Additional File 8

Tether-directed synthesis of highly substituted oxasilacycles *via* an intramolecular allylation employing allylsilanes

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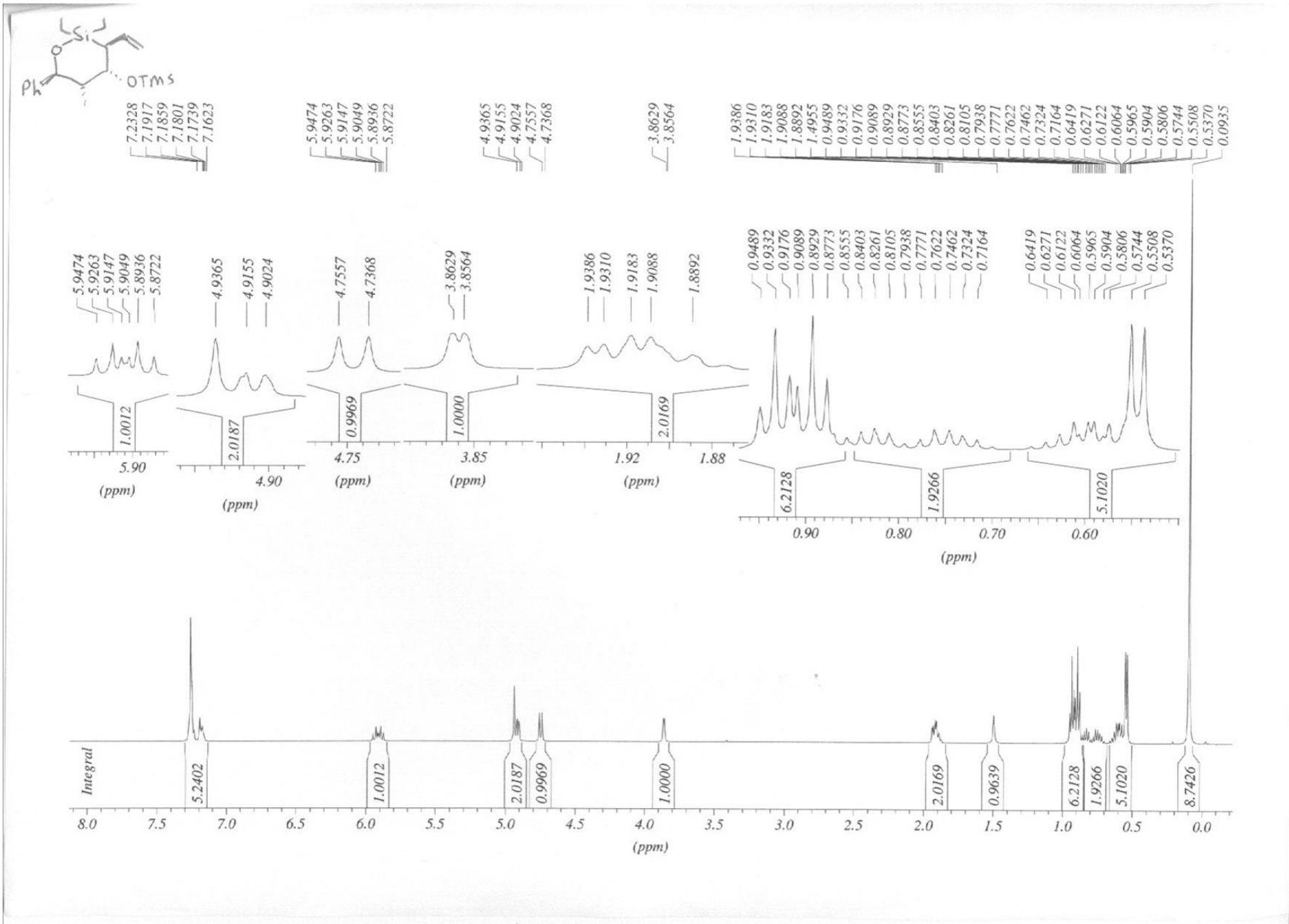
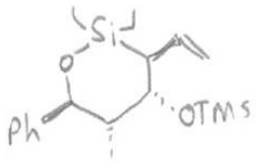
^{1}H-NMR and ^{13}C-NMR Spectra for the following compounds:

14b, 15b

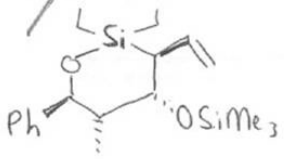

OTMS
Ph
7.2328
7.1917
7.1859
7.1801
7.1739
7.1623
5.9474
5.9263
5.9147
5.9049
5.8936
5.8722
4.9365
4.9155
4.9024
4.7557
4.7368
3.8629
3.8564
1.9386
1.9310
1.9183
1.9088
1.8892
1.4955
0.9489
0.9332
0.9176
0.9089
0.8929
0.8773
0.8555
0.8403
0.8261
0.8105
0.7938
0.7771
0.7622
0.7462
0.7324
0.7164
0.6419
0.6271
0.6122
0.6064
0.5965
0.5904
0.5806
0.5744
0.5508
0.5370
0.0935
1.0012
2.0187
0.9969
1.0000
2.0169
6.2128
1.9266
5.1020
(ppm)
Integral
5.2402
0.9639
8.7426



144.2575
137.1915
128.0716
127.2231
126.9614
113.8525
77.7930
76.1039
40.8216
38.9818
16.2057
6.6496
6.6258
6.0945
4.8891
0.2260

200 180 160 140 120 100 80 60 40 20 0 -20
(ppm)

Peter Jervis Sample 1, Barcode 3902 in CDCl3 at +27C, set temp
drx500, Gradient COSY90



Current Data Parameters

NAME	jl05pjid
EXPNO	4
PROCNO	1

F2 - Acquisition Parameters

Date_	20050705
Time	21.43
INSTRUM	drx500
PROBHD	5 mm TBI H/C
PULPROG	cosygp
TD	2048
SOLVENT	CDCl3
NS	8
DS	16
SWH	4310.345 Hz
FIDRES	2.104661 Hz
AQ	0.2376180 sec
RG	71.6
DW	116.000 usec
DE	5.50 usec
TE	300.0 K
d0	0.00000300 sec
D1	2.00000000 sec
d13	0.00000300 sec
D16	0.00010000 sec
IN0	0.00023200 sec

CHANNEL f1

NUC1	1H
P0	10.70 usec
P1	10.70 usec
PL1	1.00 dB
SFO1	500.1318867 MHz

GRADIENT CHANNEL

GPNAM1	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

NDO	1
TD	512
SFO1	500.1319 MHz
FIDRES	8.416642 Hz
SW	8.618 ppm

F2 - Processing parameters

SI	2048
SF	500.1300233 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

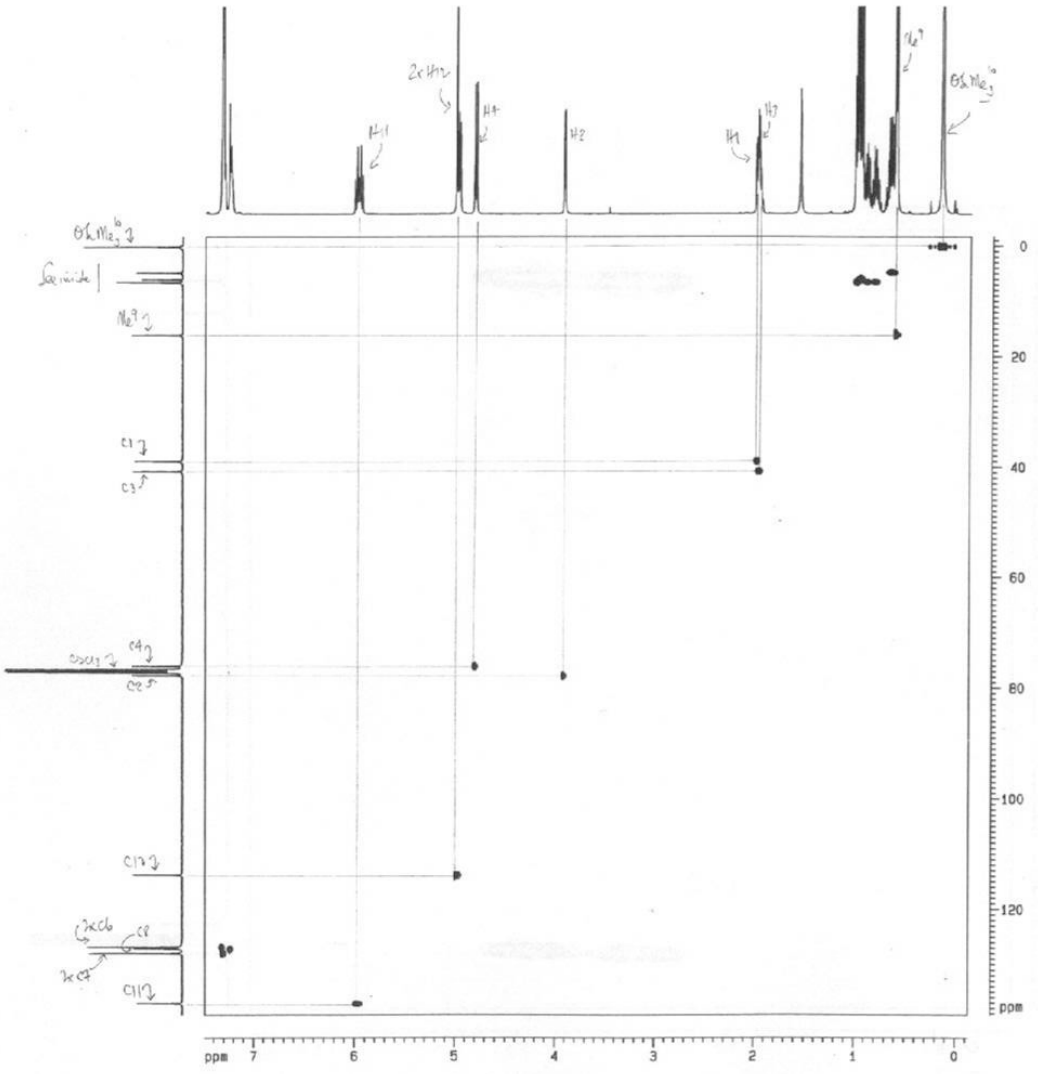
F1 - Processing parameters

SI	1024
MC2	QF
SF	500.1300233 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	20.00 cm
CX1	20.00 cm
F2PLO	7.450 ppm
F2LO	3726.08 Hz
F2PHI	-0.082 ppm
F2HI	-41.26 Hz
F1PLO	7.480 ppm
F1LO	3740.82 Hz
F1PHI	-0.061 ppm
F1HI	-30.73 Hz
F2PPMCM	0.37664 ppm/cm
F2HZCM	188.36713 Hz/cm
F1PPMCM	0.37706 ppm/cm
F1HZCM	188.57759 Hz/cm

