

## SUPPORTING INFORMATION

### Catalytic Asymmetric Synthesis Using Feedstocks. An Enantioselective Route to 2-Arylpropionic Acids and 2-Arylethyl Amines via Hydrovinylation of Vinylarenes

Craig R. Smith and T. V. RajanBabu\*

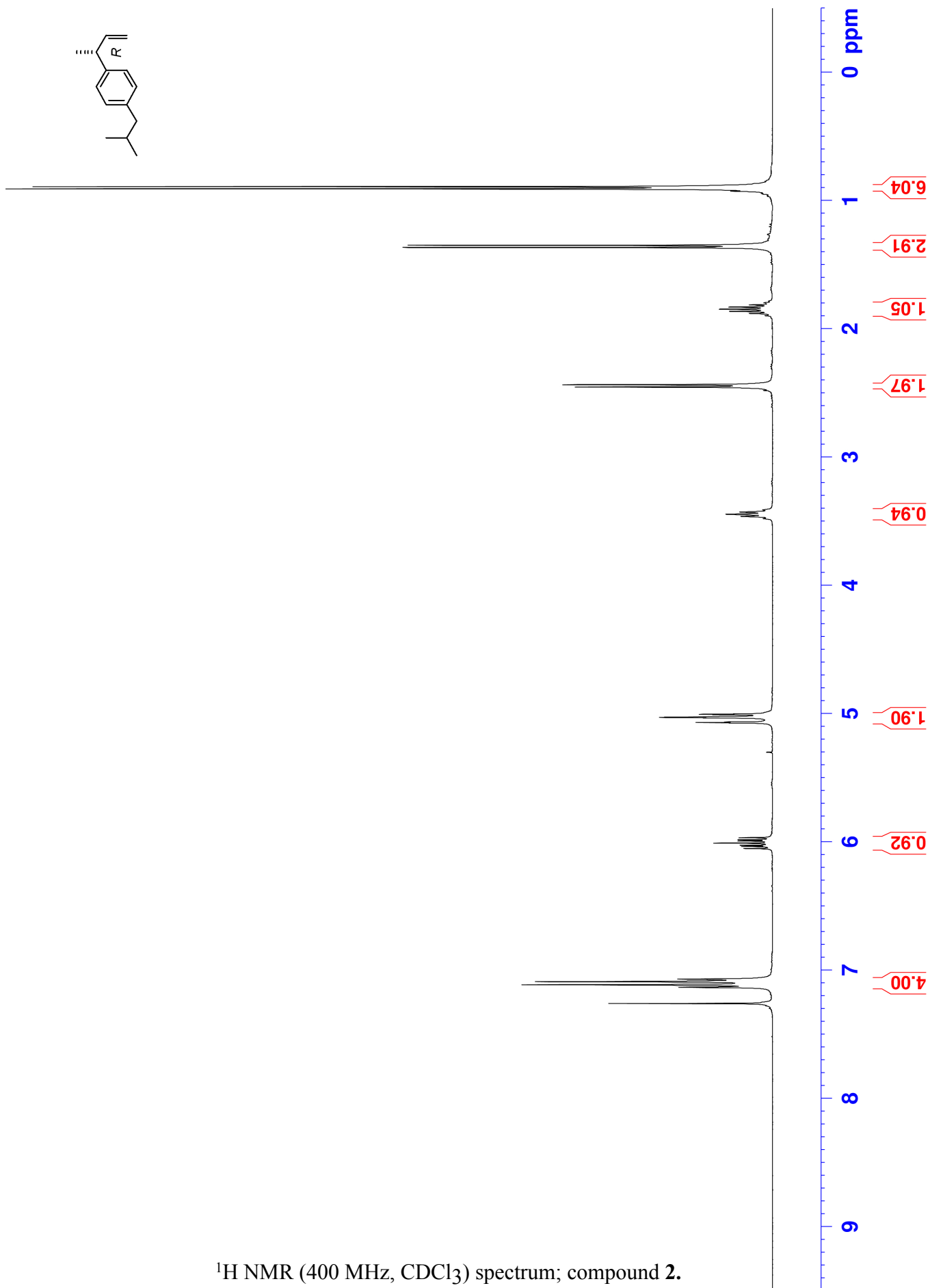
*Department of Chemistry, The Ohio State University, 100 W 18<sup>th</sup> Avenue, Columbus, OH 43210*

**General methods.** Reactions requiring air-sensitive manipulations were conducted under an inert atmosphere of nitrogen using Schlenk techniques or in a Vacuum Atmospheres glovebox. Methylene chloride was distilled from calcium hydride under a dry atmosphere and stored over molecular sieves. Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone ketyl. Olefins were made from Wittig reactions of the corresponding aldehydes with triphenylphosphonium bromide in the presence of *n*-BuLi in THF at reflux or via a palladacycle-mediated Heck reaction<sup>1</sup> of the corresponding aryl bromide with ethylene. Na<sup>+</sup>[[3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>4</sub>B]<sup>-</sup> (NaBARF) and ligand<sup>2,3</sup> were prepared according to the literature. Ethylene (99.5%) was purchased from Matheson Inc., and passed through Drierite® before use. Analytical TLC was performed on precoated (0.25 mm) silica gel 60 F254 plates (olefins stained with KMnO<sub>4</sub>; acids stained with bromocresol green). Flash column chromatography was carried out on silica gel 40. All chiral stationary phase gas chromatographic separations of the 2-arylpropionic acids were achieved via conversion of the acid to the (*L*)-menthyl ester. Enantiomeric excesses of chiral compounds **2**, **3**, **5**, **6**, and **7** were determined by chiral stationary phase gas chromatographic analyses, which were performed with Cyclodex B (25 m x 0.25 mm, 0.12 mm film thickness) capillary GC column. Enantiomeric excesses of chiral compounds **9**, **11**, **13** and **14** were determined by gas chromatographic analyses via the corresponding (*L*)-(-)-menthyl esters, which were performed on a chromatograph equipped with Chirasil-(*S*)-Val on WCOT fused silica (50 m x 0.25 mm, 0.12 mm film thickness) capillary GC column. Enantiomeric excess of compound **4** was determined by HPLC using a Daicel Chiralcel OJ-H column using hexane/isopropanol as solvents where base-line separation was obtained. Optical rotations were recorded the sodium D line in chloroform.

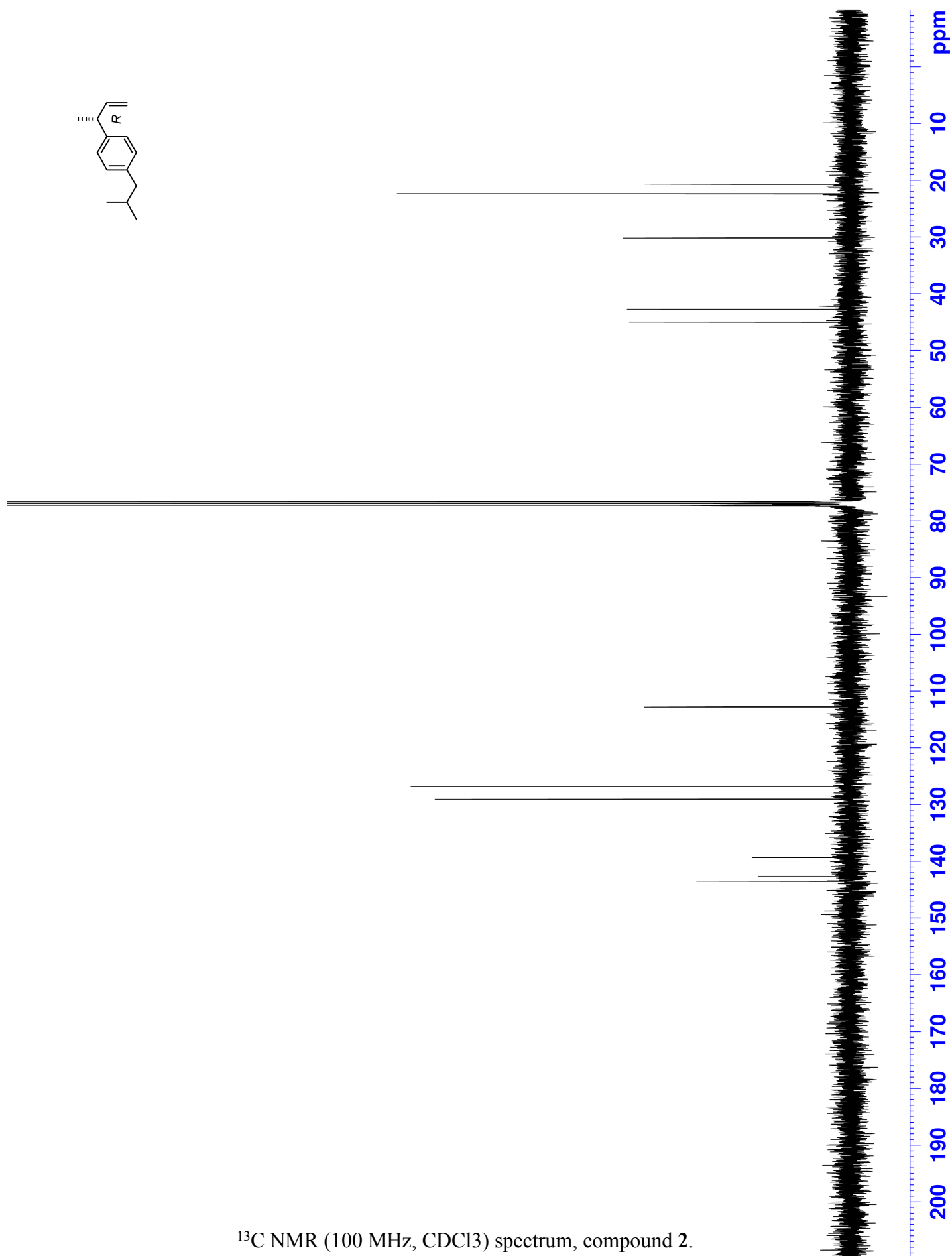
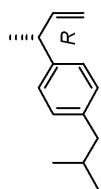
1. Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C-P. *J. Organomet. Chem.* **1999**, 576, 23.
2. Smith, C. R.; Zhang, A.; Mans, D.; RajanBabu, T. V. *Org. Synth.* **2008**, 85, 248.
3. (a) Kobayashi, H.; Sonoda, A.; Iwamoto, H.; Yoshimura, M. *Chem. Lett.* **1981**, 10, 579. (b) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics*, **1992**, 11, 3920-3922.

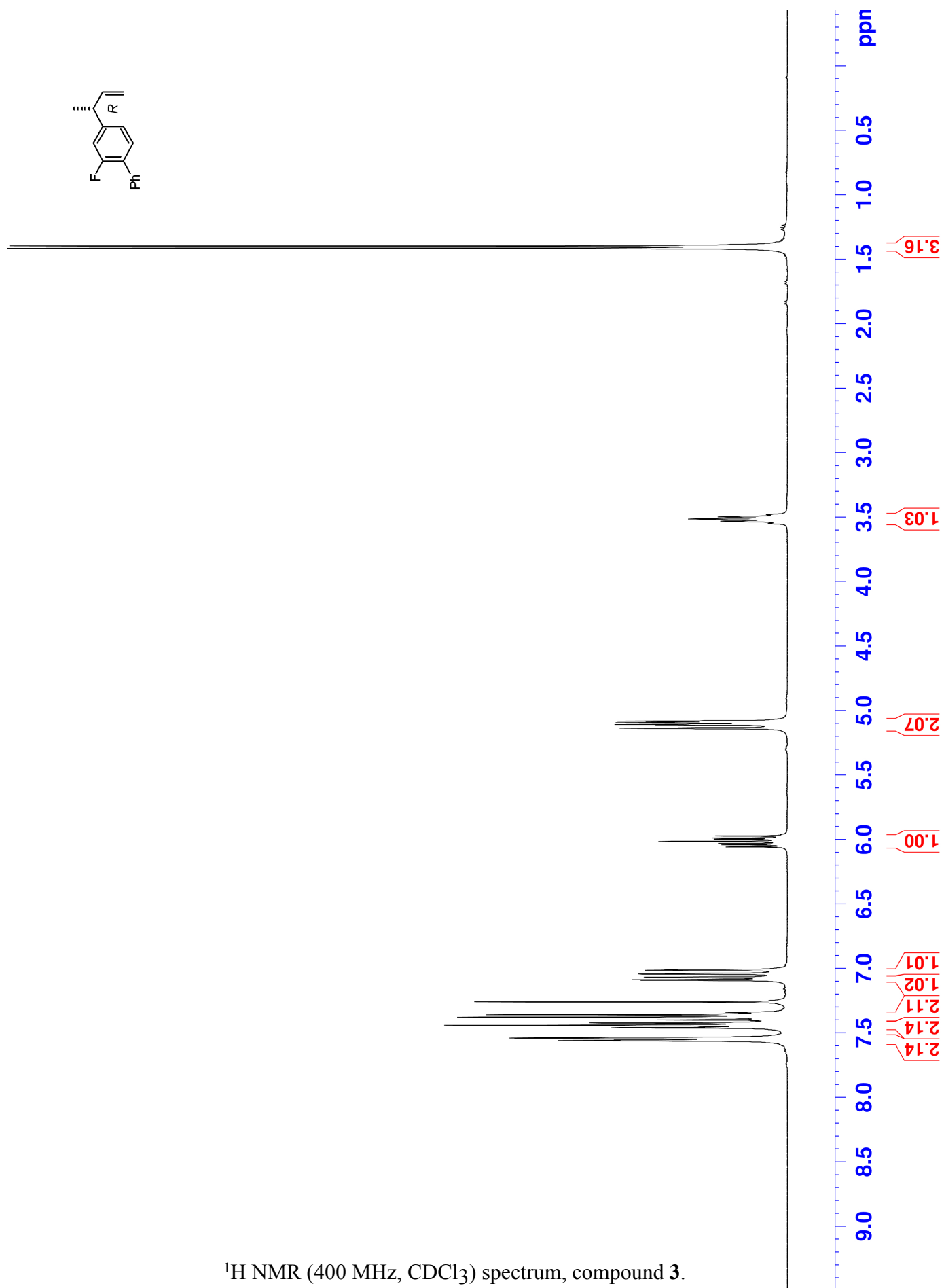
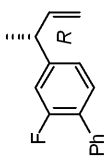
## **$^1\text{H}$ and $^{13}\text{C}$ NMR Spectra and Chromatograms of Key Compounds**

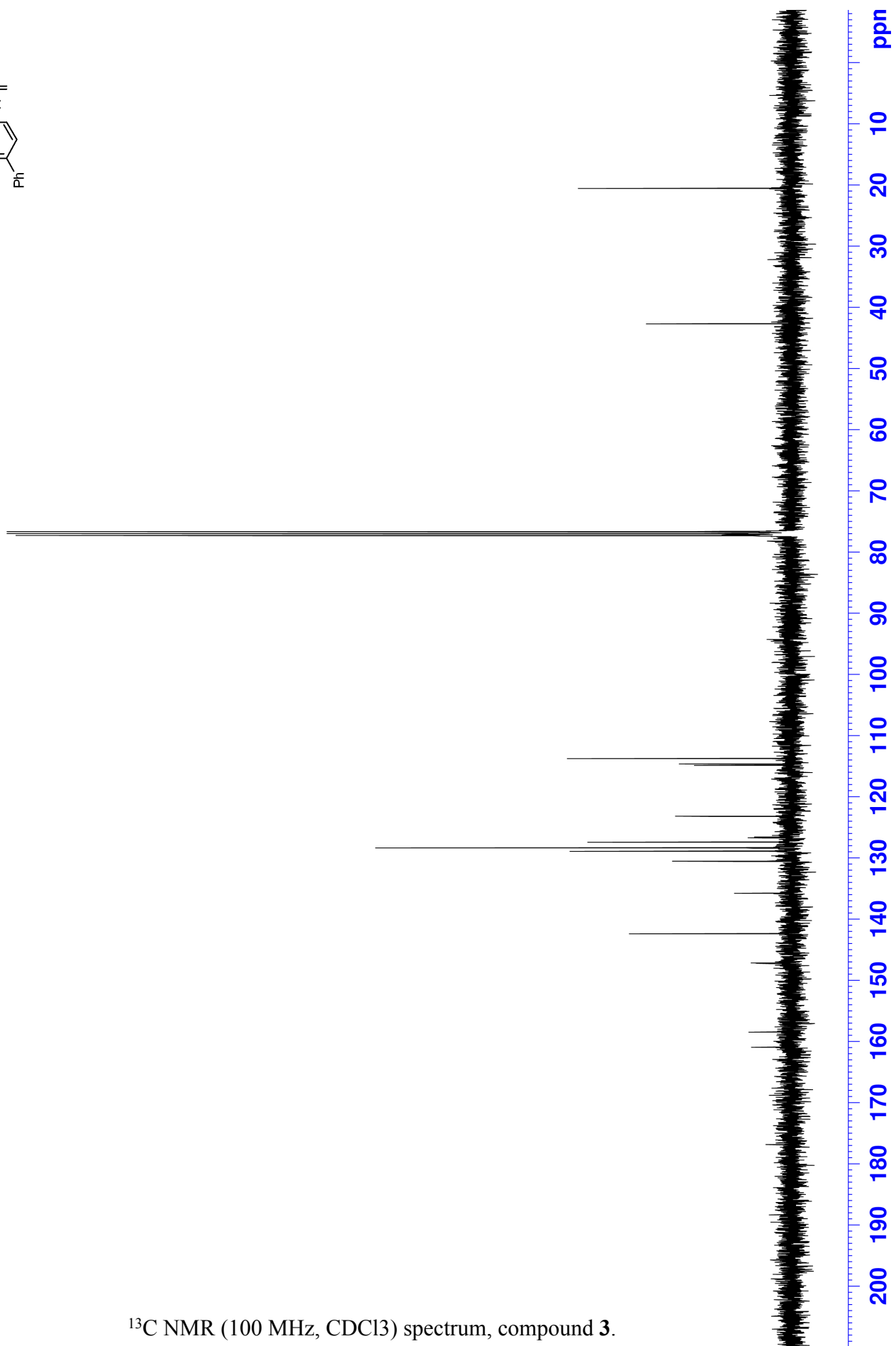
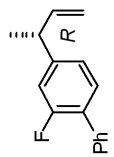
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>2</b>	S3-S4
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>3</b>	S5-S6
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>4</b>	S7-S8
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>5</b>	S9-S10
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>6</b>	S11-S12
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>7</b>	S13-S14
Gas chromatogram of racemic and enriched <b>7</b>	S15-S16
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>9</b>	S17-S18
Gas chromatogram of racemic and enriched <i>L</i> -menthyl esters of <b>9</b>	S19-S20
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>11</b>	S21-S22
Gas chromatogram of racemic and enriched <i>L</i> -menthyl esters of <b>11</b>	S23-S24
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>12</b>	S25-S26
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>13</b>	S27-S28
Gas chromatogram of racemic and enriched <i>L</i> -menthyl esters of <b>13</b>	S29-S30
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>14</b>	S31-S32
Gas chromatogram of racemic and enriched <i>L</i> -menthyl esters of <b>14</b>	S33-S34
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>17</b>	S35-S36
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>15</b>	S37-S38
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>18</b>	S39-S40
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>20</b>	S41-S42
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>21</b>	S43-S44
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>19</b>	S45-S46
$^1\text{H}$ NMR, $^{13}\text{C}$ NMR of <b>22</b>	S47-S48
Chromatogram of racemic and enriched <b>22</b>	S49-S50



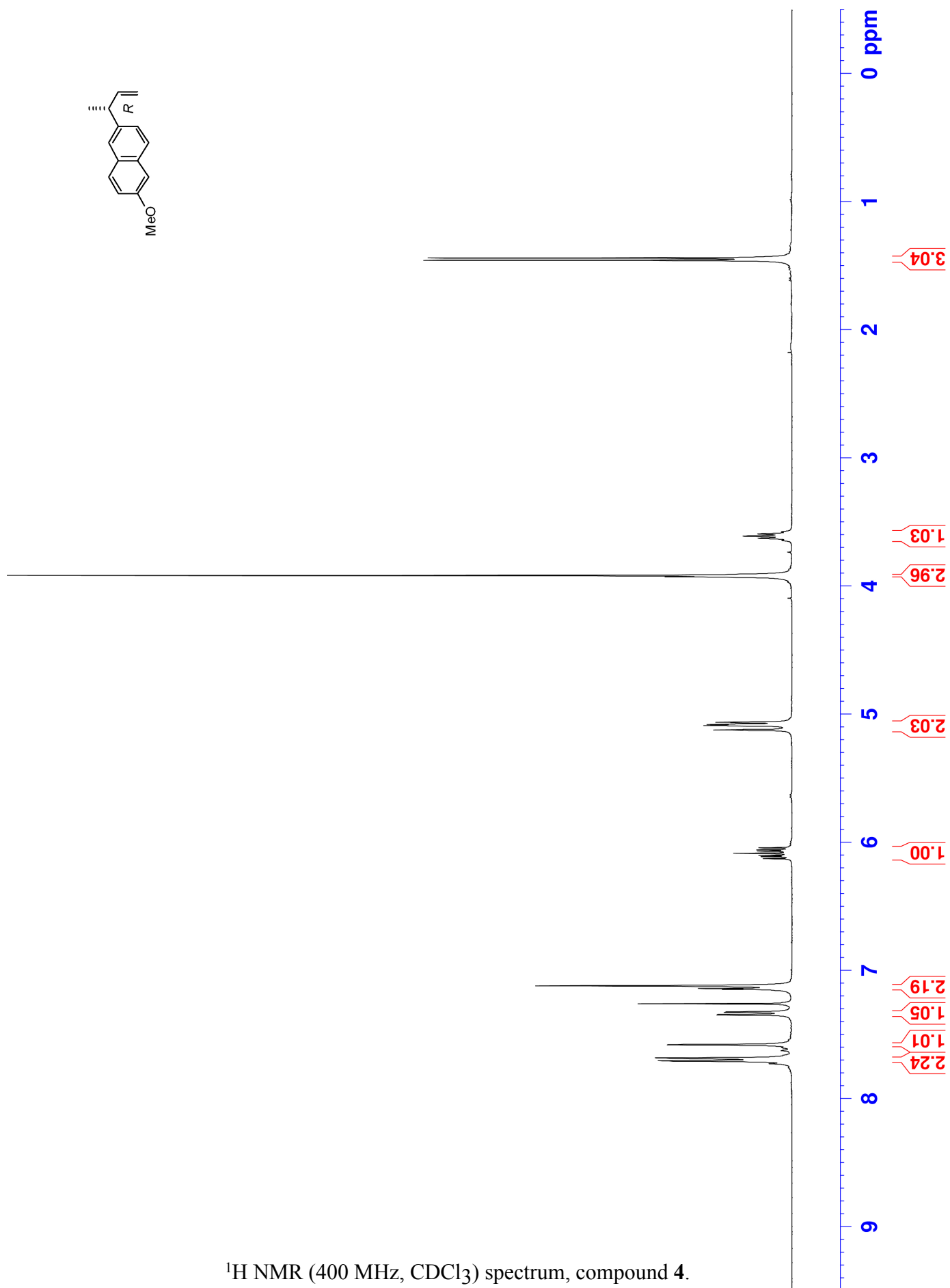
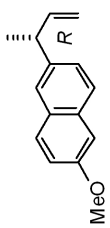
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum; compound 2.



