

Supporting Information

A General Approach to the Synthesis of the Chlorosulfolipids Danicalipin A, Mytilipin A, and Malhamensilipin A in Enantioenriched Form

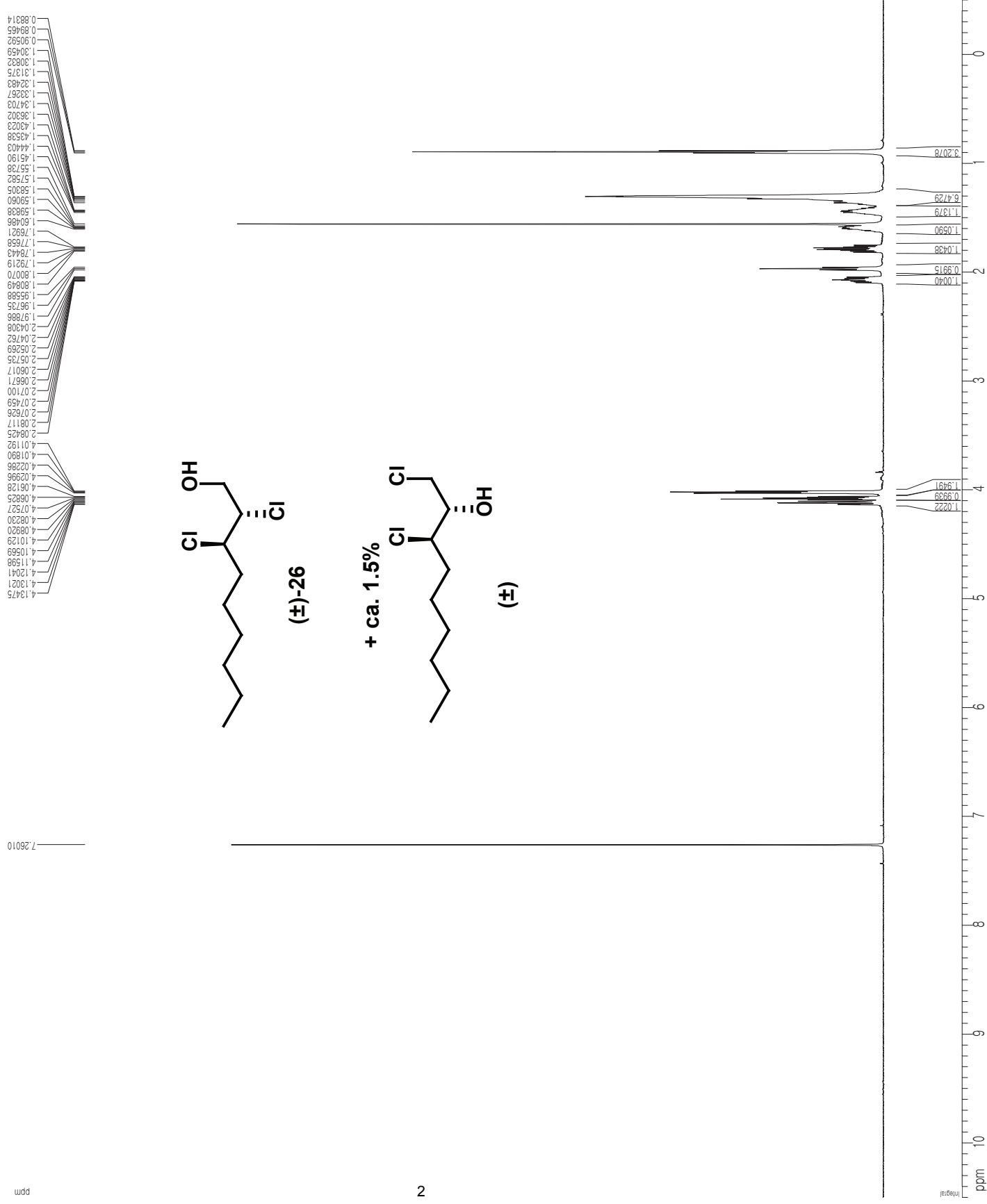
Won-jin Chung, Joseph S. Carlson, and Christopher D. Vanderwal*

1102 Natural Sciences II, Department of Chemistry, University of California, Irvine, CA 92697-2025

¹H NMR, ¹³C NMR Spectra **p. 2-40**

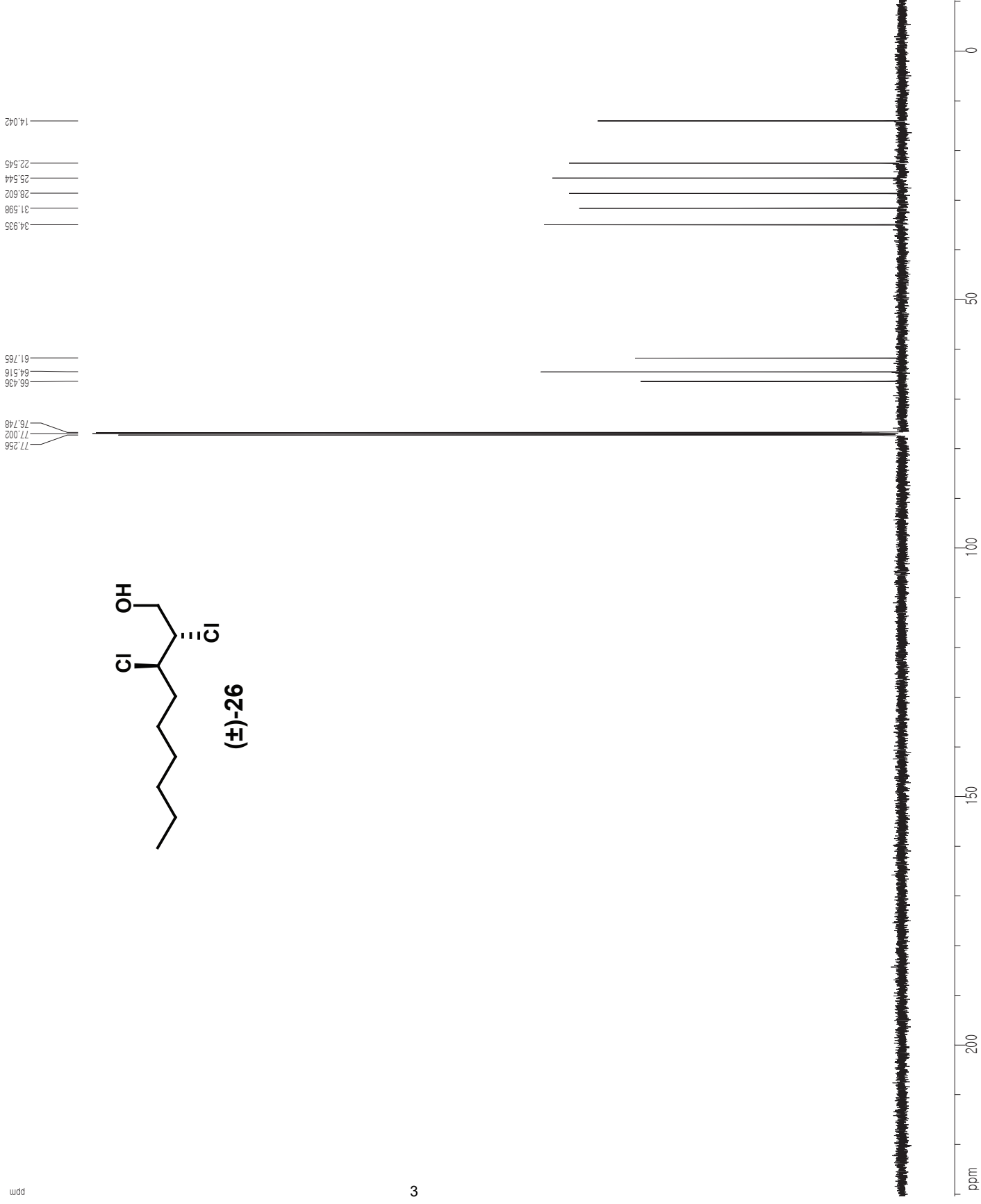
GC Chromatograms **p. 41-47**

¹H Spectrum



Z-restored spin-echo 13C spectrum with 1H decoupling

wddp



Current Data Parameters
 USER wonjin
 NAME WJC-V-129
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20130616
 Time 18.21
 INSTRUM cryo500
 PROBOH 5 mm CPTCI 1H-
 PULPROG SpineEcho30pprd
 TD 65536
 SOLVENT CDCl3
 NS 848
 DS 16
 SWH 30303.031 Hz
 FIDRES 0.462388 Hz
 AQ 1.0813940 sec
 RG 8192
 DW 18.500 usec
 DE 6.00 usec
 TE 295.1 K
 D11 0.95000000 sec
 D16 0.03000000 sec
 D17 0.00020000 sec
 d17 0.00019600 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec
 P2 31.00 usec

===== CHANNEL f1 =====
 NUC1 13C
 P1 15.50 usec
 PL1 500.00 usec
 PL2 2000.00 usec
 PL0 120.00 dB
 PL1 -1.00 dB
 SF01 125.794548 MHz
 SP1 320 dB
 SPNAM1 Cmg6015.20.1
 SPNAM2 Cmg6015.20.1
 SPOFF1 0.00 Hz
 SPOFF2 0.00 Hz

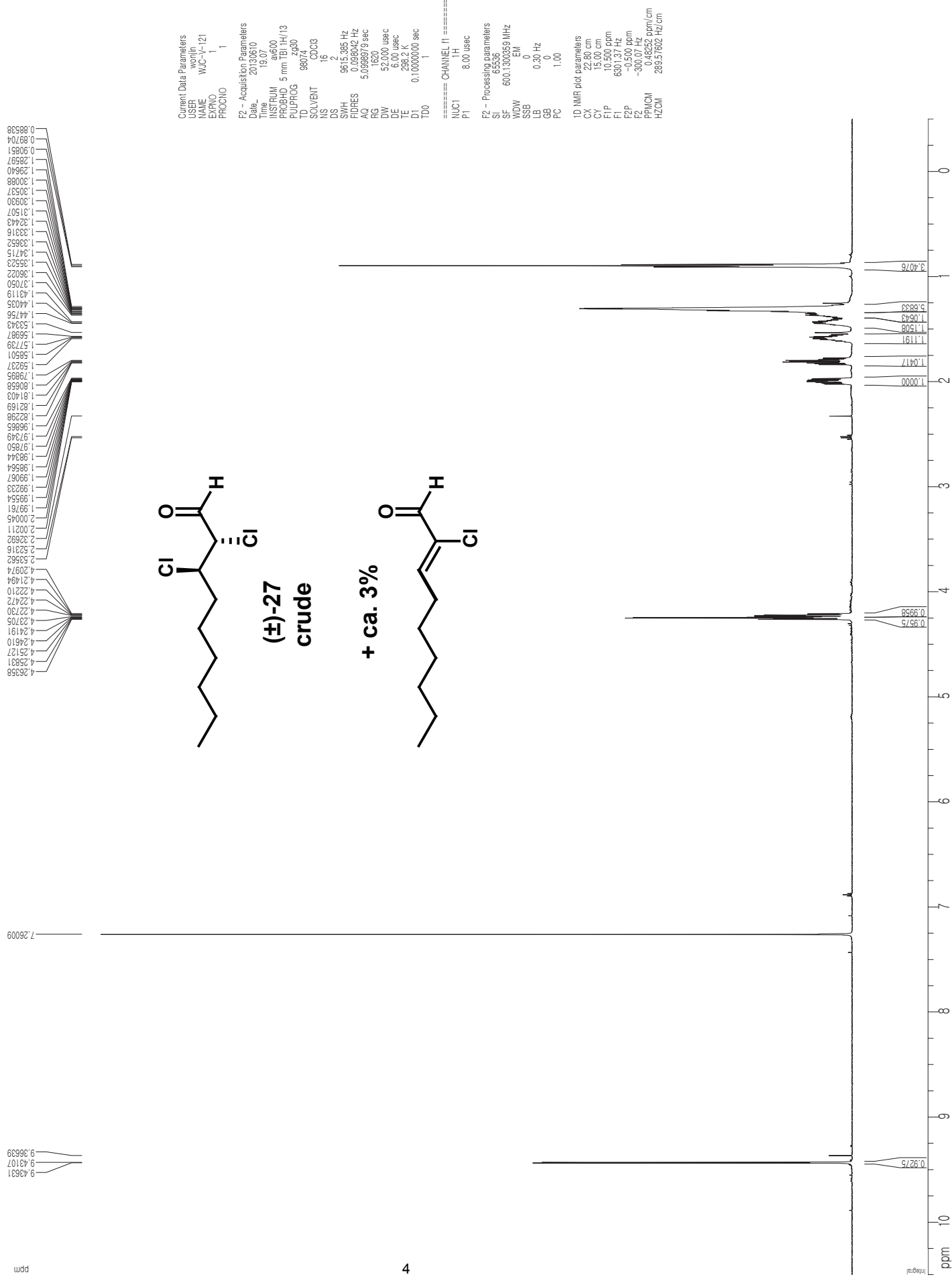
===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 P1 100.00 usec
 PL1 180.00 dB
 PL2 24.80 dB
 SF02 500.2225011 MHz

===== GRADIENT CHANNEL =====
 GPM1 SINE100
 GPM2 SINE100
 GPX1 0.00 %
 GPX2 0.00 %
 GPY1 0.00 %
 GPY2 0.00 %
 GPZ1 30.00 %
 GPZ2 50.00 %
 p15 500.00 usec
 p16 1000.00 usec

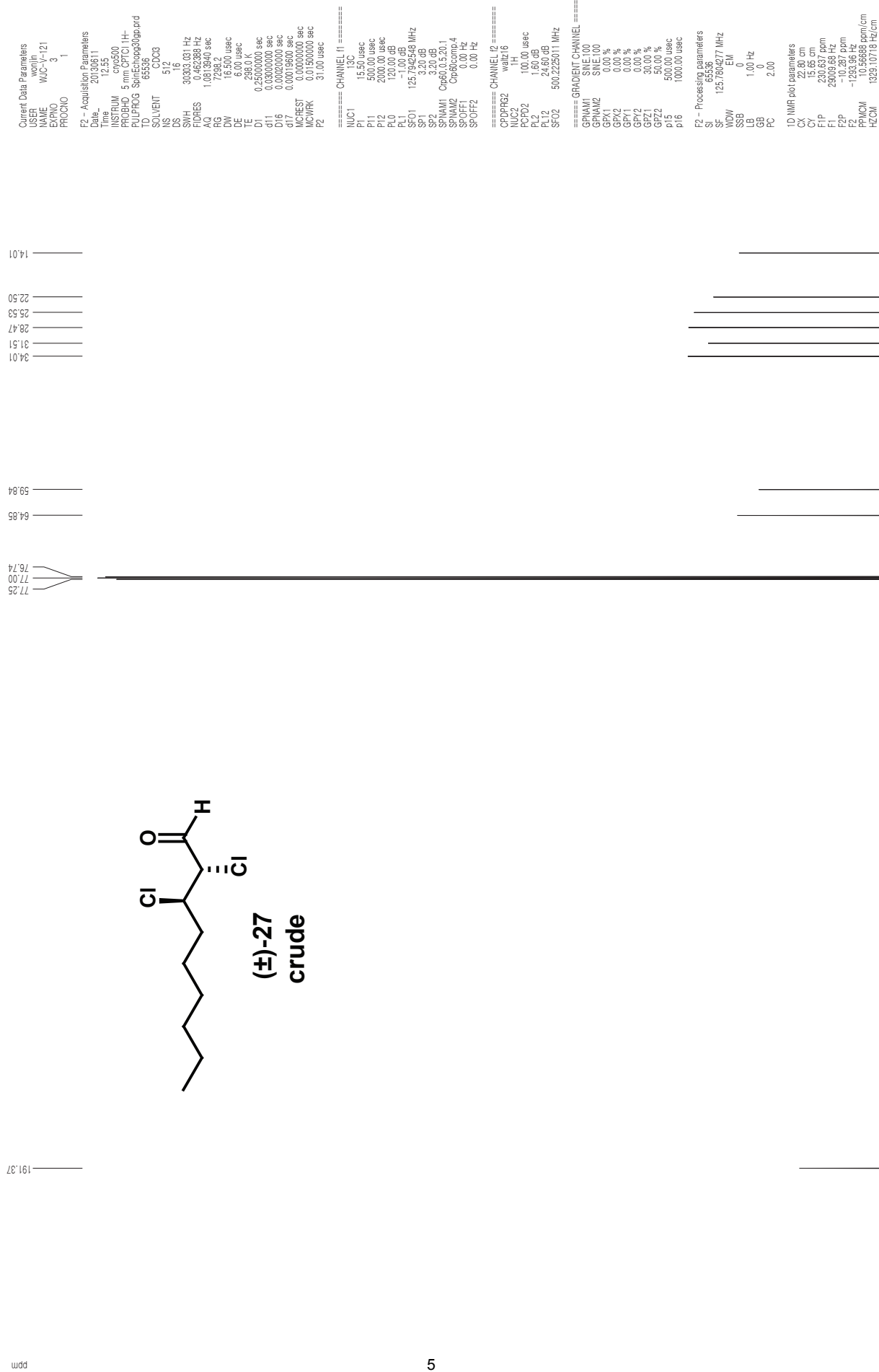
F2 - Processing parameters
 SI 65536
 SF 125.760277 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 2.00

1D NMR plot parameters
 CX 12.86 cm
 CY 12.86 cm
 F1P 230.637 ppm
 F1 23009.68 Hz
 F2P -10.287 ppm
 F2 -1293.96 Hz
 PPMCM 10.56688 ppm/cm
 HZCM 1329.10718 Hz/cm

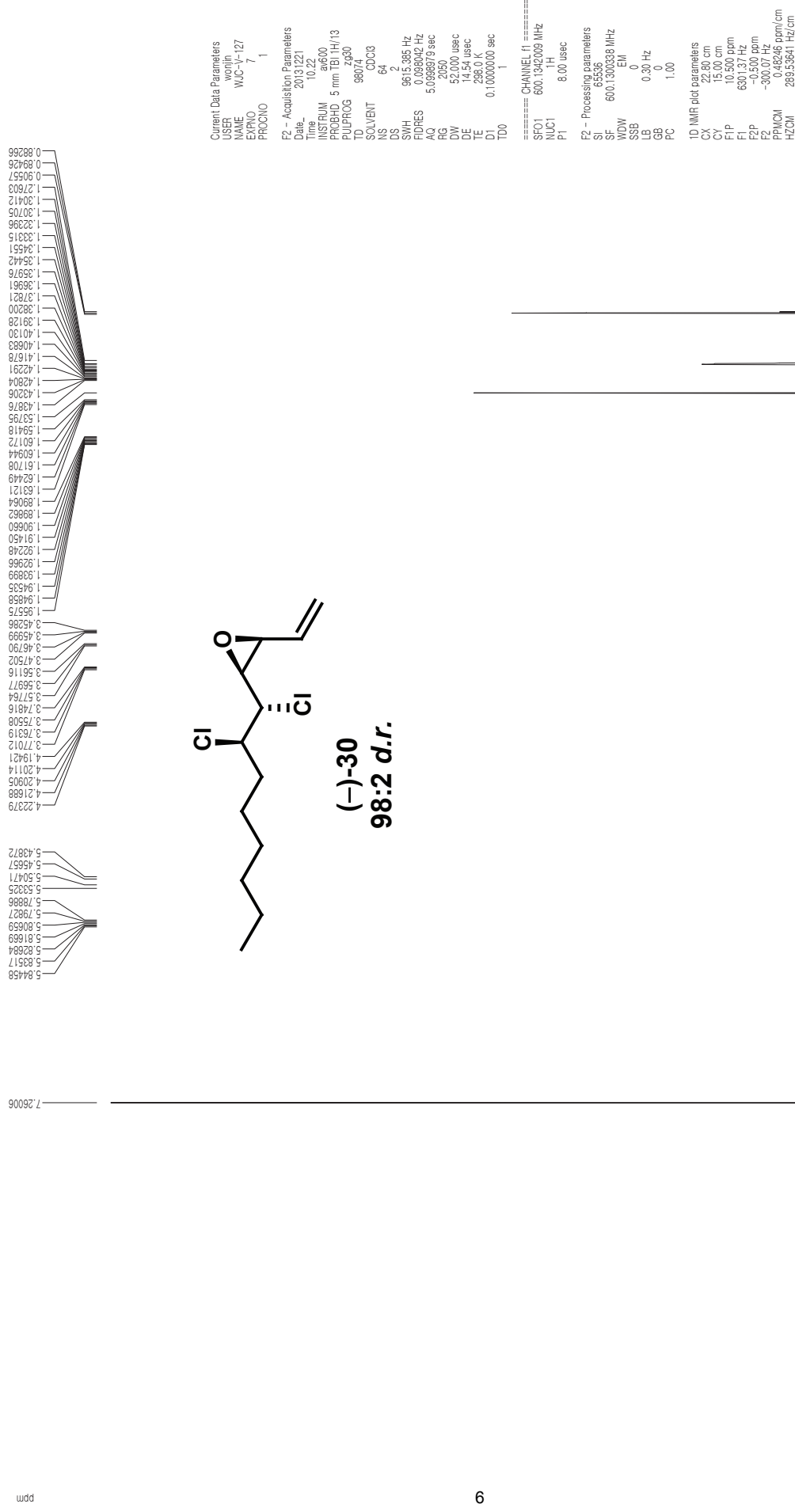
¹H Spectrum



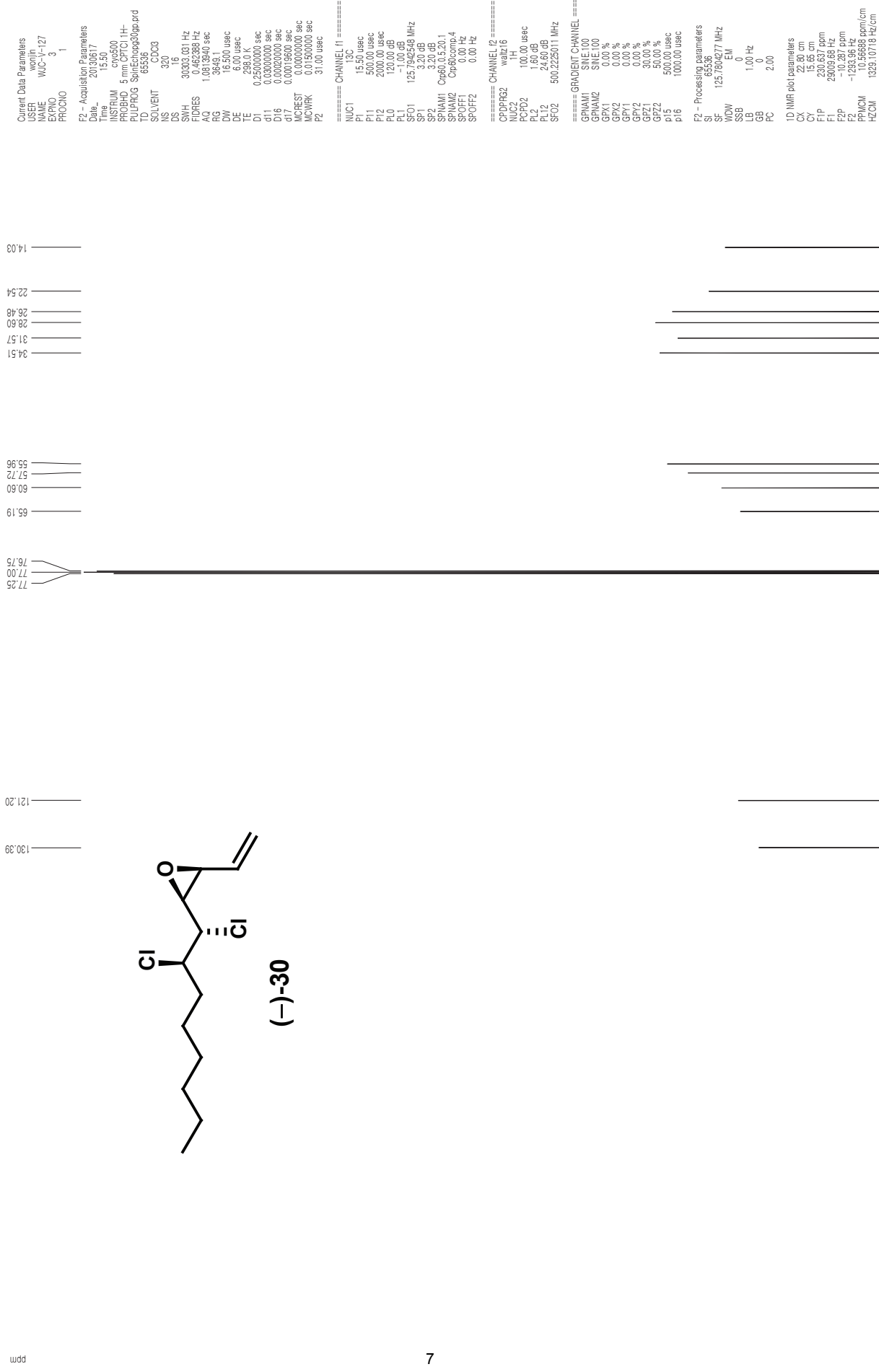
Z-restored spin-echo 13C spectrum with 1H decoupling



