Supplementary information

Otherwise inert reaction of sulfonamides/carboxamides with formamides via proton transfer-enhanced reactivity

Zaihai Niu,[a] Shaoxia Lin,[a] Zhiyong Dong,[a] Hao Sun,[a] Fushun Liang*[,a,b] and Jingping Zhang*[,a]

[a] *Department of Chemistry, Northeast Normal University, Changchun 130024, China. E-mail: liangfs112@nenu.edu.cn; zhangjingping66@yahoo.cn*

[b] *Key Laboratory for UV-Emitting Materials and Technology of Ministry of Education, Northeast Normal University, Changchun 130024, China*

Table of contents

I. General……..…….…….....S2

II. DFT-calculations on the proposed hydrogen bond interaction……..…..S2

III. DFT-calculations on the proposed halogen activated hydrogen bond interaction……...……..S3

IV. Copies of ^{1}H and ^{13}C NMR spectra for compounds **3** and **5** ..….....….…..….....S6

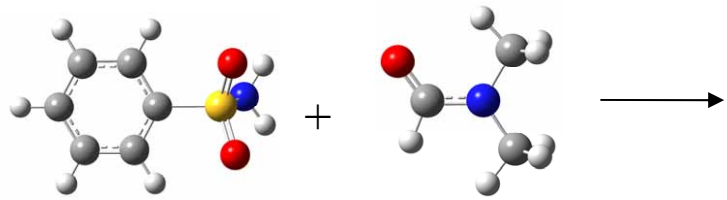
I. General

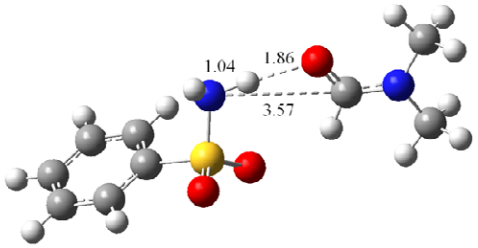
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ºC on a Varian 500 MHz and 125 MHz, respectively, and TMS as internal standard. Elemental analyses were measured on an E-2400 analyzer (Perkin-Elmer). Mass spectra were recorded on Agilient 1100 LCMsD mass spectrometer.

II. DFT-calculations on the proposed hydrogen bond activation.

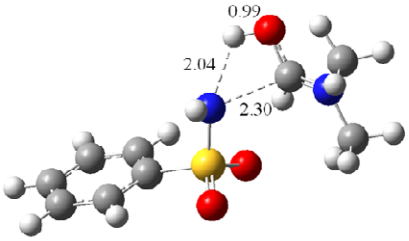
All of the DFT calculations were performed with the Gaussian 09 suite of programs. B3LYP3 method and the 6-31G* basis set were used for the geometry optimization of all the minima and transition states. Frequency analysis were carried out at the same level of theory to check the stationary points to be real minima or saddle points, and to evaluate its zero-point vibration energy (ZPVE).

Reaction a:

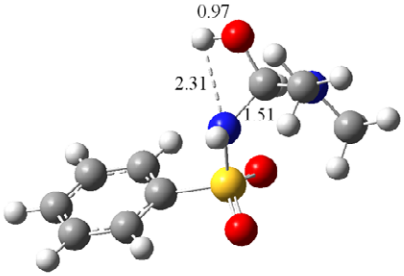




Com1a



TS1a



Int1a

Figure S1. Structures of intermediates and transition states for reaction a ($TsNH_2$ and DMF).

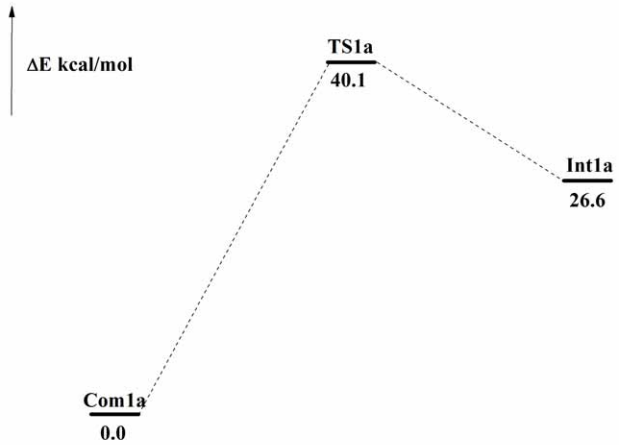
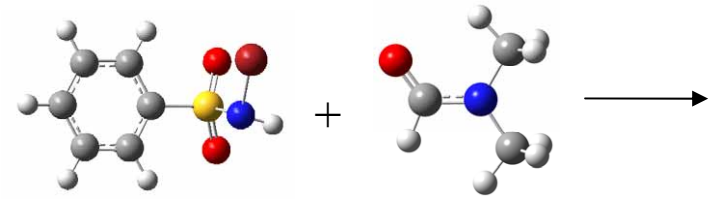
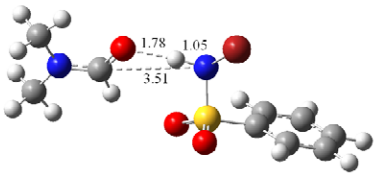


Figure S2. DFT-computed energy profile for reaction a.

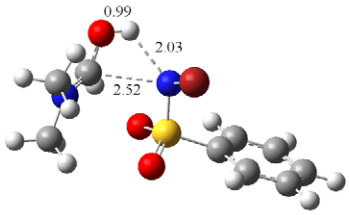
III. DFT-calculations on the proposed halogen activated hydrogen bond activation

Reaction b:

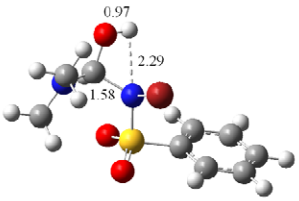




Com1b



TS1b



Int1b

Figure S3. Structures of intermediates and transition states for reaction b ($PhSO_2NHBr$ and DMF), in whichCom1b, TS1b and Int1b correspond to **6-8** in the main text, respectively.

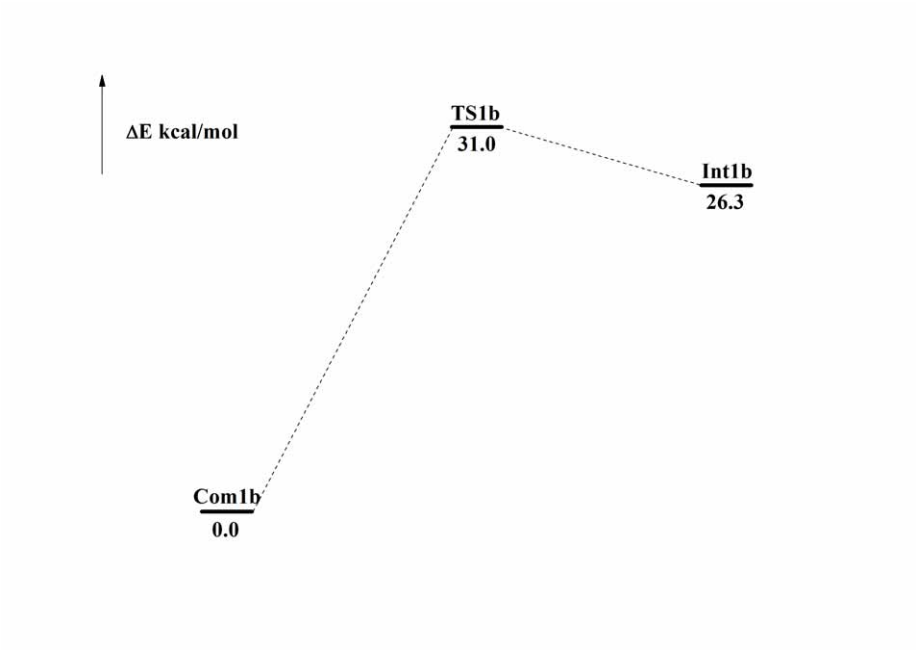
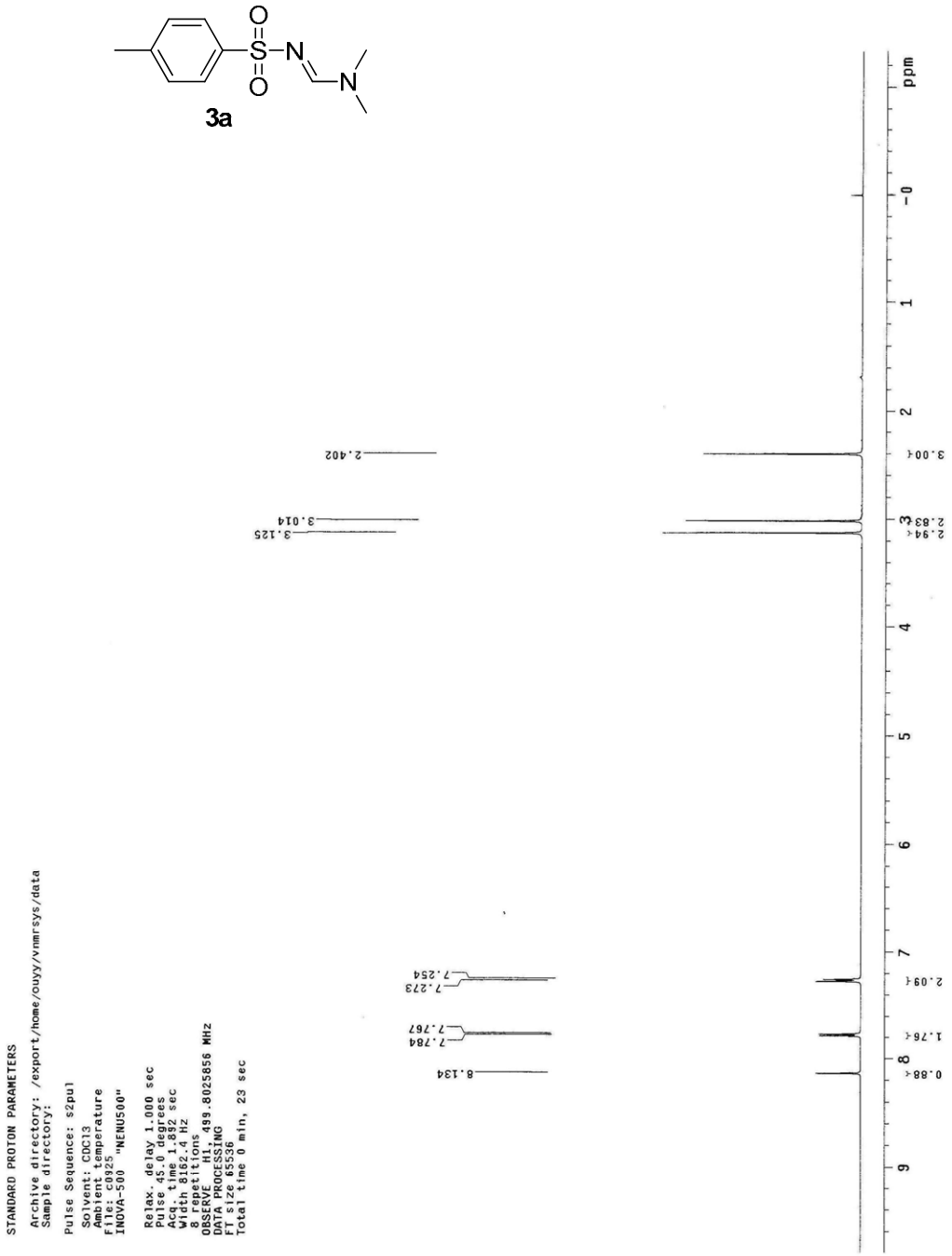
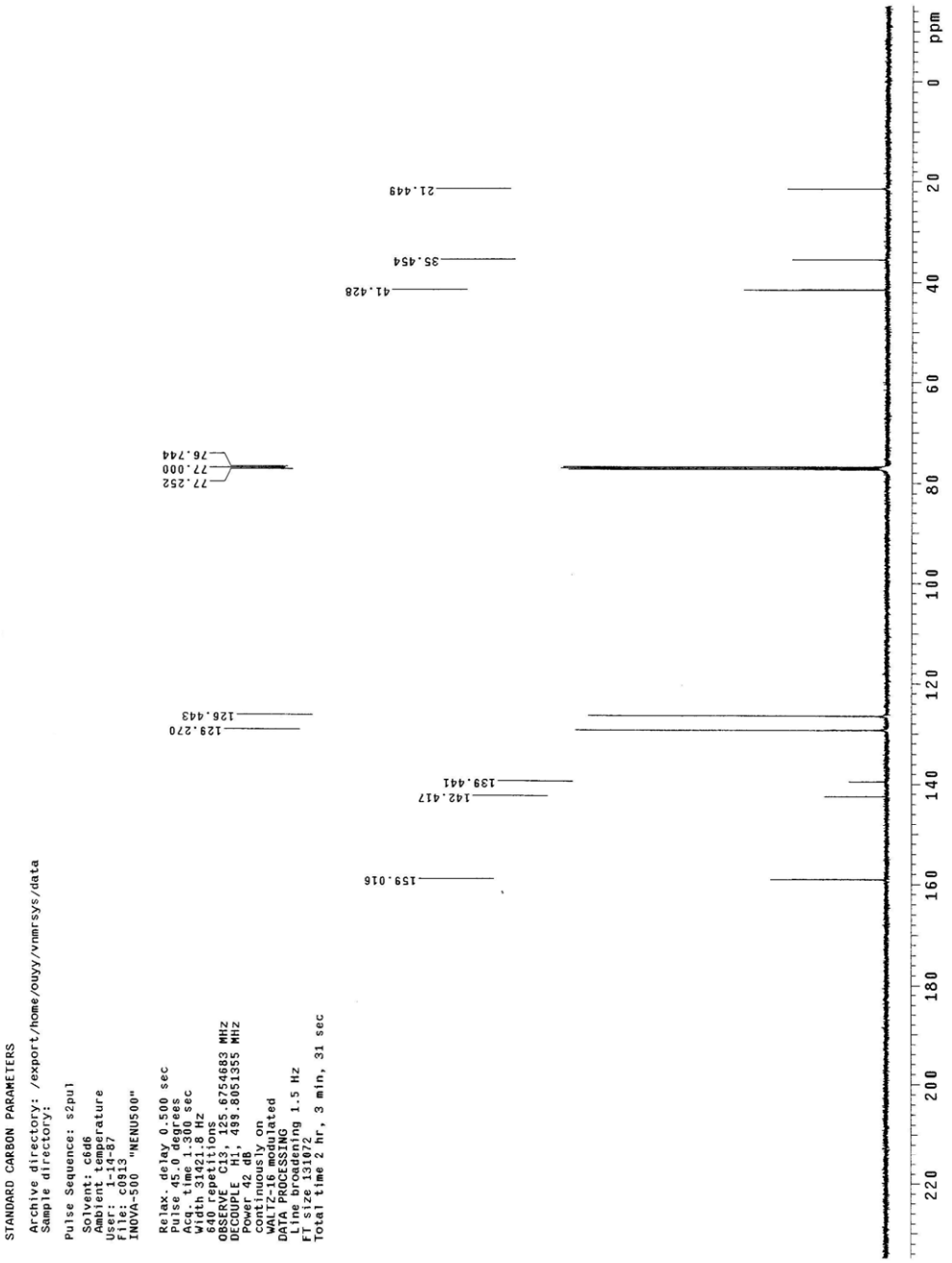
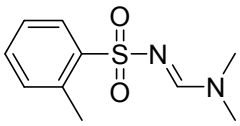


Figure S4. DFT-computed energy profile for reaction b.

