

## Electronic Supplementary Information

# Enantioselective Synthesis of $\alpha$ -Phenyl- and $\alpha$ -(Dimethylphenylsilyl)-alkylboronic Esters by Ligand Mediated Stereoinductive Reagent-Controlled Homologation Using Configurationally Labile Carbenoids

## 2. $^1\text{H}$ & $^{13}\text{C}$ NMR Spectra

Adam L. Barsamian, Zhenhua Wu and Paul R. Blakemore\*

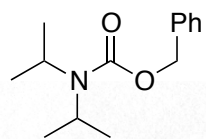
Department of Chemistry, Oregon State University, Corvallis, OR 97331-4003.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in Fourier transform mode at the field strength specified using standard 5 mm diameter tubes. Chemical shift in ppm is quoted relative to residual solvent signals calibrated as follows:

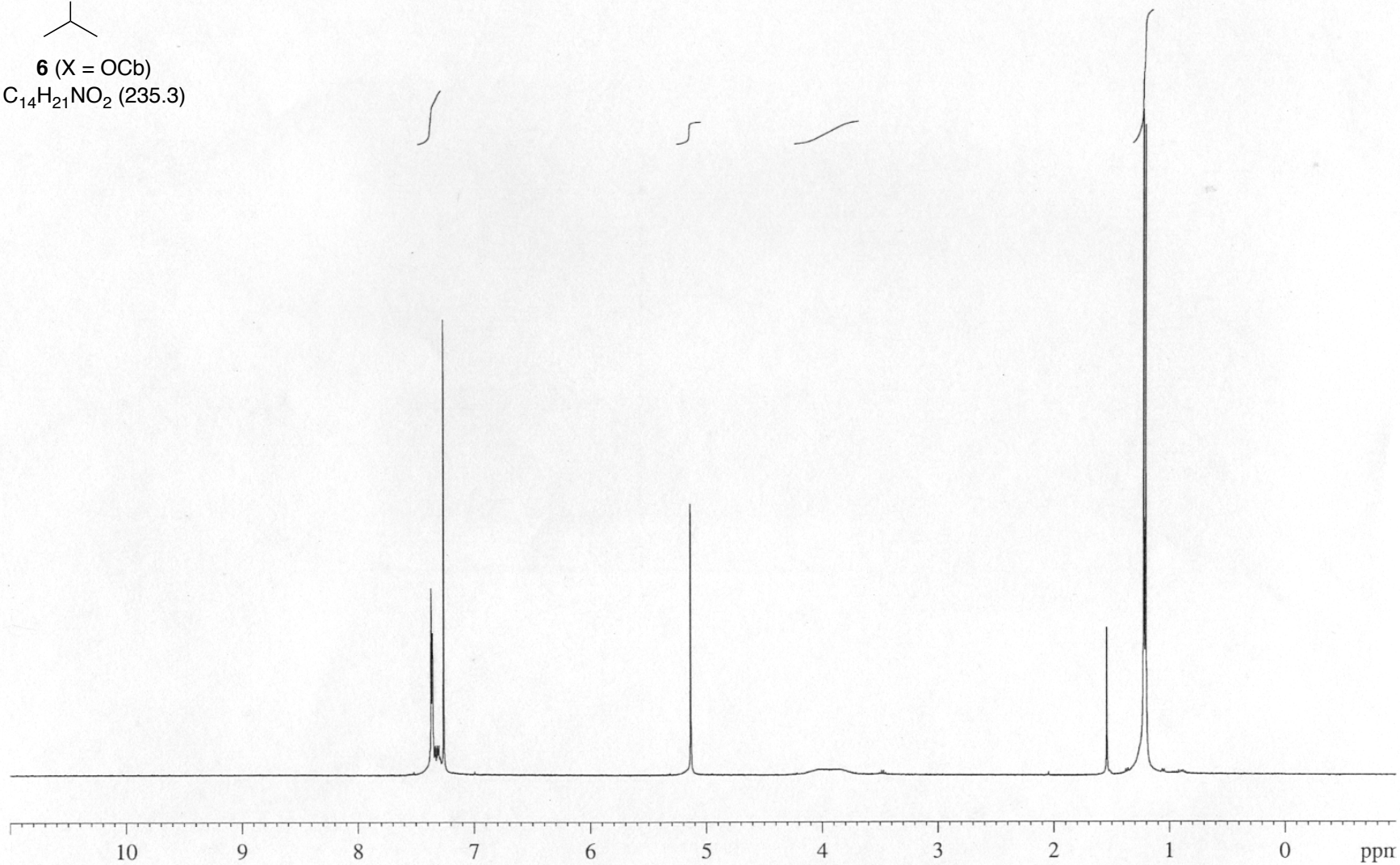
$\text{CDCl}_3$   $\delta_{\text{H}}$  ( $\text{CHCl}_3$ ) = 7.26 ppm,  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) = 77.2 ppm;  $d_6$ -DMSO  $\delta_{\text{H}}$  ( $\text{CHD}_2\text{SOCD}_3$ ) = 2.50 ppm,  $\delta_{\text{C}}$  [ $(\text{CD}_3)_2\text{SO}$ ] = 39.50 ppm

|  |         |
|--|---------|
| Carbenoid precursors <b>6</b> (X = OCb), <b>6</b> (X = OTIB), and <b>19</b>            | S23-S28 |
| Boronic ester substrates (not previously disclosed)                                    | S29-S42 |
| Products of <i>i</i> -StReCH with benzylic carbenoid <b>7</b> (Table 1 and Figure 2)   | S43-S60 |
| Products of <i>i</i> -StReCH with silylated carbenoid <b>20</b> (Table 2 and Figure 3) | S61-S72 |

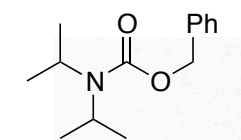
$^1\text{H}$  NMR: 400 MHz,  $\text{CDCl}_3$



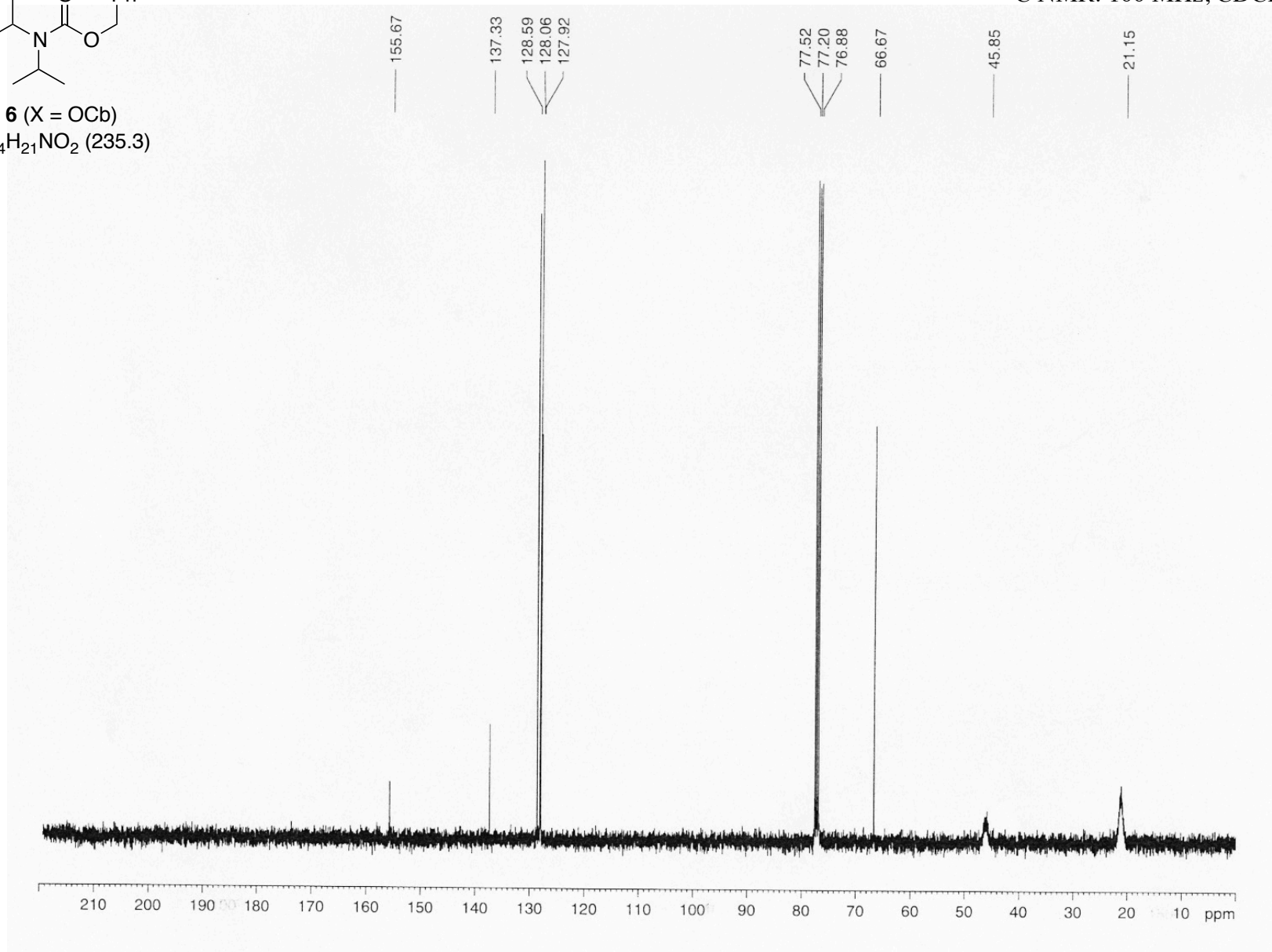
**6** (X = OCb)  
 $\text{C}_{14}\text{H}_{21}\text{NO}_2$  (235.3)



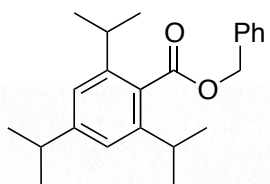
$^{13}\text{C}$  NMR: 100 MHz,  $\text{CDCl}_3$



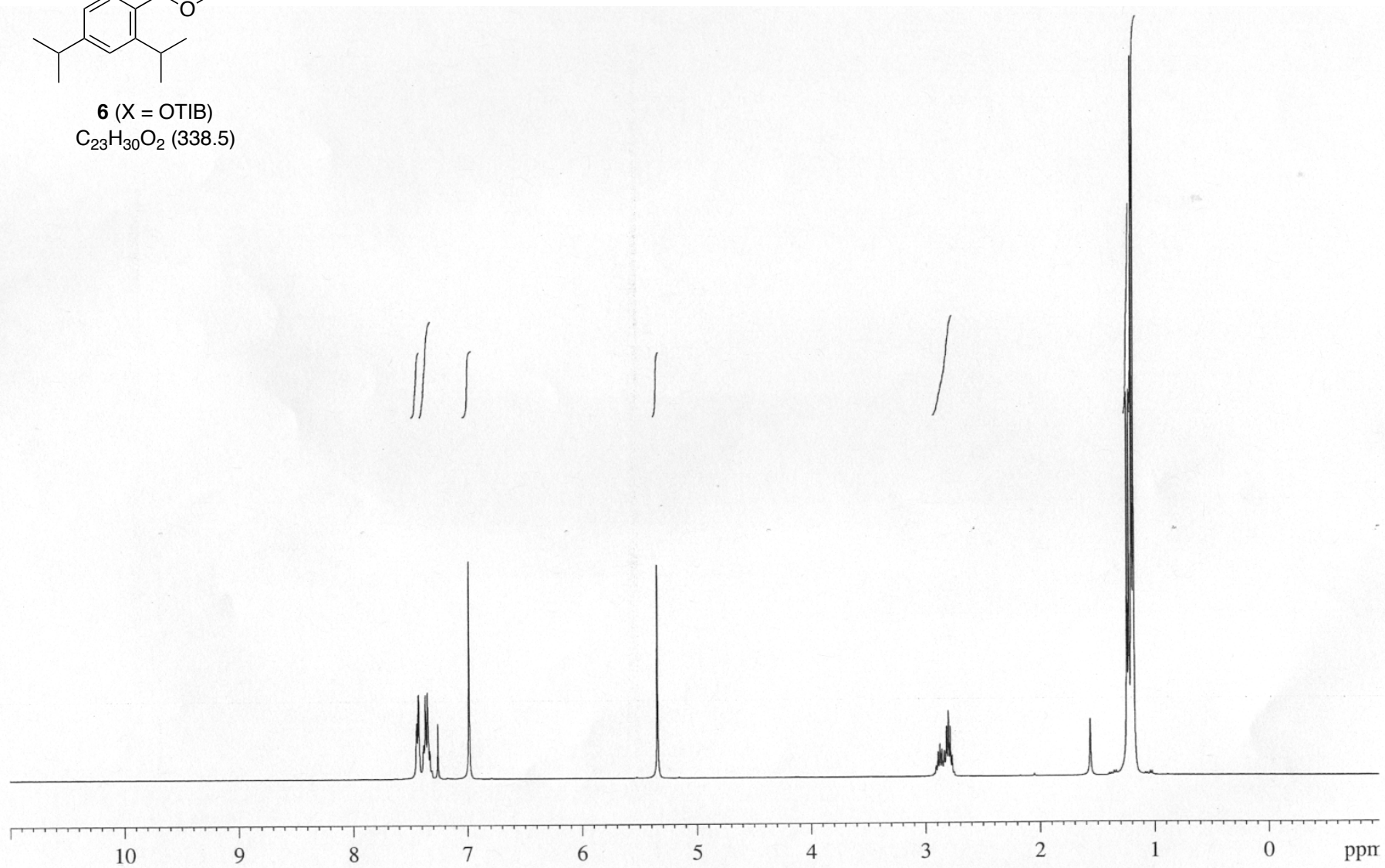
**6** (X = OCb)  
 $\text{C}_{14}\text{H}_{21}\text{NO}_2$  (235.3)

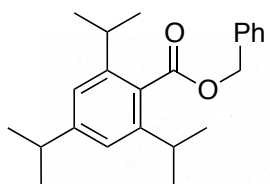


$^1\text{H}$  NMR: 400 MHz,  $\text{CDCl}_3$



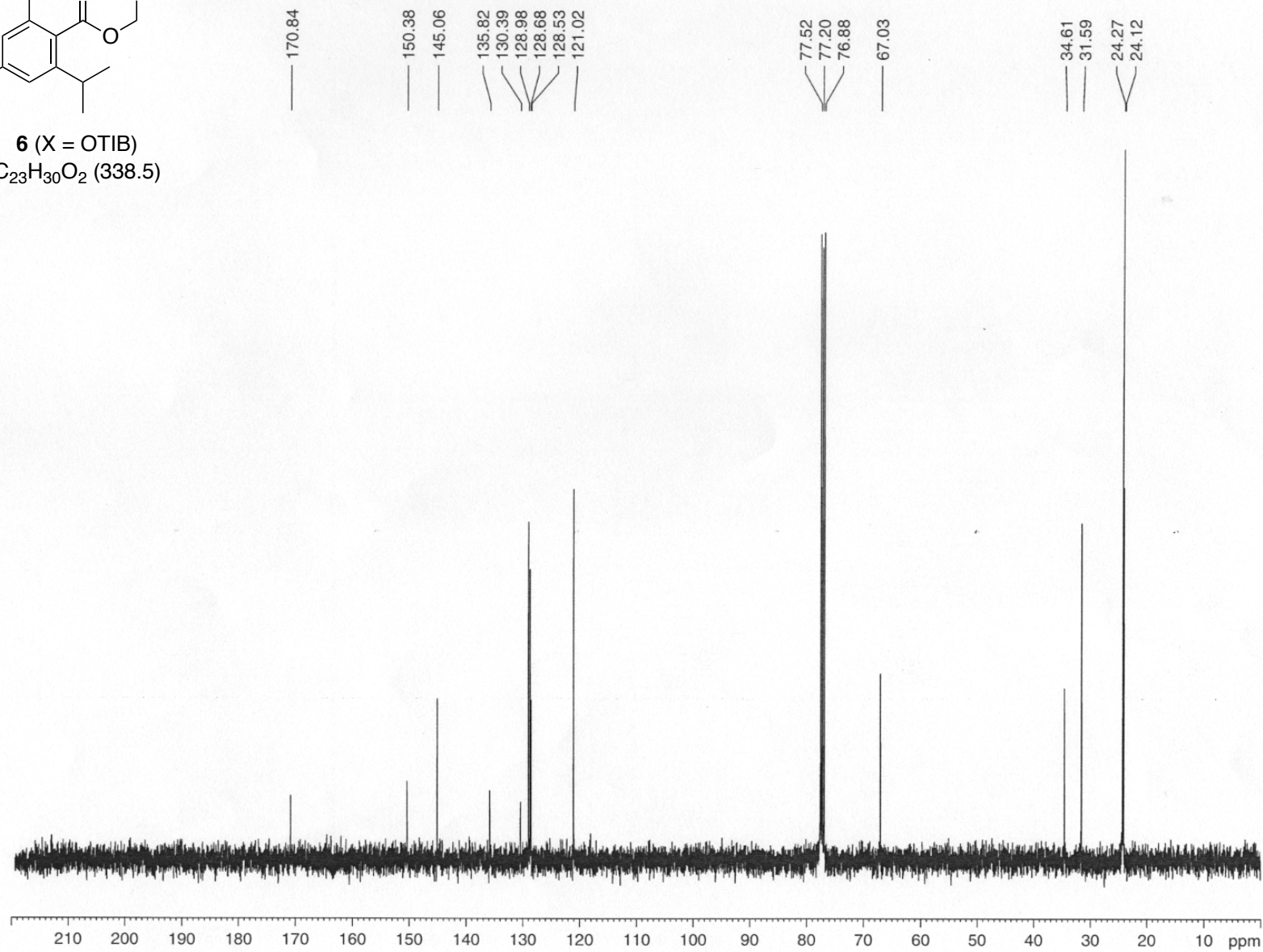
**6** (X = OTIB)  
 $\text{C}_{23}\text{H}_{30}\text{O}_2$  (338.5)

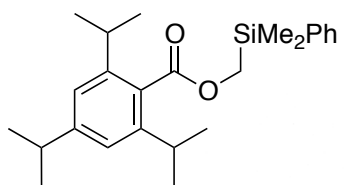




**6** (X = OTIB)  
C<sub>23</sub>H<sub>30</sub>O<sub>2</sub> (338.5)

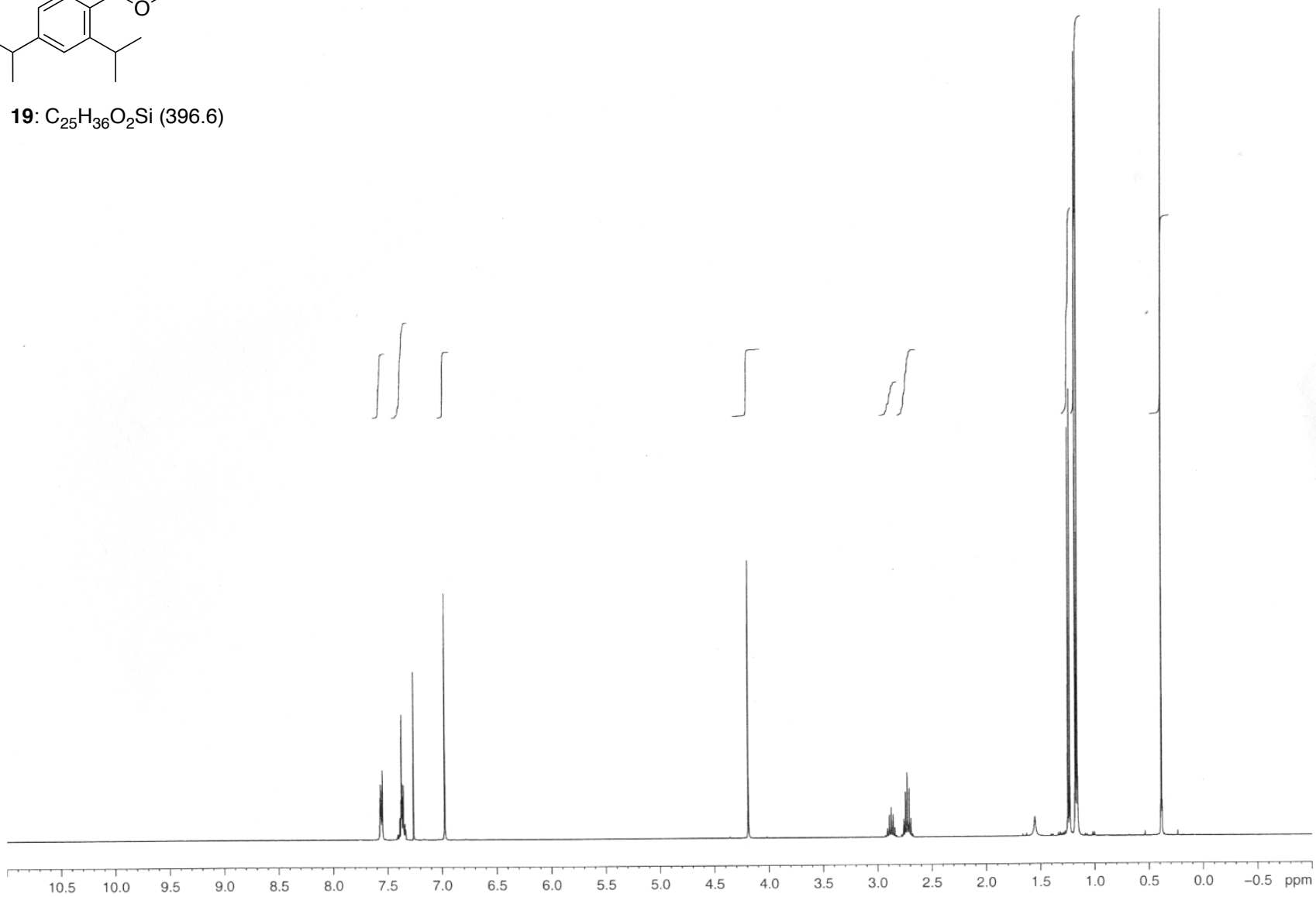
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>

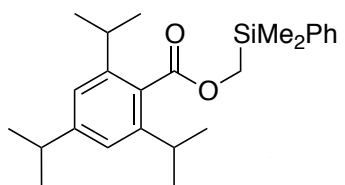




19: C<sub>25</sub>H<sub>36</sub>O<sub>2</sub>Si (396.6)

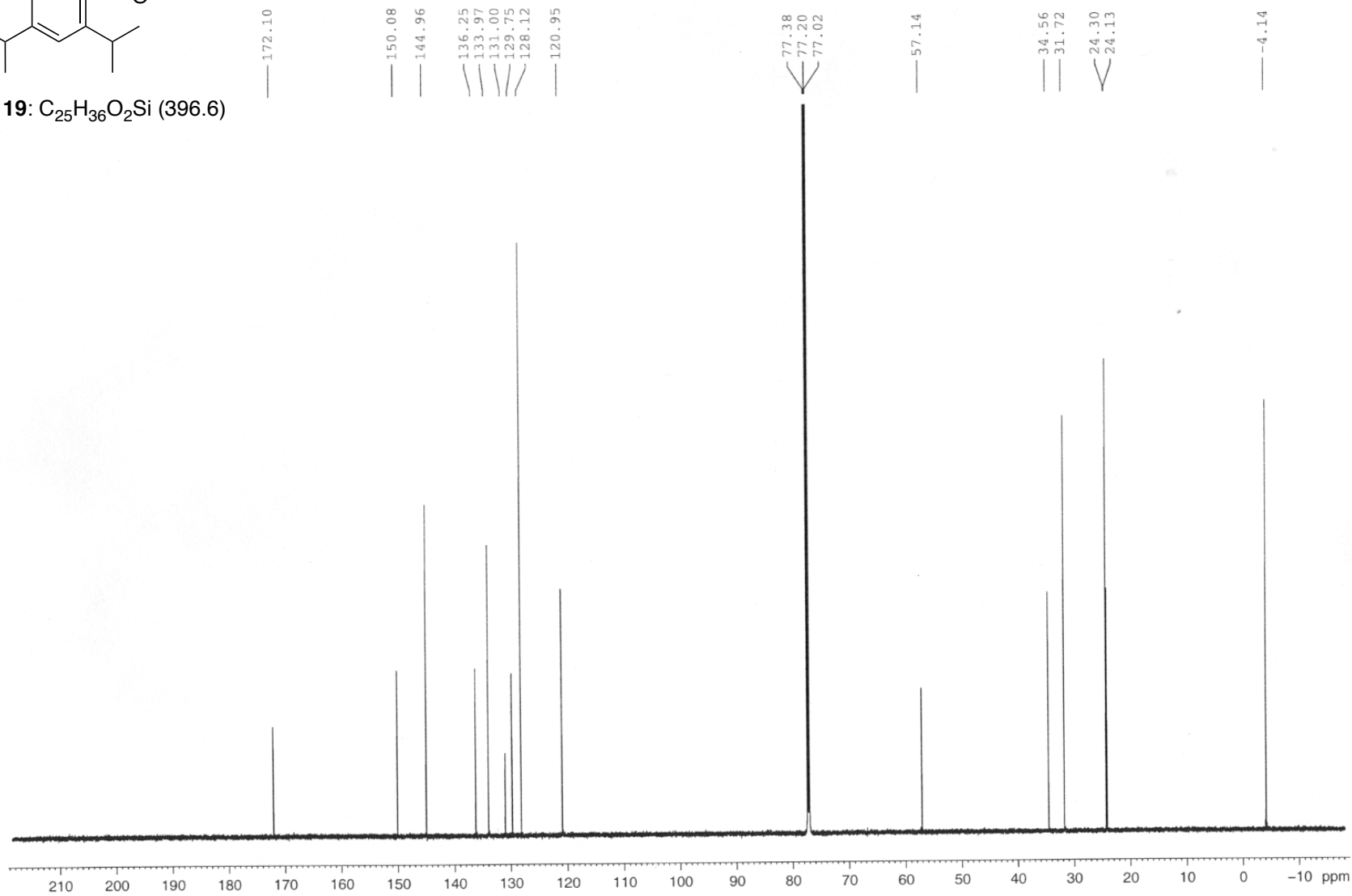
<sup>1</sup>H NMR: 400 MHz, CDCl<sub>3</sub>

