

## Supporting Information

### Metal-Catalyzed Hydrosilylation of Alkenes and Alkynes Using Dimethyl(pyridyl)silane

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#### Product Data for Rhodium-Catalyzed Hydrosilylation of Alkenes

Table 2

**Dimethyl(1-octyl)(2-pyridyl)silane (2a).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.30 (s, 6 H), 0.80–0.84 (m, 2 H), 0.86 (t,  $J$  = 7.1 Hz, 3 H), 1.20–1.37 (m, 12 H), 7.18 (ddd,  $J$  = 7.7, 5.0, 1.5 Hz, 1 H), 7.48 (dt,  $J$  = 7.7, 1.5 Hz, 1 H), 7.57 (td,  $J$  = 7.7, 1.5 Hz, 1 H), 7.77 (dt,  $J$  = 5.0, 1.5 Hz, 1 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  –3.6, 14.1, 14.8, 22.6, 23.7, 29.22, 29.23, 31.9, 33.5, 122.6, 129.0, 133.8, 150.1, 168.0; IR (neat) 1576, 1559, 1417, 1246  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{27}\text{NSi}$ : 249.1913, found 249.1911. Anal. Calcd for  $\text{C}_{15}\text{H}_{27}\text{NSi}$ : C, 72.22; H, 10.91; N, 5.61. Found: C, 72.31; H, 10.63; N, 5.63.

**Dimethyl(3-phenylpropyl)(2-pyridyl)silane (2b).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.31 (s, 6 H), 0.84–0.93 (m, 2 H), 1.60–1.72 (m, 2 H), 2.62 (dd,  $J$  = 7.8, 7.2 Hz, 2 H), 7.10–7.21 (m, 4 H), 7.22–7.30 (m, 2 H), 7.46 (ddd,  $J$  = 7.5, 1.5, 1.2 Hz, 1 H), 7.56 (td,  $J$  = 7.5, 1.8 Hz, 1 H), 8.77 (ddd,  $J$  = 4.8, 1.8, 1.2 Hz, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –3.8, 14.6, 25.8, 39.6, 122.7, 125.7, 128.2, 128.5, 129.1, 133.9, 142.6, 150.2, 167.7; IR (neat) 1574, 1497, 1453, 1246  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{21}\text{NSi}$ : 255.1443, found 255.1446.

**Dimethyl(2-pyridyl)(2-trimethylsilylethyl)silane (2c).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  –0.06 (s, 9 H), 0.29 (s, 6 H), 0.35–0.43 (m, 2 H), 0.66–0.74 (m, 2 H), 7.15 (ddd,  $J$  = 7.5, 5.1, 1.8 Hz, 1 H), 7.46 (ddd,  $J$  = 7.5, 1.8, 1.2 Hz, 1 H), 7.54 (td,  $J$  = 7.5, 1.8 Hz, 1 H), 8.76 (ddd,  $J$  = 5.1, 1.8, 1.2 Hz, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –4.4, –2.4, 6.8, 8.5, 122.6, 129.1, 133.8, 150.2, 168.0; IR (neat) 2955, 1246, 860  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$  calcd for  $\text{C}_{12}\text{H}_{23}\text{NSi}_2$ : 237.1369, found 237.1370. Anal. Calcd for  $\text{C}_{12}\text{H}_{23}\text{NSi}_2$ : C, 60.69; H, 9.76; N, 5.90. Found: C, 60.94; H, 10.06; N, 5.88.

**Dimethyl[2-(3-cyclohexenyl)ethyl](2-pyridyl)silane (2d).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.29 (s, 6 H), 0.78–0.87 (m, 2 H), 1.05–1.20 (m, 1 H), 1.23–1.33 (m, 2 H), 1.35–1.50 (m, 1 H), 1.50–1.65 (m, 1 H), 1.65–1.78 (m, 1 H), 1.90–2.05 (m, 2 H), 2.05–2.15 (m, 1 H), 5.605 (s, 1 H), 5.612 (s, 1 H), 7.15 (ddd,  $J$  = 7.8, 5.1, 1.8 Hz, 1 H), 7.46 (dm,  $J$  = 7.8 Hz, 1 H), 7.54 (td,  $J$  = 7.8, 1.5 Hz, 1 H), 8.75 (dm,  $J$  = 5.1 Hz, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –3.9, 11.6, 25.1, 28.3, 30.3, 31.5, 36.3, 122.6, 126.7, 127.0, 129.0,

133.9, 150.2, 167.9. HRMS (EI) *m/z* calcd for C<sub>15</sub>H<sub>23</sub>NSi: 245.1600, found 245.1600.

**Dimethyl(4-methoxycarbonyl-3,3-dimethylpentyl)(2-pyridyl)silane (2e).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.24 (s, 6 H), 0.66–0.74 (m, 2 H), 0.87 (s, 6 H), 1.20–1.30 (m, 2 H), 2.11 (s, 2 H), 3.52 (s, 3 H), 7.11 (ddd, *J* = 7.5, 4.8, 1.5 Hz, 1 H), 7.42 (ddd, *J* = 7.5, 1.5, 0.9 Hz, 1 H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1 H), 8.69 (ddd, *J* = 4.8, 1.2, 0.9 Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -4.1, 8.4, 26.6, 33.9, 35.8, 44.9, 50.9, 122.7, 129.1, 133.9, 150.2, 167.6, 173.0; IR (neat) 1719, 1578, 1437, 1248 cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>25</sub>NO<sub>2</sub>Si: C, 64.47; H, 9.02; N, 5.01. Found: C, 64.68; H, 9.15; N, 5.04.

**Dimethyl(3-cyanopropyl)(2-pyridyl)silane (2f).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.34 (s, 6 H), 0.93–1.01 (m, 2 H), 1.64–1.80 (m, 2 H), 2.33 (t, *J* = 7.2 Hz, 2 H), 7.21 (ddd, *J* = 7.5, 4.8, 1.5 Hz, 1 H), 7.48 (dm, *J* = 7.5 Hz, 1 H), 7.59 (td, *J* = 7.5, 1.8 Hz, 1 H), 8.76 (dm, *J* = 4.8 Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -3.9, 14.6, 20.46, 20.51, 119.8, 123.1, 129.2, 134.2, 150.3, 166.6. Anal. Calcd for C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>Si: C, 64.45; H, 7.89; N, 13.71. Found: C, 64.80; H, 8.05; N, 13.47.

