Supporting Information (Part C) for

# Allenyl Azide Cycloaddition Chemistry. Exploration of the Scope and Mechanism of Cyclopentennelated Dihydropyrrole Synthesis through Azatrimethylenemethane (ATMM) Intermediates.

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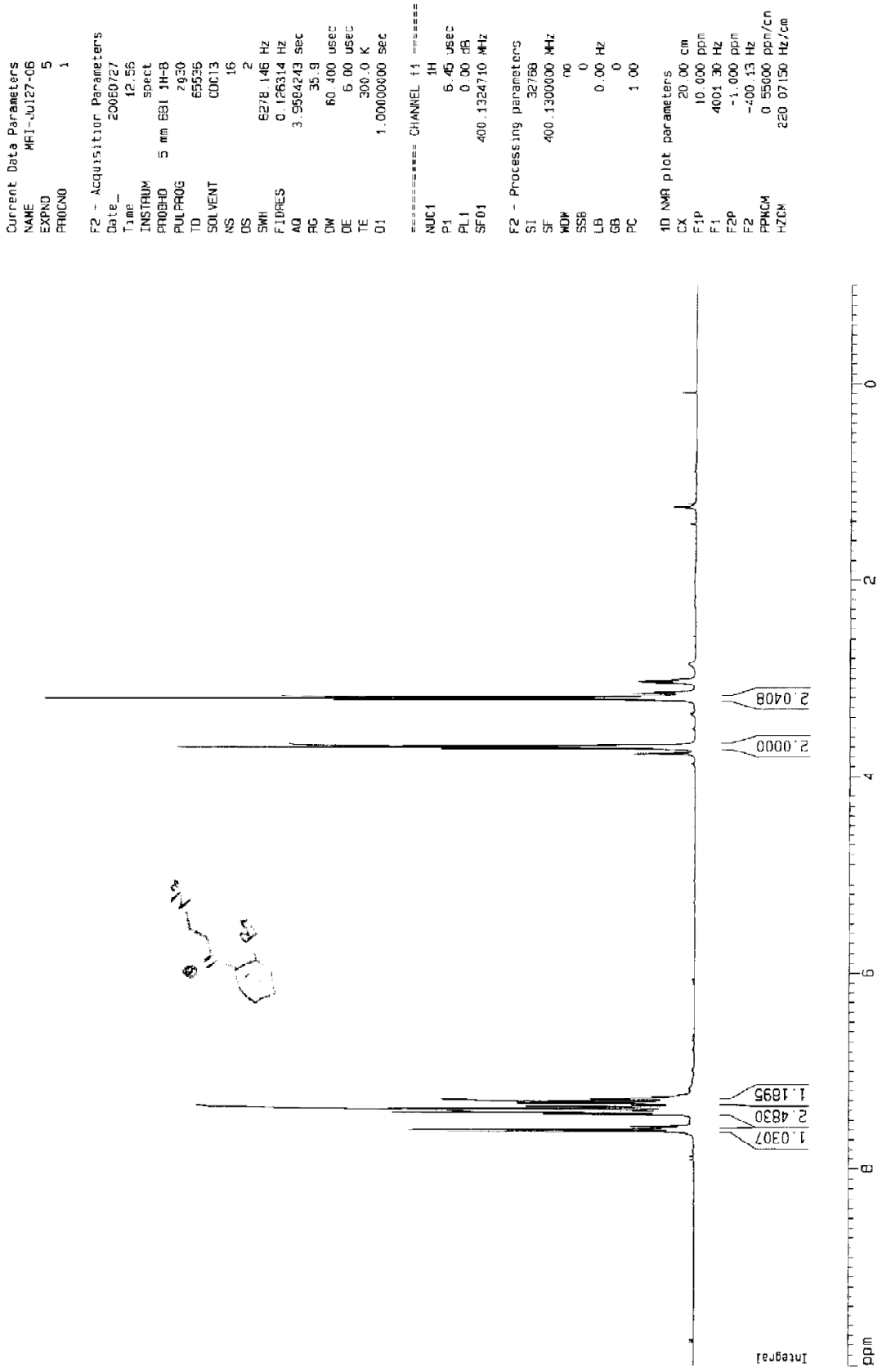
**34**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PULPROG 2g30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 35.9
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.55000 ppm/cm
HZCM 220.07150 Hz/cm
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ppm
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4
2
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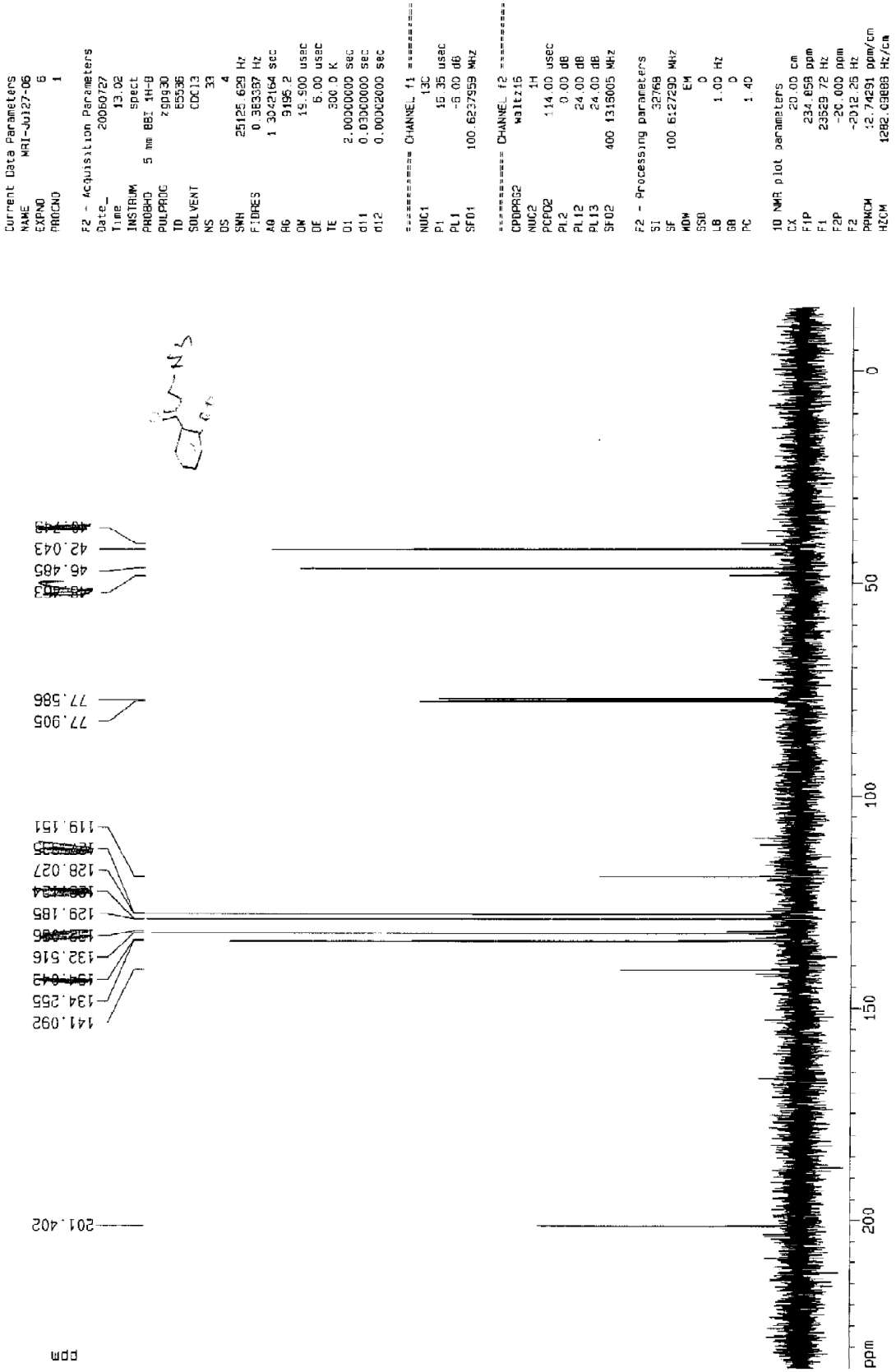
**34**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TD 65536
SOLVENT CDCl3
NS 33
DS 4
SWH 25125.629 Hz
FIDRES 0.383397 Hz
AQ 1.3042164 sec
RG 9195.2
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
NUC1 13C
P1 15.35 usec
PL1 -6.00 dB
SF01 100.6237959 MHz
CPDPRG2 waltz16
NUC2 1H
PCPD2 114.00 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SF02 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127290 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 234.658 ppm
F1 23589.72 Hz
F2P -20.000 ppm
F2 -2012.25 Hz
PPMCM 12.74291 ppm/cm
HZCM 1282.03888 Hz/cm
201.402
141.092
134.255
132.516
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ppm
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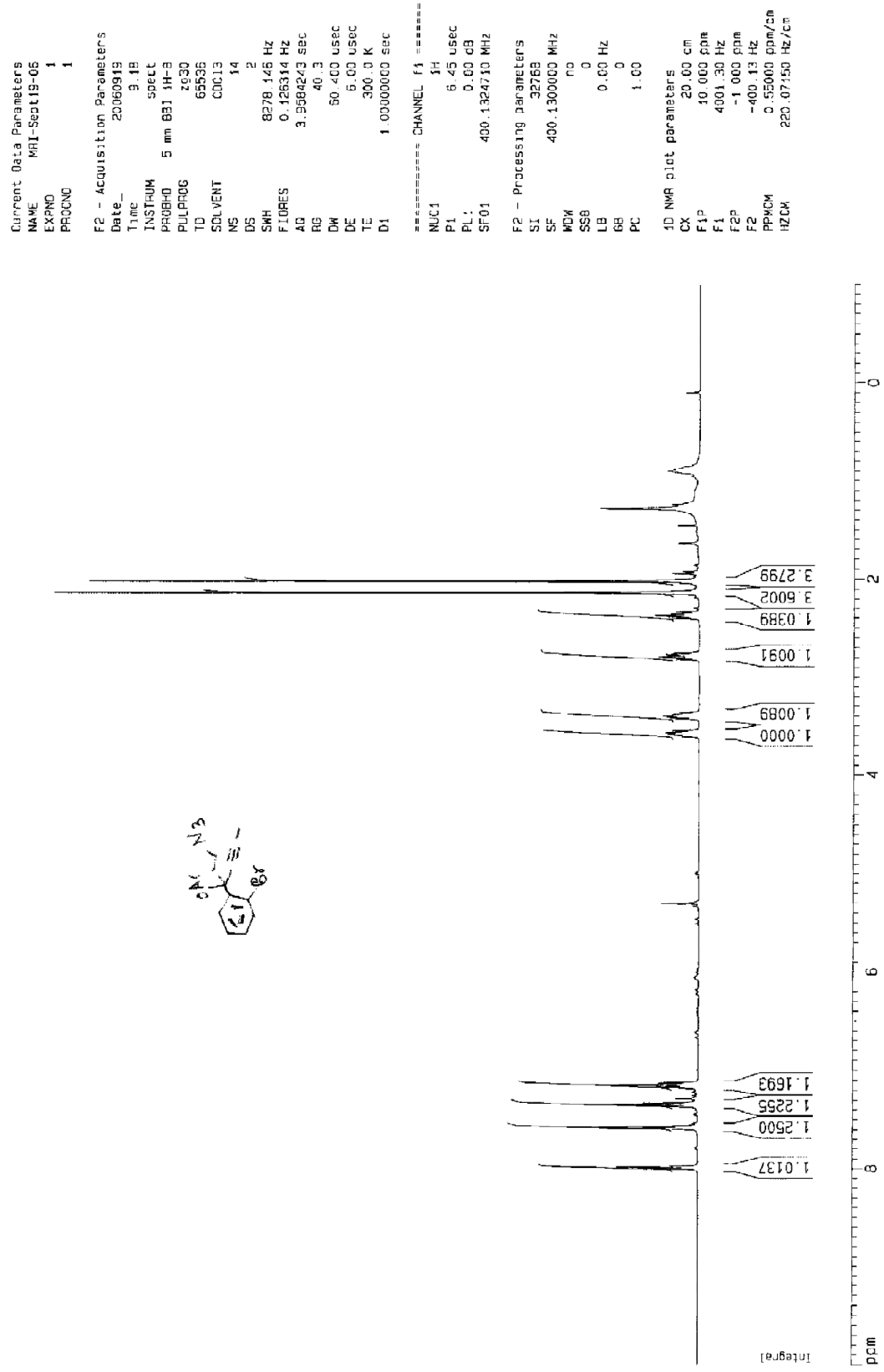
100
50
0