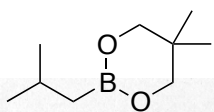




19: C<sub>25</sub>H<sub>36</sub>O<sub>2</sub>Si (396.6)

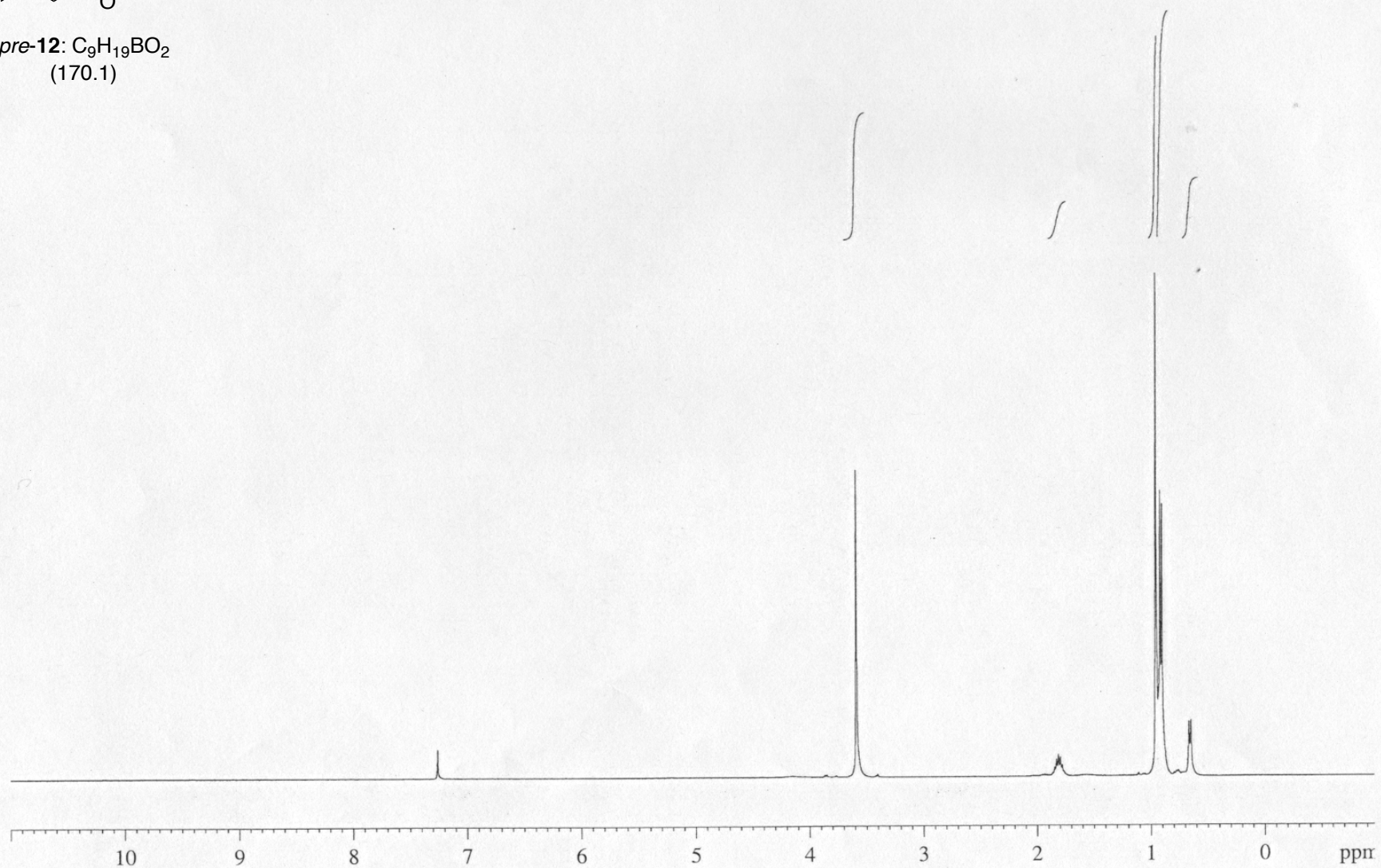
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>



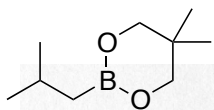


pre-12: C<sub>9</sub>H<sub>19</sub>BO<sub>2</sub>  
(170.1)

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

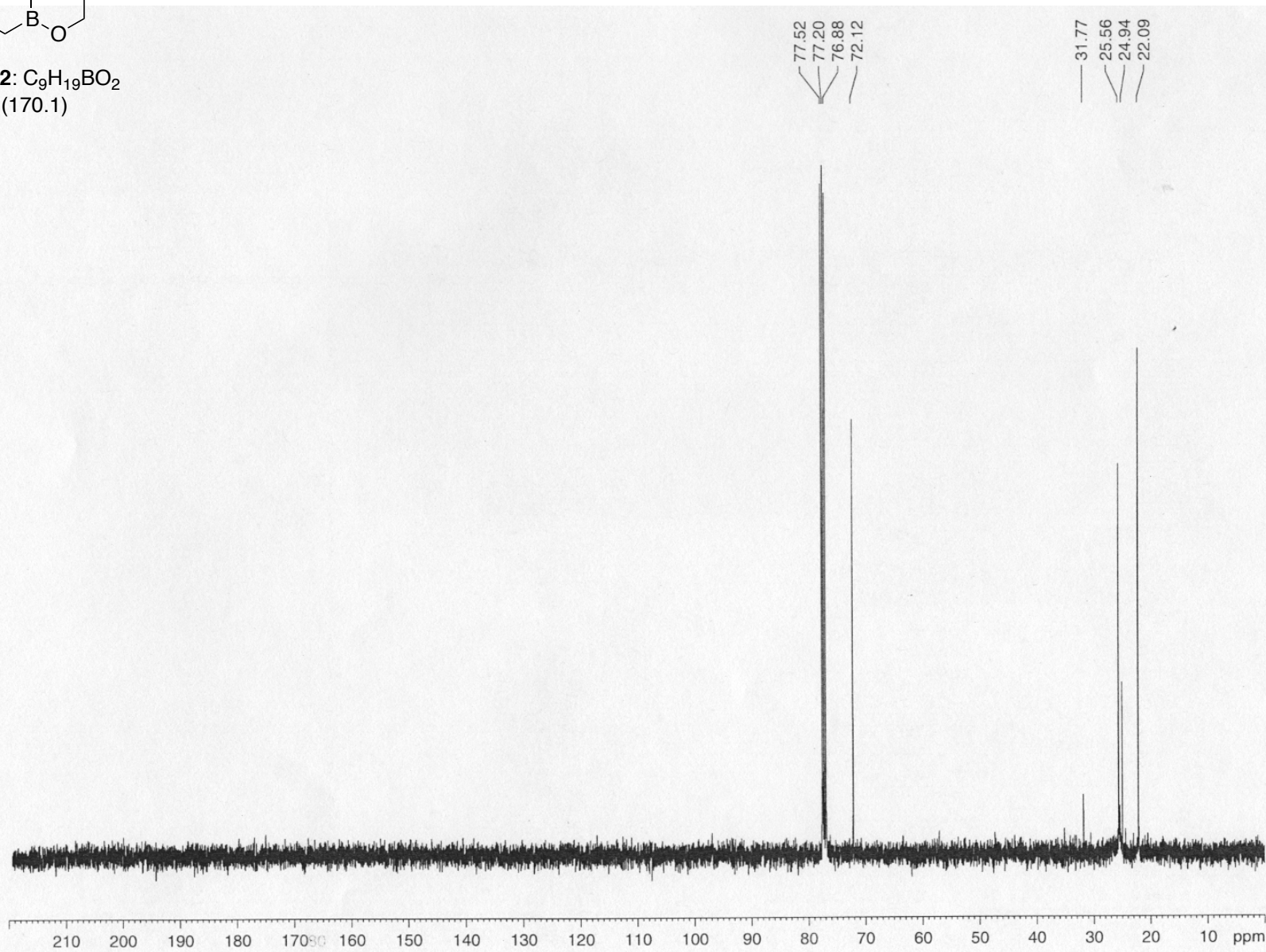


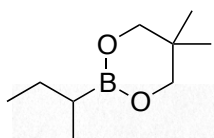




*pre-12*: C<sub>9</sub>H<sub>19</sub>BO<sub>2</sub>  
(170.1)

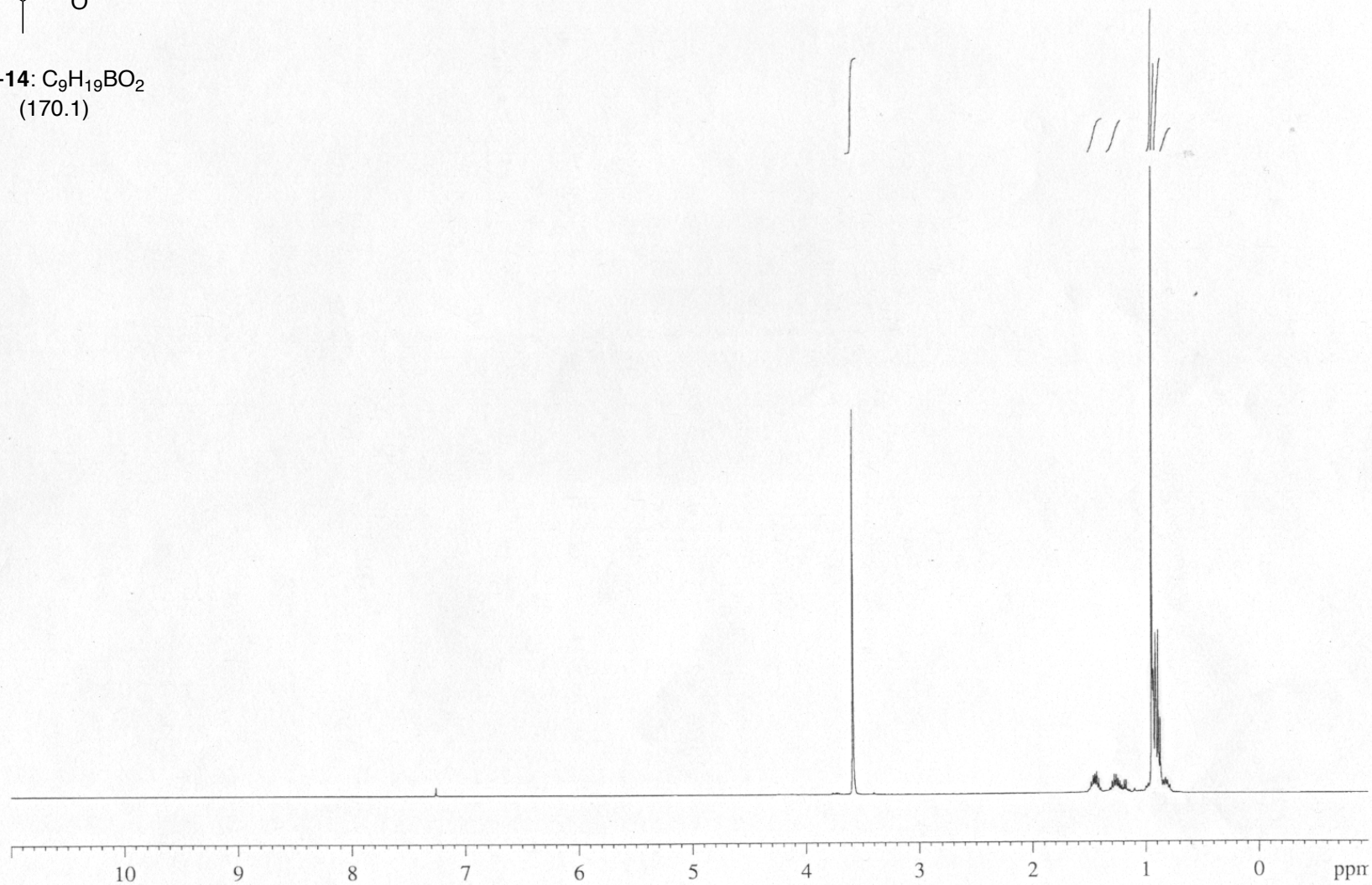
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>

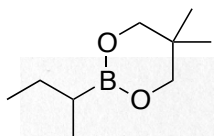




*pre-14*: C<sub>9</sub>H<sub>19</sub>BO<sub>2</sub>  
(170.1)

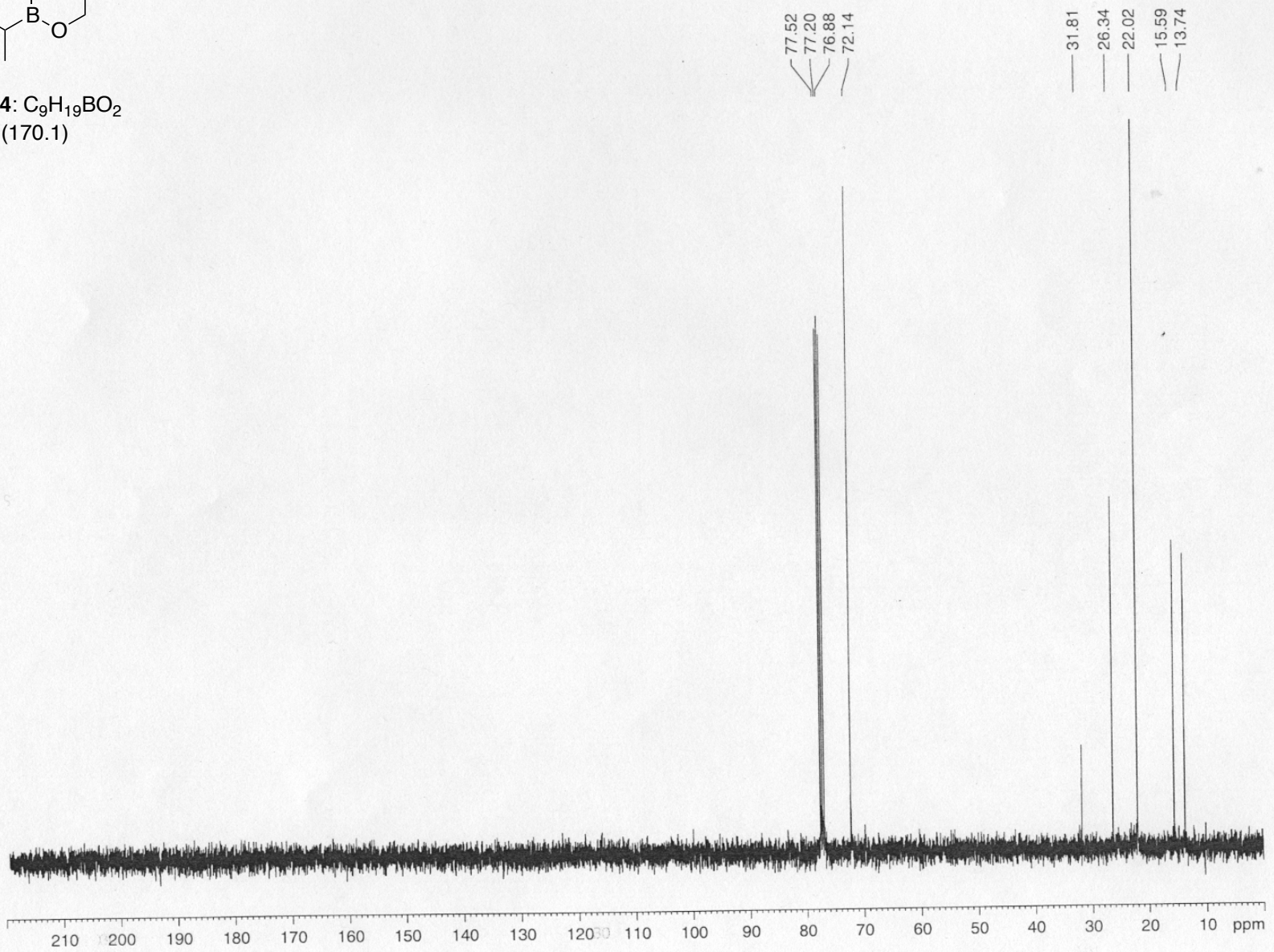
<sup>1</sup>H NMR: 400 MHz, CDCl<sub>3</sub>



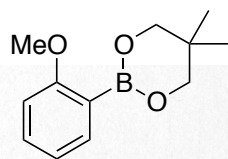


*pre-14*: C<sub>9</sub>H<sub>19</sub>BO<sub>2</sub>  
(170.1)

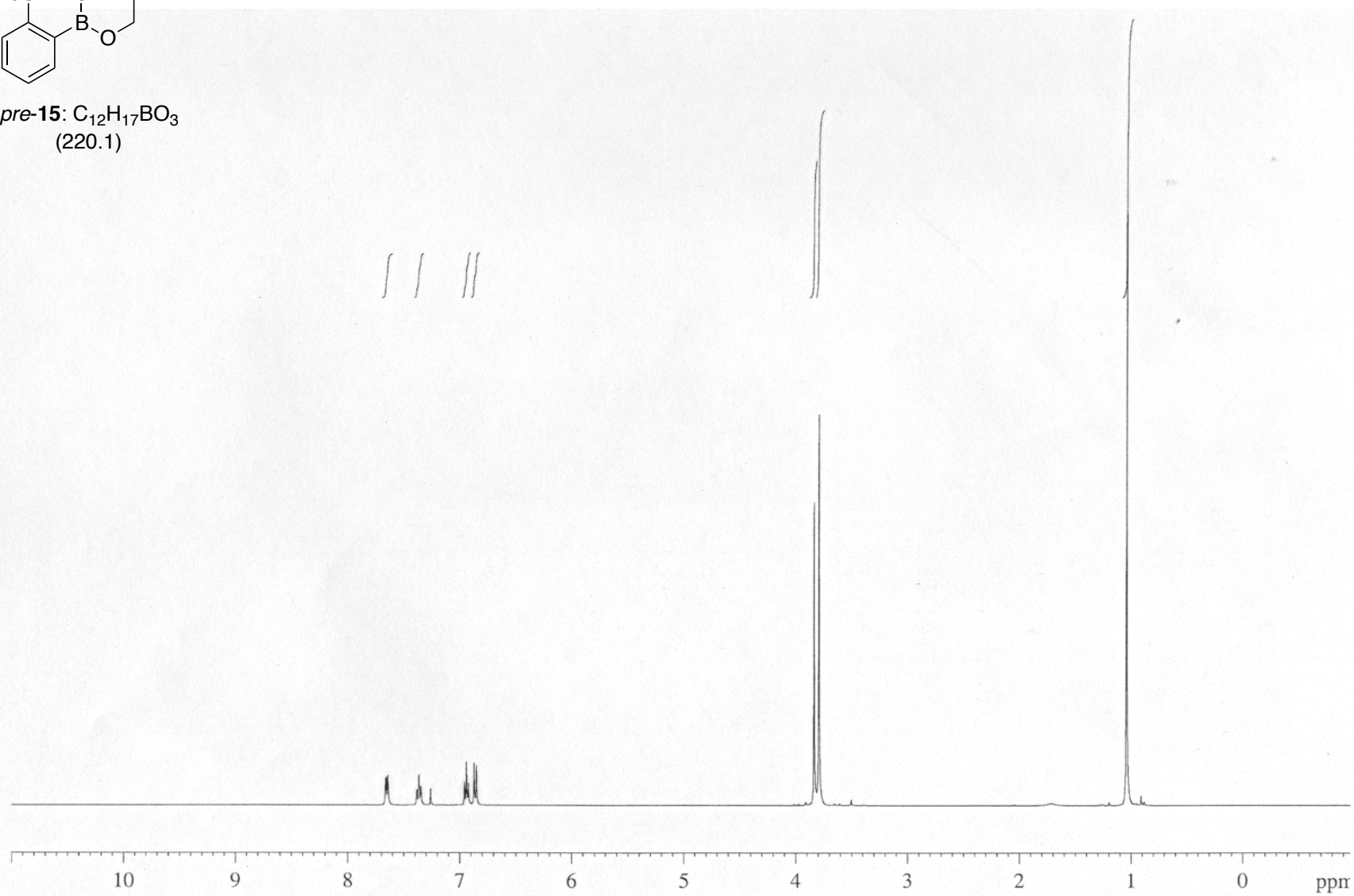
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>

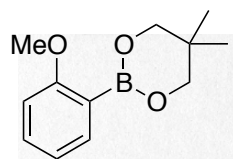


$^1\text{H NMR}$ : 400 MHz,  $\text{CDCl}_3$



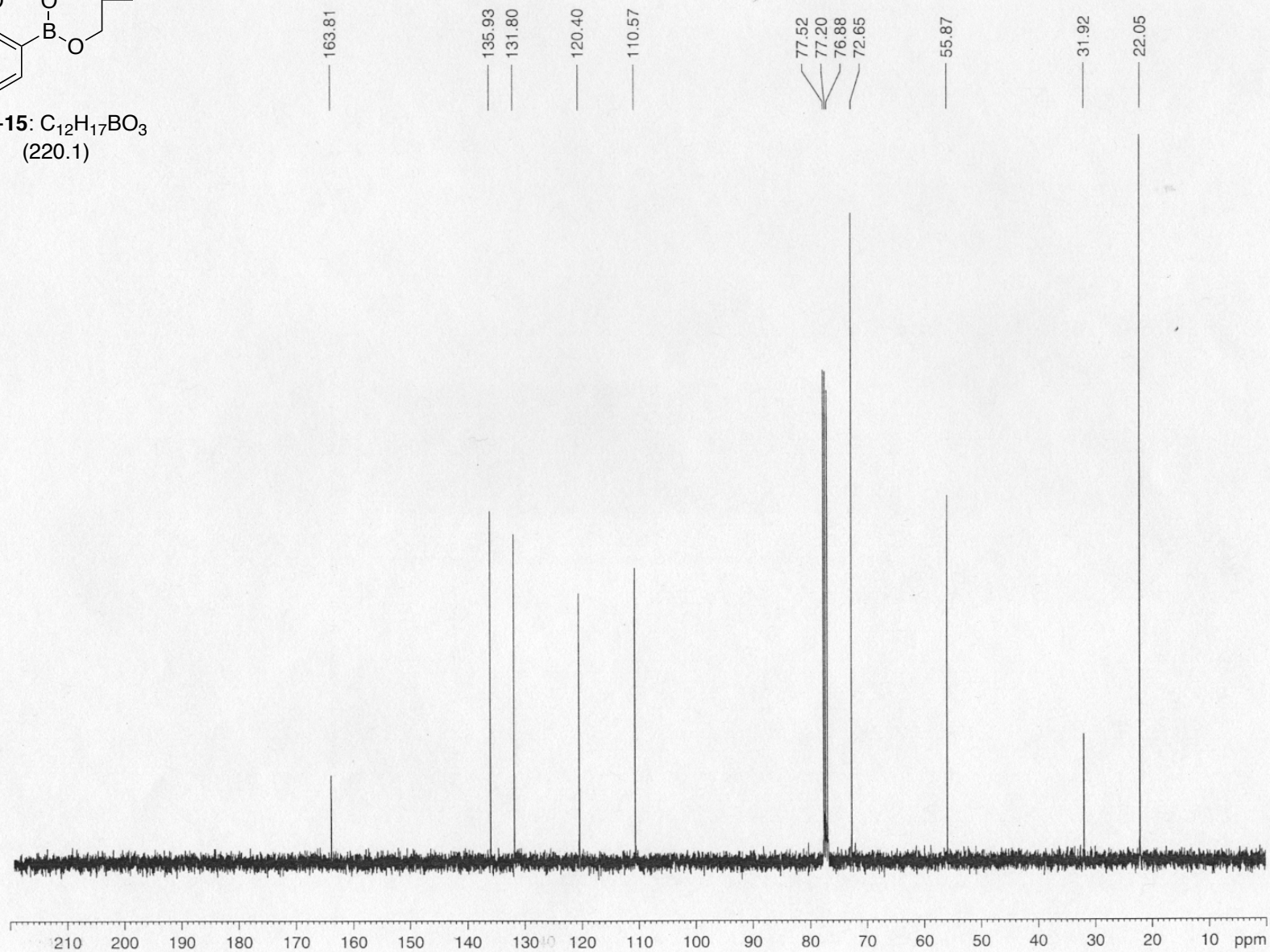
*pre-15*:  $\text{C}_{12}\text{H}_{17}\text{BO}_3$   
(220.1)



