

Supporting Information

Synthesis of α -secondary allylic amines via a modified Bruylants reaction

Claude Agami, François Couty* and Gwilherm Evano

*Laboratoire de Synthèse Asymétrique associé au CNRS, Université Pierre et Marie Curie,
4 place Jussieu, 75005 Paris, France.*

General comments

^1H and ^{13}C NMR spectra (CDCl_3 solution) were respectively recorded on a Bruker ARX 250 spectrometer at 250 and 62.9 MHz. Chemical shifts are reported in ppm from TMS as the internal standard.

All reactions were carried out under an atmosphere of argon in glassware that had been flame-dried under an inert atmosphere. THF was distilled from sodium/benzophenone ketyl.

Columns chromatographies were performed on silica gel, 230-400 mesh by using various mixtures of diethyl ether and petroleum ether.

Typical procedure for the modified Bruylants reaction

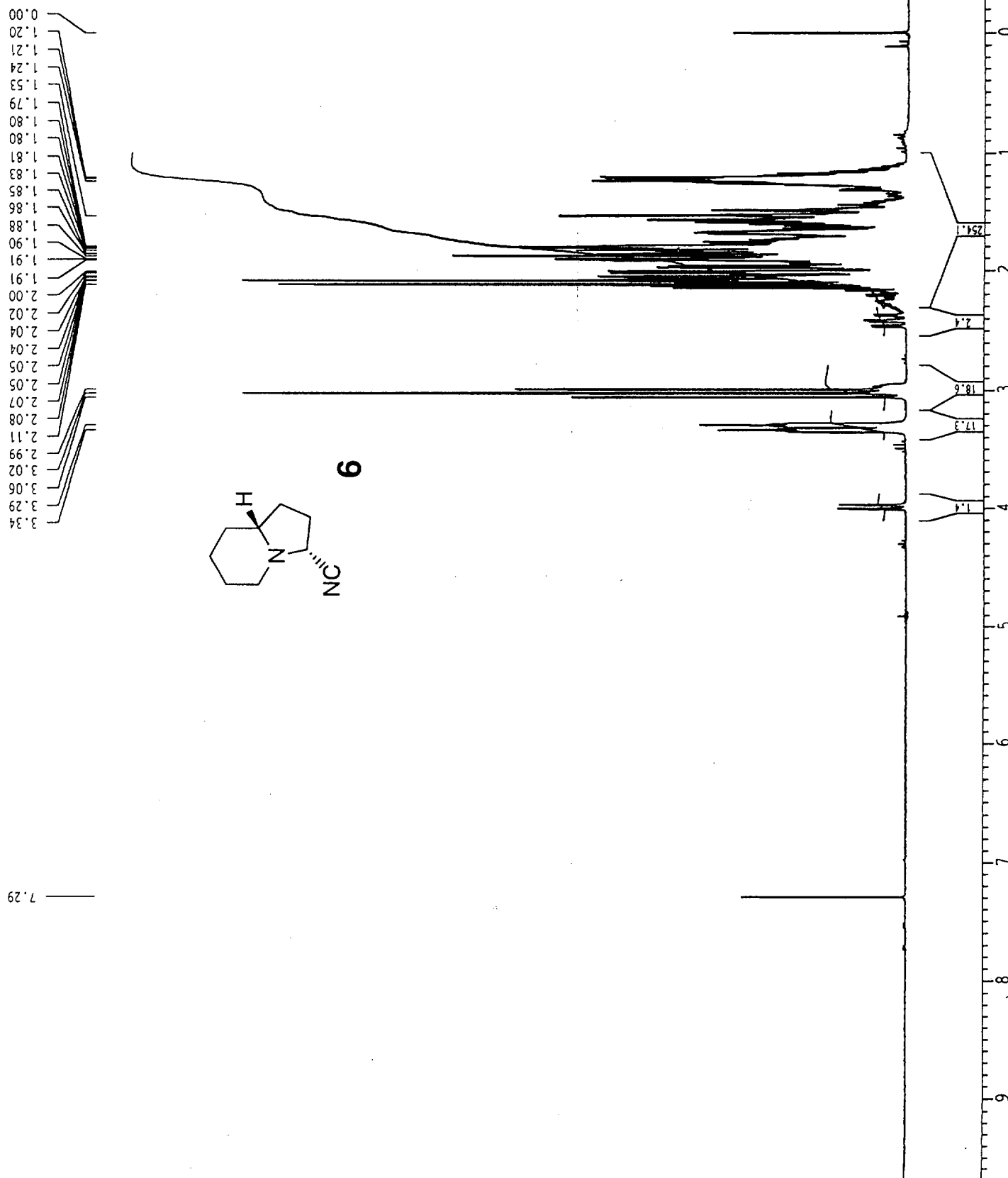
To a solution of the required α -amino nitrile (1 mmol) in THF (10 mL) was added silver tetrafluoroborate (311 mg, 1.6 mmol). The mixture was stirred at r.t. for 10 minutes and cooled at -78°C . Grignard reagent (4 mmol) was then added dropwise and the solution was allowed to reach 0°C . Completion of the reaction was ascertained by TLC and required ca. 1 h. The mixture was then hydrolyzed by dropwise addition of a saturated aqueous solution of NH_4Cl (10 mL) and extracted with ether. The combined organic layers were dried over MgSO_4 and the solvents were evaporated under reduced pressure. Crude products were further purified by flash chromatography and were obtained as oils.

Current Data Parameters
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EXPNO 2
PROCNO 1

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TE 300.0 K
D1 0.30000001 sec
P1 4.50 usec
SFO1 250.1312264 MHz
NUCLEUS 1H

F2 - Processing parameters
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SF 250.1299993 MHz
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SSB 0
LA 0
GB 0
PC 1.00

1D NMR plot parameters
CX 21.00 cm
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F1 2501.30 Hz
F2P -0.922 ppm
F2 -230.69 Hz
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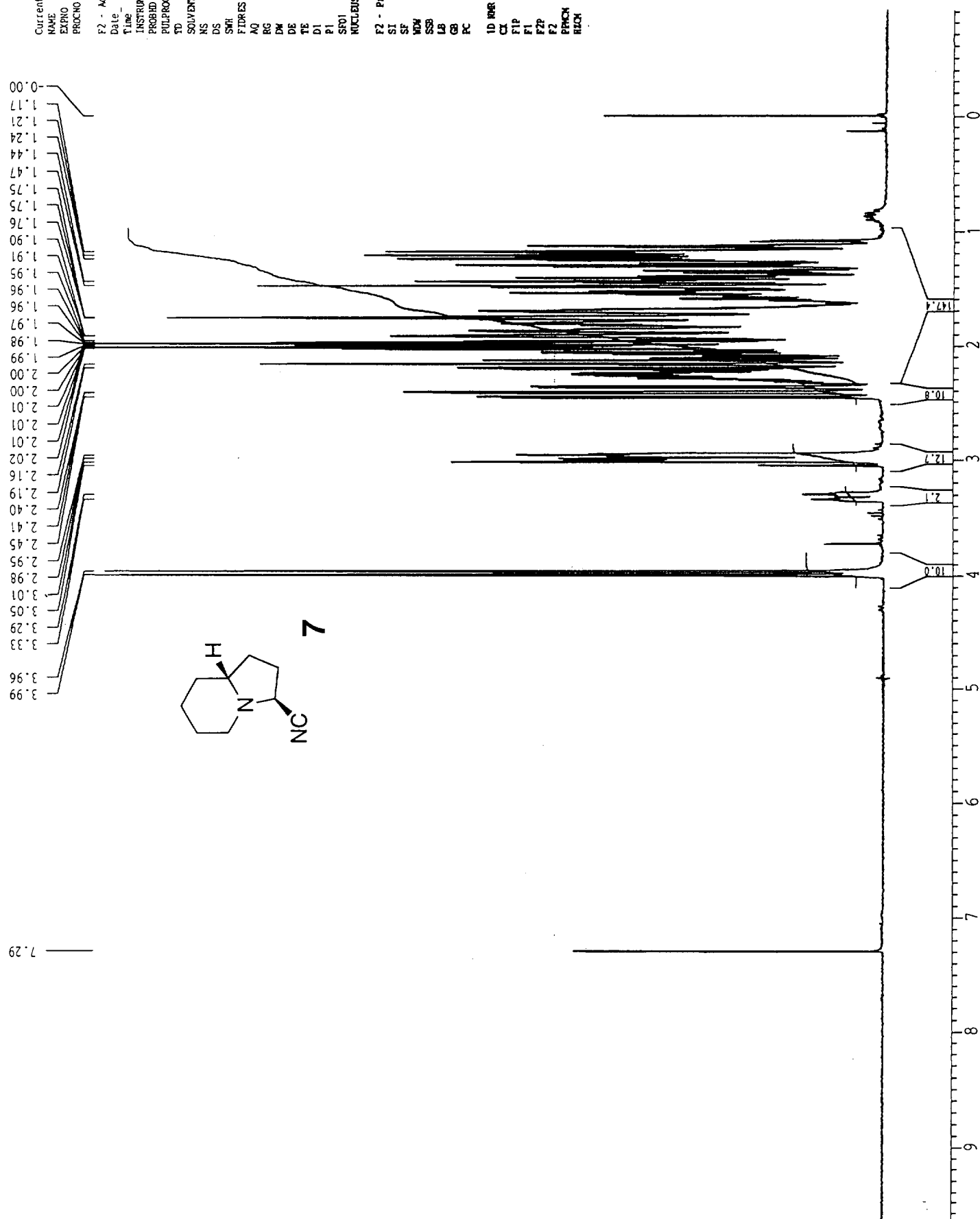


