

Name: _____

Chem 203
December 15, 2012

Final Exam Part II
Problem 2 of 3 (30 points)

Select and submit TWO OUT OF THE THREE PROBLEMS FROM PART II for grading.
Do not submit three problems.

If you wish to unstaple the pages, please initial each page.

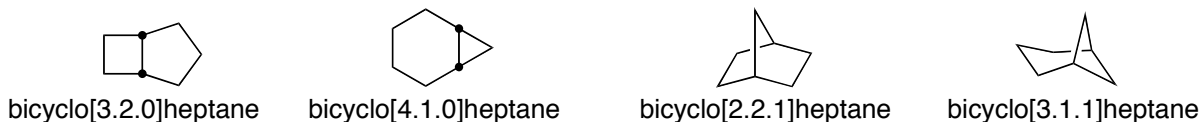
Books, notes, lecture videos, calculators, rulers, and laptop computers are permitted as is wireless (or wired) internet access and appropriate software (e.g, Pymol, Macromodel/Maestro, Excel, NMRPrediction, Chemdraw, ElComp, MolE, etc.). Catalogs of molecular structures (e.g., the Aldrich catalog, the Merck Index, etc.) or databases of molecular structures (such as wireless access to SciFinder Scholar, the Sigma-Aldrich website, etc.) are NOT PERMITTED. USE OF SUCH ITEMS CONSTITUTES ACADEMIC DISHONESTY, WILL RESULT IN A FAILING GRADE (F) IN THE CLASS, AND MAY RESULT IN EXPULSION FROM THE Ph.D. PROGRAM.

If you wish to use a laptop computer, please be willing to share briefly with others when needed.

The following spectral data are provided for a compound with a molecular formula $C_9H_{10}O_4$: IR (thin film from $CHCl_3$ solution on NaCl plates), 500 MHz 1H NMR, 125.7 MHz ^{13}C NMR, DEPT-90, DEPT-135, COSY, HMQC, HMBC, TOCSY and NOESY. Using these data, determine the structure of the compound and assign all of the 1H and ^{13}C resonances to their respective atoms in the structure. Make sure to determine the stereochemistry of the compound and to clearly assign 1H resonances to the appropriate diastereotopic protons.

All NMR spectra were measured in deuterodimethyl sulfoxide, CD_3SOCD_3 . The 1H resonance associated with the CD_3SOCD_2H isotopic impurity overlaps with resonance f and is marked on the 1H NMR spectrum.

HINT: The molecule contains a bicycloheptane ring system. Note that small bicyclic ring systems such as bicycloheptanes often show W-coupling (long-range $^4J_{HH}$ coupling) in the 1H NMR spectrum.



MAKE SURE TO COMPLETELY ANSWER THE QUESTIONS **a-e** ON PAGES 2-4.

a. Write the structure of the molecule.

If there are any aspects of your structure that don't seem to make sense, please feel free to comment on them below:

b. Tabulate the shifts of the ^1H resonances (a-j) in order of descending chemical shift. Provide an appropriate name for each multiplet (e.g., s, d, t, q, quintet, sextet, septet, octet, dd, ddd, dt, td, dddd, tt, qd, dq, etc.) and list its coupling constants in appropriate order; also list its integral [e.g., a: 3.30 (t, $J = 7.3$ Hz, 3 H)]. If a resonance is not described by a well-defined multiplet, name it as m and give its range [e.g., c: 4.43-4.37 (m, 2 H)].

a:

b:

c:

d:

e:

f:

g:

h:

i:

j:

c. Redraw the structure of the molecule below and write the letter (a-j) of each ^1H resonance next to the proton or protons to which it corresponds. If the assignment of a particular resonance is uncertain, please indicate this.

d. Tabulate the shifts of the ^{13}C resonances (1-9) in order of descending chemical shift. Make sure to report the chemical shift of each carbon resonances to the nearest tenth of ppm, unless two have the same value, in which case you may report it to the nearest hundredth.

1:

2:

3:

4:

5:

6:

7:

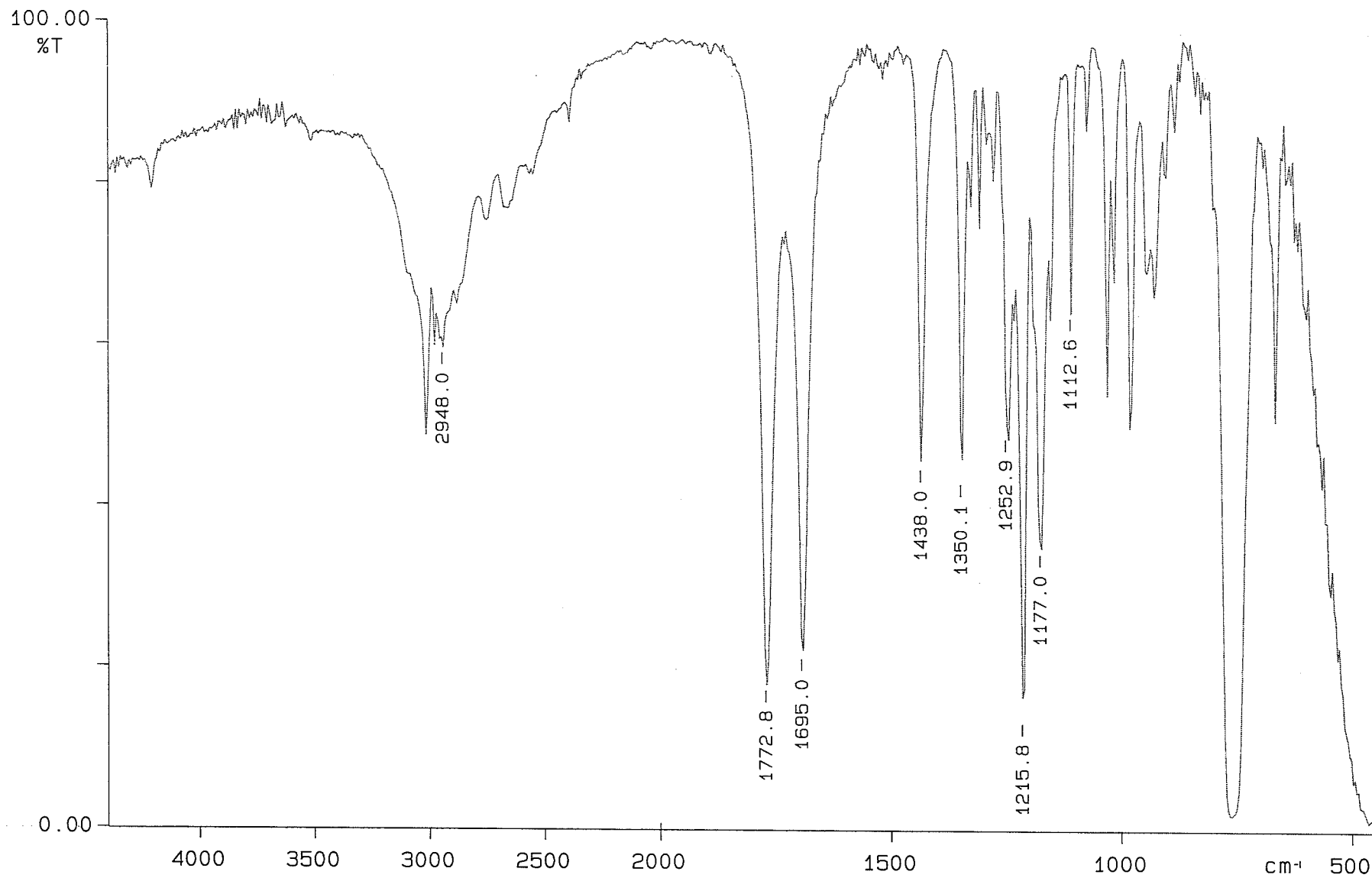
8:

9:

e. Redraw the structure of the molecule below and write the number (1-9) of each ^{13}C resonance next to the carbon or carbons to which it corresponds. If the assignment of particular resonance is uncertain, please indicate this.

