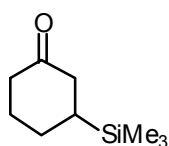


Supplementary data

Experimental:

General Procedure for the Preparation of β -Trimethylsilyl Cyclic Ketones **7,9, and 11**

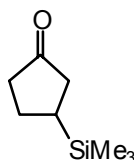
3-Trimethylsilylcyclohexan-1-one (**7**)



A solution of HMPA (20 mL) and hexamethyldisilane (5 mL, 25 mmol) under nitrogen was cooled in a dry-ice/acetone bath (the mixture became frozen). Methyl lithium (14.3 mL, 20 mmol, 1.4 M in ether) was added onto the frozen mixture followed by THF (50 mL). The dry-ice/acetone bath was replaced with an ice bath. Within a minute or two, the solid melted sufficiently and stirring was possible. The resulting red solution was then cooled to $-78\text{ }^{\circ}\text{C}$ and a solution of 2-cyclohexene-1-one (1.6 mL, 1.6 g, 17 mmol) in THF (5 mL) was added dropwise. The mixture was stirred for 10 min, quenched with water (15 mL) and stirring was continued for 5 min. The dry-ice/acetone bath was replaced with an ice/water bath and stirred for an additional 35 min. The mixture was poured onto pentane (80 mL), washed with water (5 x 80 mL), dried (MgSO_4) and concentrated under reduced pressure to obtain 3-trimethylsilylcyclohexanone (**72**) (2.465 g, 14.5 mmol, 87 %). ^1H nmr (300 MHz, CDCl_3) δ -0.06 (s, 9H, SiMe_3), 1.02 (dddd, 1H, $J = 3.2, 3.2, 13.3, 13.3$ Hz), 1.38 (dddd, 1H, $J = 3.4, 12.6, 12.6, 12.6$ Hz), 1.58-1.80 (m,

2H), 2.00-2.40 (m, 5H); ^{13}C nmr (75 MHz, CDCl_3) δ -3.85 (SiMe_3), 25.86, 27.89, 29.87, 41.86, 42.28, 212.90 ($\text{C}=\text{O}$); ν_{max} : 837-854, 1712 cm^{-1} .

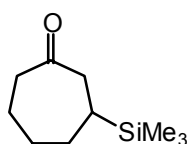
3-Trimethylsilylcyclopentan-1-one (7)



The crude product was kügelrohr distilled (80-85 °C/6 mmHg) to obtain 3-trimethylsilylcyclohexanone as a clear oil (2.981 g, 19.1 mmol, 59 %).

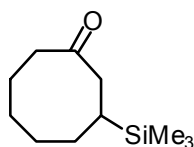
^1H nmr (300 MHz, CDCl_3) δ -0.02 (s, 9H, SiMe_3), 1.20-1.35 (m, 1H), 1.52-1.70 (m, 1H), 1.74-1.89 (m, 1H), 1.95-2.30 (m, 4H); ^{13}C nmr (75 MHz, CDCl_3) δ -3.51 (SiMe_3), 24.13, 24.74, 39.39, 39.88, 221.30 ($\text{C}=\text{O}$); ν_{max} : 836-858, 1743 cm^{-1} .

3-Trimethylsilylheptan-1-one (11)



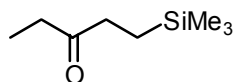
(2.990 g, 16.2 mmol, 89 %). ^1H nmr (300 MHz, CDCl_3) δ -0.02 (s, 9H, SiMe_3), 0.75-0.84 (m, 1H), 1.07-1.36 (m, 2H), 1.45-1.59 (m, 1H), 1.84-2.08 (m, 3H), 2.28-2.60 (m, 4H); ^{13}C nmr (75 MHz, CDCl_3) δ -3.59 (SiMe_3), 23.64, 24.37, 31.06, 31.86, 43.40, 44.50, 215.63 ($\text{C}=\text{O}$); ν_{max} : 837, 867, 892, 1699 cm^{-1} .

3-Trimethylsilylcyclooctan-1-one



(0.117 g, 58.9 mmol, 73 %). ^1H nmr (300 MHz, CDCl_3) δ -0.04 (s, 9H, SiMe_3), 1.16-1.49 (m, 5H), 1.55-1.73 (m, 2H), 1.75-1.89 (m, 2H), 2.12-2.40 (m, 3H), 2.46-2.58 (m, 1H); ^{13}C nmr (75 MHz, CDCl_3) δ -3.38 (SiMe_3), 24.21, 25.89, 26.07, 26.88, 27.89, 41.44, 42.83, 219.92 (C=O).

