 1.90-2.00 (1H, m, H-3), 2.16 (1H, d, J = 3.6 Hz, H-3'), 2.21-2.30 (1H, m, H-3), 2.98-3.05 (1H, m, H-2'), 4.03 (1H, dd, J = 10.4, 4.4 Hz, H-2), 7.37 (5H, m, Ar). ^{13}C NMR (100 MHz) δ -8.3 and -8.0 (SiMe_2), 16.8 (CMe_3), 26.7 (CMe_3), 35.3 (C-2), 41.2 (C-3), 51.1 and 52.9 (C-4 and C-5), 120.3 (CN), 127.2, 128.5, 129.4 and 135.5 (Ph). HRMS calcd for $\text{C}_{13}\text{H}_{16}\text{NOSi}$, 230.1001 (M^+ - *t*-Bu), found 230.1004.

3-((2*R**,3*R**)-3-(*tert*-butyldimethylsilyl)oxiran-2-yl)-2-(trimethylsilyl)propanenitrile (**12**).

To a cooled (-80 °C) solution of lithium diisopropylamide (LDA) prepared from diisopropylamine (939 μ L, 6.7 mmol) and *n*-BuLi (2.3 M in hexane, 2.91 mL, 6.7 mmol) in THF (23 mL) was added dropwise a solution of trimethylsilylacetonitrile (759 mg, 6.7 mmol) in THF (9 mL) and the solution was stirred at the same temperature for 10 min. This mixture was added to a cooled (-80 °C) solution of ((*E*)-(3-bromoprop-1-enyl)-*tert*-butyldimethylsilyl) (1.50 g, 6.38 mmol) in THF (32 mL) via cannula over a period of 30 min and the reaction mixture was warmed to -60 °C. The solution was diluted with 10% NH₄Cl solution (100 mL), and extracted with hexane (50 mL x 2). Combined organic phases were washed with saturated brine (50 mL), dried, and concentrated to give crude (*E*)-5-(*tert*-butyldimethylsilyl)-2-trimethylsilylpent-4-enenitrile.

This compound was dissolved in CHCl₃ (13 mL) and mCPBA (77%, 2.00 g, 8.9 mmol) was added. The reaction mixture was stirred at room temperature for 12 h, and diluted with Et₂O (20 mL) and saturated aqueous K₂CO₃ solution (20 mL). Phases were separated and the aqueous phase was extracted with Et₂O (10 mL x 3). Combined organic phases were washed with saturated brine (20 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 45 g, elution with hexane:AcOEt = 8:1) to give **12** (1.29 g, 71%) as a 3:4 mixture of diastereomers. This mixture was separated with MPLC (elution with hexane:AcOEt = 15:1) to give **12a** (more polar) and **12b** (less polar). **12a**: Colorless needles (EtOH-H₂O), mp 64-65 °C, *R*_f = 0.43 (hexane:AcOEt = 5:1). IR (KBr pellet) 2217 cm⁻¹. ¹H NMR (500 MHz) δ 0.03 (6H, s, SiMe₂), 0.18 (9H, s, SiMe₃), 0.95 (9H, s, *t*-Bu), 1.56 (1H, ddd, *J* = 14.0, 7.1, 3.4 Hz, H-3), 1.85 (1H, ddd, *J* = 14.0, 12.4, 4.4 Hz, H-3), 2.01 (1H, dd, *J* = 12.4, 3.4 Hz, H-2), 2.18 (1H, d, *J* = 3.4 Hz, H-3'), 2.95 (1H, ddd, *J* = 7.1, 4.4, 3.4 Hz, H-2'). ¹³C NMR (125 MHz) δ -8.37 and -8.17 (SiMe₂), -3.31 (SiMe₃), 16.4 (C-2), 16.7 (CMe₃), 26.6 (CMe₃), 32.1 (C-3), 51.2 and 54.7 (C-2' and C-3'), 121.6 (CN). HRMS calcd for C₁₀H₂₀NOSi₂, 226.1083 (M⁺ - *t*-Bu), found 226.1084. Anal. Calcd for C₁₀H₂₀NOSi₂: C 59.30, H 10.31, N 4.94, found C 59.36, H 10.05, N 4.90. **12b**: colorless prisms (EtOH-H₂O), mp 55-56 °C, *R*_f = 0.43 (hexane:AcOH = 5:1). IR (KBr) 2217 cm⁻¹. ¹H NMR (500 MHz) δ -0.05 and -0.00 (each 3H, s, SiMe₂), 0.20 (9H, s, SiMe₃), 0.96 (9H, s, *t*-Bu), 1.70 (1H, ddd, *J* = 14.2, 5.5, 3.9 Hz, H-3), 1.81 (1H, dd, *J* = 10.8, 3.9 Hz, H-2), 2.02 (1H, ddd, *J* = 14.2, 10.8, 4.8 Hz, H-3), 2.12 (1H, d, *J* = 3.4 Hz, H-3'), 2.98 (1H, ddd, *J* = 5.5, 4.8, 3.4 Hz, H-2'). ¹³C NMR (125 MHz) δ -8.35 and -8.21 (SiMe₂), -3.16 (SiMe₃), 15.2 (C-2), 16.7 (CMe₃), 26.6 (CMe₃), 30.9 (C-3), 49.3 and 54.4 (C-2' and C-3'), 121.7 (CN). HRMS calcd for C₁₀H₂₀NOSi₂, 226.1083 (M⁺ - *t*-Bu), found 226.1084.

Reaction of *trans*-**9** with NHMDS Followed by Quenching with Acetic Acid.

To a cooled (-30 °C) solution of **9** (500 mg, 2.4 mmol) in THF (19 mL) was added NHMDS (0.94 M in THF, 5.1 mL, 4.8 mmol) and the reaction mixture was warmed to 5 °C before addition of AcOH (1 M in THF, 4.8 mL, 4.8 mmol). The solution was diluted with 10% NH₄Cl solution (30 mL), and extracted with Et₂O (15 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, 15 g, elution with hexane:AcOEt = 10:1) to give (*Z*)-**13** (367 mg, 73%). *R*_f = 0.54 (hexane:AcOEt = 3:1). IR (film) 2246, 1658 cm⁻¹. ¹H NMR (400 MHz) δ 0.14 (6H, s, SiMe₂), 0.92 (9H, s, *t*-Bu), 2.35-2.45 (4H, m, H-2 and H-3), 4.51 (1H, dt, *J* = 5.6, 5.2 Hz, H-4), 6.29 (1H, d, *J* = 5.6 Hz, H-5). ¹³C NMR (100 MHz) δ -5.2 (SiMe₂), 17.6 (C-2), 20.2 (C-3), 18.4 (CMe₃), 25.7 (CMe₃), 105.6 (C-4), 120.0 (CN), 141.5 (C-5). HRMS calcd for C₇H₁₂NOSi, 154.0688 (M⁺ - *t*-Bu), found 154.0678.

General Procedure for Alkylation of *trans*-9**: Reaction of *trans*-**9** with NHMDS and MeI.** To a cooled (-30 °C) solution of **9** (100 mg, 0.470 mmol) in THF (3.9 mL) was added NHMDS (1.0 M in THF, 0.94 mL, 0.94 mmol) and the reaction mixture was warmed to 5 °C. Then the mixture was cooled to -10 °C, MeI (32 μ L, 1.1 mmol) was added, and stirred at the same temperature for 15 min before addition of 10% aqueous NH₄Cl solution (10 mL). The phases were separated, and the aqueous phase was extracted with Et₂O (5 mL x 3). Combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The

residual oil was subjected to column chromatography (silica gel, 5 g, elution with hexane:AcOEt = 10:1) to give (Z)-**15a** (67 mg, 63%).

