

Supporting Information (Part A) for

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

Ken S. Feldman,^{†} Malliga R. Iyer,[†] Carlos Silva López,[§] and Olalla Nieto Faza[§]*

Department of Chemistry, The Pennsylvania State University, University Park,
Pennsylvania 16802, USA, Departamento de Química Orgánica, Universidade de Vigo,
Lagoas Marcosende, 36200, Vigo, Galicia, Spain, and Department of Chemistry,
University of Minnesota, 207 Pleasant St. SE, Minneapolis, Minnesota 55455-0431, USA

General Experimental	S2
19 ¹ H NMR	S3
19 ¹³ C NMR	S4
20a ¹ H NMR	S5
20a ¹³ C NMR	S6
20b ¹ H NMR	S7
20b ¹³ C NMR	S8
20c ¹ H NMR	S9
20c ¹³ C NMR	S10
20d ¹ H NMR	S11
20d ¹³ C NMR	S12
20e ¹ H NMR	S13
20e ¹³ C NMR	S14
23a ¹ H NMR	S15
23a ¹³ C NMR	S16
23b ¹ H NMR	S17
23b ¹³ C NMR	S18
23c ¹ H NMR	S19
23c ¹³ C NMR	S20
23d ¹ H NMR	S21
23d ¹³ C NMR	S22

General Experimental. Moisture and oxygen sensitive reactions were carried out in flame-dried glassware under an argon or nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under an argon atmosphere, or passed through an activated alumina column, immediately before use. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride (CaH_2) under an argon atmosphere, or passed through an activated alumina column, immediately before use. All organic reagents were used as purchased. Purification of products via flash chromatography was performed with 32-63 μm silica gel and the solvent systems indicated. Hexanes, EtOAc and Et_2O used in flash chromatography were distilled from CaH_2 , or passed through an activated alumina column, prior to use. Melting points are uncorrected. Low- and high-resolution mass spectra were obtained according to the specified technique and were performed at the Pennsylvania State University, University Park, PA. Copies of ^1H and ^{13}C NMR spectra are supplied in the Supporting Information as criteria of purity.