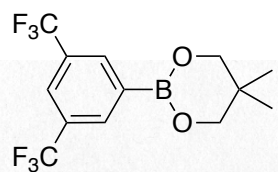


*pre-15*: C<sub>12</sub>H<sub>17</sub>BO<sub>3</sub>  
(220.1)

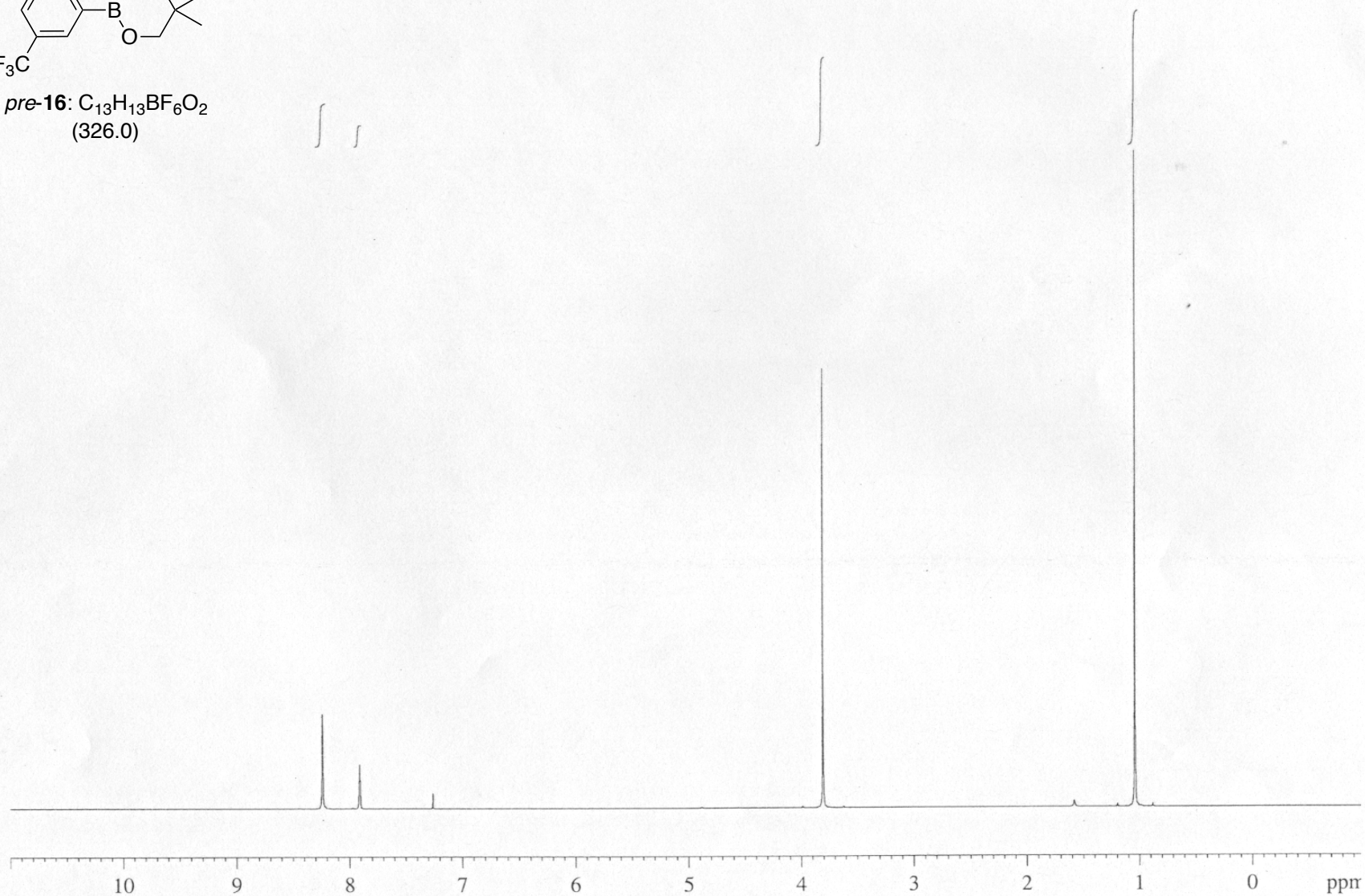
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>



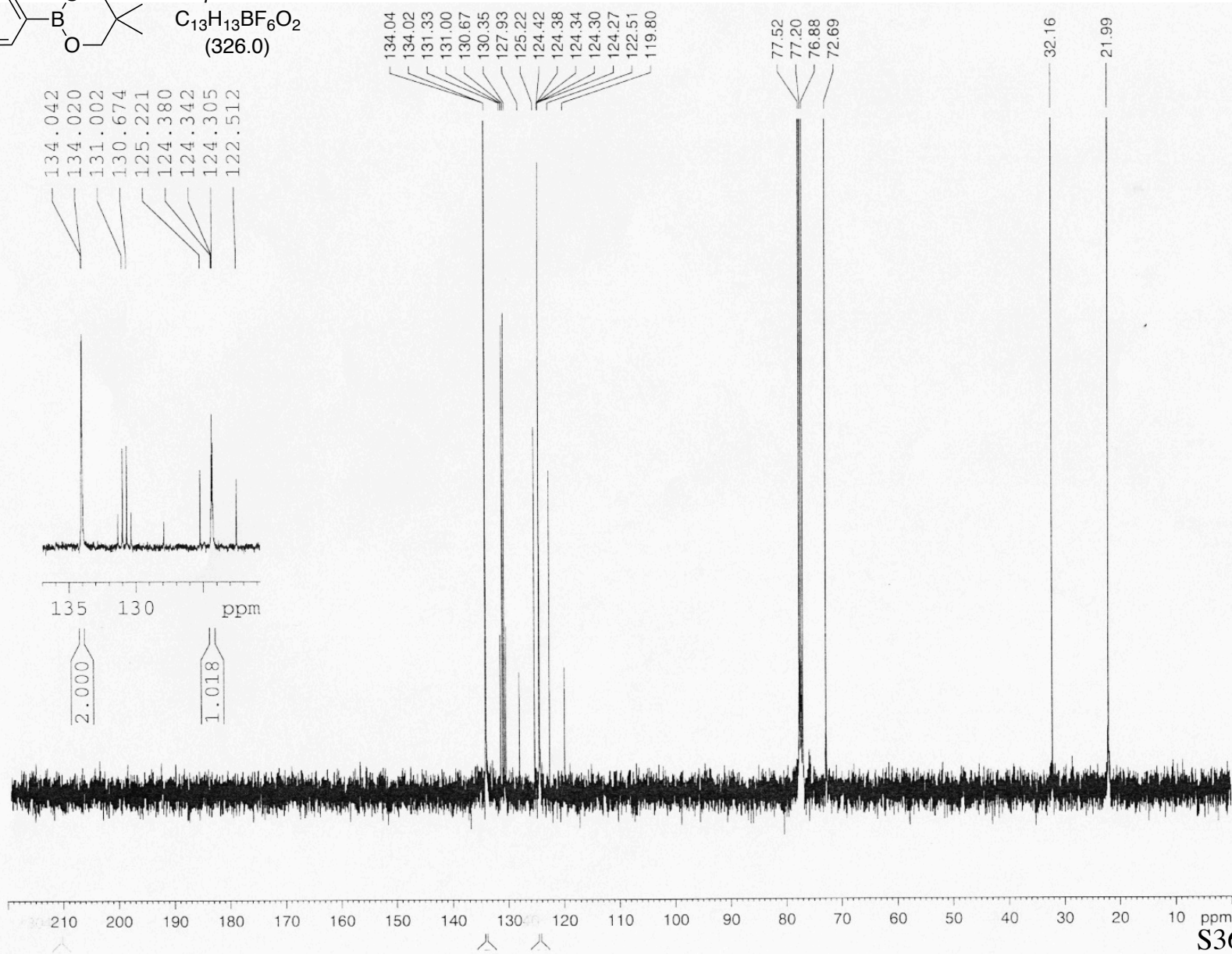
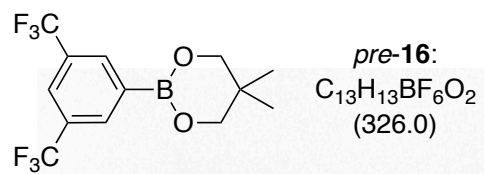
$^1\text{H}$  NMR: 400 MHz,  $\text{CDCl}_3$



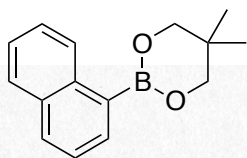
*pre-16*:  $\text{C}_{13}\text{H}_{13}\text{BF}_6\text{O}_2$   
(326.0)



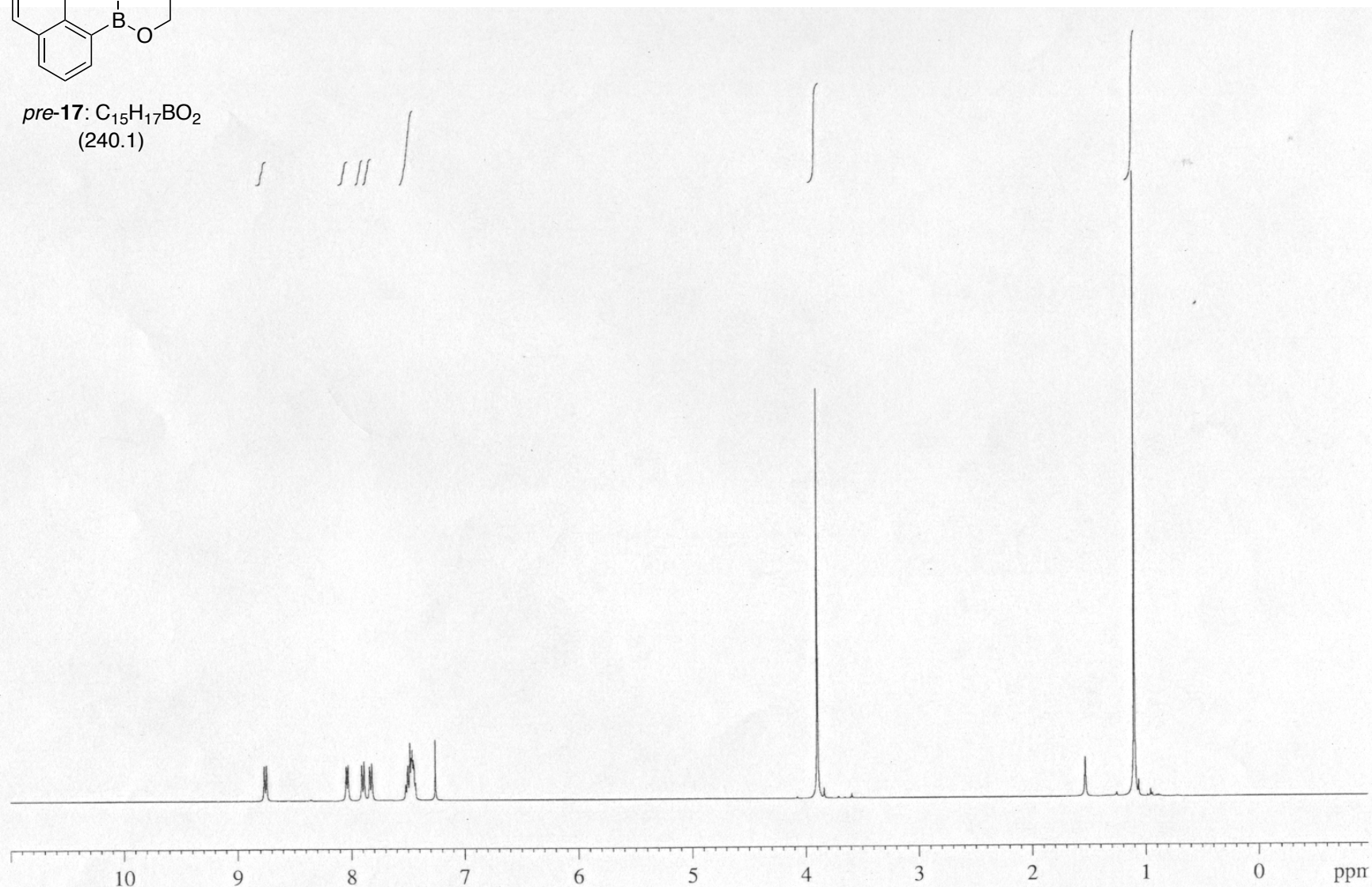
$^{13}\text{C}$  NMR: 100 MHz,  $\text{CDCl}_3$



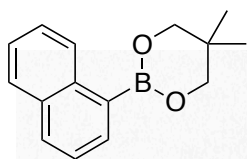
$^1\text{H}$  NMR: 400 MHz,  $\text{CDCl}_3$



*pre-17*:  $\text{C}_{15}\text{H}_{17}\text{BO}_2$   
(240.1)

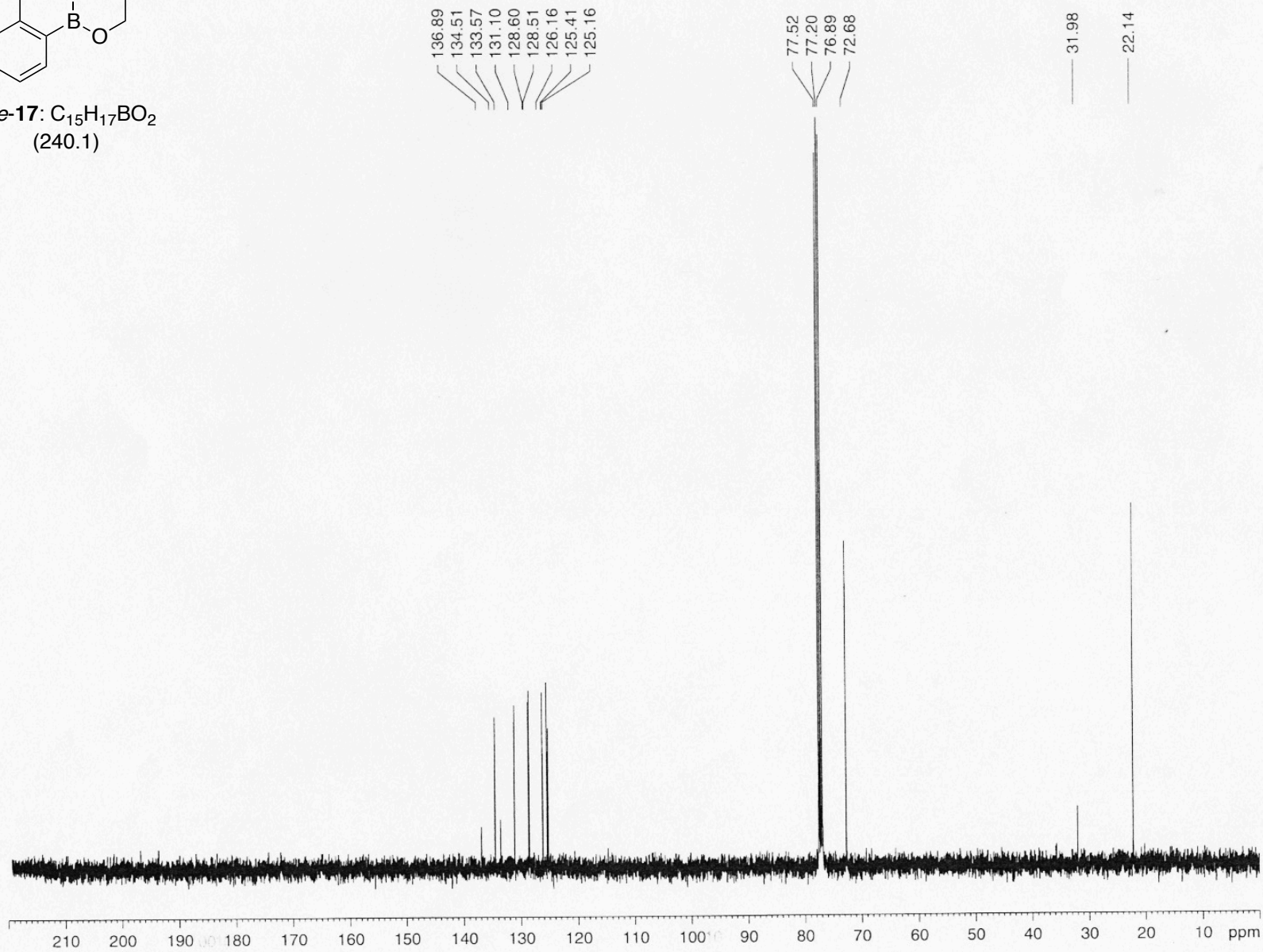




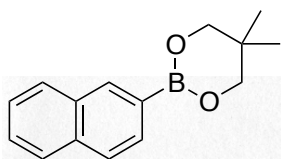


*pre-17*: C<sub>15</sub>H<sub>17</sub>BO<sub>2</sub>  
(240.1)

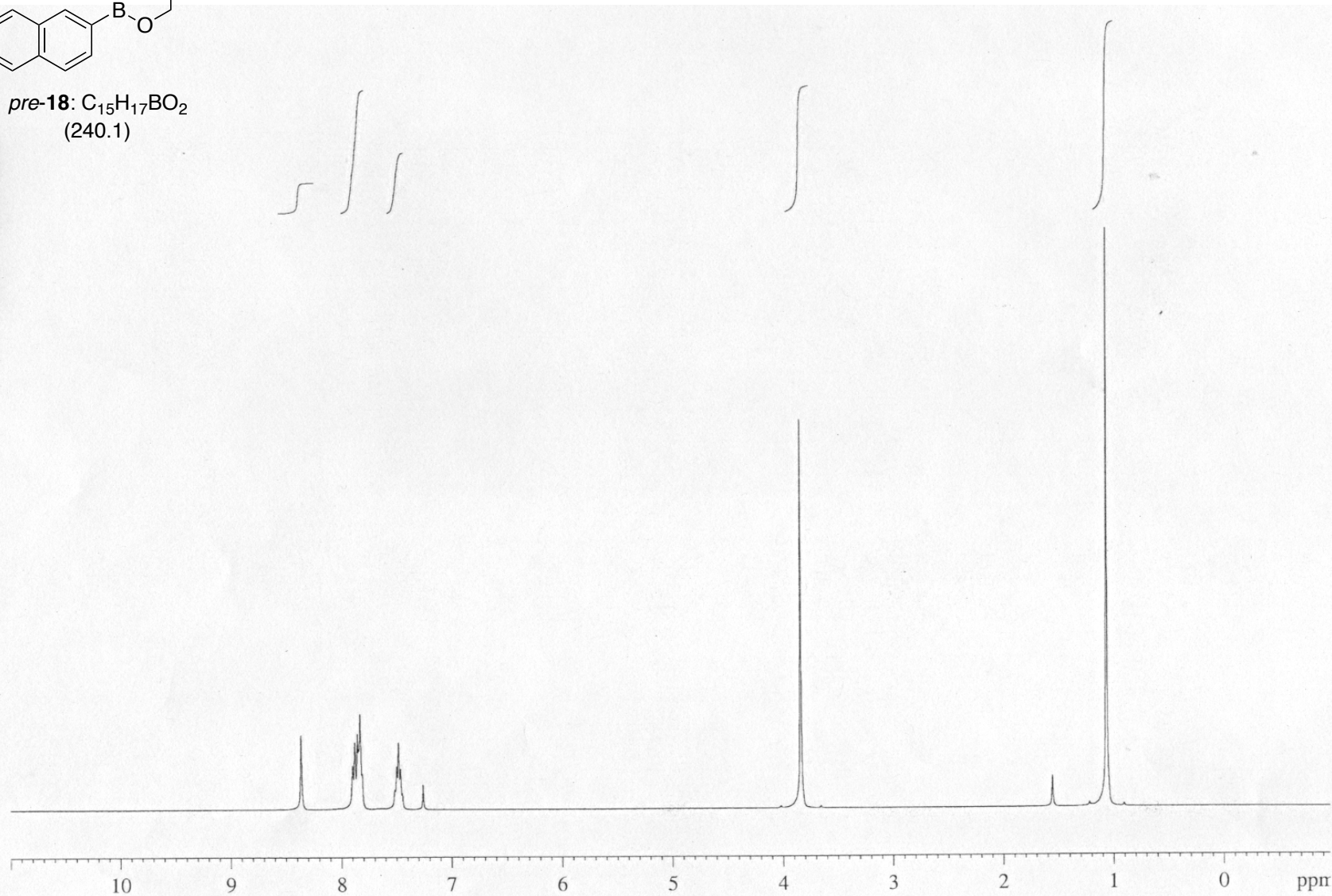
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>

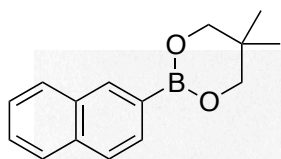


$^1\text{H NMR}$ : 400 MHz,  $\text{CDCl}_3$



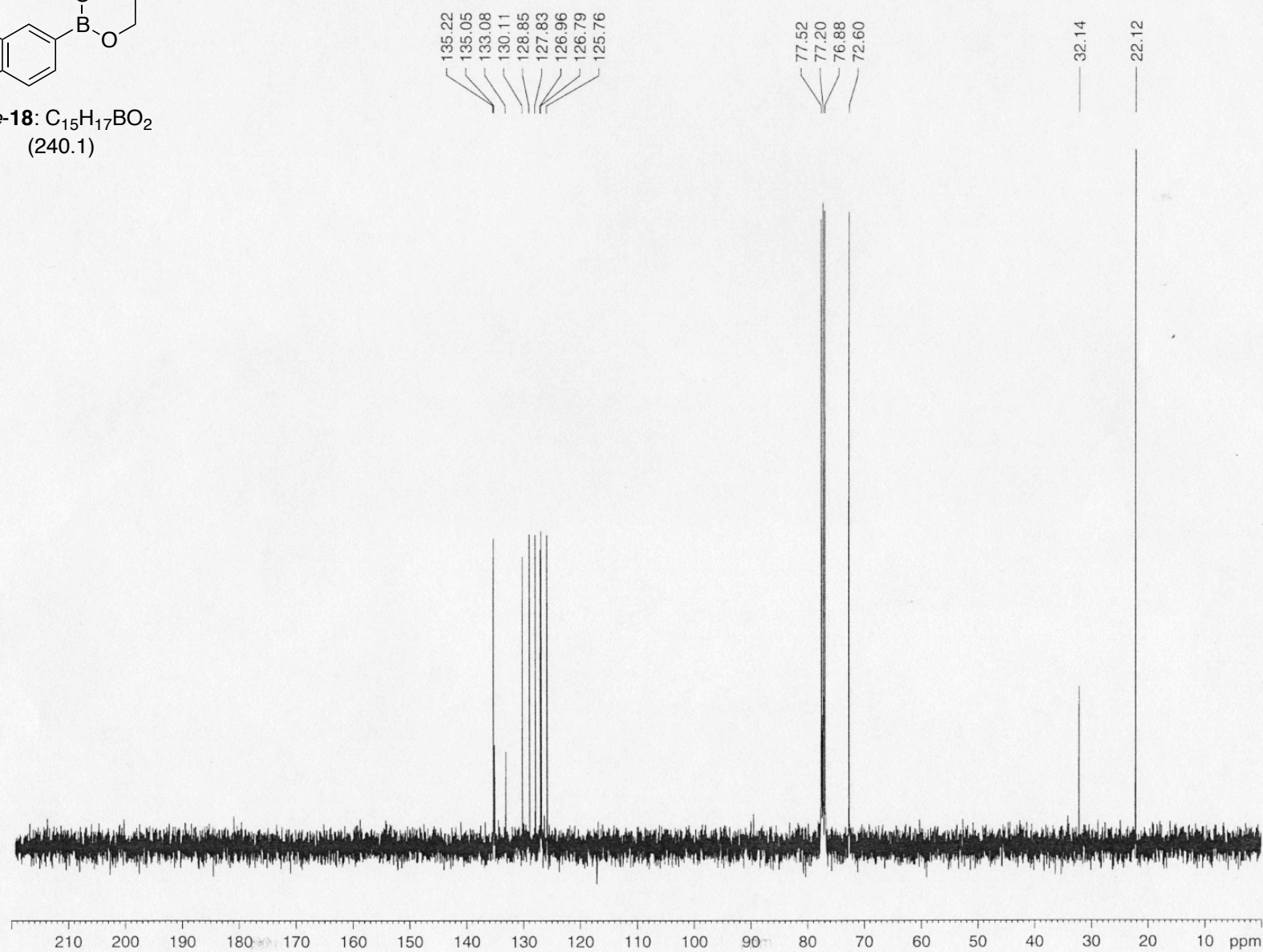
*pre-18*:  $\text{C}_{15}\text{H}_{17}\text{BO}_2$   
(240.1)

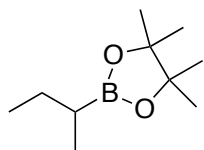




*pre-18*: C<sub>15</sub>H<sub>17</sub>BO<sub>2</sub>  
(240.1)

