Confirmation of the Structures of Synthetic Derivatives of Migrastatin in the Light of Recently Disclosed Crystallographically Based Claims

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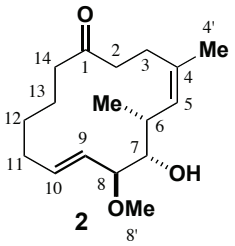
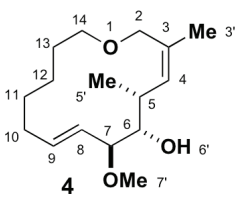
Content:

^{1}H-, COSY and NOESY NMR spectra for migrastatin ketone **2** and migrastatin ether **4** were recorded on a Bruker DRX-600 spectrometer. Chemical shifts (δ-values) are reported in ppm with residual undeuterated $CHCl_3$ as the internal standard (referenced to 7.26 ppm for H-NMR) for migrastatin ether **4** and with residual undeuterated benzene as the internal standard (referenced to 7.16 ppm for H-NMR) for migrastatin ketone **2**. Coupling constants (J) (H,H) are given in Hz, spectral splitting patterns are designated as singlet (s), doublet (d), triplet (t), quadruplet (q), multiplet or more overlapping signals (m), apparent (app), broad signal (br). 1D NOE data was extracted from the corresponding 2D NOESY spectra.



Migrastatin Ketone (**2**).[1] ^{1}H NMR (C_6D_6, 600 MHz): δ 5.70 (dq, 1H, *J* = 10.1, 1.3 Hz, C_5**H**), 5.35 (ddd, 1H, *J* = 15.2, 8.1, 6.5 Hz, C_{10}**H**), 5.04 (ddt, 1H, *J* = 15.6, 7.6, 1.1 Hz, C_9**H**), 3.46 (dd, 1H, *J* = 9.2, 1.3 Hz, C_7**H**), 3.36 (t, 1H, *J* = 7.9 Hz, C_8**H**), 3.04 (s, 3H, C_8OC**H$_3$**), 2.27 (bs, 1H, C_7O**H**), 2.43 (dqd, 1H, *J* = 9.8, 6.8, 1.0 Hz, C_6**H**), 2.16-2.03 (m, 5H, C_2**H$_2$**, C_3**H$_2$**, C_{14}**H**), 1.93 (ddd, 1H, *J* = 13.7, 10.4, 6.2 Hz, C_{14}**H**), 1.84-1.82 (m, 1H, C_{11}**H**), 1.80-1.74 (m, 1H, C_{11}**H**), 1.58 (d, 3H, *J* = 1.3 Hz, C_4C**H$_3$**), 1.47-1.37 (m, 1H, C_{13}**H**), 1.37-1.25 (m, 1H, C_{13}**H**), 1.12 (d, 3H, *J* = 6.8 Hz, C_6C**H$_3$**), 1.11-1.07 (m, 2H, C_{12}**H$_2$**).



Migrastatin Ether (**4**).[2] ^{1}H NMR ($CDCl_3$, 600 MHz): δ 5.63 (ddd, 1H, *J* = 15.1, 9.3, 5.1 Hz, C_9**H**), 5.61 (dd, 1H, *J* = 8.9, 1.2 Hz, C_4**H**), 5.22 (dd, 1H, *J* = 7.9, 15.5 Hz, C_8**H**), 3.76 (s, 2H, C_2**H$_2$**), 3.56-3.52 (m, 1H, C_{14}**H**), 3.49-3.44 (m, 1H, C_{14}**H**), 3.44-3.40 (m, 2H, C_6**H**, C_7**H**), 3.30 (s, 3H, C_7OC**H$_3$**), 2.93 (dqd, 1H, *J* = 9.9, 6.9, 0.9 Hz, C_5**H**), 2.73 (br s, 1H, C_6O**H**), 2.24 (m, 1H, C_{10}**H**), 2.09 (m, 1H, C_{10}**H**), 1.76 (d, 3H, *J* = 1.2 Hz, C_3C**H$_3$**), 1.66 (m, 1H, C_{13}**H**), 1.53 (m, 1H, C_{11}**H**), 1.45-1.36 (m, 4H, C_{11}**H**, C_{10}**H$_2$**, C_{13}**H**), 0.94 (d, 3H, *J* = 6.9 Hz, C_5C**H$_3$**). Crystallized by slow evaporation from *i*-PrOH/H_2O/Acetone or from Acetone/Hexanes/MeOH/H_2O at –20 ºC.

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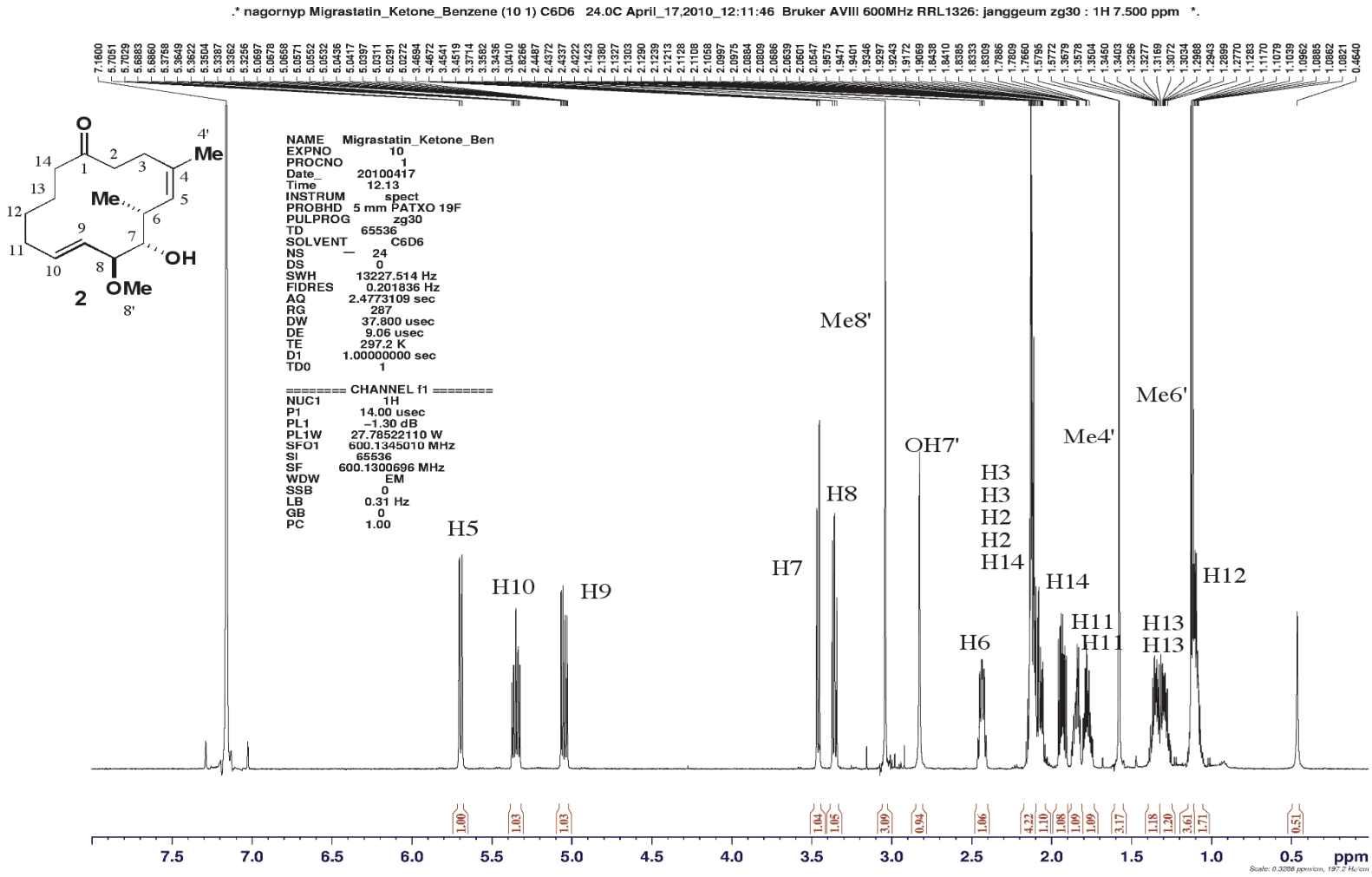
[1] For the full experimental procedures and characterization data for the preparation of **2** refer to: Gaul. C.; Njardarson, J. T.; Shan, D.; Dorn, D. C.; Wu, K.-D.; Tong, W. P.; Huang, X.-Y.; Moore, M. A. S.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2004**, *126(36)*, 11326-11337.

[2] For the full experimental procedures and characterization data for the preparation of **4** refer to: Oskarsson, T.; Nagorny, P.; Krauss, I. J.; Perez, L.; Mandal, M.; Yang, G.; Ouerfelli, O.; Xiao, D.; Moore, M. S. A.; Massague, J.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2010**, *132(9)*, 3224-3228.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TE 297.2 K
D1 1.00000000 sec
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PL1 –1.30 dB
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SI 65536
SF 600.1300696 MHz
WDW EM
SSB 0
LB 0.31 Hz
GB 0
PC 1.00
Me8'
OH7'
Me4'
Me6'
H5
H10
H9
H8
H7
H6
H3
H3
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H2
H14
H14
H11
H11
H13
H13
H12
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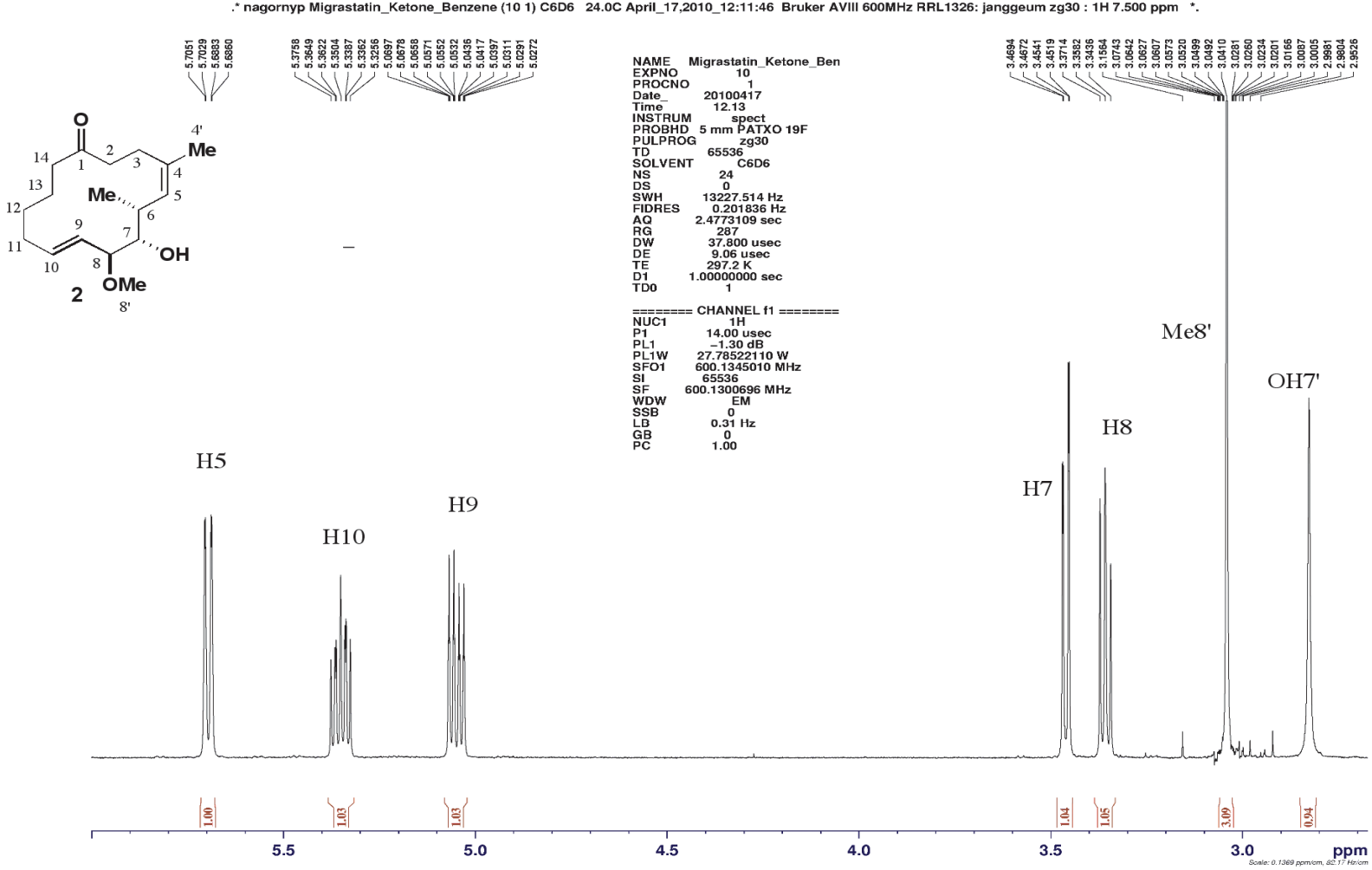
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NAME Migrastatin_Ketone_Ben
EXPNO 10
PROCNO 1
Date_ 20100417
Time 12.13
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG zg30
TD 65536
SOLVENT C6D6
NS 24
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FIDRES 0.201836 Hz
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DE 9.06 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -1.30 dB
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SI 65536
SF 600.1300696 MHz
WDW EM
SSB 0
LB 0.31 Hz
GB 0
PC 1.00
H5
H10
H9
H7
H8
Me8'
OH7'
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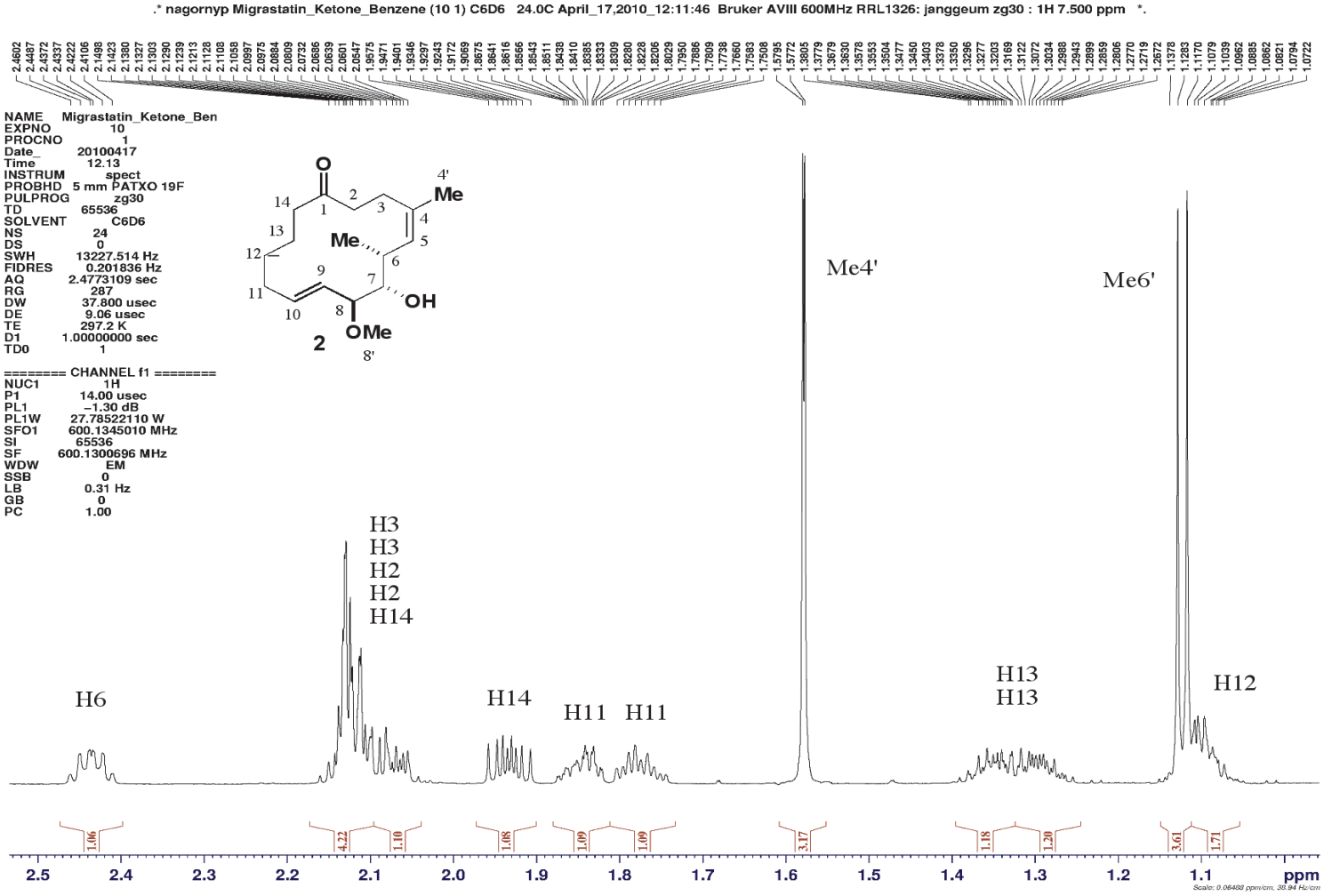
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NAME Migrastatin_Ketone_Ben
EXPNO 10
PROCNO 1
Date_ 20100417
Time 12.13
INSTRUM spect
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PULPROG zg30
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SSB 0
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H6
H3
H3
H2
H2
H14
H14
H11
H11
Me4'
H13
H13
Me6'
H12
1.06
4.22
1.10
1.08
1.09
1.09
3.17
1.18
1.20
3.61
1.71
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2.4
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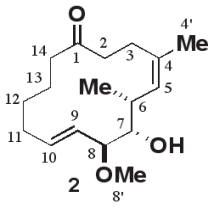

