

## Supplementary Material

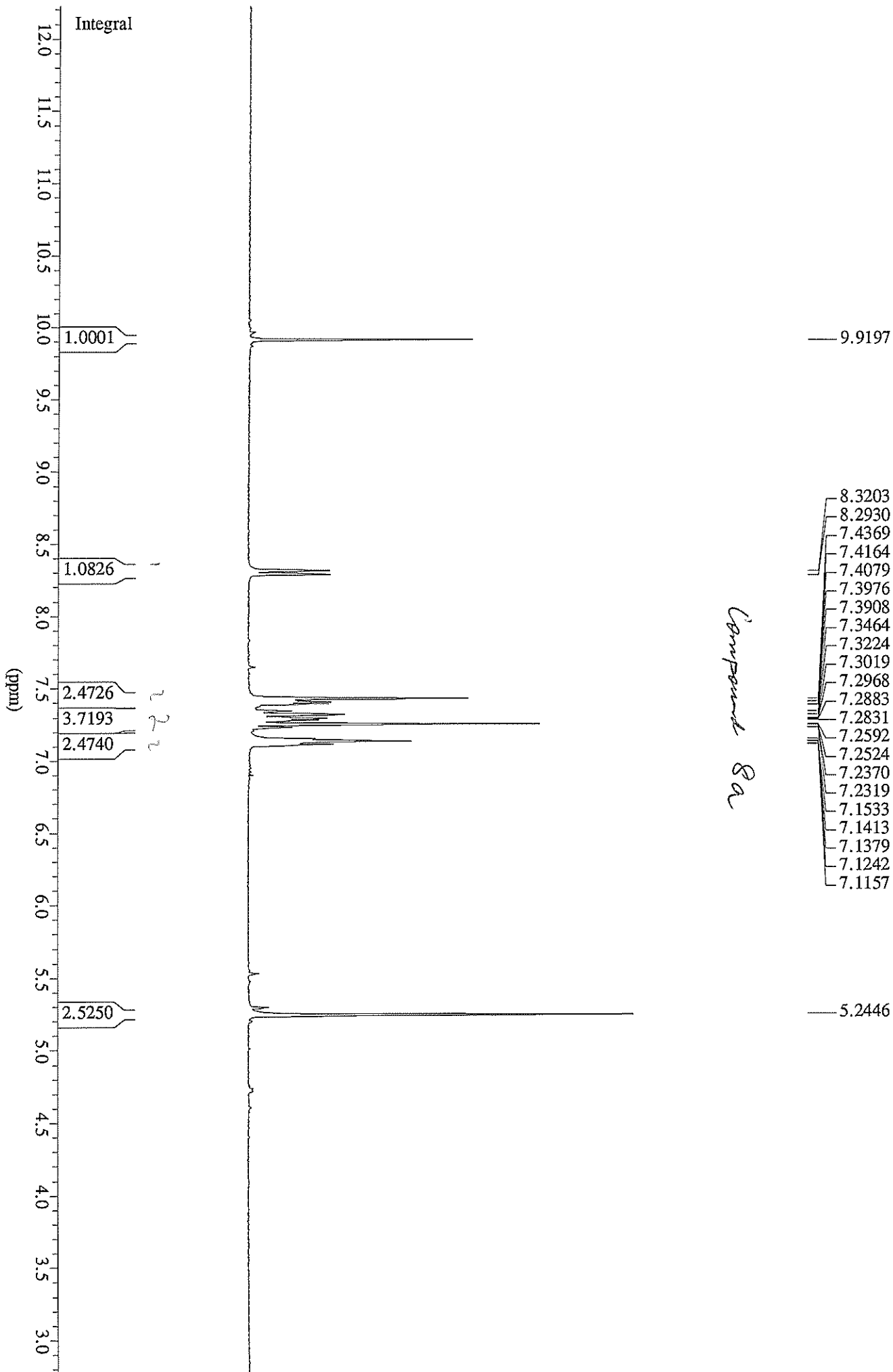
### Formaldehyde Extrusion in *ipso*-Substitution Reactions of Hydroxymethylindoles\*

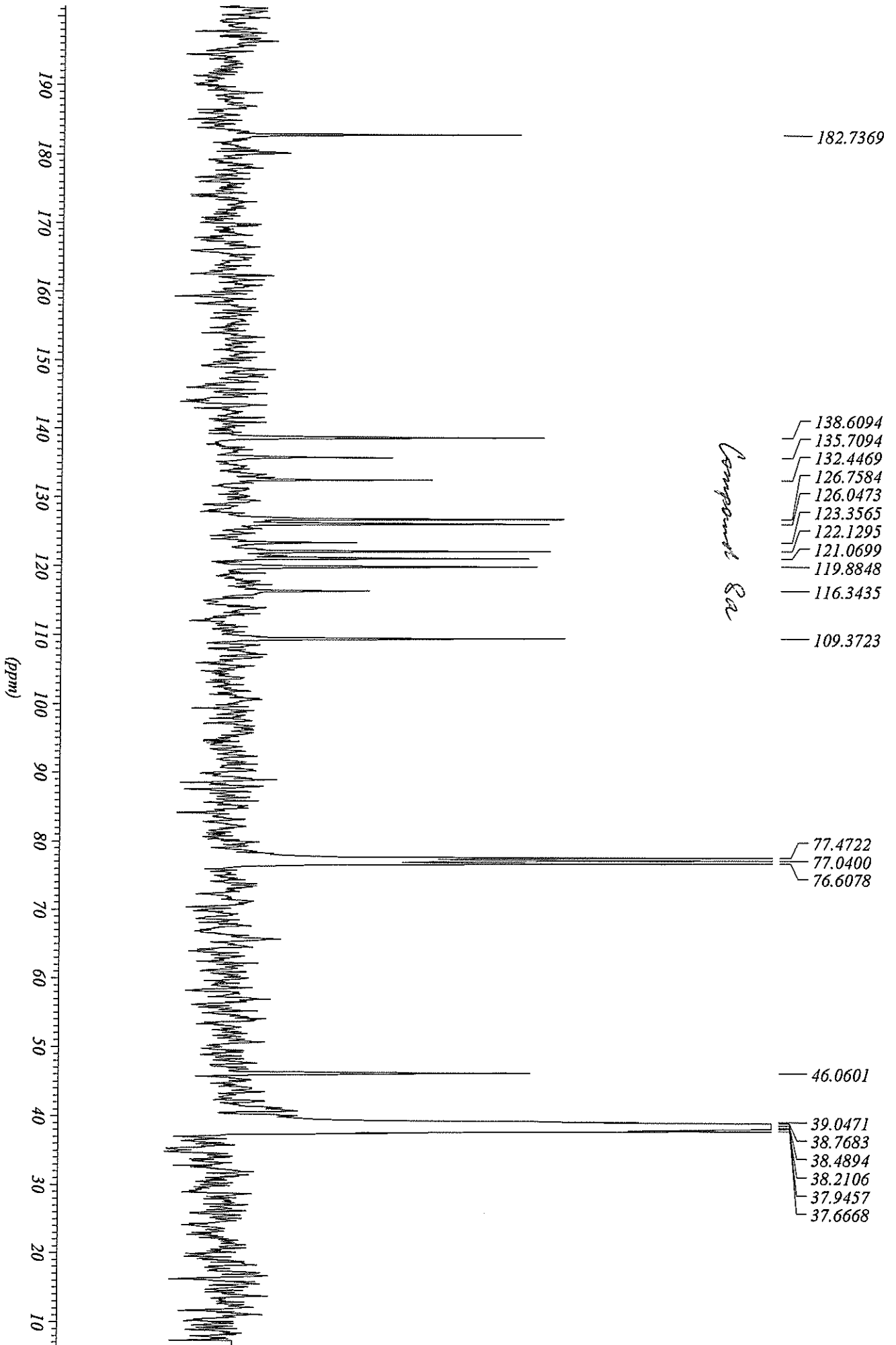
Jeremy C. Dobrowolski,<sup>A</sup> Kittiya Somphol,<sup>A</sup> Mardi Santoso,<sup>A</sup> Hung Duong,<sup>A</sup> Christopher R. Gardner,<sup>A</sup> Naresh Kumar,<sup>A</sup> and David StC. Black<sup>A,B</sup>

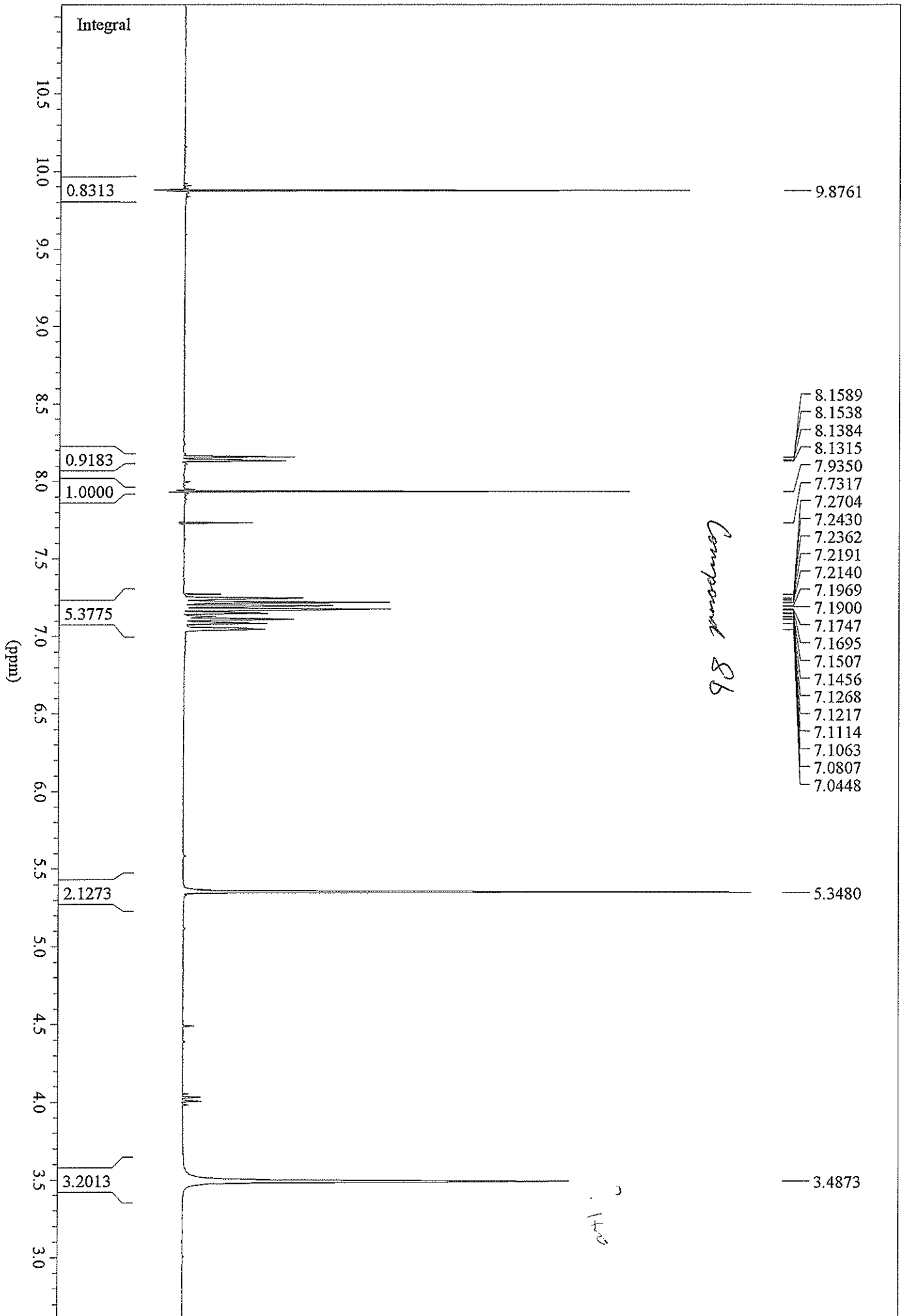
<sup>A</sup>School of Chemistry, The University of New South Wales, UNSW Australia, Sydney, NSW 2052, Australia.