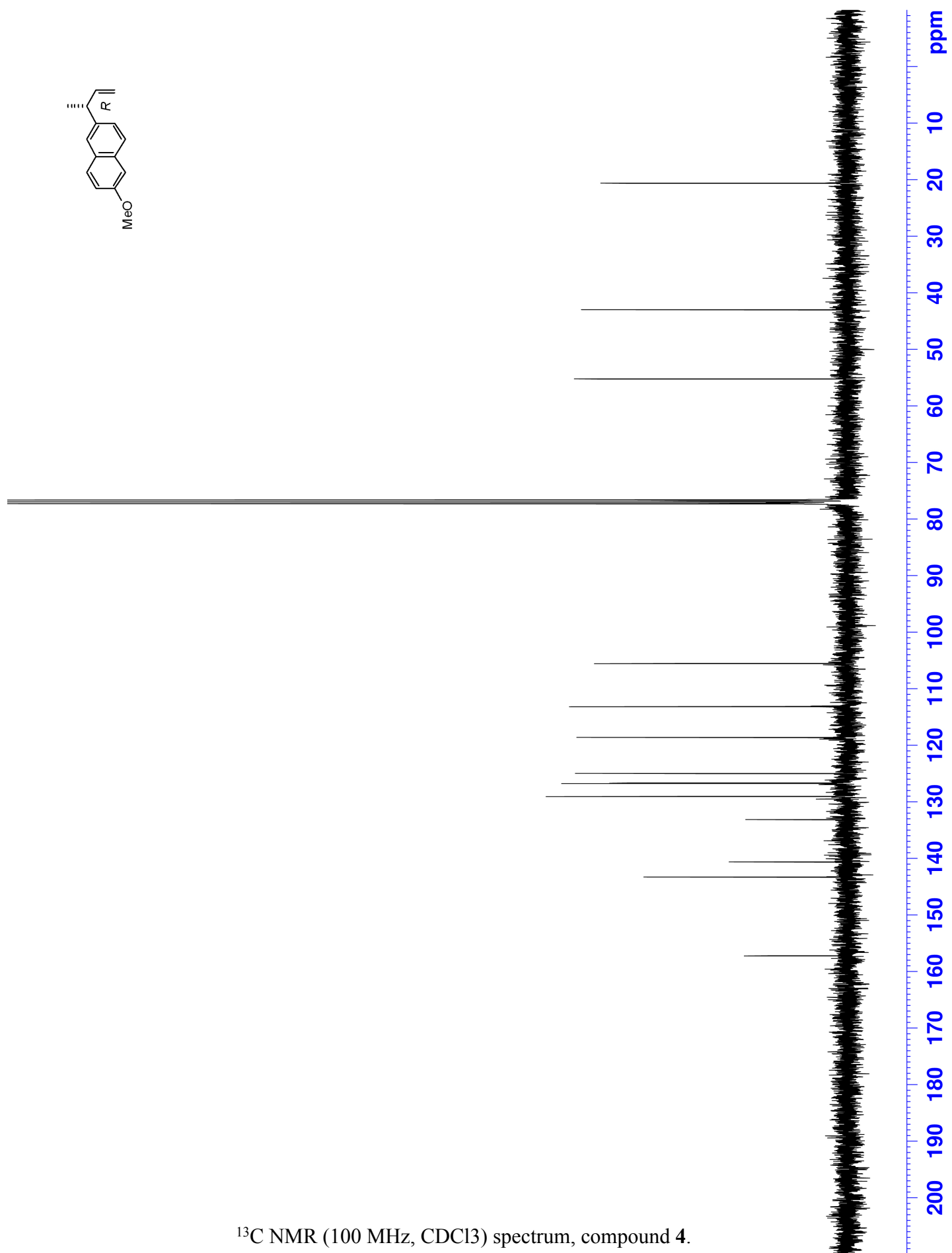
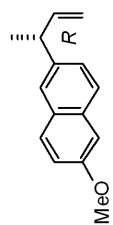




$^{13}\text{C}$  NMR (100 MHz, CDCl<sub>3</sub>) spectrum, compound 3.

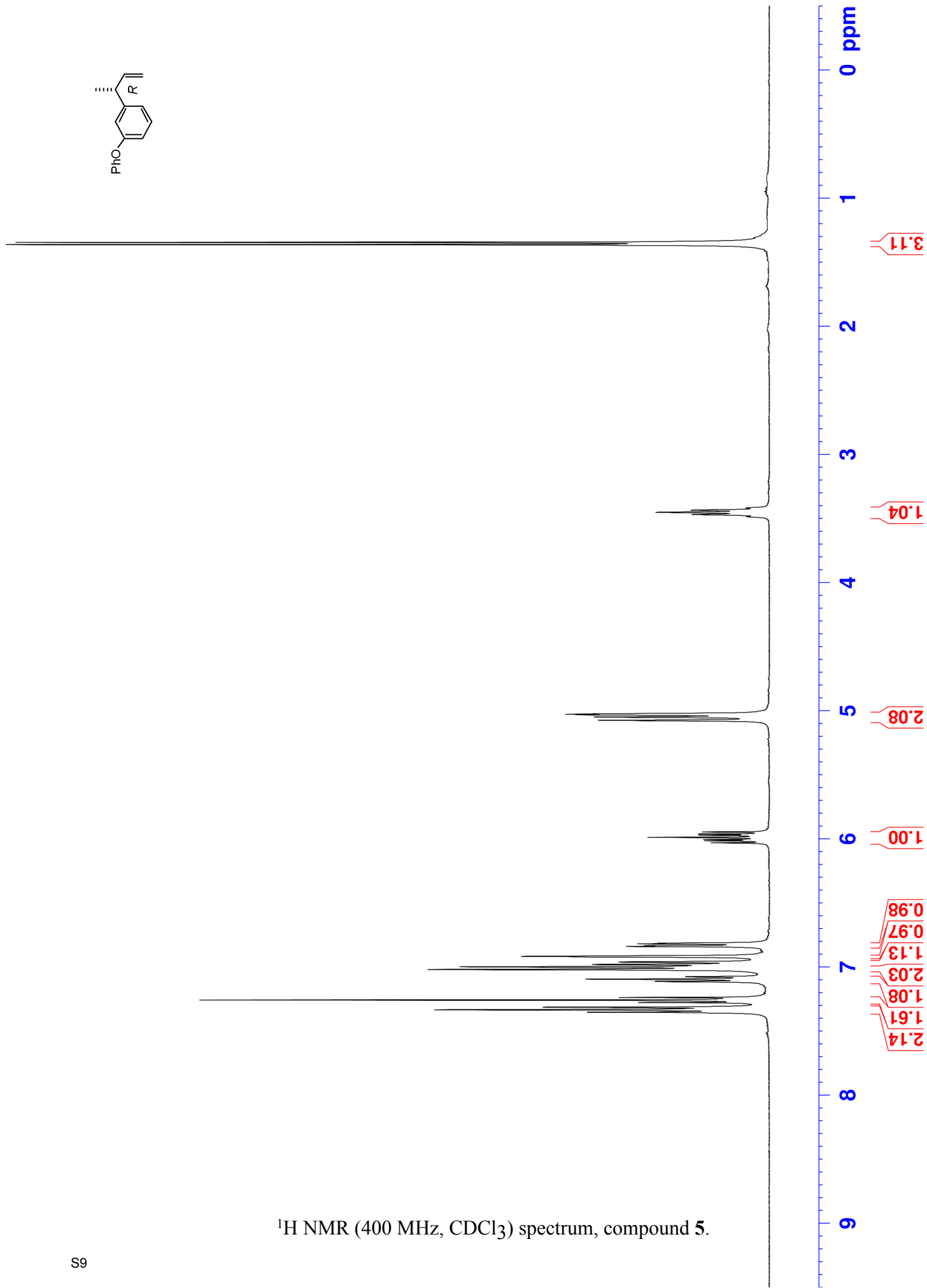
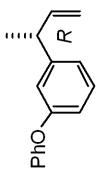


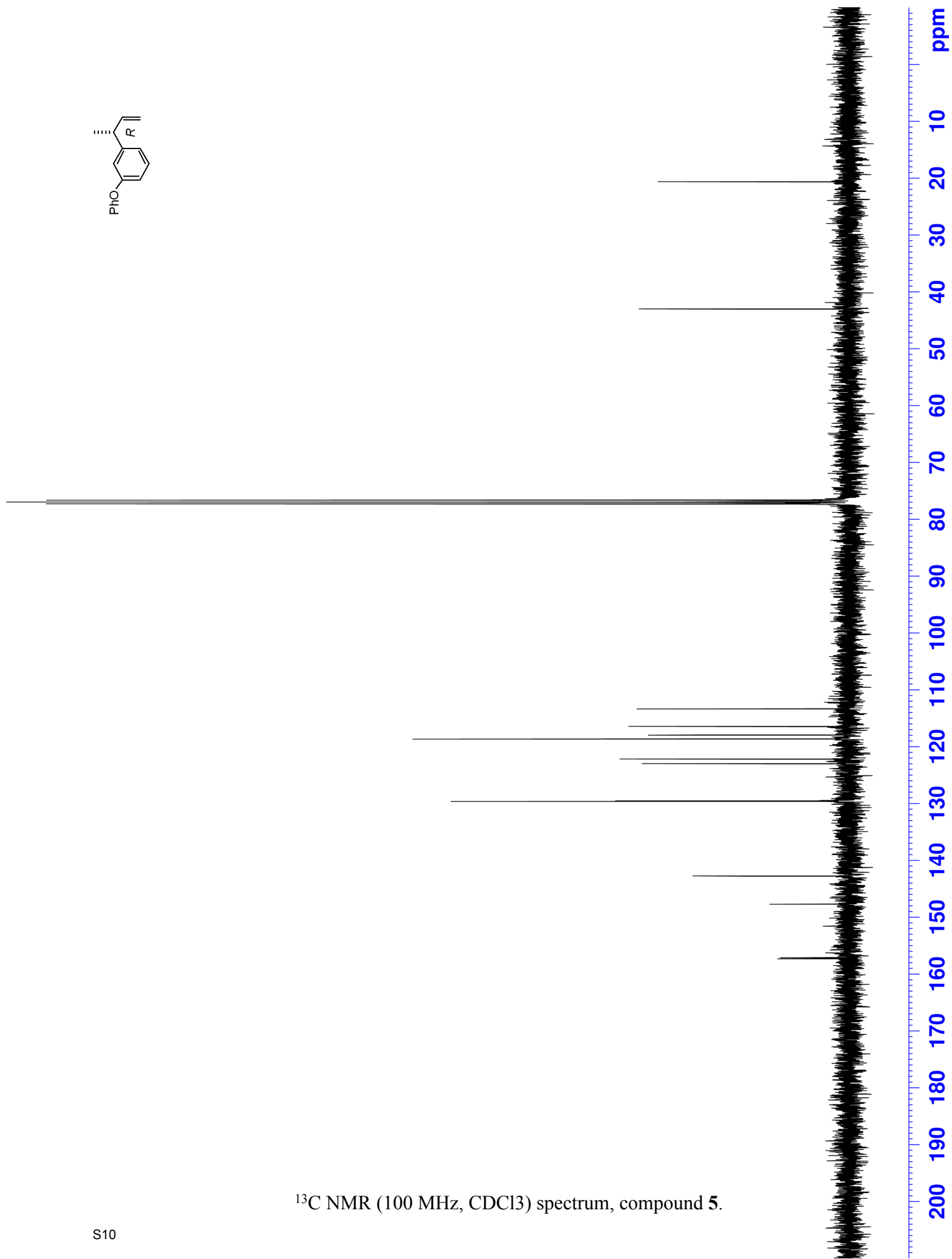
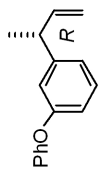
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum, compound 4.



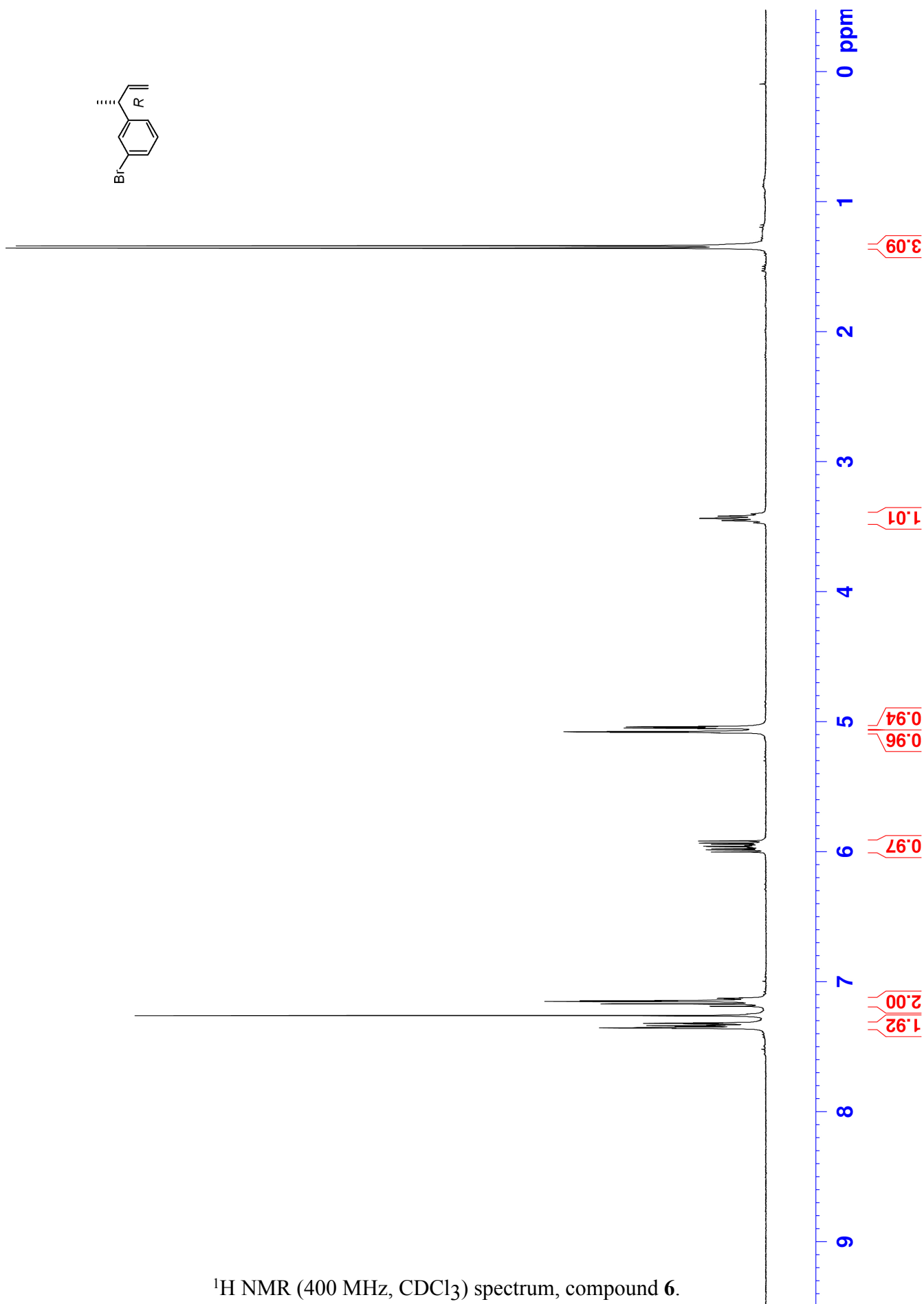
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum, compound 4.



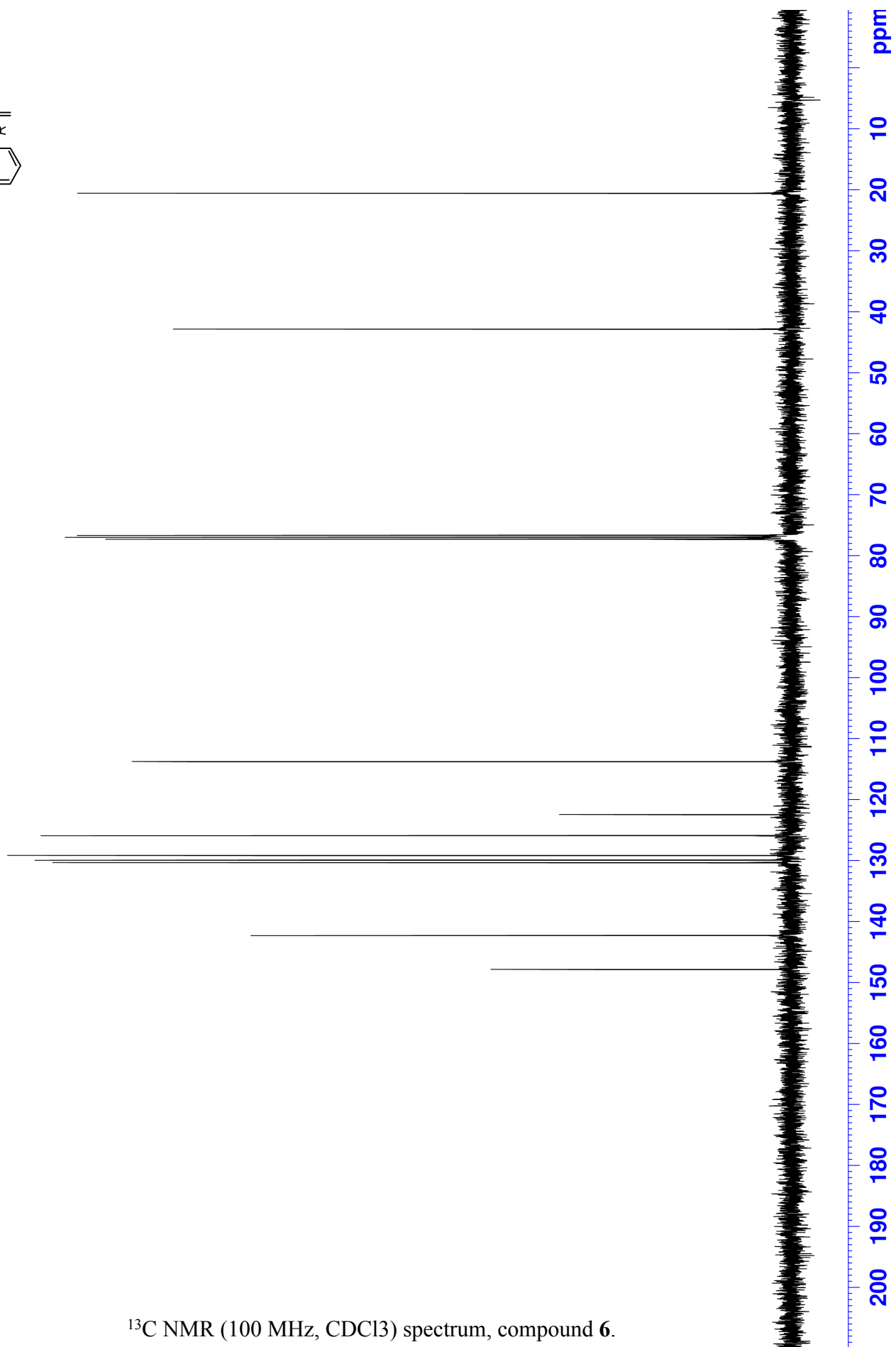
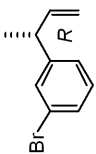




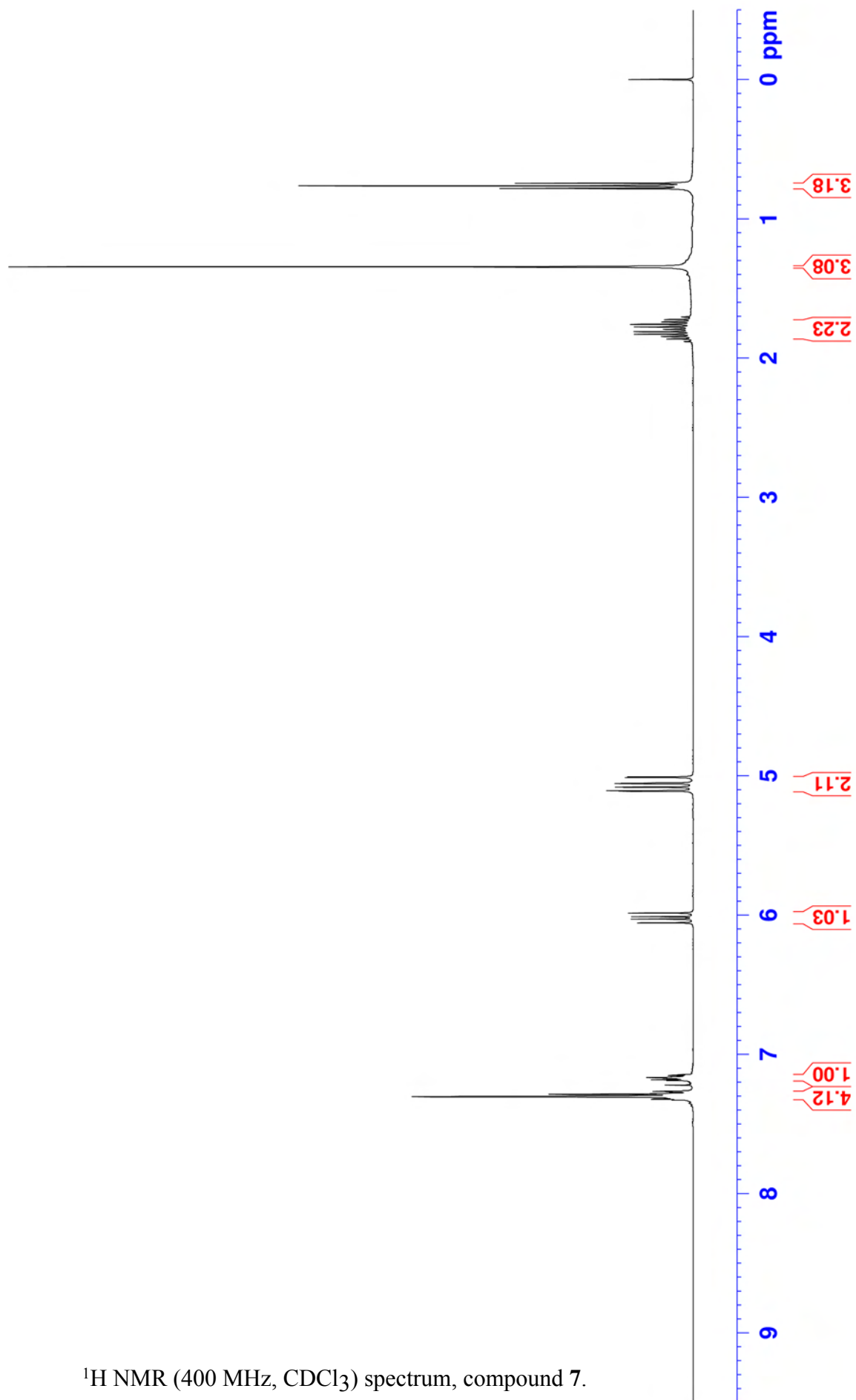
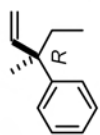
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum, compound 5.