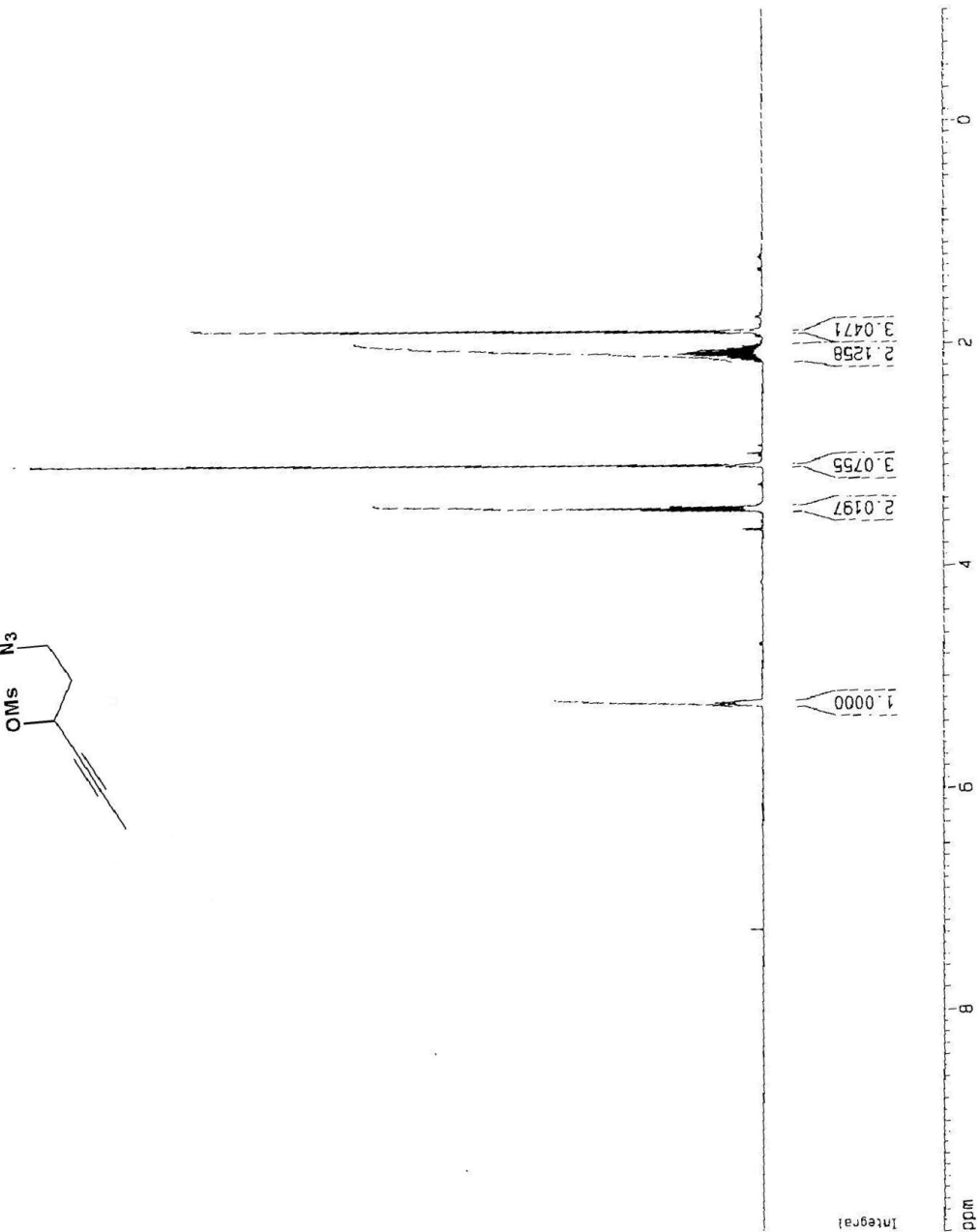
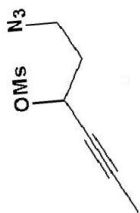
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F2 - Processing parameters
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1D NMR plot parameters
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 F2 -400.13 Hz
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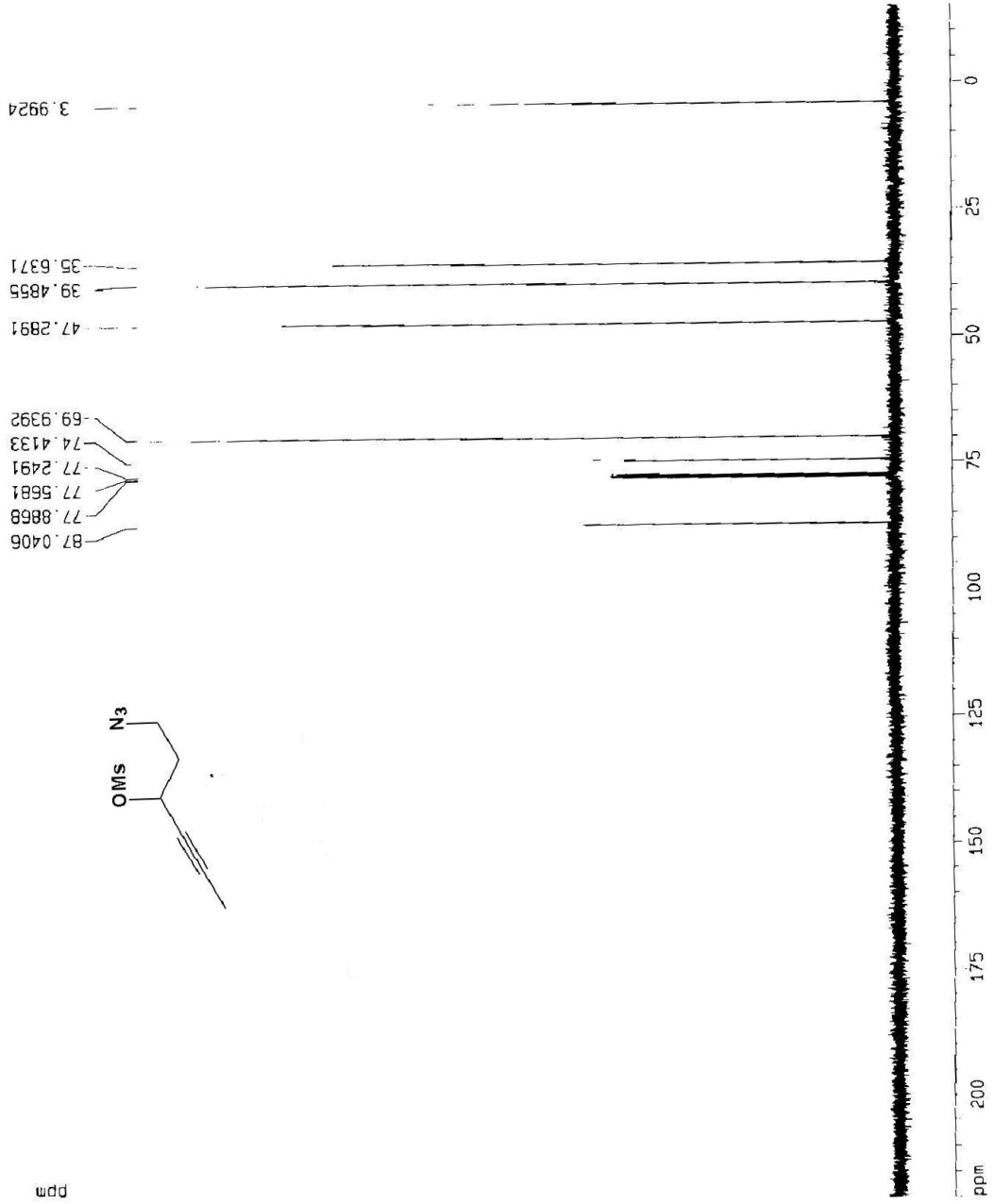
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PL13    24.00 dB
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GB       0
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F1       22134.80 Hz
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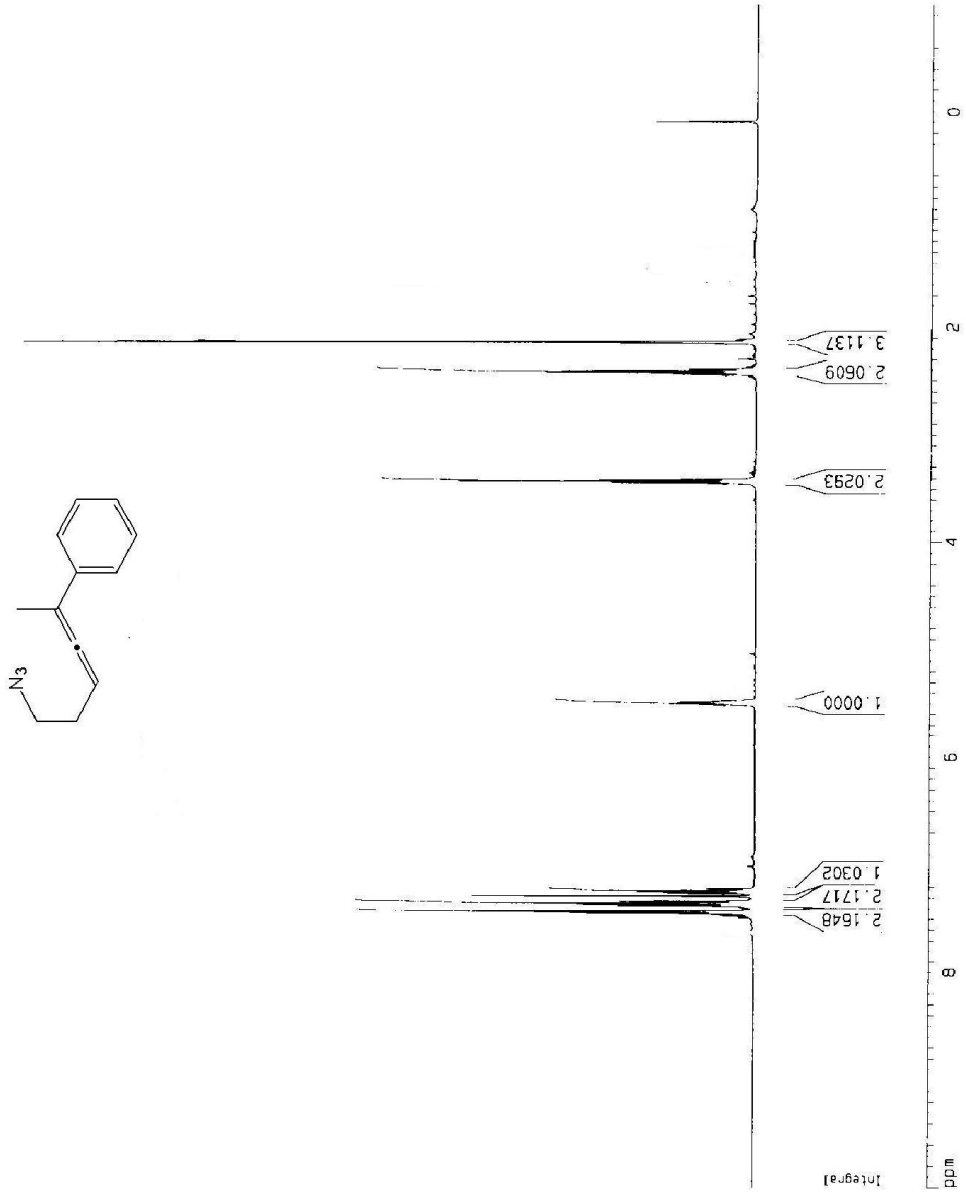
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1D NMR plot parameters
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F2      -400.13 Hz
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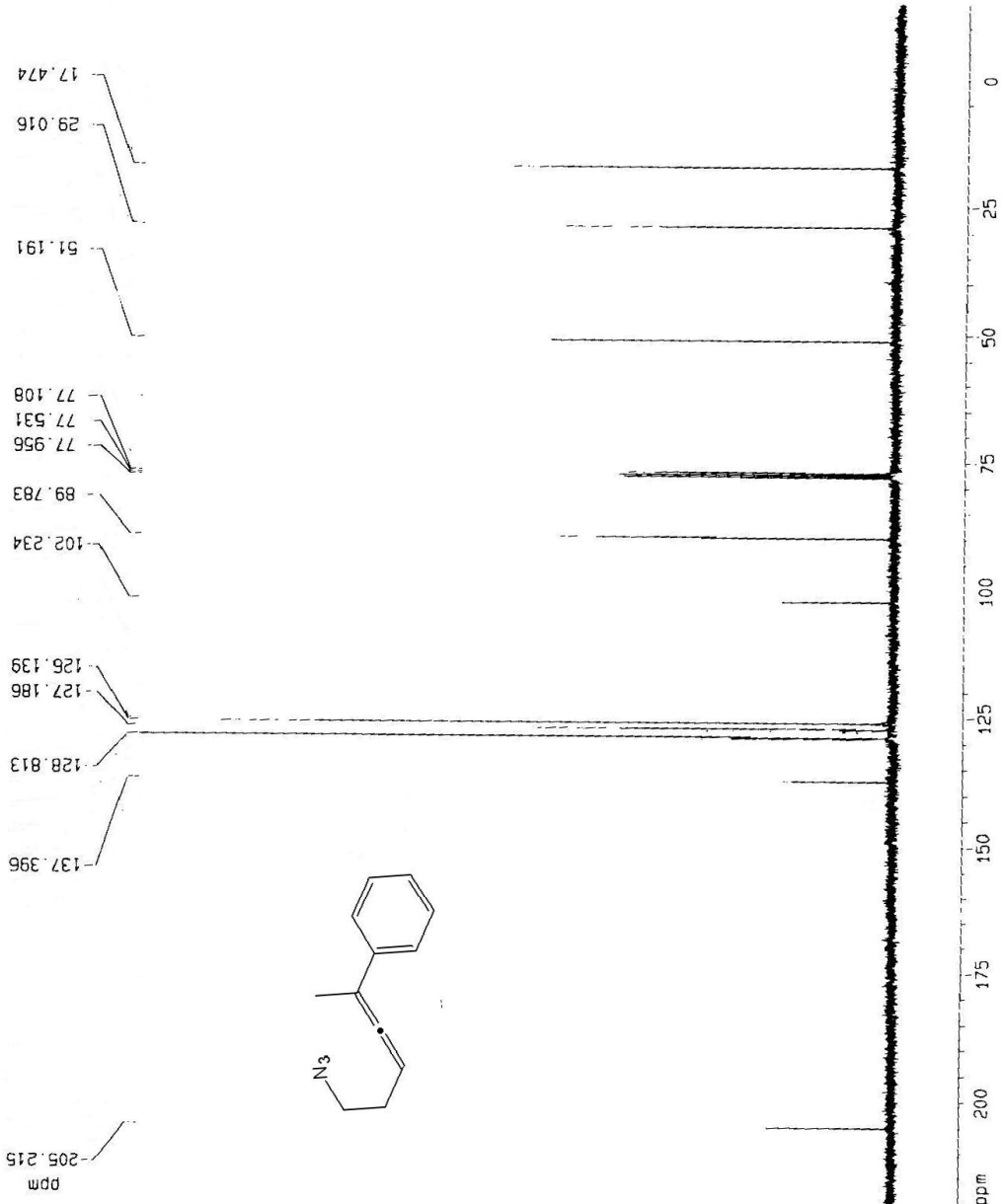
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***** CHANNEL f2 *****
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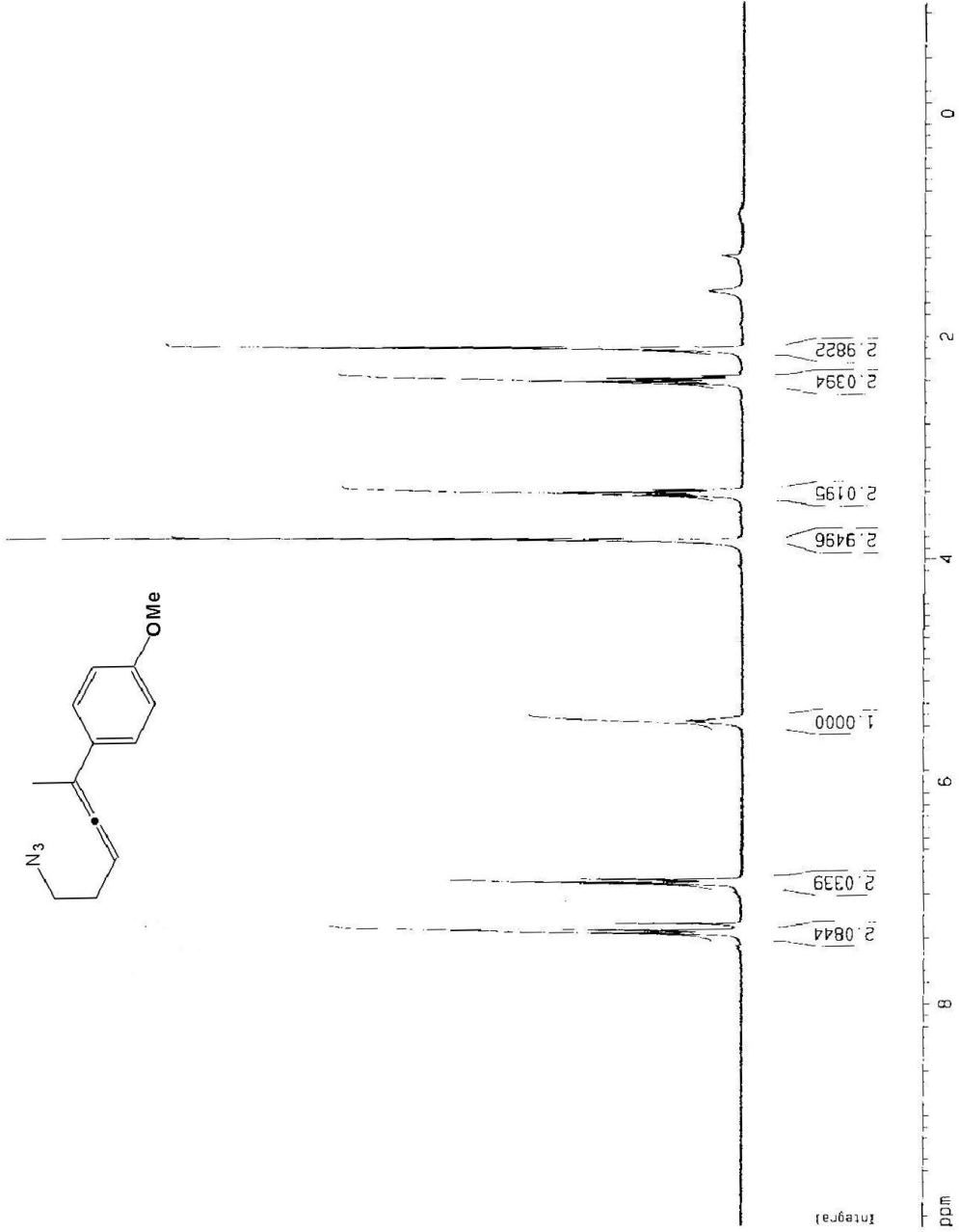
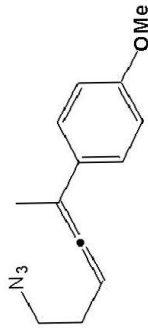
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 SOLVENT CDCl3
 NS 16
 DS 2
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 FIDRES 0.094190 Hz
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 TE 300.0 K
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 PL1 -6.00 dB
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 SF 300.1300000 MHz
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 LB 0.00 Hz
 GB 0
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1D NMR plot parameters
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 F1 3001.30 Hz
 F2P -1.000 ppm
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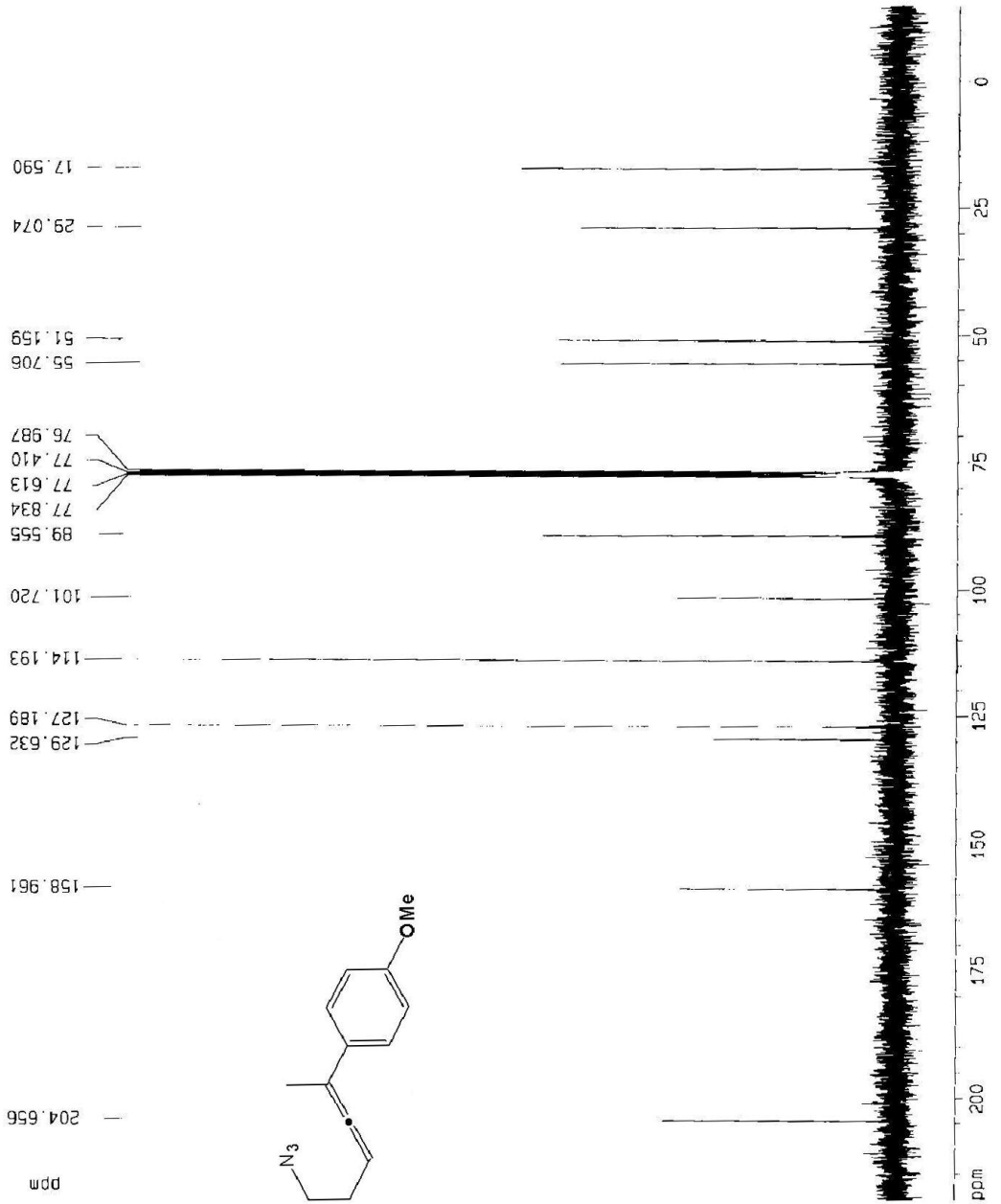
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 DS 4
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 DE 5.00 usec
 TE 300.0 K
 D1 2.0000000 sec
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 D12 0.0002000 sec

