Supplementary data

Biologically Active Metabolites from the Marine Sediment-Derived Fungus *Aspergillus flocculosus*

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Content

Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of aspilactonol F (**1**)

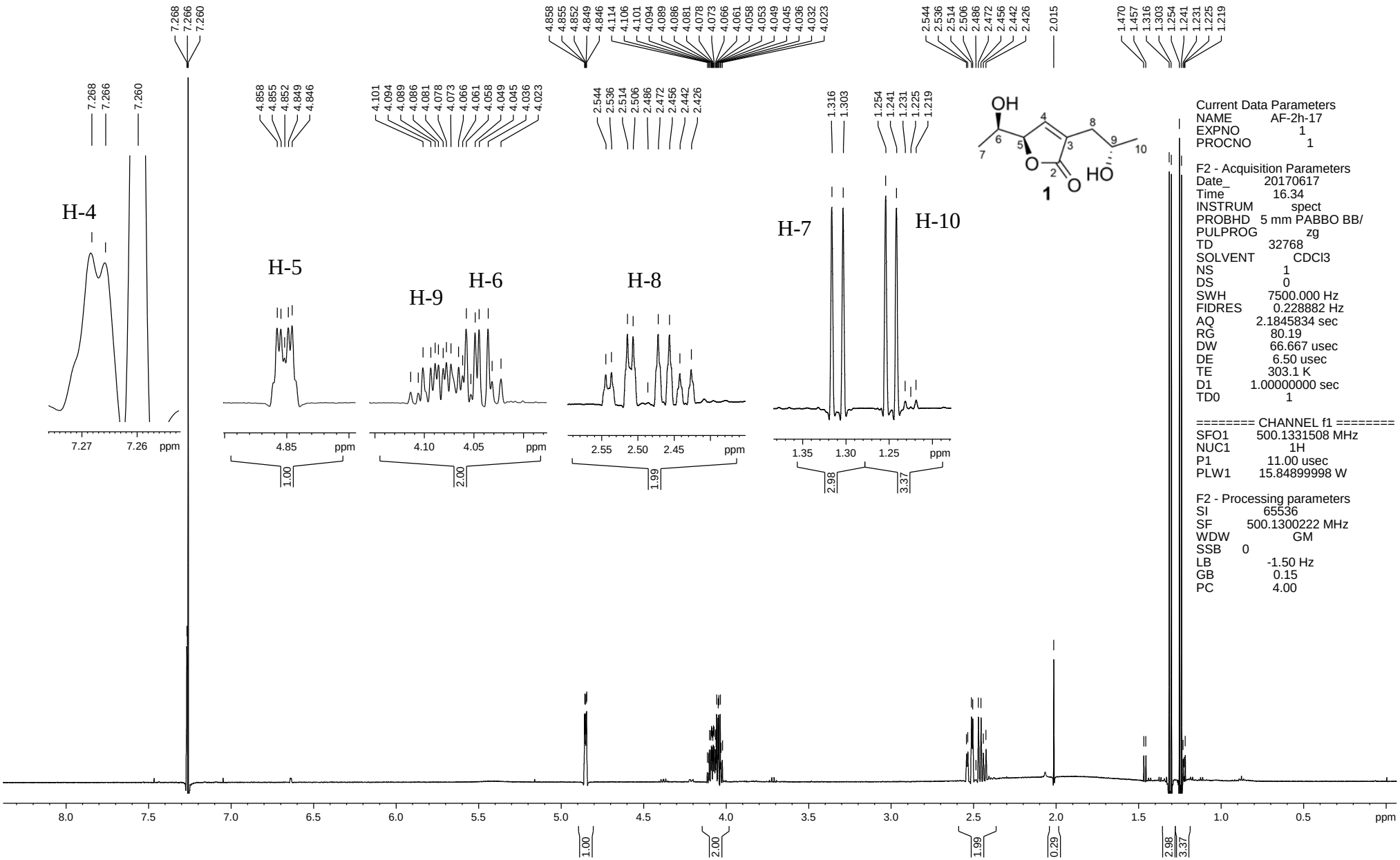


Figure S2. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of aspilactonol F (**1**)

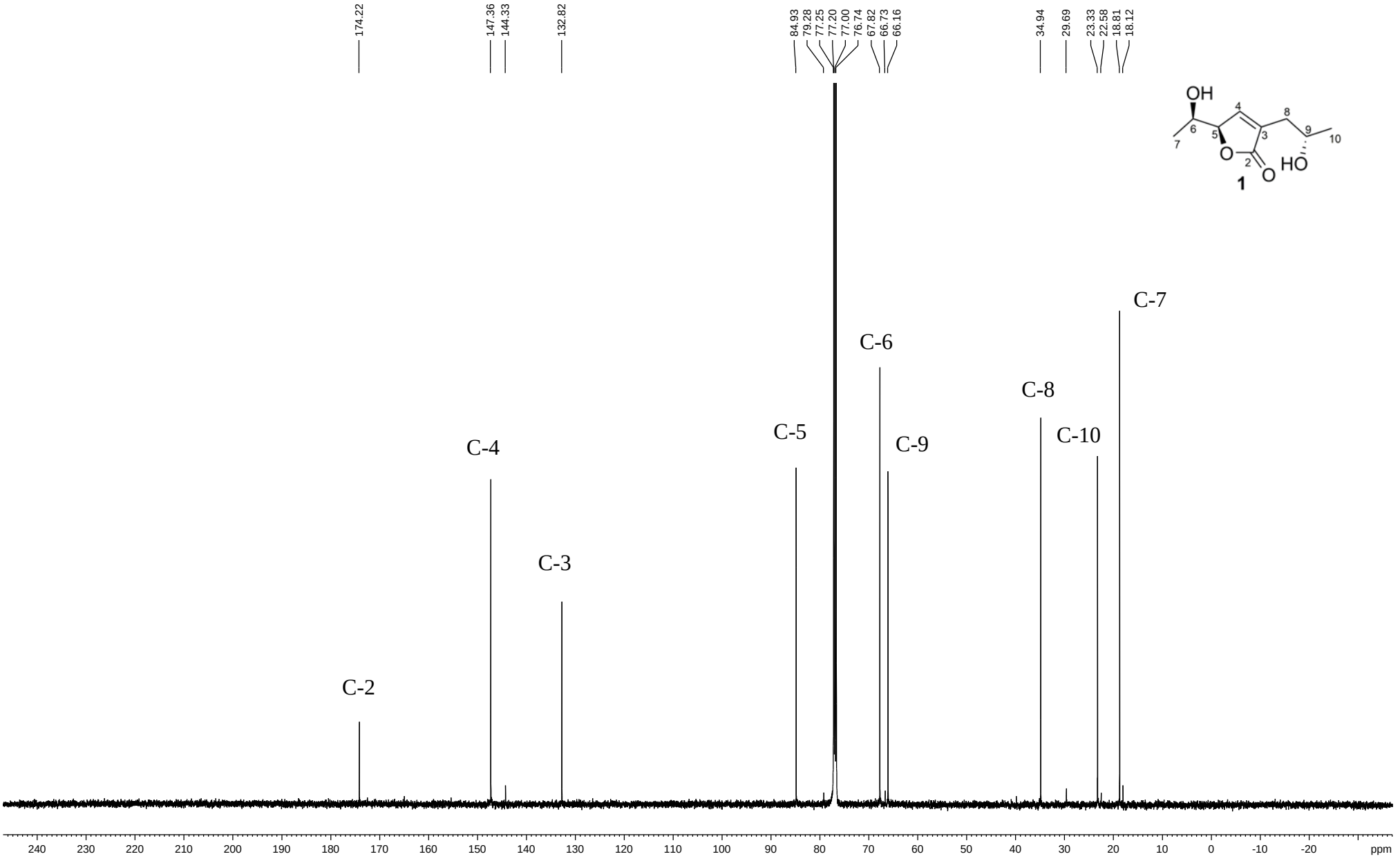


Figure S3. DEPT-135 (125 MHz, $CDCl_3$) spectrum of aspilactonol F (**1**)

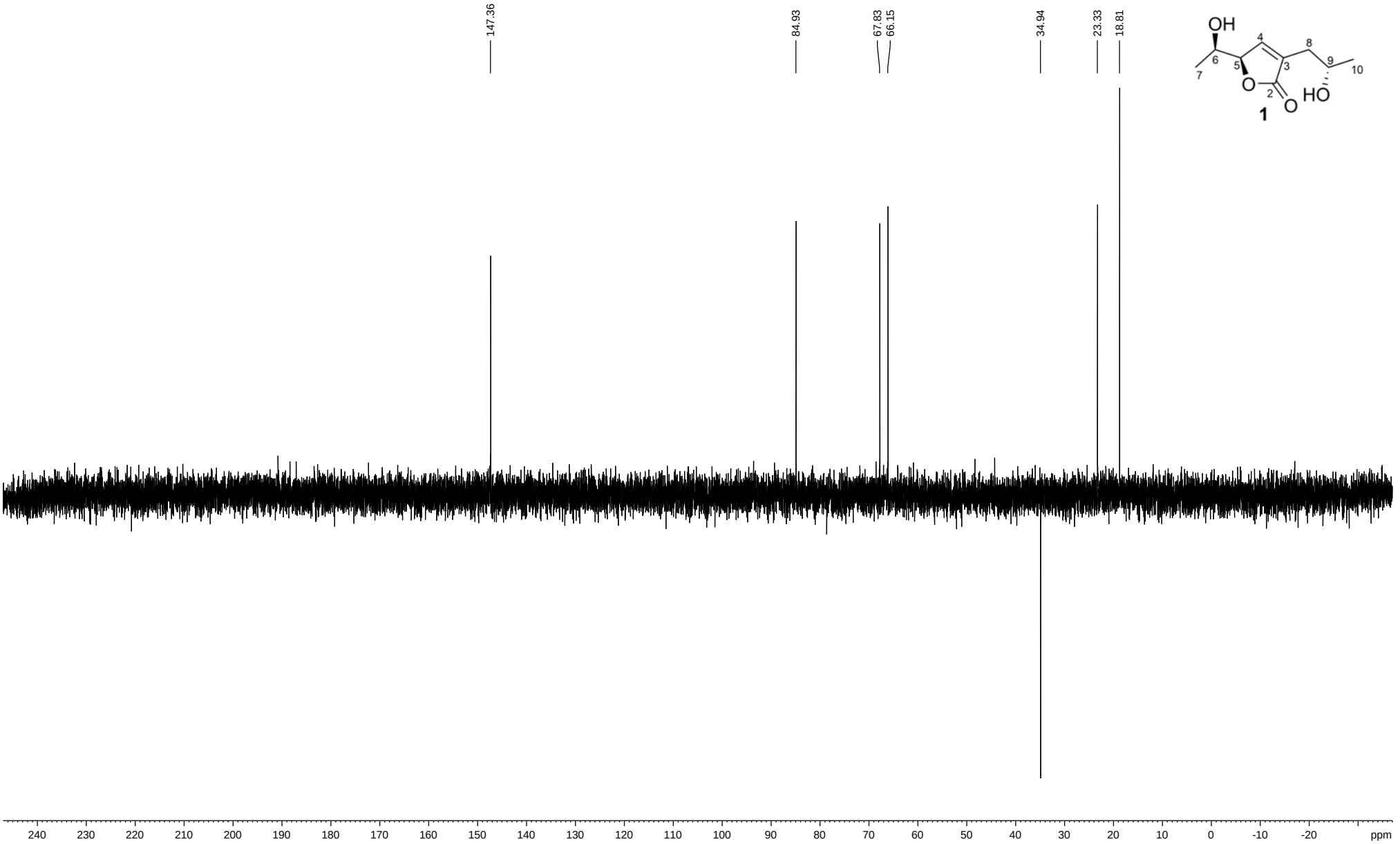
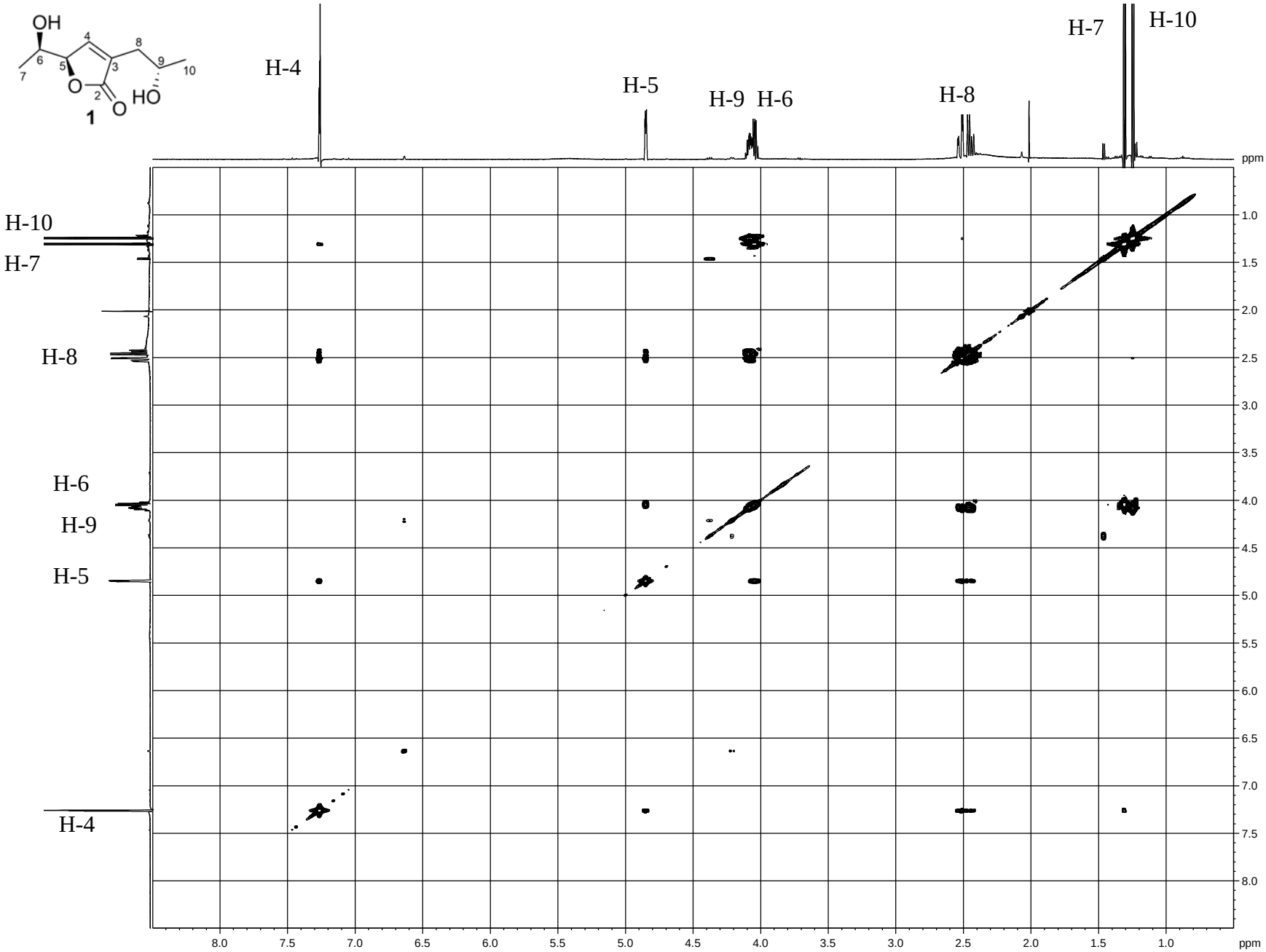


Figure S4. ^{1}H-^{1}H COSY (500 MHz, $CDCl_3$) spectrum of aspilactonol F (**1**)



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PROCNO 1

F2 - Acquisition Parameters
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INSTRUM spect
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PULPROG cosyqf45
TD 2048
SOLVENT CDCl3
NS 8
DS 16
SWH 4835.590 Hz
FIDRES 2.361128 Hz
AQ 0.2118132 sec
RG 80.19
DW 103.400 usec
DE 6.50 usec
TE 303.2 K
D0 0.00000300 sec
D1 2.00000000 sec
IN0 0.00020680 sec

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SFO1 500.1321663 MHz
NUC1 1H
P1 11.00 usec
PLW1 15.84899998 W

F1 - Acquisition parameters
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SFO1 500.1322 MHz
FIDRES 9.444511 Hz
SW 9.669 ppm
FnMODE QF

F2 - Processing parameters
SI 2048
SF 500.1300226 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 4.00

F1 - Processing parameters
SI 2048
MC2 QF
SF 500.1300226 MHz
WDW GM
SSB 0
LB 0 Hz
GB 0

Figure S5. HSQC (500 MHz, $CDCl_3$) spectrum of aspilactonol F (**1**)

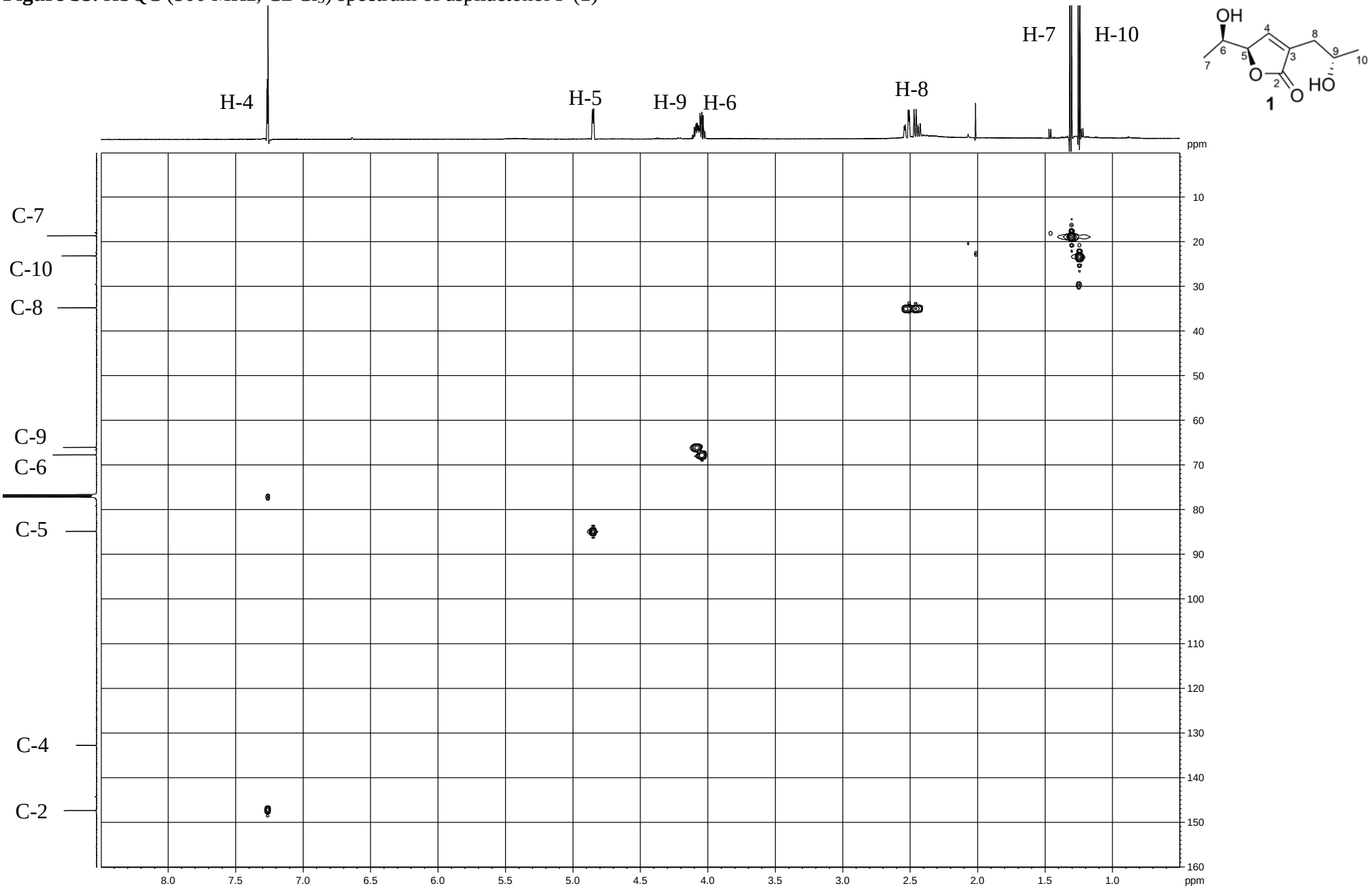


Figure S6. HMBC (500 MHz, $CDCl_3$) spectrum of aspilactonol F (**1**)

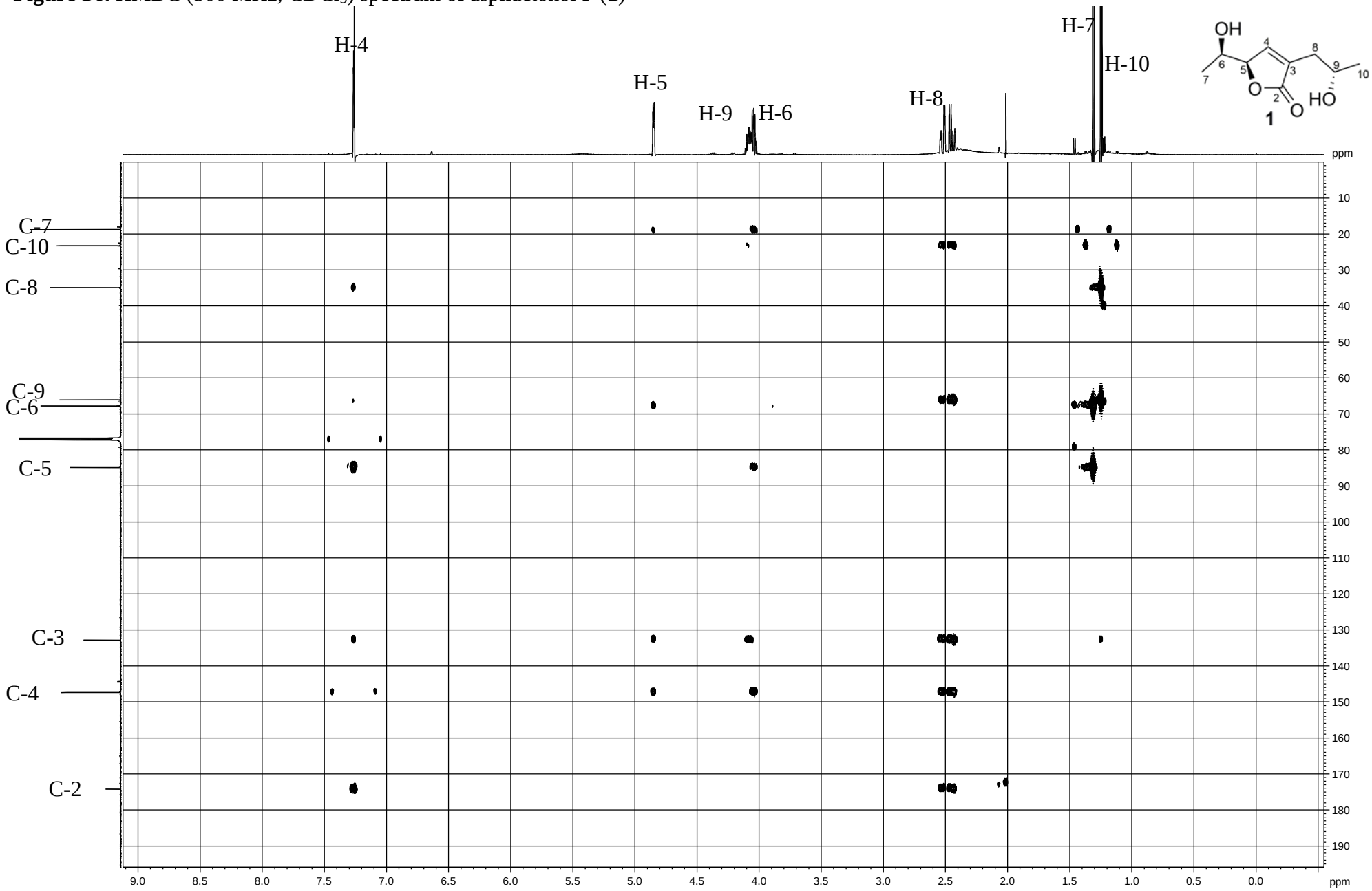
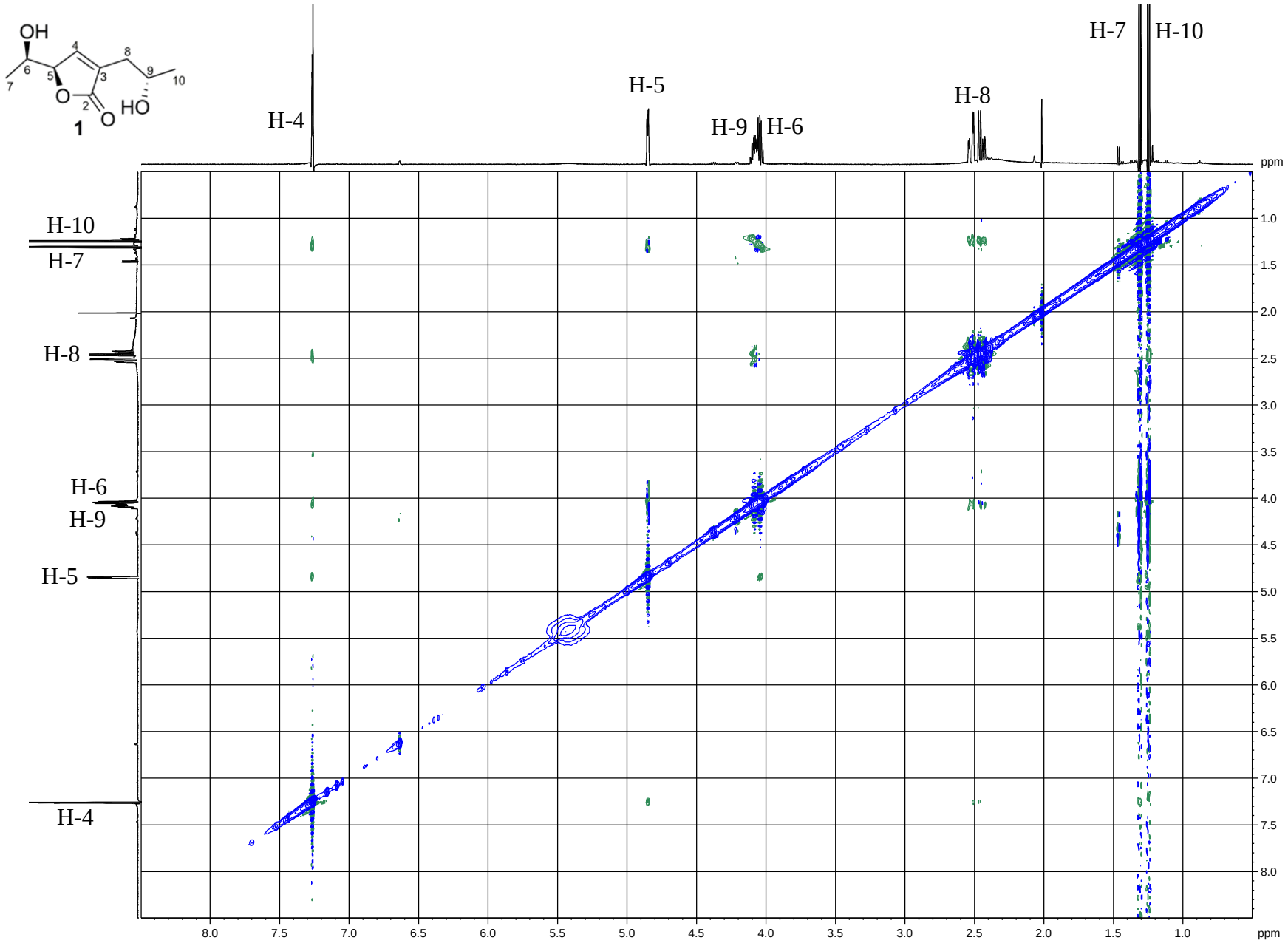


Figure S7. ROESY (500 MHz, $CDCl_3$) spectrum of aspilactonol F (**1**)



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EXPNO 23
PROCNO 1

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Date_ 20170622
Time 22.02
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG roesyph.2
TD 2048
SOLVENT CDCl3
NS 24
DS 16
SWH 4835.590 Hz
FIDRES 2.361128 Hz
AQ 0.2118132 sec
RG 4.19
DW 103.400 usec
DE 6.50 usec
TE 303.2 K
D0 0.00009240 sec
D1 2.00000000 sec
D12 0.00002000 sec
IN0 0.00020680 sec
L4 1350
P15 270000.00 usec

======== CHANNEL f1 ========
SFO1 500.1321663 MHz
NUC1 1H
P1 11.00 usec
P25 100.00 usec
PLW1 15.84899998 W
PLW27 0.76709002 W

F1 - Acquisition parameters
TD 256
SFO1 500.1322 MHz
FIDRES 18.889023 Hz
SW 9.669 ppm
FnMODE TPPI

F2 - Processing parameters
SI 2048
SF 500.1300226 MHz
WDW SINE
SSB 2
LB 0 Hz
GB 0
PC 4.00

F1 - Processing parameters
SI 512
MC2 TPPI
SF 500.1300226 MHz
WDW GM
SSB 2
LB 0 Hz
GB 0

Figure S8. ECD spectrum of aspilactonol F (**1**) in methanol

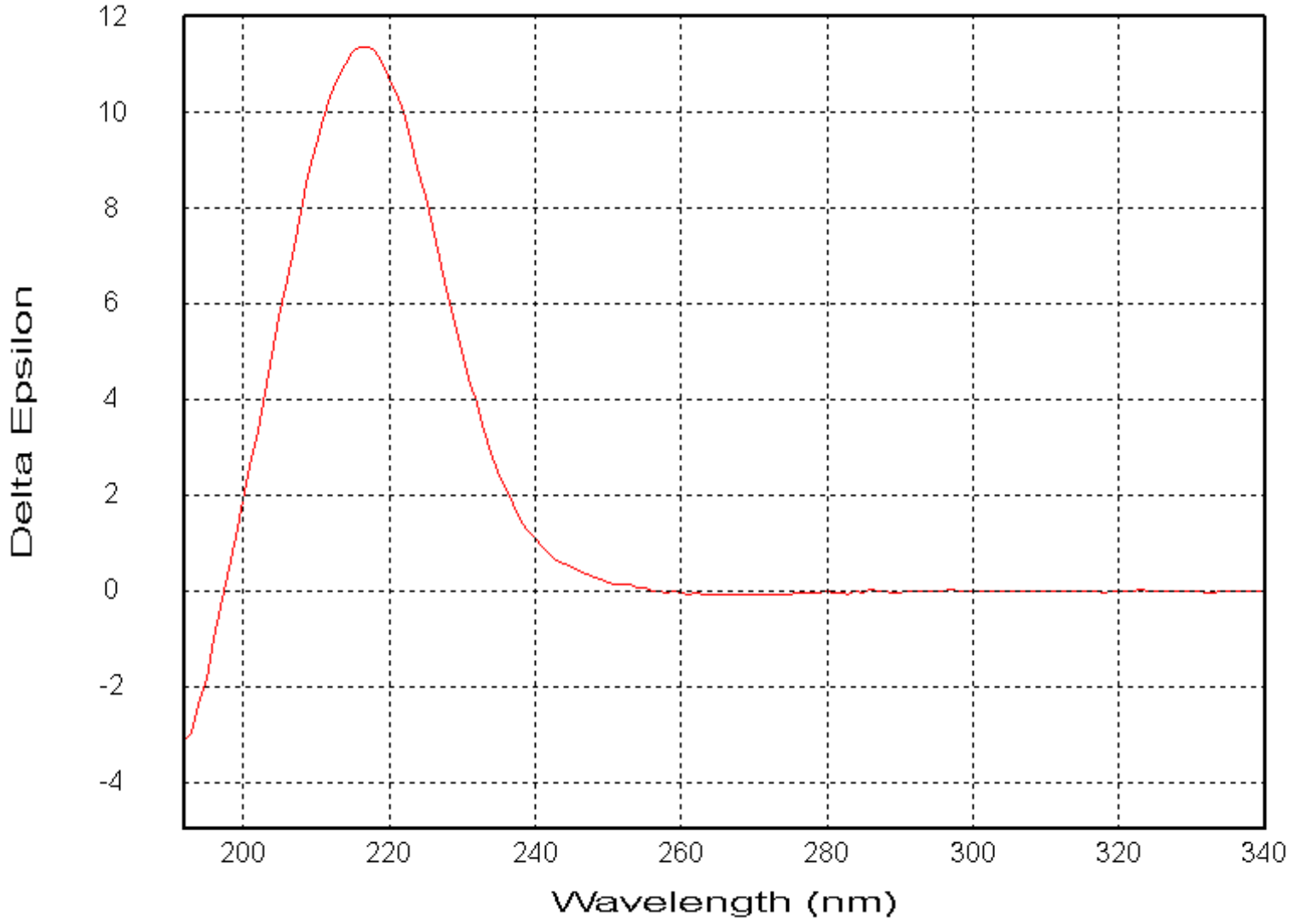


Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of aspilactonol G (**2**)