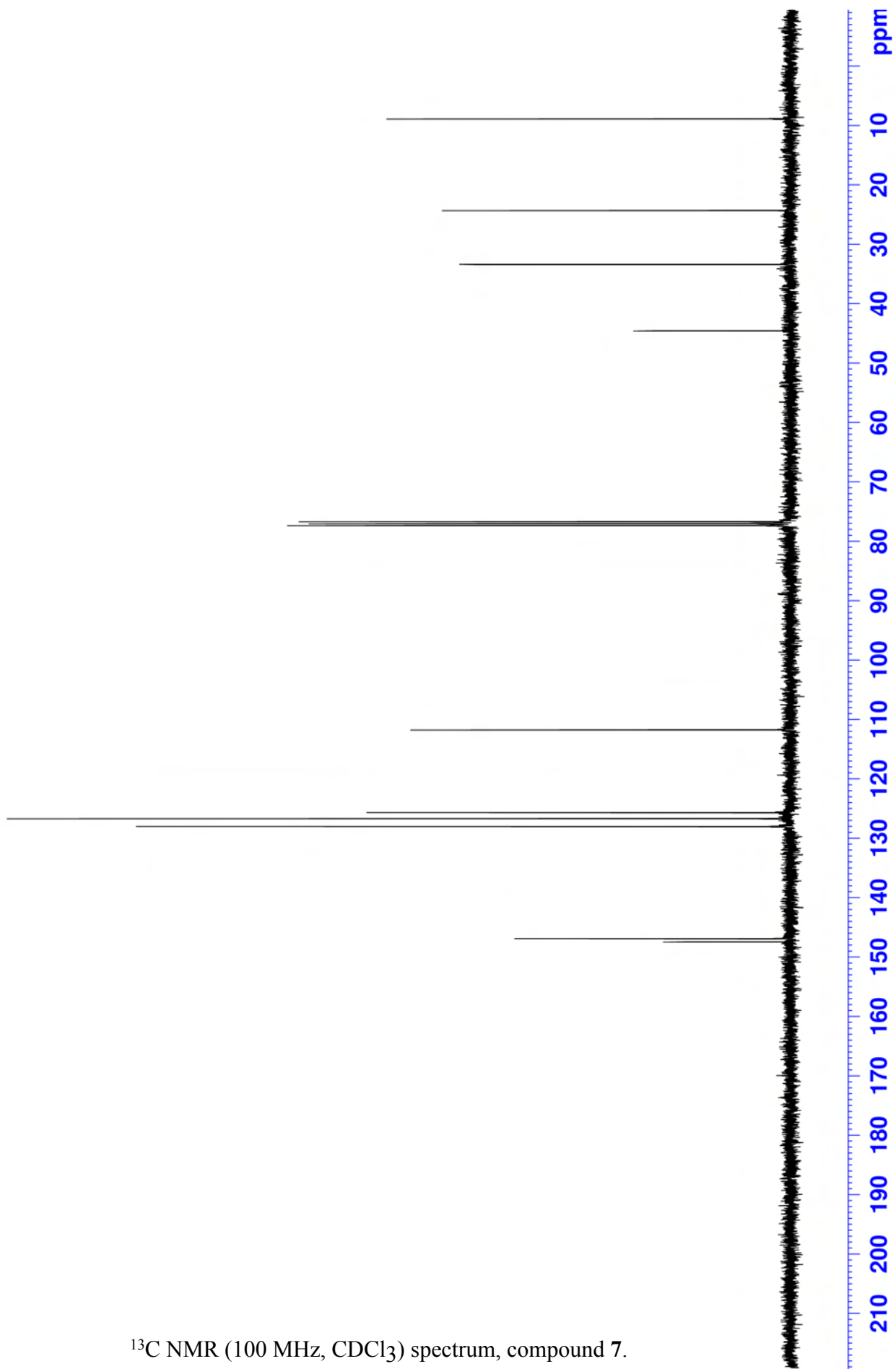
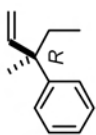


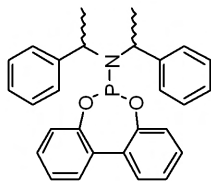
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum, compound 6.



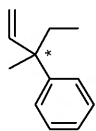
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum, compound 6.



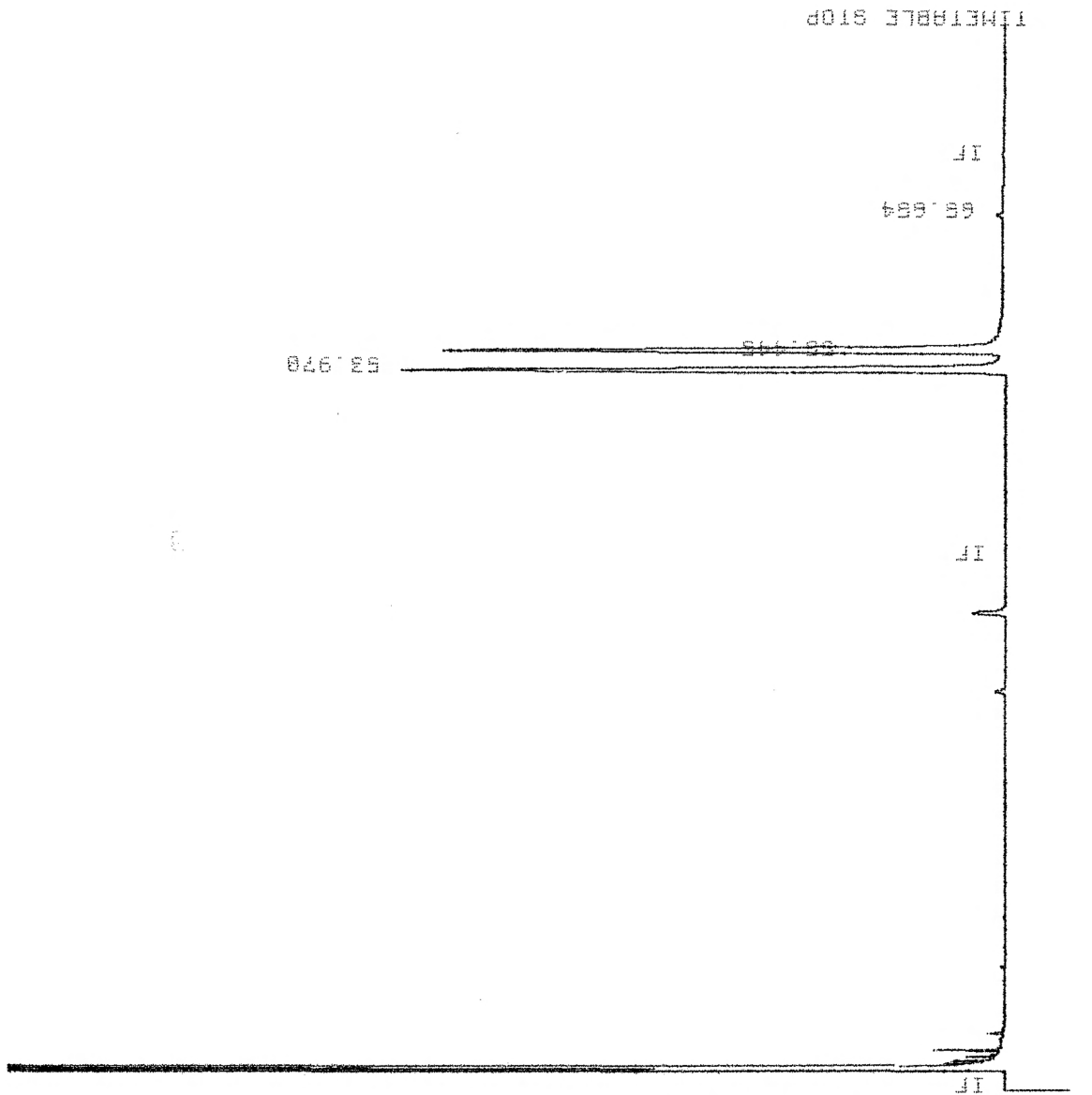




R<sub>1</sub>R<sub>2</sub> & S<sub>1</sub>S<sub>2</sub> (rac)



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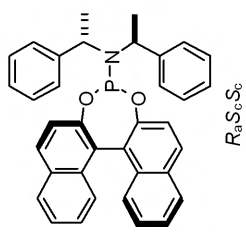
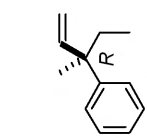


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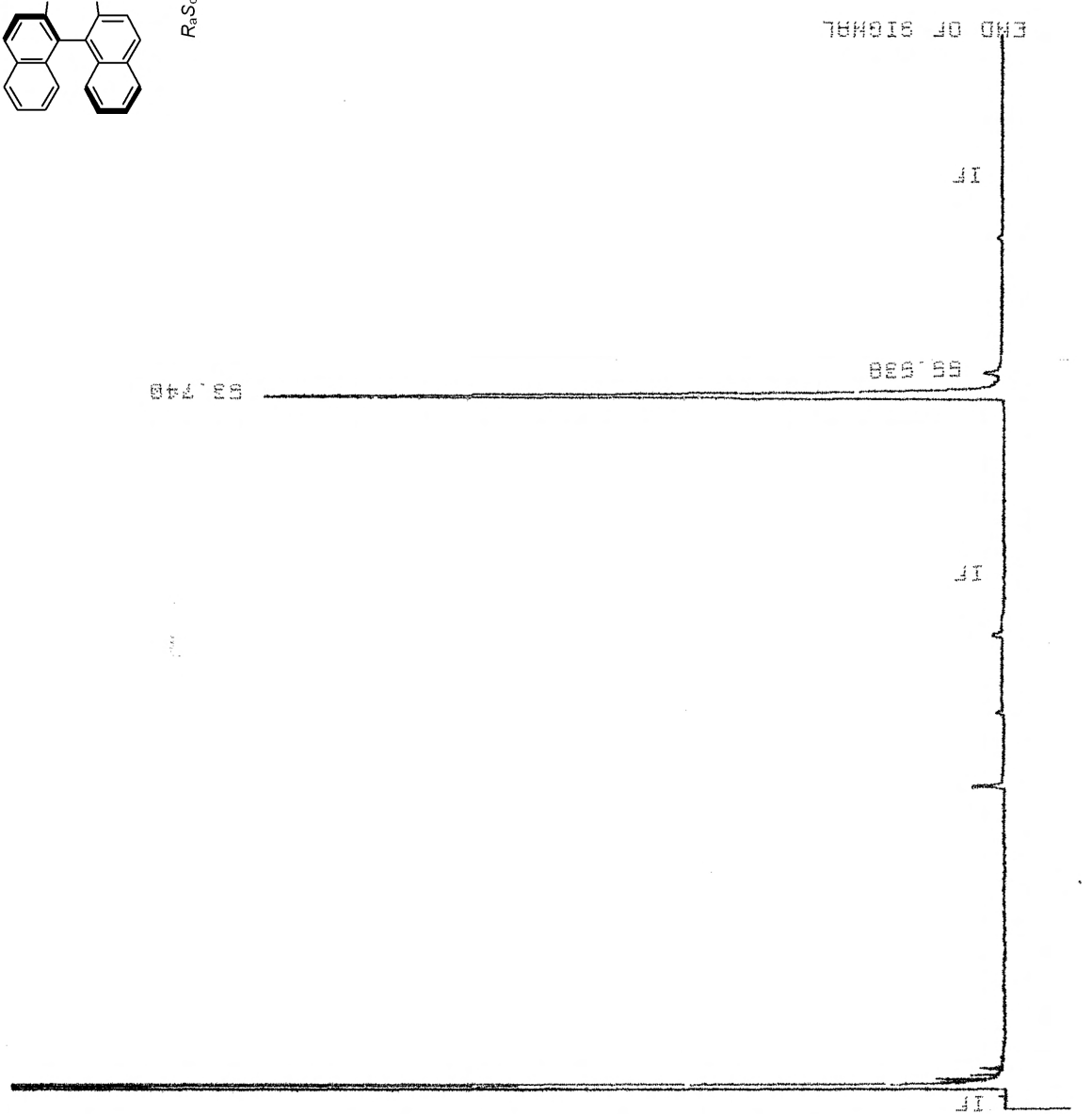
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Chiral GC (racemic mixture): 40 min at 70°C,  
 5°C/min, 10 min at 90°C, compound 7.

\* BR REL 1000 @  
 \* LIST: LIST  
 PEAK CHIRALITY: 11



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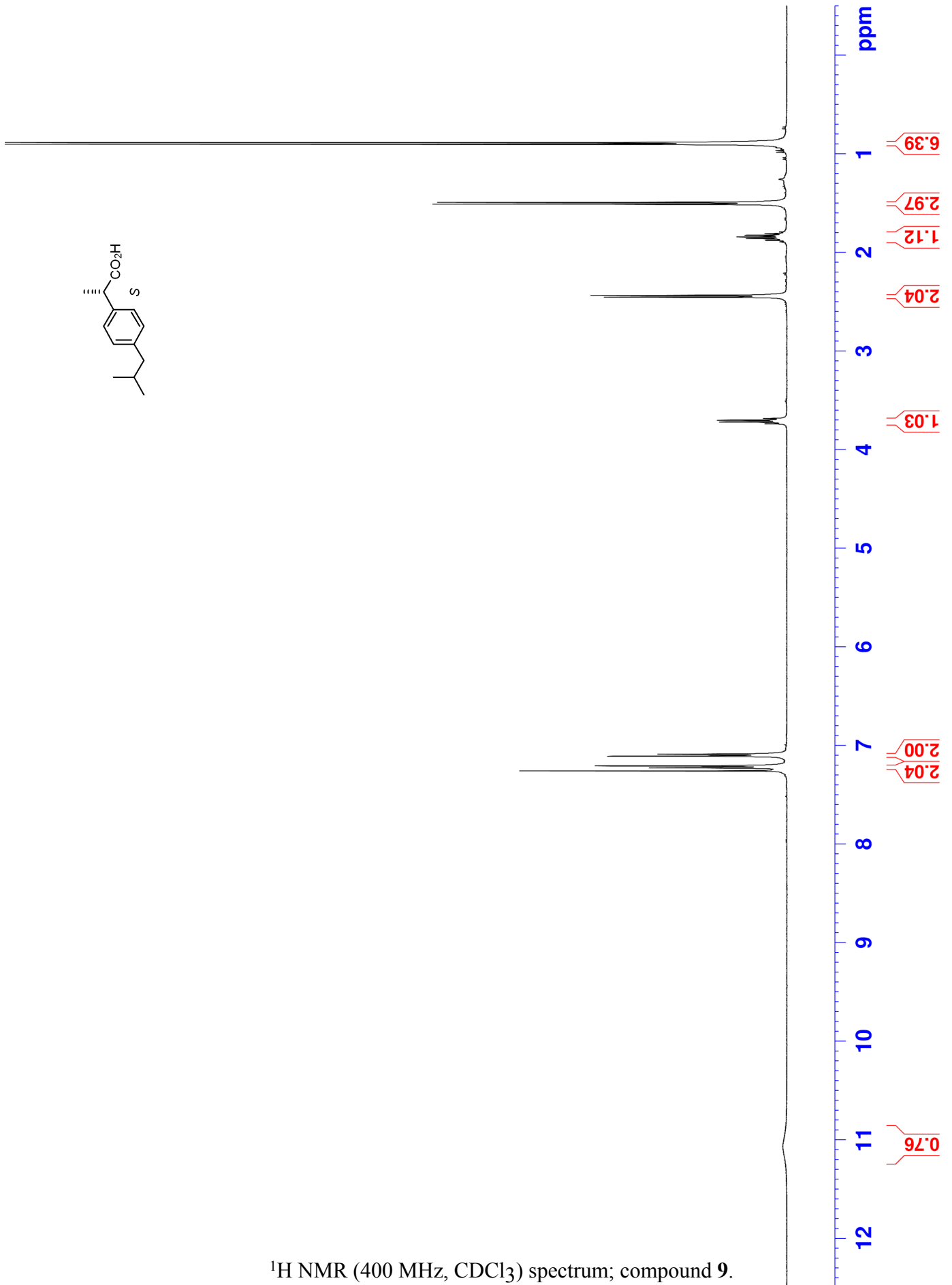
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 +  
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 +

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 PK WD = 0.10

Chiral GC: 40 min at 70°C, 5°C/min, 10 min at 90°C,  
 compound 7.

\* LIST: LIST  
 PEAK CAPACITY: 1164





<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum; compound 9.

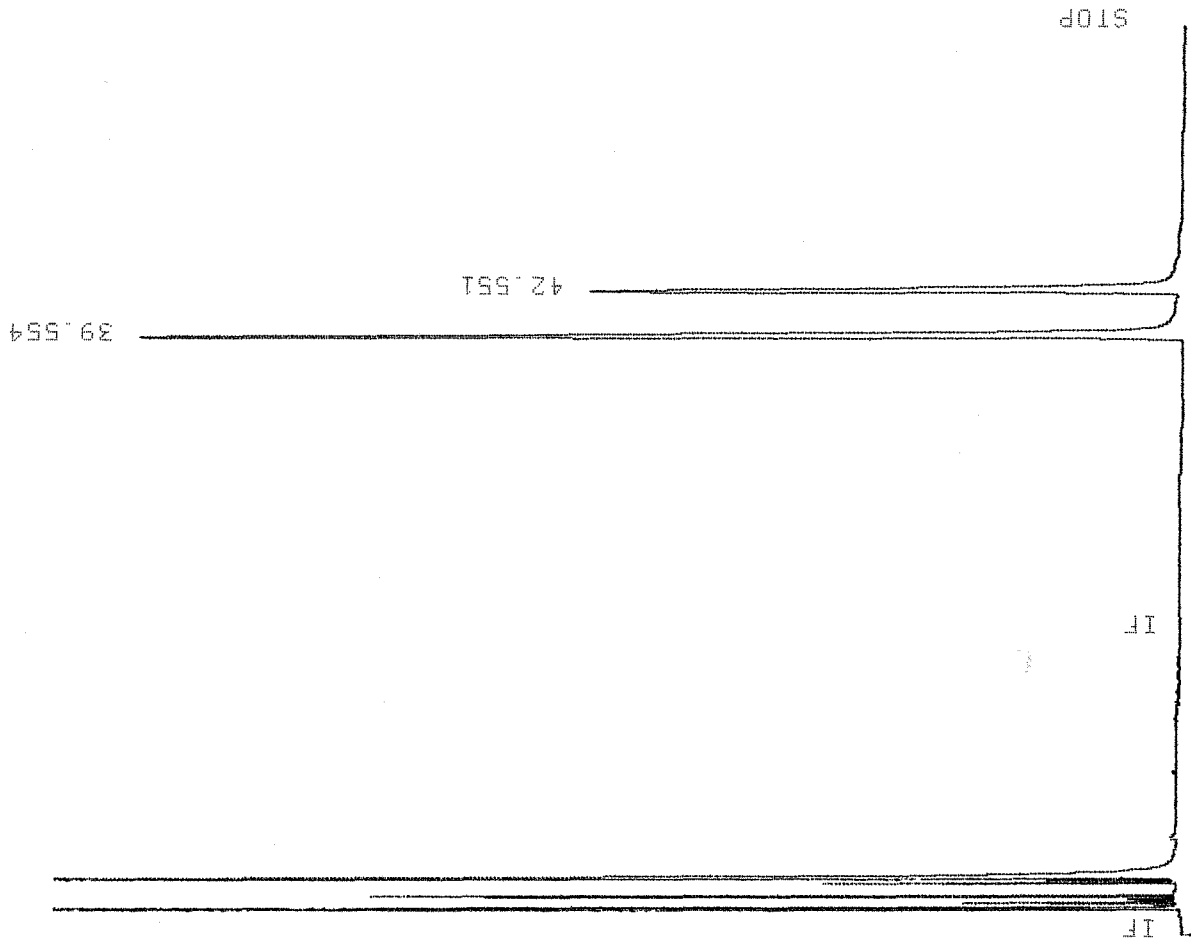
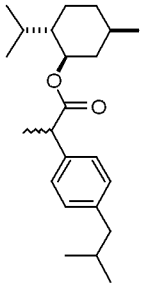


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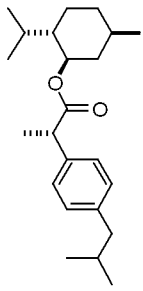
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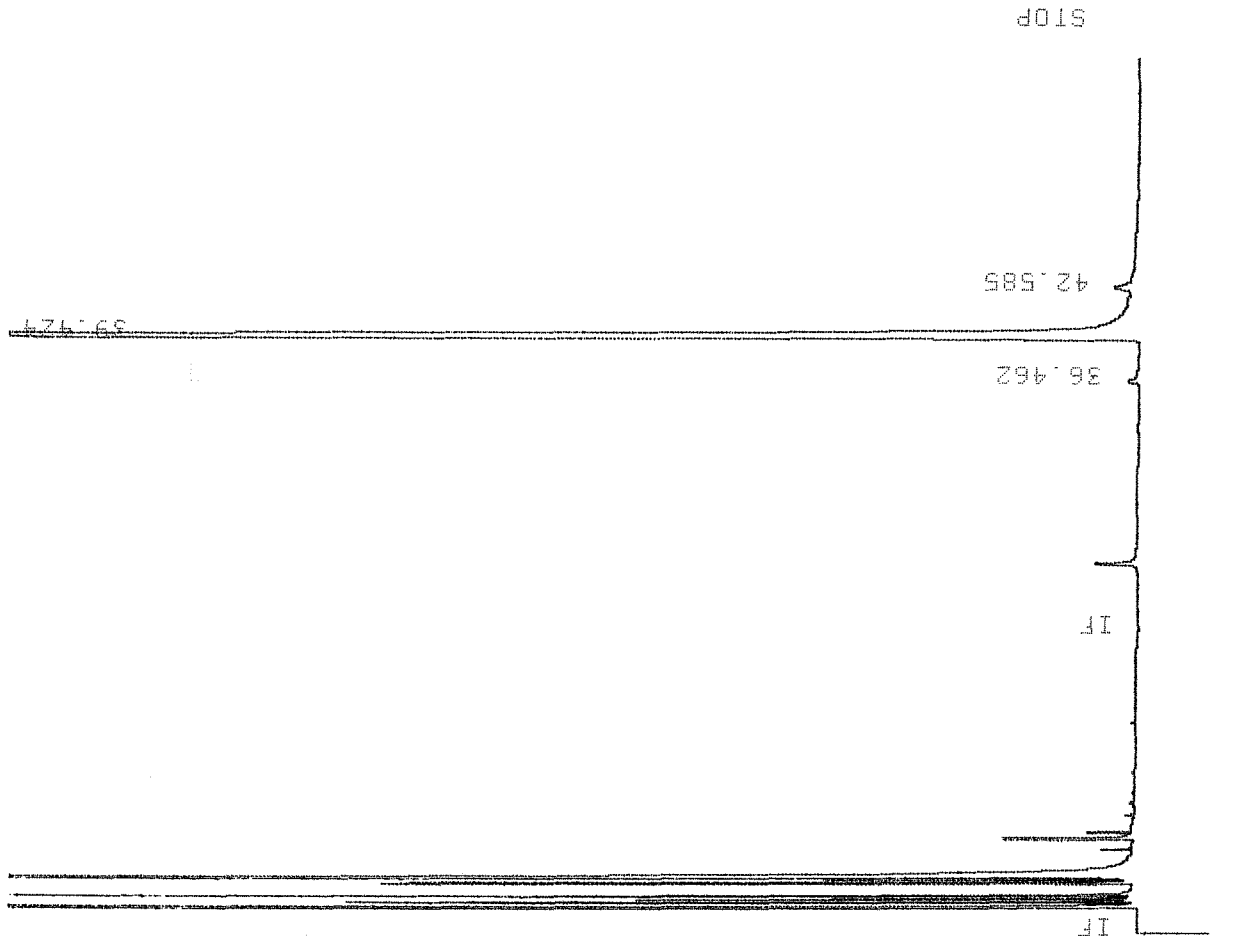


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Chiral GC (Cyclodex-β): 60 min at 160°C;  
L-menthyl ester of compound 9 (enriched).