**35**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TD 65536
SOLVENT CDCl3
NS 14
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
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DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
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P1 6.45 usec
PL1 0.00 dB
SF01 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.55000 ppm/cm
HZCM 220.07150 Hz/cm
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3.6002
1.0389
1.0091
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1.2500
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Integral
ppm
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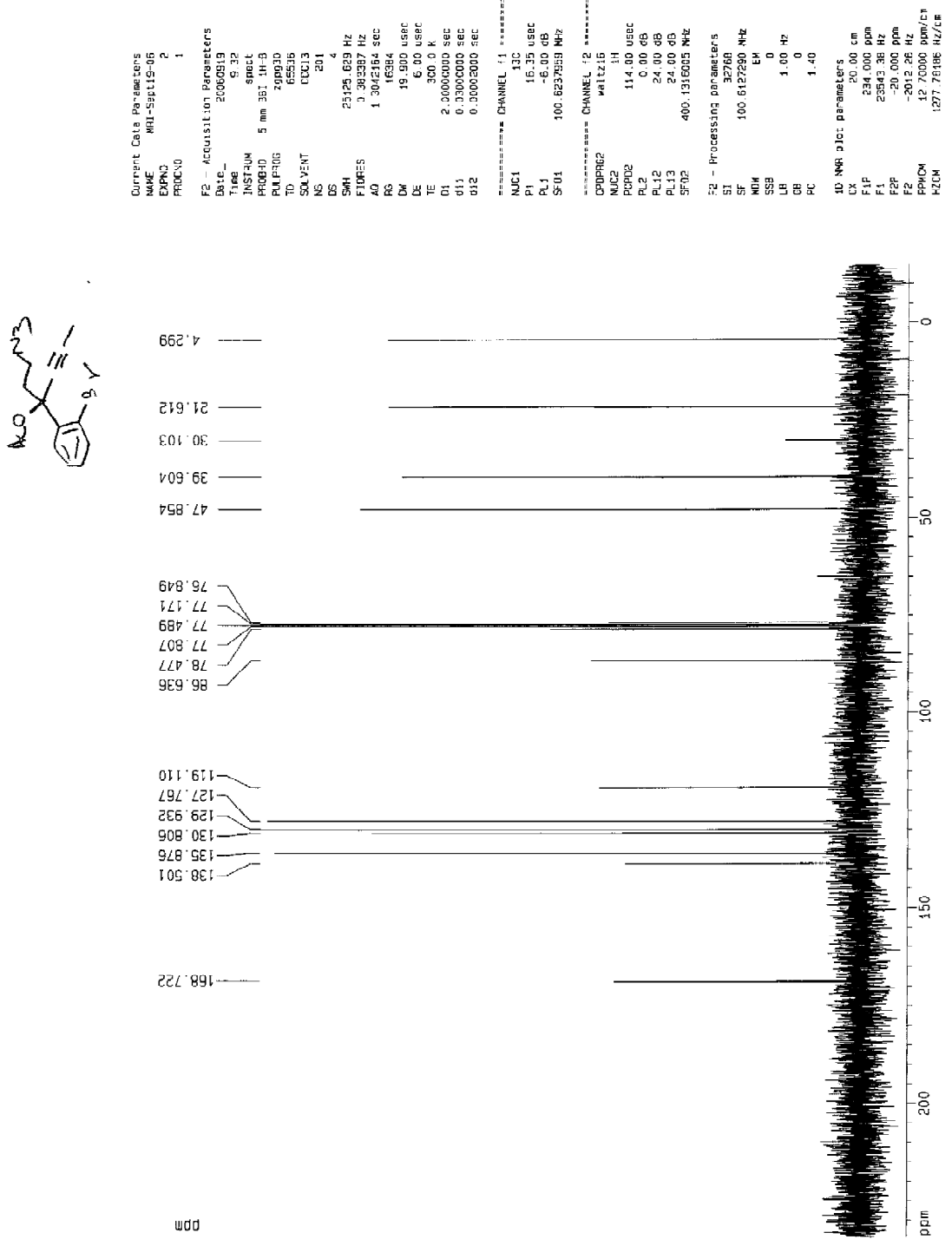
2
4
6
8