Peter Jervis Sample 1, Barcode 3902 in CDCl3 at +27C, set temp
drx500, Gradient HSQC




```
                Current Data Parameters
NAME                    jl05pjid
EXPNO                          2
PROCNO                         1

                F2 - Acquisition Parameters
Date_                   20050706
Time                       18.26
INSTRUM                  drx500
PROBHD      5 mm TBI H/C
PULPROG                 invigptp
TD                         2048
SOLVENT                    CDCl3
NS                             8
DS                            16
SWH                     4310.345 Hz
FIDRES                  2.104661 Hz
AQ                      0.2378188 sec
RG                         32768
DW                       116.000 usec
DE                         5.50 usec
TE                        300.0 K
CNST2                   145.0000000
d0                      0.00000360 sec
D1                      2.00000000 sec
d4                      0.00172414 sec
d11                     0.03000000 sec
d13                     0.00000300 sec
D16                     0.00010000 sec
d20                     0.00110000 sec
d21                     0.00061714 sec
IN0                     0.00001140 sec

============== CHANNEL f1 =============
NUC1                           1H
P1                          12.70 usec
p2                          21.40 usec
PL1                          1.00 dB
SF01                  500.1318867 MHz

============== CHANNEL f2 =============
CPDPRG2                     garp
NUC2                          13C
P3                          12.00 usec
p4                          24.00 usec
PCPD2                       76.00 usec
PL2                         -1.00 dB
PL12                        15.00 dB
SF02                  125.7667893 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                        80.00 %
GPZ2                        30.00 %
GPZ3                        20.10 %
P16                       1000.00 usec

        F1 - Acquisition parameters
ND0                            4
TD                           512
SF01                  125.7688 MHz
FIDRES                42.831688 Hz
SW                      174.369 ppm

        F2 - Processing parameters
SI                          2048
SF                    500.1300233 MHz
WDW                        QSINE
SSB                            2
LB                          0.00 Hz
GB                             0
PC                          1.00

        F1 - Processing parameters
SI                          1024
MC2                         TPPI
SF                    125.7577945 MHz
WDW                        QSINE
SSB                            2
LB                          0.00 Hz
GB                             0

        2D NMR plot parameters
CX2                         17.00 cm
CX1                         17.00 cm
F2PLO                    7.488 ppm
F2LO                    3745.03 Hz
F2PHI                   -0.129 ppm
F2HI                    -64.41 Hz
F1PLO                   139.302 ppm
F1LO                    17518.34 Hz
F1PHI                   -1.701 ppm
F1HI                    -213.98 Hz
F2PPMCM                 0.44805 ppm/cm
F2HZCM                  224.08446 Hz/cm
F1PPMCM                 8.29434 ppm/cm
F1HZCM                  1043.07764 Hz/cm
```

Peter Jarvis Sample 1, Barcode 3902 in CDCl3 at +27C, set temp
drx500, Gradient HMBC

Current Data Parameters

NAME	jl05pjld
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20050705
Time	19.01
INSTRUM	drx500
PROBHD	5 mm TBI H/C
PULPROG	inv4gp1prnd
TD	2048
SOLVENT	CDCl3
NS	8
DS	16
SWH	4310.345 Hz
FIDRES	2.104861 Hz
AQ	0.2376180 sec
RG	32768
DW	116.000 usec
DE	6.50 usec
TE	300.0 K
CNST2	160.0000000
d0	0.00000300 sec
D1	2.00000000 sec
d2	0.00312500 sec
D6	0.10000000 sec
d13	0.00000300 sec
D16	0.00010000 sec
IN0	0.00002080 sec

CHANNEL f1

NUC1	1H
P1	10.70 usec
p2	21.40 usec
PL1	1.00 dB
SFO1	500.1318867 MHz

CHANNEL f2

NUC2	13C
P3	12.00 usec
PL2	-1.00 dB
SFO2	125.7667893 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	512
SFO1	125.7668 MHz
FIDRES	42.831688 Hz
SW	174.369 ppm

F2 - Processing parameters

SI	2048
SF	500.1300233 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	0.20

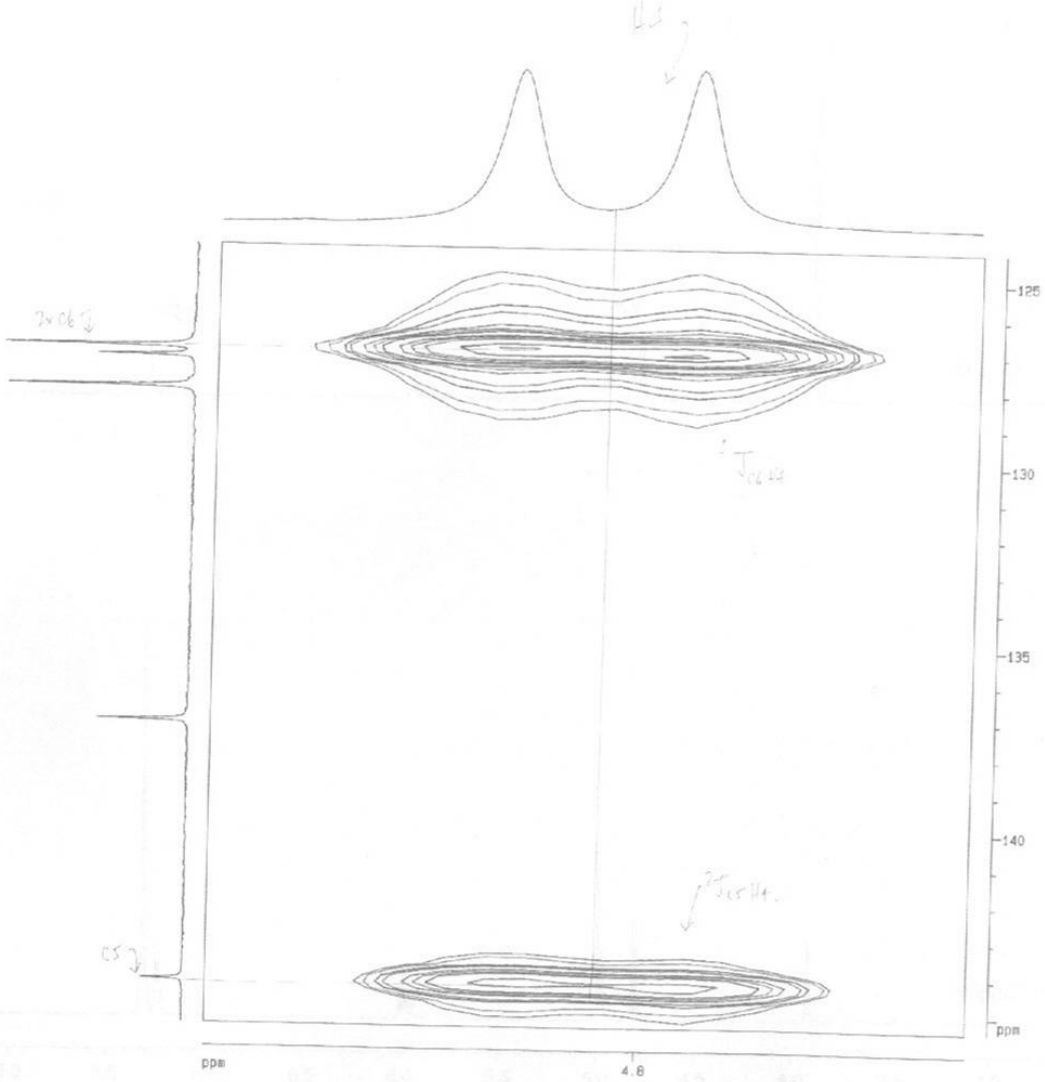
F1 - Processing parameters

SI	1024
MC2	QF
SF	125.7577945 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	17.00 cm
CX1	17.00 cm
F2PLO	6.129 ppm
F2LO	3065.22 Hz
F2PHI	5.753 ppm
F2HI	2862.12 Hz
F1PLO	81.062 ppm
F1LO	10194.12 Hz
F1PHI	36.104 ppm
F1HI	4540.34 Hz
F2PPMCM	0.02154 ppm/cm
F2HZCM	10.77091 Hz/cm
F1PPMCM	2.64457 ppm/cm
F1HZCM	332.57547 Hz/cm

Peter Jervis Sample 1, Barcode 3902 in CDCl3 at +27C, set temp
drx500, Gradient HMBC



Current Data Parameters

NAME	jl06p1d
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20050705
Time	19.01
INSTRUM	drx500
PROBHD	5 mm TBI H/C
PULPROG	inv4gp1p1rnd
TD	2048
SOLVENT	CDCl3
NS	8
DS	16
SWH	4310.345 Hz
FIDRES	2.104661 Hz
AQ	0.2376160 sec
RG	32768
DW	116.000 usec
DE	5.50 usec
TE	300.0 K
CNST2	160.0000000
d0	0.00000300 sec
d1	2.00000000 sec
d2	0.00312500 sec
d6	0.10000000 sec
d13	0.00000300 sec
d16	0.00010000 sec
INO	0.00002280 sec

CHANNEL f1

NUC1	1H
P1	10.70 usec
p2	21.40 usec
PL1	1.00 dB
SFO1	500.1318867 MHz

CHANNEL f2

NUC2	13C
P3	12.00 usec
PL2	-1.00 dB
SFO2	125.7667893 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

