Supplementary information

Enantioselective Conjugate Addition Nitro-Mannich Reactions: Solvent Controlled Synthesis of Acyclic *anti*- and *syn*-β-nitroamines with 3 Contiguous Stereocenters

James C. Anderson, Gregory J. Stepney, Matthew R. Mills, Lisa R. Horsfall, Alexander J. Blake and William Lewis.*

Department of Chemistry, 20 Gordon Street, University College London, London, WC1H 0AJ, UK

j.c.anderson@ucl.ac.uk

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General experimental

Unless otherwise stated, all reactions were carried out under an atmosphere of nitrogen. All glassware was flame dried and allowed to cool under a stream of nitrogen before use. Cooling to 0 $^{\circ}$C was effected using an ice-water bath. Cooling to temperatures below 0 $^{\circ}$C was effected using dry ice-acetone mixtures. Reactions were monitored by thin layer chromatography (TLC) using Polygram® SIL G/UV_{254} 0.25 mm silica gel precoated plastic plates with fluorescent indicator. Sheets were visualised using ultra-violet light (254 nm) and/or anisaldehyde or $KmnO_4$ solutions, as appropriate. Flash column chromatography was performed using Fluorochem silica gel 60, 35-70 μ. The liquid phase was analytical grade 40-60 petroleum ether (petrol) and ethyl acetate (EtOAc) unless otherwise noted.

Purification of Solvents and Reagents

Commercial solvents and reagents were used as supplied or purified in accordance with standard procedures, as described below.

Tetrahydrofuran (THF) was pre-dried over sodium wire and distilled under an atmosphere of dry nitrogen from sodium benzophenone ketal or obtained from a solvent tower, where degassed THF was passed through two columns of activated alumina and a 7 micron filter under 4 bar pressure.

Diethyl ether (Et_2O) was pre-dried over sodium wire and distilled under an atmosphere of dry nitrogen from sodium benzophenone ketal or obtained from a solvent tower, where degassed Et_2O was passed through two columns of activated alumina and a 7 micron filter under 4 bar pressure.

Toluene was obtained form a solvent tower, where degassed toluene was passed through two columns of activated alumina and a 7 micron filter under 4 bar pressure. Dichloromethane was distilled from calcium hydride powder or purchased as an analytical grade and stored over 4Å molecular sieves.

Characterisation

Melting points are uncorrected. Optical rotations were recorded at 25 $^{\circ}$C and are reported in deg cm^2 g^{-1}. Infrared spectra were recorded as a thin film on sodium chloride discs or as dilute chloroform solutions. ^{1}H and ^{13}C NMR spectra were recorded as dilute solutions in deuterochloroform unless otherwise stated. All chemical shifts (δ) are reported in parts per million (ppm) relative to chloroform (δ_H = 7.27 ppm, δ_c = 77.1 ppm). Coupling constants (*J*) are reported in Hertz and are recorded as observed in the spectrum without averaging. The multiplicity of an ^{1}H signal is designated by the following abbreviations: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet and quin = quintet, br = broad signal. ^{13}C multiplicities were assigned using a DEPT sequence. Where appropriate, HMQC and NOE experiments were carried out to aid assignment.

Nitroalkenes were prepared according to literature procedures[1] and their data was in accord with that published.[2]

Solvent studies

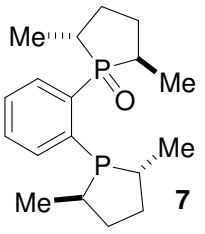
To a stirred mixture of nitroalkene (1.00 mmol) and $Cu(Otf)_2$ (0.05 mmol) in dry solvent (3 mL) at -78 °C was added Et_2Zn (1.10 mmol, 1M in hexane). The resulting orange solution was stirred for 10 min before being warmed to rt. After 1 h the brown suspension was cooled to -78 °C. A solution of imine (2.00 mmol) in dry solvent (2 mL) was added and the mixture stirred for 20 min. A solution of TFA (3.50 mmol) in dry solvent (0.6 mL) was added dropwise over 20 seconds and the reaction stirred for 1 h. The reaction was warmed to room temperature over 1 h to provide a suspension of white solid and vivid yellow supernatant. The reaction was quenched by the addition of Et_2O (5 mL) and saturated aq. $NaHCO_3$ (5 mL). The layers were separated and the aqueous phase extracted with Et_2O (2 x 5 mL). The organic layers were combined and the solvent removed *in vacuo* to provide crude β-nitroamine. Note: $MgSO_4$ was not used to dry the product β-nitroamines prior to solvent removal because the products were found to be mildy unstable towards this reagent.

Temperature studies

The reactions were carried out as above for the specified times recorded in Table 2.

Chiral ligands

The Charette ligand Bozphos (**7**) was used as the Cu(**7**)$_2$Otf complex and was prepared in two steps from commercially available Me-DuPHOS according to the literature.[3] The Hoveyda ligand **8** was prepared according to the literature[4] and was used as described.



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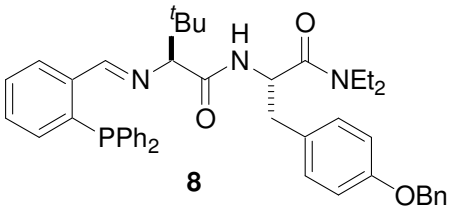
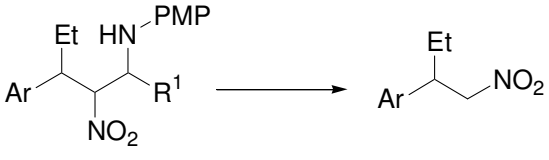


8

Determination of *ee*.

Retention times were compared to racemic standards. If the products could not be separated by a chiral stationary phase, they were measured by degradation.



***syn*, *anti*-a.** As is normal for the types of *anti*-β-nitroamines we generate, the NMR solutions gradually undergo retro addition if left in $CDCl_3$ at rt.[5] Samples were left until complete degradation

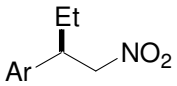
(1-2 days) by ^{1}H NMR and the crude nitroalkane was then used for HPLC analysis to measure the enantiomeric excess of the parent *β*-nitroamine.

***Syn*, *syn*-b.** If the product could not be separated by a chiral stationary phase, they were measured by degradation. *B*-Nitroamine (*ca*. 20 mg) was dissolved in THF (3 mL) and TFA (0.2 mL) was added. The yellow solution was heated at reflux for 5 h before being cooled to rt. Et_2O (2 mL) was added and the organic phase was washed with saturated aq. $NaHCO_3$ (2 mL), dried ($MgSO_4$) and the solvent removed in vacuo. The crude nitroalkane was then used for HPLC analysis to measure the enantiomeric excess of the parent *β*-nitroamine.

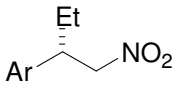
These processes were validated by subjecting entry 18, Table 4 (Ar=Ph, R=Et, R^1=*p*-Me-Ph) measured by chiral HPLC (OD-H column, 99.5 % hexane 0.5% IPA) to be 96% *ee* to the above conditions which showed the parent nitroalkane had 95% *ee*.

Assignment of absolute and relative stereochemistry

We have assumed that the initial conjugate addition with ligands **7** and **8** gives the opposite enantiomers as characterised by Charette[3] and Hoveyda.[4]



using Charette ligand **7**



using Hoveyda ligand **8**

Entry 1/15. X-ray structures of each diastereoisomer confirmed relative stereochemistry.

Entry 2/17. The relative stereochemistry of these two diastereoisomers was assigned by analogy to the other compounds, **Entry 2** slowly degraded by retro addition in $CDCl_3$ indicating *anti*-β-nitroamine stereochemistry[5] and was reactive towards trifluoroacetic anhydride. Whereas **Entry 17** was stable in $CDCl_3$, purification by chromatography and was unreactive towards trifluoroacetic anhydride, indicating *syn*-β-nitroamine stereochemistry.

Entry 3/18. **Entry 3** slowly degraded by retro addition in $CDCl_3$ indicating *anti*-β-nitroamine stereochemistry[5] and was reactive towards trifluoroacetic anhydride. X-ray confirmed relative stereochemistry of **Entry 18**, which was stable in $CDCl_3$ and purification by chromatography.

Entry 4. The same diastereoisomer was isolated as the trifluoroacetamide from a THF or PhMe nitro Mannich reaction (both homogeneous) using the Charette ligand **5** and the stereochemistry was assigned by analogy to the other compounds. The parent β-nitroamine before treatment with trifluoroacetic anhydride was unstable in $CDCl_3$ and collectively indicated *anti*-β-nitroamine stereochemistry.[5]

Entry 5/19. X-ray confirmed relative stereochemistry of **Entry 5** which slowly degraded by retro addition in $CDCl_3$ and was reactive towards trifluoroacetic anhydride. **Entry 19** was stable in $CDCl_3$ and purification by chromatography, indicating *syn*-β-nitroamine stereochemistry.

Entry 6/20. The relative stereochemistry of these two diastereoisomers was assigned by analogy to the other compounds. **Entry 6** slowly degraded by retro addition in $CDCl_3$ indicating *anti*-β-nitroamine stereochemistry[5] and was reactive towards trifluoroacetic anhydride. Whereas **Entry 20** was stable in $CDCl_3$ and purification by chromatography, indicating *syn*-β-nitroamine stereochemistry.

Entry 7/21. X-ray confirmed relative stereochemistry of **Entry 7** which slowly degraded by retro addition in $CDCl_3$ and was reactive towards trifluoroacetic anhydride. **Entry 21** was stable in $CDCl_3$ and purification by chromatography, indicating *syn*-β-nitroamine stereochemistry.

Entry 8/16. The relative stereochemistry of these two diastereoisomers was assigned by analogy to the other compounds (especially **Entry 1/15**). **Entry 8** slowly degraded by retro addition in $CDCl_3$ indicating *anti*-β-nitroamine stereochemistry[5] and was reactive towards trifluoroacetic anhydride. Whereas **Entry 16** was stable in $CDCl_3$ and purification by chromatography, indicating *syn*-β-nitroamine stereochemistry.

Entry 9/22. X-ray structures of each diastereoisomer confirmed the relative stereochemistry.

Entry 10/23. X-ray confirmed relative stereochemistry of **Entry 10** which slowly degraded by retro addition in $CDCl_3$ indicating *anti*-β-nitroamine stereochemistry[5] and was reactive towards trifluoroacetic anhydride. **Entry 23** was stable in $CDCl_3$ and purification by chromatography, indicating *syn*-β-nitroamine stereochemistry.

Entry 11/24. **Entry 11** slowly degrades by retro addition in $CDCl_3$ indicating *anti*-β-nitroamine stereochemistry[5] and was reactive towards trifluoroacetic anhydride. X-ray confirmed the relative stereochemistry of **Entry 24**, which was stable in $CDCl_3$ and purification by chromatography.

Entry 12/25. The relative stereochemistry of these two diastereoisomers was assigned by analogy to the other compounds. **Entry 12** slowly degraded by retro addition in $CDCl_3$ indicating *anti*-β-nitroamine stereochemistry[5] and was reactive towards trifluoroacetic anhydride. Whereas **Entry 25** was stable in $CDCl_3$ and purification by chromatography, indicating *syn*-β-nitroamine stereochemistry.

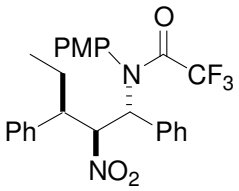
Entry 13. X-ray structure confirmed relative stereochemistry.

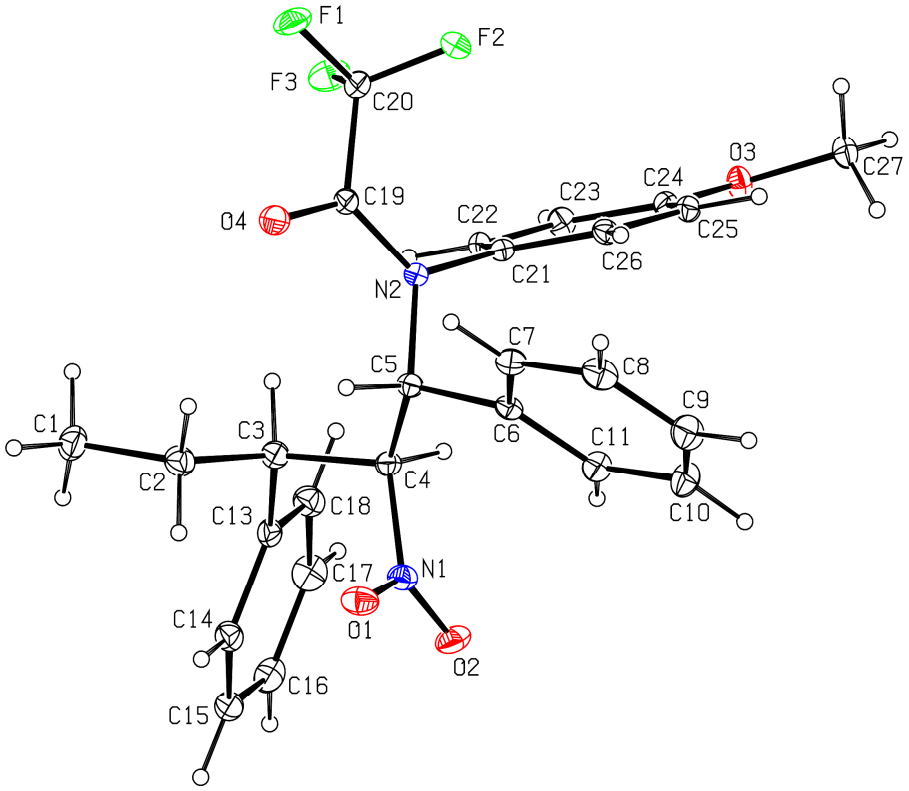
Entry 14. The relative stereochemistry of these two diastereoisomers was assigned by analogy to the other compounds. The *syn, anti*-**a** diastereoisomer slowly degraded by retro addition in $CDCl_3$ indicating *anti*-β-nitroamine stereochemistry[5] and was unstable on chromatography. Whereas *syn, syn*-**b** was stable in $CDCl_3$ and purification by chromatography, indicating *syn*-β-nitroamine stereochemistry.

Entry 26. X-ray structure confirmed relative stereochemistry.

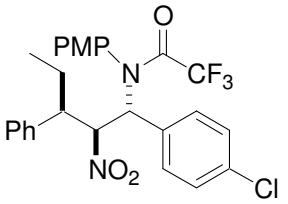
Structures and X-ray structures for compounds in Table 4

Entry 1 - Cu(**7**)$_2$OTf, THF

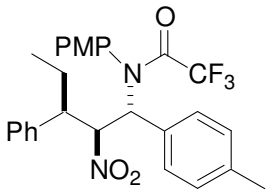




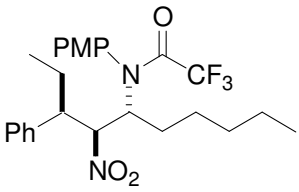
Entry 2 - Cu(**7**)$_2$OTf, THF



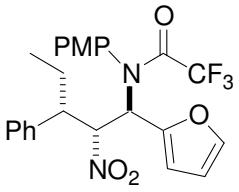
Entry 3 - Cu(**7**)$_2$OTf, THF

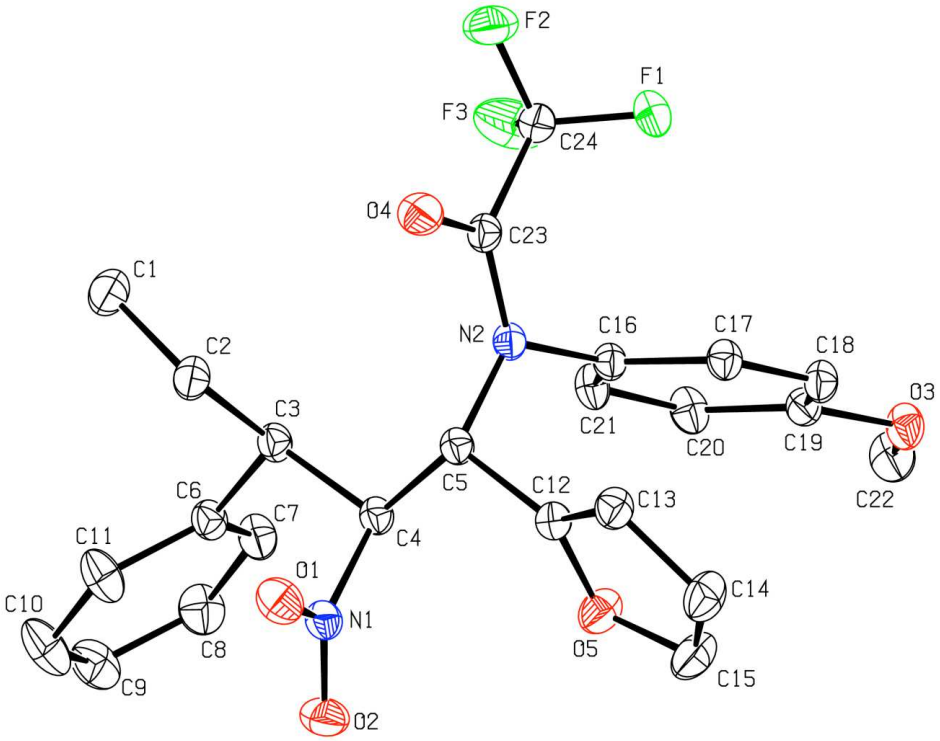


Entry 4 - Cu(**7**)$_2$OTf, THF or PhMe

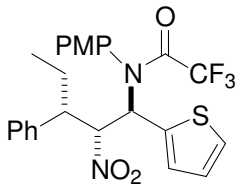


Entry 5 – Ligand **8**, THF

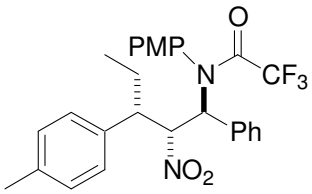


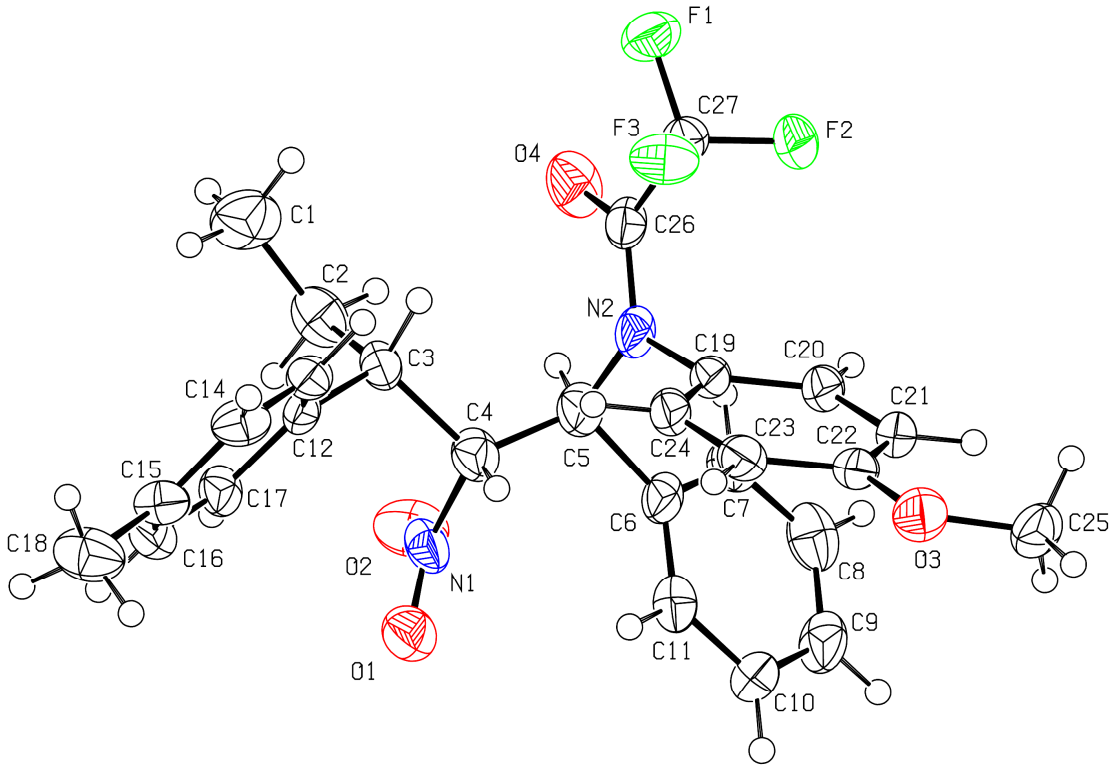


Entry 6 - Ligand **8**, THF



Entry 7 - Ligand **8**, THF





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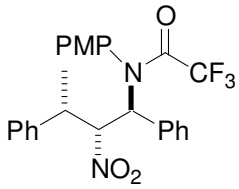

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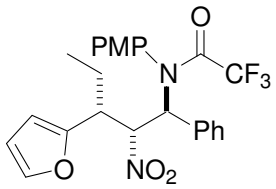
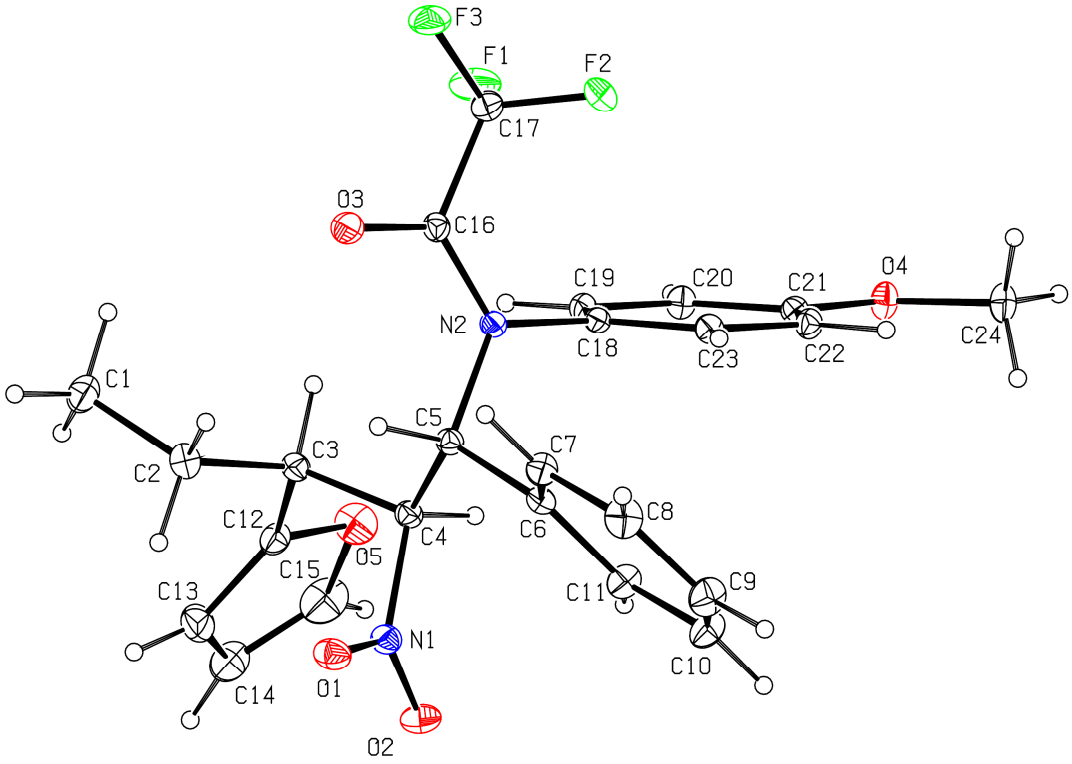
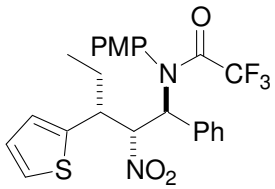
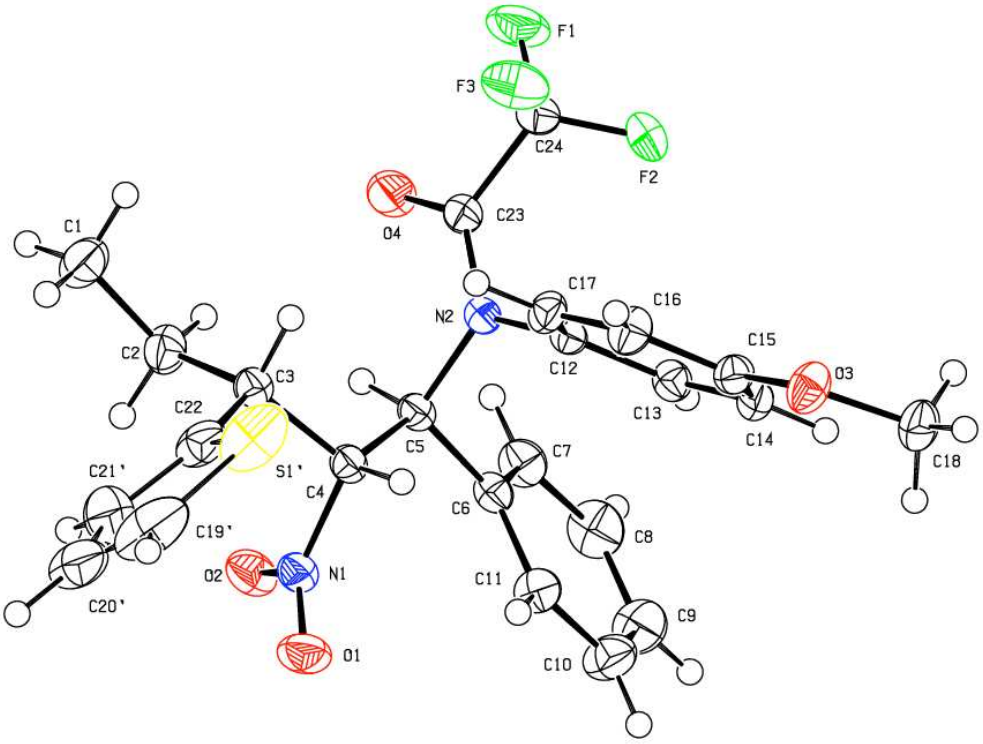


X-ray of enantiomer.



Entry 10 - Ligand **8**, THF





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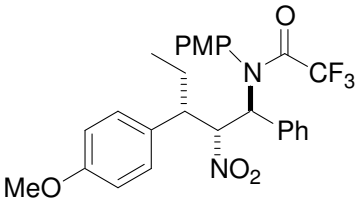
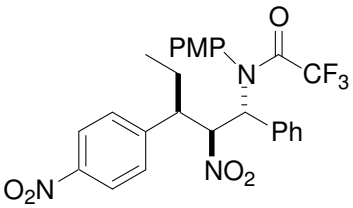
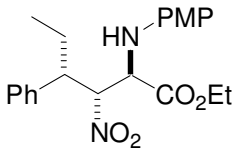


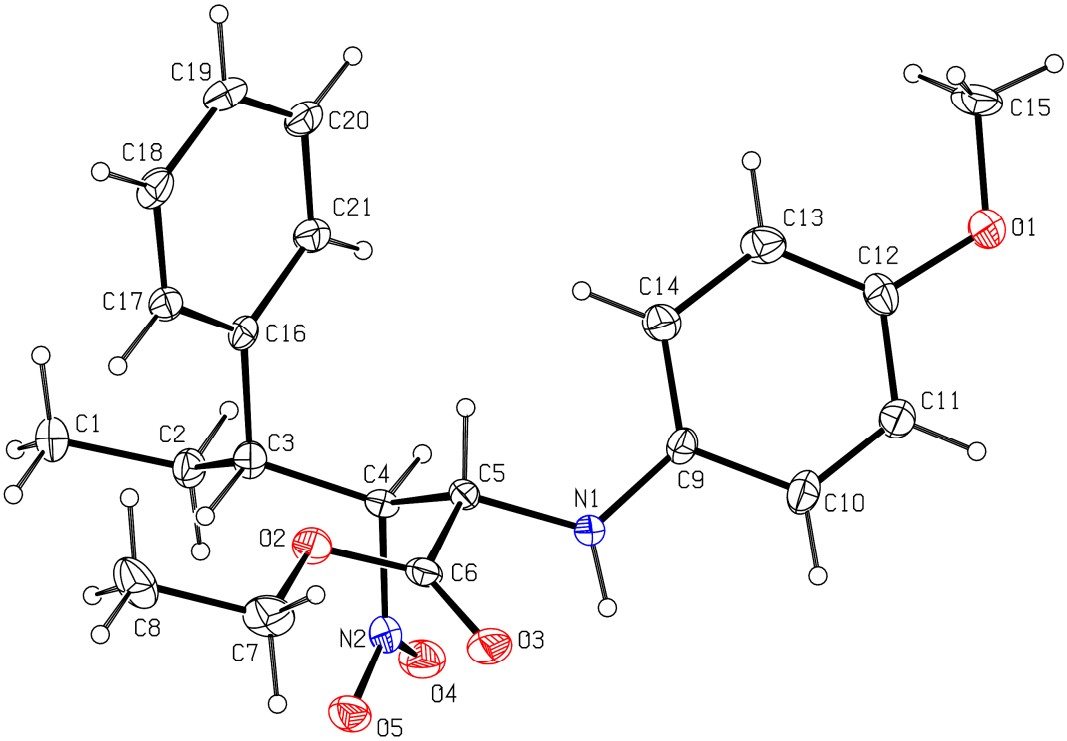
Entry 12 – no ligand, THF



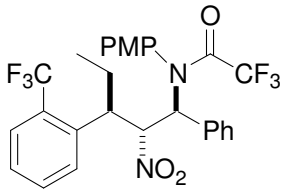
Entry 26 - Ligand **8**, PhMe

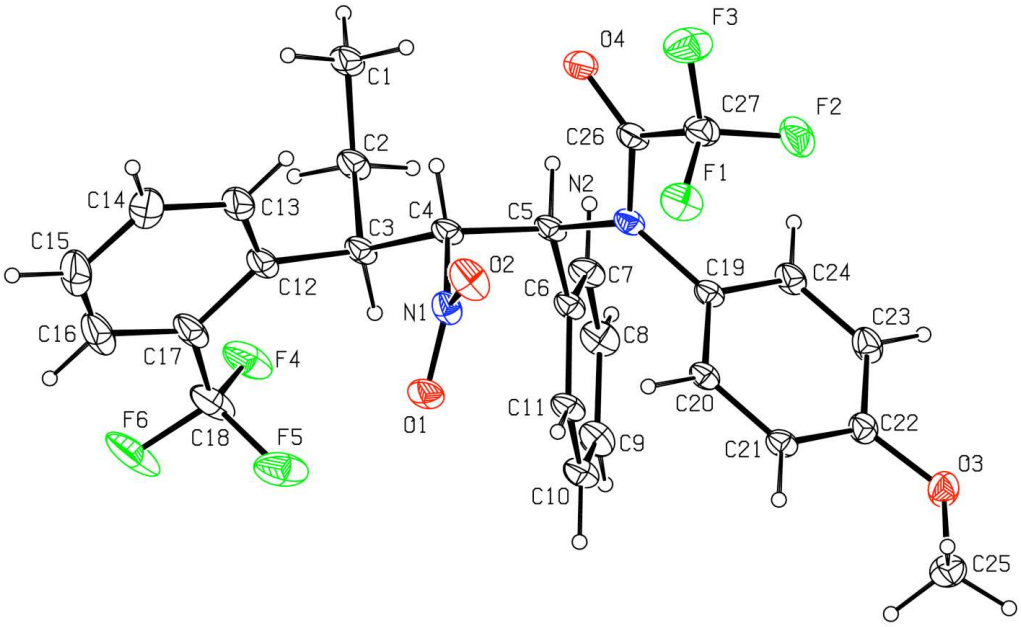


X-ray of enantiomer.