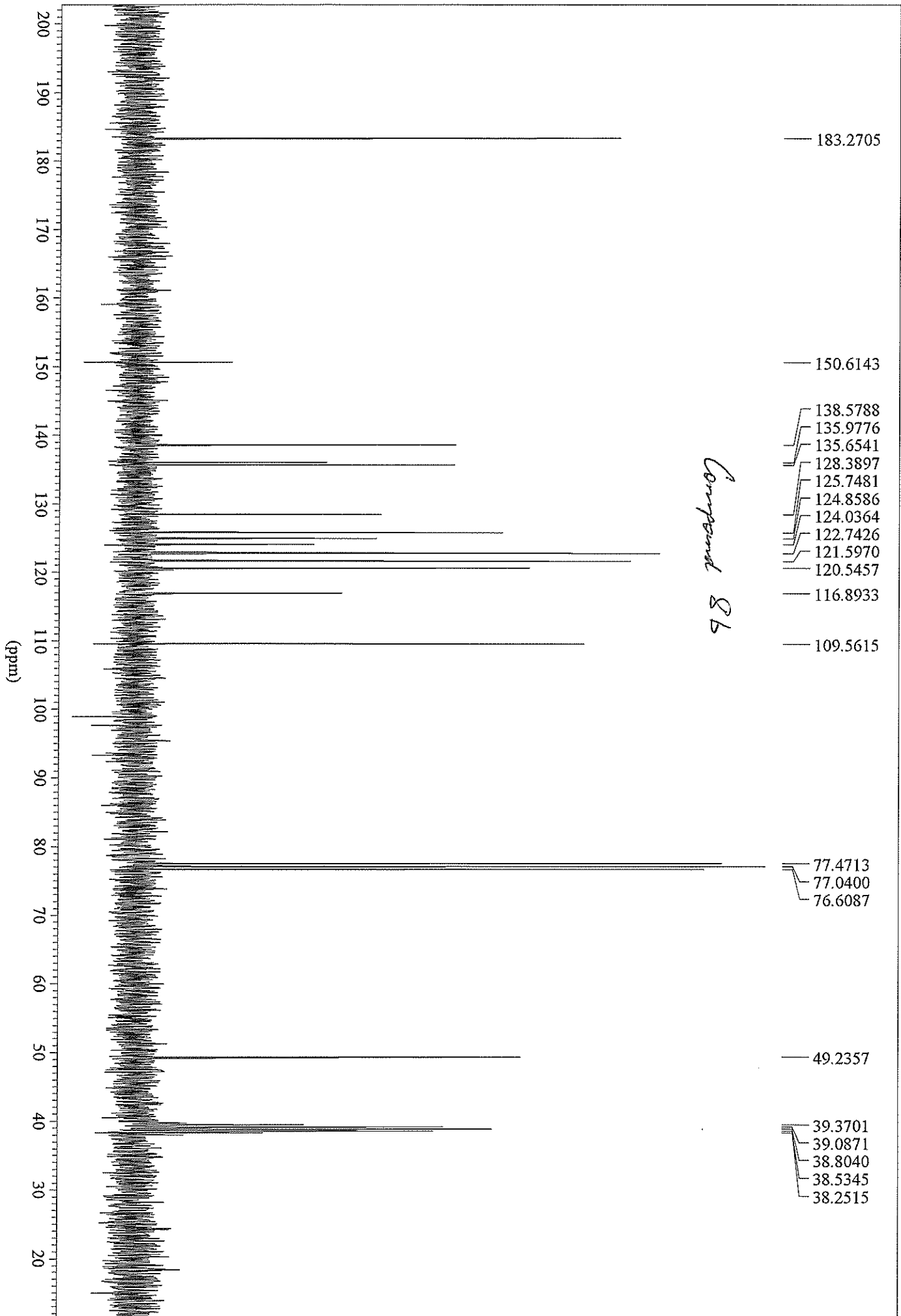
<sup>B</sup>Corresponding author. Email: d.black@unsw.edu.au

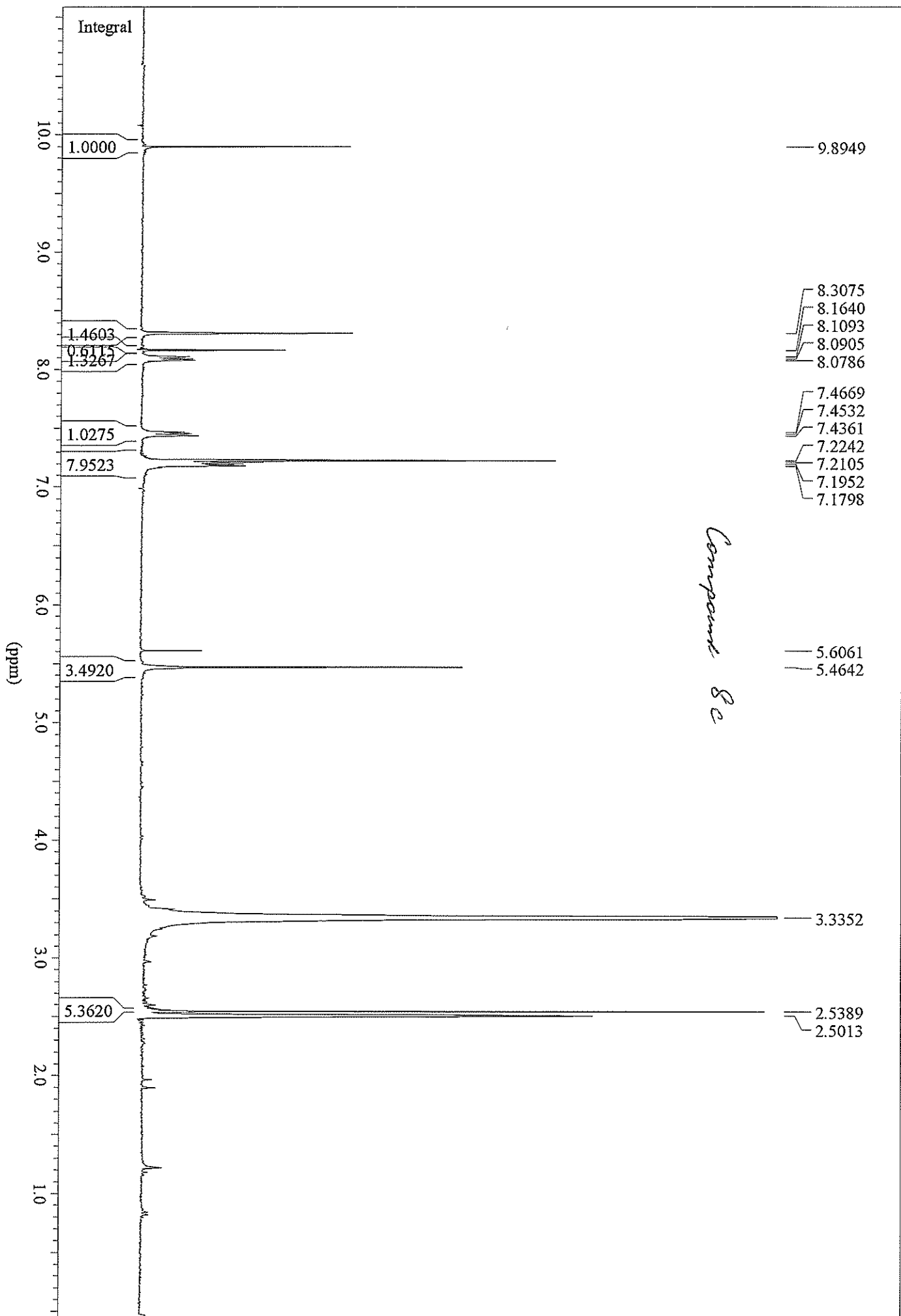
\*David StClair Black was awarded the Australian Academy of Science David Craig Medal for 2017.