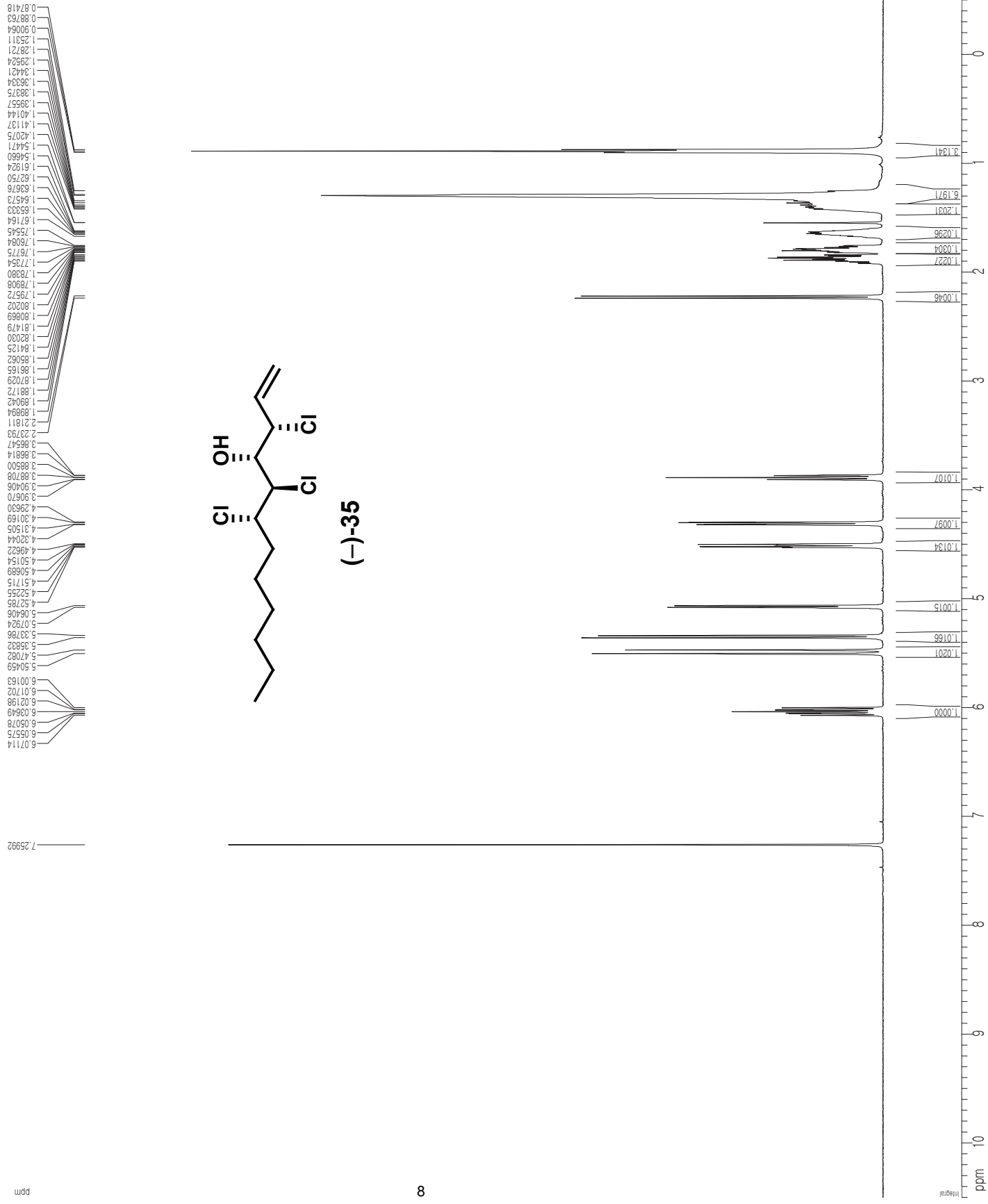
¹H Spectrum



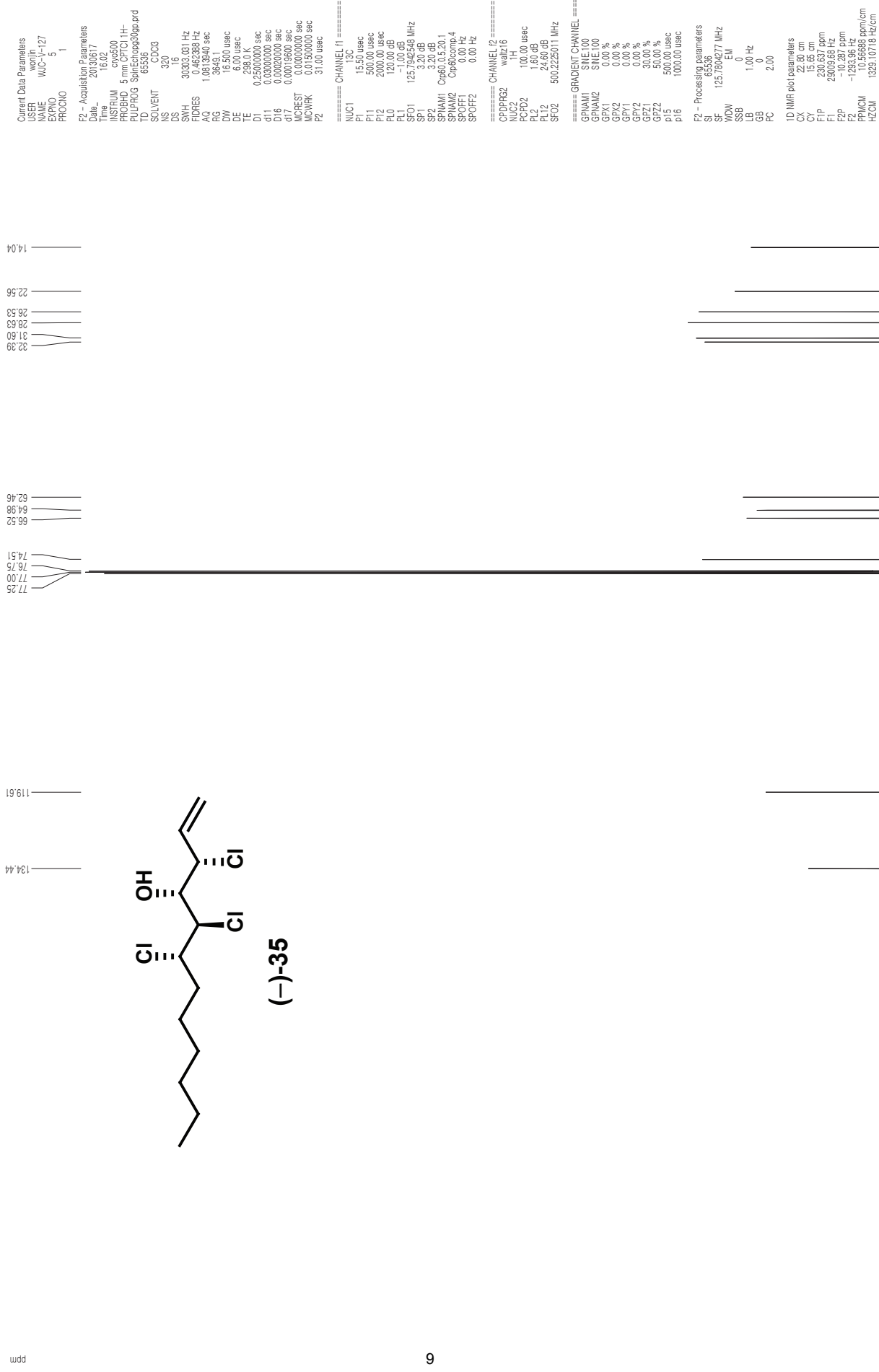
Z-restored spin-echo 13C spectrum with 1H decoupling



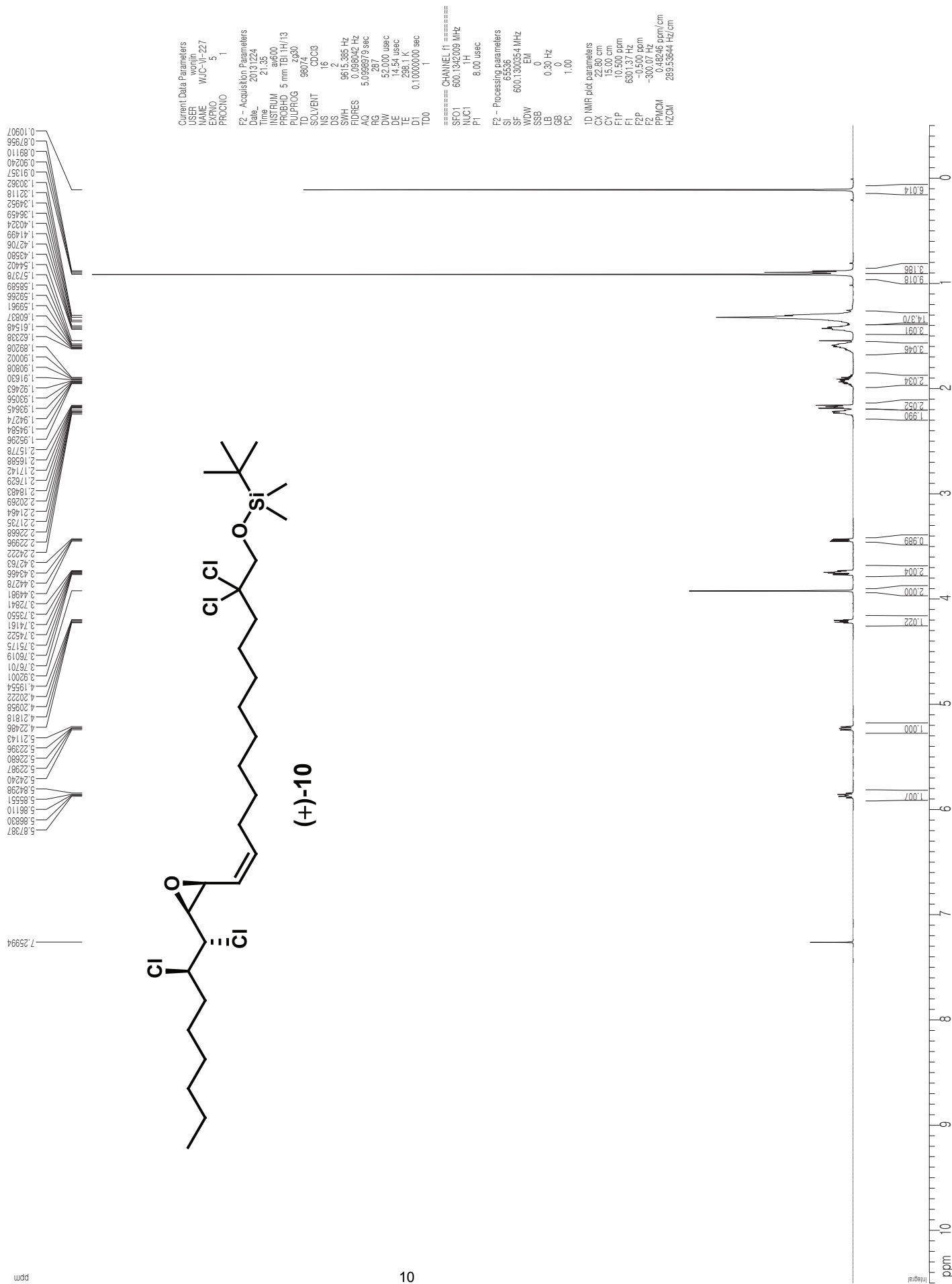
¹H Spectrum



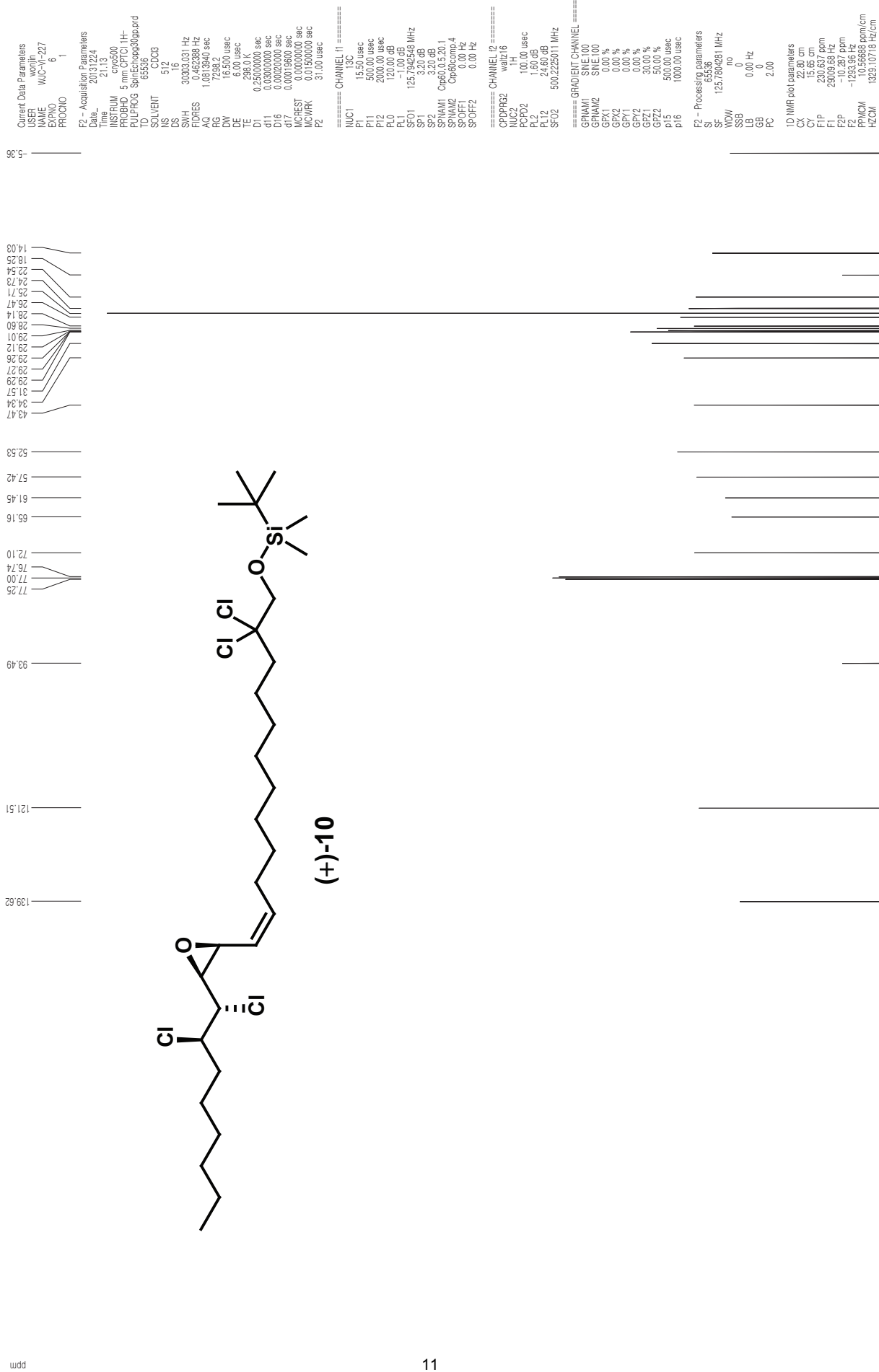
Z-restored spin-echo 13C spectrum with 1H decoupling



