Formation and Utility of Azasilacyclopentadienes Derived from Silacyclopropenes and Nitriles

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Supporting Information

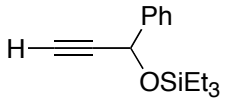
Contents:

Experimental Section

General. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature using Bruker DRX 400 or DRX 500 spectrometers, as indicated. The data are reported as follows: chemical shift in ppm from an internal tetramethylsilane standard on the δ scale, multiplicity (b = broad, vb = very broad, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were acquired on a VG analytical 7070E or Fisions Autospec spectrometer, and were obtained by peak matching. Infrared spectra were obtained using thin films on sodium chloride plates on a Perkin Elmer Spectrum RX1 FTIR spectrometer. Analytical thin layer chromatography was performed on EM reagents 0.25 mm silica gel 60-F plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system of EM reagents silica gel (SiO_2) 60 (230-400). Cyclohexene silacyclopropane, silacyclopropenes **1a-c** and **4a-d**, and azasilacyclopentadienes **2a-f**, **3**, and **5a-e** were stored and manipulated in an Innovative Technologies nitrogen-

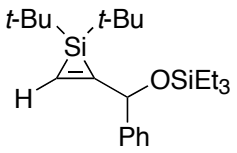
atmosphere dry box. Azasilacyclopentadienes **2a-f** were stored in a – 25 °C freezer inside the drybox. All reactions were performed under an atmosphere of nitrogen in glassware that had been flame-dried under vacuum. Solvents were distilled or filtered through alumina before use. Nitriles, alkynes, and methyl acrylate were distilled from CaH_2, degassed, and stored in the dry box. Potassium *t*-butoxide was used dry and weighed out in the nitrogen dry box. Cyclohexene silacyclopropane,[1] silacyclopropenes **1a-1c** and **4a-4d**,[2] and *t*-butyldimethylsilyl-protected, 3-hydroxyproprionitrile[3] were synthesized by known methods.

I. Synthesis of a Protected Propargylic Alcohol and Silacyclopropene 1c.[4]



S1

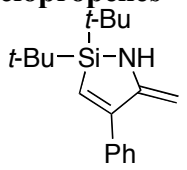
Alkyne S1. To a solution of the propargylic alcohol (1.5 mL, 12 mmol) in 100 mL of THF was added NEt_3 (3.0 mL, 22 mmol). The solution was then cooled to 0 °C and chlorotriethylsilane (2.0 mL, 12 mmol) was added. The reaction mixture was then allowed to warm to ambient temperature and stir for 12 h. At this point the mixture was partitioned between hexanes (~200 mL) and water (~200 mL). The hexanes solution was washed with brine (~50 mL), dried with $MgSO_4$, and then concentrated under vacuum. The resultant yellow oil was purified by flash chromatography (95:5 hexanes:EtOAc) to afford **S1** (2.185 g, 73%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.57 (m, 2H), 7.18-7.14 (m, 2H), 7.14-7.08 (m, 1H), 5.47 (s, 1H), 2.14 (s, 1H), 1.02-0.98 (m, 9H), 0.73-0.60 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 128.6, 126.6, 122.8, 85.0, 73.9, 65.0, 7.0, 5.2; IR (thin film) 2956, 2877, 1602, 1455, 1241, 1068 cm^{-1}; LRMS (ESI) *m/z* calcd for $C_{15}H_{22}OSiNa$ $(M+Na)^+$ 269.2, found 269.2.



1c

Silacyclopropene 1c. To a solution of alkyne **S1** (2.185 g, 8.87 mmol) in 100 mL of toluene was added cyclohexene silacyclopropane (1.990 g, 8.87 mmol) followed by Ag_3PO_4 (371 mg, 0.887 mmol). The reaction mixture was allowed to stir at ambient temperature for 24 h. At this time, the reaction mixture was filtered through Celite and concentrated under vacuum. The resultant brown oil was purified by bulb-to-bulb distillation (110 °C, ~0.5 mm Hg) to afford **1c** (2.402 g, 70%) as a clear colorless oil: ^{1}H NMR (400 MHz, C_6D_6) δ 8.02 (s, 1H), 7.52-7.50 (m, 2H), 7.22-7.13 (m, 2H), 7.08-7.05 (m, 1H), 5.77 (s, 1H), 1.07 (s, 9H), 1.01-0.95 (m, 9H), 0.90 (s, 9H), 0.69-0.61 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 144.5, 136.3, 128.3, 127.1, 126.2, 76.2, 30.0, 29.7, 21.1, 21.0, 7.1, 5.2; HRMS (ESI) *m/z* calcd for $C_{23}H_{41}OSi_2$ $(M+H)^+$ 389.2696, found 389.2703.

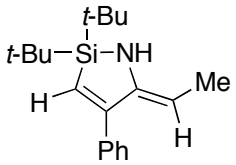
II. Nitrile Insertion Reactions of Silacyclopropenes



2a

Representative procedure for nitrile insertion reactions of silacyclopropenes (Azasilacyclopentadiene 2a, Table 1, Entry 1). To a solution of silacyclopropene **1a** (828 mg, 3.39 mmol) in 17 mL of toluene was added acetonitrile (139 mg, 3.39 mmol) followed by $(CuOTf)_2$•tol (88 mg, 0.17 mmol). The reaction mixture was then allowed to stand for 24 h at ambient temperature. At this time, the reaction mixture was concentrated under vacuum to afford a red oil. The oil was dissolved in acetonitrile (~5 mL) and extracted with hexane (~10 mL). The hexane solution was then filtered through a glass fiber filter pipet plug and concentrated under vacuum to afford azasilacyclopentadiene **2a** (786 mg, 82%) as a yellow/orange oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.47-7.37 (m, 2H), 7.22-7.08 (m, 3H), 5.94 (s, 1H), 4.33 (s, 1H), 4.27 (s, 1H), 3.16 (bs, 1H), 1.03 (s, 18H); ^{13}C NMR (125 MHz, C_6D_6) δ 159.3, 154.5, 140.6, 129.0, 128.1, 127.6, 126.8, 87.3, 28.2, 20.9; IR (thin film) 3414, 2928, 2856, 1624, 1572, 1467, 1208 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{18}H_{28}NSi$ $(M+H)^+$ 286.1991, found 286.1988.

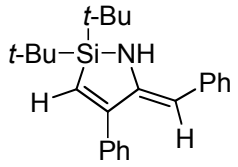
Synthesis of Azasilacyclopentadiene 2a with $Cu(OTf)_2$ as the catalyst. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **1a** (210 mg, 0.859 mmol), acetonitrile (35 mg, 0.86 mmol), $Cu(OTf)_2$ (16 mg, 0.043 mmol), and 17 mL of toluene for 24 h at ambient temperature. Isolation by extraction afforded azasilacyclopentadiene **2a** (152 mg, 62%) as a yellow/orange oil.



2b

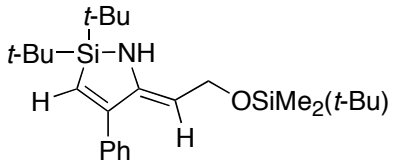
Azasilacyclopentadiene 2b, Table 1, Entry 2. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **1a** (1.015 g, 4.15 mmol), propionitrile (212 mg, 4.15 mmol), $(CuOTf)_2$•tol (107 mg, 0.207 mmol), and 17 mL of toluene for 24 h at ambient temperature. Isolation by extraction afforded **2b** (1.072 g, 86%) as a yellow/orange oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.42-7.33 (m, 2H), 7.21-7.07 (m, 3H), 5.85 (s, 1H), 4.66 (q, J = 6.9 Hz, 1H), 3.24 (bs, 1H), 1.55 (d, J = 6.9 Hz, 3H), 1.07 (s, 18H); ^{13}C NMR

(100 MHz, C_6D_6) δ 159.6, 149.3, 140.8, 129.1, 128.8, 127.4, 123.7, 97.6, 30.3, 28.2, 20.9; IR (thin film) 3459, 2929, 2855, 1636, 1488, 1387, 1154, 946 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{19}H_{30}NSi$ $(M+H)^+$ 300.2148, found 300.2137.