### Figure 1 (Figure 3)

**Dimethyl(1-octyl)(3-pyridyl)silane.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 0.27 (s, 6 H), 0.72–0.79 (m, 2 H), 0.86 (t, *J* = 7.0 Hz, 3 H), 1.19–1.32 (m, 12 H), 7.23 (ddd, *J* = 7.4, 4.9, 1.0 Hz, 1 H), 7.75 (dt, *J* = 7.4, 1.9 Hz, 1 H), 8.55 (dd, *J* = 4.9, 1.9 Hz, 1 H), 8.66 (dd, *J* = 1.9, 1.0 Hz, 1 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ -3.3, 14.1, 15.4, 22.6, 23.7, 29.17, 29.19, 31.8, 33.5, 123.1, 134.4, 141.2, 149.8, 154.0; IR (neat) 1574, 1559, 1393, 1250 cm<sup>-1</sup>. HRMS (EI) *m/z* calcd for C<sub>15</sub>H<sub>27</sub>NSi: 249.1913, found 249.1919. Anal. Calcd for C<sub>15</sub>H<sub>27</sub>NSi: C, 72.22; H, 10.91; N, 5.61. Found: C, 72.12; H, 11.19; N, 5.57.

**Dimethyl(1-octyl)(4-pyridyl)silane.** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.27 (s, 6 H), 0.70–0.78 (m, 2 H), 0.87 (t, *J* = 7.2 Hz, 3 H), 1.18–1.32 (m, 12 H), 7.41 (d, *J* = 5.4 Hz, 2 H), 8.51–8.64 (m, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ -3.6, 14.1, 15.0, 22.6, 23.6, 29.2, 31.9, 33.4, 128.4, 148.5, 149.8; IR (neat) 1584, 1402, 1250, 1125 cm<sup>-1</sup>. HRMS (EI) *m/z* calcd for C<sub>15</sub>H<sub>27</sub>NSi: 249.1913, found 249.1912. Anal. Calcd for C<sub>15</sub>H<sub>27</sub>NSi: C, 72.22; H, 10.91; N, 5.61. Found: C, 72.26; H, 11.14; N, 5.60.

**Dimethyl(1-octyl)phenylsilane.** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.26 (s, 6 H), 0.73 (t, *J* = 7.8 Hz, 2 H), 0.87 (t, *J* = 6.8 Hz, 3 H), 1.14–1.35 (m, 12 H), 7.32–7.38 (m, 3 H), 7.48–7.56 (m, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -3.0, 14.1, 15.7, 22.7, 23.8, 29.3, 31.9, 33.6, 127.7, 128.7, 133.6, 139.8.

### Figure 2 (Figure 4)

**Dimethyl(3-pyridyl)(2-trimethylsilylethyl)silane.** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ -0.04 (s, 9 H), 0.29 (s, 6 H), 0.34–0.40 (m, 2 H), 0.62–0.68 (m, 2 H), 7.27–7.35 (m, 1 H), 7.82 (dm, *J* = 7.5 Hz, 1 H), 8.54–8.62 (m, 1 H), 8.67 (s, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -3.9, -2.3, 7.5, 8.5, 123.1, 134.2, 141.3,

149.8, 154.1; IR (neat) 1248, 860, 835 cm<sup>-1</sup>. HRMS (EI) *m/z* calcd for C<sub>12</sub>H<sub>23</sub>NSi<sub>2</sub>: 237.1369, found 237.1368. Anal. Calcd for C<sub>12</sub>H<sub>23</sub>NSi<sub>2</sub>: C, 60.69; H, 9.76; N, 5.90. Found: C, 60.75; H, 10.04; N, 5.73.

**Dimethyl(4-pyridyl)(2-trimethylsilylethyl)silane.** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ -0.03 (s, 9 H), 0.27 (s, 6 H), 0.31–0.38 (m, 2 H), 0.60–0.67 (m, 2 H), 7.41 (dd, *J* = 4.2, 1.5 Hz, 2 H), 8.56 (dd, *J* = 4.2, 1.5 Hz, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -4.2, -2.3, 7.1, 7.5, 128.5, 148.4, 149.7; IR (neat) 1248, 1127, 837 cm<sup>-1</sup>. HRMS (EI) *m/z* calcd for C<sub>12</sub>H<sub>23</sub>NSi<sub>2</sub>: 237.1369, found 237.1370. Anal. Calcd for C<sub>12</sub>H<sub>23</sub>NSi<sub>2</sub>: C, 60.69; H, 9.76; N, 5.90. Found: C, 60.68; H, 10.04; N, 5.98.

**Dimethylphenyl(2-trimethylsilylethyl)silane.**<sup>2</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ -0.05 (s, 9 H), 0.34–0.42 (m, 2 H), 0.59–0.66 (m, 2 H), 7.32–7.40 (m, 3 H), 7.45–7.56 (m, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -3.5, -2.2, 7.8, 8.8, 127.7, 128.8, 133.0, 133.6, 139.5.

### Procedure for the Consecutive Use of the Recovered Rhodium Catalyst (Section 1-3)

**First Run.** To a solution of RhCl(PPh<sub>3</sub>)<sub>3</sub> (23.1 mg, 5 mol %) in CH<sub>3</sub>CN (1.0 mL) were added 1-octene (168 mg, 1.5 mmol) and **1** (69 mg, 0.5 mmol) under argon. After the mixture was stirred at room temperature for 1 h, toluene (2 mL) was added to the mixture. This mixture was extracted with 1 N aq HCl (6 × 3 mL). The evaporation of the organic phase afforded the recovered rhodium catalyst, which was used directly for the next run. The combined aqueous phase was neutralized by adding NaHCO<sub>3</sub> and then was extracted with EtOAc (3 × 10 mL). Drying over Na<sub>2</sub>SO<sub>4</sub> and removal of the solvents under reduced pressure afforded **2a** (107 mg, 86%) as colorless oil.

**Second Run.** To a solution of the recovered rhodium catalyst in CH<sub>3</sub>CN (1.0 mL) were added 1-octene (168 mg, 1.5 mmol) and **1** (69 mg, 0.5 mmol) under argon. After the reaction mixture was stirred at room temperature for 1 h, toluene (2 mL) was added to the reaction mixture. Exactly same separation procedure as a first run furnished the recovered rhodium catalyst and **2a** (84 mg, 67%).

**Third Run.** Exactly same procedure as a second run afforded the recovered rhodium catalyst and **2a** (74 mg, 59%).

**Forth Run.** Exactly same procedure as a second run afforded the recovered rhodium catalyst and **2a** (62 mg, 50%).

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(1) Matsumoto, A.; Ito, Y. *J. Org. Chem.* **2000**, *65*, 5707.

(2) Lukevic, E.; Pudova, O.; Sturkovich, R.; Gaukhman, A. *J. Organomet. Chem.* **1988**, *346*, 297.