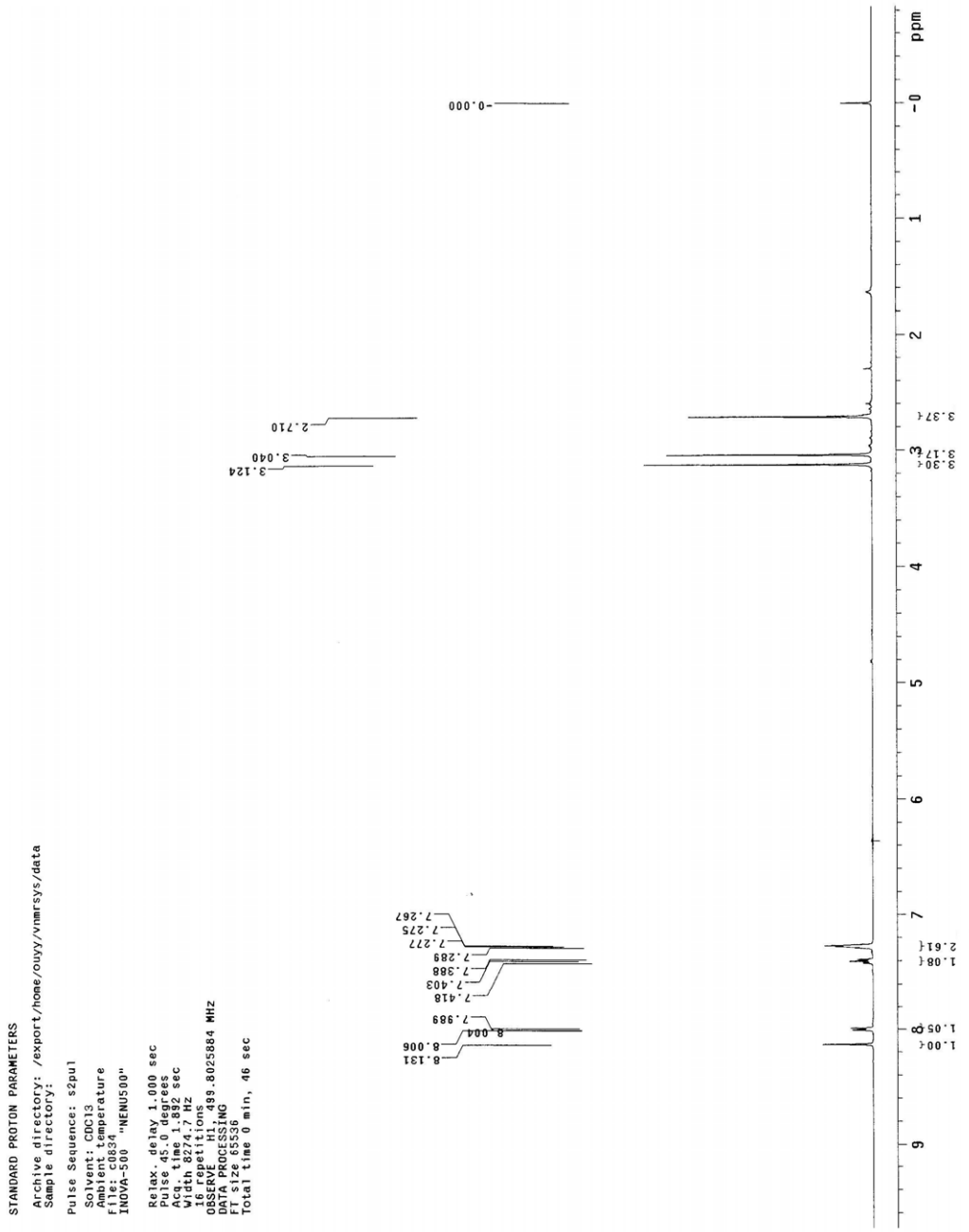
IV. Copies of ^{1}H and ^{13}C NMR spectra for compounds 3 and 5