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 PL13 18.00 dB
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1D NMR plot parameters
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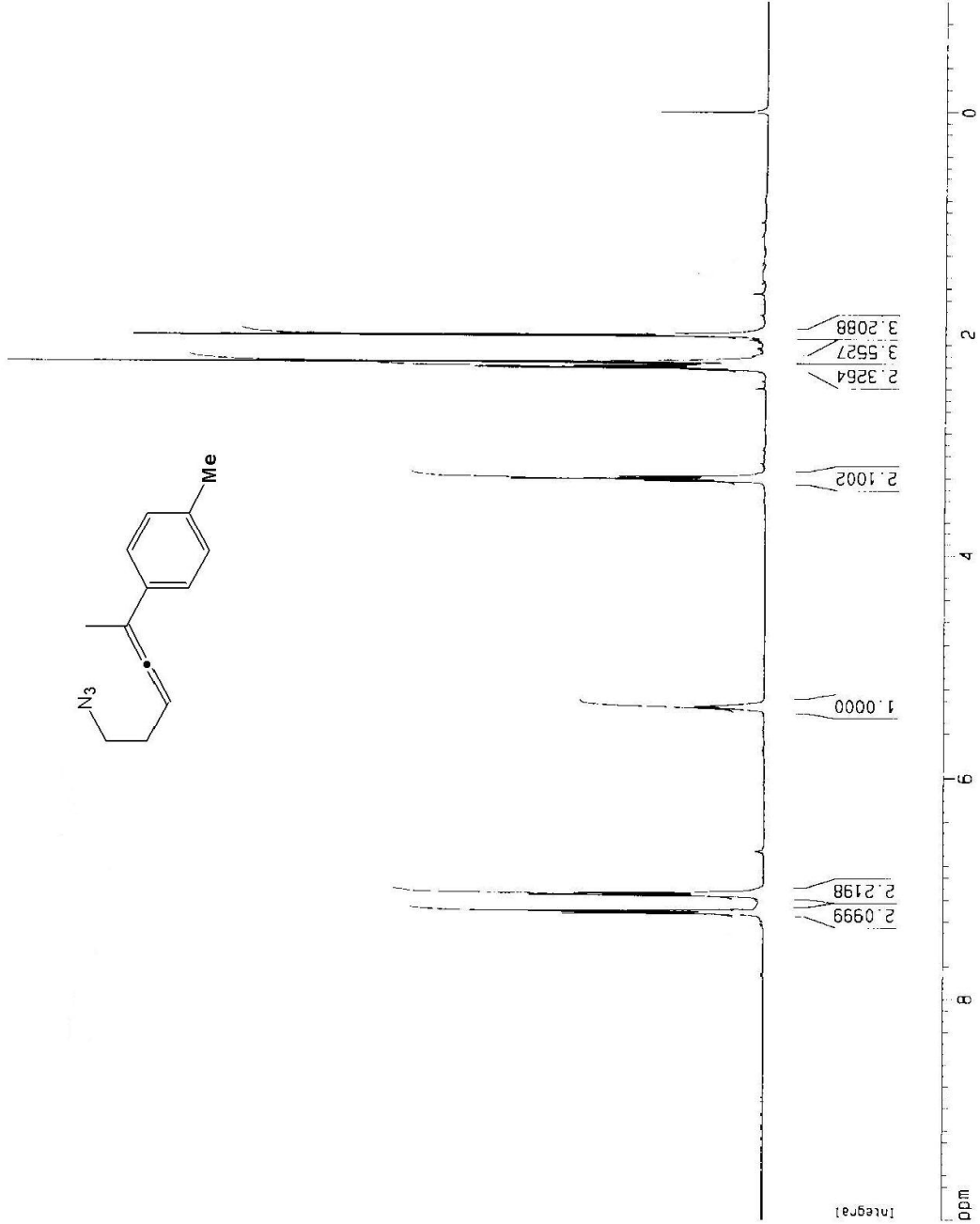
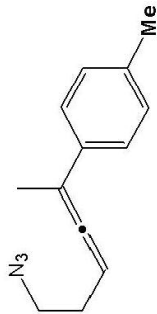


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 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 7462.687 Hz
 FIDRES 0.113872 Hz
 AQ 4.3509621 sec
 RG 256
 CW 67.000 usec
 DE 95.71 usec
 TE 300.0 K
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 O1 1.0000000 sec
 P1 12.00 usec
 SF01 360.1361620 MHz
 NUCLEUS 1H