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 SFO1 250.1312264 MHz
 NUCLEUS 1H

F2 - Processing parameters
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 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
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 F1P 10.000 ppm
 F1 2501.30 Hz
 F2P -0.922 ppm
 F2 -230.69 Hz
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 HZCN 113.83282 Hz/cm

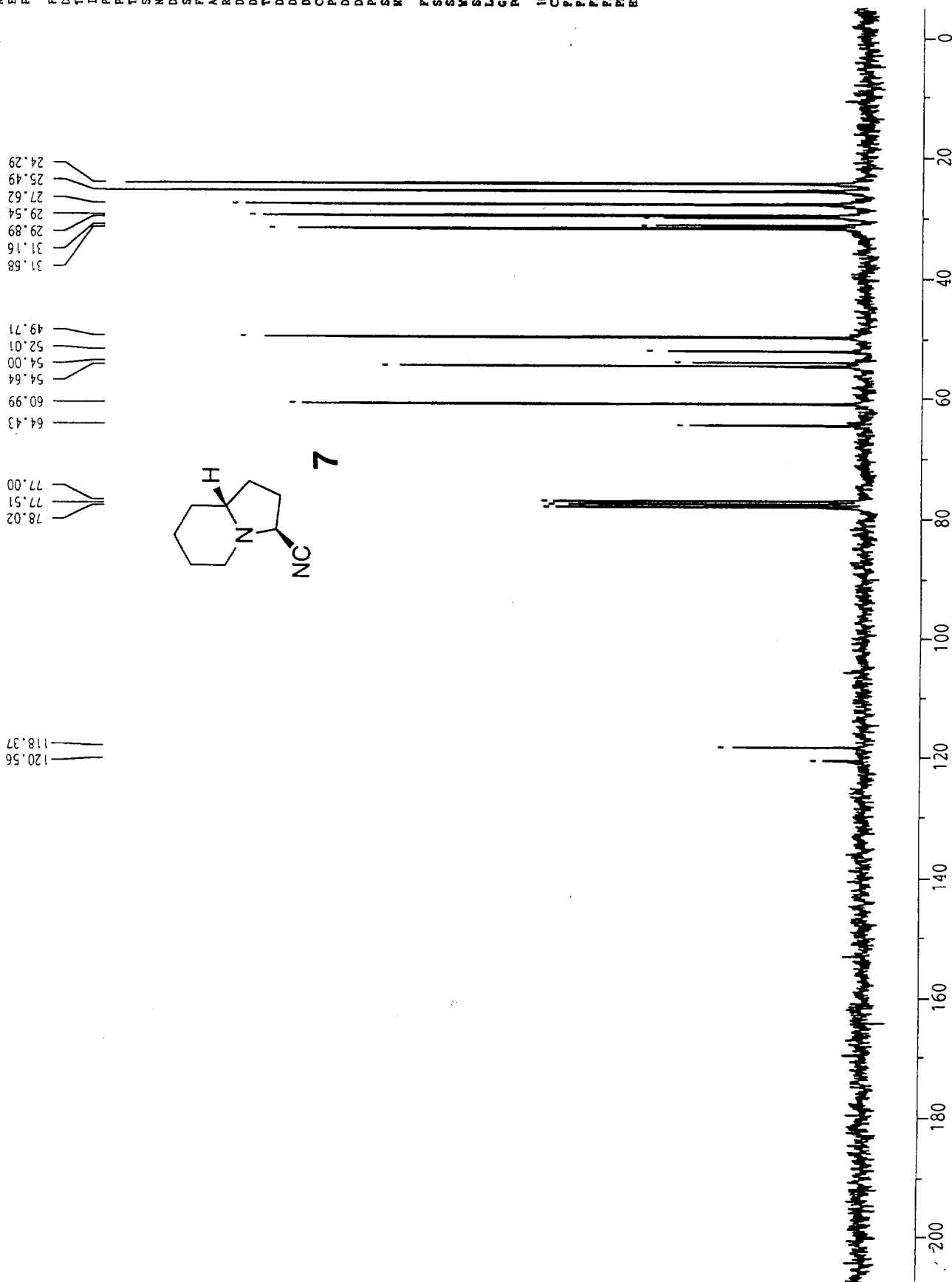


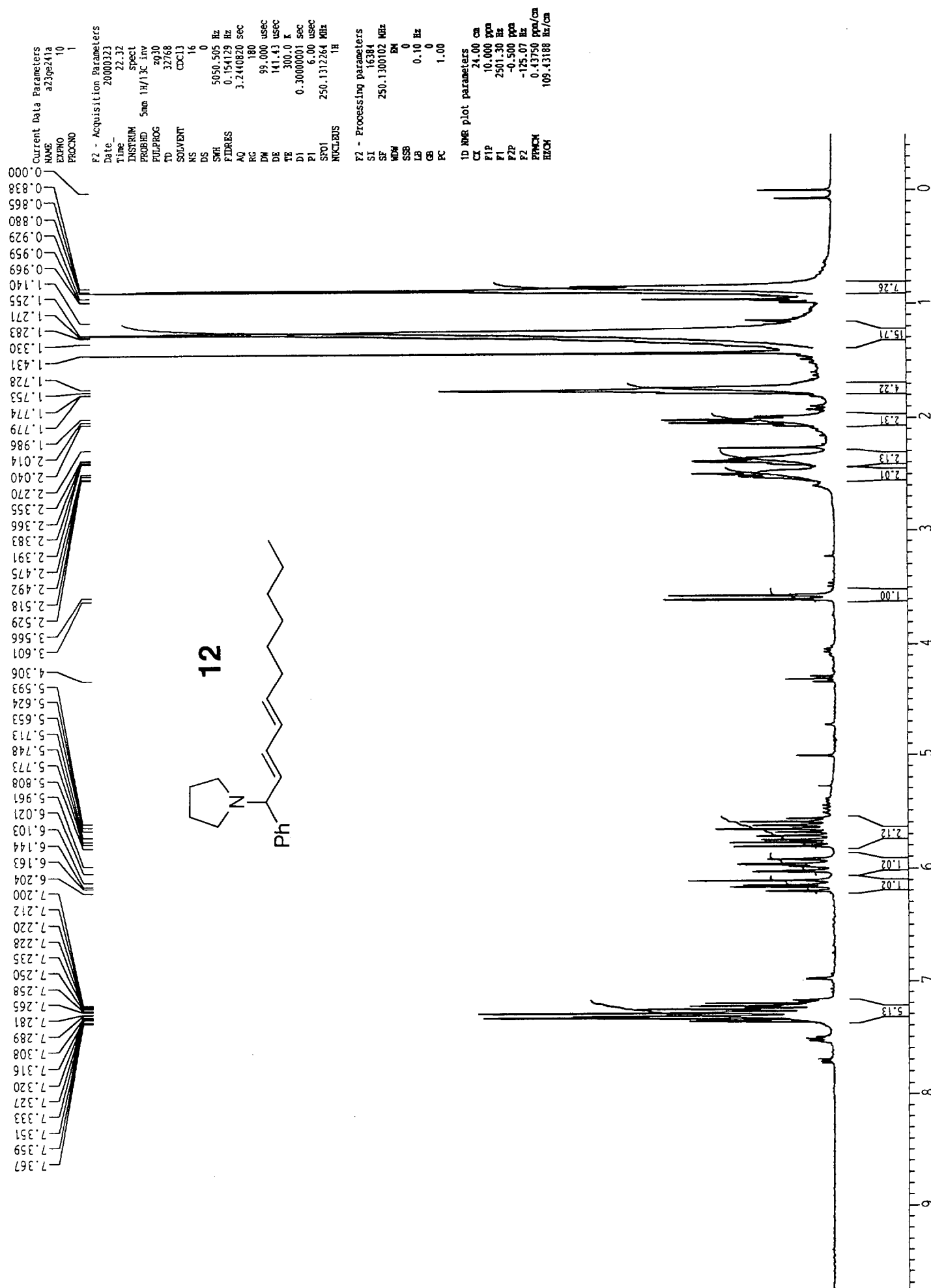
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 NS 1024
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 FIDRES 0.984438 Hz
 AQ 0.5079540 sec
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 DW 31.000 usec
 DE 44.29 usec
 TE 300.0 K
 D12 0.0002000 sec
 DL6 35.00 dB
 D1 0.80000001 sec
 CDPGPG waltz16
 P31 100.00 usec
 D11 0.03000000 sec
 DL5 26.00 dB
 P1 9.50 usec
 EXO 62.904935 MHz
 NUC13 13C