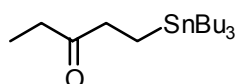
3-Trimethylsilylpentan-3-one (21)



Lithium slivers (0.4077 g, 58.74 mmol) and chlorotrimethylsilane (0.56 mL, 4.835 g, 44.5 mmol) were added to THF (45 mL) maintained at 0 °C under a nitrogen atmosphere. Ethyl vinyl ketone (1.5 g, 1.78 mL, 17.8 mmol) was added dropwise whilst maintaining the temperature below 10 °C. The mixture was warmed to room temperature and stirred overnight. The liquid was decanted from the solid lithium and solvent was removed under reduced pressure to obtain a milky/white suspension. The suspension was dissolved in a 1:1 mixture of ether/methanol (20 mL), followed by dropwise addition of concentrated HCl (3 mL). The mixture was stirred for 1 h. The solution was poured onto water (40 mL) and extracted with ether (3 x 20 mL), dried (MgSO_4) and concentrated under reduced pressure. The crude product was kügelrohr distilled (60 °C/ H_2O pressure) to give 3-trimethylsilylpentan-1-one (**103a**) (1.075 g, 6.79 mmol, 38 %). ^1H nmr (300

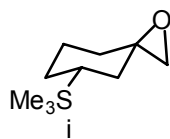
MHz, CDCl₃) δ -0.03 (s, 9H, SiMe₃), 0.69-0.76 (m, 2H, CH₂-SiMe₃), 1.04 (t, 3H, CH₃, *J* = 7.3 Hz), 2.30-2.36 (m, 2H, -CH₂CH₂C=O), 2.43 (q, 2H, *J* = 7.3 Hz); ¹³C nmr (75 MHz, CDCl₃) δ -1.92 (SiMe₃), 7.98, 10.28, 35.06, 36.80, 212.63 (C=O); ν_{max}: 836-862, 1716 cm⁻¹.

1-Tributylstannylpentan-3-one (22)



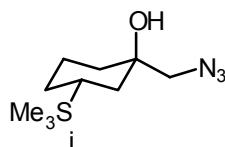
To 1-trichlorostannylpentan-3-one (2.013 g, 0.60 mmol) in THF (60 mL) at -78 °C was added *n*-butylmagnesium chloride (9.73 mL, 19.5 mmol, 2.0 M solution in ether) dropwise (changed from orange/red to cloudy white) and stirred at -78 °C for 1 h. The solution was diluted with ether (50 mL) was washed successively with 1 M HCl (2 x 30 mL), NaHCO₃ (2 x 30 mL), water (3 x 30 mL). The organic layer was dried (MgSO₄) and concentrated under reduced pressure to yield 1-tributylstannylpentan-3-one (**103c**) (2.148 g, 5.72 mmol, 88 %). ¹H nmr (400 MHz, CDCl₃) δ 0.78-0.84 (m, 6H, SnCH₂CH₂CH₂CH₃), 0.85-0.93 (m, 11H), 1.05 (t, 3H, *J* = 7.4 Hz, CH₃CH₂), 1.22-1.34 (m, 6H), 1.40-1.52 (m, 6H), 2.42 (q, 2H, CH₂CH₃, *J* = 7.4 Hz), 2.57 (t, 2H, COCH₂CH₂, *J* = 8.0 Hz); ¹³C nmr (75 MHz, CDCl₃) δ 2.06, 8.07, 8.97, 13.70, 27.38, 29.15, 35.00, 39.50, 213.22 (C=O).

cis-3-Trimethylsilyl-7-oxaspiro [6.3] Octane



A suspension of 95 % sodium hydride (1.01 g, 42.1 mmol) in DMSO (25 mL) was stirred until evolution of H₂ gas ceased (*ca.* 45 min). The solution was diluted with THF (25 mL), followed by dropwise addition of a solution of trimethylsulfoxonium iodide (4.03 g, 18.3 mmol) in DMSO (15 mL). Stirring was continued for an additional 5 min, followed by dropwise addition of 3-trimethylsilylcyclohexan-1-one (2.83 g, 16.6 mmol) in DMSO (5 mL). The cloudy-grey mixture was left to stir overnight during which time a yellow colour had formed. The reaction was quenched with water (50 mL) and the product was extracted into ether (3 x 30 mL). The combined ether extracts were washed with water (3 x 30 mL), dried (MgSO₄) and concentrated to afford 3-trimethylsilyl-7-oxaspiro-[6.3]-octane (**92**) as a yellow oil (2.53 g, 13.7 mmol, 83 %). ¹H nmr (400 MHz, CDCl₃) δ - 0.08 (s, 9H, SiMe₃), 0.92- 1.27 (m, 4H), 1.52-1.87 (m, 5H), 2.60 (bs, 2H, CH₂O); ¹³C nmr (100 MHz, CDCl₃) δ -3.73 (SiMe₃), 22.95, 25.33, 25.84, 33.10, 33.79, 54.63 (CH₂O), 58.60 (quat. C-O); ν_{max}: 832-880, 1077, 1248, 3032 cm⁻¹.

