# Supporting Information for [Bis(2-pyridyldimethylsilyl)methyl]lithium. New Reagent for the Stereoselective Synthesis of Vinylsilanes

**Kenichiro Itami, Toshiki Nokami, and Jun-ichi Yoshida***

*Department of Synthetic Chemistry & Biological Chemistry, Kyoto University*

*Yoshida, Kyoto 606-8501, Japan*

**General Experimental.**

NMR spectra were recorded on Varian GEMINI-2000 ($^1$H 300 MHz, $^{13}$C 75 MHz) and JEOL A-500 ($^1$H 500 MHz, $^{13}$C 125 MHz) spectrometers in $CDCl_3$ with internal standards (7.26 ppm $^1$H, 77.0 ppm $^{13}$C). Mass spectra were recorded with a JEOL JMS-D-300 spectrometer. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Diethyl ether ($Et_2O$) was freshly distilled under argon from sodium benzophenone ketyl prior to use.

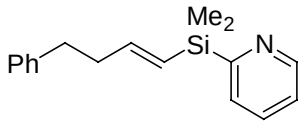
**Bis(2-pyridyldimethylsilyl)methane (2).** To a solution of 2-pyridyltrimethylsilane **1** (151 mg, 1.0 mmol) in dry $Et_2O$ (2 mL) was added dropwise a solution of *t*-BuLi (1.0 mmol, 1.64 M solution in pentane) at –78 °C. The mixture was stirred for additional 30 min. To the resultant solution of [(2-pyridyldimethylsilyl)methyl]lithium was added 2-pyridyldimethylsilane (137 mg, 1.0 mmol) at –78 °C and stirred for 1 h. The reaction was quenched with a saturated aqueous solution of $NH_4Cl$. Extractive work-up and subsequent silica gel chromatography (hexane/EtOAc = 5/1 to 5/2 as eluents) afforded **2** (180 mg, 63%) as a colorless oil: $^1$H NMR (300 MHz) δ 0.22 (s, 12 H), 0.38 (s, 2 H), 7.08 (ddd, *J* = 7.5, 4.8, 1.5 Hz, 2 H), 7.38 (ddd, *J* = 7.5, 1.5, 1.2 Hz, 2 H), 7.46 (td, *J* = 7.5, 1.8 Hz, 2 H), 8.68 (ddd, *J* = 4.8, 1.8, 1.2 Hz, 2 H); $^{13}$C NMR (75 MHz) δ -1.2, 0.1, 122.5, 128.6, 133.8, 150.0, 168.7. IR (neat) 2955, 1576, 1559, 1451, 1418, 1248, 1051 cm$^{-1}$. Anal. Calcd for $C_{15}H_{22}N_2Si_2$: C, 62.88; H, 7.74; N, 9.78. Found: C, 62.61; H, 7.78; N, 9.79. HRMS *m/e* calcd for $C_{14}H_{19}N_2Si_2$ $(M - CH_3)^+$: 271.1087, found 271.1079.

**4,4-Bis(2-pyridyldimethylsilyl)butene (3).** To a solution of **2** (60 mg, 0.21 mmol) in dry $Et_2O$ (1 mL) was added dropwise a solution of *n*-BuLi (0.23 mmol, 1.55 M in hexane) at –78 °C. After stirring for an additional 1 h, allyl bromide (38 mg, 0.31 mmol) was added and stirred for 1 h at 0°C. After stirring at room temperature for 17 h, the mixture was washed with $H_2O$ (2 × 10 mL). The organic phase was additionally extracted with 1 N aq HCl (3 × 10 mL). The aqueous phase was basified to pH 14 by

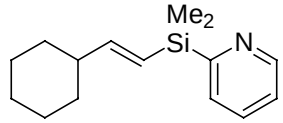
adding NaOH pellet and was extracted with $Et_2O$ (2 × 10 mL). Drying over $MgSO_4$ and removal of the solvents under reduced pressure afforded **3** (63 mg, 92%) as a pale yellow oil: $^1$H NMR (300 MHz): δ 0.21 (s, 6 H), 0.28 (s, 6 H), 0.86 (t, *J* = 6.0 Hz, 1 H), 2.26-2.34 (m, 2 H), 4.67 (ddt, *J* = 9.9, 1.8, 1.5 Hz, 1 H), 4.72 (ddt, *J* = 16.8, 1.8, 1.5 Hz, 1 H), 5.55 (ddt, *J* = 16.8, 9.9, 6.9 Hz, 1 H), 7.09 (ddd, *J* = 7.5, 4.8, 1.5 Hz, 2 H), 7.37 (ddd, *J* = 7.5, 1.5, 1.2 Hz, 2 H), 7.46 (td, *J* = 7.5, 1.5 Hz, 2 H), 8.69 (ddd, *J* = 4.8, 1.5, 1.2 Hz, 2 H); $^{13}$C NMR (75 MHz): δ -2.6, -2.1, 10.9, 30.2, 113.8, 122.5, 129.2, 133.7, 140.7, 149.9, 168.3. HRMS *m/e* calcd for $C_{18}H_{26}N_2Si_2$: 326.1635, found 326.1635.

**Typical Procedure for the Synthesis of Vinylsilanes (4).** To a solution of **2** (143 mg, 0.5 mmol) in dry $Et_2O$ (1 mL) was added dropwise a solution of *n*-BuLi (0.55 mmol, 1.50 M in hexane) at –78 °C. After stirring for an additional 1 h, carbonyl compound (0.75 mmol) was added and stirred for 30 min at –78 °C and 1 h at room temperature. The reaction was quenched with a saturated aqueous solution of $NH_4Cl$. Extractive work-up and subsequent silica gel chromatography (hexane/EtOAc = 10/1 to 5/1 as eluents) afforded **4**. Yields are sited in Table 1.

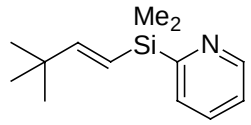
**Spectral Data of 4.**



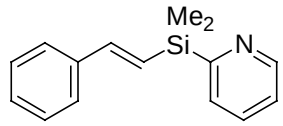

**4a:** $^1$H NMR (300 MHz) δ 0.38 (s, 6 H), 2.43-2.53 (m, 2 H), 2.70-2.79 (m, 2 H), 5.86 (dt, *J* = 18.6, 1.5 Hz, 1 H), 6.24 (dt, *J* = 18.6, 6.3 Hz, 1 H), 7.14-7.22 (m, 4 H), 7.24-7.31 (m, 2 H), 7.44 (ddd, *J* = 7.5, 1.5, 0.9 Hz, 1 H), 7.56 (td, *J* = 7.5, 1.8 Hz, 1 H), 8.79 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -3.3, 34.9, 38.4, 122.8, 125.8, 127.3, 128.3, 128.5, 129.5, 134.0, 141.9, 148.9, 150.3, 167.5. HRMS *m/e* calcd for $C_{17}H_{21}NSi$: 267.1443, found 267.1431.



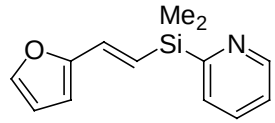

**4b:** $^1$H NMR (300 MHz) δ 0.36 (s, 6 H), 1.00-1.35 (m, 5 H), 1.58-1.80 (m, 5 H), 1.94-2.08 (m, 1 H), 5.75 (dd, *J* = 18.9, 1.2 Hz, 1 H), 6.13 (dd, *J* = 18.9, 5.7 Hz, 1 H), 7.16 (ddd, *J* = 7.5, 4.8, 1.8 Hz, 1 H), 7.50 (ddd, *J* = 7.5, 1.8, 1.2 Hz, 1 H), 7.55 (td, *J* = 7.5, 1.8 Hz, 1 H), 8.77 (ddd, *J* = 4.8, 1.8, 1.2 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -3.3, 25.9, 26.1, 32.2, 43.9, 122.7, 123.1, 129.4, 133.9, 150.3, 155.5, 167.9. IR (neat) 2924, 1612, 1574, 1449, 1418, 1244 cm$^{-1}$. HRMS *m/e* calcd for $C_{15}H_{23}NSi$: 245.1600, found 245.1604.



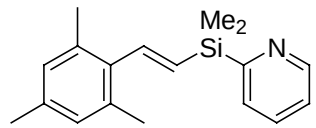

**4c:** $^{1}$H NMR (300 MHz) δ 0.38 (s, 6 H), 1.01 (s, 9 H), 5.71 (d, *J* = 18.9 Hz, 1 H), 6.18 (d, *J* = 18.9 Hz, 1 H), 7.18 (ddd, *J* = 7.5, 4.8, 1.5 Hz, 1 H), 7.48 (dt, *J* = 7.5, 1.2 Hz, 1 H), 7.57 (td, *J* = 7.5, 1.8 Hz, 1 H), 8.78 (dm, *J* = 4.8 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -3.2, 28.9, 35.2, 119.6, 122.7, 129.5, 134.1, 150.2, 160.3, 167.9. HRMS *m/e* calcd for $C_{13}H_{20}NSi$ $(M - H)^+$: 218.1365, found 218.1368.



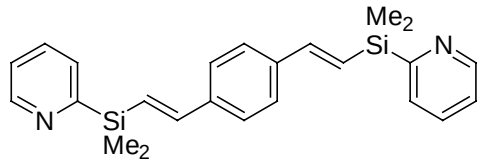

**4d:** $^{1}$H NMR (300 MHz) δ 0.50 (s, 6 H), 6.65 (d, *J* = 19.2 Hz, 1 H), 7.02 (d, *J* = 19.2 Hz, 1 H), 7.21 (ddd, *J* = 6.9, 4.8, 2.1 Hz, 1 H), 7.26-7.36 (m, 3 H), 7.44-7.49 (m, 2 H), 7.54-7.62 (m, 2 H), 8.81 (dt, *J* = 5.1, 1.2 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -3.4, 122.9, 126.1, 126.6, 128.3, 128.6, 129.5, 134.1, 138.2, 145.9, 150.4, 167.0. IR (neat) 2959, 1605, 1574, 1495, 1449, 1418, 1246 $cm^{-1}$. HRMS *m/e* calcd for $C_{15}H_{17}NSi$: 239.1131, found 239.1122.



