SUPPORTING INFORMATION

Materials and General Comments. All reactions were carried out under an atmosphere of dry nitrogen. The following reagents were obtained from commercial sources and used without further purification: n-BuLi (hexane solution, 2.5 M), 1,3-divinyltetramethyldisilazane, chlorodimethylsilane, 1,1,3,3-tetramethyldisilazane, vinyldimethylchlorosilane, diethyl ether, ammonium chloride, hydrochloric acid and sodium chloride. Tetrahydrofuran (THF) was distilled from Na/benzophenone under a N_2 atmosphere prior to use. Karstedt's catalyst in xylene (platinum-divinyltetramethyldisiloxane complex, Pt-DVTMDSO) was purchased from either Gelest, Inc. or United Chemical Technologies and used as received.

^1H and ^{13}C NMR were obtained on a 400 MHz Bruker AVANCE DRX multinuclear NMR spectrometer using $CDCl_3$ as solvent. Elemental analyses were performed by E+R Microanalytical Laboratory, Corona, NY.

Preparation of Compounds 1 and 2. These compounds were prepared using essentially the same procedure. As an example, the preparation of compound **1** is described in detail.

Preparation of Bis(dimethylvinyl)dimethylsilylamine 1. A 500-mL round-bottomed three-neck flask equipped with a magnetic stir bar, septum, a pressure equalizing addition funnel with a rubber septum on top, and a gas-inlet needle was charged with 45.0 mL of 1,3-divinyltetramethyldisilazane (0.20 mol) and 200 mL of THF. The flask was placed in a water/ice bath and then 80 mL of n-BuLi (0.20 mol, 2.5M solution in hexanes) was cannulated into the addition funnel and added dropwise to the reaction flask. After completion of addition, the clean yellow solution was stirred for an additional 15 minutes. Chlorodimethylsilane (22.2 mL, 0.20 mol) was added dropwise via syringe causing the solution to change to a milky white. After stirring cold for an additional 1 hour, the mix was allowed to warm up to room temperature and left overnight. The white suspension was poured into an ice-cold solution of saturated aqueous ammonium chloride. The layers were separated and the aqueous layer was extracted twice with ether. The organic layers were combined and washed twice with distilled water, and once with saturated aqueous sodium chloride solution. The clean yellow organic layer was dried over anhydrous magnesium sulfate and then filtered. All volatiles were removed using a rotary evaporator which provided 59.4 g of clean, colorless liquid (theoretical yield 48.7 g). This crude product was further purified by distillation to give 46.2 g of product **1** as a clean, colorless oil in 95% yield (bp 79-80.5 °C/mm Hg). ^{1}H NMR: δ 0.20 (12 H, ViSiCH_3), 0.19 (d, 6 H, HSiCH_3, ^{3}J = 3.5 Hz), 4.53 (sept, 1 H, Si*H*, ^{3}J = 3.5 Hz), 5.65 (dd, 2 H, C=C*H*H, ^{2}J = 3.7 Hz, ^{3}J = 20.3 Hz), 5.89 (dd, 2 H, C=CH*H*, ^{2}J = 3.7 Hz, ^{3}J = 14.7 Hz), 6.21 (dd, 2 H, C*H*=CH_2, ^{3}J = 14.7 Hz, ^{3}J = 20.3 Hz). ^{13}C NMR: δ 1.66 (HSiCH_3), 2.10 (ViSiCH_3), 131 (*C*H=CH_2), 142 (CH=CH_2). IR (neat) cm^{-1}: 3049 (m), 3008(w), 2956 (s), 2902(w), 2136 (s), 1593 (w), 1404 (s), 1253 (s), 1009 (s), 974 (s), 952 (s), 903 (br, s), 835 (s), 802 (s), 778 (s), 685 (m), 661 (w), 627 (w), 607 (w). Anal. Calcd for $C_{10}H_{25}NSi_3$: C, 49.51; H, 10.39. Found: C, 49.42; H, 10.29.