NDO	2
TD	512
SFO1	125.7668 MHz
FIDRES	42.831668 Hz
SW	174.369 ppm

F2 - Processing parameters

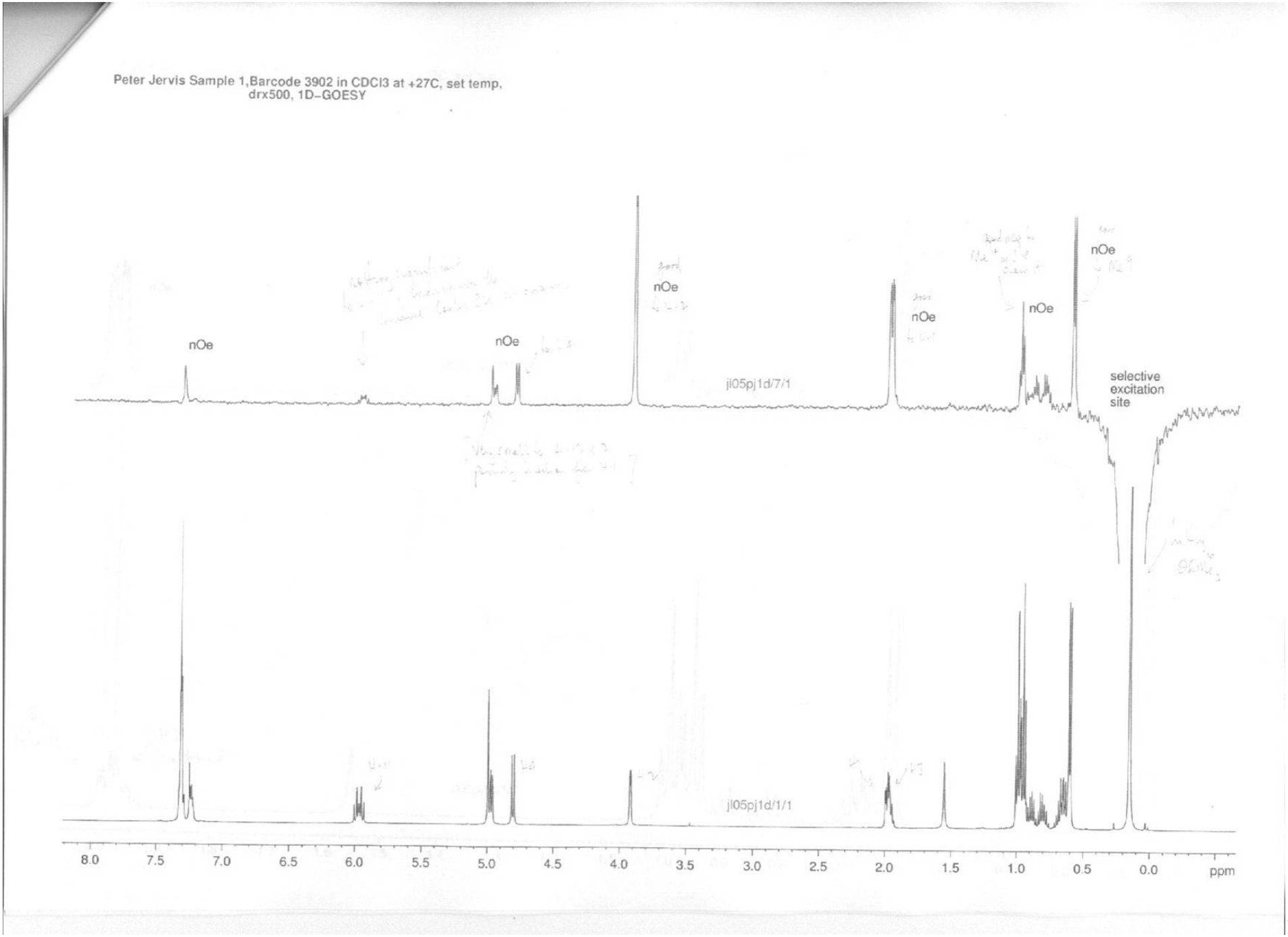
SI	2048
SF	500.1300233 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	0.20

F1 - Processing parameters

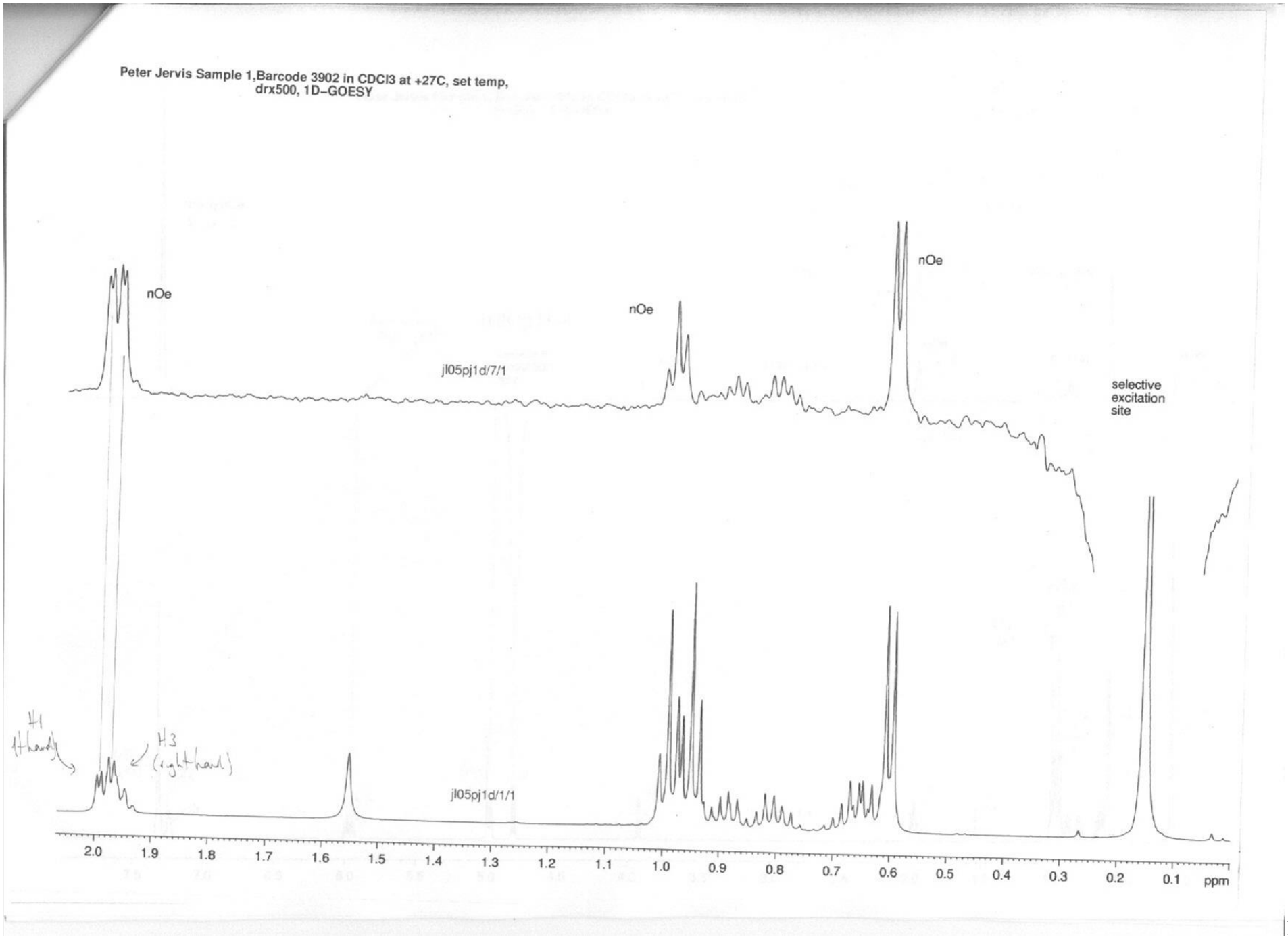
SI	1024
MC2	QF
SF	125.7577945 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

2D NMR plot parameters

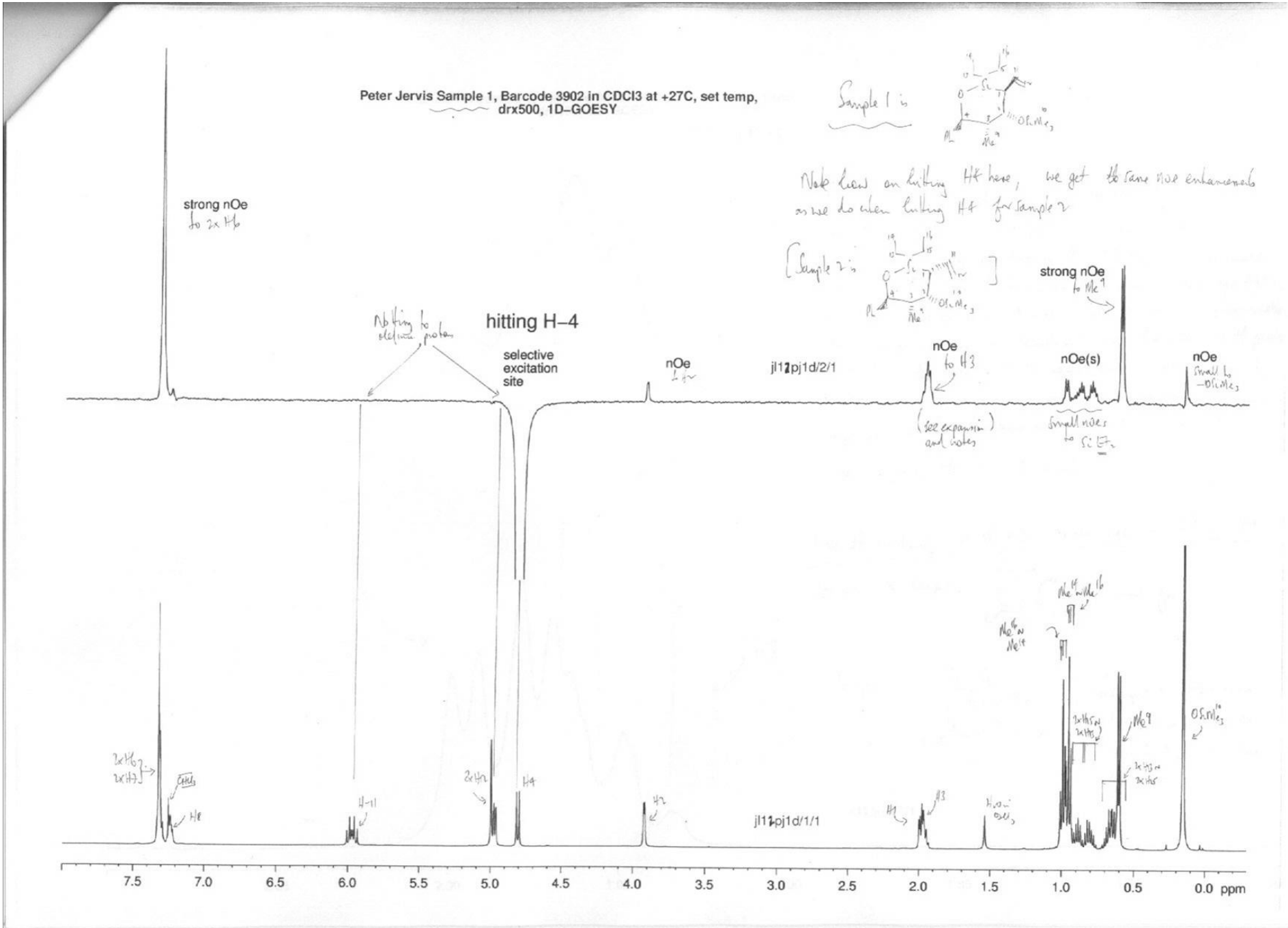
CX2	17.00 cm
CX1	17.00 cm
F2PLO	4.845 ppm
F2LO	2423.30 Hz
F2PHI	4.765 ppm
F2HI	2383.31 Hz
F1PLO	146.433 ppm
F1LO	18289.31 Hz
F1PHI	124.146 ppm
F1HI	15512.33 Hz
F2PPMCM	0.00470 ppm/cm
F2HZCM	2.35227 Hz/cm
F1PPMCM	1.25215 ppm/cm
F1HZCM	157.46945 Hz/cm