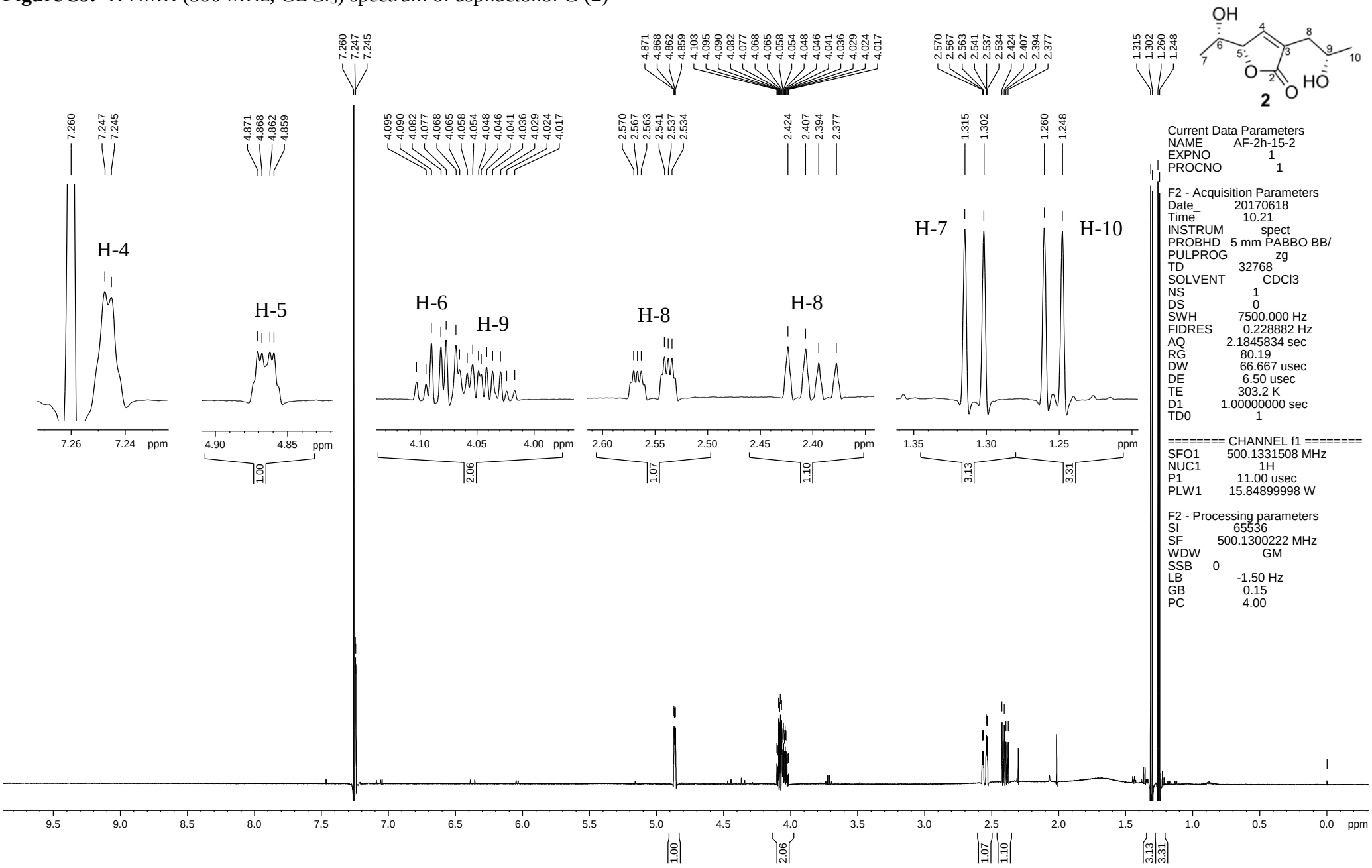


Figure S10. ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of aspilactonol G (**2**)

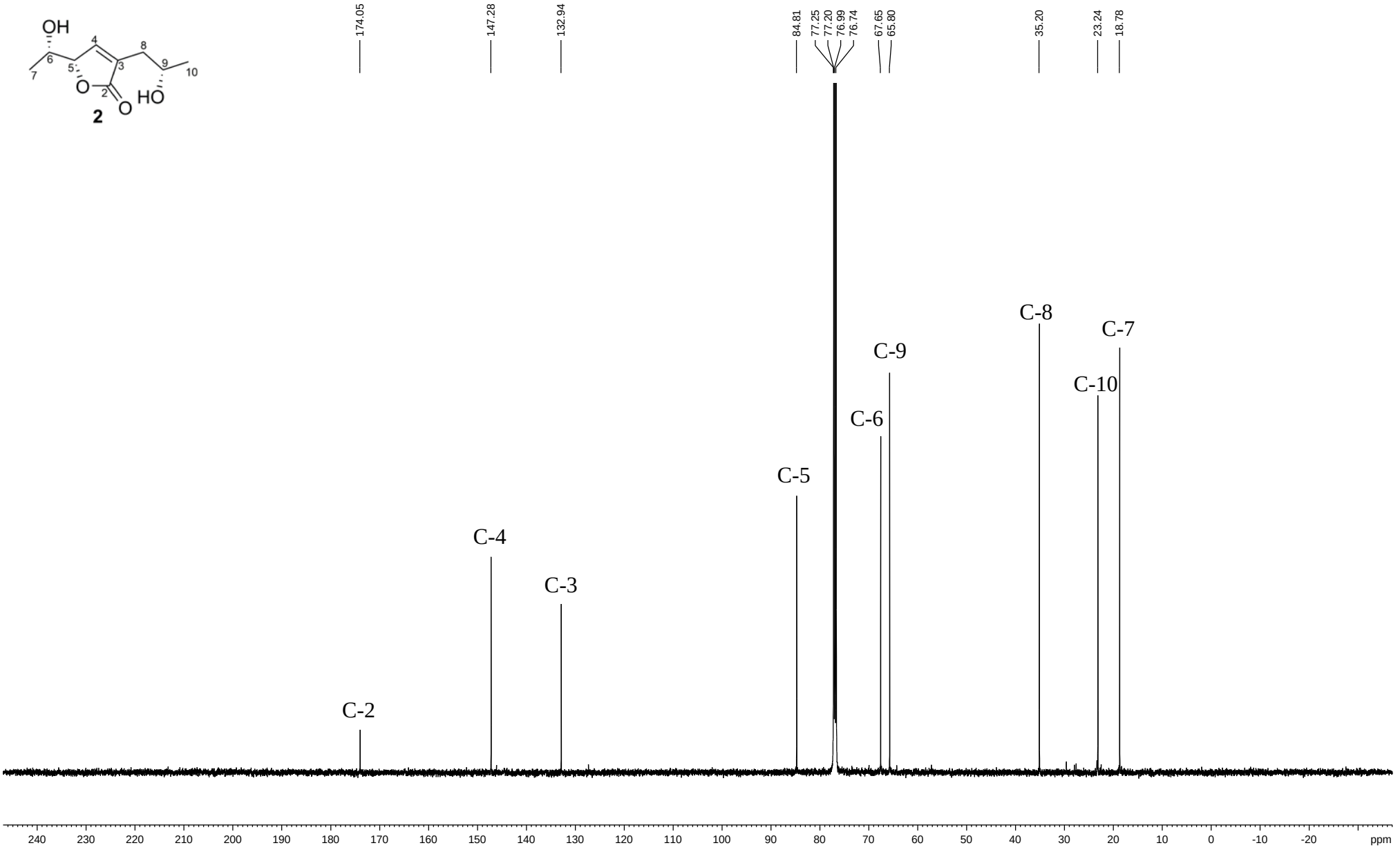


Figure S11. DEPT-135 (125 MHz, $CDCl_3$) spectrum of aspilactonol G (**2**)

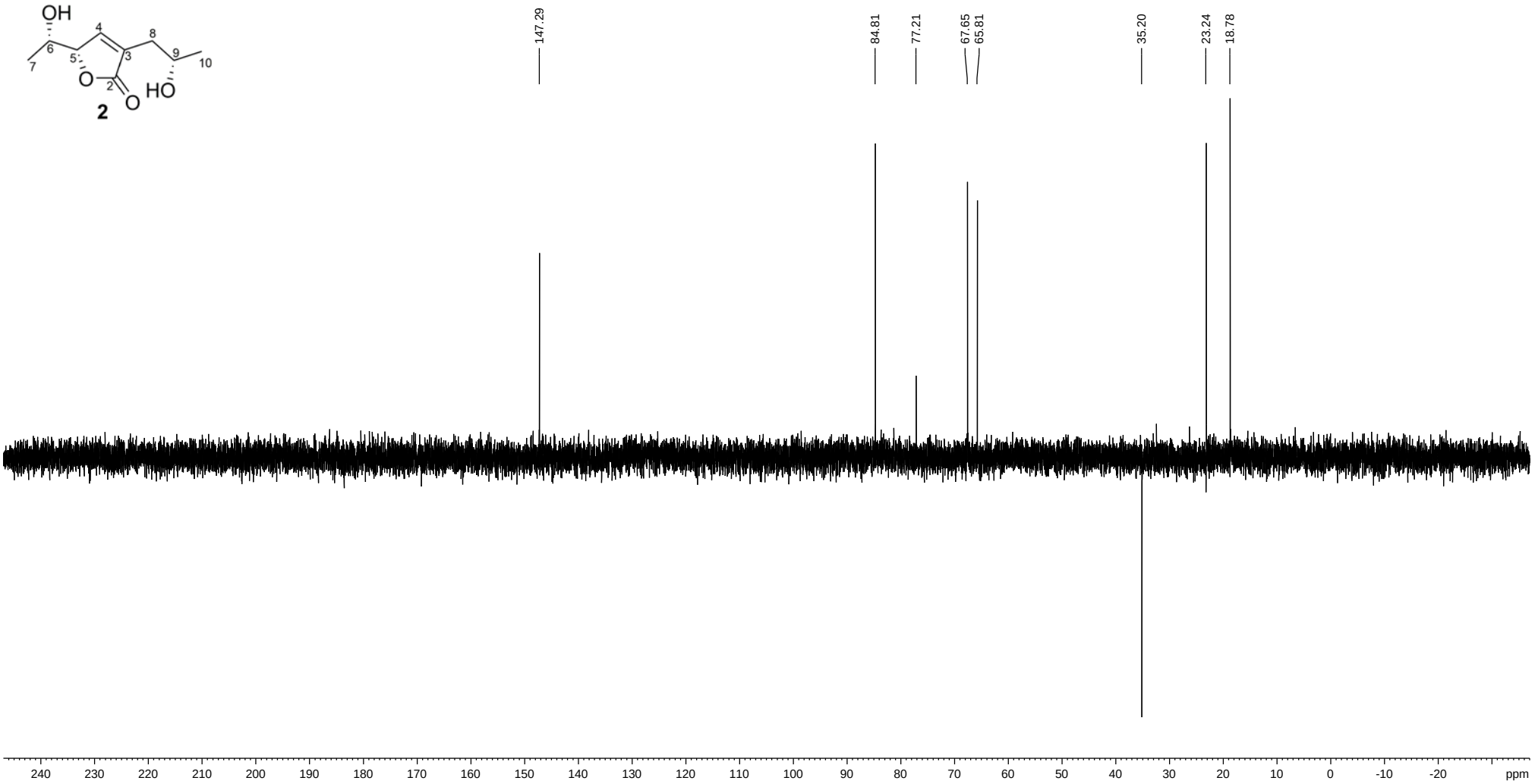


Figure S12. ^{1}H NMR (700 MHz, acetone-d_6) spectrum of aspilactonol G (**2**)

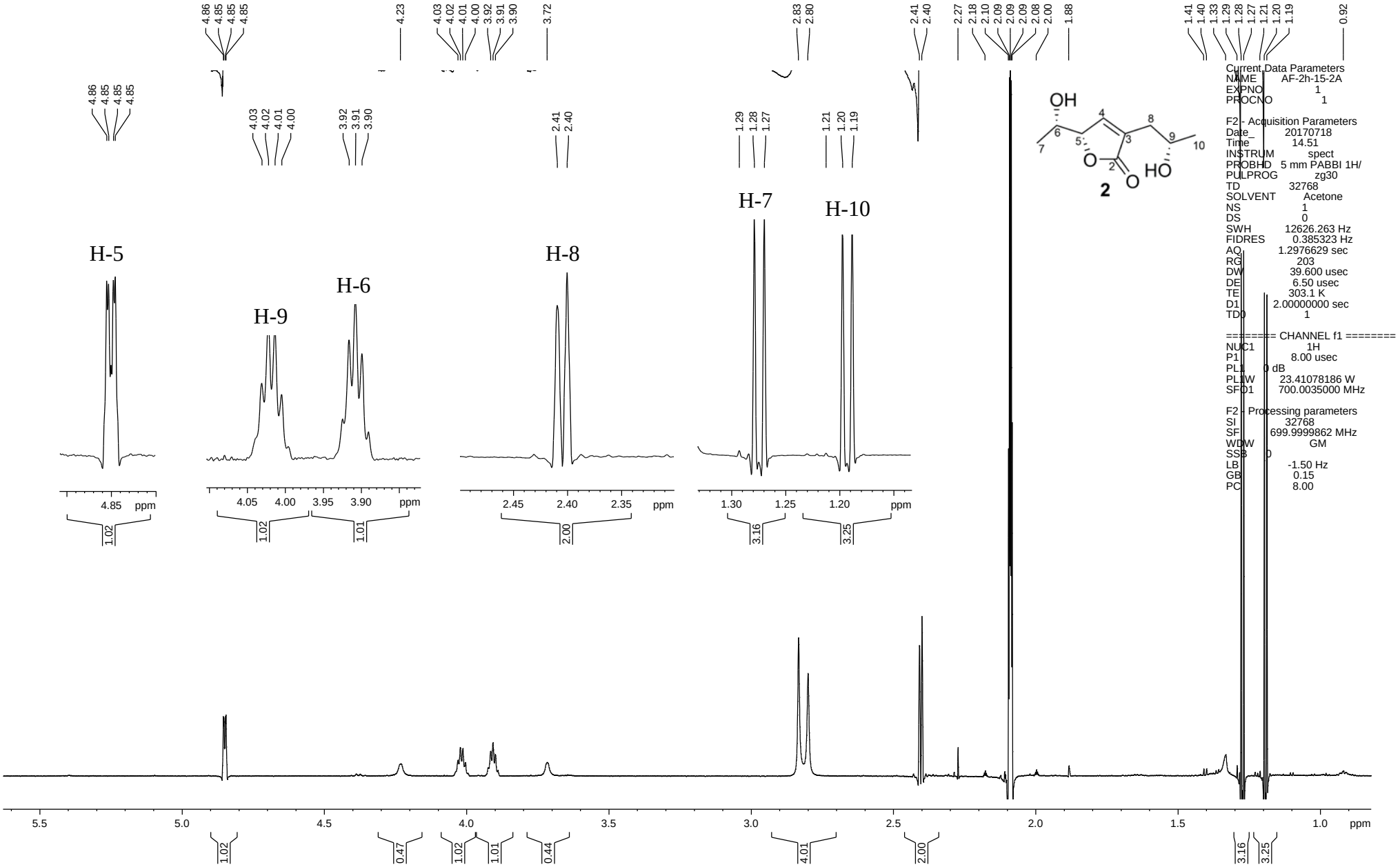


Figure S13. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of aspilactonol G (**2**)

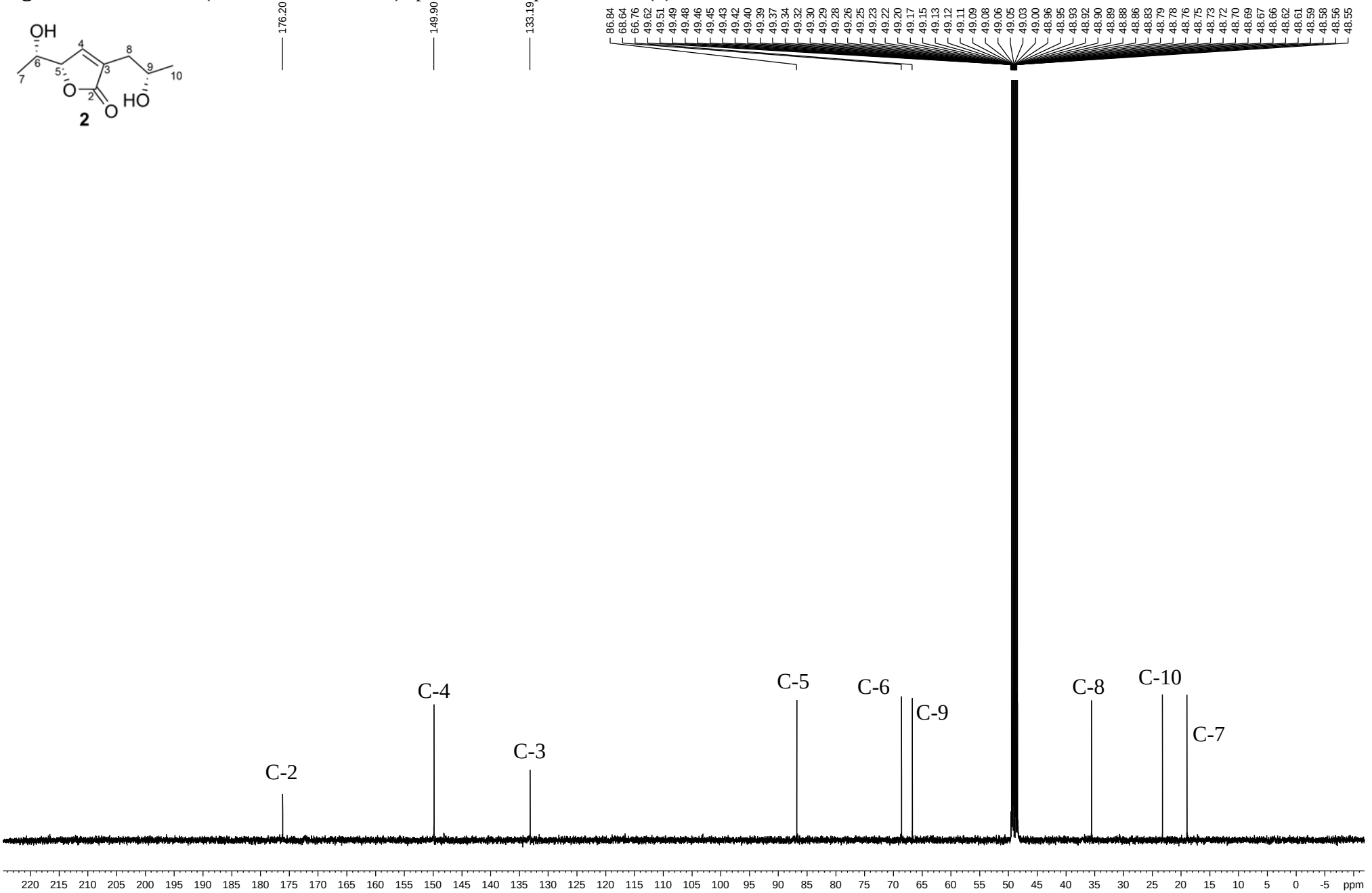
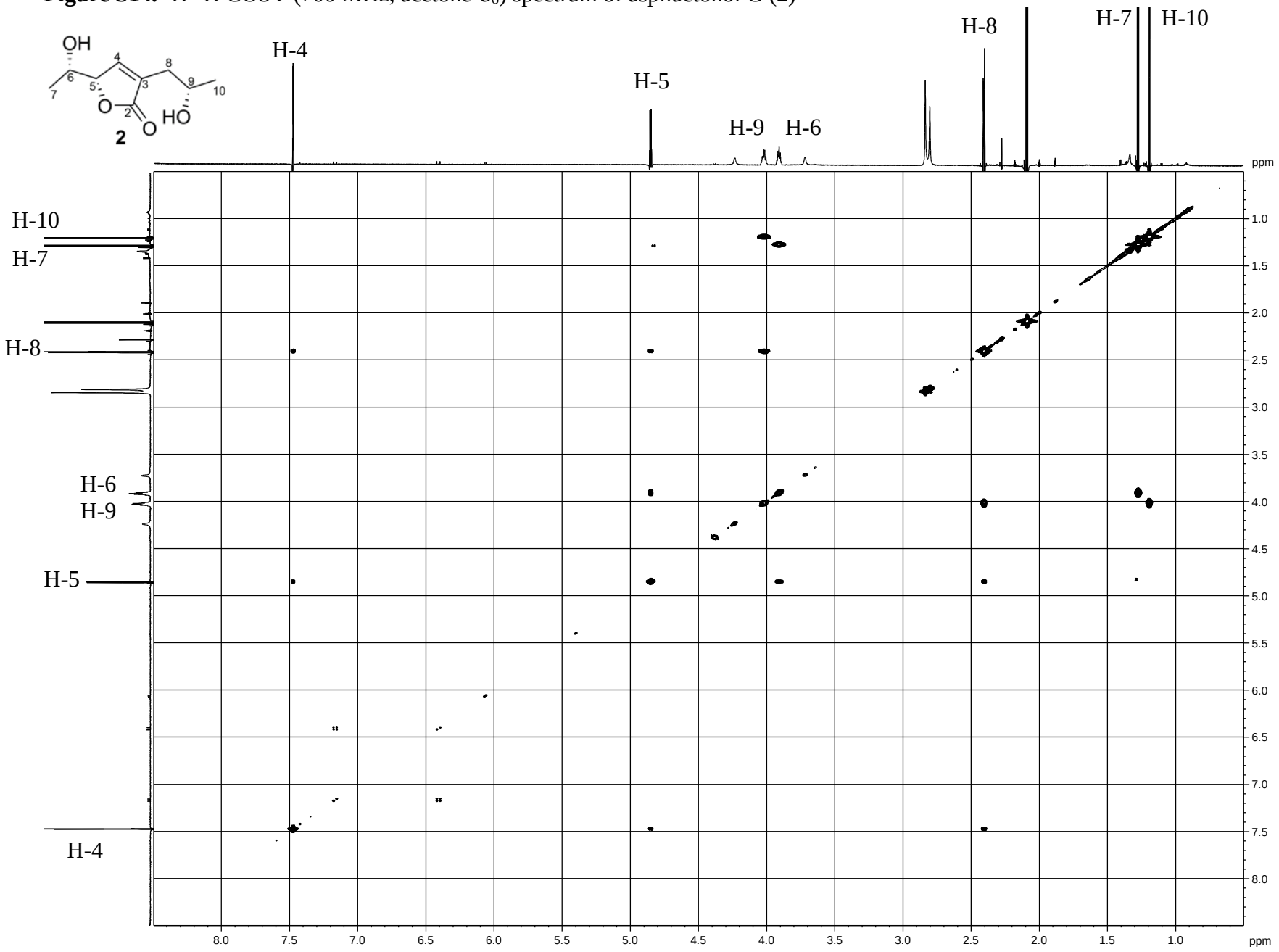


Figure S14. ^{1}H-^{1}H COSY (700 MHz, acetone-d_6) spectrum of aspilactonol G (**2**)

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EXPNO              21
PROCNO              1

F2 - Acquisition Parameters
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Time_             15.44
INSTRUM           spect
PROBHD   5 mm PABBI 1H/
PULPROG         cosygpqf
TD                2048
SOLVENT         Acetone
NS                   2
DS                  16
SWH            5597.015 Hz
FIDRES         2.732918 Hz
AQ           0.1830047 sec
RG                 203
DW              89.333 usec
DE               6.50 usec
TE               303.0 K
D0           0.00000300 sec
D1           2.00000000 sec
D13          0.00000400 sec
D16          0.00010000 sec
IN0          0.00017865 sec

======== CHANNEL f1 ========
NUC1                1H
P0               4.00 usec
P1               8.00 usec
PL1      0 dB
PL1W        23.41078186 W
SFO1        700.0031356 MHz

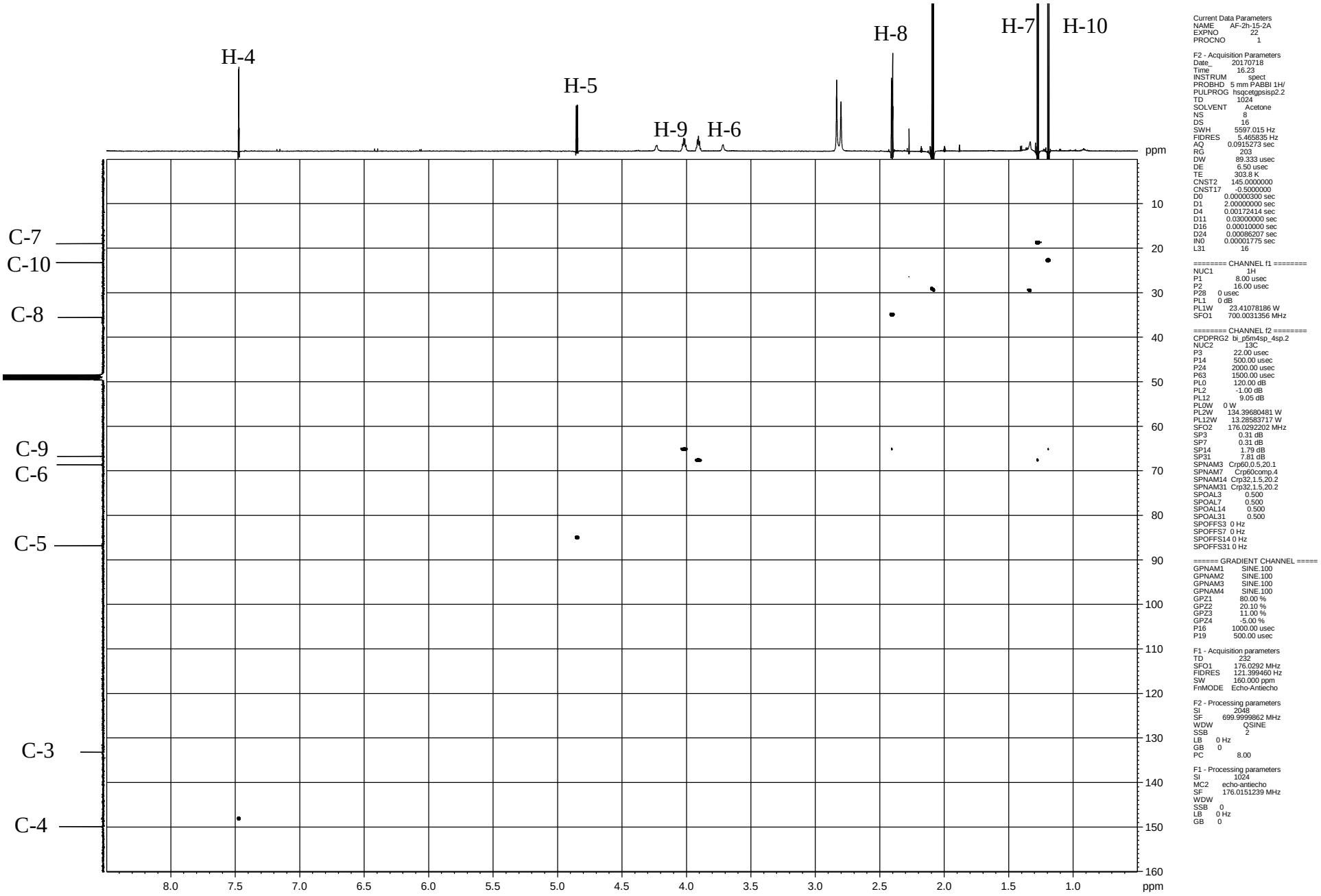
====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPZ1             10.00 %
P16            1000.00 usec

F1 - Acquisition parameters
TD                  512
SFO1            700.0031 MHz
FIDRES         10.931670 Hz
SW              7.996 ppm
FnMODE               QF

F2 - Processing parameters
SI                 2048
SF          699.9999862 MHz
WDW                SINE
SSB      0
LB       0 Hz
GB       0
PC                 8.00