Preparation of Bis(dimethylsilyl)dimethylvinylsilylamine 2. This preparation was carried out using the procedure given above. 1,1,3,3-tetramethyldisilazane (17.4 mL, 0.1 mol), n-BuLi (40 mL, 0.1 mol), and vinyldimethylchlorosilane (13.8 mL, 0.1 mol) were allowed to react in 100 mL of THF. After removing solvent using a rotary evaporator, a clean yellow oil was further purified by distillation under vacuum to provide 16.6 g of product **2** as a colorless, clean oil. The isolated yield of product was determined to be 76% (bp 53 °C/3.5 mmHg). ^{1}H NMR: δ 0.20 (6 H, ViSiC*H*$_3$), 0.17 (d, 12 H, HSiC*H*$_3$, ^{3}J = 3.4 Hz), 4.50 (sept, 2 H, Si*H*, ^{3}J = 3.4 Hz), 5.66 (dd, 1 H, C=C*H*H, ^{2}J = 3.8 Hz, ^{3}J = 20.3 Hz), 5.91 (dd, 1 H, C=CH*H*, ^{2}J = 3.8 Hz, ^{3}J = 14.7 Hz), 6.18 (dd, 1 H, C*H*=CH$_2$, ^{3}J = 14.7 Hz, ^{3}J = 20.2 Hz). ^{13}C NMR: δ 0.91 (HSi*C*H$_3$), 0.87 (ViSi*C*H$_3$), 131 (*C*H=CH$_2$), 141 (CH=*C*H$_2$). IR (neat) cm^{-1}: 3050 (w), 2957 (s), 2902 (w), 2127 (s), 1593 (w), 1406 (m), 1252 (s), 1008 (m), 982 (s), 953 (s), 908 (s), 883 (s), 831 (s), 808 (s), 777 (s), 739 (w), 693 (m), 648 (w), 632 (w), 615 (w). Anal. Calcd for $C_8H_{23}NSi_3$: C, 44.17; H, 10.66. Found: C, 44.36; H, 10.47.

Preparation of Cyclic Compound 3. A 250-mL round-bottomed three-neck flask equipped with a magnetic stir bar, a reflux condenser, septum, and a N_2 gas inlet was charged with 28.2 g of compound **1** (0.116 mol) and 100 mL of THF. Four drops of Pt-DVTMDSO were added and the mixture was stirred for 10 minutes at room temperature. The reaction mixture was then stirred at reflux for 18h. After removing all volatiles under vacuum, the light yellow crude product was purified by distillation under vacuum. Distillation provided 27.3 g of product **3** in 96.7 % yield (bp 76.5 °C/10 mmHg). ^{1}H NMR: δ 0.04 (6 H, ViSiC*H*$_3$), 0.16 (6 H, SiC*H*$_3$), 0.18 (6 H, SiC*H*$_3$), 0.50 (quat, 1 H, *H*CCH$_3$, ^{3}J = 7.9 Hz), 1.04 (d, 3 H, HCC*H*$_3$, ^{3}J = 7.9 Hz), 5.61 (dd, 1 H, C=C*H*H, ^{2}J = 4.0 Hz, ^{3}J = 20.3 Hz), 5.85 (dd, 1 H, C=CH*H*, ^{2}J = 4.0 Hz, ^{3}J = 14.7 Hz), 6.08 (dd, 1 H, C*H*=CH$_2$, ^{3}J = 14.7 Hz, ^{3}J = 20.2 Hz). ^{13}C NMR: δ 0.28 (Si*C*H$_3$), 0.41 (ViSi*C*H$_3$), 3.93 (Si*C*H$_3$), 8.07 (HC*C*H$_3$), 9.20 (H*C*CH$_3$), 131 (*C*H=CH$_2$), 141 (CH=*C*H$_2$). ^{29}Si NMR: δ -11.31 (Vi*Si*Me$_2$), 12.50 (SiCH$_3$). IR (neat) cm^{-1}: 3048 (w), 3008 (w), 2952 (s), 2903 (m), 2867 (m), 1594 (w), 1466 (w), 1405 (m), 1250 (s), 1059 (s), 1030 (s), 966 (m), 952 (m), 923 (s), 855 (s), 785 (s), 766 (m), 733 (w), 681 (m), 663 (w), 607 (m). Molecular Weight (GC-Mass), Calcd for $C_{10}H_{25}NSi_3$: 243.6. Found: 243.4. Anal. Calcd for $C_{10}H_{25}NSi_3$: C, 49.51; H, 10.39. Found: C, 49.38; H, 10.25.

