

2-1-2013

# Spectral Data for "Generation of Molecular Complexity from Cyclooctatetraene: Preparation of Optically Active Protected Aminocycloheptitols and Bicyclo[4.4.1]undecatriene"

Mohamed F. El-Mansy  
*Marquette University*

Anobick Sar  
*Marquette University*

Sergey V. Lindeman  
*Marquette University, sergey.lindeman@marquette.edu*

William A. Donaldson  
*Marquette University, william.donaldson@marquette.edu*

---

*Electronic Supporting Information*

**Generation of molecular complexity from cyclooctatetraene. Preparation of optically active protected aminocycloheptitols and bicyclo[4.4.1]undecatriene**

Mohamed F. El-Mansy, Anobick Sar, Sergey Lindeman and William A. Donaldson\*

Preparation of tricarbonyl(6-styrylcyclohepta-2,4-diene-1-ol)iron ( $\pm$ )- <b>8f</b>	S2
Reaction of ( $\pm$ )- <b>7</b> with triphenylphosphine	S3
Dimethyl 2-allyl-2-(6-styryl-2,4-cycloheptadien-1-yl)propanedioate ( $\pm$ )- <b>9b</b>	S3
10,10-Bis(methoxycarbonyl)bicyclo[4.4.1]undeca-2,4,6-triene ( $\pm$ )- <b>10</b>	S4
Dimethyl 2-(2'-propynyl)-2-(6-styryl-2,4-cycloheptadien-1-yl)propanedioate ( $\pm$ )- <b>9c</b>	S4
<i>N</i> -(6-Styryl-2,4-cycloheptadien-1-yl)- <i>N</i> -toluenesulfonyl-allylamine ( $\pm$ )- <b>9e</b>	S5
<i>N</i> -Toluenesulfonyl-2-azabicyclo[4.4.1]undeca-5,7,9-triene ( $\pm$ )- <b>12</b>	S6
6-Styryl-2,4-cycloheptadiene-1-ol ( $\pm$ )- <b>9f</b>	S6
2-Phthalimido-4-(2'-styryl)-6,7-dioxabicyclo[3.2.2]non-8-ene ( $\pm$ )- <b>13</b>	S7
4-Phthalimido-6-(2'-styryl)-3,7-dihydroxycycloheptene ( $\pm$ )- <b>14</b>	S7
<i>N</i> -(2,5-Diacetoxy-6-styryl-3-cyclohepten-1-yl)phthalimide ( $\pm$ )- <b>15</b>	S8
Bis(dinitrobenzoate) PTAD adduct (+)- <b>24</b>	S8
( <i>S</i> )-Mosher's ester of (+)- <b>17</b>	S9
( <i>S</i> )-Mosher's ester of (-)- <b>17</b>	S9
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>8a</b> (CDCl <sub>3</sub> )	S11
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>8a</b> (CDCl <sub>3</sub> )	S12
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>8d</b> (CDCl <sub>3</sub> )	S13
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>8d</b> (CDCl <sub>3</sub> )	S14
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>8f</b> (CDCl <sub>3</sub> )	S15
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>8f</b> (CDCl <sub>3</sub> )	S16
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>8g</b> (CDCl <sub>3</sub> )	S17
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>8g</b> (d <sub>6</sub> -acetone)	S18
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>9b</b> (CDCl <sub>3</sub> )	S19
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>9b</b> (CDCl <sub>3</sub> )	S20
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>9c</b> (CDCl <sub>3</sub> )	S21
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>9c</b> (CDCl <sub>3</sub> )	S22
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>9d</b> (CDCl <sub>3</sub> )	S23
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>9d</b> (CDCl <sub>3</sub> )	S24
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>9e</b> (CDCl <sub>3</sub> )	S25
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>9e</b> (CDCl <sub>3</sub> )	S26
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>9f</b> (CDCl <sub>3</sub> )	S27
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>9f</b> (CDCl <sub>3</sub> )	S28
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>10</b> (CDCl <sub>3</sub> )	S29
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>10</b> (CDCl <sub>3</sub> )	S30
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>12</b> (CDCl <sub>3</sub> )	S31
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>12</b> (CDCl <sub>3</sub> )	S32
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>13</b> (CDCl <sub>3</sub> )	S33
<sup>13</sup> C NMR spectrum of ( $\pm$ )- <b>13</b> (CDCl <sub>3</sub> )	S34
<sup>1</sup> H NMR spectrum of ( $\pm$ )- <b>14</b> (d <sub>6</sub> -acetone)	S35

<sup>13</sup> C NMR spectrum of (±)- <b>14</b> (CD <sub>3</sub> OD)	S36
<sup>1</sup> H NMR spectrum of (±)- <b>15</b> (CDCl <sub>3</sub> )	S37
<sup>13</sup> C NMR spectrum of (±)- <b>15</b> (CDCl <sub>3</sub> )	S38
<sup>1</sup> H NMR spectrum of (±)- <b>16</b> (CDCl <sub>3</sub> )	S39
<sup>13</sup> C NMR spectrum of (±)- <b>16</b> (CDCl <sub>3</sub> )	S40
<sup>1</sup> H NMR spectrum of (±)- <b>17</b> (CDCl <sub>3</sub> )	S41
<sup>13</sup> C NMR spectrum of (±)- <b>17</b> (CDCl <sub>3</sub> )	S42
<sup>1</sup> H NMR spectrum of (±)- <b>18</b> (CDCl <sub>3</sub> )	S43
<sup>13</sup> C NMR spectrum of (±)- <b>18</b> (CDCl <sub>3</sub> )	S44
<sup>1</sup> H NMR spectrum of (±)- <b>19</b> (CDCl <sub>3</sub> )	S45
<sup>13</sup> C NMR spectrum of (±)- <b>19</b> (CDCl <sub>3</sub> )	S46
<sup>1</sup> H NMR spectrum of (±)- <b>20</b> (CD <sub>3</sub> OD)	S47
<sup>13</sup> C NMR spectrum of (±)- <b>20</b> (CD <sub>3</sub> OD)	S48
<sup>1</sup> H NMR spectrum of (-)- <b>22</b> (CDCl <sub>3</sub> )	S49
<sup>13</sup> C NMR spectrum of (-)- <b>22</b> (CDCl <sub>3</sub> )	S50
<sup>1</sup> H NMR spectrum of (+)- <b>23</b> (CDCl <sub>3</sub> )	S51
<sup>13</sup> C NMR spectrum of (+)- <b>23</b> (CDCl <sub>3</sub> )	S52
<sup>1</sup> H NMR spectrum of (+)- <b>24</b> (CDCl <sub>3</sub> )	S53
<sup>13</sup> C NMR spectrum of (+)- <b>24</b> (CDCl <sub>3</sub> )	S54
<sup>1</sup> H NMR spectrum of (+)- <b>25</b> (CDCl <sub>3</sub> )	S55
<sup>13</sup> C NMR spectrum of (+)- <b>25</b> (CDCl <sub>3</sub> )	S56
<sup>1</sup> H NMR spectrum of (+)- <b>26</b> (CDCl <sub>3</sub> )	S57
<sup>13</sup> C NMR spectrum of (+)- <b>26</b> (CDCl <sub>3</sub> )	S58
<sup>1</sup> H NMR spectrum of <b>27</b> (d <sub>6</sub> -acetone)	S59
<sup>1</sup> H NMR spectrum of <b>28</b> (d <sub>6</sub> -acetone)	S60
ORTEP of (6-styryl-2,4-cycloheptadien-1-yl)phthalimide (±)- <b>9d</b>	S61

**Tricarbonyl(6-styrylcyclohepta-2,4-diene-1-ol)iron (±)-8f.** In a 500 mL round bottomed flask, solid (±)-**7** (4.10 g, 9.71 mmol) was dissolved in water (250 mL) and the mixture was stirred for 20 min. To the clear light yellow solution was added solid sodium bicarbonate (8.07 g, 95.2 mmol). After a few minutes, a yellow colored solid began to precipitate. The reaction mixture was stirred for 45 min, at which time it was extracted several times with dichloromethane. The combined extracts were washed with brine, dried (MgSO<sub>4</sub>) and concentrated. The yellow sticky, foamy residue was purified by column chromatography (Al<sub>2</sub>O<sub>3</sub>, hexanes-ethyl acetate = 4:1) to afford (±)-**8f** (2.37 g, 70%) as a yellow solid: m.p. 122-126 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ = 7.36-7.20 (m, 5H; Ar-H), 6.37 (d, *J* = 16.0 Hz, 1H; H-9), 5.98 (dd, *J* = 8.0, 16.0 Hz, 1H; H-8), 5.45-5.39 (m, 1H; H3 or H4), 5.37-5.31 (m, 1H; H3 or H4), 4.18-4.10 (m, 1H; H-1), 2.97-2.82 (m, 3H; H-2, H-5 & H-6), 1.78-1.68 (m, 2H; H-7' & OH), 1.04 ppm (q, *J* = 12.0 Hz, 1H; H-7); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 210.0 (M-C=O), 137.4, 135.7, 128.9, 128.8, 127.6, 126.4, 88.2,

88.17, 70.8, 62.2, 62.0, 43.1, 38.6 ppm. IR (KBr):  $\nu = 3200-3400, 2049, 1979, 746, 693 \text{ cm}^{-1}$ ; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Fe}+\text{Na}^+$ : 375.0296 [ $M+\text{Na}^+$ ]; found: 375.0291.

**Reaction of ( $\pm$ )-7 with triphenylphosphine.** To a stirring suspension of ( $\pm$ )-7 (300 mg, 0.710 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) at room temperature under nitrogen was added triphenylphosphine (186 mg, 0.710 mmol). The mixture was stirred for 45 min, the clear light yellow solution was concentrated and dried. The glassy solid residue was washed with pentane and dried under high vacuum to afford ( $\pm$ )-8g (410 mg, 83%) as a glassy light yellow solid: m.p. 155-158 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.85-7.70$  (m, 15H;  $\text{PPh}_3$ ), 7.37-7.15 (m, 5H;  $\text{C}_6\text{H}_5$ ), 6.44 (d,  $J = 15.2$  Hz, 1H; H-9), 5.88 (dd,  $J = 8.6, 15.2$  Hz, 1H; H-8), 5.35-5.30 (narrow m, 1H; C=CH), 5.05-4.95 (narrow m, 1H; C=CH), 4.23 (t,  $J = 12.0$  Hz, 1H; H-1), 3.13 (br t,  $J = 9.6$  Hz, 1H; H-2), 3.02 (d,  $J = 7.2$  Hz, 1H; H-5), 1.93-1.82 (m, 1H; H-7'), 1.15-1.00 ppm (m, 1H; H-7);  $^{13}\text{C}$  NMR (75 MHz,  $d_6$ -acetone)  $\delta = 206.4, 136.0$  (d,  $J_{\text{PC}} = 2.8$  Hz), 135.1 (d,  $J_{\text{PC}} = 9.2$  Hz), 134.4 (d,  $J_{\text{PC}} = 19.6$  Hz), 131.4 (d,  $J_{\text{PC}} = 11.9$  Hz), 130.0 (d,  $J_{\text{PC}} = 44.0$  Hz), 129.5 (d,  $J_{\text{PC}} = 6.6$  Hz), 129.4, 128.3, 127.1, 118.5 (d,  $J_{\text{PC}} = 81.3$  Hz), 90.9, 88.4 (d,  $J_{\text{PC}} = 1.7$  Hz), 62.5, 49.4 (d,  $J_{\text{PC}} = 6.4$  Hz), 42.8 (d,  $J_{\text{PC}} = 14.0$  Hz), 34.5 (d,  $J_{\text{PC}} = 35.8$  Hz), 30.1 ppm. A satisfactory elemental analysis was not obtained for this product.

**Dimethyl 2-allyl-2-(6-styryl-2,4-cycloheptadien-1-yl)propanedioate ( $\pm$ )-9b.** A flame dried 200 mL Schlenk flask was charged with freshly distilled ether (120 mL) at 0 °C under nitrogen. To an ethereal solution of lithium dimethyl allylmalonate (6.16 mmol, freshly prepared from dimethyl allylmalonate and *n*-BuLi, 1.6M in hexane) was added solid ( $\pm$ )-7 (2.0 g, 4.7 mmol) and the mixture was stirred for 3 h at room temperature. The reaction mixture was quenched with water and extracted several times with ether. The combined ether extracts were washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated. The residue was purified by column chromatography ( $\text{SiO}_2$ , hexanes-ethyl acetate = 4:1) to afford a mixture of product and dimethyl allylmalonate (2.608 g). The mixture (2.608 g) was dissolved in methanol (100 mL) and ceric ammonium nitrate (7.50 gm, 13.7 mmol) was added, and the mixture stirred for 1 h at room temperature. The mixture was concentrated, diluted with water and extracted several times with ether. The combined ether extracts were washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated. The residue was purified by column chromatography ( $\text{SiO}_2$ , hexanes-ethyl acetate = 20:1) to afford ( $\pm$ )-9b (1.17 gm, 67%) as a colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.34-7.15$  (m, 5H;  $\text{C}_6\text{H}_5$ ), 6.41 (d,  $J = 15.9$  Hz, 1H; H-9), 6.11 (ddd,  $J = 1.1, 8.1, 15.7$  Hz, 1H; H-8), 5.87-5.69 (br m, 5H; H-2,



H-3, H-4, H-5 &  $CH=CH_2$ ), 5.09-5.0 (m, 2H;  $C=CH_2$ ), 3.72 (s, 6H; 2 x  $OCH_3$ ), 3.48-3.38 (br m, 1H; H-6), 3.11 (br d,  $J = 8.7$  Hz, 1H; H-1), 2.78-2.60 (m, 2H;  $CH_2-CH=CH_2$ ), 2.09 (dd,  $J = 5.4$ , 13.3 Hz, 1H; H-7'), 1.68-1.55 ppm (m, 1H; H-7);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta = 171.4$  ( $CO_2Me$ ), 137.6, 137.0, 134.3, 133.2, 132.8, 129.6, 128.7, 127.3, 126.3, 124.7, 124.4, 119.1, 61.7, 52.5, 47.4, 43.0, 38.8, 37.9 ppm; HRMS (ESI):  $m/z$  calcd for  $C_{23}H_{26}O_4+Na^+$ : 389.1729 [ $M+Na^+$ ]; found: 389.1728.

**10,10-Bis(methoxycarbonyl)bicyclo[4.4.1]undeca-2,4,6-triene ( $\pm$ )-10.** To a stirring solution of ( $\pm$ )-**9b** (30.0 mg, 0.0820 mmol) in  $CH_2Cl_2$  (2 mL) at room temperature was added Grubbs 1<sup>st</sup> generation catalyst (3 mg, 5 mol%). The reaction mixture was stirred for 45 min, concentrated and the residue was purified by column chromatography ( $SiO_2$ , hexanes-ethyl acetate = 20:1) to afford ( $\pm$ )-**10** (19 mg, 88%) as a colorless oil.  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta = 6.44$ -6.39 (m, 1H), 6.31-6.26 (m, 1H), 6.18-6.12 (m, 1H), 5.57-5.66 (m, 2H), 3.84-3.76 (m, 1H), 3.75 (s, 3H;  $OMe$ ), 3.66 (s, 3H;  $OMe$ ), 3.29 (dq,  $J = 17.3$ , 2.0 Hz, 1H), 2.96-2.89 (m, 2H), 2.85-2.75 (m, 1H), 2.55 (dd,  $J = 1.5$ , 14.2 Hz, 1H), 2.27 ppm (dd,  $J = 1.2$ , 14.2 Hz, 1H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta = 173.0$ , 171.1, 146.8, 132.9, 132.5, 131.4, 128.4, 127.4, 63.0, 52.9, 52.5, 50.6, 43.6, 40.3, 32.8 ppm; HRMS (ESI):  $m/z$  calcd for  $C_{15}H_{18}O_4$ : 262.1205 [ $M^+$ ]; found: 262.1198.

**Dimethyl 2-(2'-propynyl)-2-(6-styryl-2,4-cycloheptadien-1-yl)propanedioate ( $\pm$ )-9c.** To a solution of lithium dimethyl propargylmalonate (0.462 mmol) in THF (4 mL) [freshly prepared from dimethyl propargylmalonate and *n*-BuLi] at 0 °C under nitrogen was added ( $\pm$ )-**7** (150 mg, 0.355 mmol) and the mixture was stirred for 3 h. The reaction mixture was quenched with water, extracted several times with ether, and the combined ethereal extracts were washed with brine, dried ( $Na_2SO_4$ ) and concentrated. The residue was purified by column chromatography ( $SiO_2$ , hexanes-ethyl acetate = 4:1) to afford a mixture of ( $\pm$ )-**8c** and unreacted dimethyl propargylmalonate (136 mg).  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta = 7.35$ -7.19 (m, 5H; Ar-H), 6.34 (d,  $J = 15.6$  Hz, 1H; H-9), 5.93 (dd,  $J = 8.4$ , 15.9 Hz, 1H; H-8), 5.36-5.25 (m,  $J = 6.9$  Hz, 2H; H-3 & H-4), 3.80 (s, 3H;  $OCH_3$ ), 3.77 (s, 3H;  $OCH_3$ ), 3.08-2.99 (m, 2H), 2.91-2.71 (m, 4H), 2.07 (t,  $J = 2.1$  Hz, 1H;  $C\equiv CH$ ), 1.38 (d,  $J = 12.4$  Hz, 1H; H-7'), 0.90 ppm (q,  $J = 12.3$  Hz, 1H; H-7);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta = 170.0$ , 169.8, 137.3, 136.4, 128.7, 127.5, 126.3, 89.2, 88.0, 79.3, 71.9, 62.9, 61.2, 58.2, 53.0, 52.9, 43.4, 42.3, 31.2, 22.7 ppm, the signal for the  $M-CO$  was not observed. The mixture (136 mg) was dissolved in methanol (4 mL) and ceric ammonium nitrate (0.44 g, 0.81 mmol) was added. The mixture stirred for 2 h at room temperature and then

concentrated. Water was added to the residue and this mixture was extracted several times with  $\text{CH}_2\text{Cl}_2$ . The combined  $\text{CH}_2\text{Cl}_2$  extracts were washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. The residue was purified by column chromatography ( $\text{SiO}_2$ , hexanes–ethyl acetate = 4:1) to afford a ( $\pm$ )-**9c** (42 mg, 33%) as a yellow oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.36–7.17 (m, 5H;  $\text{C}_6\text{H}_5$ ), 6.46 (d,  $J$  = 15.9 Hz, 1H; H-9), 6.14 (dd,  $J$  = 7.8, 15.9 Hz, 1H; H-8), 5.85–5.76 (m, 4H; H-2, H-3, H-4 & H-5), 3.76 (s, 6H; 2 x OMe), 3.59–3.47 (br m, 1H; H-6), 3.41 (br d,  $J$  = 9.3 Hz, 1H; H-1), 2.94 (d,  $J$  = 2.4 Hz, 2H;  $\text{CH}_2\text{C}\equiv\text{CH}$ ), 2.19 (dd,  $J$  = 5.7, 13.2 Hz, 1H; H-7'), 2.06 (t,  $J$  = 2.7 Hz, 1H;  $\text{C}\equiv\text{CH}$ ), 1.69 ppm (td,  $J$  = 9.0, 12.6 Hz, 1H; H-7);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  = 170.3 ( $\text{CO}_2\text{Me}$ ), 137.5, 137.1, 133.4, 132.6, 129.6, 128.6, 127.3, 126.2, 124.8, 124.5, 79.1, 71.9, 60.2, 52.8 (OMe), 47.2, 42.5 (C-6), 37.4 (C-7), 27.0, 23.8 ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{24}\text{O}_4+\text{Na}^+$ : 387.1567 [ $M+\text{Na}^+$ ]; found: 387.1569.

***N*-(6-Styryl-2,4-cycloheptadien-1-yl)-*N*-toluenesulfonyl-allylamine ( $\pm$ )-**9e**.** To a solution of ( $\pm$ )-**7** (0.10 g, 0.24 mmol) in acetonitrile (10 mL), under  $\text{N}_2$ , was added the potassium salt of tosyl allylamine (0.140 g, 0.562 mmol). The mixture was stirred for 2 h, at which time TLC indicated the disappearance of **7**. The reaction mixture was dried under reduced pressure and the solid residue was purified by column chromatography ( $\text{SiO}_2$ , hexanes–ethyl acetate = 4:1) to give the product (0.113 g, 86%) as a yellow foam: m.p. 47–48 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.77 (d,  $J$  = 8.0 Hz, 2H; Ar-H), 7.38–7.20 (m, 7H; Phth and ArH), 6.33 (d,  $J$  = 15.2 Hz, 1H; H-9), 5.94–5.80 (m, 2H), 5.33–5.22 (m, 3H), 5.14 (d,  $J$  = 10.4 Hz, 1H;  $\text{C}=\text{CH}_2$ ), 4.38 (dd,  $J$  = 3.6, 12.0 Hz, 1H; H-1), 3.93 (dd,  $J$  = 5.2, 16.8 Hz, 1H;  $\text{NCH}_2\text{CH}=\text{CH}_2$ ), 3.68 (dd,  $J$  = 6.0, 16.8 Hz, 1H;  $\text{NCH}_2\text{CH}=\text{CH}_2$ ), 2.92–2.82 (m, 2H), 2.40 (s, 3H;  $\text{PhCH}_3$ ), 1.91 (d,  $J$  = 7.2 Hz, 1H), 1.55 (br d,  $J$  = 13.2 Hz, 1H), 1.14 ppm (q,  $J$  = 12.4 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 143.8, 137.9, 137.1, 136.5, 135.2, 130.1, 129.1, 128.8, 127.6, 127.3, 126.3, 117.0, 88.6, 88.3, 61.5, 58.6, 57.1, 46.2, 44.0, 36.4, 21.6 ppm; IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu$  = 2047, 1965, 1338, 1157  $\text{cm}^{-1}$ . This compound was utilized in the next step without further characterization. To the prior complex (0.277 g, 0.509 mmol) in acetonitrile (15 mL), under  $\text{N}_2$ , was added cerium ammonium nitrate (0.47 g, 0.858 mmol). The mixture was stirred at room temperature for 1 h, at which time TLC indicated complete disappearance of starting material. The reaction mixture was filtered through a short column of silica gel, which was washed with  $\text{CH}_2\text{Cl}_2$  until all of the product was eluted. These fractions were combined, concentrated, and the residue was purified by column chromatography ( $\text{SiO}_2$ , hexanes–ethyl acetate = 17:3) to give ( $\pm$ )-**9e** (0.106 g, 51%) as a faint yellow oil.  $^1\text{H}$  NMR

NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.77 (d,  $J$  = 8.0 Hz, 2H; Ar-H), 7.38-7.20 (m, 7H; Phth and Ar-H), 6.39 (d,  $J$  = 15.9 Hz, 1H; H-9), 6.11 (dd,  $J$  = 8.4, 15.9 Hz, 1H; H-8), 5.91 (tdd,  $J$  = 6.0, 10.5, 17.1 Hz, 1H; CH=CH<sub>2</sub>), 5.75-5.6 (m, 3H; CH=CH-CH=H), 5.39 (br d,  $J$  = 11.1 Hz, 1H; CH=CH<sub>2</sub>), 5.23 (dd,  $J$  = 1.5, 16.8 Hz, 1H; CH=CH<sub>2</sub>), 5.13 (dd,  $J$  = 0.9, 8.7 Hz, 1H), 4.94-4.85 (m, 1H; H-1), 3.85 (dd,  $J$  = 6.0, 16.5 Hz, 1H; NCH<sub>2</sub>CH=CH<sub>2</sub>), 3.73 (dd,  $J$  = 6.0, 16.5 Hz, 1H; NCH<sub>2</sub>CH=CH<sub>2</sub>), 3.42-3.30 (m, 1H; H-6), 2.42 (s, 3H; PhCH<sub>3</sub>), 2.08 (td,  $J$  = 10.9, 12.6 Hz, 1H; H-7'), 1.96 ppm (br d,  $J$  = 12.6 Hz, 1H; H-7); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 143.5, 137.9, 137.6, 137.3, 136.1, 134.4, 132.6, 129.9, 129.8, 128.8, 127.5, 127.4, 126.3, 125.1, 123.9, 117.6, 59.1, 47.9, 43.2, 39.0, 21.7 ppm. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  = 1336, 1162 cm<sup>-1</sup>; HRMS (ESI):  $m/z$  calcd for C<sub>25</sub>H<sub>27</sub>NO<sub>4</sub>S+Na<sup>+</sup>: 428.1660 [ $M$ +Na<sup>+</sup>]; found: 428.1657.

***N*-Toluenesulfonyl-2-azabicyclo[4.4.1]undeca-5,7,9-triene (±)-12.** To a solution of (±)-**9e** (60 mg, 0.15 mmol) in freshly distilled dichloromethane (20 mL), was added Grubbs' 2<sup>nd</sup> generation catalyst (7 mg, 0.008 mmol, 5 mol %). The reaction mixture was stirred under N<sub>2</sub> and the reaction progress was monitored by <sup>1</sup>H NMR spectroscopy. After 4 h all signals for the starting material had disappeared. The reaction mixture was concentrated under a flow of N<sub>2</sub>, and the residue purified by column chromatography (SiO<sub>2</sub>, hexanes-ethyl acetate = 4:1) to afford (±)-**12** (37 mg, 82%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.73 and 7.3 (ABq,  $J_{AB}$  = 8.2 Hz, 4H; ArH), 6.43 (qd,  $J$  = 2.0, 5.4 Hz, 1H), 6.30 (qd,  $J$  = 1.2, 5.4 Hz, 1H), 6.24-6.20 (m, 1H), 5.60-5.56 (narrow m, 2H), 4.59 (td,  $J$  = 4.0, 8.4 Hz, 1H), 4.09-4.06 (narrow m, 2H), 3.06 (ddd,  $J$  = 1.2, 3.6, 14.4 Hz, 1H), 2.99-2.97 (narrow m, 2H), 2.81 (ddd,  $J$  = 1.2, 8.8, 14.4 Hz, 1H), 2.43 ppm (s, 3H; ArCH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 144.5, 143.7, 134.8, 132.6, 131.9, 130.1, 130.0, 129.5, 127.6, 125.0, 67.6, 55.9, 44.6, 38.0, 21.7 ppm. This compound decomposed upon standing and thus a satisfactory HRMS was not obtained.

**6-Styryl-2,4-cycloheptadiene-1-ol (±)-9f.** To a solution of (±)-**8f** (0.30 g, 0.85 mmol) in methanol (12 mL), at 0 °C under N<sub>2</sub>, was added a solution of H<sub>2</sub>O<sub>2</sub> (5.70 mL, 51.0 mmol, 30 wt %). A solution of NaOH (240.0 mg, 5.950 mmol) in methanol (8 mL) was added to the reaction mixture dropwise. The reaction mixture immediately turned deep brown in color. The mixture was stirred for 30 min at 0 °C followed by another 30 min at room temperature. The mixture was quenched with water (30 mL) and extracted several times with ether. The combined extracts were washed with brine, dried (MgSO<sub>4</sub>) and concentrated. The residue was purified by column chromatography (SiO<sub>2</sub>, hexanes-ethyl acetate = 4:1) to afford (±)-**9f** (90.0 mg, 50%) as a

colorless foamy solid; m.p. = 59-63 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.42-7.20 (m, 5H;  $\text{C}_6\text{H}_5$ ), 6.48 (d,  $J$  = 16.0 Hz, 1H; H-9), 6.24 (dd,  $J$  = 8.2, 16.0 Hz, 1H; H-8), 5.90-5.69 (m, 4H; olefinic H), 4.67 (d,  $J$  = 8.0 Hz, 1H; H-1), 3.50-3.42 (m, 1H; H-6), 2.30-2.15 ppm (m, 2H; H7 & H-7');  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 137.9, 137.4, 136.8, 132.5, 129.5, 128.7, 127.4, 126.3, 124.2, 122.6, 71.0, 41.9, 41.8 ppm; IR (KBr):  $\nu$  = 3400-3200, 746, 692  $\text{cm}^{-1}$ .

**2-Phthalimido-4-(2'-styryl)-6,7-dioxabicyclo[3.2.2]non-8-ene ( $\pm$ )-13.** To a 50 ml two-necked round-bottom flask equipped with condenser, was charged ( $\pm$ )-**9d** (1.00 g, 2.93 mmol) in dry  $\text{CHCl}_3$  (40 mL) and tetraphenylporphorine (36 mg, 3 mol %). The resulting deep purple solution was cooled with an ice bath and irradiated for 8 h with a 100-W halogen lamp, while ultra pure  $\text{O}_2$  was bubbled through the solution. The organic solvent was removed and the residue was purified by column chromatography ( $\text{SiO}_2$ , hexanes-ethyl acetate = 1:1) to give ( $\pm$ )-**13** (923 mg, 91%) as a colorless solid: m.p. 175-177 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 7.90-7.70 (m, 4H; Phth), 7.35-7.20 (m, 5H;  $\text{C}_6\text{H}_5$ ), 6.89 (dd,  $J$  = 8.0, 8.4 Hz, 1H; CH=CH), 6.49 (d,  $J$  = 16.2 Hz, 1H; CH=CHPh), 6.47-6.43 (m, 1H; CH=CH), 5.98 (dd,  $J$  = 8.3, 16.2 Hz, 1H; CH=CHPh), 4.85 (dd,  $J$  = 4.0, 12.8 Hz, 1H; H-2), 4.82-4.78 (m, 2H; H-1 & H-5), 3.10-2.98 (m, 1H; H-4), 2.11 (q,  $J$  = 12.7 Hz, 1H; H-3'), 1.77 ppm (td,  $J$  = 4.4, 12.8 Hz, 1H; H-3);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 167.8, 136.9, 134.5, 131.9, 131.8, 130.9, 128.8, 128.7, 127.9, 126.4, 123.9, 123.6, 81.1, 80.4, 52.0, 45.8, 29.9 ppm; elemental analysis calcd (%) for  $\text{C}_{23}\text{H}_{19}\text{NO}_4$ : C 73.98, H 5.13; found: C 73.87, H 5.27.