F1 - Processing parameters
SI                 2048
MC2                  QF
SF          699.9999862 MHz
WDW                  GM
SSB      0
LB       0 Hz
GB       0
```

Figure S15. HSQC (700 MHz, acetone-d_6) spectrum of aspilactonol G (**2**)



Current Data Parameters
NAME AF-2h-15-2A
EXPNO 22
PROCNO 1

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Time 16.23
INSTRUM spect
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PULPROG hsqcetgpsisp2.2
TD 1024
SOLVENT Acetone
NS 8
DS 16
SWH 5597.015 Hz
FIDRES 5.465835 Hz
AQ 0.0915273 sec
RG 203
DW 89.333 usec
DE 6.50 usec
TE 303.8 K
CNST2 145.0000000
CNST17 -0.5000000
D0 0.00000300 sec
D1 2.00000000 sec
D4 0.00172414 sec
D11 0.03000000 sec
D16 0.00010000 sec
D24 0.00086207 sec
IN0 0.00001775 sec
L31 16

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
P2 16.00 usec
P28 0 usec
PL1 0 dB
PL1W 23.41078186 W
SFO1 700.0031356 MHz

======== CHANNEL f2 ========
CPDPRG2 bi_p5m4sp_4sp.2
NUC2 13C
P3 22.00 usec
P14 500.00 usec
P24 2000.00 usec
P63 1500.00 usec
PL0 120.00 dB
PL2 -1.00 dB
PL12 9.05 dB
PL0W 0 W
PL2W 134.39680481 W
PL12W 13.28583717 W
SFO2 176.0292202 MHz
SP3 0.31 dB
SP7 0.31 dB
SP14 1.79 dB
SP31 7.81 dB
SPNAM3 Crp60,0.5,20.1
SPNAM7 Crp60comp.4
SPNAM14 Crp32,1.5,20.2
SPNAM31 Crp32,1.5,20.2
SPOAL3 0.500
SPOAL7 0.500
SPOAL14 0.500
SPOAL31 0.500
SPOFFS3 0 Hz
SPOFFS7 0 Hz
SPOFFS14 0 Hz
SPOFFS31 0 Hz

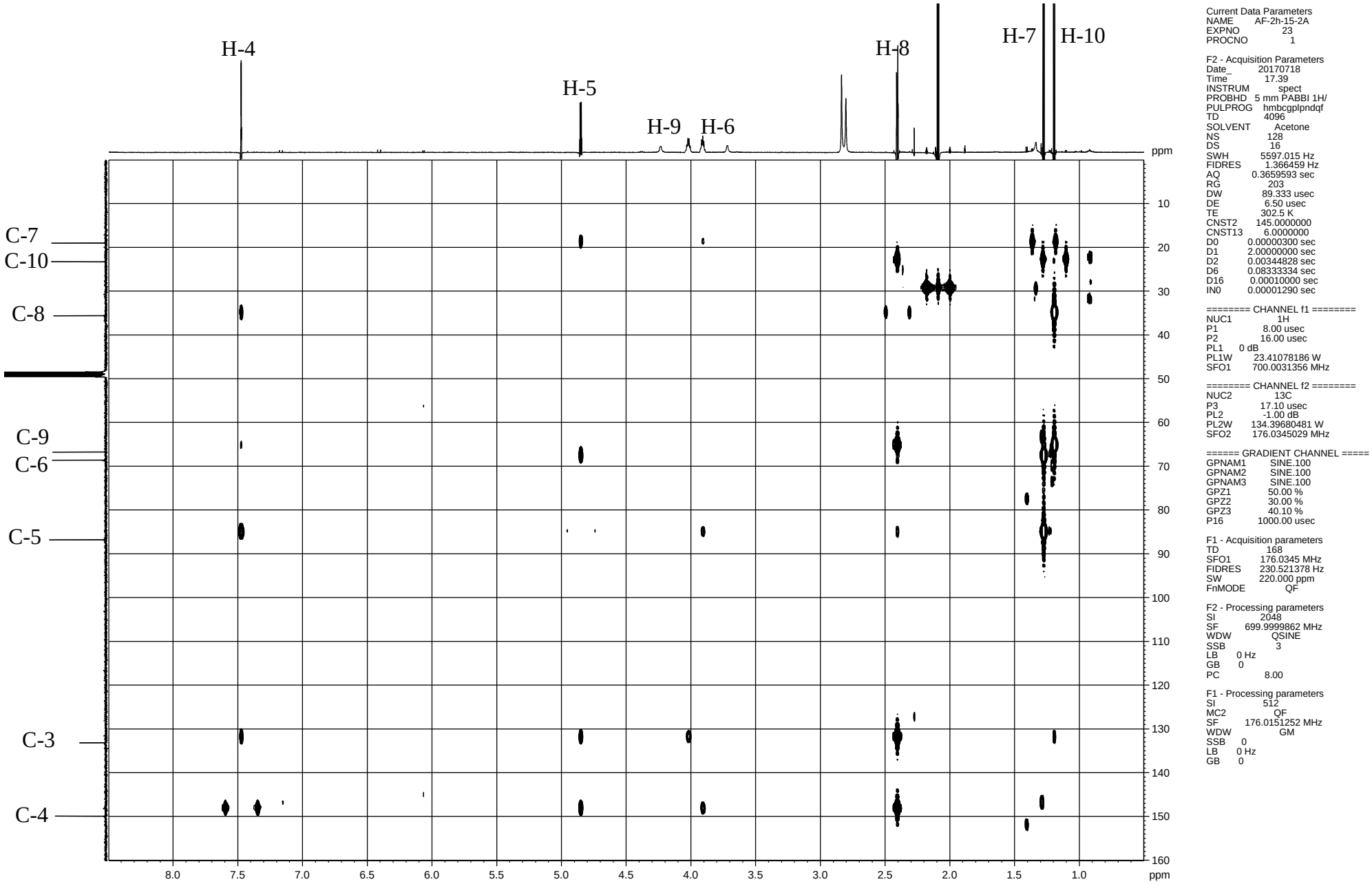
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPNAM3 SINE.100
GPNAM4 SINE.100
GPZ1 80.00 %
GPZ2 20.10 %
GPZ3 11.00 %
GPZ4 -5.00 %
P16 1000.00 usec
P19 500.00 usec

F1 - Acquisition parameters
TD 232
SFO1 176.0292 MHz
FIDRES 121.399460 Hz
SW 160.000 ppm
FnMODE Echo-Antiecho

F2 - Processing parameters
SI 2048
SF 699.9999862 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 8.00

F1 - Processing parameters
SI 1024
MC2 echo-antiecho
SF 176.0151239 MHz
WDW
SSB 0
LB 0 Hz
GB 0

Figure S16. HMBC (700 MHz, acetone-d_6) spectrum of aspilactonol G (**2**)



Current Data Parameters
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EXPNO 23
PROCNO 1

F2 - Acquisition Parameters
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INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG hmbcgplpndqf
TD 4096
SOLVENT Acetone
NS 128
DS 16
SWH 5597.015 Hz
FIDRES 1.366459 Hz
AQ 0.3659593 sec
RG 203
DW 89.333 usec
DE 6.50 usec
TE 302.5 K
CNST2 145.0000000
CNST13 6.0000000
D0 0.00000300 sec
D1 2.00000000 sec
D2 0.00344828 sec
D6 0.08333334 sec
D16 0.00010000 sec
IN0 0.00001290 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
P2 16.00 usec
PL1 0 dB
PL1W 23.41078186 W
SFO1 700.0031356 MHz

======== CHANNEL f2 ========
NUC2 13C
P3 17.10 usec
PL2 -1.00 dB
PL2W 134.39680481 W
SFO2 176.0345029 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPNAM3 SINE.100
GPZ1 50.00 %
GPZ2 30.00 %
GPZ3 40.10 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 168
SFO1 176.0345 MHz
FIDRES 230.521378 Hz
SW 220.000 ppm
FnMODE QF

F2 - Processing parameters
SI 2048
SF 699.9999862 MHz
WDW QSINE
SSB 3
LB 0 Hz
GB 0
PC 8.00

F1 - Processing parameters
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MC2 QF
SF 176.0151252 MHz
WDW GM
SSB 0
LB 0 Hz
GB 0

Figure S17. ECD spectrum of aspilactonol G (**2**) in methanol

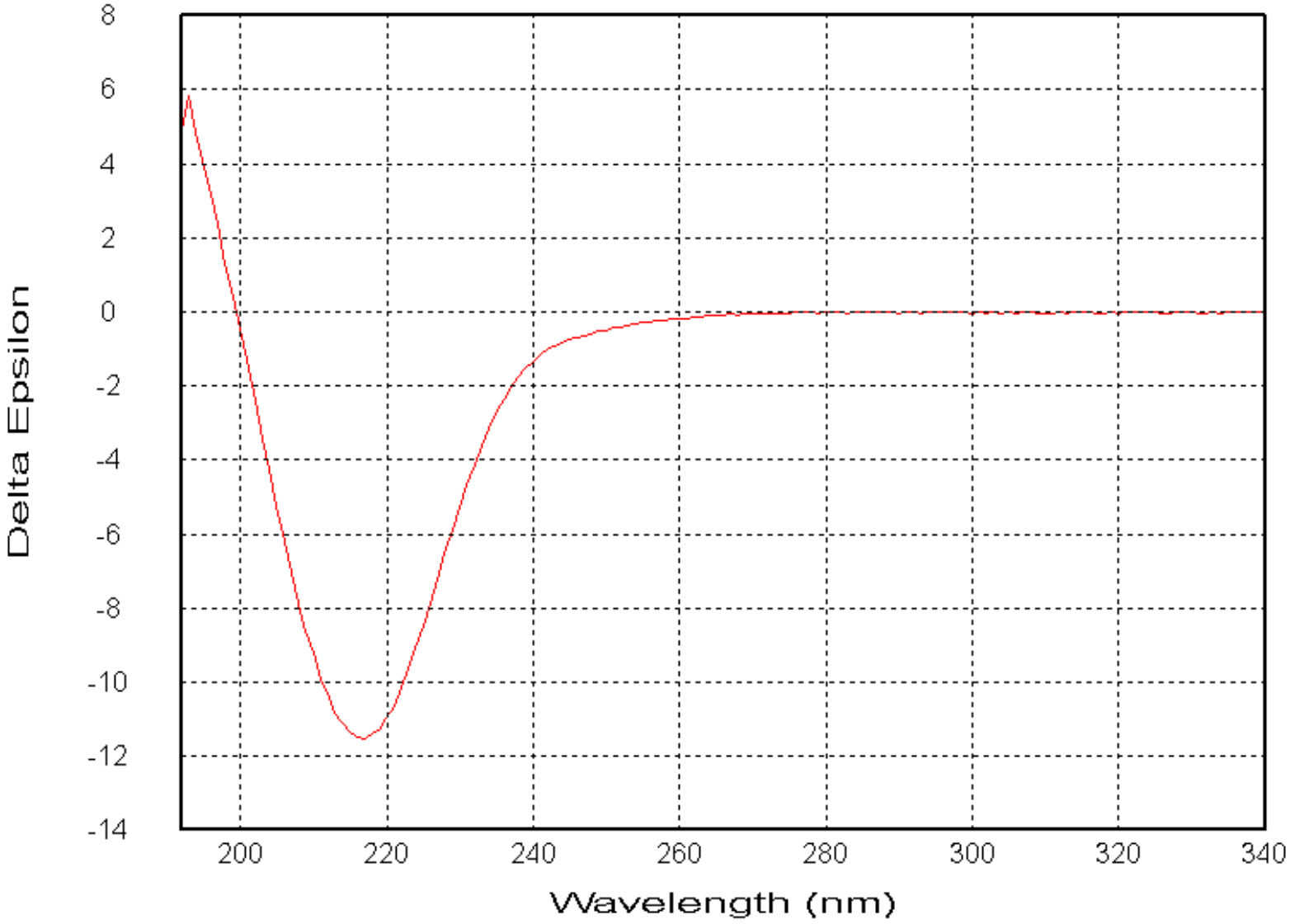


Figure S18. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of dihydroaspirone (**3**)