F2 - Processing parameters
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 VOP EN
 SSF 0
 LB 3.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters
 CX 24.00 cm
 P1P 220.000 ppm
 F1 13836.95 Hz
 F2P -5.000 ppm
 F2 -314.48 Hz
 FPMCH 9.37500 ppm/cm
 BECH 589.64264 Hz/cm



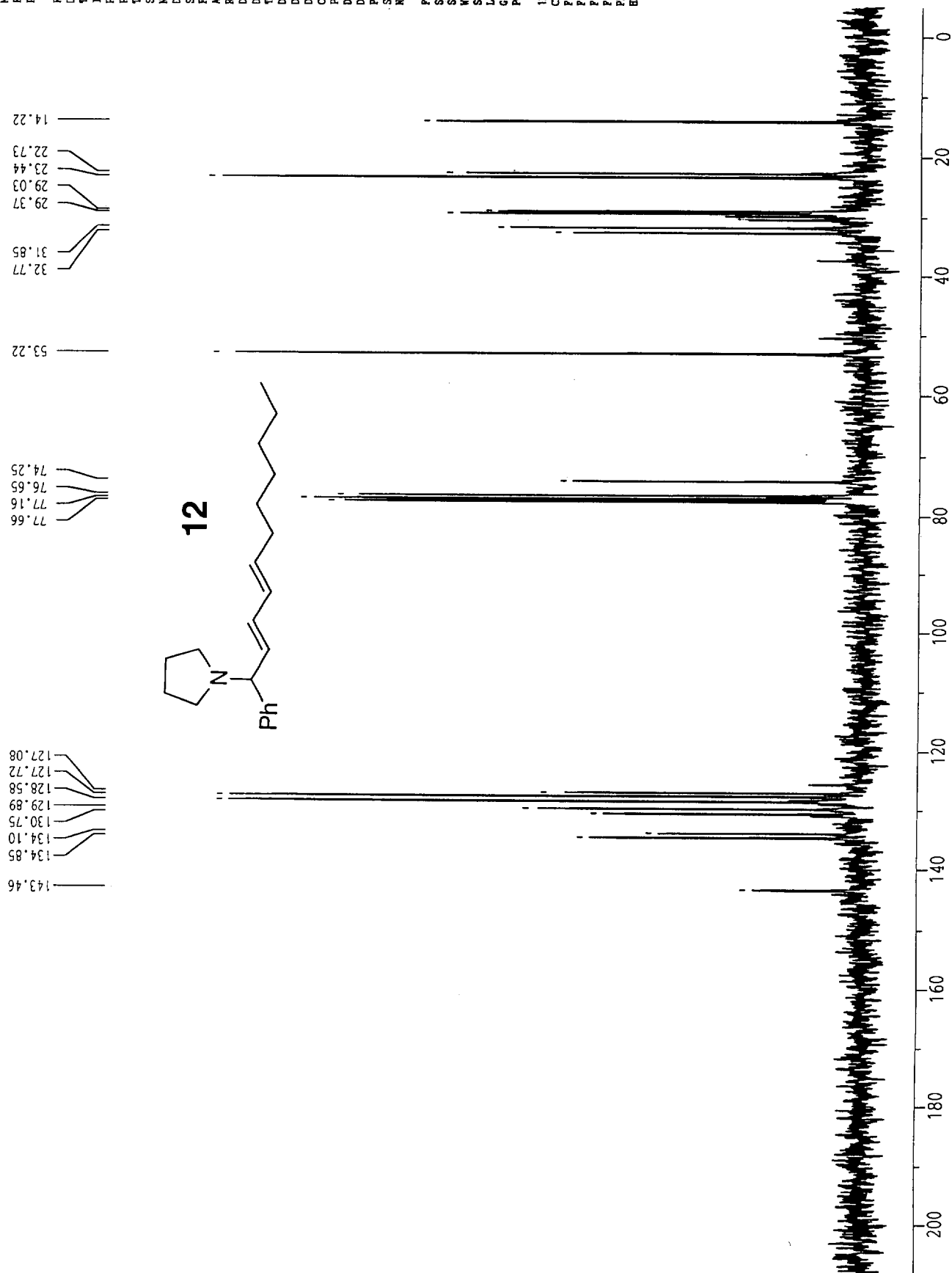


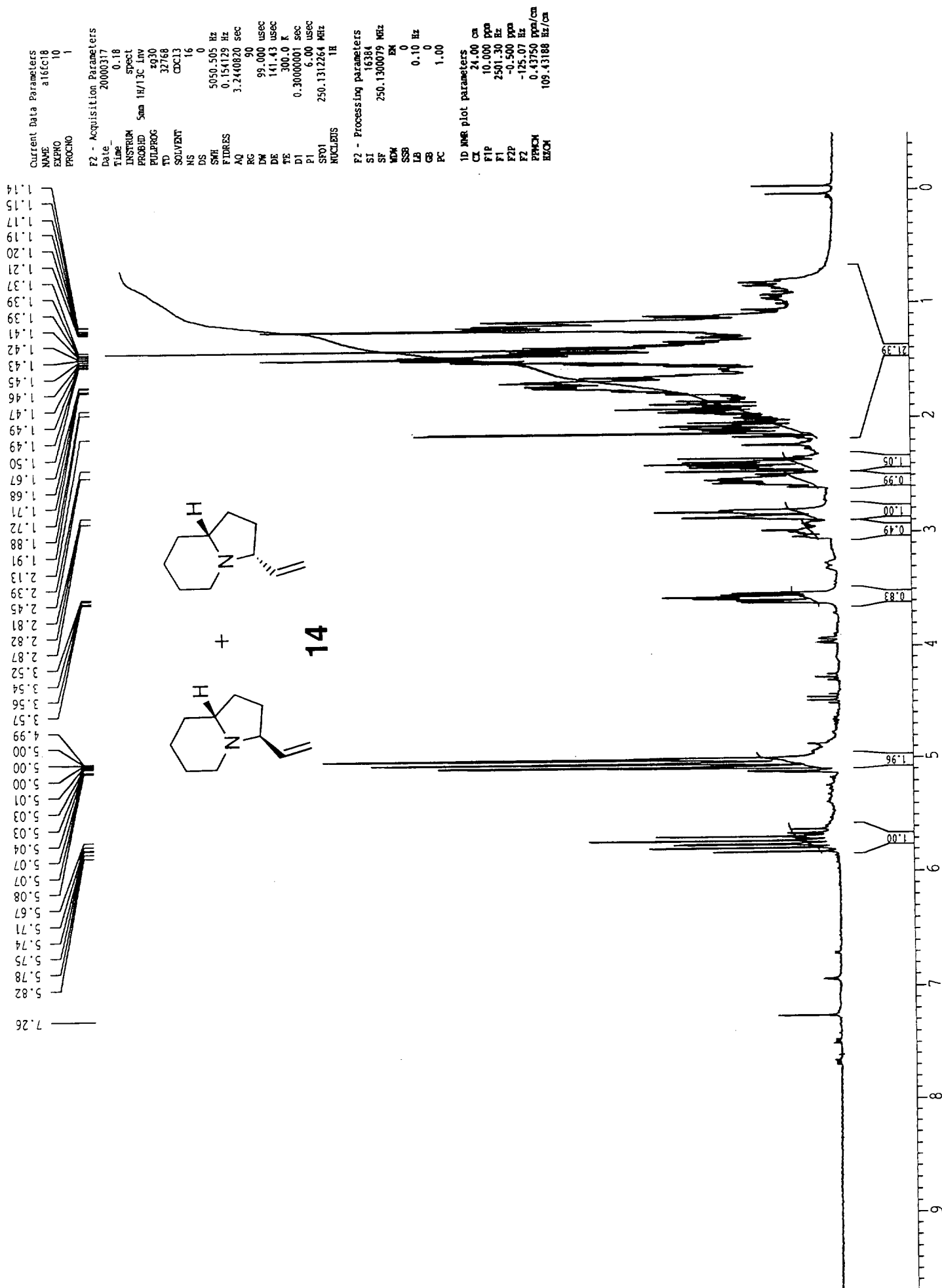
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 P1 9.50 usec
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 NUCLEUS 13C

F2 - Processing parameters
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 GB 0
 PC 1.40

1D NMR plot parameters
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 F2P -5.000 ppm
 F2 -314.48 Hz
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 BECN 589.64282 Hz/cm