**4-Phthalimido-6-(2'-styryl)-3,7-dihydroxycycloheptene ( $\pm$ )-14.** To a solution of ( $\pm$ )-**13** (50 mg, 0.145 mmol) in  $\text{CH}_2\text{Cl}_2$  (1 mL) was added activated zinc dust (50 mg). To the resulting suspension was added a solution of glacial acetic acid (0.02 mL, 0.34 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) in 3 portions over 30 min. The reaction mixture was stirred at room temperature for 15 min, after which the entire mixture was loaded onto a column chromatography ( $\text{SiO}_2$ , hexanes-ethyl acetate = 2:3) to give ( $\pm$ )-**14** (47 mg, 92%) as a colorless solid; m.p. = 225-227 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  = 7.88-7.75 (m, 4H; Phth), 7.37 (d,  $J$  = 7.6 Hz, 2H; Ar-H), 7.25 (t,  $J$  = 7.6 Hz, 2H; Ar-H), 7.16 (t,  $J$  = 7.4, 1H; Ar-H), 6.46 (d,  $J$  = 16.4 Hz, 1H; H-9), 6.19 (dd,  $J$  = 9.0, 16.4 Hz, 1H; H-8), 5.80 (td,  $J$  = 2.8, 12.6 Hz, 1H; CH=CH), 5.70 (td,  $J$  = 2.8, 12.6 Hz, 1H; CH=CH), 4.99-4.93 (m, 1H; H-4), 4.25-4.10 (m, 2H; H-3 and H-7), 2.70 (td,  $J$  = 11.8, 14.0 Hz, 1H; H-5'), 2.47 (dq,  $J$  = 2.8, 10.1 Hz, 1H; H-6), 1.95 ppm (td,  $J$  = 2.8, 14.0 Hz, 1H; H-5);  $^1\text{H}$  NMR (400 MHz,  $d_6$ -acetone)  $\delta$  = 7.82 (s, 4H; Phth), 7.39 (d,  $J$  = 8.0 Hz, 2H; Ar-H), 7.28 (t,  $J$  = 7.2 Hz, 2H; Ar-H),

7.18 (tt,  $J = 1.6, 7.4$  Hz, 1H; Ar-H), 6.50 (d,  $J = 16.0$  Hz, 1H; H-9), 6.28 (dd,  $J = 8.8, 16.0$  Hz, 1H; H-8), 5.82 (td,  $J = 2.7, 12.8$  Hz, 1H, CH=CH), 5.73 (td,  $J = 2.8, 12.4$  Hz, 1H; CH=CH), 4.99-4.93 (m, 1H; H-3), 4.53 (d,  $J = 5.6$  Hz, 1H; OH), 4.31-4.25 (m, 1H; H-7), 4.16 (ddd,  $J = 3.2, 10.4, 12.4$  Hz, 1H; H-4), 3.99 (d,  $J = 4.8$  Hz, 1H; OH), 2.73 (td,  $J = 11.8, 14.4$  Hz, 1H; H-5), 2.53-2.42 (m, 1H; H-6), 2.01 ppm (td,  $J = 2.8, 14.0$  Hz, 1H; H-5');  $^{13}\text{C}$  NMR (75 MHz,  $d_6$ -acetone)  $\delta = 168.9, 138.6, 137.4, 134.9, 134.5, 133.4, 133.2, 131.9, 129.3, 127.9, 127.1, 123.7, 73.5, 70.2, 55.5, 50.5, 37.6$  ppm; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{NO}_4 + \text{Na}^+$ : 398.1363 [ $M + \text{Na}^+$ ]; found: 398.1358.

**(1S\*,2S\*,5S\*,6S\*) *N*-(2,5-Diacetoxy-6-styryl-3-cyclohepten-1(S\*)-yl)phthalimide ( $\pm$ )-15.** To a mixture of ( $\pm$ )-14 (400 mg, 1.108 mmol) and *p*-toluenesulfonyl chloride (21 mg, 0.111 mmol) was added acetic anhydride (5 mL). The resulting suspension was heated at reflux under  $\text{N}_2$  for 1 h. The reaction mixture was concentrated and the residue was purified by column chromatography ( $\text{SiO}_2$ , hexanes-ethyl acetate = 3:2) to afford ( $\pm$ )-15 (406 mg, 82%) as a colorless solid: m.p. = 65-66 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta = 7.80$ -7.63 (m, 4H; Phth), 7.25-7.10 (m, 5H;  $\text{C}_6\text{H}_5$ ), 6.34 (d,  $J = 15.6$  Hz, 1H; H-9), 6.02 (br d,  $J = 10.4$  Hz, 1H; H-2), 5.86 (dd,  $J = 9.4, 15.6$  Hz, 1H; H-8), 5.70 (br d,  $J = 13.2$  Hz, 1H; CH=CH), 5.57-5.49 (br m, 2H; H-5 & C=CH), 4.42 (t,  $J = 10.8$  Hz, 1H; H-1), 2.85 (q,  $J = 12.8$  Hz, 1H; H-7'), 2.63 (br q,  $J = 9.6$  Hz, 1H; H-6), 2.01 (br d,  $J = 14.4$  Hz, 1H; H-7), 1.87 (s, 3H; OAc), 1.75 ppm (s, 3H; OAc);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 170.3, 169.6, 167.9, 137.0, 134.4, 132.7, 131.9, 131.6, 130.3, 130.2, 128.8, 127.7, 126.4, 123.6, 74.1, 72.1, 51.4, 47.6, 36.2, 21.2, 20.9$  ppm; elemental analysis calcd (%) for  $\text{C}_{27}\text{H}_{25}\text{NO}_6$ : C 70.58, H 5.48; found: C 70.28, H 5.45.

**Bis(dinitrobenzoate) PTAD adduct (+)-24.** To a solution of less polar diol (–)-22 (69.0 mg, 0.184 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.5 mL) at room temperature was added dropwise a solution of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) in  $\text{CH}_2\text{Cl}_2$  and the mixture was occasionally stirred. The process was continued until the light red color of PTAD persisted. The mixture was concentrated and the residue purified by column chromatography ( $\text{SiO}_2$ , hexanes-ethyl acetate = 1:4) to afford the cycloadduct (94 mg, 93%) as a colorless solid. This compound was used in the next step without further characterization. To a stirring solution of the PTAD adduct (94 mg, 0.171 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (2 mL) at room temperature under nitrogen was added 4-(dimethylamino)pyridine (45 mg, 0.376 mmol). After stirring for 15 min, 3,5-dinitrobenzoyl chloride (85 mg, 0.376 mmol) was added and the mixture was stirred for 3 h. The reaction

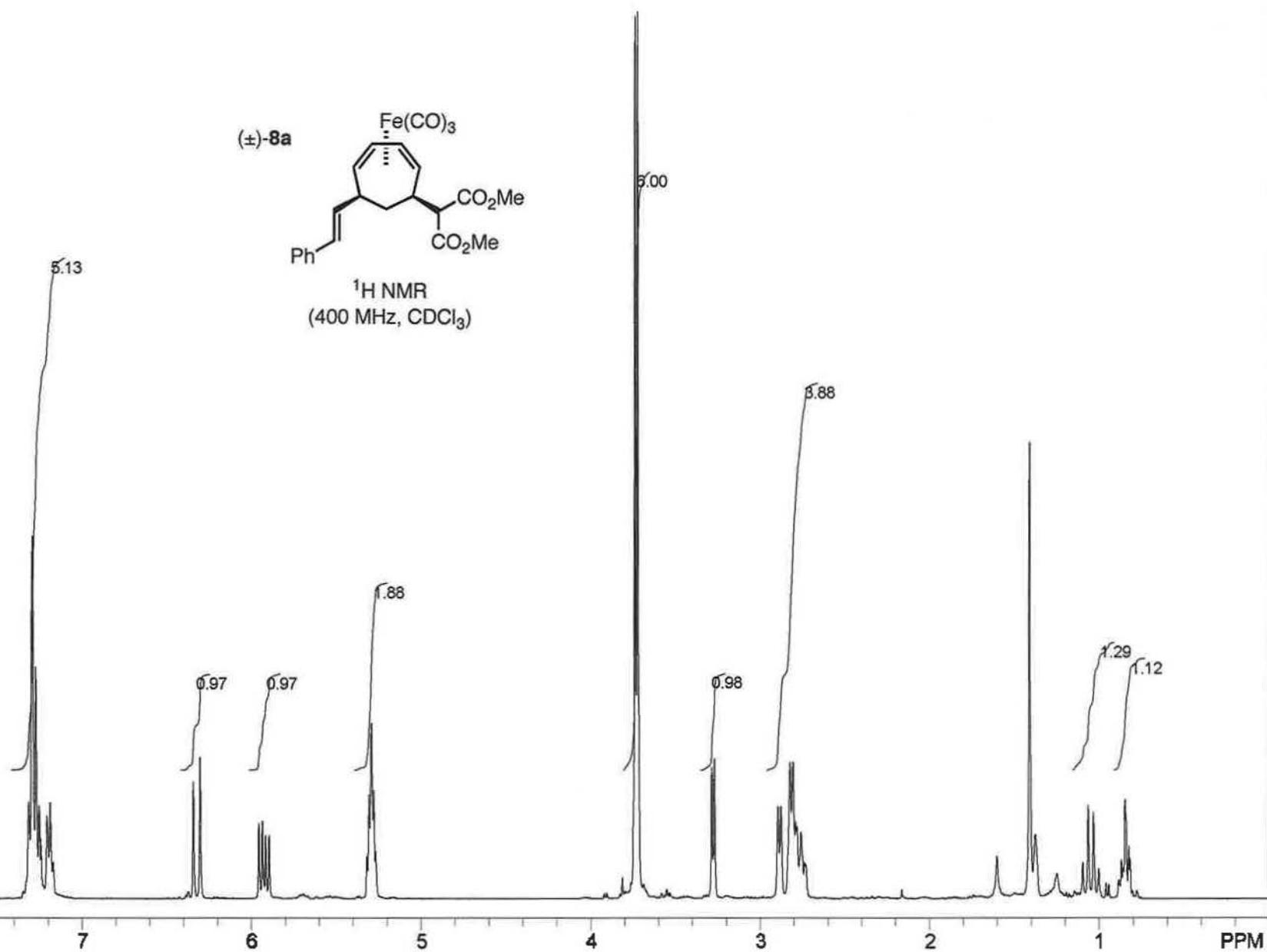
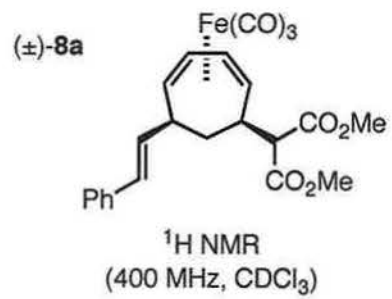
mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (4 mL) and washed with 0.1 M HCl solution. The combined  $\text{CH}_2\text{Cl}_2$  fractions were washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. The residue was purified by column chromatography ( $\text{SiO}_2$ , hexanes-ethyl acetate = 1:1) to afford (+)-**24** (131 mg, 81%) as a light yellow solid. Recrystallization from hexanes-ethyl acetate gave crystals suitable for X-ray diffraction analysis; m.p. = 240-242 °C;  $[\alpha]_D^{20} = +50.1$  (c 0.357,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta = 9.33$ -8.94 (m, 7H; Ar-H), 7.84-7.72 (m, 5H; Ar-H), 7.49-7.33 (m, 8H; Ar-H), 6.68 (dd,  $J = 6.9, 8.8$  Hz, 1H; CH=CH), 6.59 (d,  $J = 8.4$  Hz, 1H; H-10), 6.47 (dd,  $J = 7.0, 8.6$  Hz, 1H; CH=CH), 5.86 (dd,  $J = 2.4, 9.0$  Hz, 1H; H-9), 5.55 (d,  $J = 6.9$  Hz, 1H; H-1), 5.06 (d,  $J = 6.9$  Hz, 1H; H-5), 4.55 (dd,  $J = 4.2, 12.0$  Hz, 1H; H-1), 2.35 (br d,  $J = 12.3$  Hz, 1H; H-4), 2.20 (q,  $J = 12.3$  Hz, 1H; H-3), 1.80-1.70 ppm (m, 1H; H-3');  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta = 167.4, 162.5, 161.6, 152.4, 151.6, 148.9, 148.8, 134.7, 134.2, 132.8, 132.2, 131.4, 131.3, 130.5, 129.6, 129.5, 129.4, 128.6, 127.4, 125.6, 124.6, 123.7, 123.4, 123.0, 78.7, 78.3, 54.9, 51.3, 50.7, 41.4, 28.7$  ppm; elemental analysis calcd (%) for  $\text{C}_{45}\text{H}_{30}\text{N}_8\text{O}_{16}\cdot\text{C}_4\text{H}_8\text{O}_2$ : C 57.31, H 3.73; found: C 57.04, H 3.58.

**(S)-Mosher's ester of (+)-17.** To a solution of (+)-**17** (20 mg, 0.066 mmol) in dry THF (3 mL) was added (S)-(-)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetic acid (50 mg, 0.213 mmol) followed by *N,N'*-dicyclohexylcarbodiimide (44 mg, 0.213 mmol) and 4-dimethylaminopyridine (5 mg, 0.004 mmol). The reaction mixture was stirred for 2 h, and then concentrated and water (5 mL) was added. The mixture was extracted several times with ether, and the combined extracts were washed with 10% HCl, and concentrated. The residue was purified by column chromatography ( $\text{SiO}_2$ , hexanes-ethyl acetate = 7:3) to give **27** (34 mg, 100%) as a colorless oil:  $^1\text{H}$  NMR (400 MHz,  $d_6$ -acetone)  $\delta = 7.85$  (s, 4H; Phth), 7.51-7.56 (m, 2H; Ph), 7.37-7.47 (m, 3H; Ph), 6.65 (ddd,  $J = 0.9, 7.2, 9.2$  Hz, 1H), 6.22 (ddd,  $J = 1.2, 7.2, 9.2$  Hz, 1H; CH=CH), 4.92 (br d,  $J = 7.2$  Hz, 1H; CH=CH), 4.72 (br d,  $J = 7.2$  Hz, 1H), 4.63 (ddd,  $J = 0.9, 4.5, 12.7$  Hz, 1H; H-1), 4.39 (dd,  $J = 5.4, 11.2$  Hz, 1H;  $\text{CH}_2\text{O}$ ), 4.27 (dd,  $J = 7.0, 11.2$  Hz, 1H;  $\text{CH}_2\text{O}$ ), 3.58 (q,  $J_{\text{H-F}} = 1.2$  Hz, 3H;  $\text{OCH}_3$ ), 2.54-2.44 (m, 1H; H-6), 2.03 (q,  $J = 12.7$  Hz, 1H; H-7), 1.64 ppm (td, 4.4, 12.8 Hz, 1H; H-7');  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta = 167.5, 166.5, 134.4, 132.0, 131.6, 130.1, 129.8, 128.6, 127.1, 124.6, 123.7, 123.5, 121.8, 79.8, 77.8, 66.6, 55.7, 51.7, 41.1, 26.2$  ppm.

**(S)-Mosher's ester of (-)-17.** The esterification of (-)-**17** (20 mg, 0.066 mmol) with (S)-(-)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetic acid was carried out in a fashion to the esterification of (+)-**17**, to afford **28** (32 mg, 94%). mp 43-45 °C;  $^1\text{H}$  NMR (400 MHz,  $d_6$ -acetone)  $\delta = 7.85$  (s,

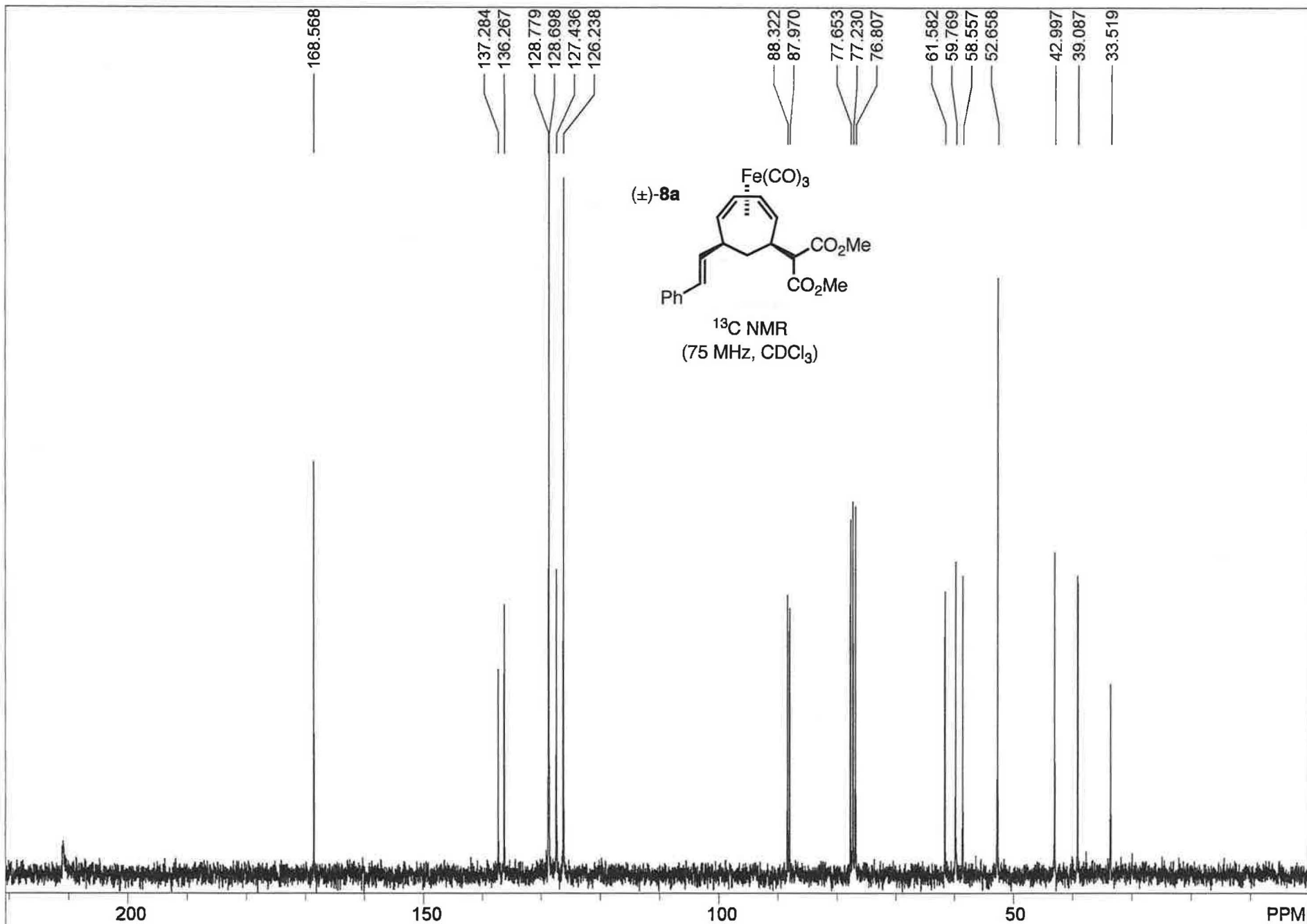


4H; Phth), 7.53-7.58 (m, 2H; Ph), 7.45-7.51 (m, 3H; Ph), 6.66 (ddd,  $J = 0.9, 7.3, 9.1$  Hz, 1H; CH=CH), 6.31 (ddd,  $J = 0.8, 7.1, 9.1$  Hz, 1H; CH=CH), 4.93 (br d,  $J = 7.2$  Hz, 1H), 4.74 (br d,  $J = 7.2$  Hz, 1H), 4.64 (dd,  $J = 5.0, 13.2$  Hz, 1H; H-1), 4.38-4.27 (m, 2H; CH<sub>2</sub>O), 3.55 (s, 3H; OCH<sub>3</sub>), 2.54-2.45 (m, 1H; H-6), 1.99 (q,  $J = 12.8$  Hz, 1H; H-7), 1.67 ppm (td,  $J = 4.6, 12.8$  Hz, 1H; H-7'); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 167.4, 166.5, 134.3, 131.8, 131.6, 130.2, 129.8, 128.6, 127.2, 124.6, 123.6, 123.4, 121.7, 79.8, 77.6, 66.5, 55.4, 51.5, 41.1, 26.2$  ppm.



:blank line						USER: -- DATE: Apr 3 2010
F1: 399.746	F2: 100.525	SW1: 6410		OF1: 2392.0		PTS1d: 13132 , 16384
EX: s2pul		PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$ase486dp.fid





$^{13}\text{C}$  OBSERVE: blank line

USER: -- DATE: Jun 26 2009

F1: 75.476

F2: 300.133

SW1: 18868

OF1: 8292.2

PTS1d: 34246 65536

EX: s2pul

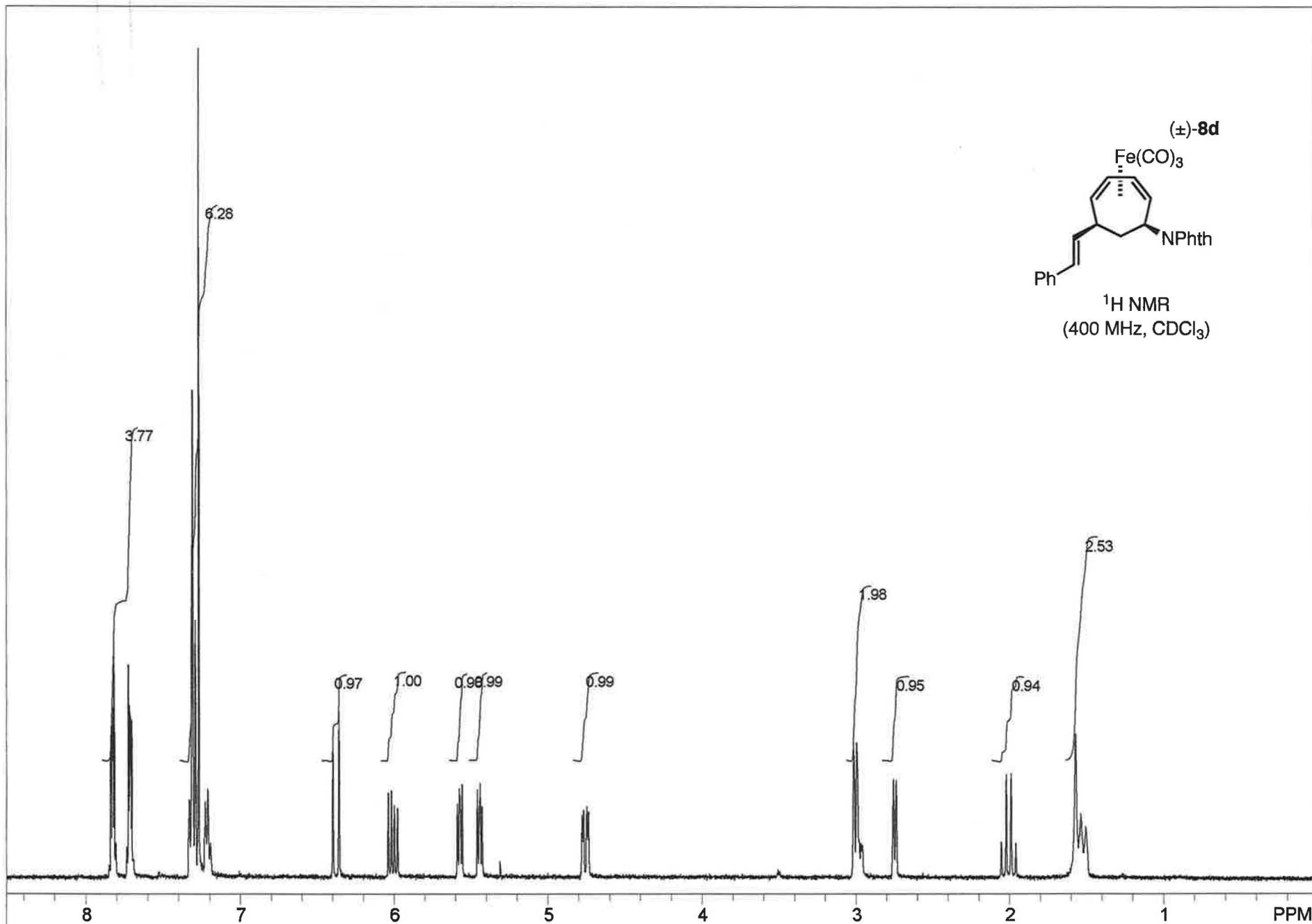
PW: 7.3 us

PD: 1.0 sec

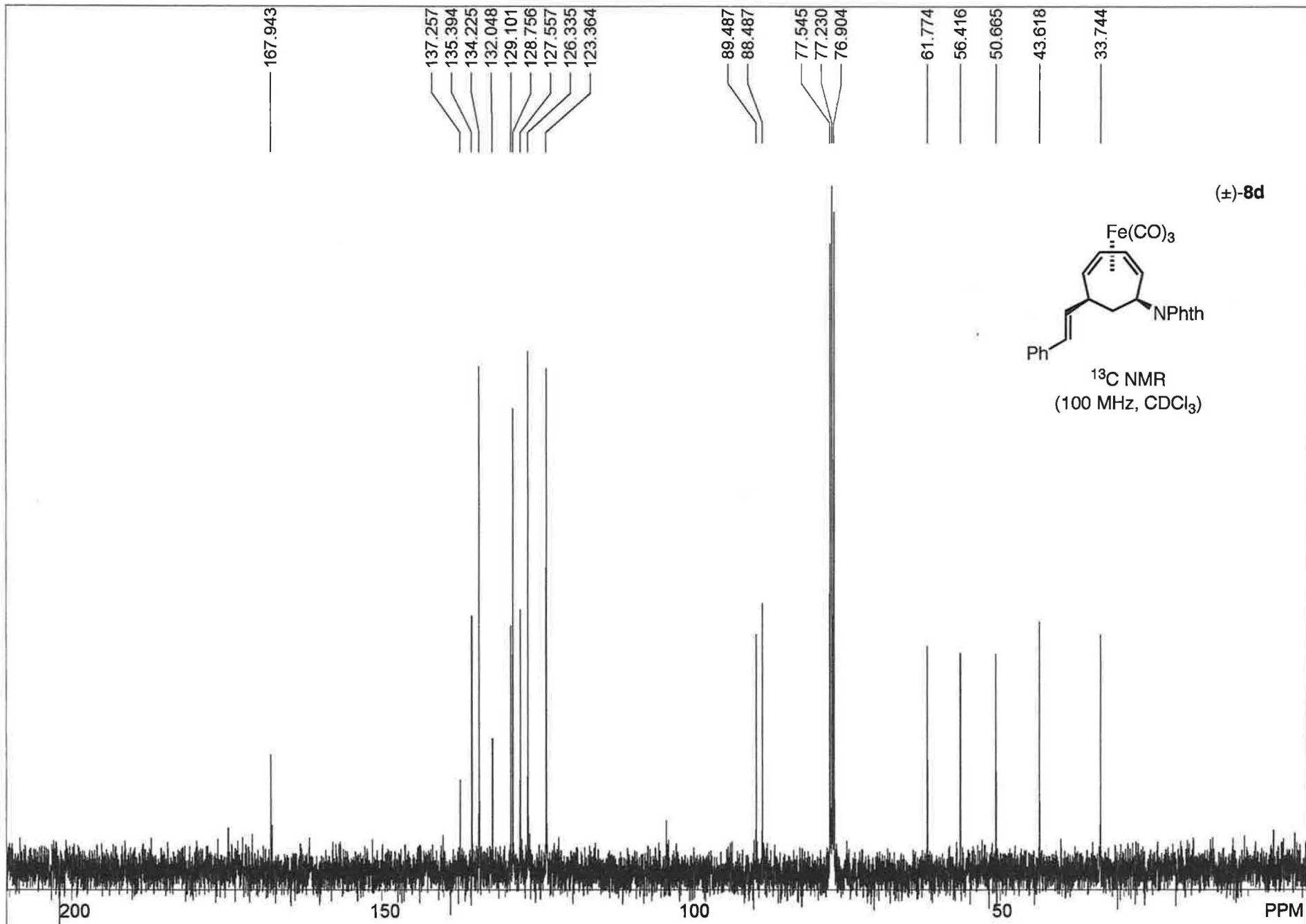
NA: 128

LB: 1.5

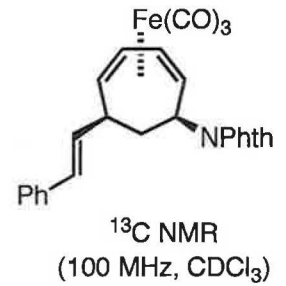
Nuts - \$ase316f1c13.fid



:blank line					USER: -- DATE: Nov 4 2009	
F1: 399.746	F2: 100.525	SW1: 6410		OF1: 2403.3		PTS1d: 13132 . 16384
EX: s2pul	PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$as110409iron.fid

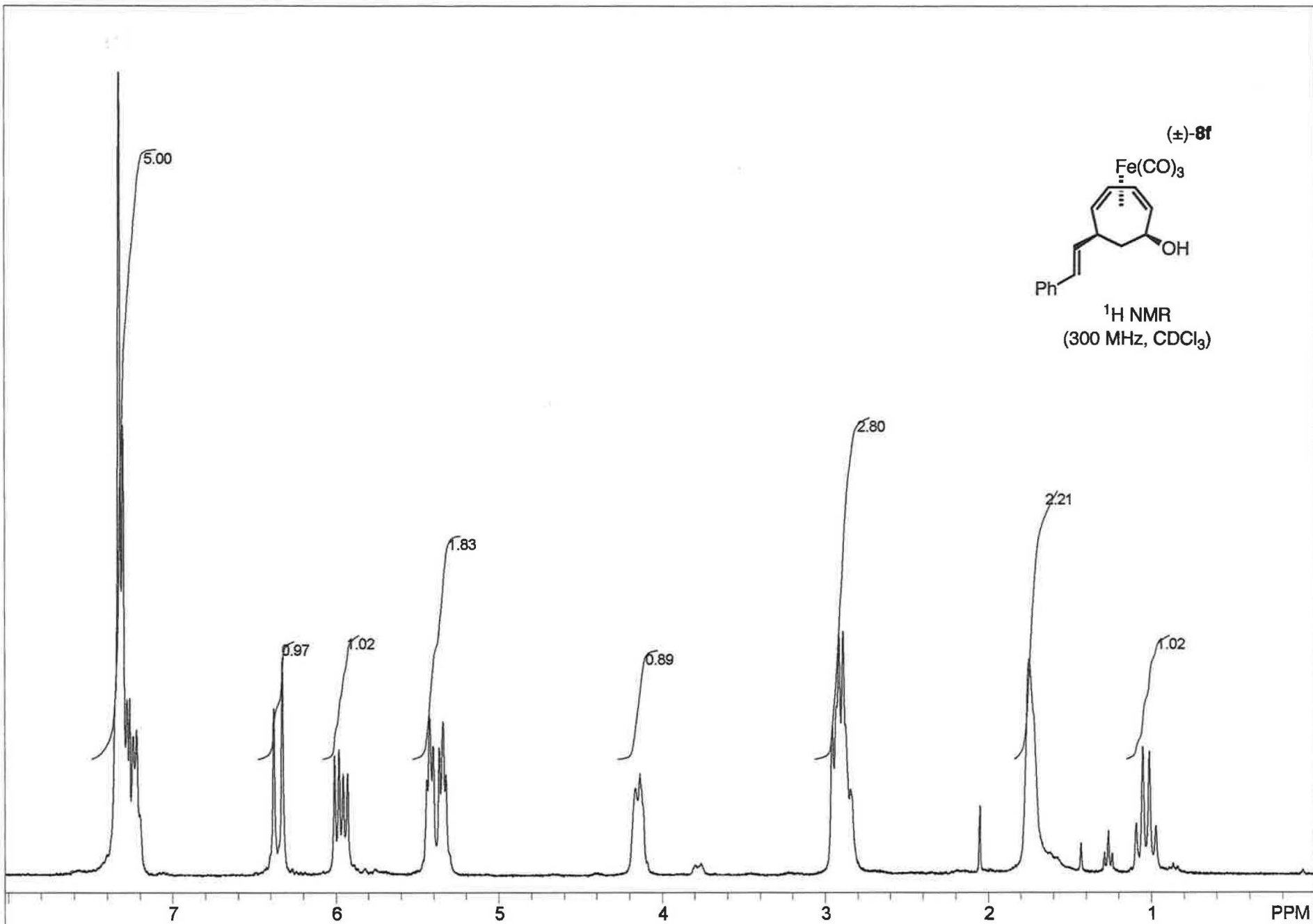


(±)-8d



:blank line				USER: -- DATE: Nov 4 2009		
F1: 100.526	F2: 399.745	SW1: 24510	OF1: 10574.9	PTS1d: 31875	32768	
EX: s2pul	PW: 5.8 us	PD: 1.0 sec	NA: 256	LB: 1.5	Nuts - \$as110409c13.fid	