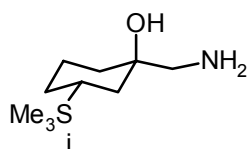
1-Azidomethyl-3-trimethylsilylcyclohexanol (**19**)



A mixture of ammonium chloride (1.802 g, 33.7 mmol), sodium azide (2.15 g, 33.1 mmol), 3-trimethylsilyl-7-oxaspiro-[6.3]-octane (1.204 g, 6.53 mmol), methanol (20 mL)

and water (8 mL) were heated at reflux for 2.5 h. Water was added to the mixture and extracted with ether (3 x 20 mL), dried (MgSO₄), filtered and concentrated under reduced pressure (no heating) to yield 1-azidomethyl-3-trimethylsilylcyclohexanol (**78a**) (1.062 g, 4.67 mmol, 72 %). ¹H nmr (300 MHz, CDCl₃) δ -0.05 (s, 9H, SiMe₃), 0.80-1.04 (m, 2H), 1.05-1.15 (t, 1H, *J* = 13.5 Hz), 1.18-1.30 (m, 1H), 1.50-1.80 (m, 6H), 3.20 (s, 2H); ¹³C nmr (75 MHz, CDCl₃) δ -3.66 (SiMe₃), 19.49, 22.22, 26.29, 34.57, 35.34, 62.89 (CH₂N₃), 70.96 (C-OH); ν_{max}: 836-869, 2102, 3429 cm⁻¹.

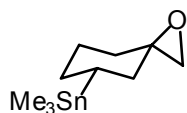
Method B: *cis*-1-Aminomethyl-3-trimethylsilylcyclohexanol (14)



To a mixture of 1-azidomethyl-3-trimethylsilylcyclohexanol (2.1638 g, 9.516 mmol) and sodium borohydride (1.156 g, 30.6 mmol) in boiling THF (35 mL) was added methanol (5.1 mL) dropwise over a 40 min period (H₂ gas is given off). Heating at reflux was continued for a further 2.5 h, followed by cooling to RT. Hydrochloric acid (1.0 M, 20 mL) was added (vigorous bubbling) and the mixture was extracted with hexane (2 x 20 mL). The combined organic extracts were washed with hydrochloric acid (1 M, 2 x 20 mL). The aqueous layers were combined and made alkaline (pH 11) with conc. aqueous sodium hydroxide. The mixture was extracted with dichloromethane (3 x 50 mL) and the organic phase dried (MgSO₄) and concentrated under reduced pressure to give 1-aminomethyl-3-trimethylsilyl-cyclohexanol (**16**) (1.037 g, 5.12 mmol, 54 %). ¹H nmr (300 MHz, CDCl₃) δ -0.09 (s, 9H, SiMe₃), 0.86-1.24 (m, 4H), 1.44-1.72 (m, 5H), 2.02 (bs, 3H), 2.51 (bs, 2H, CH₂NH₂); ¹³C nmr (75 MHz, CDCl₃) δ -3.67 (SiMe₃), 19.67,

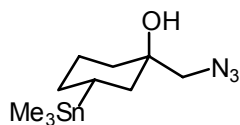
22.59, 26.63, 34.83, 35.56, 53.14 (CH₂NH₂), 69.52 (COH); ν_{\max} : 833-869, 1247, 1645, 2856, 2928, 2953, 3398 cm⁻¹; MS (ESI) m/z : 202.16 (M⁺).