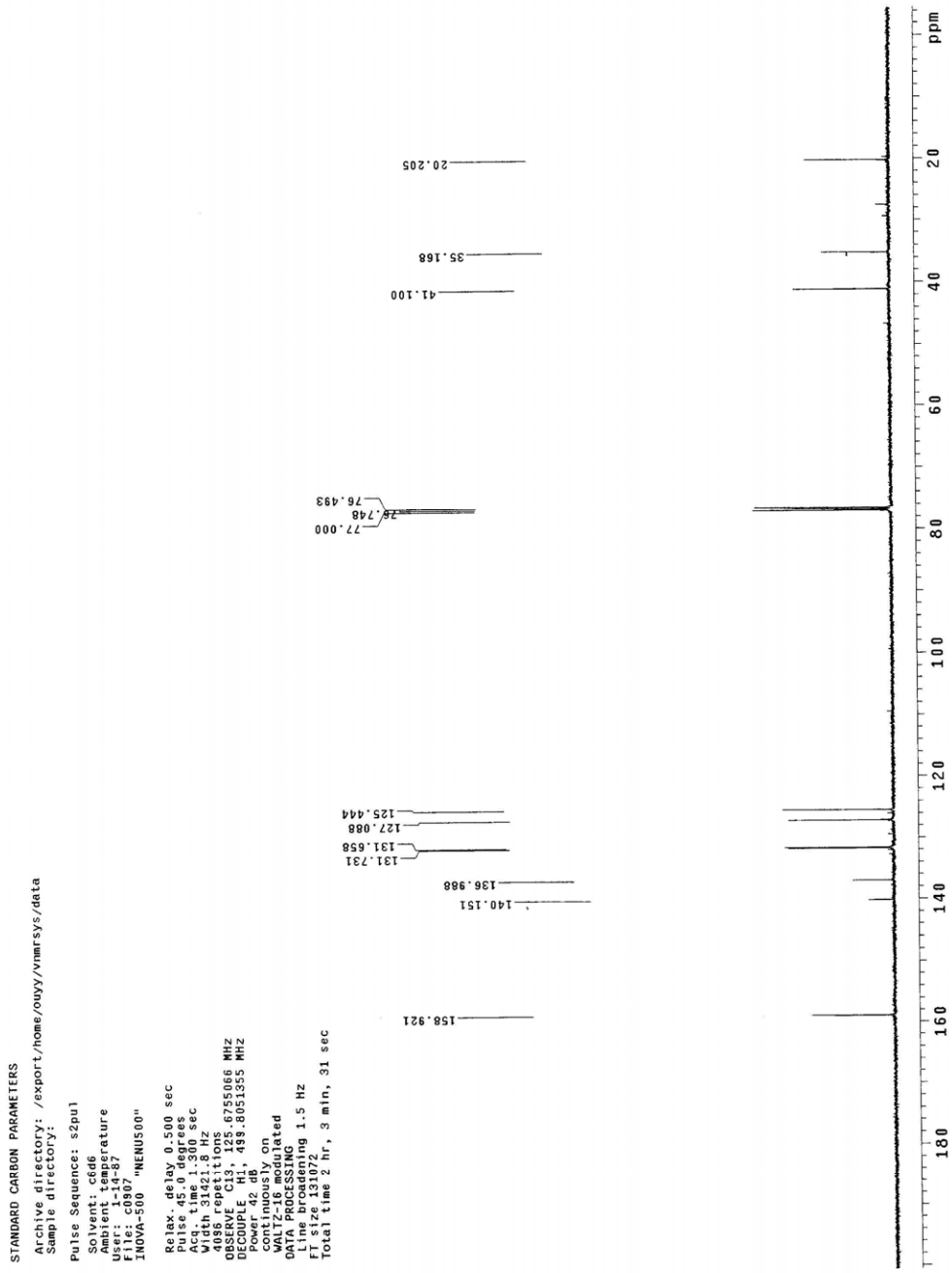


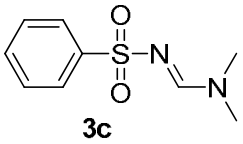




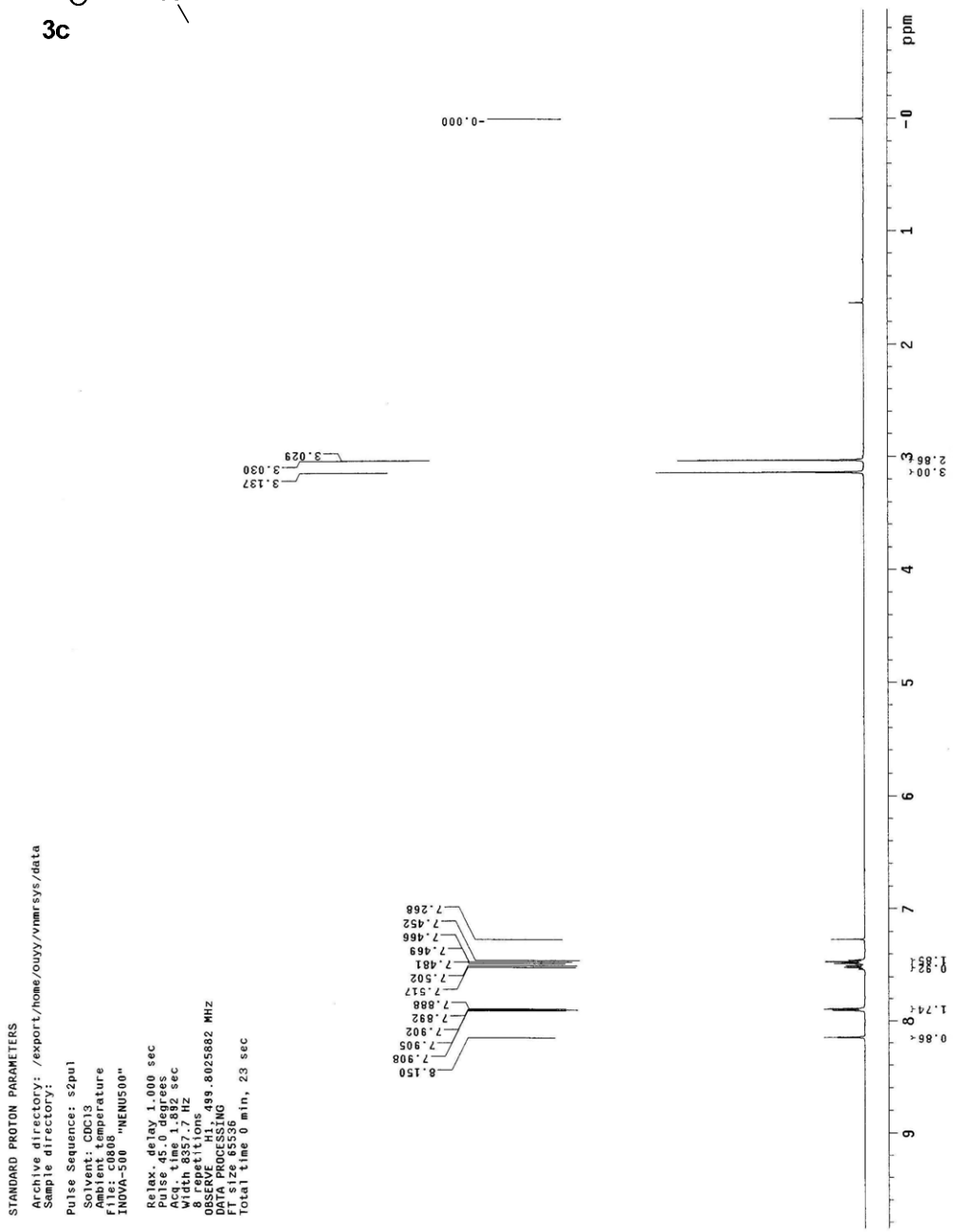
3b

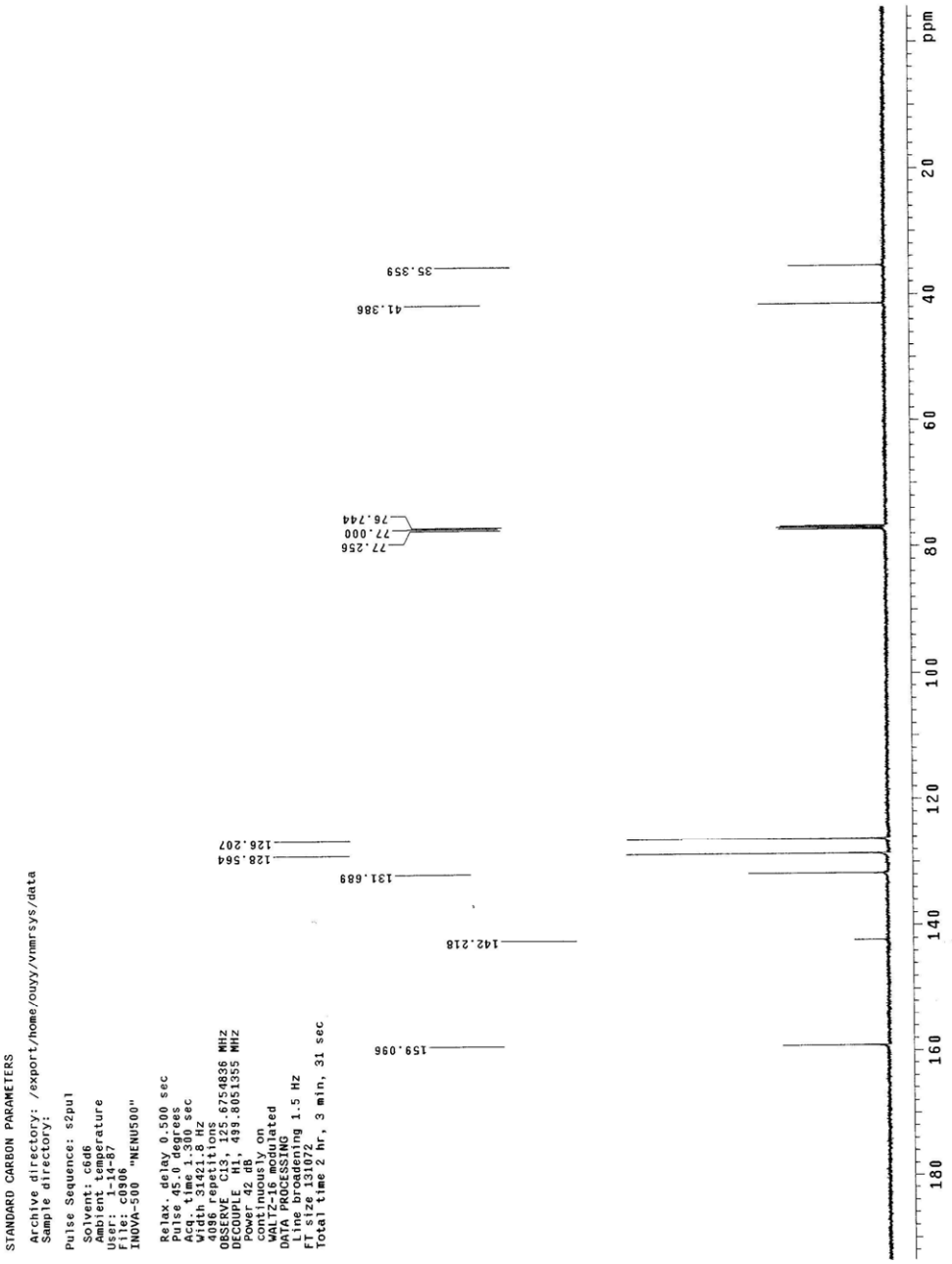


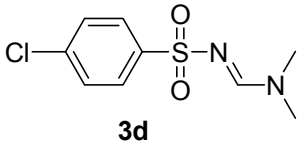




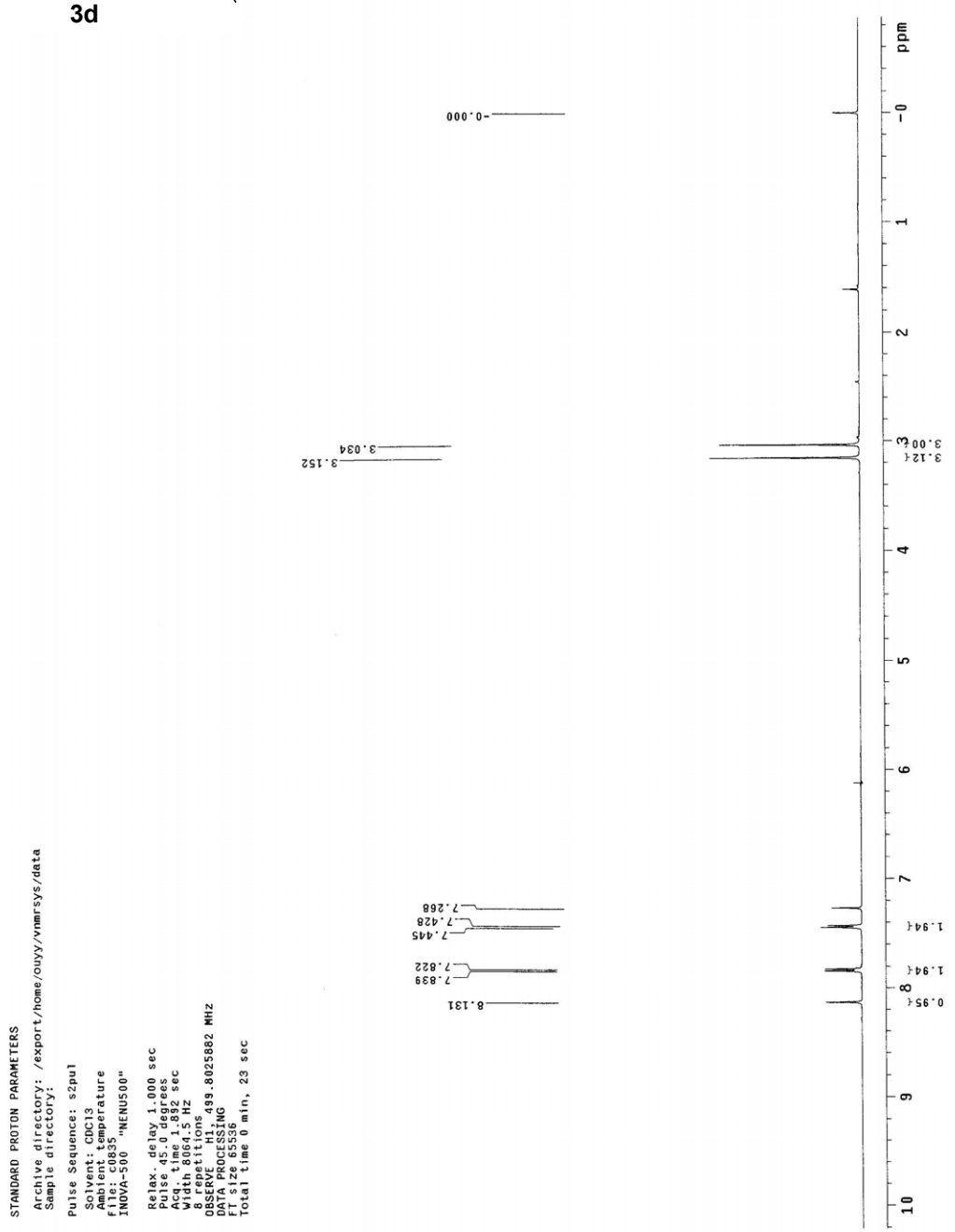
3c

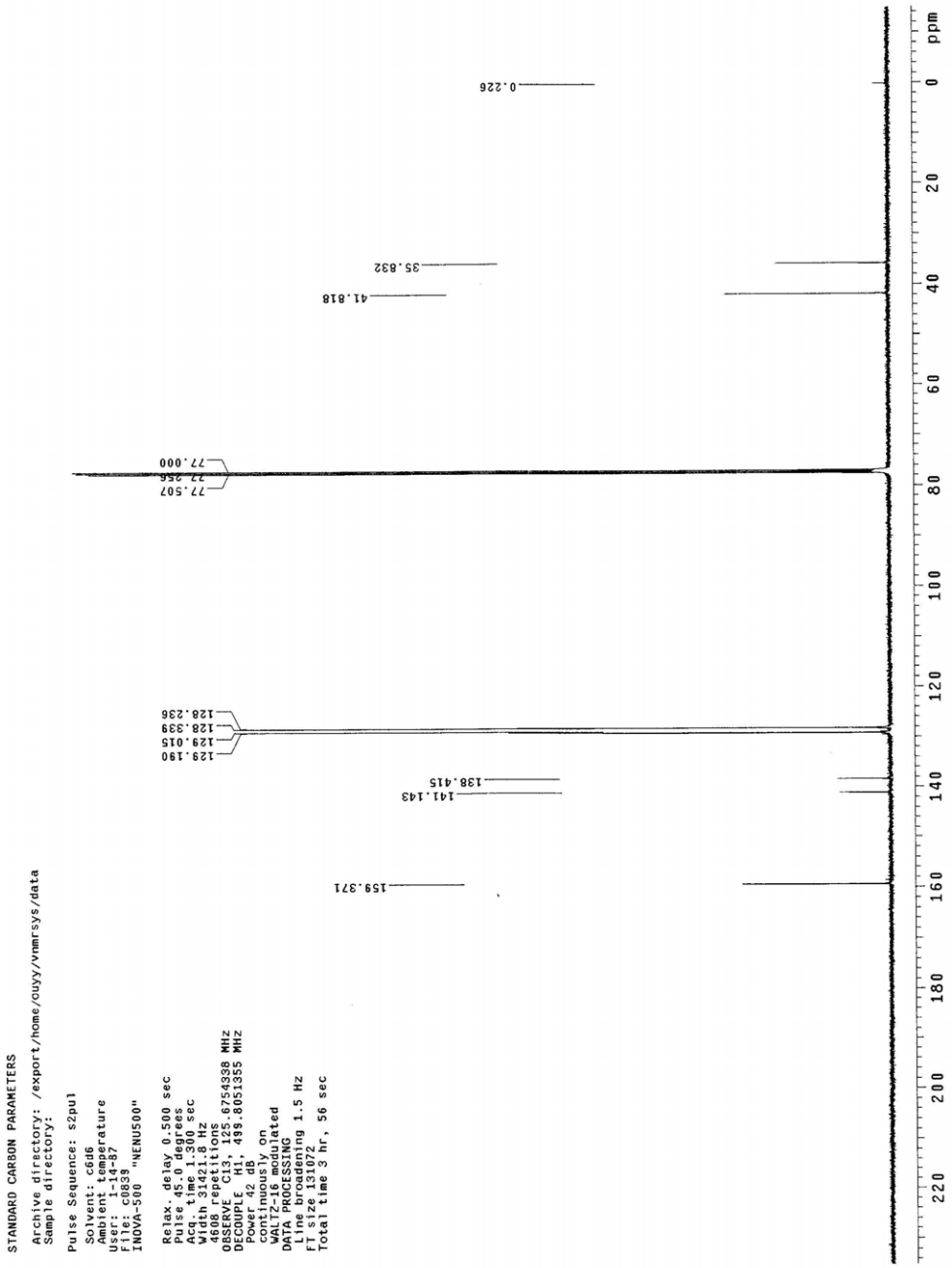


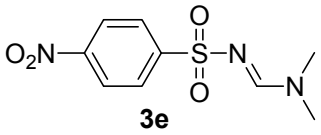




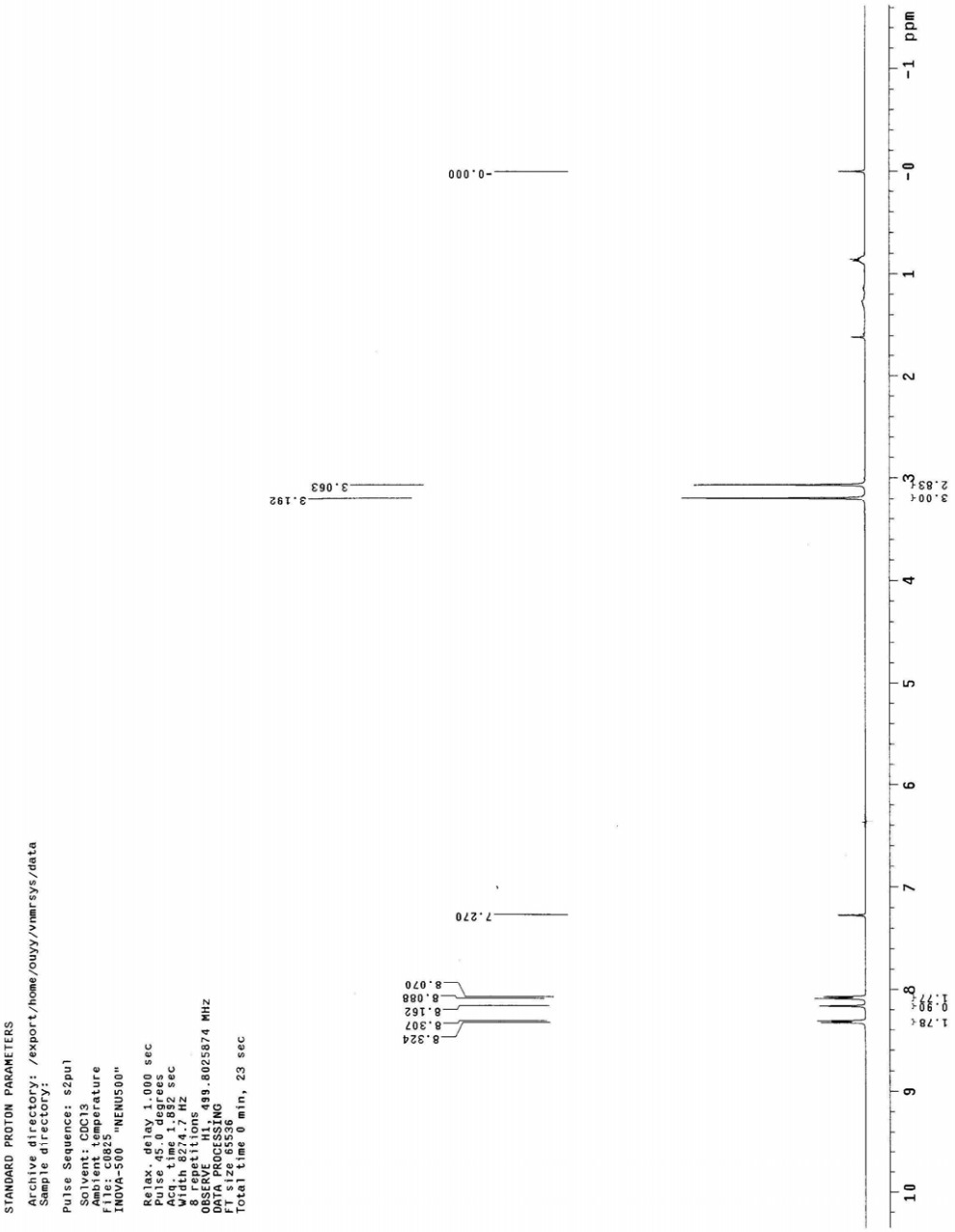
3d

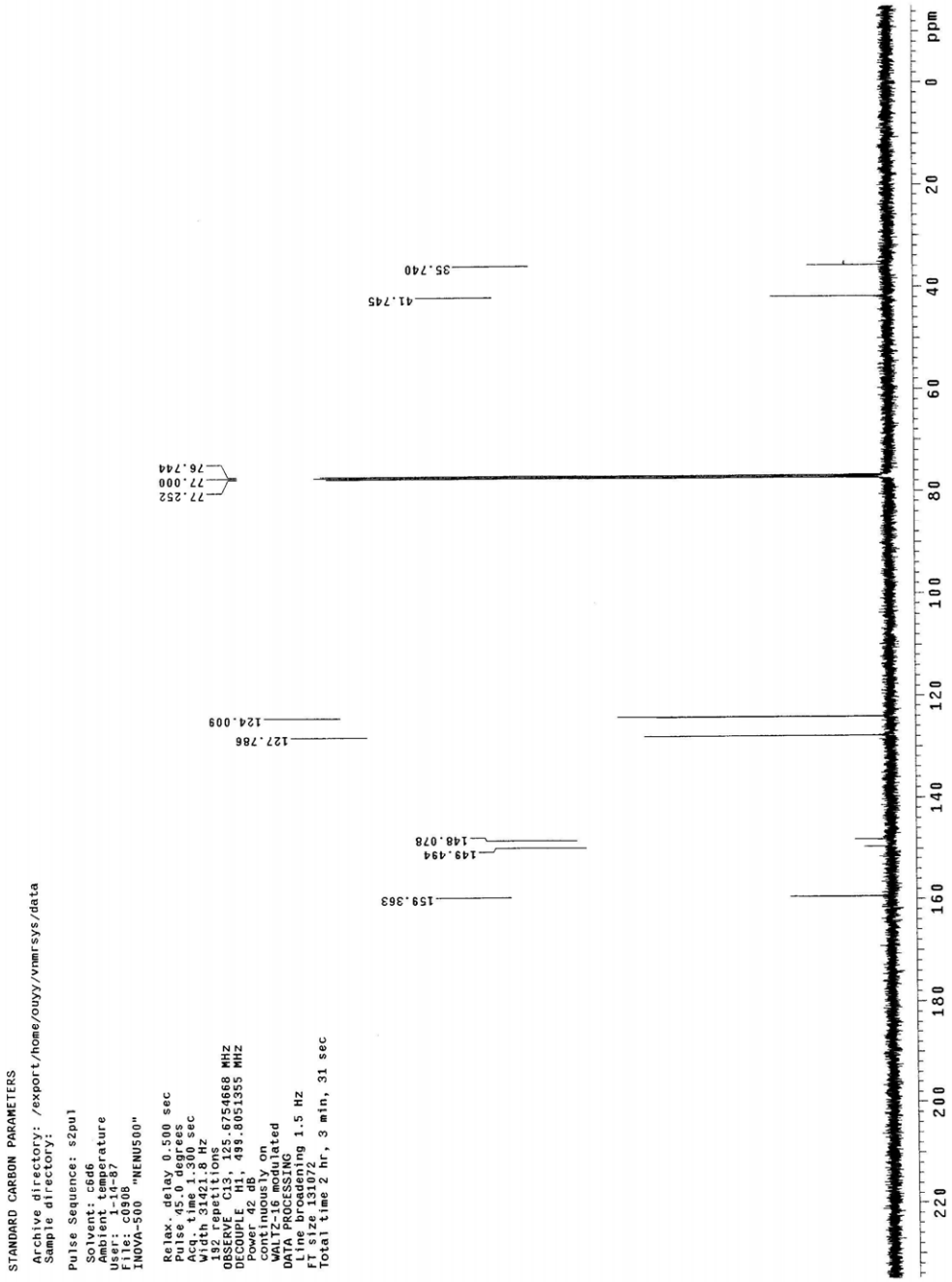


