

Supporting Information

Use of *N*-Methylformamide as a Solvent in Indium Promoted Barbier Reactions *En Route* to Ene-diyne and Epoxydiyne Formation: Comparison of Rate and Stereoselectivity in C-C Bond Forming Reactions with Water

Kwame Frimpong, Joseph Wzorek, Claire Lawlor, Katharine Spencer, and Thomas Mitzel*

Department of Chemistry, Trinity College, 300 Summit Street, Hartford, CT 06106
thomas.mitzel@trincoll.edu

Table of Contents

General Experimental Methods.....	S3
Proton NMR for I.a.1.....	S4
Carbon NMR for I.a.1.....	S5
Proton NMR for I.a.2 (syn-isomer).....	S6
Carbon NMR for I.a.2 (syn-isomer).....	S7
Proton NMR for I.a.2 (anti-isomer).....	S8
Carbon NMR for I.a.2 (anti-isomer).....	S9
Proton NMR for I.a.3 (syn-isomer).....	S10
Carbon NMR for I.a.3 (syn-isomer).....	S11
Proton NMR for I.a.3 (anti-isomer).....	S12
Carbon NMR for I.a.3 (anti-isomer).....	S13
Proton NMR for I.a.4.....	S14
Carbon NMR for I.a.4.....	S15
Proton NMR for II.a.1.....	S16
Carbon NMR for II.a.1.....	S17
Proton NMR for II.a.2 (syn-isomer).....	S18
Carbon NMR for II.a.2 (syn-isomer).....	S19
Proton NMR for II.a.2 (anti-isomer).....	S20

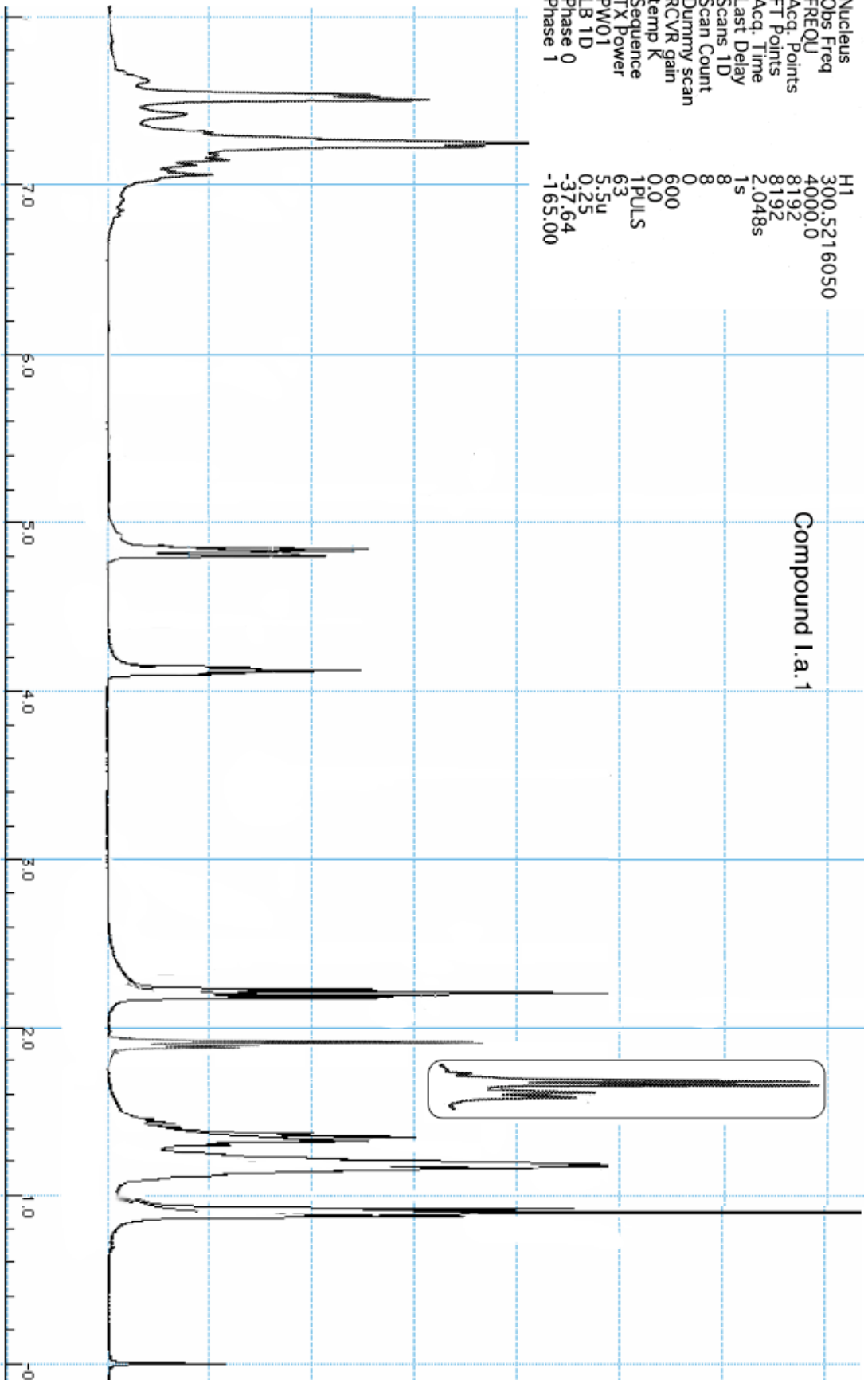
Carbon NMR for II.a.2 (anti-isomer).....	S21
Proton NMR for II.a.3 (syn-isomer).....	S22
Carbon NMR for II.a.3 (syn-isomer).....	S23
Proton NMR for II.a.3 (anti-isomer)	S24
Carbon NMR for II.a.3 (anti-isomer)	S25
Proton NMR for II.a.4	S26
Carbon NMR for II.a.4	S27
Proton NMR for III.a.1	S28
Carbon NMR for III.a.1	S29
Proton NMR for III.a.2	S30
Carbon NMR for III.a.2.....	S31
Proton NMR for III.a.2 (anti-isomer)	S32
Carbon NMR for III.a.2 (anti-isomer)	S33
Proton NMR for III.a.3	S34
Carbon NMR for III.a.3.....	S35
Proton NMR for III.a.3 (anti-isomer).....	S36
Carbon NMR for III.a.3 (anti-isomer).....	S37
Proton NMR for III.a.4	S38
Carbon NMR for III.a.4	S39

General Methods:

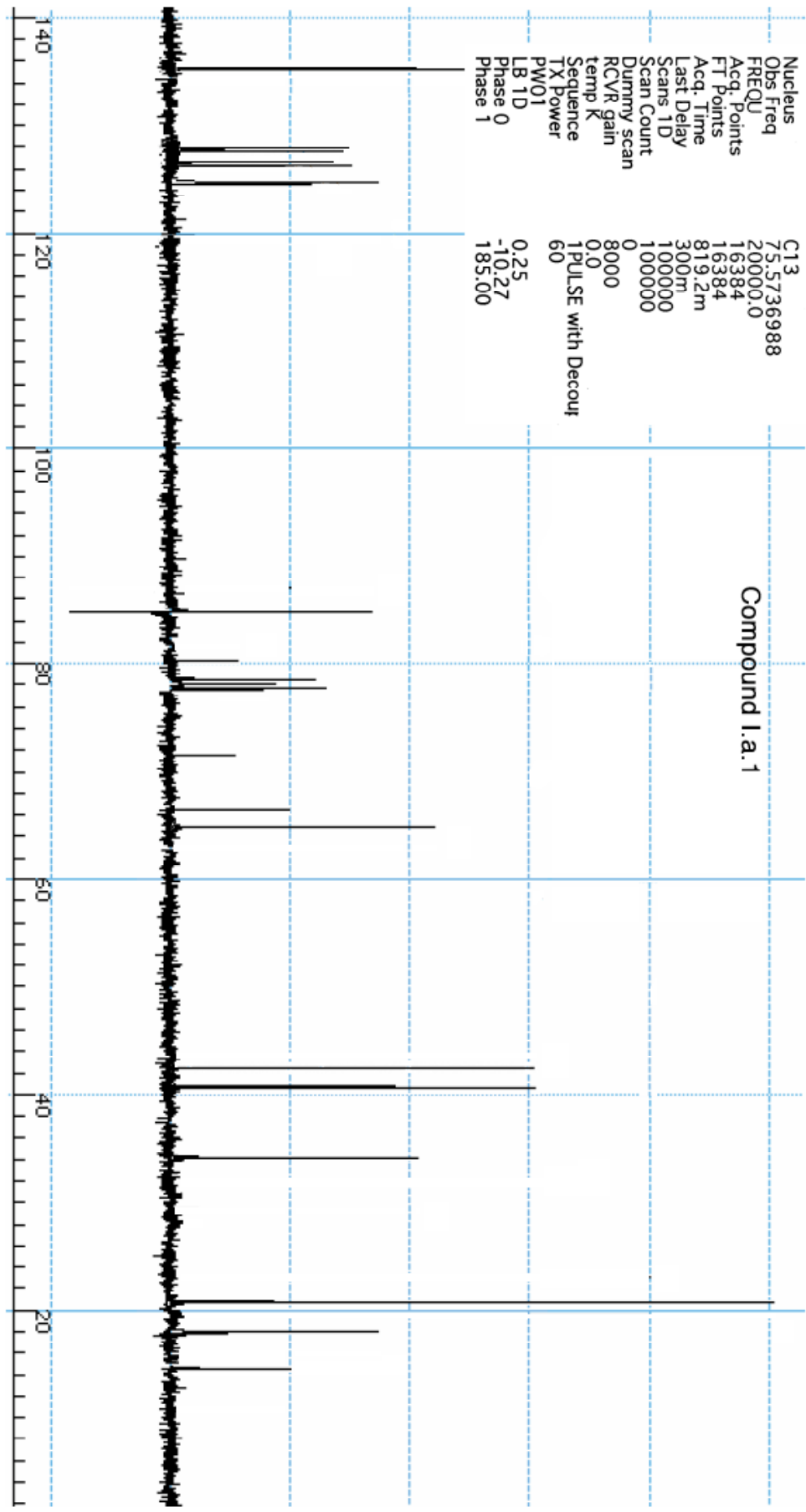
All spectra were obtained using a GE NMR with a tecmag upgrade. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) were obtained in CDCl_3 at room temperature. Chemical shifts are reported in parts per million upfield/downfield from CDCl_3 (δ 7.26 ppm and 77.3 ppm) Tetramethylsilane was used as an internal standard (δ 0.00 ppm).

Nucleus H1
 Obs.Freq 300.5216050
 FREQU 4000.0
 Acq. Points 8192
 FT Points 8192
 Acq. Time 2.048s
 Last Delay 1s
 Scans 1D 8
 Scan Count 8
 Dummy scan 0
 RCVR gain 600
 temp K 0.0
 Sequence 1PULS
 TX Power 63
 PW01 5.5u
 LB 1D 0.25
 Phase 0 -37.64
 Phase 1 -165.00