**35**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PROCNO 1
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 201
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 360.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
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NUC1 13C
P1 16.35 usec
PL1 -6.00 dB
SF01 100.6237559 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 114.00 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SF02 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127290 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 234.000 ppm
F1 23543.38 Hz
F2P -20.000 ppm
F2 -2012.26 Hz
PPMCM 12.70000 ppm/cm
HZCM 1277.78186 Hz/cm
4.299
21.612
30.103
39.604
47.854
75.849
77.174
77.489
77.807
78.477
86.636
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130.806
135.876
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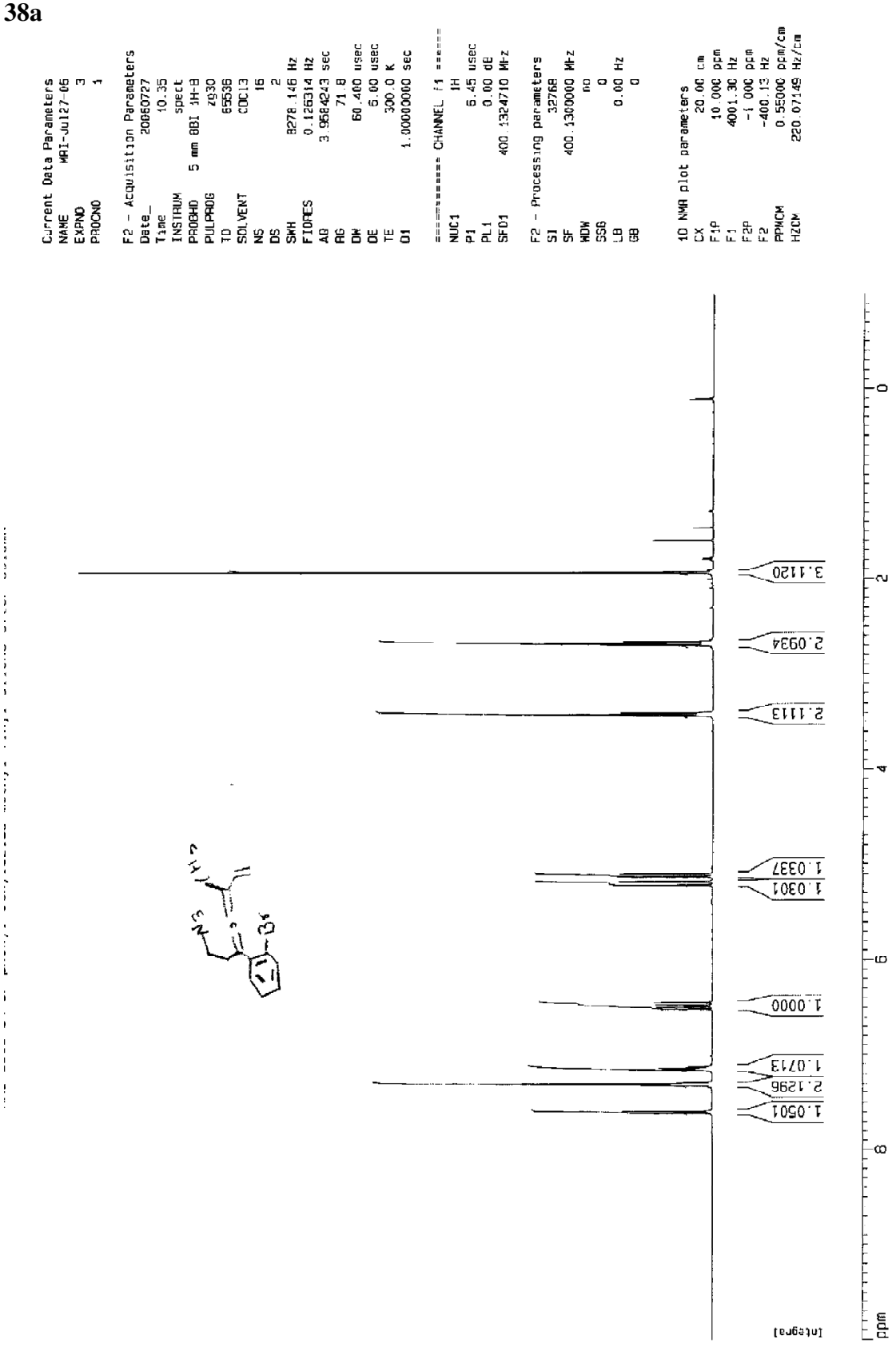
168.722
ppm
0
50
100
150
200

**38a**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PROCNO 1
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Time 10.35
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 71.8
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 5.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
10 NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.55000 ppm/cm
HZCM 220.07149 Hz/cm
3.1120
2.0934
2.1113
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1.0301
1.0000
1.0713
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integral
ppm
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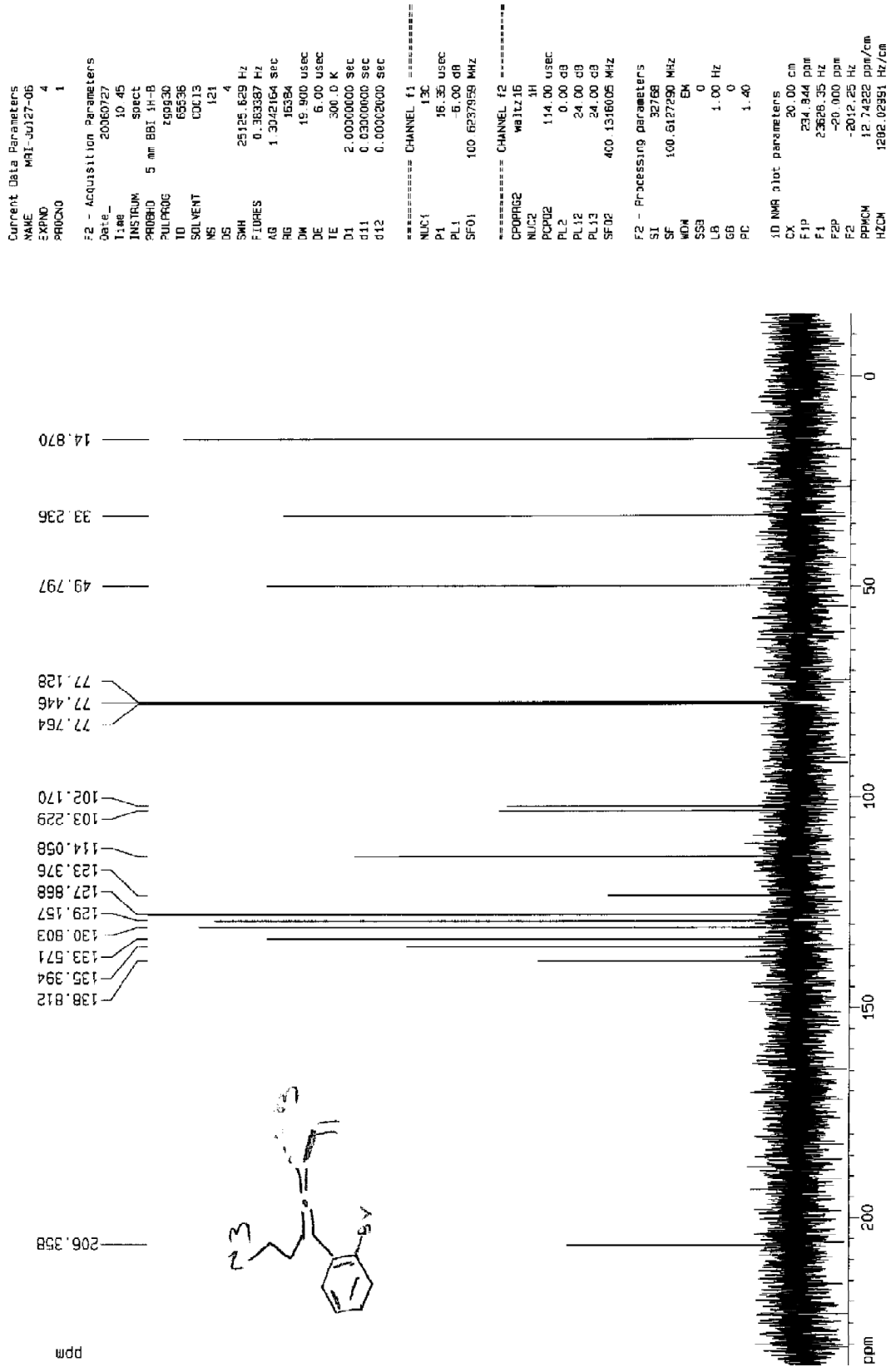
2
4
6
8