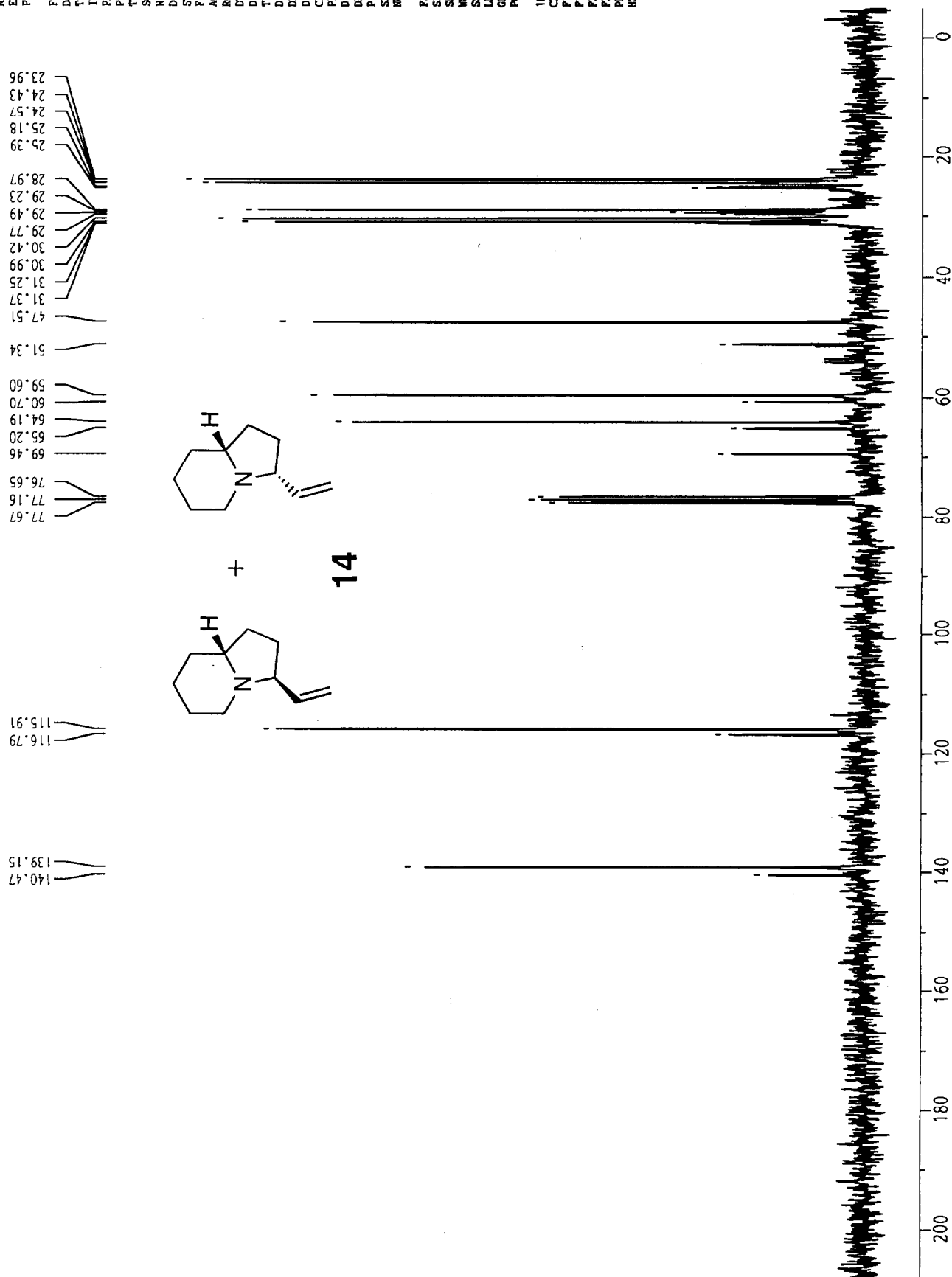


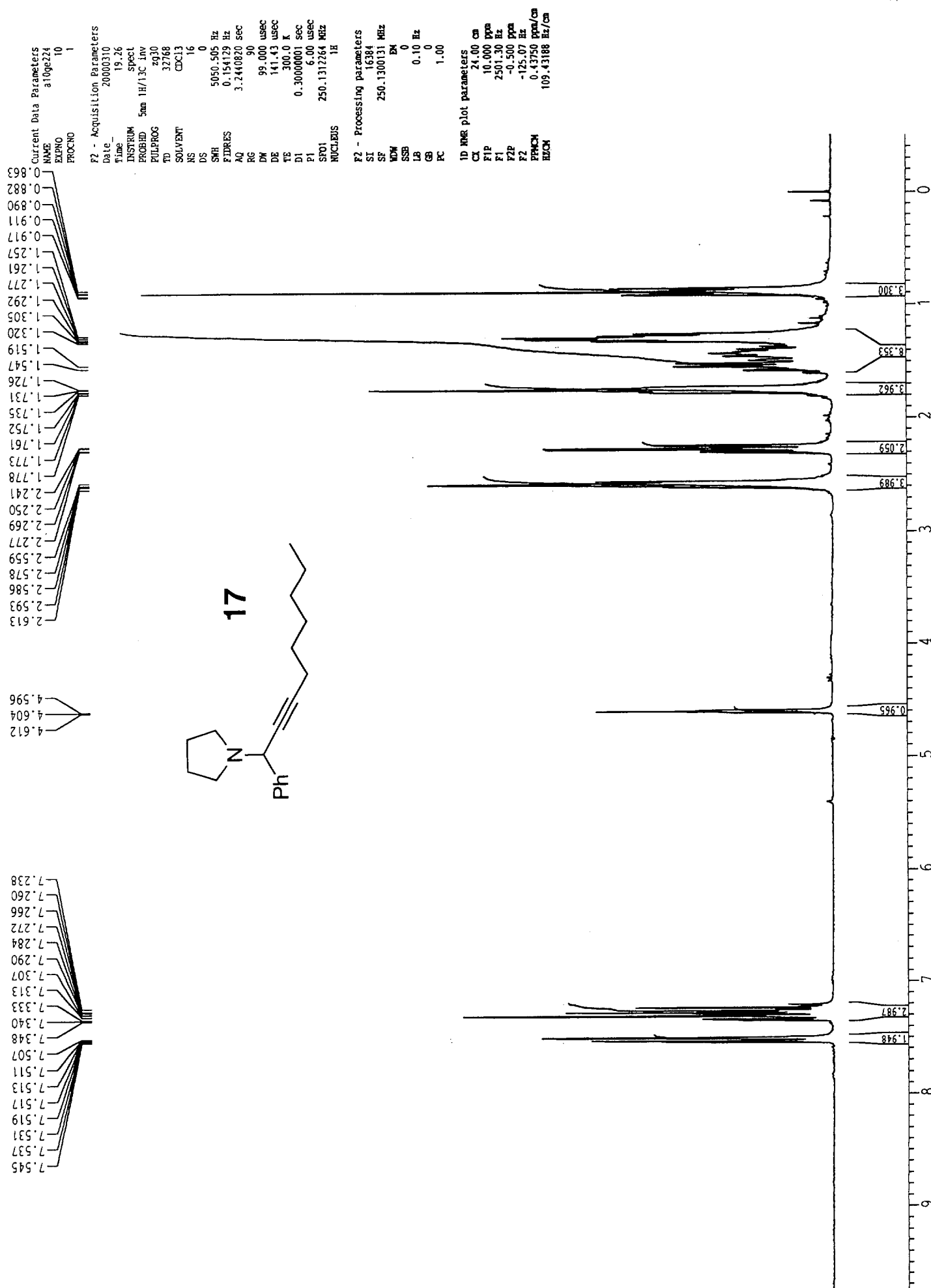
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NS 1024
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FIDRES 0.984438 Hz
AQ 0.5079540 sec
RG 45500
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DE 44.29 usec
TE 300.0 K
D12 0.0002000 sec
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D1 0.80000001 sec
CPOPRG waltz16
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P1 9.50 usec
SFO1 62.9029305 MHz
NUC1 13C