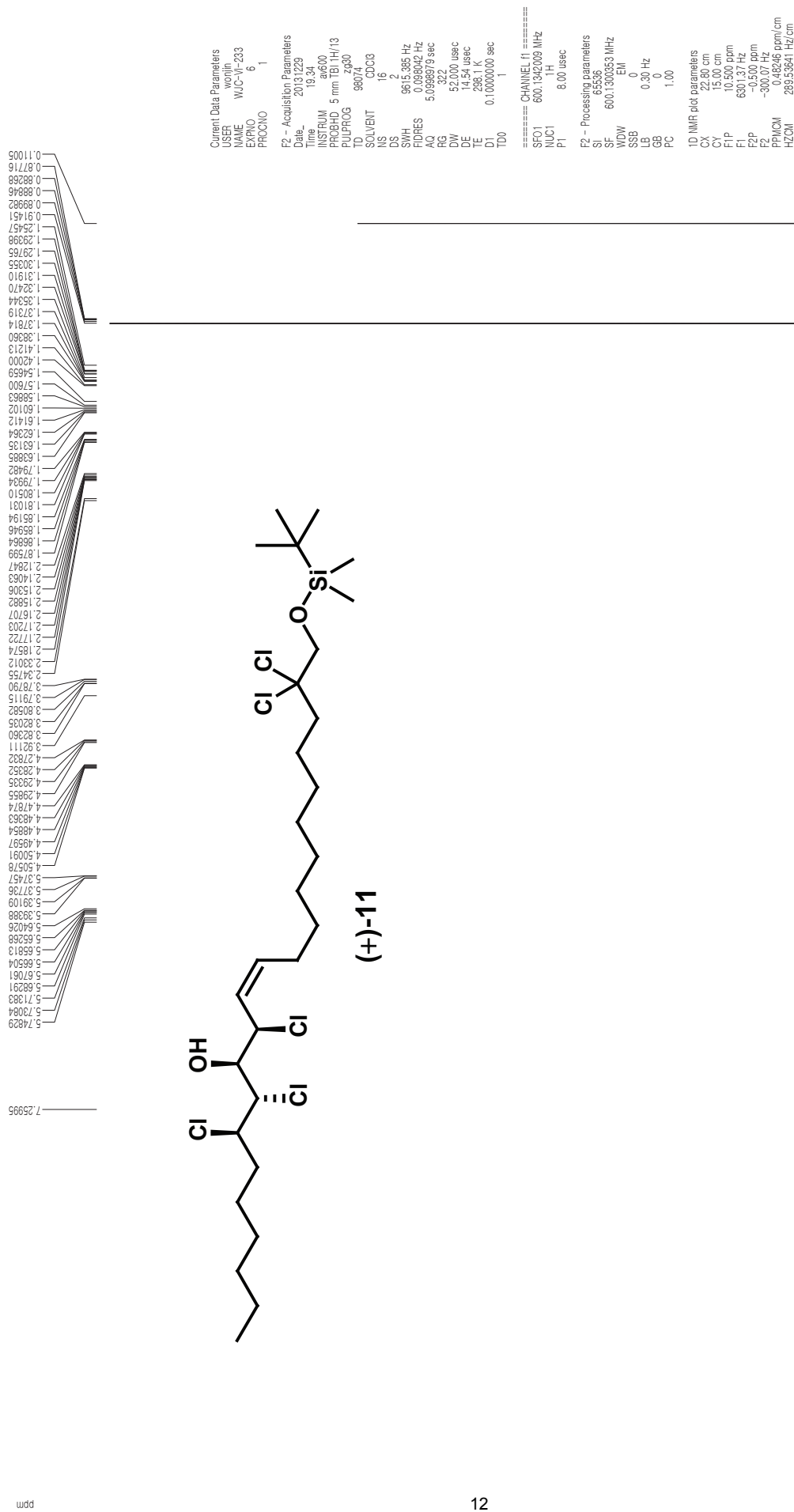
¹H Spectrum



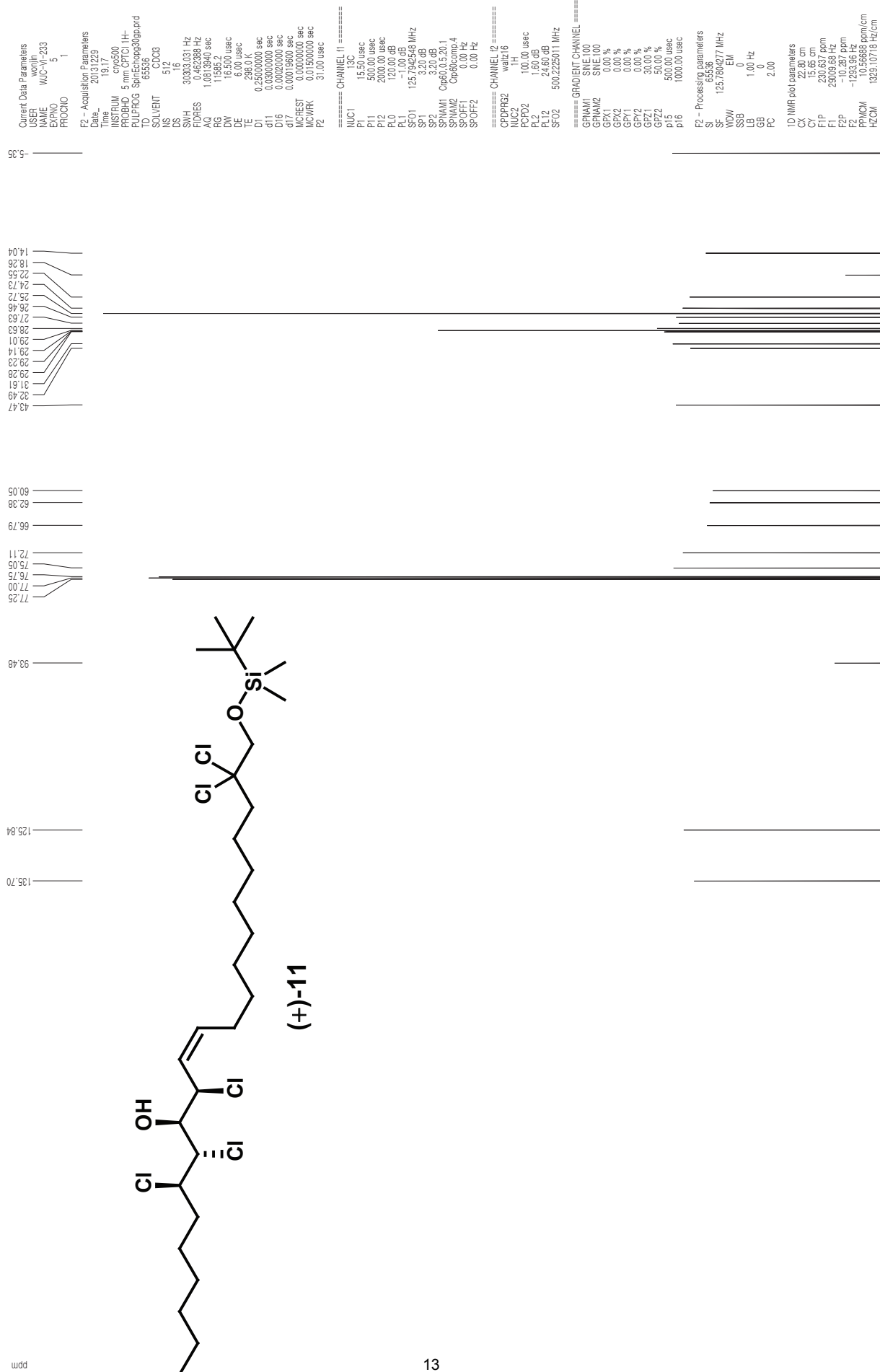
Z-restored spin-echo 13C spectrum with 1H decoupling



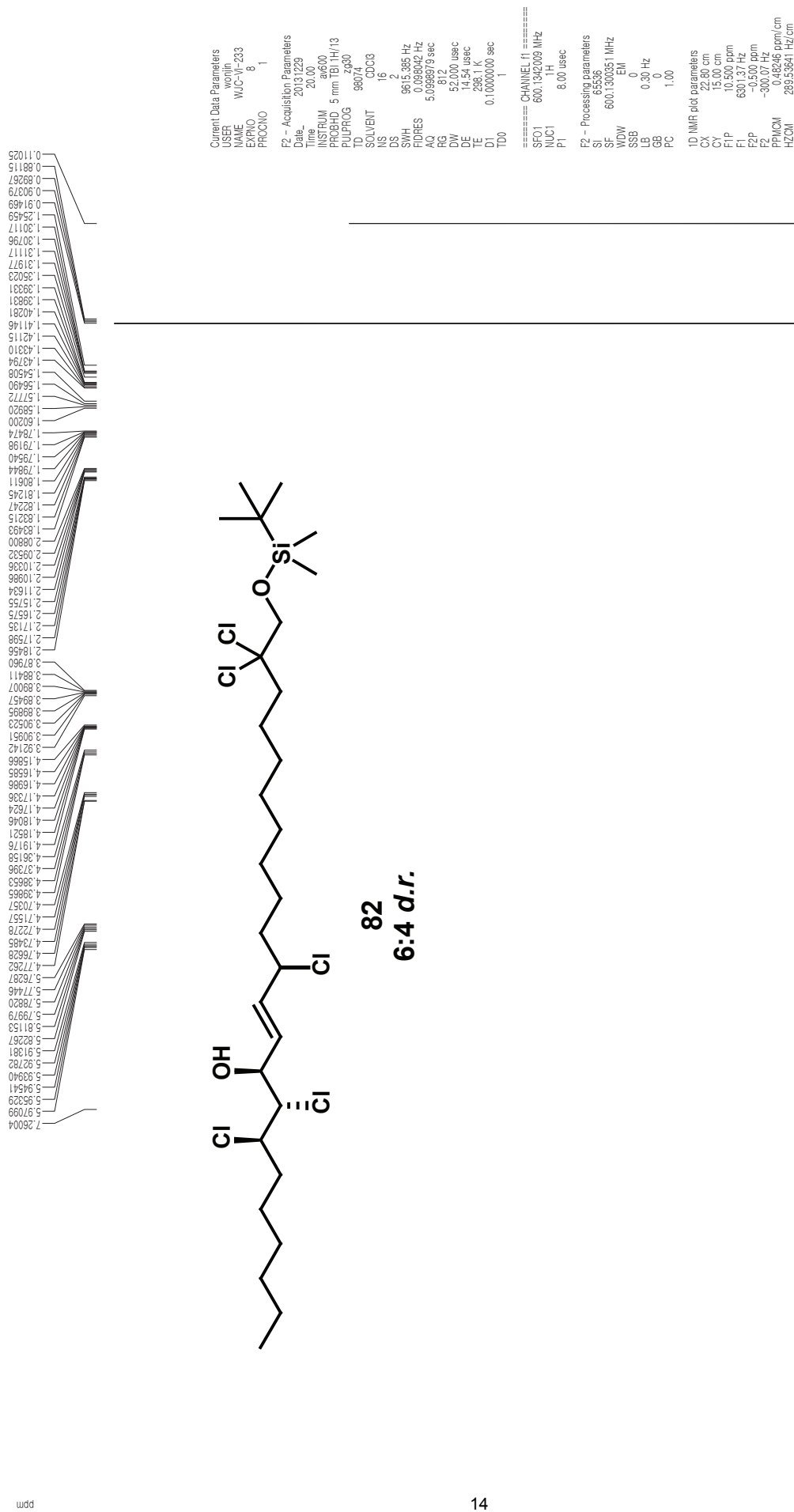
¹H Spectrum



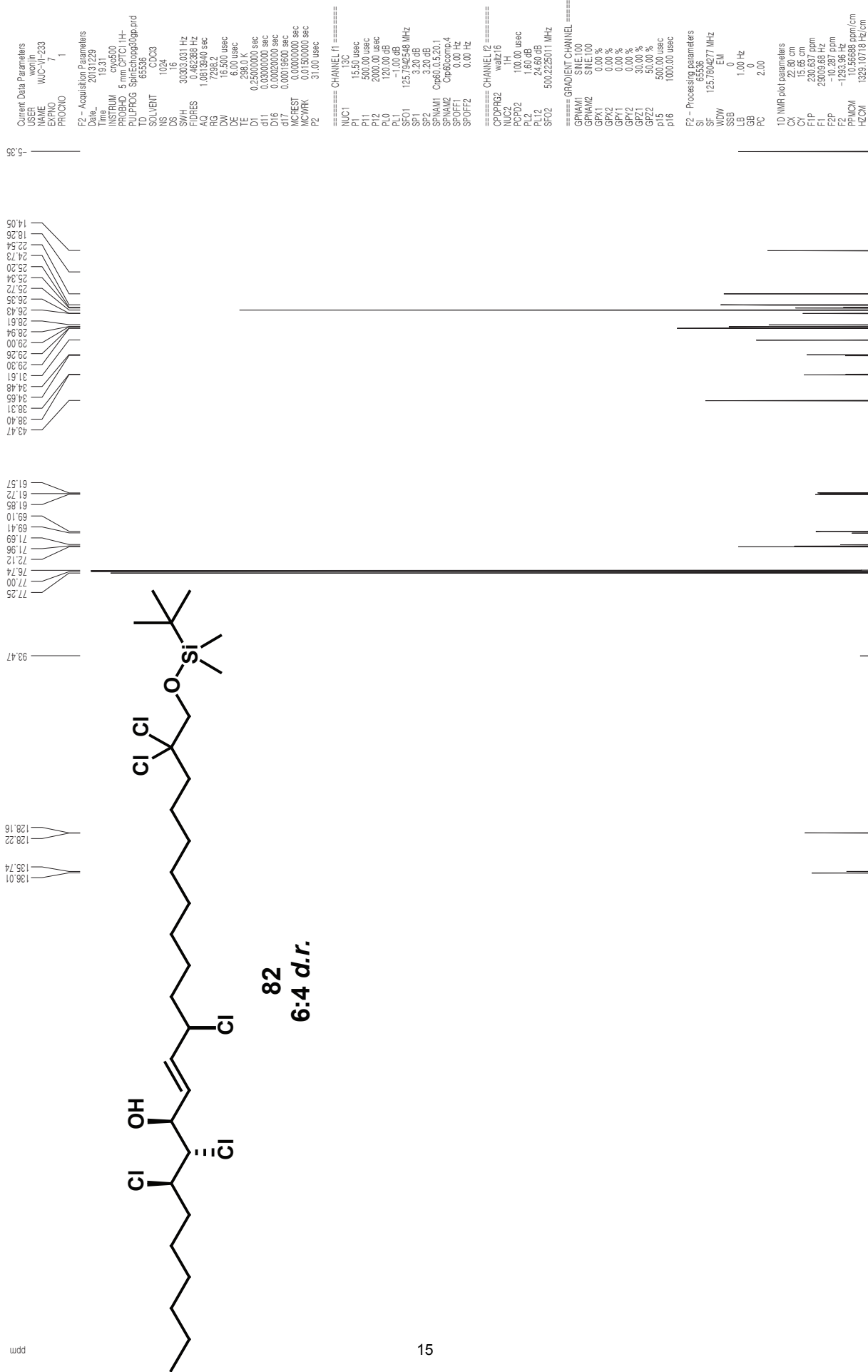
Z-restored spin-echo 13C spectrum with 1H decoupling



¹H Spectrum



Z-restored spin-echo 13C spectrum with 1H decoupling

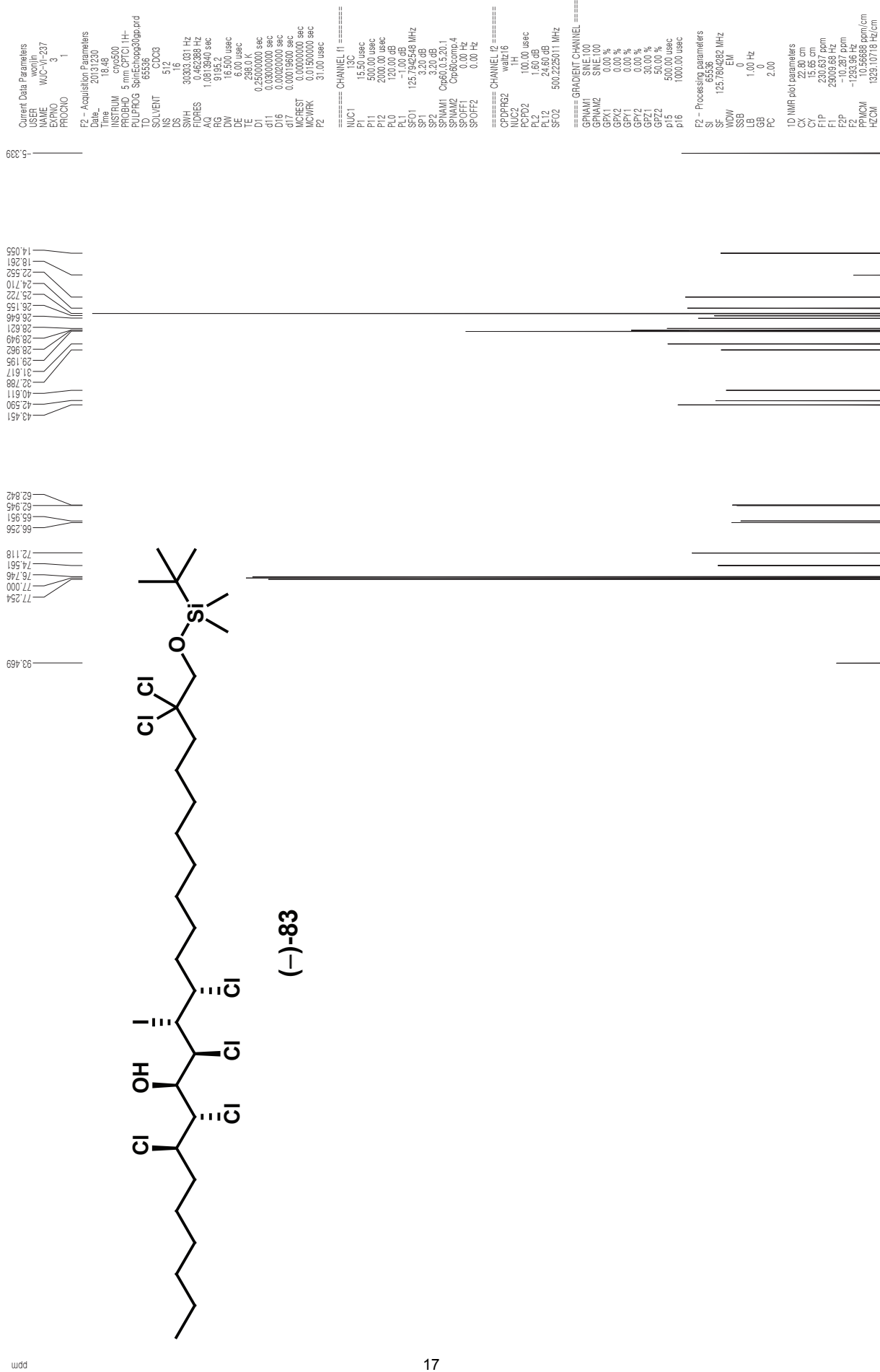


wdd

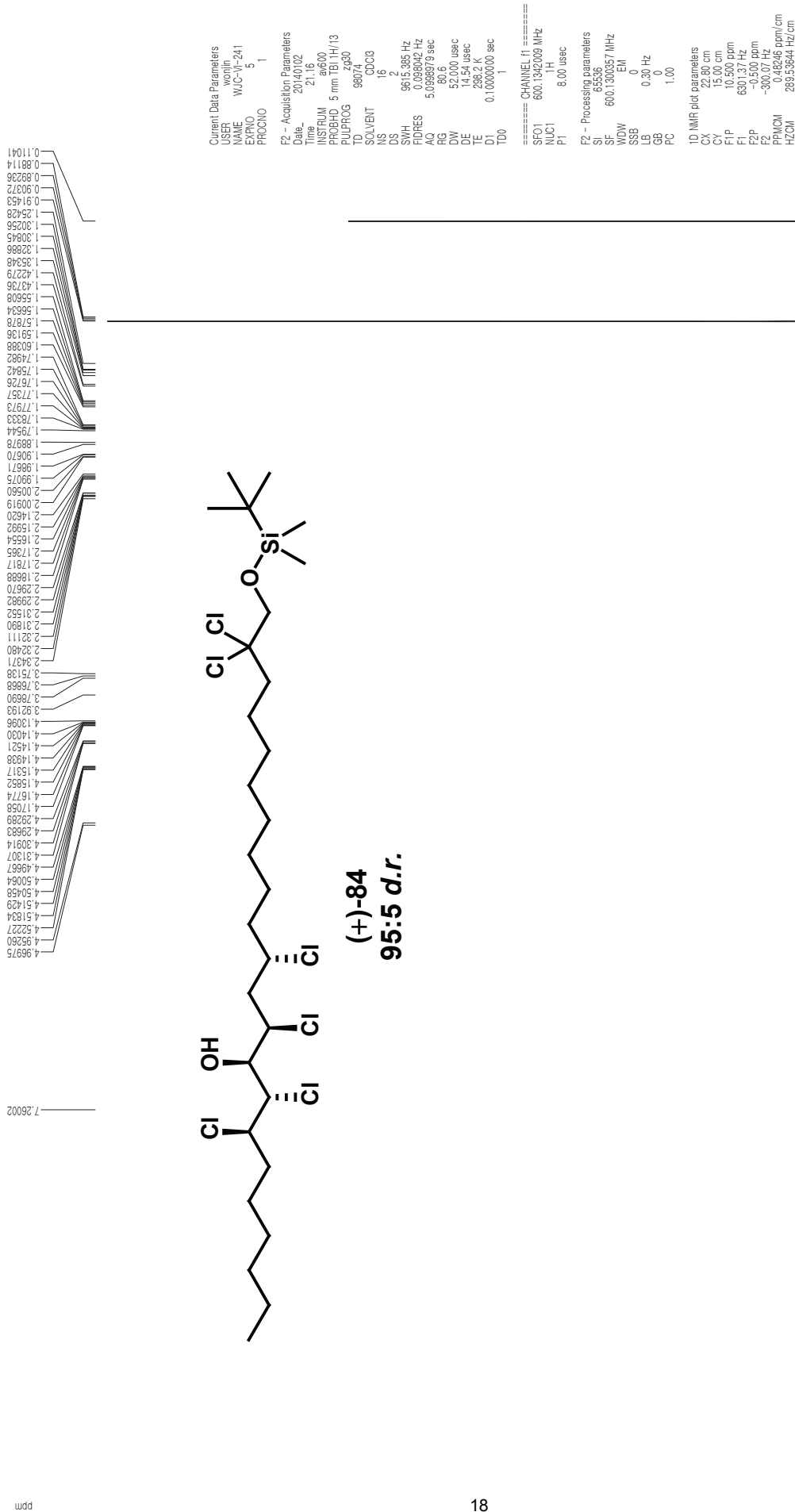


Current Data Parameters	
WOLIN	4
WJC-W1237	1
EXPNO	4
PROCNO	1
F2 - Acquisition Parameters	
Date_	2013.230
Time	19.05
INSTRUM	ax600
PROBHD	5 mm TBI/H1/13
PULPROG	zg30
TD	98074
NS	1
DS	4
SWH	9615.385 Hz
FIDRES	0.090402 Hz
AQ	5.0988979 sec
RG	322
DD	52.00 usec
DW	14.54 usec
DE	298.0 K
TE	0.1000000 sec
TD0	1
===== CHANNEL f1 =====	
SFO1	600.1342009 MHz
NUC1	1H
P1	8.00 usec
F2 - Processing parameters	
SF	600.1300533 MHz
WDW	EM
SSB	0
LB	0.20 Hz
GB	0
PC	1.00
TD NMR data parameters	
SI	22.80 cm
CV	15.00 cm
F1	10.500 ppm
F2	6301.37 Hz
F22	-300.00 ppm
F23	-900.07 Hz
PPMCM	2893.3641 Hz/cm
HZCM	