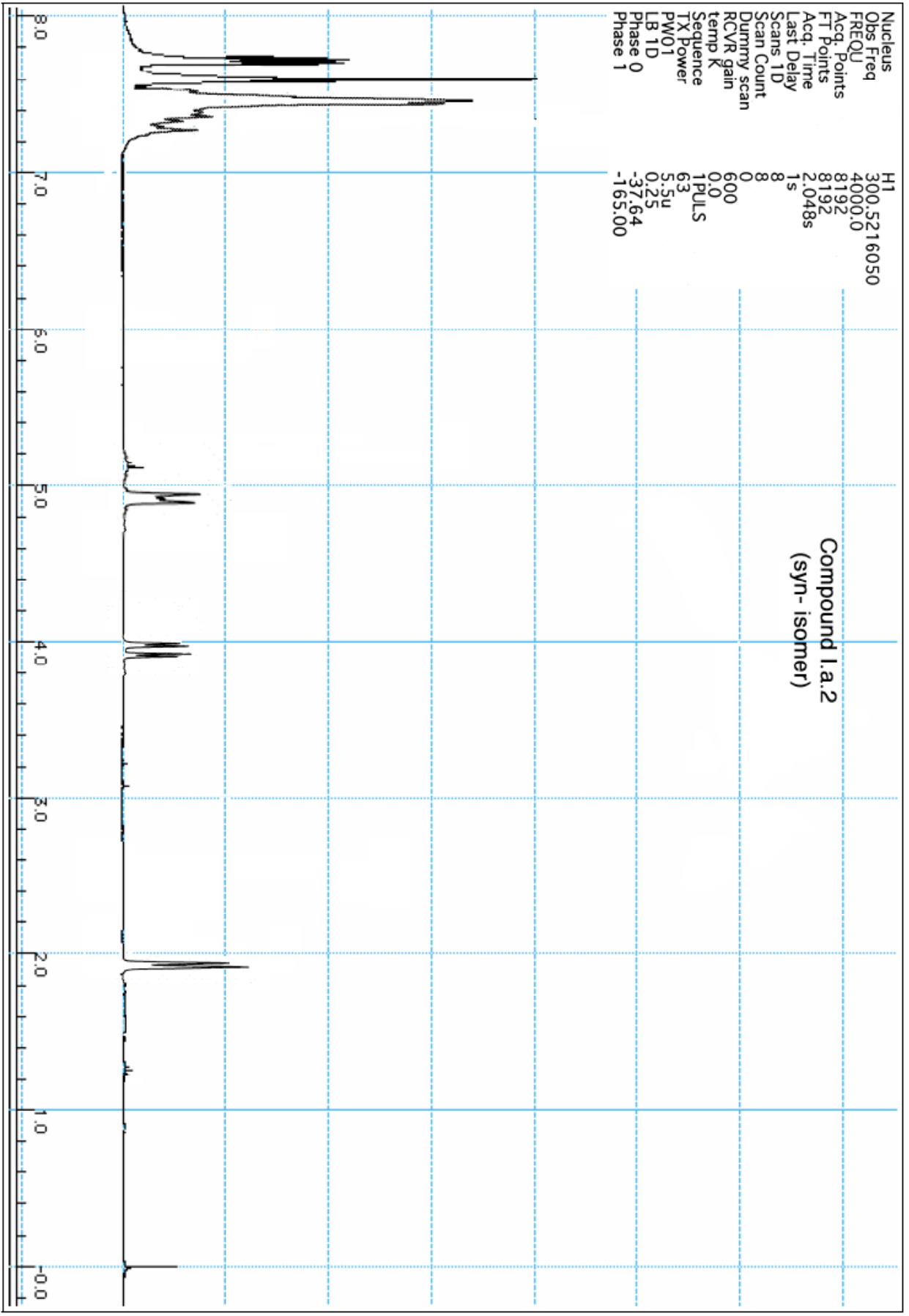
Compound 1.a.1



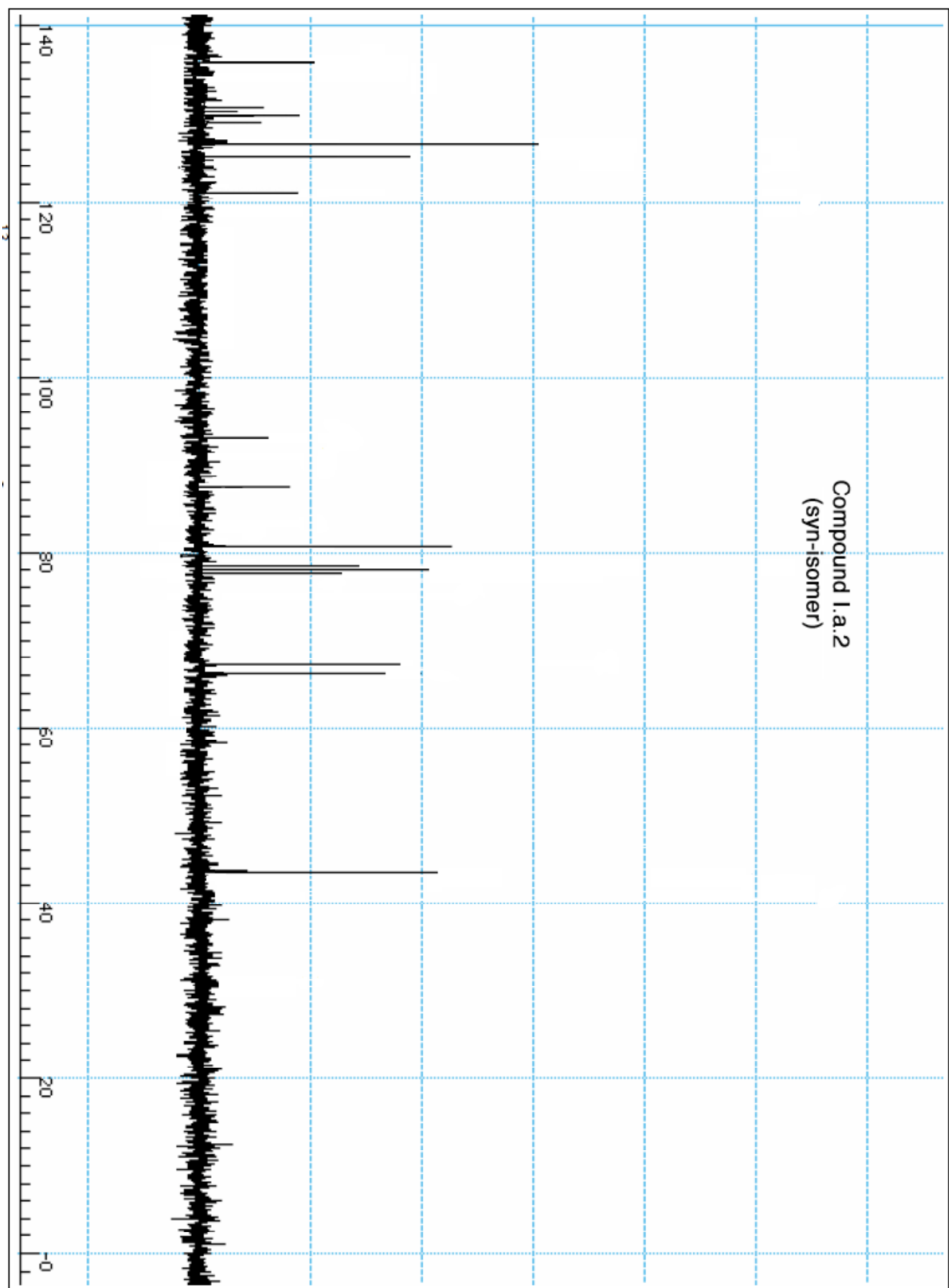
tecmaq

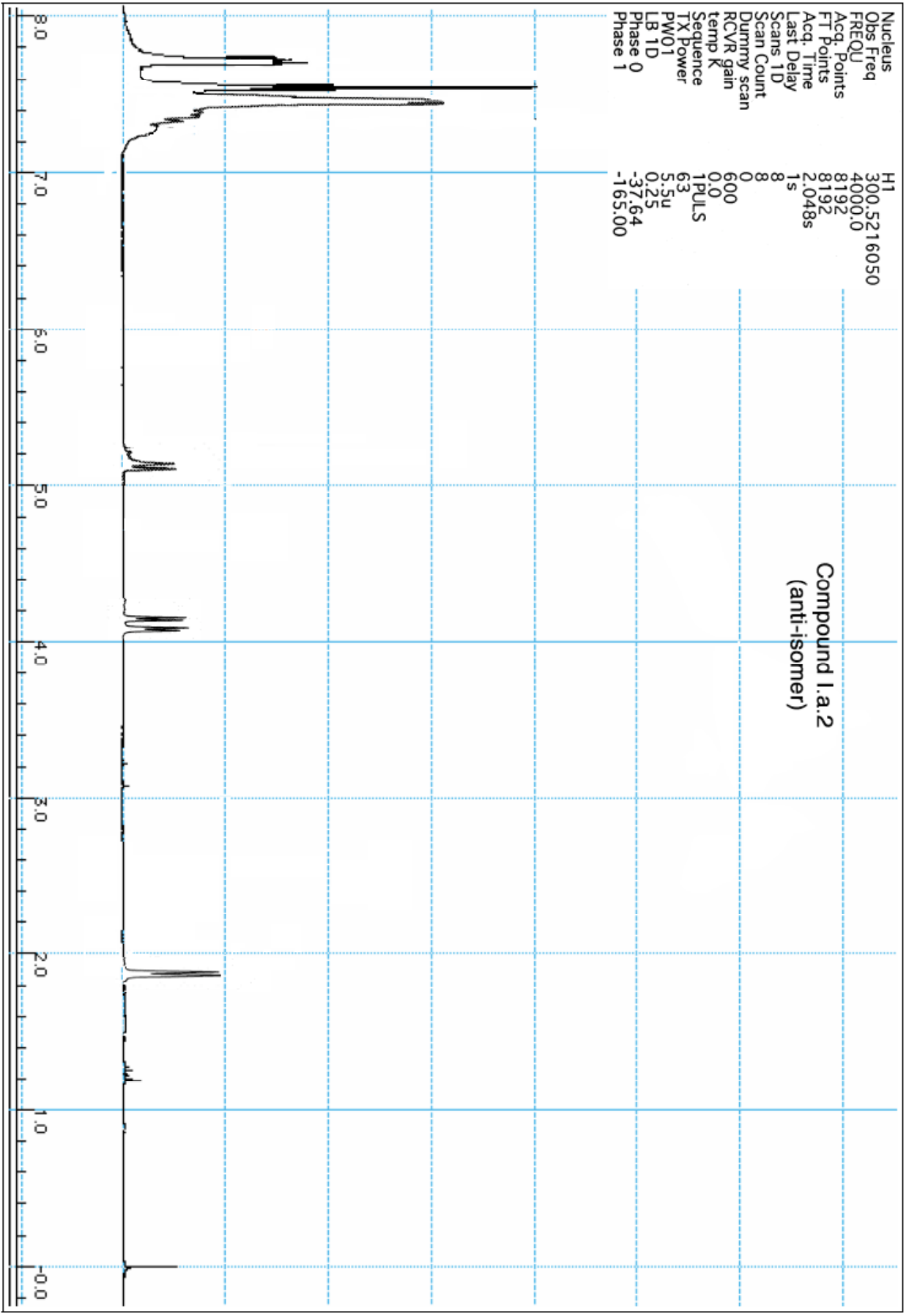


tecmag

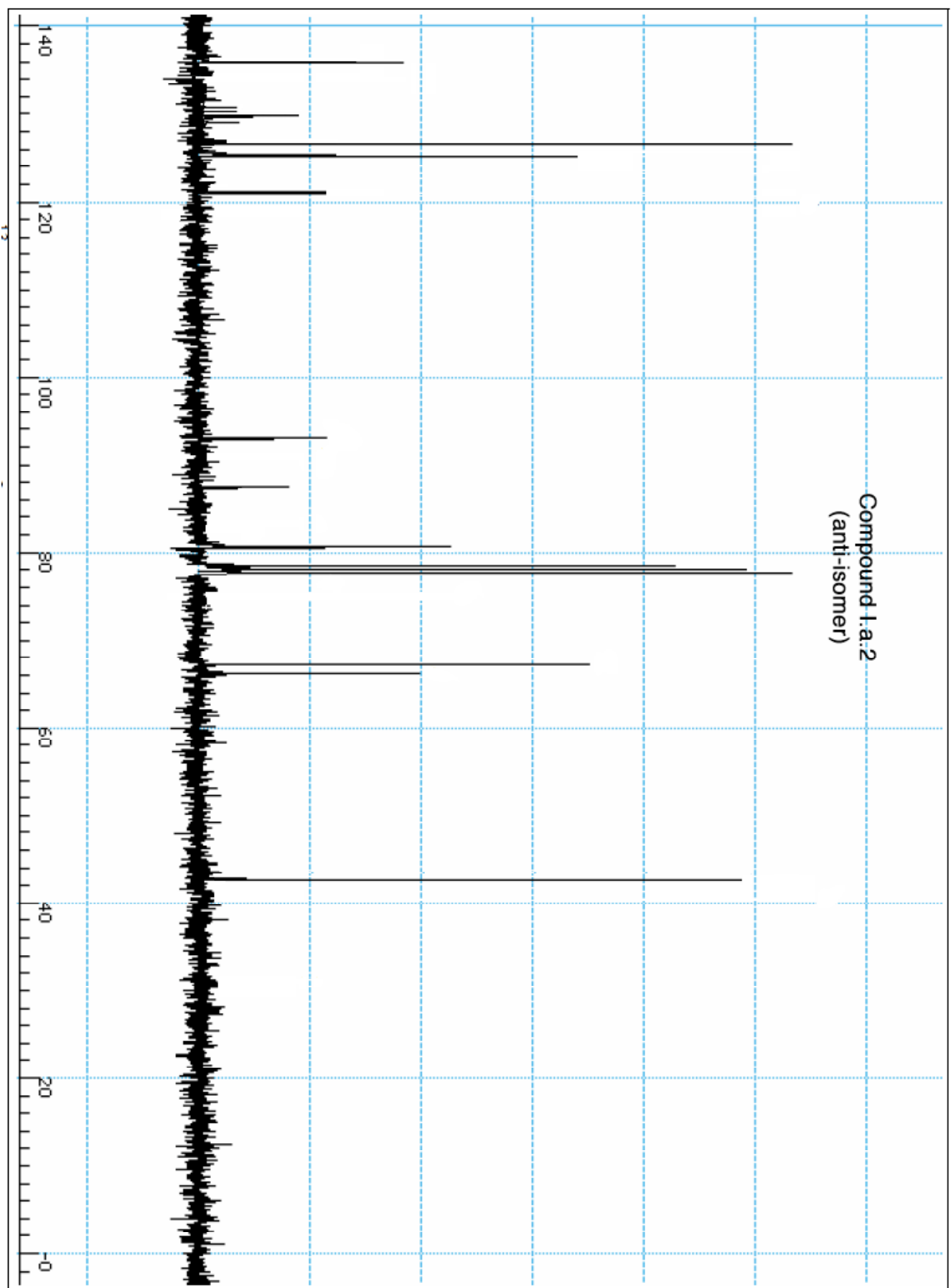


Compound I.a.2
(syn-isomer)



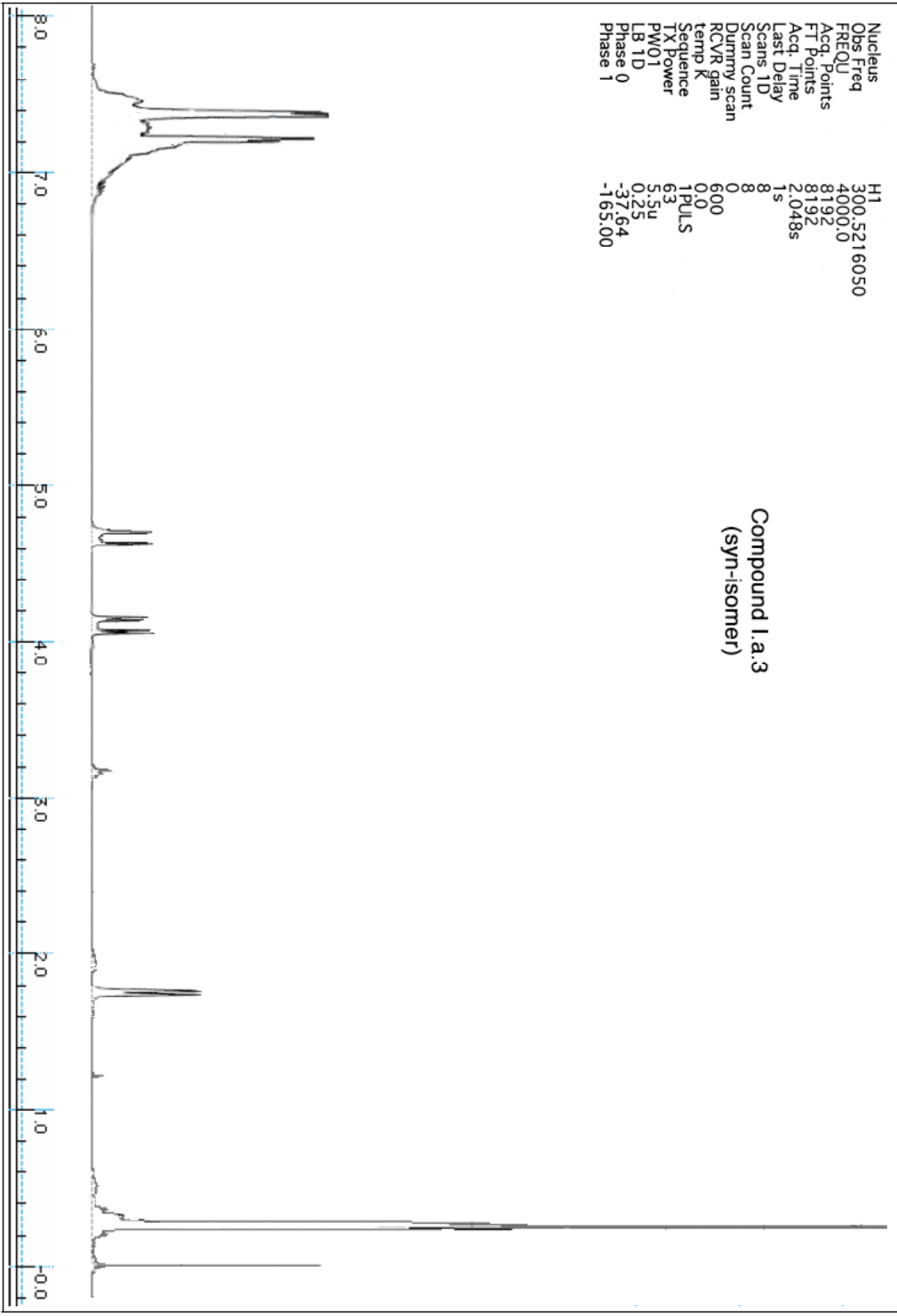


Compound 1.a.2
(anti-isomer)