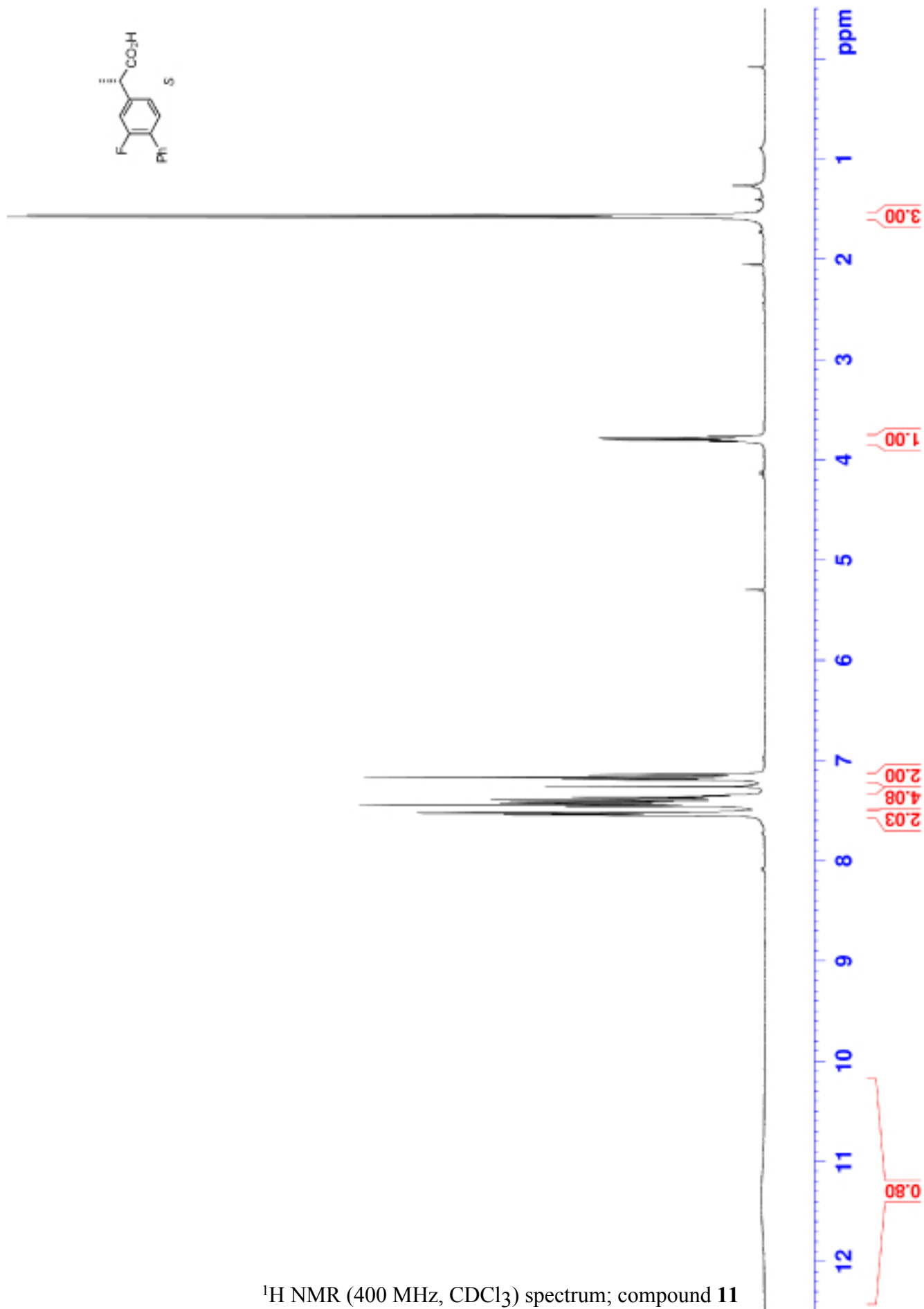
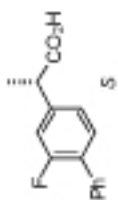


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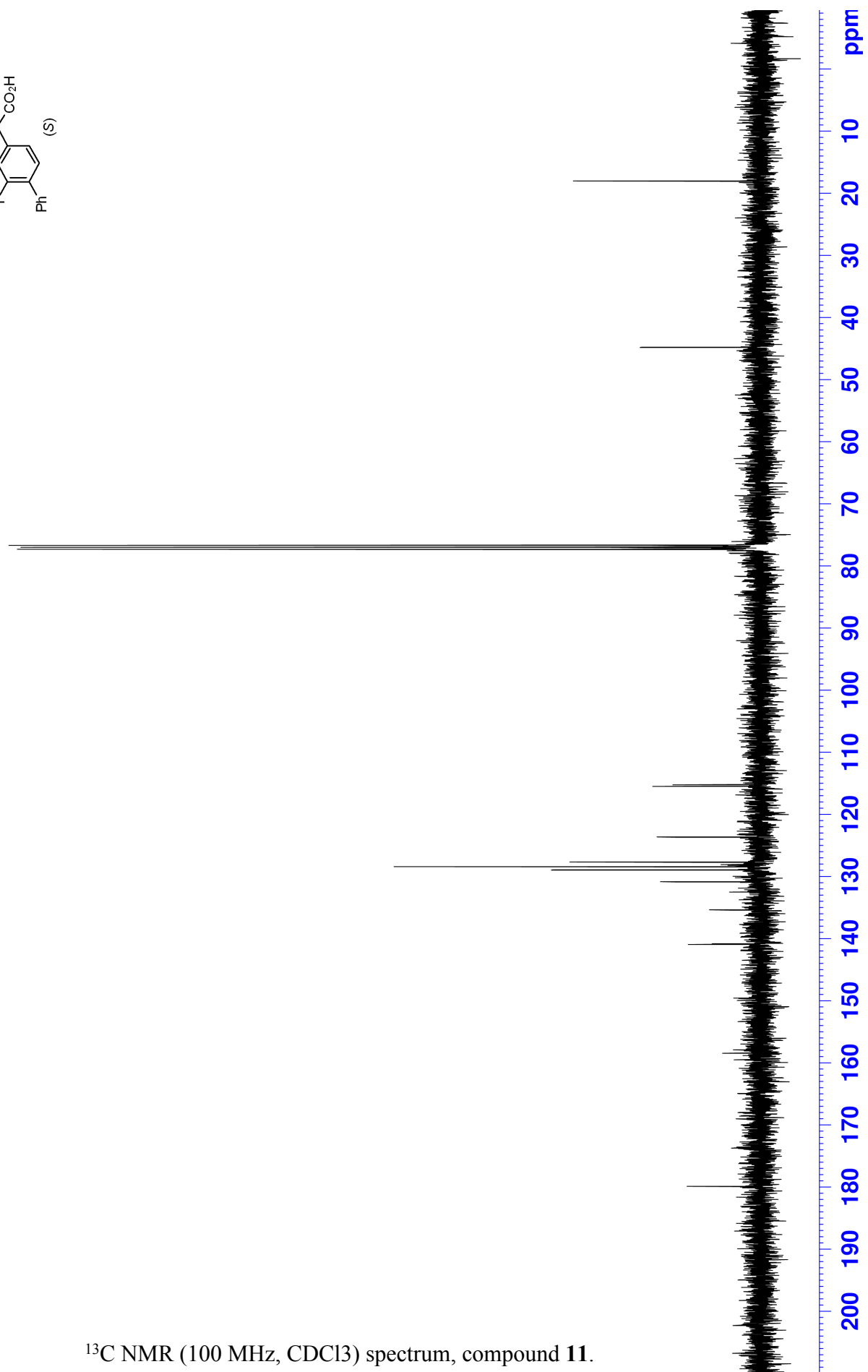
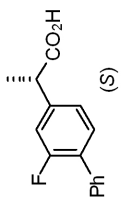


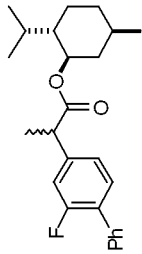
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Chiral GC (Cyclodex- $\beta$ ): 60 min at 160°C;  
 L-menthyl ester of compound **9** (from **2**).



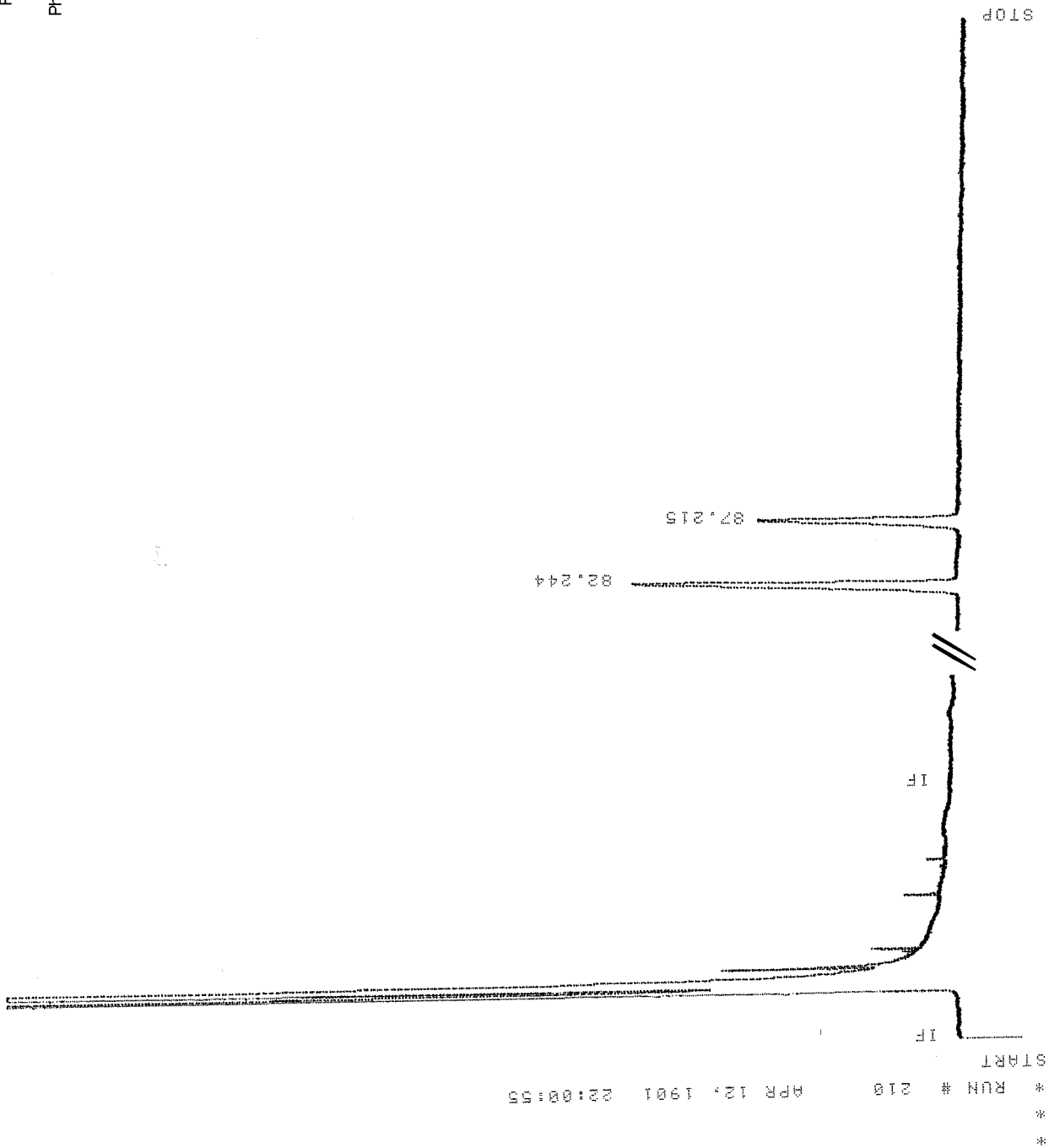
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum; compound 11





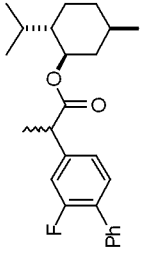
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Chiral GC (Chirasil-S-Val): 120 min at 200°C;  
 L-menthyl ester of compound 11 (enriched).

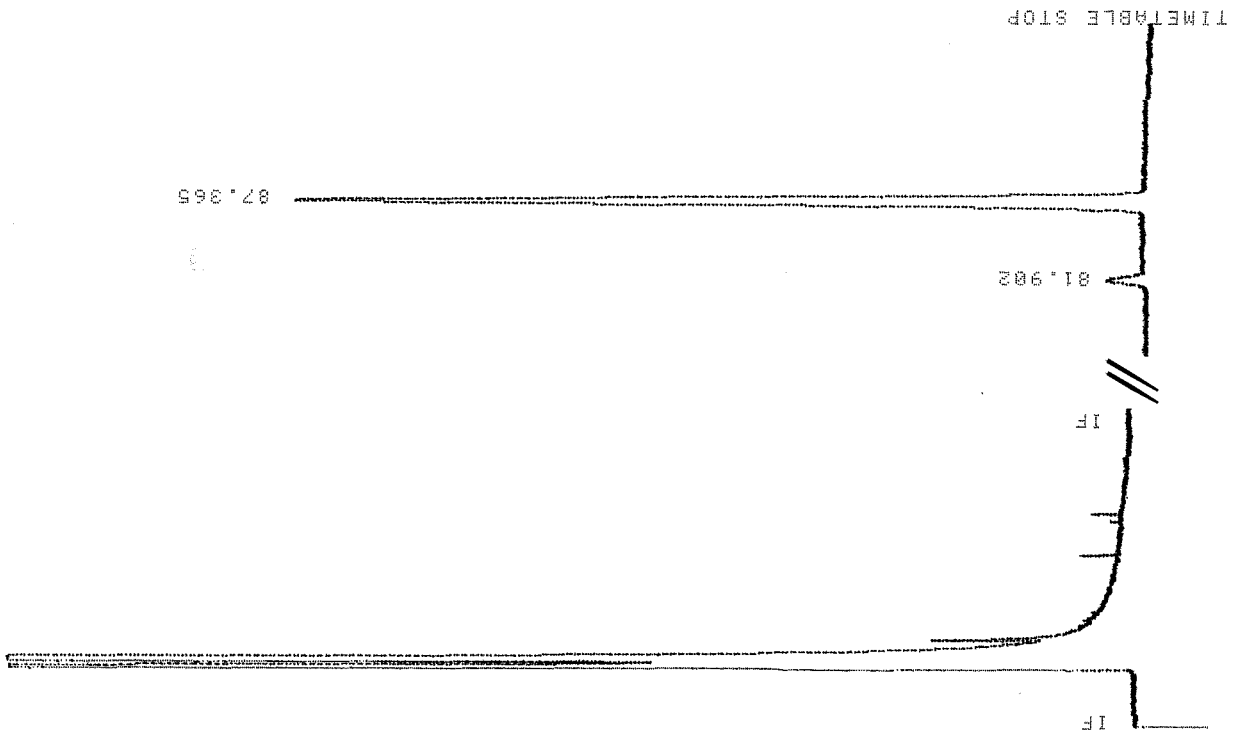


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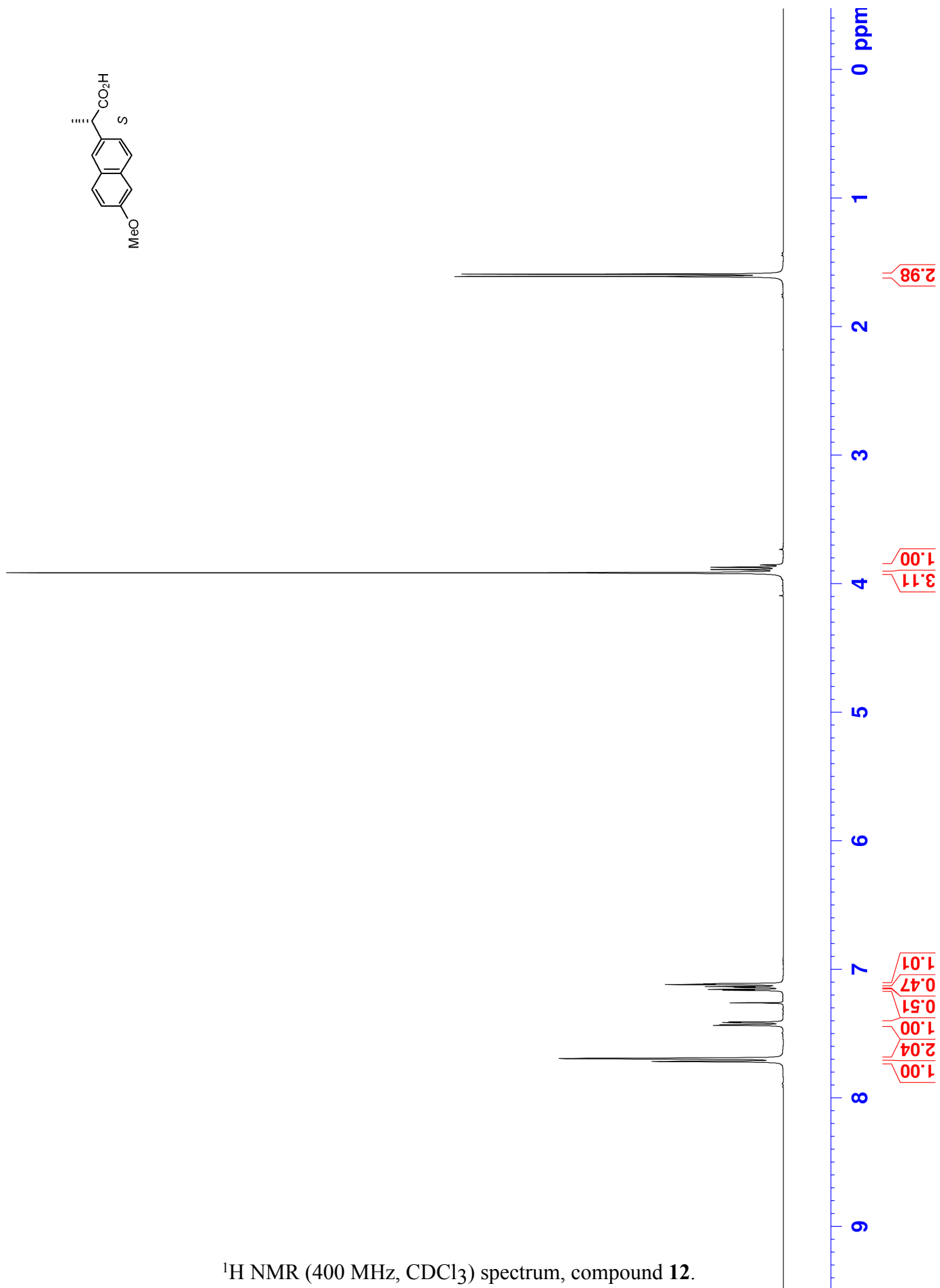
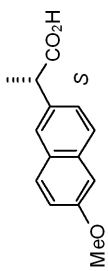