#3 NaCl

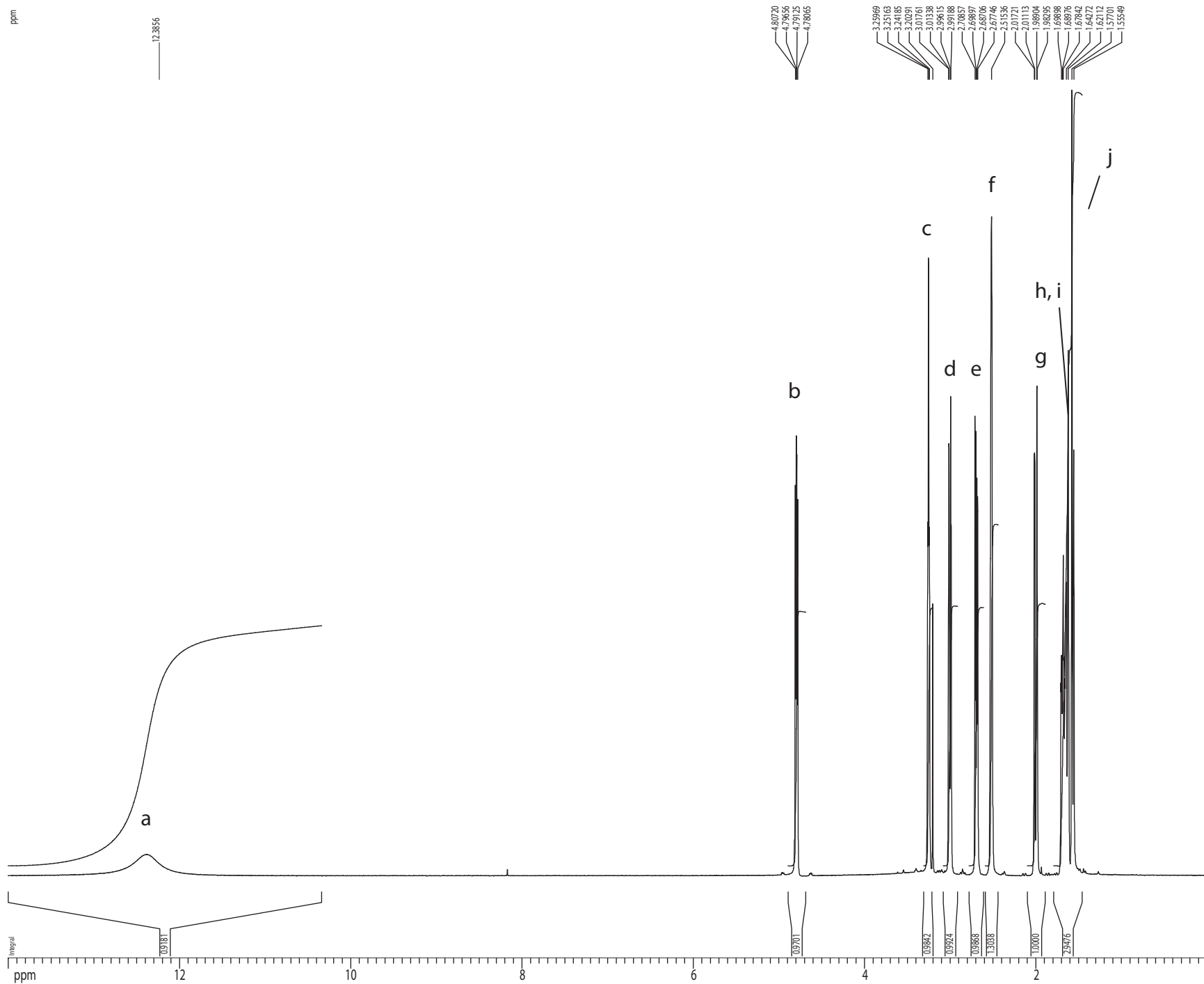
PERKIN ELMER



12/12/12 14:50

X: 4 scans, 4.0cm⁻¹

¹H spectrum

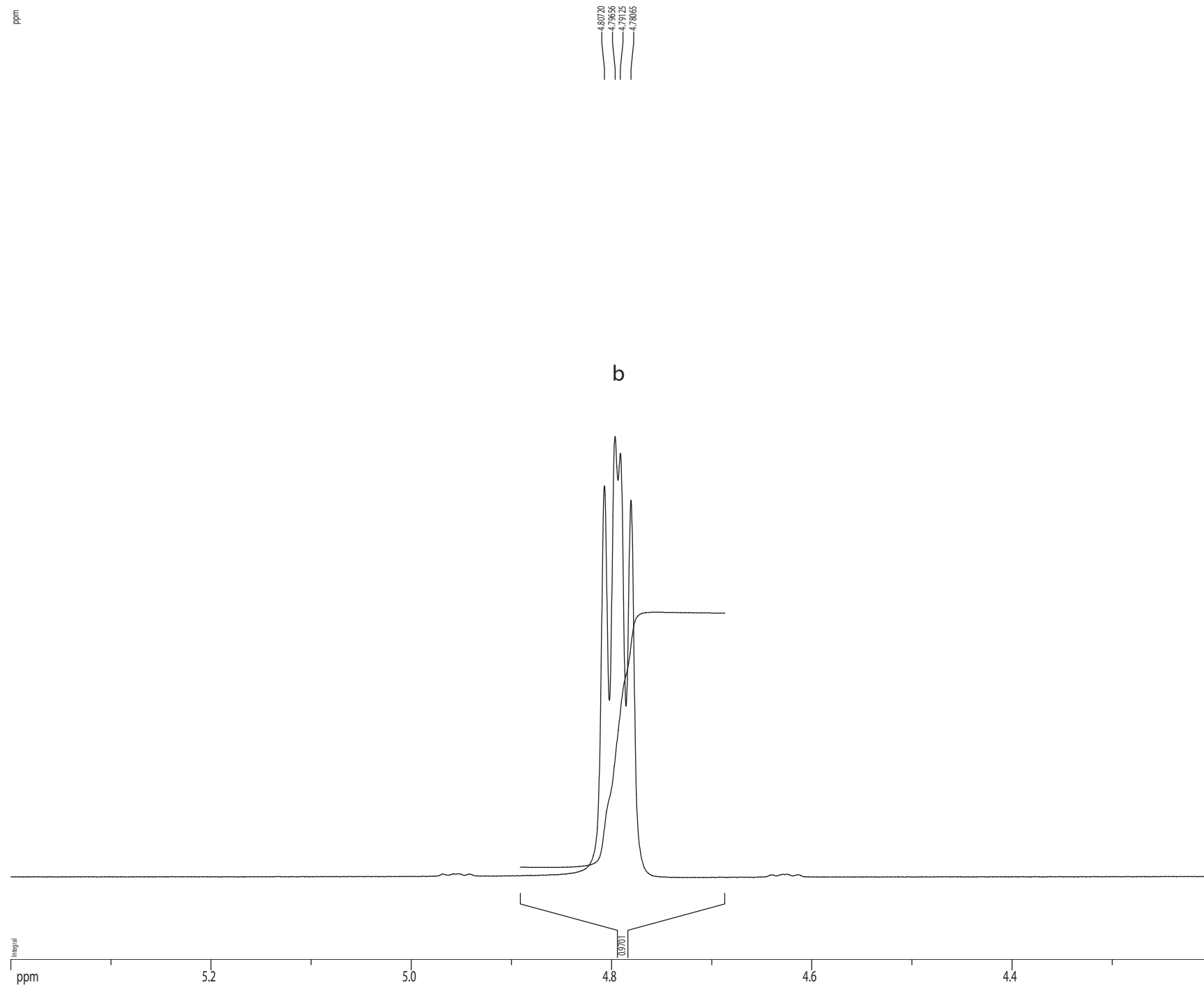


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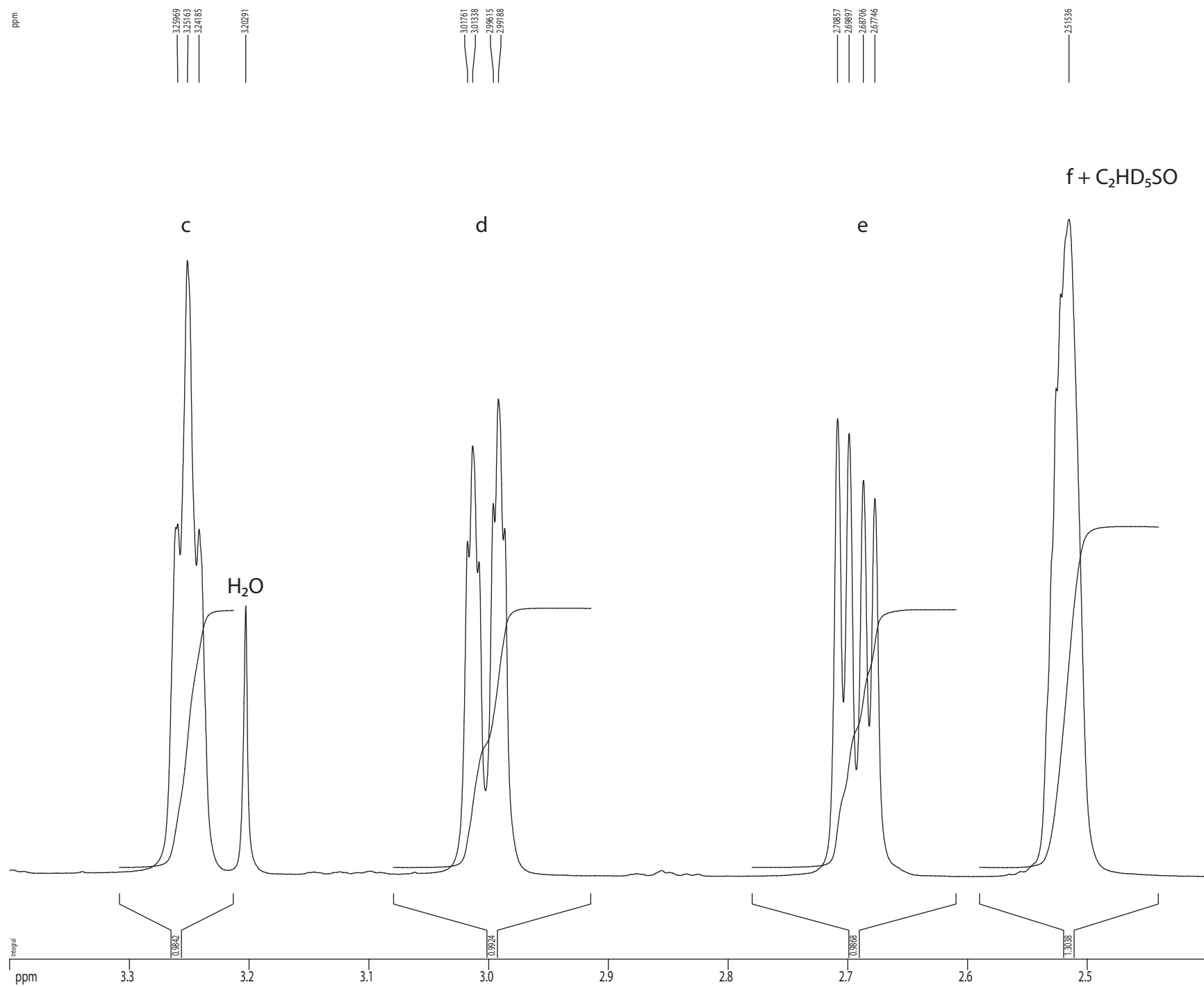
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#	ADDRESS	FREQUENCY		INTENSITY
		[Hz]	[PPM]	
1	10734.1	6195.539	12.3856	0.47
2	41739.3	2404.656	4.8072	7.49
3	41782.8	2399.337	4.7966	8.43
4	41804.6	2396.680	4.7913	8.11
5	41847.9	2391.378	4.7807	7.22
6	48070.5	1630.564	3.2597	6.80
7	48103.5	1626.532	3.2516	11.81
8	48143.6	1621.636	3.2418	6.70
9	48302.8	1602.161	3.2029	5.24
10	49061.0	1509.469	3.0176	6.47
11	49078.3	1507.353	3.0134	8.28
12	49148.8	1498.734	2.9962	7.18
13	49166.2	1496.599	2.9919	9.17
14	50325.3	1354.880	2.7086	8.80
15	50364.6	1350.079	2.6990	8.52
16	50413.3	1344.121	2.6871	7.63
17	50452.6	1339.320	2.6775	7.28
18	51115.8	1258.233	2.5154	12.60
19	53153.8	1009.049	2.0172	8.08
20	53178.7	1006.005	2.0111	8.10
21	53269.1	994.957	1.9890	9.30
22	53294.0	991.909	1.9829	9.37
23	54455.8	849.864	1.6990	4.25
24	54493.5	845.254	1.6898	4.13
25	54539.9	839.578	1.6784	6.16
26	54686.0	821.722	1.6427	5.65
27	54774.3	810.917	1.6211	10.05
28	54954.8	788.852	1.5770	15.00
29	55042.8	778.087	1.5555	8.16