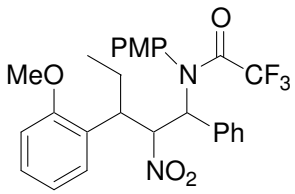


Entry 13 – no ligand, THF





Entry 14 – no ligand THF



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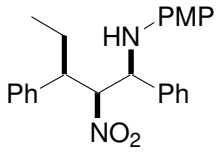
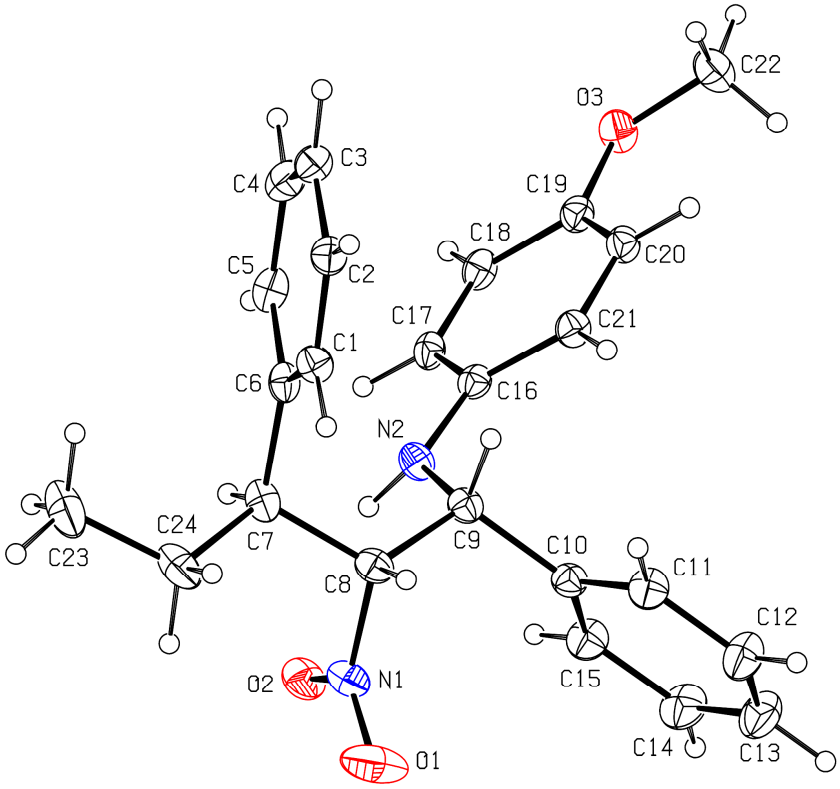
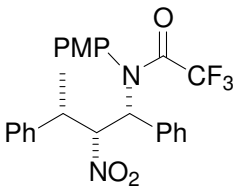
Entry 15 - Cu(**7**)$_2$OTf, Et$_2$O



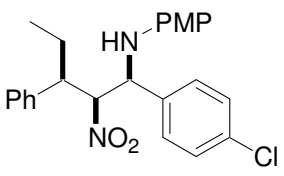
X-ray of enantiomer



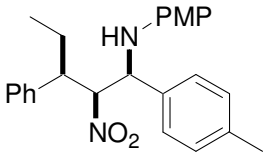
Entry 16 – Ligand **8**, PhMe

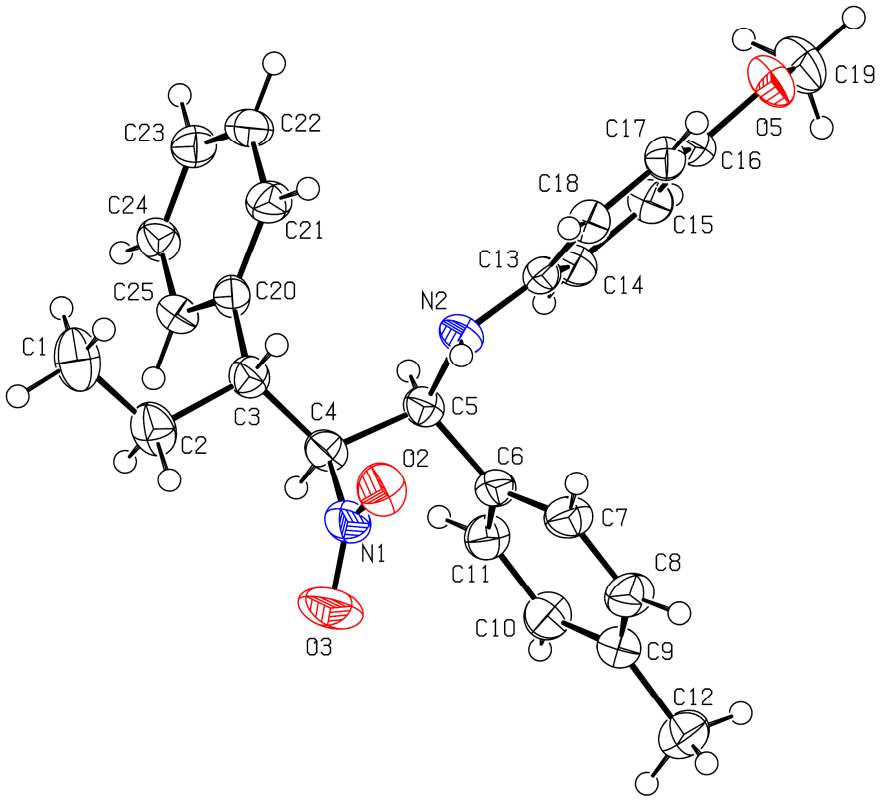


Entry 17 - Cu(**7**)$_2$OTf, Et$_2$O



Entry 18 - Cu(**7**)$_2$OTf, Et$_2$O





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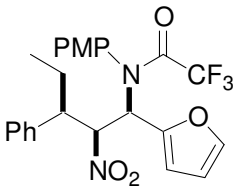

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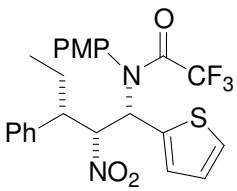

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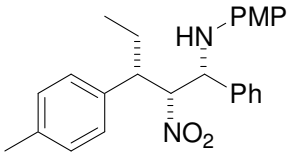

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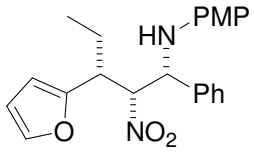

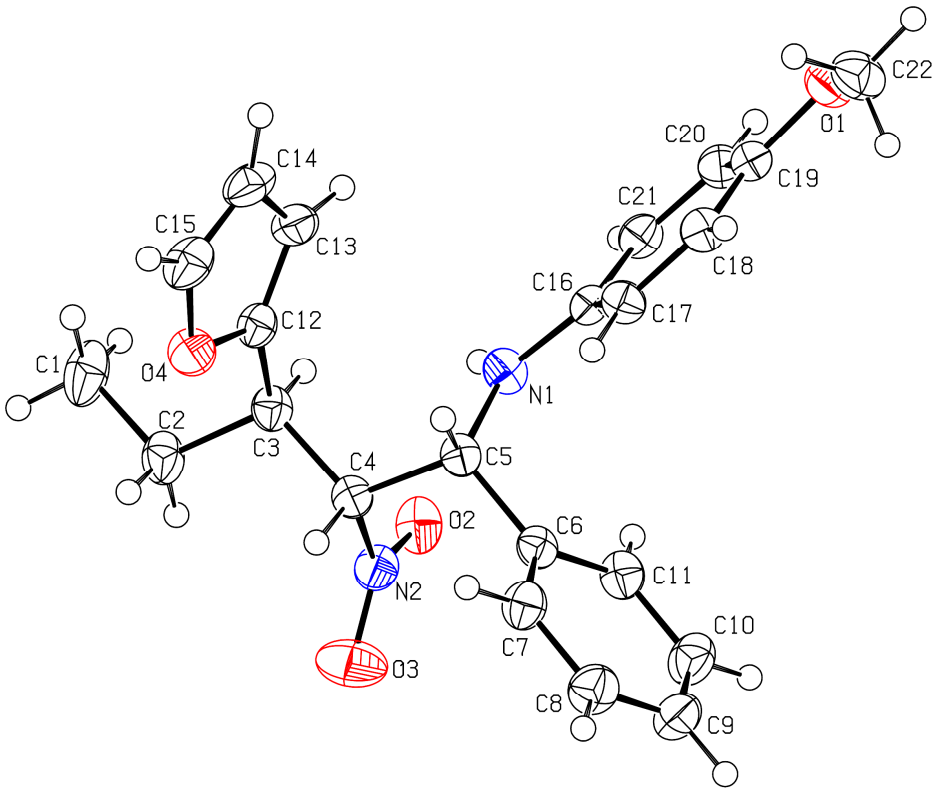

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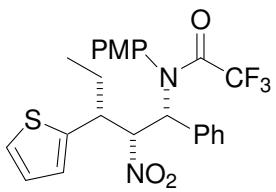
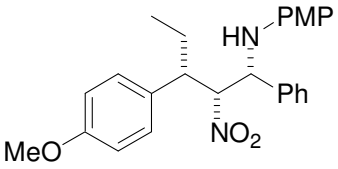
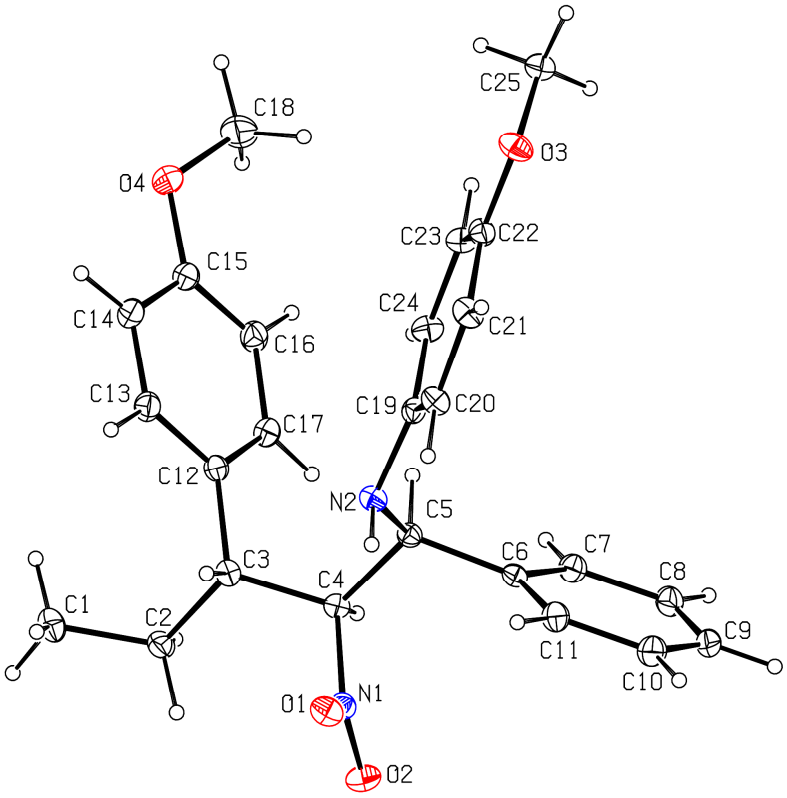


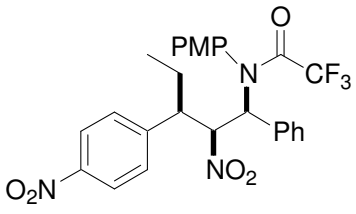
Entry 24 - Ligand **8**, PhMe



X-ray of enantiomer.

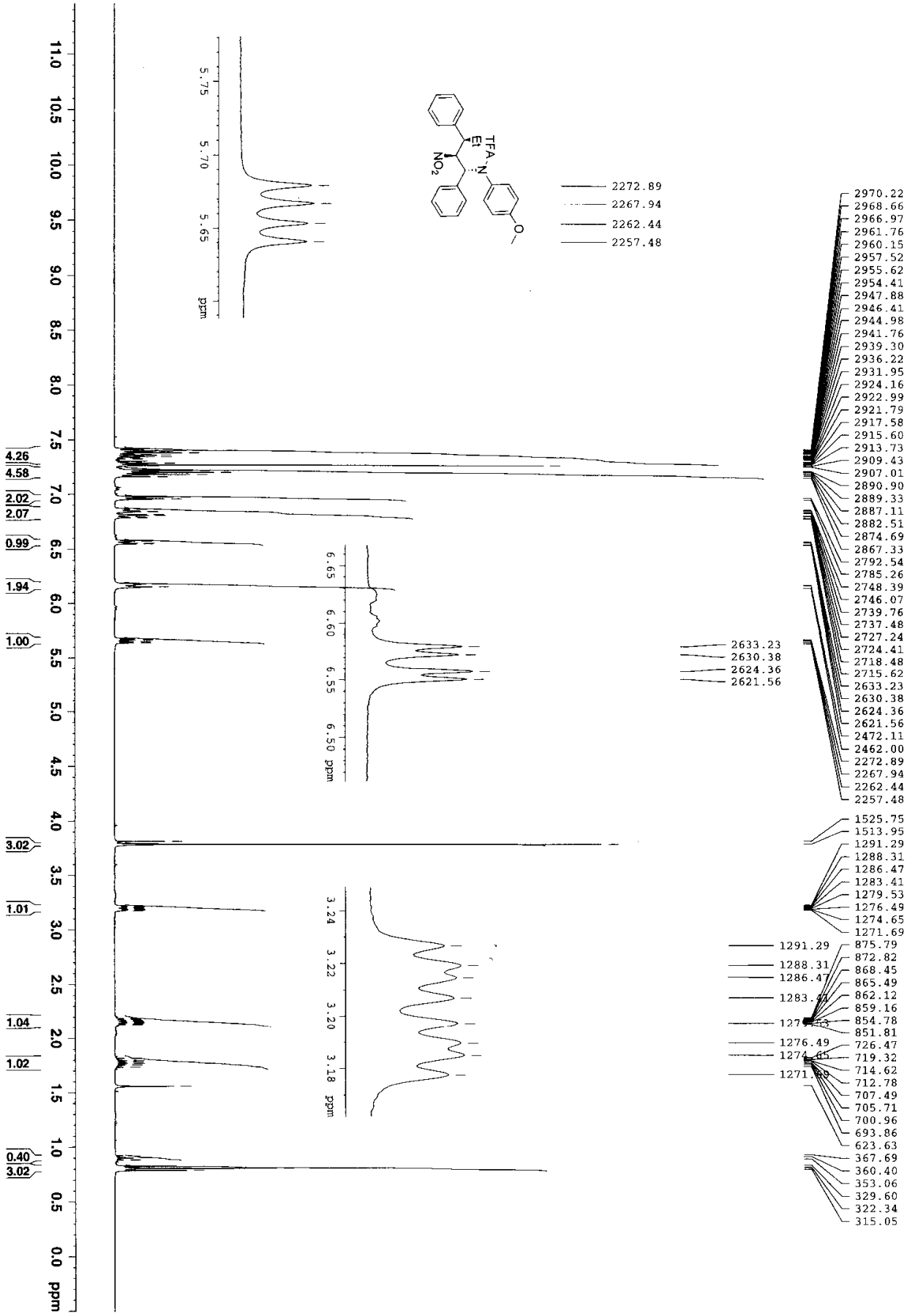


Entry 25 – no ligand, diethyl zinc addition in THF, nitro-Mannich in Et_2O

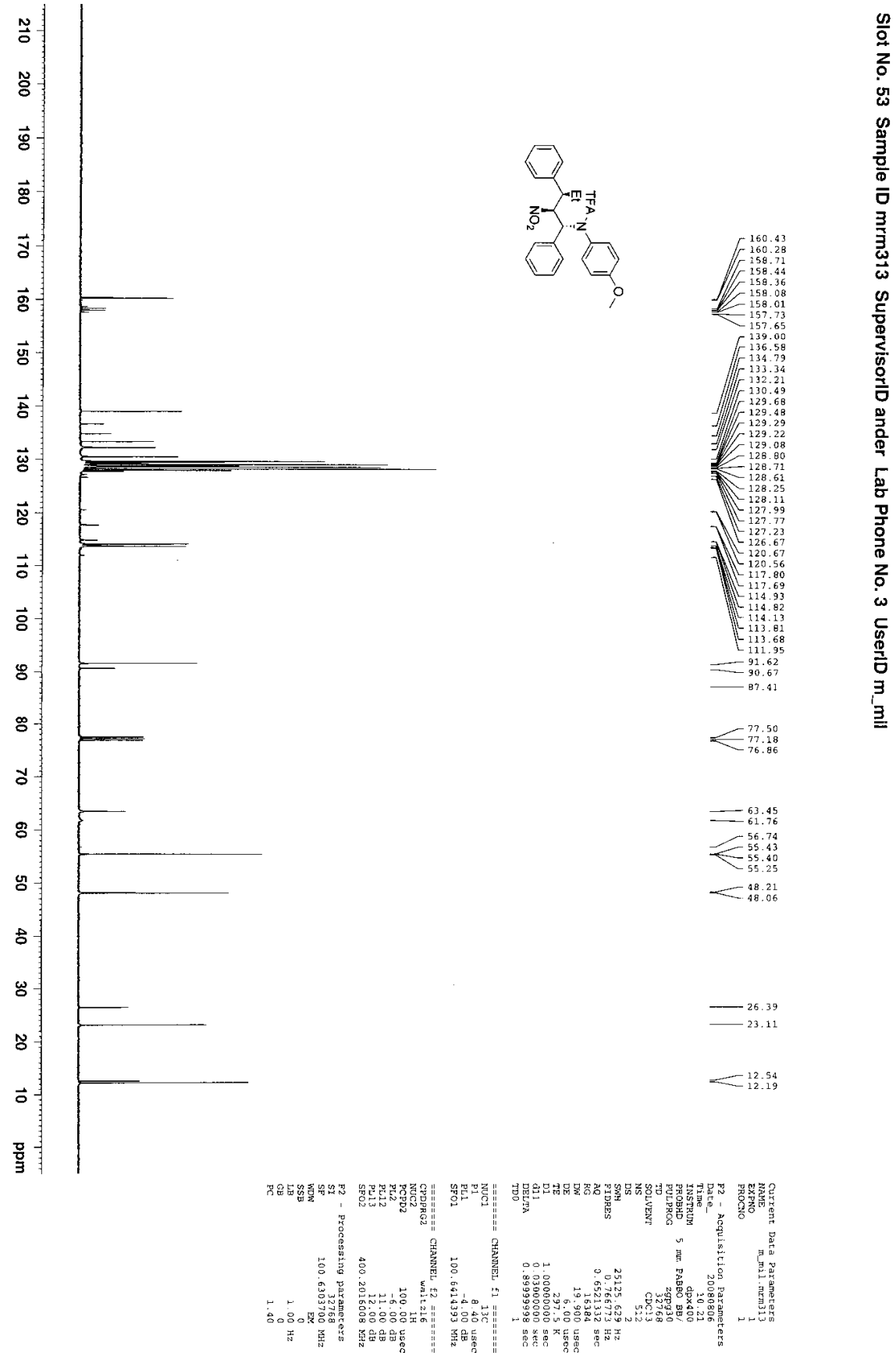


1. a) Fieser, L. F.; Gates, M. *J. Am. Chem. Soc.* **1946**, *68*, 2249. b) Melton, J.; McMurry, J. E. *J. Org. Chem.* **1975**, *40*, 2138.
2. a) Kumaran, G.; Kulkarni, G.H. *Synthesis*, **1995**, 1545. b) Enders, D.; Wiedemann, J. *Synthesis*, **1996**, 1443.
3. Côté, A.; Charette, A.B. J. Org. Chem. **2005**, *70*, 10864.
4. Mampreian, D. M.; Hoveyda, A. H. Org. Lett. 2004, *6*, 2829.
5. Adams, H.; Anderson, J. C.; Peace, S.; Pennell, A. M. K. *J. Org Chem.* **1998**, *63*, 9932.