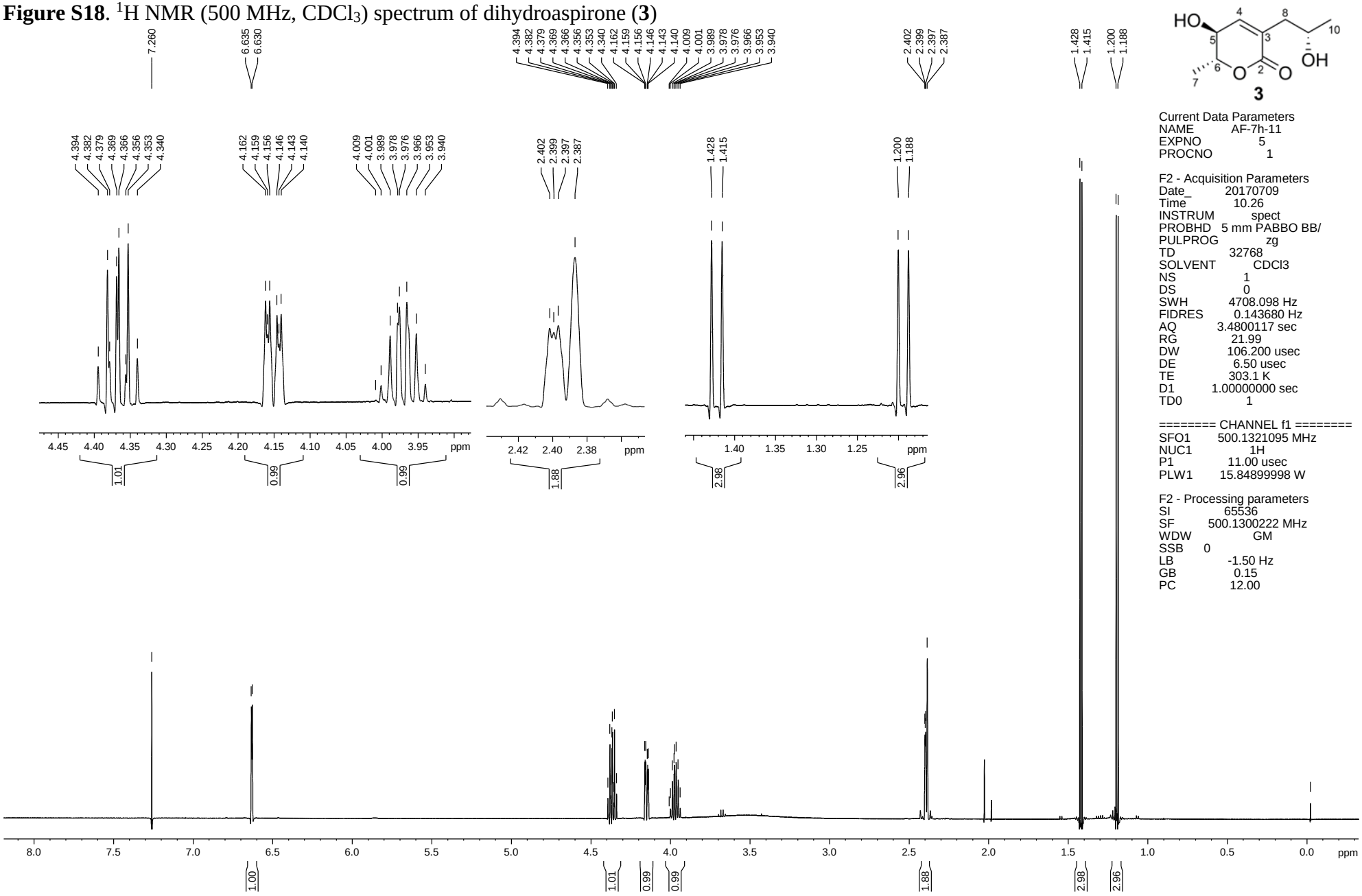


Figure S19. ^{13}C NMR (176 MHz, $CDCl_3$) spectrum of dihydroaspirone (**3**)

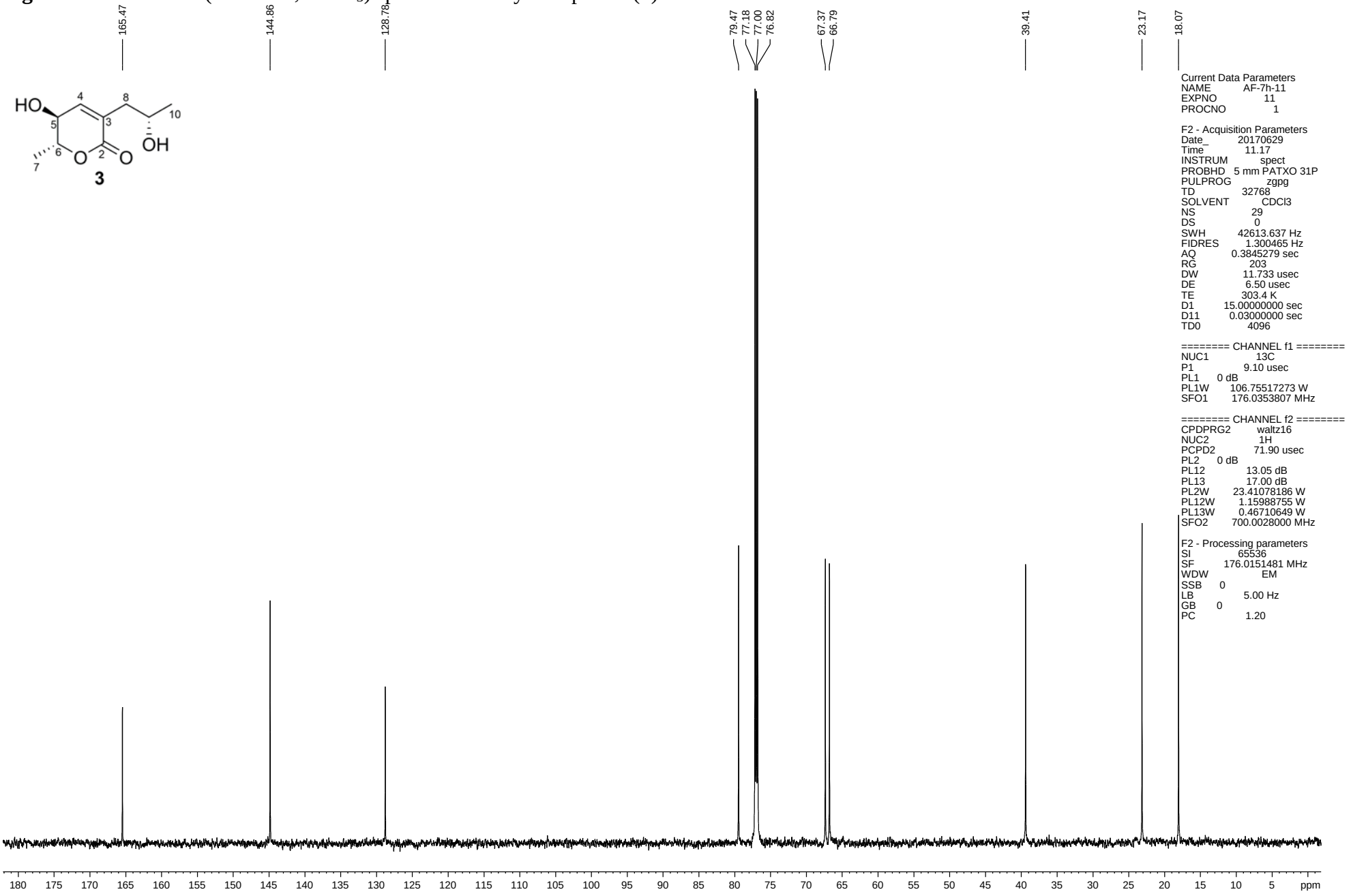
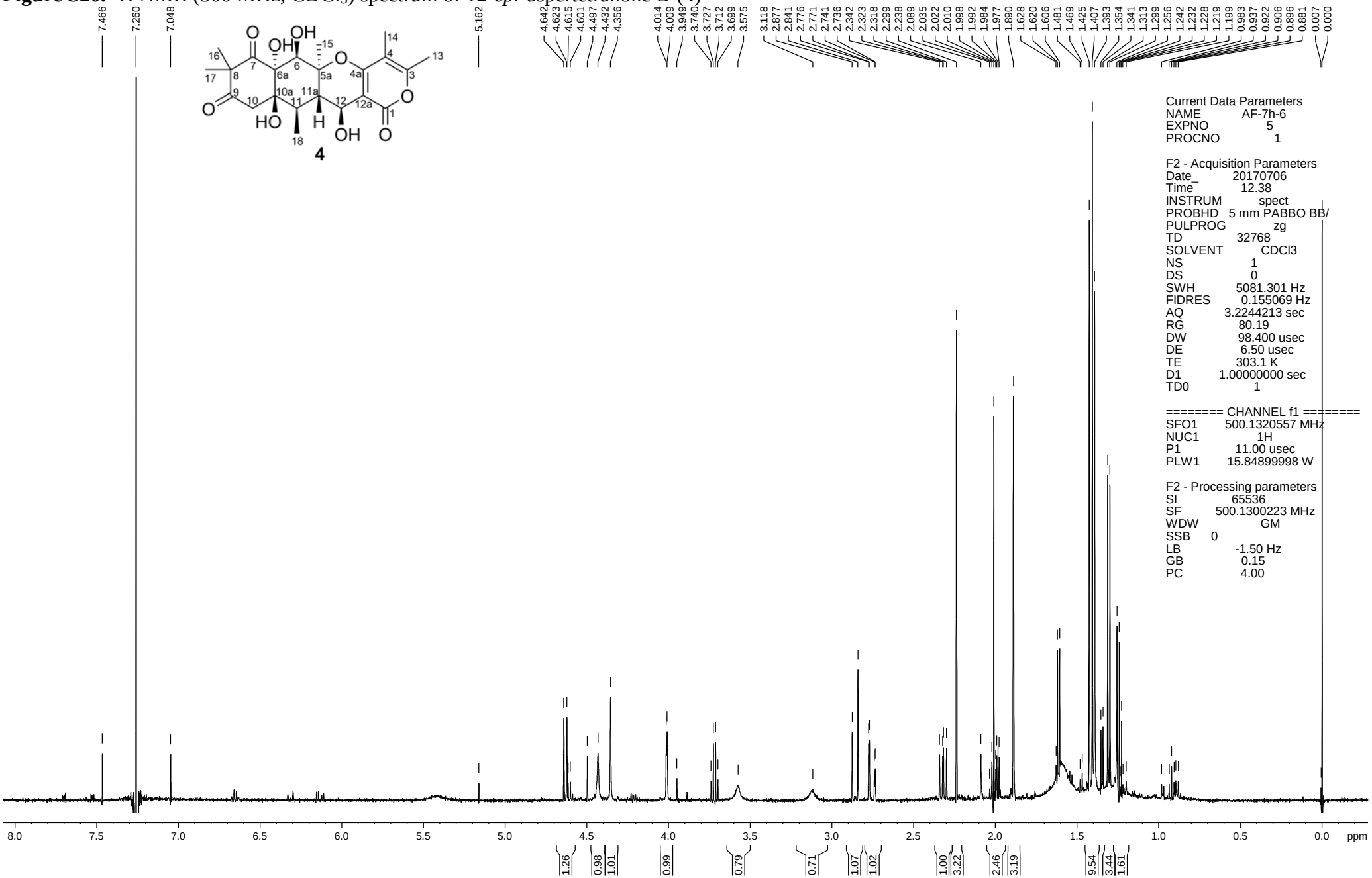
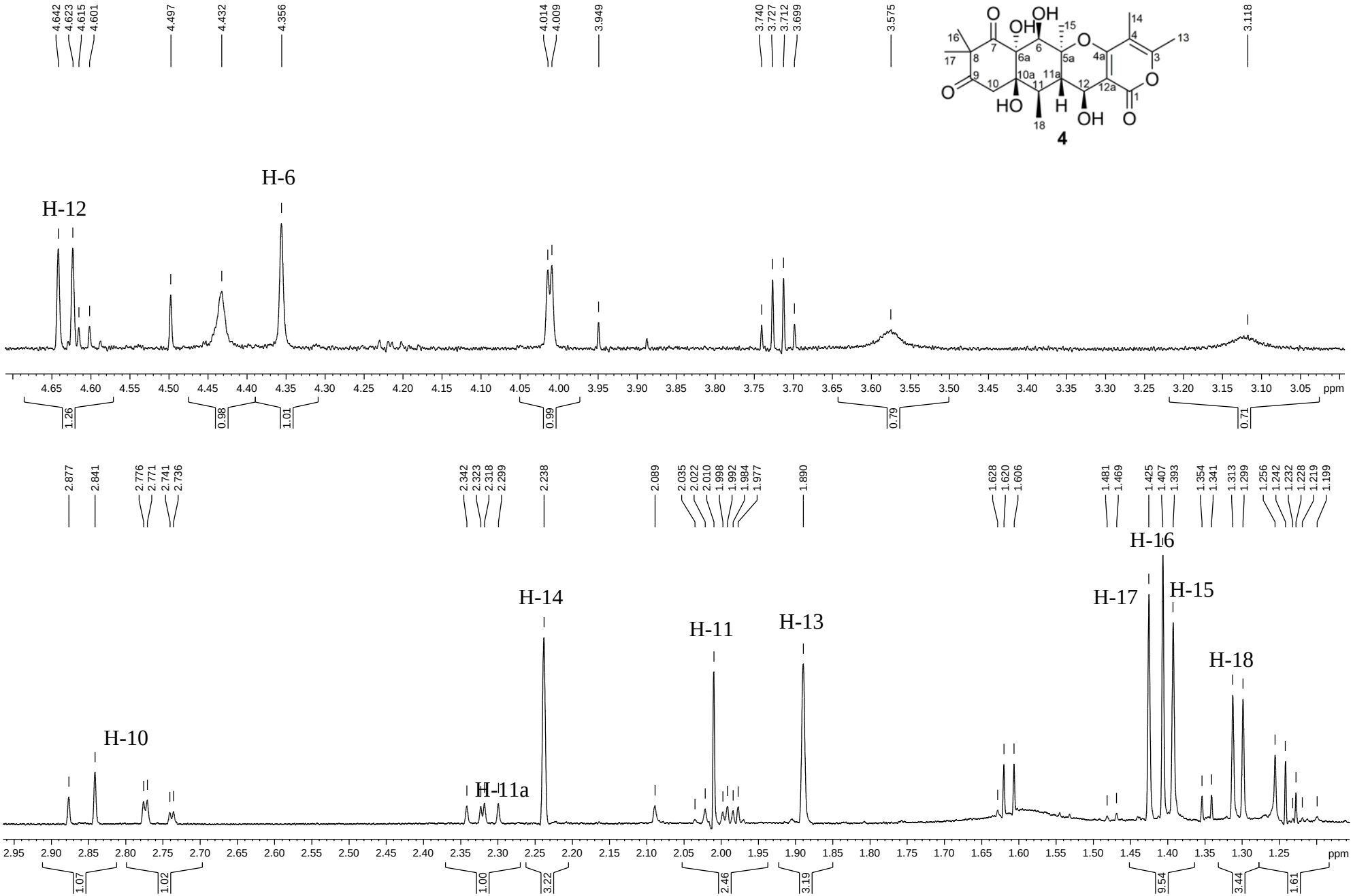


Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 12-*epi*-aspertetranone D (**4**)




4.642
4.623
4.615
4.601
4.497
4.432
4.356
4.014
4.009
3.949
3.740
3.727
3.712
3.699
3.575
3.118
H-12
H-6
4
2.877
2.841
2.776
2.771
2.741
2.736
2.342
2.323
2.318
2.299
2.238
2.089
2.035
2.022
2.010
1.998
1.992
1.984
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1.890
1.628
1.620
1.606
1.481
1.469
1.425
1.407
1.393
1.354
1.341
1.313
1.299
1.256
1.242
1.232
1.228
1.219
1.199
H-10
H-11a
H-14
H-11
H-13
H-17
H-16
H-15
H-18
ppm

Figure S21. ^{13}C NMR (176 MHz, $CDCl_3$) spectrum of 12-*epi*-aspertetranone D (**4**)

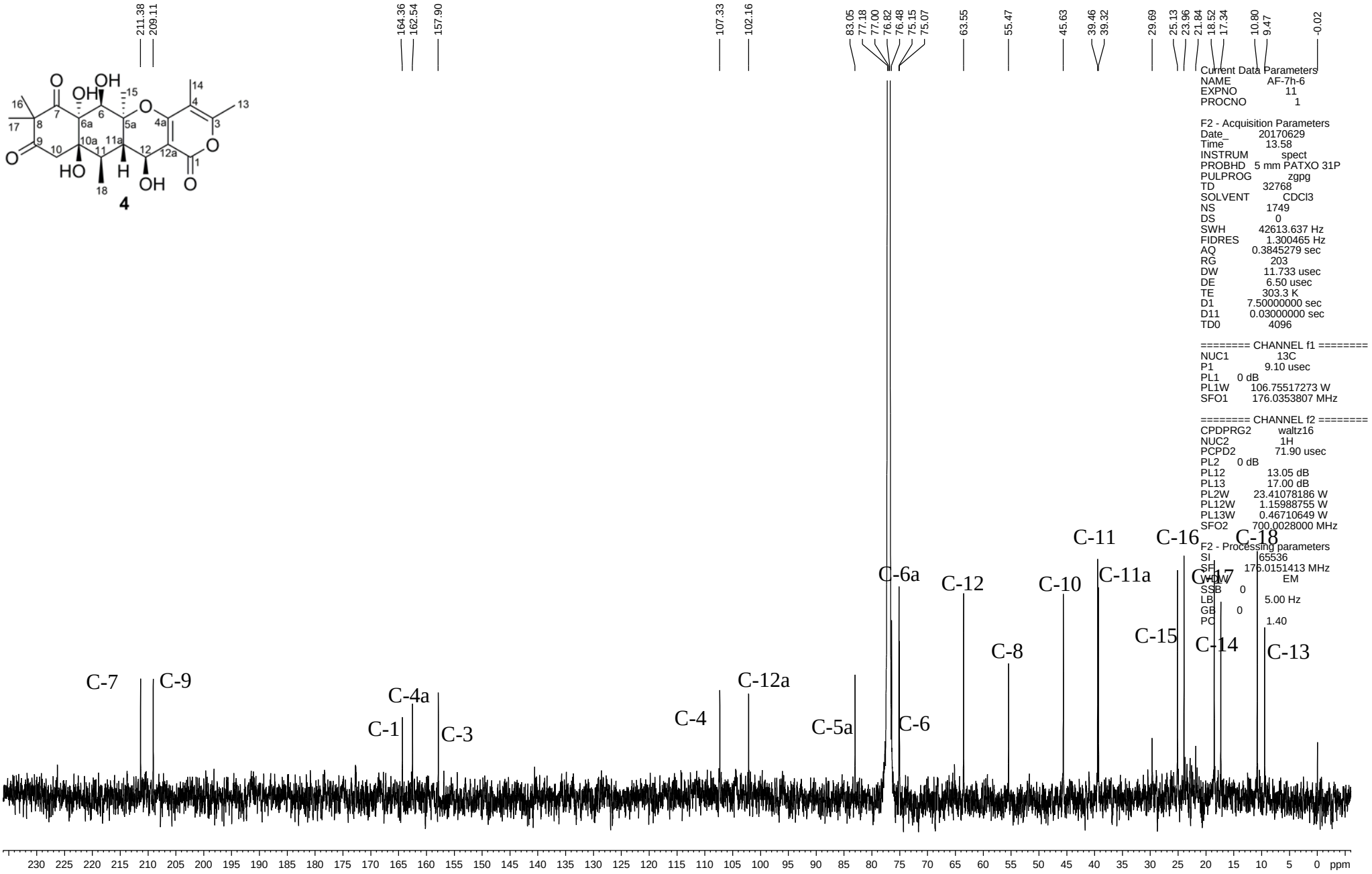


Figure S22.DEPT-135 (500 MHz, $CDCl_3$) spectrum of 12-*epi*-aspertetranone D (**4**)

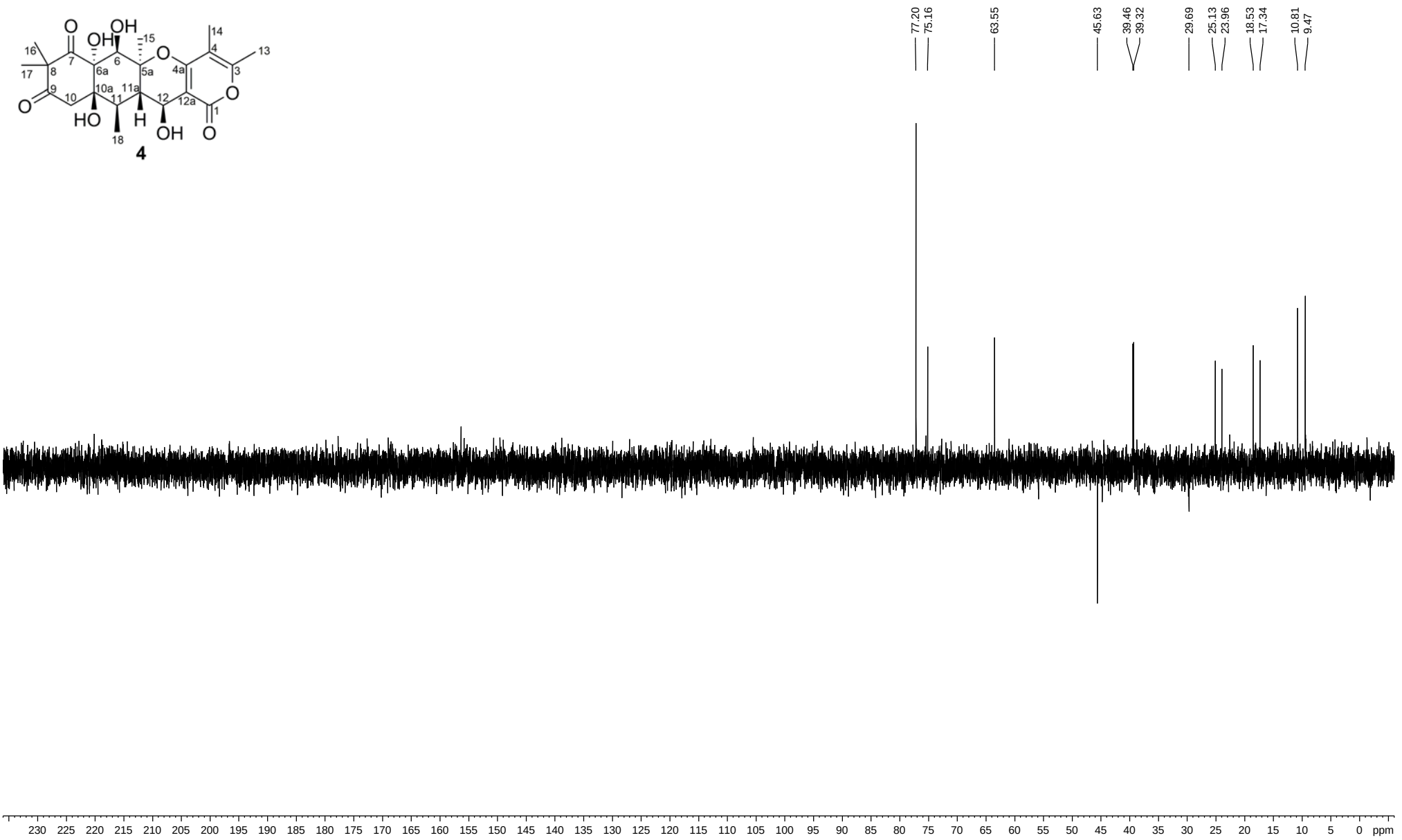
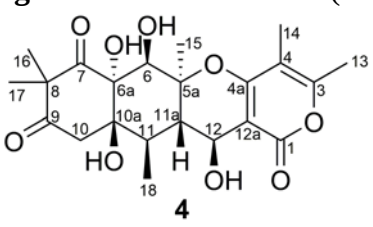


Figure S23. ^{1}H-^{1}H COSY (500 MHz, $CDCl_3$) spectrum of 12-*epi*-aspertetranone D (**4**)



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PULPROG cosyqf45
TD 2048
SOLVENT CDCl3
NS 8
DS 16
SWH 5081.301 Hz
FIDRES 2.481104 Hz
AQ 0.2015732 sec
RG 80.19
DW 98.400 usec
DE 6.50 usec
TE 303.1 K
D0 0.00000300 sec
D1 2.00000000 sec
IN0 0.00019680 sec

======== CHANNEL f1 ========
SFO1 500.1320557 MHz
NUC1 1H
P1 11.00 usec
PLW1 15.84899998 W

F1 - Acquisition parameters
TD 512
SFO1 500.1321 MHz
FIDRES 9.924416 Hz
SW 10.160 ppm
FnMODE QF

F2 - Processing parameters
SI 2048
SF 500.1300223 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 4.00

F1 - Processing parameters
SI 2048
MC2 QF
SF 500.1300223 MHz
WDW GM
SSB 0
LB 0 Hz
GB 0

Figure S24. HSQC (500 MHz, $CDCl_3$) spectrum of 12-*epi*-aspertetranone D (**4**)

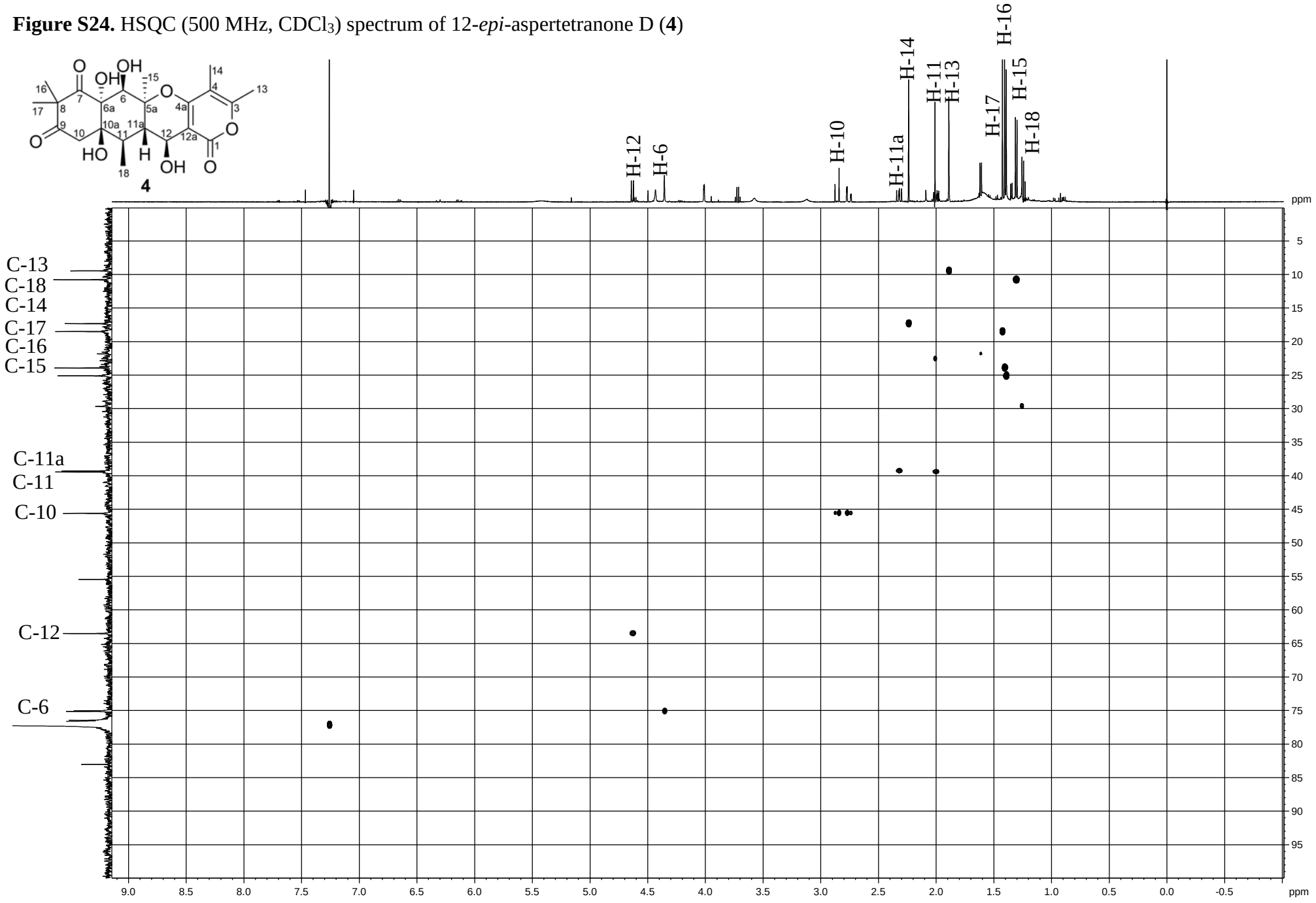
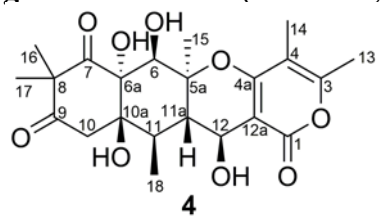
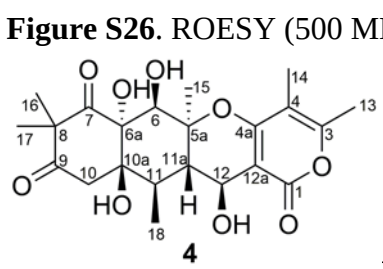


Figure S25. HMBC (500 MHz, $CDCl_3$) spectrum of 12-*epi*-aspertetranone D (**4**)



4

Figure S26. ROESY (500 MHz, $CDCl_3$) spectrum of 12-*epi*-aspertetranone D (**4**)



4

Current Data Parameters
NAME AF-7h-6
EXPNO 23
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170706
Time 18.49
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG roesyph.2
TD 2048
SOLVENT CDCl3
NS 24
DS 16
SWH 5081.301 Hz
FIDRES 2.481104 Hz
AQ 0.2015732 sec
RG 4.19
DW 98.400 usec
DE 6.50 usec
TE 303.2 K
D0 0.00008740 sec
D1 2.00000000 sec
D12 0.00002000 sec
IN0 0.00019680 sec
L4 1350
P15 270000.00 usec

======== CHANNEL f1 ========
SFO1 500.1320557 MHz
NUC1 1H
P1 11.00 usec
P25 100.00 usec
PLW1 15.84899998 W
PLW27 0.76709002 W

F1 - Acquisition parameters
TD 256
SFO1 500.1321 MHz
FIDRES 19.848831 Hz
SW 10.160 ppm
FnMODE TPPI

F2 - Processing parameters
SI 2048
SF 500.1300224 MHz
WDW SINE
SSB 2
LB 0 Hz
GB 0
PC 4.00

F1 - Processing parameters
SI 512
MC2 TPPI
SF 500.1300185 MHz
WDW GM
SSB 2
LB 0 Hz
GB 0

Figure S27. ECD spectrum of 12-*epi*-aspertetranone D (**4**) in methanol

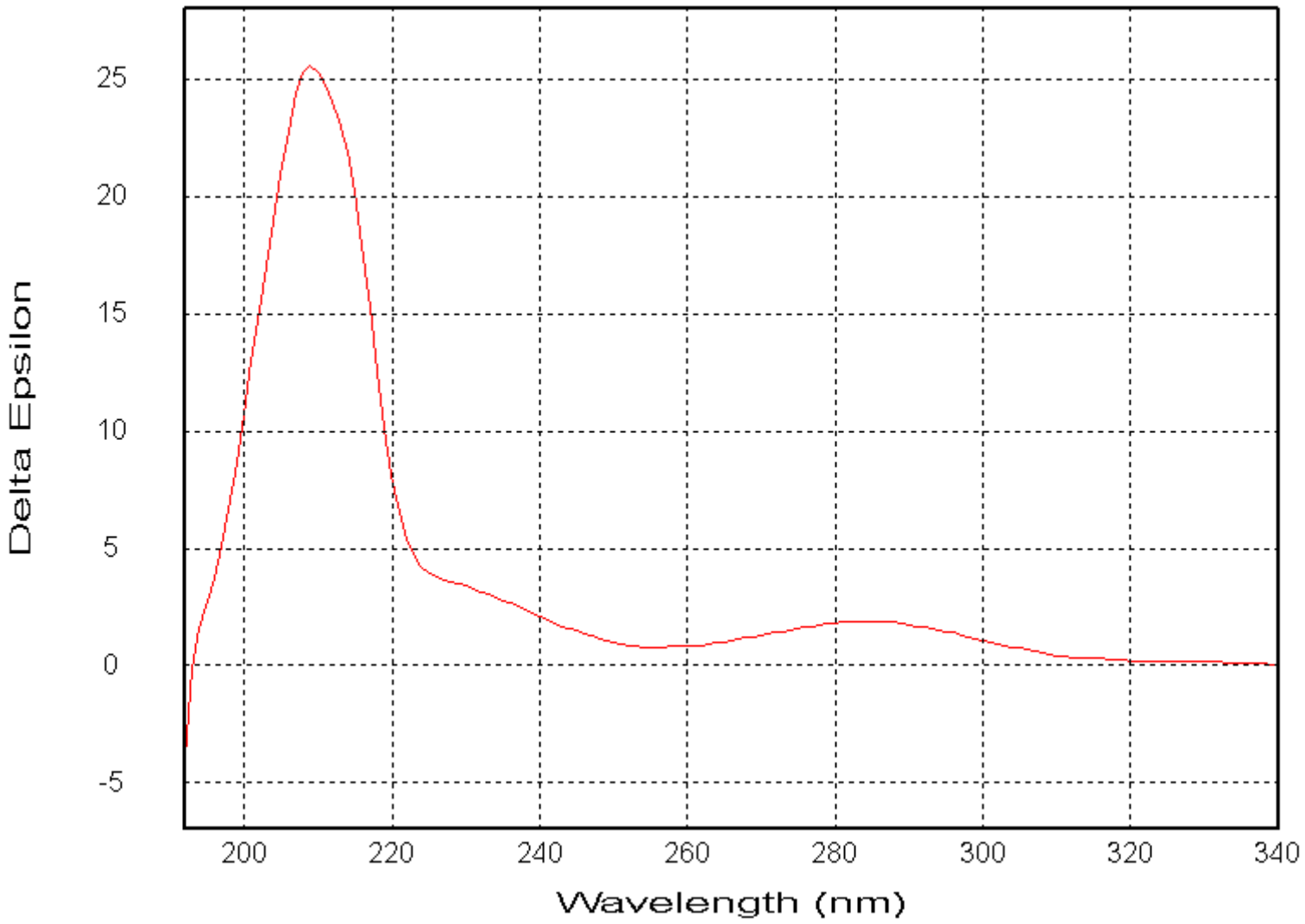


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of aspertetranone D (**5**)

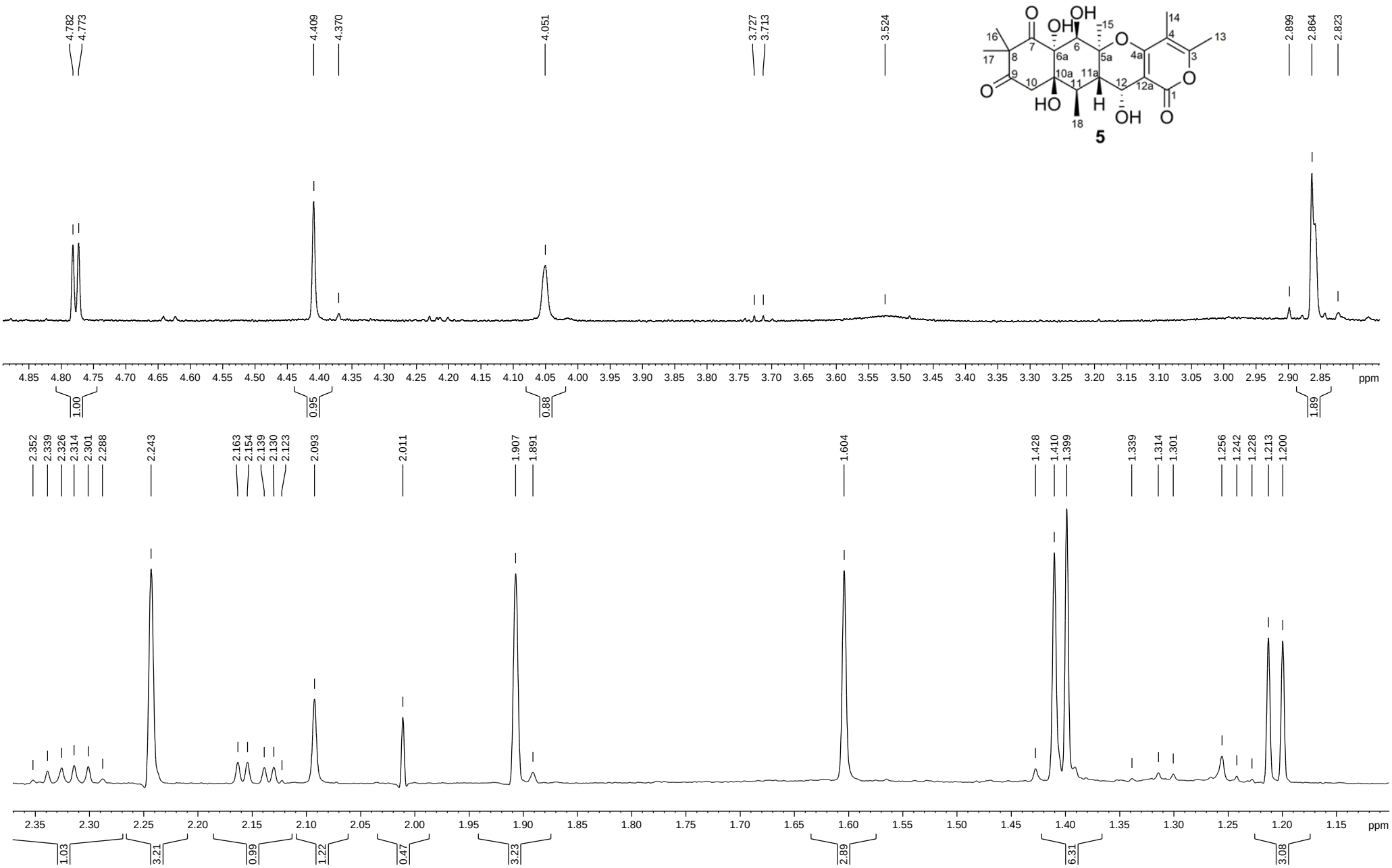


Figure S29. ^{13}C NMR (176 MHz, $CDCl_3$) spectrum of aspertetranone D (**5**)

