Electronic Supplementary Information

A New Synthetic Access to Bicyclic Polyhydroxylated Alkaloid Analogues from Pyranosides

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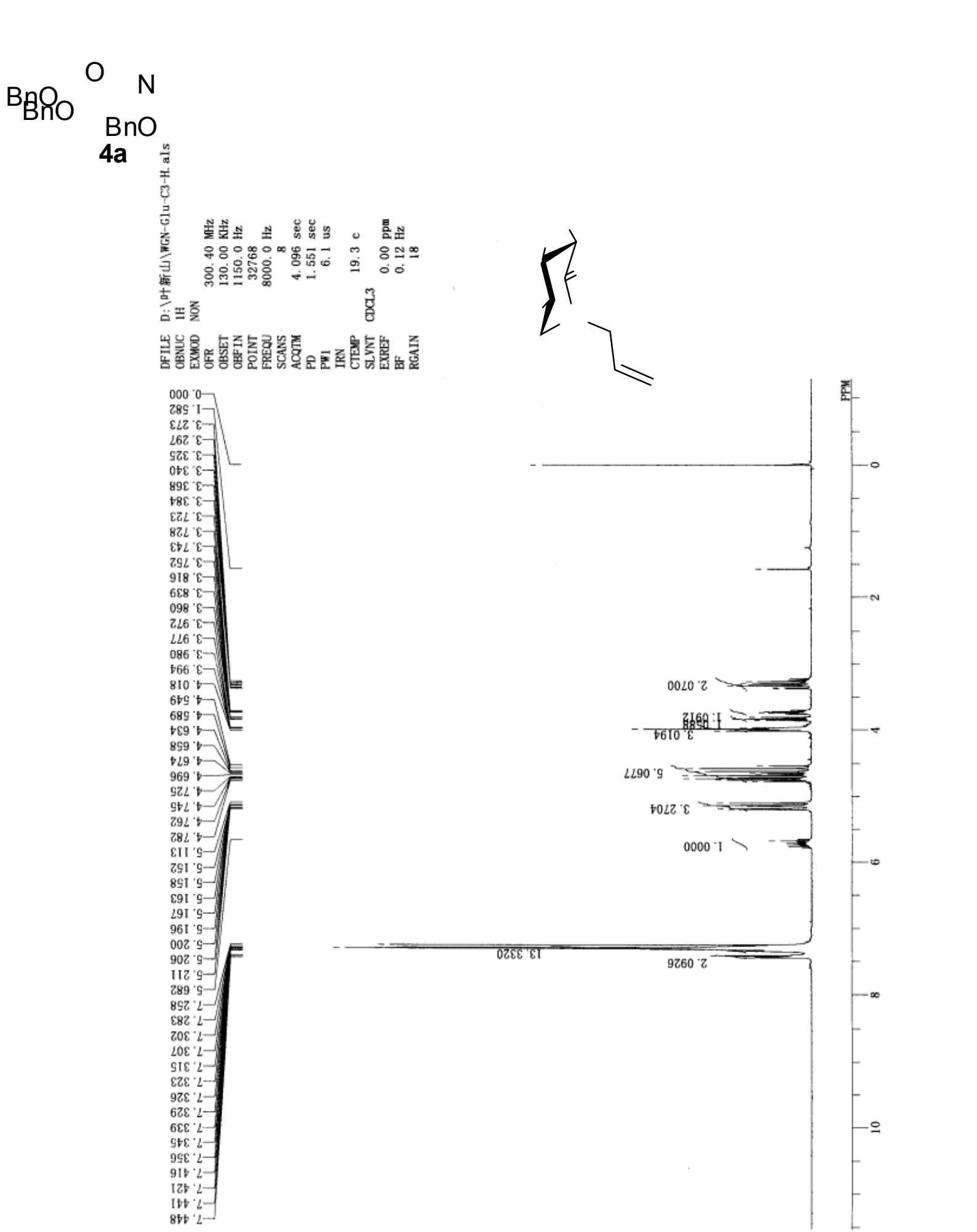

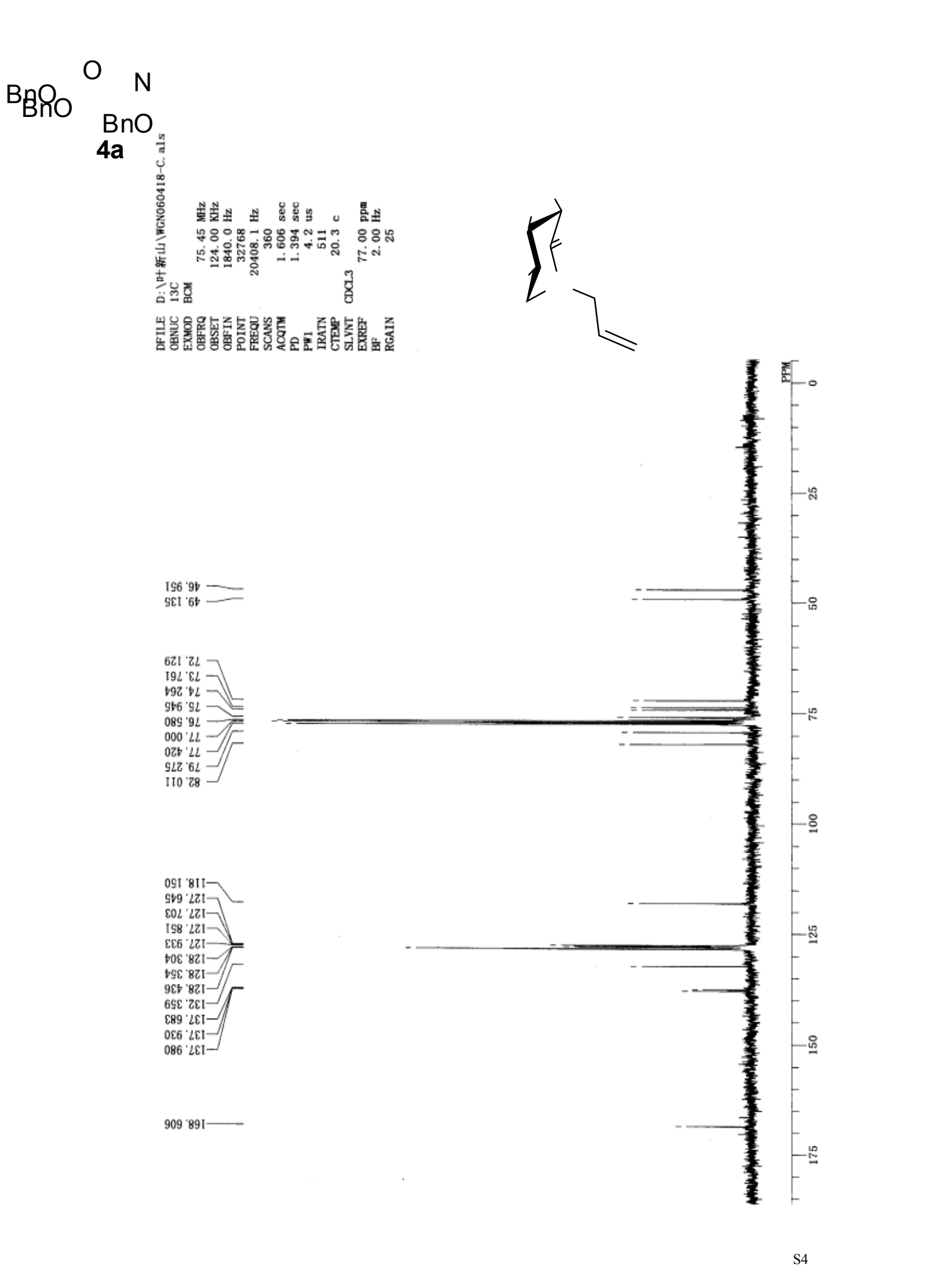

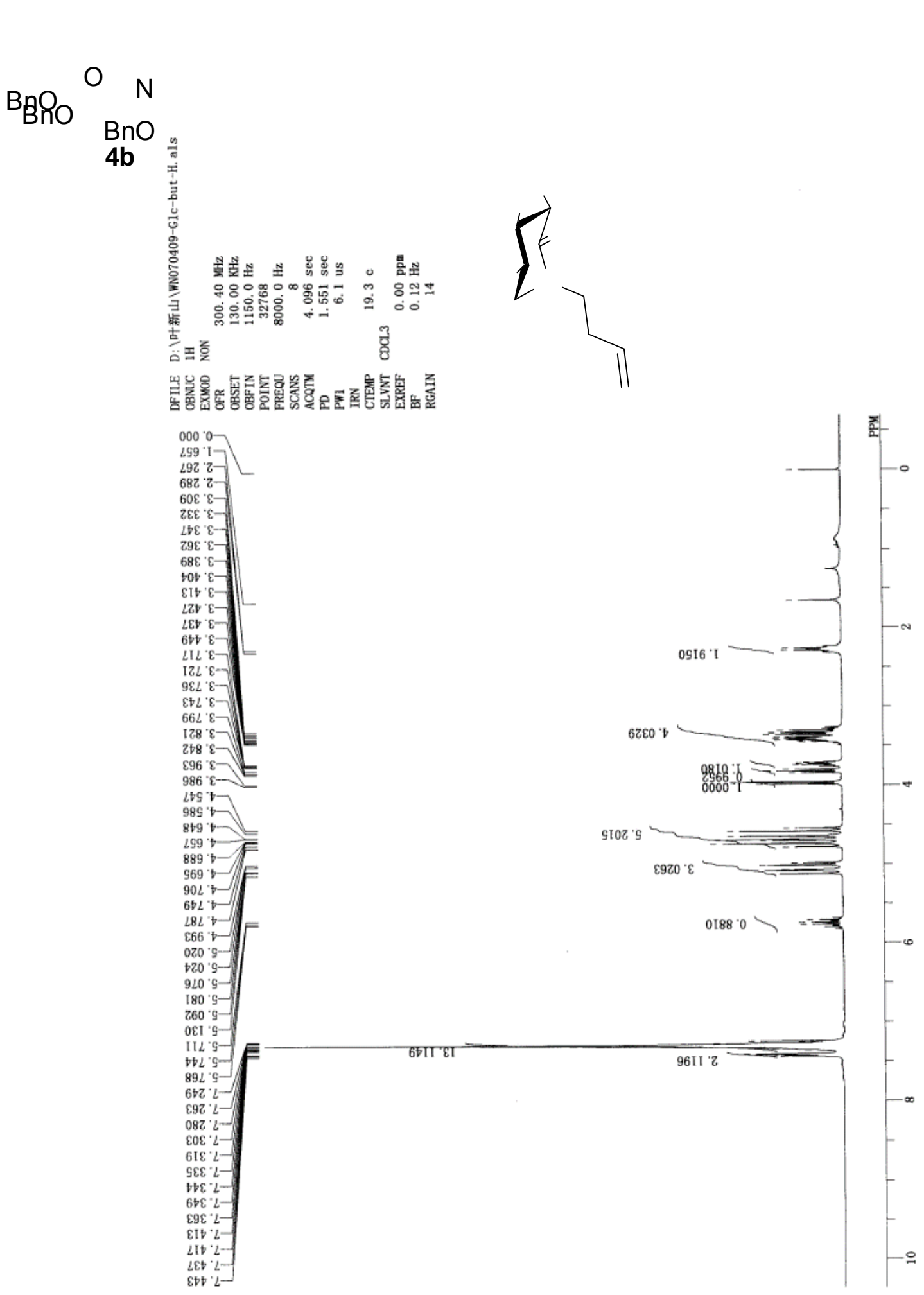

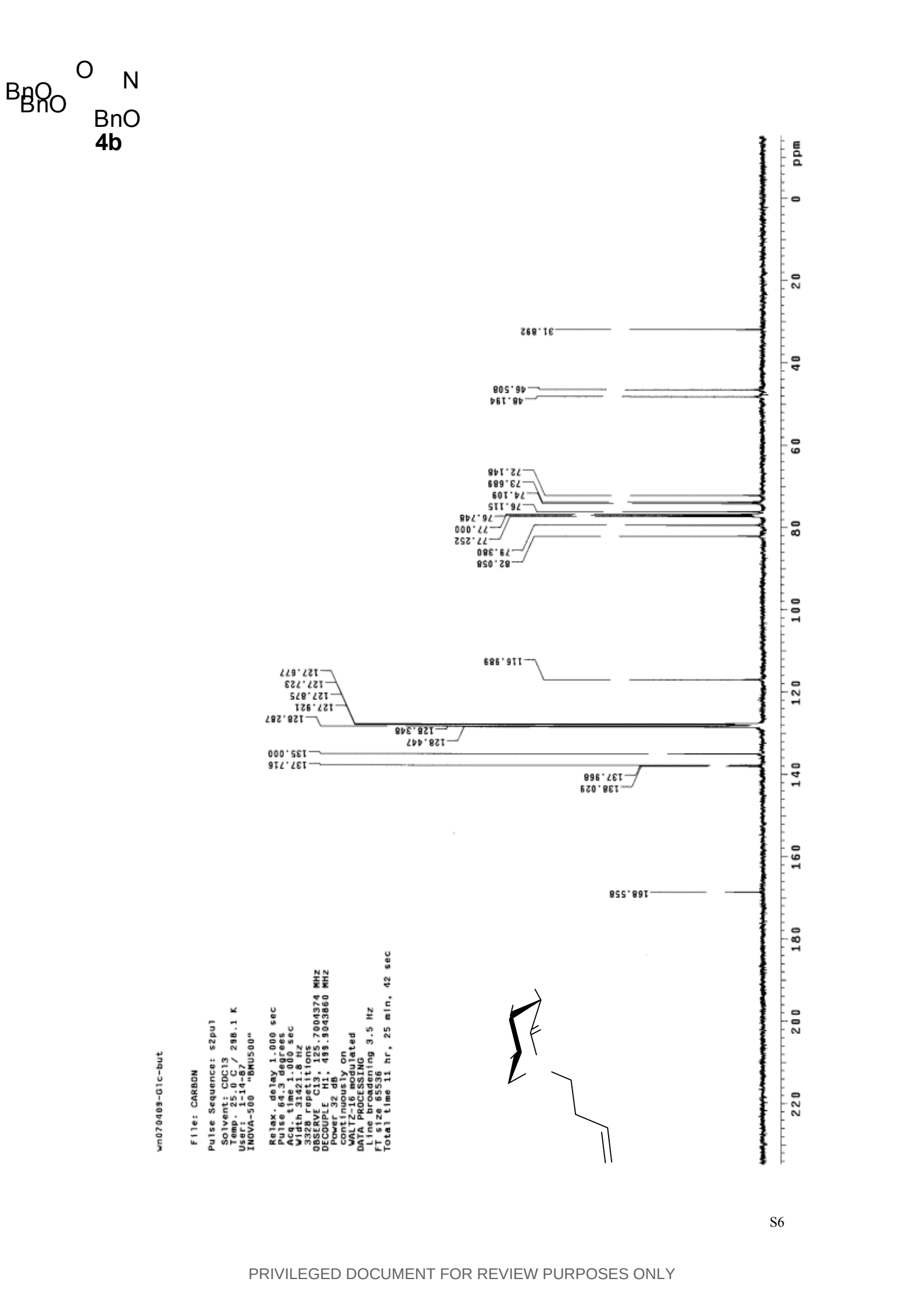

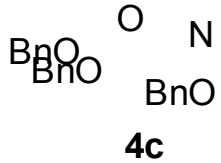

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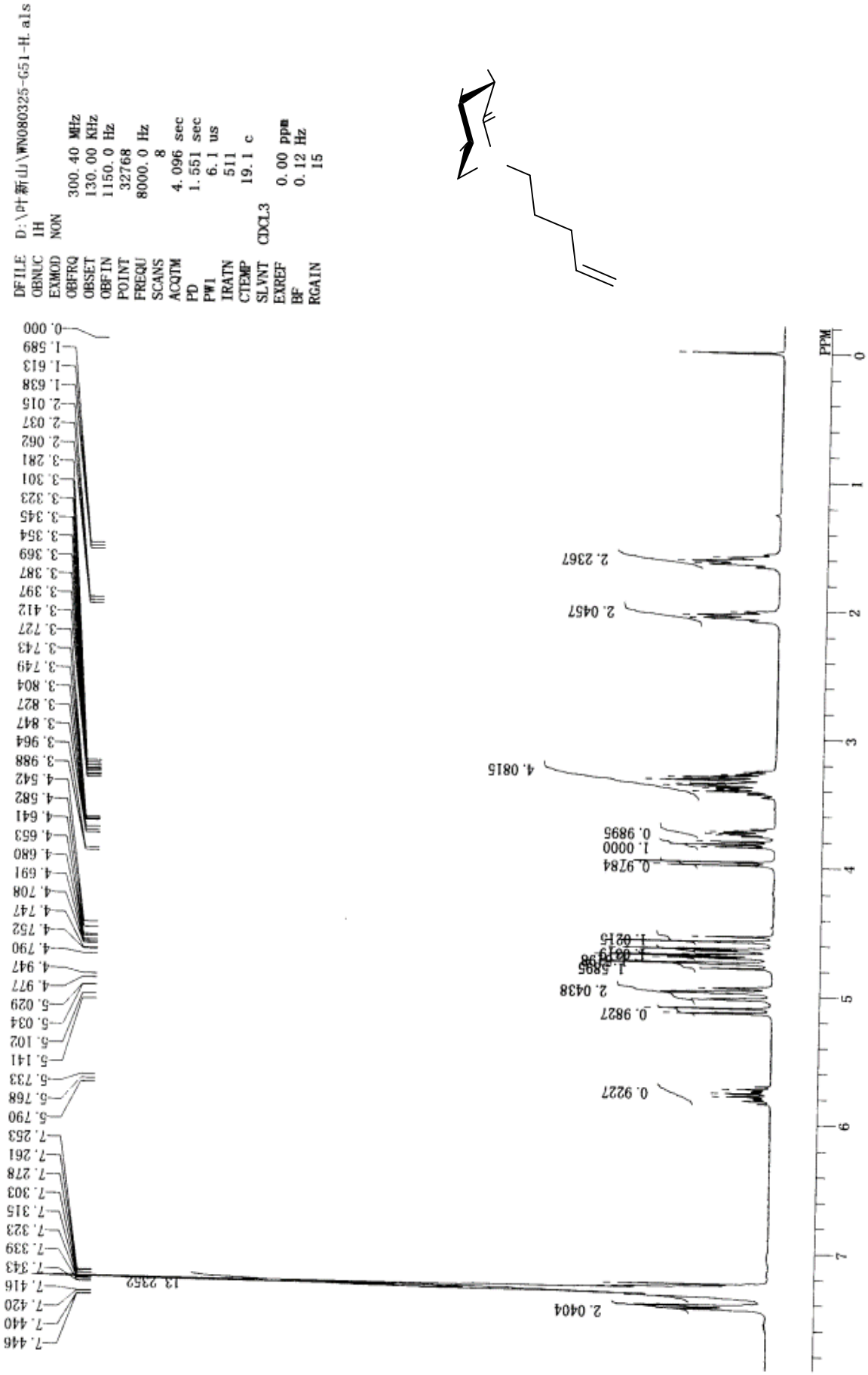

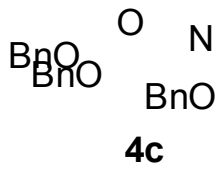

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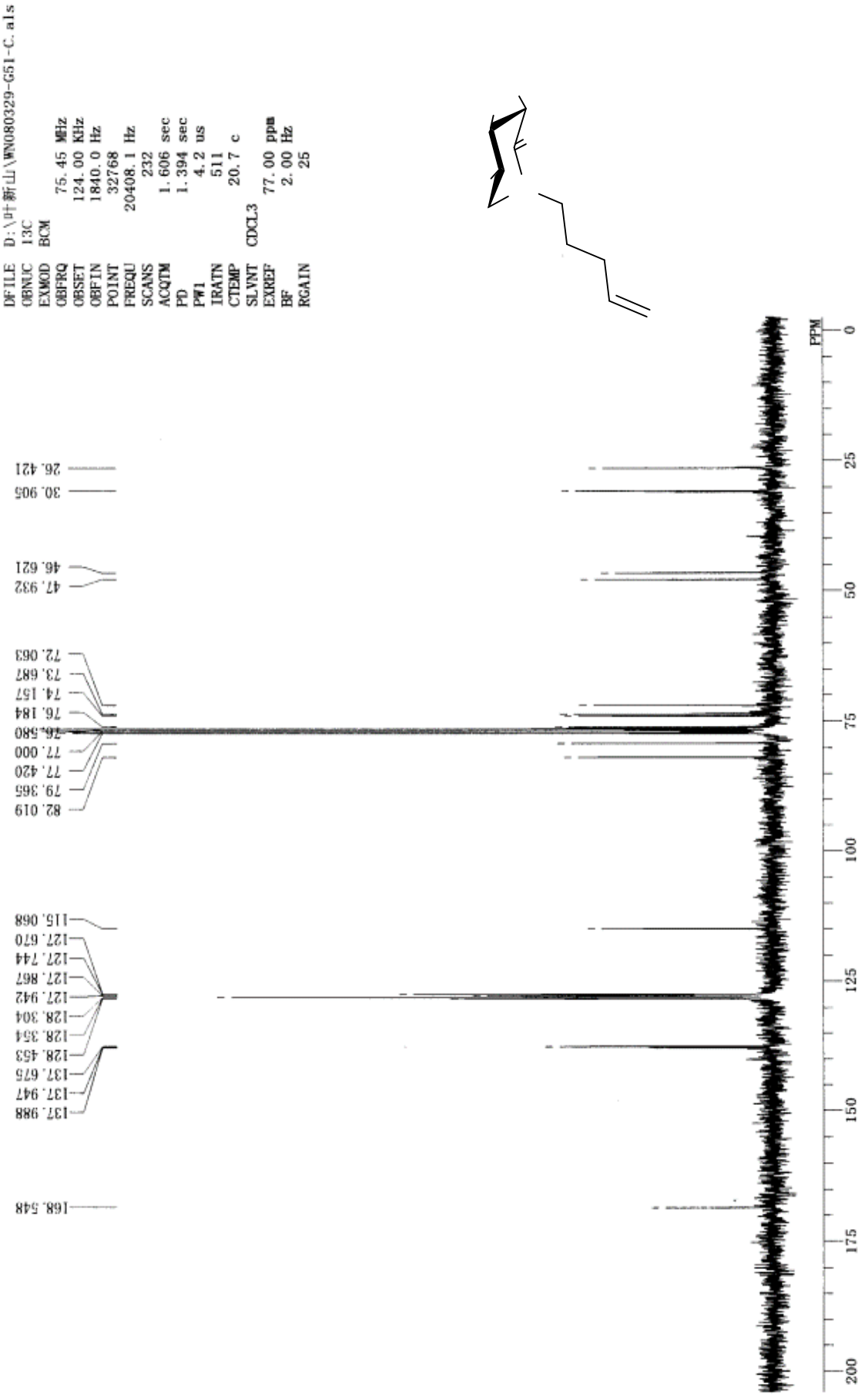

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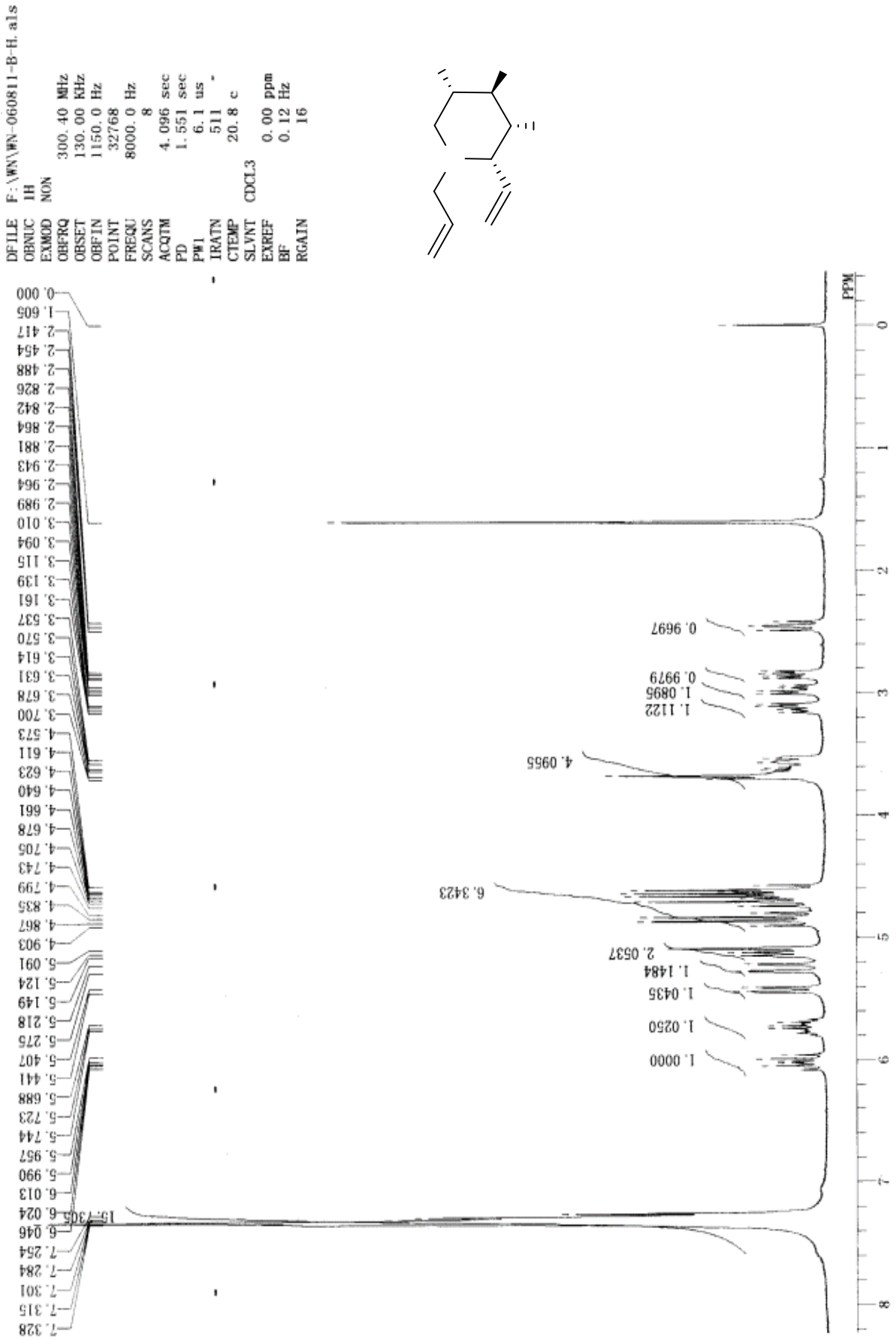

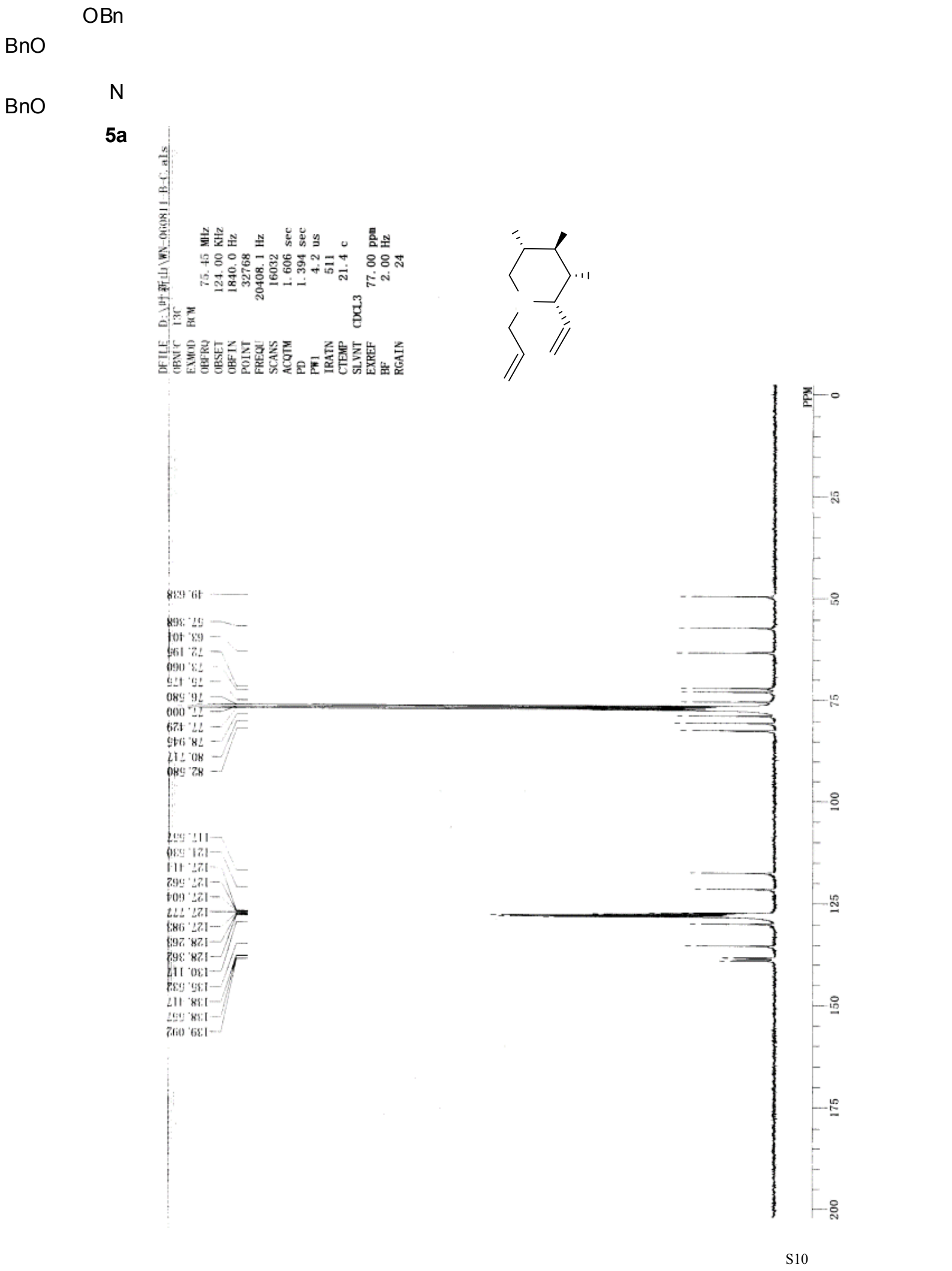

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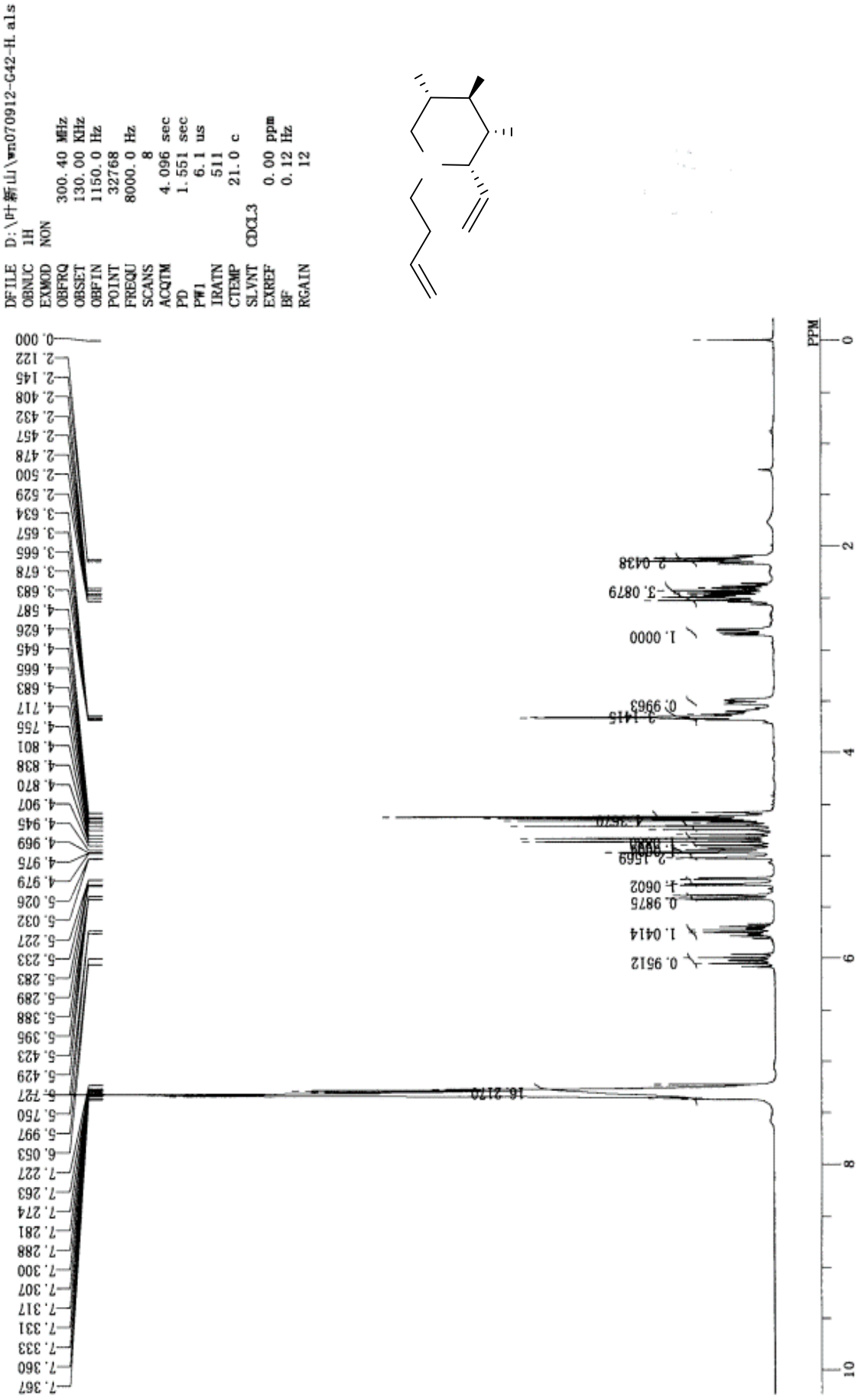