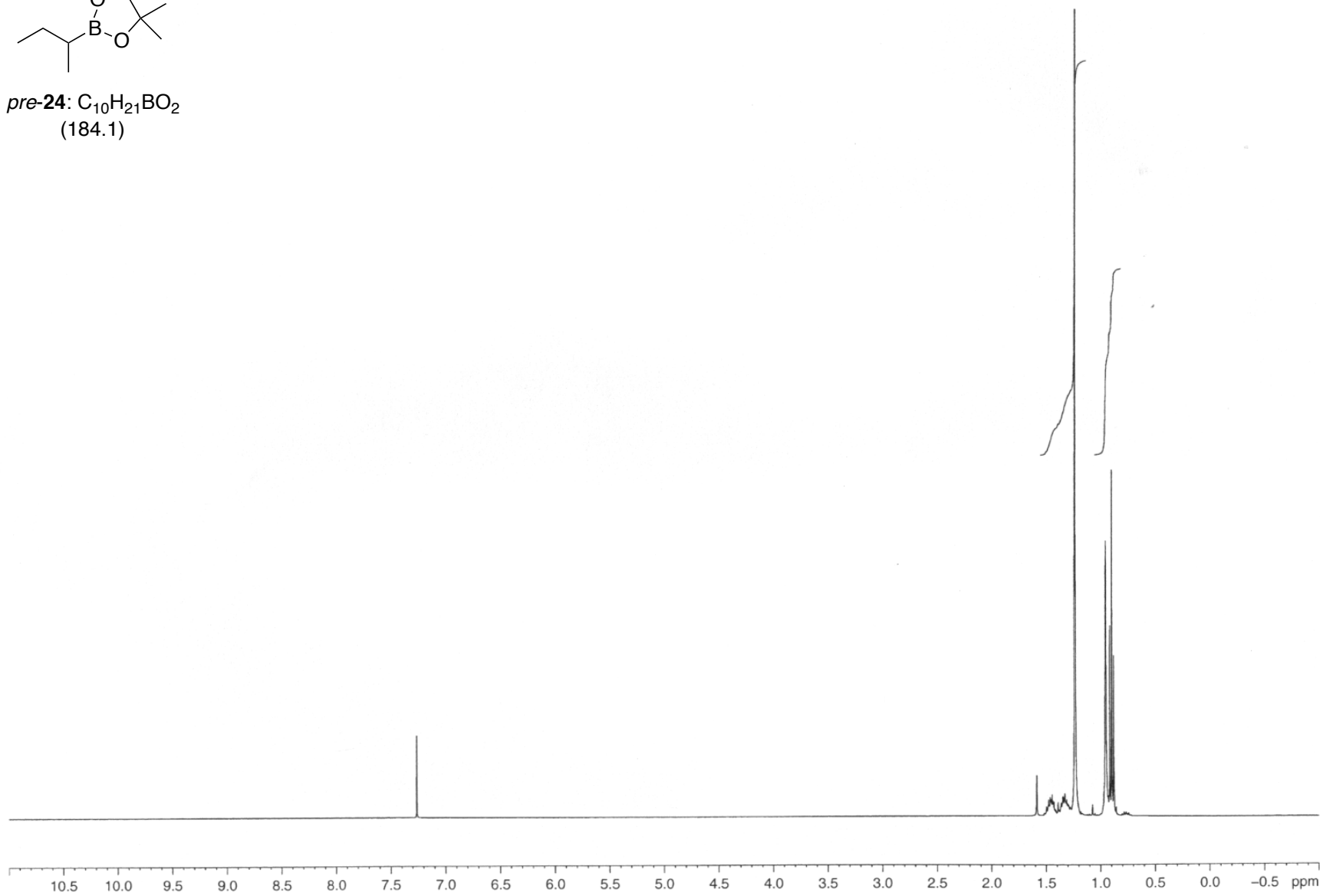
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>

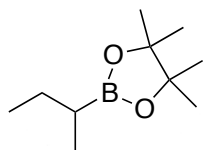




*pre-24*: C<sub>10</sub>H<sub>21</sub>BO<sub>2</sub>  
(184.1)

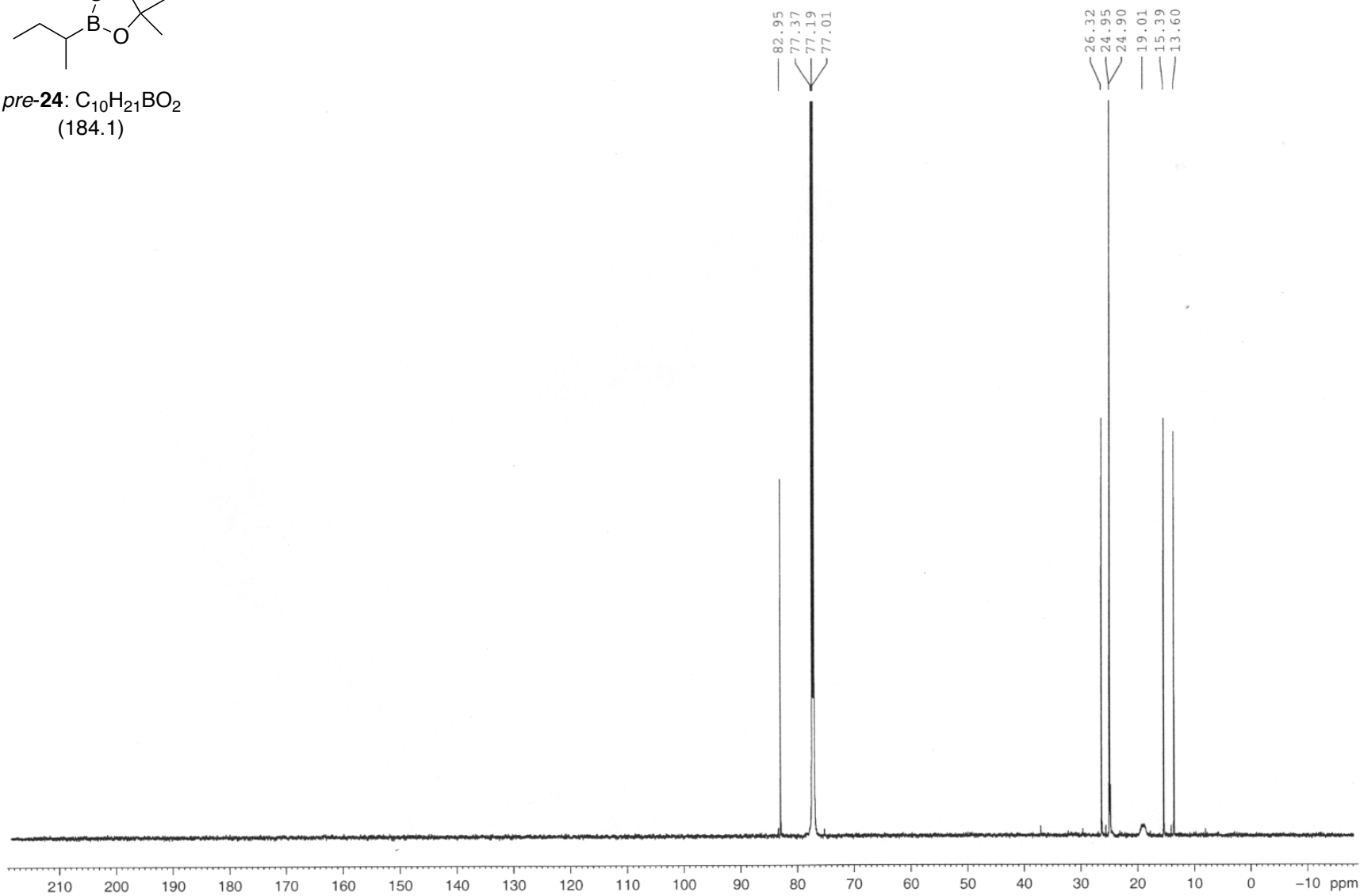
<sup>1</sup>H NMR: 400 MHz, CDCl<sub>3</sub>

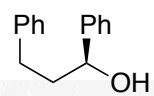




*pre-24*: C<sub>10</sub>H<sub>21</sub>BO<sub>2</sub>  
(184.1)

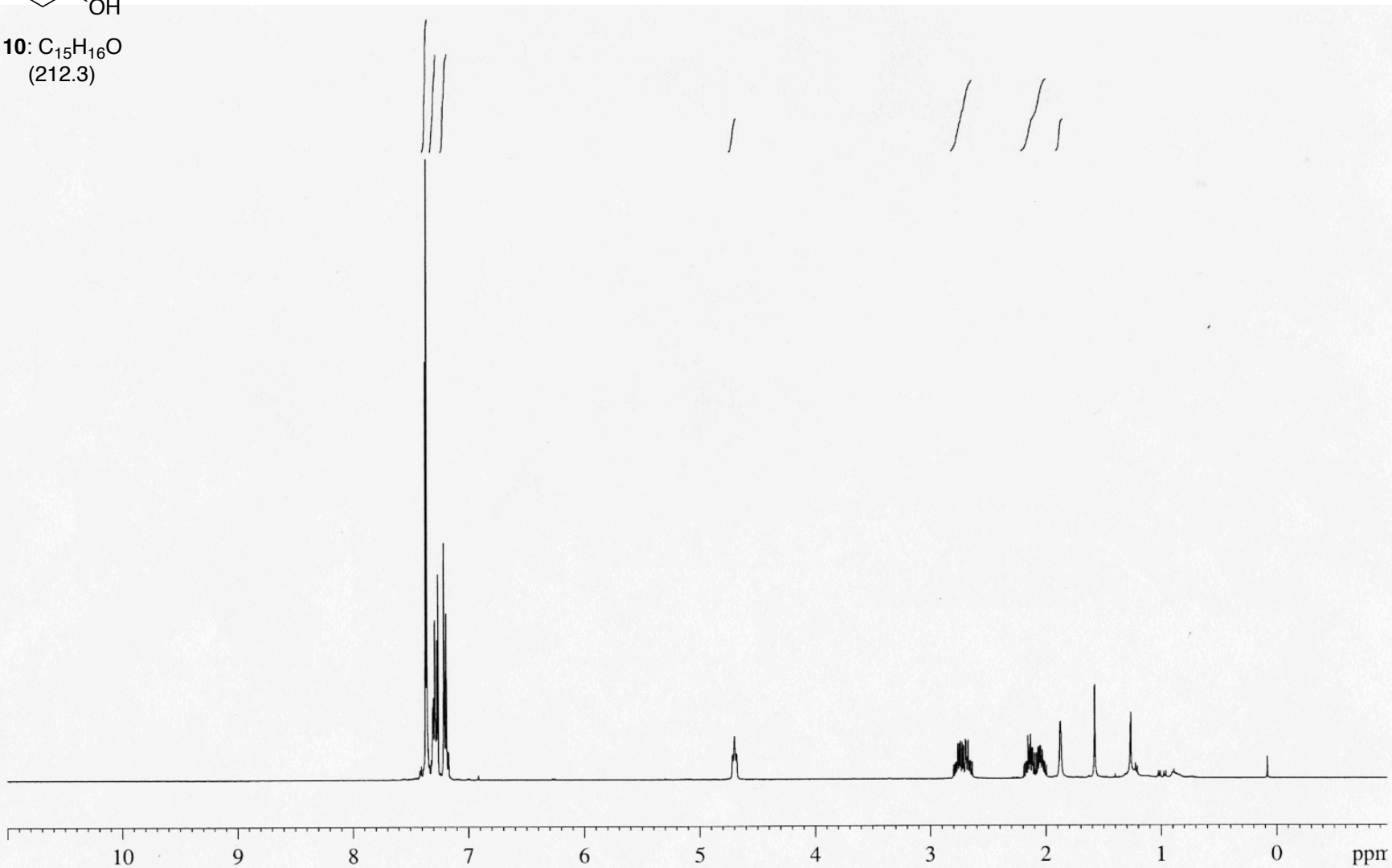
<sup>13</sup>C NMR: 175 MHz, CDCl<sub>3</sub>

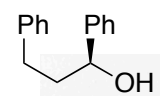




**10:** C<sub>15</sub>H<sub>16</sub>O  
(212.3)

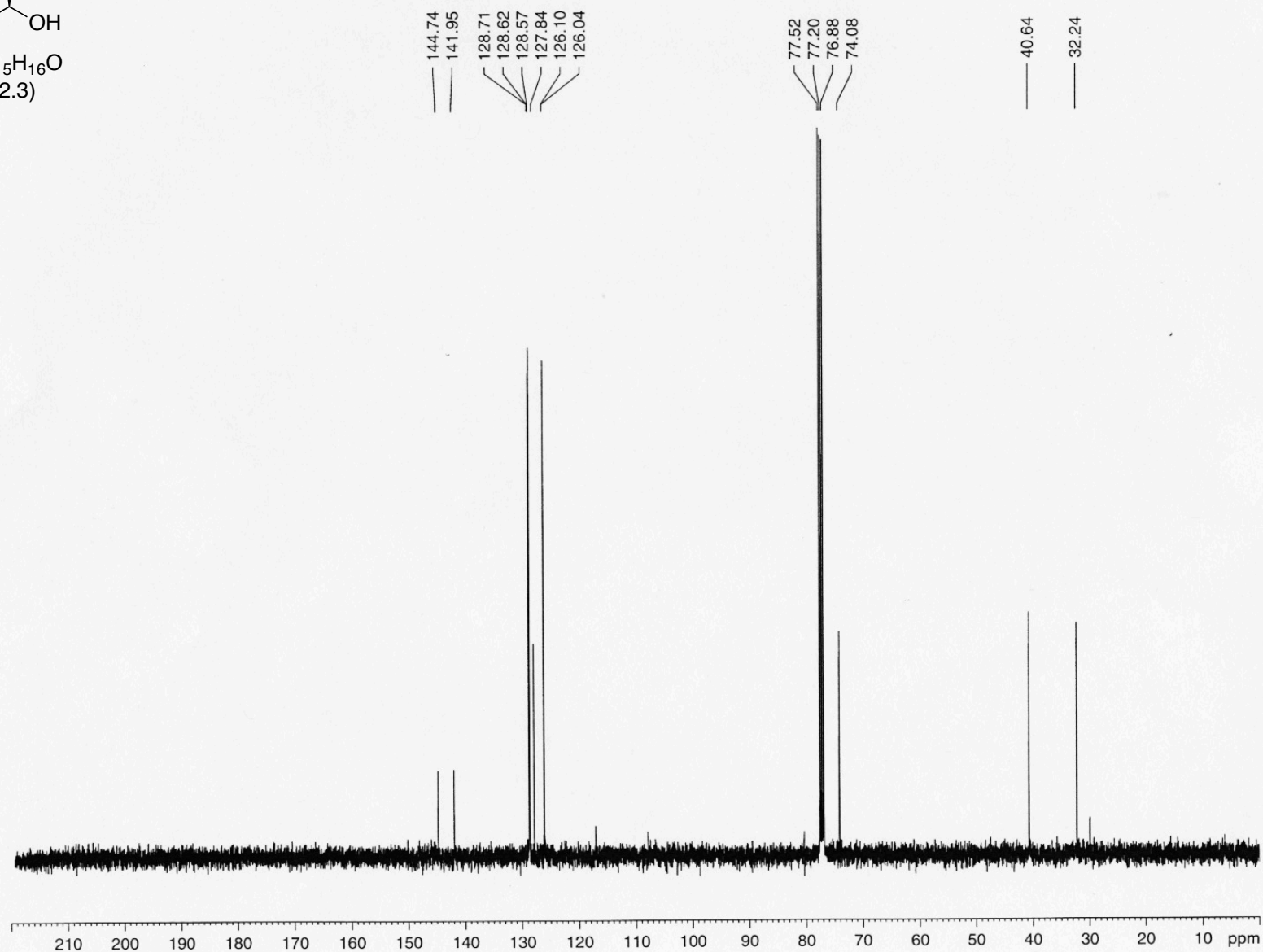
<sup>1</sup>H NMR: 400 MHz, CDCl<sub>3</sub>

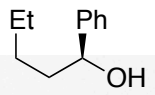




**10**: C<sub>15</sub>H<sub>16</sub>O  
(212.3)

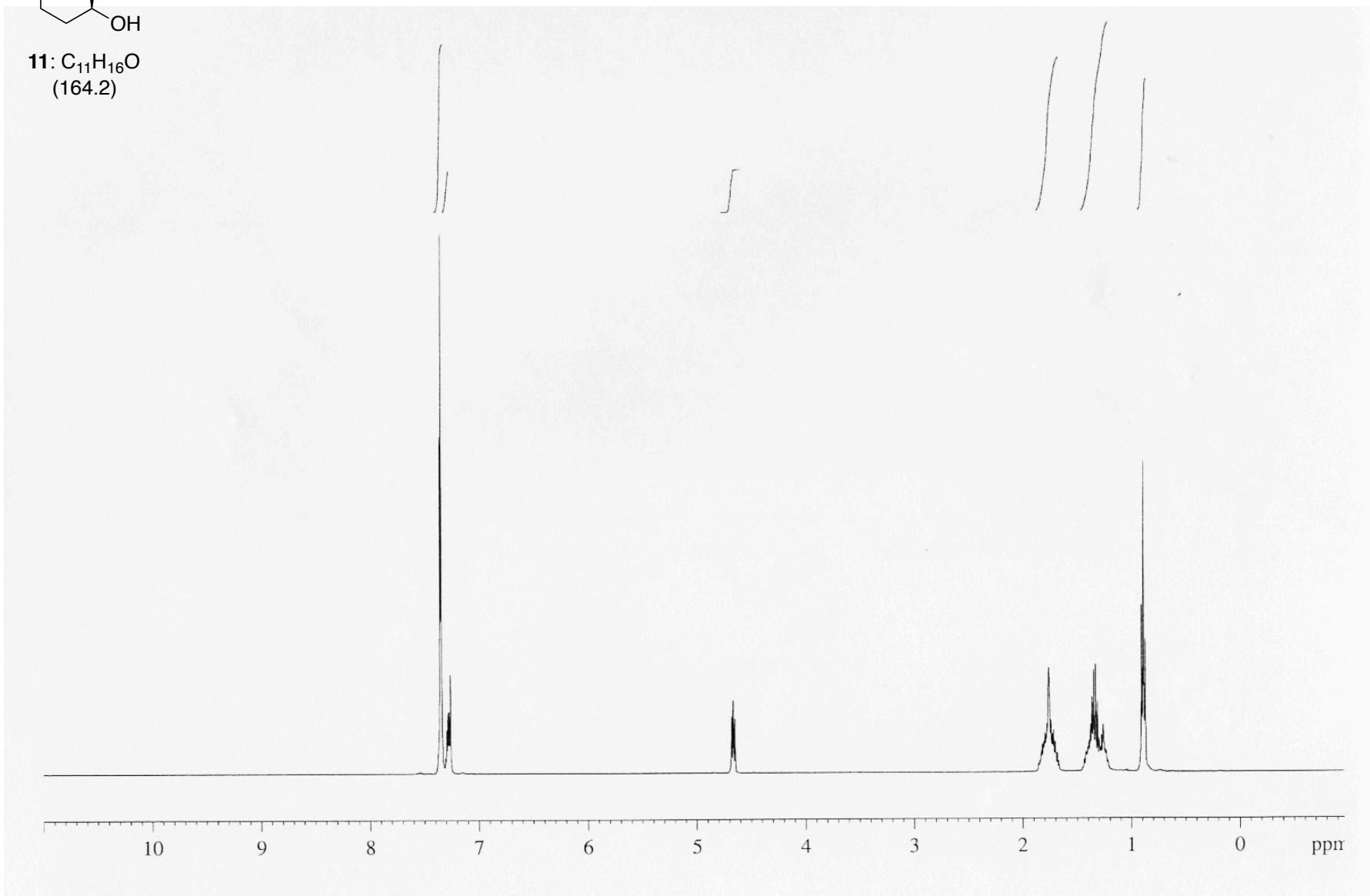
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>



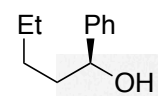


**11:** C<sub>11</sub>H<sub>16</sub>O  
(164.2)

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

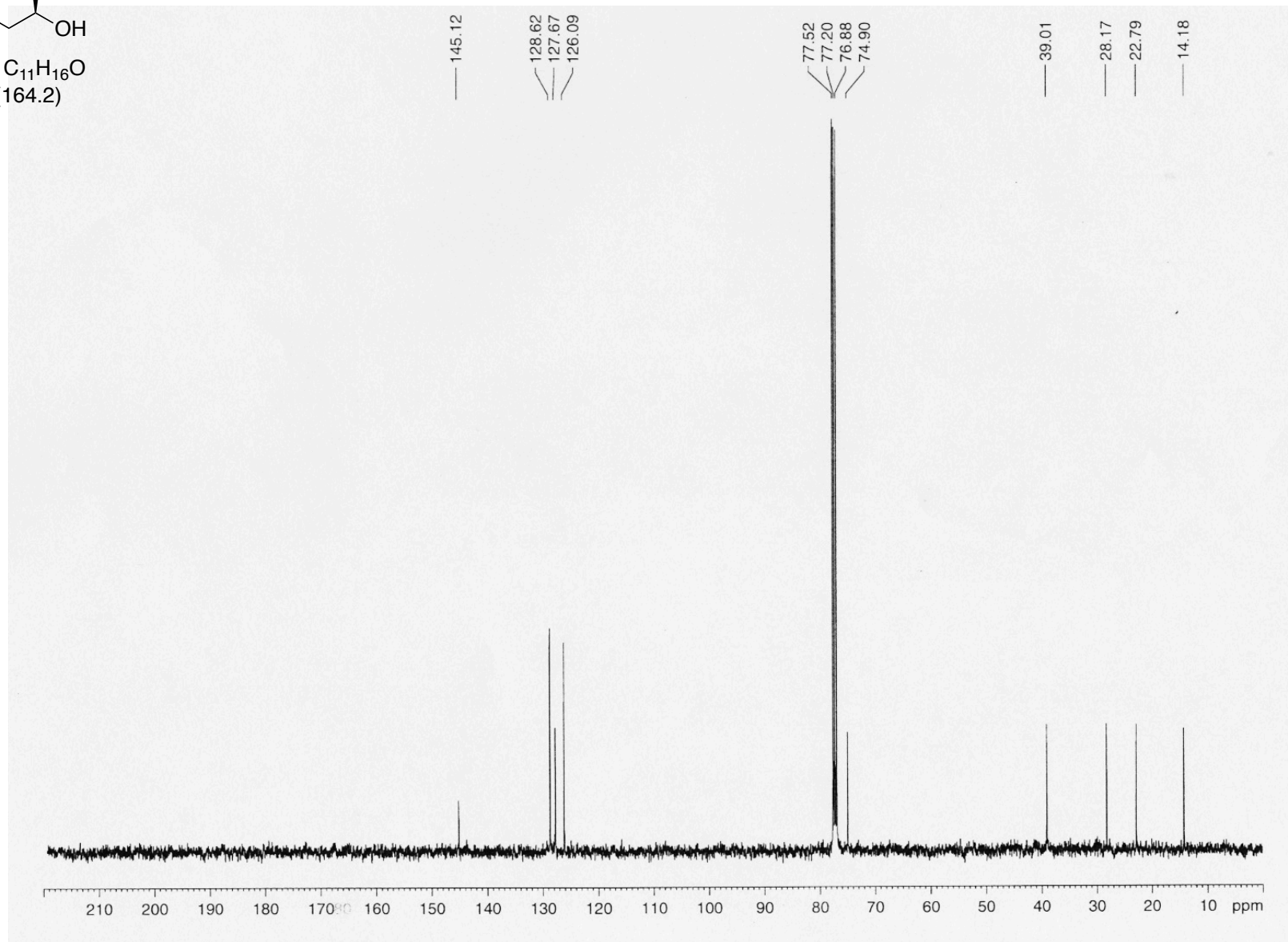




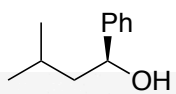


**11:** C<sub>11</sub>H<sub>16</sub>O  
(164.2)

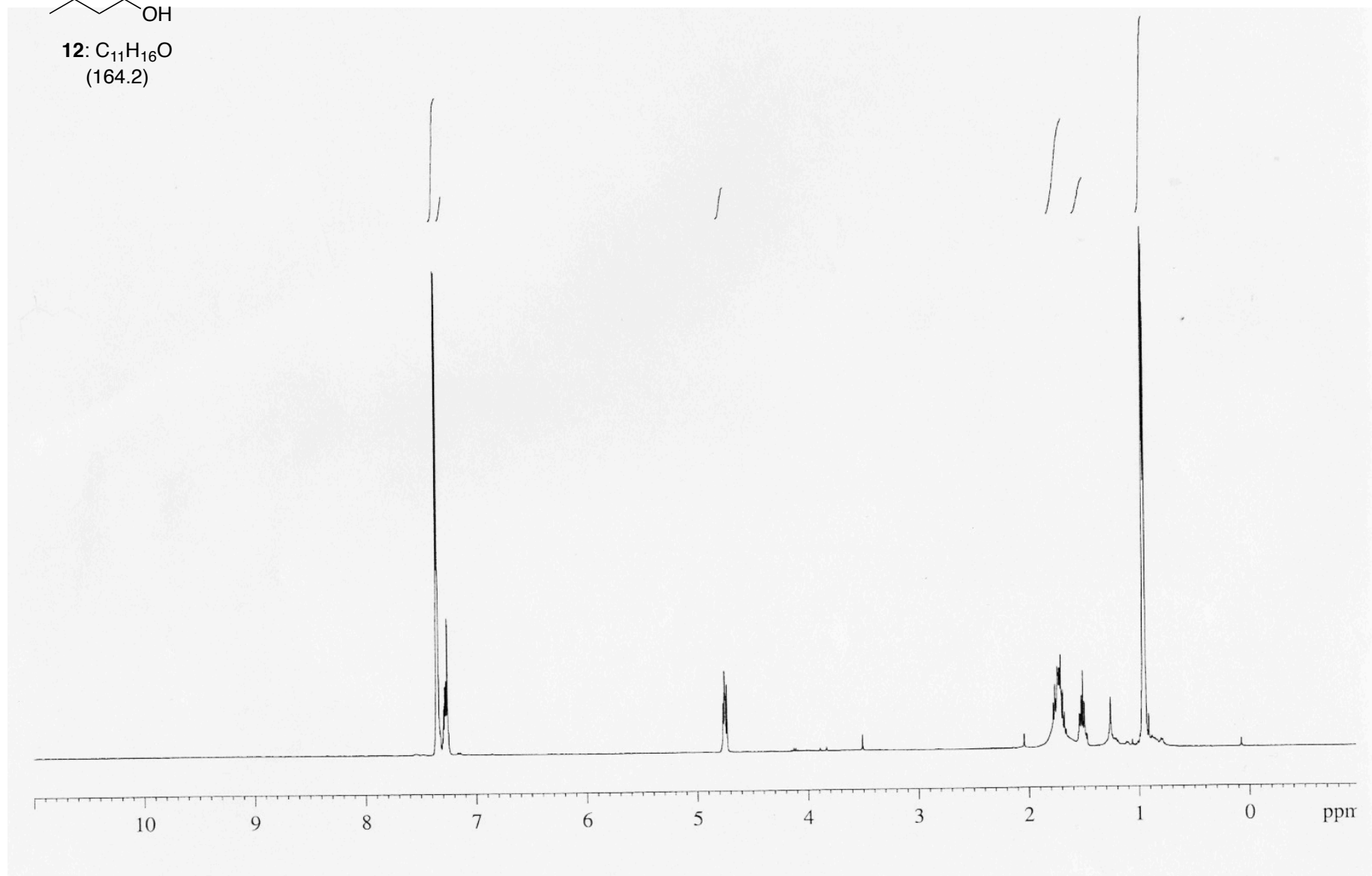
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>