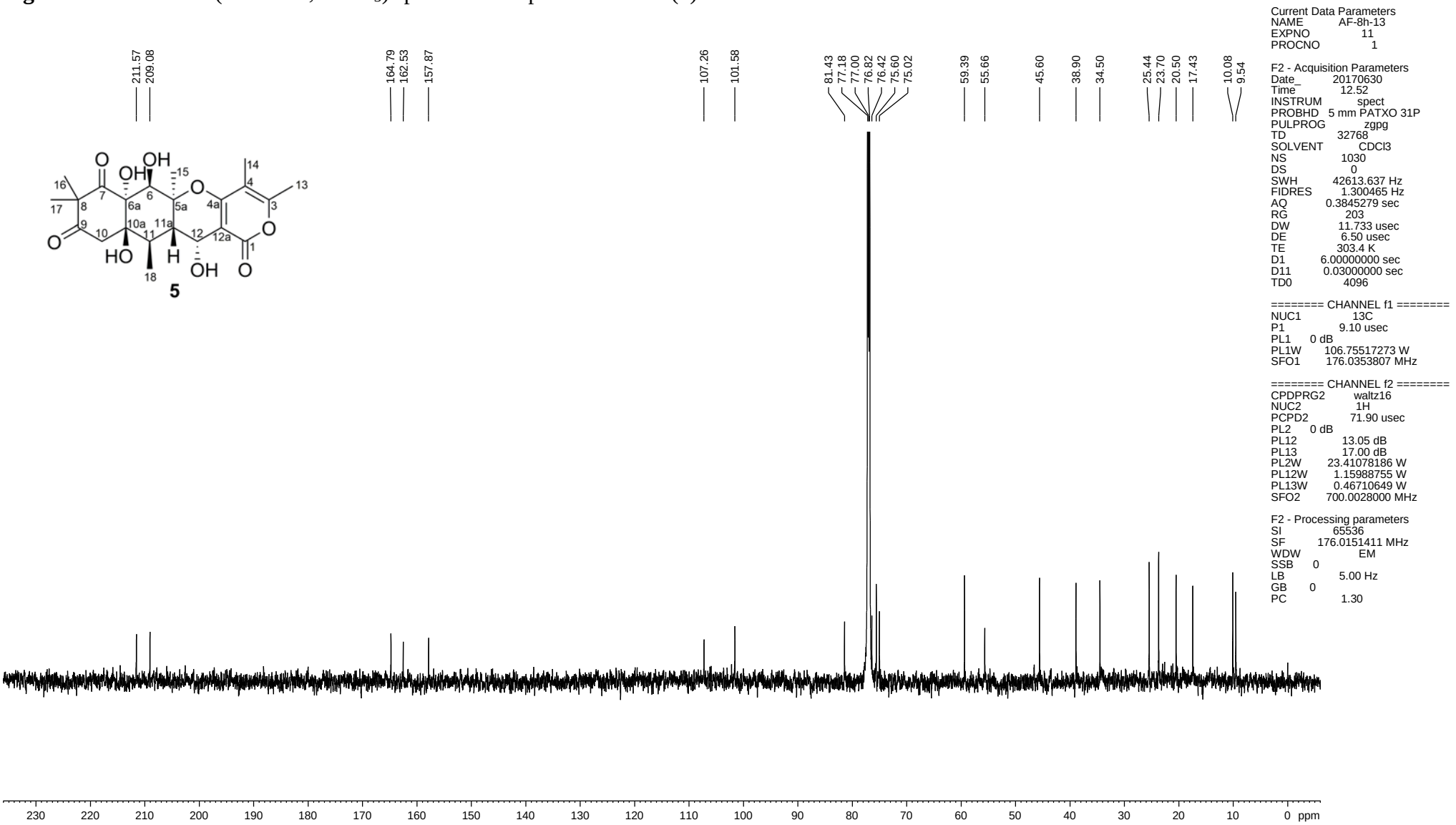


Figure S30. ^{1}H NMR (500 MHz, acetone-d_6) spectrum of aspertetranone A (**6**)

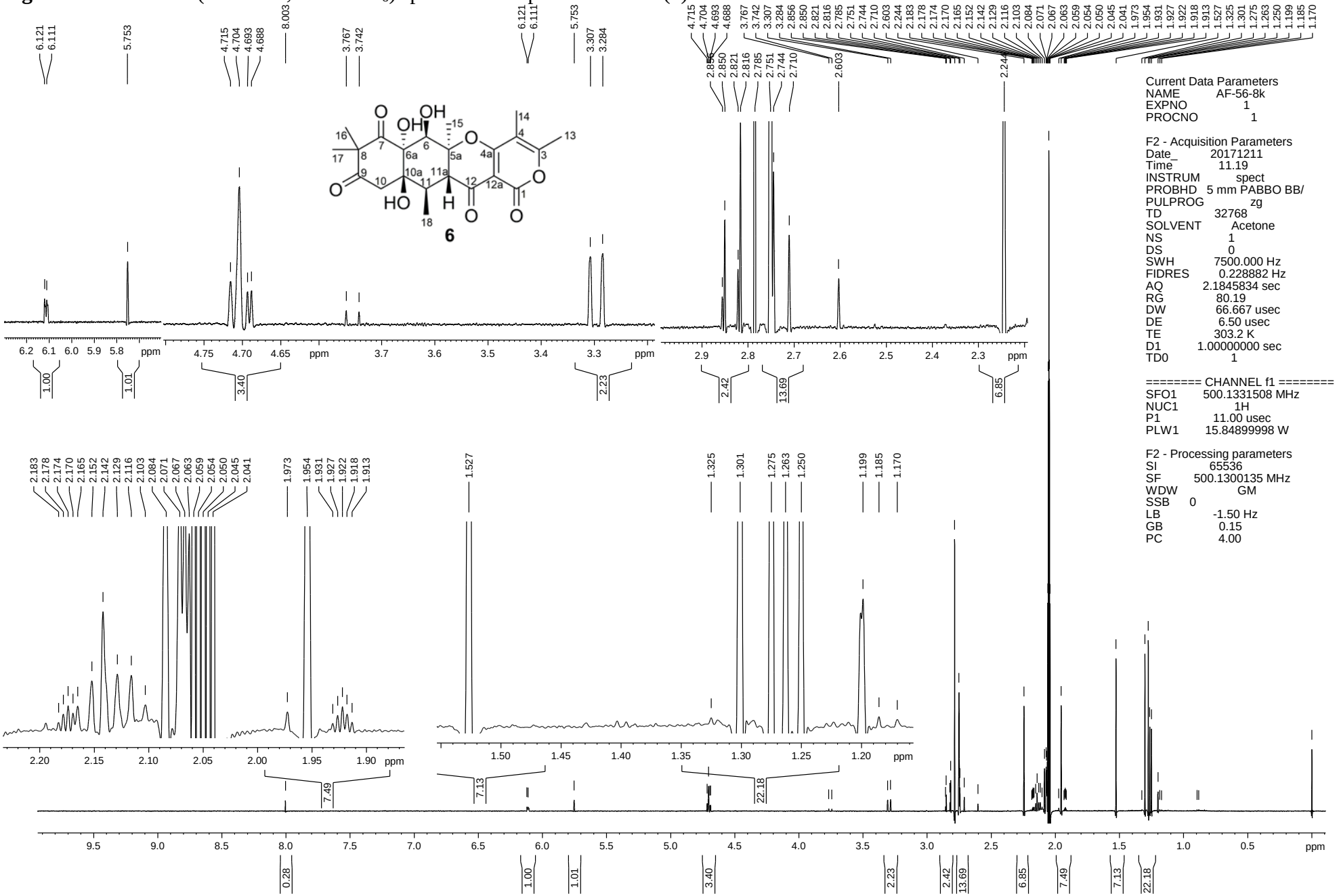


Figure S31. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of aspertetranone A (**6**)

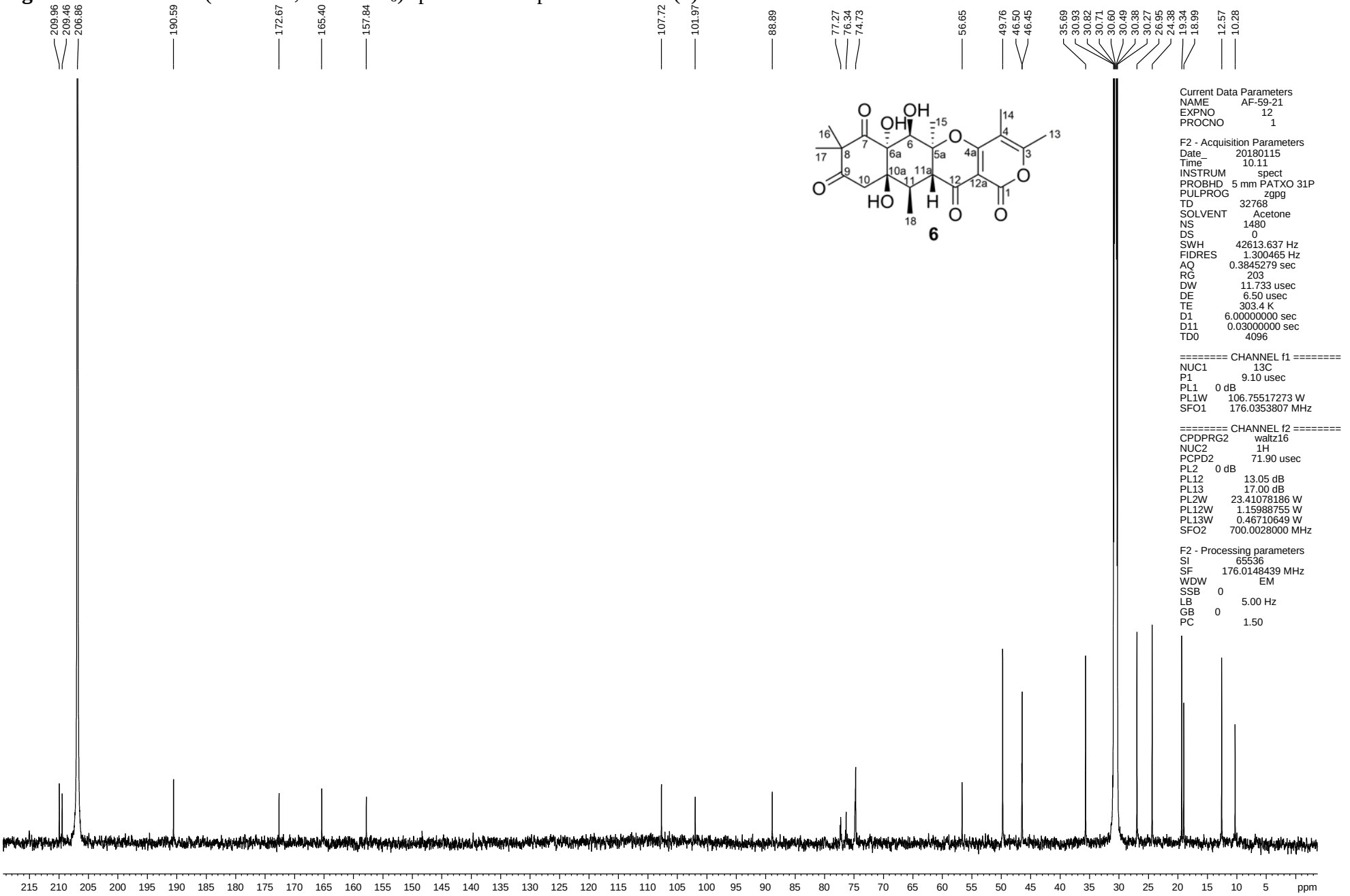


Figure S32. DEPT-135 (125 MHz, acetone-d_6) spectrum of aspertetranone A (**6**)

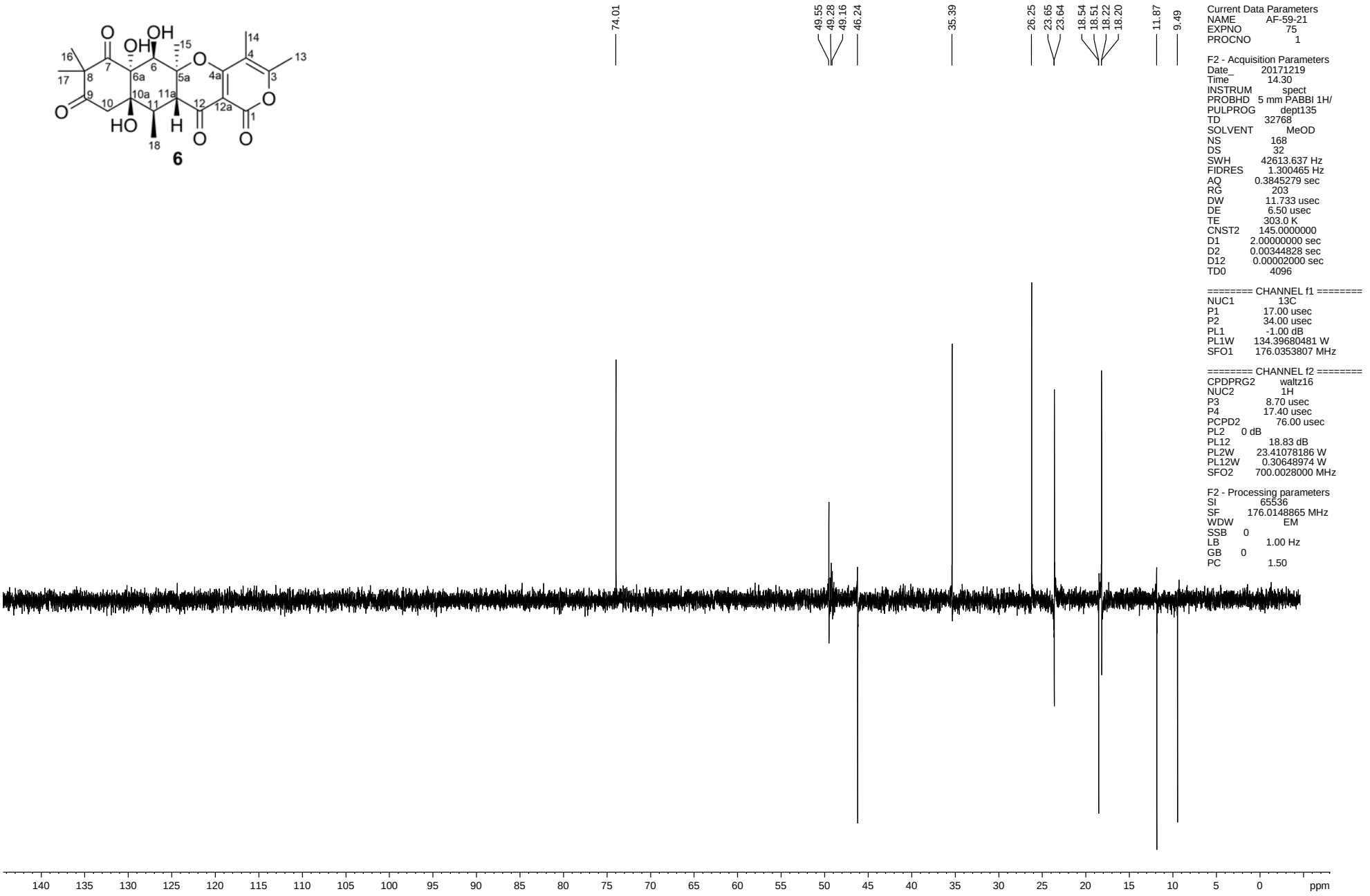


Figure S33. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 6β,9α,14-trihydroxycinnamolide (**7**)

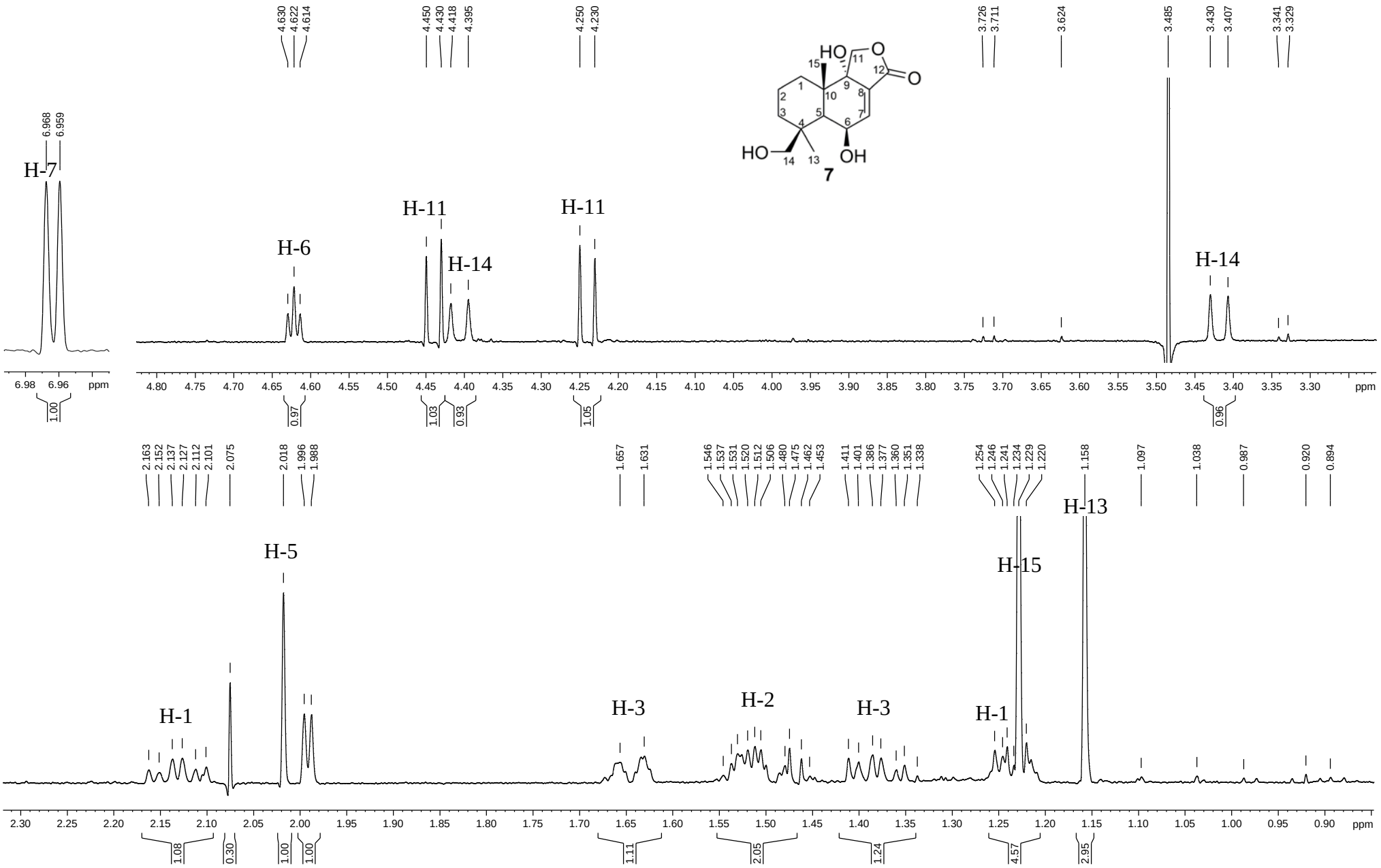


Figure S34. ^{13}C NMR (500 MHz, $CDCl_3$) spectrum of 6β,9α,14-trihydroxycinnamolide (**7**)

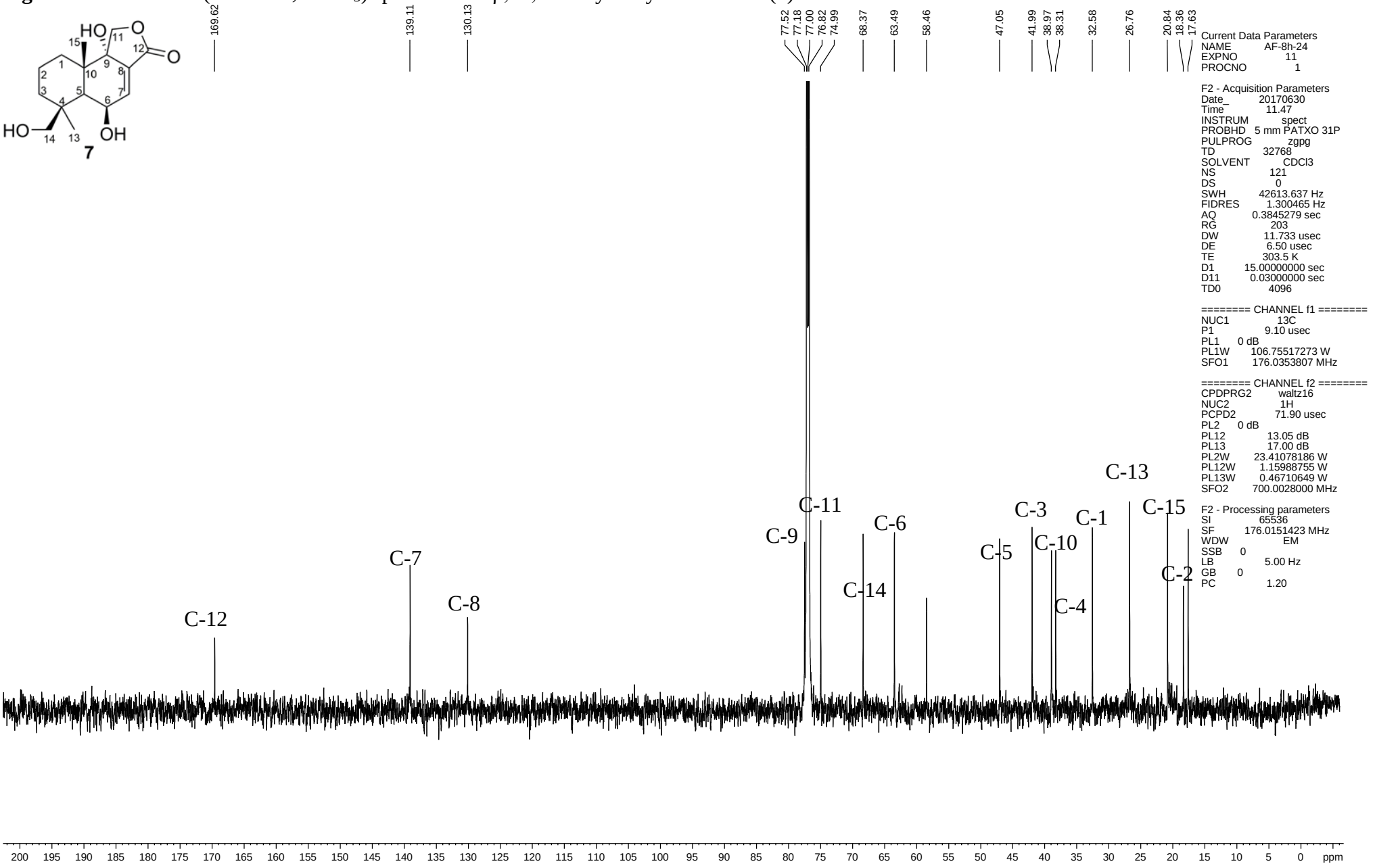


Figure S35. DEPT-135 (500 MHz, $CDCl_3$) spectrum of 6β,9α,14-trihydroxycinnamolide (**7**)

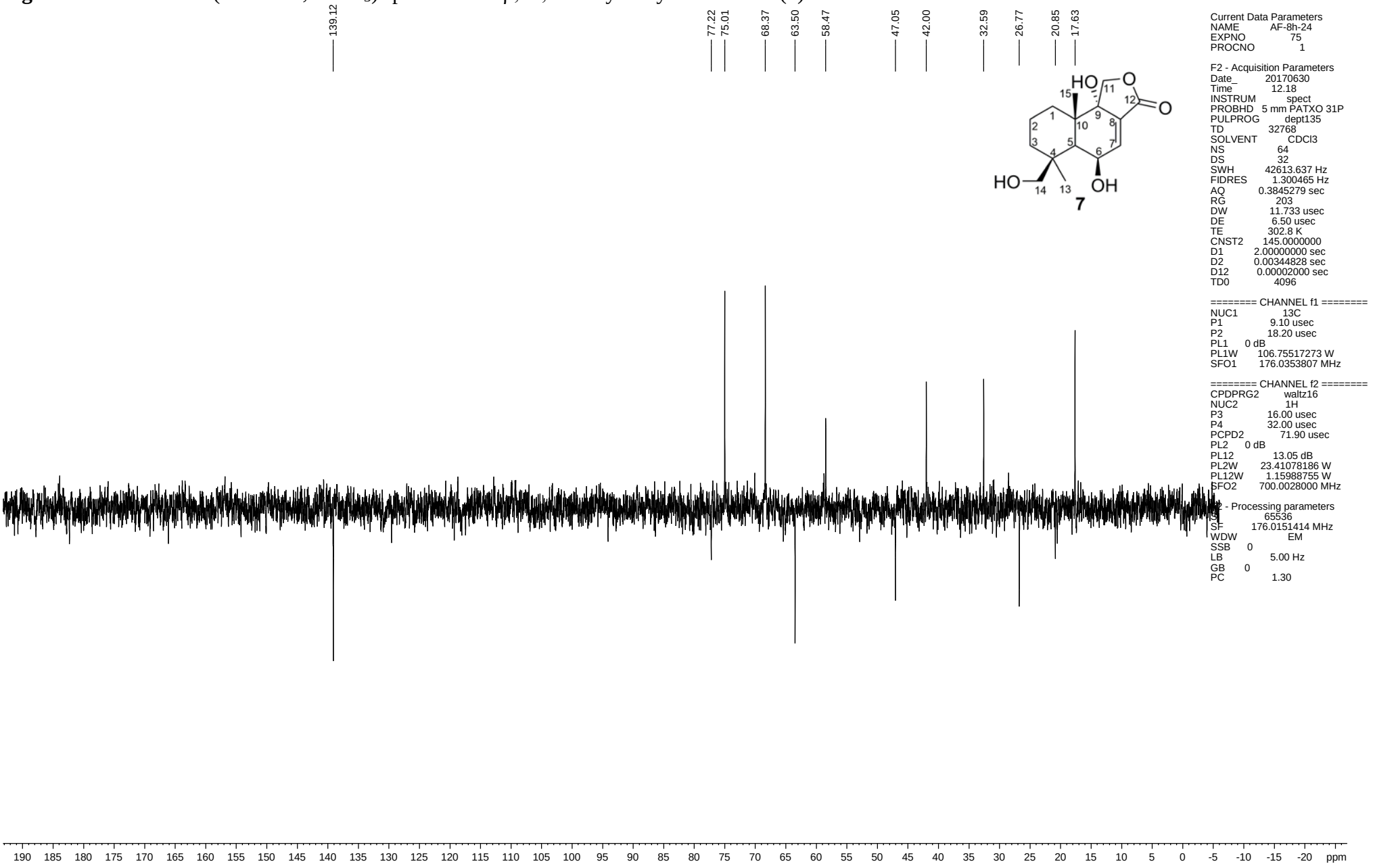
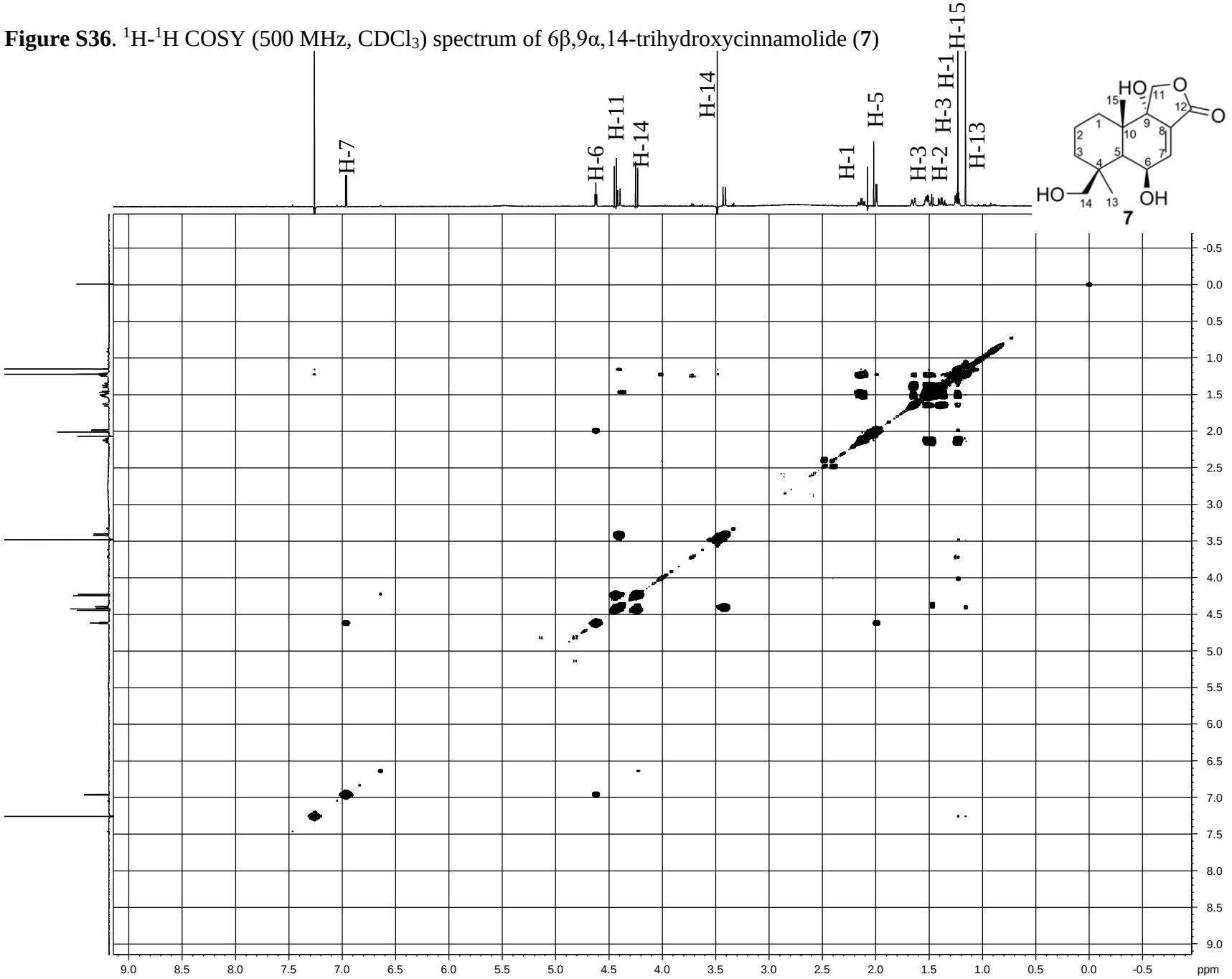


Figure S36. ^{1}H-^{1}H COSY (500 MHz, $CDCl_3$) spectrum of 6β,9α,14-trihydroxycinnamolide (**7**)



Current Data Parameters
NAME AF-8h-24
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180417
Time 13.31
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG cosyqf45
TD 2048
SOLVENT CDCl3
NS 4
DS 16
SWH 5241.090 Hz
FIDRES 2.559126 Hz
AQ 0.1954292 sec
RG 62.26
DW 95.400 usec
DE 6.50 usec
TE 303.2 K
D0 0.00000300 sec
D1 2.00000000 sec
IN0 0.00019080 sec

======== CHANNEL f1 ========
SFO1 500.1321619 MHz
NUC1 1H
P1 11.00 usec
PLW1 15.84899998 W

F1 - Acquisition parameters
TD 512
SFO1 500.1322 MHz
FIDRES 10.236505 Hz
SW 10.479 ppm
FnMODE QF

F2 - Processing parameters
SI 2048
SF 500.1300223 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 4.00

F1 - Processing parameters
SI 2048
MC2 QF
SF 500.1300223 MHz
WDW GM
SSB 0
LB 0 Hz
GB 0

Figure S37. HSQC (500 MHz, $CDCl_3$) spectrum of 6β,9α,14-trihydroxycinnamolide (**7**)

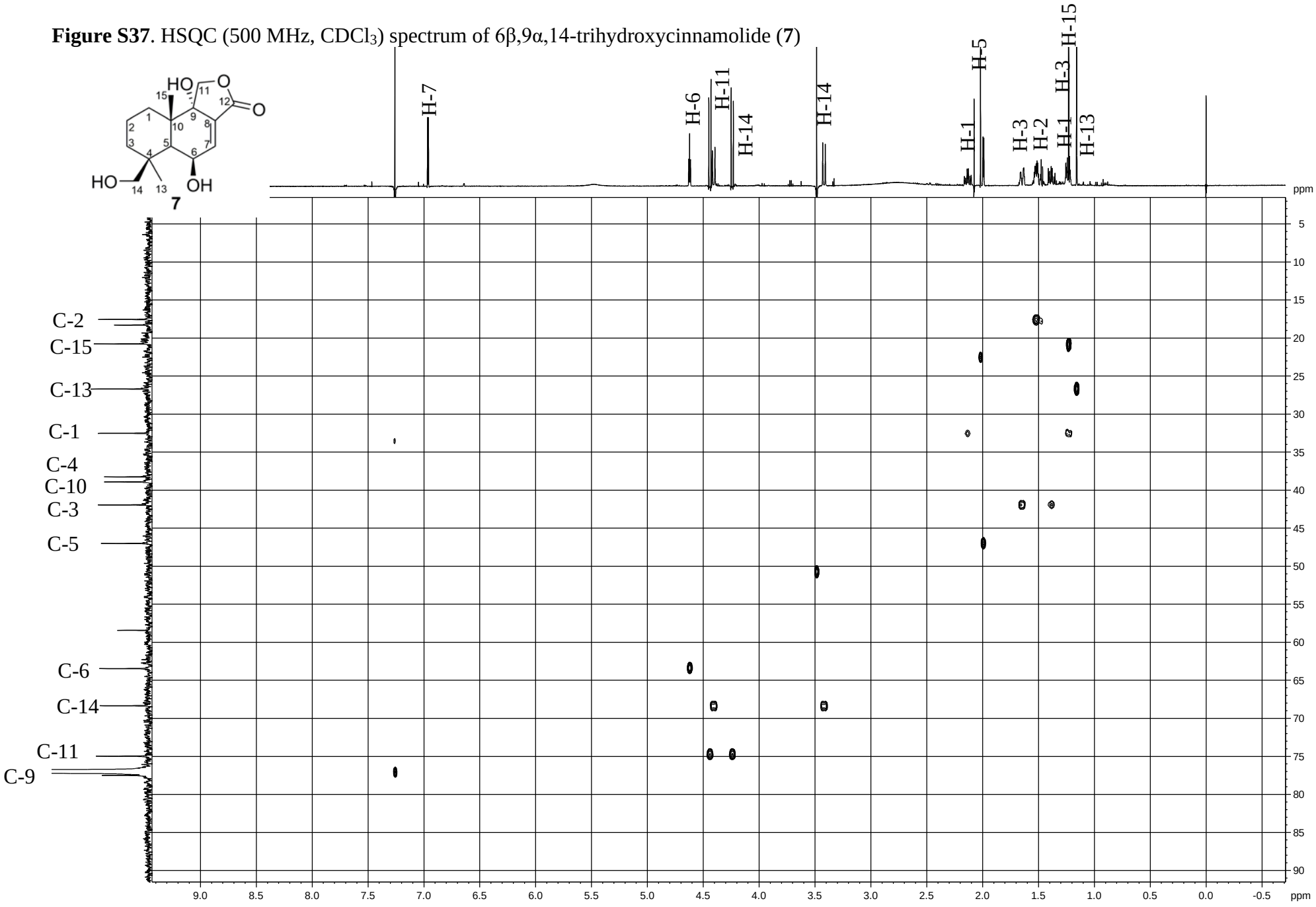
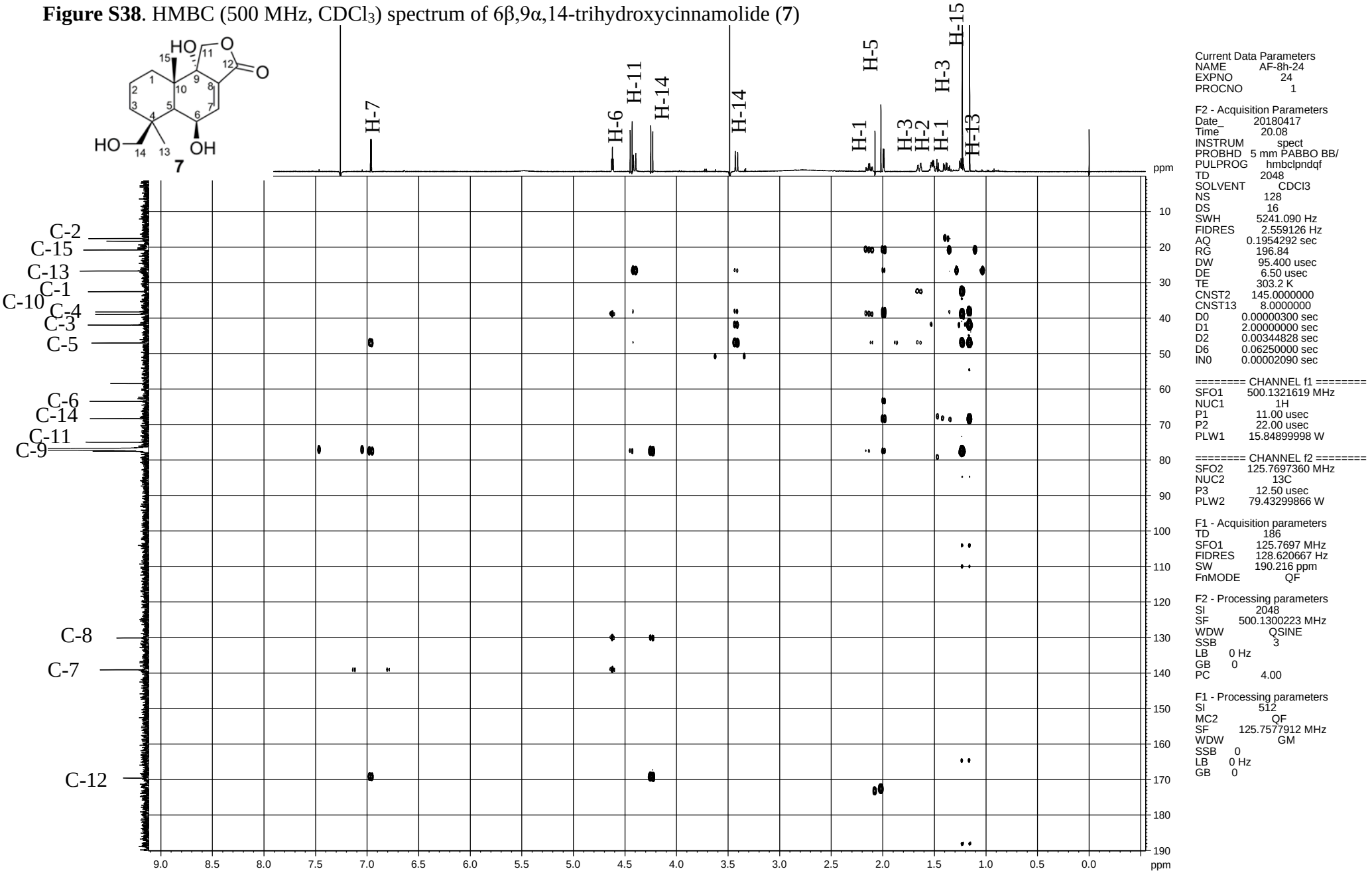


Figure S38. HMBC (500 MHz, $CDCl_3$) spectrum of 6β,9α,14-trihydroxycinnamolide (**7**)



Current Data Parameters
NAME AF-8h-24
EXPNO 24
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180417
Time 20.08
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG hmbclpndqf
TD 2048
SOLVENT CDCl3
NS 128
DS 16
SWH 5241.090 Hz
FIDRES 2.559126 Hz
AQ 0.1954292 sec
RG 196.84
DW 95.400 usec
DE 6.50 usec
TE 303.2 K
CNST2 145.0000000
CNST13 8.0000000
D0 0.00000300 sec
D1 2.00000000 sec
D2 0.00344828 sec
D6 0.06250000 sec
IN0 0.00002090 sec

======== CHANNEL f1 ========
SFO1 500.1321619 MHz
NUC1 1H
P1 11.00 usec
P2 22.00 usec
PLW1 15.84899998 W

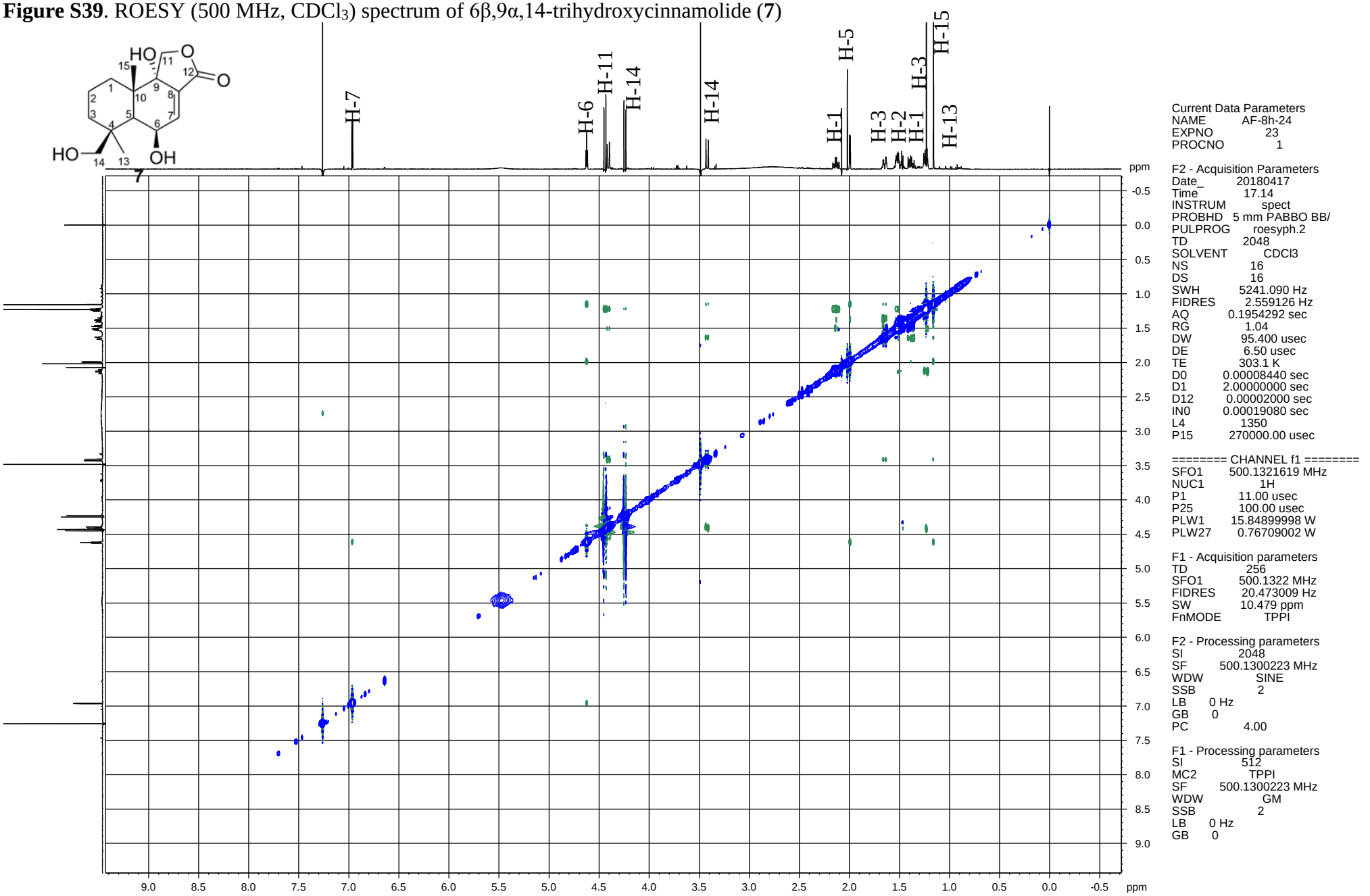
======== CHANNEL f2 ========
SFO2 125.7697360 MHz
NUC2 13C
P3 12.50 usec
PLW2 79.43299866 W

F1 - Acquisition parameters
TD 186
SFO1 125.7697 MHz
FIDRES 128.620667 Hz
SW 190.216 ppm
FnMODE QF

F2 - Processing parameters
SI 2048
SF 500.1300223 MHz
WDW QSINE
SSB 3
LB 0 Hz
GB 0
PC 4.00

F1 - Processing parameters
SI 512
MC2 QF
SF 125.7577912 MHz
WDW GM
SSB 0
LB 0 Hz
GB 0

Figure S39. ROESY (500 MHz, $CDCl_3$) spectrum of 6β,9α,14-trihydroxycinnamolide (**7**)



Current Data Parameters
NAME AF-8h-24
EXPNO 23
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180417
Time 17.14
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG roesyph.2
TD 2048
SOLVENT CDCl3
NS 16
DS 16
SWH 5241.090 Hz
FIDRES 2.559126 Hz
AQ 0.1954292 sec
RG 1.04
DW 95.400 usec
DE 6.50 usec
TE 303.1 K