## Product Data for Platinum-Catalyzed Hydrosilylation of Alkynes

**Table 4**

**(E)-1-Dimethyl(2-pyridyl)silyl-1-octene (3a).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.38 (s, 6 H), 0.87 (t,  $J$  = 6.9 Hz, 3 H), 1.25–1.32 (m, 6 H), 1.35–1.45 (m, 2 H), 2.15 (dd,  $J$  = 6.3, 1.5 Hz, 2 H), 5.81 (dt,  $J$  = 18.3, 1.5 Hz, 1 H), 6.19 (dt,  $J$  = 18.3, 6.3 Hz, 1 H), 7.19 (ddd,  $J$  = 7.5, 5.1, 1.2 Hz, 1 H), 7.51 (dt,  $J$  = 7.5, 1.2 Hz, 1 H), 7.58 (td,  $J$  = 7.5, 1.2 Hz, 1 H), 8.78 (dt,  $J$  = 5.1, 1.2 Hz, 1 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  –3.2, 14.0, 22.5, 28.5, 28.8, 31.7, 36.8, 122.6, 126.1, 129.3, 133.9, 150.08, 150.09, 167.6; IR (neat) 1617, 1576, 1559, 1246  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{25}\text{NSi}$ : 247.1756, found 247.1759. Anal. Calcd for  $\text{C}_{15}\text{H}_{25}\text{NSi}$ : C, 72.81; H, 10.18; N, 5.66. Found: C, 72.76; H, 10.39; N, 5.50.

**2-Dimethyl(2-pyridyl)silyl-1-octene (4a).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.42 (s, 6 H), 0.84 (t,  $J$  = 6.8 Hz, 3 H), 1.13–1.38 (m, 8 H), 2.13 (tm,  $J$  = 7.5 Hz, 2 H), 5.44 (dt,  $J$  = 3.0, 0.9 Hz, 1 H), 5.71 (dt,  $J$  = 3.0, 1.2 Hz, 1 H), 7.18 (ddd,  $J$  = 7.5, 4.8, 1.5 Hz, 1 H), 7.50 (ddd,  $J$  = 7.5, 1.5, 1.2 Hz, 1 H), 7.56 (td,  $J$  = 7.5, 1.8 Hz, 1 H), 8.78 (ddd,  $J$  = 4.8, 1.8, 1.2 Hz, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –3.5, 14.1, 22.6, 28.8, 29.1, 31.7, 36.1, 122.7, 126.2, 129.4, 133.9, 149.7, 150.2, 166.9; IR (neat) 1576, 1559, 1418, 1246  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{25}\text{NSi}$ : 247.1756, found 247.1758.

**(E)-1-Dimethyl(2-pyridyl)silyl-6-chloro-1-hexene (3b).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.39 (s, 6 H), 1.50–1.62 (m, 2 H), 1.72–1.83 (m, 2 H), 2.19 (dtd,  $J$  = 7.5, 6.0, 1.5 Hz, 2 H), 3.54 (t,  $J$  = 6.6 Hz, 2 H), 5.84 (dt,  $J$  = 18.6, 1.5 Hz, 1 H), 6.17 (dt,  $J$  = 18.6, 6.0 Hz, 1 H), 7.21 (ddm,  $J$  = 7.5, 4.5 Hz, 1 H), 7.51 (dm,  $J$  = 7.5 Hz, 1 H), 7.60 (tm,  $J$  = 7.5 Hz, 1 H), 8.78 (dm,  $J$  = 4.5 Hz, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –3.2, 25.6, 32.0, 35.8, 44.8, 122.6, 127.1, 129.2, 133.9, 148.8, 150.1, 167.2; IR (neat) 1617, 1574, 1451, 1418, 1246  $\text{cm}^{-1}$ . HRMS (FAB)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{21}\text{ClNSi}$  ( $M + H$ ): 254.1132, found 254.1128. Anal. Calcd for  $\text{C}_{13}\text{H}_{20}\text{ClNSi}$ : C, 61.51; H, 7.94; N, 5.52. Found: C, 61.73; H, 8.22; N, 5.44.

**(E)-1-Dimethyl(2-pyridyl)silyl-6-methoxy-1-hexene (3c).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.38 (s, 6 H), 1.41–1.63 (m, 4 H), 2.18 (dt,  $J$  = 7.2, 6.2 Hz, 2 H), 3.32 (s, 3 H), 3.37 (t,  $J$  = 6.3 Hz, 2 H), 5.82 (dt,  $J$  = 18.3, 1.5 Hz, 1 H), 6.18 (dt,  $J$  = 18.3, 6.2 Hz, 1 H), 7.19 (ddd,  $J$  = 7.5, 4.8, 1.2 Hz, 1 H), 7.50 (dt,  $J$  = 7.5, 1.2 Hz, 1 H), 7.58 (td,  $J$  = 7.5, 1.5 Hz, 1 H), 8.78 (ddd,  $J$  = 4.8, 1.5, 1.2 Hz, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –3.2, 24.9, 29.1, 36.4, 58.4, 72.6, 122.6, 126.5, 129.2, 133.8, 149.4, 150.0, 167.3; IR (neat) 1617, 1574, 1559, 1418, 1246  $\text{cm}^{-1}$ . HRMS (FAB)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{24}\text{ONSi}$  ( $M + H$ ): 250.1627, found 250.1628.

**(E)-b-Dimethyl(2-pyridyl)silyl-styrene (3d).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  –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  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{17}\text{NSi}$ : 239.1131, found 239.1122. Anal.

Calcd for C<sub>15</sub>H<sub>17</sub>NSi: C, 75.26; H, 7.16; N, 5.85. Found: C, 75.49; H, 7.25; N, 5.83.

**a-Dimethyl(2-pyridyl)silyl-styrene (4d).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.51 (s, 6 H), 5.75 (d, *J*=2.7 Hz, 1 H), 6.05 (d, *J*=2.7 Hz, 1 H), 7.13–7.27 (m, 6 H), 7.52 (dt, *J*=7.2, 1.5 Hz, 1 H), 7.57 (td, *J*=7.2, 1.5 Hz, 1 H), 8.81 (dt, *J*=4.8, 1.5 Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -2.9, 122.9, 126.5, 126.9, 128.1, 129.6, 129.8, 134.1, 143.8, 150.0, 150.2, 166.5; IR (neat) 1574, 1418, 1248 cm<sup>-1</sup>. HRMS (EI) *m/z* calcd for C<sub>15</sub>H<sub>17</sub>NSi: 239.1130, found 239.1133.