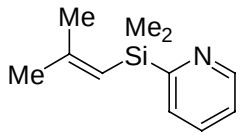

**4e:** $^{1}$H NMR (300 MHz) δ 0.47 (s, 6 H), 6.30 (d, *J* = 3.3 Hz, 1 H), 6.37 (dd, *J* = 3.3, 1.8 Hz, 1 H), 6.48 (d, *J* = 18.9 Hz, 1 H), 6.79 (d, *J* = 18.9 Hz, 1 H), 7.19 (ddd, *J* = 7.2, 4.8, 2.1 Hz, 1 H), 7.36 (d, *J* = 1.8 Hz, 1 H), 7.51-7.62 (m, 2 H), 8.79 (dm, *J* = 4.8 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -3.4, 108.7, 111.5, 122.9, 124.1, 129.6, 133.2, 134.1, 142.5, 150.4, 154.0, 166.8. IR (neat) 2959, 1617, 1576, 1545, 1478, 1417, 1248 $cm^{-1}$. HRMS *m/e* calcd for $C_{13}H_{15}NOSi$: 229.0923, found 229.0927.



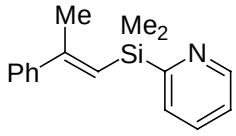

**4f:** $^{1}$H NMR (300 MHz) δ 0.52 (s, 6 H), 2.28 (s, 3 H), 2.29 (s, 6 H), 6.12 (d, *J* = 19.8 Hz, 1 H), 6.87 (s, 2 H), 7.04 (d, *J* = 19.8 Hz, 1 H), 7.17-7.25 (m, 1 H), 7.56-7.62 (m, 2 H), 8.81 (dt, *J* = 4.8, 1.2 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -3.3, 20.6, 20.8, 122.8, 128.7, 129.5, 132.3, 134.0, 135.4, 136.2, 136.3, 144.9, 150.3, 167.3. HRMS *m/e* calcd for $C_{18}H_{23}NSi$: 281.1600, found 281.1591.



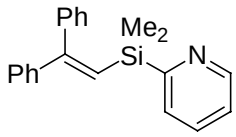

**4g:** $^{1}$H NMR (300 MHz) δ 0.49 (s, 12 H), 6.64 (d, *J* = 19.2 Hz, 2 H), 6.99 (d, *J* = 19.2 Hz, 2 H), 7.17-7.24 (m, 2 H), 7.43 (s, 4 H), 7.52-7.63 (m, 4 H), 8.80 (dm, *J* = 5.1 Hz, 2 H); $^{13}$C NMR (75 MHz) δ -3.4, 122.9, 126.3, 126.8, 129.5, 134.1, 138.0, 145.4, 150.3, 166.9. IR (KBr) 1603, 1574, 1557, 1509, 1451, 1420, 1248 cm$^{-1}$. HRMS *m/e* calcd for $C_{24}H_{28}N_2Si_2$: 400.1791, found 400.1793.



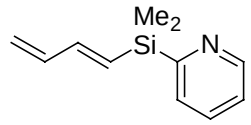

**4h:** $^{1}$H NMR (300 MHz) δ 0.40 (s, 6 H), 1.72 (s, 3 H), 1.88 (d, *J* = 1.5 Hz, 3 H), 5.41 (br, 1 H), 7.17 (ddd, *J* = 7.5, 4.8, 1.8 Hz, 1 H), 7.50-7.60 (m, 2 H), 8.78 (dm, *J* = 4.8 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -1.8, 23.6, 29.4, 121.1, 122.6, 129.3, 134.0, 150.3, 154.6, 168.3. HRMS *m/e* calcd for $C_{11}H_{17}NSi$: 191.1130, found 191.1139.



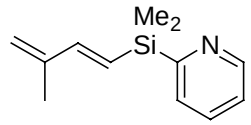

**4i:** $^{1}$H NMR (300 MHz) δ 0.52 (s, 6 H), 2.17 (d, *J* = 0.6 Hz, 3 H), 6.12 (d, *J* = 0.6 Hz, 1 H), 7.19-7.24 (m, 1 H), 7.28-7.35 (m, 3 H), 7.50 (dt, *J* = 6.9, 1.8 Hz, 2 H), 7.59 (dt, *J* = 4.5, 1.2 Hz, 2 H), 8.81 (dt, *J* = 4.8, 1.5 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -1.8, 21.4, 122.8, 124.0, 125.6, 127.7, 128.2, 129.5, 134.2, 144.0, 150.3, 154.0, 167.7. IR (neat) 3061, 2959, 1597, 1574, 1493, 1445, 1418, 1246, 1138 cm$^{-1}$. HRMS *m/e* calcd for $C_{16}H_{19}NSi$: 253.1287, found 253.1284.



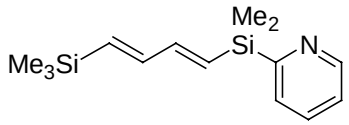

**4j:** $^{1}$H NMR (300 MHz) δ 0.16 (s, 6 H), 6.55 (s, 1 H), 7.10-7.19 (m, 3 H), 7.22-7.36 (m, 8 H), 7.37-7.45 (m, 1 H), 7.53 (td, *J* = 7.5, 1.8 Hz, 1 H), 8.78 (dm, *J* = 5.1 Hz, 1 H); $^{13}$C NMR (125 MHz) δ -2.0, 122.5, 126.34, 126.35, 127.3, 127.4, 127.8, 128.0, 129.3, 129.6, 133.9, 142.3, 142.9, 150.0, 158.8, 167.8. IR (neat) 3058, 2957, 1574, 1489, 1443, 1418, 1246 cm$^{-1}$. HRMS *m/e* calcd for $C_{21}H_{21}NSi$: 315.1443, found 315.1444.




**4k:** $^{1}$H NMR (300 MHz) δ 0.42 (s, 6 H), 5.15 (ddd, *J* = 9.9, 1.5, 0.6 Hz, 1 H), 5.25 (ddd, *J* = 16.8, 1.5, 0.6 Hz, 1 H), 6.05 (dd, *J* = 18.3, 0.9 Hz, 1 H), 6.39 (dtd, *J* = 16.8, 9.9, 0.9 Hz, 1 H), 6.64 (ddt, *J* = 18.3, 9.9, 0.6 Hz, 1 H), 7.18 (ddd, *J* = 7.5, 4.8, 1.8 Hz, 1 H), 7.50 (ddd, *J* = 7.5, 1.8, 1.2 Hz, 1 H), 7.57 (td, *J* = 7.5, 1.8 Hz, 1 H), 8.78 (ddd, *J* = 4.8, 1.8, 1.2 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -3.5, 118.6, 122.9, 129.5, 131.2, 134.1, 139.7, 146.8, 150.4, 167.0. IR (neat) 2959, 1574, 1256 cm$^{-1}$. Anal. Calcd for $C_{11}H_{15}NSi$: C, 69.78; H, 7.99; N, 7.40. Found: C, 69.69; H, 8.17; N, 7.37. HRMS *m/e* calcd for $C_{11}H_{15}NSi$: 189.0974, found 189.0977.




**4l:** $^{1}$H NMR (300 MHz) δ 0.43 (s, 6 H), 1.86 (s, 3 H), 5.04 (d, *J* = 1.5 Hz, 1 H), 5.09 (d, *J* = 1.5 Hz, 1 H), 6.00 (d, *J* = 18.9 Hz, 1 H), 6.74 (d, *J* = 18.9 Hz, 1 H), 7.19 (ddd, *J* = 7.5, 4.8, 1.8 Hz, 1 H), 7.51 (ddd, *J* = 7.5, 1.8, 1.2 Hz, 1 H), 7.58 (td, *J* = 7.5, 1.8 Hz, 1 H), 8.79 (ddd, *J* = 4.8, 1.8, 1.2 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -3.4, 17.8, 118.0, 122.8, 125.9, 129.5, 134.0, 143.5, 148.8, 150.3, 167.2. IR (neat) 2988, 1576, 1246 cm$^{-1}$. HRMS *m/e* calcd for $C_{12}H_{17}NSi$: 203.1130, found 203.1121.




**4m:** $^{1}$H NMR (300 MHz) δ 0.07 (s, 9 H), 0.41 (s, 6 H), 5.94 (dd, *J* = 18.0, 2.4 Hz, 1 H), 6.07 (dd, *J* = 18.0, 2.4 Hz, 1 H), 6.57 (dd, *J* = 18.0, 9.6 Hz, 1 H), 6.65 (dd, *J* = 18.0, 9.6 Hz, 1 H), 7.18 (ddd, *J* = 7.5, 4.8, 1.5 Hz, 1 H), 7.50 (dt, *J* = 7.5, 1.5 Hz, 1 H), 7.57 (td, *J* = 7.5, 1.5 Hz, 1 H), 8.77 (dt, *J* = 4.8, 1.5 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -3.5, -1.6, 122.9, 129.5, 131.1, 134.1, 136.0, 146.5, 148.8, 150.3, 167.0.

**2-Pyridyldimethyl-(phenyldimethylsilyl)methylsilane (5).** To a solution of 2-pyridyltrimethylsilane **1** (3.03 g, 20 mmol) in dry $Et_2O$ (20 mL) was added dropwise a solution of *tert*-butyllithium (20 mmol, 1.31 M solution in pentane) at –78 °C. The mixture was stirred for additional 30 min. To the resultant solution of [(2-pyridyldimethylsilyl)methyl]lithium was added chlorodimethylphenylsilane (3.76 g, 22 mmol) at –78 °C and stirred for 1 h. After stirring for 3 h at room temperature, the reaction was quenched with $H_2O$ (20 mL). Extractive work-up and subsequent silica gel chromatography

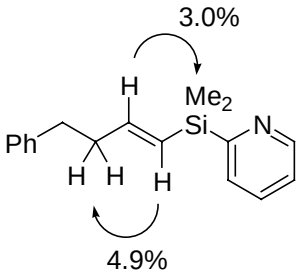
(hexane/EtOAc = 10/1 as eluents) afforded **5** (5.64 g, 99%) as a colorless oil: $^1$H NMR (300 MHz) δ 0.23 (s, 6 H), 0.27 (s, 6 H), 0.35 (s, 2 H), 7.16 (ddd, *J* = 7.5, 4.8, 1.5 Hz, 1 H), 7.29-7.33 (m, 3 H), 7.42-7.49 (m, 3 H), 7.54 (td, *J* = 7.5, 1.8 Hz, 1 H), 8.76 (ddd, *J* = 4.8, 1.8, 1.2 Hz, 1 H); $^{13}$C NMR (75 MHz) δ -1.1, -0.5, 1.1, 122.6, 127.7, 128.68, 128.71, 133.4, 134.0, 140.9, 150.1, 168.9. IR (neat) 3067, 2955, 1576, 1559, 1428, 1248, 1113 cm$^{-1}$. HRMS *m/e* calcd for $C_{16}H_{23}NSi_2$: 285.1369, found 285.1358.