(Z)-5-(tert-butyldimethylsilyloxy)-2-methylpent-4-enenitrile ((Z)-15a).

Colorless oil. R_f = 0.54 (hexane:AcOEt = 3:1). IR (film) 2243, 1658 cm^{-1} . ^1H NMR (400 MHz) δ 0.14 (6H, s, SiMe_2), 0.92 (9H, s, $t\text{-Bu}$), 1.29 (3H, d, J = 7.2 Hz, 2-Me), 2.37 (2H, dd, J = 6.8, 6.0 Hz, H-3), 2.50-2.68 (1H, m, 1H, H-2), 4.5 (1H, dt, J = 6.0, 6.0 Hz, H-4), 6.35 (1H, d, J = 6.0 Hz, H-5). ^{13}C NMR (100 MHz) δ -5.2 (SiMe_2), 17.6 (Me), 18.4 (CMe_3), 25.7 (CMe_3), 25.8 (C-2), 28.3 (C-3), 104.4 (C-4), 123.3 (CN), 141.8 (C-5). HRMS calcd for $\text{C}_8\text{H}_{14}\text{NOSi}$, 168.0845 ($\text{M}^+ - t\text{-Bu}$), found 168.0814.

(Z)-5-(tert-butyldimethylsilyloxy)-2-ethylpent-4-enenitrile ((Z)-15b).

Colorless oil. R_f = 0.55 (hexane:AcOEt = 3:1). IR (film) 2239, 1658 cm^{-1} . ^1H NMR (400 MHz) δ 0.13 (6H, s, SiMe_2), 0.91 (9H, s, $t\text{-Bu}$), 1.06 (3H, t, J = 7.2 Hz, CH_2CH_3), 1.58-1.68 (2H, m, CH_2CH_3), 2.37 (2H, m, H-3), 2.42-2.53 (1H, m, H-2), 4.50 (1H, dt, J = 6.0, 6.0 Hz, H-4), 6.31 (1H, d, J = 6.0 Hz, H-5). ^{13}C NMR (100 MHz) δ -5.3 (SiMe_2), 11.7 (CH_2CH_3), 18.3 (CMe_3), 25.0 and 26.1 (CH_2CH_3 and C-2), 25.7 (CMe_3), 33.5 (C-3), 104.6 (C-4), 122.4 (CN), 141.6 (C-5). HRMS calcd for $\text{C}_9\text{H}_{16}\text{NOSi}$, 182.1001 ($\text{M}^+ - t\text{-Bu}$), found 182.0998.

General Procedure for alkylation of 11: Reaction of 11 with NHMDS and MeI. To a cooled (-30 $^\circ\text{C}$) solution of a mixture of **11a** and **11b** (100 mg, 0.350 mmol) in THF (2.1 mL) was added NHMDS (1.0 M in THF, 1.40 mL, 1.40 mmol) and the reaction mixture was warmed to 15 $^\circ\text{C}$. Then the mixture was cooled to -10 $^\circ\text{C}$, MeI (85 μL , 1.40 mmol) was added, and stirred at the same temperature for 15 min before addition of 10% aqueous NH_4Cl solution (10 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (5 mL x 3). Combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 5 g, elution with hexane:AcOEt = 18:1) to give (Z)-**16a** (89 mg, 84%).

(Z)-5-(tert-butyldimethylsilyloxy)-2-methyl-2-phenylpent-4-enenitrile ((Z)-16a)

Colorless oil. R_f = 0.55 (hexane:AcOH = 5:1). IR (film) 2236, 1658, 1602 cm^{-1} . ^1H NMR (400 MHz) δ 0.12 and 0.13 (each 3H, s, SiMe_2), 0.93 (9H, s, $t\text{-Bu}$), 1.71 (3H, s, Me), 2.66-2.80 (2H, m, H-3), 4.45 (1H, dt, J = 6.0, 6.0 Hz, H-4), 6.32 (1H, d, J = 6.0 Hz, H-5), 7.25-7.49 (5H, m, Ph). ^{13}C NMR (100 MHz) δ -5.2, -5.2 (SiMe_2), 18.3 (CMe_3), 25.8 (CMe_3), 26.7 (Me), 36.3 (C-3), 42.5 (C-2), 103.3 (C-4), 123.9 (CN), 125.8, 127.8, 128.9 and 140.7 (Ph), 142.0 (C-5). HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{NOSi}$, 244.3885 ($\text{M}^+ - t\text{-Bu}$), found 244.3848.

(Z)-5-(tert-butyldimethylsilyloxy)-2-ethyl-2-phenylpent-4-enenitrile ((Z)-16b)

Colorless oil. R_f = 0.31 (hexane:AcOH = 16:1). IR (film) 2236, 1658, 1602 cm^{-1} . ^1H NMR (400 MHz) δ 0.10 and 0.12 (each 3H, s, SiMe_2), 0.92 (3H, t, J = 7.6 Hz, CH_2CH_3), 0.93 (9H, s, $t\text{-Bu}$), 1.88-1.98 and 2.03-2.13 (each 1H, m, CH_2CH_3), 2.69 (1H, ddd, J = 14.4, 6.8, 1.2 Hz, H-3), 2.84 (1H, ddd, J = 14.4, 7.6, 1.2 Hz, H-3), 4.40 (1H, ddd, J = 7.6, 6.8, 6.0 Hz, H-4), 6.27 (1H, ddd, J = 6.0, 1.2, 1.2 Hz, H-5), 7.25-7.44 (5H, m, Ph). ^{13}C NMR (100 MHz) δ -5.2 and -5.2 (SiMe_2), 9.8 (CH_2CH_3), 18.3 (CMe_3), 25.8 (CMe_3), 33.1 and 34.9 (C-3, CH_2CH_3), 48.9 (C-2), 103.3 (C-4), 122.7 (CN), 126.4, 127.6, 128.8 and 138.7 (Ph), 141.7 (C-5). HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{NOSi}$, 258.1350 ($\text{M}^+ - t\text{-Bu}$), found 258.1314.

(Z)-5-(tert-butyldimethylsilyloxy)-2-(1-methylethyl)-2-phenylpent-4-enenitrile ((Z)-16c).

Colorless oil. R_f = 0.29 (hexane:AcOH = 18:1). IR (film) 2235, 1658, 1599 cm^{-1} . ^1H NMR (400 MHz) δ 0.01 and 0.03 (each 3H, s, SiMe_2), 0.74 and 1.12 (each 3H, d, J = 7.6 Hz, $\text{CH}(\text{CH}_3)_2$), 0.85 (9H, s, $t\text{-Bu}$), 2.10 (1H, sep, J = 7.6 Hz, $\text{CH}(\text{CH}_3)_2$), 2.65 (1H, ddd, J = 14.4, 7.2, 1.2 Hz, H-3), 2.90 (1H, ddd, J = 14.4, 6.8, 1.2 Hz, H-3), 4.16 (1H, ddd, J = 7.2, 6.8, 6.0 Hz, H-4), 6.1 (1H, ddd, J = 6.0, 1.2, 1.2 Hz, H-5), 7.17-7.34 (5H, m, Ph). ^{13}C NMR (100 MHz) δ -5.2 and -5.2 (SiMe_2), 18.3 (CMe_3), 18.7 and 19.0 ($\text{CH}(\text{CH}_3)_2$), 25.8 ($t\text{-Bu}$), 31.9 (C-3), 37.0 ($\text{CH}(\text{CH}_3)_2$), 53.6 (C-2), 103.8 (C-4), 121.7 (CN), 127.0, 127.5,

128.5, and 138.3 (Ph), 141.3 (C-5). HRMS calcd for $C_{16}H_{22}NOSi$, 272.1471 ($M^+ - t\text{-Bu}$), found 272.1462.