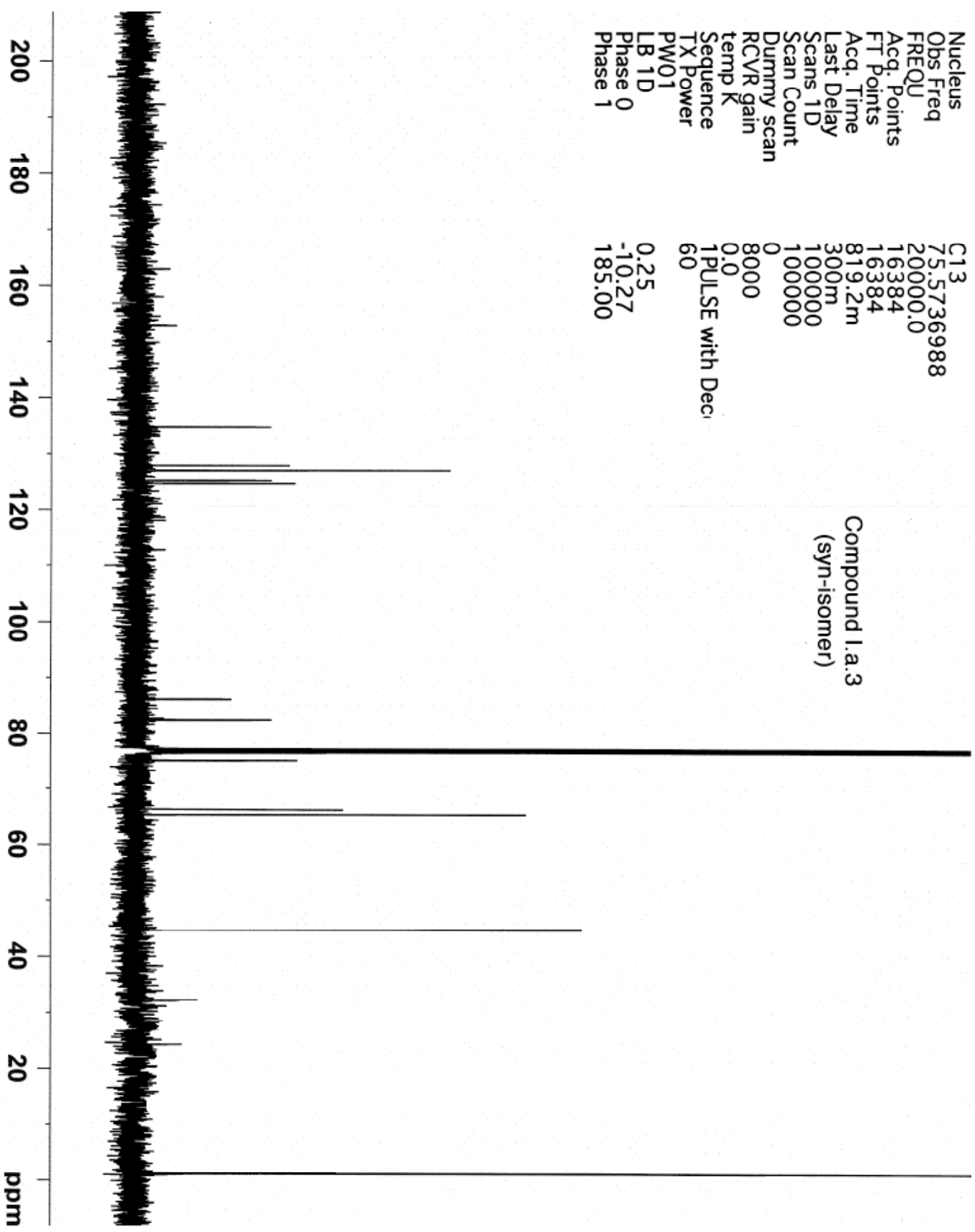
Nucleus H1
Obs Freq 300.5216050
FREQU 4000.0
Acq. Points 8192
FT Points 8192
Acq. Time 2.048s
Last Delay 1s
Scans 1D 8
Scan Count 8
Dummy scan 0
RCVR gain 600
temp K 0.0
Sequence 1PULS
TX Power 63
PW01 5.5u
LB 1D 0.25
Phase 0 -37.64
Phase 1 -165.00

Compound 1.a.3
(syn-isomer)



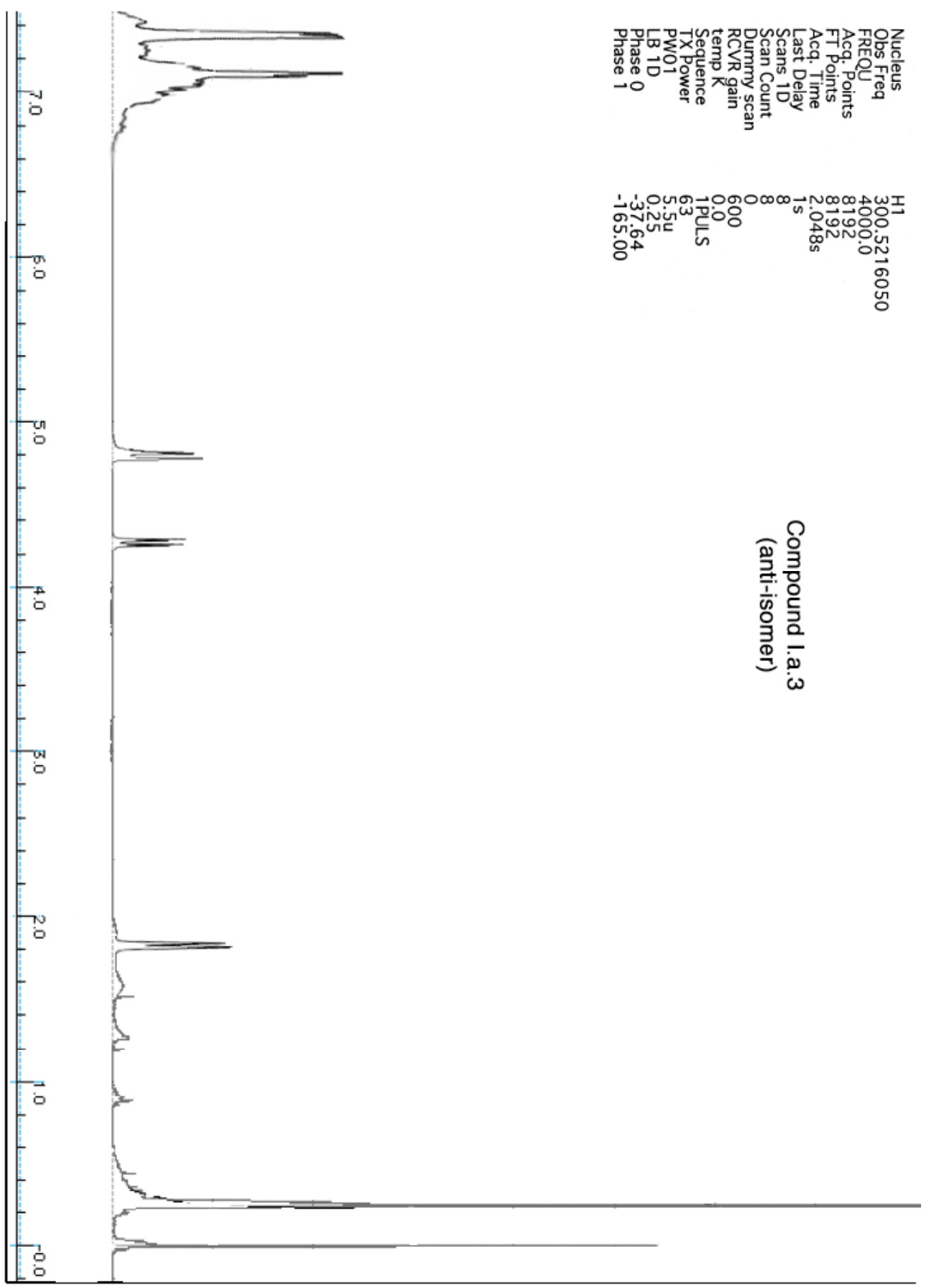
Nucleus C13
Obs Freq 75.5736988
FREQU 20000.0
Acq. Points 16384
FT Points 16384
Acq. Time 819.2m
Last Delay 300m
Scans 1D 100000
Scan Count 100000
Dummy scan 0
RCVR gain 8000
temp K 0.0
Sequence 1PULSE with Dec
TX Power 60
PW01
LB 1D 0.25
Phase 0 -10.27
Phase 1 185.00

Compound 1.a.3
(syn-isomer)



Nucleus H1
Obs Freq 300.5216050
FREQJ 4000.0
Acq. Points 8192
FT Points 8192
Acq. Time 2.048s
Last Delay 1s
Scans 1D 8
Scan Count 8
Dummy scan 0
RCVR gain 600
temp K 0.0
Sequence 1PULS
TX Power 63
PW01 5.5u
LB 1D 0.25
Phase 0 -37.64
Phase 1 -165.00

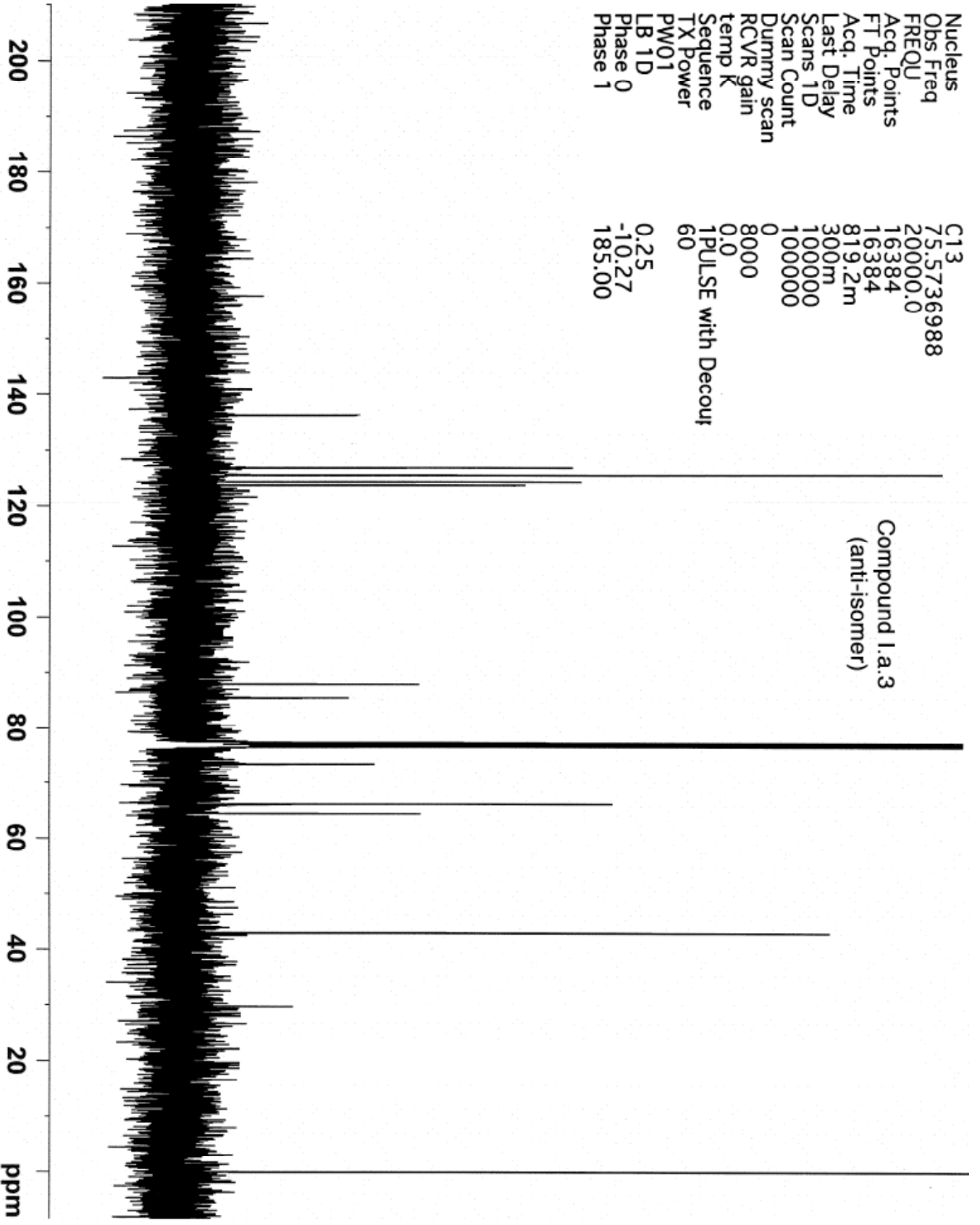
Compound 1.a.3
(anti-isomer)



Nucleus C13
Obs Freq 75.5736988
FREQU 20000.0
Acq. Points 16384
FT Points 16384
Acq. Time 819.2m
Last Delay 300m
Scans 1D 100000
Scan Count 100000
Dummy scan 0
RCVR gain 8000
temp K 0.0
Sequence 1PULSE with Decouf
TX Power 60
PW01
LB 1D
Phase 0
Phase 1

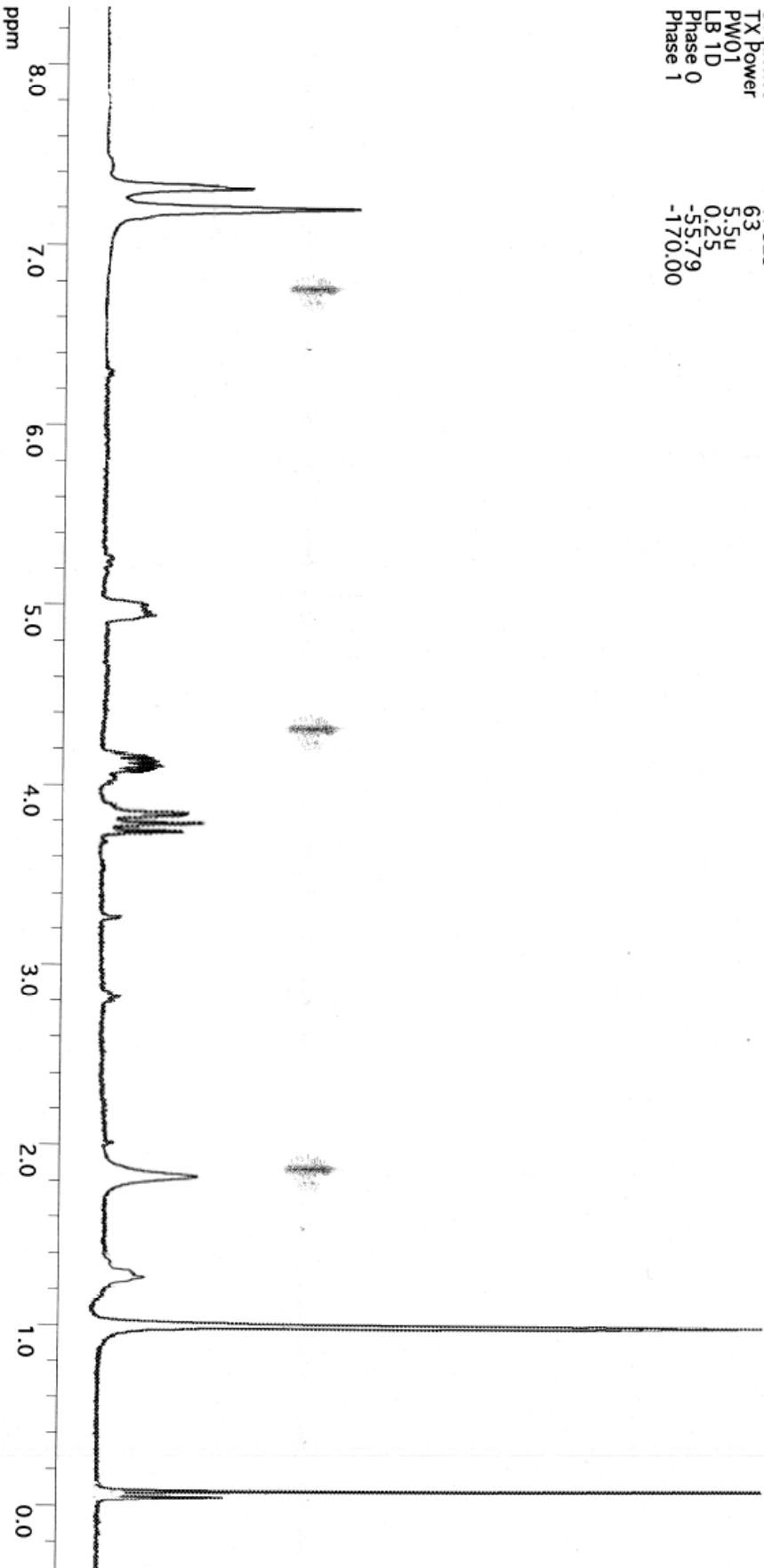
0.25
-10.27
185.00

Compound 1.a.3
(anti-isomer)