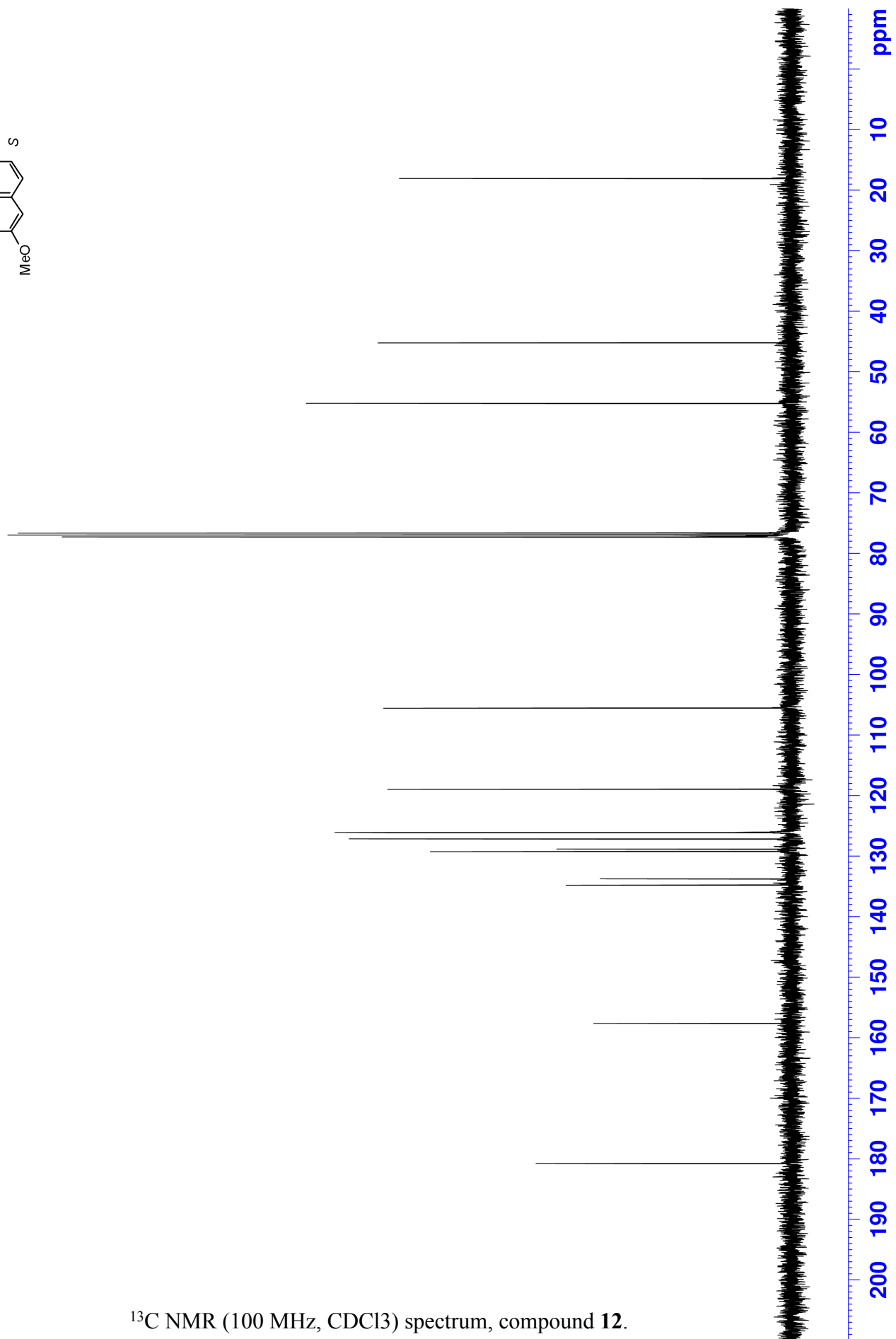
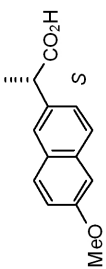
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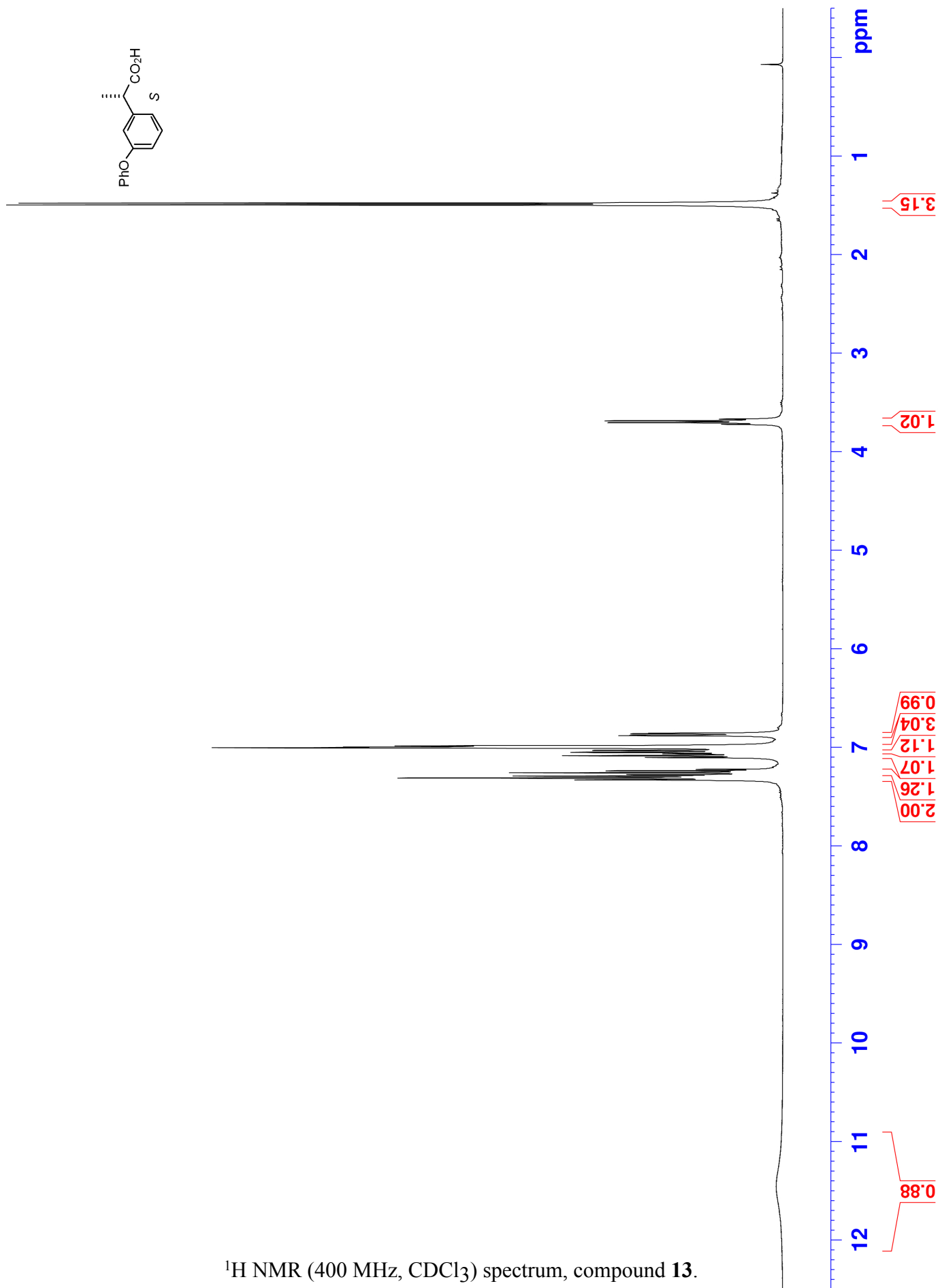
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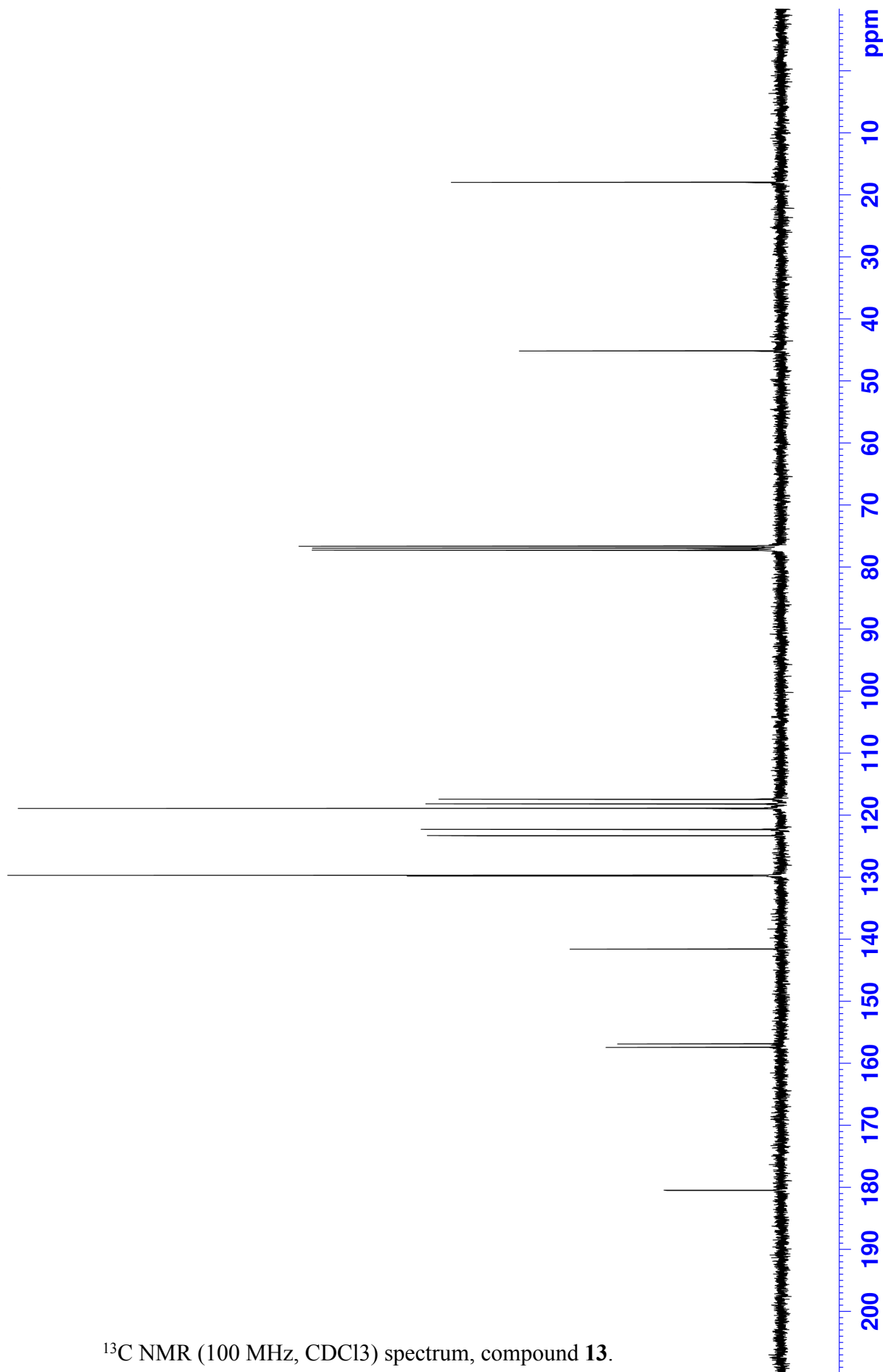
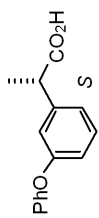
Chiral GC (Chirasil-S-Val): 120 min at 200°C;  
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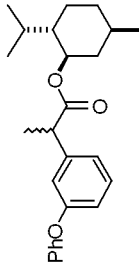




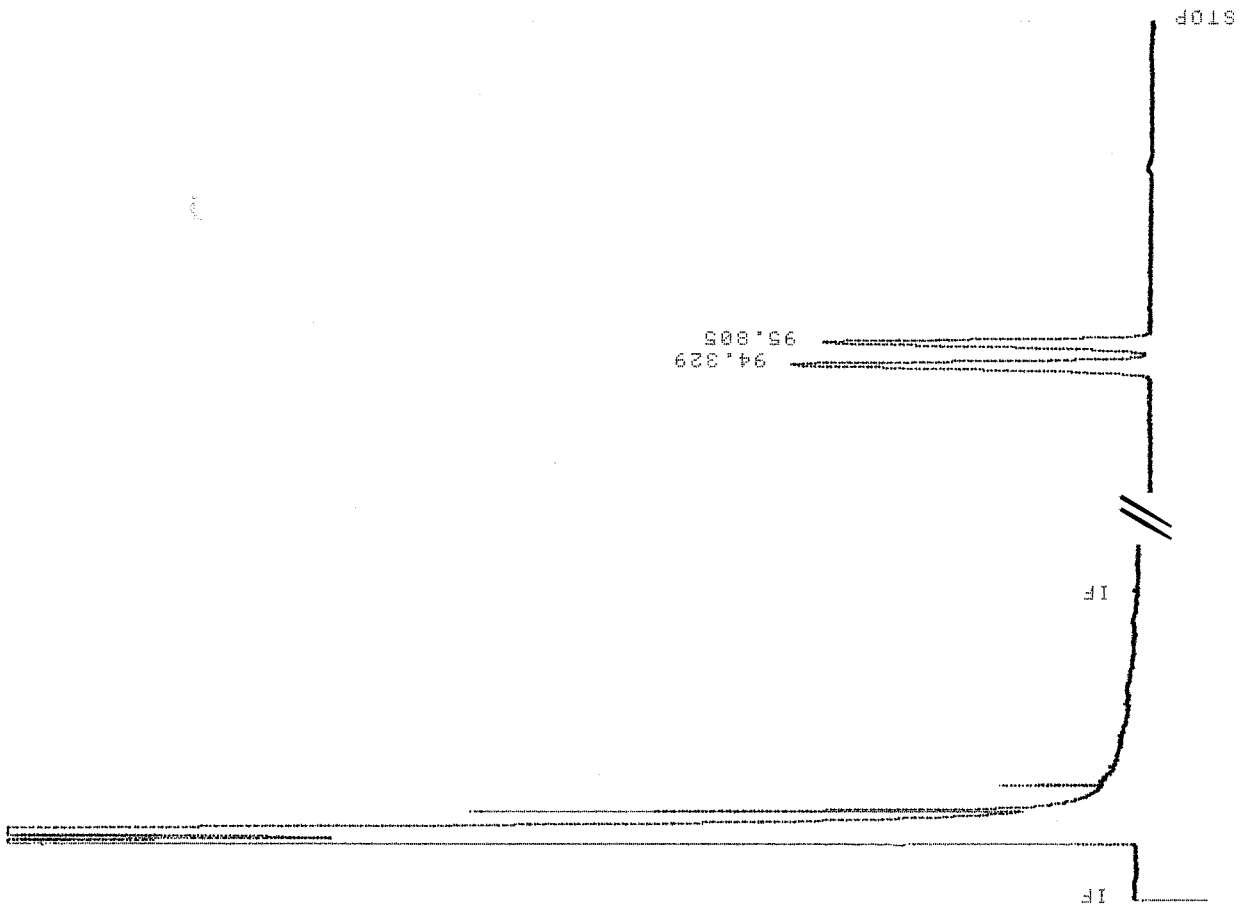




<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum, compound 13.

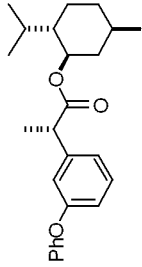


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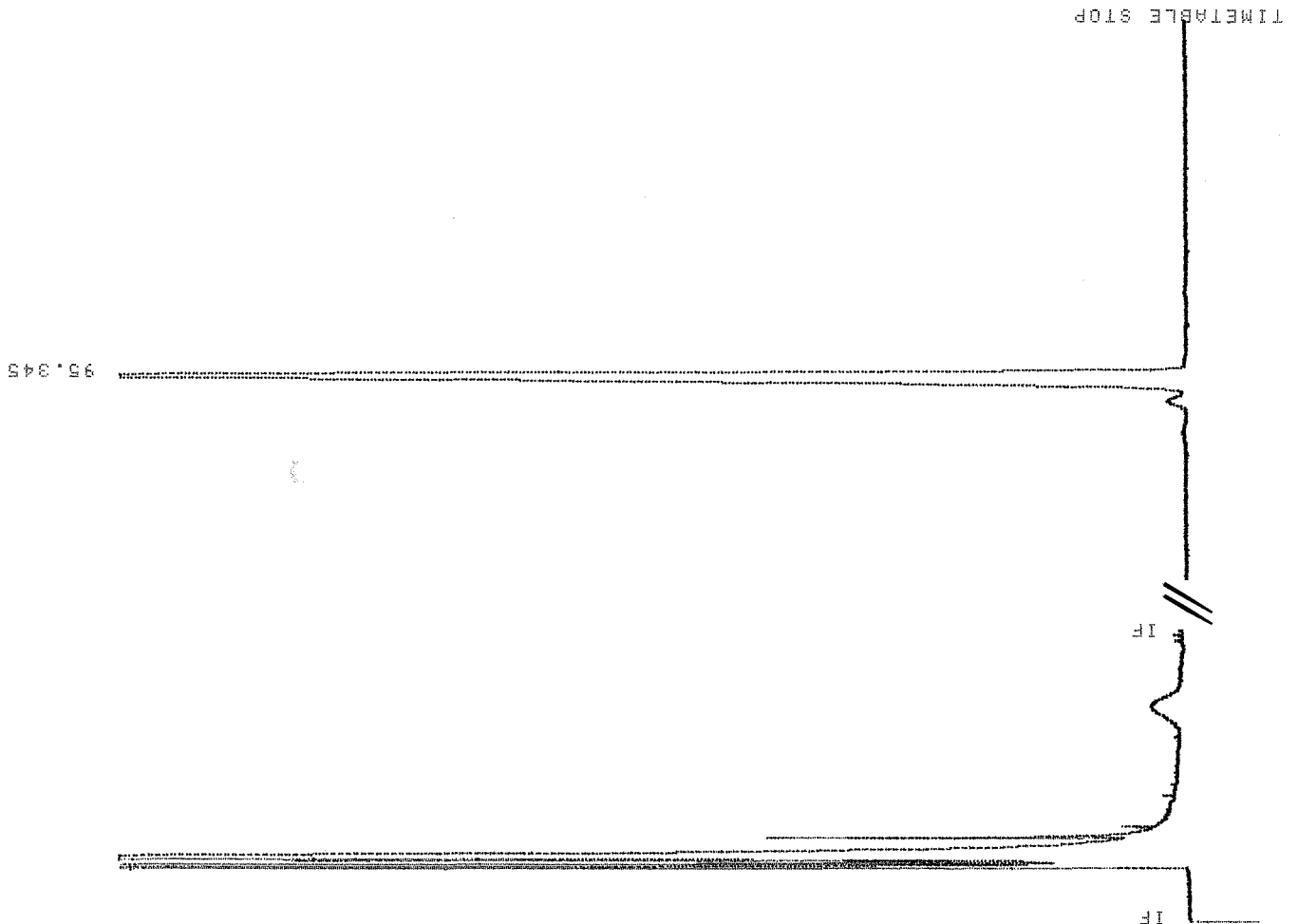


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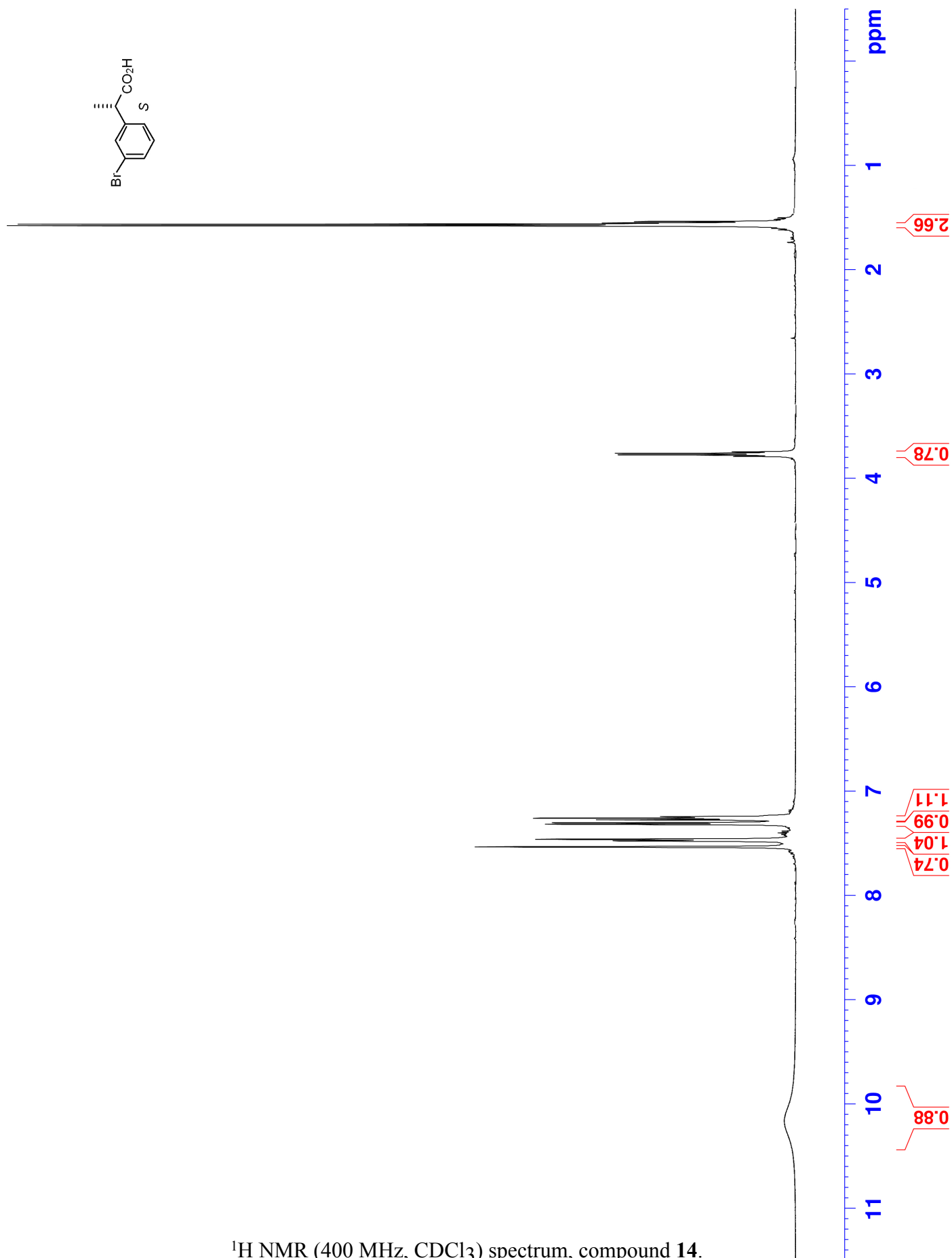
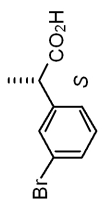


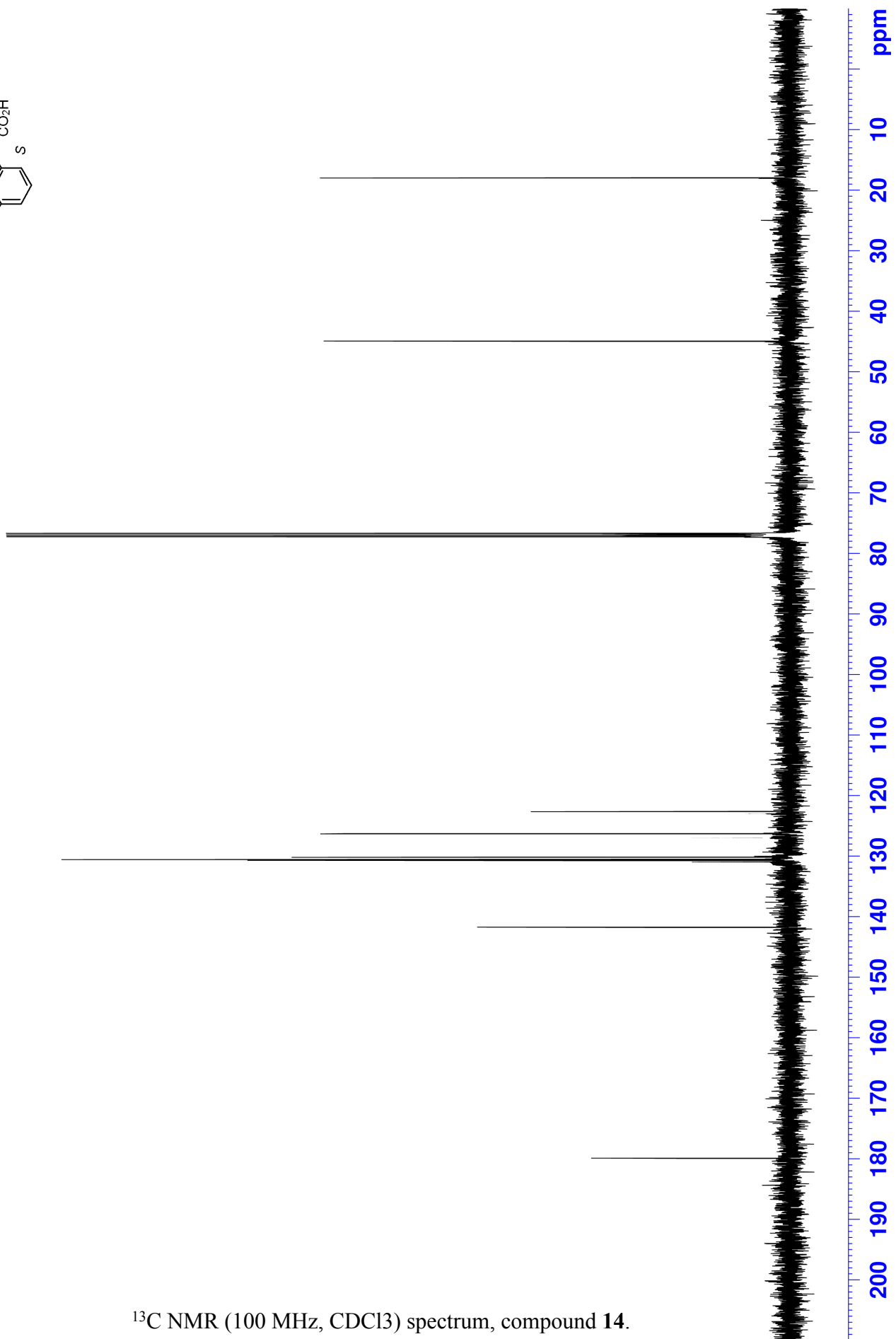
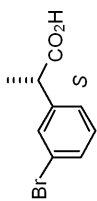
START  
 \* RUN # 221 APR 14, 1901 21:42:26

\* AR REJ 2500 @  
 \*  
 \*  
 ZERO = 0.2660  
 ATT 2 = 2  
 CH1 SP = 0.2  
 AR REJ = 250  
 THRS = 1  
 PK WD = 0.04

\* LIST: LIST  
 PEAK CAPACITY: 1243

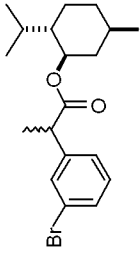
Chiral GC (Chirasil-S-Val): 120 min at 195°C;  
 L-menthyl ester of compound 13 (from 5).



