

## Supporting Information

### **Contents**

Optimization of Catalytic Reaction Conditions

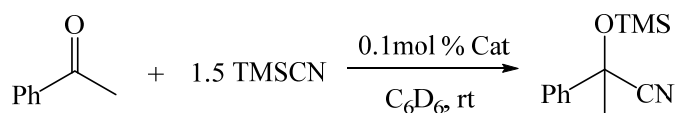
General Procedure for Catalytic Cyanosilylation of Ketones and Aldehydes

NMR Spectra of Cyanosilylation Products

All air-sensitive compounds were carried out using standard Schlenk-line or glove box techniques under high-purity argon.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra were recorded at 25 °C on Bruker Avance III 600 MHz spectrometer in deuterated solvents and were referenced to the resonances of the solvent used.  $\text{C}_6\text{D}_6$  was dried over sodium mirror and freeze-thawed twice prior to use. Complexes **1-3** were prepared according to the literature procedure. Aldehydes, ketones and  $\text{Me}_3\text{SiCN}$  were purchased from Sigma-Aldrich Ltd, Alfa-Aesar, and Acros and used without further purification.

### Optimization of Catalytic Reaction Conditions

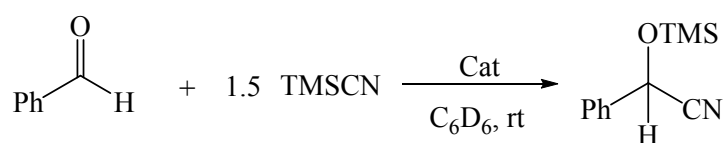
**Table S1** Optimization of ketones cyanosilylation



Entry	Cat	Time (h)	Yield (%) <sup>a</sup>
1	<b>1</b>	1	>99
2	<b>2</b>	1.2	>99
3	<b>3</b>	1.3	>99

<sup>a</sup> The reaction was monitored by  $^1\text{H}$  NMR spectroscopy.

**Table S2** Optimization of aldehydes cyanosilylation



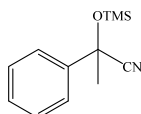
Entry	Cat	Catalyst loading (mol %)	Time (min)	Yield <sup>a</sup> (%)
1	<b>1</b>	0.1	<10	>99
2	<b>2</b>	0.1	< 15	>99
3	<b>3</b>	0.1	15	>99
4	<b>1</b>	0.05	30	>99

<sup>a</sup> The reaction was monitored by  $^1\text{H}$  NMR spectroscopy.

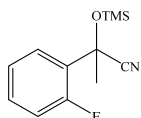
## General Procedure for Catalytic Cyanosilylation of Aldehydes or Ketones

In a glove box, catalyst **1** (0.1 mol%) was added to a solution of aldehyde (1 mmol) and TMSCN (1.5 mmol) at room temperature or catalyst **1** was added to a solution of ketones (1 mmol) and TMSCN (1.5 mmol) at room temperature or 60°C in a J. Young NMR tube equipped with a Teflon screw cap, which was charged with C<sub>6</sub>D<sub>6</sub> (0.5 mL). The progress of the reaction was monitored by <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>29</sup>Si NMR.

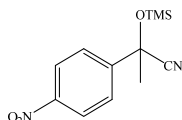
## Spectroscopic data for Ketone or Aldehyde Cyanosilylation Products



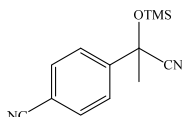
<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.48–7.46 (m, 2H, Ar-*H*), 7.07–7.01 (m, 3H, Ar-*H*), 1.56 (s, 3H, *CMe*), 0.12 (s, 9H, OSiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 142.6, 128.9, 128.8, 124.9 (Ar-*C*), 121.8 (CN), 72.0 (*CMe*), 33.5 (*CMe*), 1.1 (OSiMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>): δ 19.8.



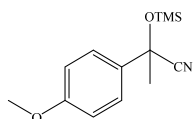
<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.53–7.52 (m, 1H, Ar-*H*), 6.85–6.69 (m, 3H, Ar-*H*), 1.71 (s, 3H, *CMe*), 0.17 (s, 9H, OSiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 160.7, 159.1, 130.9, 127.0, 124.4, 120.9 (Ar-*C*), 116.8 (CN), 69.1 (*CMe*), 30.8 (*CMe*), 1.1 (OSiMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>): δ 20.2.



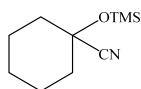
<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.14 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H, Ar-*H*), 6.98 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H, Ar-*H*), 1.36 (s, 3H, *CMe*), 0.08 (s, 9H, OSiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 146.8, 132.5, 125.4, 120.9, 118.2 (Ar-*C*), 113.2 (CN), 71.2 (*CMe*), 33.0 (*CMe*), 1.0 (OSiMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>): δ 21.2.



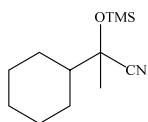
<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.74–7.73 (m, 2H, Ar-*H*), 7.20–7.19 (m, 2H, Ar-*H*), 1.40 (s, 3H, *CMe*), 0.11 (s, 9H, OSiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 148.6, 129.1, 125.9, 125.6, 124.0, 123.5 (Ar-*C*), 120.9, 94.4 (CN), 71.1 (*CMe*), 33.1 (*CMe*), 1.0 (OSiMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>): δ 21.2.



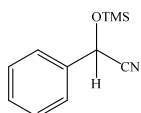
$^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.39 (d,  $^3J_{\text{HH}} = 8.4$  Hz, 2H, Ar-H), 6.67 (d,  $^3J_{\text{HH}} = 8.4$  Hz, 2H, Ar-H), 3.28 (s, 3H, OMe), 1.62 (s, 3H, CMe), 0.14 (s, 9H, OSiMe<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  160.3, 134.5, 130.7, 126.4, 122.1, 114.2 (Ar-C), 113.9 (CN), 71.7 (CMe), 54.9 (OCH<sub>3</sub>), 33.4 (CMe), 1.1 (OSiMe<sub>3</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  19.3.



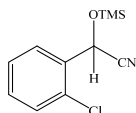
$^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.39–1.35 (m, 10H, C<sub>6</sub>H<sub>10</sub>), 0.21 (s, 9H, OSiMe<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  122.0 (CN), 103.6, 70.8, 39.6, 30.4, 24.7, 22.8 (C<sub>6</sub>H<sub>10</sub>), 1.5 (OSiMe<sub>3</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  16.9.



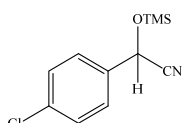
$^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  2.41–2.40 (m, 2H, C<sub>6</sub>H<sub>10</sub>), 2.37 (s, 3H, CMe), 1.88–1.32 (m, 9H, C<sub>6</sub>H<sub>10</sub>), 0.03 (s, 9H, OSiMe<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  119.0 (CN), 109.3 (CMe), 32.6 (CMe), 32.2, 24.8, 23.2, 22.5 (C<sub>6</sub>H<sub>11</sub>), 1.0 (OSiMe<sub>3</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  17.7.



$^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.29–7.28 (m, 2H, Ar-H), 7.06–7.02 (m, 3H, Ar-H), 5.08 (s, 1H, CH), 0.02 (s, 9H, OSiMe<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  137.1, 129.4, 129.1, 126.7 (Ar-C), 119.5 (CN), 64.0 (CH), -0.4 (OSiMe<sub>3</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  23.6.

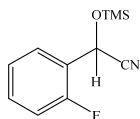


$^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.62–6.71 (m, 4H, Ar-H), 5.71 (s, 1H, CH), 0.05 (s, 9H, OSiMe<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  134.5, 132.4, 130.7, 129.9, 128.7, 127.7 (Ar-C), 118.5 (CN), 61.3 (CH), -0.5 (OSiMe<sub>3</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  24.8.

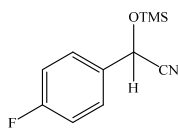


$^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.99 (s, 4H, Ar-H), 4.92 (s, 1H, CH), 0.01 (s, 9H,

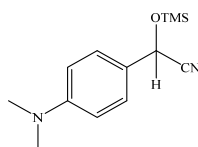
OSiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 135.5, 135.4, 129.3 (Ar-C), 119.1 (CN), 63.2 (CH), -0.4 (OSiMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>): δ 24.2.



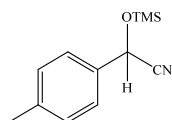
<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.52–7.49 (m, 1H, Ar-H), 6.80–6.62 (m, 3H, Ar-H), 5.52 (s, 1H, CH), 0.03 (s, 9H, OSiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 160.8, 159.1, 131.4, 128.8, 124.9, 118.6 (Ar-C), 115.8 (CN), 58.3 (CH), -0.6 (OSiMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>): δ 24.7.



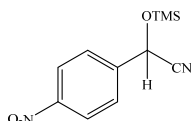
<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.07–7.05 (m, 2H, Ar-H), 6.69–6.66 (m, 2H, Ar-H), 4.96 (s, 1H, CH), 0.01 (s, 9H, OSiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 164.2, 162.7, 132.9, 128.7, 119.3, 116.1 (Ar-C), 115.9 (CN), 63.2 (CH), -0.4 (OSiMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>): δ 23.9.



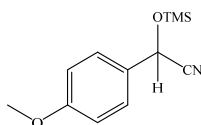
<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.27 (d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 2H, Ar-H), 6.42 (d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 2H, Ar-H), 5.15 (s, 1H, CH), 2.44 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 0.06 (s, 9H, OSiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 151.3, 128.3, 124.5, 120.1 (Ar-C), 112.5 (CN), 64.2 (CH), 39.9 (N(CH<sub>3</sub>)<sub>2</sub>), -0.1 (OSiMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>): δ 22.0.



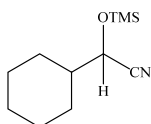
<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.23 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H, Ar-H), 6.88 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H, Ar-H), 5.09 (s, 1H, CH), 2.01 (s, Ar-Me), 0.03 (s, 9H, OSiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 139.3, 134.3, 129.8, 126.8 (Ar-C), 119.7 (CN), 63.9 (CH), 21.0 (Ar-Me), -0.3 (OSiMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>): δ 23.3.



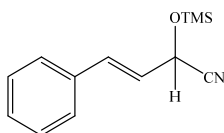
<sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.73 (d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 2H, Ar-H), 7.01 (d, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 2H, Ar-H), 4.93 (s, 1H, CH), 0.04 (s, 9H, OSiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>): δ 148.6, 142.8, 127.0, 124.0 (Ar-C), 118.5 (CN), 62.8 (CH), -0.6 (OSiMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (119 MHz, C<sub>6</sub>D<sub>6</sub>): δ 22.5.



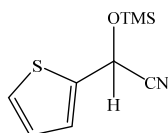
$^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.21 (d,  $^3J_{\text{HH}} = 8.4$  Hz, 2H, Ar-H), 6.65 (d,  $^3J_{\text{HH}} = 8.4$  Hz, 2H, Ar-H), 5.08 (s, 1H, CH), 3.24 (s, 3H, OCH<sub>3</sub>), 0.04 (s, 9H, OSiMe<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  160.8, 129.2, 128.4, 119.7 (Ar-C), 114.5 (CN), 63.8 (CH), 54.9 (OCH<sub>3</sub>), -0.3 (OSiMe<sub>3</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  23.0.



$^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  3.82 (s, 1H, CH), 1.74–0.93 (m, 11H, C<sub>6</sub>H<sub>11</sub>), 0.07 (s, 9H, OSiMe<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  119.5 (CN), 66.7 (CH), 43.2, 28.2, 26.3, 25.8 (C<sub>6</sub>H<sub>11</sub>), -0.5 (OSiMe<sub>3</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  17.7.



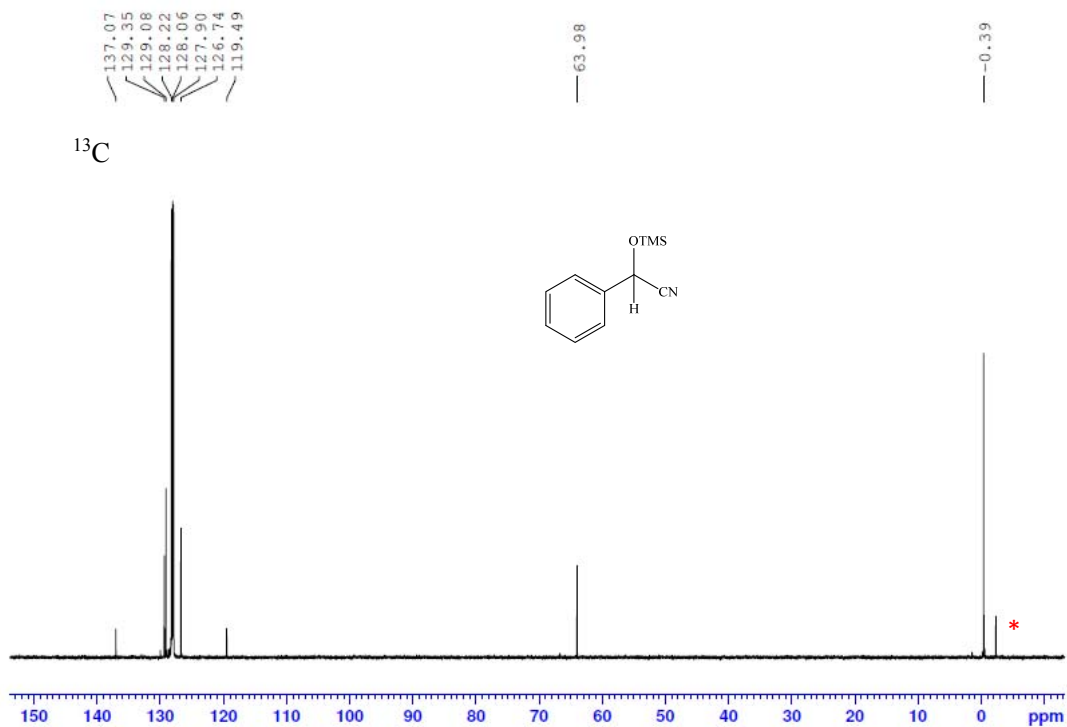
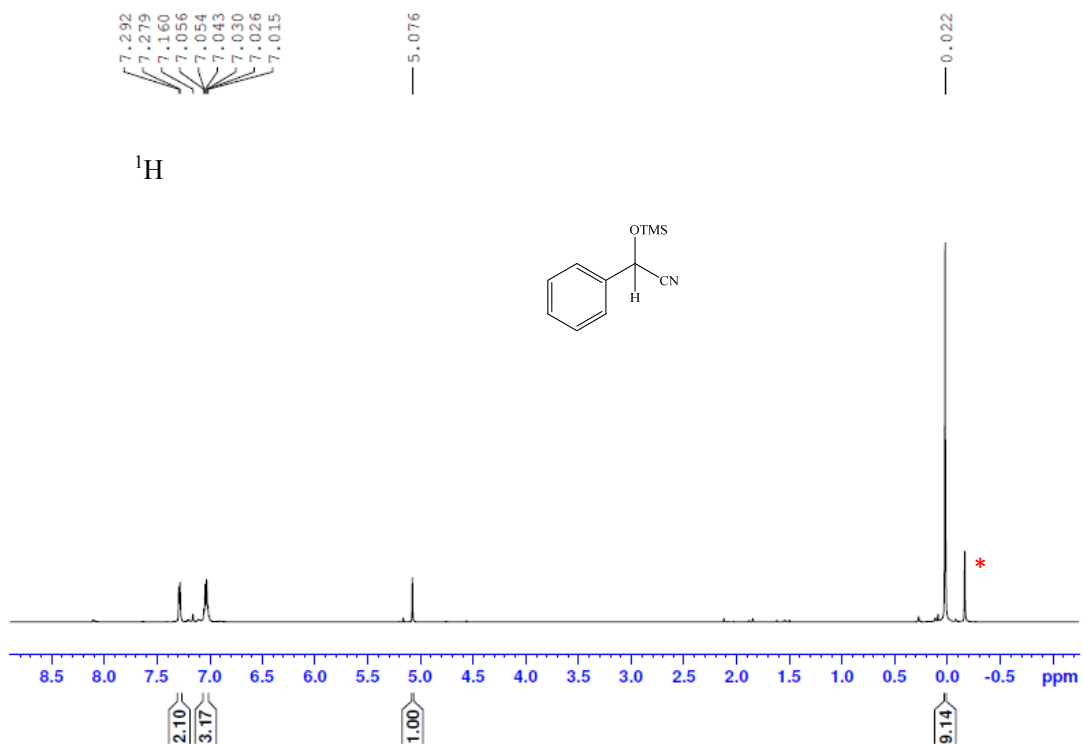
$^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.07–7.04 (m, 5H, Ar-H), 6.59 (d, 1H, PhCH=CH), 5.94 (dd, 1H, PhCH=CH), 4.66 (m, 1H, CH), 0.08 (s, 9H, OSiMe<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  135.5, 133.9, 128.9, 128.9 (Ar-C), 127.3, 124.3 (PhCH=CH), 118.8 (CN), 62.5 (CH), -0.2 (OSiMe<sub>3</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  23.3.