(Z)-5-(tert-butyldimethylsilyloxy)-2-(2-propen-1-yl)-2-phenylpent-4-enenitrile ((Z)-16d).

Colorless oil. R_f = 0.21 (hexane:AcOH = 18:1). IR (film) 2237, 1729, 1657, 1602 cm^{-1} . ^1H NMR (400 MHz) δ 0.11 and 0.13 (each 3H, s, SiMe_2), 0.93 (9H, s, $t\text{-Bu}$), 2.63-2.77 (3H, m, H-3 and $\text{CH}_2\text{CH}=\text{CH}_2$), 2.86 (1H, dd, J = 14.4, 7.6 Hz, H-3), 4.42 (1H, ddd, J = 7.6, 7.6, 6.0 Hz,

H-4), 5.05-5.15 (2H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 5.60-5.75 (1H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 6.29 (1H, dm, J = 6.0 Hz, H-5), 7.25-7.45 (5H, Ph). ^{13}C NMR (100 MHz) δ -5.2 and -5.2 (SiMe_2), 18.3 (CMe_3), 25.8 (CMe_3), 34.4 (C-3), 44.3 ($\text{CH}_2\text{CH}=\text{CH}_2$), 48.0 (C-2), 103.1 (C-4), 119.9 ($\text{CH}_2\text{CH}=\text{CH}_2$), 122.3 (CN), 126.5, 127.8, 128.8, and 138.5 (Ph), 132.3 ($\text{CH}_2\text{CH}=\text{CH}_2$), 141.9 (C-5). HRMS calcd for $C_{16}H_{20}NOSi$, 270.1314 ($M^+ - t\text{-Bu}$), found 270.1336.

(Z)-5-(tert-butyldimethylsilyloxy)-2-benzyl-2-phenylpent-4-enenitrile ((Z)-16e).

Colorless oil. R_f = 0.36 (hexane:AcOH = 9:1), IR (film) 2237, 1657, 1601 cm^{-1} . ^1H NMR (400 MHz) δ 0.07 and 0.07 (each 3H, s, SiMe_2), 0.88 (9H, s, $t\text{-Bu}$), 2.78 (1H, ddd, J = 14.4, 7.2, 1.2 Hz, H-3), 2.89 (1H, dd, J = 14.4, 7.6, 1.2 Hz, H-3), 3.07 and 3.20 (each 1H, d, J = 13.6 Hz, CH_2Ph), 4.42 (1H, ddd,

J = 7.6, 7.2, 6.4 Hz, H-4), 6.24 (1H, ddd, J = 6.4, 1.2, 1.2 Hz, H-5), 6.92-7.30 (10H, m, Ph). ^{13}C NMR (100 MHz) δ -5.2 and -5.2 (SiMe_2), 18.3 (CMe_3), 25.8 (CMe_3), 33.6 (C-3), 47.0, 49.5 (C-2, CH_2Ph), 103.4 (C-4), 122.2 (CN), 122.2, 126.8, 127.3, 127.8, 128.7, 128.6, 130.5, 135.4, and 138.3 (Ph), 141.9 (C-5). HRMS calcd for $C_{20}H_{22}NOSi$, 320.1471 ($M^+ - t\text{-Bu}$), found 320.1446.

Reaction of 12 with $n\text{-BuLi}$ and MeI.

To a cooled ($-50\text{ }^\circ\text{C}$) solution of **12** (80 mg, 0.28 mmol) in THF (2.8 mL) was added $n\text{-BuLi}$ (2.3 M in hexane, 130 μL , 0.3 mmol), and the reaction mixture was warmed to $15\text{ }^\circ\text{C}$. Then the mixture was cooled to $-10\text{ }^\circ\text{C}$, MeI (35 μL , 0.56 mmol) was added, and stirred at the same temperature for 15 min before

addition of 10% aqueous NH_4Cl solution (5 mL). The phases were separated, and the aqueous phase was extracted with hexane (5 mL x 3). Combined organic phases were washed with saturated brine (5 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 4 g, elution with hexane:AcOEt = 10:1) to give **17** (58 mg, 70%). Pale yellow oil, R_f = 0.45 (hexane:AcOEt = 5:1). IR (film) 1656, 2215 cm^{-1} . ^1H NMR (500 MHz) δ 0.12 and 0.12 (each 3H, s, SiMe_2), 0.17 (9H, s, SiMe_3), 0.90 (9H, s, $t\text{-Bu}$), 1.23 (3H, s, 2-Me), 2.29 (1H, ddd, J = 14.2, 8.2, 1.1 Hz, H-3), 2.35 (1H, ddd, J = 14.2, 6.6, 1.4 Hz, H-3), 4.60 (1H, ddd, J = 8.2, 6.6, 5.7 Hz, H-4), 6.37 (1H, ddd, J = 5.7, 1.4, 1.1 Hz, H-5). ^{13}C NMR (125 MHz) δ -5.32 and -5.28 (SiMe_2), -4.22 (SiMe_3), 18.2 (CMe_3), 18.3 (2-Me), 22.5 (C-2), 25.6 (CMe_3), 28.1 (C-3), 104.4 (C-4), 125.2 (CN), 141.3 (C-5). HRMS calcd for $C_{11}H_{22}NOSi_2$, 240.1240 ($M^+ - t\text{-Bu}$), found 240.1242.

(Z)-(3-Bromoprop-1-enyl)-tert-butyldimethylsilane.

To a cooled ($0\text{ }^\circ\text{C}$) solution of DIBAL-H (31.5 mL, 177 mmol) in Et_2O was added dropwise 3-(tert-butyldimethylsilyl)-2-propyne-1-ol (10.0 g, 58.7 mmol) in Et_2O (13 mL). After refluxing for 2 h, the reaction mixture was cooled to $-30\text{ }^\circ\text{C}$, 10:1 mixture of $\text{Et}_2\text{O}/\text{MeOH}$ (100 mL), water (100 mL) and 1N hydrochloric acid (50 mL) were added.

Phases are separated and aqueous phase was extracted with Et_2O (100 mL x 3). Combined organic phases were washed with saturated brine, dried, and concentrated to give crude (*E*)-3-(tert-butyldimethylsilyl)-2-propene-1-ol. The product was used in the following step without further purification.

