

*Supporting Information*

**Catalytic Cyanosilylation Using Germylene Stabilized Platinum(II)  
Dicyanide**

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## Experimental Section:

All the manipulations were performed using either standard Schlenk techniques or a Jacomex glove box [GP(Concept)-T2]. Compound **1** was synthesized by following literature procedure.<sup>51</sup> Solvents (THF and hexane) were initially dried by refluxing them over sodium/benzophenone. Then, they were further dried over potassium mirror. DCM was dried by refluxing over P<sub>2</sub>O<sub>5</sub>, and CDCl<sub>3</sub> was dried over activated molecular sieves (4 Å). All the required chemicals were purchased from Sigma Aldrich and used without further purification. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded on a 300 MHz Bruker Topspin spectrometer. The chemical shifts  $\delta$  are reported in ppm and are referenced internally to the residual solvent (<sup>1</sup>H NMR) and solvent (<sup>13</sup>C NMR) resonances. In the <sup>19</sup>F NMR spectroscopic studies, CFCl<sub>3</sub> was used as an external reference. IR spectra of compounds **3**, and **6** were recorded using an Agilent Resolutions Pro IR spectrophotometer as KBr pellets. Melting points were recorded using Unitech Sales digital melting point apparatus by sealing the samples in glass capillaries and the reported melting points are uncorrected. Elemental analyses were carried out using a Perkin-Elmer CHN analyzer.

**Caution:** Organic and inorganic azides can be shock- and heat-sensitive, and can explode violently. Further, their solutions in chlorinated solvents can also explode. Therefore, standard/suitable safety norms should be followed while working with them.

**Synthesis of  $\{(\text{iBu})_2\text{ATiGe}^i\text{Pr}\}_2\text{PtCl}_2$  (**2**):** A solution of germylene **1** (2.00 g, 5.76 mmol) in THF (20 mL) was transferred to a suspension of Pt(cod)Cl<sub>2</sub> (1.08 g, 2.88 mmol) in THF (10 mL) and stirred for 12 h at room temperature. Then, the volatiles were removed under reduced pressure to get a yellow solid. It was washed with cold hexane (20 mL) and dried in *vacuo* to afford an analytically pure sample of compound **2**. Single crystals of compound **2** suitable for X-ray diffraction studies were grown by the slow evaporation of its saturated solution in a mixture of dichloromethane and hexane at room temperature. Yield: 2.69 g, 97%. Mp: 139 °C (dec.). Anal. Calcd for C<sub>36</sub>H<sub>60</sub>Cl<sub>2</sub>Ge<sub>2</sub>N<sub>4</sub>Pt (M = 960.15): C, 45.03; H, 6.30; N, 5.84; Found: C, 45.15; H, 6.18; N, 5.90. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.85 (d, <sup>3</sup>J<sub>HH</sub> = 6.2 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.07 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.17-2.25 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.27-2.34 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.14-3.28 (m, 8H, CH<sub>2</sub>), 6.63 (d, <sup>3</sup>J<sub>HH</sub> = 11.1 Hz, 6H, CH), 7.20 (t, <sup>3</sup>J<sub>HH</sub> = 10.5 Hz, 4H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  18.14 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.18 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.00 (CH(CH<sub>3</sub>)<sub>2</sub>),

27.77 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.91 (CH(CH<sub>3</sub>)<sub>2</sub>), 53.38 (CH<sub>2</sub>), 115.56 (C<sub>4</sub>), 122.85 (C<sub>2,6</sub>), 137.65 (C<sub>3,5</sub>), 160.65 (C<sub>1,7</sub>).

**Synthesis of  $\{(i\text{Bu})_2\text{ATiGe}^i\text{Pr}\}_2\text{Pt}(\text{CN})_2$  (**3**):** To a solution of compound **2** (1.00 g, 1.04 mmol) in THF (10 mL), trimethylsilylcyanoide (0.28 mL, 2.15 mmol) was added, and the resulting mixture was stirred for 5 minutes at room temperature. Then, all the volatiles were removed under reduced pressure to get an orange solid. It was washed with cold hexane (5 mL) and dried in *vacuo* to afford an analytically pure sample of compound **3**. Single crystals of compound **3** suitable for X-ray diffraction studies were grown by cooling its saturated solution in THF at -40 °C temperature. Yield: 0.96 g, 98%. Mp: 157 °C (dec.). Anal. Calcd for C<sub>38</sub>H<sub>60</sub>Ge<sub>2</sub>N<sub>6</sub>Pt (M = 941.28): C, 48.49; H, 6.42; N, 8.93; Found: C, 48.57; H, 6.55; N, 8.83. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.02 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.25 (d, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.82-1.87 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.15-2.28 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.38-3.51 (m, 8H, CH<sub>2</sub>), 6.49 (t, <sup>3</sup>J<sub>HH</sub> = 9.3 Hz, 2H, CH), 6.65 (d, <sup>3</sup>J<sub>HH</sub> = 11.1 Hz, 4H, CH), 7.11 (t, <sup>3</sup>J<sub>HH</sub> = 10.2 Hz, 4H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 18.46 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.40 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.72 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.48 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.67 (CH(CH<sub>3</sub>)<sub>2</sub>), 54.56 (CH<sub>2</sub>), 115.85 (C<sub>4</sub>), 122.46 (C<sub>2,6</sub>), 137.90 (C<sub>3,5</sub>), 161.41 (C<sub>1,7</sub>). IR (cm<sup>-1</sup>): ν = 2100. In the <sup>13</sup>C NMR spectrum of compound **3**, carbon atoms of the cyanide ligands are not observed.

**Synthesis of  $\{(i\text{Bu})_2\text{ATiGe}^i\text{Pr}\}_2\text{PtCl}_2[\text{OTf}]_2$  (**4**):** To a solution of compound **2** (0.50 g, 0.52 mmol) in dichloromethane (10 mL), silver triflate (0.14 g, 0.54 mmol) was added at 0 °C and stirred for 60 min at room temperature. It was then filtered using a G4 frit containing celite, and all the volatiles were removed under reduced pressure to get a yellow solid. It was washed with hexane (5 mL) and dried in *vacuo* to afford an analytically pure sample of compound **4**. Single crystals of compound **4** suitable for X-ray diffraction studies were obtained by the slow evaporation of its saturated solution in a mixture of dichloromethane and hexane at room temperature. Yield: 0.54 g, 97%. Mp: 167 °C (dec.). Anal. Calcd for C<sub>74</sub>H<sub>120</sub>Cl<sub>2</sub>F<sub>6</sub>Ge<sub>4</sub>N<sub>8</sub>O<sub>6</sub>Pt<sub>2</sub>S<sub>2</sub> (M = 2147.54): C, 41.39; H, 5.63; N, 5.22; Found: C, 41.32; H, 5.73; N, 5.29. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.95 (d, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.01 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.18 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.84-1.91 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.11-2.22 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.09-3.24 (m, 8H, CH<sub>2</sub>), 6.97 (t, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 6H, CH), 7.55 (t, <sup>3</sup>J<sub>HH</sub> = 10.5 Hz, 4H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 17.90 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.10 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.90

(CH(CH<sub>3</sub>)<sub>2</sub>), 25.67 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.12 (CH(CH<sub>3</sub>)<sub>2</sub>), 53.58 (CH<sub>2</sub>), 117.65 (C<sub>4</sub>), 126.68 (C<sub>2,6</sub>), 139.41 (C<sub>3,5</sub>), 160.30 (C<sub>1,7</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (282 MHz, CDCl<sub>3</sub>): δ -77.90.

**Synthesis of [(<sup>i</sup>Bu)<sub>2</sub>ATI*Ge*<sup>i</sup>Pr]<sub>2</sub>PtCl(DMAP)][OTf] (5):** A solution of 4-(*N,N*-dimethylamino)pyridine (0.057 g, 0.46 mmol) in dichloromethane (5 mL) was transferred to a solution of compound **4** (0.50 g, 0.23 mmol) in dichloromethane (15 mL), and the resultant solution was stirred for 10 minutes at room temperature. All the volatiles were then removed under reduced pressure to get a yellow solid. It was washed with hexane (5 mL) and dried in *vacuo* to afford an analytically pure sample of compound **5**. Single crystals of compound **5** suitable for X-ray diffraction studies were obtained by the slow evaporation of its saturated solution in a mixture of dichloromethane and hexane at room temperature. Yield: 0.54 g, 98%. Mp: 151 °C (dec.). Anal. Calcd for C<sub>44</sub>H<sub>70</sub>ClF<sub>3</sub>Ge<sub>2</sub>N<sub>6</sub>O<sub>3</sub>PtS (M = 1195.94): C, 44.19; H, 5.90; N, 7.03; Found: C, 44.25; H, 5.85; N, 7.09. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.02 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.14 (t, <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.08 (br, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.27 (br, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.37-2.40 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.00 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 3.24-3.44 (m, 8H, CH<sub>2</sub>), 6.35 (br, 2H, py), 6.66 (d, <sup>3</sup>J<sub>HH</sub> = 11.1 Hz, 2H, CH), 6.74-6.85 (m, 4H, CH), 7.29-7.39 (m, 4H, CH), 7.95 (br, 2H, py). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 21.37; 21.42 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.02; 22.07 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.95; 27.14 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.12; 29.25 (CH(CH<sub>3</sub>)<sub>2</sub>), 39.43 (N(CH<sub>3</sub>)<sub>2</sub>), 53.33; 54.00 (CH<sub>2</sub>), 116.60; 116.94 (C<sub>4</sub>), 124.54; 125.49 (C<sub>2,6</sub>), 138.40; 138.83 (C<sub>3,5</sub>), 150.00 (py), 154.13 (py), 160.65; 160.89 (C<sub>1,7</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (282 MHz, CDCl<sub>3</sub>): δ -77.92.

**Synthesis of [(<sup>i</sup>Bu)<sub>2</sub>ATI*Ge*<sup>i</sup>Pr]<sub>2</sub>Pt(N<sub>3</sub>)<sub>2</sub> (6):** Compound **6** was synthesized through the same procedure used for compound **3** using compound **2** (0.80 g, 0.83 mmol) and trimethylsilylazide (0.23 mL, 1.74 mmol). Single crystals of compound **6** suitable for X-ray diffraction studies were grown by cooling its saturated THF solution at -40 °C temperature. Yield: 0.79 g, 98%. Mp: 153 °C (dec.). Anal. Calcd for C<sub>36</sub>H<sub>60</sub>Ge<sub>2</sub>N<sub>10</sub>Pt (M = 973.29): C, 44.43; H, 6.21; N, 14.39; Found: C, 44.35; H, 6.29; N, 14.47. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 0.92 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.02 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.09 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.82-1.90 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.11-2.20 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.10 (dd, <sup>3</sup>J<sub>HH</sub> = 13.5, 9.3 Hz, 4H, CH<sub>2</sub>), 3.24 (dd, <sup>3</sup>J<sub>HH</sub> = 13.5, 5.1 Hz, 4H, CH<sub>2</sub>), 6.64 (t, <sup>3</sup>J<sub>HH</sub> = 11.7 Hz, 6H, CH), 7.18-7.26 (m, 4H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>): δ 18.05 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.17 (CH(CH<sub>3</sub>)<sub>2</sub>), 21.77 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.64 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.87 (CH(CH<sub>3</sub>)<sub>2</sub>), 53.53 (CH<sub>2</sub>), 115.65 (C<sub>4</sub>), 123.24 (C<sub>2,6</sub>), 137.83 (C<sub>3,5</sub>), 160.77 (C<sub>1,7</sub>). IR (cm<sup>-1</sup>): ν = 2040.

**Alternate Procedure for the Synthesis of  $\{(i\text{Bu})_2\text{ATiGe}^i\text{Pr}\}_2\text{Pt}(\text{CN})_2$  (**3**):** Excess TMSCN was added to a solution of germylene stabilized platinum(II) complexes **4-6** in THF and stirred for 5 minutes at room temperature. After that, all the volatiles were removed under reduced pressure and the resultant solids were washed with hexane to afford an analytically pure sample of compound **3** in almost quantitative yields.

**General Procedure for the Cyanosilylation of Aldehydes/Ketones Using Compound **3** as Catalyst:**

To a solution of aldehyde/ketone (1 mmol) and catalyst **3** (0.25-1 mol%) in  $\text{CDCl}_3$  (1 mL), trimethylsilyl cyanide (1.2 mmol) was added and the resulting solution was stirred for an appropriate time period (1.5 to 7 h) at 50 °C. Then, excess of trimethylsilyl cyanide was removed under reduced pressure and the resultant crude product was characterized by  $^1\text{H}$  NMR spectroscopy. Yield of the product was calculated based on the  $^1\text{H}$  NMR spectroscopic data on the basis of consumption of aldehyde/ketone. The crude product was then distilled under reduced pressure to get an analytically pure sample of cyanohydrin trimethylsilyl ether.

**NMR Data of Cyanosilylated Products:**

Data for cyanosilylated product of benzaldehyde:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.23 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 5.50 (s, 1H,  $\text{CHOSi}(\text{CH}_3)_3$ ), 7.40-7.48 (m, 5H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.14 ( $\text{Si}(\text{CH}_3)_3$ ), 63.80 ( $\text{CHOSi}(\text{CH}_3)_3$ ), 119.29 (CN), 126.47 ( $\text{C}_{\text{Ar}}$ ), 129.05 ( $\text{C}_{\text{Ar}}$ ), 129.44 ( $\text{C}_{\text{Ar}}$ ), 136.43 ( $\text{C}_{\text{Ar}}$ ).

**Data for cyanosilylated product reported in Table 2**

**Entry 1:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.19 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 1.01-1.06 (t,  $^3J_{\text{H,H}} = 6$  Hz, 3H,  $\text{CH}_3$ ), 1.76-1.86 (m, 2H,  $\text{CH}_2$ ), 4.35 (t,  $^3J_{\text{H,H}} = 6$  Hz, 1H,  $\text{CHOSi}(\text{CH}_3)_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.27 ( $\text{Si}(\text{CH}_3)_3$ ), 9.06 ( $\text{CH}_3$ ), 29.74 ( $\text{CH}_2$ ), 62.86 ( $\text{COSi}(\text{CH}_3)_2$ ), 120.05 (CN).

**Entry 2:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.20 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 0.95 (t, 3H,  $^3J_{\text{H,H}} = 7.2$  Hz,  $\text{CH}_3$ ), 1.46-1.52 (m, 2H,  $\text{CH}_2$ ), 1.73-1.78 (m, 2H,  $\text{CH}_2$ ), 4.39 (t,  $^3J_{\text{H,H}} = 6$  Hz, 1H, CH).  $^{13}\text{C}\{^1\text{H}\}$

NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  -0.30 (Si(CH<sub>3</sub>)<sub>3</sub>), 13.51 (CH<sub>3</sub>), 18.00 (CH<sub>2</sub>), 38.33 (CH<sub>2</sub>), 61.34 (COSi(CH<sub>3</sub>)<sub>2</sub>), 120.22 (CN).

**Entry 3:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  0.24 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 5.47 (s, 1H, CHOSi(CH<sub>3</sub>)<sub>3</sub>), 7.40 (br, 4H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  0.13 (Si(CH<sub>3</sub>)<sub>3</sub>), 63.14 (CHOSi(CH<sub>3</sub>)<sub>3</sub>), 118.93 (CN), 127.82 (C<sub>Ar</sub>), 129.32 (C<sub>Ar</sub>), 134.98 (C<sub>Ar</sub>), 135.50 (C<sub>Ar</sub>).

**Entry 4:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  0.26 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 5.76 (s, 1H, CHOSi(CH<sub>3</sub>)<sub>3</sub>), 7.26 (t, <sup>3</sup>J<sub>H,H</sub> = 6.0 Hz, 1H, Ph), 7.42 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 1H, Ph), 7.58 (d, <sup>3</sup>J<sub>H,H</sub> = 8.1 Hz, 1H, Ph), 7.72 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 1H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  -0.15 (Si(CH<sub>3</sub>)<sub>3</sub>), 63.30 (CHOSi(CH<sub>3</sub>)<sub>3</sub>), 118.45 (CN), 121.82 (C<sub>Ar</sub>), 128.29 (C<sub>Ar</sub>), 128.71 (C<sub>Ar</sub>), 131.00 (C<sub>Ar</sub>), 133.10 (C<sub>Ar</sub>), 135.58 (C<sub>Ar</sub>).

**Entry 5:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  0.28 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 6.22 (s, 1H, CHOSi(CH<sub>3</sub>)<sub>3</sub>), 7.60 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 1H, Ph), 7.77 (t, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 1H, Ph), 8.02 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 1H, Ph), 8.16 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 1H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  -0.30 (Si(CH<sub>3</sub>)<sub>3</sub>), 60.31 (CHOSi(CH<sub>3</sub>)<sub>3</sub>), 118.00 (CN), 125.46 (C<sub>Ar</sub>), 128.69 (C<sub>Ar</sub>), 130.35 (C<sub>Ar</sub>), 132.25 (C<sub>Ar</sub>), 134.60 (C<sub>Ar</sub>), 146.56 (C<sub>Ar</sub>).

**Entry 6:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  0.20 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 5.54 (s, 1H, CHOSi(CH<sub>3</sub>)<sub>3</sub>), 7.60 (d, <sup>3</sup>J<sub>H,H</sub> = 8.1 Hz, 2H, Ph), 7.73 (d, <sup>3</sup>J<sub>H,H</sub> = 8.1 Hz, 2H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  -0.19 (Si(CH<sub>3</sub>)<sub>3</sub>), 62.97 (CHOSi(CH<sub>3</sub>)<sub>3</sub>), 113.51 (C<sub>Ar</sub>), 118.22 (CN), 118.37 (CN), 127.00 (C<sub>Ar</sub>), 132.91 (C<sub>Ar</sub>), 141.26 (C<sub>Ar</sub>).

**Entry 7:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  0.24 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 5.54 (s, 1H, CHOSi(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  -0.53 (Si(CH<sub>3</sub>)<sub>3</sub>), 53.37 (CHOSi(CH<sub>3</sub>)<sub>3</sub>), 116.58 (CN), 136.64 (C<sub>Ar</sub>), 139.20 (C<sub>Ar</sub>), 143.77 (C<sub>Ar</sub>), 146.27 (C<sub>Ar</sub>). <sup>19</sup>F{<sup>1</sup>H} NMR (282 MHz, CDCl<sub>3</sub>):  $\delta$  -141.68 (m, 2F, *ortho*-C<sub>6</sub>F<sub>5</sub>), -150.54 (t, 2F, *para*-C<sub>6</sub>F<sub>5</sub>), -160.22 (m, 1F, *meta*-C<sub>6</sub>F<sub>5</sub>).

**Entry 8:** <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  0.22 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 2.37 (s, 3H, CH<sub>3</sub>), 5.46 (s, 1H, CHOSi(CH<sub>3</sub>)<sub>3</sub>), 7.22 (d, <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz, 2H, Ph), 7.35 (d, <sup>3</sup>J<sub>H,H</sub> = 8.4 Hz, 2H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  -0.08 (Si(CH<sub>3</sub>)<sub>3</sub>), 21.34 (CH<sub>3</sub>), 63.74 (CHOSi(CH<sub>3</sub>)<sub>3</sub>), 119.45 (CN), 126.55 (C<sub>Ar</sub>), 129.75 (C<sub>Ar</sub>), 133.59 (C<sub>Ar</sub>), 139.53 (C<sub>Ar</sub>).

**Entry 9:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.21 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 3.82 (s, 3H,  $\text{CH}_3$ ), 5.44 (s, 1H,  $\text{CHOSi}(\text{CH}_3)_3$ ), 6.92 (d,  $^3J_{\text{H,H}} = 8.5$  Hz, 2H, *Ph*), 7.38 (d,  $^3J_{\text{H,H}} = 9.0$  Hz, 2H, *Ph*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.08 ( $\text{Si}(\text{CH}_3)_3$ ), 55.49 ( $\text{OCH}_3$ ), 63.51 ( $\text{CHOSi}(\text{CH}_3)_3$ ), 114.44 ( $\text{C}_{\text{Ar}}$ ), 119.48 (CN), , 128.08 ( $\text{C}_{\text{Ar}}$ ), 128.65 ( $\text{C}_{\text{Ar}}$ ), 160.52 ( $\text{C}_{\text{Ar}}$ ).

**Entry 10:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.22 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 2.44 (s, 3H,  $\text{CH}_3$ ), 5.57 (s, 1H,  $\text{CHOSi}(\text{CH}_3)_3$ ), 7.20-7.30 (m, 3H, *Ph*), 7.53 (d,  $^3J_{\text{H,H}} = 6.0$  Hz, 1H, *Ph*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.11 ( $\text{Si}(\text{CH}_3)_3$ ), 18.93 ( $\text{CH}_3$ ), 62.10 ( $\text{CHOSi}(\text{CH}_3)_3$ ), 118.95 (CN), 126.60 ( $\text{C}_{\text{Ar}}$ ), 127.16 ( $\text{C}_{\text{Ar}}$ ), 129.55 ( $\text{C}_{\text{Ar}}$ ), 131.22 ( $\text{C}_{\text{Ar}}$ ), 134.23 ( $\text{C}_{\text{Ar}}$ ), 135.78 ( $\text{C}_{\text{Ar}}$ ).

**Entry 11:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.24 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 3.92 (s, 3H,  $\text{CH}_3$ ), 5.54 (s, 1H, CH), 7.54 (d,  $^3J_{\text{H,H}} = 6.6$  Hz, 2H, *Ph*), 8.07 (d,  $^3J_{\text{H,H}} = 6.4$  Hz, 2H, *Ph*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.17 ( $\text{Si}(\text{CH}_3)_3$ ), 52.41 ( $\text{CH}_3$ ), 62.29 ( $\text{CHOSi}(\text{CH}_3)_3$ ), 118.77 (CN), 126.34 ( $\text{C}_{\text{Ar}}$ ), 129.12 ( $\text{C}_{\text{Ar}}$ ), 130.33 ( $\text{C}_{\text{Ar}}$ ), 131.19 ( $\text{C}_{\text{Ar}}$ ), 140.96 ( $\text{C}_{\text{Ar}}$ ), 166.45 (CO).

**Entry 12:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.19 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 2.14 (s, 3H,  $\text{CH}_3$ ), 5.45 (s, 1H,  $\text{CHOSi}(\text{CH}_3)_3$ ), 7.35 (d,  $^3J_{\text{H,H}} = 6.0$  Hz, 2H, *Ph*), 7.58 (d,  $^3J_{\text{H,H}} = 6.0$  Hz, 2H, *Ph*), 8.51 (s, 1H, NH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.26 ( $\text{Si}(\text{CH}_3)_3$ ), 24.32 ( $\text{CH}_3$ ), 63.30 ( $\text{CHOSi}(\text{CH}_3)_3$ ), 119.37 (CN), 120.22 ( $\text{C}_{\text{Ar}}$ ), 127.08 ( $\text{C}_{\text{Ar}}$ ), 131.67 ( $\text{C}_{\text{Ar}}$ ), 139.27 ( $\text{C}_{\text{Ar}}$ ), 169.50 (CO).

**Entry 13:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.23 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 0.96 (t,  $^3J_{\text{H,H}} = 7.2$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.47-1.62 (m, 5H,  $\text{CH}_2$  &  $\text{CH}_3$ ), 1.63-1.71 (m, 2H,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.40 ( $\text{Si}(\text{CH}_3)_3$ ), 13.92 ( $\text{CH}_3$ ), 17.78 ( $\text{CH}_2$ ), 29.05 ( $\text{CH}_2$ ), 45.64 ( $\text{CH}_2$ ), 69.73 ( $\text{COSi}(\text{CH}_3)_2$ ), 122.32 (CN).

**Entry 14:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.22 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 0.99–1.03 (m, 6H,  $\text{C}(\text{CH}_3)_2$ ), 1.51 (s, 3H,  $\text{C}(\text{CH}_3)$ ), 1.79–1.88 (m, 1H,  $\text{CH}(\text{CH}_3)_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.32 ( $\text{Si}(\text{CH}_3)_3$ ), 17.08 ( $\text{C}(\text{CH}_3)_2$ ), 17.29 ( $\text{C}(\text{CH}_3)_2$ ), 26.14 ( $\text{C}(\text{CH}_3)_2$ ), 39.21 (CO( $\text{CH}_3$ )), 73.60 (COCH<sub>3</sub>), 121.74 (CN).

**Entry 15:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.21 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 1.73-1.82 (m, 4H,  $\text{CH}_2$ ), 1.95-2.08 (m, 4H,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.14 ( $\text{Si}(\text{CH}_3)_3$ ), 22.69 ( $\text{CH}_2$ ), 41.80 ( $\text{CH}_2$ ), 74.53 ( $\text{COSi}(\text{CH}_3)_2$ ), 122.64 (CN).



**Entry 16:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.22 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 1.50-1.61 (m, 6H,  $\text{CH}_2$ ), 1.70-1.75 (m, 2H,  $\text{CH}_2$ ), 2.00-2.05 (m, 2H,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.48 ( $\text{Si}(\text{CH}_3)_3$ ), 22.72 ( $\text{CH}_2$ ), 24.61 ( $\text{CH}_2$ ), 39.45 ( $\text{CH}_2$ ), 70.71 ( $\text{COSi}(\text{CH}_3)_2$ ), 122.01 (CN).

**Entry 17:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.22 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 1.58 (br, 8H,  $\text{CH}_2$ ), 1.88-1.95 (m, 2H,  $\text{CH}_2$ ), 2.06-2.13 (m, 2H,  $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.45 ( $\text{Si}(\text{CH}_3)_3$ ), 21.38 ( $\text{CH}_2$ ), 27.76 ( $\text{CH}_2$ ), 42.48 ( $\text{CH}_2$ ), 73.26 ( $\text{COSi}(\text{CH}_3)_2$ ), 123.11 (CN).

**Entry 19:**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  0.25 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ), 2.61 (s, 3H,  $\text{CH}_3$ ), 5.55 (s, 1H, CH), 7.55 (d,  $^3J_{\text{H,H}} = 6.6$  Hz, 2H, *Ph*), 7.99 (d,  $^3J_{\text{H,H}} = 6.6$  Hz, 2H, *Ph*).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.16 ( $\text{Si}(\text{CH}_3)_3$ ), 26.83 ( $\text{CH}_3$ ), 63.28 ( $\text{CHOSi}(\text{CH}_3)_3$ ), 118.73 (CN), 126.58 ( $\text{C}_{\text{Ar}}$ ), 129.06 ( $\text{C}_{\text{Ar}}$ ), 129.06 ( $\text{C}_{\text{Ar}}$ ), 137.94 ( $\text{C}_{\text{Ar}}$ ), 141.10 ( $\text{C}_{\text{Ar}}$ ), 197.452 (CO).

**X-ray Crystal Structure Determination for Compounds 2-6:** For compounds **2-6** the single crystal X-ray diffraction data were collected using a Bruker SMART APEX diffractometer either at room temperature or low temperature using  $\text{Mo}_{K\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ).<sup>S2</sup> After covering the crystals with a cryoprotectant, the crystals were mounted on a glass capillary. Integration of data and empirical absorption correction were done using SAINT and SADABS, respectively.<sup>S3</sup> The structures were solved by direct methods and refined by full matrix least-square on  $F^2$  using SHELXTL or SHELXL-2013 incorporated in OLEX2.<sup>S4, S5</sup> In compound **3**, large regions of diffused electron density that could not be modelled (disordered solvents) were removed from the refinement using SHELXL-2013 incorporated in OLEX2.<sup>S5</sup> All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were fixed according to a riding model and were isotropically refined. Important crystallographic data are provided in Tables S1 and S2.

**Table S1.** Crystal Data and Structure Refinement Parameters for Compounds **2-4**:

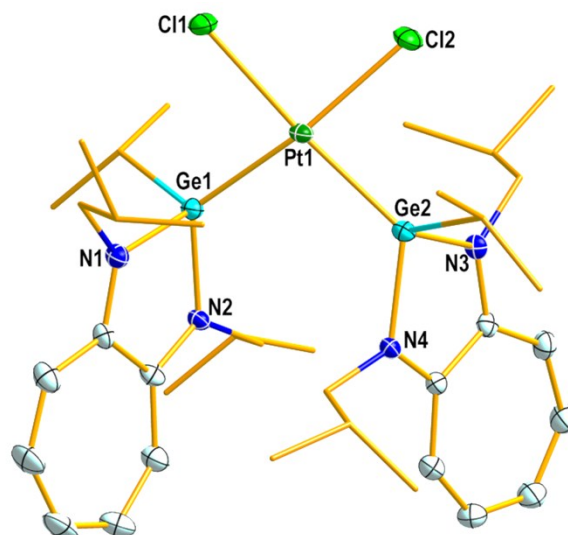
	<b>2</b>	<b>3</b>	<b>4</b>
Empirical formula	C <sub>36</sub> H <sub>60</sub> Cl <sub>2</sub> Ge <sub>2</sub> N <sub>4</sub> Pt·CH <sub>2</sub> Cl <sub>2</sub>	C <sub>38</sub> H <sub>60</sub> Ge <sub>2</sub> N <sub>6</sub> Pt	C <sub>74</sub> H <sub>120</sub> Cl <sub>2</sub> F <sub>6</sub> Ge <sub>4</sub> N <sub>8</sub> O <sub>6</sub> Pt <sub>2</sub> S <sub>2</sub>
Formula weight	1045.01	941.22	2147.40
Temperature, K	150(2)	120(2)	120(2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>p</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions	a = 17.8516(18) Å b = 13.4971(14) Å c = 19.508(2) Å $\beta$ = 112.457(2)°	a = 11.9108(16) Å b = 12.3525(16) Å c = 17.527(2) Å $\alpha$ = 72.036(2)° $\beta$ = 80.201(2)° $\gamma$ = 75.546(3)°	a = 10.799(2) Å b = 17.921(3) Å c = 22.042(4) Å $\beta$ = 91.711(4)°
Volume, Å <sup>3</sup>	4343.9(8)	2363.2(5)	4263.9(13)
Z	4	2	2
Density (calculated), Mg/m <sup>3</sup>	1.598	1.323	1.673
Absorption coefficient, mm <sup>-1</sup>	4.863	4.244	4.837
<i>F</i> (000)	2088.0	944.0	2144.0
Crystal size, mm <sup>3</sup>	0.34 x 0.26 x 0.15	0.20 x 0.19 x 0.15	0.34 x 0.27 x 0.15
$\theta$ range for data collection, °	1.23 to 25.00	1.775 to 25.03	1.85 to 25.00
Limiting indices	-21 ≤ <i>h</i> ≤ 13, -16 ≤ <i>k</i> ≤ 14, -22 ≤ <i>l</i> ≤ 23	-14 ≤ <i>h</i> ≤ 13, -14 ≤ <i>k</i> ≤ 9, -20 ≤ <i>l</i> ≤ 18	-12 ≤ <i>h</i> ≤ 12, -21 ≤ <i>k</i> ≤ 17, -16 ≤ <i>l</i> ≤ 26
Reflections collected	18479	12332	22043
Independent reflections	7642 [ <i>R</i> <sub>(int)</sub> = 0.0356]	8173 [ <i>R</i> <sub>(int)</sub> = 0.0430]	7497 [ <i>R</i> <sub>(int)</sub> = 0.0950]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on	Full-matrix least-squares	Full-matrix least-squares

	$F^2$	on $F^2$	on $F^2$
Data/restraints/parameter	7642 / 0 / 451	8173 / 7 / 422	7497 / 0 / 475
Goodness-of-fit on $F^2$	1.074	1.068	0.983
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0328$ , $wR_2 = 0.0775$	$R_1 = 0.0430$ , $wR_2 = 0.0935$	$R_1 = 0.0522$ , $wR_2 = 0.1069$
$R$ indices (all data)	$R_1 = 0.0433$ , $wR_2 = 0.0928$	$R_1 = 0.060$ , $wR_2 = 0.1327$	$R_1 = 0.0867$ , $wR_2 = 0.1271$
Largest diff. peak and hole, $e\text{\AA}^{-3}$	1.145 and -0.828	2.307 and -4.108	1.995 and -1.062

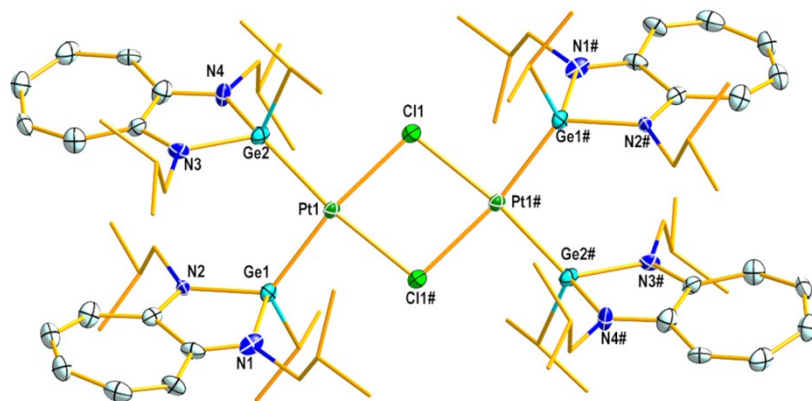
**Table S2.** Crystal Data and Structure Refinement Parameters for Compounds **5** and **6**.

	<b>5</b>	<b>6</b>
Empirical formula	$C_{44}H_{70}ClF_3Ge_2N_6O_3PtS$	$C_{40}H_{68}Ge_2N_{10}OPt$
Formula weight	1195.87	1045.34
Temperature, K	100(2)	150(2)
Wavelength, $\text{\AA}$	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P 2_1/c$	$P 2_1/c$
Unit cell dimensions	$a = 14.300(4) \text{\AA}$ $b = 17.928(4) \text{\AA}$ $c = 20.470(5) \text{\AA}$ $\beta = 105.098(5)^\circ$	$a = 17.510(2) \text{\AA}$ $b = 13.7732(18) \text{\AA}$ $c = 20.114(3) \text{\AA}$ $\beta = 113.278(2)^\circ$
Volume, $\text{\AA}^3$	5067(2)	4455.9(10)
$Z$	4	4
Density (calculated), $\text{Mg/m}^3$	1.568	1.558
Absorption coefficient, $\text{mm}^{-1}$	4.080	4.514
$F(000)$	2408.0	2112.0
Crystal size, $\text{mm}^3$	0.34 x 0.28 x 0.15	0.34 x 0.27 x 0.16
$\theta$ range for data collection, $^\circ$	1.53 to 25.00	1.27 to 25.00

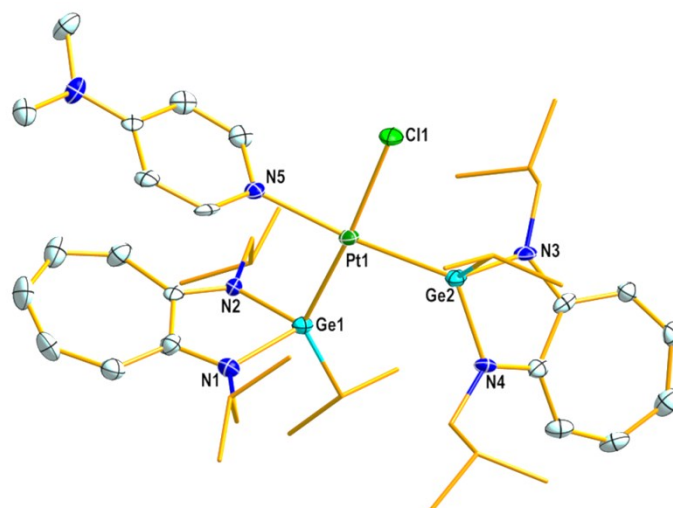
Limiting indices	$-16 \leq h \leq 17, -19 \leq k \leq 21, -24 \leq l \leq 24$	$-20 \leq h \leq 20, -14 \leq k \leq 16, -16 \leq l \leq 23$
Reflections collected	26256	23033
Independent reflections	8897 [ $R_{\text{(int)}} = 0.0864$ ]	7824 [ $R_{\text{(int)}} = 0.0632$ ]
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data /restraints/ parameter	8897 / 0 / 564	7824 / 0 / 502
Goodness-of-fit on $F^2$	1.034	1.051
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0576, wR_2 = 0.1332$	$R_1 = 0.0490, wR_2 = 0.0919$
$R$ indices (all data)	$R_1 = 0.0859, wR_2 = 0.1516$	$R_1 = 0.0694, wR_2 = 0.0992$
Largest diff. peak and hole, $\text{e}\text{\AA}^{-3}$	2.524 and -2.284	0.653 and -0.221



**Figure S1.** Molecular structure of compound **2**. Thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms and a solvent molecule ( $\text{CH}_2\text{Cl}_2$ ) are deleted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles (deg): Pt1-Ge1 2.326(6), Pt1-Ge2 2.329(6), Pt1-Cl1 2.407(1), Pt1-Cl2 2.389(1), Ge1-C16 1.984(6), Ge2-C34 1.992(6), Ge1-N1 1.915(4), Ge1-N2 1.916(4), Ge2-N3 1.910(4), Ge2-N4 1.933(4); N1-Ge1-N2 82.34(2), N3-Ge2-N4 82.72(2), C16-Ge1-Pt1 115.93(2), C34-Ge2-Pt1 116.33(2), Cl1-Pt1-Cl2 89.39(5), Ge1-Pt1-Cl1 85.27(4), Ge2-Pt1-Cl2 84.34(4), Ge1-Pt1-Ge2 102.25(2).

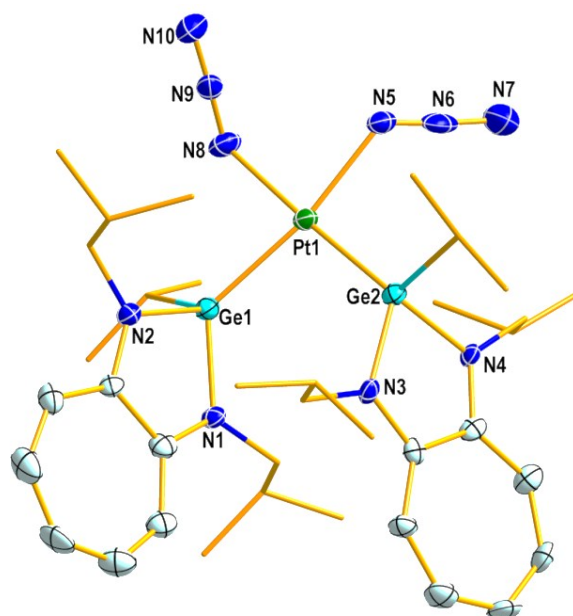


**Figure S2.** Molecular structure of compound **4**. Thermal ellipsoids are drawn at the 30% probability level. The cationic part is displayed. All hydrogen atoms and triflate counter anions are deleted for clarity. Selected bond lengths (Å) and angles (deg): Pt1-Ge1 2.335(1), Pt1-Ge2 2.334(1), Pt1-Cl1 2.441(2), Ge1-C16 1.956(9), Ge2-C34 2.00(1), Ge1-N1 1.899(8), Ge1-N2 1.894(7), Ge2-N3 1.896(7), Ge2-N4 1.883(7); N1-Ge1-N2 84.3(3), N3-Ge2-N4 83.4(3), C16-Ge1-Pt1 113.4(3), C34-Ge2-Pt1 114.0(3), Cl1#1-Pt1-Cl1 82.93(8), Ge1-Pt1-Cl1 89.75(6), Ge1-Pt1-Ge2 100.31(4). #Symmetry transformation used to generate equivalent atoms: -x, -y+1, -z.



**Figure S3.** Molecular structure of compound **5**. Thermal ellipsoids are drawn at the 30% probability level. The cationic part is displayed. All hydrogen atoms and triflate counter anion are deleted for clarity. Selected bond lengths (Å) and angles (deg): Pt1-Ge1 2.344(1), Pt1-Ge2 2.341(1), Pt1-Cl1 2.388(2), Pt1-N5 2.132(7), Ge1-C16 1.981(9), Ge2-C34 1.972(8), Ge1-N1 1.918(7), Ge1-N2 1.921(7), Ge2-N3 1.905(7), Ge2-N4 1.914(7); N1-Ge1-N2 82.5(3), N3-Ge2-N4 83.2(3), C16-Ge1-Pt1 132.4(3), C34-Ge2-Pt1 113.0(3), N5-Pt1-Cl1 85.9(2), Ge1-Pt1-Cl1 170.41(6), Ge2-Pt1-Cl1 85.32(6), Ge1-Pt1-Ge2 99.92(4).

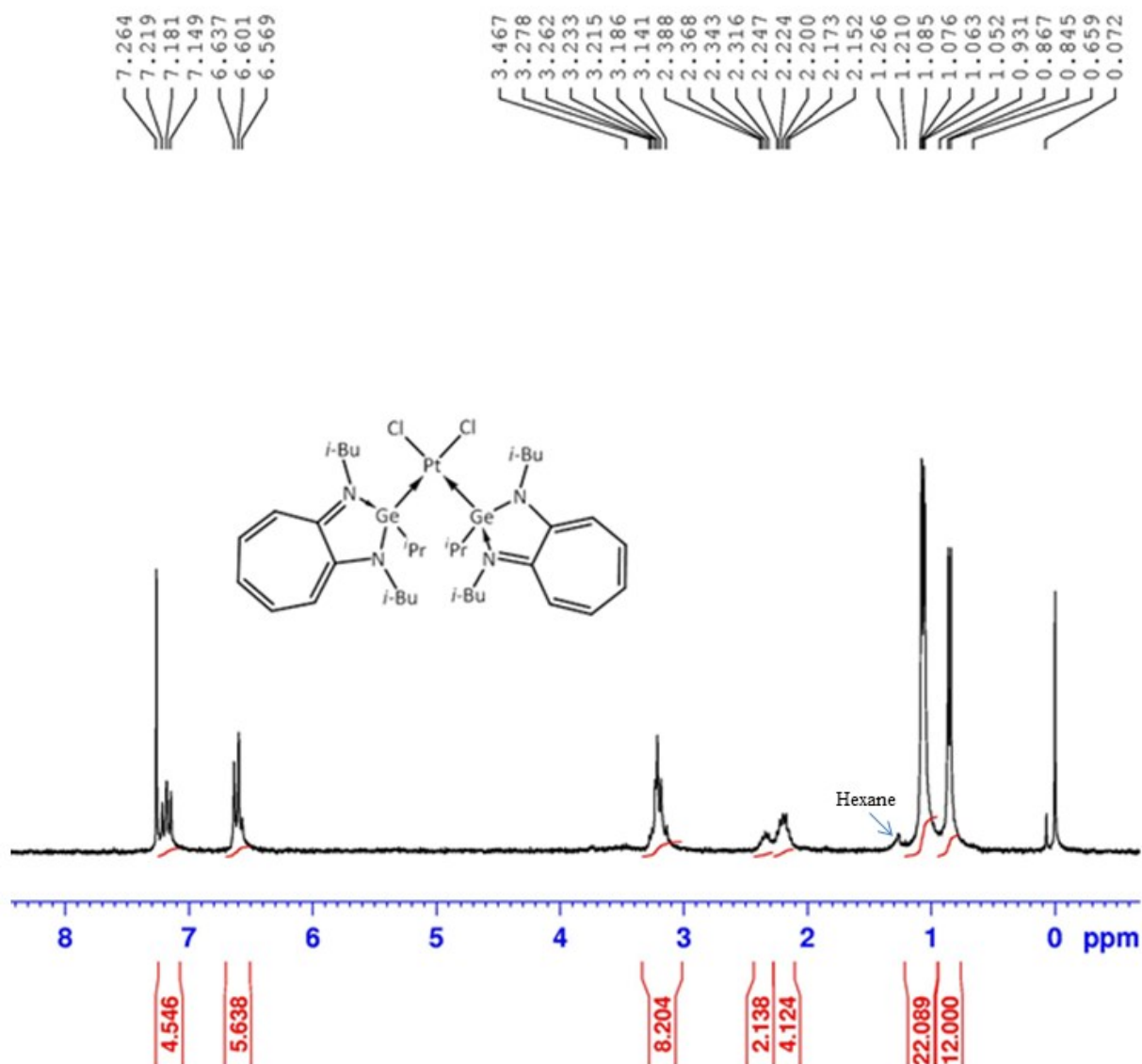




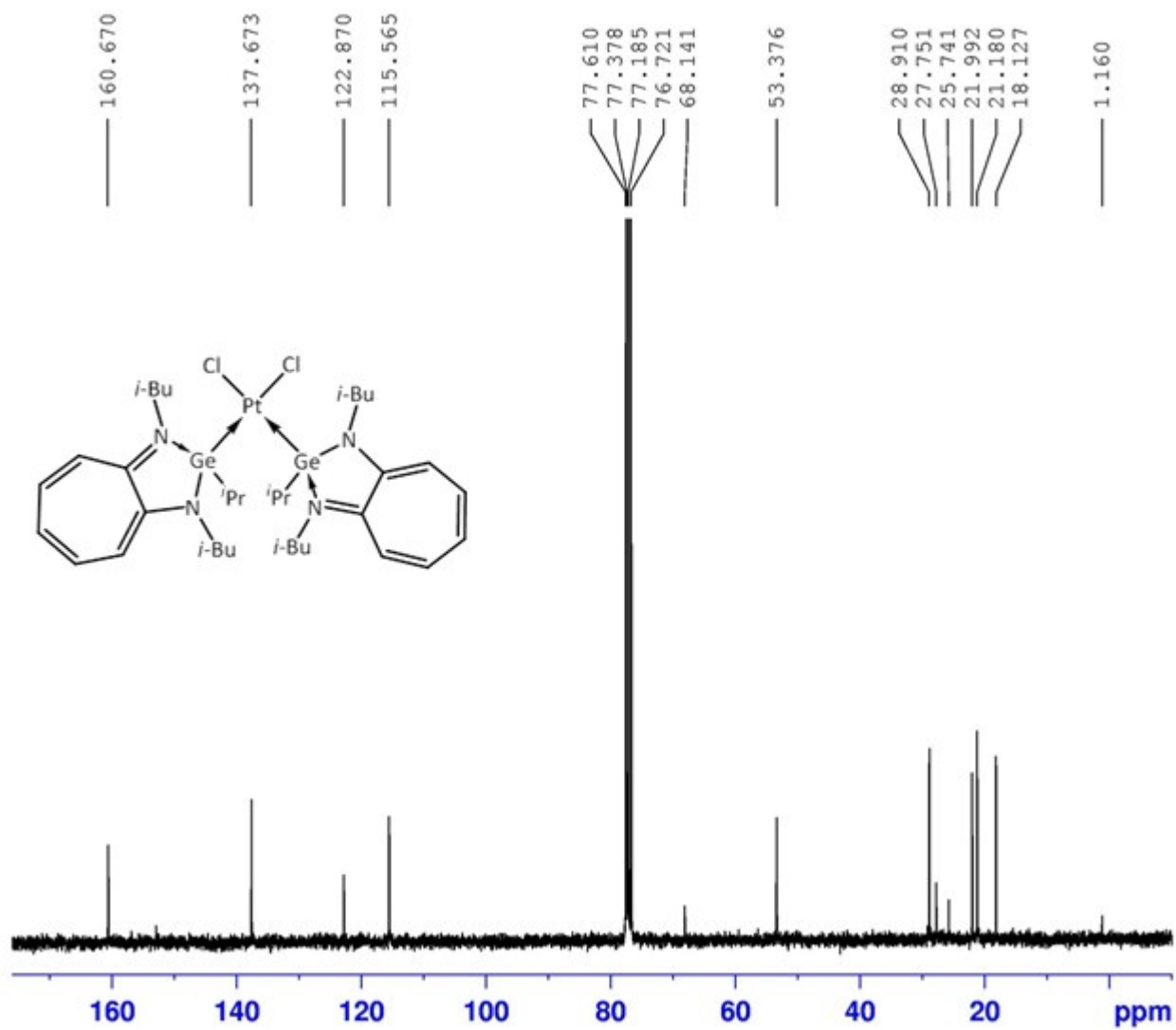
**Figure S4.** Molecular structure of compound **6**. Thermal ellipsoids are drawn at the 40% probability level. All hydrogen atoms and a solvent molecule (THF) are deleted for clarity. Selected bond lengths (Å) and angles (deg): Pt1-Ge1 2.326(8), Pt1-Ge2 2.335(8), Pt1-N5 2.137(6), Pt1-N8 2.116(6), Ge1-C16 1.978(7), Ge2-C34 1.973(7), Ge1-N1 1.910(5), Ge1-N2 1.908(5), Ge2-N3 1.918(5), Ge2-N4 1.917(5); N1-Ge1-N2 82.8(2), N4-Ge2-N3 83.0(2), C16-Ge1-Pt1 116.1(2), C34-Ge2-Pt1 114.6(2), N5-Pt1-Ge1 168.88(2), N8-Pt1-Ge2 174.55(2), Ge1-Pt1-Ge2 101.09(3), N8-Pt1-N5 87.2(2).

# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds 2-6:

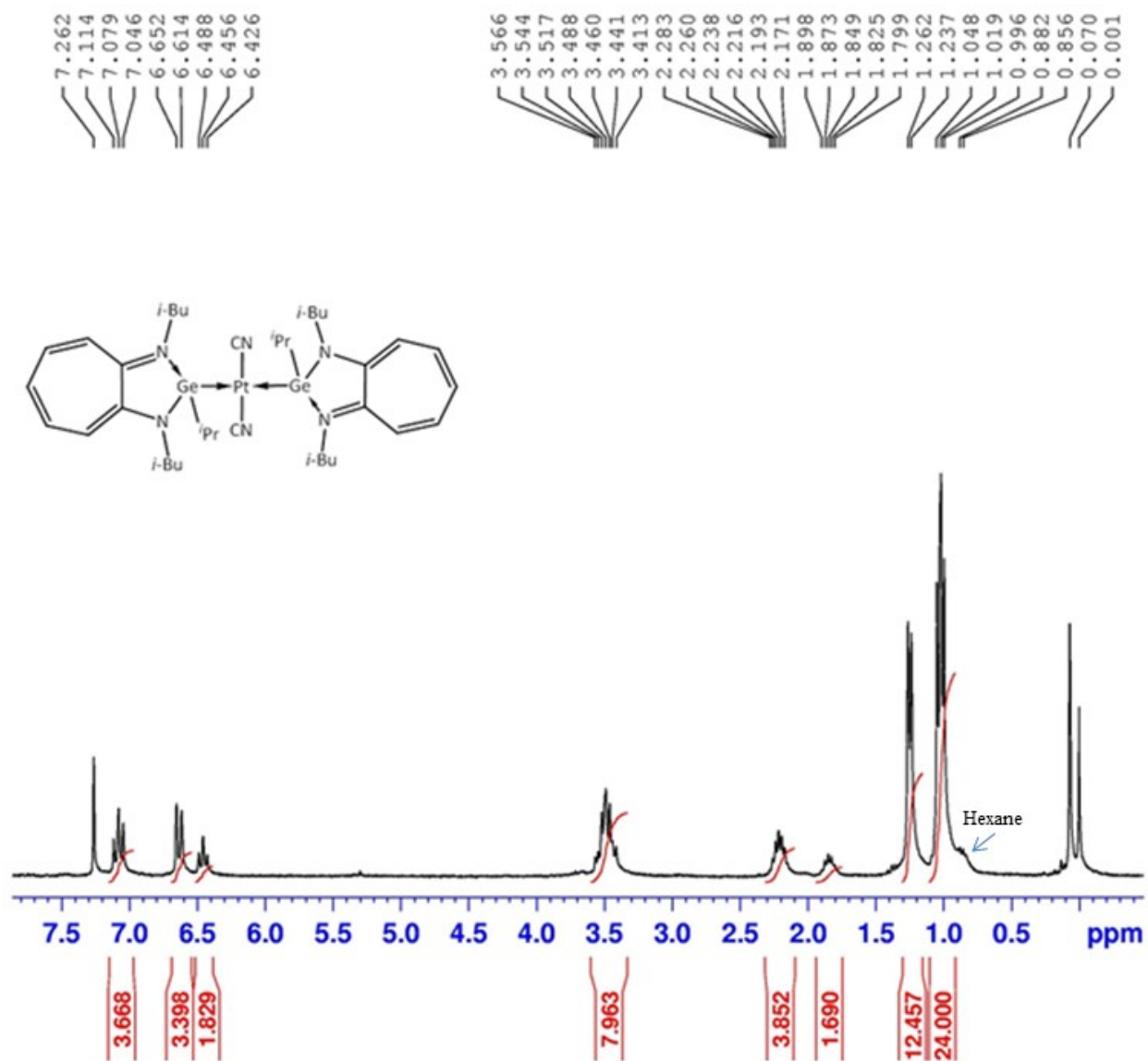
<sup>1</sup>H NMR spectrum of compound 2:



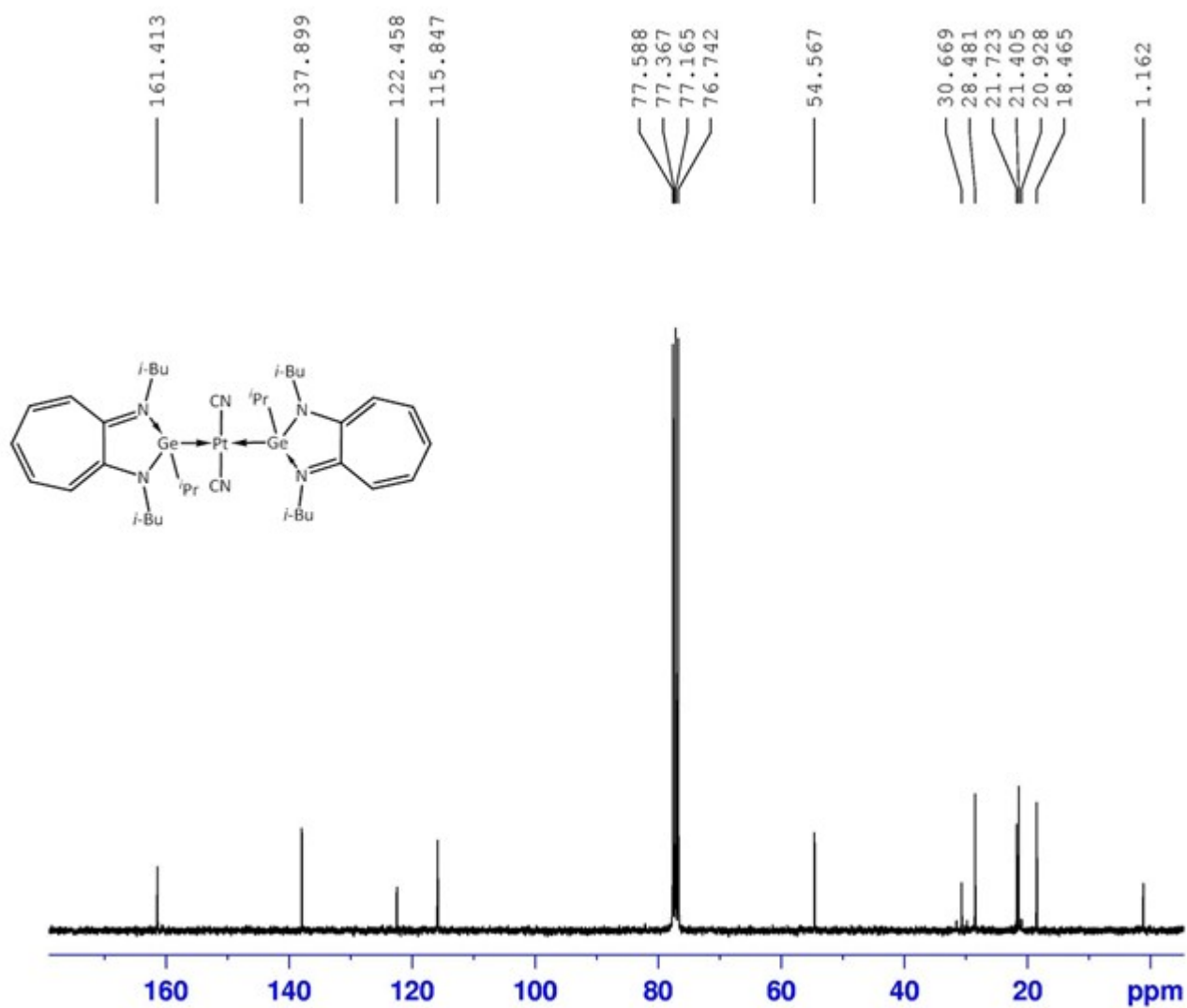
$^{13}\text{C}$  NMR spectrum of compound **2**:



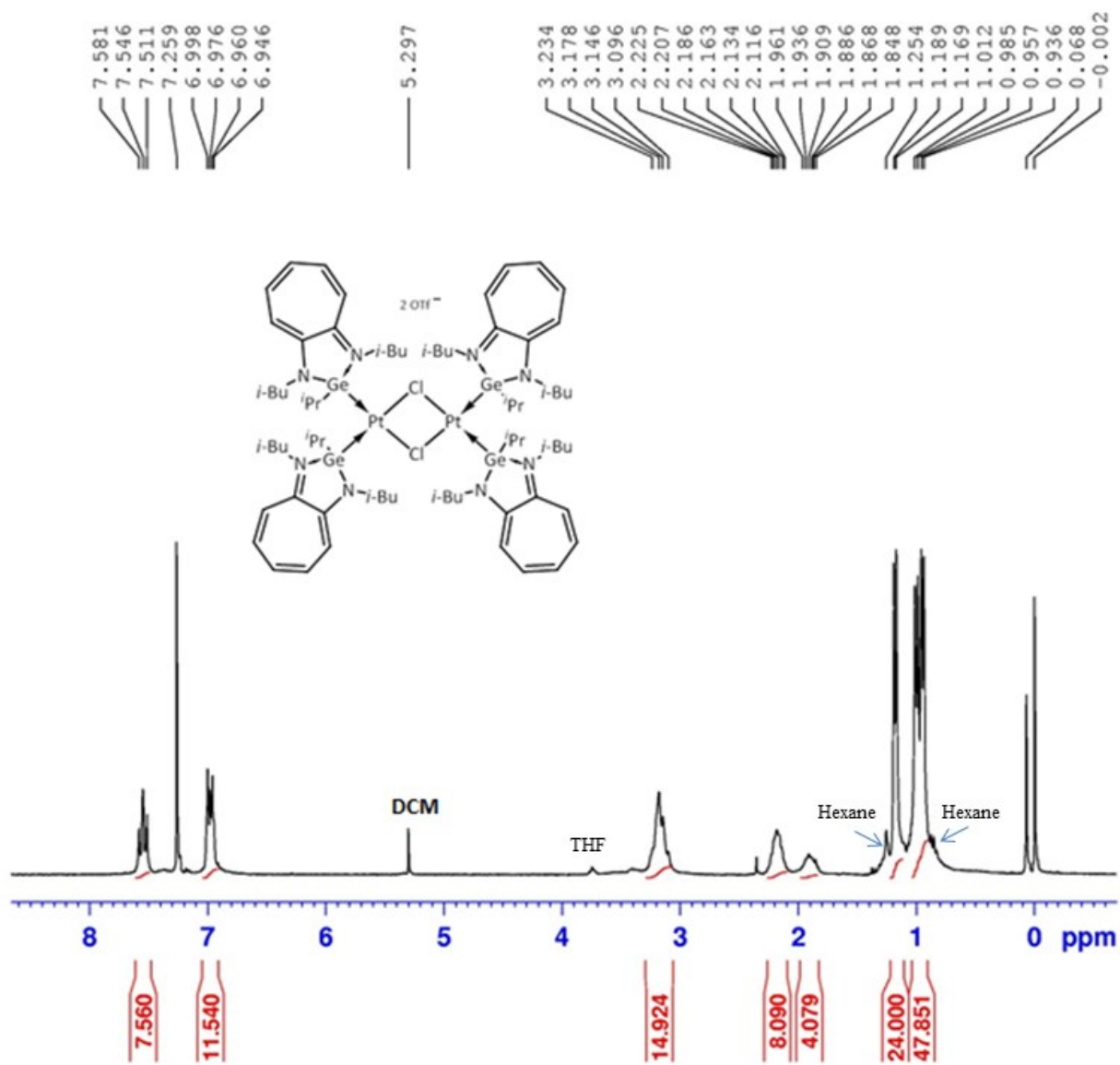
<sup>1</sup>H NMR spectrum of compound **3**:



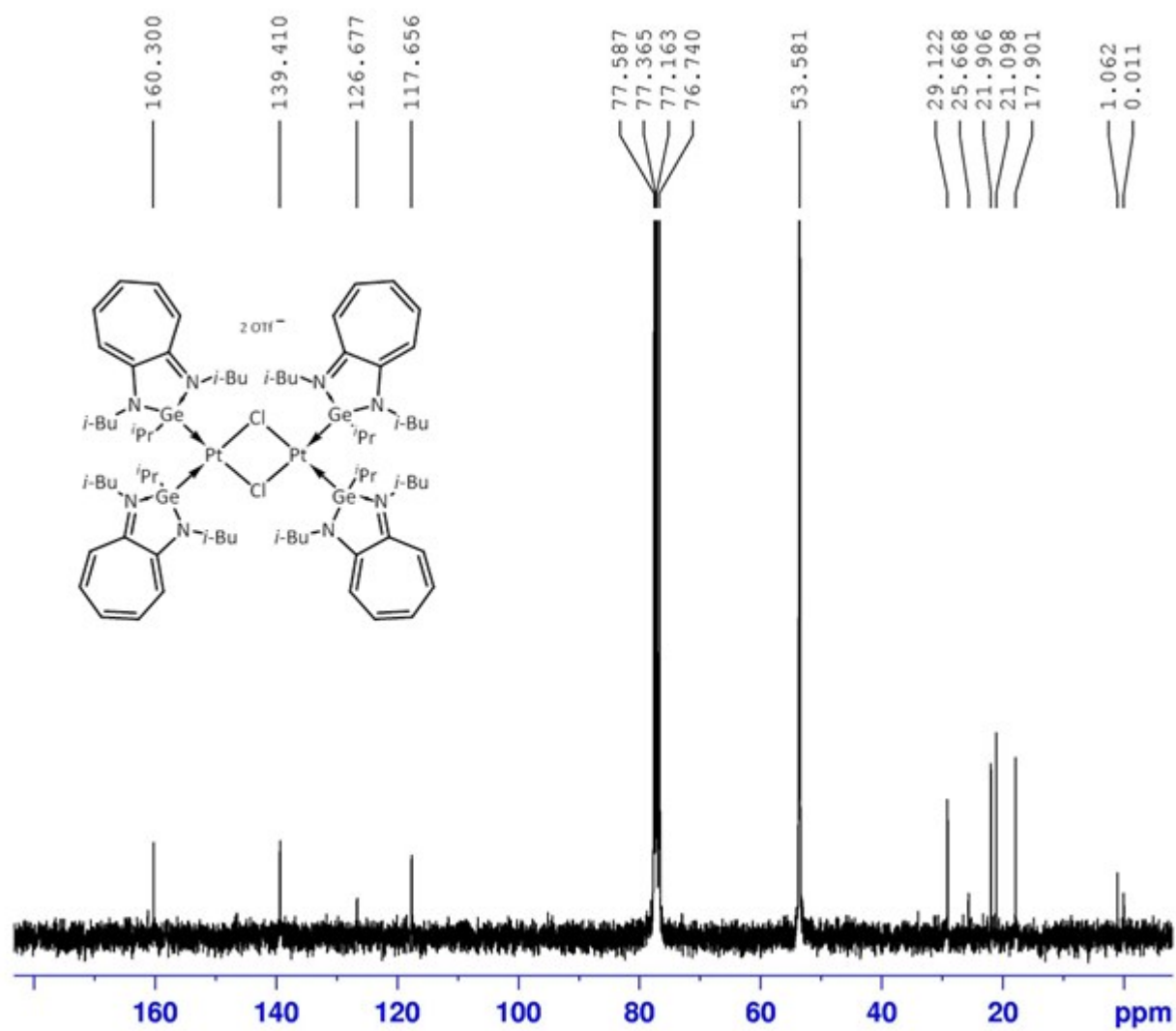
$^{13}\text{C}$  NMR spectrum of compound **3**:



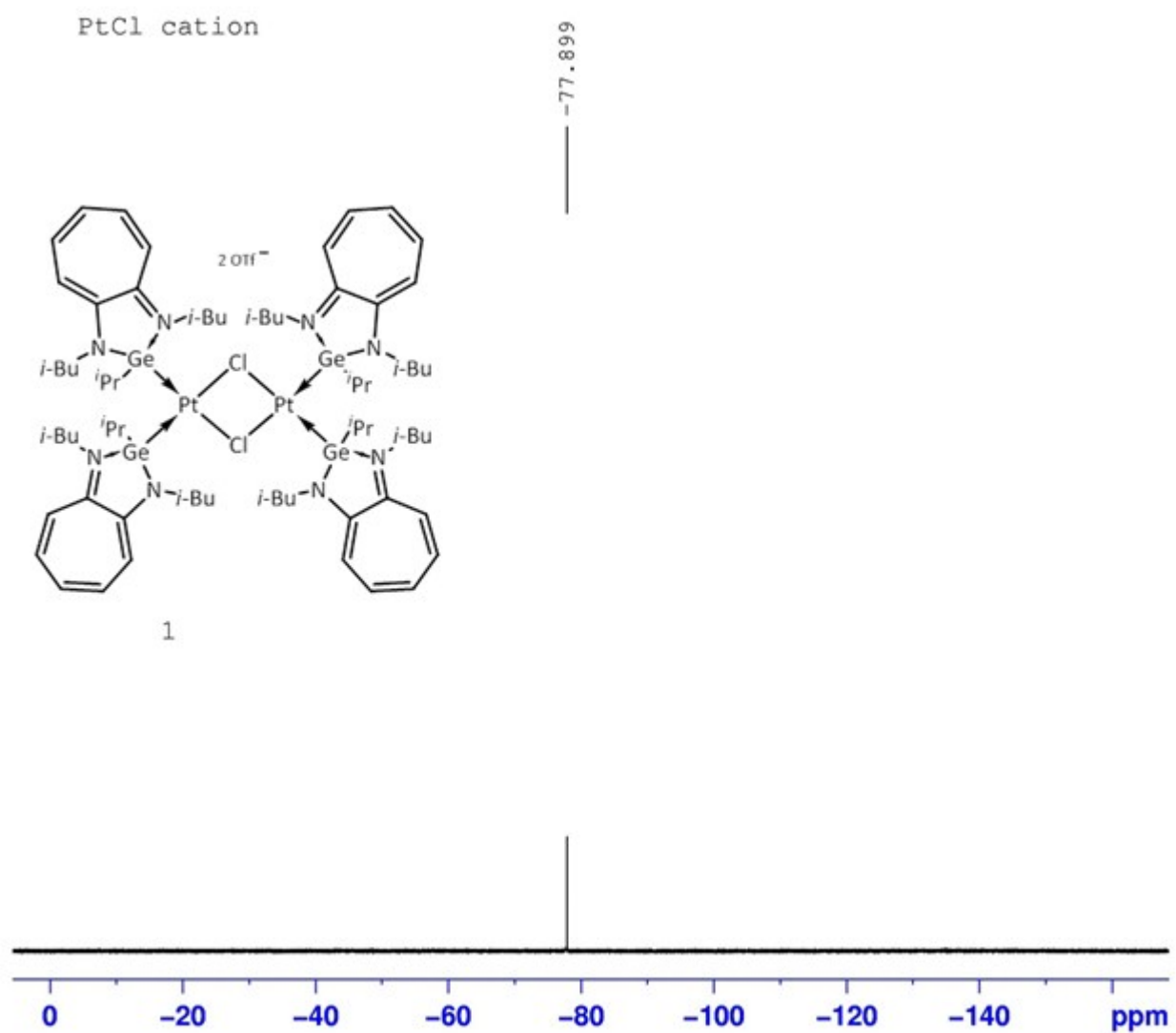
<sup>1</sup>H NMR spectrum of compound **4**:



$^{13}\text{C}$  NMR spectrum of compound **4**:

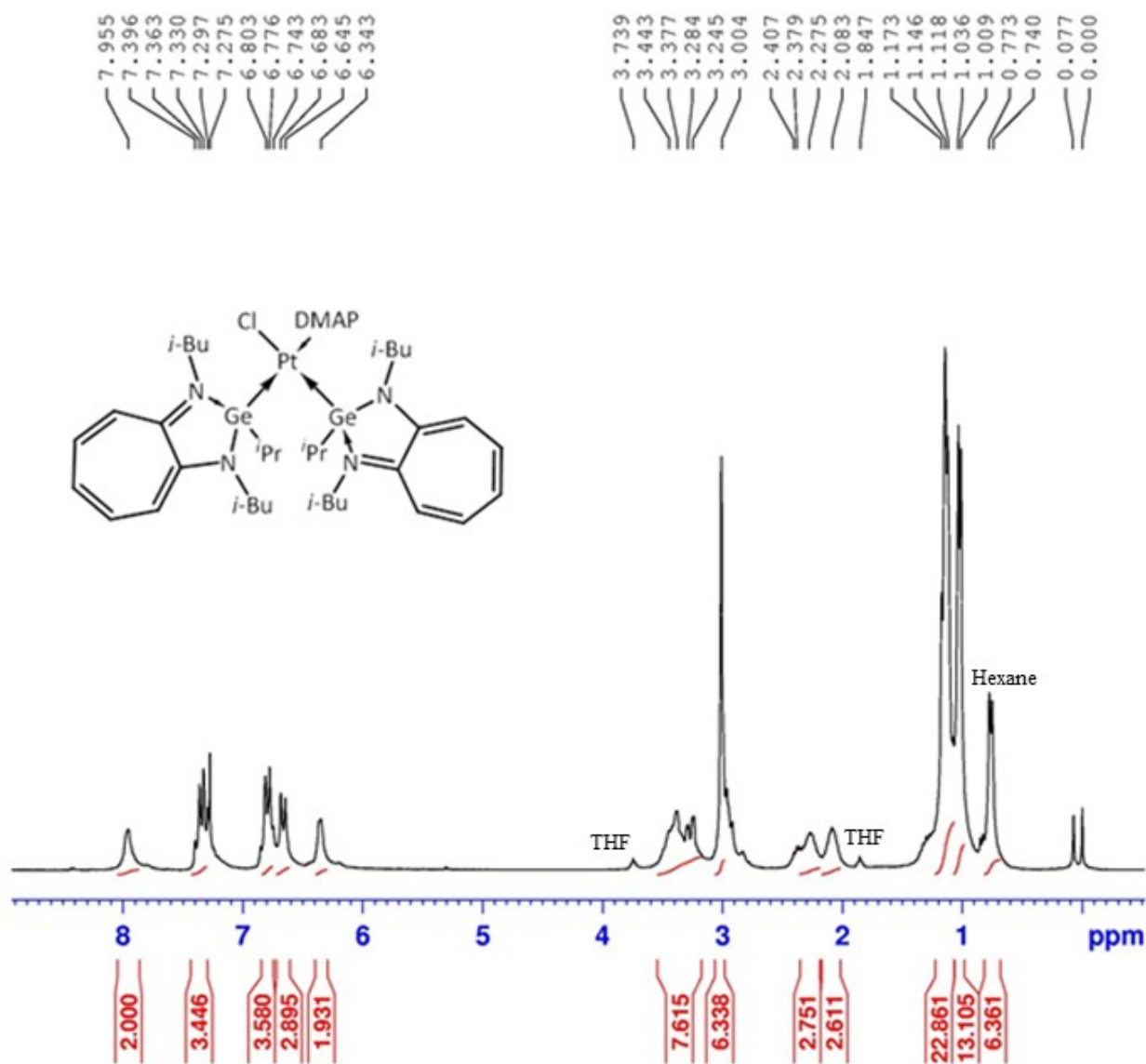


$^{19}\text{F}$  NMR spectrum of compound **4**:

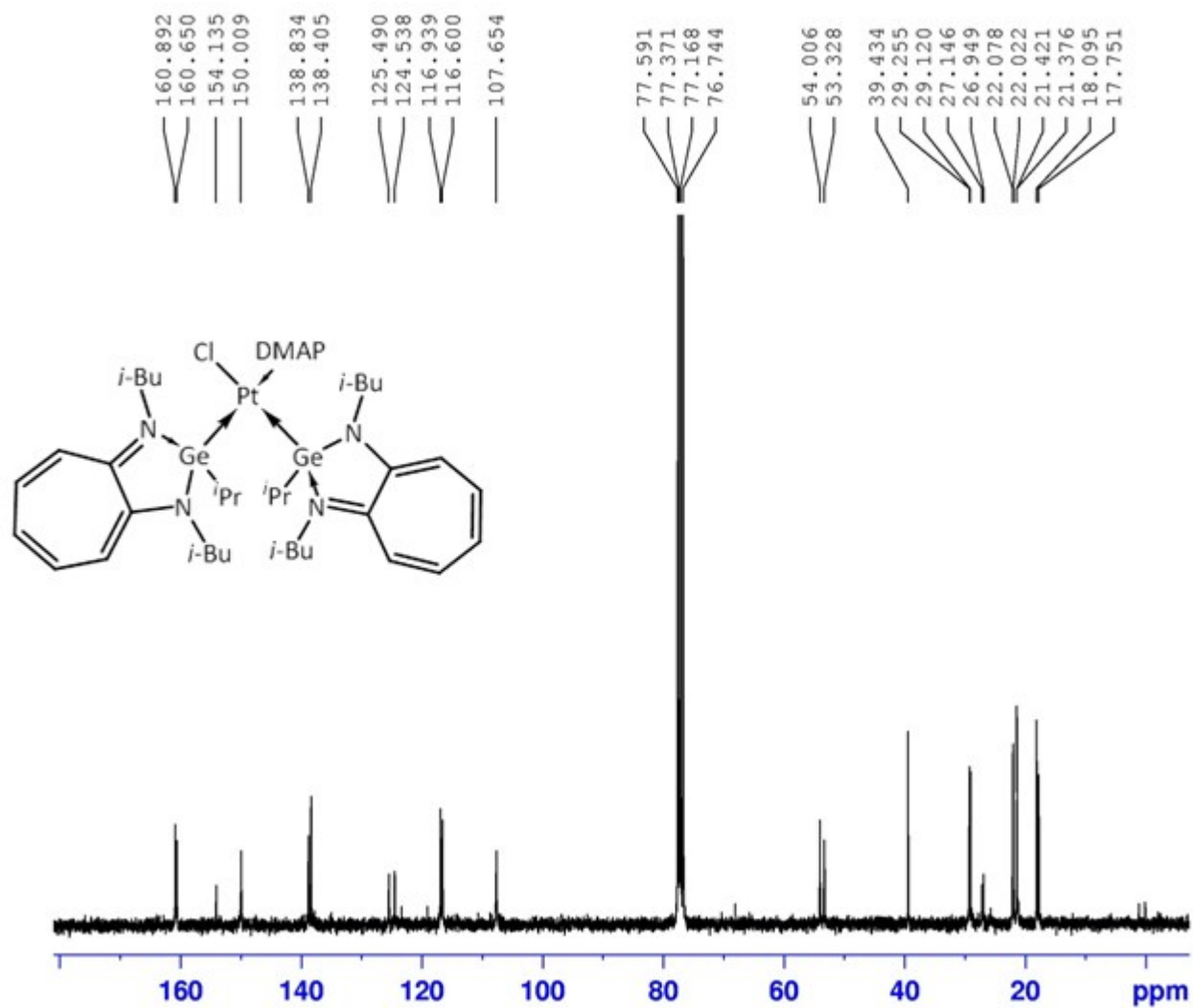




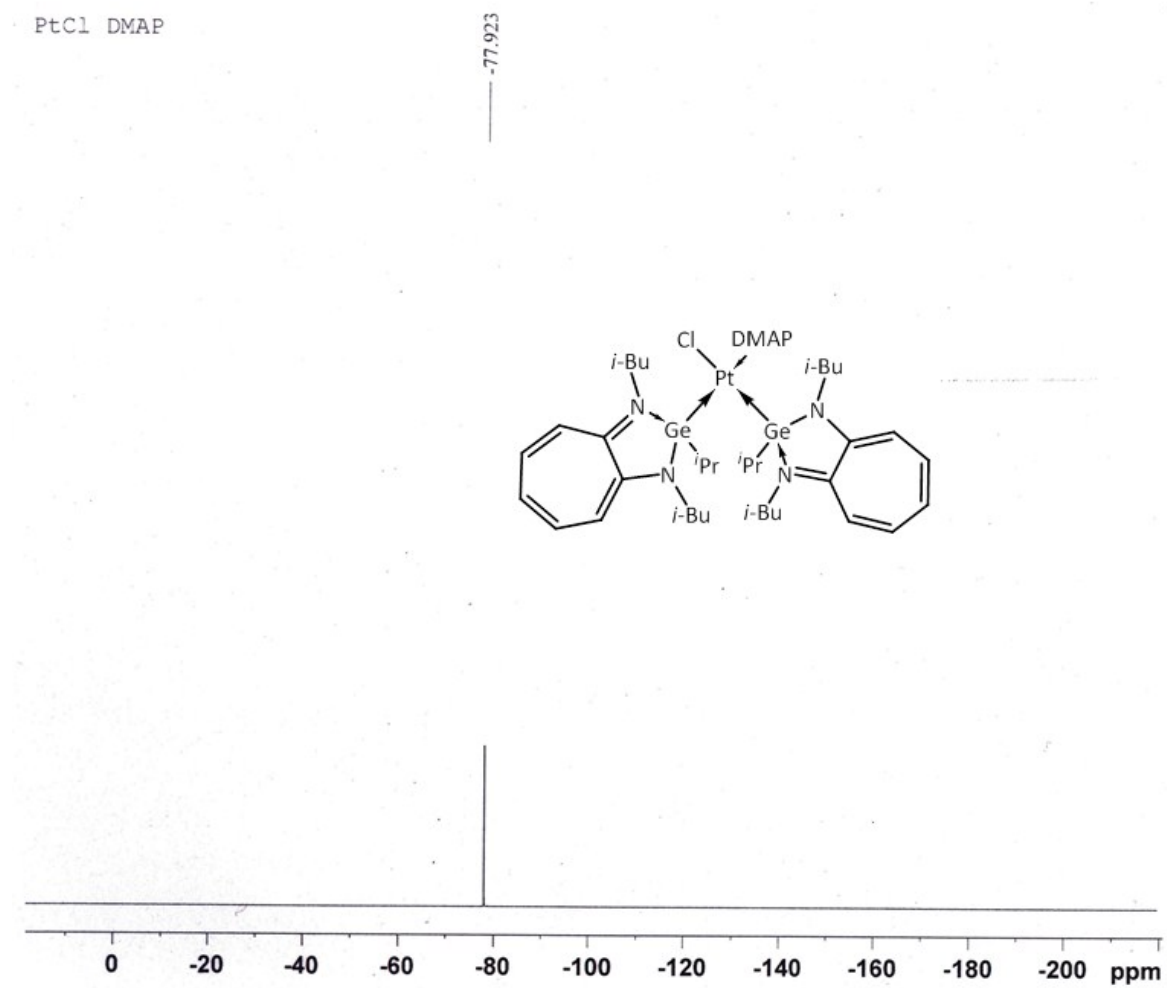
$^1\text{H}$  NMR spectrum of compound **5**:



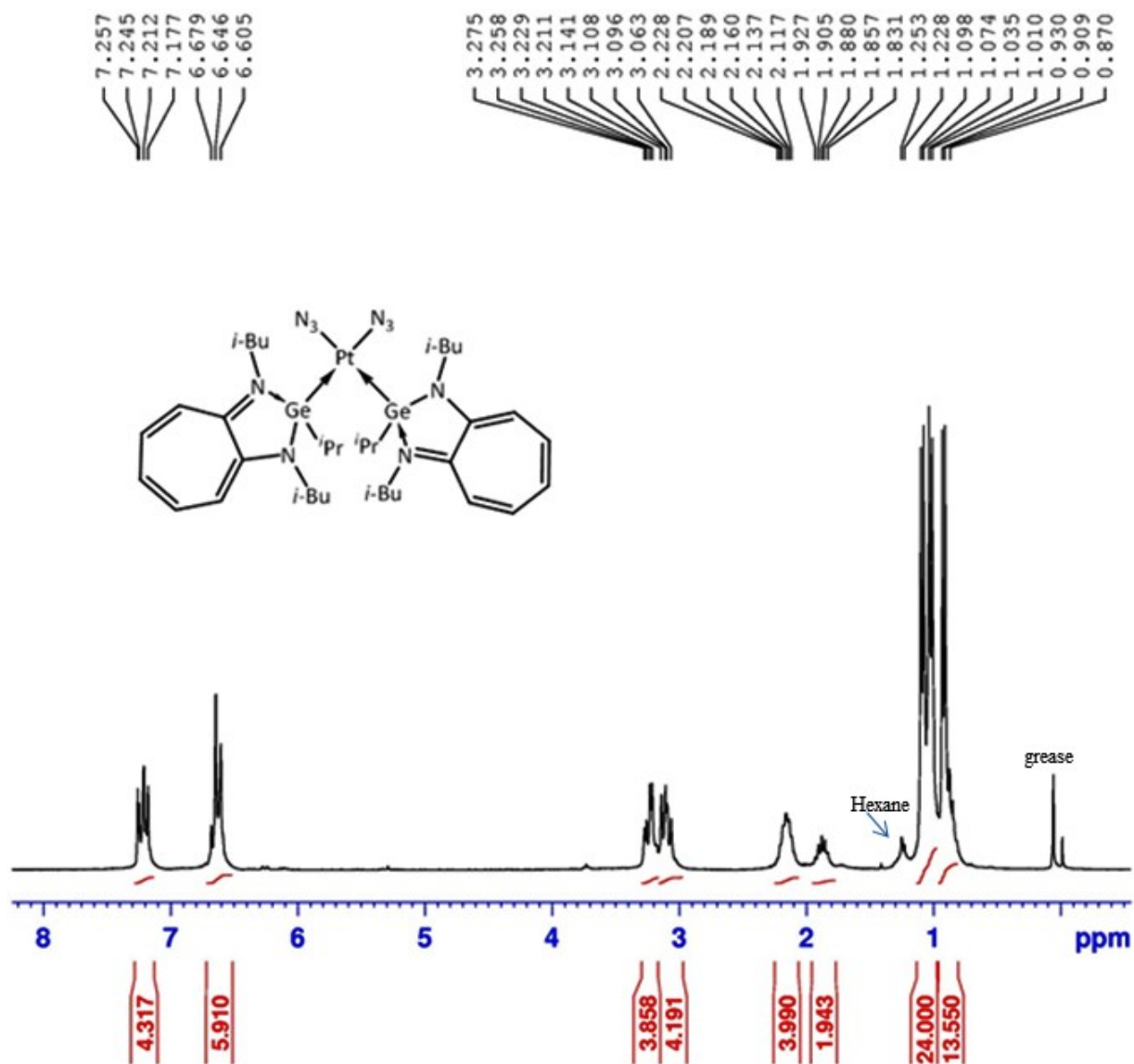
<sup>13</sup>C NMR spectrum of compound **5**:



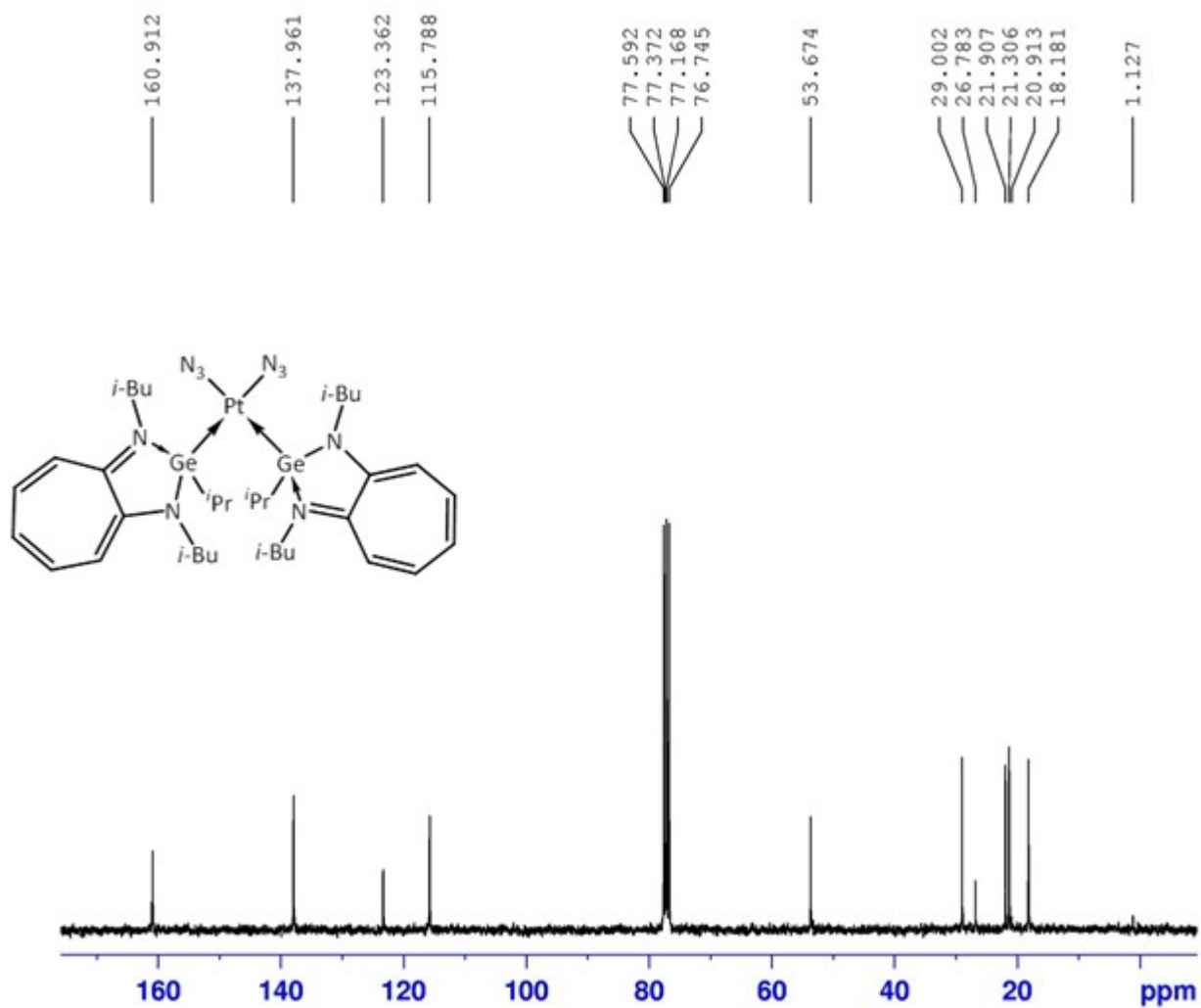
$^{19}\text{F}$  NMR spectrum of compound **5**:



<sup>1</sup>H NMR spectrum of compound 6:



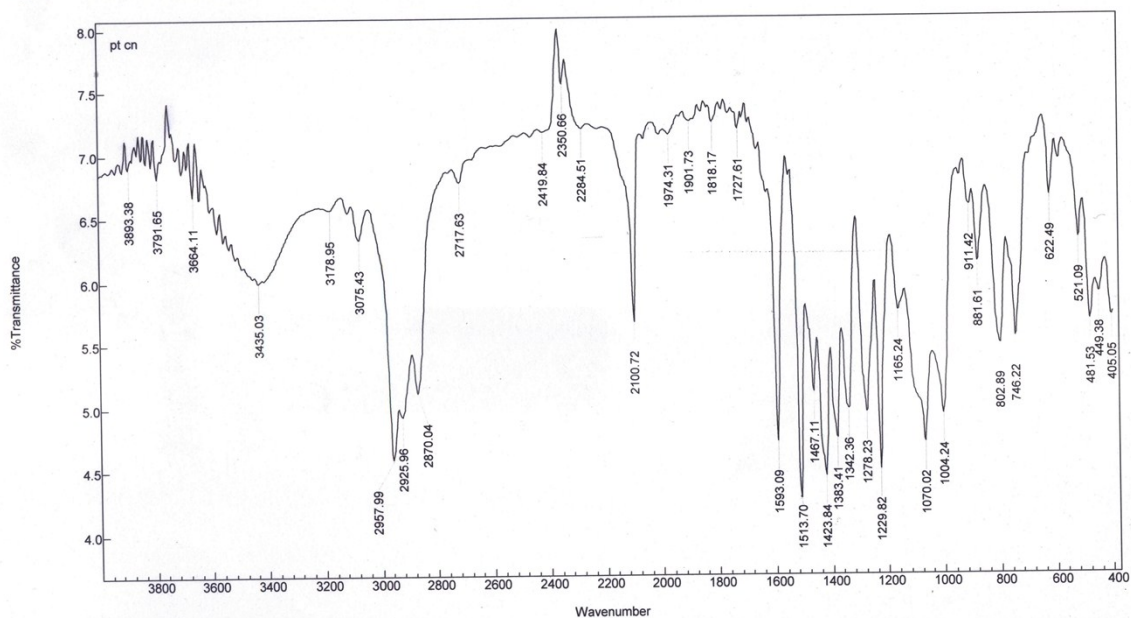
$^{13}\text{C}$  NMR spectrum of compound **6**:



## IR Spectra of Compounds 3 and 6:

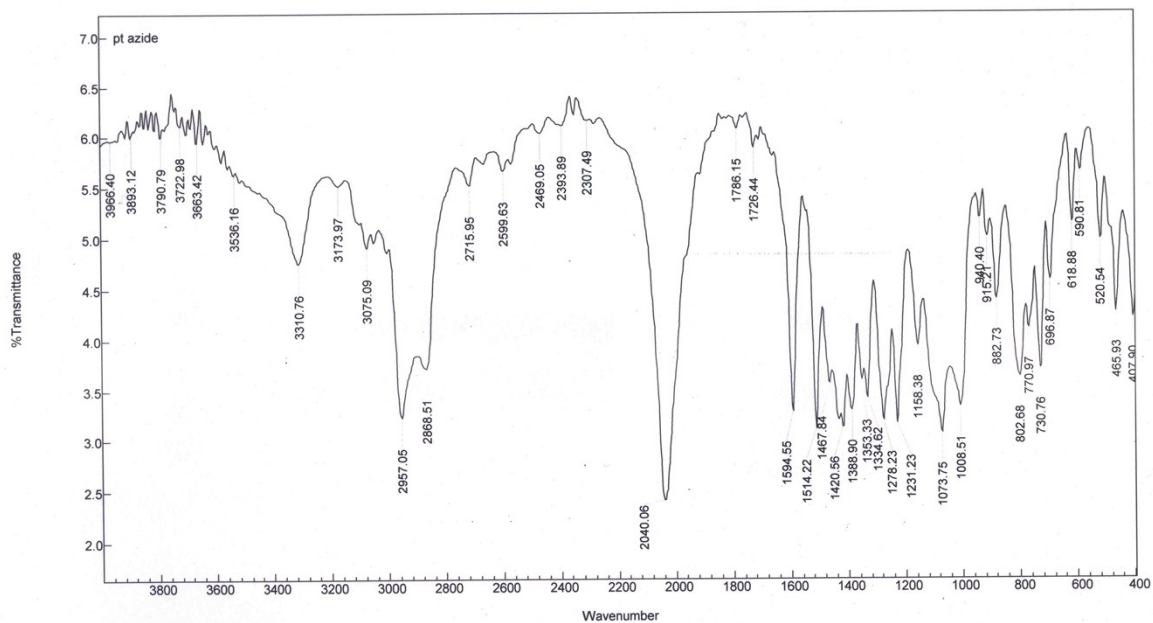
### IR Spectrum of compound 3:

Agilent Resolutions Pro

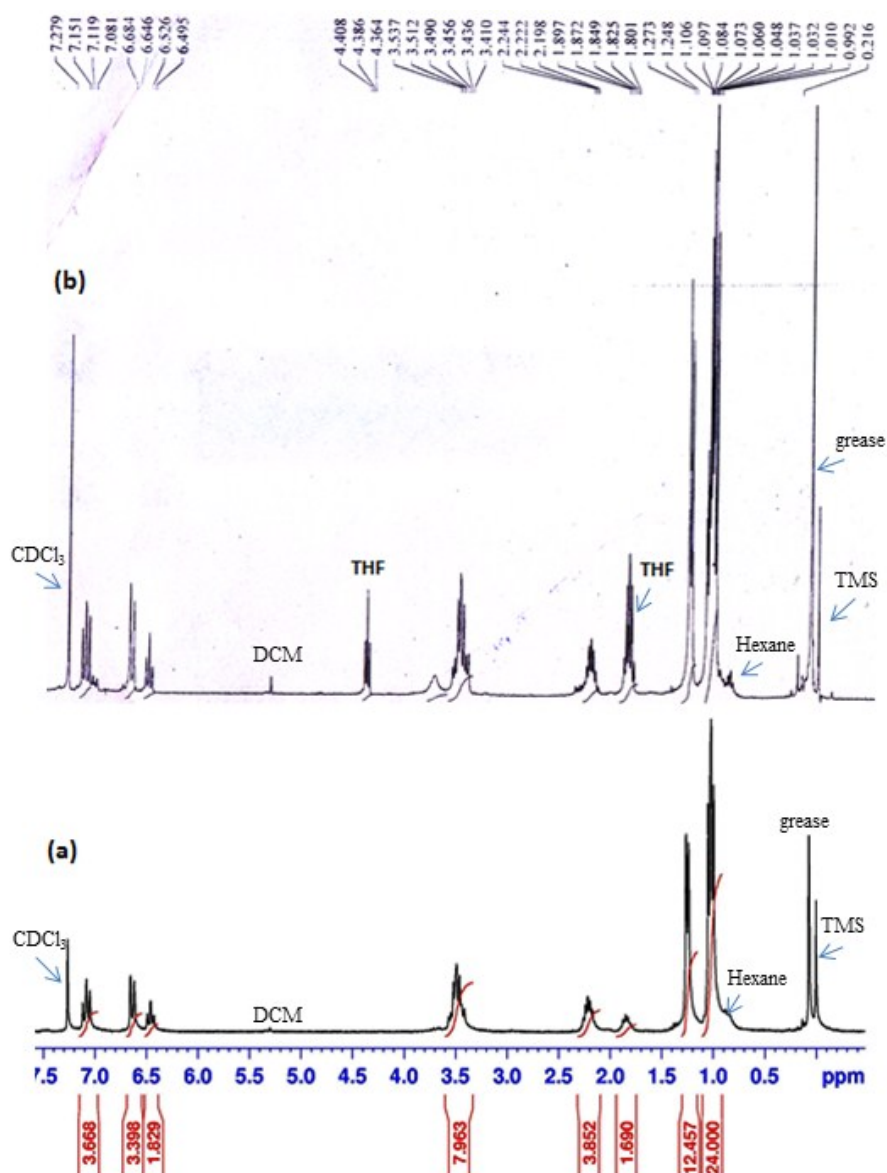


### IR Spectrum of compound 6:

Agilent Resolutions Pro

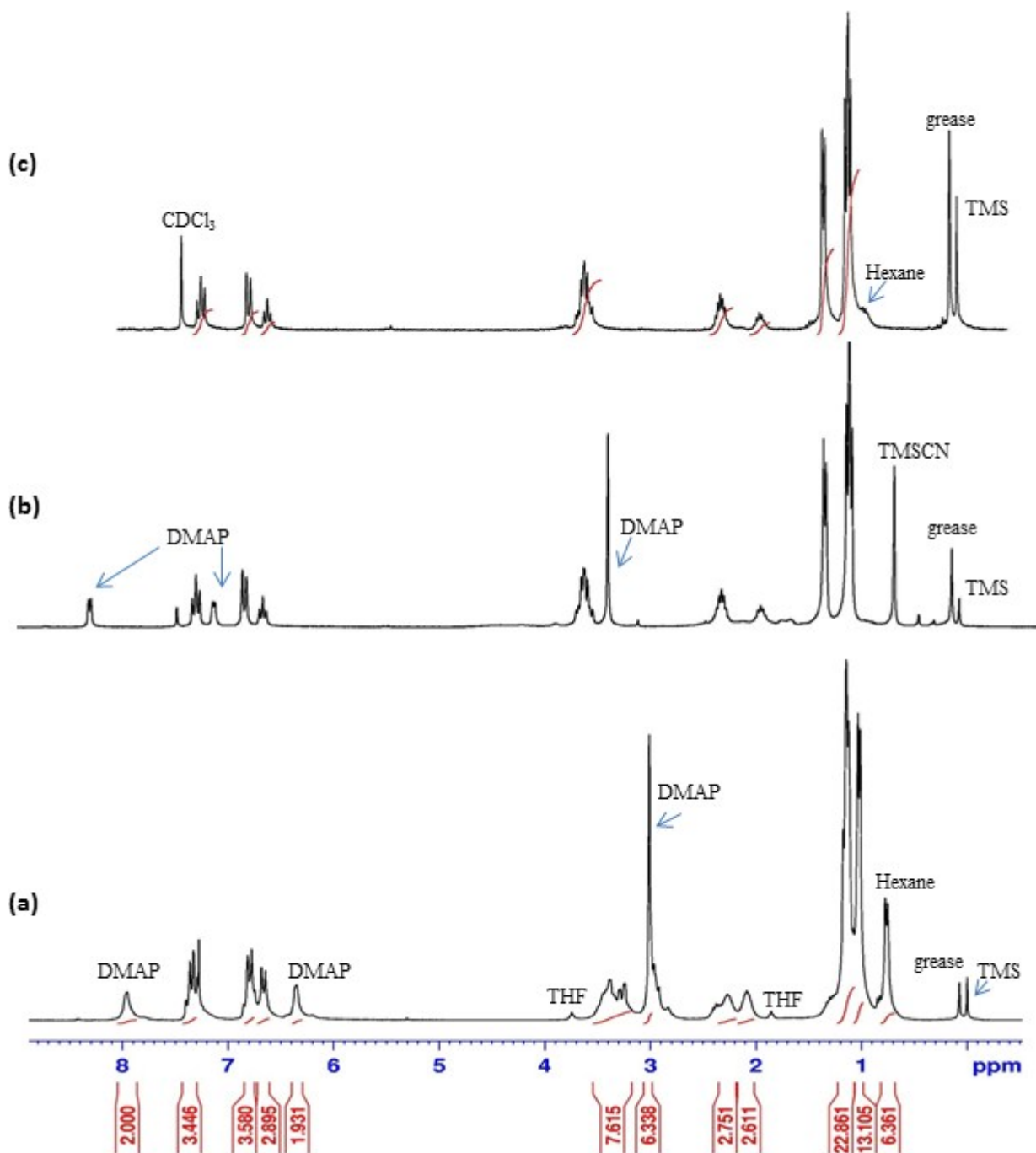


**Procedure followed for recovering compound 3 after a catalytic reaction:** The reaction of benzaldehyde with 1.2 equiv of TMS-CN was carried out in  $\text{CDCl}_3$  at  $50^\circ\text{C}$  in the presence of 1 mol% of compound 3. After 1.5 h, the reaction mixture was cooled to room temperature and the excess TMS-CN and solvent ( $\text{CDCl}_3$ ) was evaporated to obtain a viscous liquid. It was stirred with a mixture of hexane and THF (90:10) to remove majority of the cyanohydrin trimethylsilylether formed during the reaction, and during with a yellow solid precipitates out. It was separated, washed with hexane, dried under reduced pressure, and  $^1\text{H}$  NMR spectrum was recorded. The spectrum (Figure 5b) shows the presence of compound 3 (for an instant comparison, spectrum of compound 3 is shown in Figure 5a) with some left out cyanohydrin trimethylsilylether and solvent impurities.



**Figure S5.** (a)  $^1\text{H}$  NMR spectrum of compound 3 (b)  $^1\text{H}$  NMR spectrum of crude compound 3 recovered from a catalytic reaction.

**Conversion of Compound 5 to Compound 3:** Compounds **2** and **4-6** react with TMSCN and produce exclusively compound **3** within 5 min. For example, the conversion of compound **5** to compound **3** is shown in Figures S6(a)-S6(c).

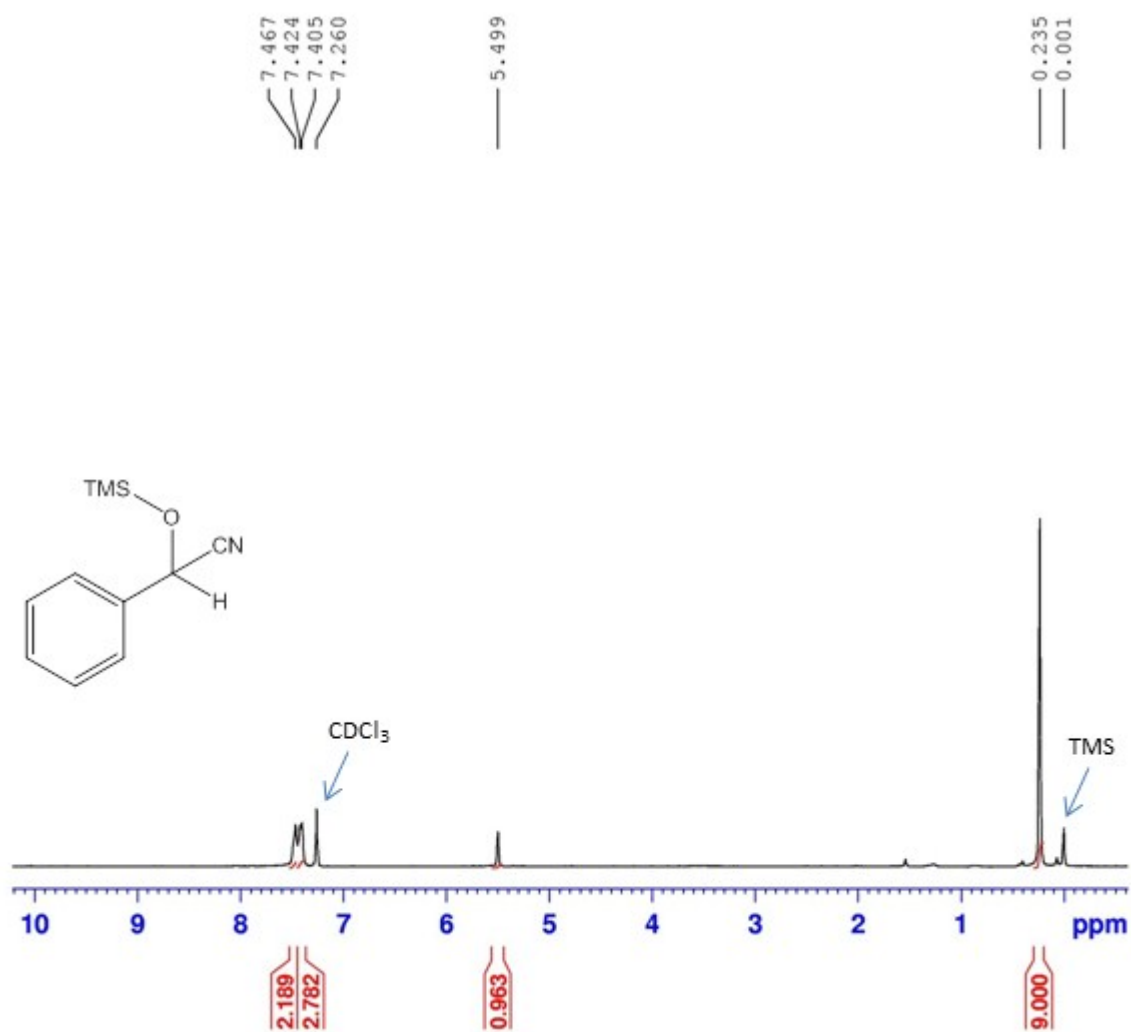


**Figure S6.** (a)  $^1\text{H}$  NMR spectrum of compound **5** in dry  $\text{CDCl}_3$  (b)  $^1\text{H}$  NMR spectrum of the reaction mixture after 5 minutes from the addition of slight excess TMSCN to compound **5**, and (c)  $^1\text{H}$  NMR spectrum of compound **3** for an instant comparison with Figure S6b to see the conversion of compound **5** to compound **3**.

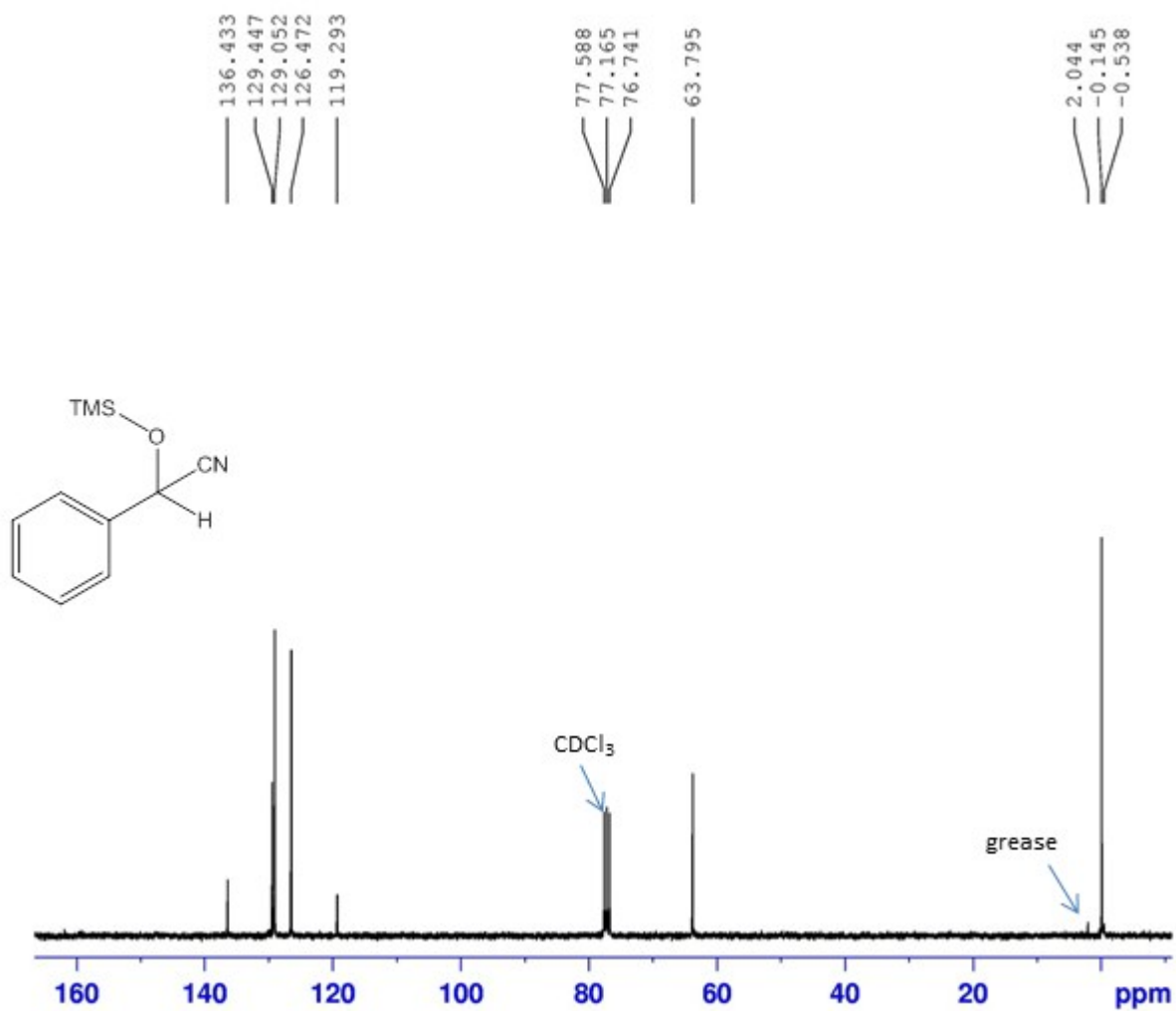


## $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Cyanosilylated Products:

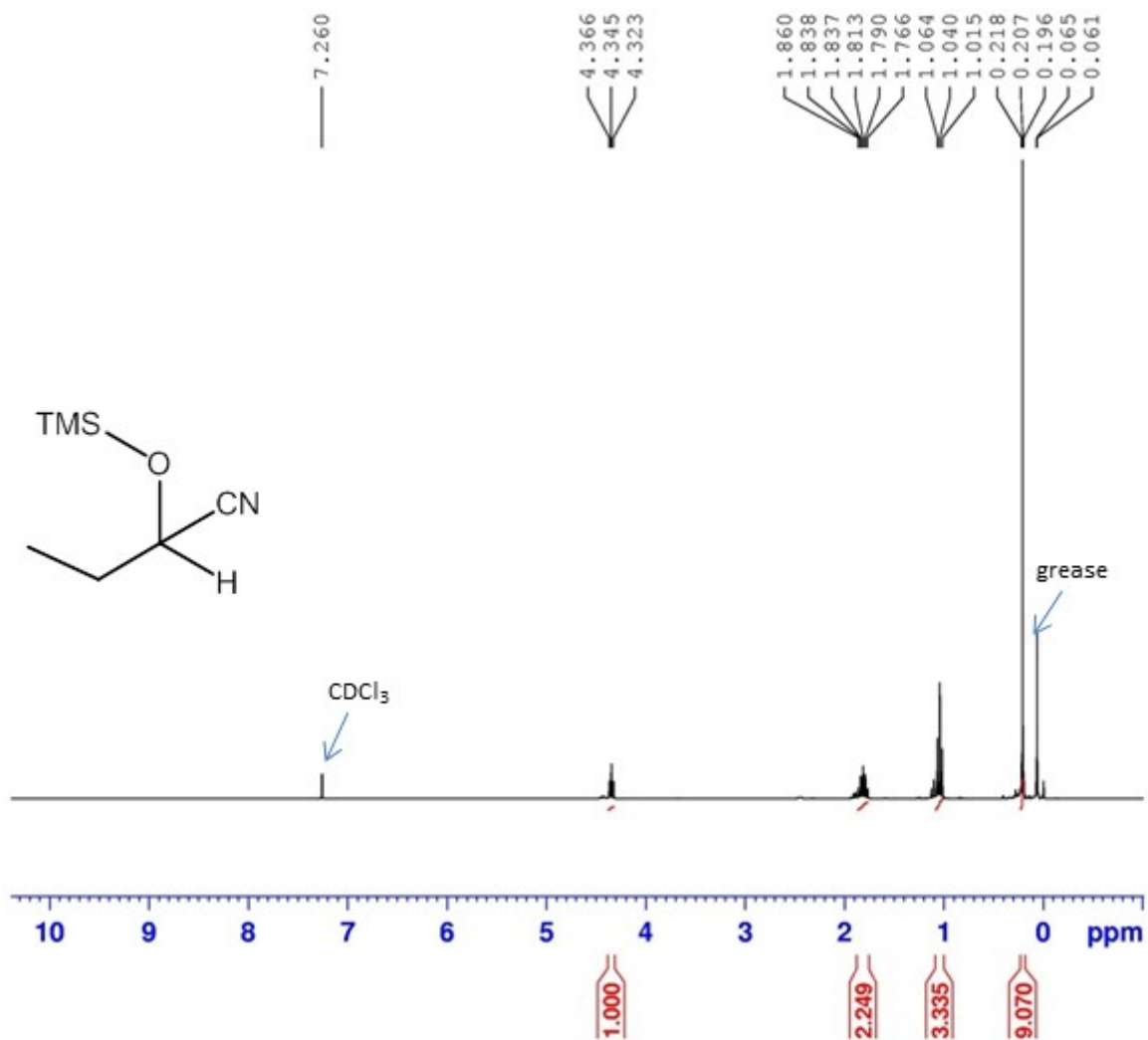
$^1\text{H}$  NMR spectrum of the cyanosilylated product of benzaldehyde:



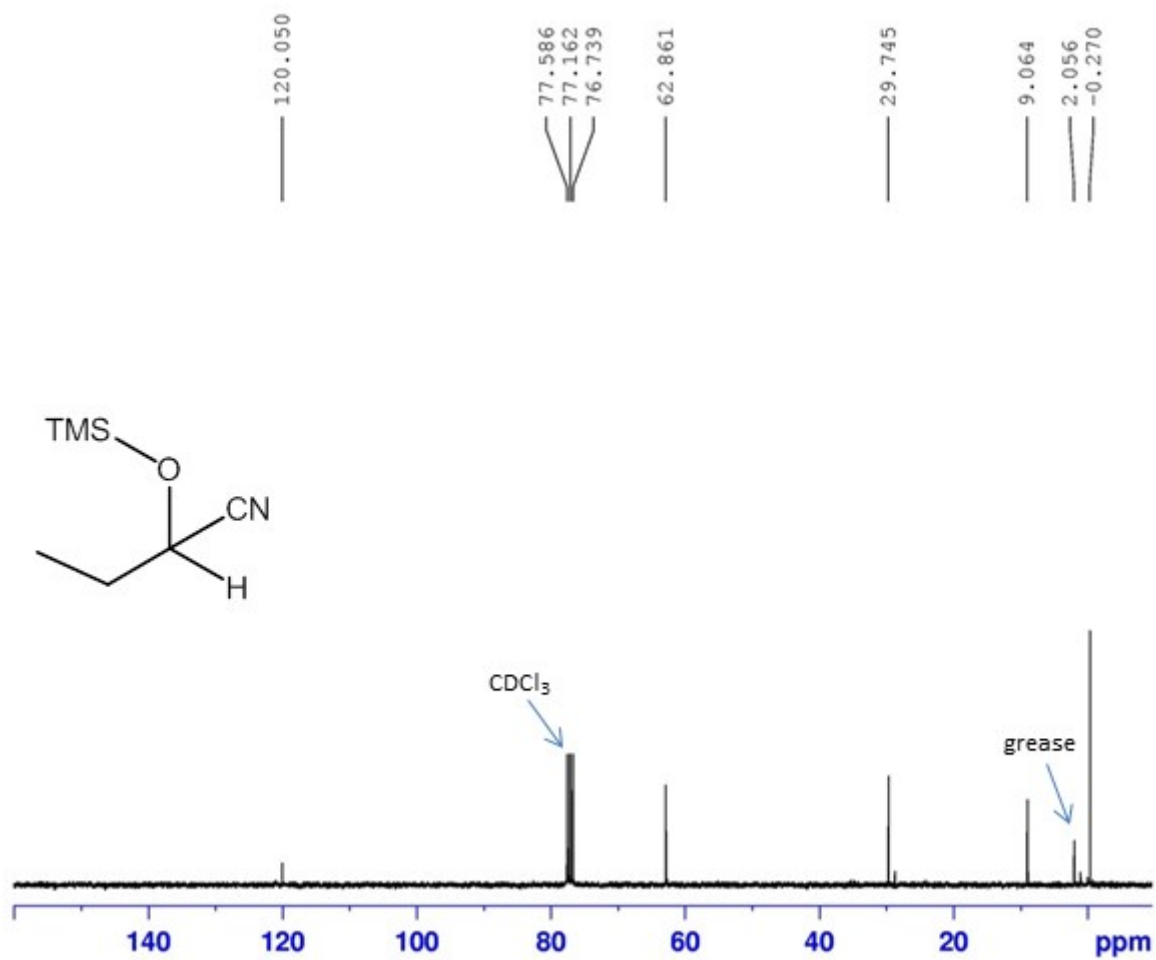
$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of benzaldehyde:



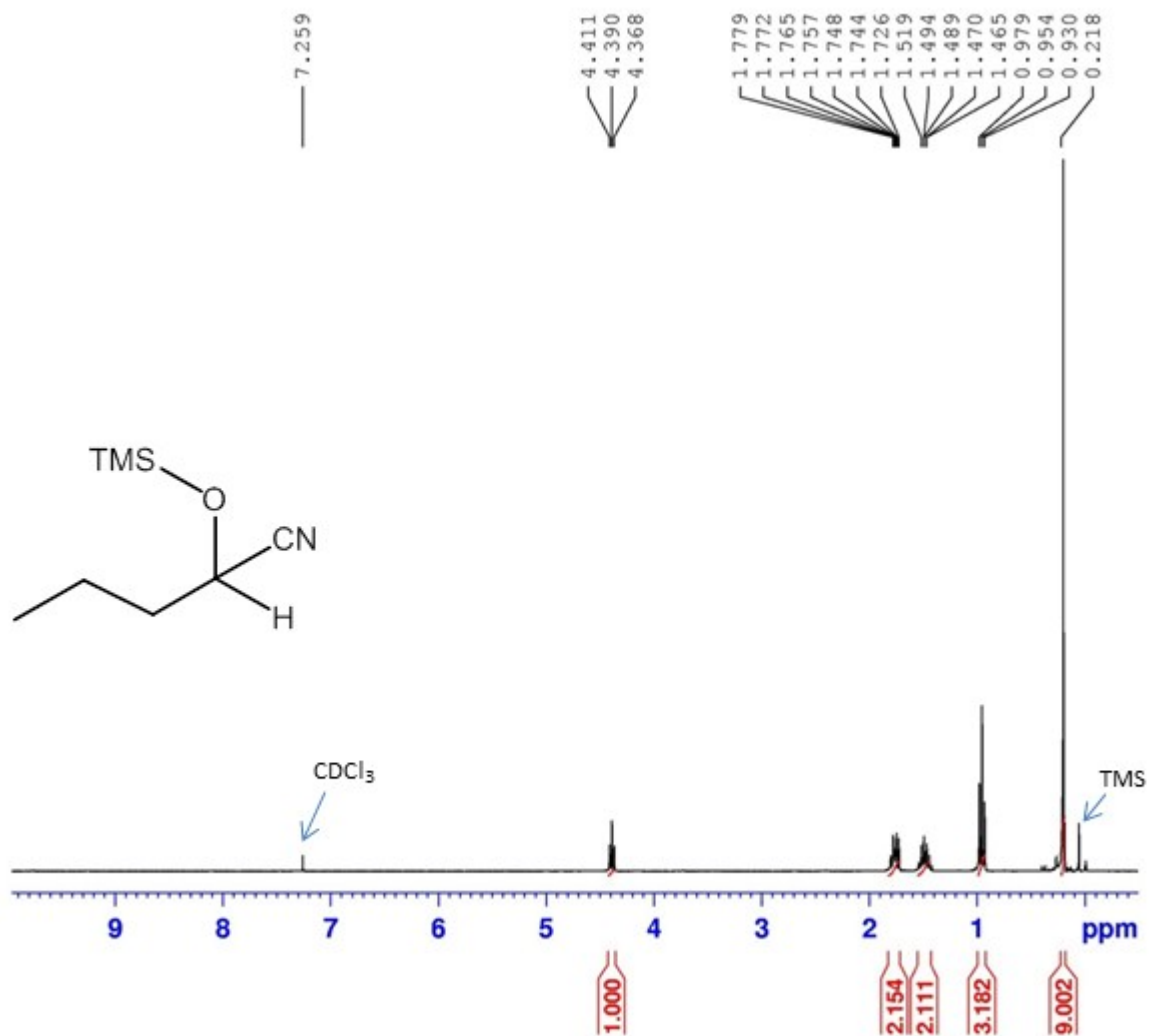
$^1\text{H}$  NMR spectrum of the cyanosilylated product of propionaldehyde:



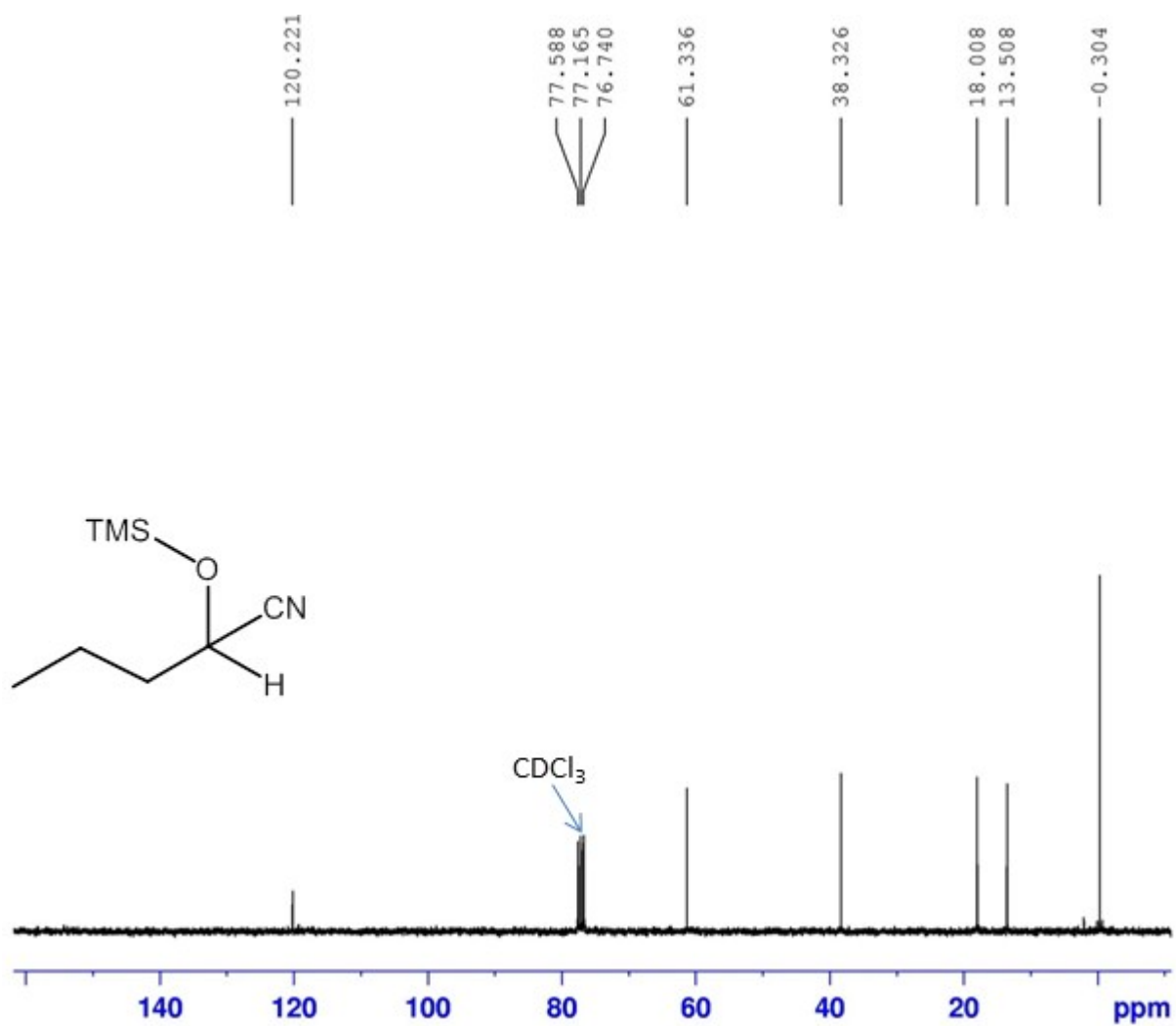
$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of propionaldehyde:



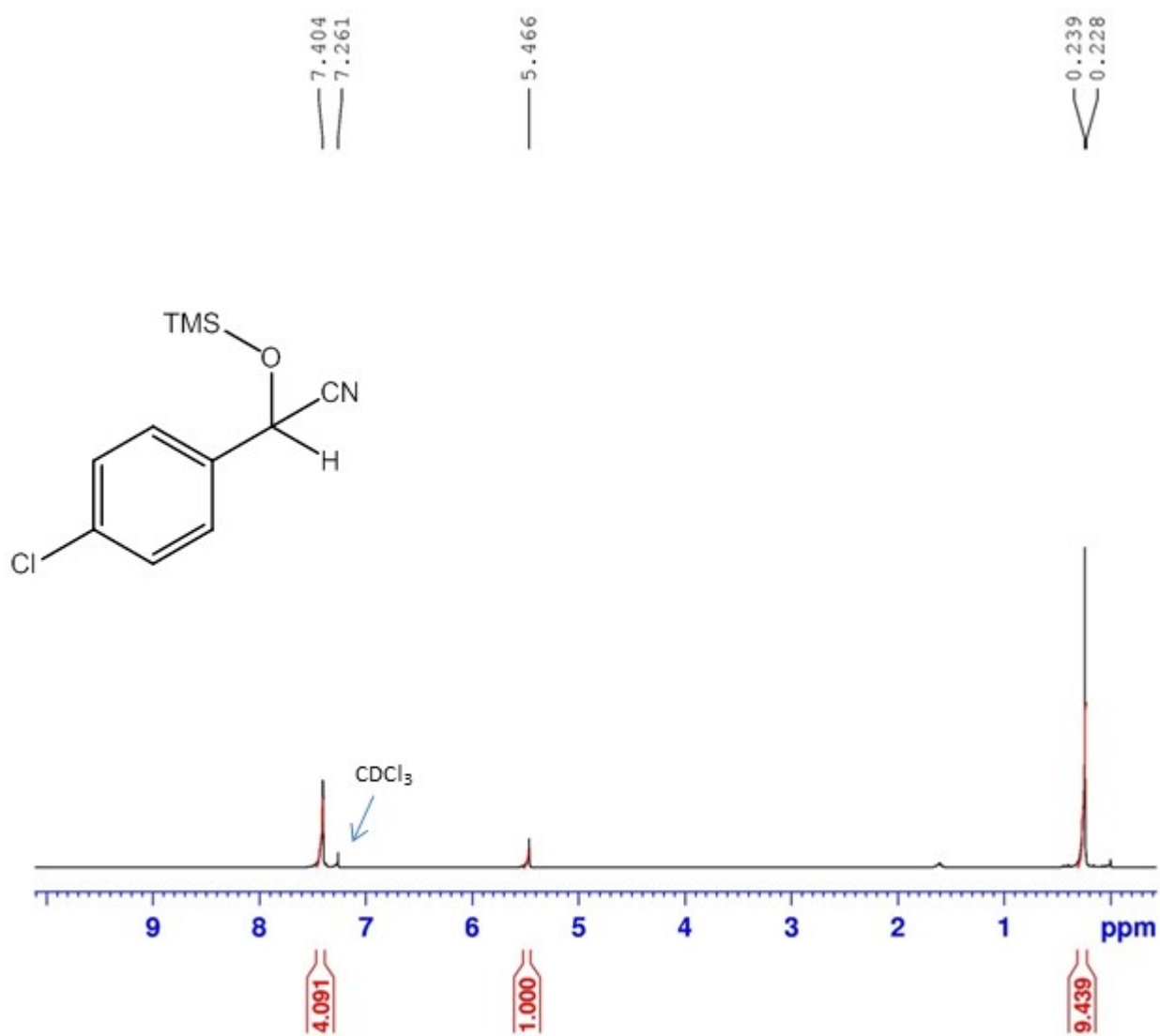
$^1\text{H}$  NMR spectrum of the cyanosilylated product of *n*-butyraldehyde:



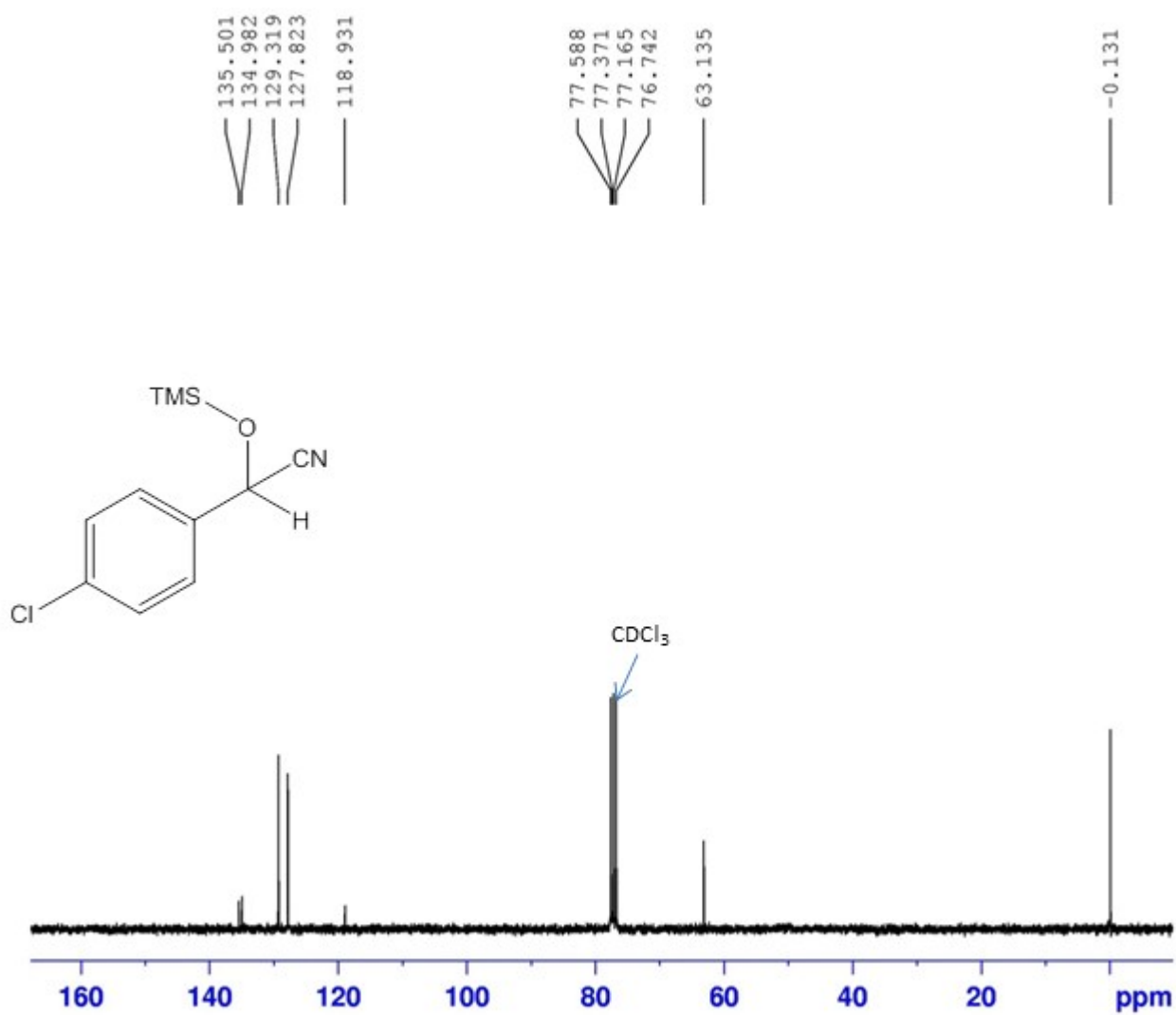
$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of *n*-butyraldehyde:



$^1\text{H}$  NMR spectrum of the cyanosilylated product of 4-chlorobenzaldehyde:

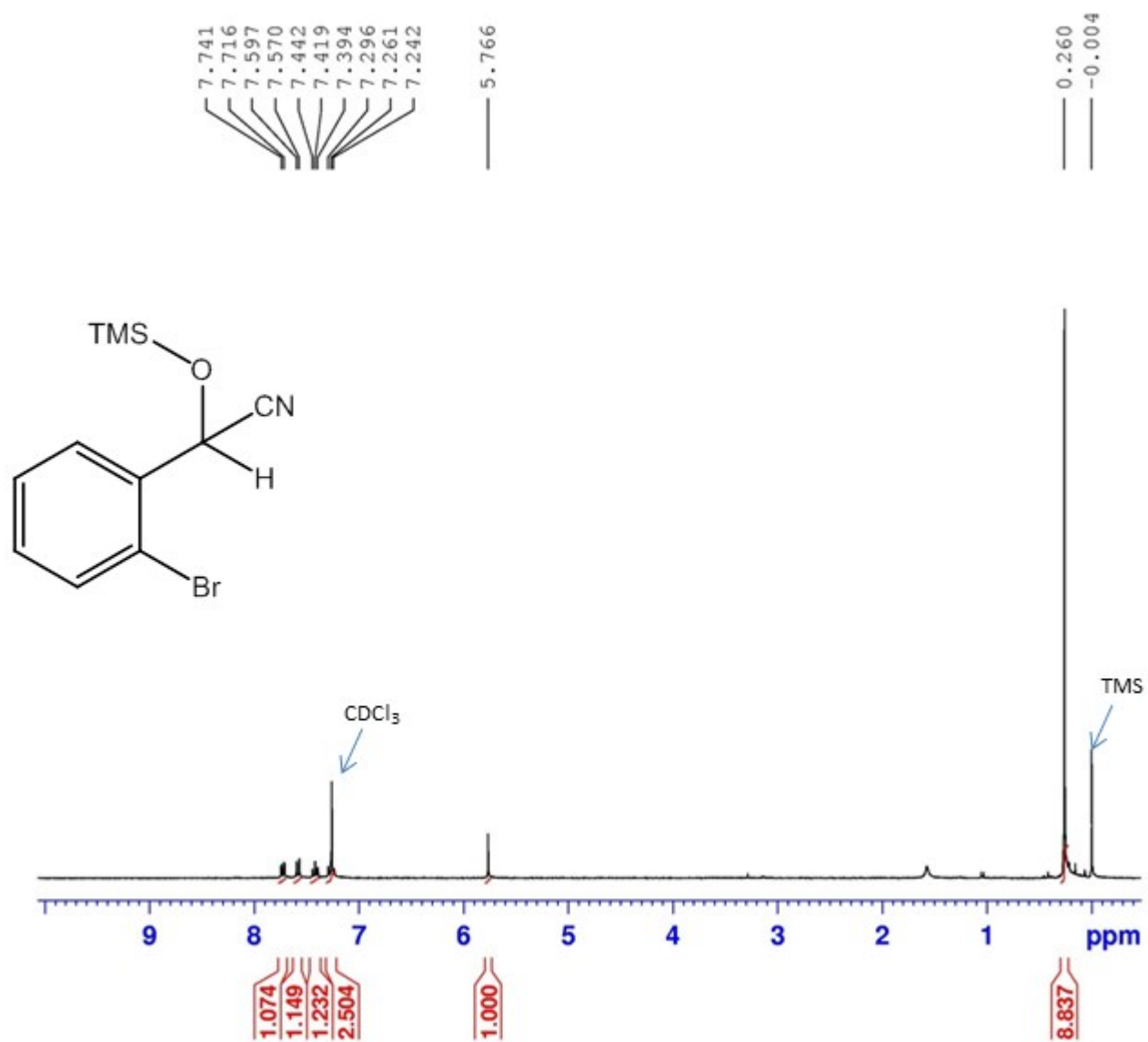


$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of 4-chlorobenzaldehyde:

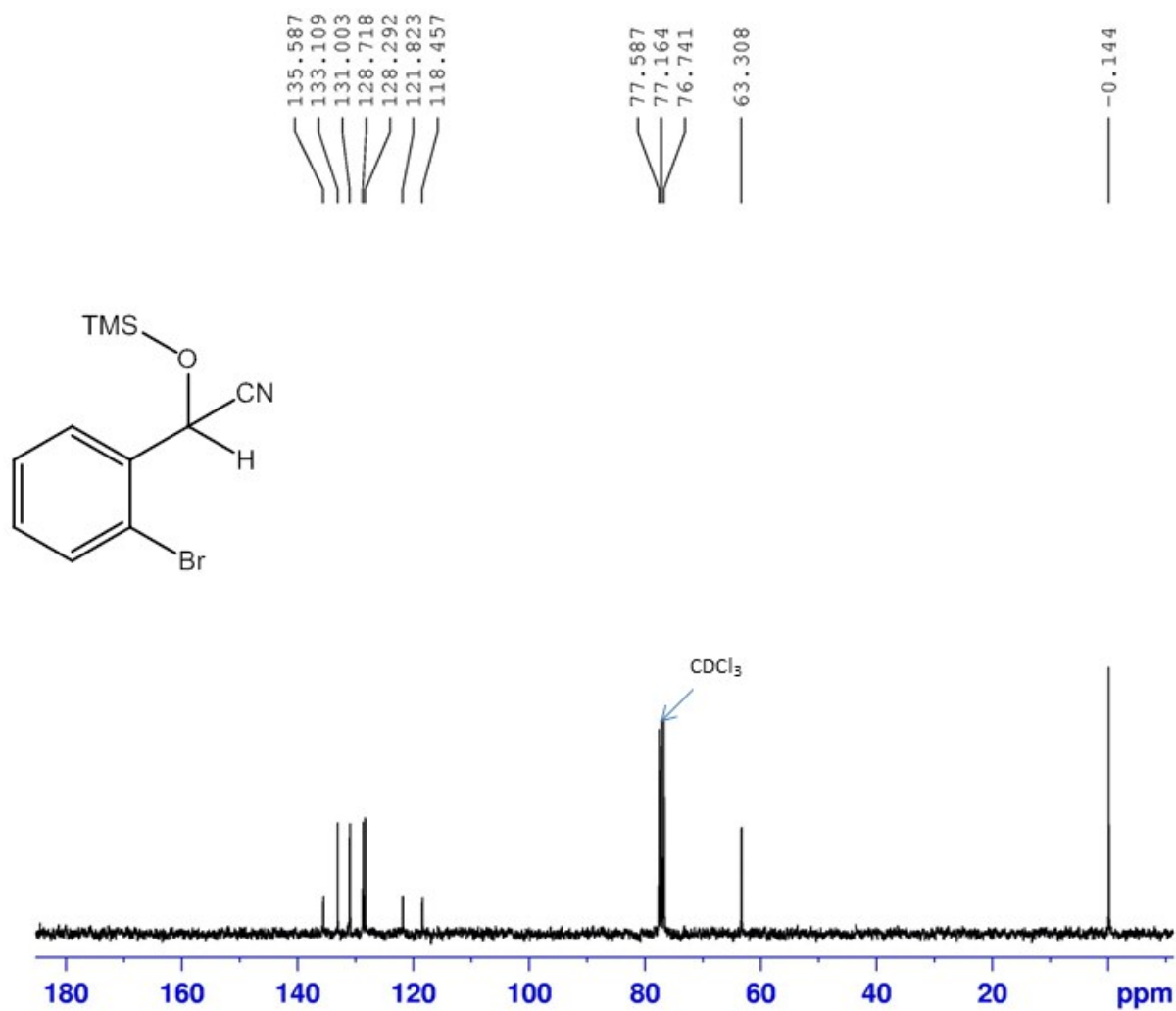




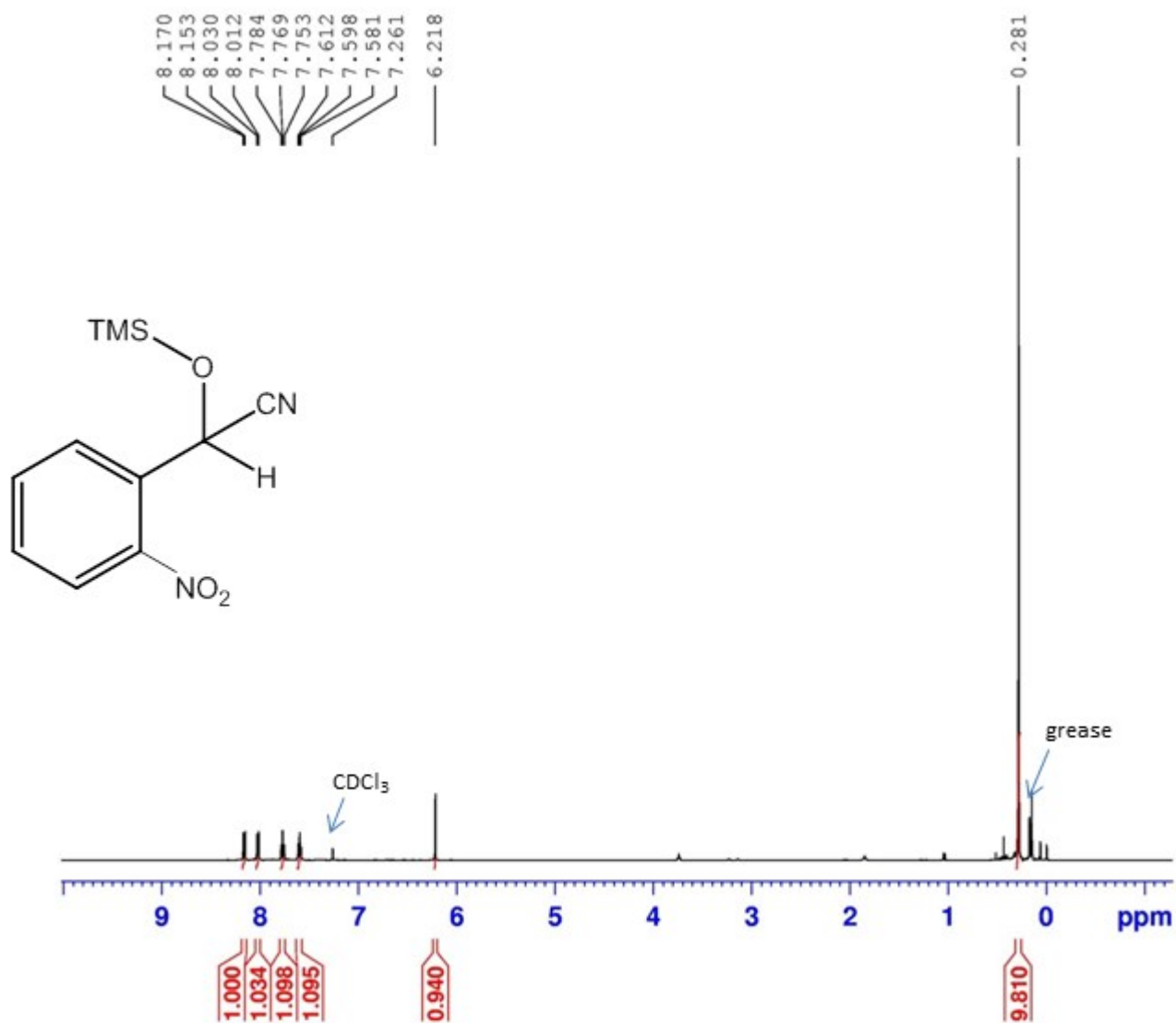
$^1\text{H}$  NMR spectrum of the cyanosilylated product of 2-bromobenzaldehyde:



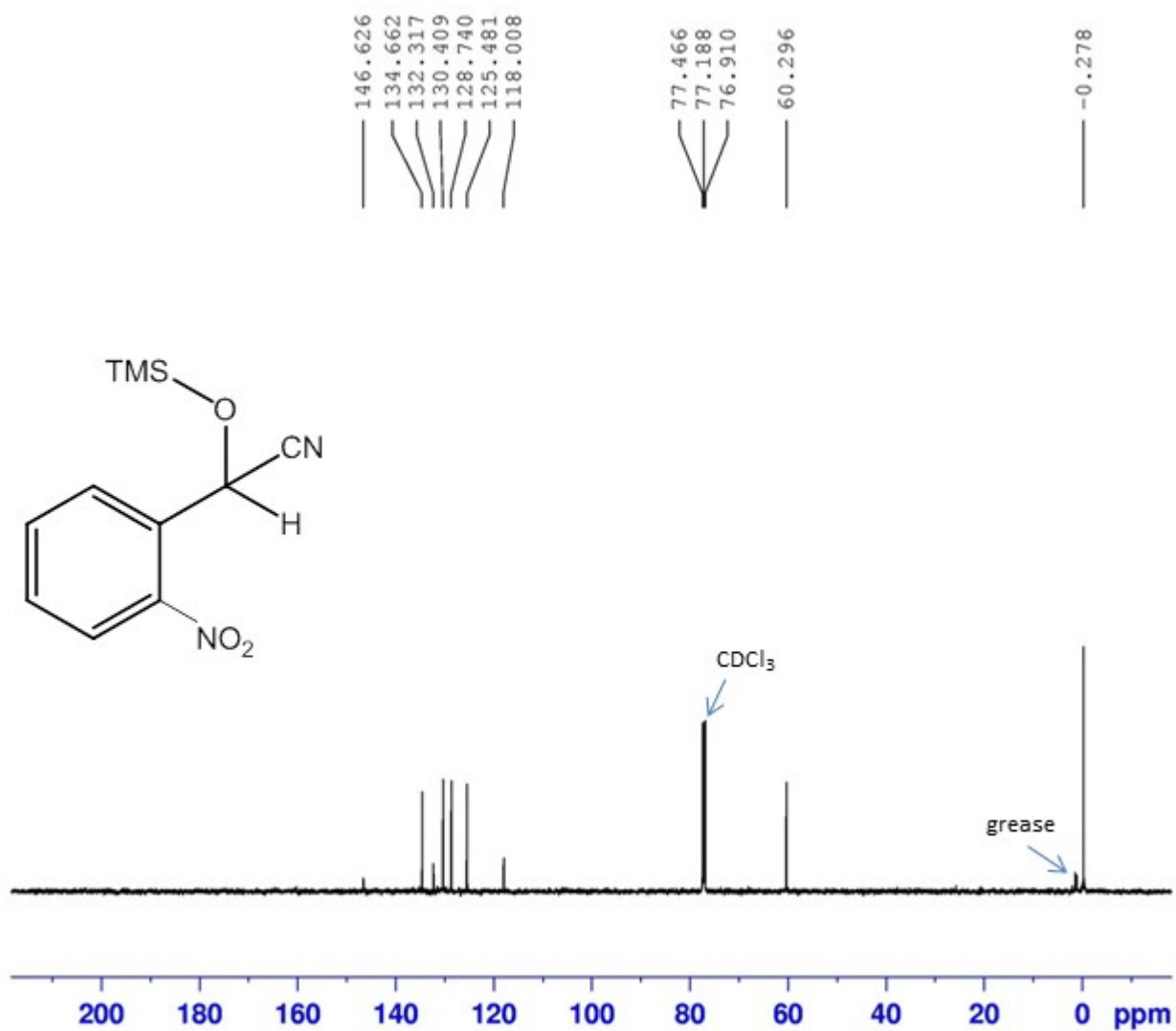
$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of 2-bromobenzaldehyde:



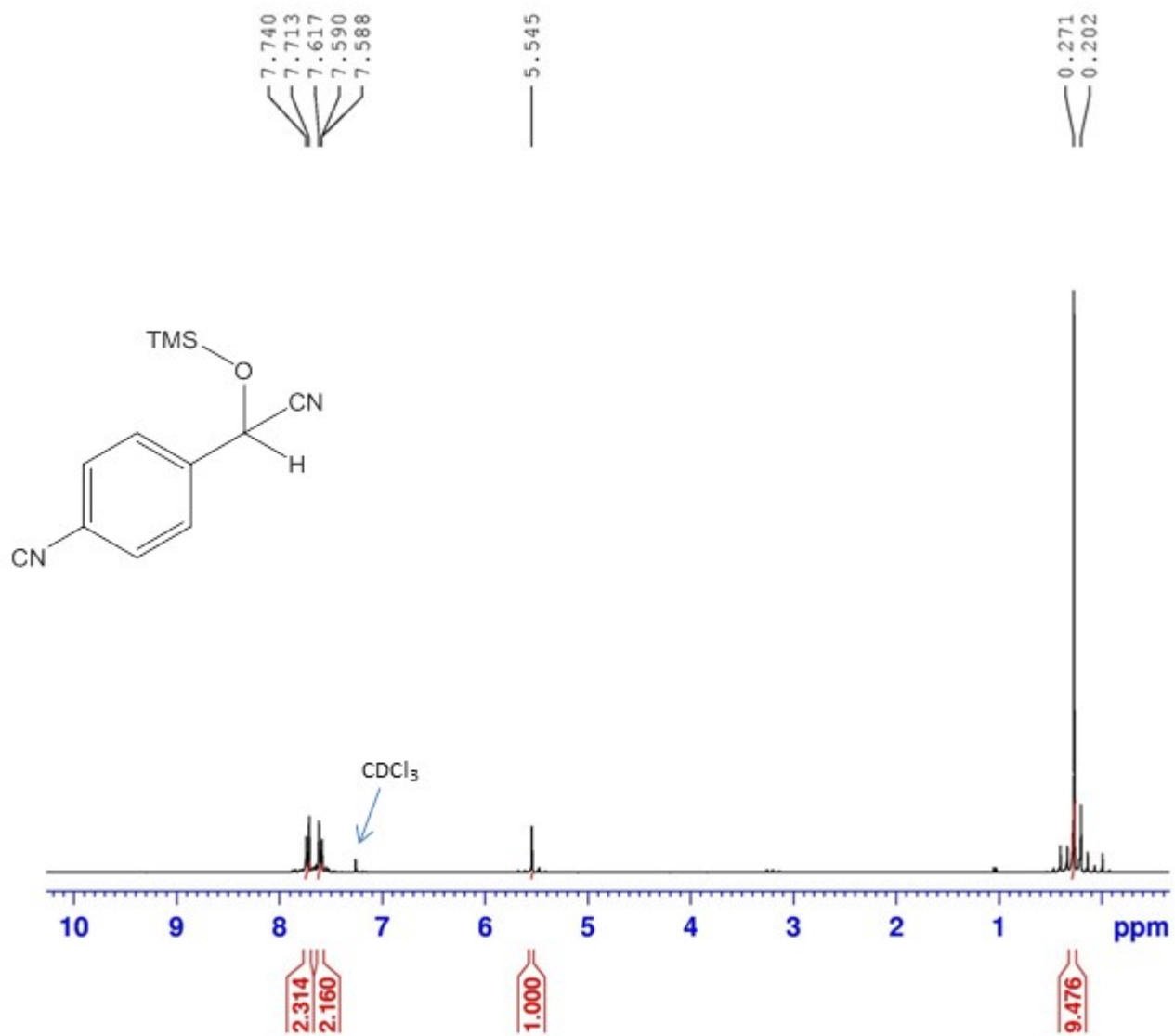
<sup>1</sup>H NMR spectrum of the cyanosilylated product of 2-nitrobenzaldehyde:



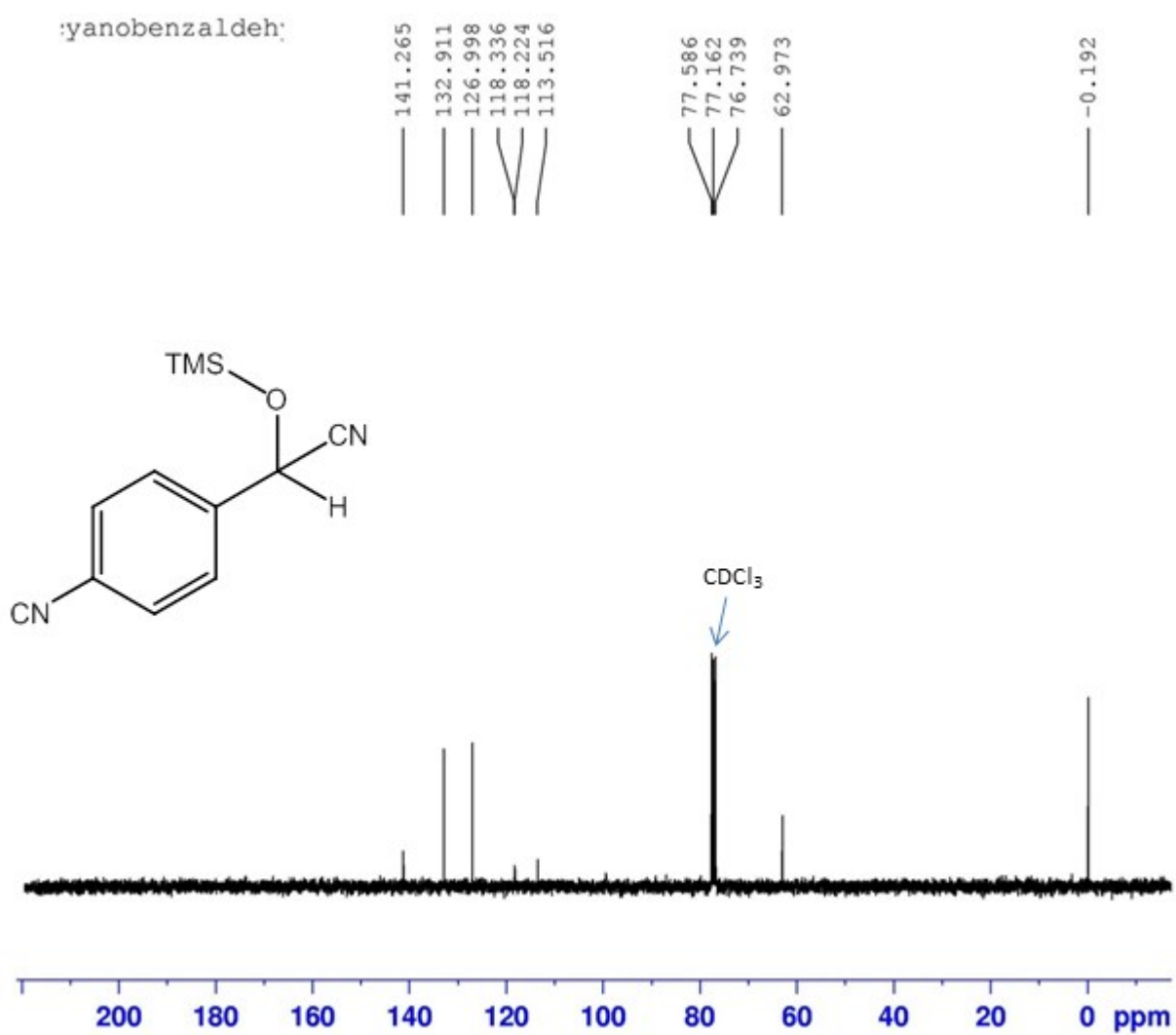
$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of 2-nitrobenzaldehyde:



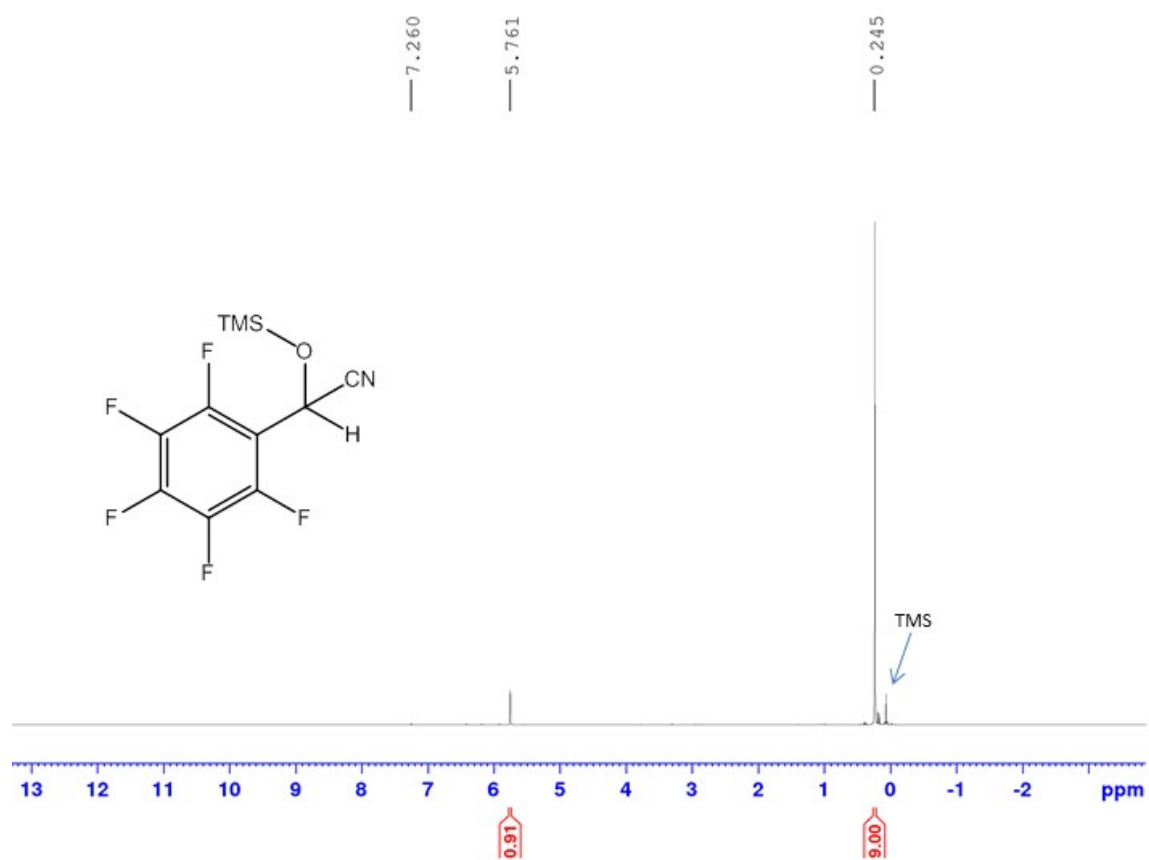
<sup>1</sup>H NMR spectrum of the cyanosilylated product of 4-cyanobenzaldehyde:



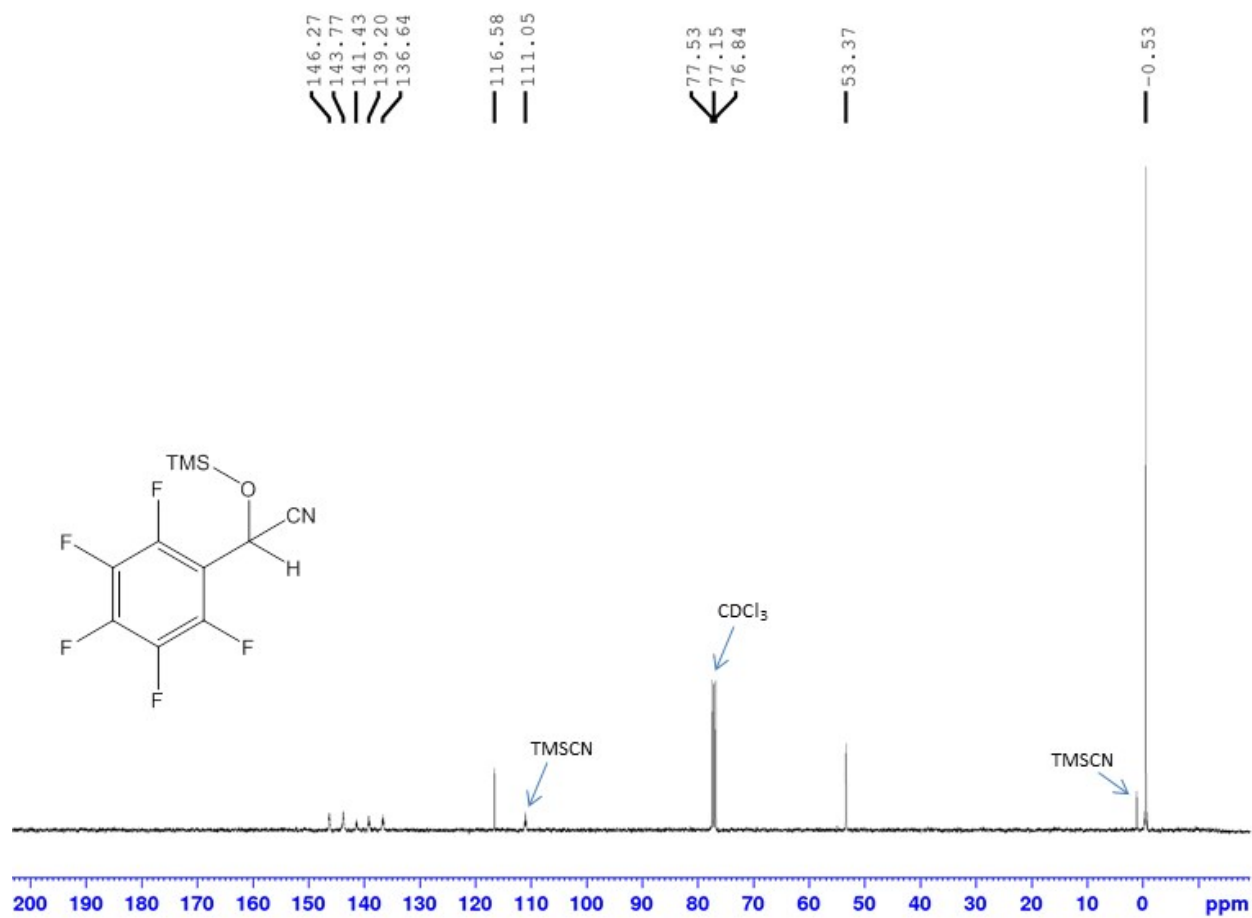
<sup>13</sup>C NMR spectrum of the cyanosilylated product of 4-cyanobenzaldehyde:



$^1\text{H}$  NMR spectrum of the cyanosilylated product of pentafluorobenzaldehyde:

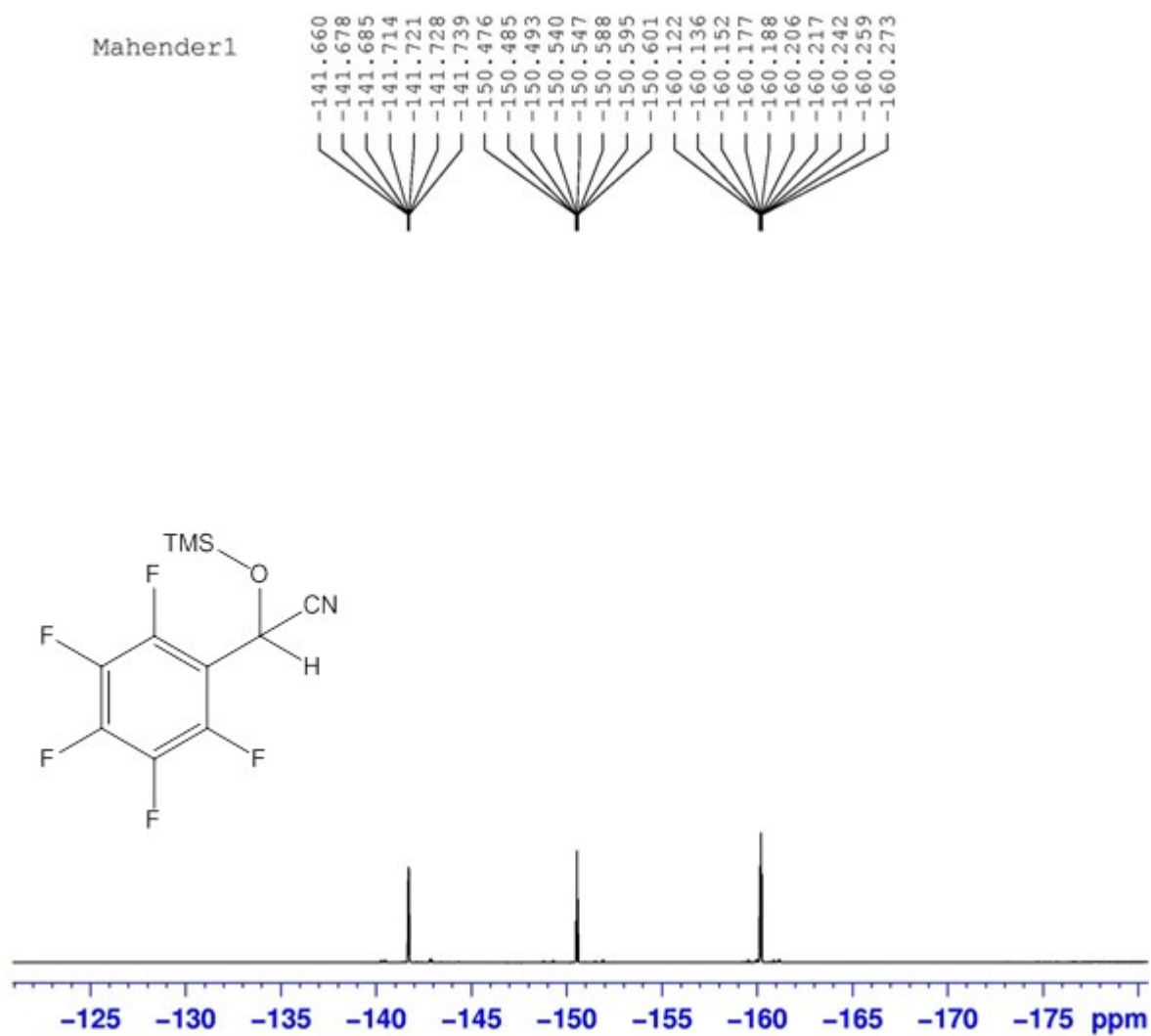


$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of pentafluorobenzaldehyde:

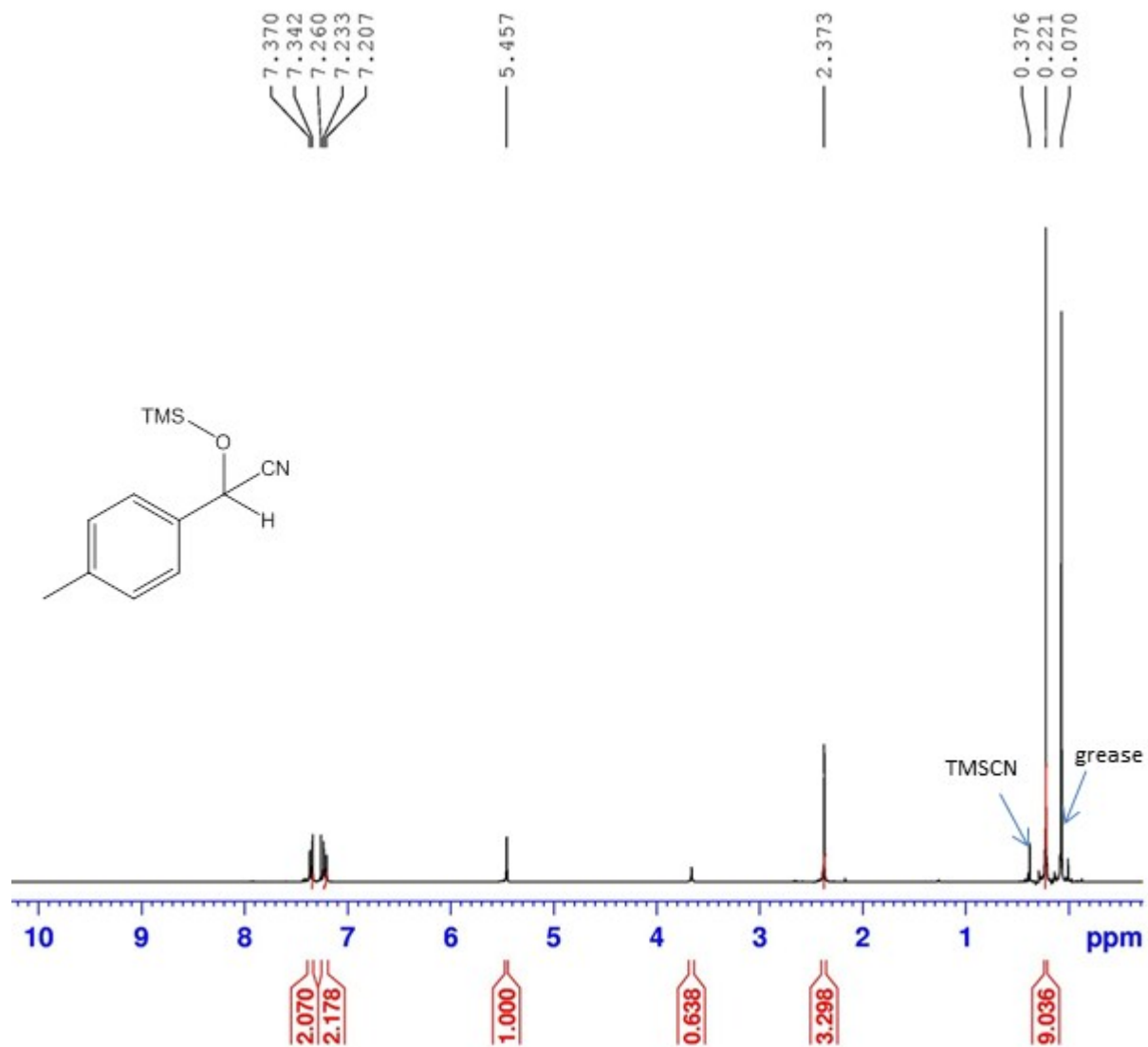




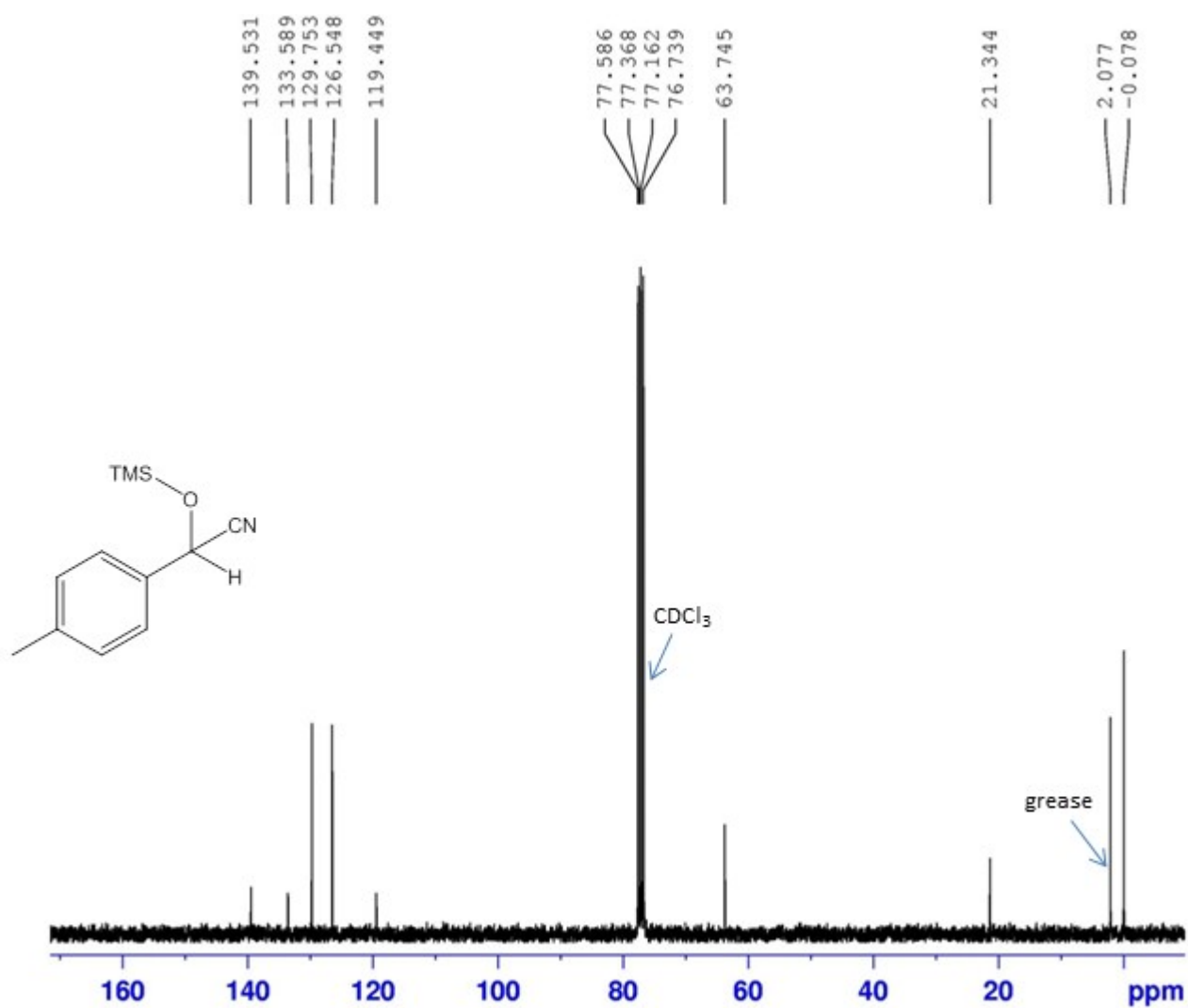
<sup>19</sup>F NMR spectrum of the cyanosilylated product of pentafluorobenzaldehyde:



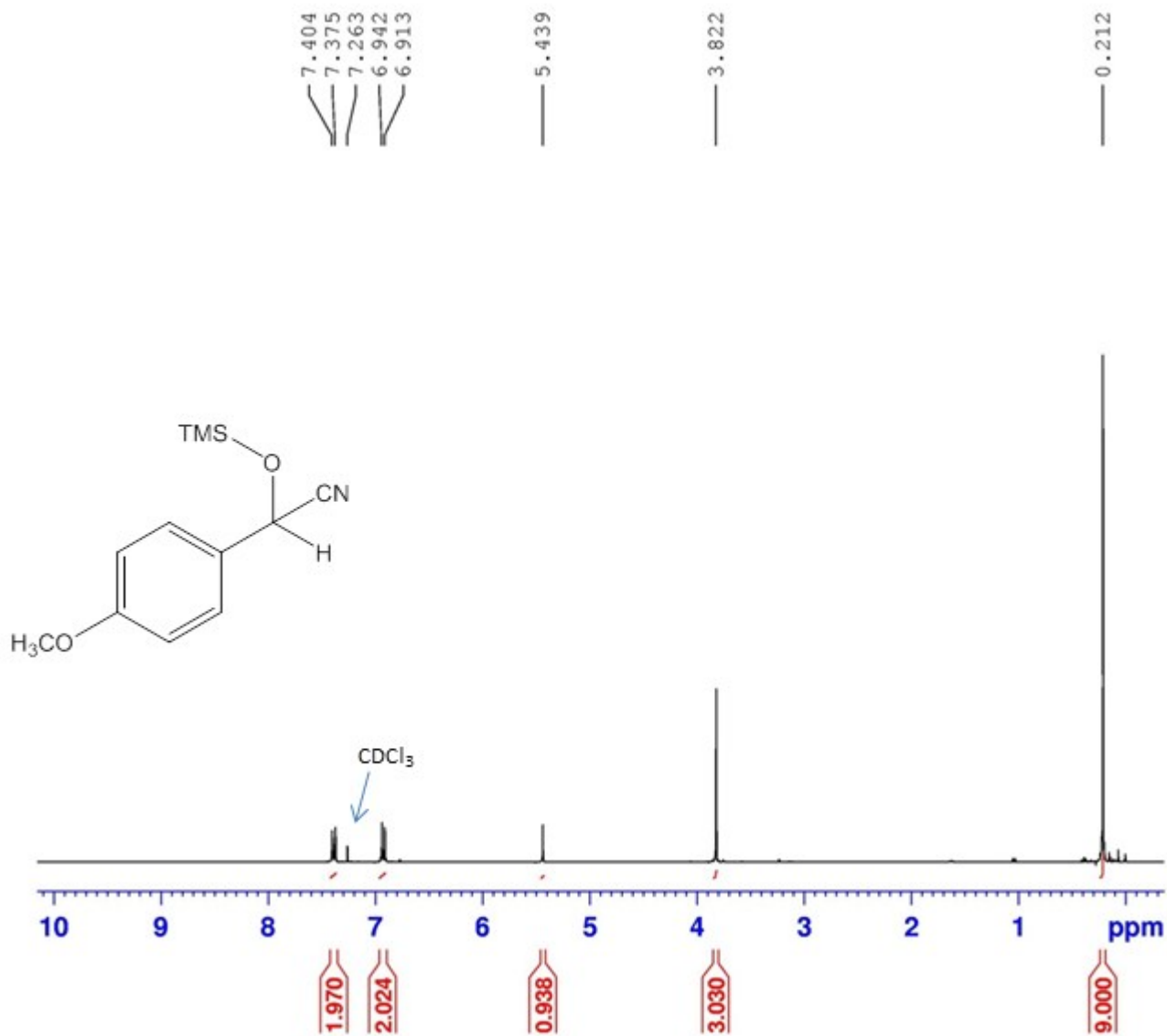
<sup>1</sup>H NMR spectrum of the cyanosilylated product of 4-methylbenzaldehyde:



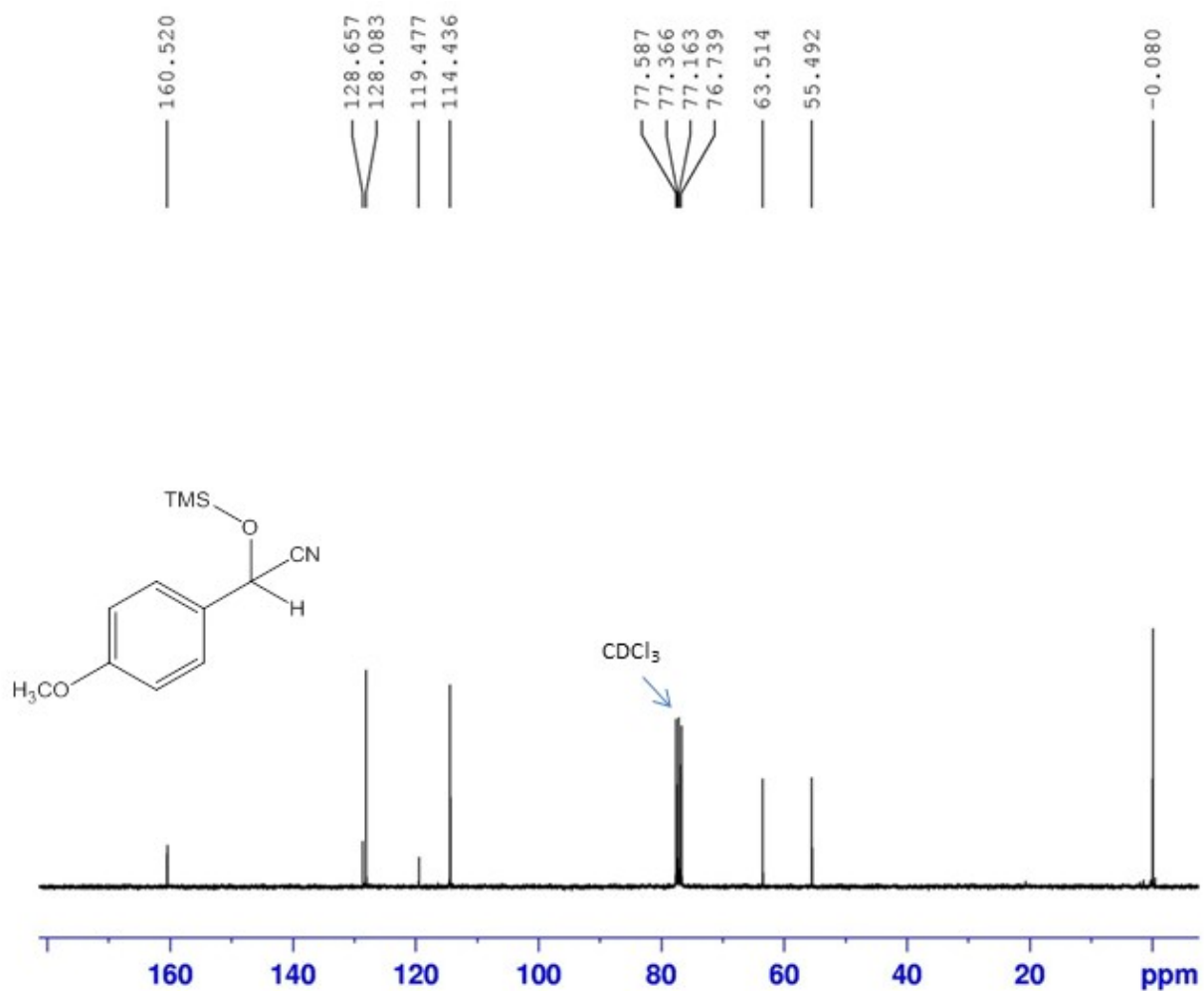
$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of 4-methylbenzaldehyde:



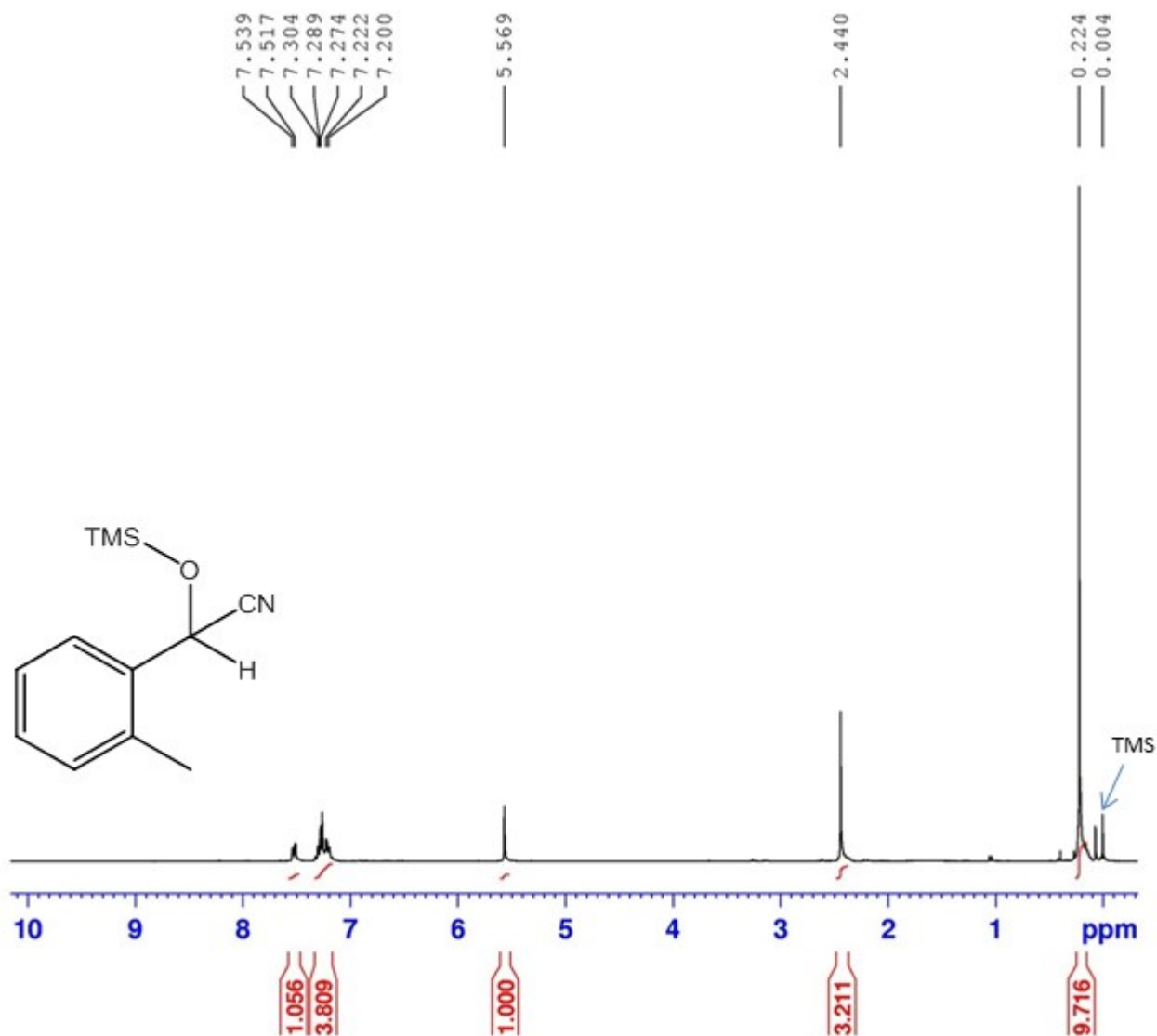
<sup>1</sup>H NMR spectrum of the cyanosilylated product of 4-methoxybenzaldehyde:



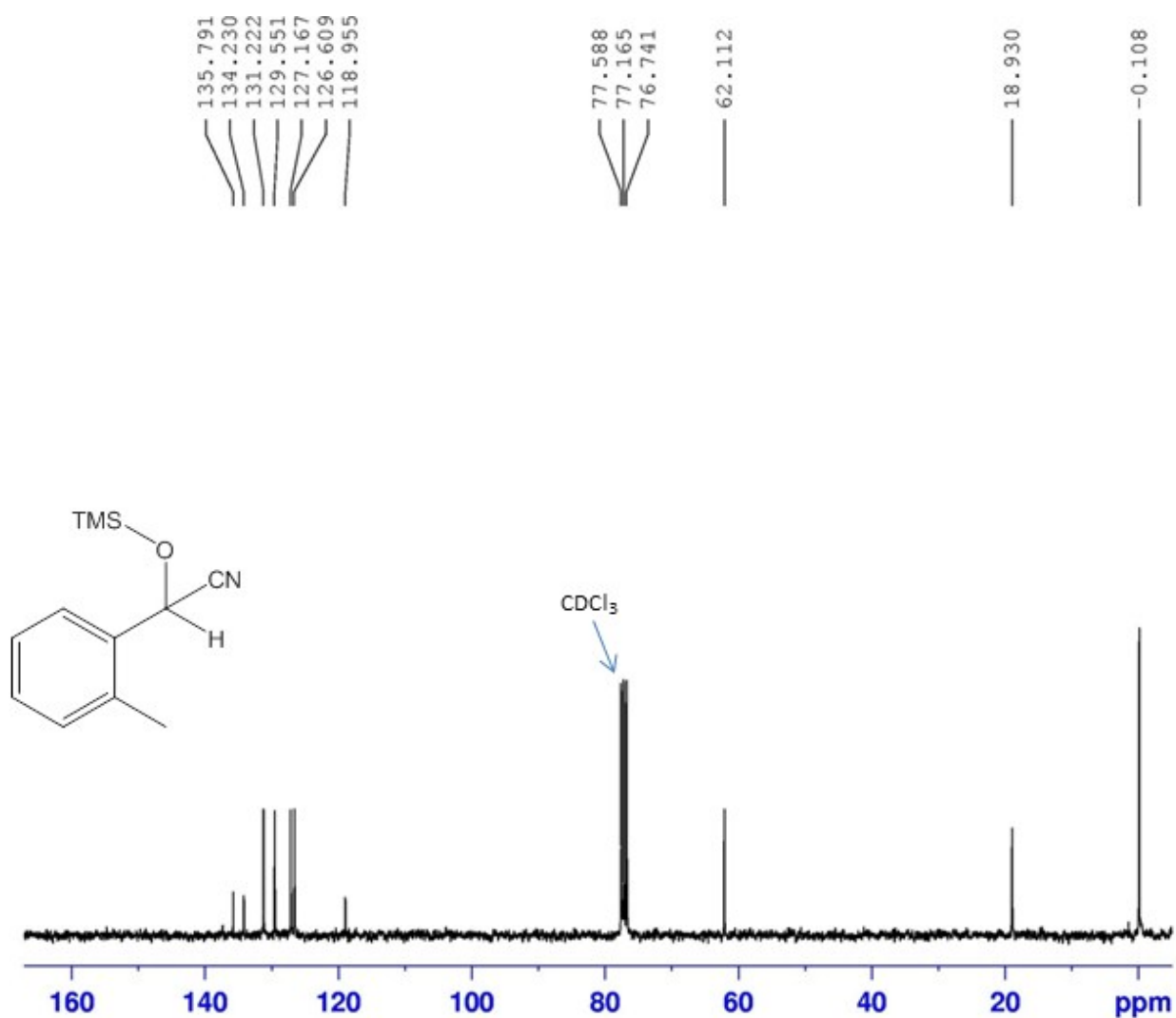
<sup>13</sup>C NMR spectrum of the cyanosilylated product of 4-methoxybenzaldehyde:



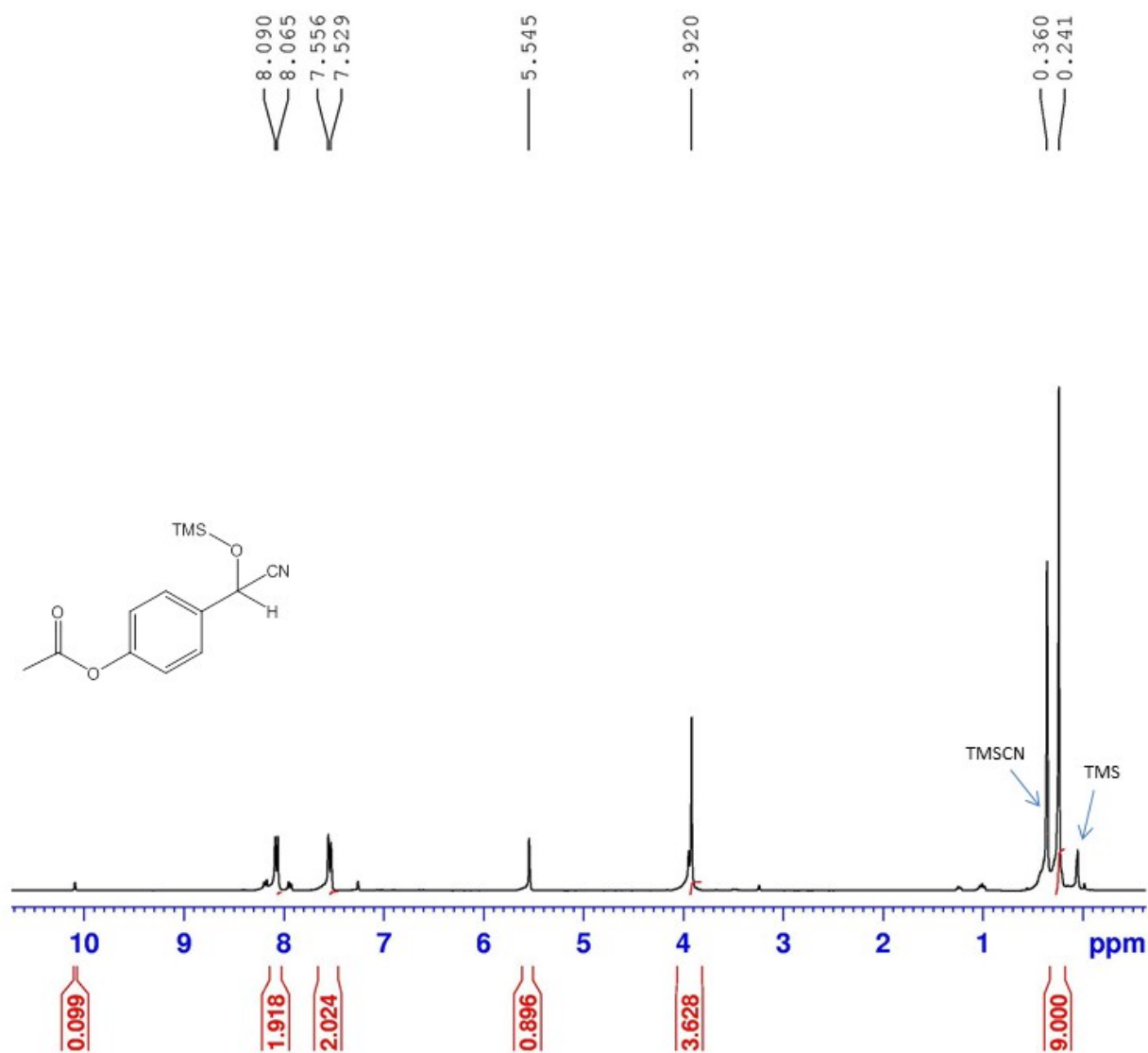
<sup>1</sup>H NMR spectrum of the cyanosilylated product of 2-methylbenzaldehyde:



<sup>13</sup>C NMR spectrum of the cyanosilylated product of 2-methylbenzaldehyde:

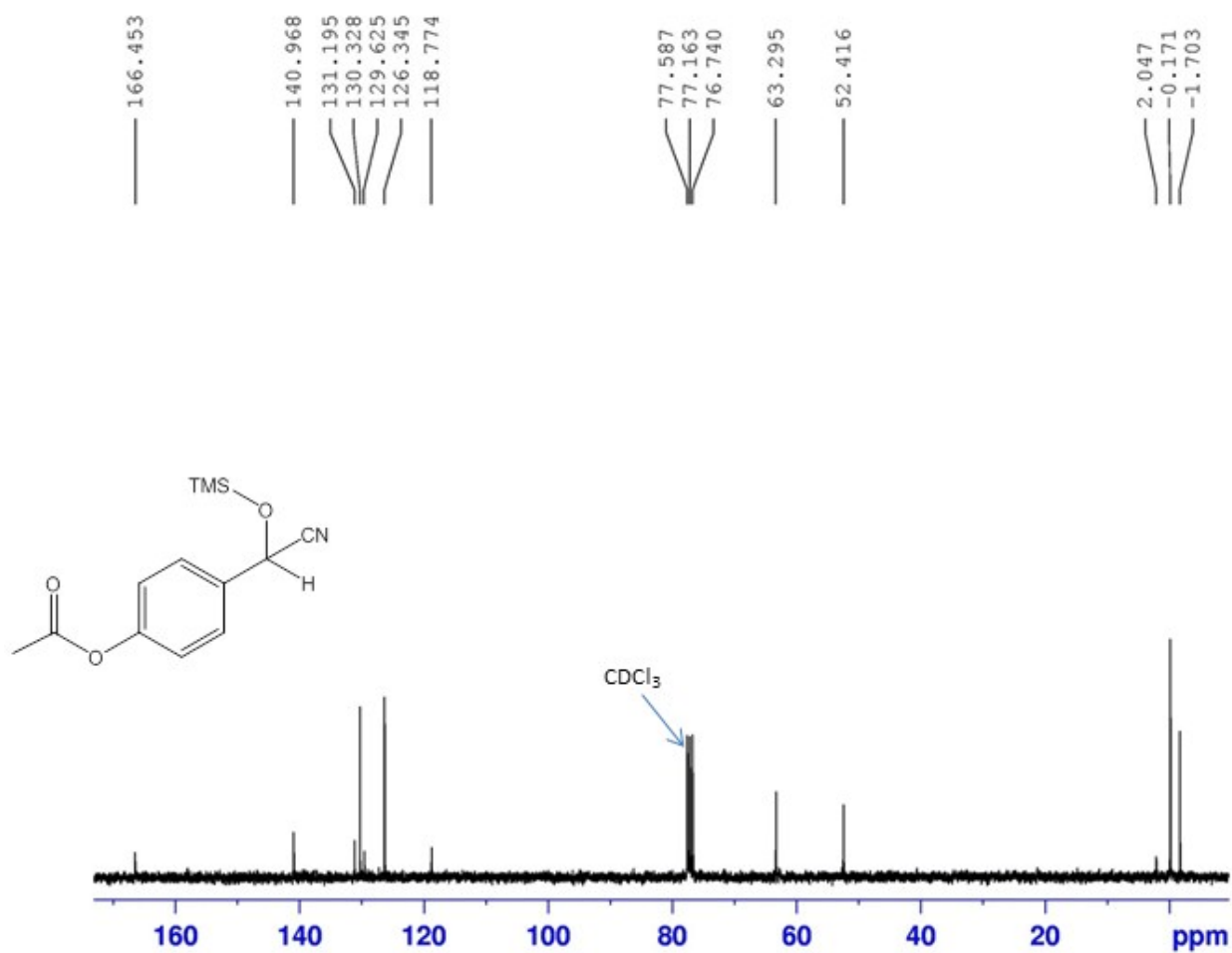


$^1\text{H}$  NMR spectrum of the **crude** cyanosilylated product of methyl 4-formylbenzoate:

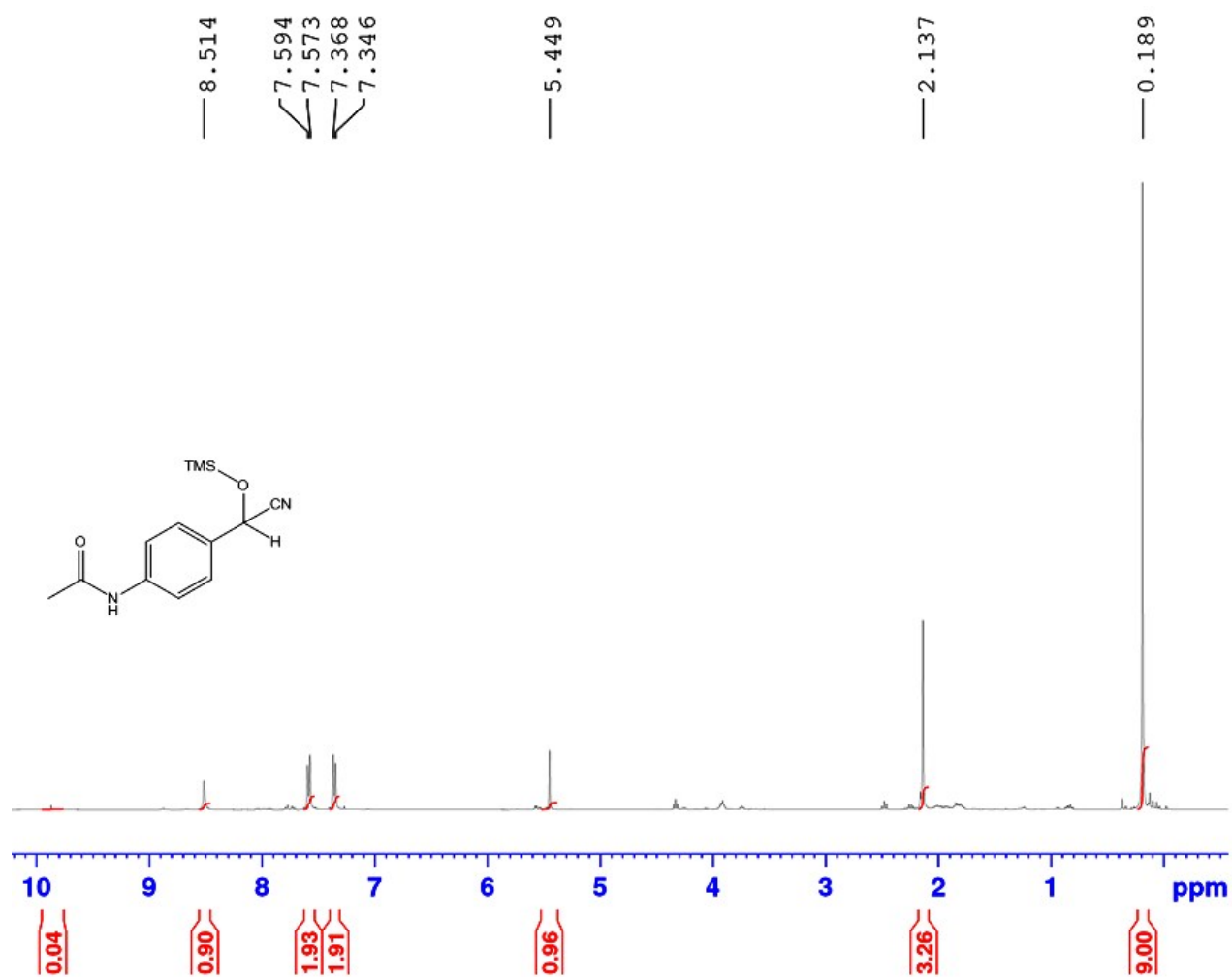




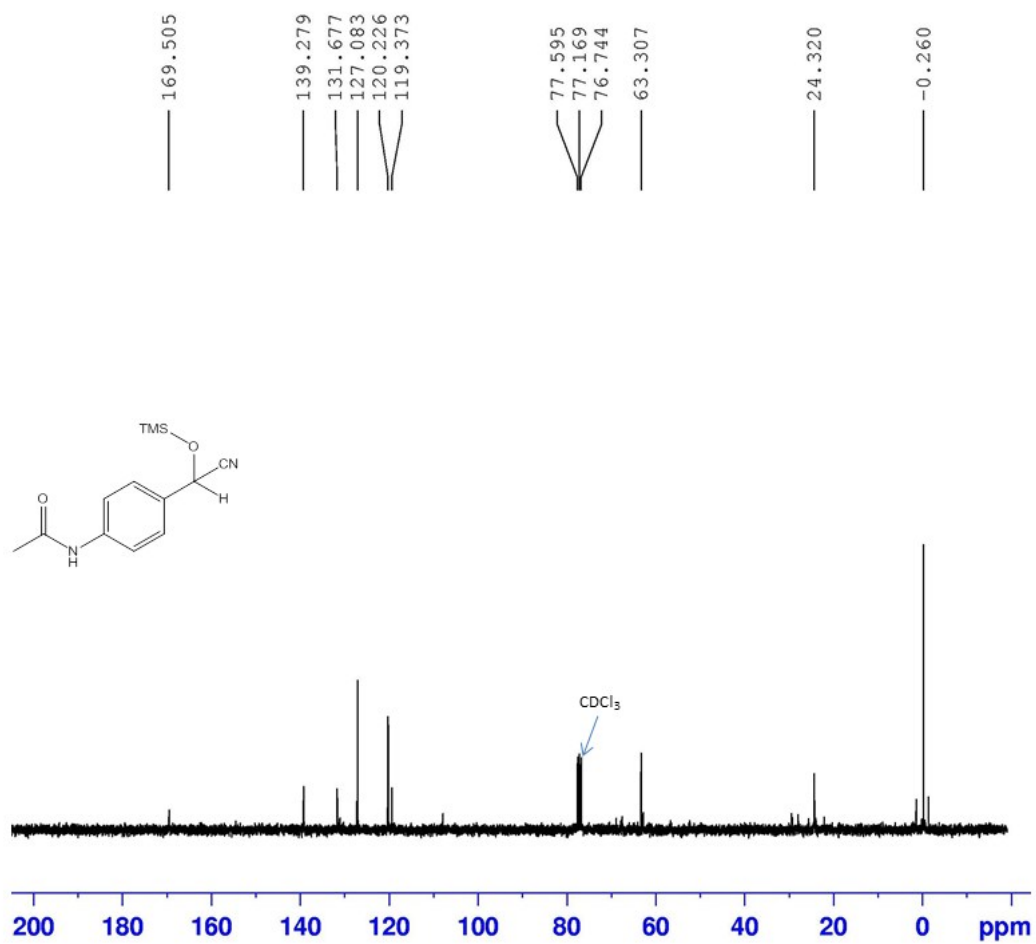
<sup>13</sup>C NMR spectrum of the crude cyanosilylated product of methyl 4-formylbenzoate:



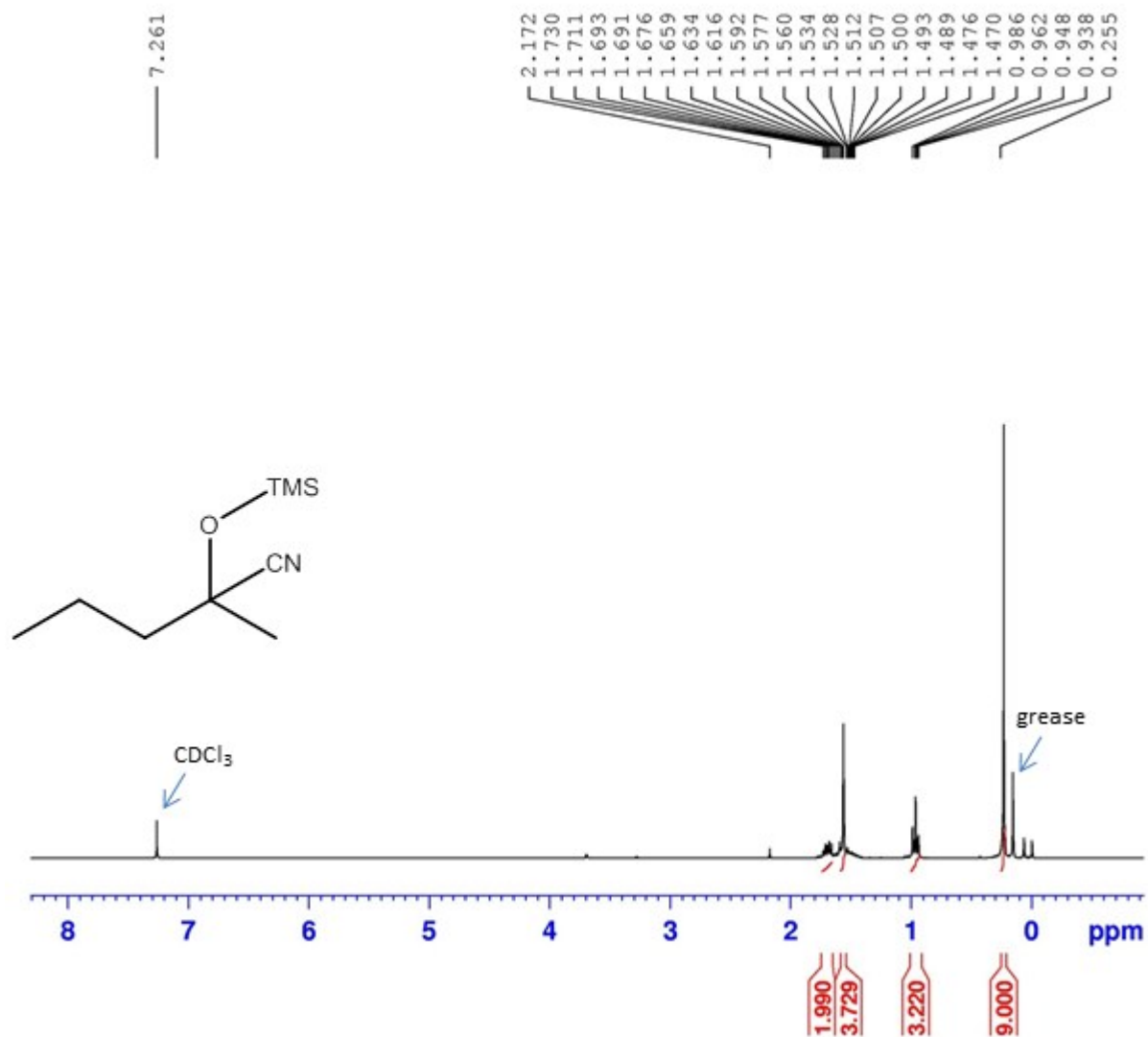
<sup>1</sup>H NMR spectrum of the **crude** cyanosilylated product of 4-acetamidobenzaldehyde<sup>S6</sup>:



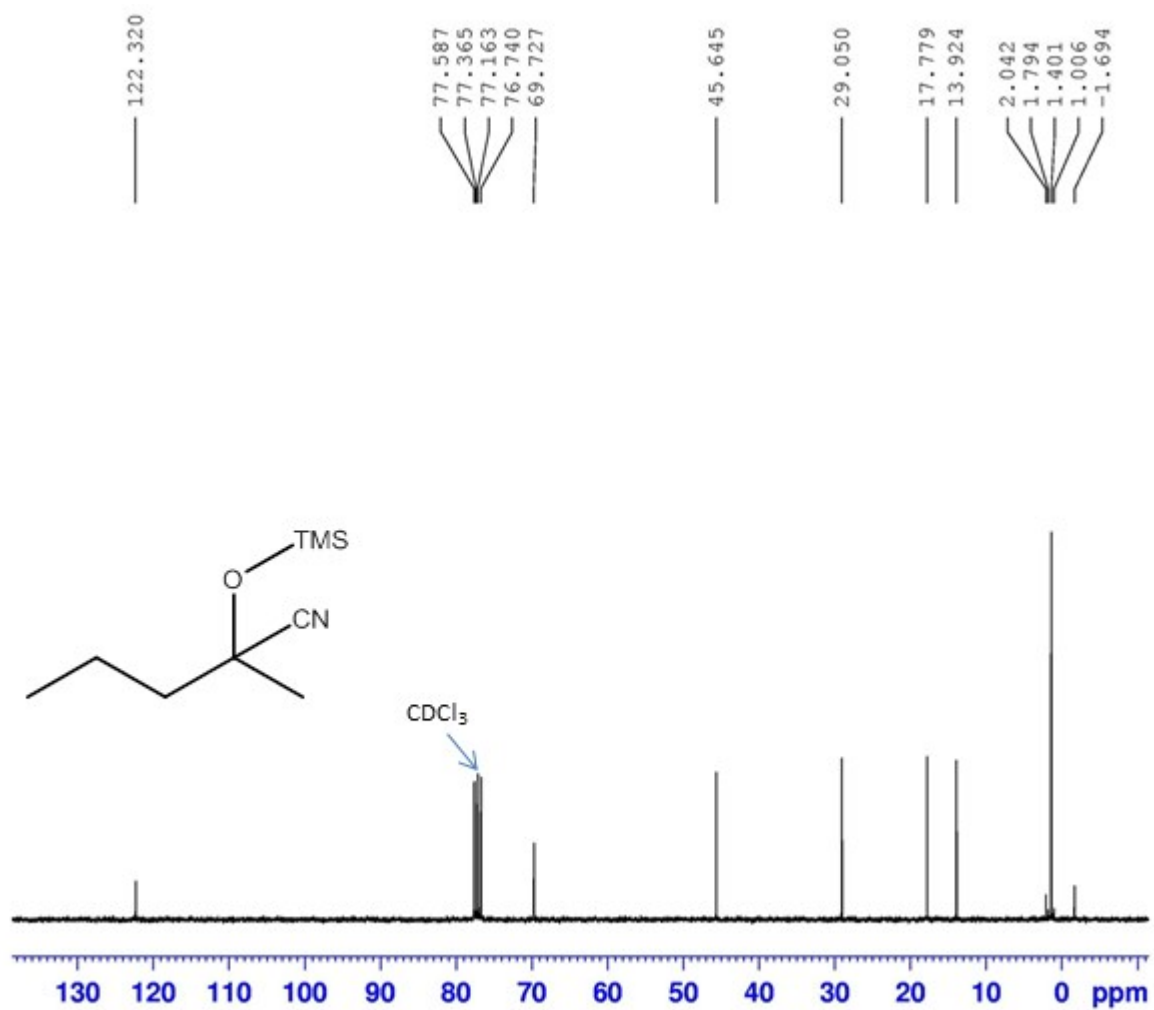
$^{13}\text{C}$  NMR spectrum of the **crude** cyanosilylated product of 4-acetamidobenzaldehyde<sup>S6</sup>:



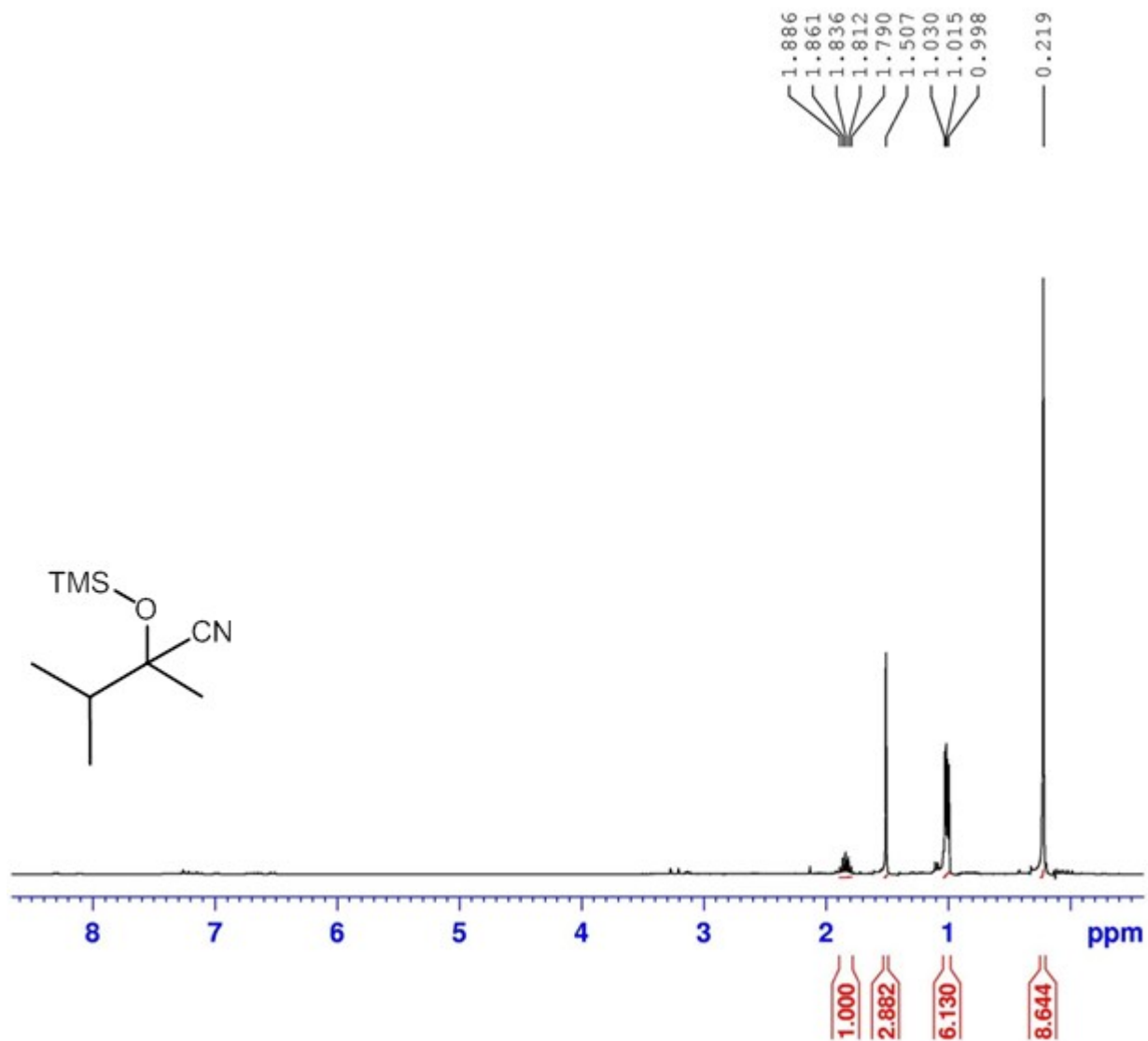
$^1\text{H}$  NMR spectrum of the cyanosilylated product of 2-pentanone:



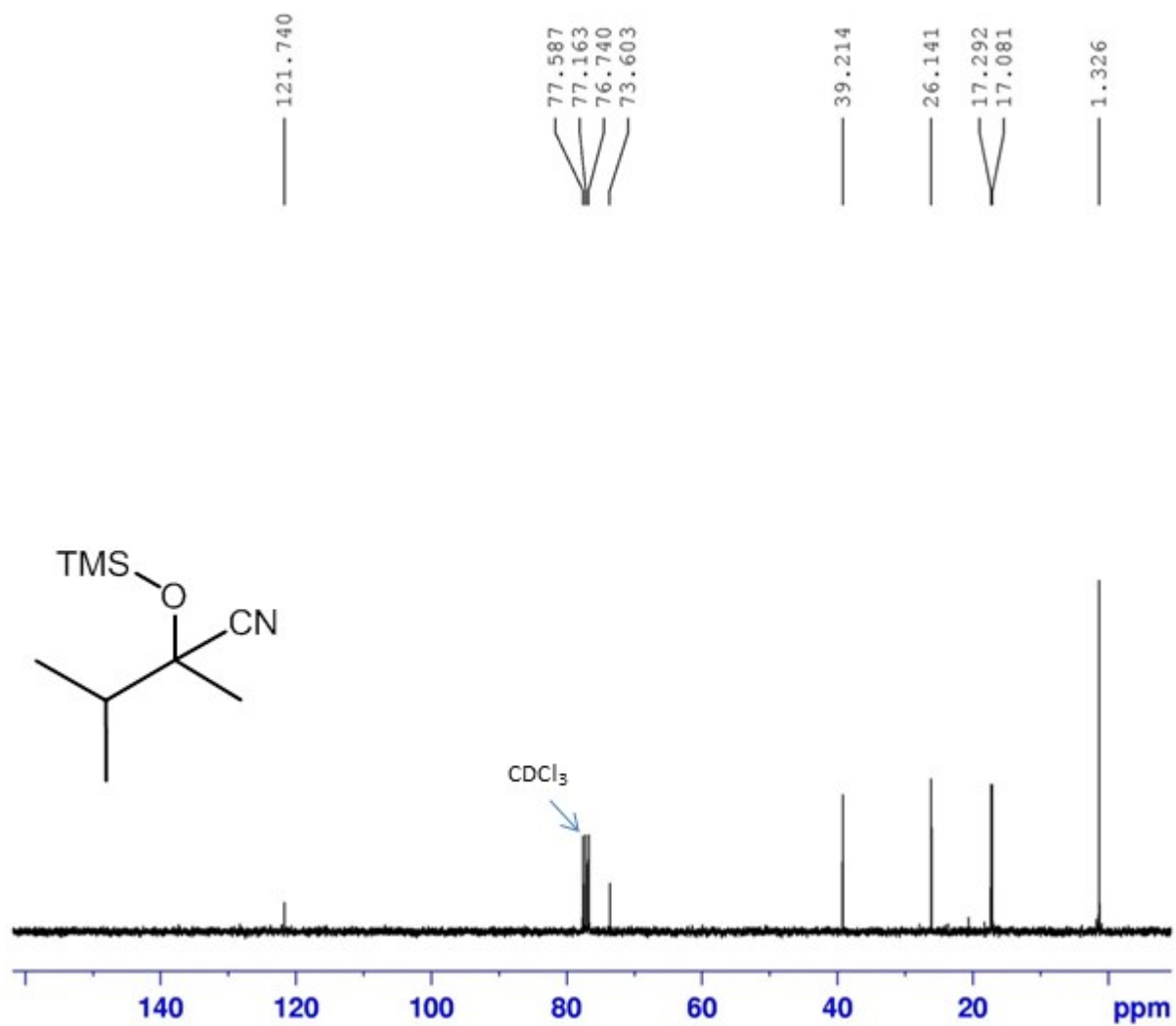
<sup>13</sup>C NMR spectrum of the cyanosilylated product of 2-pentanone:



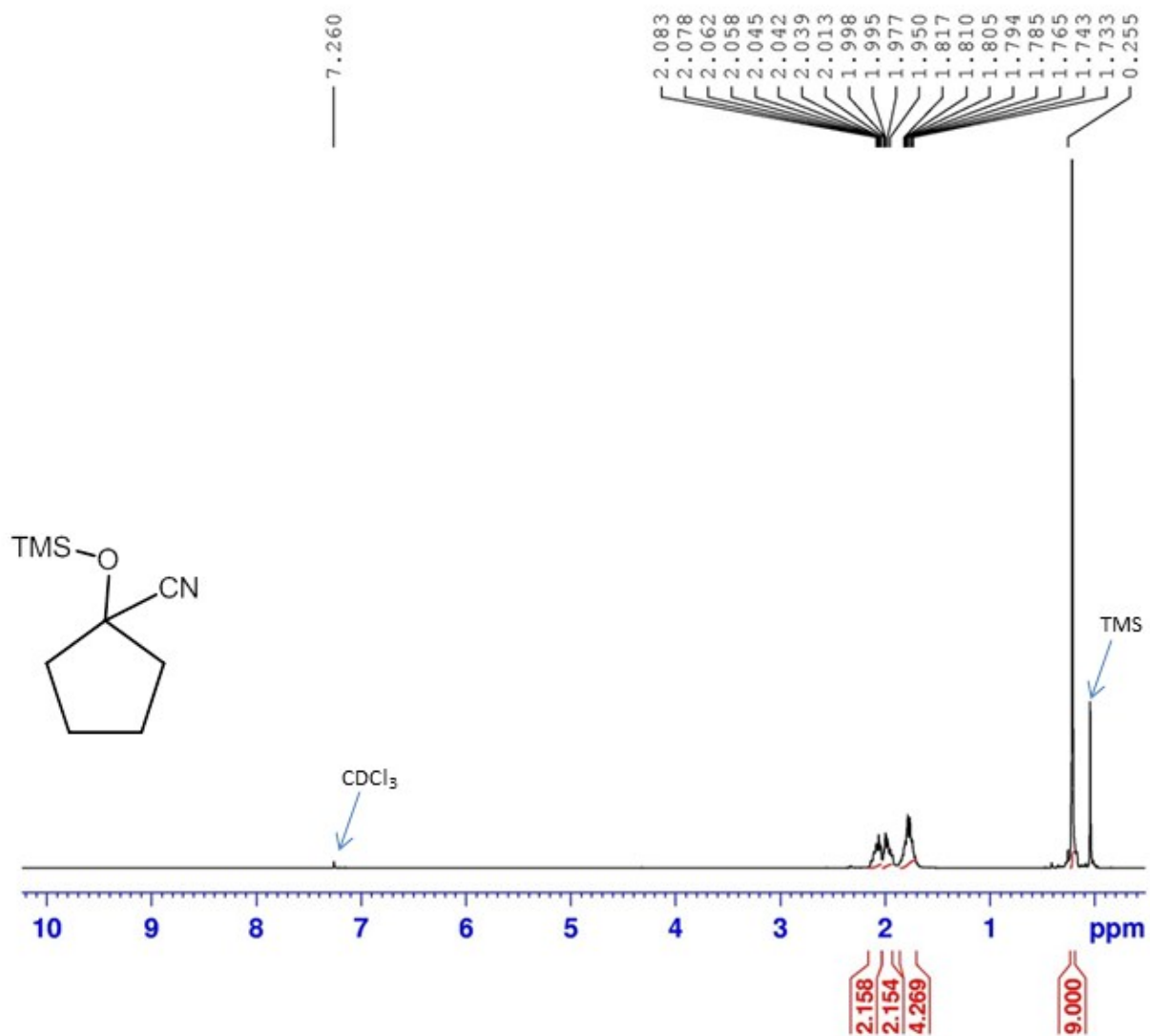
<sup>1</sup>H NMR spectrum of the cyanosilylated product of methylisopropylketone:



$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of methylisopropylketone:

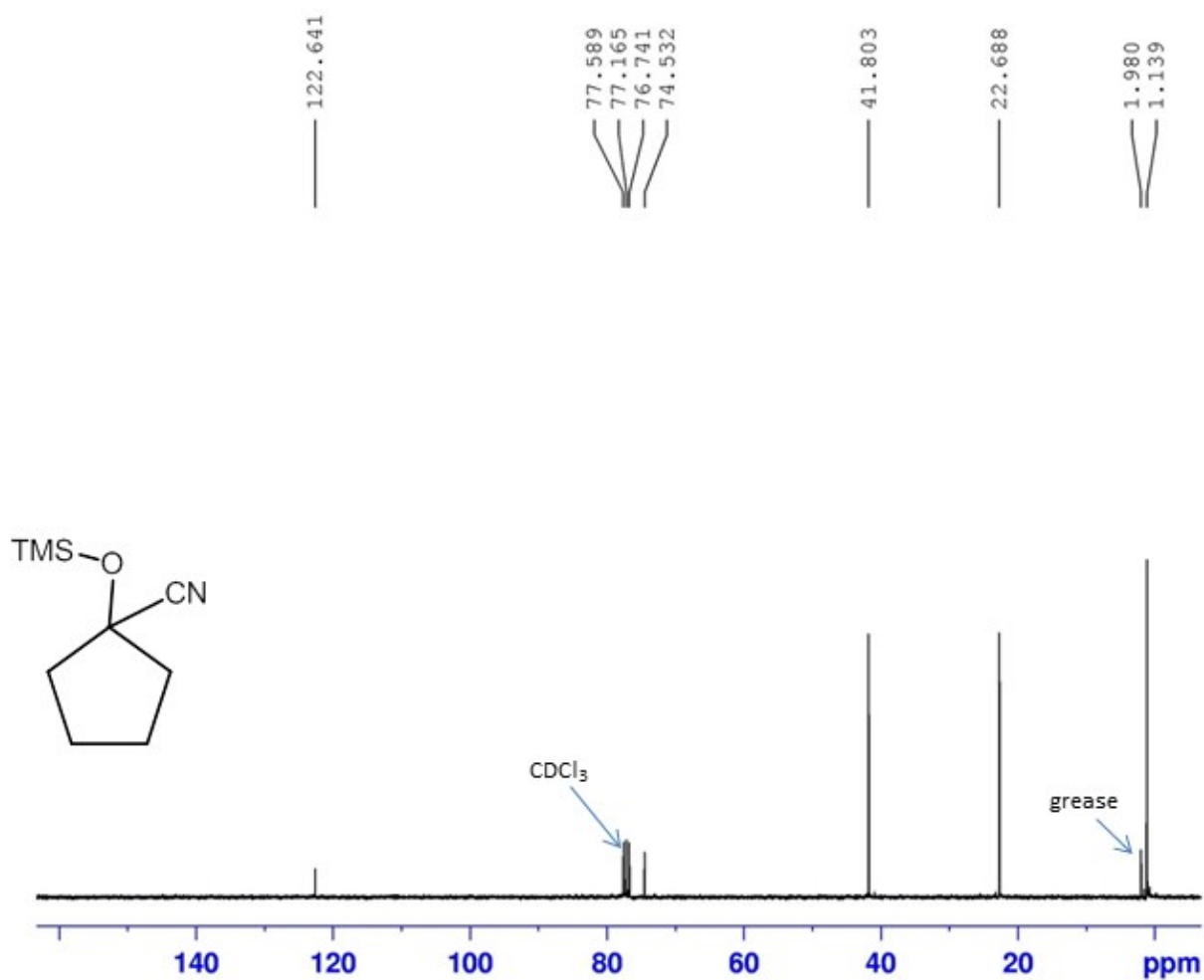


<sup>1</sup>H NMR spectrum of the cyanosilylated product of cyclopentanone:

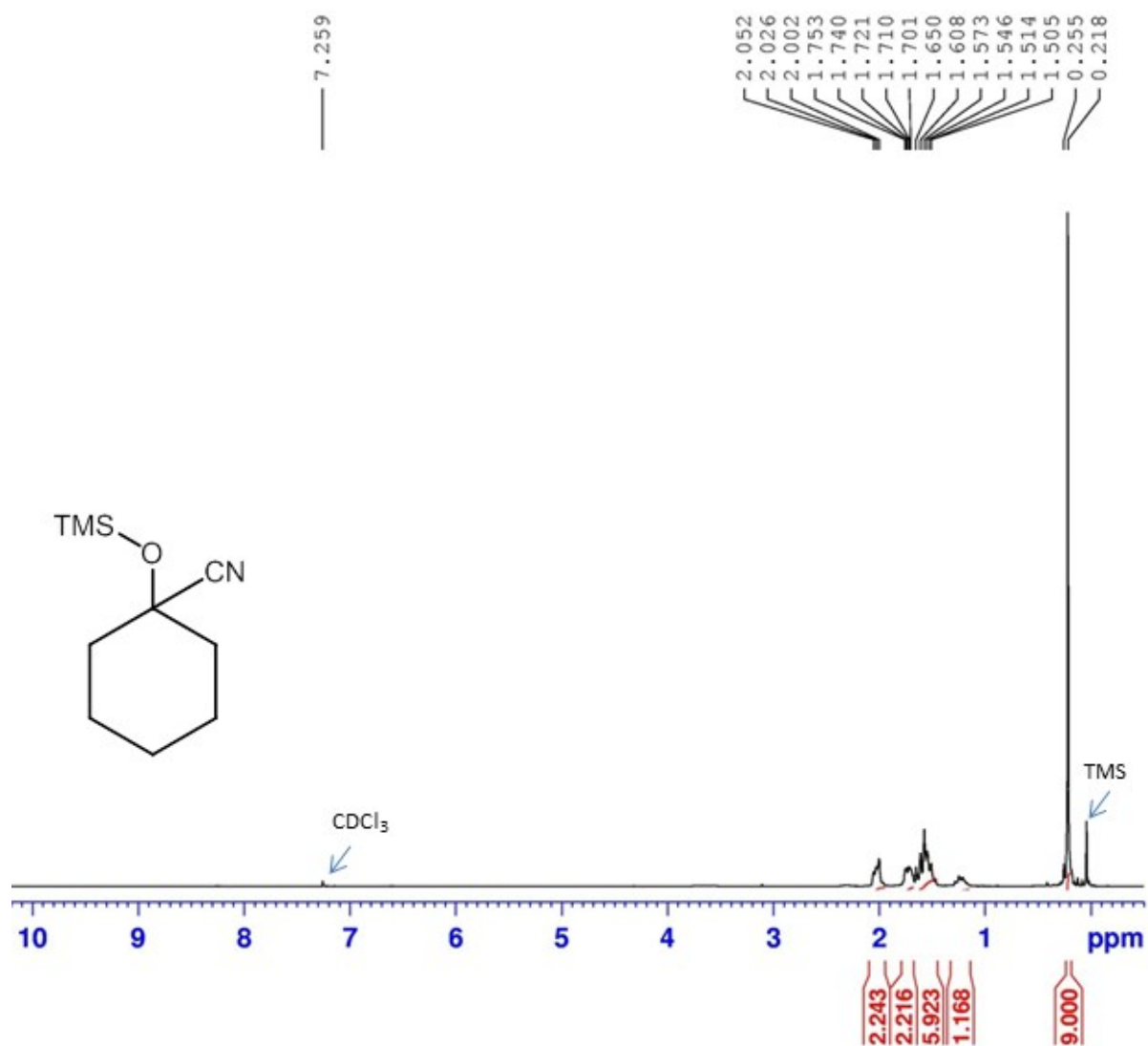




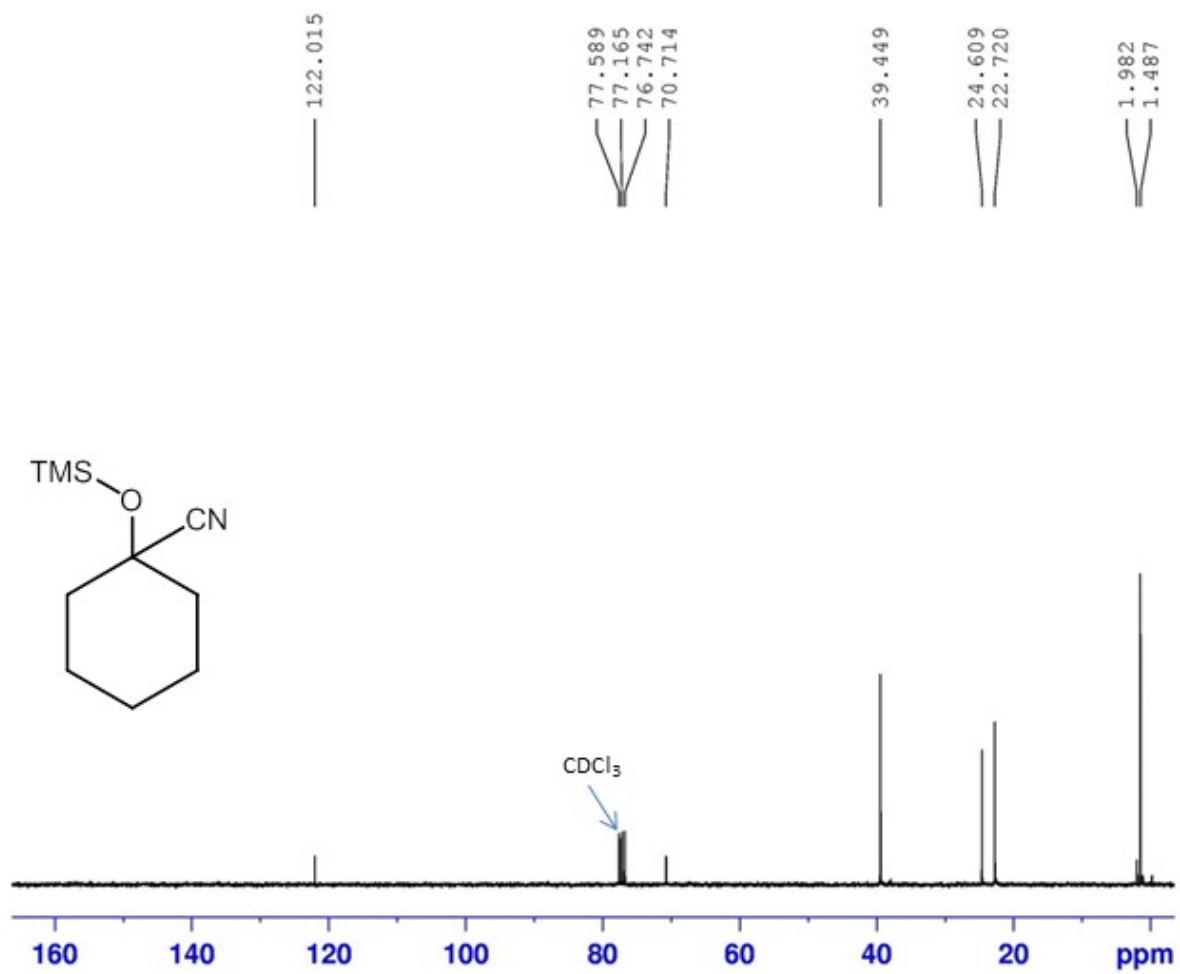
$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of cyclopentanone:



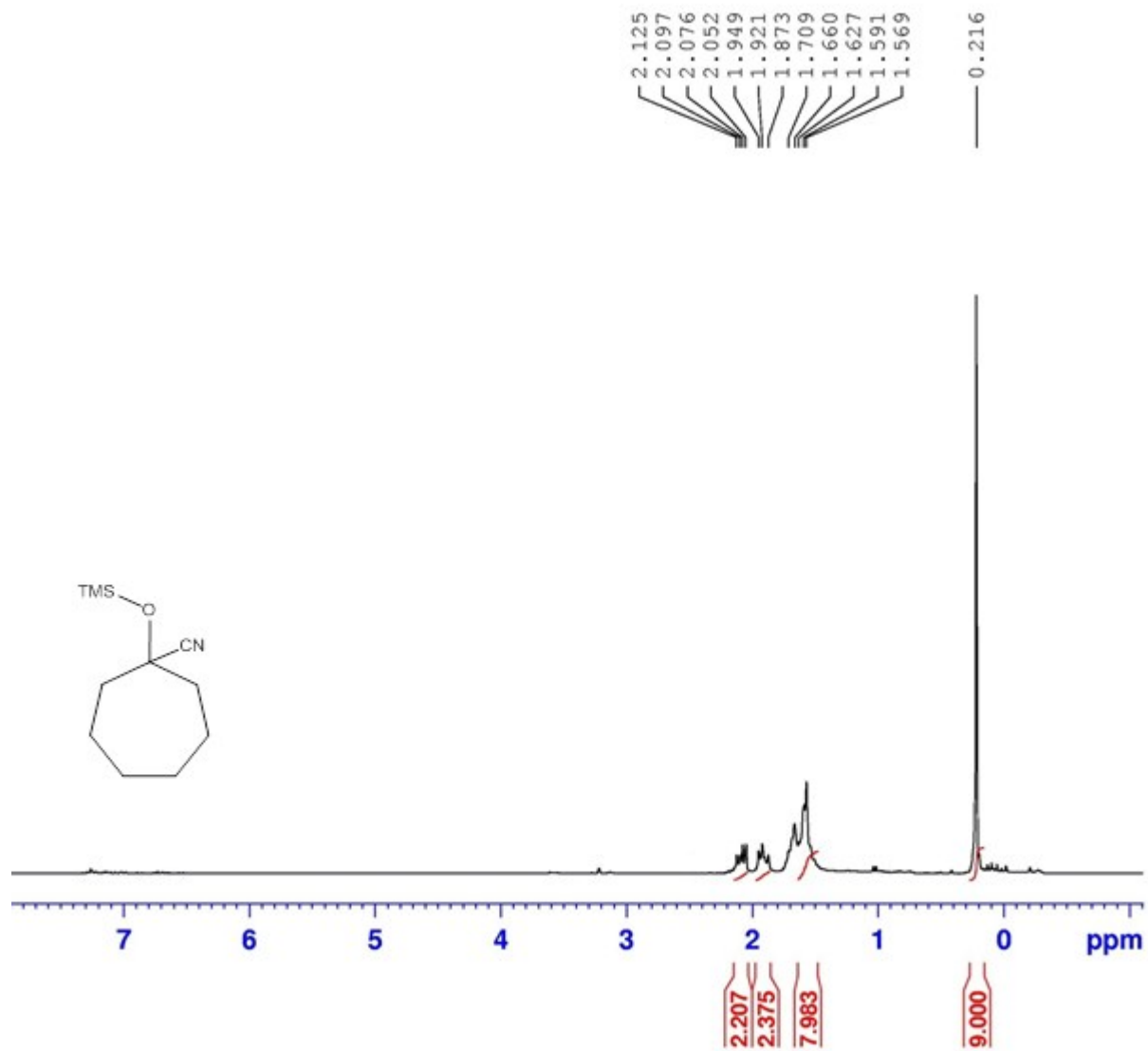
<sup>1</sup>H NMR spectrum of the cyanosilylated product of cyclohexanone:



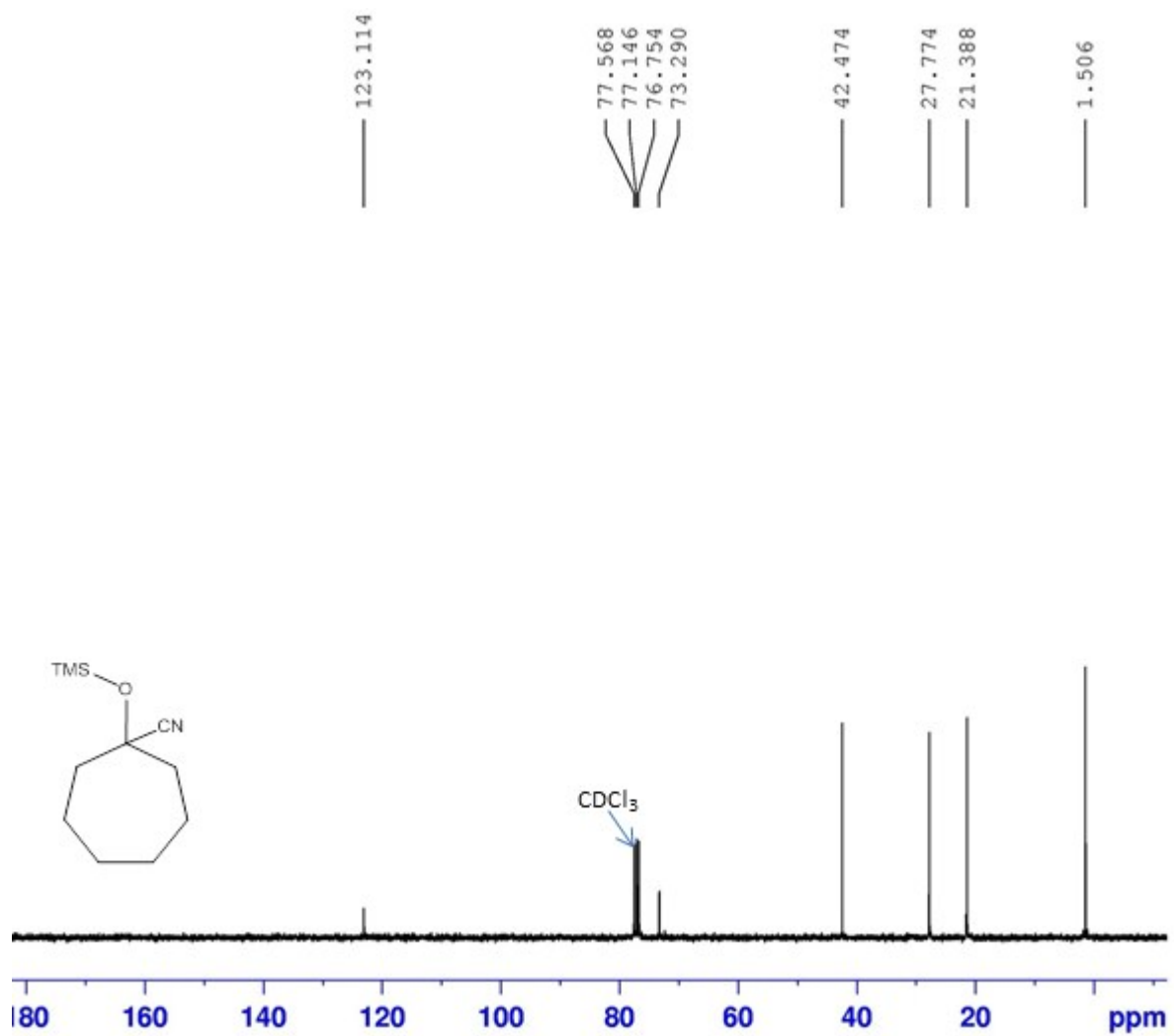
$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of cyclohexanone:



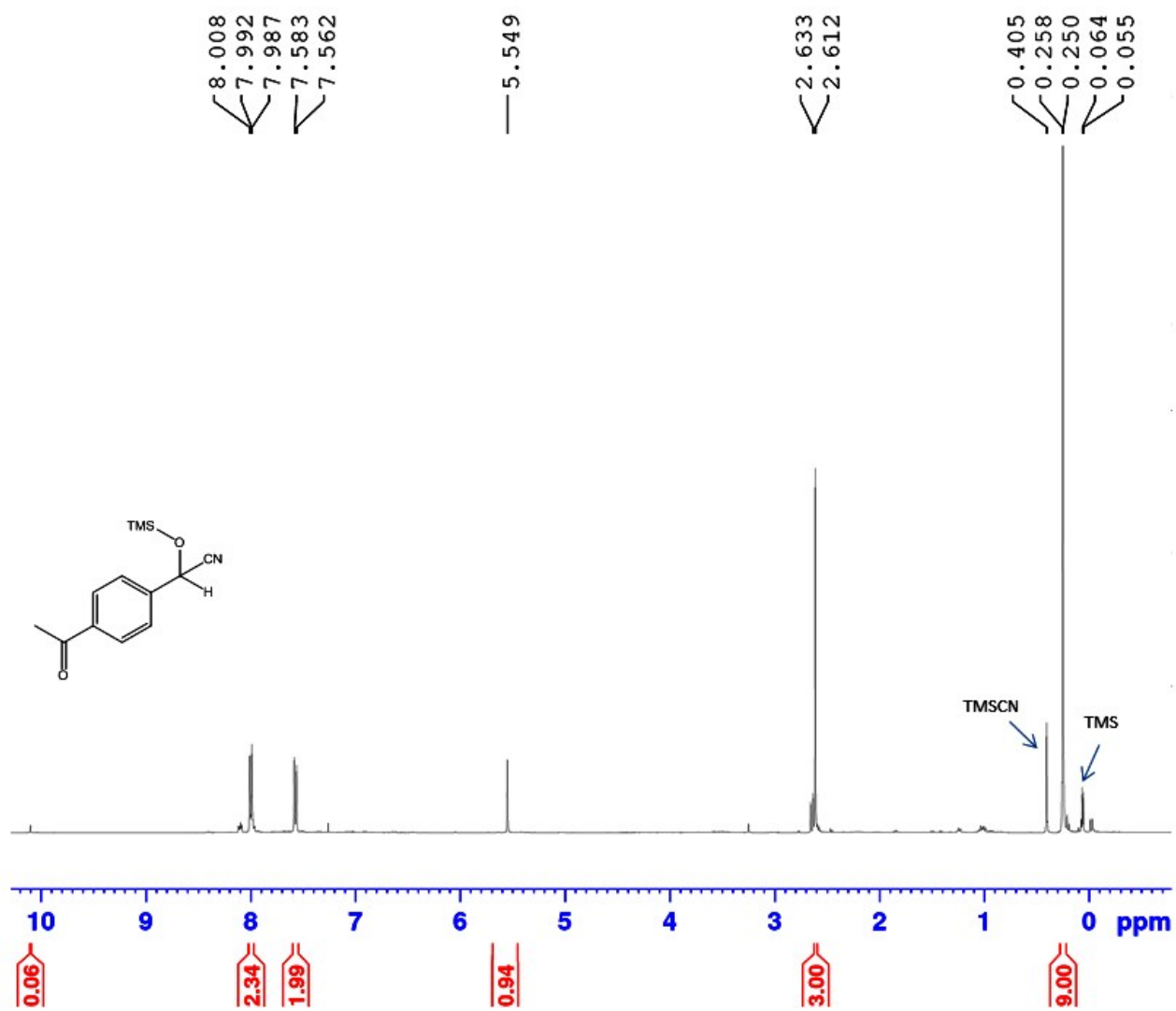
$^1\text{H}$  NMR spectrum of the cyanosilylated product of cycloheptanone:



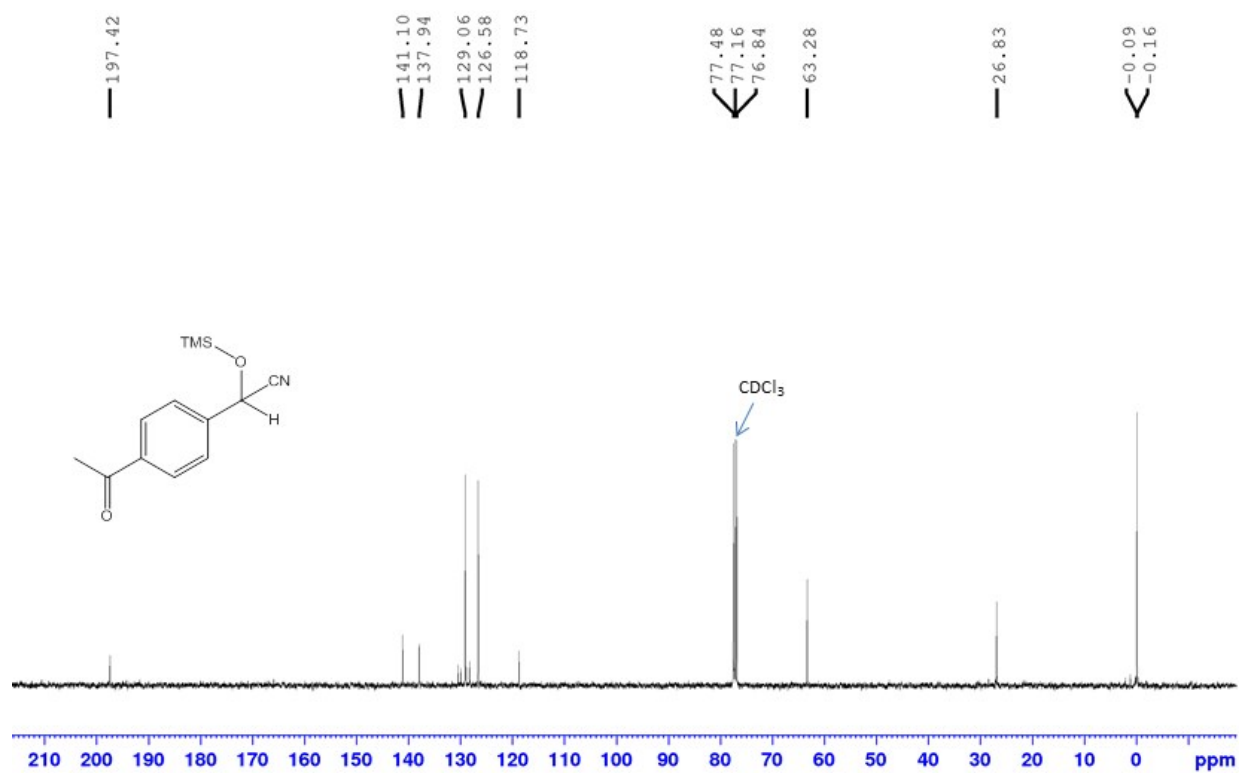
$^{13}\text{C}$  NMR spectrum of the cyanosilylated product of cycloheptanone:

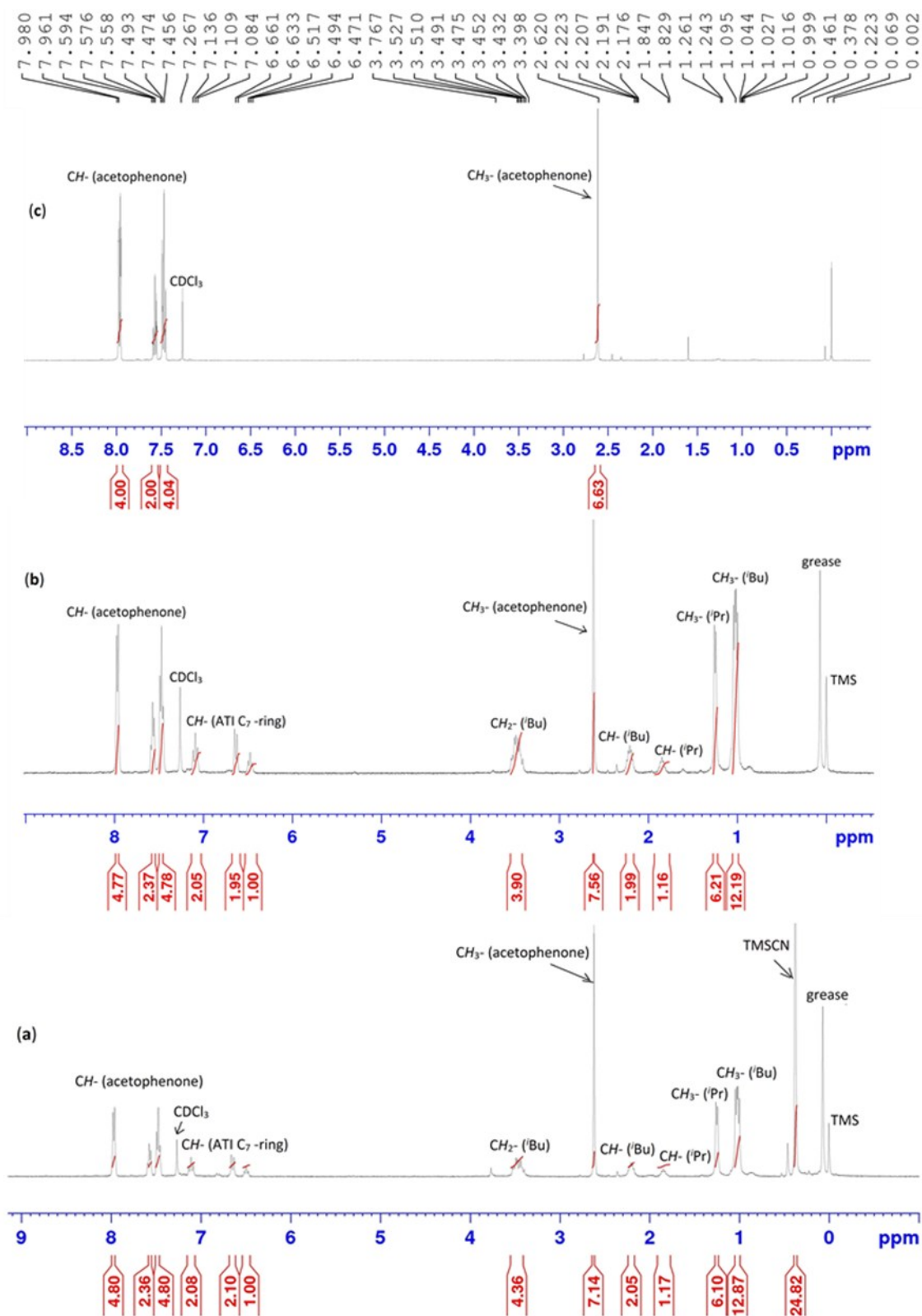


<sup>1</sup>H NMR spectrum of the **crude** cyanosilylated product of 4-acetylbenzaldehyde:



$^{13}\text{C}$  NMR spectrum of the **crude** cyanosilylated product of 4-acetylbenzaldehyde:





**Figure S7.** (a)  $^1\text{H}$  NMR spectrum of the crude reaction mixture from the reaction of one equiv of acetophenone and 1.2 equiv of TMS-CN with 25 mol% of compound **3**, (b)  $^1\text{H}$  NMR spectrum of the crude reaction mixture from the reaction of one equiv of acetophenone with 25 mol% of compound **3**, and (c)  $^1\text{H}$  NMR spectrum of acetophenone in dry  $\text{CDCl}_3$ .



## References:

- S1. S. Sinhababu, D. Yadav, S. Karwasara, M. K. Sharma, G. Mukherjee, G. Rajaraman and S. Nagendran, *Angew. Chem. Int. Ed.*, 2016, **55**, 7742.
- S2. SMART: Bruker Molecular Analysis Research Tool, Version 5.618; Bruker AXS: Madison, WI, 2000.
- S3. SAINT-NT, Version 6.04; Bruker AXS: Madison, WI, 2001.
- S4. SHELXTL-NT, Version 6.10; Bruker AXS: Madison, WI, 2000.
- S5. (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program, *J. Appl. Crystallogr.* 2009, **42**, 339. (b) G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3-8.
- S6. This reaction did not give the anticipated product cleanly in  $\text{CDCl}_3$  and  $\text{CH}_2\text{Cl}_2$ .