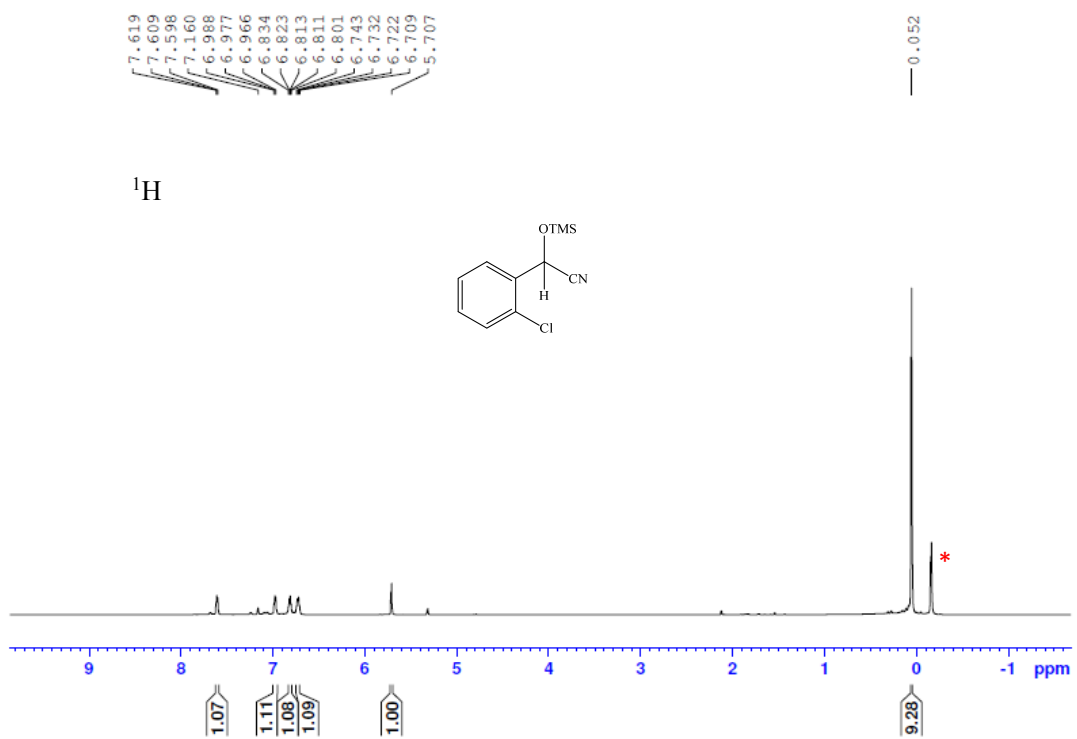
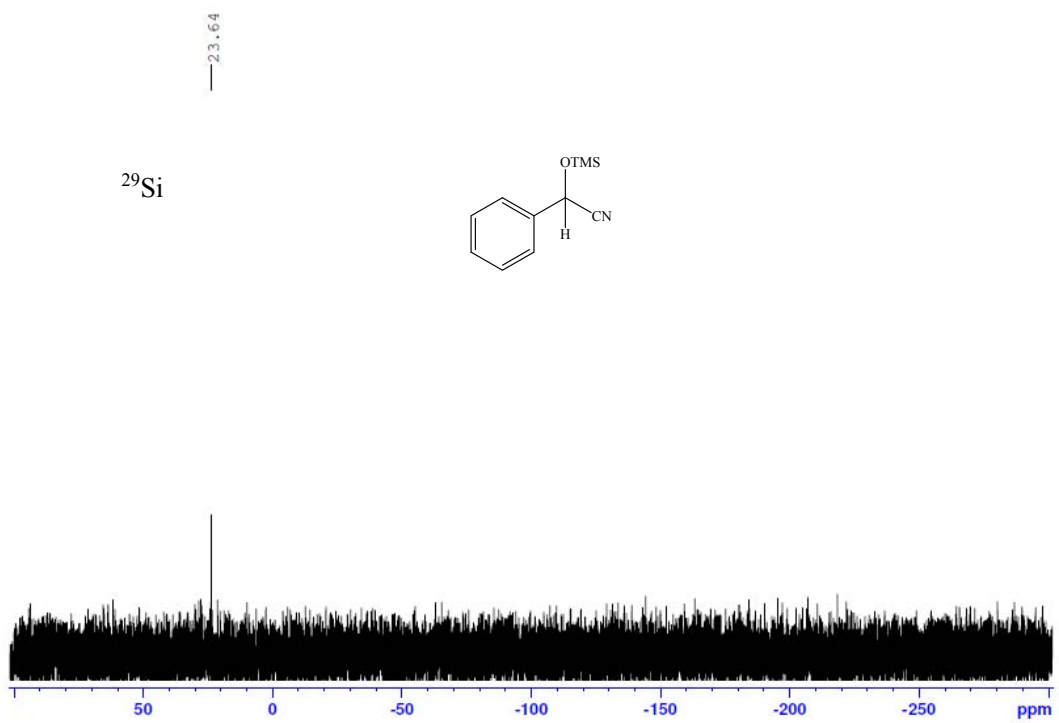


$^1\text{H}$  NMR (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.86 (d,  $^3J_{\text{HH}} = 4.8$  Hz, 1H, C<sub>4</sub>H<sub>3</sub>S), 6.76 (d,  $^3J_{\text{HH}} = 4.8$  Hz, 1H, C<sub>4</sub>H<sub>3</sub>S), 6.54 (m, 1H, C<sub>4</sub>H<sub>3</sub>S), 5.22 (s, 1H, CH), 0.01 (s, 9H, OSiMe<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  140.3, 127.2, 127.0, 126.6 (C<sub>4</sub>H<sub>3</sub>S), 118.7 (CN), 59.8 (CH), -0.5 (OSiMe<sub>3</sub>).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (119 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  24.2.

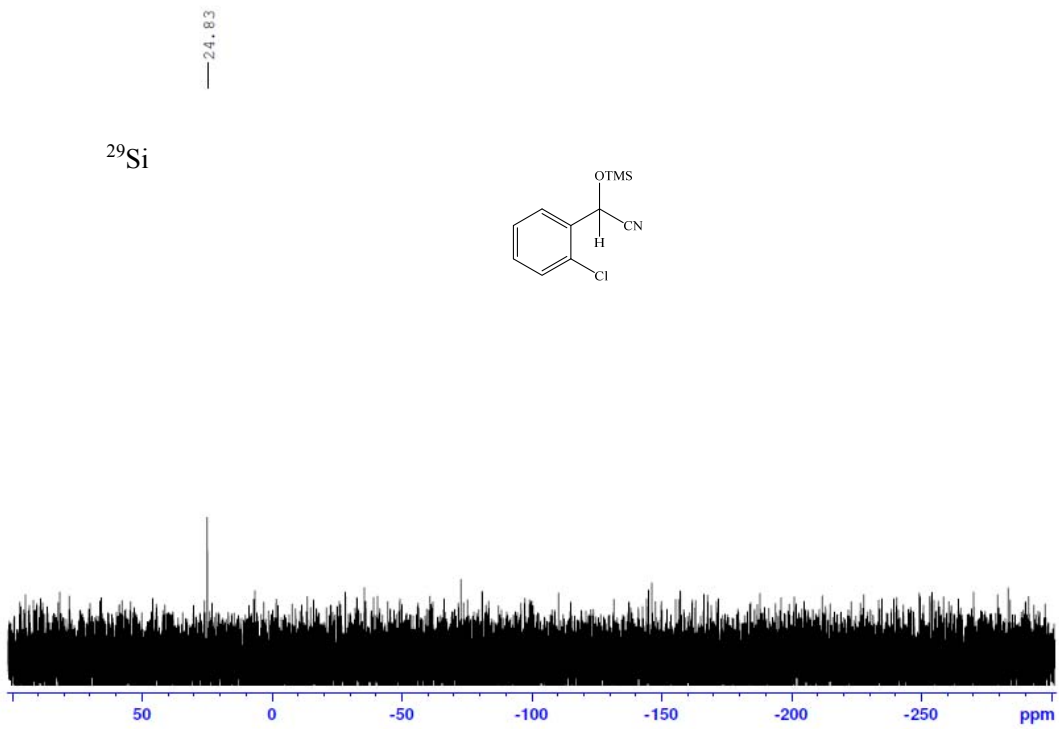
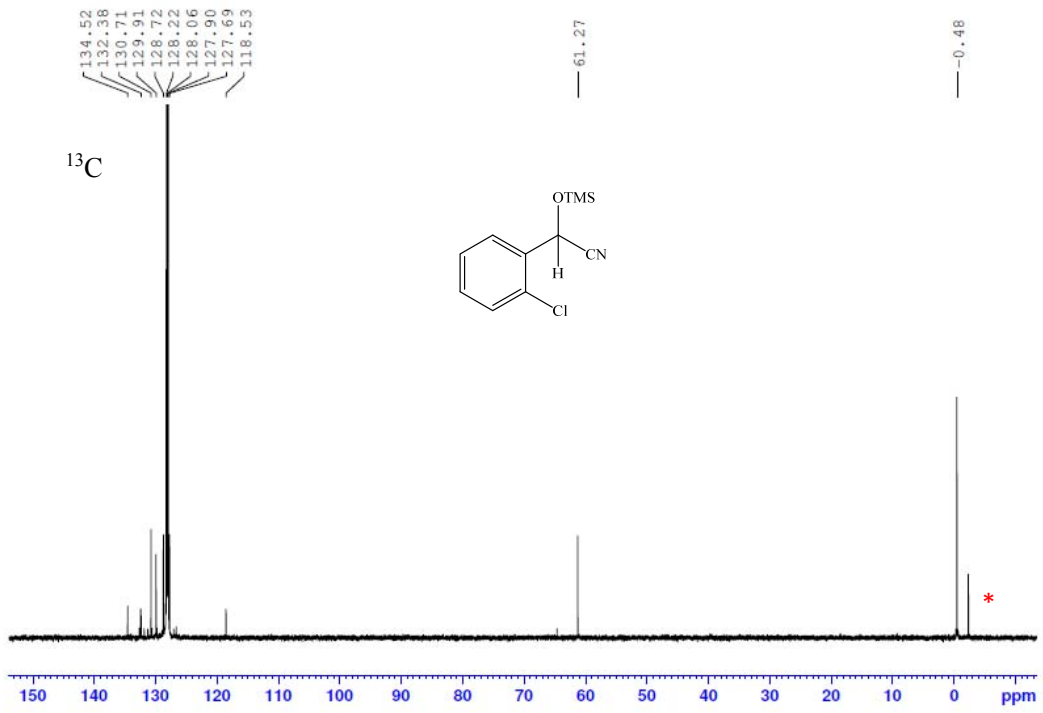
## NMR Spectra of Cyanosilylation Products

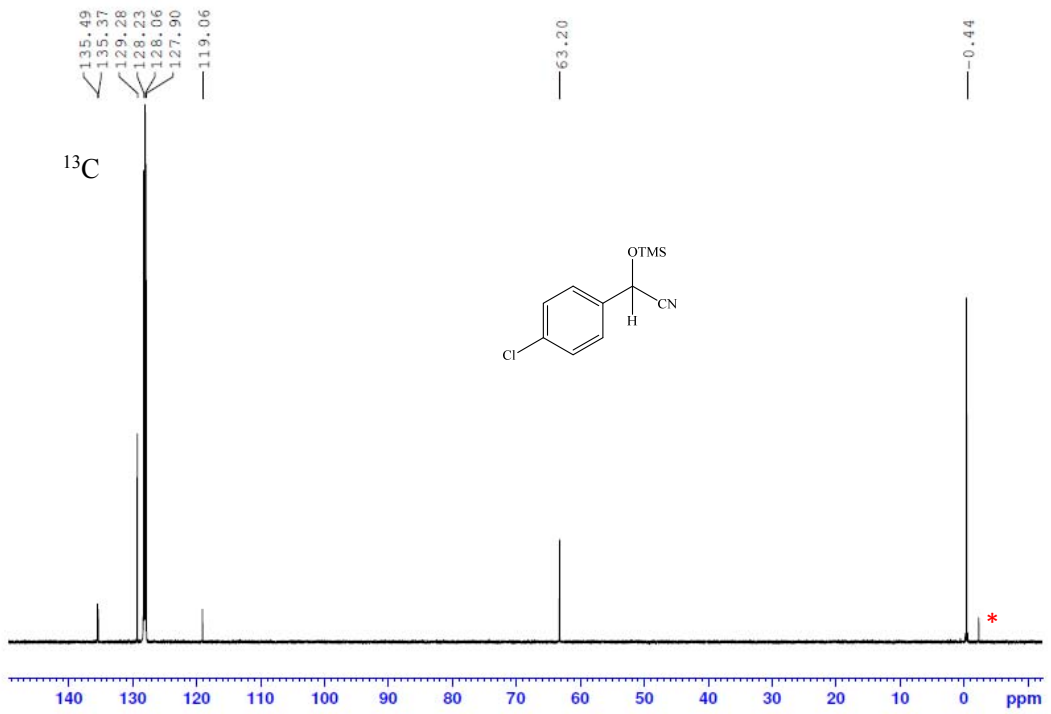
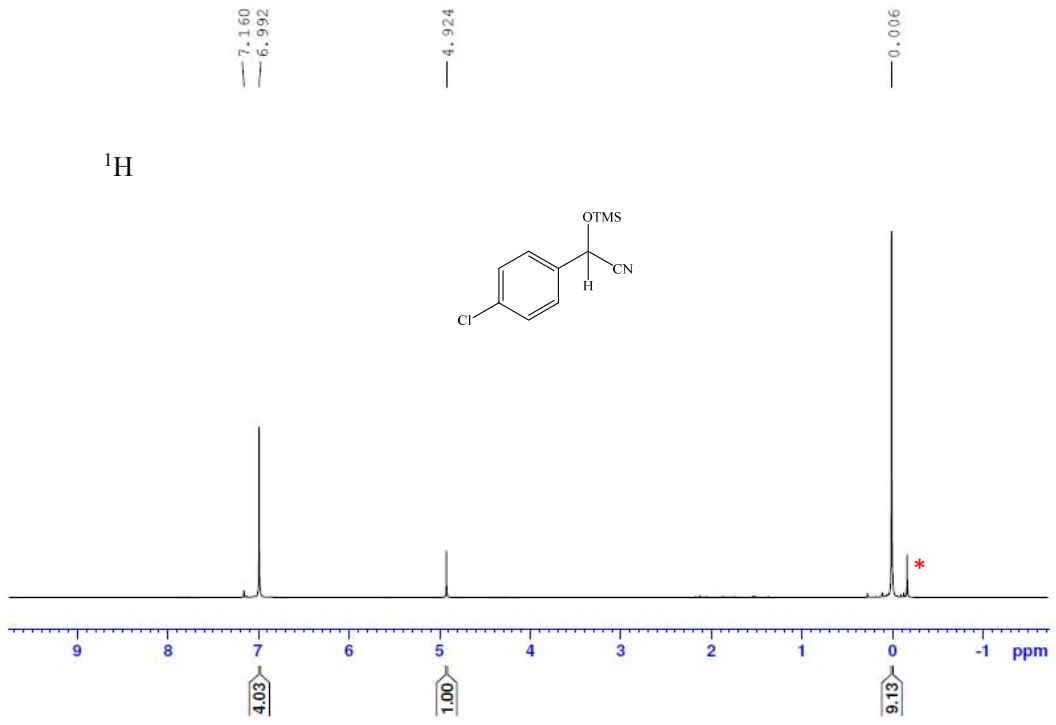
General: The cyanosilylation products are shown along with the spectra. Resonances are denoted as follows: excess TMS-CN (\*).





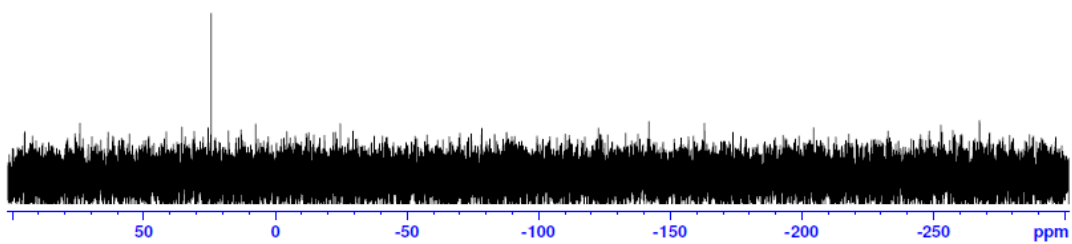
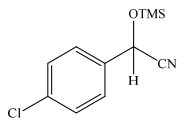






$^{29}\text{Si}$

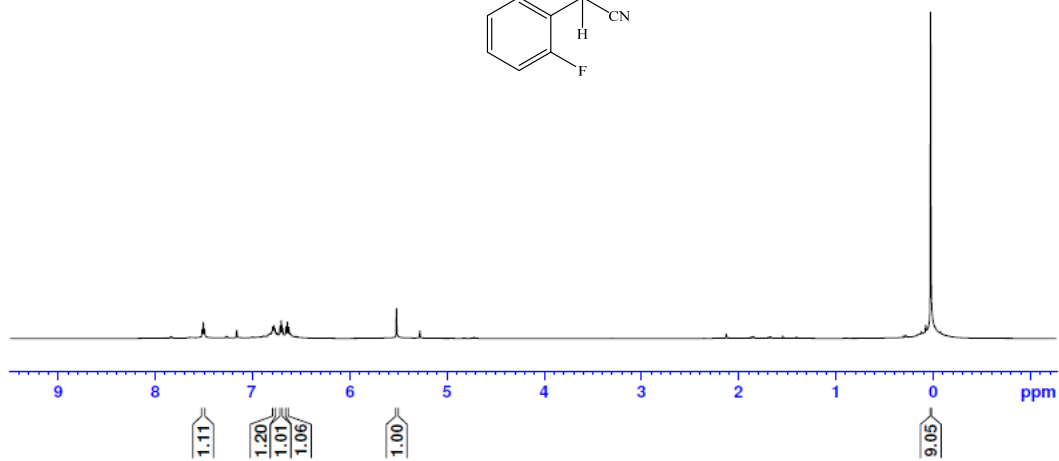
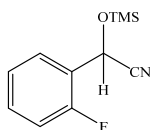
— 24.24