Cyclization of 1 in the Presence of Rh(I) Catalyst. This preparation was performed using the exact same procedure used in the preparation of compound **3** except tris-(triphenylphosphine)-Rh(I)chloride was used as catalyst instead of Pt-DVTMDSO. At room temperature, 2.31 g of compound **1** (9.50 mmol) and 0.088g (1 mol%) of Tris-(triphenylphosphine)-Rh(I)chloride were stirred in 10 mL of THF for 10 minutes, resulting in a clean yellow solution. The mixture was then refluxed for 24 h. Volatiles were removed under full vacuum to give a brown suspension. The ^{1}H NMR spectra was compared with the one of compound **3**. ^{1}H NMR: δ 0.04 (6 H, ViSiCH_3), 0.09 (12 H, five-membered ring, SiCH_3), 0.16 (6 H, four-membered ring, SiCH_3), 0.19 (6 H, four-membered ring, SiCH_3), 0.51 (quat, 1 H, HCCH_3, ^{3}J = 7.9 Hz), 0.65 (4H, five-membered ring, CH_2CH_2), 1.04(3H, HCCH_3, ^{3}J = 7.9 Hz), 5.59 – 6.22 (two sets, vinyl). IR (neat) cm^{-1}: 3048 (m), 3008 (w), 2951 (s), 2903 (m), 2867 (m), 1466 (w), 1456 (w), 1405 (m), 1249 (s), 1059 (s), 1032 (s), 974 (s), 952 (s), 923 (s), 895 (s), 861 (br, s), 786 (br, s), 733 (m), 681 (m), 663 (m), 609 (m).

Preparation of Cyclic Compound 4. Compound **4** was prepared using essentially the same procedure used in the preparation of compound **3**. At room temperature, 10.8 g of compound **2** (49.5 mmol) and several drops of Pt-DVTMDSO were stirred in 50 mL of THF for 10 minutes and the mixture was then refluxed for 18 h. Distillation of the crude mixture provided 6.3 g of **4** as a clean, colorless liquid in 59% yield (bp 49 °C/4.1 mmHg). ^{1}H NMR: δ 0.04 (d, 6 H, HSiCH_3, ^{3}J = 3.1 Hz), 0.17 (6 H, SiCH_3), 0.20 (6 H, SiCH_3), 0.54 (quat, 1 H, *H*CCH$_3$, ^{3}J = 7.9 Hz), 1.05 (d, 3 H, HCC*H*$_3$, ^{3}J = 7.9 Hz), 4.33 (sept, 1 H, SiH, ^{3}J = 3.1 Hz). ^{13}C NMR: δ 0.07 (Si*C*H$_3$), 0.46 (HSi*C*H$_3$), 3.51 (Si*C*H$_3$), 8.07 (HC*C*H$_3$), 9.93 (H*C*CH$_3$). ^{29}Si NMR: δ -17.08 (H*Si*Me$_2$, J$_{(SiH)}$ = 190.2 Hz), 12.86 (*Si*CH$_3$). IR (neat) cm^{-1}: 2952 (s), 2903 (m), 2867 (m), 2100 (s), 1466 (w), 1456 (w), 1403 (br, w), 1250 (s), 1067 (s), 1036 (s), 966 (w), 909 (s), 853 (s), 818 (s), 787 (s), 766 (m), 720 (m), 690 (m), 662 (w), 612 (m). Molecular Weight (GC-Mass), Calcd for $C_8H_{23}NSi_3$: 217.5. Found: 217.3. Anal. Calcd for $C_8H_{23}NSi_3$: C, 44.17; H, 10.66. Found: C, 44.37; H, 10.41.

Cyclization of 2 in the Presence of Rh(I) Catalyst. This preparation was performed using the exact same procedure used in the preparation of compound **4** except tris-(triphenylphosphine)-Rh(I)chloride was used as catalyst instead of Pt-DVTMDSO. At room temperature, 2.02 g of compound **2** (9.31 mmol) and 0.086 g (1 mol%) of Tris-(triphenylphosphine)-Rh(I)chloride were stirred in 10 mL of THF for 10 minutes and the mixture was then refluxed for 24 h. Volatiles were removed under full vacuum to get a crude product. The ^{1}H NMR spectrum was compared with the one of compound **4**. The ^{1}H NMR spectrum was messy but we observed that the percentage of five-membered ring product in the mixture was increased compared to the mixture from **1** and Rh(I) catalyst.