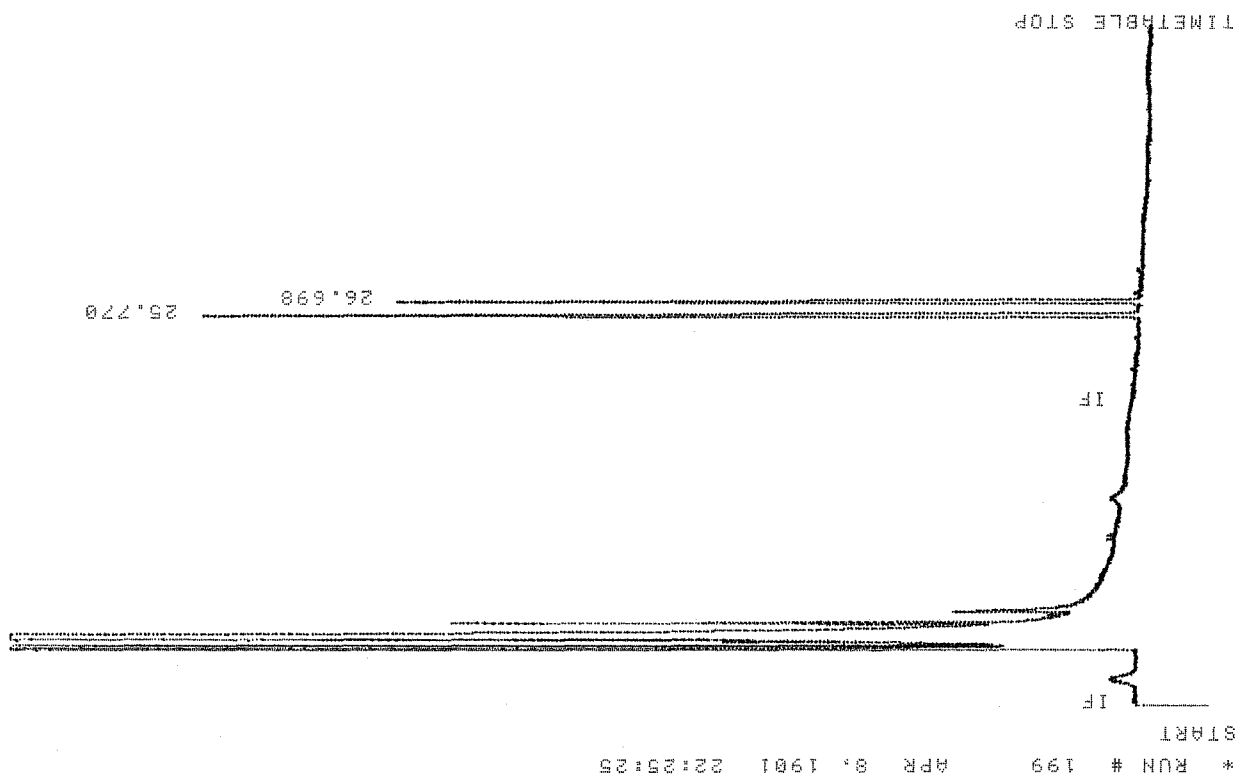


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum, compound 14.



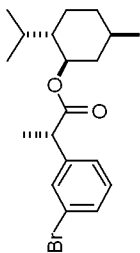


MUL FACTOR=1.0000E+00  
 TOTAL AREA= 424005  
 26.698 191996 VP .151 45.28154  
 25.720 232009 BP .145 54.71845  
 AREA% RT AREA TYPE WIDTH AREA  
 RUN# 199 APR 8, 1901 22:25:25  
 Error storing signal to M: SIGNAL .BNC  
 ATTEMPTED WRITE PAST END OF FILE



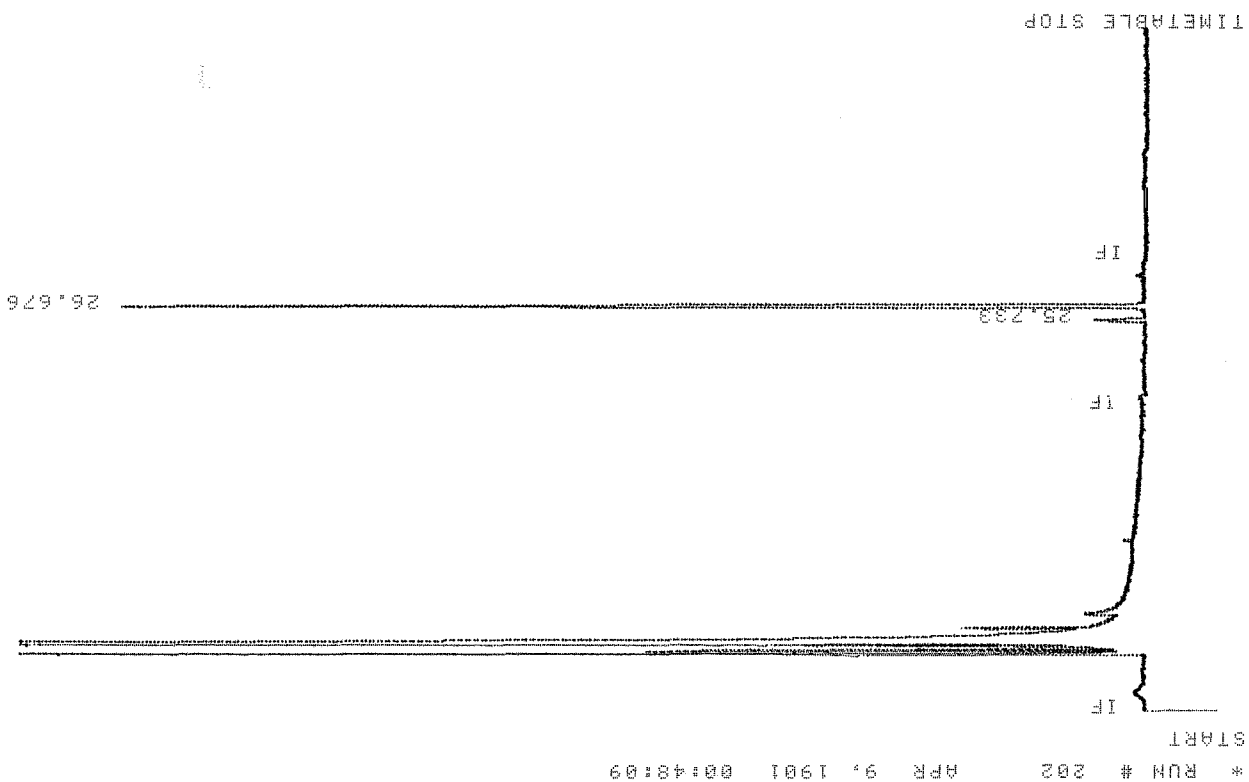
\* LIST: LIST  
 PEAK CAPACITY: 1243  
 ZERO = 0.9425  
 ATT 2 = 2  
 CHT SP = 0.2  
 AR REJ = 5000  
 THRSH = 2  
 PK WD = 0.04

Chiral GC (Chirasil-S-Val): 45 min at 190°C;  
 (racemic mixture) (L)-menthyl esters of **14**  
 (enriched).



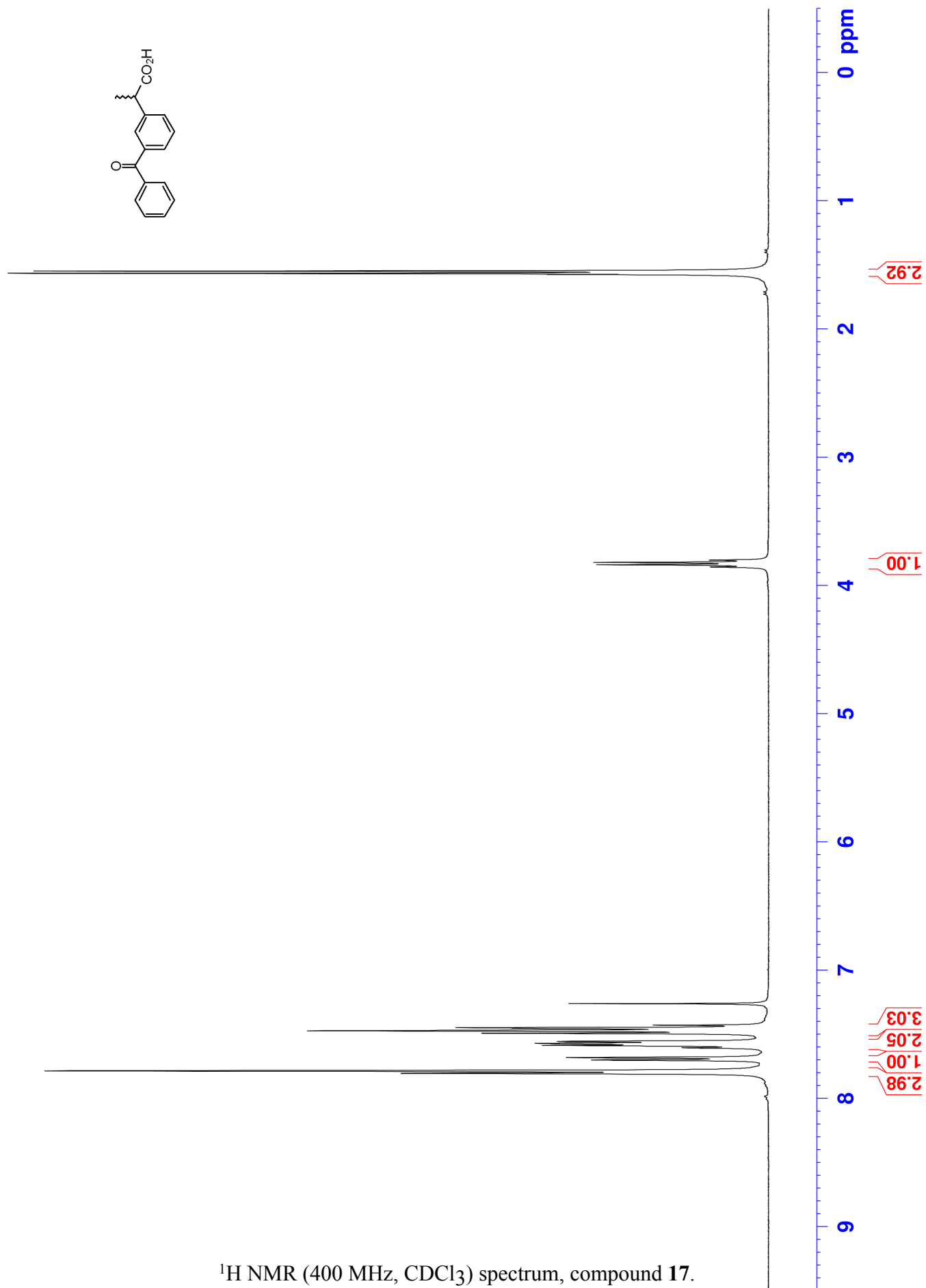
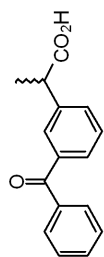
MULTI FACTOR=1.0000E+00  
 TOTAL AREA= 274143  
 26.676 262038 BP .150 95.58445  
 25.733 12105 PP .139 4.41550  
 RT AREA TYPE WIDTH AREA%  
 RUN# 202 APR 9, 1901 00:48:09

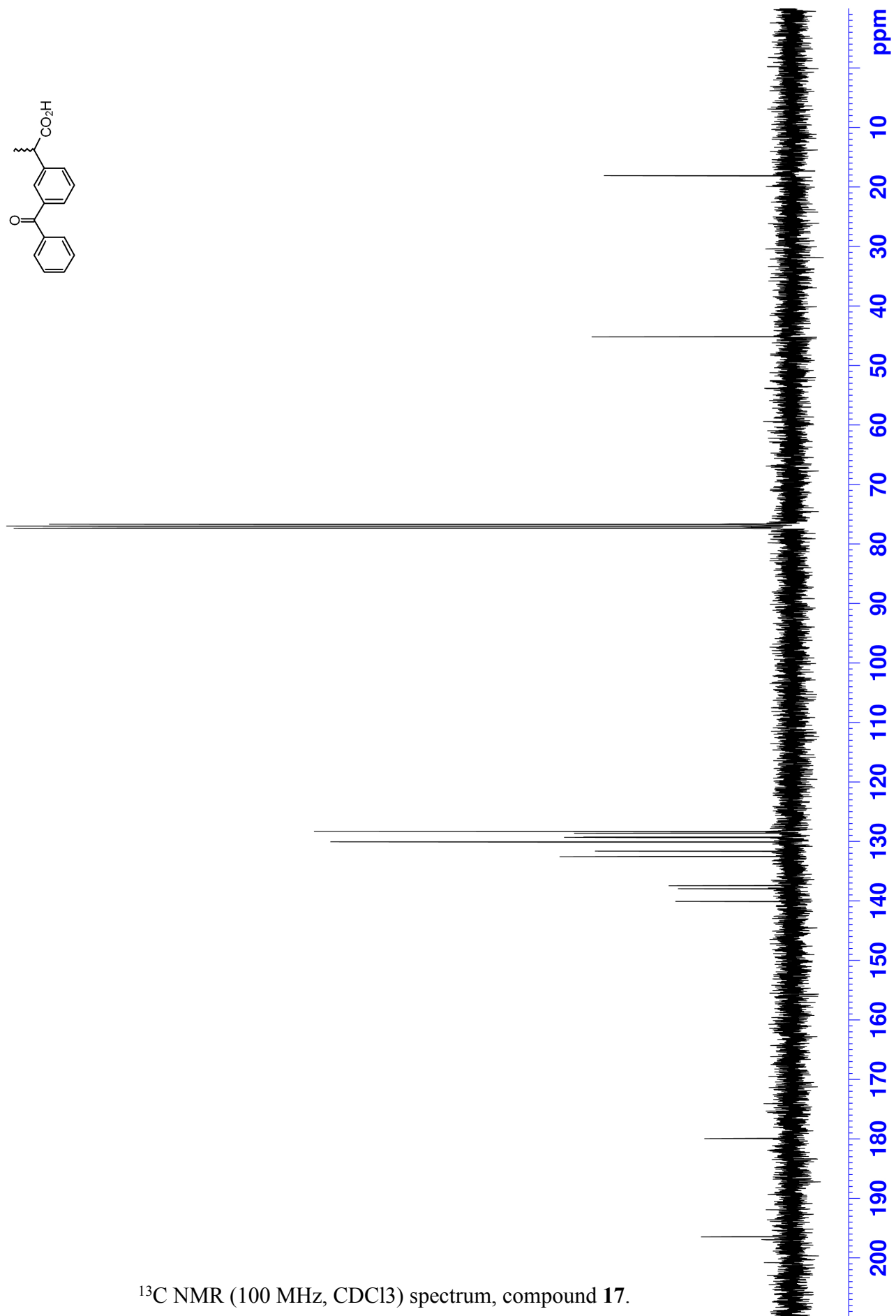
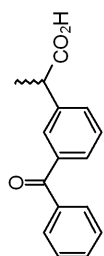
ERROR STOPPING SIGNAL TO M: SIGNAL .BNC  
 ATTEMPTED WRITE PAST END OF FILE



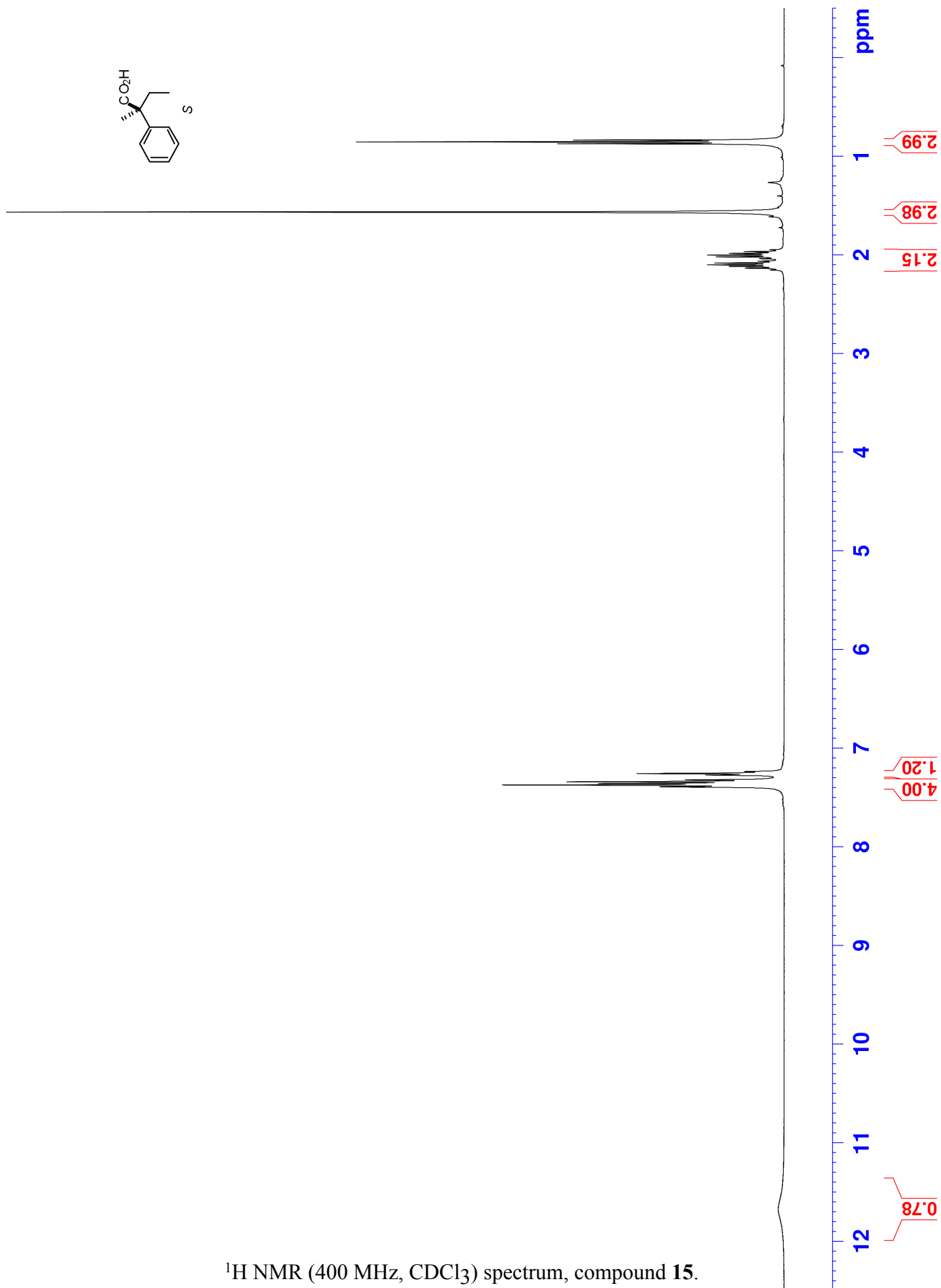
\* RUN # 202 APR 9, 1901 00:48:09  
 START  
 ZERO = 0, 9,304  
 ATT 2 = 2  
 CHT SP = 0.2  
 AR REJ = 5000  
 THRESH = 2  
 PK WD = 0.04  
 \* LIST: LIST  
 PEAK CAPACITY: 1243

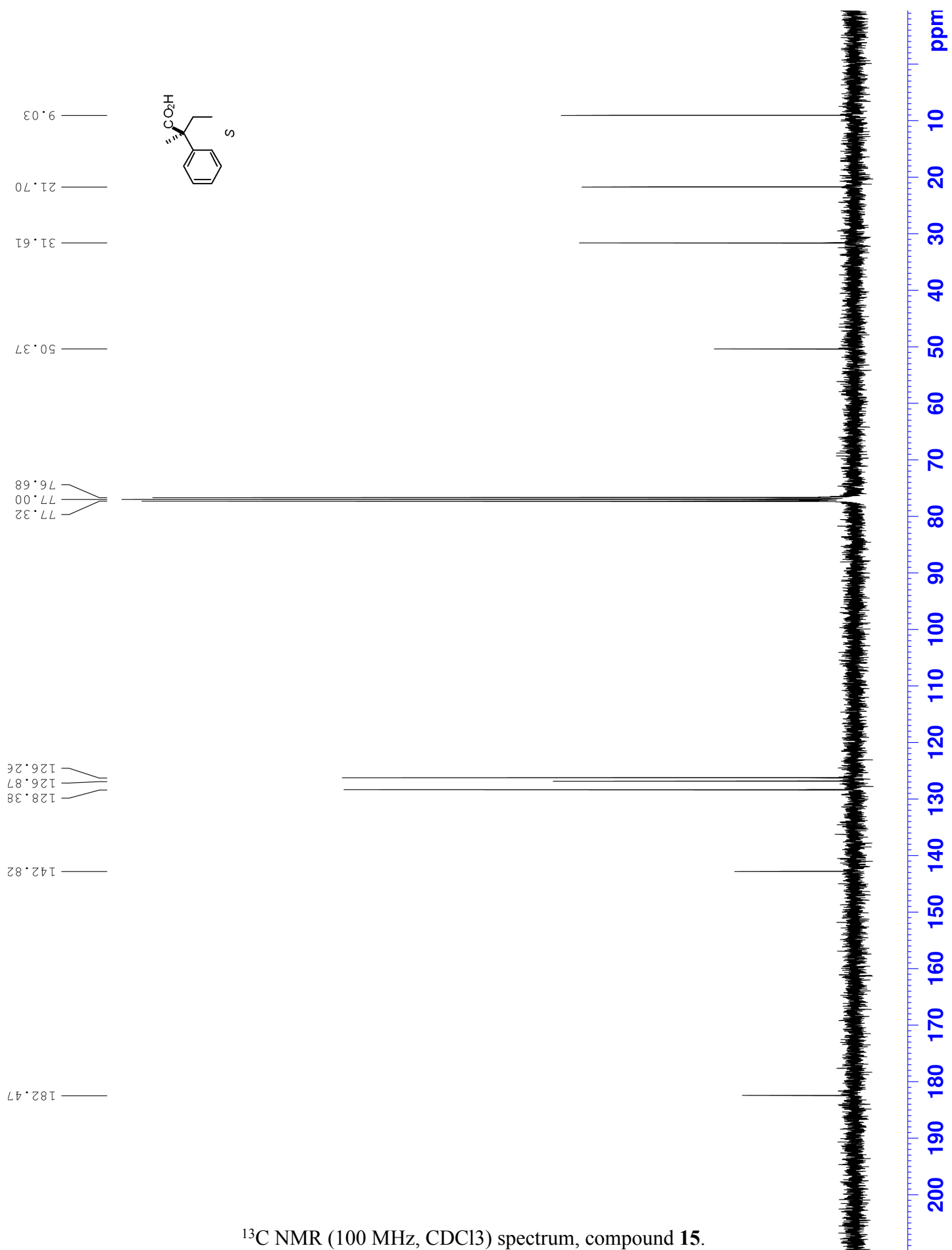
Chiral GC (Chirasil-S-Val): 45 min at 190°C;  
 (L)-menthyl ester of **14** from **6**.