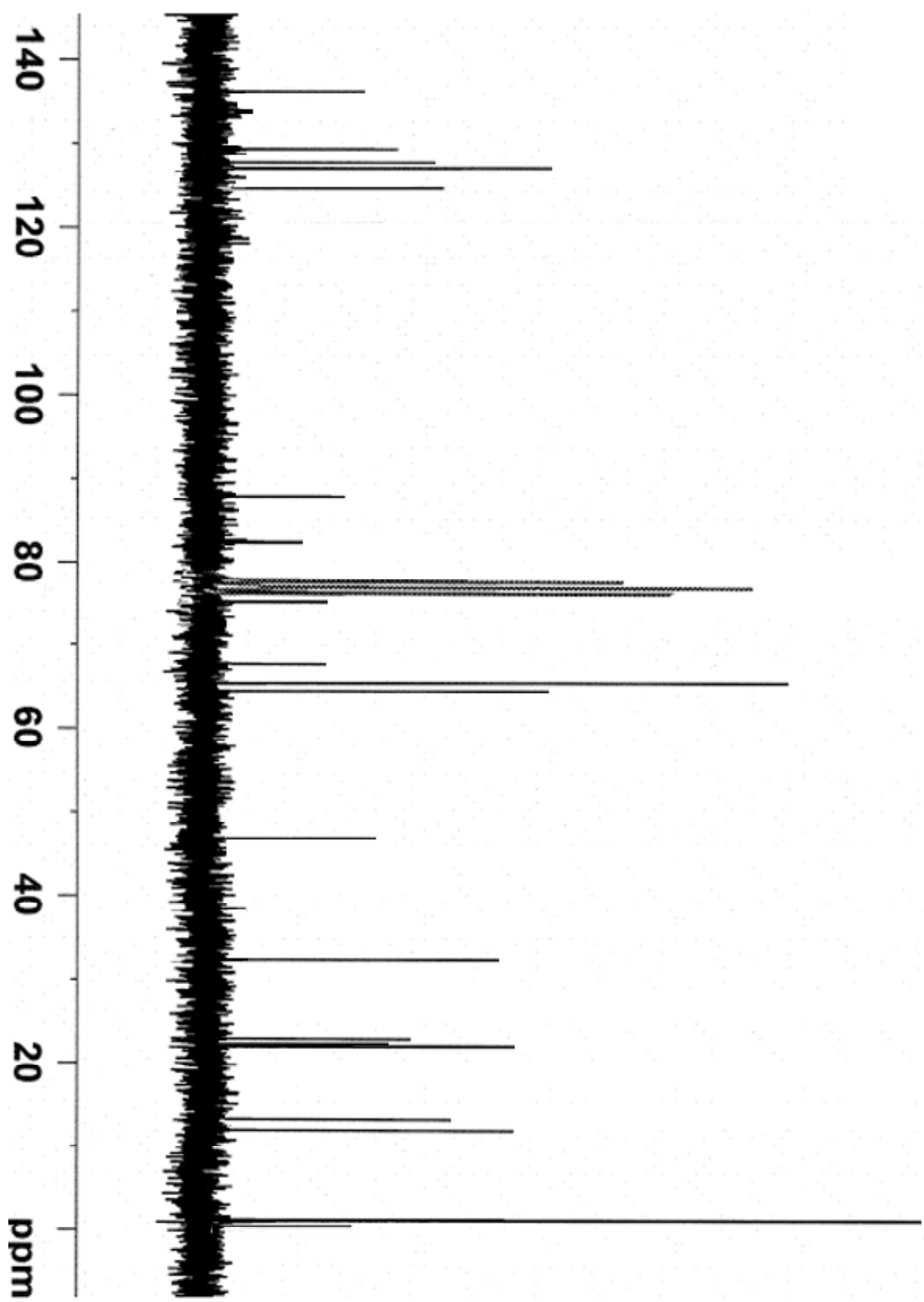


Nucleus	H1
Obs.Freq	300.5216050
FREQU	4000.0
Acq. Points	8192
FT Points	8192
Acq. Time	2.048s
Last Delay	1s
Scans 1D	24
Scan Count	24
Dummy scan	0
RCVR gain	480
temp K	0.0
Sequence	1PULS
TX Power	63
PW01	5.5u
LB 1D	0.25
Phase 0	-55.79
Phase 1	-170.00

Compound I.a.4
(mixture)

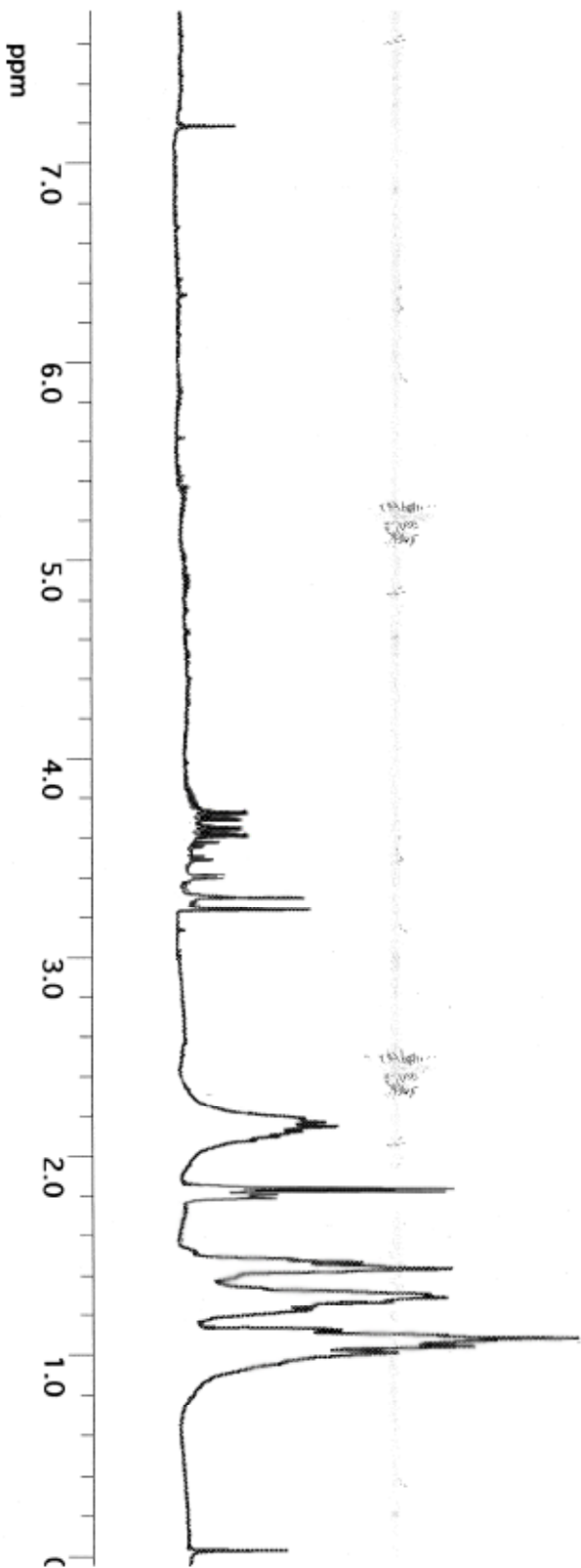


Compound 1.a.4



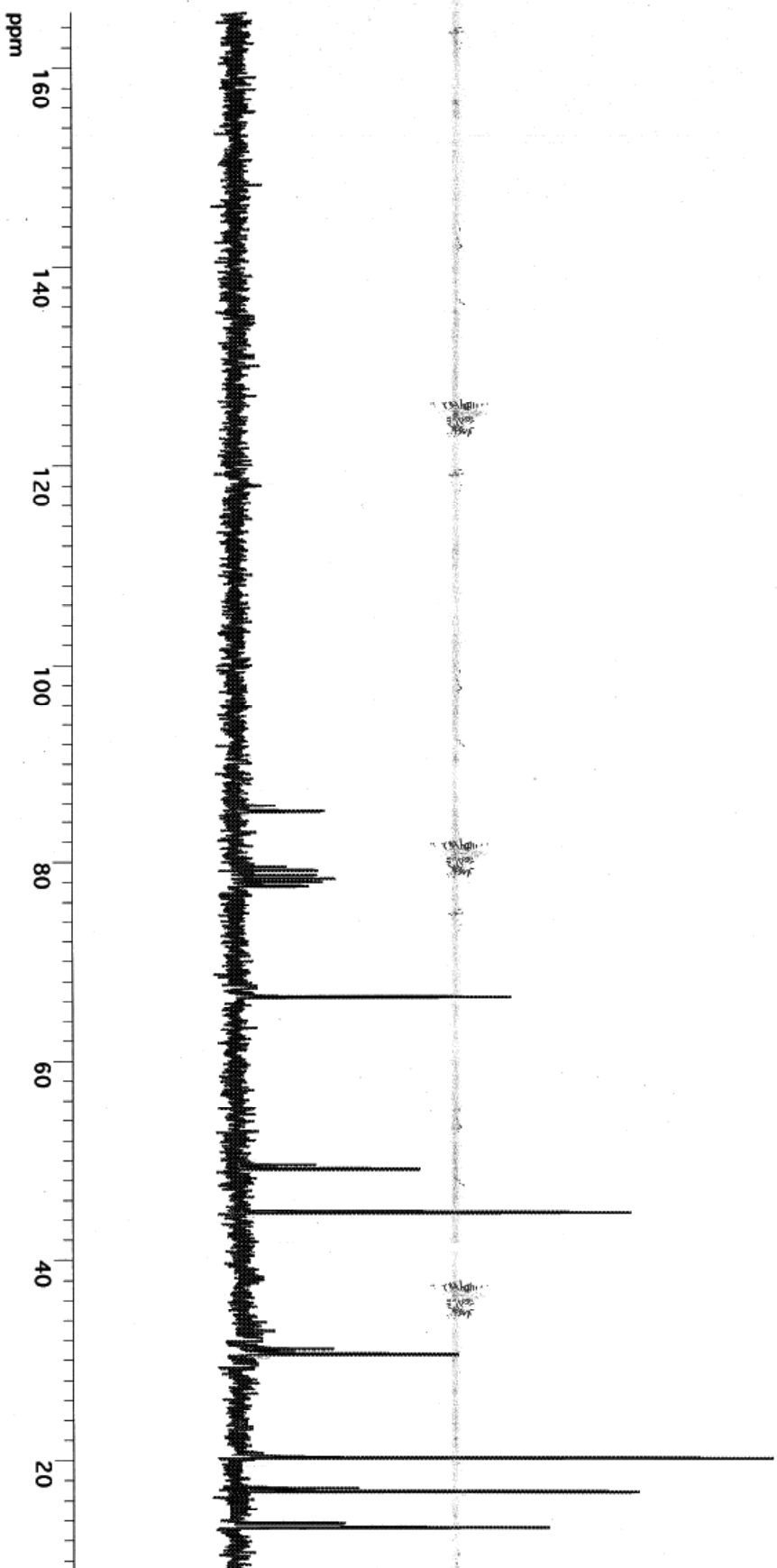
Nucleus H1
Obs Freq 300.5216050
FREQU 4000.0
Acq. Points 8192
FT Points 8192
Acq. Time 2.048s
Last Delay 1s
Scans 1D 16
Scan Count 0
Dummy scan 80
RCVR gain 0.0
TX Power 1PULS
Sequence 63
PW01 5.5u
LB 1D 0.25
Phase 0 -47.49
Phase 1 -149.00

Compound II.a.1



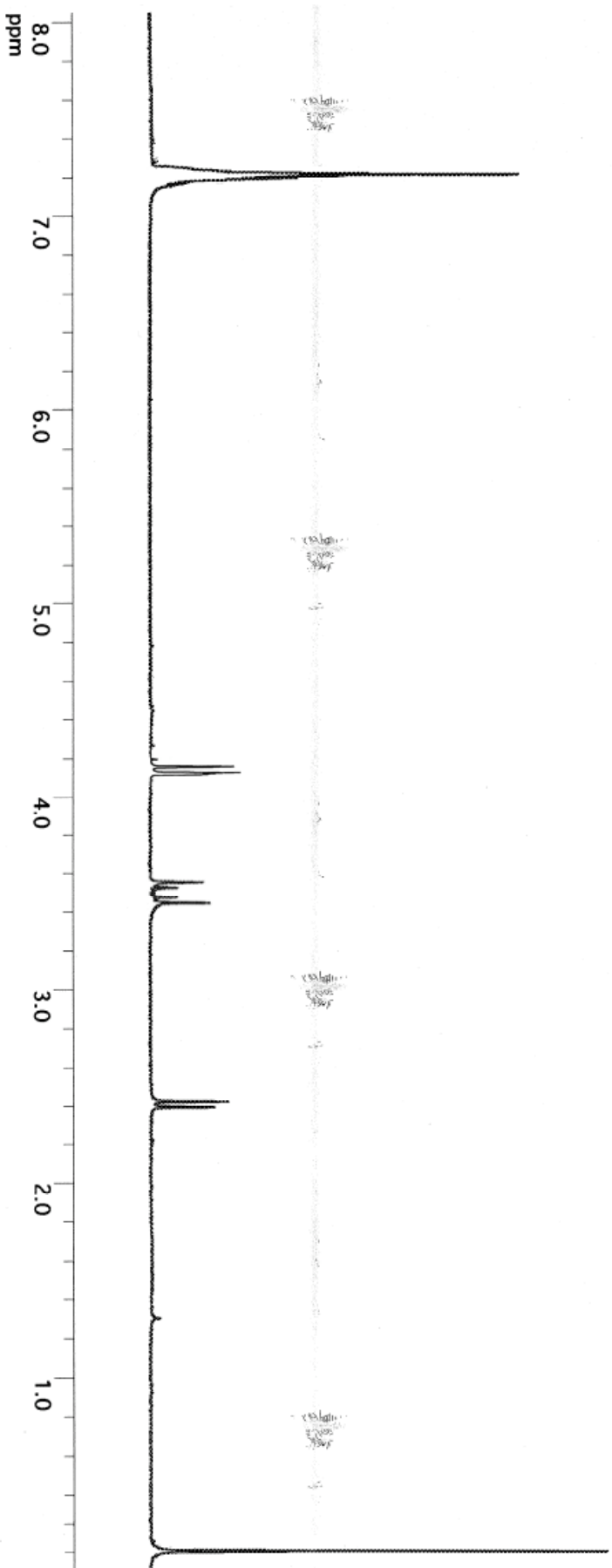
Nucleus C13
Dwell 1D 50u
SW +/- 10000.0
FILTER 10000
Scans 1D 1000
Scan Count 500
Points 1D 8192
Last Delay 200m
Obs Freq 75.5736988
F1 base 75.5736988
F1 offset 0.0000 KHz
RCVR gain 9999
F2 freq 300.5210900
F2 base 300.1036340
F2 offset 417.4560 KHz
DEC Power 70
DEC Scheme WALTZ 16
Dummy scan 0