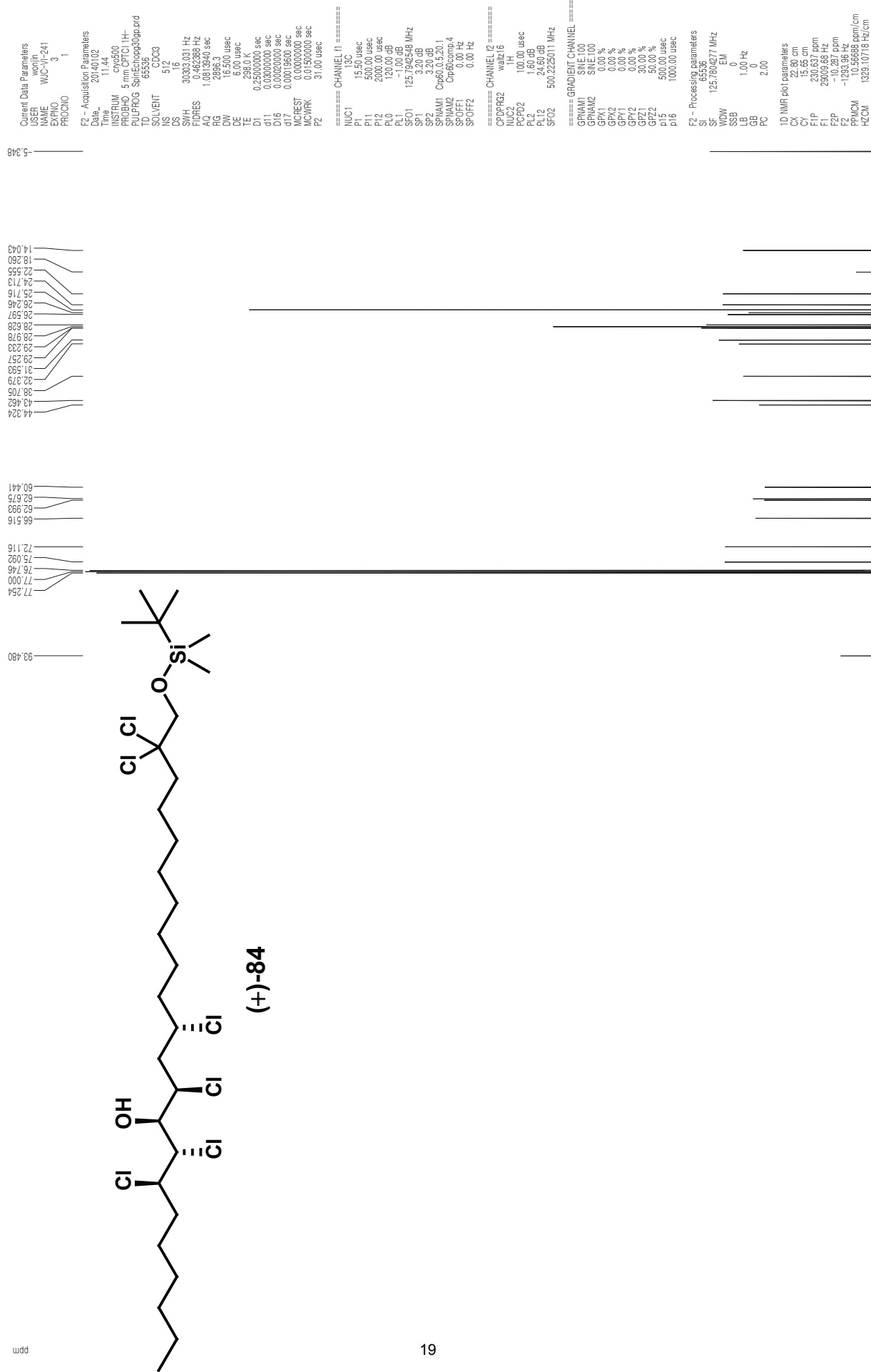
Z-restored spin-echo 13C spectrum with 1H decoupling



¹H Spectrum



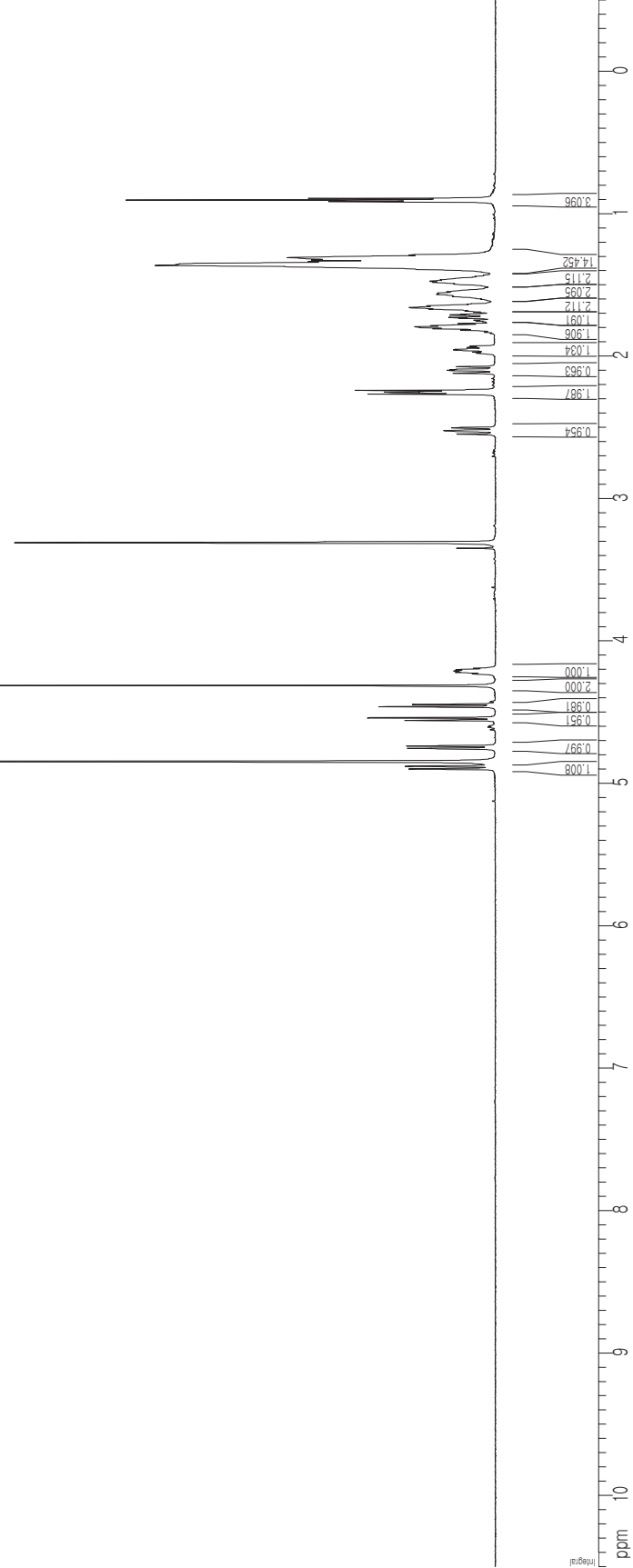
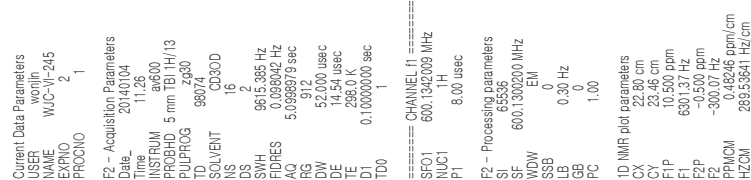
Z-restored spin-echo 13C spectrum with 1H decoupling



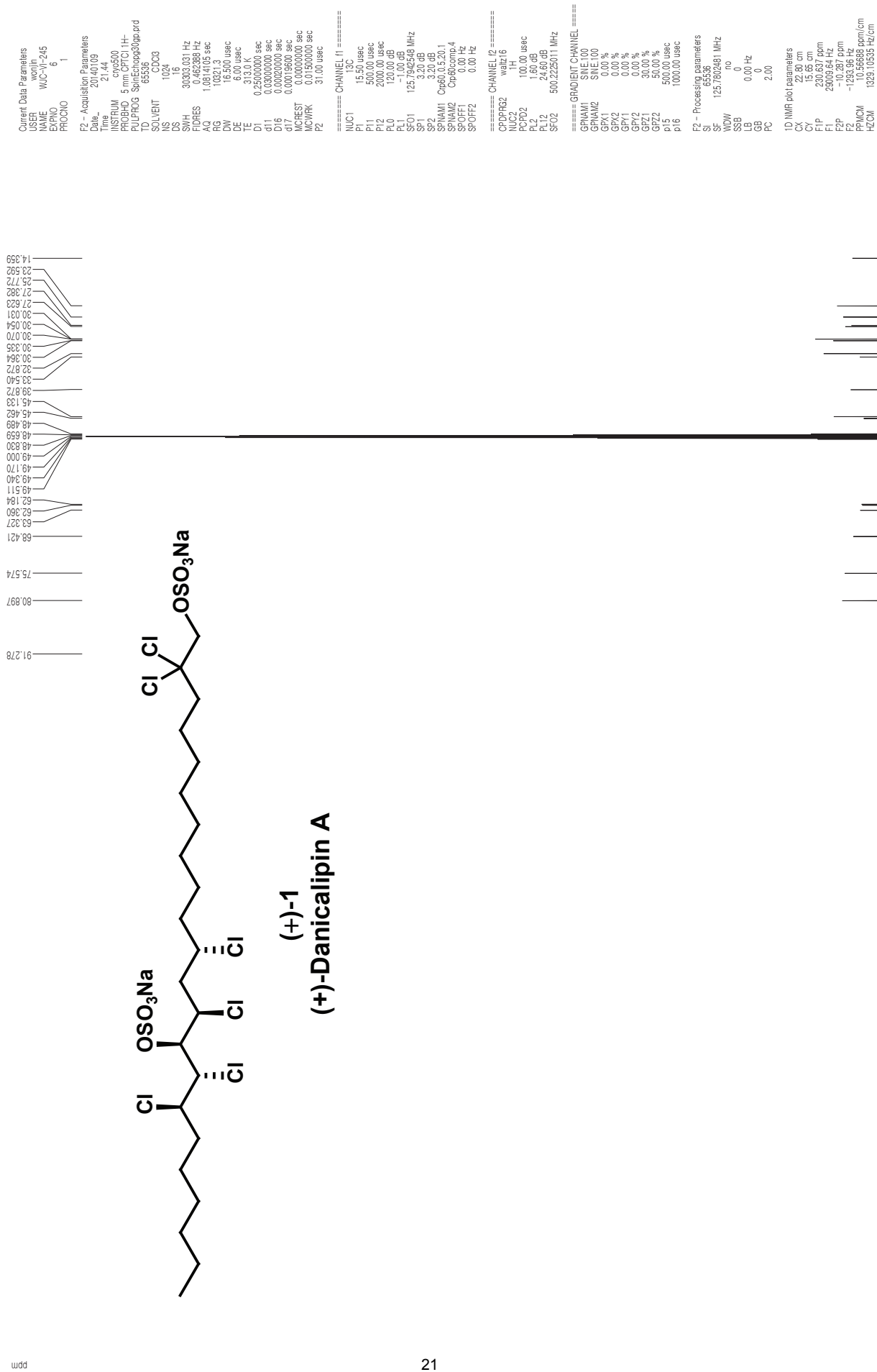
wpd



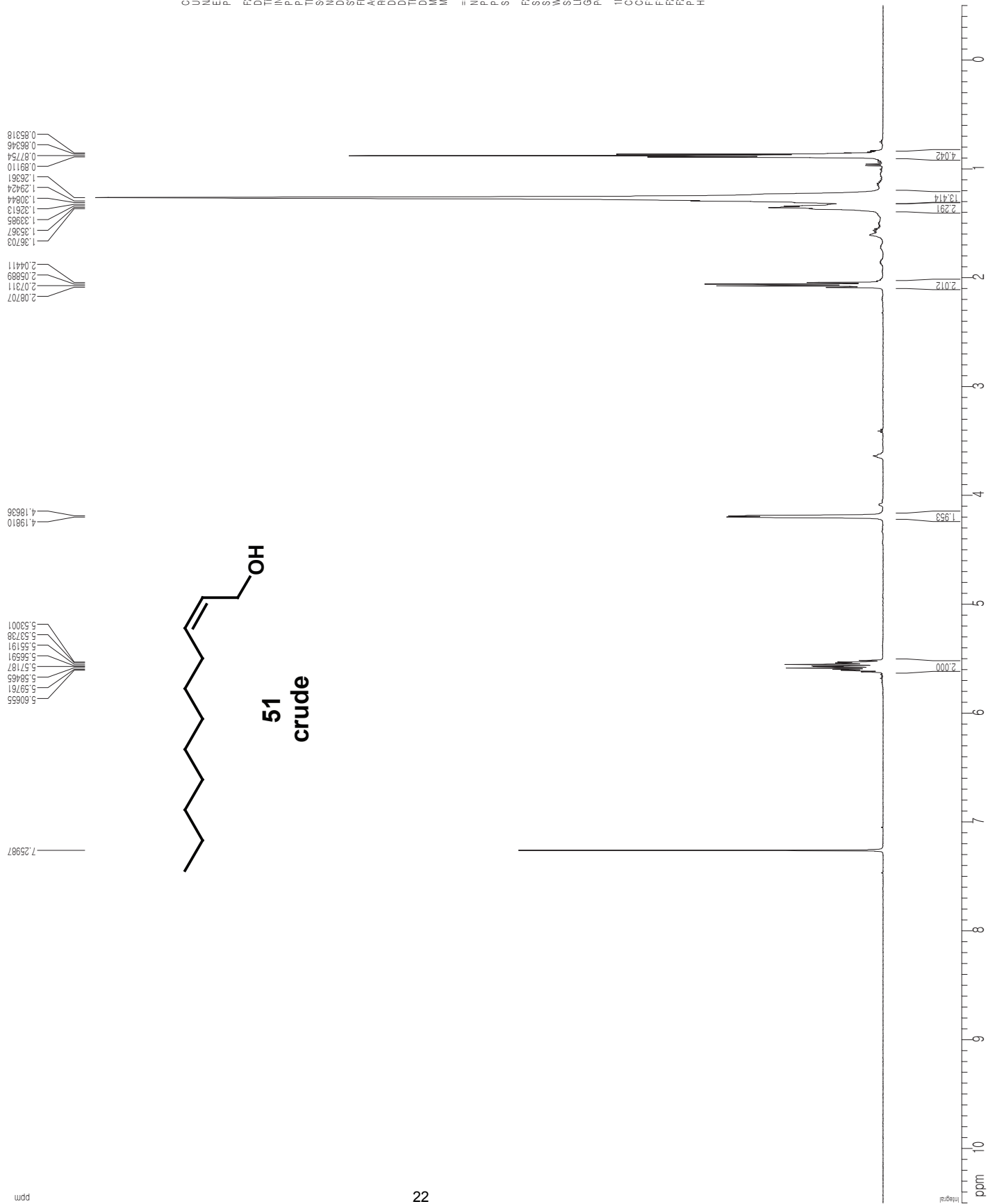
**(+)-1
(+)-Danicalipin A
95:5 d.r.**



Z-restored spin-echo ^{13}C spectrum with ^1H decoupling

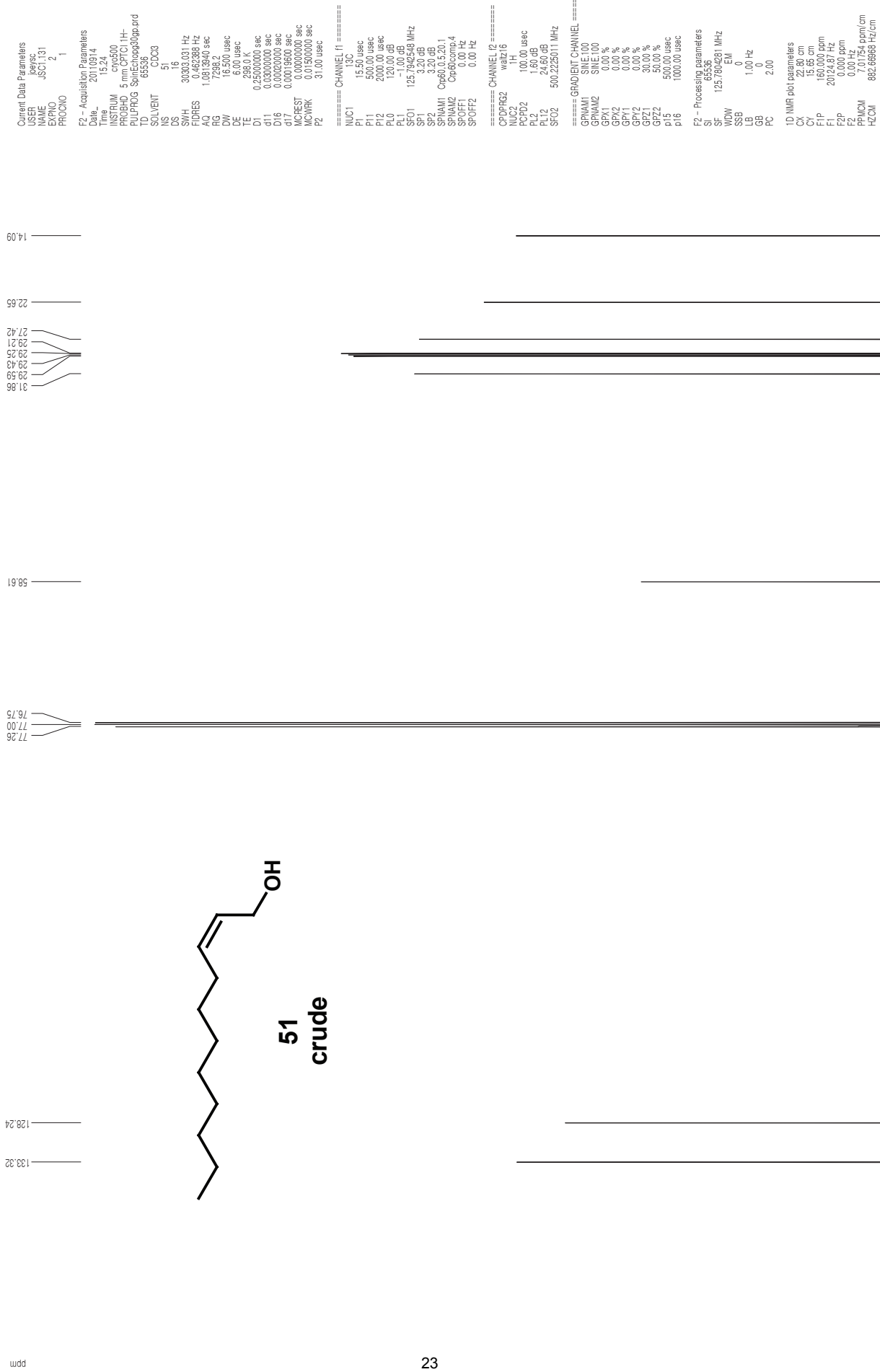


¹H spectrum

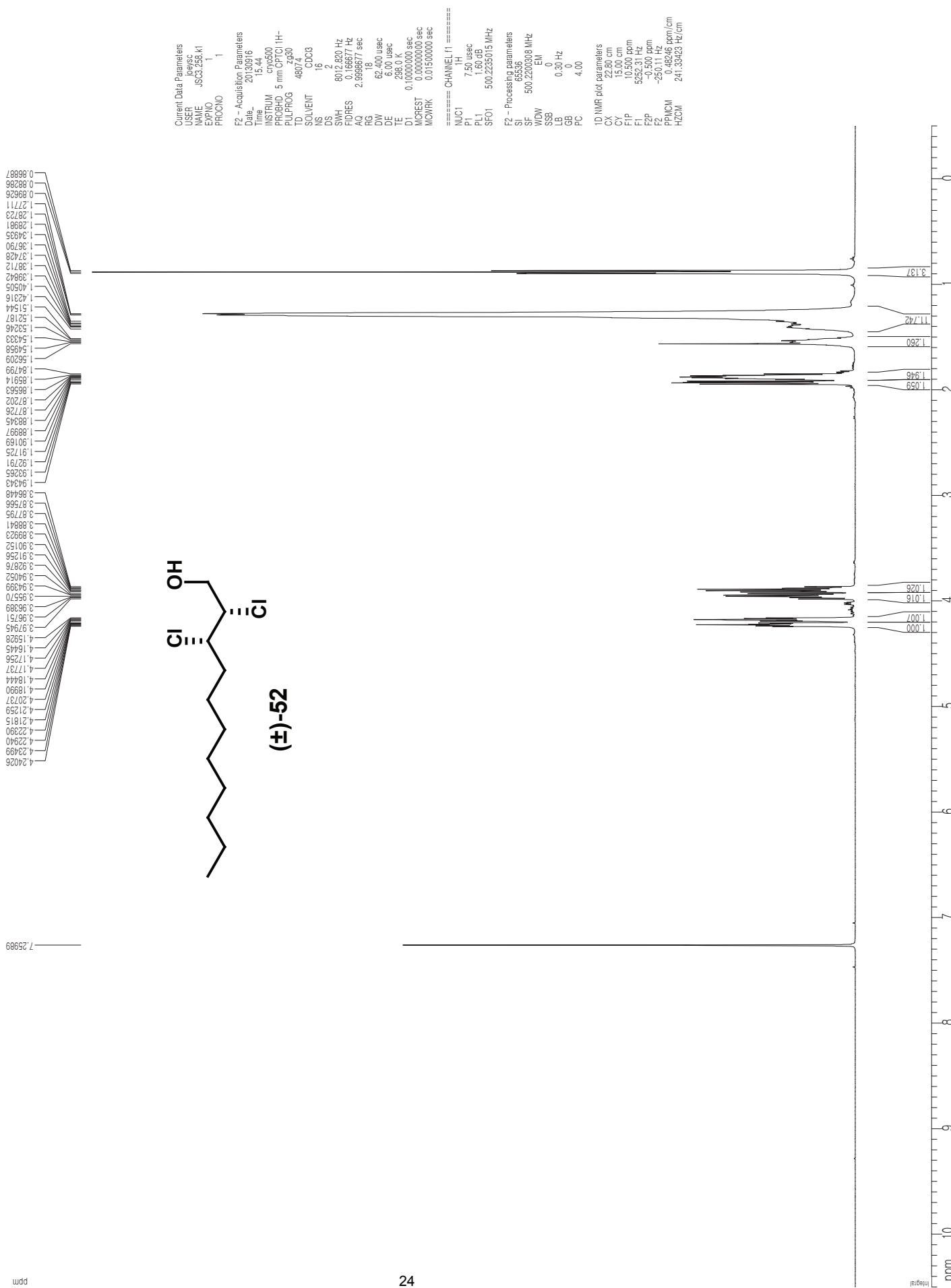


Current Data Parameters
 USER jesc
 NAME JSC1131
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20110914
 Time 15.22
 INSTRUM cryo500
 PROBHD 5 mm CP1CI IH-
 PULPROG zgpg30
 TO 817.960
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.059043 Hz
 AQ 5.0998774 sec
 RG 6.3
 DW 62.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.1000000 sec
 MCREST 0.0000000 sec
 MCNMR 0.0150000 sec
 ===== CHANNEL f1 =====
 NUC1 ¹H
 P1 7.50 usec
 PL1 1.50 dB
 SFO1 500.2235015 MHz
 F2 - Processing parameters
 SI 65536
 SF 500.2200316 MHz
 WDW 0
 SSB 0
 GB 0.30 Hz
 PC 4.00
 1D NMR plot parameters
 CX 22.80 cm
 CY 15.00 cm
 FIP 10.500 ppm
 F1 5252.31 Hz
 F2P -0.500 ppm
 F2 -250.11 Hz
 PPMCM 0.48246 ppm/cm
 HZCM 241.33423 Hz/cm