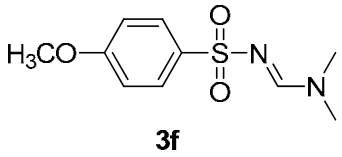




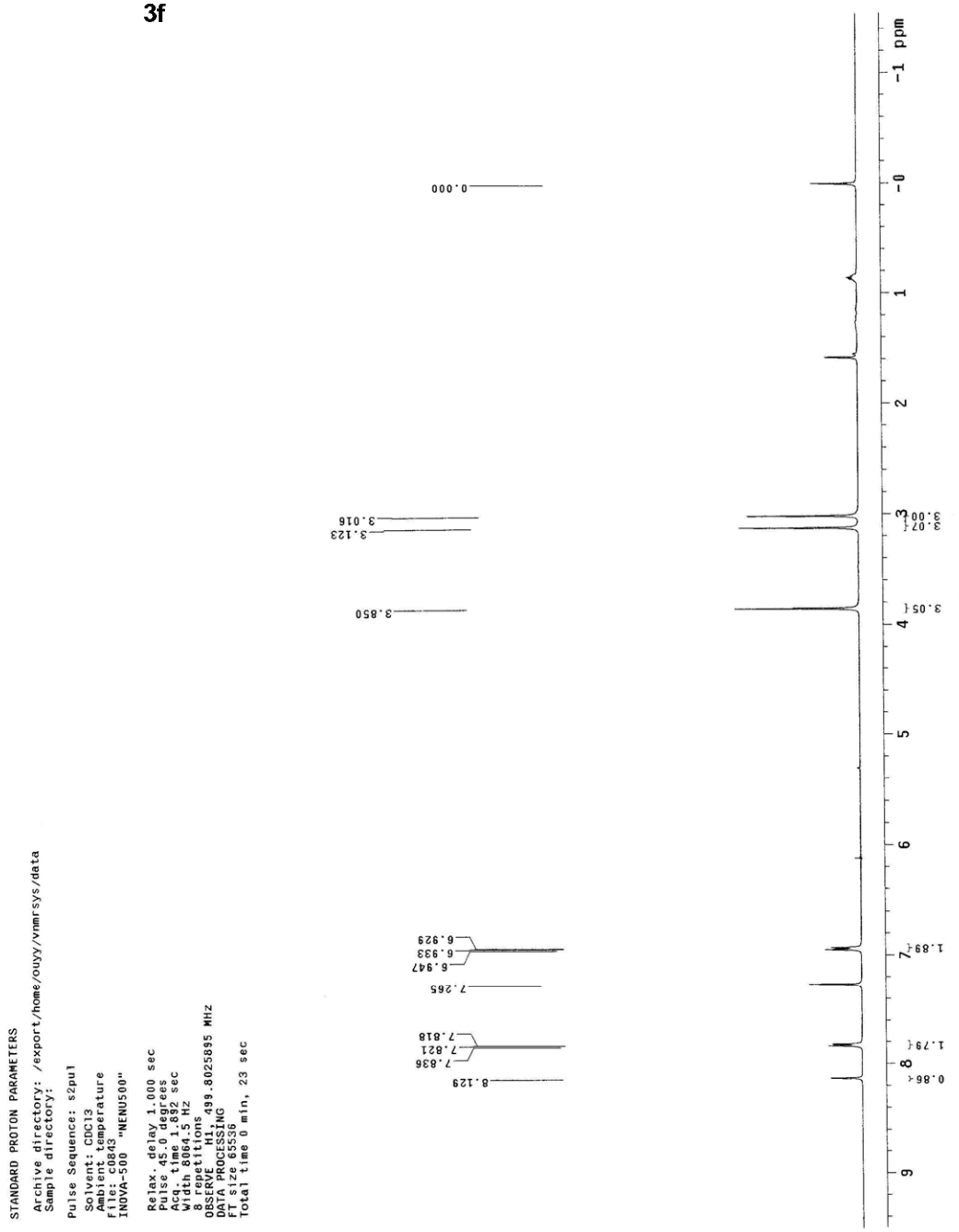
3e

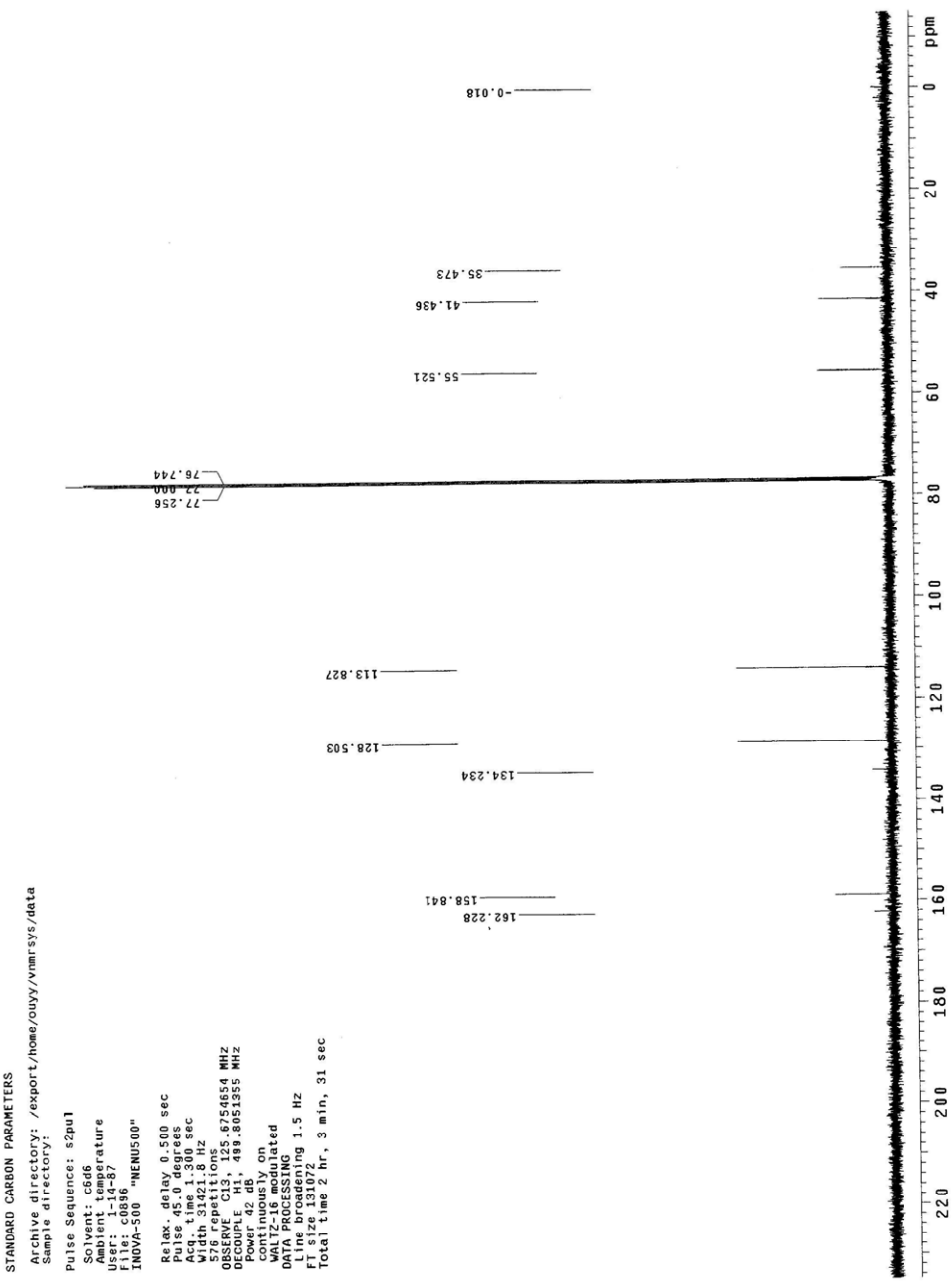

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: C0825
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.832 sec
Width 8274.7 Hz
8 repetitions
OBSERVE H1, 499.8025874 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
8.324
8.307
8.162
8.088
8.070
7.270
3.192
3.063
0.000
1.778
0.904
1.777
2.834
3.000
ppm