Compound II.a.1



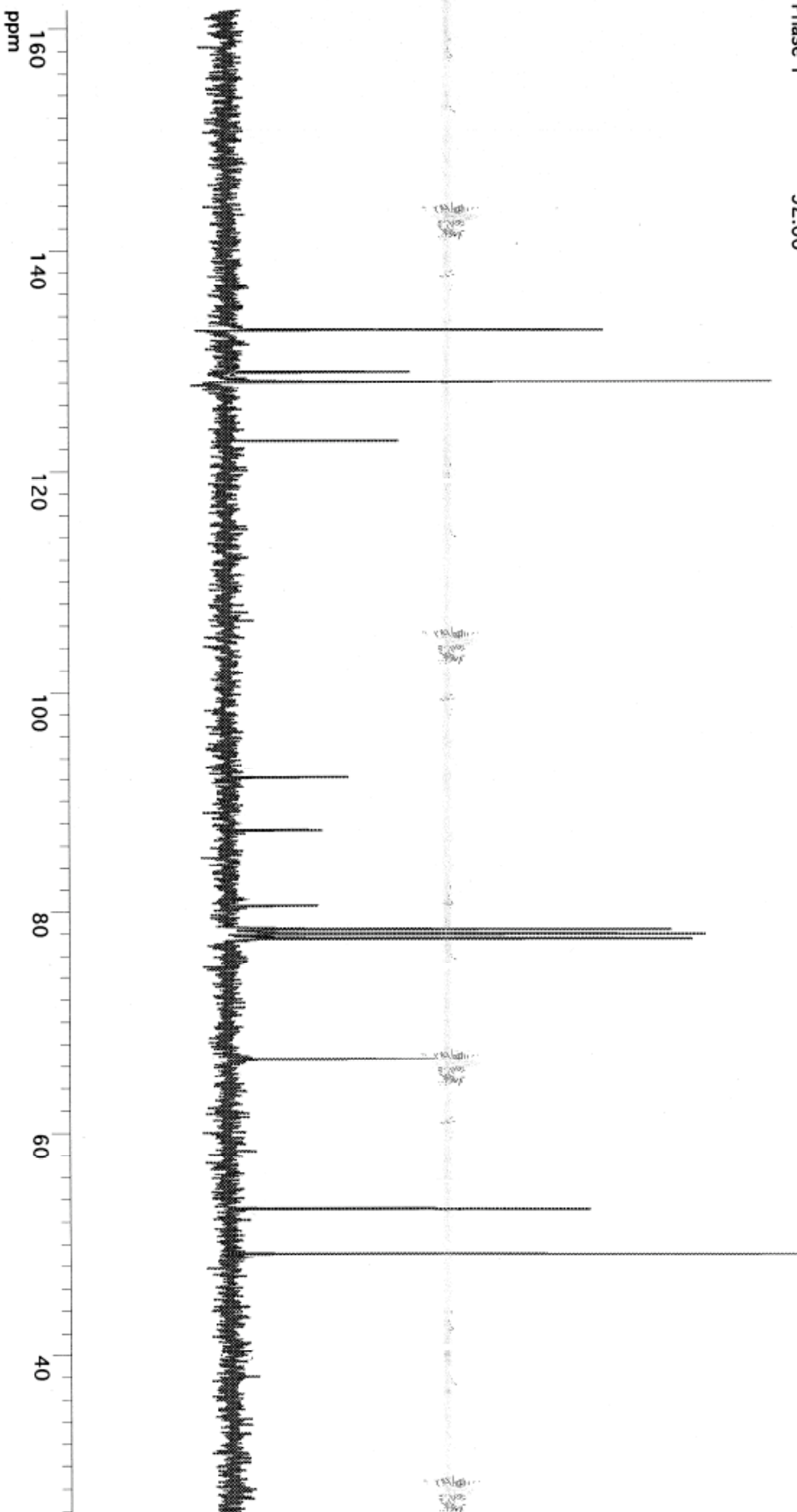
Nucleus H1
Obs Freq 300.5216050
FREQU 4000.0
Acq. Points 8192
FT Points 8192
Acq. Time 2.048s
Last Delay 1s
Scans 1D 8
Scan Count 8
Dummy scan 0
RCVR gain 600
temp K 0.0
Sequence 1PULS
TX Power 63
PW01 5.5u
LB 1D 0.25
Phase 0 -37.64
Phase 1 -165.00

Compound II.a.2
(syn-isomer)



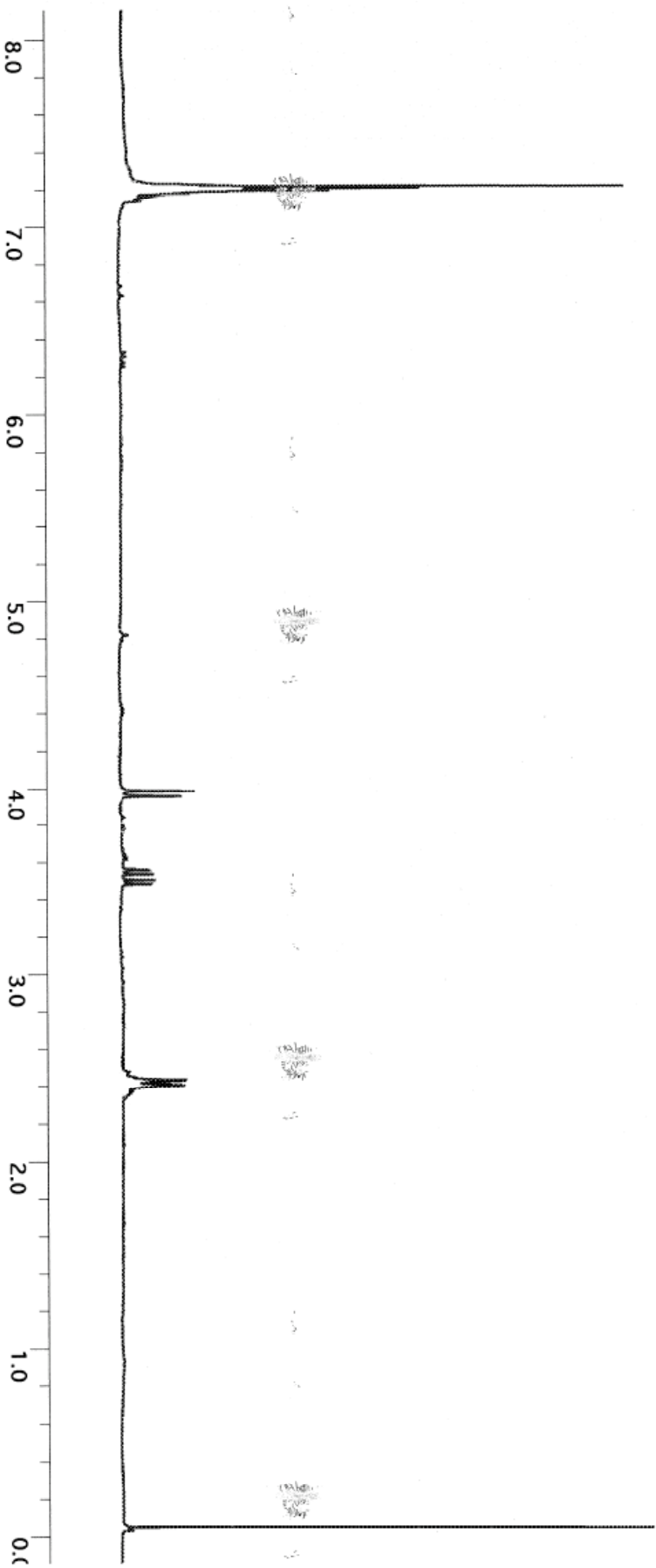
Compound II.a.2
(syn-isomer)

Nucleus	C13
Obs Freq	75.5736988
FREQ	20000.0
Acq. Points	8192
FT Points	8192
Acq. Time	409.6m
Last Delay	200m
Scans 1D	5000
Scan Count	5000
Dumpry scan	0
RCVR gain	8000
temp K	0.0
Sequence	1PULSE with Decoupl
TX Power	60
PW01	0.25
LB 1D	-60.53
Phase 0	92.00
Phase 1	



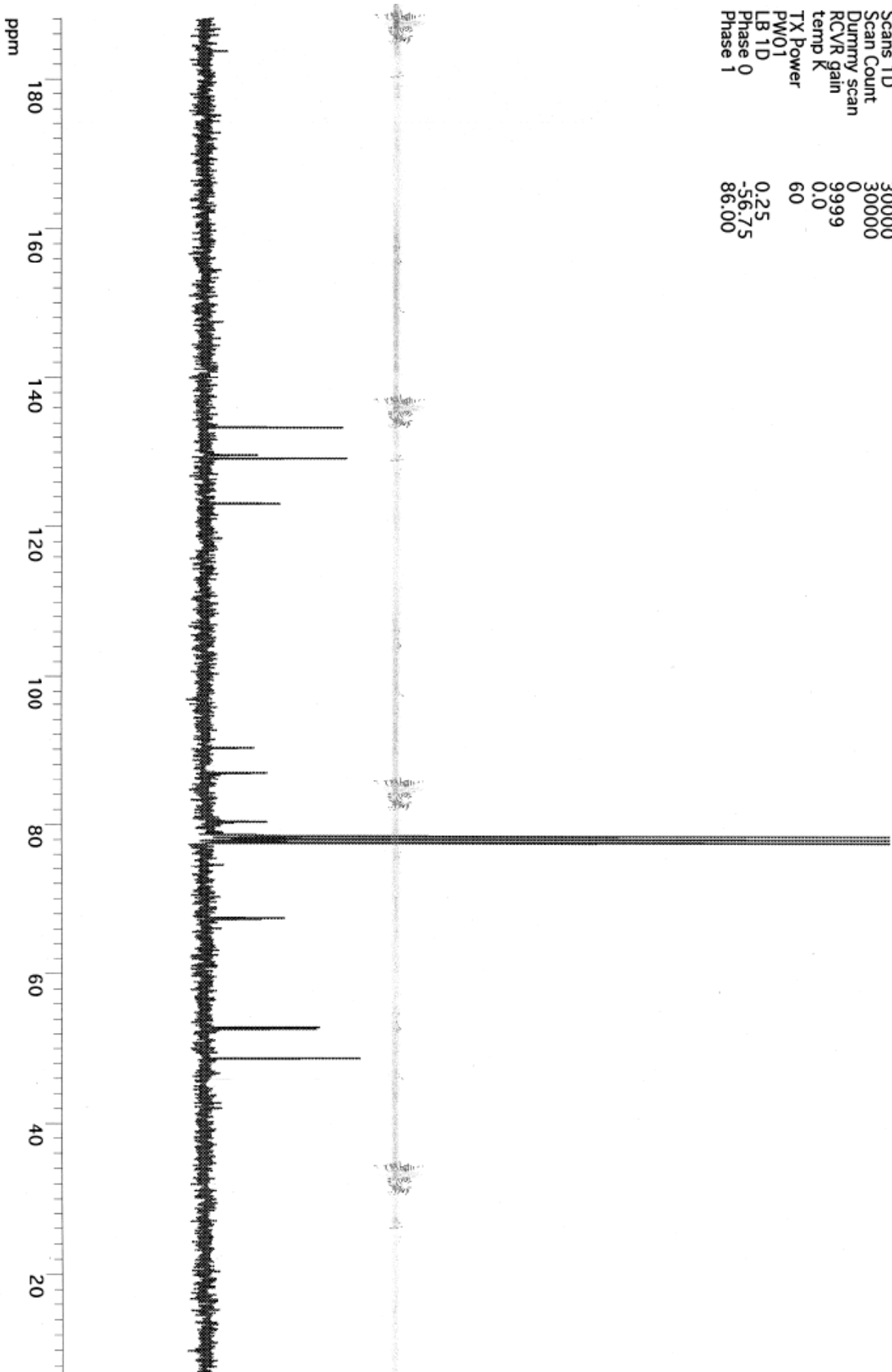
Nucleus H1
Obs Freq 300.5216050
FREQU 4000.0
Acq. Points 8192
FT Points 8192
Acq. Time 2.048s
Last Delay 1s
Scans 1D 16
Scan Count 16
Dummy scan 0
RCVR gain 200
temp K 0.0
TX Power 63
PW01 5.5u
LB 1D 0.25
Phase 0 -59.83
Phase 1 -163.00

Compound II.a.2
(anti-isomer)



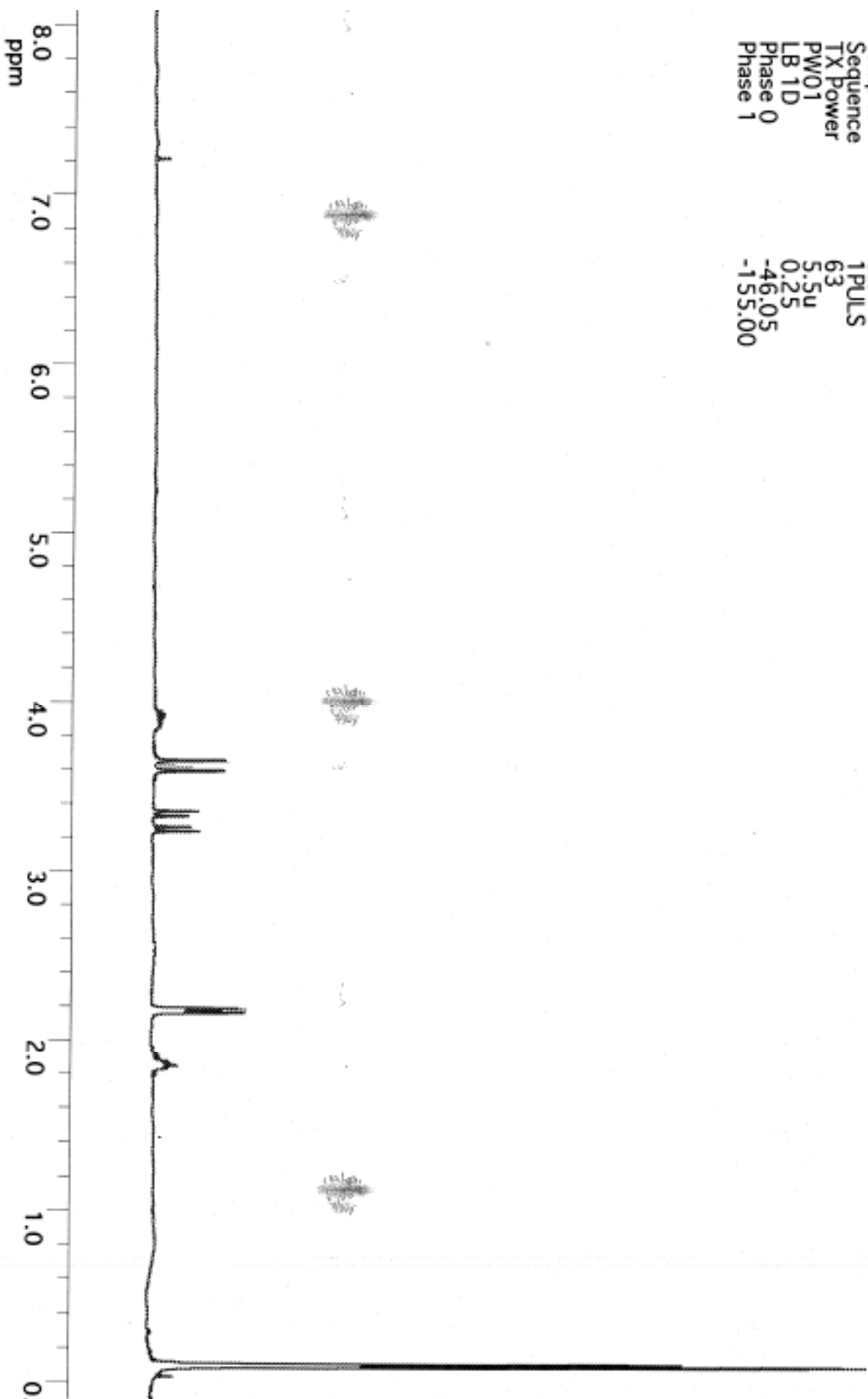
Nucleus	C13
Obs Freq	75.5736988
FREQ	20000.0
Acq. Points	8192
FT Points	8192
Acq. Time	409.6m
Last Delay	200m
Scans 1D	30000
Scan Count	30000
Dummy scan	0
RCVR gain	9999
temp K	0.0
TX Power	60
PW01	0.25
LB 1D	-56.75
Phase 0	86.00
Phase 1	

Compound II.a.2
(anti-isomer)