**(E)-1-Dimethyl(2-pyridyl)silyl-2-trimethylsilylethene (3e).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.06 (s, 9 H), 0.39 (s, 6 H), 6.75 (s, 2 H), 7.17 (ddd, *J*=7.5, 4.8, 1.2 Hz, 1 H), 7.47 (dt, *J*=7.5, 1.2 Hz, 1 H), 7.56 (td, *J*=7.5, 1.8 Hz, 1 H), 8.77 (ddd, *J*=4.8, 1.8, 1.2 Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -3.6, -1.7, 122.7, 129.4, 133.9, 147.0, 150.2, 153.8, 167.0; IR (neat) 1576, 1558, 1418, 1248 cm<sup>-1</sup>. HRMS (EI) *m/z* calcd for C<sub>12</sub>H<sub>21</sub>NSi<sub>2</sub>: 235.1213, found 235.1215. Anal. Calcd for C<sub>12</sub>H<sub>21</sub>NSi<sub>2</sub>: C, 61.21; H, 8.99; N, 5.95. Found: C, 61.50; H, 9.09; N, 5.70.

**1-Dimethyl(2-pyridyl)silyl-1-trimethylsilylethene (4e).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ -0.02 (s, 9 H), 0.44 (s, 6 H), 6.38 (d, *J*=4.8 Hz, 1 H), 6.44 (d, *J*=4.8 Hz, 1 H), 7.17 (ddd, *J*=7.5, 4.8, 1.5 Hz, 1 H), 7.48 (ddd, *J*=7.5, 1.5, 0.9 Hz, 1 H), 7.57 (td, *J*=7.5, 1.5 Hz, 1 H), 8.78 (ddd, *J*=4.8, 1.5, 0.9 Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -2.4, -0.5, 122.6, 129.6, 133.8, 142.4, 150.1, 151.6, 167.4; IR (neat) 1576, 1559, 1418, 1248 cm<sup>-1</sup>. HRMS (EI) *m/z* calcd for C<sub>12</sub>H<sub>21</sub>NSi<sub>2</sub>: 235.1213, found 235.1212.

**(E)-4-Dimethyl(2-pyridyl)silyl-4-octene (3f).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.40 (s, 6 H), 0.81 (t, *J*=7.2 Hz, 3 H), 0.91 (t, *J*=7.2 Hz, 3 H), 1.14–1.28 (m, 2 H), 1.33–1.47 (m, 2 H), 2.07–2.16 (m, 4 H), 5.86 (t, *J*=6.6 Hz, 1 H), 7.19 (ddd, *J*=7.5, 4.8, 1.5 Hz, 1 H), 7.50 (dm, *J*=7.5 Hz, 1 H), 7.58 (td, *J*=7.5, 1.5 Hz, 1 H), 8.78 (ddd, *J*=4.8, 1.5, 0.9 Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -3.1, 13.9, 14.4, 22.6, 23.3, 30.7, 32.1, 122.5, 129.4, 133.7, 138.2, 143.1, 150.0, 167.8; IR (neat) 1574, 1559, 1418, 1244 cm<sup>-1</sup>. HRMS (EI) *m/z* calcd for C<sub>15</sub>H<sub>25</sub>NSi: 247.1756, found 247.1752. Anal. Calcd for C<sub>15</sub>H<sub>25</sub>NSi: C, 72.81; H, 10.18; N, 5.66. Found: C, 72.80; H, 10.45; N, 5.62.

**(E)-1-Dimethyl(2-pyridyl)silyl-1,2-diphenylethene (3g).** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.50 (s, 6 H), 6.92–7.01 (m, 5 H), 7.05–7.11 (m, 3 H), 7.14–7.28 (m, 4 H), 7.52 (dt, *J*=7.5, 1.5 Hz, 1 H), 7.57 (td, *J*=7.5, 1.5 Hz, 1 H), 8.84 (dt, *J*=4.8, 1.5 Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ -3.6, 122.8, 125.7, 127.1, 127.6, 127.8, 128.5, 129.5, 129.9, 133.8, 137.1, 139.8, 142.1, 143.8, 150.1, 166.1; IR (neat) 1574, 1559, 1246, 826 cm<sup>-1</sup>. HRMS (EI) *m/z* calcd for C<sub>21</sub>H<sub>21</sub>NSi: 315.1443, found 315.1445. Anal. Calcd for C<sub>21</sub>H<sub>21</sub>NSi: C, 79.95; H, 6.71; N, 4.44. Found: C, 79.73; H, 6.72; N, 4.47.

## Figure 5

**(E)-1-Dimethyl(3-pyridyl)silyl-1-octene.** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.32 (s, 6 H), 0.85 (t, *J*=6.6 Hz, 3 H), 1.16–1.44 (m, 8 H), 2.13 (q, *J*=6.6 Hz, 2 H), 5.71 (dt, *J*=18.6, 1.5 Hz, 1 H), 6.13 (dt, *J*=

18.6, 6.6 Hz, 1 H), 7.21 (ddd,  $J = 7.5, 5.1, 0.6$  Hz, 1 H), 7.74 (dt,  $J = 7.5, 1.5$  Hz, 1 H), 8.54 (dd,  $J = 5.1, 1.5$  Hz, 1 H), 8.65 (d,  $J = 1.5$  Hz, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –2.7, 14.0, 22.5, 28.4, 28.8, 31.6, 36.7, 123.0, 125.9, 134.1, 141.4, 149.8, 150.5, 154.2; IR (neat) 1574, 1393, 1250, 990  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{25}\text{NSi}$ : 247.1756, found 247.1761.

**2-Dimethyl(3-pyridyl)silyl-1-octene.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.39 (s, 6 H), 0.84 (t,  $J = 6.6$  Hz, 3 H), 1.12–1.38 (m, 8 H), 2.09 (t,  $J = 7.5$  Hz, 2 H), 5.38–5.42 (m, 1 H), 5.69–5.73 (m, 1 H), 7.25 (ddd,  $J = 7.8, 3.6, 0.6$  Hz, 1 H), 7.77 (dt,  $J = 7.8, 1.8$  Hz, 1 H), 8.57 (d,  $J = 3.6$  Hz, 1 H), 8.67 (s, 1 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –3.1, 14.1, 22.6, 28.8, 29.0, 31.6, 35.9, 123.2, 126.5, 133.5, 141.7, 149.3, 149.9, 154.3; IR (neat) 1574, 1395, 1250  $\text{cm}^{-1}$ . HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{25}\text{NSi}$ : 247.1756, found 247.1757.

**(E)-1-Dimethyl(4-pyridyl)silyl-1-octene.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.33 (s, 6 H), 0.88 (t,  $J = 7.2$  Hz, 3 H), 1.23–1.31 (m, 6 H), 1.32–1.45 (m, 2 H), 2.15 (q,  $J = 6.6$  Hz, 2 H), 5.70 (dt,  $J = 18.6, 1.5$  Hz, 1 H), 6.15 (dt,  $J = 18.6, 6.6$  Hz, 1 H), 7.44 (d,  $J = 3.0$  Hz, 2 H), 8.74 (brs, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –3.1, 14.1, 22.6, 28.4, 28.8, 31.6, 36.8, 125.3, 129.3, 148.7, 149.7, 150.9. HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{25}\text{NSi}$ : 247.1756, found 247.1758.