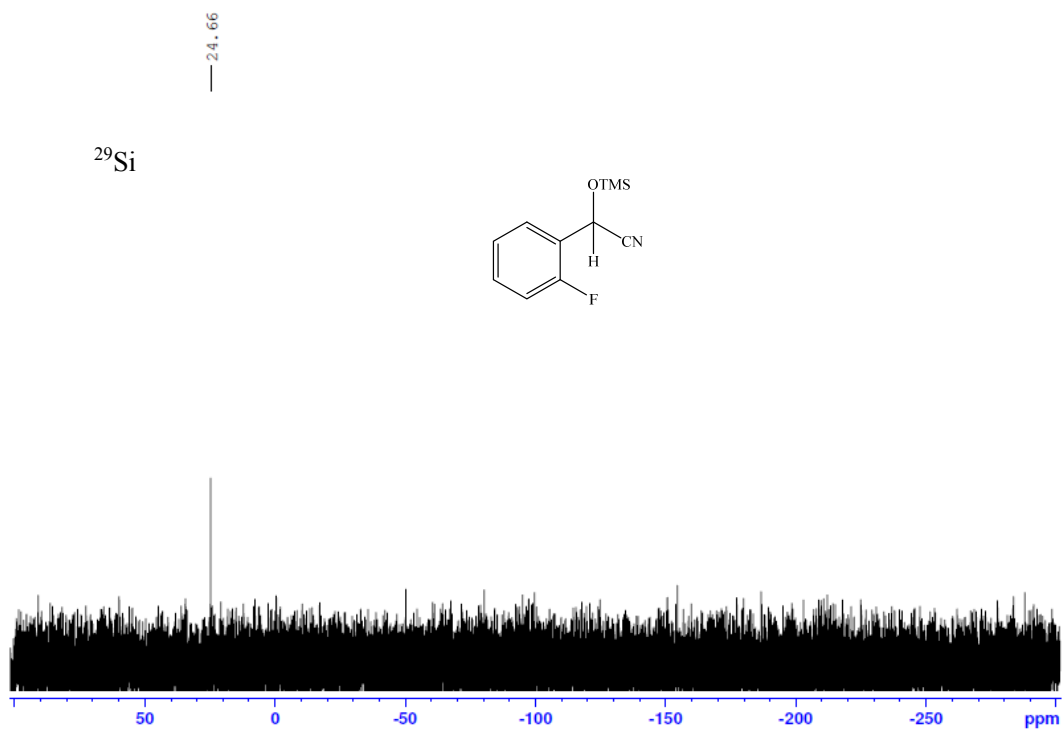
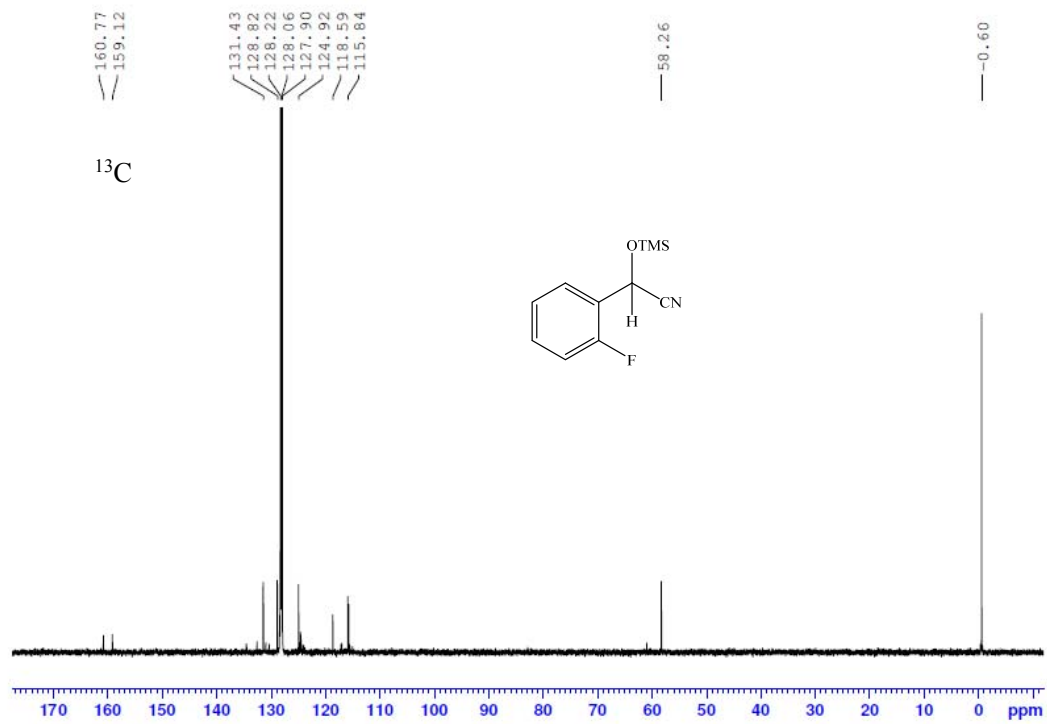


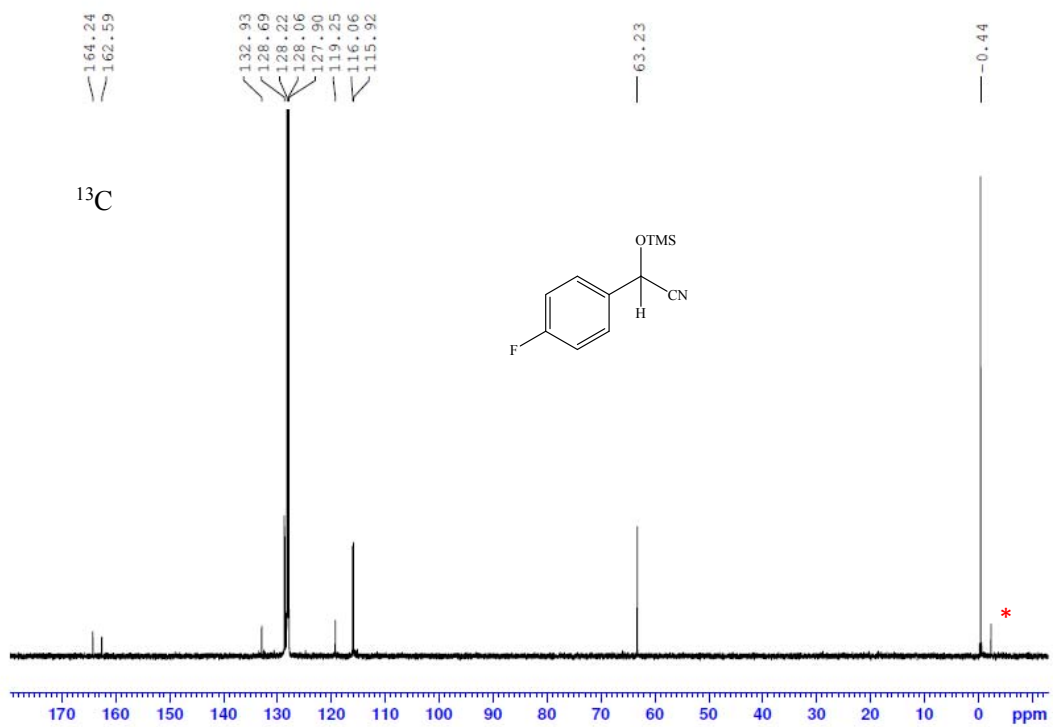
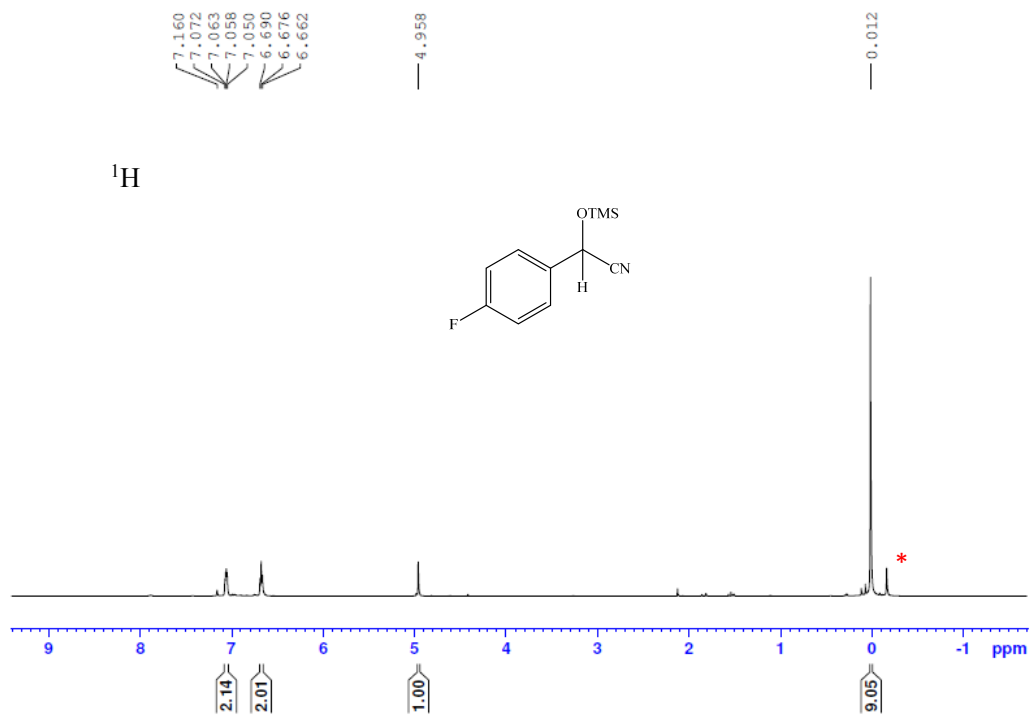
$^1\text{H}$

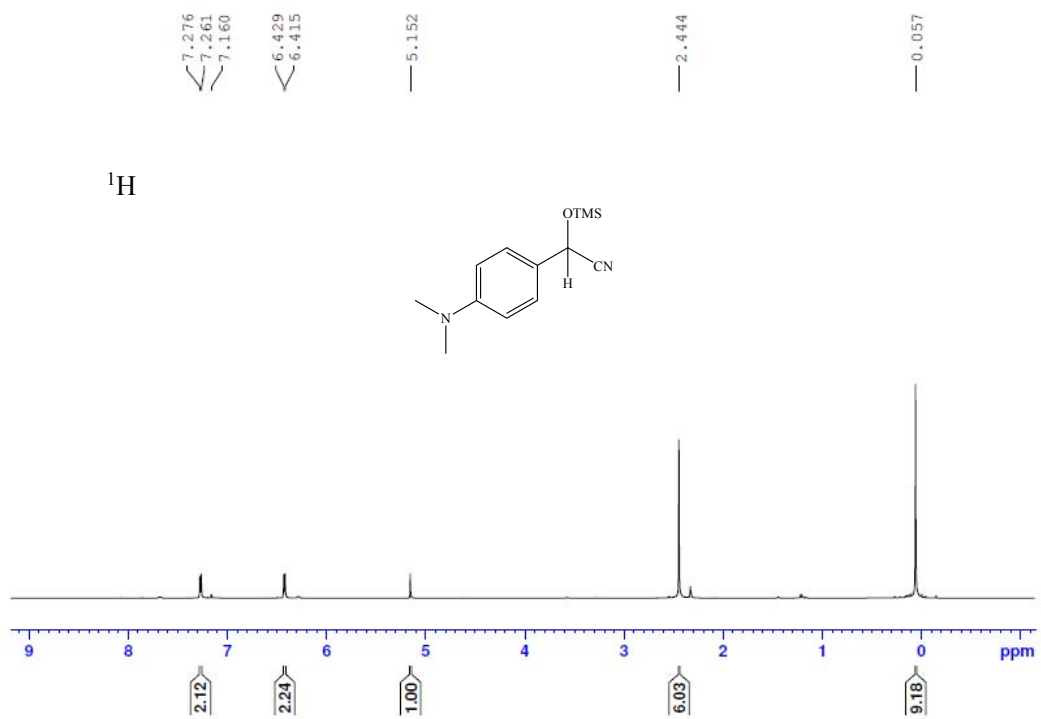
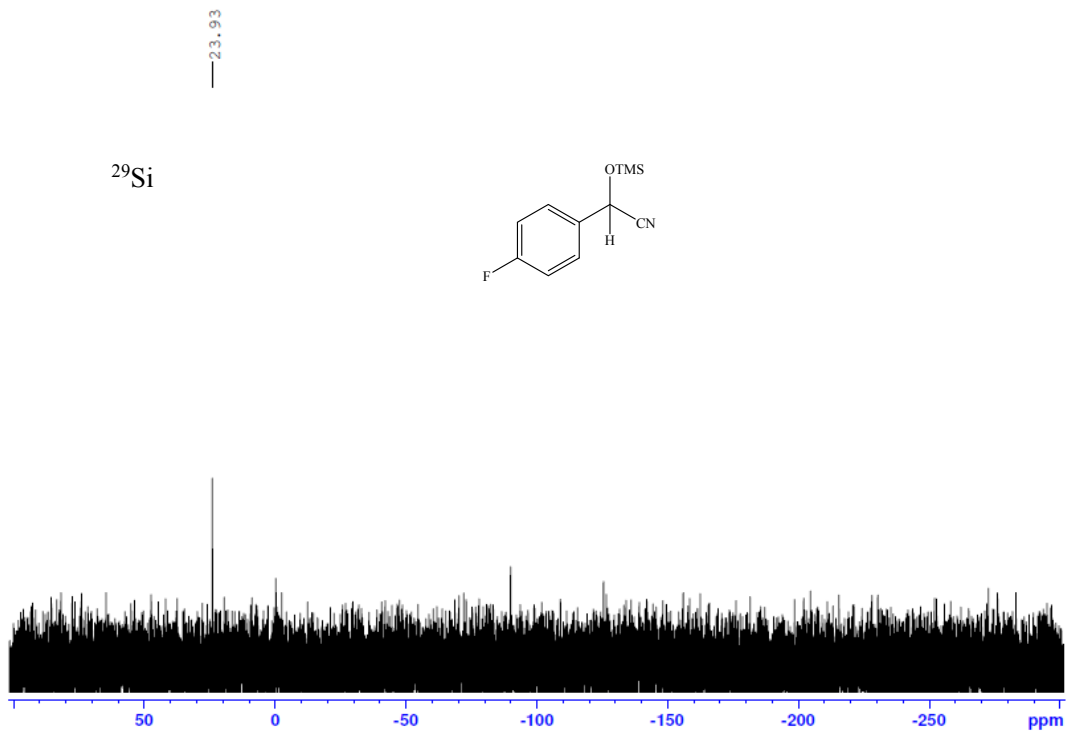
7.517  
7.504  
7.492  
7.160  
6.802  
6.789  
6.779  
6.776  
6.770  
6.767  
6.714  
6.702  
6.689  
6.655  
6.639  
6.638  
6.624  
5.517

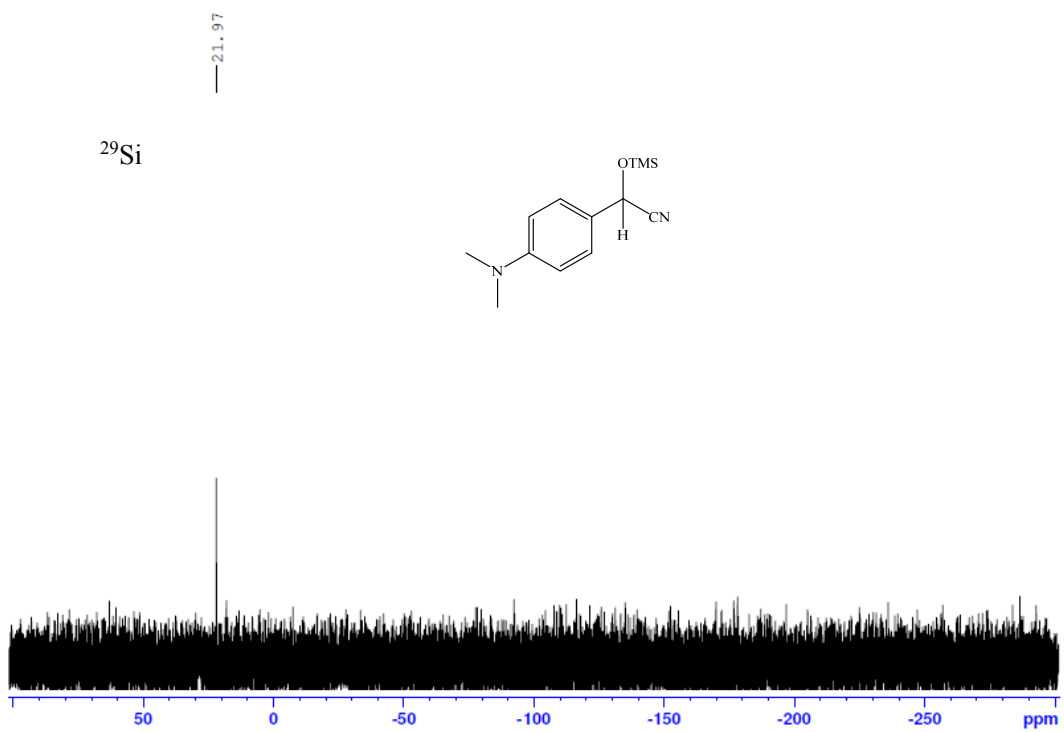
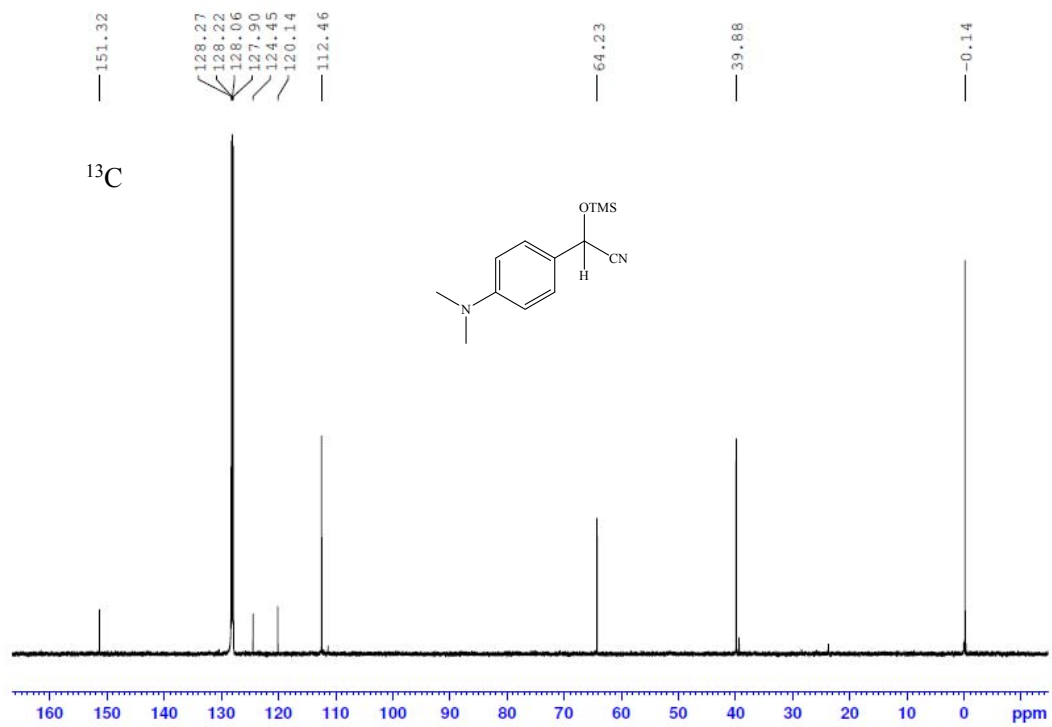
— 0.025