D0 0.00008440 sec
D1 2.00000000 sec
D12 0.00002000 sec
IN0 0.00019080 sec
L4 1350
P15 270000.00 usec

======== CHANNEL f1 ========
SFO1 500.1321619 MHz
NUC1 1H
P1 11.00 usec
P25 100.00 usec
PLW1 15.84899998 W
PLW27 0.76709002 W

F1 - Acquisition parameters
TD 256
SFO1 500.1322 MHz
FIDRES 20.473009 Hz
SW 10.479 ppm
FnMODE TPPI

F2 - Processing parameters
SI 2048
SF 500.1300223 MHz
WDW SINE
SSB 2
LB 0 Hz
GB 0
PC 4.00

F1 - Processing parameters
SI 512
MC2 TPPI
SF 500.1300223 MHz
WDW GM
SSB 2
LB 0 Hz
GB 0

Figure S40. ECD spectrum of 6β,9α,14-trihydroxycinnamolide (**7**) in methanol

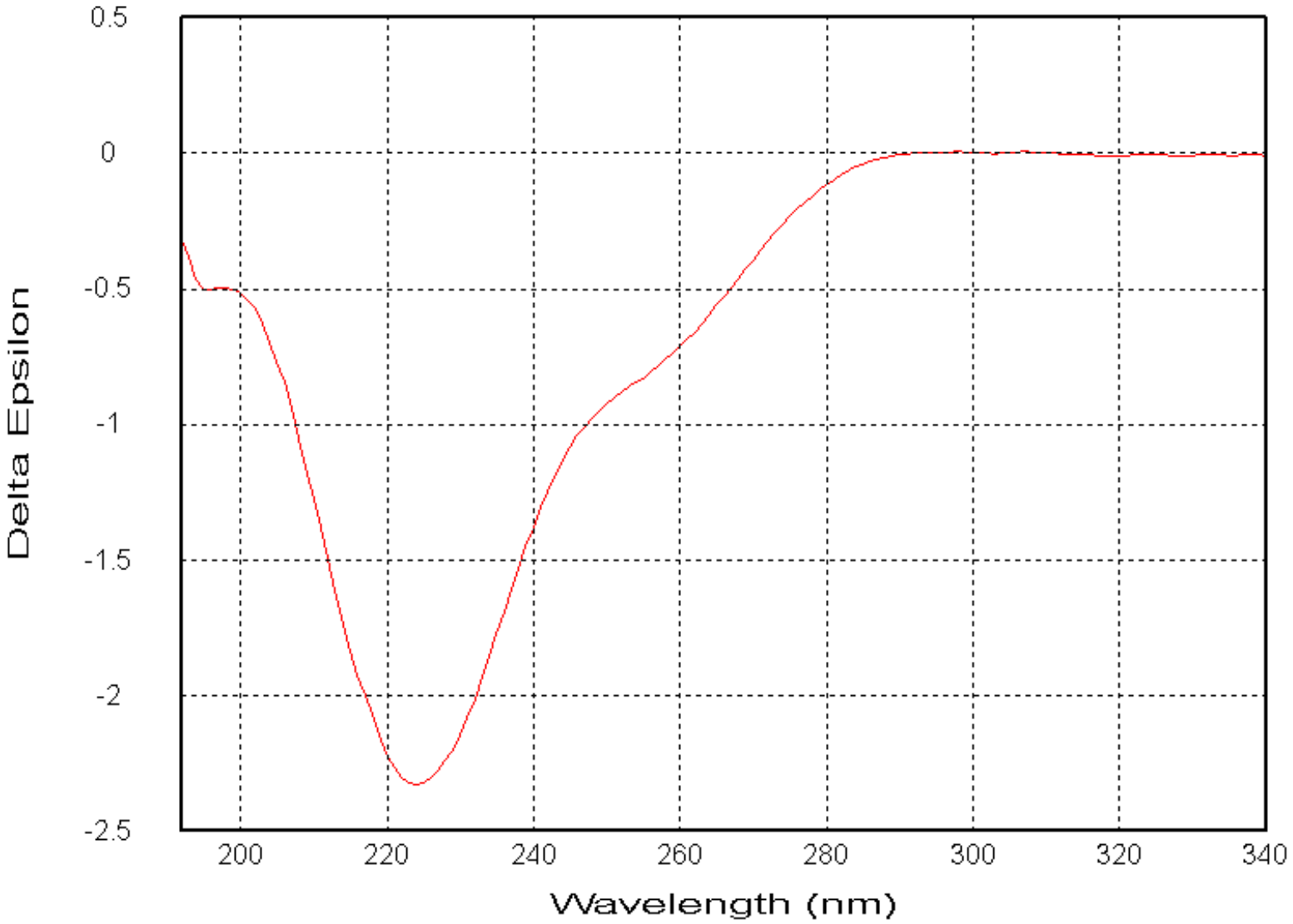
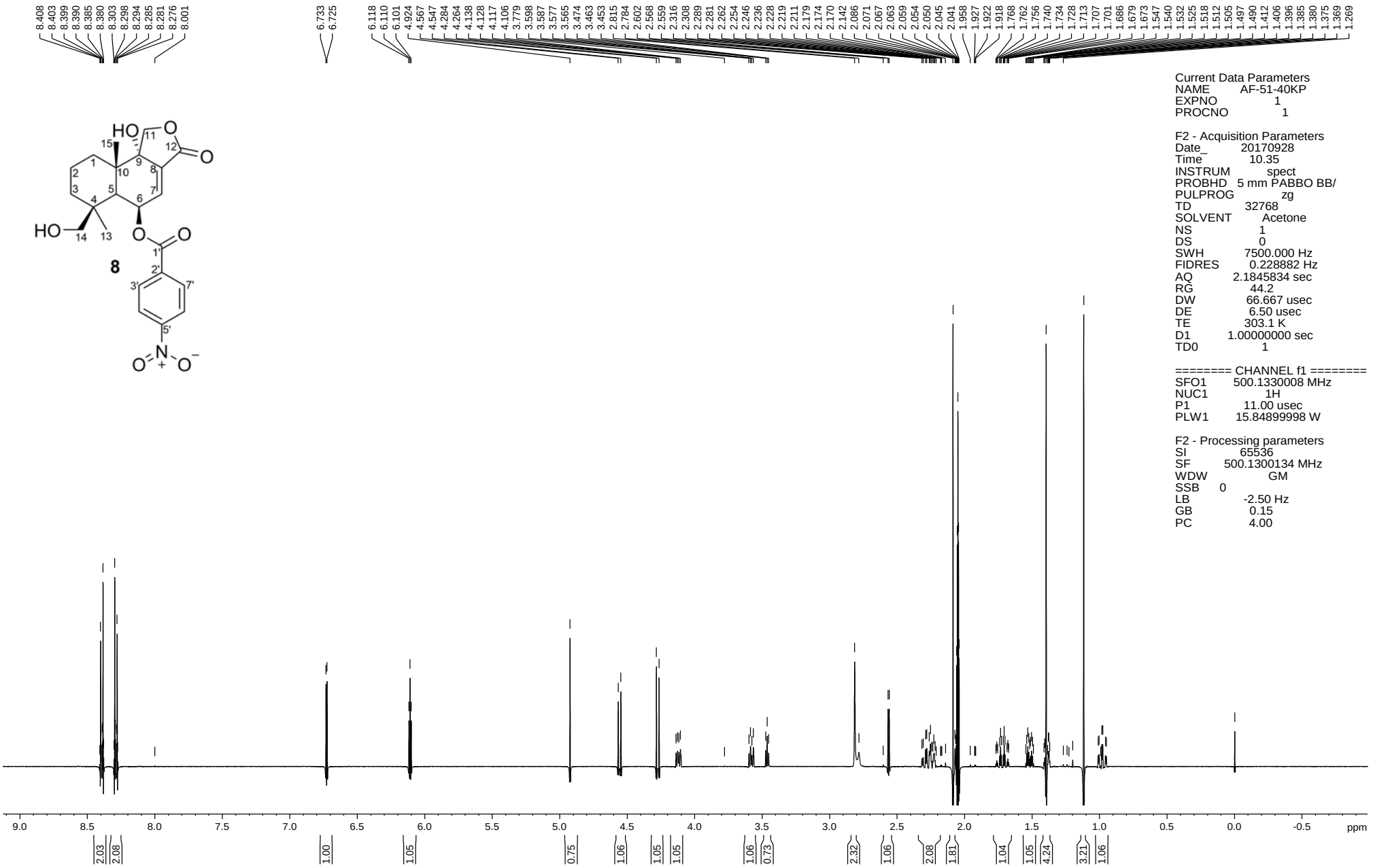


Figure S41. ^{1}H NMR (500 MHz, acetone-d_6) spectrum of insulicolide A (**8**)



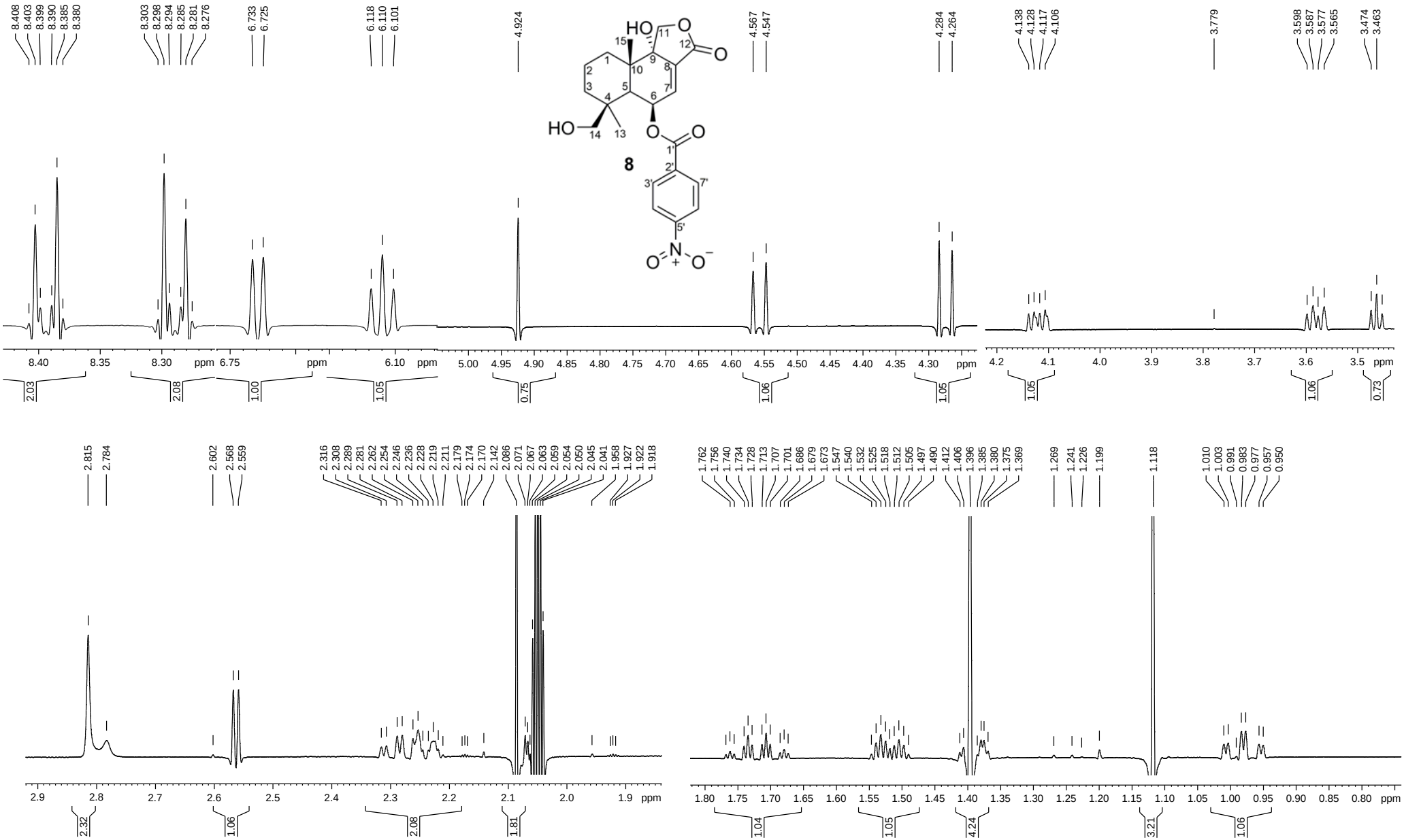

8.408
8.403
8.399
8.390
8.385
8.380
8.303
8.298
8.294
8.285
8.281
8.276
6.733
6.725
6.118
6.110
6.101
4.924
4.567
4.547
4.284
4.264
4.138
4.128
4.117
4.106
3.779
3.598
3.587
3.577
3.565
3.474
3.463
HO
O
O
HO
O
O
O
N
O
8
ppm
2.815
2.784
2.602
2.568
2.559
2.316
2.308
2.289
2.281
2.262
2.254
2.246
2.236
2.228
2.219
2.211
2.179
2.174
2.170
2.142
2.086
2.071
2.067
2.063
2.059
2.054
2.050
2.045
2.041
1.958
1.927
1.922
1.918
1.762
1.756
1.740
1.734
1.728
1.713
1.707
1.701
1.686
1.679
1.673
1.547
1.540
1.532
1.525
1.518
1.512
1.505
1.497
1.490
1.412
1.406
1.396
1.385
1.380
1.375
1.369
1.269
1.241
1.226
1.199
1.118
1.010
1.003
0.991
0.983
0.977
0.957
0.950

Figure S42. ^{13}C NMR (125 MHz, acetone-d_6) spectrum of insulicolide A (**8**)

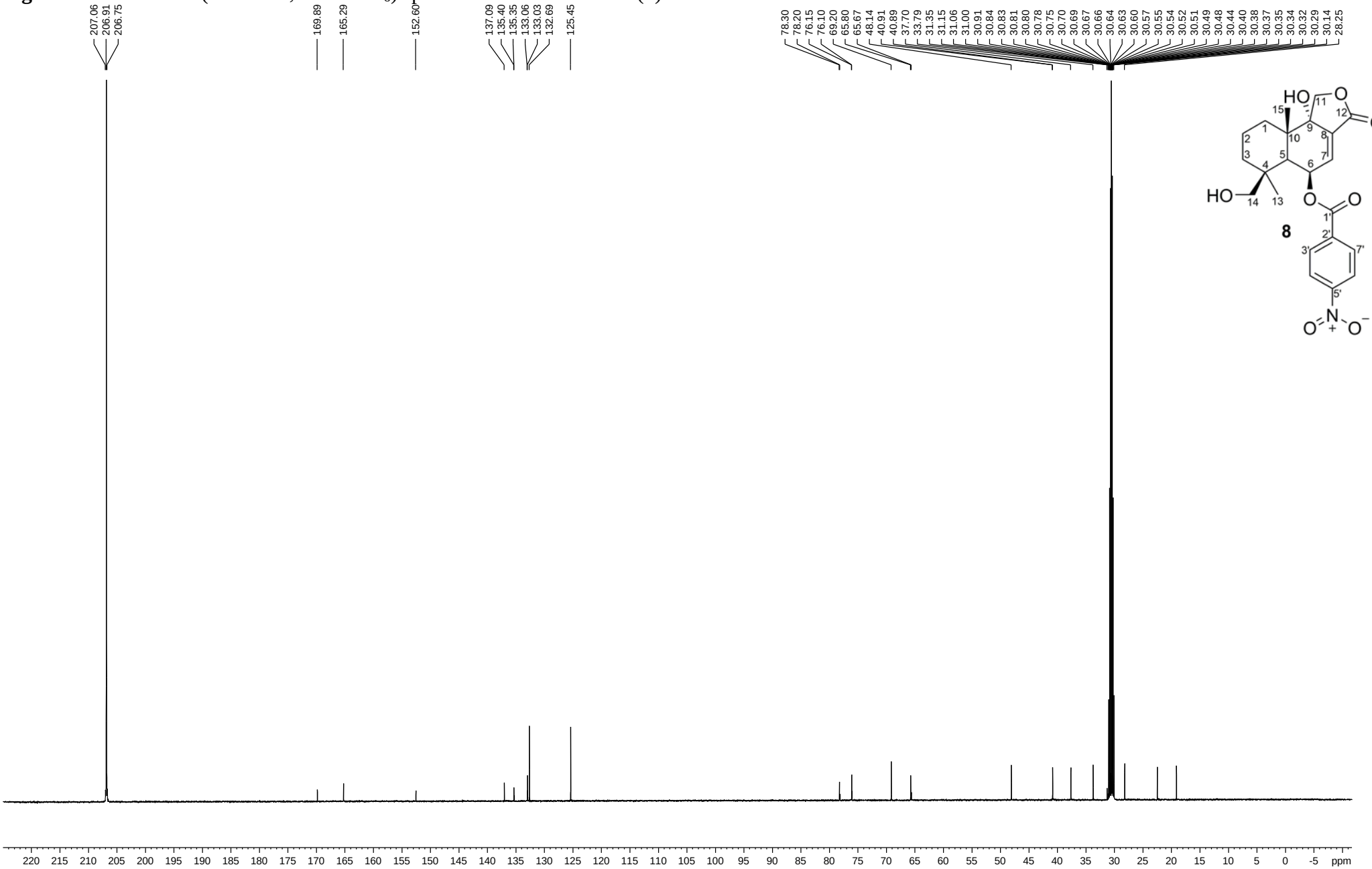


Figure S43. DEPT-135 (125 MHz, acetone-d_6) spectrum of insulicolide A (**8**)

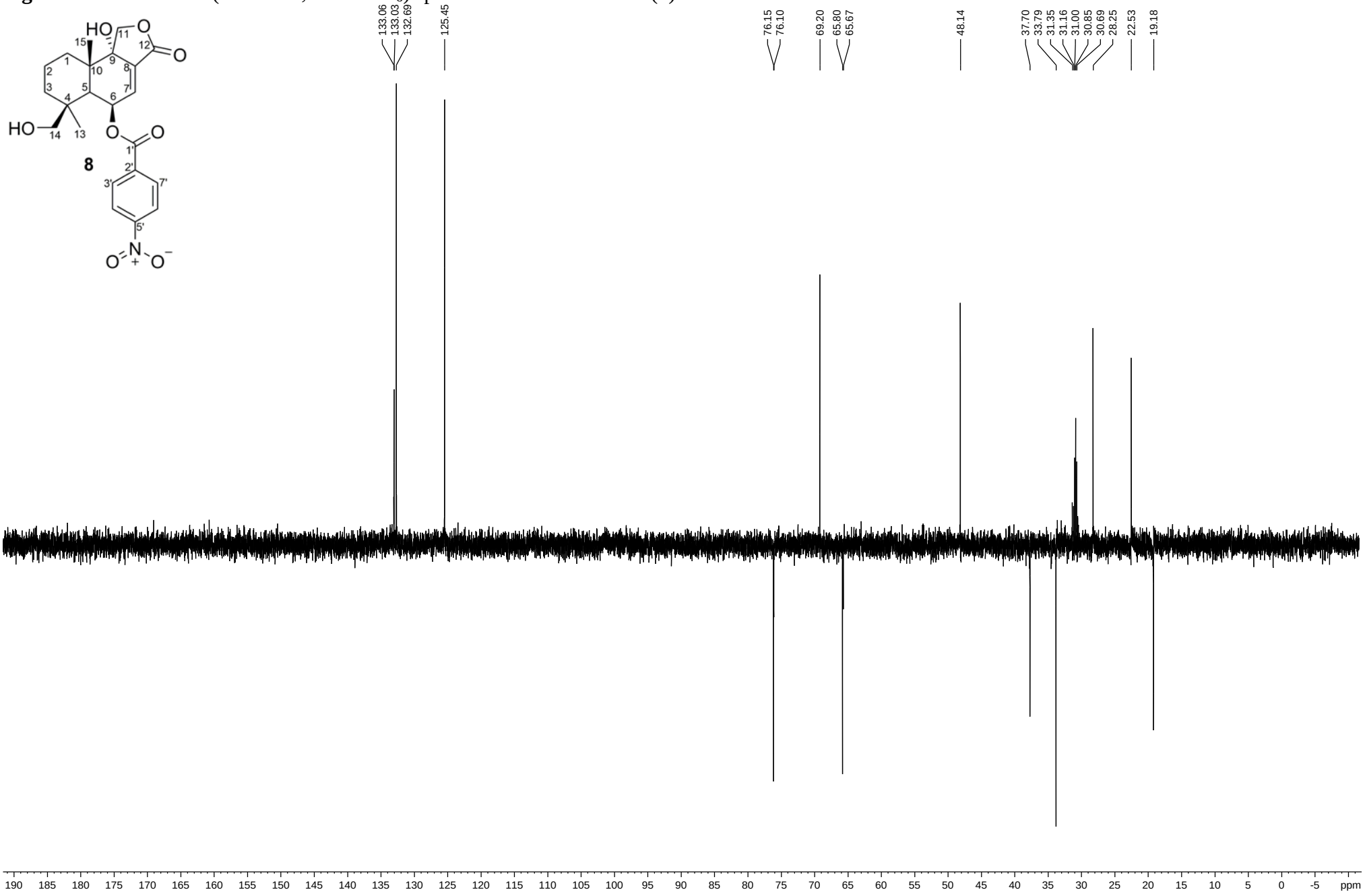


Figure S44. ECD spectrum of insulicolide A (**8**) in methanol

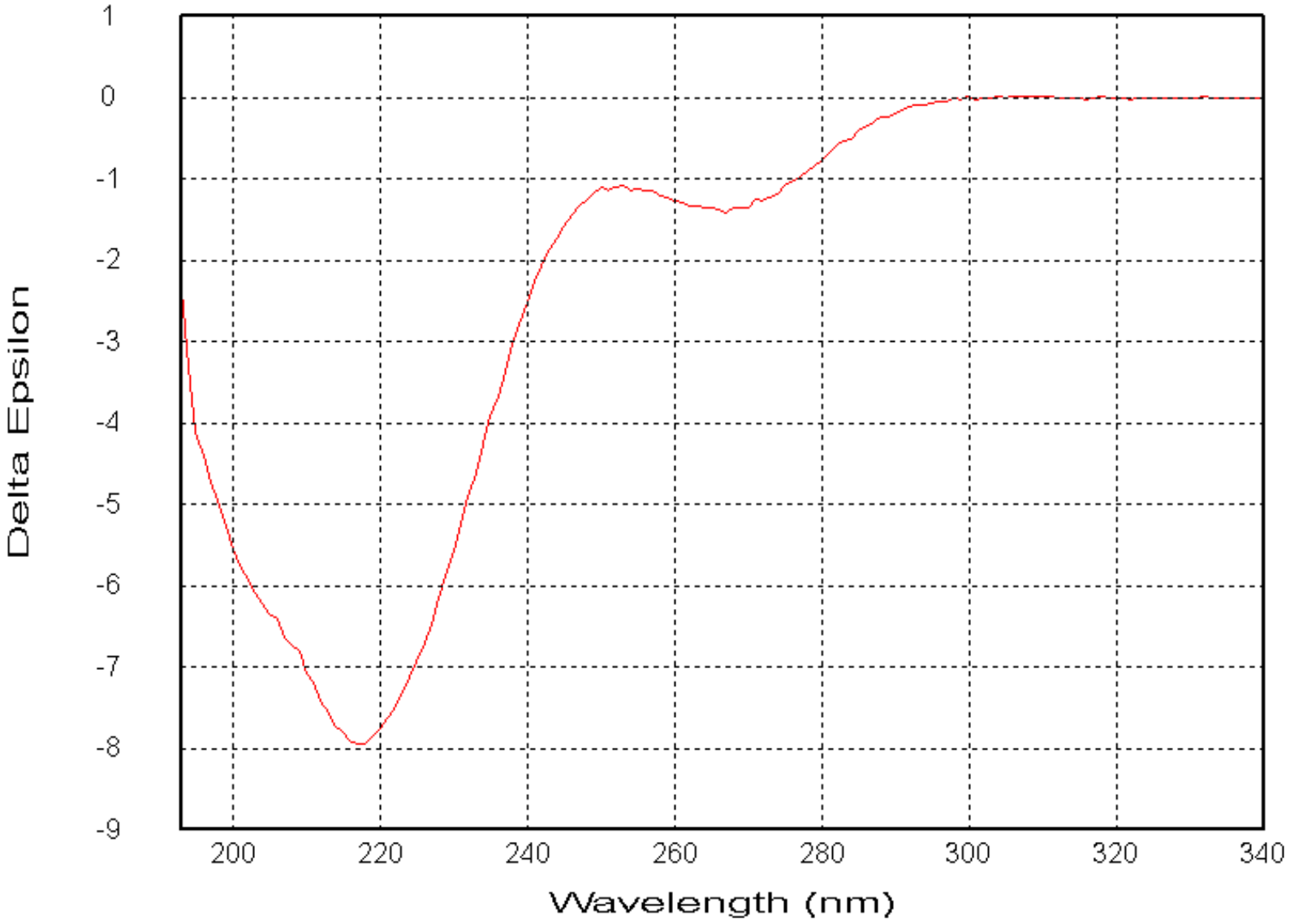
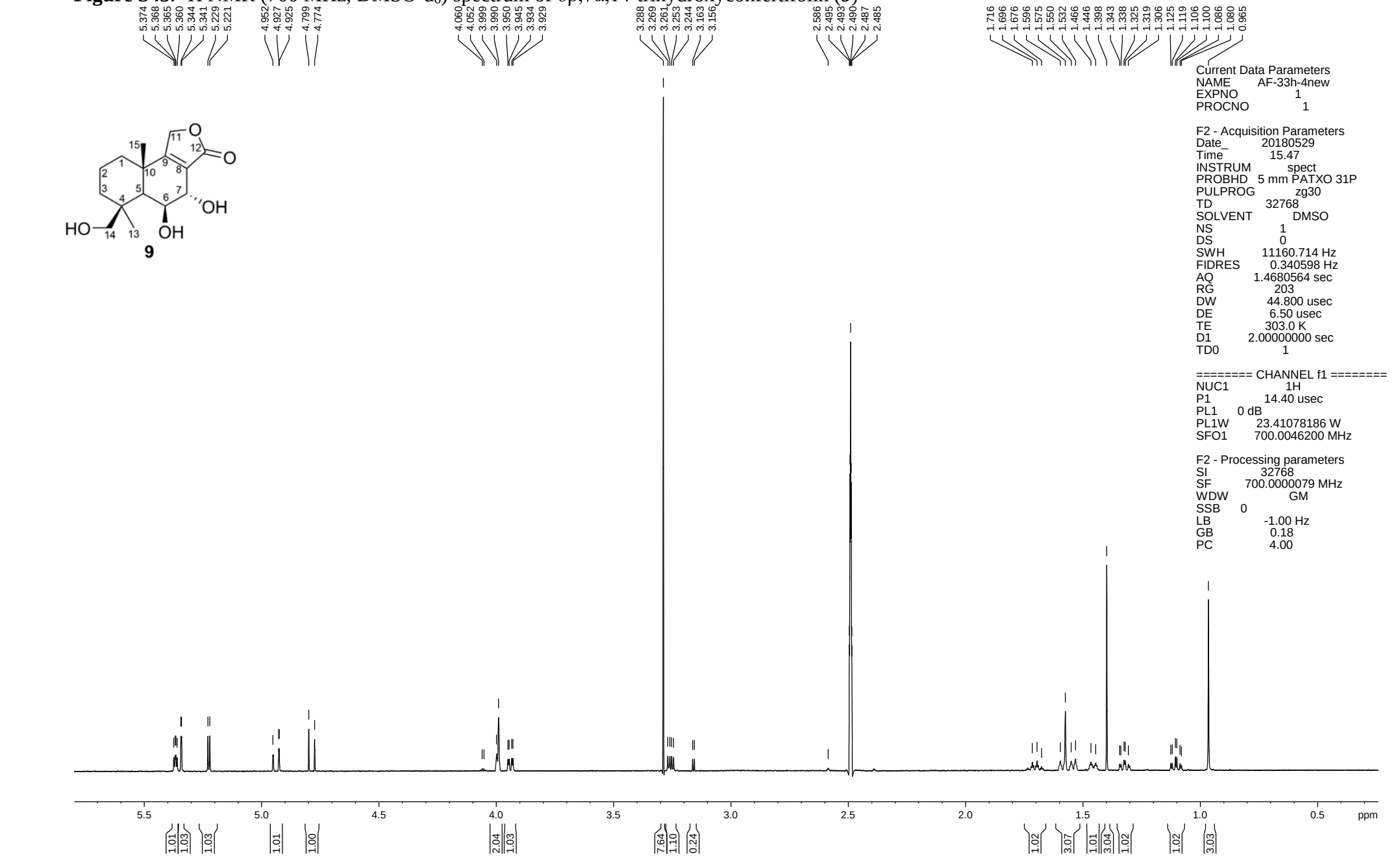


Figure S45. ^{1}H NMR (700 MHz, DMSO-d_6) spectrum of 6β,7α,14-trihydroxyconfertifolin (**9**)



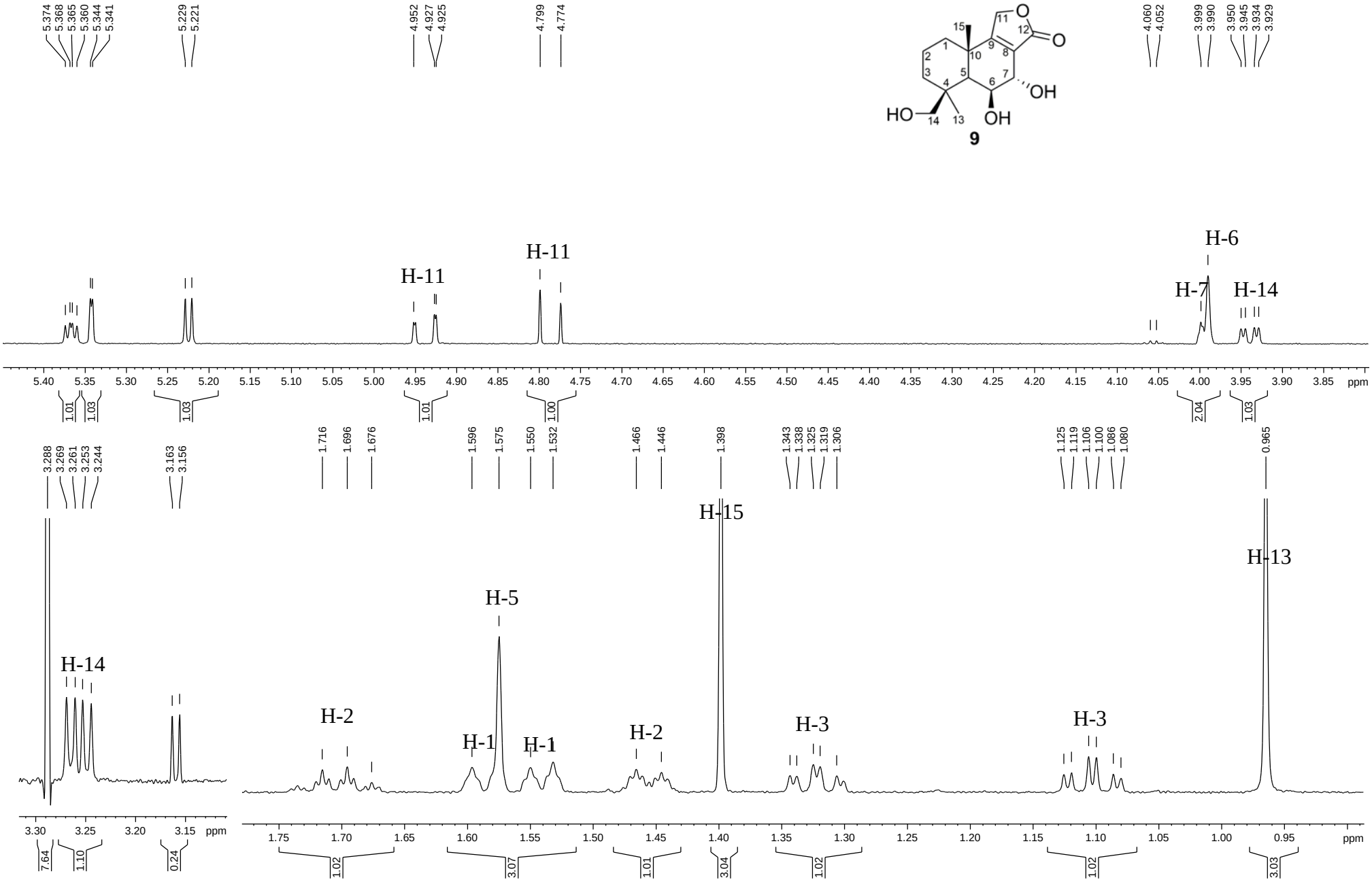

5.374
5.368
5.365
5.360
5.344
5.341
5.229
5.221
4.952
4.927
4.925
4.799
4.774
4.060
4.052
3.999
3.990
3.950
3.945
3.934
3.929
O
O
OH
HO
OH
9
H-11
H-11
H-6
H-7
H-14
ppm
3.288
3.269
3.261
3.253
3.244
3.163
3.156
1.716
1.696
1.676
1.596
1.575
1.550
1.532
1.466
1.446
1.398
1.343
1.338
1.325
1.319
1.306
1.125
1.119
1.106
1.100
1.086
1.080
0.965
H-15
H-13
H-5
H-14
H-2
H-1
H-1
H-2
H-3
H-3
ppm

Figure S46. ^{13}C NMR (125 MHz, DMSO-d_6) spectrum of 6β,7α,14-trihydroxyconfertifolin (**9**)

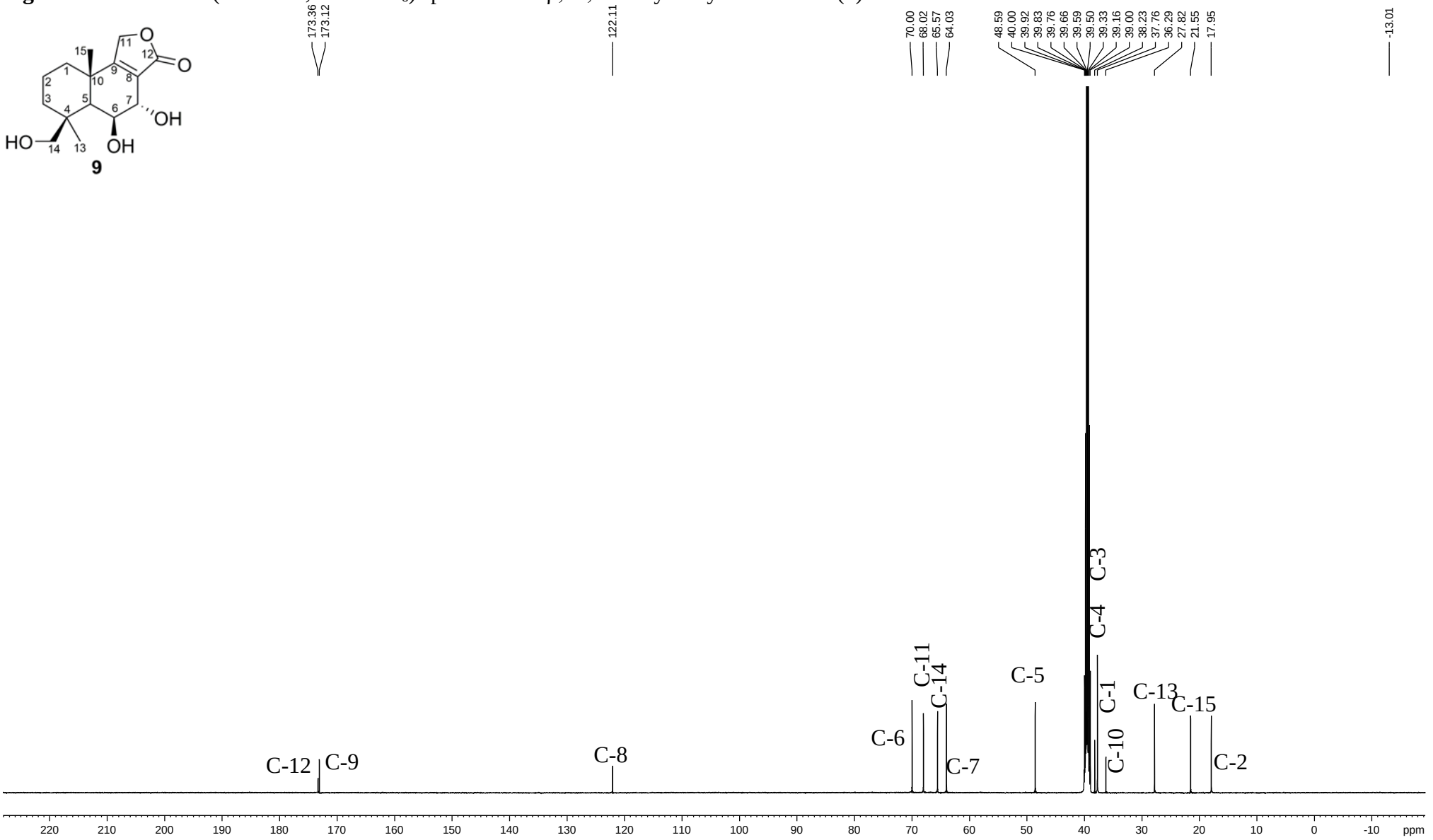
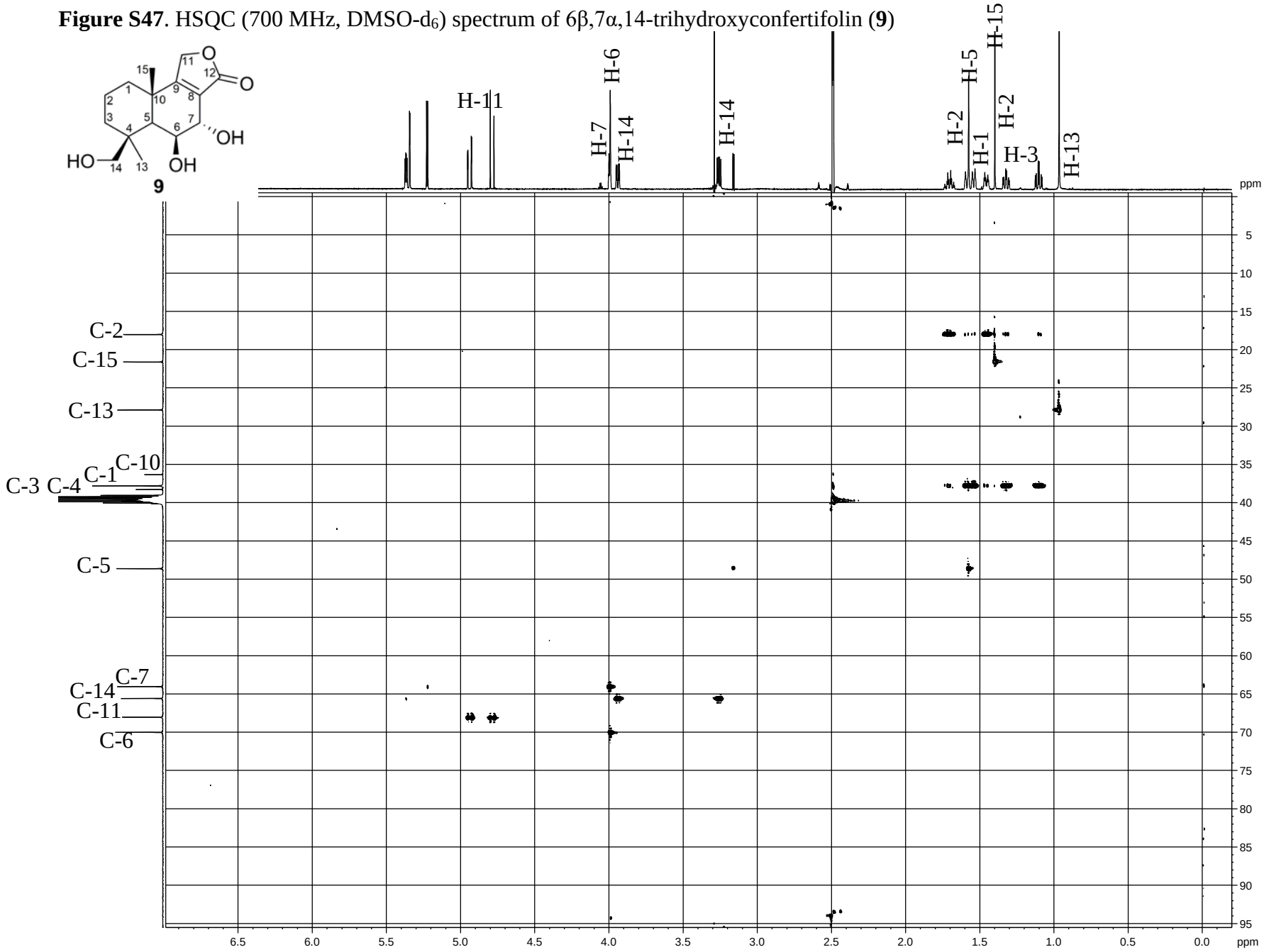


Figure S47. HSQC (700 MHz, DMSO-d_6) spectrum of 6β,7α,14-trihydroxyconfertifolin (**9**)



Current Data Parameters
NAME AF-33h-4new
EXPNO 22
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180529
Time 16.22
INSTRUM spect
PROBHD 5 mm PATXO 31P
PULPROG hsqcetgpsisp2.2
TD 2048
SOLVENT DMSO
NS 48
DS 16
SWH 5030.181 Hz
FIDRES 2.456143 Hz
AQ 0.2036212 sec
RG 203
DW 99.400 usec
DE 6.50 usec
TE 303.4 K
CNST2 145.0000000
CNST17 -0.5000000
D0 0.00000300 sec
D1 2.00000000 sec
D4 0.00172414 sec
D11 0.03000000 sec
D16 0.00010000 sec
D24 0.00086207 sec
IN0 0.00002960 sec
L31 16

======== CHANNEL f1 ========
NUC1 1H
P1 14.40 usec
P2 28.80 usec
P28 0 usec
PL1 0 dB
PL1W 23.41078186 W
SFO1 700.0023824 MHz

======== CHANNEL f2 ========
CPDPRG2 bi_p5m4sp_4sp.2
NUC2 13C
P3 9.20 usec
P14 500.00 usec
P24 2000.00 usec