F2 - Processing parameters
 SI 32768
 SF 360.1340131 MHz
 WDM no
 SSB 0
 -B 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
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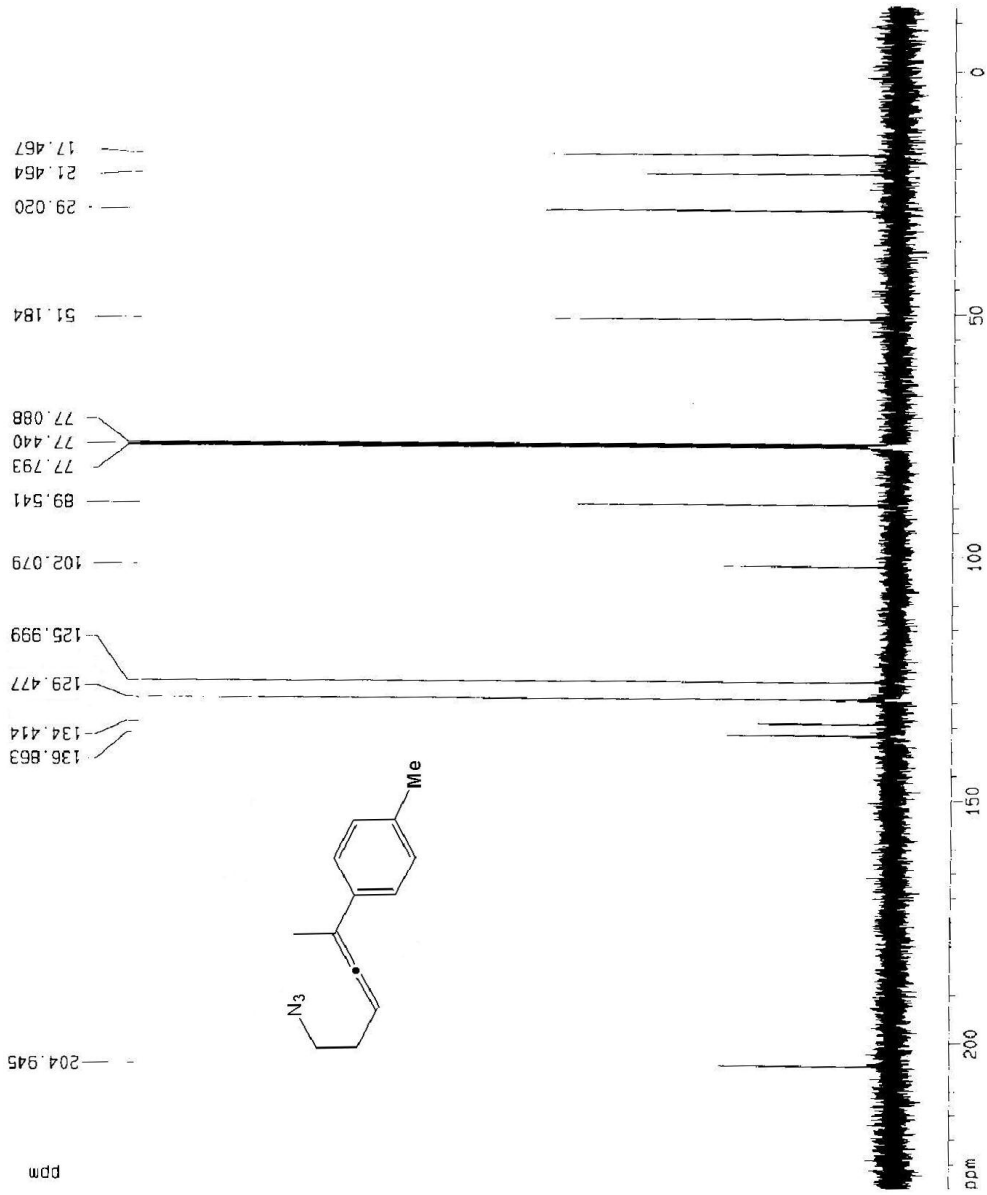
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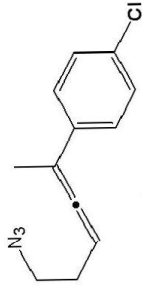
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EXPNO 3
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TD 65536
SOLVENT CDCl3
NS 156
DS 4
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FIDRES 0.346791 Hz
AQ 1.4418420 sec
RG 32768
DM 22.900 usec
DE 31.43 usec
TE 300.0 K
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J1 2.00000000 sec
CPDPRG waltz16
P31 106.00 usec
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D11 0.03000000 sec
p1 30 dB
S2 30 dB
p1 7.90 usec
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NUCLEUS 13C

F2 - Processing parameters
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1D NMR plot parameters
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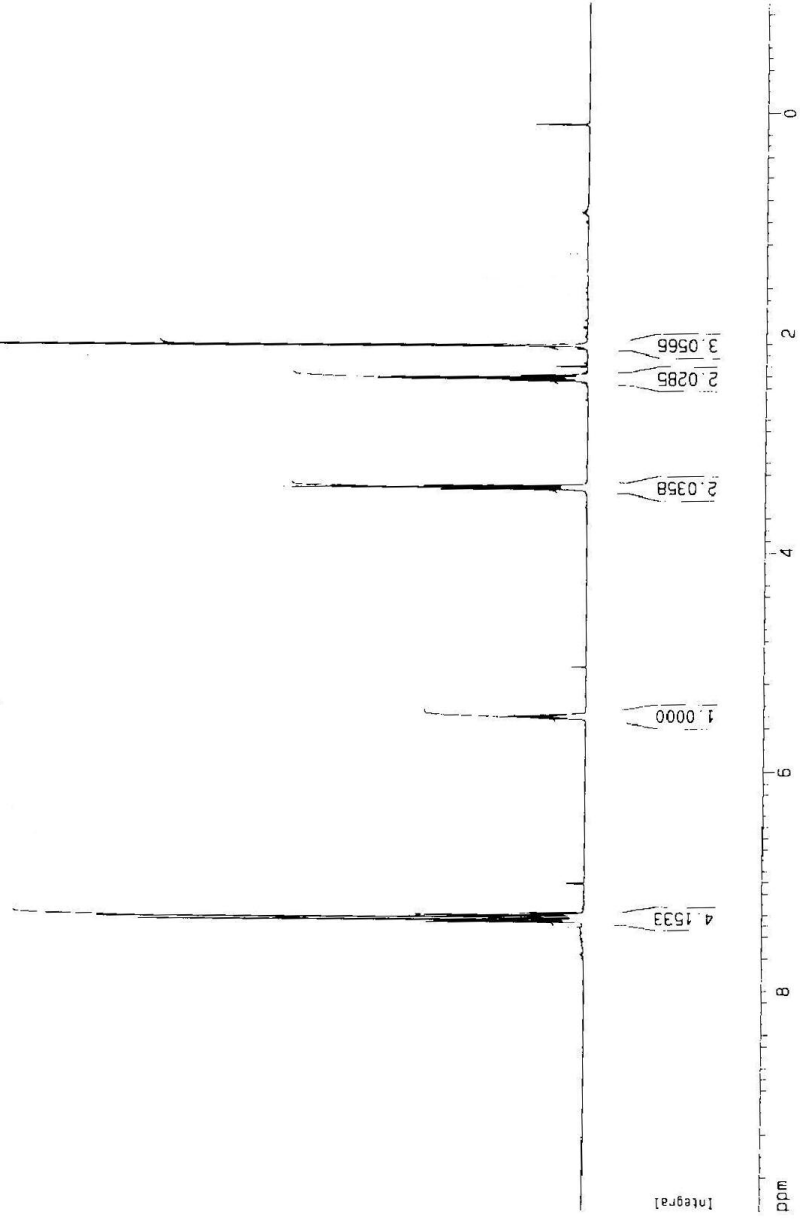
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 SOLVENT CCl3
 NS 16
 DS 2
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 FIDRES 0.126314 Hz
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 TE 300.0 K
 D1 1.00000000 sec

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F2 - Processing parameters
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 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
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 HzCM 220.07150 Hz/cm



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Current Data Parameters
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PROCNO   1

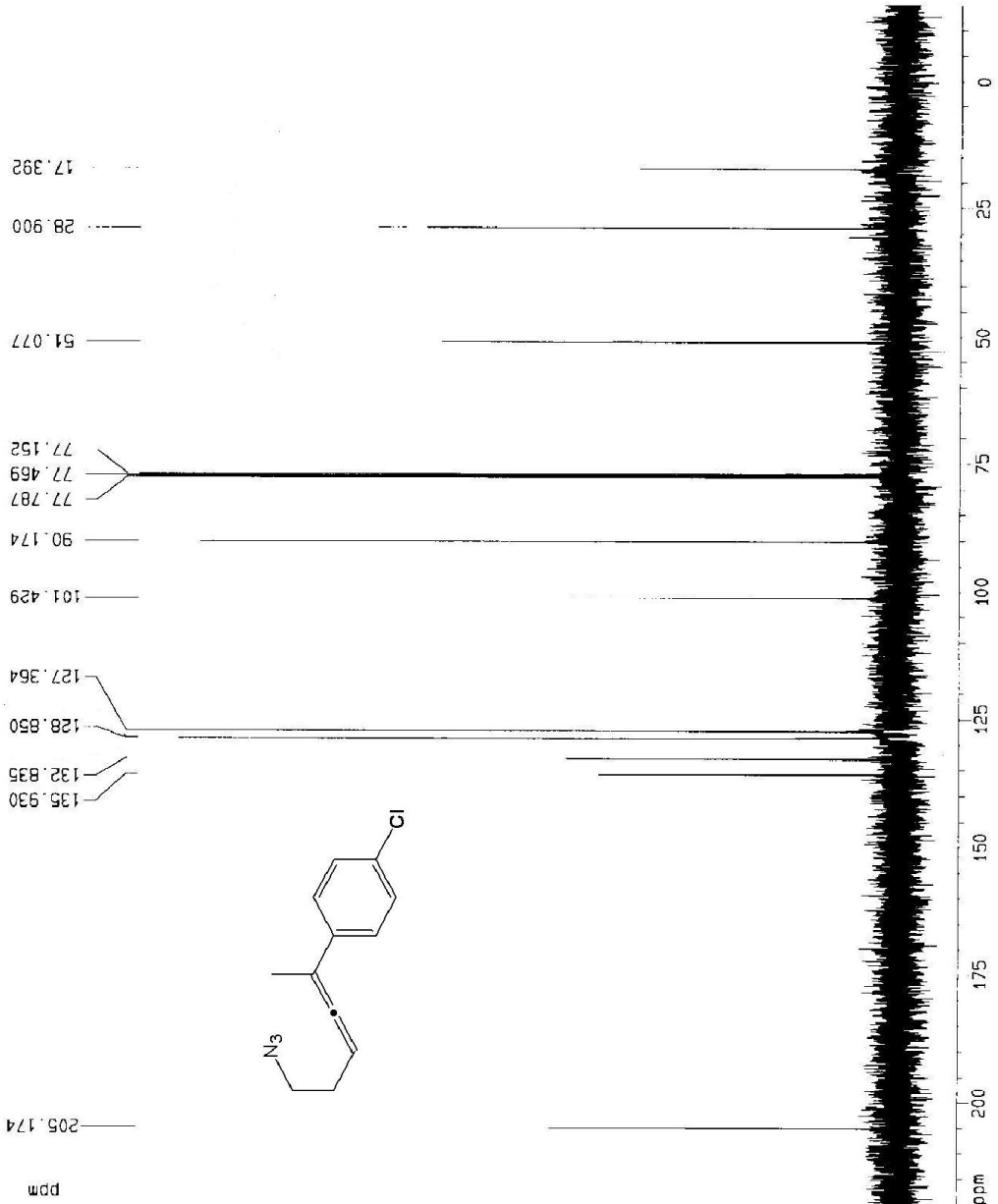
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SOLVENT  CDCl3
NS        154
DS        4
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FIDRES   0.383387 Hz
AQ        1.3042164 sec
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DE        6.00 usec
TE        300.0 K
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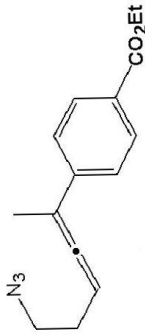
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NUC2      1H
PCPD2     114.00 usec
PL2       0.00 dB
PL12      24.00 dB
PL13      24.00 dB
SFO2      400.1316005 MHz