To a cooled ($0\text{ }^\circ\text{C}$) solution of NBS (16.1 g, 90.5 mmol) in CH_2Cl_2 (120 mL) was added dropwise Me_2S (8.4 mL, 108.5 mmol). The solution was stirred at the same temperature for 20 min and cooled to $-15\text{ }^\circ\text{C}$ before addition of a solution of above compound in CH_2Cl_2 (30 mL). The mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was poured into hexane- Et_2O (1:1, 100 mL) and ice-water (200 mL). Phases were separated and the aqueous phase was extracted with hexane (100 mL x 2). Combined organic phases were washed with saturated brine (100 mL), dried, and concentrated. The residual oil was filtered through a short pad of silica gel to give the title compound (8.24 g, 65%). Colorless oil, R_f = 0.75

(hexane:AcOEt = 3:1). IR (film) 1601 cm^{-1} . ^1H NMR (400 MHz) δ 0.15 (6H, s, SiMe_2), 0.90 (9H, s, SiMe_3), 3.99 (2H, d, $J = 8.1$ Hz, H-3), 5.71 (1H, d, $J = 13.9$ Hz, H-1), 6.57 (1H, dt, $J = 13.9, 8.1$ Hz, H-2). ^{13}C NMR (100 MHz) δ -4.15 (SiMe_2), 17.0 (CMe_3), 26.5 (CMe_3), 32.3 (C-3), 132.4 (C-2), 143.5 (C-1). MS 177 ($\text{M}^+ - t\text{-Bu}$).

3-((2*R**,3*S**)-3-(*tert*-butyldimethylsilyl)oxiran-2-yl)propanenitrile (*cis*-9).

To a cooled ($-80\text{ }^\circ\text{C}$) solution of MeCN (537 μL , 10.2 mmol) in THF (43 mL) was added dropwise *n*-BuLi (2.3 M in hexane, 4.43 mL, 10.2 mmol) and the solution was stirred at the same temperature for 10 min. This mixture was added to a solution of (Z)-(3-bromoprop-1-enyl)-*tert*-butyldimethylsilane (2.00 g, 8.5 mmol) in THF (43 mL) via cannula over a period of 30 min. The reaction mixture was stirred at the same temperature for 5 min and diluted with 10% aqueous NH_4Cl solution (50 mL). Phases were separated and the aqueous phase was extracted with hexane (20 mL x 3). Combined organic phases were washed with saturated brine (50 mL), dried, and concentrated to give crude (Z)-4-(*tert*-butyldimethylsilyl)but-3-enenitrile.

This compound was dissolved in CHCl_3 (17 mL) and mCPBA (70%, 2.9 g, 11.9 mmol) was added. The reaction mixture was stirred at room temperature for 12 h, and diluted with Et_2O (20 mL) and saturated aqueous K_2CO_3 solution (20 mL). Phases were separated and the aqueous phase was extracted with Et_2O (10 mL x 2). Combined organic phases were washed with saturated brine (20 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 60 g, elution with hexane:AcOEt = 3:1) to give *cis*-9 (1.19 g, 66%). Colorless oil, $R_f = 0.32$ (hexane:AcOEt = 3:1). IR (film) 2248 cm^{-1} . ^1H NMR (400 MHz) δ 0.03 and 0.07 (each 3H, s, SiMe_2), 0.96 (9H, s, *t*-Bu), 1.57-1.66 (1H, m, H-3), 2.03-2.11 (1H, m, H-3), 2.36 (1H, d, $J = 5.1$ Hz, H-3'), 2.48-2.56 (2H, m, H-2), 3.16-3.20 (1H, m, H-2'). ^{13}C NMR (100 MHz) δ -6.15 and -5.88 (SiMe_2), 15.2 (C-2), 16.9 (CMe_3), 26.6 (CMe_3), 28.1 (C-3), 49.1 and 55.4 (C-2' and C-3'), 119.1 (CN). HRMS calcd for $\text{C}_7\text{H}_{12}\text{NOSi}$, 154.0688 ($\text{M}^+ - t\text{-Bu}$), found 154.0688.

Reaction of *cis*-9 with NHMDS Followed by Quenching with Acetic Acid.

To a cooled ($-30\text{ }^\circ\text{C}$) solution of *cis*-9 (100 mg, 0.470 mmol) in THF (4.2 mL) was added NHMDS (0.94 M in THF, 1.0 mL, 0.94 mmol) and the reaction mixture was warmed to $5\text{ }^\circ\text{C}$ before addition of AcOH (1 M in THF, 0.94 mL,

0.94 mmol). The solution was diluted with 10% NH_4Cl solution (5 mL), and extracted with Et_2O (5 mL x 2). Combined organic phases were washed with saturated brine (5 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 5 g, elution with hexane:AcOEt = 10:1) to give (*E*)-13 ($\text{R} = \text{H}$) (62 mg, 62%). Colorless oil, $R_f = 0.48$ (hexane:AcOEt = 5:1). IR (film) 1664, 2247 cm^{-1} . ^1H NMR (400 MHz) δ 0.15 (6H, s, SiMe_2), 0.92 (9H, s, *t*-Bu), 2.25 (2H, dt, $J = 7.3, 6.6$ Hz, H-3), 2.35 (2H, t, $J = 6.6$ Hz, H-2), 4.98 (1H, dt, $J = 11.7, 7.3$ Hz, H-4), 6.38 (1H, d, $J = 11.7$ Hz, H-5). ^{13}C NMR (100 MHz) δ -5.15 (SiMe_2), 18.4 (CMe_3), 19.0 (C-2), 25.1 (C-3), 25.8 (CMe_3), 107.1 (C-4), 119.4 (CN), 143.2 (C-5). HRMS calcd for $\text{C}_{11}\text{H}_{22}\text{NOSi}$, 212.1471 ($\text{M}^+ + 1$), found 212.1479.

General Procedure for Alkylation of *cis*-9: Reaction of *cis*-9 with NHMDS and MeI. To a cooled ($-30\text{ }^\circ\text{C}$) solution of *cis*-9 (100 mg, 0.470 mmol) in THF (3.9 mL) was added NHMDS (0.94 M in THF, 1.0 mL, 0.94 mmol) and the reaction mixture was warmed to $5\text{ }^\circ\text{C}$. Then the mixture was cooled to $-10\text{ }^\circ\text{C}$, MeI (32 μL , 0.52 mmol) was added, and stirred at the same temperature for 15 min before addition of 10% aqueous NH_4Cl solution (10 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (5 mL x 3). Combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 5 g, elution with hexane:AcOEt = 10:1) to give (*E*)-15a (75 mg, 71%).

(*E*)-5-(*tert*-butyldimethylsilyloxy)-2-methylpent-4-enenitrile ((*E*)-15a).

Colorless oil, $R_f = 0.52$ (hexane:AcOEt = 3:1), IR (film) 1664, 2240 cm^{-1} . ^1H NMR (500 MHz) δ 0.13 (6H, s, SiMe_2), 0.90 (9H, s, *t*-Bu), 1.27 (3H, d, $J = 7.1$ Hz, 2-Me), 2.11-2.21 (2H, m, H-3), 2.57 (1H, ddq, $J = 7.1, 7.1, 7.1$ Hz, H-2), 4.97 (1H, ddd, $J = 11.7, 7.8, 7.8$ Hz, H-4), 6.34 (1H, d, $J = 11.7$ Hz, H-5). ^{13}C

NMR (125 MHz) δ -5.22 (SiMe₂), 17.3 (Me), 18.3 (CMe₃), 25.7 (CMe₃), 26.8 (C-2), 32.2 (C-3), 105.7 (C-4), 122.7 (CN), 143.7 (C-5). HRMS calcd for C₈H₁₄NOSi, 168.0845 (M⁺ - *t*-Bu), found 168.0842.

(*E*)-5-(*tert*-butyldimethylsilyloxy)-2-ethylpent-4-enitrile ((*E*)-15b).