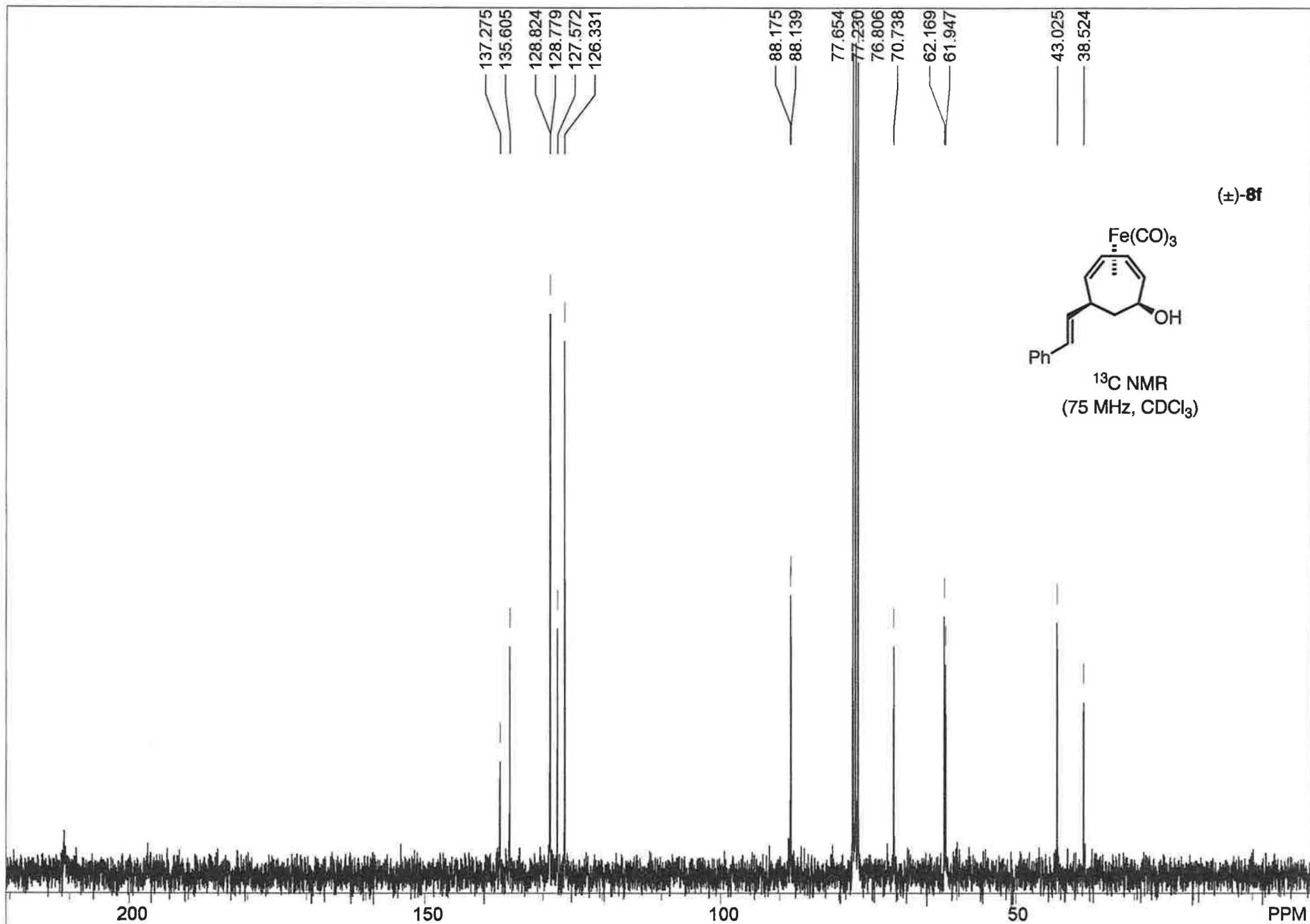
HS



STANDARD 1H OBSERVE:blank line

USER: -- DATE: May 23 2011

F1: 300.133	F2: 75.476	SW1: 4803	OF1: 1802.8	PTS1d: 9596	16384
EX: s2pul	PW: 6.2 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$ase662fd.fid



$^{13}\text{C}$  OBSERVE:blank line

USER: -- DATE: May 23 2011

F1: 75.476

F2: 300.133

SW1: 18868

OF1: 8298.4

PTS1d: 34246 65536

EX: s2pul

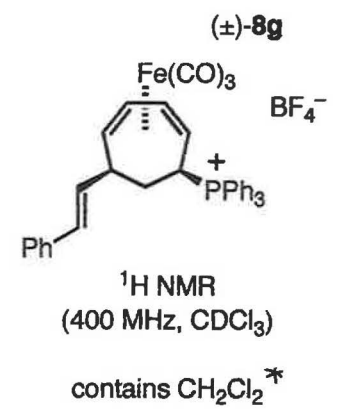
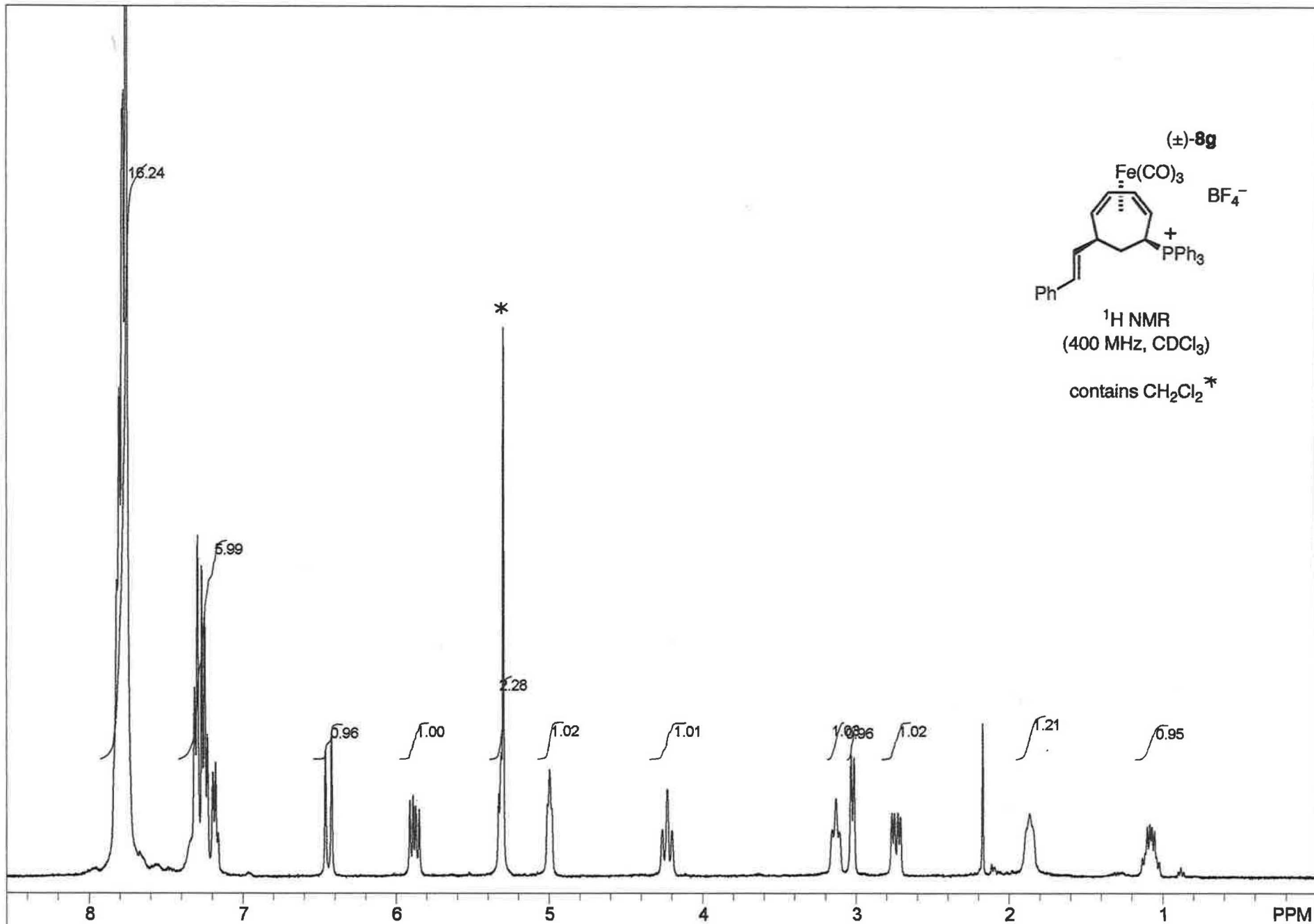
PW: 7.3 us

PD: 1.0 sec

NA: 256

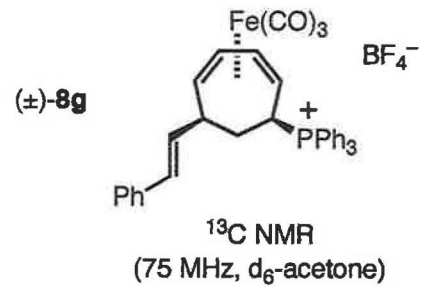
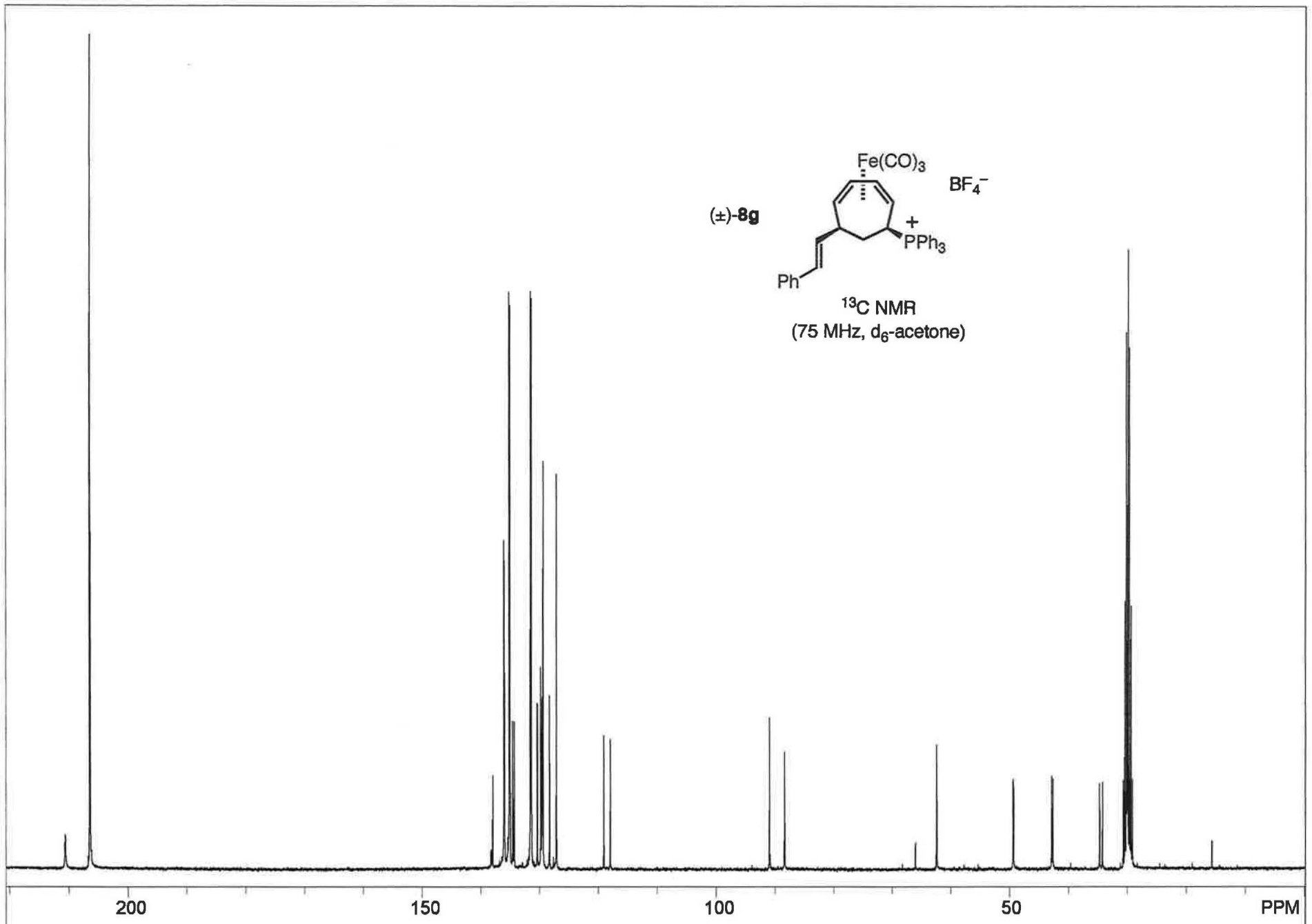
LB: 1.5

Nuts - \$ase662fd13c.fid



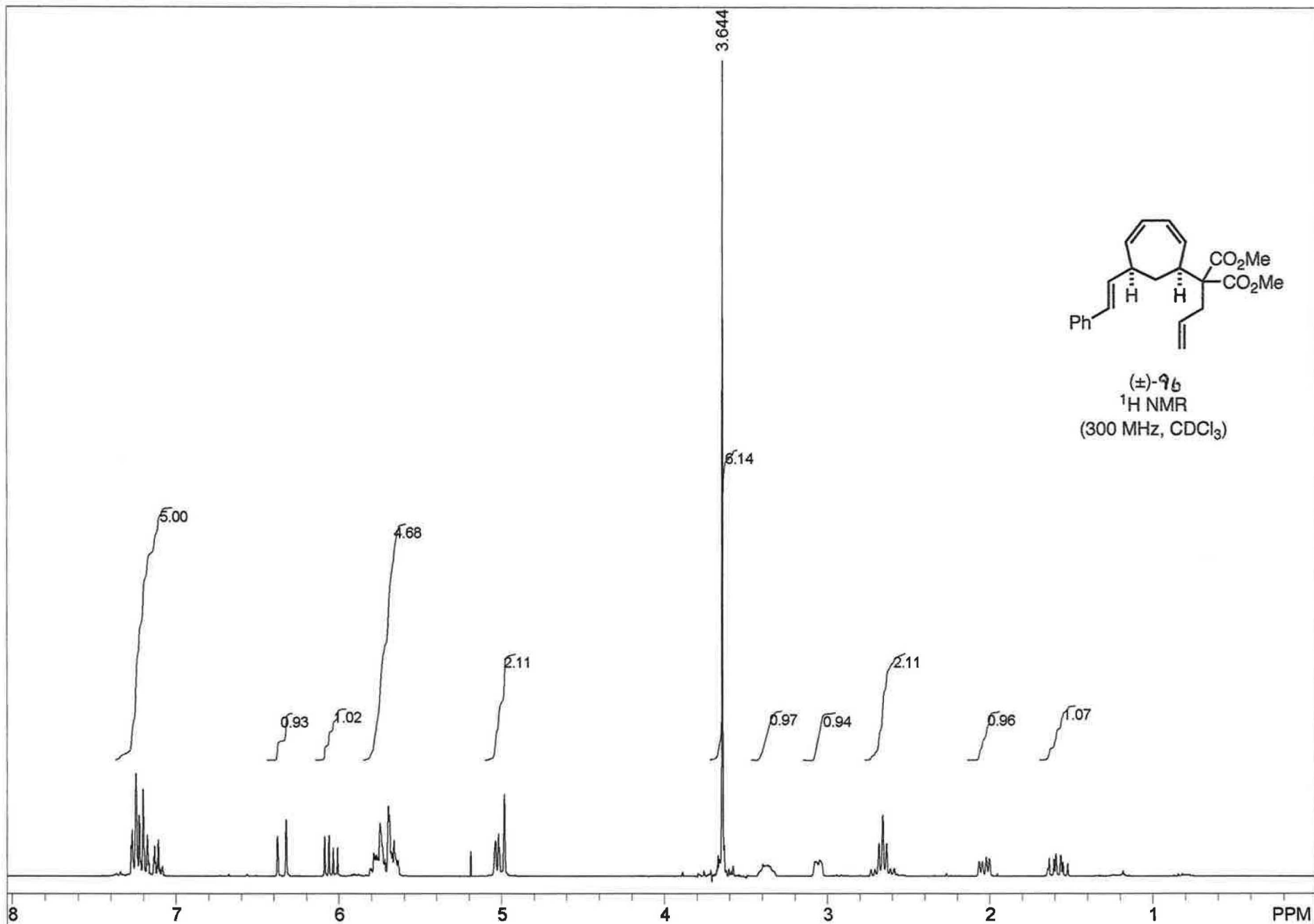
:blank line				USER: -- DATE: Mar 23 2011			
F1: 399.746	F2: 100.525	SW1: 6410		OF1: 2402.3		PTS1d: 13132 , 16384	
EX: s2pul		PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$as032311salt2.fid	

517



13C OBSERVE:blank line				USER: -- DATE: Apr 7 2010		
F1: 75.477	F2: 300.134	SW1: 18868		OF1: 8332.3		PTS1d: 34246 . 65536
EX: s2pul		PW: 8.5 us	PD: 1.0 sec	NA:	LB: 1.0	Nuts - \$aspsalt.fid

5/8



STANDARD 1H OBSERVE:blank line

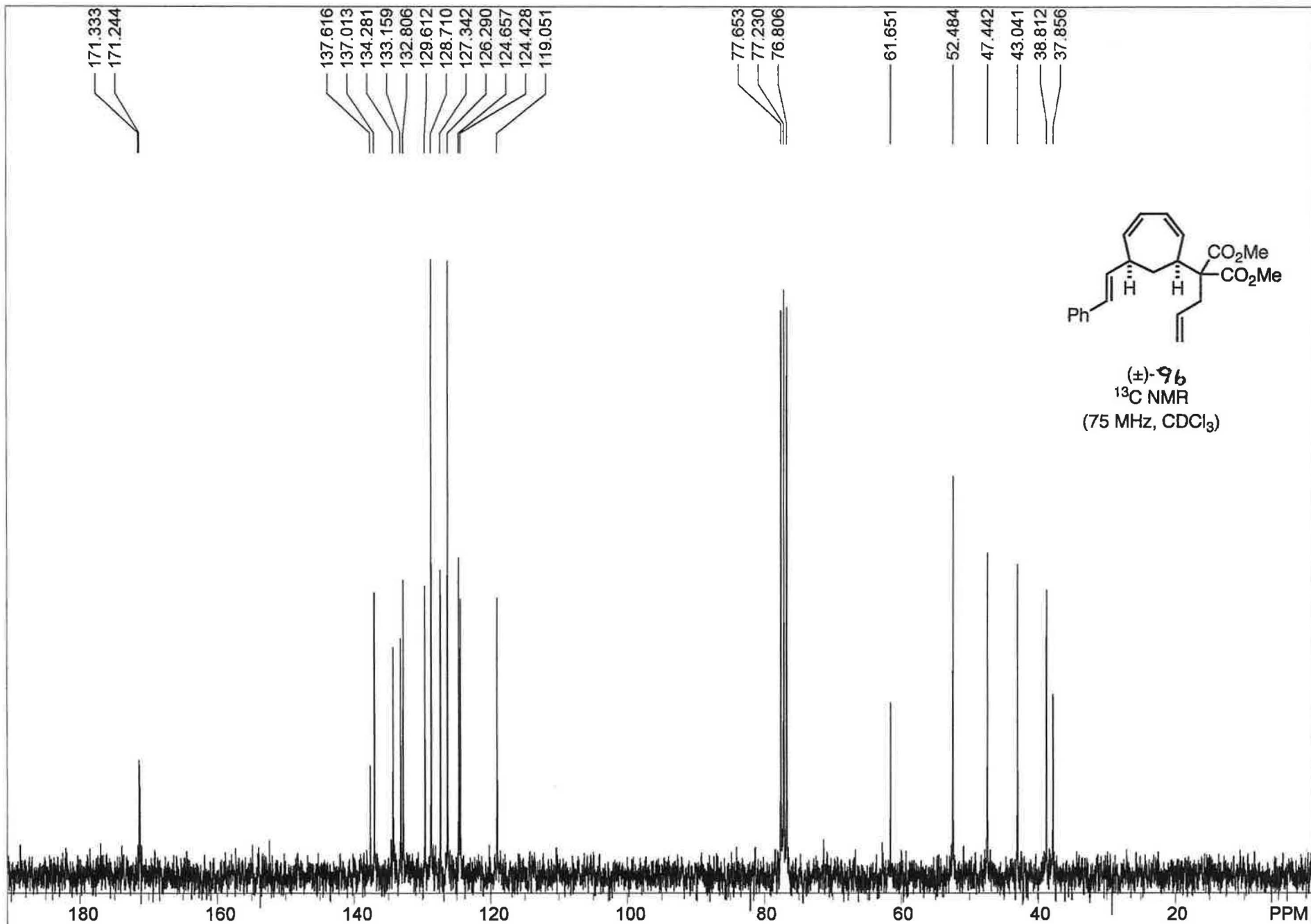
USER: -- DATE: May 11 2010

F1: 300.133	F2: 75.476	SW1: 4803	OF1: 1771.8	PTS1d: 9596 , 16384
EX: s2pul	PW: 6.3 us	PD: 1.0 sec	NA: 8	LB: 0.0

Nuts - \$as051110p.fid

5  
10

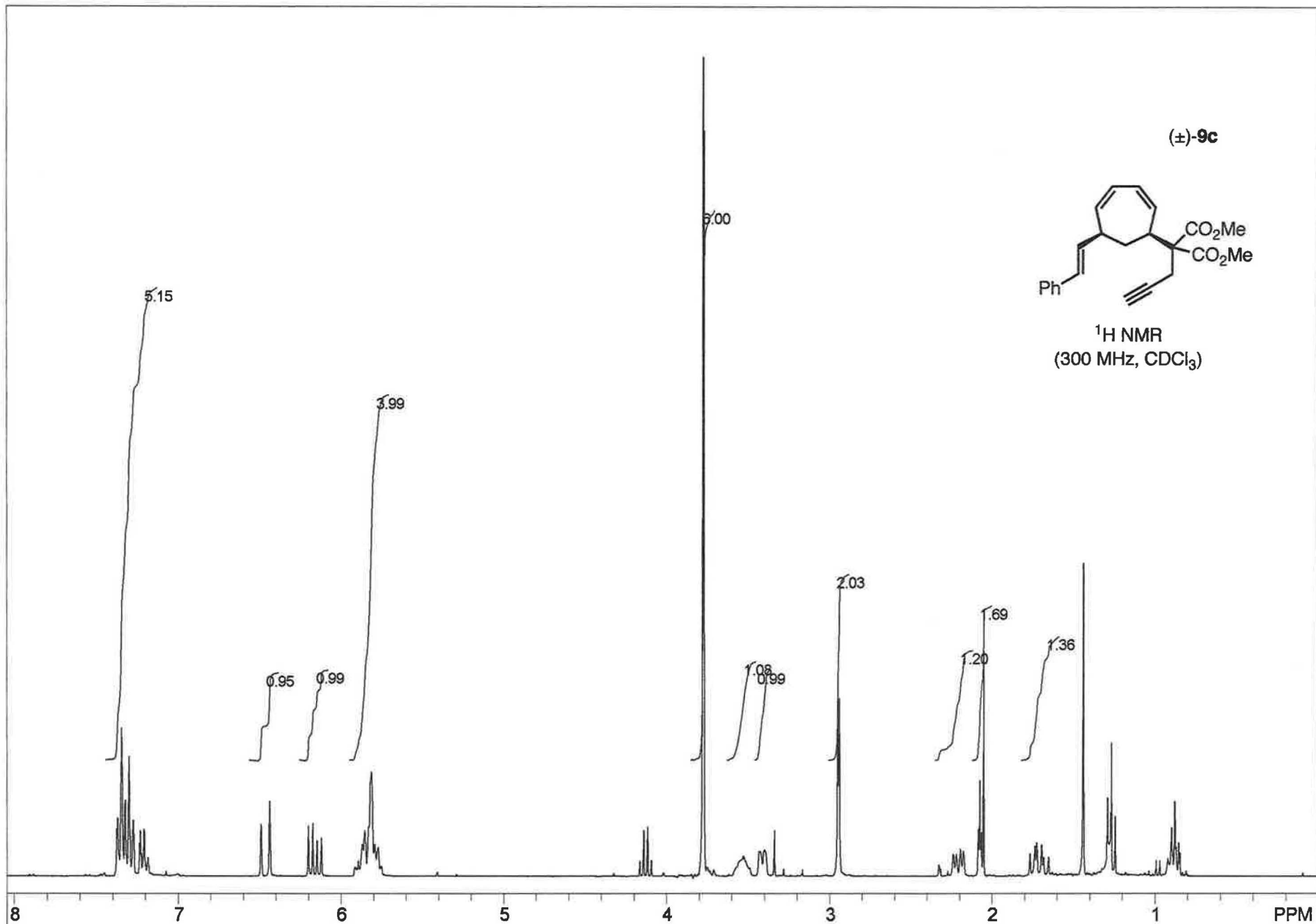




<sup>13</sup>C OBSERVE: blank line

USER: -- DATE: May 3 2010

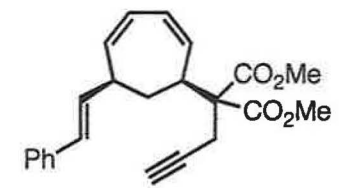
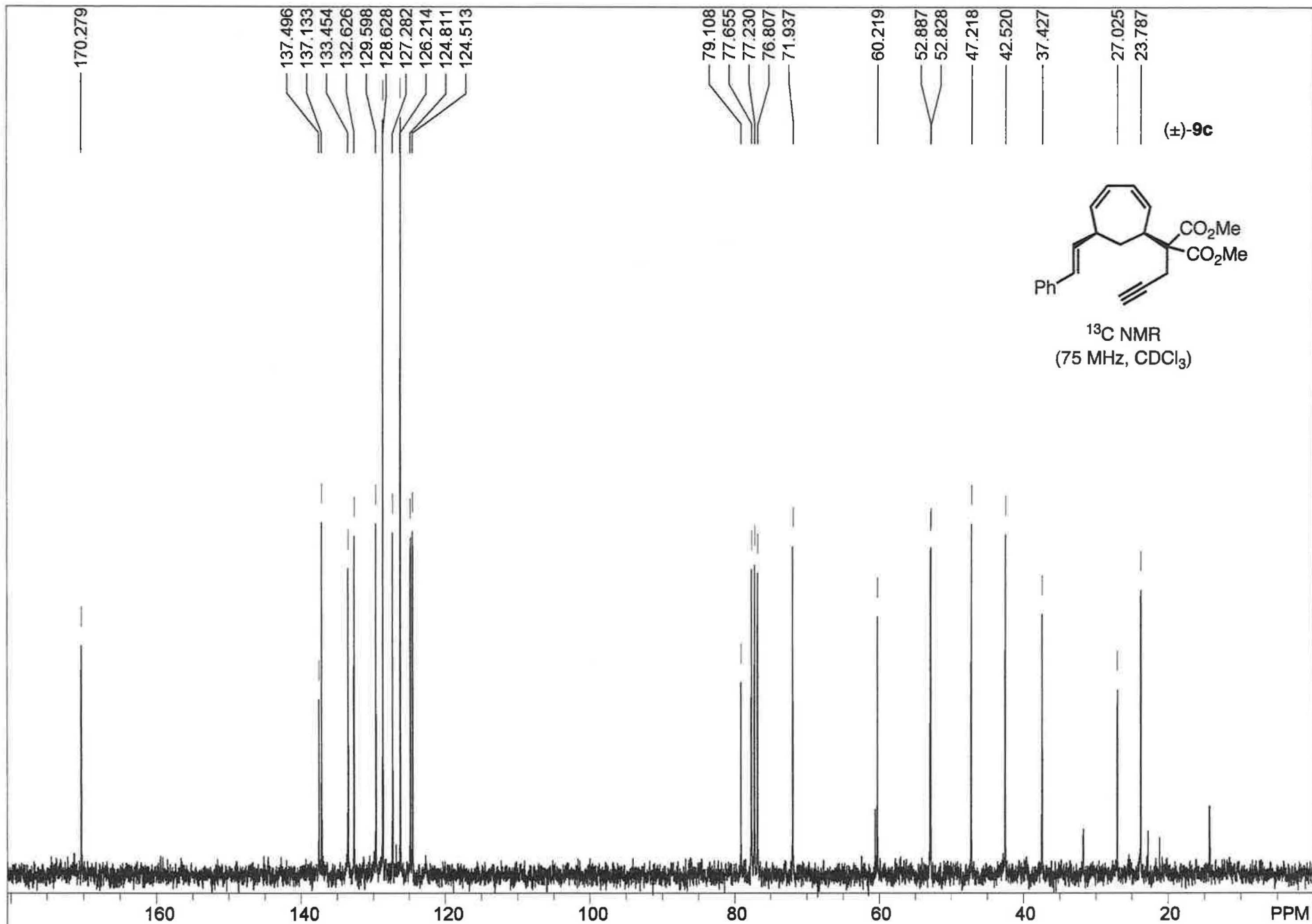
F1: 75.476	F2: 300.133	SW1: 18868	OF1: 8299.2	PTS1d: 34246	65536
EX: s2pul	PW: 8.5 us	PD: 1.0 sec	NA: 256	LB: 2.0	Nuts - \$ase501pp13c.fid