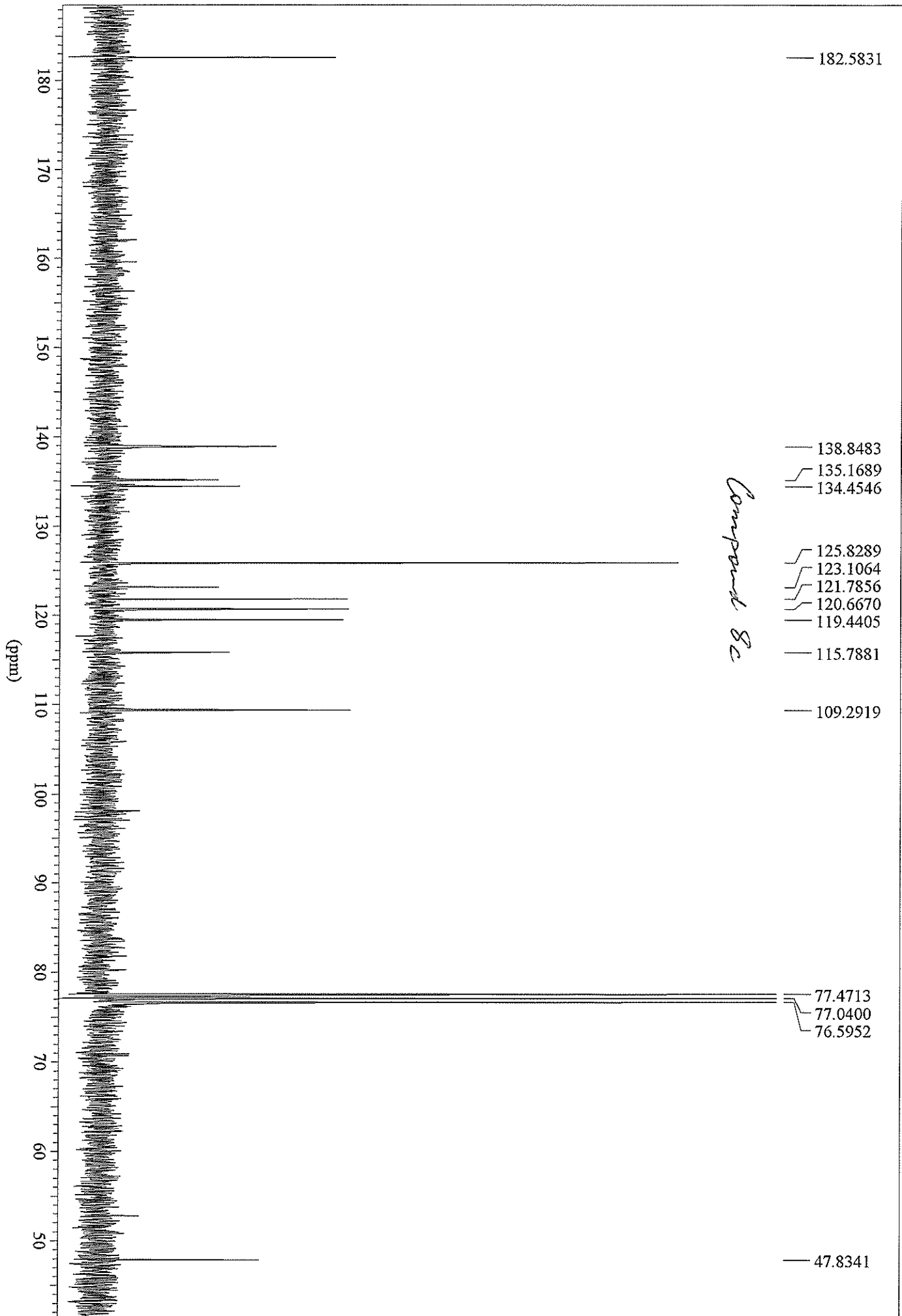


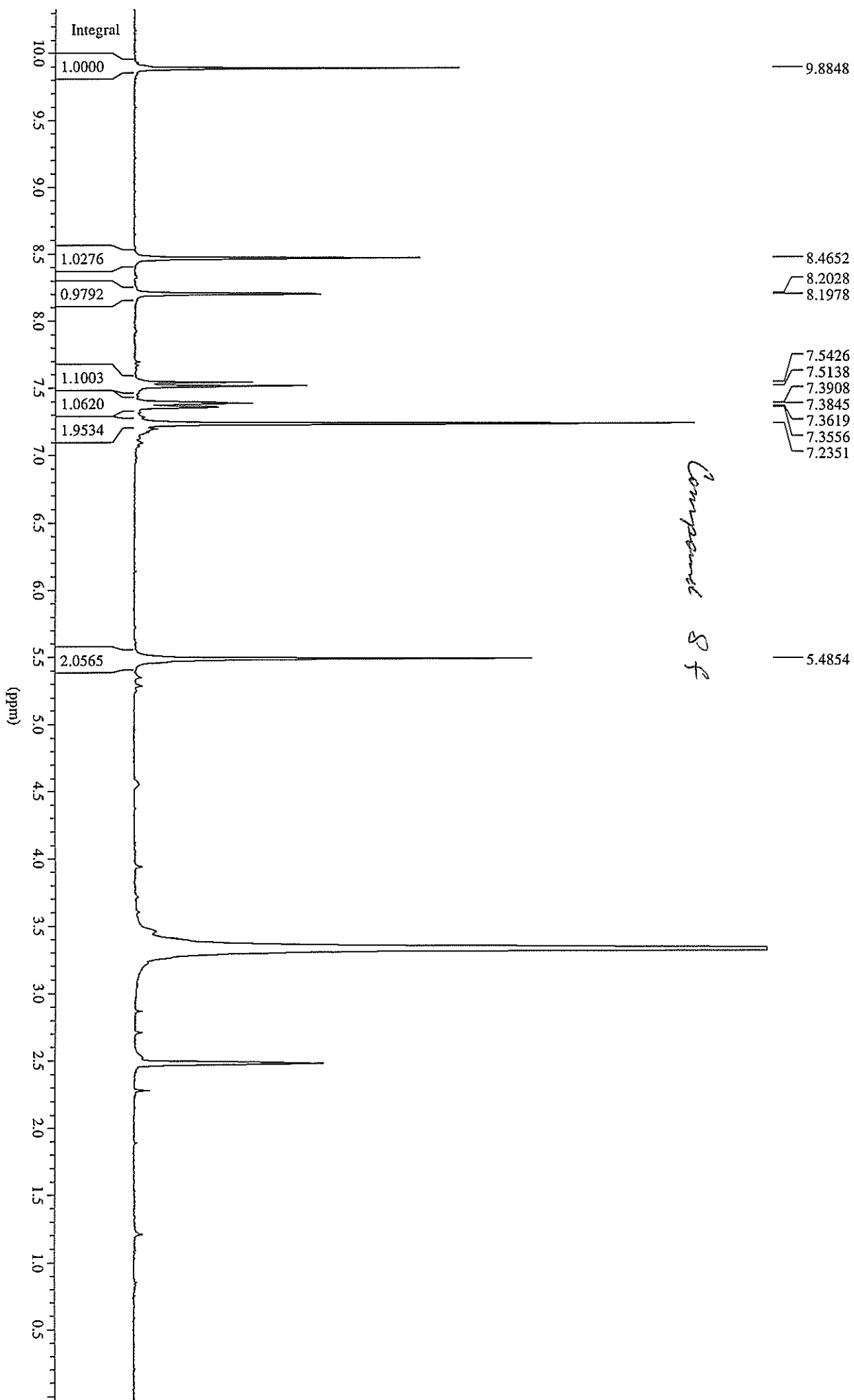




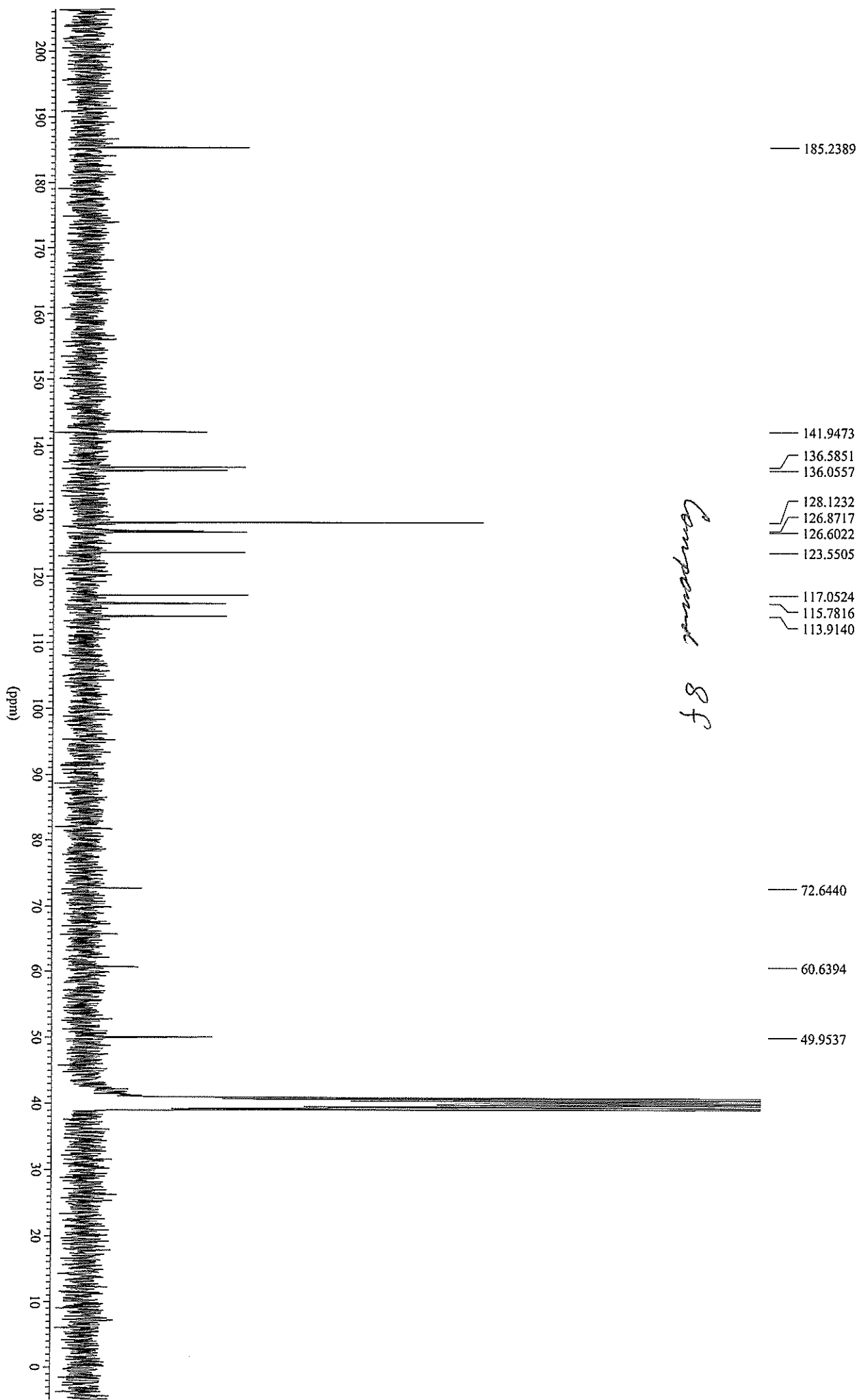


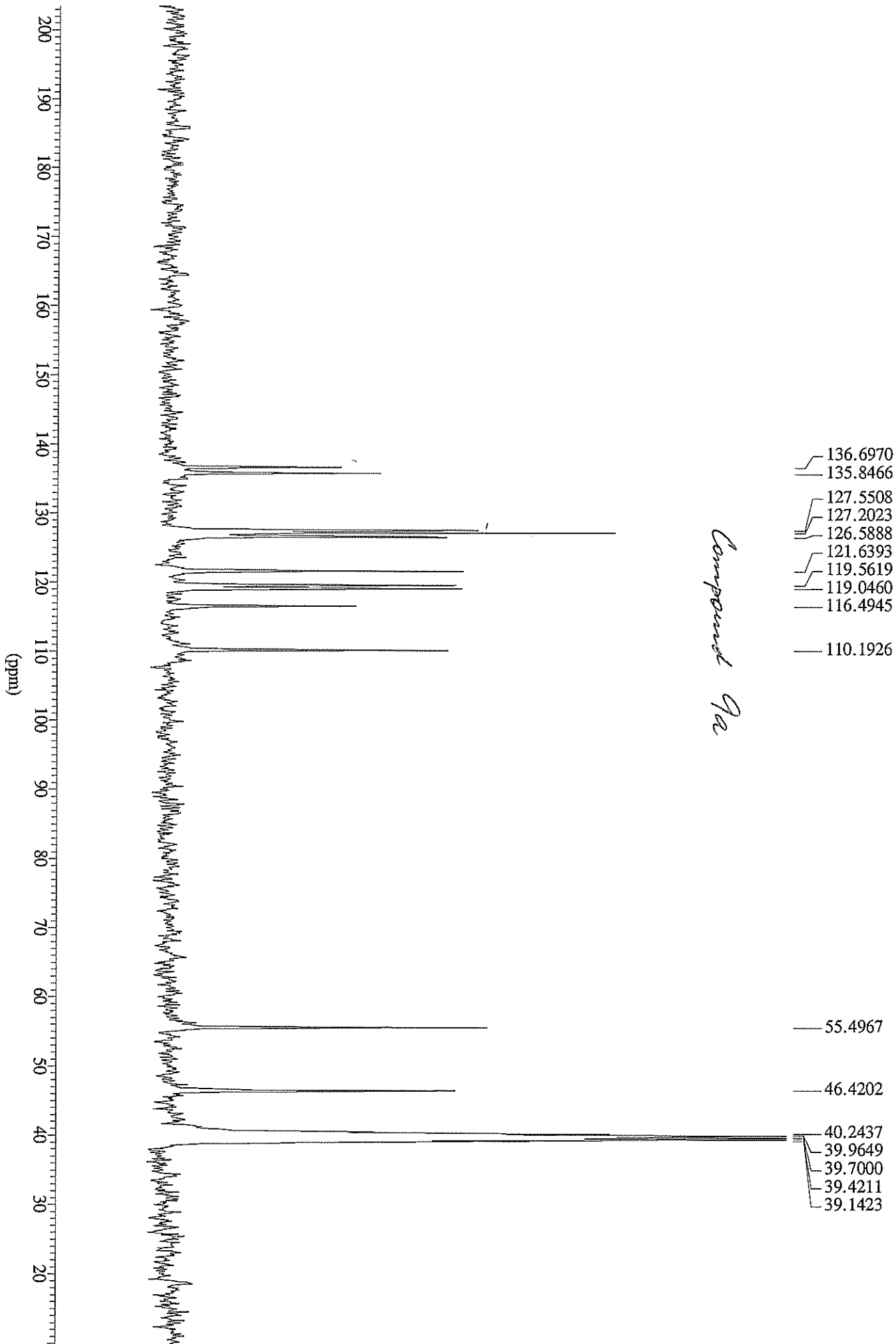


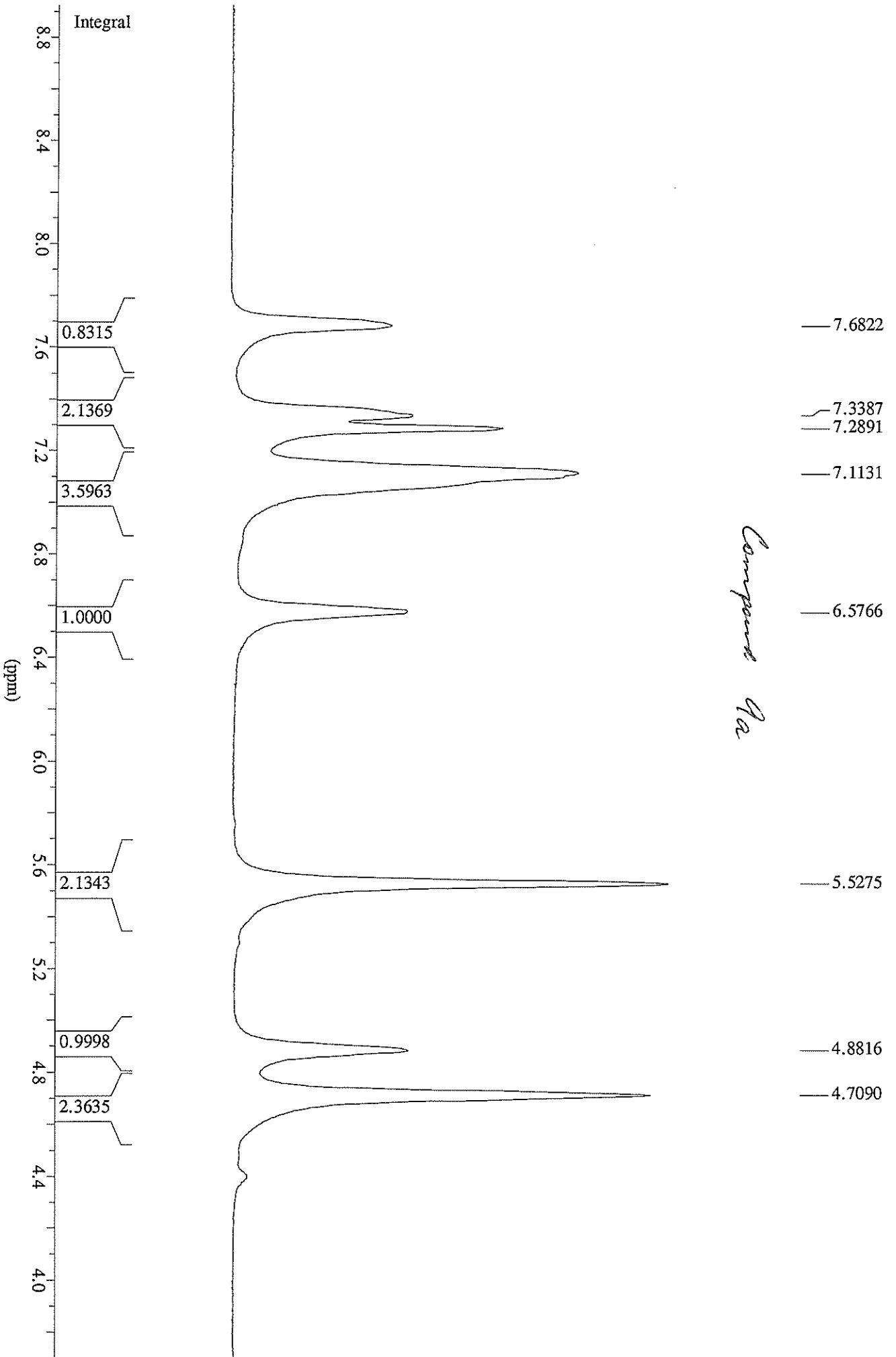


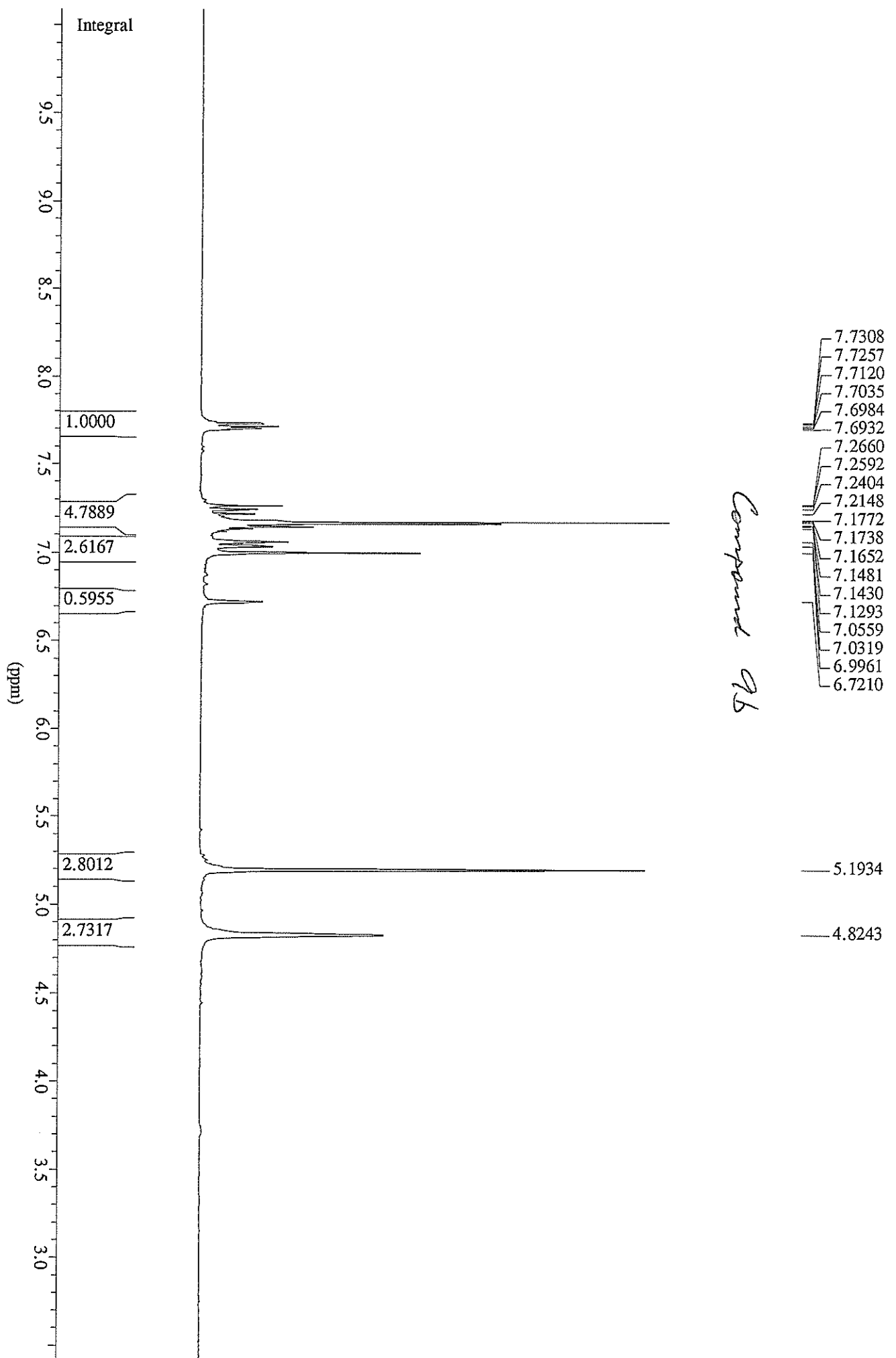


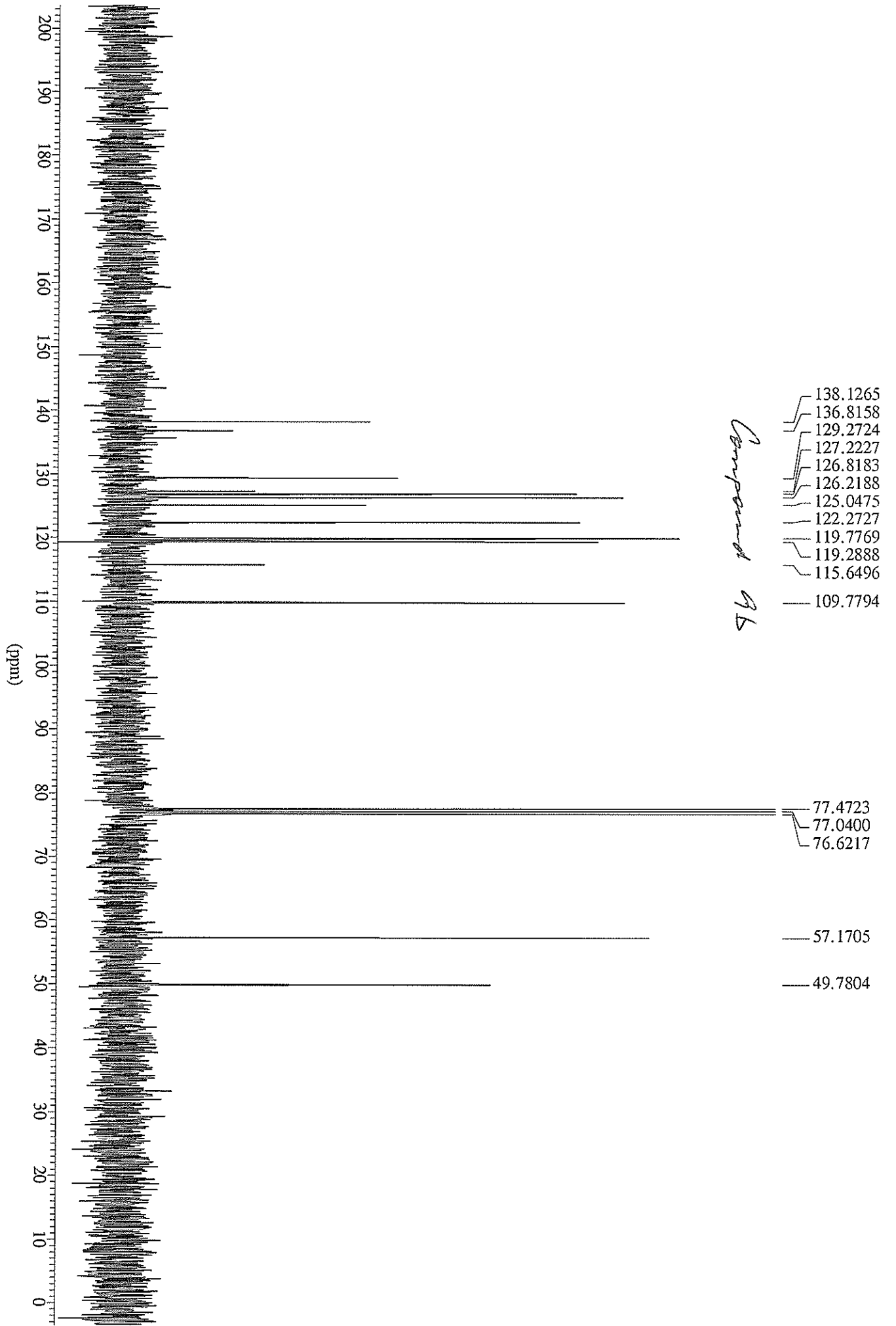


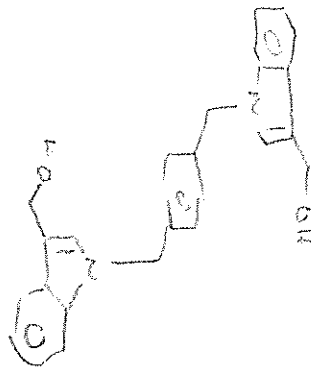