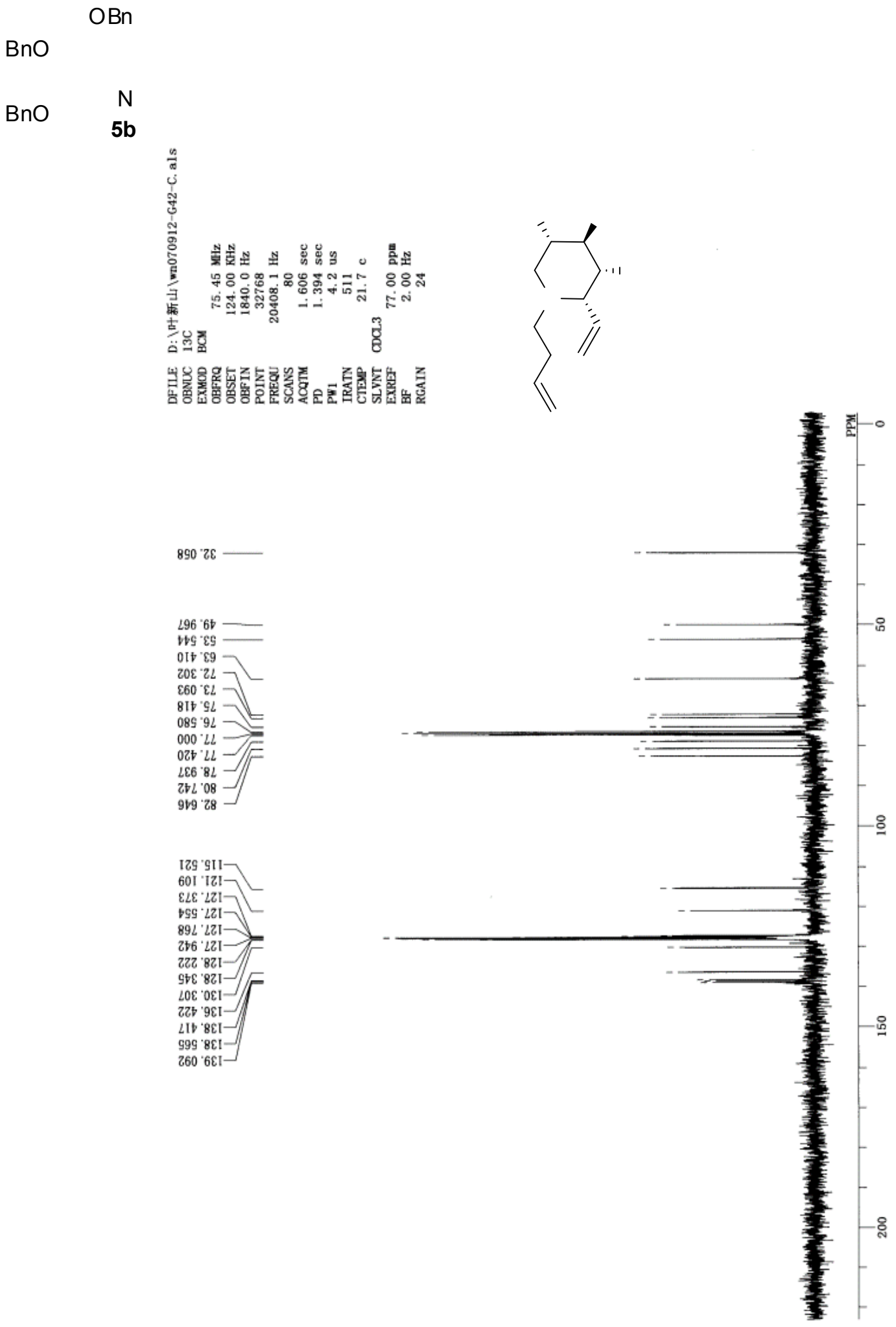

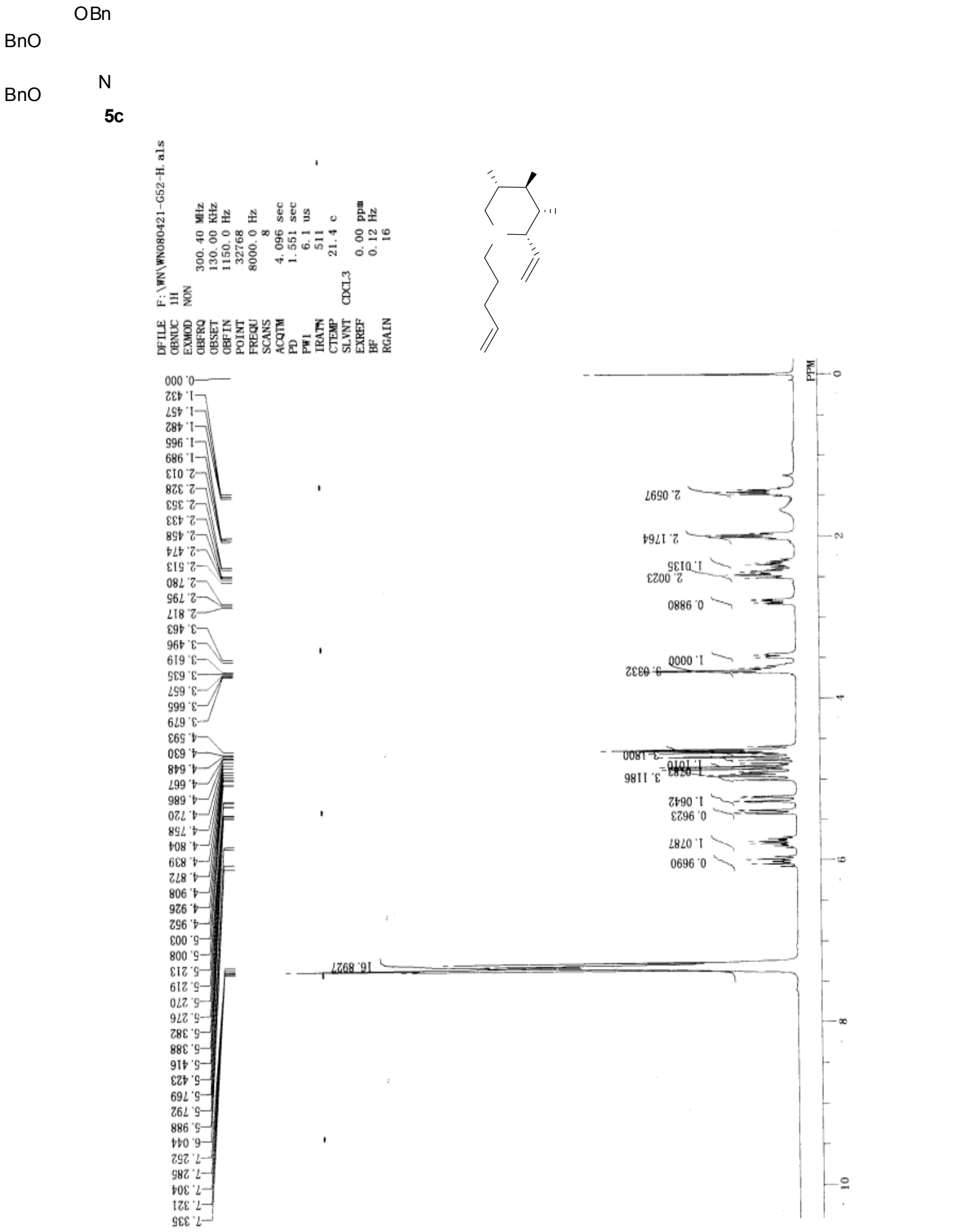

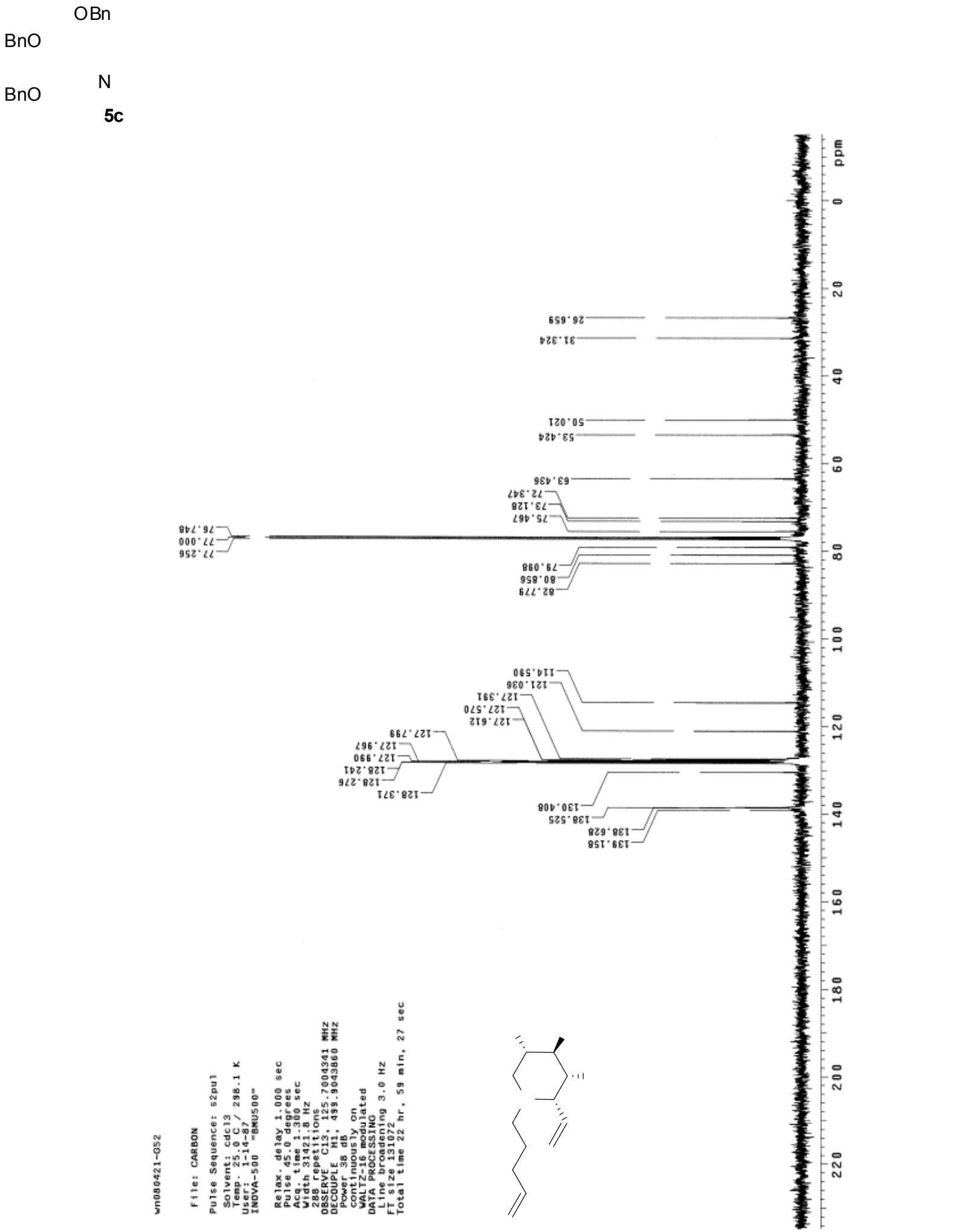

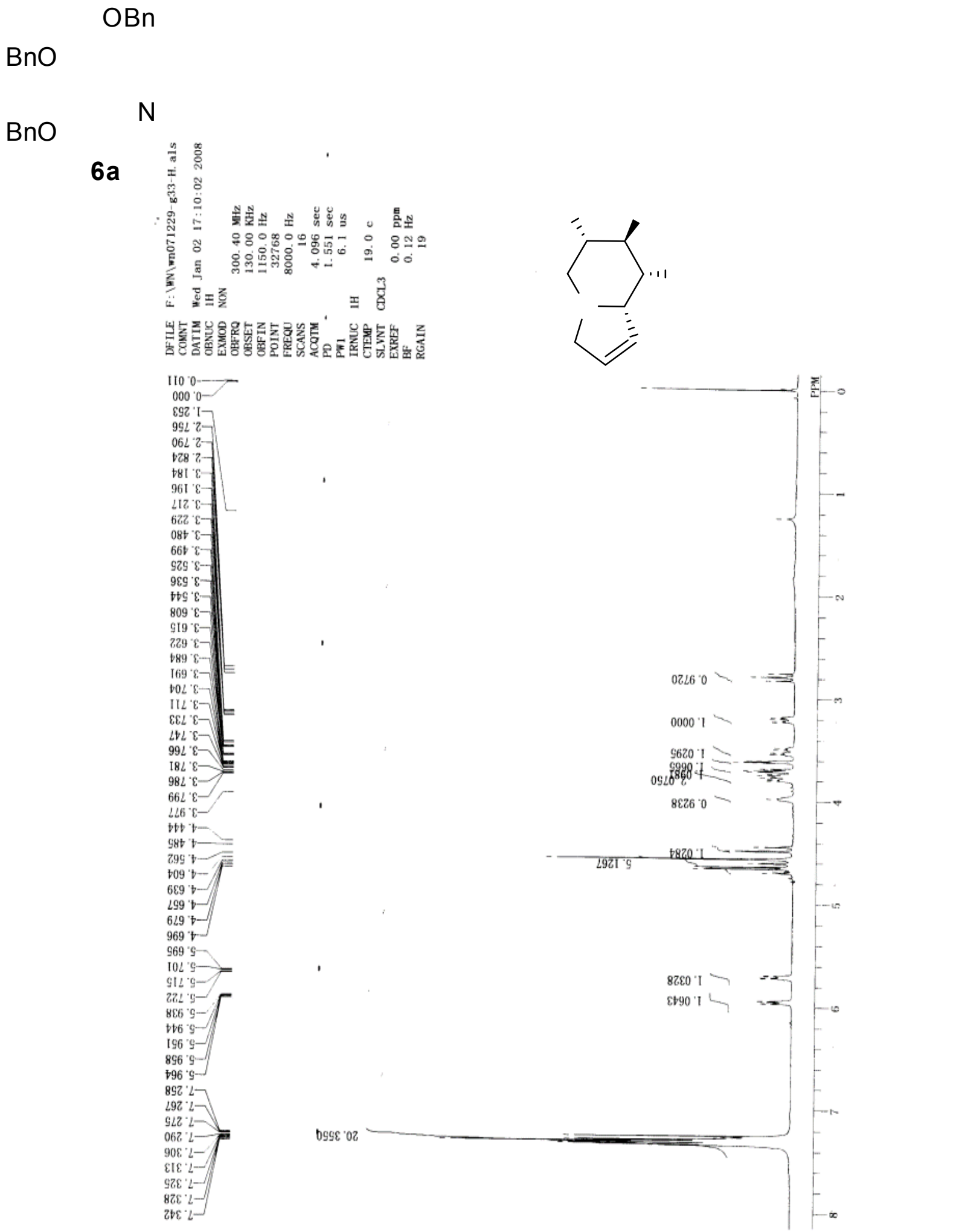

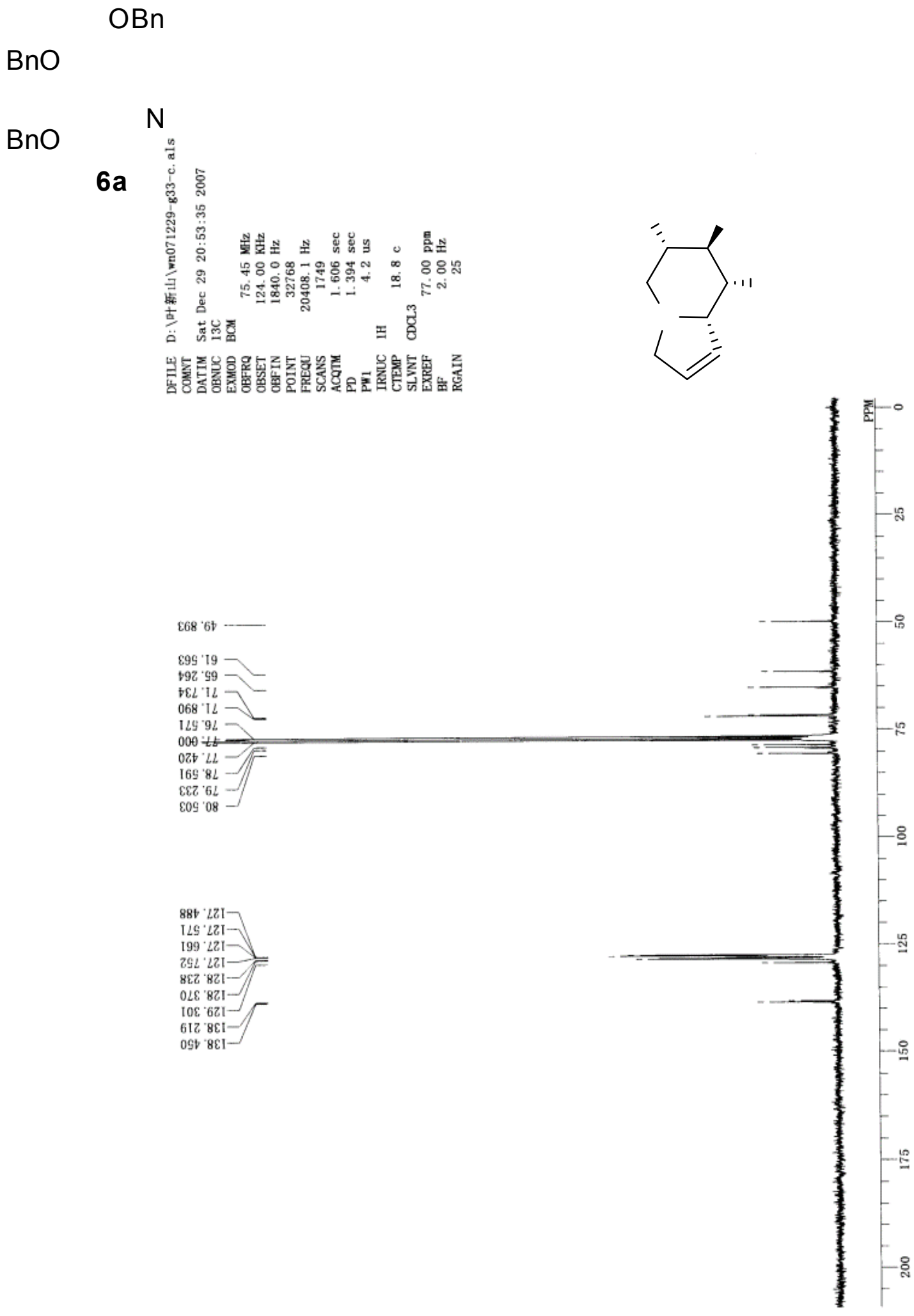

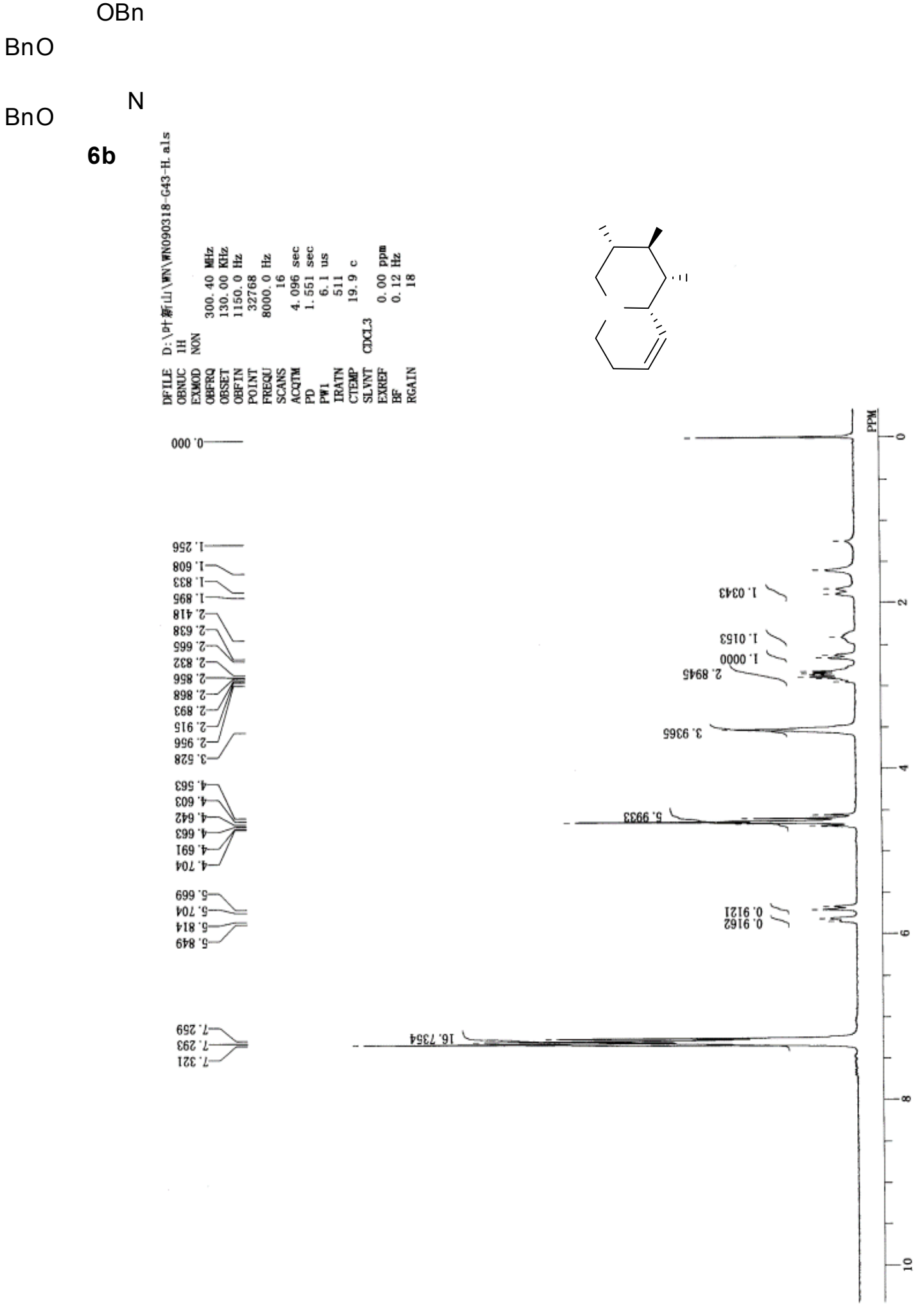

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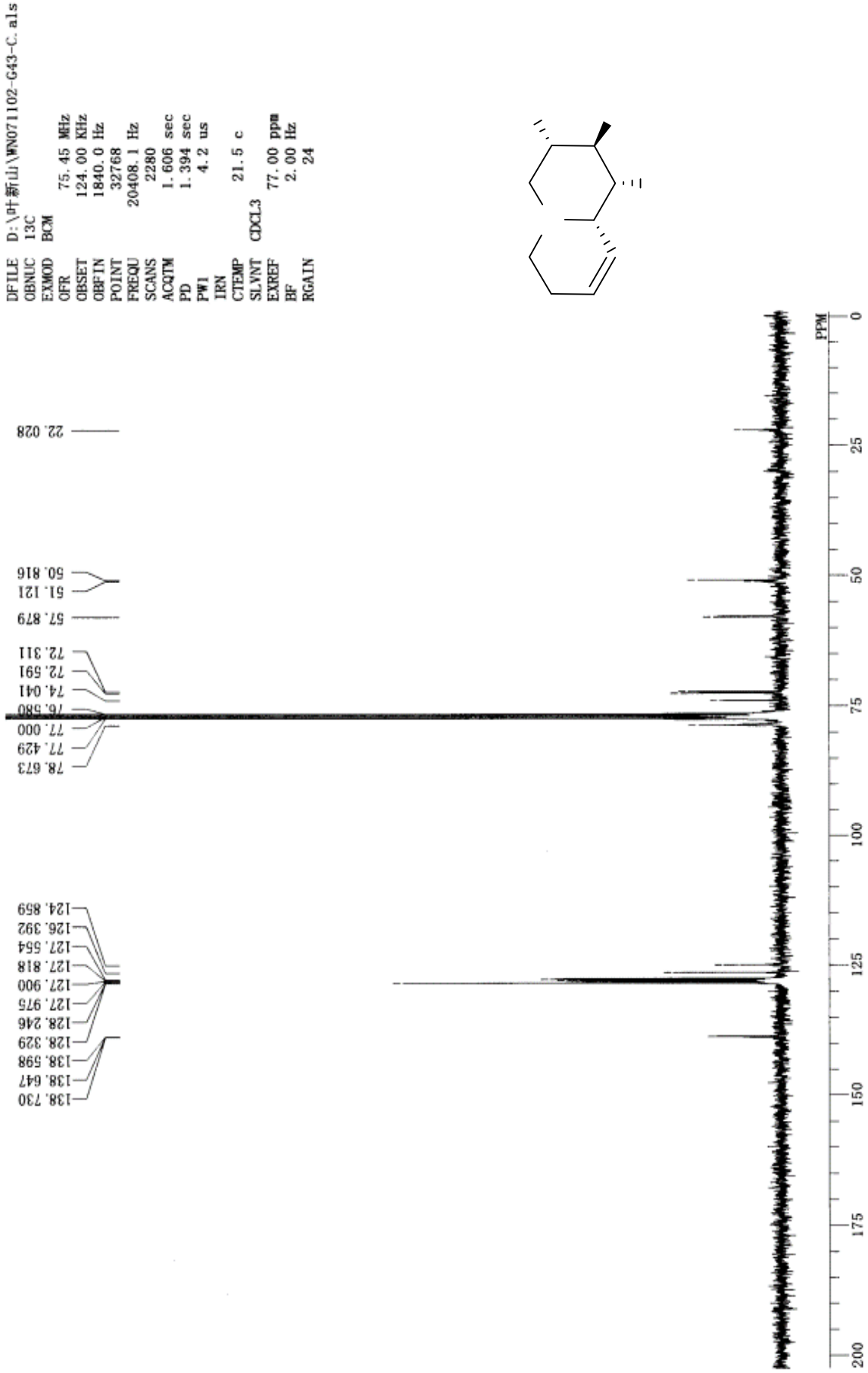