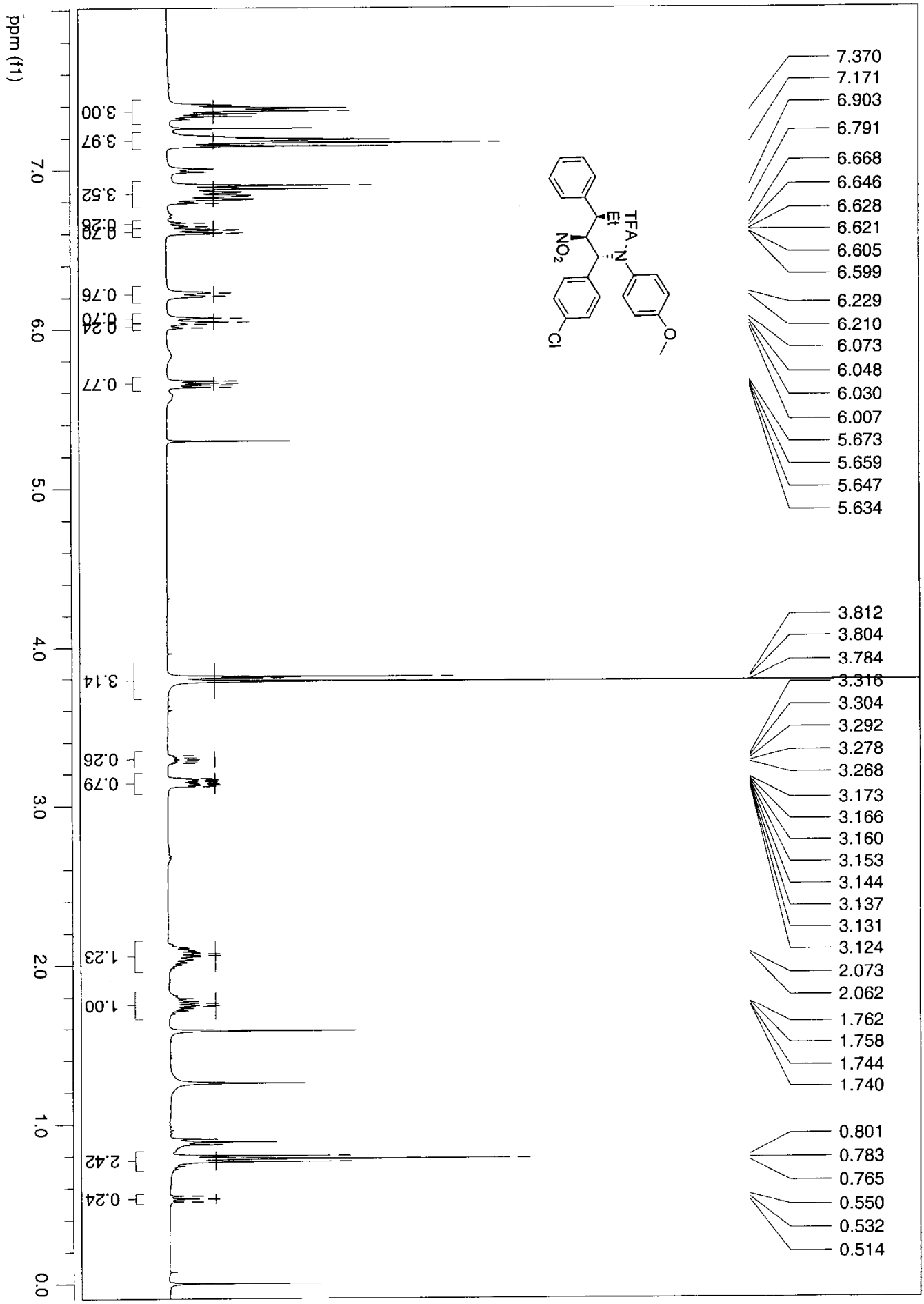
^{1}H NMR **Entry 1**



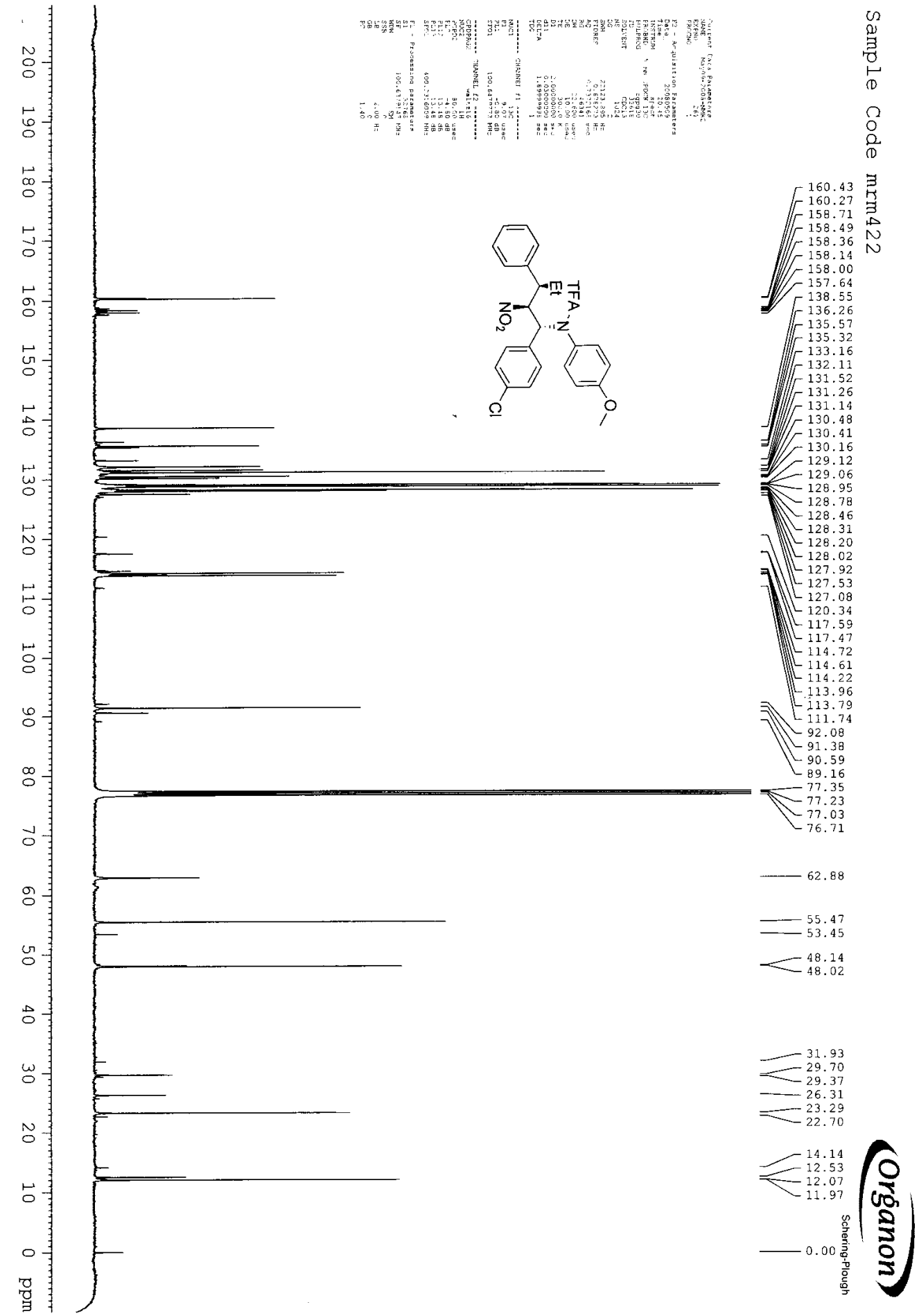
^{13}C NMR **Entry 1**



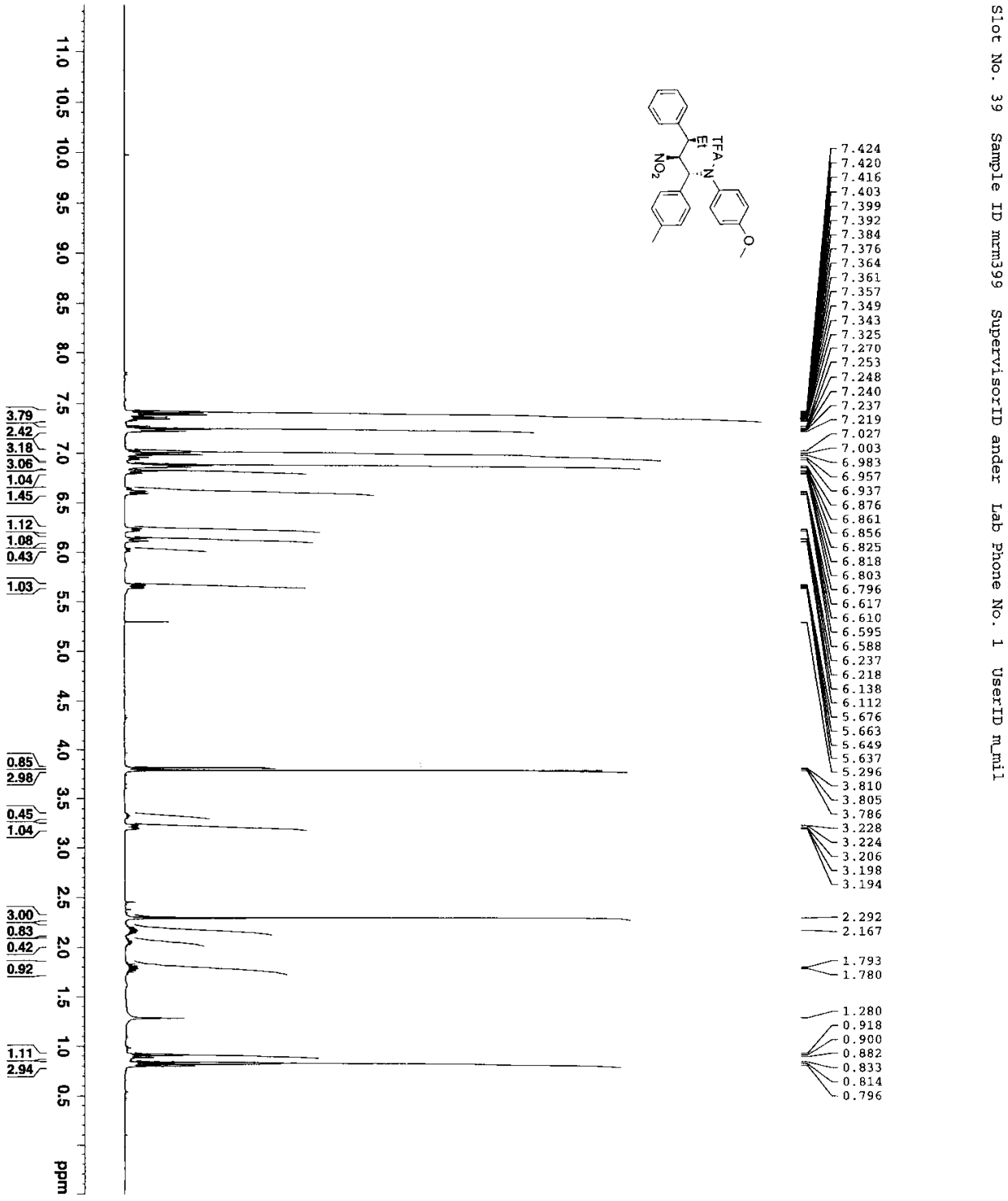
^{1}H NMR **Entry 2**



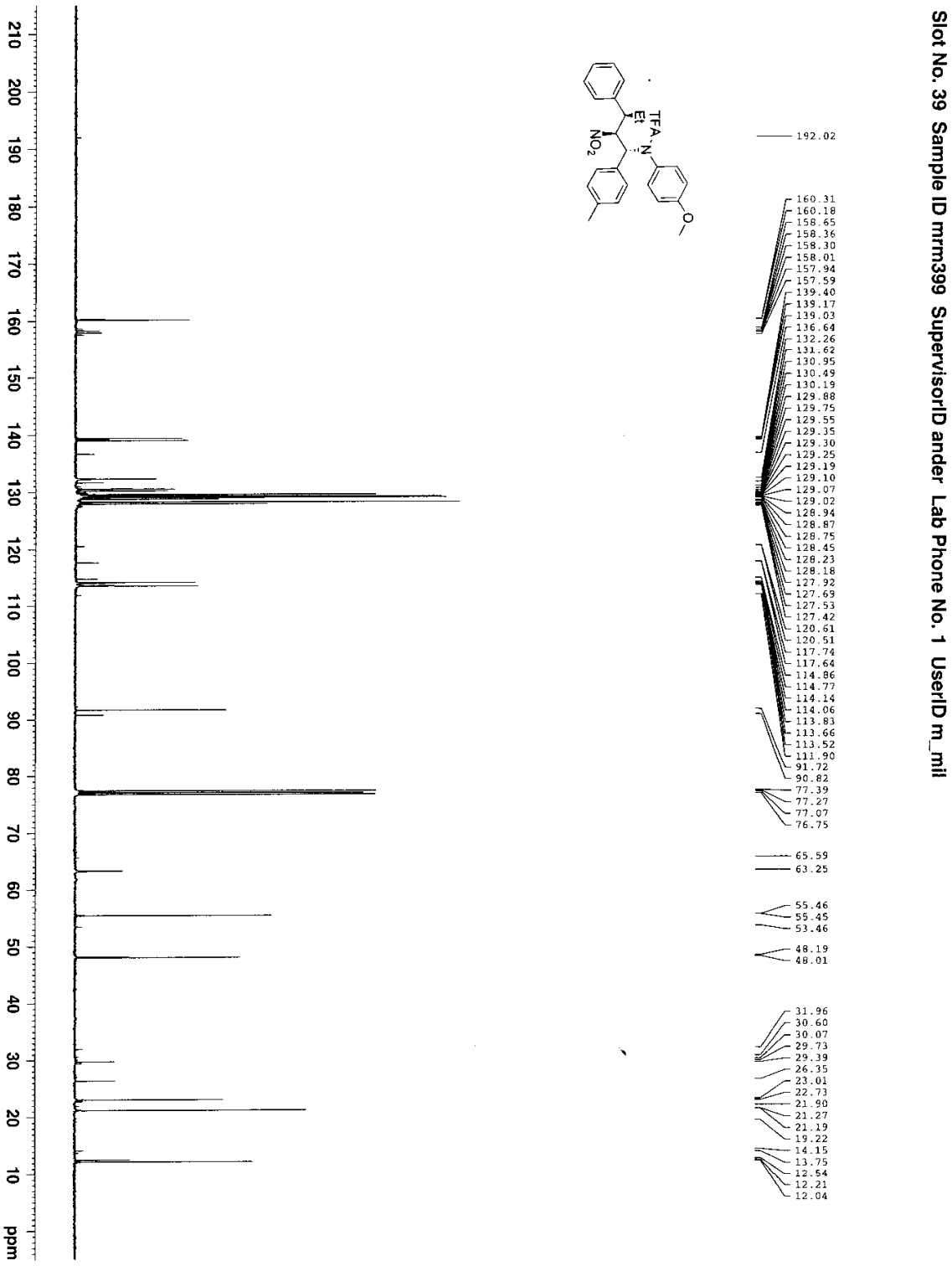
^{13}C NMR **Entry 2**



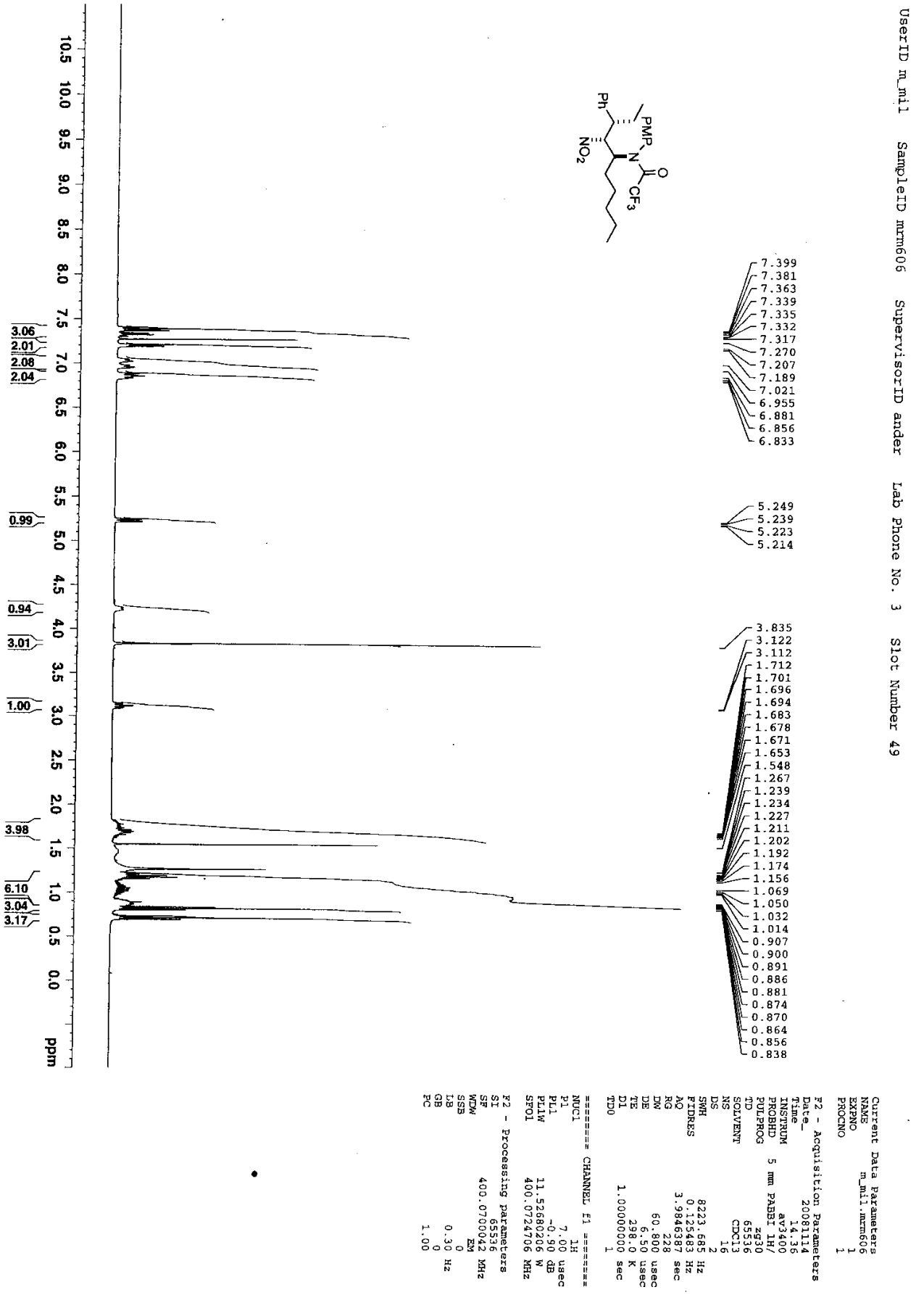
^{1}H NMR **Entry 3**



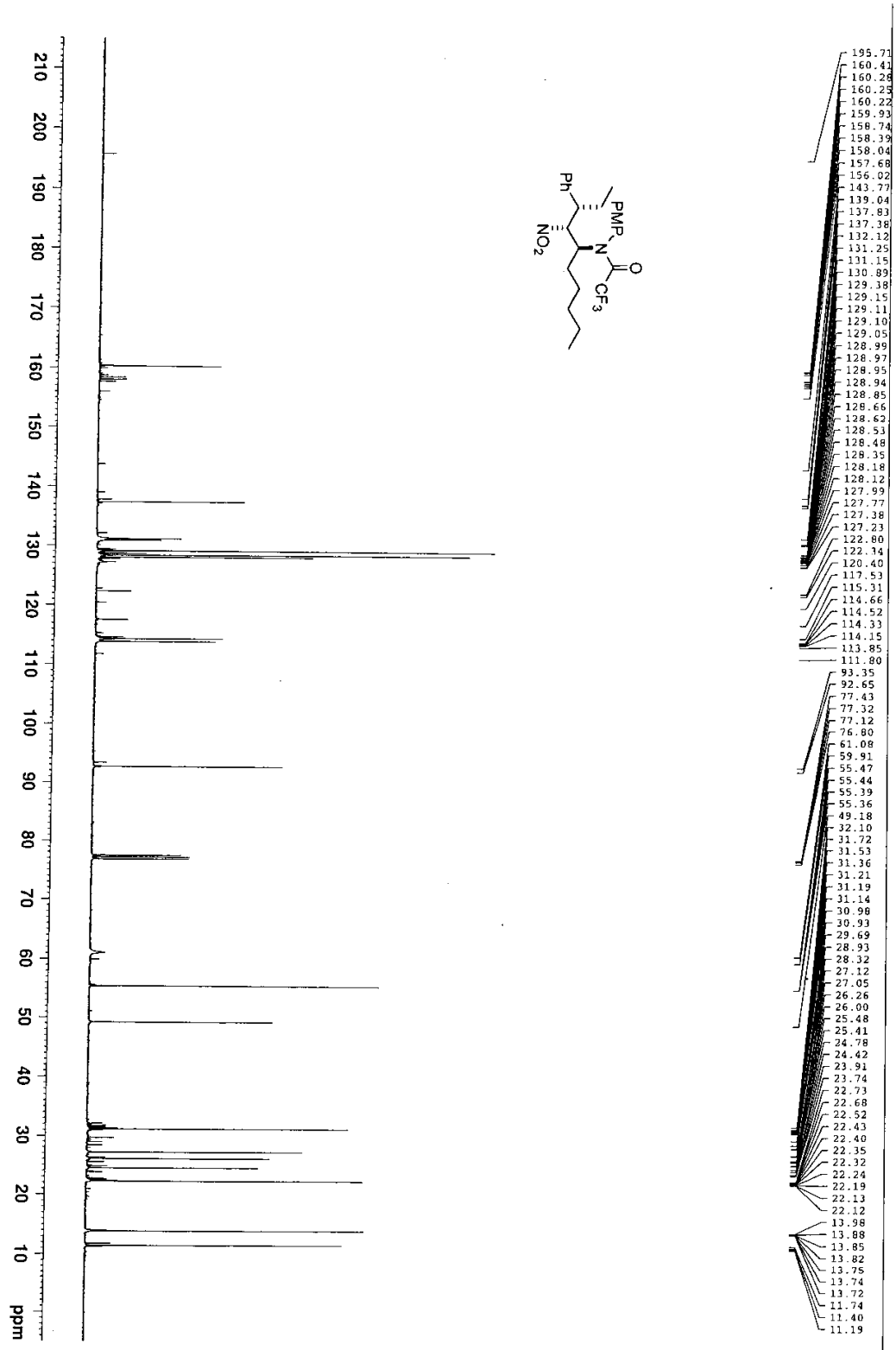
^{13}C NMR **Entry 3**



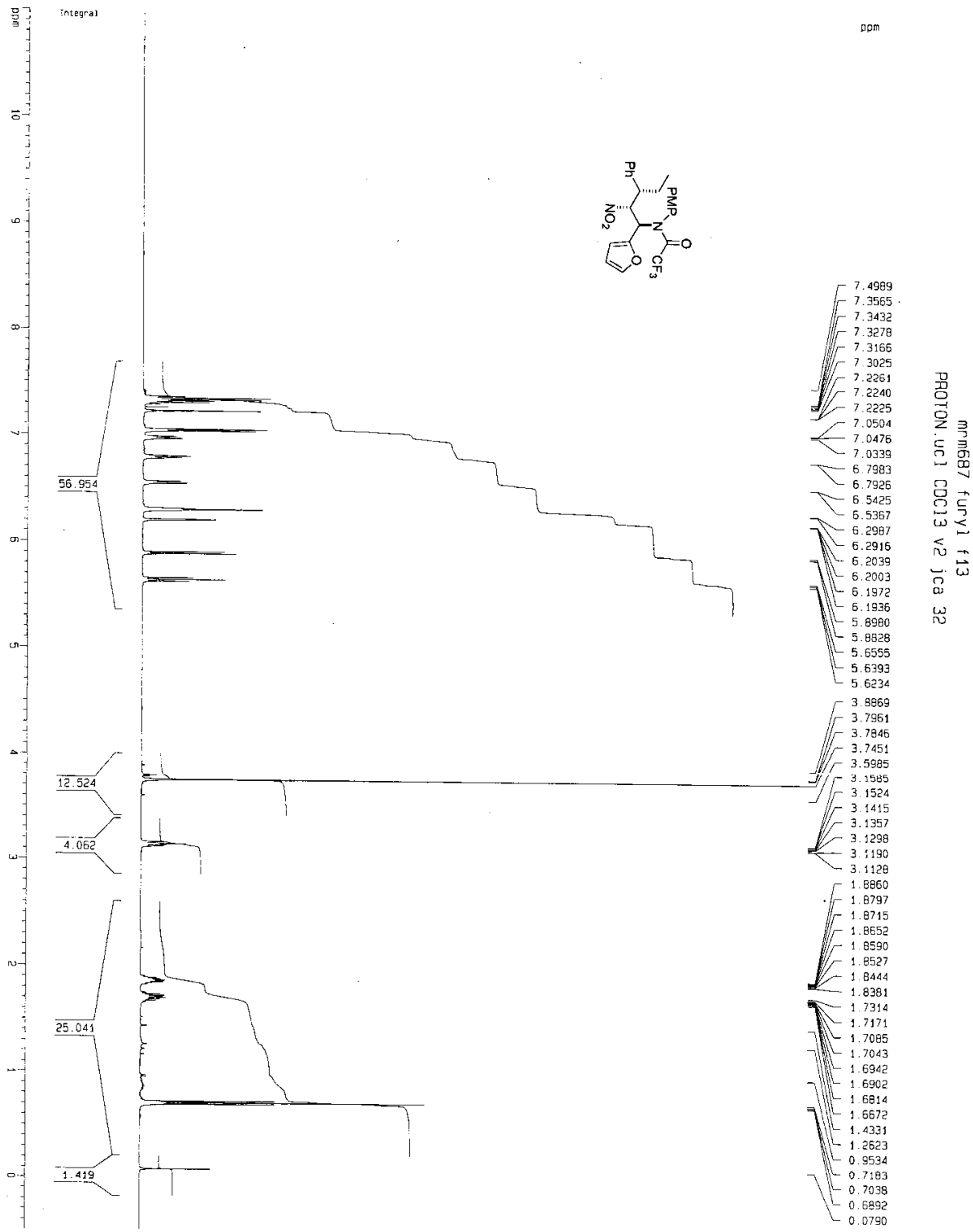
^{1}H NMR **Entry 4**



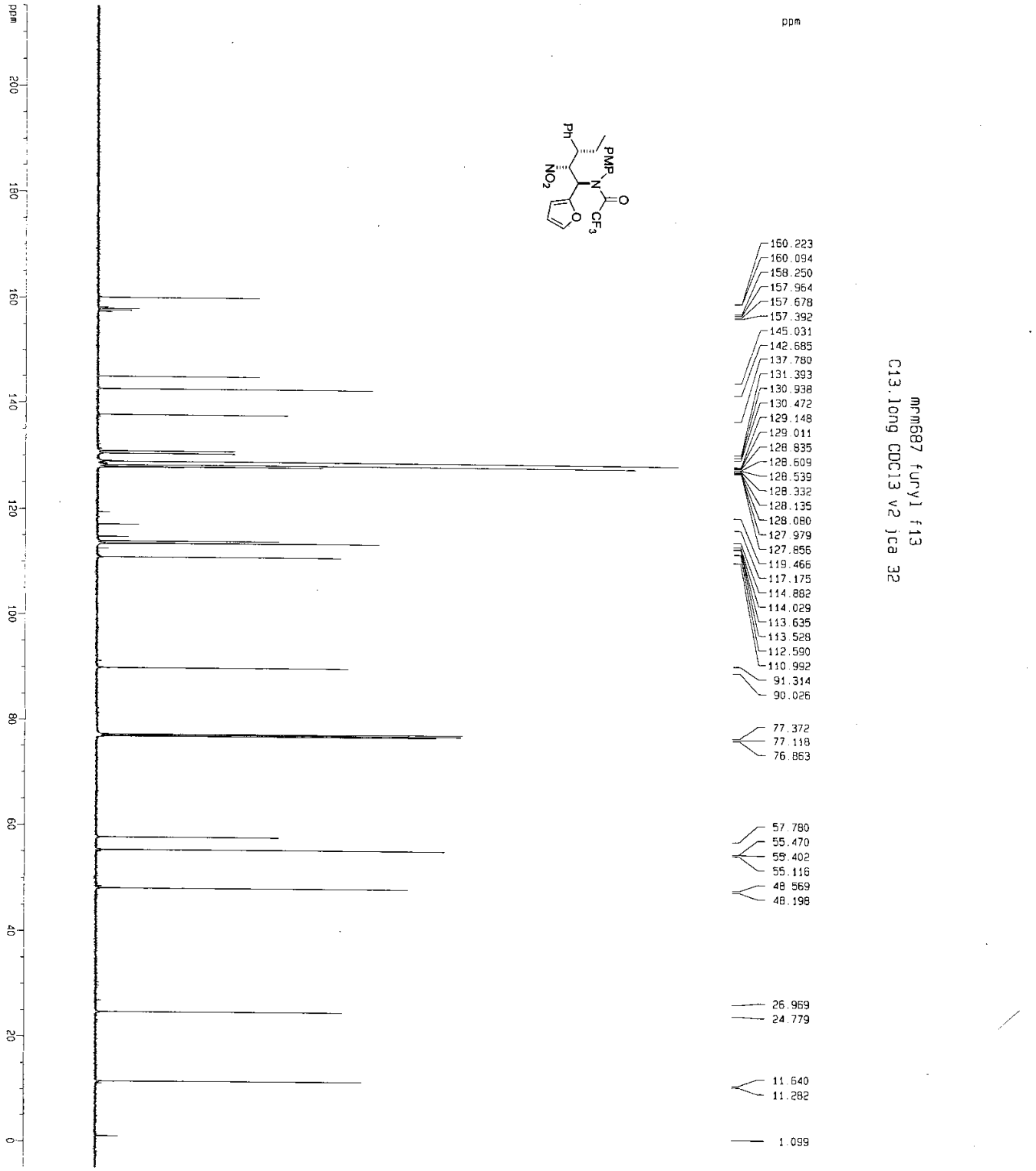
^{13}C NMR **Entry 4**



^{1}H NMR **Entry 5**



^{13}C NMR **Entry 5**

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EXPNO                        103
PROCNO                         1

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Time                        1.14
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PULPROG                  zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                         1024
DS                            4
SWH                  31446.541 Hz
FIDRES                0.479836 Hz
AQ                    1.0420724 sec
RG                         3649.1
DW                        15.900 usec
DE                         6.00 usec
TE                        300.0 K
D1                    2.00000000 sec
d11                   0.03000000 sec
d12                   0.00002000 sec

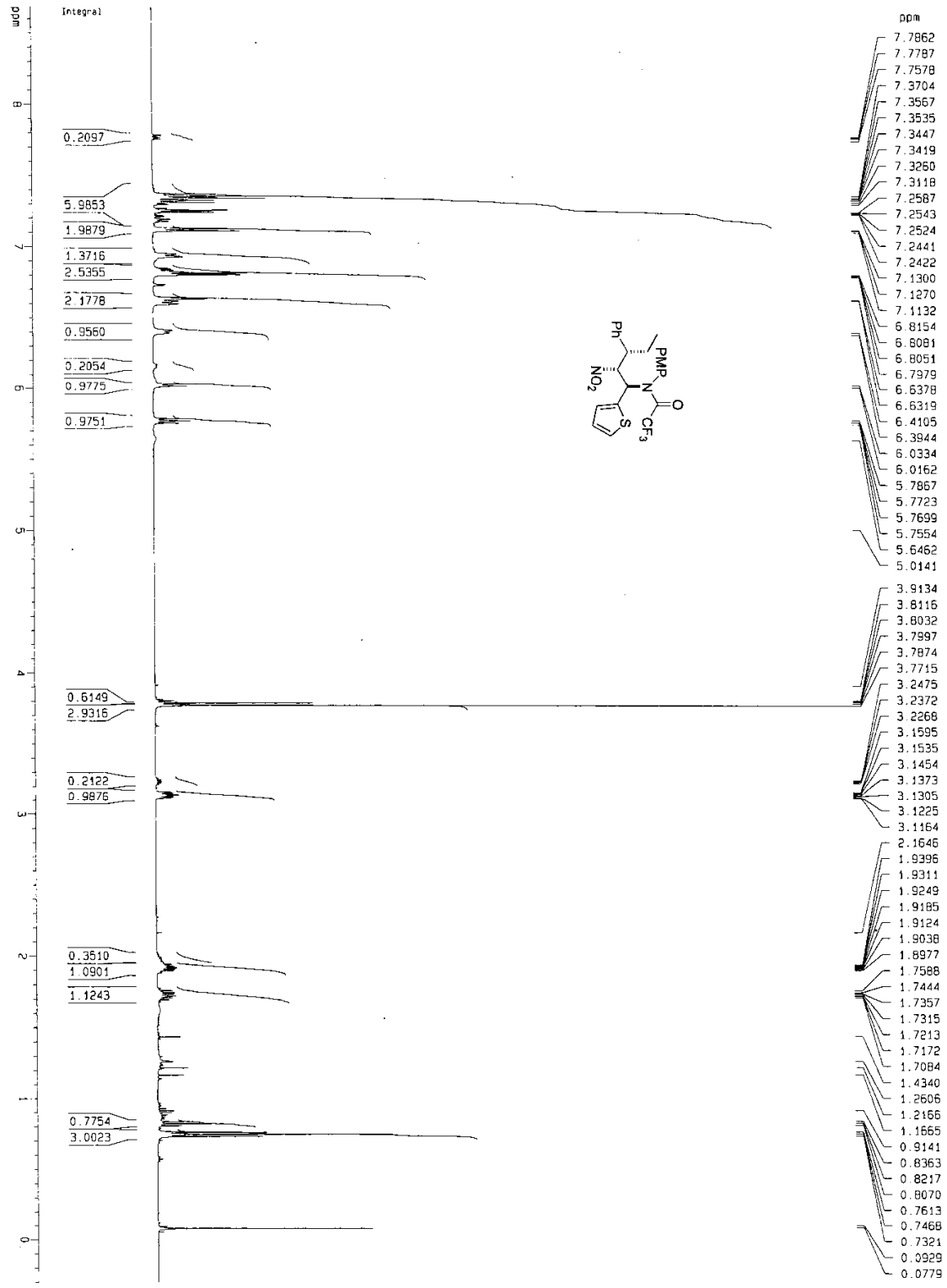
======== CHANNEL f1 ========
NUC1                         13C
P1                          5.50 usec
PL1                         0.00 dB
SFO1                 125.7715719 MHz

======== CHANNEL f2 ========
CPDPRG2                   waltz16
NUC2                          1H
PCPD2                     95.00 usec
PL2                        0.00 dB
PL12                      19.00 dB
PL13                      19.00 dB
SFO2                 500.1320005 MHz

F2 - Processing parameters
SI                           32768
SF                   125.7577814 MHz
WDW                             EM
SSB                              0
LB                        1.00 Hz
GB                               0
PC                        1.40

1D NMR plot parameters
CX                           32.00 cm
F1P                         215.000 ppm
F1                        27037.93 Hz
F2P                        -5.000 ppm
F2                        -628.79 Hz
PPMCM                      6.87500 ppm/cm
HZCM                     864.58478 Hz/cm
```

^{1}H NMR **Entry 6**

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NAME                  Jul07-2009
EXPNO                         22
PROCNO                         1

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Time                        3.24
INSTRUM                  drx500
PROBHD     5 mm Multinu
PULPROG                    1930
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            0
SWH                  10330.578 Hz
FIDRES                0.157632 Hz
AQ                    3.1719923 sec
RG                         90.5
DW                       48.400 usec
DE                        5.00 usec
TE                       300.0 K
D1                    1.00000000 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                        15.50 usec
PL1                        0.00 dB
SFO1              500.1330885 MHz

F2 - Processing parameters
SI                        65536
SF                500.1300140 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        32.00 cm
F1P                       8.683 ppm
F1                     4342.65 Hz
F2P                      -0.302 ppm
F2                     -151.14 Hz
PPMCM                  0.28079 ppm/cm
HZCM                 140.43115 Hz/cm
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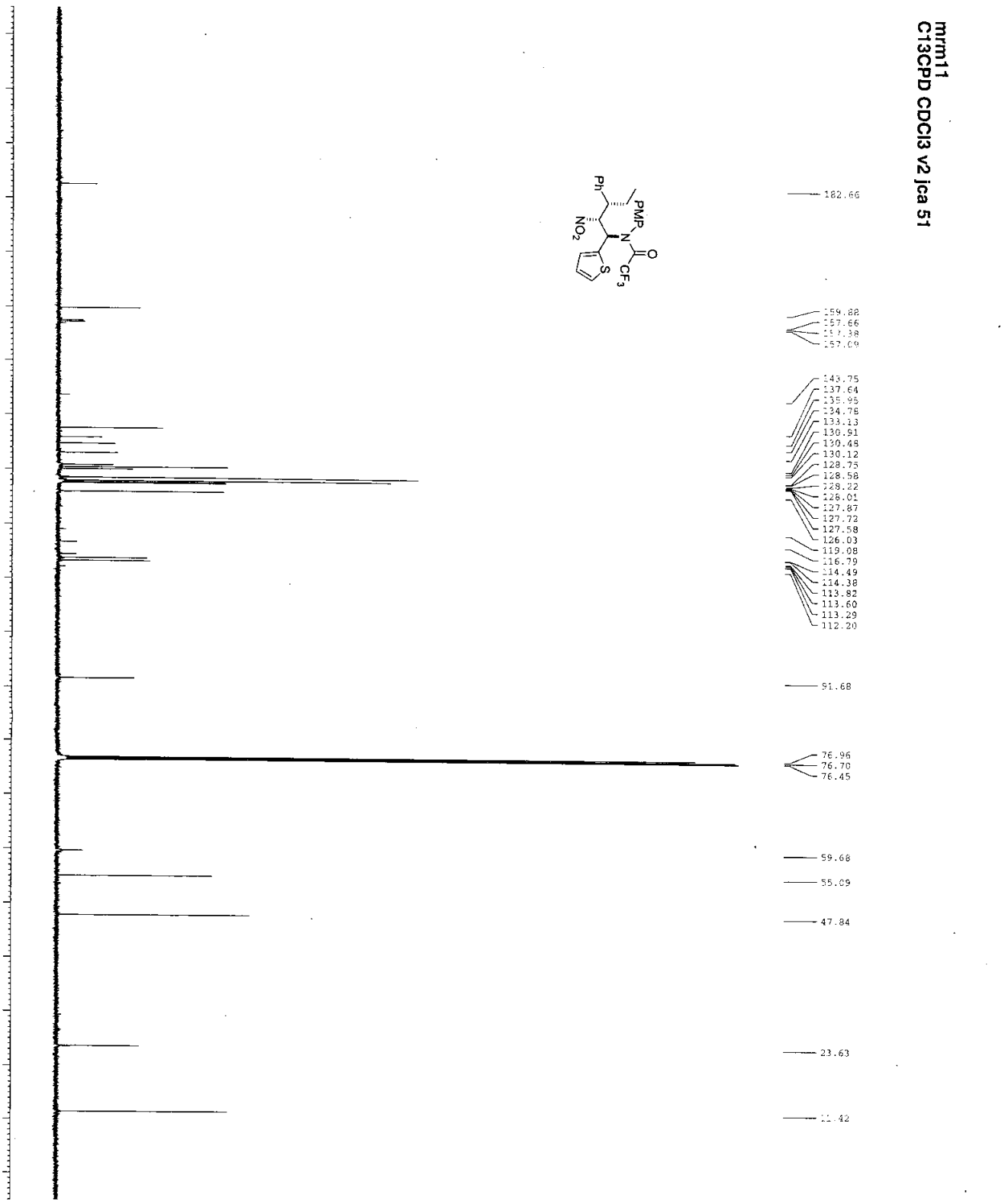
^{13}C NMR **Entry 6**



Current Data Parameters
NAME Dec01-2009
EXPNO 30
PROCNO 1

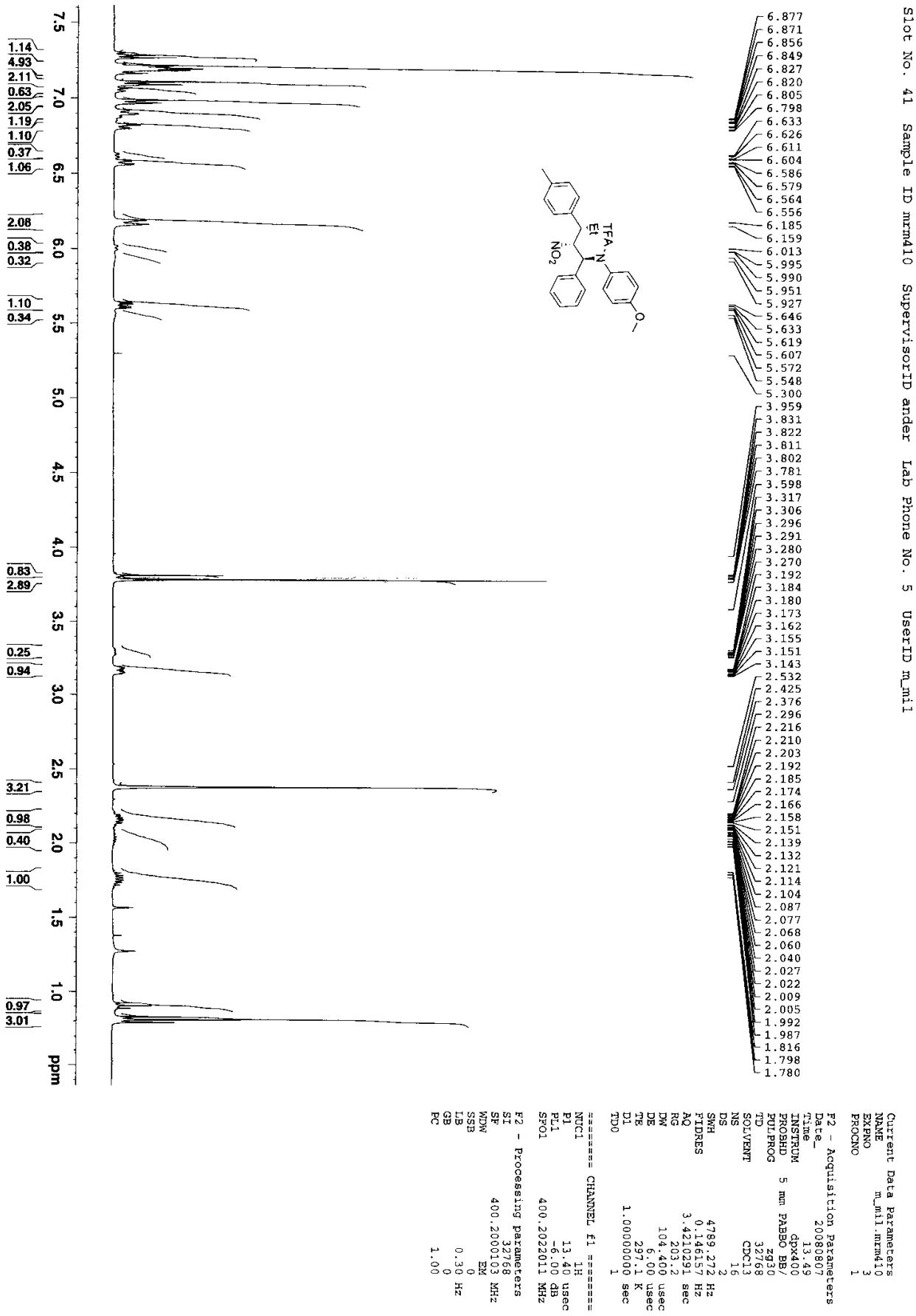
F2 - Acquisition Parameters
Date_ 20091201
Time 14.03
INSTRUM drx500
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 9195.2
DW 16.650 use
DE 6.00 use
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 5.50 use
PL1 0.00 dB
SFO1 125.7703643 MHz

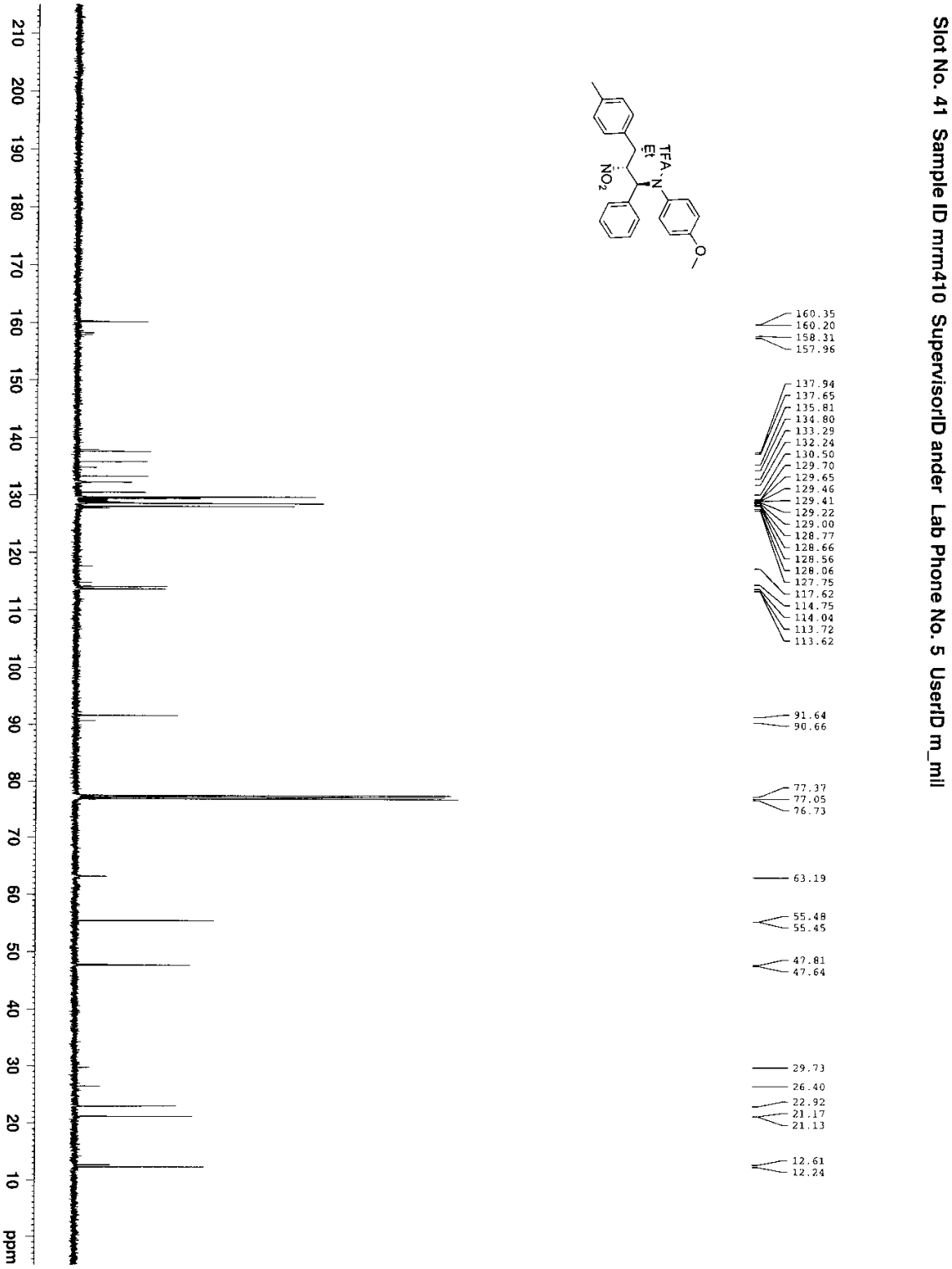
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 use
PL2 0.00 dB
PL12 19.00 dB
PL13 19.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7578314 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

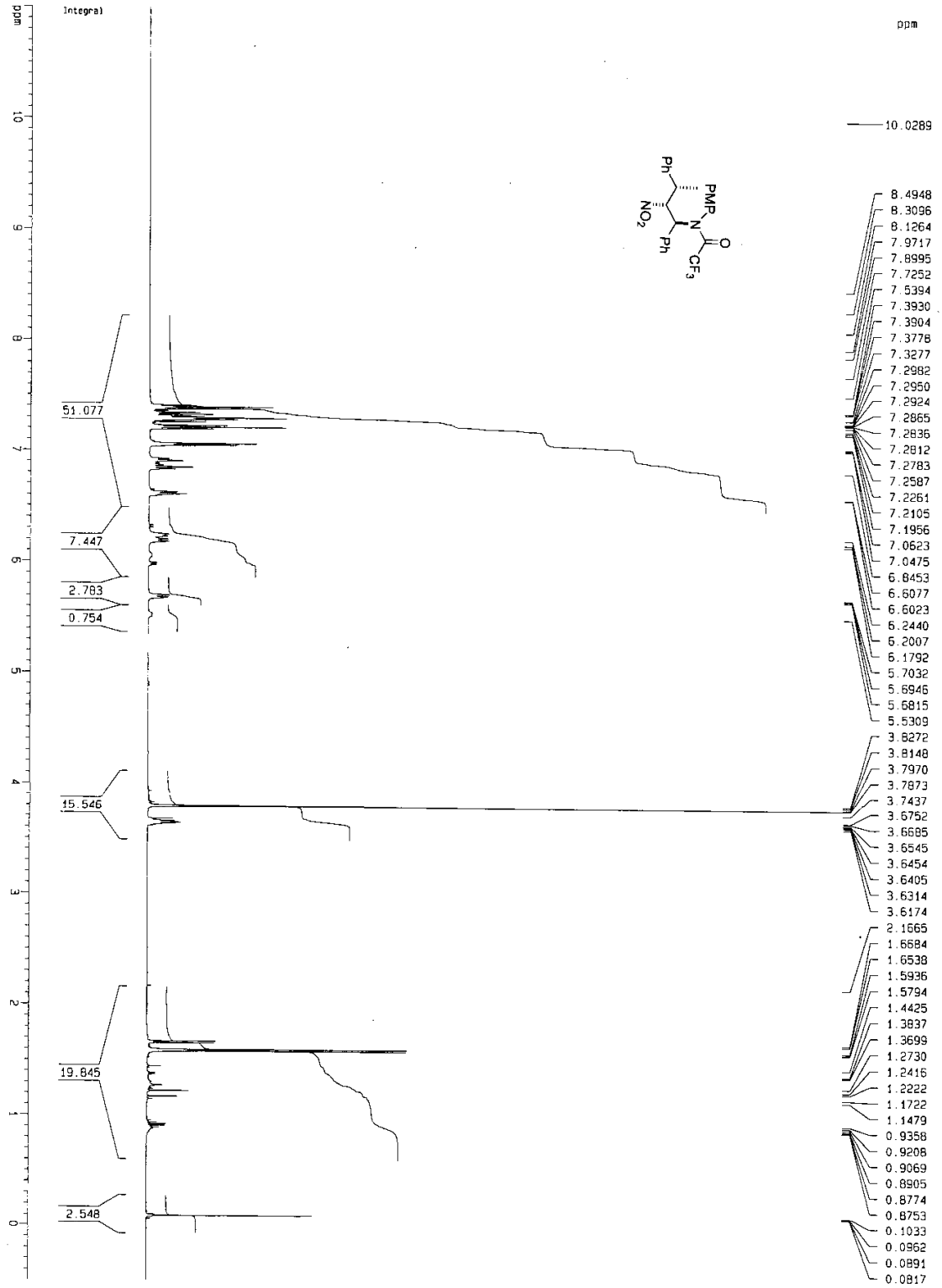
^{1}H NMR **Entry 7**



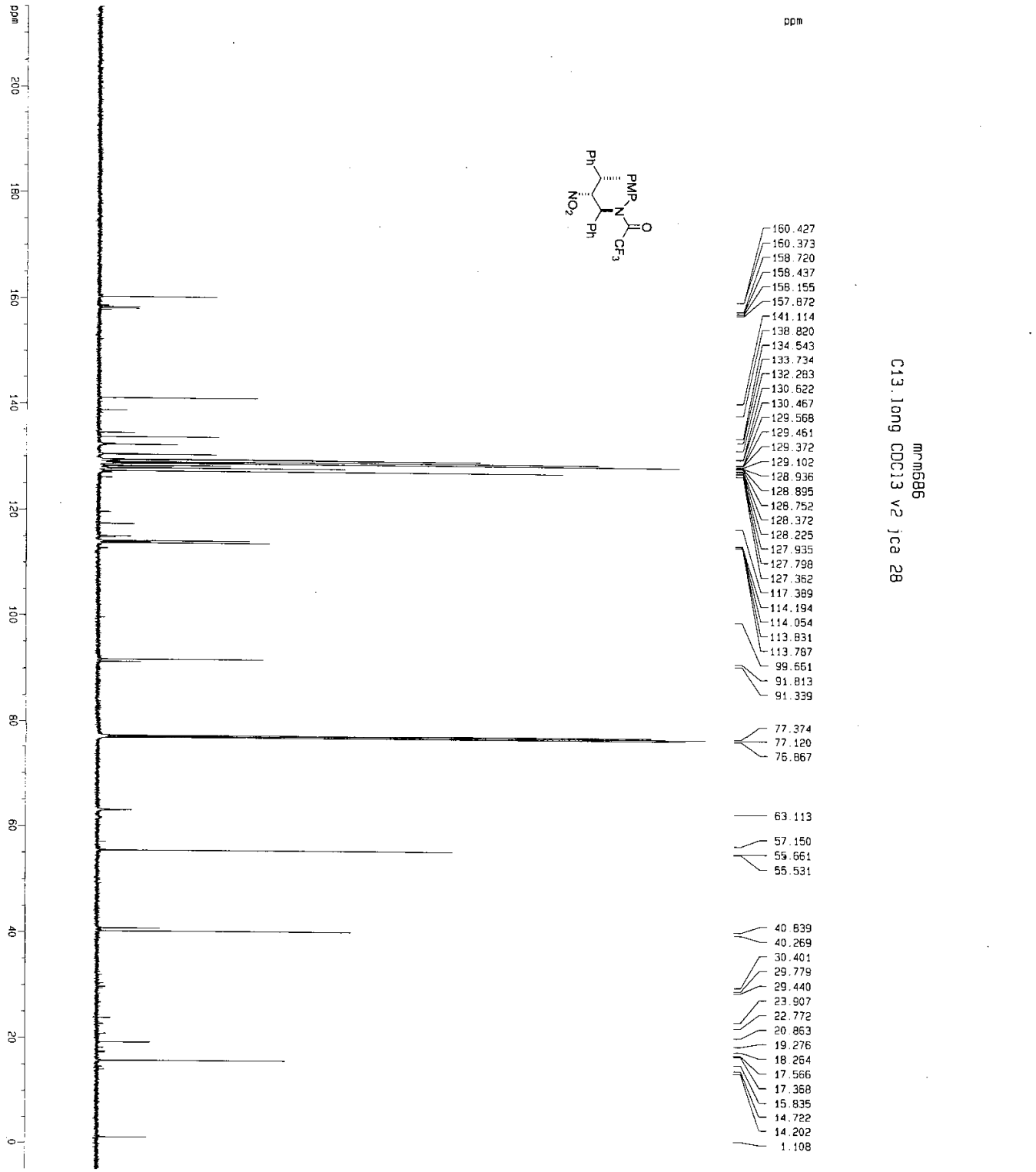
^{13}C NMR **Entry 7**



^{1}H NMR **Entry 8**



^{13}C NMR **Entry 8**

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PROCNO                          1

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Time                    5.00
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PROBHD     5 mm Multinu
PULPROG                 zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1024
DS                          4
SWH                 31446.541 Hz
FIDRES              0.479836 Hz
AQ                  1.0420724 sec
RG                      3649.1
DW                     15.900 usec
DE                      6.00 usec
TE                     300.0 K
D1                  2.00000000 sec
d11                 0.03000000 sec
d12                 0.00002000 sec

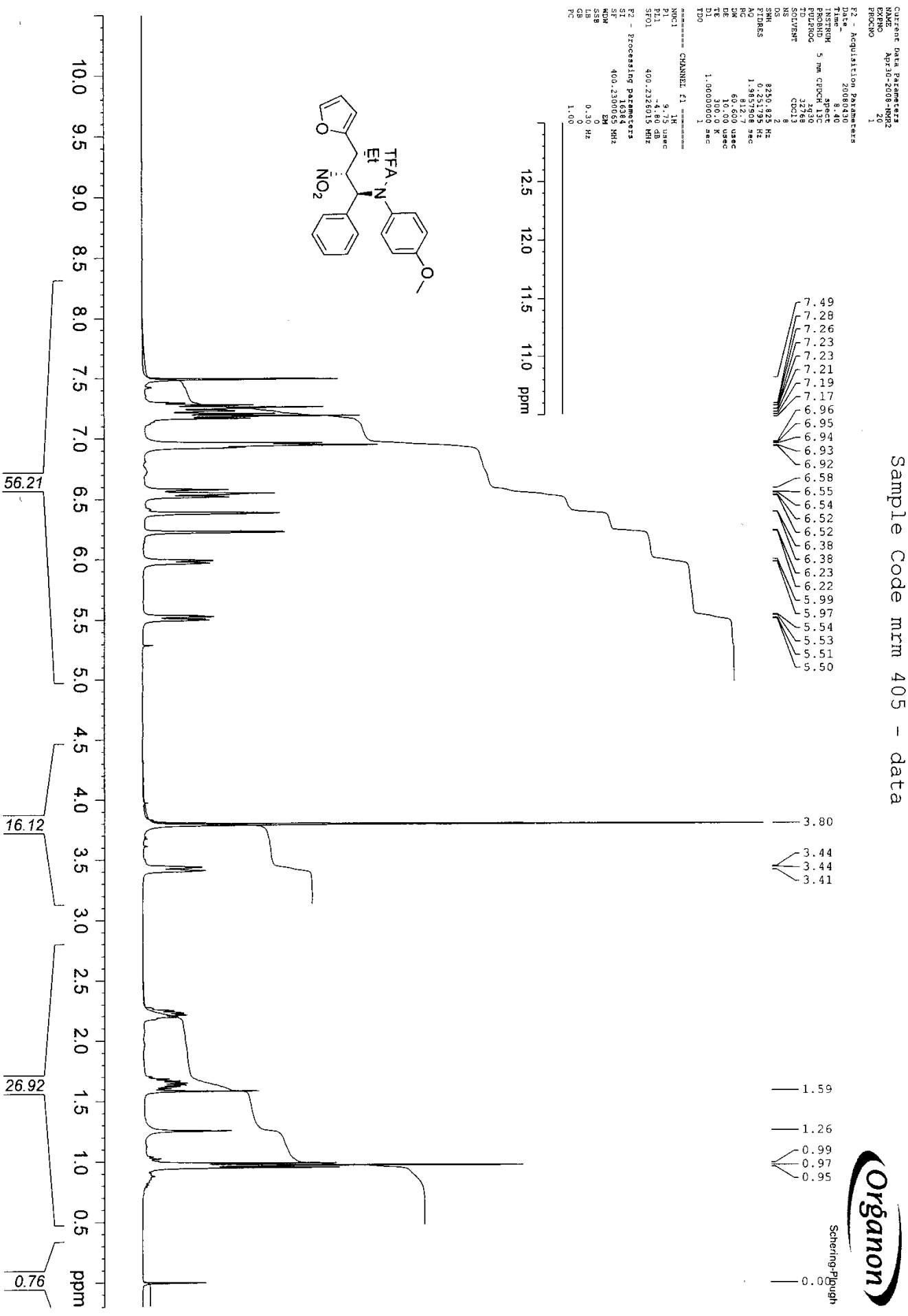
======== CHANNEL f1 ========
NUC1                       13C
P1                        5.50 usec
PL1                       0.00 dB
SFO1                125.7715719 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                    95.00 usec
PL2                       0.00 dB
PL12                     19.00 dB
PL13                     19.00 dB
SFO2                500.1320005 MHz

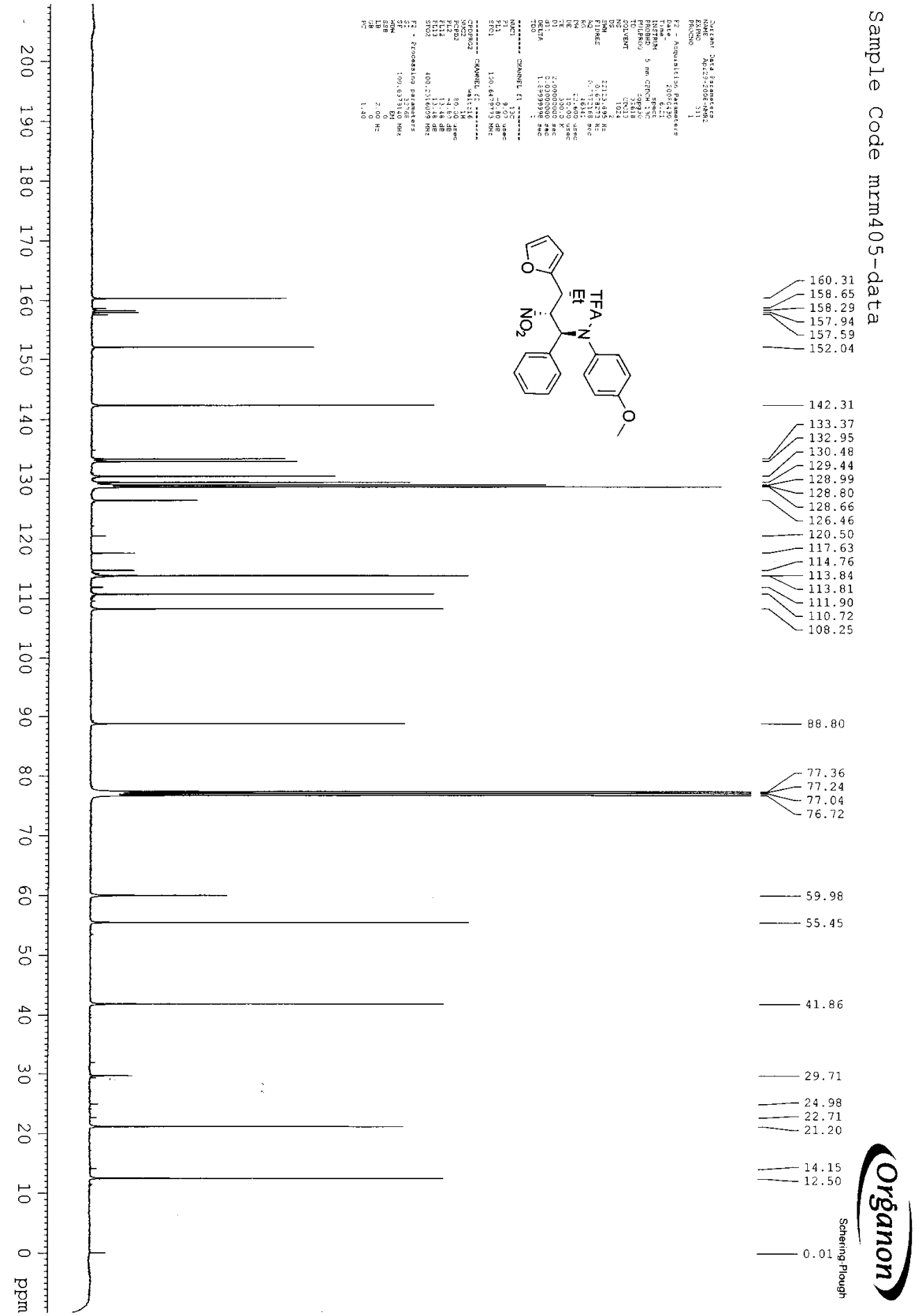
F2 - Processing parameters
SI                         32768
SF                  125.7577814 MHz
WDW                            EM
SSB                             0
LB                       1.00 Hz
GB                              0
PC                           1.40

1D NMR plot parameters
CX                        32.00 cm
F1P                     215.000 ppm
F1                     27037.93 Hz
F2P                     -5.000 ppm
F2                     -628.79 Hz
PPMCM                  6.87500 ppm/cm
HZCM                 864.58478 Hz/cm
```