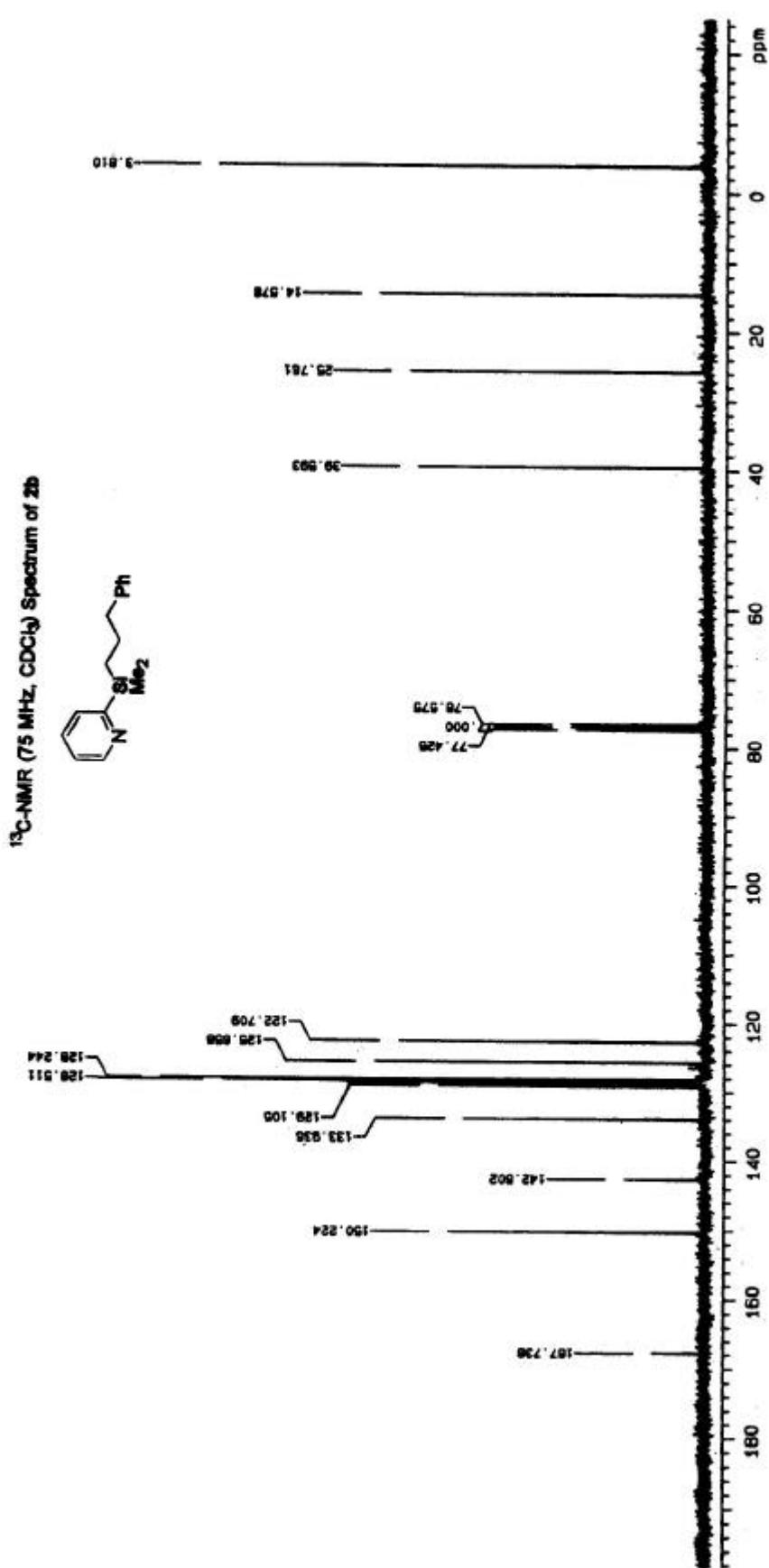
**2-Dimethyl(4-pyridyl)silyl-1-octene.**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.38 (s, 6 H), 0.85 (t,  $J = 7.2$  Hz, 3 H), 1.15–1.35 (m, 8 H), 2.08 (t,  $J = 7.5$  Hz, 2 H), 5.40–5.43 (m, 1 H), 5.72–5.74 (m, 1 H), 7.41 (d,  $J = 4.5$  Hz, 2 H), 8.59 (brs, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –3.5, 14.0, 22.6, 28.8, 29.0, 31.6, 35.9, 126.8, 128.9, 148.3, 148.8, 149.3. HRMS (EI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{25}\text{NSi}$ : 247.1756, found 247.1757.

**(E)-1-Dimethylphenylsilyl-1-octene.<sup>3</sup>**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.39 (s, 6 H), 0.96 (t,  $J = 7.2$  Hz, 3 H), 1.31–1.39 (m, 6 H), 1.40–1.53 (m, 2 H), 2.21 (q,  $J = 6.6$  Hz, 2 H), 5.83 (dt,  $J = 18.3, 1.5$  Hz, 1 H), 6.20 (dt,  $J = 18.3, 6.3$  Hz, 1 H), 7.38–7.43 (m, 3 H), 7.56–7.62 (m, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –2.4, 14.1, 22.6, 28.6, 28.9, 31.7, 36.8, 127.2, 127.7, 128.8, 133.8, 139.4, 149.5.