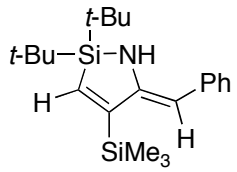
2c

Azasilacyclopentene 2c, Table 1, Entry 3. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **1a** (873 mg, 3.57 mmol), phenylacetonitrile (418 mg, 3.57 mmol), $(CuOTf)_2$•tol (92 mg, 0.18 mmol), and 17 mL of toluene for 24 h at ambient temperature. Isolation by extraction afforded **2c** (1.087 g, 84%) as an orange oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.47-7.36 (m, 4H), 7.22-7.12 (m, 5H), 7.00-6.91 (m, 1H), 6.01 (s, 1H), 5.75 (s, 1H), 4.60 (bs, 1H), 1.02 (s, 18H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.3, 149.3, 140.2, 139.3, 129.0, 128.8, 128.0, 127.6, 127.4, 126.2, 125.1, 104.1, 27.8, 20.4; IR (thin film) 3444, 2957, 2855, 1612, 1595, 1484, 1288, 1127, 882 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{24}H_{32}NSi$ $(M+H)^+$ 362.2304, found 362.2304.



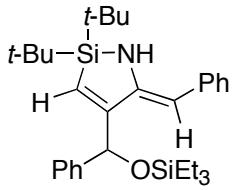
2d

Azasilacyclopentene 2d, Table 1, Entry 4. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **1a** (440 mg, 1.80 mmol), TBS protected, 3-hydroxypropionitrile (334 mg, 1.80 mmol), $(CuOTf)_2$•tol (47 mg, 0.090 mmol), and 12 mL of toluene for 24 h at ambient temperature. Isolation by extraction afforded **2d** (642 mg, 83%) as an orange oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.43-7.35 (m, 2H), 7.23-7.10 (m, 3H), 5.91 (s, 1H), 4.75 (t, J = 5.6 Hz, 1H), 4.70 (bs, 1H), 4.31 (d, J = 5.6 Hz, 2H), 1.11 (s, 18H), 0.98 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 159.9, 151.7, 140.7, 129.1, 127.9, 127.5, 125.5, 100.9, 60.8, 28.3, 26.2, 20.9, 18.5, -5.1; IR (thin film) 3426, 2956, 2856, 1627, 1472, 1363, 1149, 937 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{25}H_{44}NOSi_2$ $(M+H)^+$ 430.2961, found 430.2950.



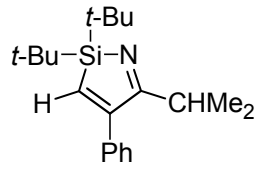
2e

Azasilacyclopentene 2e, Table 1, Entry 5. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **1b** (198 mg, 0.824 mmol), phenylacetonitrile (96 mg, 0.82 mmol), $Cu(OTf)_2$ (15 mg, 0.041 mmol), and 8 mL of toluene for 24 h at ambient temperature. Isolation by extraction afforded **2e** (191 mg, 65%) as an orange oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.58-7.49 (m, 2H), 7.29-7.19 (m, 2H), 7.06-6.97 (m, 1H), 6.76 (s, 1H), 5.88 (s, 1H), 4.59 (bs, 1H), 0.97 (s, 18H), 0.35 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 164.1, 152.3, 139.8, 128.8, 128.0, 127.8, 125.0, 104.4, 27.9, 20.3, -0.06; IR (thin film) 3448, 2957, 2856, 1610, 1470, 1365, 1138 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{21}H_{36}NSi_2$ $(M+H)^+$ 358.2386, found 358.2375.



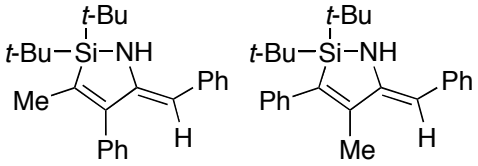
2f

Azasilacyclopentene 2f, Table 1, Entry 6. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **1c** (692 mg, 1.78 mmol), phenylacetonitrile (209 mg, 1.78 mmol), $(CuOTf)_2$•tol (46 mg, 0.089 mmol), and 15 mL of toluene for 24 h at ambient temperature. Isolation by extraction afforded **2f** (741 mg, 82%) as an orange oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.62-7.54 (m, 2H), 7.46-7.38 (m, 2H), 7.24-7.10 (m, 2H), 7.09-7.01 (m, 2H), 6.98-6.89 (m, 2H), 6.71 (s, 1H), 5.91 (s, 1H), 5.86 (s, 1H), 4.40 (bs, 1H), 1.04 (s, 9H), 1.01 (t, J = 8.0 Hz, 9H), 0.94 (s, 9H), 0.67 (q, J = 8.0 Hz, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 160.6, 147.1, 144.1, 139.0, 128.7, 128.1, 127.9, 127.2, 126.8, 125.0, 123.1, 101.0, 73.6, 27.9, 27.8, 20.4, 20.3, 6.9, 4.9; IR (thin film) 3449, 2932, 2877, 1616, 1598, 1470, 1387, 1239 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{31}H_{48}NOSi_2$ $(M+H)^+$ 506.3275, found 506.3298.



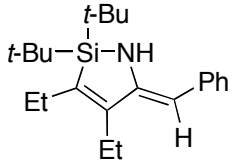
3

Azasilacyclopentadiene 3. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **1a** (108 mg, 0.442 mmol), isobutyronitrile (31 mg, 0.44 mmol), $(CuOTf)_2$•tol (12 mg, 0.022 mmol), and 10 mL of toluene for 4 d at ambient temperature. Isolation by extraction afforded **3** (87 mg, 62%) as a yellow oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.23-7.10 (m, 5H), 6.40 (s, 1H), 3.06 (sept, J = 6.5 Hz, 1H), 1.18 (s, 18H), 1.16 (d, J = 6.5 Hz, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 189.5, 161.4, 142.3, 140.9, 128.2, 127.4, 127.2, 33.1, 28.3, 20.8, 19.3; IR (thin film) 2931, 2856, 1618, 1547, 1471, 1387, 1302, 1013, 822, 698 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{20}H_{32}NSi$ $(M+H)^+$ 314.2304, found 314.2313.



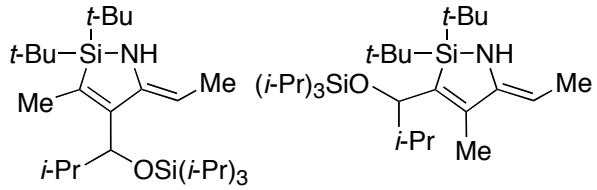
10 : 1
5a

Azasilacyclopentene 5a, Table 2, Entry 1. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **4a** (840 mg, 3.25 mmol), phenyl acetonitrile (381 mg, 3.25 mmol), $(CuOTf)_2$•tol (84 mg, 0.16 mmol), and 20 mL of toluene for 24 h at 55°C. Isolation by extraction afforded a 10:1 regioisomeric mixture of **5a** (1.038 g, 85%) as a light yellow oil: ^{1}H NMR of major regioisomer (400 MHz, C_6D_6) δ 7.42-7.34 (m 2H), 7.26-7.19 (m, 4H), 7.18-7.11 (m, 3H), 6.97-6.89 (m, 1H), 5.40 (s, 1H), 4.57 (bs, 1H), 1.78 (s, 3H), 1.04 (s, 18H); ^{1}H NMR of minor regioisomer (400 MHz, C_6D_6) δ 7.62-7.51 (m, 2H), 7.26-7.19 (m, 4H), 7.18-7.11 (m, 4H), 5.85 (s, 1H), 2.63 (bs, 1H), 1.92 (s, 3H), 1.12 (s, 18H); ^{13}C NMR of major regioisomer (125 MHz, C_6D_6) δ 153.8, 150.9, 139.9, 137.9, 135.0, 130.2, 129.0, 128.3, 127.92, 127.3, 125.0, 103.1, 28.2, 21.0, 16.6; ^{13}C NMR of minor regioisomer (125 MHz, C_6D_6) δ150.2, 148.1, 142.1, 140.0, 139.8, 129.2, 128.7, 128.1, 127.97, 126.1, 125.3, 100.2, 28.4, 21.3, 13.8; IR (thin film) 3446, 2928, 2855, 1613, 1594, 1469, 1444, 1383, 1157 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{25}H_{34}NSi$ $(M+H)^+$ 376.2461, found 376.2464. The major and minor regioisomers were not separated. The ^{1}H and ^{13}C NMR resonances were assigned based on relative peak intensity that matched the regioisomeric ratio and a ^{1}H-^{13}C HMQC experiment.