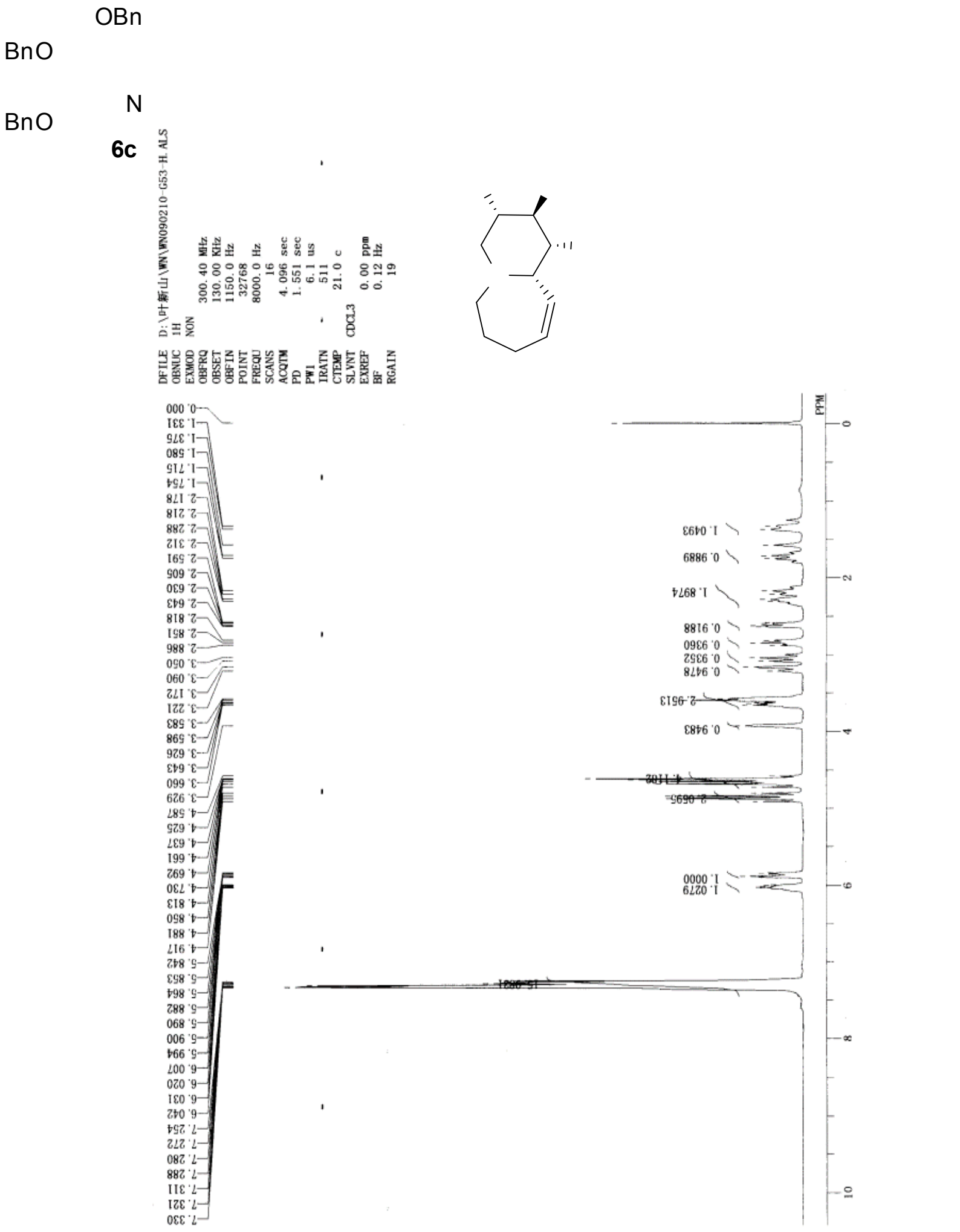

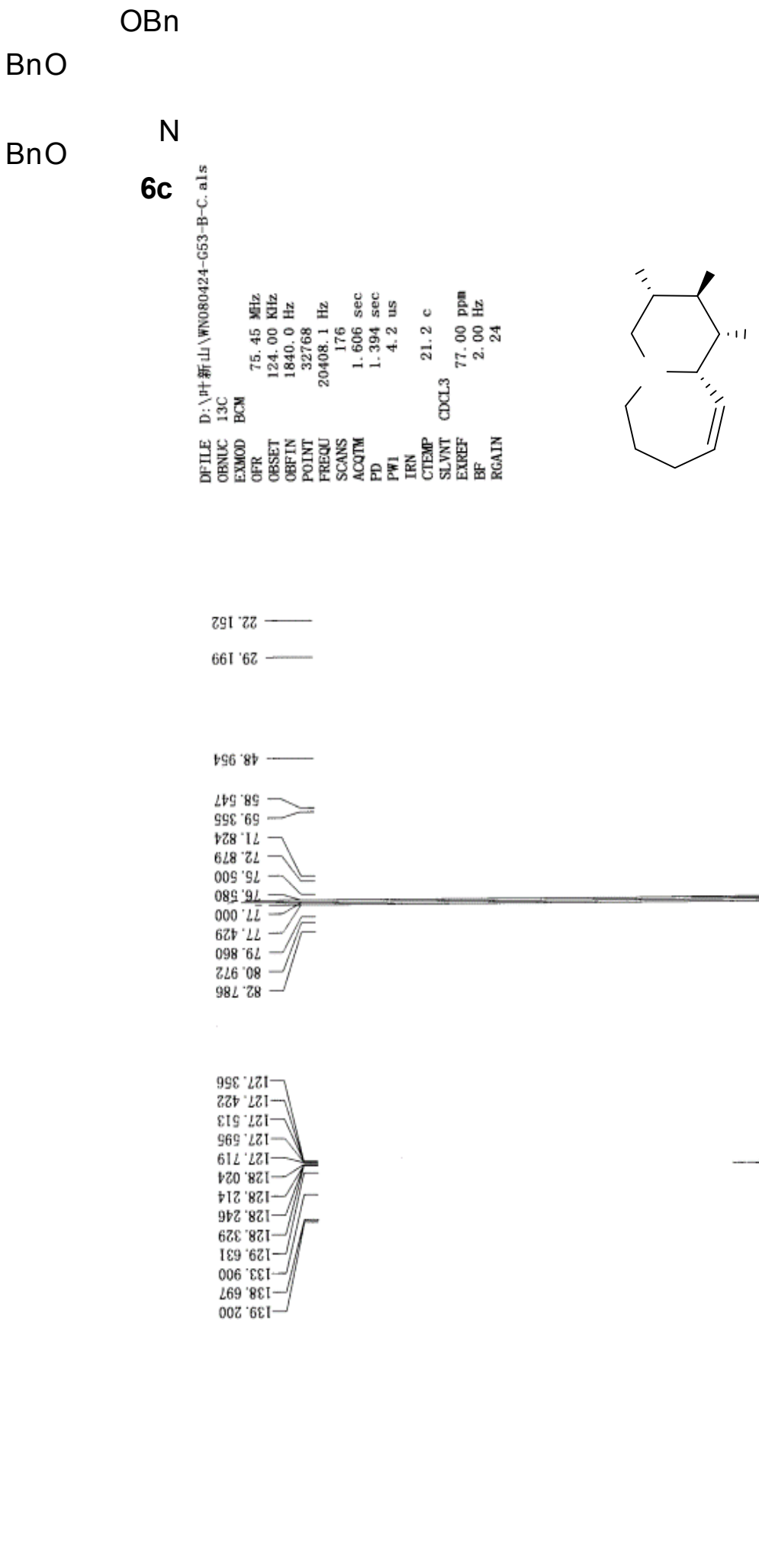

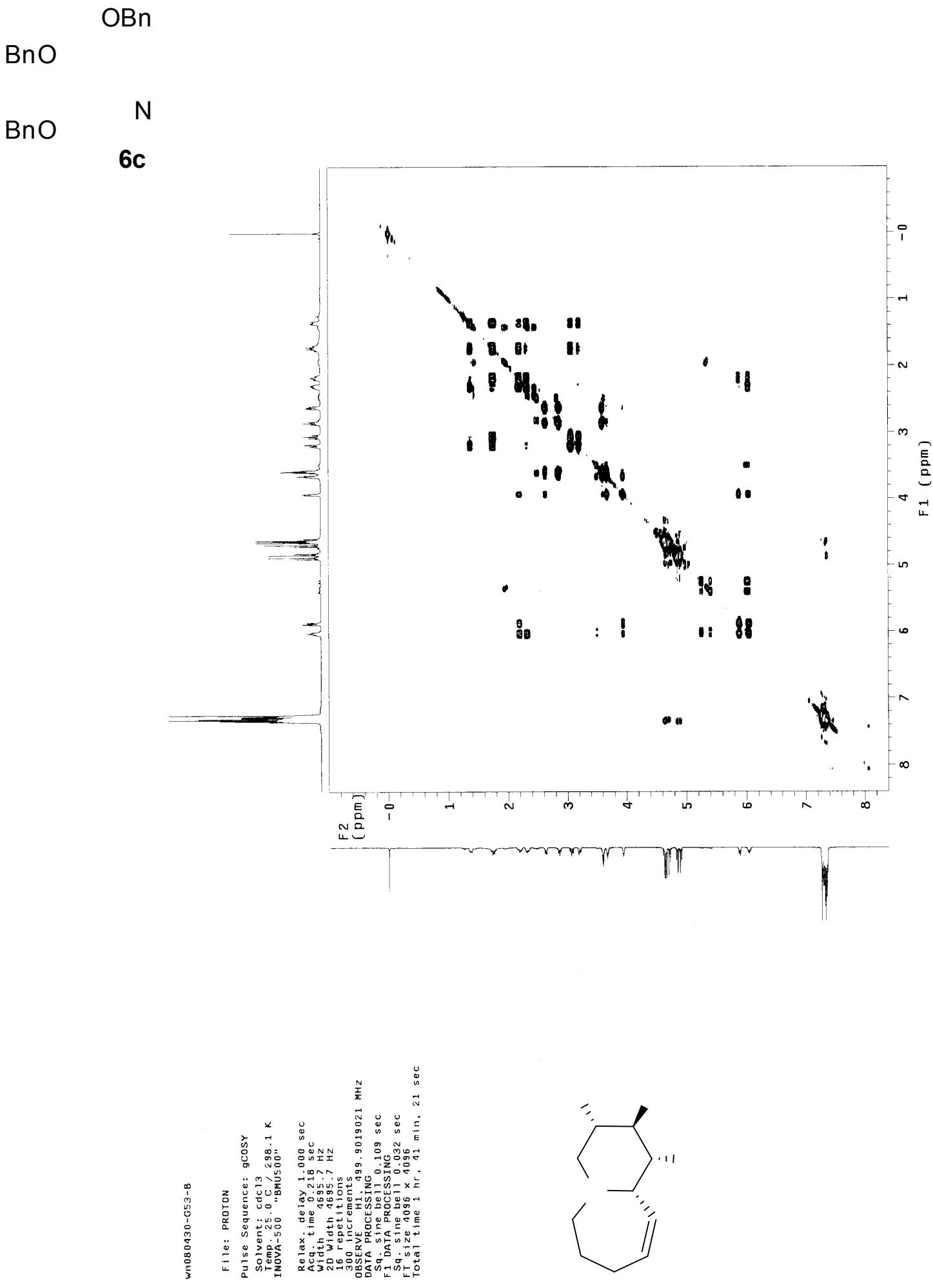

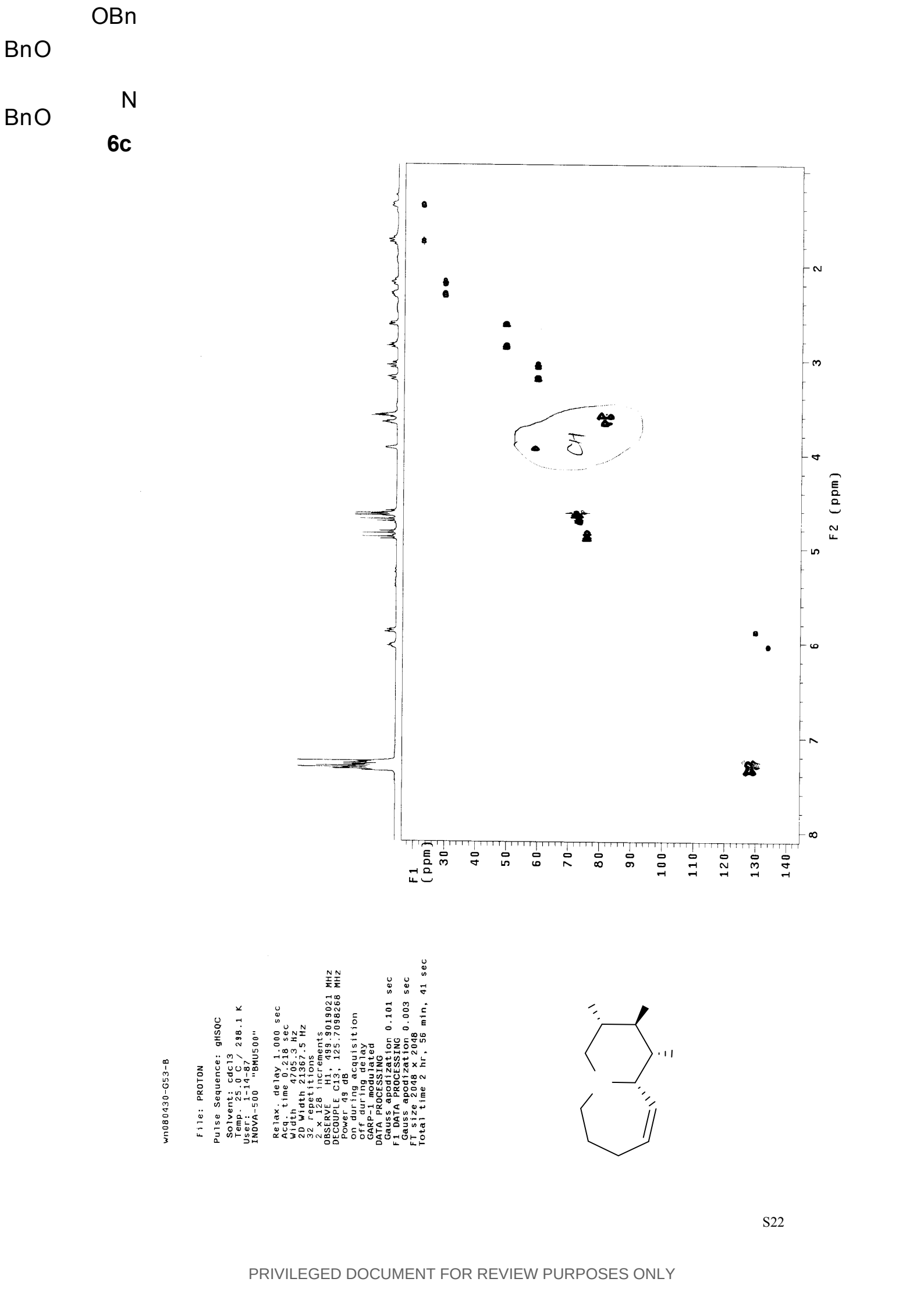

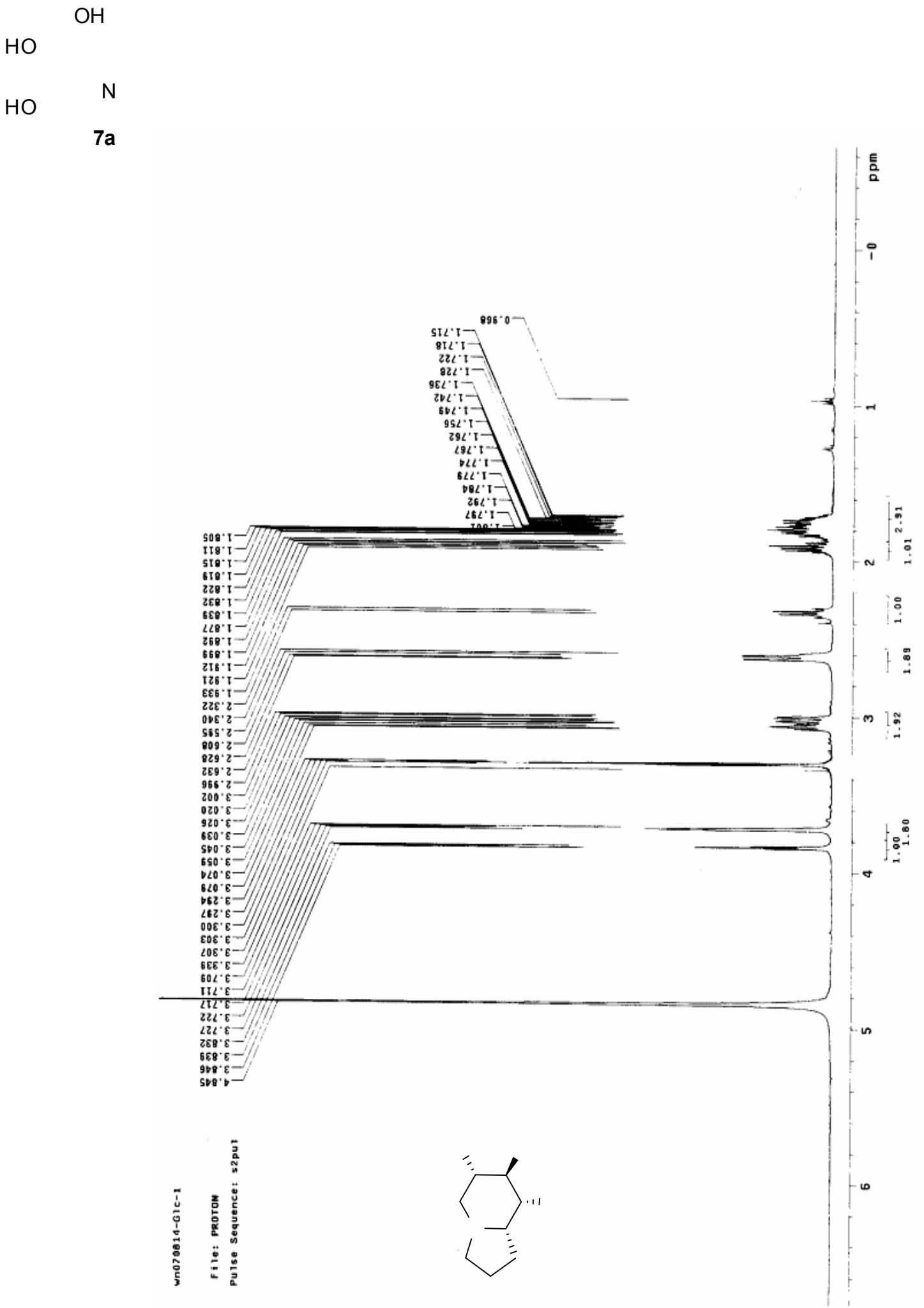

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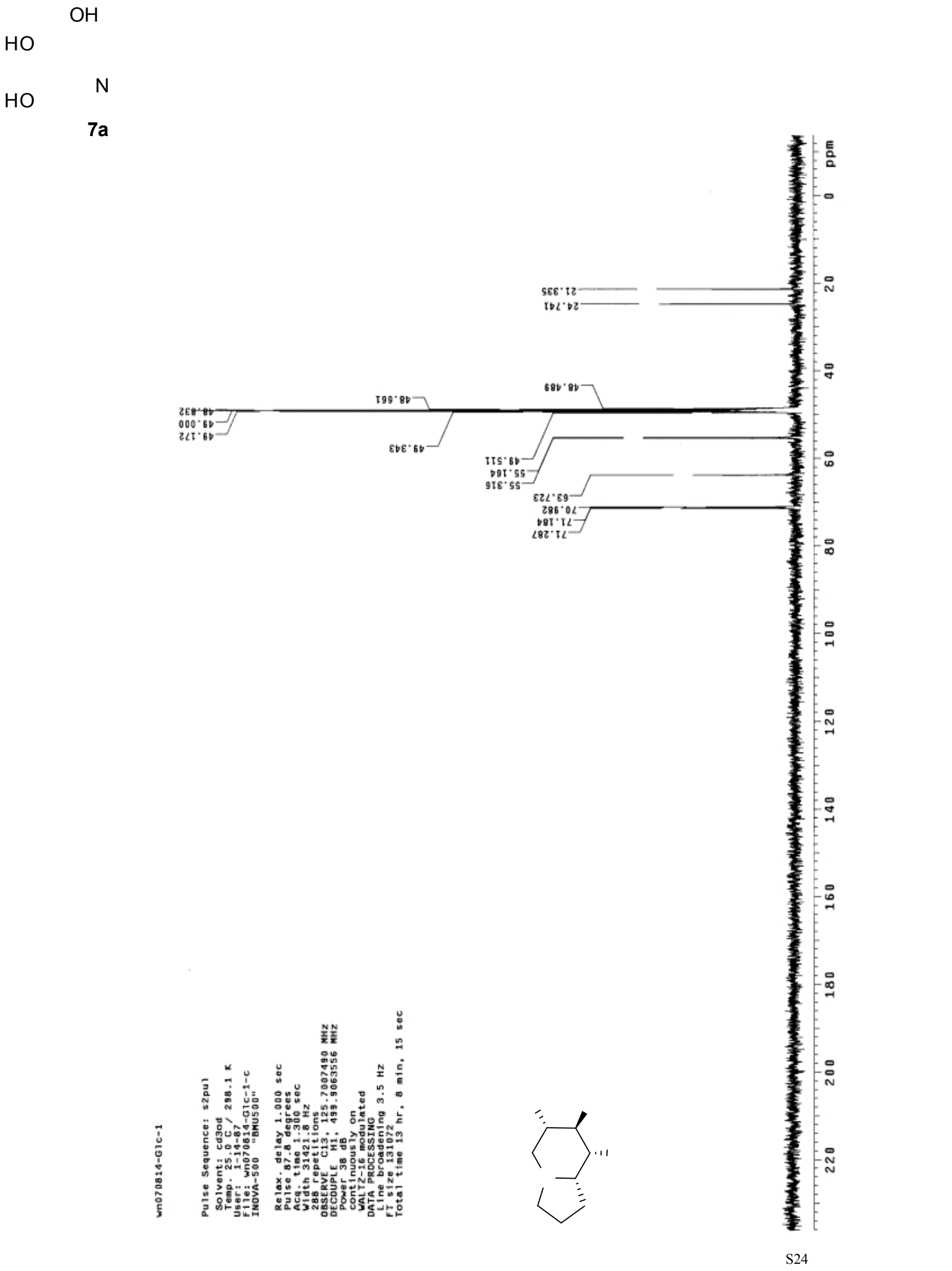
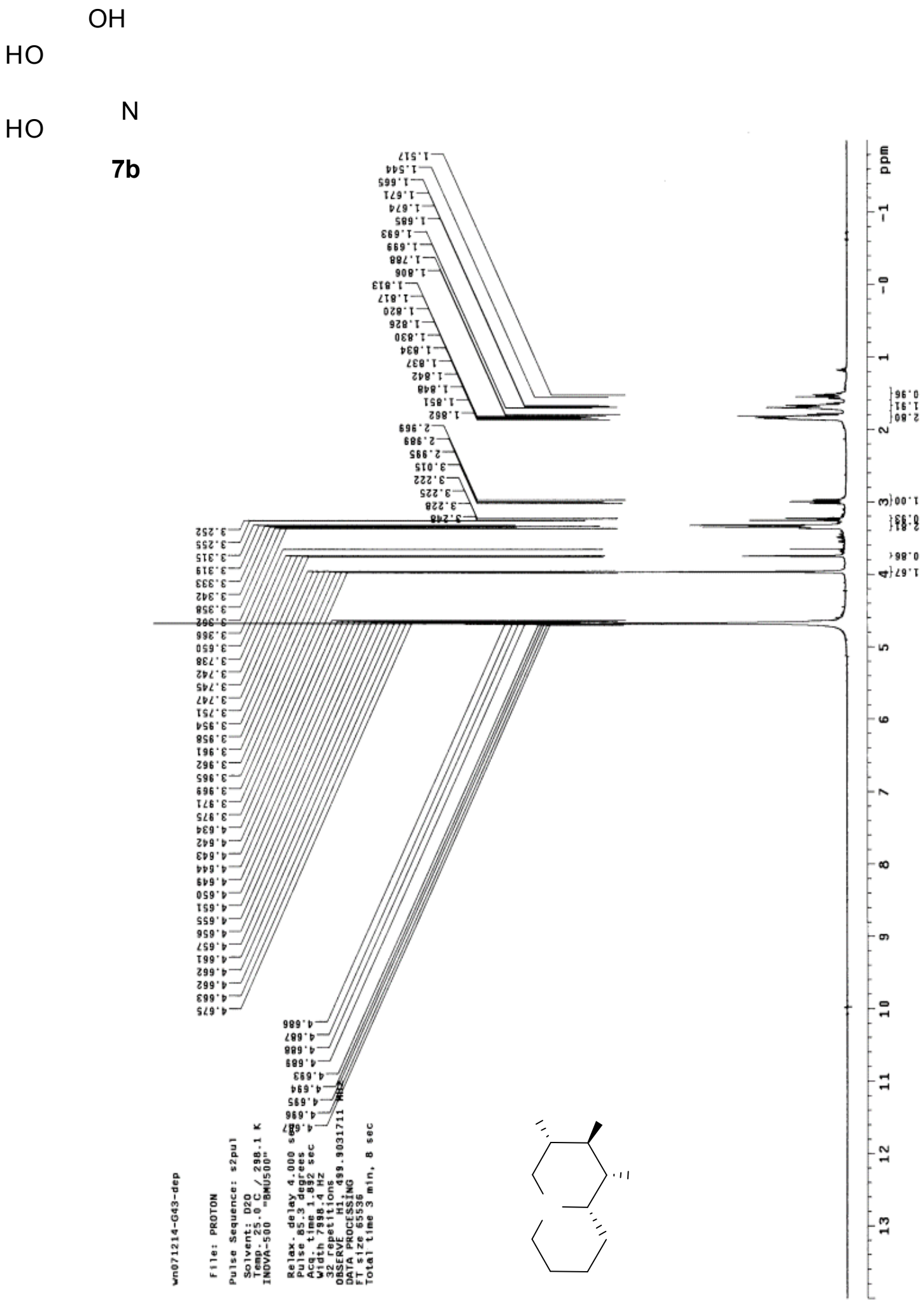
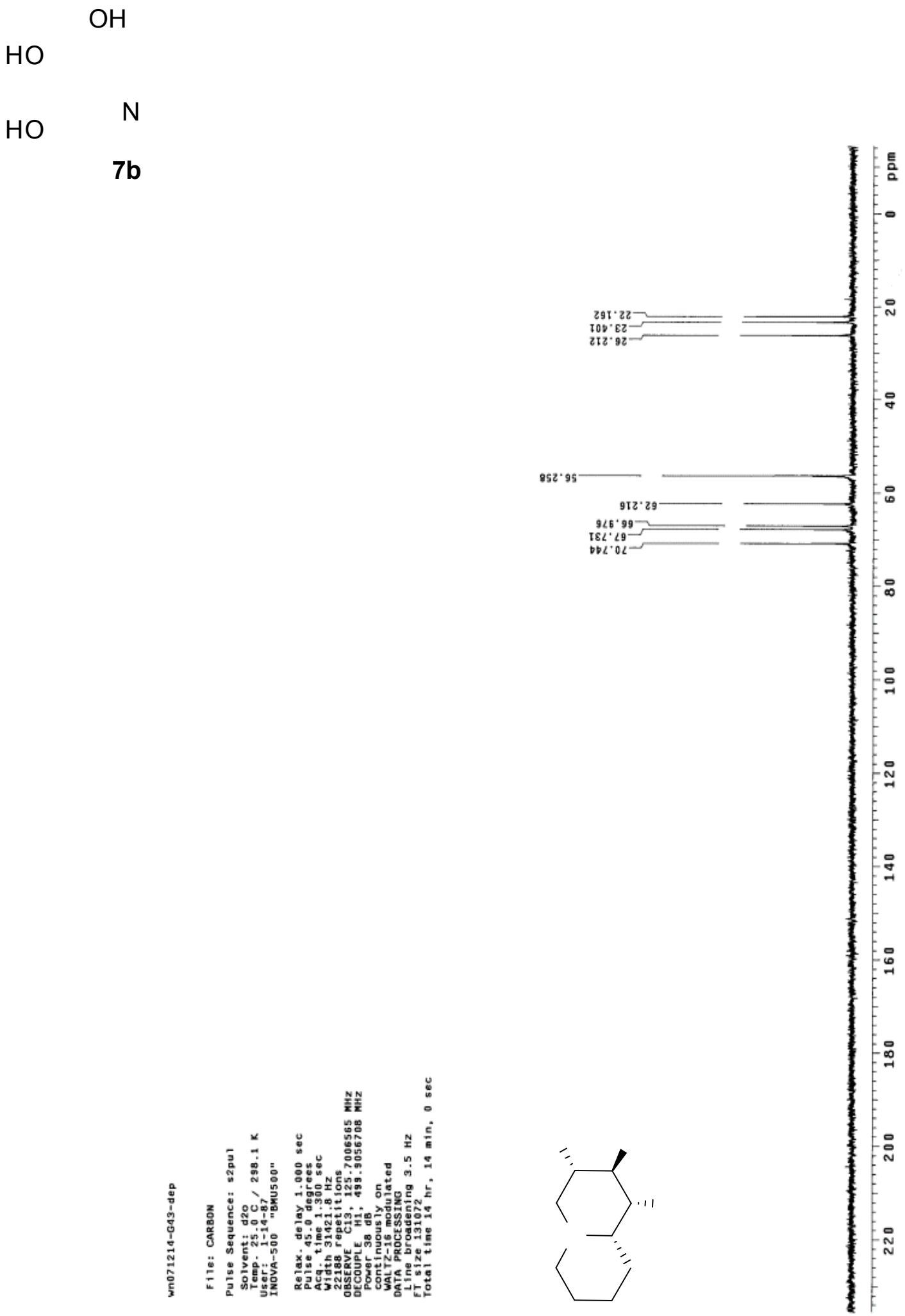
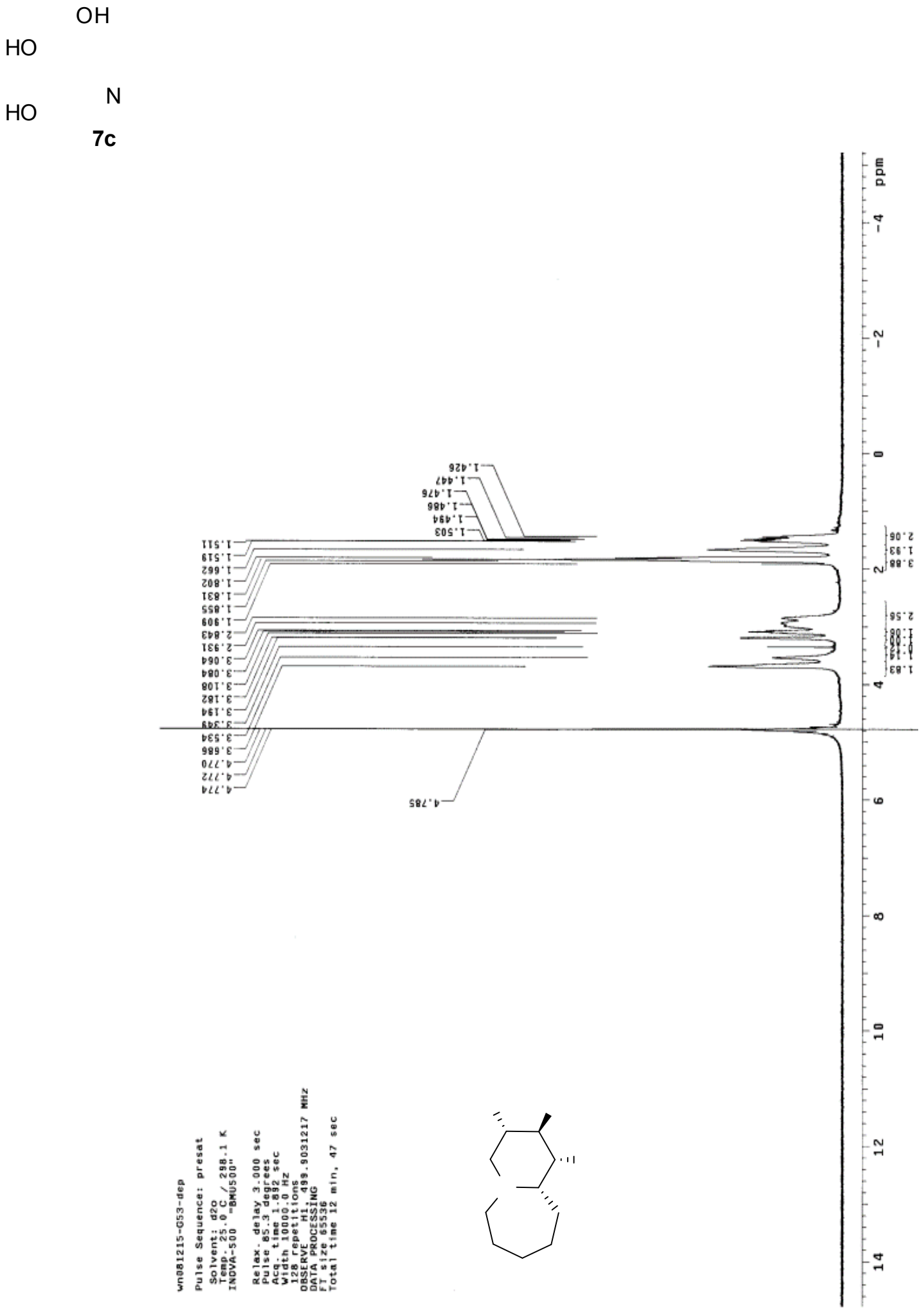
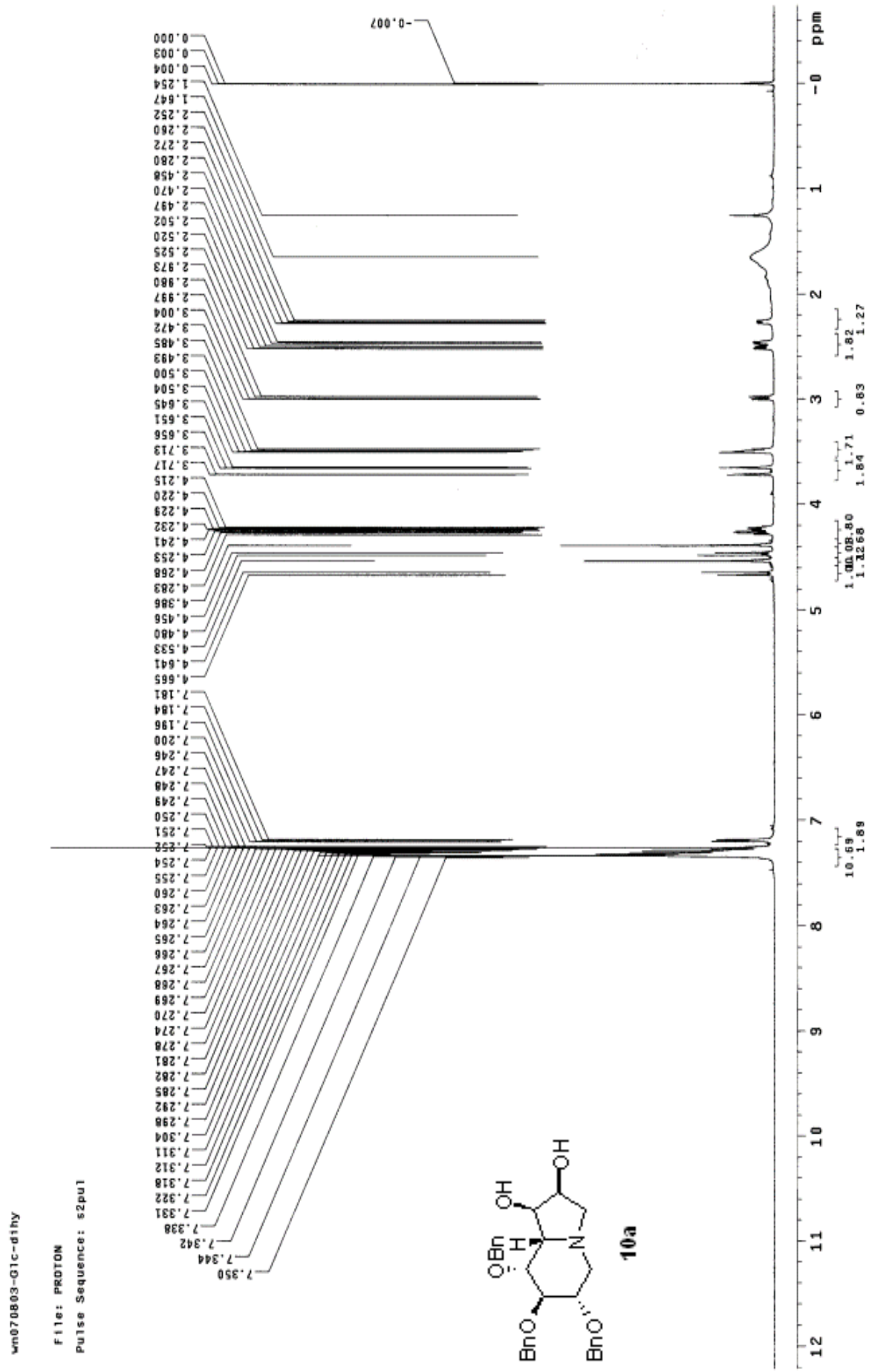
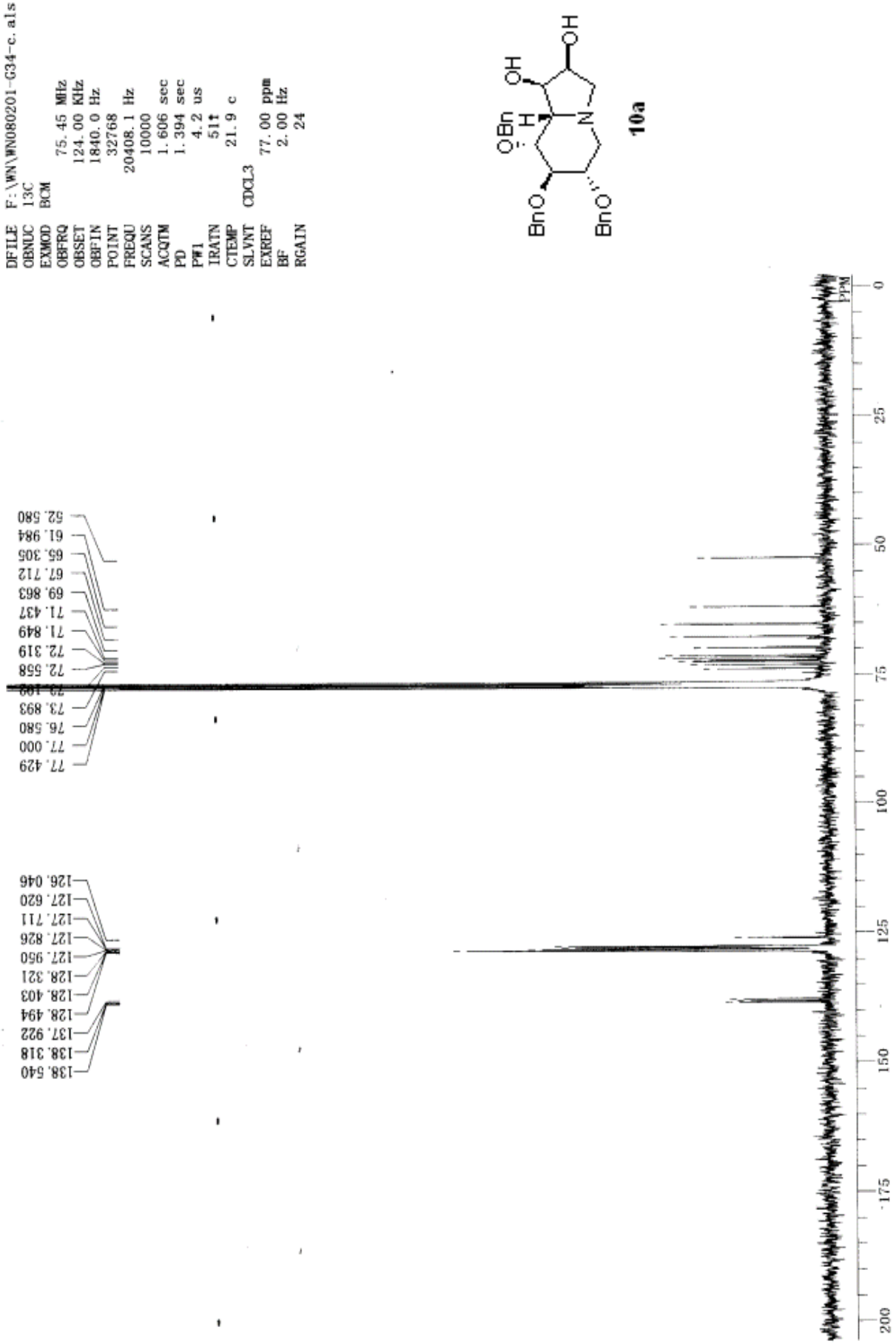










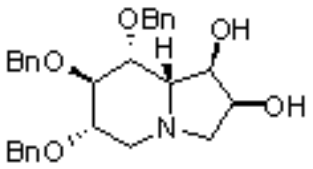


wn071231-G34

File: PROTON

Pulse Sequence: gCOSY
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.208 sec
Width 4916.1 Hz
2D Width 4916.1 Hz
24 repetitions
300 increments
OBSERVE H1, 499.9018980 MHz
DATA PROCESSING
Sq. sine bell 0.104 sec
F1 DATA PROCESSING
Sq. sine bell 0.031 sec
FT size 4096 x 4096
Total time 2 hr, 30 min, 31 sec



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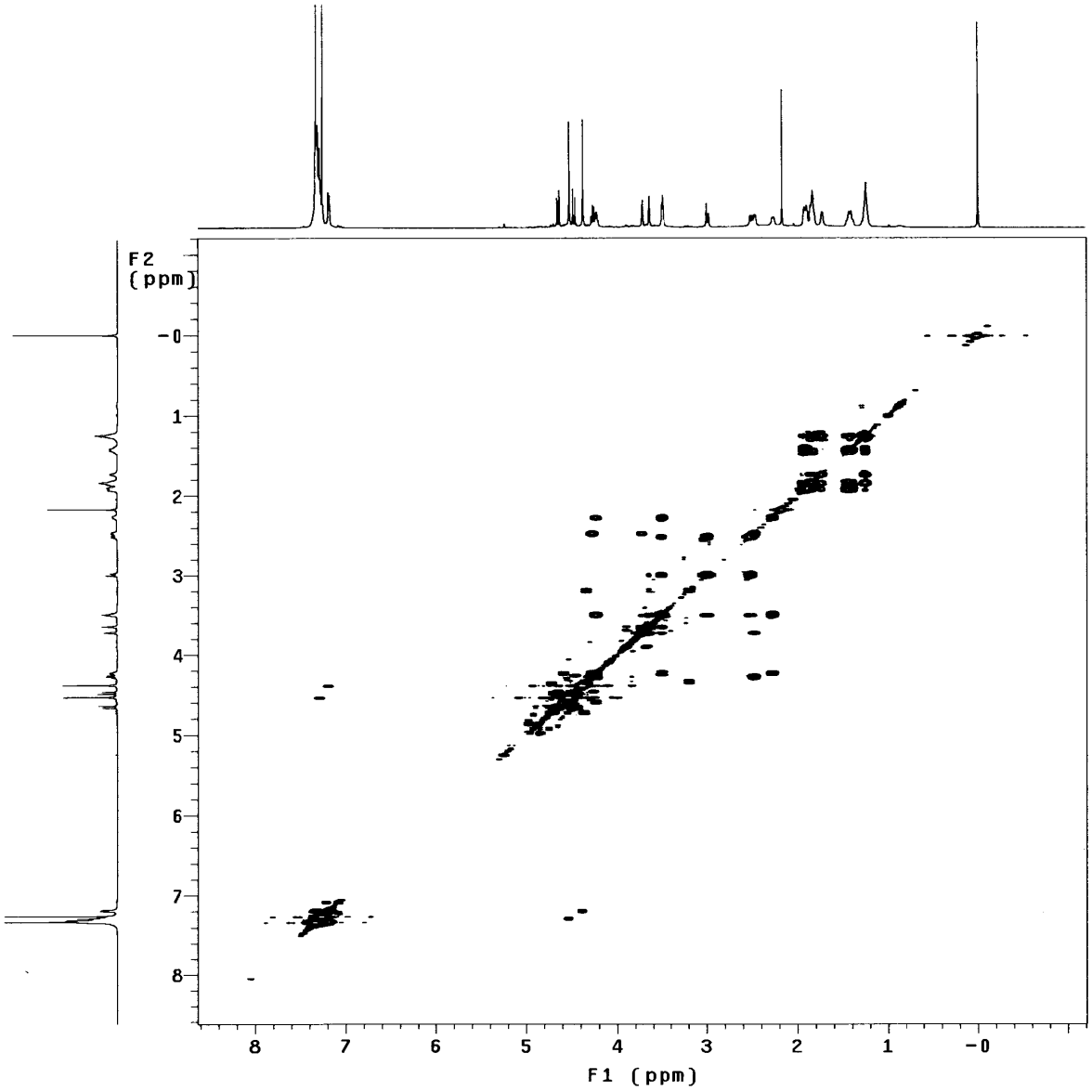
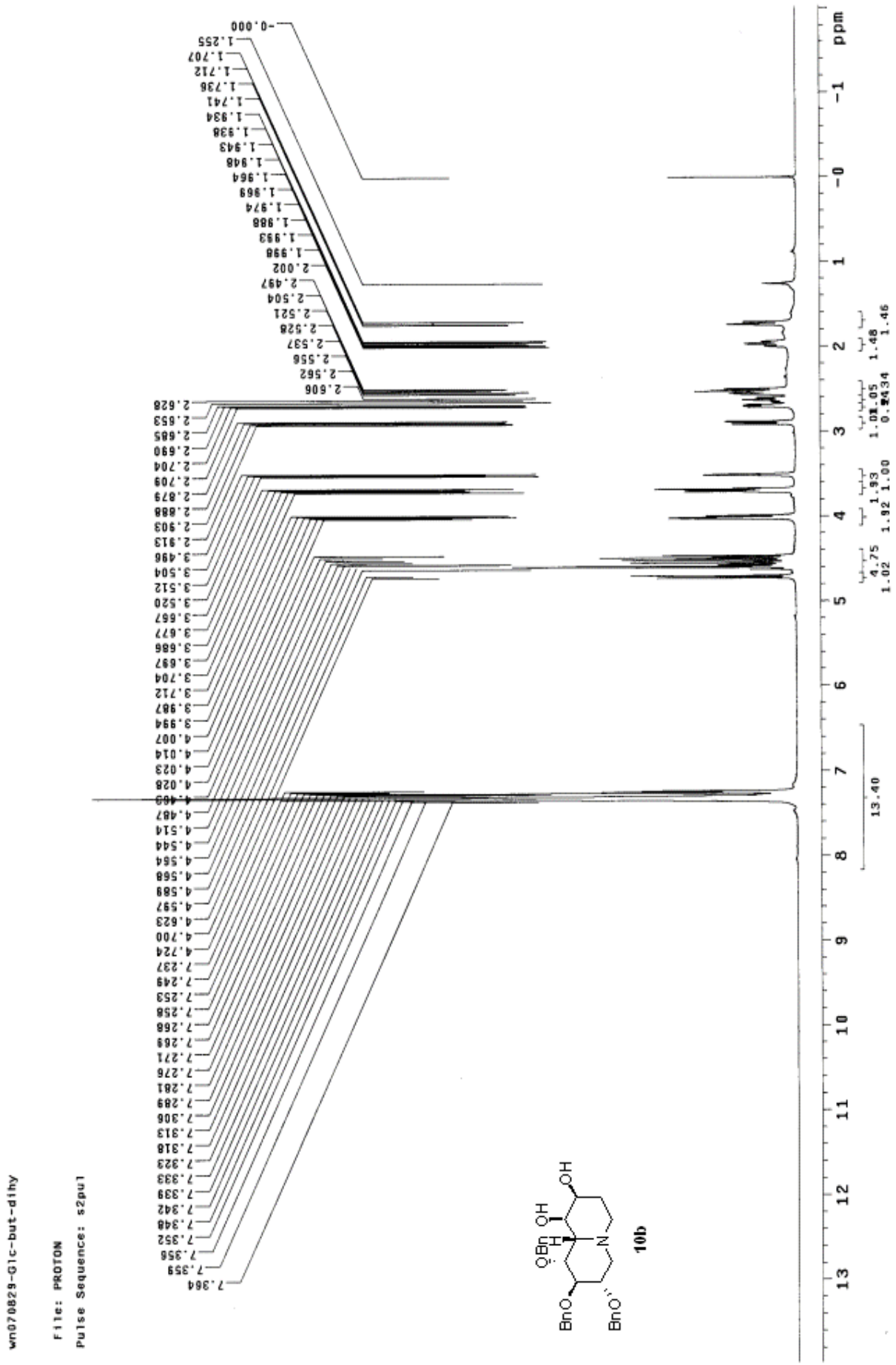
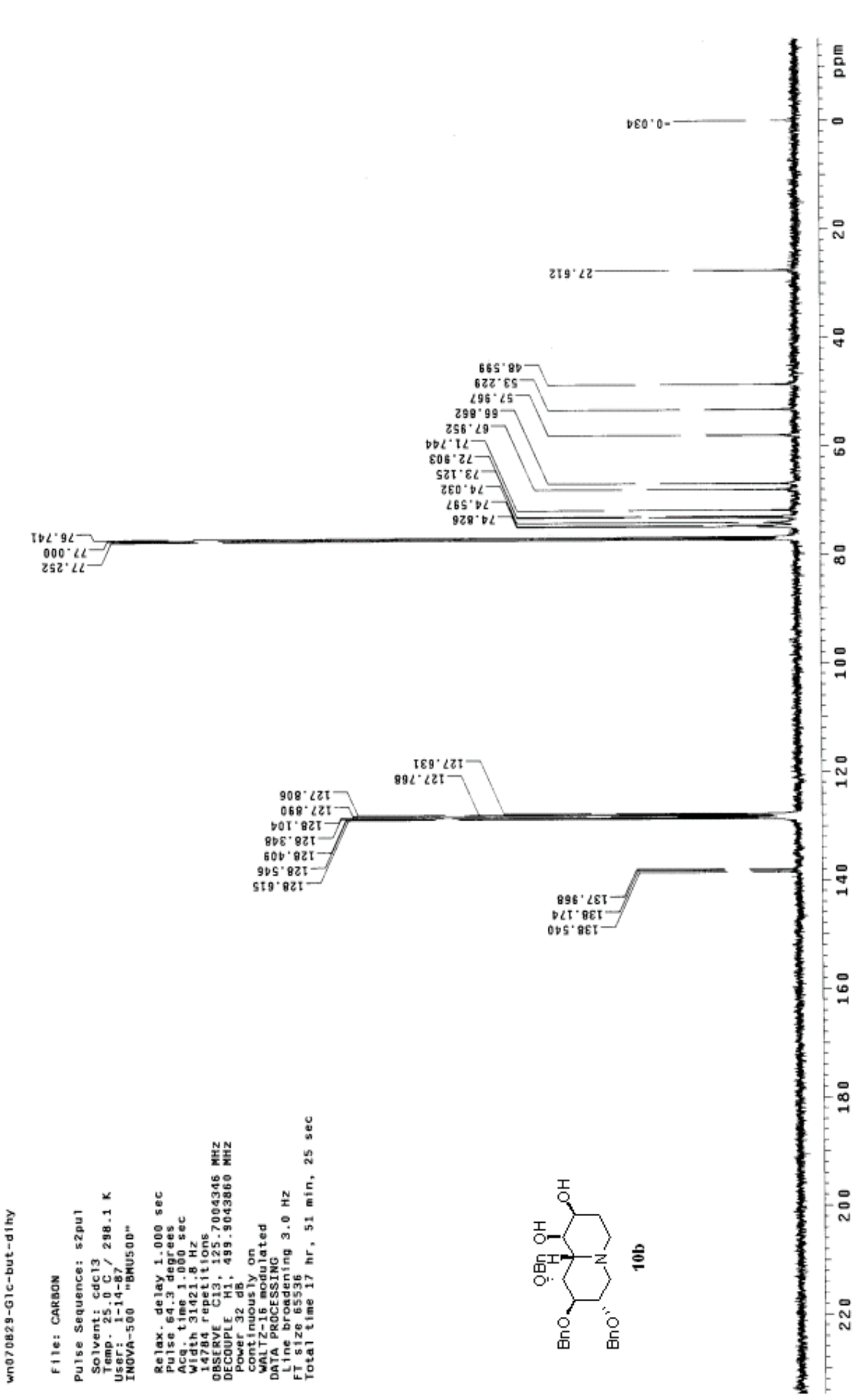




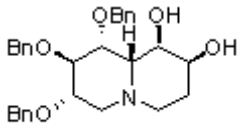


wn070829-Glc-but-dihy

File: PROTON

Pulse Sequence: gCOSY
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.197 sec
Width 5200.5 Hz
2D Width 5200.5 Hz
16 repetitions
300 increments
OBSERVE H1, 499.9019006 MHz
DATA PROCESSING
Sq. sine bell 0.098 sec
F1 DATA PROCESSING
Sq. sine bell 0.029 sec
FT size 4096 x 4096
Total time 1 hr, 39 min, 24 sec



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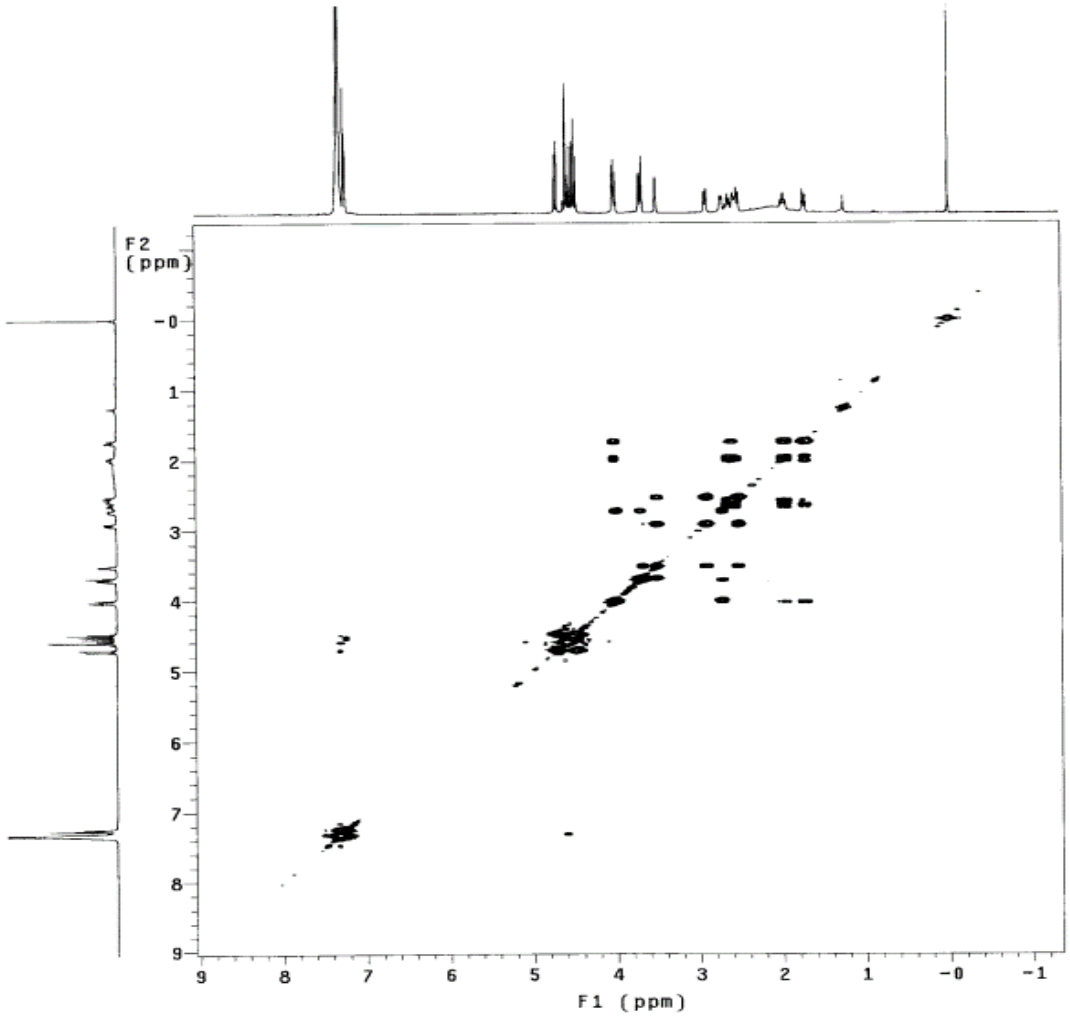
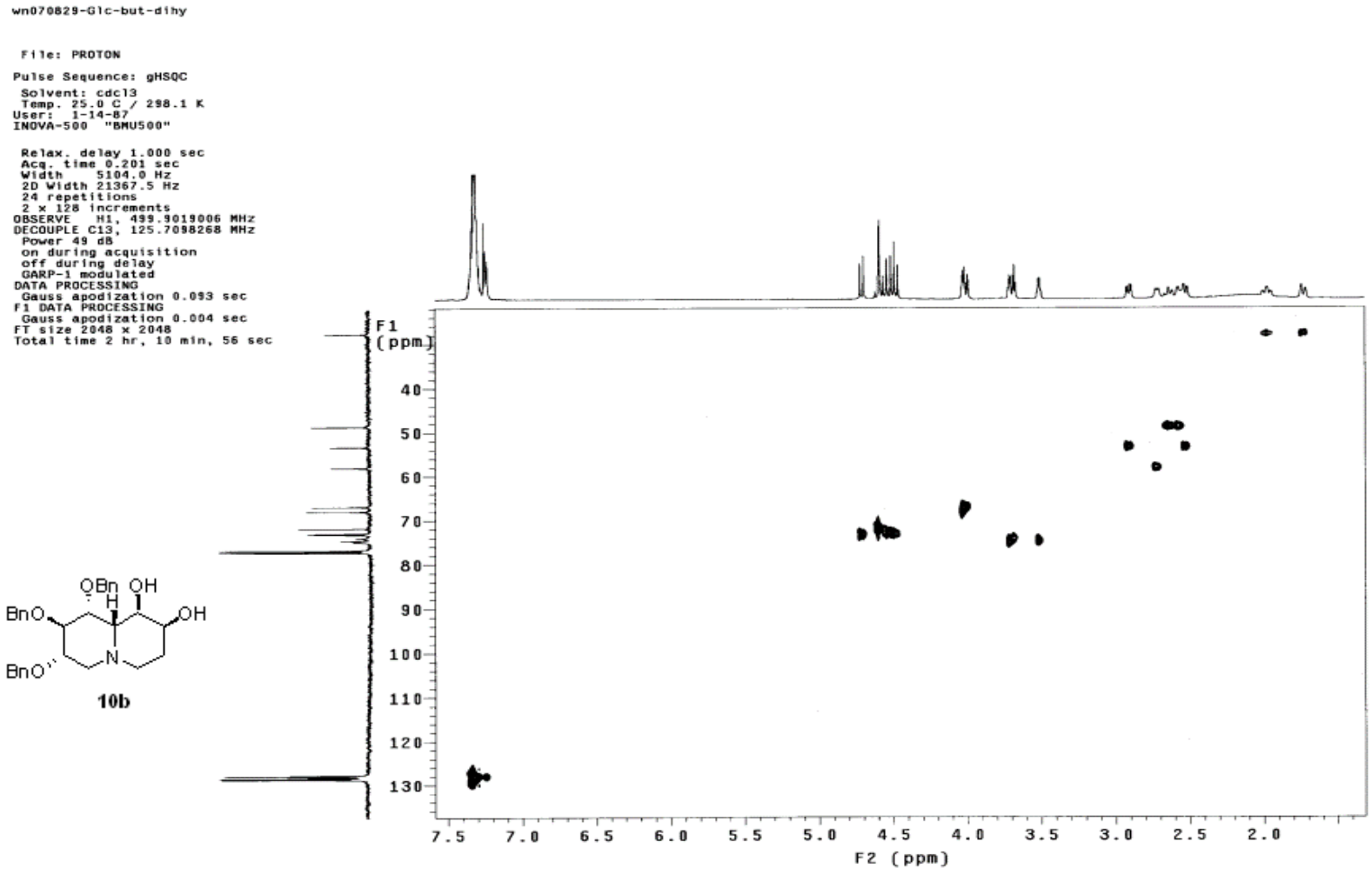
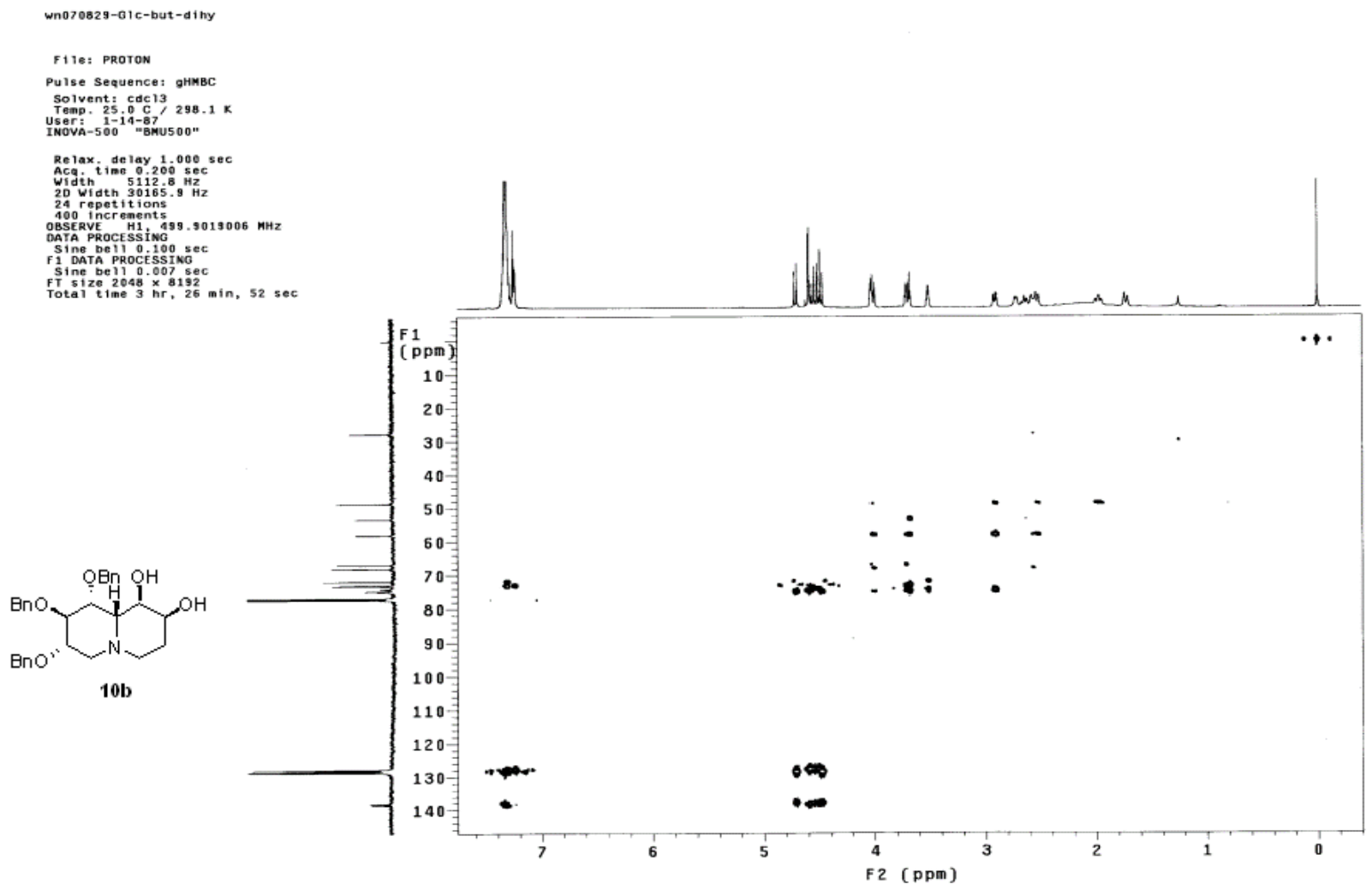