STANDARD 1H OBSERVE:blank line

USER: -- DATE: Jun 7 2011

F1: 300.133	F2: 75.476	SW1: 4803	OF1: 1803.5	PTS1d: 9596	16384
EX: s2pul	PW: 6.2 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$ase669fd.fid



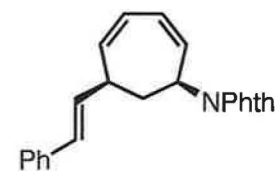
<sup>13</sup>C NMR  
(75 MHz, CDCl<sub>3</sub>)

<sup>13</sup>C OBSERVE: blank line

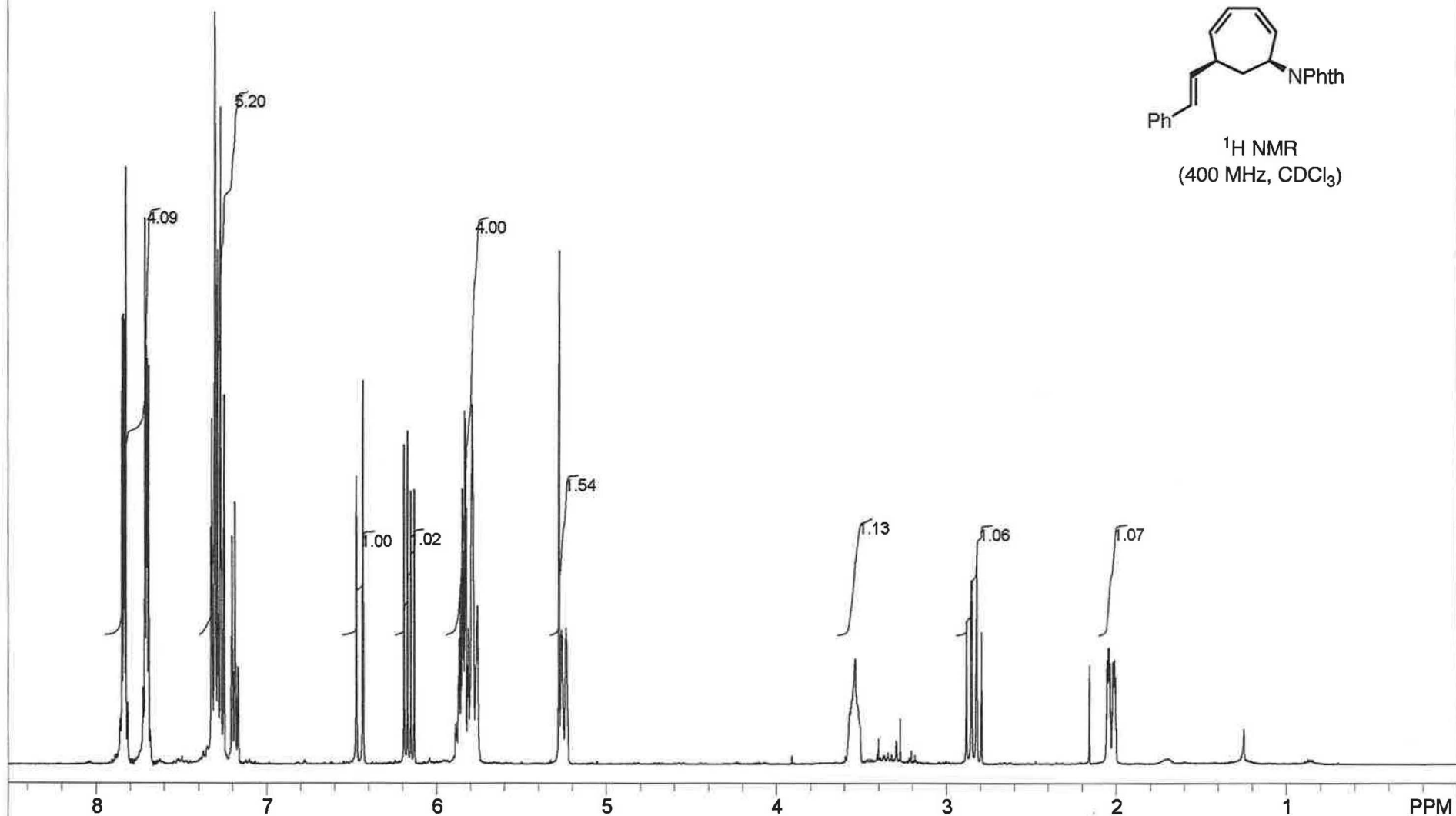
USER: -- DATE: Jun 7 2011

F1: 75.476	F2: 300.133	SW1: 18868	OF1: 8292.1	PTS1d: 34246	65536
EX: s2pul	PW: 7.3 us	PD: 1.0 sec	NA: 64	LB: 1.5	Nuts - \$ase669fd13c.fid

(±)-9d



<sup>1</sup>H NMR  
(400 MHz, CDCl<sub>3</sub>)

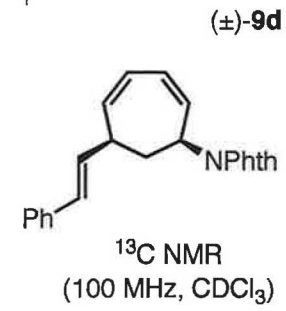
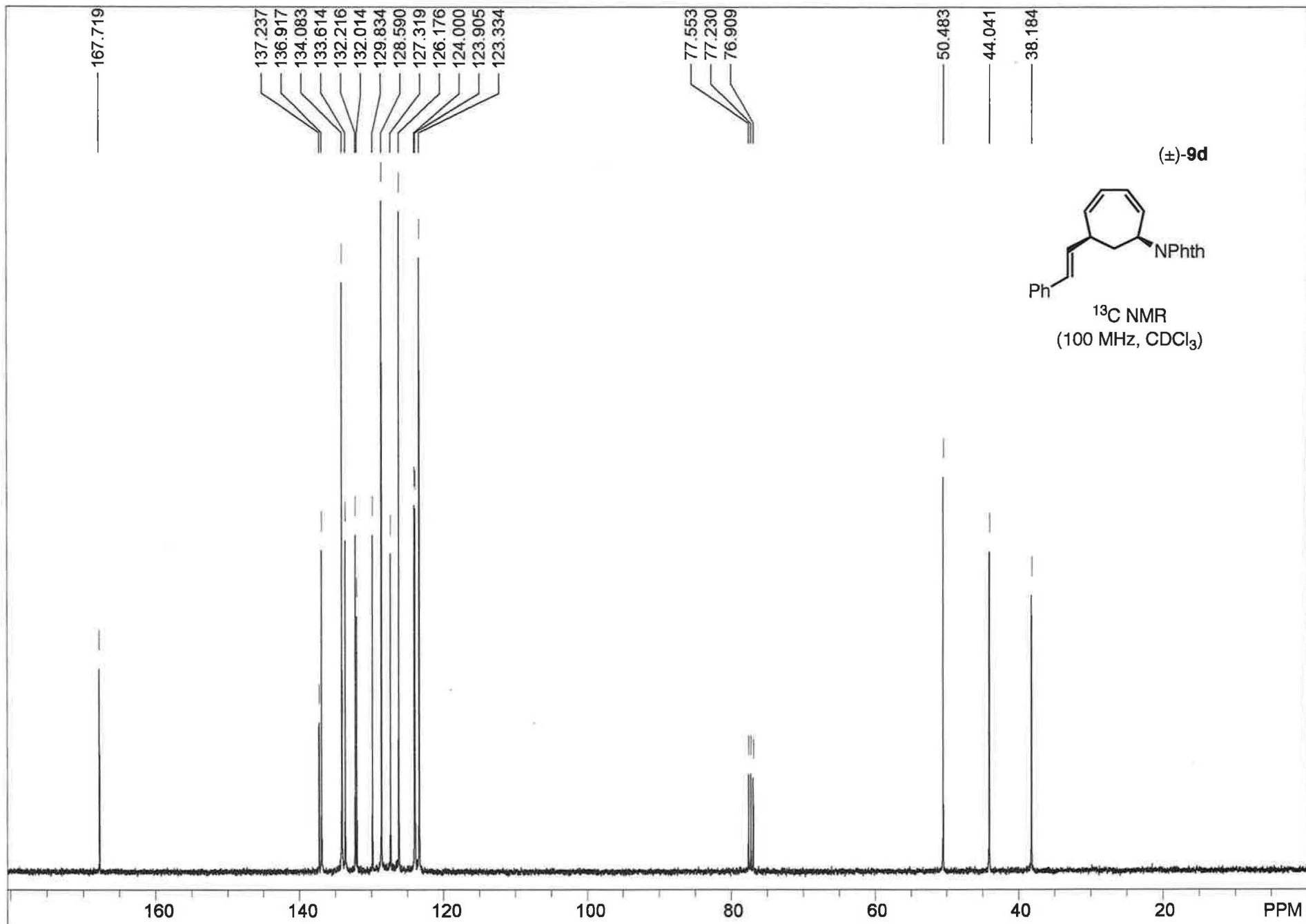


:blank line

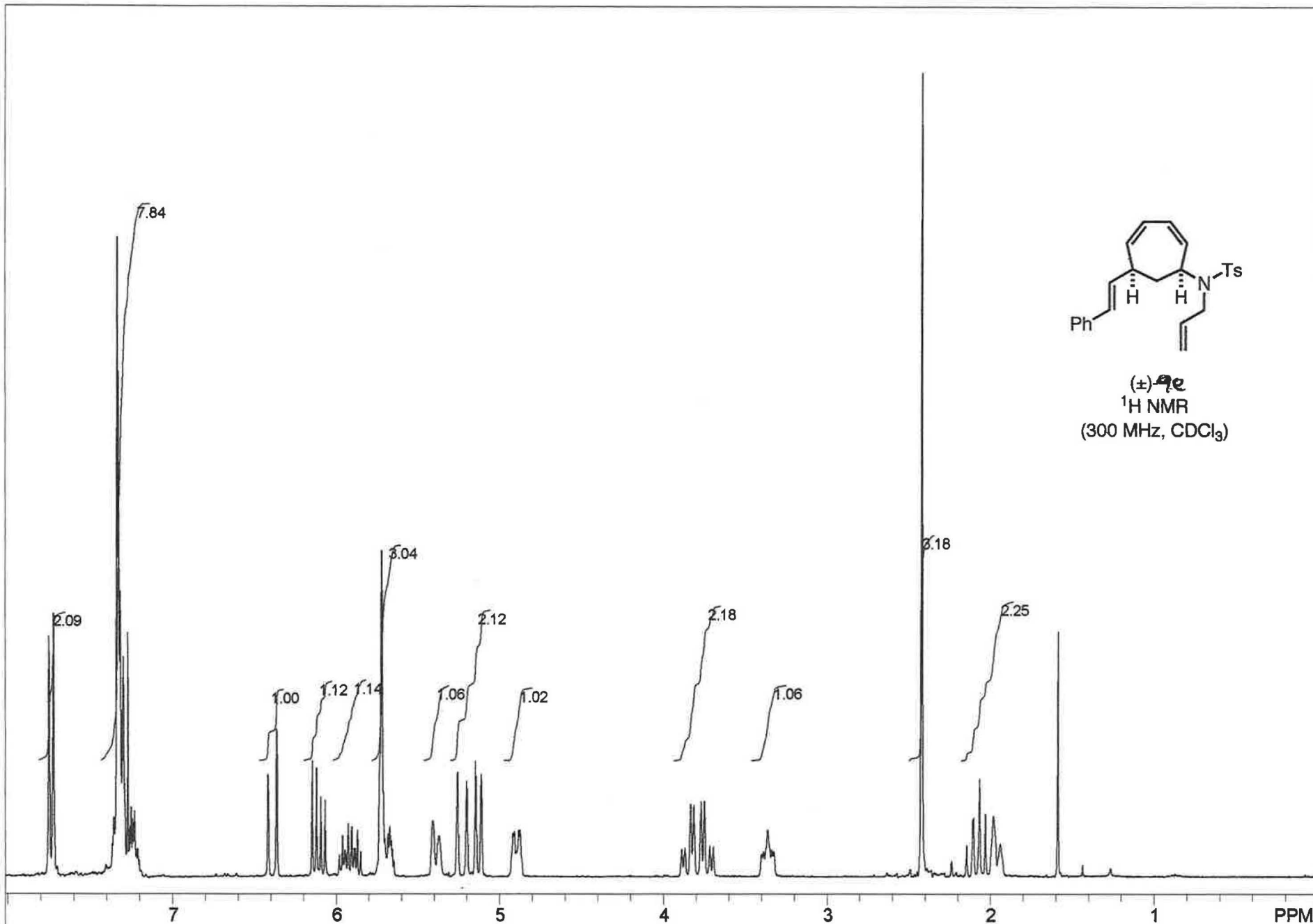
USER: -- DATE: Oct 21 2008

F1: 399.751	F2: 100.526	SW1: 6410	OF1: 2396.7	PTS1d: 13132 , 16384
EX: s2pul	PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0

Nuts - \$ase163cr.fid



:blank line						USER: -- DATE: Oct 21 2008
F1: 100.527	F2: 399.751	SW1: 24510		OF1: 10324.3		PTS1d: 31875 . 32768
EX: s2pul		PW: 4.0 us	PD: 1.0 sec	NA: 256	LB: 1.0	Nuts - \$ase163fde13.fid

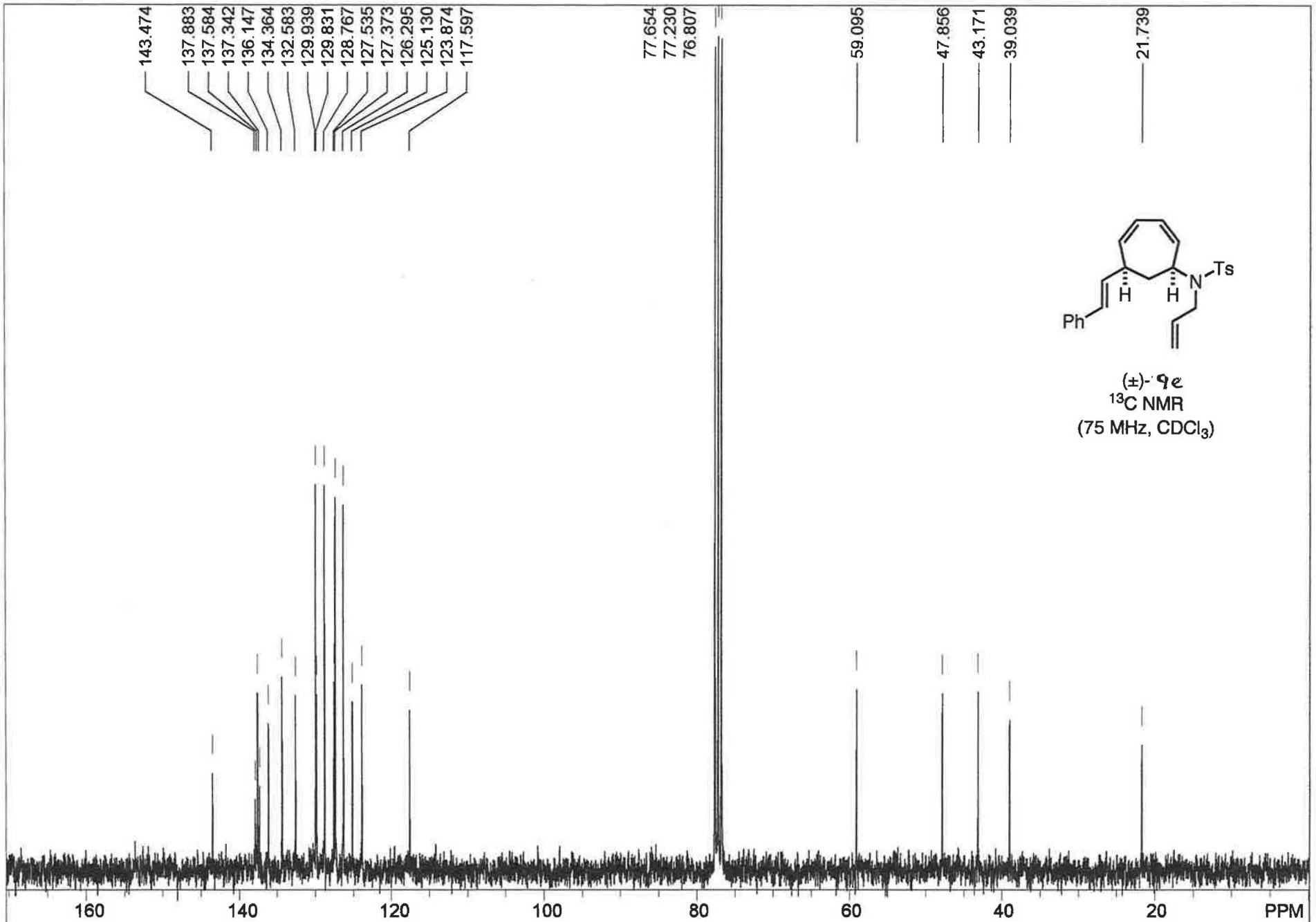


STANDARD 1H OBSERVE:blank line

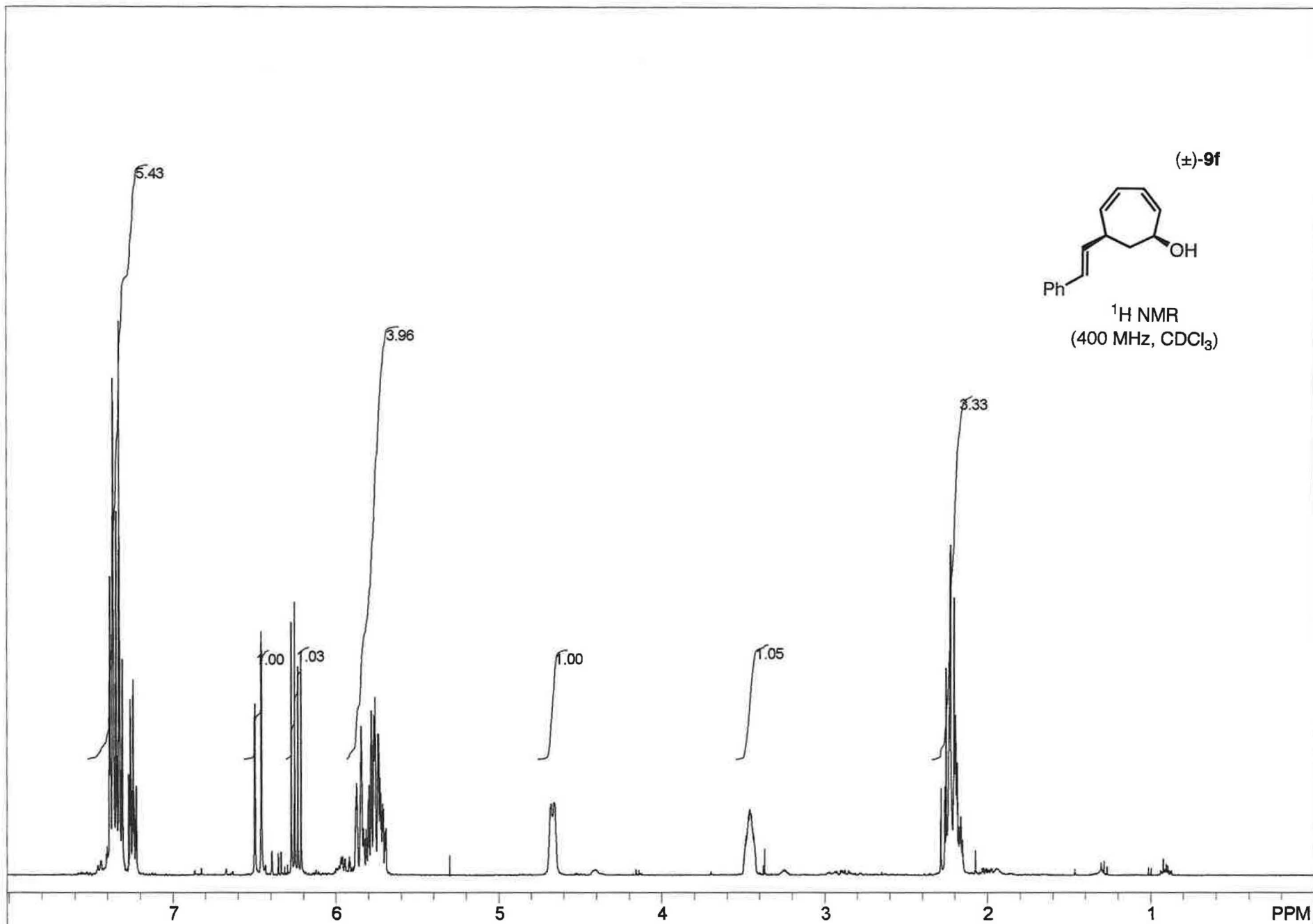
USER: -- DATE: Aug 18 2011

F1: 300.133	F2: 75.476	SW1: 4803	OF1: 1803.8	PTS1d: 9596 , 16384
EX: s2pul	PW: 6.2 us	PD: 1.0 sec	NA: 8	LB: 0.0

Nuts - \$ml46free.fid



13C OBSERVE:blank line				USER: -- DATE: Aug 18 2011		
F1: 75.476	F2: 300.133	SW1: 18868		OF1: 8298.8		PTS1d: 34246 . 65536
EX: s2pul		PW: 7.3 us	PD: 1.0 sec	NA: 256	LB: 1.5	Nuts - \$ml46freec.fid



:blank line					USER: -- DATE: Feb 4 2008	
F1: 399.751	F2: 100.526	SW1: 6410	OF1: 2404.8	PTS1d: 13132	16384	
EX: s2pul	PW: 8.0 us	PD: 1.0 sec	NA: 1	LB: 0.0	Nuts - \$as0204081h.fid	

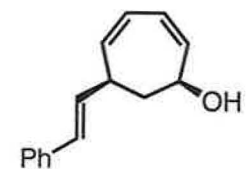


137.946  
137.407  
136.846  
132.551  
129.460  
128.709  
127.412  
126.286  
124.174  
122.552

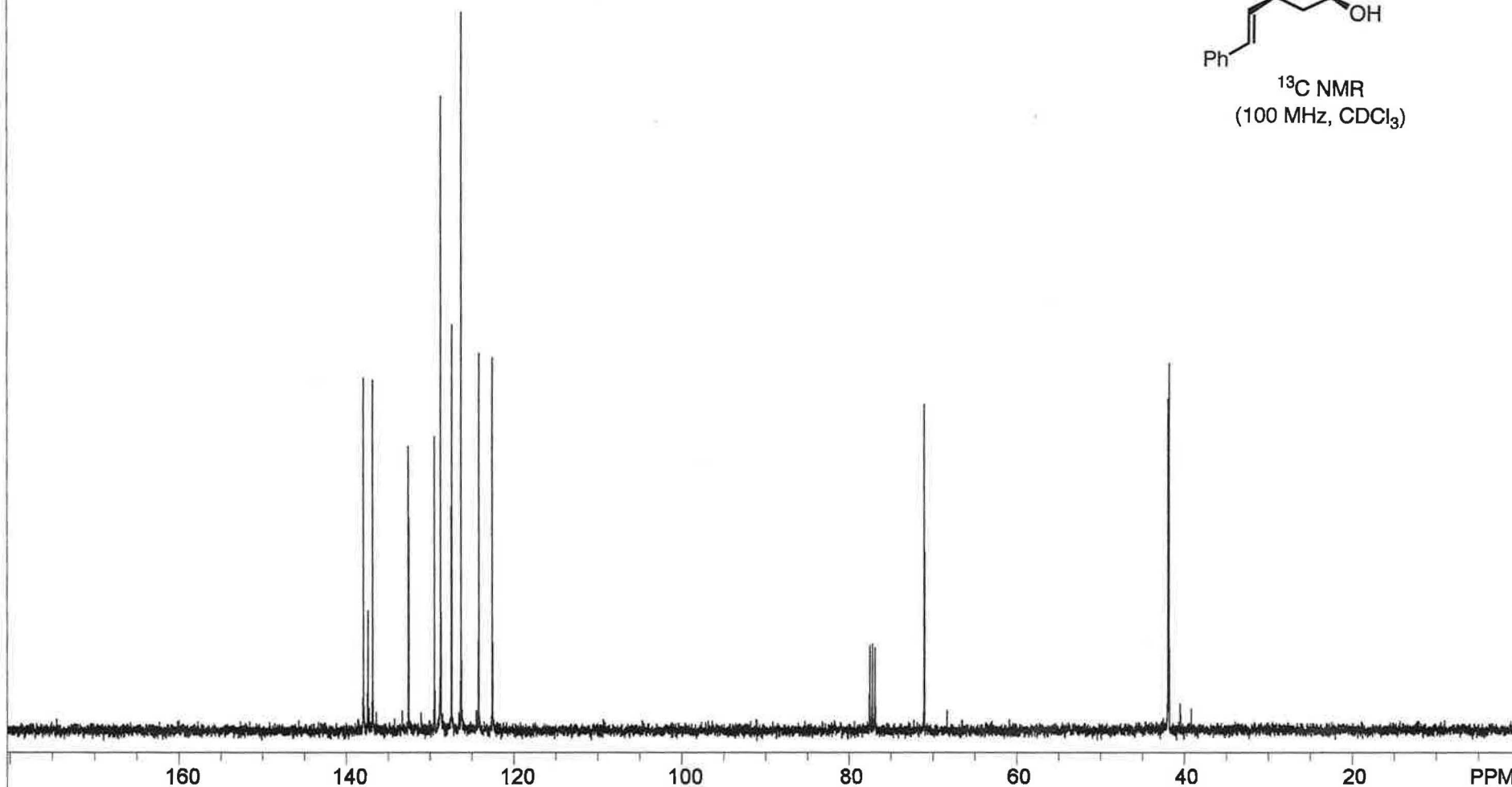
77.553  
77.230  
76.914  
71.042

41.926  
41.800

(±)-**9f**



<sup>13</sup>C NMR  
(100 MHz, CDCl<sub>3</sub>)



:blank line

USER: -- DATE: Feb 4 2008

F1: 100.527

F2: 399.751

SW1: 24510

OF1: 10544.0

PTS1d: 31875 . 32768

EX: s2pul

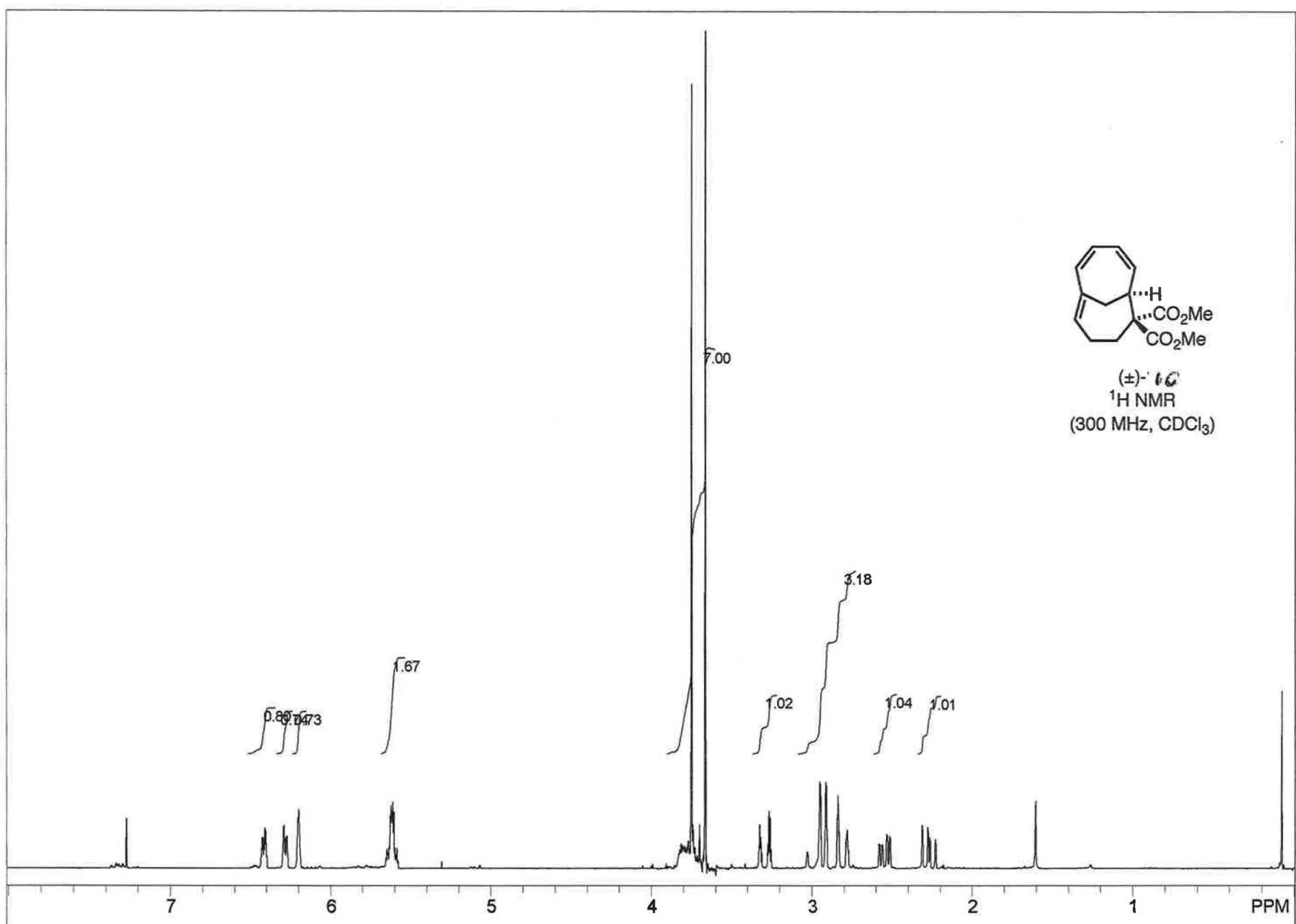
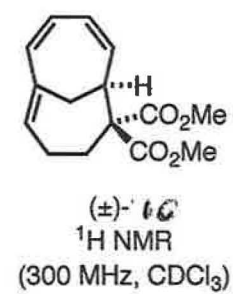
PW: 7.5 us