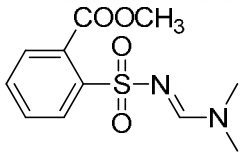




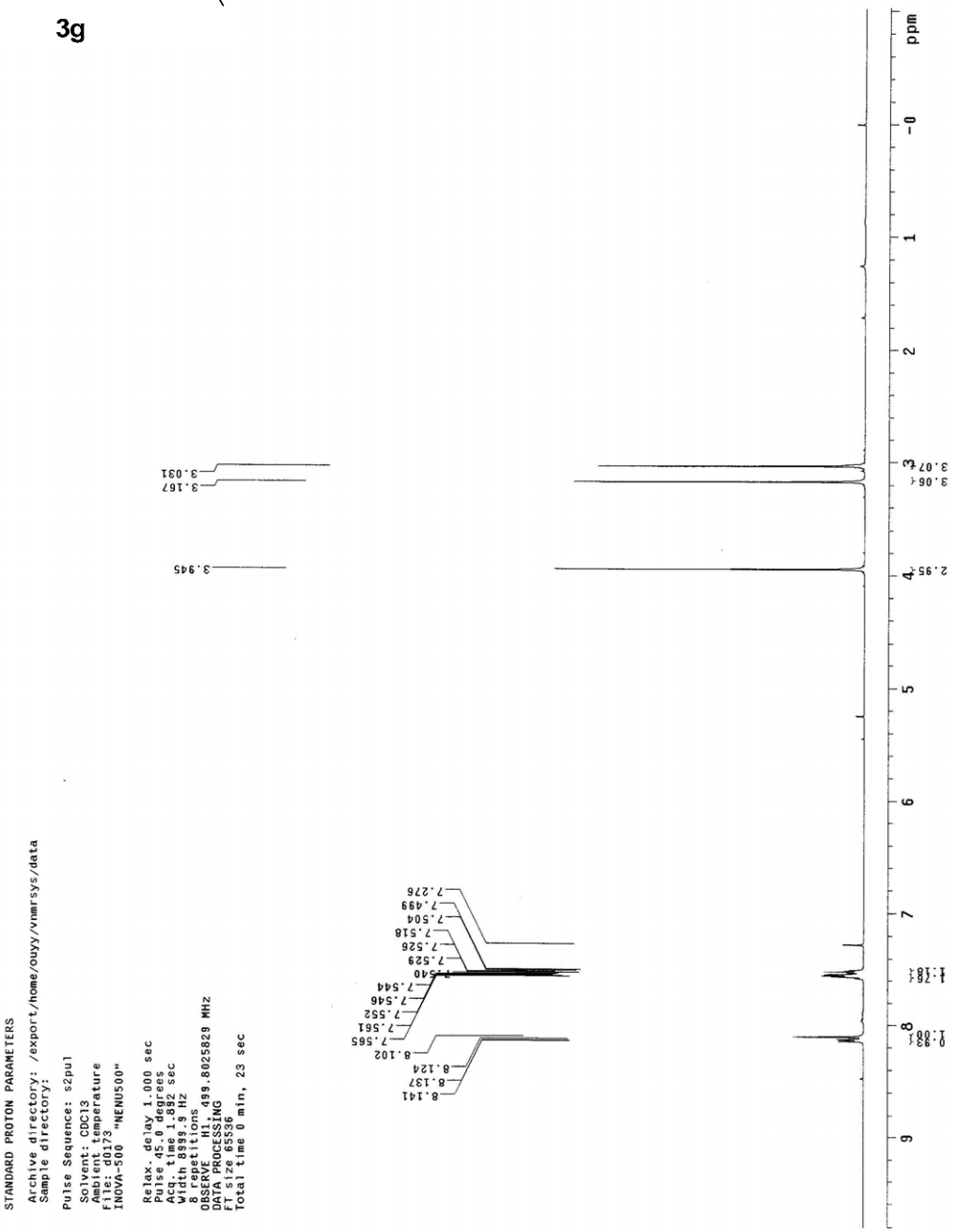
3f

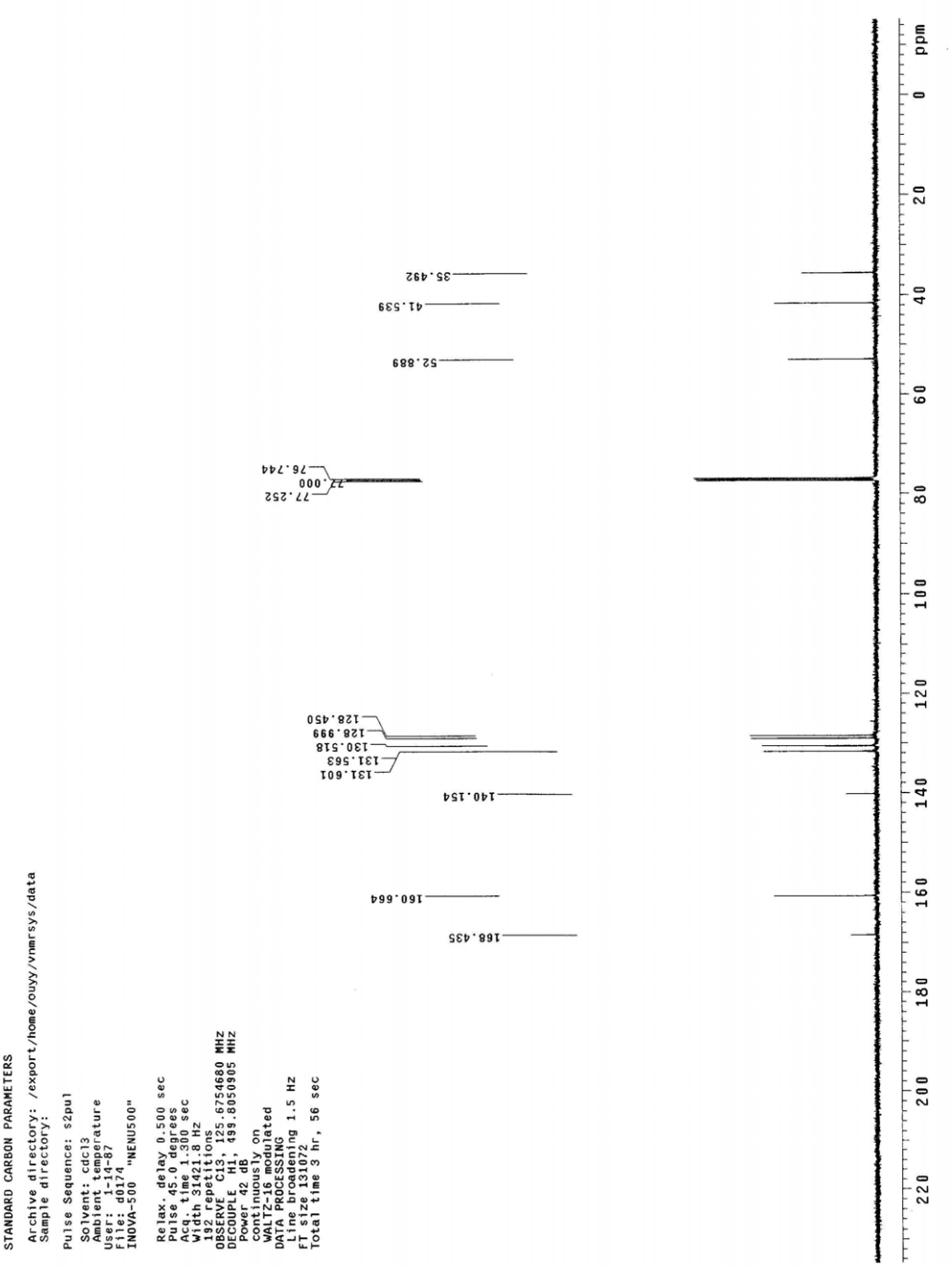






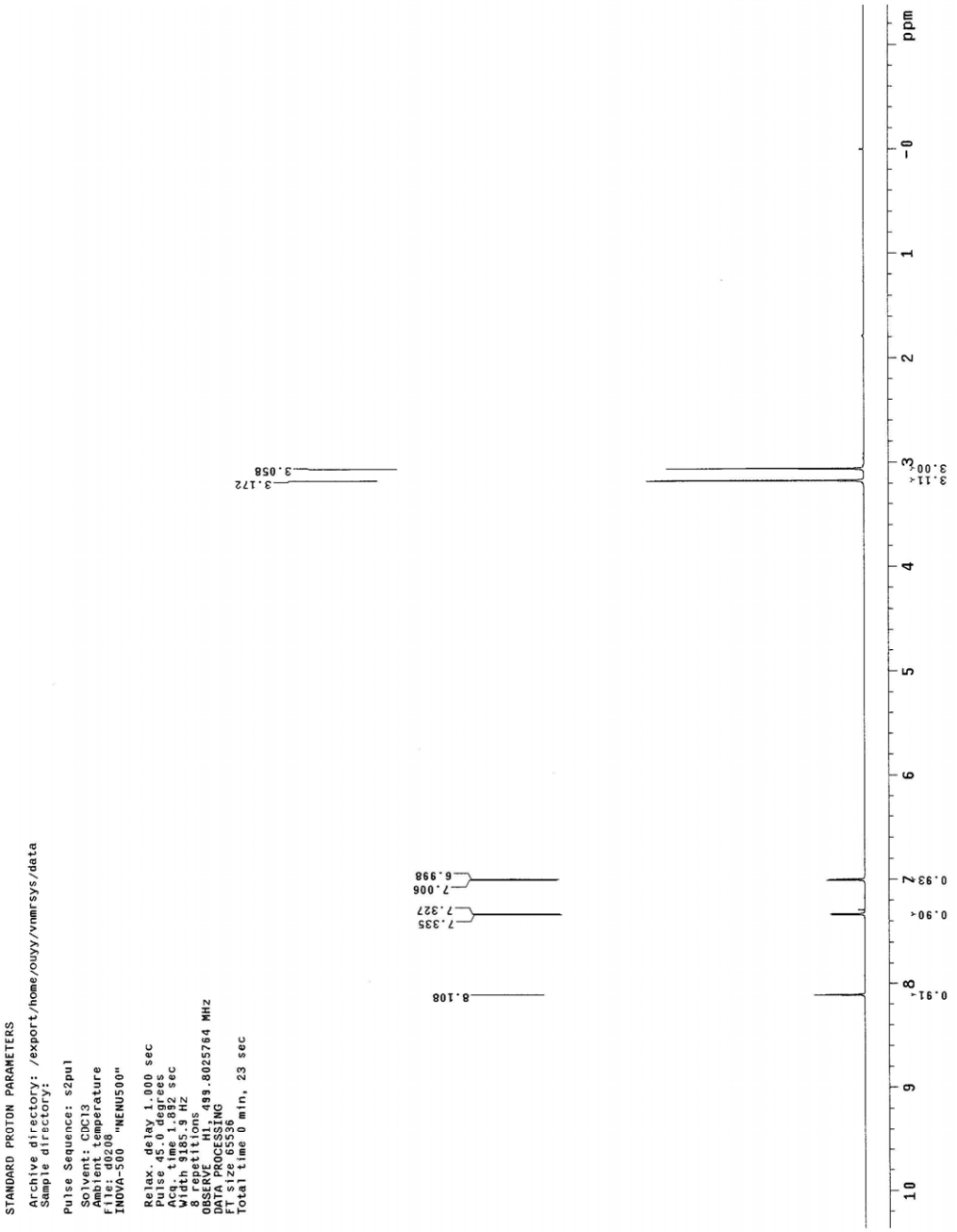
3g

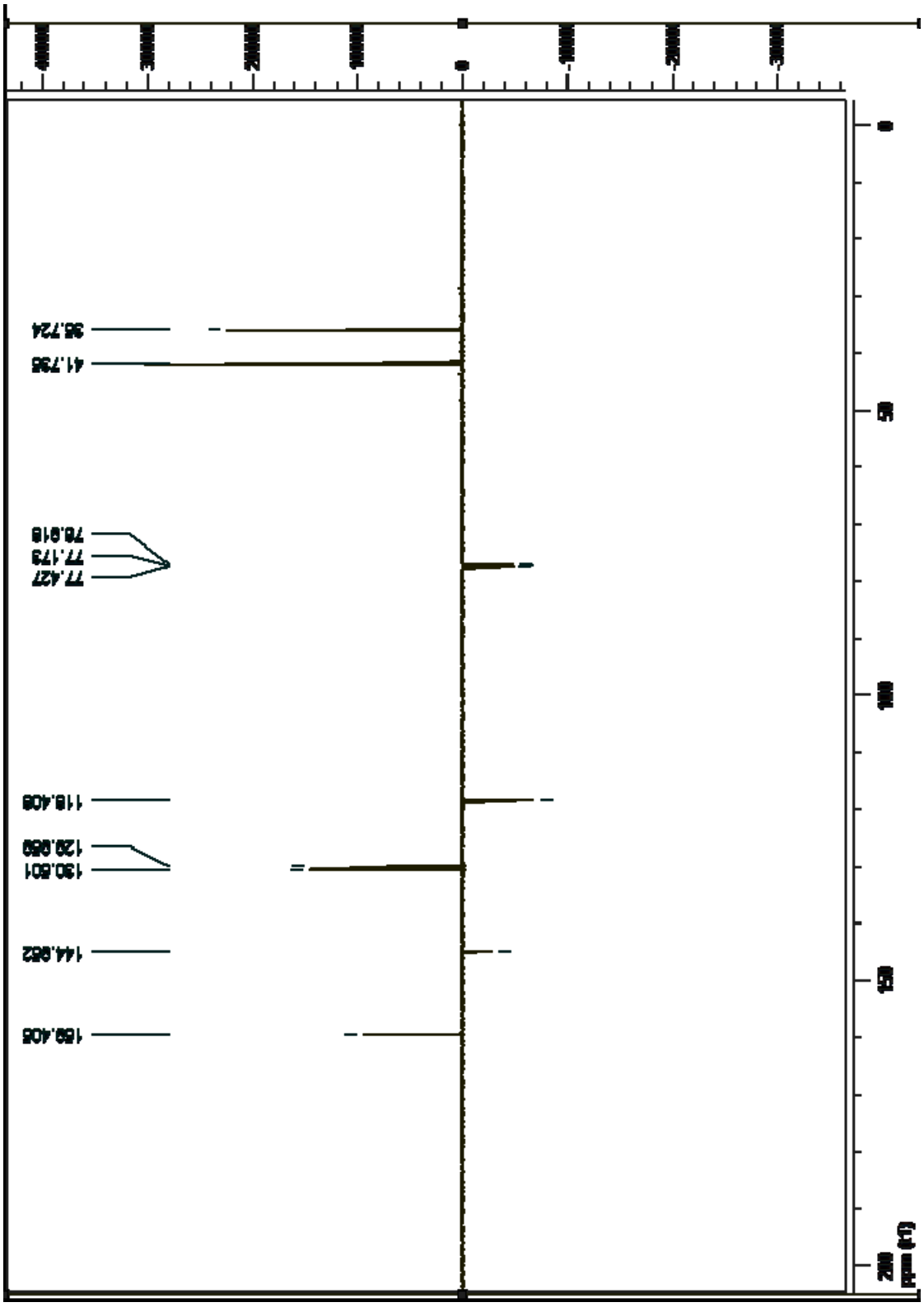


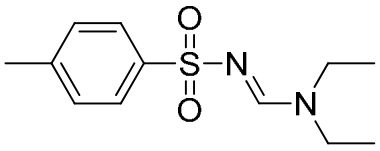



Br
S
O
S
O
N
N

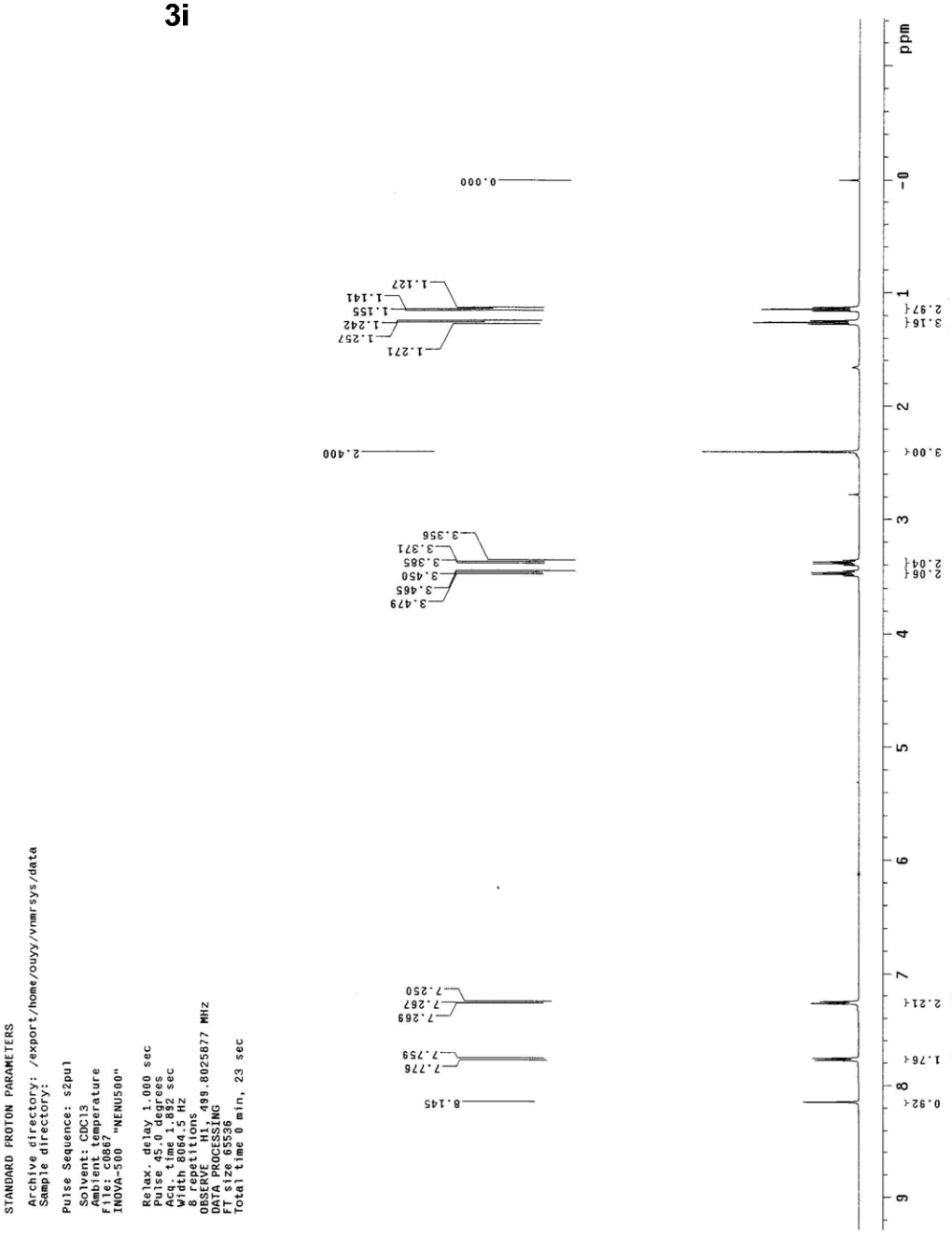
3h

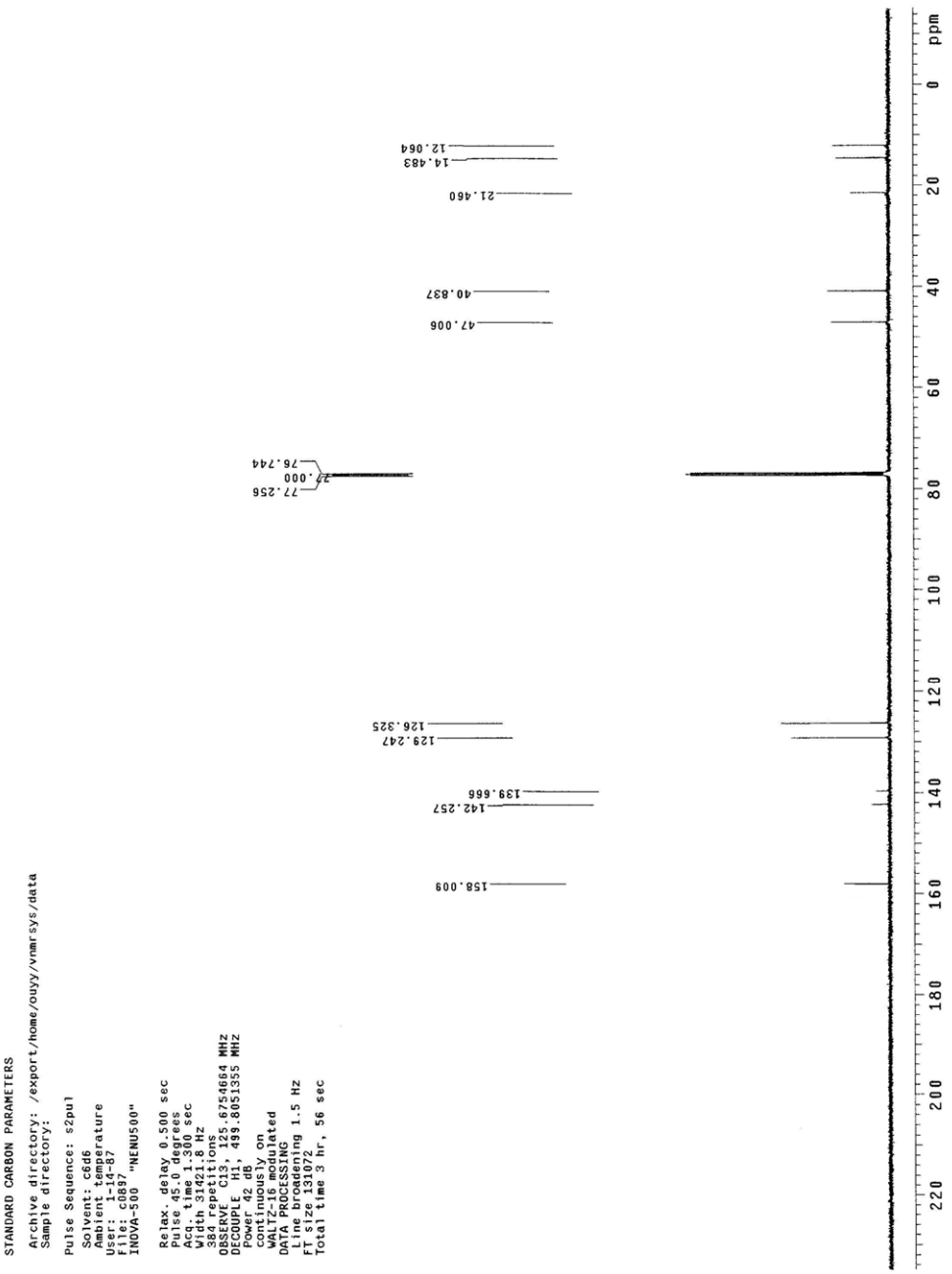

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: d0208
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 9165.9 Hz
8 repetitions
OBSERVE H1, 499.8025764 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
3.172
3.058
7.998
7.335
7.327
8.108
3.11
3.00
0.93
0.90
0.91
ppm

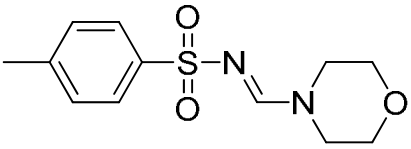




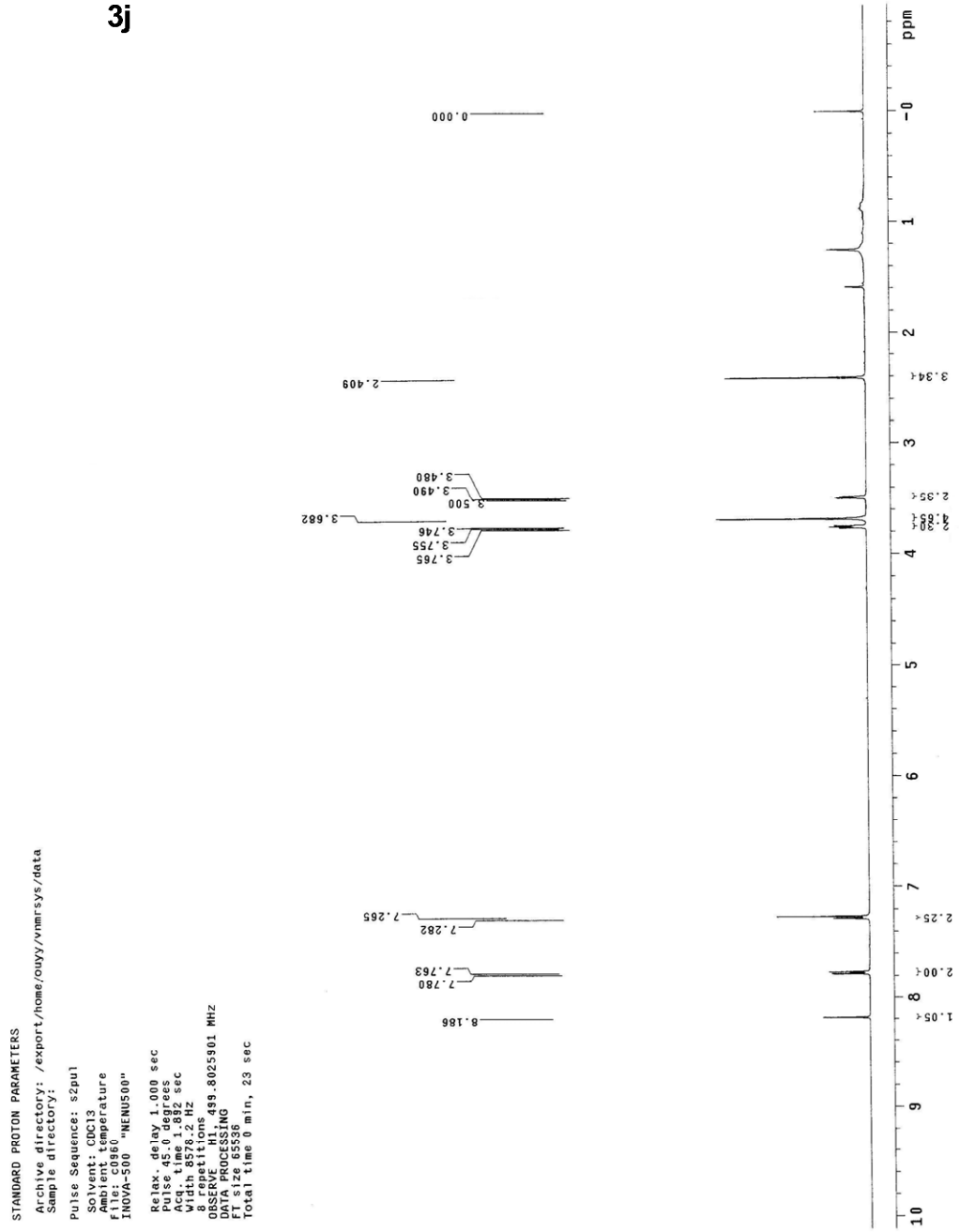
3i

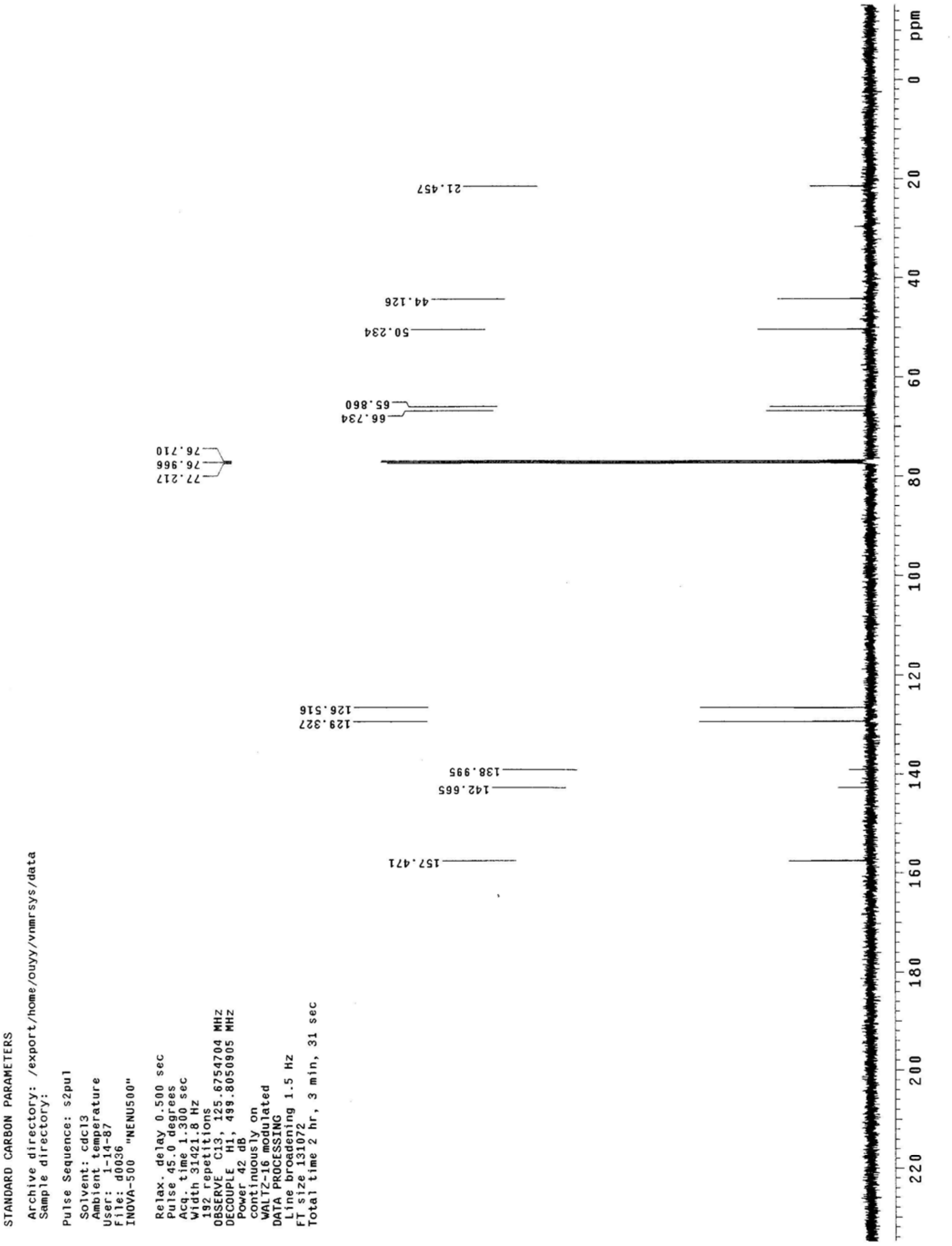


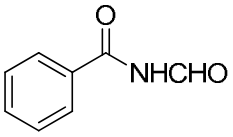

STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: c6d6
Ambient temperature
User: lab-87
File: c087
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
384 repetitions
OBSERVE C13, 125.6754664 MHz
DECOUPLE H1, 499.8051355 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 3 hr, 56 sec
158.009
142.257
139.666
129.247
126.325
77.256
77.000
76.744
47.006
40.837
21.460
14.483
12.064
ppm