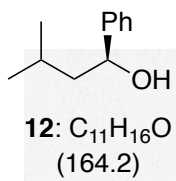
$^1\text{H}$  NMR: 400 MHz,  $\text{CDCl}_3$



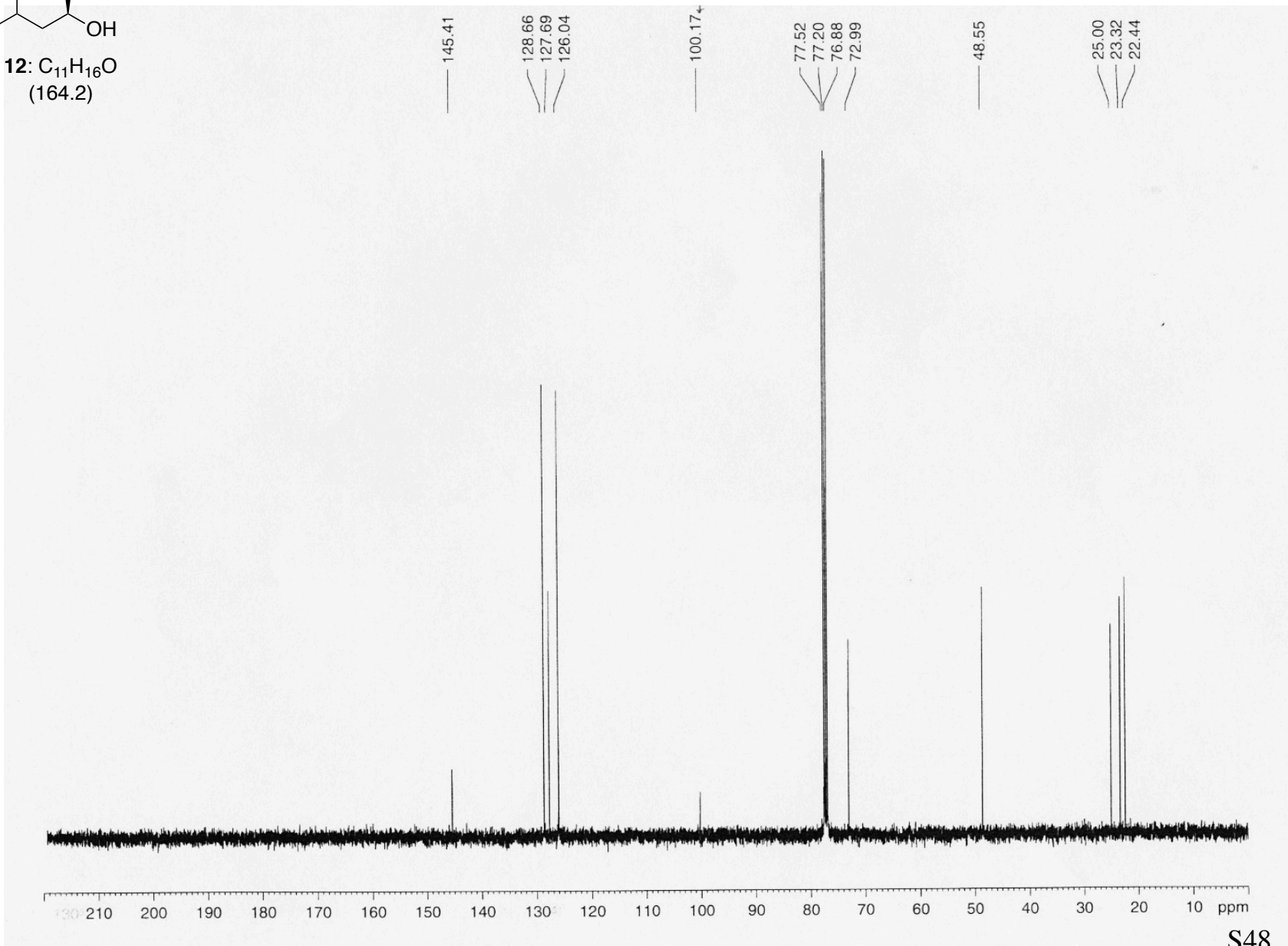
**12:**  $\text{C}_{11}\text{H}_{16}\text{O}$   
(164.2)



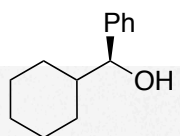
S47



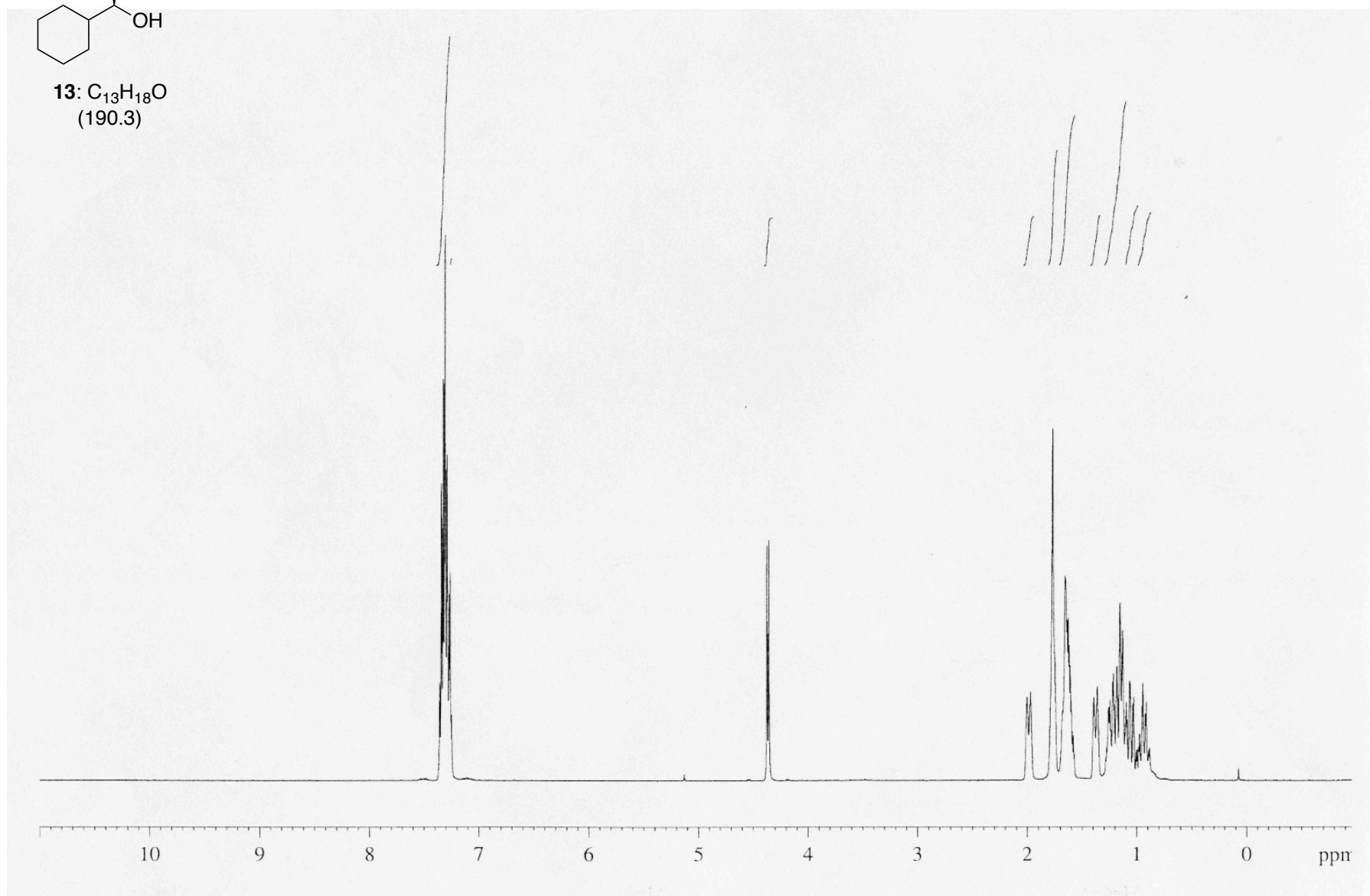
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>

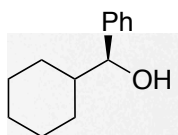


$^1\text{H}$  NMR: 400 MHz,  $\text{CDCl}_3$



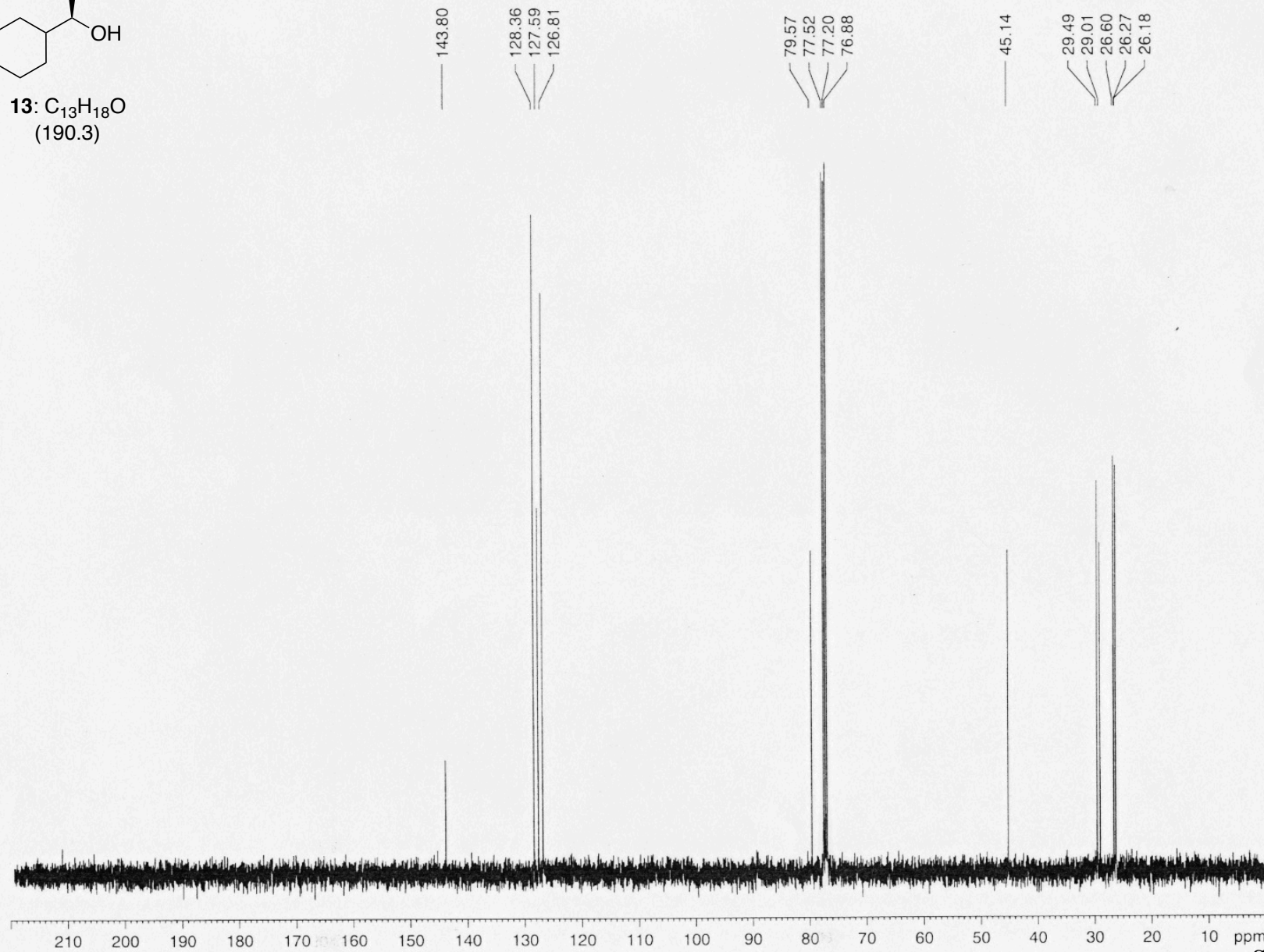
**13:**  $\text{C}_{13}\text{H}_{18}\text{O}$   
(190.3)

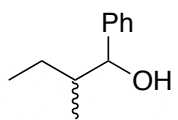




**13**: C<sub>13</sub>H<sub>18</sub>O  
(190.3)

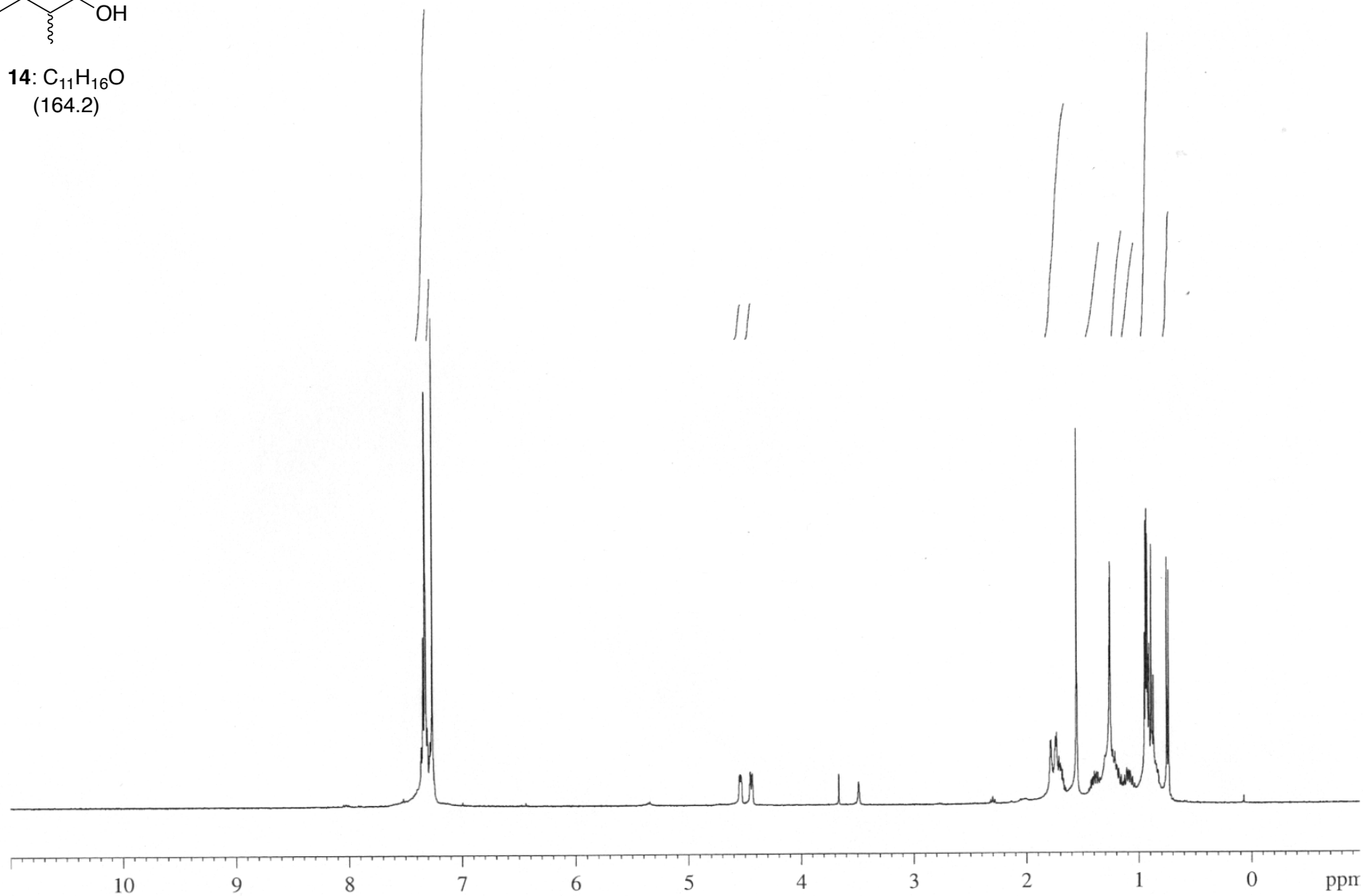
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>

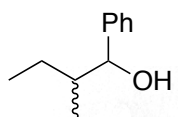




**14:** C<sub>11</sub>H<sub>16</sub>O  
(164.2)

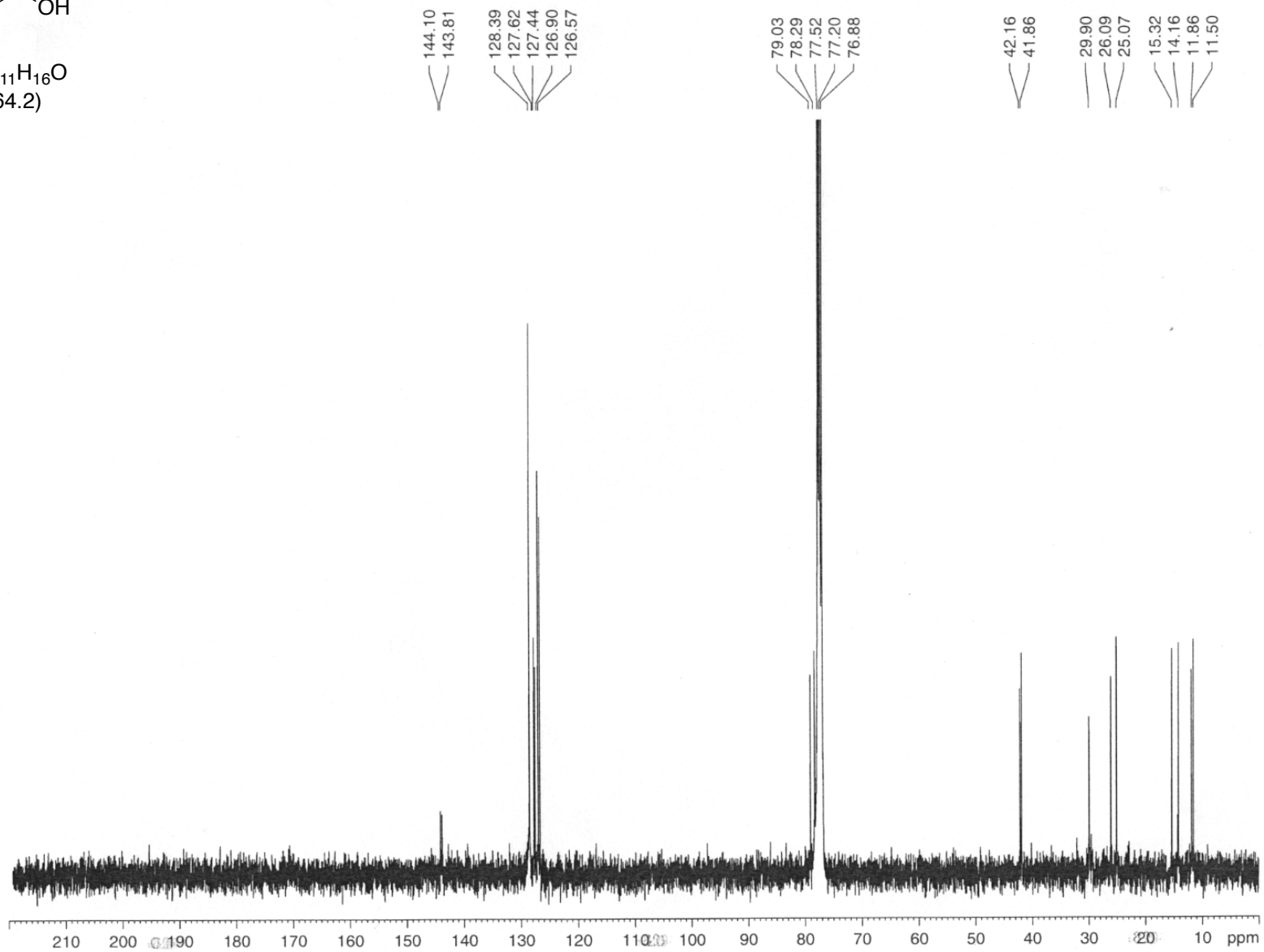
<sup>1</sup>H NMR: 400 MHz, CDCl<sub>3</sub>



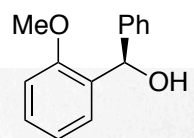


**14:** C<sub>11</sub>H<sub>16</sub>O  
(164.2)

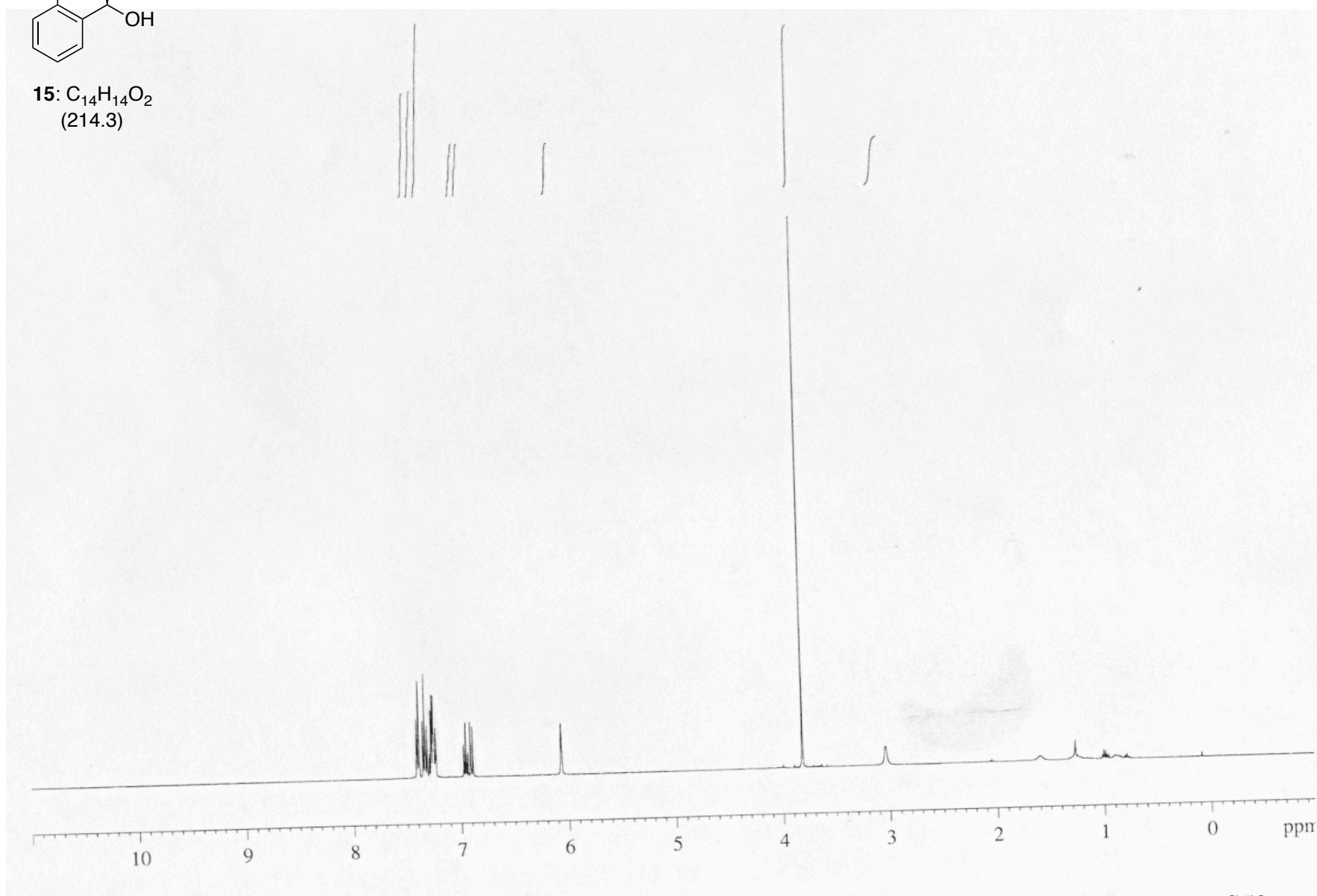
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>