PD: 1.0 sec

NA: 256

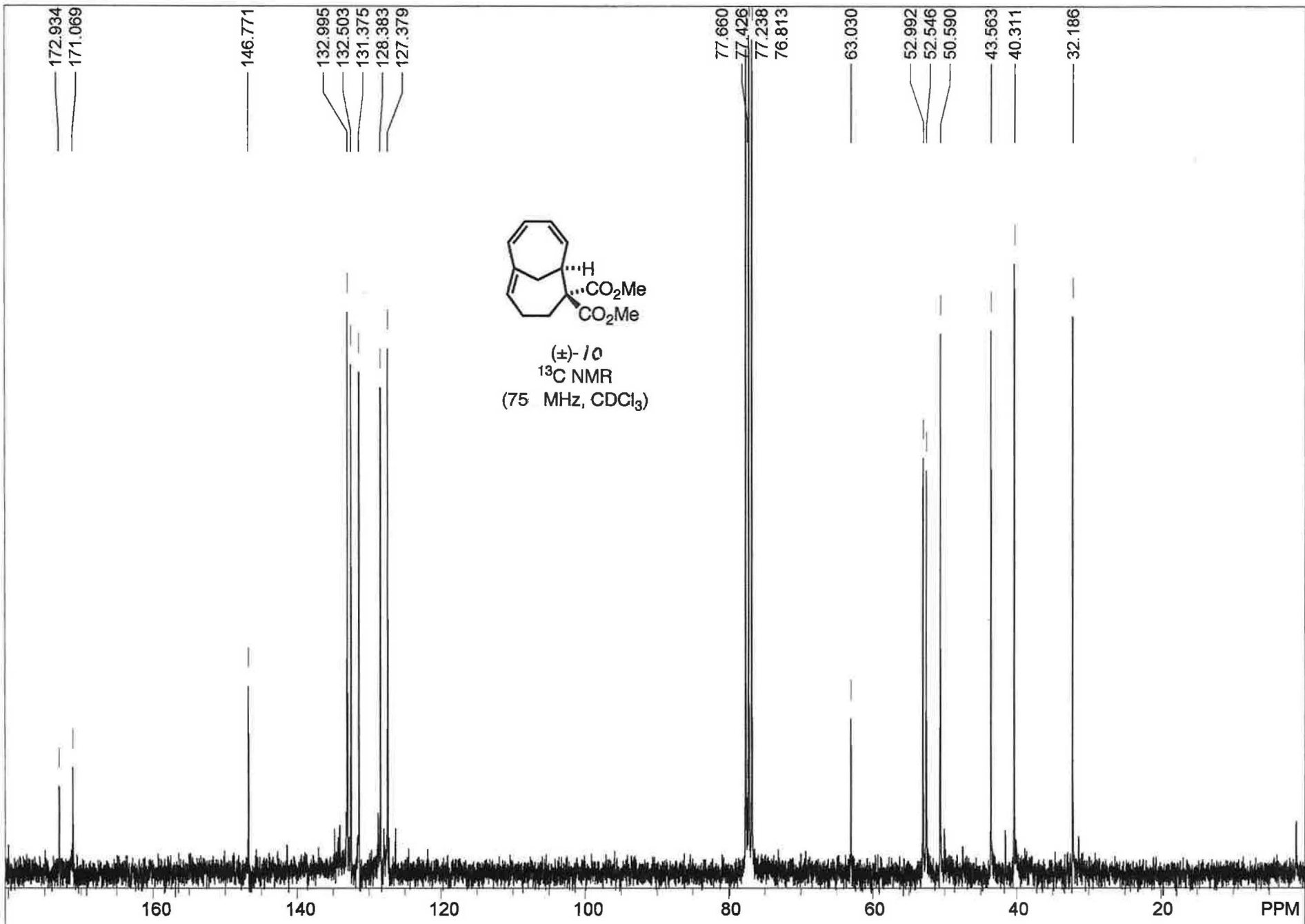
LB: 1.0

Nuts - \$as020408c13.fid



STANDARD 1H OBSERVE:blank line				USER: -- DATE: May 11 2010			
F1: 300.133	F2: 75.476	SW1: 4803		OF1: 1803.0		PTS1d: 9596	16384
EX: s2pul		PW: 6.3 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$as051110IVp.fid	

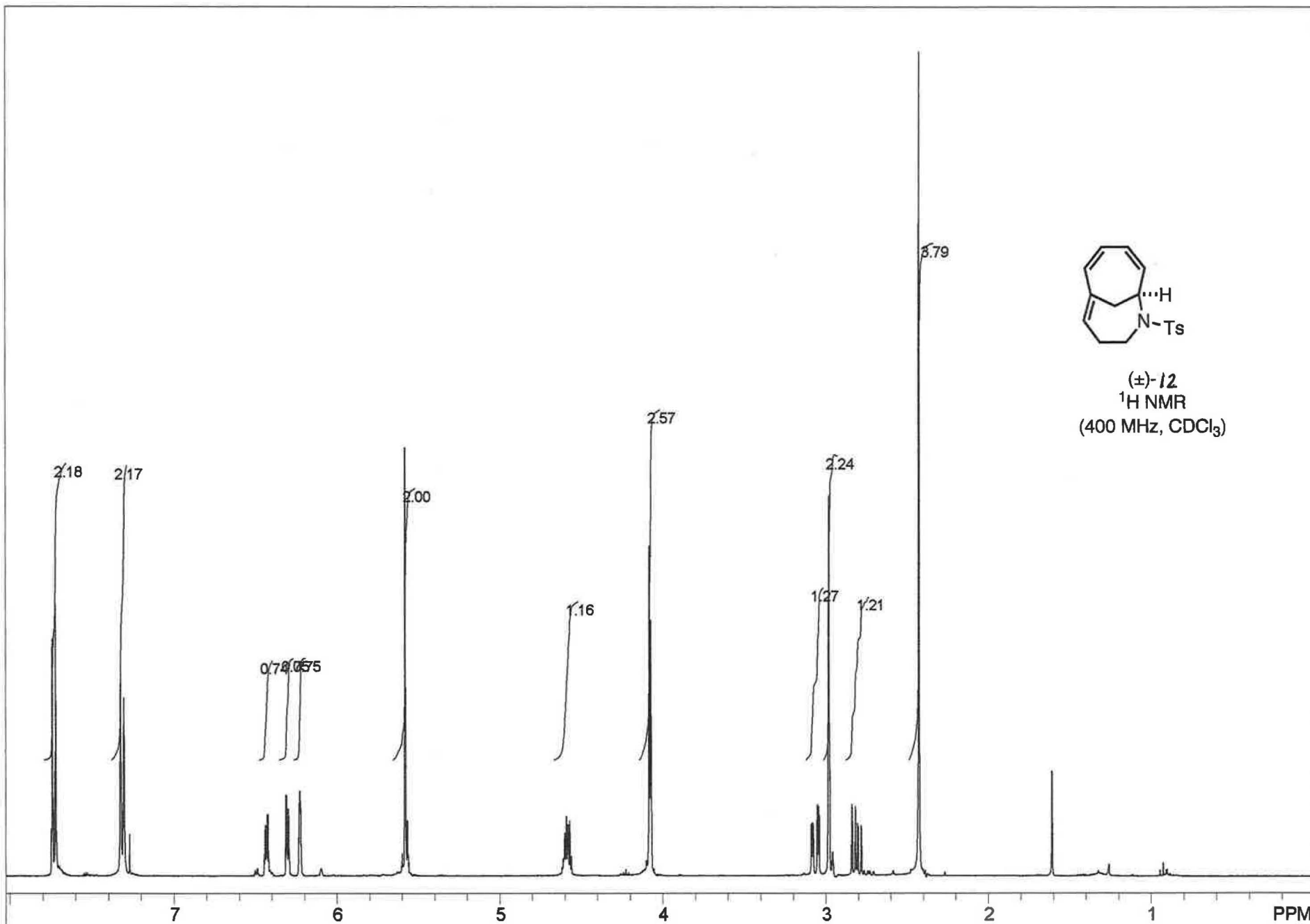
S 29



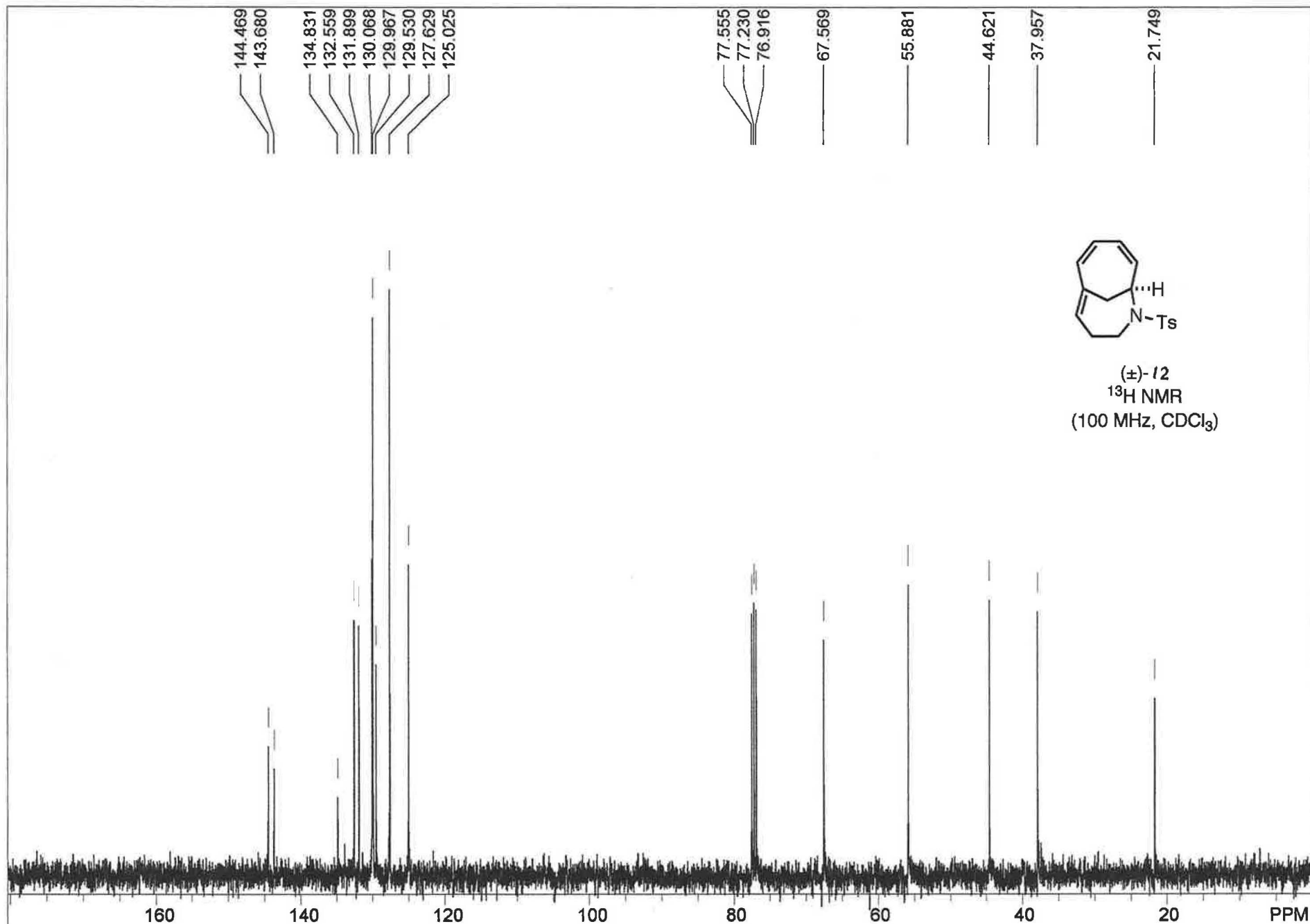
13C OBSERVE:blank line

USER: -- DATE: May 11 2010

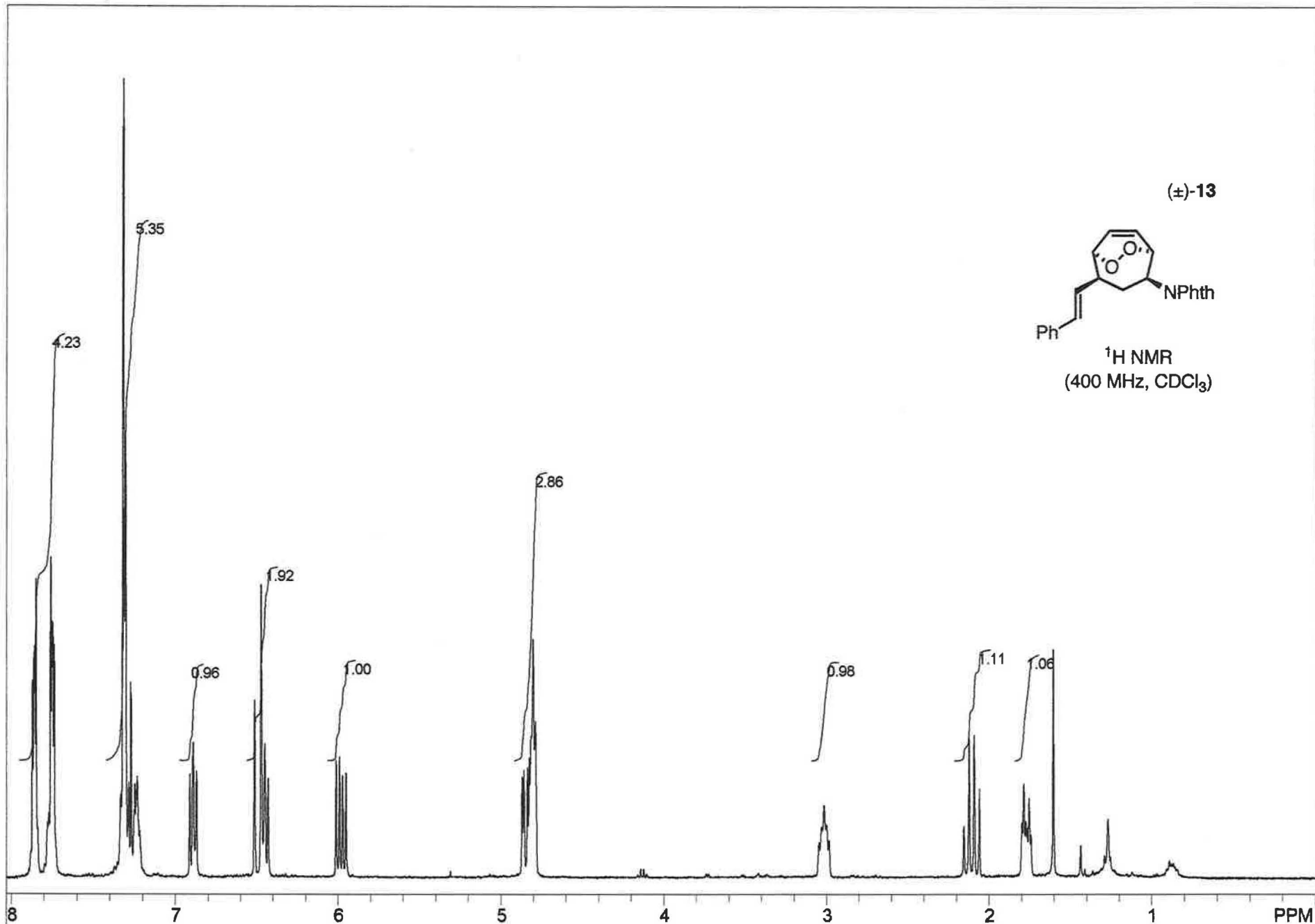
F1: 75.476	F2: 300.133	SW1: 18868	OF1: 8287.1	PTS1d: 34246	65536
EX: s2pul	PW: 8.5 us	PD: 1.0 sec	NA:	LB: 1.0	Nuts - \$as051210p13c.fid



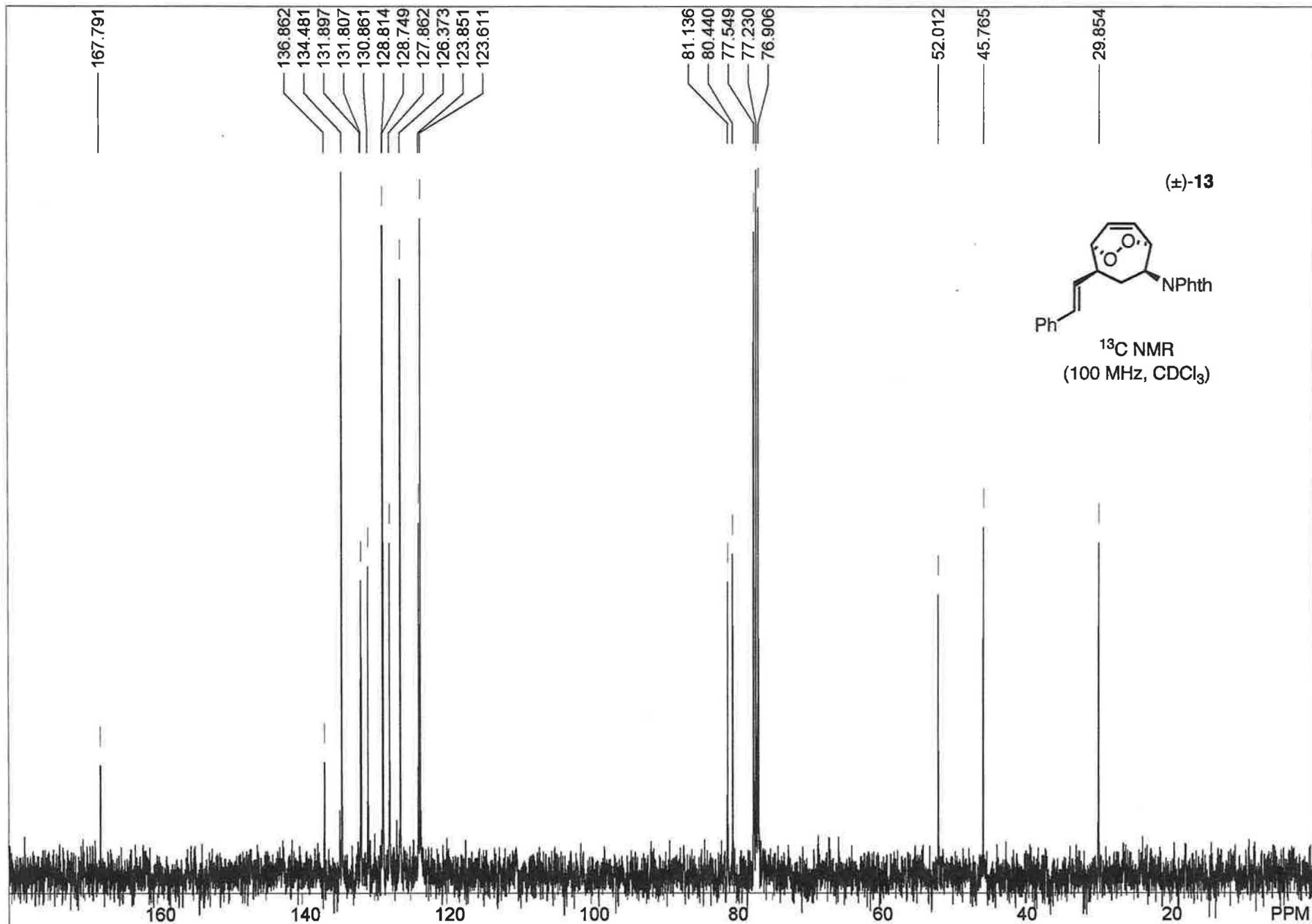
:blank line				USER: -- DATE: Dec 5 2011		
F1: 399.746	F2: 100.525	SW1: 6410		OF1: 2403.2		PTS1d: 13132 , 16384
EX: s2pul		PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$m176chloroform.fid



:blank line				USER: -- DATE: Dec 5 2011			
F1: 100.526	F2: 399.745	SW1: 24510		OF1: 10577.0		PTS1d: 31875	32768
EX: s2pul		PW: 5.8 us	PD: 1.0 sec	NA: 256	LB: 1.5	Nuts - \$m176chloroformc.fid	



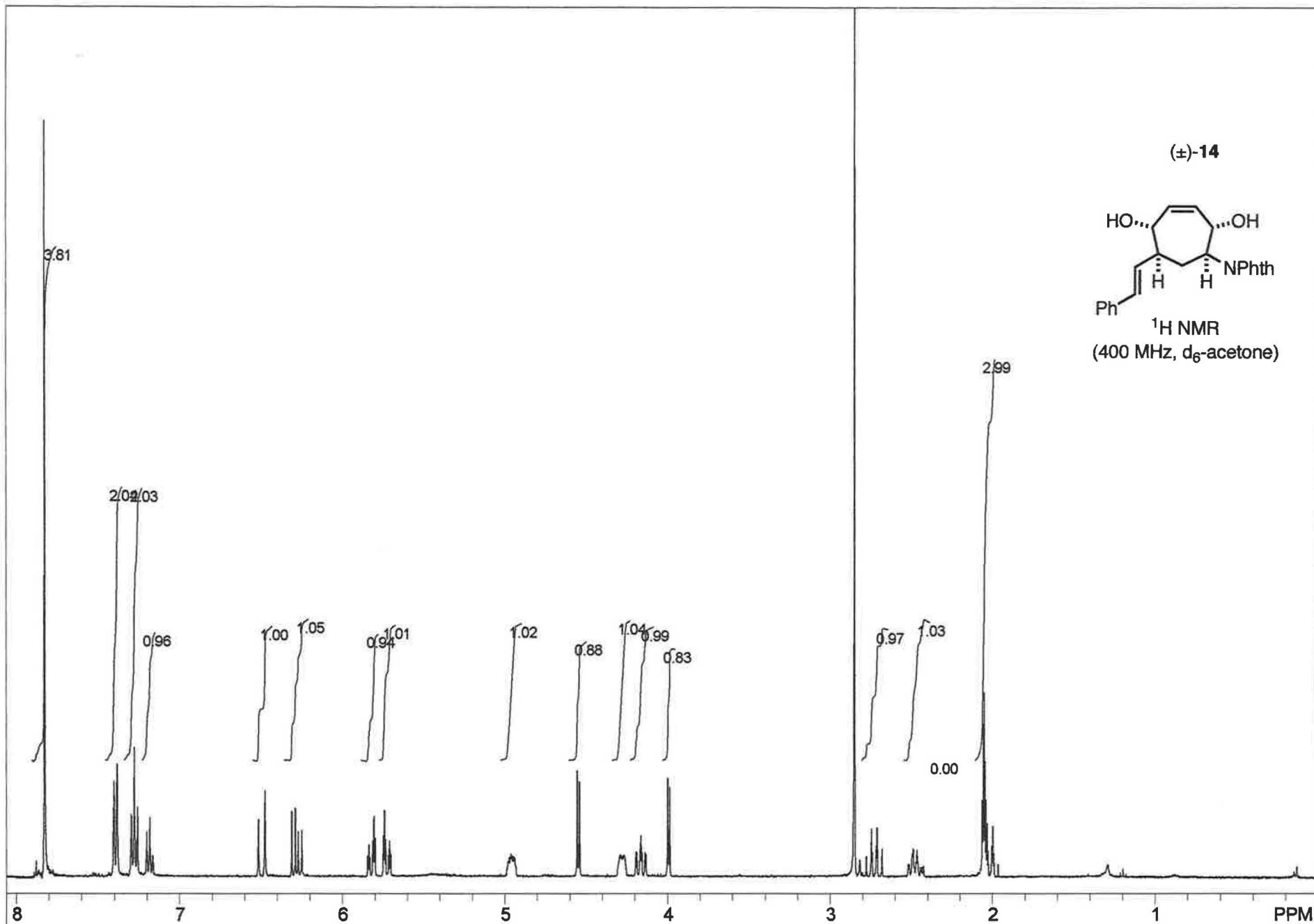
:blank line				USER: -- DATE: Nov 16 2010		
F1: 399.746	F2: 100.525	SW1: 6410		OF1: 2403.8		PTS1d: 13132 , 16384
EX: s2pul	PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$ase604p.fid



:blank line

USER: -- DATE: Nov 16 2010

F1: 100.526	F2: 399.745	SW1: 24510	OF1: 10575.1	PTS1d: 31875 , 32768
EX: s2pul	PW: 5.8 us	PD: 1.0 sec	NA: 256	LB: 2.0
				Nuts - \$ase604p13c.fid



:blank line

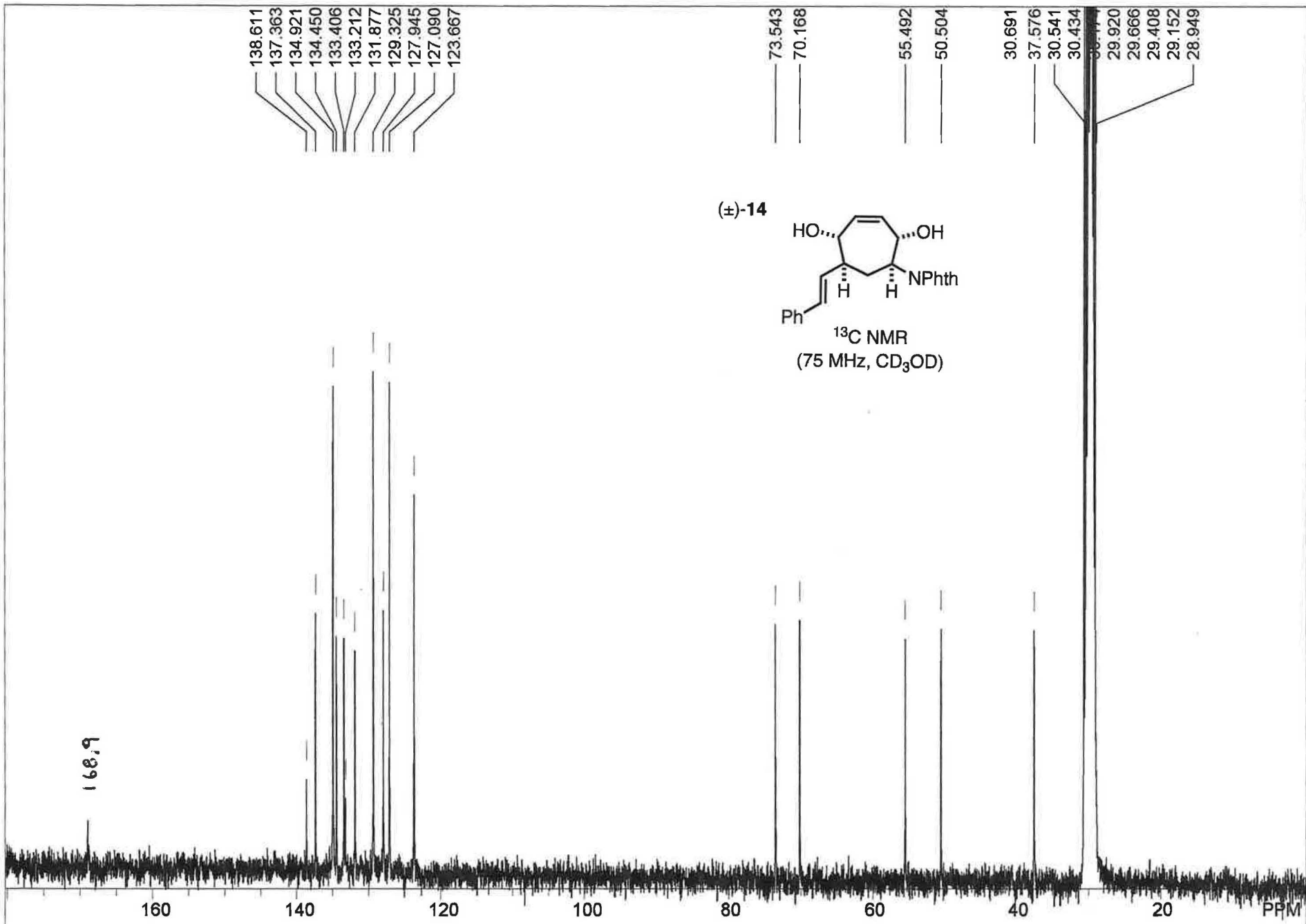
USER: -- DATE: Aug 6 2011

F1: 399.748	F2: 100.526	SW1: 6410	OF1: 2398.3	PTSId: 13132 , 16384
EX: s2pul	PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0