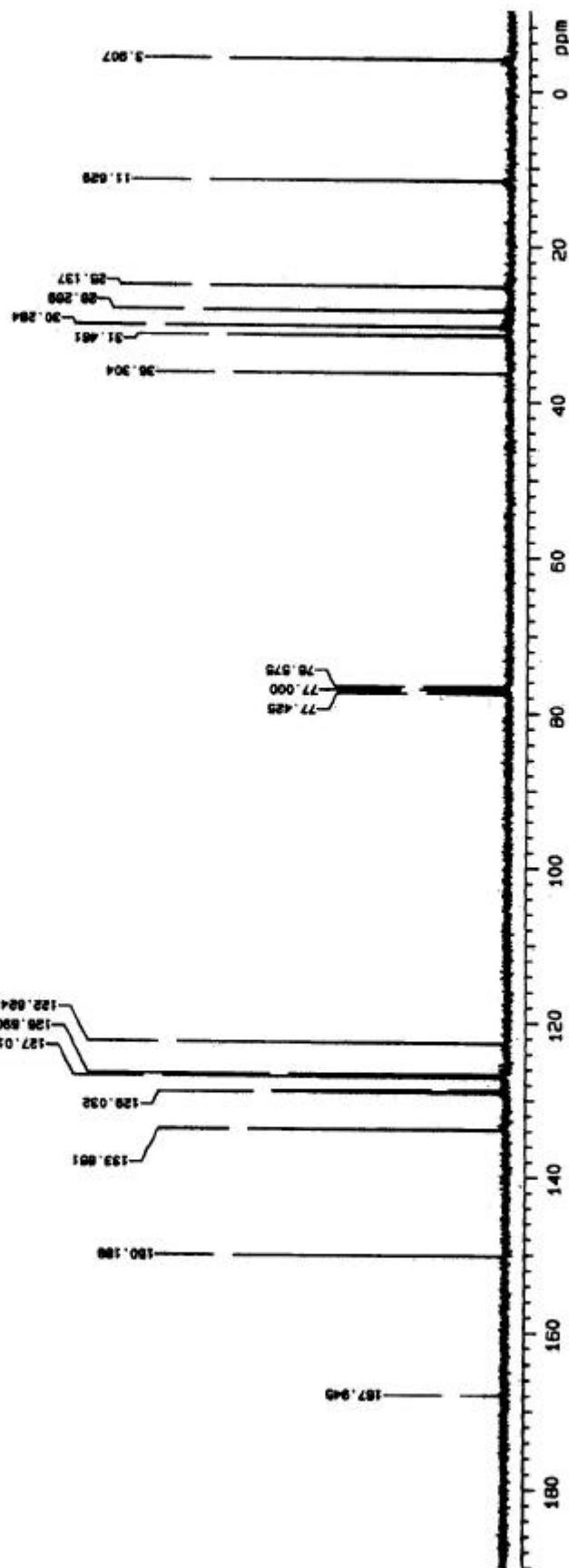
**2-Dimethylphenylsilyl-1-octene.<sup>3</sup>**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.38 (s, 6 H), 0.87 (t,  $J = 7.2$  Hz, 3 H), 1.17–1.25 (m, 6 H), 1.25–1.40 (m, 2 H), 2.12 (t,  $J = 6.9$  Hz, 2 H), 5.39–5.42 (m, 1 H), 5.68–5.71 (m, 1 H), 7.33–7.39 (m, 3 H), 7.50–7.56 (m, 2 H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  –2.9, 14.1, 22.6, 28.8, 29.1, 31.7, 36.0, 125.6, 127.7, 128.9, 133.9, 138.5, 150.6.

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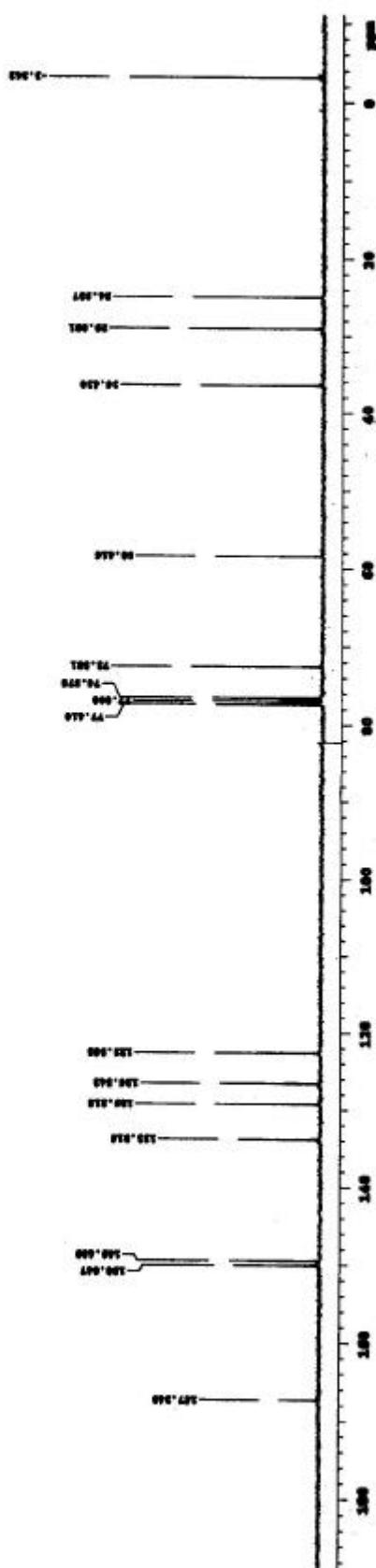
(3) Fugami, K.; Hibino, J.; Nakatsukasa, S.; Matsubara, S.; Oshima, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1988**, 44, 4277.



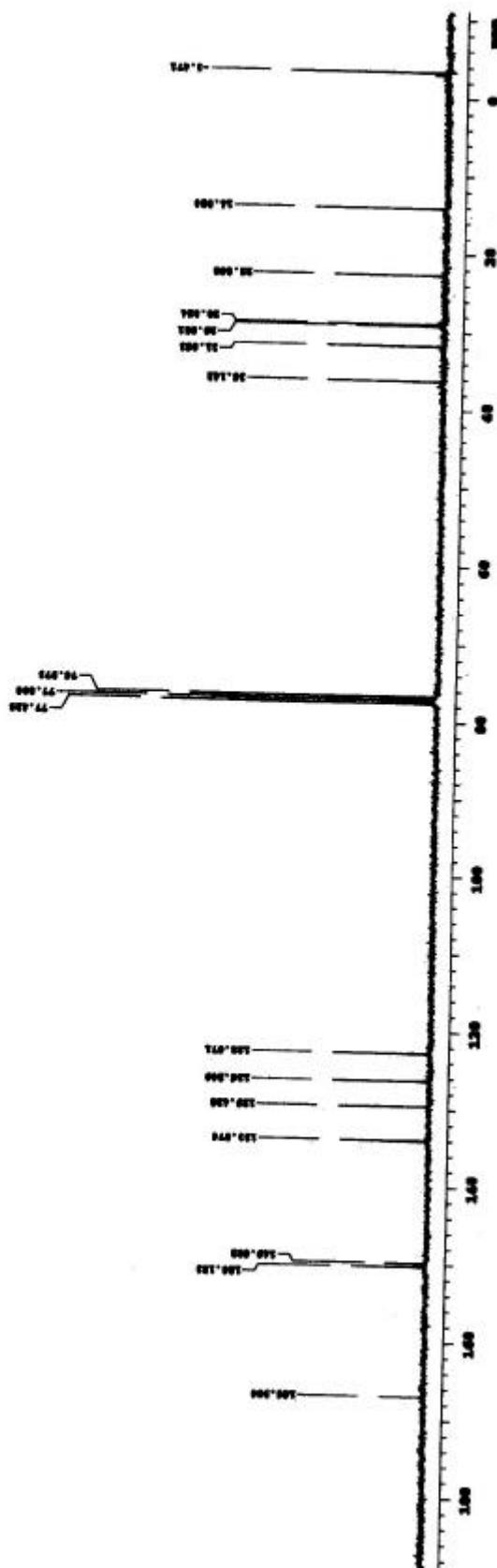
<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) Spectrum of 2d