$^1\text{H}$  NMR: 400 MHz,  $\text{CDCl}_3$

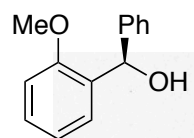


**15:**  $\text{C}_{14}\text{H}_{14}\text{O}_2$   
(214.3)

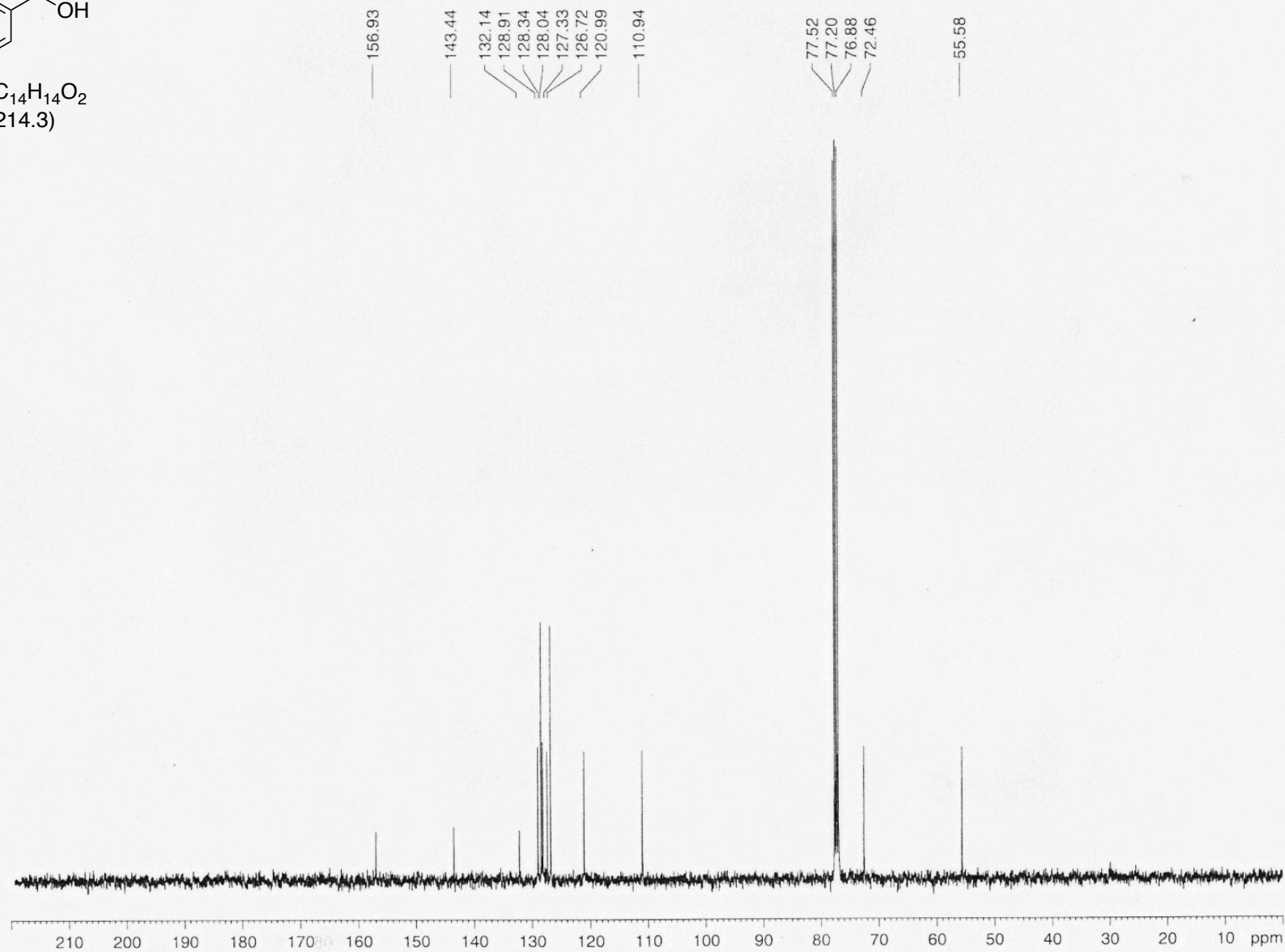




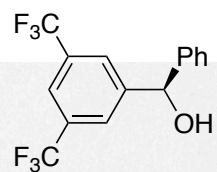
$^{13}\text{C}$  NMR: 100 MHz,  $\text{CDCl}_3$



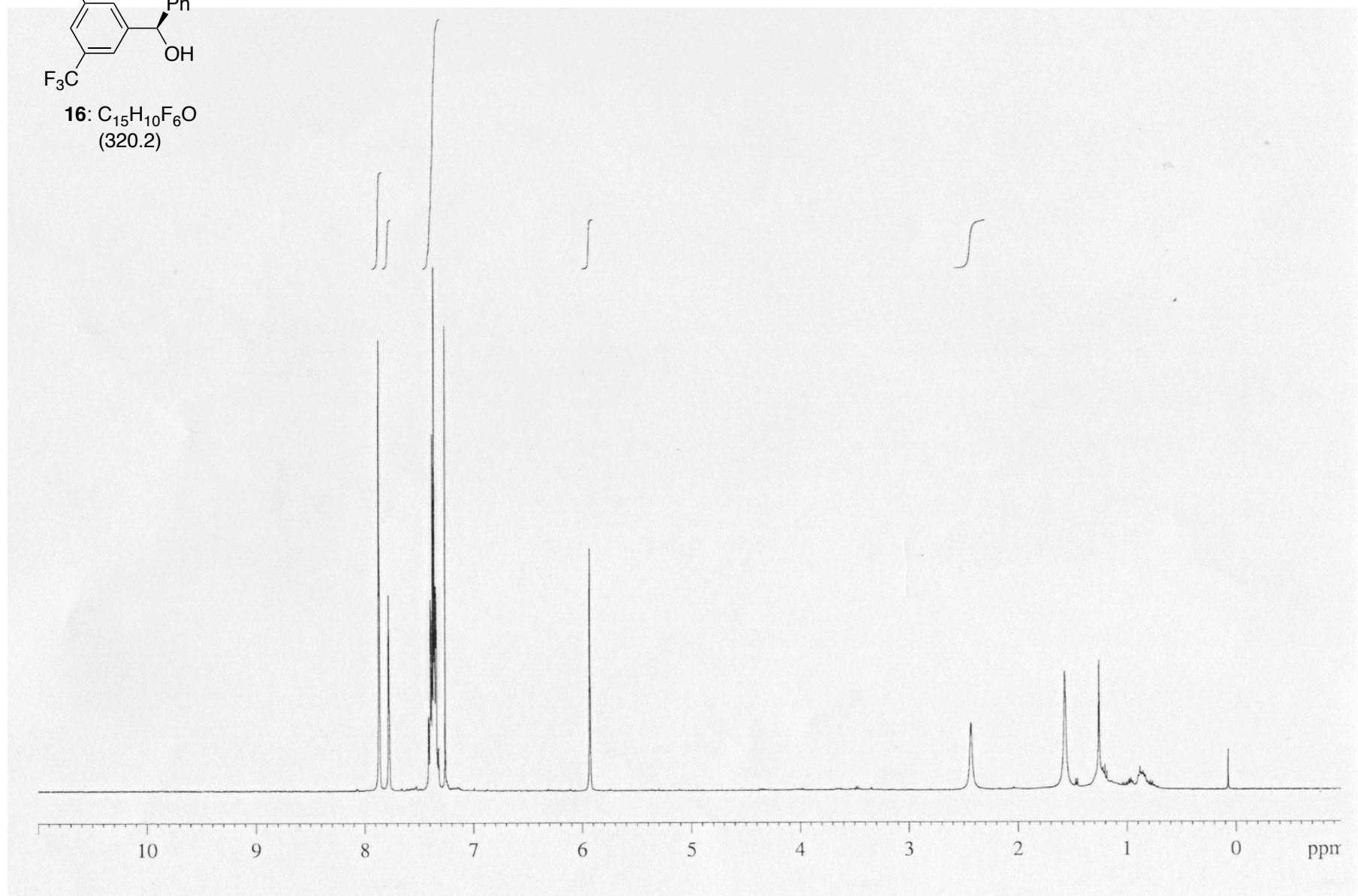
**15:**  $\text{C}_{14}\text{H}_{14}\text{O}_2$   
(214.3)



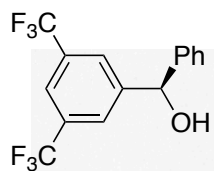
$^1\text{H}$  NMR: 400 MHz,  $\text{CDCl}_3$



**16:**  $\text{C}_{15}\text{H}_{10}\text{F}_6\text{O}$   
(320.2)

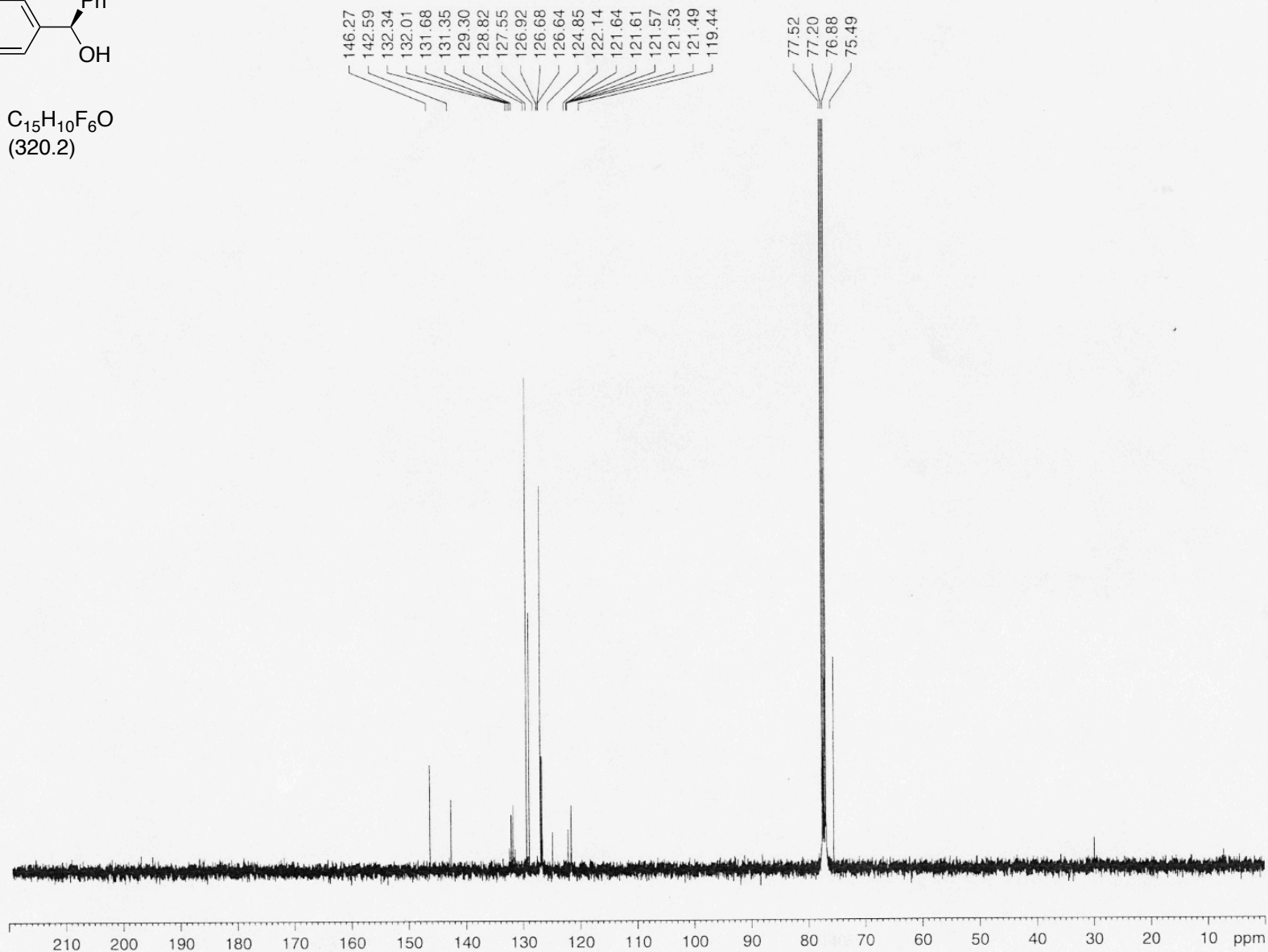


S55

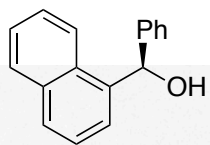


**16:** C<sub>15</sub>H<sub>10</sub>F<sub>6</sub>O  
(320.2)

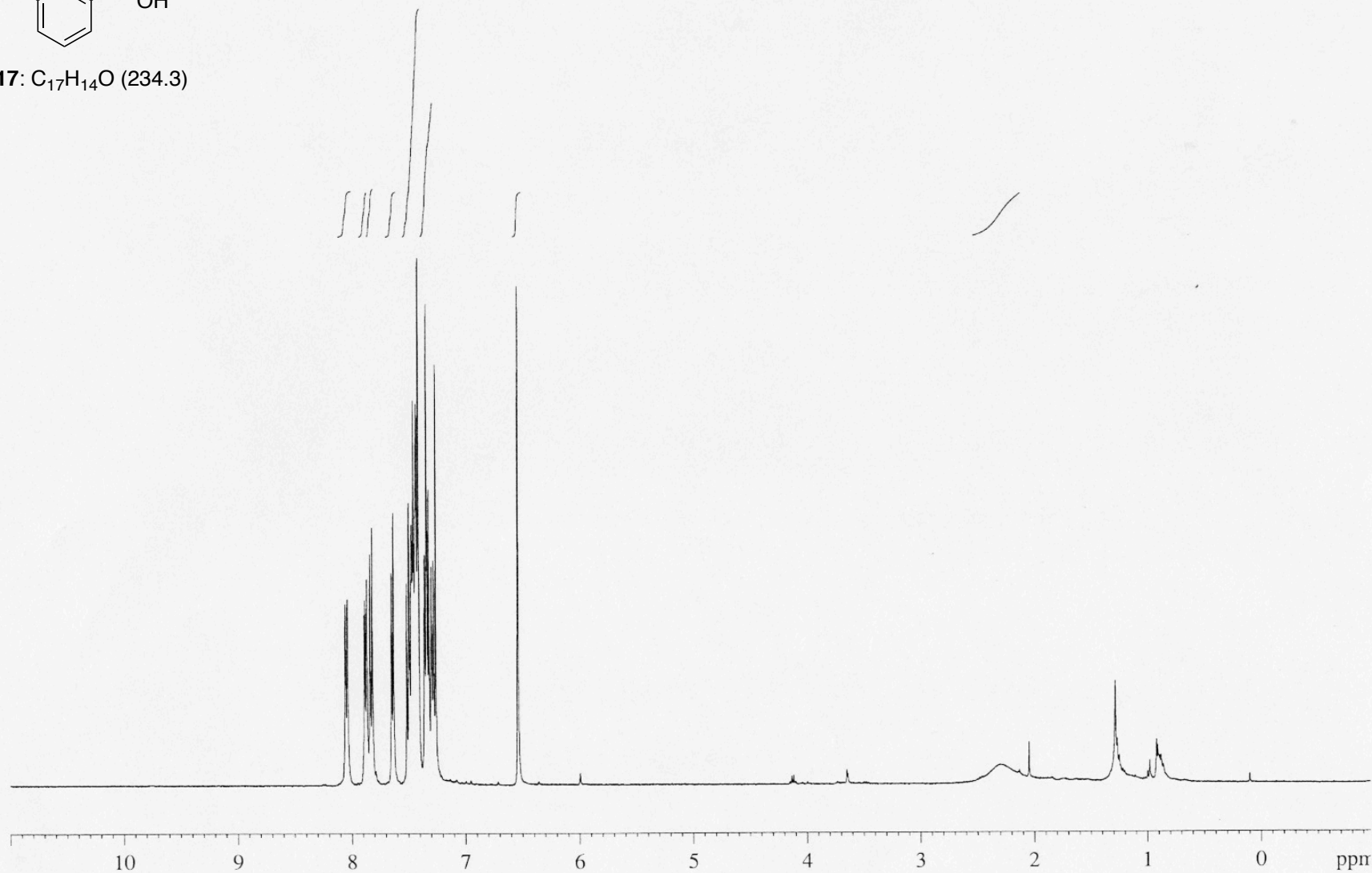
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>



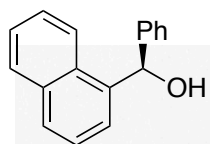
$^1\text{H}$  NMR: 400 MHz,  $\text{CDCl}_3$



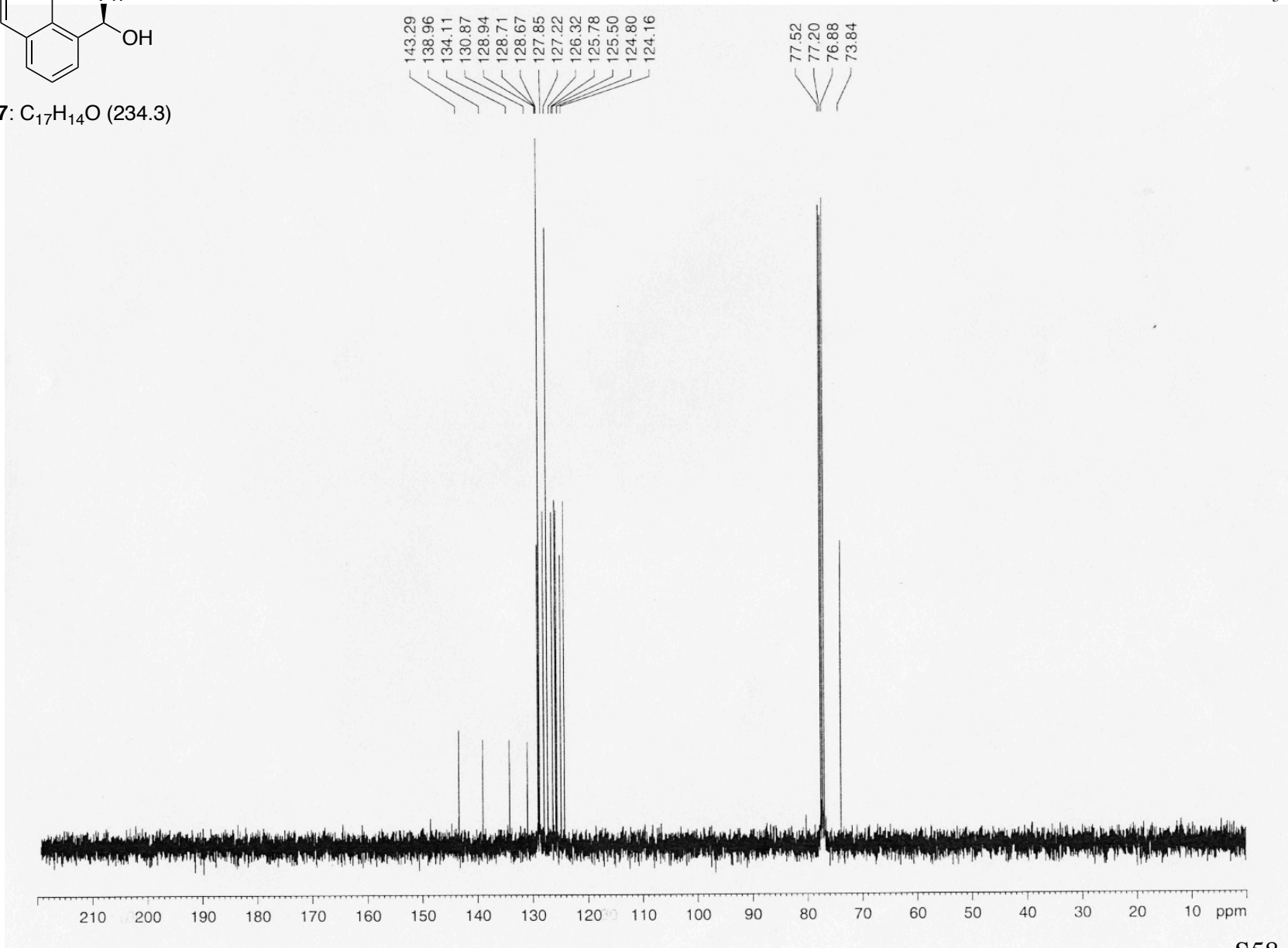
17:  $\text{C}_{17}\text{H}_{14}\text{O}$  (234.3)



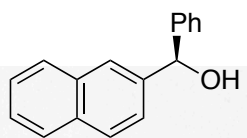
$^{13}\text{C}$  NMR: 100 MHz,  $\text{CDCl}_3$



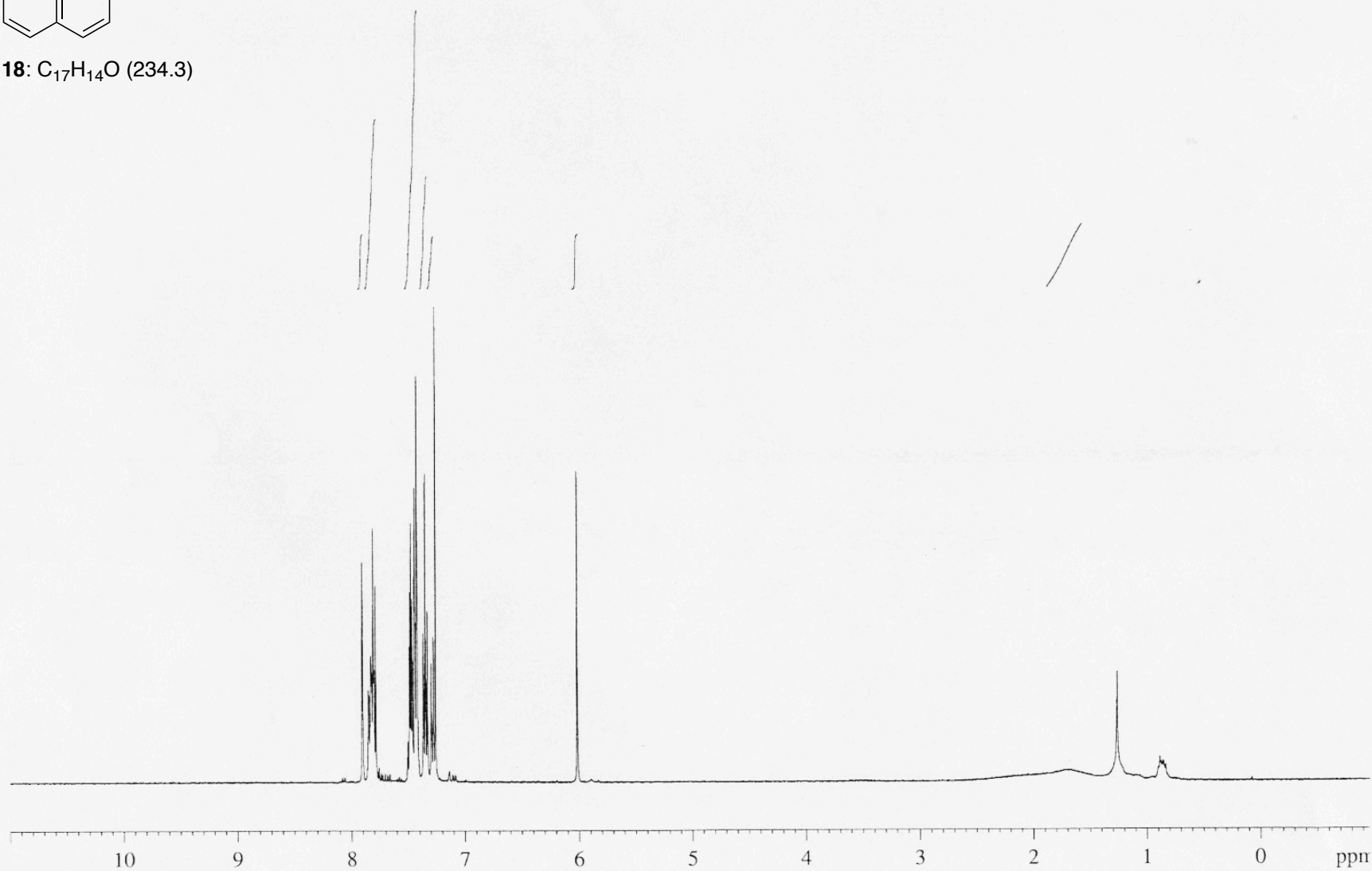
17:  $\text{C}_{17}\text{H}_{14}\text{O}$  (234.3)