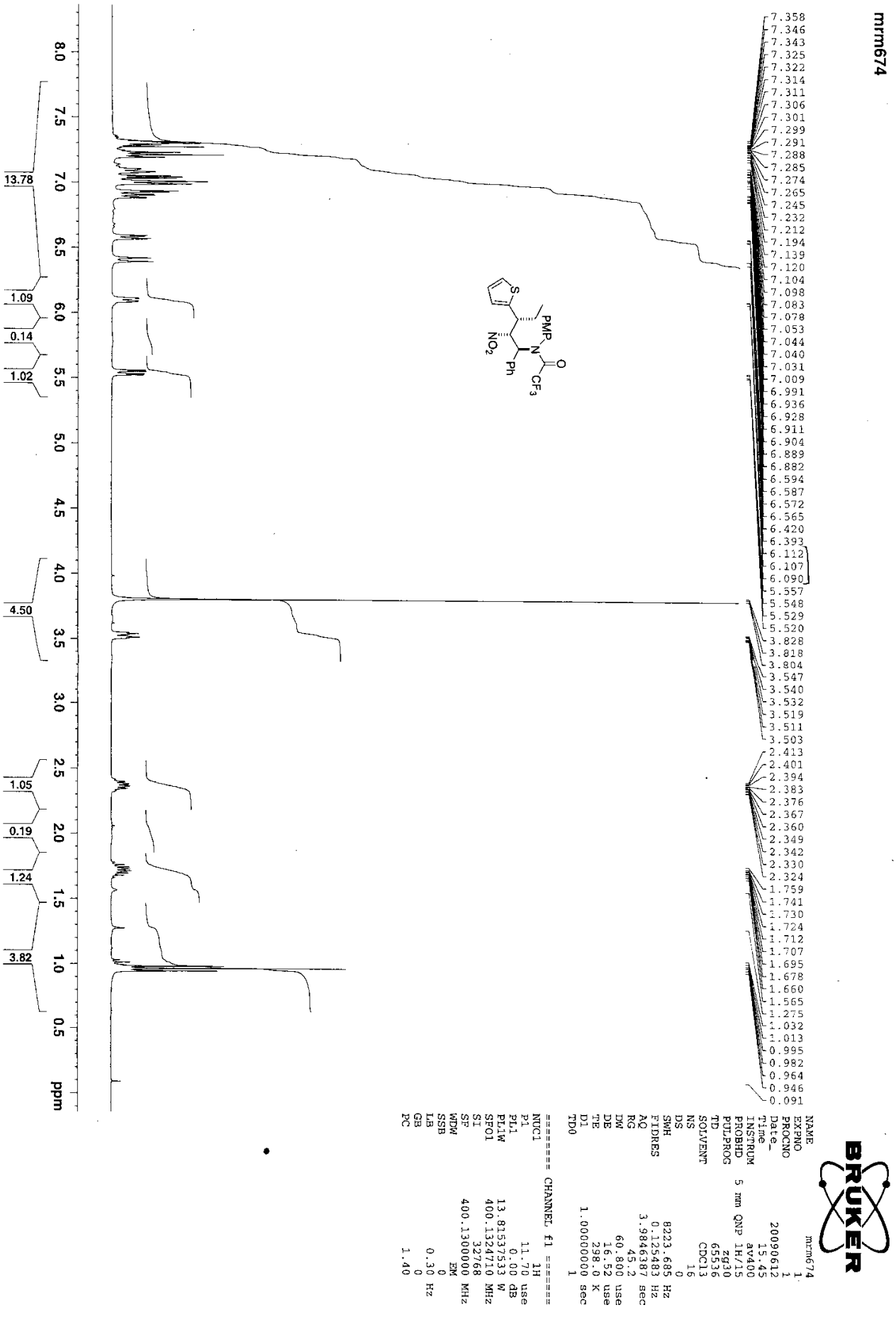
[1]H NMR **Entry 9**



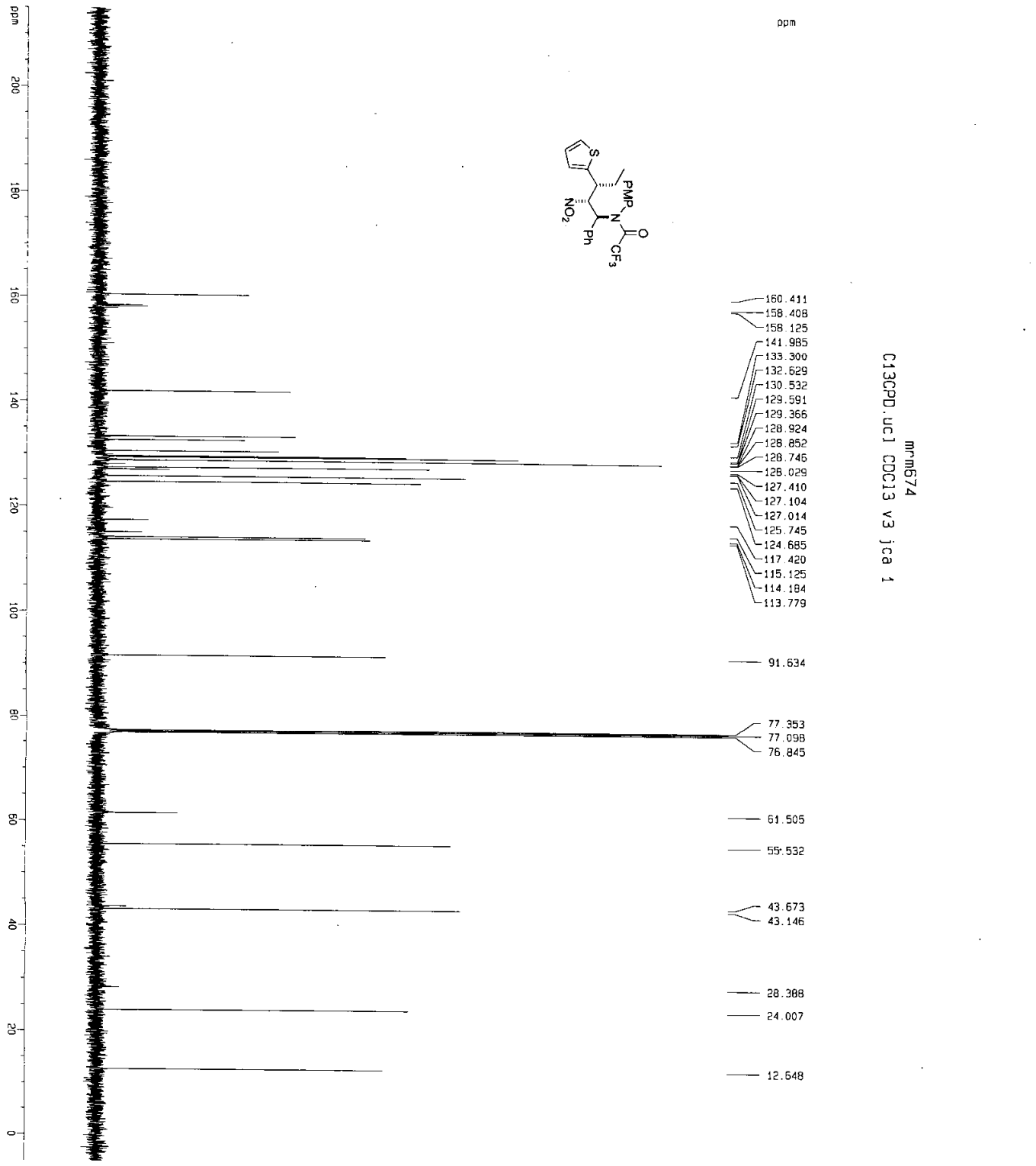
^{13}C NMR **Entry 9**



^{1}H NMR **Entry 10**



^{13}C NMR **Entry 10**

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Current Data Parameters
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PROCNO                         1

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Time                      20.08
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PROBHD     5 mm Multinu
PULPROG                 zgpg30
TD                       65536
SOLVENT                 CDCl3
NS                          256
DS                            4
SWH                 31446.541 Hz
FIDRES               0.479636 Hz
AQ                   1.0420724 sec
RG                        3649.1
DW                      15.900 usec
DE                       6.00 usec
TE                      300.0 K
D1                   2.00000000 sec
d11                  0.03000000 sec
d12                  0.00002000 sec

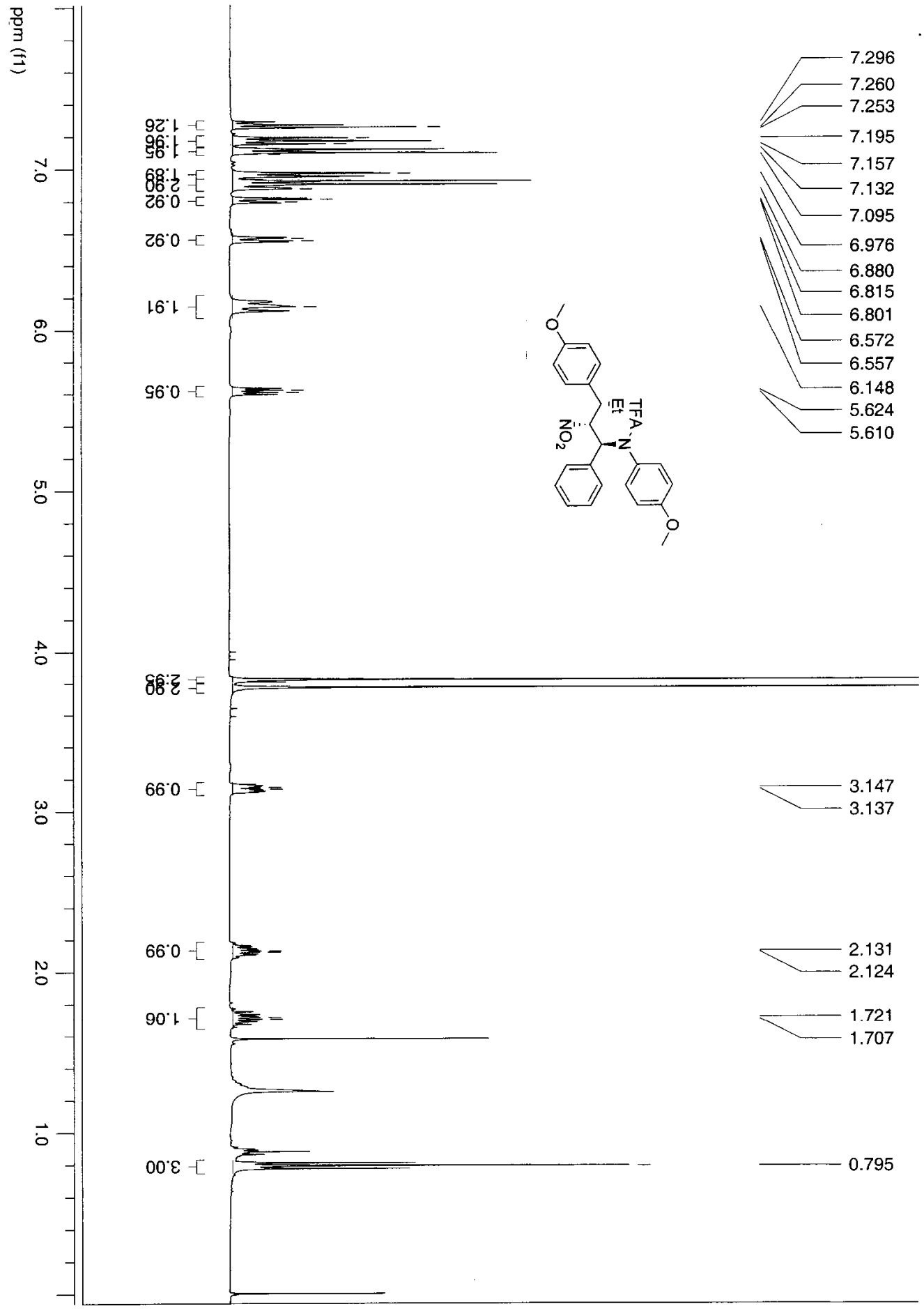
======== CHANNEL f1 ========
NUC1                       13C
P1                        5.50 usec
PL1                       0.00 dB
SFO1               125.7715719 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                   95.00 usec
PL2                       0.00 dB
PL12                     19.00 dB
PL13                     19.00 dB
SFO2               500.1320005 MHz

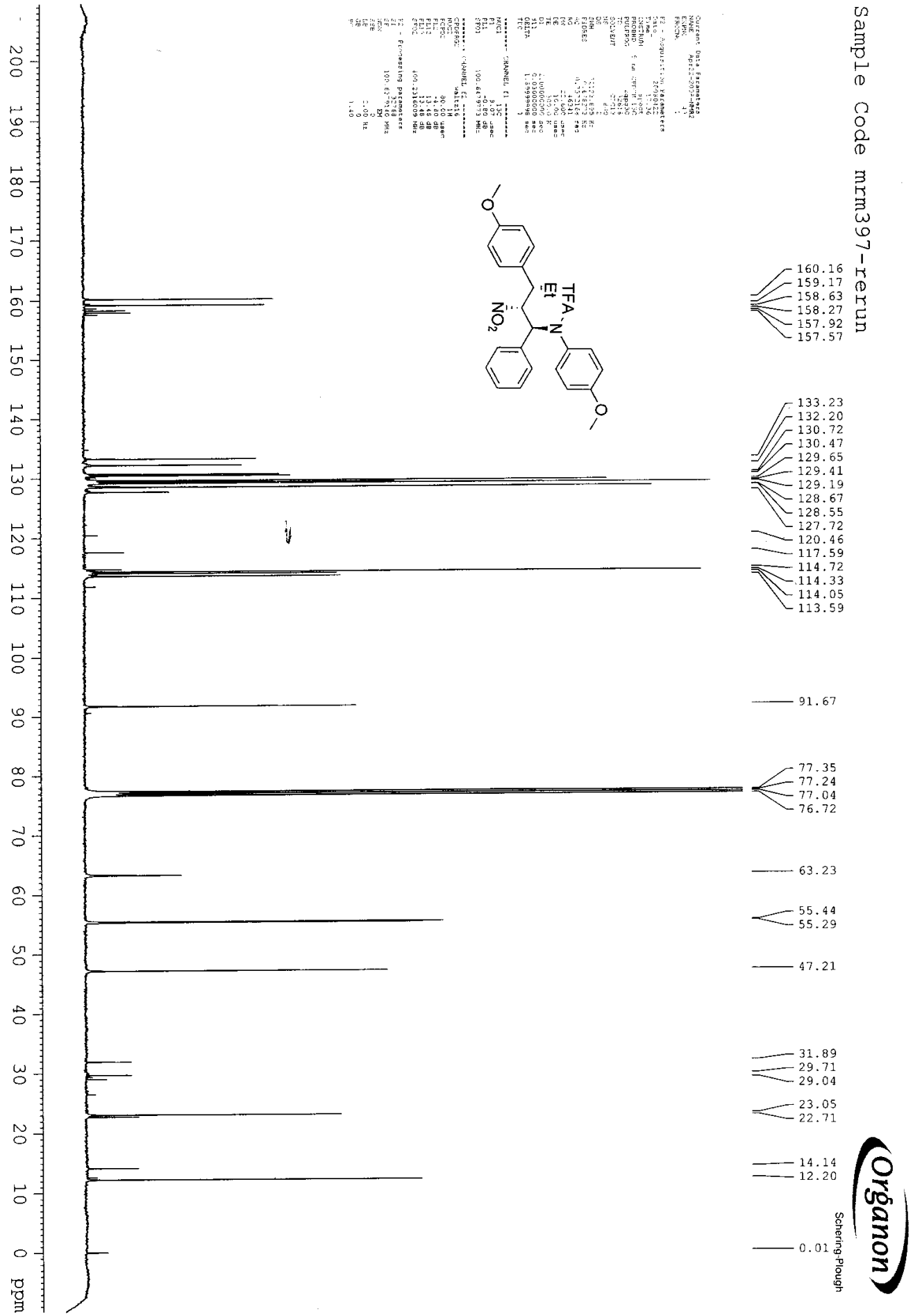
F2 - Processing parameters
SI                        32768
SF                 125.7577814 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40