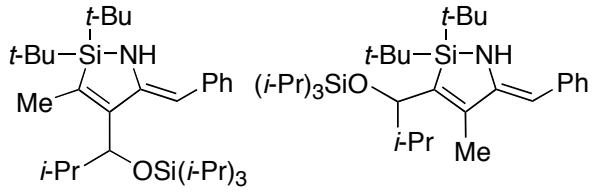
5b

Azasilacyclopentene 5b, Table 2, Entry 2. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **4b** (804 mg, 3.59 mmol), phenylacetonitrile (420 mg, 3.59 mmol), $(CuOTf)_2$•tol (93 mg, 0.18 mmol), and 20 mL of toluene for 24 h at 55 °C. Isolation by extraction afforded **5b** (1.053 g, 86%) as a light yellow oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.60-7.52 (m, 2H), 7.30-7.21 (m, 2H), 7.04-6.97 (m, 1H), 5.76 (s, 1H), 4.46 (bs, 1H), 2.39 (q, J = 7.4 Hz, 2H), 2.30 (q, J = 7.6 Hz, 2H), 1.14-1.07 (m, 6H), 1.00 (s, 18H); ^{13}C NMR (400 MHz, C_6D_6) δ 153.2, 148.8, 140.1, 138.4, 129.0, 127.9, 124.7, 98.0, 28.3, 22.7, 20.8, 19.6, 15.2, 15.1; IR (thin film) 3449, 2964, 2857, 1614, 1555, 1469, 1380, 1159, cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{22}H_{36}NSi$ $(M+H)^+$ 342.2617, found 342.2608.



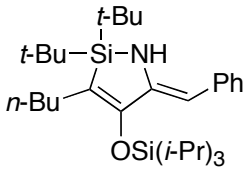
3 : 2
5c

Azasilacyclopentene 5c, Table 2, Entry 3. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **5c** (189 mg, 0.460 mmol), propionitrile (24 mg, 0.46 mmol), $(CuOTf)_2$•tol (12 mg, 0.023 mmol), and 15 mL of toluene for 24 h at 55 °C. Isolation by extraction afforded the 3:2 regioisomeric mixture **5c** (193 mg, 96%) as a light yellow oil: ^{1}H NMR of major regioisomer (500 MHz, C_6D_6) δ 5.54 (q, J = 6.8 Hz, 1H), 4.75-4.62 (m, 1H), 3.03 (bs, 1H), 2.48-2.38 (m, 1H), 1.92 (s, 3H), 1.68 (d, J = 6.8 Hz, 3H), 1.24-1.13 (m, 24H), 1.08 (s, 9H), 1.04 (s, 9H), 1.00 (d, J = 6.8 Hz, 3H); ^{1}H NMR of minor regioisomer (500 MHz, C_6D_6) δ 4.75-4.62 (m, 2H), 3.10 (bs, 1H), 2.35 (s, 3H), 2.19 (sept, J = 6.8 Hz, 1H), 1.60 (d, J = 6.8 Hz, 3H), 1.24-1.13 (m, 24H), 1.10 (s, 9H), 1.06 (s, 9H), 0.87 (d, J = 6.8 Hz, 3H); ^{13}C NMR of major regioisomer (125 MHz, C_6D_6) δ 151.0, 145.9, 131.7, 96.0, 75.6, 35.7, 28.43, 28.3, 20.8, 20.6, 19.8, 18.3, 15.7, 13.0, 11.6; ^{13}C NMR of minor regioisomer (125 MHz, C_6D_6) δ 149.9, 149.7, 133.8, 90.4, 76.1, 36.1, 28.48, 28.2, 20.9, 20.7, 19.9, 18.4, 17.2, 12.9, 11.7; IR (thin film) 3462, 2943, 2866, 1630, 1470, 1363, 1161, 1056 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{27}H_{56}NOSi_2$ $(M+H)^+$ 466.3900, found 466.3898. The major and minor regioisomers were not separated. The ^{1}H and ^{13}C NMR resonances were assigned based on relative peak intensity that matched the regioisomeric ratio and a ^{1}H-^{13}C HMQC experiment.



5d

Azasilacyclopentene 5d, Table 2, Entry 4. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **4c** (428 mg, 1.04 mmol), phenyl acetonitrile (122 mg, 1.04 mmol), $(CuOTf)_2$•tol (27 mg, 0.052 mmol), and 15 mL of toluene for 24 h at 55 °C. Isolation by extraction afforded the 3:1 regioisomeric mixture **5d** (459 mg, 83%) as a light yellow oil: ^{1}H NMR of major regioisomer (400 MHz, C_6D_6) δ 7.68-7.62 (m, 2H), 7.29-7.23 (m, 2H), 7.01-6.95 (m, 1H), 6.71 (s, 1H), 4.79 (m, 1H), 4.39 (bs, 1H), 2.57-2.46 (m, 1H), 1.94 (s, 3H), 1.25-1.18 (m, 24H), 1.02 (s, 9H), 0.97 (s, 9H), 0.89 (d, J = 6.7 Hz, 3H); ^{1}H NMR of minor regioisomer, (400 MHz, C_6D_6) δ 7.55-7.49 (m, 2H), 7.24-7.19 (m, 2H), 7.01-6.95 (m, 1H), 5.79 (s, 1H), 4.87 (d, J = 7.6 Hz, 1H), 4.45 (bs, 1H), 2.26 (sept, J = 6.9 Hz, 1H), 2.39 (s, 3H), 1.16-1.13 (m, 24H), 1.09-1.04 (m, 3H), 1.02 (s, 9H), 0.99 (s, 9H); ^{13}C NMR of major regioisomer (125 MHz, C_6D_6) δ 151.5, 146.8, 140.1, 134.8, 128.8, 128.0, 124.6, 103.3, 75.5, 35.8, 28.3, 28.2, 20.9, 20.5, 19.5, 18.5, 15.9, 13.0; ^{13}C NMR of minor regioisomer (125 MHz, C_6D_6) δ 150.5, 150.2, 139.7, 137.4, 128.9, 127.6, 124.9, 98.3, 76.1, 36.1, 28.01, 28.05, 20.6, 20.1, 19.9, 18.4, 17.4, 12.9; IR (thin film) 3444, 2941, 2864, 1609, 1594, 1381, 1252, 1149 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{32}H_{58}NOSi_2$ $(M+H)^+$ 528.4057, found 528.4074. The major and minor regioisomers were not separated. The ^{1}H and ^{13}C NMR resonances were assigned based on relative peak intensity that matched the regioisomeric ratio and a ^{1}H-^{13}C HMQC experiment.



5e

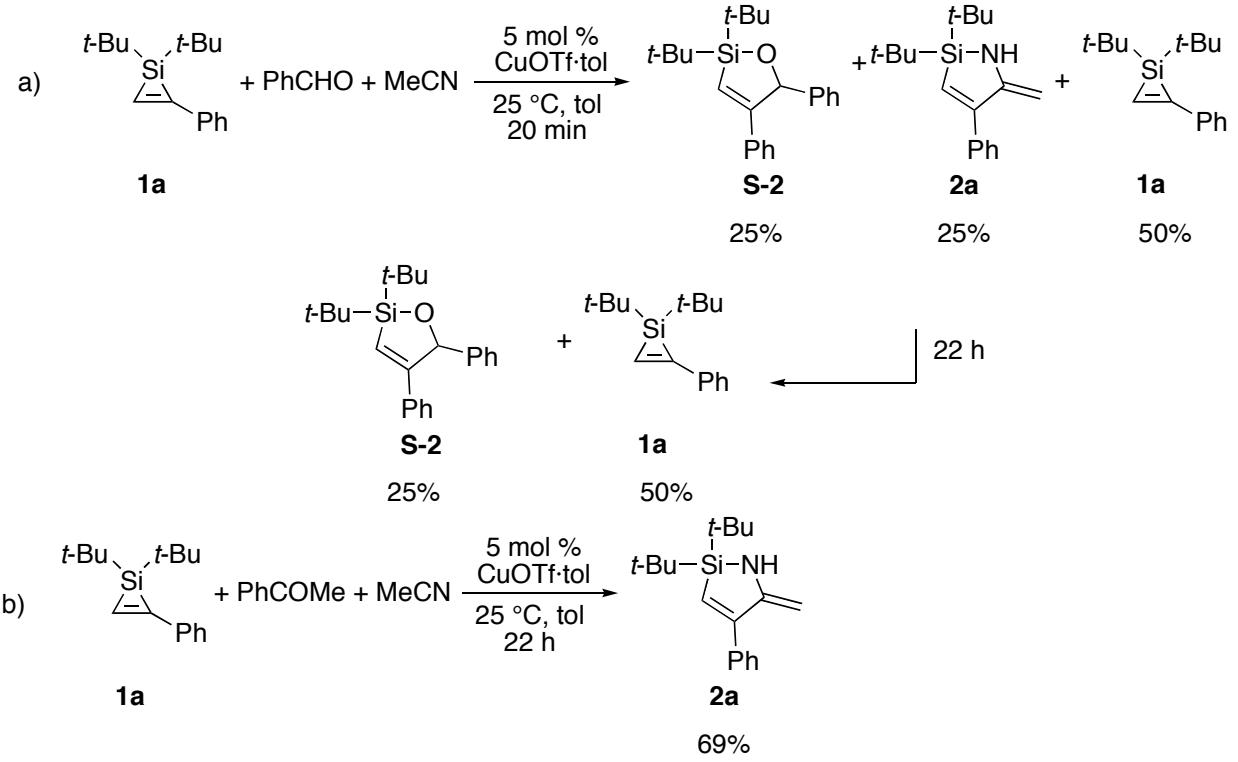
Azasilacyclopentene 5e, Table 2, Entry 5. The representative procedure for the synthesis of azasilacyclopentadienes was followed using silacyclopropene **4d** (920 mg, 2.32 mmol), phenyl acetonitrile (272 mg, 2.32 mmol), $(CuOTf)_2$•tol (60 mg, 0.12 mmol), and 20 mL of toluene for 24 h at 55 °C. Isolation by extraction afforded **5e** (1.012 g, 85%) as a light yellow oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.64-7.55 (m, 2H), 7.30-7.20 (m, 2H), 7.04-6.96 (m, 1H), 6.09 (s, 1H), 4.27 (bs, 1H), 2.52-2.42 (m, 2H), 1.77-1.64 (m, 3H), 1.55-1.34 (m, 4H), 1.27-1.16 (m, 12H), 1.14-1.07 (m, 6H), 1.05 (s, 18H), 0.99 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 156.7, 145.8,