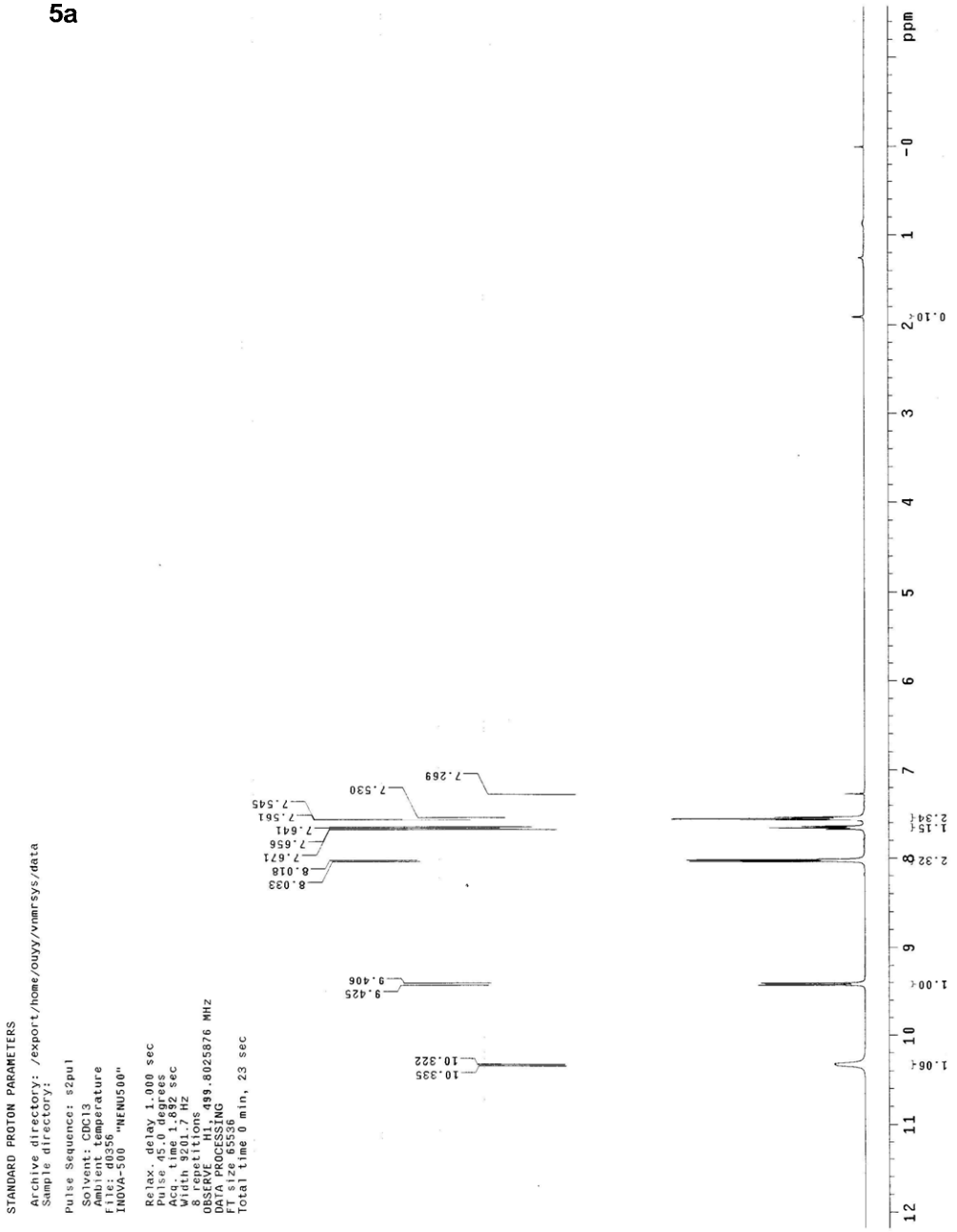
3j

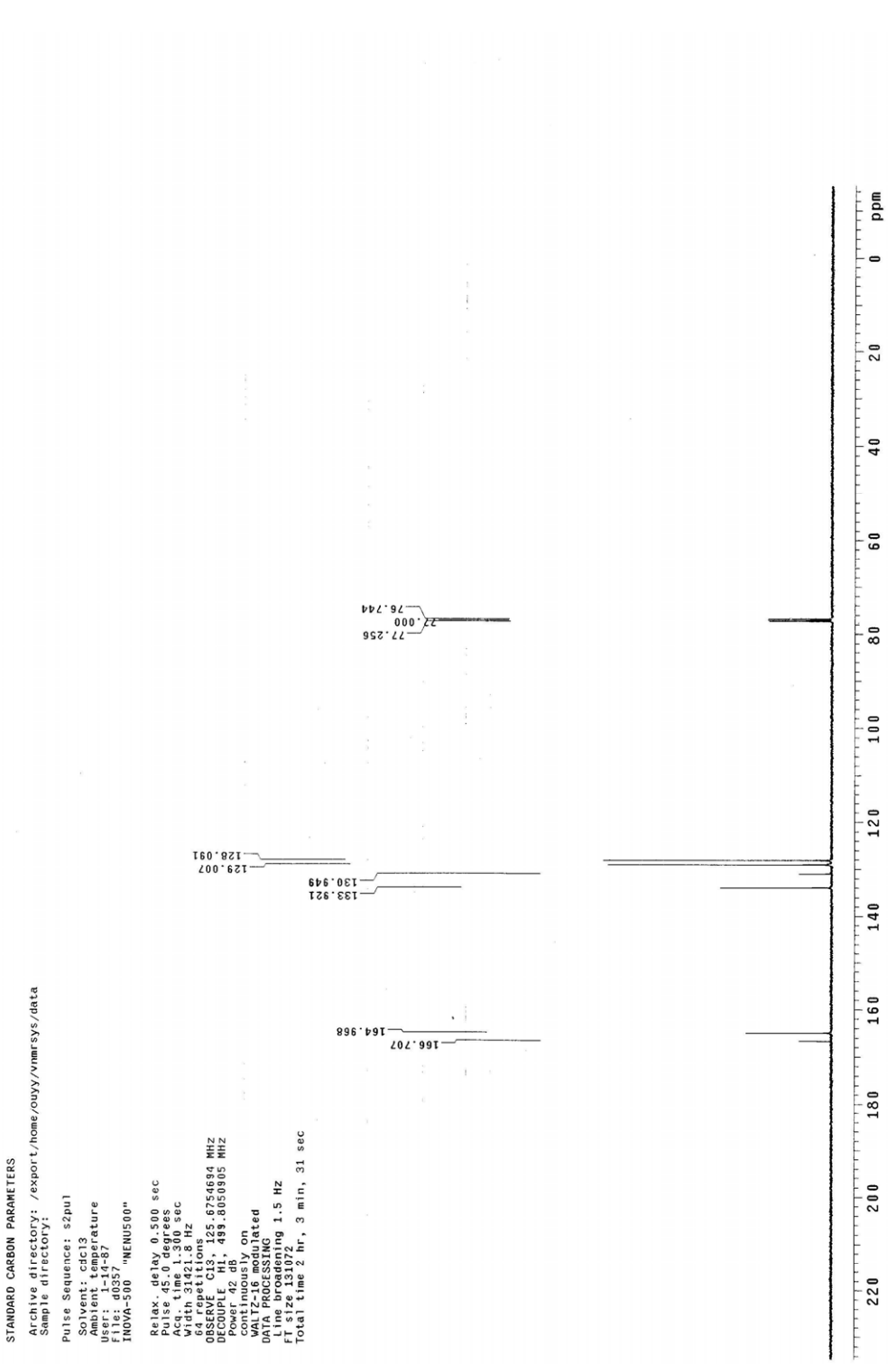


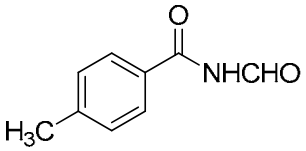

STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: d0036
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
192 repetitions
OBSERVE C13, 125.6754704 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 131072
Total time 2 hr, 3 min, 31 sec
157.471
142.665
138.995
129.327
126.516
77.217
76.966
76.710
66.734
65.860
50.234
44.126
21.457
220
200
180
160
140
120
100
80
60
40
20
0
ppm