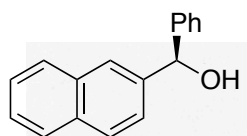
$^1\text{H}$  NMR: 400 MHz,  $\text{CDCl}_3$



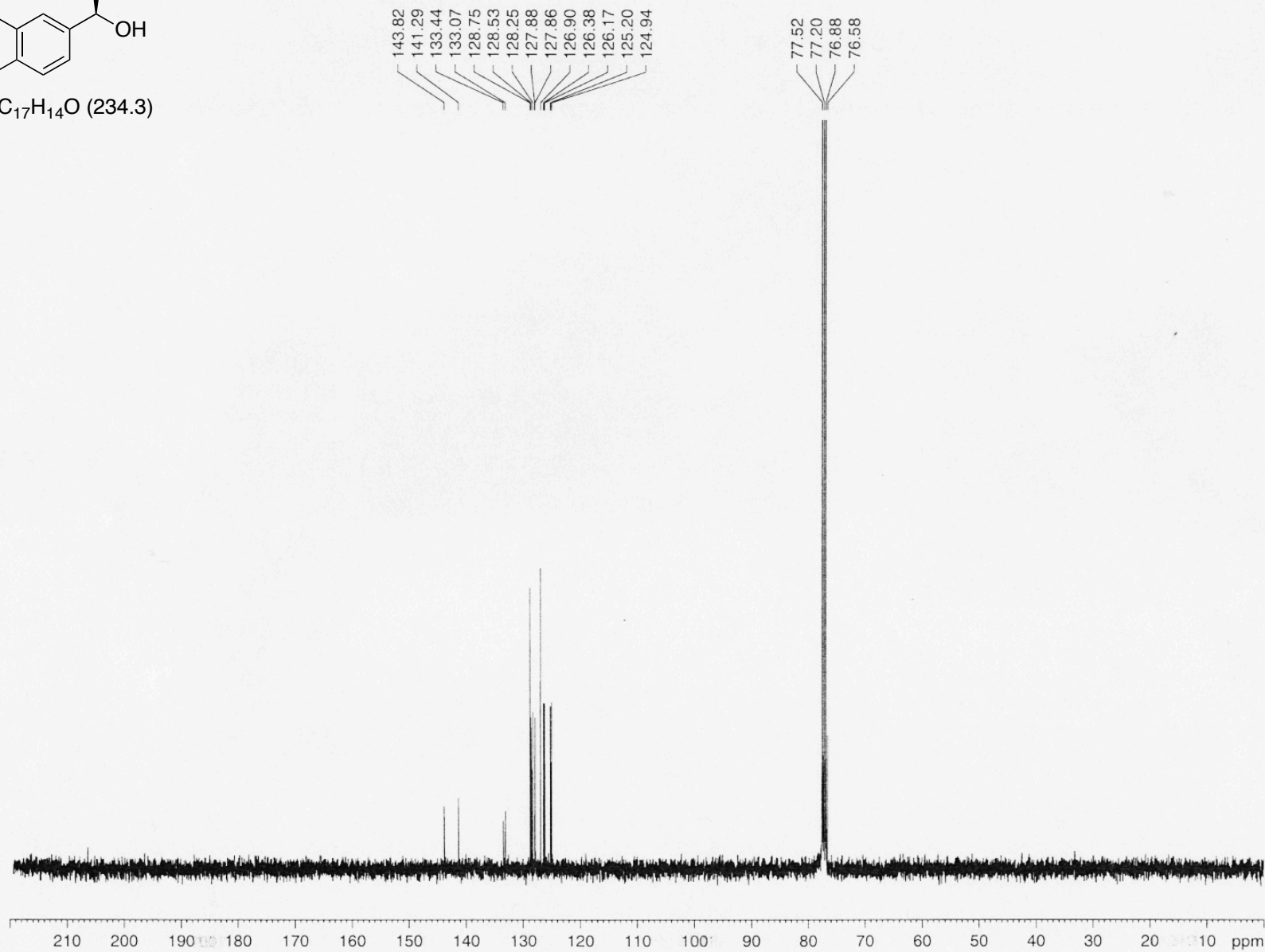
**18:**  $\text{C}_{17}\text{H}_{14}\text{O}$  (234.3)



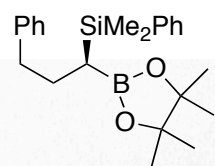
$^{13}\text{C}$  NMR: 100 MHz,  $\text{CDCl}_3$



**18:**  $\text{C}_{17}\text{H}_{14}\text{O}$  (234.3)

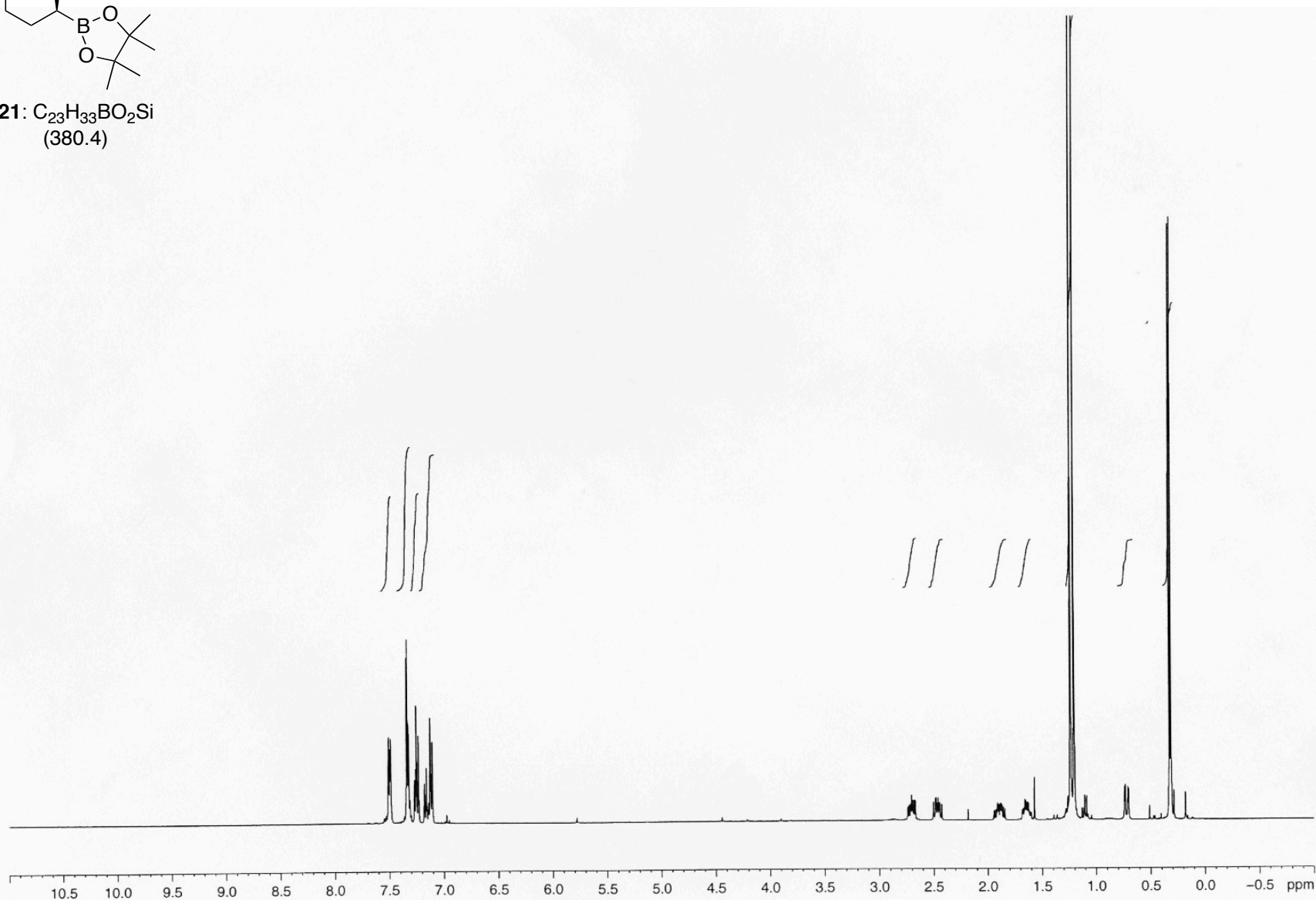


S60



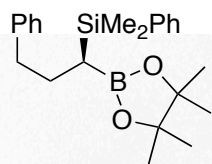
**21:** C<sub>23</sub>H<sub>33</sub>BO<sub>2</sub>Si  
(380.4)

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



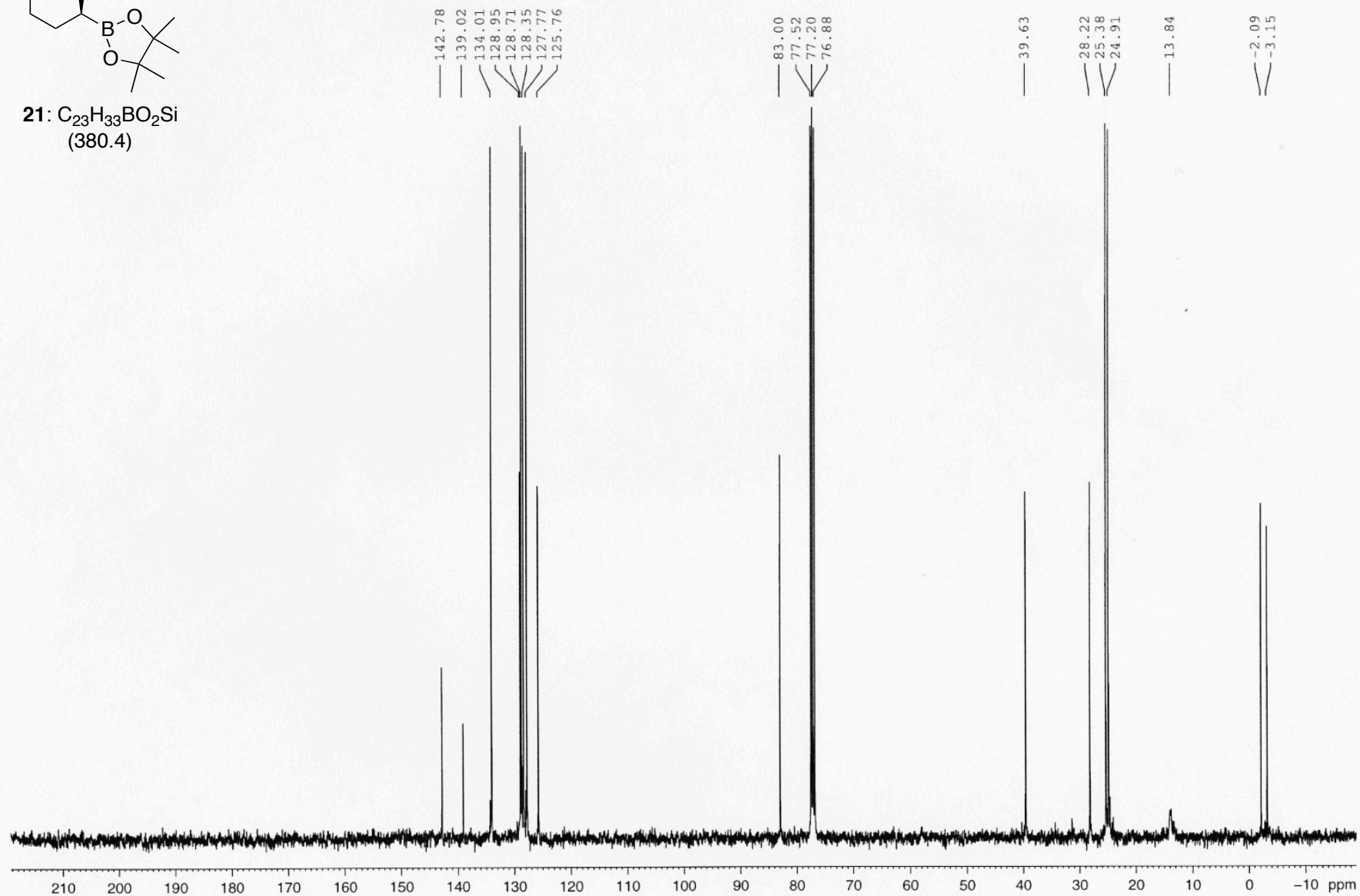
S61

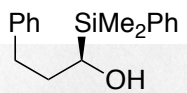




**21**: C<sub>23</sub>H<sub>33</sub>BO<sub>2</sub>Si  
(380.4)

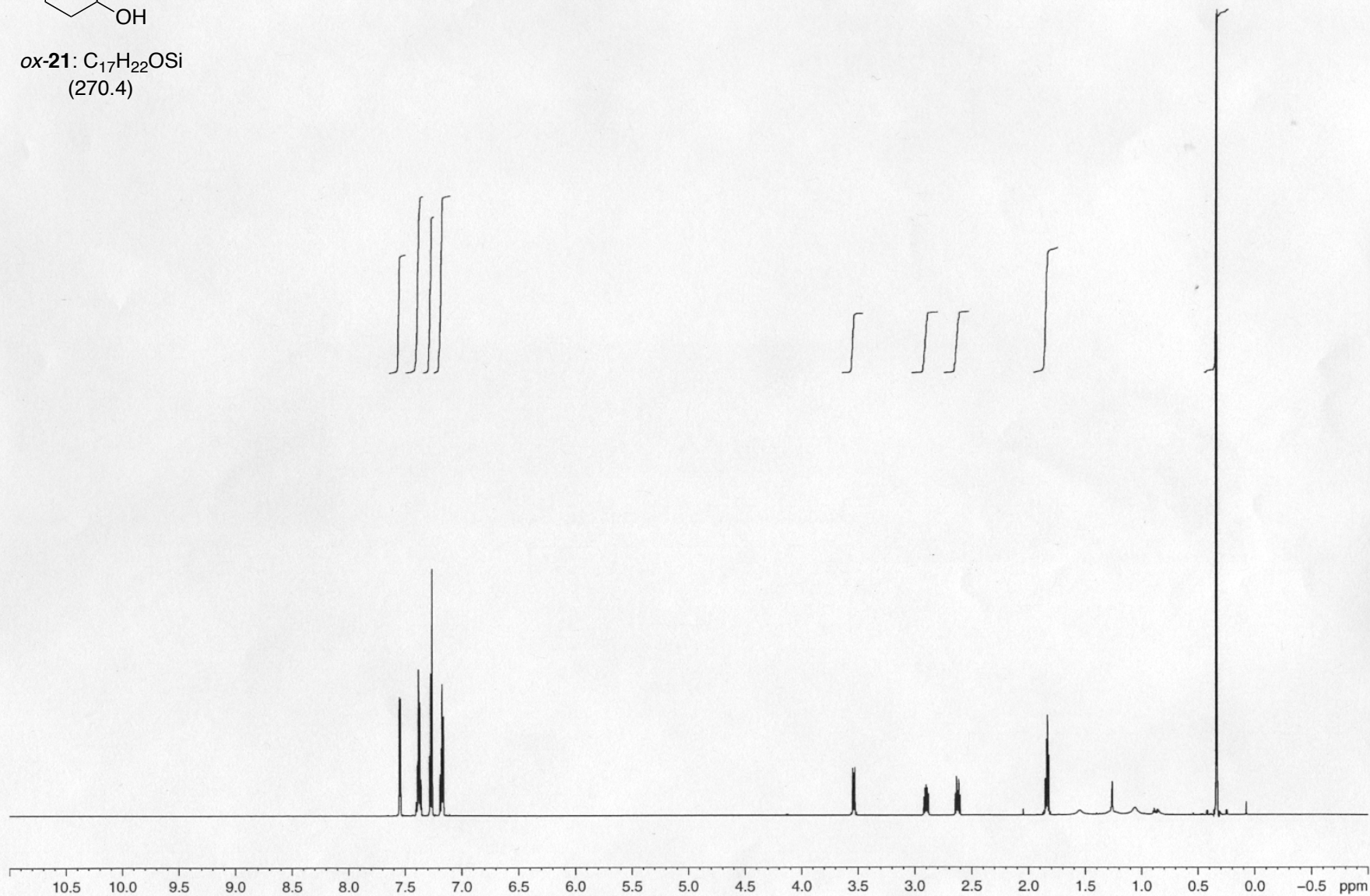
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>

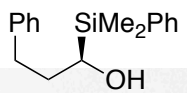




$^1\text{H}$  NMR: 700 MHz,  $\text{CDCl}_3$

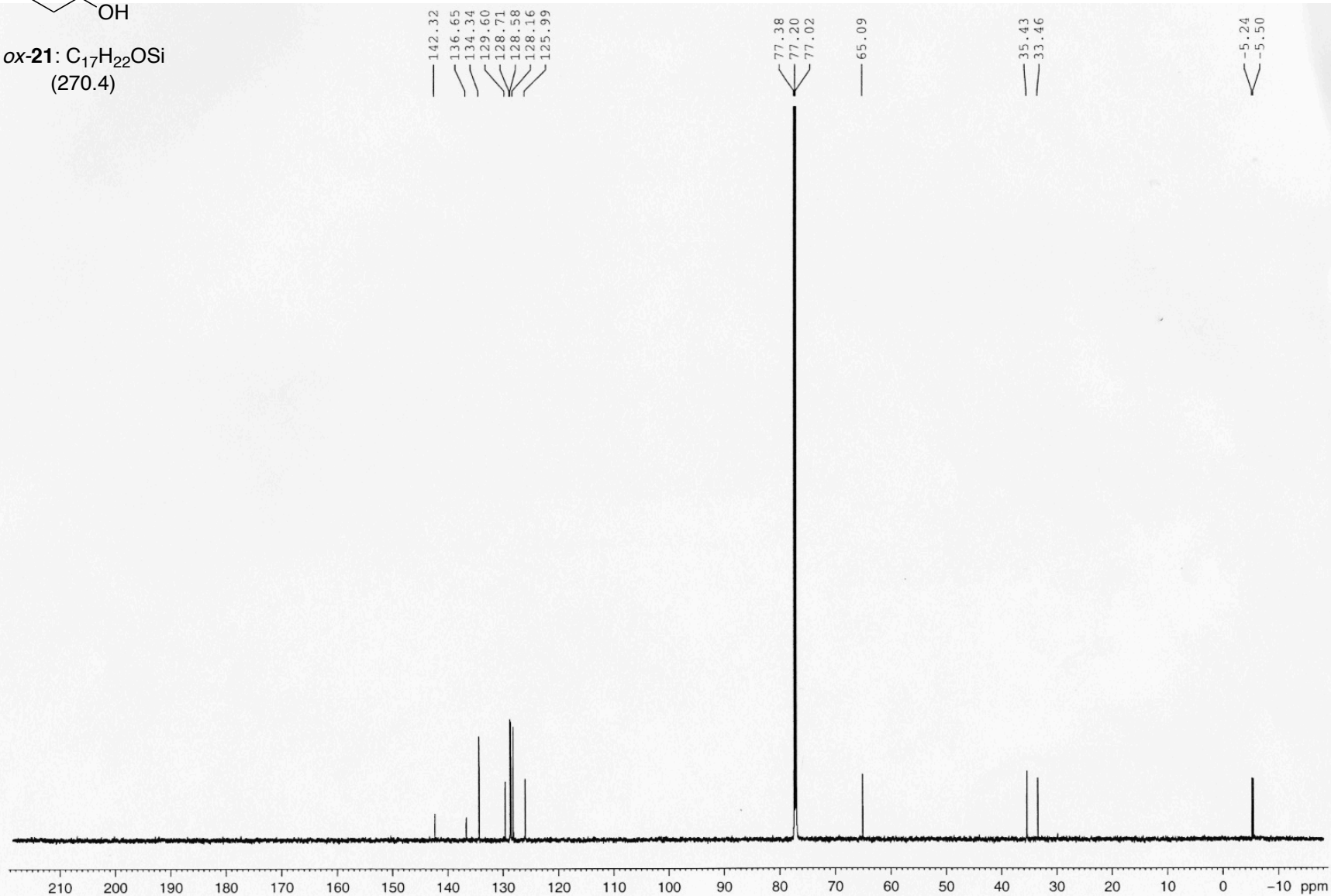
ox-21:  $\text{C}_{17}\text{H}_{22}\text{OSi}$   
(270.4)

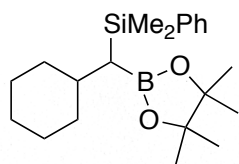




$^{13}\text{C}$  NMR: 175 MHz,  $\text{CDCl}_3$

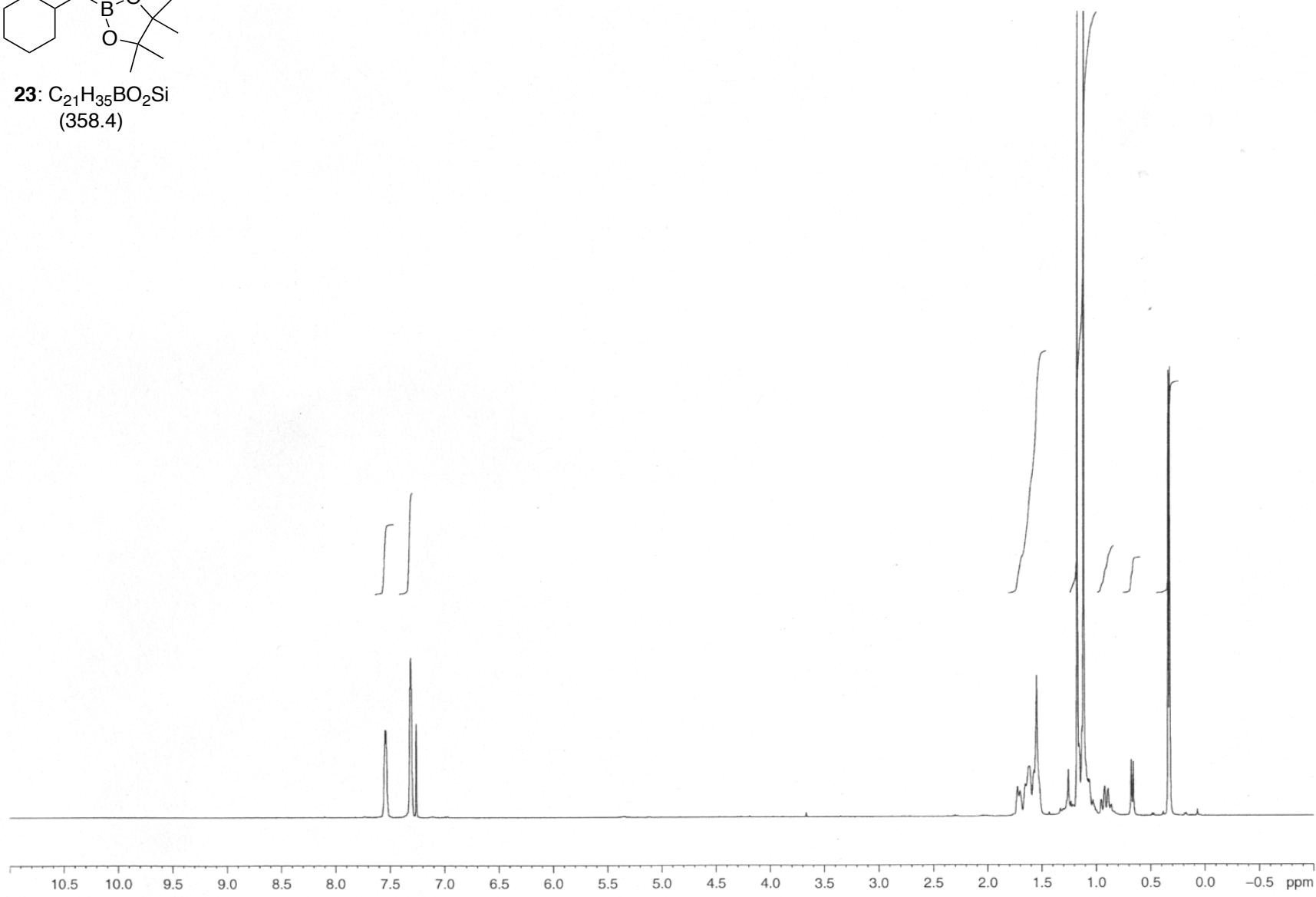
ox-21:  $\text{C}_{17}\text{H}_{22}\text{OSi}$   
(270.4)