Nuts - \$ase674pp.fid

535





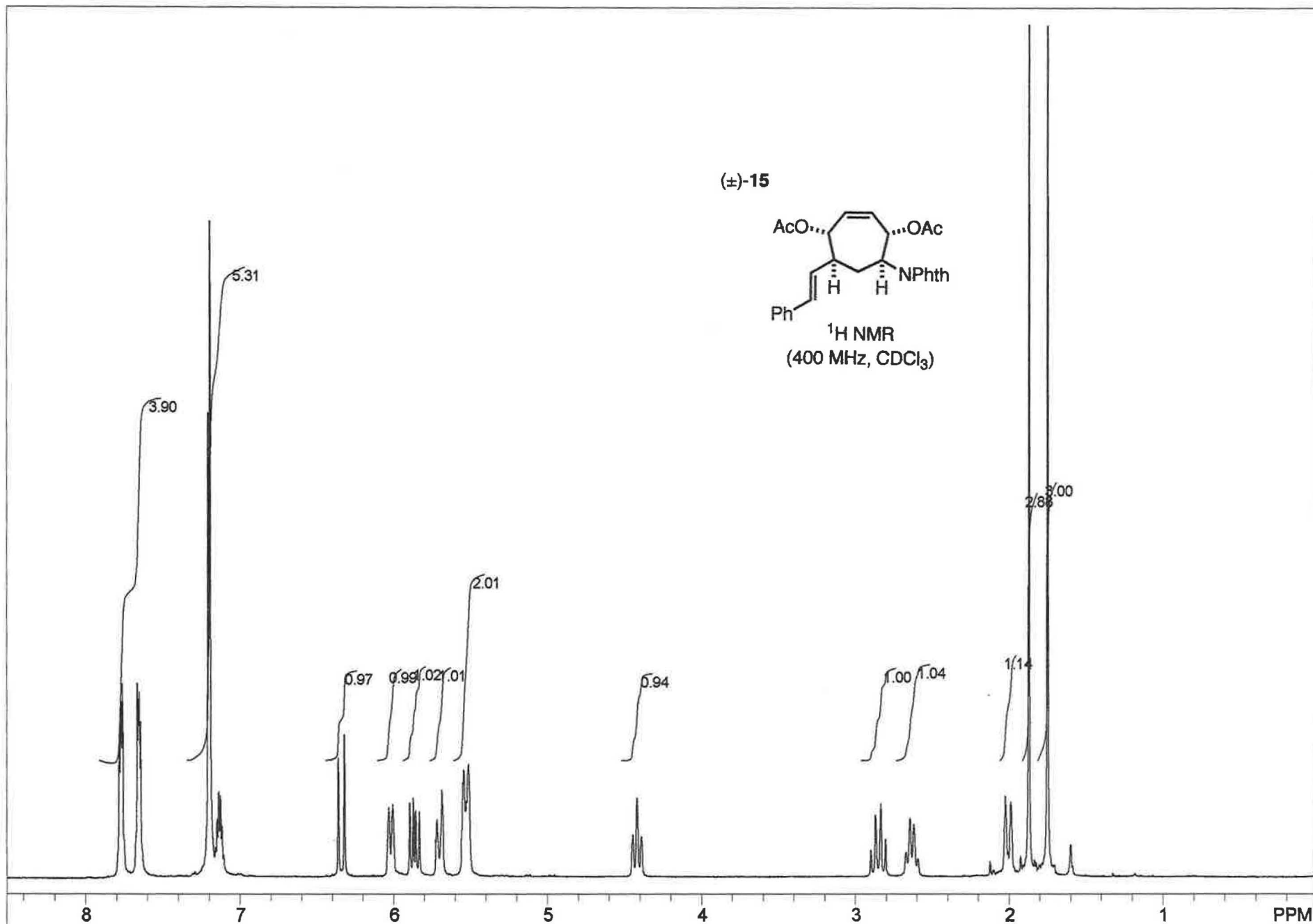
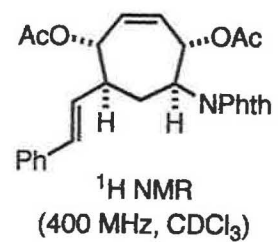
<sup>13</sup>C OBSERVE: blank line

USER: -- DATE: Aug 6 2011

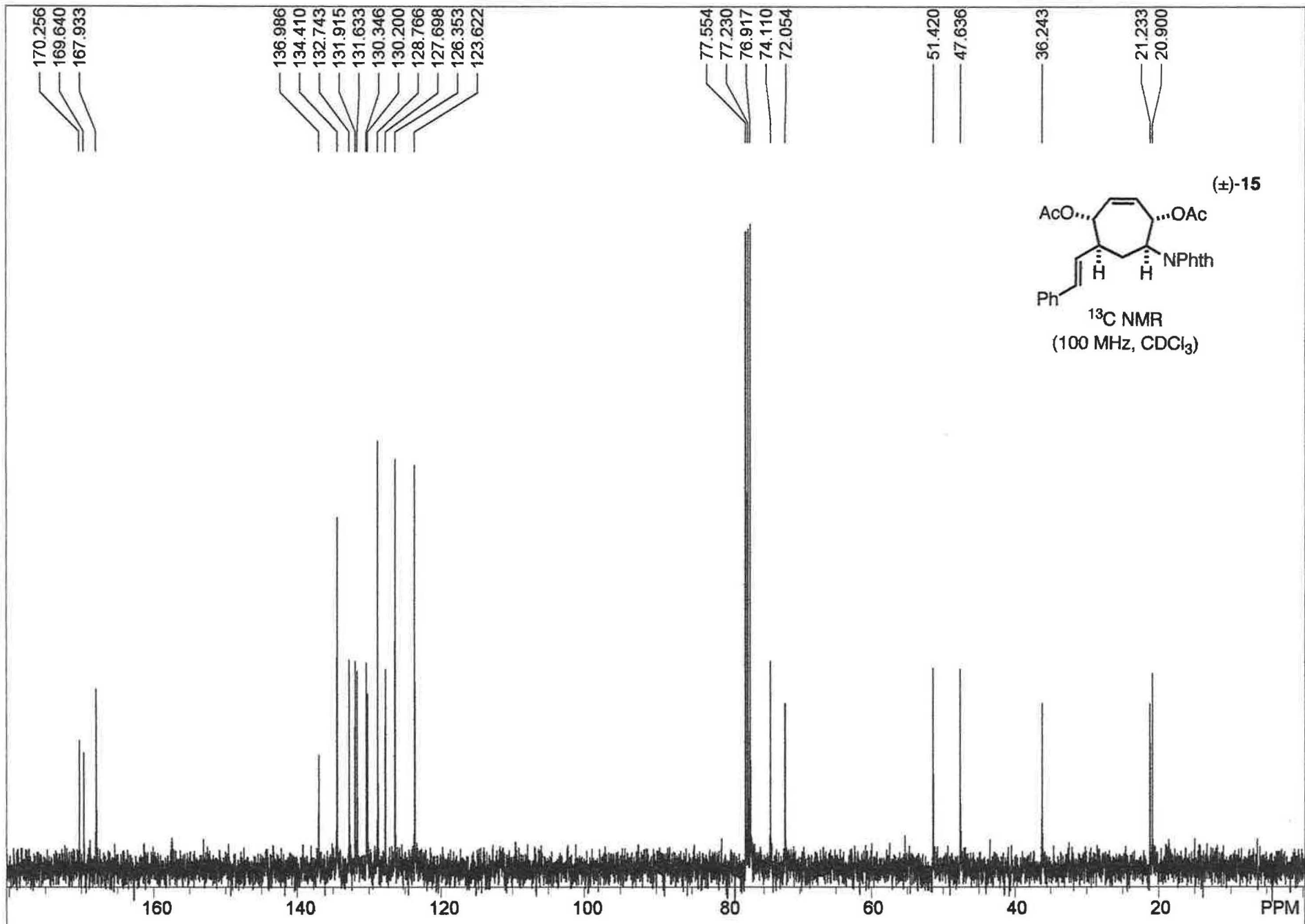
F1: 75.477	F2: 300.134	SW1: 18868	OF1: 8336.6	PTS1d: 34246 , 65536
EX: s2pul	PW: 7.3 us	PD: 1.0 sec	NA:	LB: 1.5

Nuts - \$ase67413c.fid

(±)-15

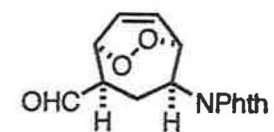


:blank line				USER: -- DATE: Apr 11 2012		
F1: 399.746	F2: 100.525	SW1: 6410	OF1: 2372.2	PTS1d: 13132 , 16384		
EX: s2pul	PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$ml143pure.fid	

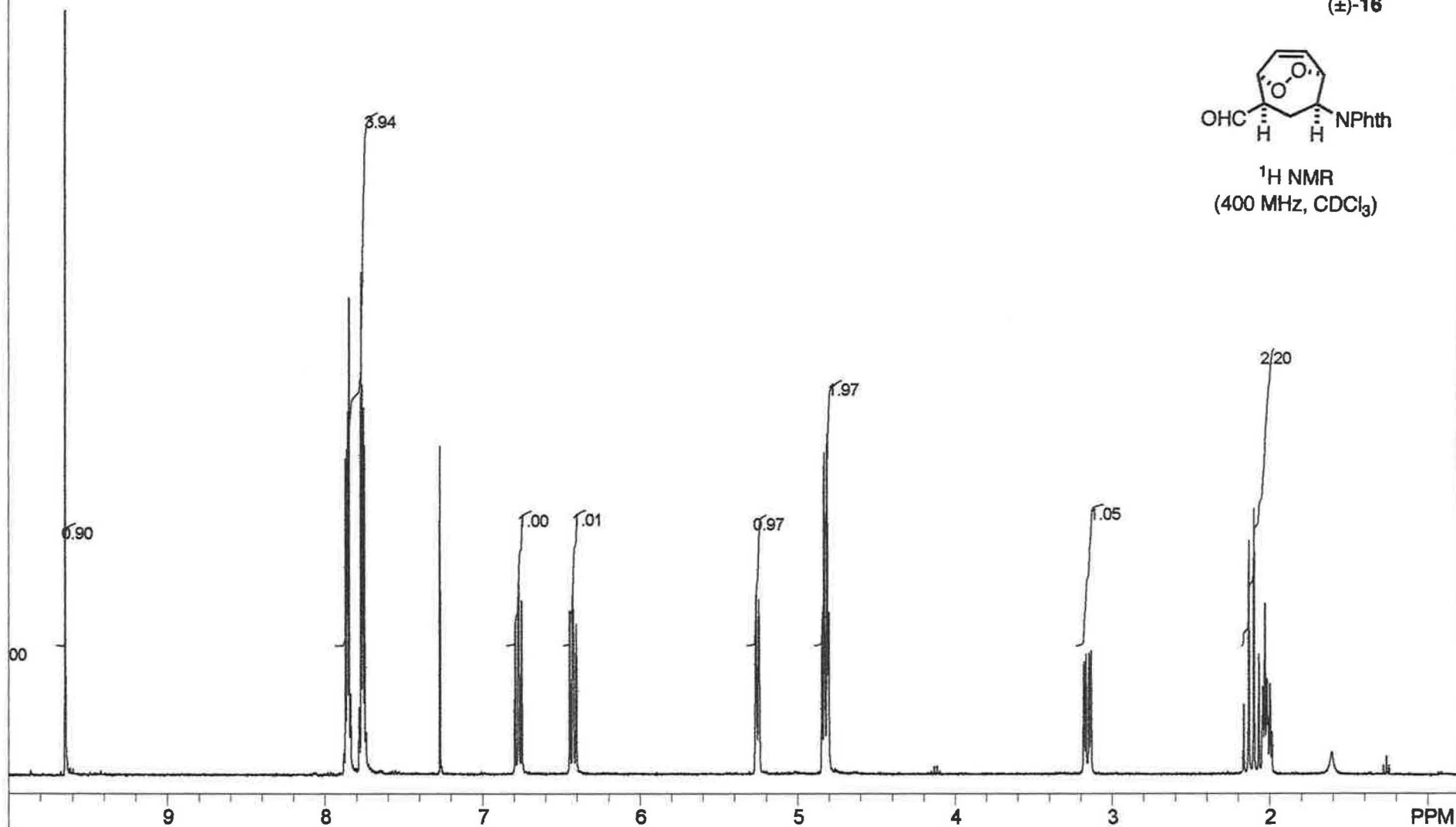


:blank line				USER: -- DATE: Apr 11 2012		
F1: 100.526	F2: 399.745	SW1: 24510		OF1: 10574.0		PTS1d: 31875 . 32768
EX: s2pul		PW: 5.8 us	PD: 1.0 sec	NA: 256	LB: 1.5	Nuts - \$ml143C.fid

(±)-16



<sup>1</sup>H NMR  
(400 MHz, CDCl<sub>3</sub>)



:blank line

USER: -- DATE: Apr 24 2012

F1: 399.746

F2: 100.525

SW1: 6410

OF1: 2403.7

PTS1d: 13132 , 16384

EX: s2pul

PW: 8.0 us

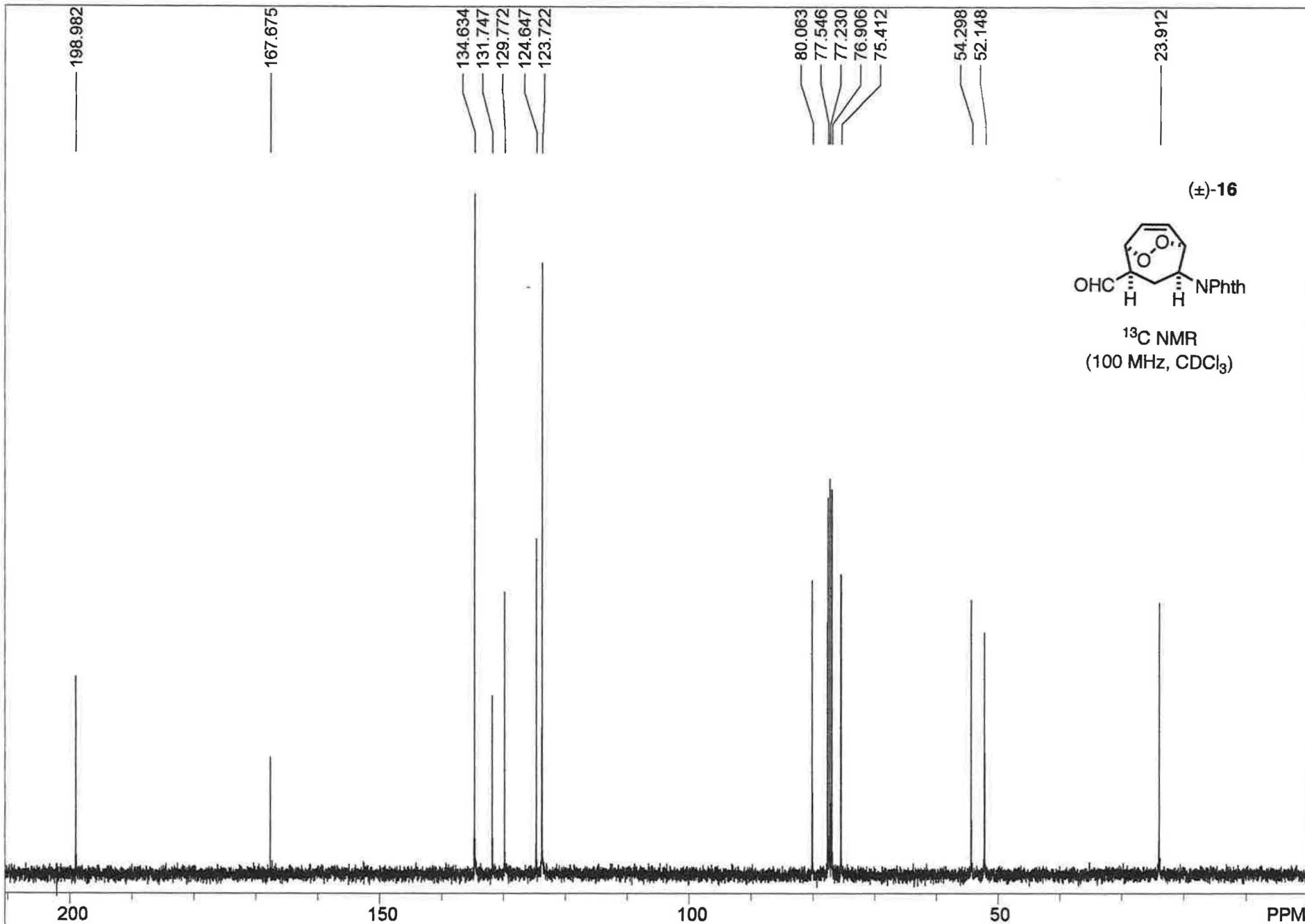
PD: 1.0 sec

NA: 8

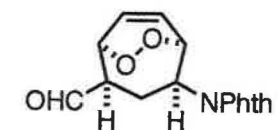
LB: 0.0

Nuts - \$ml156.fid

S 39



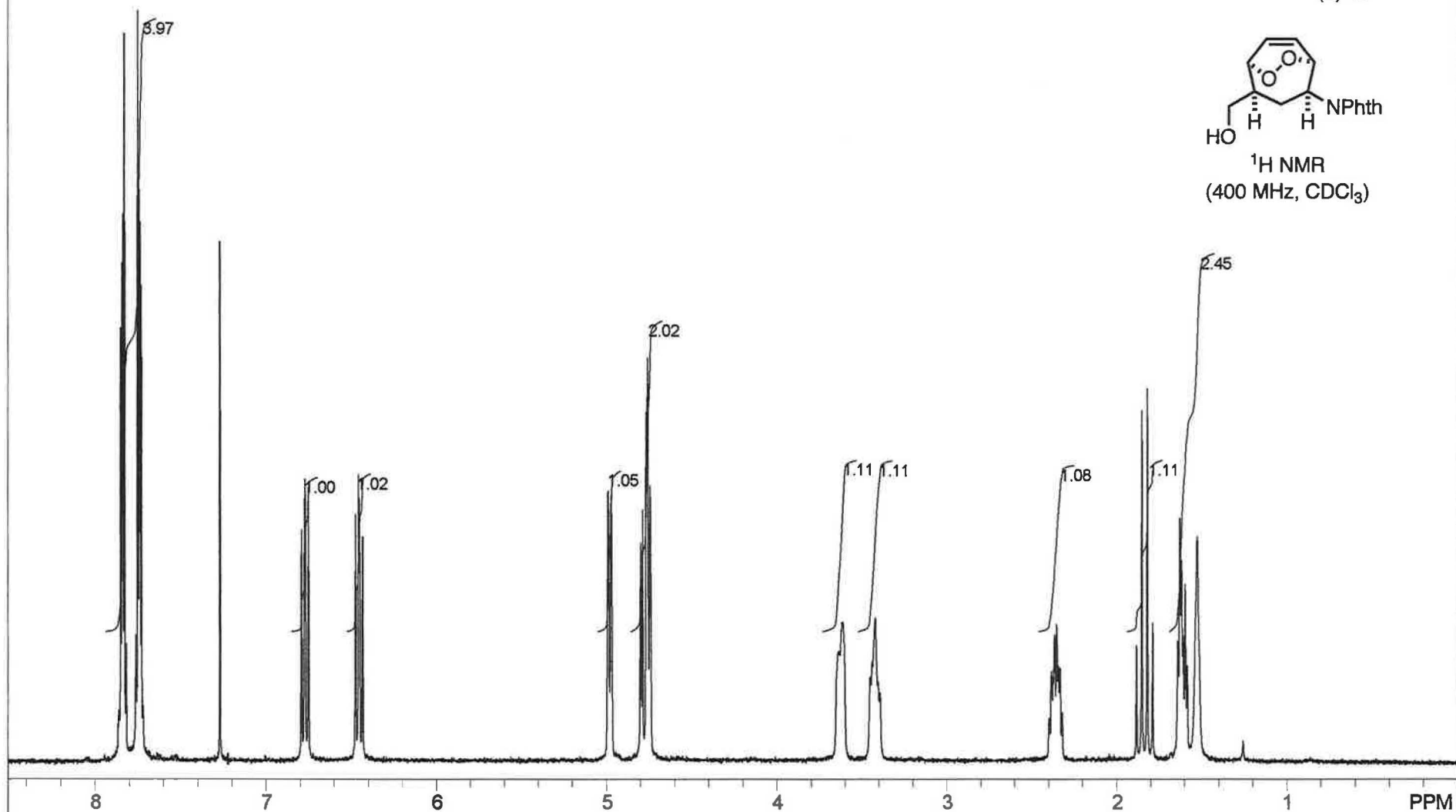
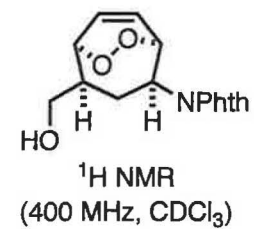
(±)-16



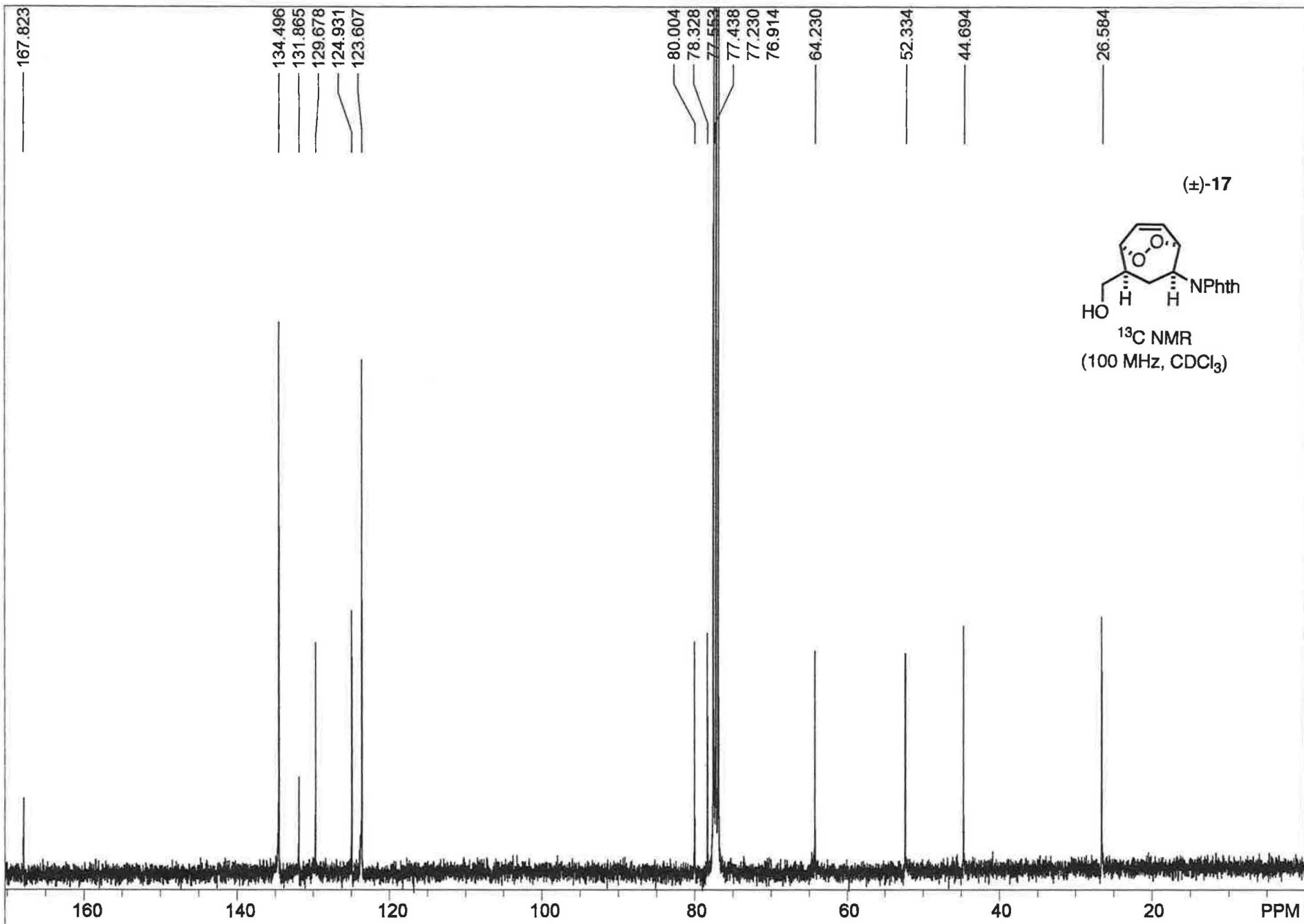
<sup>13</sup>C NMR  
(100 MHz, CDCl<sub>3</sub>)

:blank line				USER: -- DATE: Apr 24 2012		
F1: 100.526	F2: 399.745	SW1: 24510		OF1: 10575.7		PTS1d: 31875 . 32768
EX: s2pul		PW: 5.8 us	PD: 1.0 sec	NA: 1500	LB: 1.0	Nuts - \$ml156C.fid

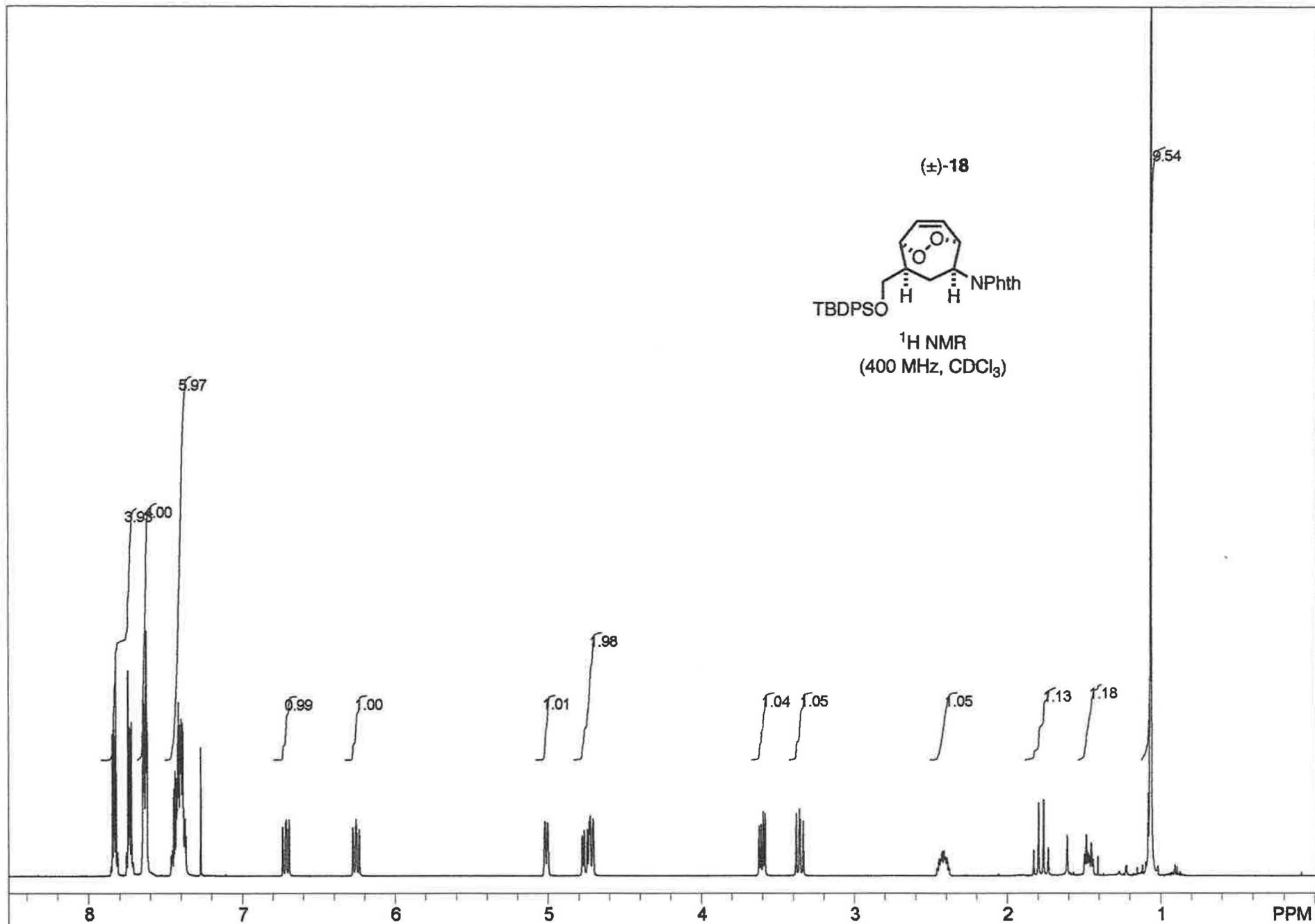
(±)-17



:blank line				USER: -- DATE: May 21 2012		
F1: 399.746	F2: 100.525	SW1: 6410		OF1: 2402.8		PTS1d: 13132 , 16384
EX: s2pul		PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$ml172final.fid

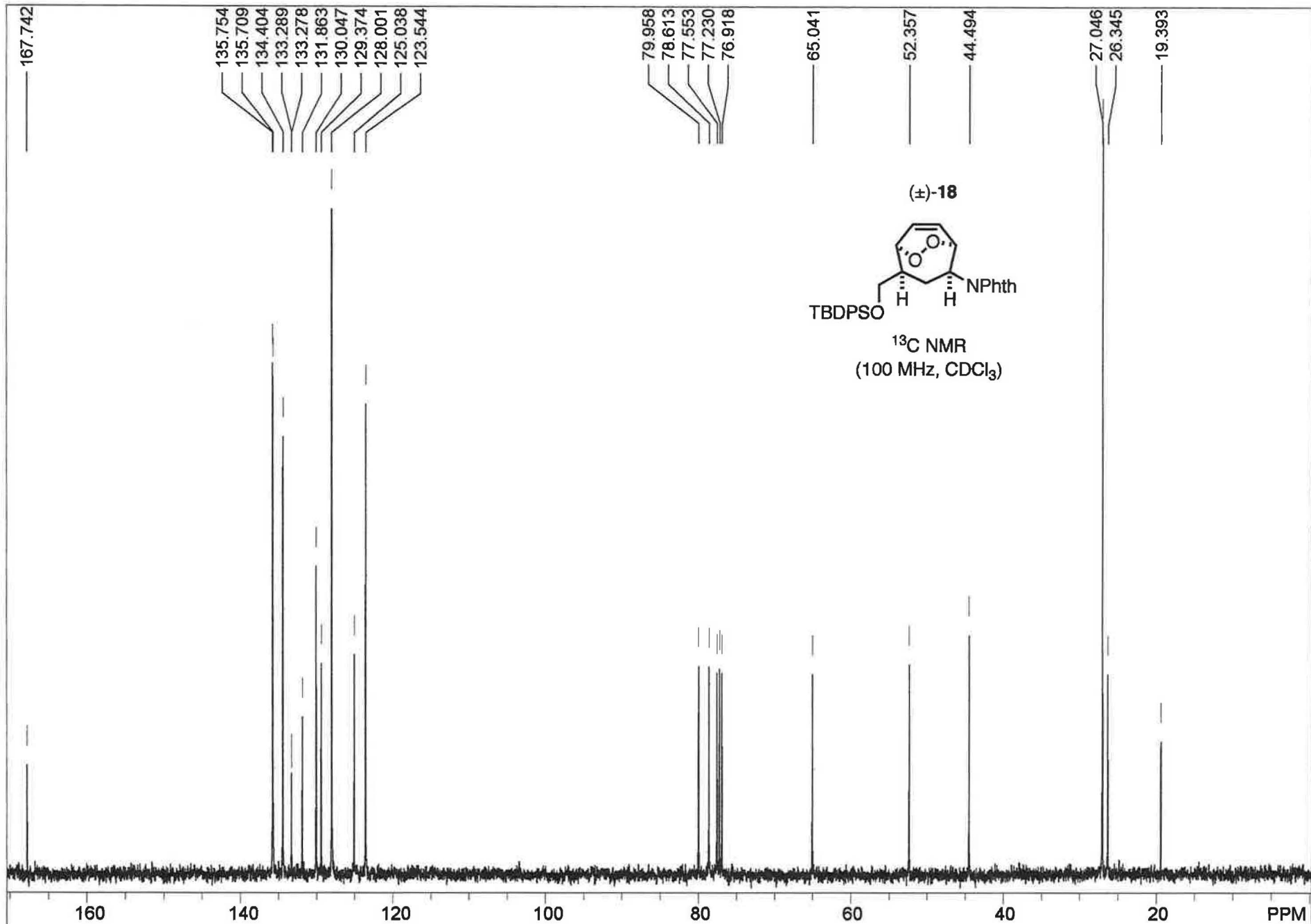


:blank line				USER: -- DATE: Apr 28 2012		
F1: 100.526	F2: 399.745	SW1: 24510		OF1: 10576.1		PTS1d: 31875 , 32768
EX: s2pul		PW: 5.8 us	PD: 1.0 sec	NA: 11968	LB: 1.0	Nuts - \$ml158f1pureC.fid