3-Trimethylstannyl-7-oxaspiro [6.3] octane



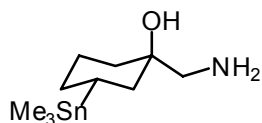
A suspension of 95% sodium hydride (1.05g, 41.6 mmol) and DMSO (40 ml) was stirred until evolution of H₂ gas ceased. THF (40 ml) was added, followed by a dropwise mixture of trimethylsulfoxonium iodide (9.11g, 41.4 mmol) dissolved in DMSO (20 ml). Again, stirring continued until the evolution of H₂ gas ceased, after which **3-trimethylstannylcyclohexanone** (10.8g, 41.4 mmol) was added in a dropwise manner. The cloudy-grey mixture gradually became yellow, then left to stir for 12 hrs. The reaction mixture was quenched with water (100 ml) and the product was extracted with ether (3x40 ml), washed with water (3x50 ml), dried (MgSO₄) and evaporated to afford a yellow oil of **3-trimethylstannyl-7-oxaspiro [6.3] octane** (10.3g, 37.4 mmol, 90%) as a mixture of diastereoisomers with a ratio of ca 3:2. ¹H NMR δ : 2.54 (major), 2.52 (minor) (s, 2H, CH₂-O), 1.9-1.2 (m, 9H, both isomers), -0.023 (s, SnMe₃, minor), -0.042 (s, SnMe₃, major); ¹³C NMR δ : (major) 58.81 (quat. C-O), 54.35 (CH₂-O), 37.15, 33.08, 29.30, 26.09, 21.54, -11.94 (SnMe₃); (minor) 59.93 (quat. C-O), 54.57 (CH₂-O), 37.89, 33.94, 29.35, 27.89, 23.03, -11.80 (SnMe₃); ν_{\max} : 3032(CH-O), 2932 (C-H) cm⁻¹.

1-Azidomethyl-3-trimethylstannylcyclohexanol (18)



Ammonium chloride (3.06g, 57.2 mmol), sodium azide (3.72g, 57.2 mmol), **3-trimethylstannyl-7-oxaspiro [6.3] octane** (3.15g, 11.5 mmol), ethanol (30 ml) and water (10 ml) was allowed to reflux for 15 hrs, then cooled to RT. Water (100 ml) was added, after which the product was extracted with ether (3x50 ml), dried (MgSO₄) and evaporated to yield a viscous, yellow-brown oil of crude 1-azidomethyl-3-trimethylstannylcyclohexanol (3.19g, 10.0 mmol, 88%) as a mixture of diastereoisomers in a ratio of ca 3:1. The azide was purified through a dry flash column with petroleum spirits/ether. ¹H NMR δ: 3.65-3.20 (m, 2H, CH₂-N₃, both isomers), 1.75-1.05 (m, 9H, both isomers), -0.033 (s, SnMe₃, minor), -0.050 (s, SnMe₃, major); ¹³C NMR δ: (major) 71.32 (C-OH), 58.00, 38.58, 34.50, 29.86, 22.97, 17.92, -12.08 (SnMe₃); (minor) 72.49 (C-OH), 62.61, 39.76, 35.94, 29.43, 24.92, 20.67, -11.70 (SnMe₃); ν_{max} (mixture): 3392 (O-H), 2924 (C-H), 2103 and 2068 (N₃) cm⁻¹.

1-Aminomethyl-3-trimethylstannylcyclohexanol 15

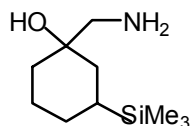


A mixture of **1-azidomethyl-3-trimethylstannylcyclohexanol** (1.00g, 3.15 mmol), sodium borohydride (0.357g, 9.44 mmol) in boiling THF (20 ml) was allowed to reflux followed by dropwise addition of methanol (1.6 ml, 39.4 mmol). After 3 hrs, the reaction mixture was cooled to RT. After the addition of HCl (10 ml, 1.0M), the organic layer was separated and the aqueous layer was washed with hexane (2x10 ml). The combined organic layers were extracted with HCl (2x10 ml, 1.0M). The aqueous layers were combined and made alkaline (pH = 13) with NaOH (10%). This mixture was extracted

with CH₂Cl₂ (3x20 ml), dried (MgSO₄) and evaporated under reduced pressure to yield yellow crystals of **1-aminomethyl-3-trimethylstannylcyclohexanol (12a)** (0.81g, 2.77 mmol, 88%) as a mixture of diastereoisomers in a ratio of ca 5:1. ¹H NMR δ: 2.74 (minor), 2.51 (major) (s, 2H, CH₂-NH₂), 1.72-1.1 (m, 9H, both isomers), -0.01 (s, Sn-Me₃, minor), -0.03 (s, Sn-Me₃, major); ¹³C NMR δ: (major) 67.88 (C-OH), 52.99 (CH₂-NH₂), 39.12, 34.92, 30.37, 23.48, 18.65, -12.00 (Sn-Me₃); (minor) 70.05 (C-OH), 53.50 (CH₂-NH₂), 40.11, 36.15, 29.89, 24.89, 21.01, -11.33 (Sn-Me₃)..