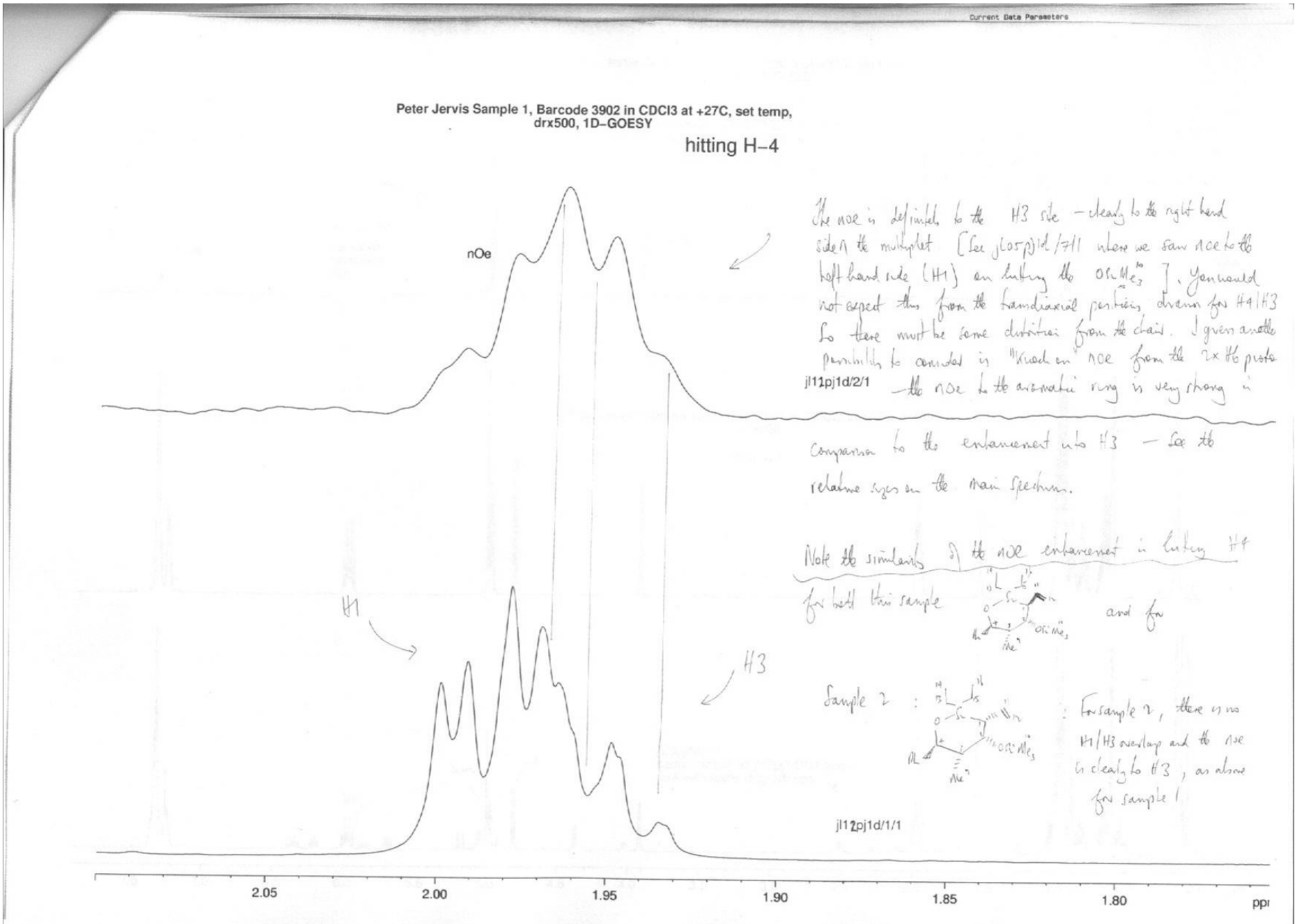

Peter Jervis Sample 1,Barcode 3902 in CDCl3 at +27C, set temp,
drx500, 1D-GOESY
nOe
nOe
nOe
nOe
nOe
nOe
jl05pj1d/7/1
selective
excitation
site
jl05pj1d/1/1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

14b


Peter Jervis Sample 1,Barcode 3902 in CDCl3 at +27C, set temp,
drx500, 1D–GOESY
nOe
nOe
nOe
jl05pj1d/7/1
selective
excitation
site
H1
(left hand)
H3
(right hand)
jl05pj1d/1/1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
ppm

14b

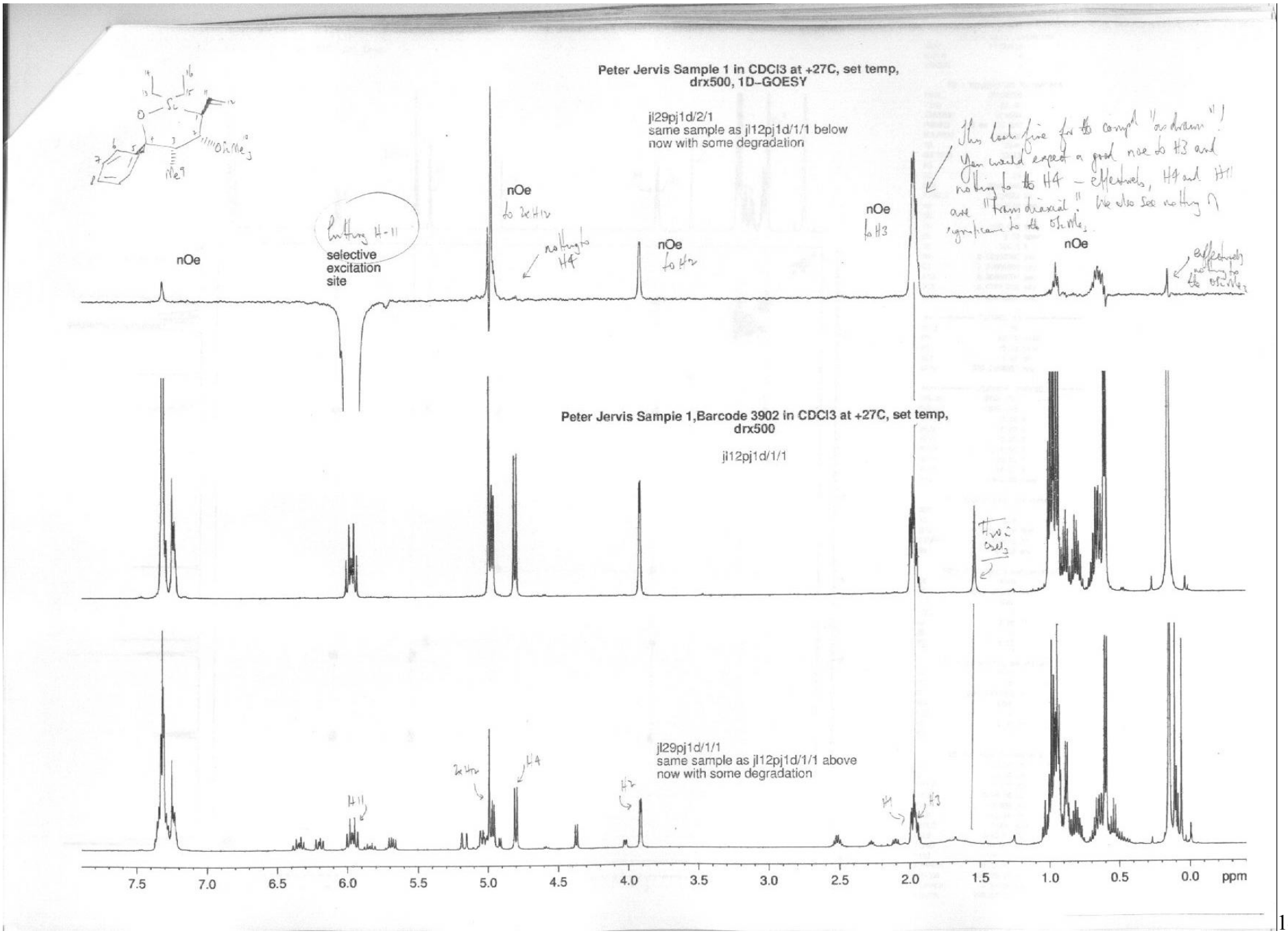

Peter Jervis Sample 1, Barcode 3902 in CDCl3 at +27C, set temp,
drx500, 1D–GOESY
Sample 1 is
Note here on hitting H4 here, we get the same nOe enhancements as we do when hitting H4 for sample 2
[Sample 2 is]
strong nOe to 2x H6
hitting H–4
selective excitation site
Nothing to selective protons
nOe
jl11pj1d/2/1
nOe to H3
(see expansion and notes)
nOe(s)
small nOes to SiEt2
strong nOe to Me9
nOe small to OSiMe3
jl11pj1d/1/1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0 ppm