1D NMR plot parameters
CX                        32.00 cm
F1P                     215.000 ppm
F1                     27037.93 Hz
F2P                     -5.000 ppm
F2                     -628.79 Hz
PPMCM                   6.87500 ppm/cm
HZCM                  864.58478 Hz/cm
```

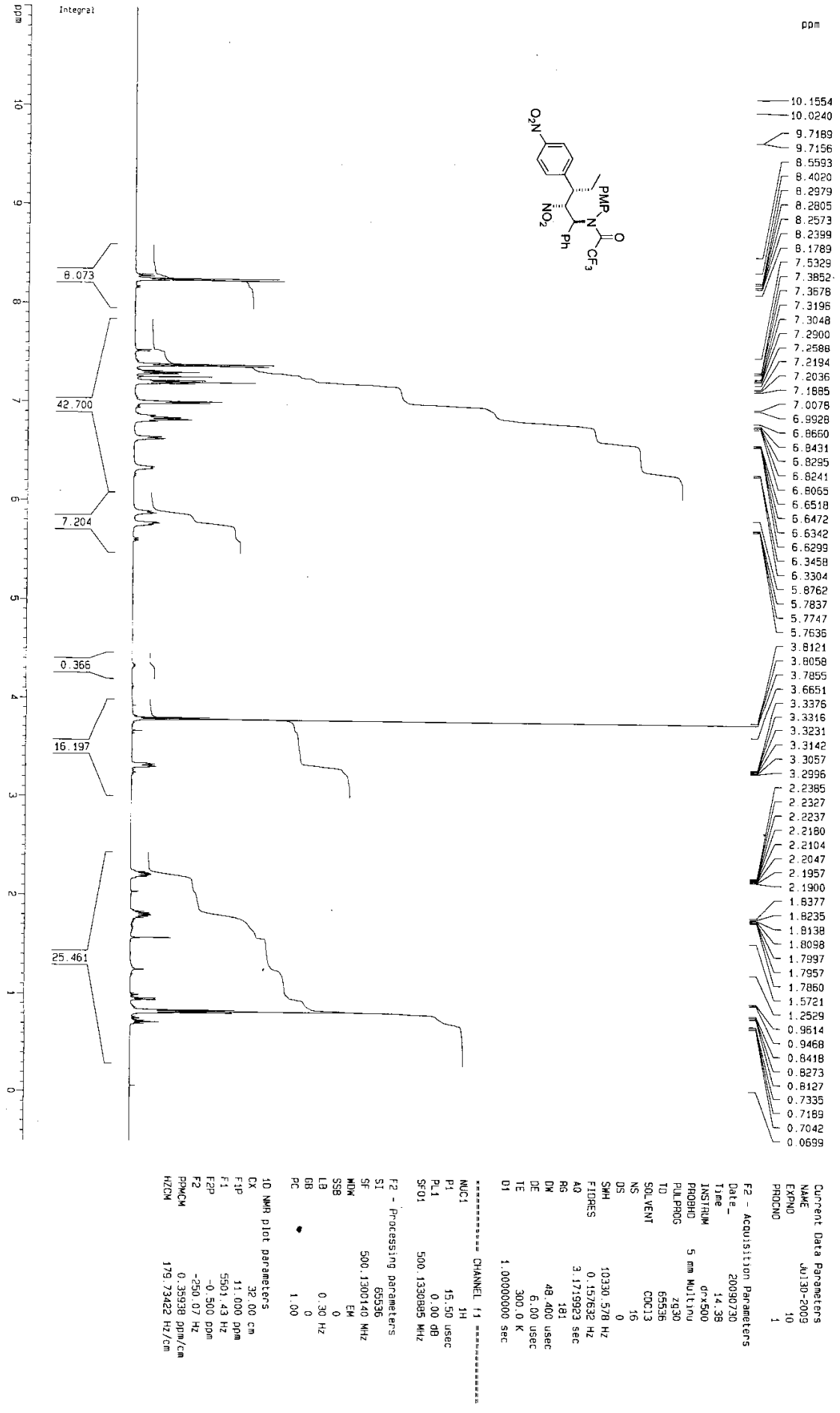
^{1}H NMR **Entry 11**



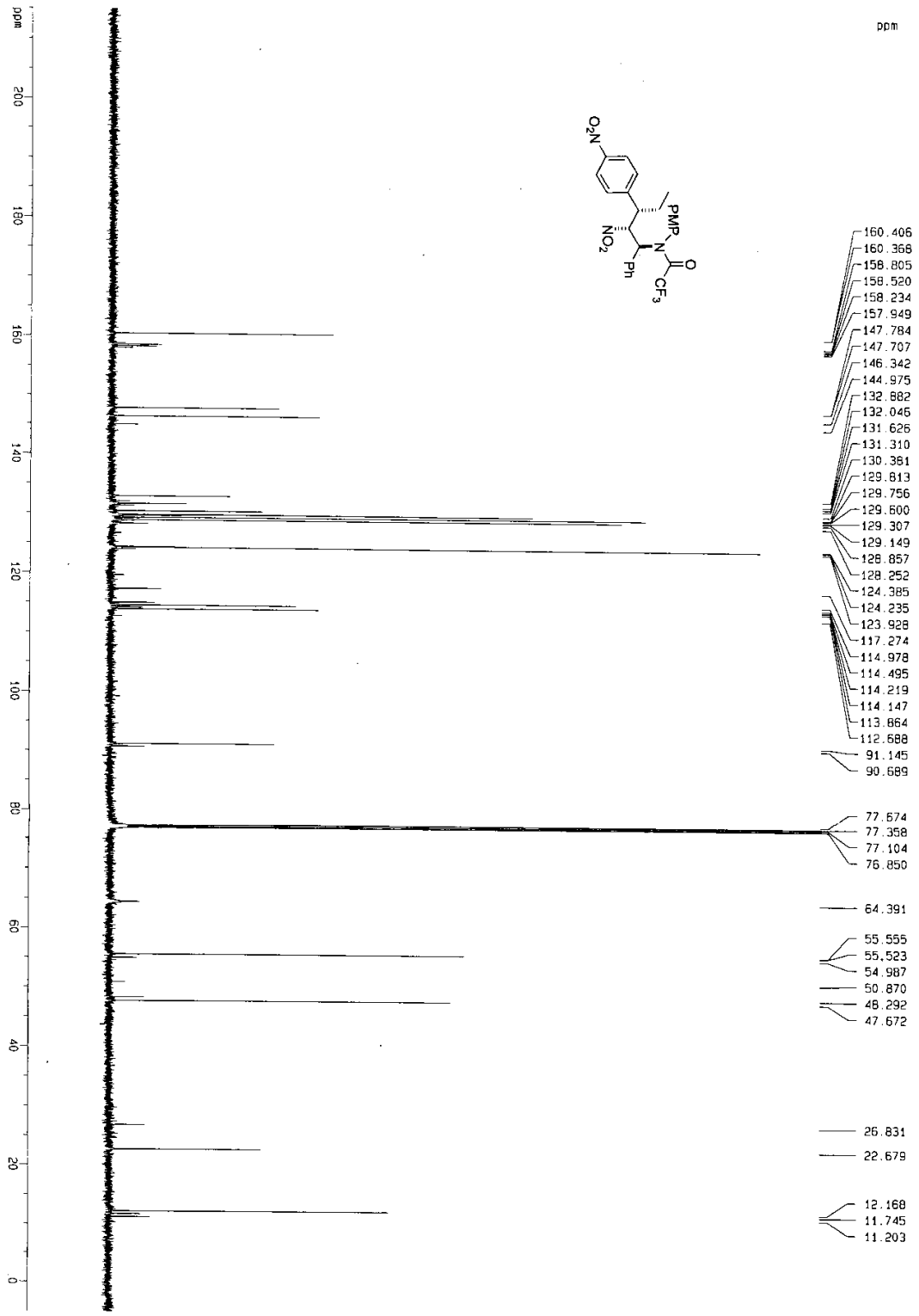
^{13}C NMR **Entry 11**



^{1}H NMR **Entry 12**



^{13}C NMR **Entry 12**



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NAME Jul30-2009
EXPNO 11
PROCNO 1

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PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 31446.541 Hz
FIDRES 0.479836 Hz
AQ 1.0420724 sec
RG 3649.1
DW 15.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

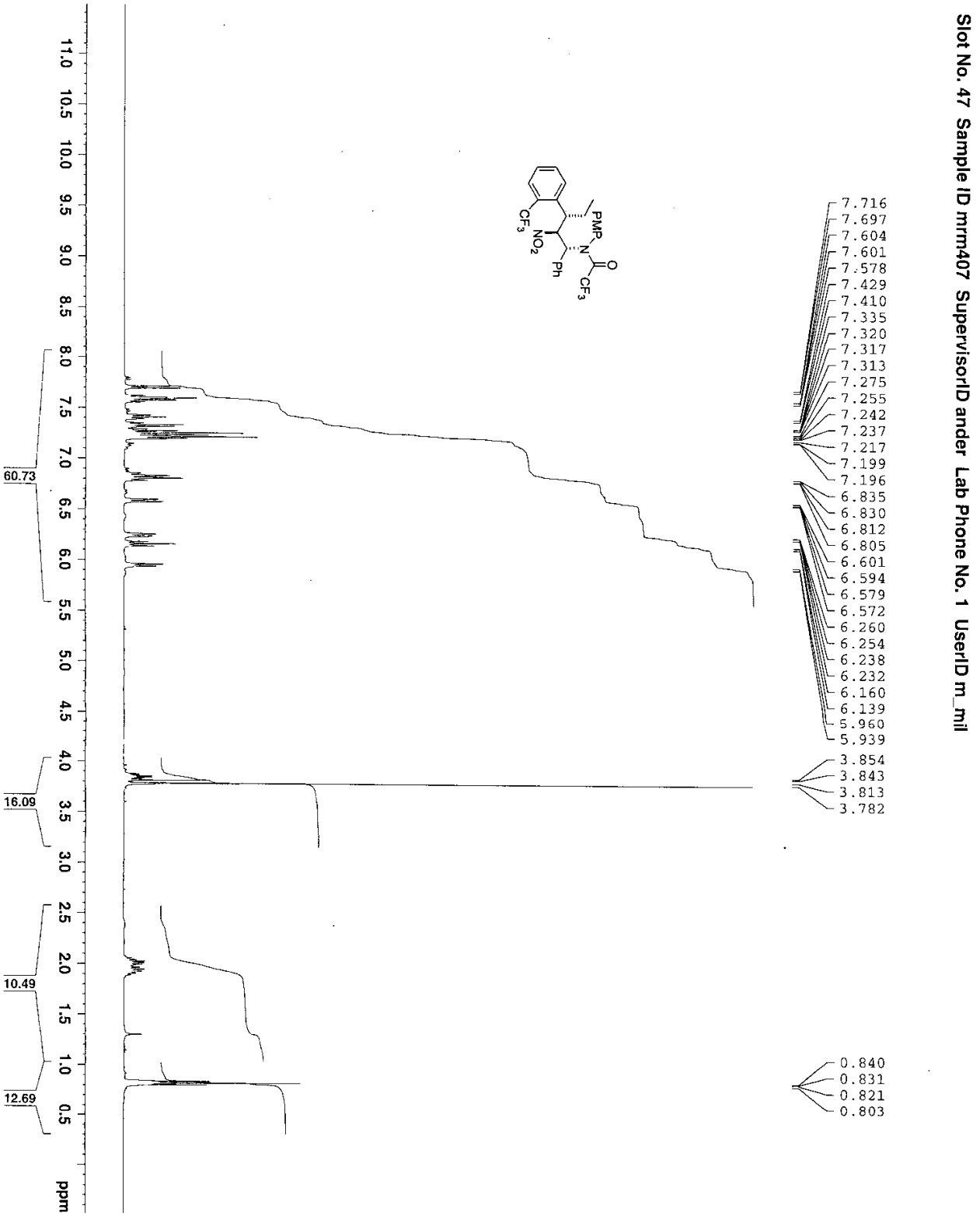
======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 0.00 dB
SF01 125.7715719 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 0.00 dB
PL12 19.00 dB
PL13 19.00 dB
SFO2 500.1320005 MHz

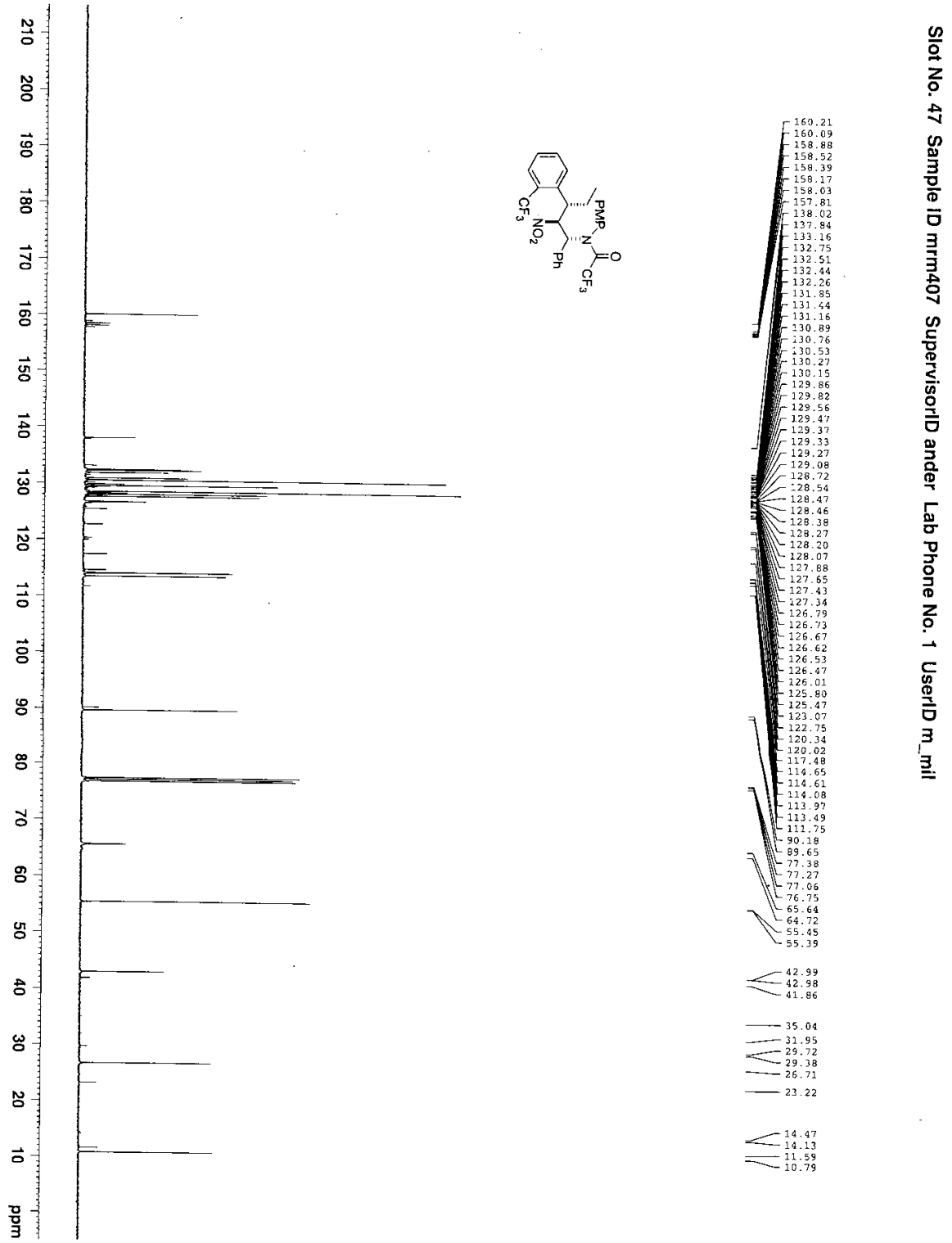
F2 - Processing parameters
SI 32768
SF 125.7577814 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 32.00 cm
F1P 215.000 ppm
F1 27037.93 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 6.87500 ppm/cm
HZCM 864.58478 Hz/cm

^{1}H NMR **Entry 13**



^{13}C NMR **Entry 13**

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Current Data Parameters
NAME            m_mil.mrm407
EXPNO                      5
PROCNO                     1

F2 - Acquisition Parameters
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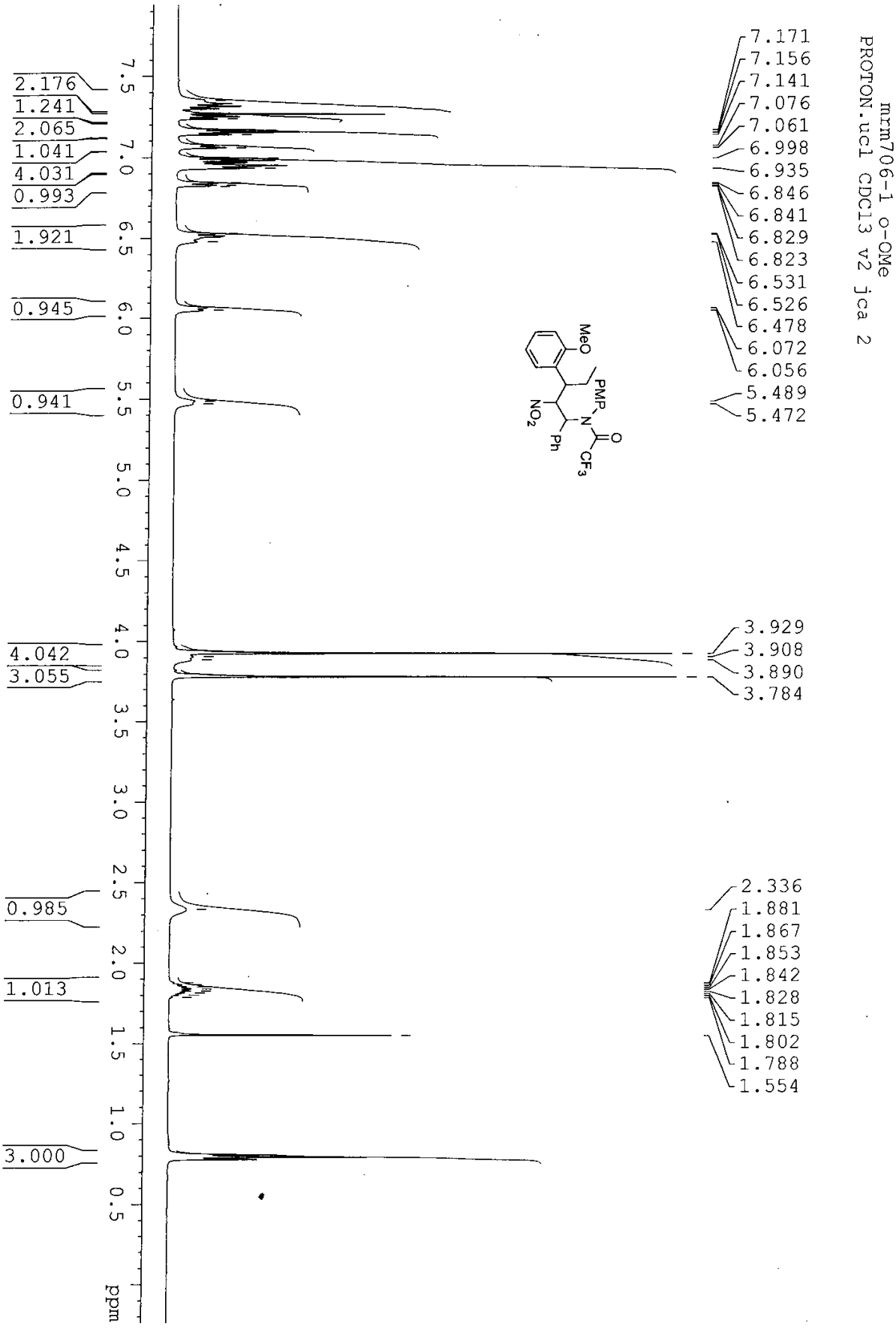
Time_                5.10
INSTRUM           dpx400
PROBHD  5 mm PABBO BB/
PULPROG         zgpg30
TD                32768
SOLVENT           CDCl3
NS                 4096
DS                    2
SWH           25125.629 Hz
FIDRES            0.766773 Hz
AQ                0.6521332 sec
RG                  16384
DW                19.900 usec
DE                 6.00 usec
TE                 297.6 K
D1                1.0000000 sec
D11               0.0300000 sec
DELTA             0.8999998 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.40 usec
PL1                  -4.00 dB
SFO1          100.6414393 MHz

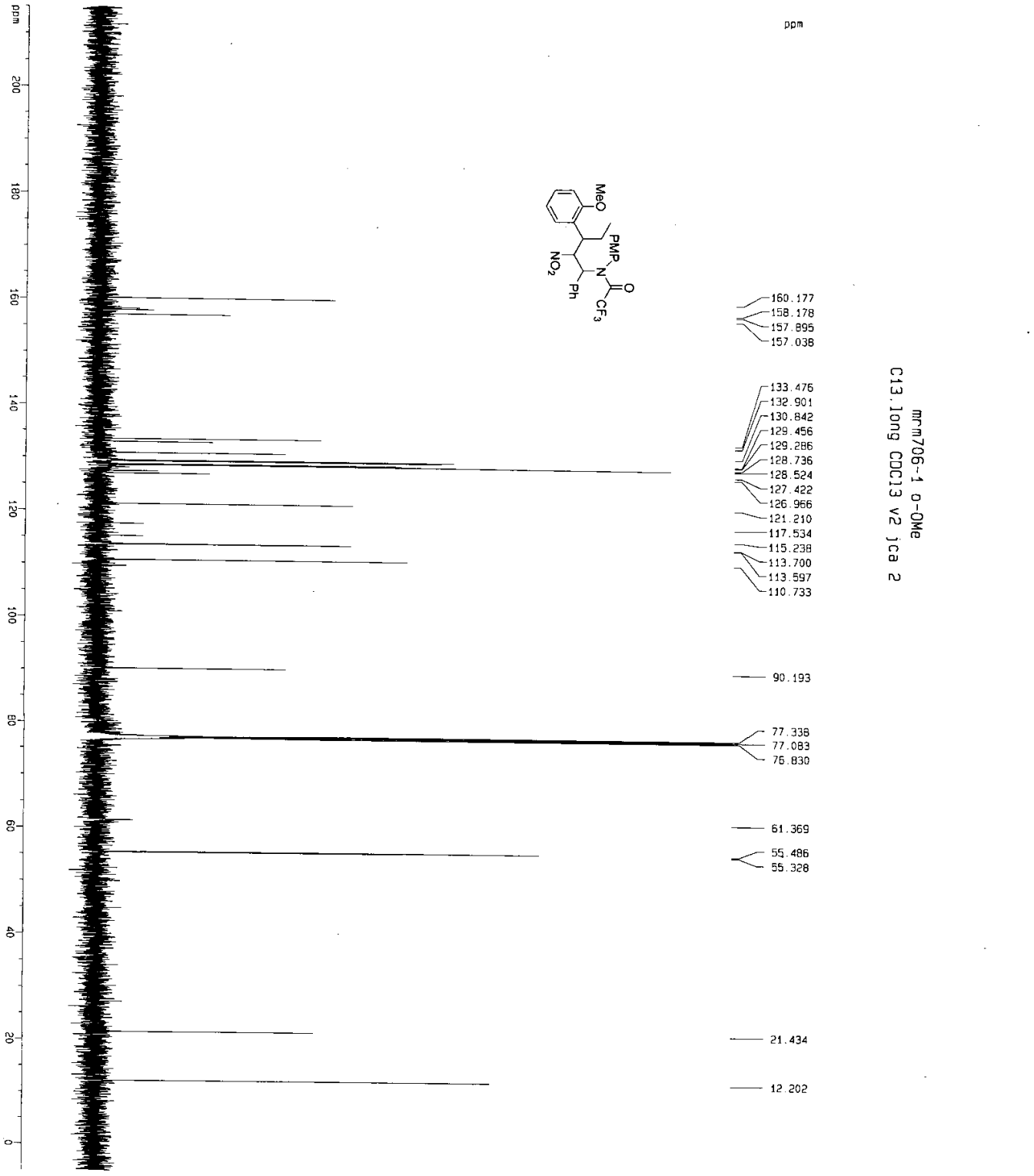
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2             100.00 usec
PL2                  15.00 dB
PL12                 11.00 dB
PL13                 12.00 dB
SFO2          400.2016008 MHz

F2 - Processing parameters
SI                    32768
SF            100.6303700 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{1}H NMR **Entry 14**



^{13}C NMR **Entry 14**

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Current Data Parameters
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EXPNO                         20
PROCNO                         1

F2 - Acquisition Parameters
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Time                    17.38
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PROBHD     5 mm Multinu
PULPROG                 zgpg30
TD                       65536
SOLVENT                 CDCl3
NS                        1024
DS                           4
SWH                 31446.541 Hz
FIDRES               0.479836 Hz
AQ                   1.04207724 sec
RG                       4597.6
DW                   15.900 usec
DE                    6.00 usec
TE                      300.0 K
D1                   2.00000000 sec
d11                  0.03000000 sec
d12                  0.00002000 sec

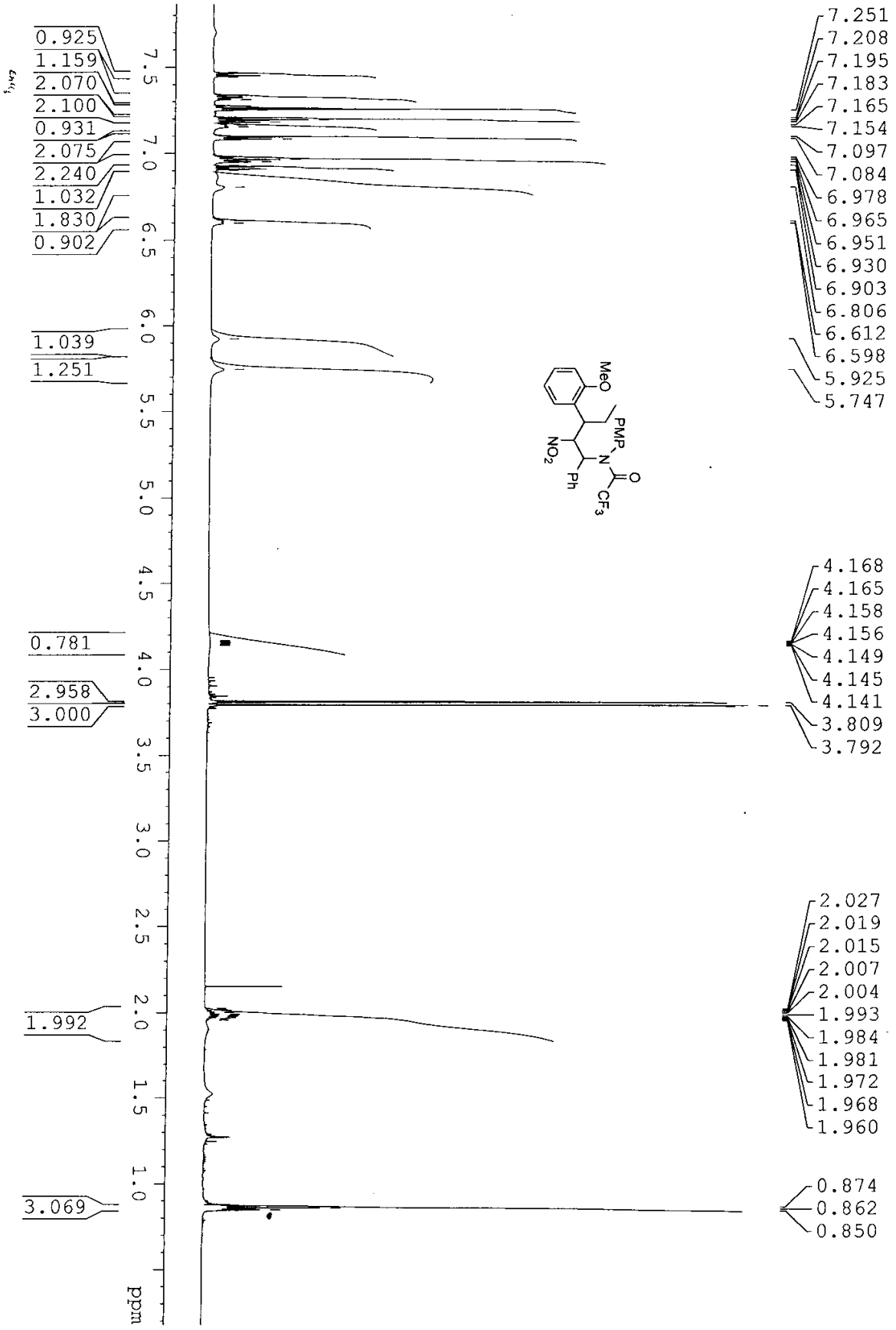
======== CHANNEL f1 ========
NUC1                       13C
P1                    5.50 usec
PL1                    0.00 dB
SFO1             125.7715719 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 95.00 usec
PL2                    0.00 dB
PL12                  19.00 dB
PL13                  19.00 dB
SFO2             500.1320005 MHz

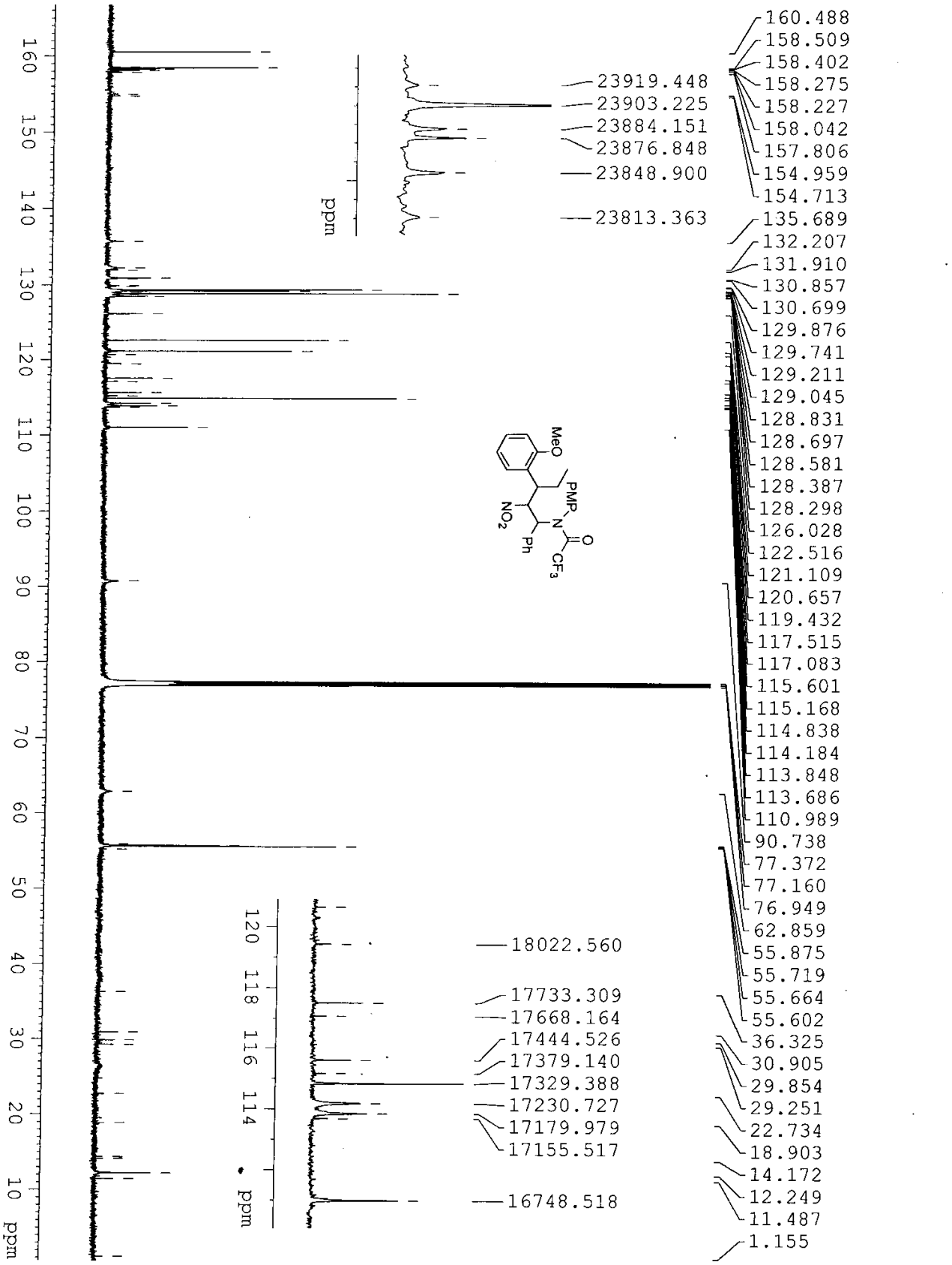
F2 - Processing parameters
SI                        32768
SF               125.7577814 MHz
WDW                          EM
SSB                           0
LB                     1.00 Hz
GB                            0
PC                         1.40

1D NMR plot parameters
CX                        32.00 cm
F1P                  215.000 ppm
F1                  27037.93 Hz
F2P                  -5.000 ppm
F2                  -628.79 Hz
PPMCM                6.87500 ppm/cm
HZCM               864.56478 Hz/cm
```