F2 - Processing parameters
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SF 62.8952325 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 24.00 cm
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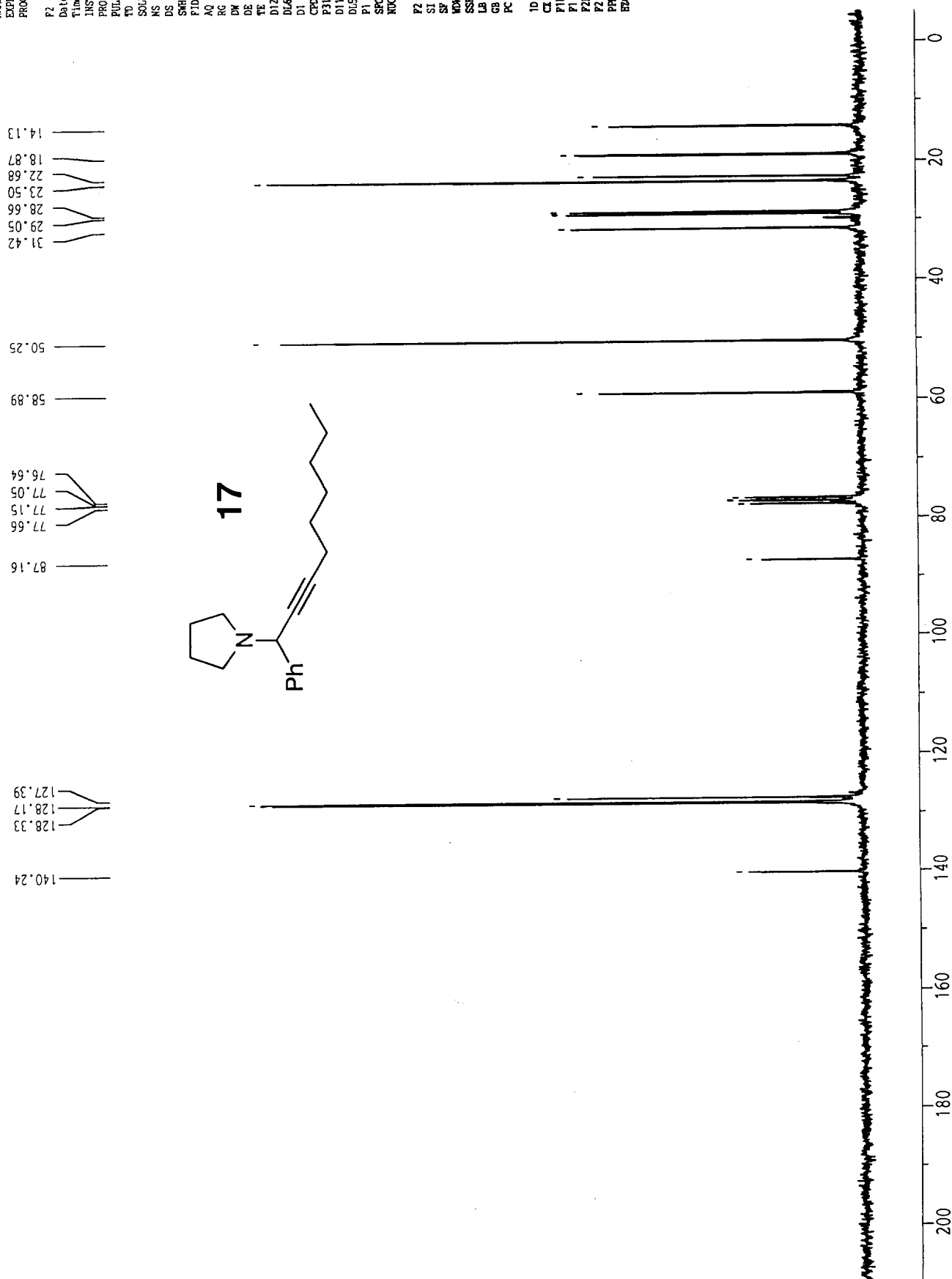


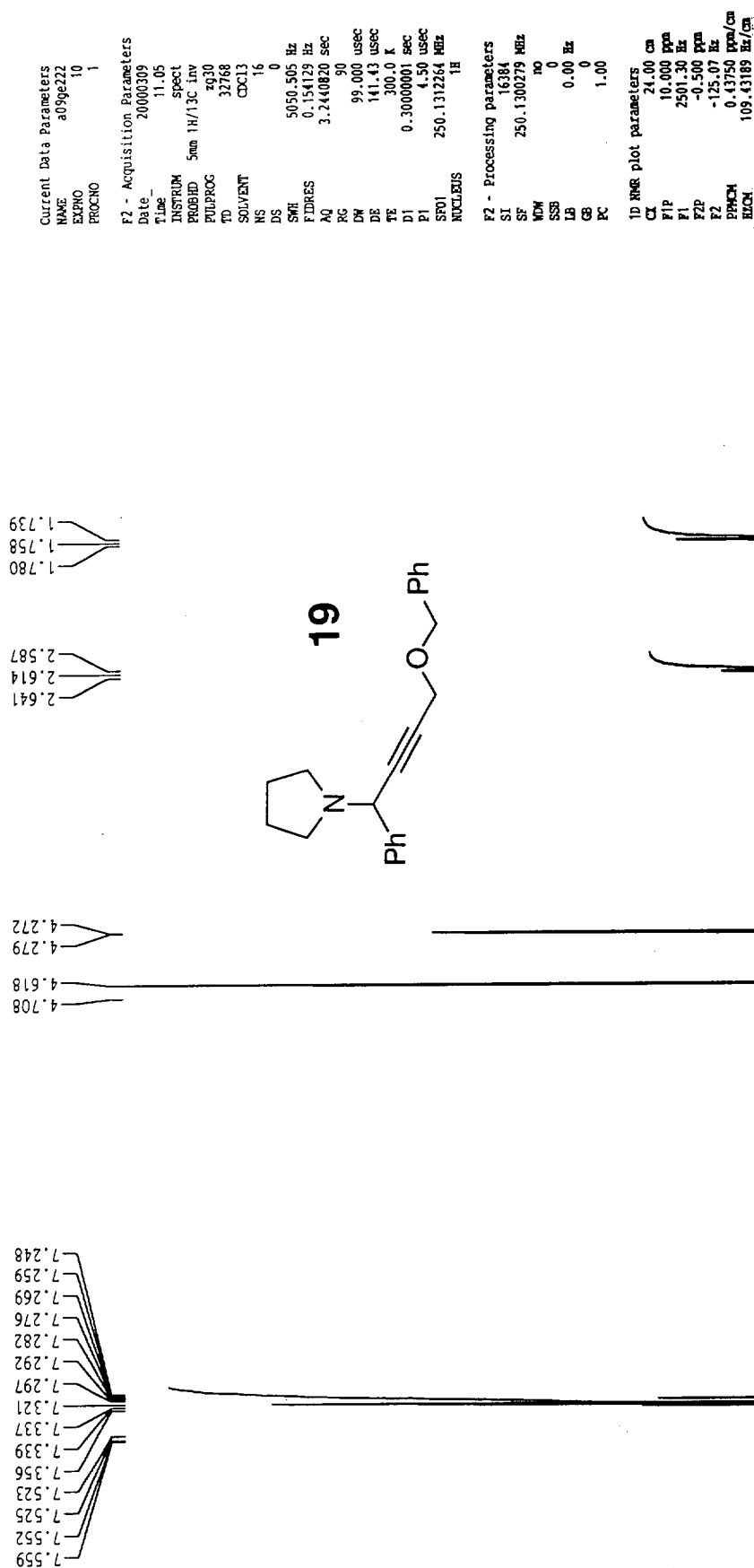
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RG 45500
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DE 44.29 usec
TE 300.0 K
D12 0.00002000 sec
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D1 0.80000001 sec
CPOPRG waltz16
P31 100.00 usec
D11 0.03000000 sec
D15 26.00 dB
P1 9.50 usec
SFO1 62.9029305 MHz
NUC1A15 13C

F2 - Processing parameters
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SF 62.8952344 MHz
WDW BN
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
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F1 13636.35 Hz
F2P -5.000 ppm
F2 -314.48 Hz
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BEZCM 589.64282 Hz/cm