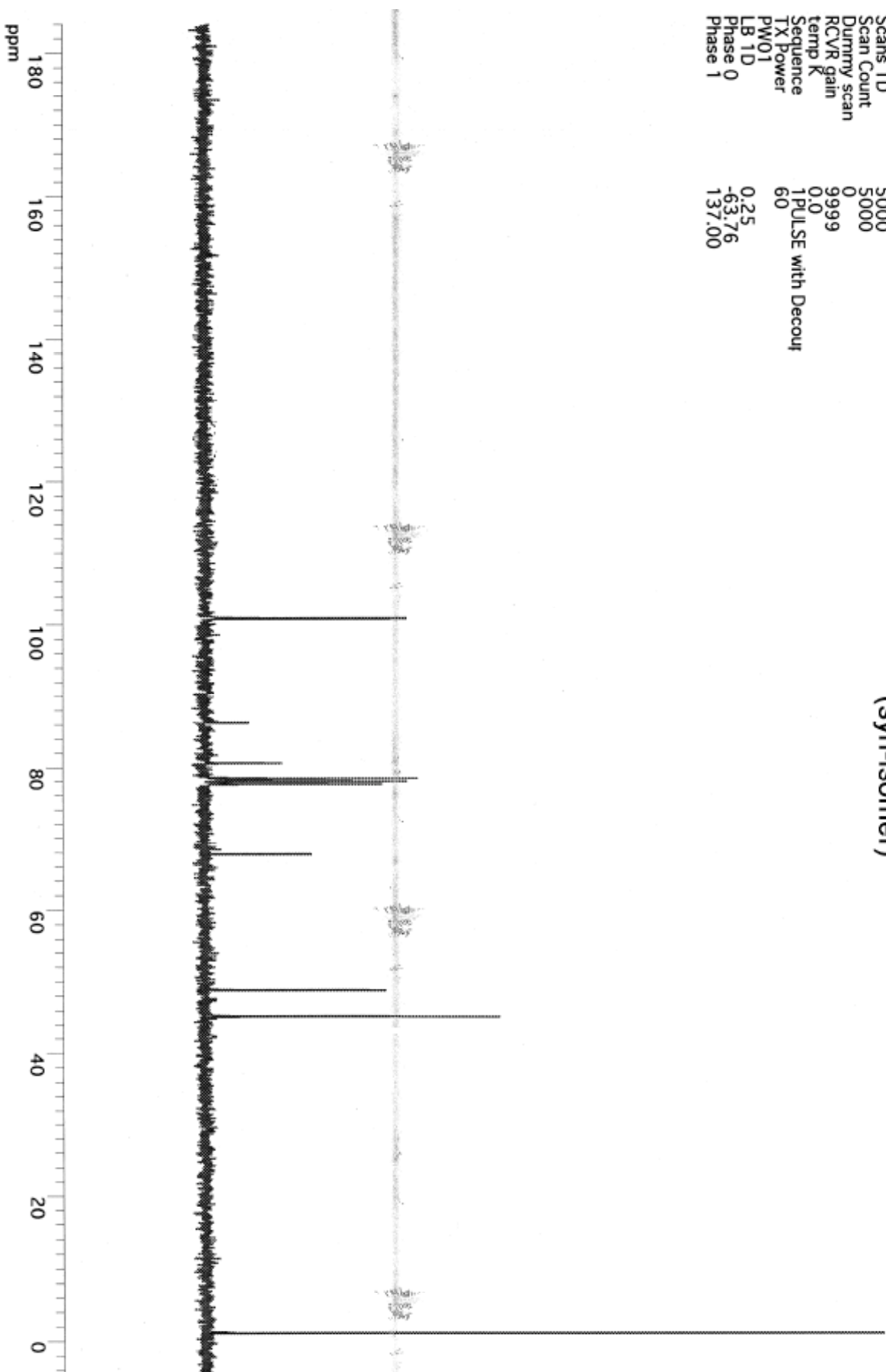
Nucleus H1
Obs Freq 300.5216050
FREQ 4000.0
Acq. Points 8192
FT Points 8192
Acq. Time 2.048s
Last Delay 1s
Scans 1D 8
Scan Count 8
Dummy scan 0
RCVR gain 10
temp K 0.0
Sequence 1PULS
TX Power 63
PW01 5.5u
LB 1D 0.25
Phase 0 -46.05
Phase 1 -155.00

Compound II.a.3
(syn-isomer)



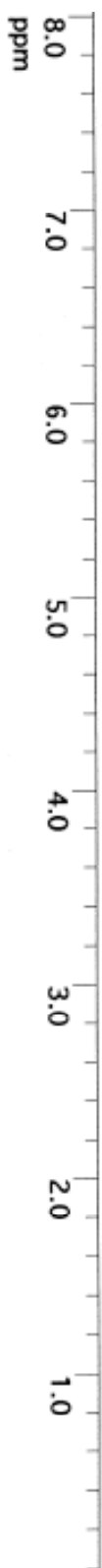
Nucleus	C13
Obs Freq	75.5736988
FREQU	20000.0
Acq. Points	8192
FT Points	8192
Acq. Time	409.6m
Last Delay	200m
Scans 1D	5000
Scan Count	5000
Dummy scan	0
RCVR gain	9999
temp K	0.0
Sequence	1PULSE with Decouf
TX Power	60
PW01	
LB 1D	0.25
Phase 0	-63.76
Phase 1	137.00

Compound II.a.3
(syn-isomer)



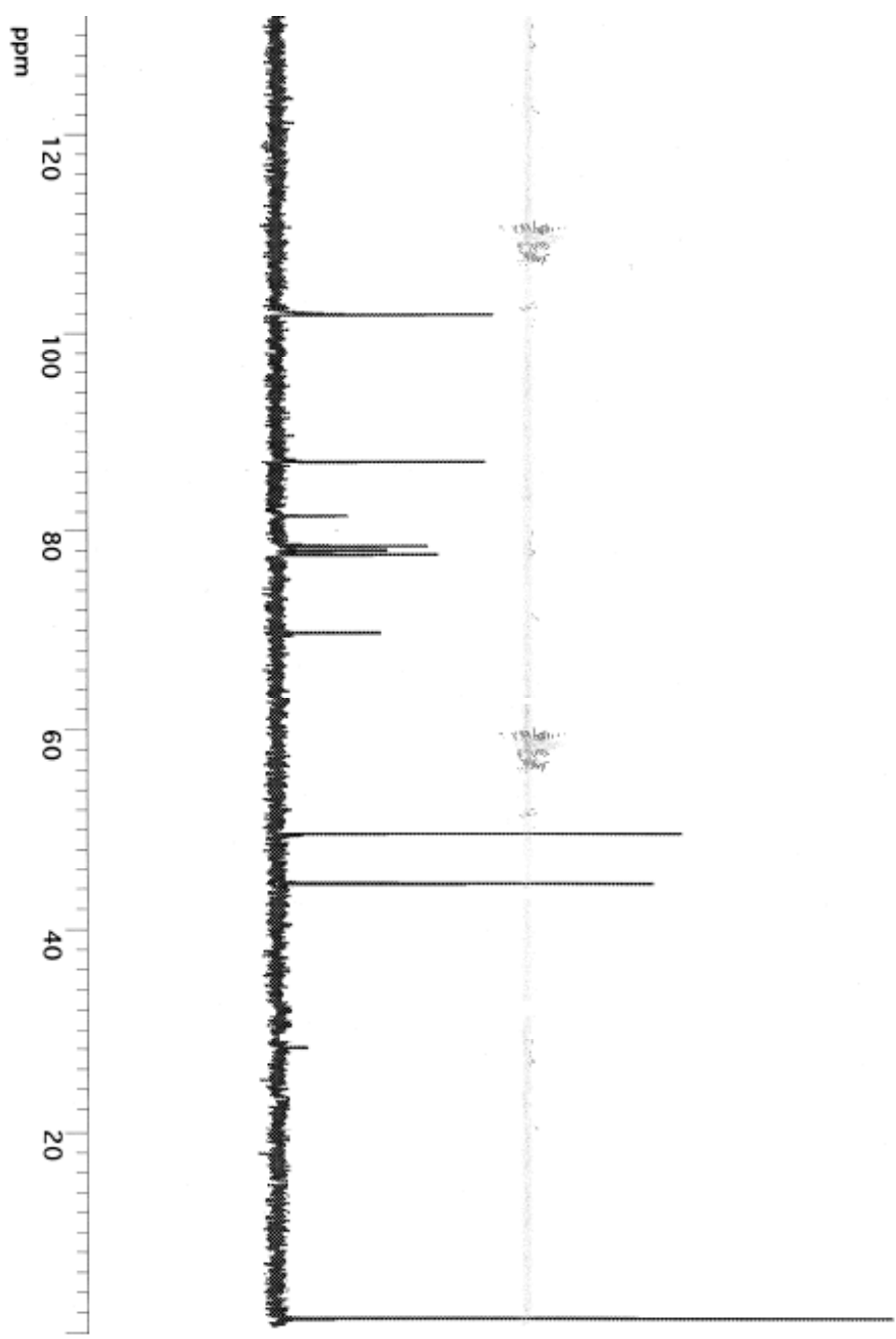
Nucleus H1
Obs Freq 300.5216050
FREQU 4000.0
Acq. Points 8192
FT Points 8192
Acq. Time 2.048s
Last Delay 1s
Scans 1D 8
Scan Count 8
Dummy scan 0
RCVR gain 0
temp K 90
Sequence 0.0
TX Power 1PULS
LB 1D 63
Phase 0 -57.53
Phase 1 -169.00

Compound II.a.3
(anti-isomer)



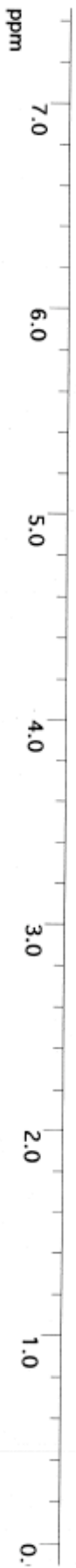
Nucleus	C13
Obs Freq	75.5736988
FREQU	16000.0
Acq. Points	8192
FT Points	8192
Acq. Time	512m
Last Delay	200m
Scans 1D	5000
Scan Count	2000
Dummy scan	0
RCVR gain	9900
temp K	0.0
Sequence	1PULSE with f
TX Power	60
PWM01	
LB 1D	0.25
Phase 0	-54.52
Phase 1	54.00

**Compound II.a.3
(anti-isomer)**



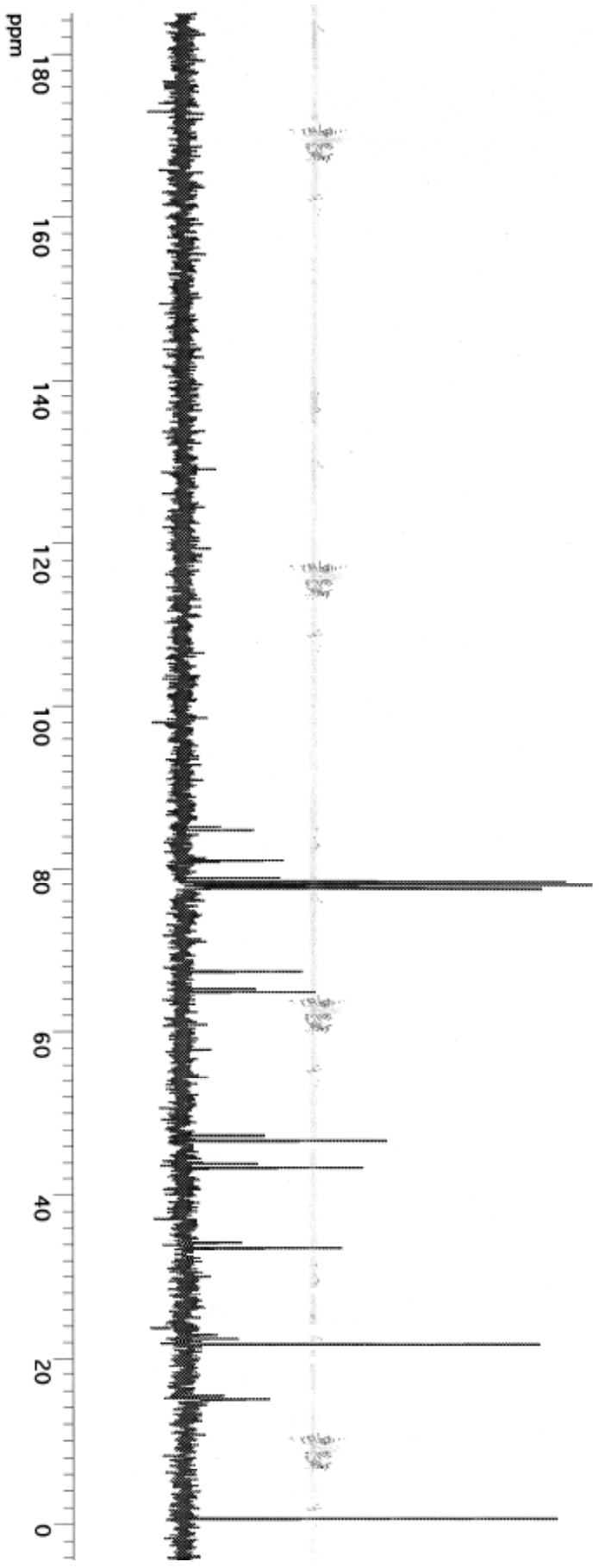
Nucleus H1
Obs Freq 300.5216050
FREQU 40000.0
Acq. Points 8192
FT Points 8192
Acq. Time 2.048s
Last Delay 1s
Scans 1D 8
Scan Count 0
Dummy scan 0
RCVR gain 30
temp K 0.0
Sequence 1PULS
TX Power 63
PW01 5.5u
LB 1D 0.25
Phase 0 -58.34
Phase 1 -136.00

Compound II.a.4



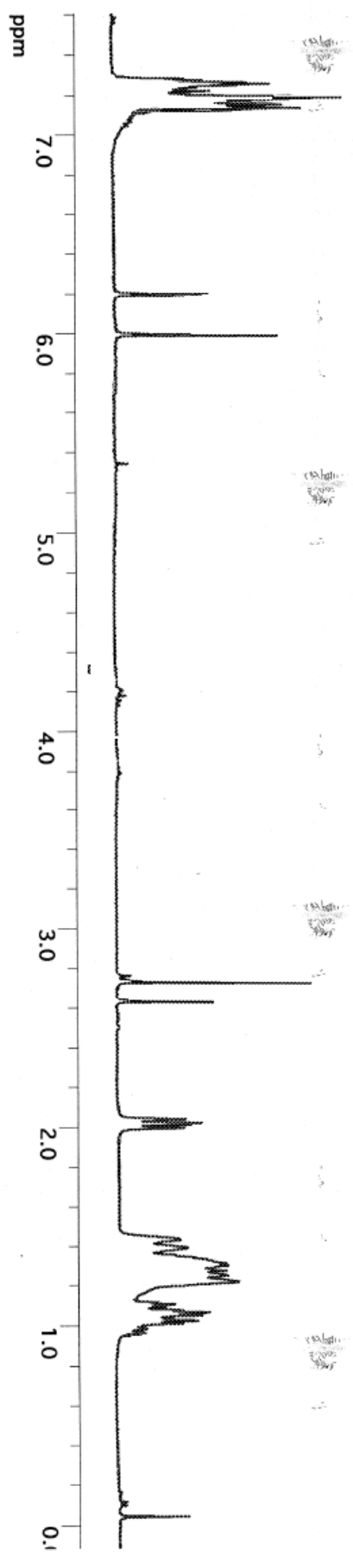
Nucleus C13
Obs Freq 75.5736988
FREQ 20000.0
Acq. Points 8192
FT Points 8192
Acq. Time 409.6m
Last Delay 200m
Scans 1D 20000
Scan Count 16668
Dummy scan 0
RCVR gain 7400
temp K 0.0
Sequence 1PULSE with Decoupl
TX Power 60
PW01 0.25
LB 1D -53.21
Phase 0 0.00
Phase 1