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SF        100.6127250 MHz
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GB        0
-PC       1.40

1D NMR Plot parameters
CX        20.00 cm
F1P       220.000 ppm
F1        22134.80 Hz
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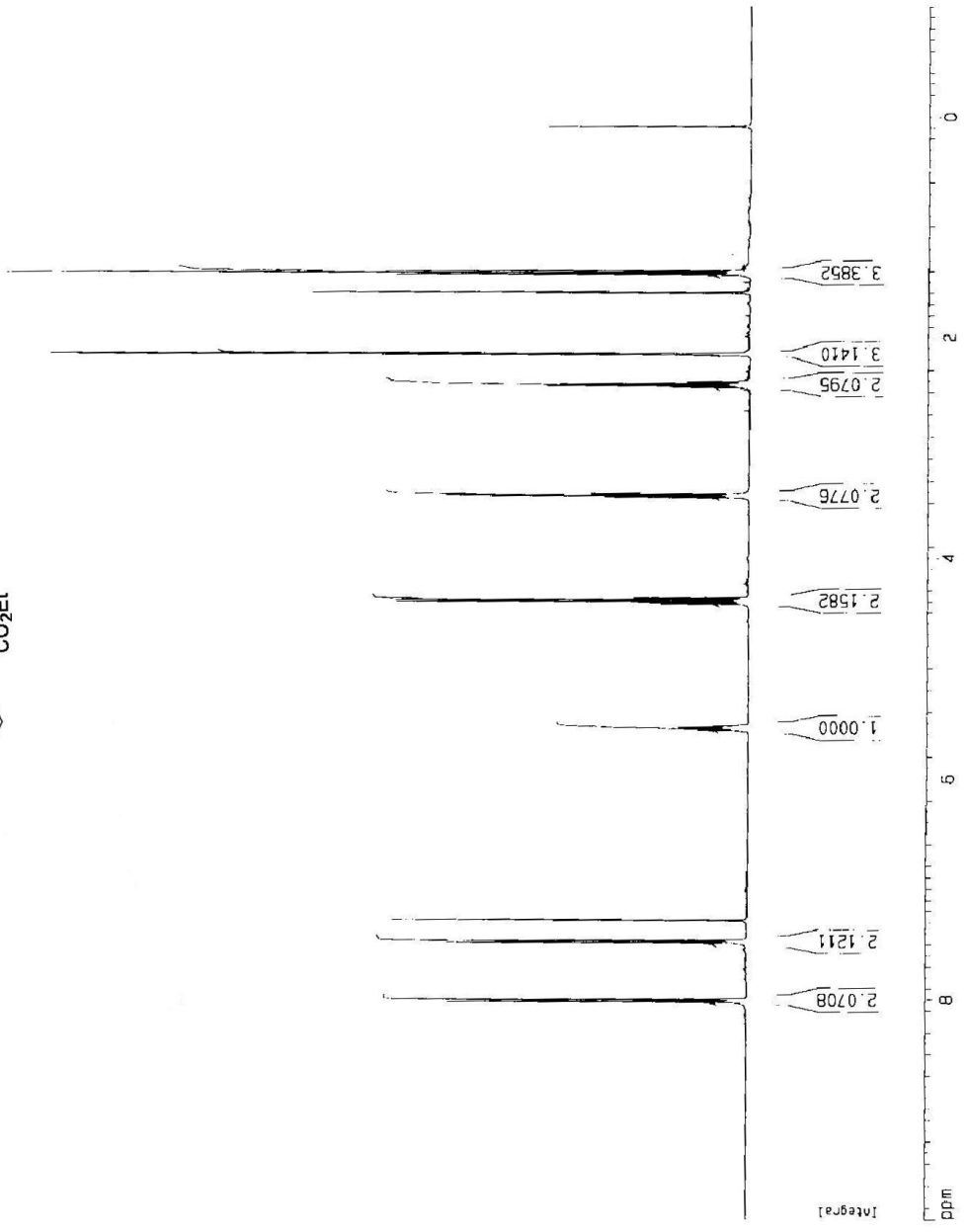
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===== CHANNEL f1 =====
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 PL1 0.00 dB
 SFO1 400.1324710 MHz

F2 - Processing parameters
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 SF 400.1300000 MHz
 WDW no
 SSB 0
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 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 FIP 10.000 ppm
 F1 4001.30 Hz
 F2P -1.000 ppm
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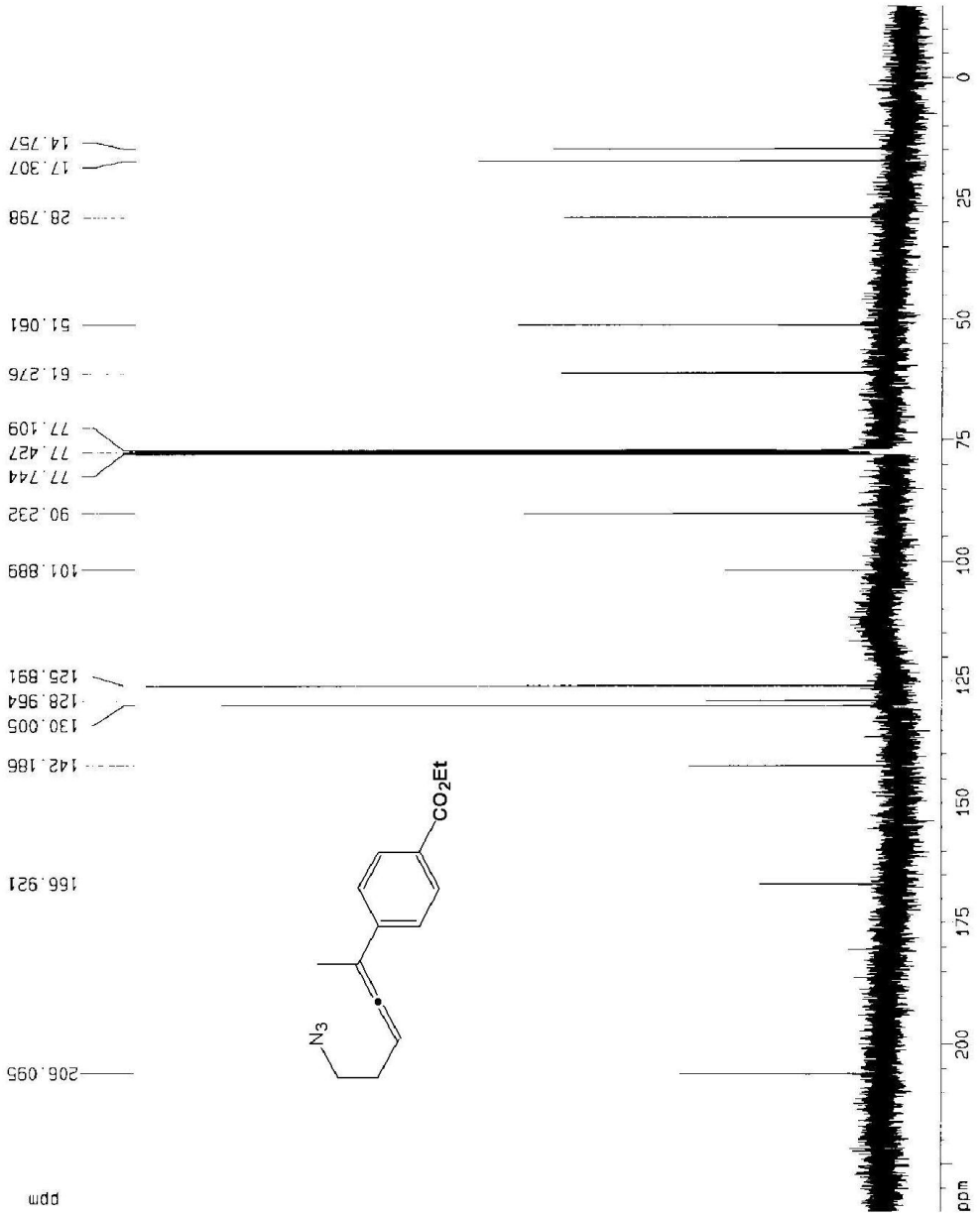
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DS        4
SWH       25125.629 Hz
FIDRES    0.383387 Hz
AQ         1.3042164 sec
RG         6132
DM         19.900 usec
DE         6.00 usec
TE         300.0 K
SI         2.0000000 sec
LI         0.0300000 sec
PI2       0.0000200 sec

***** CHANNEL f1 *****
NUC1      13C
P1         16.35 usec
PL1        -6.00 dB
SFO1      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
SFO2      400.1315005 MHz