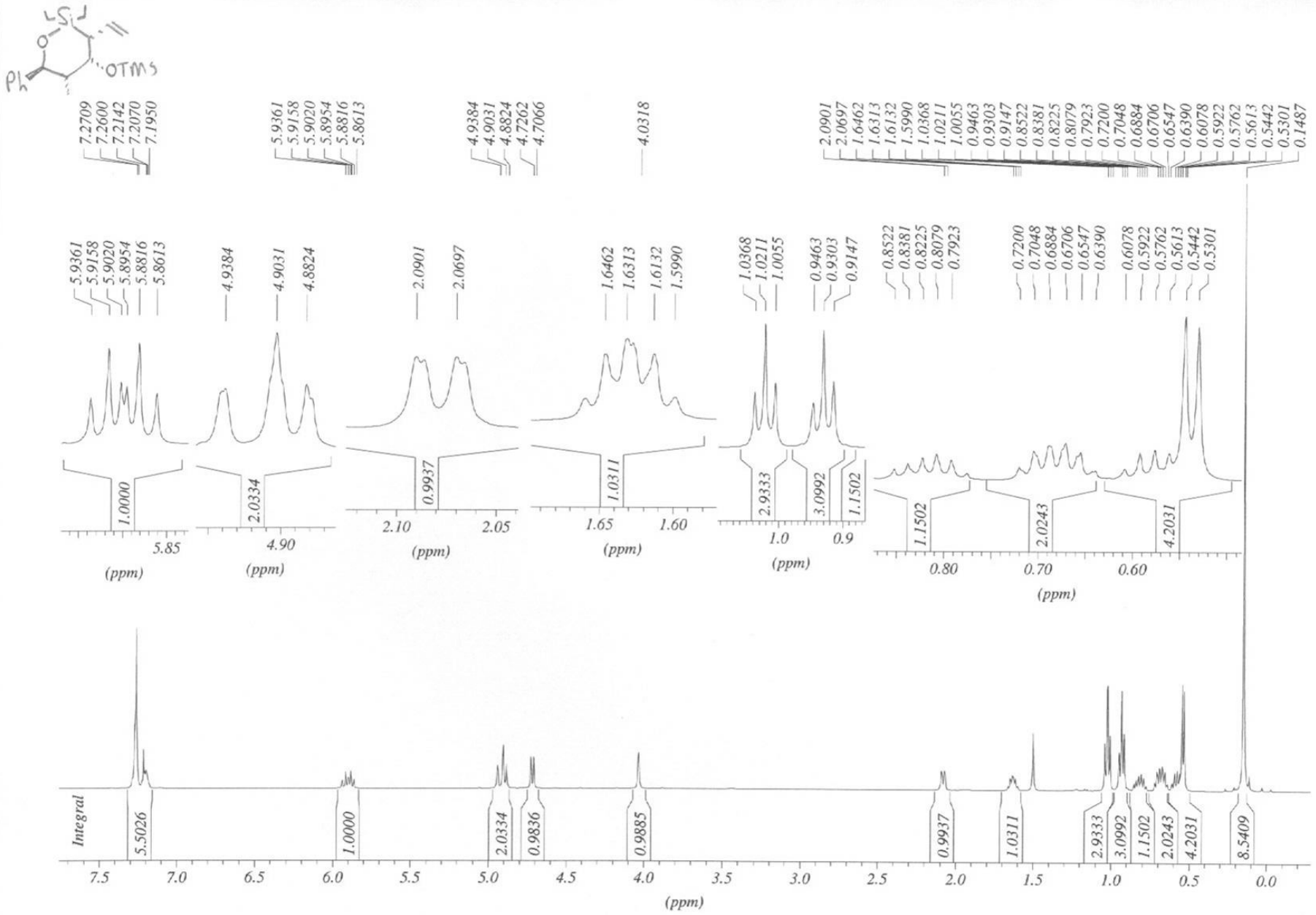


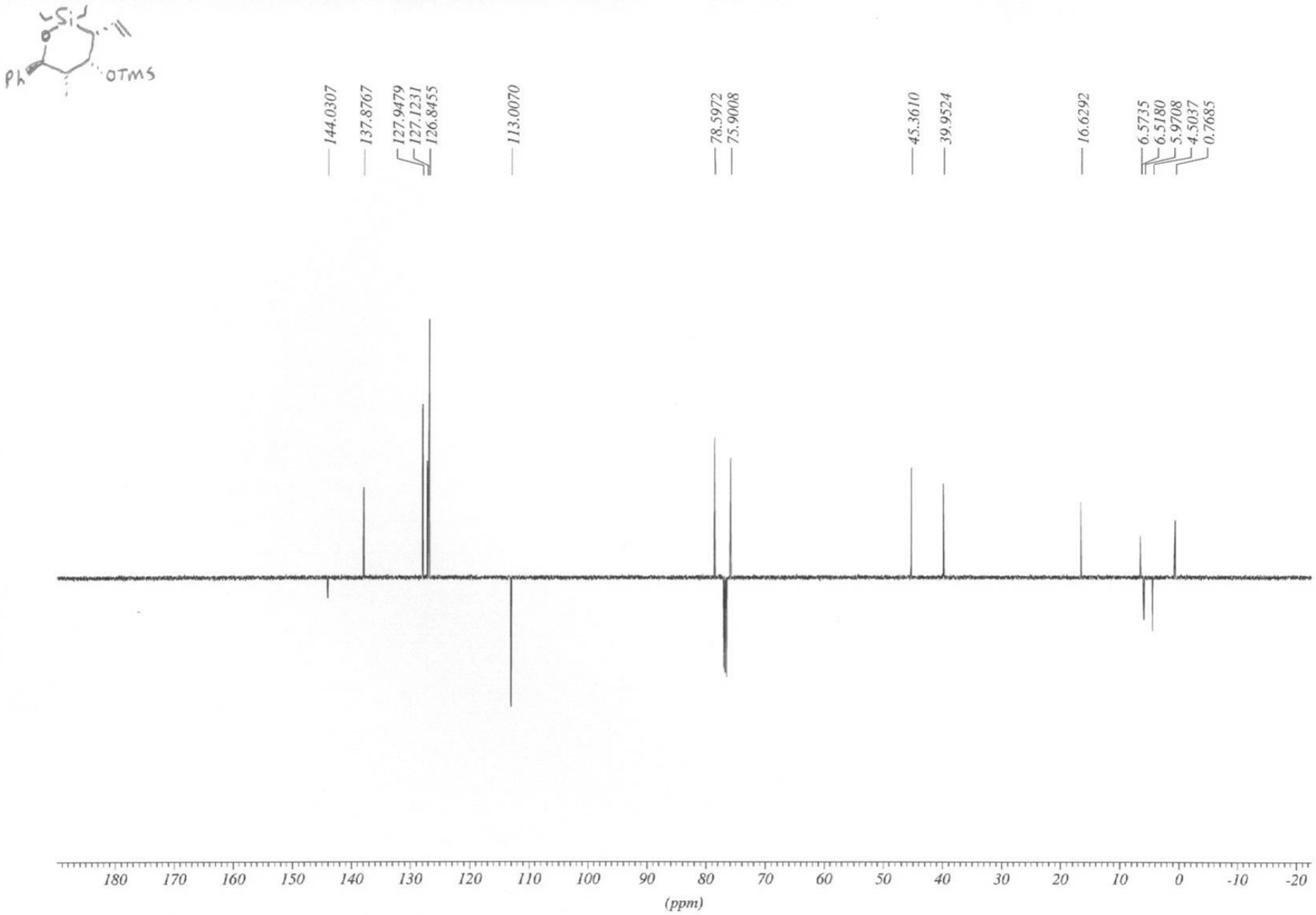
The noe is definitely to the H3 side – clearly to the right hand side of the multiplet [See jl05pj1d/7/1 where we saw noe to the left hand side (H1) on hitting the $OSiMe_3$]. You would not expect this from the transdiaxial positioning of H4/H3 so there must be some distortion from the chair. I guess another possibility to consider is "knock on" noe from the 2x H6 protons – the noe to the aromatic ring is very strong in comparison to the enhancement into H3 – see the relative sizes on the main spectrum.

Note the similarity of the noe enhancement in hitting H4 for both this sample and for

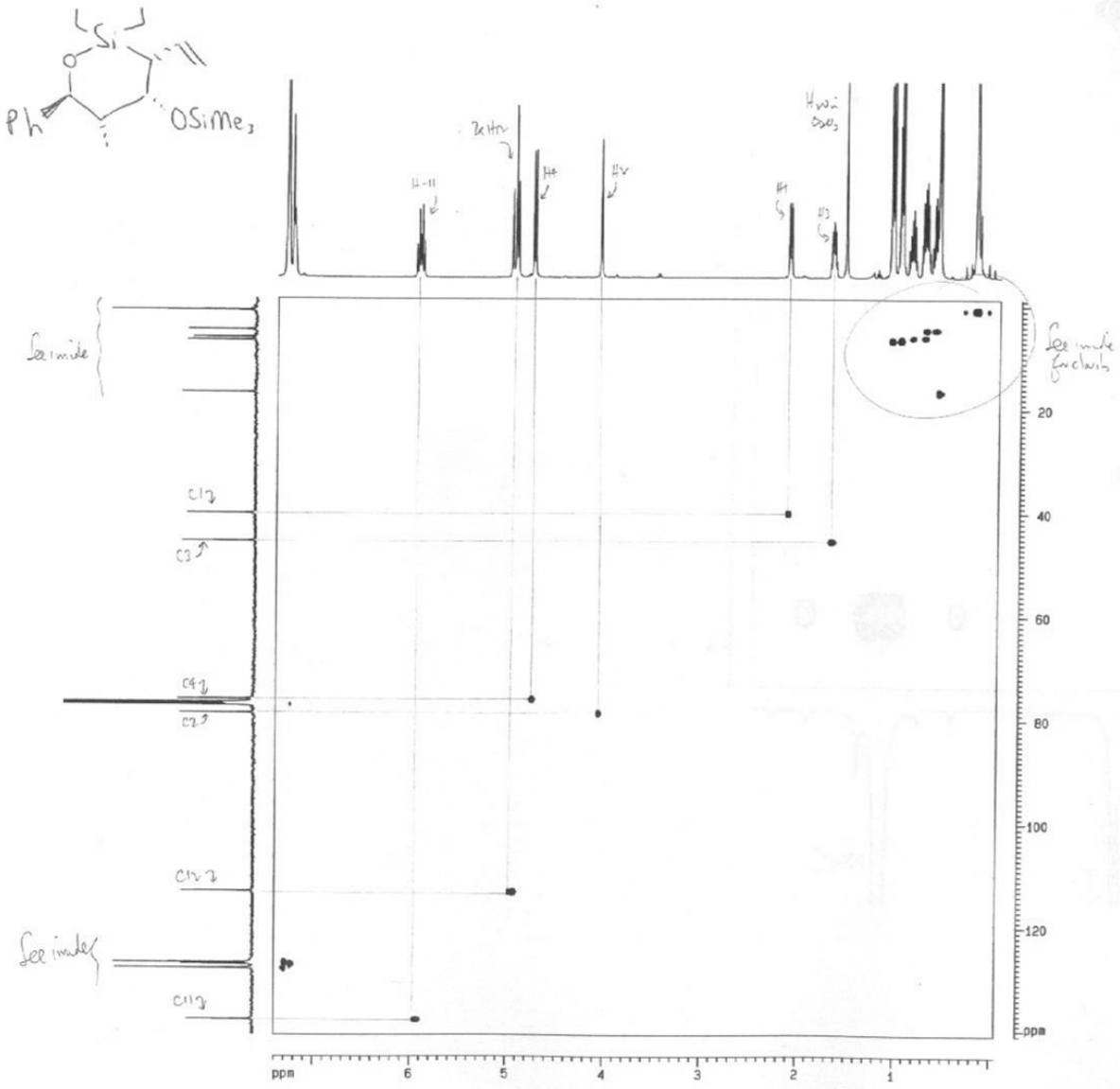
Sample 2 : : For sample 2, there is no H1/H3 overlap and the noe is clearly to H3, as above for sample 1


Peter Jervis Sample 1 in CDCl3 at +27C, set temp,
drx500, 1D-GOESY
jl29pj1d/2/1
same sample as jl12pj1d/1/1 below
now with some degradation
nOe
selective
excitation
site
nOe
nOe
nOe
nOe
Peter Jervis Sample 1,Barcode 3902 in CDCl3 at +27C, set temp,
drx500
jl12pj1d/1/1
jl29pj1d/1/1
same sample as jl12pj1d/1/1 above
now with some degradation
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


OTMS
Ph
7.2709
7.2600
7.2142
7.2070
7.1950
5.9361
5.9158
5.9020
5.8954
5.8816
5.8613
4.9384
4.9031
4.8824
4.7262
4.7066
4.0318
2.0901
2.0697
1.6462
1.6313
1.6132
1.5990
1.0368
1.0211
1.0055
0.9463
0.9303
0.9147
0.8522
0.8381
0.8225
0.8079
0.7923
0.7200
0.7048
0.6884
0.6706
0.6547
0.6390
0.6078
0.5922
0.5762
0.5613
0.5442
0.5301
0.1487
1.0000
2.0334
0.9937
1.0311
2.9333
3.0992
1.1502
2.0243
4.2031
(ppm)
Integral
5.5026
1.0000
2.0334
0.9836
0.9885
0.9937
1.0311
2.9333
3.0992
1.1502
2.0243
4.2031
8.5409