**1-Phenyl-2-(dimethylphenylsilyl)ethylene (6).** To a solution of **5** (294 mg, 1.03 mmol) in dry $Et_2O$ (1 mL) was added dropwise a solution of *t*-BuLi (1.10 mmol, 1.31 M in pentane) at –78 °C and stirred for 30 min. To the resultant solution of carbanion was added benzaldehyde (127 mg, 1.20 mmol) at –78 °C and stirred for 30 min. After stirring overnight at room temperature, the reaction was quenched with $H_2O$ (5 mL). Extractive work-up and subsequent silica gel chromatography (hexane as eluent) afforded **6** (234 mg, 95%) as a mixture of stereoisomers (*E*/*Z* = 1/1). These isomers were separated by gel permeation chromatography. ***E*-isomer**[1]: $^1$H NMR (300 MHz) δ 0.46 (s, 6 H), 6.61 (d, *J* = 18.9 Hz, 1 H), 6.97 (d, *J* = 18.9 Hz, 1 H), 7.27-7.40 (m, 6 H), 7.47 (d, *J* = 6.9 Hz, 2 H), 7.58-7.62 (m, 2 H); $^{13}$C NMR (75 MHz) δ -2.7, 126.6, 127.1, 127.9, 128.2, 128.6, 129.1, 134.0, 138.2, 138.6, 145.4; IR (neat) 3067, 3022, 2957, 1605, 1574, 1495, 1248, 1113, 990 cm$^{-1}$. ***Z*-isomer**[1]: $^1$H NMR (300 MHz) δ 0.26 (d, *J* = 0.6 Hz, 6 H), 6.01 (d, *J* = 15.0 Hz, 1 H), 7.22 (s, 5 H), 7.32-7.36 (m, 3 H), 7.50 (d, *J* = 15.0 Hz, 1 H), 7.52-7.57 (m, 2 H); $^{13}$C NMR (75 MHz) δ -1.1, 127.4, 127.8 (two peaks as judged by integration), 128.2, 128.8, 130.2, 133.7, 139.58, 139.61, 148.1; IR (neat) 2961, 1592, 1570, 1493, 1428, 1248, 1111 cm$^{-1}$.

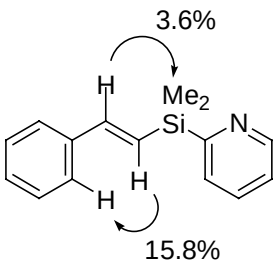
**Reference**

(1) Watanabe, H.; Kitahara, T.; Motegi, T.; Nagai *J. Organomet. Chem.* **1977**, *139*, 215.

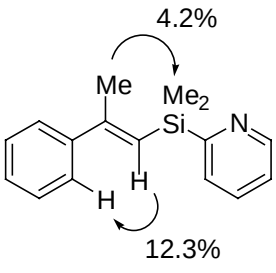
The *E* stereochemistry of **4** was assigned based on the results of the NOE experiments and the coupling constants between the two vinylic protons (18.0-19.8 Hz) in $^1$H NMR. The selected NOE data are as follows:




**4a**

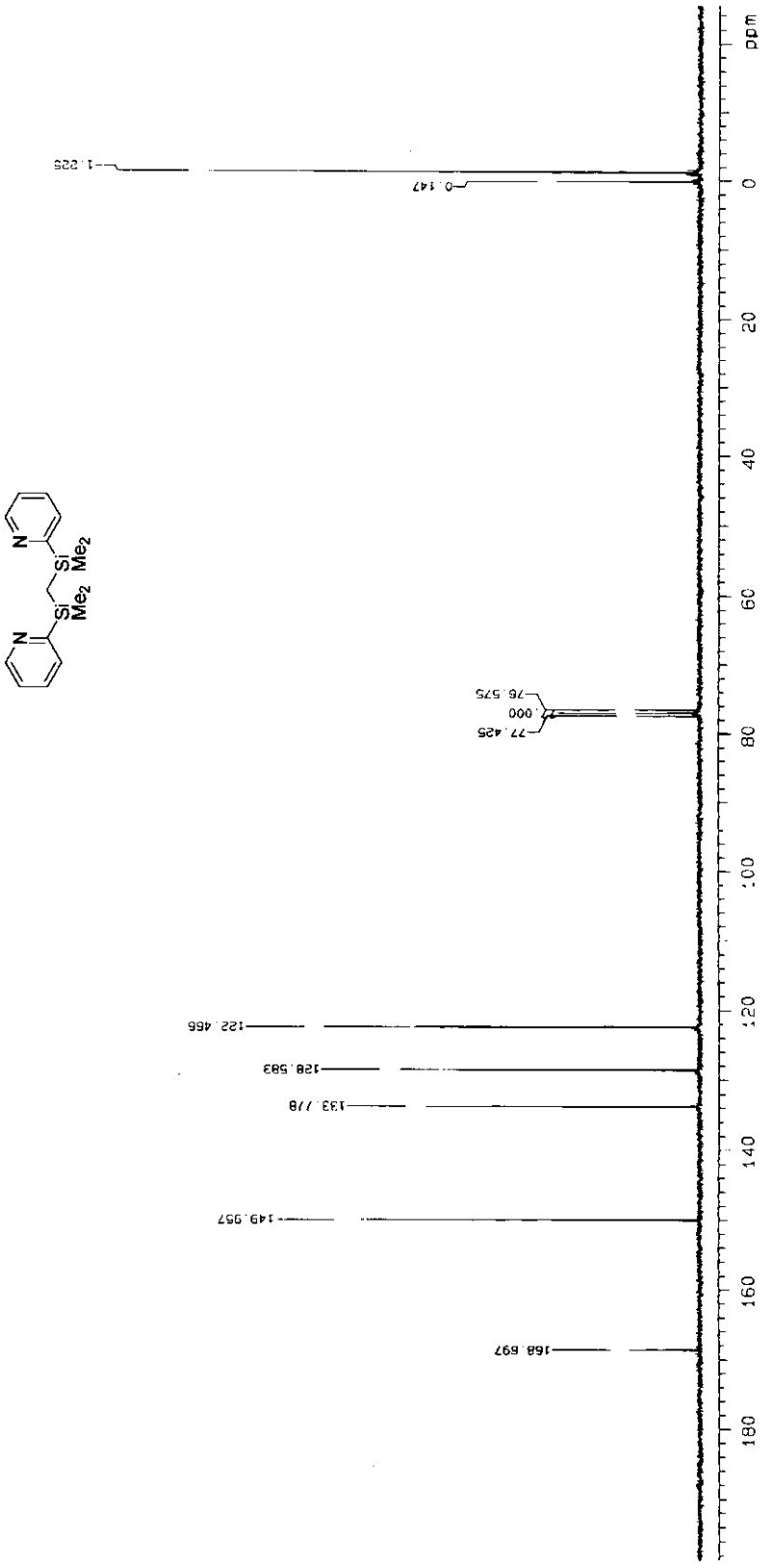



**4d**

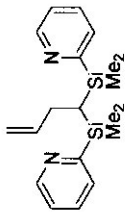


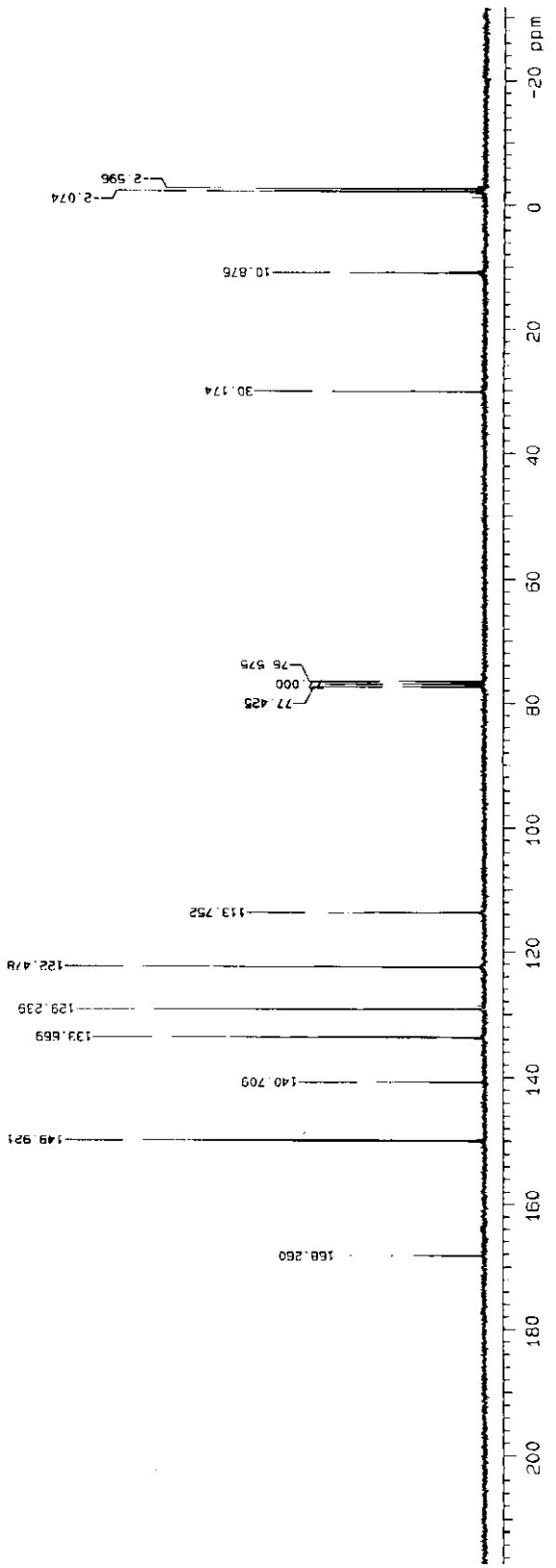

**4i**

$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **2**

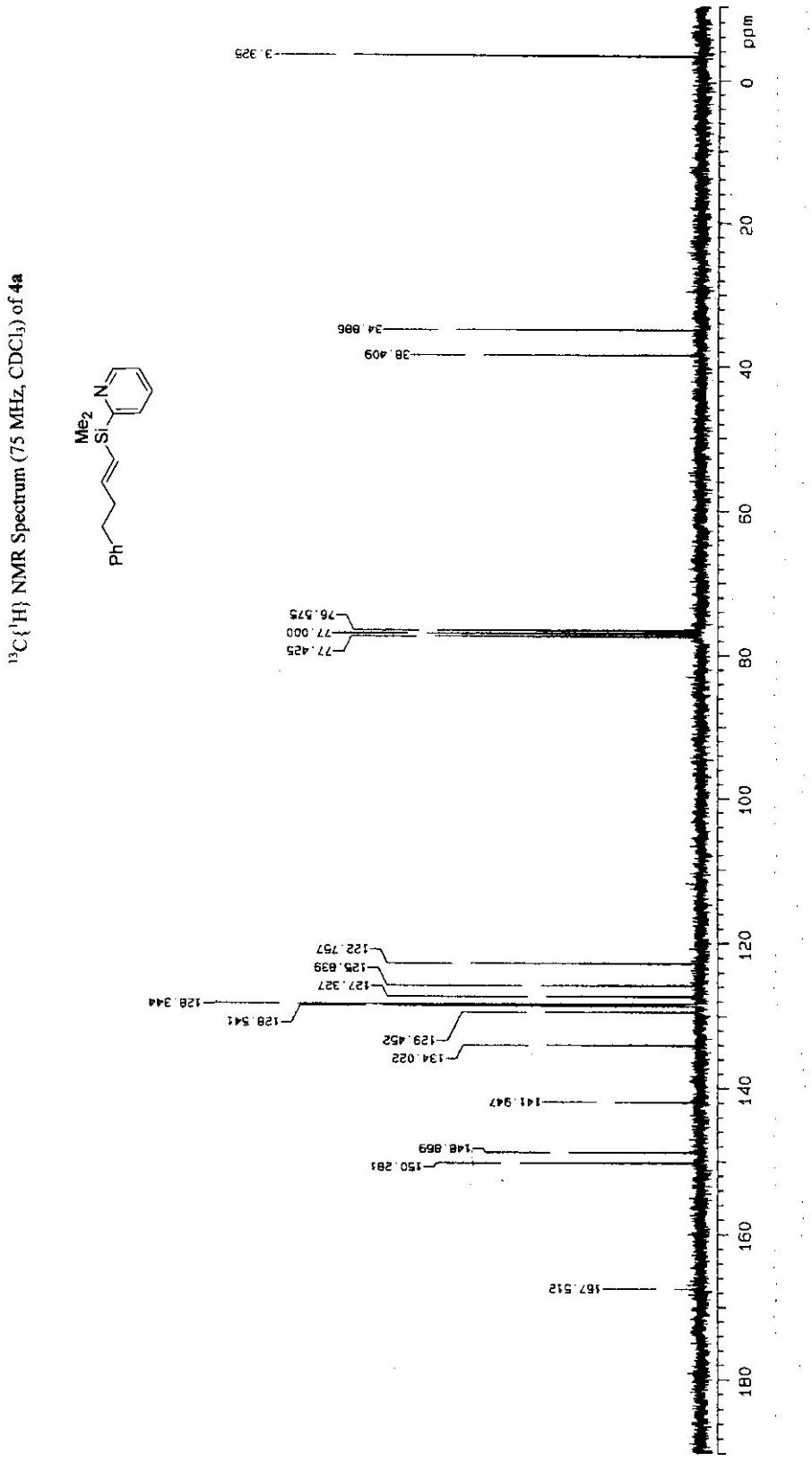


$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **3**