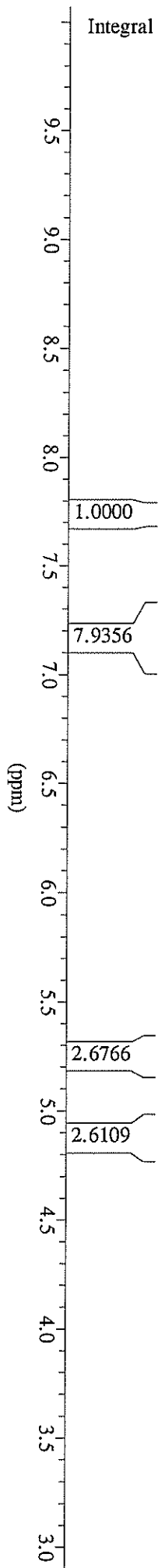












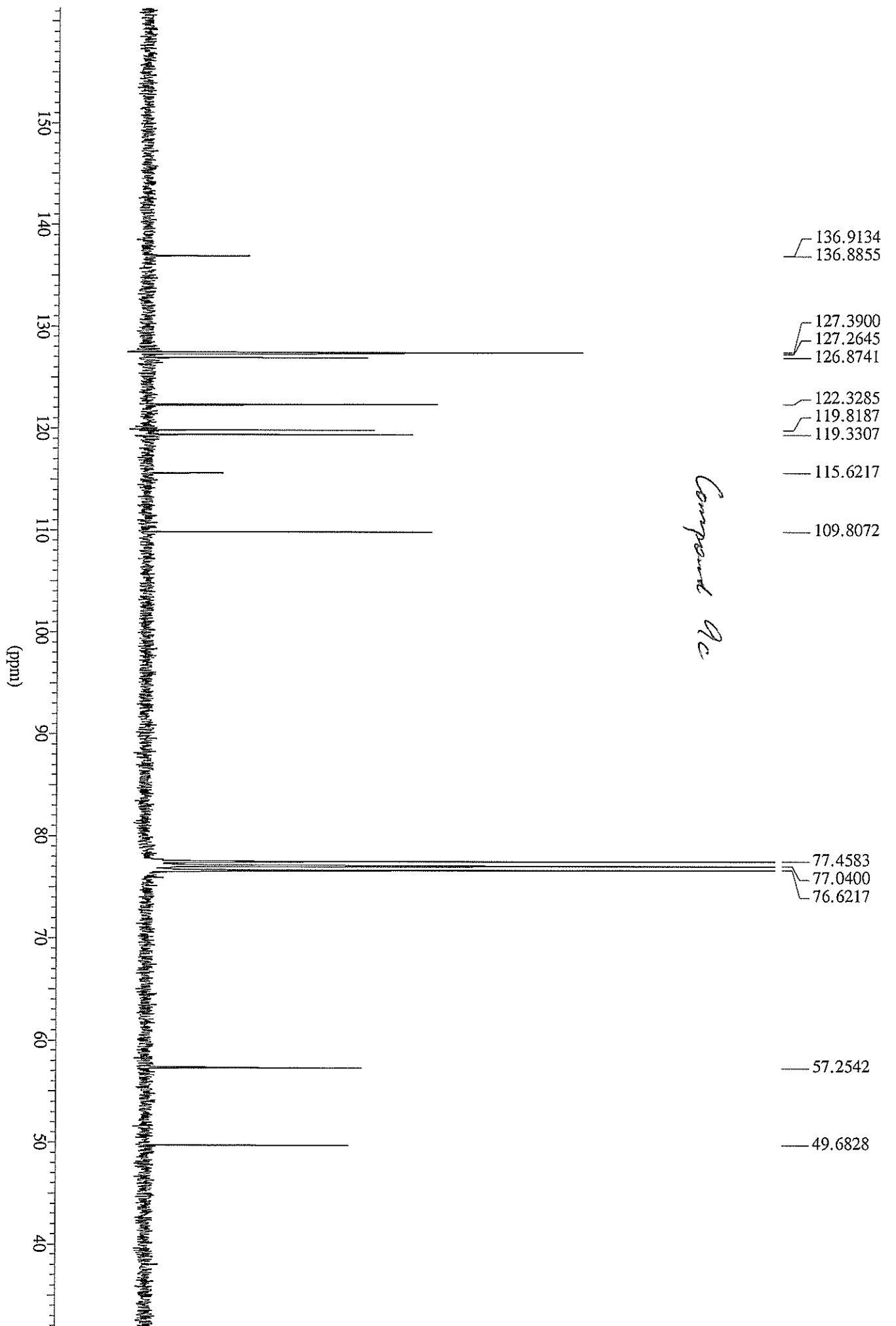
*Compound 9c*

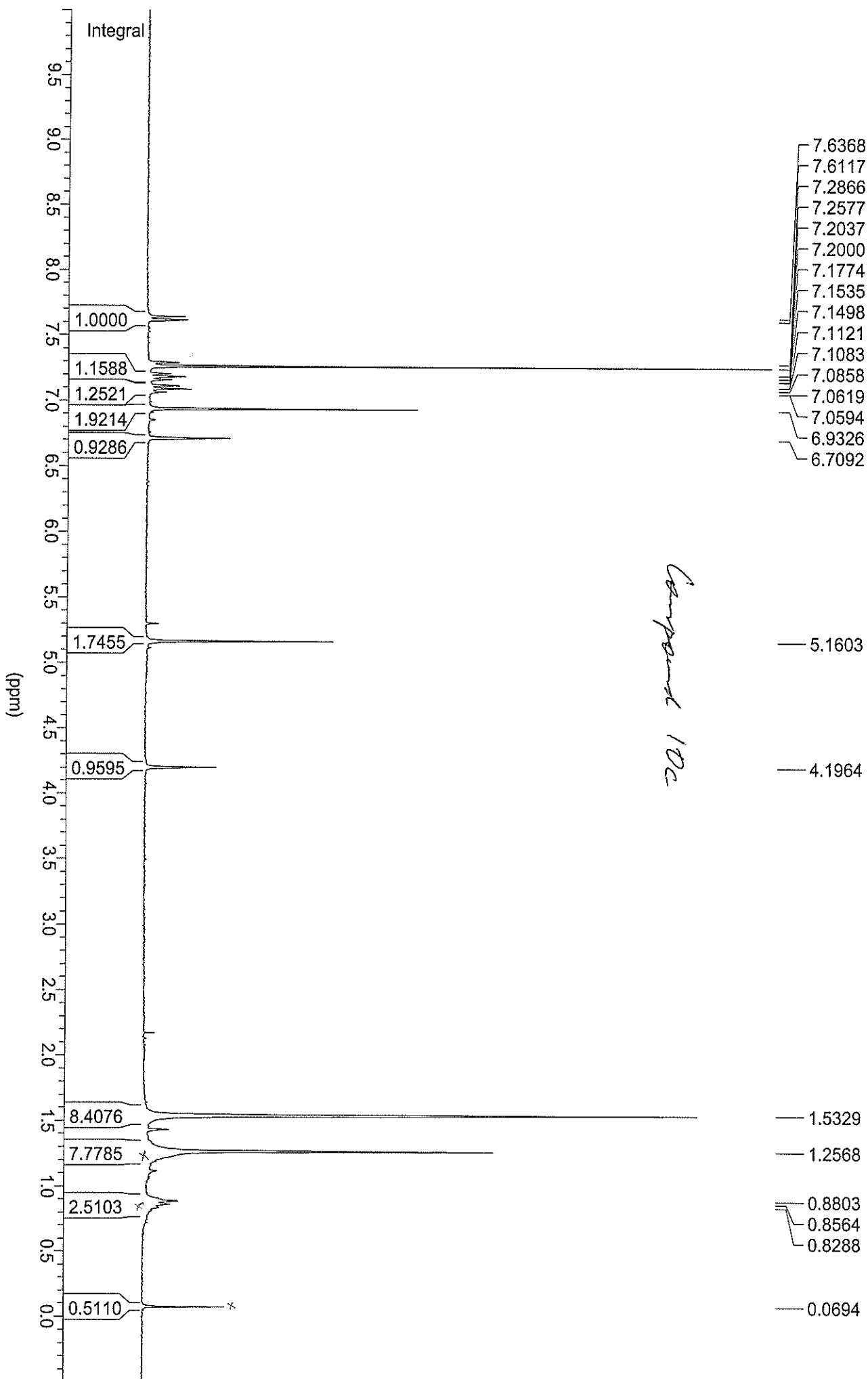
- 7.7445
- 7.7394
- 7.7206
- 7.7171
- 7.2592
- 7.2421
- 7.2353
- 7.2199
- 7.2165
- 7.1977
- 7.1926
- 7.1721
- 7.1652
- 7.1447
- 7.1413
- 7.1225
- 7.1174
- 7.0900
- 7.0490