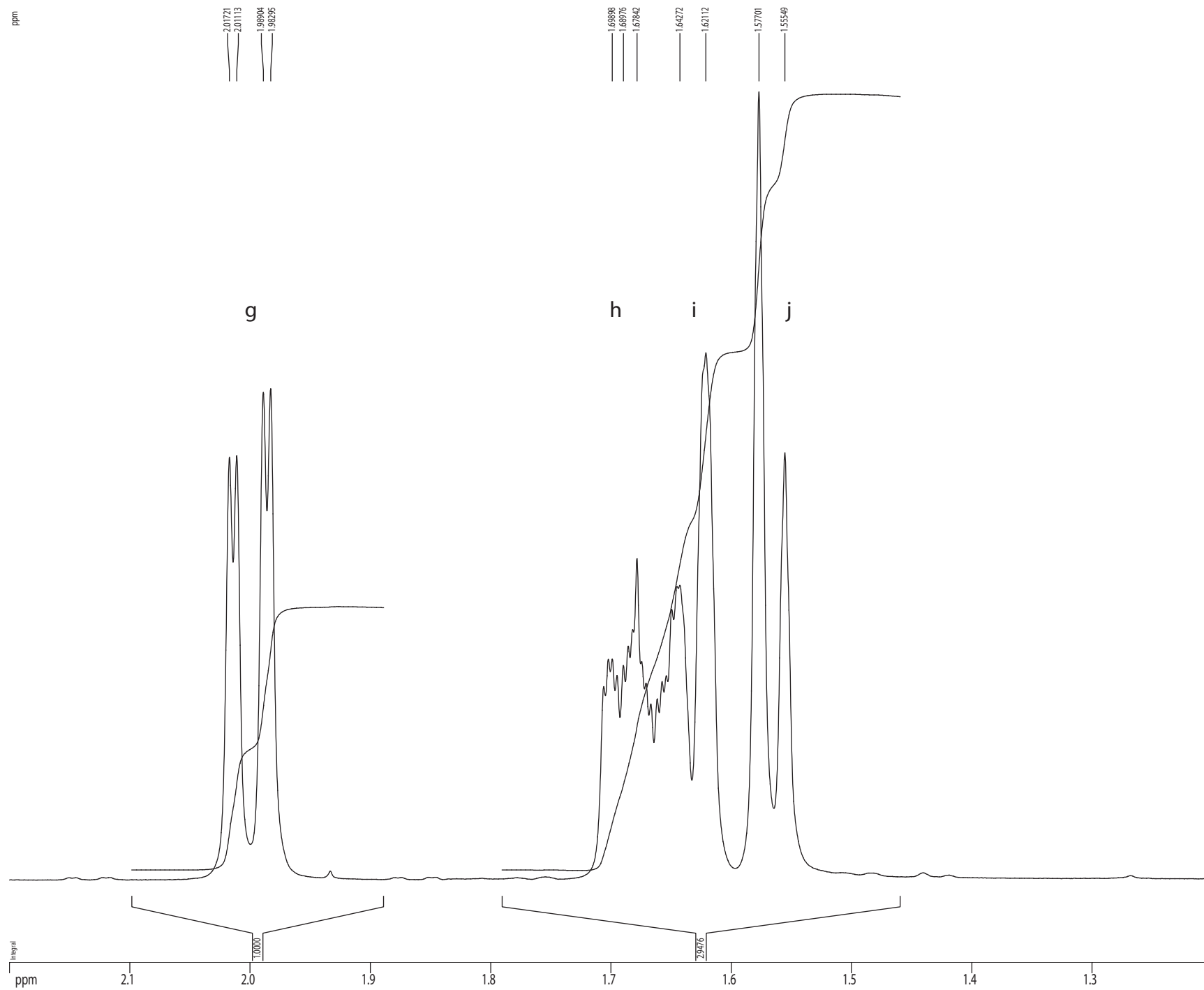
¹H spectrum



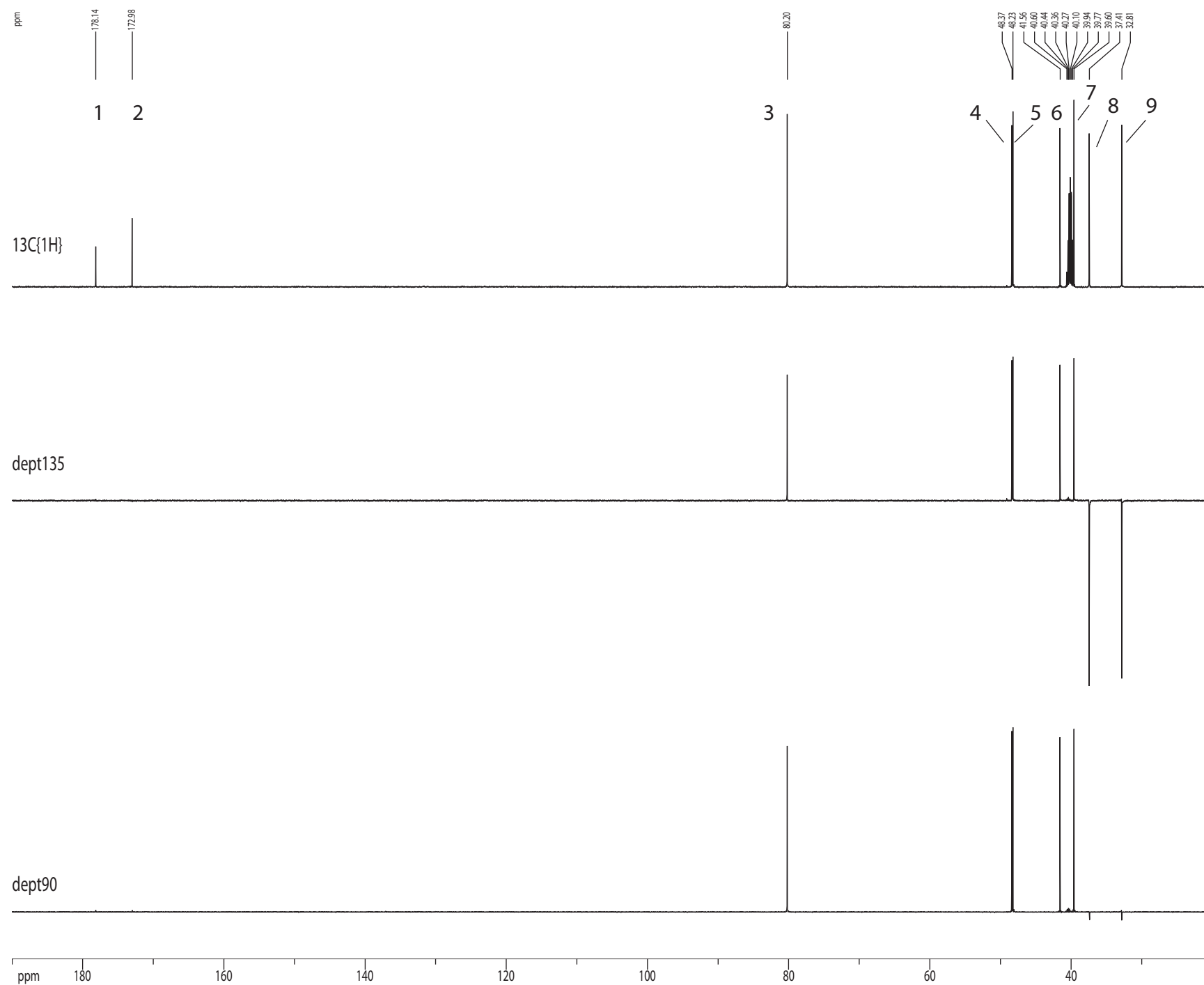
¹H spectrum



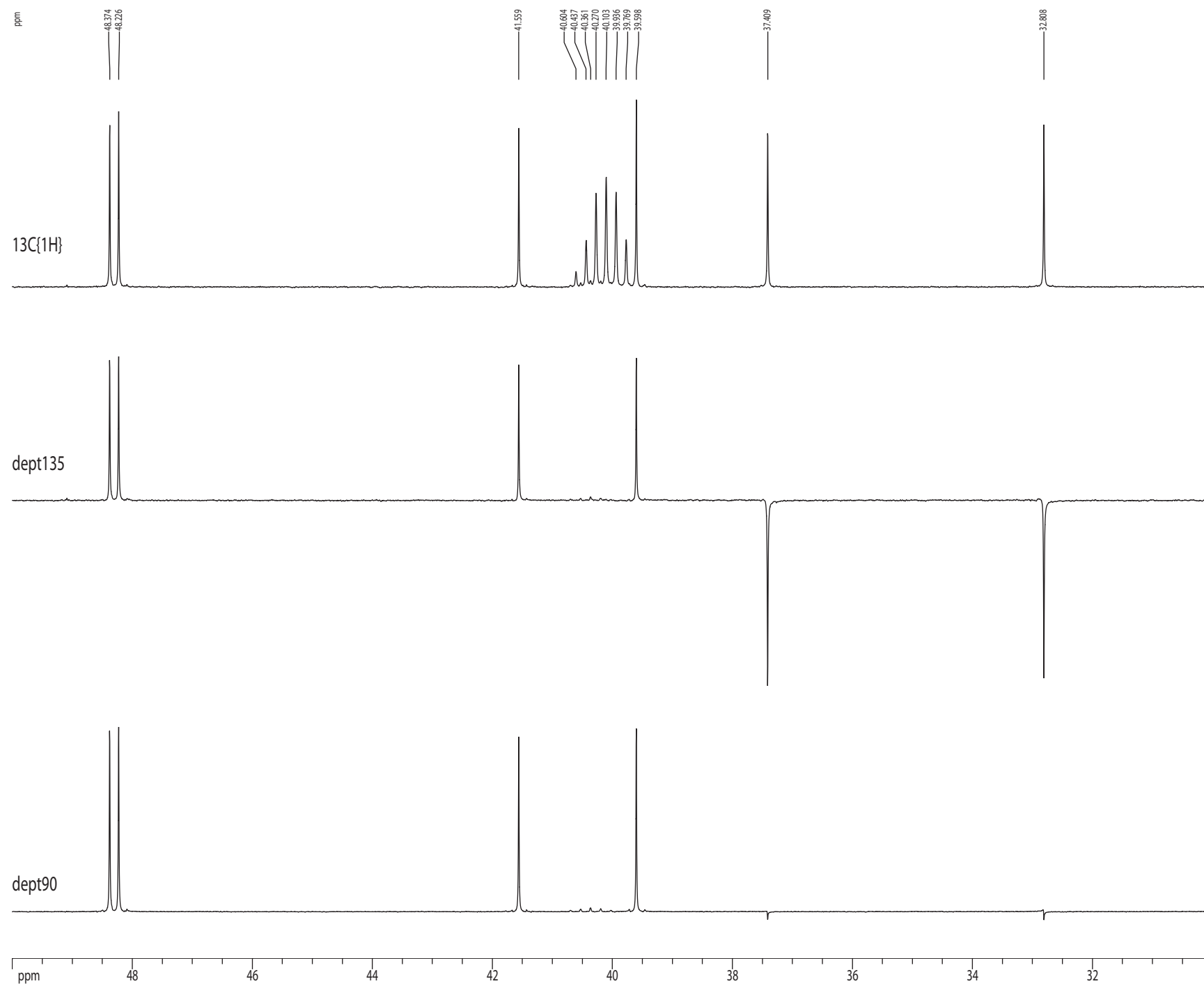