139.3, 128.9, 127.6, 124.7, 114.8, 97.1, 32.7, 29.5, 28.2, 23.7, 20.8, 18.6, 18.1, 14.2; IR (thin film) 3450, 2959, 2865, 1630, 1596, 1466, 1385, 1260, 1054 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{31}H_{56}NOSi_2$ $(M+H)^+$ 514.3901, found 514.3915.

III. Intermolecular Competition Experiment for Acetonitrile Insertion of 1a.

This competition experiment is not described in the text but was conducted to relate the results of this project to previous carbonyl compound insertion reactions of silacyclopropenes and silacyclopropanes developed in our group.[2,5]

Scheme S-1

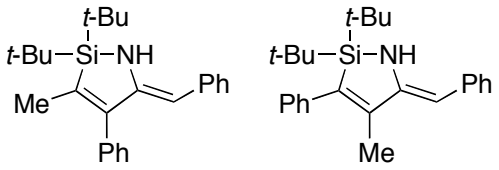


Competition experiment between benzaldehyde and acetonitrile (Scheme S-1a). To a solution of silacyclopropene **1a** (38 mg, 0.16 mmol) and phenyltrimethylsilane (13 mg, 0.084 mmol) in 0.25 mL of C_6D_6 was added a solution of benzaldehyde (17 mg, 0.16 mmol) and acetonitrile (6 mg, 0.2 mmol) in 0.25 mL of C_6D_6. $(CuOTf)_2$•tol (4 mg, 0.08 mmol) was added to the reaction mixture and the solution was transferred to an NMR tube. After 20 min a ^1H NMR experiment showed 25% conversion to oxasilacyclopentene **S-2**, 25% conversion to azasilacyclopentadiene **2a**, and 50% remaining **1a**. After 22 h at ambient temperature, a ^1H NMR experiment showed 25% conversion to oxasilacyclopentene **S-2**, decomposition of **2a**, and 45% **1a**. Published ^1H NMR data for oxasilacyclopentene **S-2**[2a]: ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 4H), 7.19 (m, 6H), 6.57 (d, J = 2.0 Hz, 1H), 6.12 (d, J = 2.0 Hz, 1H), 1.07 (s, 9H), 1.05 (s, 9H). Experimental data for oxasilacyclopentene **S-2** from the competition experiment: ^1H

NMR (400 MHz, C_6D_6) δ 7.45 (m, 4H), 7.22 (m, 6H), 6.50 (bs, 1H), 6.24 (bs, 1H), 1.19 (s, 9H), 1.14 (s, 9H).

Competition experiment between acetophenone and acetonitrile (Scheme S1-b). To a solution of silacyclopropene **1a** (48 mg, 0.20 mmol) and phenyltrimethylsilane (16 mg, 0.11 mmol) in 0.25 mL of C_6D_6 was added a solution of acetophenone (24 mg, 0.20 mmol) and acetonitrile (8 mg, 0.2 mmol) in 0.25 mL of C_6D_6. $(CuOTf)_2$•tol (5 mg, 0.01 mmol) was added to the reaction mixture and the solution was transferred to an NMR tube. After 20 min. a ^{1}H NMR experiment showed 50% conversion to azasilacyclopentadiene **2a**, 15% remaining **1a**, and no evidence of the oxasilacyclopentene product. After 22 h at ambient temperature, a ^{1}H NMR experiment showed 69% conversion to **2a**, no remaining **1a**, and no oxasilacyclopentene product.

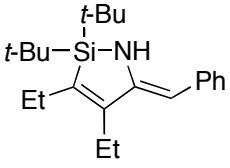
IV. Two-Step, One-Flask Procedure for Nitrile Insertion Reactions



10 : 1

5a

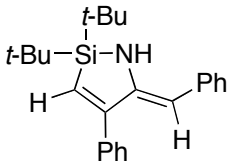
Two-Step, One-Pot Synthesis of Azasilacyclopentadiene 5a. To a solution of 1-phenylpropyne (150 mg, 1.29 mmol) and cyclohexene silacyclopropane (289 mg, 1.29 mmol) in 15 mL of toluene was added $Cu(OTf)_2$ (47 mg, 0.13 mmol). The reaction mixture was then allowed to stir at ambient temperature for 24 h. At this time, phenylacetonitrile was added and the reaction mixture was allowed to stir for an additional 24 h at 55 °C. The reaction mixture was then concentrated under vacuum, dissolved in acetonitrile (~5 mL), and extracted with hexanes (~10 mL). The hexanes solution was filtered through a glass fiber filter pipet plug and concentrated under vacuum to give **5a** (286 mg, 59%) as a yellow oil. The oil was > 90% pure by ^{1}H NMR spectroscopy.



5b

Two-Step, One-Pot Synthesis of Azasilacyclopentadiene 5b. To a solution of 3-hexyne (105 mg, 1.28 mmol) and cyclohexene silacyclopropane (286 mg, 1.28 mmol) in 15 mL of toluene was added $Cu(OTf)_2$ (46 mg, 0.13 mmol). The reaction mixture was then allowed to stir at ambient temperature for 24 h. At this time phenylacetonitrile was added and the reaction

mixture was allowed to stir for an additional 24 h at 55 °C. At this time, the reaction mixture was concentrated under vacuum, dissolved in acetonitrile (~5 mL), and extracted with hexanes (~10 mL). The hexanes solution was filtered through a glass fiber filter pipet plug and concentrated under vacuum to give **5b** (192 mg, 67%) as a yellow oil. The oil was > 90% pure by ^{1}H NMR spectroscopy.

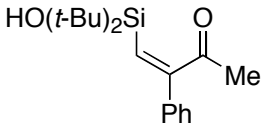


2c

Two-Step, One-Pot Synthesis of Azasilacyclopentadiene 2c. To a solution of phenylacetylene (116 mg, 1.14 mmol) and cyclohexene silacyclopropane (255 mg, 1.14 mmol) in 15 mL of toluene was added Ag_3PO_4 (48 mg, 0.11 mmol). The reaction mixture was then allowed to stir at ambient temperature for 24 h. At this time, the reaction mixture was filtered through a glass fiber filter pipet plug. Phenylacetonitrile (133 mg, 1.14 mmol) and $Cu(OTf)_2$ (39 mg, 0.11 mmol) were then added to the solution and the reaction mixture was allowed to stir for an additional 24 h at ambient temperature. At this time, the reaction mixture was concentrated under vacuum and dissolved in acetonitrile (~5 mL) and extracted with hexanes (~10 mL). The hexanes solution was then filtered through a glass fiber filter pipet plug and concentrated under vacuum to give **2c** (210 mg, 51%) as a yellow oil. The oil was > 90% pure by ^{1}H NMR spectroscopy.

VII. Hydrolysis of Azasilacyclopentadienes

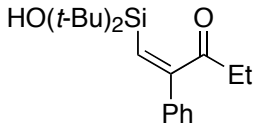
Several azasilacyclopentadienes were hydrolyzed to confirm the identity of the nitrile insertion products.