Method A: General Procedure for the Preparation of the β-Substituted Methylene Amino Alcohols 12, 14, 16;

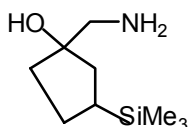
***cis and trans*-1-Aminomethyl-3-trimethylsilylcyclohexanol 14 (mixture of isomers ca 1:1)**



A mixture of 3-trimethylsilylcyclohexan-1-one (2.5508 g, 15.0 mmol), 18-crown-6 (0.128 g, 0.482 mmol) and potassium cyanide (0.034 g, 0.519 mmol) was stirred for 35 min at ambient temperature. The mixture was cooled in an ice-water bath and trimethylsilylcyanide (3.4 mL, 2.698 g, 27.2 mmol) was added and the mixture allowed to stir overnight (turned a deep brown/red colour). A suspension of LiAlH₄ (1.329 g, 35 mmol) in ether (55 mL) was stirred under N₂ for 30 min and allowed to settle. The clearer part of the LiAlH₄/ether mixture was added slowly to the ice-cold 3-trimethylsilyl-cyclohexanone cyanohydrin ether and the remainder added by bore pipette. The mixture was allowed to stir for 2 h, after which the excess LiAlH₄ was quenched

cautiously with water (1.3 mL), 15 % NaOH (1.3 mL) and finally water (4.0 mL). The mixture was stirred for 1 h (formed a white granular solid). The solid was filtered through a plug of celite and extracted thoroughly with ether (5 x 50 mL) and the combined ether extracts were washed with 8.6 % sulphuric acid (5 x 50 mL). The acidic extract was made basic with 15 % NaOH whilst cooling in an ice bath. The basic layer was then extracted with chloroform (3 x 50 mL), dried (MgSO₄) and evaporated under reduced pressure to give 1-aminomethyl-3-trimethylsilylcyclohexanol (**16**) as a ca 1:1 mixture of diastereoisomers (2.648 g, 13.2 mmol, 88 %) as a viscous oil in a 1.0:1.0 ratio of isomers. ¹H nmr (400 MHz, CDCl₃) δ -0.09 (s, 9H, SiMe₃, eq. isomer), -0.08 (s, 9H, SiMe₃, ax. isomer), 0.55 (dddd, 1H, *J* = 3.1, 3.1, 13.6, 13.6 Hz, ax. isomer), 0.88-1.80 (m, 23H), 2.51 (bs, 2H, CH₂NH₂, eq. isomer), 2.72 (d, 1H, CH₂NH₂, ax. isomer, *J* = 13.6 Hz), 2.74 (d, 1H, CH₂NH₂, ax. isomer, *J* = 13.6 Hz); ¹³C nmr (75 MHz, CDCl₃) δ (ax. isomer) -3.87 (SiMe₃), 22.39, 24.70, 26.06, 35.96, 36.73, 46.14 (CH₂NH₂), 70.90 (COH); δ (eq. isomer) -3.82 (SiMe₃), 19.41, 22.39, 26.48, 34.61, 35.33, 53.22 (CH₂NH₂), 69.39 (COH); ν_{max}: 797-866, 1195-1247, 1596, 3368 cm⁻¹.

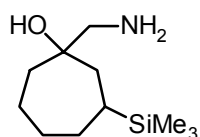
1-Aminomethyl-3-trimethylsilylcyclopentan-1-ol (**12**)



(1.746 g, 9.32 mmol, 77 %) as a mixture of isomers in a ratio of *ca.* 2:1. ¹H nmr (300 MHz, CDCl₃) δ -0.11 (s, 9H, SiMe₃, minor), -0.09 (s, 9H, SiMe₃, major), 0.83-0.92 (m, 1H), 1.10-1.17 (m, 1H), 1.26-2.07 (m, 18H), 2.60-2.68 (m, 4H); ¹³C nmr (75 MHz,

CDCl_3) (major) δ -3.24 (SiMe_3), 25.28, 26.21, 39.34, 39.42, 50.74 (CH_2NH_2), 82.23
(COH); (minor) δ -3.28 (SiMe_3), 23.83, 25.87, 38.32, 39.92, 50.94 (CH_2NH_2), 82.76
(COH); ν_{max} : 835-860, 1249, 1597, 3308-3368 cm^{-1} ; MS (ESI) m/z : 188.07 (M^+).