Compound II.a.4



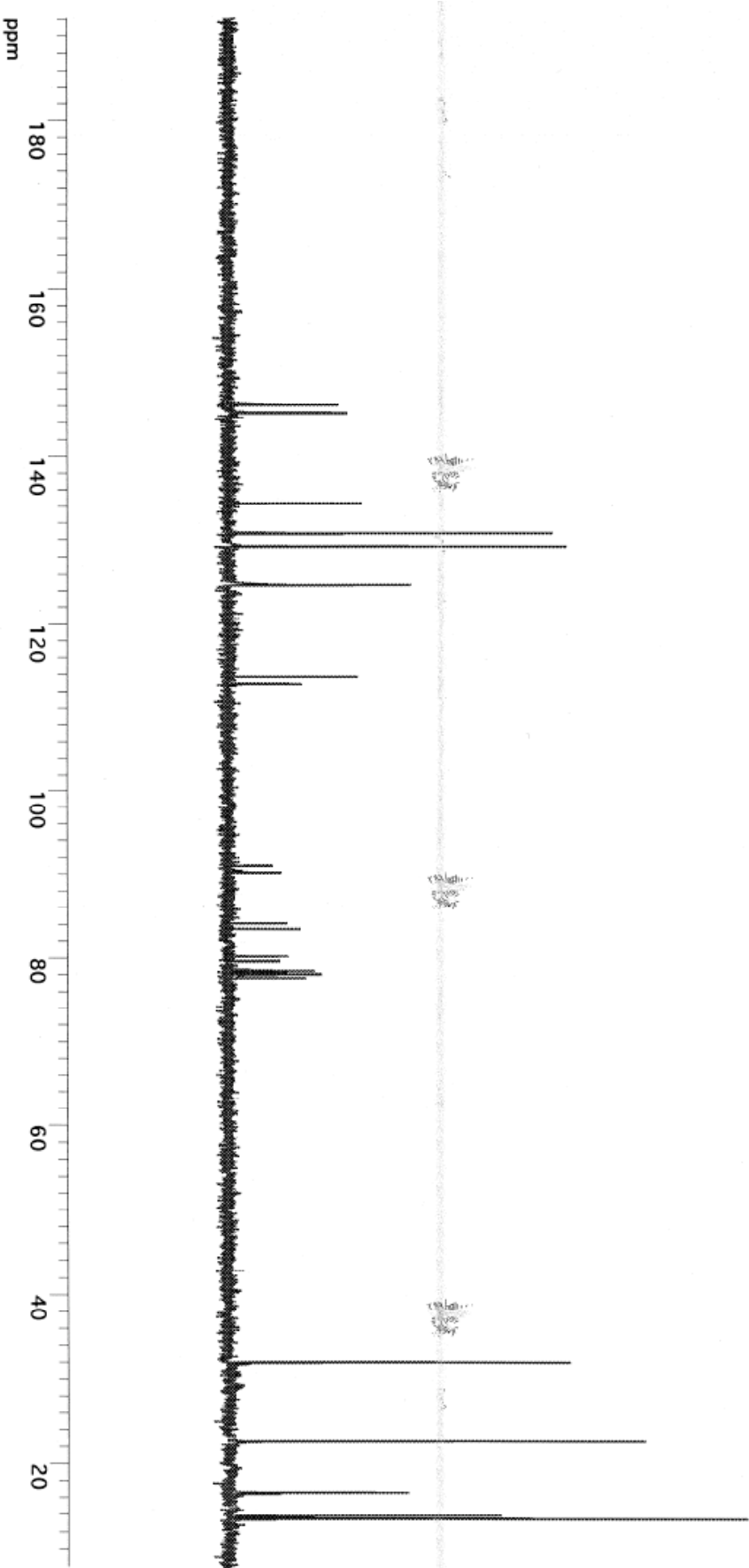
Nucleus H1
Obs Freq 300.5216050
FREQ 4000.0
Acq: Points 8192
FT Points 8192
Acq: Time 2.048s
Last Delay 1s
Scans 1D 8
Scan Count 8
Dummy scan 0
RCVR gain 150
temp K 0.0
Sequence 1PULS
TX Power 63
LB 1D 5.5u
Phase 0 0.25
Phase 1 -56.49
-151.00

Compound III.a.1



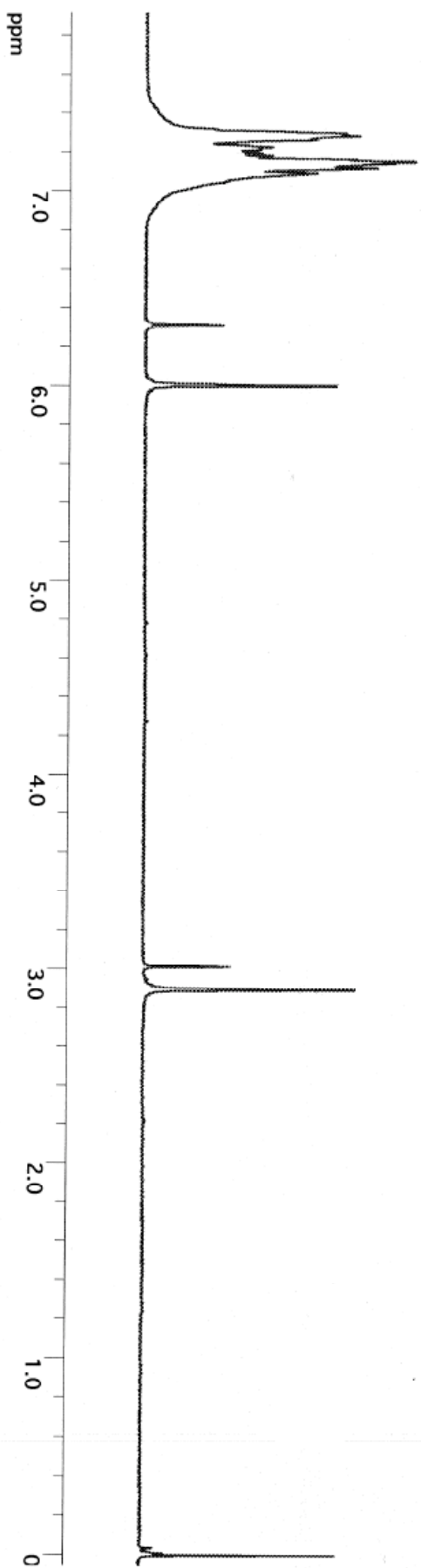
Nucleus C13
Obs Freq 75.5736988
FREQU 16000.0
Acq. Points 8192
FT Points 8192
Acq. Time 51.2m
Last Delay 200m
Scans 1D 5000
Scan Count 2000
Dummy scan 0
RCVR gain 9900
temp K 0.0
Sequence 1 PULSE with Decoupl
TX Power 60
PW01 0.25
LB 1D -54.52
Phase 0 54.00
Phase 1

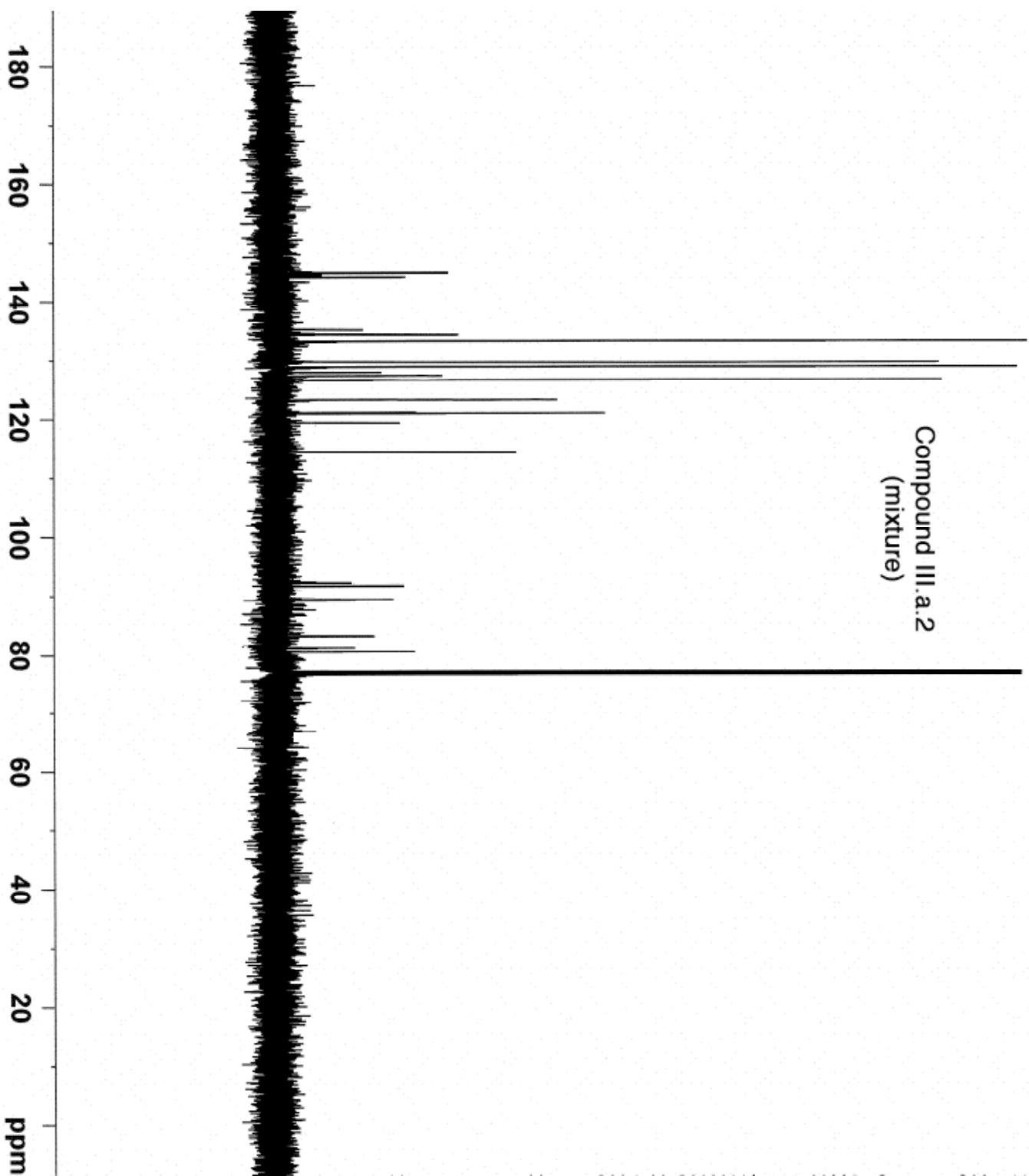
Compound III.a.1
(mixture)



Nucleus H1
 Obs Freq 300.5216050
 FREQU 4000.0
 Acq. Points 8192
 FT Points 8192
 Acq. Time 2.048s
 Last Delay 1s
 Scans 1D 8
 Scan Count 0
 Dummy scan 0
 RCVR gain 600
 temp K 0.0
 Sequence 1PULS
 TX Power 63
 PW01 5.5u
 LB 1D 0.25
 Phase 0 -37.64
 Phase 1 -165.00

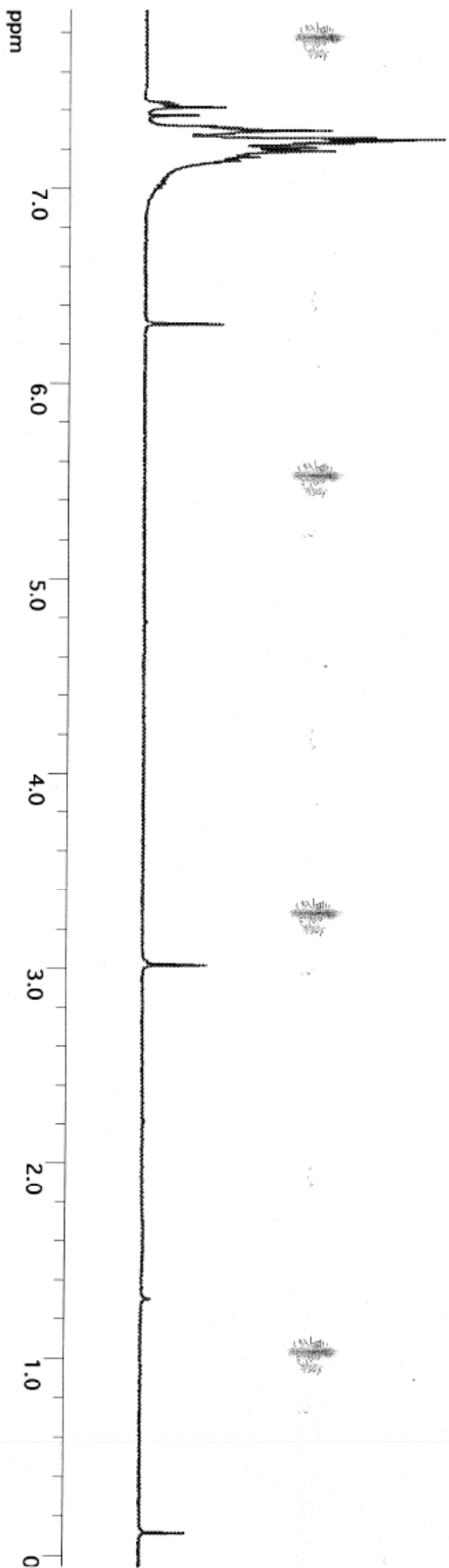
Compound III. a.2
 (mixture)



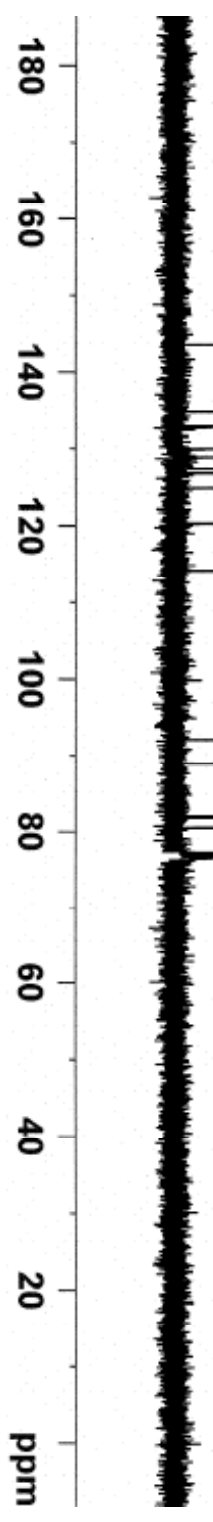


Nucleus	H1
Obs Freq	300.5216050
FREQU	4000.0
Acq. Points	8192
FT Points	8192
Acq. Time	2.048s
Last Delay	1s
Scans 1D	8
Scan Count	0
Dummy scan	0
RCVR gain	600
temp K	0.0
Sequence	1PULS
TX Power	63
PW01	5.5u
LB 1D	0.25
Phase 0	-37.64
Phase 1	-165.00

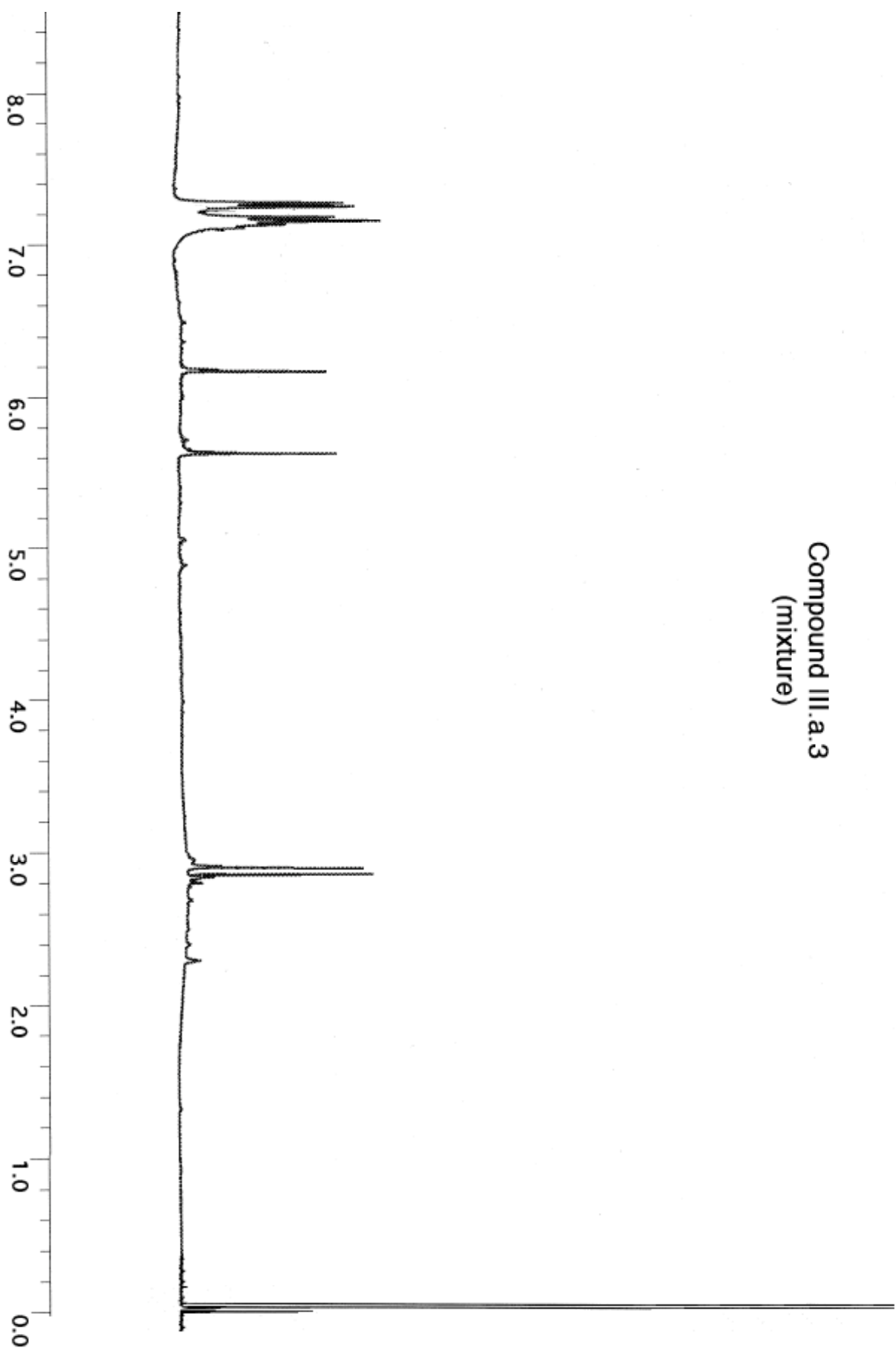
Compound III.a.2
(anti-isomer)



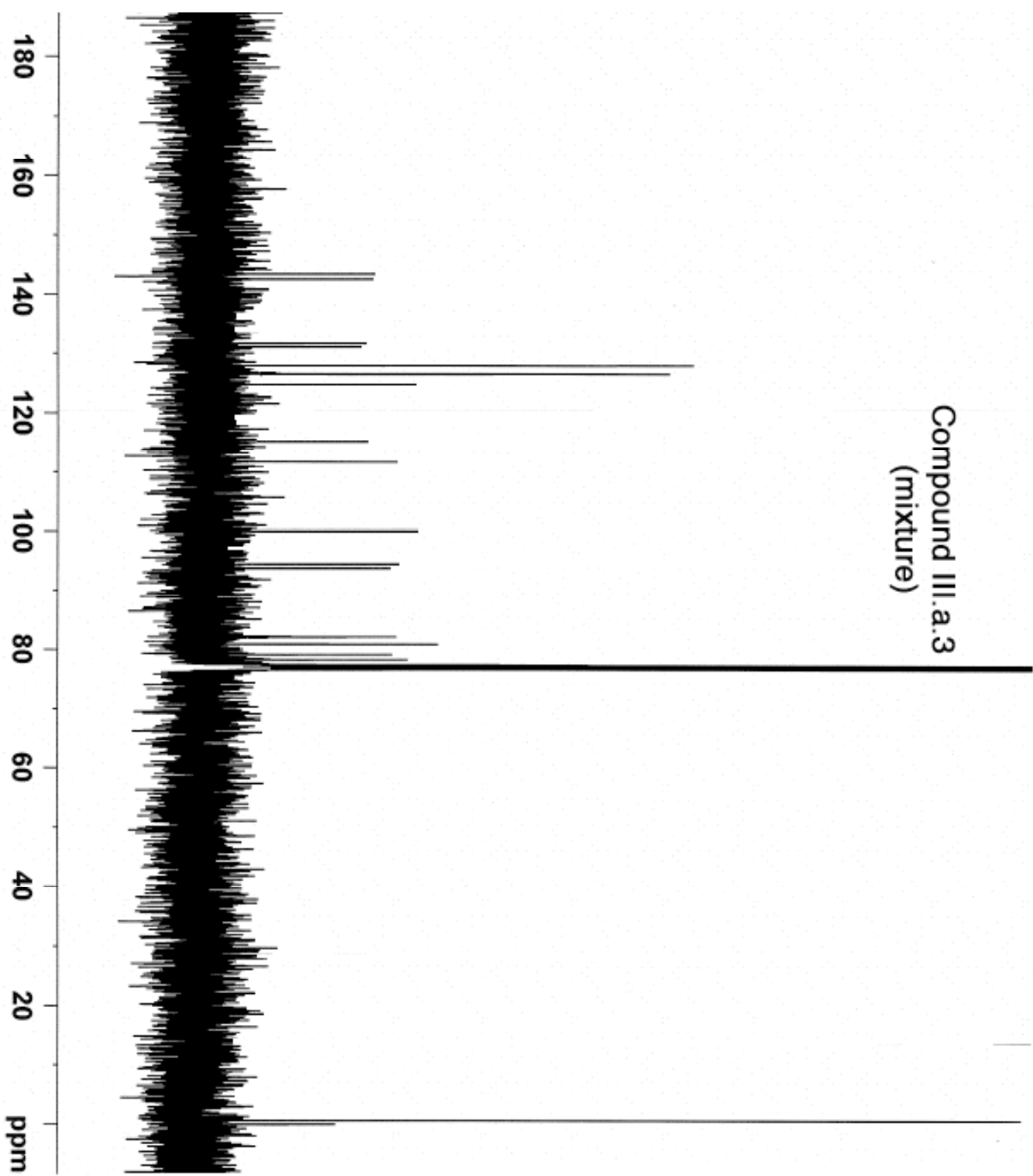
Compound III.a.2
(anti-isomer)



Compound III.a.3
(mixture)

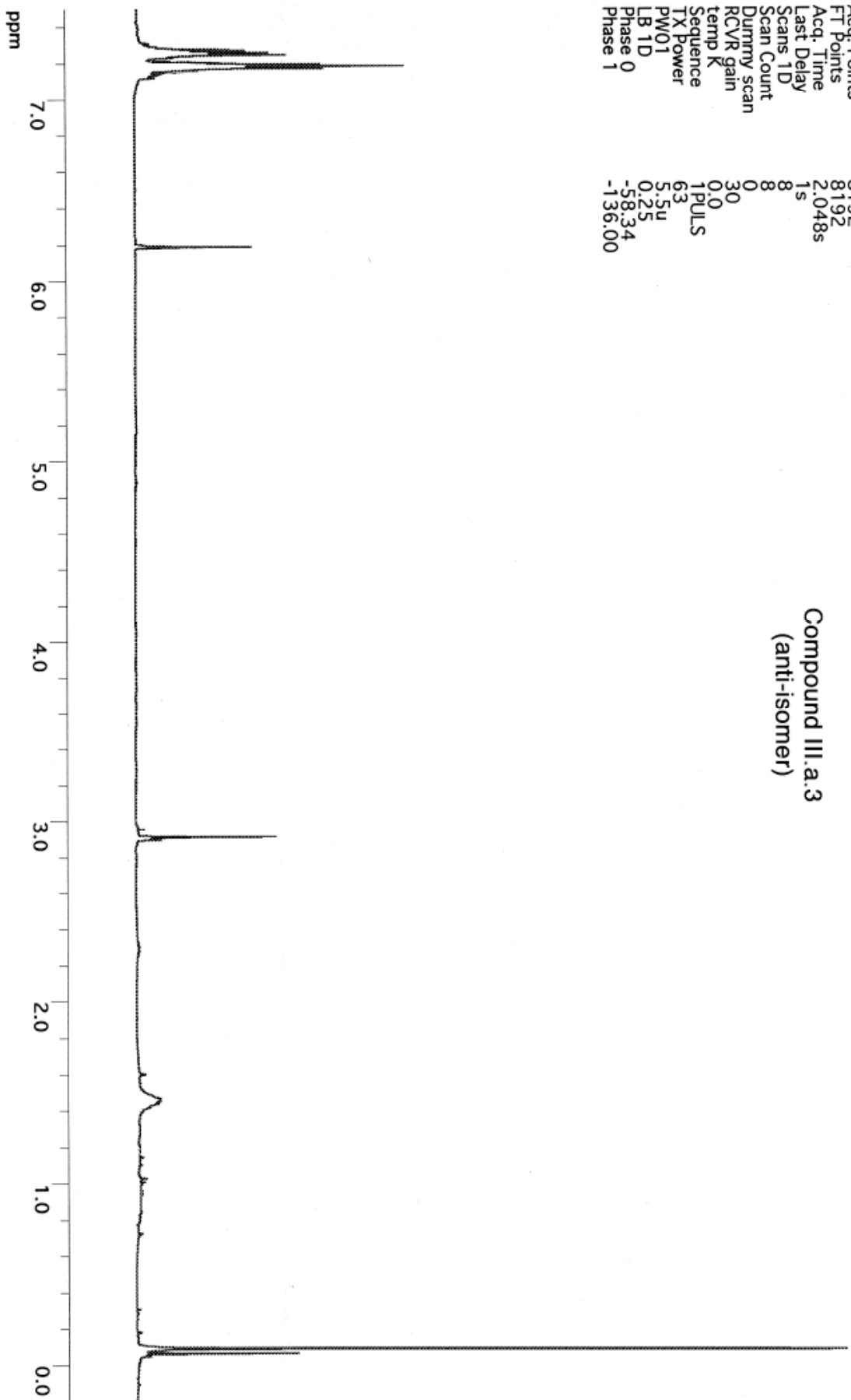


Compound III.a.3
(mixture)

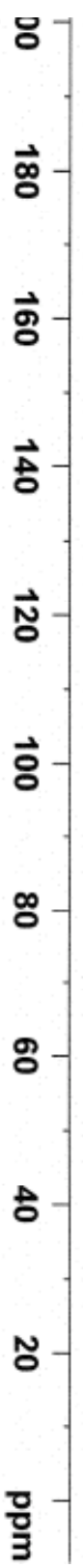


Nucleus	H1
Obs Freq	300.5216050
FREQU	4000.0
Acq. Points	8192
FT Points	8192
Acq. Time	2.048s
Last Delay	1s
Scans 1D	8
Scan Count	0
Dummy scan	30
RCVR gain	0.0
temp K	0.0
Sequence	1PULS
TX Power	63
PW01	5.5u
LB 1D	0.25
Phase 0	-58.34
Phase 1	-136.00

Compound III.a.3
(anti-isomer)

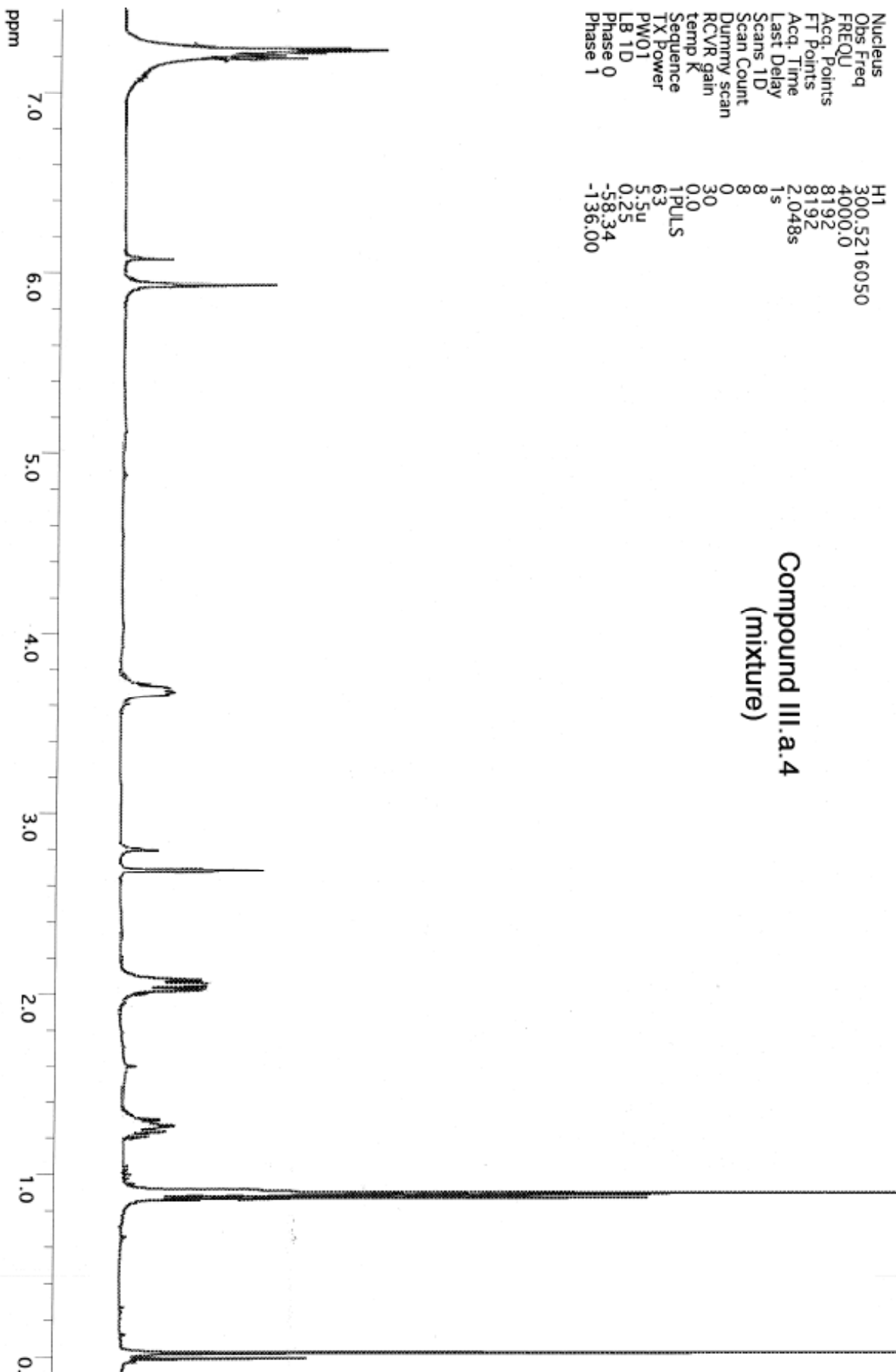


Compound III.a.3
(anti-isomer)



Nucleus H1
Obs Freq 300.5216050
FREQU 4000.0
Acq. Points 8192
FT Points 8192
Acq. Time 2.048s
Last Delay 1s
Scans 1D 8
Scan Count 8
Dummy scan 0
RCVR gain 30
temp. K 0.0
Sequence 1PULS
TX Power 63
PW01 5.5u
LB 1D 0.25
Phase 0 -58.34
Phase 1 -136.00

Compound III.a.4
(mixture)



Compound III.a.4
(mixture)