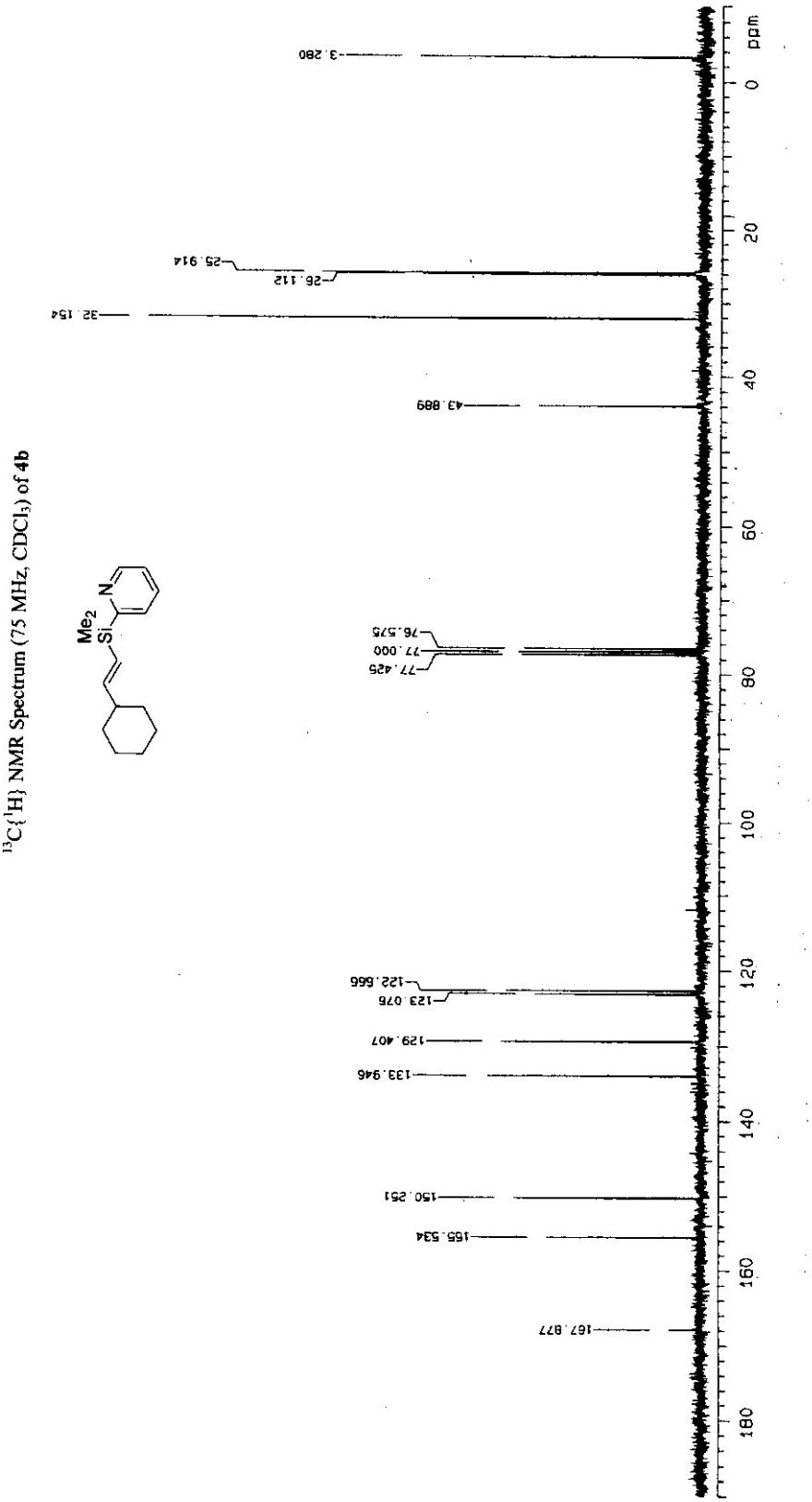


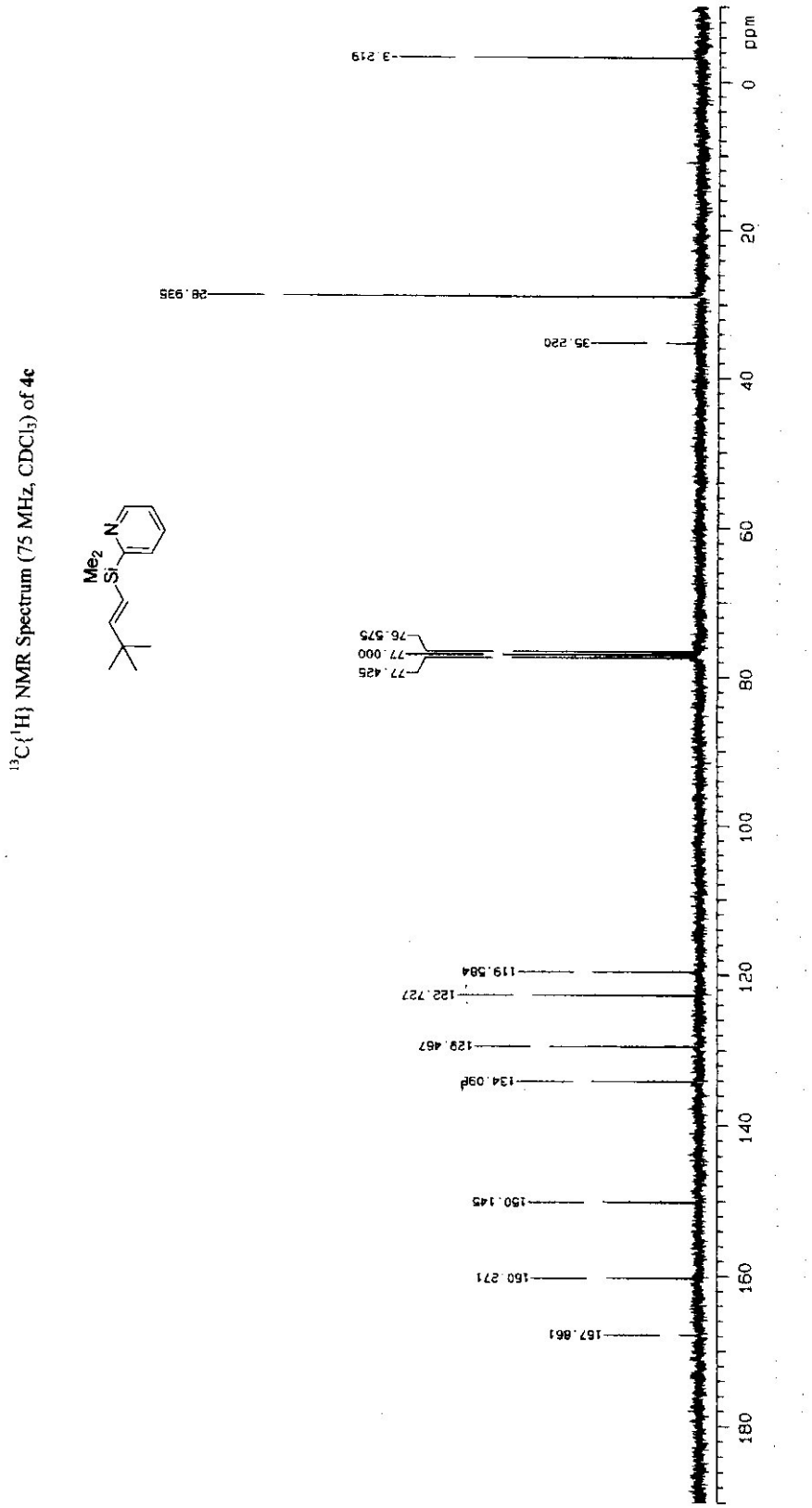
$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4a**



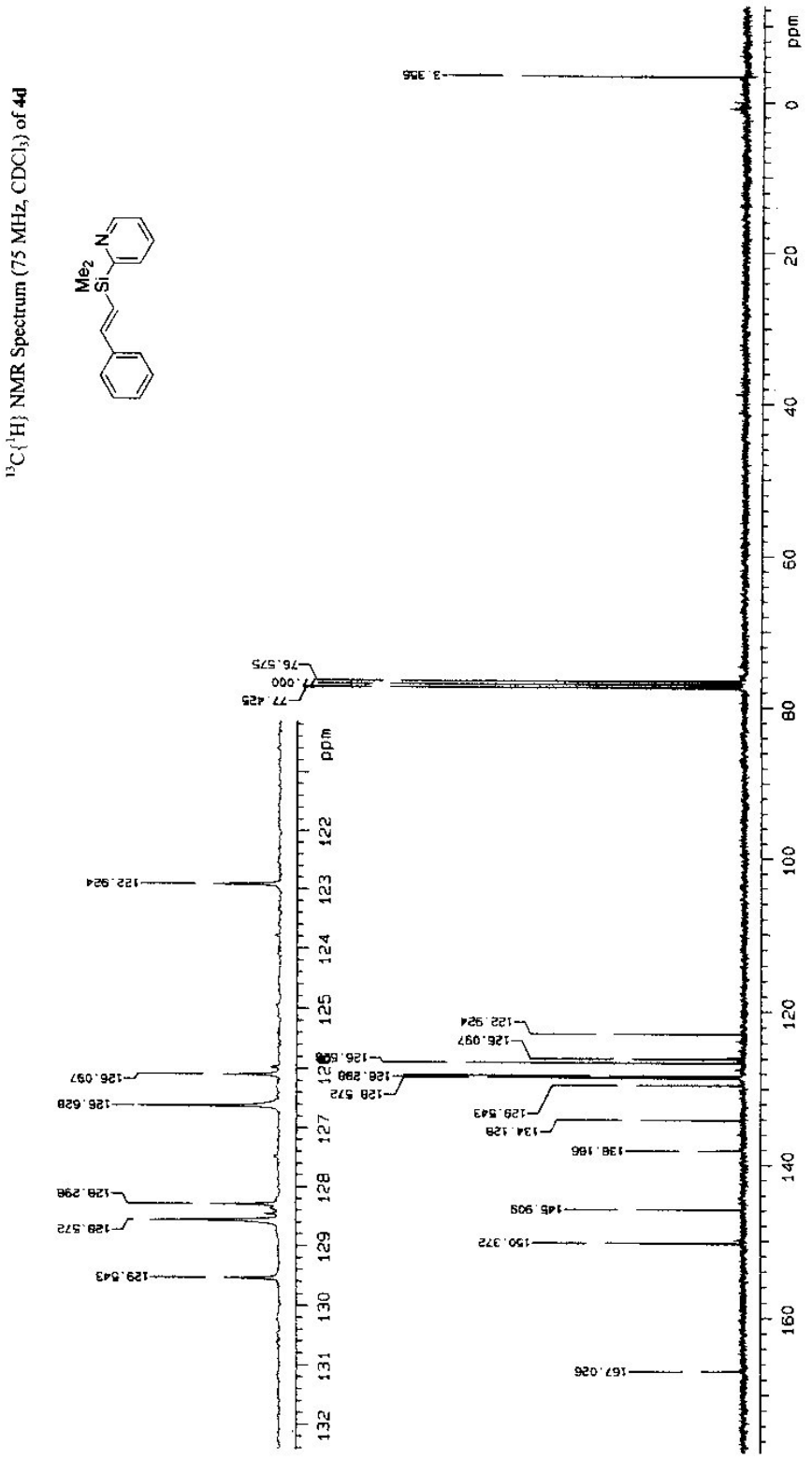
$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4b**



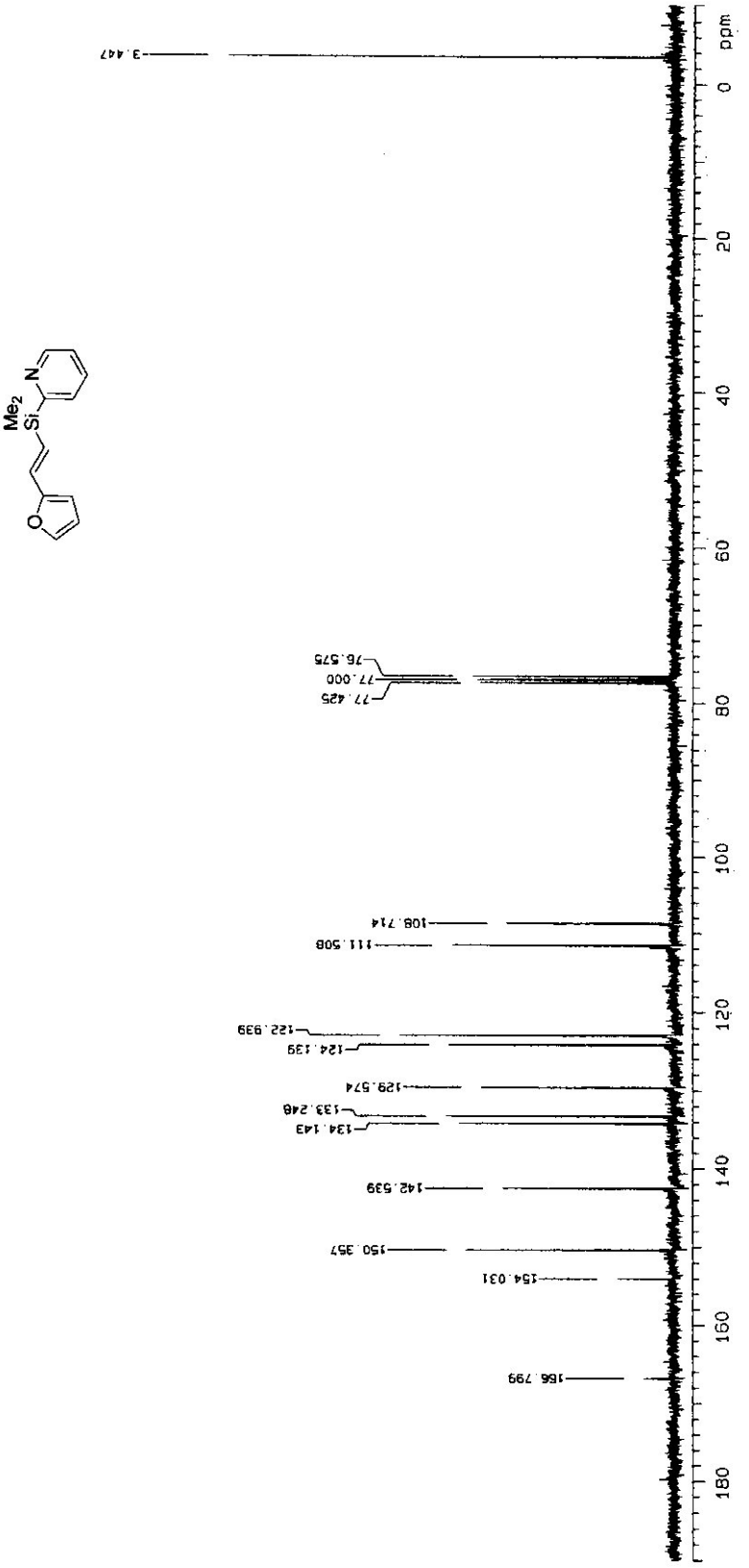
$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4c**