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EXPNO11
PROCNO1

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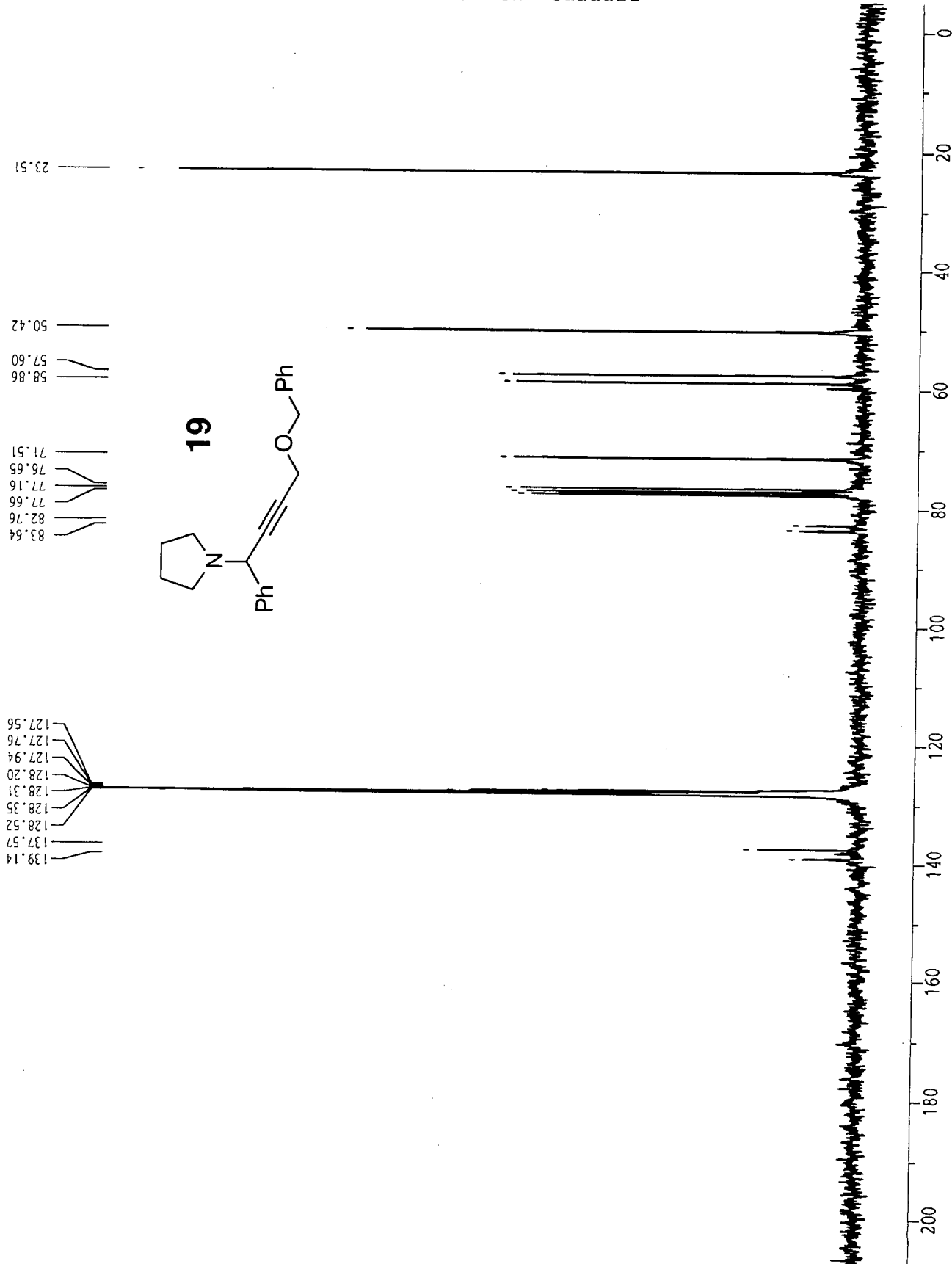
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FIDRES0.984438 Hz
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RG45500
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DE44.29 usec
TE300.0 K
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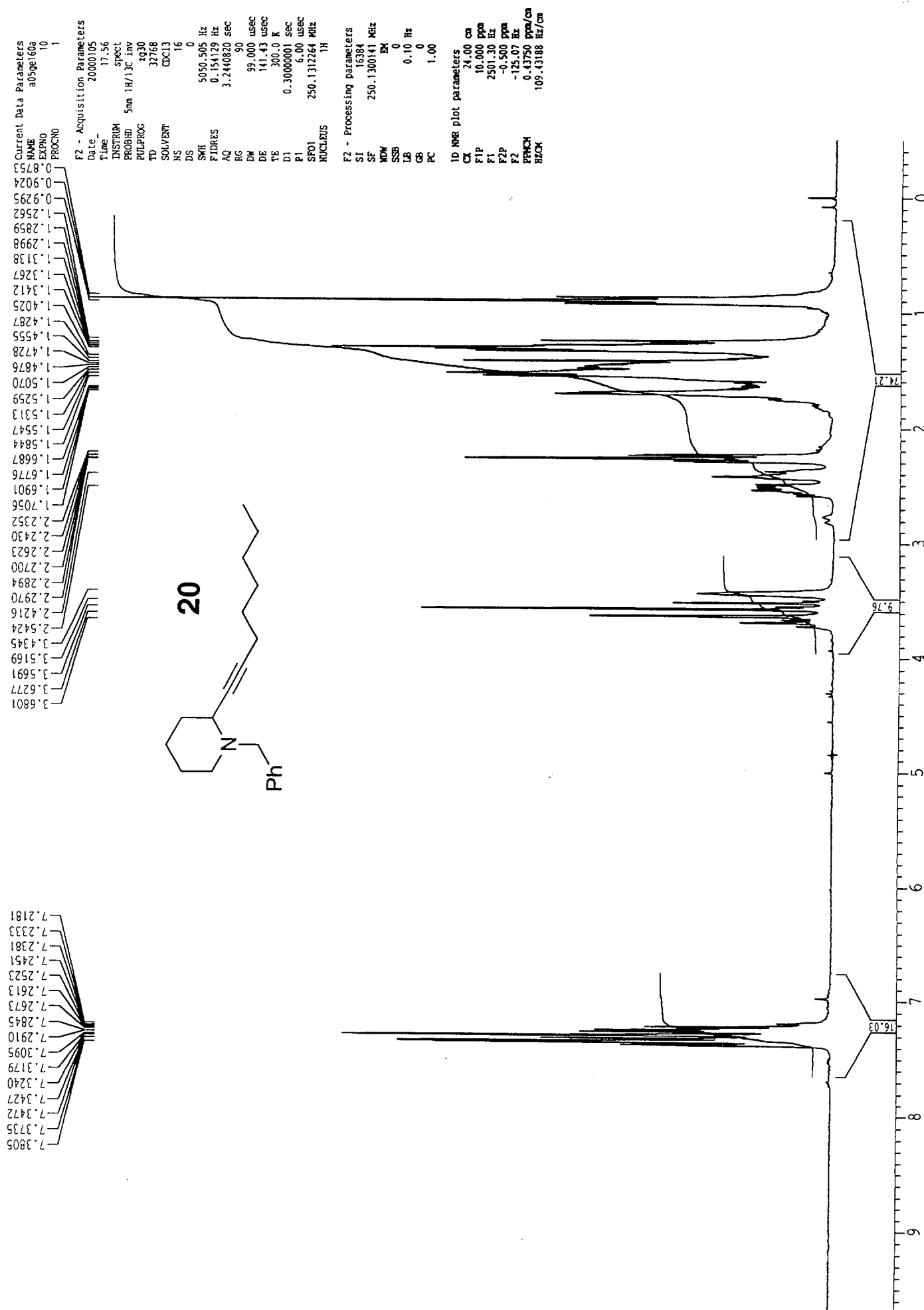
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1D NMR plot parameters