Colorless oil, R_f = 0.63 (hexane:AcOEt = 3:1), IR (film) 1664, 2239 cm⁻¹. ¹H NMR (500 MHz) δ 0.13 (6H, s, SiMe₂), 0.90 (9H, s, *t*-Bu), 1.05 (3H, t, J = 7.6 Hz, CH₂CH₃), 1.57-1.64 (2H, m, CH₂CH₃), 2.12-2.22 (2H, m, H-3), 2.42 (1H, ddt, J = 7.7, 7.7, 6.3 Hz, H-2), 4.96 (1H, ddd, J = 11.9, 7.8, 7.8 Hz, H-4), 6.33 (1H, ddd, J = 11.9, 1.1, 1.1 Hz, H-5). ¹³C NMR (125 MHz) δ -5.22 (SiMe₂), 11.5 (CH₂CH₃), 18.3 (CMe₃), 24.8 (C-2), 25.7 (CMe₃), 30.1 (CH₂CH₃), 34.6 (C-3), 105.9 (C-4), 121.8 (CN), 143.5 (C-5). HRMS calcd for C₉H₁₆NOSi, 182.1001 (M⁺ - *t*-Bu), found 182.1003.

2-Bromo-1-(*tert*-butyldimethylsilyl)prop-2-enone (23).

To a cooled (0 °C) solution of 1-(*tert*-butyldimethylsilyl)prop-2-enone (3.00 g, 17.6 mmol) in CH₂Cl₂ (59 mL) was added dropwise bromine (1.00 mL, 19.4 mmol) and the solution was stirred at the same temperature for 10 min. The solution was concentrated to give crude 2,3-dibromo-1-(*tert*-butyldimethylsilyl)propanone. The product was used in the following step without further purification.

To cooled (0 °C) solution of above compound in CH₂Cl₂ (176 mL) was added Et₃N (12 mL, 86.1 mmol) and the solution was stirred for 10 min. The mixture was diluted with 1N HCl solution (100 mL), and extracted with hexane (50 mL x 3). Combined organic phases were successively washed with saturated Na₂CO₃ solution and saturated brine, dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 50 g, elution with hexane:AcOEt = 10:1) to give **23** (4.2 g, 96%). Orange oil, R_f = 0.37 (hexane:CH₂Cl₂ = 2:1), IR (film) 1624 cm⁻¹. ¹H NMR (500 MHz) δ 0.31 (6H, s, SiMe₂), 0.93 (9H, s, *t*-Bu), 6.75 and 6.82 (each 1H, d, J = 2.5 Hz, H-3). ¹³C NMR (125 MHz) δ -4.61 (SiMe₂), 17.1 (CMe₃), 26.6 (CMe₃), 132.0 (C-3), 140.4 (C-2), 224.6 (C-1). MS 191 (M⁺ - *t*-Bu).

(*tert*-Butyldimethylsilyl)-(2,2-dicyanocyclopropyl)methanol (26a).

To cooled (-80 °C) solution of malononitrile (872 mg, 13.2 mmol) in THF (50 mL) was added dropwise *n*-BuLi (2.3 M in hexane, 5.7 mL, 13.2 mmol) and the solution was stirred at the same temperature for 5 min before addition of a solution of **23** (3.00 g, 12.0 mmol) in THF (10 mL). After warming to -20 °C, the mixture was diluted with 10% NH₄Cl solution (100 mL), and extracted with hexane (50 mL x 2).

Combined organic phases were washed with saturated brine, dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 60 g, elution with hexane:AcOEt = 3:1) to give 2-(*tert*-butyldimethylsilyl)carbamoylcyclopropane-1,1-dicarbonitrile (2.13 g, 76%). yellow oil, R_f = 0.37 (hexane:AcOEt = 5:1), IR (film) 1642, 2251 cm⁻¹. ¹H NMR (500 MHz) δ 0.29 and 0.30 (each 3H, s, SiMe₂), 0.97 (9H, s, *t*-Bu), 1.92 (1H, dd, J = 8.5, 5.3 Hz, H-4), 2.19 (1H, dd, J = 7.8, 5.3 Hz, H-4), 3.37 (1H, dd, J = 8.5, 7.8 Hz, H-2). ¹³C NMR (125 MHz) δ -7.45 and -7.37 (SiMe₂), 7.02 (C-3), 17.0 (CMe₃), 21.3 (C-4), 26.4 (CMe₃), 36.8 (C-2), 111.6 and 114.5 (CN), 234.9 (C-1). HRMS calcd for C₈H₉N₂OSi, 177.0484 (M⁺ - *t*-Bu), found 177.0453.

To a cooled (0 °C) solution of the above compound (80 mg, 0.34 mmol) in MeOH/THF (1:10, 3.4 mL) was added NaBH₄ (3 mg, 0.085 mmol) and the solution was stirred at the same temperature for 15 min. The reaction mixture was diluted with 10% NH₄Cl solution (10 mL), and extracted Et₂O (5 mL x 3). Combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 3 g, elution with hexane:AcOEt = 4:1) to give **26a** (30 mg, 30%). colorless needles (Et₂O-hexane), mp 107-109 °C, R_f = 0.35 (hexane:AcOEt = 5:1), IR (KBr) 2254, 3484 cm⁻¹. ¹H NMR (500 MHz) δ 0.045 and 0.14 (each 3H, s, SiMe₂), 0.98 (9H, s, *t*-Bu), 1.62 (1H, dd, J = 8.5, 6.2 Hz, H-4), 1.85 (1H, d, J = 5.1 Hz, OH), 2.0 (1H, dd, J = 9.2, 6.2 Hz, H-4), 2.32 (1H, ddd, J = 11.0, 9.2, 8.5 Hz, H-2), 3.21 (1H, dd, J = 11.0, 5.1 Hz, H-1). ¹³C NMR (125 MHz) δ -8.37 and -6.96 (SiMe₂), 4.23 (C-3), 16.9 (CMe₃), 23.5 (C-4), 26.9 (CMe₃), 36.9 (C-2), 64.9 (C-1), 114.4 and 115.3 (CN). HRMS calcd for C₈H₁₁N₂OSi, 179.0641 (M⁺ - *t*-Bu), found 179.0634. Anal. Calcd for C₈H₁₁N₂OSi: C 60.97, H 8.53, N 11.85,

found C 60.92, H 8.49, N 11.74. X-ray data: crystal system, monoclinic; space group, P2(1)/c; unit cell dimensions, $a = 18.120(7)$ Å, $\alpha = 90^\circ$, $b = 6.607(2)$ Å, $\beta = 107.072(5)^\circ$, $c = 12.804(5)$ Å; volume, 1465.4(9) Å³; $Z = 4$; $R = 0.061$.

2-(*tert*-Butyldimethylsilanecarbonyl)-1-phenylcyclopropanecarbonitrile (**25**).

To a cooled (-80°C) solution of benzyl cyanide (515 mg, 4.40 mmol) in THF (37 mL) was added dropwise *n*-BuLi (2.25 M in hexane, 1.96 mL, 4.40 mmol) and the solution was stirred at the same temperature for 15 min before addition of a solution of **23** (1.0 g, 4.01 mmol) in THF (3 mL). After warming to -60°C , the mixture was diluted with 10% NH_4Cl solution (30 mL), and extracted Et_2O (20 mL x 3).

Combined organic phases were washed with saturated brine (30 mL), dried, and concentrated to give **24**. This was used in the following step without further purification.