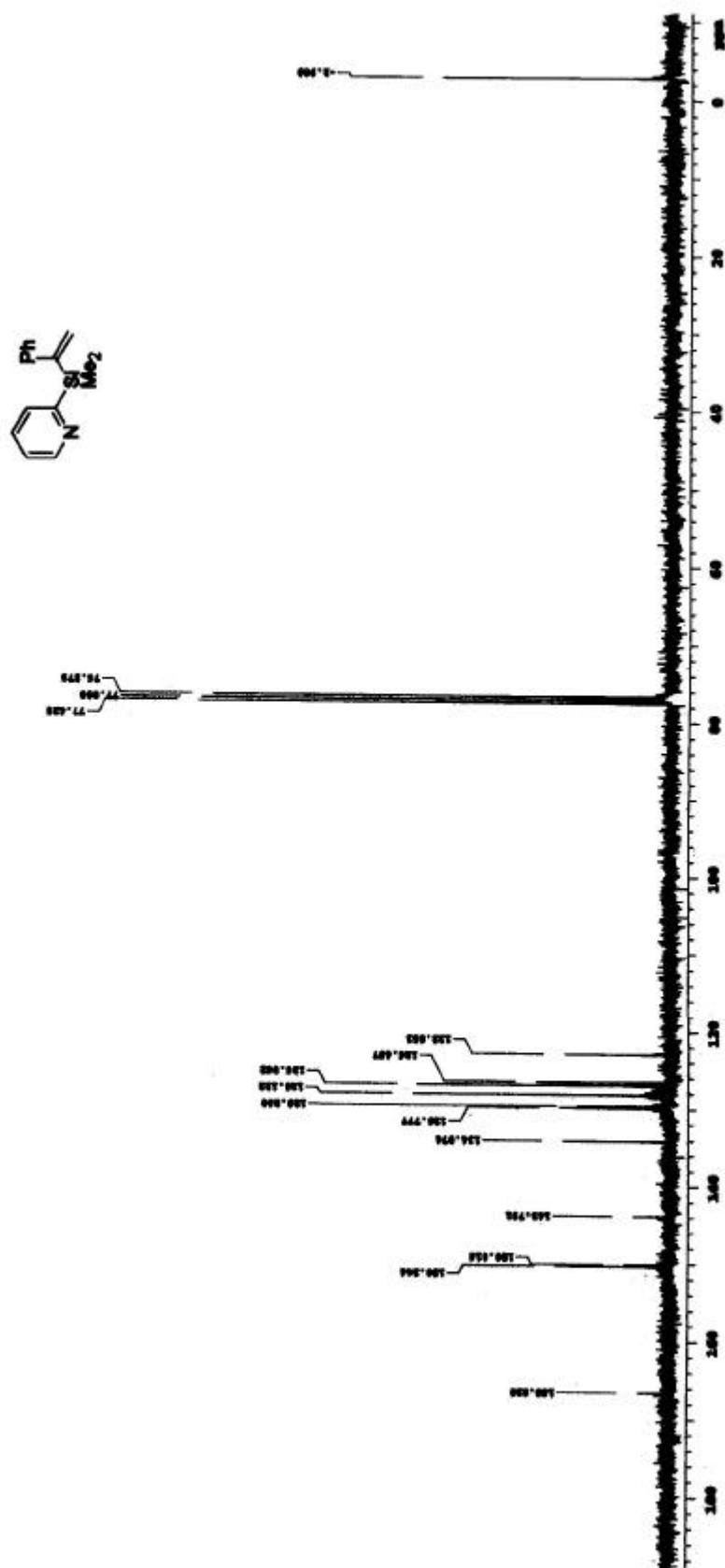
<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) Spectrum of 3c



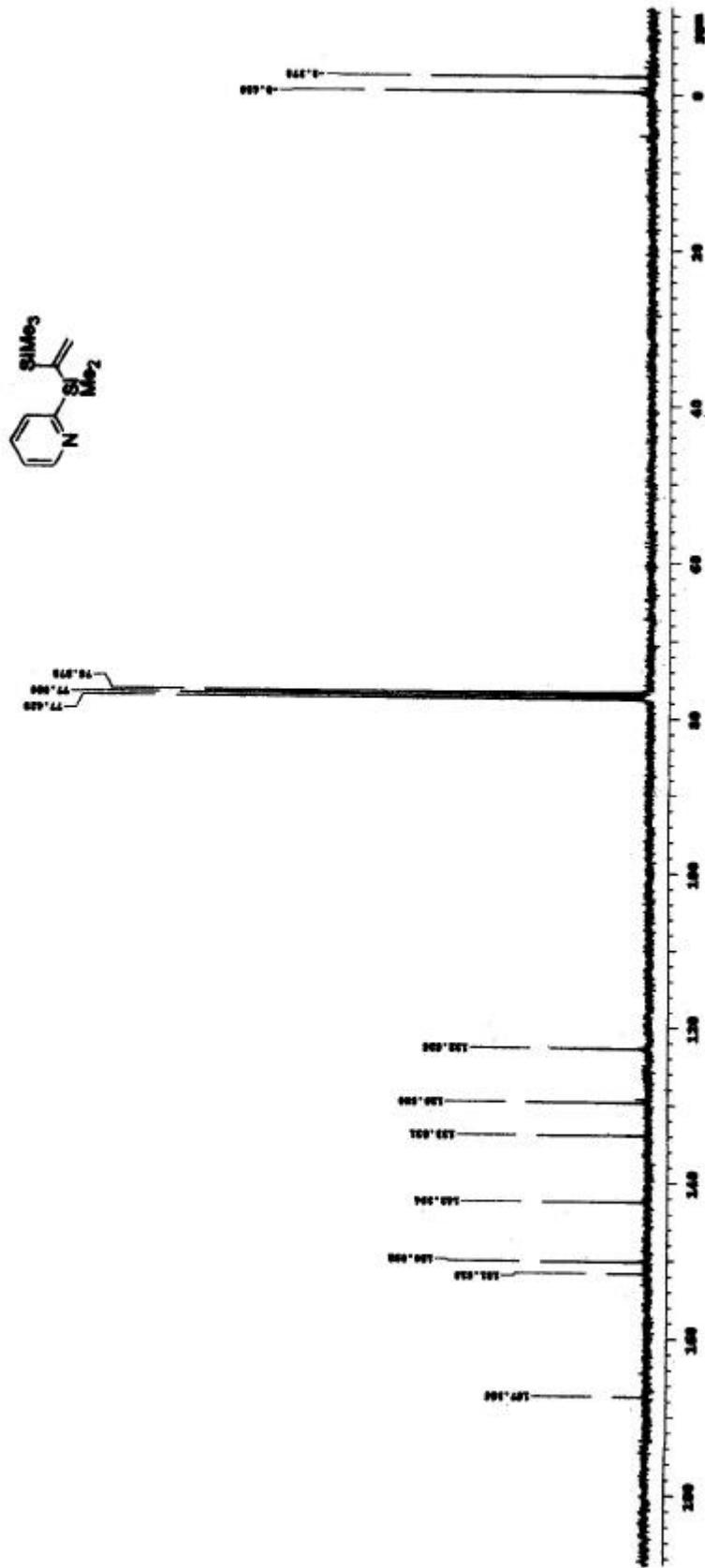
<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) Spectrum of 4a