**38a**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EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
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Time 10.45
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 121
DS 4
SWH 25125.629 Hz
FIDRES 0.383387 Hz
AQ 1.3042164 sec
RG 16384
DW 19.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 16.35 usec
PL1 -6.00 dB
SFO1 100.6237959 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 114.00 usec
PL2 0.00 dB
PL12 24.00 dB
PL13 24.00 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127290 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 234.944 ppm
F1 23628.35 Hz
F2P -20.000 ppm
F2 -2012.25 Hz
PPMCM 12.74222 ppm/cm
HZCM 1282.02991 Hz/cm
14.870
33.236
49.797
77.128
77.446
77.764
102.170
103.229
114.058
123.376
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130.803
133.571
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ppm
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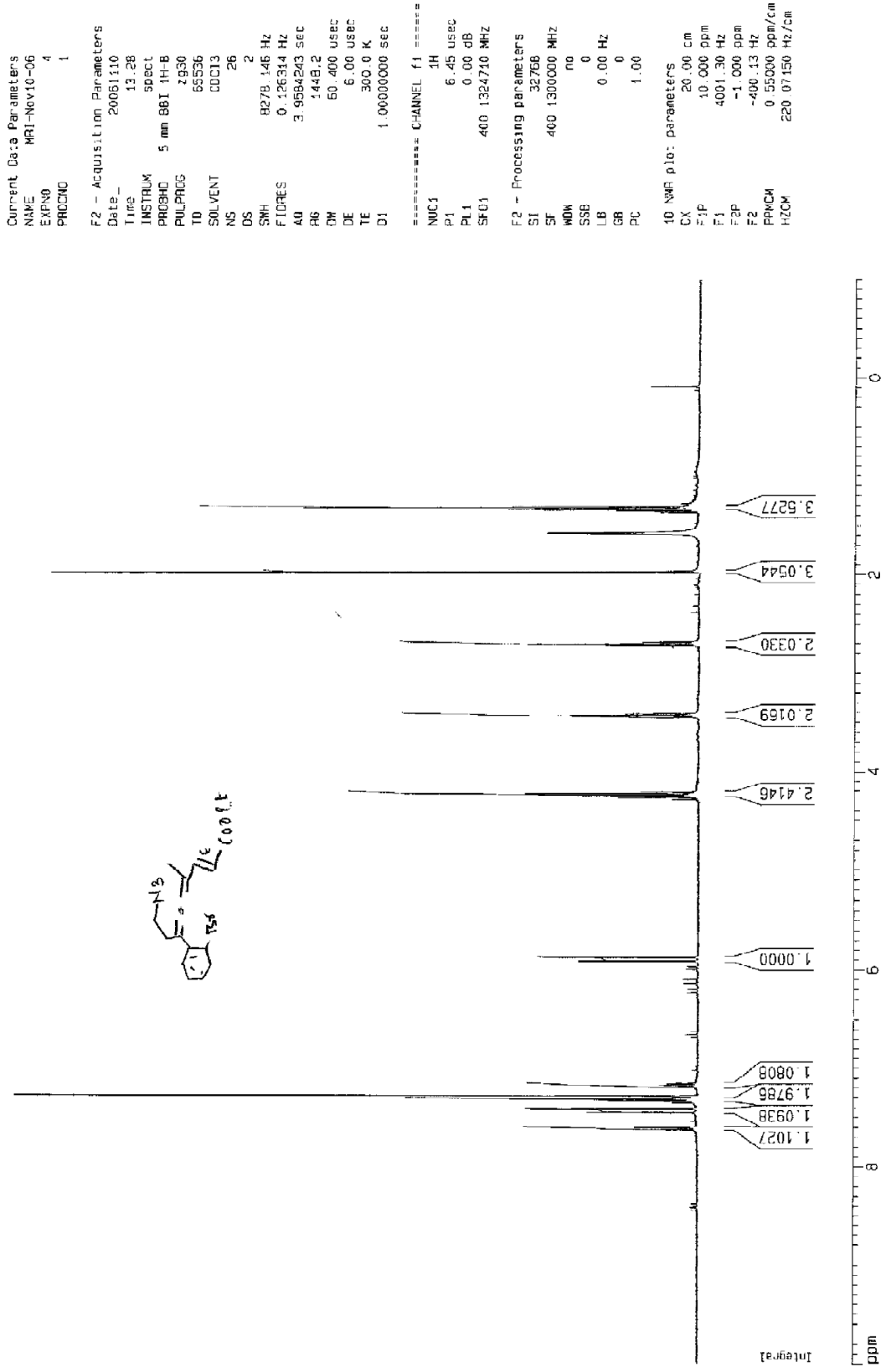
100
150
200

**38b**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PROCNO 1
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Time 13.28
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 26
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 1448.2
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.55000 ppm/cm
HZCM 220.07150 Hz/cm
3.5277
3.0544
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2.4146
1.0000
1.0808
1.9786
1.0938
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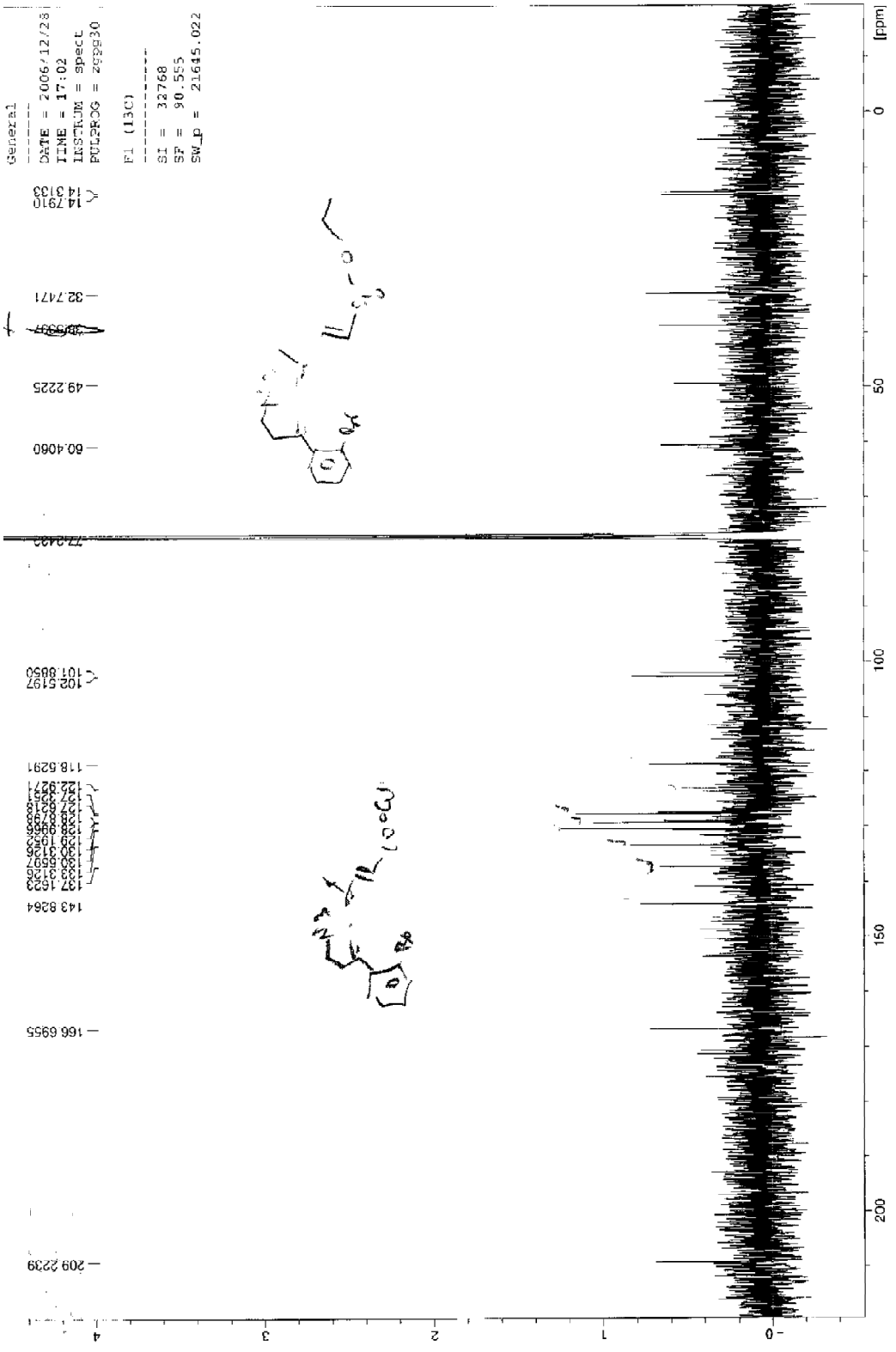
Integral
ppm

**38b**


General
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TIME = 17:02
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PULPROG = zgpg30
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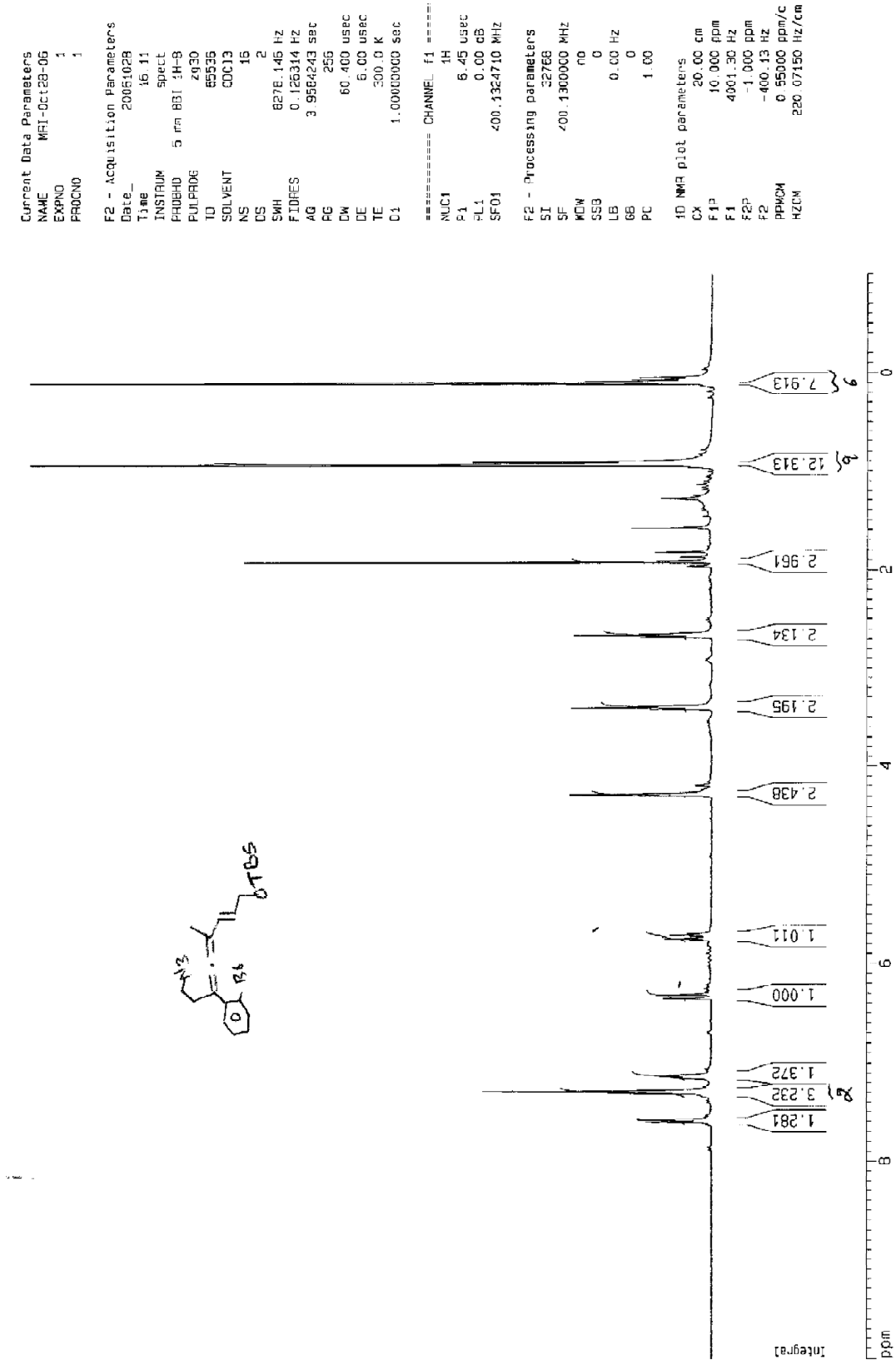
SW_p = 21645.022
[ppm]