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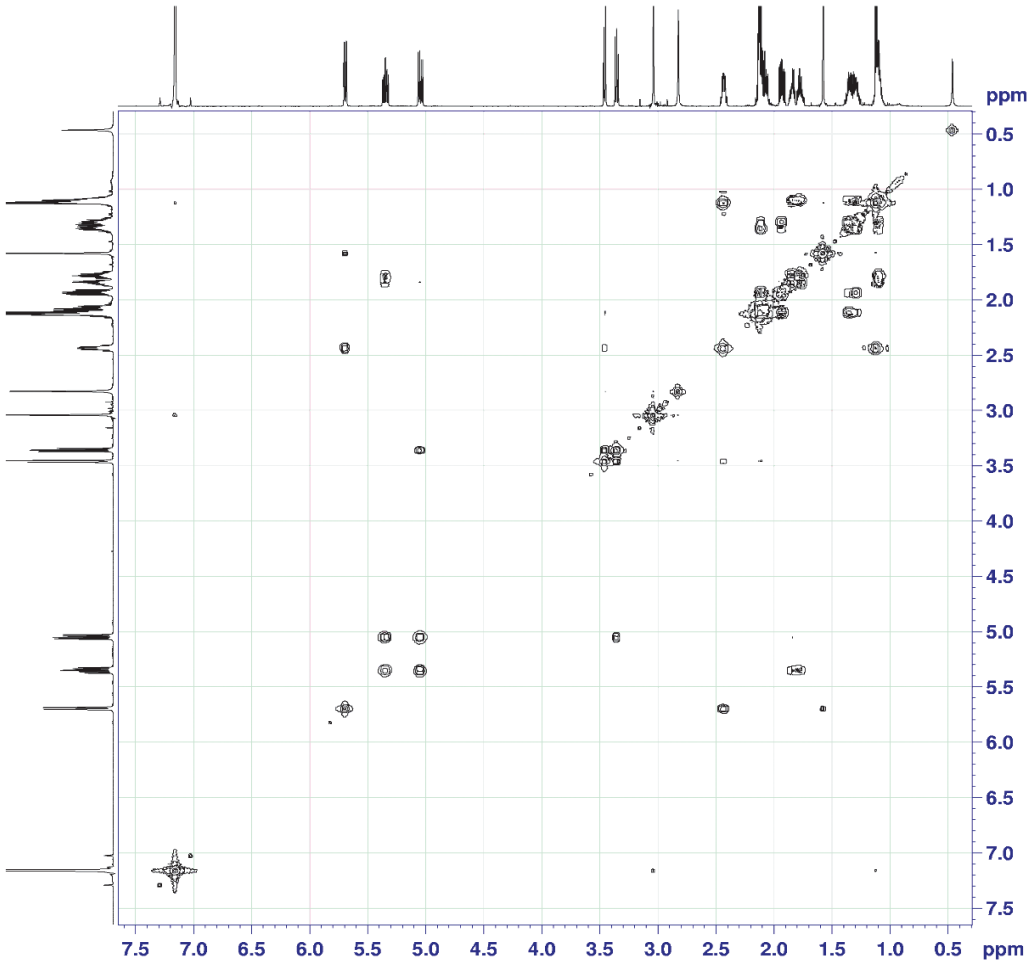

MEMORIAL SLOAN-KETTERING CANCER CENTER
ESTABLISHED 1884
NMR Analytical Core Facility
Rockefeller Research Laboratories
430 E 67th St
New York, NY 10021

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EXPNO 11
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Date_ 20100417
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PULPROG cosygpqf
TD 2048
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FIDRES 2.260361 Hz
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DE 6.50 usec
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D1 1.39350293 sec
D13 0.00030400 sec
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TD0 0.00021600 sec
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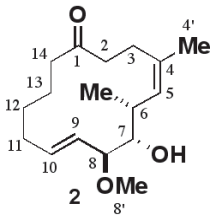
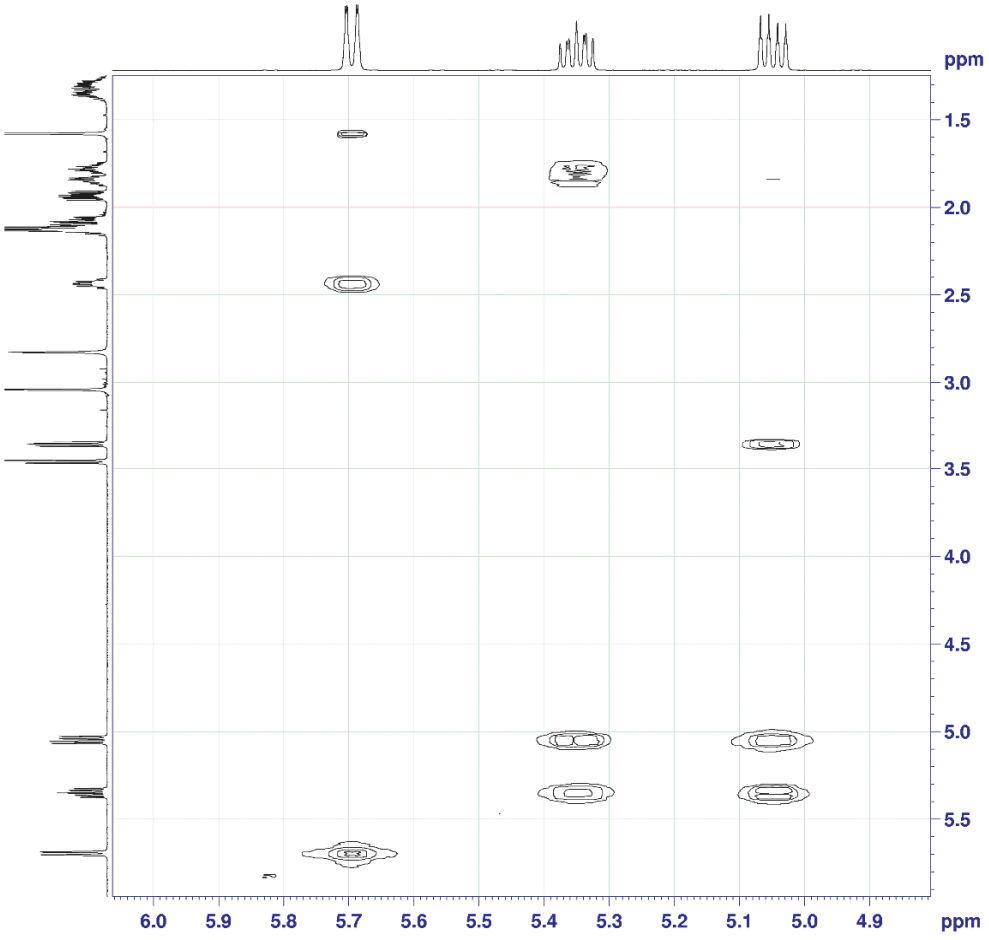


n_Ketone_Benzene (11 1) C6D6 24.0C April_17,2010_12:13:53 Bruker AVIII 600MHz RRL1326: janggeum cosy



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DE 6.00 usec
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D1 1.95350290 sec
D13 0.00000400 sec
D16 0.00020000 sec
IAC 0.00001600 sec

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P1 14.00 usec
PL1 -1.30 dB
PLW1 27.78522110 W
SFO1 600.1323439 MHz

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FnMODE QF
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SF 600.1300865 MHz
WDW SINE
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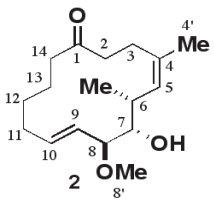

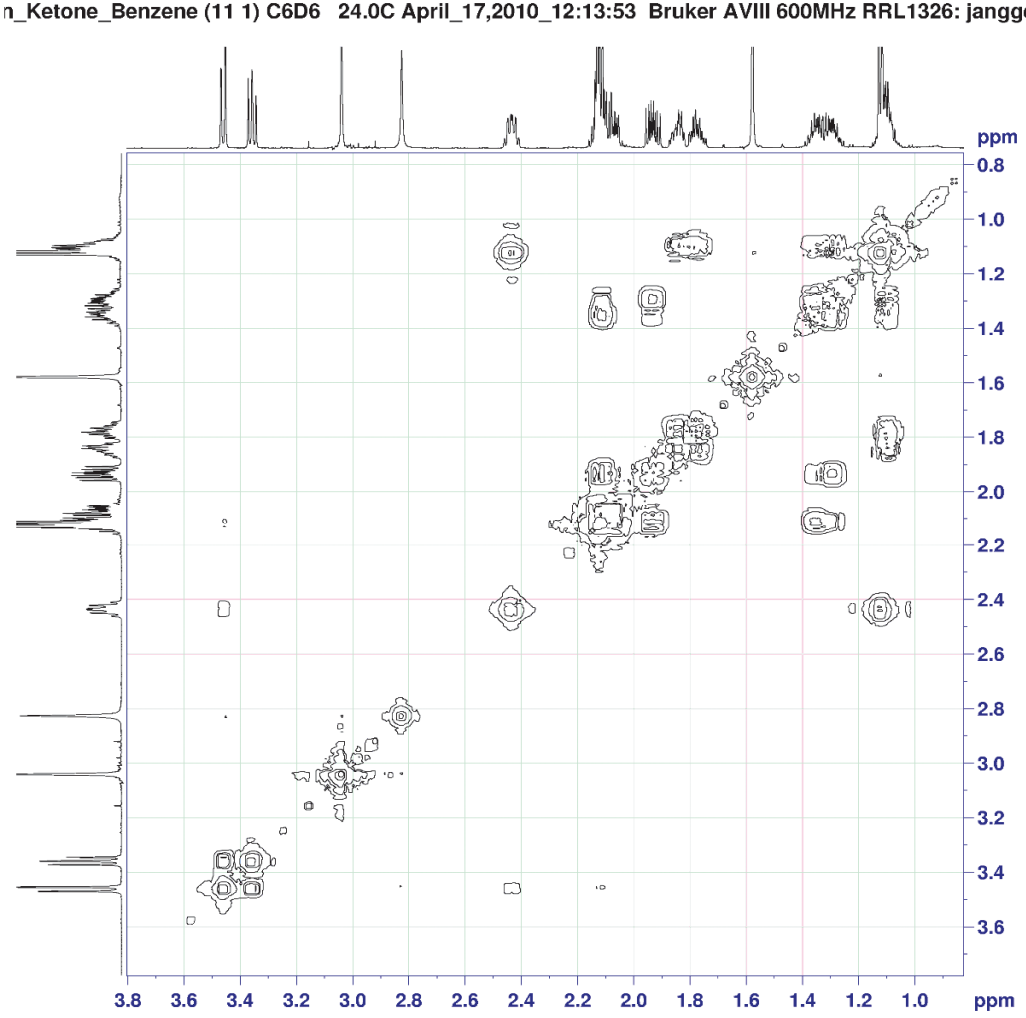

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EXPNO	11
PROCNO	1
Date_	20100417
Time	12.14
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RG	128
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DE	6.00 usec
TE	297.2 K
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D1	1.30350255 sec
D13	0.00004000 sec
D16	0.00020000 sec
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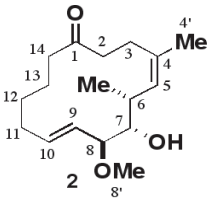

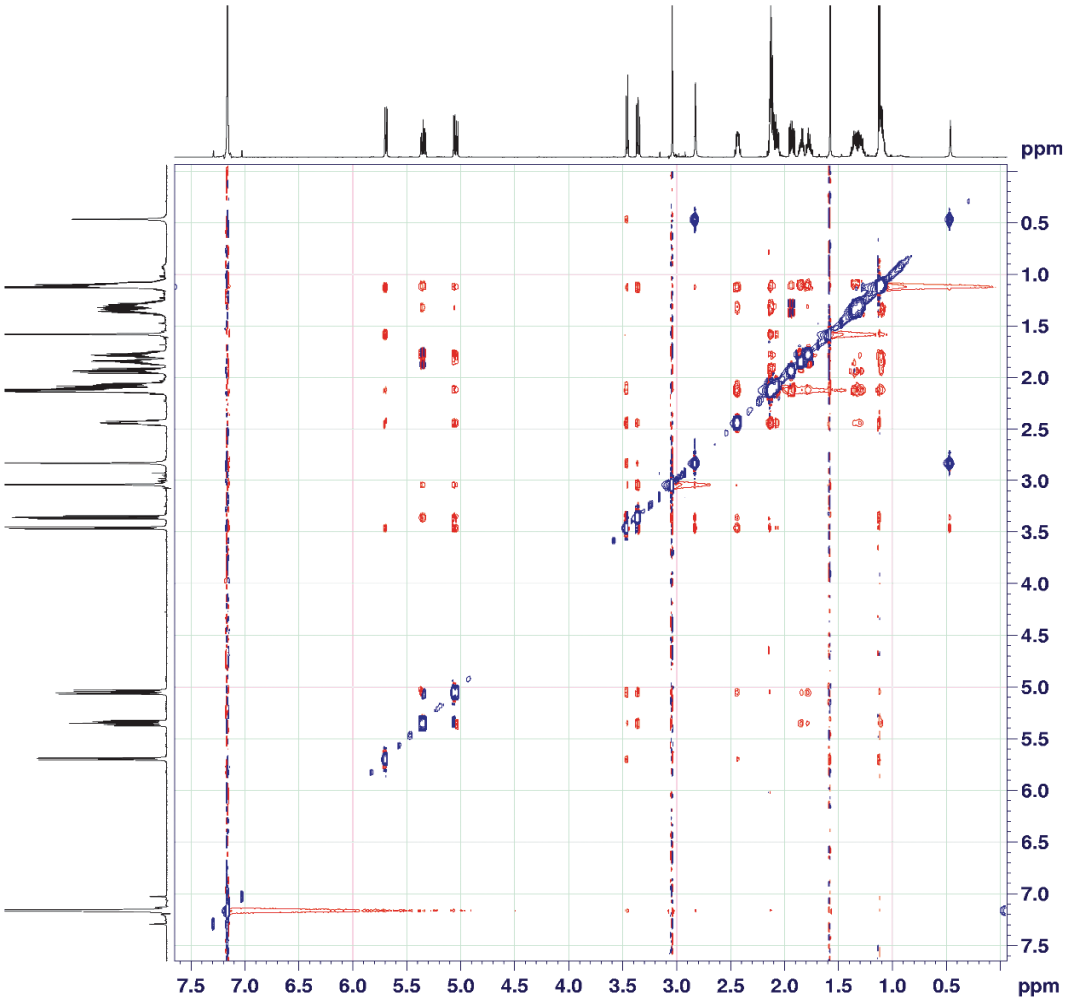

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======== CHANNEL f1 ========
NUC1 1H
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P2 28.00 usec
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SFO1 600.1323439 MHz