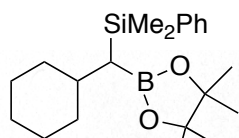


**23:** C<sub>21</sub>H<sub>35</sub>BO<sub>2</sub>Si  
(358.4)

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

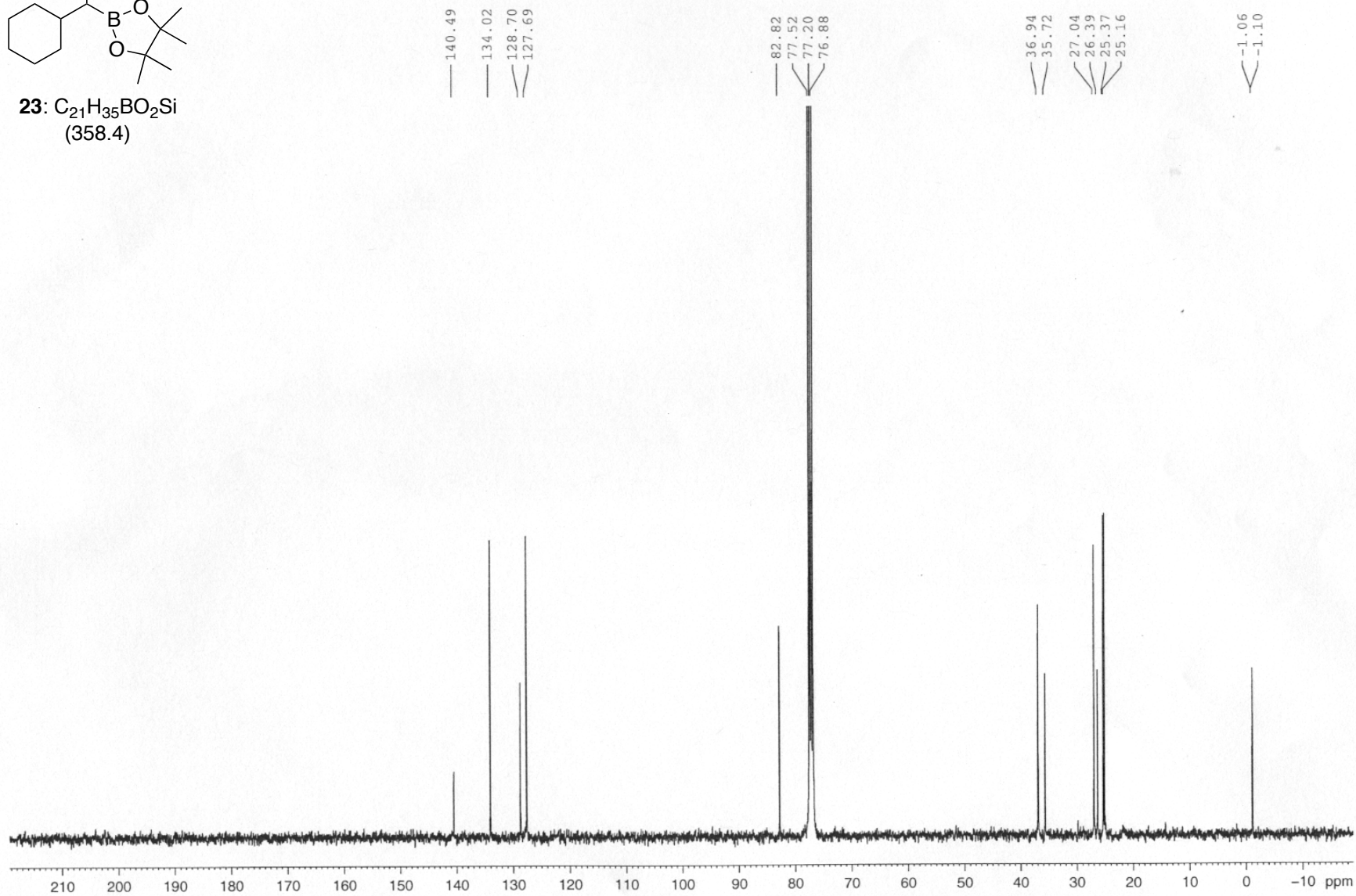


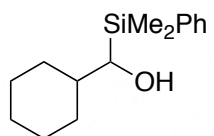
S65



**23:** C<sub>21</sub>H<sub>35</sub>BO<sub>2</sub>Si  
(358.4)

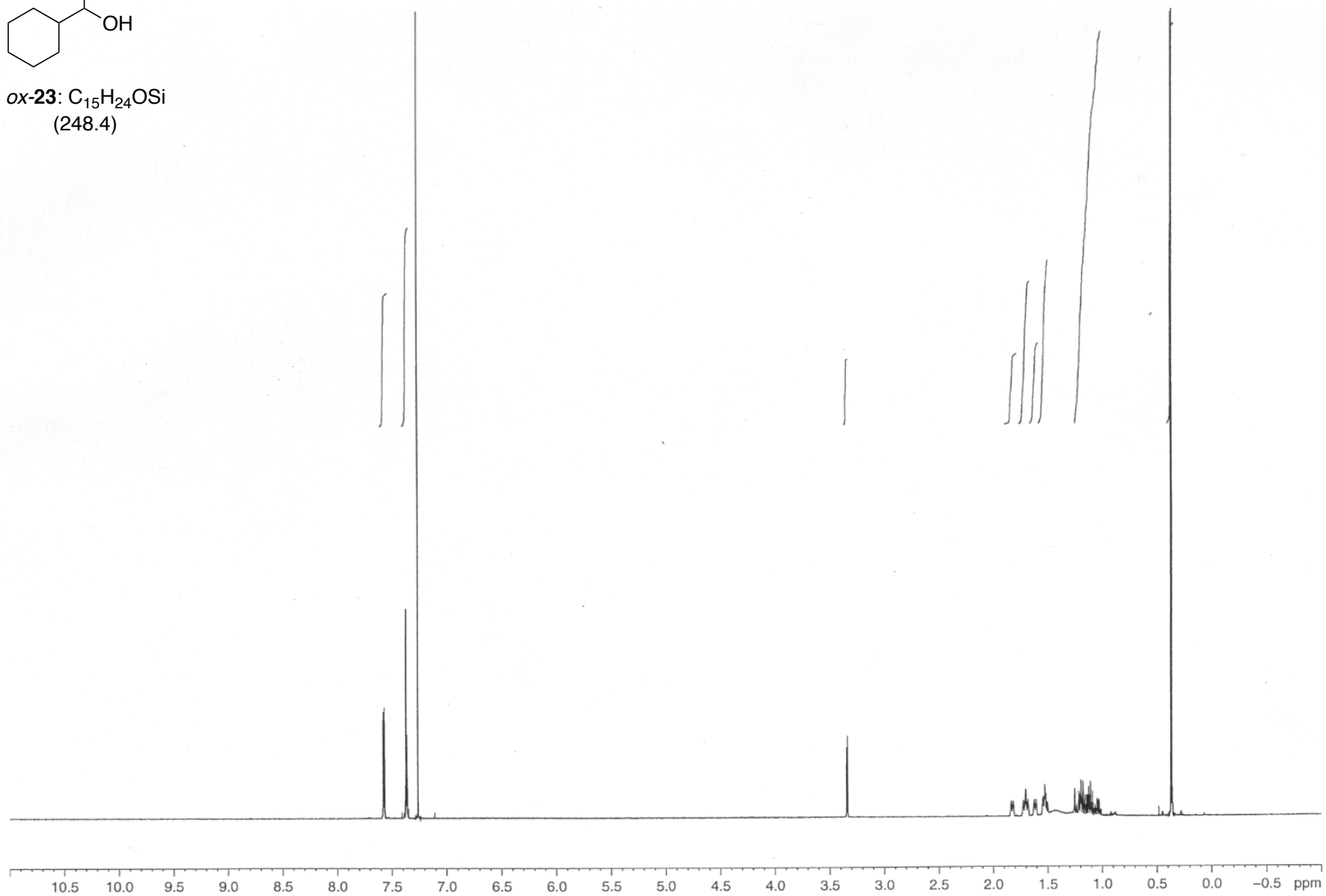
<sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub>

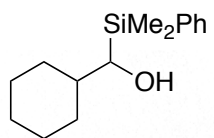




ox-23: C<sub>15</sub>H<sub>24</sub>OSi  
(248.4)

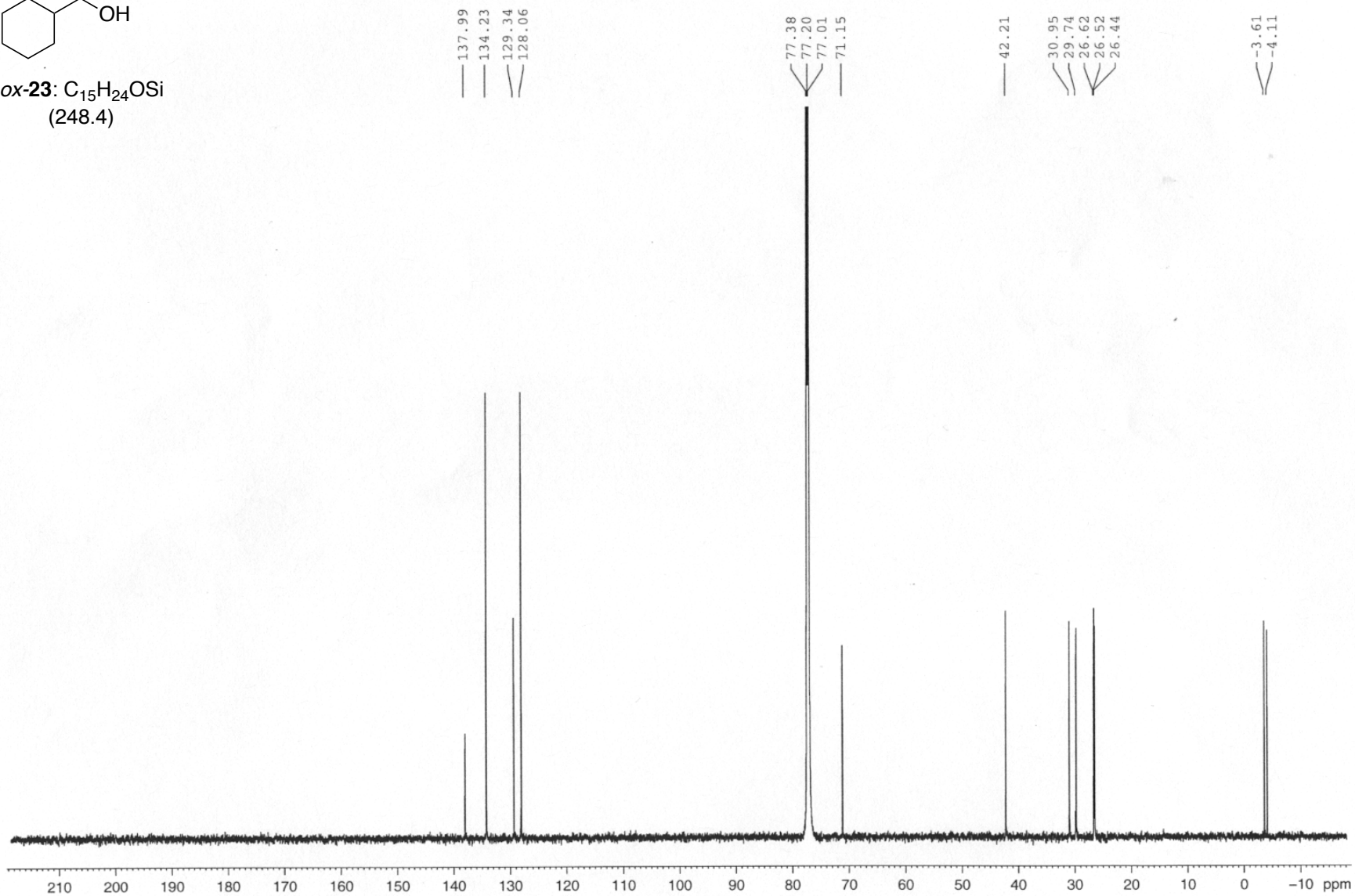
<sup>1</sup>H NMR: 700 MHz, CDCl<sub>3</sub>



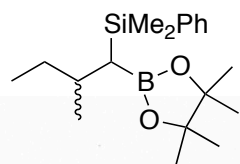


ox-23: C<sub>15</sub>H<sub>24</sub>OSi  
(248.4)

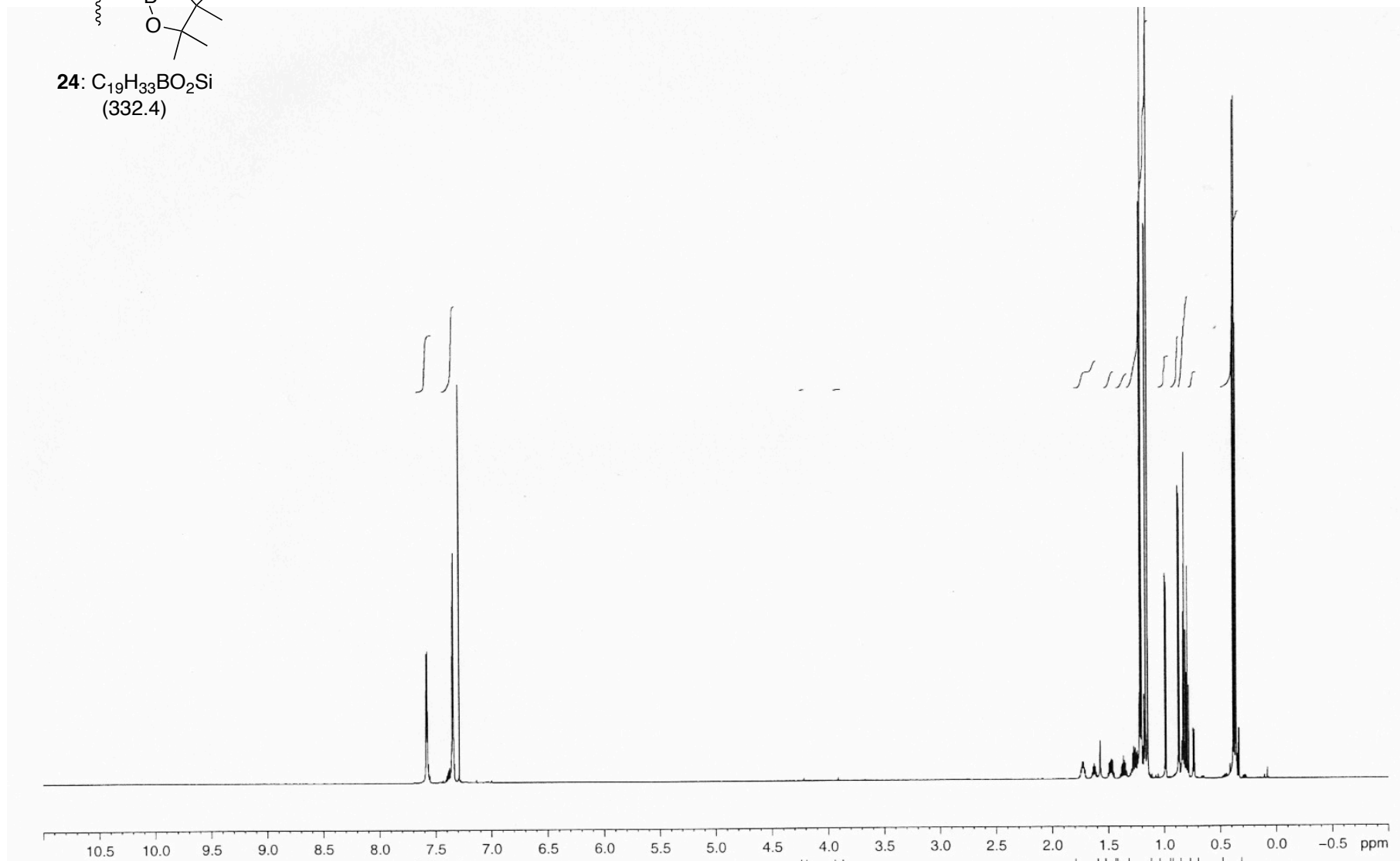
<sup>13</sup>C NMR: 175 MHz, CDCl<sub>3</sub>



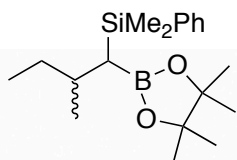
$^1\text{H NMR}$ : 700 MHz,  $\text{CDCl}_3$



**24:**  $\text{C}_{19}\text{H}_{33}\text{BO}_2\text{Si}$   
(332.4)

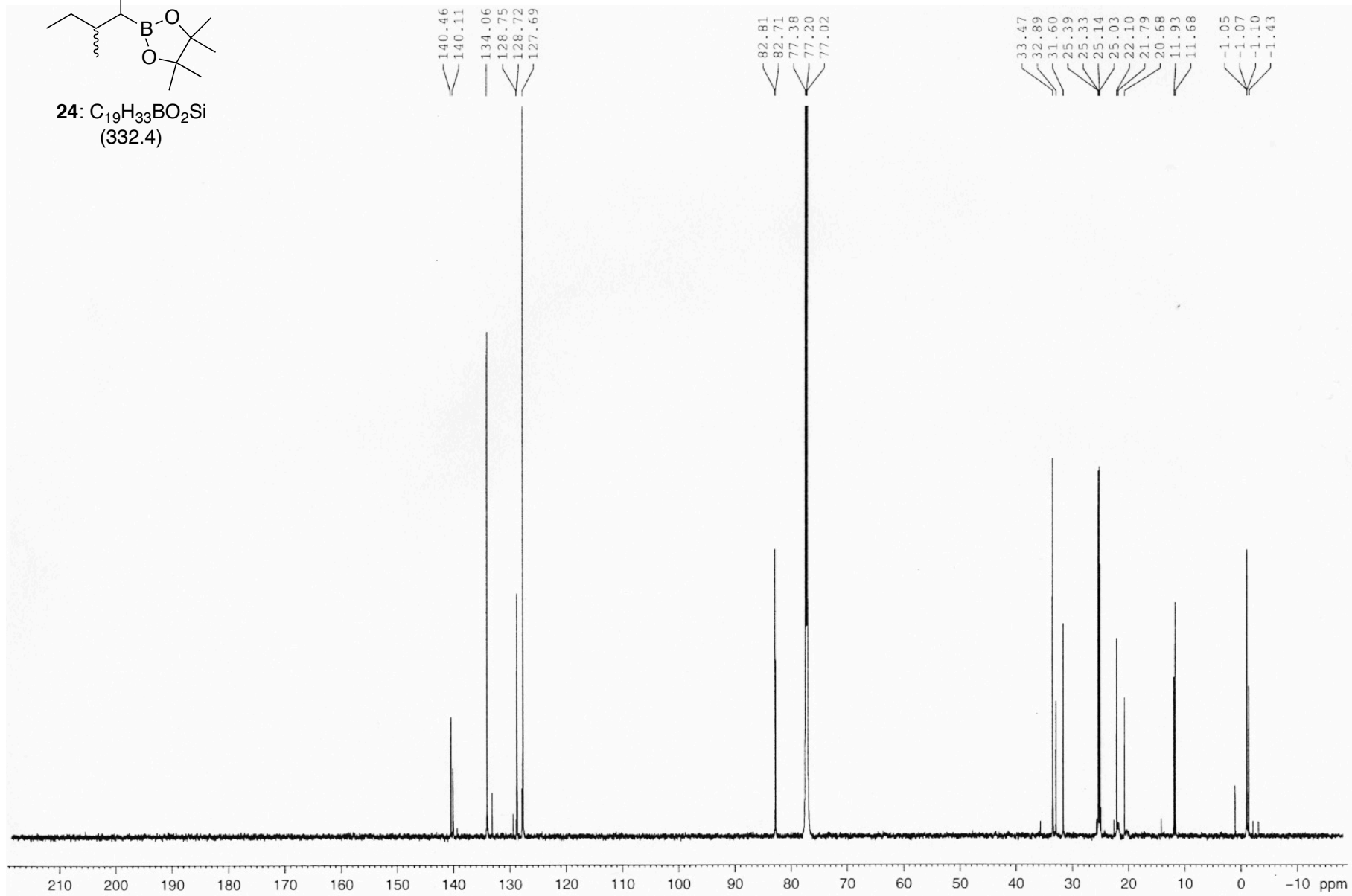




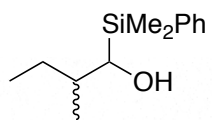


**24:** C<sub>19</sub>H<sub>33</sub>BO<sub>2</sub>Si  
(332.4)

<sup>13</sup>C NMR: 175 MHz, CDCl<sub>3</sub>

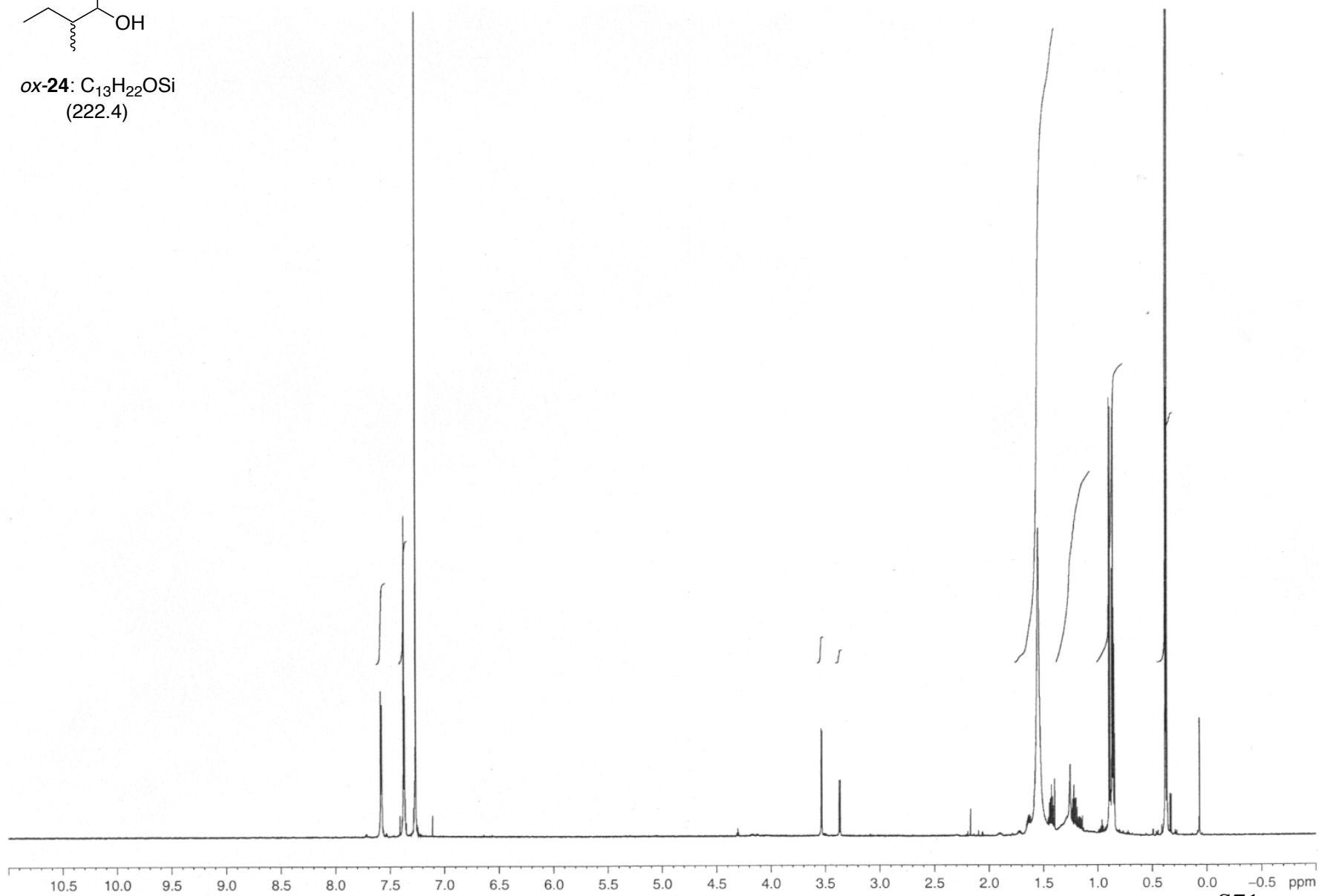


S70

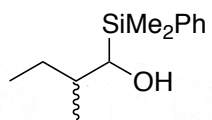


ox-24: C<sub>13</sub>H<sub>22</sub>OSi  
(222.4)

<sup>1</sup>H NMR: 700 MHz, CDCl<sub>3</sub>



S71



ox-24: C<sub>13</sub>H<sub>22</sub>O<sub>2</sub>Si  
(222.4)

<sup>13</sup>C NMR: 175 MHz, CDCl<sub>3</sub>