:blank line				USER: -- DATE: May 22 2012		
F1: 399.746	F2: 100.525	SW1: 6410		OF1: 2404.5		PTS1d: 13132 , 16384
EX: s2pul	PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$ml173f2pure.fid

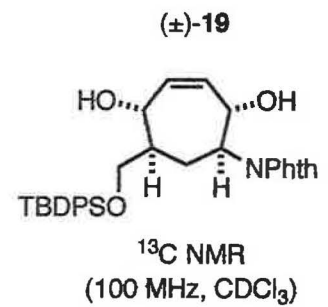
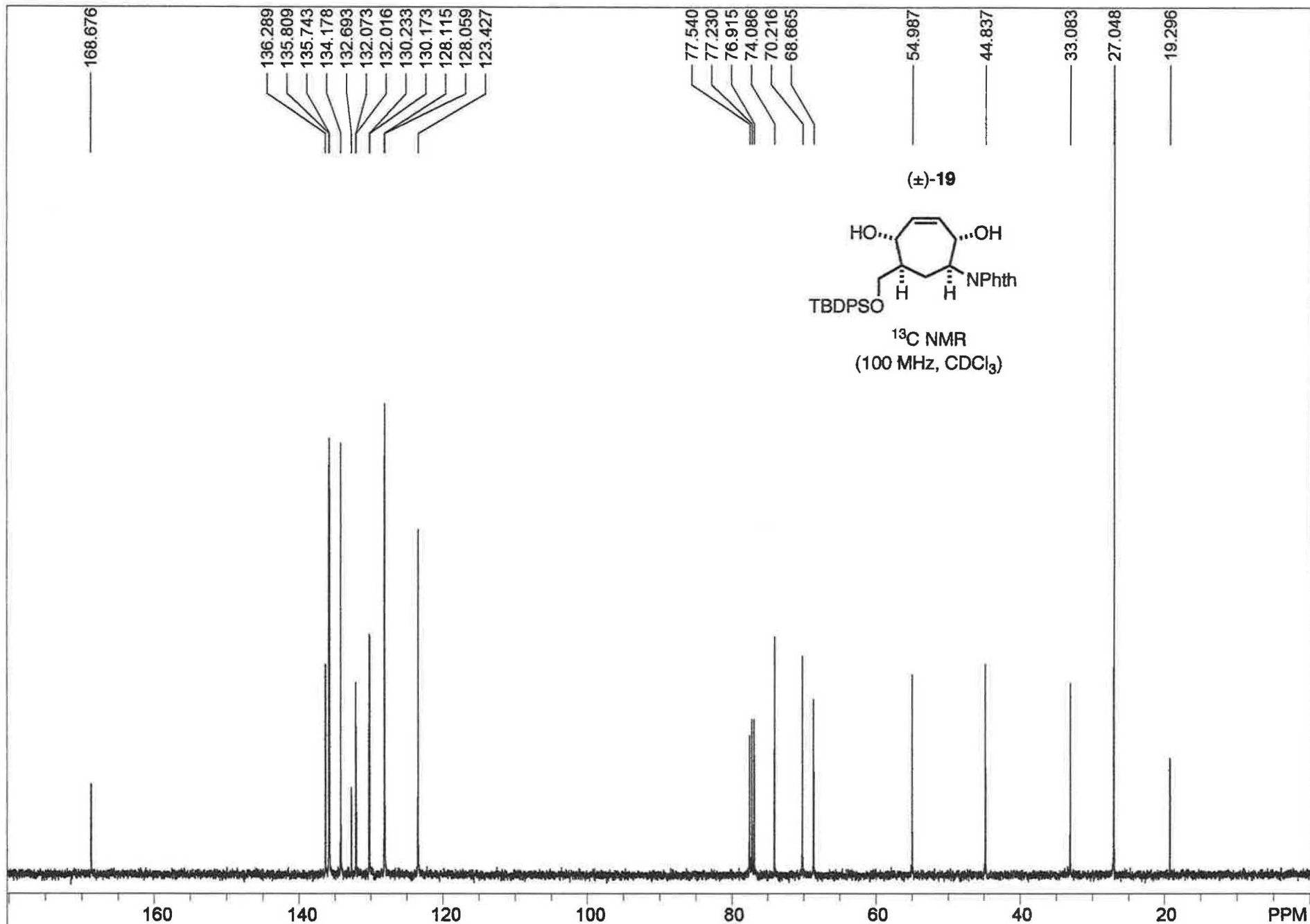




:blank line		USER: -- DATE: May 21 2012				
F1: 100.526	F2: 399.745	SW1: 24510		OF1: 10573.3		PTS1d: 31875 , 32768
EX: s2pul		PW: 5.8 us	PD: 1.0 sec	NA: 128	LB: 1.5	Nuts - \$ml173f2C.fid

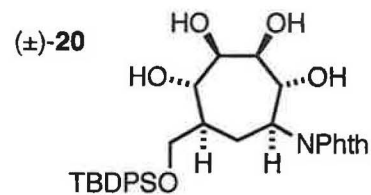
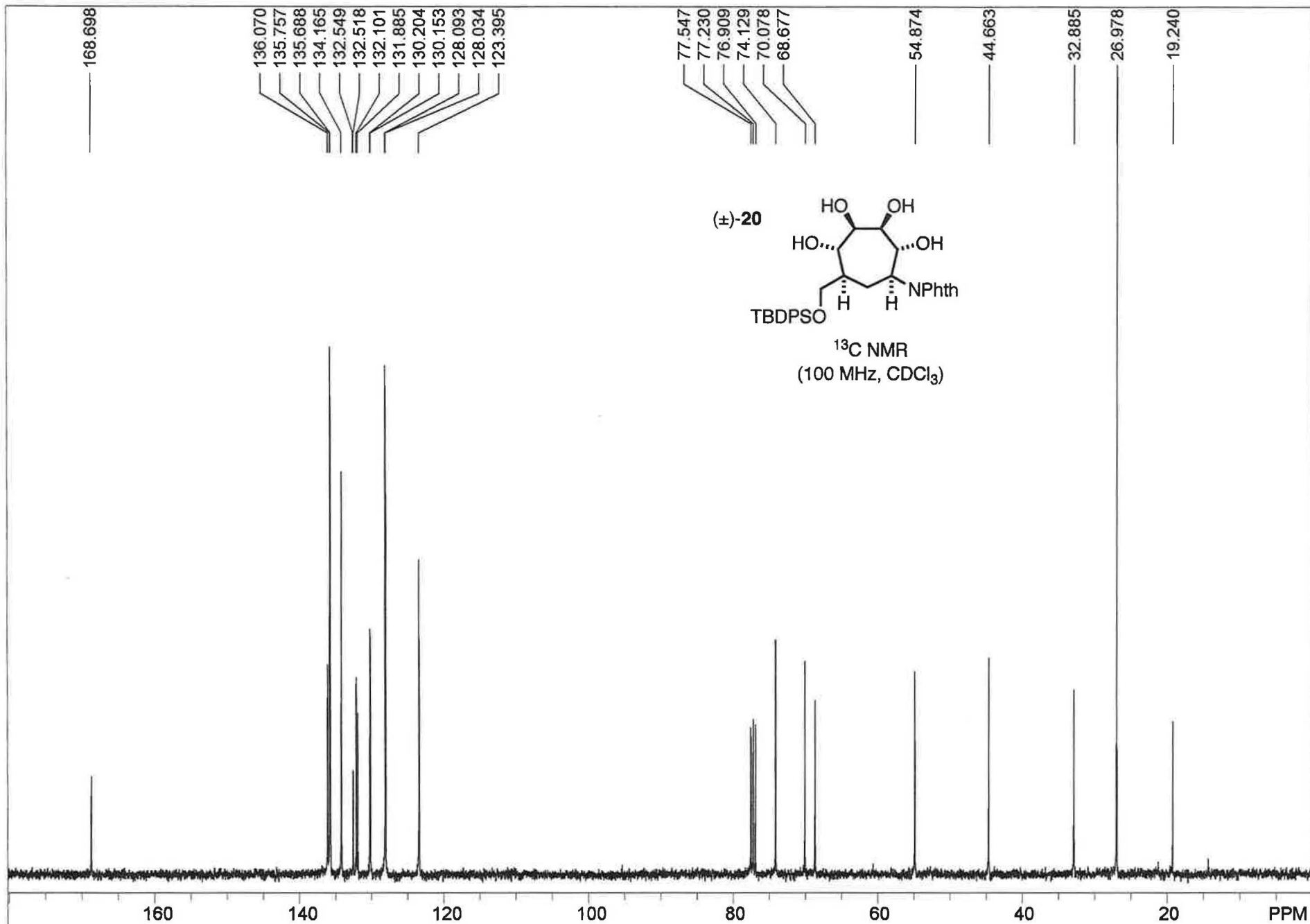
HTS





:blank line				USER: -- DATE: May 22 2012			
F1: 100.526	F2: 399.745	SW1: 24510		OF1: 10576.2		PTS1d: 31875 , 32768	
EX: s2pul		PW: 5.8 us	PD: 1.0 sec	NA: 64	LB: 1.0	Nuts - \$ml175_againC.fid	

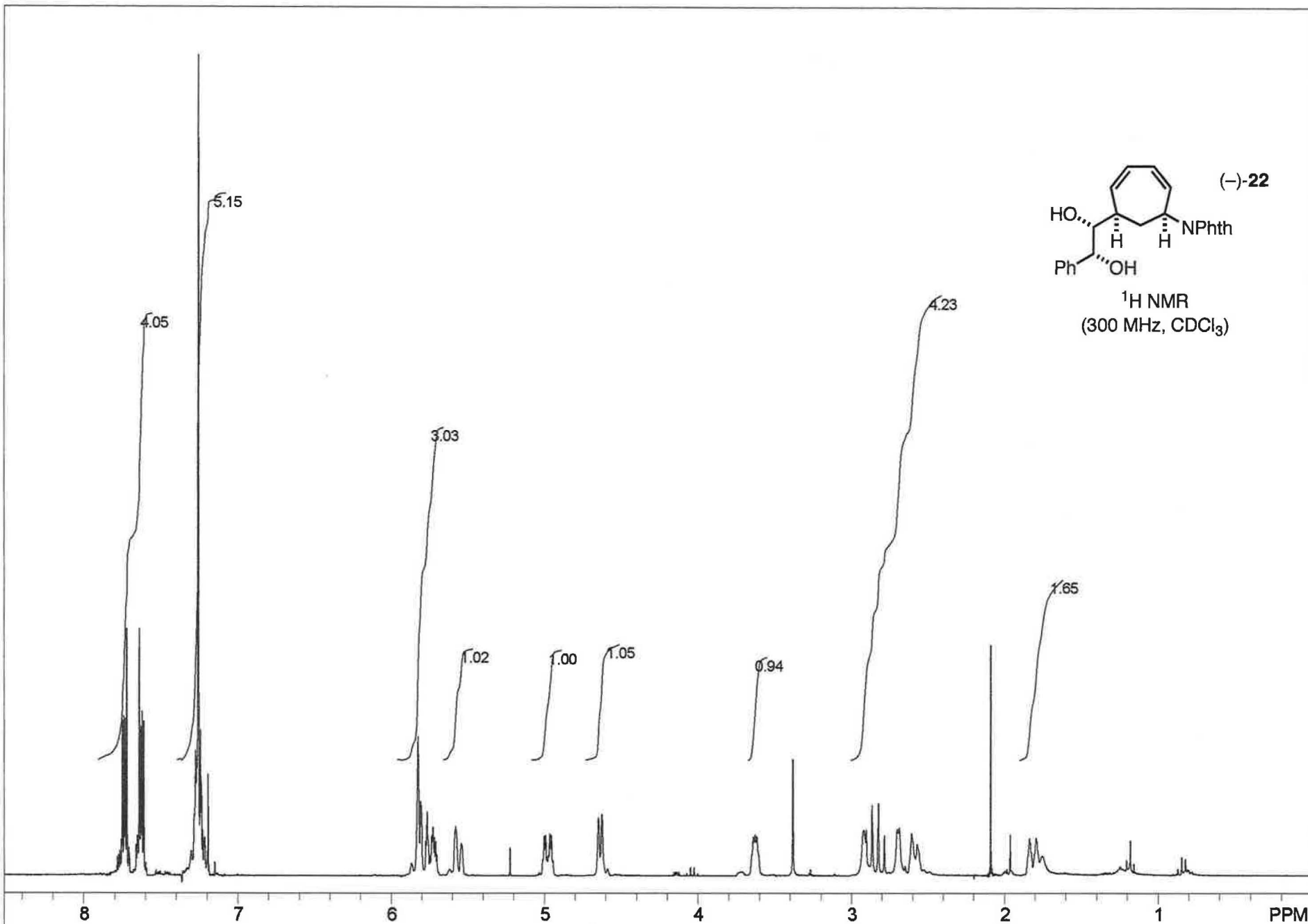




<sup>13</sup>C NMR  
(100 MHz, CDCl<sub>3</sub>)

:blank line				USER: -- DATE: Jul 4 2012			
F1: 100.526	F2: 399.745	SW1: 24510		OF1: 10570.0		PTS1d: 31875	32768
EX: s2pul		PW: 5.8 us	PD: 1.0 sec	NA: 256	LB: 1.5	Nuts - \$ml192C.fid	

875

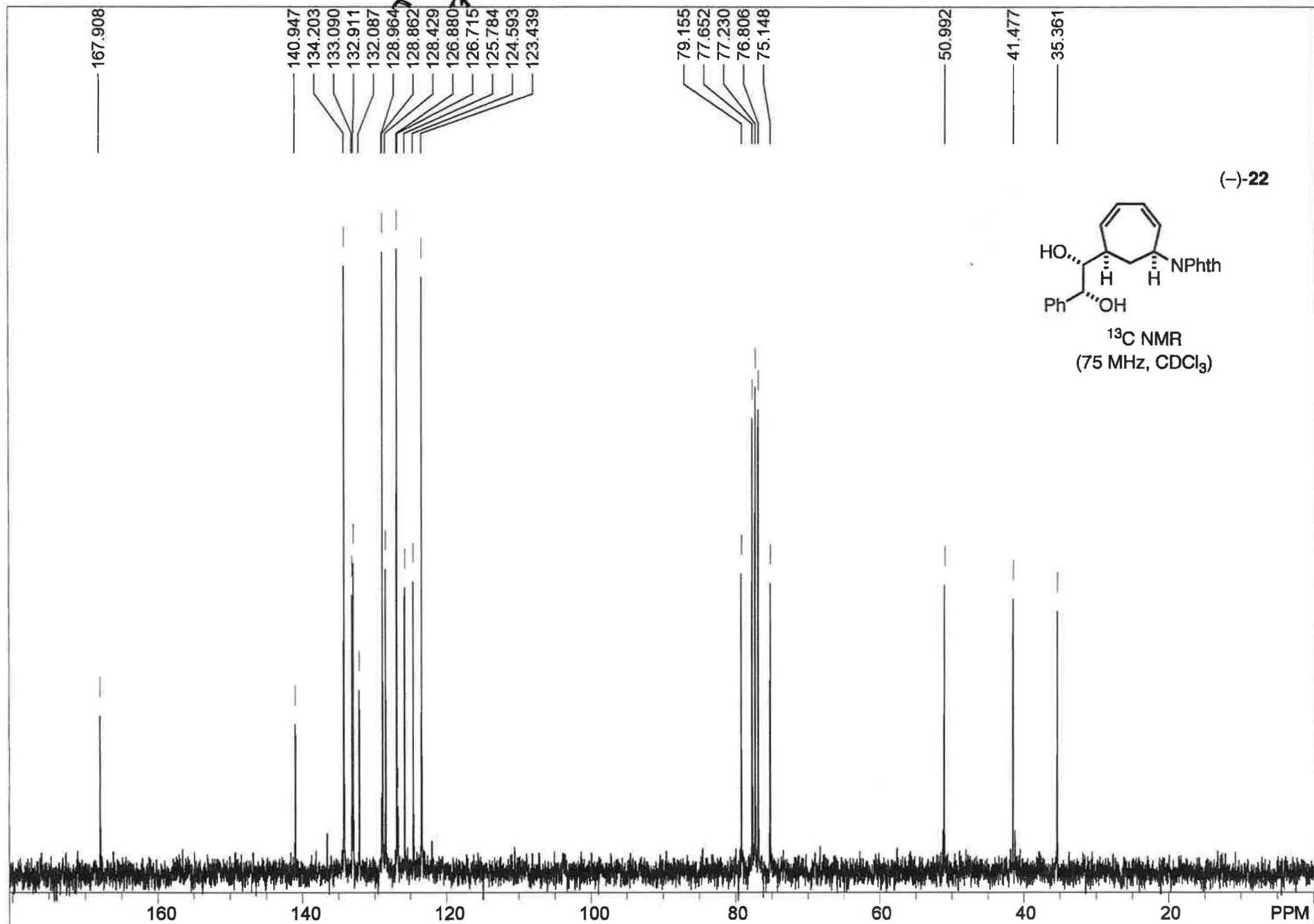


STANDARD 1H OBSERVE:blank line

USER: -- DATE: Jun 17 2010

F1: 300.133	F2: 75.476	SW1: 4803	OF1: 1781.3	PTS1d: 9596	16384
EX: s2pul	PW: 6.3 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$ase536f11.fid

549

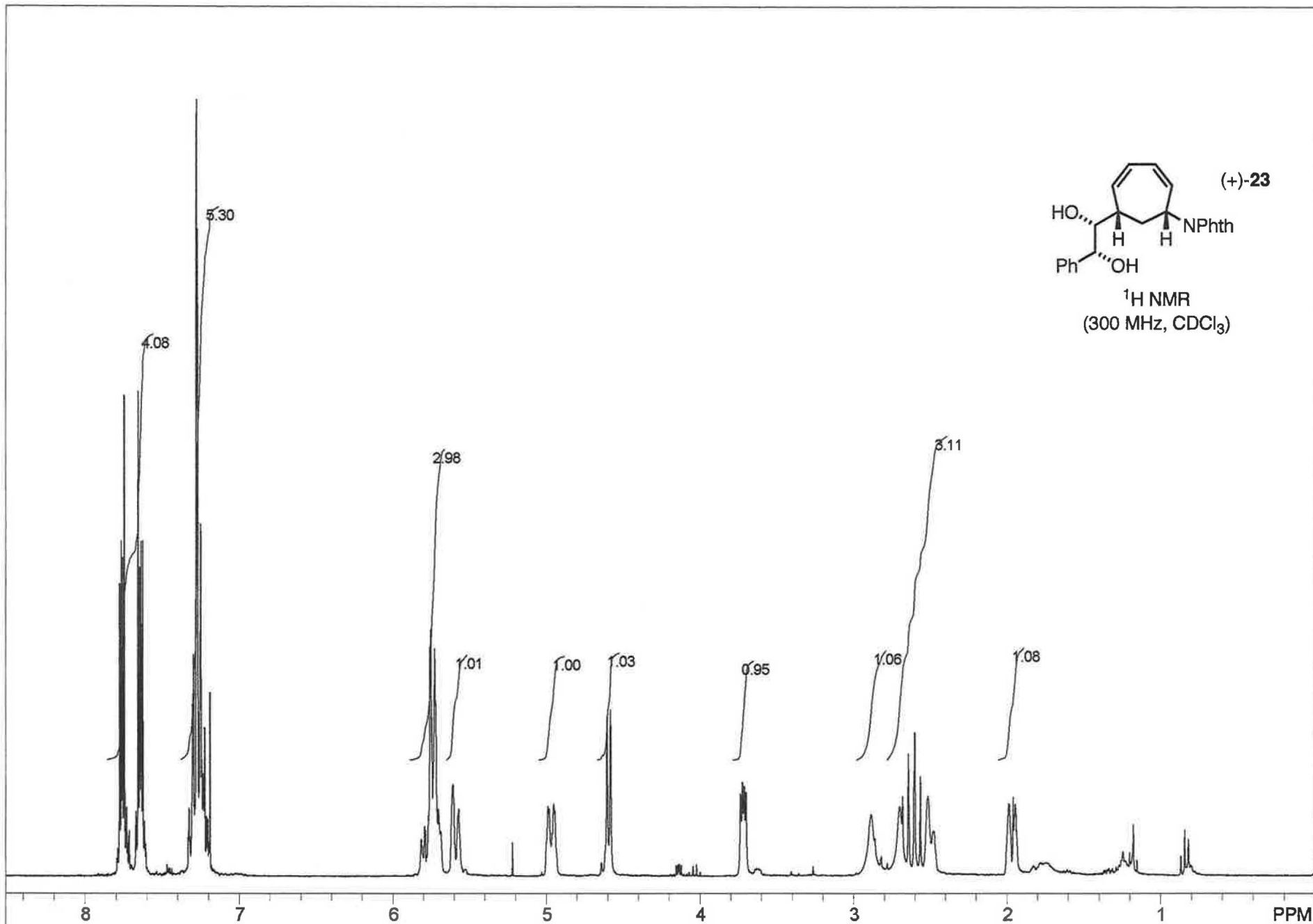


13C OBSERVE:blank line

USER: -- DATE: Jun 17 2010

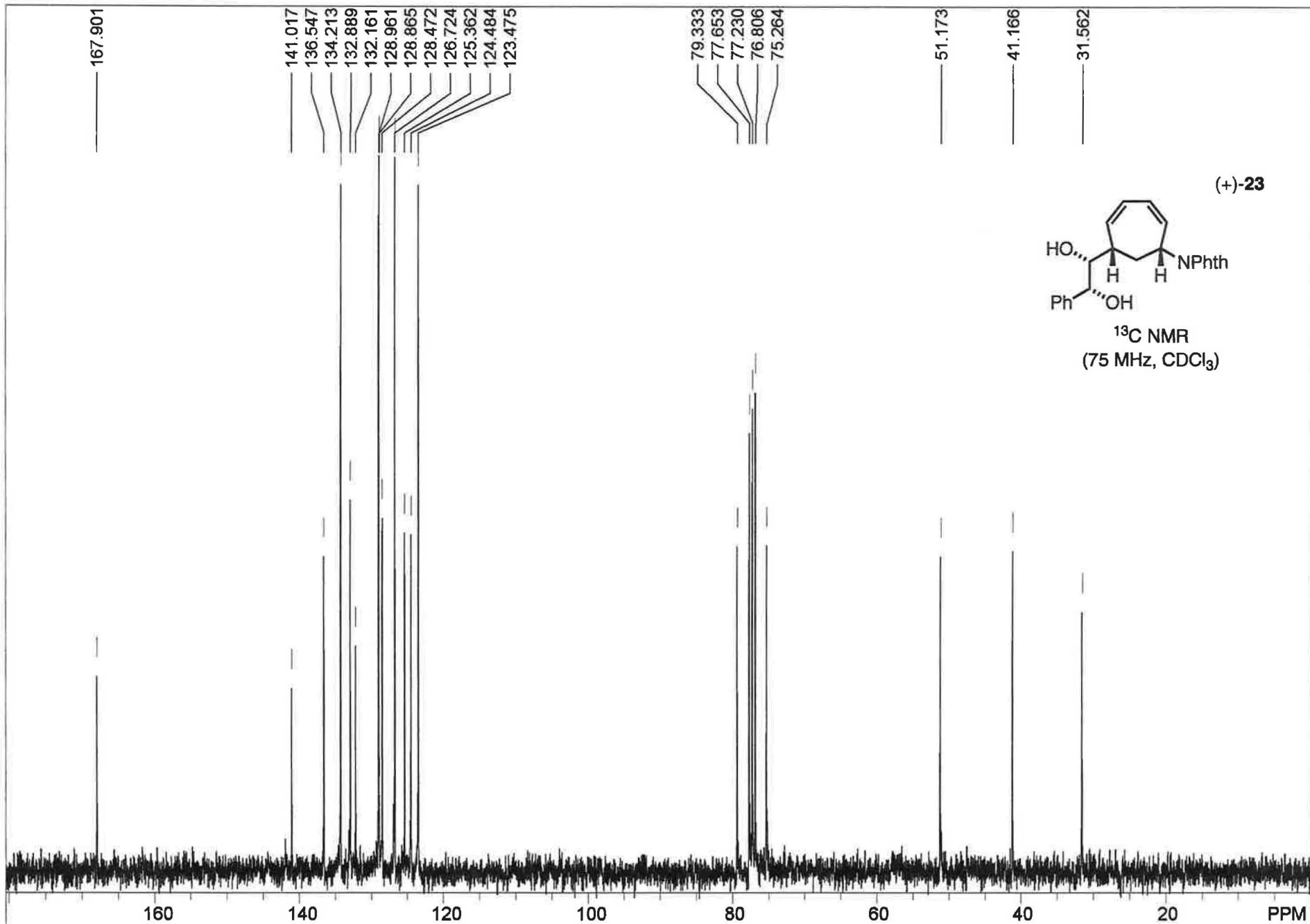
F1: 75.476 F2: 300.133 SW1: 18868 OF1: 8297.3 PTS1d: 34246 65536

EX: s2pul PW: 8.5 us PD: 1.0 sec NA: 256 LB: 1.5 Nuts - \$ase536f13c.fid



STANDARD 1H OBSERVE:blank line				USER: -- DATE: Jun 17 2010			
F1: 300.133	F2: 75.476	SW1: 4803		OF1: 1780.4		PTS1d: 9596	16384
EX: s2pul		PW: 6.3 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$ase536f2II.fid	





13C OBSERVE:blank line

USER: -- DATE: Jun 17 2010

F1: 75.476

F2: 300.133

SW1: 18868

OF1: 8297.2

PTS1d: 34246 . 65536

EX: s2pul

PW: 8.5 us

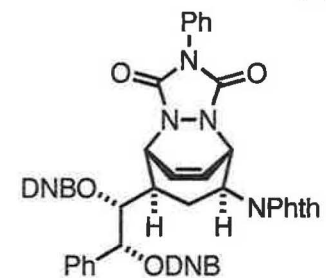
PD: 1.0 sec

NA: 256

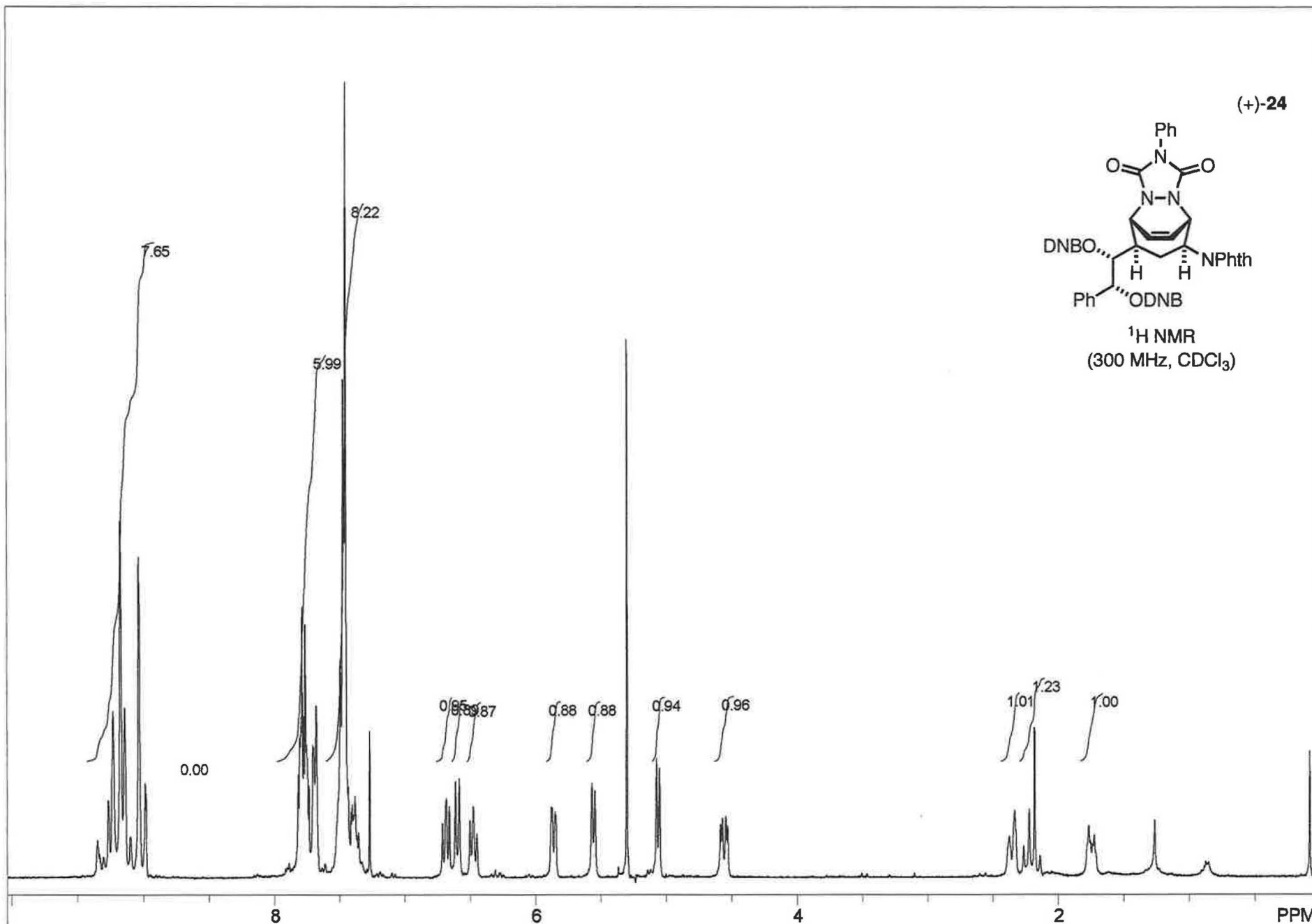
LB: 1.5

Nuts - \$ase536f2c13.fid

(+)-24



<sup>1</sup>H NMR  
(300 MHz, CDCl<sub>3</sub>)