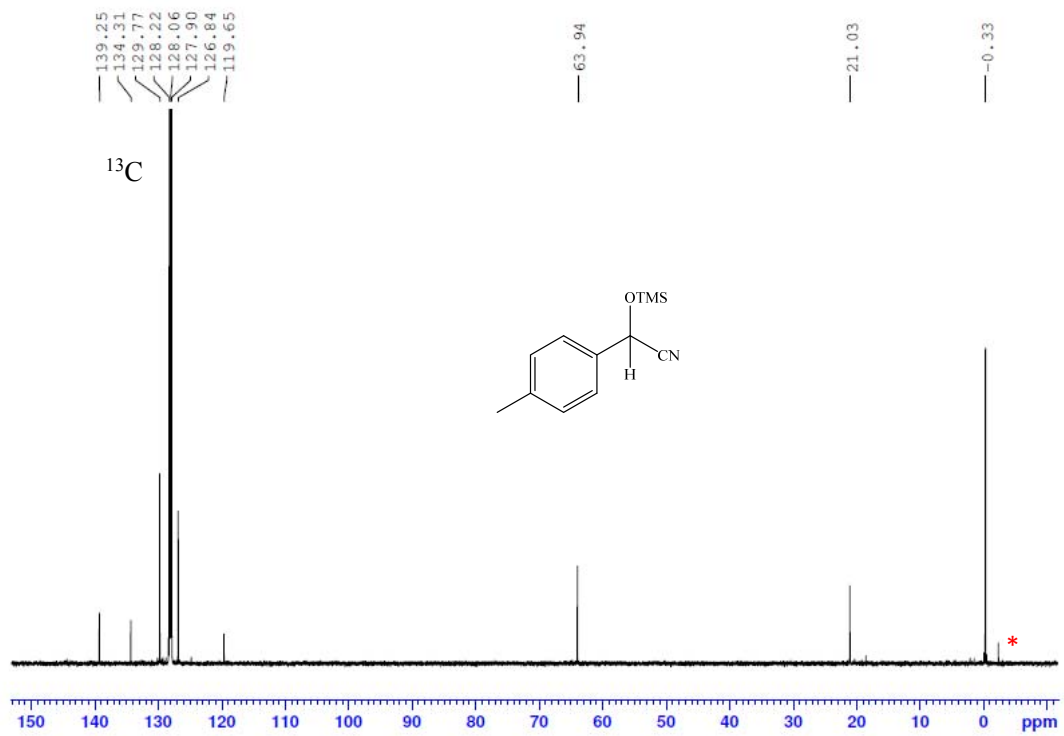
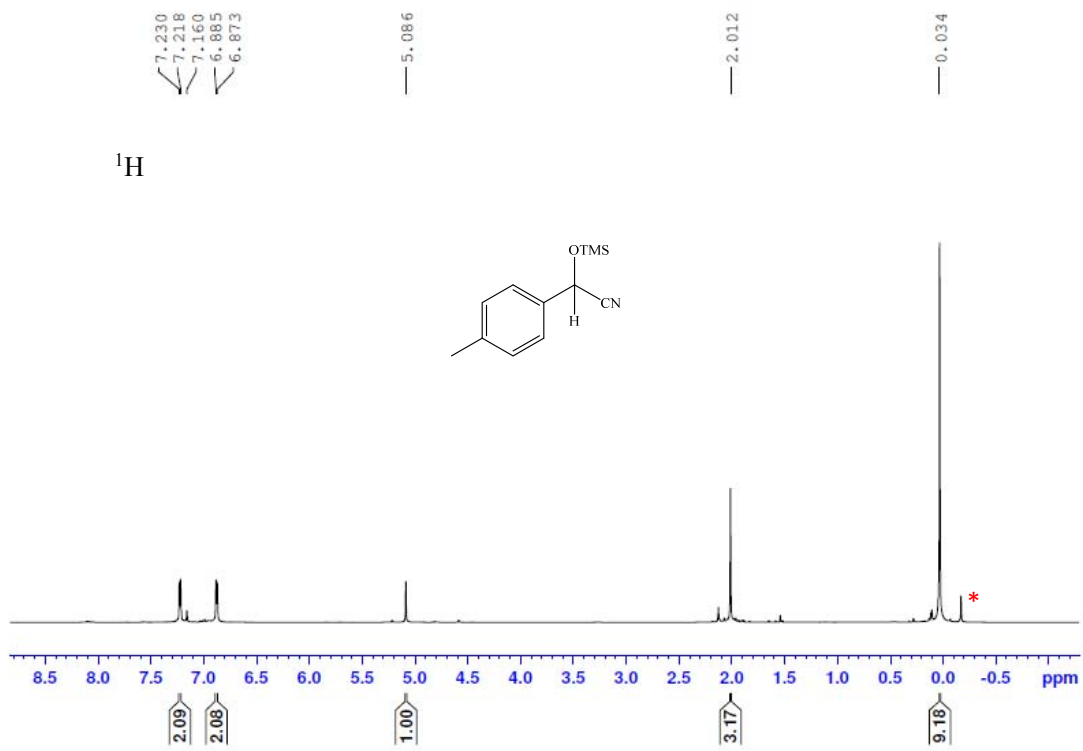




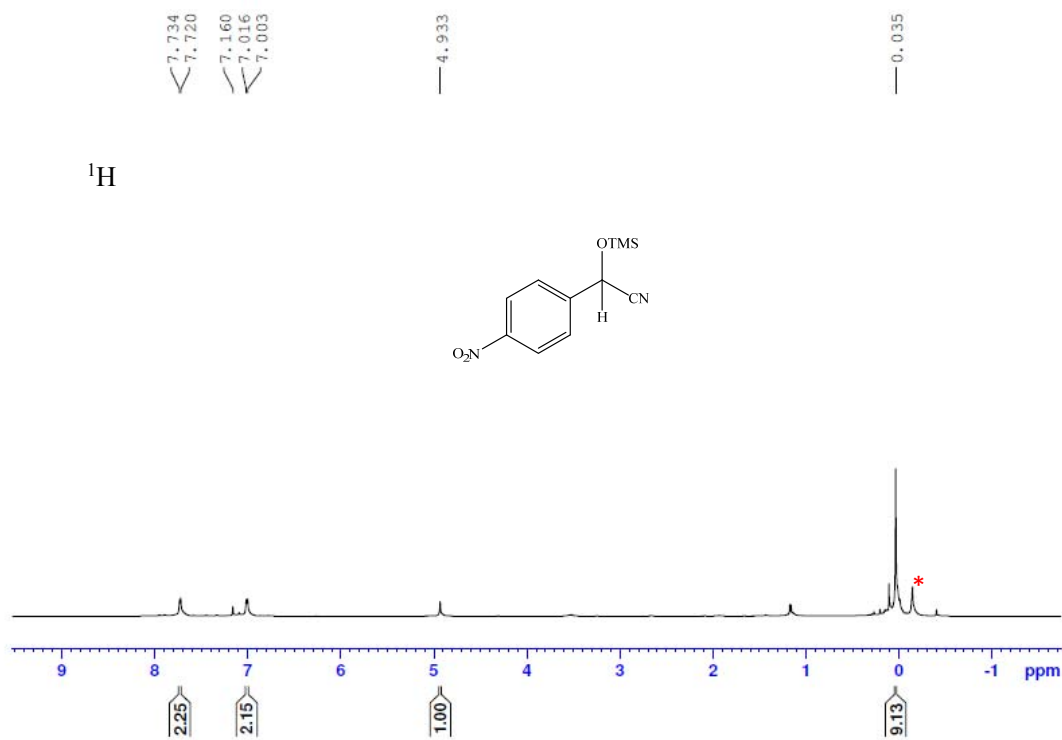
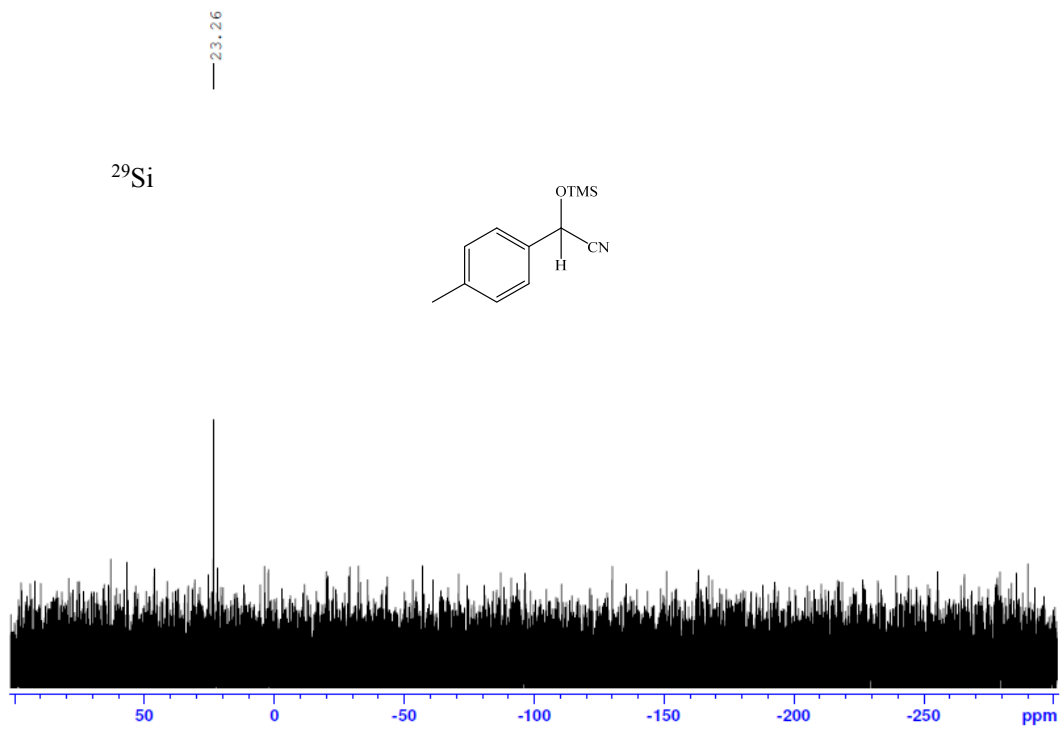


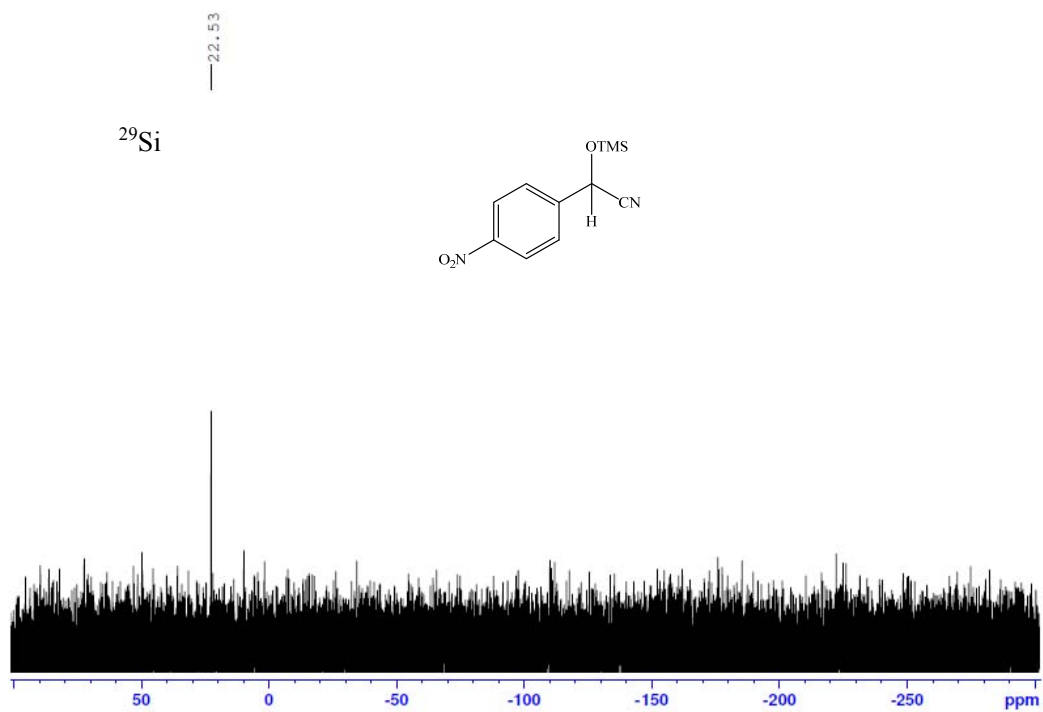
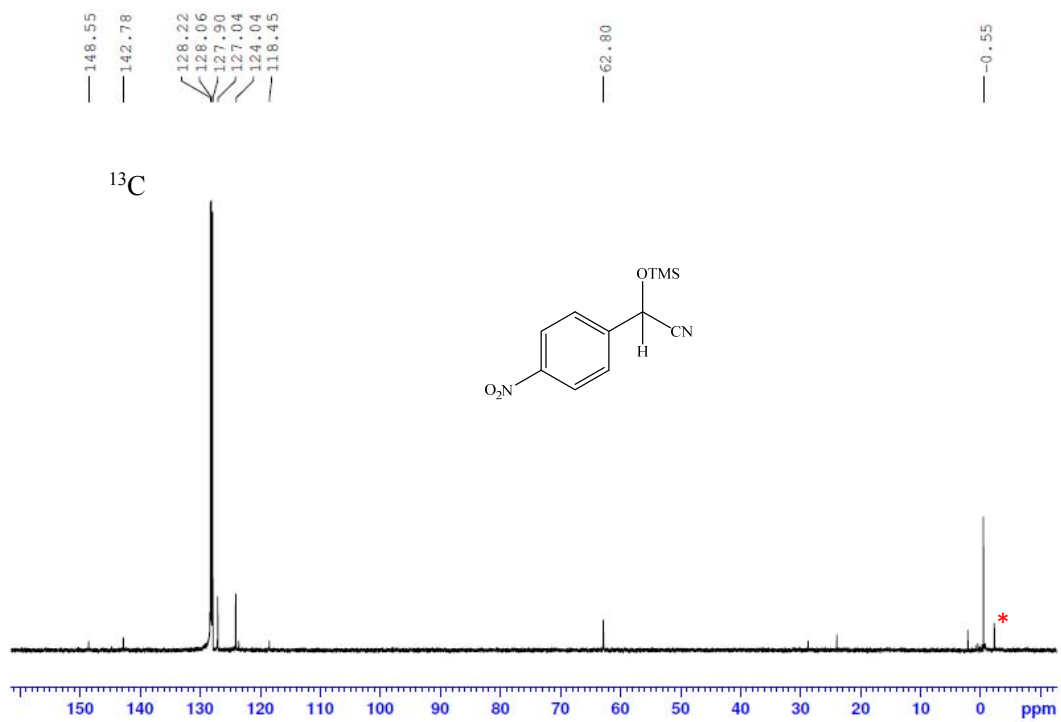