====== GRADIENT CHANNEL =====
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SF 600.1300669 MHz
WDW QSINE
SSB 2
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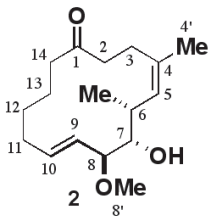

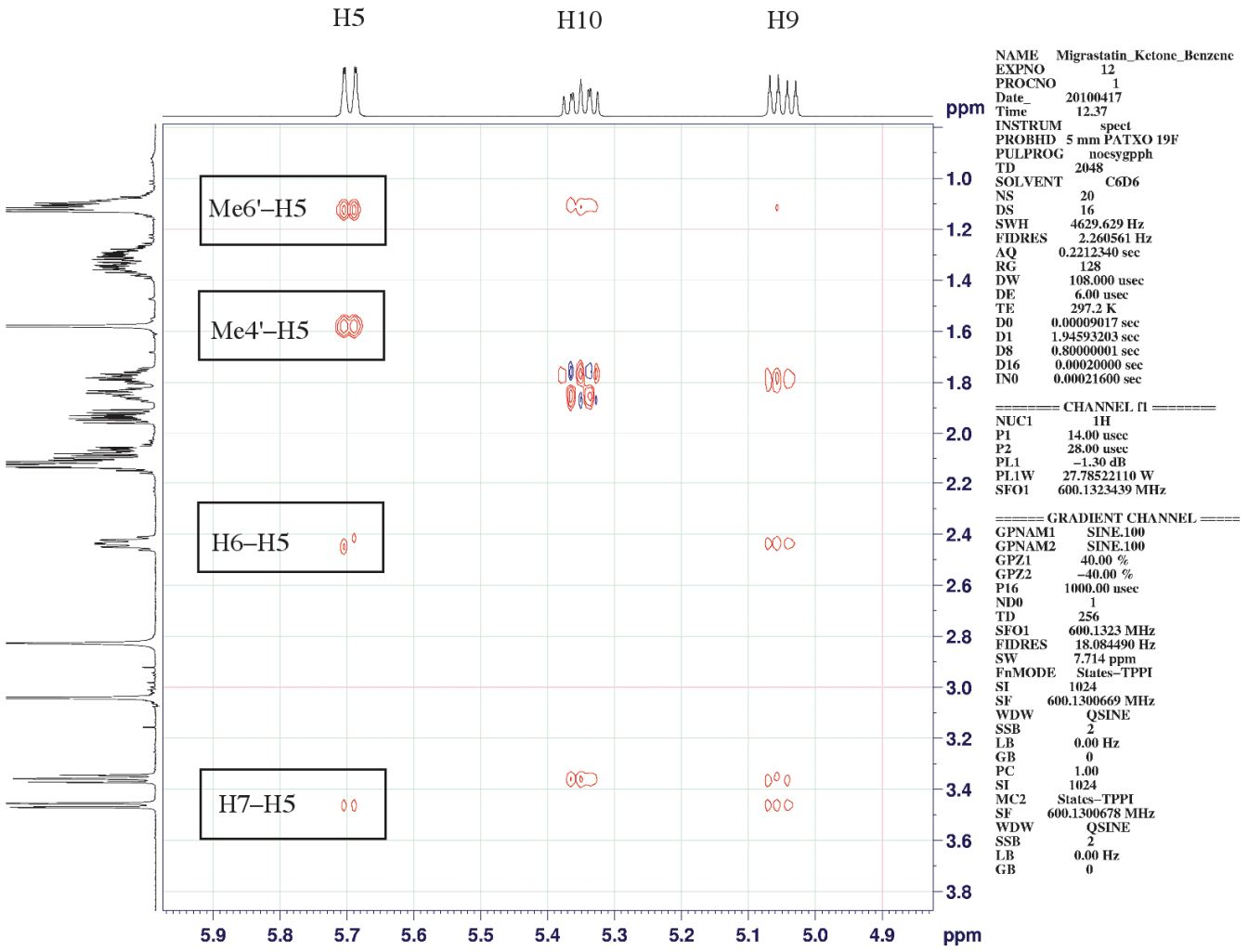

NAME Migrastatin_Ketone_Benzene
EXPNO 12
PROCNO 1
Date_ 20100417
Time 12.37
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PULPROG noesygpph
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NS 20
DS 16
SWH 4629.629 Hz
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AQ 0.2212340 sec
RG 128
DW 108.000 usec
DE 6.00 usec
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D1 1.94593203 sec
D8 0.80000001 sec
D16 0.00020000 sec
IN0 0.00021600 sec

======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
P2 28.00 usec
PL1 –1.30 dB
PL1W 27.78522110 W
SFO1 600.1323439 MHz

====== GRADIENT CHANNEL =====
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GPNAM2 SINE.100
GPZ1 40.00 %
GPZ2 –40.00 %
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SW 7.714 ppm
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WDW QSINE
SSB 2
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GB 0
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WDW QSINE
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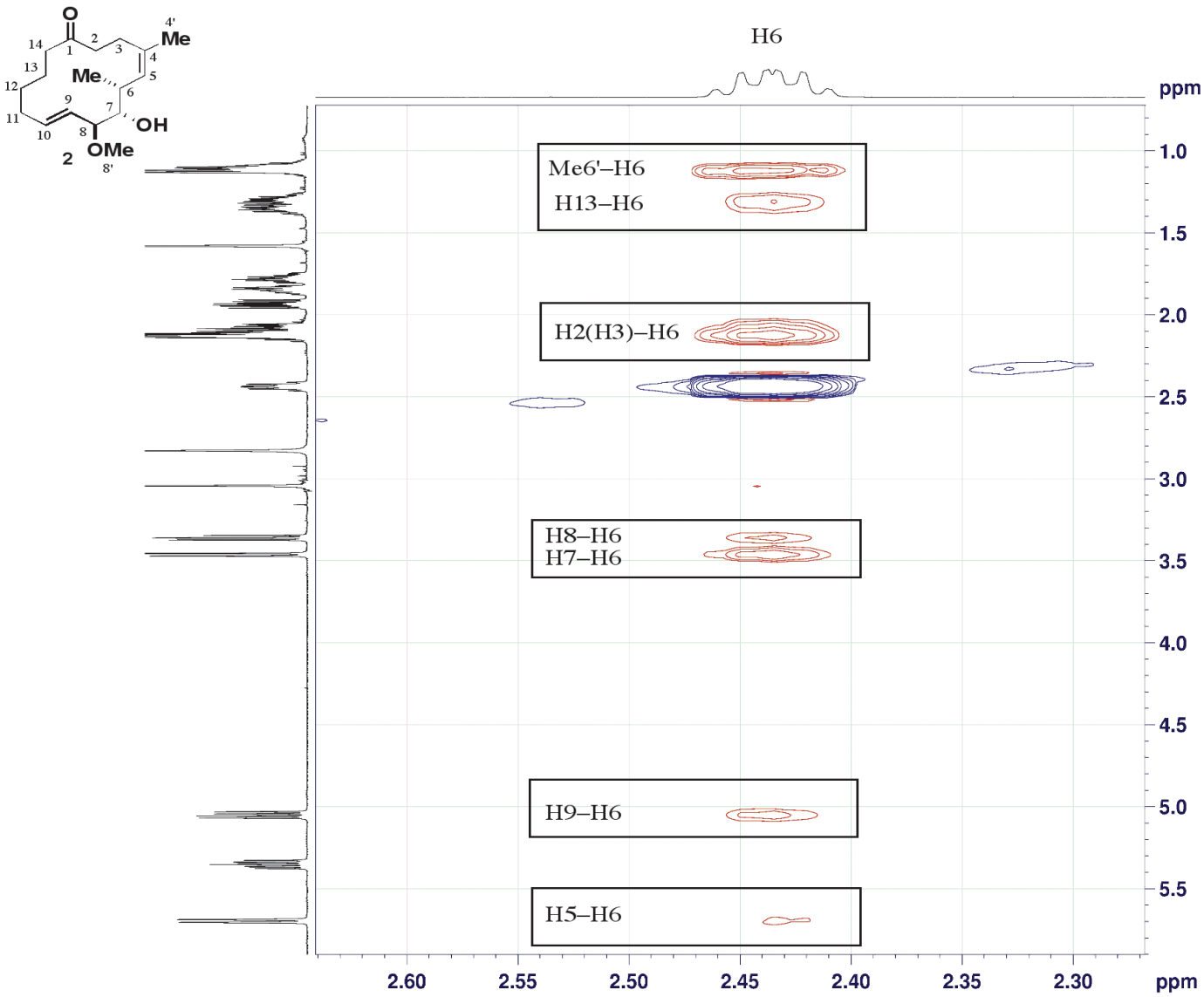
GB 0



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DE 6.00 usec
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D1 1.94593203 sec
D8 0.80000001 sec
D16 0.00020000 sec
IN0 0.00021600 sec

======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
P2 28.00 usec
PL1 −1.30 dB
PL1W 27.78522110 W
SFO1 600.1323439 MHz

====== GRADIENT CHANNEL =====
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GPNAM2 SINE.100
GPZ1 40.00 %
GPZ2 −40.00 %
P16 1000.00 usec
ND0 1
TD 256
SFO1 600.1323 MHz
FIDRES 18.084490 Hz
SW 7.714 ppm
FnMODE States−TPPI
SI 1024
SF 600.1300669 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
SI 1024
MC2 States−TPPI
SF 600.1300678 MHz
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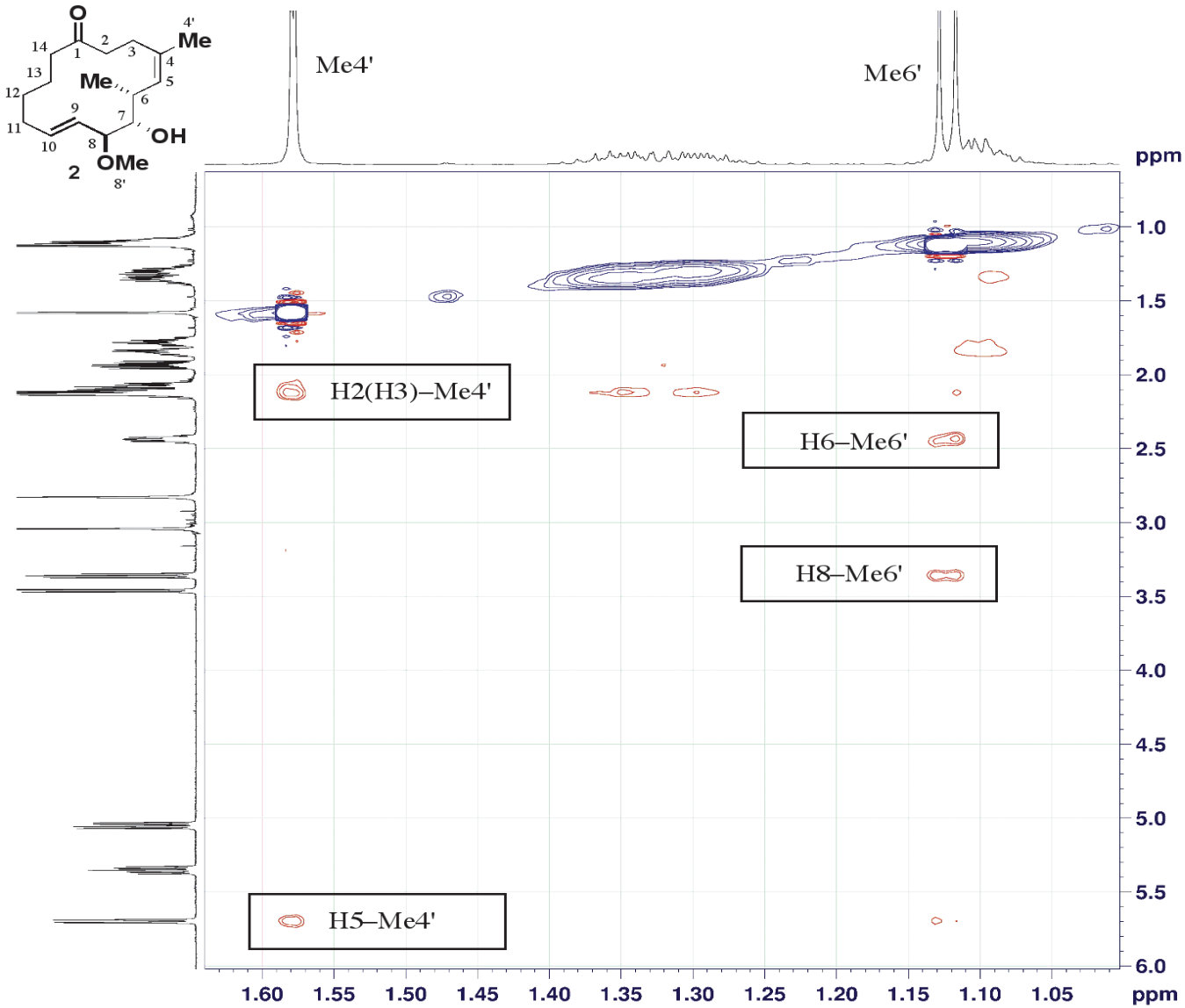
SSB 2
LB 0.00 Hz
GB 0