Preparation of compound 5, bis(vinyldimethylsilyl)methylphenylsilylamine.

A 100-mL round-bottomed single-neck flask equipped with septum, N_2 gas inlet, and a magnetic stir bar was charged with 6.76 mL of 1,3-divinyltetramethyldisilazane (0.03 mol) and 30 mL of THF. The flask was placed in a water/ice bath and then 12 mL of n-BuLi (0.03 mol, 2.5M solution in hexanes) was added dropwise to the reaction flask via syringe. After the addition was complete, the clean yellow solution was stirred for an additional 15 min. Chloromethylphenylsilane (3.96 mL, 0.03 mol) was added dropwise via syringe causing the solution to change to a milky white mixture. After stirring cold for an additional 1 h, the mixture was allowed to warm up to room temperature and left overnight. The white suspension was poured into an ice-cold solution of saturated aqueous ammonium chloride. The layers were separated and the aqueous layer was extracted twice with ether. The organic layers were combined and washed twice with distilled water, and once with saturated aqueous sodium chloride solution. The clean yellow organic layer was dried over anhydrous magnesium sulfate and then filtered. All volatiles were removed using a rotary evaporator which provided 8.47 g of a clean, yellow solution (theoretical yield 9.17g). This crude product was purified by distillation to give 6.63 g of **5** as a clean, colorless oil in 72.3 % yield (bp 84 °C/0.001 mmHg). ^{1}H NMR: δ 0.18 (6 H, ViSiC*H*$_3$), 0.20 (6 H, ViSiC*H*$_3$), 0.51 (3 H, HSiC*H*$_3$, ^{3}J = 3.6 Hz), 5.00 (quat, 1 H, Si*H* ^{3}J = 3.6 Hz), 5.64 (dd, 2 H, C=C*H*H, ^{2}J = 3.6 Hz, ^{3}J = 20.4 Hz), 5.88 (dd, 2 H, C=C*H*H, ^{2}J = 3.7 Hz, ^{3}J = 14.7 Hz), 6.19 (dd, 2 H, CH=CH$_2$, ^{3}J = 14.7 Hz, ^{3}J = 20.3 Hz), 7.34 (multi, 3 H, aromatic), 7.55 (multi, 2 H, aromatic). IR (neat) cm^{-1}: 3049 (m), 3008 (m), 2955 (m), 2902 (w), 2134 (m), 1591 (w), 1404 (m), 1254 (s), 1113 (m), 1009 (m), 963 (s), 911 (br, s), 864 (s), 828 (s), 772 (s), 725 (s), 698 (s). Anal. Calcd for $C_{15}H_{27}NSi_3$: C, 58.95; H, 8.90. Found: C, 58.70; H, 9.09.

Reaction of 5 and Pt-catalyst.

A 25-mL round-bottomed single-neck flask equipped with a magnetic stir bar, a reflux condensor, and N_2-gas inlet was charged with 10 mL of THF and 2.44 g (7.98 mmol) of **5**. Several drops of Karstedt's catalyst solution were added at room temperature and the mixture was then stirred for an additional 10 min. The mixture was refluxed for 18 h to give a clean colorless liquid. All volatiles were removed using a rotary evaporator and the crude product was distillated using Kugerohr which provided 2.06 g of product as a clean, colorless oil in 84.5 % yield. The ^{1}H NMR data showed that the product contains a mixture of four-membered (64 %) and five-membered cyclic products (36 %). GC-MS data showed the ratio of four- and five-membered ring compounds as 100:56.4. ^{1}H NMR: δ -0.07 (3 H, four-membered ring, MeSiCH_3), -0.04 (3 H, four-membered ring, MeSiCH_3), 0.006 (3 H, five-membered ring, MeSiCH_3), 0.022 (3 H, five-membered ring, MeSiCH_3), 0.26 (3 H, four-membered ring, ViSiCH_3), 0.27 (3 H, five-membered ring, ViSiCH_3), 0.29 (3 H, five-membered ring, ViSiCH_3) 0.31 (3 H, four-membered ring, ViSiCH_3), 0.50 (3 H, four-membered ring, PhSiCH_3), 0.51 (3 H, five-membered ring, PhSiCH_3), 0.67 - 0.80 (multi, 1 H, four-membered ring, HCCH$_3$ and 4 H, five-membered ring, CH_2CH$_2$), 1.11 (d, 3 H, four-membered ring, HCCH_3, ^{3}J = 7.9 Hz), 5.50 - 6.11 (two sets, vinyl), 7.35 (multi, aromatic), 7.55 (multi, aromatic). GC-MS data: two compounds with MW = 305 (theoretically 305.64), ratio % = 56.5 : 100.

