

Supporting Information

Activation of sp^3 C-H Bonds with Cobalt(I): Catalytic Synthesis of Enamines

*Andrew D. Bolig and Maurice Brookhart**

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

Email: mbrookhart@unc.edu

I. General Considerations. All reactions, unless stated otherwise, were conducted under an atmosphere of dry, oxygen-free argon using standard Schlenk or drybox techniques¹. Argon was purified by passage through BASF R3-11 catalyst (Chemalog) and 4Å molecular sieves. Catalysts and transfer products were stored in an Argon-filled M. Braun glovebox freezer at -35°C. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX 400MHz or Bruker 400MHz AVANCE spectrometer. ¹H and ¹³C chemical shifts were referenced to residual ¹H NMR signals and to the ¹³C NMR signals of the deuterated solvents, respectively. High resolution mass spectrometry was performed with a Bruker BioTOF II reflectron time-of-flight mass spectrometer (Billerica, MA) equipped with the Apollo electrospray ionization source. Data was collected in positive ionization mode, and samples were injected at a flow rate of 65 μL/hr.

II. Materials. Alkanes were dried by passage over columns of activated alumina² and deoxygenated by sparging with nitrogen.³ THF was dried by distillation from sodium/benzophenone ketyl under nitrogen. CDCl₃, C₆D₆, and C₆D₁₂ were dried over 4Å molecular sieves and degassed via three freeze-pump-thaw cycles. Amines and n-BuLi (2.5M in hexanes) were purchased from Aldrich and used as received. Chlorodimethylvinylsilane was purchased from Gelest and used as received. [(Cp*)Co(VTMS)₂] (**1**)⁴ and [(Cp*)Rh(VTMS)₂] (**2**)⁵ were synthesized by literature procedures.

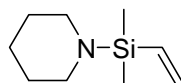
III. Preparation of (vinyl)silyl-protected amines. The general procedures for the synthesis of all N-(dimethylvinyl)silyl amines are analogous to those described below for N-(dimethylvinyl)silyl morpholine.

Morpholine (8.75 mL, 100 mmol) was dissolved in 30 mL THF in a 100mL Schlenk flask and cooled to 0°C. 40 mL of a 2.5M solution of n-butyl lithium were added dropwise over 15 minutes from a dropping funnel. The solution was allowed to warm to room temperature and stirred for one hour. The solution was again cooled to 0°C and chlorodimethylvinyl silane (13.8 mL, 100 mmol) was added dropwise via addition funnel over 30 minutes. White precipitate formed, and the solution was stirred for 3h at room temperature after addition was complete. Cessation of stirring allowed most LiCl to precipitate. The supernatant was transferred via cannula into a Schlenk frit containing a pad of oven-dried Celite; filtrate was collected in a 50mL round-bottom flask by applying partial vacuum. Distillation under argon removed residual THF and hexanes. The resultant oil was purified by vacuum distillation through a short Vigreux column. Fraction with boiling point 76-78°C (2.0mm Hg) was collected: 14.05g (82%). Effective separations were generally achieved with a vacuum of ca. 2mm Hg (determined by Hg manometer), with the exception of less volatile **17**, **19**, and **21** which required ca. 0.2 mm Hg vacuum, measured by an Edwards Pirani 501 analog vacuum gauge.

IV. Procedure for Catalytic Hydrogen Transfer. Method 1 (NMR scale): An oven-dried J. Young Teflon screw-cap NMR tube was charged with catalyst **1** or **2** (0.01mmol, 4 mol%), substrate (0.25 mmol), and 500 mg dry, degassed C₆D₁₂ in an argon-filled M.Braun glovebox. The tube was sealed, then submerged (~80%) in an oil bath (80°C for reactions with **1** or 140°C for reactions with **2**) for the desired reaction time. Conversion was monitored by cooling the tube to room temperature then collecting NMR spectra without further workup.

Method 2: (Preparative Scale) A flame dried 10-mL Kontes flask with Teflon screw-cap and stir bar was charged with catalyst **1** or **2** (0.1 mmol, 2 mol%), substrate (5 mmol), and 8 mL dry, degassed pentane in an Argon-filled M.Braun glovebox. The flask was sealed, then submerged in an oil bath (80°C for reactions with **1** or 140°C for reactions with **2**) for the desired reaction time. The crude reaction mixture was cooled to room temperature and transferred to a flame-dried round bottom flask with stir bar via cannula. The solvent was distilled off under argon. The collector was switched under Ar flow, and the product then vacuum distilled away from the catalyst residues. Products may be handled briefly on the benchtop, but were stored in an argon-filled M.Braun glovebox to prevent decomposition.

V. Characterization of Substrates



3

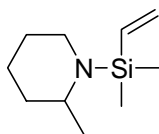
1-(dimethyl(vinyl)silyl)piperidine

¹H NMR (400 MHz, 20°C, CDCl₃) δ6.09 (dd, J = 20.2 Hz, 14.6 Hz, -CH=CH₂, 1H), 5.92 (dd, J = 14.8 Hz, 4.0Hz, -CH=C(*H cis*)H, 1H), 5.67(dd, J = 20.2 Hz, 4.2 Hz, -CH=C(*H trans*)H, 1H), 2.79 (t, 5.2 Hz, N-(CH₂)₂, 4H), 1.53 (m, CH₂(CH₂CH₂)₂N, 2H), 1.37 (m, CH₂CH₂)₂ N, 4H), 0.08 (s, 6H, Si(CH₃)₂)

^{13}C NMR (100.6 MHz, 20°C, CDCl_3) δ 139.33 (Si-C(H)=), 131.55 (-C(H)=CH₂), 46.46 ((CH₂)₂N), 27.77 ((CH₂CH₂)₂N), 25.55 (CH₂(CH₂CH₂)₂N), -2.57 (Si-(CH₃)₂)

Collected distillate 69-71°C (2.0mm Hg)

HRMS-ESI (m/z): [M-H]⁺ calcd for [C₉H₁₉NSi + H⁺], 170.137; found, 170.137.



5

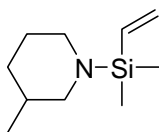
2-methyl-1-(dimethyl(vinyl)silyl)piperidine

^1H NMR (400 MHz, 20°C, CDCl_3) δ 6.10 (dd, J = 20.2 Hz, 14.6 Hz, -CH=CH₂, 1H), 5.89 (dd, J = 14.4 Hz, 4.0 Hz, -CH=C(*H cis*)H, 1H), 5.67 (dd, J = 20.0 Hz, 4.0 Hz, -CH=C(*H trans*)H, 1H), 3.27 (m, NC(Me)H, 1H), 2.9-2.7 (m, 2H, NCH₂), 1.6-1.2 (m, (CH₂)₃, 6H), 1.14 (t, J = 6.8 Hz, (CH₃)C(H)N), 0.12 (s, Si-(CH₃)₂, 6H)

^{13}C NMR (100.6 MHz, 20°C, CDCl_3) δ 140.21 (Si-C(H)=), 131.14 (-C(H)=CH₂), 46.87 (NCH(Me)), 39.81 (CH₂N), 32.23 (CH₂C(H)(Me)N), 28.03 (CH₂(CH₂)N), 20.18 (CH₂(CH₂)₂N), 17.77 (NC(H)-CH₃), -1.83 (Si-CH₃)₂

Collected distillate 79-80°C (2.0mm Hg)

HRMS-ESI (m/z): [M-H]⁺ calcd for [C₁₀H₂₁NSi + H⁺], 184.152; found, 184.153.



7

3-methyl-1-(dimethyl(vinyl)silyl)piperidine

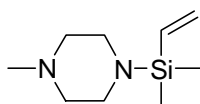
^1H NMR (400 MHz, 20°C, CDCl_3) δ 6.08 (dd, J = 20.2 Hz, 14.6 Hz, -CH=CH₂, 1H), 5.92 (dd, J = 14.8 Hz, 4.2 Hz, -CH=C(*H cis*)H, 1H), 5.67 (dd, J = 20.4 Hz, 4.2 Hz, -CH=C(*H trans*)H, 1H), 3.01 (m, 2H),

2.46 (m, 1H), 2.14 (m, 1H), 1.73 (m, 1H), 1.50 (m, 1H), 1.28 (m, 2H), 0.94 (m, CH(Me)CH₂N, 1H), 0.74 (d, J = 6.6 Hz, HC(CH₃)), 0.06 (s, Si-CH₃), 6H)

¹³C NMR (100.6 MHz, 20°C, CDCl₃) δ 139.31 (Si-C(H)=), 131.58 (-C(H)=CH₂), 53.87 (C(Me)(H)-CH₂N), 45.98 (CH₂CH₂N), 34.15 (CH₂(CH₂)₂N), 32.31 (C(H)(Me)CH₂N), 27.45(CH₂CH₂N), 19.54(-CH-CH₃), -2.52 (Si-(CH₃)₂)

Collected distillate 77-78°C (2.0mm Hg)

HRMS-ESI (*m/z*): [M-H]⁺ calcd for [C₁₀H₂₁NSi + H⁺], 184.152; found, 184.154.



9

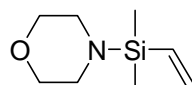
1-methyl-4-(dimethyl(vinyl)silyl)piperazine

¹H NMR (400 MHz, 20°C, CDCl₃) δ 6.05 (dd, J = 20.0 Hz, 14.7 Hz, -CH=CH₂, 1H), 5.92 (dd, J = 14.7 Hz, 4.3Hz, -CH=C(*H cis*)H, 1H), 5.67 (dd, J = 20.0 Hz, 4.2 Hz, -CH=C(*H trans*)H, 1H), 2.86 (t, 4.7 Hz, (CH₂)₂N, 4H), 2.21 (broad s, (CH₂)₂N, overlapping (N-CH₃) 7H), 0.08 (s, 6H, Si(CH₃)₂)

¹³C NMR (100.6 MHz, 20°C, CDCl₃) δ 138.68 (Si-C(H)=), 132.22 (-C(H)=CH₂), 56.74 ((CH₂)₂N-Me), 46.77 (N-CH₃), 45.25 ((CH₂)₂N-Si), -2.71 (Si-(CH₃)₂)

Collected distillate 84-85°C (2.1mm Hg)

HRMS-ESI (*m/z*): [M-H]⁺ calcd for [C₉H₂₀N₂Si + H⁺], 185.147; found, 185.144.