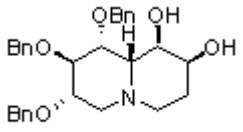


wn070829-Glc-but-dihy

File: PROTON

Pulse Sequence: NOESY
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Mixing 0.600 sec
Acq. time 0.205 sec
Width 5000.0 Hz
2D Width 5000.0 Hz
32 repetitions
2 x 320 increments
OBSERVE H1, 499.9019006 MHz
DATA PROCESSING
Gauss apodization 0.095 sec
F1 DATA PROCESSING
Gauss apodization 0.033 sec
FT size 4096 x 4096
Total time 10 hr, 32 min, 34 sec



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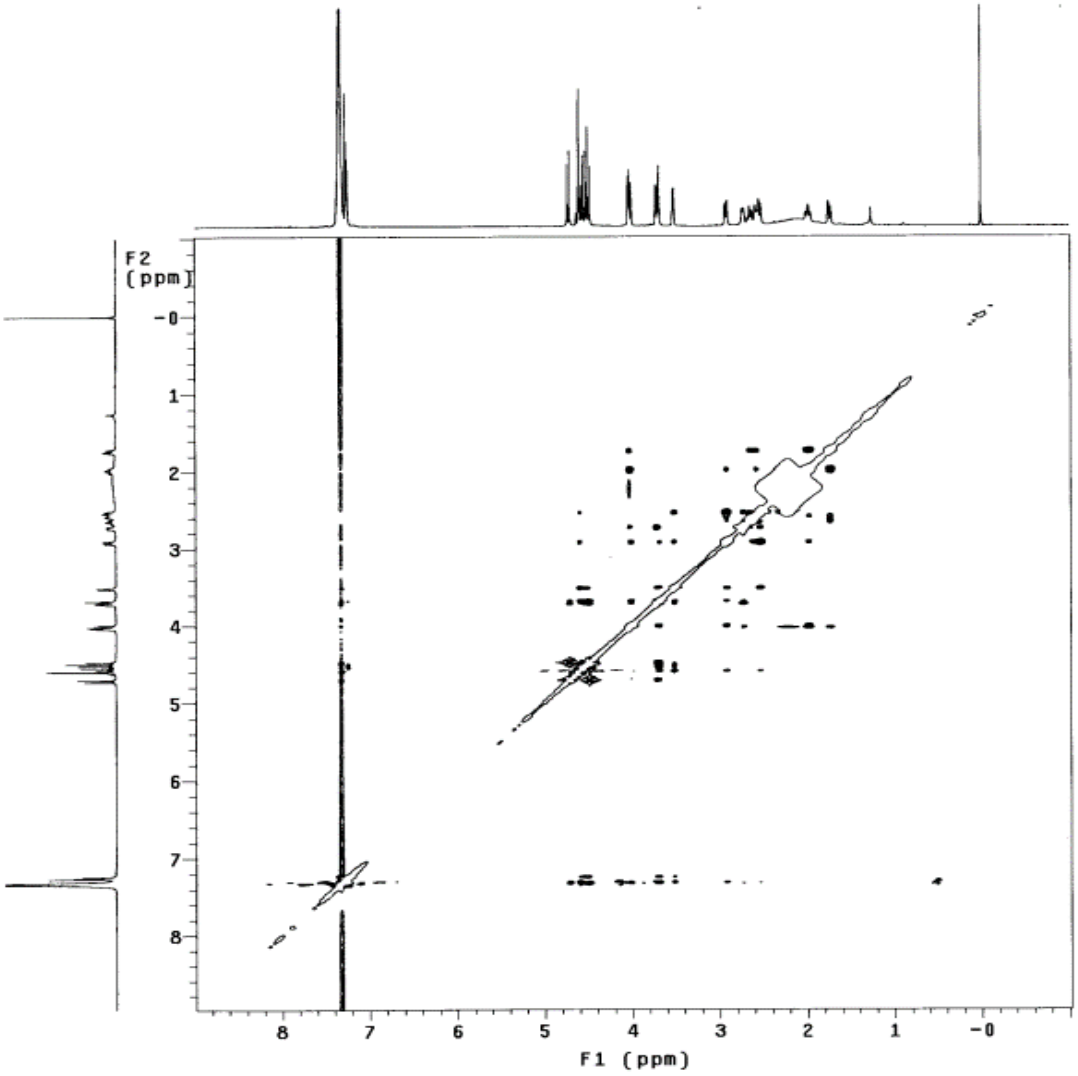

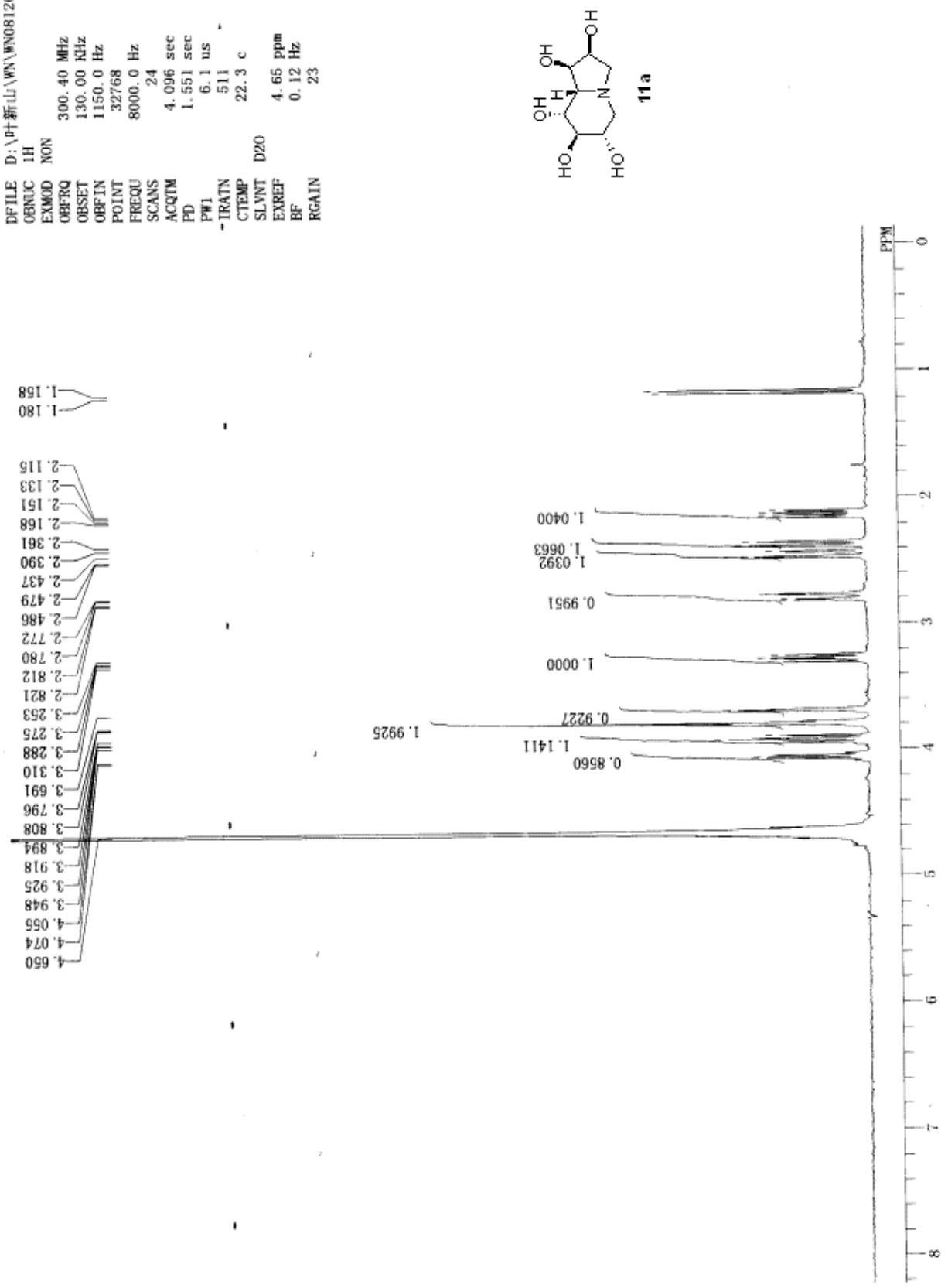

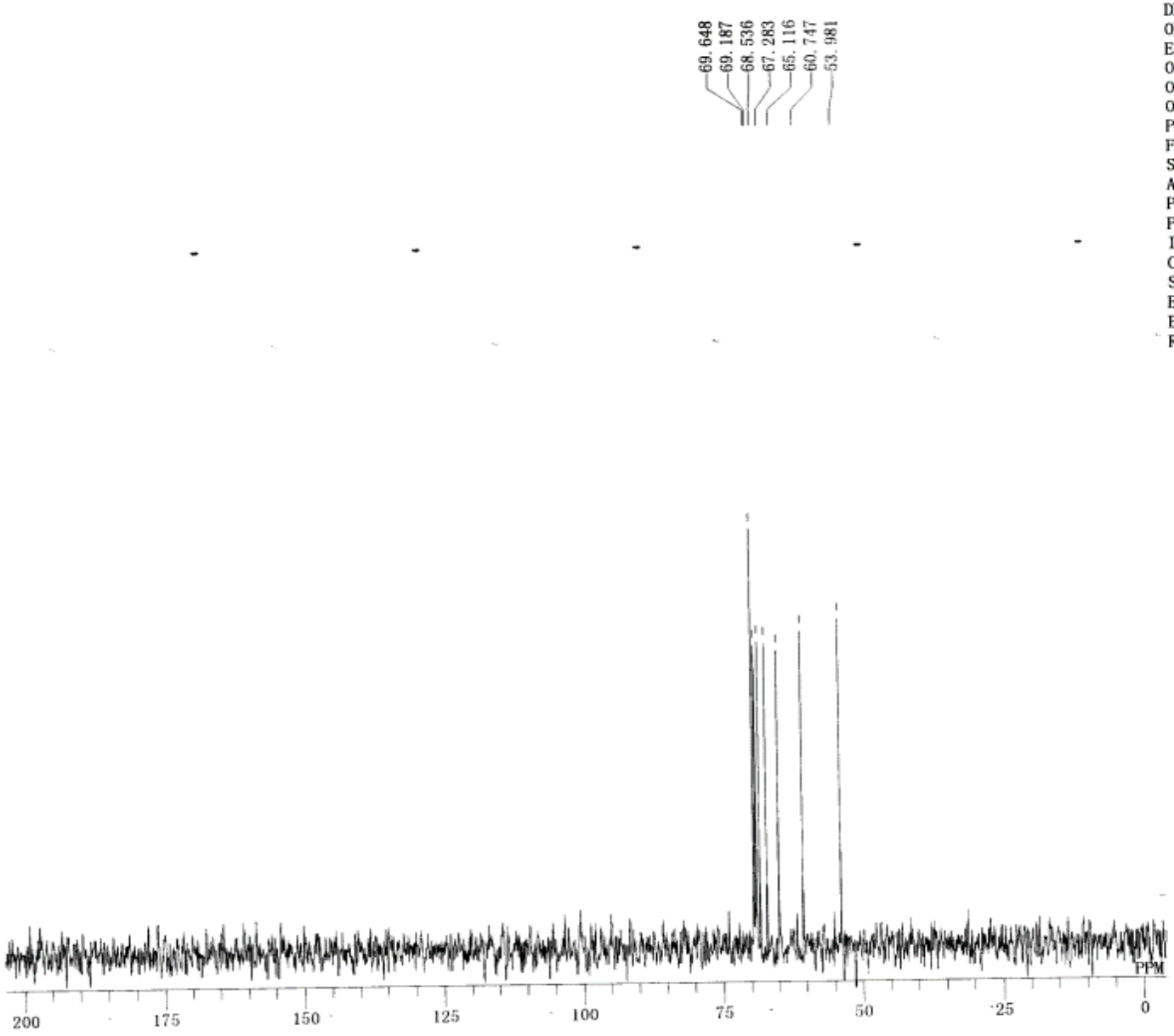

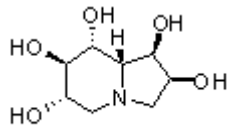

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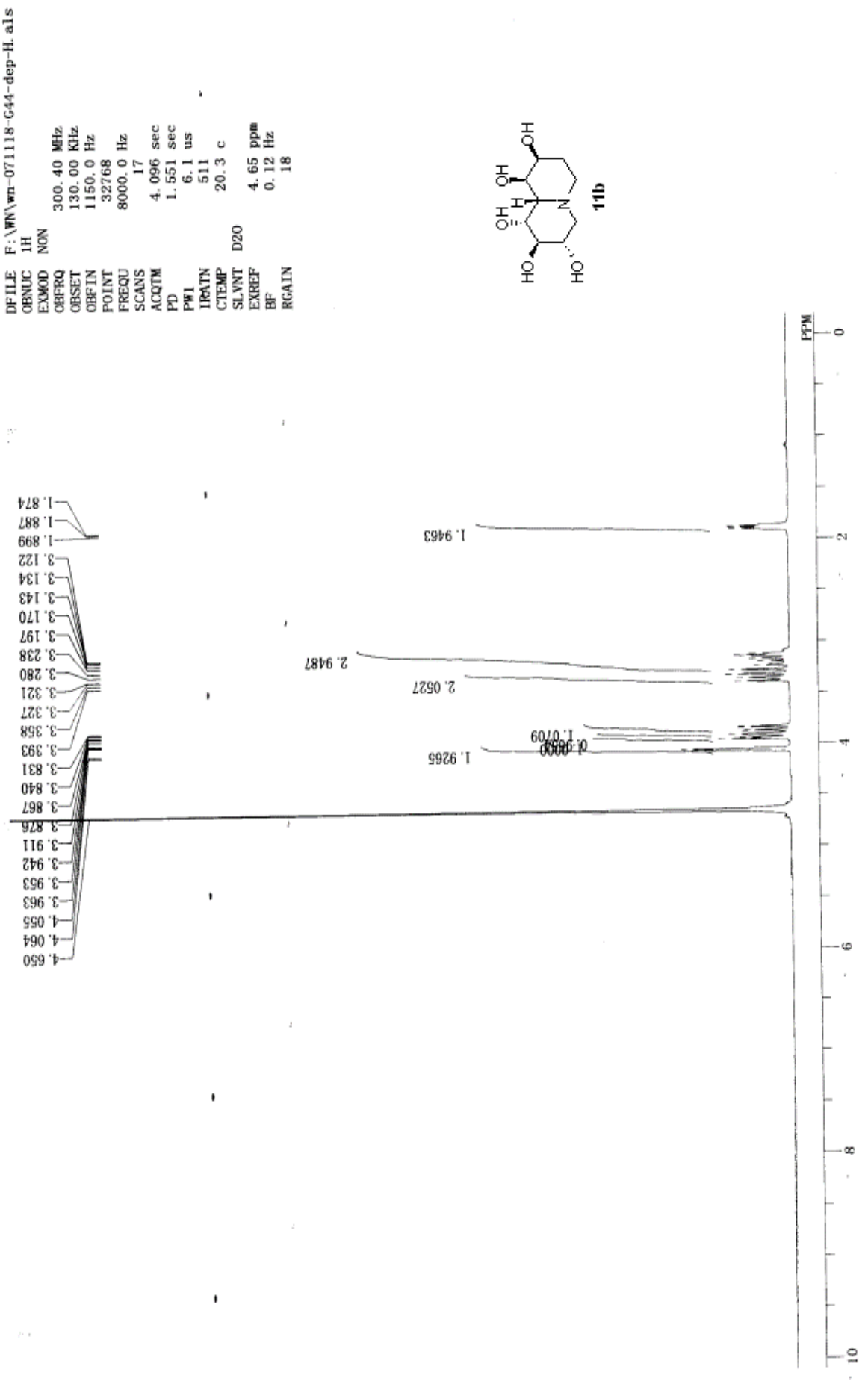
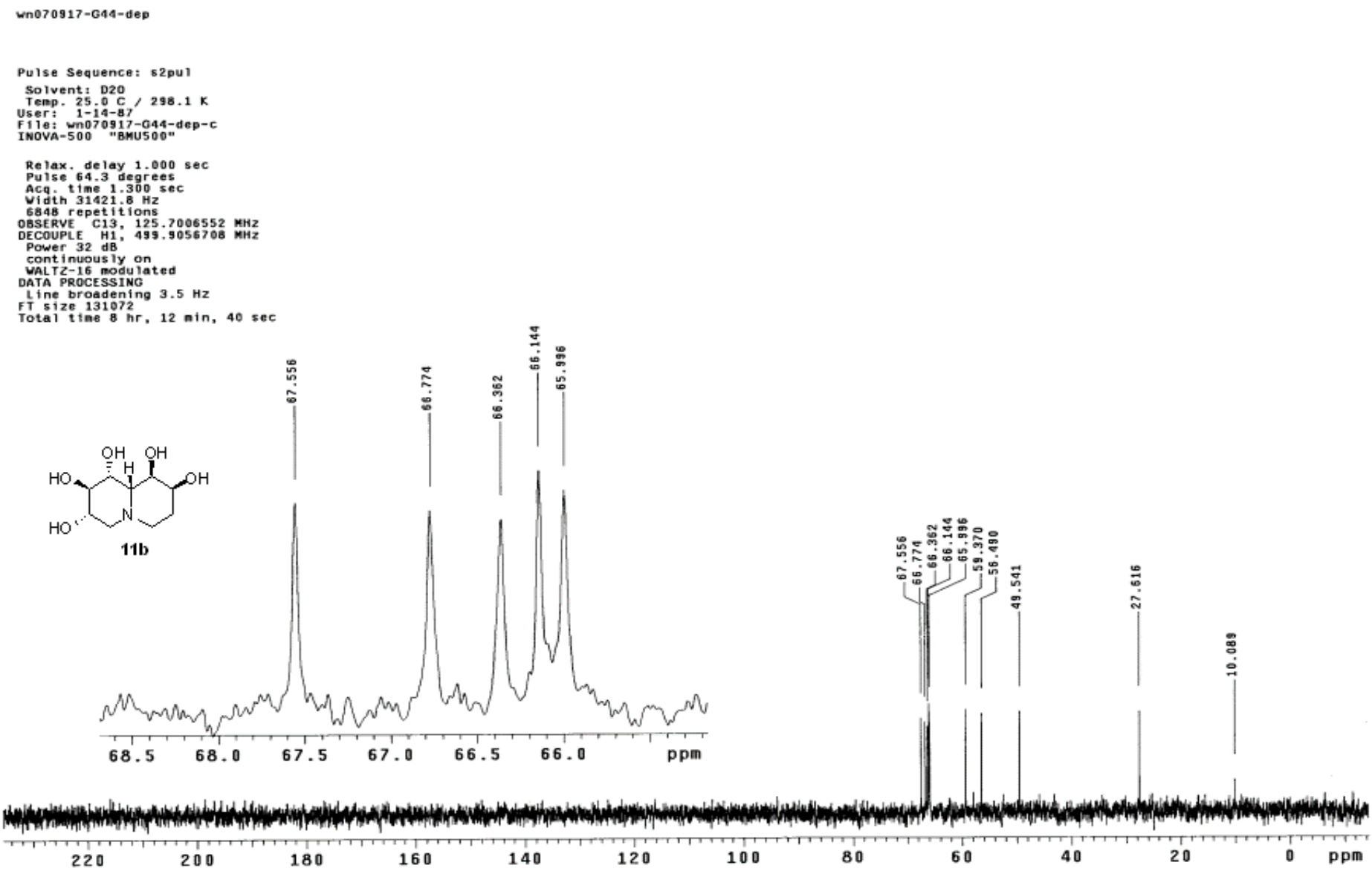
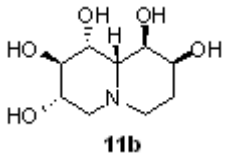




wn070917-G44-dep

Pulse Sequence: gCOSY
Solvent: d2o
Temp. 25.0 C / 298.1 K
File: wn070917-G44-dep-cosy
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.171 sec
Width 2992.2 Hz
2D Width 2992.2 Hz
16 repetitions
512 increments
OBSERVE H1, 499.9031226 MHz
DATA PROCESSING
Sq. sine bell 0.086 sec
F1 DATA PROCESSING
Sq. sine bell 0.091 sec
FT size 8192 x 8192
Total time 2 hr, 53 min, 38 sec



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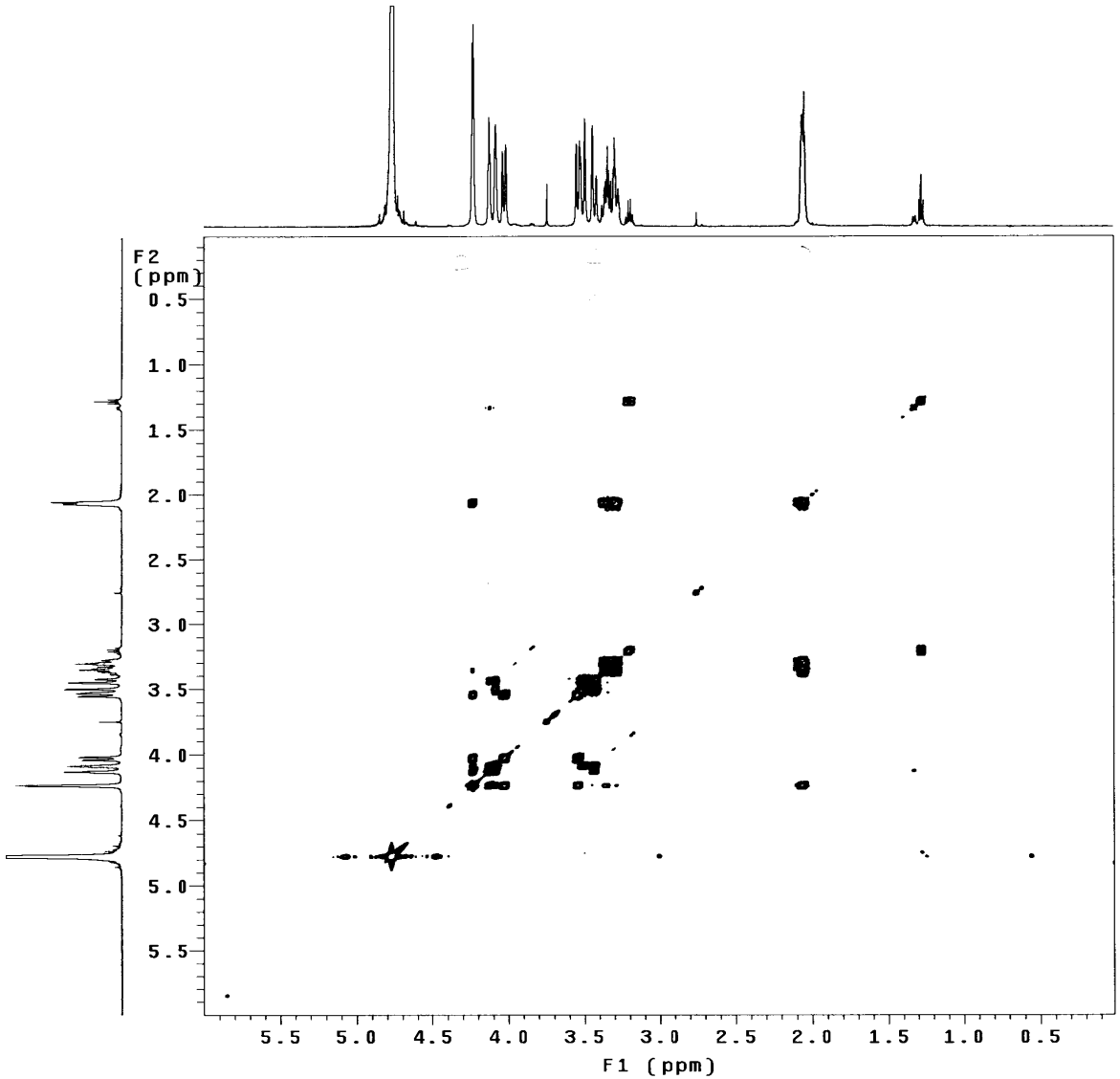
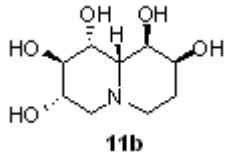


wn070917-G44-dep

Pulse Sequence: gHSQC
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: wn070917-G44-dep-qc
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.340 sec
Width 3014.2 Hz
2D Width 10093.4 Hz
16 repetitions
2 x 128 increments
OBSERVE H1, 499.9031397 MHz
DECOUPLE C13, 125.7056833 MHz
Power 49 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Gauss apodization 0.078 sec
F1 DATA PROCESSING
Gauss apodization 0.006 sec
FT size 1024 x 2048
Total time 1 hr, 37 min, 18 sec



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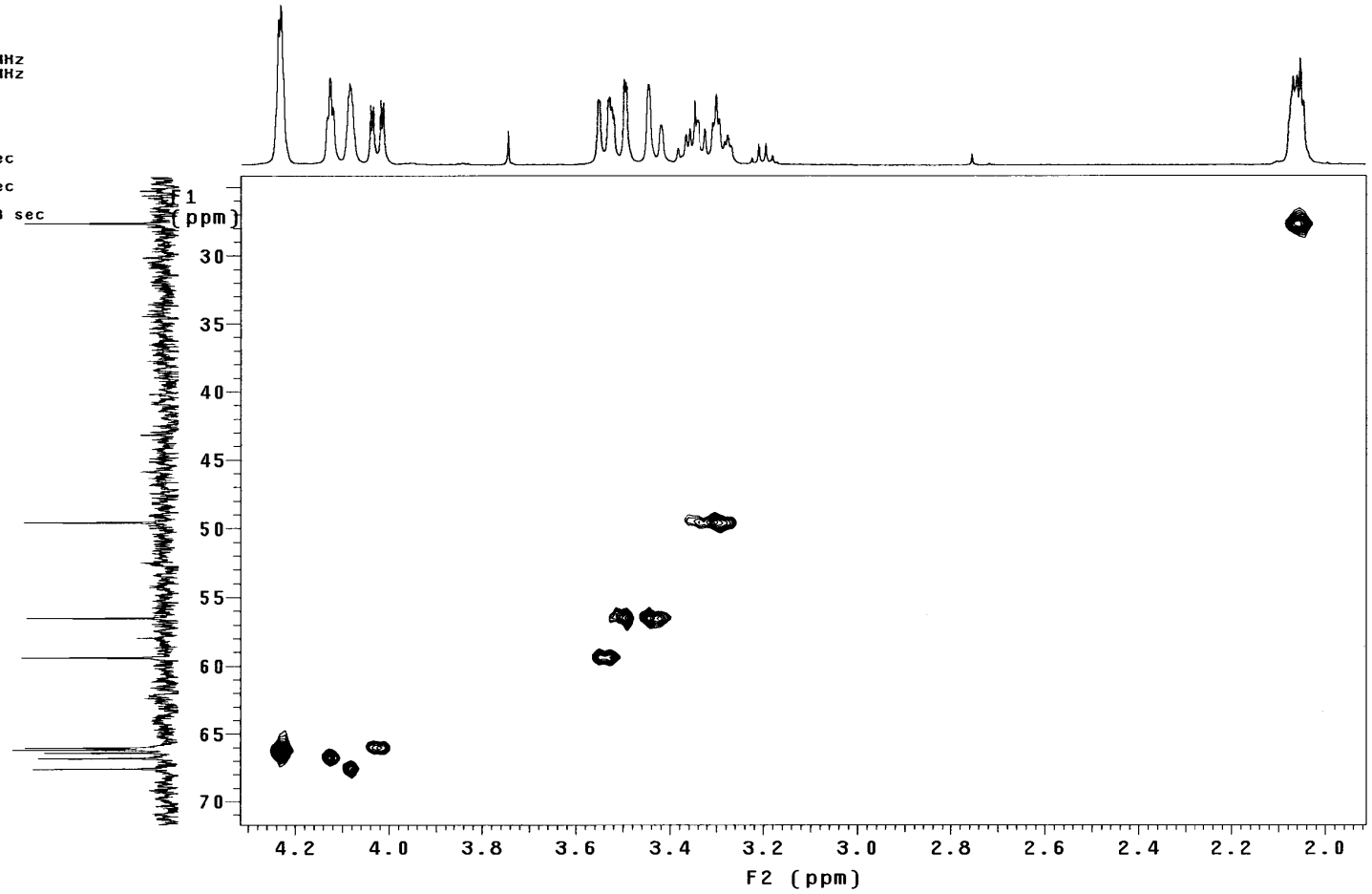