**38c**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EXPNO 1
PROCNO 1
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Time 16.11
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9564243 sec
RG 256
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.55000 ppm/c
HZCM 220.07150 Hz/cm
7.913
12.313
2.961
2.134
2.195
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1.011
1.000
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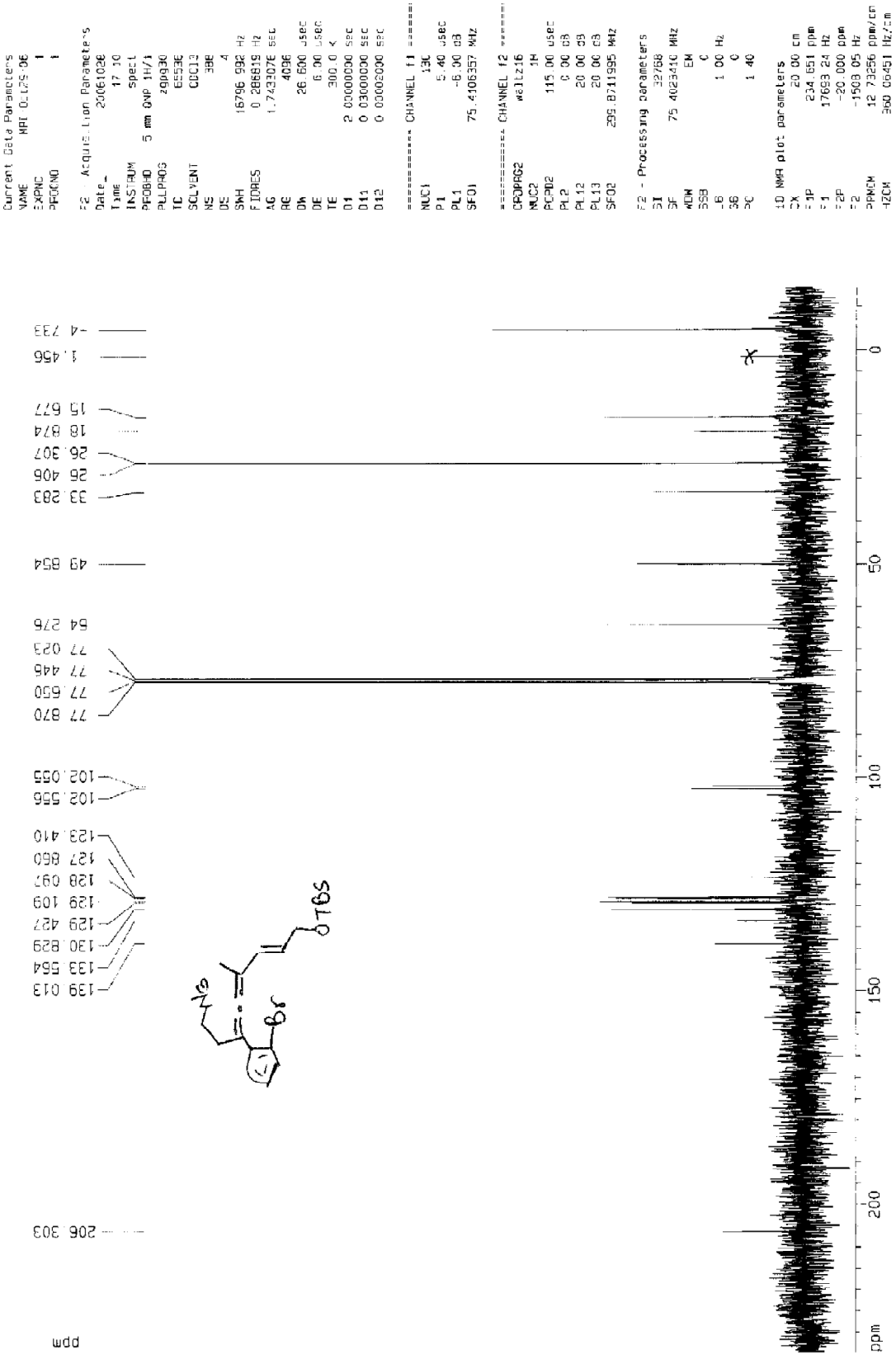
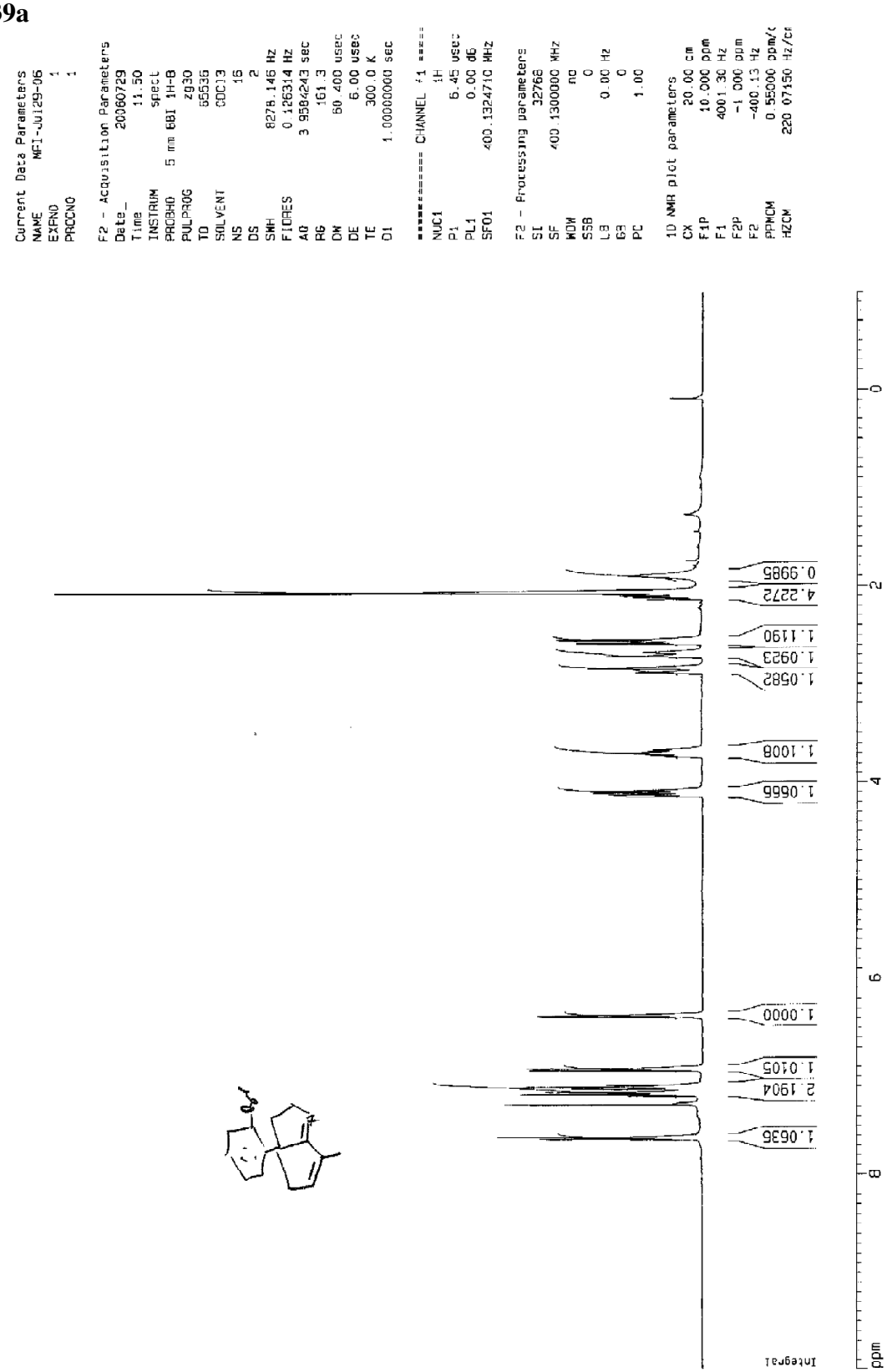
3.232
1.281
Integral
ppm
OTBS
Me
Bn