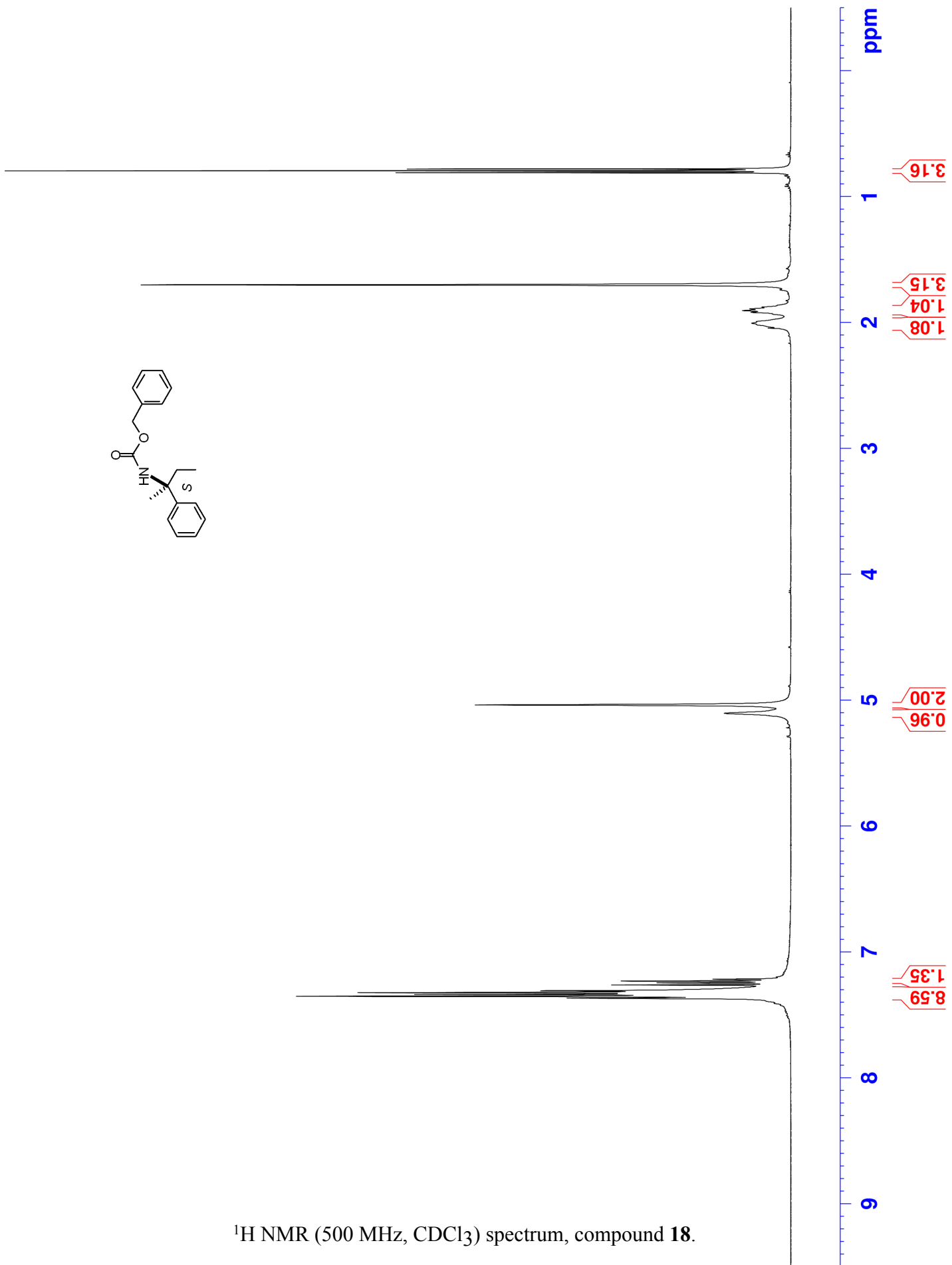
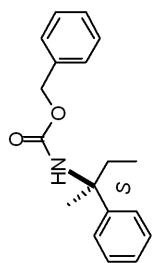


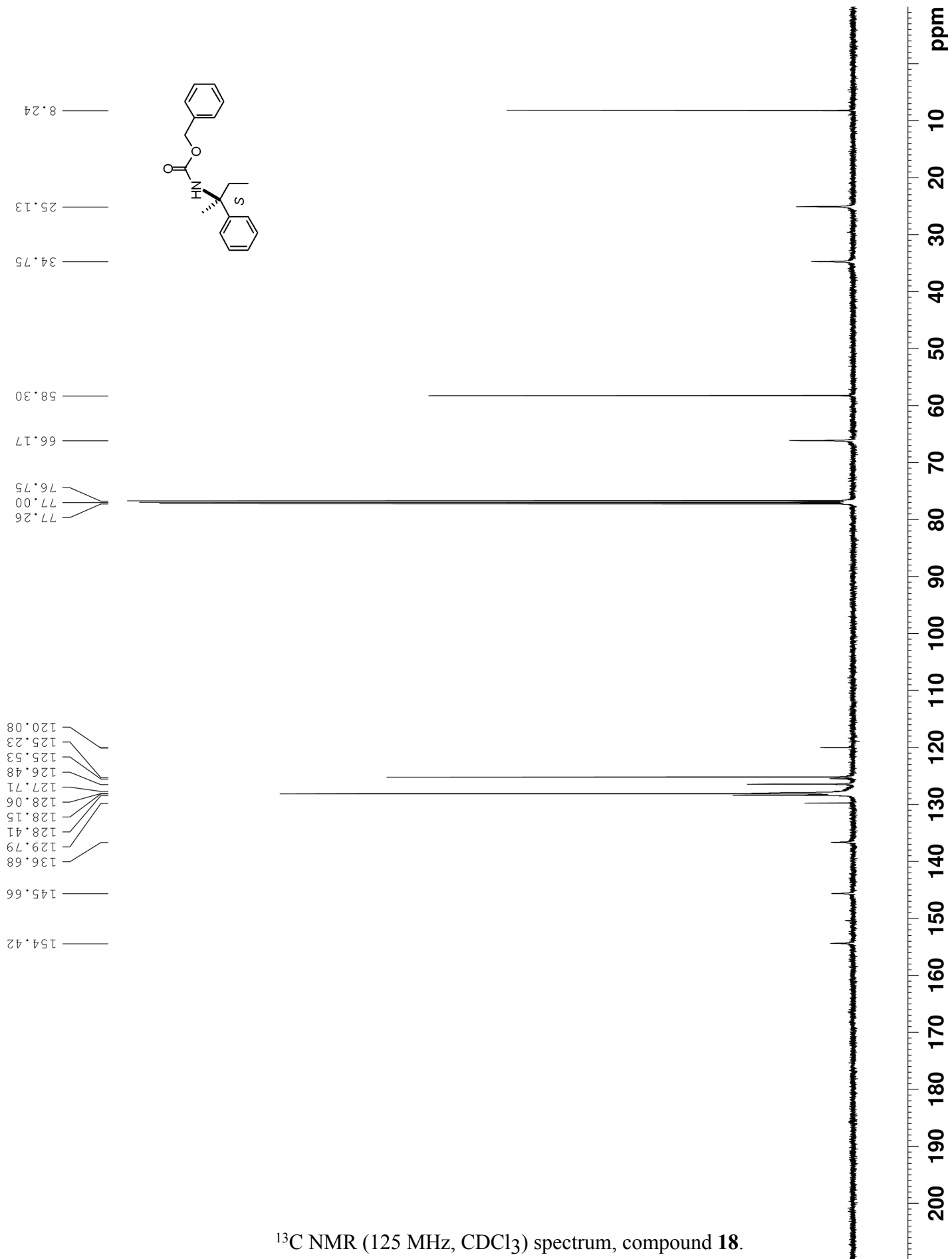


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectrum, compound 17.

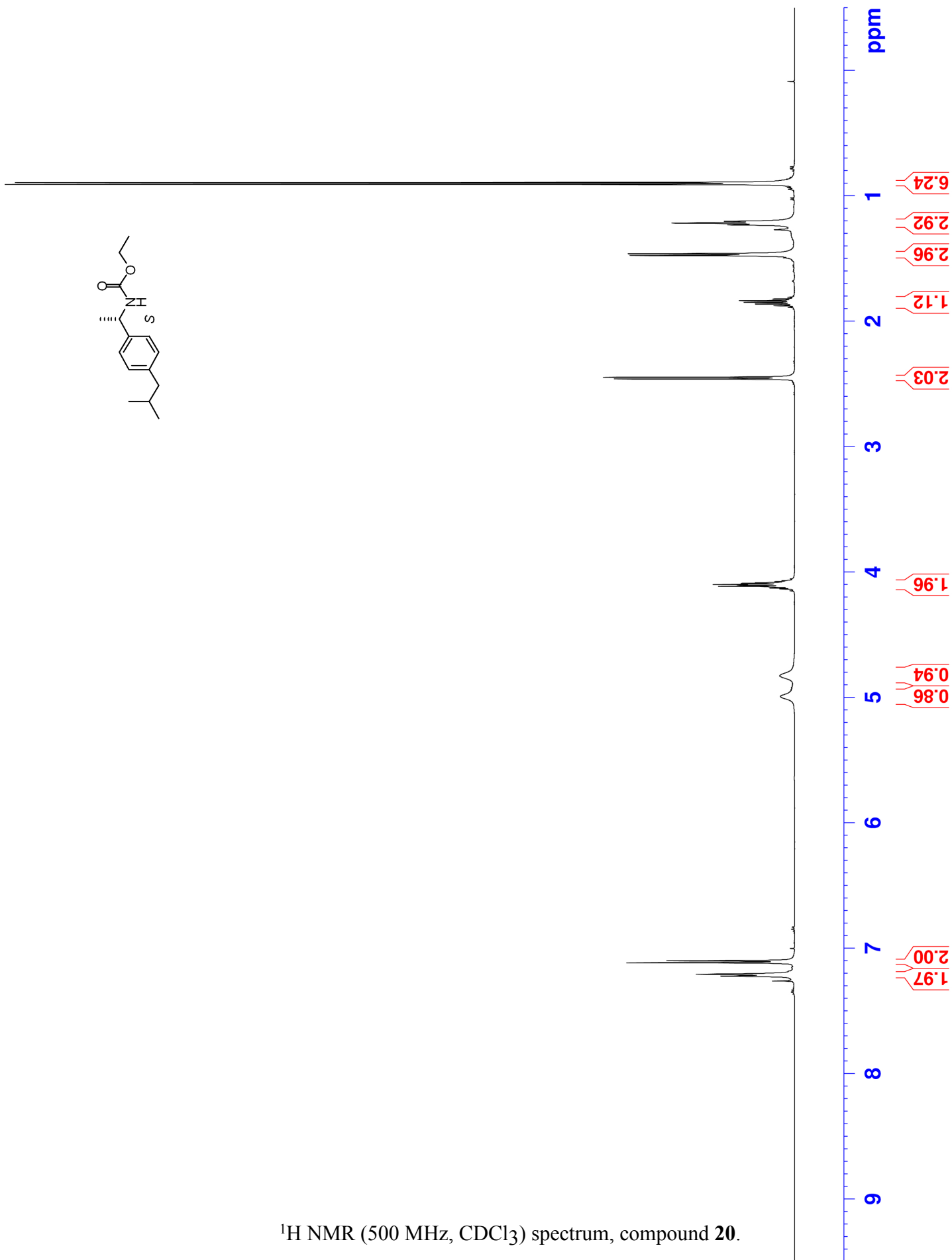
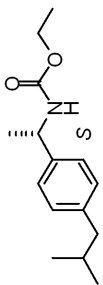


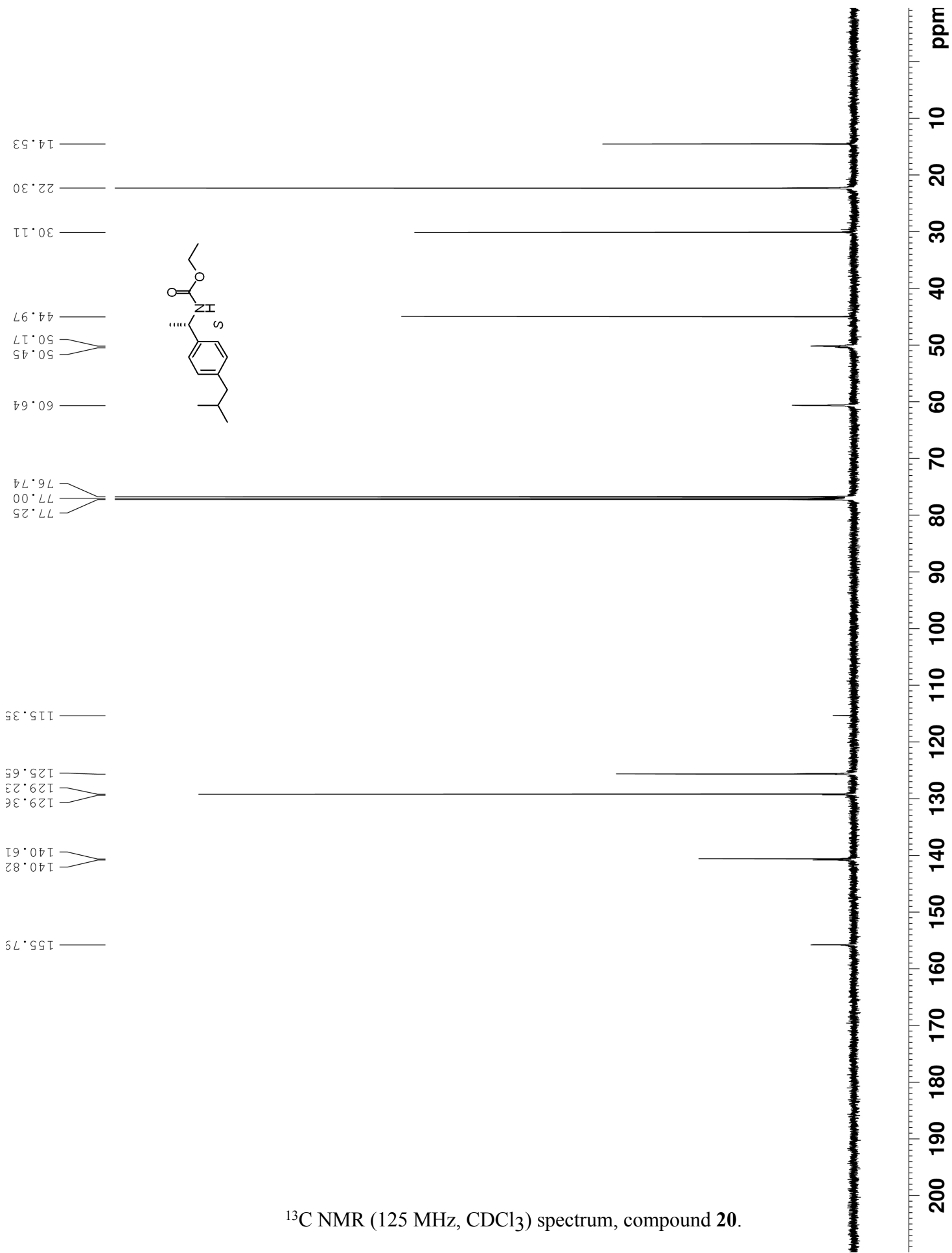




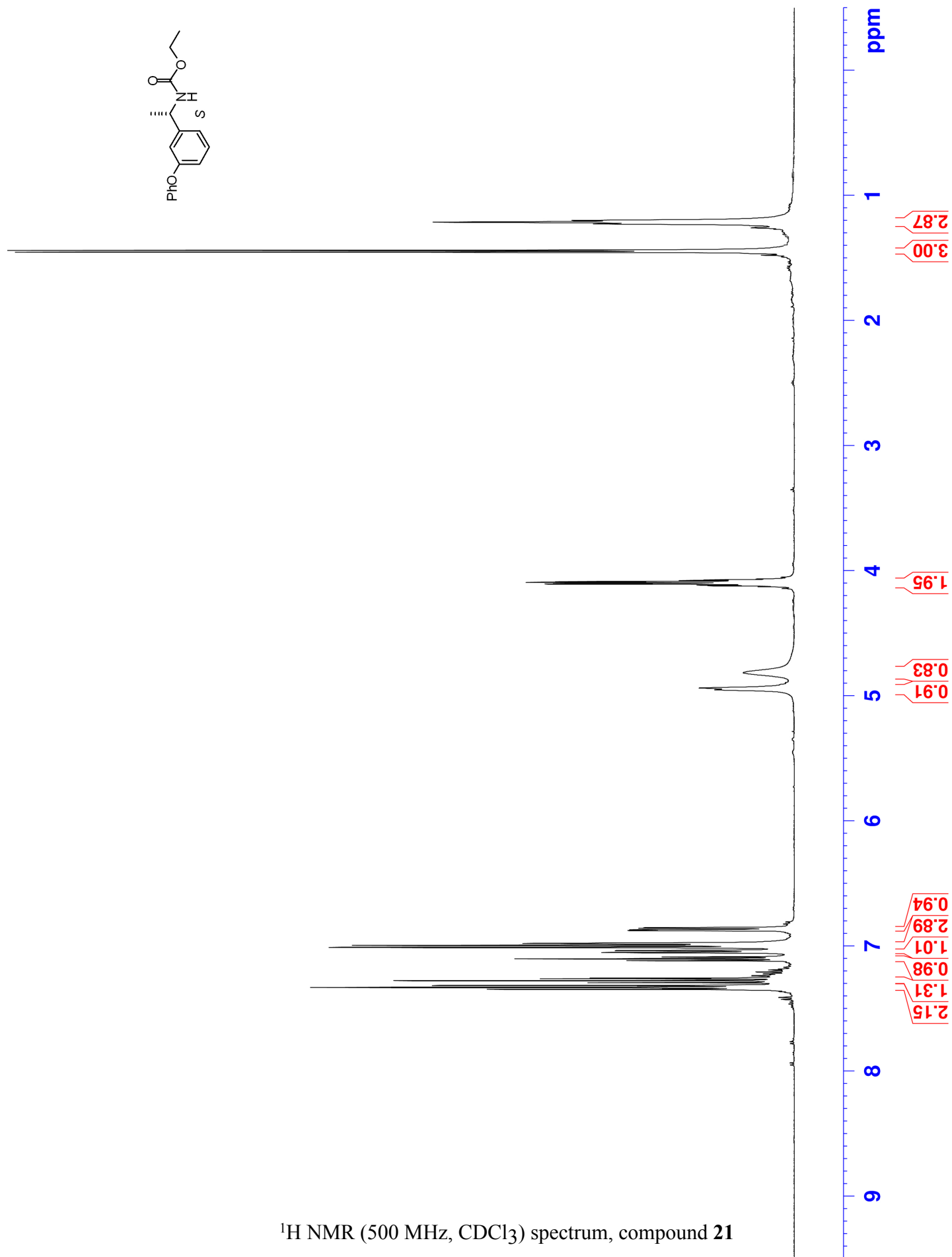
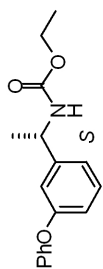