¹H spectrum



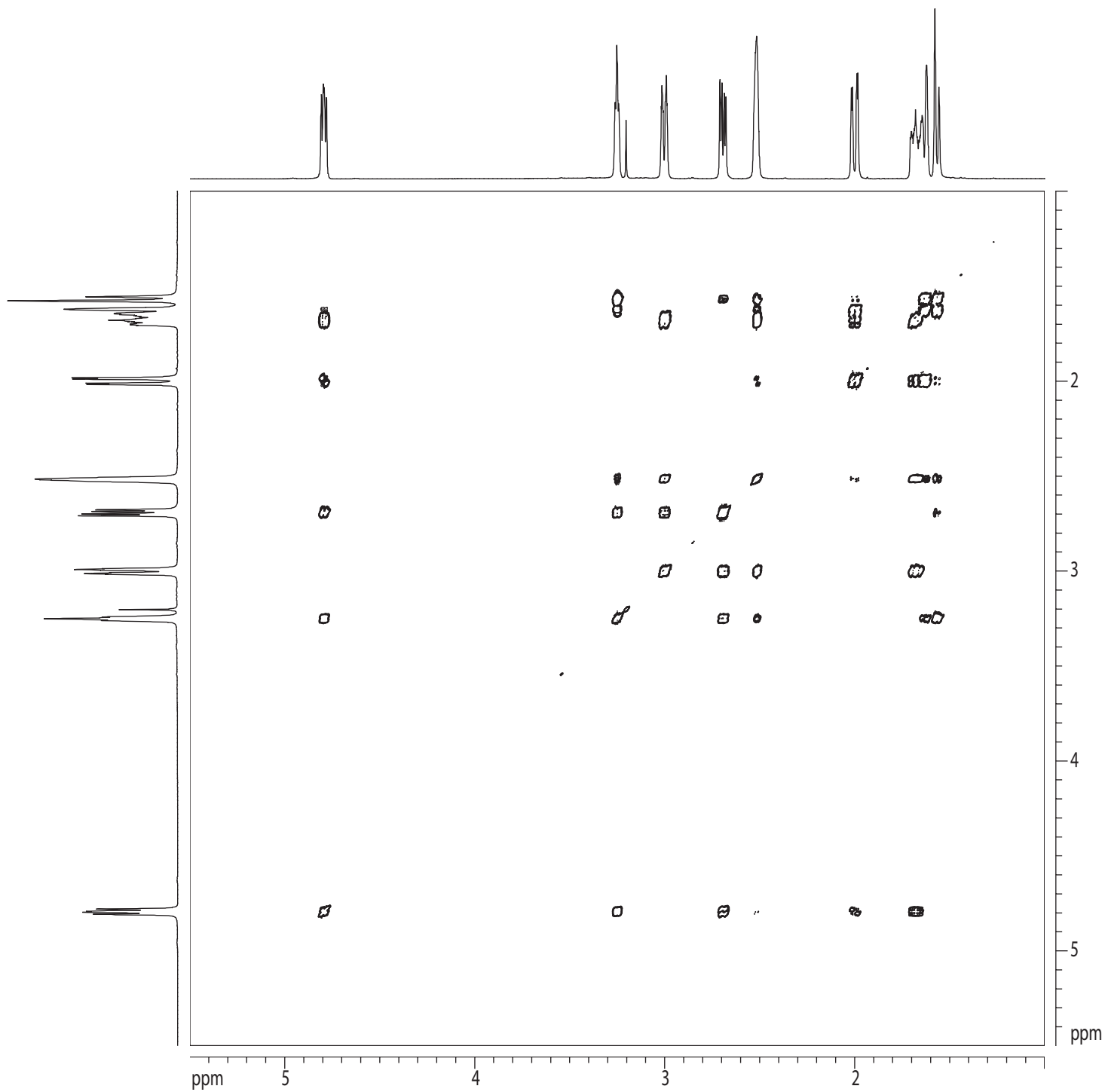
Z-restored spin-echo ^{13}C spectrum with ^1H decoupling