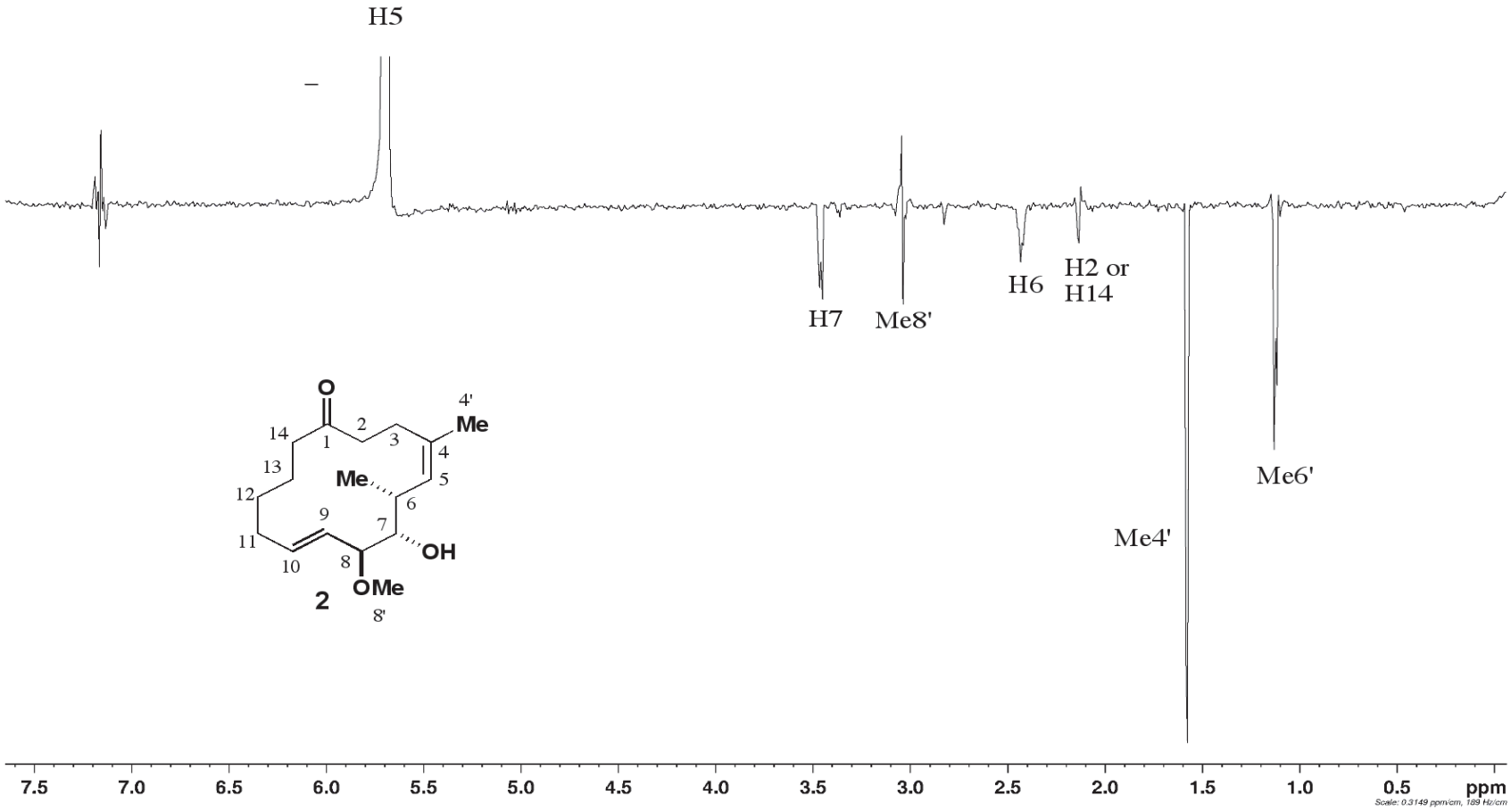


NAME Migrastatin_Ketone_Benzene
EXPNO 12
PROCNO 1
Date_ 20100417
Time 12.37
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG noesygpph
TD 2048
SOLVENT C6D6
NS 20
DS 16
SWH 4629.629 Hz
FIDRES 2.260561 Hz
AQ 0.2212340 sec
RG 128
DW 108.000 usec
DE 6.00 usec
TE 297.2 K
D0 0.00009017 sec
D1 1.94593203 sec
D8 0.80000001 sec
D16 0.00020000 sec
IN0 0.00021600 sec

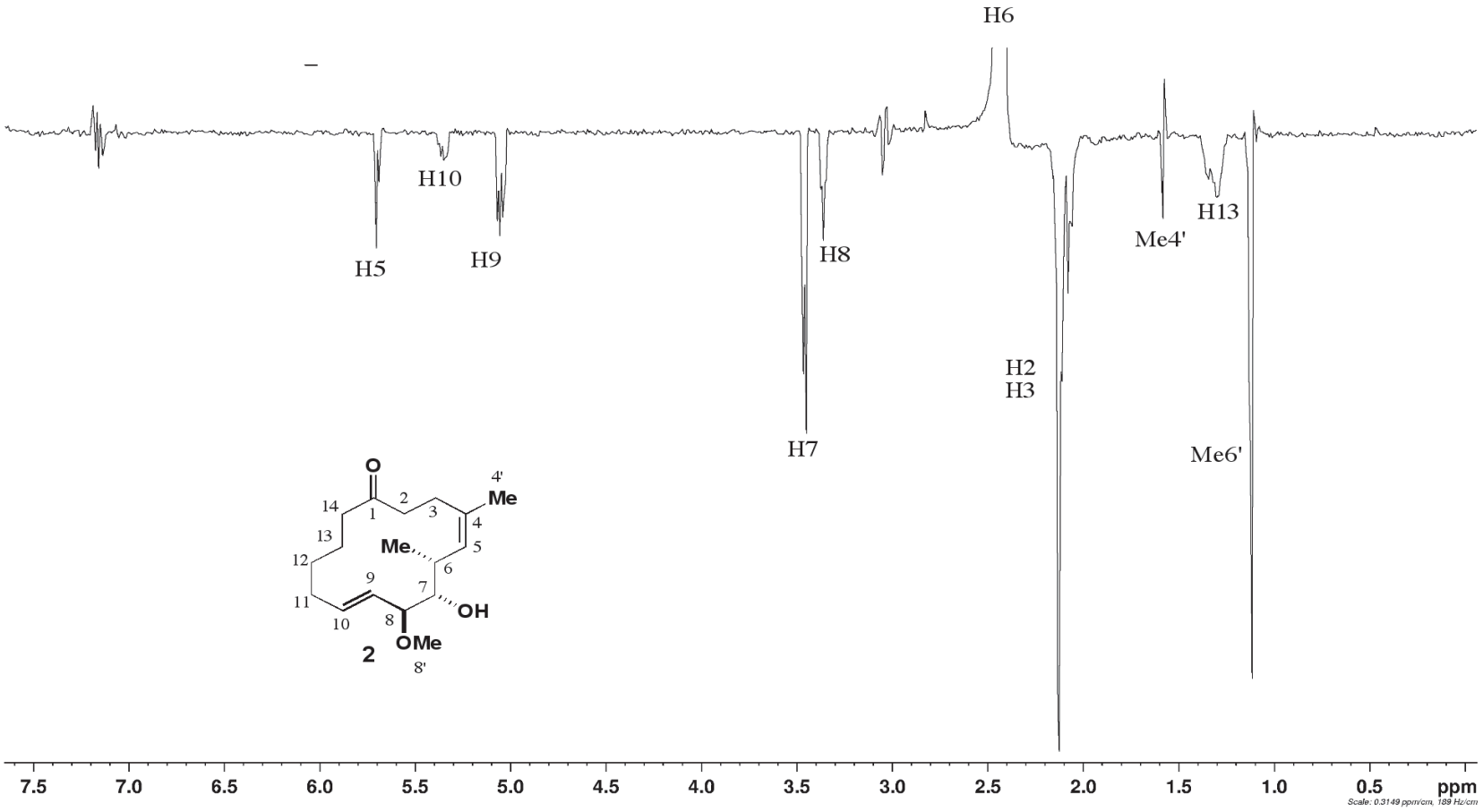
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
P2 28.00 usec
PL1 −1.30 dB
PL1W 27.78522110 W
SFO1 600.1323439 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 40.00 %
GPZ2 −40.00 %
P16 1000.00 usec
ND0 1
TD 256
SFO1 600.1323 MHz
FIDRES 18.084490 Hz
SW 7.714 ppm
FnMODE States−TPPI
SI 1024
SF 600.1300669 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
SI 1024
MC2 States−TPPI
SF 600.1300678 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0

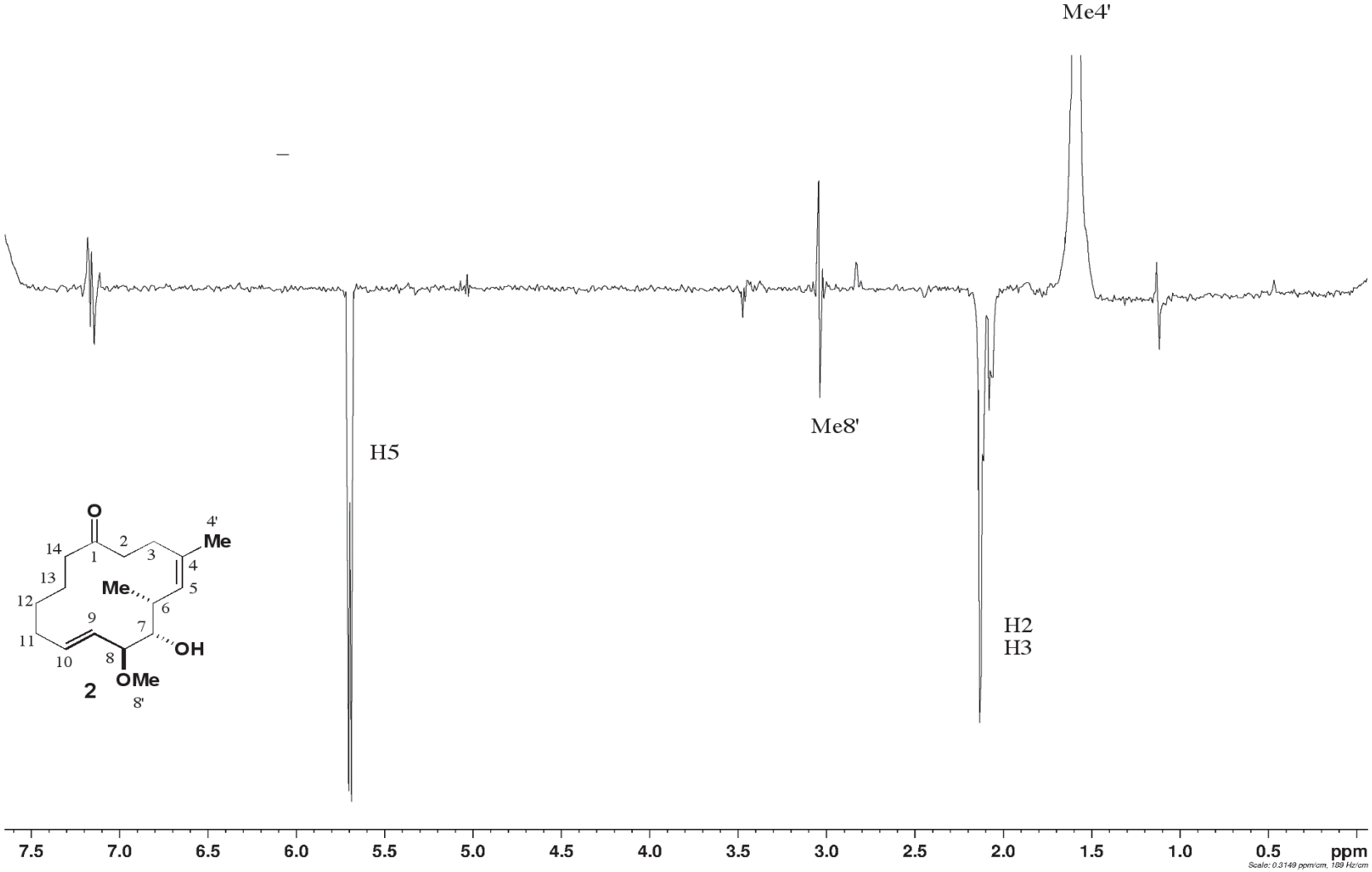
1D NOE Data Obtained from 2D NOESY of migrastatin ketone (2) recorded in benzene.
Correlations for the H5 olefin.