**38c**



**39a**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F2 - Acquisition Parameters
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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 161.3
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
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NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.55000 ppm/c
HZCM 220.07150 Hz/cm
0.9985
4.2272
1.1190
1.0923
1.0582
1.1008
1.0666
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Integral
ppm
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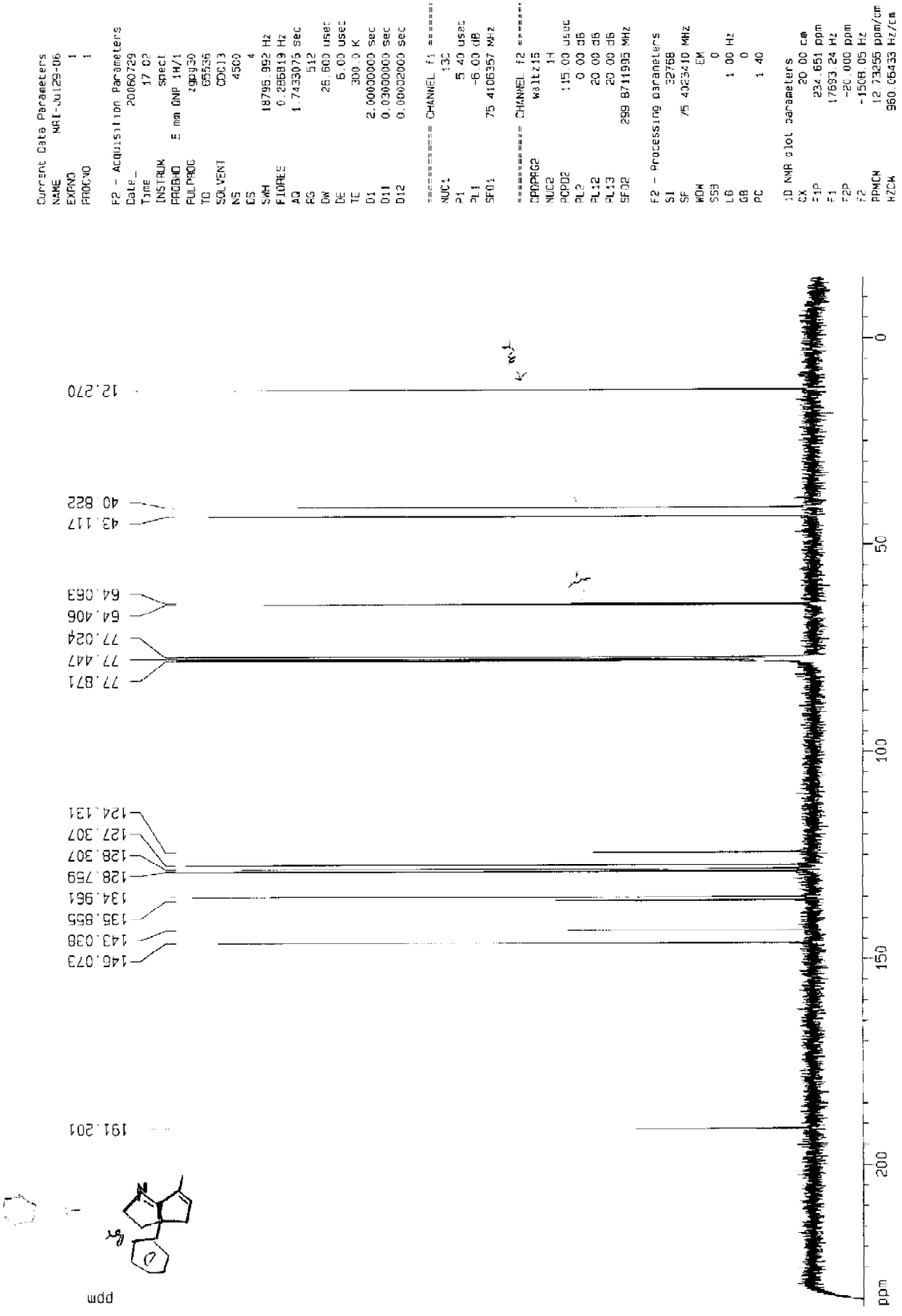
2
4
6
8

**39a**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TD 65536
SOLVENT CDCl3
NS 4500
DS 4
SWH 18796.992 Hz
FIDRES 0.286819 Hz
AQ 1.7433075 sec
RG 512
DW 26.600 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000003 sec
D11 0.03000000 sec
D12 0.00002000 sec
CHANNEL f1
NUC1 13C
P1 5.40 usec
PL1 -6.00 dB
SFO1 75.4106357 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 115.00 usec
PL2 0.00 dB
PL12 20.00 dB
PL13 20.00 dB
SFO2 299.8711995 MHz
F2 - Processing parameters
SI 32768
SF 75.4023410 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 234.651 ppm
F1 17693.24 Hz
F2P -20.000 ppm
F2 -1508.05 Hz
PPMCM 12.73255 ppm/cm
HZCM 960.06433 Hz/cm
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146.073
143.038
135.855
134.961
128.759
128.307
127.307
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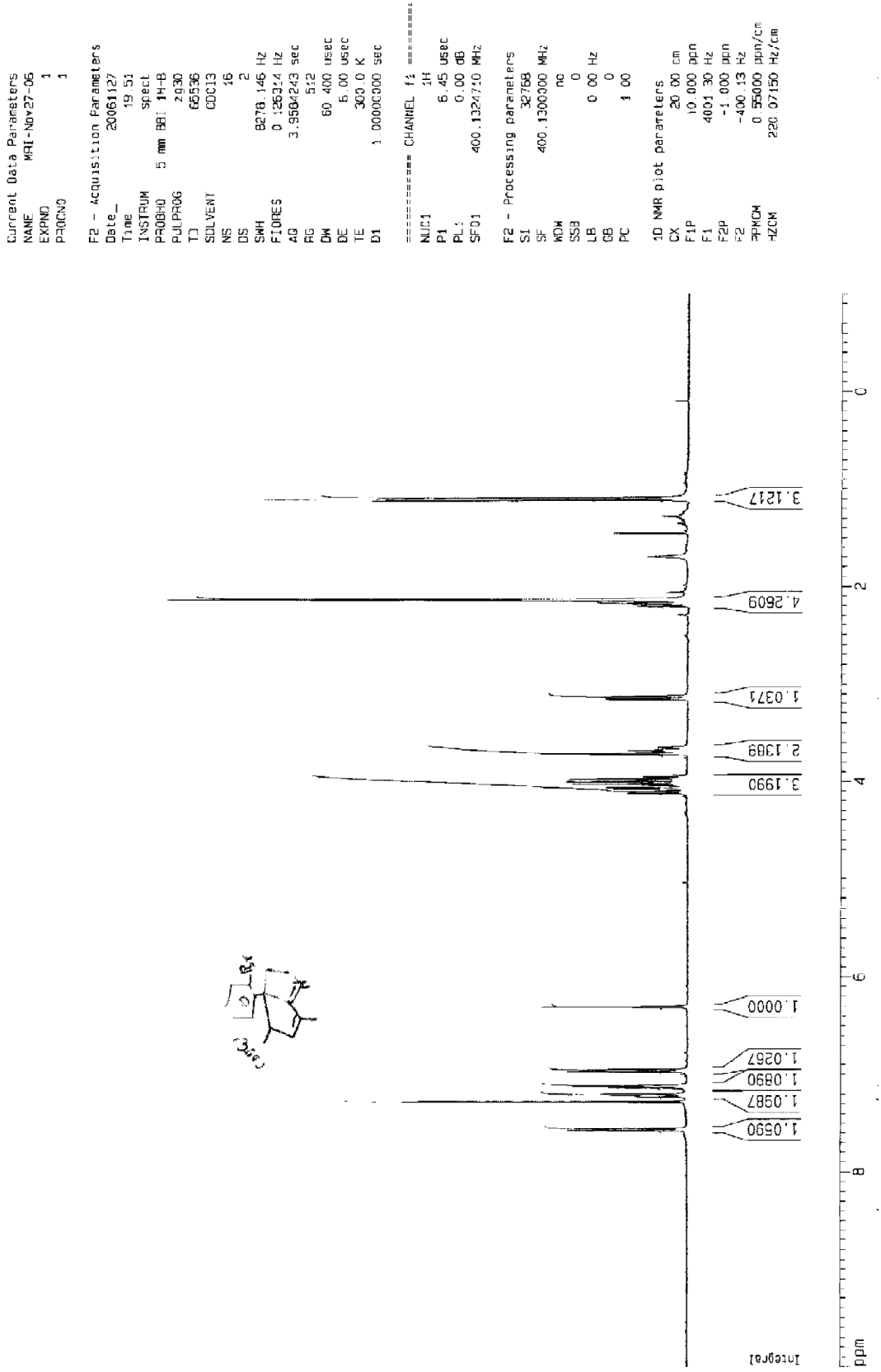
ppm