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



gcosy60



Current Data Parameters
USER nmr12t
NAME Fin_3_500
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
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INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG cosygp60.prd
TD 2048
SOLVENT DMSO
NS 4
DS 16
SWH 2500.000 Hz
FIDRES 1.220703 Hz
AQ 0.4096500 sec
RG 4
DW 200.000 usec
DE 6.00 usec
TE 318.0 K
d0 0.00000300 sec
D1 1.00000000 sec
d13 0.00000300 sec
D16 0.00020000 sec
IN0 0.00040000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
PL1 1.60 dB
SFO1 500.2215006 MHz

===== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPNAM2 sine.100
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GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 17.00 %
GPZ2 17.00 %
PT6 1000.00 usec

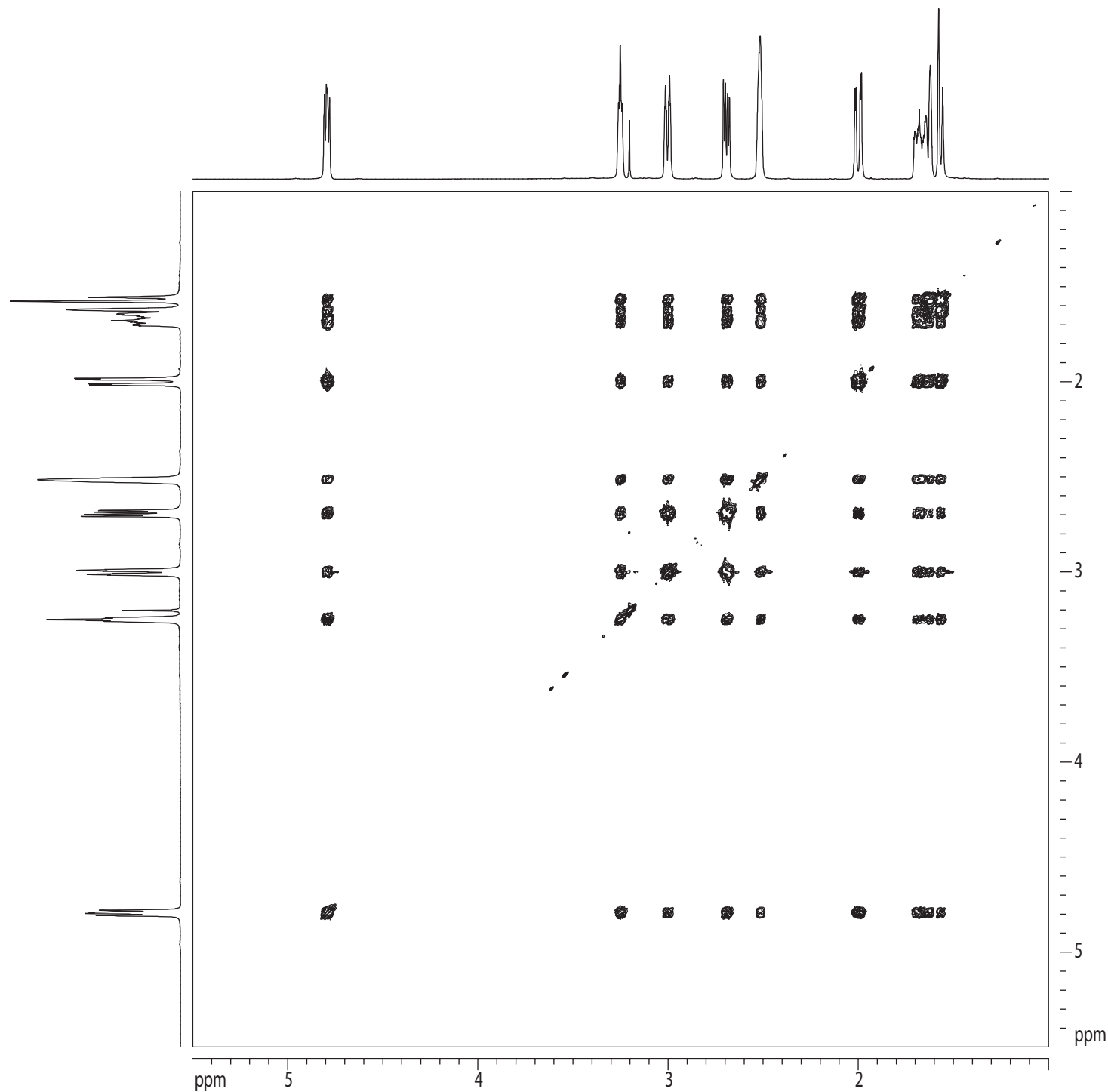
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SFO1 500.2215 MHz
FIDRES 4.882812 Hz
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F2 - Processing parameters
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SF 500.2200000 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 QF
SF 500.2200000 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

2D NMR plot parameters
CX2 15.00 cm
CX1 15.00 cm
F2PLO 5.499 ppm
F2LO 2750.65 Hz
F2PHI 1.000 ppm
F2HI 500.22 Hz
F1PLO 5.499 ppm
F1LO 2750.65 Hz
F1PHI 0.999 ppm
F1HI 499.67 Hz
F2PPMCM 0.29992 ppm/cm
F2HZCM 150.02838 Hz/cm
F1PPMCM 0.30000 ppm/cm
F1HZCM 150.06511 Hz/cm

gtocsy



Current Data Parameters
USER nmr12t
NAME Fin_3_500
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121210
Time 21.29
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG mlevup_mo
TD 2048
SOLVENT DMSO
NS 4
DS 16
SWH 2500.000 Hz
FIDRES 1.220703 Hz
AQ 0.4096500 sec
RG 4
DW 200.000 usec
DE 6.00 usec
TE 318.0 K
d0 0.00000300 sec
D1 2.00000000 sec
D9 0.06000000 sec
d12 0.00002000 sec
D16 0.00020000 sec
FACTOR1 4
INO 0.00040000 sec
I1 24
SCALEF 6

===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
p5 23.34 usec
P6 35.00 usec
p7 70.00 usec
P17 2500.00 usec
PL1 1.60 dB
PL10 15.20 dB
SFO1 500.2215006 MHz

===== GRADIENT CHANNEL =====
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GPNAM2 sine.100
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GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 10.00 %
GPZ2 10.00 %
P16 1000.00 usec

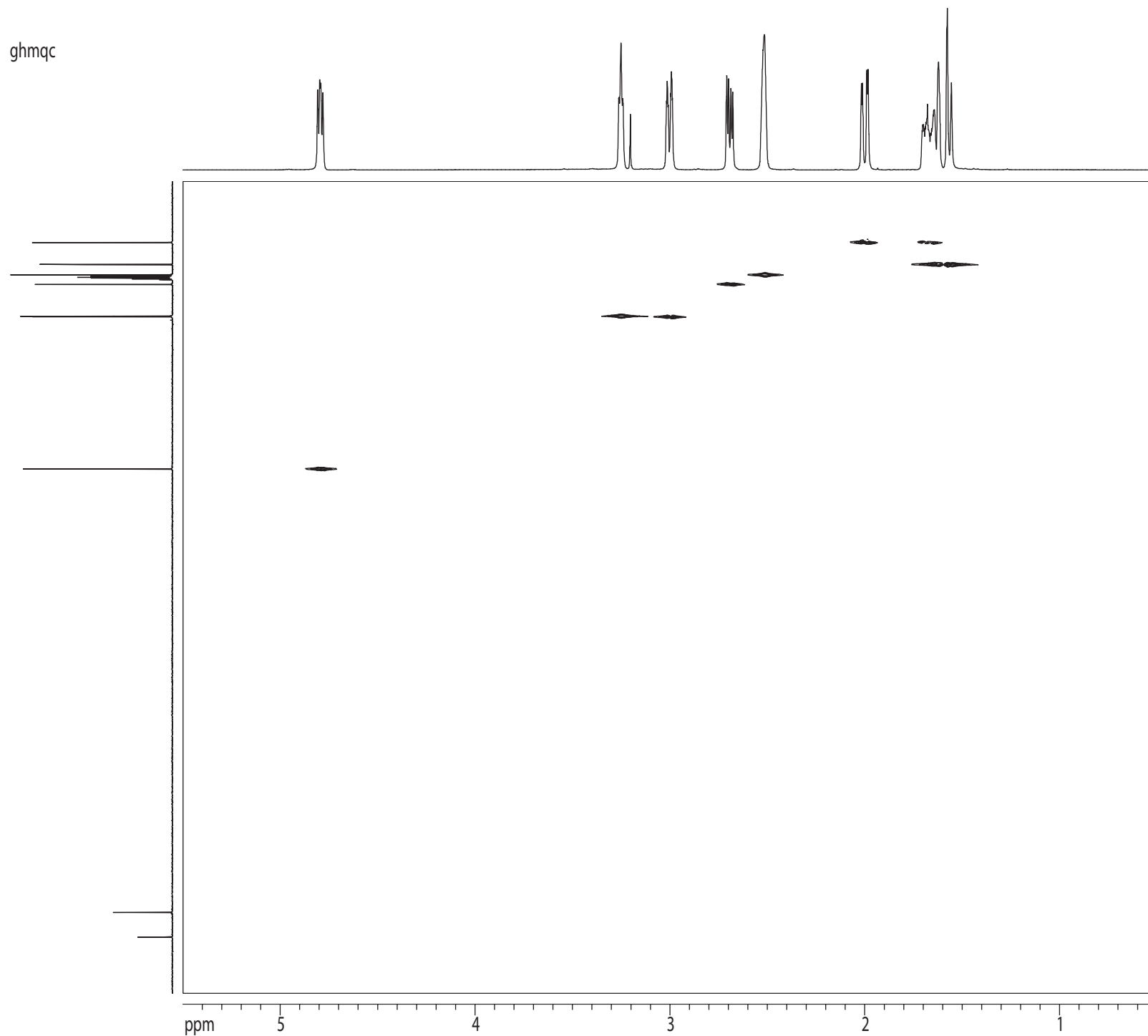
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SFO1 500.2215 MHz
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SW 4.998 ppm
FnMODE undefined