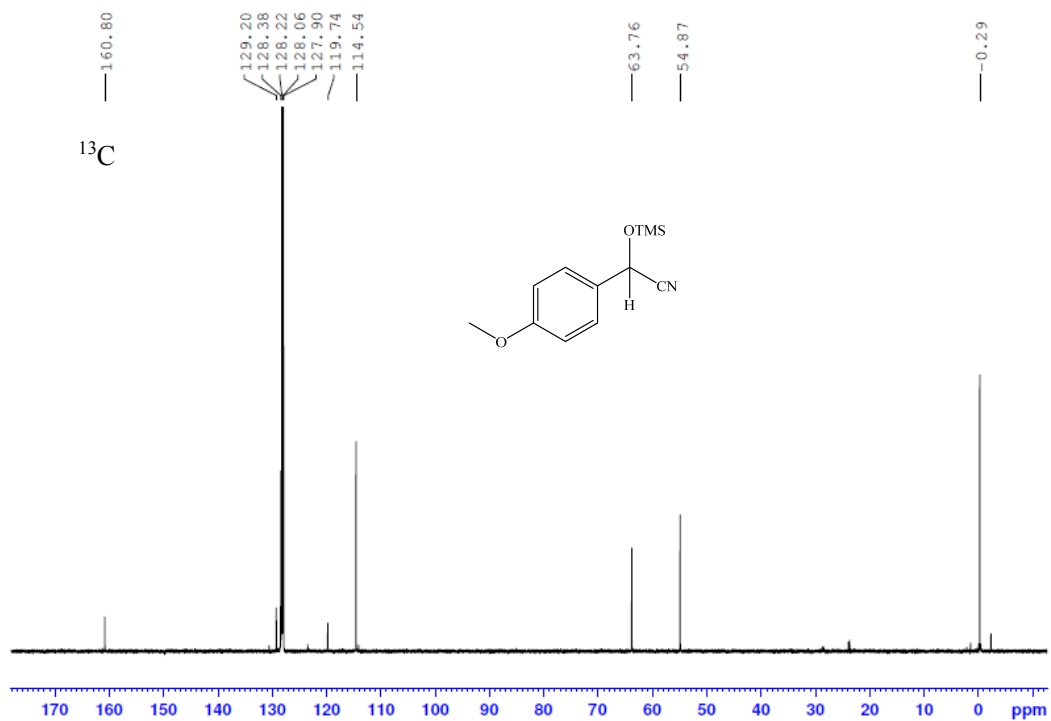
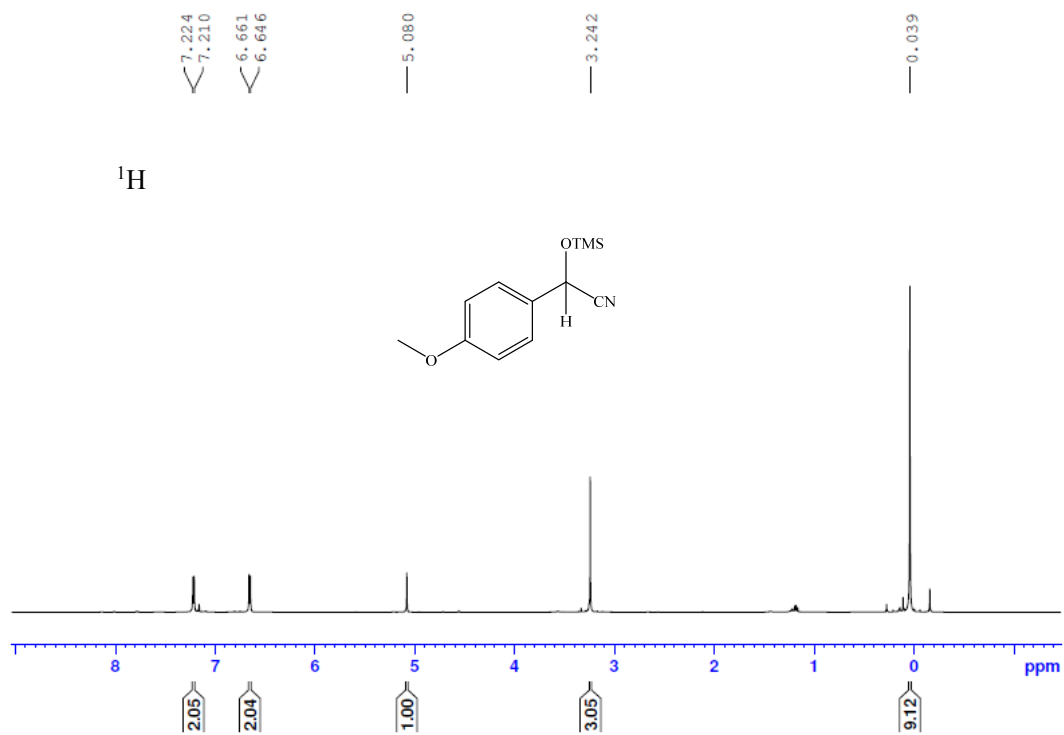


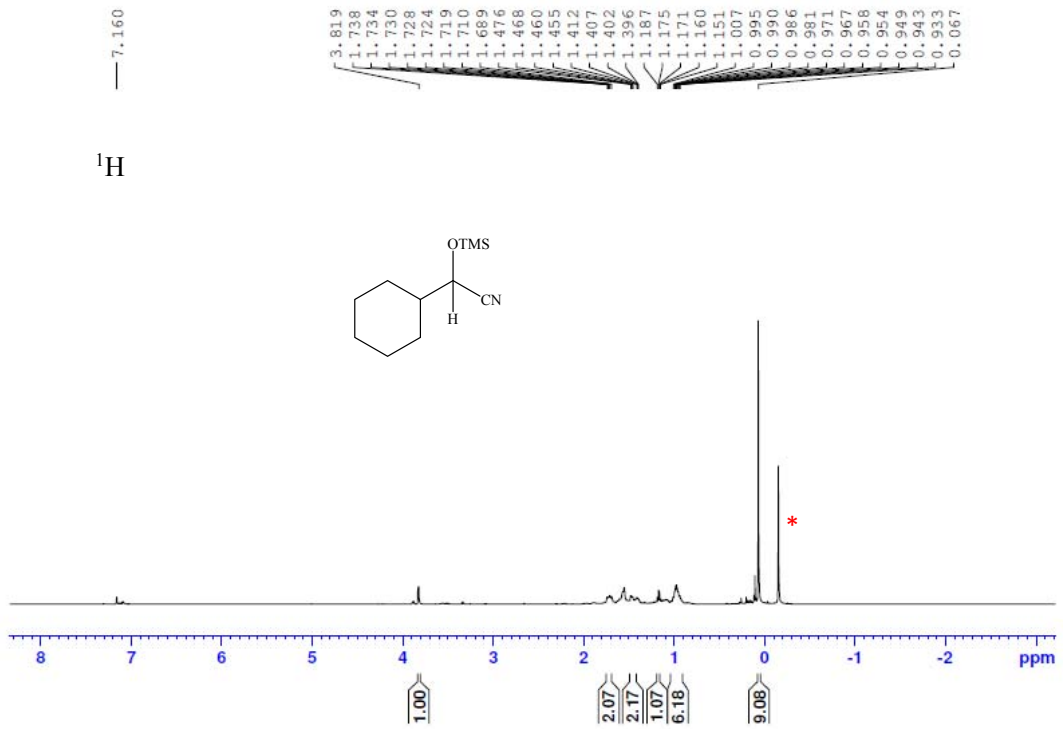
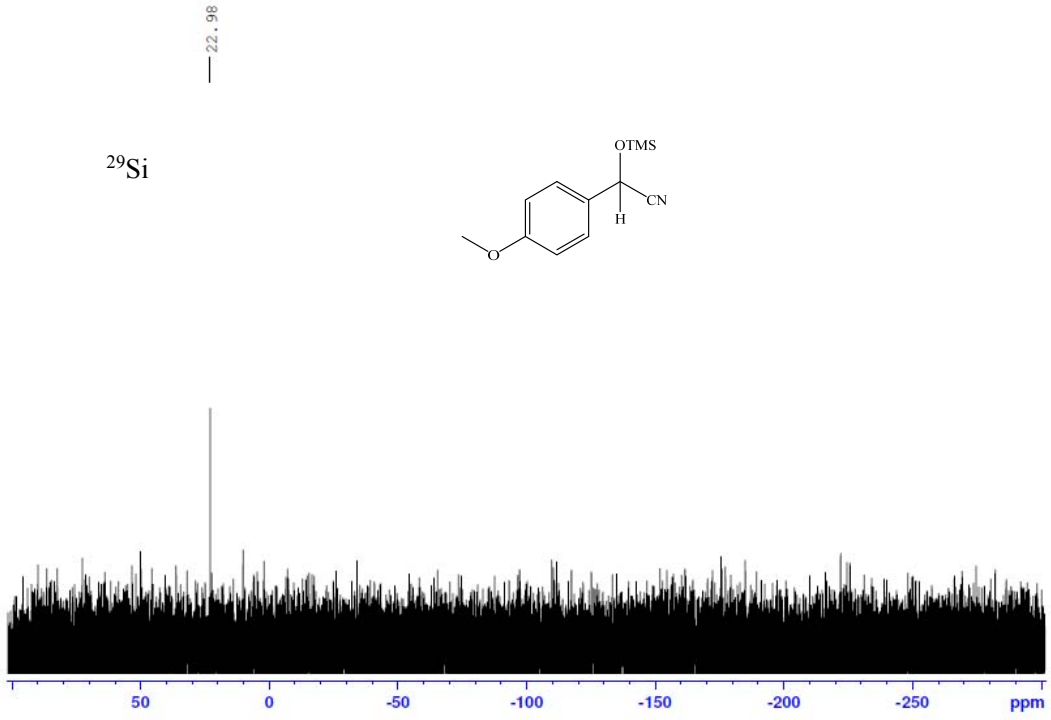


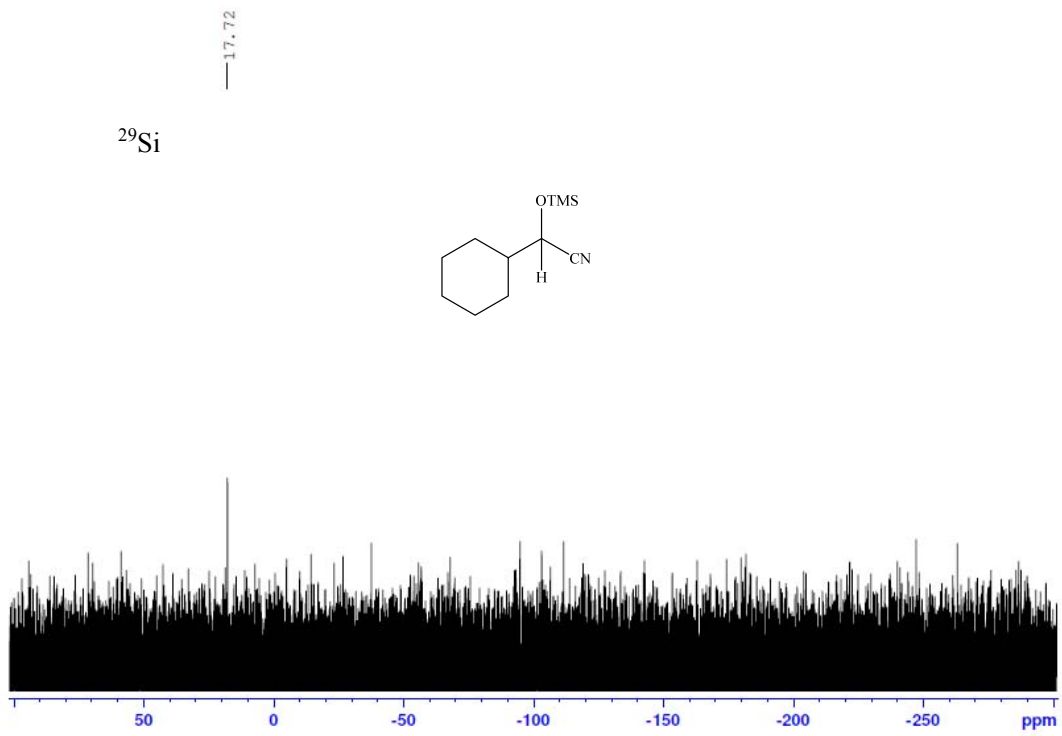
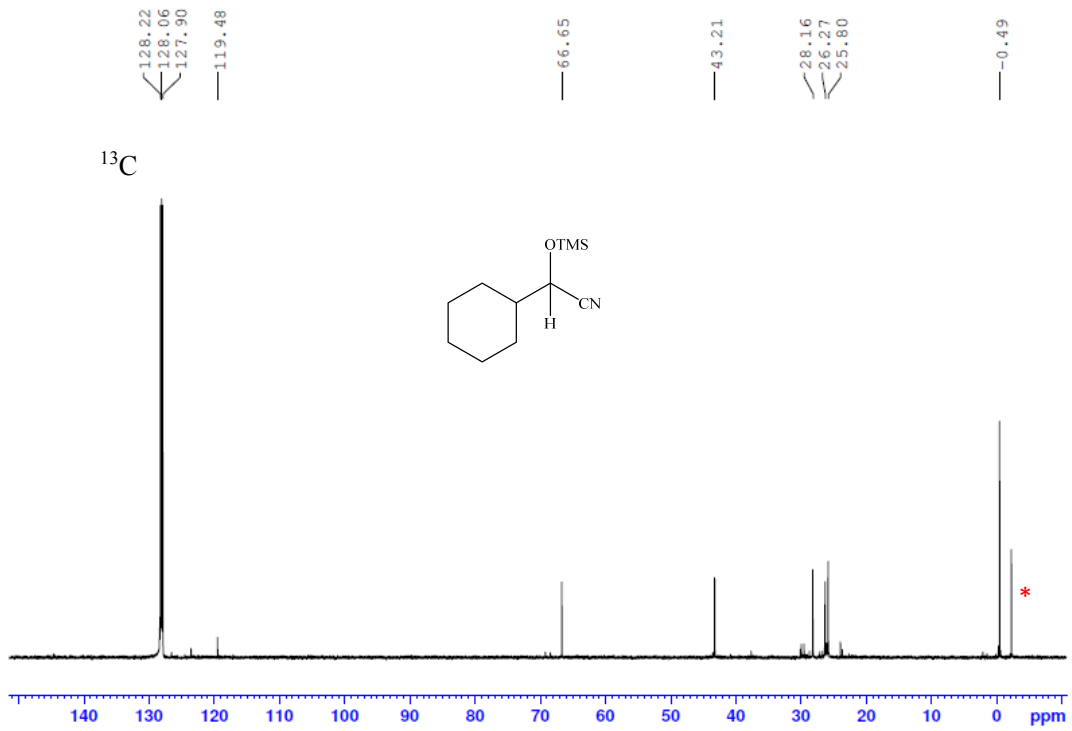


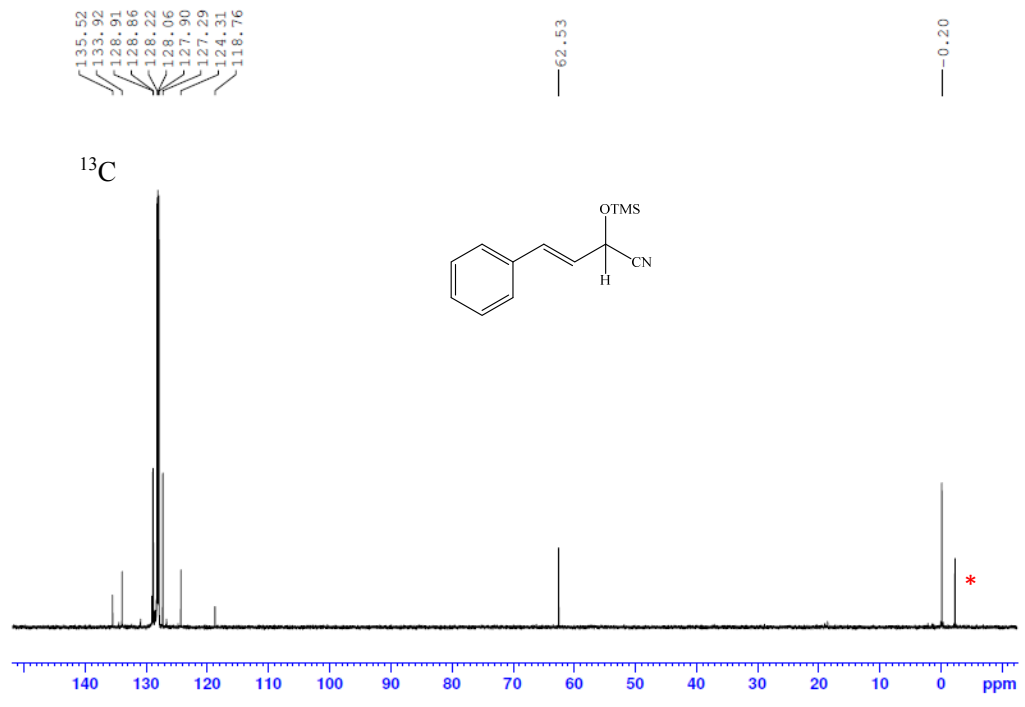
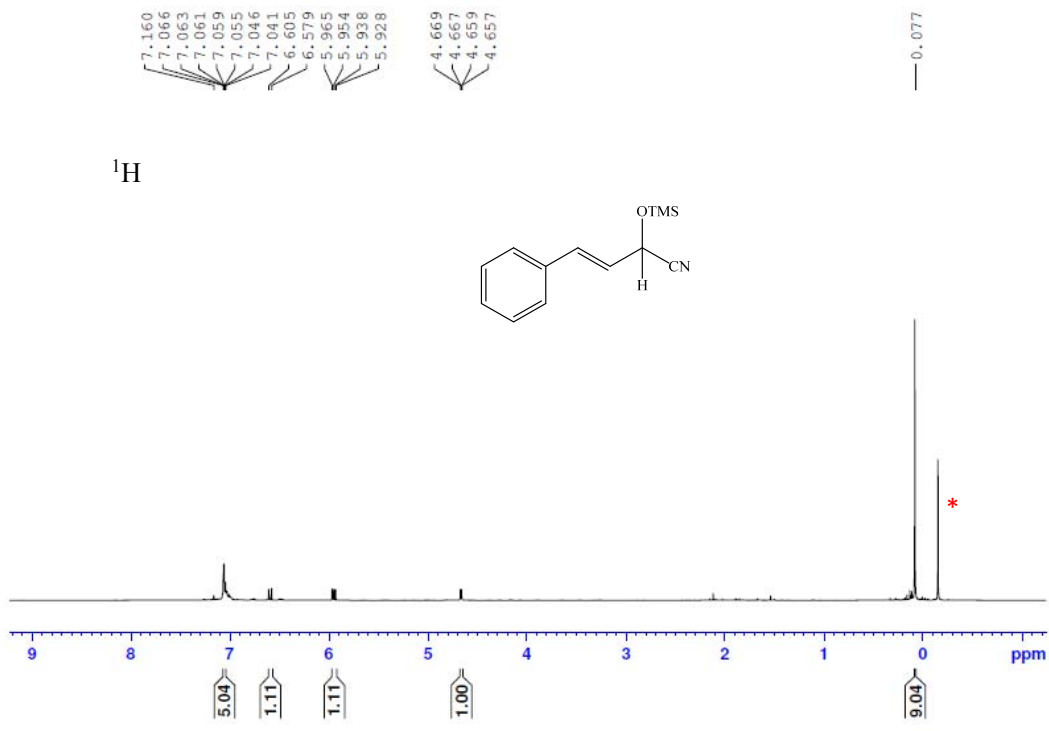