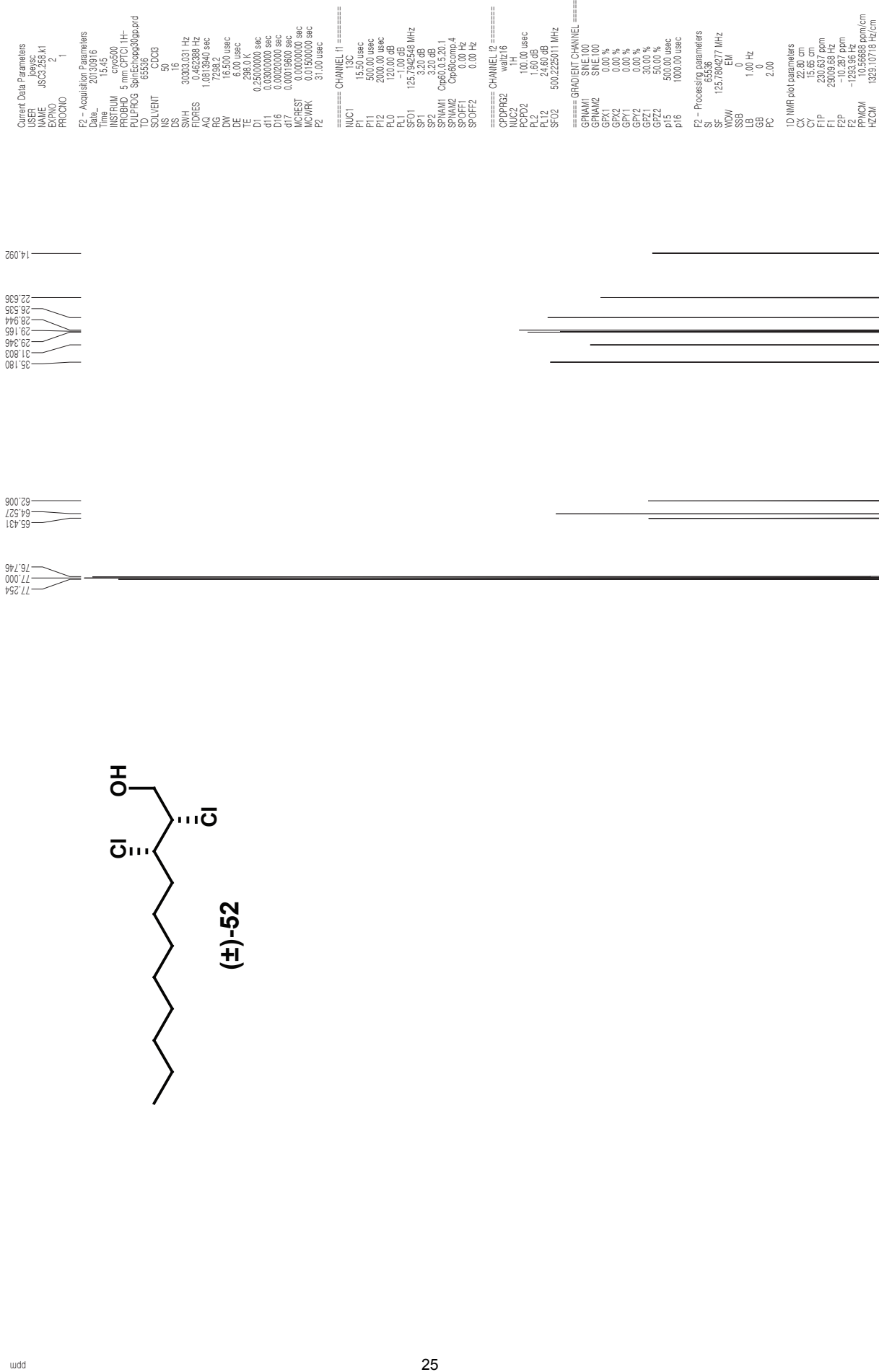
Z-restored spin-echo 13C spectrum with 1H decoupling

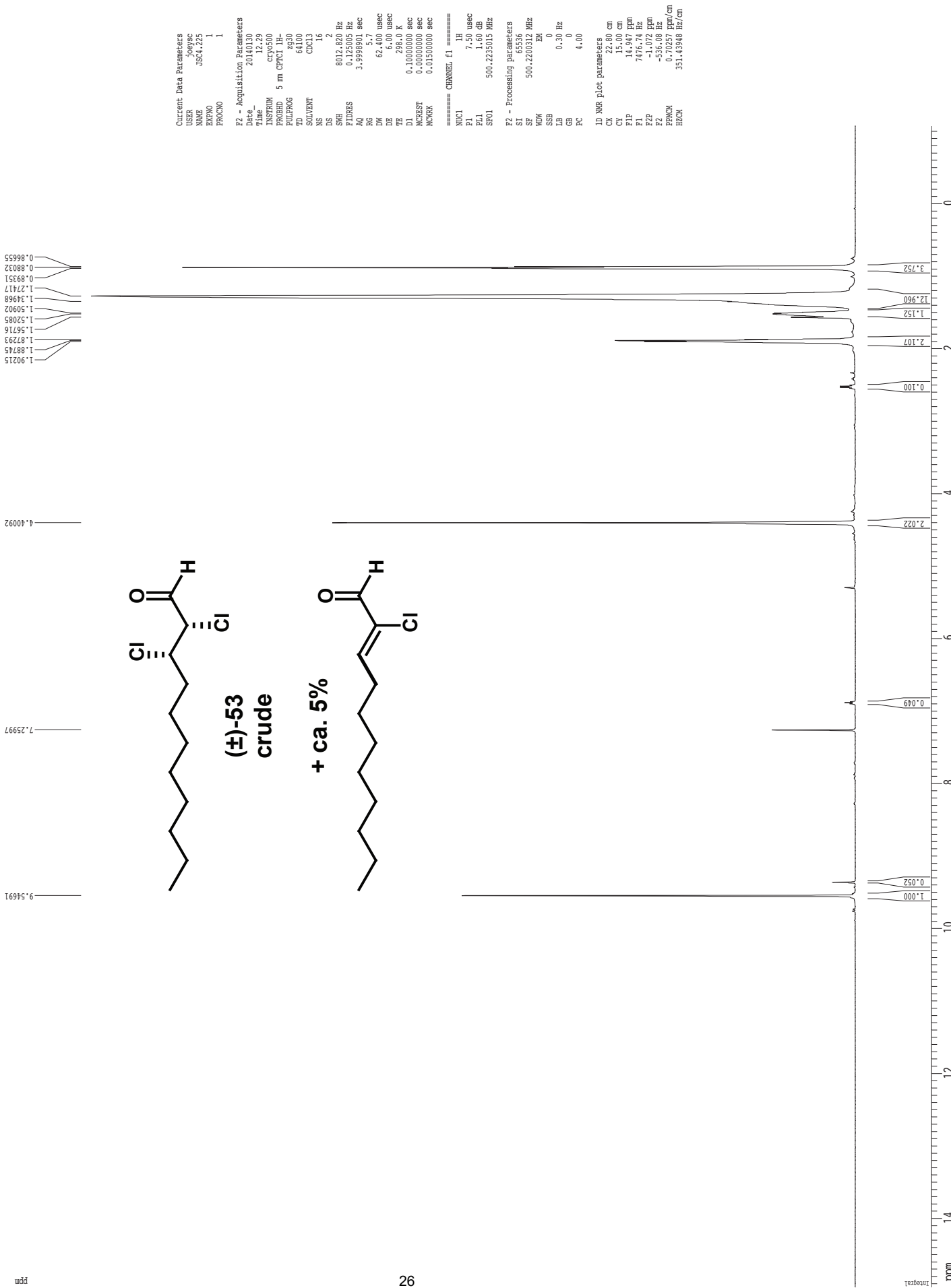


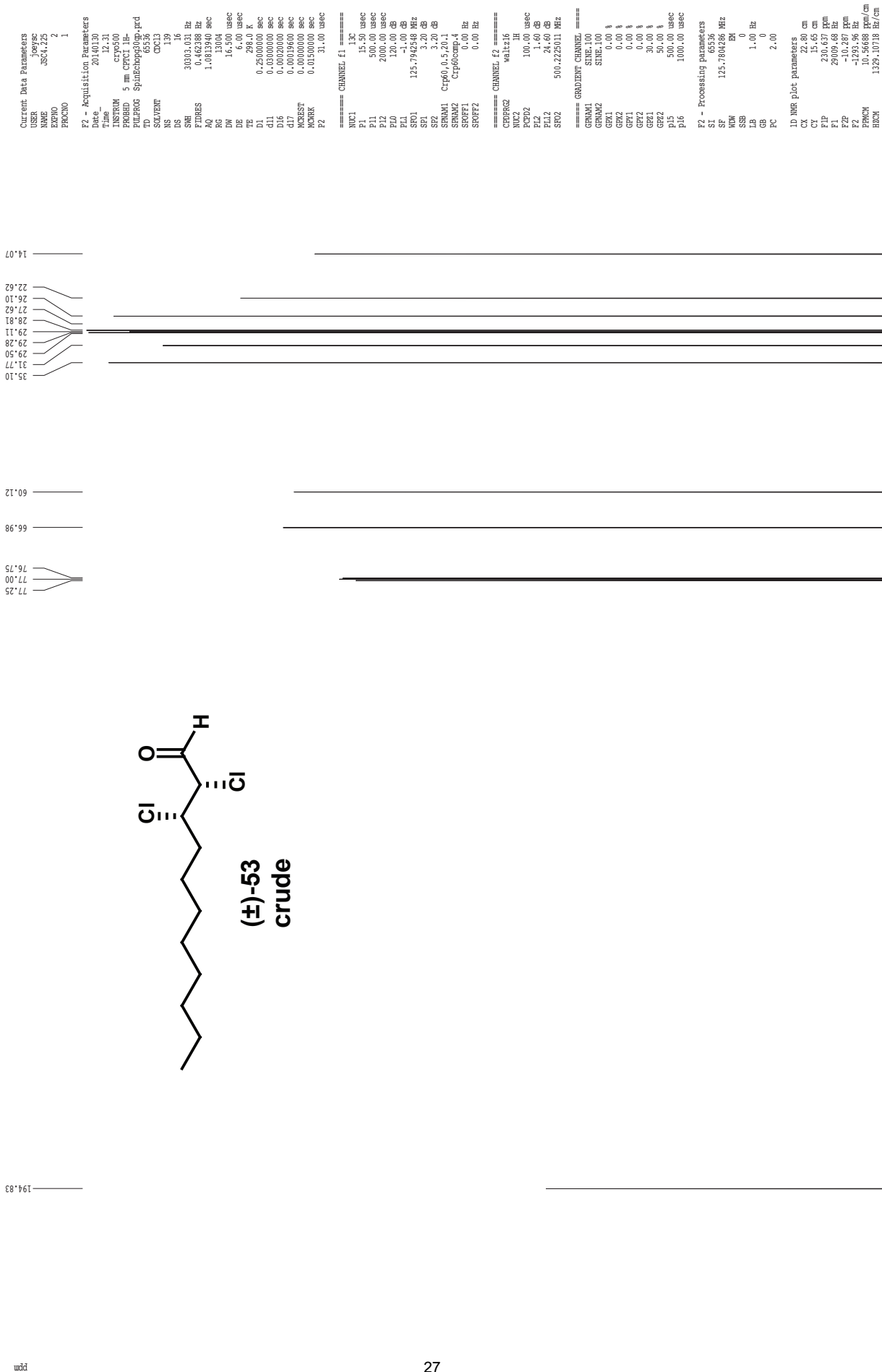
¹H spectrum



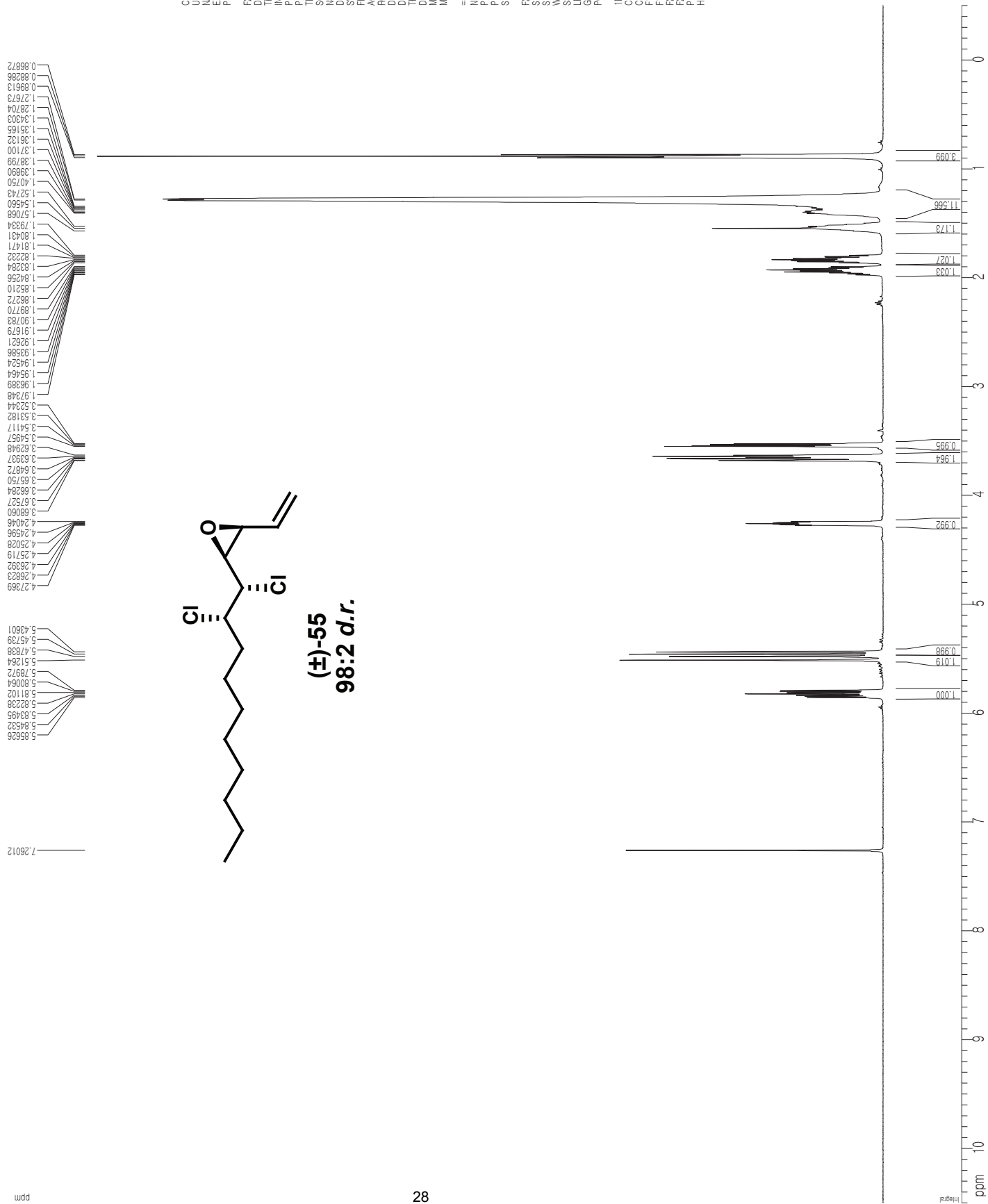
Z-restored spin-echo 13C spectrum with 1H decoupling



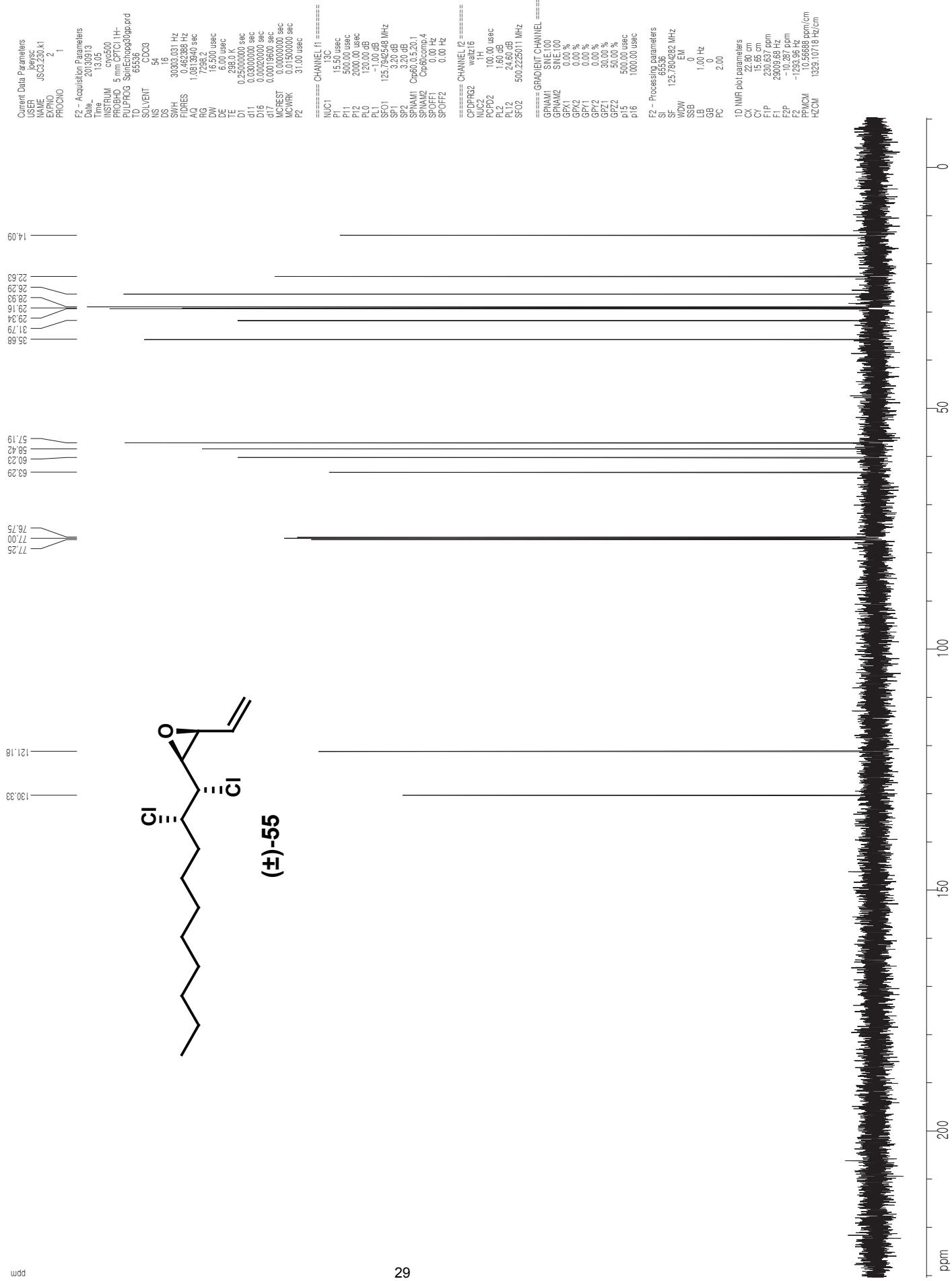


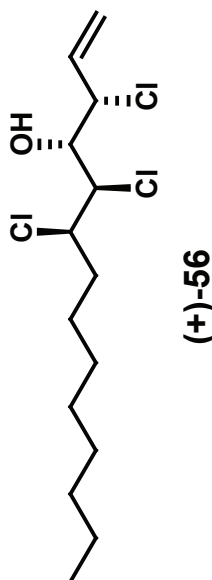
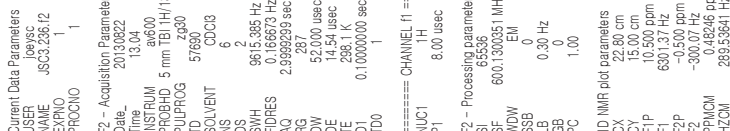