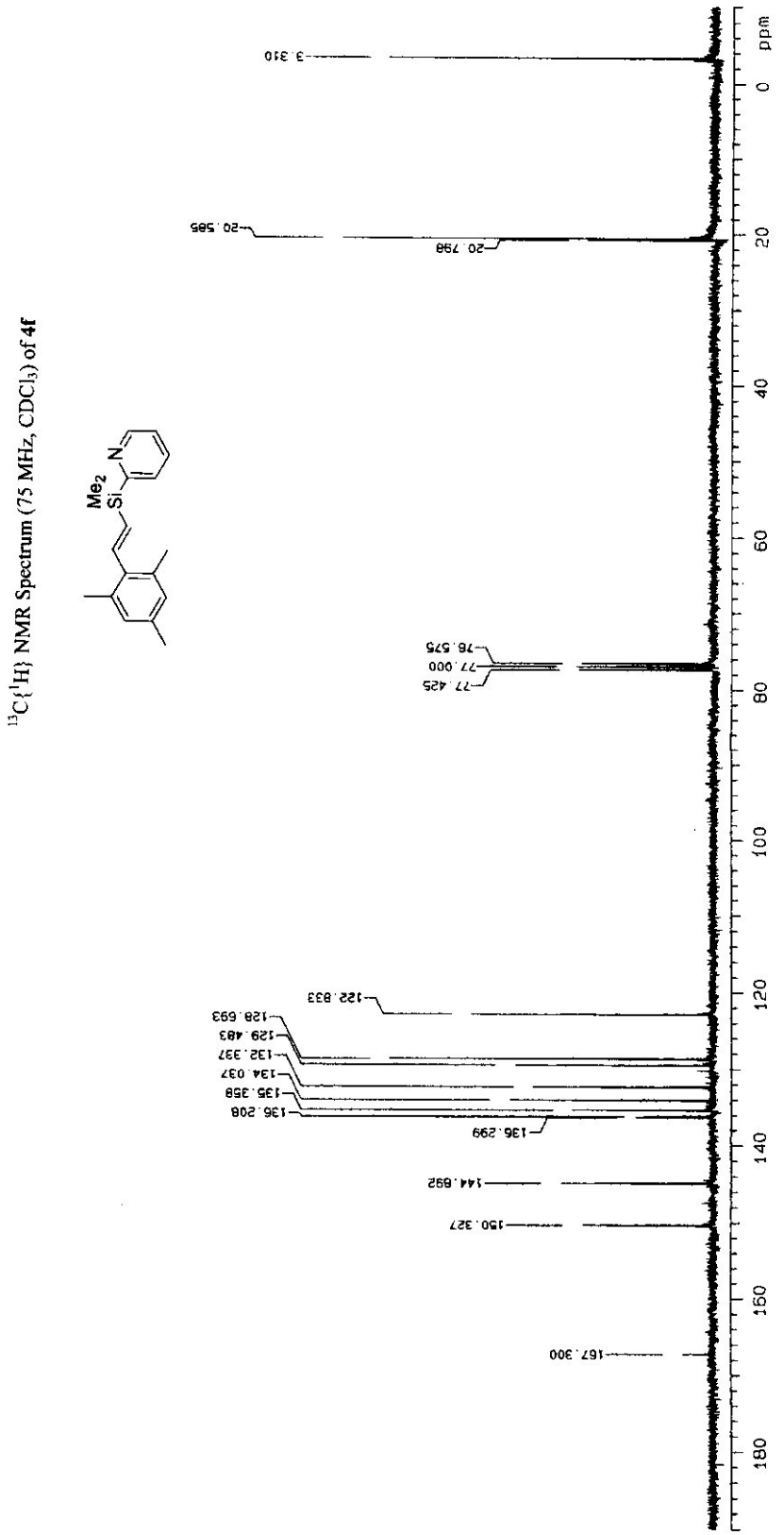
$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4d**



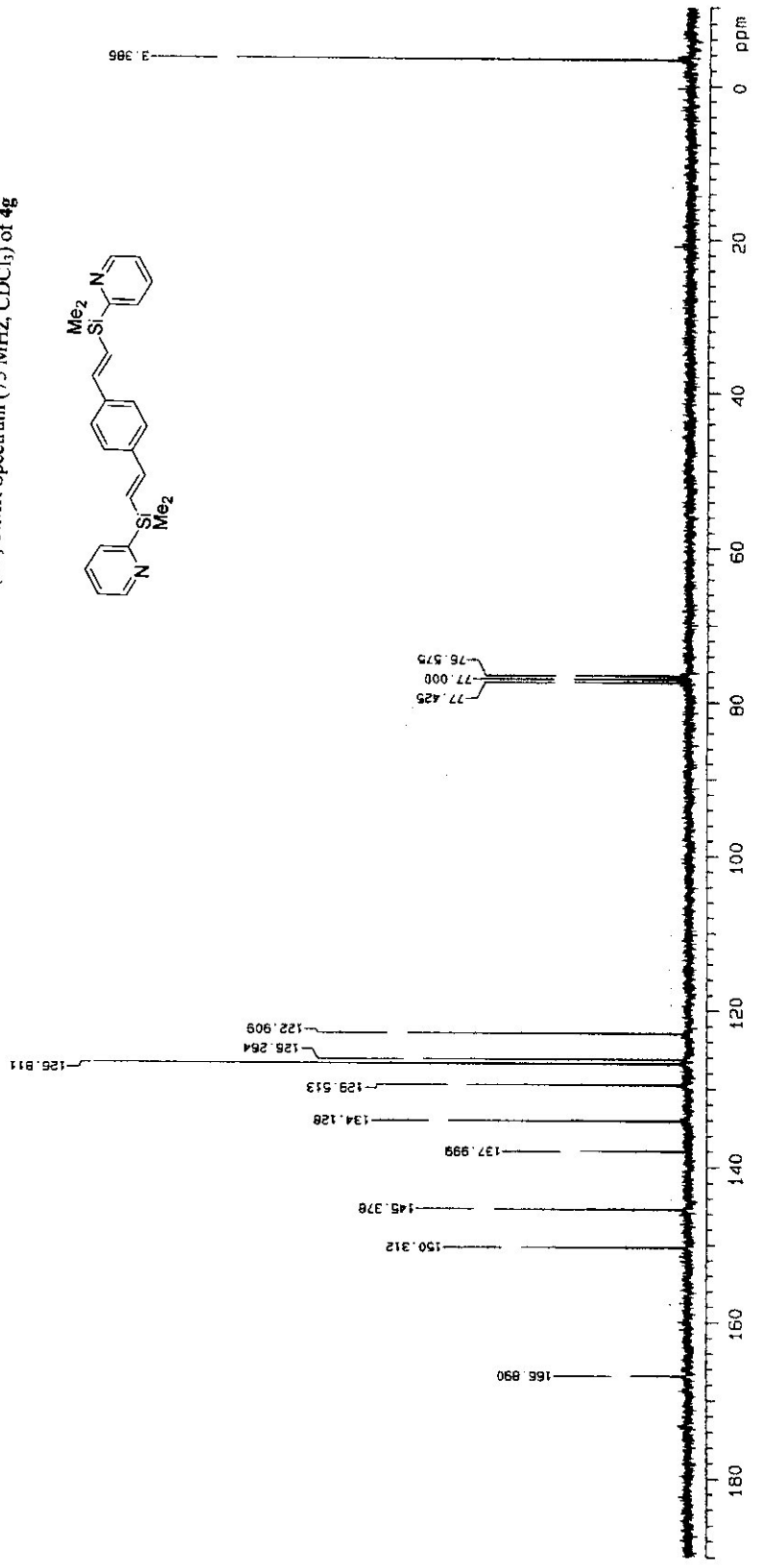
$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4e**



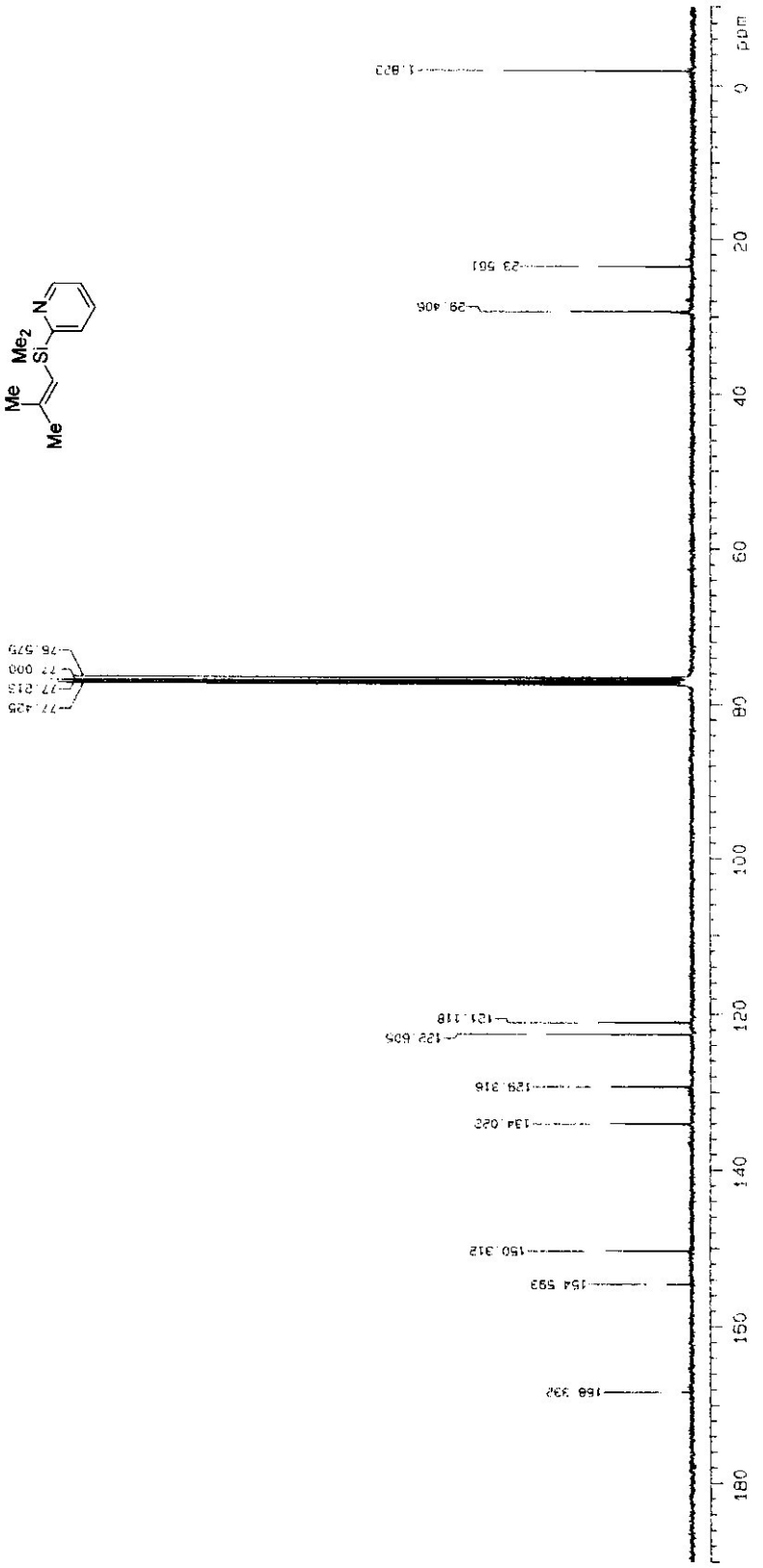
$^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4f**