**39b**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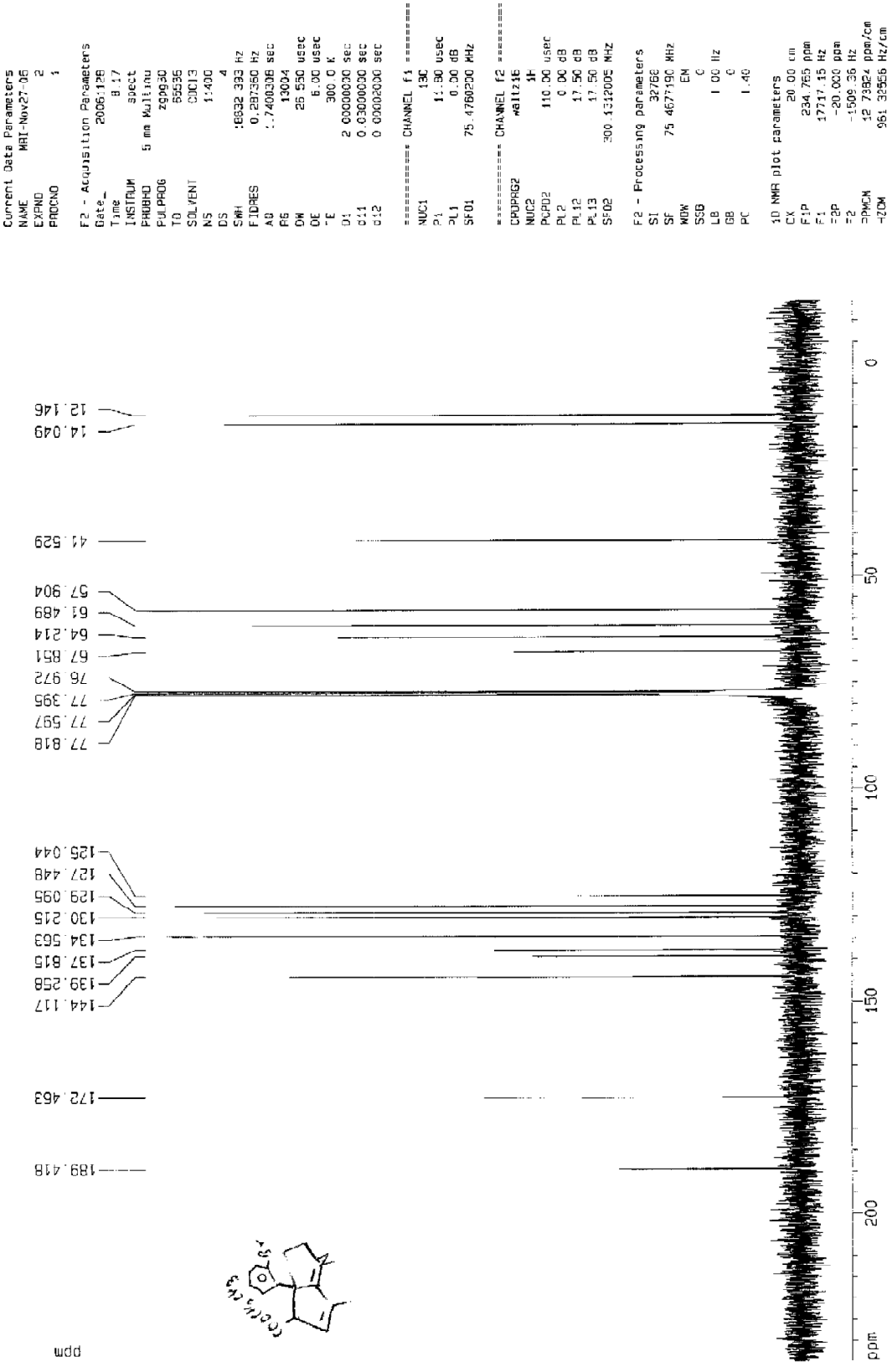
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9504243 sec
RG 512
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.55000 ppm/cm
HZCM 220.07150 Hz/cm
3.1217
4.2609
1.0371
2.1389
3.1990
1.0000
1.0287
1.0890
1.0987
1.0590
Integral
ppm
8
6
4
2
0

**39b**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PROCNO 1
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TD 65536
SOLVENT CDCl3
NS 1400
DS 4
SWH 19832.393 Hz
FIDRES 0.287360 Hz
AQ 1.7408036 sec
RG 13004
DW 25.550 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 11.90 usec
PL1 0.00 dB
SFO1 75.4760200 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 110.00 usec
PL2 0.00 dB
PL12 17.50 dB
PL13 17.50 dB
SFO2 300.1312005 MHz
F2 - Processing parameters
SI 32768
SF 75.4677190 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 20.00 cm
F1P 234.765 ppm
F1 17717.15 Hz
F2P -20.000 ppm
F2 -1509.36 Hz
PPMCM 12.73824 ppm/cm
HZCM 961.38556 Hz/cm
12.146
14.049
41.529
57.904
61.489
64.214
67.851
76.972
77.395
77.597
77.818
125.044
127.448
129.095
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137.815
139.258
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ppm
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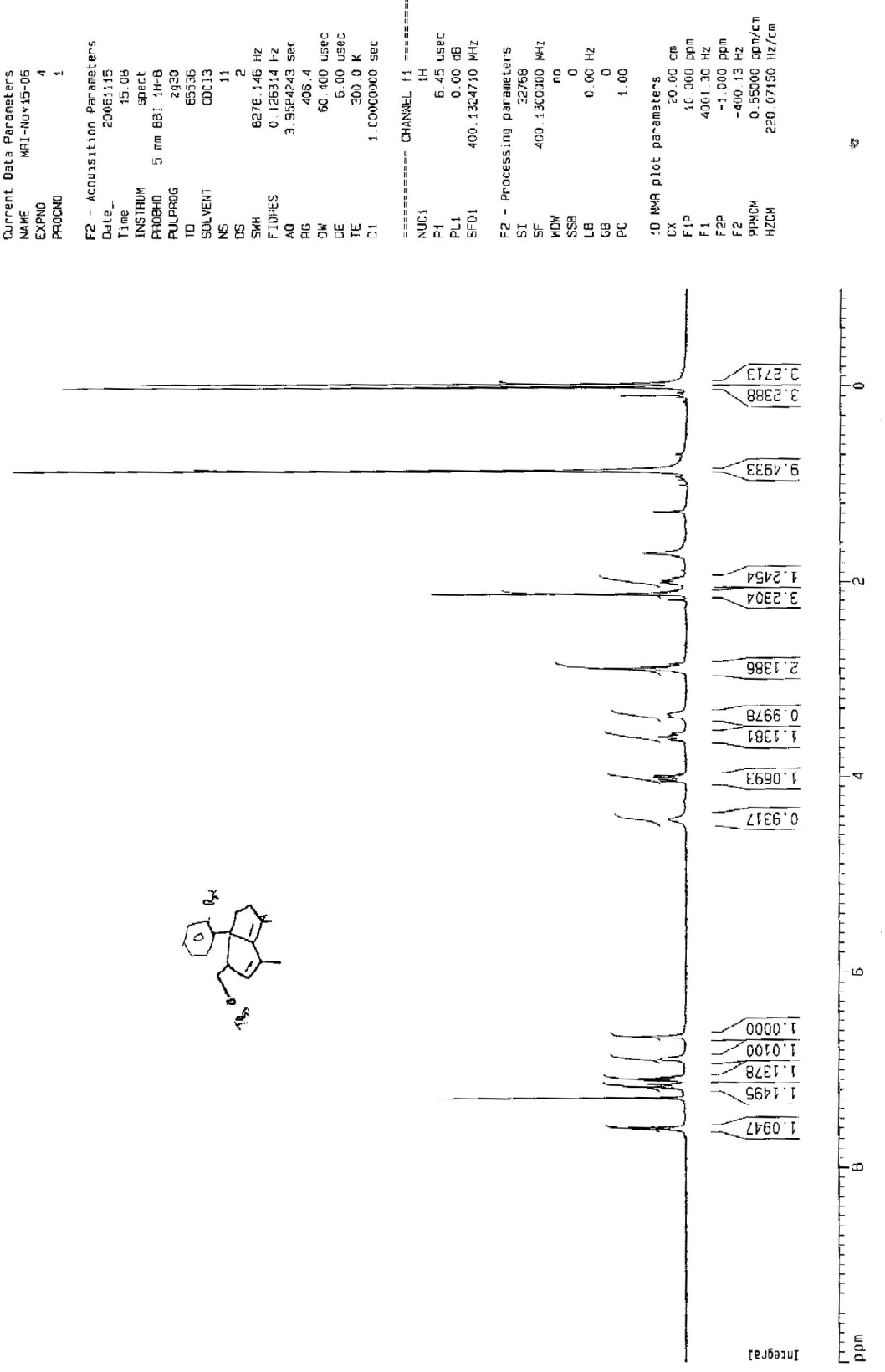
100
150
200