1-Aminomethyl-3-trimethylsilylcycloheptanol (16)

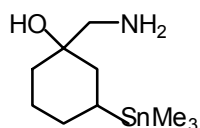


(0.274 g, 1.27 mmol, 18 %) as fine white platelets: mp 61.0-62.5 °C (pentane). ^1H nmr (300 MHz, CDCl_3) δ -0.08 (s, 9H, SiMe_3), 0.92-1.83 (m, 11H), 2.33 (bs, 3H), 2.58 (bs, 2H); ^{13}C nmr (75 MHz, CDCl_3) δ -3.45, 18.92, 22.36, 30.00, 30.82, 38.10, 39.48, 51.96 (CH_2NH_2), 74.42 (COH).

1-Aminomethyl-3-trimethylstannylcyclopentanol (13) (diastereoisomers, ratio ca

1.1:1, 53%) had ^1H NMR δ : 2.65 (m, 2H), 2.2 (m, 2H, NH_2), 2.2-1.1 (m, 7H), -0.01 (br. s, Sn-Me_3); ^{13}C NMR δ : (major isomer) 81.99 (C-OH), 50.99 ($\text{CH}_2\text{-NH}_2$), 42.23, 38.57, 29.07, 22.24, -11.21 (Sn-Me_3); (minor) 82.28 (C-OH), 51.13 ($\text{CH}_2\text{-NH}_2$), 42.81, 39.39, 29.28, 21.08, -11.51 (Sn-Me_3).

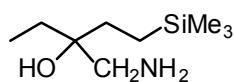
1-Aminomethyl-3-trimethylstannylcyclohexanol 15.



(3.039 g, 10.4 mmol, 54 %) as a mixture of isomers in a ratio of ca. 3.0:1.0. ^1H nmr (300 MHz, CDCl_3) δ -0.02 (minor) and 0.00 (major) (s, 9H, SnMe_3), 1.09-1.88 (m, 12H), 2.50

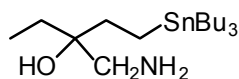
(minor) and 2.72 (major) (bs, 2H, CH₂NH₂); ¹³C nmr (75 MHz, CDCl₃) (major) δ -11.34 (SnMe₃), 20.97, 24.90, 29.88, 36.15, 40.07, 47.04 (CH₂NH₂), 71.03 (C-OH); (minor) δ -12.00 (SnMe₃), 18.64, 23.48, 30.37, 34.90, 39.09, 53.06 (CH₂NH₂), 70.08 (C-OH); MS (ESI) *m/z*: 294.1 (M⁺).

3-Aminomethyl-1-trimethylsilylpentan-3-ol (21)



(0.593 g, 4.52 mmol, 53 %). ¹H nmr (300 MHz, CDCl₃) δ -0.03 (s, 9H, SiMe₃), 0.30-0.45 (m, 2H), 0.82 (t, 3H, *J* = 9.2 Hz), 1.30-1.48 (m, 4H), 1.84 (bs, 3H), 2.58 (s, 2H); ¹³C nmr (75 MHz, CDCl₃) δ -1.96 (SiMe₃), 7.72 (m, 2H), 9.64, 28.36, 29.85, 47.84 (CH₂NH₂), 73.95 (COH). ν_{\max} : 837-887, 1594, 3306-3373 cm⁻¹. MS (ESI) *m/z*: 190.13 (M⁺).

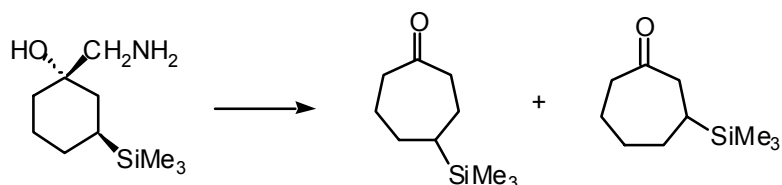
3-Aminomethyl-1-tributylsilylpentan-3-ol (22)



(0.527 g, 1.30 mmol, 49 %). ¹H nmr (400 MHz, CDCl₃) δ 0.70-0.98 (m, 17H), 1.12- 1.71 (m, 19H), 1.96 (bs, 1H, COH), 2.55-2.74 (m, 2H, CH₂NH₂), 2.90 (m, 2H, NH₂); ¹³C nmr (100 MHz, CDCl₃) δ 1.31, 7.80, 8.62, 13.69, 27.36, 28.18, 29.20, 32.82, 47.41 (CH₂NH₂), 74.51 (COH).