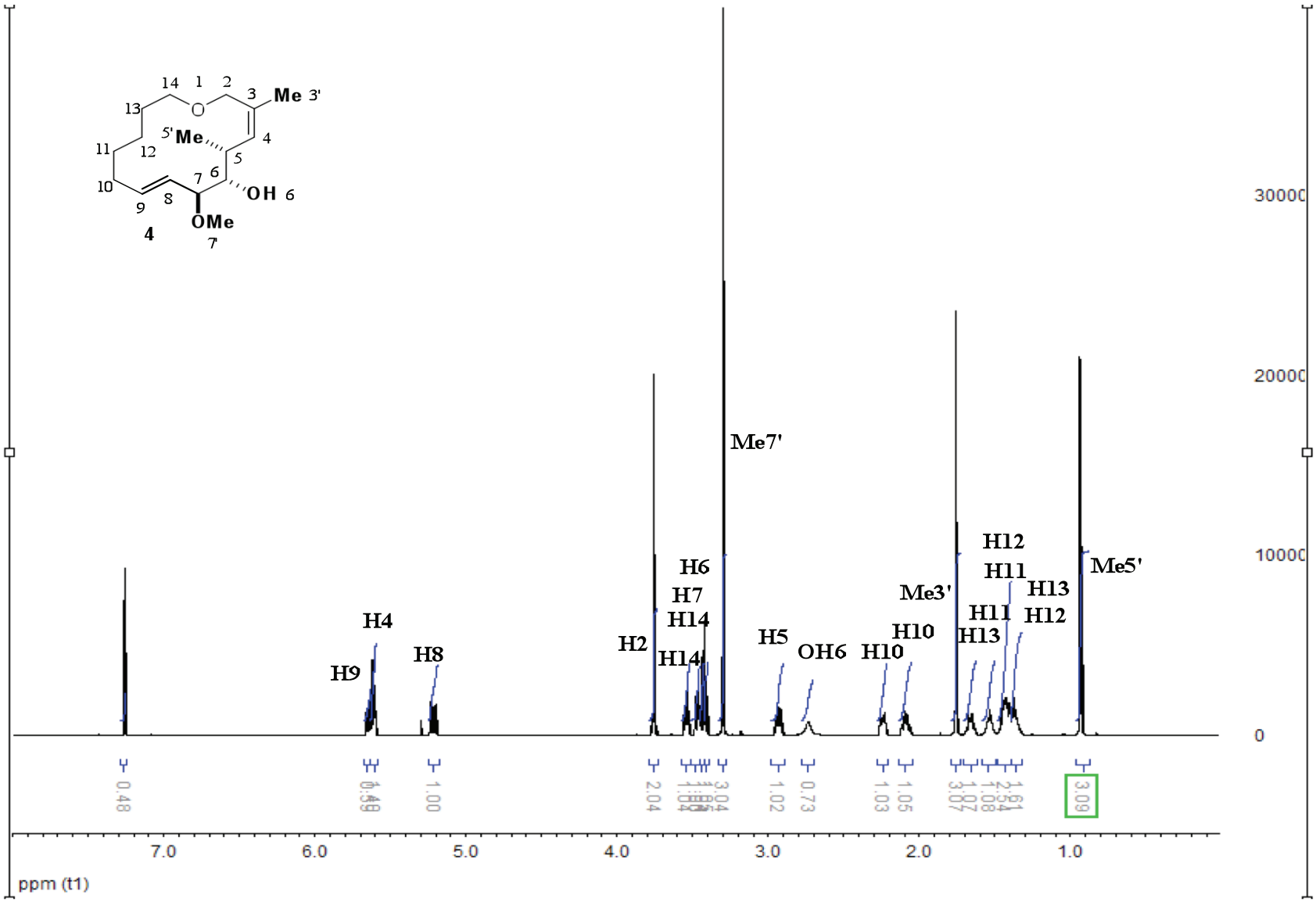


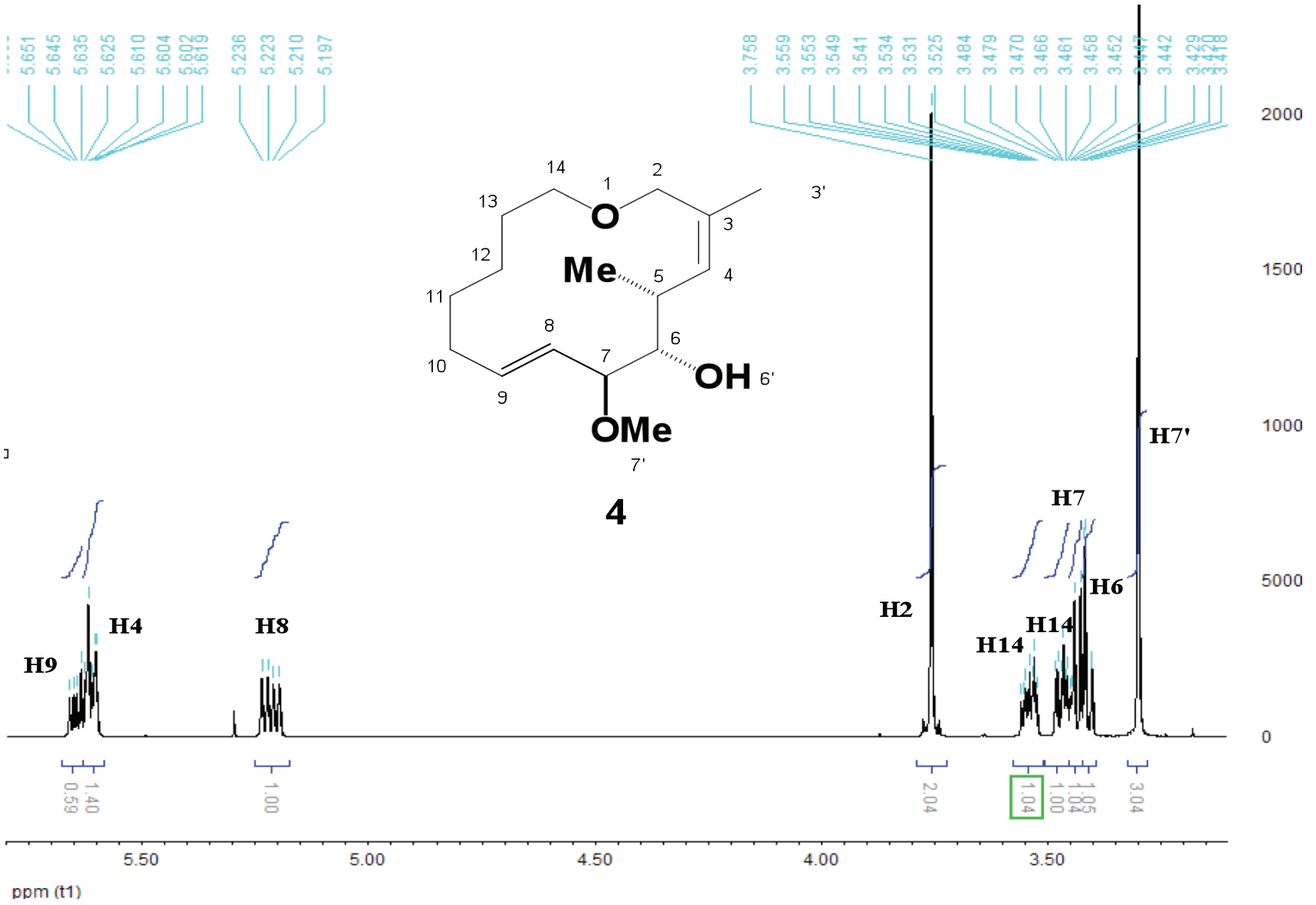
1D NOE Data Extracted from 2D NOESY Spectrum of Migrastatin Ketone (2) recorded in benz
Correlations for H5

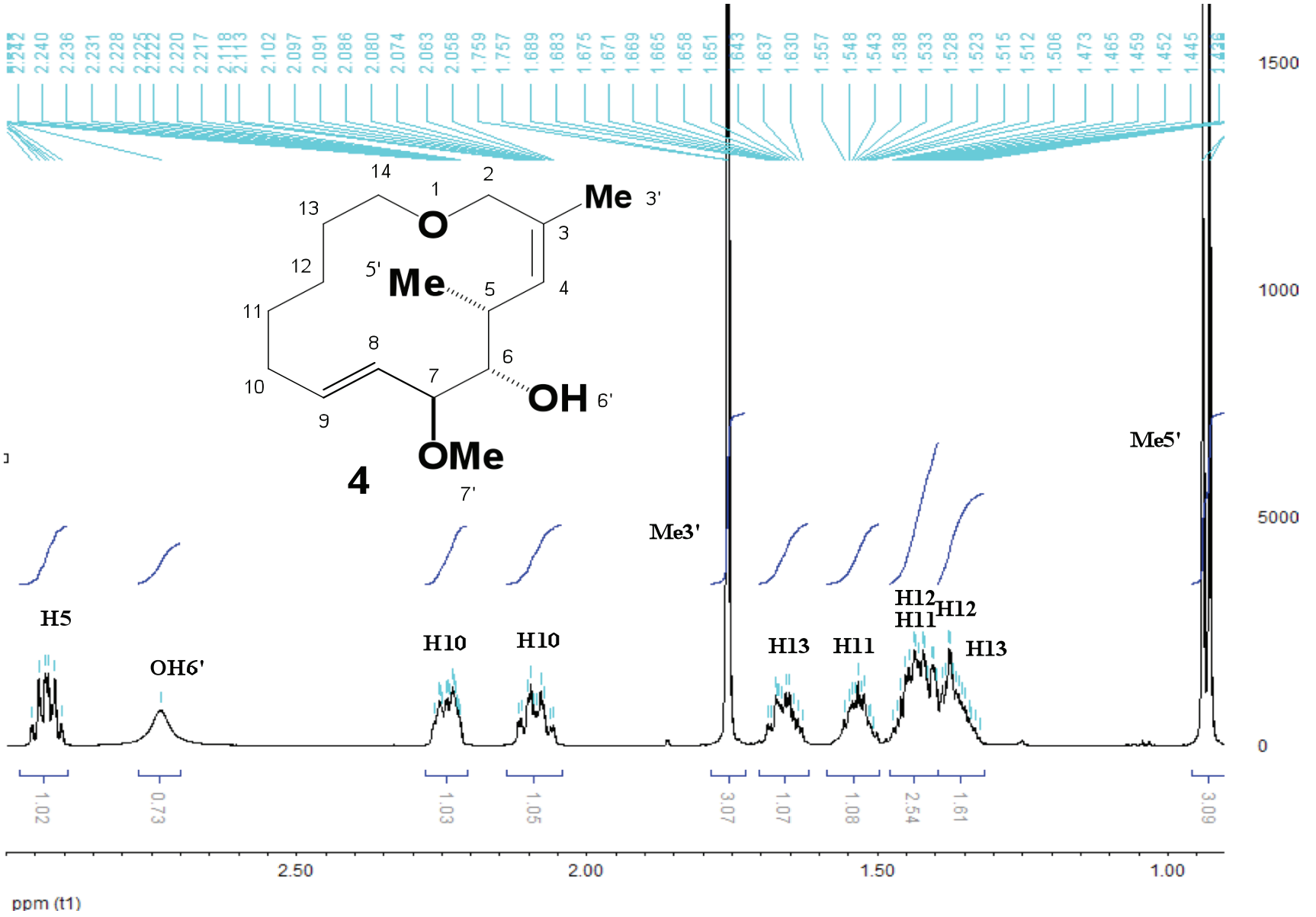


1D NOE data extracted from 2D NOESY spectrum for migrastatin ketone (2) in benzene.
The correlations for the Me4′ of the C4–C5 olefin.

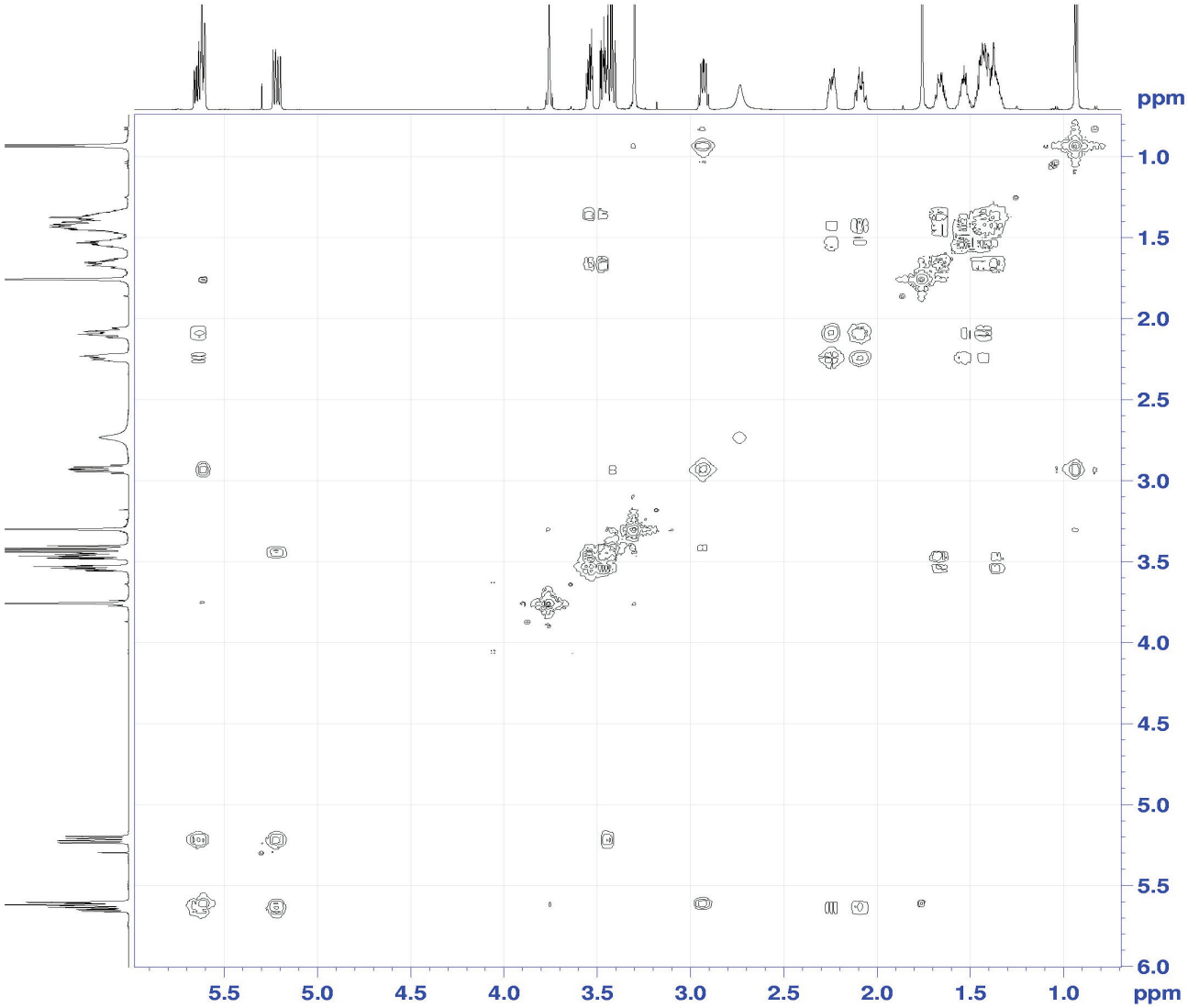


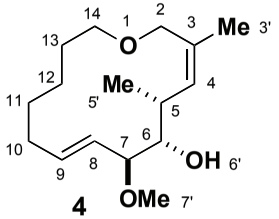

14 1 2 3 Me 3'
13 O 4
5'Me 5
11 12 6
10 7 OH 6
9 8
OMe
4 7'
H4
H9
H8
H2
H6
H7
H14
H14'
Me7'
H5
OH6
H10
H10
Me3'
H12
H11
H13
H11
H13
H12
Me5'
0.48
0.49
1.00
2.04
3.04
1.02
0.73
1.03
1.05
3.07
1.08
1.61
2.54
3.09
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
30000
20000
10000
0


5.651
5.645
5.635
5.625
5.610
5.604
5.602
5.619
5.236
5.223
5.210
5.197
3.758
3.559
3.553
3.549
3.541
3.534
3.531
3.525
3.484
3.479
3.470
3.466
3.461
3.458
3.452
3.447
3.442
3.429
3.420
3.418
14
1
2
13
O
3
12
Me
5
4
11
8
6
10
7
OH
6'
9
OMe
7'
3'
4
H9
H4
H8
H2
H14
H14
H7
H6
H7'
0.59
1.40
1.00
2.04
1.04
1.00
1.04
1.05
3.04
2000
1500
1000
5000
0
5.50
5.00
4.50
4.00
3.50
ppm (t1)


14
1
2
13
O
Me
3'
3
12
5'
Me
5
4
11
8
6
10
7
OH
6'
9
OMe
4
7'
Me5'
Me3'
H5
OH6'
H10
H10
H13
H11
H12
H11
H12
H13
1.02
0.73
1.03
1.05
3.07
1.07
1.08
2.54
1.61
3.09
1500
1000
5000
0
2.50
2.00
1.50
1.00
ppm (t1)