**39c**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EXPNO 4
PROCNO 1
F2 - Acquisition Parameters
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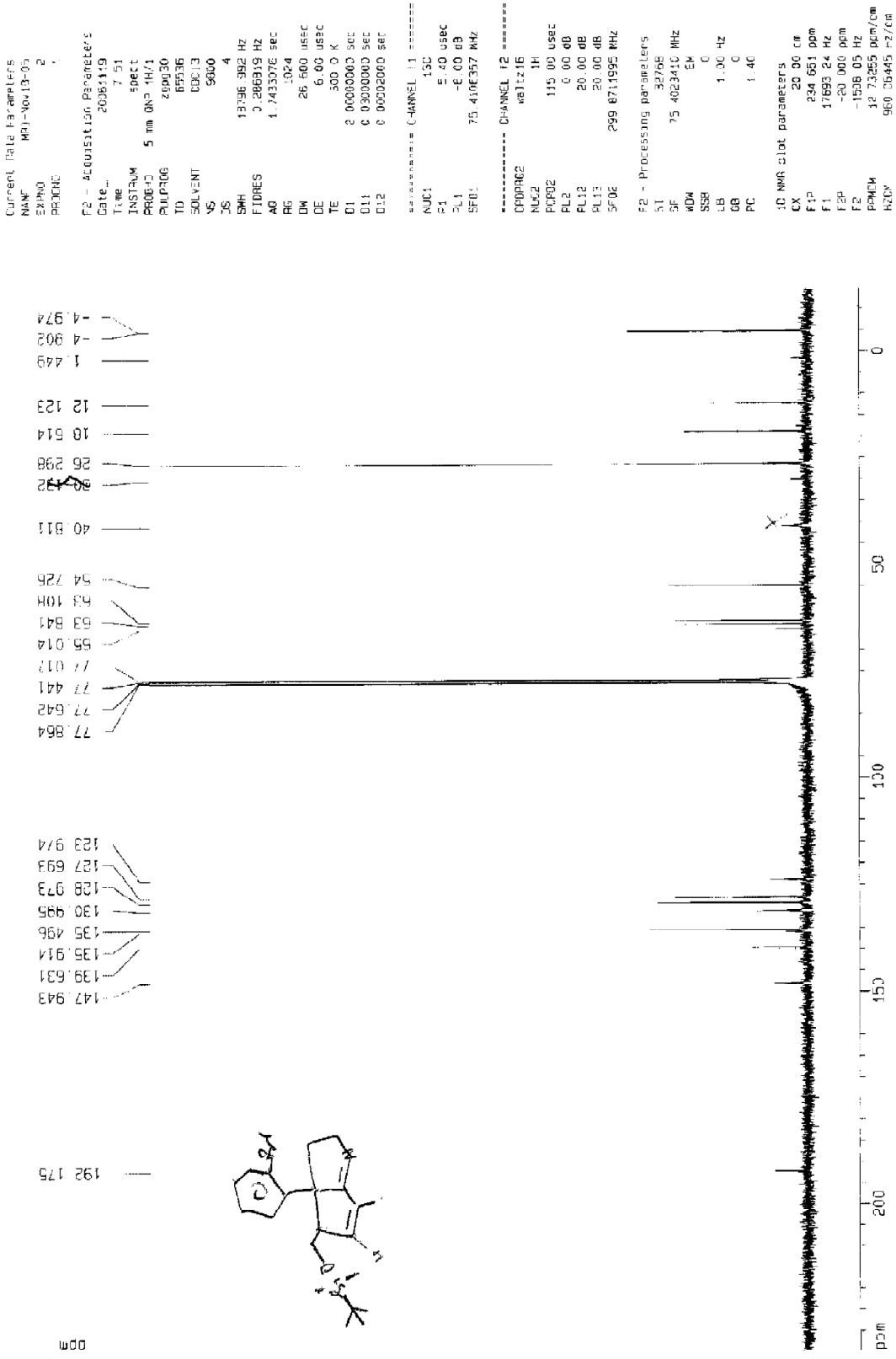
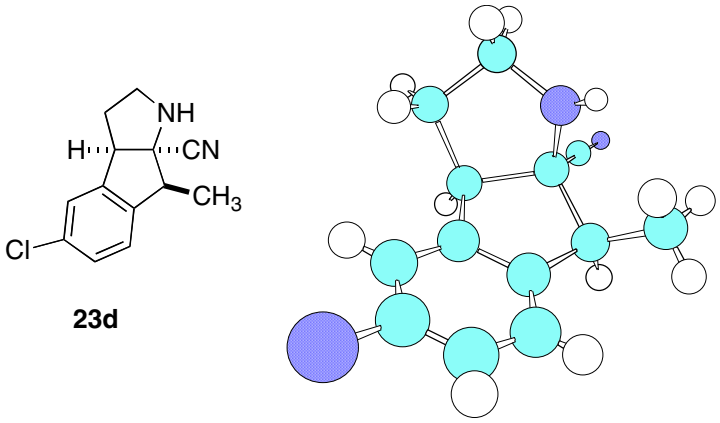
Time 15.08
INSTRUM spect
PROBHD 5 mm BBI 1H-B
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 11
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 406.4
DW 60.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 6.45 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 20.00 cm
F1P 10.000 ppm
F1 4001.30 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.35000 ppm/cm
HZCM 220.07150 Hz/cm
3.2713
3.2388
2.4933
1.2454
1.2304
1.1386
0.9978
0.9817
0.9317
1.0693
1.0000
1.0100
1.1378
1.1495
1.0947
Integral
ppm

**39c**



**X-Ray structural Determination of 23d**



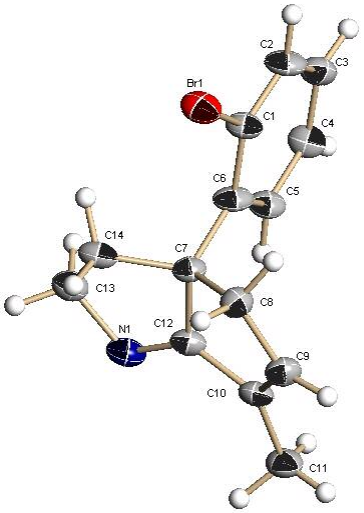

**23d**

A clear plate shaped crystal of **23d** (C13 H13 Cl N2) with approximate dimensions 0.1 x 0.17 x 0.25 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 98(2) K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073≈) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 5 seconds/frame. The total data collection time was about 4 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Monoclinic unit cell yielded a total of 7319 reflections to a maximum θ angle of 28.29° (0.90 ≈ resolution), of which 2783 were independent, completeness = 95.5 %, $R_{int}$ = 0.0290, $R_{sig}$ = 0.0322 and 2483 were greater than 2σ(I). The final cell constants: a = 9.6258(16)≈, b = 7.7123(13)≈, c = 16.200(3)≈, α = 90∞, β = 103.750(3)∞, γ = 90∞, volume = 1168.2(3)≈$^3$, are based upon the refinement of the XYZ-centroids of 4472 reflections above 20σ(I) with 2.588∞ <θ <28.289∞ . Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.927354.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P2(1)/c, with Z = 4 for the formula unit, C13 H13 Cl N2. The final anisotropic full-matrix least-squares refinement on $F^2$ with 146 variables converged at R1 = 5.03 %, for the observed data and wR2 = 12.77 % for all data. The goodness-of-fit was 1.079. The largest peak on the final difference map was 0.690 $e^-/\approx^3$ and the largest hole was -0.677 $e^-/\approx^3$. Based on the final model, the calculated density of the crystal is 1.323 $g/cm^3$ and F(000) amounts to 488 electrons.

**X-Ray Structural Determination of 39a.**




A colorless block shaped crystal of **39a** ($C_{14}H_{14}BrN$) with approximate dimensions 0.08 x 0.09 x 0.15 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 133(2) K, cooled by Rigaku-MSC X-Stream 2000, on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a MoKα fine-focus sealed tube (λ = 0.71073Å) operated at 1600 watts power (50 kV, 32 mA). The detector was placed at a distance of 5.8 cm from the crystal.

A total of 1850 frames were collected with a scan width of 0.3º in ω and an exposure time of 10 seconds/frame. The total data collection time was about 8 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 4946 reflections to a maximum θ angle of 28.47° (0.90 Å resolution), of which 3003 were independent, completeness = 96 %, $R_{int}$ = 0.0591, $R_{sig}$ = 0.1088 and 1766 were greater than 2σ(I). The final cell constants: a = 7.433(8)Å, b = 7.991(8)Å, c = 10.455(11)Å, α = 85.140(17)°, β = 79.187(19)°, γ = 78.799(17)°, volume = 597.6(11)$Å^3$, are based upon the refinement of the XYZ-centroids of 2783 reflections above 20σ(I) with 2.843° <θ <28.24°. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using the multiscan technique (SADABS). The ratio of minimum to maximum apparent transmission was 0.0426.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group P-1, with Z = 2 for the formula unit, $C_{14}H_{14}BrN$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 146 variables converged at R1 = 6.93 %, for the observed data and wR2 = 20.91 % for all data. The goodness-of-fit was 0.987. The largest peak on the final difference map was 1.453 $e^-/Å^3$ and the largest hole was -1.009 $e^-/Å^3$. Based on the final model, the calculated density of the crystal is 1.535 $g/cm^3$ and F(000) amounts to 280 electrons.