¹H spectrum

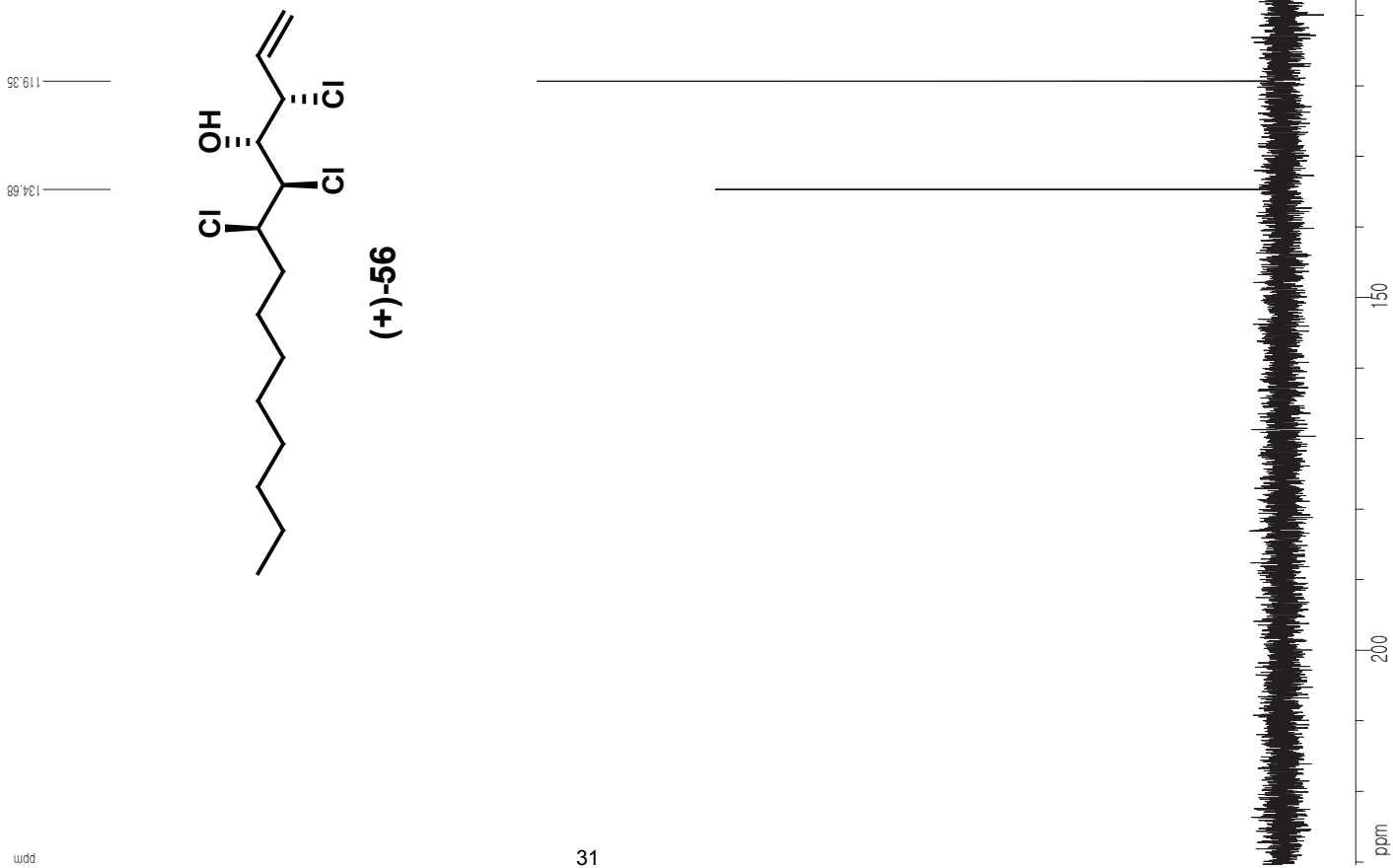


Z-restored spin-echo 13C spectrum with 1H decoupling

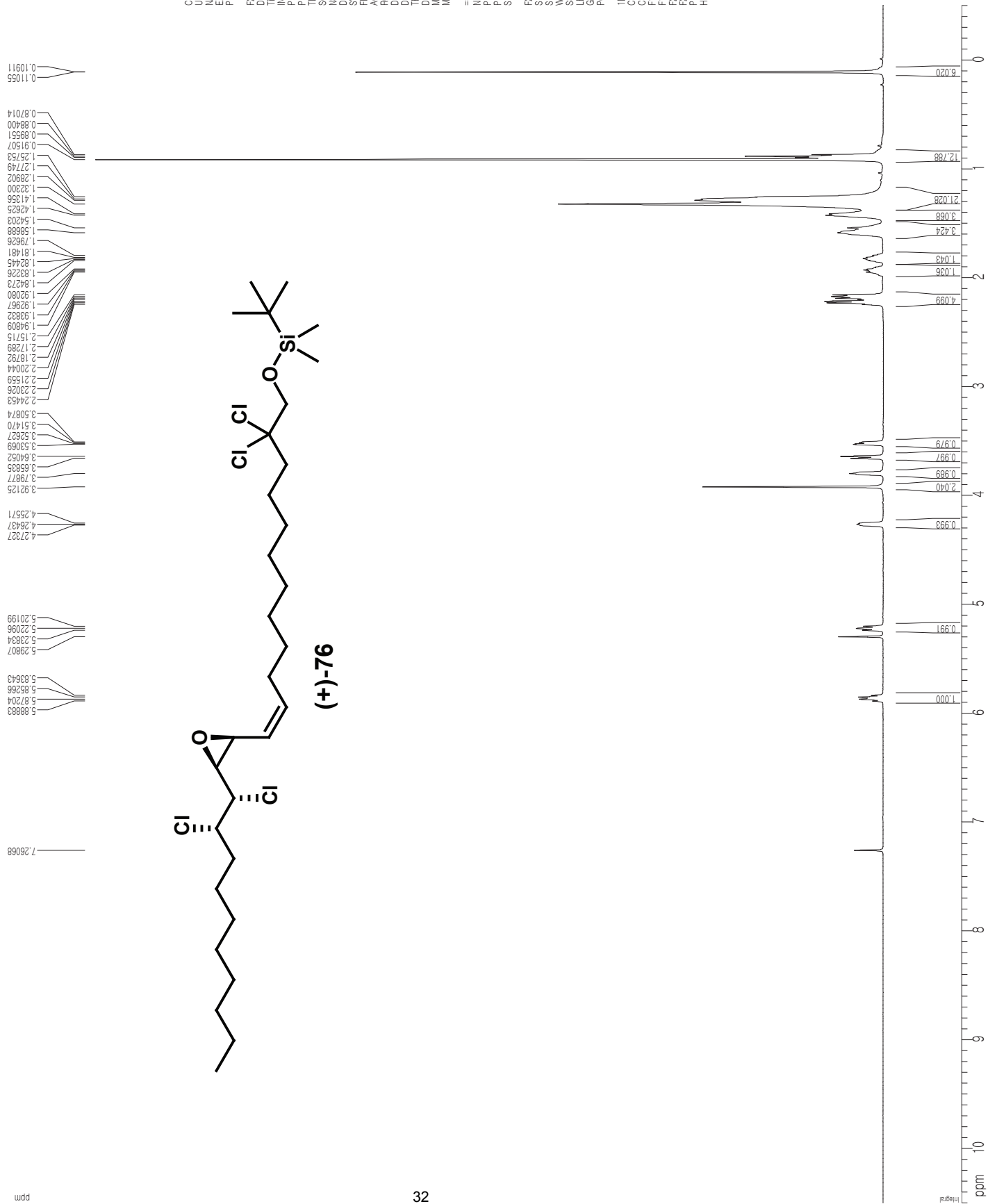


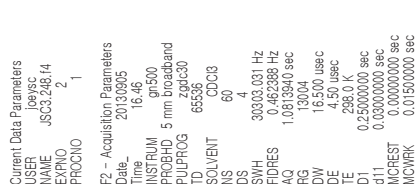


Z-restored spin-echo 13C spectrum with 1H decoupling



¹H spectrum



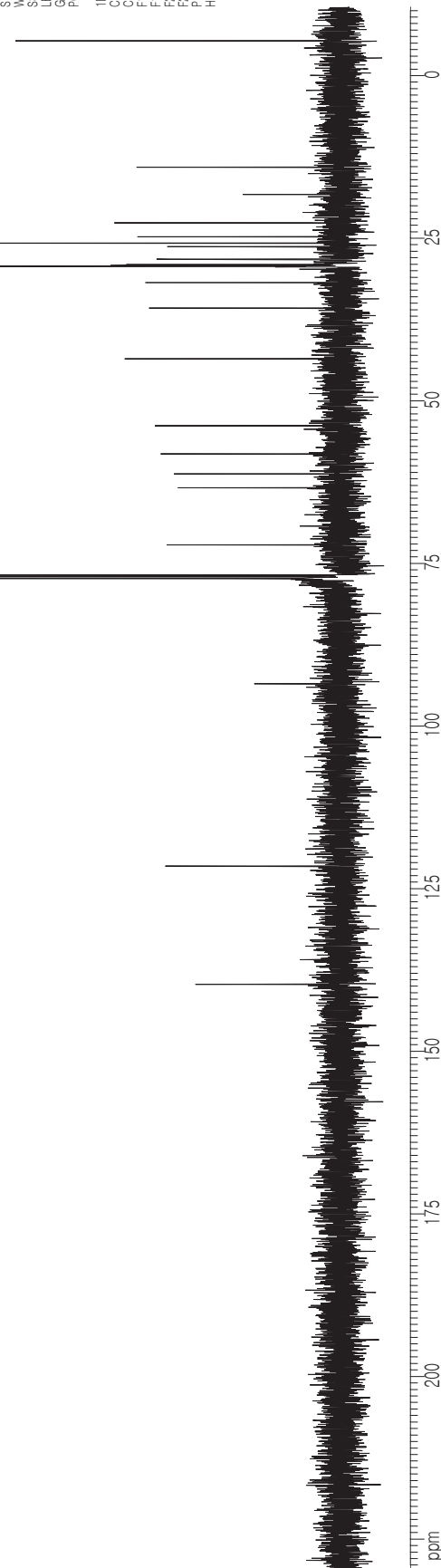


```
===== CHANNEL f1 =====
NUC1      13C
P1        7.70 usec
PL1       0.00 dB
SFO1     125.5603801 MHz
```

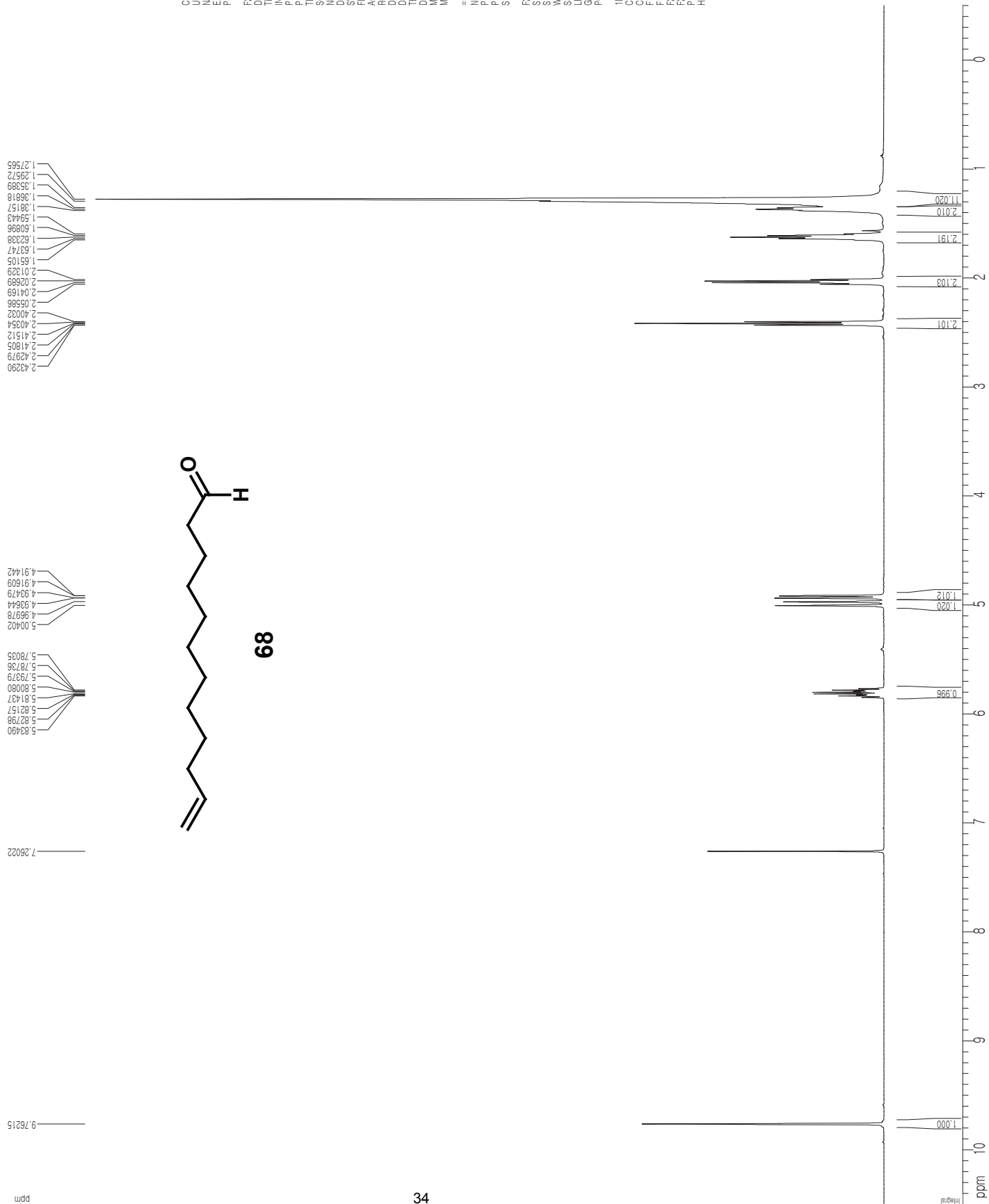
```
===== CHANNEL f2 =====
CPDRG2      waltz 16
NUC2        1H
PCPD2       80.00 usec
PL2         -3.00 dB
PL12        13.20 dB
SFO2        499.2924964 MHz
```

F2 - Processing parameters	
SI	6536
SF	125.5465774 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	2.00

1D NMR plot parameters	
CX	22.80 cm
CY	15.65 cm
F1P	229.520 ppm
F1	28815.41 Hz
F2P	-10.507 ppm
F2	-1319.07 Hz
PPMCM	10.52747 ppm/cm
HZCM	1321.68762 Hz/cm



¹H spectrum



Current Data Parameters
 USER jensc
 NAME JSC3.9.13
 EXPNO 1
 PROCNO 1

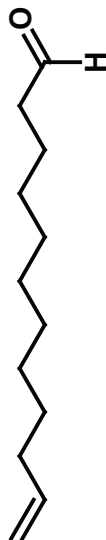
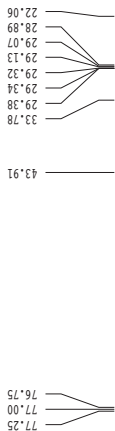
F2 - Acquisition Parameters
 Date_ 20121221
 Time 9:27
 INSTRUM cryo500
 PROBHD 5 mm CPTCI 1H-
 PULPROG zgpg30
 TO 6417.7980
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.125005 Hz
 AQ 3.9998901 sec
 RG 3.2
 DW 62.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.10000000 sec
 INCREST 0.00000000 sec
 MCNHR 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 7.50 usec
 PL1 1.50 dB
 SFO1 500.2235015 MHz

F2 - Processing parameters
 SI 65536
 SF 500.2200305 MHz
 Evt
 WDW 0
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 4.00

1D NMR plot parameters
 CX 22.80 cm
 CY 15.00 cm
 FIP 10.500 ppm
 F1 5252.31 Hz
 F2P -0.500 ppm
 F2 -250.11 Hz
 PPMCM 0.48246 ppm/cm
 HZCM 241.33423 Hz/cm

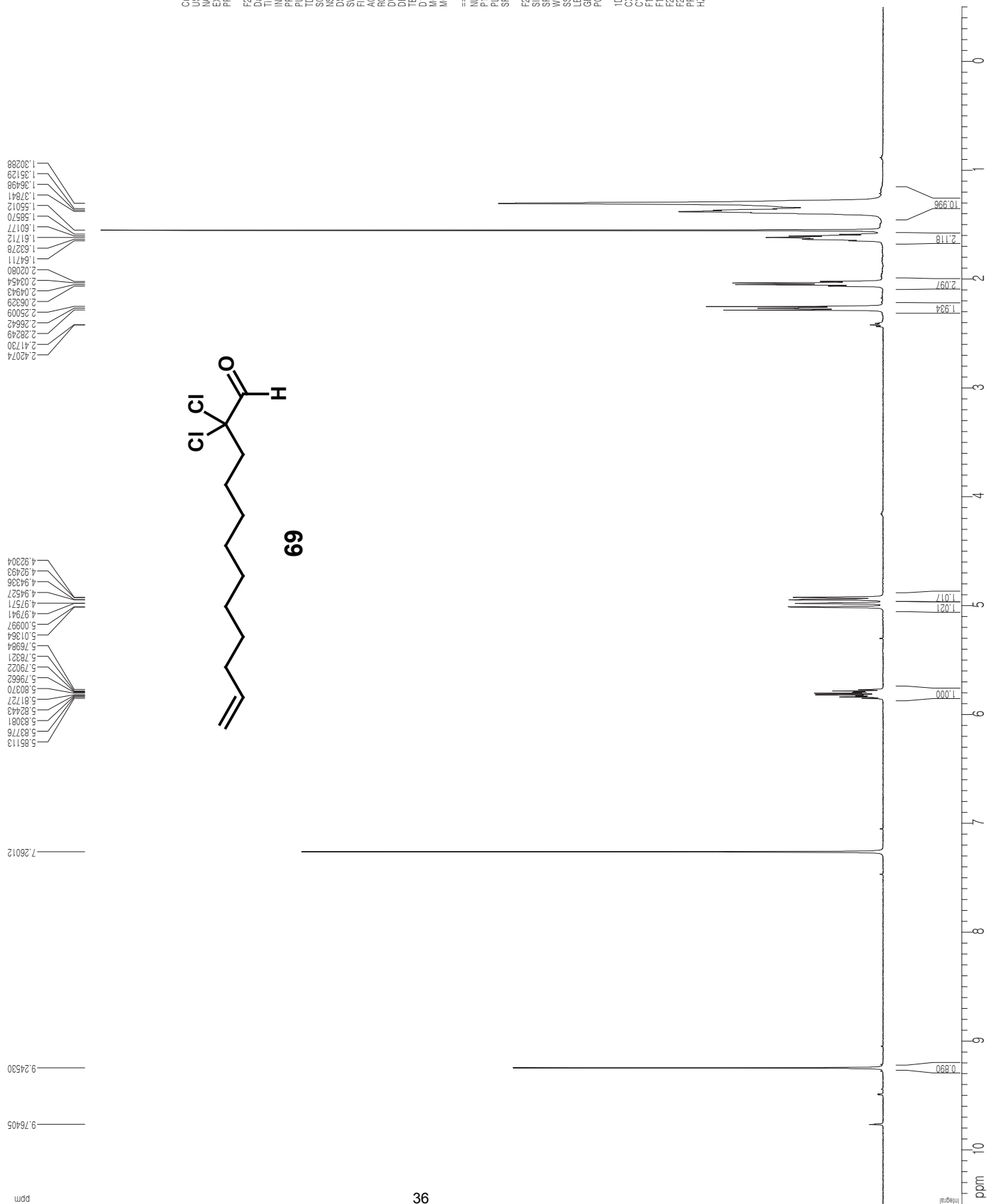
ppm



68

Current Data Parameters
USER joyesc
NAME JSC3.9.f3
EXPNO 2
PROCNO 1
F2 - Acquisition Parameters
Date_ 20121221
Time_ 9.29
INSTRUM cryo500
PROBHD 5 mm CPXI 1H-
PULPROG zgpg300p.prd
TD 65536
SOLVENT CHCl3
NS 69
DS 4
SWH 30303.031 Hz
FIDRES 0.462388 Hz
AQ 1.0813940 sec
RG 7298.2
DW 16.500 usec
DE 6.00 usec
TE 298.0 K
D1 0.2500000 sec
d11 0.0000000 sec
D16 0.0002000 sec
d17 0.0003600 sec
MCREST 0.0000000 sec
MCWRE 0.0150000 sec
PC 31.00 usec
===== CHANNEL f1 =====
NUC1 15N
P1 15.50 usec
P11 500.00 usec
P12 2000.00 usec
PL0 120.00 dB
PL1 -1.00 dB
SFO1 125.7942548 MHz
SFO2 500.2225011 MHz
SE1 3.20 dB
SE2 3.20 dB
SFO1 C1p60,0.5240.1
SFO2 C1p60,0.5240.1
SFO1 0.00 Hz
SFO2 0.00 Hz
===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
P2 100.00 usec
P21 100.00 usec
P22 24.60 dB
SFO2 500.2225011 MHz
===== GRADIENT CHANNEL =====
GRAM1 SINE.100
GRAM2 SINE.100
GB1 0.00 A
GB2 0.00 A
GB3 0.00 A
GB4 0.00 A
GB5 30.00 A
GB6 50.00 A
p15 500.00 usec
p16 1000.00 usec
F2 - Processing parameters
SI 65536
SF 125.7804254 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.80 cm
CY 22.80 cm
FID 230.637 KHz
F1 28009.68 Hz
F2 -10.287 ppm
F2 -1293.96 Hz
PRCM 10.5668 ppm/cm
HSCM 1329.10718 Hz/cm

¹H Spectrum



Current Data Parameters
 USER wujin
 NAME WJC-137
 EXPNO 7
 PROCNO 1

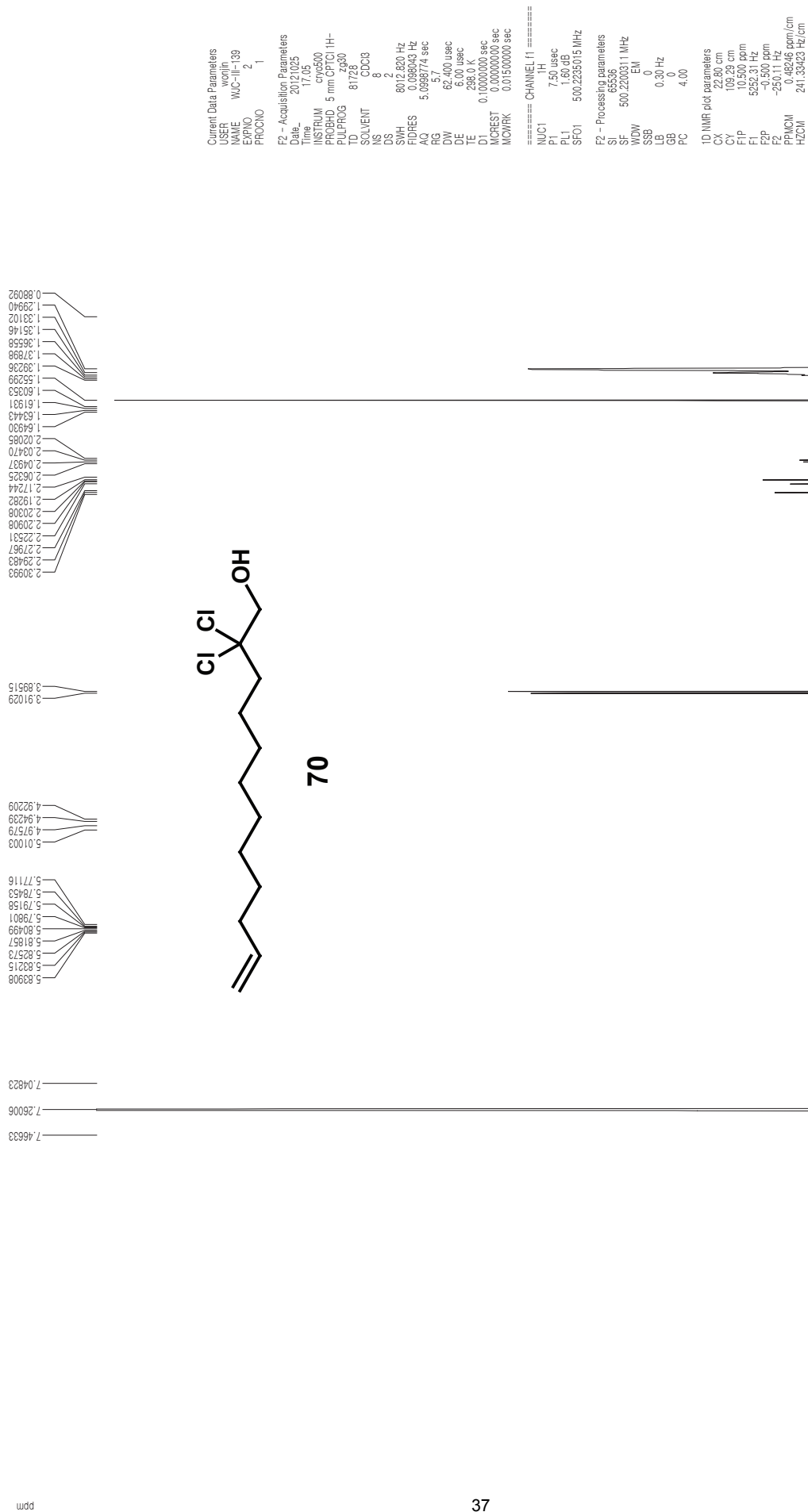
F2 - Acquisition Parameters
 Date_ 20121016
 Time 14.24
 INSTRUM cryo500
 PROBHD 5 mm CPTCI IH-
 PULPROG zgpg30
 TO 817.950
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8012.820 Hz
 FIDRES 0.059043 Hz
 AQ 5.0998774 sec
 RG 4.5
 DW 62.400 usec
 DE 6.00 usec
 TE 298.0 K
 D1 0.10000000 sec
 DCREST 0.00000000 sec
 MCNMR 0.01500000 sec