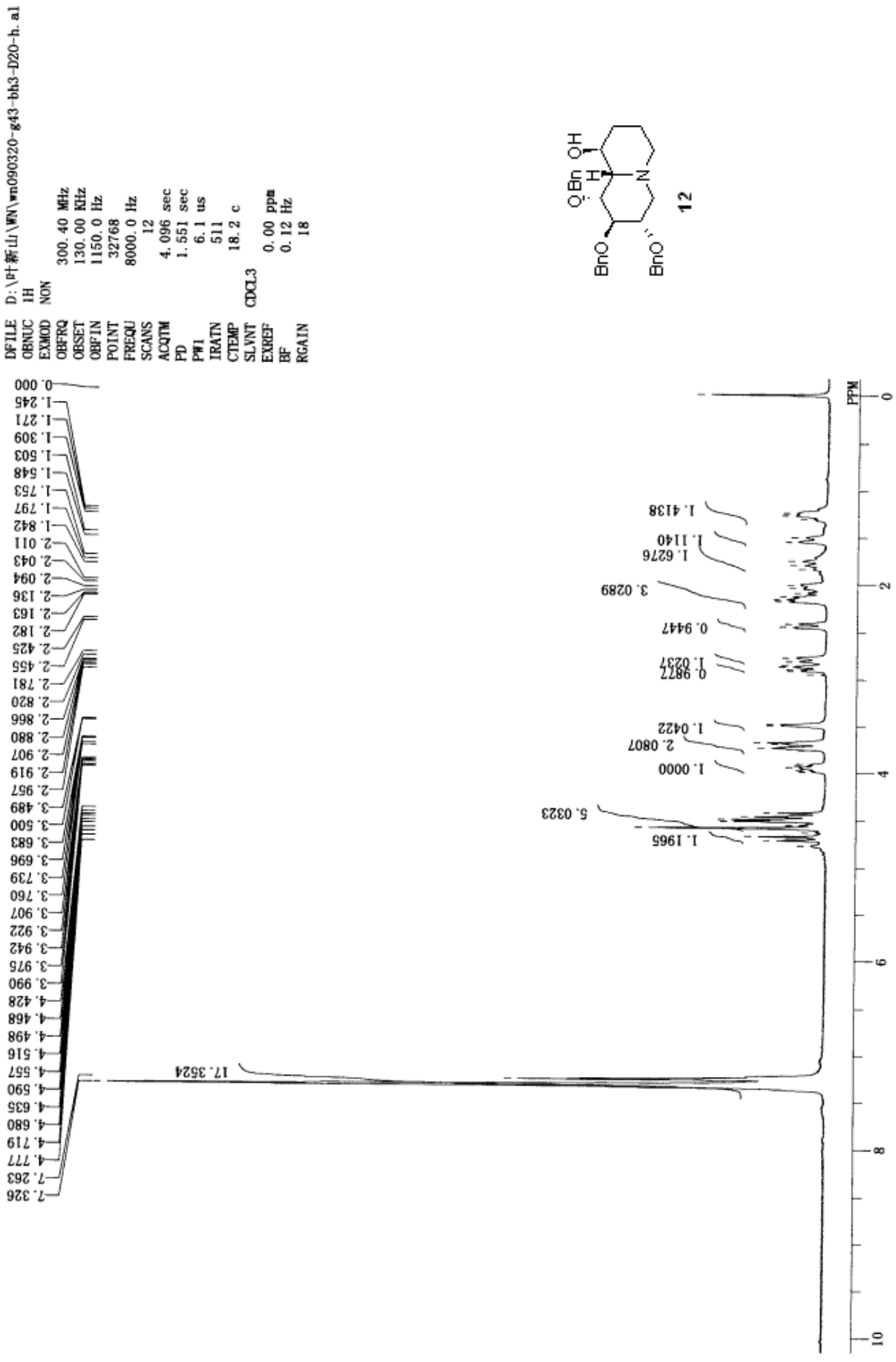

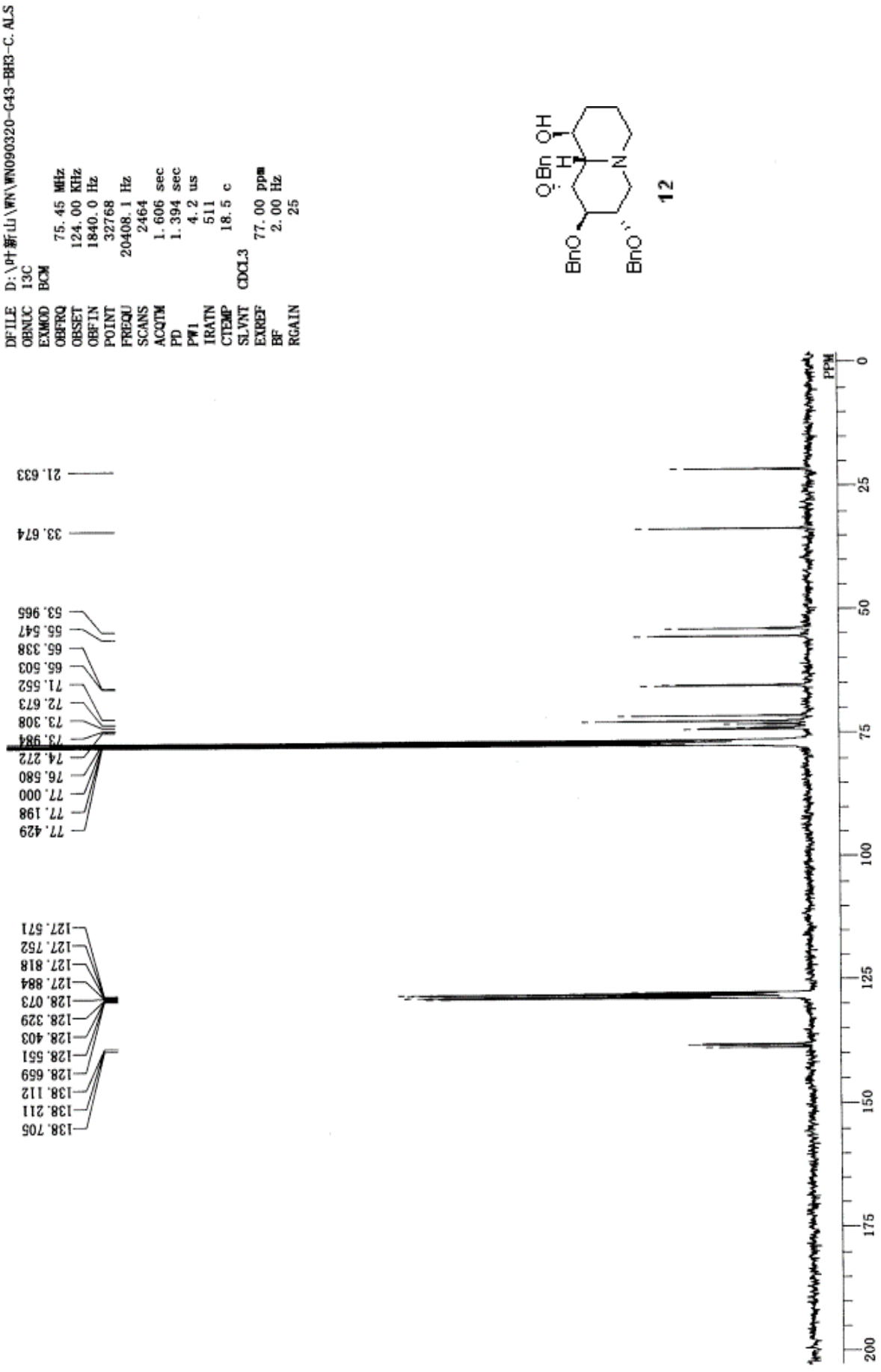

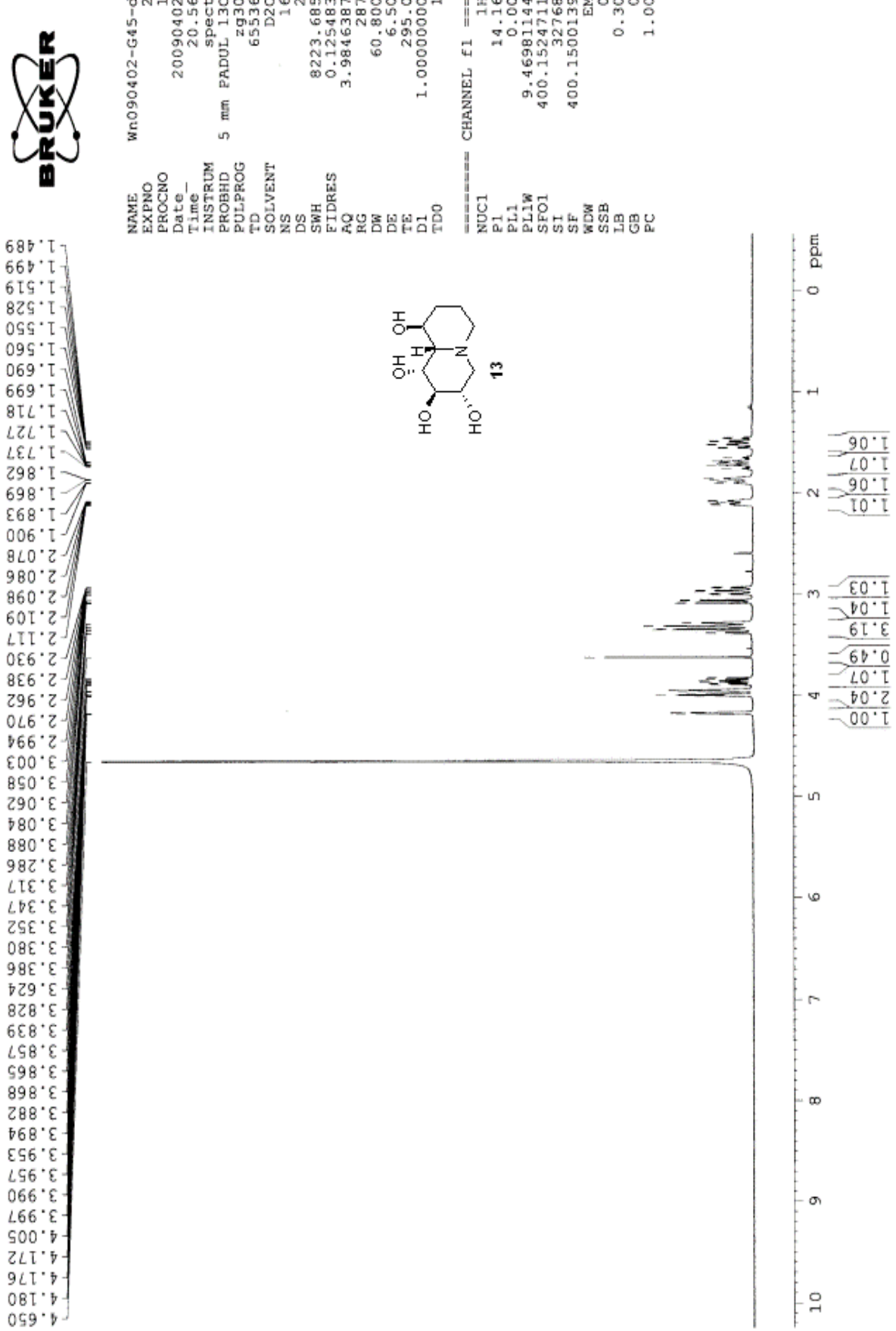

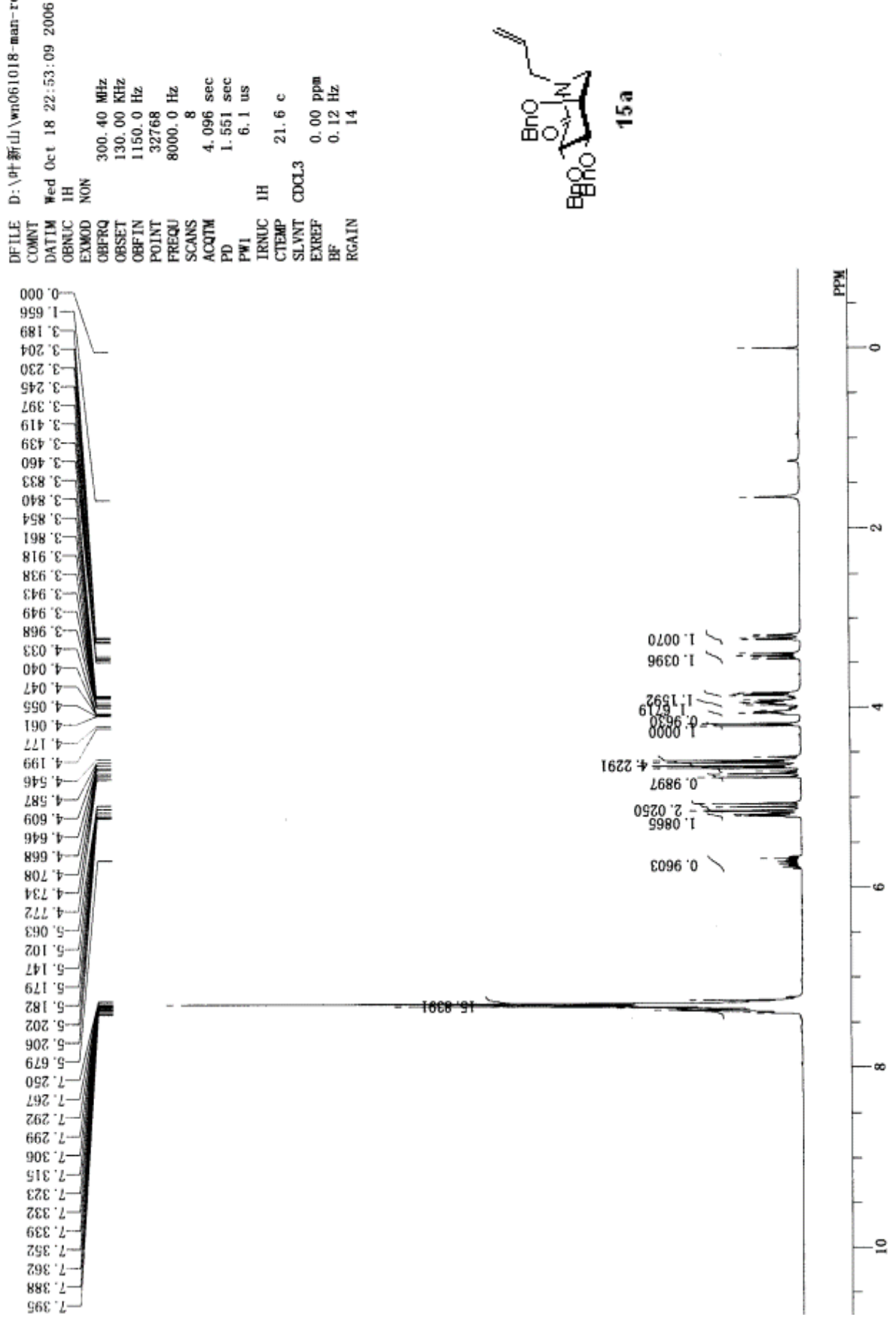

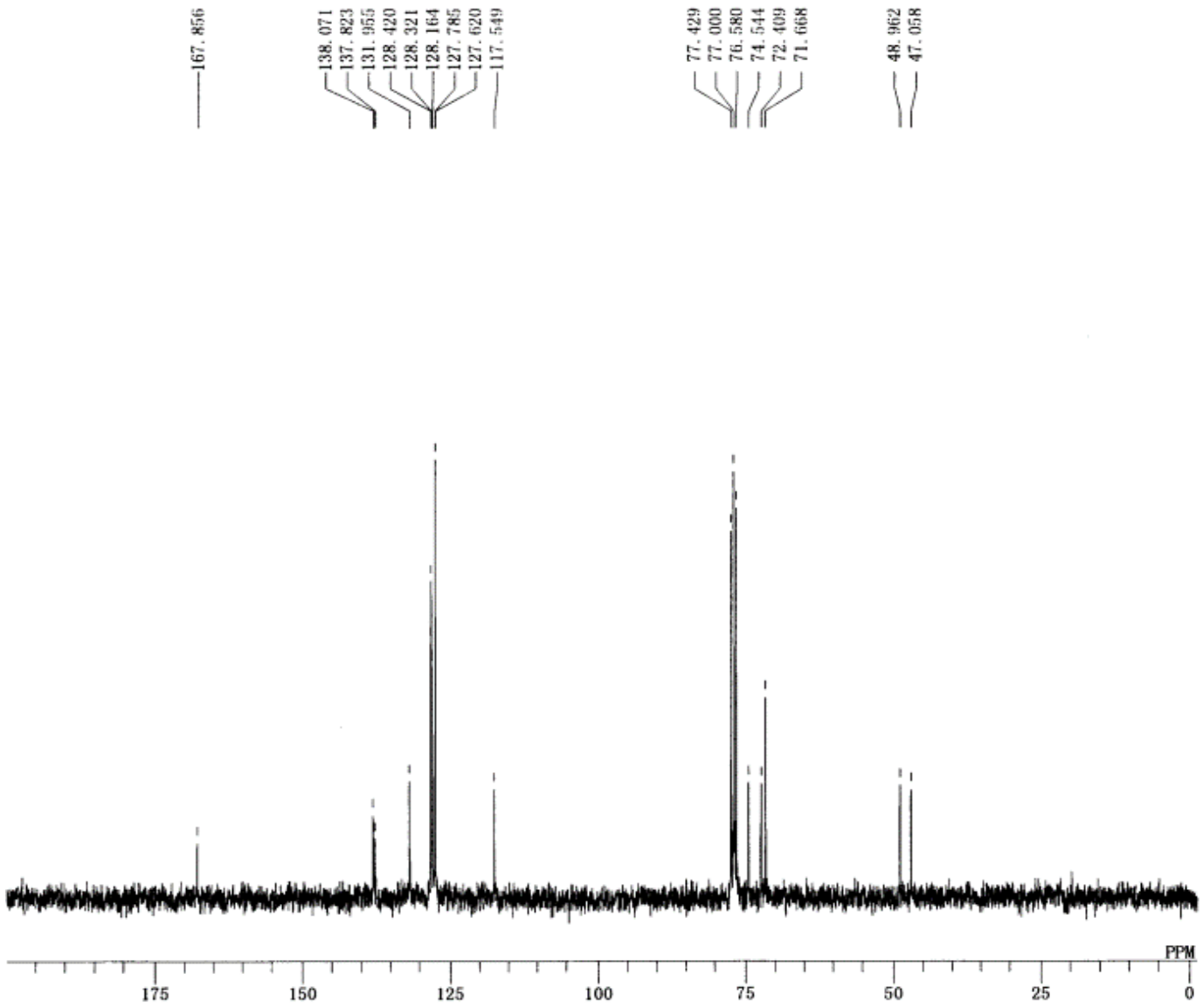


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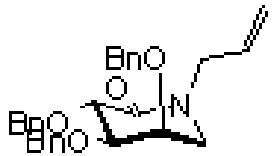
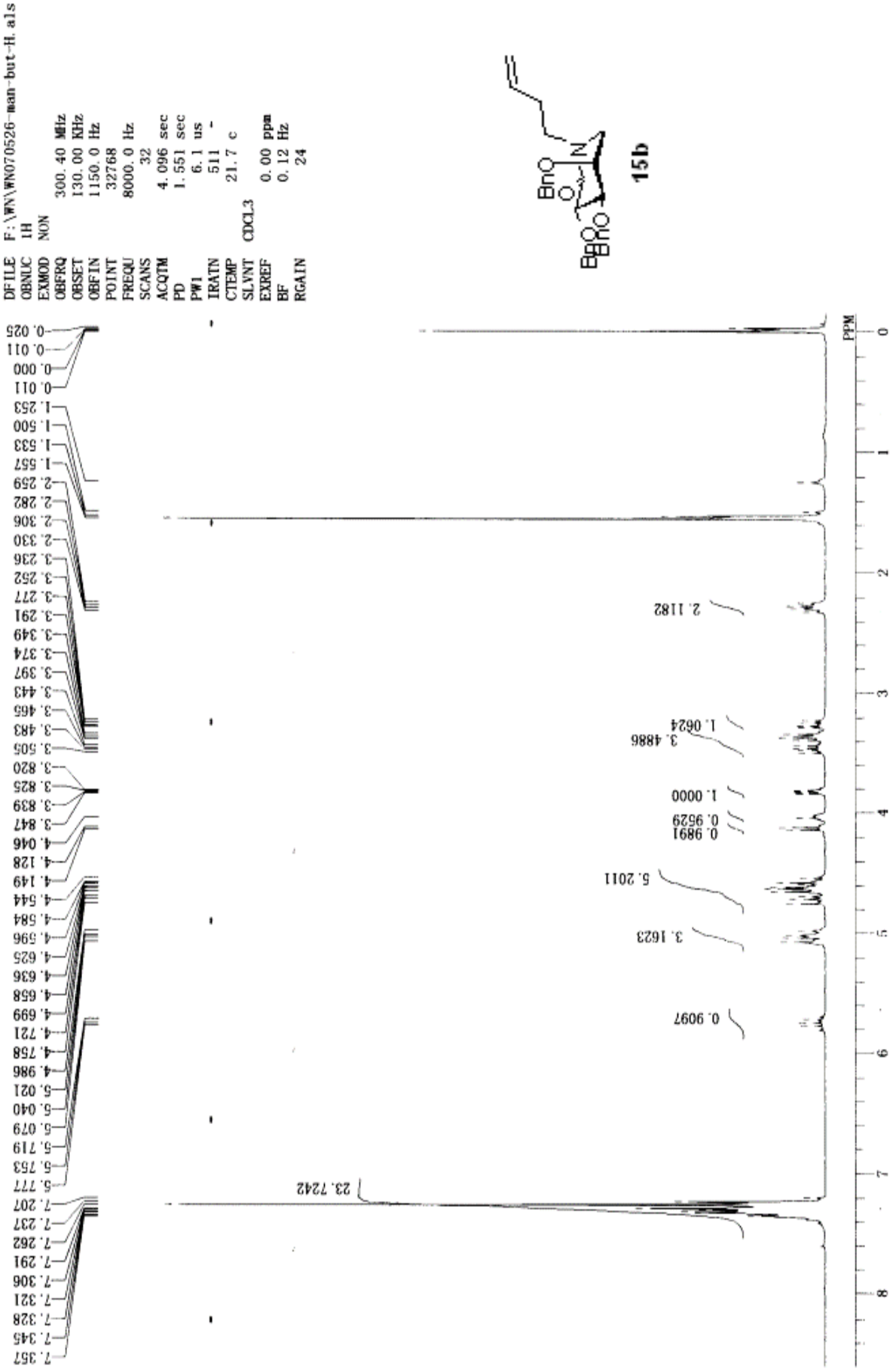
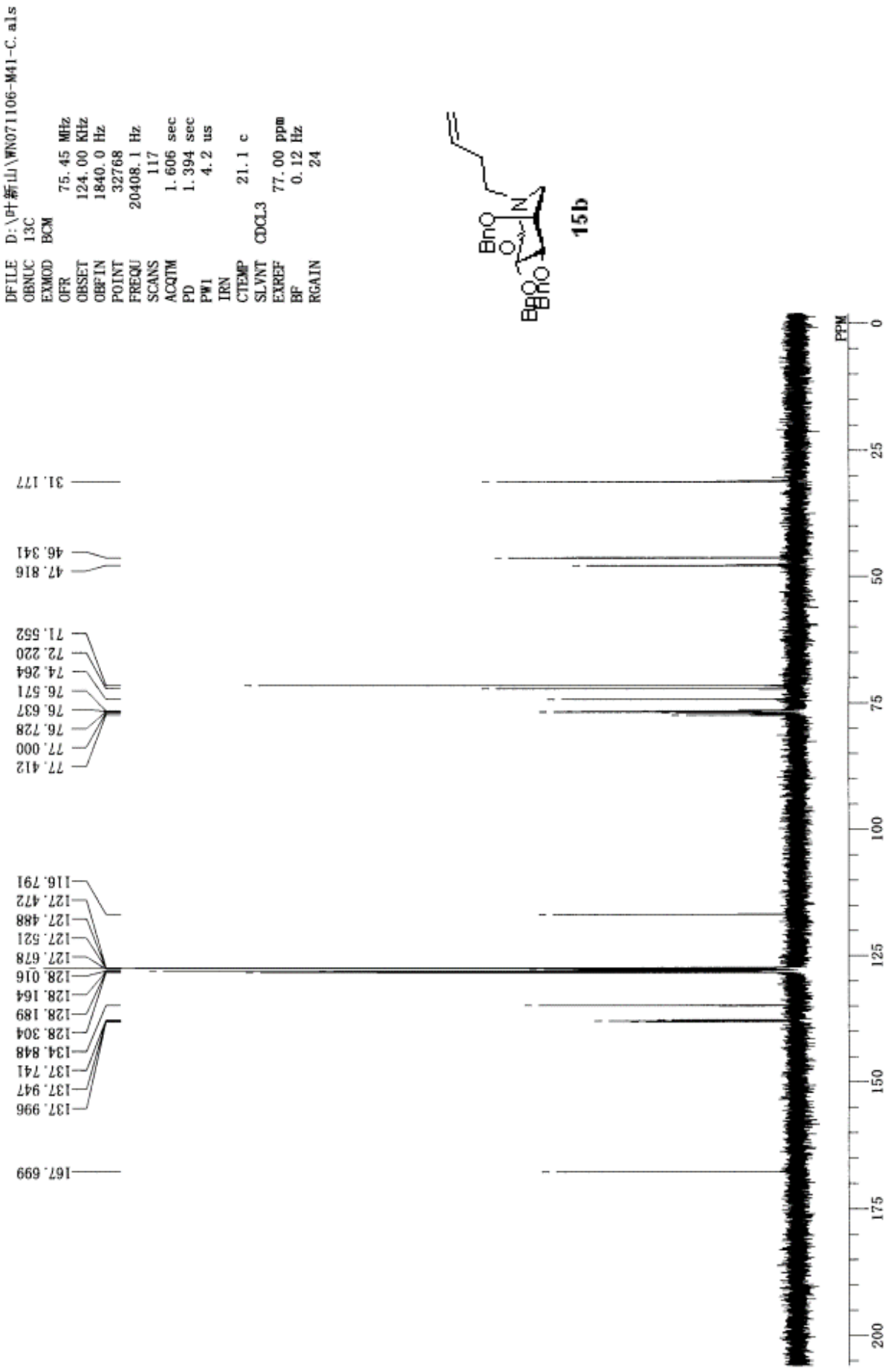
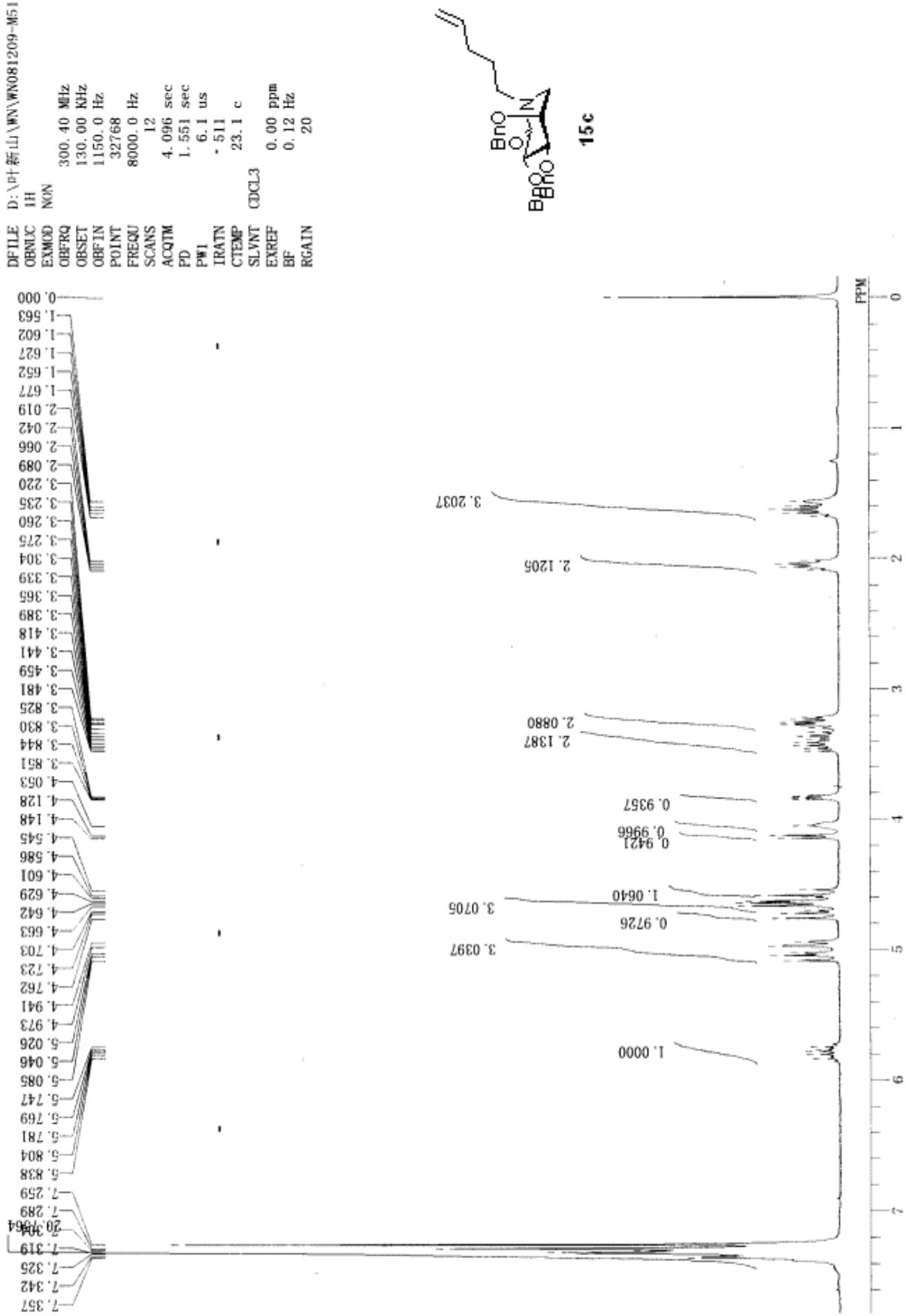
DFILE  D:\叶新山\wn061018-man-rearr-C.als
COMNT
DATIM  Sun Oct 22 17:27:17 2006
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS           81
ACQTM        1.606 sec
PD           1.394 sec
PW1            4.2 us
IRNUC  1H
CTEMP         21.8 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            2.00 Hz
RGAIN           24
```

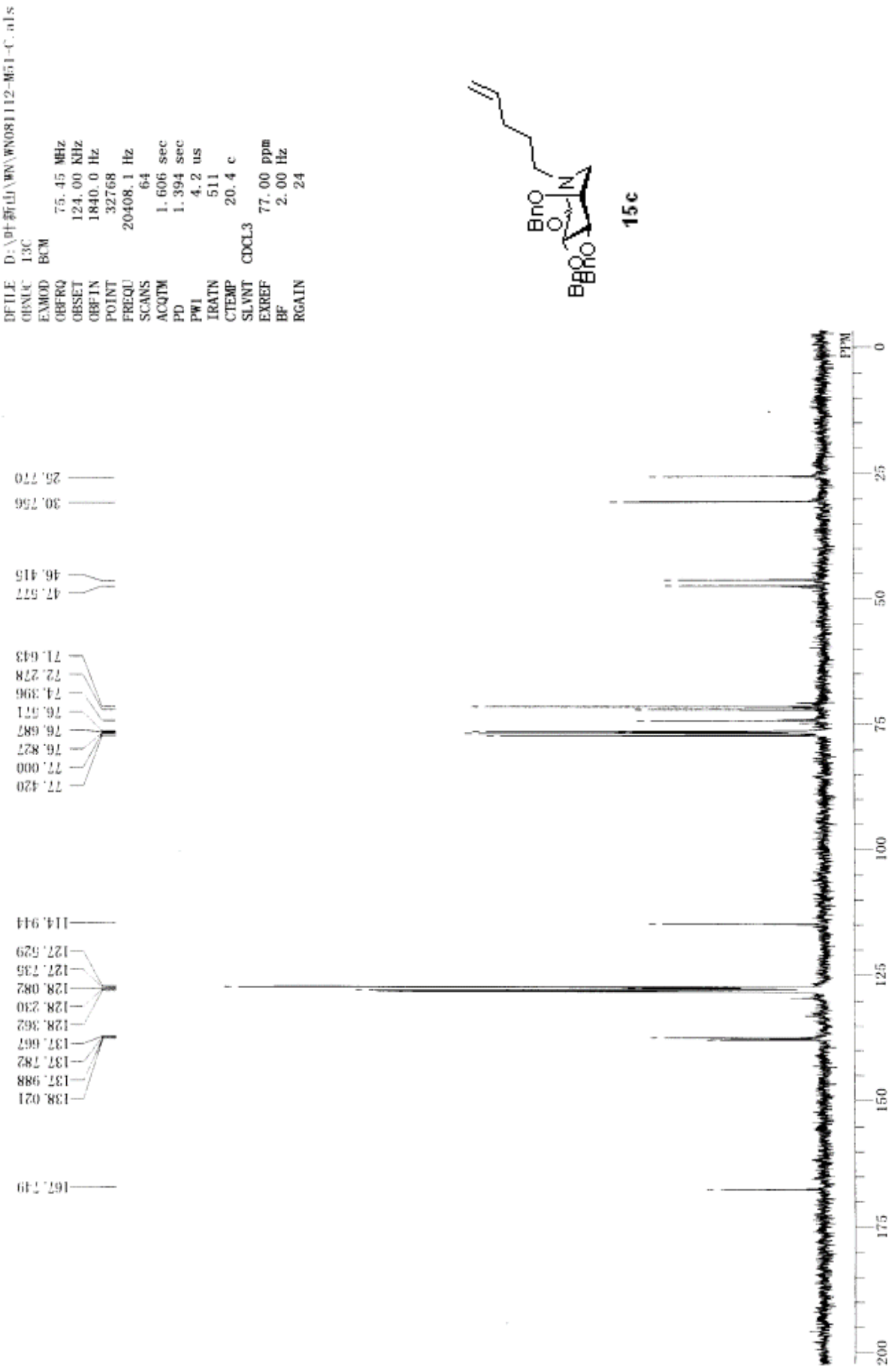


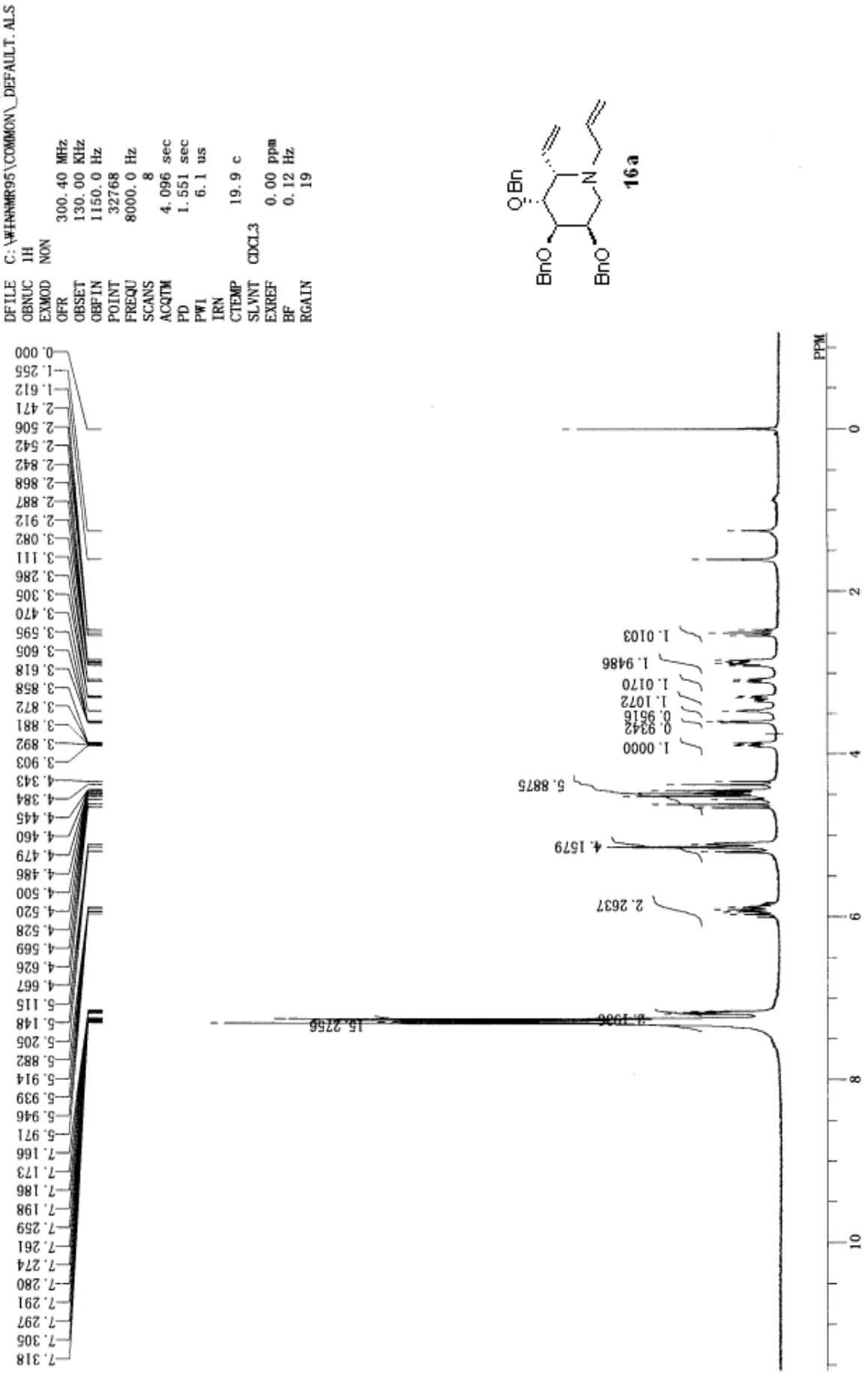
15a

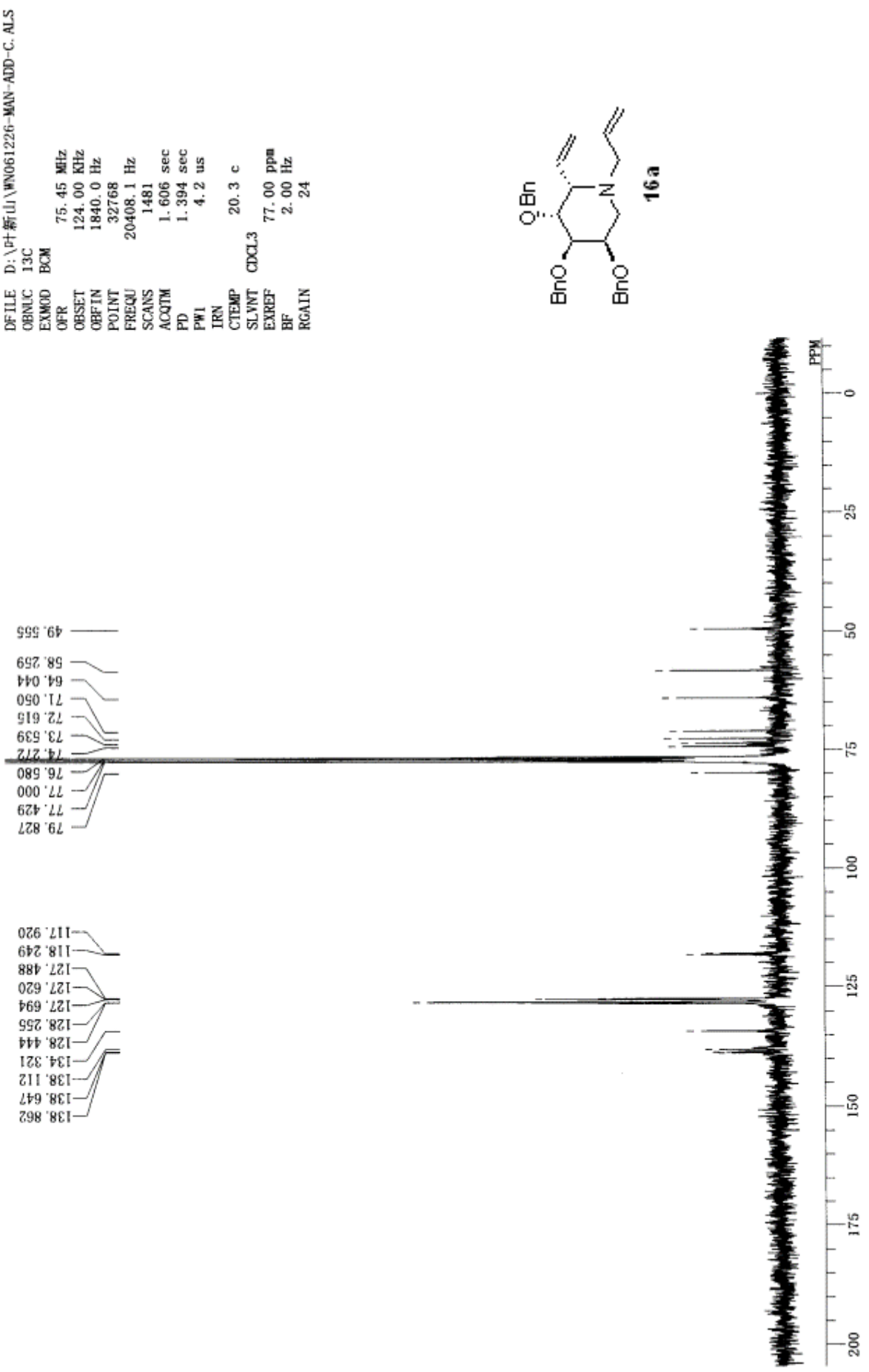








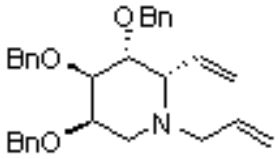




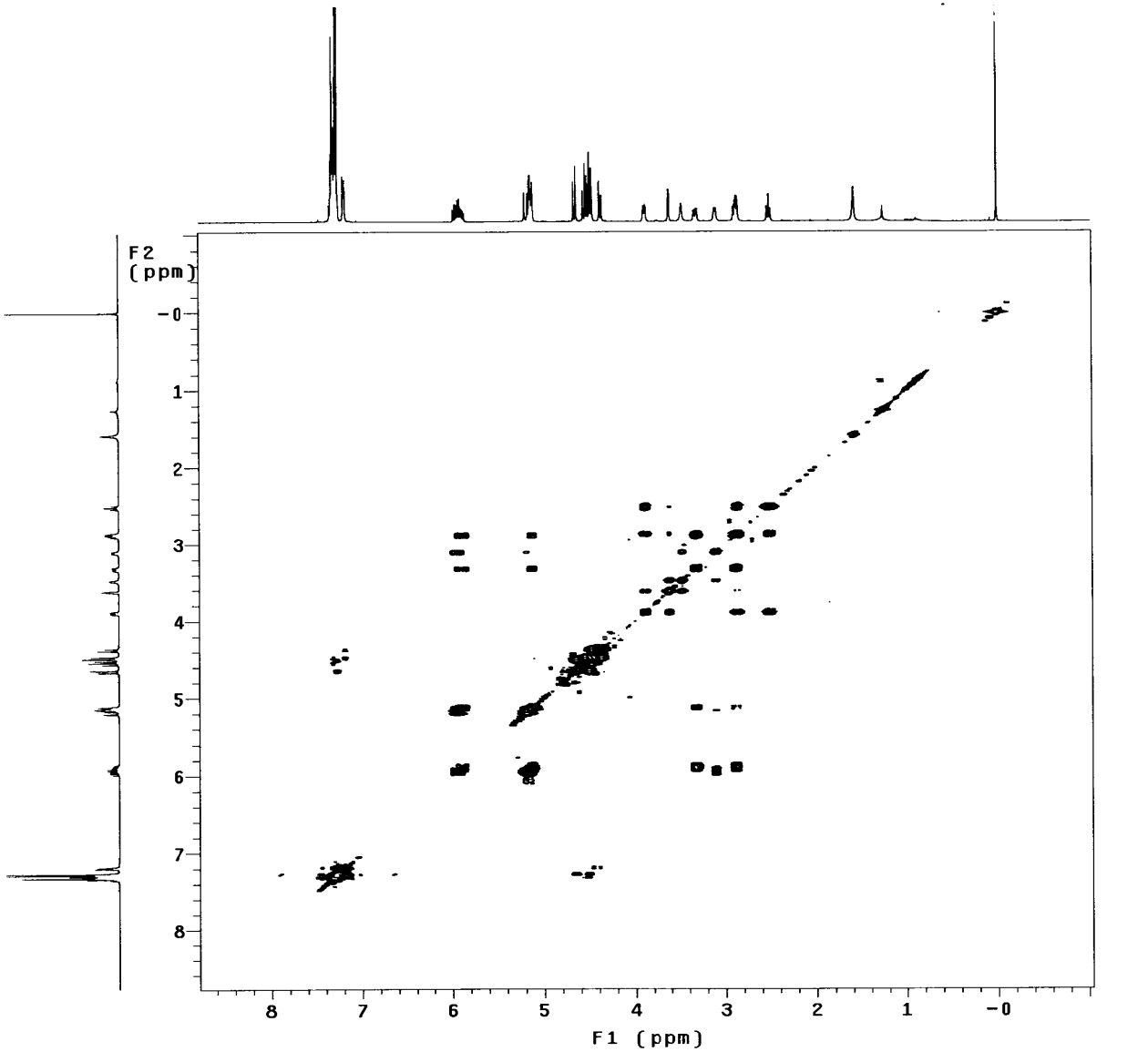
wn061226-man-add

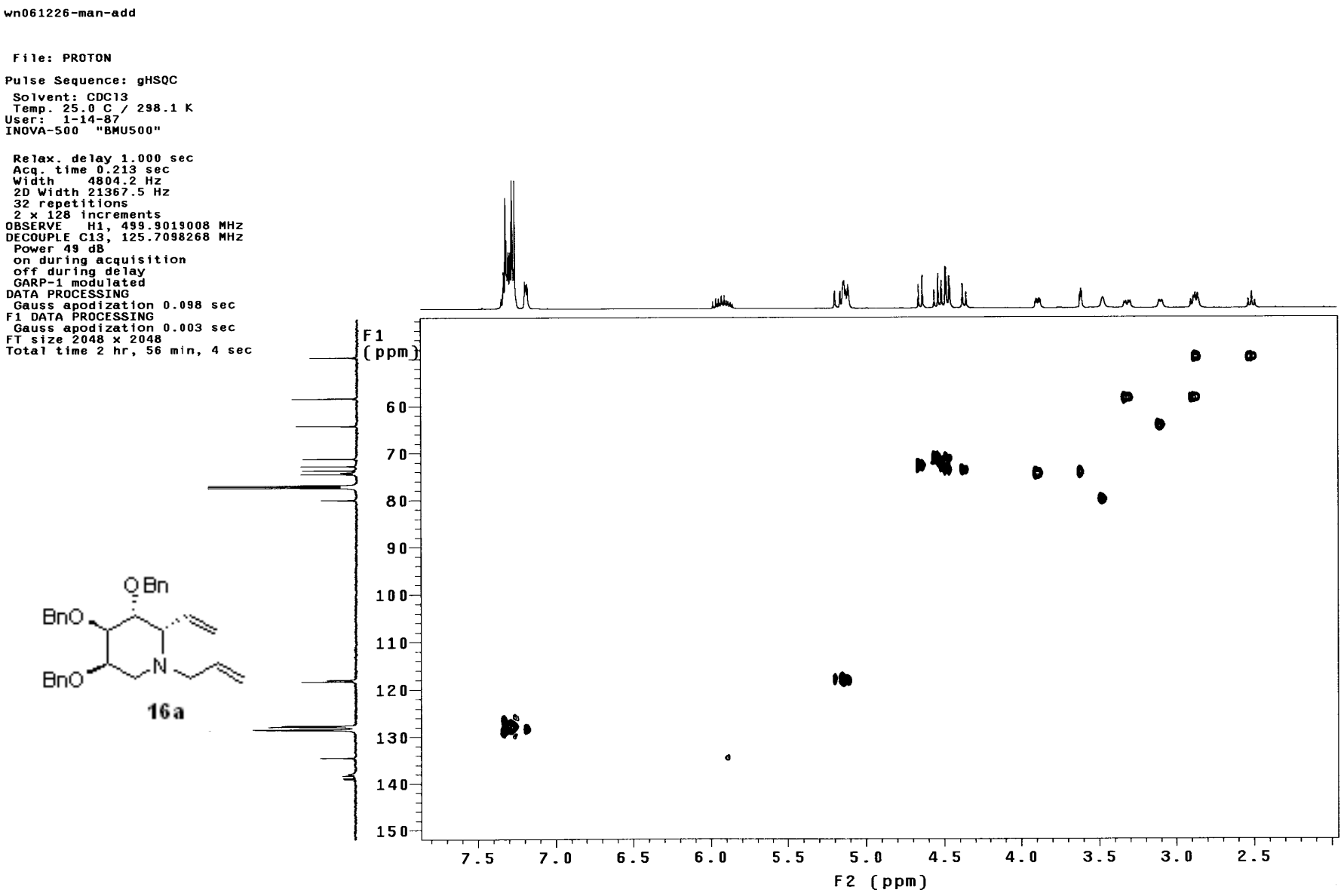
Pulse Sequence: gCOSY
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: wn061226-man-add-cosy
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.209 sec
Width 4909.8 Hz
2D Width 4909.8 Hz
16 repetitions
400 increments
OBSERVE H1, 499.9019008 MHz
DATA PROCESSING
Sq. sine bell 0.104 sec
F1 DATA PROCESSING
Sq. sine bell 0.042 sec
FT size 8192 x 8192
Total time 2 hr, 14 min, 57 sec



16a



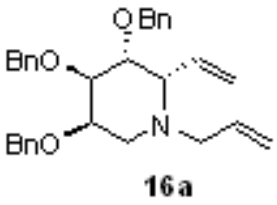


wn061226-man-add

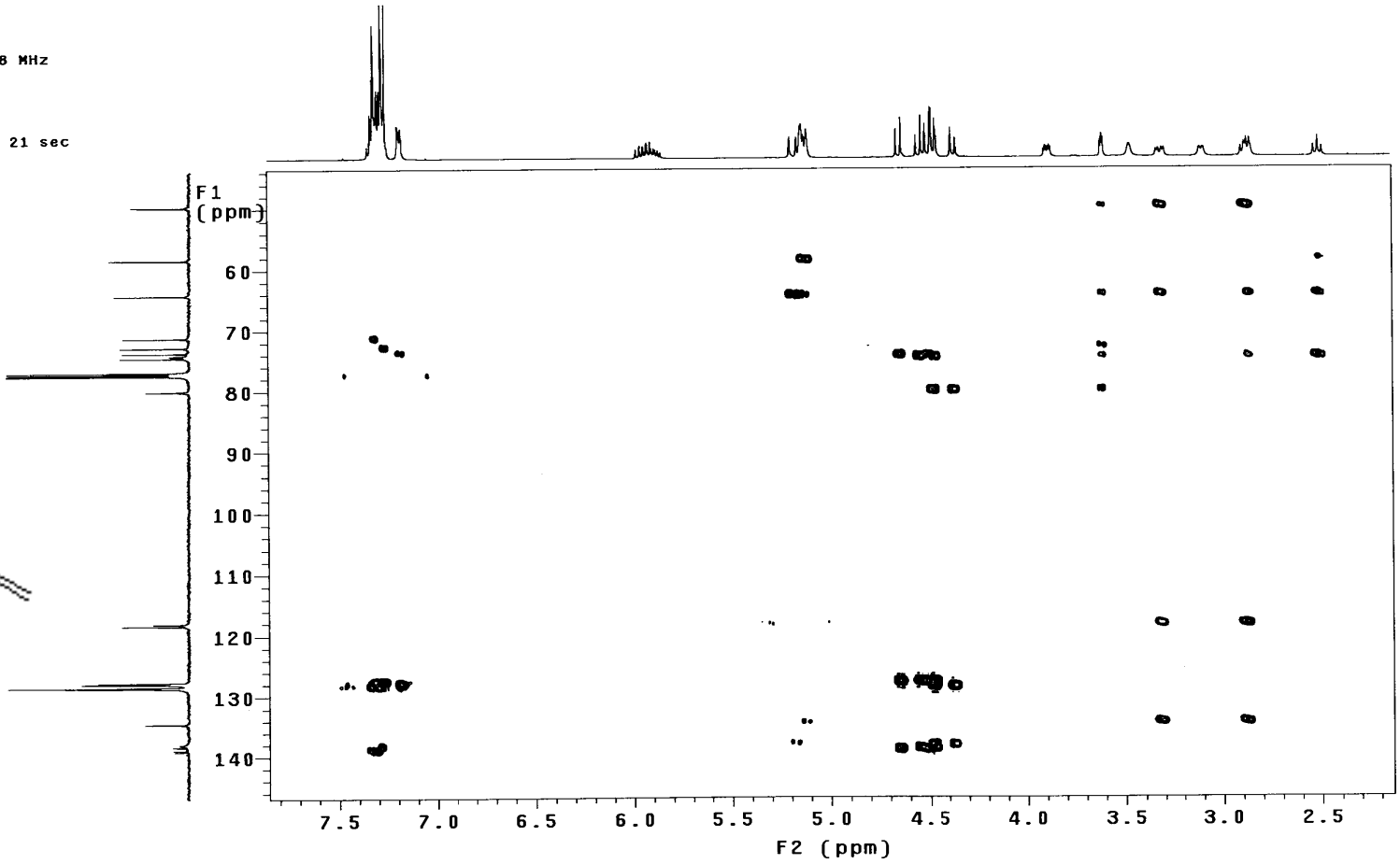
File: PROTON

Pulse Sequence: gHMBC