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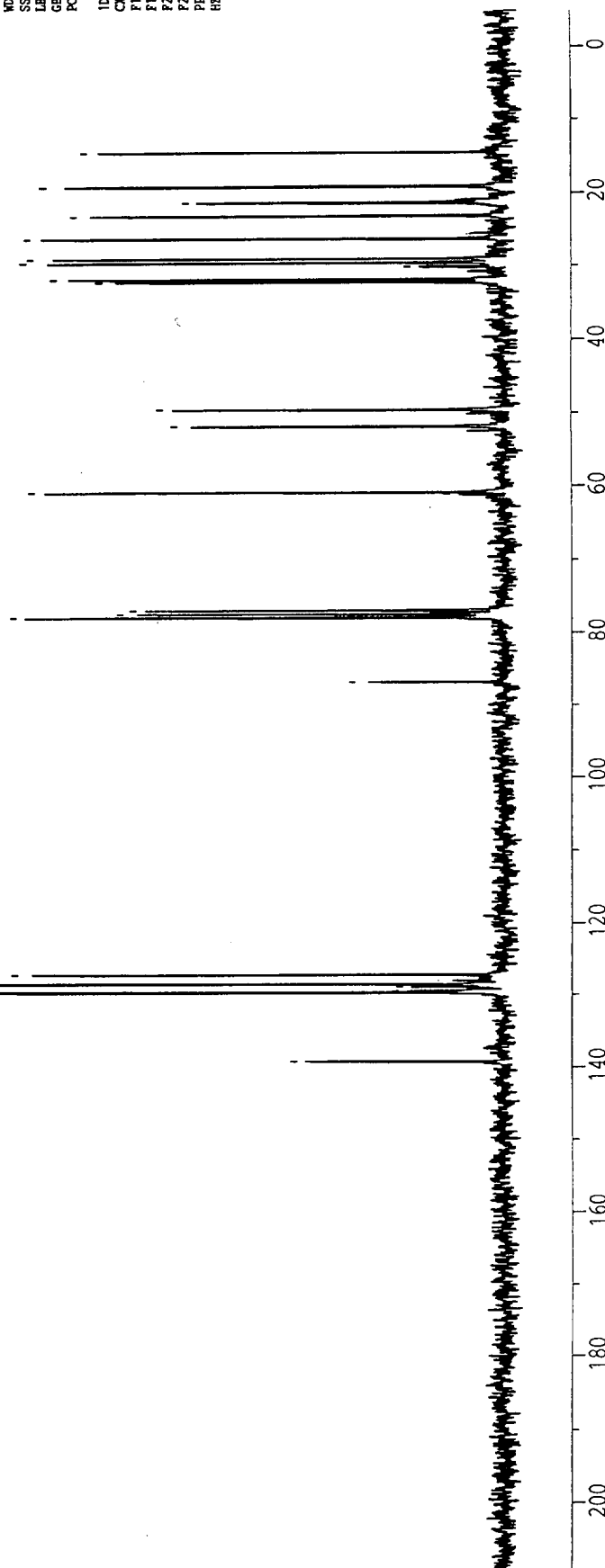
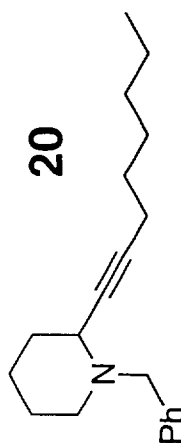
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 NS 1024
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 RG 45500
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 TE 300.0 K
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 P1 9.50 usec
 SFO1 62.9029305 MHz
 NUCLEUS 13C
 F2 - Processing parameters
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 GB 0
 PC 1.40
 1D NMR plot parameters
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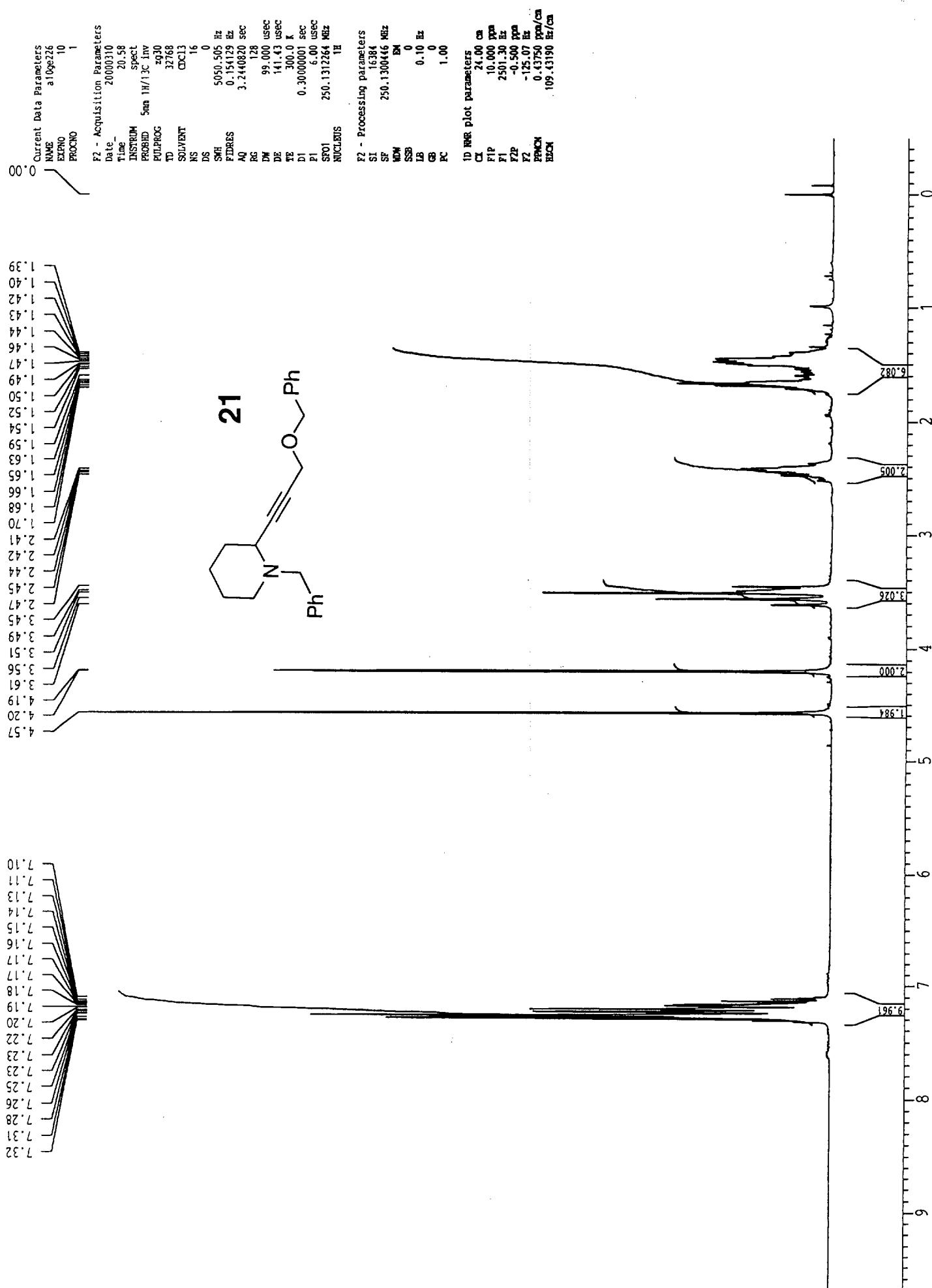
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129.69
139.22



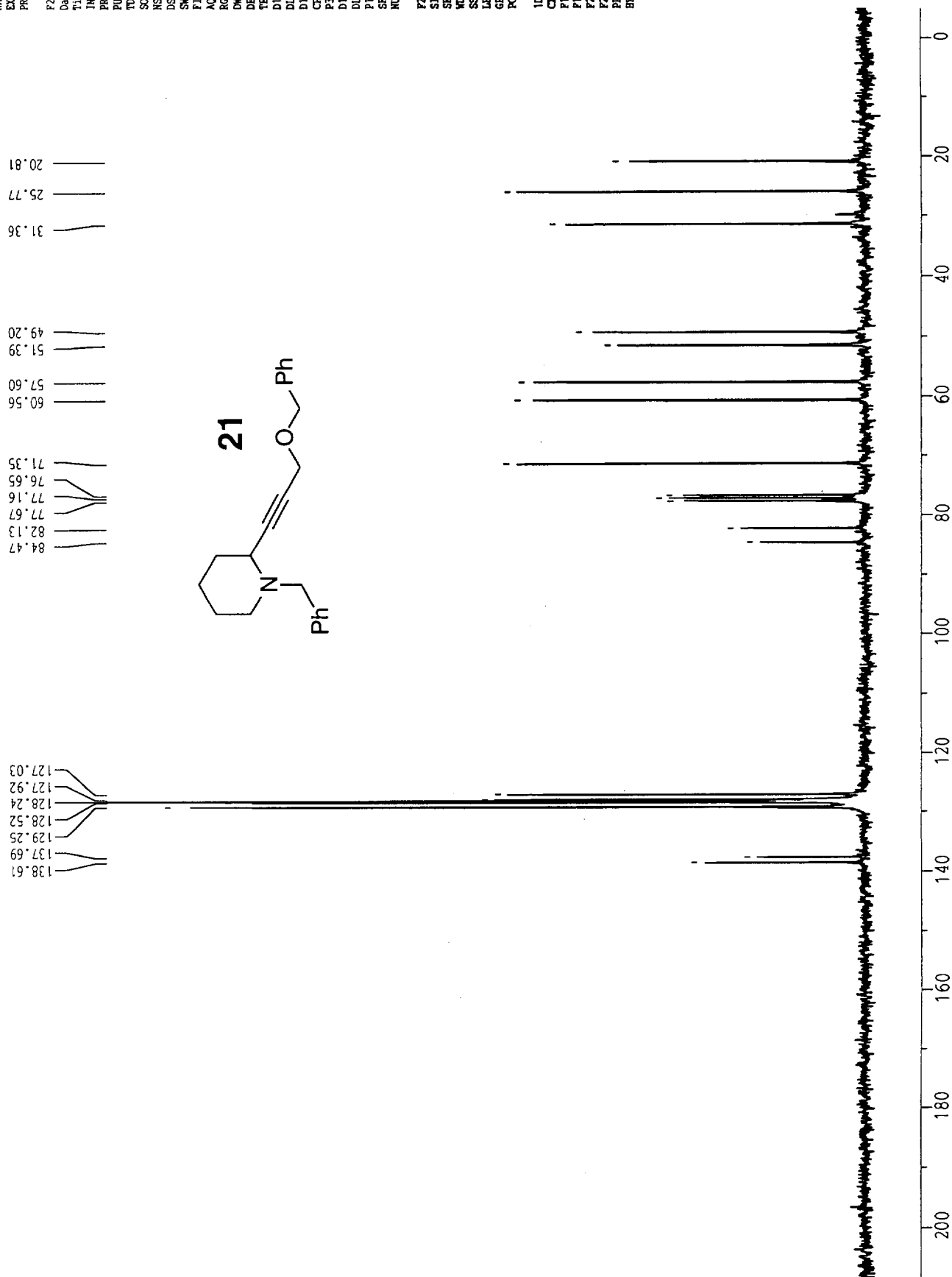


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EXPNO 11
PROCNO 1

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PULPROG zgpg30
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FIDRES 0.00000001 sec
RG 45500
DM 31.000 usec
DE 44.29 usec
TE 300.0 K
D12 0.00002000 sec
DL6 35.00 dB
D1 0.80000001 sec
CPDPRG waltz16
P31 100.00 usec
D11 0.03000000 sec
DL5 26.00 dB
P1 9.50 usec
SFO1 62.9029305 MHz
NUCL13C 13C