F2 - Processing parameters
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SF 500.2200000 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 OF
SF 500.2200000 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

2D NMR plot parameters
CX2 15.00 cm
CX1 15.00 cm
F2PLO 5.499 ppm
F2LO 2750.65 Hz
F2PHI 0.999 ppm
F2HI 499.67 Hz
F1PLO 5.499 ppm
F1LO 2750.65 Hz
F1PHI 0.999 ppm
F1HI 499.67 Hz
F2PPMCM 0.30000 ppm/cm
F2HZCM 150.06511 Hz/cm
F1PPMCM 0.30000 ppm/cm
F1HZCM 150.06511 Hz/cm

ghmqc



Current Data Parameters
USER nmr12t
NAME Fin_3_500
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121210
Time 22:58
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG inv4gp.wu
TD 2048
SOLVENT DMSO
NS 8
DS 16
SWH 2500.000 Hz
FIDRES 1.220703 Hz
AQ 0.4096500 sec
RG 3251
DW 200.000 usec
DE 6.50 usec
TE 318.0 K
CN22 145.0000000
d0 0.00000300 sec
d1 1.00000000 sec
d2 0.00344628 sec
d12 0.00002000 sec
d13 0.00000300 sec
D16 0.00020000 sec
d20 0.00242528 sec
IN0 0.00002340 sec

===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
p2 15.00 usec
PL1 1.60 dB
SFO1 500.2215006 MHz

===== CHANNEL f2 =====
CPDPRG2 garp
NUC2 13C
P3 15.50 usec
PCPD2 65.00 usec
PL2 -1.00 dB
PL12 11.30 dB
SFO2 125.7936259 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 30.00 %
GPZ2 18.00 %
GPZ3 24.00 %
P16 1000.00 usec

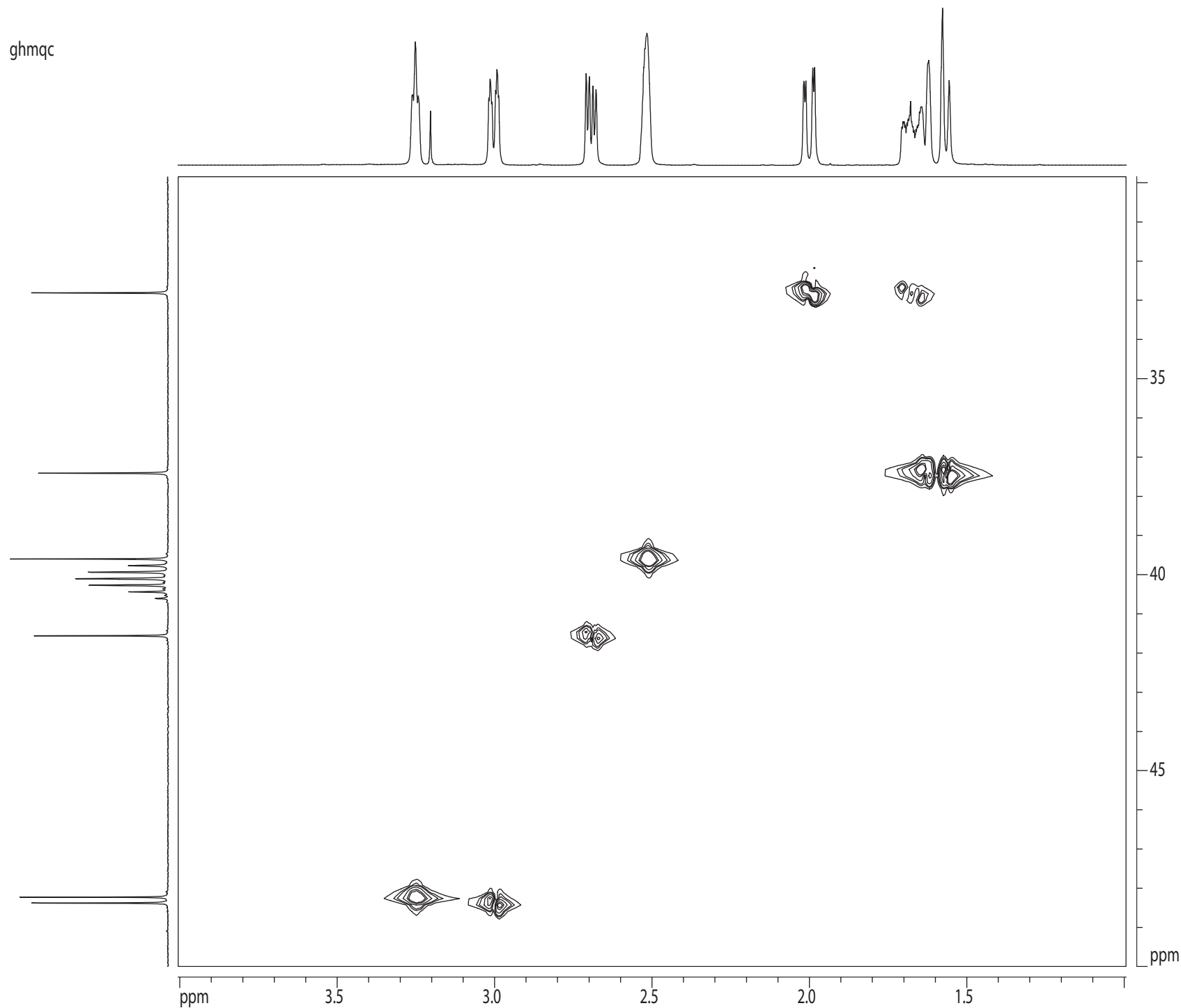
F1 - Acquisition parameters
ND0 2
TD 512
SFO1 125.7936 MHz
FIDRES 41.733440 Hz
SW 169.862 ppm
FrnMODE undefined

F2 - Processing parameters
SI 1024
SF 500.2200000 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

F1 - Processing parameters
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MC2 QF
SF 125.7804190 MHz
WDW QSINE
SSB 3
LB 0.00 Hz
GB 0

2D NMR plot parameters
CK2 18.00 cm
CK1 15.00 cm
F2PLO 5.499 ppm
F2LO 2750.65 Hz
F2PHI 0.501 ppm
F2HI 250.65 Hz
F1PLO 189.940 ppm
F1LO 23890.70 Hz
F1PHI 20.660 ppm
F1HI 2523.17 Hz
F2PPMCM 0.27766 ppm/cm
F2HZCM 138.8889 Hz/cm
F1PPMCM 11.32530 ppm/cm
F1HZCM 1424.50146 Hz/cm

ghmqc



Current Data Parameters
USER nmr12t
NAME Fin_3_500
EXPNO 7
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121210
Time 22:58
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG inv4gp.wu
TD 2048
SOLVENT DMSO
NS 8
DS 16
SWH 2500.000 Hz
FIDRES 1.220703 Hz
AQ 0.4096500 sec
RG 3251
DW 200.000 usec
DE 6.50 usec
TE 318.0 K
CNST2 145.0000000
d0 0.00000300 sec
d1 1.00000000 sec
d2 0.00344628 sec
d12 0.00002000 sec
d13 0.00000300 sec
D16 0.00020000 sec
d20 0.00242528 sec
INO 0.00002340 sec

===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
p2 15.00 usec
PL1 1.60 dB
SFO1 500.2215006 MHz

===== CHANNEL f2 =====
CPDPRG2 garp
NUC2 13C
P3 15.50 usec
PCPD2 65.00 usec
PL2 -1.00 dB
PL12 11.30 dB
SFO2 125.7936259 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 30.00 %
GPZ2 18.00 %
GPZ3 24.00 %
P16 1000.00 usec