F2 - Processing parameters
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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
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F2P        23629.72 Hz
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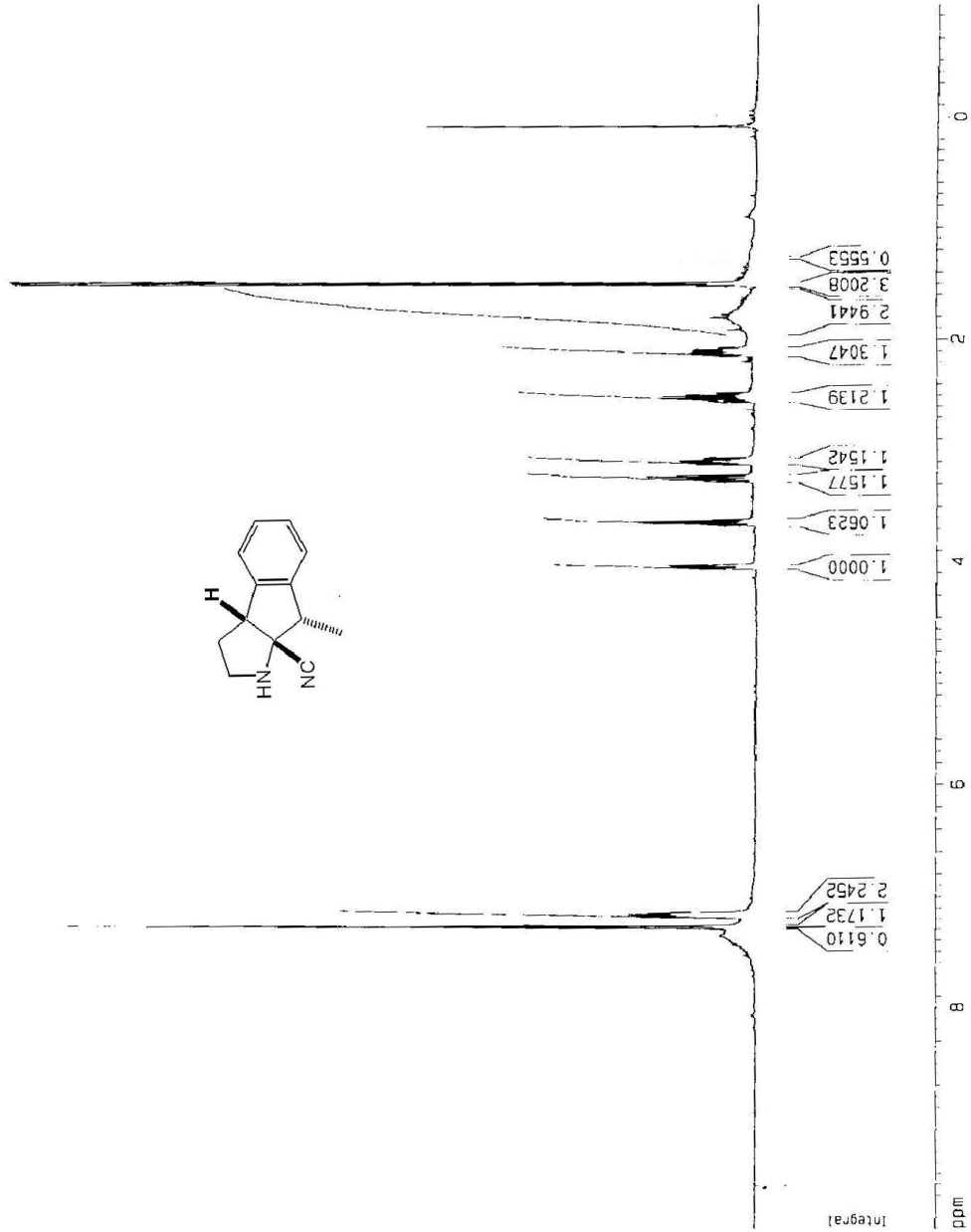
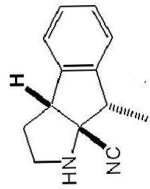
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PROCNO   1

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SOLVENT  CDCl3
NS        16
DS        2
SWH       8278.146 Hz
FIDRES    0.126314 Hz
AQ        3.9584243 sec
RG        203.2
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TE        300.0 K
D1        1.00000000 sec

===== CHANNEL f1 =====
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P1        6.45 usec
PL1       0.00 dB
SF01      400.1324710 MHz

F2 - Processing parameters
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SF        400.1300000 MHz
RG        nc
SSB       0
-B        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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PROCNO   1

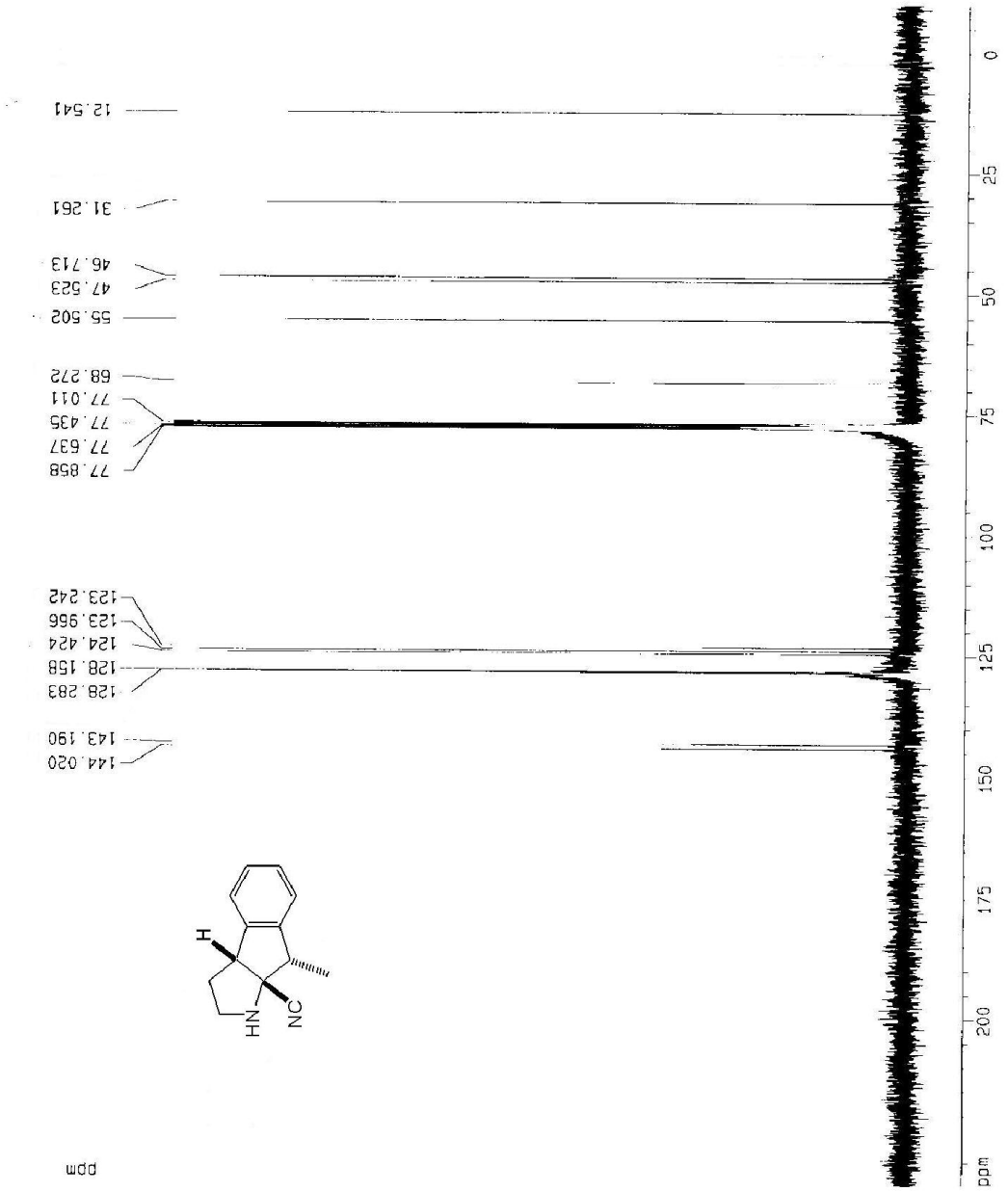
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SOLVENT  DMS-D
NS       13993
DS       4
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FIDRES   0.288819 Hz
AQ       1.7433076 sec
RG       2048
DM       26.608 usec
DE       5.00 usec
TE       300.0 K
D1       2.0000000 sec
D11      0.0300000 sec
D12      0.0000200 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     299.6711995 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
CK       20.00 cr
F1P      234.651 ppm
F2       17693.24 Hz
F2P      -10.000 ppm
F2       -754.02 Hz
ppmMCH  12.23255 ppm/cm
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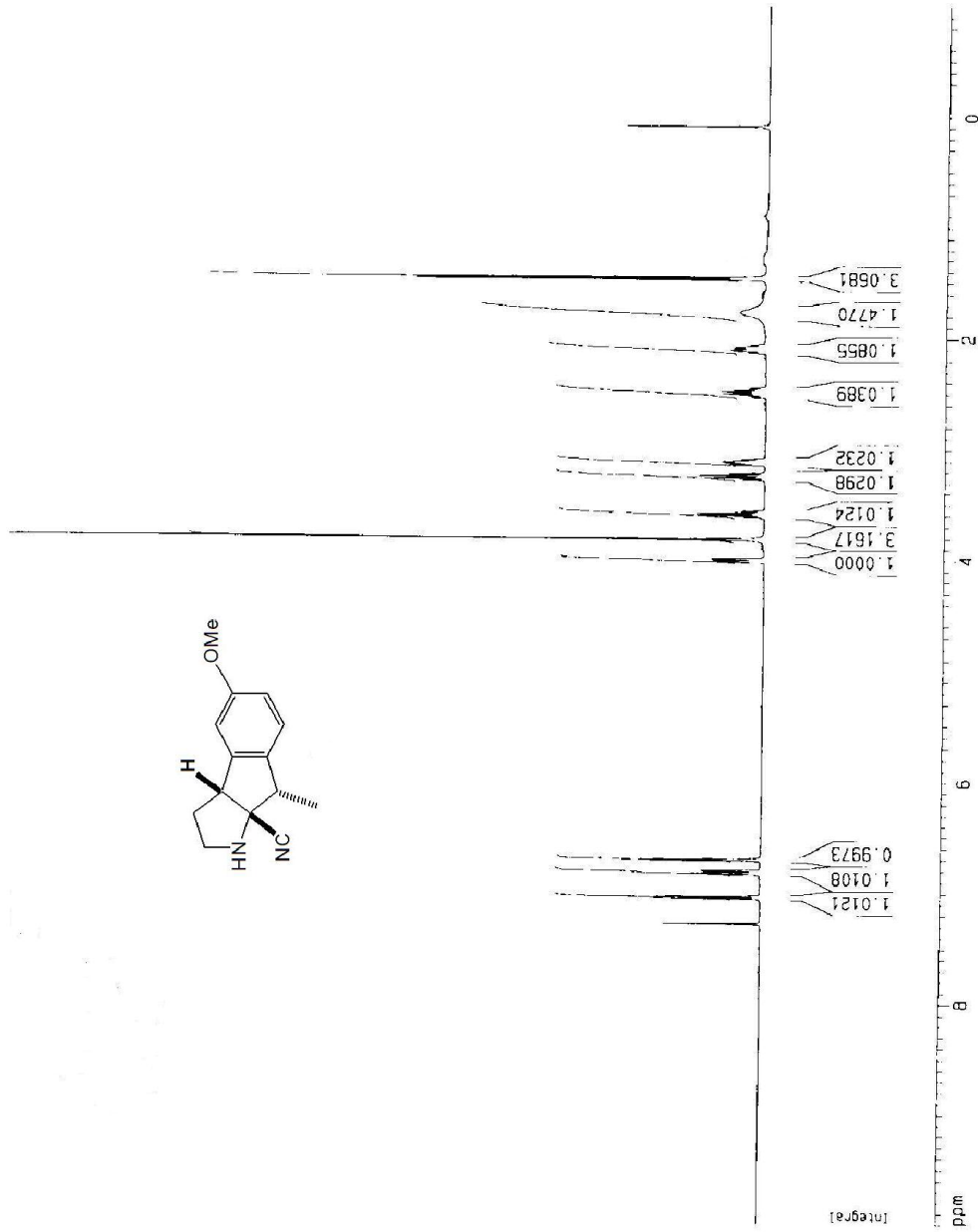
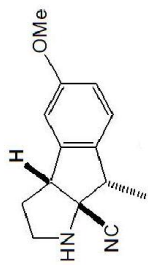
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EXPNO    3
PROCNO   1