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4804.2 Hz
2D Width 30165.9 Hz
32 repetitions
400 increments
OBSERVE H1, 499.9019008 MHz
DATA PROCESSING
Sine bell 0.107 sec
F1 DATA PROCESSING
Sine bell 0.007 sec
FT size 2048 x 8192
Total time 4 hr, 38 min, 21 sec



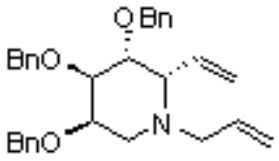
16a



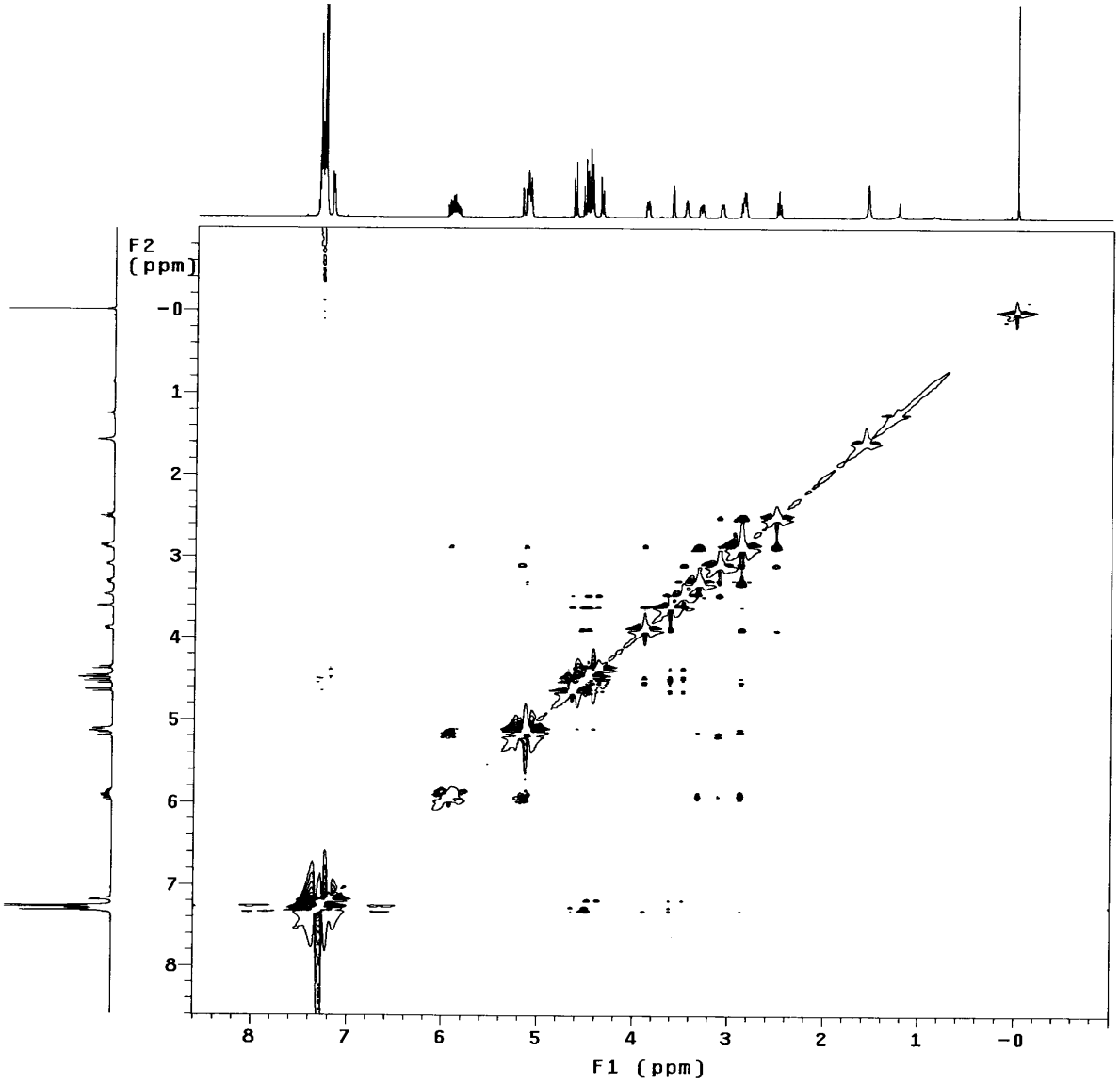
wn061226-man-add

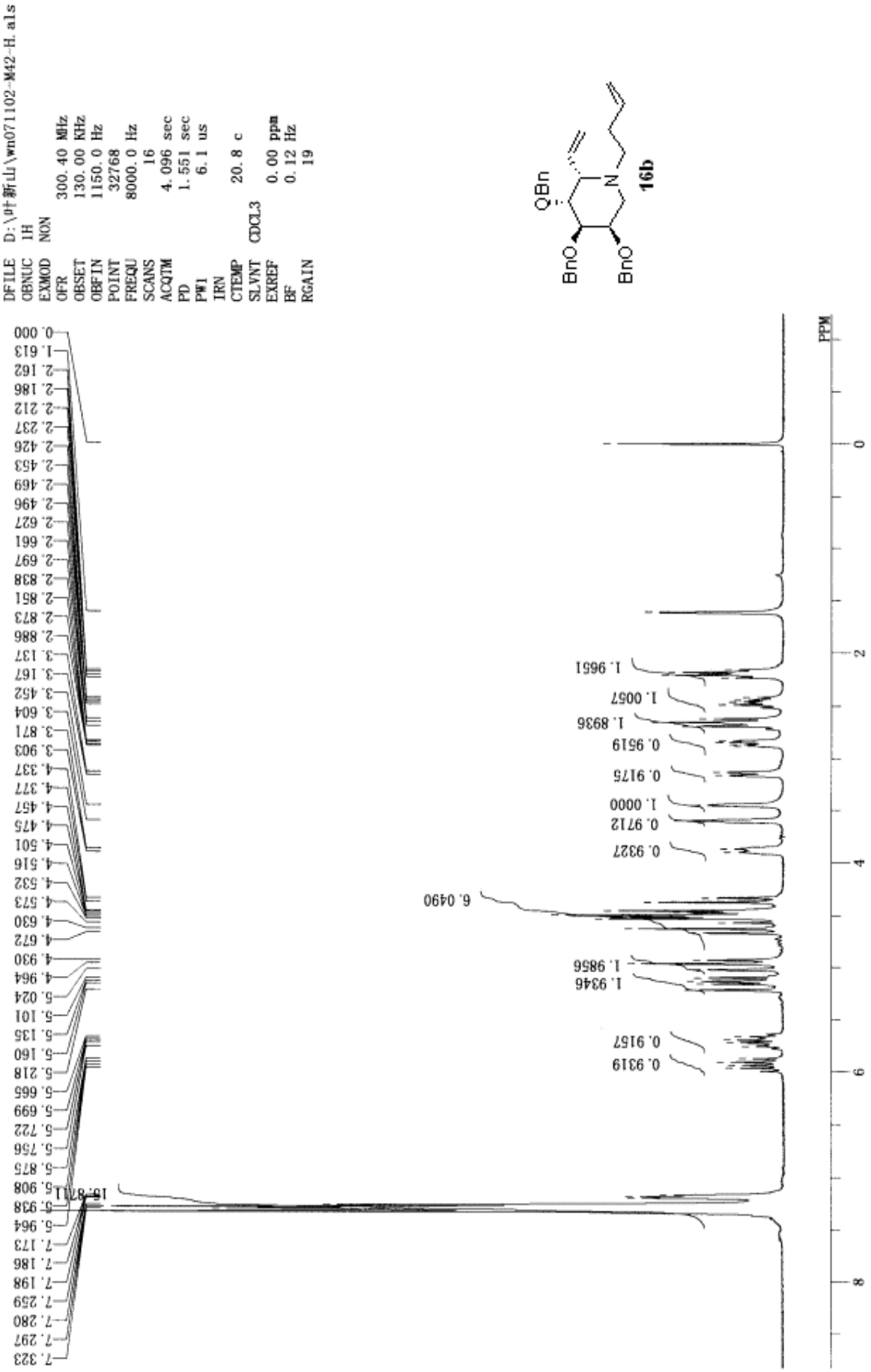
Pulse Sequence: NOESY
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: wn061226-man-add-noesy
INOVA-500 "BMU500"

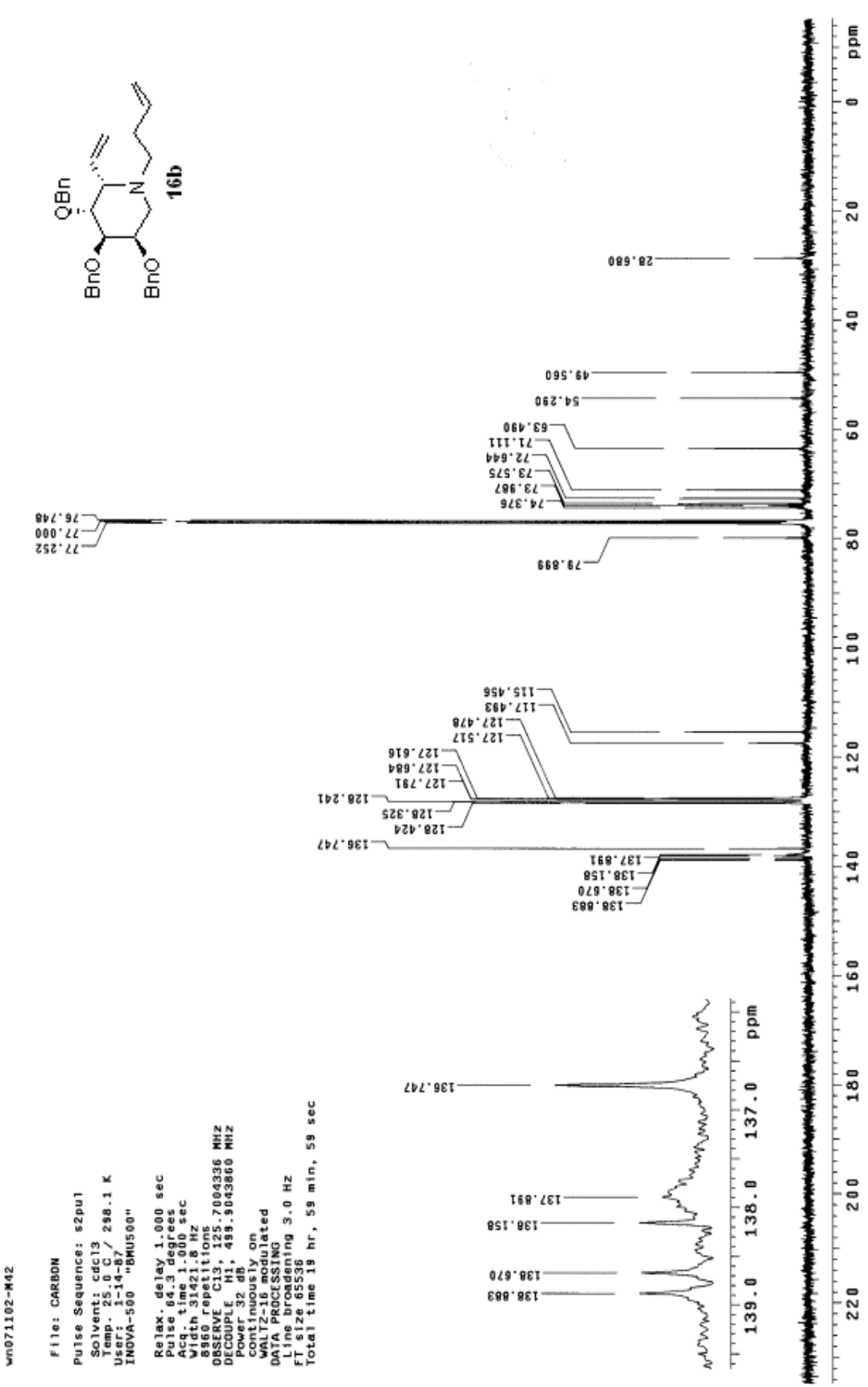
Relax. delay 1.000 sec
Mixing 0.500 sec
Acq. time 0.213 sec
Width 4804.2 Hz
2D Width 4804.2 Hz
32 repetitions
2 x 300 increments
OBSERVE H1, 499.9019008 MHz
DATA PROCESSING
Gauss apodization 0.098 sec
F1 DATA PROCESSING
Gauss apodization 0.031 sec
FT size 4096 x 4096
Total time 9 hr, 23 min, 28 sec

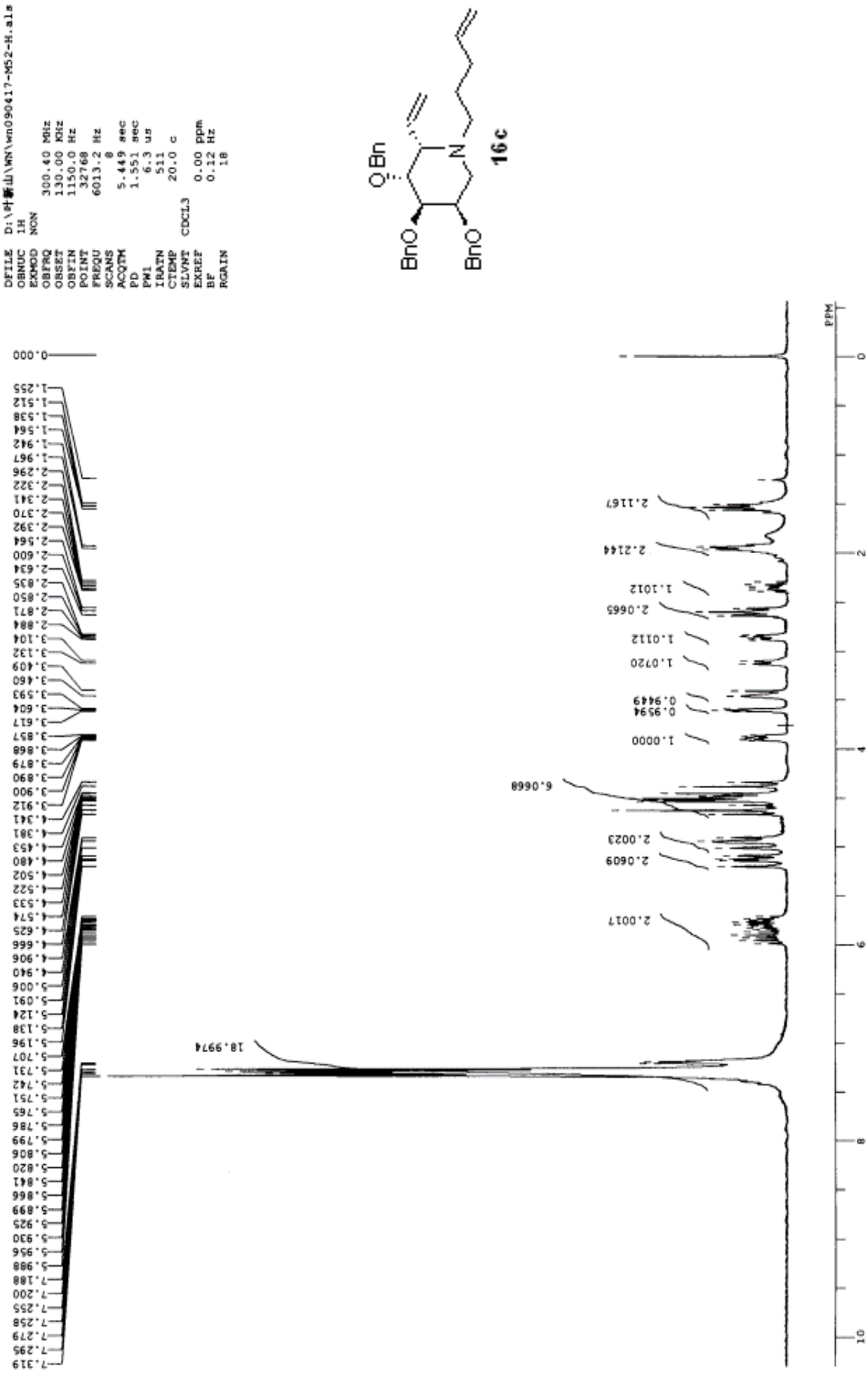


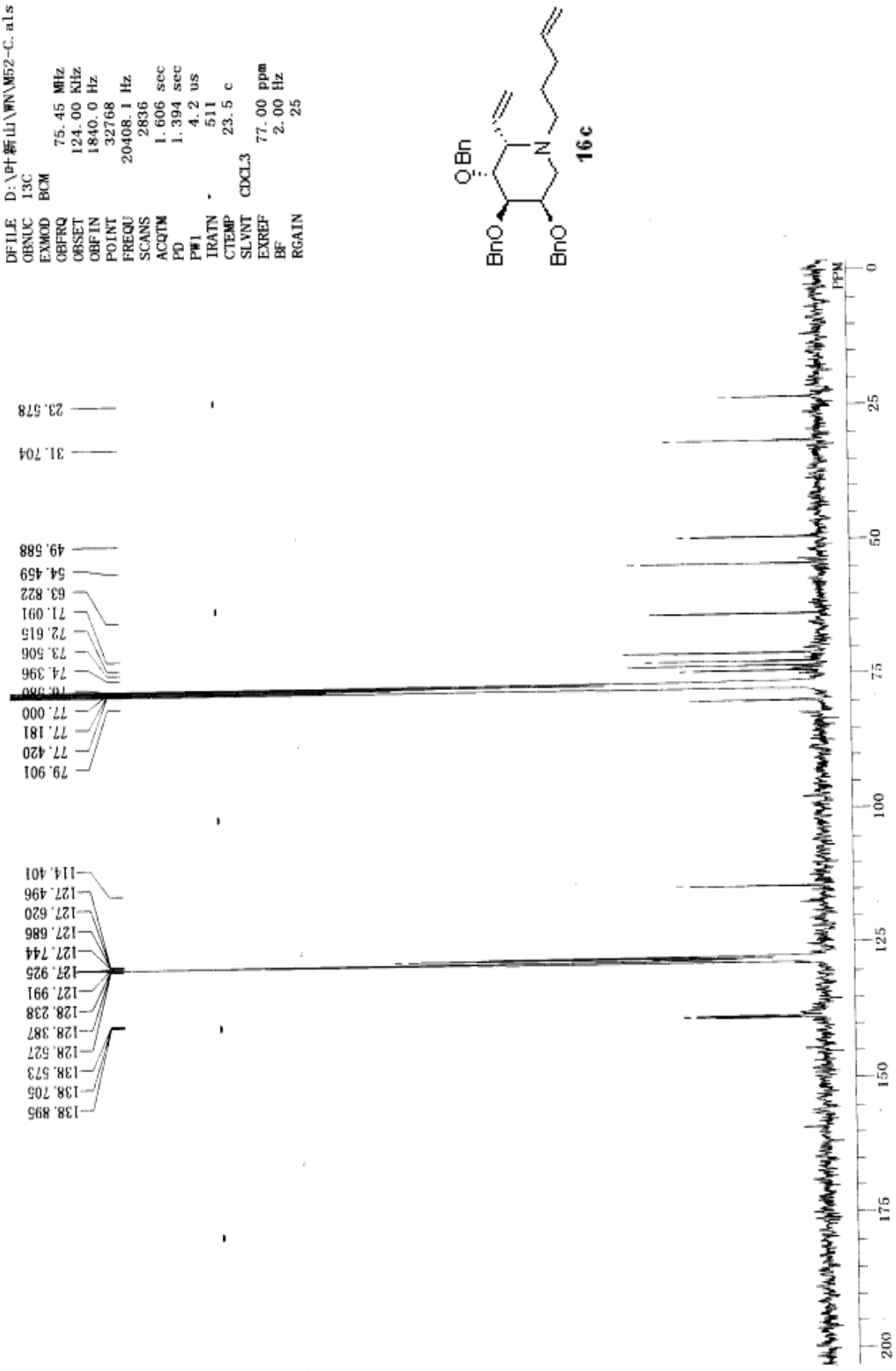
16a

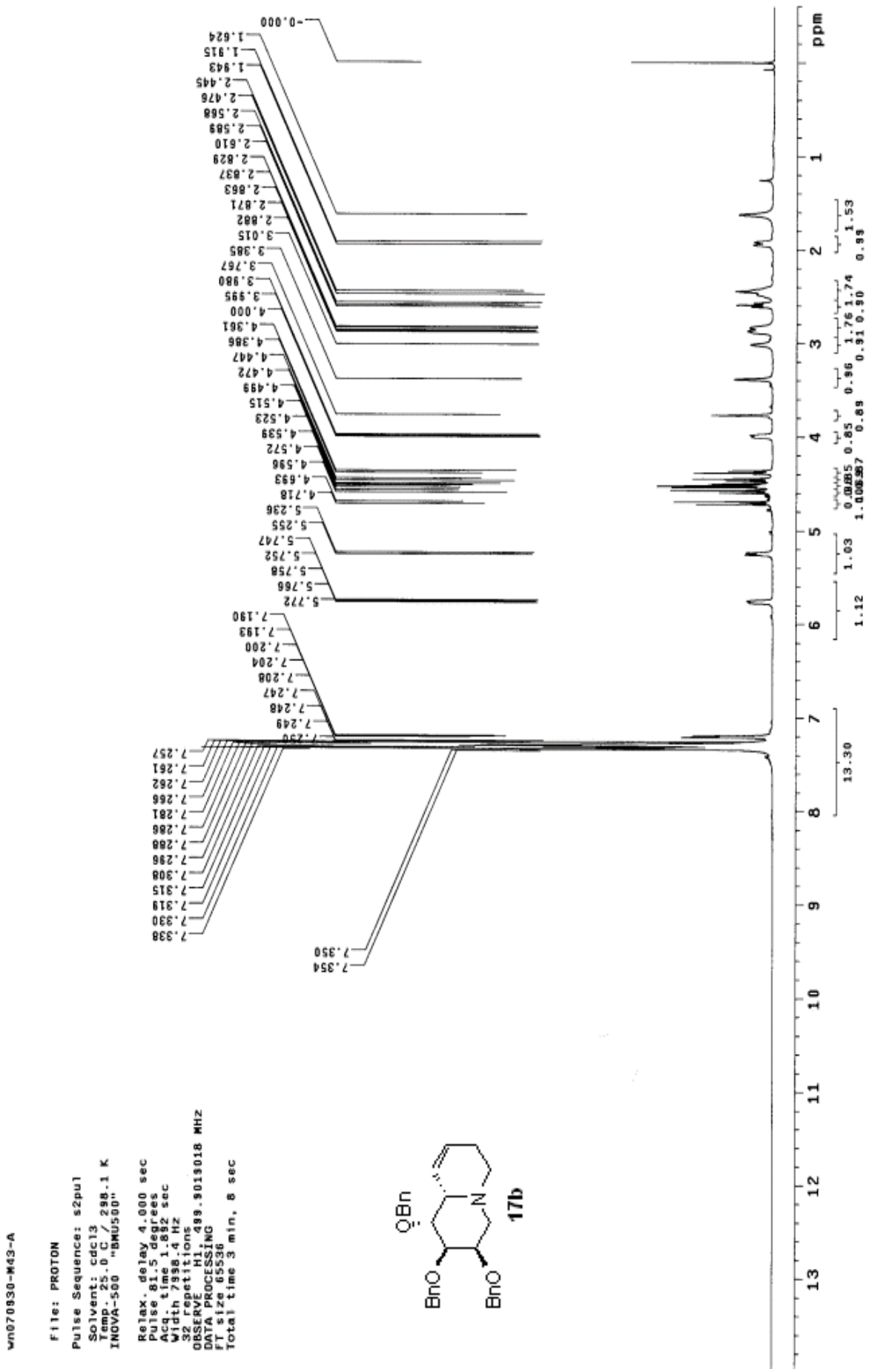


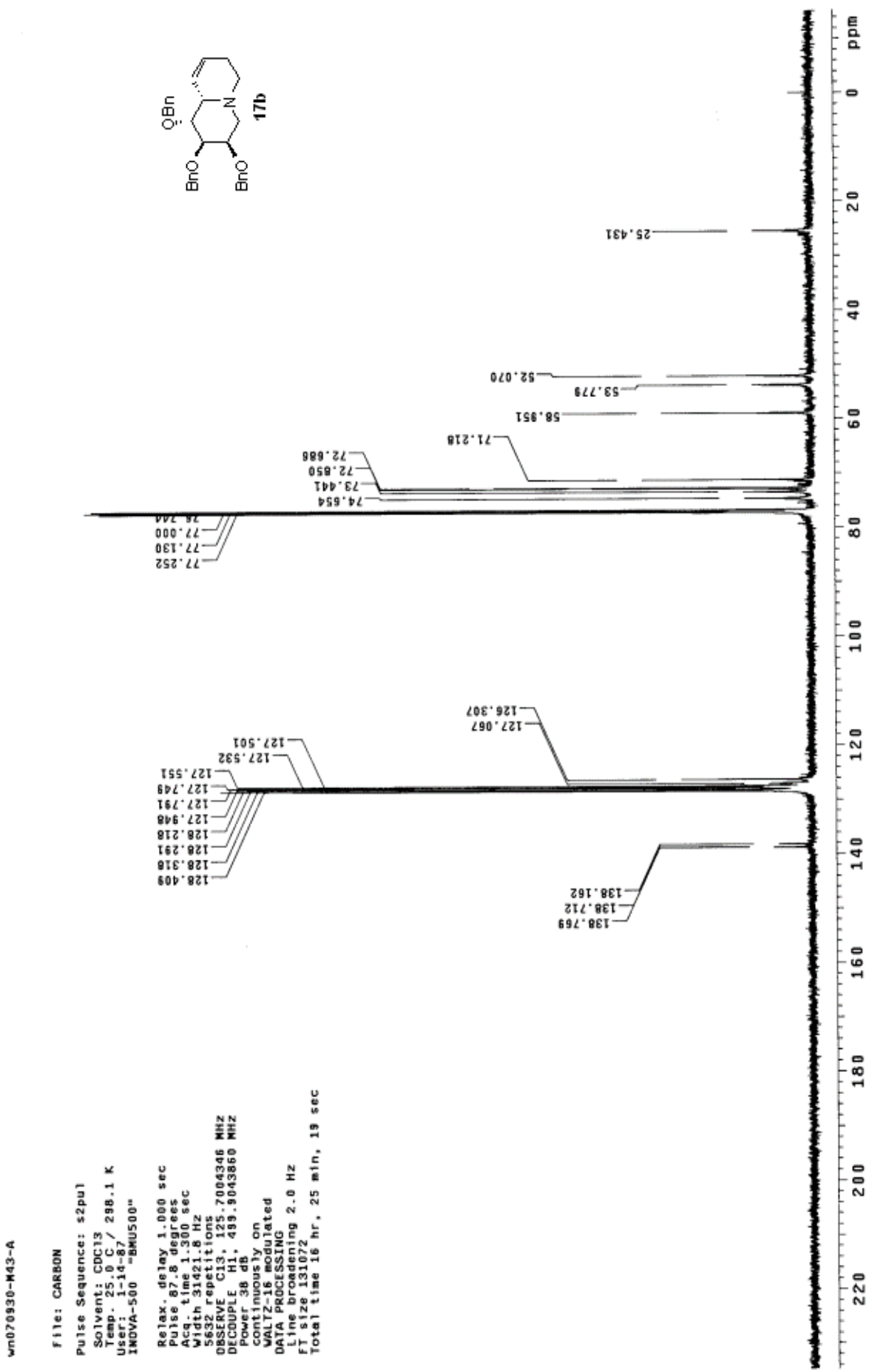


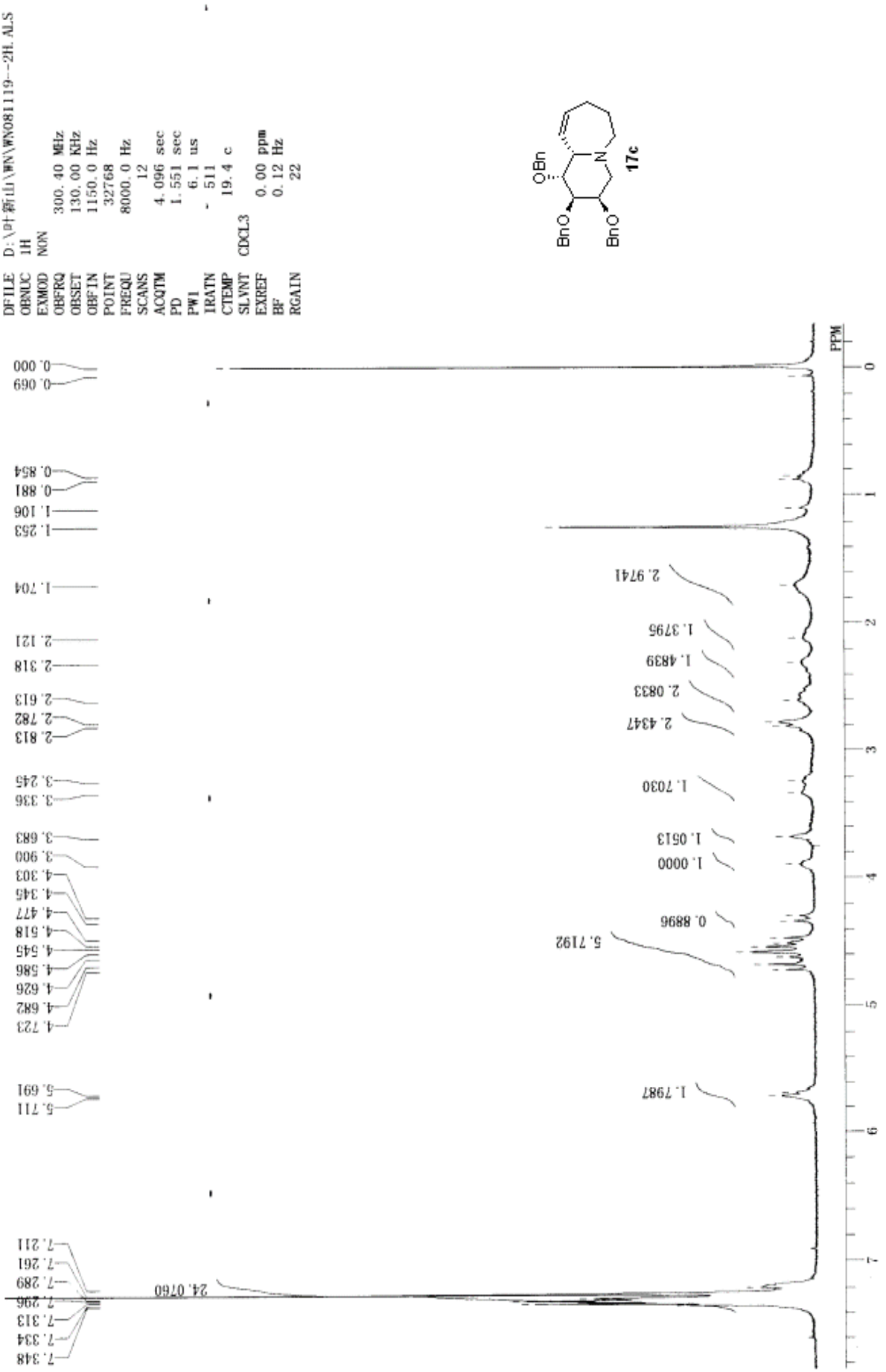


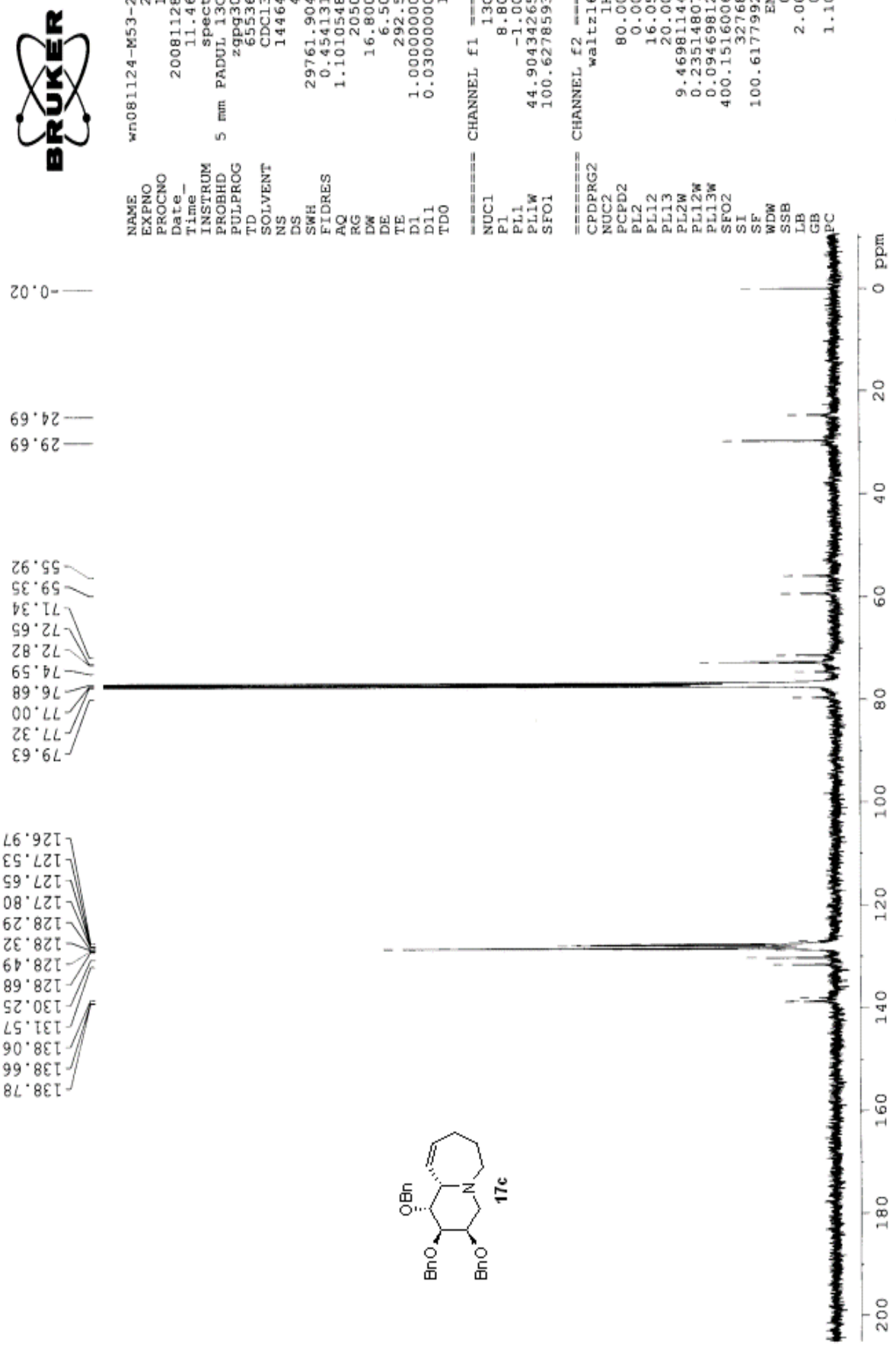


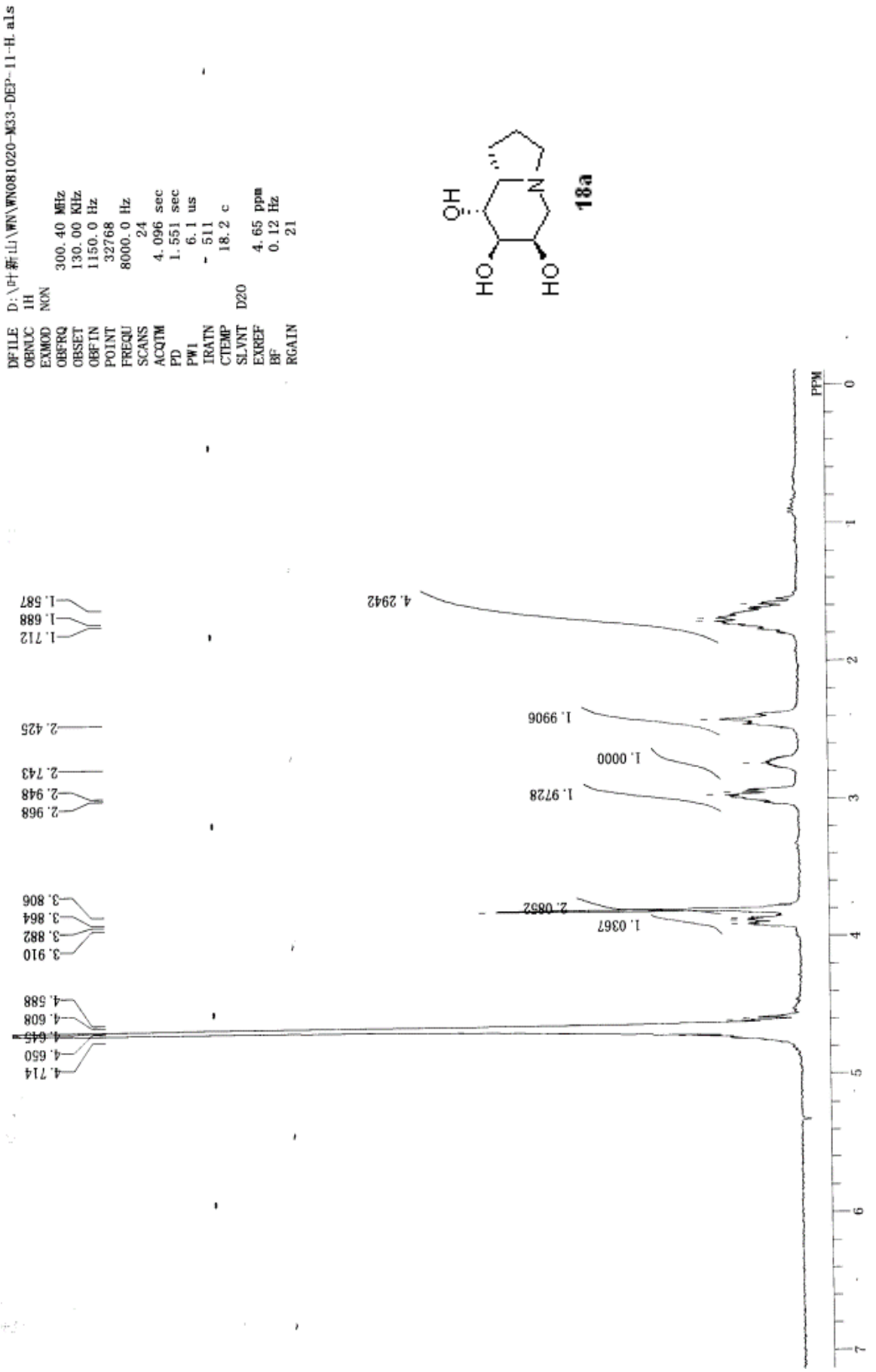










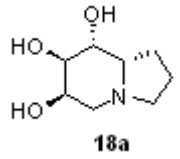


wn081020-M33-dep-11

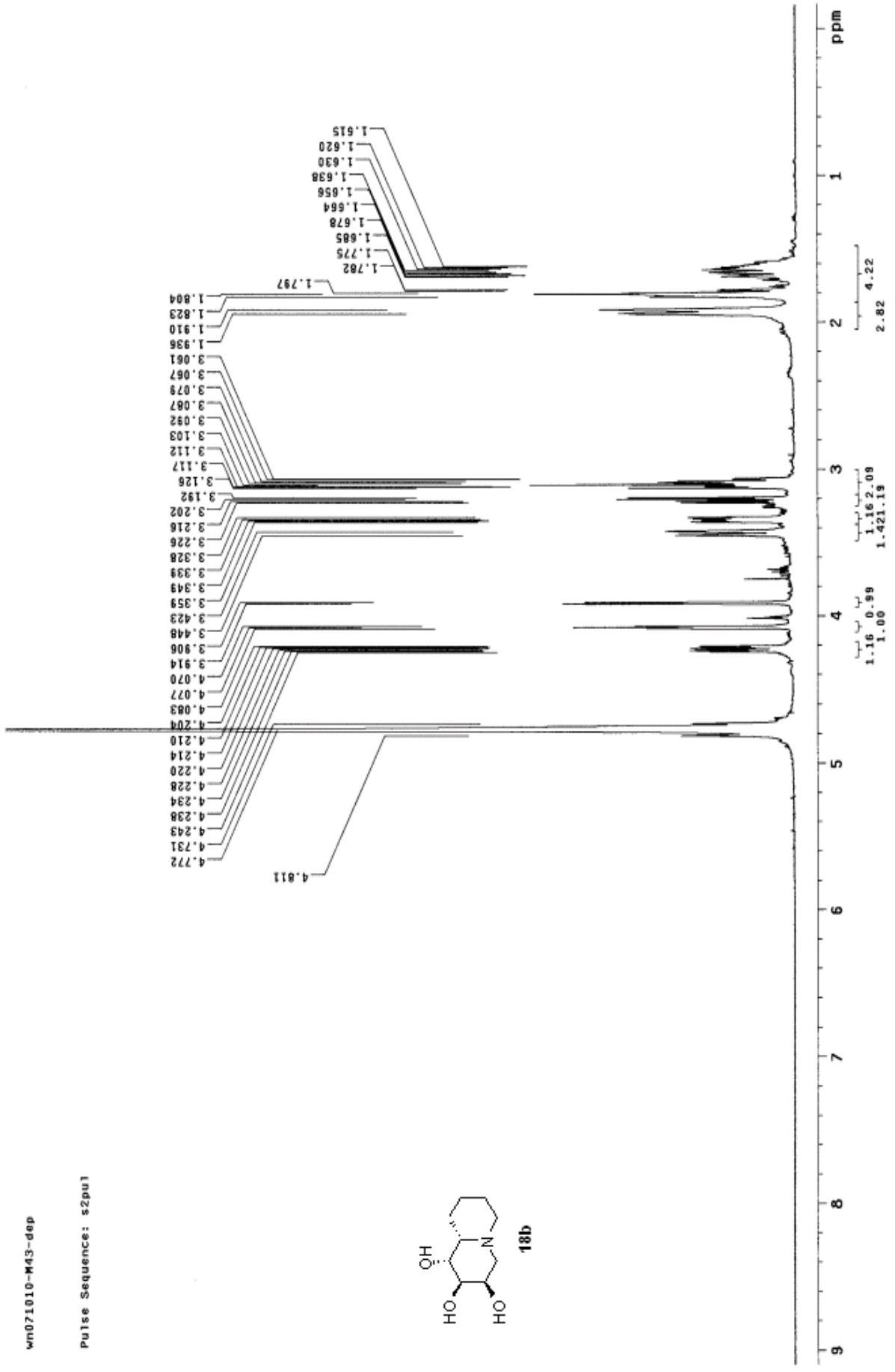
File: CARBON

Pulse Sequence: s2pul
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
25600 repetitions
OBSERVE C13, 125.7006556 MHz
DECOUPLE H1, 499.9056708 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 131072
Total time 19 hr, 42 min, 23 sec



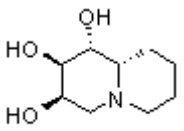
18a



JL-1008-C

Pulse Sequence: s2pul