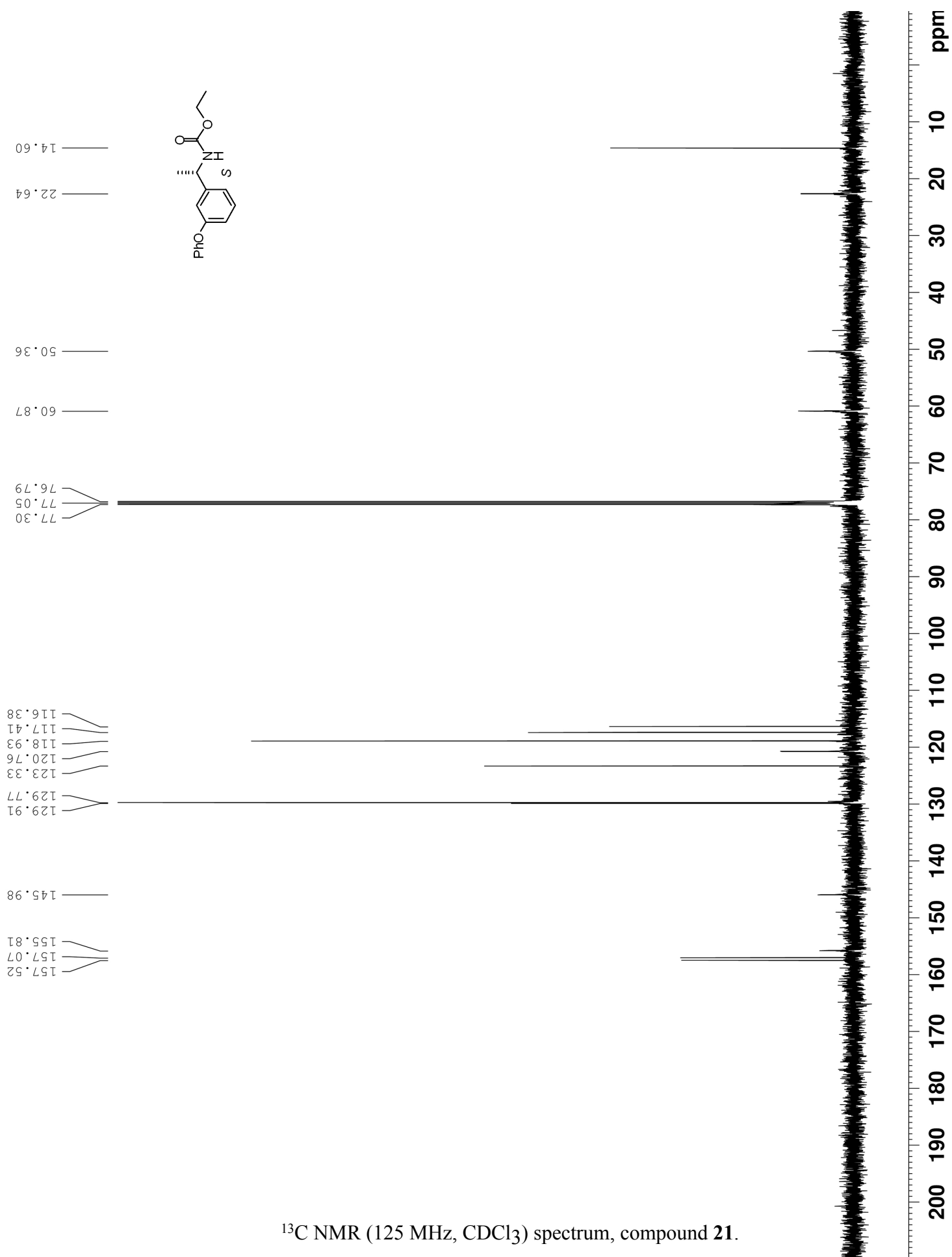


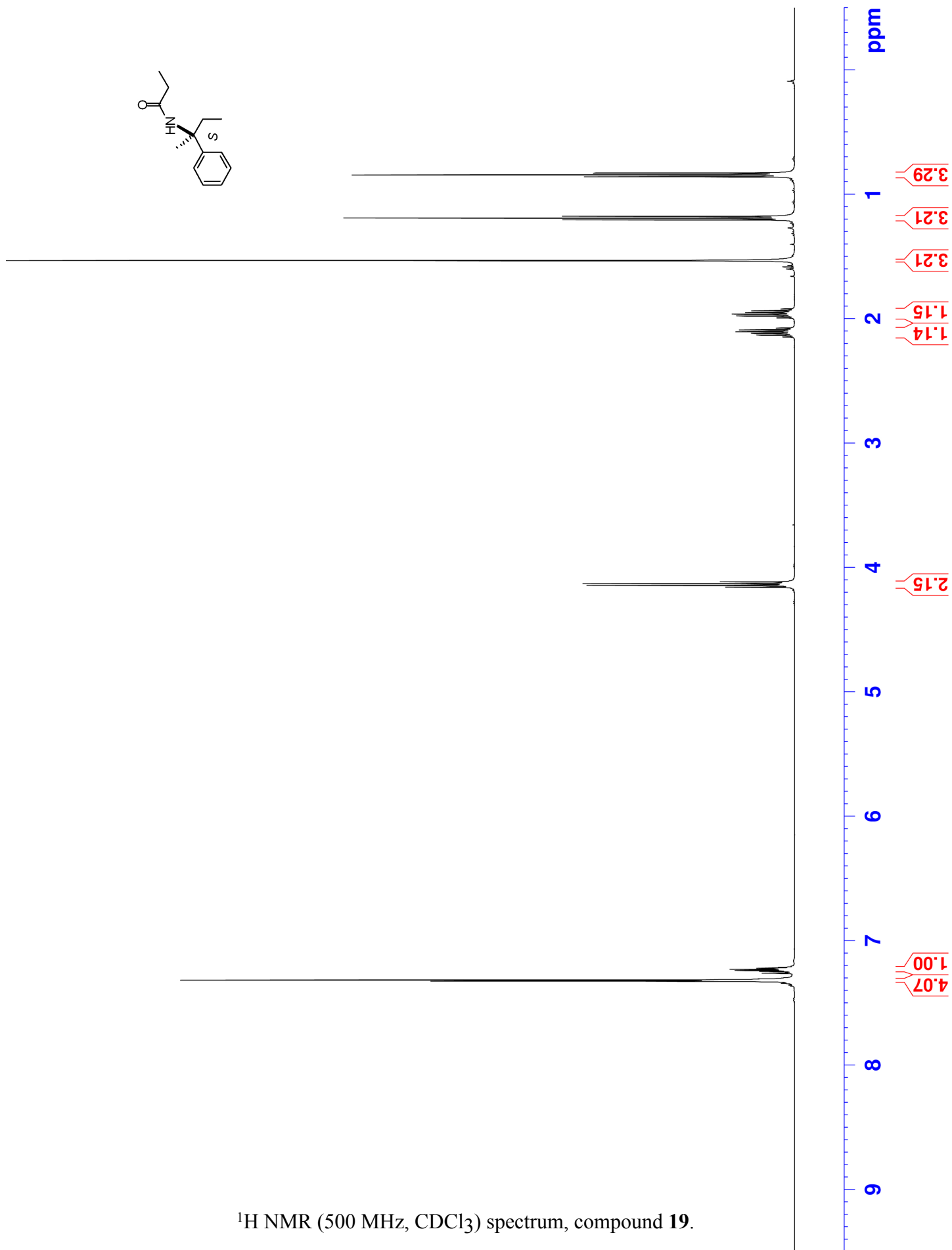
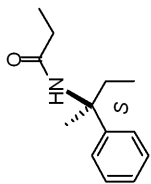


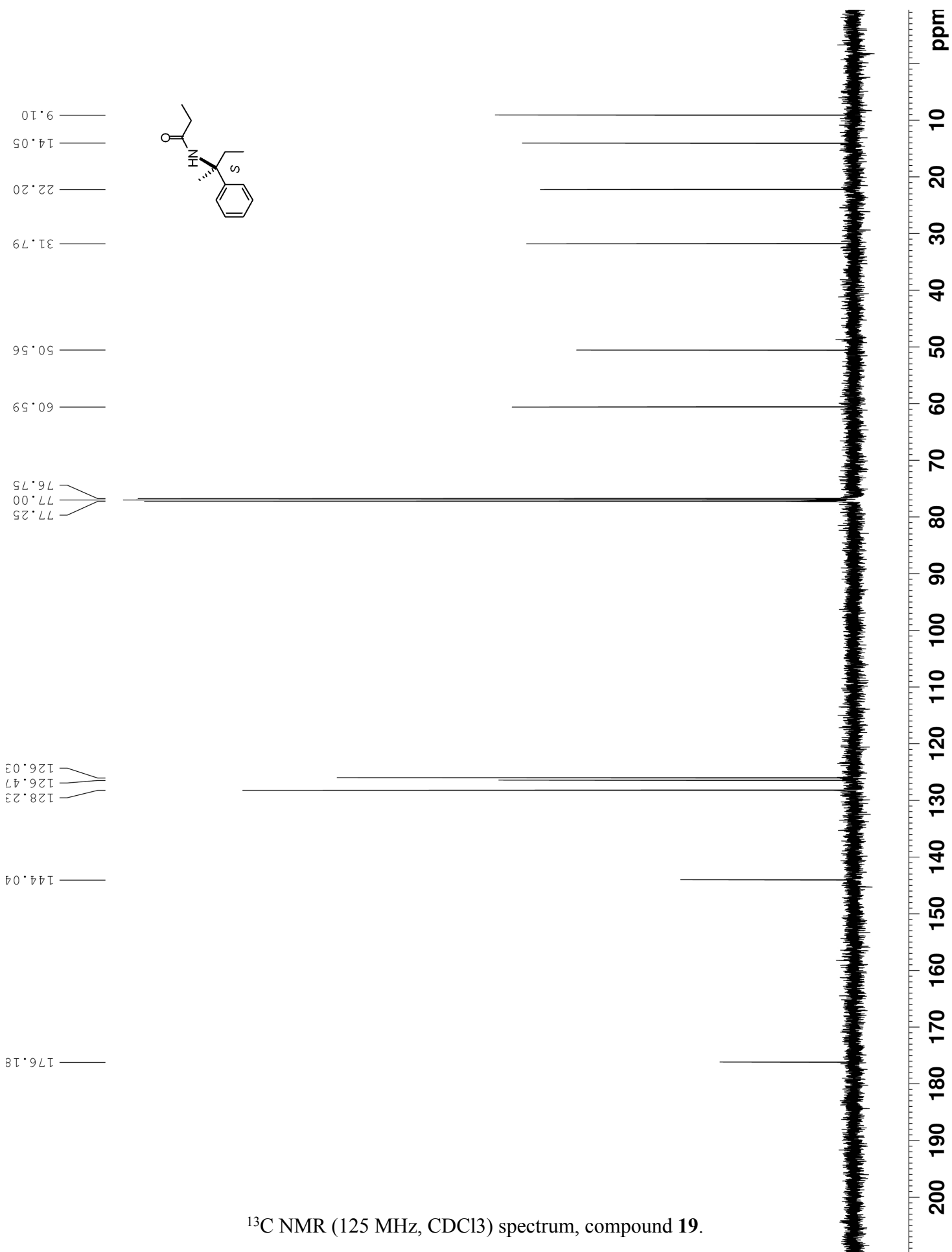


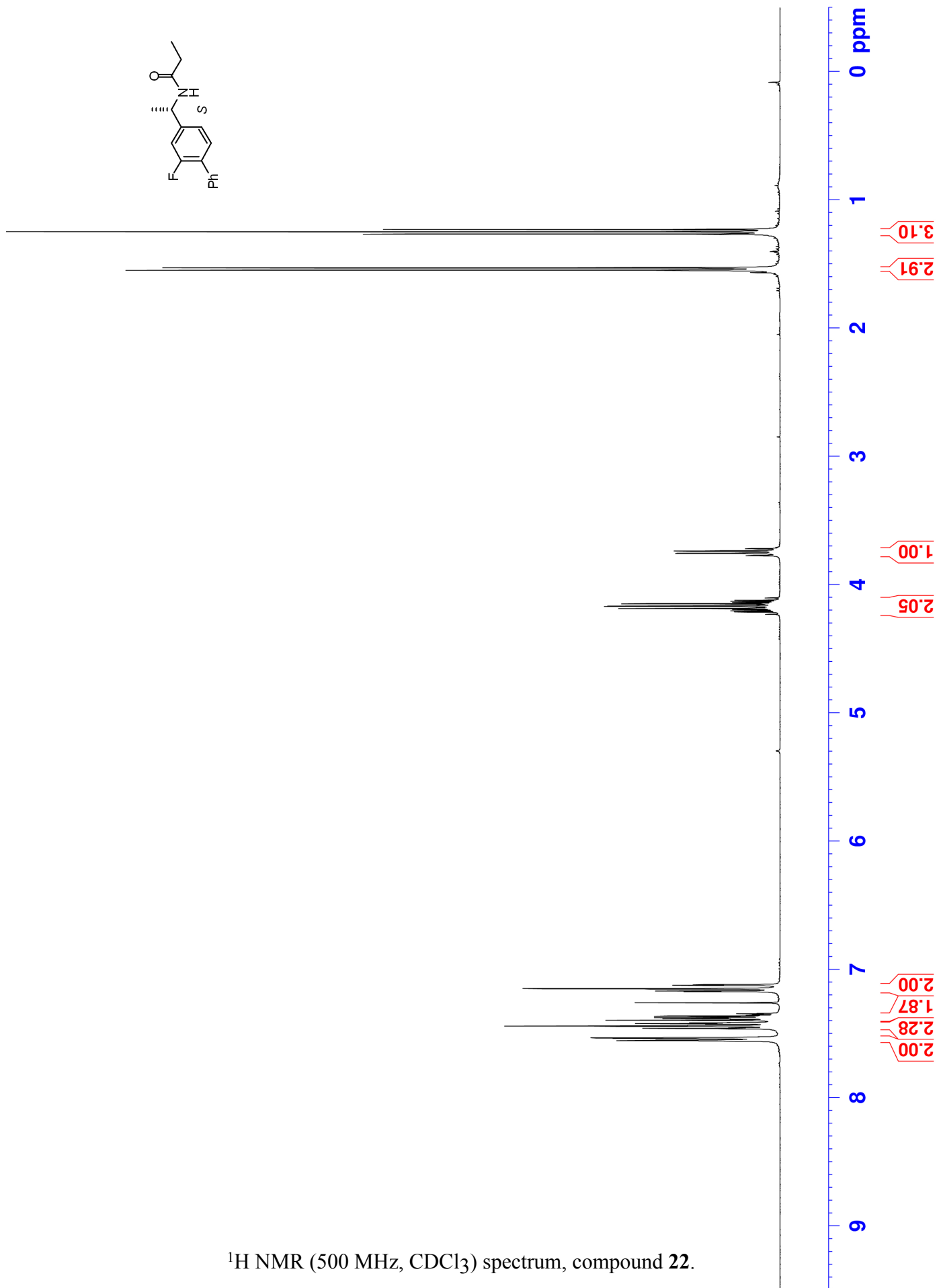
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectrum, compound 20.

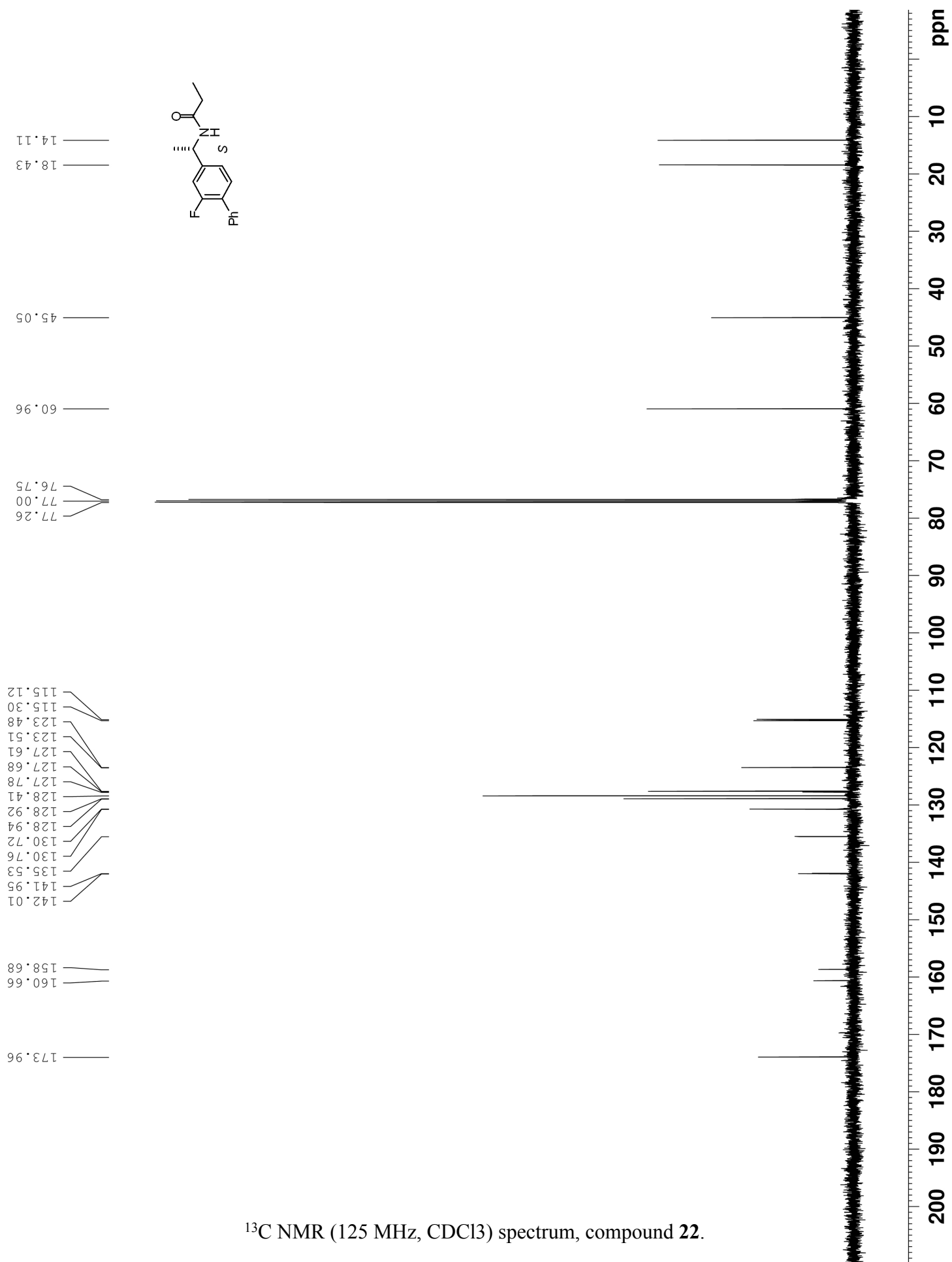






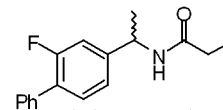




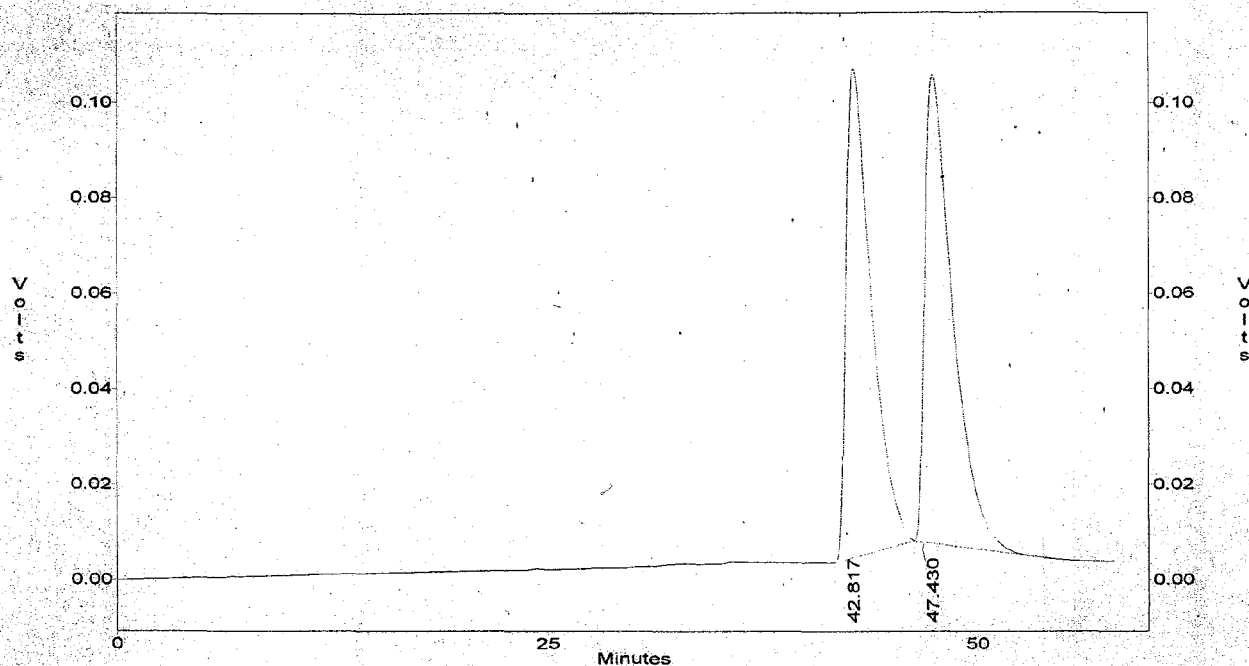




File : c:\users\craig\Cs5209.3  
 Method : c:\class-vp\methods\C-0%05.met  
 Sample ID : CS-5-209-rac-3  
 Acquired : Nov 24, 2008 12:40:06  
 Printed : Nov 24, 2008 13:41:09  
 User : System



c:\users\craig\Cs5209.3 - Channel A

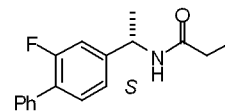


Channel A Results

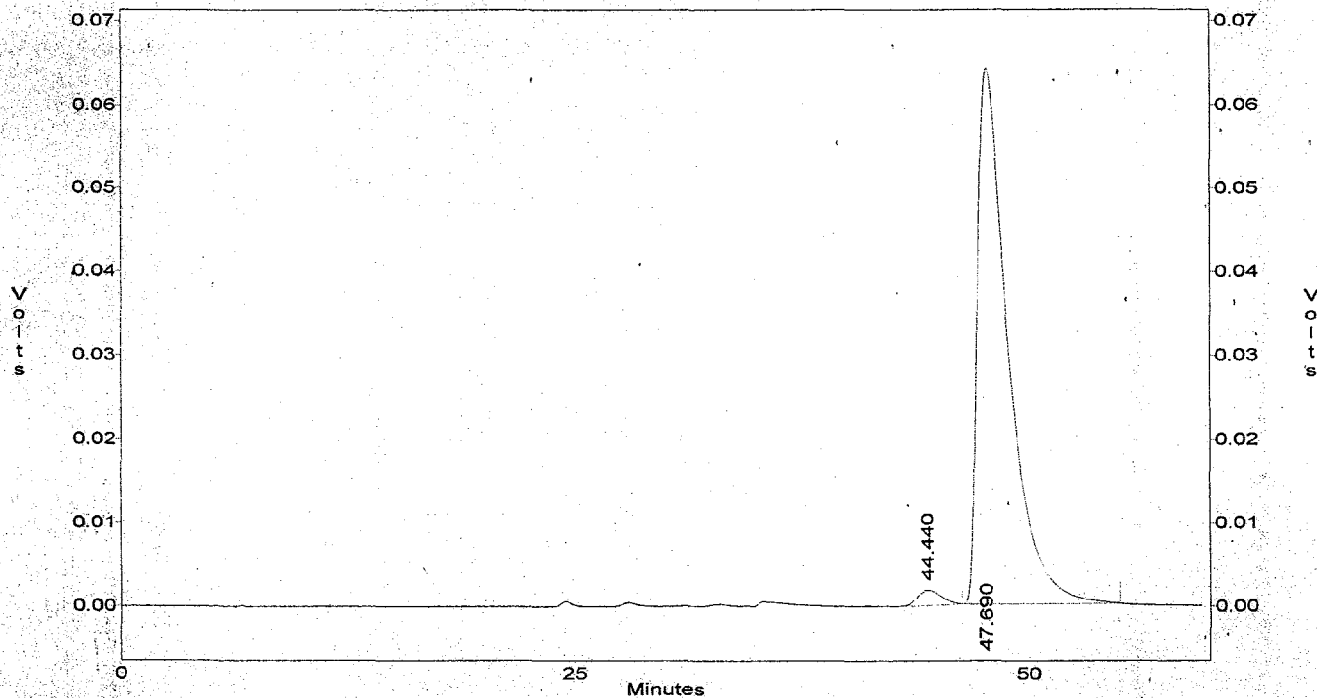
Peak	Time	Area	Area %
1	42.82	10484576	48.830
2	47.43	10986850	51.170
Totals :		21471426	100.000

Chiral HPLC (racemic mixture): hexanes  
 60 min at 0.50 mL/min, compound 22.

File : c:\users\craig\Cs5209.4  
Method : c:\class-vp\methods\C-0%05.met  
Sample ID : CS-5-209-s-1  
Acquired : Nov 24, 2008 14:07:38  
Printed : Nov 24, 2008 15:08:43  
User : System



c:\users\craig\Cs5209.4 -- Channel A



## Channel A Results

Peak	Time	Area	Area %
1	44.44	162945	2.149
2	47.69	7418323	97.851
Totals :		7581268	100.000

Chiral HPLC: hexanes; 60 min at 0.50 mL/min,  
compound 22 from 7.