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PULPROG zg30
TD       65536
SOLVENT  DMS-D6
NS       16
DS       2
SWH      8276.146 Hz
FIDRES   0.126314 Hz
AQ       3.9584243 sec
RG       143.7
DM       60.400 usec
DE       6.00 usec
TE       300.0 K
D1       1.0000000 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      nd
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
    
```



```

Current Data Parameters
NAME      MRI-Aug-2-04
EXPNO    1
PROCNO   1

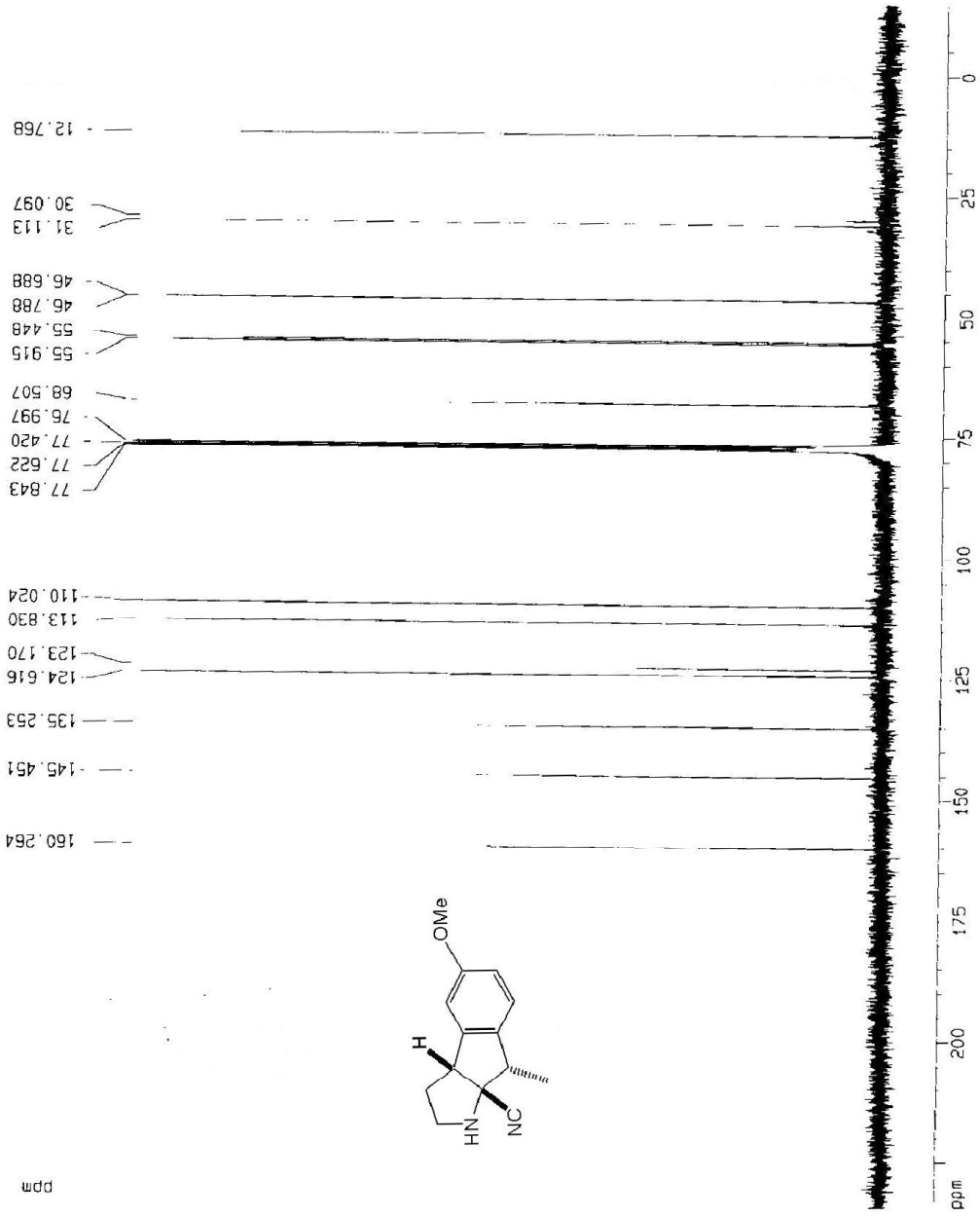
F2 - Acquisition Parameters
Date_     20040814
Time      8.12
Spect     5
PROBHD    5 mm Multinu
PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS        12828
DS        4
SWH        18632.393 Hz
FIDRES    0.287360 Hz
AQ        1.7400308 sec
RG        16384
Dw        26.550 usec
DE        6.00 usec
TE        300.0 K
D1        2.0000000 sec
d11       0.0300000 sec
d12       0.0002000 sec

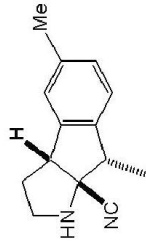
===== CHANNEL f1 =====
NUC1      13C
P1        5.60 usec
PL1       -8.00 dB
SFO1      75.4760200 MHz

===== CHANNEL f2 =====
CPDPRG2   mltz15
NUC2      1H
P2        114.00 usec
PL2       -6.00 dB
P3        18.00 dB
P4        18.00 dB
SFO2      300.1312005 MHz

F2 - Processing parameters
SI        32768
SF        75.4671950 MHz
WDW       EM
SSB       C
LB        1.00 Hz
GB        0
PC        1.40

1D NMR pict parameters
CX        20.00 cm
F1P       234.765 ppm
F2P       177.745 Hz
F2Q       -24.778 ppm
PP4CM     -1115.24 Hz
PZCM      12.47712 ppm/cm
RZCM      941.61963 Hz/cm
    
```





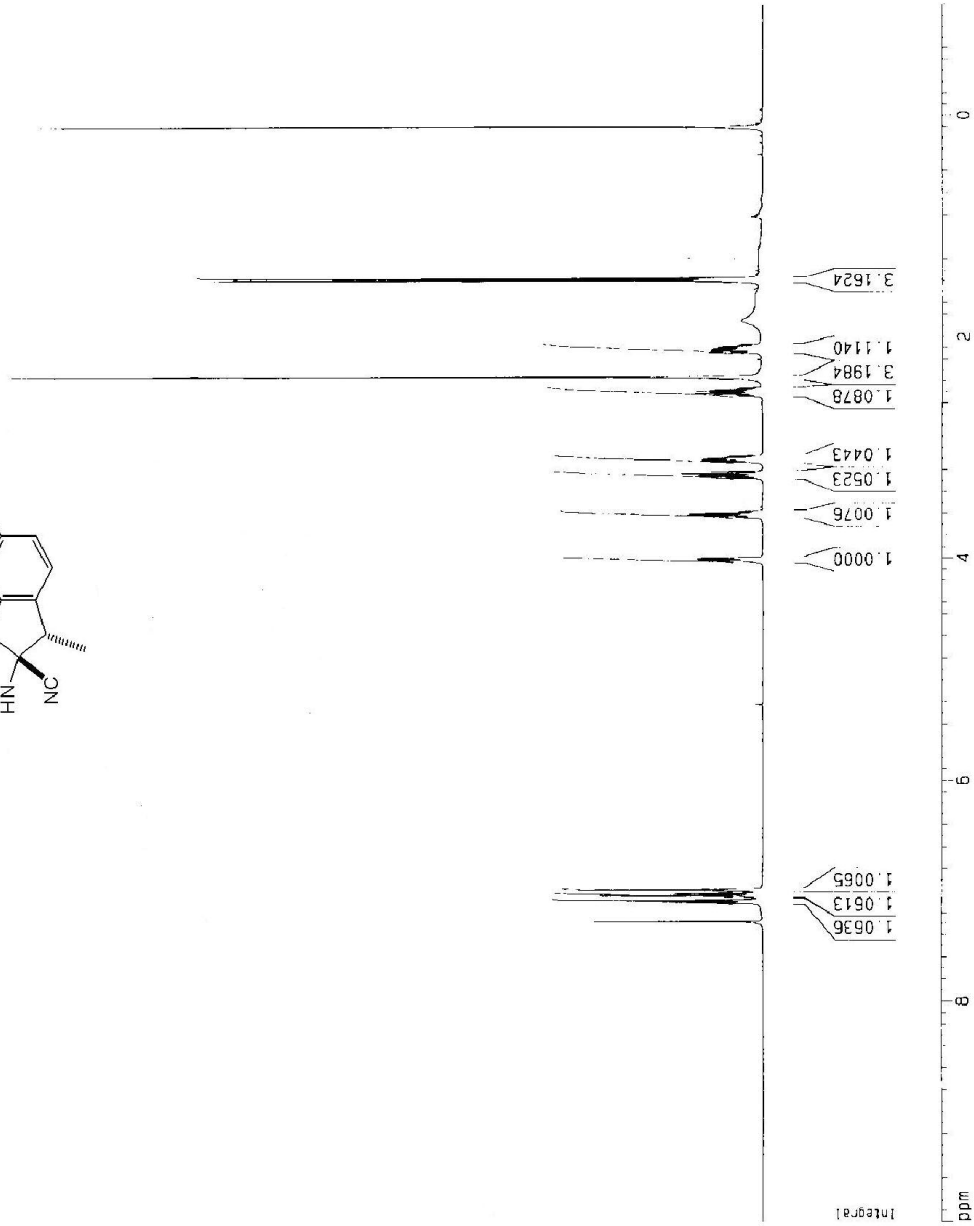
Current Data Parameters
 NAME MRI-Aug04-04
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20040804
 Time 17.54
 INSTRUM spect
 PROBHD 5 mm BBI 1H-B
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9564243 sec
 RG 128
 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
 SF01 400.1324710 MHz

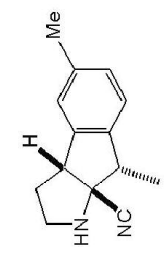
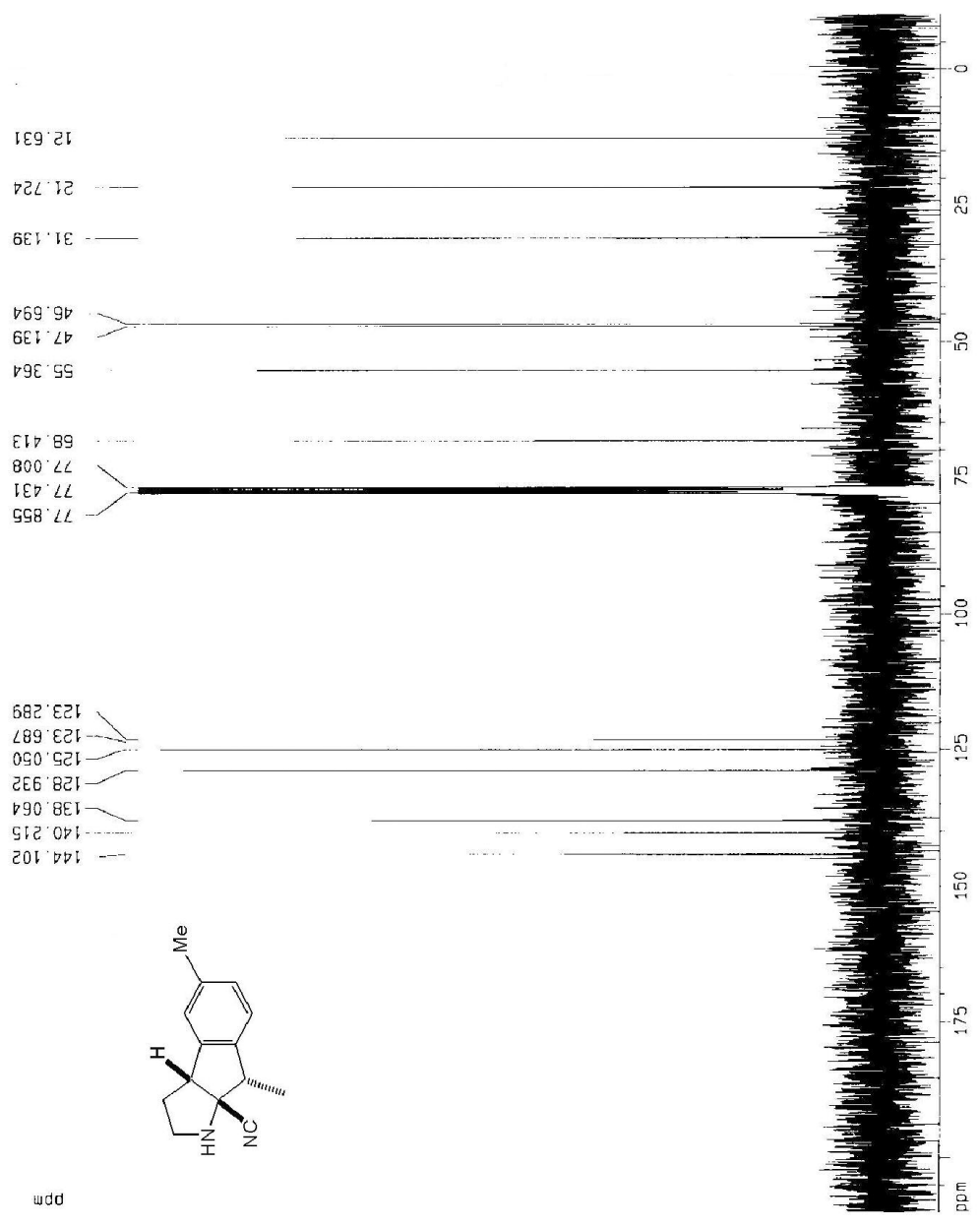
F2 - Processing parameters
 S1 32768
 SF 400.1300000 MHz
 NDM rd
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 F4P 10.000 ppm
 F1 4001.30 Hz
 F2P -1.000 ppm
 F2 -400.13 Hz
 PPMCK 0.55000 ppm/cm
 HZCM 220.07150 hz/cm