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: wn071010-M43-dep-c
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
20480 repetitions
OBSERVE C13, 125.7006556 MHz
DECOUPLE H1, 499.9056708 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.5 Hz
FT size 65536
Total time 11 hr, 25 min, 42 sec



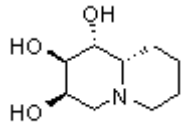
18b

wn071010-M43-dep

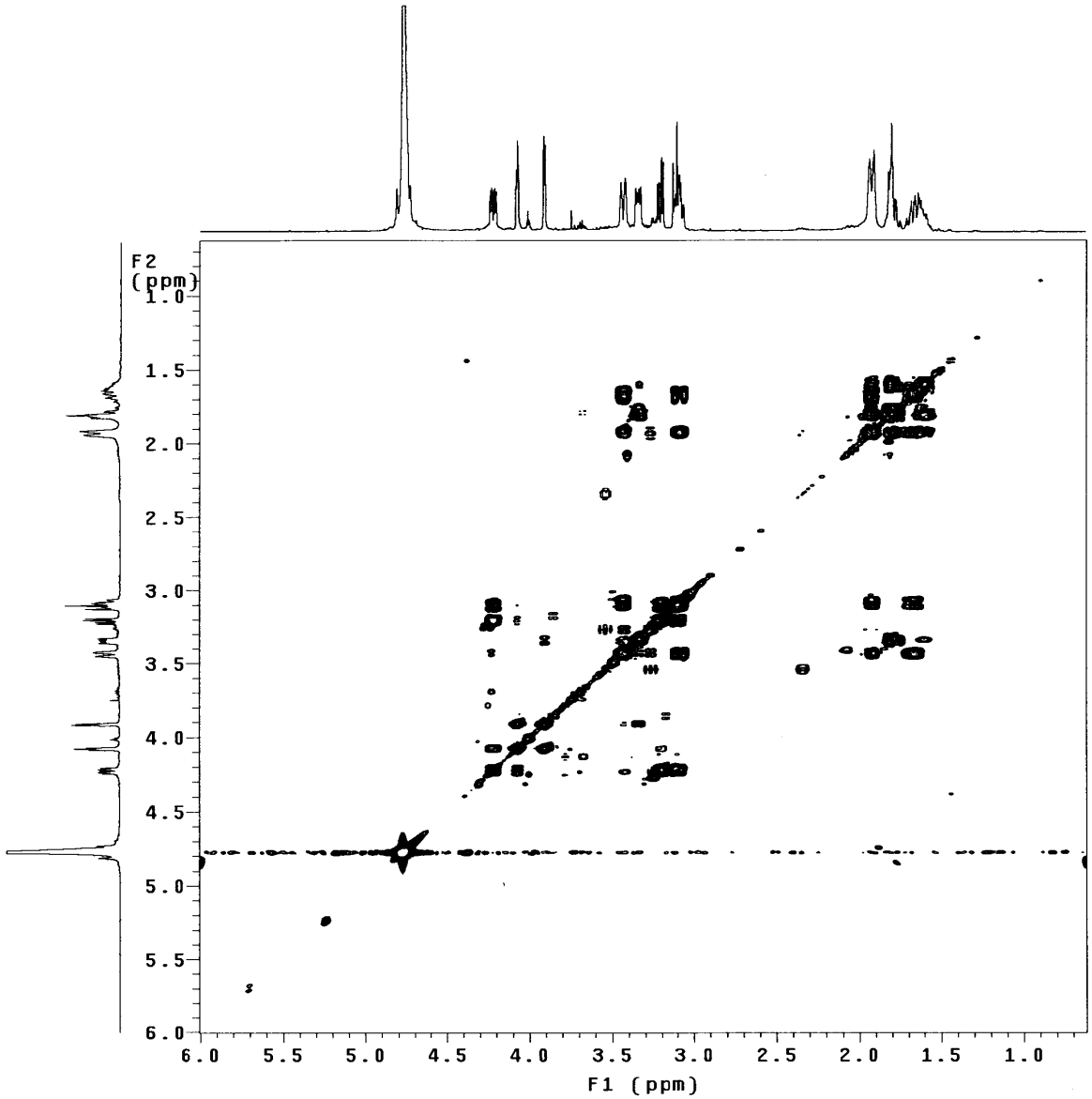
File: PROTON

Pulse Sequence: gCOSY
Solvent: d2o
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.380 sec
Width 2692.2 Hz
2D Width 2692.2 Hz
16 repetitions
300 increments
OBSERVE H1, 499.9031220 MHz
DATA PROCESSING
Sq. sine bell 0.095 sec
F1 DATA PROCESSING
Sq. sine bell 0.059 sec
FT size 4096 x 4096
Total time 1 hr, 56 min, 16 sec



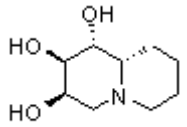
18b



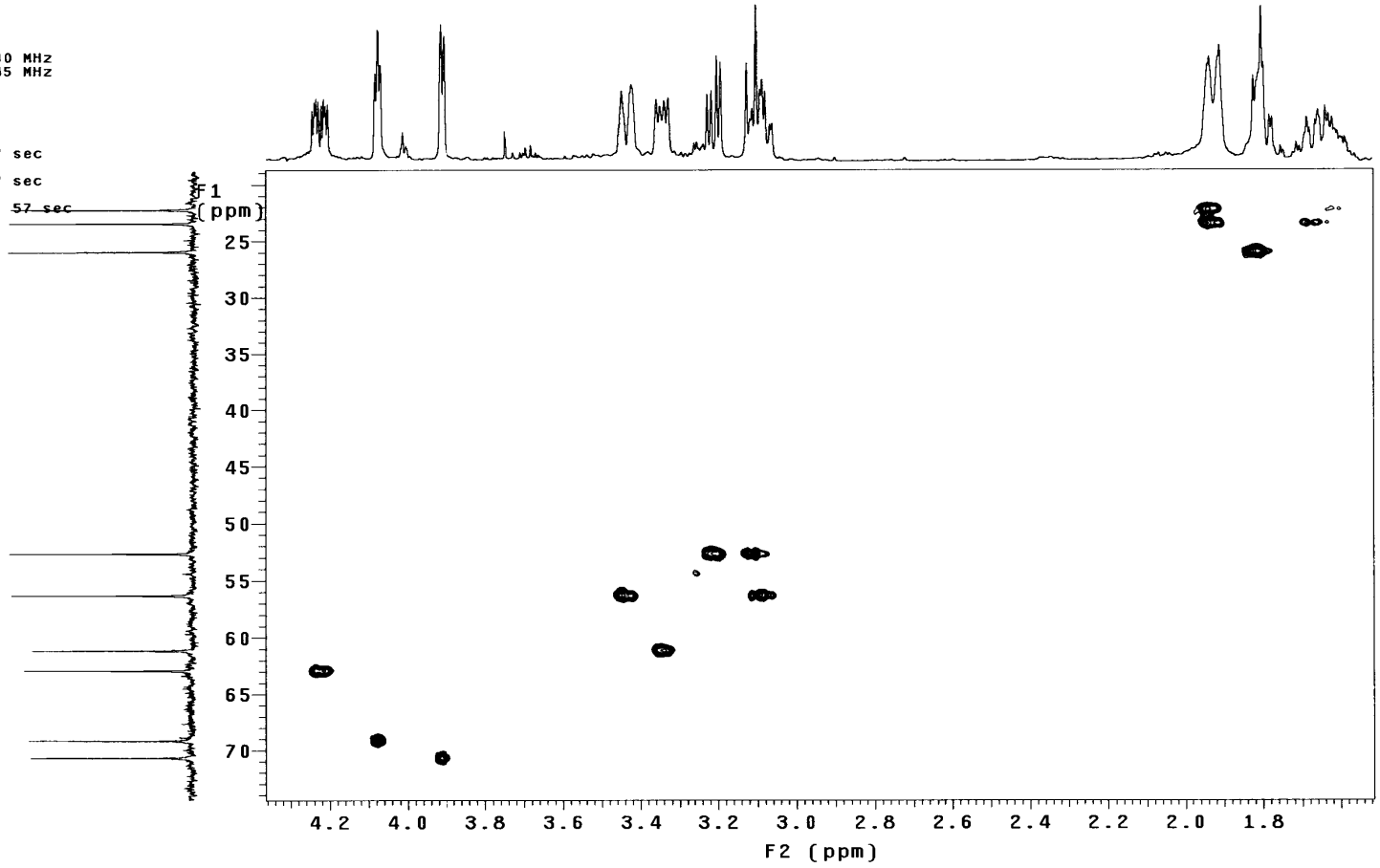
wn071010-M43-dep

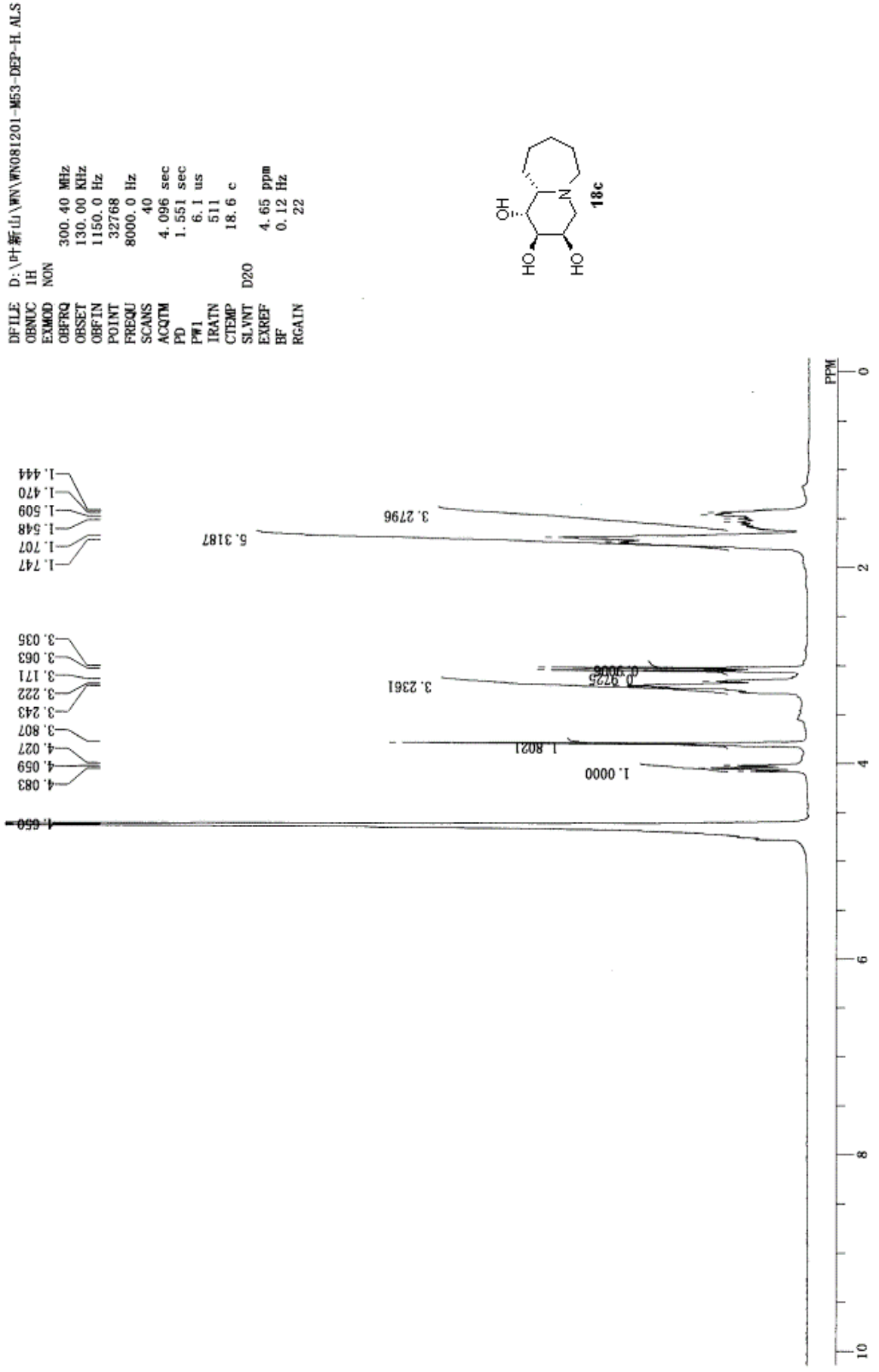
Pulse Sequence: gHSQC
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: wn071010-M43-dep-qc
INOVA-500 "BMU500"

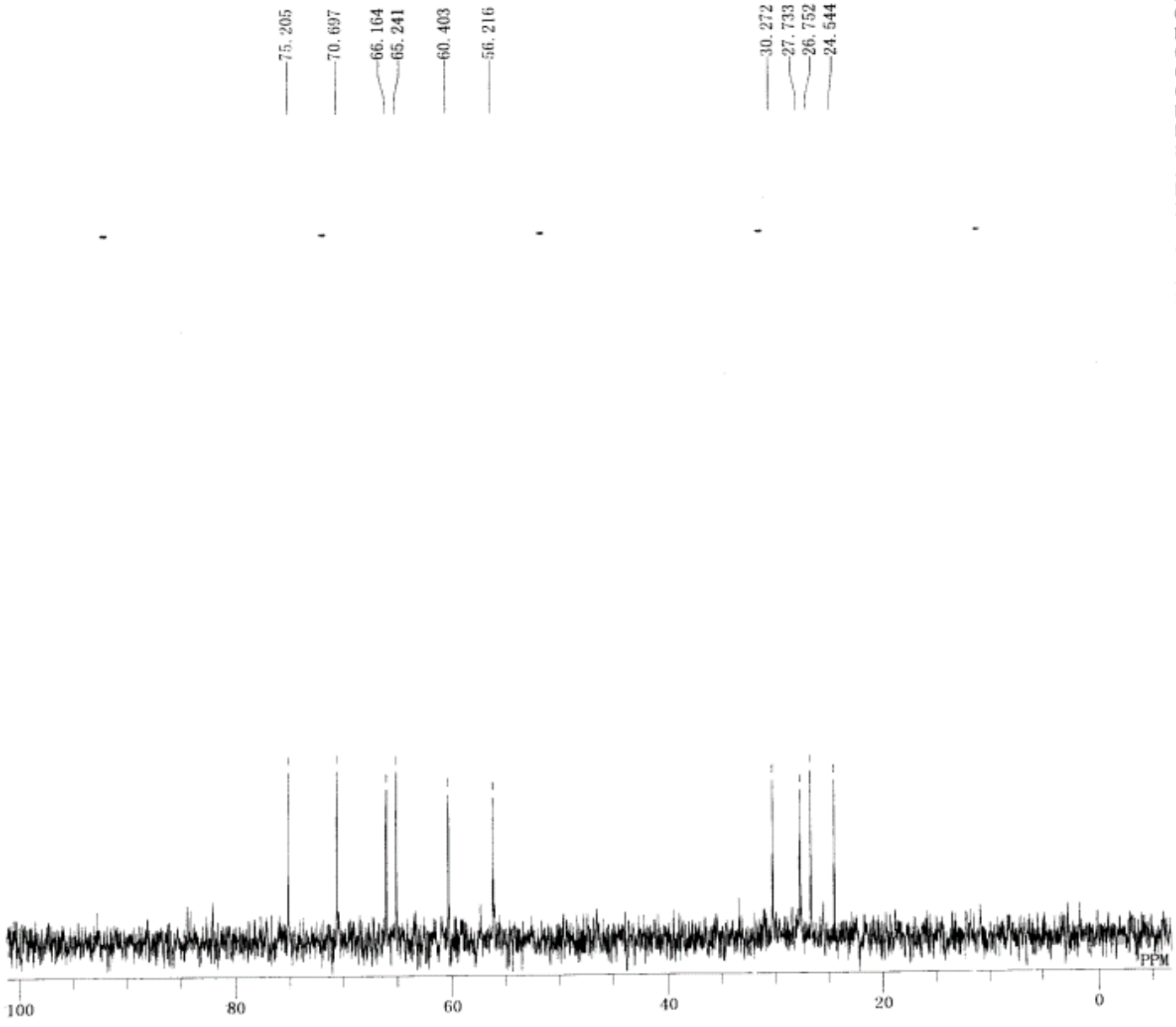
Relax. delay 1.000 sec
Acq. time 0.378 sec
Width 2709.8 Hz
2D Width 9615.4 Hz
16 repetitions
2 x 128 increments
OBSERVE H1, 499.9031390 MHz
DECOUPLE C13, 125.7065245 MHz
Power 49 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Gauss apodization 0.087 sec
F1 DATA PROCESSING
Gauss apodization 0.007 sec
FT size 1024 x 2048
Total time 1 hr, 39 min, 57 sec



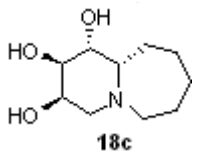
18b



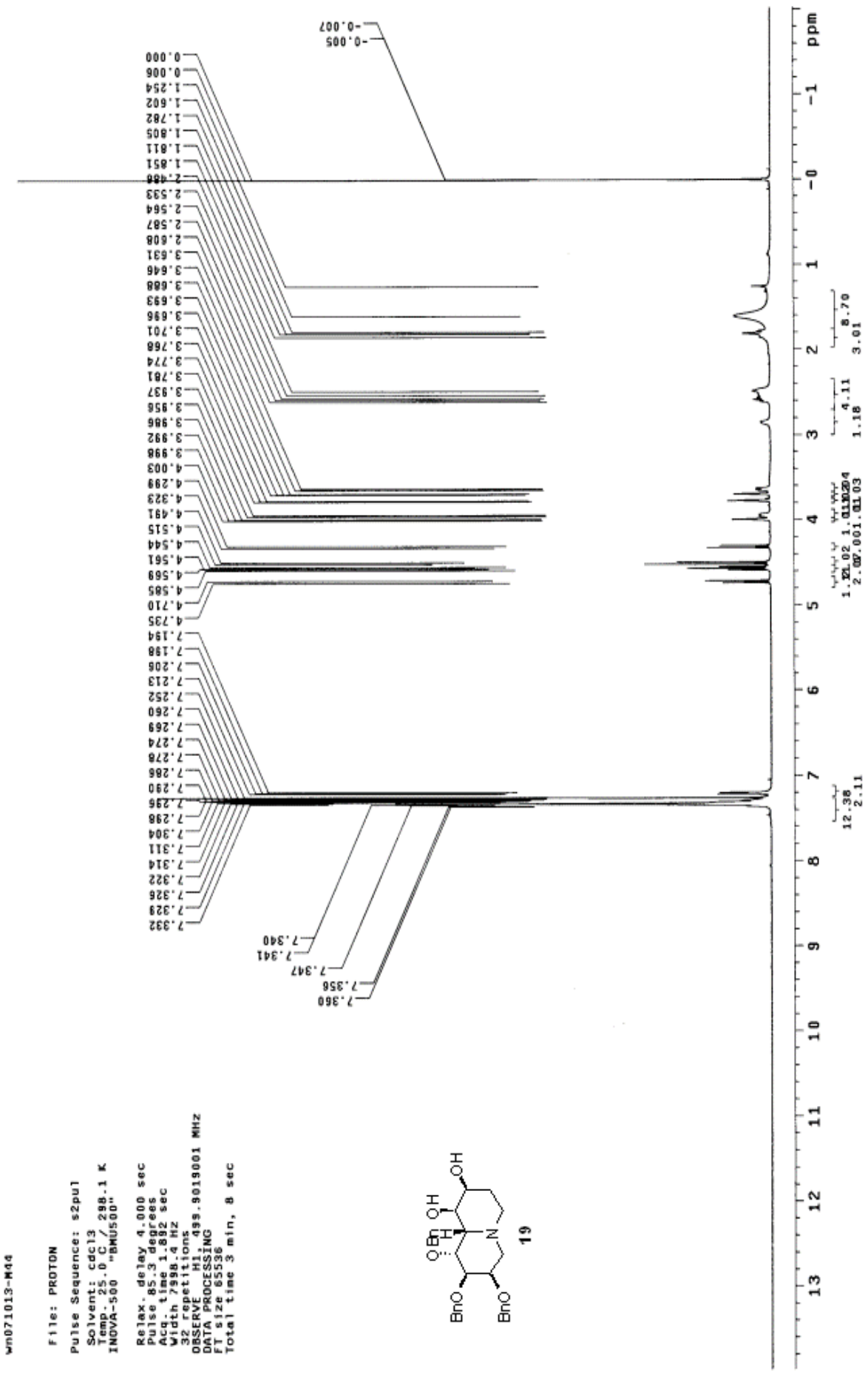


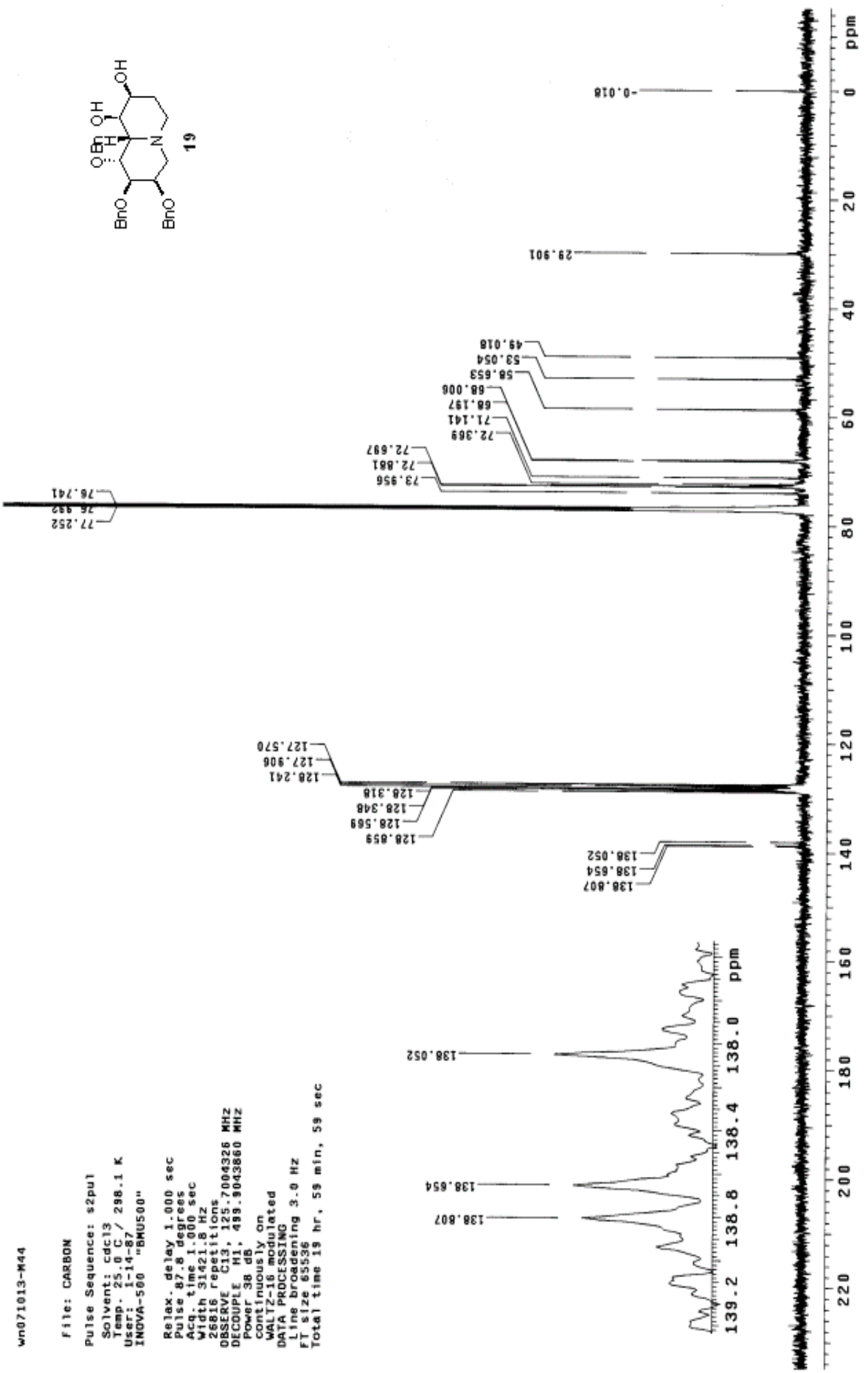


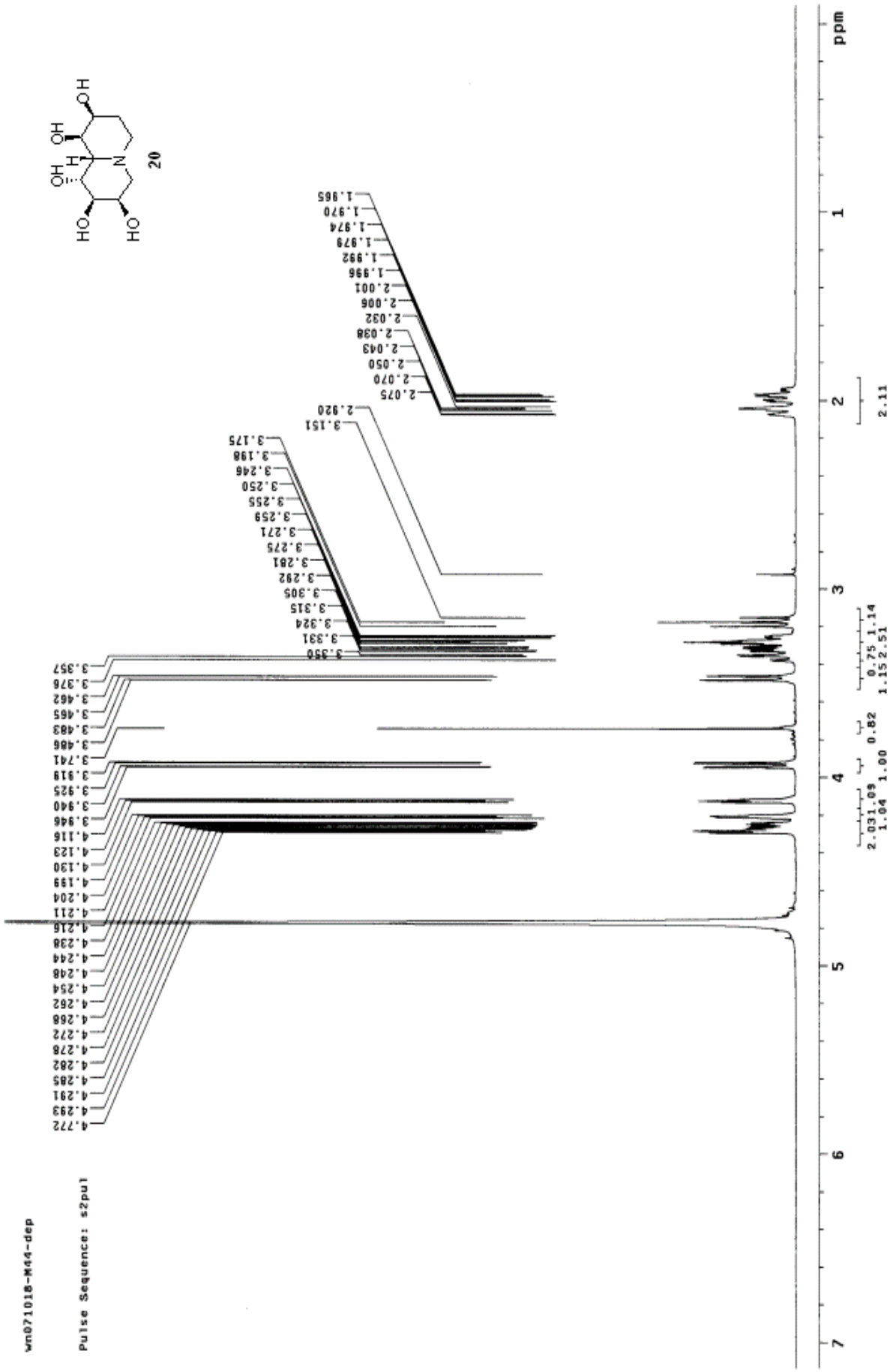