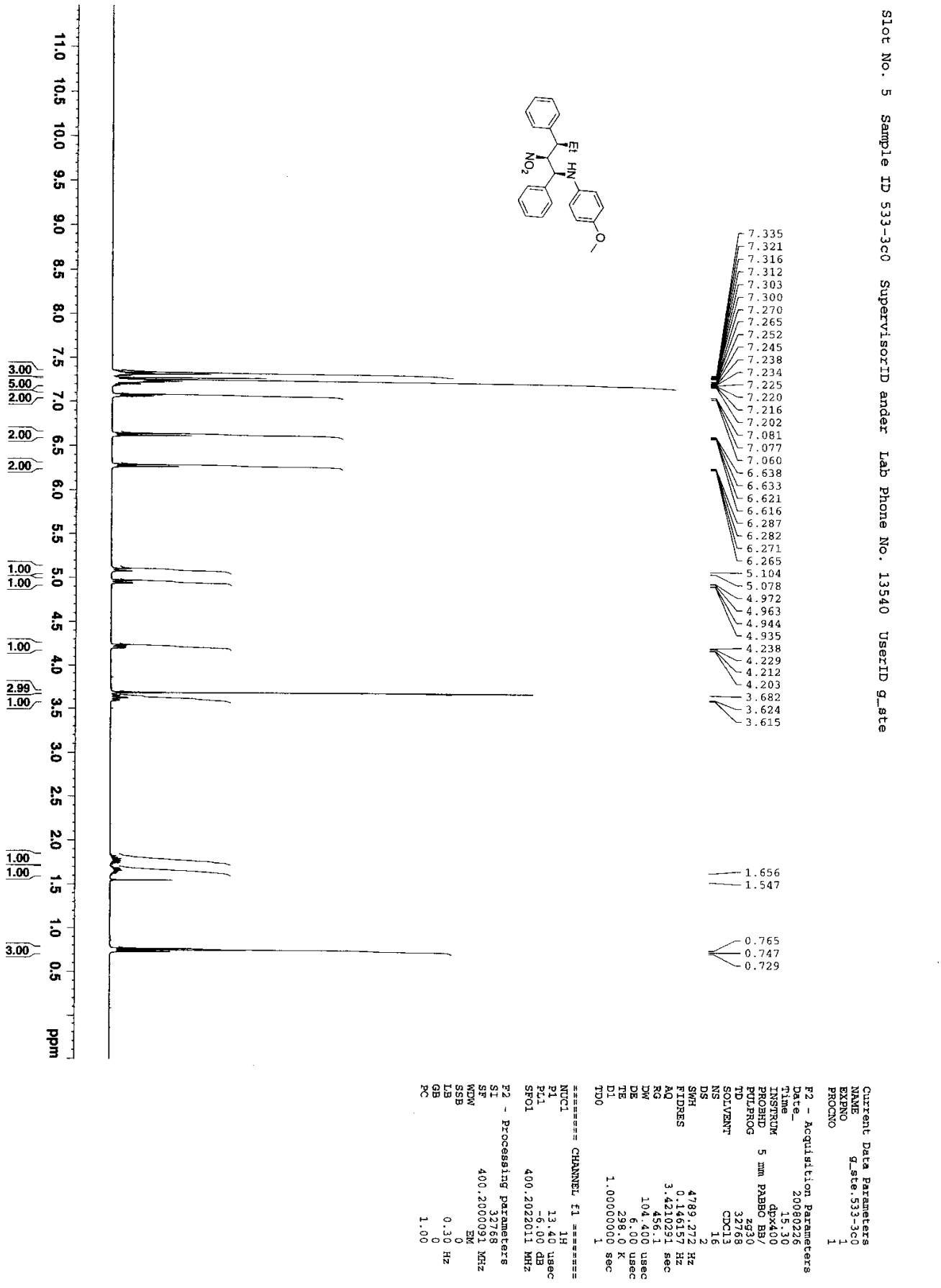
[1]H NMR **Entry 14**



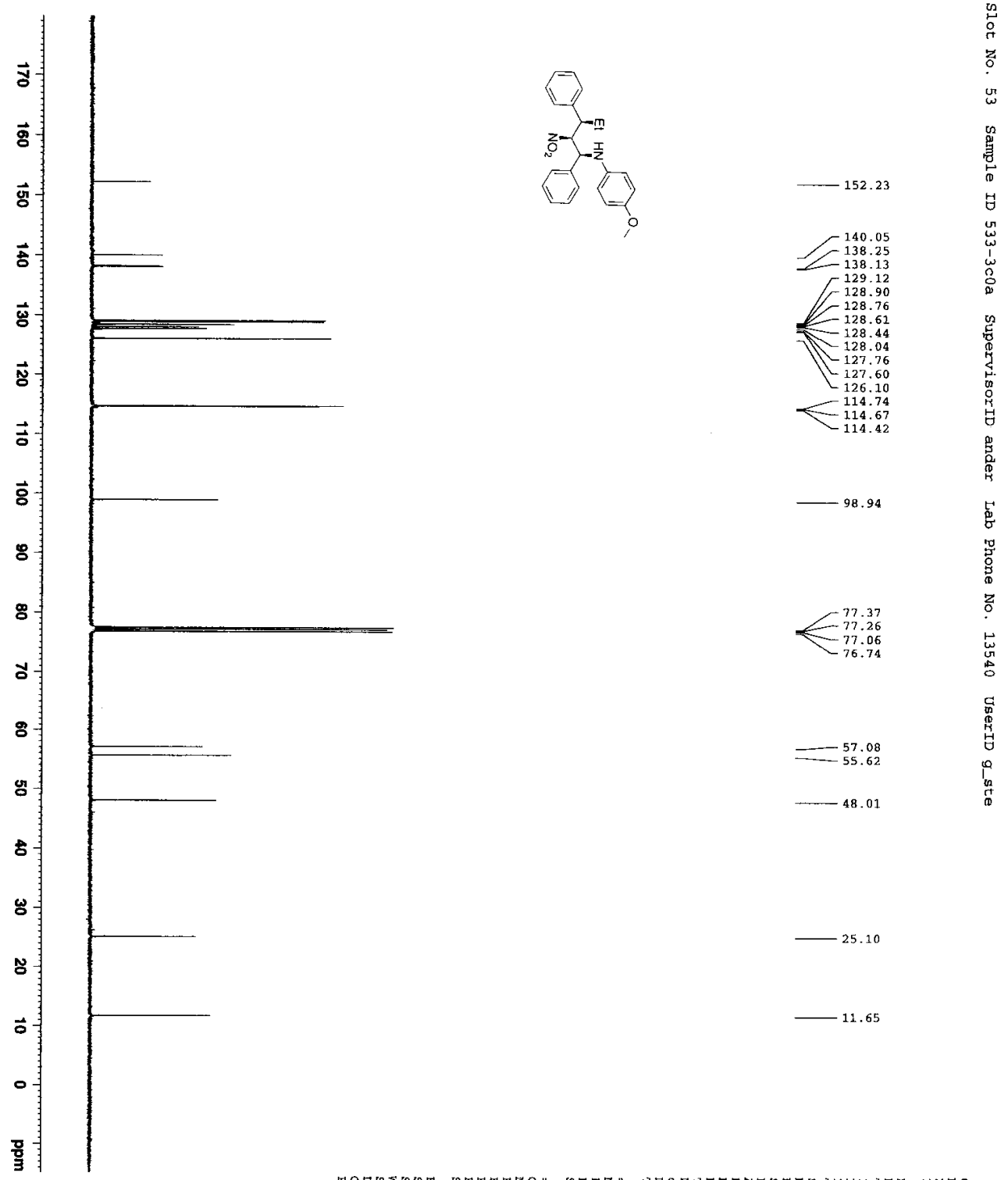
^{13}C NMR **Entry 14**



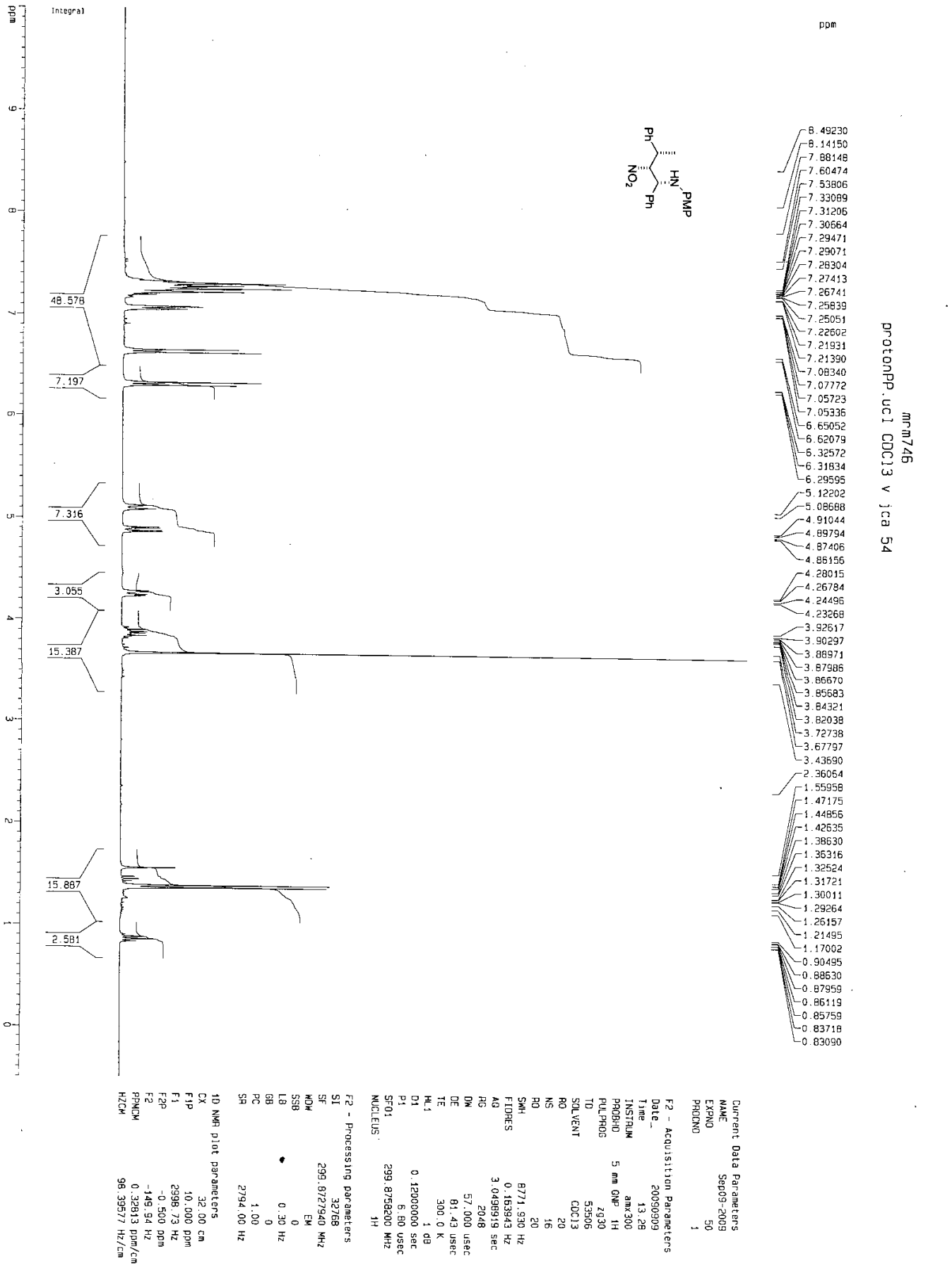
^{1}H NMR **Entry 15**



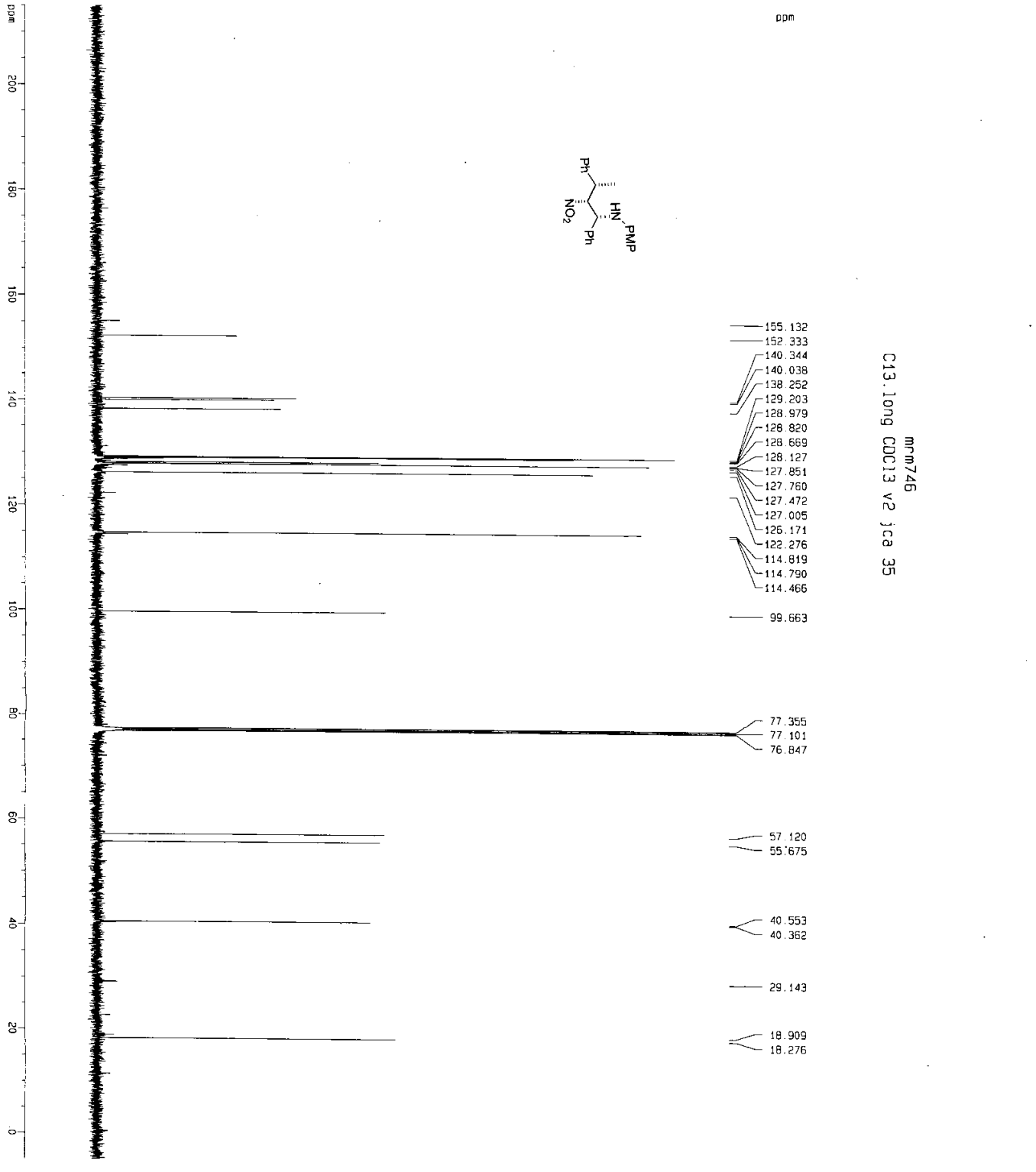
^{13}C NMR **Entry 15**



^{1}H NMR **Entry 16**



^{13}C NMR **Entry 16**



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EXPNO 20
PROCNO 1

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PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 31446.541 Hz
FIDRES 0.479836 Hz
AQ 1.0420724 sec
RG 6502
DW 15.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

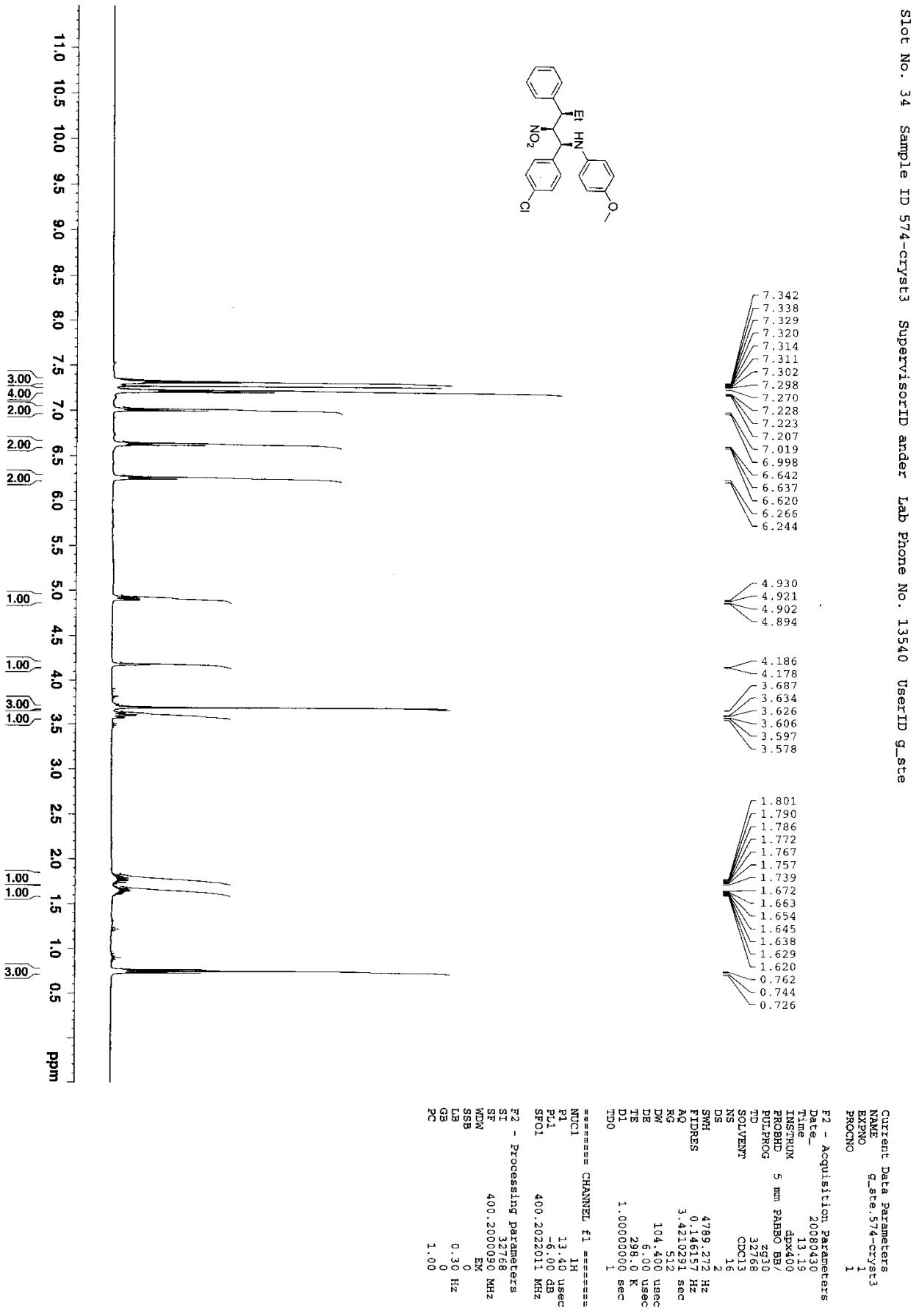
======== CHANNEL f1 ========
NUC1 13C
P1 5.60 usec
PL1 0.00 dB
SFO1 125.7715719 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 0.00 dB
PL12 19.00 dB
PL13 19.00 dB
SFO2 500.1320005 MHz

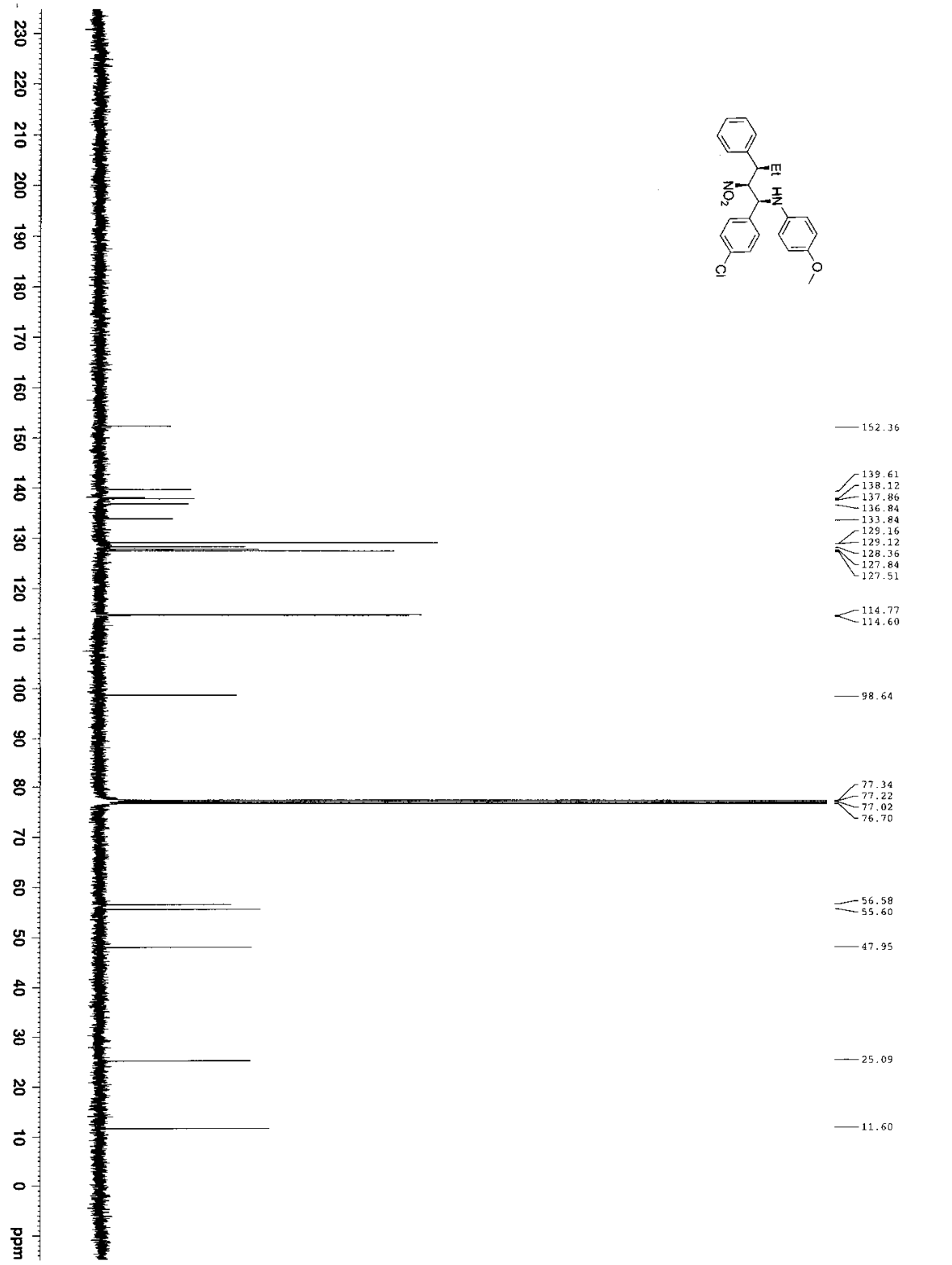
F2 - Processing parameters
SI 32768
SF 125.7577814 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 32.00 cm
F1P 215.000 ppm
F1 27037.93 Hz
F2P -5.000 ppm
F2 -626.79 Hz
PPMCM 6.87500 ppm/cm
HZCM 864.58478 Hz/cm

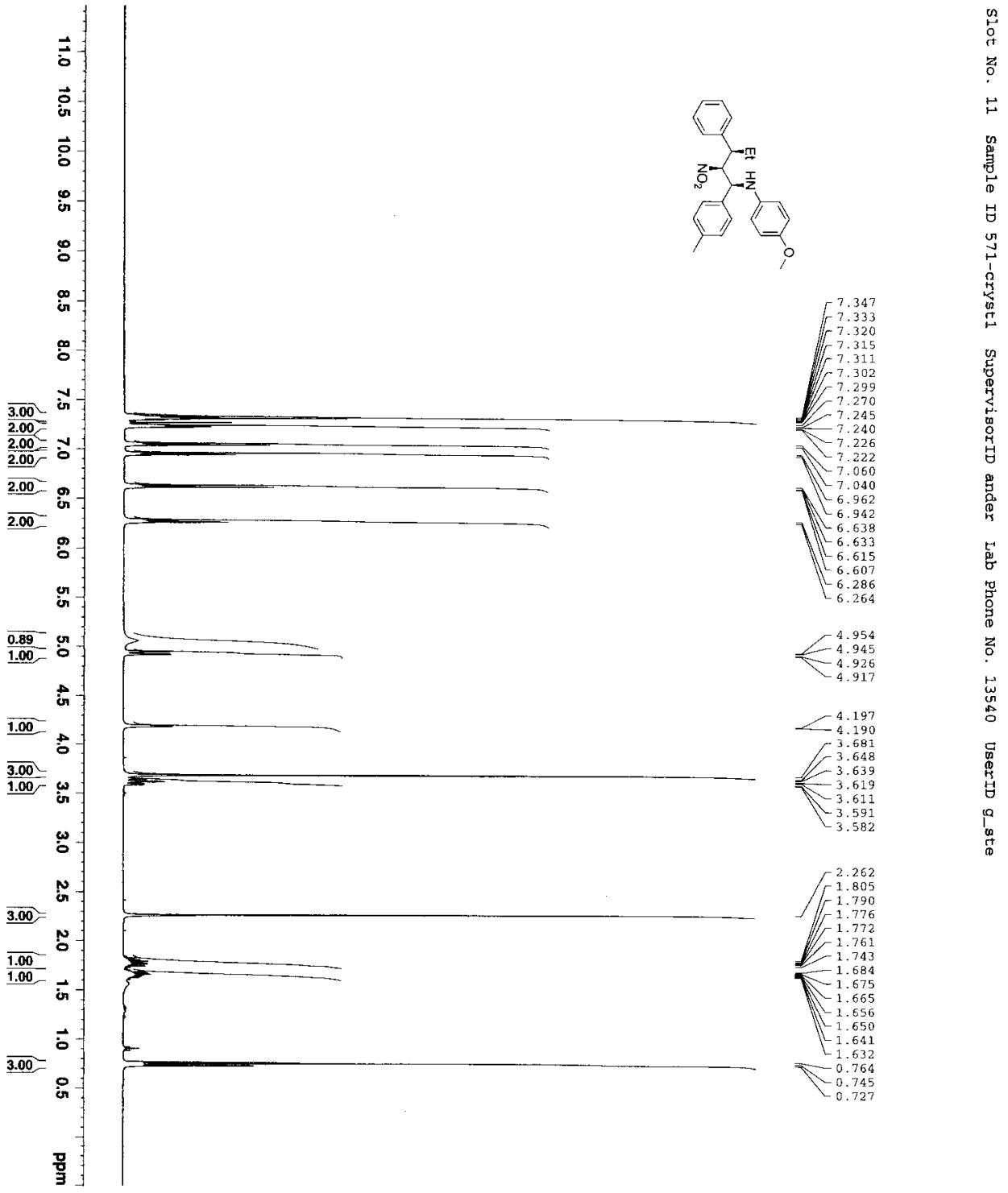
^{1}H NMR **Entry 17**



^{13}C NMR **Entry 17**



^{1}H NMR **Entry 18**

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EXPNO                              1
PROCNO                             1

F2 - Acquisition Parameters
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Time                           18.36
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PROBHD                5 mm PABBO BB/
PULPROG                      zg30
TD                          32768
SOLVENT                     CDCl3
NS                             16
DS                              2
SWH                       4789.272 Hz
FIDRES                    0.146157 Hz
AQ                        3.4210291 sec
RG                           287.4
DW                        104.400 usec
DE                          6.00 usec
TE                          298.0 K
D1                    1.00000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                          1H
P1                         13.40 usec
PL1                        -6.00 dB
SFO1                  400.2022011 MHz

F2 - Processing parameters
SI                          32768
SF                    400.2000090 MHz
WDW                            EM
SSB                             0
LB                           0.30 Hz
GB                              0
PC                           1.00
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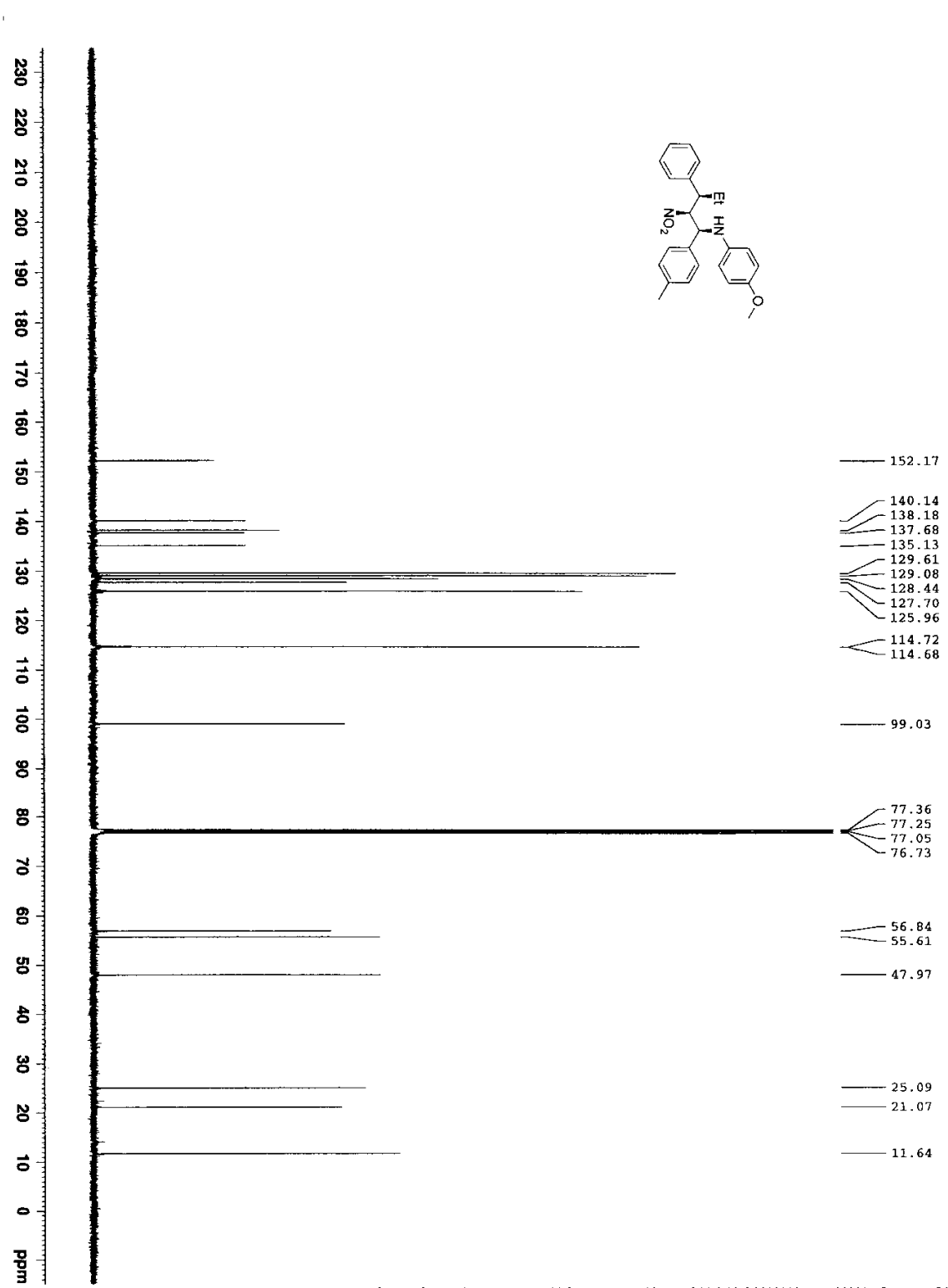
^{13}C NMR **Entry 18**

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Current Data Parameters
NAME                  g_ste.571-crystl
EXPNO                              2
PROCNO                             1

F2 - Acquisition Parameters
Date_                       20080329
Time                           20.47
INSTRUM                       dpx400
PROBHD                5 mm PABBO BB/
PULPROG                       zgpg30
TD                             32768
SOLVENT                       CDCl3
NS                              4096
DS                                 2
SWH                        25125.629 Hz
FIDRES                      0.766773 Hz
AQ                          0.6521332 sec
RG                             9195.2
DW                         19.900 usec
DE                          6.00 usec
TE                             298.0 K
D1                        1.00000000 sec
d11                       0.03000000 sec
DELTA                     0.89999998 sec
TD0                                1

======== CHANNEL f1 ========
NUC1                             13C
P1                            8.40 usec
PL1                          -4.00 dB
SFO1                  100.6414393 MHz

======== CHANNEL f2 ========
CPDPRG2                     waltz16
NUC2                             1H
PCPD2                     100.00 usec
PL2                         -6.00 dB
PL12                        11.00 dB
PL13                        12.00 dB
SFO2                  400.2016008 MHz

F2 - Processing parameters
SI                             32768
SF                    100.6303700 MHz
WDW                               EM
SSB                                0
LB                              1.00 Hz
GB                                 0
PC                              1.40
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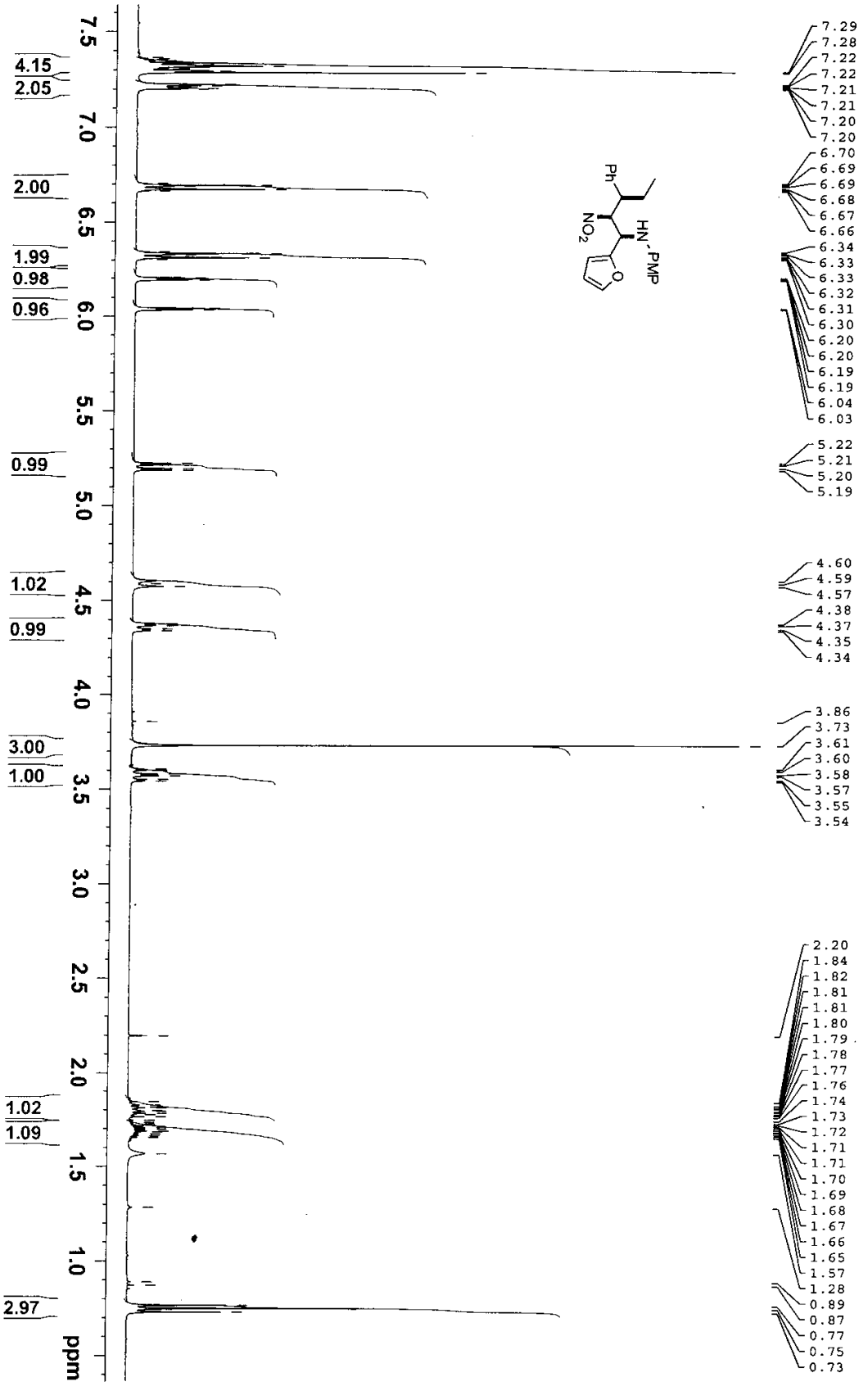
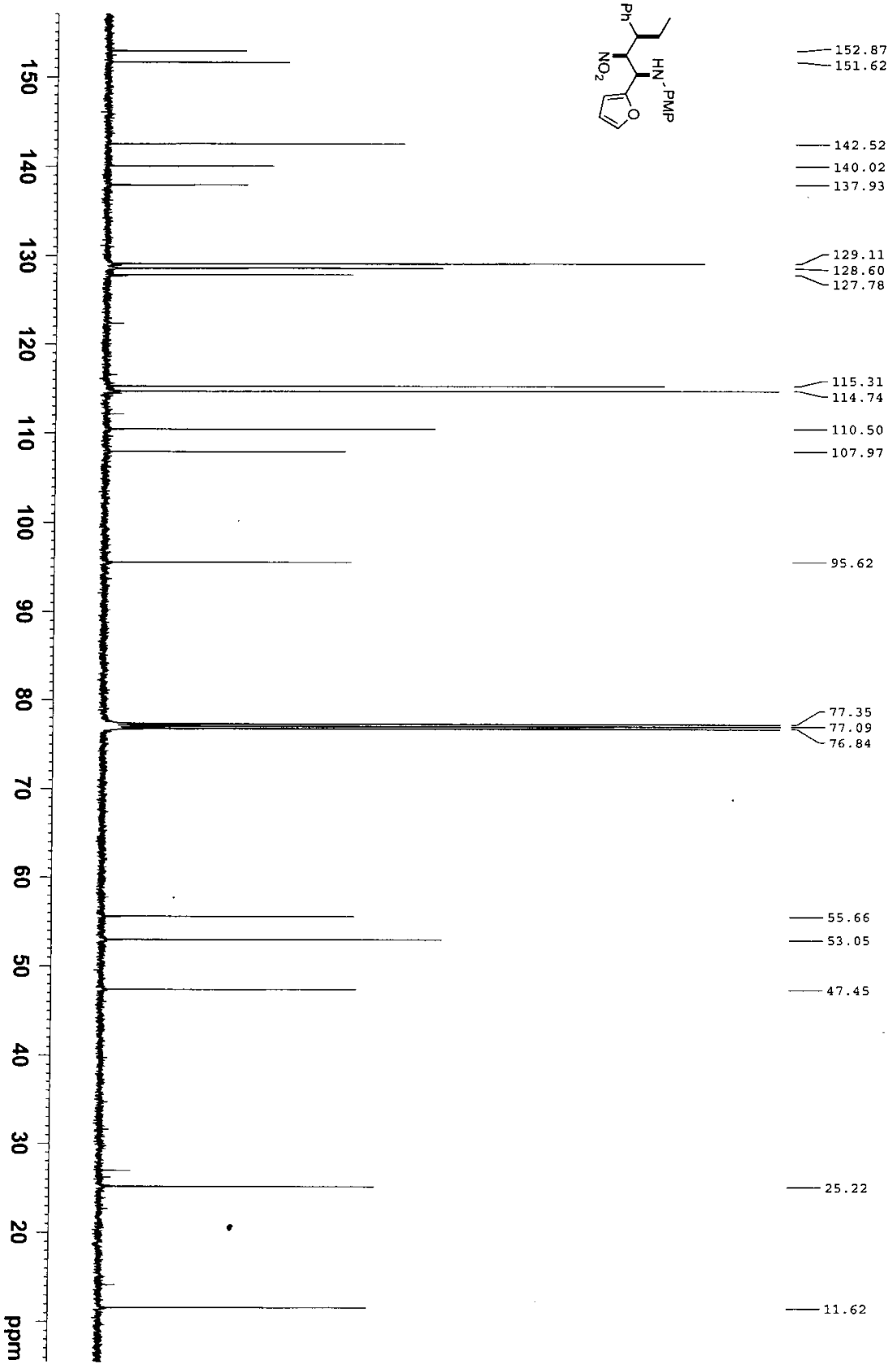
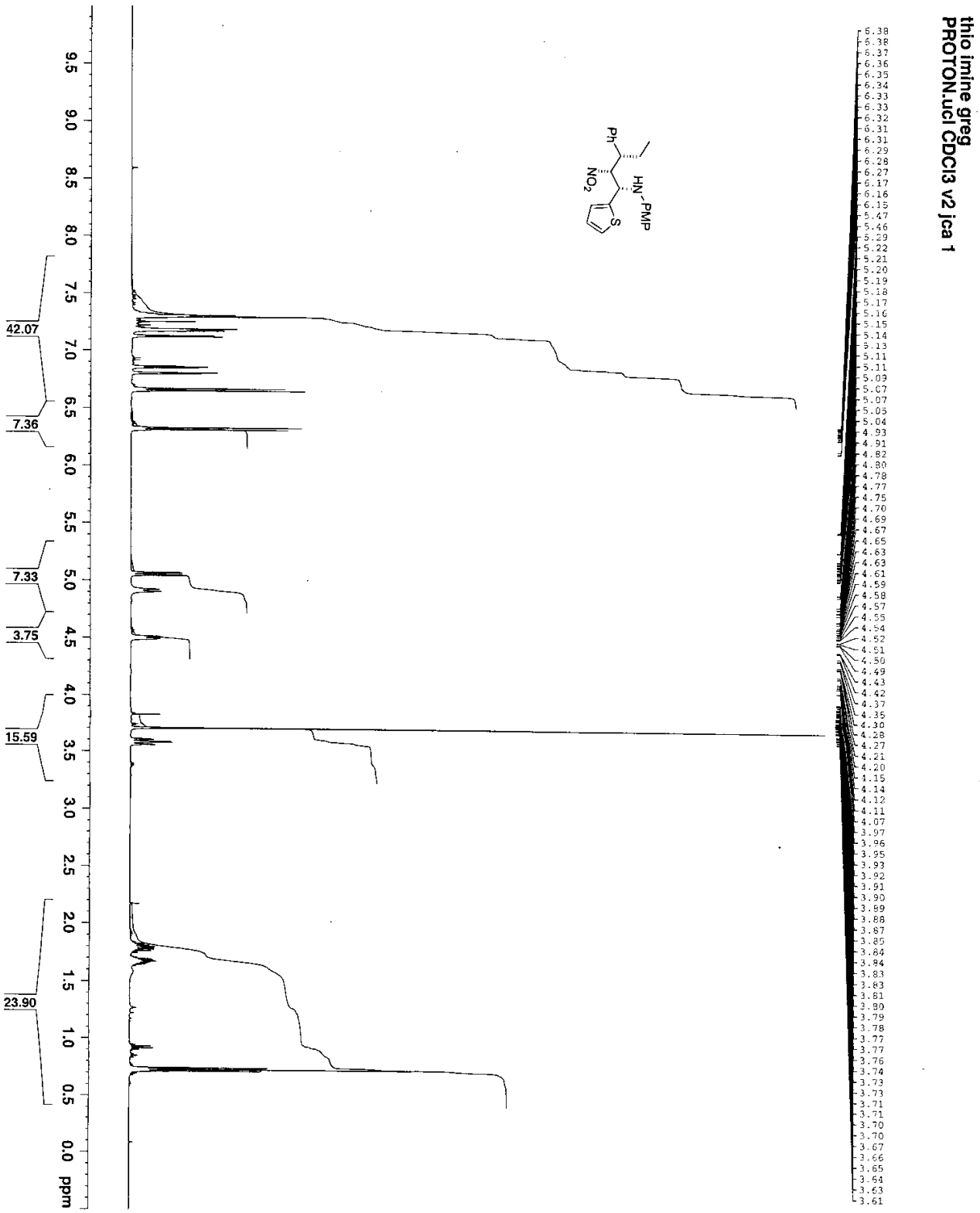
^{1}H NMR **Entry 19**