```

Current Data Parameters
NAME      M01-AUG08-04
EXPNO    1
PROCNO   1
-----
F2 - Acquisition Parameters
Date_    23040807
Time     9.48
INSTRUM  spect
PROBHD   5 mm WJ111Pv
PULPROG  zgpg30
TD       65536
SOLVENT  DMS-D6
NS       14000
DS       4
SFO1     18832.393 Hz
FIDRES   0.2812660 Hz
AQ       1.74003508 sec
RG       16384
CW       28.560 usec
DE       6.00 usec
TE       300.0 K
C1       2.00000000 sec
C2       0.03000000 sec
C3       0.00020000 sec
-----
CHANNEL f1
NUC1     13C
P1       5.00 usec
PL1     -6.00 dB
SFO1    75.4760200 MHz
-----
CHANNEL f2
CPDPRG2  waltz16
NUC2     1H
PCPD2    114.00 usec
PL2     -6.00 dB
PL12    18.00 dB
PL13    18.00 dB
SFO2    300.1312005 MHz
-----
F2 - Processing parameters
SI       32768
SF       75.4677190 MHz
RG       0
SBB      EM
GB       0
PC       1.40
-----
1D NMR plot parameters
CX       20.00 cm
F1P      210.000 ppm
F1       45648.22 Hz
F2P      -10.000 ppm
F2       -754.68 Hz
SFOCK    31.00000 ppm/cm
SFOCV    630.14450 Hz/cm
    
```



```

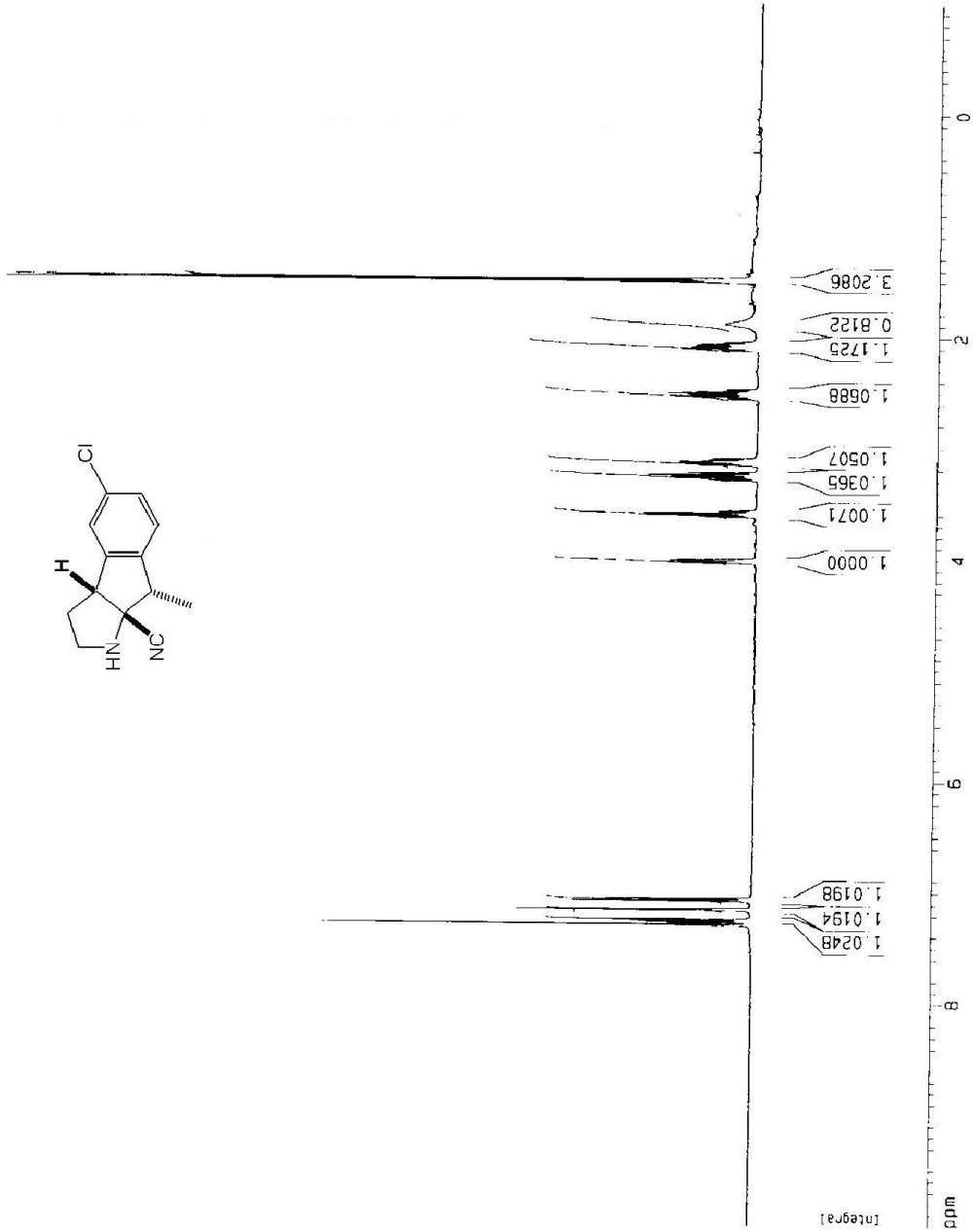
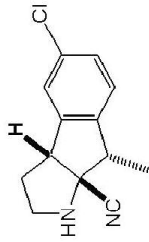
Current Data Parameters
NAME      MRI-Aug12-04
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20040812
Time     18.42
INSTRUM spect
PROBHD   5 mm BBI 1H-B
PULPROG zg30
TD       65536
SOLVENT  CDCl3
NS       12
DS       2
SWH      8278.146 Hz
FIDRES   0.126314 Hz
AQ       3.9584243 sec
RG       256
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      nc
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
SFOCM   0.55000 ppm/cm
HZCM    220.07149 Hz/cm
    
```



```

Current Data Parameters
NAME      MRI-Aug10-04
EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
Date_    20040811
Time     8:45
INSTRUM  spect
PROBHD   5 mm DNP 1H/1
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        13000
DS        4
SWH       18796.992 Hz
FIDRES    0.286819 Hz
AQ        1.7433076 sec
RG         1024
CM        26.600 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        5.40 usec
PL1       -6.00 dB
SFO1      75.4106357 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
P2        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

10 MHz plot parameters
CX        20.00 cm
FIP       220.000 ppm
F1        16588.51 Hz
F2P       -10.000 ppm
F2        -754.02 Hz
PPMCM     11.50000 ppm/cm
HZCM      867.12695 Hz/cm
    
```