— 5.2429

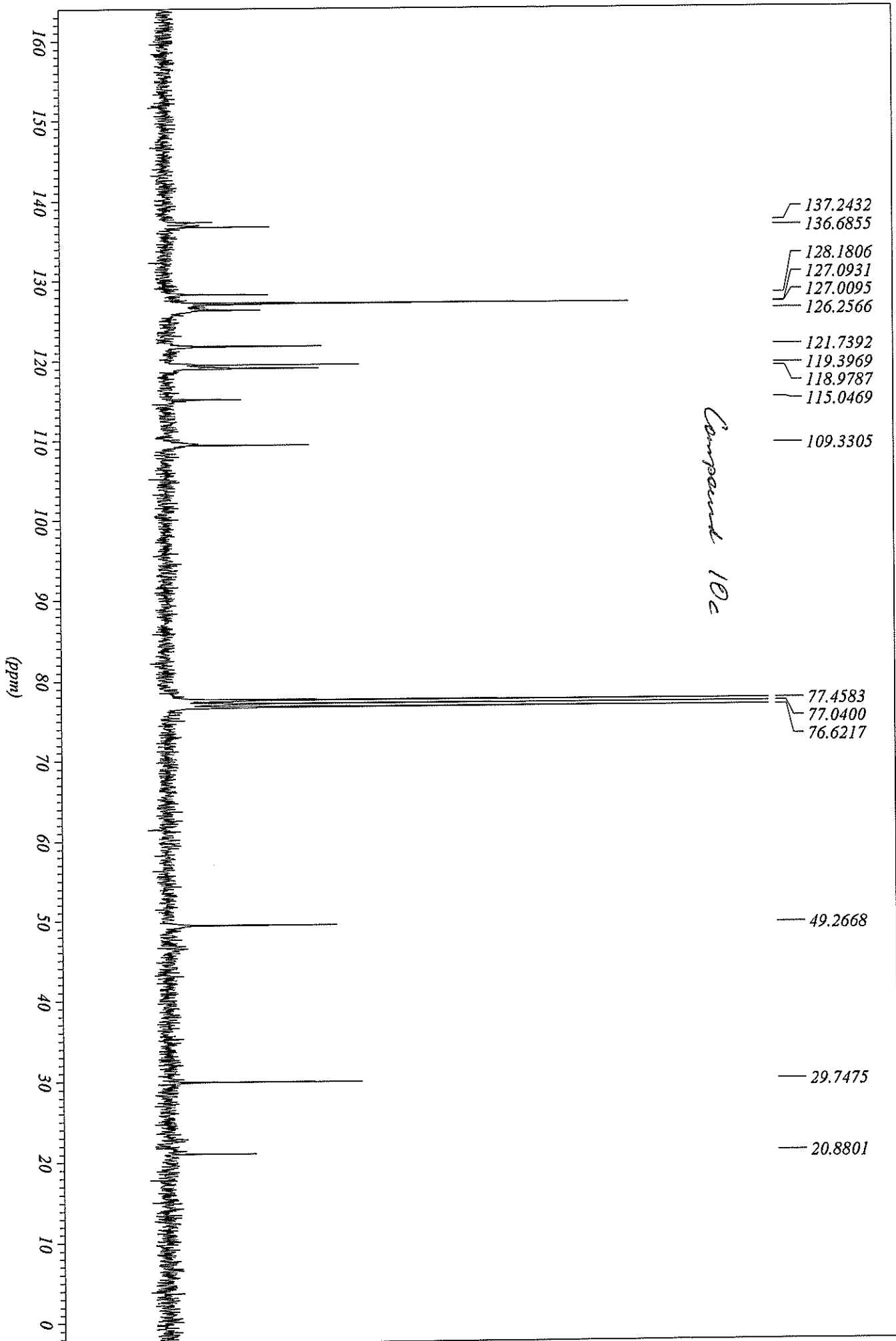
— 4.8602

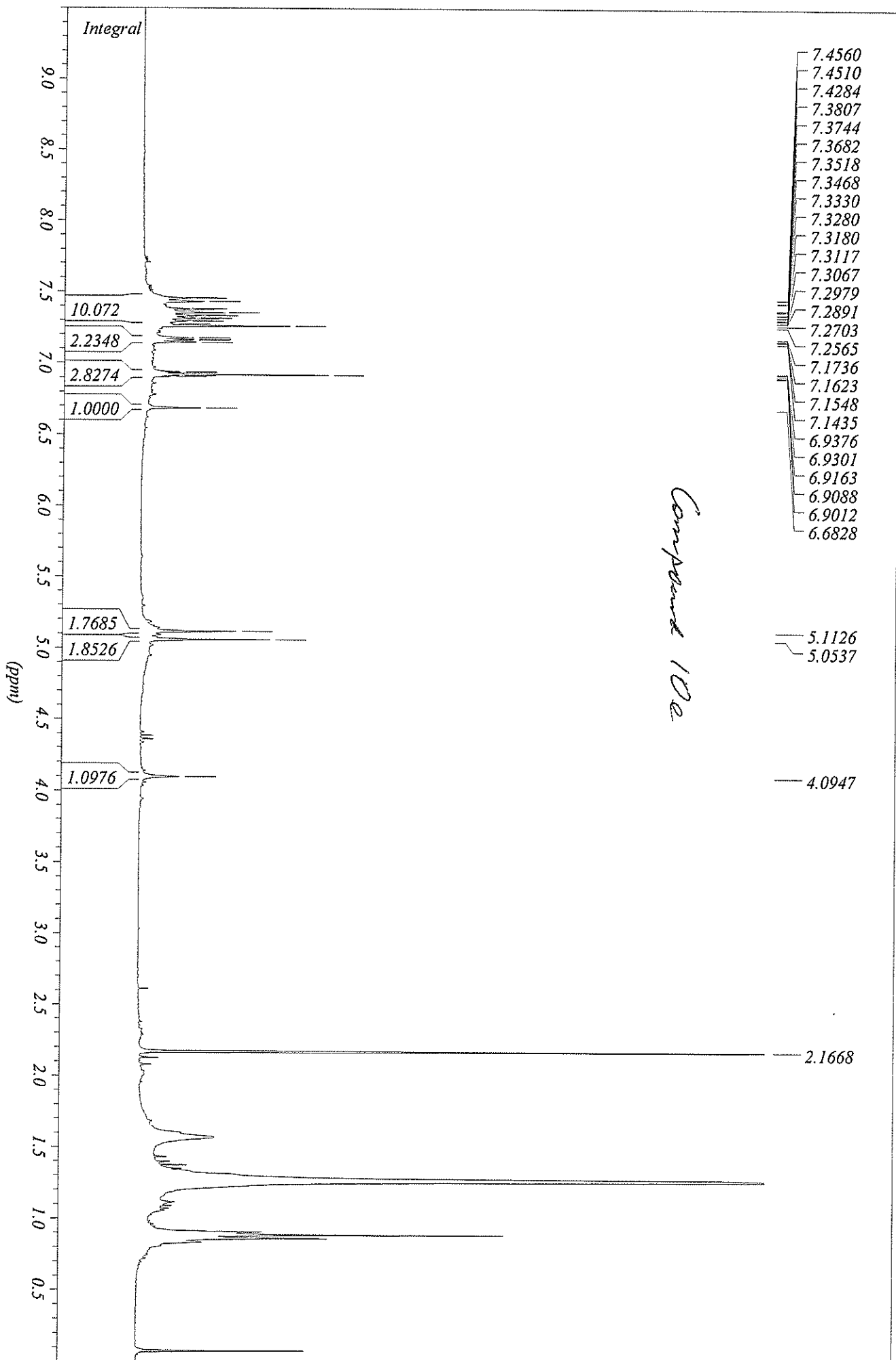
*Compound Ac*

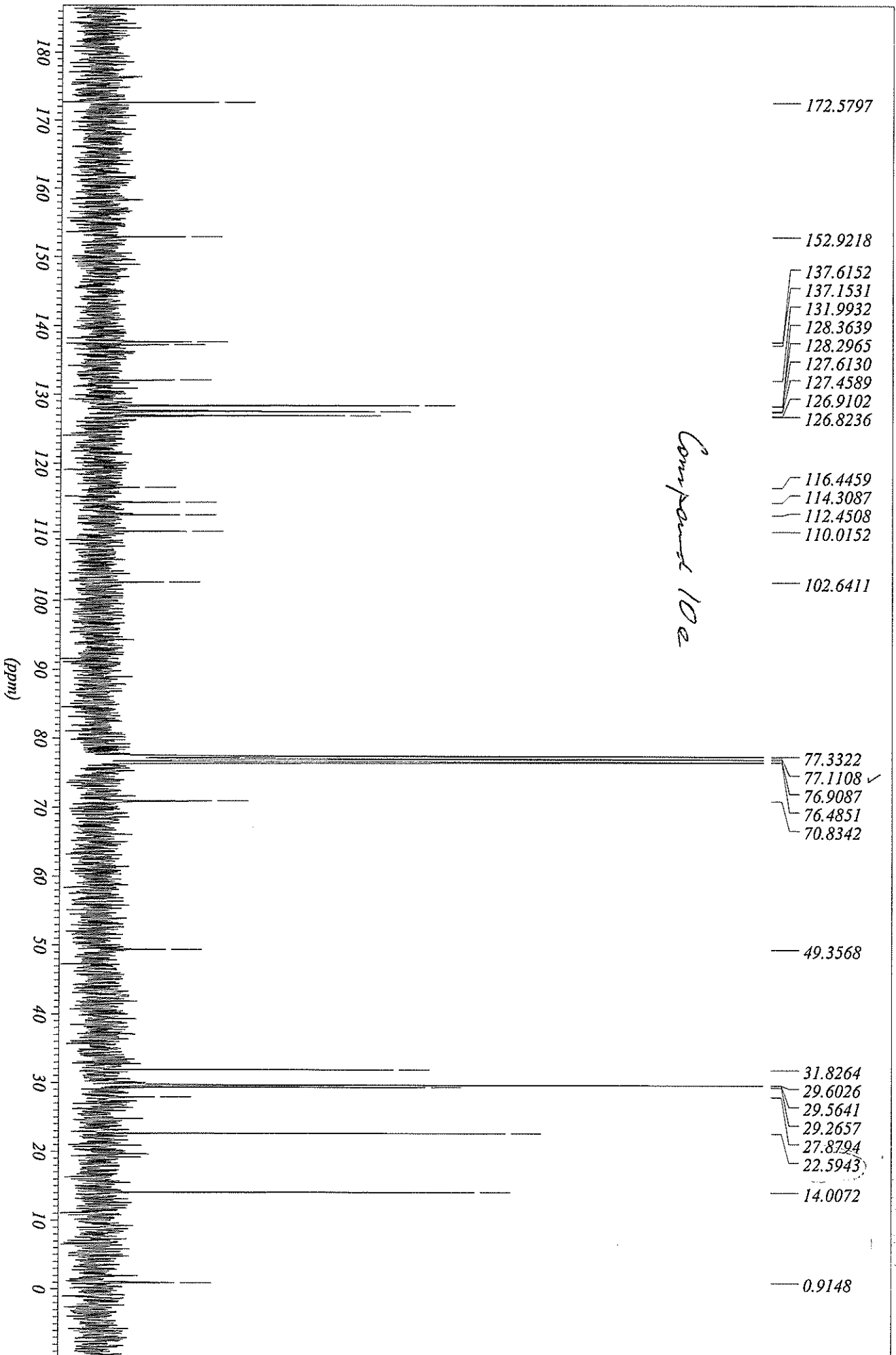


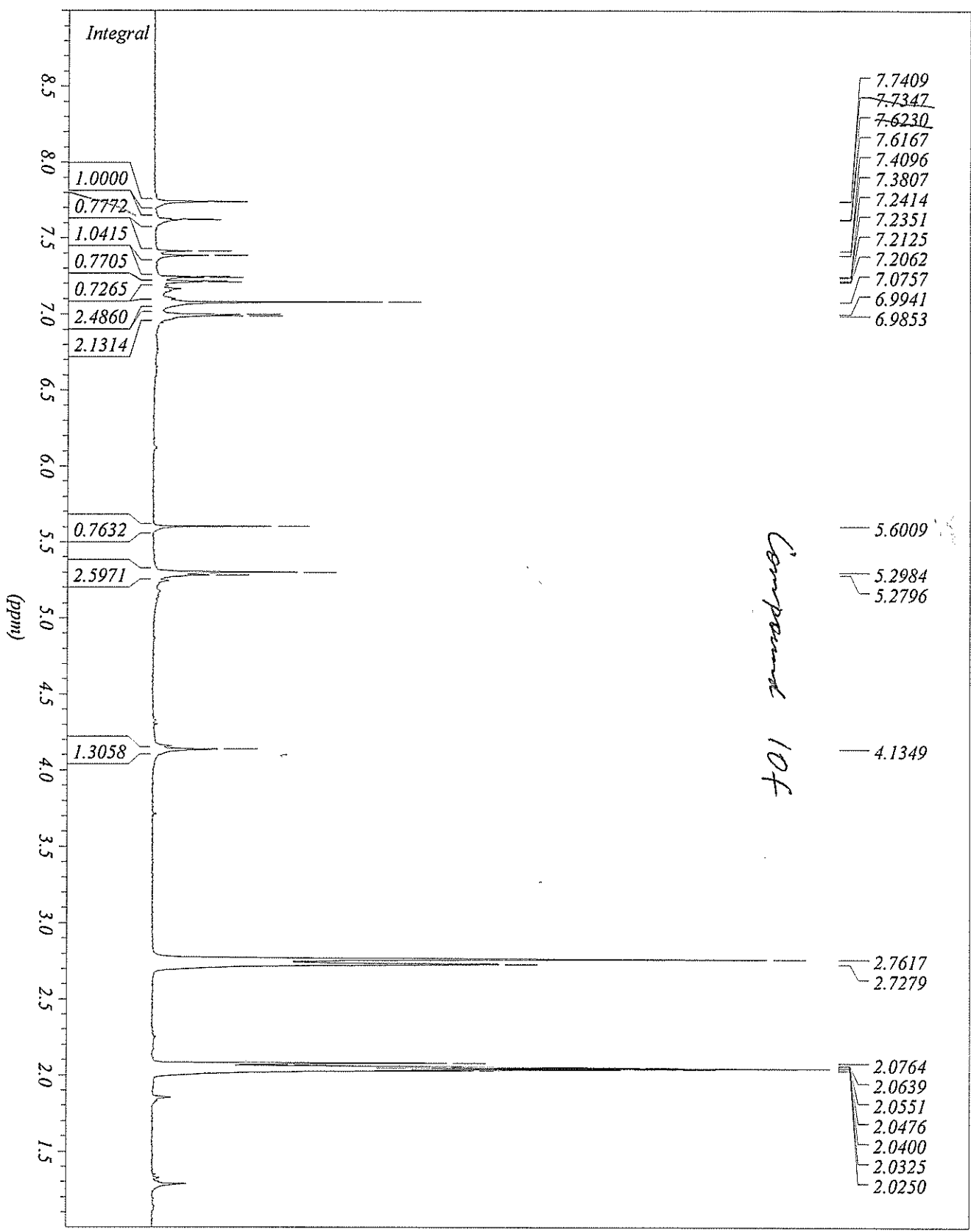






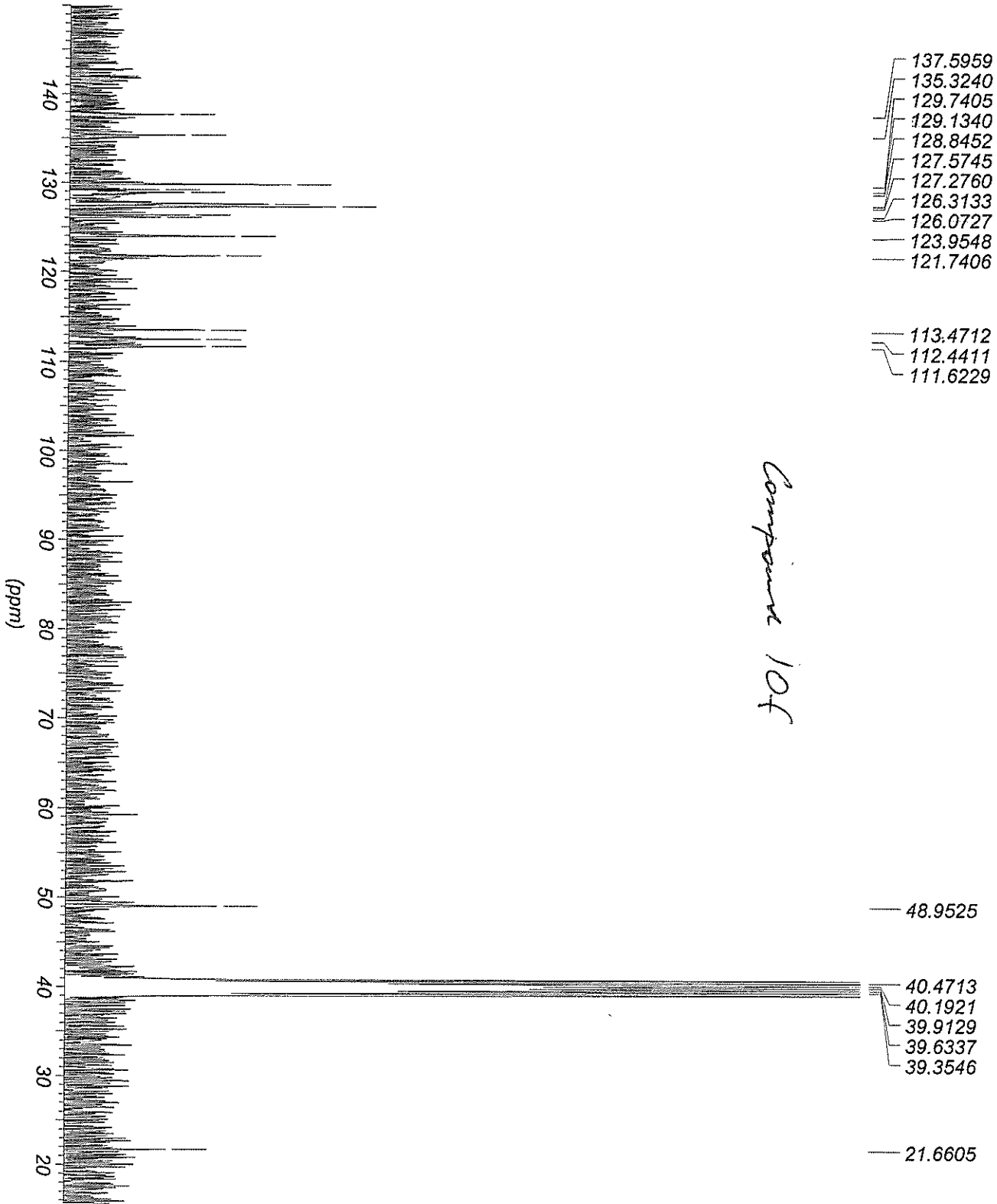






*Compound 10f*

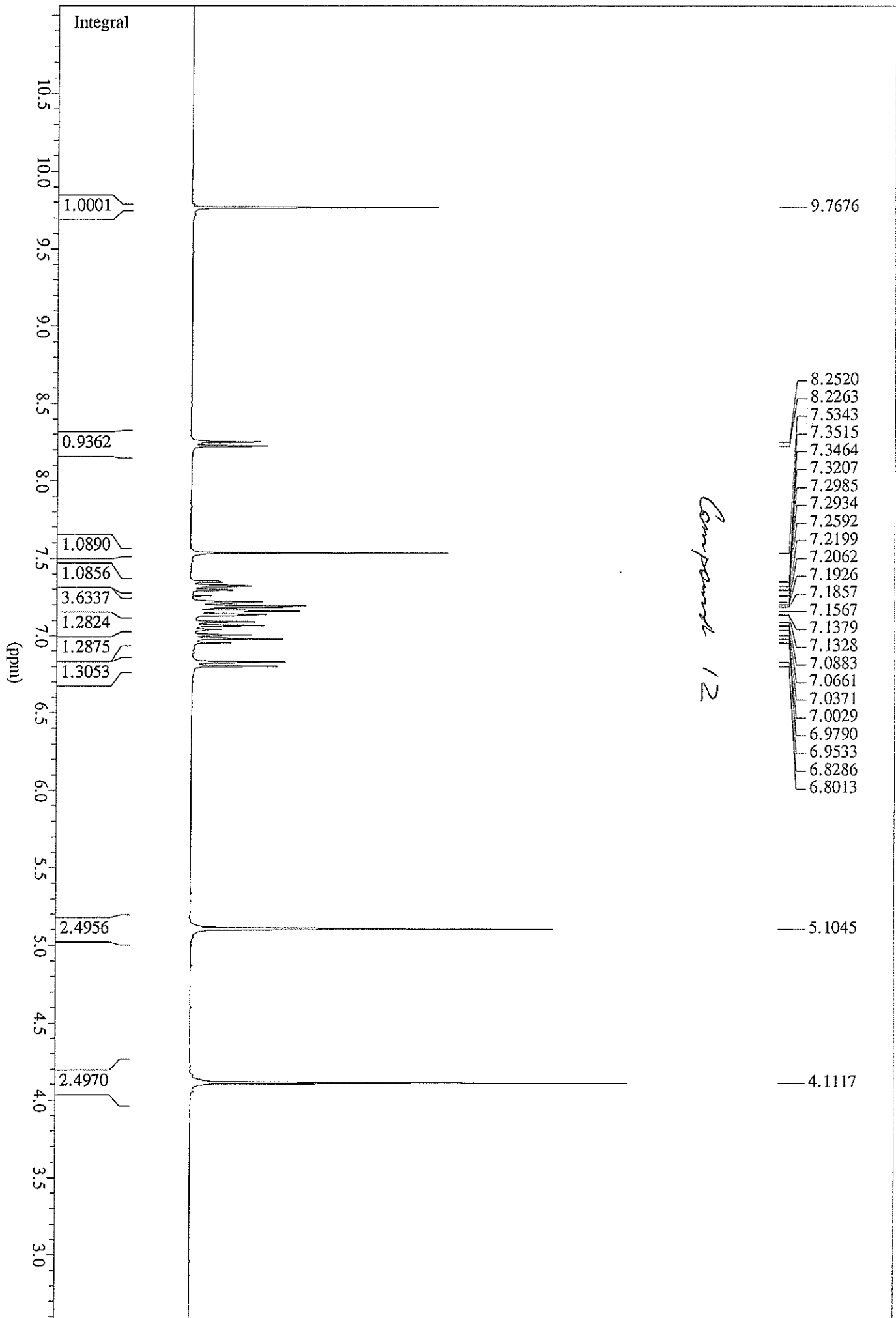
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 NAME : 07\_09k1s  
 EXPNO : 40  
 PROCNO : 1  
 \*\*\* Acquisition Parameters \*\*\*  
 D11 : 1.0000000 sec  
 DATE\_1 : 19-18-42  
 DATE\_2 : Sep 06 2004  
 DE : 12.0 usec  
 DS : 2  
 EXP : PS done  
 INSTRUM : dpx1  
 NS : 16  
 O1 : 1853.67 Hz  
 P10 : 10.1 usec  
 P11 : 10.1 usec  
 P12 : -3.0 dB  
 PULPROG : zg30  
 RG : 912.2999878  
 RO : 20 Hz  
 SFO1 : 300.1718537 MHz  
 SFO2 : 300.1718537 MHz  
 SW : 20.5644 ppm  
 SW\_h : 6172.840 Hz  
 TD : 32768  
 TE : 303.2 K  
 \*\*\* Processing Parameters \*\*\*  
 TDof : 32768  
 \*\*\* 1D NMR Plot Parameters \*\*\*  
 SR : 11.95 Hz  
 AQ\_time : 2.6542080 sec