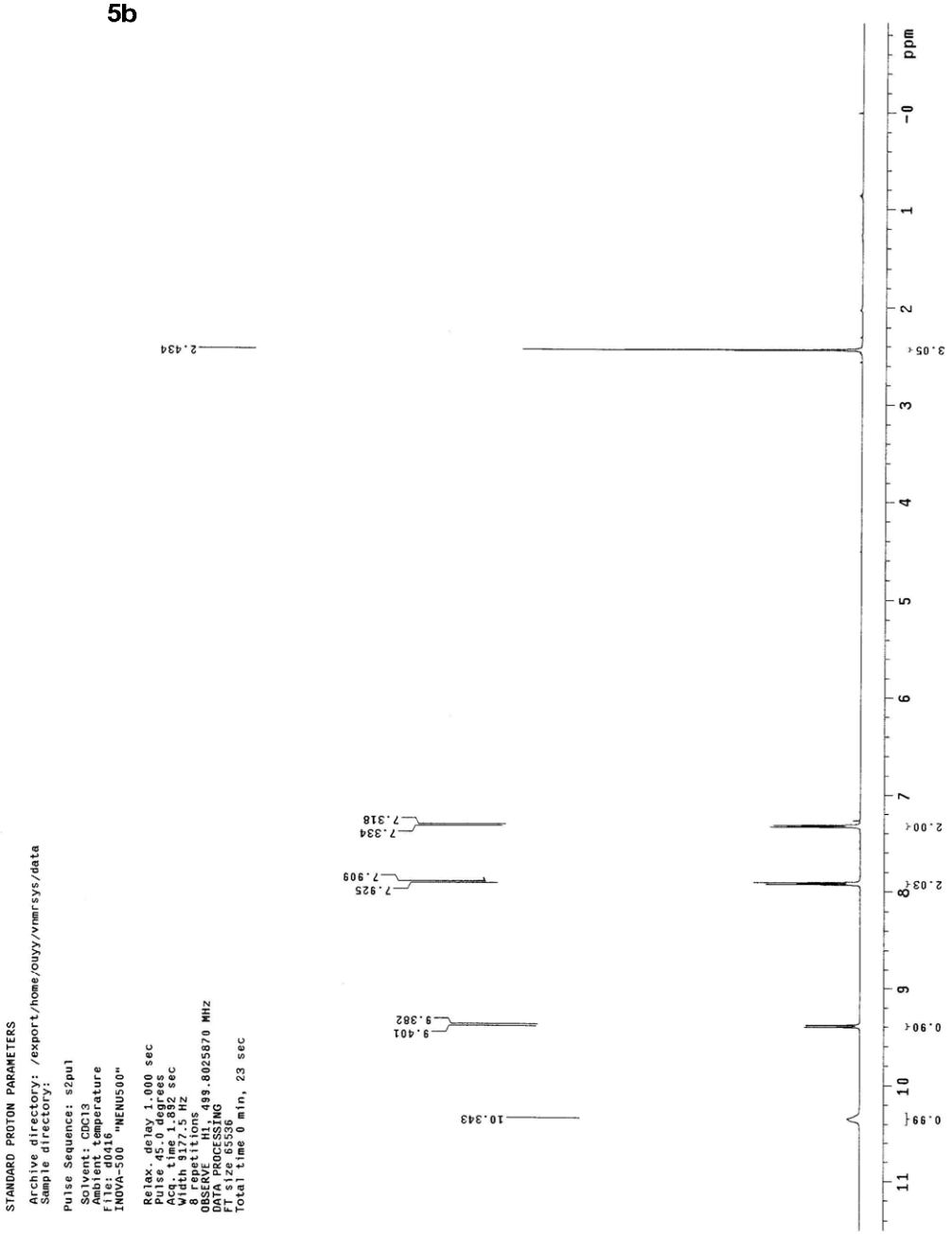
5a

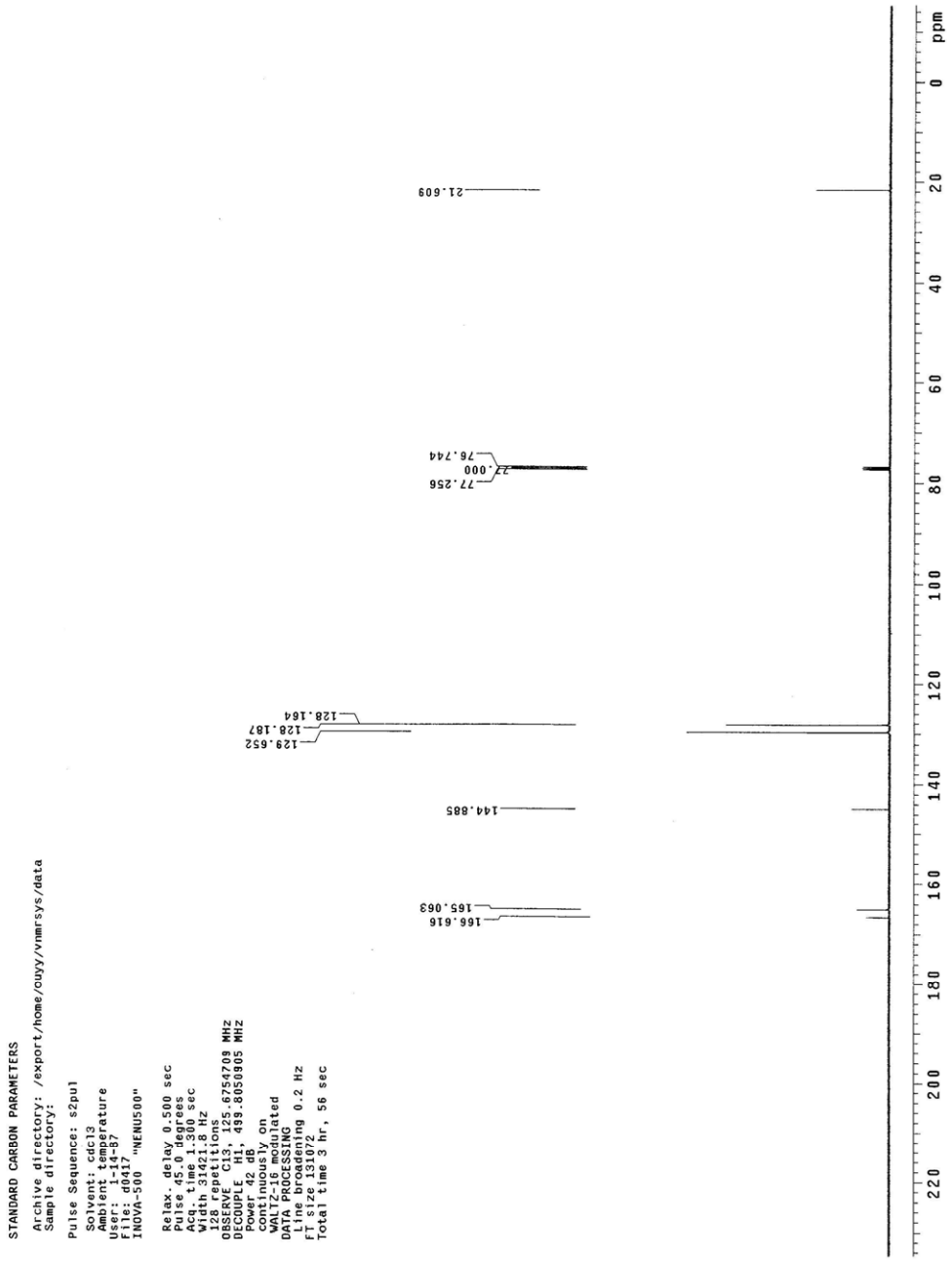


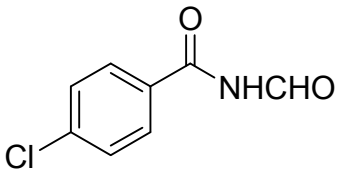




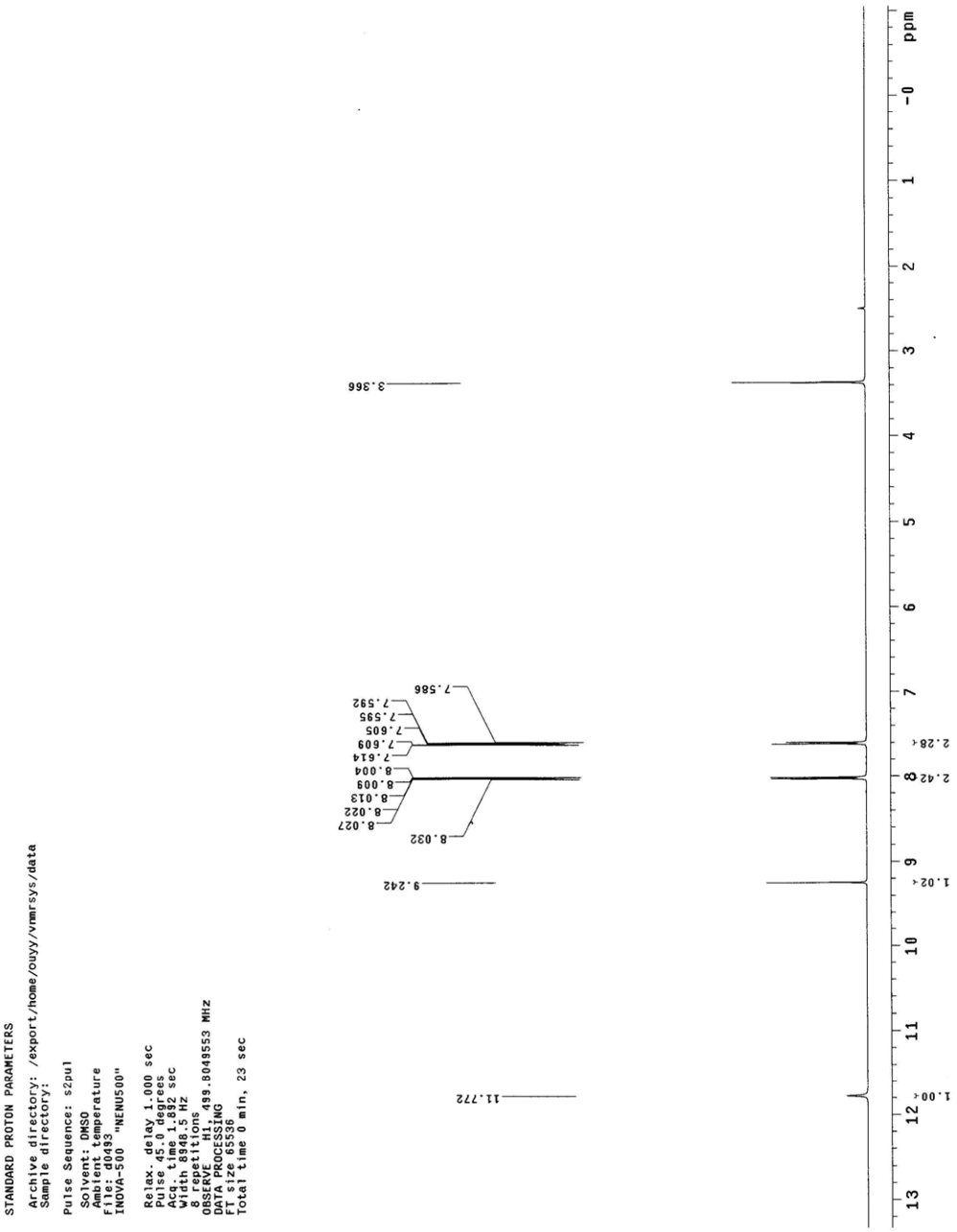
5b

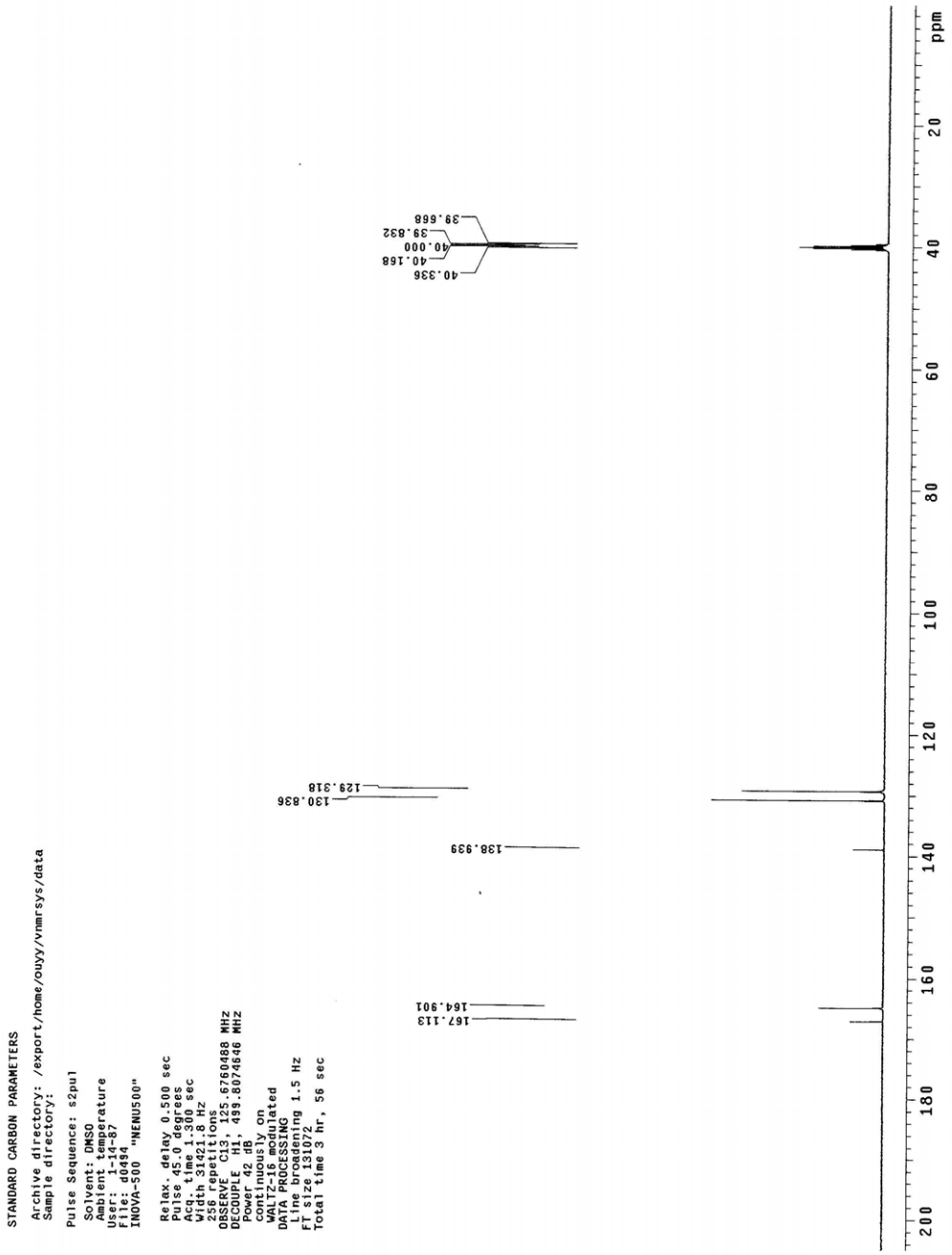


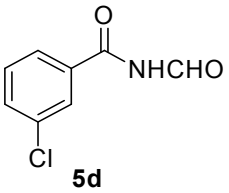

STANDARD CARBON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
User: 1-14-87
File: d041
INOVA-500 "NENU500"
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
128 repetitions
OBSERVE C13, 125.6754709 MHz
DECOUPLE H1, 499.8050905 MHz
Power 42 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
Line broadening 0.2 Hz
FT size 131072
Total time 3 hr, 56 sec
21.609
76.744
77.000
77.256
128.164
128.187
129.652
144.885
165.063
166.616
220
200
180
160
140
120
100
80
60
40
20
0
ppm


O
NHCHO
Cl

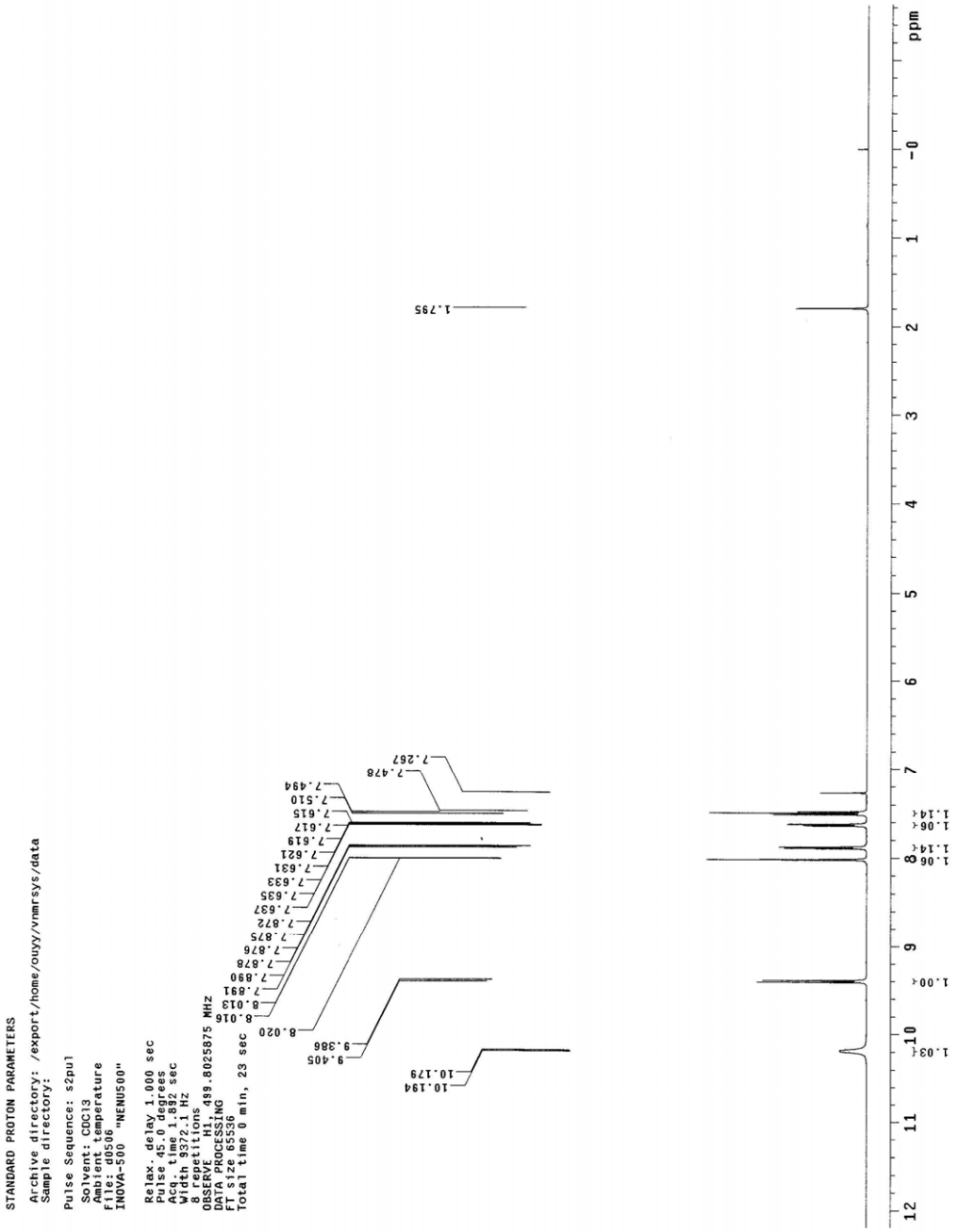
5c

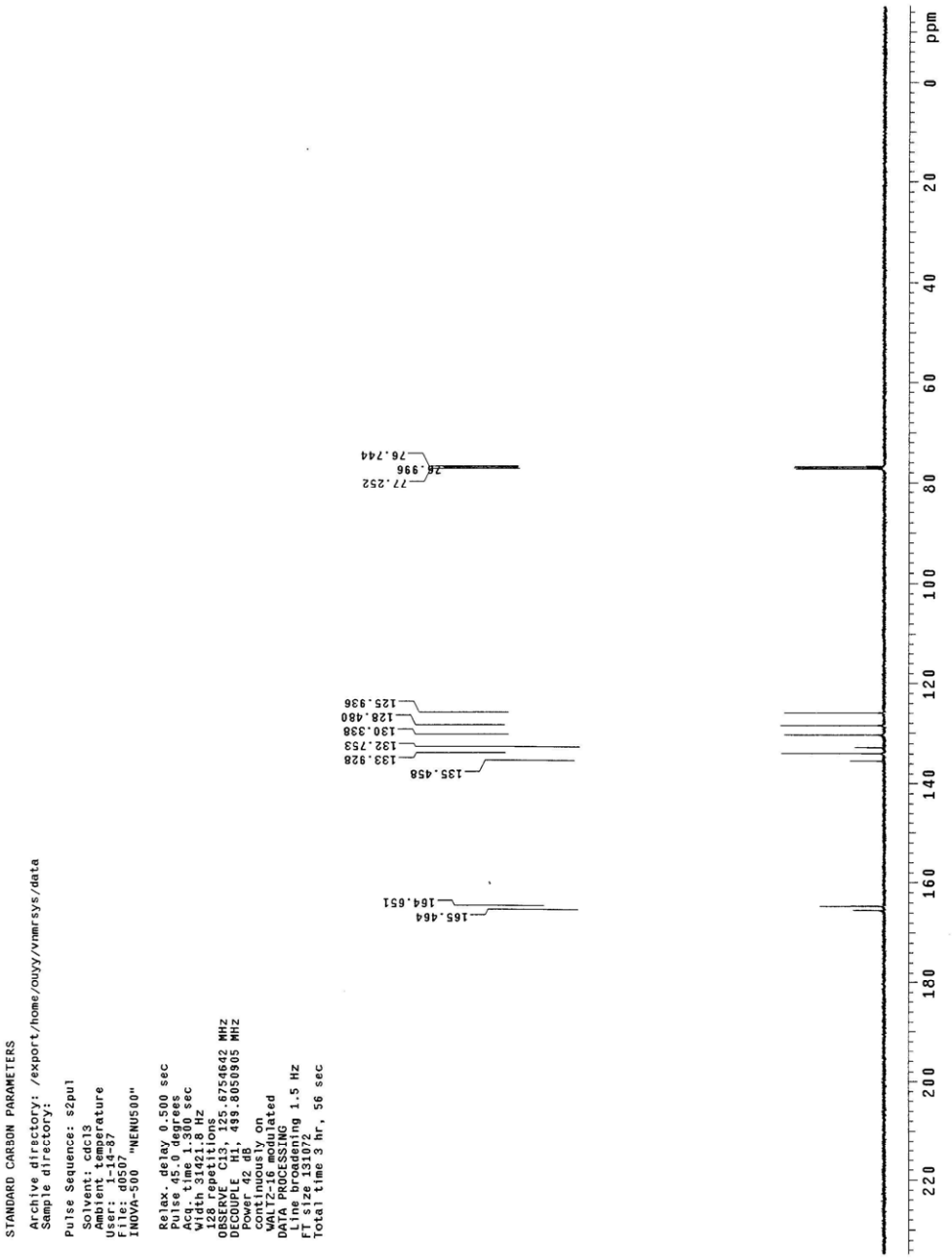

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: DMSO
Ambient temperature
File: d0493
INOVA-500 "WENUS00"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8013.5 Hz
8 repetitions
OBSERVE H1, 499.8049553 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
3.366
7.586
7.592
7.595
7.605
7.609
7.614
8.004
8.009
8.013
8.022
8.027
8.032
9.242
11.772
2.28
2.42
1.02
1.00
ppm