P63 1500.00 usec
PL0 120.00 dB
PL2 0 dB
PL12 16.00 dB
PL0W 0 W
PL2W 106.75517273 W
PL12W 2.68156862 W
SFO2 176.0235899 MHz
SP3 8.88 dB
SP7 8.88 dB
SP14 10.36 dB
SP31 16.38 dB
SPNAM3 Crp60,0.5,20.1
SPNAM7 Crp60comp.4
SPNAM14 Crp32,1.5,20.2
SPNAM31 Crp32,1.5,20.2
SPOAL3 0.500
SPOAL7 0.500
SPOAL14 0.500
SPOAL31 0.500
SPOFFS3 0 Hz
SPOFFS7 0 Hz
SPOFFS14 0 Hz
SPOFFS31 0 Hz

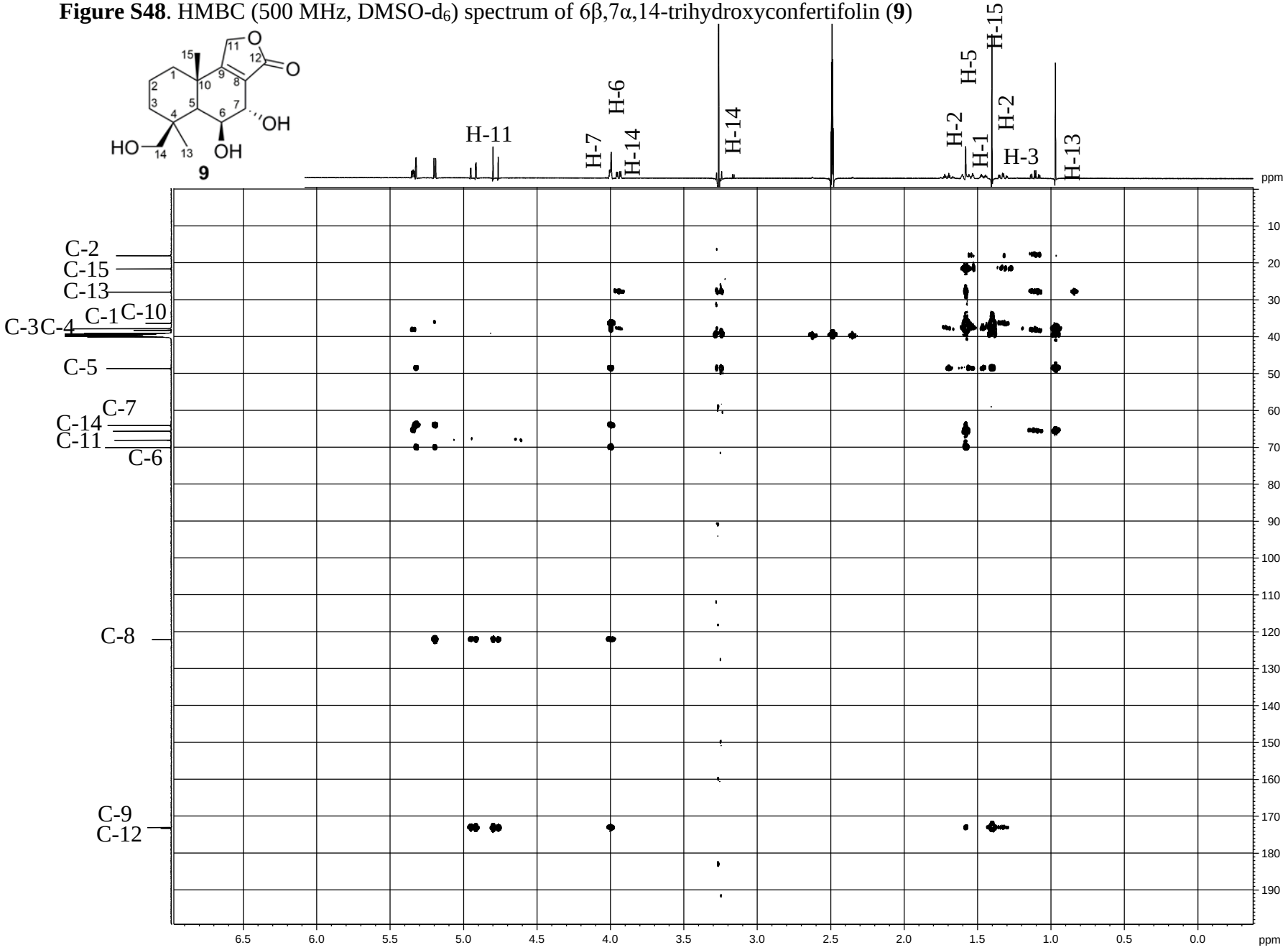
====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPNAM3 SINE.100
GPNAM4 SINE.100
GPZ1 80.00 %
GPZ2 20.10 %
GPZ3 11.00 %
GPZ4 -5.00 %
P16 1000.00 usec
P19 500.00 usec

F1 - Acquisition parameters
TD 256
SFO1 176.0236 MHz
FIDRES 66.008842 Hz
SW 96.000 ppm
FnMODE Echo-Antiecho

F2 - Processing parameters
SI 2048
SF 700.0000062 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 4.00

F1 - Processing parameters
SI 1024
MC2 echo-antiecho
SF 176.0152282 MHz
WDW
SSB 2
LB 0 Hz
GB 0

Figure S48. HMBC (500 MHz, DMSO-d_6) spectrum of 6β,7α,14-trihydroxyconfertifolin (**9**)



Current Data Parameters
NAME AF-33h-4
EXPNO 23
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180627
Time 9.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG hmbclpndqf
TD 2048
SOLVENT DMSO
NS 160
DS 16
SWH 3676.471 Hz
FIDRES 1.795152 Hz
AQ 0.2785780 sec
RG 196.84
DW 136.000 usec
DE 6.50 usec
TE 308.2 K
CNST2 145.0000000
CNST13 8.0000000
D0 0.00000300 sec
D1 2.00000000 sec
D2 0.00344828 sec
D6 0.06250000 sec
IN0 0.00001990 sec

======== CHANNEL f1 ========
SFO1 500.1316629 MHz
NUC1 1H
P1 11.00 usec
P2 22.00 usec
PLW1 15.84899998 W

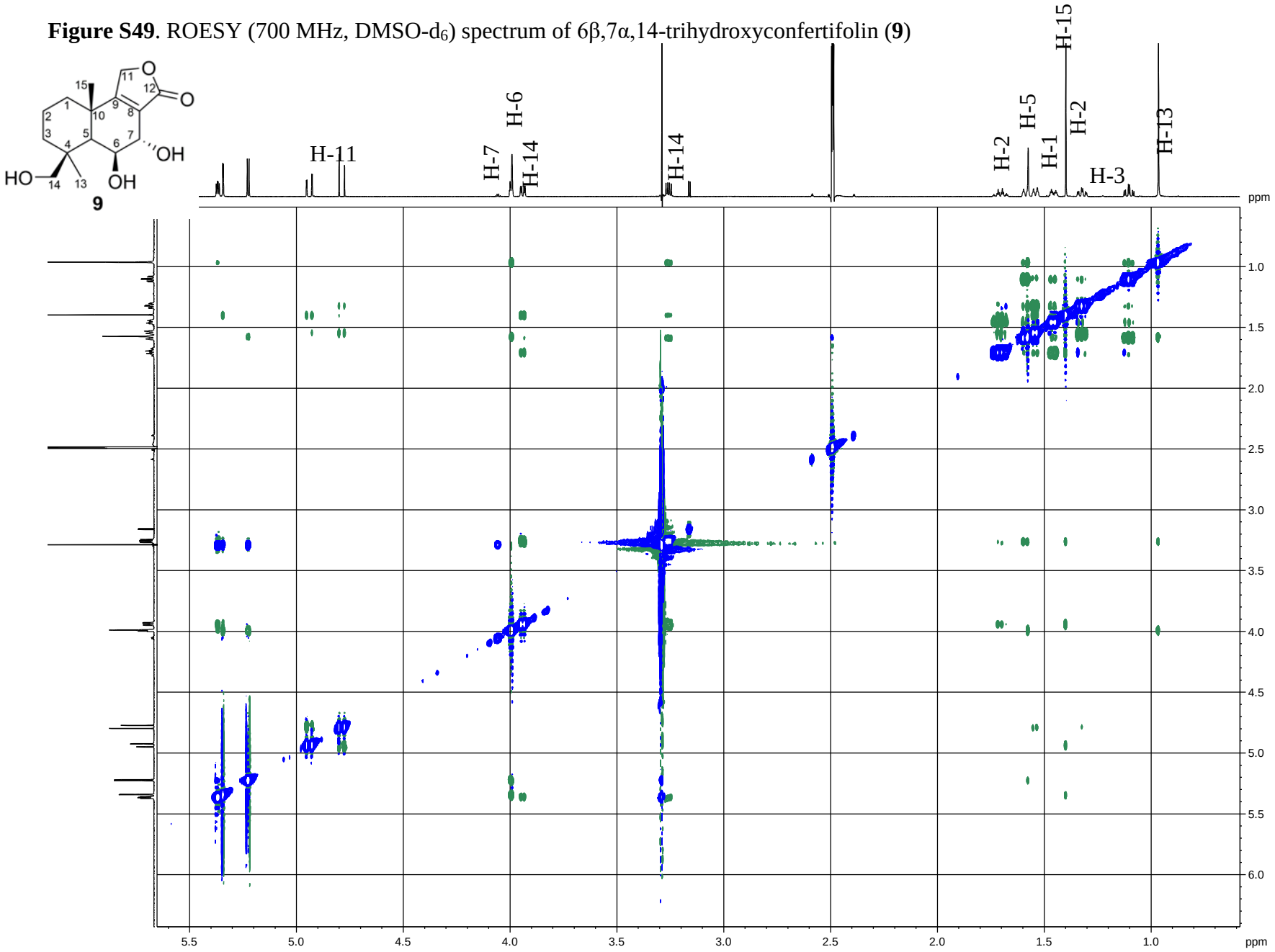
======== CHANNEL f2 ========
SFO2 125.7703643 MHz
NUC2 13C
P3 12.50 usec
PLW2 79.43299866 W

F1 - Acquisition parameters
TD 203
SFO1 125.7704 MHz
FIDRES 123.771568 Hz
SW 199.774 ppm
FnMODE QF

F2 - Processing parameters
SI 2048
SF 500.1300133 MHz
WDW QSINE
SSB 3
LB 0 Hz
GB 0
PC 3.00

F1 - Processing parameters
SI 1024
MC2 QF
SF 125.7578634 MHz
WDW GM
SSB 0
LB 0 Hz
GB 0

Figure S49. ROESY (700 MHz, DMSO-d_6) spectrum of 6β,7α,14-trihydroxyconfertifolin (**9**)



Current Data Parameters
NAME AF-33h-4new
EXPNO 23
PROCNO 1

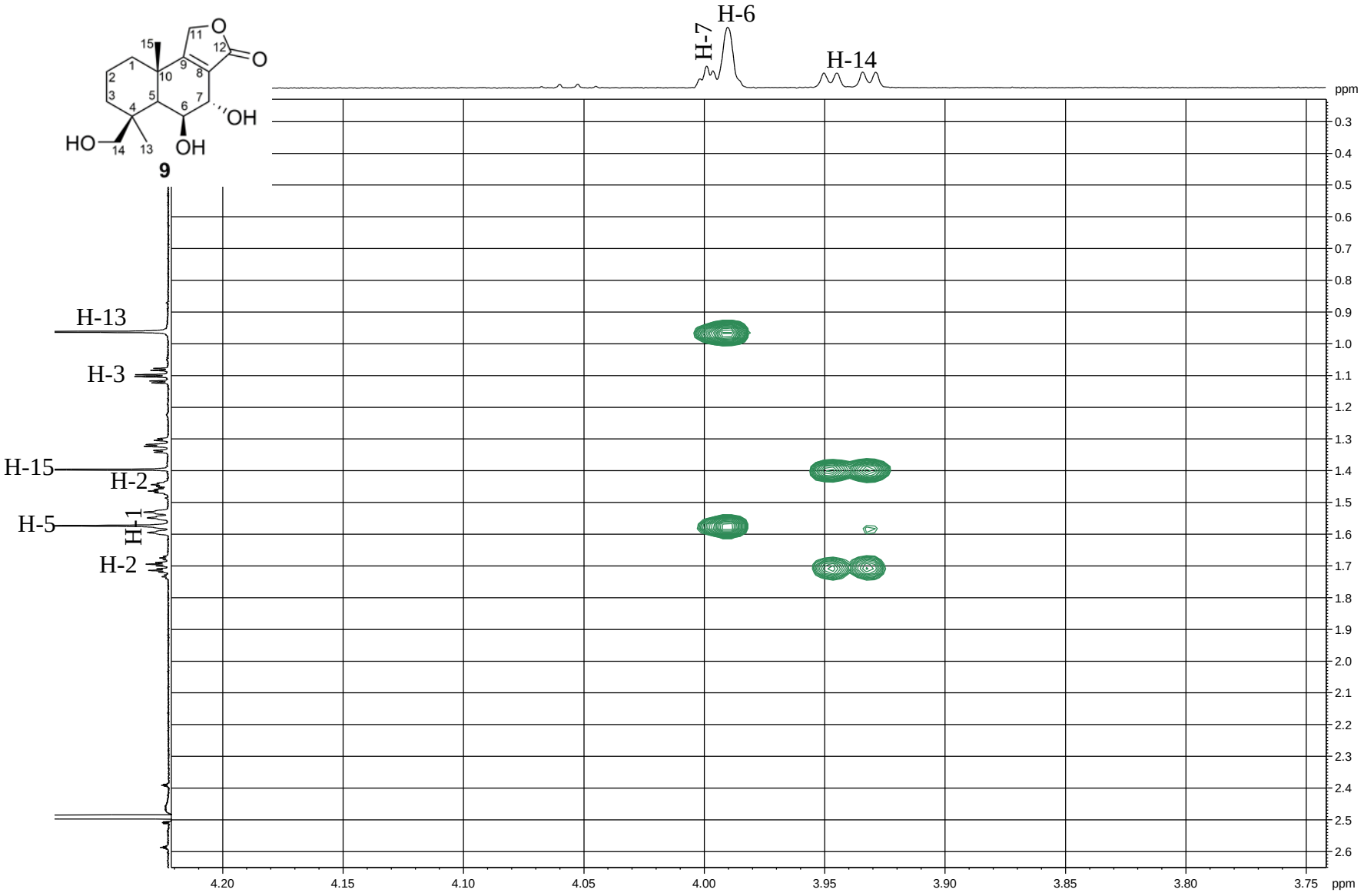
F2 - Acquisition Parameters
Date_ 20180529
Time 23.59
INSTRUM spect
PROBHD 5 mm PATXO 31P
PULPROG roesyph.2
TD 2048
SOLVENT DMSO
NS 48
DS 16
SWH 5030.181 Hz
FIDRES 2.456143 Hz
AQ 0.2036212 sec
RG 1.12
DW 99.400 usec
DE 6.50 usec
TE 302.7 K
D0 0.00008623 sec
D1 2.00000000 sec
D12 0.00002000 sec
IN0 0.00019880 sec
L4 613
P15 270000.00 usec

======== CHANNEL f1 ========
NUC1 1H
P1 14.40 usec
P25 220.00 usec
PL1 0 dB
PL27 17.66 dB
PL1W 23.41078186 W
PL27W 0.40125081 W
SFO1 700.0023824 MHz

F1 - Acquisition parameters
TD 256
SFO1 700.0024 MHz
FIDRES 19.649145 Hz
SW 7.186 ppm
FnMODE TPPI

F2 - Processing parameters
SI 2048
SF 700.0000067 MHz
WDW SINE
SSB 2
LB 0 Hz
GB 0
PC 4.00

F1 - Processing parameters
SI 512
MC2 TPPI
SF 700.0000026 MHz
WDW
SSB 2
LB 0 Hz
GB 0



Current Data Parameters
NAME AF-33h-4new
EXPNO 23
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180529
Time 23.59
INSTRUM spect
PROBHD 5 mm PATXO 31P
PULPROG roesyph.2
TD 2048
SOLVENT DMSO
NS 48
DS 16
SWH 5030.181 Hz
FIDRES 2.456143 Hz
AQ 0.2036212 sec
RG 1.12
DW 99.400 usec
DE 6.50 usec
TE 302.7 K
D0 0.00008623 sec
D1 2.00000000 sec
D12 0.00002000 sec
IN0 0.00019880 sec
L4 613
P15 270000.00 usec

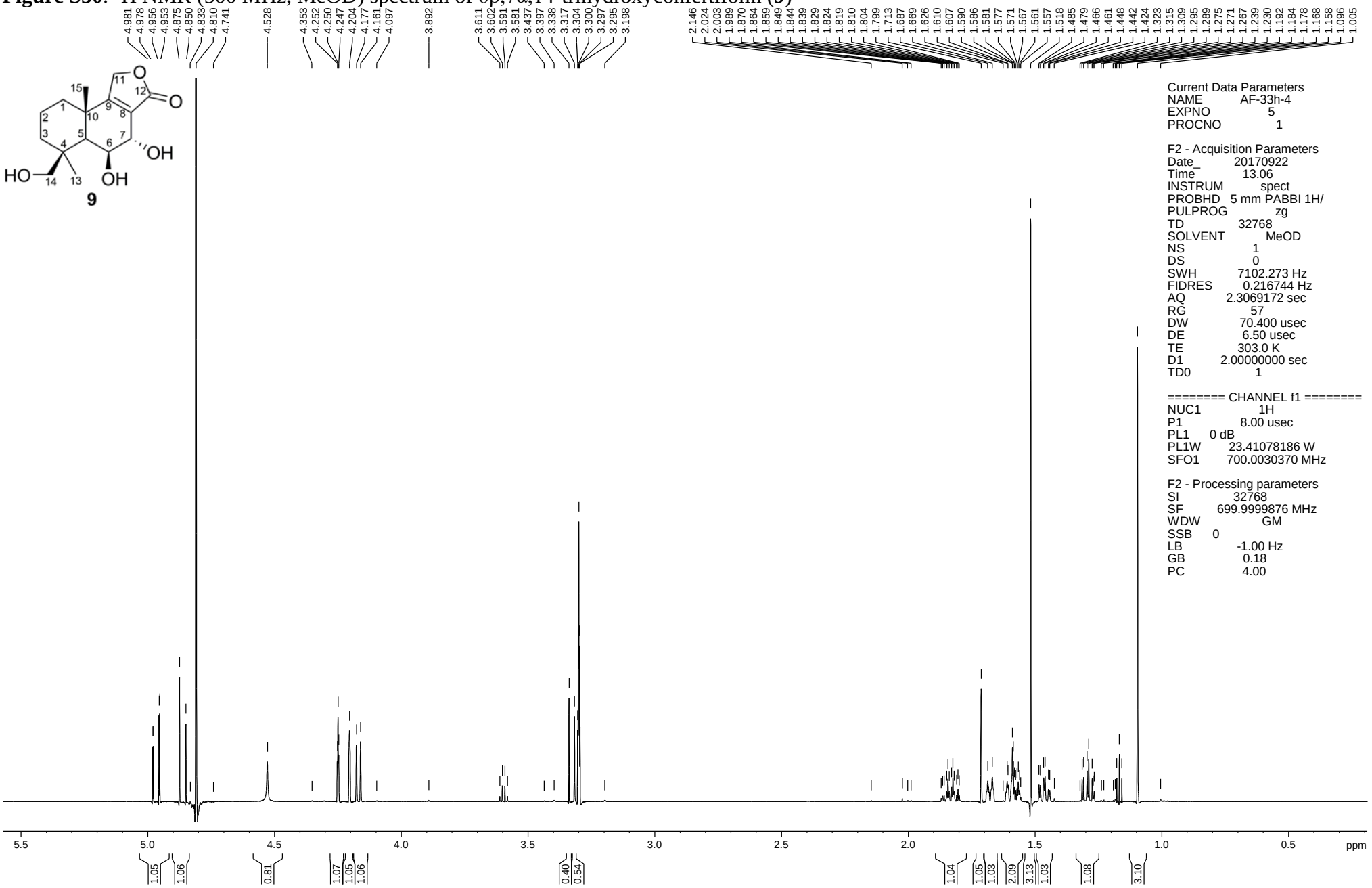