11

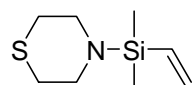
4-(dimethyl(vinyl)silyl)morpholine

^1H NMR (400 MHz, 20°C, CDCl_3) δ 6.04(dd, $J = 20.0$ Hz, 14.6 Hz, $-\text{CH}=\text{CH}_2$, 1H), 5.93 (dd, $J = 14.8$ Hz, 4.4Hz, $-\text{CH}=\text{C}(\text{H } cis)\text{H}$, 1H), 5.68(dd, $J = 20.0$ Hz, 4.4 Hz, $-\text{CH}=\text{C}(\text{H } trans)\text{H}$, 1H), 3.50 (t, 4.4 Hz, $(\text{CH}_2)_2\text{N}$, 4H), 2.80 (t, 4.4 Hz, $(\text{CH}_2)_2\text{O}$, 4H), 0.08 (s, 6H, $\text{Si}(\text{CH}_3)_2$)

^{13}C NMR (100.6 MHz, 20°C, CDCl_3) δ 138.16 ($\text{Si}-\text{C}(\text{H})=$), 132.50 ($-\text{C}(\text{H})=\text{CH}_2$), 68.43 ($(\text{CH}_2)\text{O}$), 45.48($(\text{CH}_2)\text{N}$), -3.03 ($\text{Si}-\text{CH}_3$)₂

Collected distillate 76-78°C (2.0mm Hg)

HRMS-ESI (m/z): $[\text{M}-\text{H}]^+$ calcd for $[\text{C}_8\text{H}_{17}\text{NOSi} + \text{H}^+]$, 172.116; found, 172.117.



13

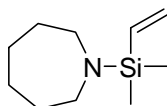
4-(dimethyl(vinyl)silyl)thiomorpholine

^1H NMR (400 MHz, 20°C, CDCl_3) δ 6.05 (dd, $J = 20.0$ Hz, 14.6 Hz, $-\text{CH}=\text{CH}_2$, 1H), 5.94 (dd, $J = 14.8$ Hz, 4.4Hz, $-\text{CH}=\text{C}(\text{H } cis)\text{H}$, 1H), 5.68(dd, $J = 20.0$ Hz, 4.4 Hz, $-\text{CH}=\text{C}(\text{H } trans)\text{H}$, 1H), 3.13 (m, $(\text{CH}_2)_2\text{N}$, 4H), 2.41 (m, $(\text{CH}_2)_2\text{S}$, 4H), 0.08 (s, 6H, $\text{Si}(\text{CH}_3)_2$)

^{13}C NMR (100.6 MHz, 20°C, CDCl_3) δ 138.60 ($\text{Si}-\text{C}(\text{H})=$), 132.32 ($-\text{C}(\text{H})=\text{CH}_2$), 47.33 ($(\text{CH}_2)_2\text{N}$ -), 28.14($(\text{CH}_2)_2\text{S}$ -), -2.43 ($\text{Si}-\text{CH}_3$)₂

Collected distillate 105-106°C (2.0mm Hg)

HRMS-ESI (m/z): $[\text{M}-\text{H}]^+$ calcd for $[\text{C}_8\text{H}_{17}\text{NSSi} + \text{H}^+]$, 188.093; found, 188.095.



15

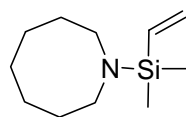
1-(dimethyl(vinyl)silyl)azepane

^1H NMR (400 MHz, 20°C, CDCl_3) δ 6.14 (dd, $J = 20.2$ Hz, 14.8 Hz, $-\text{CH}=\text{CH}_2$, 1H), 5.93 (dd, $J = 14.4$ Hz, 4.2 Hz, $-\text{CH}=\text{C}(\text{H } cis)\text{H}$, 1H), 5.69 (dd, $J = 20.0$ Hz, 4.0 Hz, $-\text{CH}=\text{C}(\text{H } trans)\text{H}$, 1H), 2.91 (t, 5.0 Hz, $\text{N}-(\text{CH}_2)_2$, 4H), 1.57 (broad s, $(\text{CH}_2)_4(\text{CH}_2)_2\text{N}$, 8H), 0.13 (s, 6H, $\text{Si}(\text{CH}_3)_2$)

^{13}C NMR (100.6 MHz, 20°C, CDCl_3) δ 139.73 ($\text{Si}-\text{C}(\text{H})=$), 131.20 ($-\text{C}(\text{H})=\text{CH}_2$), 49.21 ($(\text{CH}_2)_2\text{N}$), 32.64 ($(\text{CH}_2\text{CH}_2)_2\text{N}$), 26.90 ($(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{N}$), -2.04 ($\text{Si}-(\text{CH}_3)_2$)

Collected distillate 86-87°C (2.0mm Hg)

HRMS-ESI (m/z): $[\text{M}-\text{H}]^+$ [$\text{C}_{10}\text{H}_{21}\text{NSi} + \text{H}^+$], 184.152; found, 184.150.



17

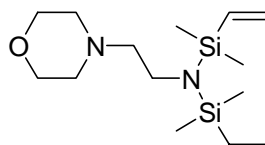
1-(dimethyl(vinyl)silyl)azocane

^1H NMR (400 MHz, 20°C, CDCl_3) δ 6.12 (dd, $J = 20.4$ Hz, 14.8 Hz, $-\text{CH}=\text{CH}_2$, 1H), 5.91 (dd, $J = 14.8$ Hz, 4.0 Hz, $-\text{CH}=\text{C}(\text{H } cis)\text{H}$, 1H), 5.66 (dd, $J = 20.2$ Hz, 4.2 Hz, $-\text{CH}=\text{C}(\text{H } trans)\text{H}$, 1H), 2.85 (t, 5.8 Hz, $\text{N}-(\text{CH}_2)_2$, 4H), 1.55 (broad s, 6H), 1.47 (broad s, 4H), 0.11 (s, 6H, $\text{Si}(\text{CH}_3)_2$)

^{13}C NMR (100.6 MHz, 20°C, CDCl_3) δ 139.58 ($\text{Si}-\text{C}(\text{H})=$), 131.19 ($-\text{C}(\text{H})=\text{CH}_2$), 49.30 ($(\text{CH}_2)_2\text{N}$), 30.27 ($(\text{CH}_2\text{CH}_2)_2\text{N}$), 28.11 ($(\text{CH}_2)(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{N}$), 24.87 ($(\text{CH}_2\text{CH}_2\text{CH}_2)_2\text{N}$), -2.14 ($\text{Si}-(\text{CH}_3)_2$)

Collected distillate 39-41°C (0.18 Torr)

HRMS-ESI (m/z): $[\text{M}-\text{H}]^+$ calcd for [$\text{C}_{11}\text{H}_{23}\text{NSi} + \text{H}^+$], 198.168; found, 198.170.



19

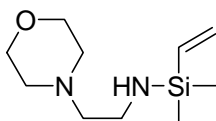
N-(ethyl dimethylsilyl)-N-(dimethyl(vinyl)silyl)-2-morpholinoethanamine

^1H NMR (400 MHz, 20°C, CDCl_3) δ 6.12 (dd, $J = 20.2$ Hz, 14.6 Hz, $-\text{CH}=\text{CH}_2$, 1H), 5.88 (dd, $J = 14.8$ Hz, 3.8 Hz, $-\text{CH}=\text{C}(\text{H } cis)\text{H}$, 1H), 5.64 (dd, $J = 20.4$ Hz, 3.8 Hz, $-\text{CH}=\text{C}(\text{H } trans)\text{H}$, 1H), 3.65 (t, $J = 4.6$ Hz, $(\text{CH}_2)_2\text{O}$, 4H), 2.88 (m, CH_2N , 2H), 2.41 (t, $J = 4.4$ Hz, $(\text{CH}_2)_2\text{N}$, 4H), 2.24 (m, CH_2N , 2H), 0.86 (t, $J = 8.0$ Hz, $\text{Si}-\text{CH}_2\text{CH}_3$, 3H), 0.51 (q, $J = 8.0$ Hz, $\text{Si}-\text{CH}_2\text{CH}_3$, 2H), 0.12 (s, $\text{Si}(\text{CH}_3)_2$, 6H), 0.05 (s, $\text{Si}(\text{CH}_3)_2$, 6H)

^{13}C NMR (100.6 MHz, 20°C, CDCl_3) δ 140.72 ($\text{Si}-\text{C}(\text{H})=$), 131.28 ($-\text{C}(\text{H})=\text{CH}_2$), 66.87 ($(\text{CH}_2)\text{O}$), 62.90 ($(\text{CH}_2)\text{N}$), 54.23 ($(\text{CH}_2)_2\text{N}$ morpholine), 42.16 ($(\text{CH}_2)\text{N}$), 9.79 ($\text{Si}-\text{CH}_2\text{CH}_3$), 7.43 ($\text{Si}-\text{CH}_2\text{CH}_3$), 0.31 ($\text{Si}-(\text{CH}_3)_2$), -0.37 ($\text{Si}-(\text{CH}_3)_2$)

Collected distillate 78-81°C (0.25 Torr)

HRMS m/z [$\text{M}-\text{H}^+$] calc'd for [$\text{C}_{14}\text{H}_{32}\text{N}_2\text{OSi}_2 + \text{H}^+$], 301.213; found, 301.211.