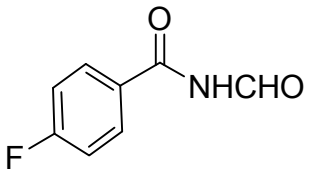



O
NHCHO
Cl

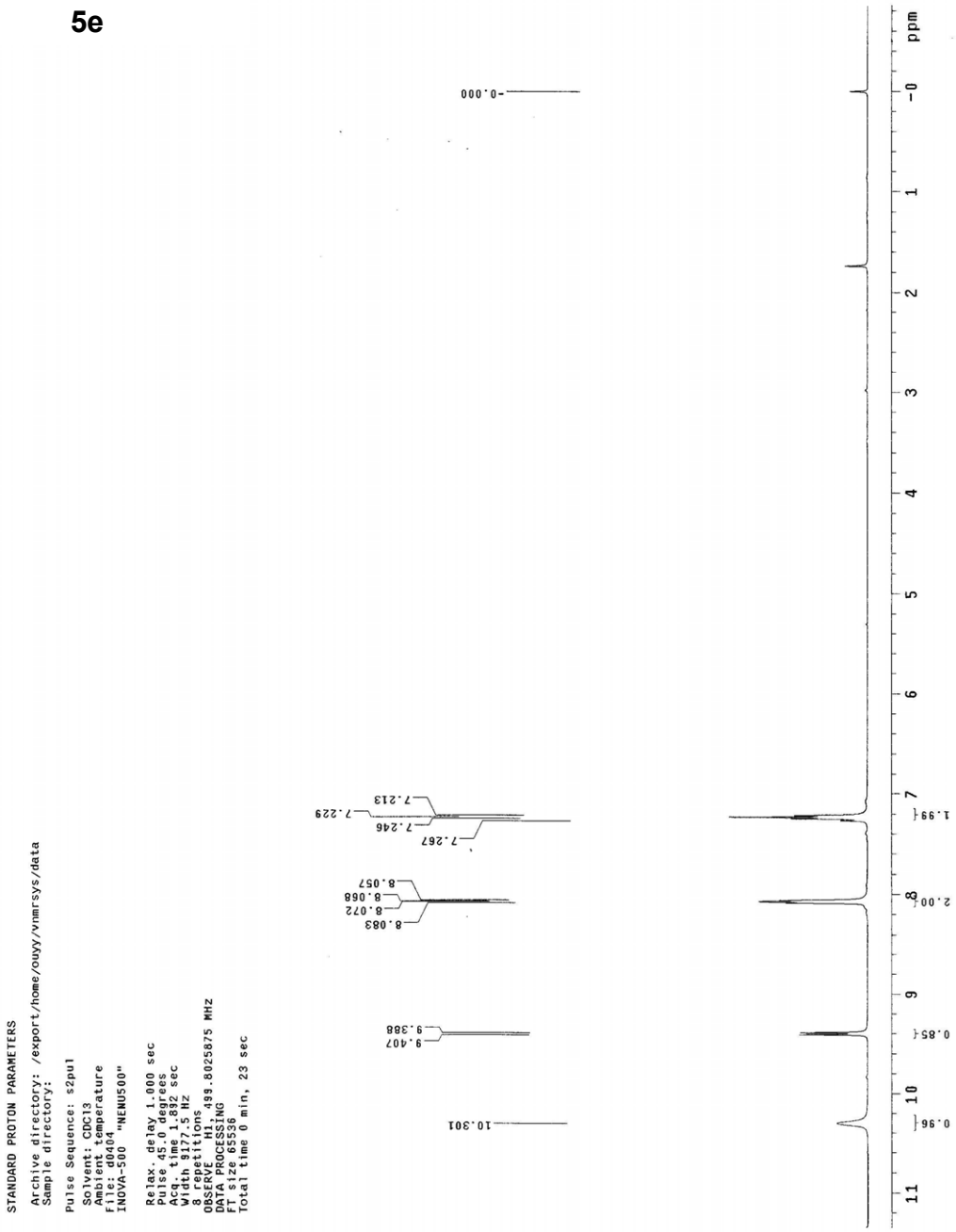
5d

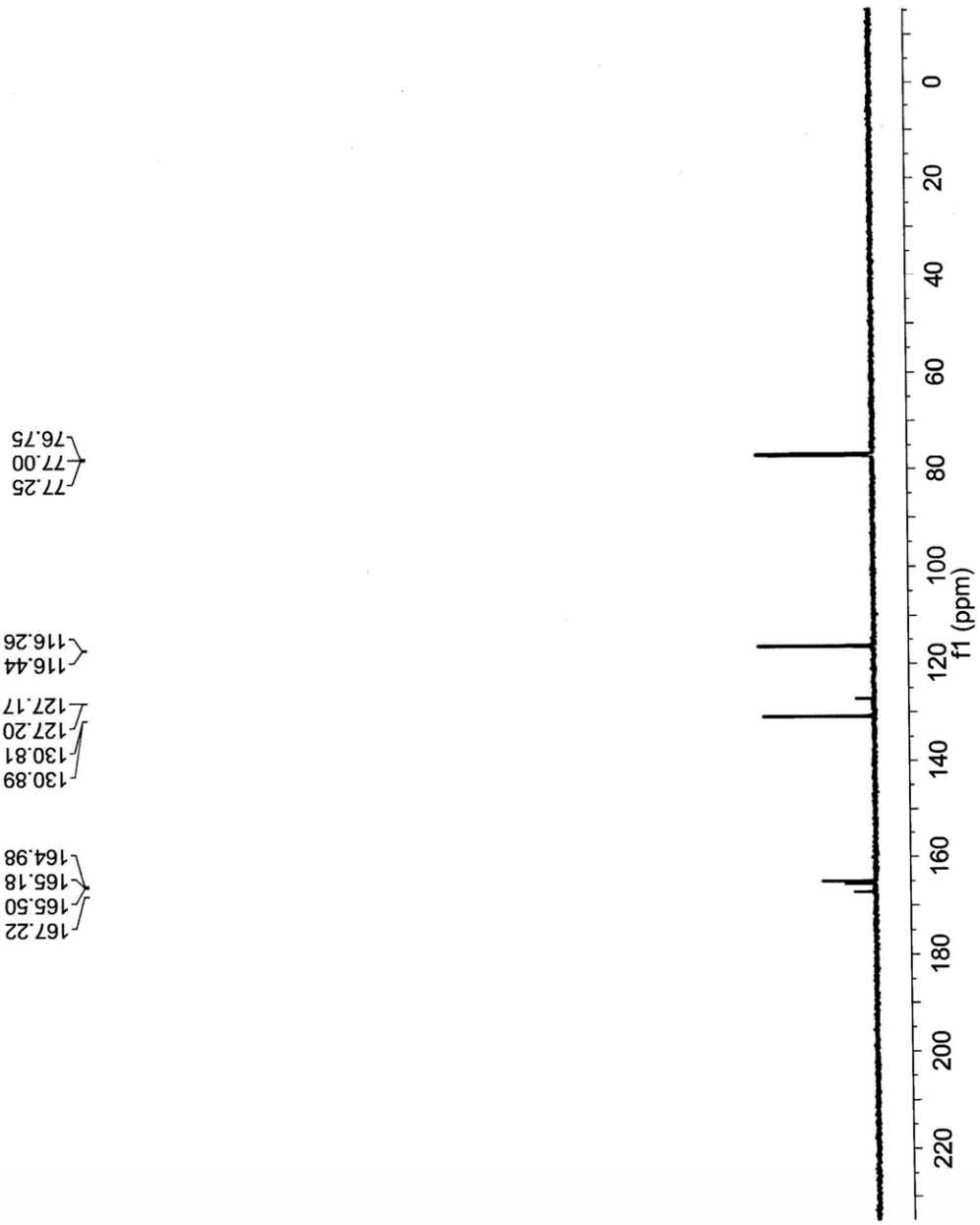

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: d0506 "NENUS00"
INOVA-500 "NENUS00"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.882 sec
Width 9372.1 Hz
8 repetitions
OBSERVE H1, 499.8025875 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
1.795
7.267
7.478
7.494
7.510
7.615
7.617
7.619
7.621
7.631
7.633
7.635
7.637
7.872
7.875
7.876
7.878
7.890
7.891
8.013
8.016
8.020
9.386
9.405
10.179
10.194
ppm

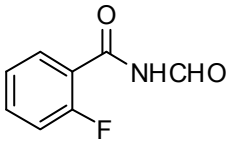



O
NHCHO
F

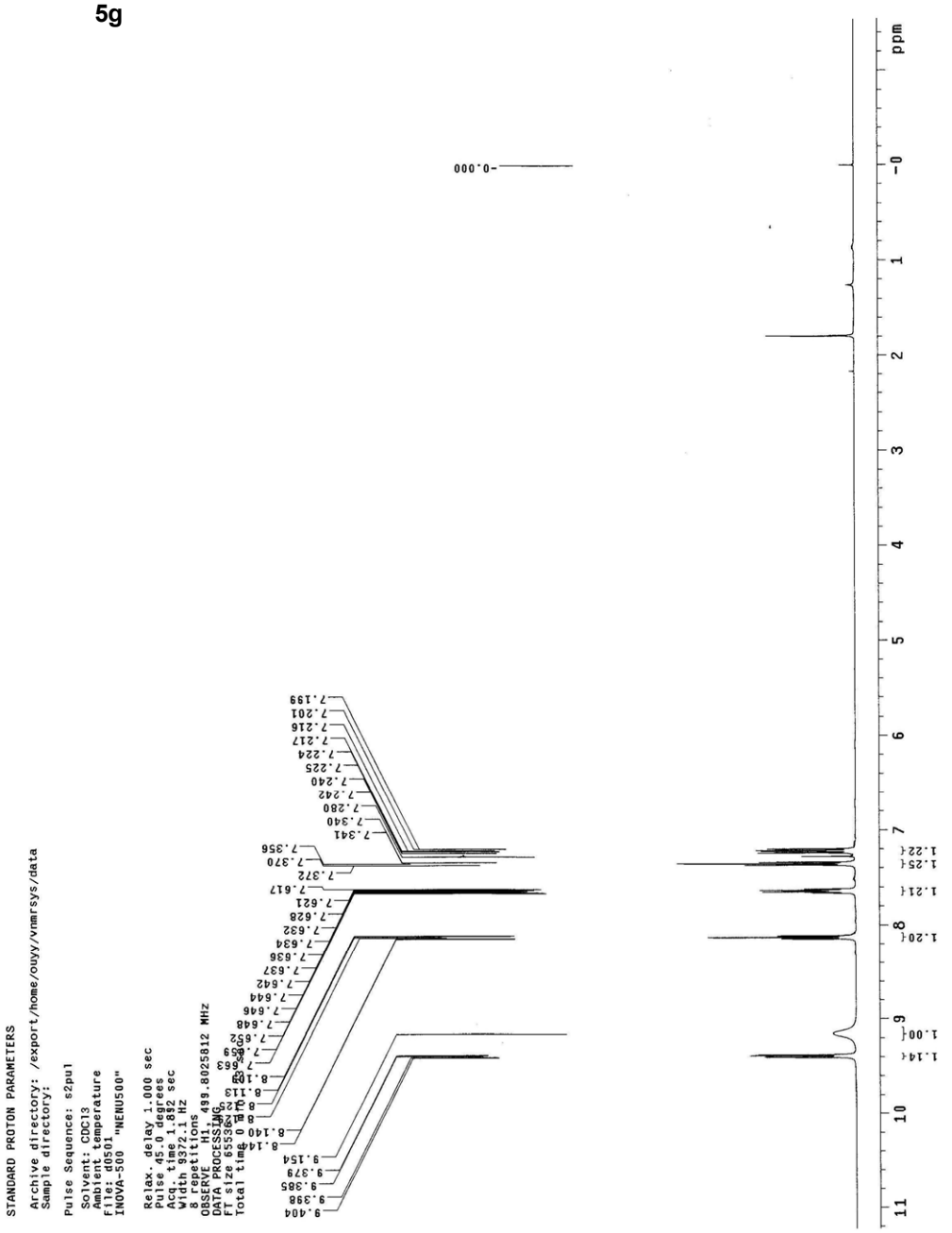
5e

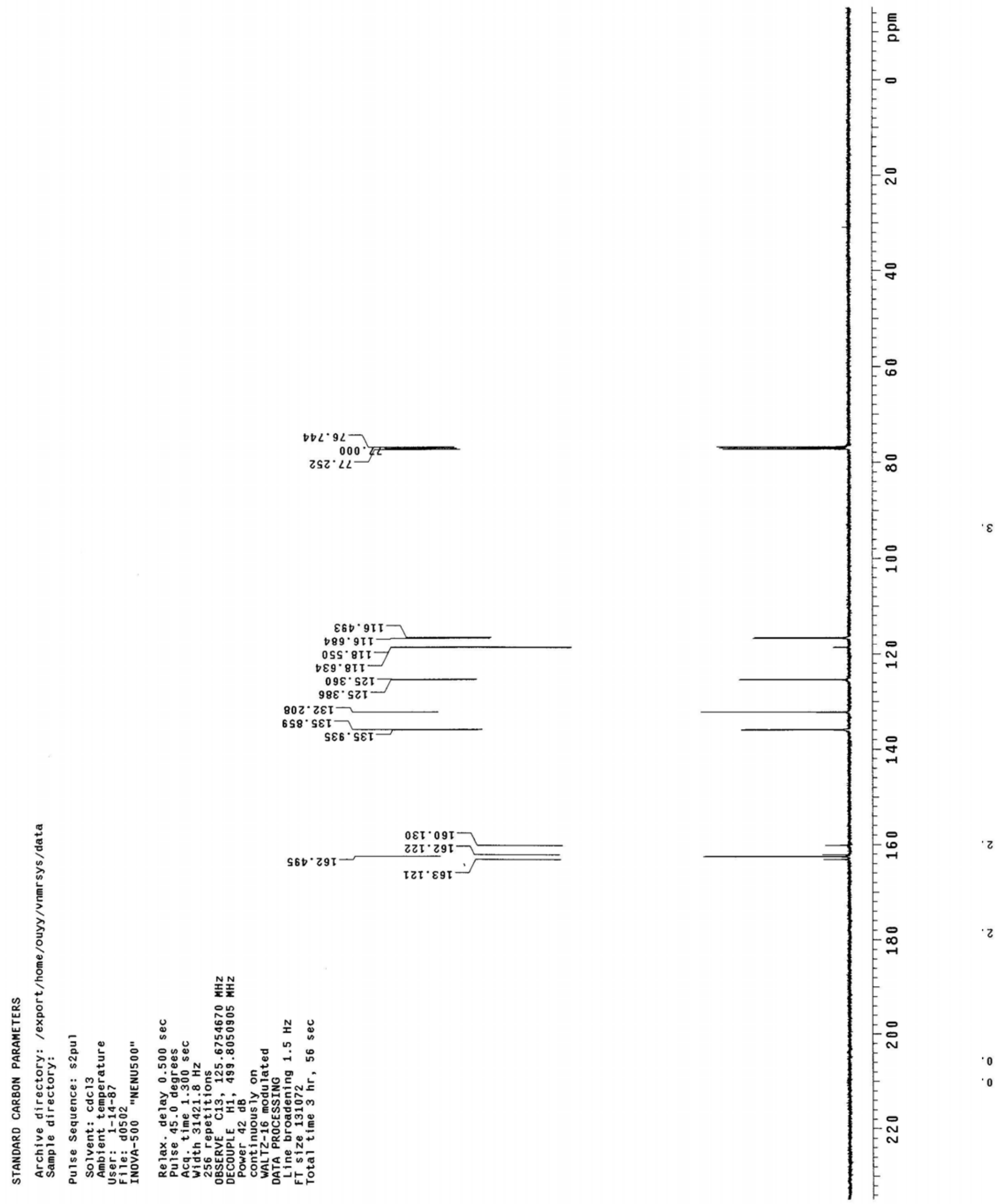

STANDARD PROTON PARAMETERS
Archive directory: /export/home/ouyy/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: dd04
INOVA-500 "NENU500"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 9177.5 Hz
8 repetitions
OBSERVE H1, 499.8025875 MHz
DATA PROCESSING
FT size 65536
Total time 0 min, 23 sec
0.000
7.213
7.229
7.246
7.267
8.057
8.068
8.072
8.083
9.388
9.407
10.301
ppm
1.99
2.00
0.85
0.96

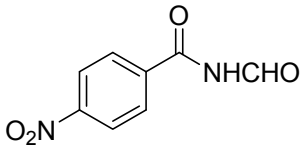




5g







5g