To cooled (-80°C) solution of lithium diisopropylamide (LDA) prepared from diisopropylamine (560 μL , 4.01 mmol) and *n*-BuLi (2.25 M in hexane, 1.78 mL, 4.01 mmol) in THF (25 mL) was added dropwise a solution of above compound in THF (15 mL). After warming to -60°C , the reaction mixture was diluted with 10% NH_4Cl solution (30 mL), and extracted Et_2O (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 = 10:1) and MPLC (elution with hexane:AcOEt = 10:1) to give **25** (36 mg, 3%). Yellow oil, $R_f = 0.52$ (hexane:AcOEt = 3:1), IR (film) 1663, 2239 cm^{-1} . ^1H NMR (500 MHz) δ 0.24 and 0.27 (each 3H, s, SiMe_2), 0.96 (9H, s, *t*-Bu), 1.75 (1H, dd, $J = 7.8, 5.0$ Hz, H-4), 2.36 (1H, dd, $J = 7.1, 5.0$ Hz, H-4), 3.06 (1H, dd, $J = 7.8, 7.1$ Hz, H-2), 7.31-7.42 (5H, m, Ph). ^{13}C NMR (100 MHz) δ -7.38 and -7.28 (SiMe_2), 17.0 (CMe_3), 20.9 (C-4), 24.7 (C-3), 26.4 (CMe_3), 41.5 (C-2), 118.2 (CN), 126.0, 128.3, 129.2 and 135.0 (Ph), 237.9 (C-1). HRMS calcd for $\text{C}_{17}\text{H}_{23}\text{NOSi}$, 285.1554 (M^+), found 285.1552.

(*tert*-Butyldimethylsilyl)-(2-cyano-2-phenylcyclopropyl)methanol (**26b**).

To a cooled (-80°C) solution of **25** (36 mg, 0.126 mmol) in THF was added dropwise DIBAL-H (0.95 M in hexane, 146 μL , 0.139 mmol), and the solution was stirred at the same temperature for 30 min before addition of MeOH (0.3 mL) and water (0.3 mL). The mixture was diluted with 10% NH_4Cl solution (5 mL), and extracted Et_2O (5 mL x 3). Combined organic phases were washed with saturated

brine (5 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 500 mg, elution with hexane:AcOEt = 5:1) to give **26b** (25 mg, 69%). Pale yellow oil, $R_f = 0.21$ (hexane:AcOEt = 5:1), IR (film) 1602, 1635, 1722, 2236, 3483 cm^{-1} . ^1H NMR (500 MHz) δ 0.05 and 0.12 (each 3H, s, SiMe_2), 1.00 (9H, s, *t*-Bu), 1.53 (1H, dd, $J = 7.3, 5.7$ Hz, H-4), 1.71 (1H, dd, $J = 8.7, 5.7$ Hz, H-4), 1.85 (1H, ddd, $J = 11.2, 8.7, 7.3$ Hz, H-2), 1.97 (1H, br, 1-OH), 3.41 (1H, d, $J = 11.2$ Hz, H-1) 7.27-7.40 (5H, m, Ph). ^{13}C NMR (125 MHz) δ -8.3 and -6.9 (SiMe_2), 16.9 (CMe_3), 20.6 (C-3), 22.8 (C-4), 27.0 (CMe_3), 35.9 (C-2), 66.8 (C-1), 121.5 (CN), 126.3, 127.8, 129.0 and 136.0 (Ph). HRMS calcd for $\text{C}_{13}\text{H}_{16}\text{NOSi}$, 230.1001 ($\text{M}^+ - t\text{-Bu}$), found 230.0967.

Reaction of **26a** with NHMDS Followed by Quenching with Acetic Acid.

To a cooled (-80°C) solution of **26a** (10 mg, 0.04 mmol) in THF (0.4 mL) was added NHMDS (0.94 M in THF, 48 μL , 0.044 mmol), and the solution was stirred at the same temperature for 5 min before addition of AcOH (1.0 M in THF, 44 μL , 0.044 mmol). The reaction mixture was diluted with water (2 mL),

and extracted with Et_2O (2 mL x 3). Combined organic phases were washed with saturated brine (2 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 1 g, elution with hexane:AcOEt = 5:1) to give (*E*)-**27** (7.6 mg, 76%). Colorless oil, $R_f = 0.36$ (hexane:AcOEt = 5:1), IR (film) 1664, 2254 cm^{-1} . ^1H NMR (500 MHz) δ 0.17 (6H, s, SiMe_2), 0.92 (9H, s, *t*-Bu), 2.62 (2H, ddd, $J = 8.0, 6.4, 1.2$ Hz, H-3), 3.65 (1H, t, $J = 6.4$ Hz, H-2), 5.00 (1H, dt, $J = 11.9, 8.0$ Hz, H-4), 6.52 (1H, dt, $J = 11.9, 1.2$ Hz, H-5). ^{13}C NMR (100 MHz) δ -5.34 (SiMe_2), 24.6 (C-2), 25.5 (CMe_3), 26.7 (CMe_3), 30.1 (C-3), 101.8 (C-4), 112.9 (CN), 146.6 (C-5). HRMS calcd for $\text{C}_8\text{H}_{11}\text{N}_2\text{OSi}$, 179.0639 ($\text{M}^+ - t\text{-Bu}$), found 179.0641.

Reaction of **26a** with NHMDS and MeI.

To a cooled (-80 °C) solution of **26a** (50 mg, 0.21 mmol) and CH₃I (14 μL, 0.23 mmol) in THF (1.9 mL) was added NHMDS (0.94 M in THF, 0.24 mL, 0.23 mmol). After warming to -20 °C, the reaction mixture was diluted with 10% NH₄Cl solution (5 mL), and extracted Et₂O (5 mL x 3). Combined organic phases were washed with saturated brine (5 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 2 g, elution with hexane:AcOEt = 5:1) to give (E)-**28** (40 mg, 76%). Colorless oil, *R_f* = 0.46 (hexane:AcOEt = 5:1), IR (film) 1663, 2251 cm⁻¹. ¹H NMR (500 MHz) δ 0.16 (6H, s, SiMe₂), 0.92 (9H, s, *t*-Bu), 1.73 (3H, s, 2-Me), 2.53 (2H, dd, *J* = 8.0, 0.9 Hz, H-3), 5.00 (1H, dt, *J* = 11.9, 8.0 Hz, H-4), 6.49 (1H, dt, *J* = 11.9, 0.9 Hz, H-5). ¹³C NMR (125 MHz) δ -5.23 (SiMe₂), 18.4 (CMe₃), 23.7 (2-Me), 25.6 (CMe₃), 33.0 (C-2), 38.0 (C-3), 101.1 (C-4), 116.2 (CN), 147.1 (C-5). HRMS calcd for C₉H₁₃N₂OSi, 193.0797 (M⁺ - *t*-Bu), found 179.0818.

Reaction of **26b** with NHMDS and MeI.