STANDARD 1H OBSERVE:blank line

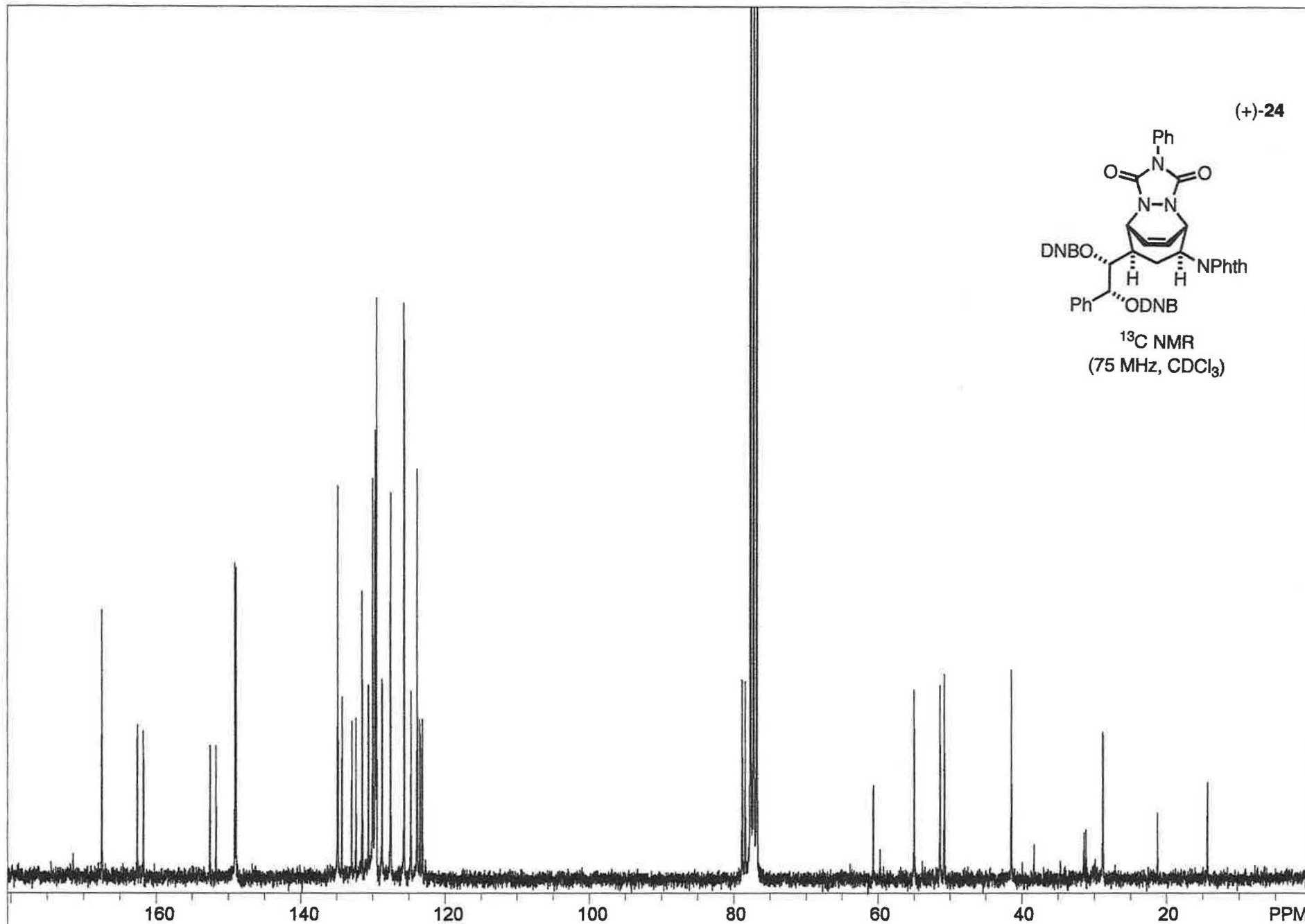
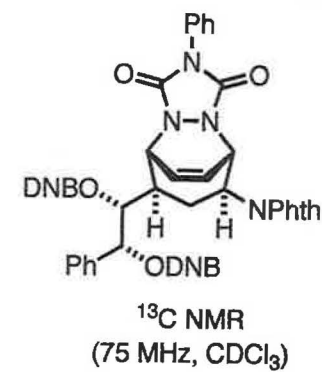
USER: -- DATE: Mar 15 2011

F1: 300.133	F2: 75.476	SW1: 4803	OF1: 1801.5	PTS1d: 9596 . 16384
EX: s2pul	PW: 6.2 us	PD: 1.0 sec	NA: 8	LB: 0.0

Nuts - \$as011511diolf1adp.fid

53

(+)-24

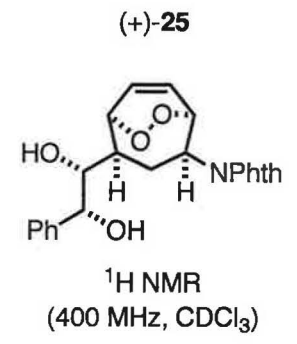
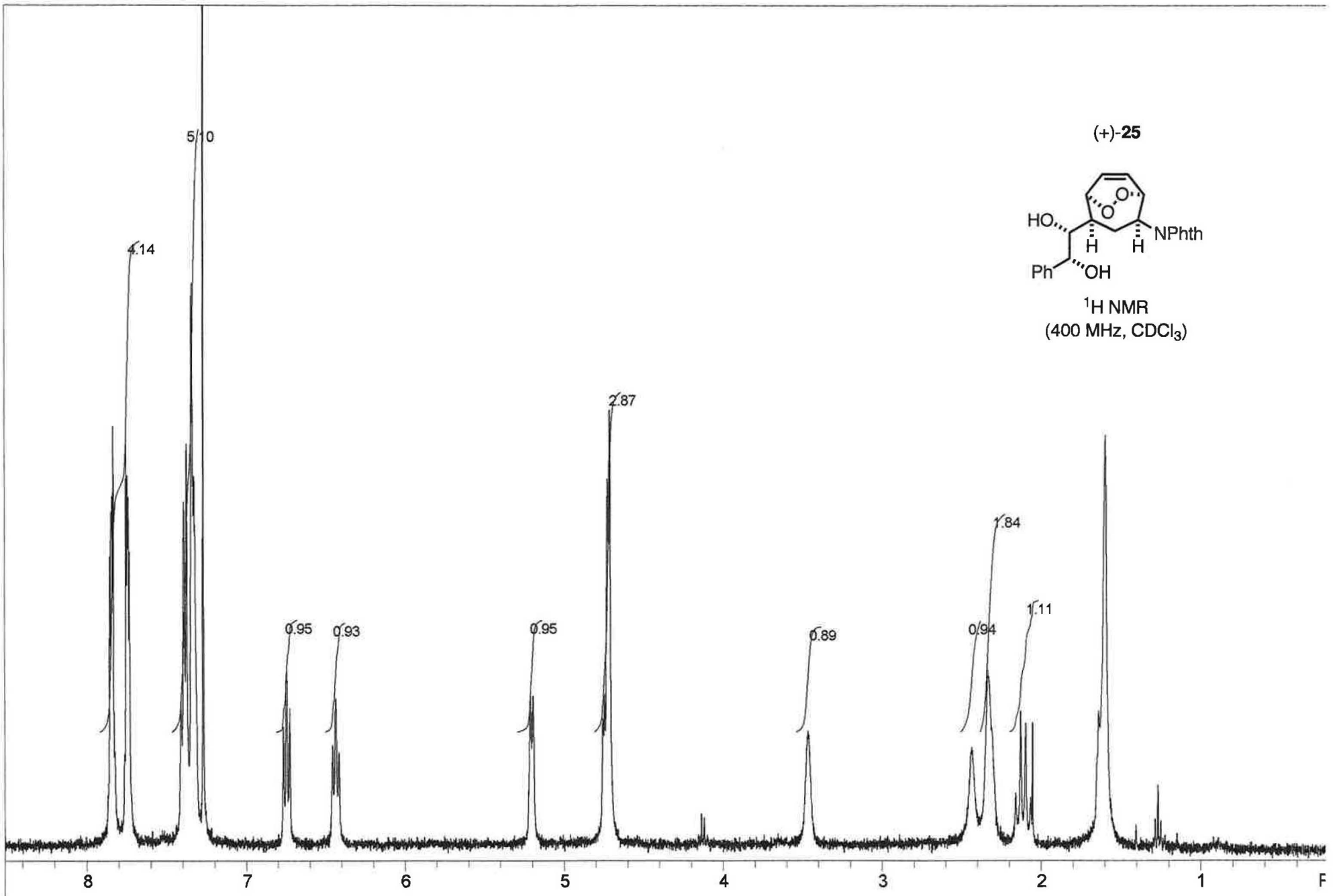


13C OBSERVE:blank line

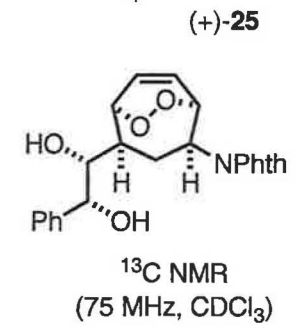
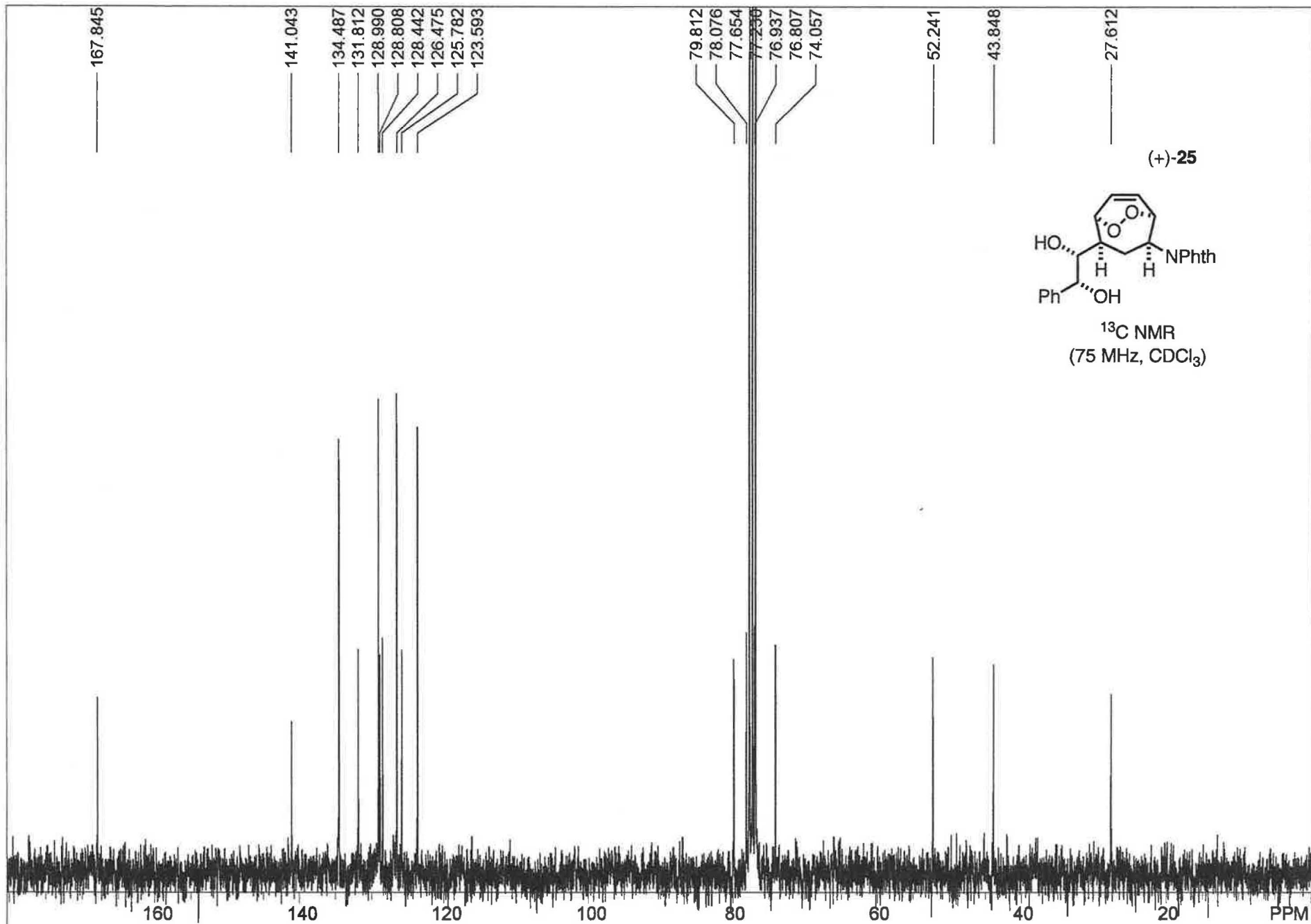
USER: -- DATE: Apr 15 2011

F1: 75.476	F2: 300.133	SW1: 18868	OF1: 8283.2	PTS1d: 34246 , 65536
EX: s2pul	PW: 7.3 us	PD: 1.0 sec	NA:	LB: 1.0

Nuts - \$ase636pp13c.fid

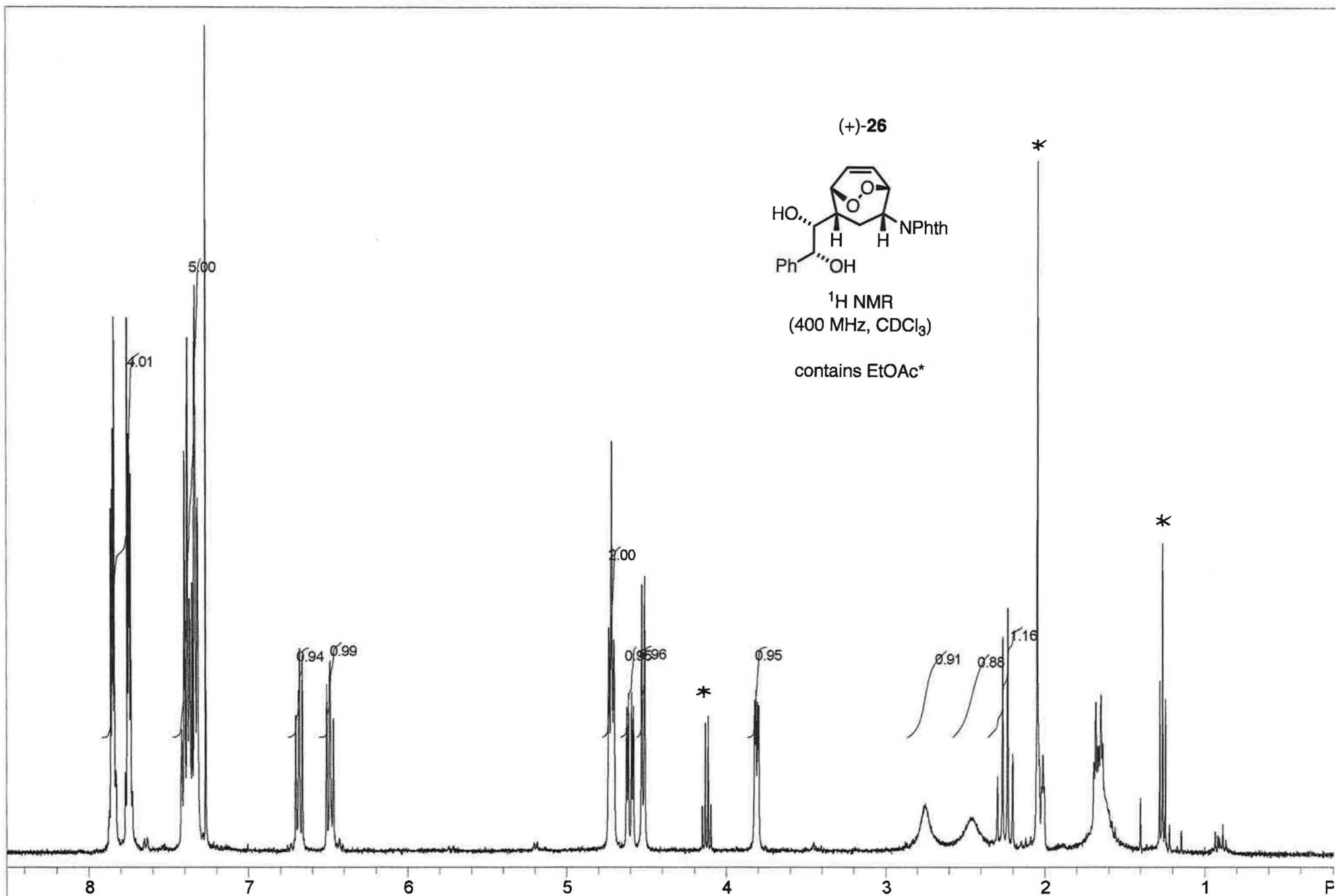


:blank line				USER: -- DATE: Jun 21 20		
F1: 399.746	F2: 100.525	SW1: 6410	OF1: 2403.7	PTS1d: 13132 , 16384		
EX: s2pul	PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$ml184fl	



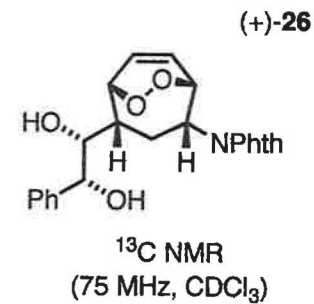
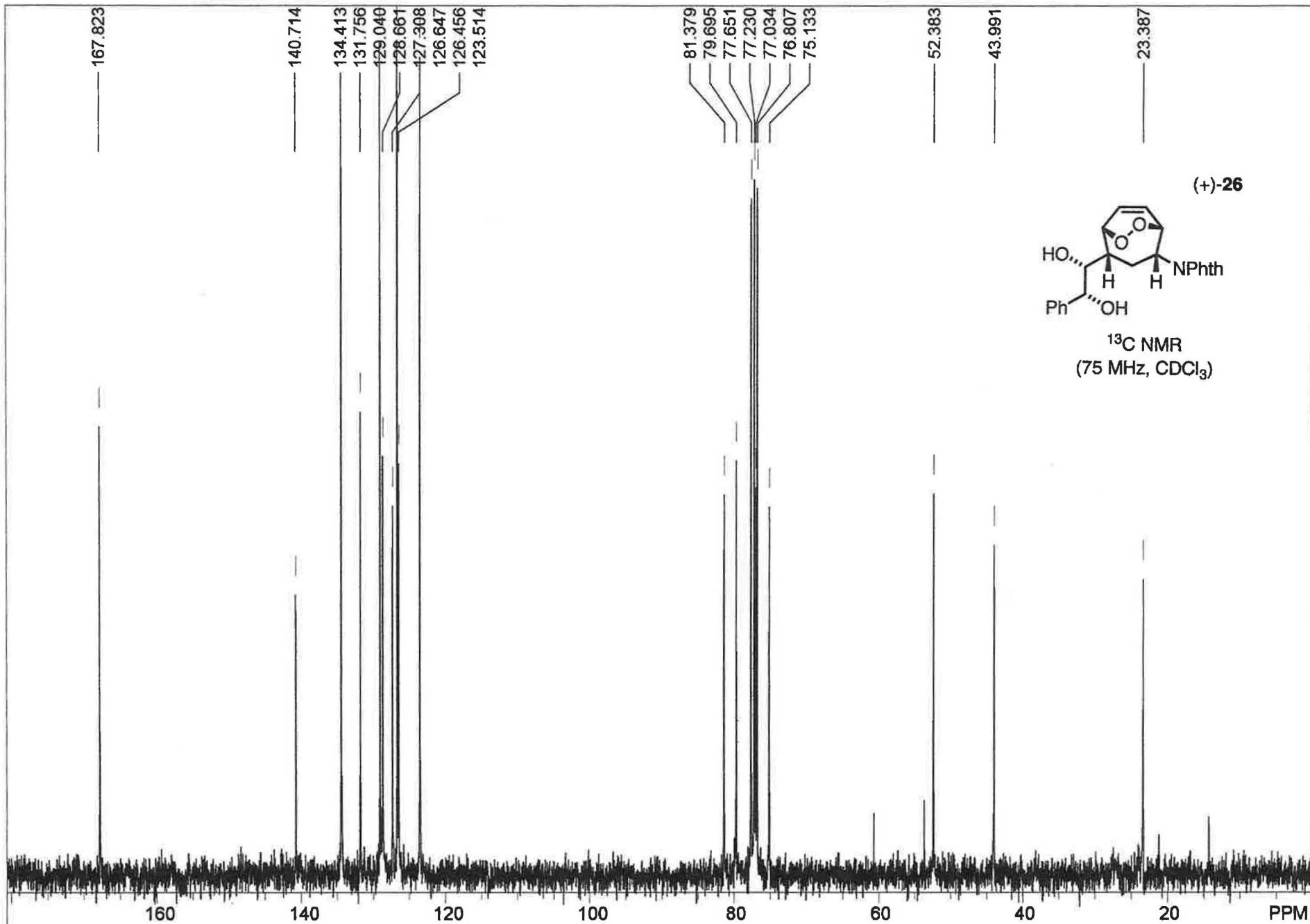
13C OBSERVE:blank line				USER: -- DATE: Apr 18 2011			
F1: 75.476	F2: 300.133	SW1: 18868		OF1: 8298.4		PTS1d: 34246 , 65536	
EX: s2pul		PW: 7.3 us	PD: 1.0 sec	NA: 256	LB: 1.5	Nuts - \$ase646p13c.fid	

955



:blank line						USER: -- DATE: Jun 21 20
F1: 399.746	F2: 100.525	SW1: 6410	OF1: 2403.4	PTS1d: 13132 . 16384		
EX: s2pul	PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0	Nuts - \$m1184F2	

S57

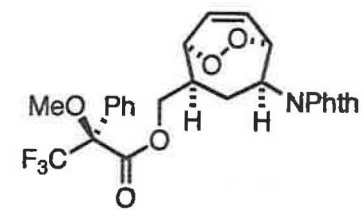


<sup>13</sup>C OBSERVE: blank line

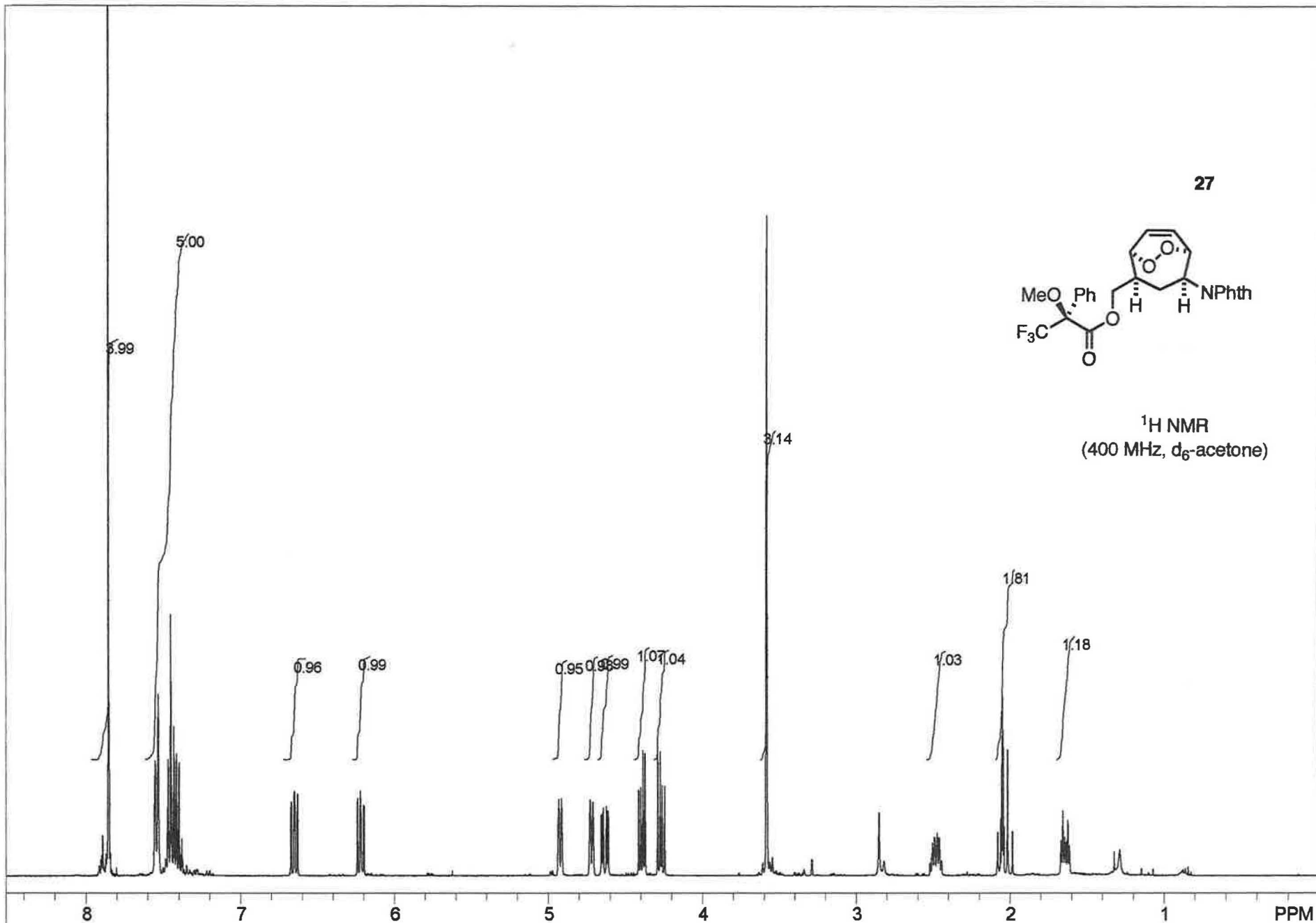
USER: -- DATE: Jan 4 2011

F1: 75.476	F2: 300.133	SW1: 18868	OF1: 8294.5	PTS1d: 34246	65536
EX: s2pul	PW: 7.3 us	PD: 1.0 sec	NA: 256	LB: 1.5	Nuts - \$ase618f2c13.fid

27



<sup>1</sup>H NMR  
(400 MHz, d<sub>6</sub>-acetone)



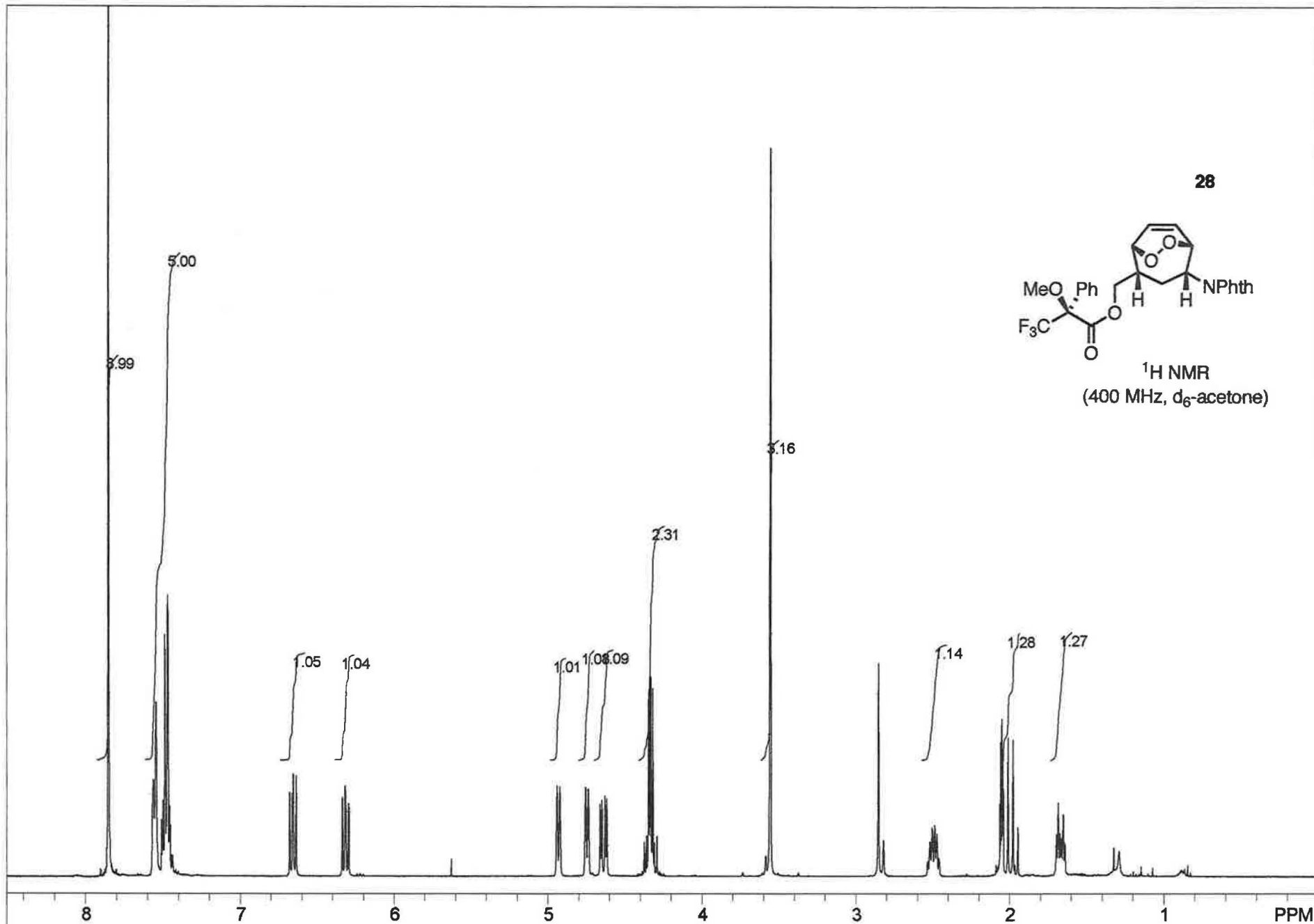
:blank line

USER: -- DATE: Aug 22 2012

F1: 399.748	F2: 100.526	SW1: 6410	OF1: 2397.8	PTS1d: 13132 , 16384
EX: s2pul	PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0

Nuts - \$ml190acetone.fid





:blank line				USER: -- DATE: Aug 22 2012		
F1: 399.748	F2: 100.526	SW1: 6410		OF1: 2398.1		PTS1d: 13132 , 16384
EX: s2pul	PW: 8.0 us	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - \$ml201acetone.fid

50

ORTEP of (6-styryl-2,4-cycloheptadien-1-yl)phthalimide ( $\pm$ )-**9d**