Si
Ph
OTMS
144.0307
137.8767
127.9479
127.1231
126.8455
113.0070
78.5972
75.9008
45.3610
39.9524
16.6292
6.5735
6.5180
5.9708
4.5037
0.7685
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
(ppm)

Peter Jervis Sample 2, Barcode 3901 in CDCl3 at +27C, set temp
drx500, Gradient HSQC



Current Data Parameters

NAME	jl06pjid
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20050706
Time	17.09
INSTRUM	drx500
PROBHD	5 mm TBI H/C
PULPROG	invigptp
TD	2048
SOLVENT	CDCl3
NS	8
DS	16
SWH	4310.345 Hz
FIDRES	2.104881 Hz
AQ	0.2378180 sec
RG	32768
DW	116.000 usec
DE	5.50 usec
TE	300.0 K
CNST2	145.0000000
d0	0.00000300 sec
D1	2.00000000 sec
d4	0.00172414 sec
d11	0.03000000 sec
d13	0.00000300 sec
D16	0.00010000 sec
d20	0.00110000 sec
d21	0.00061714 sec
IN0	0.00001140 sec

CHANNEL f1

NUC1	1H
P1	10.70 usec
p2	21.40 usec
PL1	1.00 dB
SFO1	500.1318887 MHz

CHANNEL f2

CPDPRG2	garp
NUC2	13C
P3	12.00 usec
p4	24.00 usec
PCPD2	78.00 usec
PL2	-1.00 dB
PL12	15.00 dB
SFO2	125.7667893 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	80.00 %
GPZ2	30.00 %
GPZ3	20.10 %
P16	1000.00 usec

F1 - Acquisition parameters

ND0	4
TD	512
SFO1	125.7688 MHz
FIDRES	42.831688 Hz
SW	174.368 ppm

F2 - Processing parameters

SI	2048
SF	500.1300233 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	1.00

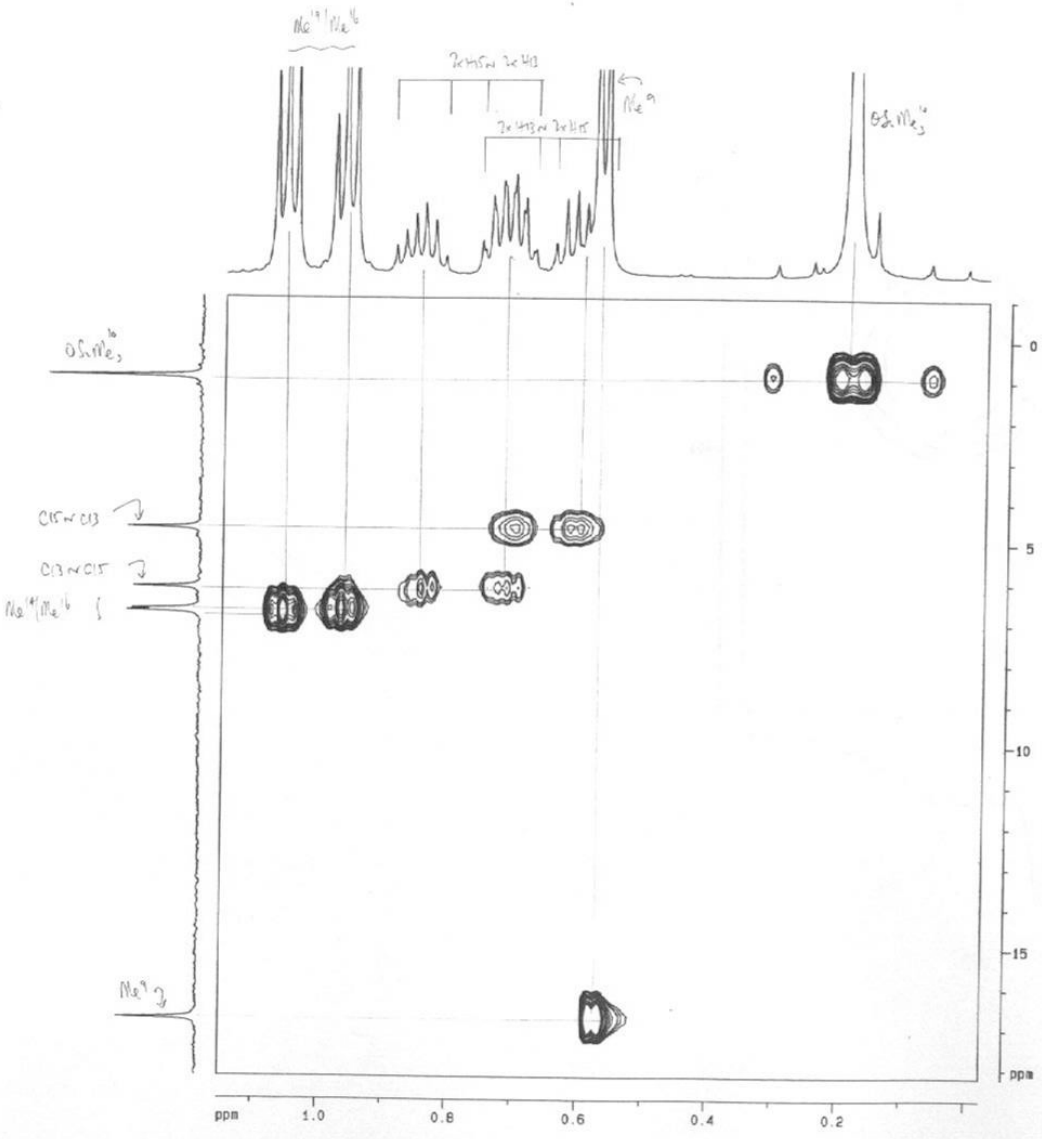
F1 - Processing parameters

SI	1024
MC2	TPPI
SF	125.7577945 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

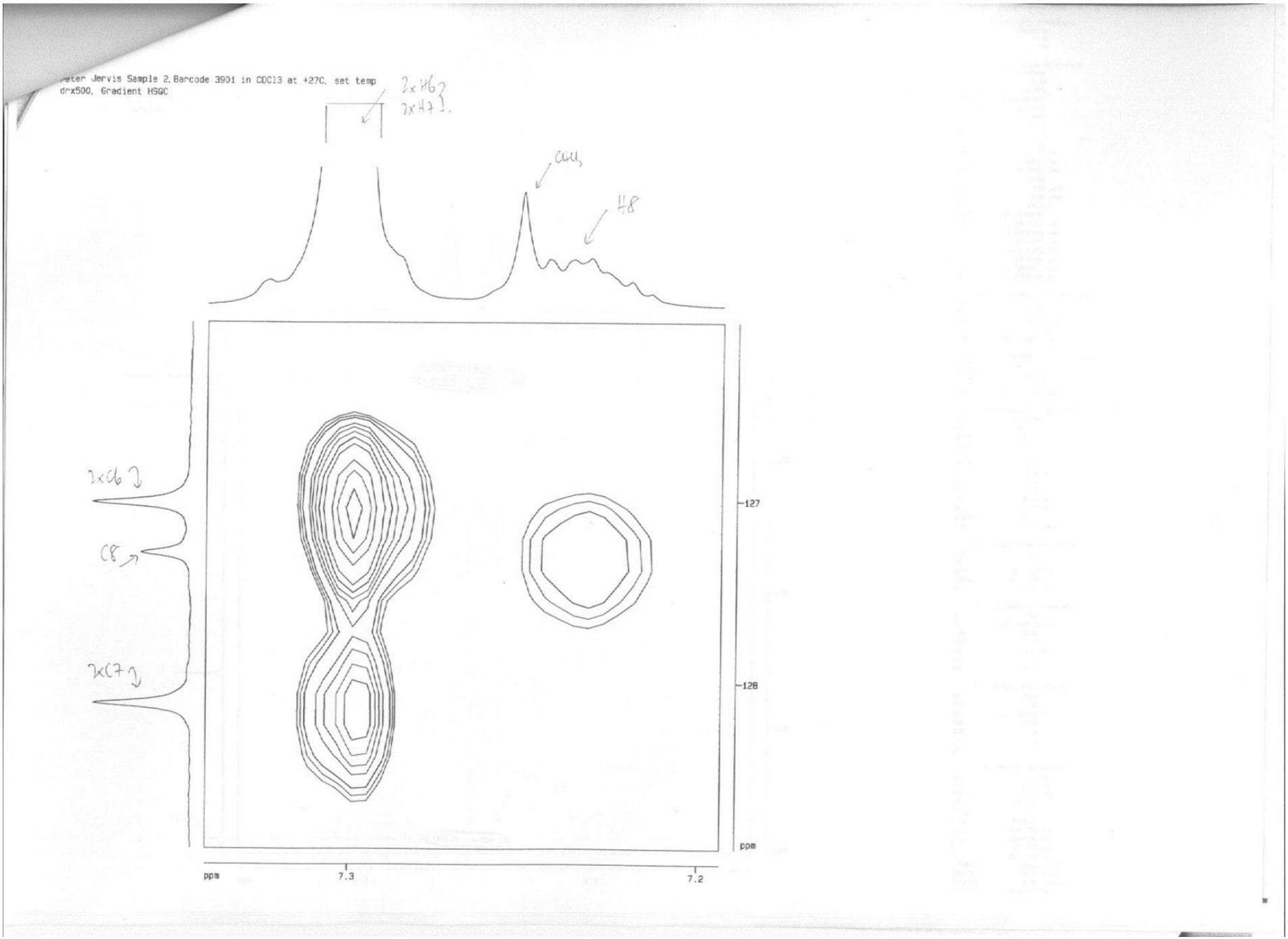
2D NMR plot parameters

CX2	17.00 cm
CX1	17.00 cm
F2PLO	7.404 ppm
F2LO	3702.93 Hz
F2PHI	-0.057 ppm
F2HI	-28.62 Hz
F1PLO	141.005 ppm
F1LO	17732.50 Hz
F1PHI	-1.381 ppm
F1HI	-171.14 Hz
F2PPMCM	0.43889 ppm/cm
F2HZCM	219.50372 Hz/cm
F1PPMCM	8.37448 ppm/cm
F1HZCM	1053.15564 Hz/cm

Peter Jervis Sample 2, Barcode 3901 in CDCl3 at +27C, set temp
drx500, Gradient HSQC