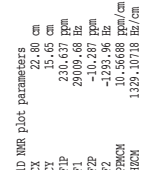
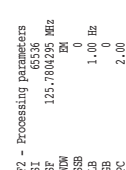
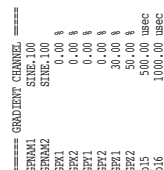
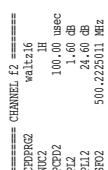
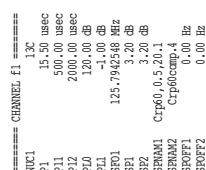
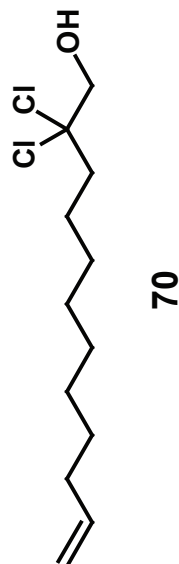
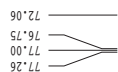
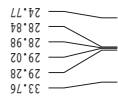
===== CHANNEL f1 =====
 NUC1 1H
 P1 7.50 usec
 PL1 1.50 dB
 SFO1 500.225015 MHz

F2 - Processing parameters
 SI 65536
 SF 500.220038 MHz
 WDW Em
 SSB 0
 GB 0
 CB 0.30 Hz
 PC 4.00

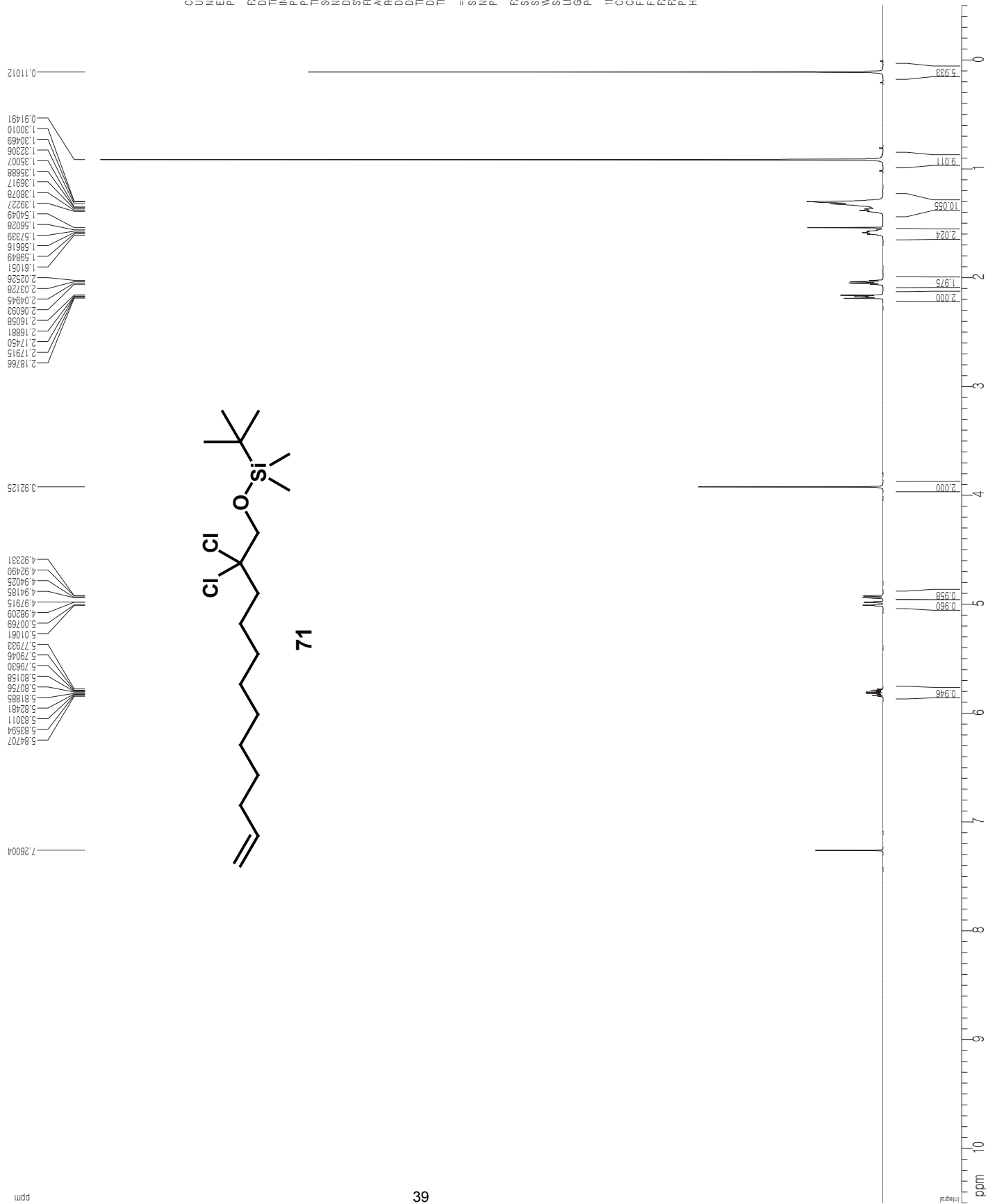
1D NMR plot parameters
 CX 22.80 cm
 CY 15.00 cm
 FIP 10.500 ppm
 F1 5252.31 Hz
 F2P -0.500 ppm
 F2 -250.11 Hz
 PPMCM 0.48246 ppm/cm
 HZCM 241.33423 Hz/cm

¹H Spectrum

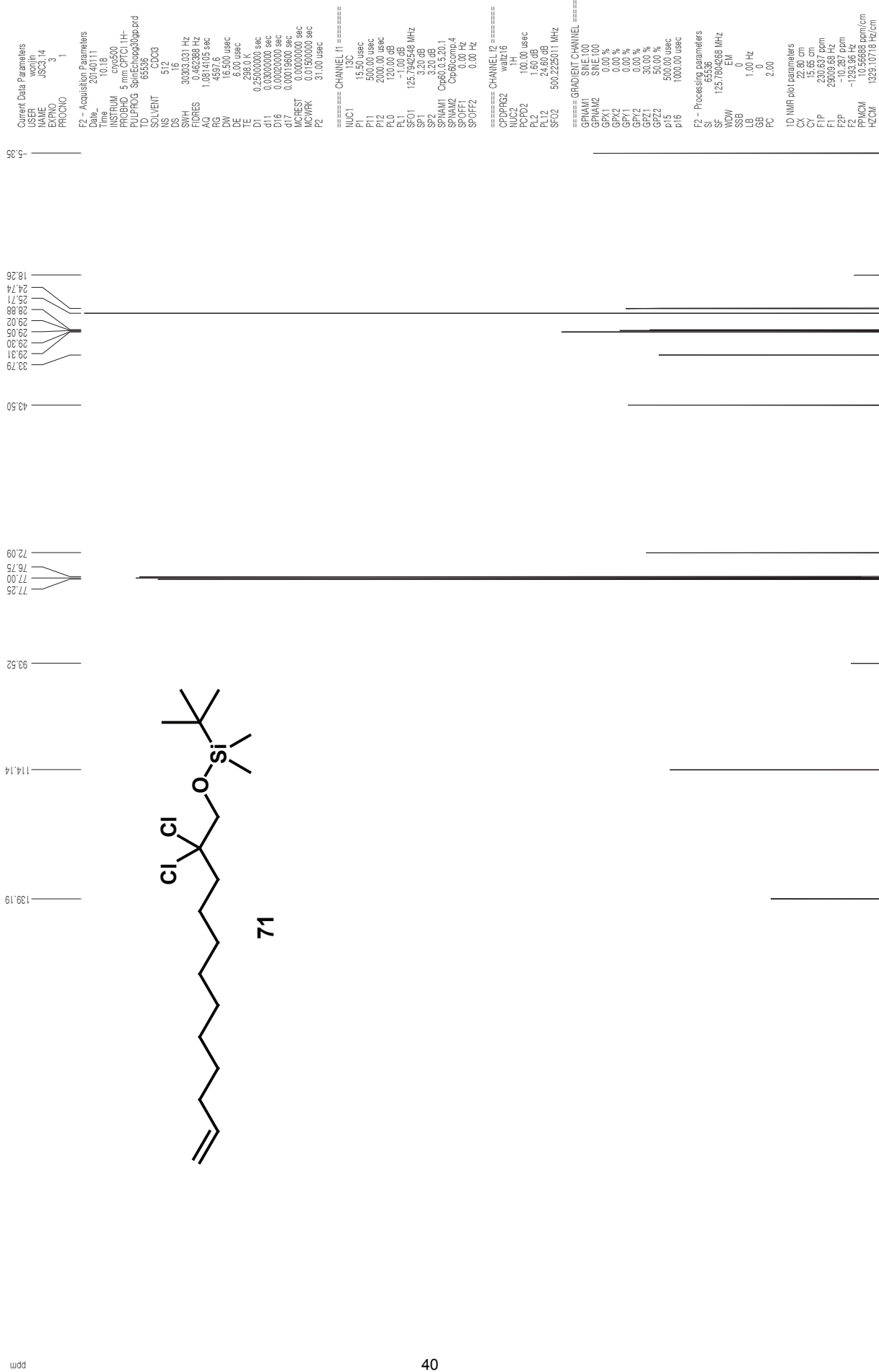




¹H Spectrum



Z-restored spin-echo 13C spectrum with 1H decoupling



CHIRALDEX B, 30 psi, 145 C

Injection Date : 12/21/13 1:08:31 PM

Sample Name : WJC-V-127-1

Location : Vial 1

Acq. Operator : WJC

Inj Volume : Manually

Acq. Method : C:\HPCHEM\2\METHODS\RIGHT.M

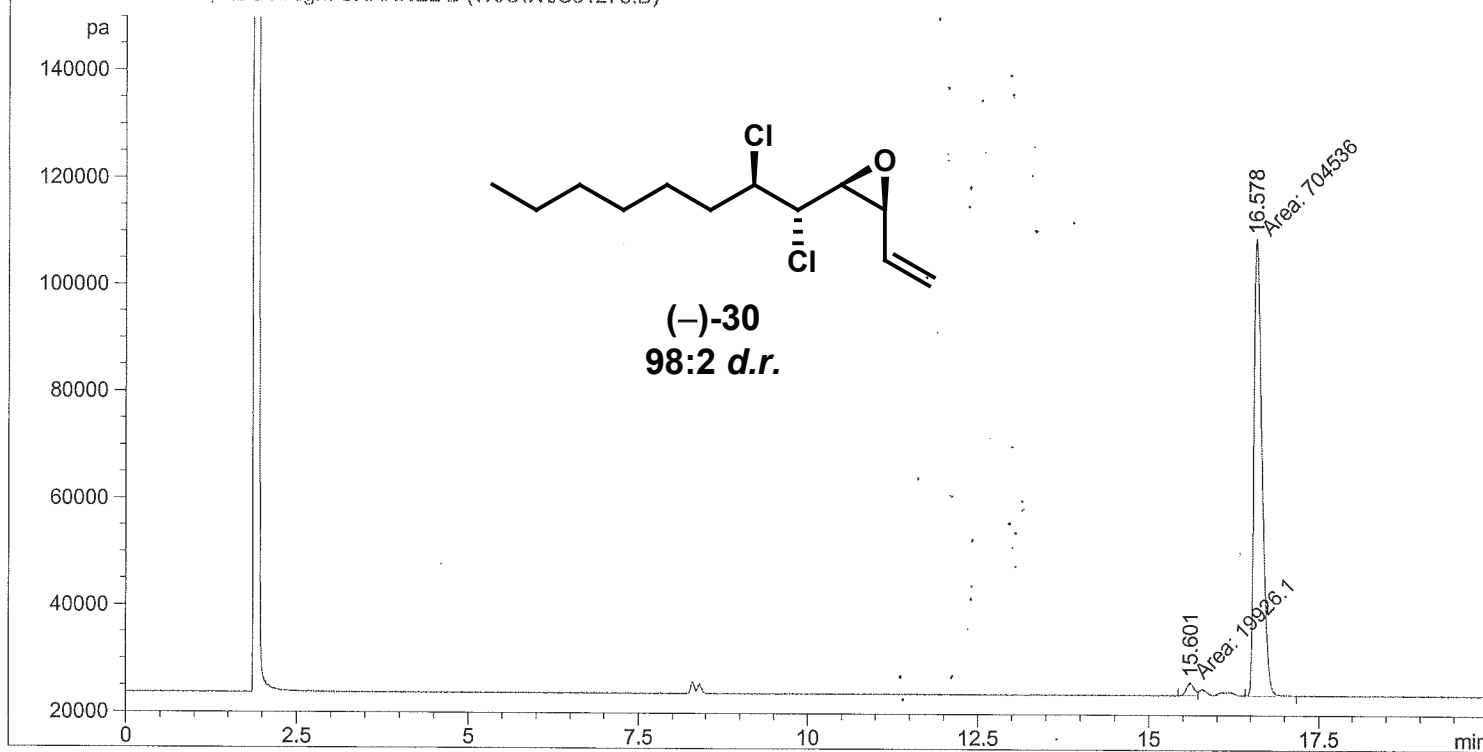
Last changed : 12/21/13 1:07:03 PM by WJC
(modified after loading)

Analysis Method : C:\HPCHEM\2\METHODS\RIGHT.M

Last changed : 12/21/13 1:32:58 PM by WJC
(modified after loading)

Checkout of Right 5890 GC, oven at 39'C, Fid on. Zones on.

ADC1 B, ADC1 Right CHANNEL B (WJCWJC51279.D)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: ADC1 B, ADC1 Right CHANNEL B

Peak #	RetTime [min]	Type	Width [min]	Area [pa*s]	Height [pa]	Area %
1	15.601	MM	0.1333	1.99261e4	2490.71655	2.75046
2	16.578	MM	0.1368	7.04536e5	8.58330e4	97.24954

Totals : 7.24463e5 8.83237e4

Results obtained with enhanced integrator!

*** End of Report ***

CHIRALDEX B, 145 C, 30 psi
rac-vinyl epoxide for danicalipin A

Injection Date : 5/13/13 8:17:54 PM

Sample Name : rac-danicalipin

Acq. Operator : WJC

Location : Vial 1

Inj Volume : Manually

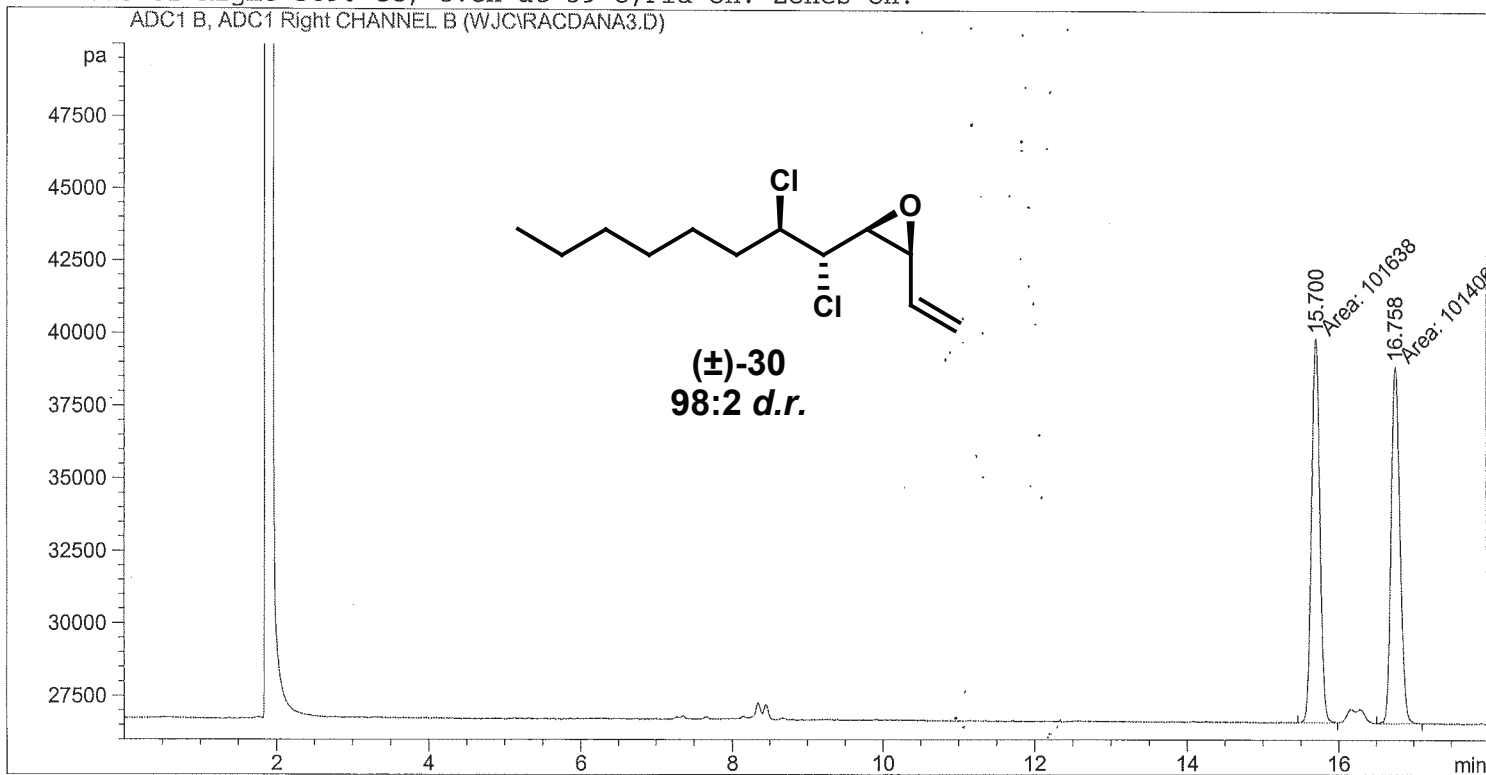
Acq. Method : C:\HPCHEM\2\METHODS\RIGHT.M

Last changed : 5/13/13 8:34:59 PM by WJC
(modified after loading)

Analysis Method : C:\HPCHEM\2\METHODS\RIGHT.M

Last changed : 5/13/13 8:36:43 PM by WJC
(modified after loading)

Checkout of Right 5890 GC, oven at 39'C, Fid on. Zones on.