```
DFILE   D:\叶新山\WN\081201-M53-DEP-C.ALS
OBNUC   13C
EXMOD   BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN      1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS        10988
ACQTM        1.606 sec
PD           1.394 sec
PW1            4.2 us
IRATN          511
CTEMP         23.7 c
SLVNT   D2O
EXREF         0.00 ppm
BF            2.00 Hz
RGAIN           26
```

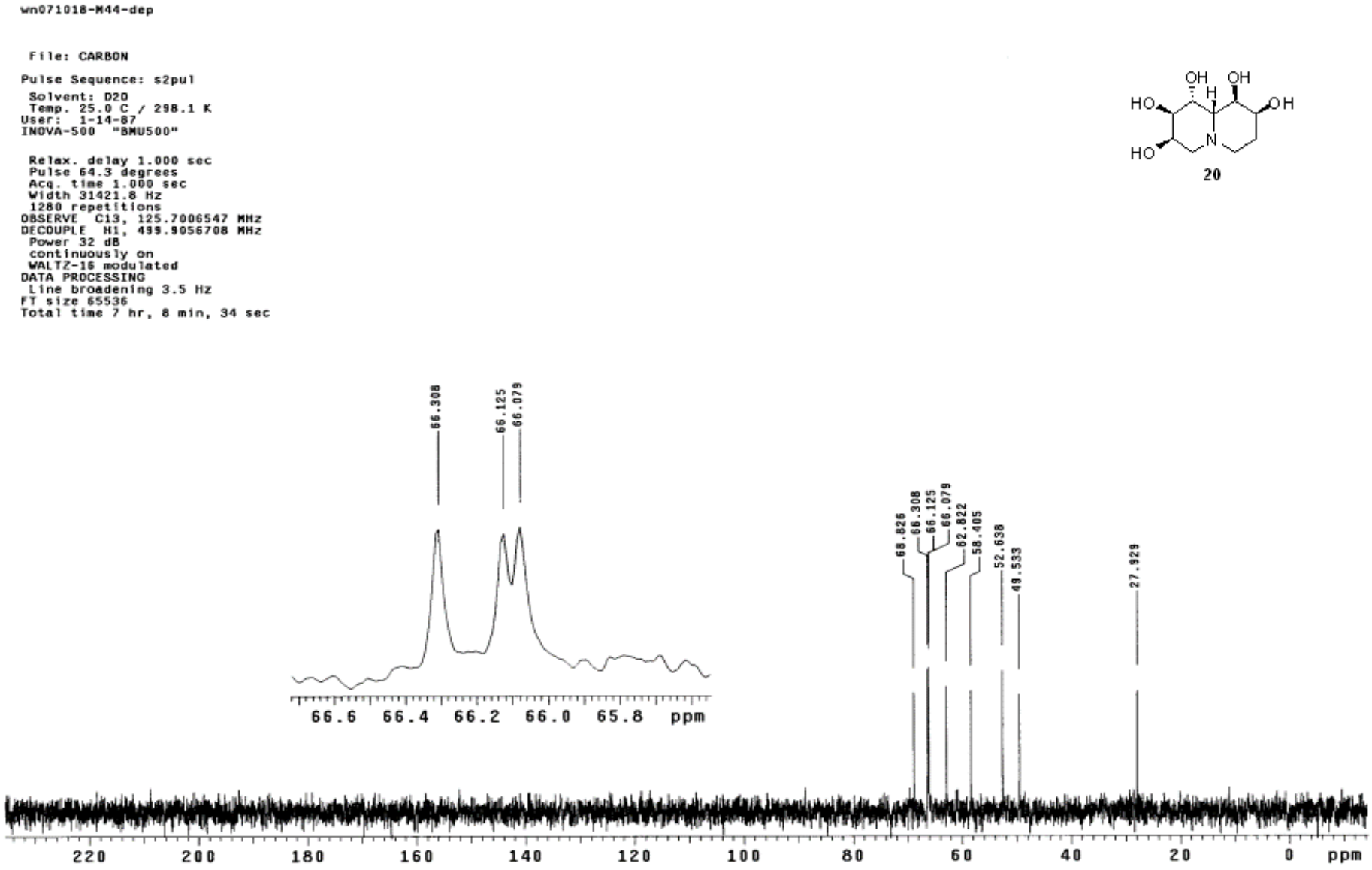


18c







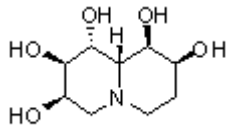


wn071018-M44-dep

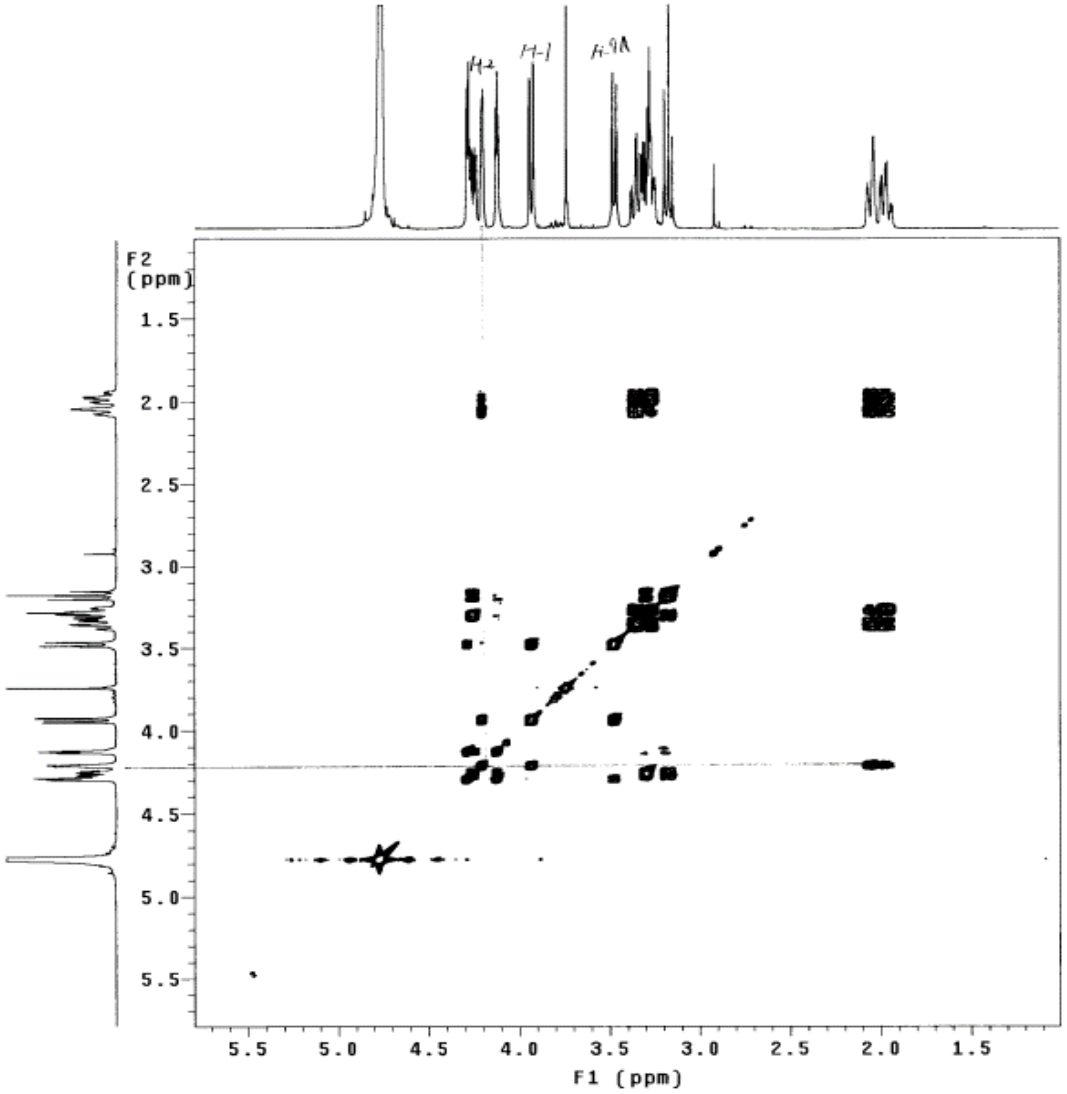
File: PROTON

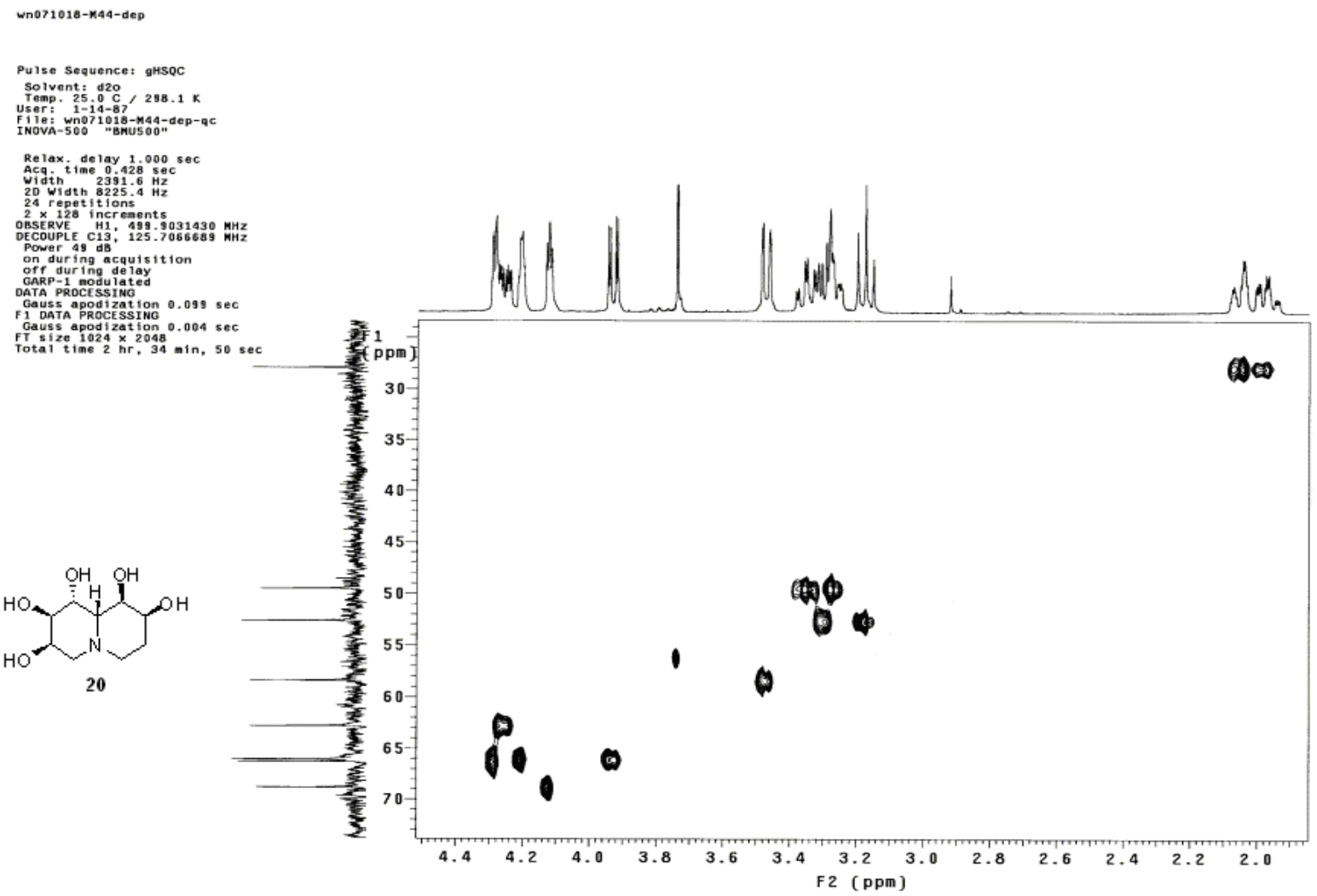
Pulse Sequence: gCOSY
Solvent: d2o
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.214 sec
Width 2391.6 Hz
2D Width 2391.6 Hz
16 repetitions
400 increments
OBSERVE H1, 499.9031222 MHz
DATA PROCESSING
Sq. sine bell 0.107 sec
F1 DATA PROCESSING
Sq. sine bell 0.091 sec
FT size 8192 x 8192
Total time 2 hr, 20 min, 6 sec



20

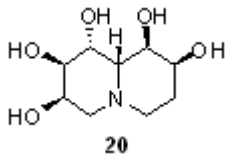




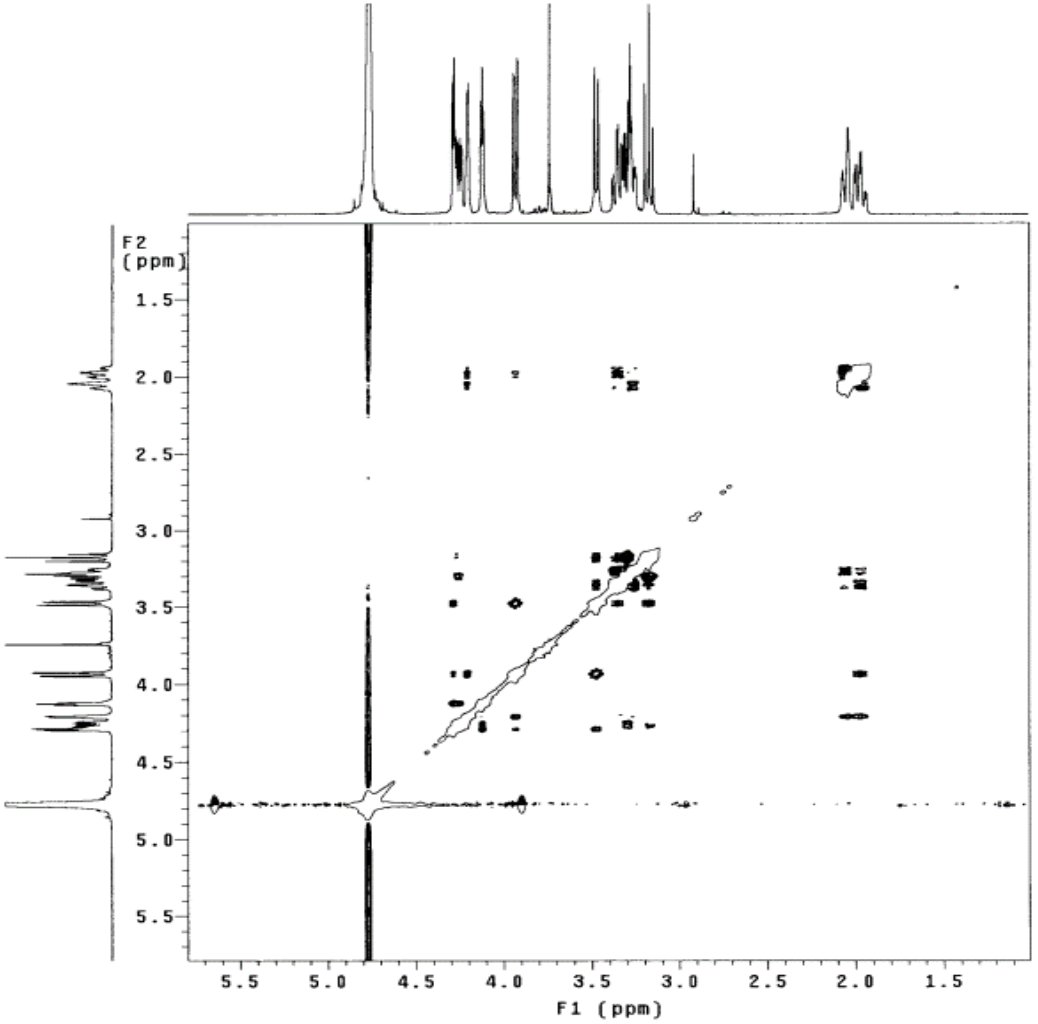
wn071018-M44-dep

Pulse Sequence: NOESY
Solvent: d2o
Temp. 25.0 C / 298.1 K
File: wn071018-M44-dep-noesy
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Mixing 0.600 sec
Acq. time 0.214 sec
Width 2391.6 Hz
2D Width 2391.6 Hz
32 repetitions
2 x 270 increments
OBSERVE H1, 499.9031222 MHz
DATA PROCESSING
Gauss apodization 0.099 sec
F1 DATA PROCESSING
Gauss apodization 0.060 sec
FT size 4096 x 4096
Total time 9 hr, 3 min, 34 sec

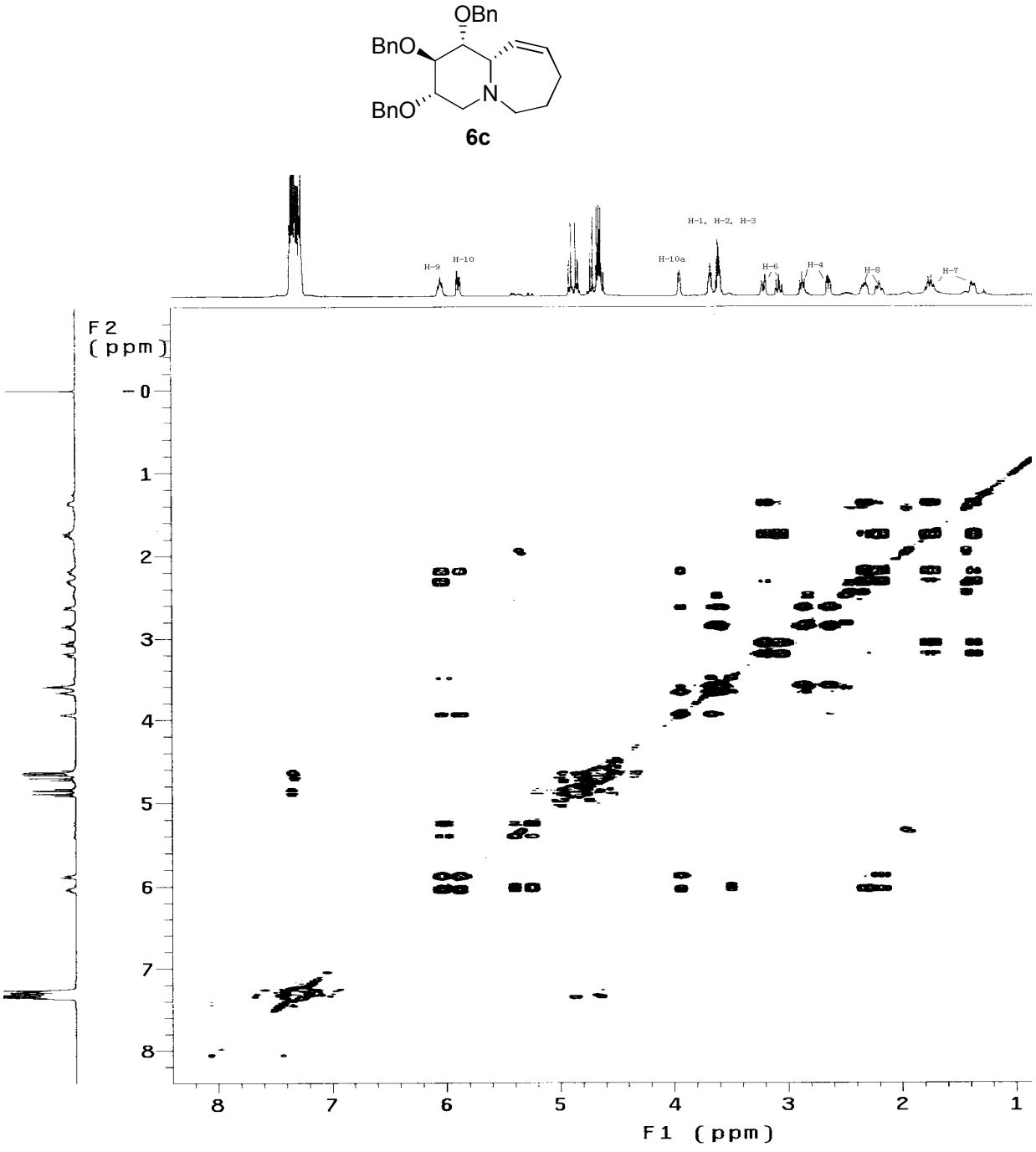


20



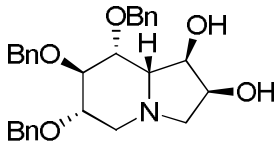
Supplementary Section

(1R,2R,3S,10aS,Z)-1,2,3-Tris(benzyloxy)-1,2,3,4,6,7,8,10a-octahydropyrido[1,2-a]azepine (6c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33-1.38 (m, 1H, H-7), 1.67-1.80 (m, 1H, H-7), 2.13-2.22 (m, 1H, H-8), 2.29-2.34 (m, 1H, H-8), 2.62 (dd, J = 3.9 Hz, J = 11.1 Hz, 1H, H-4), 2.82-2.89 (m, 1H, H-4), 3.01-3.09 (m, 1H, H-6), 3.17-3.22 (m, 1H, H-6), 3.57-3.69 (m, 3H, H-1, H-2, H-3), 3.94 (br.s, 1H, H-10a), 4.63-4.92 (m, 6H, $PhCH_2$), 5.86-5.90 (m, 1H, H-10), 6.03-6.04 (m, 1H, H-9), 7.27-7.36 (m, 15H, Ar). Proton NMR assignment was proceeded by analysis of COSY and other 2D NMR spectra.

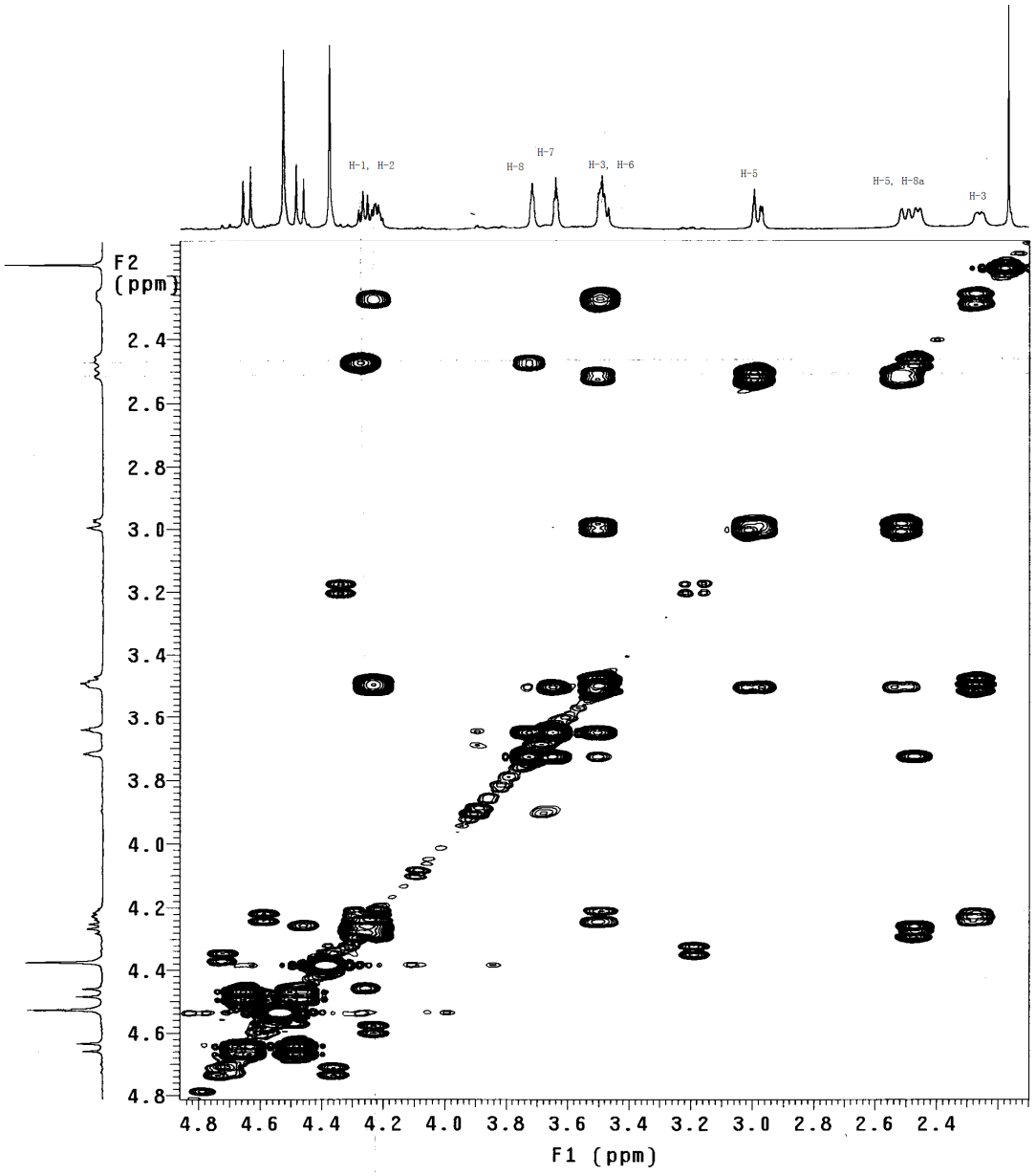


COSY spectra of **6c**

(1R,2S,6S,7R,8R,8aS)-6,7,8-Tris(benzyloxy)octahydroindolizine-1,2-diol (10a). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.27 (dd, J = 4.0 Hz, J = 10.0 Hz, 1H, H-3), 2.46-2.52 (m, 2H, H-5, H-8a), 2.99 (dd, J = 3.5 Hz, J = 12.0 Hz, 1H, H-5), 3.47-3.50 (m, 2H, H-3, H-6), 3.65 (t, J = 2.5 Hz, 1H, H-7), 3.72 (br.s, 1H, H-8), 4.22-4.28 (m, 2H, H-1, H-2), 4.38-4.68 (m, 6H, $PhCH_2$), 7.18-7.35 (m, 15H, Ar). Proton NMR assignment was proceeded by analysis of COSY.



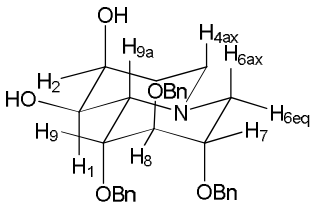
10a



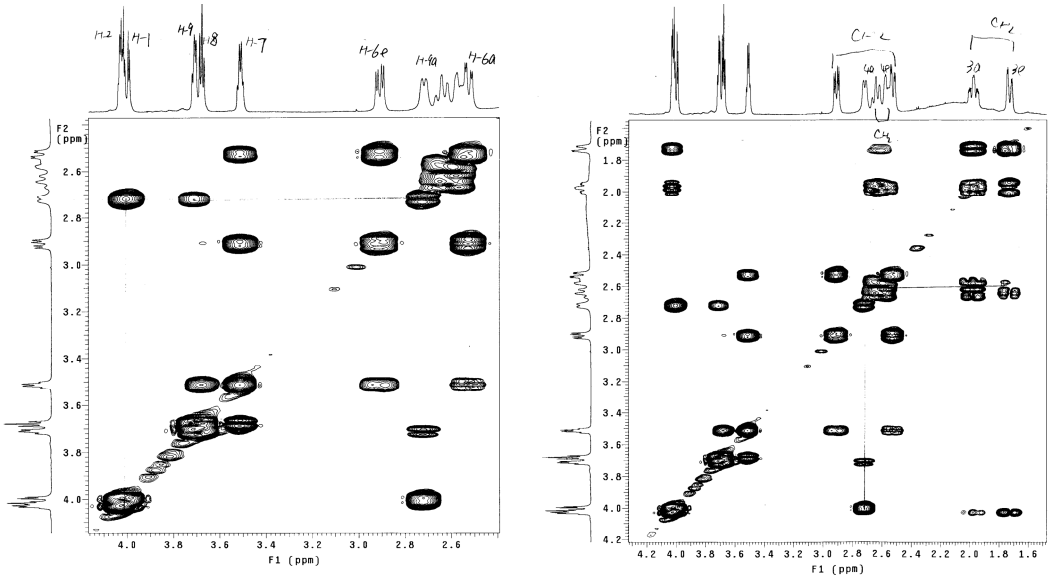
COSY spectra of **10a**

(1R,2S,7S,8R,9R,9aS)-7,8,9-Tris(benzyloxy)octahydro-1H-quinolizine-1,2-diol (10b). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.71-1.74 (m, 1H, H-3), 1.93-2.00 (m, 1H, H-3), 2.51 (dd, J = 3.5 Hz,

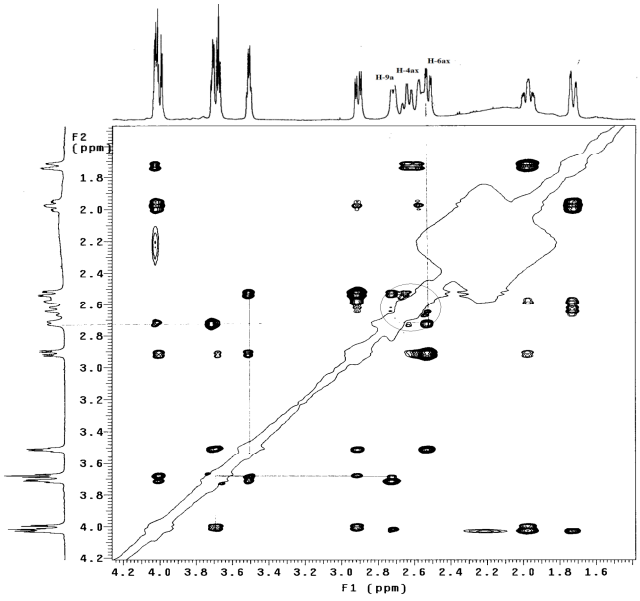
J = 12.0 Hz, 1H, H-6ax), 2.53-2.56 (m, 1H, H-4eq), 2.61-2.65 (m, 1H, H-4ax), 2.70 (dd, *J* = 2.5 Hz, *J* = 9.5 Hz, 1H, H-9a), 2.90 (dd, *J* = 5.0 Hz, *J* = 12.5 Hz, 1H, H-6eq), 3.51 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H, H-7), 3.67-3.71 (m, 2H, H-8, H-9), 4.00 (dd, *J* = 3.5 Hz, *J* = 10.0 Hz, 1H, H-1), 4.01-4.03 (m, 1H, H-2), 4.46-4.62 (m, 5H, $PhCH_2$), 4.71 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 7.25-7.35 (m, 15H, Ar). Proton NMR assignment was proceeded by analysis of COSY and other 2D NMR spectra. The axial orientations of H_{4ax}, H_{6ax} and H_{9a} were proved by the NOESY spectrum which showed their intimacy in geometry.



10b

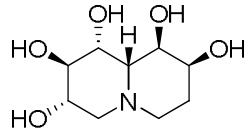


COSY spectra of **10b**

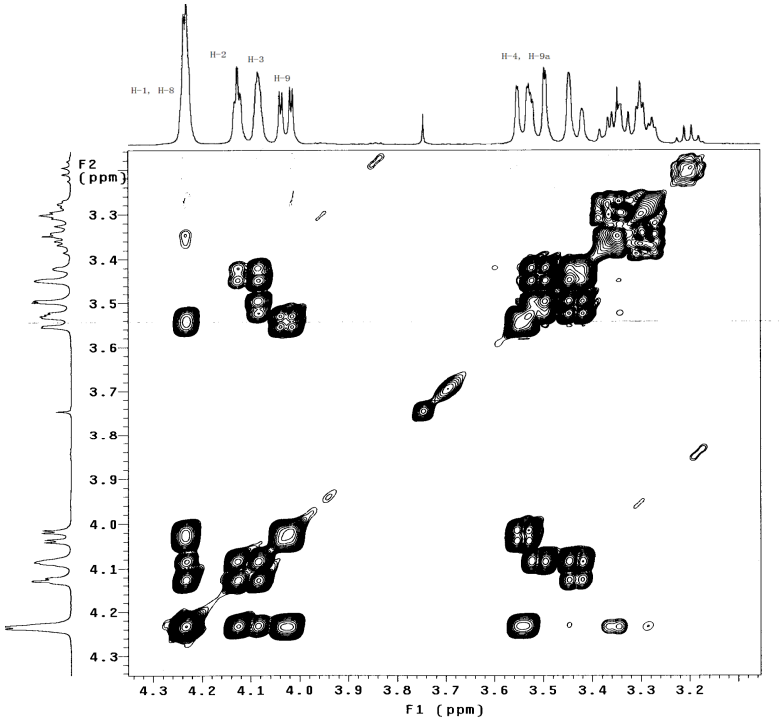


NOESY spectra of **10b**

(1R,2R,3S,8S,9R,9aS)-Octahydro-1H-quinolizine-1,2,3,8,9-pentaol (11b). ^{1}H NMR (300 MHz, D_2O) δ 1.87-1.90 (m, 2H, H-7), 3.12-3.28 (m, 3H, H-4, H-6), 3.32-3.39 (m, 2H, H-4, H-9a), 3.85 (dd, J = 2.7 Hz, J = 10.8 Hz, 1H, H-9), 3.91-3.94 (m, 1H, H-3), 3.95-3.96 (m, 1H, H-2), 4.05-4.06 (m, 2H, H-1, H-8). Proton NMR assignment was proceeded by analysis of COSY and other 2D NMR spectra.

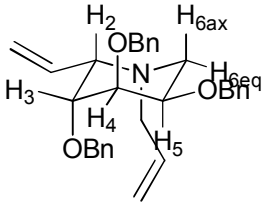


11b

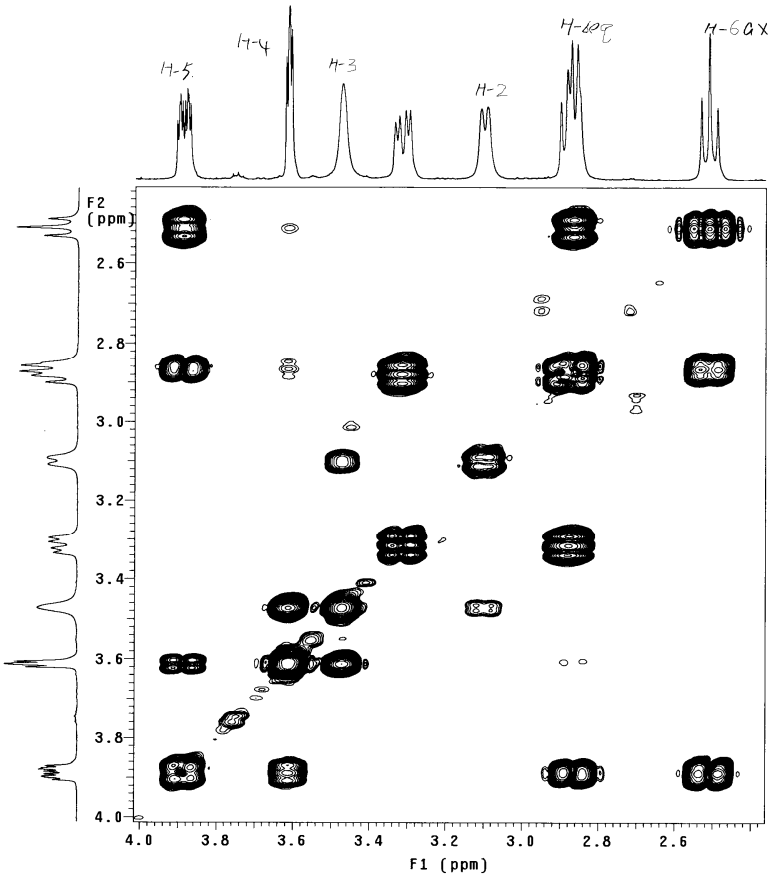


COSY spectra of **11b**

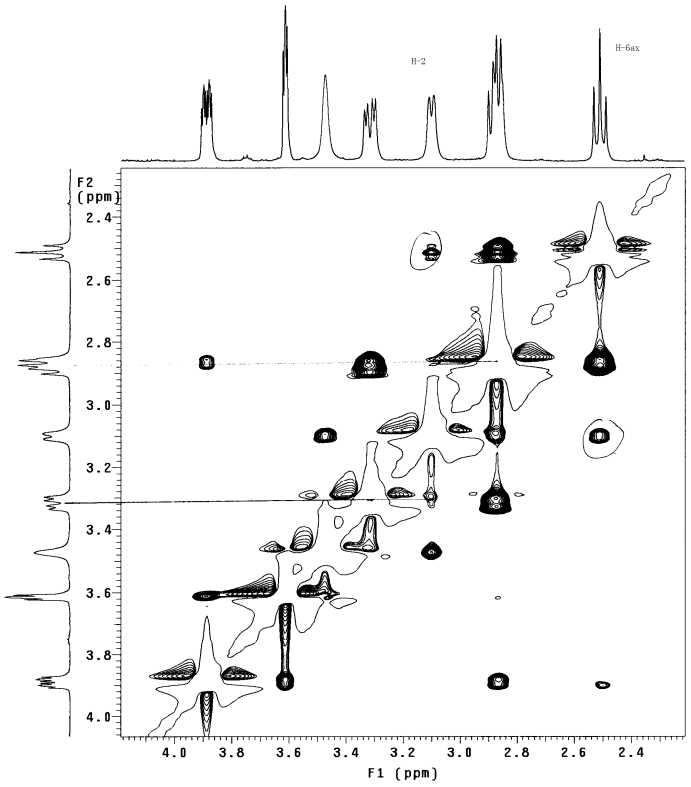
(2S,3R,4R,5R)-1-Allyl-3,4,5-tris(benzyloxy)-2-vinylpiperidine (16a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.51 (t, J = 10.5 Hz, 1H, H-6ax), 2.84-2.91 (m, 2H, H-6eq, NCH_2), 3.09 (d, J = 8.7 Hz, 1H, H-2), 3.32 (dd, J = 5.7 Hz, J = 13.8 Hz, 1H, NCH_2), 3.47 (br.s, 1H, H-3), 3.61 (t, J = 3.3 Hz, 1H, H-4), 3.86-3.90 (m, 1H, H-5), 4.34-4.67 (m, 6H, $PhCH_2$), 5.12-5.21 (m, 4H, $=CH_2$), 5.83-6.00 (m, 2H, -CH=), 7.17-7.32 (m, 15H, Ar). Proton NMR assignment was proceeded by analysis of COSY and other 2D NMR spectra. The axial orientations of H_{6ax} and H_2 were also proved by the NOESY spectrum which showed their intimacy in geometry.



16a

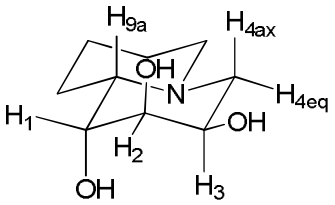


COSY spectra of **16a**

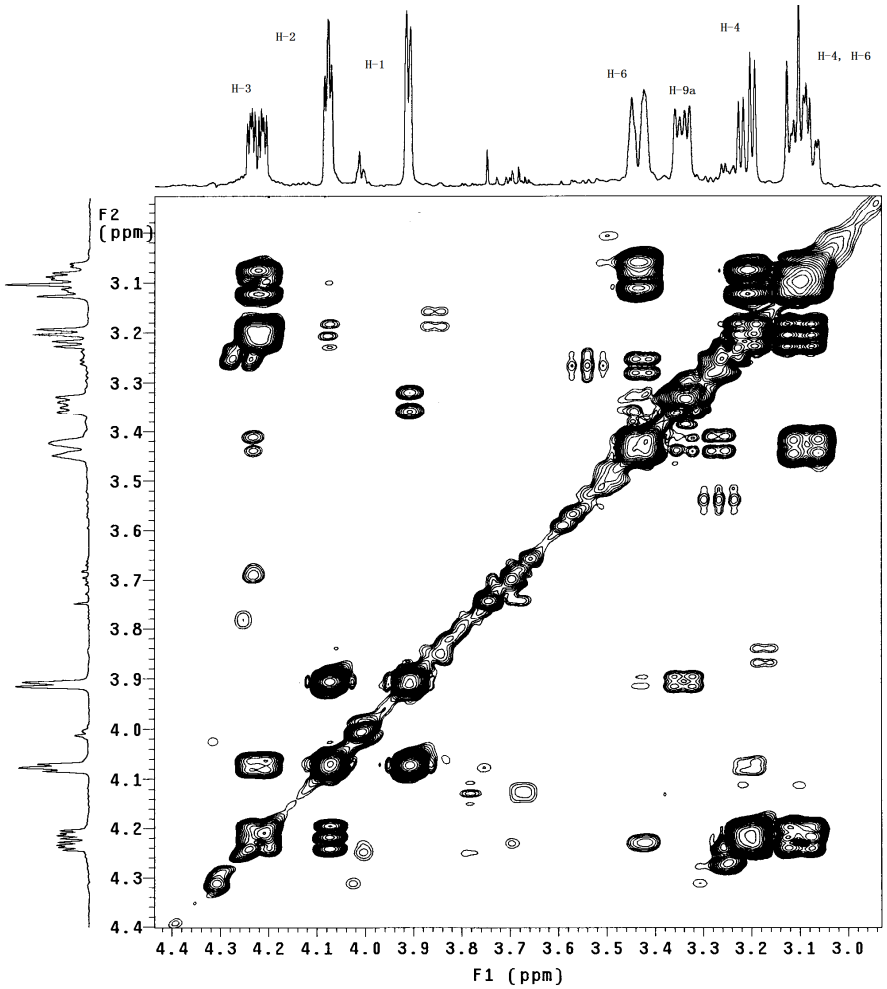


NOESY spectra of **16a**

(1R,2R,3R,9aS)-Octahydro-1H-quinolizine-1,2,3-triol (18b). ^{1}H NMR (500 MHz, D_2O) δ 1.57-1.82 (m, 4H, H-7, H-8, H-9), 1.91-1.94 (m, 2H, H-7, H-8), 3.06-3.13 (m, 2H, H-4, H-6), 3.21 (dd, J = 5.0 Hz, J = 12.0 Hz, 1H, H-4), 3.34 (dd, J = 5.0 Hz, J = 10.0 Hz, 1H, H-9a), 3.42-3.45 (m, 1H, H-6), 3.91 (d, J = 4.0 Hz, 1H, H-1), 4.08 (t, J = 3.5 Hz, 1H, H-2), 4.22 (ddd, J = 3.0 Hz, J = 5.0 Hz, J = 12.0 Hz, 1H, H-3). Proton NMR assignment was proceeded by analysis of COSY and other 2D NMR spectra.



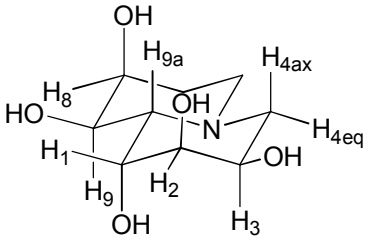
18b



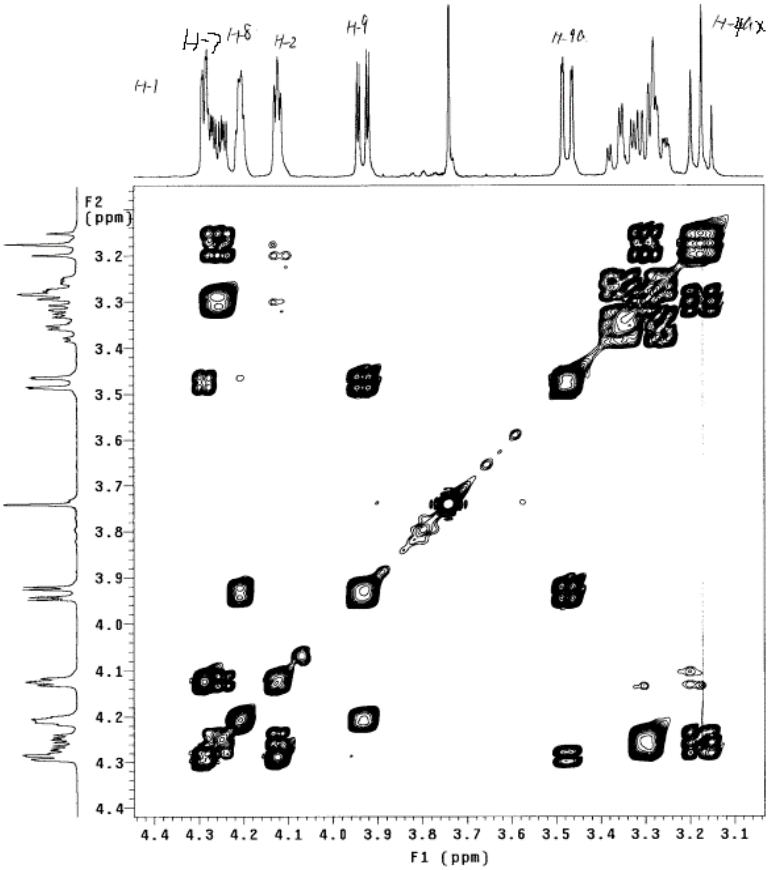
COSY spectra of **18b**

(1R,2R,3R,8S,9R,9aS)-Octahydro-1H-quinolizine-1,2,3,8,9-pentaol (20). ^{1}H NMR (500 MHz, D_2O) δ 1.93-2.08 (m, 2H, H-7), 3.18 (t, J = 12.0 Hz, 1H, H-4ax), 3.25-3.38 (m, 3H, H-4eq, H-6), 3.47 (dd, J = 1.5 Hz, J =10.5 Hz, 1H, H-9a), 3.93 (dd, J = 3.0 Hz, J = 10.5 Hz, 1H, H-9), 4.12 (t, J = 3.5 Hz, 1H, H-2), 4.21 (dd, J = 2.5 Hz, J = 6.0 Hz, 1H, H-8), 4.24-4.28 (m, 1H, H-3), 4.29 (dd, J

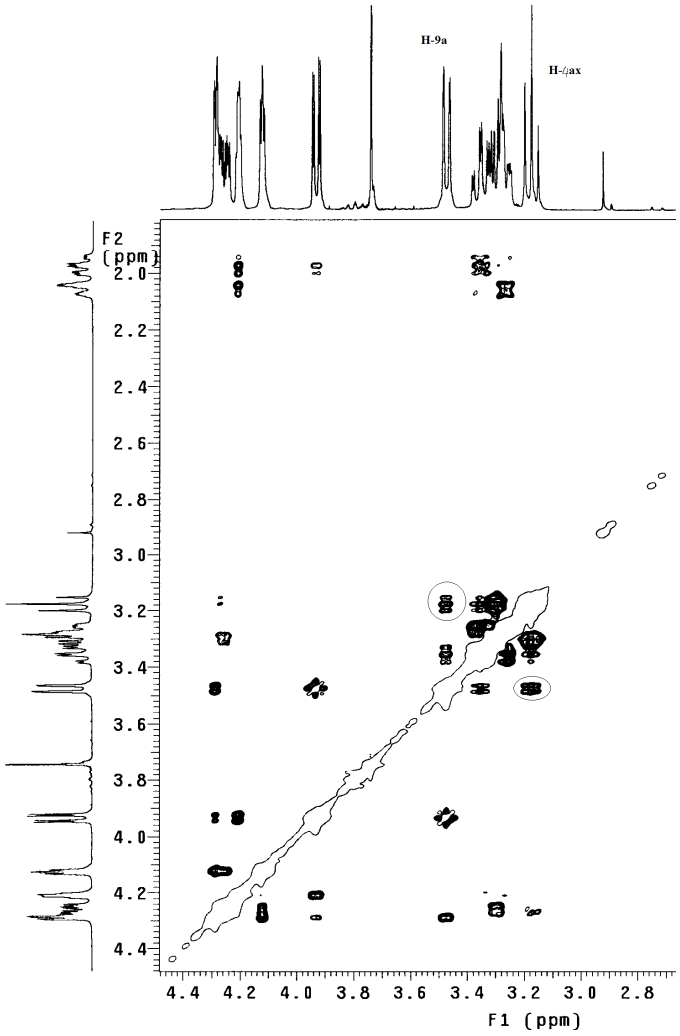
= 1.0 Hz, *J* = 4.0 Hz, 1H, H-1). Proton NMR assignment was proceeded by analysis of COSY and other 2D NMR spectra. The axial orientations of H_{4ax} and H_{9a} were also proved by the NOESY spectrum which showed their intimacy in geometry.



20



COSY spectra of **20**



NOESY spectra of **20**