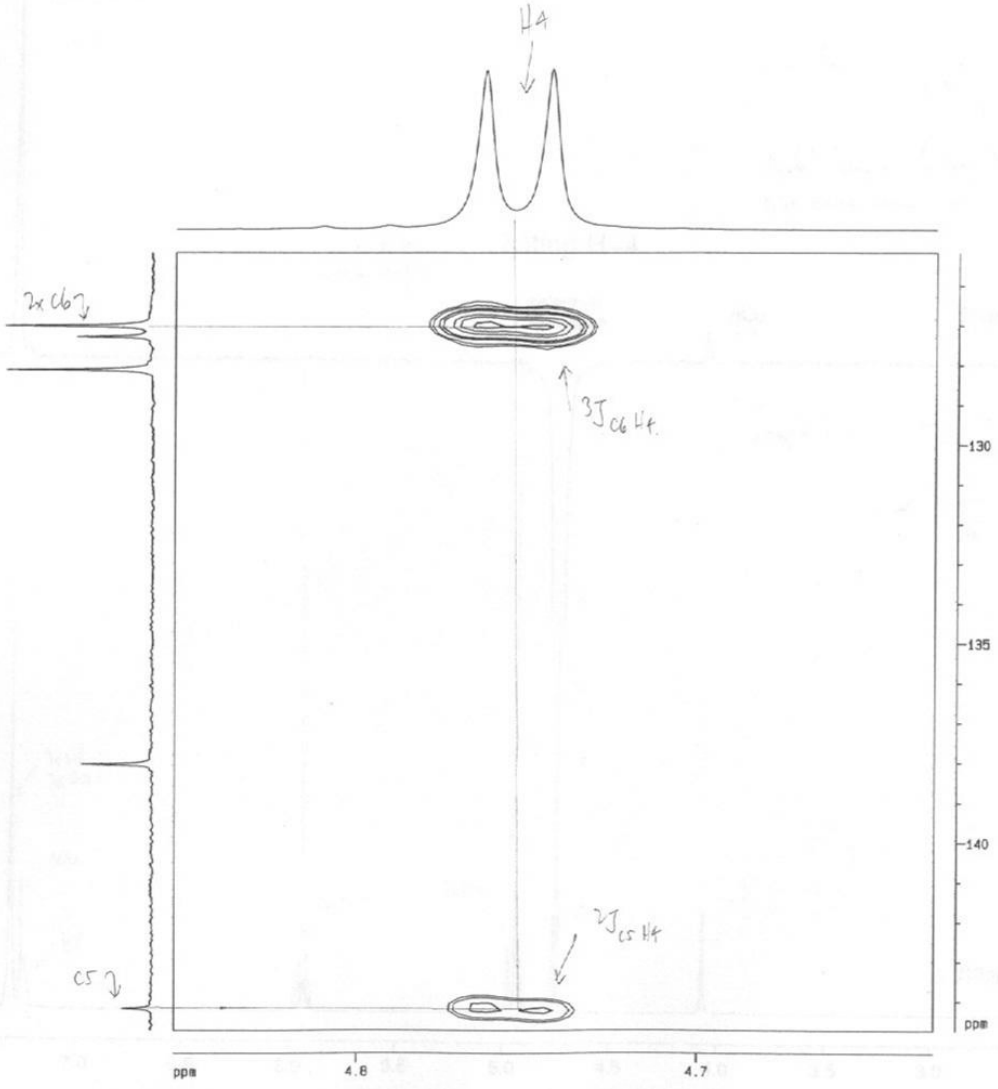


15b


eter Jervis Sample 2, Barcode 3901 in CDCl3 at +27C, set temp
drx500, Gradient HSQC
2xH6?
2xH7?.
CH3
H8
2xC6
C8
2xC7
127
128
ppm
ppm
7.3
7.2

15b

Peter Jervis Sample 2, Barcode 3901 in CDCl3 at +27C, set temp
drx500, Gradient HMBC



Current Data Parameters

NAME	1108pjid
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20050706
Time	19.44
INSTRUM	drx500
PROBHD	5 mm TBI H/C
PULPROG	inv4gplplrnd
TD	2048
SOLVENT	CDCl3
NS	8
DS	16
SWH	4310.345 Hz
FIDRES	2.104661 Hz
AQ	0.2376160 sec
RG	32768
DW	116.000 usec
DE	5.50 usec
TE	300.0 K
CNST2	150.0000000
d0	0.00000300 sec
D1	2.00000000 sec
d2	0.00312500 sec
D6	0.10000000 sec
d13	0.00000300 sec
D16	0.00010000 sec
IN0	0.00002280 sec

CHANNEL f1

NUC1	1H
P1	10.70 usec
p2	21.40 usec
PL1	1.00 dB
SFO1	500.1318857 MHz

CHANNEL f2

NUC2	13C
P3	12.00 usec
PL2	-1.00 dB
SFO2	125.7667893 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	512
SFO1	125.7668 MHz
FIDRES	42.831688 Hz
SW	174.369 ppm

F2 - Processing parameters

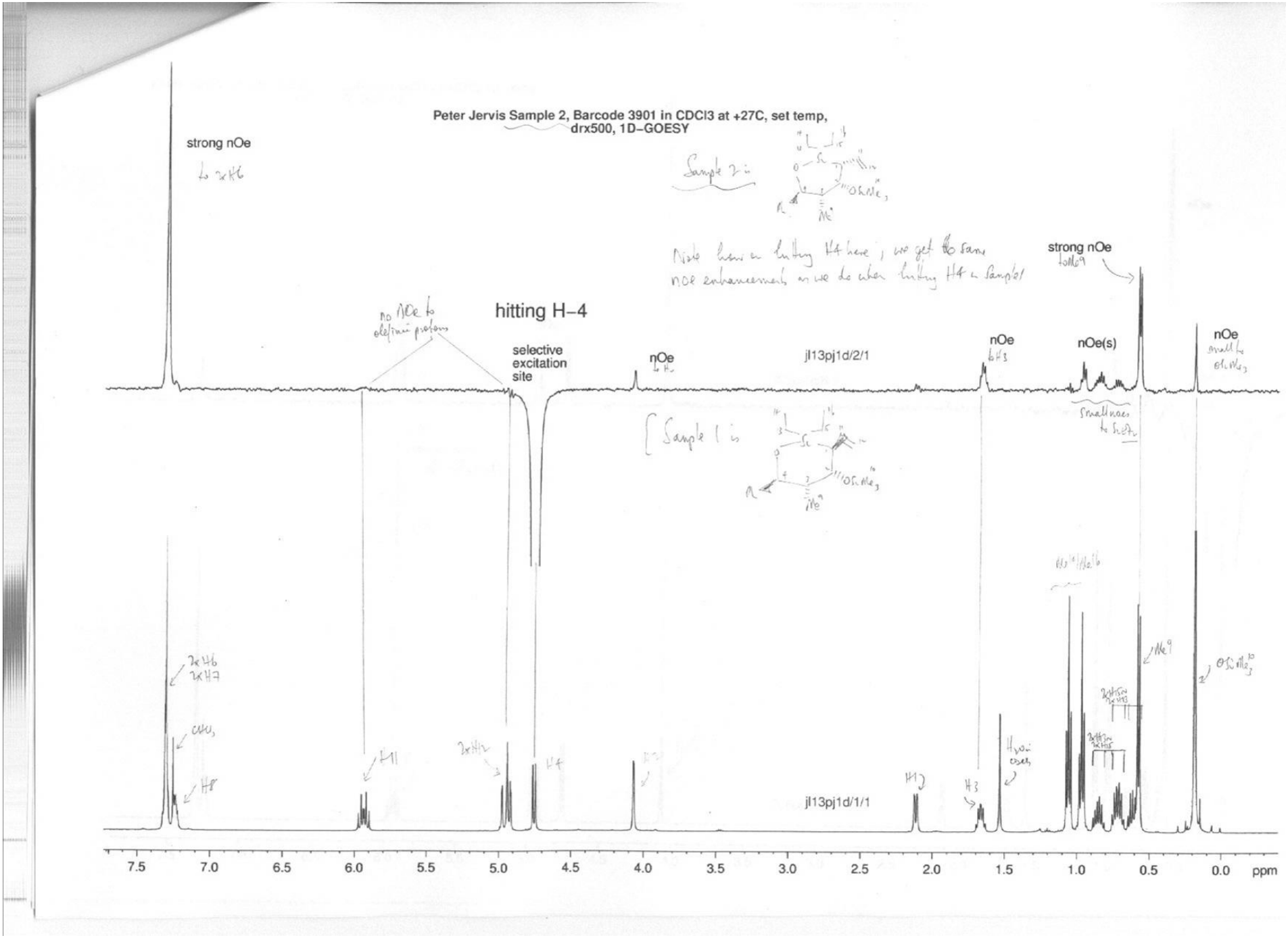
SI	2048
SF	500.1300233 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0
PC	0.20