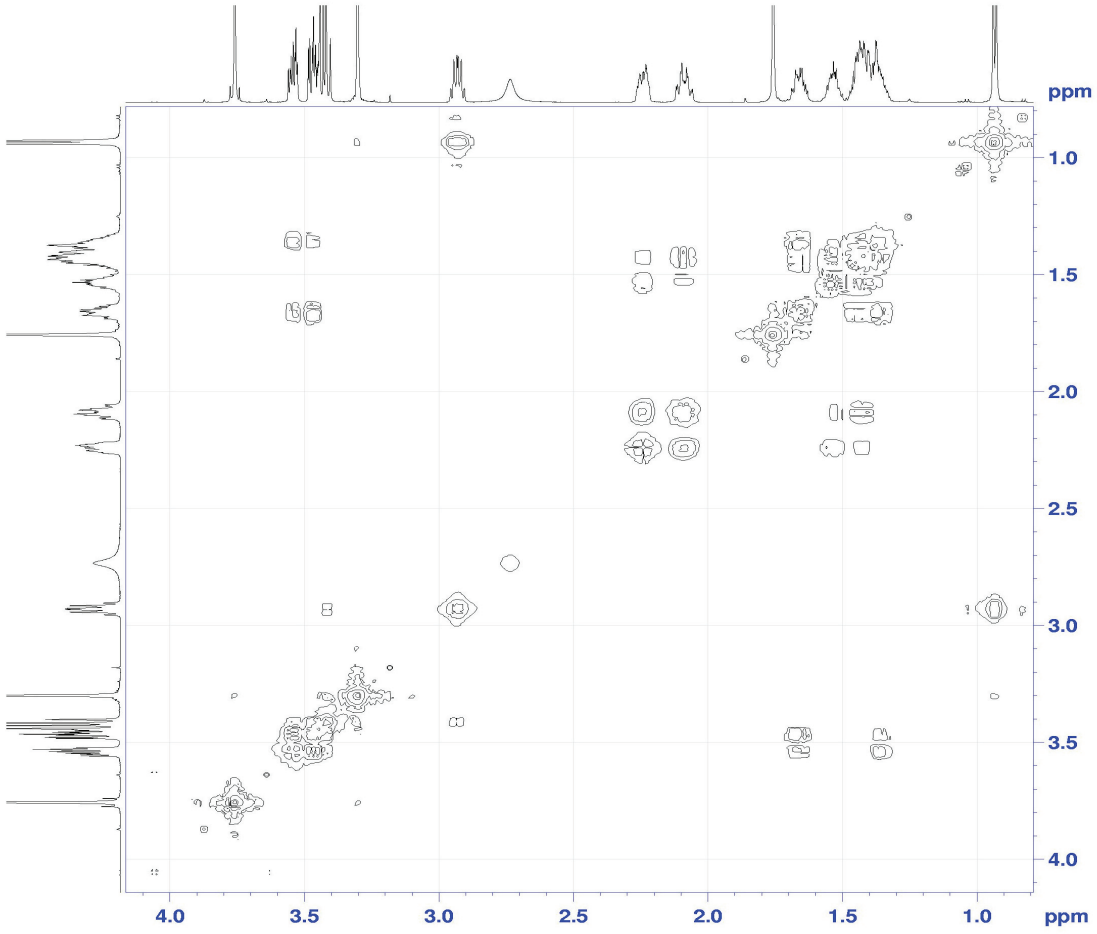
ɜstatin_Ether (11 1) CDCl3 24.0C April_16,2010_10:25:40 Bruker AVIII 600MHz RRL1326: janggeum cosygpqf

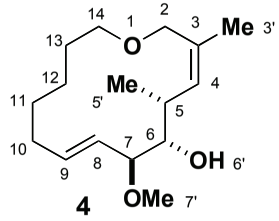




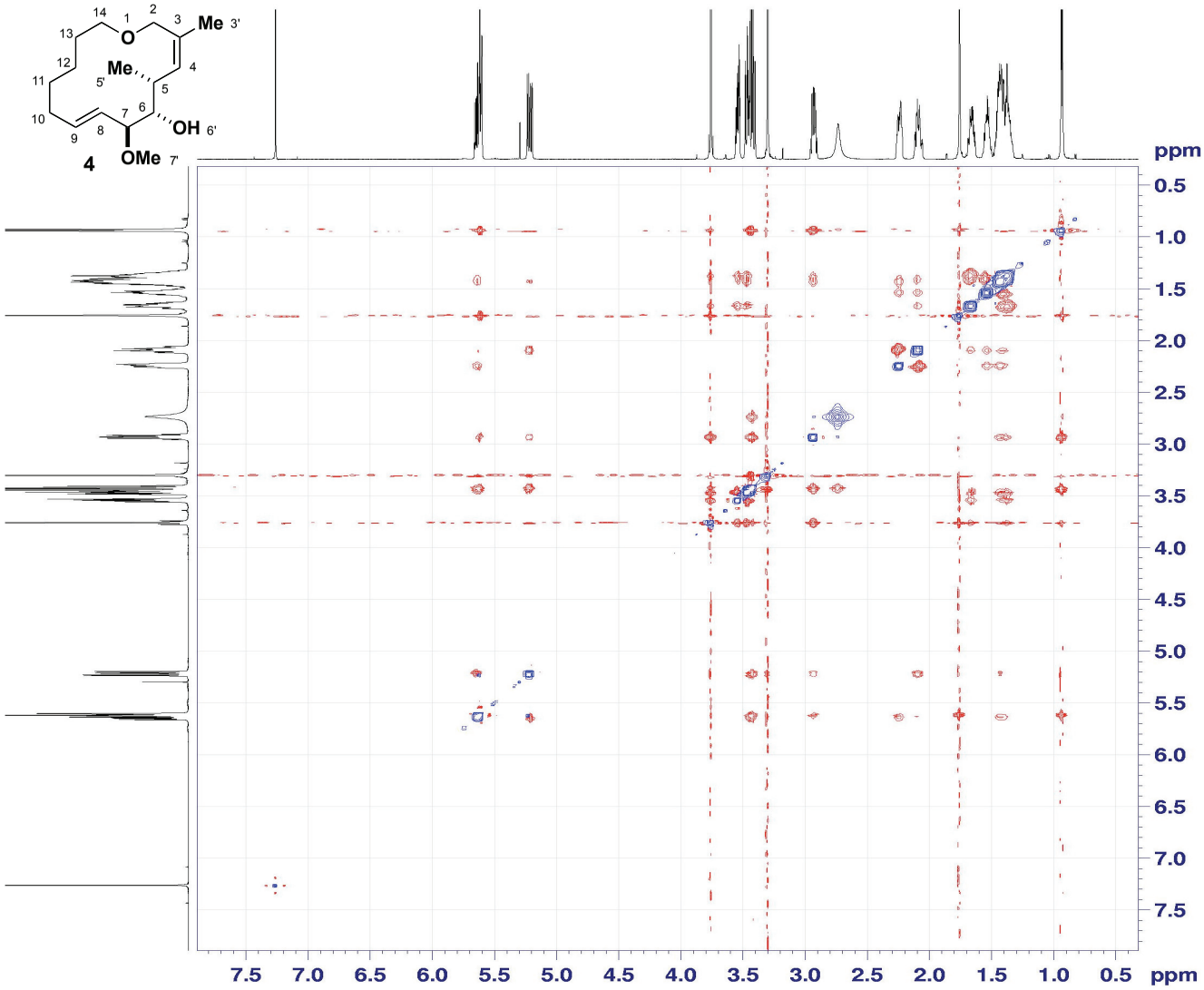
NAME	Migrastatin_Ether	
EXPNO	11	
PROCNO	1	
Date_	20100416	
Time	10.26	
INSTRUM	spect	
PROBHD	5 mm PATXO 19F	
PULPROG	cosygpqf	
TD	2048	
SOLVENT	CDCl3	
NS	3	
DS	16	
SWH	4545.455	Hz
FIDRES	2.219460	Hz
AQ	0.2253300	sec
RG	64	
DW	110.000	usec
DE	6.00	usec
TE	297.1	K
D0	0.00000300	sec
D1	1.38940704	sec
D13	0.00000400	sec
D16	0.00020000	sec
IN0	0.00022000	sec
-------- CHANNEL f1 --------		
NUC1	1H	
P0	14.00	usec
P1	14.00	usec
PL1	-1.30	dB
PL1W	27.78522110	W
SFO1	600.1324788	MHz
------ GRADIENT CHANNEL -----		
GPNAM1	SINE.100	
GPZ1	10.00	%
P16	1000.00	usec
ND0	1	
TD	128	
SFO1	600.1325	MHz
FIDRES	35.511364	Hz
SW	7.574	ppm
FnMODE	QF	
SI	1024	
SF	600.1300153	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	
PC	1.40	
SI	1024	
MC2	QF	
SF	600.1300157	MHz
WDW	SINE	
SSB	0	
LB	0.00	Hz
GB	0	

ıstatin_Ether (11 1) CDCl3 24.0C April_16,2010_10:25:40 Bruker AVIII 600MHz RRL1326: janggeum cosygpqf

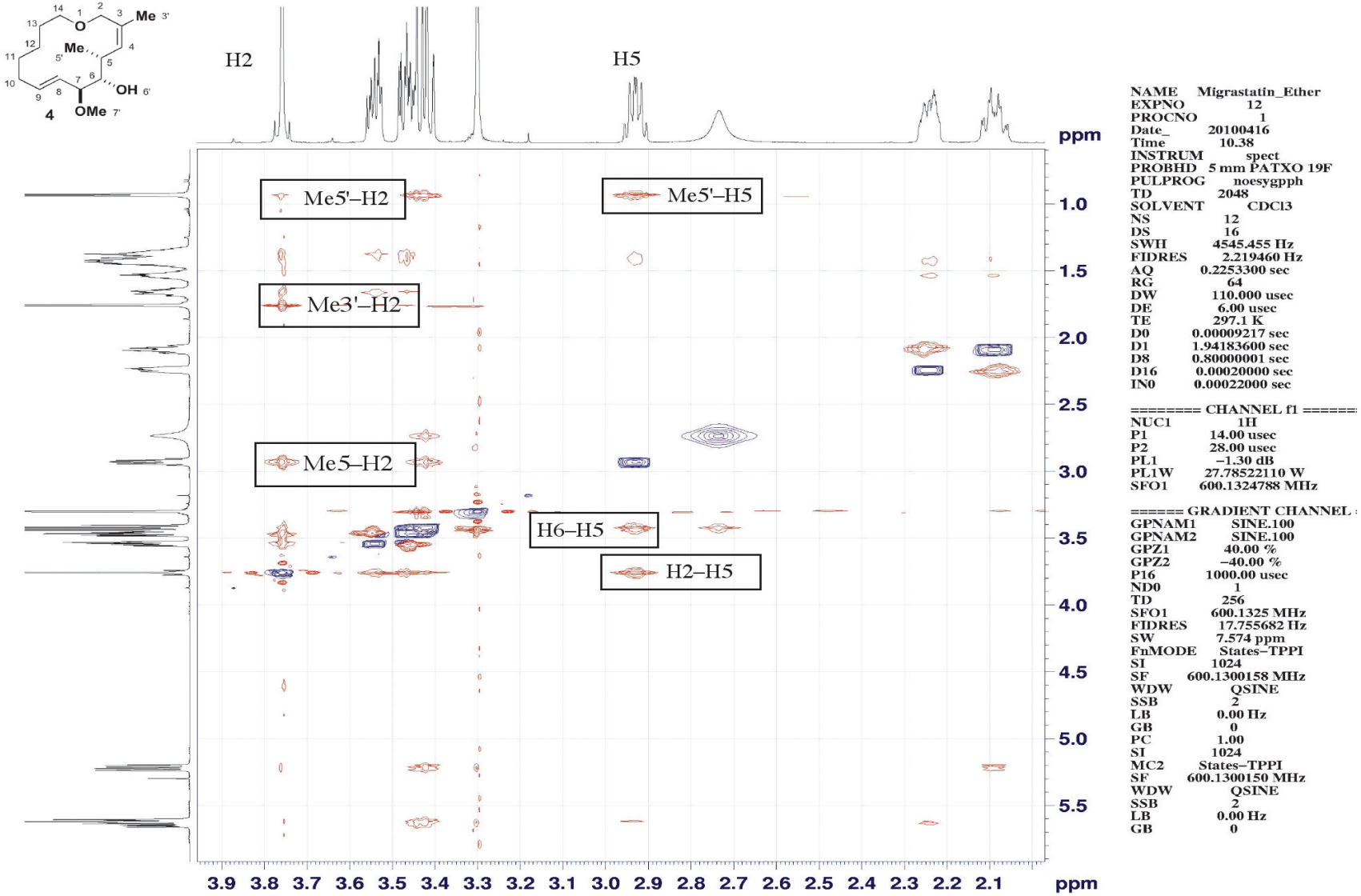





```
NAME          Migrastatin_Ether
EXPNO                        11
PROCNO                        1
Date_                  20100416
Time                      10.26
INSTRUM                   spect
PROBHD    5 mm PATXO 19F
PULPROG                cosygpqf
TD                         2048
SOLVENT                   CDCl3
NS                            3
DS                           16
SWH                    4545.455 Hz
FIDRES                 2.219460 Hz
AQ                     0.2253300 sec
RG                           64
DW                      110.000 usec
DE                        6.00 usec
TE                      297.1 K
D0                     0.00000300 sec
D1                     1.38940704 sec
D13                    0.00000400 sec
D16                    0.00020000 sec
IN0                    0.00022000 sec

======== CHANNEL f1 ========
NUC1                         1H
P0                        14.00 usec
P1                        14.00 usec
PL1                       -1.30 dB
PL1W                  27.78522110 W
SFO1                 600.1324788 MHz

====== GRADIENT CHANNEL =====
GPNAM1                  SINE.100
GPZ1                      10.00 %
P16                     1000.00 usec
ND0                           1
TD                          128
SFO1                 600.1325 MHz
FIDRES                35.511364 Hz
SW                        7.574 ppm
FnMODE                       QF
SI                         1024
SF                   600.1300153 MHz
WDW                        SINE
SSB                           0
LB                         0.00 Hz
GB                            0
PC                         1.40
SI                         1024
MC2                          QF
SF                   600.1300157 MHz
WDW                        SINE
SSB                           0
LB                         0.00 Hz
GB                            0
```



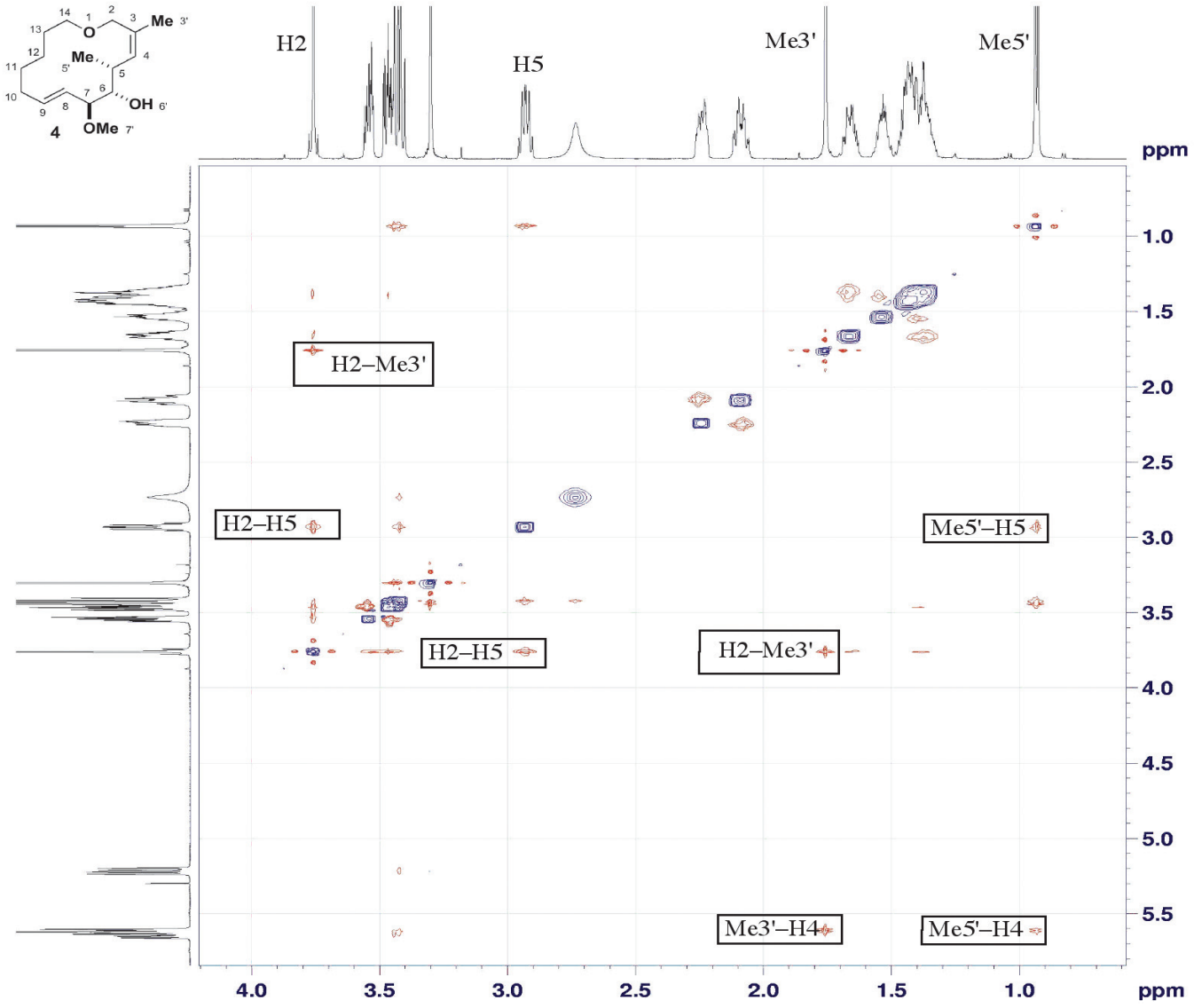

```
NAME      Migrastatin_Ether
EXPNO             12
PROCNO             1
Date_          20100416
Time              10.38
INSTRUM           spect
PROBHD   5 mm PATXO 19F
PULPROG        noesygpph
TD                2048
SOLVENT           CDCl3
NS                  12
DS                  16
SWH           4545.455 Hz
FIDRES          2.219460 Hz
AQ            0.2253300 sec
RG                  64
DW             110.000 usec
DE               6.00 usec
TE               297.1 K
D0            0.00009217 sec
D1            1.94183600 sec
D8            0.80000001 sec
D16           0.00020000 sec
IN0           0.00022000 sec

======== CHANNEL f1 =====
NUC1                1H
P1              14.00 usec
P2              28.00 usec
PL1             -1.30 dB
PL1W        27.78522110 W
SFO1       600.1324788 MHz

====== GRADIENT CHANNEL
GPNAM1          SINE.100
GPNAM2          SINE.100
GPZ1             40.00 %
GPZ2            -40.00 %
P16           1000.00 usec
ND0                 1
TD                256
SFO1         600.1325 MHz
FIDRES        17.755682 Hz
SW            7.574 ppm
FnMODE       States-TPPI
SI               1024
SF         600.1300158 MHz
WDW               QSINE
SSB                 2
LB              0.00 Hz
GB                  0
PC              1.00
SI              1024
MC2          States-TPPI
SF         600.1300150 MHz
WDW               QSINE
SSB                 2
LB              0.00 Hz
GB                  0
```