To a cooled (-80 °C) solution of **26b** (35 mg, 0.12 mmol) and CH₃I (15 μL, 0.24 mmol) in THF (1.1 mL) was added dropwise NHMDS (0.94 M in THF, 143 μL, 0.134 mmol). After warming to -70 °C, the reaction mixture was diluted with 10% NH₄Cl solution (5 mL), and extracted Et₂O (5 mL x 3). Combined organic phases were washed with saturated brine (5 mL), dried, and concentrated. The residual oil was subjected to column chromatography (silica gel, 2 g, elution with hexane:AcOEt = 10:1) to give (E)-**16a** (25 mg, 69%). pale yellow oil, *R_f* = 0.44 (hexane:AcOEt = 8:1), IR (film) 1660, 1730, 2243 cm⁻¹. ¹H NMR (500 MHz) δ 0.08 (6H, s, SiMe₂), 0.87 (9H, s, *t*-Bu), 1.69 (3H, s, 2-Me), 2.44 (1H, ddd, *J* = 14.2, 8.2, 0.9 Hz, H-3), 2.49 (1H, ddd, *J* = 14.2, 7.6, 1.1 Hz, H-3), 4.86 (1H, ddd, *J* = 11.9, 8.2, 7.6 Hz, H-4), 6.25 (1H, dt, *J* = 11.9, 1.1, 0.9 Hz, H-5). ¹³C NMR (125 MHz) δ -5.32 (SiMe₂), 18.2 (CMe₃), 25.6 (CMe₃), 26.2 (2-Me), 40.8 (C-3), 43.1 (C-2), 104.3 (C-4), 123.3 (CN), 125.7, 127.7, 128.8 and 140.0 (Ph), 144.4 (C-5). HRMS calcd for C₁₄H₁₈NOSi, 244.1158 (M⁺ - *t*-Bu), found 244.1133.

(*tert*-Butyldimethylsilyl)-(2-trimethylsilanylcyclopropyl)methanol (**30**).

To a cooled (-15 °C) solution of 1-(*tert*-butyldimethylsilyl)-3-trimethylsilylpropenone (2.00 g, 8.2 mmol) in MeOH/THF (1:10, 82 mL) was added NaBH₄ (310 mg, 8.2 mmol) and the solution was stirred at the same temperature for 10 min. The reaction mixture was diluted with 10% NH₄Cl solution (50 mL), and extracted with Et₂O (30 mL x 3). Combined organic phases were washed with saturated brine (50 mL), dried, and concentrated to give crude 1-(*tert*-butyldimethylsilyl)-3-trimethylsilylprop-2-en-1-ol. This was used in the following step without further purification.

To a cooled (-10 °C) solution of the above compound and CH₂I₂ (3.9 mL, 48.4 mmol) in CH₂Cl₂ (65 mL) was added dropwise ZnEt₂ (1.0 M in hexane, 48.4 mL, 48.4 mmol) and the solution was stirred at the same temperature for 2 hour. The reaction mixture was diluted with 10% NH₄Cl solution (50 mL), and extracted with Et₂O (30 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, 60 g, elution with hexane:Et₂O = 3:1) to give **30** (1.17 g, 55%). Pale yellow oil, *R_f* = 0.27 (hexane:Et₂O = 3:1), IR (film) 3462 cm⁻¹. ¹H NMR (500 MHz) δ -0.43--0.02 (1H, m, H-3), -0.05 (9H, s, SiMe₃), -0.02 and 0.05 (each 3H, s, SiMe₂), 0.39-0.42 (2H, m, H-4), 0.95 (9H, s, *t*-Bu), 0.97-1.03 (1H, m, H-2), 2.60 (1H, d, *J* = 10.1 Hz, H-1). ¹³C NMR (100 MHz) δ -8.56 and -6.53 (SiMe₂), -2.11 (SiMe₃), 3.55 (C-3), 7.78 (C-4), 16.8 (CMe₃), 20.9 (C-2), 27.0 (CMe₃), 71.6 (C-1). HRMS calcd for C₉H₂₁OSi₂, 201.1131 (M⁺ - C₄H₉), found 201.1128.

(*tert*-Butyldimethylsilyl)-(2-trimethylsilanylcyclopropyl)methyl methyl ether (**31**).

To a cooled (-80 °C) solution of **30** (100 mg, 0.41 mmol) and CH₃I (28 μL, 0.43 mmol) in THF (4.1 mL) was added NHMDS (1.0 M in THF, 0.43 mL, 0.43 mmol). After warming to room temperature, the solution was diluted with 10% NH₄Cl solution (10 mL), and extracted with Et₂O (5 mL x 3). Combined organic phases were washed with saturated brine (10 mL), dried, and concentrated. The

residual oil was subjected to column chromatography (silica gel, 6 g, elution with hexane:Et₂O = 10:1) to give **30** (20 mg, 20%) and **31** (54 mg, 48%). colorless oil, R_f = 0.74 (hexane:AcOEt = 5:1), IR (film) 2951 cm⁻¹. ¹H NMR (500 MHz) δ -0.67--0.62 (1H, m, H-3), -0.05 and 0.03 (each 3H, s, SiMe₂), -0.04 (9H, s, SiMe₃), 0.54-0.57 (2H, m, H-4), 0.76-0.81 (1H, m, H-2), 0.92 (9H, s, *t*-Bu), 2.25 (1H, d, J = 9.9 Hz, H-1), 3.42 (3H, s, Me). ¹³C NMR (125 MHz) δ -8.05 and -5.58 (SiMe₂), -1.95 (SiMe₃), -0.47 (C-3), 10.8 (C-4), 16.7 (C-2), 17.1 (CMe₃), 27.1 (CMe₃), 59.4 (C-1), 81.2 (OMe). HRMS calcd for C₁₀H₂₃OSi₂, 215.1287 (M⁺ - *t*-Bu), found 215.1291.

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JEOL

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JEOL

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Mod_return = 1
X_points = 32768
X_prescans = 0
X_domain = 1H
X_offset = 5[ppm]
X_freq = 500.15991521[MHz]
X_resolution = 7.50750751[kHz]
X_acq_duration = 0.22911095[Hz]
Digital_filter = 4.3646976[s]
Filter_factor = FALSE
Delay_of_start = 1[s]
Actual_start_time = 4-JUN-2004 19:56
Acq_delay = 0.1295[ms]
X90 = 14.8[us]
Irr90 = 10[us]
Tri90 = 10[us]
Qua90 = 10[us]
X90_hi = 12[us]
Irr90_hi = 10[us]
Tri90_hi = 10[us]
Qua90_hi = 10[us]
X90_lo = 45[us]
Irr90_lo = 50[us]
Tri90_lo = 10[us]
Qua90_lo = 10[us]
Spin_lock_90 = 1[us]
Spin_lock_attn = 29[us]
Deut_grad_shim_90 = 63.875[us]
Deut_grad_shim_attn = 16/1MHz/20
Acq_card = BUTTERWORTH
Field_strength = 11.7473579[T]
Filter_mode = BUTTERWORTH
Filter_width = 3.75375375[kHz]
Recvr_gain = 17
Irr_code = 146
Obs_noise = 1[us]
Wdth = 57[us]
Irr_noise = 57[us]
Tri_noise = 1[us]
Qua_noise = 1[us]
Solvent = CHLOROFORM-D
Lock_strength = 844
Lock_level = 180
Lock_gain = 22
Lock_osc_offset = 70.3331[kHz]
Lock_phase = 218.21deg
Lock_osc_state = 2H OSC ON