======== CHANNEL f1 ========
NUC1 1H
P1 14.40 usec
P25 220.00 usec
PL1 0 dB
PL27 17.66 dB
PL1W 23.41078186 W
PL27W 0.40125081 W
SFO1 700.0023824 MHz

F1 - Acquisition parameters
TD 256
SFO1 700.0024 MHz
FIDRES 19.649145 Hz
SW 7.186 ppm
FnMODE TPPI

F2 - Processing parameters
SI 2048
SF 700.0000067 MHz
WDW SINE
SSB 2
LB 0 Hz
GB 0
PC 4.00

F1 - Processing parameters
SI 512
MC2 TPPI
SF 700.0000026 MHz
WDW
SSB 2
LB 0 Hz
GB 0

Figure S50. ^{1}H NMR (500 MHz, MeOD) spectrum of 6β,7α,14-trihydroxyconfertifolin (**9**)



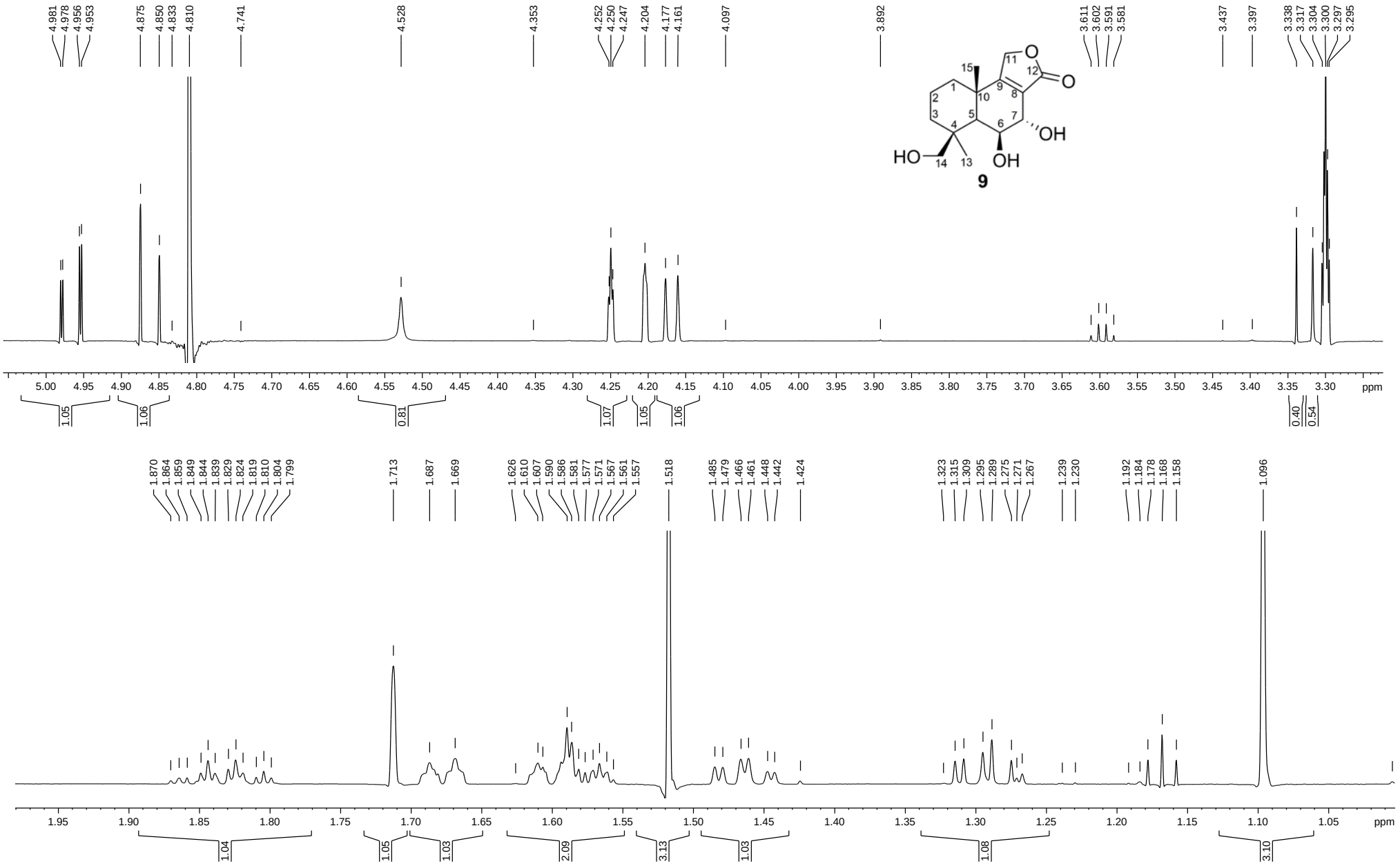

4.981
4.978
4.956
4.953
4.875
4.850
4.833
4.810
4.741
4.528
4.353
4.252
4.250
4.247
4.204
4.177
4.161
4.097
3.892
3.611
3.602
3.591
3.581
3.437
3.397
3.338
3.317
3.304
3.300
3.297
3.295
O
O
OH
HO
OH
15
11
12
1
9
8
2
10
3
5
7
4
6
14
13
9
5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 3.80 3.75 3.70 3.65 3.60 3.55 3.50 3.45 3.40 3.35 3.30 ppm
1.05
1.06
0.81
1.07
1.05
1.06
0.40
0.54
1.870
1.864
1.859
1.849
1.844
1.839
1.829
1.824
1.819
1.810
1.804
1.799
1.713
1.687
1.669
1.626
1.610
1.607
1.590
1.586
1.581
1.577
1.571
1.567
1.561
1.557
1.518
1.485
1.479
1.466
1.461
1.448
1.442
1.424
1.323
1.315
1.309
1.295
1.289
1.275
1.271
1.267
1.239
1.230
1.192
1.184
1.178
1.168
1.158
1.096
1.95 1.90 1.85 1.80 1.75 1.70 1.65 1.60 1.55 1.50 1.45 1.40 1.35 1.30 1.25 1.20 1.15 1.10 1.05 ppm
1.04
1.05
1.03
2.09
3.13
1.03
1.08
3.10

Figure S51. ^{13}C NMR (125 MHz, MeOD) spectrum of 6β,7α,14-trihydroxyconfertifolin (**9**)

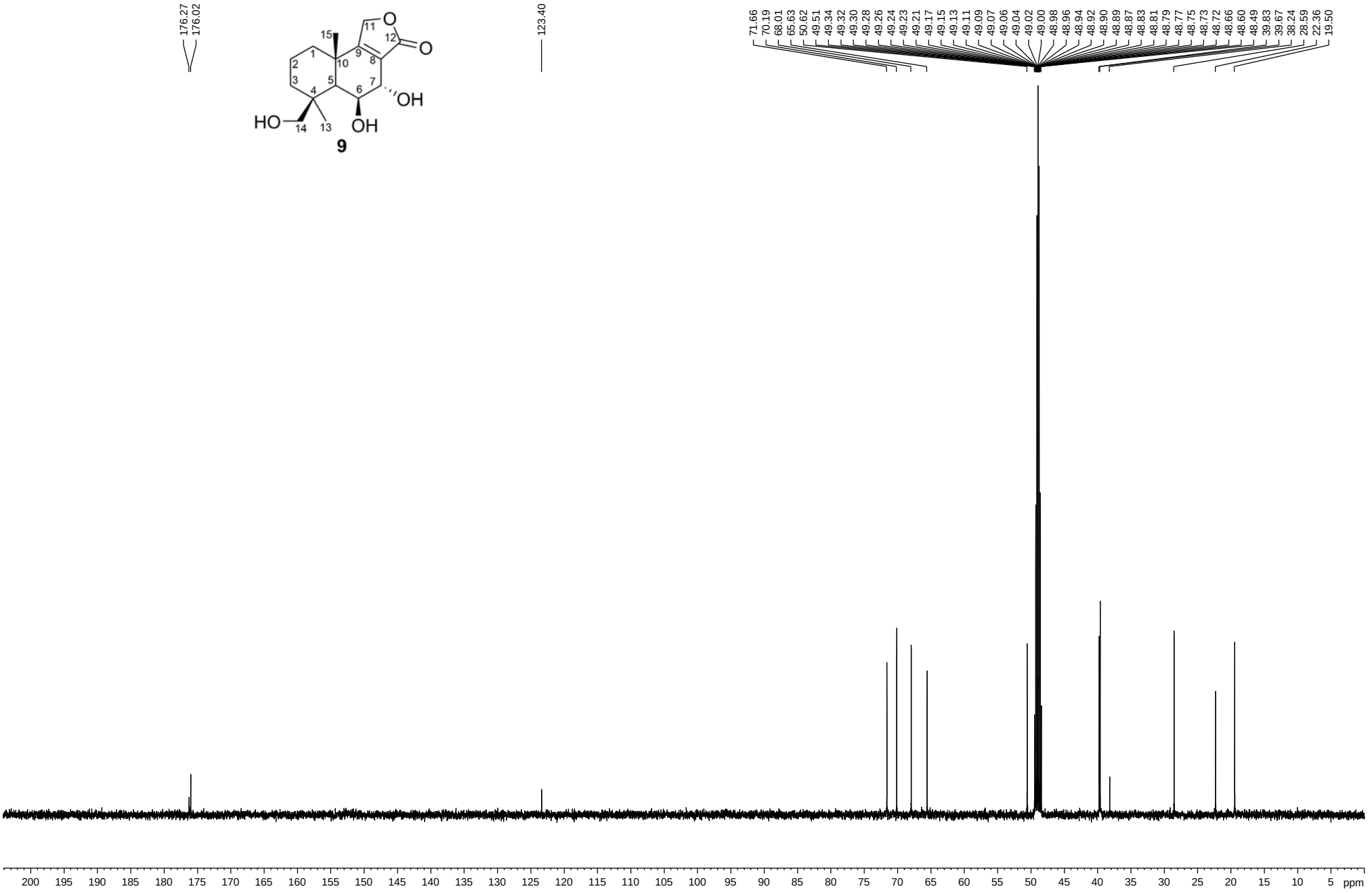


Figure S52. DEPT-135 (125 MHz, MeOD) spectrum of 6β,7α,14-trihydroxyconfertifolin (**9**)

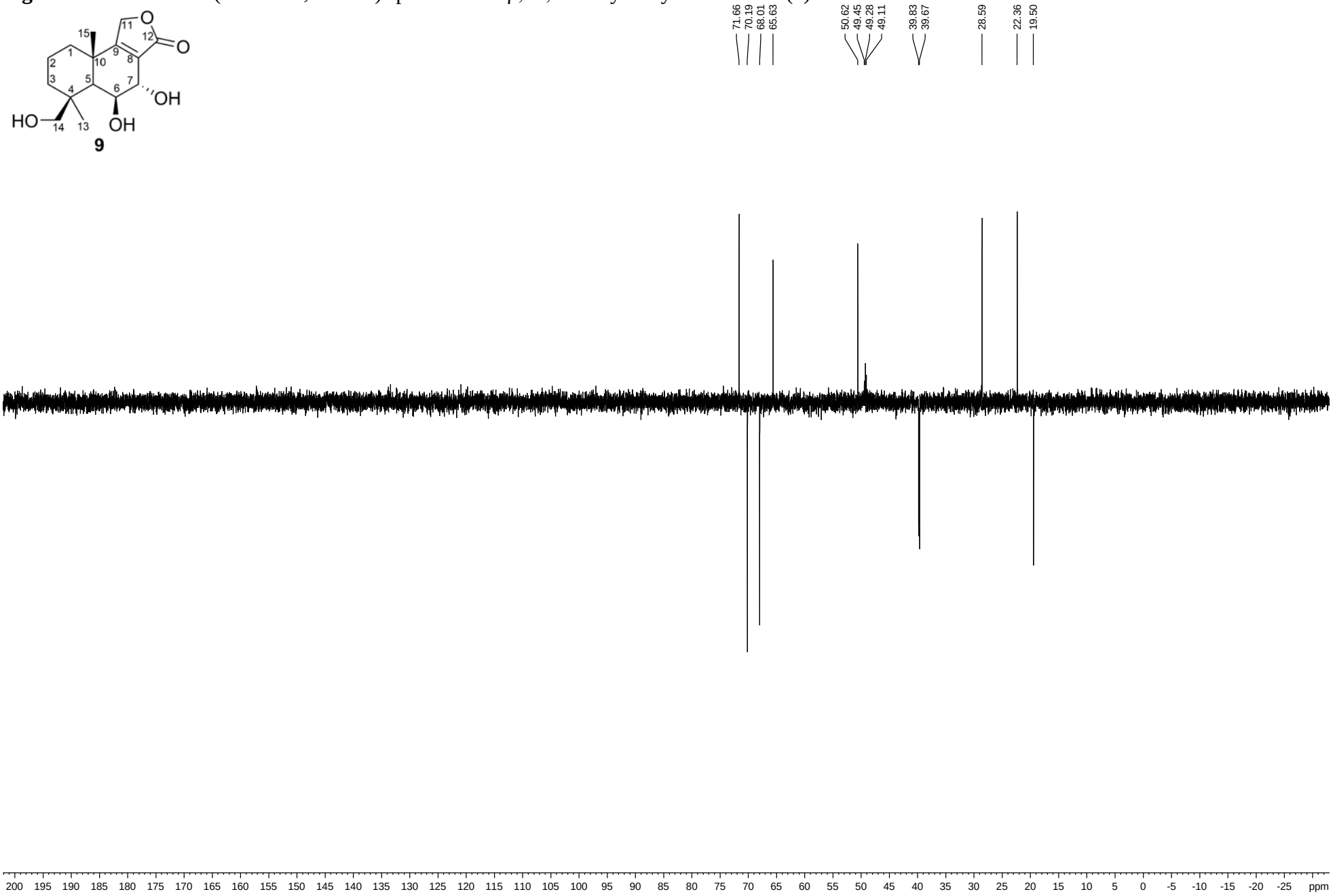
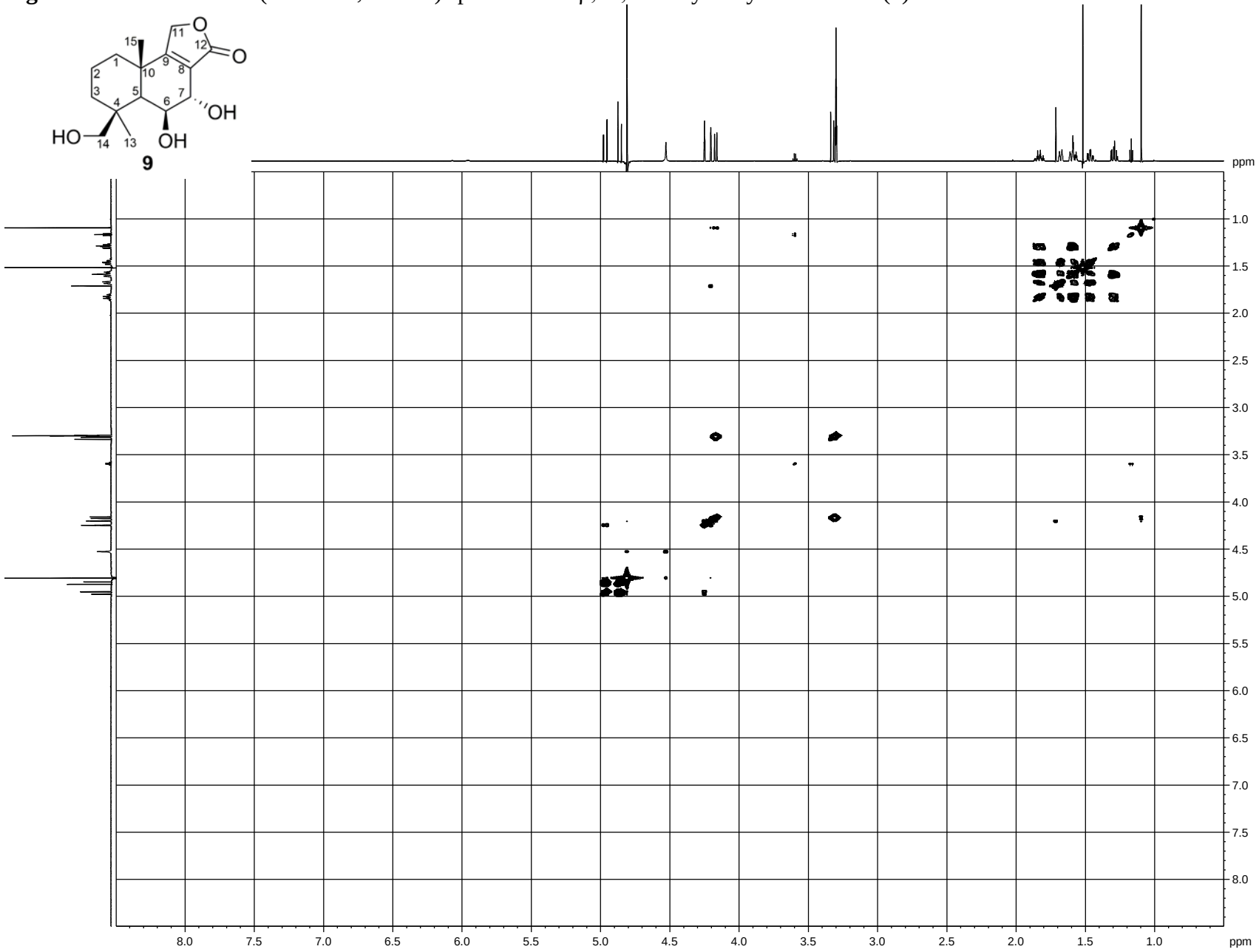


Figure S53. ^{1}H-^{1}H COSY (700 MHz, MeOD) spectrum of 6β,7α,14-trihydroxyconfertifolin (**9**)



Current Data Parameters
NAME AF-33h-4
EXPNO 21
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170922
Time 13.28
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG cosyqf45
TD 2048
SOLVENT MeOD
NS 8
DS 16
SWH 7102.273 Hz
FIDRES 3.467907 Hz
AQ 0.1442292 sec
RG 57
DW 70.400 usec
DE 6.50 usec
TE 303.0 K
D0 0.00000300 sec
D1 2.00000000 sec
IN0 0.00014080 sec

======== CHANNEL f1 ========
NUC1 1H
P1 8.00 usec
PL1 0 dB
PL1W 23.41078186 W
SFO1 700.0030370 MHz

F1 - Acquisition parameters
TD 512
SFO1 700.003 MHz
FIDRES 13.871627 Hz
SW 10.146 ppm
FnMODE QF

F2 - Processing parameters
SI 2048
SF 699.9999876 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 4.00

F1 - Processing parameters
SI 2048
MC2 QF
SF 699.9999876 MHz
WDW GM
SSB 0
LB 0 Hz
GB 0

Figure S54. ECD spectrum of 6β,7α,14-trihydroxyconfertifolin (**9**) in methanol

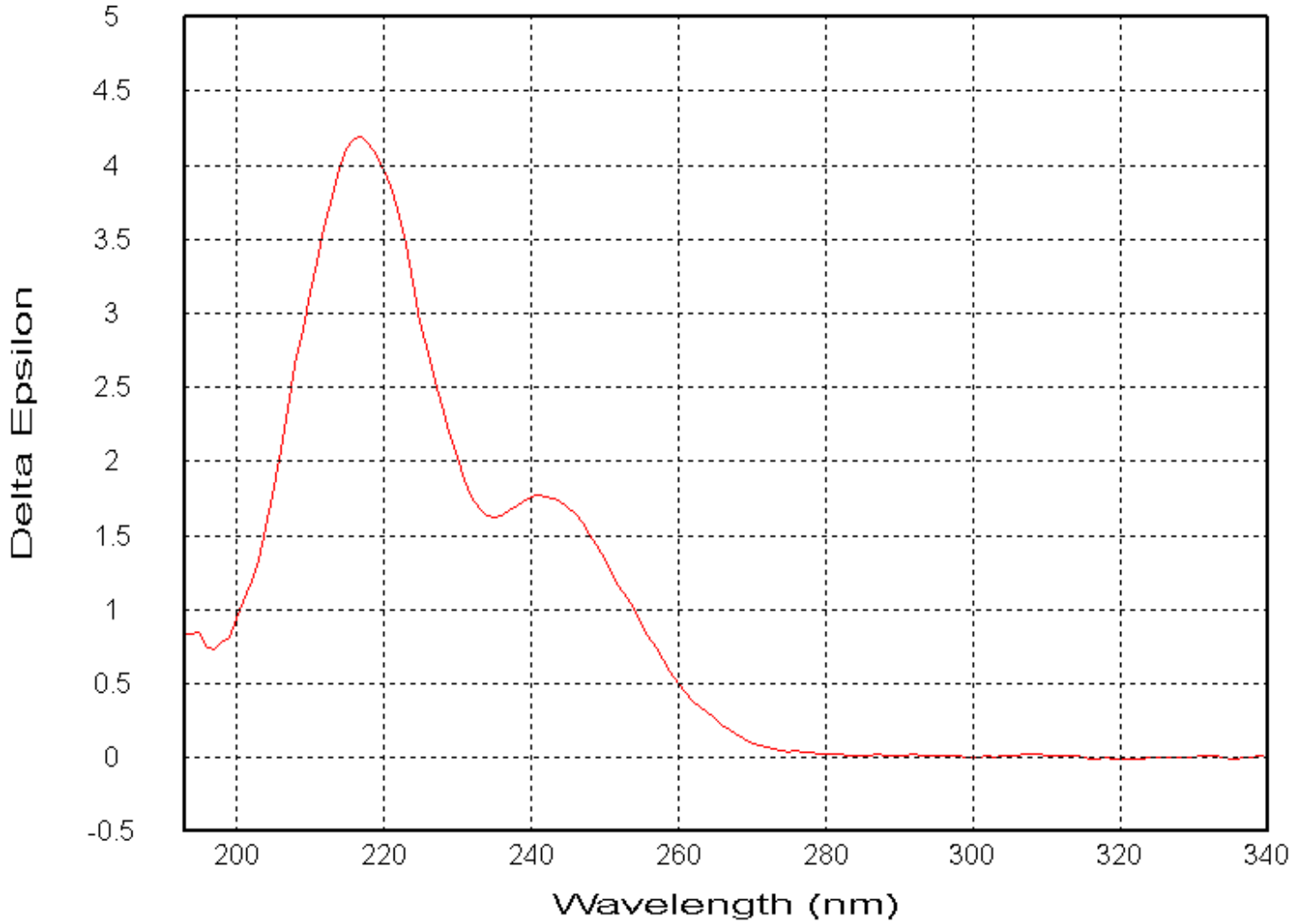
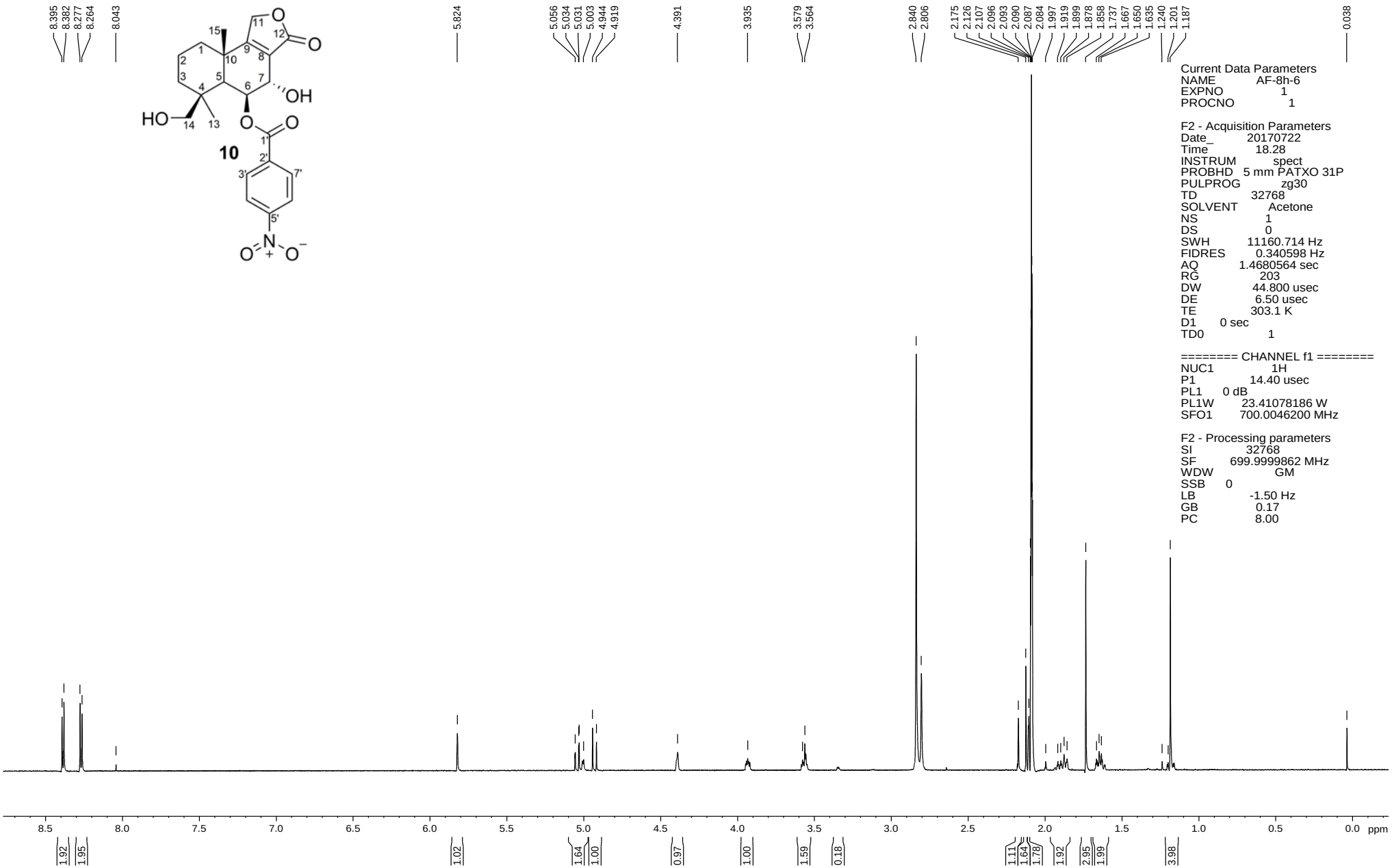


Figure S55. ^{1}H NMR (700 MHz, acetone-d_6) spectrum of 7α,14-dihydroxy-6β-p-nitrobenzoylconfertifolin (**10**)



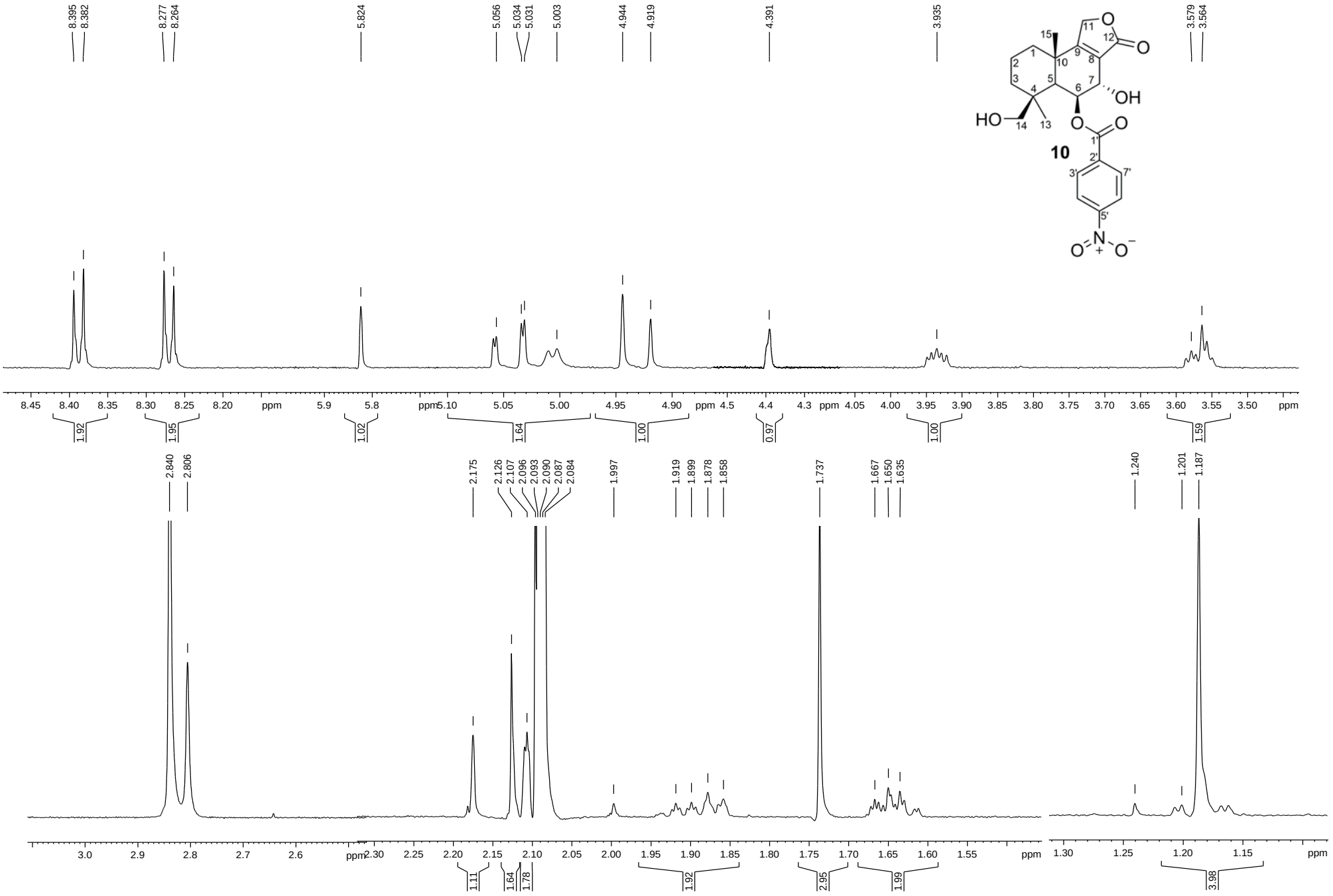

8.395
8.382
8.277
8.264
5.824
5.056
5.034
5.031
5.003
4.944
4.919
4.391
3.935
3.579
3.564
10
2.840
2.806
2.175
2.126
2.107
2.096
2.093
2.090
2.087
2.084
1.997
1.919
1.899
1.878
1.858
1.737
1.667
1.650
1.635
1.240
1.201
1.187
ppm

Figure S56. ^{13}C NMR (175 MHz, acetone-d_6) spectrum of 7α,14-dihydroxy-6β-p-nitrobenzoylconfertifolin (**10**)

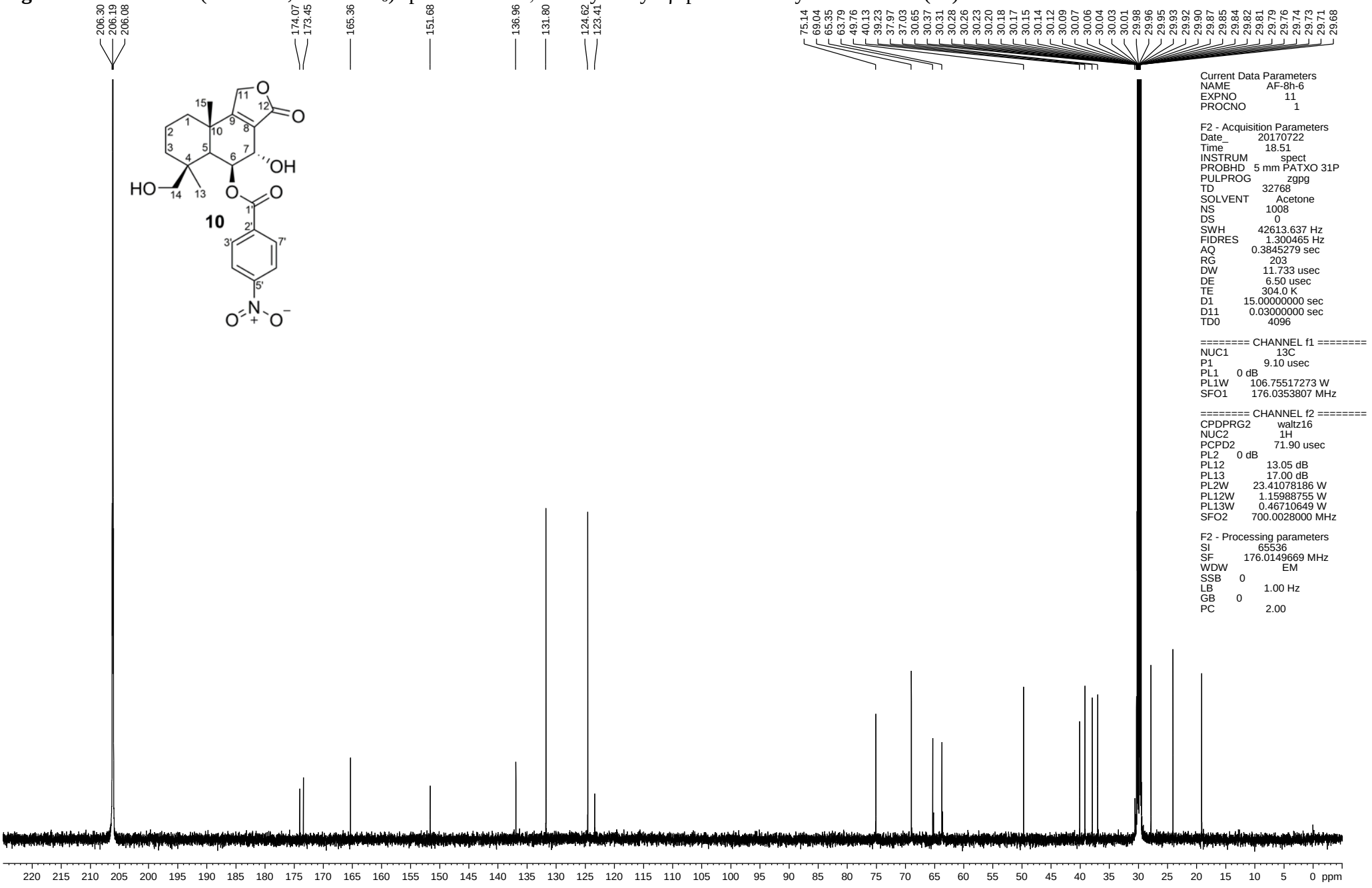


Figure S57. ECD spectrum of 7α,14-dihydroxy-6β-p-nitrobenzoylconfertifolin (**10**) in methanol