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: ADC1 B, ADC1 Right CHANNEL B

Peak #	RetTime [min]	Type	Width [min]	Area [pa*s]	Height [pa]	Area %
1	15.700	MM	0.1273	1.01638e5	1.33040e4	50.05713
2	16.758	MM	0.1366	1.01406e5	1.23741e4	49.94287

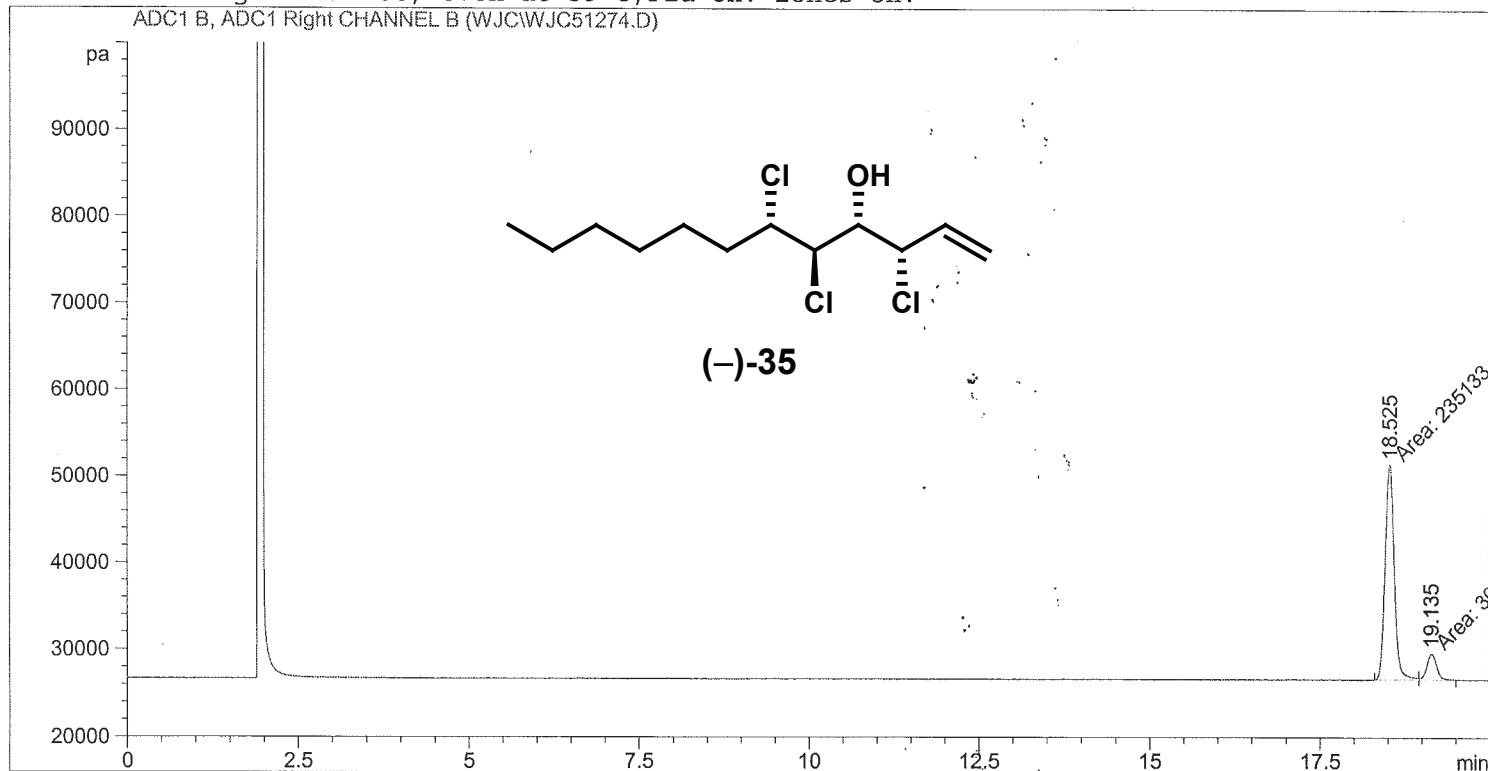
Totals : 2.03044e5 2.56782e4

Results obtained with enhanced integrator!

*** End of Report ***

CHIRALDEX B, 30 psi, 165 C

=====
Injection Date : 6/17/13 6:53:22 PM
Sample Name : WJC-V-127-2 Location : Vial 1
Acq. Operator : WJC Inj Volume : Manually
Acq. Method : C:\HPCHEM\2\METHODS\RIGHT.M
Last changed : 6/17/13 6:47:58 PM by WJC
(modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\RIGHT.M
Last changed : 12/21/13 2:00:06 PM by WJC
(modified after loading)
Checkout of Right 5890 GC, oven at 39'C, Fid on. Zones on.



=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: ADC1 B, ADC1 Right CHANNEL B

Peak #	RetTime [min]	Type	Width [min]	Area [pa*s]	Height [pa]	Area %
1	18.525	MF	0.1573	2.35133e5	2.49056e4	88.45260
2	19.135	FM	0.1685	3.06963e4	3035.53394	11.54740

Totals : 2.65829e5 2.79412e4

Results obtained with enhanced integrator!

=====
*** End of Report ***

CHIRALDEX B, 30 psi, 165 C

Injection Date : 5/28/13 12:37:21 PM

Sample Name : WJC-V-097

Location : Vial 1

Acq. Operator : WJC

Inj Volume : Manually

Acq. Method : C:\HPCHEM\2\METHODS\RIGHT.M

Last changed : 5/28/13 12:33:54 PM by WJC

(modified after loading)

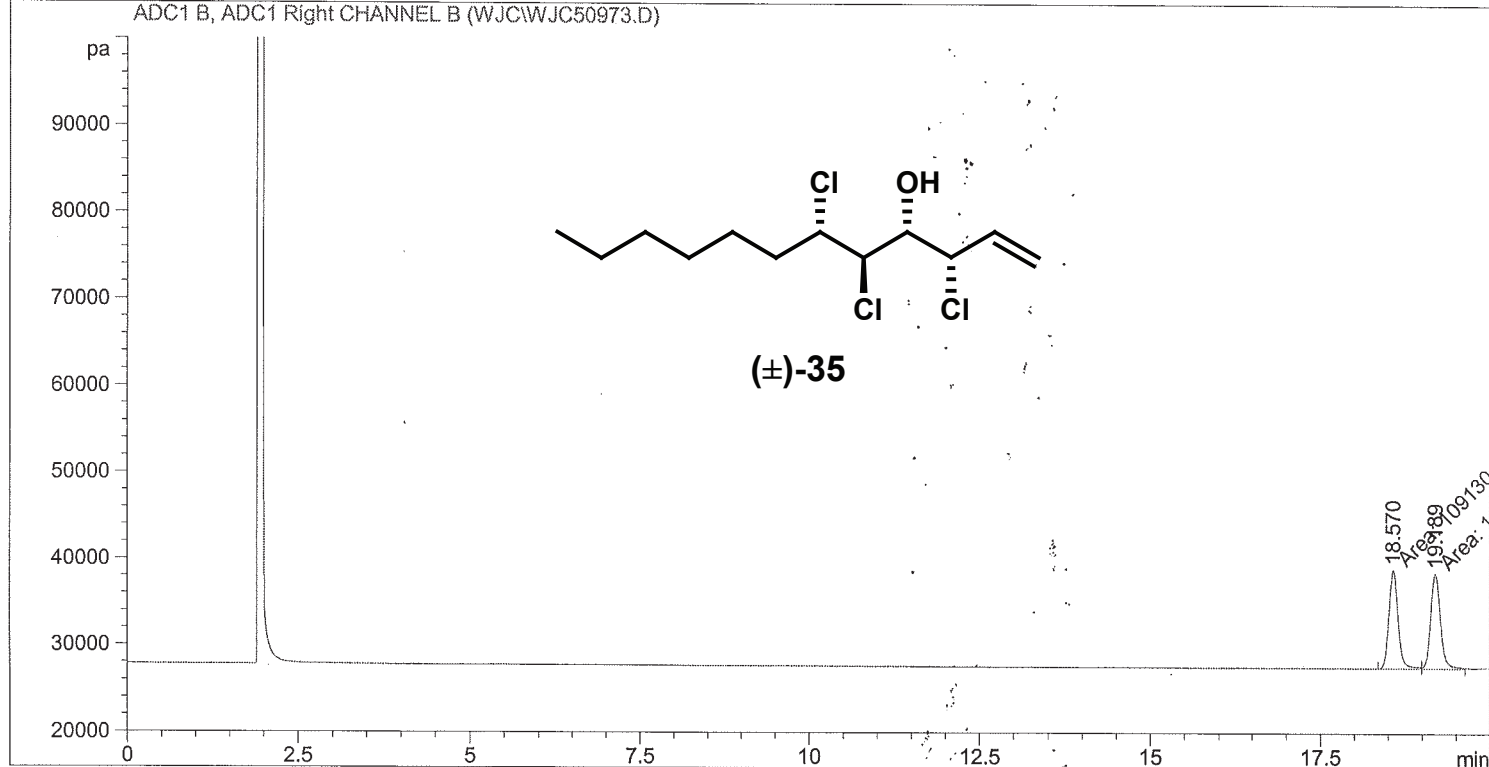
Analysis Method : C:\HPCHEM\2\METHODS\RIGHT.M

Last changed : 12/21/13 2:05:05 PM by WJC

(modified after loading)

Checkout of Right 5890 GC, oven at 39'C, Fid on. Zones on.

ADC1 B, ADC1 Right CHANNEL B (WJC\WJC50973.D)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: ADC1 B, ADC1 Right CHANNEL B

Peak #	RetTime [min]	Type	Width [min]	Area [pa*s]	Height [pa]	Area %
1	18.570	MF	0.1593	1.09130e5	1.14164e4	49.54654
2	19.189	FM	0.1681	1.11128e5	1.10150e4	50.45346

Totals : 2.20258e5 2.24314e4

Results obtained with enhanced integrator!

*** End of Report ***

CHIRALDEX B, 30 psi, 180 deg C
mal resolution, chlorohydrin from SM

Injection Date : 8/22/13 7:57:03 PM

Sample Name : JSC3.236.f1_2

Location : Vial 1

Acq. Operator : JSC

Inj Volume : Manually

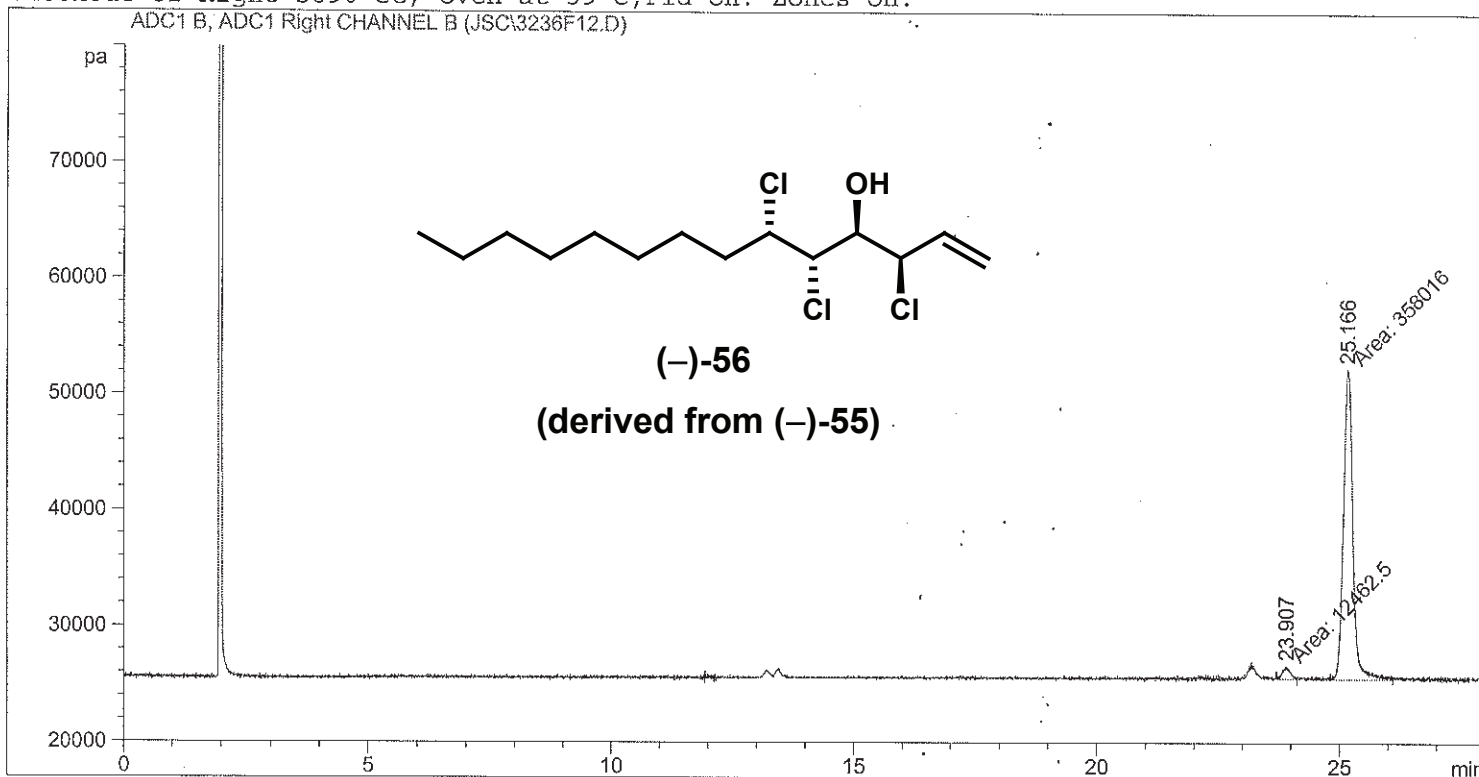
Acq. Method : C:\HPCHEM\2\METHODS\RIGHT.M

Last changed : 8/22/13 7:53:55 PM by JSC
(modified after loading)

Analysis Method : C:\HPCHEM\2\METHODS\RIGHT.M

Last changed : 1/13/14 2:31:47 PM by WJC
(modified after loading)

Checkout of Right 5890 GC, oven at 39'C, Fid on. Zones on.



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: ADC1 B, ADC1 Right CHANNEL B

Peak #	RetTime [min]	Type	Width [min]	Area [pa*s]	Height [pa]	Area %
1	23.907	MM	0.1850	1.24625e4	1122.51733	3.36390
2	25.166	MM	0.2222	3.58016e5	2.68558e4	96.63610

Totals : 3.70478e5 2.79783e4

Results obtained with enhanced integrator!

*** End of Report ***

CHIRALDEX B, 30 psi, 180 deg C
malham. resolution chlorohydrin prod

Injection Date : 8/22/13 2:23:58 PM

Sample Name : JSC3.236.f2

Location : Vial 1

Acq. Operator : JSC

Inj Volume : Manually

Acq. Method : C:\HPCHEM\2\METHODS\RIGHT.M

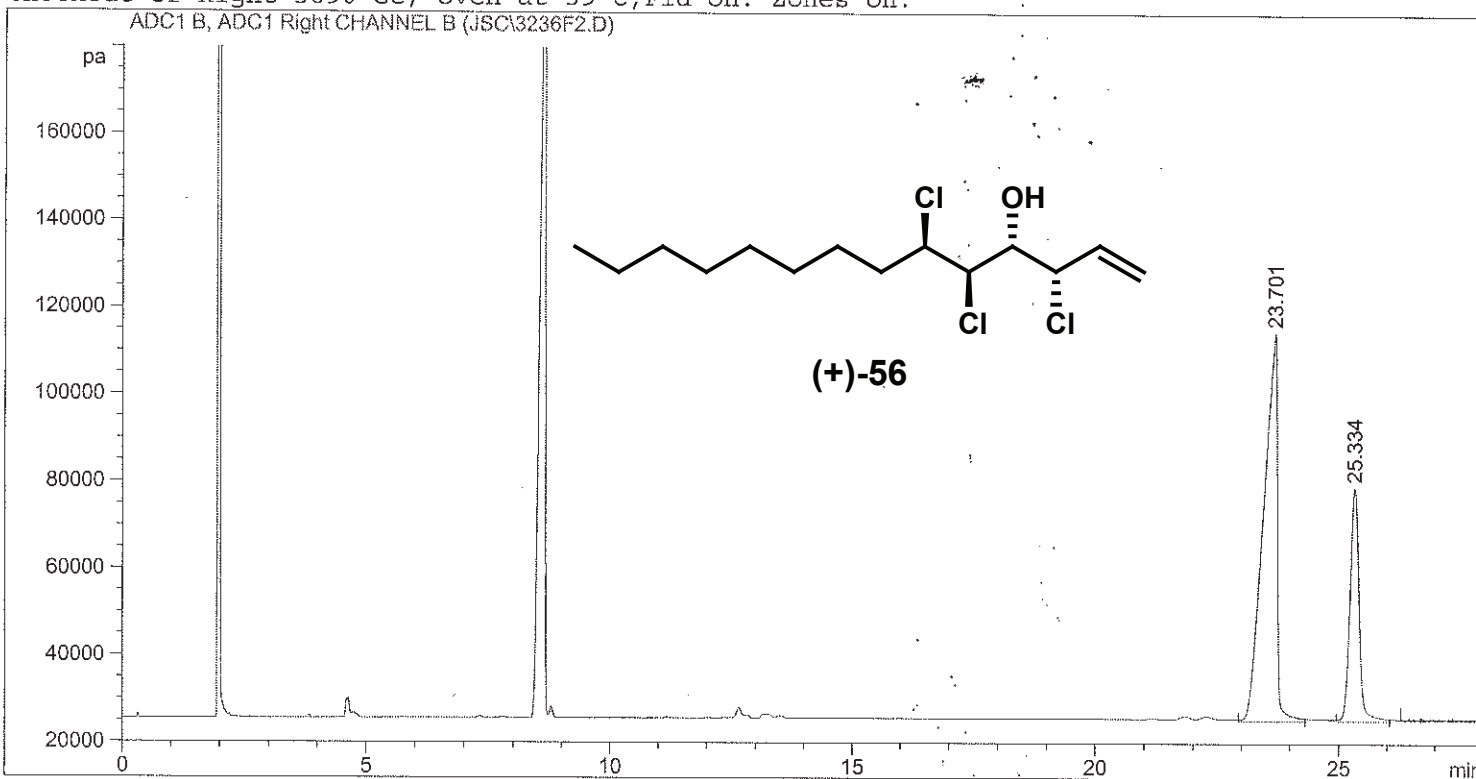
Last changed : 1/26/06 2:19:25 PM

Analysis Method : C:\HPCHEM\2\METHODS\RIGHT.M

Last changed : 1/13/14 2:36:14 PM by WJC

(modified after loading)

Checkout of Right 5890 GC, oven at 39'C, Fid on. Zones on.



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: ADC1 B, ADC1 Right CHANNEL B

Peak #	RetTime [min]	Type	Width [min]	Area [pa*s]	Height [pa]	Area %
1	23.701	VV	0.2548	1.81696e6	8.95359e4	71.43658
2	25.334	VV	0.1933	7.26499e5	5.38667e4	28.56342

Totals : 2.54346e6 1.43403e5

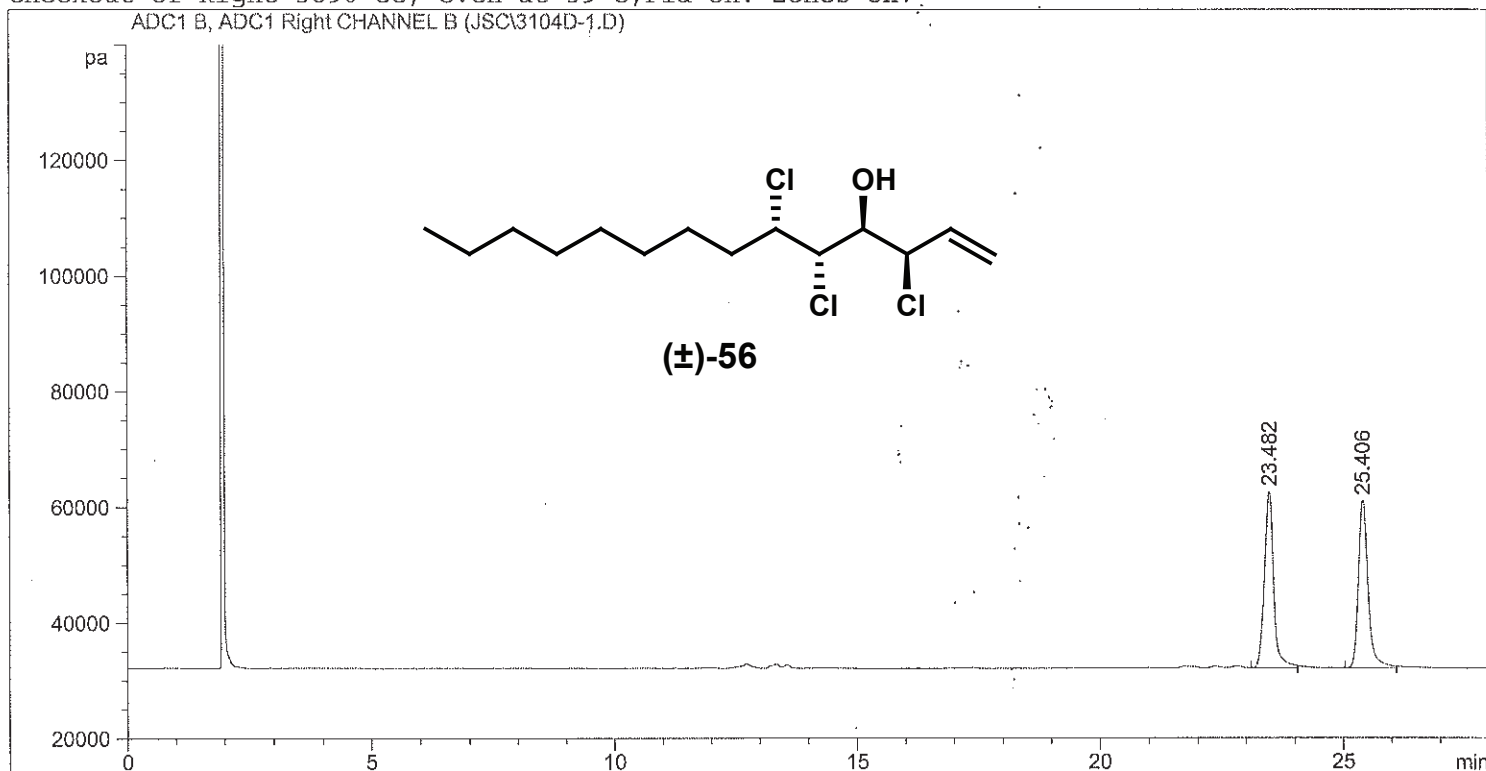
Results obtained with enhanced integrator!

*** End of Report ***

CHIRALDEX B, 30 psi, 180 C
malhamensilipin A: SM opened chlorohydrin from kinetic
resolution
JSC3.104D

=====
Injection Date : 5/21/13 1:34:08 PM
Sample Name : mal chlorohydrin Location : Vial 1
Acq. Operator : JSC Inj Volume : Manually

Acq. Method : C:\HPCHEM\2\METHODS\RIGHT.M
Last changed : 5/21/13 1:35:18 PM by JSC
(modified after loading)
Analysis Method : C:\HPCHEM\2\METHODS\RIGHT.M
Last changed : 1/13/14 2:38:27 PM by WJC
(modified after loading)
Checkout of Right 5890 GC, oven at 39'C, Fid on. Zones on.



=====
Area Percent Report
=====

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000

Signal 1: ADC1 B, ADC1 Right CHANNEL B

Peak #	RetTime [min]	Type	Width [min]	Area [pa*s]	Height [pa]	Area %
1	23.482	VV	0.1889	4.10963e5	3.05644e4	50.07526
2	25.406	VV	0.1765	4.09728e5	2.90554e4	49.92474

Totals : 8.20691e5 5.96198e4

Results obtained with enhanced integrator!