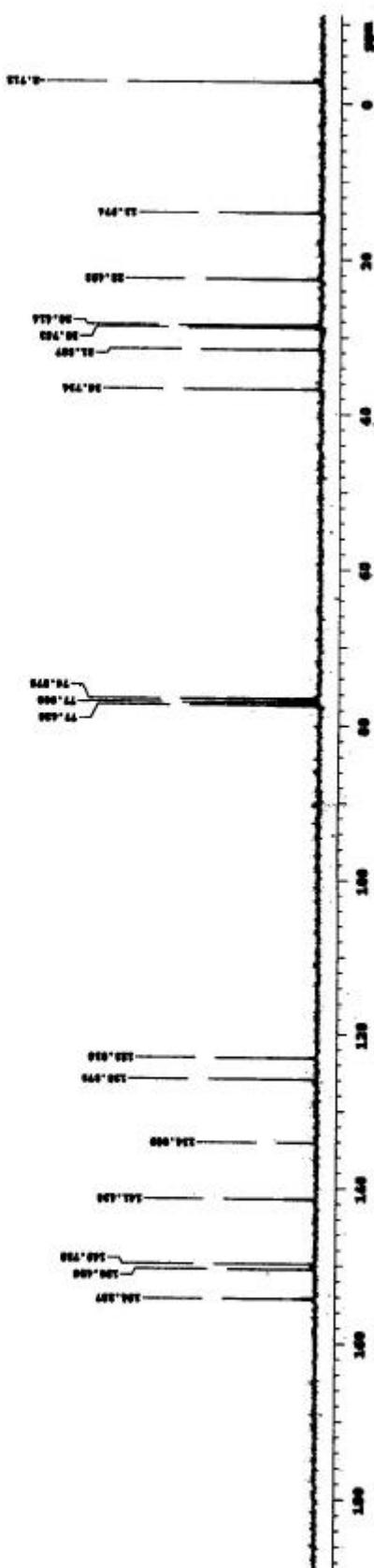
$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ) spectrum of 4d



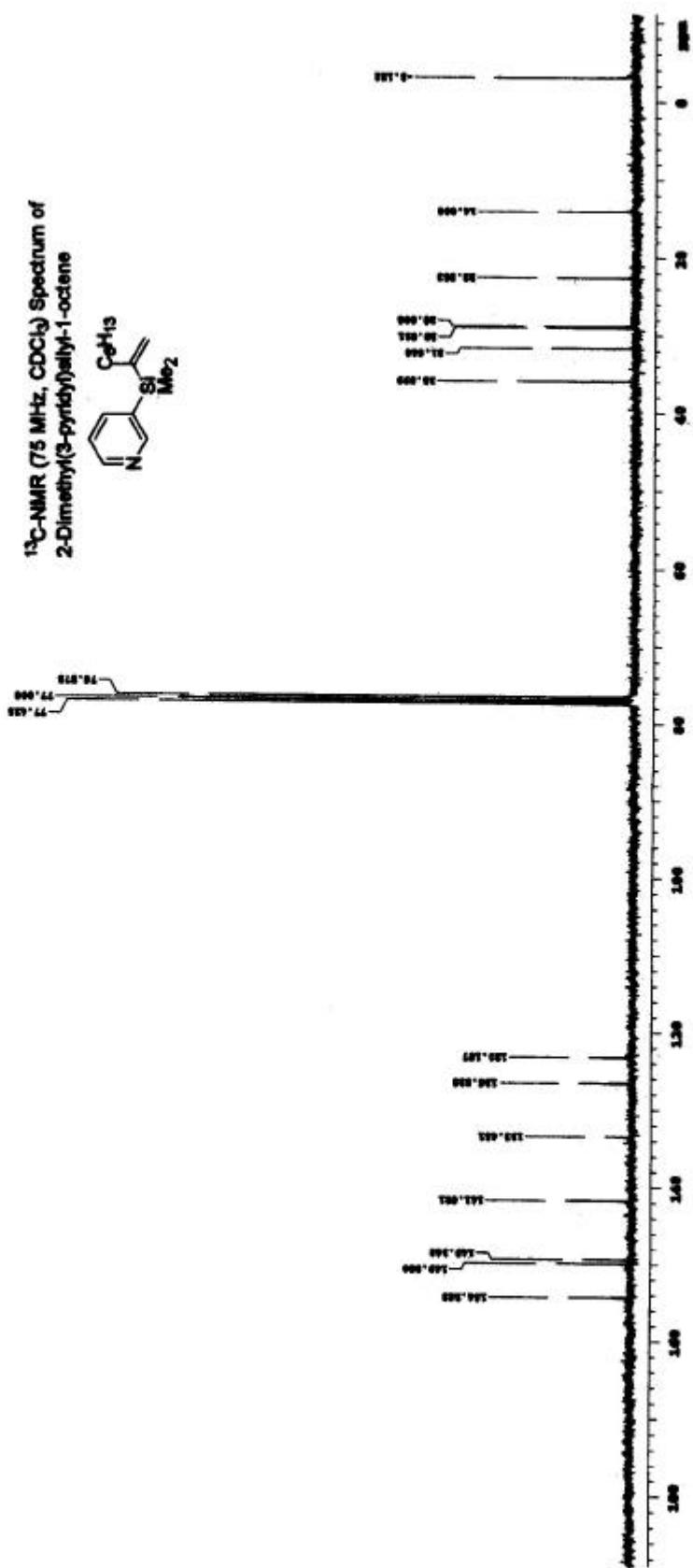
$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ) Spectrum of 4e



$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ) Spectrum of  
(E)-1-Dimethyl(3-pyridyl)silyl-1-octene



$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ) Spectrum of  
2-Dimethyl(3-Pyridyl)allyl-1-octene



$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ) Spectrum of  
(E)-1-Dimethyl(4-pyridyl)allyl-1-octene