Reaction of 5 and Rh(I)-catalyst.

A mixture of **5** (1.53 g, 5.0 mmol) and Rh(PPh$_3$)$_3$Cl catalyst (0.0046 g , 0.1 mol% of trisilylamine, 0.005 mmol) in 8 mL of THF was refluxed for 18 h. After removing solvent using a rotary evaporator, a brownish clean oil was further purified by Kugelrohr distillation to provide 1.31 g of product as a colorless, clean oil in 85.7 % yield. The product is a mixture of four-membered (60 %) and five-membered ring compound (40 %). ^{1}H NMR: δ -0.06 (3 H, four-membered ring, MeSiCH_3), -0.03 (3 H, four-membered ring, MeSiCH_3), 0.006 (3 H, five-membered ring, MeSiCH_3), 0.03 (3 H, five-membered ring, MeSiCH_3), 0.27 (3 H, four-membered ring, ViSiC*H*$_3$), 0.29 (3 H, five-membered ring, ViSiC*H*$_3$), 0.30 (3 H, five-membered ring, ViSiC*H*$_3$) 0.32 (3 H, four-membered ring, ViSiC*H*$_3$), 0.51 (3 H, four-membered ring, PhSiC*H*$_3$), 0.52 (3 H, five-membered ring, PhSiC*H*$_3$), 0.69 - 0.82 (multi, 1 H, four-membered ring, *H*CCH$_3$ and 4 H, five-membered ring, C*H*$_2$CH$_2$), 1.12 (d, 3 H, four-membered ring, HCC*H*$_3$, ^{3}J = 7.9 Hz), 5.51 - 6.12 (two sets, vinyl), 7.36 (multi, aromatic), 7.56 (multi, aromatic).

Preparation of Compound 6. A 250-mL round-bottomed two-neck flask equipped with a magnetic stir bar, a reflux condenser, septum, and a N$_2$ gas inlet was charged with 9.96 g of compound **3** (40.9 mmol), triphenylsilane (10.7 g, 40.9 mmol), and 85 mL of THF. Four drops of Pt-DVTMDSO were added and the mixture was stirred for 10 minutes at room temperature. The reaction mixture was then stirred at reflux for 96 h. After the reaction was complete, volatiles were removed under full vacuum for several days to give a light yellowish white waxy solid in quantitative yield. ^{1}H NMR: δ -0.03 (6 H, SiC*H*$_3$), 0.10 (6 H, cyc-SiC*H*$_3$), 0.12 (6 H, cyc-SiC*H*$_3$), 0.45 – 0.52 (multi, 1 H, CH$_3$C*H*), 0.49 (multi, 2 H, CH$_2$CH$_2$), 1.02 (d, 3 H, C*H*$_3$CH, J = 7.9 Hz), 1.23 (multi, 2 H, CH$_2$CH$_2$), 7.24 – 7.53 (multi, 15 H, aromatic). ^{13}C NMR: δ -0.34 (cyc-Si*C*H$_3$), 0.61 (Si*C*H$_3$), 4.12 (cyc-Si*C*H$_3$), 5.10 (*C*H$_2$CH$_2$), 8.18 (CH*C*H$_3$), 8.93 (*C*H$_2$CH$_2$), 11.04 (*C*HCH$_3$), 127.5 (aromatic), 129.0 (aromatic), 135.1 (aromatic), 135.5 (aromatic). IR (neat) cm^{-1}: 3066 (m), 2926 (s), 2858 (s), 1588 (w), 1460 (m), 1428 (m), 1377 (w), 1251 (s), 1187 (w), 1110 (s), 1029 (s), 967 (w), 922 (m), 857 (s), 788 (s), 707 (s), 616 (m).