F2 - Processing parameters
SI 16384
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SSB 0
LB 3.00 Hz
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PC 1.40

1D NMR plot parameters
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BZCN 589.64282 Hz/cm

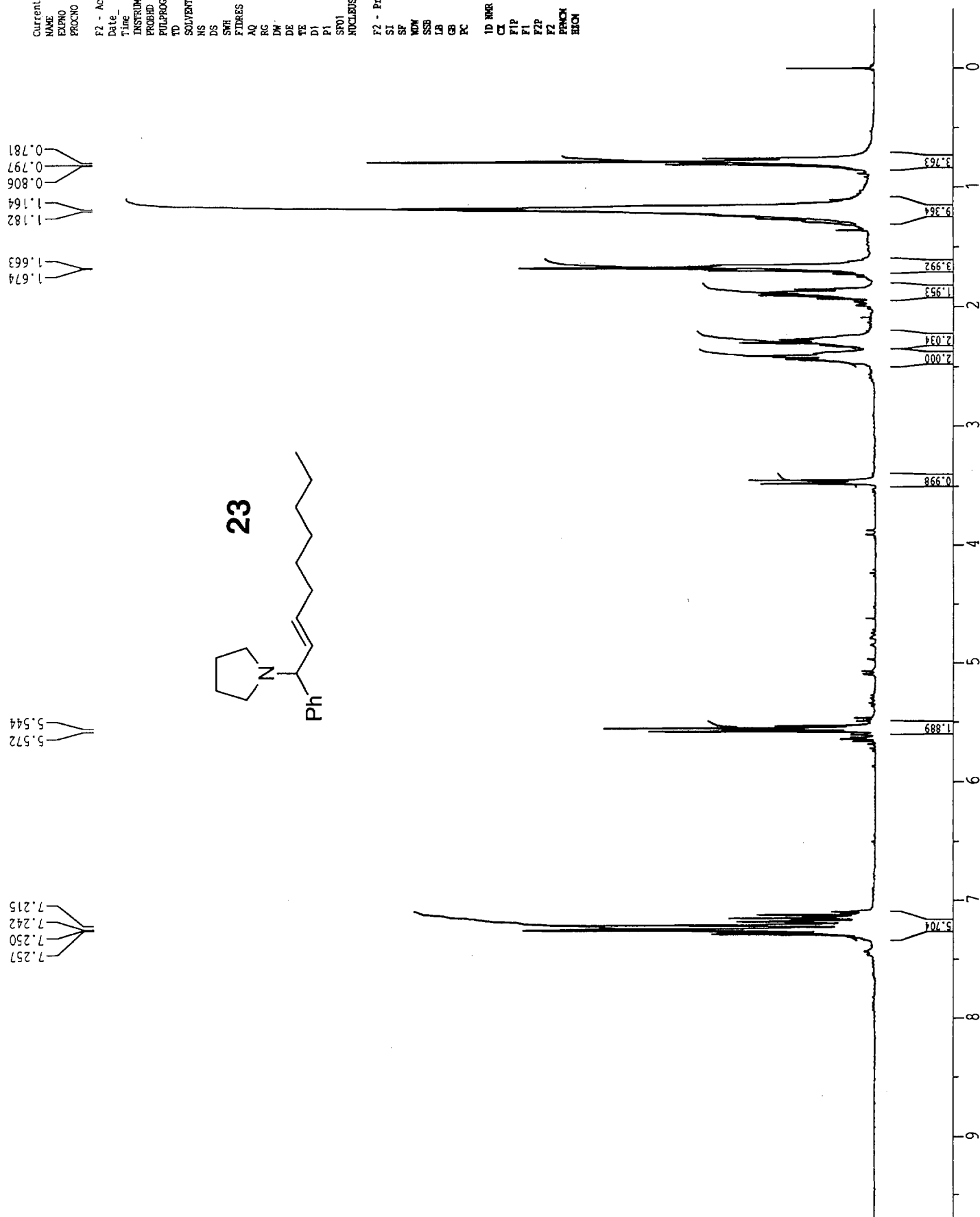


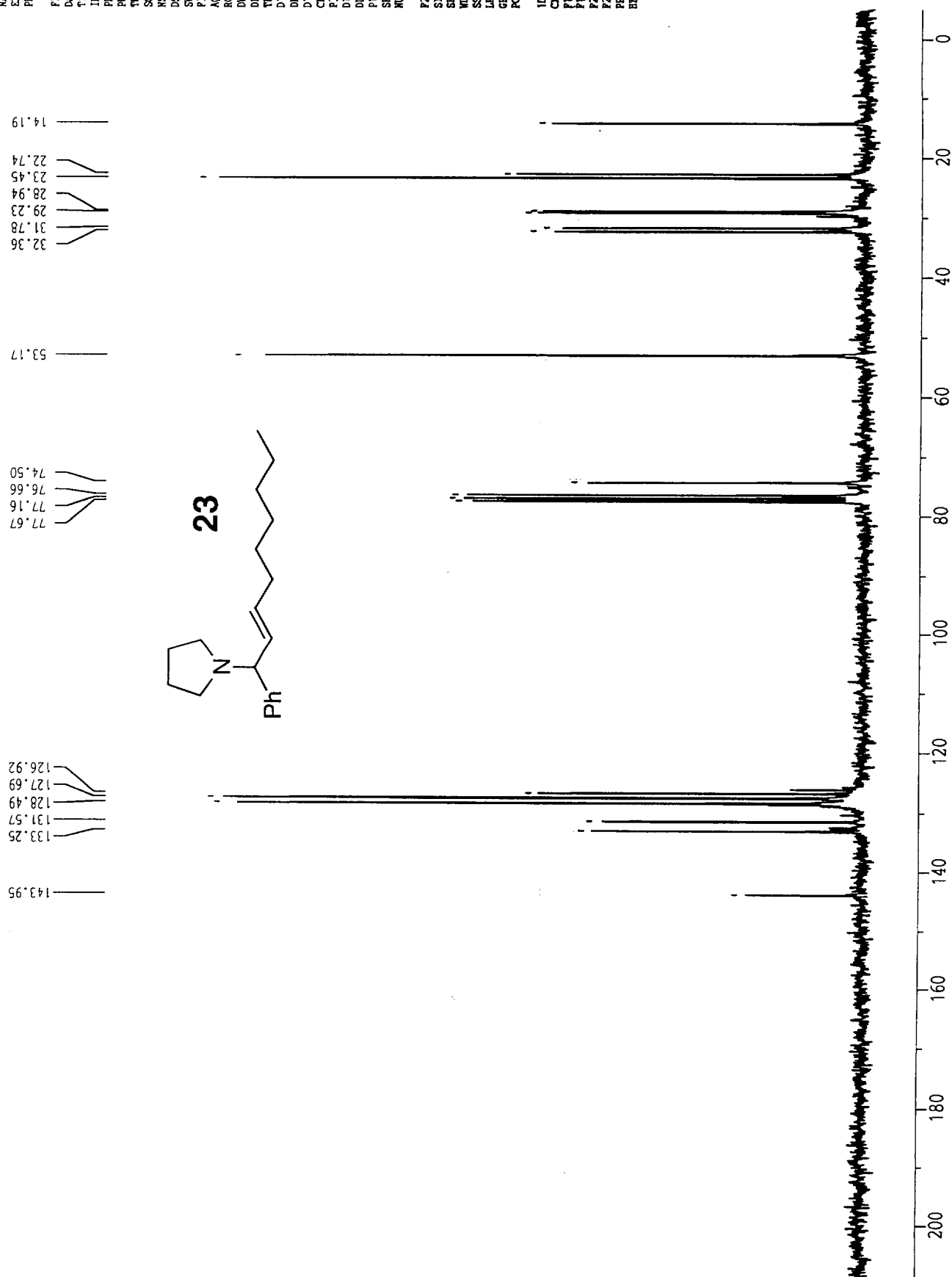
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 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 0
 SWH 5050.505 Hz
 FIDRES 0.154129 Hz
 AQ 3.2440820 sec
 RG 180
 DW 99.000 usec
 DE 141.43 usec
 TE 300.0 K
 D1 0.30000001 sec
 P1 6.00 usec
 SFO1 250.1312264 MHz
 NUC1 1H

F2 - Processing parameters
 SI 16384
 SF 250.1300292 MHz
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 SSF 0
 LB 0.10 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
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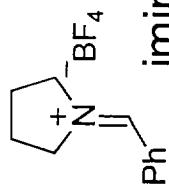




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PROCNO 1

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FIDRES 0.154129 Hz
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RG 2860
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D1 0.30000001 sec
P1 4.50 usec
SFO1 250.1312264 MHz
NUC1 13C

F2 - Processing parameters
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PC 1.00

1D NMR plot parameters
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F2P -0.500 ppm
F2 -125.07 Hz
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