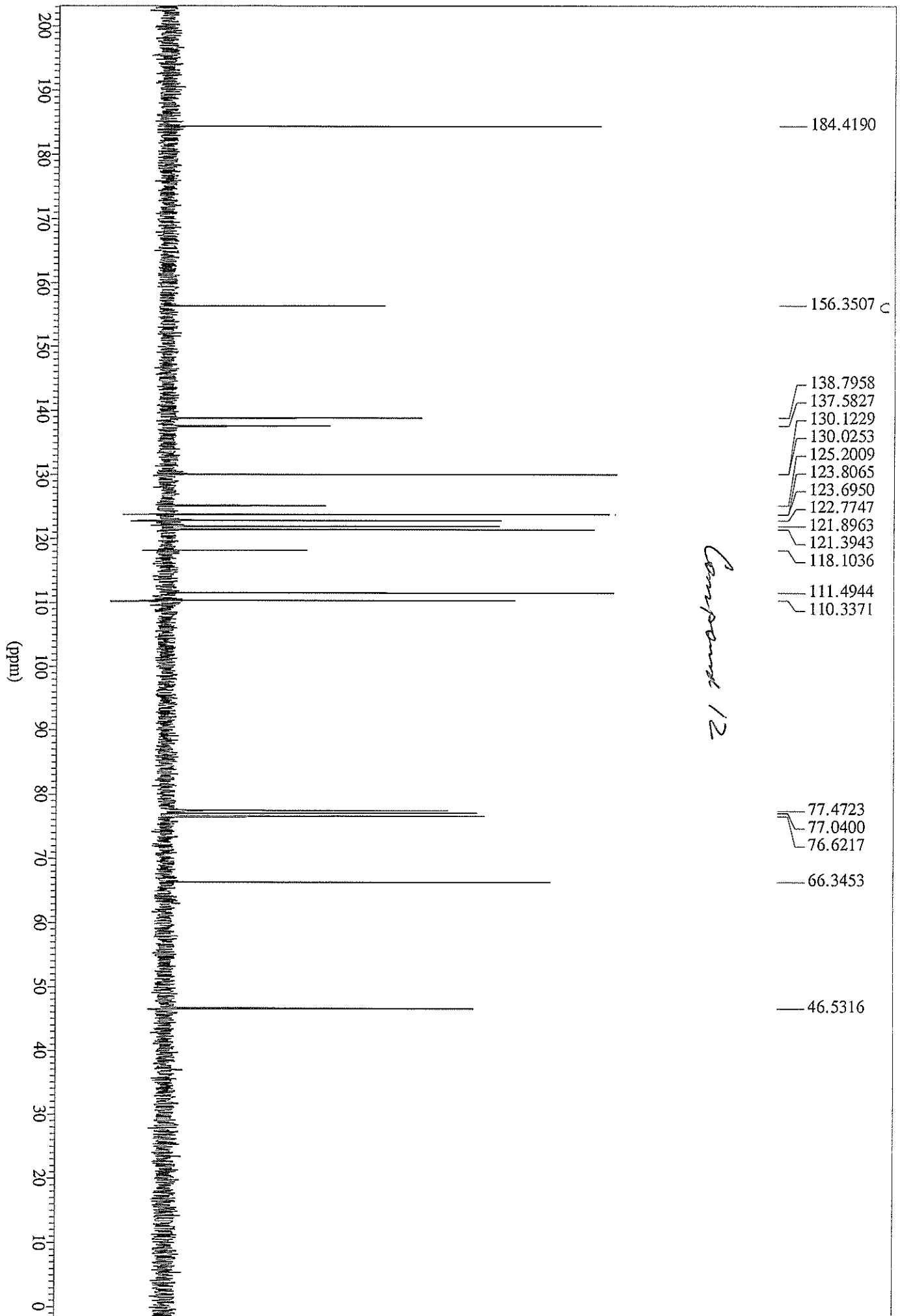


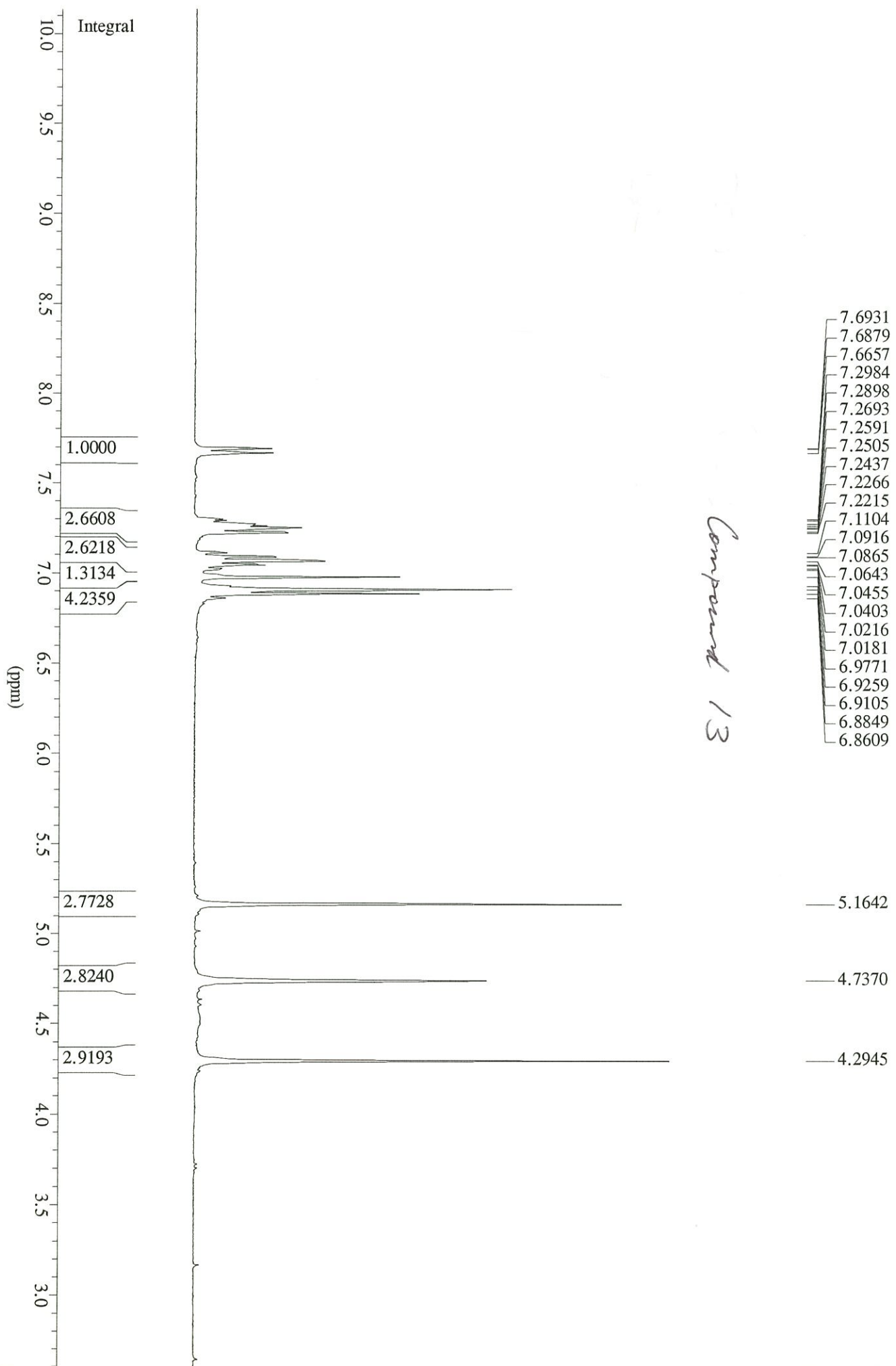
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*** Current Data Parameters ***
NAME       :      Ks25.08
EXPNO     :      10
PROCNO    :      1
*** Acquisition Parameters ***
DATE_1    :      05:06:33
DATE_d    :      Aug 25 2006
DS        :      2
INSTRUM   :      dpx1
NS        :      2048
O1        :      9532.38 Hz
P1[0]    :      7.5 usec
PROBHD    :      5 mm QNP 1H/13C/31
PULPROG   :      zgpg30
RG        :      14596.5000000
RO        :      20 Hz
SFO1     :      75.4873094 MHz
SW       :      315.4109 ppm
SW_h     :      23809.524 Hz
TD       :      65536
TE       :      301.2 K
*** 1D NMR Plot Parameters ***
SR       :      38.49 Hz
AQ_time  :      1.3762560 sec

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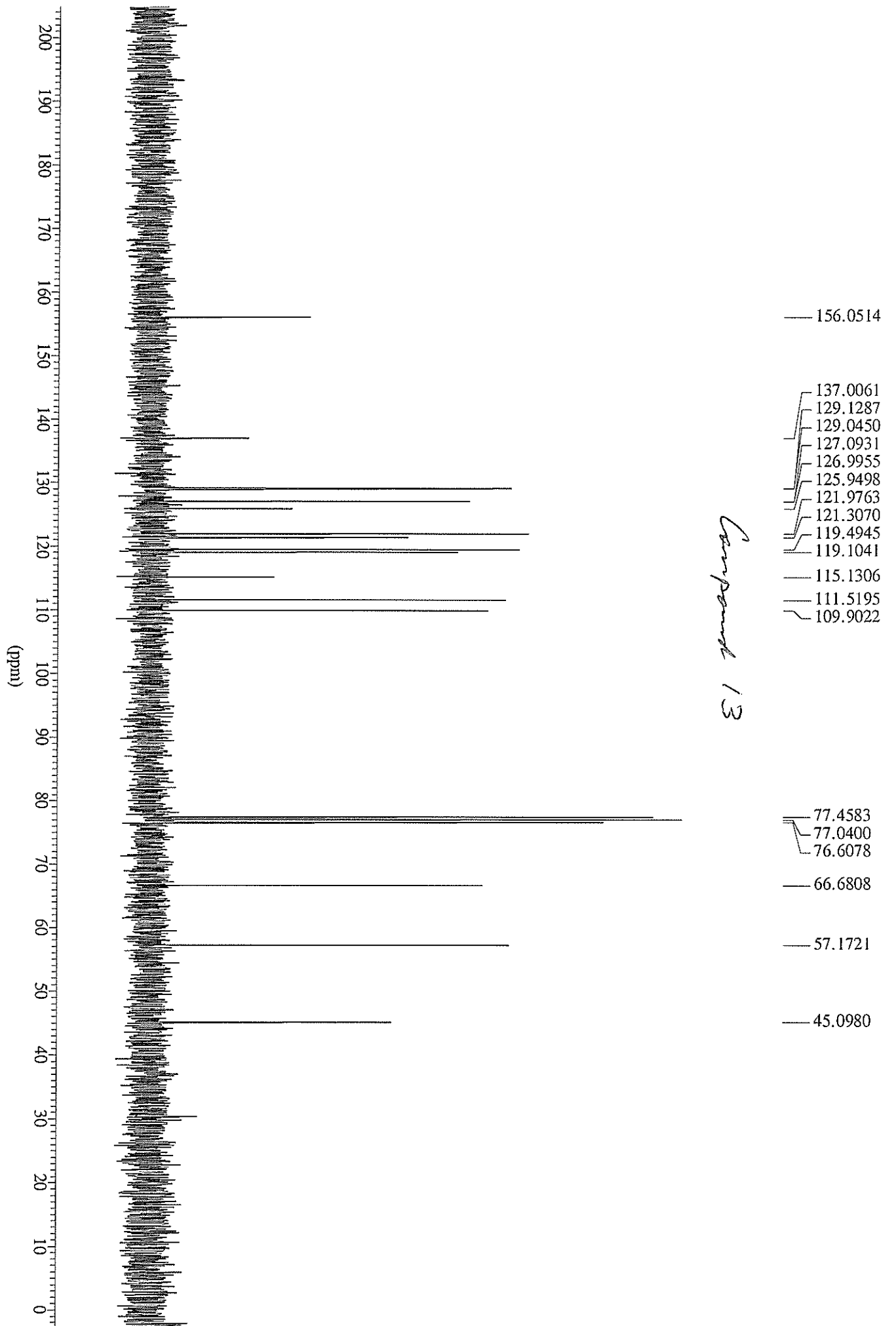


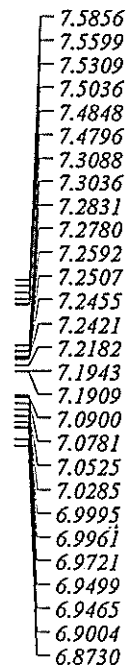
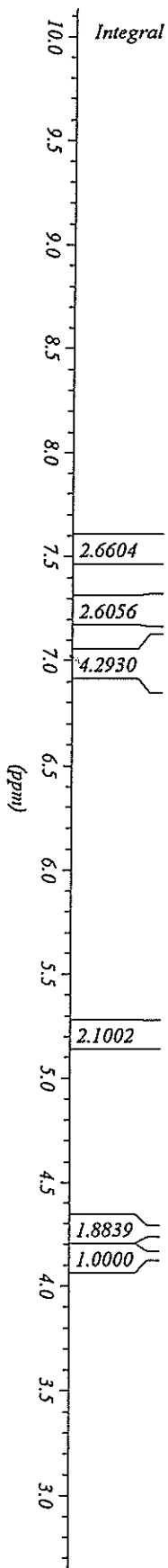