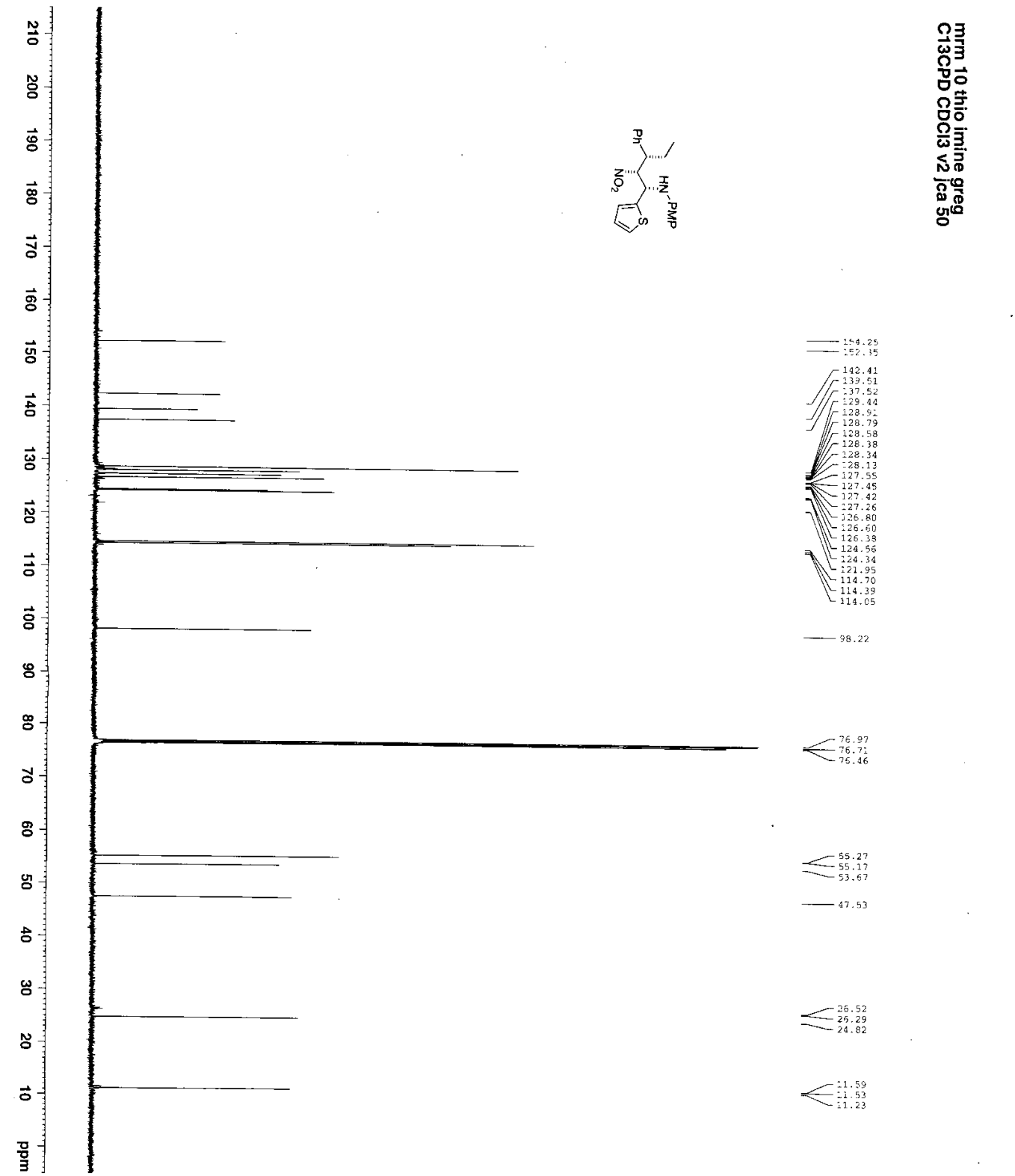
^{13}C NMR **Entry 19**



^{1}H NMR **Entry 20**



^{13}C NMR **Entry 20**



Current Data Parameters
NAME Dec01-2009
EXPNO 70
PROCNO 1

F2 - Acquisition Parameters
Date_ 20091201
Time 17.32
INSTRUM drx500
PROBHD 5 mm Multinucl
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0912410 sec
RG 4096
DW 16.650 usec
DE 6.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 5.50 usec
PL1 0.00 dB
SFO1 125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 0.00 dB
PL12 19.00 dB
PL13 19.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
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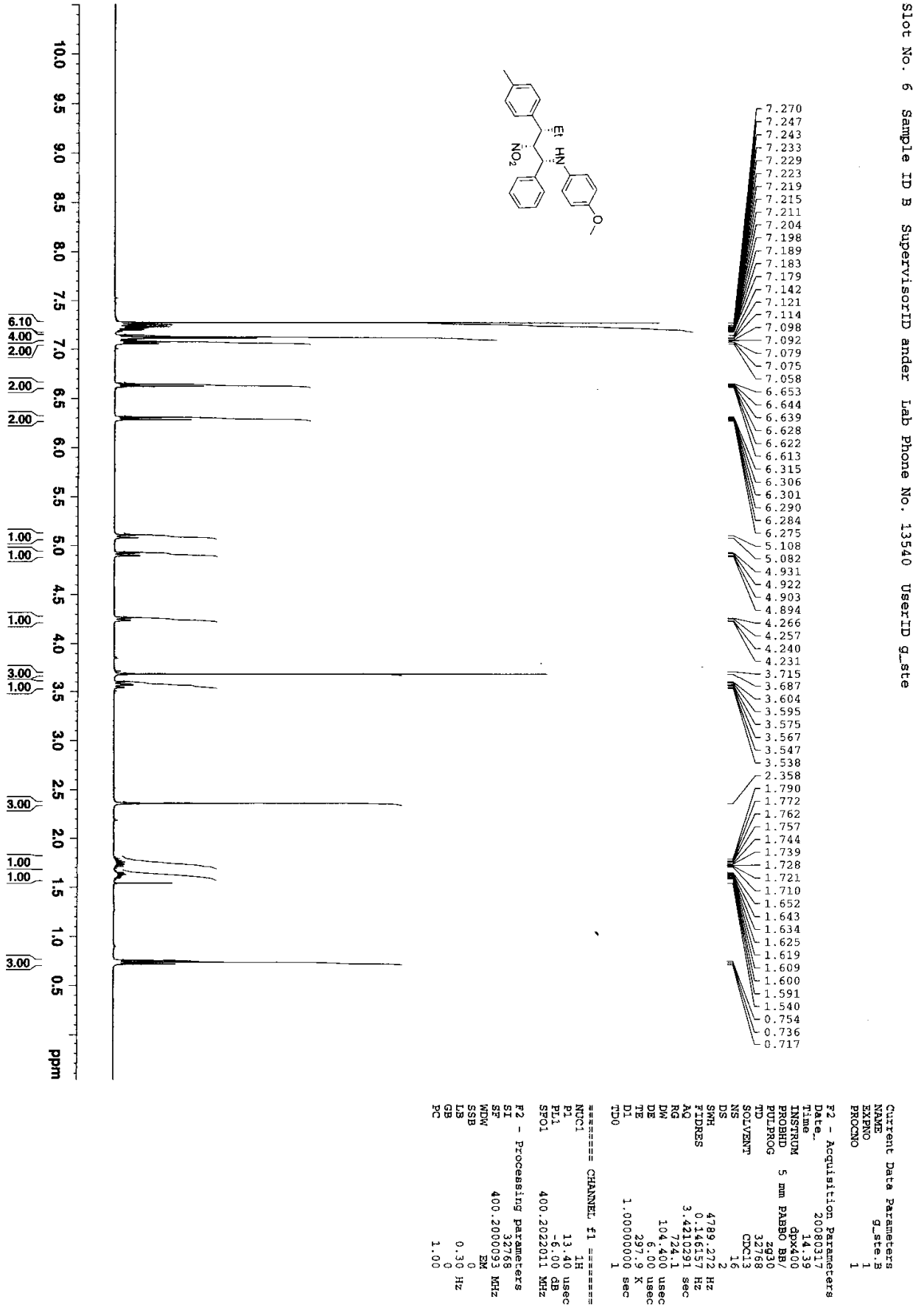
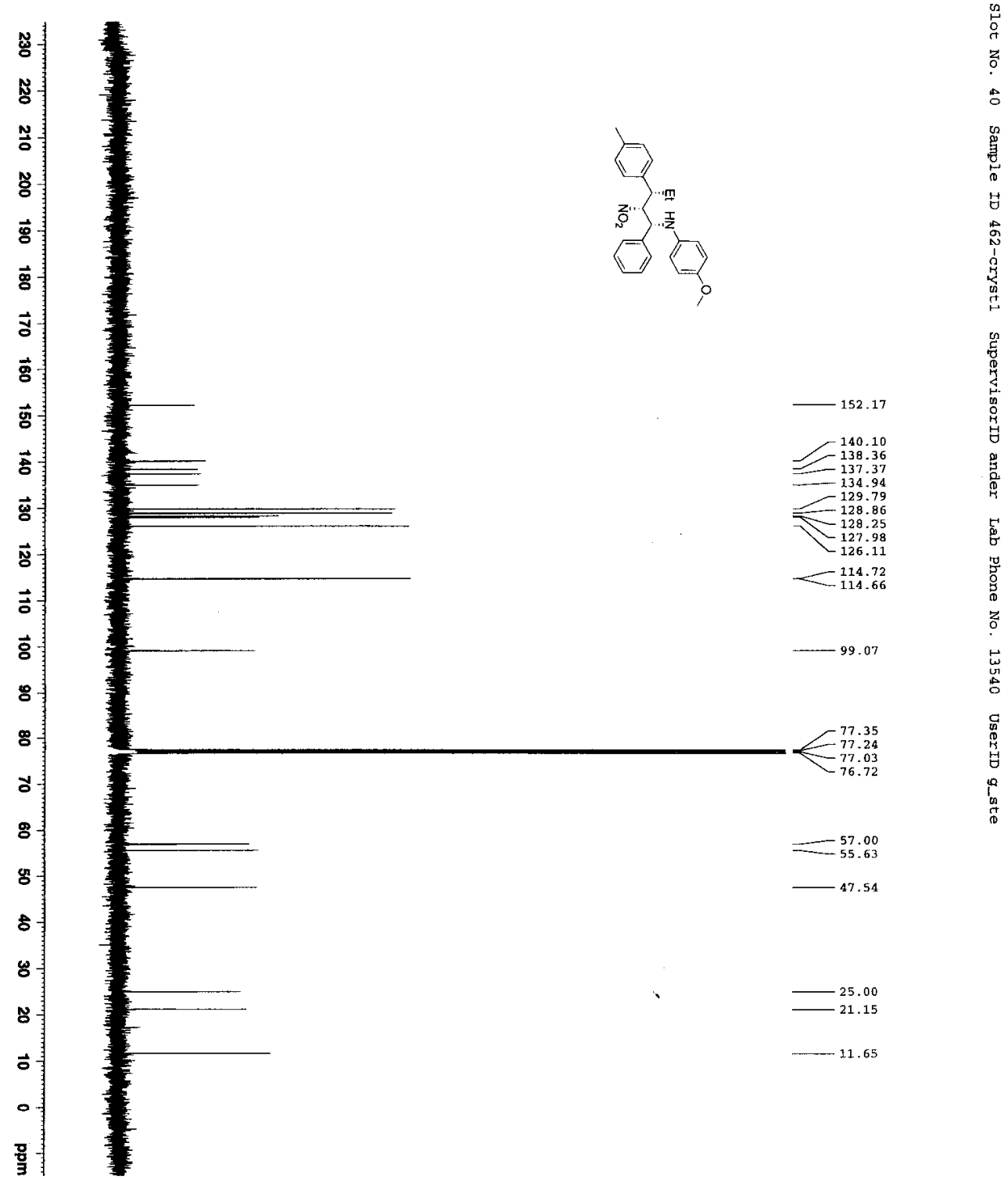
SF 125.7578314 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

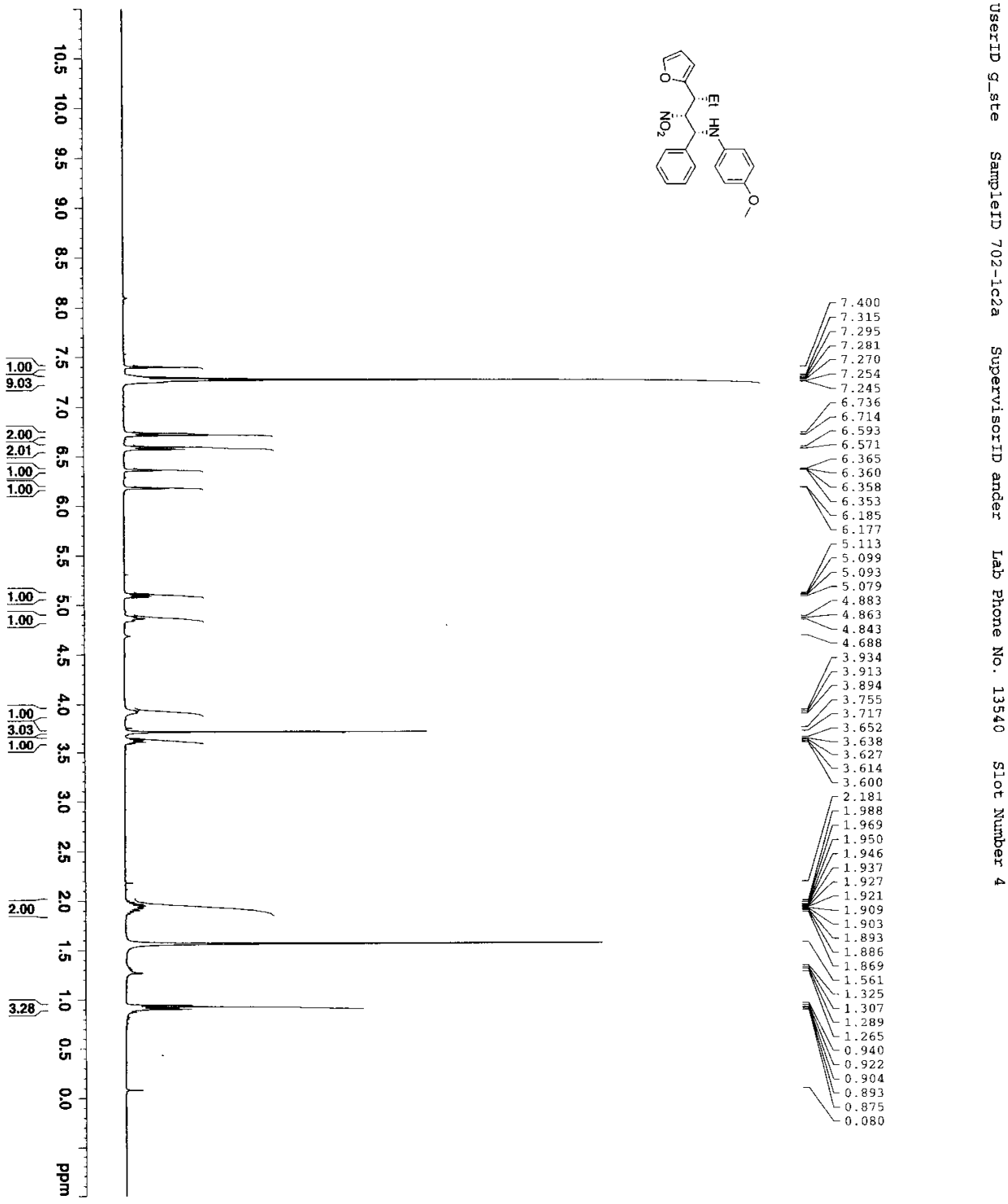
[1]H NMR **Entry 21**



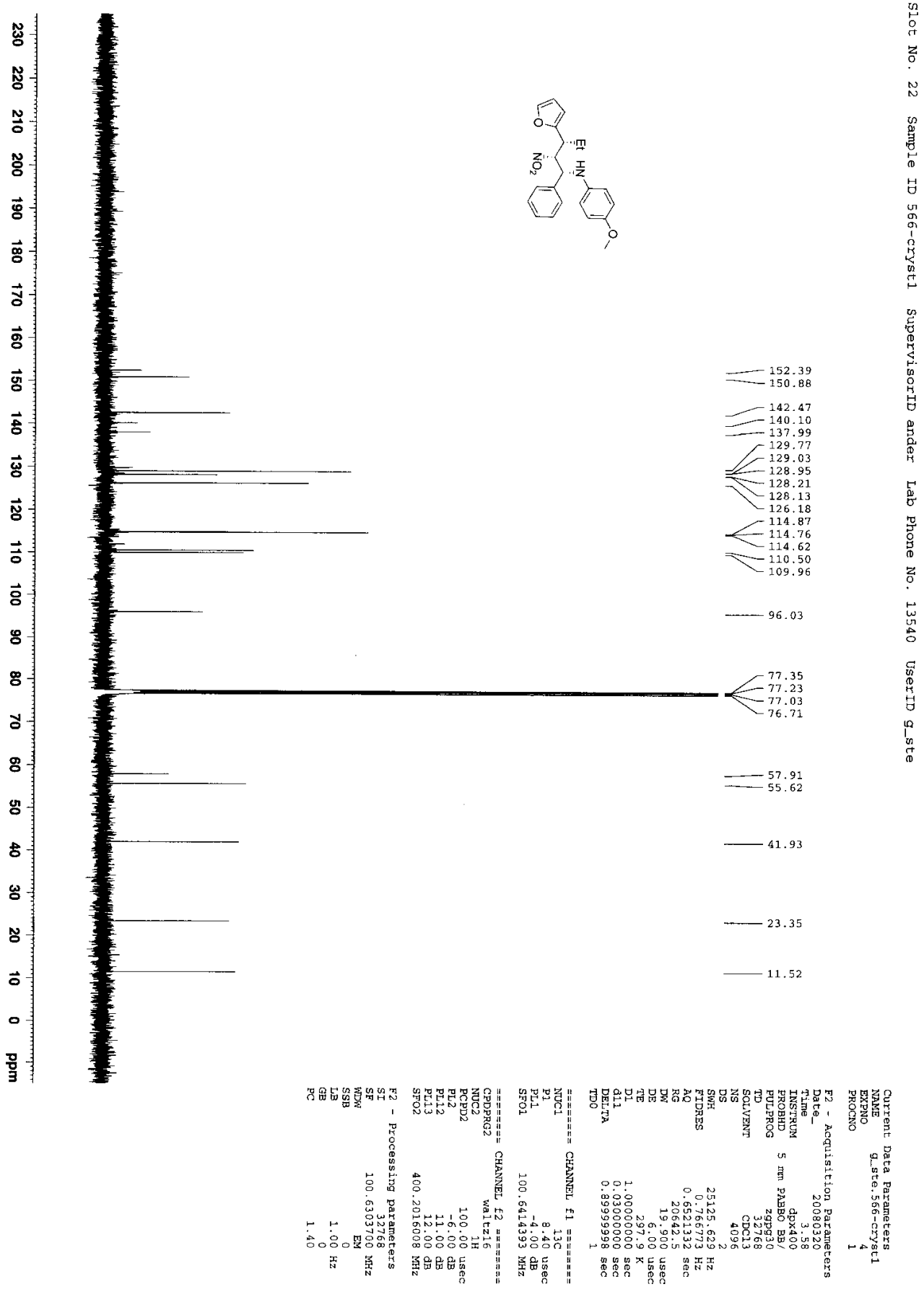
^{13}C NMR **Entry 21**



^{1}H NMR **Entry 22**



^{13}C NMR **Entry 22**



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NAME g_ste.566-crystl
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080320
Time 3.58
INSTRUM dpx400
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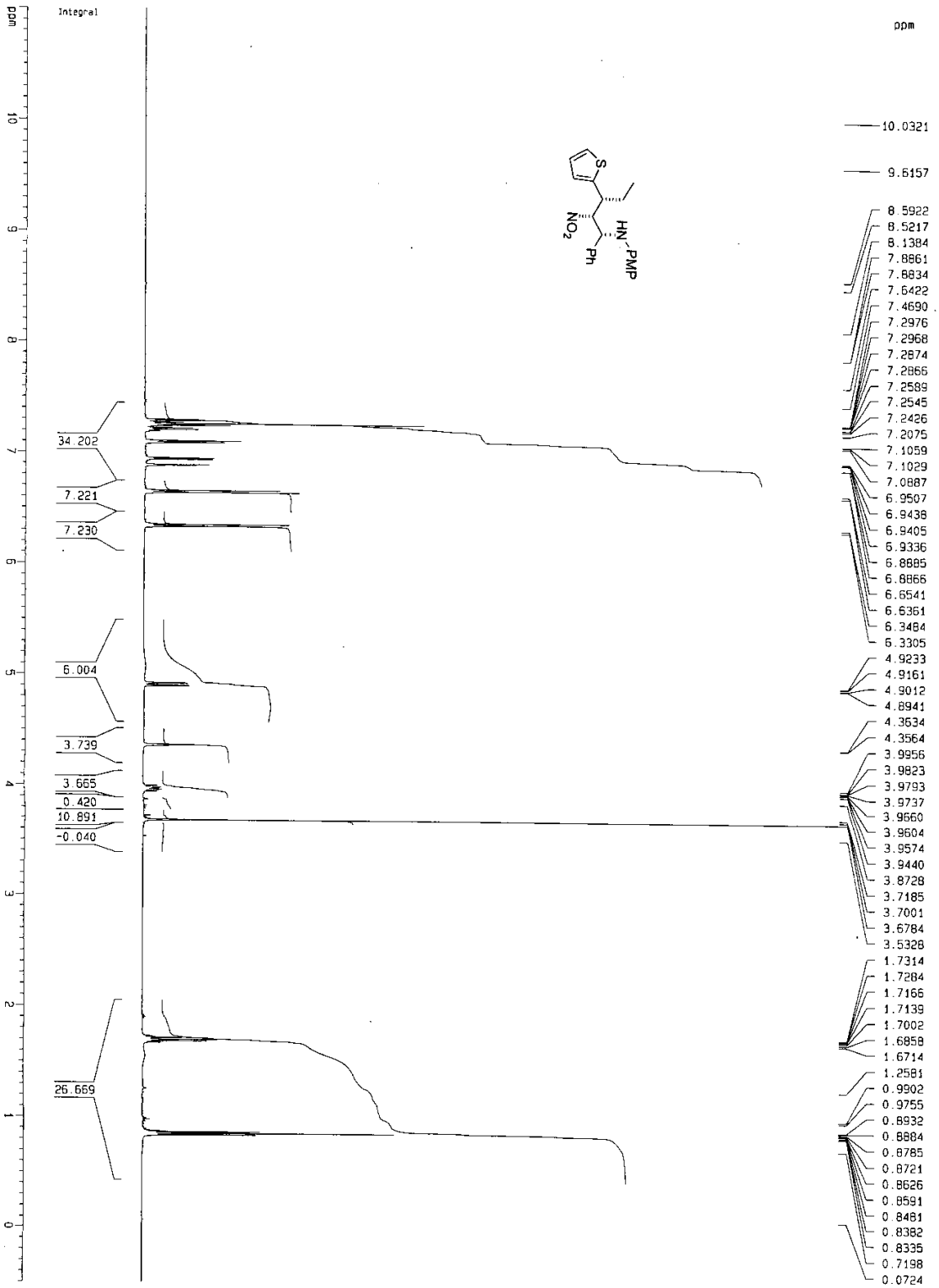
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 4096
DS 2
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 20642.5
DW 19.900 usec
DE 6.00 usec
TE 297.9 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.40 usec
PL1 -4.00 dB
SFO1 100.6414393 MHz

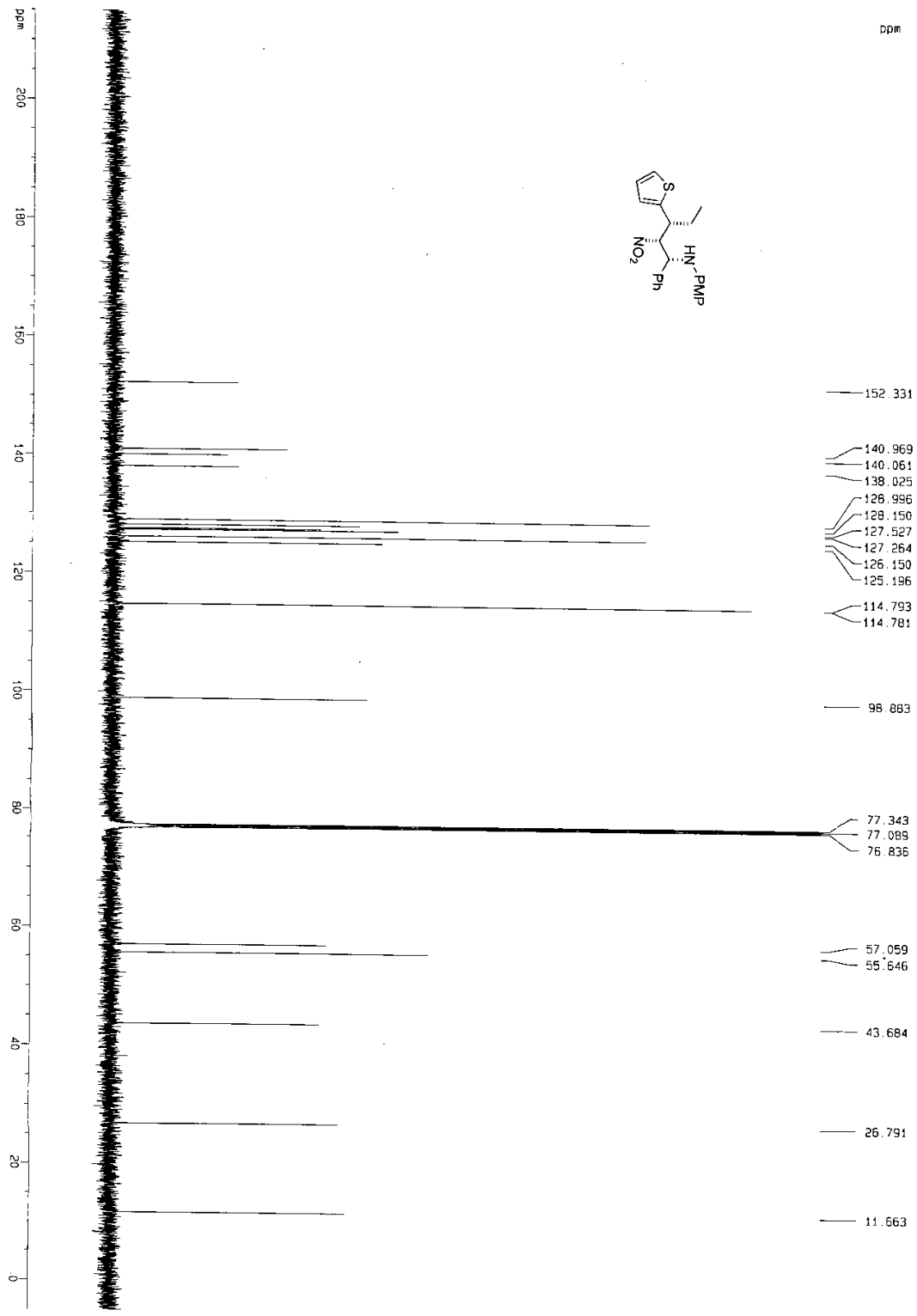
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 11.00 dB
PL13 12.00 dB
SFO2 400.2016008 MHz

F2 - Processing parameters
SI 32768
SF 100.6303700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{1}H NMR **Entry 23**



^{13}C NMR **Entry 23**



Current Data Parameters
NAME Sep17-2009
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
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Time 18.16
INSTRUM drx500
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 31446.541 Hz
FIDRES 0.479836 Hz
AQ 1.0420724 sec
RG 3649.1
DW 15.900 usec
DE 6.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.00002000 sec

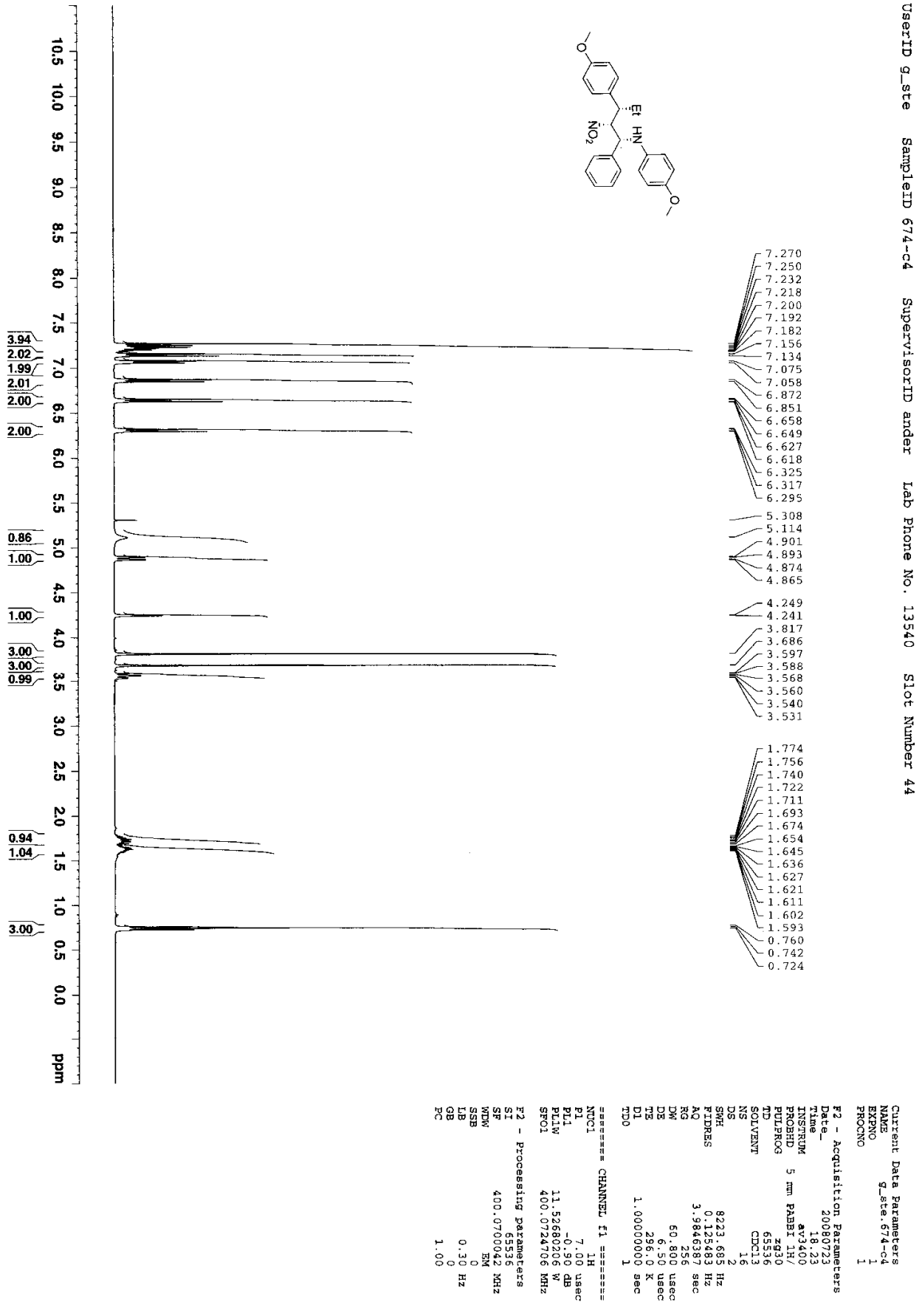
======== CHANNEL f1 ========
NUC1 13C
P1 5.60 usec
PL1 0.00 dB
SFO1 125.7715719 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 95.00 usec
PL2 0.00 dB
PL12 19.00 dB
PL13 19.00 dB
SFO2 500.1320005 MHz

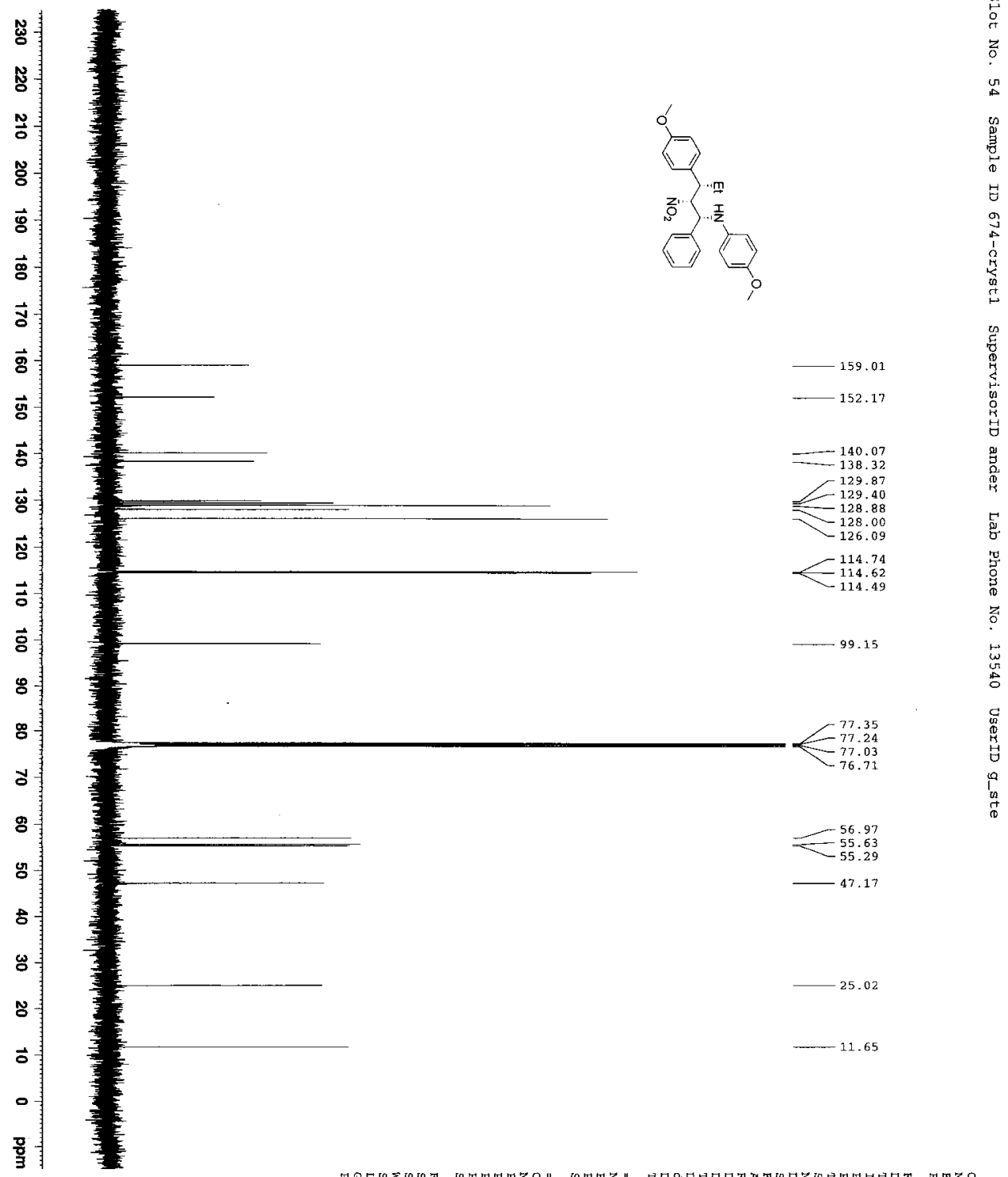
F2 - Processing parameters
SI 32768
SF 125.7577814 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 32.00 cm
F1P 215.000 ppm
F1 27037.93 Hz
F2P -5.000 ppm
F2 -628.79 Hz
PPMCM 6.87500 ppm/cm
HZCM 864.59478 Hz/cm