S-3

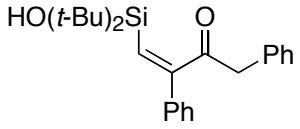
Representative procedure for the hydrolysis of azasilacyclopentadienes. Hydrolysis of azasilacyclopentadiene 2a. To a solution of **2a** (161 mg, 0.563 mmol) in 10 mL of THF was added 10 mL of a saturated aqueous solution of $CuSO_4$. The reaction mixture was allowed to stir for 2 d. At this time the reaction mixture was extracted with MTBE (~50 mL) and water (~30 mL). The MTBE solution was washed with water (~20 mL) and brine (~20 mL), dried with

$MgSO_4$, and concentrated under vacuum to give **S-3** (143 mg, 83%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H), 7.31-7.27 (m, 3H), 6.18 (s, 1H), 3.22 (bs, 1H), 2.25 (s, 3H), 1.10 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 158.9, 140.2, 134.1, 129.0, 128.6, 127.8, 30.8, 28.4, 21.1; HRMS (ESI) *m/z* calcd for $C_{18}H_{28}O_2SiNa$ $(M+Na)^+$ 327.1756, found 327.1758.



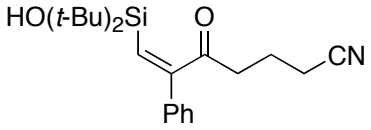
S-4

Hydrolysis of Azasilacyclopentadiene 2b. The representative procedure for the hydrolysis of azasilacyclopentadienes was followed using azasilacyclopentadiene **2b** (256 mg, 0.856 mmol) in 10 mL of THF and 10 mL of a saturated aqueous solution of $CuSO_4$. The reaction mixture was allowed to stir for 2 d at ambient temperature. Purification by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) gave **S-4** (184 mg, 67%) as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 3H), 7.27-7.25 (m, 2H), 6.15 (s, 1H), 2.90 (bs, 1H), 2.53 (q, *J* = 7.2 Hz, 2H), 1.10-1.03 (m, 21H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.1, 158.9, 140.1, 132.9, 128.8, 128.3, 127.0, 36.1, 27.8, 20.5, 8.0; IR (thin film) 3583, 2931, 2856, 1691, 1570, 1491, 1363, 1117 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{30}O_2SiNa$ $(M+Na)^+$ 341.1913, found 341.1917.



S-5

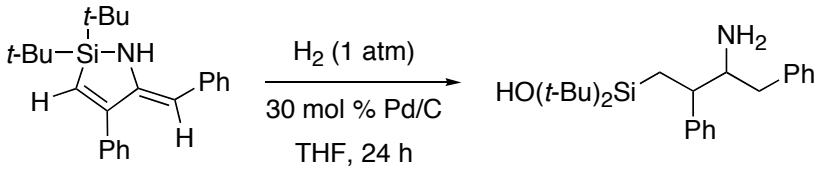
Hydrolysis of Azasilacyclopentadiene 2c. The representative procedure for the hydrolysis of azasilacyclopentadienes was followed using azasilacyclopentadiene **2c** (163 mg, 0.452 mmol) in 10 mL of THF and 10 mL of a saturated aqueous $CuSO_4$ solution. The reaction mixture was allowed to stir for 5 d at ambient temperature. Purification by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) gave **S-5** (77 mg, 45%) as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 3H), 7.29-7.23 (m, 5H), 7.06-7.04 (m, 2H), 6.21 (s, 1H), 3,84 (s, 2H), 2.64 (bs, 1H), 1.05 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.4, 158.6, 139.9, 134.4, 133.8, 130.0, 129.0, 128.7, 128.3, 127.4, 106.8, 49.3, 28.2, 20.7; IR (thin film) 3568, 2930, 2856, 1684, 1560, 1470, 1364, 1073 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{32}O_2SiNa$ $(M+Na)^+$ 403.2069, found 403.2064.



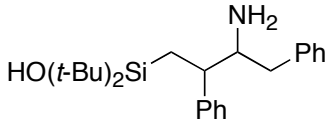
S-6

Hydrolysis of 1,4-Addition Product 10. The representative procedure for the hydrolysis of azasilacyclopentadienes was followed using azasilacyclopentadiene **10** (131 mg, 0.386 mmol) in 10 mL of THF and 10 mL of a saturated aqueous $CuSO_4$ solution. The reaction mixture was allowed to stir for 5 d at ambient temperature. Purification by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) gave **S-6** (90 mg, 66%) as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.37 (m, 2H), 7.33-7.25 (m, 3H), 6.18 (s, 1H), 2.71 (t, J = 6.8 Hz, 2H), 2.42 (t, J = 6.8 Hz, 2H), 1.96 (t, J = 6.9 Hz, 2H), 1.10 (s, 18H) (the Si-OH proton resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 158.5, 139.5, 133.2, 129.2, 128.9, 127.0, 40.9, 30.5, 28.1, 21.1, 16.6; HRMS (ESI) *m/z* calcd for $C_{24}H_{35}NO_2SiNa$ $(M+Na)^+$ 380.2022, found 380.2018.

VIII. Reductions of Azasilacyclopentadienes

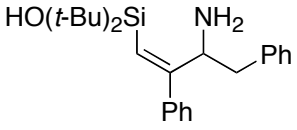


2c **S-7**



S-7

Hydrogenation of azasilacyclopentadiene 2c and synthesis of alkyl amine S-7 (Scheme S-2). To a solution of **2c** (208 mg, 0.576 mmol) in 15 mL of THF was added 10% Pd/C (185 mg, 0.174 mmol). The reaction slurry was then sparged with a balloon of hydrogen for 15 min and then stirred under 1 atm of hydrogen for 24 h. At this time, the reaction mixture was filtered through Celite and concentrated under vacuum. The resultant light yellow oil was purified by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) to give **S-7** as a 1:1 mixture of diastereomers (134 mg, 61%) as a light yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.26 (m, 6H), 7.25-7.18 (m, 8H), 7.18-7.09 (m, 2H), 7.06-7.00 (m, 2H), 7.00-6.93 (m, 2H), 3.22-3.13 (m, 2H), 3.04-2.94 (m, 1H), 2.92-2.80 (m, 2H), 2.92-2.53 (vbs, 6H), 2.64-2.55 (m, 1H), 2.46-2.35 (m, 1H), 2.10-1.97 (m, 1H), 1.40-1.29 (m, 1H), 1.29-1.18 (m, 2H), 1.05 (s, 9H), 0.97 (s, 9H), 0.94 (s, 18H), 1.01-0.99 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 147.1, 139.5, 139.4, 129.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.1, 127.6, 126.6, 126.58, 126.52, 126.4, 60.3, 59.2, 48.7, 47.5, 42.8, 37.9, 28.2, 28.1, 28.0, 27.8, 21.3, 20.9, 20.8, 18.0, 11.8, 11.7; IR (thin film) 3651, 3358, 1878, 1601, 1469, 1363, 1242, 1178 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{38}NOSi$ $(M+H)^+$ 384.2723, found 384.2731.

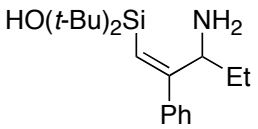


6a

Representative procedure for the selective reduction of the enamine functional group of azasilacyclopentadienes (Table 3, Entry 1, silanol-substituted allylic amine 6a). To a solution of azasilacyclopentadiene **2c** (369 mg, 1.02 mmol) and CSA (594 mg, 2.56 mmol) in 20 mL of THF was added $NaBH_4$ (77 mg, 2.1 mmol). The reaction mixture was allowed to stir at ambient temperature for 36 h. At this time the reaction mixture was partitioned between MTBE (~50 mL) and a saturated solution of aqueous $NaHCO_3$ (~20 mL). The organic layer was washed with water (~20 mL) and brine (~20 mL), dried with $MgSO_4$, and concentrated under vacuum to afford **6a** (349 mg, 90%) as a light yellow oil. Purity of product was > 90% by 1H NMR spectroscopy.

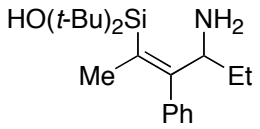
Representative procedure for the selective reduction of the enamine functional group of azasilacyclopentadienes with purification (Table 3, Entry 1, silanol-substituted allylic amine 6a). To a solution of azasilacyclopentadiene **2c** (583 mg, 1.62 mmol) and CSA (939 mg, 4.04 mmol) in 20 mL of THF was added $NaBH_4$ (122 mg, 3.23 mmol). The reaction mixture was allowed to stir at ambient temperature for 36 h. At this time the reaction mixture was partitioned between MTBE (~50 mL) and a saturated solution of aqueous $NaHCO_3$ (~20 mL). The organic layer was washed with water (~20 mL) and brine (~20 mL), dried with $MgSO_4$, and concentrated under vacuum. The resultant light yellow oil was purified by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) to afford **6a** (615 mg, 59%) as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 4H), 7.36-7.27 (m, 3H), 7.26-7.21 (m, 3H), 5.95 (s, 1H), 4.43-1.47 (vbs, 3H), 4.33-4.26 (m, 1H), 3.06-2.86 (m, 2H), 1.17 (s, 9H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 146.4, 139.0, 129.4, 129.0, 128.6, 127.8, 127.7, 127.0, 126.9, 57.8, 43.4, 28.7, 28.4, 21.1, 20.5; IR (thin film) 3363, 3298, 2929, 2854, 1654, 1592, 1570, 1493, 1362, 1214 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{36}NOSi$ $(M+H)^+$ 382.2566, found 382.2573.

Evidence that silanol-substituted allylic amines stick to silica gel and that a significant decrease in yield is observed after purification by flash chromatography. Purified compound **6a** (615 mg, 1.62 mmol) was resubjected to flash chromatography conditions (98:2 hexanes: EtOAc – 80:20 hexanes: EtOAc). Chromatography afforded compound **6a** (468 mg, 78%) as a light yellow oil. No other products were isolated. This experiment suggests that when silanol-substituted allylic amines are purified by chromatography, only 78% of the product present in the crude material will be recovered.



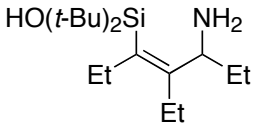
6b

Table 3, Entry 2, silanol-substituted allylic amine 6b. The representative procedure for the synthesis of siloxy-substituted allylic amines was followed using azasilacyclopentadiene **2b** (190 mg, 0.635 mmol), CSA (438 mg, 1.59 mmol), $NaBH_4$ (57 mg, 1.3 mmol), and 15 mL of THF for 36 h at ambient temperature. The product **6b** (193 mg, 95%) was isolated as a light yellow oil. Purification by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) afforded **6b** (121 mg, 60%) as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.13 (m, 5H), 5.85 (s, 1H), 4.38-3.28 (vbs, 3H), 4.07-3.99 (m, 1H), 1.87-1.65 (m, 2H), 1.10 (s, 9H), 1.04 (s, 9H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 147.0, 128.4, 127.4, 127.1, 126.9, 57.7, 30.6, 28.6, 28.4, 21.1, 20.4, 11.9; IR (thin film) 3359, 3279, 2930, 2855, 1591, 1471, 1385, 1119 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{34}NOSi$ $(M+H)^+$ 320.2410, found 320.2411.



6c

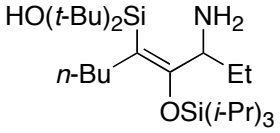
Table 3, Entry 4, silanol-substituted allylic amine 6c. The representative procedure for the synthesis of siloxy-substituted allylic amines was followed using azasilacyclopentadiene **5a** (234 mg, 0.91 mmol), CSA (367 mg, 2.26 mmol), $NaBH_4$ (48 mg, 1.8 mmol), and 15 mL of THF for 36 h at ambient temperature. The reaction afforded **6c** (199 mg, 80%) as a light yellow oil. Purification by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) afforded **6c** (79 mg, 32%) as a light yellow foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.36 (m, 2H), 7.32-7.22 (m, 4H), 7.18-7.12 (m, 2H), 7.09-7.02 (m, 2H), 4.06-3.96 (m, 1H), 3.06-2.98 (m, 1H), 2.92-2.79 (m, 1H), 2.00-1.47 (vbs, 3H), 1.56 (s, 3H), 1.19 (s, 9H), 1.13 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) δ 156.9, 141.0, 139.5, 129.6, 128.9, 128.7, 128.6, 127.0, 126.3, 123.2, 67.2, 45.0, 28.9, 28.4, 21.8, 20.6, 16.2; IR (thin film) 3449, 3026, 2928, 2853, 1603, 1470, 1362, 1285, 1103 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{38}NOSi$ $(M+H)^+$ 396.2723, found 396.2719.



6d

Table 3, Entry 3, silanol-substituted allylic amine 6d. The representative procedure for the synthesis of siloxy-substituted allylic amines was followed using azasilacyclopentadiene **5b** (291 mg, 1.30 mmol), CSA (496 mg, 3.25 mmol), $NaBH_4$ (65 mg, 2.6 mmol), and 15 mL of THF for 36 h at ambient temperature. The product **6d** (253 mg, 82%) was isolated as a light yellow oil:

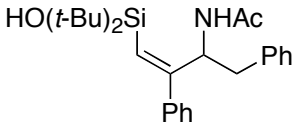
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 4H), 7.13-7.05 (m, 1H), 4.13-4.05 (m, 1H), 3.15-3.06 (m, 1H), 2.44-2.32 (m, 1H), 2.32-2.23 (m, 1H), 2.23-2.15 (m, 2H), 2.08-1.96 (m, 1H), 1.15-1.07 (m, 12H), 1.02 (t, J = 7.2 Hz, 3H), 0.94 (s, 9H), (Si-OH and NH_2 resonances were too broad to be observed); ^{13}C NMR (100 MHz, C_6D_6) δ 158.1, 141.1, 133.4, 129.7, 128.8, 126.4, 64.3, 44.7, 29.2, 28.6, 22.4, 21.8, 21.1, 20.4, 15.5, 13.8; IR (thin film) 3452, 2930, 2854, 1603, 1591, 1469, 1383, 1088 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{22}H_{40}NOSi$ $(M+H)^+$ 362.2879, found 362.2876.



6e

Table 3, Entry 5, silanol-substituted allylic amine 6e. The representative procedure for the synthesis of siloxy-substituted allylic amines was followed using azasilacyclopentadiene **5e** (190 mg, 0.371 mmol), CSA (215 mg, 0.925 mmol), $NaBH_4$ (28 mg, 0.74 mmol), and 15 mL of THF for 36 h at ambient temperature. The product **6e** (174 mg, 88%) was isolated as a light yellow oil: ^{1}H NMR (400 MHz, C_6D_6) δ 7.37-7.31 (m, 2H), 7.18-7.13 (m, 2H), 7.10-7.03 (m, 1H), 3.50-3.35 (m, 2H), 3.15-3.07 (m, 1H), 2.40-2.29 (m, 1H), 2.22-2.12 (m, 1H), 2.09-1.96 (m, 1H), 1.73-1.58 (m, 2H), 1.45 (s, 9H), 1.29 (s, 9H), 1.15-1.08 (m, 22H), 1.06-1.00 (m, 3H) (Si-OH and NH_2 resonances were too broad to be observed); ^{13}C NMR (100 MHz, C_6D_6) δ 161.4, 139.2, 129.7, 129.1, 127.1, 114.2, 59.4, 43.5, 35.0, 32.0, 31.5, 31.0, 30.1, 29.6, 24.2, 22.3, 18.5, 14.4; IR (thin film) 3453, 2944, 2865, 1592, 1467, 1364, 1258, 1196, 1050 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{31}H_{60}NO_2Si_2$ $(M+H)^+$ 534.4163, found 534.4164.

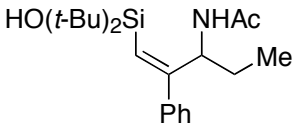
IX. Reduction and Protection of Azasilacyclopentadienes



7

Silanol-substituted allylic amide 7. To a solution of azasilacyclopentadiene **2c** (369 mg, 1.02 mmol) and CSA (594 mg, 2.56 mmol) in 20 mL of THF was added $NaBH_4$ (77 mg, 2.0 mmol). The reaction mixture was allowed to stir at ambient temperature for 36 h. At this time the

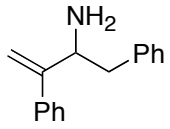
reaction mixture was partitioned between MTBE (~ 50 mL) and a saturated solution of aqueous $NaHCO_3$ (~20 mL). The organic layer was washed with water (~20 mL) and brine (~20 mL), dried with $MgSO_4$, and concentrated under vacuum to afford **6a** (349 mg) as a light yellow oil. To a solution of **6a** (349 mg, 0.916 mmol) and DMAP (246 mg, 2.13 mmol) in 4 mL of CH_2Cl_2 was added acetic anhydride (173 μL, 1.93 mmol). The reaction was allowed to stir at ambient temperature for 24 h. At this time, the reaction mixture was partitioned between CH_2Cl_2 (~ 30 mL) and water (~30 mL). The organic layer was washed with water (~20 mL) and brine (~20 mL), dried with $MgSO_4$, and concentrated under vacuum. The resultant light yellow foam was purified by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) to afford **7** (347.8 mg, 82%) as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.32 (m, 3H), 7.31-7.18 (m, 5H), 7.17-7.12 (m, 2H), 5.89 (bs, 1H), 5.79-5.70 (m, 1H), 5.65 (s, 1H), 3.10-3.01 (m, 1H), 2.58-2.46 (m, 1H), 1.87 (s, 3H), 1.14 (s, 9H), 1.06 (s, 9H) (Si-OH resonance was too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 158.7, 143.7, 137.3, 128.6, 128.4, 128.2, 128.1, 127.9, 127.2, 126.5, 53.6, 40.2, 27.87, 27.86, 23.2, 20.4, 20.3; IR (thin film) 3411, 2931, 2856, 1644, 1495, 1347, 1266 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{26}H_{38}NO_2Si$ $(M+H)^+$ 424.2672, found 424.2659.



8

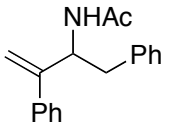
Silanol-substituted allylic amide 8. To a solution of azasilacyclopentadiene **2b** (254 mg, 0.850 mmol) and CSA (494 mg, 2.13 mmol) in 20 mL of THF was added $NaBH_4$ (64 mg, 1.7 mmol). The reaction mixture was allowed to stir at ambient temperature for 36 h. At this time the reaction mixture was extracted partitioned between MTBE (~50 mL) and a saturated solution of aqueous $NaHCO_3$ (~20 mL). The organic layer was washed with water (~20 mL) and brine (~20 mL), dried with $MgSO_4$, and concentrated under vacuum to afford **6b** (250 mg) as a light yellow oil. To a solution of **6b** (250 mg, 0.783 mmol) and DMAP (242 mg, 1.96 mmol) in 4 mL of CH_2Cl_2 was added acetic anhydride (113 μL, 1.57 mmol). The reaction was allowed to stir at ambient temperature for 24 h. At this time, the reaction mixture was partitioned between CH_2Cl_2 (~30 mL) and water (~20 mL). The organic layer was washed with water (~20 mL) and brine (~20 mL), dried with $MgSO_4$, and concentrated under vacuum. The resultant light yellow foam was purified by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) to afford **8** (160 mg, 56%) as a light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.24 (m, 3H), 7.21-7.12 (m, 2H), 6.00 (bs, 1H), 5.83 (bs, 1H), 5.57 (s, 1H), 5.21-5.08 (m, 1H), 2.02 (s, 3H), 1.71-1.54 (m, 1H), 1.45-1.29 (m, 1H), 1.09 (s, 9H), 1.03 (s, 9H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 170.4, 158.4, 144.0, 128.5, 128.2, 128.1, 127.2, 55.1, 28.1, 28.0, 27.8, 23.7, 20.7, 20.3, 11.3; IR (thin film) 3272, 2963, 2856, 1645, 1550, 1471, 1383, 856, 822, 699 cm^{-1}; HRMS (ESI) *m/z* calc for $C_{21}H_{36}NO_2Si$ $(M+H)^+$ 384.2335, found 384.2337.

X. Protodesilylation of Silanol-Substituted Allylic Amines.



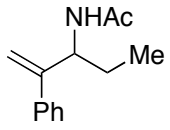
9a

Representative procedure for the protodesilylation of silanol-substituted allylic amines and allylic amides (Table 4, Entry 1, allylic amine 9a). To a slurry of KO(*t*-Bu) (609 mg, 5.42 mmol) in 20 mL of DMSO was added a mixture of **6a** (345 mg, 0.906 mmol) in 5.4 mL (5.4 mmol) of a 1.0 M THF solution of TBAF. The reaction mixture was heated to 120 °C for 36 h. At this time the reaction mixture was cooled and extracted with MTBE (~30 mL) and water (~50 mL). The MTBE solution was washed with water (~50 mL) and brine (~30 mL), dried with $MgSO_4$, and concentrated under vacuum. The resultant orange oil was purified by flash chromatography (98:2 hexanes: EtOAc – 60:40 hexanes:EtOAc) to give **9a** (150 mg, 74%) as a light yellow foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2H), 7.41-7.35 (m, 2H), 7.35-7.28 (m, 3H), 7.25-7.17 (m, 3H), 5.34-5.29 (m, 2H), 4.21-4.13 (m, 1H), 3.01-2.94 (m, 1H), 2.54-2.45 (m, 1H), 1.50 (bs, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 153.2, 141.6, 139.5, 129.8, 128.8, 128.2, 128.0, 127.3, 126.8, 112.6, 56.2, 43.5; IR (thin film) 3358, 3027, 2932, 2855, 1668, 1628, 1600, 1494, 1453, 1386, 1060, 1028, 907, 778, 698 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{18}N$ $(M+H)^+$ 224.1439, found 224.1431.



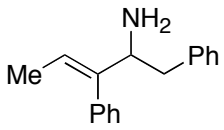
9b

Table 4, Entry 2, allylic amide 9b. The representative procedure for the synthesis of allylic amines was followed using silanol-substituted allylic amide **7** (239 mg, 0.562 mmol), KO(*t*-Bu) (380 mg, 3.39 mmol), a 1M THF solution of TBAF (3.4 mL, 3.4 mmol), and 14 mL of DMSO. The reaction mixture was heated to 120 °C for 36 h. Purification by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) afforded **9b** (103 mg, 55%) as a light yellow foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.40-7.35 (m, 2H), 7.35-7.29 (m, 1H), 7.29-7.25 (m, 2H), 7.24-7.18 (m, 1H), 7.18-7.13 (m, 2H), 5.77-5.67 (bd, 1H), 5.40-5.32 (m, 1H), 5.32-5.29 (m, 1H), 5.15-5.07 (m, 1H), 3.04-2.95 (m, 1H), 2.83-2.73 (m, 1H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 149.3, 140.4, 137.4, 129.5, 128.7, 128.5, 128.0, 127.1, 126.8, 113.2, 53.0, 39.9, 23.5; IR (thin film) 3648, 3269, 2929, 2856, 1752, 1647, 1551, 1495, 1454, 1372, 1302 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{20}NO$ $(M+H)^+$ 288.1364, found 288.1366.



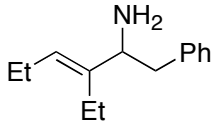
9c

Table 4, Entry 3, allylic amide 9c. The representative procedure for the synthesis of allylic amines was followed using silanol-substituted allylic amide **8** (123 mg, 0.341 mmol), KO(*t*-Bu) (230 mg, 2.05 mmol), a 1.0 M THF solution of TBAF (2.1 mL, 2.1 mmol), and 9 mL of DMSO. The reaction mixture was heated to 120 °C for 36 h. Purification by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) afforded **9** (51 mg, 74%) as a light yellow foam: ^{1}H NMR (400 MHz, C_6D_6) δ 7.51-7.41 (m, 2H), 7.21-7.11 (m, 2H), 7.11-7.02 (m, 1H), 5.50 (bs, 1H), 5.24-5.18 (m, 1H), 5.15-5.07 (m, 1H), 5.07-5.04 (m, 1H), 1.62 (s, 3H), 1.58-1.54 (m, 1H), 1.35-1.24 (m, 1H), 0.79 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 168.6, 151.2, 141.3, 128.6, 127.9, 127.2, 112.1, 53.7, 27.6, 22.9, 10.8; IR (thin film) 3200, 3059, 2966, 2875, 1651, 1538, 1443, 1373, 1298, 1101, 1040, 905, 778, 700 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{18}NO$ $(M+H)^+$ 226.1208, found 226.1210.



9d

Table 4, Entry 4, allylic amine 9d. The representative procedure for the synthesis of allylic amines was followed using silanol-substituted allylic amine **6c** (401 mg, 1.02 mmol), KO(*t*-Bu) (684 mg, 6.09 mmol), a 1.0 M THF solution of TBAF (6.1 mL, 6.1 mmol), and 24 mL of DMSO. The reaction mixture was heated to 120 °C for 36 h. Purification by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) afforded **9d** (131 mg, 54%) as a light yellow foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.37 (m, 2H), 7.34-7.26 (m, 3H), 7.24-7.14 (m, 5H), 5.88-5.72 (m, 1H), 3.90-3.83 (m, 1H), 2.94-2.87 (m, 1H), 2.48-2.38 (m, 1H), 1.55 (d, J = 6.8 Hz, 3H), 1.28 (bs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 139.8, 139.5, 129.42, 129.41, 128.5, 128.3, 126.9, 126.4, 121.5, 59.2, 43.3, 14.6; IR (thin film) 3372, 3305, 3025, 2915, 2856, 1601, 1493, 1335, 1075, 1030 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{17}H_{20}N$ $(M+H)^+$ 238.1596, found 238.1589.