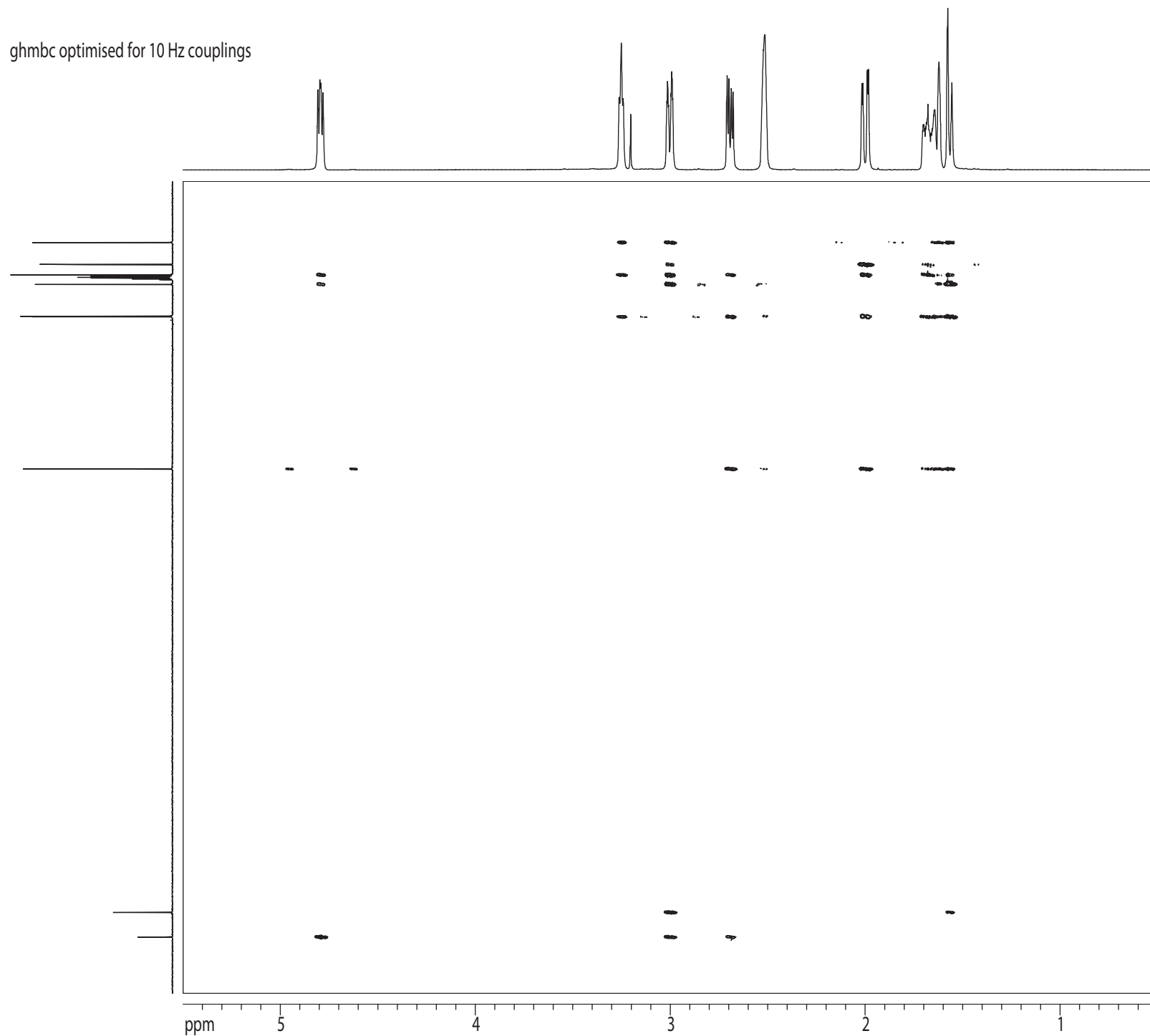
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TD 512
SFO1 125.7936 MHz
FIDRES 41.733440 Hz
SW 169.862 ppm
FrnMODE undefined

F2 - Processing parameters
SI 1024
SF 500.2200000 MHz
WDW EM
SSB 0
LB 5.00 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 125.7804190 MHz
WDW QSINE
SSB 3
LB 0.00 Hz
GB 0

2D NMR plot parameters
CX2 18.00 cm
CX1 15.00 cm
F2PLO 4.005 ppm
F2LO 2003.58 Hz
F2PHI 0.994 ppm
F2HI 497.23 Hz
F1PLO 50.000 ppm
F1LO 6289.02 Hz
F1PHI 29.848 ppm
F1HI 3754.31 Hz
F2PPMCM 0.16730 ppm/cm
F2HZCM 83.68597 Hz/cm
F1PPMCM 1.34346 ppm/cm
F1HZCM 168.98074 Hz/cm

ghmbc optimised for 10 Hz couplings



Current Data Parameters
USER nm12t
NAME Fin_3_500
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121211
Time 0.37
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PROBHD 5 mm CPTCI 1H-
PULPROG ghmbcwu
TD 4096
SOLVENT DMSO
NS 8
DS 16
SWH 2500.000 Hz
FIDRES 0.610352 Hz
AQ 0.8192500 sec
RG 11585.2
DW 200.000 usec
DE 6.00 usec
TE 318.0 K
CNST2 145.0000000
d0 0.00000300 sec
D1 1.25000000 sec
d2 0.00344828 sec
D6 0.05000000 sec
d13 0.00000300 sec
D16 0.00020000 sec
IN0 0.00002340 sec

===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
p2 15.00 usec
PL1 1.60 dB
SFO1 500.2215006 MHz

===== CHANNEL f2 =====
NUC2 13C
P3 15.50 usec
PL2 -1.00 dB
SFO2 125.7936259 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 40.00 %
P16 1000.00 usec

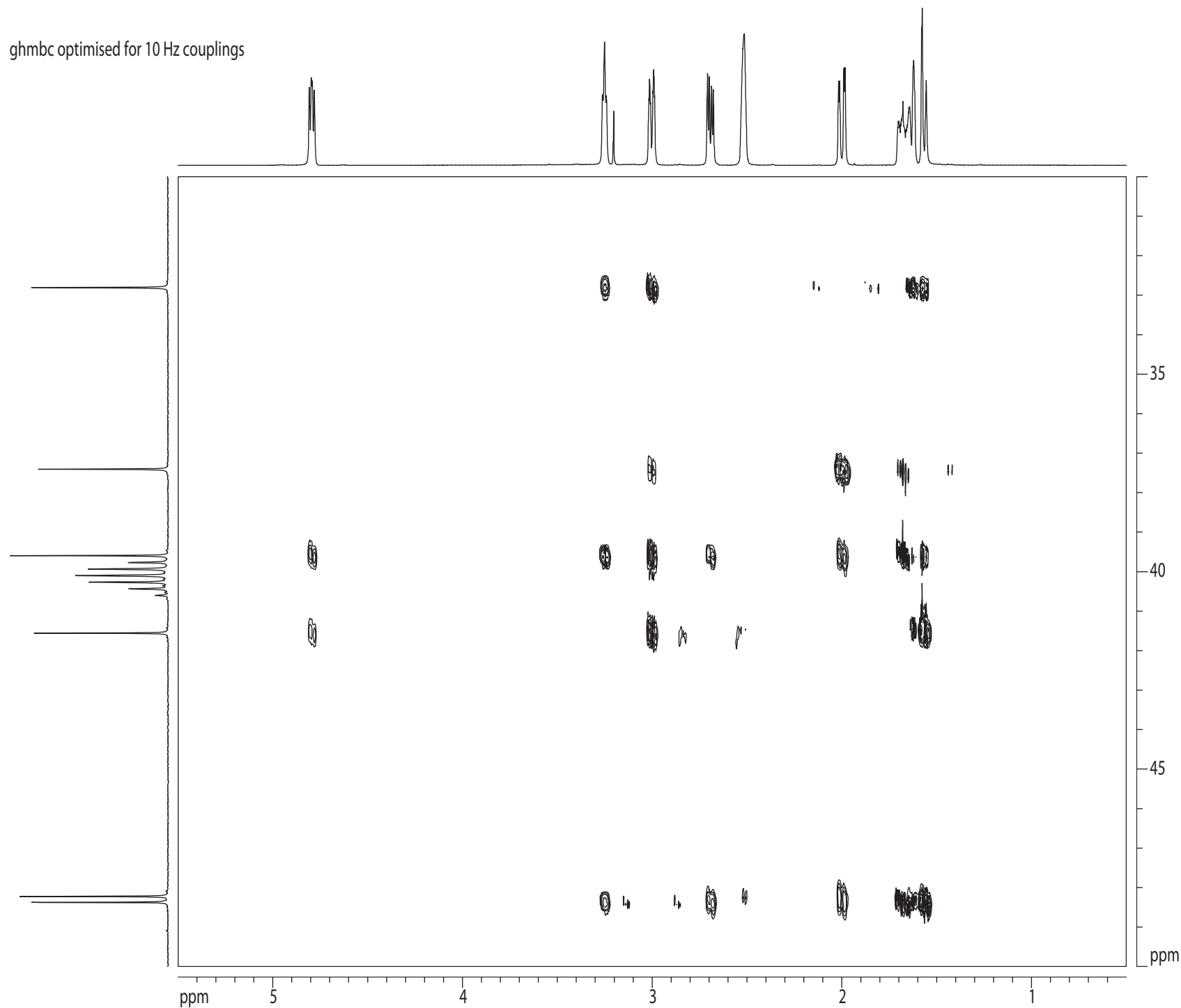
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ND0 2
TD 512
SFO1 125.7936 MHz
FIDRES 41.733440 Hz
SW 169.862 ppm
F1MODE undefined