^{1}H NMR **Entry 24**



^{13}C NMR **Entry 24**



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EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
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INSTRUM dpx400
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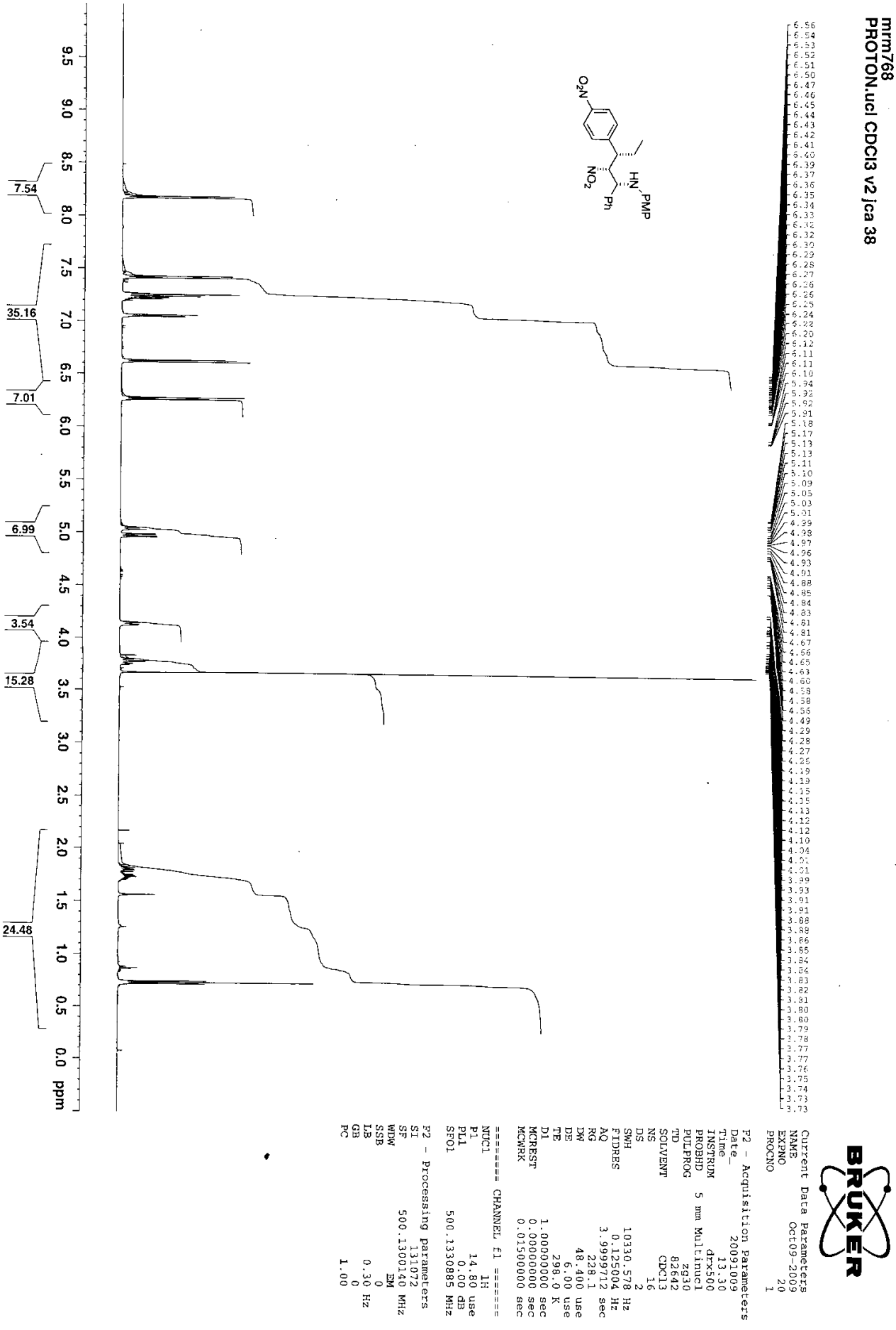
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 4096
DS 2
SWH 25125.629 Hz
FIDRES 0.766773 Hz
AQ 0.6521332 sec
RG 4096
DW 19.900 usec
DE 6.00 usec
TE 298.0 K
D1 1.00000000 sec
d11 0.03000000 sec
DELTA 0.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 8.40 usec
PL1 -4.00 dB
SFO1 100.6414393 MHz

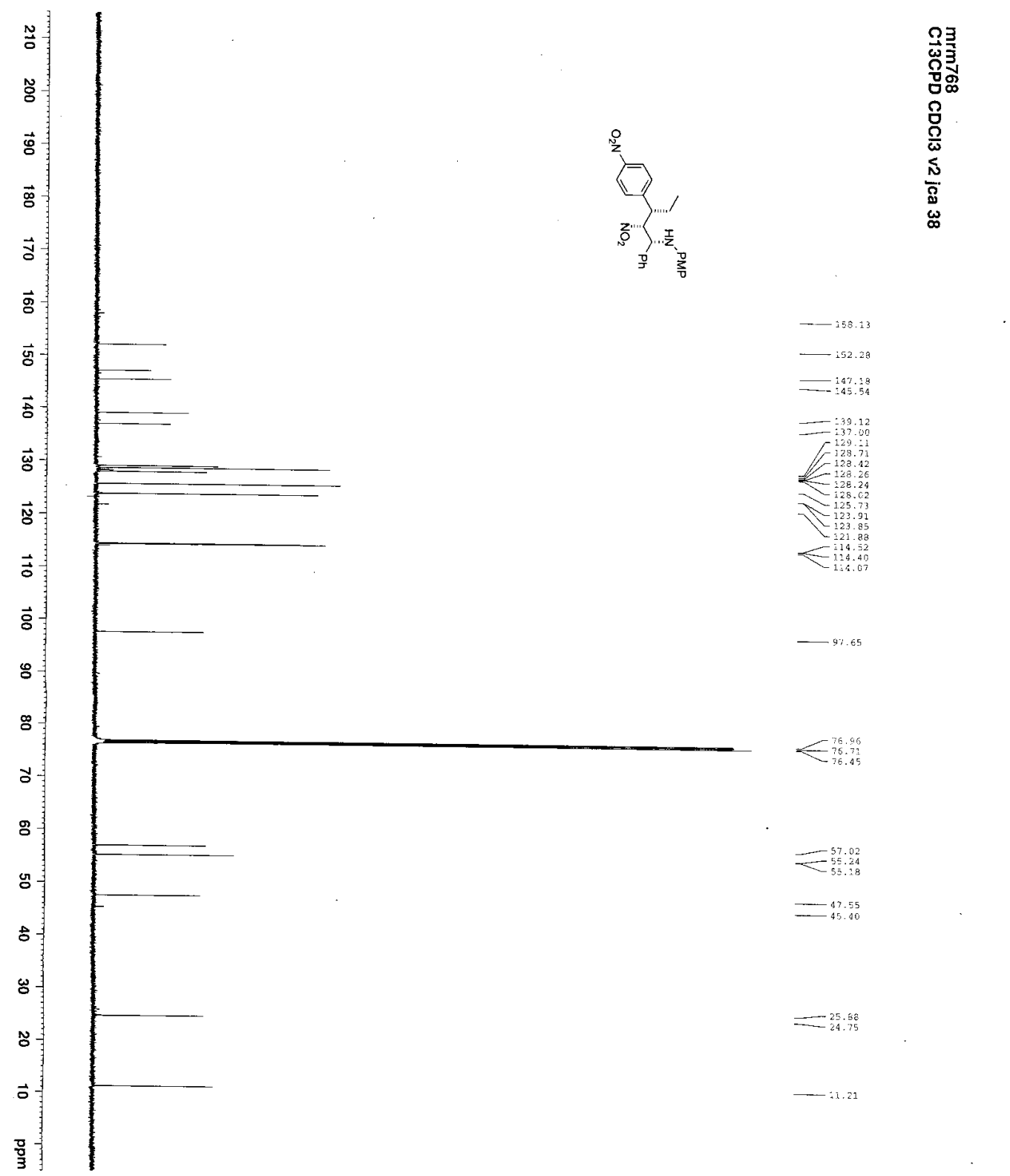
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -6.00 dB
PL12 11.00 dB
PL13 12.00 dB
SFO2 400.2016008 MHz

F2 - Processing parameters
SI 32768
SF 100.6303700 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

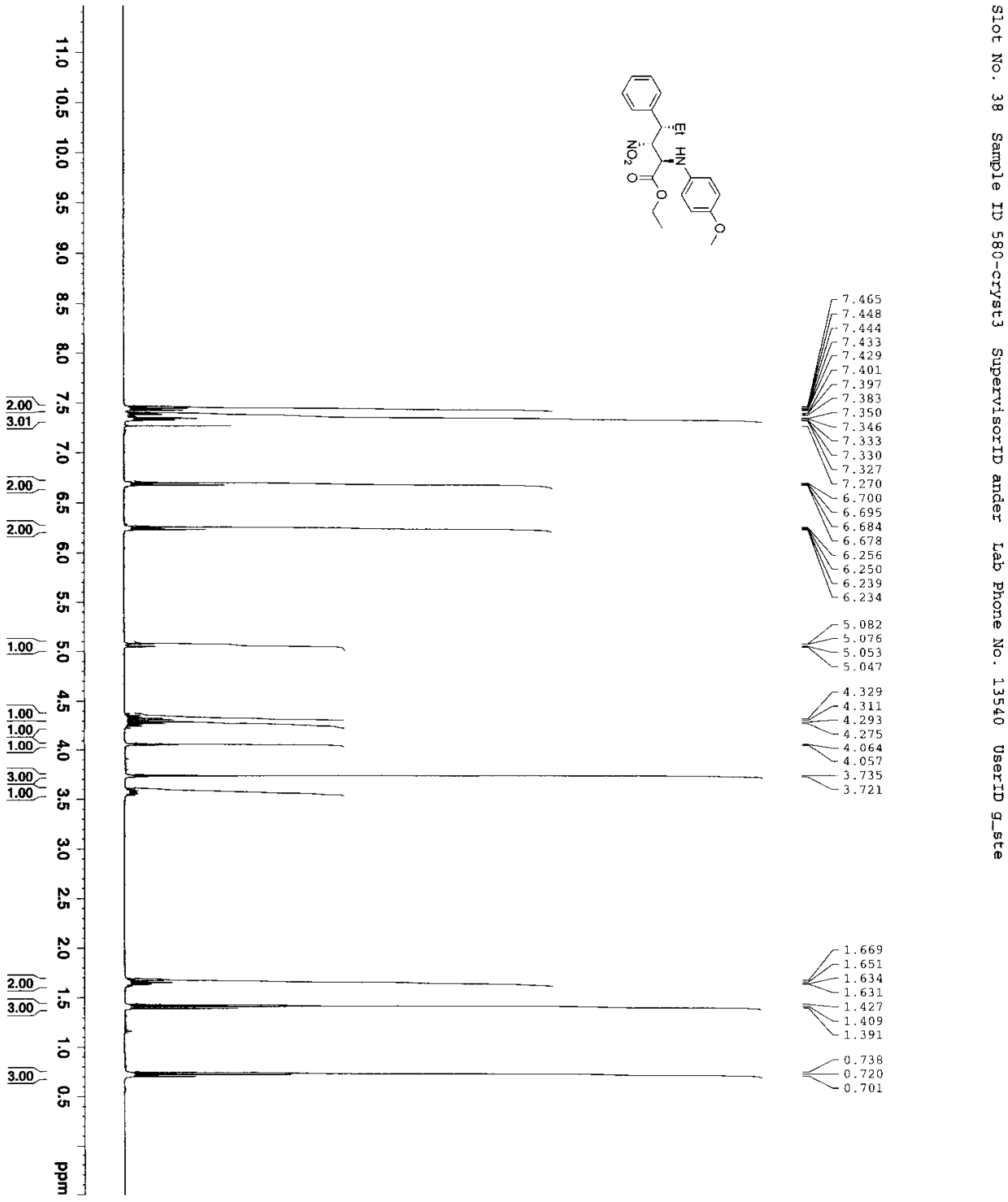
^{1}H NMR **Entry 25**



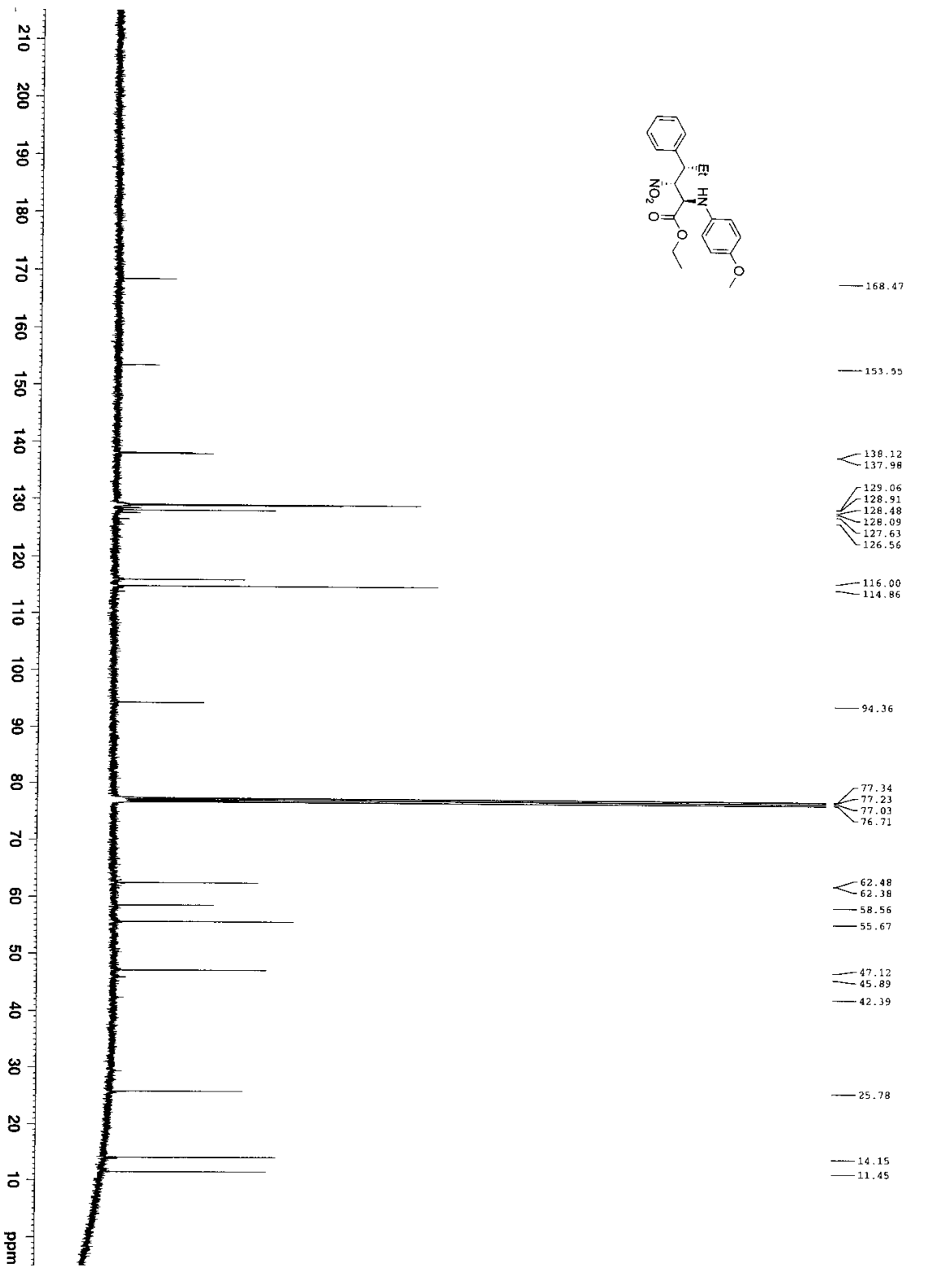
^{13}C NMR **Entry 25**



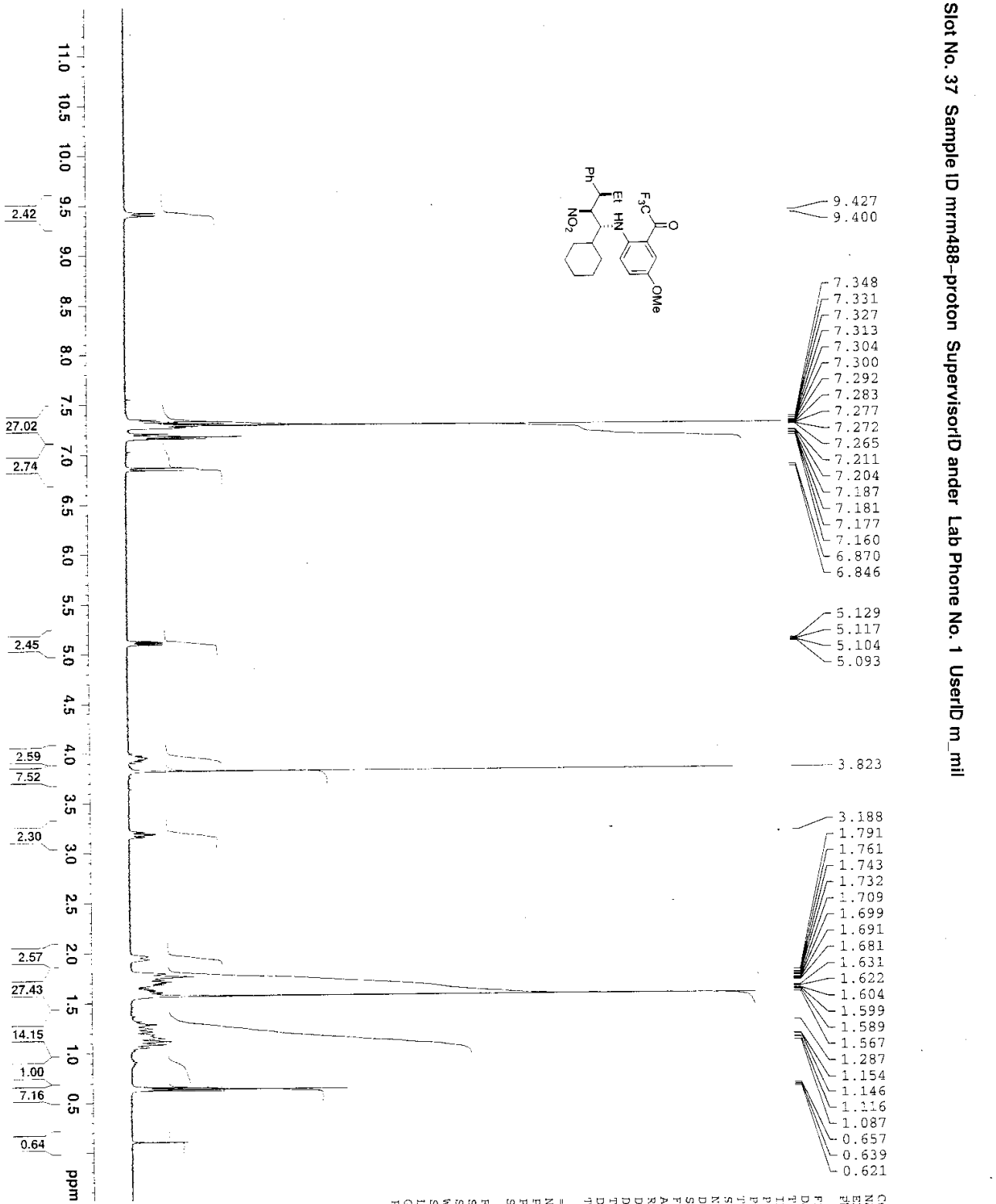
^{1}H NMR **Entry 26**



^{13}C NMR **Entry 26**



^{1}H NMR **9**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F3C
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OMe
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7.181
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5.093
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1.599
1.589
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1.154
1.146
1.116
1.087
0.657
0.639
0.621
2.42
27.02
2.74
2.45
2.59
7.52
2.30
2.57
27.43
14.15
1.00
7.16
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ppm
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PROCNO 1
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Time 15.16
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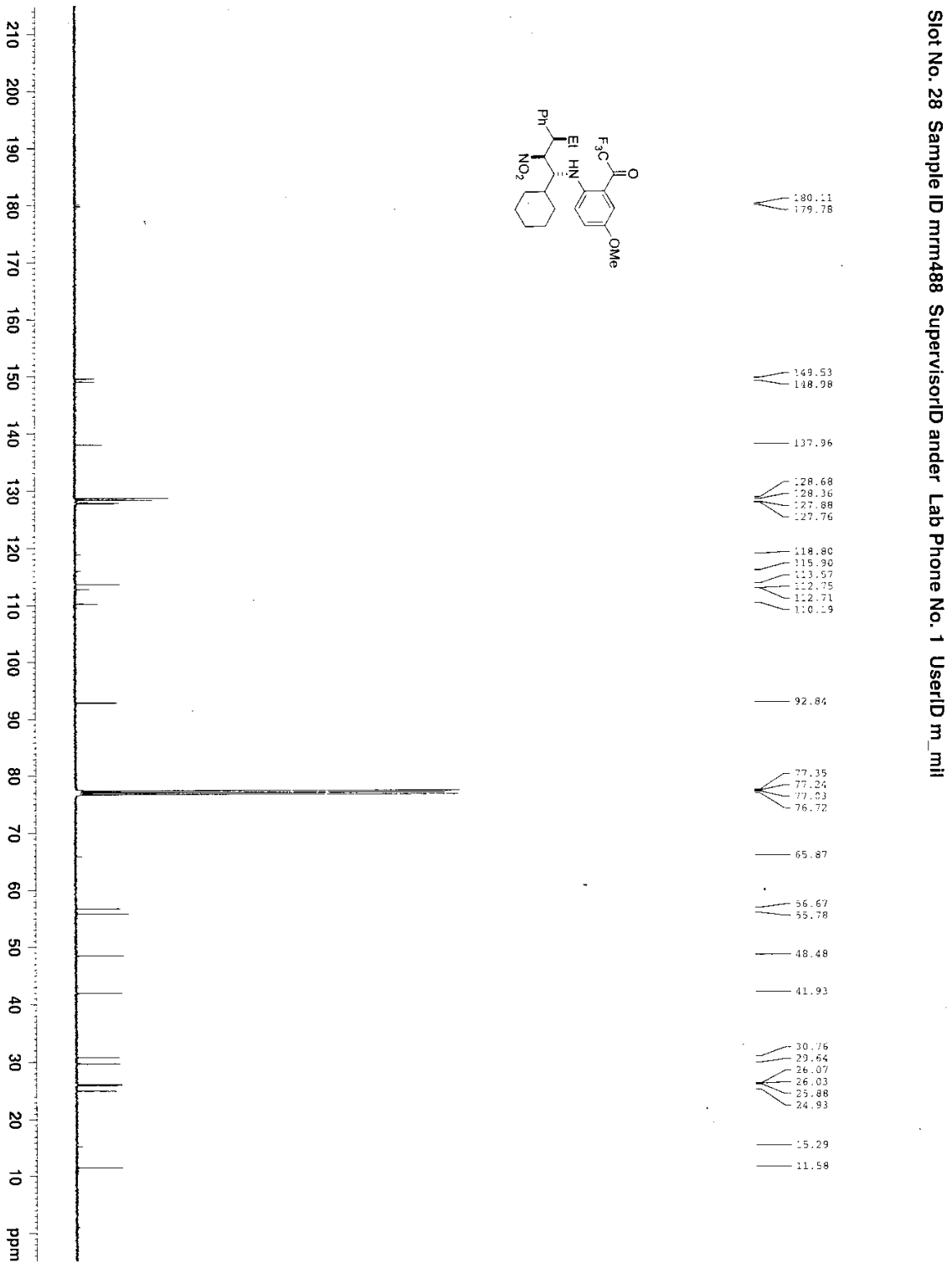
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 4789.272 Hz
FIDRES 0.146157 Hz
AQ 3.4210291 sec
RG 912.3
DW 104.400 use
DE 6.00 use
TE 298.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.40 use
PL1 -6.00 dB
SFO1 400.7022011 MHz
F2 - Processing parameters
SI 32768
SF 400.2000000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{13}C NMR **9**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Ph
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HN
NO2
F3C
O
OMe
180.11
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149.53
148.98
137.96
128.68
128.36
127.88
127.76
118.80
115.90
113.57
112.75
112.71
110.29
92.84
77.35
77.24
77.03
76.72
65.87
56.67
55.78
48.48
41.93
30.76
29.64
26.07
26.03
25.88
24.93
15.29
11.58
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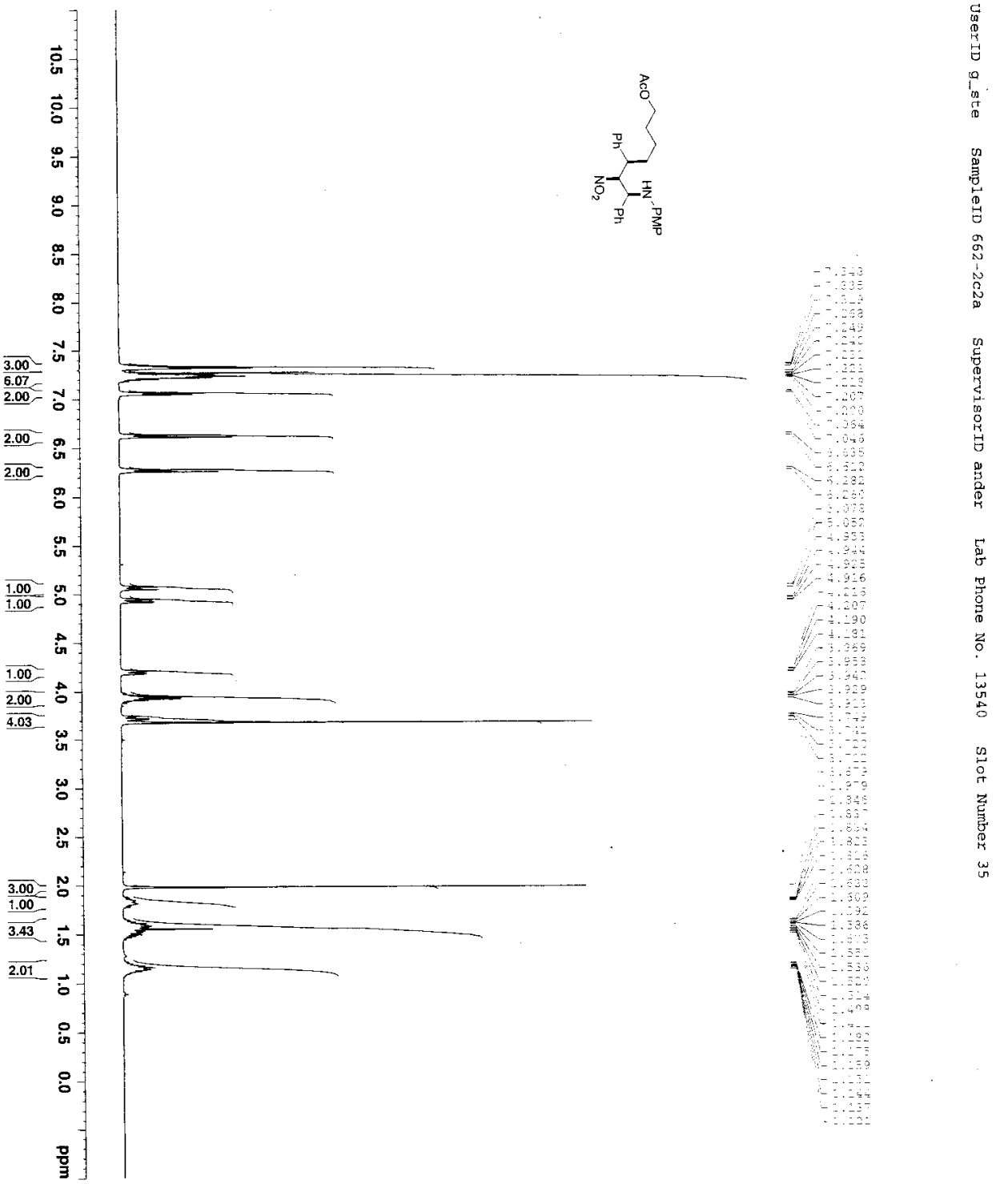
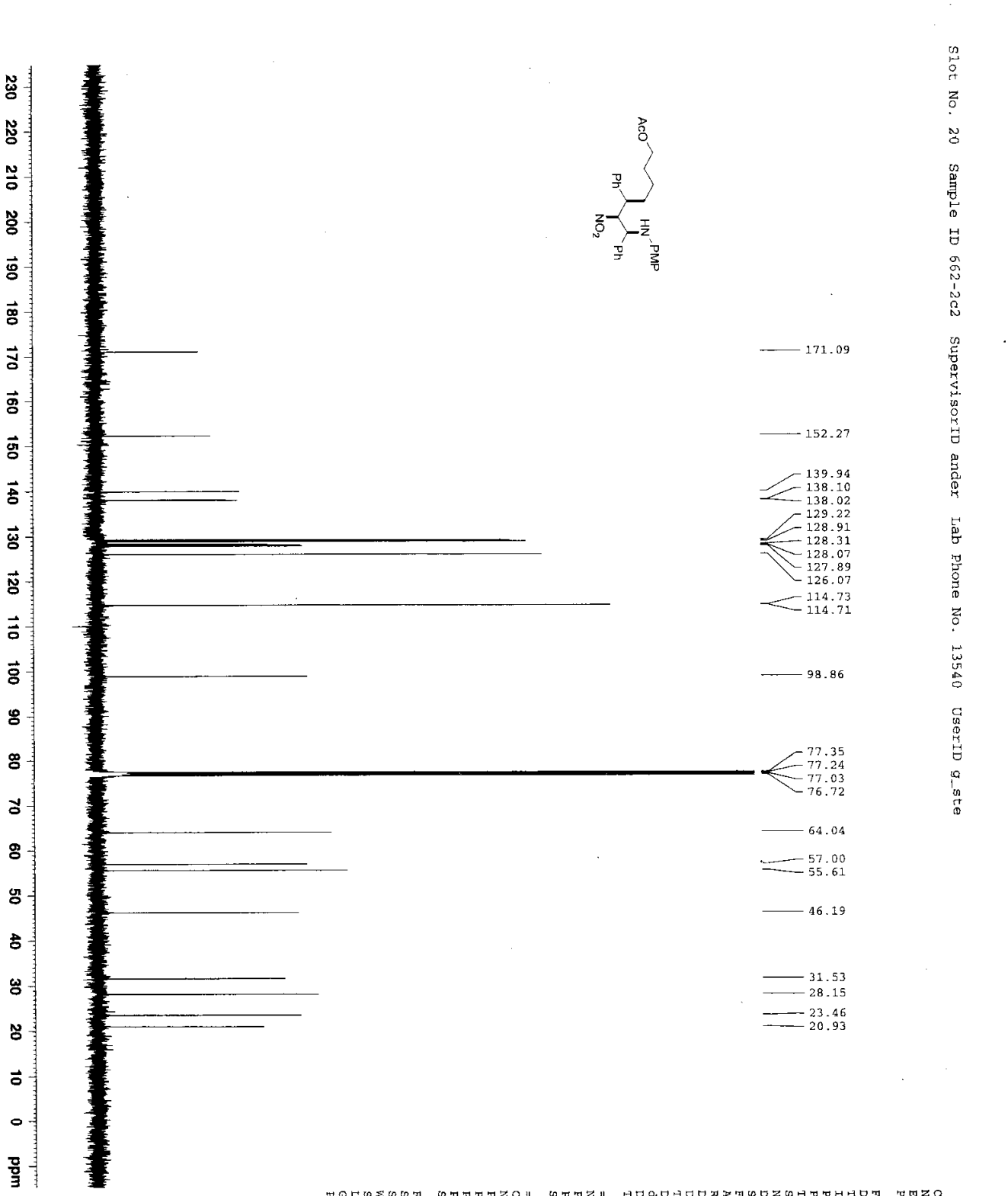
^{1}H NMR **11**


UserID g_ste SampleID 662-2c2a SupervisorID ander Lab Phone No. 13540 Slot Number 35
Current Date Parameters
NAME g_ste.662-2c2a
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20080708
Time 15.52
INSTRUM av3400
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 287
DW 60.800 usec
DE 6.50 usec
TE 295.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.00 usec
PL1 -0.90 dB
PL1W 11.52680206 W
SFO1 400.0724706 MHz
F2 - Processing parameters
SI 65536
SF 400.0700050 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
AcO
Ph
HN
PMP
NO2
Ph
3.00
6.07
2.00
2.00
2.00
1.00
1.00
1.00
2.00
4.03
3.00
1.00
3.43
2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

^{13}C NMR **11**




```
Current Data Parameters
NAME                  g_ste.662-2c2
EXPNO                            4
PROCNO                           1

F2 - Acquisition Parameters
Date_                     20080709
Time                          7.35
INSTRUM                    dpx400
PROBHD     5 mm PABBO BB/
PULPROG                   zgpg30
TD                         32768
SOLVENT                    CDCl3
NS                              2
DS                           4096
SWH                     25125.629 Hz
FIDRES                      0.766773 Hz
AQ                      0.6521332 sec
RG                           9195.2
DW                          19.900 usec
DE                           6.00 usec
TE                          298.0 K
D1                      1.00000000 sec
D11                     0.03000000 sec
DELTA                   0.89999998 sec
TD0                              1

========== CHANNEL f1 ==========
NUC1                           13C
P1                            8.40 usec
PL1                          -4.00 dB
SFO1                  100.6414393 MHz

========== CHANNEL f2 ==========
CPDPRG2                    waltz16
NUC2                           1H
PCPD2                       100.00 usec
PL2                          -6.00 dB
PL12                         11.00 dB
PL13                         12.00 dB
SFO2                  400.2016008 MHz

F2 - Processing parameters
SI                             32768
SF                    100.6303700 MHz
WDW                               EM
SSB                                0
LB                              1.00 Hz
GB                                 0
PC                              1.40
```