NAME Migrastatin_Ether
EXPNO 12
PROCNO 1
Date_ 20100416
Time 10.38
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG noesygpph
TD 2048
SOLVENT CDCl3
NS 12
DS 16
SWH 4545.455 Hz
FIDRES 2.219460 Hz
AQ 0.2253300 sec
RG 64
DW 110.000 usec
DE 6.00 usec
TE 297.1 K
D0 0.00009217 sec
D1 1.94183600 sec
D8 0.80000001 sec
D16 0.00020000 sec
IN0 0.00022000 sec

======== CHANNEL f1 ======
NUC1 1H
P1 14.00 usec
P2 28.00 usec
PL1 −1.30 dB
PL1W 27.78522110 W
SFO1 600.1324788 MHz

====== GRADIENT CHANNEL
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 40.00 %
GPZ2 −40.00 %
P16 1000.00 usec
ND0 1
TD 256
SFO1 600.1325 MHz
FIDRES 17.755682 Hz
SW 7.574 ppm
FnMODE States−TPPI
SI 1024
SF 600.1300158 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
SI 1024
MC2 States−TPPI
SF 600.1300150 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0

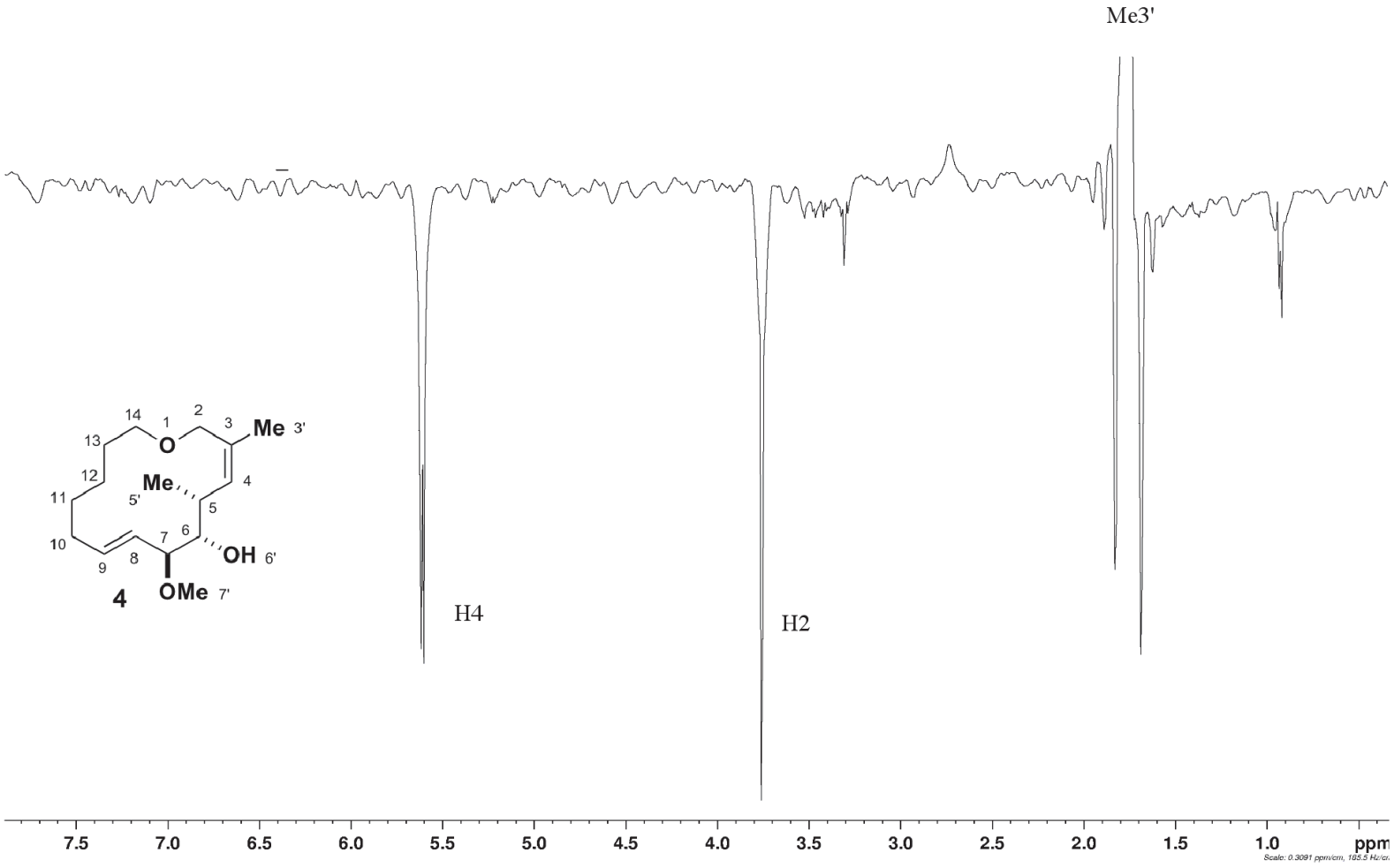


NAME Migrastatin_Ether
EXPNO 12
PROCNO 1
Date_ 20100416
Time 10.38
INSTRUM spect
PROBHD 5 mm PATXO 19F
PULPROG noesygpph
TD 2048
SOLVENT CDCl3
NS 12
DS 16
SWH 4545.455 Hz
FIDRES 2.219460 Hz
AQ 0.2253300 sec
RG 64
DW 110.000 usec
DE 6.00 usec
TE 297.1 K
D0 0.00009217 sec
D1 1.94183600 sec
D8 0.80000001 sec
D16 0.00020000 sec
IN0 0.00022000 sec

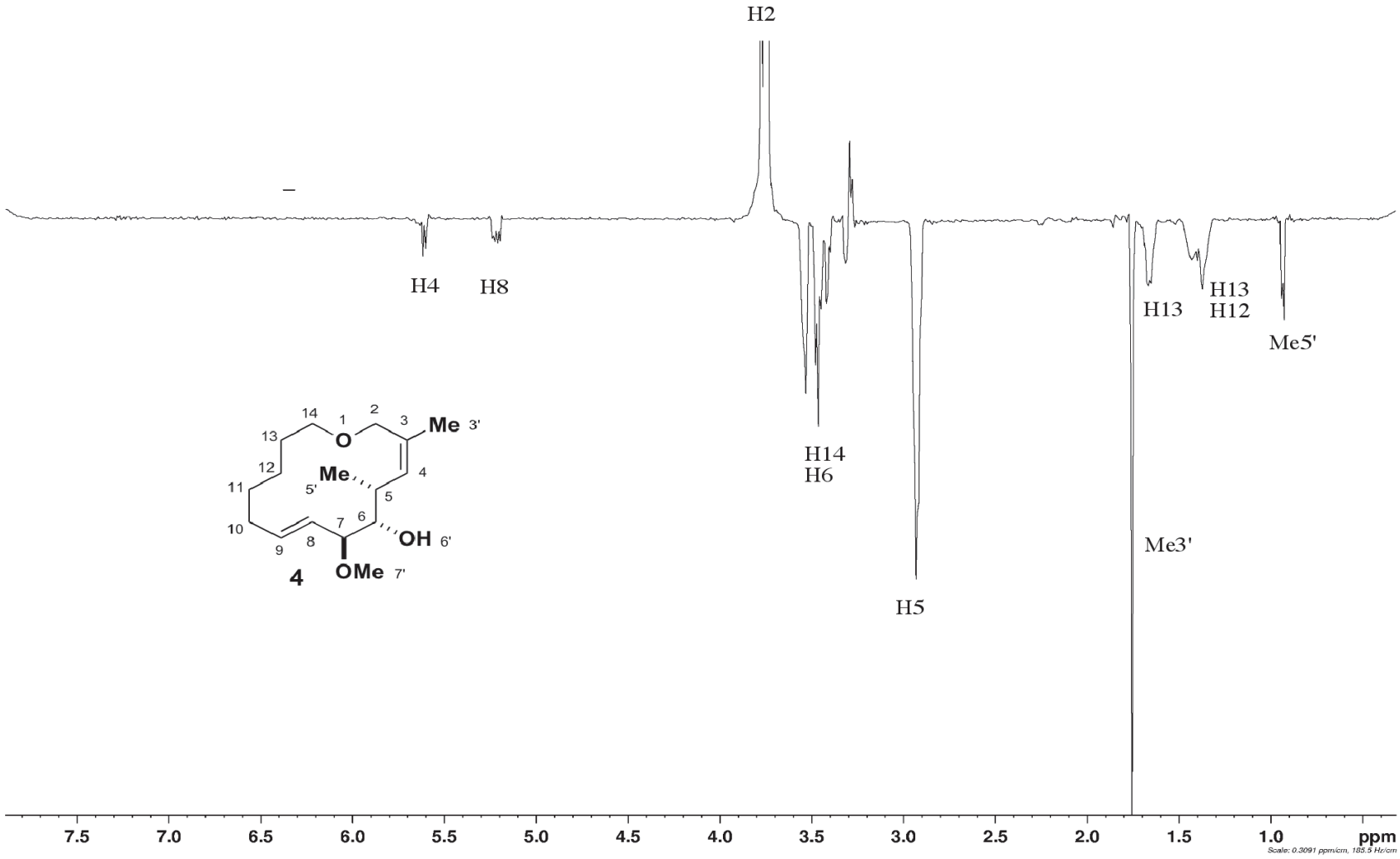
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
P2 28.00 usec
PL1 −1.30 dB
PL1W 27.78522110 W
SFO1 600.1324788 MHz

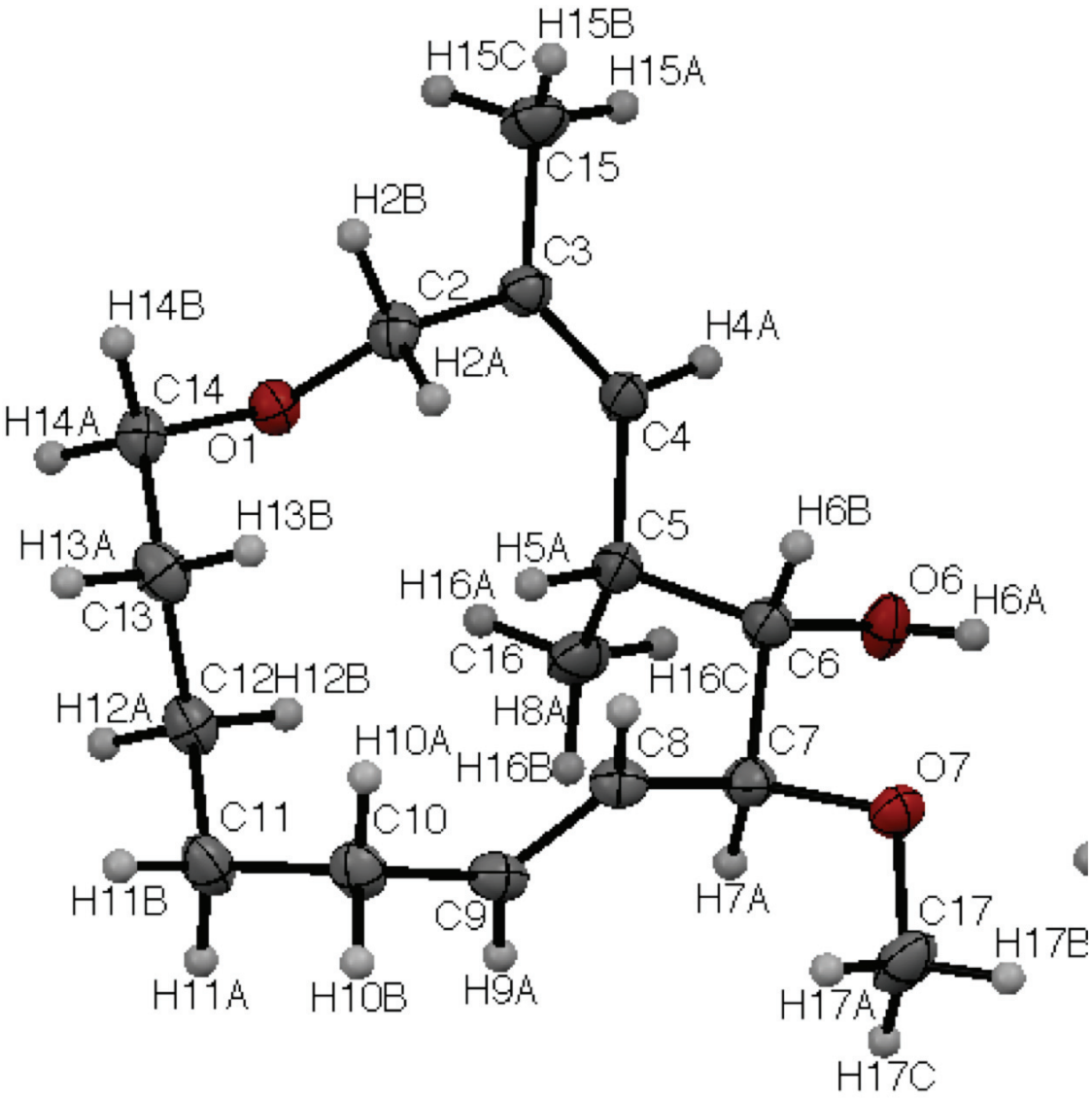
====== GRADIENT CHANNEL =
GPNAM1 SINE.100
GPNAM2 SINE.100
GPZ1 40.00 %
GPZ2 −40.00 %
P16 1000.00 usec
ND0 1
TD 256
SFO1 600.1325 MHz
FIDRES 17.755682 Hz
SW 7.574 ppm
FnMODE States−TPPI
SI 1024
SF 600.1300158 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00
SI 1024
MC2 States−TPPI
SF 600.1300150 MHz
WDW QSINE
SSB 2
LB 0.00 Hz
GB 0

1D NOE data extracted from 2D NOESY spectrum of Migrastatin Ether (4) recorded in chloroform.
Correlations for Me3



1D NOE data extracted from 2D NOESY spectrum of Migrastatin Ketone (4) recorded in chloroform. Correlations for H2 protons.