21

N-(dimethyl(vinyl)silyl)-2-morpholinoethanamine

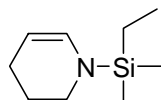
^1H NMR (400 MHz, 20°C, CDCl_3) δ 6.08 (dd, $J = 20.1$ Hz, 14.7 Hz, $-\text{CH}=\text{CH}_2$, 1H), 5.92 (dd, $J = 14.8$ Hz, 4.1 Hz, $-\text{CH}=\text{C}(\text{H } cis)\text{H}$, 1H), 5.69 (dd, $J = 20.1$ Hz, 4.1 Hz, $-\text{CH}=\text{C}(\text{H } trans)\text{H}$, 1H), 3.67 (t, $J = 4.5$ Hz, $(\text{CH}_2)_2\text{O}$, 4H), 2.88 (q, 6.7 Hz, CH_2N , 2H), 2.40 (broad s, $(\text{CH}_2)_2\text{N}$, 4H), 2.33 (t, $J = 6.5$ Hz, CH_2N , 2H), 0.87 (broad s, $\text{N}-\text{H}$, 1H), 0.51 (q, $J = 8.0$ Hz, $\text{Si}-\text{CH}_2\text{CH}_3$, 2H), 0.12 (s, $\text{Si}(\text{CH}_3)_2$, 6H), 0.03 (s, $\text{Si}(\text{CH}_3)_2$, 6H)

^{13}C NMR (100.6 MHz, 20°C, CDCl_3) δ 139.48 ($\text{Si}-\text{C}(\text{H})=$), 131.81 ($-\text{C}(\text{H})=\text{CH}_2$), 67.02 ($(\text{CH}_2)\text{O}$), 62.23 ($(\text{CH}_2)\text{N}$), 53.73 ($(\text{CH}_2)_2\text{N}$ morpholine), 38.30 ($(\text{CH}_2)\text{N}$), -1.90 ($\text{Si}-(\text{CH}_3)_2$)

Collected distillate 60-62°C (0.3 Torr)

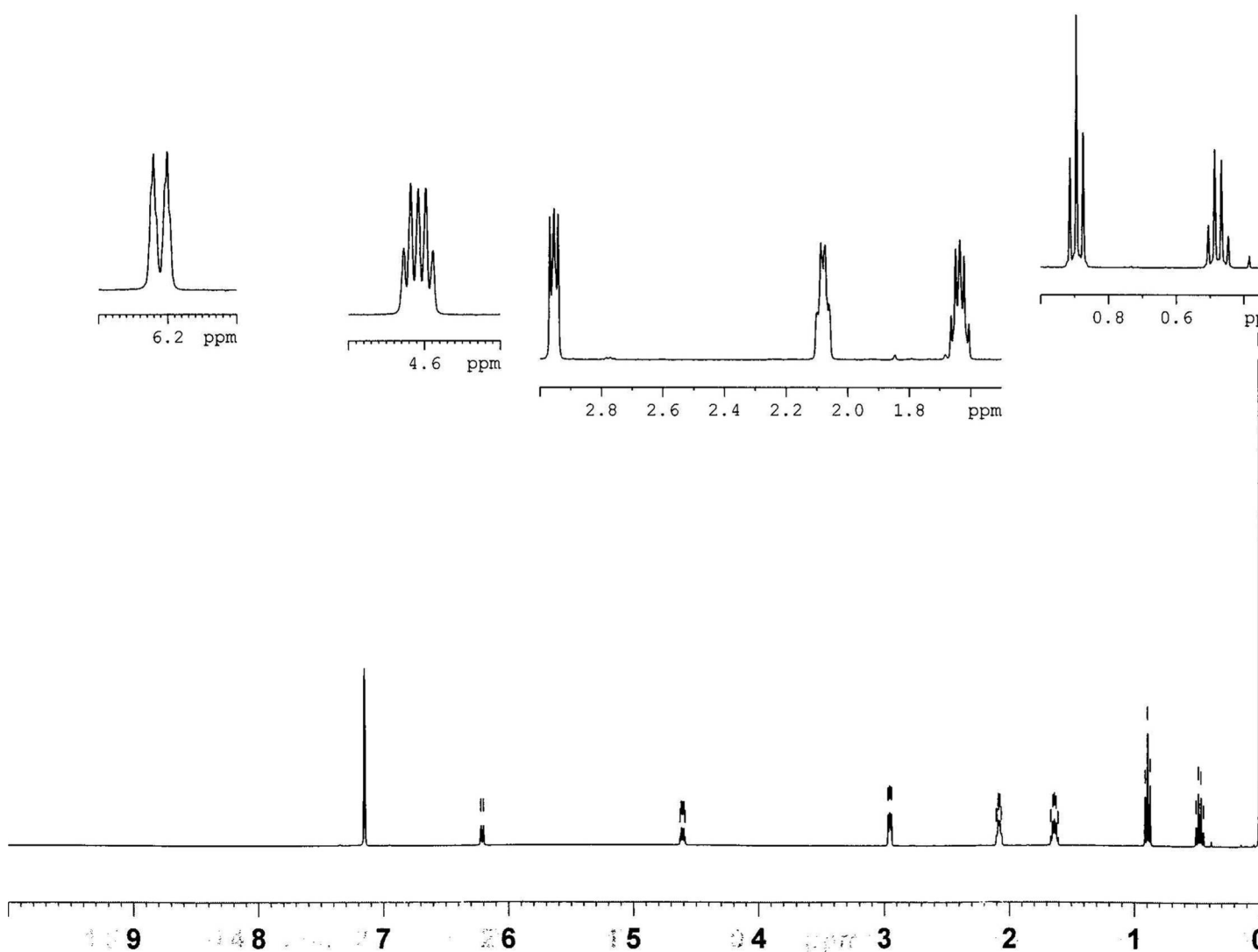
MS m/z [$\text{M}-\text{H}^+$] calc'd for [$\text{C}_{10}\text{H}_{22}\text{N}_2\text{OSi} + \text{H}^+$], 215.158; found, 215.1.

VI. Characterization of Transfer Hydrogenation Products



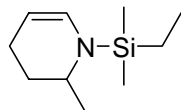
4

1-(ethyldimethylsilyl)-1,2,3,4-tetrahydropyridine



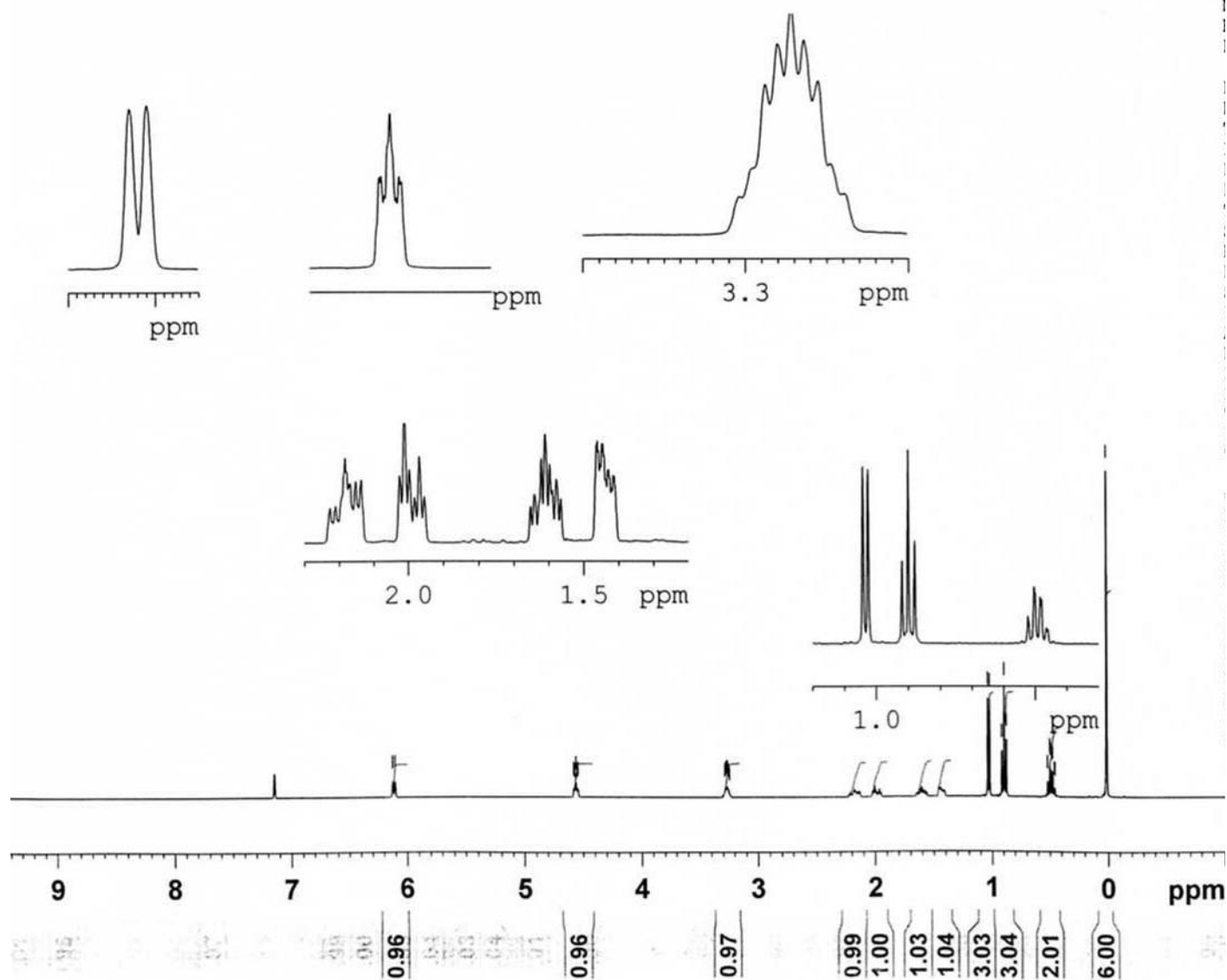
^1H NMR (400 MHz, 20°C , C_6D_6) δ 6.21 (d, $J = 8.0$ Hz, HC-N , 1H), 4.61 (m, $\text{HC}=\text{C}(\text{H})\text{N}$, 1H), 2.95 (t, $J = 5.2$ Hz, $(\text{CH}_2)\text{N}$, 2H), 2.08 (m, $(\text{H}_2\text{C}-\text{C}(\text{H})_2-\text{N})$, 2H), 1.64 (m, $(\text{H}_2\text{C}-(\text{CH}_2)-\text{N})$, 2H), 0.89 (t, $J = 8.0$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)$, 3H), 0.48 (q, $J = 8.0$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)$, 2H), 0.00 (s, $\text{Si}(\text{CH}_3)_2$, 6H)

^{13}C NMR (100.6 MHz, 20°C, C_6D_6) δ 132.30 (N-C(H)=C), 97.20 (C(H)=C(H)-N), 42.87 ((CH₂)N), 23.80 ((CH₂)(CH₂)₂N), 22.47 ((CH₂)CH₂-N), 7.71 (Si-CH₂CH₃), 7.22 (Si-CH₂CH₃), -3.43 (Si-(CH₃)₂)



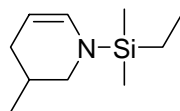
6

1-(ethyldimethylsilyl)-1,2,3,4-tetrahydro-2-methylpyridine



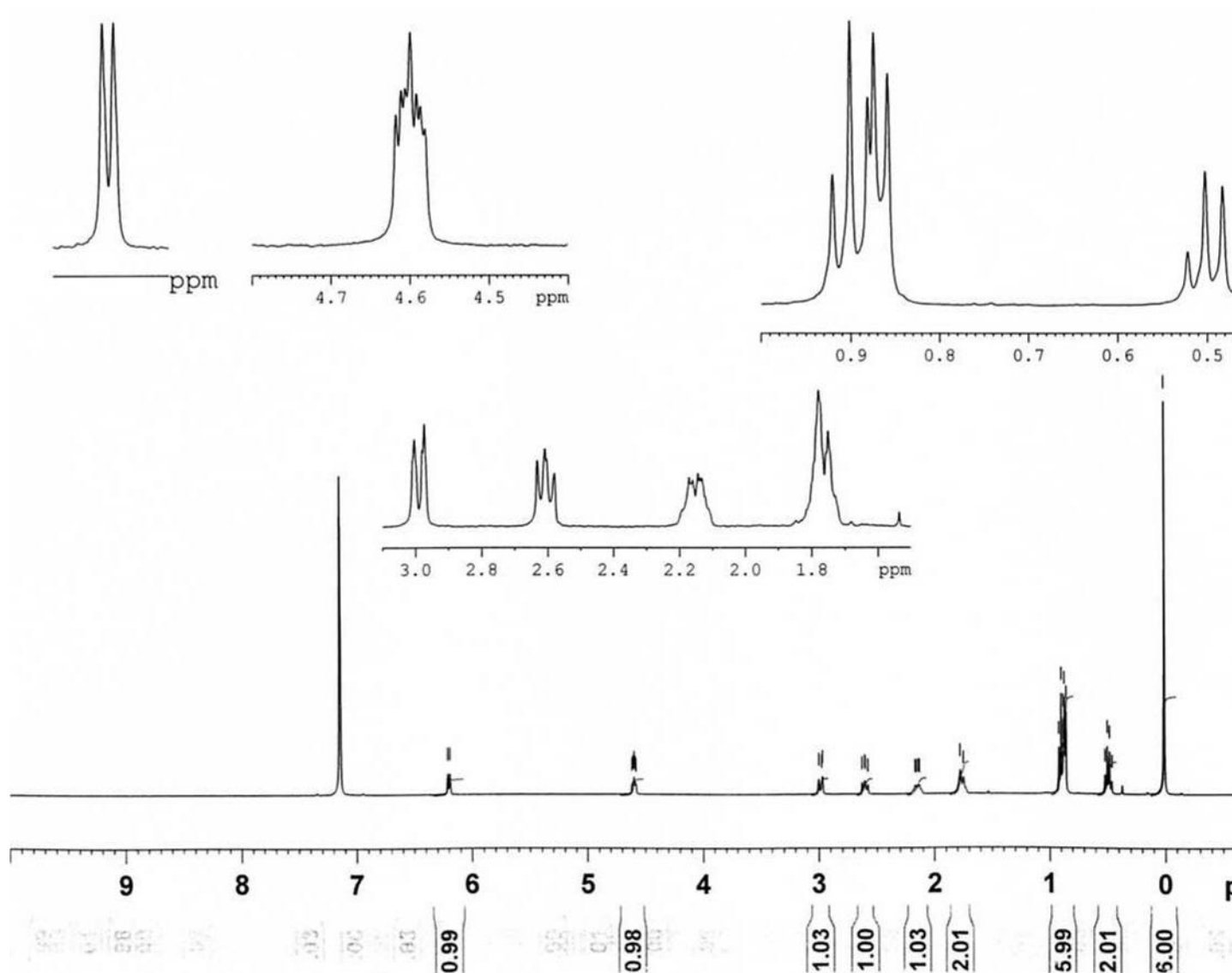
^1H NMR (400 MHz, 20°C , C_6D_6) δ 6.12 (d, $J = 8.0$ Hz, HC-N 1H), 4.56 (m, $\text{HC}=\text{C}(\text{H})\text{N}$, 1H), 3.27 (m, $\text{HC}(\text{CH}_3)\text{-N}$, 1H), 1.4-2.25 (m, $(\text{CH}_2)_2$, 4H), 1.03 (d, $J = 6.4$ Hz, N-C-CH_3 , 3H) 0.90 (t, $J = 8.0$ Hz, $(\text{Si-CH}_2\text{CH}_3)$, 3H), 0.49 (q, $J = 8.0$ Hz, $(\text{Si-CH}_2\text{CH}_3)$, 2H), 0.02 (s, $\text{Si}(\text{CH}_3)_2$, 6H)

^{13}C NMR (100.6 MHz, 20°C , C_6D_6) δ 130.23 ($\text{NC}(\text{H})=\text{C}$), 96.33 ($\text{C}(\text{H})=\text{C}(\text{H})\text{-N}$), 46.04 ($(\text{CH}(\text{Me}))\text{N}$), 28.18 ($\text{C}(\text{H}_2)(\text{CH}_2)\text{N}$), 19.30 ($\text{N-C}(\text{H})\text{-CH}_3$), 17.95 ($\text{CH}_2\text{C}(\text{H})\text{-CH}_3$), 8.05 ($\text{Si-CH}_2\text{CH}_3$), 7.28 ($\text{Si-CH}_2\text{CH}_3$), -2.93 ($\text{Si-}(\text{CH}_3)$), -3.16 ($\text{Si-}(\text{CH}_3)$).



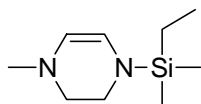
8

1-(ethyldimethylsilyl)-1,2,3,4-tetrahydro-3-methylpyridine



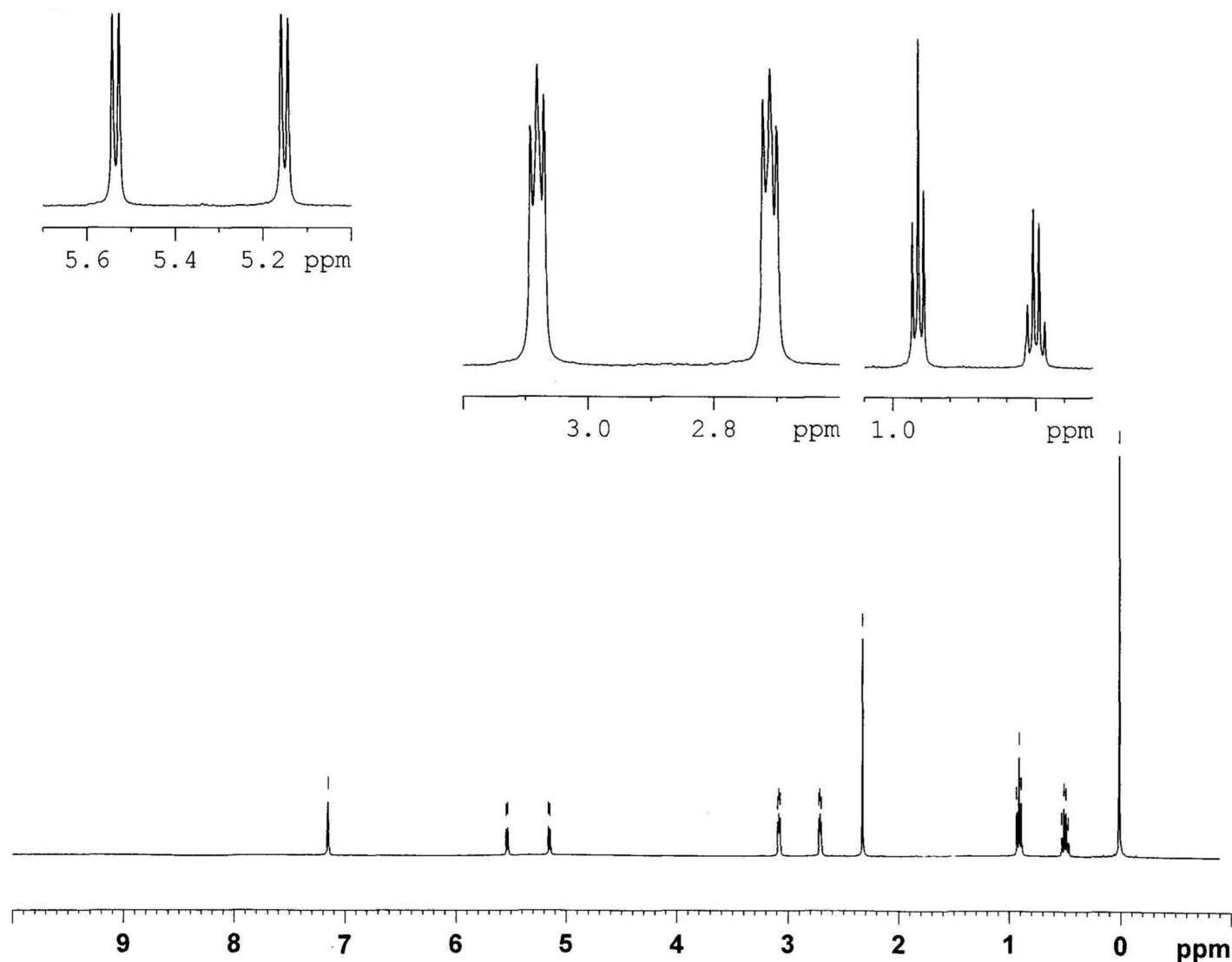
^1H NMR (400 MHz, 20°C , C_6D_6) δ 6.20 (d, $J = 7.6$ Hz, HC-N 1H), 4.60 (m, $\text{HC}=\text{C}(\text{H})\text{N}$, 1H), 3.27 (m, $\text{HC}(\text{CH}_3)\text{-N}$, 1H), 2.98 (m, methylene, 1H), 2.60 (m, methylene, 1H), 2.15 (m, methylene, 1H), 1.76 (m, methylene, 1H), 0.90 (t, $J = 7.8$ Hz, $(\text{Si-CH}_2\text{CH}_3)$, 3H), 0.87 (d, $J = 6.4$ Hz, 3-methyl, 3H), 0.51 (q, $J = 8.0$ Hz, $(\text{Si-CH}_2\text{CH}_3)$, 2H), -0.01 (s, $\text{Si}(\text{CH}_3)_2$, 6H)

^{13}C NMR (100.6 MHz, 20°C , C_6D_6) δ 131.76 ($\text{N-C}(\text{H})=\text{C}$), 96.43 ($\text{C}(\text{H})=\text{C}(\text{H})\text{-N}$), 49.52 ($(\text{CH}_2)\text{N}$), 30.79 ($(\text{CH}_2)\text{C}(\text{H})=$), 28.01 ($\text{CH}(\text{Me})$), 19.39 ($(\text{C}(\text{H})\text{-CH}_3)$), 7.76 ($\text{Si-CH}_2\text{CH}_3$), 7.23 ($\text{Si-CH}_2\text{CH}_3$), -3.28 ($\text{Si-}(\text{CH}_3)$), -3.36 ($\text{Si-}(\text{CH}_3)$).



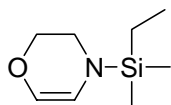
10

1-(ethyldimethylsilyl)-1,2,3,4-tetrahydro-4-methylpyrazine



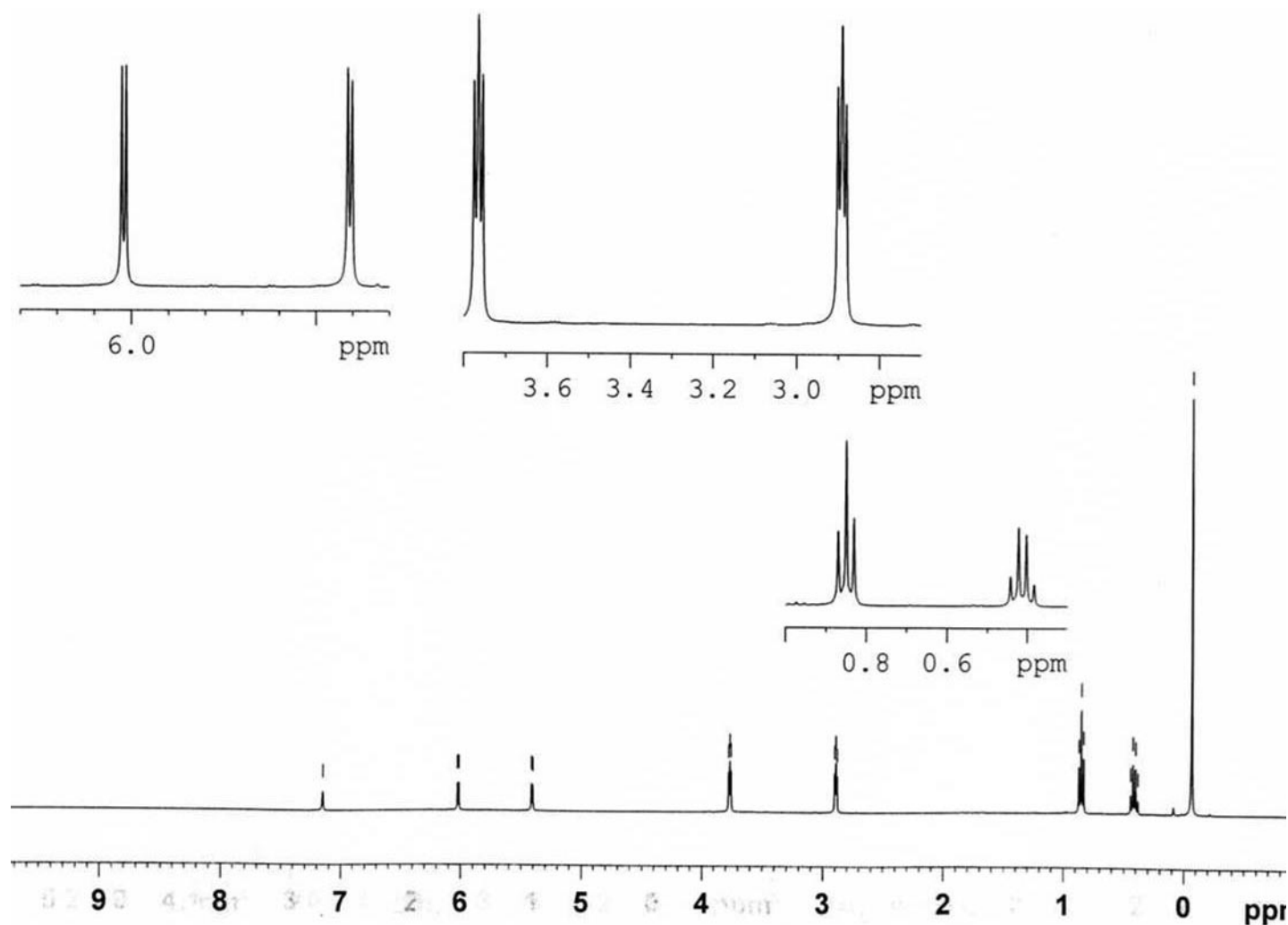
^1H NMR (400 MHz, 20°C , C_6D_6) δ 5.53 (d, $J = 6.0$ Hz, NC(H)=C , 1H), 5.14 (d, $J = 6.0$ Hz, NC(H)=C , 1H), 3.08 (t, $J = 4.2$ Hz, $(\text{CH}_2)\text{N}$, 2H), 2.71 (t, $J = 4.4$ Hz, $(\text{CH}_2)\text{N}$, 2H), 2.33 (s, N-CH_3 , 3H), 0.91 (t, $J = 8.0$ Hz, $(\text{Si-CH}_2\text{CH}_3)_2$, 3H), 0.50 (q, $J = 8.0$ Hz, $(\text{Si-CH}_2\text{CH}_3)_2$, 2H), 0.01 (s, $(\text{Si}(\text{CH}_3)_2)$, 6H)

^{13}C NMR (100.6 MHz, 20°C , C_6D_6) δ 116.63 (N(Me)-C(H)=), 113.30 ($(\text{Si})\text{N-C(H)=}$), 51.67 ($(\text{CH}_2)\text{N(Me)}$), 43.78 ($\text{N-(CH}_3)$), 41.59 ($(\text{CH}_2)\text{N(Si)}$), 7.60 ($\text{Si-CH}_2\text{CH}_3$) 7.28 ($\text{Si-CH}_2\text{CH}_3$), -3.62 ($\text{Si-(CH}_3)_2$)



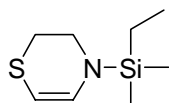
12

4-(ethyldimethylsilyl)-3,4-dihydro-2H-1,4-oxazine



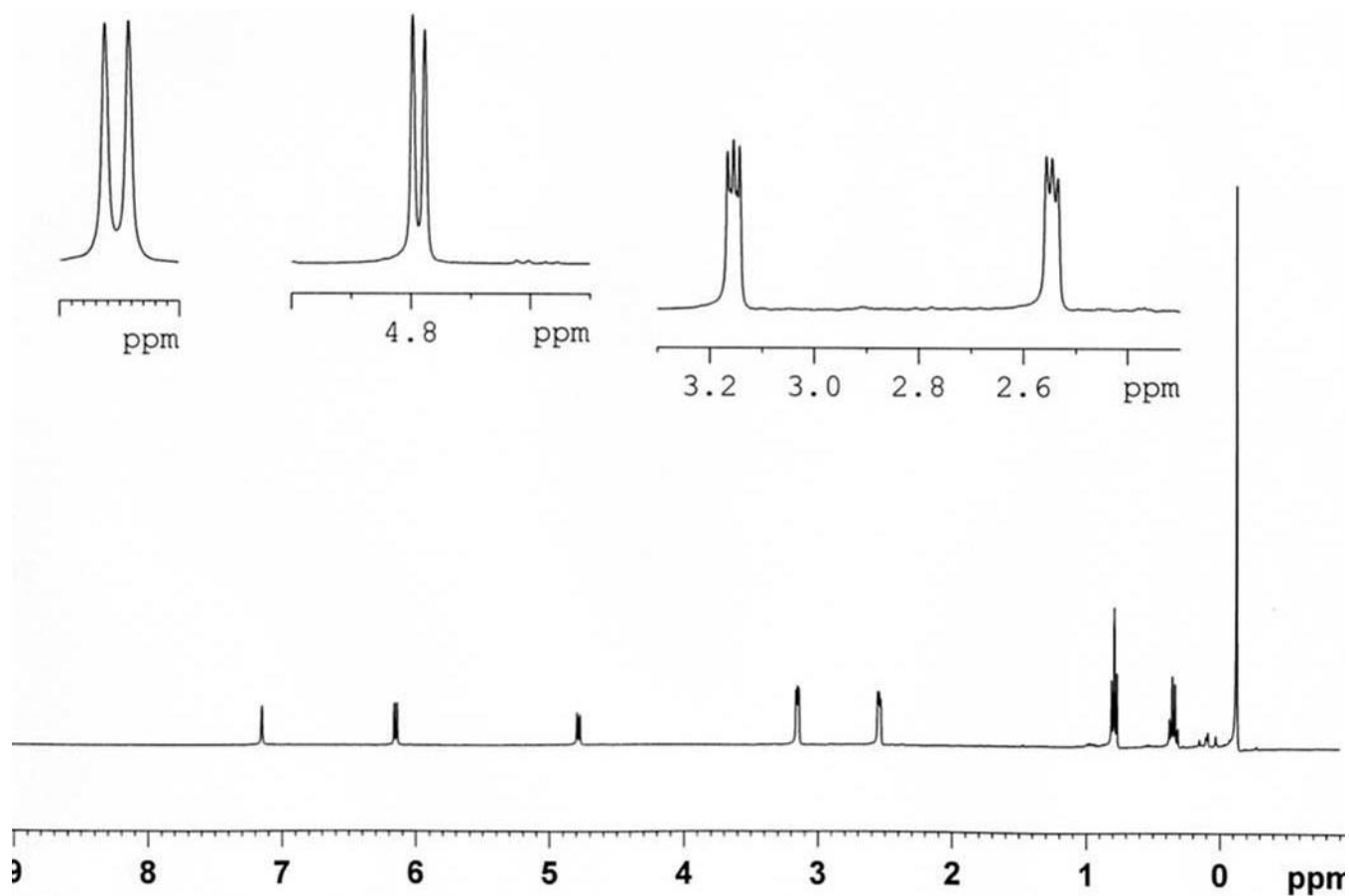
^1H NMR (400 MHz, 20°C , C_6D_6) δ 6.02 (d, $J = 4.8$ Hz, $\text{C}(\text{H})\text{O}$, 1H), 5.41 (d, $J = 4.8$ Hz, $\text{C}(\text{H})\text{N}$, 1H), 3.77 (t, $J = 4.0$ Hz, $(\text{CH}_2)\text{O}$, 2H), 2.89 (t, $J = 4.0$ Hz, $(\text{CH}_2)\text{N}$, 2H), 0.85 (t, $J = 8.0$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)$, 3H), 0.41 (q, $J = 8.0$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)$, 2H), -0.07 (s, $\text{Si}(\text{CH}_3)_2$, 6H)

^{13}C NMR (100.6 MHz, 20°C , C_6D_6) δ 125.63 ($\text{OC}(\text{H})=\text{C}$), 112.79 ($\text{NC}(\text{H})=\text{C}$), 65.55 ($(\text{CH}_2)\text{O}$), 42.97 ($(\text{CH}_2)\text{N}$), 7.34 ($\text{Si}-\text{CH}_2\text{CH}_3$), 7.12 ($\text{Si}-\text{CH}_2\text{CH}_3$), -3.87 ($\text{Si}-(\text{CH}_3)_2$)



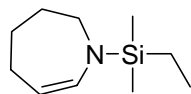
14

4-(ethyldimethylsilyl)-3,4-dihydro-2H-1,4-thiazine



^1H NMR (400 MHz, 20°C , C_6D_6) δ 6.15 (d, $J = 8.0$ Hz, $\text{HC}=\text{C}$, 1H), 4.80 (d, $J = 8.1$ Hz, $\text{HC}=\text{C}$, 1H), 3.16 (m, $(\text{CH}_2)\text{N}$, 2H), 2.55 (m, $(\text{CH}_2)\text{S}$, 2H), 0.80 (t, $J = 8.0$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)$, 3H), 0.35 (q, $J = 8.0$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)$, 2H), -0.12 (s, $\text{Si}(\text{CH}_3)_2$, 6H)

^{13}C NMR (100.6 MHz, 20°C , C_6D_{12}) δ 127.64, 89.77, 44.53, 26.14, 8.05 ($\text{Si}-\text{CH}_2\text{CH}_3$), 7.25 ($\text{Si}-\text{CH}_2\text{CH}_3$), -3.33 ($\text{Si}-(\text{CH}_3)_2$)



16

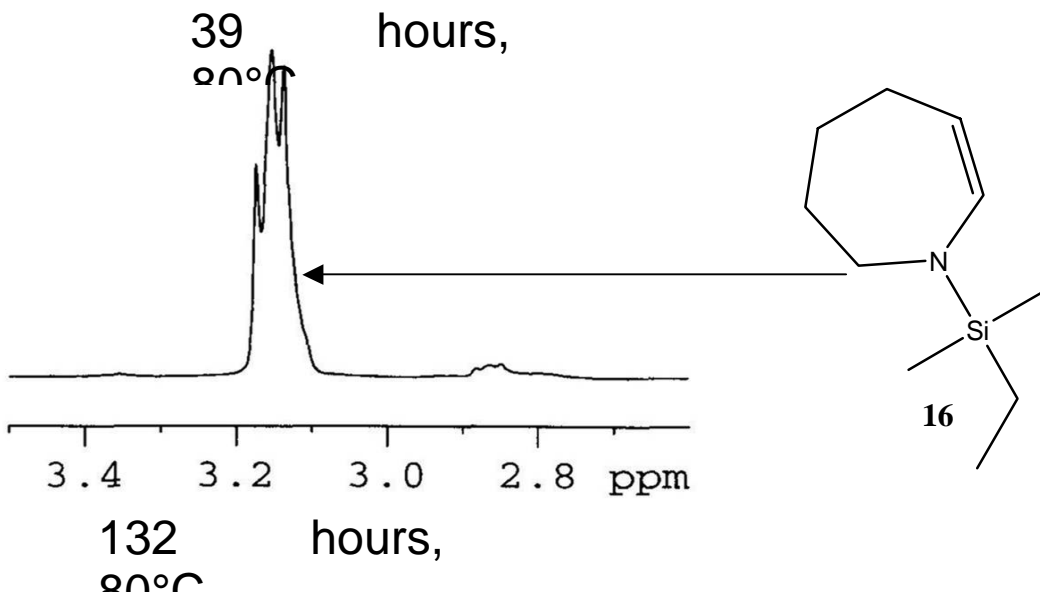
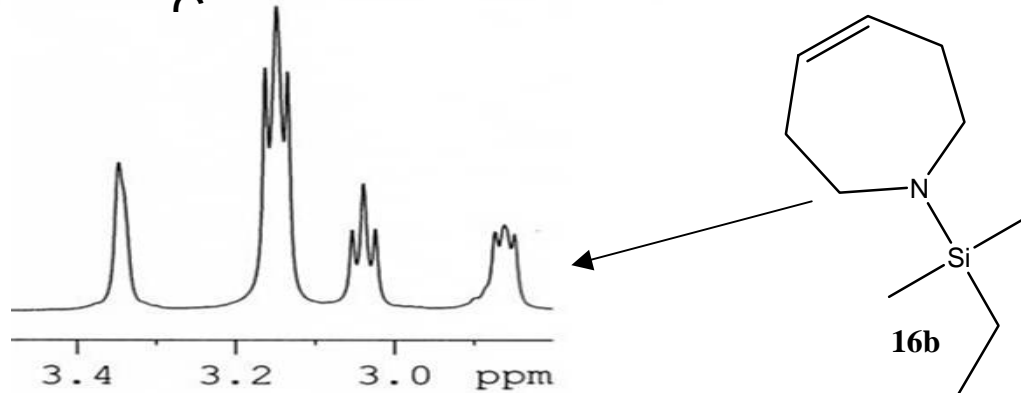
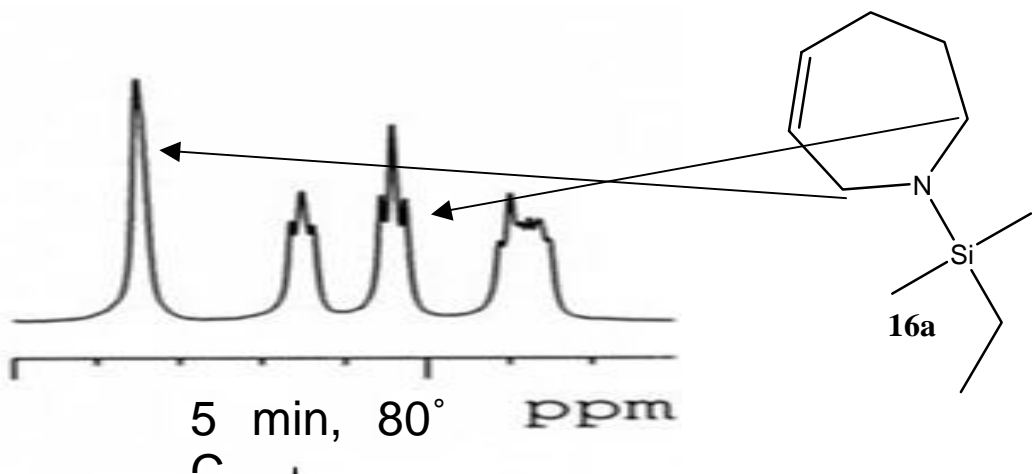
1-(ethyldimethylsilyl)-2,3,4,5-tetrahydro-1H-azepine

^{13}C NMR (100.6 MHz, 20°C , C_6D_6) δ 136.80 ($\text{N}-\text{C}(\text{H})=\text{C}$), 105.51 ($\text{C}(\text{H})=\text{C}(\text{H})-\text{N}$), 48.39 ($(\text{CH}_2)\text{N}$), 32.44 (CH_2), 27.71 (CH_2), 27.23 (CH_2), 8.19 ($\text{Si}-\text{CH}_2\text{CH}_3$), 7.29 ($\text{Si}-\text{CH}_2\text{CH}_3$), -2.84 ($\text{Si}-(\text{CH}_3)_2$)

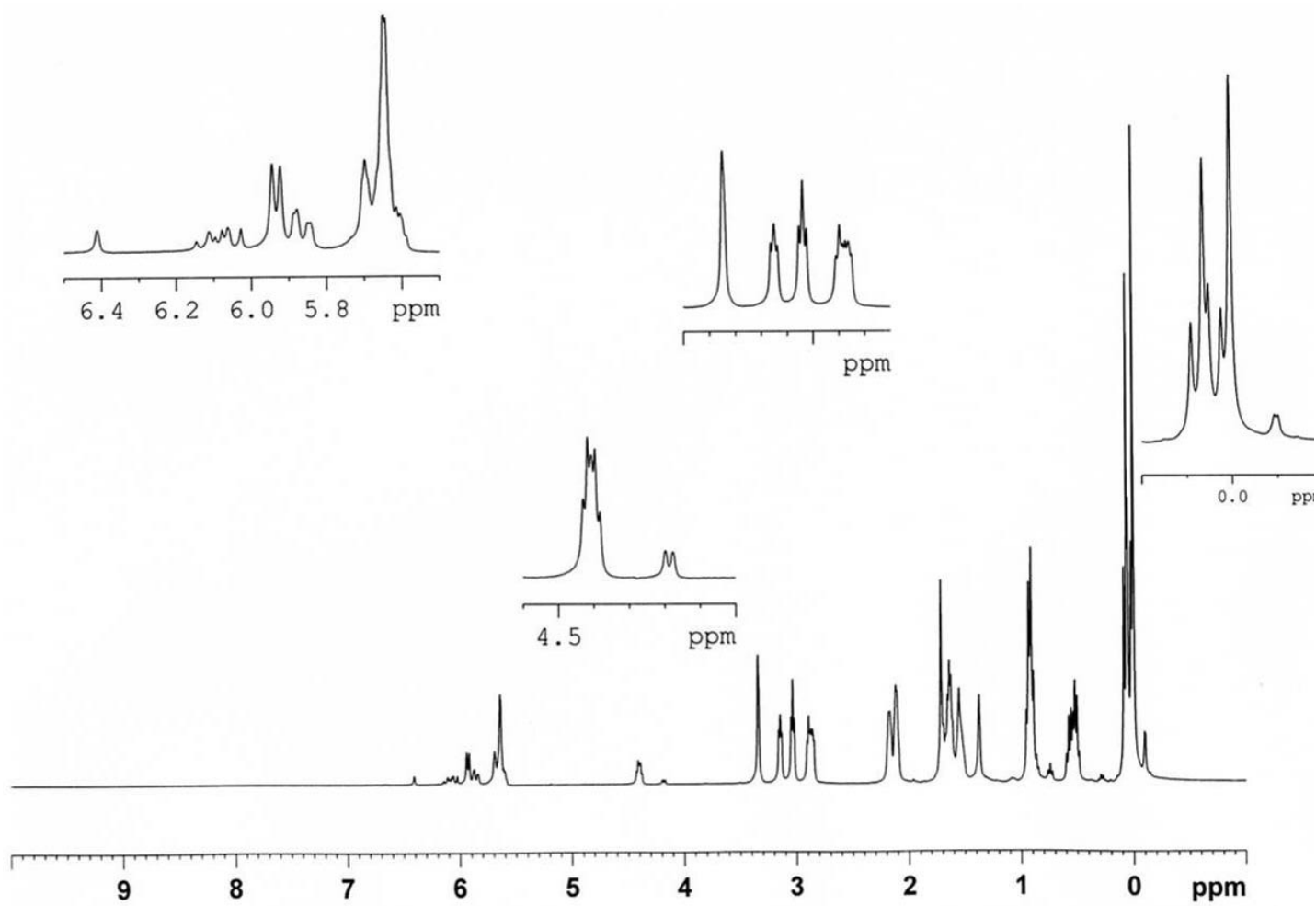
^1H NMR (400 MHz, 20°C , C_6D_6) δ 6.13 (d, $J = 8.8$ Hz, $\text{HC}-\text{N}$, 1H), 4.65 (m, $\text{HC}=\text{C}(\text{H})\text{N}$, 1H), 3.10 (t, $J = 5.6$ Hz, $(\text{CH}_2)\text{N}$, 2H), 2.21 (q, $J = 5.4$ Hz, $\text{CH}_2(\text{CH})_2\text{N}$, 2H), 1.74 (m, CH_2 , 2H), 1.55 (m, CH_2 , 2H), 0.92 (t, $J = 8.0$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)$, 3H), 0.52 (q, $J = 8.0$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)$, 2H), 0.03 (s, $\text{Si}(\text{CH}_3)_2$, 6H)