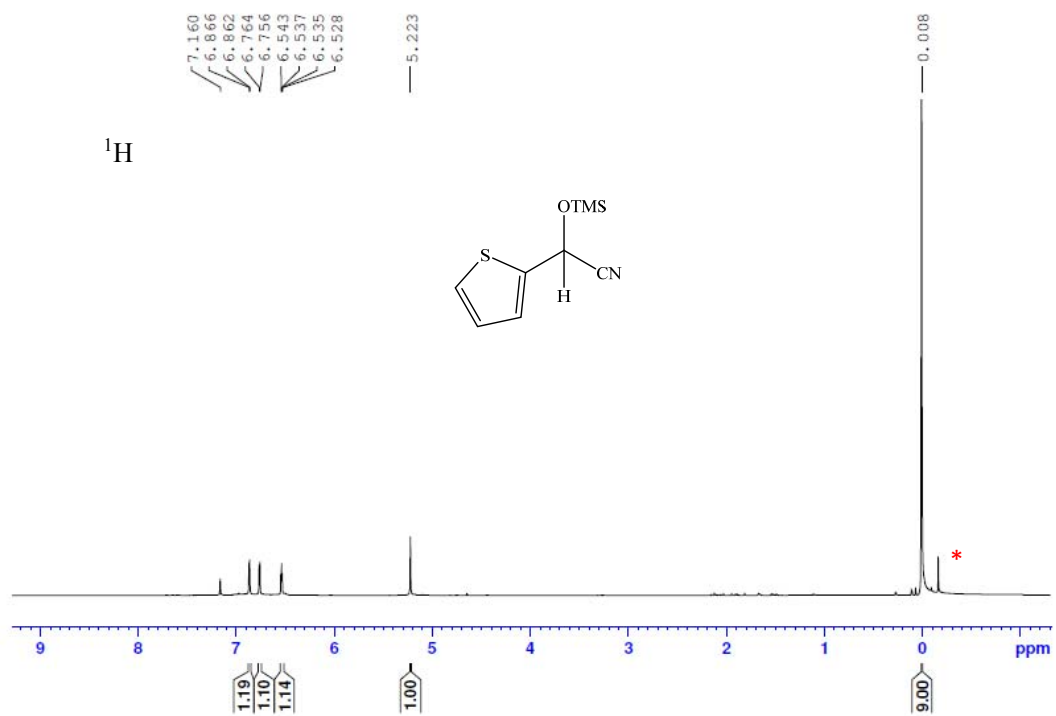
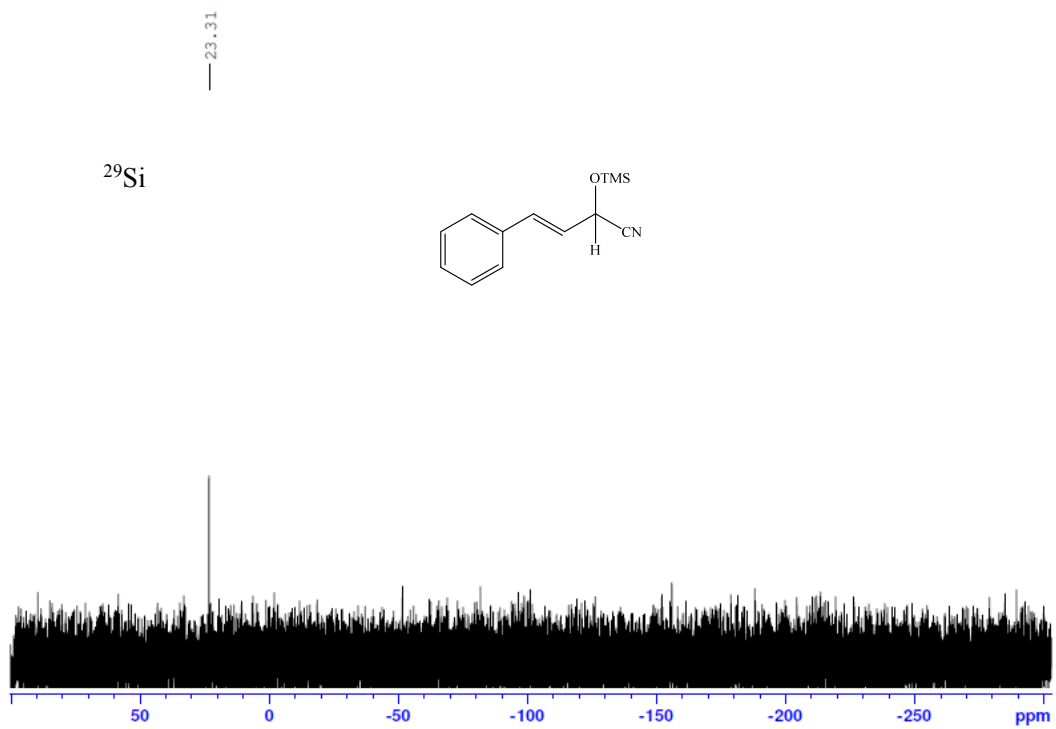


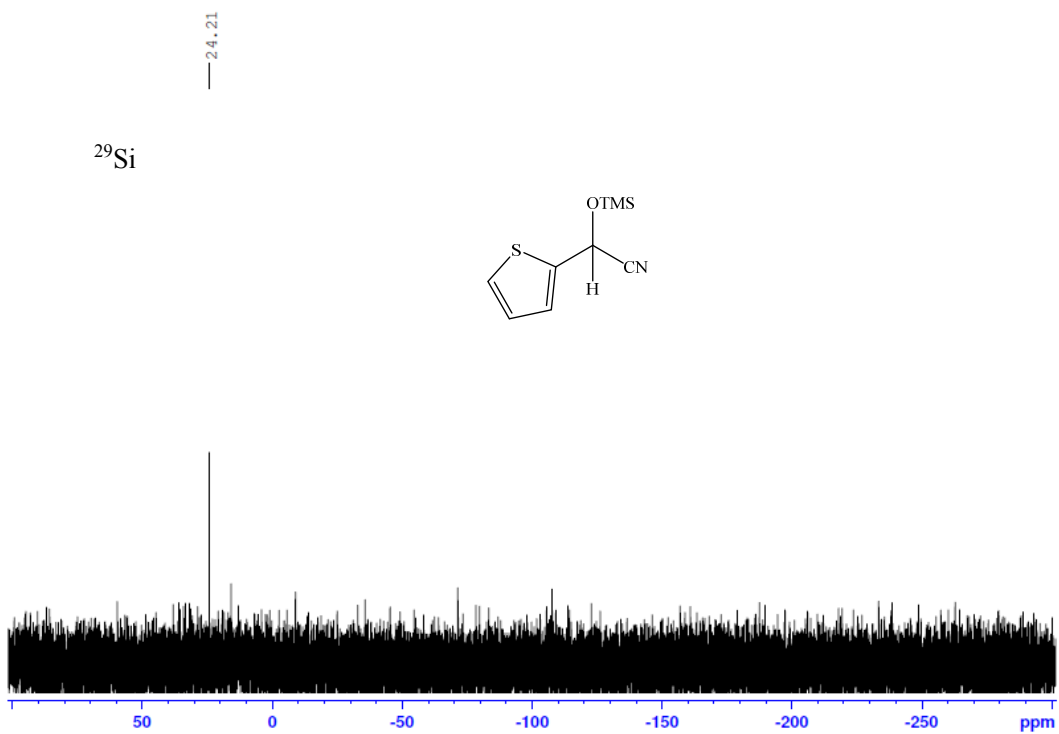
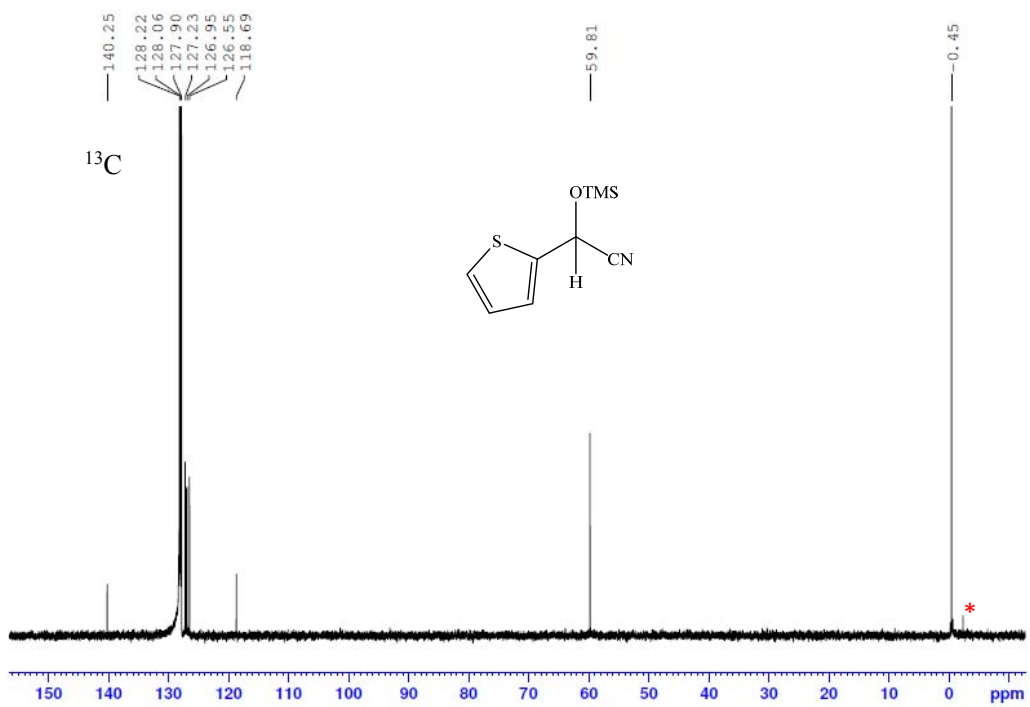












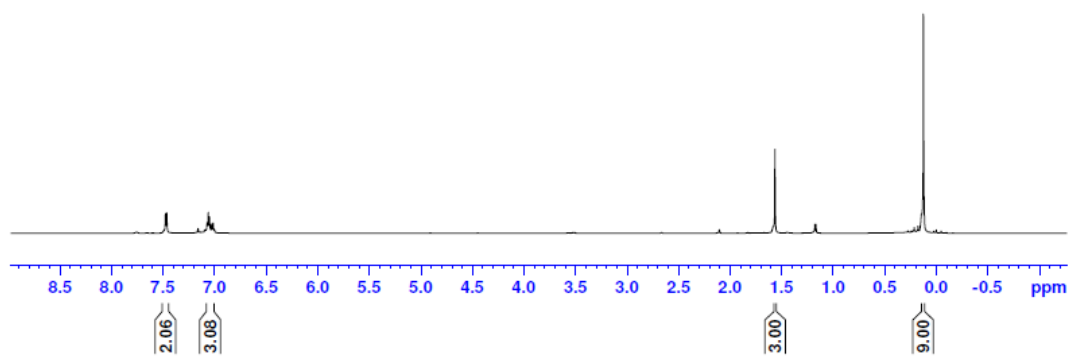
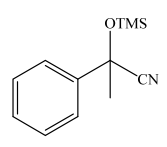


7.476  
7.463  
7.160  
7.073  
7.061  
7.048  
7.027  
7.026  
7.015

1.563

0.123

<sup>1</sup>H



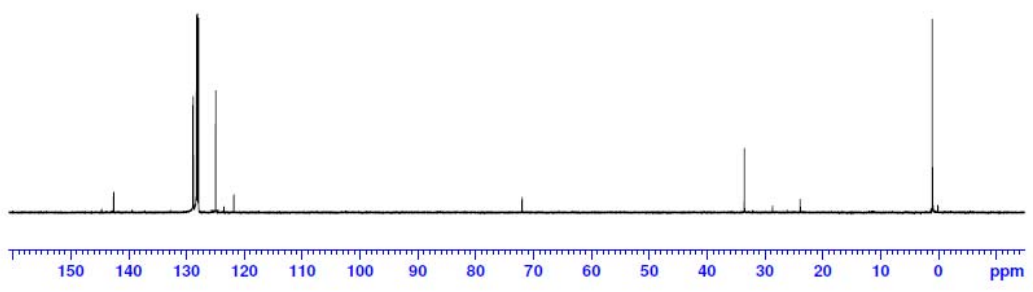
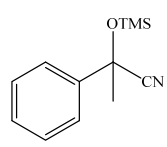
142.59  
128.89  
128.79  
128.22  
128.06  
127.90  
124.94  
121.81

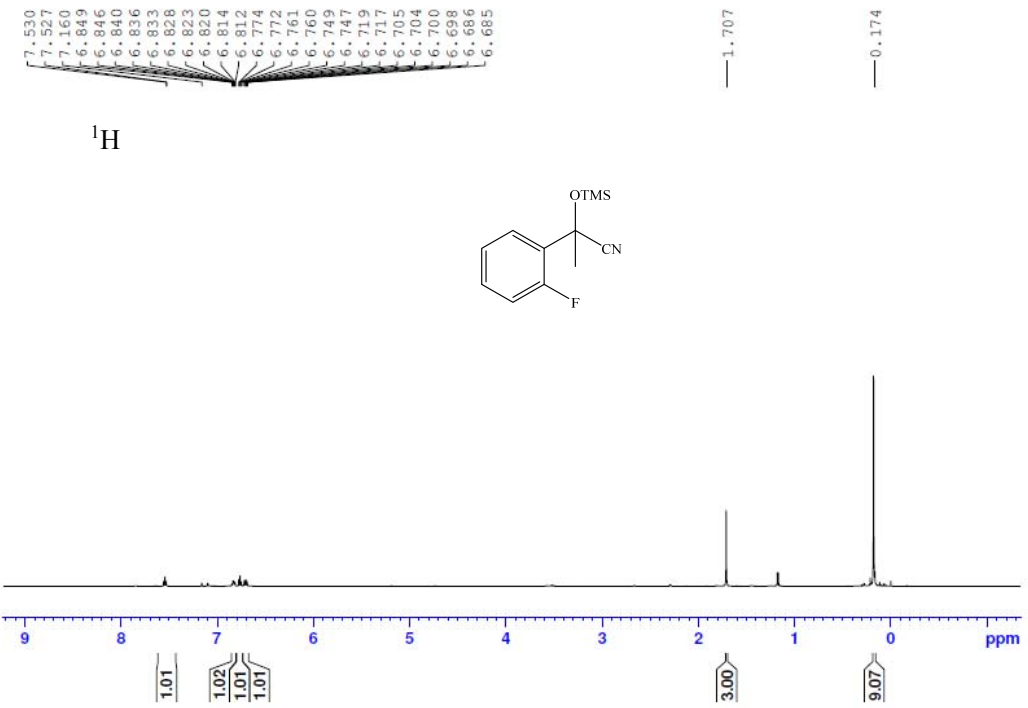
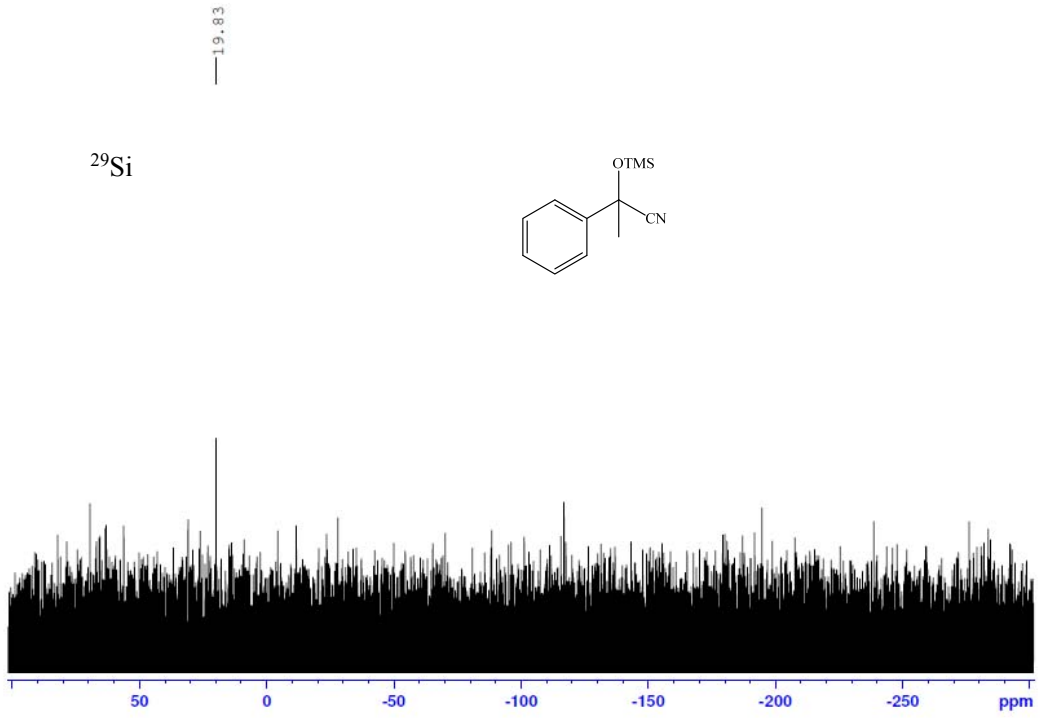
71.98

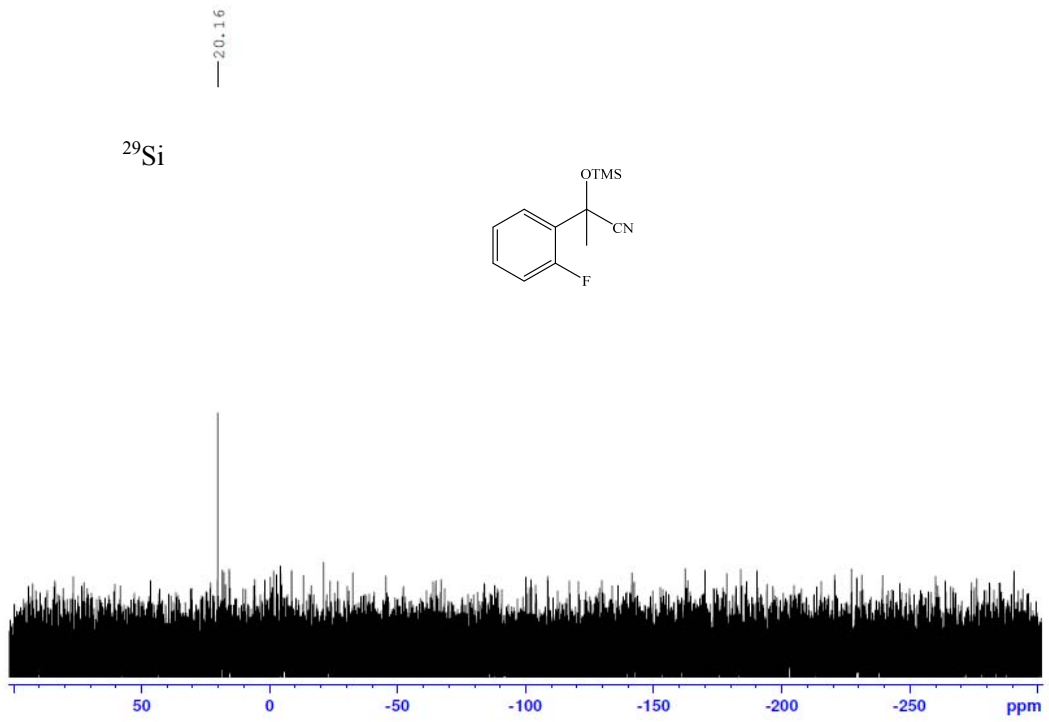
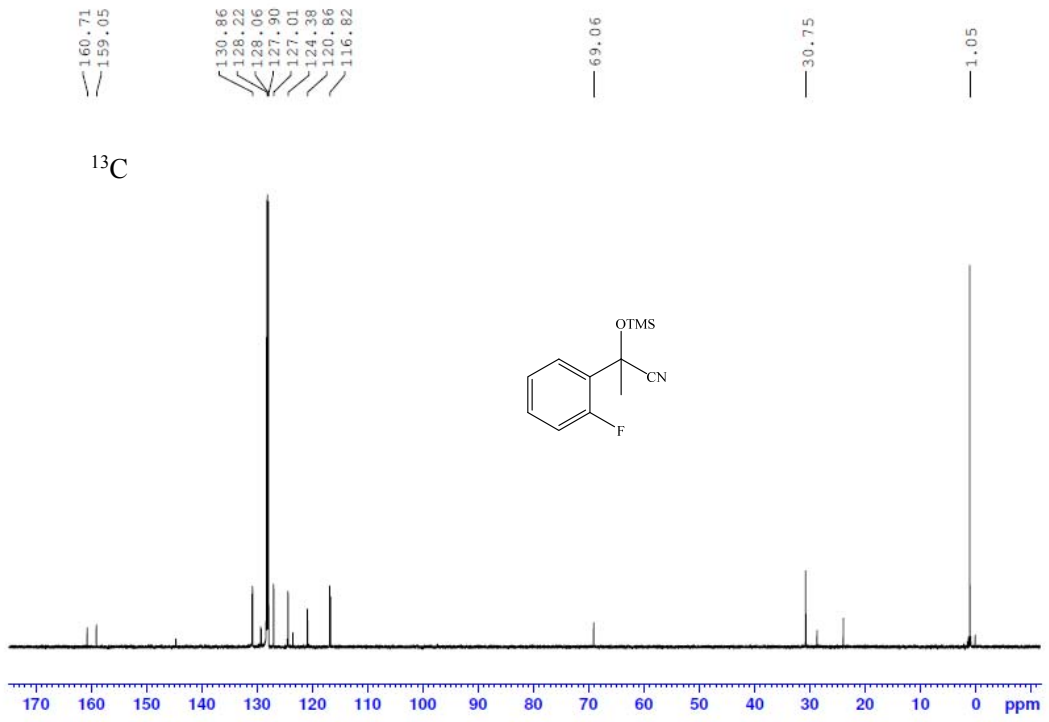
33.51

1.07

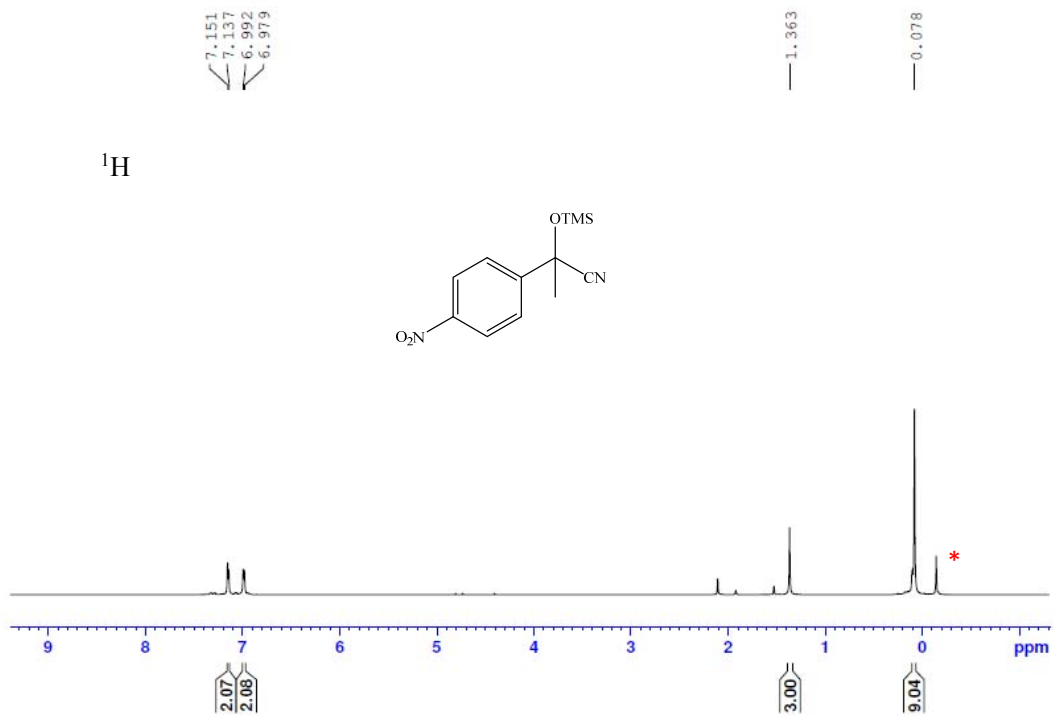
<sup>13</sup>C



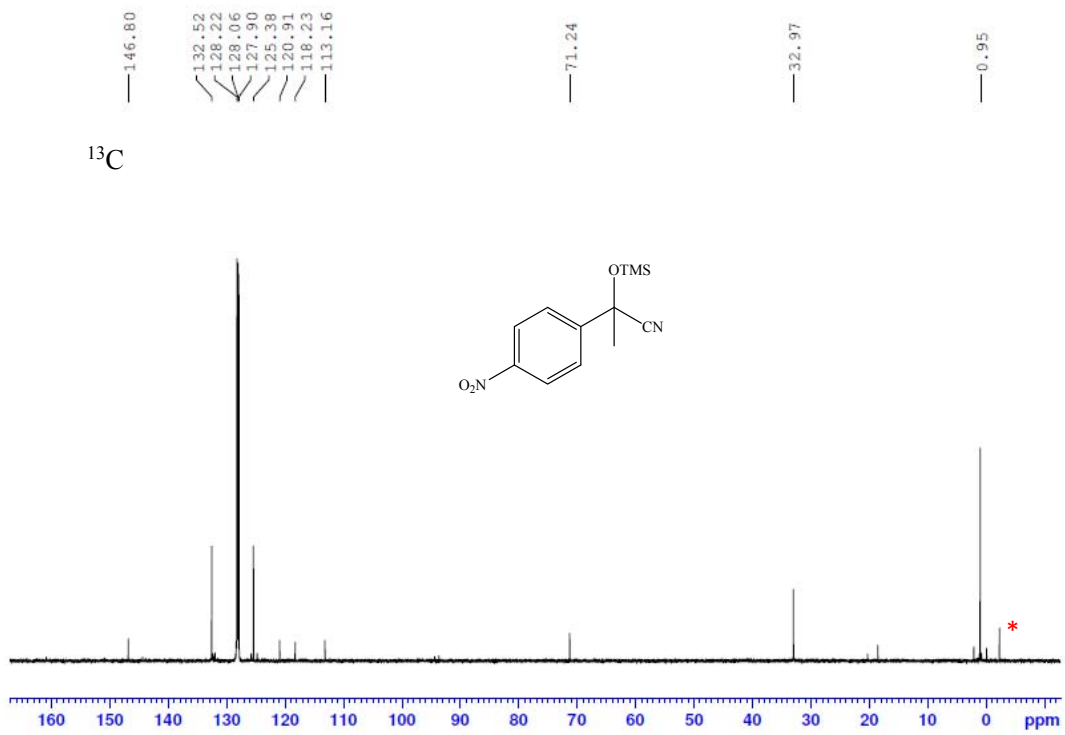


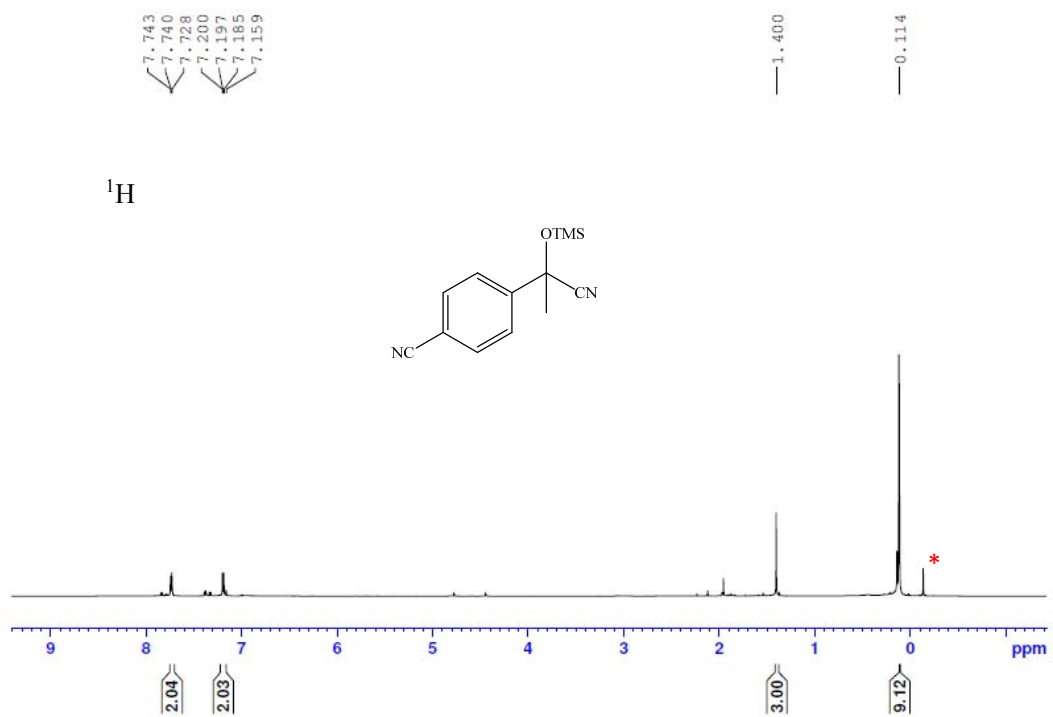
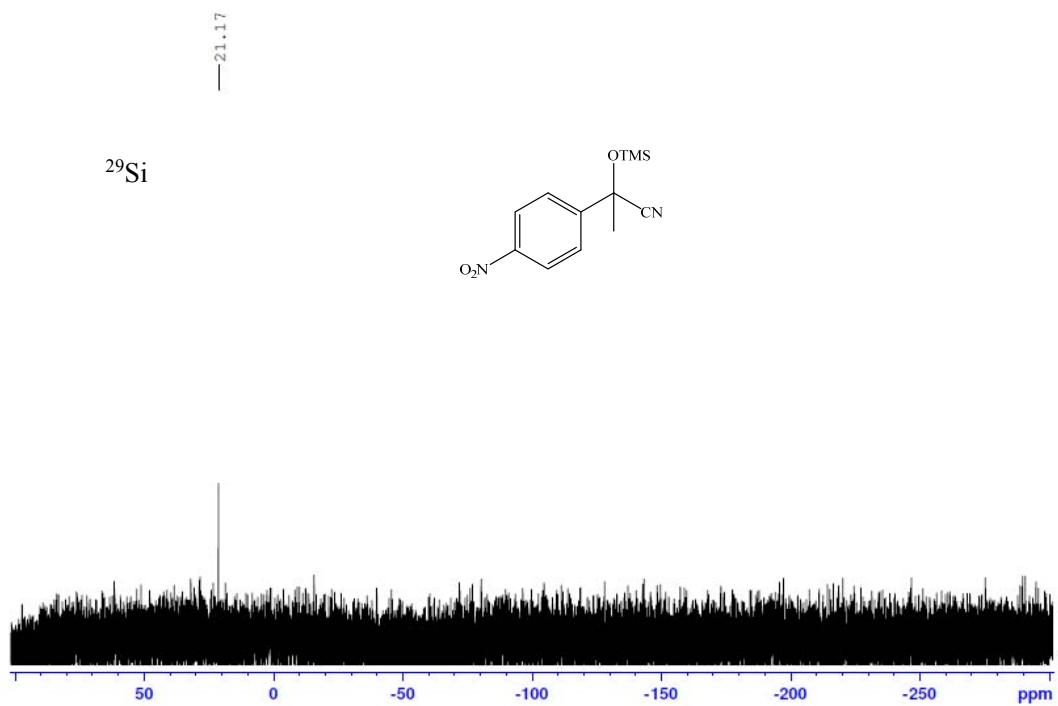


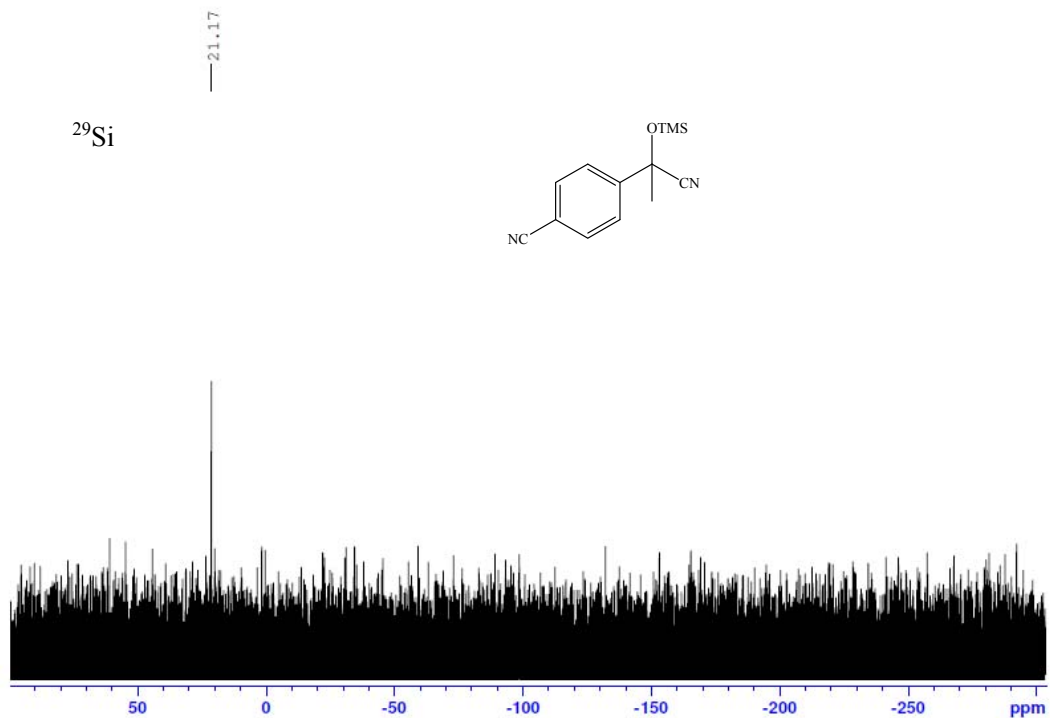
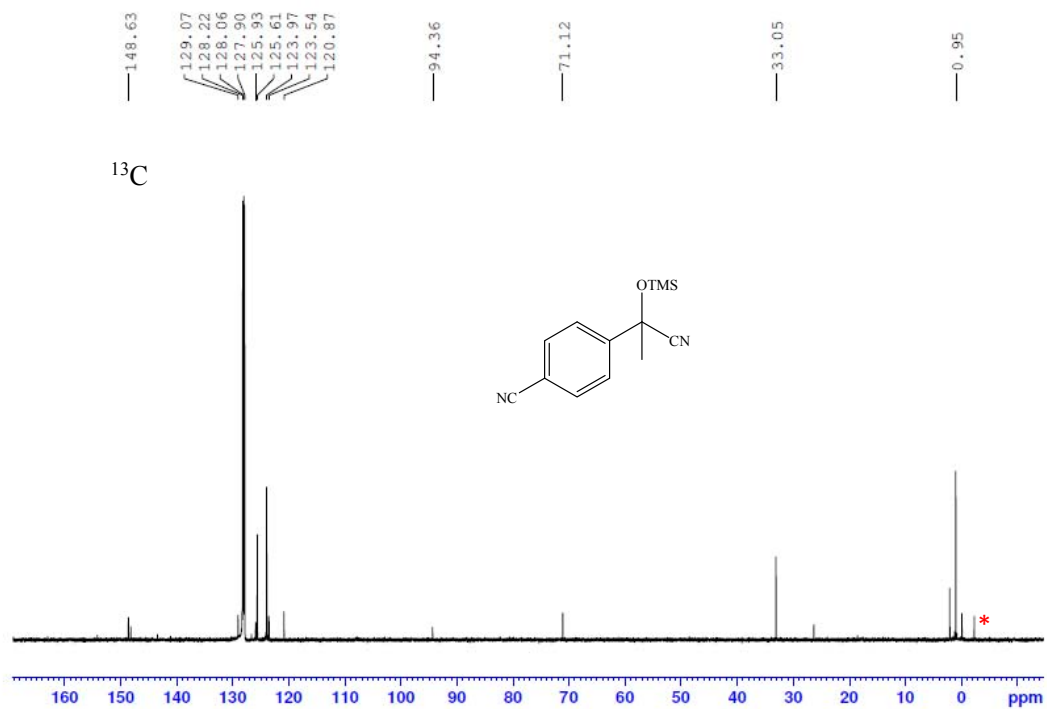
$^1\text{H}$



$^{13}\text{C}$







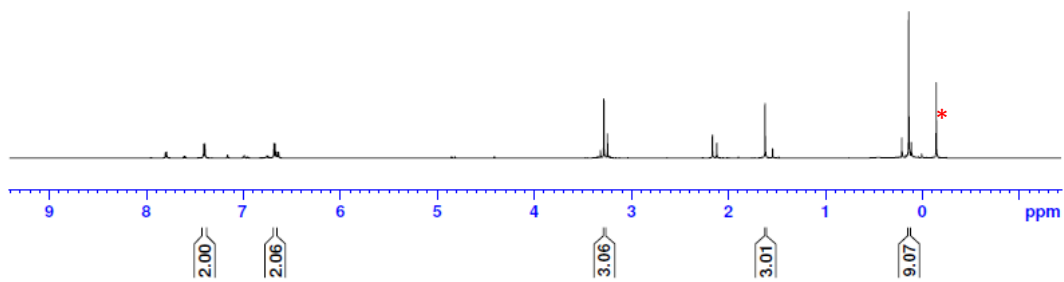
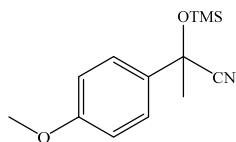
7.407  
7.393  
7.160  
6.681  
6.666

3.279

1.619

0.137

$^1\text{H}$



160.32

134.45  
130.73  
128.22  
128.06  
127.90  
126.41  
122.06  
114.24  
113.86

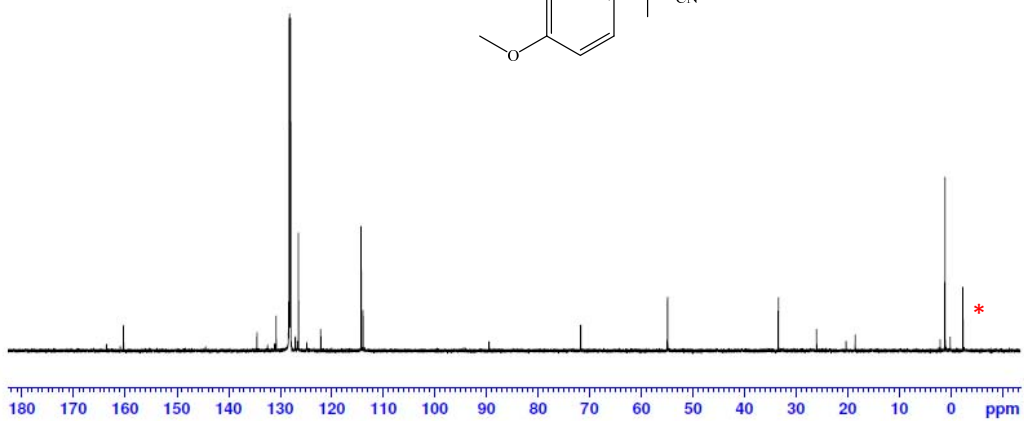
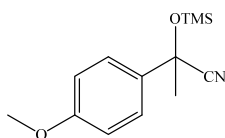
71.72

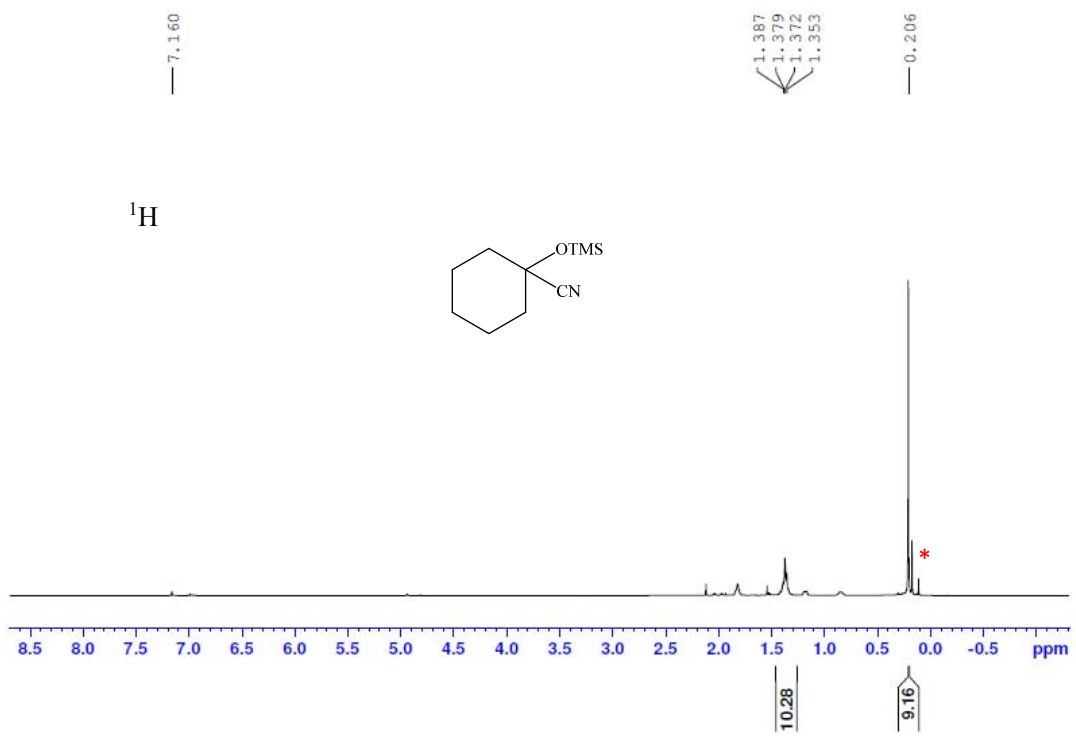
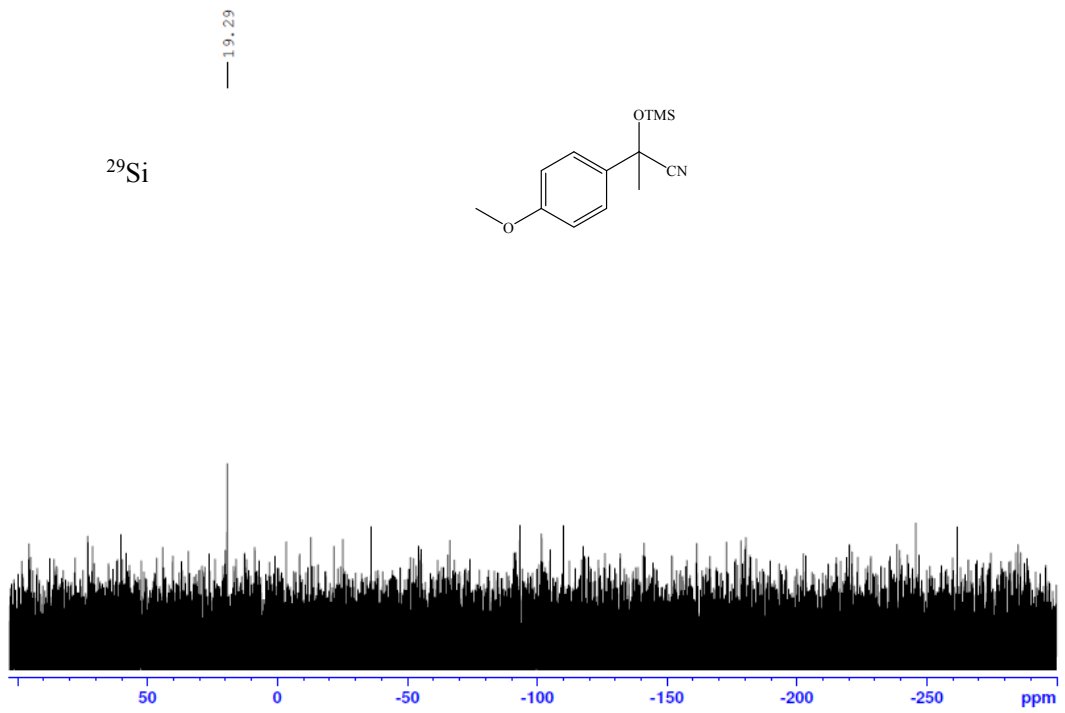
54.87

33.42

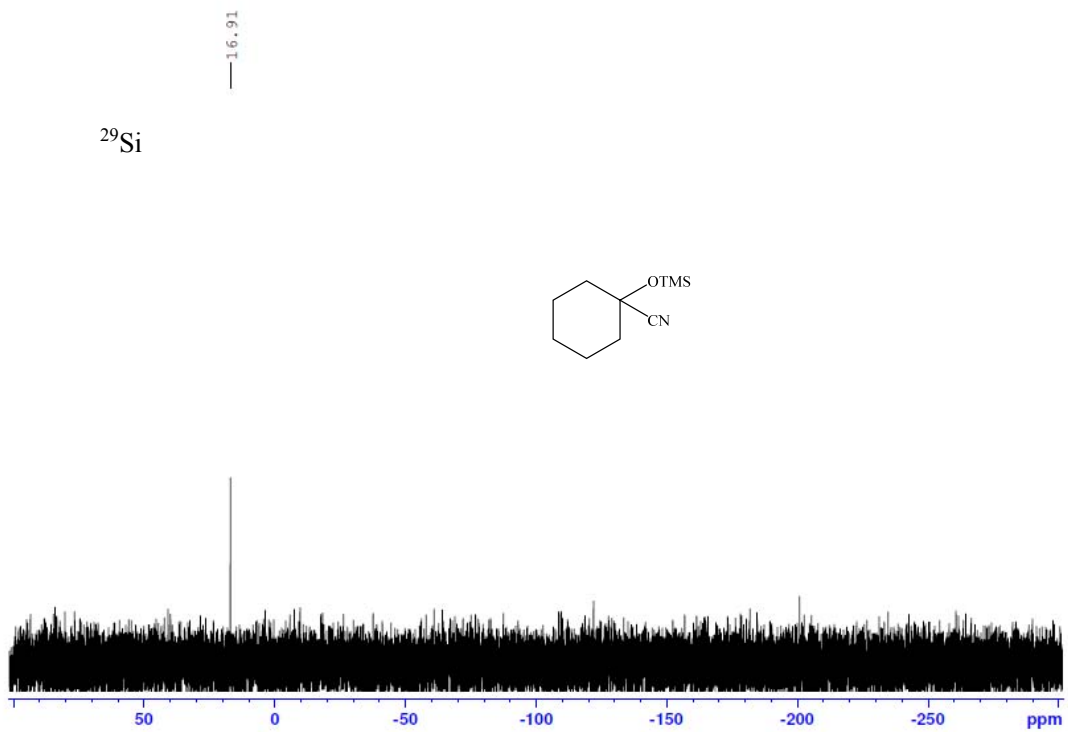
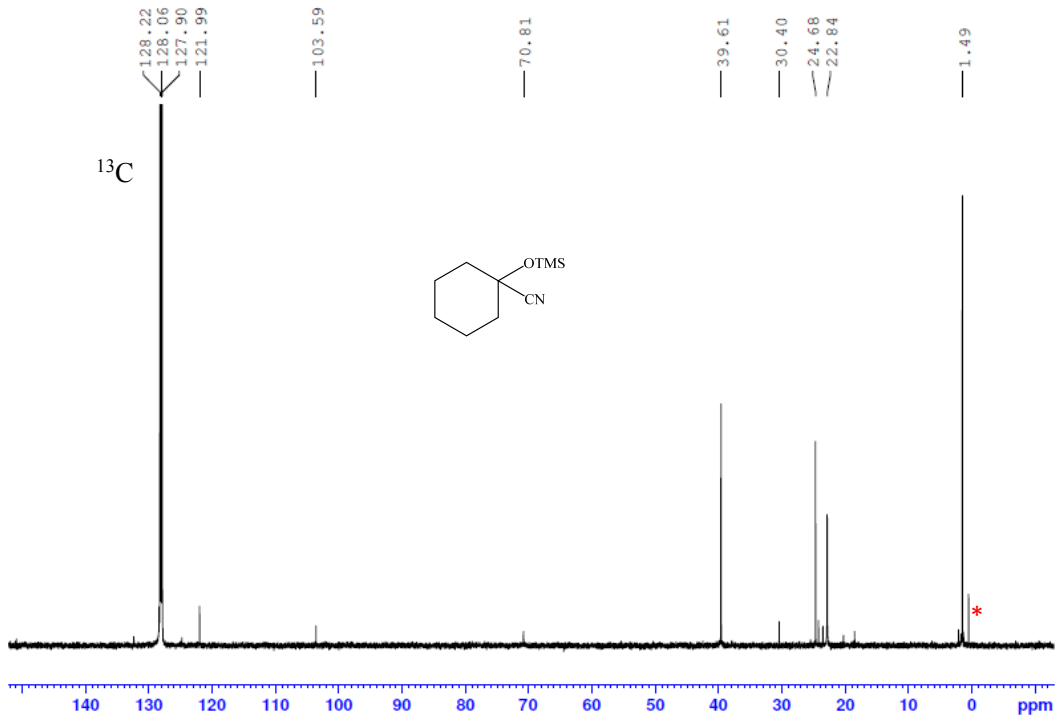
1.13

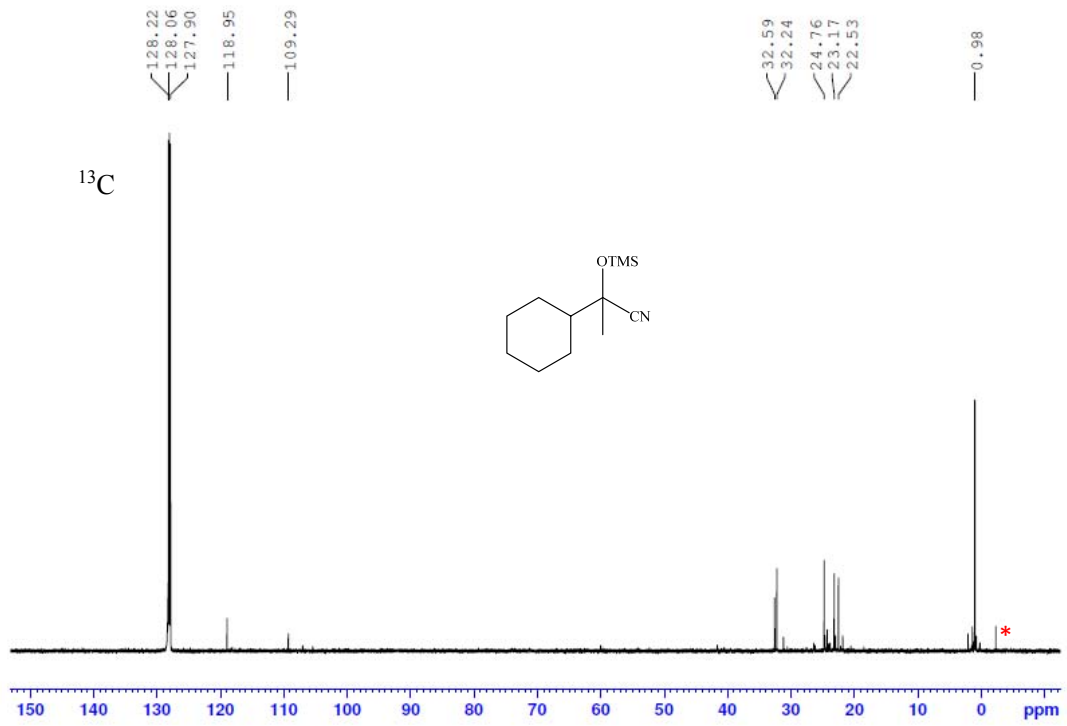
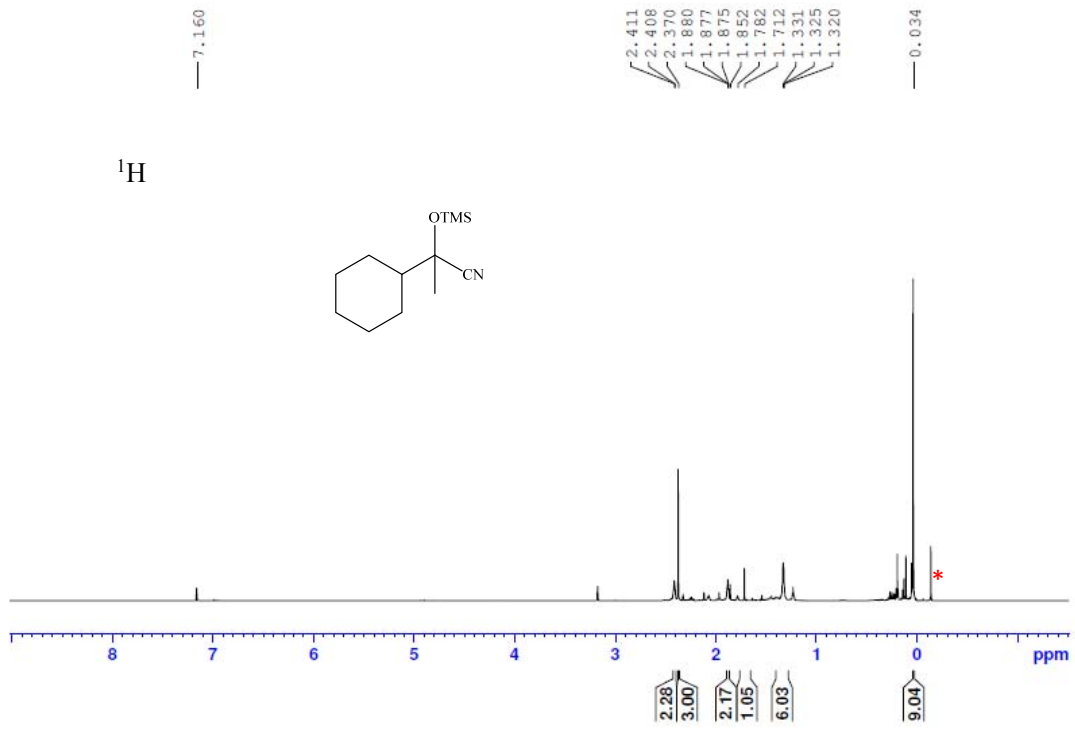
$^{13}\text{C}$











—17.72

$^{29}\text{Si}$