H15B
H15C
H15A
C15
H2B
C3
C2
H14B
H4A
H2A
C14
H14A
O1
C4
H13B
H6B
H13A
C5
H5A
H16A
O6
H6A
C13
C16
H16C
C6
C12H12B
H12A
H8A
H10A
C8
C7
H16B
O7
C11
C10
H11B
H7A
C9
C17
H17B
H11A
H10B
H9A
H17A
H17C

Single-Crystal X-ray Diffraction. The intensity data for **I** were measured on a Bruker-Nonius KappaCCD diffractometer (graphite-monochromated Mo $K\alpha$ radiation, λ = 0.71073 Å, ϕ-ω scans) at 100 (1) K. The data were not corrected for absorption. Details of the solution and refinements for this compound are presented below:

$C_{16}H_{28}O_3$ (I): The crystal of **I**, with approximate dimensions 0.050 x 0.10 x 0.36 mm, were monoclinic with space group $P2_1$. The final unit-cell constants of **I** were a = 9.069(2), b = 11.990(2), c = 14.787(3) Å, β = 94.81(3)°, V = 1602.2(6) Å^3, Z = 4, ρ = 1.113 g cm^{-1}, μ = 0.075 mm^{-1}, formula weight = 268.38. The structure of **I** was solved with SHELXS-97 and refined by full-matrix least squares on F^2 with SHELXL-97. The unit cell of **I** contains two independent molecules. The hydrogen atoms were included in the structure-factor calculations, but their parameters were not refined. The final discrepancy indices for the 4874 reflections (θ < 30.04°) were R = 0.0612 (calculated on F) and R_w = 0.1143 (calculated on F^2) with 352 parameters varied. The final difference map peaks are < 0.25 e Å^{-3}.

Table 1. Thermal Parameters (U's) for PN-V-ME at 100 K

Atom	U11/U	U22	U33	U12	U13	U23
O1	0.023(1)	0.024(1)	0.021(1)	-0.0013(9)	0.0012(9)	0.0001(9)
O6	0.024(1)	0.026(1)	0.027(1)	-0.0038(9)	-0.006(1)	0.0077(9)
O7	0.030(1)	0.019(1)	0.027(1)	-0.0022(9)	0.000(1)	0.0018(9)
C2	0.020(2)	0.028(2)	0.023(2)	0.003(1)	0.003(1)	0.002(1)
C3	0.025(2)	0.019(1)	0.023(2)	-0.001(1)	0.004(1)	-0.000(1)
C4	0.025(2)	0.020(1)	0.022(2)	-0.003(1)	-0.004(1)	0.000(1)
C5	0.029(2)	0.020(1)	0.023(2)	0.001(1)	-0.004(1)	0.001(1)
C6	0.023(2)	0.021(1)	0.023(2)	-0.001(1)	-0.002(1)	0.000(1)

C7	0.024(2)	0.020(1)	0.023(2)	0.001(1)	0.004(1)	-0.002(1)
C8	0.020(2)	0.023(1)	0.025(2)	-0.001(1)	0.004(1)	-0.002(1)
C9	0.027(2)	0.021(1)	0.027(2)	-0.002(1)	0.006(1)	-0.004(1)
C10	0.027(2)	0.027(2)	0.024(2)	-0.007(1)	-0.001(1)	-0.000(1)
C11	0.035(2)	0.031(2)	0.020(2)	-0.009(1)	-0.001(1)	-0.000(1)
C12	0.025(2)	0.031(2)	0.020(2)	-0.004(1)	0.001(1)	-0.000(1)
C13	0.023(2)	0.035(2)	0.024(2)	-0.004(1)	-0.000(1)	-0.003(1)
C14	0.024(2)	0.027(2)	0.022(2)	0.002(1)	-0.000(1)	0.003(1)
C15	0.034(2)	0.021(2)	0.039(2)	-0.004(1)	0.001(2)	-0.004(1)
C16	0.049(2)	0.019(2)	0.031(2)	-0.000(1)	0.012(2)	0.002(1)
C17	0.038(2)	0.019(2)	0.046(2)	-0.003(1)	-0.006(2)	0.006(2)
O1'	0.019(1)	0.024(1)	0.023(1)	0.0011(9)	0.0003(9)	-0.0019(9)
O6'	0.032(1)	0.028(1)	0.020(1)	0.010(1)	-0.005(1)	-0.0025(9)
O7'	0.025(1)	0.018(1)	0.025(1)	0.0022(9)	-0.000(1)	-0.0016(8)
C2'	0.024(2)	0.025(2)	0.022(2)	0.004(1)	0.005(1)	0.001(1)
C3'	0.018(1)	0.020(1)	0.027(2)	0.001(1)	0.002(1)	-0.004(1)
C4'	0.025(2)	0.020(1)	0.021(2)	0.001(1)	-0.002(1)	-0.003(1)
C5'	0.026(2)	0.019(1)	0.021(2)	-0.000(1)	-0.003(1)	-0.001(1)
C6'	0.021(2)	0.021(1)	0.021(2)	0.003(1)	0.001(1)	-0.001(1)
C7'	0.020(2)	0.020(1)	0.022(2)	0.001(1)	-0.000(1)	-0.001(1)
C8'	0.024(2)	0.019(1)	0.021(2)	-0.000(1)	0.003(1)	-0.001(1)
C9'	0.023(2)	0.022(1)	0.020(2)	-0.000(1)	0.003(1)	-0.003(1)
C10'	0.026(2)	0.026(2)	0.023(2)	0.001(1)	-0.001(1)	-0.004(1)
C11'	0.025(2)	0.026(2)	0.024(2)	-0.002(1)	-0.002(1)	-0.002(1)
C12'	0.022(2)	0.024(1)	0.022(2)	0.001(1)	0.002(1)	-0.000(1)
C13'	0.025(2)	0.029(2)	0.022(2)	0.001(1)	0.004(1)	-0.002(1)
C14'	0.027(2)	0.025(2)	0.022(2)	0.003(1)	0.001(1)	0.001(1)
C15'	0.029(2)	0.023(2)	0.031(2)	-0.001(1)	0.006(1)	-0.001(1)
C16'	0.024(2)	0.023(2)	0.039(2)	0.001(1)	-0.003(2)	0.000(1)
C17'	0.033(2)	0.021(2)	0.028(2)	0.004(1)	0.004(2)	-0.001(1)

Table 2. Coordinates for PN-V-ME at 100 K

Atom	x	y	z
O1	0.3376(2)	0.6858(2)	-0.0009(1)
O6	0.6182(2)	0.3782(2)	0.2478(2)
O7	0.3993(2)	0.2136(2)	0.2296(1)

C2	0.2927(3)	0.6848(3)	0.0890(2)
C3	0.4270(3)	0.6893(2)	0.1567(2)
C4	0.5152(4)	0.6015(2)	0.1741(2)
C5	0.4972(4)	0.4894(2)	0.1288(2)
C6	0.4790(4)	0.3965(2)	0.1984(2)
C7	0.4182(3)	0.2882(2)	0.1544(2)
C8	0.2763(3)	0.3081(2)	0.0980(2)
C9	0.2545(4)	0.2855(2)	0.0100(2)
C10	0.1188(4)	0.3142(3)	-0.0501(2)
C11	0.1561(4)	0.3777(3)	-0.1350(2)
C12	0.2341(4)	0.4894(3)	-0.1168(2)
C13	0.1337(4)	0.5809(3)	-0.0831(2)
C14	0.2144(4)	0.6911(3)	-0.0681(2)
C15	0.4550(4)	0.8011(2)	0.2021(2)
C16	0.6265(4)	0.4676(3)	0.0705(2)
C17	0.3535(4)	0.1043(3)	0.2003(3)
O1'	0.9337(2)	-0.1786(2)	0.5993(1)
O6'	0.6710(3)	0.1122(2)	0.3162(1)
O7'	0.6108(2)	0.2859(2)	0.4298(1)
C2'	0.7784(4)	-0.1616(3)	0.5778(2)
C3'	0.7428(3)	-0.1828(2)	0.4774(2)
C4'	0.7580(3)	-0.1041(2)	0.4154(2)
C5'	0.8149(3)	0.0124(2)	0.4332(2)
C6'	0.6936(4)	0.1002(2)	0.4123(2)
C7'	0.7317(3)	0.2117(2)	0.4590(2)
C8'	0.7492(3)	0.1985(2)	0.5601(2)
C9'	0.8729(4)	0.2222(2)	0.6099(2)
C10'	0.9022(4)	0.2016(3)	0.7097(2)
C11'	1.0499(4)	0.1423(2)	0.7328(2)
C12'	1.0610(4)	0.0260(2)	0.6916(2)
C13'	0.9676(4)	-0.0600(3)	0.7365(2)
C14'	0.9754(4)	-0.1763(3)	0.6951(2)
C15'	0.6947(4)	-0.3003(3)	0.4538(2)
C16'	0.9518(4)	0.0335(3)	0.3818(2)
C17'	0.6310(4)	0.3961(2)	0.4668(2)

Table 3. Bond Distances and Bond Angles for PN-V-ME at 100 K

	Bond Distance		Bond Angle
O1 - C2	1.423(4) Å	C2 - O1 - C14	112.4(2)°
O1 - C14	1.433(4) Å		
O6 - C6	1.422(4) Å		
O7 - C7	1.449(3) Å	C7 - O7 - C17	112.6(2)°
O7 - C17	1.430(4) Å		
C2 - O1	1.423(4) Å	O1 - C2 - C3	109.9(2)°
C2 - C3	1.511(4) Å		
C3 - C2	1.511(4) Å	C2 - C3 - C4	122.4(3)°
C3 - C4	1.334(4) Å	C2 - C3 - C15	115.0(2)°
C3 - C15	1.511(4) Å	C4 - C3 - C15	122.6(3)°
C4 - C3	1.334(4) Å	C3 - C4 - C5	125.3(3)°
C4 - C5	1.505(4) Å		
C5 - C4	1.505(4) Å	C4 - C5 - C6	111.3(2)°
C5 - C6	1.535(4) Å	C4 - C5 - C16	110.0(3)°
C5 - C16	1.535(5) Å	C6 - C5 - C16	112.5(2)°
C6 - O6	1.422(4) Å	O6 - C6 - C5	108.4(2)°
C6 - C5	1.535(4) Å	O6 - C6 - C7	111.1(2)°
C6 - C7	1.534(4) Å	C5 - C6 - C7	112.6(2)°
C7 - O7	1.449(3) Å	O7 - C7 - C6	105.0(2)°
C7 - C6	1.534(4) Å	O7 - C7 - C8	112.1(2)°
C7 - C8	1.493(4) Å	C6 - C7 - C8	111.3(2)°
C8 - C7	1.493(4) Å	C7 - C8 - C9	124.4(3)°
C8 - C9	1.328(4) Å		
C9 - C8	1.328(4) Å	C8 - C9 - C10	125.6(3)°
C9 - C10	1.496(5) Å		
C10 - C9	1.496(5) Å	C9 - C10 - C11	112.0(3)°
C10 - C11	1.530(4) Å		

C11 - C10	1.530(4) Å	C10 - C11 - C12	115.0(3)°
C11 - C12	1.528(5) Å		
C12 - C11	1.528(5) Å	C11 - C12 - C13	113.9(3)°
C12 - C13	1.535(5) Å		
C13 - C12	1.535(5) Å	C12 - C13 - C14	112.2(3)°
C13 - C14	1.518(5) Å		
C14 - O1	1.433(4) Å	O1 - C14 - C13	113.7(3)°
C14 - C13	1.518(5) Å		
C15 - C3	1.511(4) Å		
C16 - C5	1.535(5) Å		
C17 - O7	1.430(4) Å		
O1' - C2'	1.432(4) Å	C2' - O1' - C14'	112.9(2)°
O1' - C14'	1.435(4) Å		
O6' - C6'	1.427(4) Å		
O7' - C7'	1.449(3) Å	C7' - O7' - C17'	112.5(2)°
O7' - C17'	1.436(3) Å		
C2' - O1'	1.432(4) Å	O1' - C2' - C3'	108.6(2)°
C2' - C3'	1.514(4) Å		
C3' - C2'	1.514(4) Å	C2' - C3' - C4'	122.0(2)°
C3' - C4'	1.331(4) Å	C2' - C3' - C15'	114.7(2)°
C3' - C15'	1.507(4) Å	C4' - C3' - C15'	123.2(3)°
C4' - C3'	1.331(4) Å	C3' - C4' - C5'	126.3(3)°
C4' - C5'	1.505(3) Å		
C5' - C4'	1.505(3) Å	C4' - C5' - C6'	111.8(2)°
C5' - C6'	1.535(4) Å	C4' - C5' - C16'	110.3(2)°
C5' - C16'	1.530(4) Å	C6' - C5' - C16'	112.6(2)°
C6' - O6'	1.427(4) Å	O6' - C6' - C5'	108.1(2)°
C6' - C5'	1.535(4) Å	O6' - C6' - C7'	111.7(2)°
C6' - C7'	1.531(4) Å	C5' - C6' - C7'	112.2(2)°

C7' - O7'	1.449(3) Å	O7' - C7' - C6'	105.4(2)°
C7' - C6'	1.531(4) Å	O7' - C7' - C8'	112.1(2)°
C7' - C8'	1.498(4) Å	C6' - C7' - C8'	111.0(2)°
C8' - C7'	1.498(4) Å	C7' - C8' - C9'	123.2(2)°
C8' - C9'	1.320(4) Å		
C9' - C8'	1.320(4) Å	C8' - C9' - C10'	125.9(3)°
C9' - C10'	1.498(4) Å		
C10' - C9'	1.498(4) Å	C9' - C10' - C11'	112.1(3)°
C10' - C11'	1.530(5) Å		
C11' - C10'	1.530(5) Å	C10' - C11' - C12'	114.9(3)°
C11' - C12'	1.528(4) Å		
C12' - C11'	1.528(4) Å	C11' - C12' - C13'	112.7(3)°
C12' - C13'	1.522(4) Å		
C13' - C12'	1.522(4) Å	C12' - C13' - C14'	113.4(3)°
C13' - C14'	1.527(5) Å		
C14' - O1'	1.435(4) Å	O1' - C14' - C13'	113.3(3)°
C14' - C13'	1.527(5) Å		
C15' - C3'	1.507(4) Å		
C16' - C5'	1.530(4) Å		
C17' - O7'	1.436(3) Å		