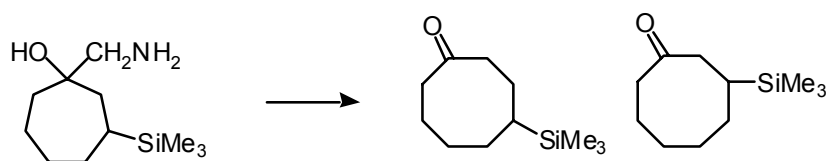
Typical Procedure for the Tiffeneau-Demjanov Ring Enlargements and Related Chain Extensions;

Ring Enlargement of Amine 14 (cis)



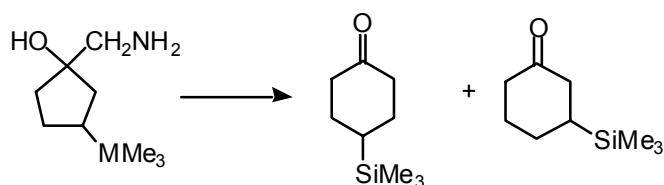
A suspension of 1-aminomethyl-3-trimethylsilylcyclohexanol (**16**) (0.966 g, 4.79 mmol), acetic acid (10 mL) and ice-cold water (40 mL) was stirred at -5 °C in an ice-salt bath. Once dissolved, a solution of sodium nitrite (0.681 g, 9.89 mmol) dissolved in ice-cold water (5 mL) was added in a dropwise manner. The reaction mixture was sustained at -5 °C for an additional hour, then allowed to stir overnight as the ice-salt bath melted. The yellow product mixture was neutralised with sat. aqueous NaHCO₃ then extracted into ether (3 x 30 mL). The organic layer was washed with water (3 x 30 mL), dried (MgSO₄) and concentrated under reduced pressure to yield a mixture of 4-trimethylsilylcycloheptan-1-one (**27**) and 3-trimethylsilylheptan-1-one (**11**) (0.695 g, 3.77 mmol, 79 %) as a pale yellow oil in a ratio of *ca* 2.6:1.0. ¹H nmr (300 MHz, CDCl₃) δ - 0.09 (s, 9H, SiMe₃, minor), -0.07 (s, 9H, SiMe₃, major), 0.50-0.66 (m, 1H), 0.68-2.20 (m, 15H), 2.25-2.70 (m, 6H); ¹³C nmr (75 MHz, CDCl₃) δ (major) -3.50 (SiMe₃), 25.10, 26.00, 30.00, 30.89, 43.63, 45.61, 215.47 (C=O); δ (minor) -3.76 (SiMe₃), 23.60, 24.30, 31.00, 31.78, 43.33, 44.38, 215.63 (C=O).

Ring Enlargement of Amine 16



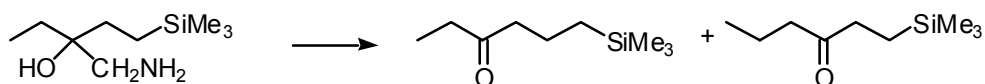
Yielded 4-trimethylsilylcyclooctan-1-one (**30**) and 3-trimethylsilylcyclooctan-1-one (**31**) as a pale orange oil (0.165 g, 0.83 mmol, 73 %) as a mixture of isomers in a ratio of *ca.* 1.7:1.0. ¹H nmr (400 MHz, CDCl₃) δ -0.12 (s, 9H, SiMe₃, major), -0.08 (s, 9H, SiMe₃, minor), 0.22-0.53 (m, 1H), 0.87-2.60 (m, 25H); ¹³C nmr (100 MHz, CDCl₃) δ (major) - 3.42 (SiMe₃), 22.79, 24.89, 26.16, 28.94, 29.03, 41.98, 43.51, 218.47 (C=O); δ (minor) - 3.40 (SiMe₃), 24.18, 25.88, 26.05, 26.85, 27.87, 41.41, 42.81, 219.83 (C=O).

Ring Enlargement of Amine 12



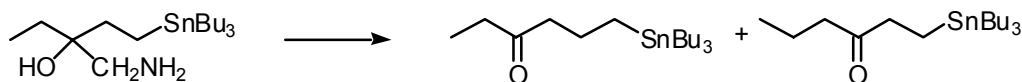
Yielded 4-trimethylsilylcyclohexan-1-one (**25**) and 3-trimethylsilylcyclohexan-1-one (**11**) (0.154 g, 0.91 mmol, 67 %) as a mixture of isomers in a ratio of *ca.* 1.4:1.0. ¹H nmr (400 MHz, CDCl₃) δ -0.61 (9H, SiMe₃), 0.82-1.08 (m, 1H), 1.31-1.51 (m, 2H), 1.59-1.80 (m, 1H), 1.98-2.40 (m, 5H); ¹³C nmr (100 MHz, CDCl₃) δ (major) -3.50 (SiMe₃), 24.87, 28.42, 43.16, 212.73 (C=O); δ (minor) -3.82 (SiMe₃), 25.88, 27.92, 29.88, 41.87, 42.30, 213.08 (C=O).