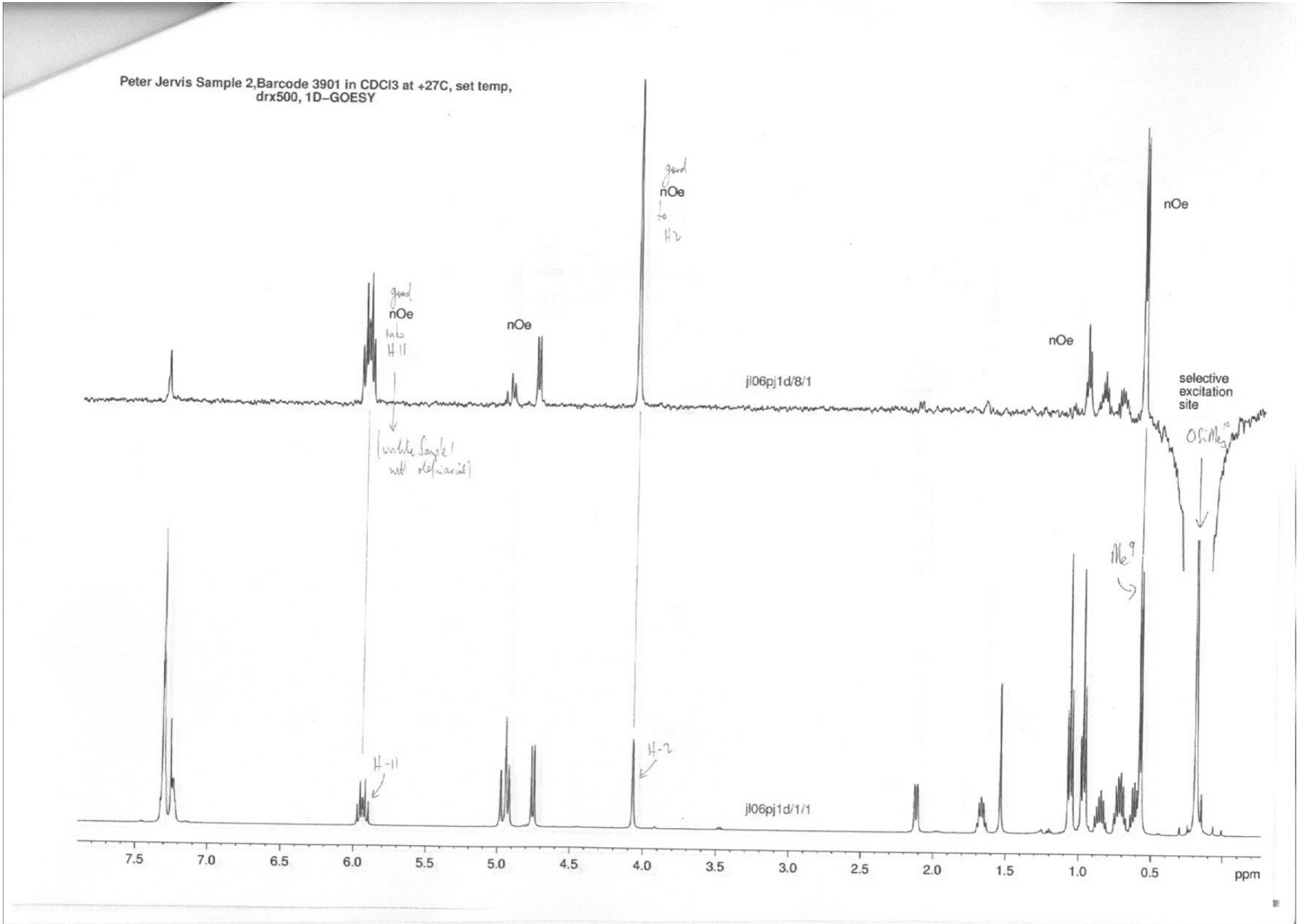
F1 - Processing parameters

SI	1024
MC2	QF
SF	125.7577945 MHz
WDW	QSINE
SSB	2
LB	0.00 Hz
GB	0

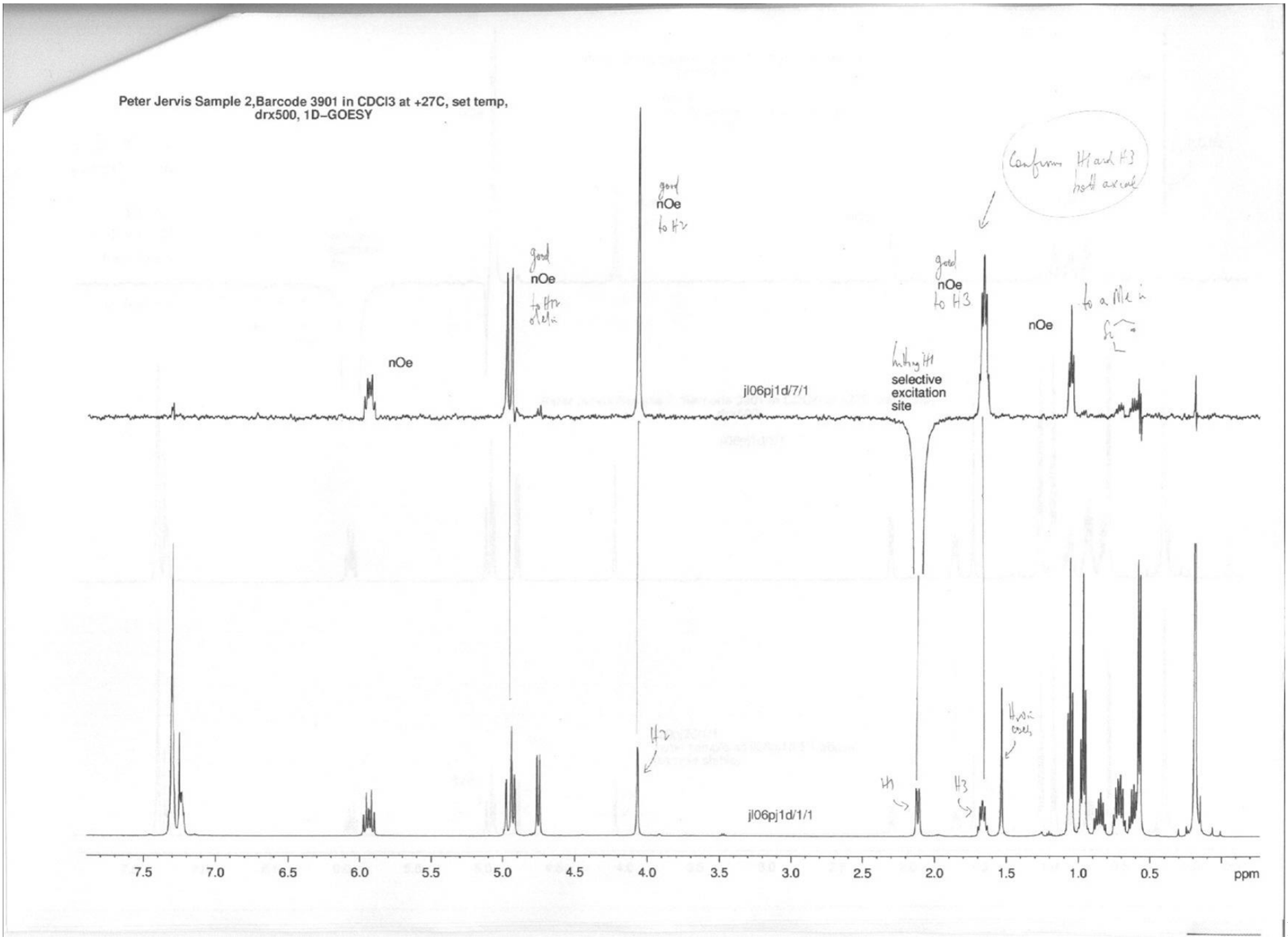
2D NMR plot parameters

CX2	17.00 cm
CX1	17.00 cm
F2PLO	4.854 ppm
F2LO	2427.51 Hz
F2PHI	4.631 ppm
F2HI	2315.96 Hz
F1PLO	144.752 ppm
F1LO	18203.65 Hz
F1PHI	125.168 ppm
F1HI	15740.83 Hz
F2PPMCM	0.01312 ppm/cm
F2HZCM	6.56156 Hz/cm
F1PPMCM	1.15199 ppm/cm
F1HZCM	144.87190 Hz/cm

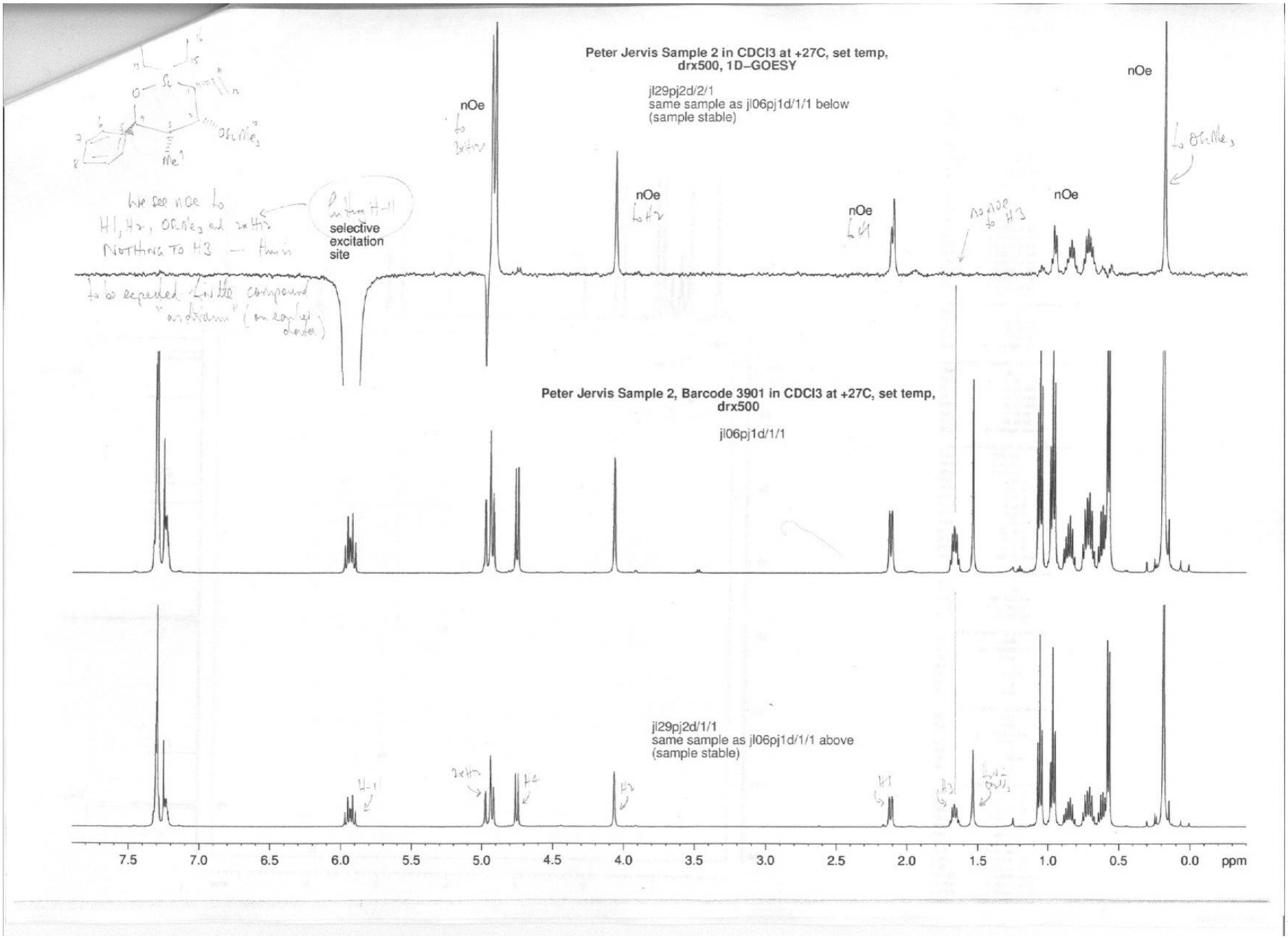

Peter Jervis Sample 2, Barcode 3901 in CDCl3 at +27C, set temp,
drx500, 1D–GOESY
strong nOe
hitting H–4
selective excitation site
nOe
nOe(s)
jl13pj1d/2/1
jl13pj1d/1/1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


Peter Jervis Sample 2,Barcode 3901 in CDCl3 at +27C, set temp,
drx500, 1D–GOESY
good
nOe
to
H2
nOe
nOe
nOe
good
nOe
to
H11
jl06pj1d/8/1
selective
excitation
site
OSiMe3
(unlabelled Sample
with olefin acid)
Me9
H-11
H-2
jl06pj1d/1/1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

15b


Peter Jervis Sample 2,Barcode 3901 in CDCl3 at +27C, set temp,
drx500, 1D–GOESY
Confirms H1 and H3 both axial
good nOe to H2
good nOe to H2
good nOe to H3
nOe
nOe
to a Me in
jl06pj1d/7/1
selective excitation site
jl06pj1d/1/1
H2
H1
H3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

15b


Peter Jervis Sample 2 in CDCl3 at +27C, set temp,
drx500, 1D–GOESY
jl29pj2d/2/1
same sample as jl06pj1d/1/1 below
(sample stable)
nOe
nOe
nOe
nOe
nOe
selective
excitation
site
Peter Jervis Sample 2, Barcode 3901 in CDCl3 at +27C, set temp,
drx500
jl06pj1d/1/1
jl29pj2d/1/1
same sample as jl06pj1d/1/1 above
(sample stable)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm