

A New Ring Expansion for a Chiral Hexahydroazulene Skeleton Possessing an Angular Methyl Group

Masaatsu Adachi*, Takema Komada, Toshio Nishikawa

Laboratory of Organic Chemistry, Graduate School of Bioagricultural Sciences,
Nagoya University, Chikusa, Nagoya 464-8601, Japan

Supporting Information

Index

General Experimental.....	S1
Spectra.....	S2-S17

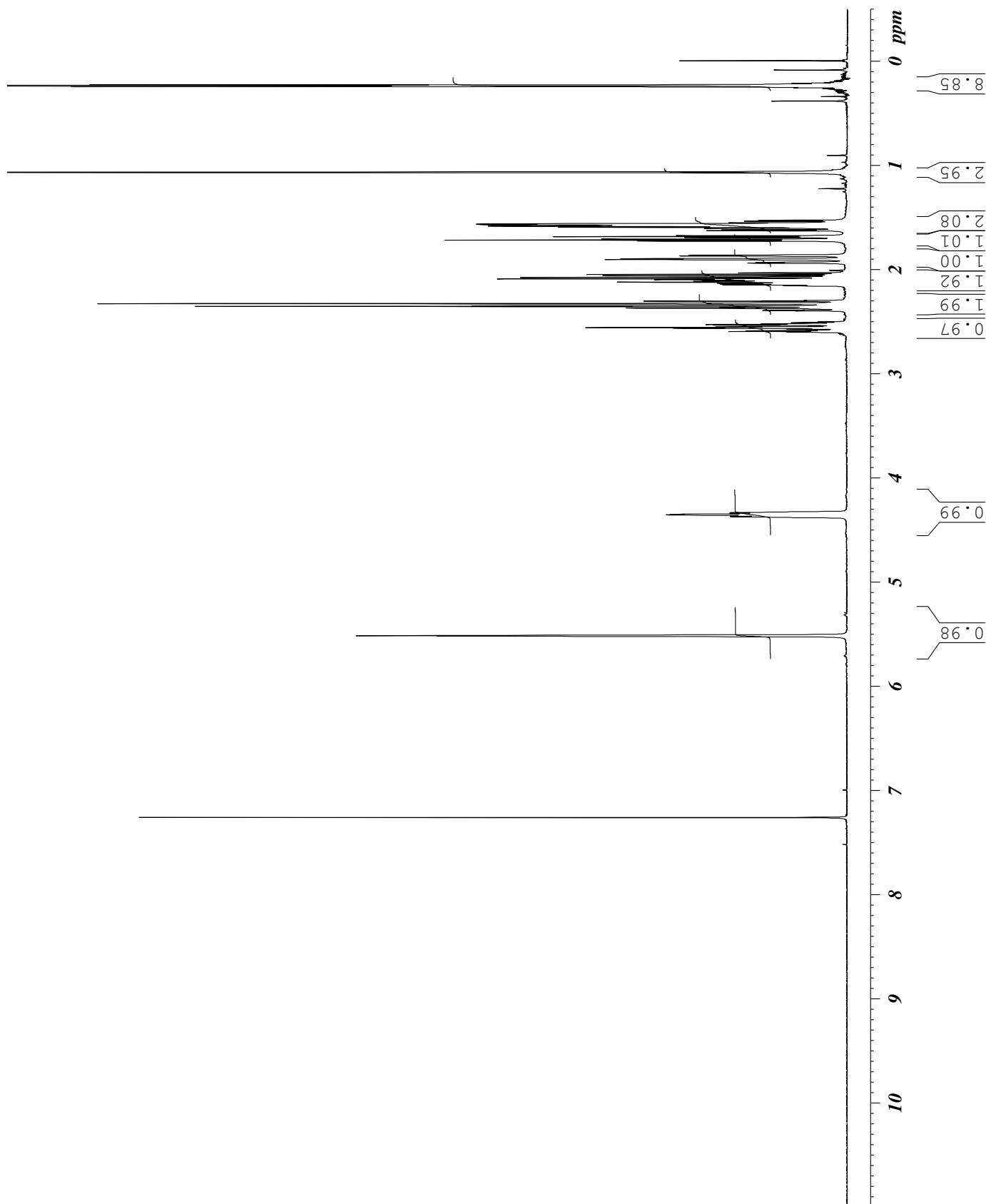
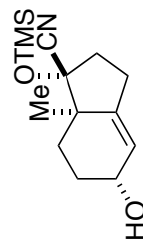
General Experimental: Melting points (mp) are not corrected. Infrared spectra (IR) are reported in wave number (cm^{-1}). Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on 600 MHz or 400 MHz spectrometer. NMR samples were dissolved in CDCl_3 , CD_3OD and C_6D_6 , and chemical shifts are reported in ppm relative to the residual undeuterated solvent (CDCl_3 as $\delta = 7.26$ ppm, CD_3OD as $\delta = 3.31$ ppm, C_6D_6 as $\delta = 7.15$ ppm). ^1H NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broadened, m = multiplet), coupling constant, and assignment. ^{13}C NMR spectra were recorded on 150 MHz or 100 MHz spectrometer. The samples were dissolved in CDCl_3 , CD_3OD and C_6D_6 , and chemical shifts are reported in ppm relative to the solvent (CDCl_3 as $\delta = 77.0$ ppm, CD_3OD as $\delta = 49.0$ ppm, C_6D_6 as $\delta = 128.0$ ppm). ^1H NMR and ^{13}C NMR spectra were measured at 300 K unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm silica gel coated glass plate 60 F₂₅₄ (Merck, #1.05715). Silica gel 60 (particle size 63-200 μm , 70-230 mesh ASTM, purchased from Merck Ltd.) was used for open column chromatography. Silica gel 60 (spherical, particle size 40-50 μm , purchased from Kanto Chemical Co., Inc.) or Silica gel 60 N (spherical, neutral, particle size 40-50 μm , purchased from Kanto Chemical Co., Inc.) were used for flash column chromatography. Unless otherwise noted, non-aqueous reactions were carried out in oven-dried (120 $^\circ\text{C}$) or flame-dried glassware under nitrogen. All commercially available reagents were used as received.

Current Data Parameters
 NAME komaV400_4
 EXPNO 26
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20090105
 Time_ 11.36
 INSTRUM av-400
 PROBHHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 181
 DW 60.400 usec
 DE 6.00 usec
 TE 300.0 K
 DI 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 8.60 usec
 PL1 -4.00 dB
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300089 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.40



Current Data Parameters
 NAME komaV400_4
 EXPNO 28
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20090105
 Time 12.17
 INSTRUM av400
 PROBHD 5 mm QNP 1H/13
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 512
 DS 4
 SWH 23980.814 Hz
 FIDRES 0.365918 Hz
 AQ 1.3664756 sec
 RG 32
 DW 20.850 usec
 DE 6.00 usec
 TE 300.0 K
 DI 1.00000000 sec
 d11 0.03000000 sec
 d12 0.0002000 sec

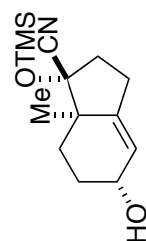
===== CHANNEL f1 =====

NUC1 13C
 P1 9.00 usec
 PL1 -3.00 dB
 SFO1 100.628298 MHz

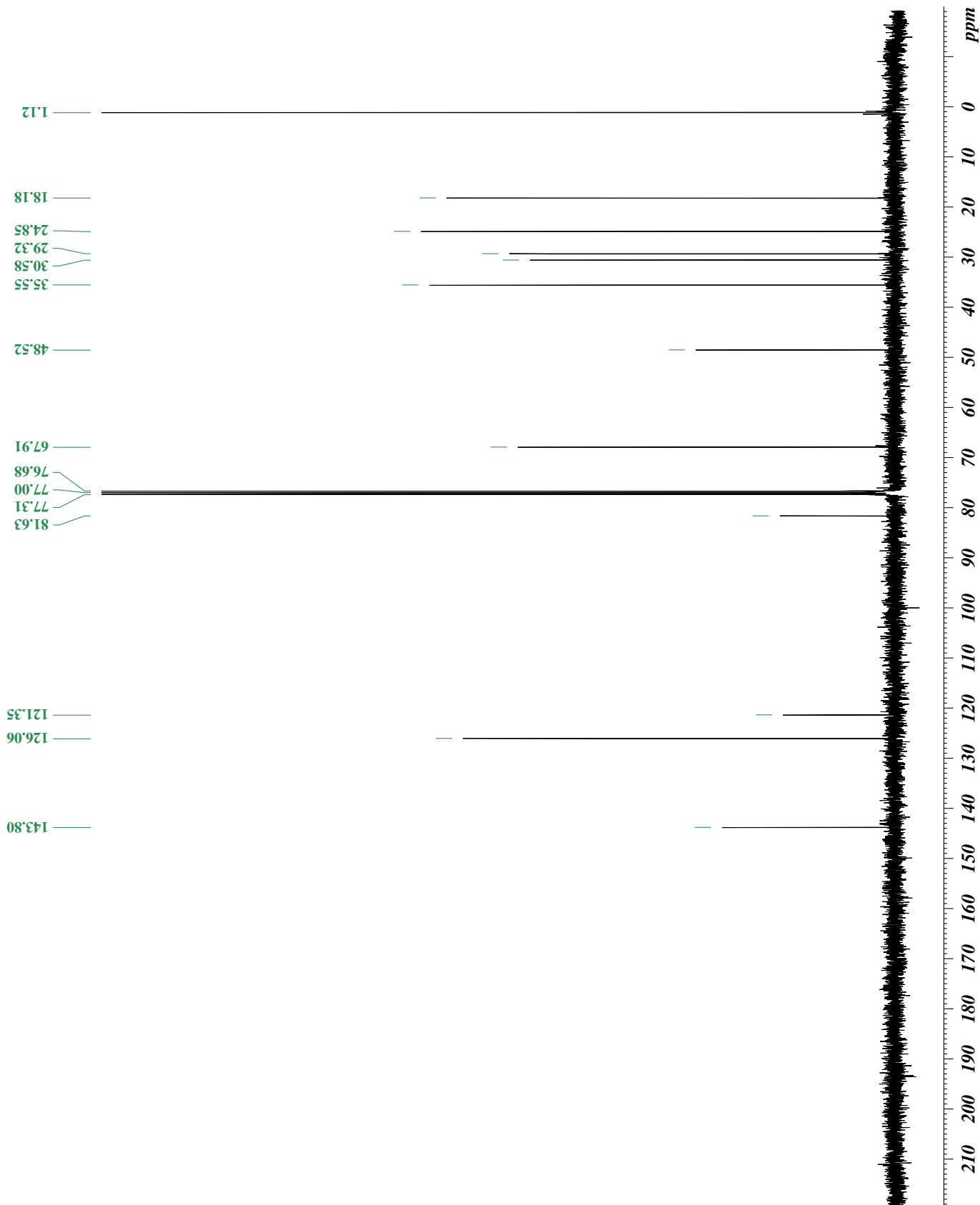
===== CHANNEL f2 =====

CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -4.00 dB
 PL12 14.80 dB
 PL13 14.80 dB
 SFO2 400.1316005 MHz

F2 - Processing parameters
 SI 32768
 SF 100.6127715 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



1

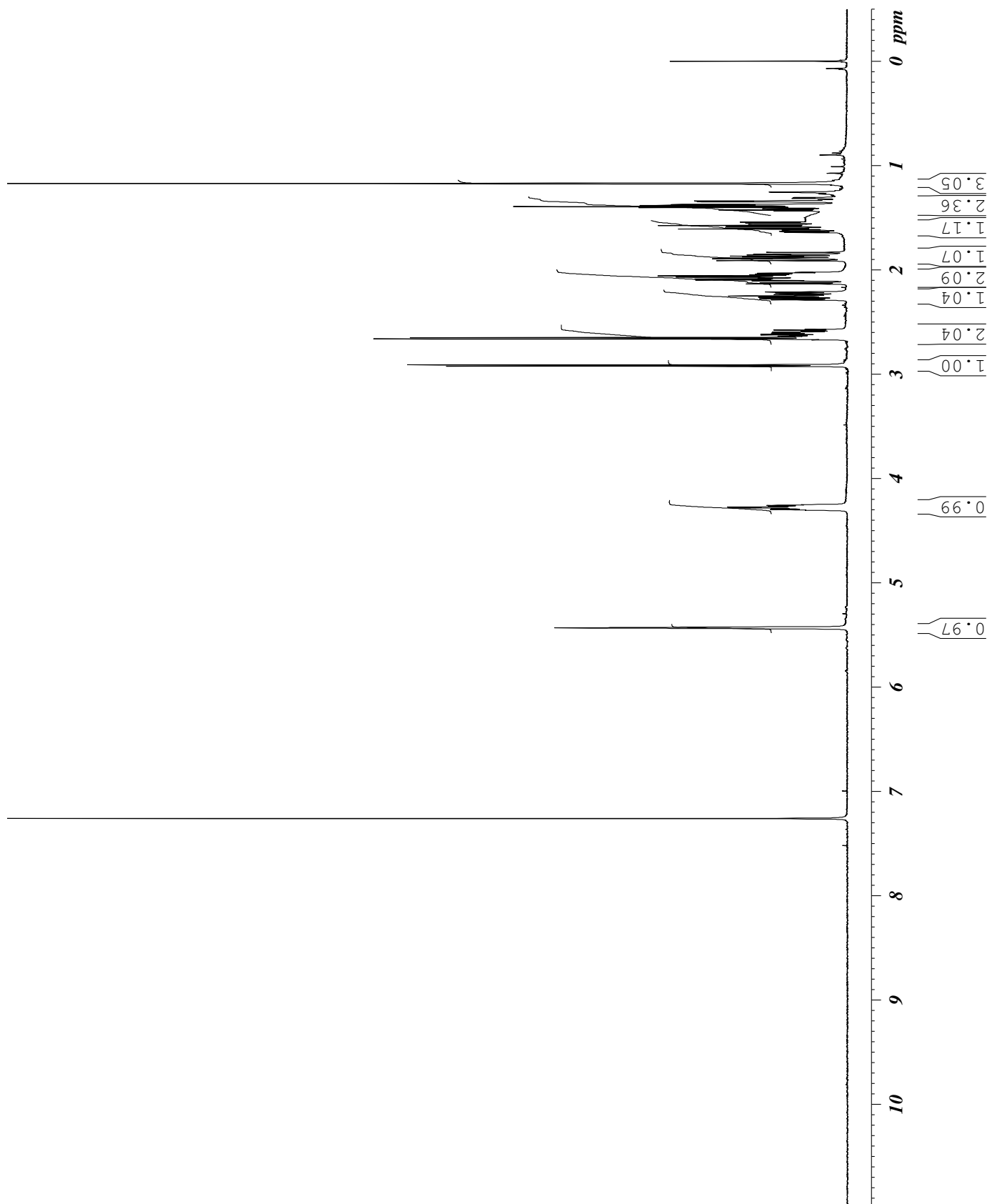
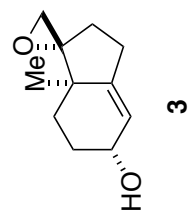


Current Data Parameters
 NAME komaV400_4
 EXPNO 44
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20090105
 Time_ 20.42
 INSTRUM av-400
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 406.4
 DW 60.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 8.60 usec
 PL1 -4.00 dB
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300091 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.40



21.18
 27.00
 29.13
 29.57
 31.20
 40.38
 53.71
 68.22
 69.99
 76.68
 77.00
 77.32
 122.13
 149.47

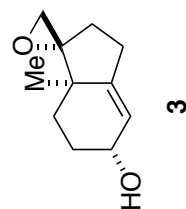
Current Data Parameters
 NAME komaV400_4
 EXPNO 46
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20090105
 Time_ 21.22
 INSTRUM avn000
 PROBHD 5 mm QNP 1H/13
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 512
 DS 4
 SWH 23980.814 Hz
 FIDRES 0.365918 Hz
 AQ 1.3664756 sec
 RG 40.3
 DW 20.850 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 d11 0.03000000 sec
 d12 0.0002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.00 usec
 PL1 -3.00 dB
 SFO1 100.628298 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -4.00 dB
 PL12 14.80 dB
 PL13 14.80 dB
 SFO2 400.1316005 MHz

F2 - Processing parameters
 SI 32768
 SF 100.6127700 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

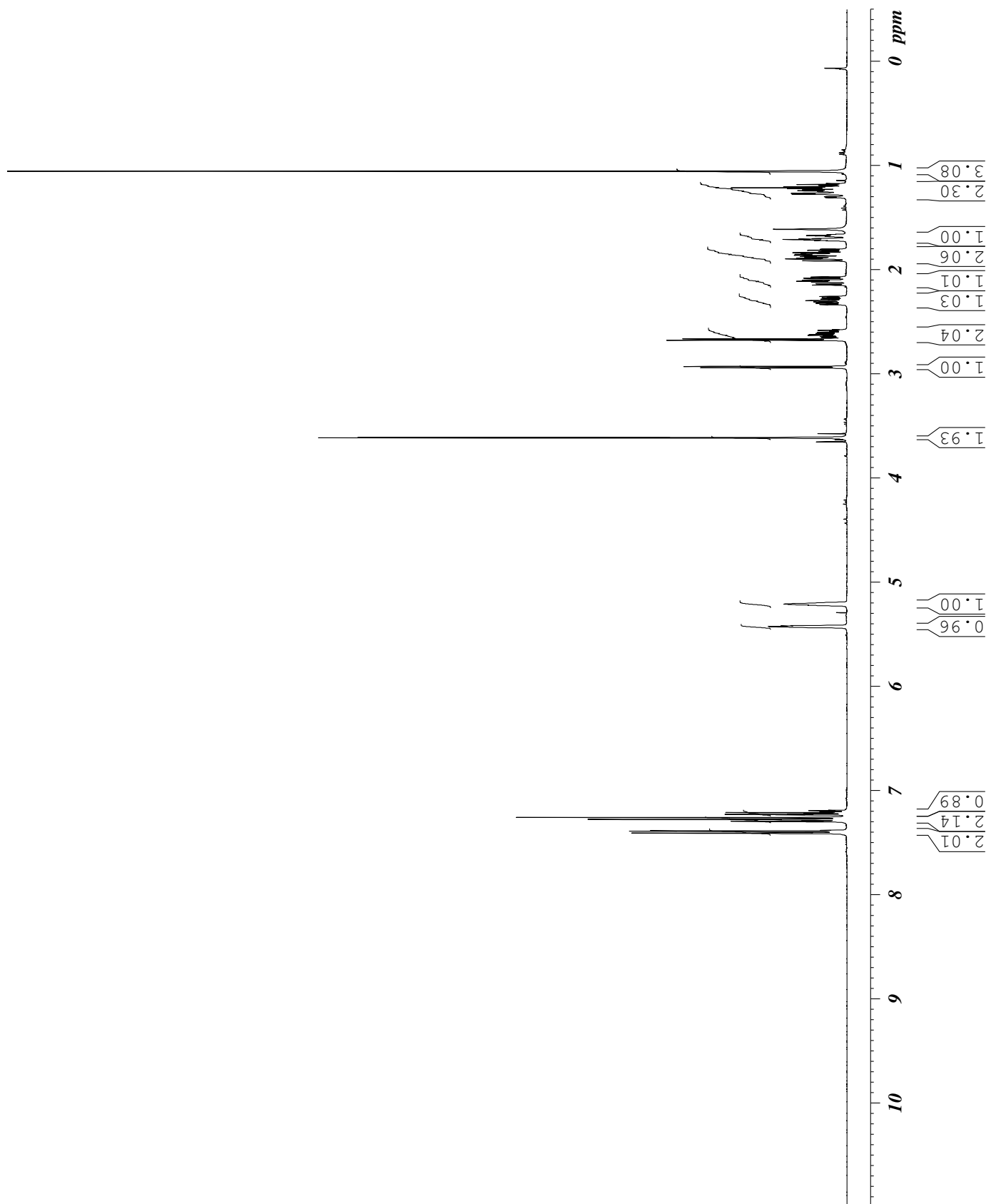
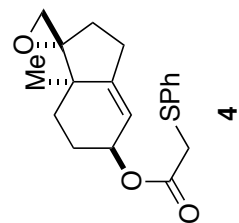


Current Data Parameters
 NAME komaV400_8
 EXPNO 19
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20110512
 Time_ 21.47
 INSTRUM av400
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 203.2
 DW 60.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 8.60 usec
 PL1 -4.00 dB
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.40



169.25
 153.16
 134.95
 129.97
 128.91
 126.85
 115.73
 77.32
 77.00
 76.68
 69.98
 68.08
 53.73
 40.22
 36.80
 28.96
 27.24
 26.81
 24.76
 19.74

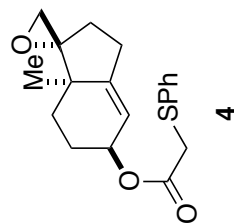
Current Data Parameters
 NAME komaV400_8
 EXPNO 20
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20110512
 Time 22.06
 INSTRUM dss000
 PROBHD 5 mm QNP 1H/13
 PULPROG zgpg30
 TD 65536
 SOLVENT CDC13
 NS 512
 DS 4
 SWH 23980.814 Hz
 FIDRES 0.365918 Hz
 AQ 1.3664756 sec
 RG 16384
 DW 20.850 usec
 DE 300.0 K
 TE 300.0 K
 DI 1.00000000 sec
 d11 0.03000000 sec
 d12 0.0002000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.00 usec
 PL1 -3.00 dB
 SFO1 100.628298 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -4.00 dB
 PL12 14.80 dB
 PL13 14.80 dB
 SFO2 400.1316005 MHz

F2 - Processing parameters
 SI 32768
 SF 100.6127729 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



4

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

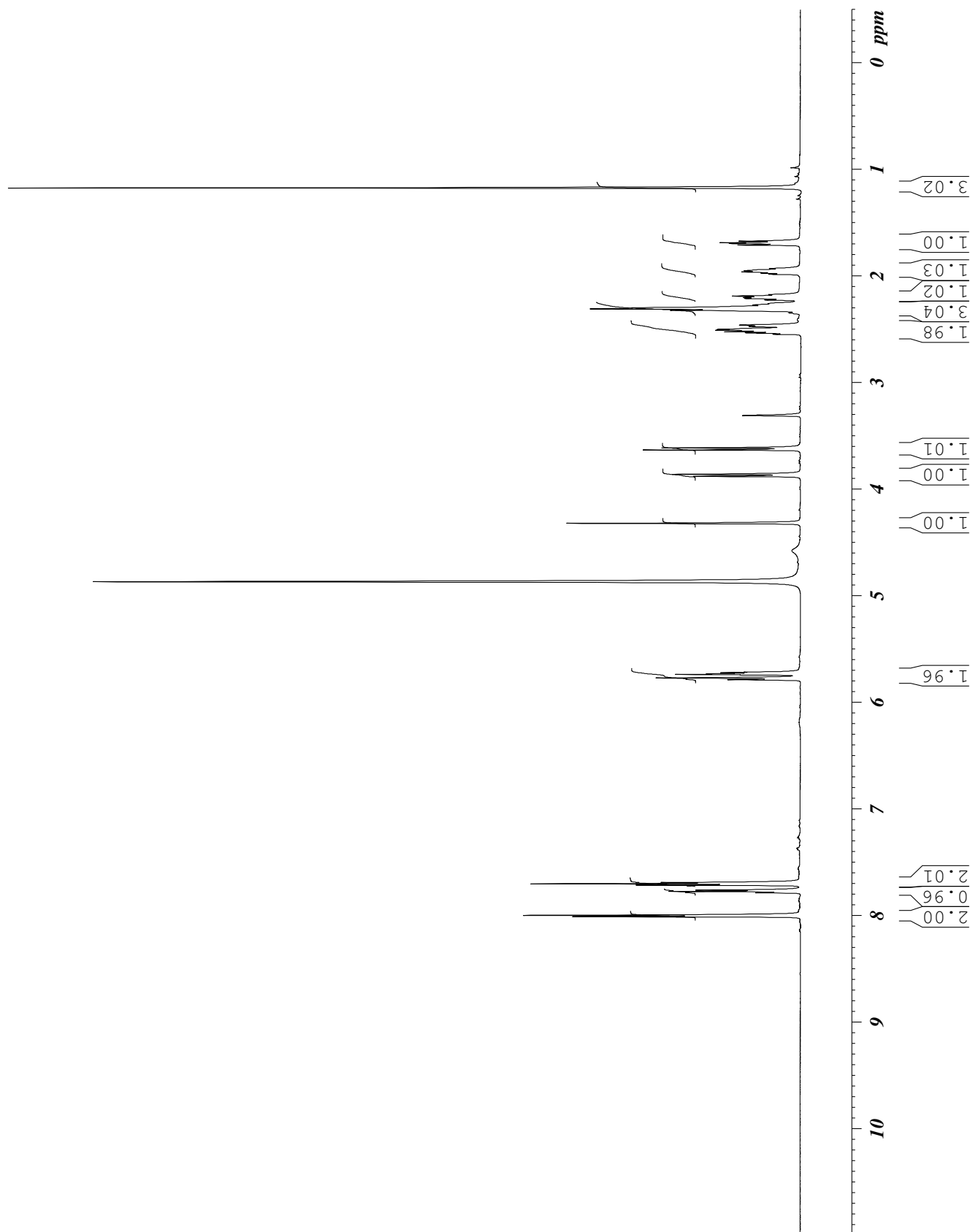
Current Data Parameters
 NAME komada600-3
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters

Date_ 710918
 Time 17.52
 INSTRUM AMX2600
 PROBHD 5 mm Dual 19
 PULPROG zg0
 TD 32768
 SOLVENT MeOH
 NS 16
 DS 2
 SWH 8474.576 Hz
 FIDRES 0.258624 Hz
 AQ 1.9333620 sec
 RG 64
 DW 59.000 usec
 DE 84.29 usec
 TE 300.0 K

F2 - Processing parameters

SI 16384
 SF 600.1388200 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00





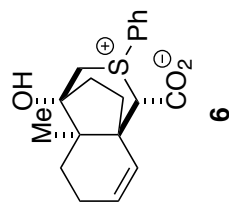
Current Data Parameters
 NAME komada600-3
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters

Date_ 710918
 Time 21.22
 INSTRUM AMX2600
 PROBHD 5 mm Dual 19
 PULPROG zgpgdc
 TD 65536
 SOLVENT CD3OD
 NS 2048
 DS 2
 SWH 35714.285 Hz
 FIDRES 0.54957 Hz
 AQ 0.9175540 sec
 RG 4096
 DW 14.000 usec
 DE 20.00 usec
 TE 300.0 K

F2 - Processing parameters

SI 65536
 SF 150.9048185 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.00



Current Data Parameters
 NAME komada600-3
 EXPNO 4
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 710918
 Time 22.02

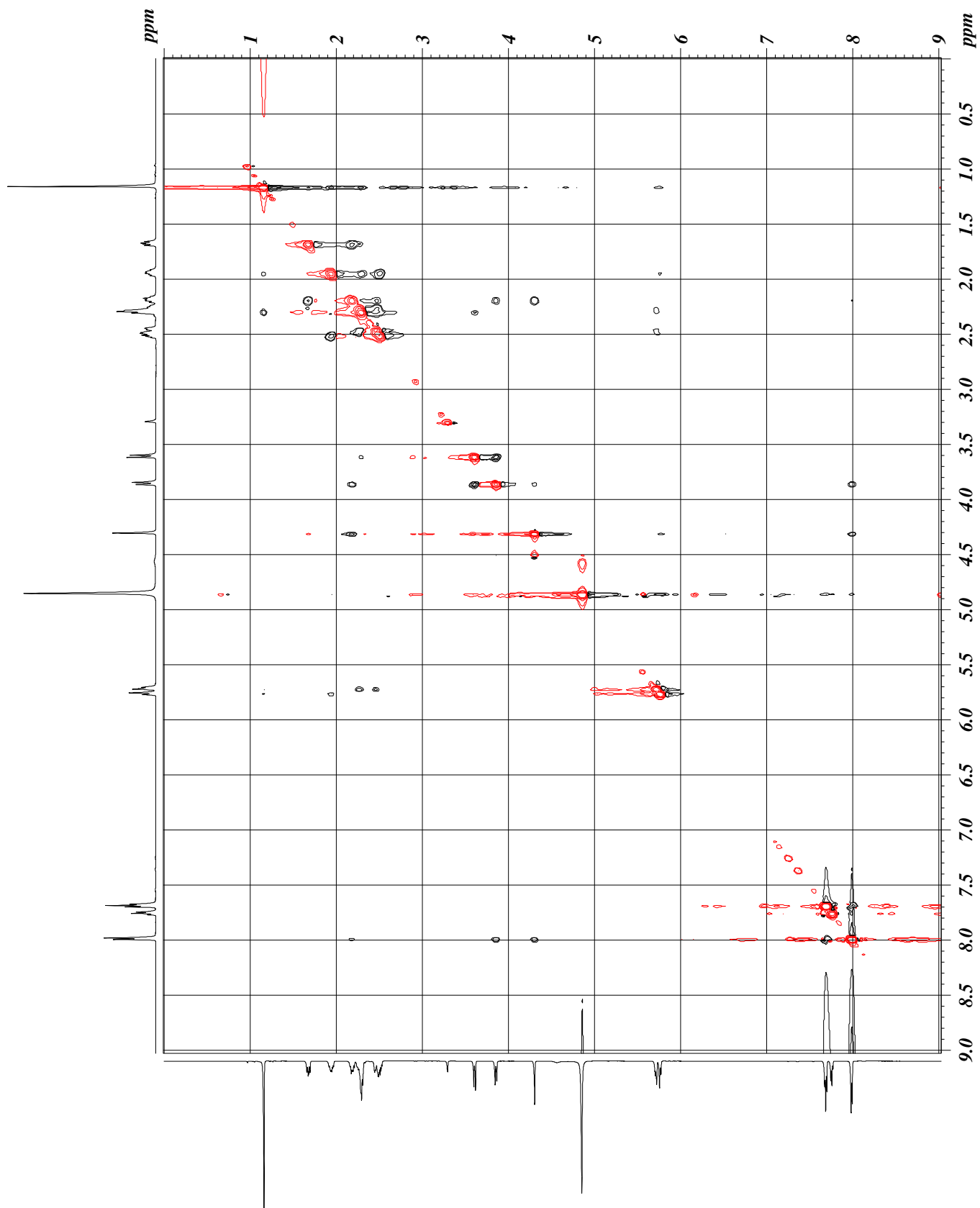
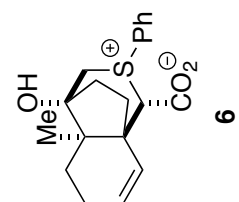
INSTRUM AMX2600
 PROBHD 5 mm Dual 19
 PULPROG noesyyp
 TD 1024
 SOLVENT MeOD
 NS 16
 DS 4

SWH 5434.783 Hz
 FIDRES 5.307405 Hz
 AQ 0.0942580 sec
 RG 64
 DW 92.000 usec
 DE 131.43 usec
 TE 300.0 K