Chain Extension of Amine 21



Yielded a mixture of 1-trimethylsilylhexan-4-one (**32**) and 1-trimethylsilylhexan-3-one (**34**) (0.247 g, 1.43 mmol, 74 %) in a ratio of *ca.* 2:1. ^1H nmr (300 MHz, CDCl_3) δ -0.03 (s, 9H, SiMe_3 both isomers), 0.42-0.50 (major), 0.70-0.77 (minor), (m, 2H, CH_2SiMe_3), 0.90 (minor), 1.13 (major), (t, 3H, CH_2CH_3), 1.51-1.66 (m, 2H, both isomers), 2.30-2.45 (m, 4H, both isomers); ^{13}C nmr (75 MHz, CDCl_3) δ (major) -1.82 (SiMe_3), 7.76, 16.49, 18.64, 35.92, 46.08, 211.95 ($\text{C}=\text{O}$); δ (minor) -1.90 (SiMe_3), 10.22, 13.77, 17.41, 37.24, 43.94, 210.57 ($\text{C}=\text{O}$); ν_{max} : 840, 1251, 1718 cm^{-1} .

Chain Extension of Amine 22



Yielded a mixture of 1-tributylstannylhexan-4-one (**31**) and 1-tributylstannylhexan-3-one (**33**) (0.259 g, 0.637 mmol, 72 %) in a ratio of 1.8:1.0. ^1H nmr (300 MHz, CDCl_3) δ 0.65-2.60 (m, 19 H); ^{13}C nmr (75 MHz, CDCl_3) δ (major) 7.72, 8.60, 8.94, 13.65, 21.77, 27.33, 29.15, 35.86, 47.08, 211.76 ($\text{C}=\text{O}$); δ (minor) 1.88, 9.62, 13.56, 13.76, 17.43, 27.93, 29.20, 39.88, 43.82, 212.67 ($\text{C}=\text{O}$).

Typical Procedure of β -trimethylstannyl Cyclic Ketones **8** **10** **26**

(3-Trimethylstannylcyclohexanone. **10**)

Under N₂ was stirred a suspension of lithium metal (0.63g, 90 mmol) in THF (50 ml), then syringed in trimethyltin chloride (36 ml, 36 mmol) in one portion. The colourless solution gradually turned dark green after 3hrs. **2-cyclohexen-1-one** (2.9 ml, 30 mmol) was added in a slow, dropwise manner and the mixture allowed to stir for 1 hr. Excess lithium metal was removed, followed by the addition of water (100 ml). The product was extracted into ether (3x30 ml), washed with water (3x50 ml), dried (MgSO₄) and solvent evaporated under reduced pressure. The crude product was kugelrohr-distilled to yield a light yellow oil of **3-trimethylstannylcyclohexanone (10)** (6.31g, 24 mmol, 81%). B.p. 120⁰C (kugelrohr-distilled); ¹H NMR δ: 2.38-1.45 (m, 8H, CH₂), -0.034 (s, SnMe₃); ¹³C NMR δ: 212.01 (C=O), 45.47, 41.84, 30.60, 29.11, 24.93, -11.84 (SnMe₃); ν_{max}: 2925 (C-H), 1710 (C=O) cm⁻¹.

3-Trimethylstannylcyclopentanone (8) (72%) had ¹H NMR δ: 2.4-1.5 (m, 7H), 0.04 (s, SnMe₃); ¹³C NMR δ: 218.41 (C=O), 42.09 (αC=O), 39.13 (αC=O), 27.75, 20.16, -11.58 (SnMe₃); ν_{max}: 2958 (C-H), 1738 (C=O) cm⁻¹.

3-Trimethylstannylcycloheptanone (27) (76%) had ¹H NMR δ: 2.7-1.15 (m, 11H), 0.09 (s, SnMe₃); ¹³C NMR δ: (C=O) missing, 47.29, 43.51, 34.84, 32.56, 23.98, 21.68, -11.14 (SnMe₃).