X : parts per Million : 1H

JEOL

```

---- ACQUISITION PARAMETERS ----
File Name      = SO_II_C_1
Author         =
Sample ID      = 1
Content        = SO-II-C
Creation Date   = 10-JUN-2

Revision Date   = 10-JUN-2
Spec Site      = ECP500

Spec Type      = DELTA NMU
Data Format     = 1D COMPL
Dimensions     = X
Dim Title      = 13C
Dim Size       = 32768
Dim Units      = [ppm]
Scans          = 260
Mod_return     = 1
X_points       = 32768
X_prescans     = 4
X_domain       = 13C
X_offset       = 100 [ppm]
X_freq         = 125.7652
X_sweep        = 31.44654
X_resolution   = 0.959672
Irr_domain     = 1H
Irr_offset     = 4.3 [ppm]
Irr_freq       = 500.1599
X_acq_duration = 1.042022
Digital_filter = FALSE
Filter_factor   = 1
Delay_of_start = 1 [s]
Actual_start_time = 10-JUN-2
Acq_delay      = 33.2 [us]
X90            = 12.8 [us]
Irr90          = 14.8 [us]
Tri90          = 10 [us]
Qua90          = 10 [us]
X90_hi         = 13.4 [us]
Irr90_hi       = 12 [us]
Tri90_hi       = 10 [us]
Qua90_hi       = 10 [us]
X90_lo         = 57 [us]
Irr90_lo       = 45 [us]
Tri90_lo       = 10 [us]
Qua90_lo       = 10 [us]
Spin_lock_90   = 1 [us]
Spin_lock_attn = 29 [dB]
Deut_grad_shim_90 = 63.875 [d]
Deut_grad_shim_attn = 16 / 1MHz /
Field_strength = 11.74735
Filter_mode     = BUTTERWO
Filter_width    = 15.72327
Recvr_gain      = 30
Irr_code        = 146
Obs_width       = 1 [us]
Obs_noise       = WAUGH
Irr_width       = 45 [us]
Irr_noise       = 45 [us]
Tri_width       = WALTZ
Tri_noise       = WALTZ
Qua_width       = WALTZ
Qua_noise       = 1 [us]
Solvent         = CHLOROFO
Lock_strength    = 1163
  
```

30.0

20.0

10.0

(Millions)

X : parts per Million : 1H

S63

DFILE C:\WINALPHA\COMMON_DEFAULT
COMNT SO-II-345C-C
DATIM Tue Jan 04 16:06:36 2005
OBNUC 13C
EXMOD SINGL
OBFRQ 100.40 MHz
OBFIN 135500.00 Hz
POINT 32768
FREQU 28169.01 Hz
SCANS 200
ACQTM 1.1633 sec
PD 0.7941 sec
PWL 5.60 usec
IRNUC 1H
CTEMP 22.1 C
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.73 Hz
RGAIN 29

```
File Name      = SO-II-337B.3
Author        =
Sample ID     = 1
Content       = SO-II-337B
Creation Date  = 8-JUN-2004 15:21
Revision Date = 8-JUN-2004 15:21
Spec Site     = MCP500
```

```

- DELTA_NMR
- ID_COMPLEX
- X
- 1H
- 32768
- [ppm]
- 4
- 1
- 32768
- 0
- 1H
- 5[ppm]
- 500.15991521[MHz]
- 7.50750751[kHz]
- 0.229110951[Hz]
- 4.3646976[s]
- FALSE
- Digital
- Digital

```

```

Delay of start
Actual_start_time
Acq_delay
X90
X90
Irr90
= 1[s]
= 8-JUN-2004 15:20
= 0.1295[ms]
= 14.8[us]
= 14.8[us]

```

-	10[us]	
-	10[us]	
-	10[us]	
-	12[us]	
-	12[us]	
-	10[us]	
-	10[us]	
-	45[us]	
-	45[us]	
-	10[us]	
-	10[us]	
-	10[us]	
-	1[us]	
-	29[db]	
-	10[us]	
-	63.875[db]	

```

Adc_card      = 16/1MHz/20
Field_strength = 11.7473579[T]
Filter_mode    = BUTTERWORTH
Filter_width   = 3.75375375[kHz]

```

```
Recvr_gain = 19
Irr_code = 146
Obs_pwidth = 1[us]
Obs_noise = WAUGH
Irr_pwidth = 45[us]
```

```

- Irr_noise
- Tri_width
- Tri_noise
- Qua_width
- Qua_noise
- WALTZ
- 1[us]
- WALTZ
- 1[us]
- WAUGH
- WAUGH

```

Solvent	= CHLOROFORM-D
Lock_strength	= 2082
Lock_level	= 180
Lock_gain	= 25
Lock on offset	= 70 3231 (150-1)

```
Lock_osc_offset = 70.3331[kHz]
Lock_phase      = 218.2[deg]
Lock_osc_state  = 2H OSC ON
```

C:\WINALPHA\COMMON\DEFAULT.ALS
SO-II-337B.C

DFILE
OBNUC
EXMOD
OBFRQ
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRATN
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\WINALPHA\COMMON\DEFAULT
13C
SINGL
100.40 MHz
135500.00 Hz
32768
27173.91 Hz
300
1.2059 sec
0.7941 sec
5.60 usec
511
26.2 c
CDCL3
77.00 ppm
0.12 Hz
28

JEOL

----- ACQUISITION PARAMETERS -----
 File Name = SO_II_336B.3
 Author =
 Sample ID = 1
 Content = SO-II-336B
 Creation Date = 7-JUN-2004 17:11
 Revision Date = 7-JUN-2004 17:10
 Spec Site = ECP500
 Spec Type = DELTA_NMR
 Data Format = 1D COMPLEX
 Dimensions = X
 Dim Title = 1H
 Dim Size = 32768
 Dim Units = [ppm]
 Scans = 4
 Mod_return = 1
 X_points = 32768
 X_prescans = 0
 X_domain = 1H
 X_offset = 5[ppm]
 X_freq = 500.15991521[MHz]
 X_sweep = 7.50750751[KHz]
 X_resolution = 0.22911095[Hz]
 X_acq_duration = 4.3646976[s]
 Digital_filter = FALSE
 Filter_factor = 1
 Delay_of_start = 1[s]
 Actual_start_time = 7-JUN-2004 17:10
 Acq_delay = 0.1295[ms]
 X90 = 14.8[us]
 Irr90 = 10[us]
 Tri90 = 10[us]
 Qua90 = 10[us]
 X90_hi = 12[us]
 Irr90_hi = 10[us]
 Tri90_hi = 10[us]
 Qua90_hi = 10[us]
 X90_lo = 45[us]
 Irr90_lo = 45[us]
 Tri90_lo = 10[us]
 Qua90_lo = 10[us]
 Spin_lock_90 = 1[us]
 Spin_lock_attn = 29[db]
 Deut_grad_shim_90 = 10[us]
 Deut_grad_shim_attn = 63.875[db]
 Adc_card = 16/1MHz/20
 Field_strength = 11.7473579[T]
 Filter_mode = BUTTERWORTH
 Filter_width = 3.75375375[KHz]
 Recvr_gain = 11
 Irr_code = 146
 Obs_width = 1[us]
 Obs_noise = WAUGH
 Irr_width = 45[us]
 Irr_noise = WALTZ
 Tri_width = 1[us]
 Tri_noise = WALTZ
 Qua_width = 1[us]
 Qua_noise = WAUGH
 Solvent = CHLOROFORM-D
 Lock_strength = 823
 Lock_level = 180
 Lock_gain = 22
 Lock_osc_offset = 70.3331[KHz]
 Lock_phase = 218.2[deg]
 Lock_osc_state = 2H OSC ON

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRQ
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\WINALPHA\COMMON_DEFAULT
SO-II-436B
Wed Jan 05 18:43:22 2005
13C
SINGL
100.40 MHz
135500.00 Hz
32768
27173.91 Hz
200
1.2059 sec
0.7941 sec
5.60 usec
1H
23.9 C
CDCL3
77.00 ppm
0.73 Hz
29

77.3217
77.0000
76.6865
71.5636
26.9834
20.8705
16.8283
7.7704
3.5466
2.1125
6.5342
8.5553