F2 - Processing parameters
SI 2048
SF 500.2200000 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 125.7804190 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

2D NMR plot parameters
CX2 18.00 cm
CX1 15.00 cm
F2PLO 5.499 ppm
F2LO 2750.65 Hz
F2PHI 0.501 ppm
F2HI 250.65 Hz
F1PLO 189.940 ppm
F1LO 23890.70 Hz
F1PHI 20.060 ppm
F1HI 2523.17 Hz
F2PPMCM 0.27766 ppm/cm
F2HZCM 138.88889 Hz/cm
F1PPMCM 11.32530 ppm/cm
F1HZCM 1424.50146 Hz/cm

ghmbc optimised for 10 Hz couplings



Current Data Parameters

USER	nm12t
NAME	Fin_3_500
EXPNO	8
PROCNO	1

F2 - Acquisition Parameters

Date_	20121211
Time	0.37
INSTRUM	cryo500
PROBHD	5 mm CPTCI 1H-
PULPROG	ghmbcwu
TD	4096
SOLVENT	DMSO
NS	8
DS	16
SWH	2500.000 Hz
FIDRES	0.610352 Hz
AQ	0.8192500 sec
RG	11585.2
DW	200.000 usec
DE	6.00 usec
TE	318.0 K
CNST2	145.0000000
d0	0.00000300 sec
D1	1.25000000 sec
d2	0.00344828 sec
D6	0.05000000 sec
d13	0.00000300 sec
D16	0.00020000 sec
IN0	0.00002340 sec

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

NUC1	1H
P1	7.50 usec
p2	15.00 usec
PL1	1.60 dB
SFO1	500.2215006 MHz

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

NUC2	13C
P3	15.50 usec
PL2	-1.00 dB
SFO2	125.7936259 MHz

===== GRADIENT CHANNEL =====

GPVAM1	sine.100
GPVAM2	sine.100
GPVAM3	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	40.00 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	2
TD	512
SFO1	125.7936 MHz
FIDRES	41.733440 Hz
SW	169.862 ppm
FMODE	undefined

F2 - Processing parameters

SI	2048
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SSB	0
LB	0.00 Hz
GB	0
PC	1.40

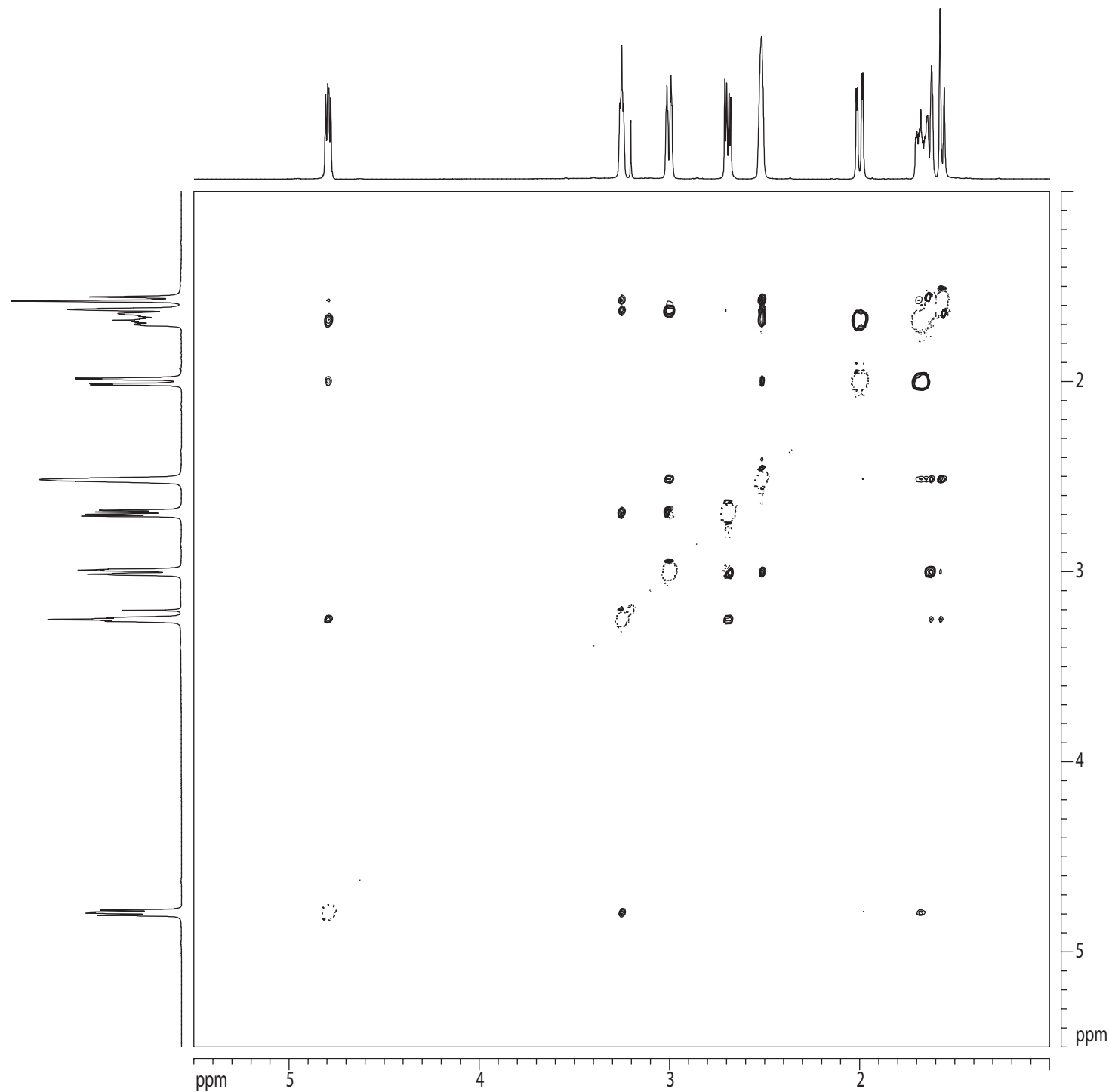
F1 - Processing parameters

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SF	125.7804190 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	18.00 cm
CX1	15.00 cm
F2PLO	5.499 ppm
F2LO	2750.65 Hz
F2PHI	0.501 ppm
F2HI	250.65 Hz
F1PLO	50.000 ppm
F1LO	6289.02 Hz
F1PHI	30.000 ppm
F1HI	3773.41 Hz
F2PPMCM	0.27766 ppm/cm
F2HZCM	138.8889 Hz/cm
F1PPMCM	1.33333 ppm/cm
F1HZCM	167.70723 Hz/cm

full proton
gnoesy



Current Data Parameters
USER nmrl2t
NAME Fin_3_500
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121211
Time 6.49
INSTRUM cryo500
PROBHD 5 mm CPTCI 1H-
PULPROG noesygtp
TD 2048
SOLVENT DMSO
NS 2
DS 16
SWH 6510.417 Hz
FIDRES 3.178914 Hz
AQ 0.1573364 sec
RG 4
DW 76.800 usec
DE 6.00 usec
TE 318.0 K
D0 0.00000300 sec
D1 2.00000000 sec
D8 0.80000001 sec
D16 0.00020000 sec
d20 0.39880002 sec
INO 0.00007680 sec

===== CHANNEL f1 =====
NUC1 1H
P1 7.50 usec
P2 15.00 usec
PL1 1.60 dB
SFO1 500.2235015 MHz

===== GRADIENT CHANNEL =====
GPNAM1 sine.100
GPNAM2 sine.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 40.00 %
GPZ2 -40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
ND0 2
TD 512
SFO1 500.2235 MHz
FIDRES 12.715657 Hz
SW 13.015 ppm
FnMODE undefined

F2 - Processing parameters
SI 1024
SF 500.2200000 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 TPPI
SF 500.2200000 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0

2D NMR plot parameters
CX2 15.00 cm
CX1 15.00 cm
F2PLO 5.500 ppm
F2LO 2751.21 Hz
F2PHI 1.000 ppm
F2HI 500.22 Hz
F1PLO 5.500 ppm
F1LO 2751.21 Hz
F1PHI 1.000 ppm
F1HI 500.22 Hz
F2PPMCM 0.30000 ppm/cm
F2HZCM 150.06599 Hz/cm
F1PPMCM 0.30000 ppm/cm
F1HZCM 150.06599 Hz/cm