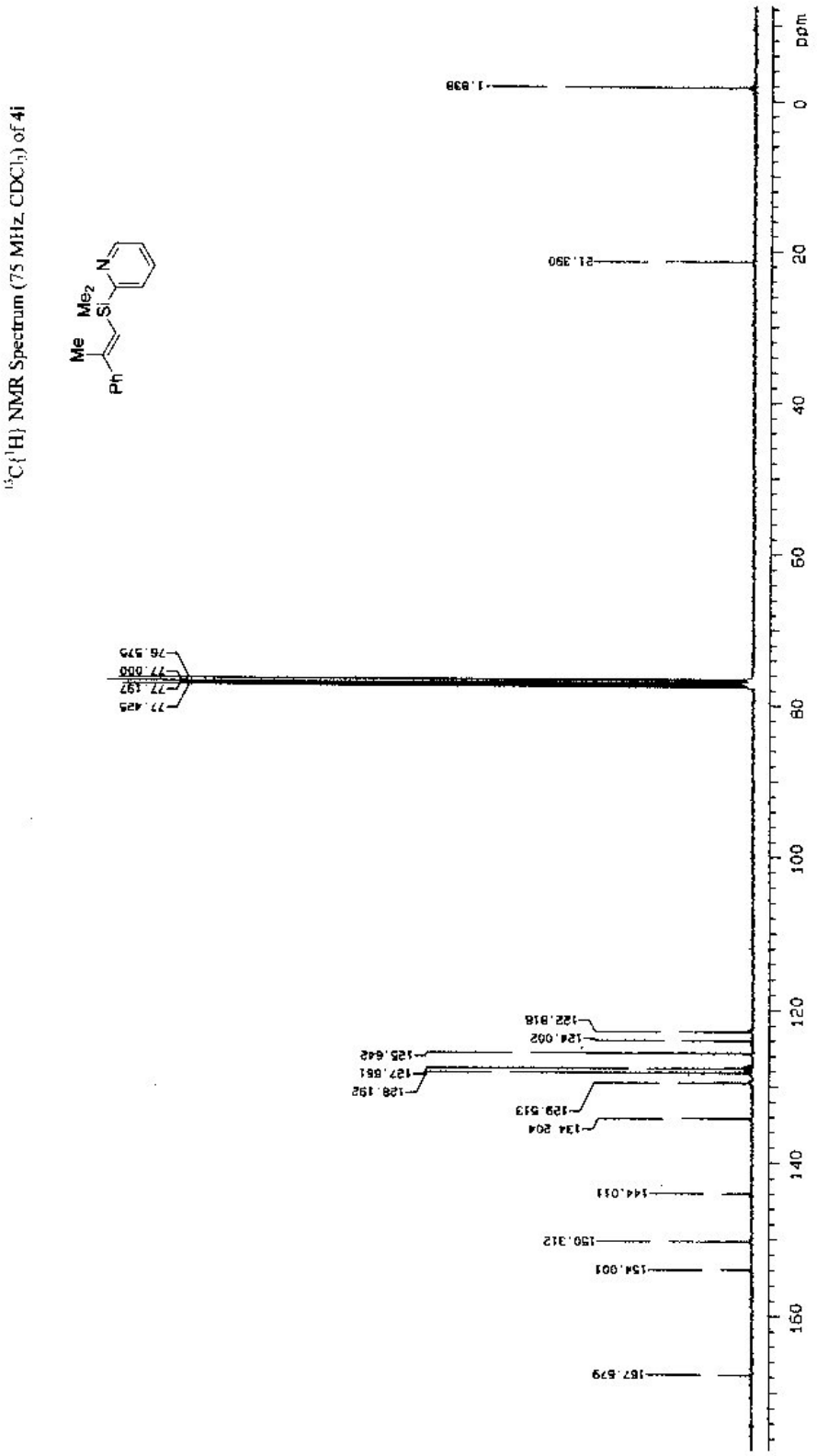
$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4g**



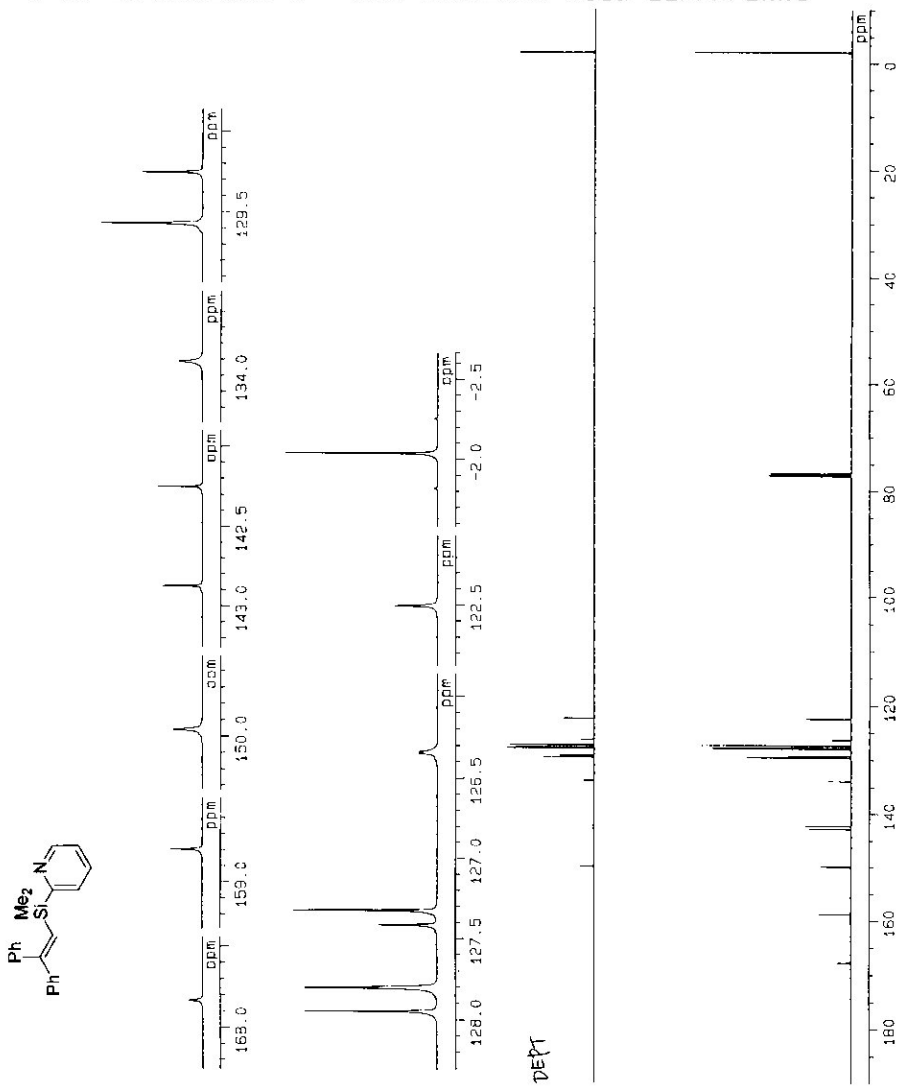
$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4h**