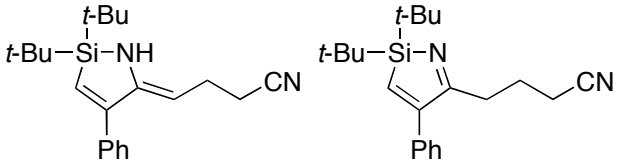


9e

Table 4, Entry 5, allylic amine 9e. The representative procedure for the synthesis of allylic amines was followed using silanol-substituted allylic amine **6d** (141 mg, 0.388 mmol), KO(*t*-Bu) (263 mg, 2.34 mmol), a 1.0 M THF solution of TBAF (2.3 mL, 2.3 mmol), and 10 mL of

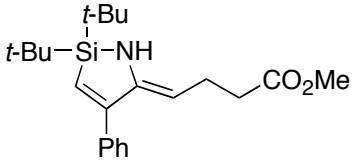
DMSO. The reaction mixture was heated to 120 °C for 36 h. Purification by flash chromatography (98:2 hexanes:EtOAc – 80:20 hexanes:EtOAc) afforded **9e** (46 mg, 58%) as a light yellow foam: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.31 (m, 2H), 7.29-7.23 (m, 3H), 5.37 (t, J = 7.2 Hz, 1H), 3.61-3.54 (m, 1H), 2.98-2.92 (m, 1H), 2.63-2.55 (m, 1H), 2.30-2.20 (m, 1H), 2.17-2.07 (m, 3H), 1.32 (bs, 2H), 1.11 (t, J = 7.5Hz, 3H), 1.02 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 140.0, 129.5, 128.5, 126.9, 126.3, 58.7, 43.9, 21.6, 21.0, 14.8, 14.7; IR (thin film) 3372, 3305, 3025, 2915, 2856, 1601, 1493, 1335, 1075 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{22}N$ $(M+H)^+$ 204.1752, found 204.1754.

V. 1,4-Addition Reactions of Azasilacyclopentadienes



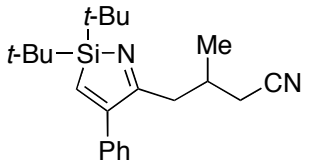
3 : 1
10

Representative procedure for 1,4-addition reactions of azasilacyclopentadiene 2a. Synthesis of 1,4-addition product 10. To a solution of **2a** (217 mg, 0.759 mmol) in 10 mL of toluene was added acrylonitrile (40 mg, 0.76 mmol) followed by $ZnOTf_2$ (28 mg, 0.076 mmol). The reaction mixture was then allowed to stir at ambient temperature for 48 h. At this time the reaction mixture was concentrated under vacuum. The resultant red oil was extracted with hexanes (~10 mL), filtered through a glass fiber filter pipet plug, and concentrated under vacuum to give a 3:1 tautomeric mixture of **10** (152 mg, 59%) as a red foam: ^{1}H NMR of enamine tautomer (500 MHz, $CDCl_3$) δ 7.46-7.39 (m, 2H), 7.34-7.19 (m, 3H), 5.99 (s, 1H), 4.34 (t, J = 7.3 Hz, 1H), 3.46 (bs, 1H), 1.98-1.89 (m, 2H), 1.55 (t, J = 7.3 Hz, 2H), 1.14 (s, 18H); ^{1}H NMR of imine tautomer (500 MHz, $CDCl_3$) δ 7.46-7.39 (m, 2H), 7.34-7.19 (m, 3H), 6.37 (s, 1H), 3.02-2.93 (m, 2H), 1.84-1.75 (m, 2H), 1.70-1.56 (m, 2H), 1.19 (s, 18H); ^{13}C NMR of enamine tautomer (125 MHz, $CDCl_3$) δ 159.0, 149.8, 143.4, 140.2, 128.9, 127.92, 125.7, 119.5, 99.0, 28.0, 23.4, 20.7, 16.7; ^{13}C NMR of imine tautomer (125 MHz, $CDCl_3$) δ 184.5, 160.6, 149.0, 139.0, 128.6, 127.98, 127.4, 118.8, 40.8, 30.1, 28.2, 19.2, 14.1; IR (thin film) 3410, 2930, 2856, 1631, 1471, 1371, 1328, 1139 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{22}H_{31}N_2Si$ $(M+H)^+$ 339.2256, found 339.2263.



11

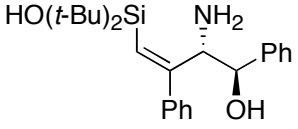
Synthesis of 1,4-addition product 11. The representative procedure for 1,4-addition reactions was followed using insertion product **2a** (79 mg, 0.28 mmol), methylacrylate (24 mg, 0.28 mmol), $ZnOTf_2$ (10 mg, 0.028 mmol), and 10 mL of toluene. The reaction mixture was allowed to stir at ambient temperature for 48 h. Isolation by hexanes extraction afforded **11** (91 mg, 88%) as a red oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.22-7.14 (m, 3H), 5.92 (s, 1H), 4.54 (t, J = 7.2 Hz, 1H), 3.97 (bs, 1H), 3.31 (s, 3H), 2.36 (q, J = 7.2 Hz, 2H), 2.13 (t, J = 7.0 Hz, 2H), 1.11 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 159.5, 149.4, 140.6, 129.0, 128.1, 127.2, 125.1, 101.7, 50.8, 33.9, 28.0, 22.6, 20.8; IR (thin film) 2929, 2855, 1736, 1632, 1471, 1364, 1171 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{22}H_{34}N_2Si$ $(M+H)^+$ 372.2359, found 372.2371.



12

Synthesis of 1,4-addition product 12. The representative procedure for 1,4-addition reactions was followed using insertion product **2a** (191 mg, 0.668 mmol), methylacrylonitrile (45 mg, 0.67 mmol), $ZnOTf_2$ (24 mg, 0.067 mmol), and 10 mL of toluene. The reaction mixture was allowed to stir at 55°C for 48 h. Isolation by hexanes extraction afforded **12** (100 mg, 42%) as a purple foam: ^{1}H NMR (400 MHz, C_6D_6) δ 7.39-7.31 (m, 2H), 7.23-7.10 (m, 3H), 5.89 (s, 1H), 4.21 (d, J = 9.1 Hz, 2H), 2.40-2.26 (m, 1H), 1.69-1.59 (m, 1H), 1.50-1.41 (m, 1H), 1.11 (s, 9H), 1.07 (s, 9H), 0.77 (d, J = 6.6 Hz, 3H); ^{13}C NMR (400 MHz, C_6D_6) δ 159.4, 148.9, 140.5, 129.1, 128.1, 127.6, 126.2, 119.4, 105.6, 30.4, 29.6, 28.3, 24.4, 21.0, 20.9, 20.4; IR (thin film) 3402, 2929, 2856, 2280, 1629, 1471, 1381, 1169 cm^{-1}; HRMS (APCI) *m/z* calcd for $C_{22}H_{33}N_2Si$ $(M+H)^+$ 353.2413, found 353.2416.

VI. Hydroboration and Oxidation of an Azasilacyclopentadiene



13

Synthesis of amino alcohol 13. To a solution of **2c** (243 mg, 0.673 mmol) in 10 mL of THF cooled to 0°C was added BH_3•SMe_2 (55.0 μL, 0.65 mmol). The reaction mixture was allowed to warm to ambient temperature and stir for 48 h. At this time the reaction mixture was vented to air with a needle and cooled to 0 °C. 2.5 mL of a 15% aqueous solution of NaOH and 2.5 mL of a 50% aqueous solution of H_2O_2 were added to the cooled reaction mixture, which was then allowed to warm to ambient temperature and stir for 12 h. At this time, the reaction mixture was partitioned between a 1M aqueous solution of KCO_3 (~20 mL) and MTBE (~20 mL). The MTBE solution was then washed with water (~ 20 mL) and brine(~20 mL), dried with $MgSO_4$, and concentrated under vacuum to give **13** (228 mg, 85%) as a light yellow foam. Purification

by flash chromatography (98:2 hexanes;EtOAc – 80:20 hexanes:EtOAc) afforded **10** (118 mg, 44%) as a light yellow foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.50 (m, 4H), 7.46-7.31 (m, 6H), 6.19 (s, 1H), 5.07 (d, J = 9.1 Hz, 1H), 4.28 (d, J = 9.1Hz, 1H), 1.20 (s, 9H), 1.10 (s, 9H) (NH_2, Si-OH, and C-OH resonances were too broad to be observed); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 146.9, 141.8, 129.6, 129.0, 128.6, 128.5, 127.6, 127.3, 127.2, 79.4, 61.1, 28.5, 28.3, 21.2, 20.5; IR (thin film) 3356, 3060, 2929, 2855, 1590, 1570, 1471, 1080, 1025 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{34}NO_2Si$ $(M+H)^+$ 398.2515, found 398.2520.

XI. References

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