F1 - Acquisition parameters
 ND0 2
 TD 300
 SFO1 600.1415 MHz
 FIDRES 18.115942 Hz
 SW 9.056 ppm
 F1MODE undefined

F2 - Processing parameters
 SI 512
 SF 600.1388200 MHz
 WDW QSINE
 SSB 2
 LB 0.00 Hz
 GB 0
 PC 1.00

F1 - Processing parameters
 SI 512
 MC2 TPPI
 SF 600.1388200 MHz
 WDW QSINE
 SSB 2
 LB 0.00 Hz
 GB 0



Current Data Parameters
NAME komada600-2
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20001026
Time 12.04

INSTRUM AMX2600
PROBHD 5 mm Dual 1H
PULPROG inv4gsplmnd
TD 2048
SOLVENT CD3OD

NS 16
DS 16
SWH 5434.783 Hz
FIDRES 2.653702 Hz
AQ 0.1884660 sec
RG 512
DW 92.000 usec
DE 131.43 usec
TE 300.0 K

F1 - Acquisition parameters
ND0 2
TD 300

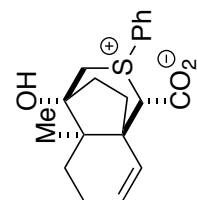
SFO1 150.9207 MHz
FIDRES 128.205124 Hz
SW 254.846 ppm
FnMODE undefined

F2 - Processing parameters
SI 1024
SF 600.1364358 MHz

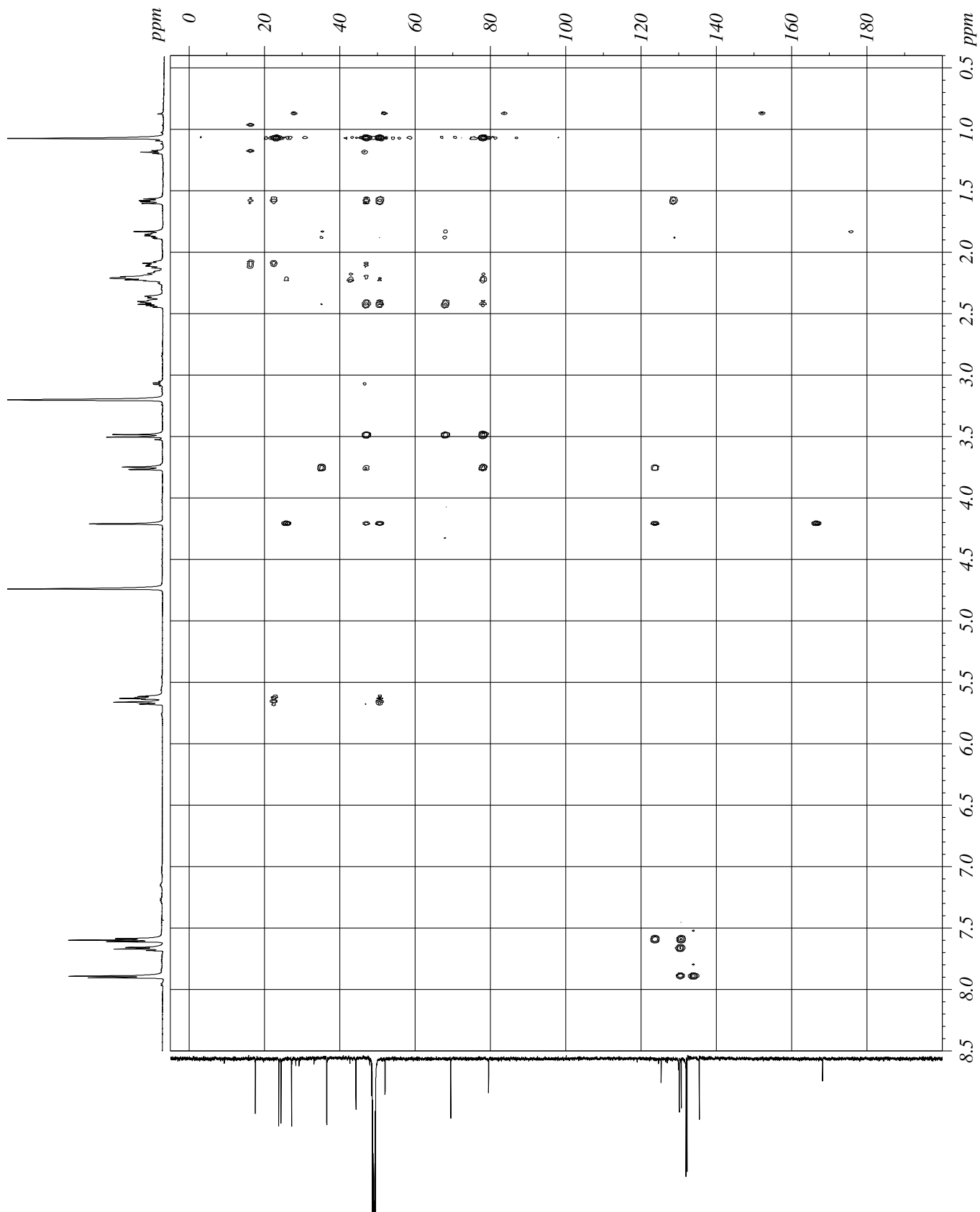
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 512
MC2 QF

SF 150.9048100 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0



6



Current Data Parameters
 NAME komada600-2
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20001027
 Time 21.37
 INSTRUM AMX2600
 PROBDH 5 mm Dual 19
 PULPROG inv4gsp
 TD 2048
 SOLVENT CD3OD
 NS 16
 DS 16
 SWH 9259.259 Hz
 FIDRES 4.521122 Hz
 AQ 0.1106420 sec
 RG 512
 DW 54.000 usec
 DE 77.14 usec
 TE 300.0 K

F1 - Acquisition parameters

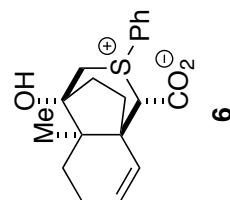
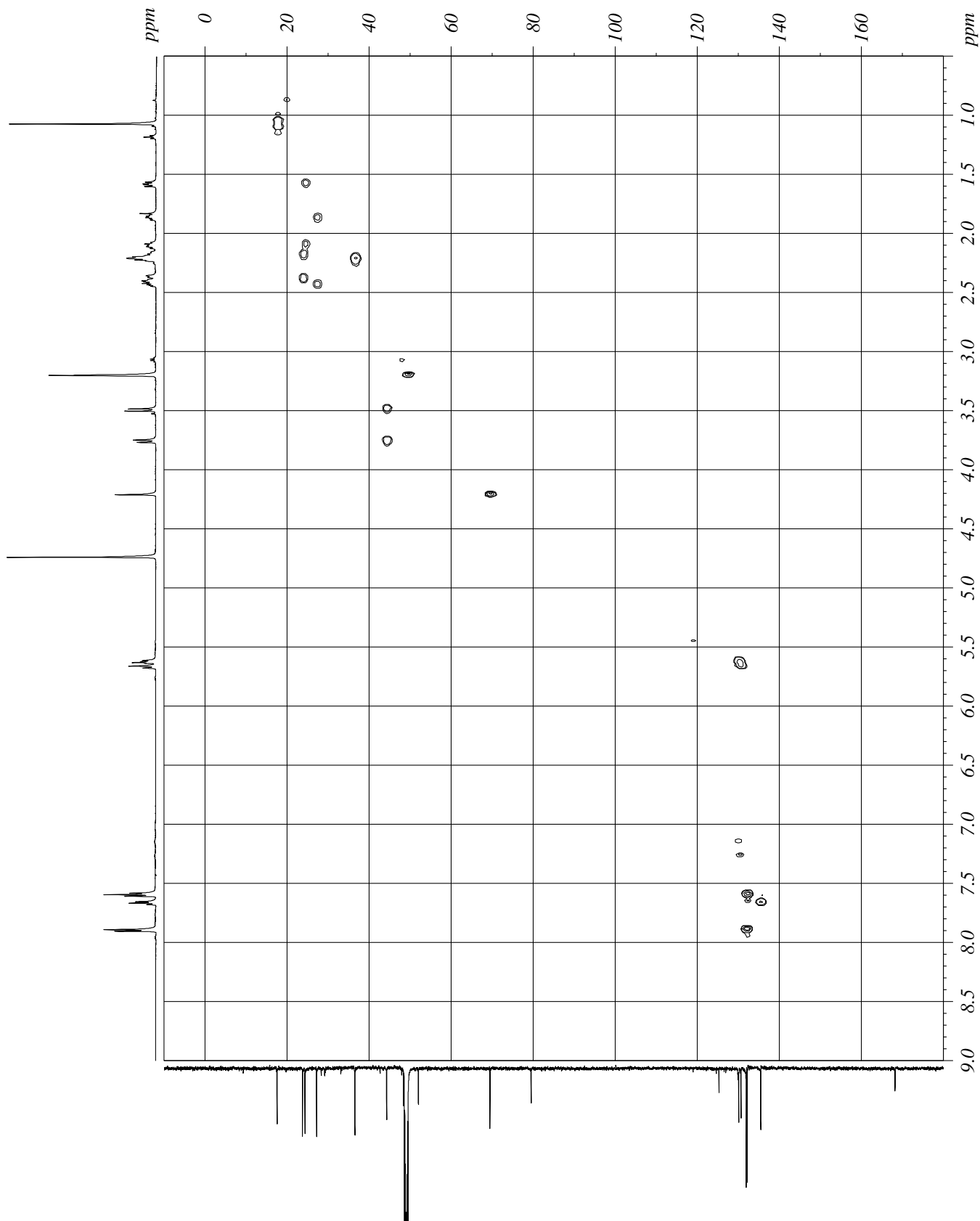
ND0 4
 TD 300
 SF01 150.9199 MHz
 FIDRES 119.047615 Hz
 SW 236.644 ppm
 FMODE undefined

F2 - Processing parameters

SI 1024
 SF 600.1379125 MHz
 WDW QSINE
 SSB 2
 LB 0.00 Hz
 GB 0
 PC 1.00

F1 - Processing parameters

SI 512
 MC2 TPPI
 SF 150.9048099 MHz
 WDW QSINE
 SSB 2
 LB 0.00 Hz
 GB 0

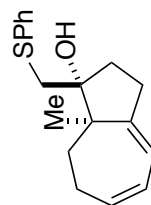
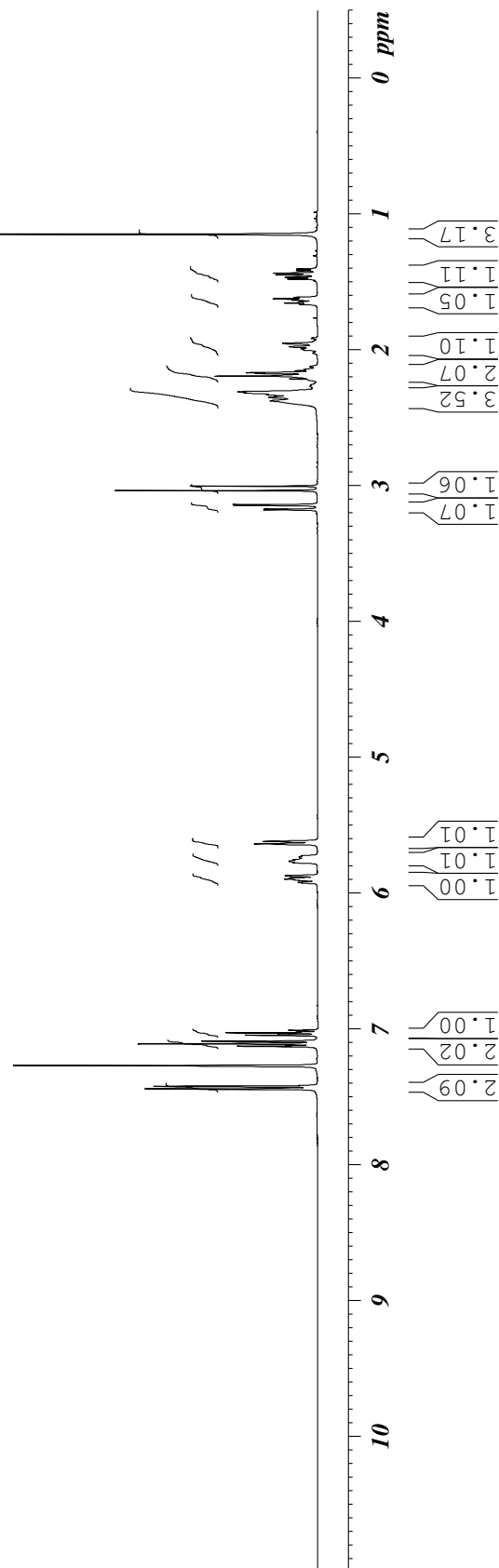


Current Data Parameters
 NAME komaV400_8
 EXPNO 13
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20110507
 Time_ 15.03
 INSTRUM av400
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT C6D6
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 64
 DW 60.400 usec
 DE 6.00 usec
 TE 300.0 K
 DI 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 8.60 usec
 PL1 -4.00 dB
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1299988 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



7

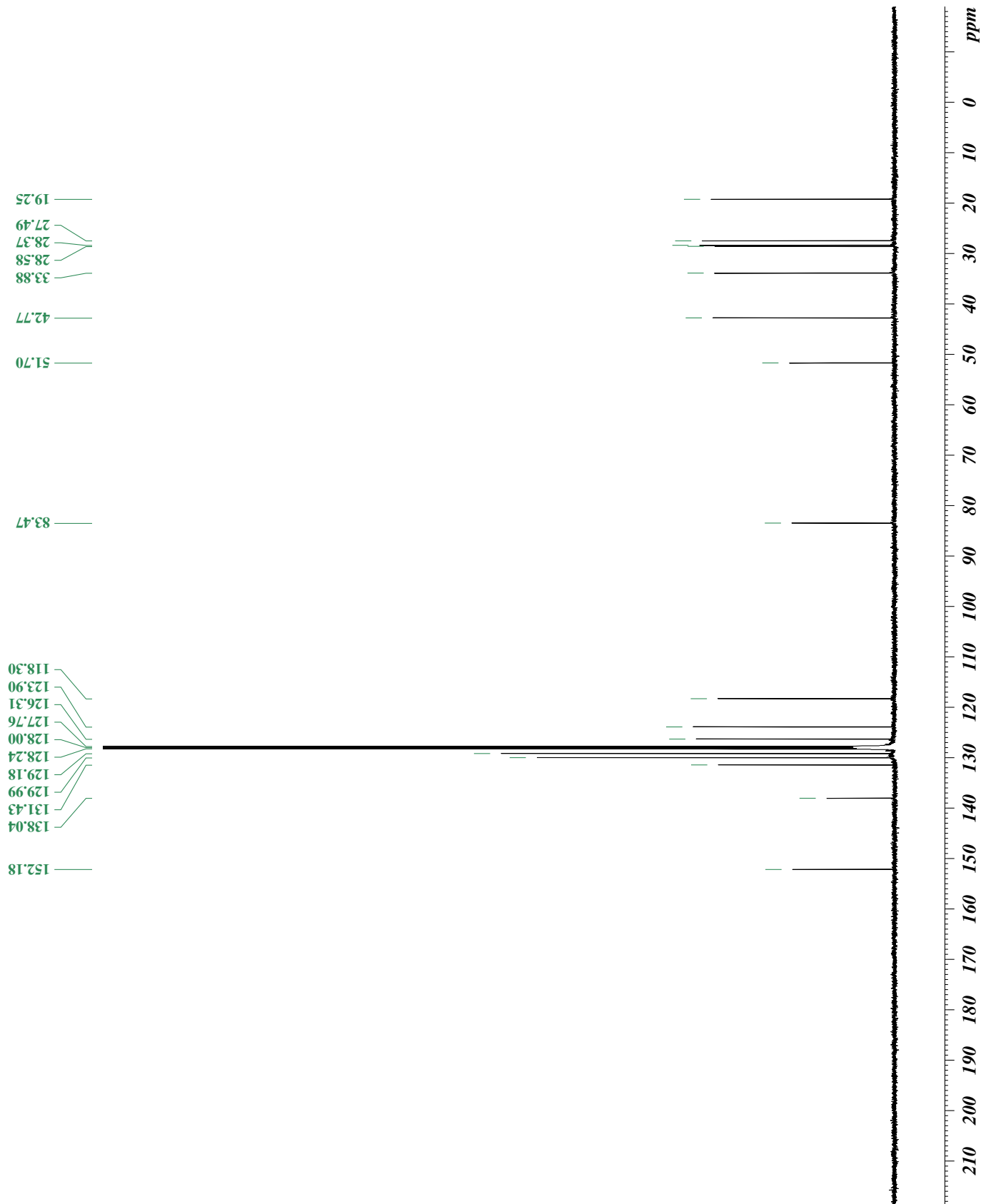
Current Data Parameters
NAME komaV400_8
EXPNO 2
PROCNO 99

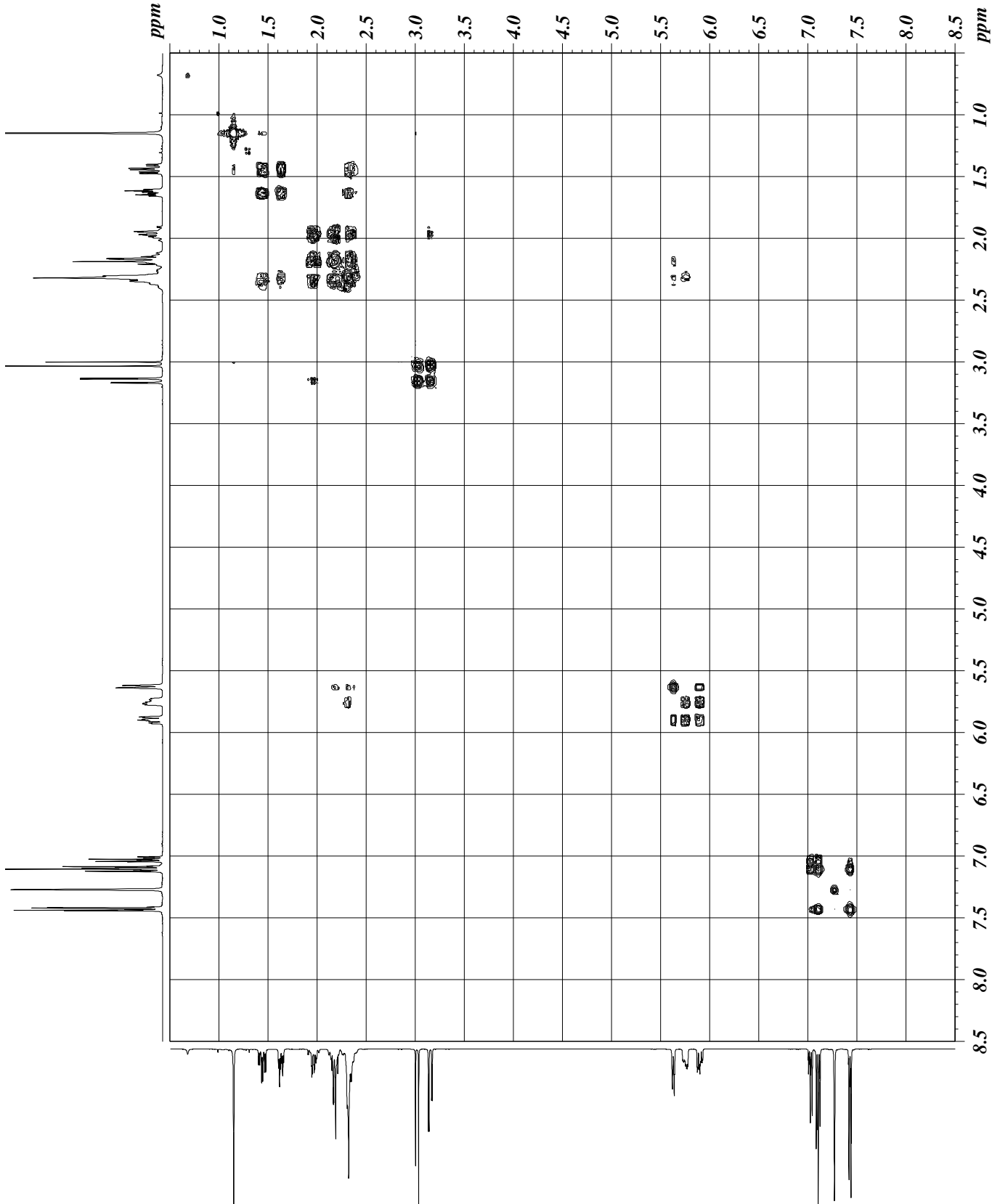
F2 - Acquisition Parameters
Date_ 20110503
Time 11:27
INSTRUM dvt000
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT C6D6
NS 528
DS 4
SWH 16129.032 Hz
FIDRES 0.246110 Hz
AQ 2.0316660 sec
RG 7298.2
DW 31.000 usec
DE 30.00 usec
TE 300.0 K
D1 2.00000000 sec
d11 0.03000000 sec
d12 0.0002000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 9.00 usec
PL1 -3.00 dB
SFO1 100.6208180 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -4.00 dB
PLI2 14.80 dB
PLI3 14.80 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127499 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40





Current Data Parameters
 NAME komuV400_8
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20110503
 Time 11.17
 INSTRUM av400
 PROBHD 5 mm QNP 1H/13
 PULPROG cosygpgf
 TD 2048

SOLVENT CDCl₃
 NS 1
 DS 8

SWH 3324.468 Hz
 FIDRES 1.623275 Hz
 AQ 0.3080692 sec

RG 80
 DW 150.400 usec
 DE 6.00 usec
 TE 300.0 K

d0 0.00003300 sec
 d1 1.37138498 sec
 d13 0.00000400 sec

d16 0.00010000 sec
 INO 0.00030080 sec
 MCREST 0.00000000 sec

MCWRK 1.37138498 sec
 ===== CHANNEL f1 =====
 NUC1 ¹H
 P0 8.60 usec
 P1 8.60 usec

PL1 -4.00 dB
 SFO1 400.1316466 MHz
 ===== GRADIENT CHANNEL =====

GPNAME1 SINE.100
 GPNAM2 SINE.100
 GPX1 0.00 %

GPX2 0.00 %
 GPY1 0.00 %
 GPY2 0.00 %

GPZ1 10.00 %
 GPZ2 10.00 %
 P16 1000.00 usec

F1 - Acquisition parameters
 ND0 1
 TD 128

SFO1 400.1316 MHz
 FIDRES 25.972406 Hz
 SW 8.308 ppm

FnMODE QF
 F2 - Processing parameters
 SI 1024

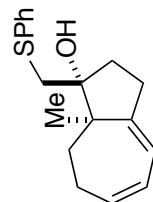
SF 400.1300000 MHz
 WDW SINE
 LB 0

SSB 0
 GB 0
 PC 1.40

F1 - Processing parameters
 SI 1024
 MC2 QF

SF 400.1300000 MHz
 WDW SINE
 SSB 0

LB 0
 GB 0



Current Data Parameters
 NAME komeAV400_8
 EXPNO 6
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20110503
 Time 12:42
 INSTRUM 400
 PROBRID 5 mm QNP 1H/13
 PULPROG zgpg30
 TD 1024
 SOLVENT C6D6
 NS 16
 DS 16
 SWH 3324.468 Hz
 FIDRES 32.46551 Hz
 AQ 0.1540596 sec
 RG 100
 DE 150.00 usec
 TE 300.0 K
 CNST2 1.45.0000000
 d0 0.00000300 sec
 d1 1.44265497 sec
 d2 0.00344828 sec
 d3 0.06500000 sec
 d16 0.00000400 sec
 INO 0.00010000 sec
 INO 0.0002085 sec
 MCRESY 0.0000000 sec
 MCWRK 1.4265997 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 8.60 usec
 P2 17.20 usec
 PL1 -4.00 dB
 SFO1 400.1316466 MHz

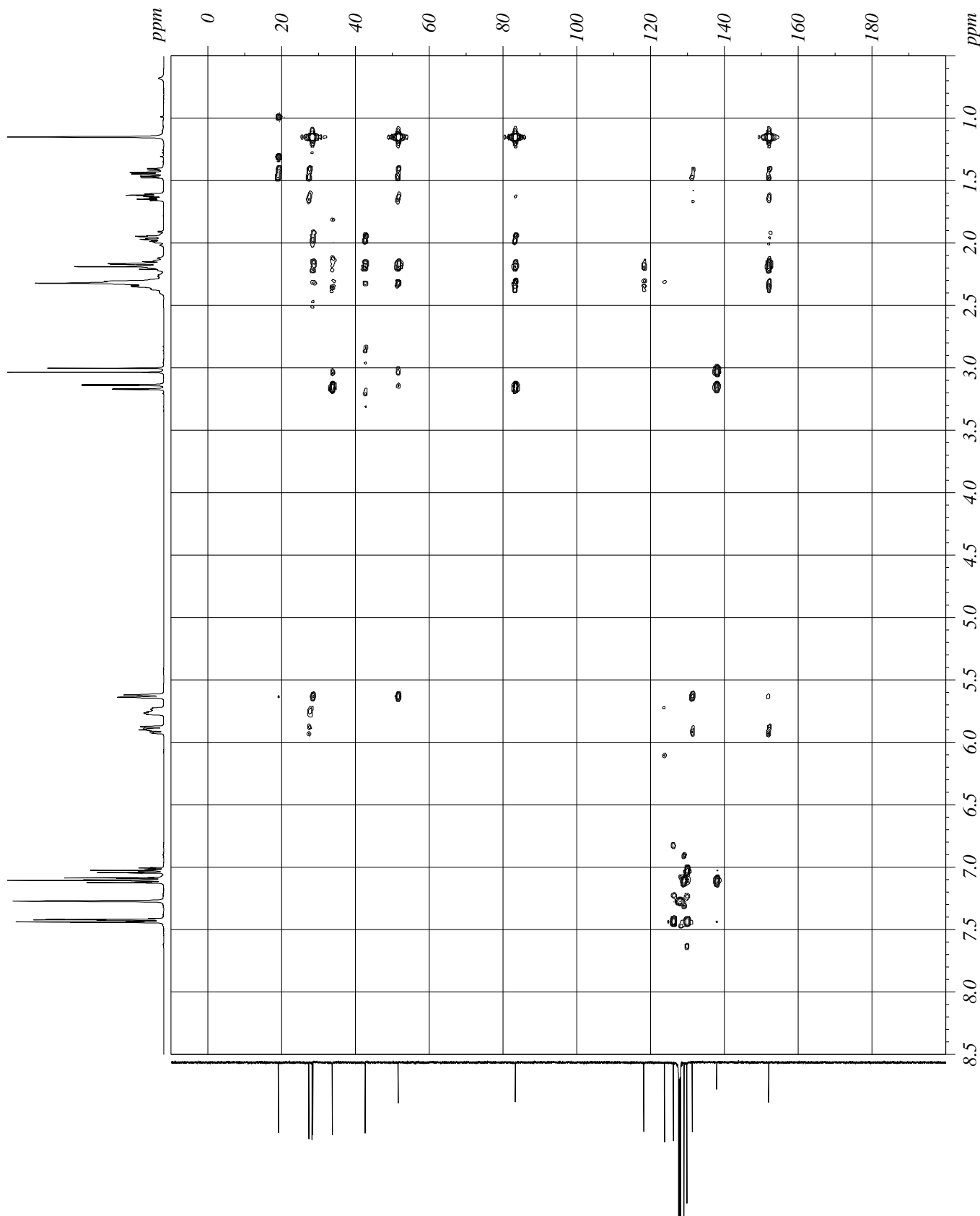
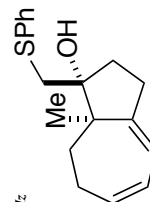
===== CHANNEL f2 =====
 NUC2 13C
 P3 9.00 usec
 P4 15.00 usec
 SFO2 100.628298 MHz

===== GRADIENT CHANNEL =====
 GPNAM1 SINE.100
 GPNAM2 SINE.100
 GPNAM3 SINE.100
 GPX1 0.00 %
 GPX2 0.00 %
 GPX3 0.00 %
 GPY1 0.00 %
 GPY2 0.00 %
 GPY3 0.00 %
 GPZ1 50.00 %
 GPZ2 30.00 %
 GPZ3 40.10 %
 P16 1000.00 usec

F1 - Acquisition parameters
 ND0 2
 TD 256
 SFO1 100.628 MHz
 FIDRES 93.675056 Hz
 SW 238.324 ppm
 FhMODE QF

F2 - Processing parameters
 SI 1034
 SF 400.1300000 MHz
 WDW 0
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.40

F1 - Processing parameters
 SI 1034
 SF 100.627690 MHz
 WDW 0
 SSB 0
 LB 0.00 Hz
 GB 0



Current Data Parameters
 NAME komaAV-400_8
 EXPNO 7
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20110503
 Time 14.37
 INSTRUM av400
 PROBDH 5 mm QNP 1H/13
 PULPROG zgpg30
 SOLVENT 1024 C6D6
 NS 8
 DS 16
 SWH 3324.468 Hz
 FIDRES 0.1540596 sec

AQ 100.000000 sec
 RG 327.680
 DW 150.00 usec
 DE 6.00 usec
 TE 300.0 K
 CNST2 145.0000000
 d0 0.00000300 sec
 d1 1.9424596 sec
 d4 0.00172414 sec
 d13 0.00000000 sec
 d16 0.00010000 sec
 d20 0.00100000 sec
 d21 0.00061614 sec
 IN0 0.00002085 sec
 MCREST 0.00000000 sec
 MCKW 0.97112298 sec
 STCNT 45

===== CHANNEL f1 =====
 NUC1 1H
 P1 8.60 usec
 PL1 17.20 usec
 PL2 -4.00 dB
 SFO1 400.1516466 MHz

===== CHANNEL f2 =====
 CPDPRG2 gcp
 NUC2 13C
 P3 9.00 usec
 PL3 18.00 usec
 PL4 3.00 usec
 PL5 -3.00 dB
 PL12 14.82 dB
 SFO2 100.628298 MHz

===== GRADIENT CHANNEL =====
 GPNAM1 SINE.100
 GPNAM2 SINE.100
 GPNAM3 SINE.100
 GPX1 0.00 %
 GPX2 0.00 %
 GPX3 0.00 %
 GPY1 0.00 %
 GPY2 0.00 %
 GPY3 0.00 %
 GPZ1 0.00 %
 GPZ2 0.00 %
 GPZ3 20.10 %
 P16 1000.00 usec

F1 - Acquisition parameters
 ND0 2
 TD 256
 SFO1 100.628298 MHz
 FIDRES 0.1540596 Hz
 SW 238.330 ppm
 F0MODE States-TPI

F2 - Processing parameters
 SI 1024
 SF 400.1300000 MHz
 WDW Q5INE
 SSB 0
 LB 0.00 Hz
 GB 0
 PC 1.40

F1 - Processing parameters
 SI 1024
 SF 100.627600 MHz
 WDW Q5INE
 SSB 0
 LB 0.00 Hz
 GB 0