Compound 13

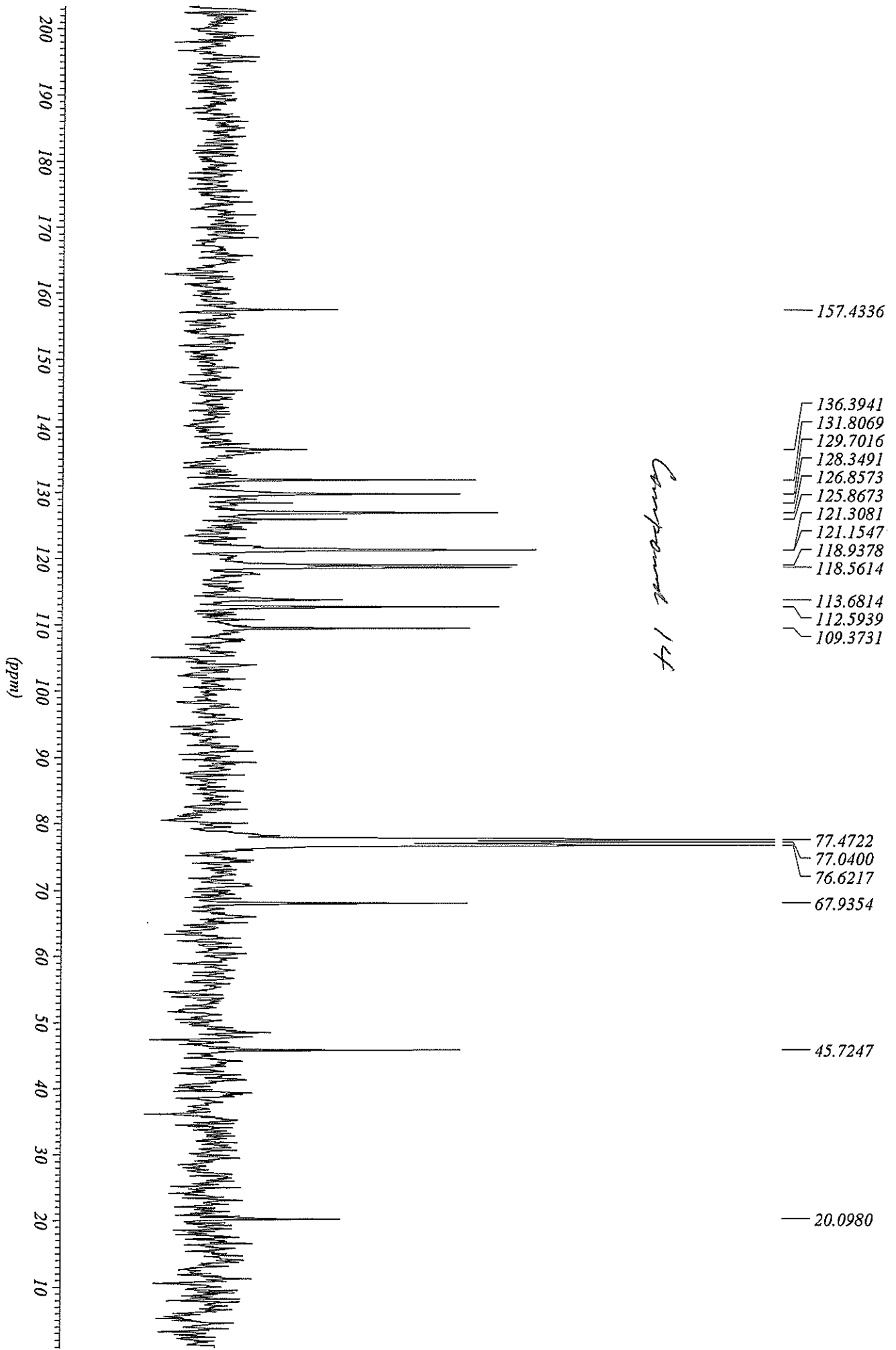


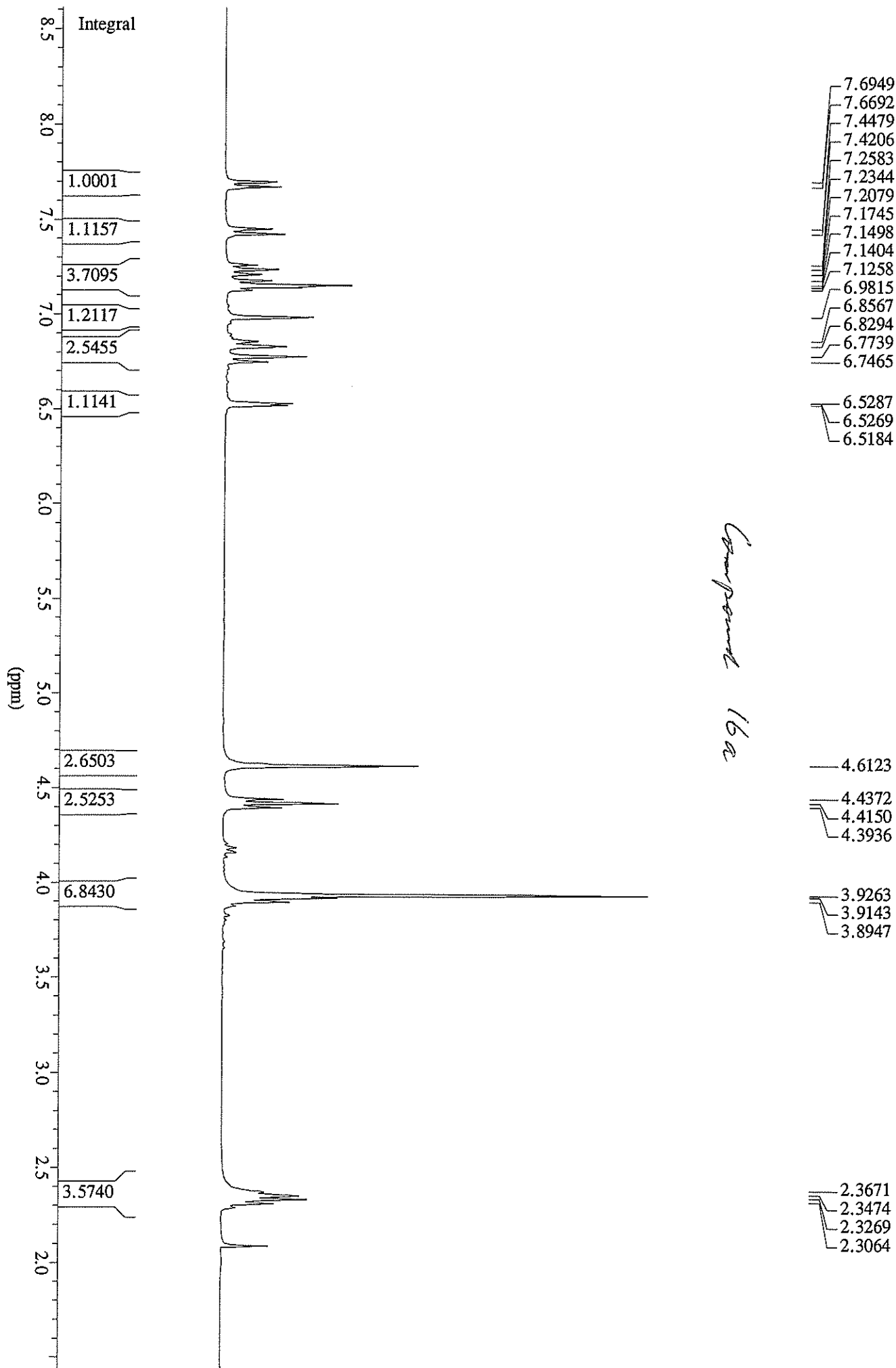


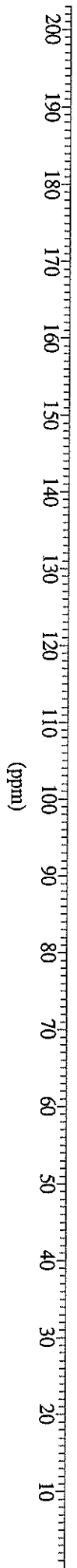


*Compound 14*



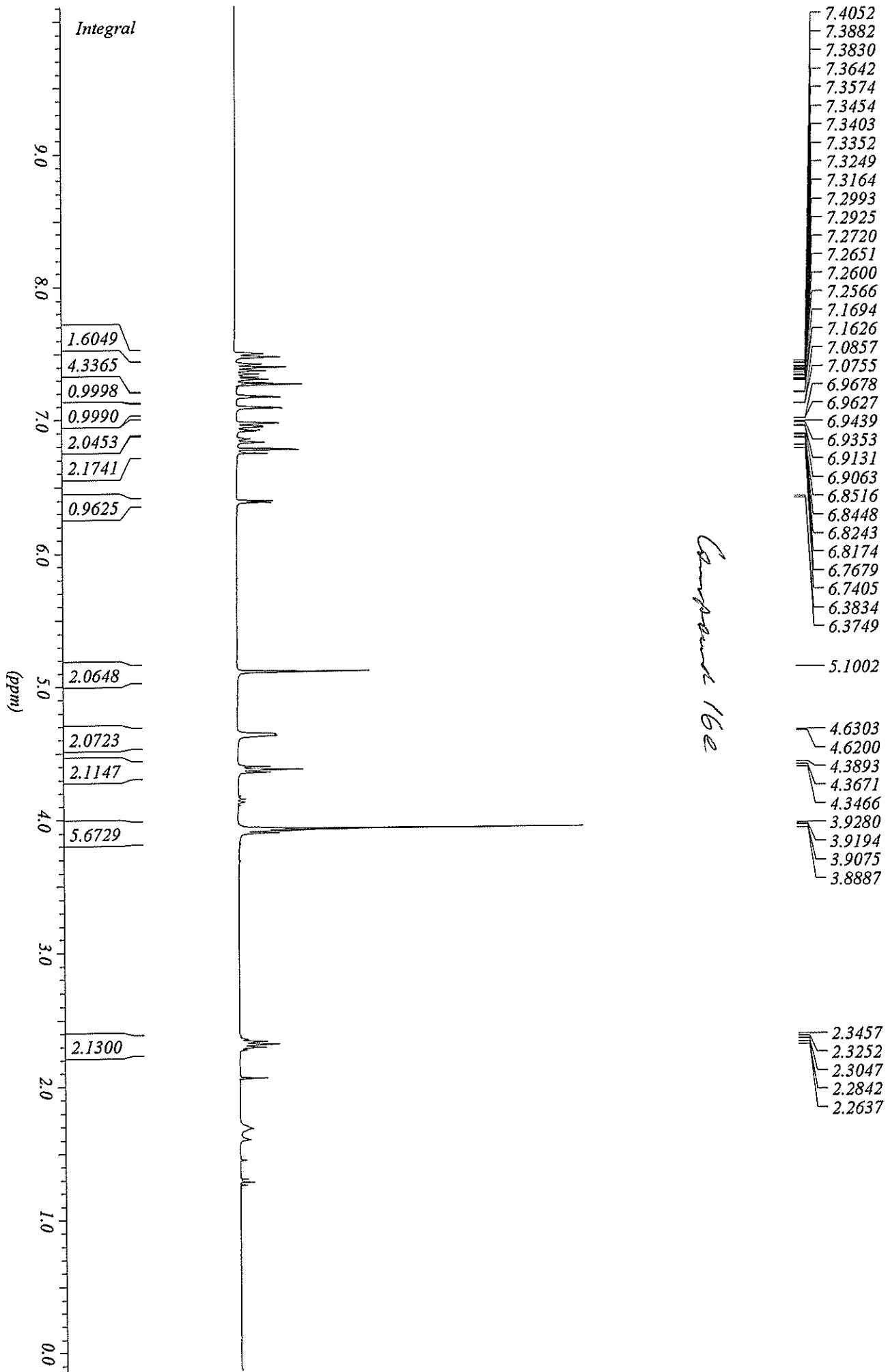




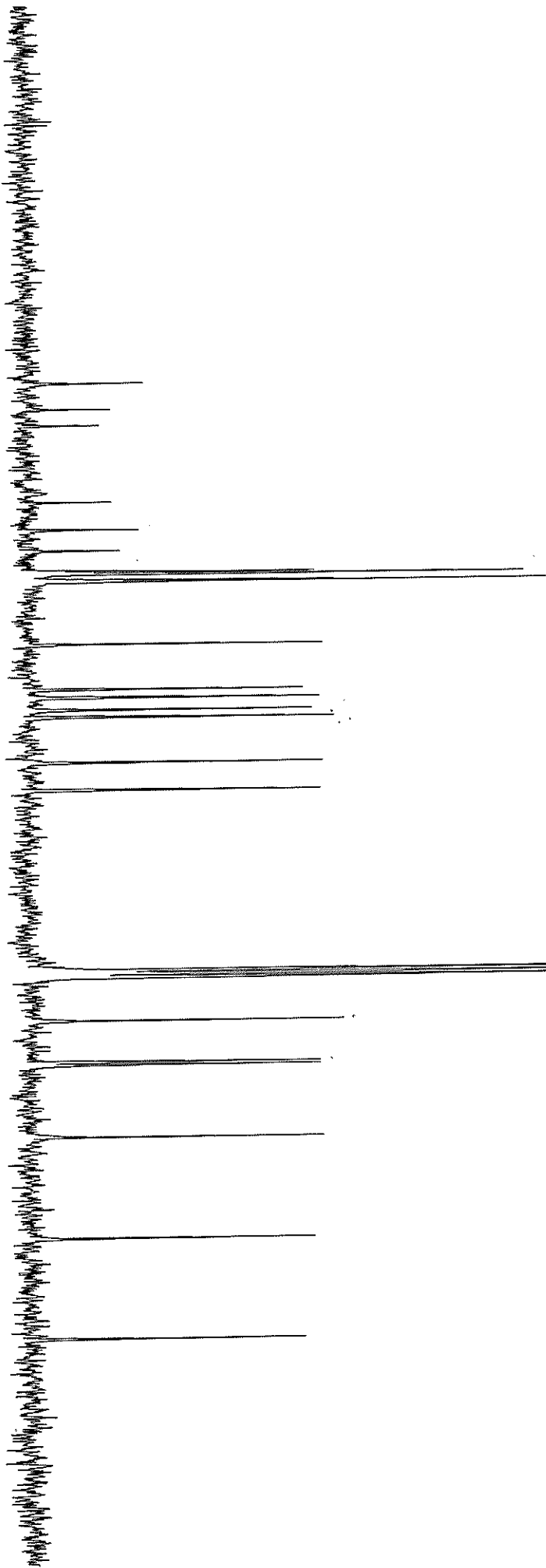


*Compound 16a*

- 149.5560
- 147.4646
  
- 135.8363
- 134.2050
- 128.5164
- 128.0563
- 121.3359
- 120.8061
- 119.2585
- 119.1748
  
- 113.4723
- 110.8510
- 109.2755
  
- 101.0354
  
  
- 77.4722
- 77.0400
- 76.6217
  
- 65.5512
- 64.8820
  
- 55.7634
  
  
- 42.5318
  
  
- 29.6488



190  
180  
170  
160  
150  
140  
130  
120  
110  
100  
90  
80  
70  
60  
50  
40  
30  
20  
10  
(ppm)



*Compound 16c*

- 153.2090
- 149.8209
- 147.7295
- 137.8023
- 134.2608
- 131.5420
- 128.9347
- 128.7256
- 128.4886
- 127.7217
- 127.5265
  
- 119.4537
- 113.6675
- 112.6078
- 111.0184
- 110.0981
- 104.2562
- 100.8123
  
- 77.4583
- 77.0400
- 76.6078
- 70.9610
- 65.6906
- 65.3003
  
- 55.9447
  
- 42.8664
  
- 29.8997