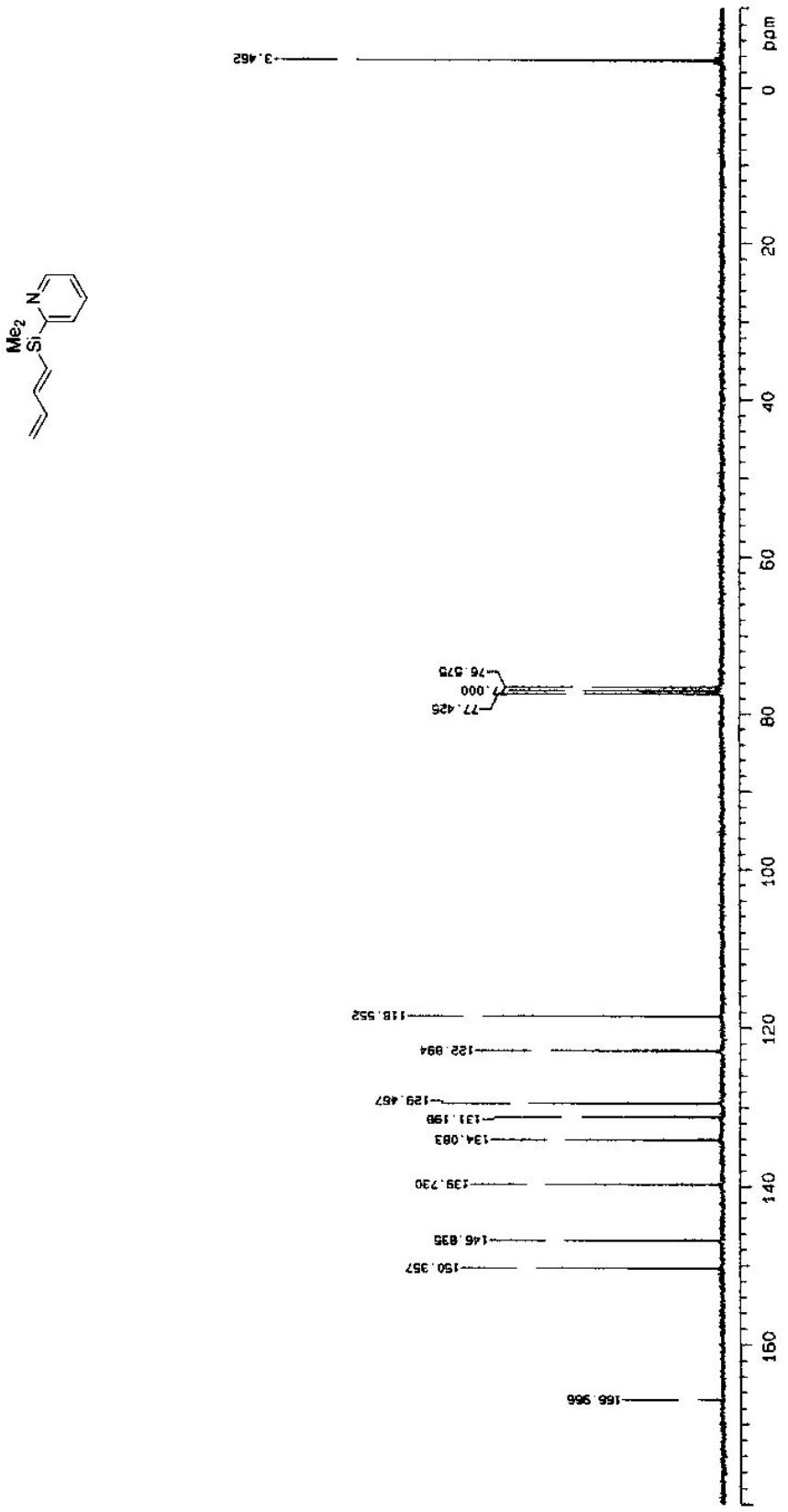
$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4i**



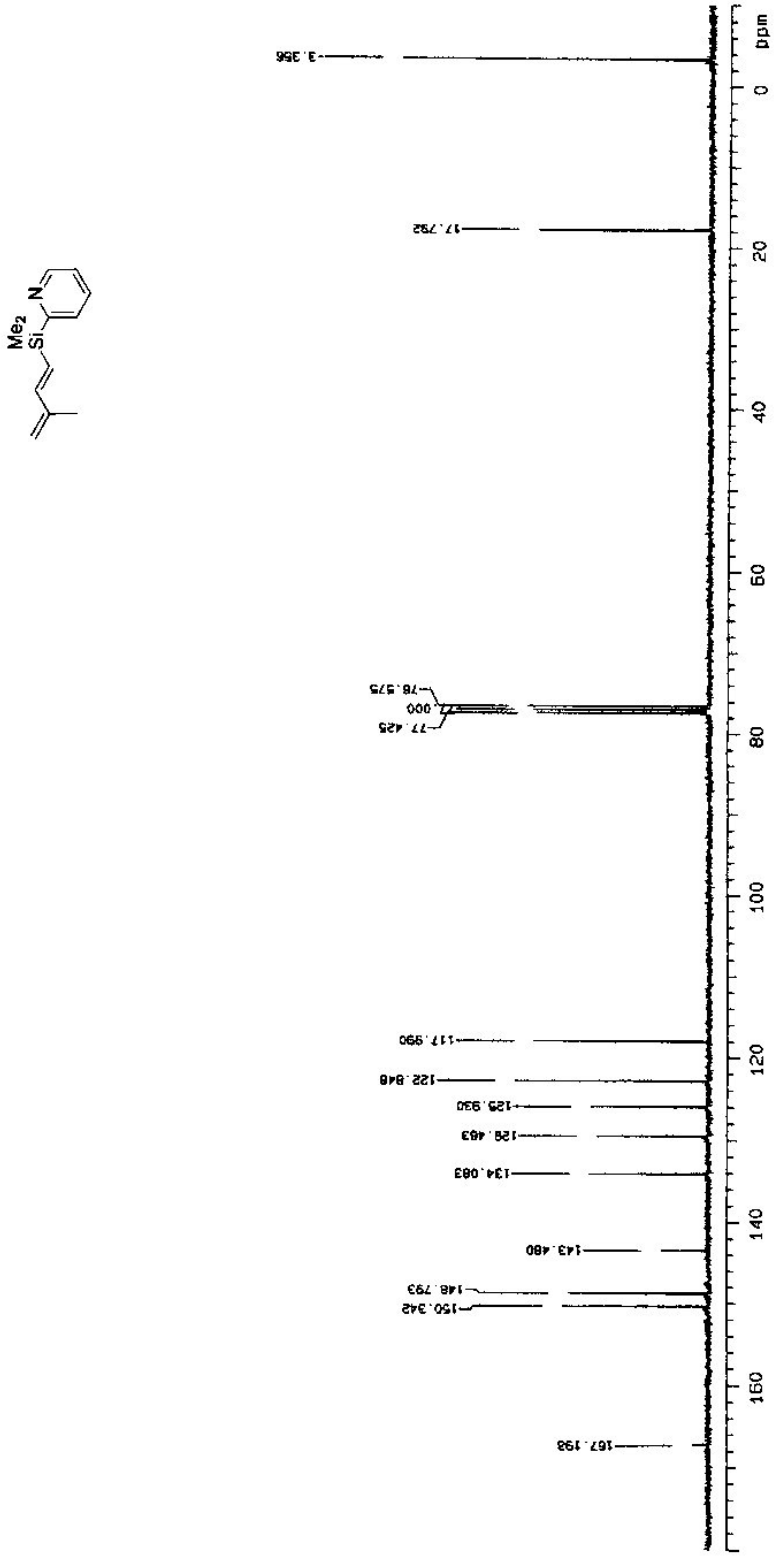
$^{13}C\{^1H\}$ NMR Spectrum (125 MHz, $CDCl_3$) of **4j**



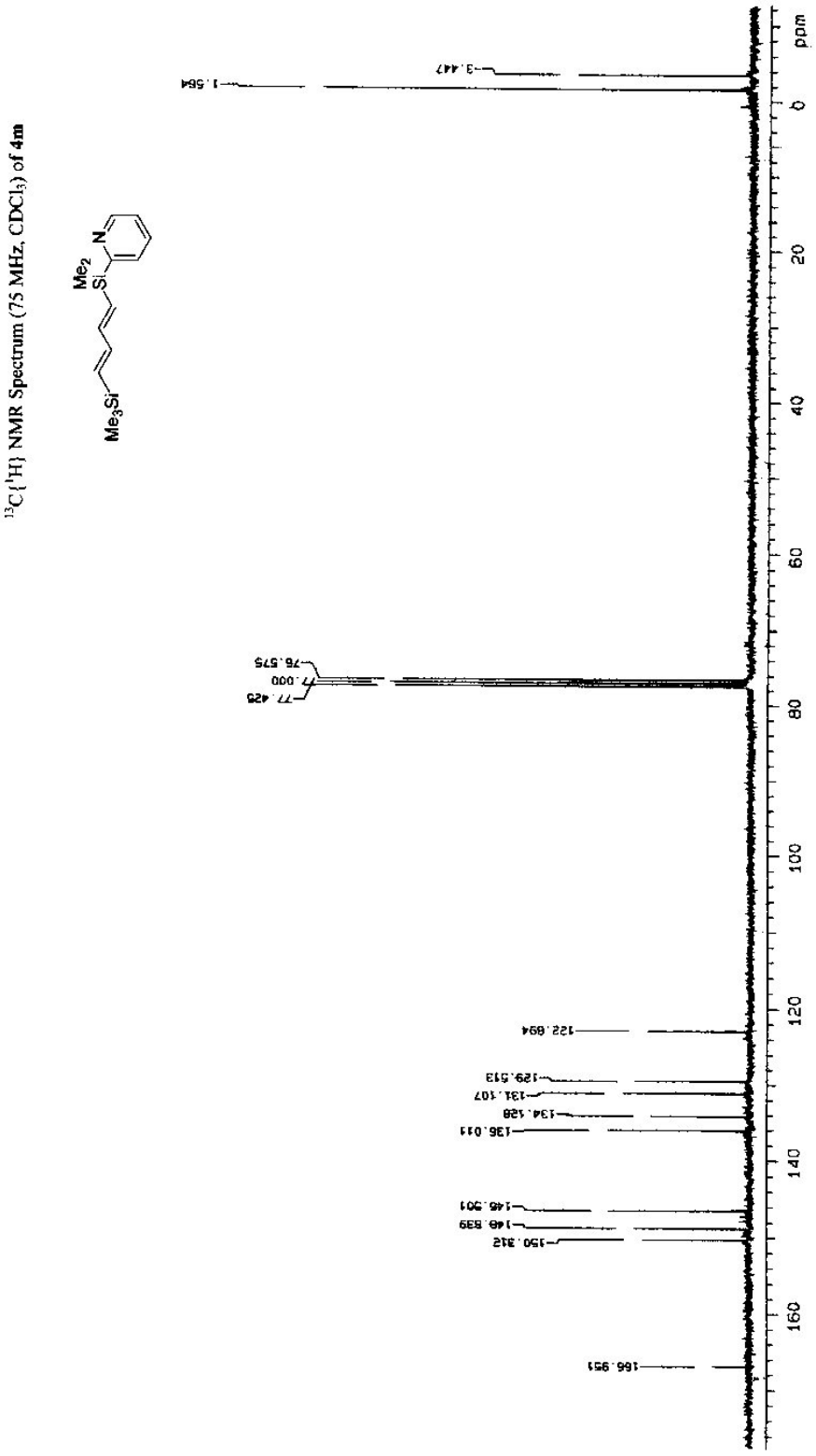
$^{13}C\{^{1}H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4k**



$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4l**



$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **4m**



$^{13}C\{^1H\}$ NMR Spectrum (75 MHz, $CDCl_3$) of **5**