Isomerization to Enamine of (Protected) Homopiperidine (16)

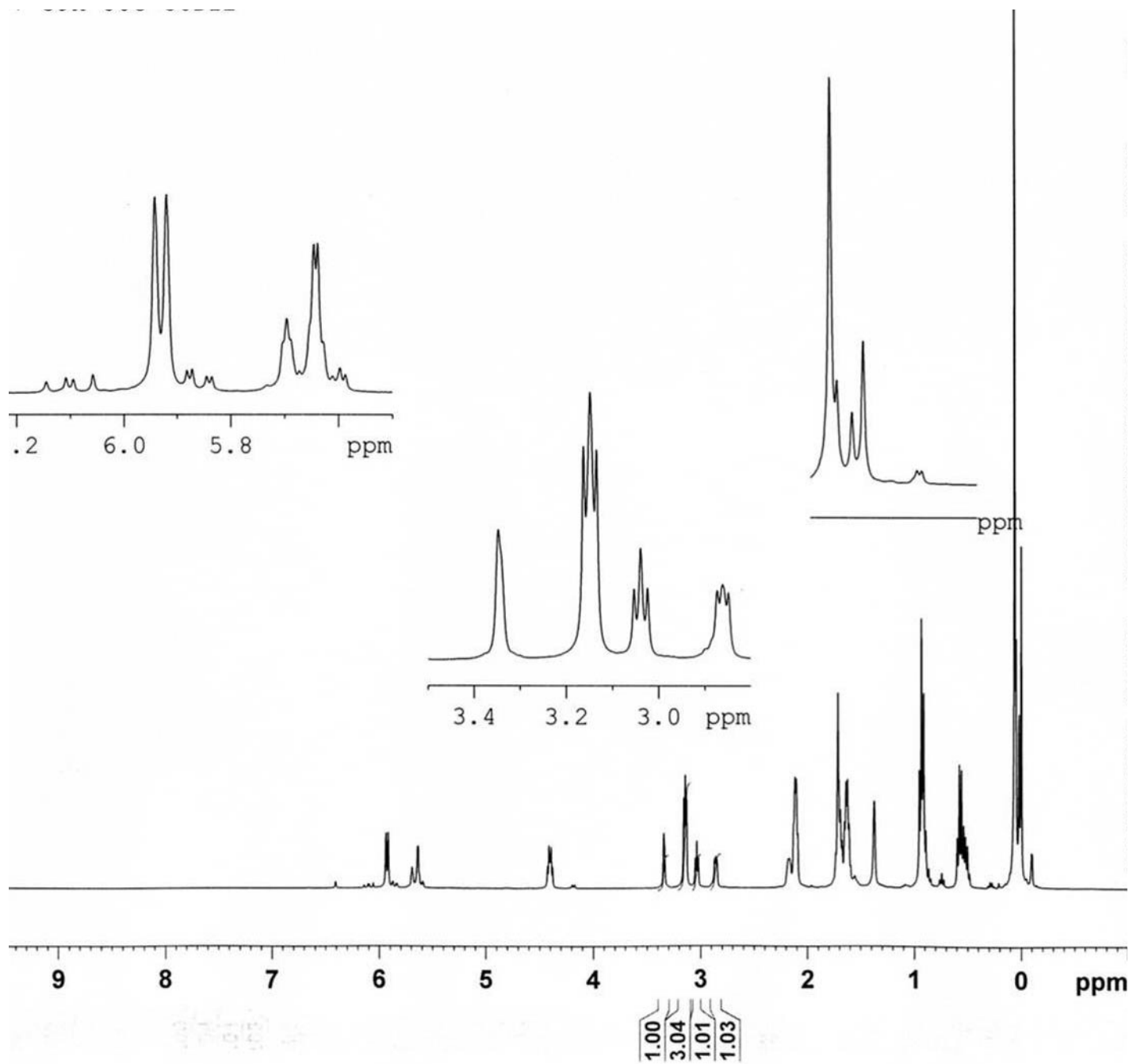
Direct observation of transfer hydrogenation with **1** in C_6D_{12} revealed very rapid consumption of starting material, with formation of 3 isomers. Characteristic, discrete signals for the protons on the carbon α to nitrogen (see expanded portions of spectra below) were monitored. Initially, the major product is the allyl amine **16a**, with two inequivalent sets of α -protons. In addition, enamine **16** and the symmetric homoallylic amine **16b** are observed; the latter isomerizes very slowly. In the 5 minute reaction shown, this triplet overlaps with residual starting material (completely consumed in next spectrum). After 39h, enamine is the major product. On the preparative scale (2% catalyst loading), >10days was required for practical conversion to the enamine **16**.



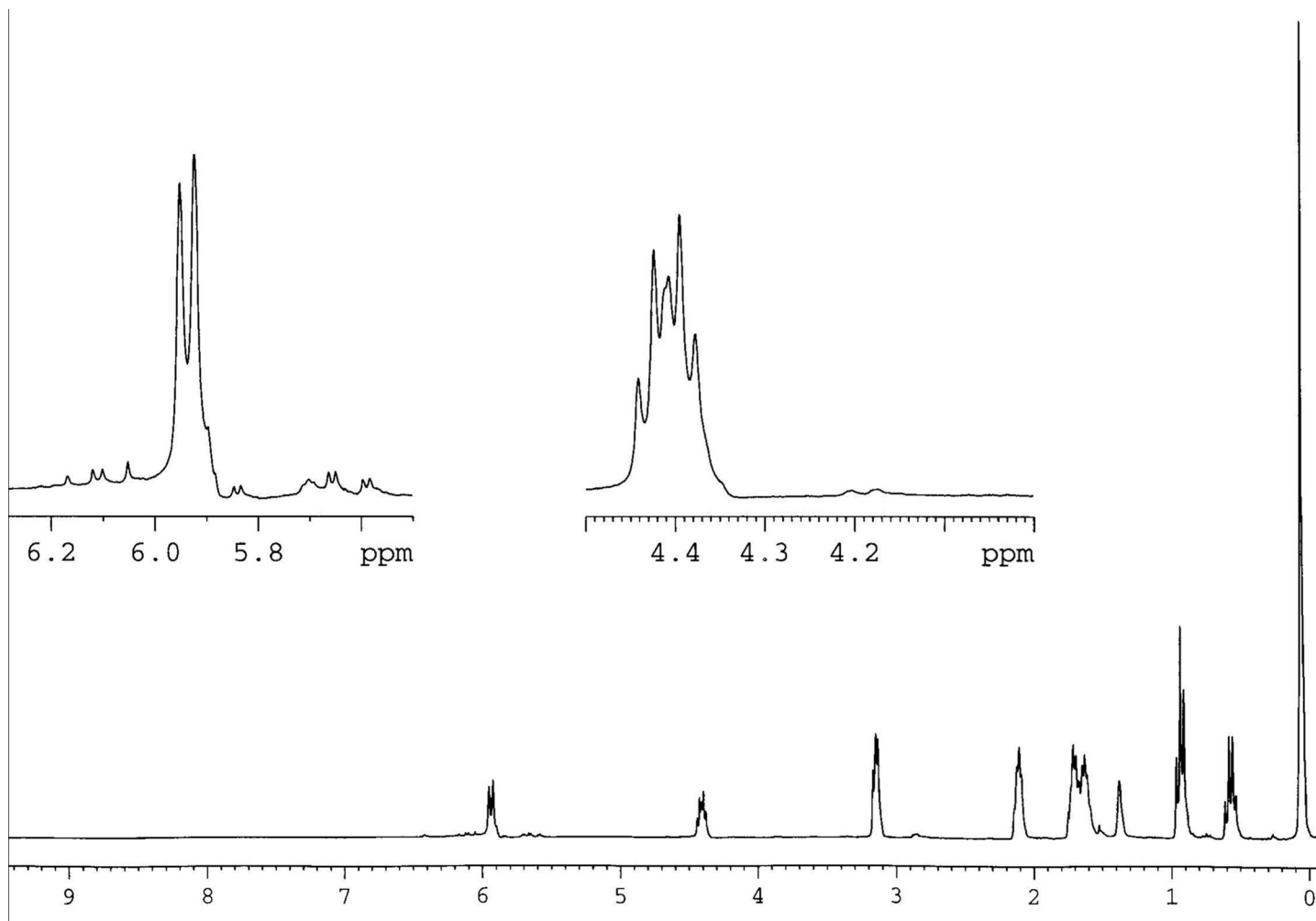
Isomerization of 16: Full Spectra



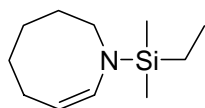
5 min, 80°C



39 hours, 80°C

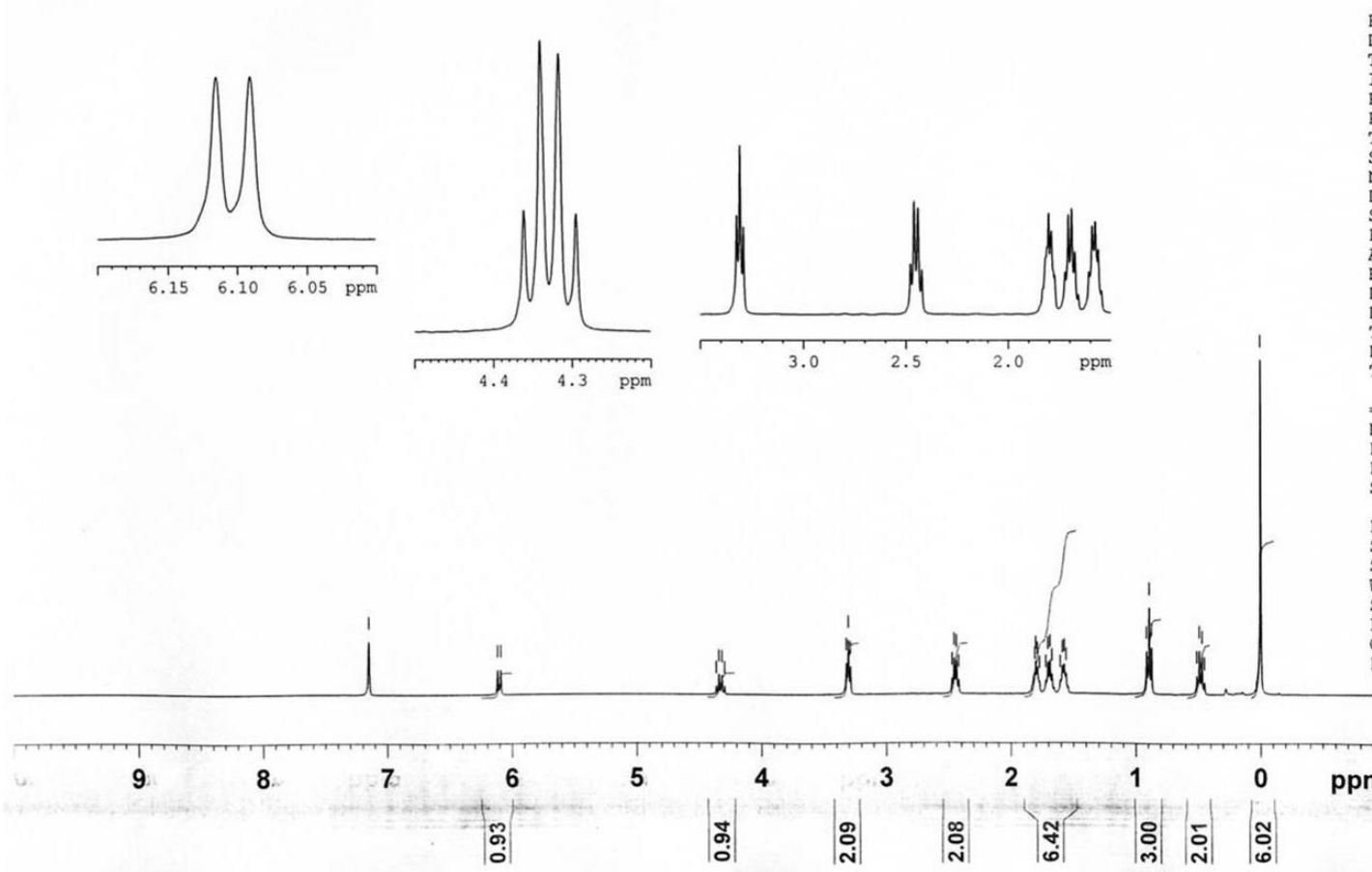


132 hours, 80°C



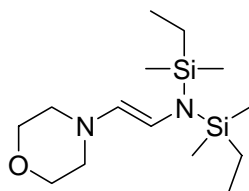
18

1-(ethyldimethylsilyl)-1,2,3,4,5,6-hexahydroazocine



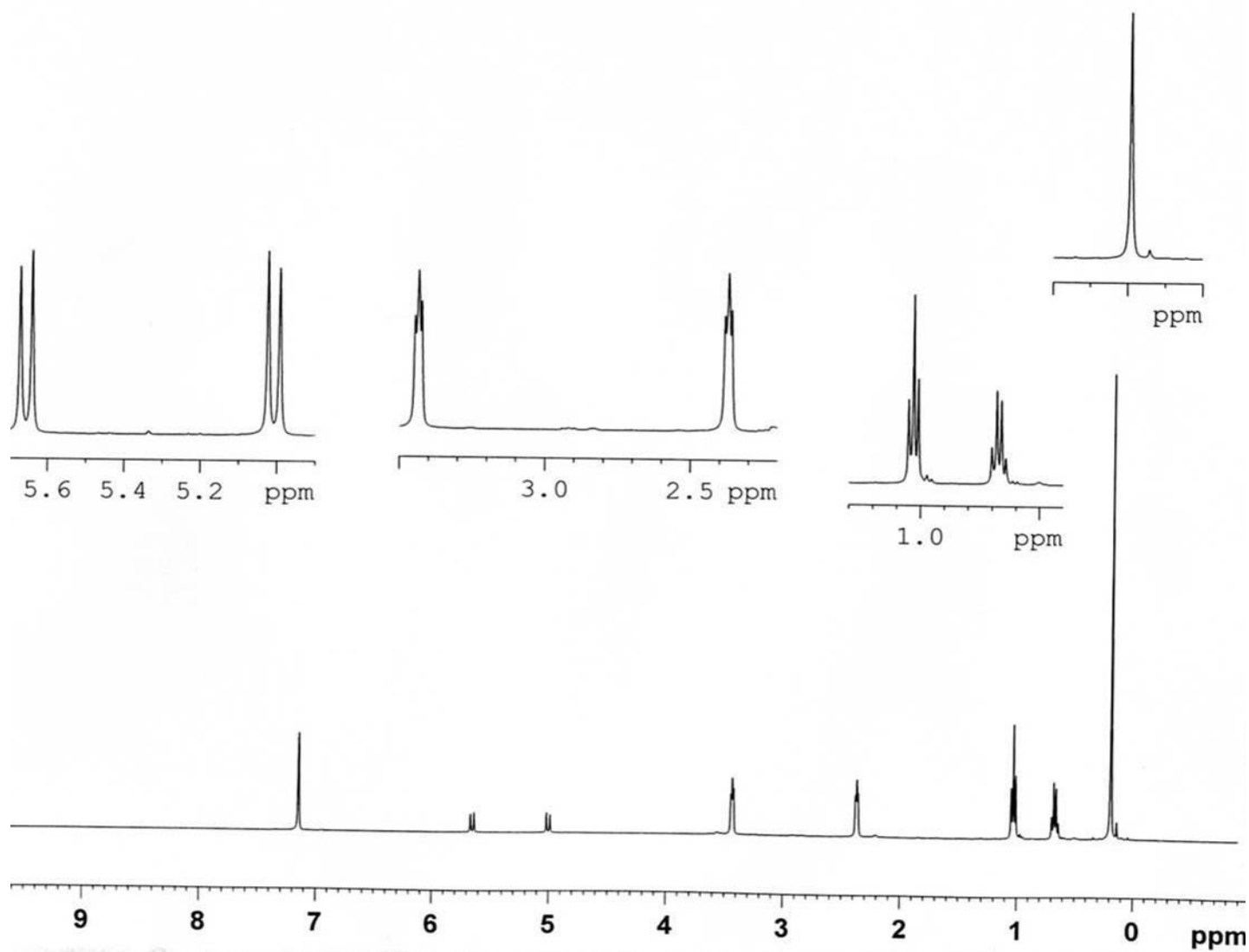
^1H NMR (400 MHz, 20°C , C_6D_6) δ 6.10 (d, $J = 9.6$ Hz, HC-N , 1H), 4.28 (dt (partial overlap), $J = 9.6$ Hz, 8.4 Hz, $\text{HC}=\text{C}(\text{H})\text{N}$, 1H), 3.31 (t, $J = 6.4$ Hz, $(\text{CH}_2)\text{N}$, 2H), 2.45 (m, $(\text{CH}_2)(\text{CH})_2\text{N}$, 2H), 1.50-1.85 (m, $(\text{CH}_2)_3$, 6H), 0.89 (t, $J = 7.8$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)$, 3H), 0.50 (q, $J = 7.9$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)$, 2H), 0.00 (s, $\text{Si}(\text{CH}_3)_2$, 6H)

^{13}C NMR (100.6 MHz, 20°C , C_6D_6) δ 136.29 ($\text{NC}(\text{H})=\text{C}$), 96.68 ($\text{C}(\text{H})=\text{C}-\text{N}$), 44.09 ($(\text{CH}_2)\text{N}$), 32.83 (CH_2), 30.79 (CH_2), 24.82 (CH_2), 21.97 ((CH_2)), 8.17 ($\text{Si}-\text{CH}_2\text{CH}_3$), 7.25 ($\text{Si}-\text{CH}_2\text{CH}_3$), -2.72 ($\text{Si}(\text{CH}_3)_2$)



20

E-*N,N*-bis(ethyldimethylsilyl)-2-morpholinoethenamine



^1H NMR (400 MHz, 20°C, C_6D_6) δ 5.66 (d, $J = 12.0$ Hz, $\text{C}(\text{H})\text{N}$, 1H), 5.01 (d, $J = 12.4$ Hz, $\text{C}(\text{H})\text{N}$, 1H), 3.44 (t, $J = 4.6$ Hz, $(\text{CH}_2)_2\text{O}$, 4H), 2.38 (t, $J = 4.6$ Hz, $(\text{CH}_2)_2\text{N}$, 4H), 1.03 (t, $J = 7.8$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)_2$, 6H), 0.68 (q, $J = 8.0$ Hz, $(\text{Si}-\text{CH}_2\text{CH}_3)_2$, 4H), 0.20 (s, $(\text{Si}(\text{CH}_3)_2)_2$, 12H)

^{13}C NMR (100.6 MHz, 20°C, C_6D_6) δ 140.88 ($\text{NC}(\text{H})=\text{C}(\text{H})\text{N}$), 109.73 ($\text{NC}(\text{H})=\text{C}(\text{H})\text{N}$), 66.39 ($(\text{CH}_2)_2\text{O}$), 50.19 ($(\text{CH}_2)_2\text{N}$), 9.71 ($\text{Si}-\text{CH}_2\text{CH}_3$), 7.71 ($\text{Si}-\text{CH}_2\text{CH}_3$), -0.24 ($\text{Si}-(\text{CH}_3)_2$)

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³ Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Educ.* **2001**, *78*, 64.

⁴ Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 6965.

⁵ Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1999**, *121*, 4385.