SUPPLEMENTARY MATERIAL

Virescenosides from the holothurian-associated fungus *Acremonium striatisporum* KMM 4401

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Virescenosides from the holothurian-associated fungus *Acremonium striatisporum* KMM 4401

Ten new diterpene glycosides virescenosides Z_9-Z_{18} (**1**–**10**) together with three known analogues (**11**–**13**) and aglycon of virescenoside A (**14**) were isolated from the marine-derived fungus *Acremonium striatisporum* KMM 4401. These compounds were obtained by cultivating fungus on wort agar medium with the addition of potassium bromide. Structures of the isolated metabolites were established based on spectroscopic methods. The effects of some isolated glycosides and aglycons **15**–**18** on urease activity and regulation of Reactive Oxygen Species (ROS) and Nitric Oxide (NO) production in macrophages stimulated with lipopolysaccharide (LPC) were evaluated.

Keywords: *Acremonium striatisporum*, secondary metabolites, diterpene glycosides, urease activity

Content

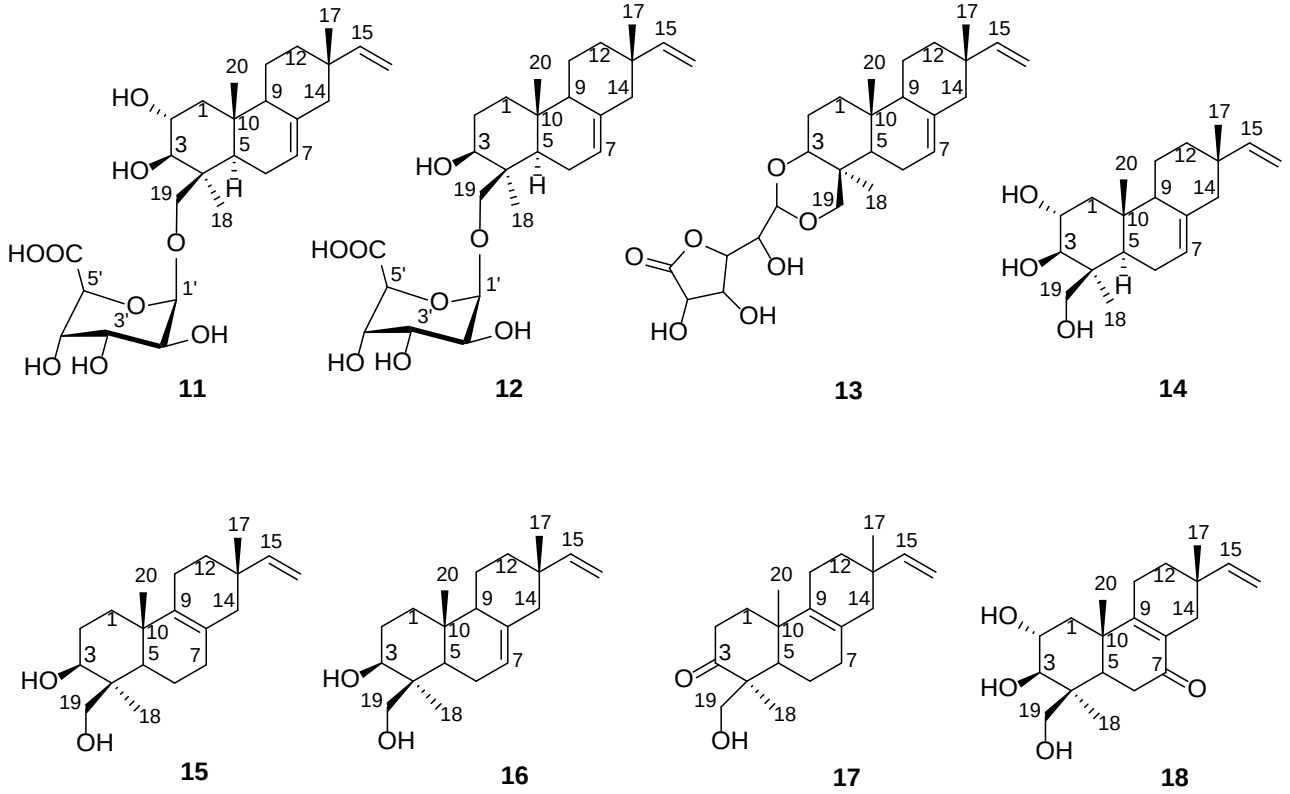


Figure S1. Chemical structures of **11**–**18**

Experimental Section

Spectral Data

Aglycon of virescenoside B ($\Delta^{8,9}$) (**15**): white powder; ^{1}H NMR (500MHz, $CDCl_3$) δ: 5.72 (1H, dd, *J* = 10.8, 17.5 Hz, H-15), 4.89 (1H, dd, *J* = 1.6, 10.8 Hz, H-16b), 4.84 (1H, dd, *J* = 1.6, 17.5 Hz, H-16a), 4.24 (1H, d, *J* = 11.1 Hz, H-19b), 3.46 (1H, dd, *J* = 4.5, 11.4 Hz, H-3), 3.34 (1H, d, *J* = 11.1 Hz, H-19a), 1.93 (2H, m, H_2-7), 1.87 (2H, m, H_2-11), 1.83 (1H, m, H-2a), 1.80 (1H, d, *J* = 16.1 Hz, H-14a), 1.77 (1H, m, H-1a), 1.75 (1H, m, H-6a), 1.74 (1H, m, H-2b), 1.71 (1H, d, *J* = 16.1 Hz, H-14b), 1.50 (1H, d, *J* = 11.1 Hz, H-12a), 1.40 (1H, dd, *J* = 4.0, 12.5 Hz, H-6b), 1.30 (1H, dd, *J* = 11.1 Hz, H-12b), 1.25 (3H, s, Me-18), 1.21 (1H, dd, *J* = 1.7, 12.7 Hz, H-5), 1.13 (1H, m, H-1b), 0.96 (3H, s, Me-17), 0.92 (3H, s, Me-20). ^{13}C NMR (125MHz, $CDCl_3$) δ: 146.1 (C-15), 136.1 (C-9), 124.7 (C-8), 110.8 (C-16), 80.8 (C-3), 64.3 (C-19), 51.8 (C-5), 42.9 (C-4), 41.8 (C-14), 37.1 (C-10), 35.1 (C-13), 34.9 (C-12), 34.5 (C-1), 32.8 (C-7), 28.2 (C-2), 28.0 (C-17), 22.3 (C-18), 21.3 (C-11), 20.1 (C-20), 18.7 (C-6); EI MS $[M]^+$ 304.

Genuine aglycon of virescenoside B ($\Delta^{7,8}$) (**16**): white powder; ^{1}H NMR (700MHz, $CDCl_3$) δ: 5.79 (1H, dd, *J* = 10.8, 17.5 Hz, H-15), 5.35 (1H, brs, H-7), 4.92 (1H, dd, *J* = 1.6, 10.8 Hz, H-16b), 4.87 (1H, dd, *J* = 1.6, 17.5 Hz, H-16a), 4.33 (1H, d, *J* = 11.1 Hz, H-19b), 3.49 (1H, dd, *J* = 4.5, 12.0 Hz, H-3), 3.48 (1H, d, *J* = 11.1 Hz, H-19a), 2.00 (1H, m, H-6a), 1.95 (1H, brd, H-14a), 1.90 (1H, dd, *J* = 2.7, 13.7 Hz, H-14b), 1.89 (1H, td, *J* = 3.6, 13.5 Hz, H-1a), 1.86 (1H, m, H-6b), 1.83 (1H, dd, *J* = 3.4, 13.6 Hz, H-2a), 1.72 (1H, qd, *J* = 3.8, 13.2 Hz, H-2b), 1.63 (1H, brs, H-9), 1.55 (1H, m, H-11a), 1.48 (1H, td, *J* = 3.0, 9.3 Hz, H-12a), 1.34 (1H, m, H-11b), 1.33 (1H, d, *J* = 9.6 Hz, H-12b), 1.27 (1H, dd, *J* = 4.1, 12.4 Hz, H-5), 1.24 (3H, s, Me-18), 1.18 (1H, dt, *J* = 3.8, 13.4 Hz, H-1b), 0.85 (3H, s, Me-17), 0.81 (3H, s, Me-20). ^{13}C NMR (175MHz, $CDCl_3$) δ: 150.2 (C-15), 135.5 (C-8), 121.2 (C-7), 109.3 (C-16), 81.3 (C-3), 64.4 (C-19), 51.9 (C-9), 51.3 (C-5), 45.9 (C-14), 42.3 (C-4), 37.8 (C-1), 36.8 (C-13), 36.1 (C-12), 35.0 (C-10), 28.0 (C-2), 23.0 (C-6), 22.5 (C-18), 21.5 (C-17), 20.4 (C-11), 16.0 (C-20); EI MS $[M]^+$ 304.

Aglycon of virescenoside C ($\Delta^{8,9}$) (**17**): white powder; ^{1}H NMR (500MHz, $CDCl_3$) δ: 5.72 (1H, dd, *J* = 10.7, 17.5 Hz, H-15), 4.91 (1H, dd, *J* = 1.6, 10.7 Hz, H-16b), 4.83 (1H, dd, *J* = 1.6, 17.5 Hz, H-16a), 4.02 (1H, d, *J* = 11.3 Hz, H-19b), 3.44 (1H, d, *J* = 11.3 Hz, H-19a), 2.58 (1H, m, H-2a), 2.45 (1H, m, H-2b), 1.98 (1H, m, H-1a), 1.96 (2H, m, H_2-7), 1.91 (1H, m, H-11), 1.90 (1H, dd, *J* = 2.3, 13.0 Hz, H-5), 1.89 (1H, m, H-11), 1.87 (1H, dd, *J* = 16.1 Hz, H-14a), 1.75 (1H, brd, *J* = 16.1 Hz, H-14b), 1.66 (1H, m, H-6a), 1.64 (1H, m, H-1b),1.52 (1H, m, H-12a), 1.45 (1H, dd, *J* = 4.0, 12.5 Hz, H-6b), 1.34 (1H, m, H-12b), 1.29 (3H, s, Me-18), 1.01 (3H, s, Me-20), 0.98 (3H, s, Me-17). ^{13}C NMR (125MHz, $CDCl_3$) δ: 221.1 (C-3), 145.8 (C-15), 134.3 (C-9), 125.8 (C-8), 110.9 (C-16), 65.8 (C-19), 52.1 (C-5), 50.7 (C-4), 41.7 (C-14), 36.9 (C-10), 35.1 (C-13), 34.7 (C-12), 34.6 (C-2), 34.4 (C-1),32.3 (C-7), 28.2 (C-17), 22.1 (C-18), 21.3 (C-11), 19.8 (C-20), 19.3 (C-6); EI MS $[M]^+$ 302.

Aglycon of virescenoside M (**18**): white powder; ^{1}H NMR (500MHz, $CDCl_3$) δ: 5.66 (1H, dd, *J* = 10.7, 17.5 Hz, H-15), 4.93 (1H, dd, *J* = 1.2, 10.7 Hz, H-16b), 4.83 (1H, dd, *J* = 1.2, 17.5 Hz, H-16a), 4.18 (1H, d, *J* = 11.2 Hz, H-19b), 3.99 (1H, ddd, *J* = 4.3, 9.6, 11.6 Hz, H-2), 3.48 (1H, dd, *J* = 1.2, 11.2 Hz, H-19a), 3.20 (1H, dd, *J* = 1.2, 9.6 Hz, H-3), 2.56 (1H, dd, *J* = 3.4, 16.9 Hz, H-6a), 2.35 (1H, d, *J* = 17.5 Hz, H-14a), 2.33 (1H, dd, *J* = 14.4, 16.9 Hz, H-6b), 2.21 (1H, dd, *J* = 4.1, 12.6 Hz, H-1a), 2.20 (1H, m, H_2-11), 2.01 (1H, dt, *J* = 2.4, 17.7 Hz, H-14b), 1.83 (1H, dd, *J* = 3.5, 14.6 Hz, H-5), 1.61 (1H, m, H-12a), 1.33 (1H, m, H-12b), 1.29 (1H, t, *J* = 11.6 Hz, H-1b), 1.28 (3H, s, Me-18), 1.14 (3H, s, Me-20), 1.01 (3H, s, Me-17). ^{13}C NMR (125MHz, $CDCl_3$) δ: 198.4 (C-7), 163.8 (C-9), 144.9 (C-15), 129.0 (C-8), 111.8 (C-16), 84.4 (C-3), 68.8 (C-2), 65.0 (C-19), 49.6 (C-5), 42.7 (C-4), 41.7 (C-1), 40.3 (C-10), 34.7 (C-6), 34.4 (C-13), 33.5 (C-12), 33.3 (C-14), 28.1 (C-17), 23.3 (C-11), 22.4 (C-18), 19.6 (C-20); EI MS $[M]^+$ 334.

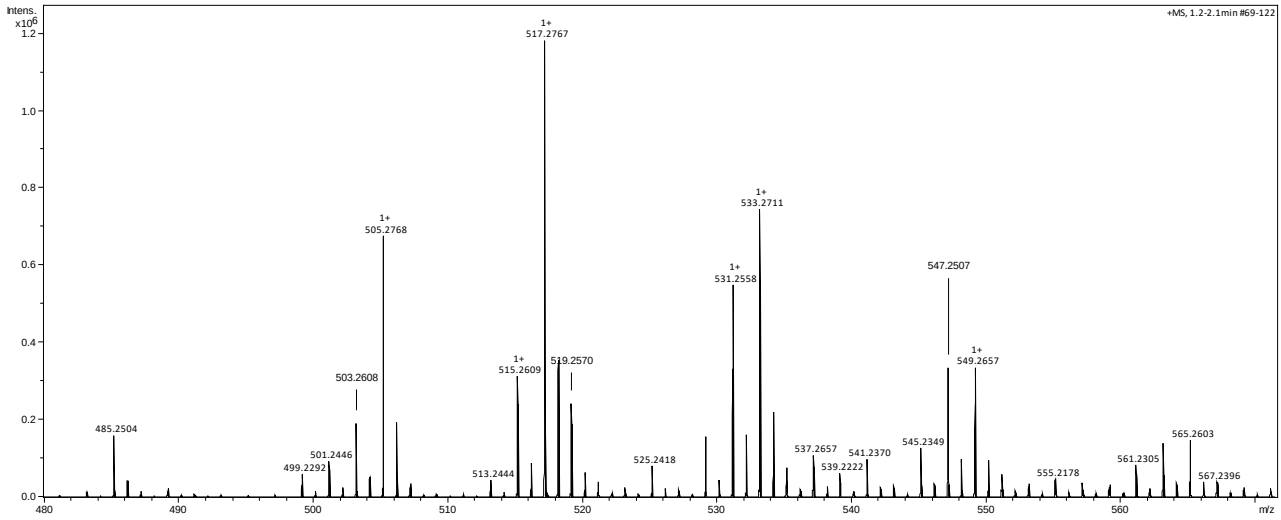
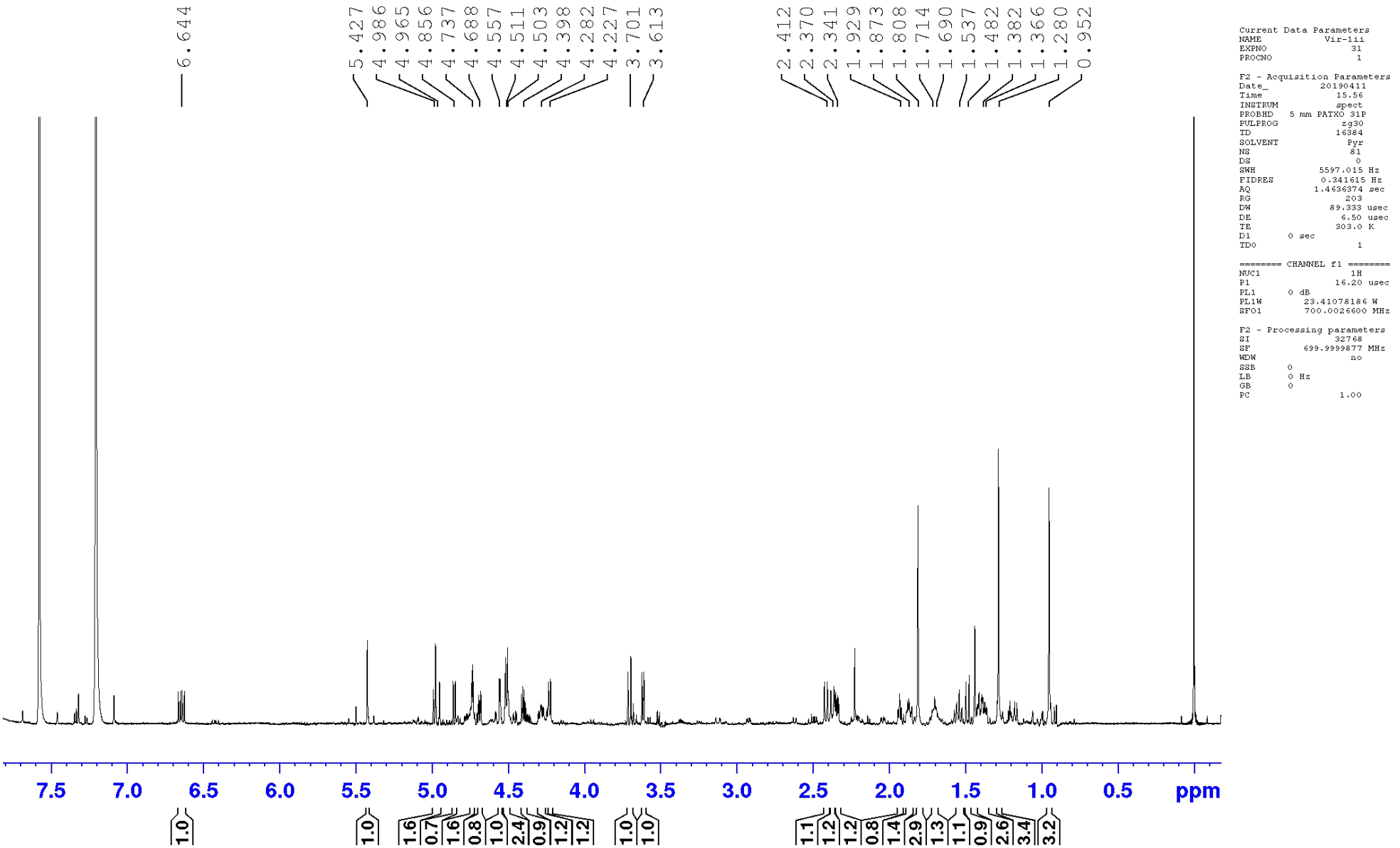


Figure S2. HPLC-MS data for subfraction II

Virescenoside Z_{12} (**4**) $[M+Na]^+$ 517.2767
Virescenoside Z_{13} (**5**) $[M+Na]^+$ 533.2711
Virescenoside Z_{14} (**6**) $[M+Na]^+$ 547.2507
Virescenoside Z_{15} (**7**) $[M+Na]^+$ 547.2507
Virescenoside Z_{16} (**8**) $[M+Na]^+$ 515.2609
Virescenoside Z_{18} (**10**) $[M+Na]^+$ 517.2767

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PROCNO                      1

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PULPROG                zg30
TD                    16384
SOLVENT                 Pyr
NS                       81
DS                        0
SWH                5597.015 Hz
FIDRES              0.341615 Hz
AQ                 1.4636374 sec
RG                       203
DW                  89.333 usec
DE                    6.50 usec
TE                   303.0 K
D1          0 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                    16.20 usec
PL1          0 dB
PL1W          23.41078186 W
SFO1          700.0026600 MHz

F2 - Processing parameters
SI                       32768
SF              699.9999877 MHz
WDW                         no
SSB          0
LB           0 Hz
GB           0
PC                      1.00
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Figure S3. ^{1}H NMR spectrum (700 MHz, Pyr-d_5) of **1**

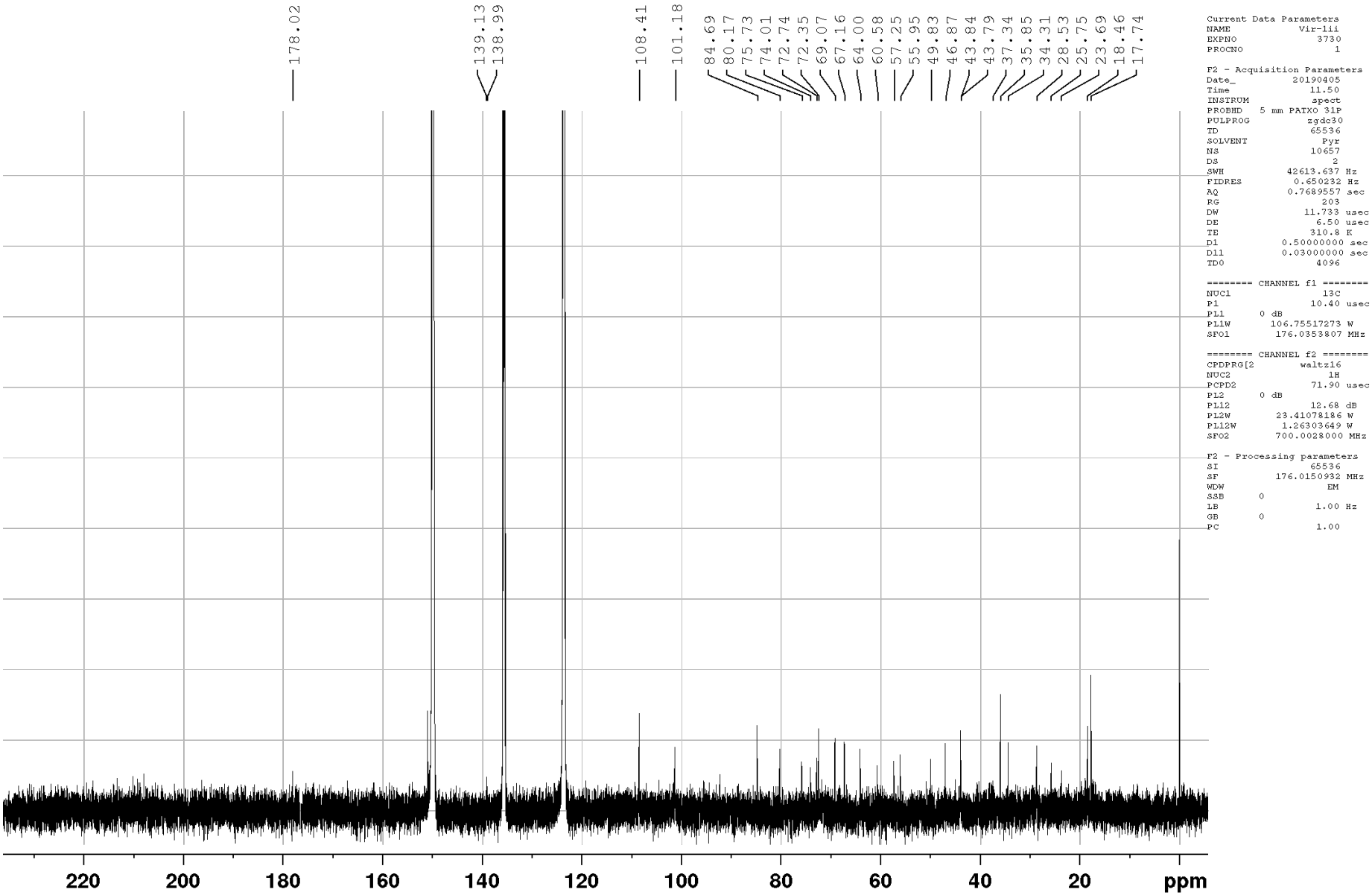


Figure S4. ^{13}C NMR spectrum (176 MHz, Pyr-d_5) of **1**

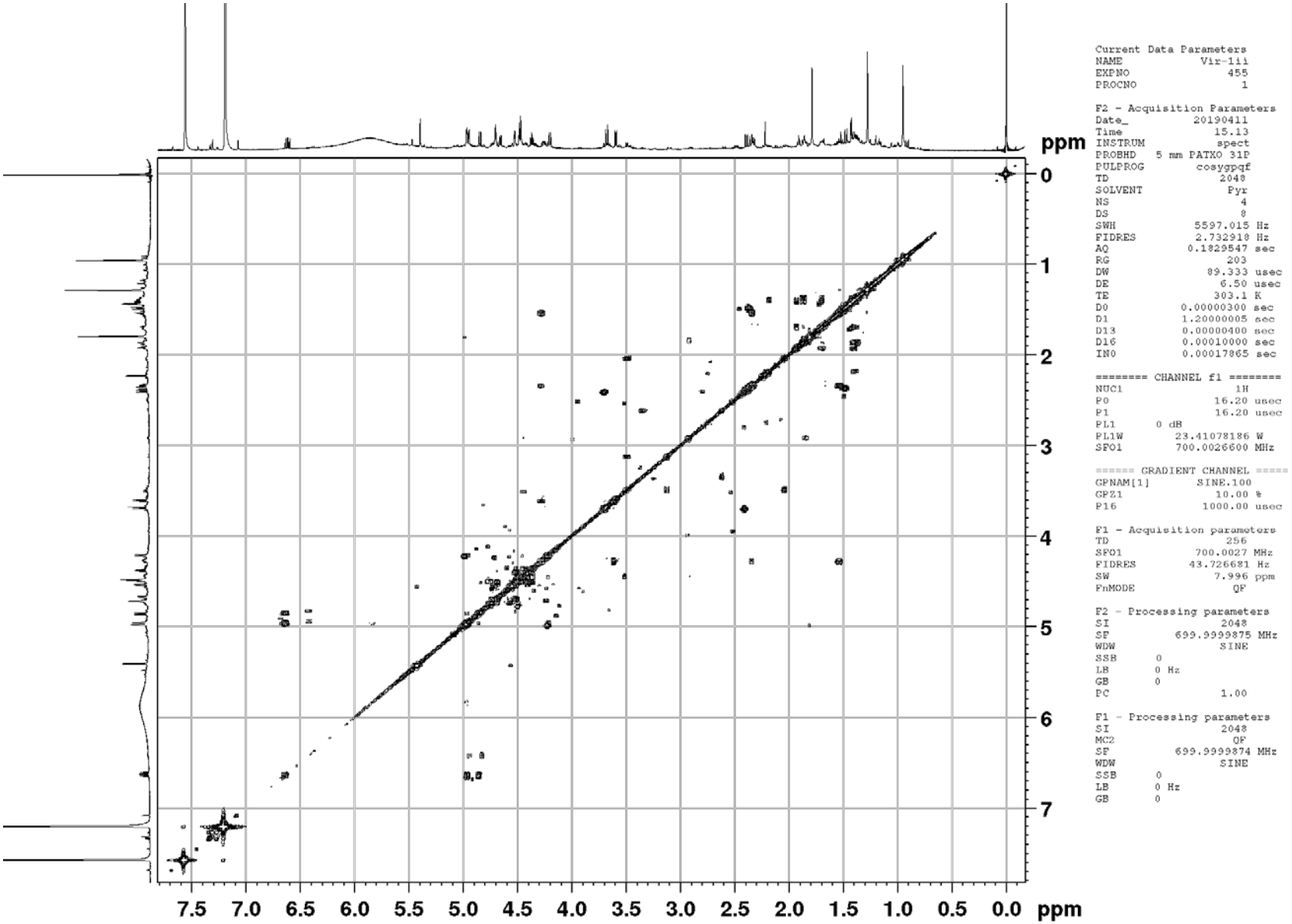
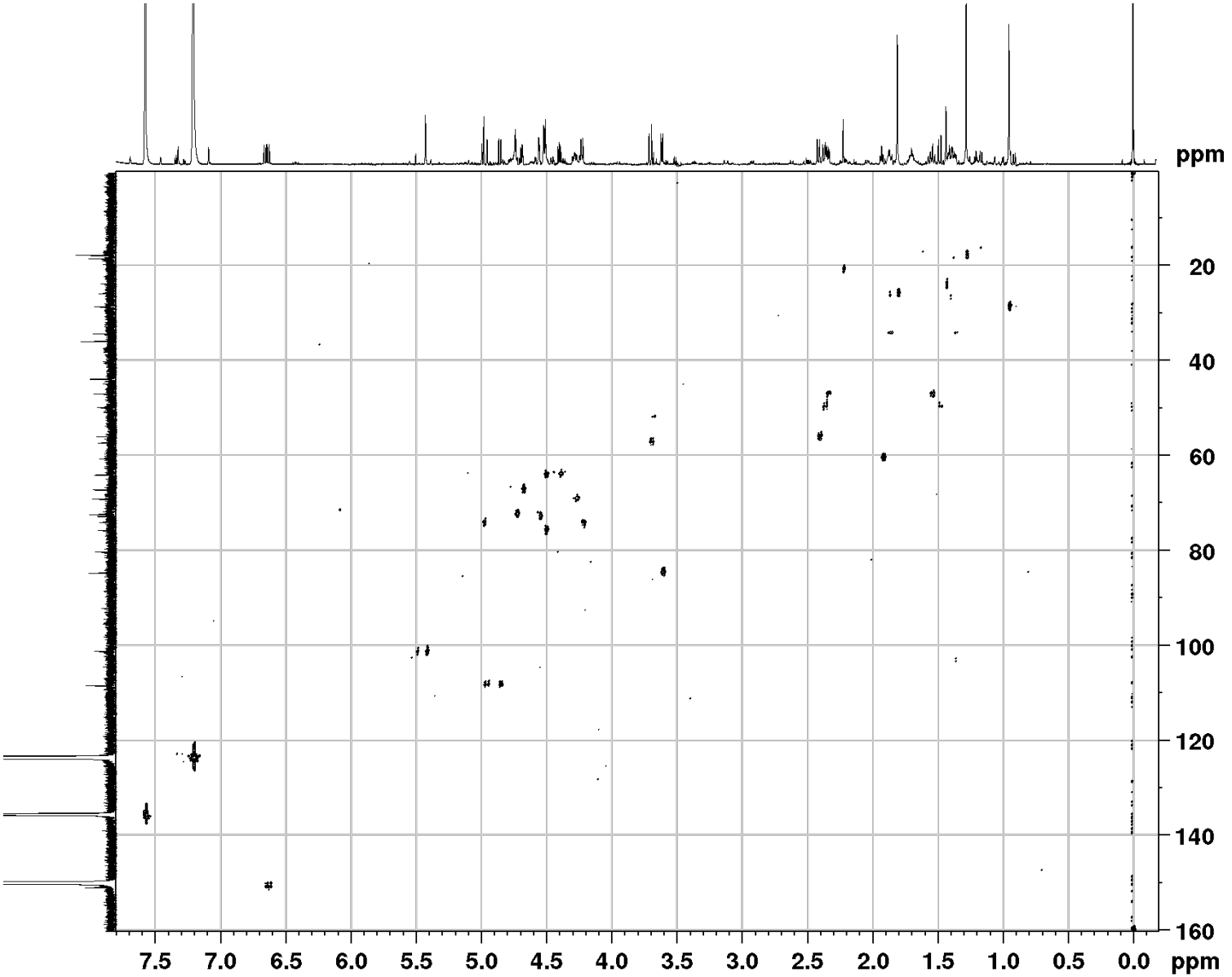


Figure S5. COSY-45 spectrum (700 MHz, Pyr-d_5) of **1**

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EXPNO                    7130
PROCNO                      2

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PROBHD    5 mm PATXO 31P
PULPROG   hsqcetgpsisp2.2
TD                       2048
SOLVENT                   Pyr
NS                          4
DS                         64
SWH                 5597.015 Hz
FIDRES              2.732918 Hz
AQ                  0.1829547 sec
RG                        203
DW                     89.333 usec
DE                       6.50 usec
TE                      303.5 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                      16.20 usec
P2                      32.40 usec
PL1        0 dB
PL1W            23.41078186 W
SFO1           700.0026600 MHz

-------- CHANNEL f2 --------
CPDPRG[2 bi_p5m4sp_4sp.2
NUC2                      13C
P3                      10.00 usec
P14                    500.00 usec
P24                   2000.00 usec
P63                   1500.00 usec
PL0                    120.00 dB
PL2        0 dB
PL12                    15.56 dB
PL0W       0 W
PL2W           106.75517273 W
PL12W            2.96748734 W
SFO2           176.0292202 MHz
SP3                      8.16 dB
SP7                      8.16 dB
SP14                     9.64 dB
SP31                    15.66 dB
SPNAM[3] Crp60,0.5,20.1
SPNAM[7]    crp60comp.4
SPNAM[14 Crp32,1.5,20.2
SPNAM[31 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 -----
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPNAM[3]          SINE.100
GPNAM[4]          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           176.0292 MHz
FIDRES         220.036530 Hz
SW                 160.000 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                       2048
SF             699.9999970 MHz
WDW                     QSINE
SSB                         2
LB         0 Hz
GB         0
PC                      1.00

F1 - Processing parameters
SI                       4096
MC2          echo-antiecho
SF             176.0150955 MHz
WDW                     QSINE
SSB                         8
LB         0 Hz
GB         0
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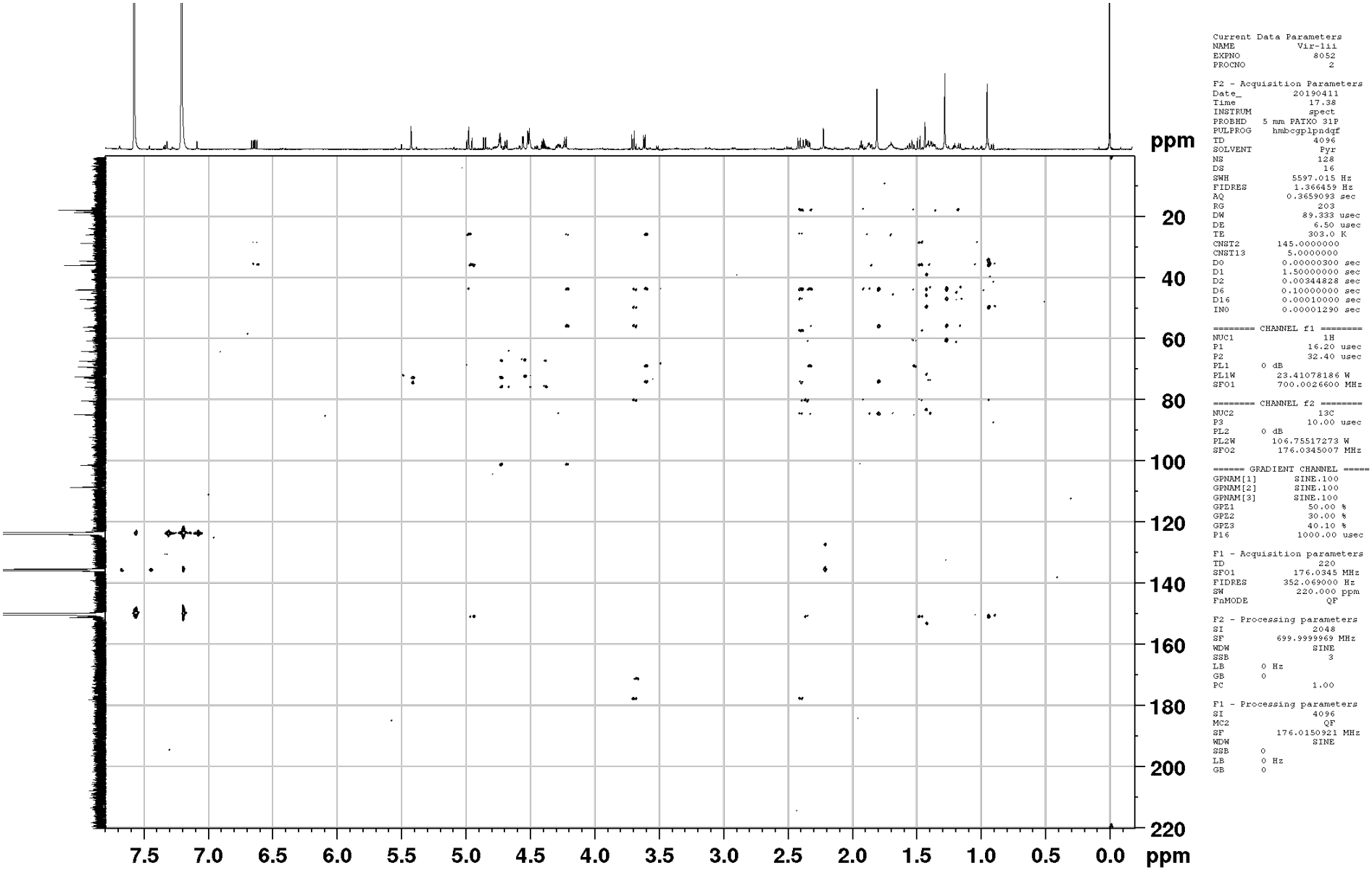
Figure S6. HSQC spectrum (700 MHz, Pyr-d_5) of **1**

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PROCNO                      2

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PULPROG     hmbcgplpndqf
TD                       4096
SOLVENT                   Pyr
NS                        128
DS                         16
SWH                  5597.015 Hz
FIDRES               1.366459 Hz
AQ                   0.3659093 sec
RG                         203
DW                    89.333 usec
DE                     6.50 usec
TE                     303.0 K
CNST2               145.0000000
CNST13                5.0000000
D0                   0.00000300 sec
D1                   1.50000000 sec
D2                   0.00344828 sec
D6                   0.10000000 sec
D16                  0.00010000 sec
IN0                  0.00001290 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      16.20 usec
P2                      32.40 usec
PL1          0 dB
PL1W            23.41078186 W
SFO1           700.0026600 MHz

======== CHANNEL f2 ========
NUC2                      13C
P3                      10.00 usec
PL2          0 dB
PL2W           106.75517273 W
SFO2           176.0345007 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]             SINE.100
GPNAM[2]             SINE.100
GPNAM[3]             SINE.100
GPZ1                    50.00 %
GPZ2                    30.00 %
GPZ3                    40.10 %
P16                   1000.00 usec

F1 - Acquisition parameters
TD                         220
SFO1                176.0345 MHz
FIDRES              352.069000 Hz
SW                   220.000 ppm
FnMODE                      QF

F2 - Processing parameters
SI                        2048
SF                699.9999969 MHz
WDW                       SINE
SSB                          3
LB           0 Hz
GB           0
PC                        1.00

F1 - Processing parameters
SI                        4096
MC2                         QF
SF                176.0150921 MHz
WDW                       SINE
SSB          0
LB           0 Hz
GB           0
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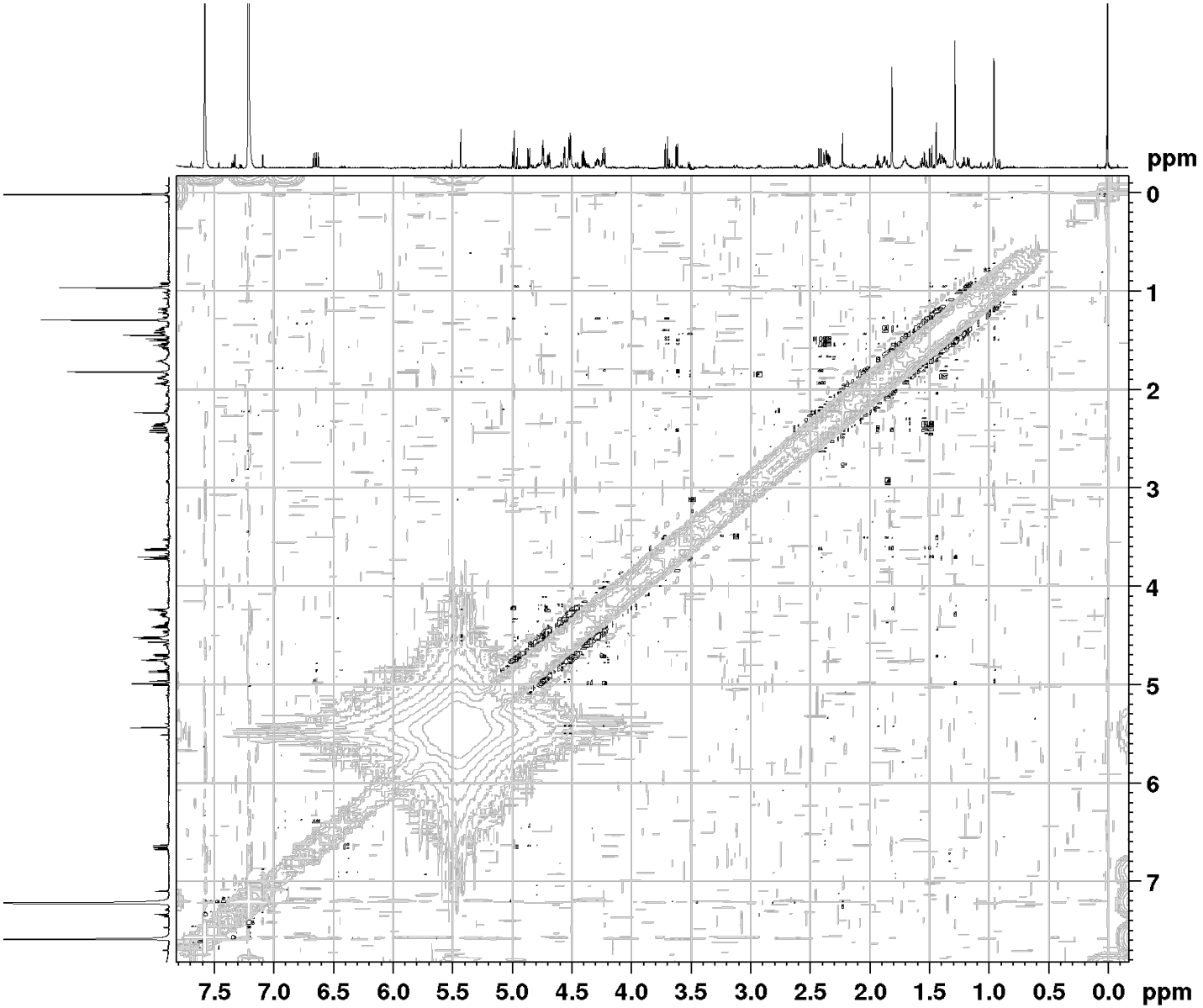
Figure S7. HMBC spectrum (700 MHz, Pyr-d_5) of **1**

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PROCNO                      2

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INSTRUM               spect
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PULPROG           noesygpph
TD                     2048
SOLVENT                 Pyr
NS                       16
DS                       16
SWH                5597.015 Hz
FIDRES             2.732918 Hz
AQ                 0.1829547 sec
RG                       203
DW                  89.333 usec
DE                    6.50 usec
TE                   303.0 K
D0                 0.00006871 sec
D1                 1.00000000 sec
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D16                0.00010000 sec
IN0                0.00017865 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                    16.20 usec
P2                    32.40 usec
PL1         0 dB
PL1W          23.41078186 W
SFO1          700.0026600 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]           SINE.100
GPZ1                 20.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                       81
SFO1               700.0027 MHz
FIDRES          138.197601 Hz
SW                   7.996 ppm
FnMODE                TPPI

F2 - Processing parameters
SI                     2048
SF              699.9999859 MHz
WDW                   QSINE
SSB                       2
LB          0 Hz
GB          0
PC                     1.00

F1 - Processing parameters
SI                     2048
MC2                   TPPI
SF              699.9999859 MHz
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SSB                       2
LB          0 Hz
GB          0
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Figure S8. NOESY spectrum (700 MHz, Pyr-d_5) of **1**

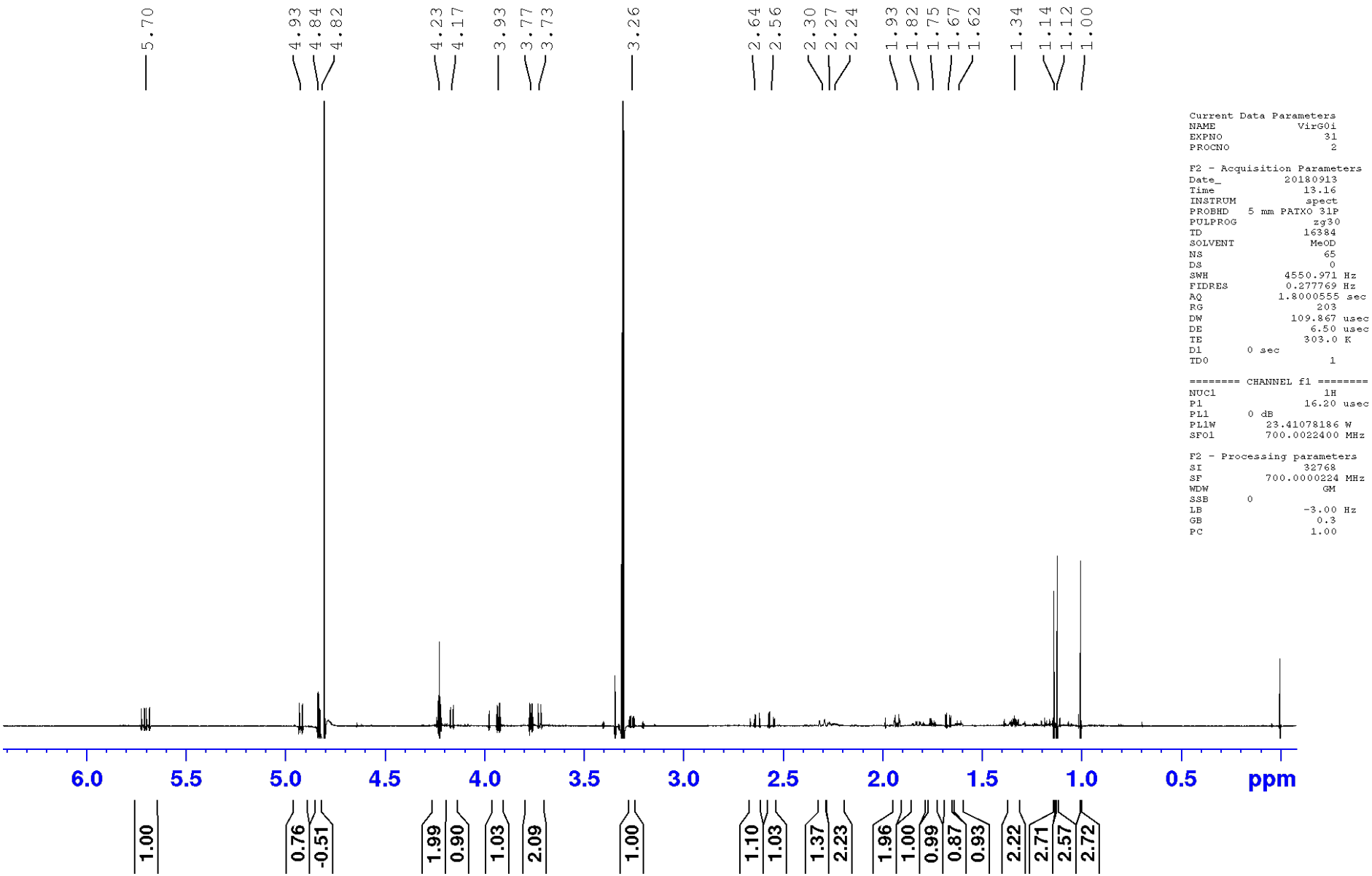
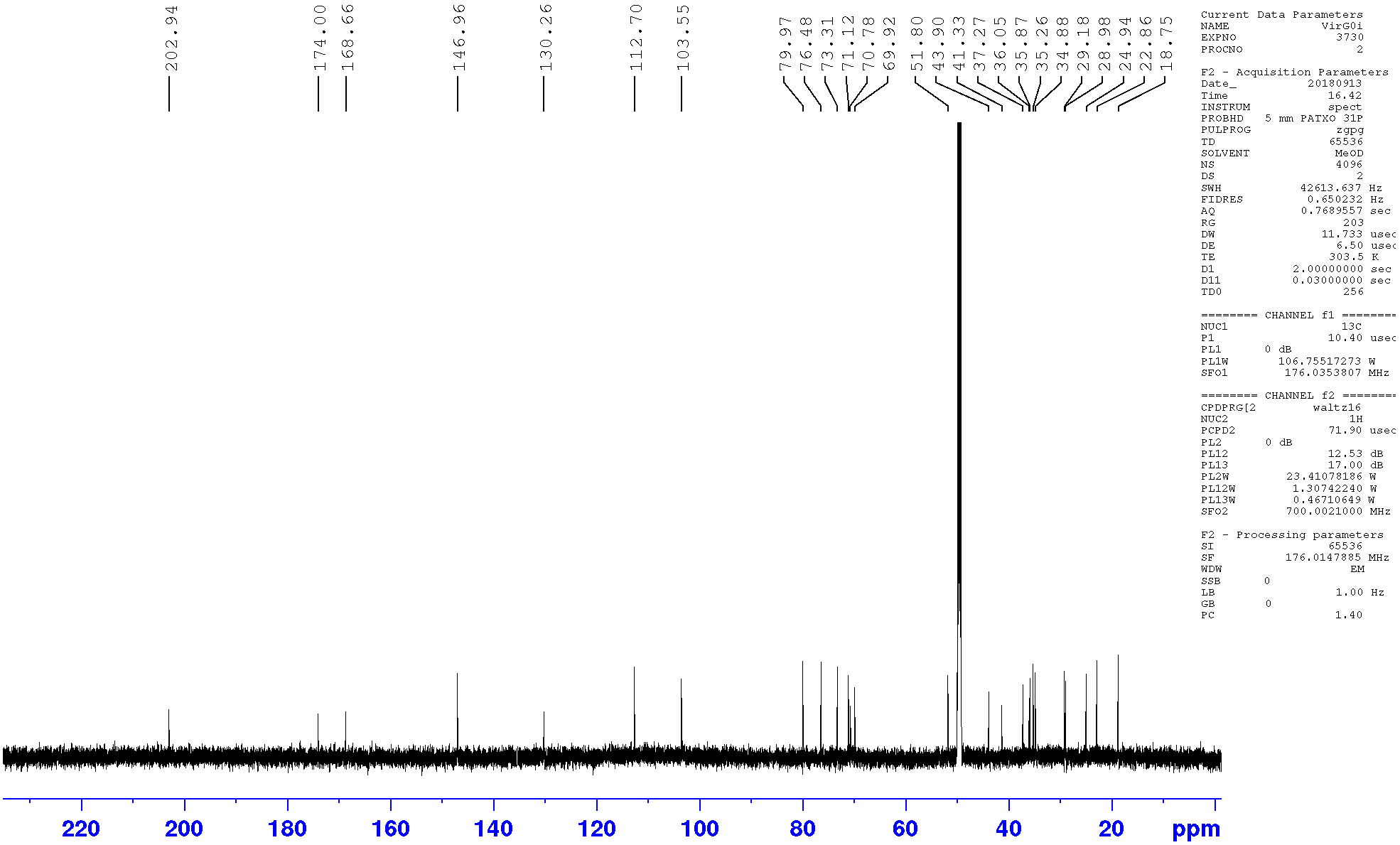


Figure S9. ^{1}H NMR spectrum (700 MHz, CD_3OD) of **2**

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PROCNO                    2

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PULPROG               zgpg
TD                   65536
SOLVENT               MeOD
NS                    4096
DS                       2
SWH             42613.637 Hz
FIDRES           0.650232 Hz
AQ               0.7689557 sec
RG                     203
DW                11.733 usec
DE                 6.50 usec
TE                 303.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    256

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.40 usec
PL1        0 dB
PL1W         106.75517273 W
SFO1          176.0353807 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              71.90 usec
PL2        0 dB
PL12               12.53 dB
PL13               17.00 dB
PL2W         23.41078186 W
PL12W         1.30742240 W
PL13W         0.46710649 W
SFO2          700.0021000 MHz

F2 - Processing parameters
SI                 65536
SF           176.0147885 MHz
WDW                   EM
SSB        0
LB                 1.00 Hz
GB         0
PC                 1.40
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Figure S10. ^{13}C NMR spectrum (176 MHz, CD_3OD) of **2**

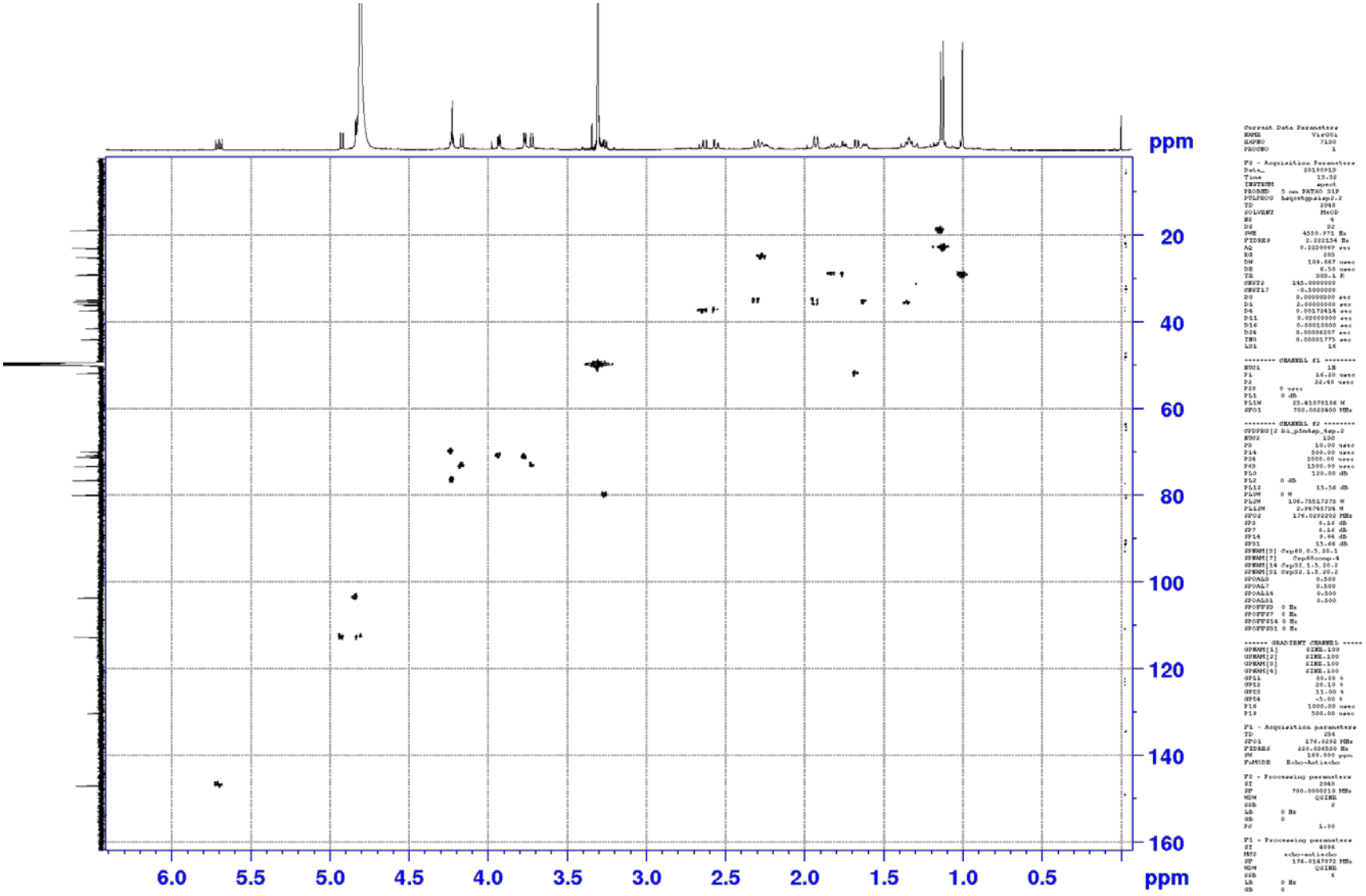


Figure S11. HSQC spectrum (700 MHz, CD_3OD) of **2**

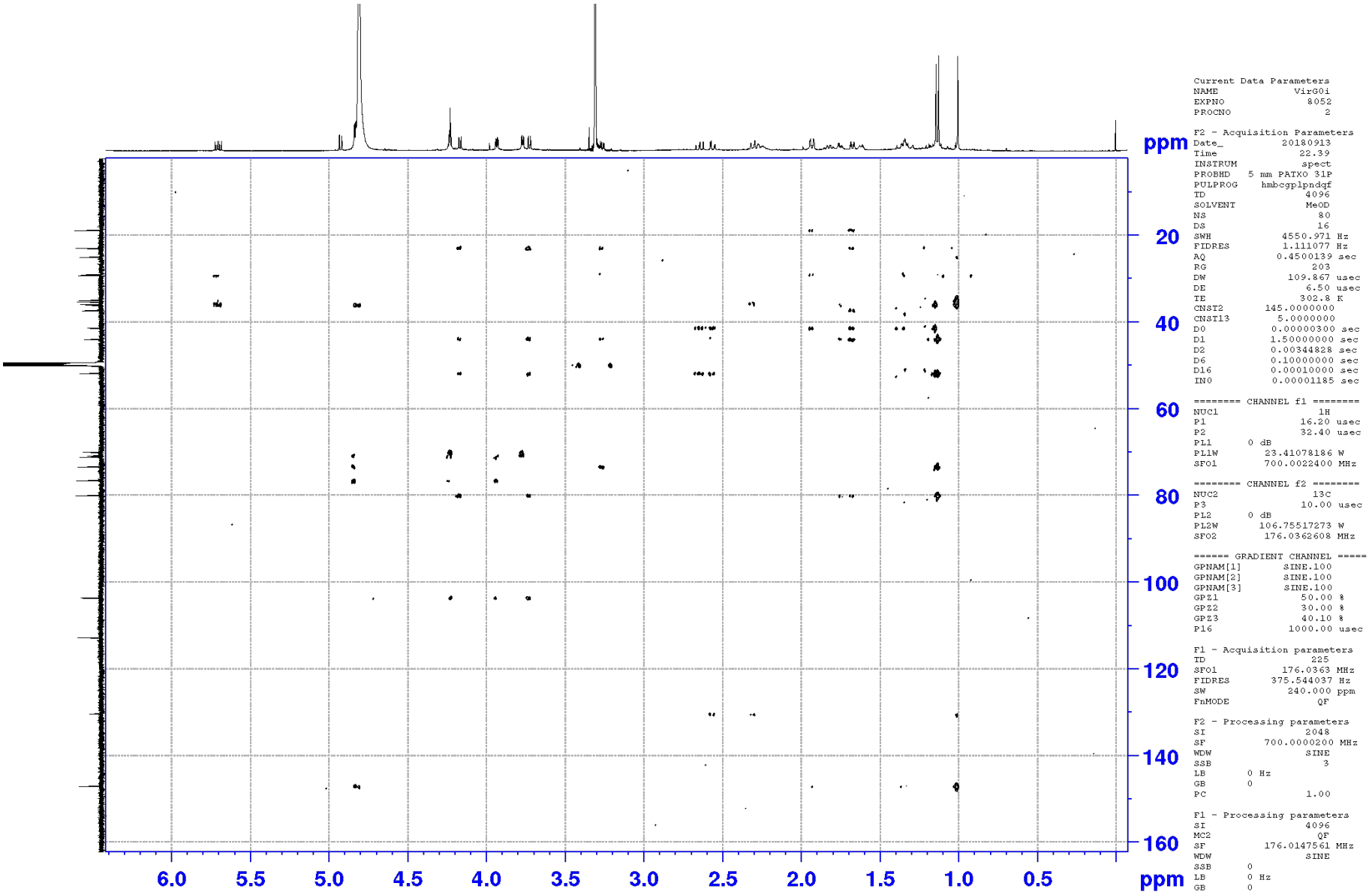
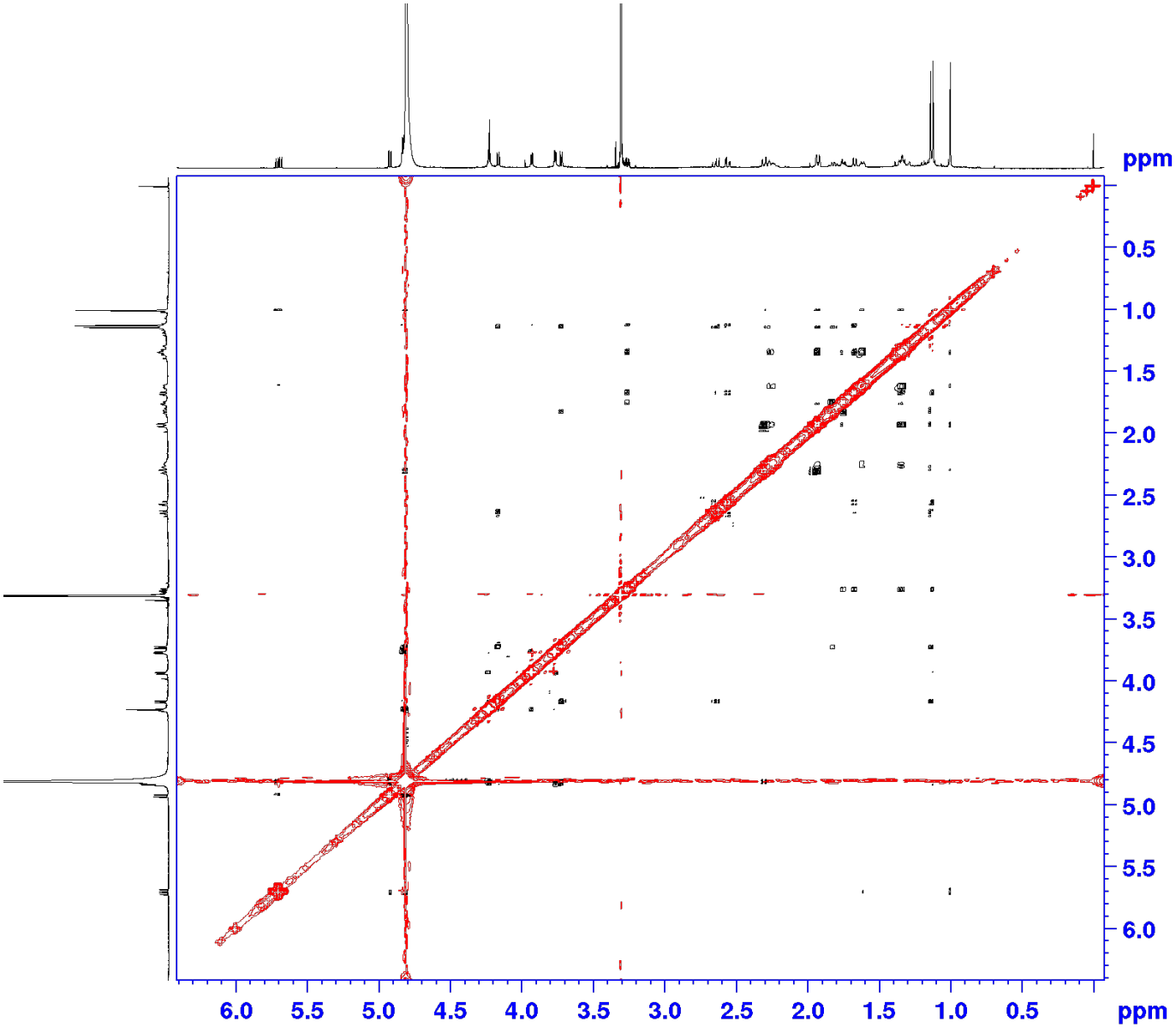


Figure S12. HMBC spectrum (700 MHz, CD_3OD) of **2**




```
Current Data Parameters
NAME                 VirG0i
EXPNO                  6030
PROCNO                    2

F2 - Acquisition Parameters
Date_              20180913
Time                  14.15
INSTRUM               spect
PROBHD   5 mm PATXO 31P
PULPROG          noesygpph
TD                     2048
SOLVENT                MeOD
NS                       16
DS                       16
SWH                4550.971 Hz
FIDRES             2.222154 Hz
AQ                 0.2250069 sec
RG                       203
DW                   109.867 usec
DE                     6.50 usec
TE                    302.9 K
D0                 0.00008924 sec
D1                 1.00000000 sec
D8                 1.00000000 sec
D16                0.00010000 sec
IN0                0.00021975 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     16.20 usec
P2                     32.40 usec
PL1          0 dB
PL1W           23.41078186 W
SFO1          700.0022400 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]           SINE.100
GPZ1                  20.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                       229
SFO1               700.0022 MHz
FIDRES            39.746361 Hz
SW                     6.501 ppm
FnMODE                  TPPI

F2 - Processing parameters
SI                       2048
SF              700.0000213 MHz
WDW                    QSINE
SSB                        2
LB           0 Hz
GB           0
PC                      1.00

F1 - Processing parameters
SI                       2048
MC2                     TPPI
SF              700.0000211 MHz
WDW                    QSINE
SSB                        2
LB           0 Hz
GB           0
```

Figure S13. NOESY spectrum (700 MHz, CD_3OD) of **2**

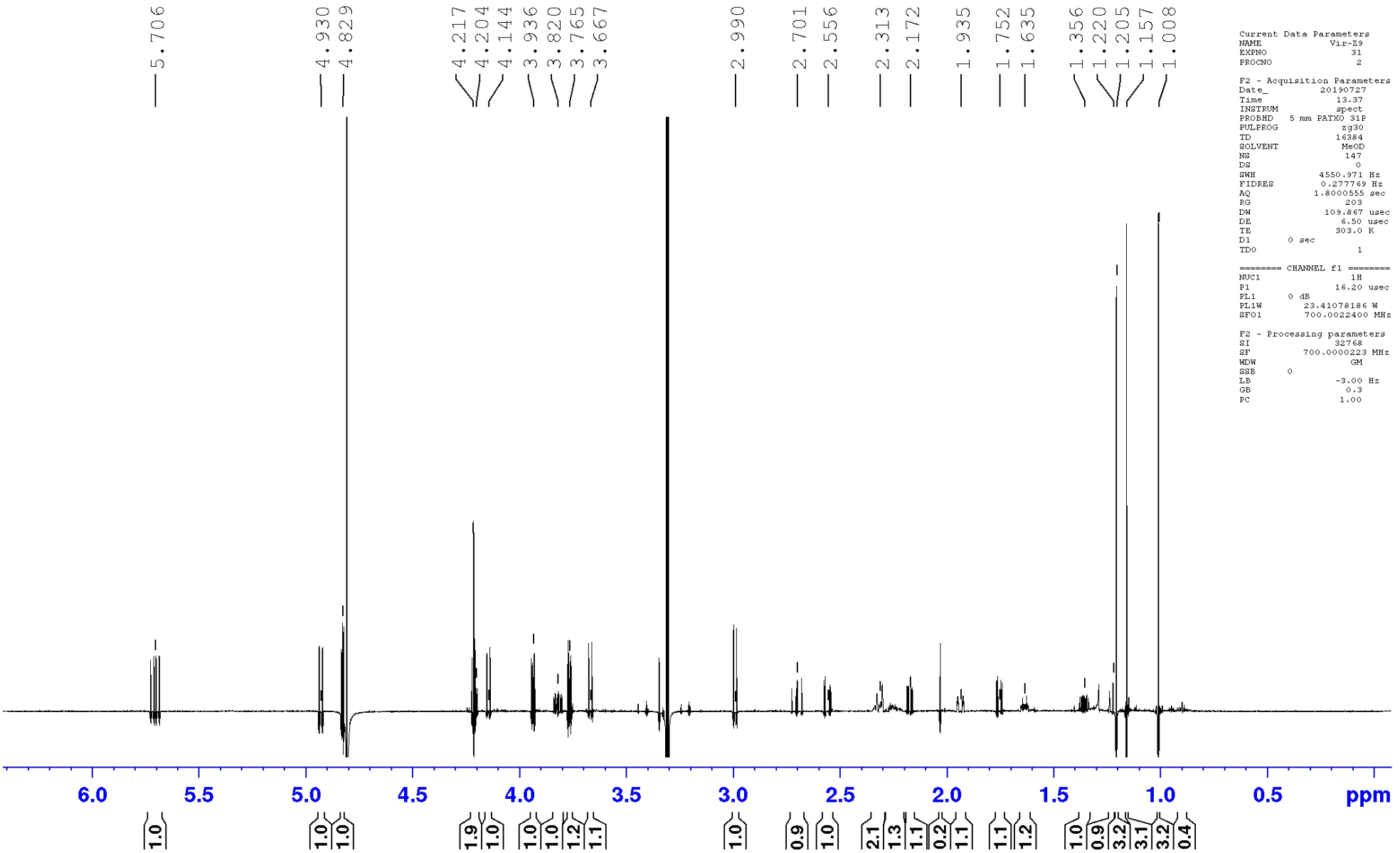


Figure S14. ^{1}H NMR spectrum (700 MHz, CD_3OD) of **3**

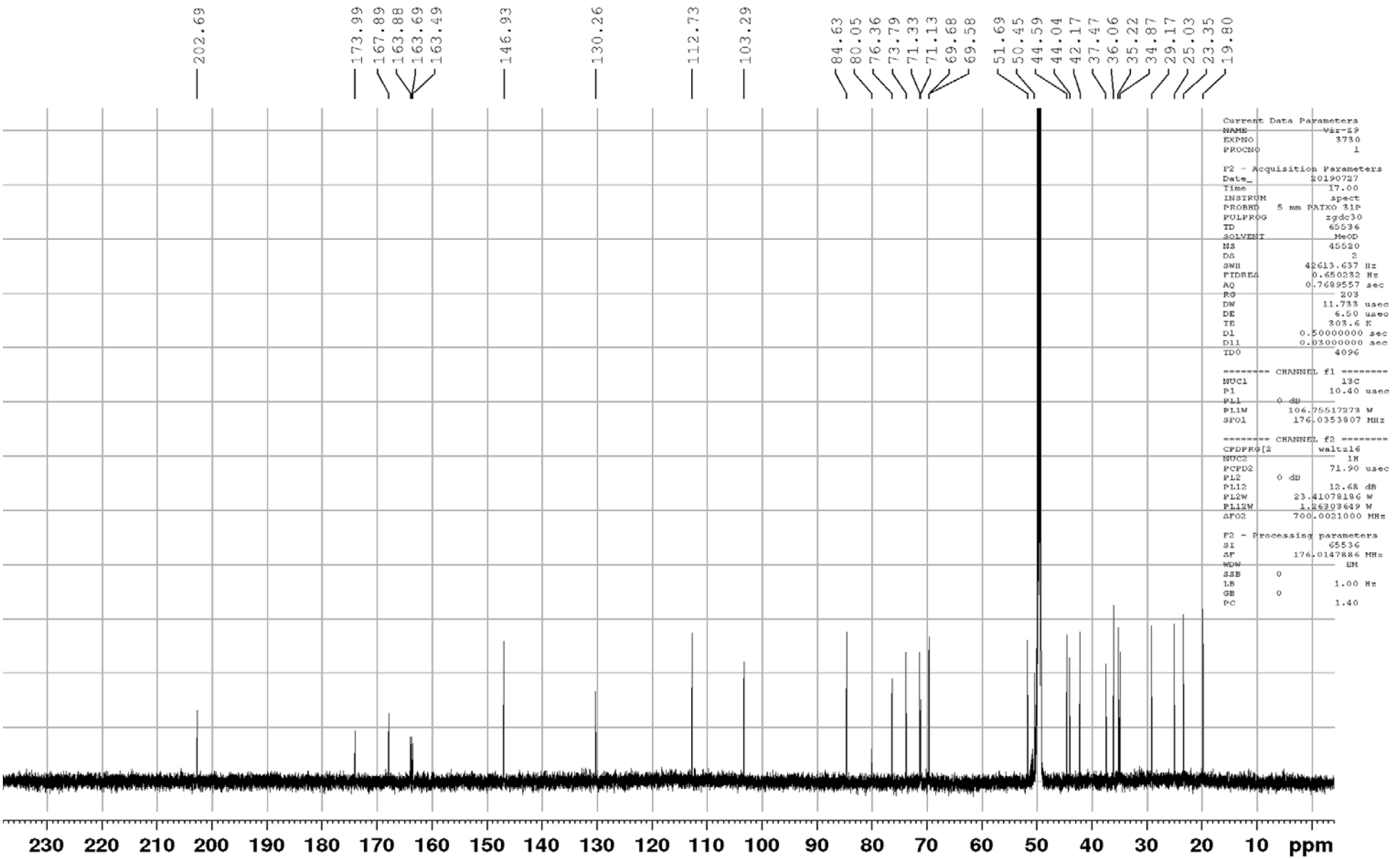


Figure S15. ^{13}C NMR spectrum (176 MHz, CD_3OD) of **3**

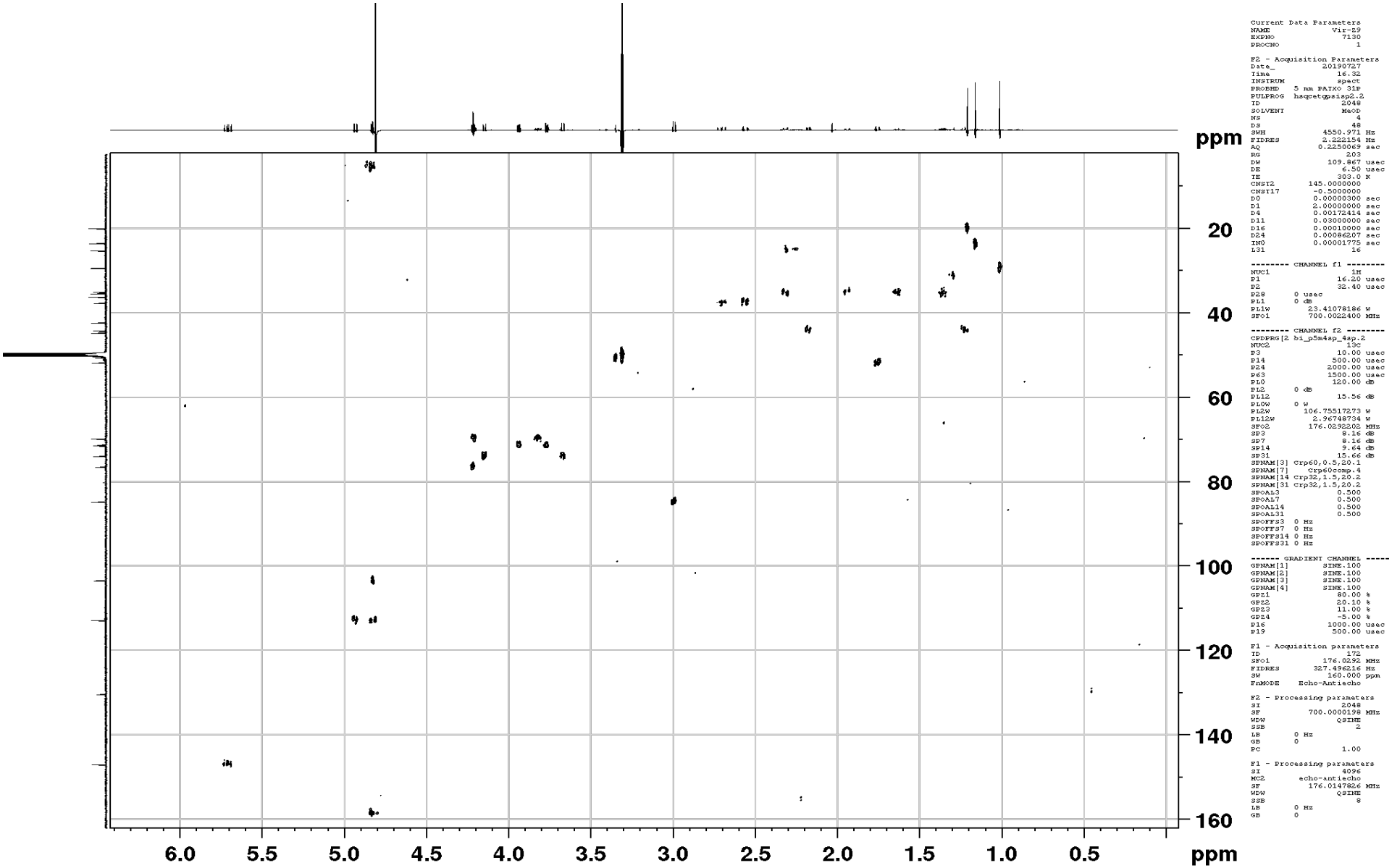
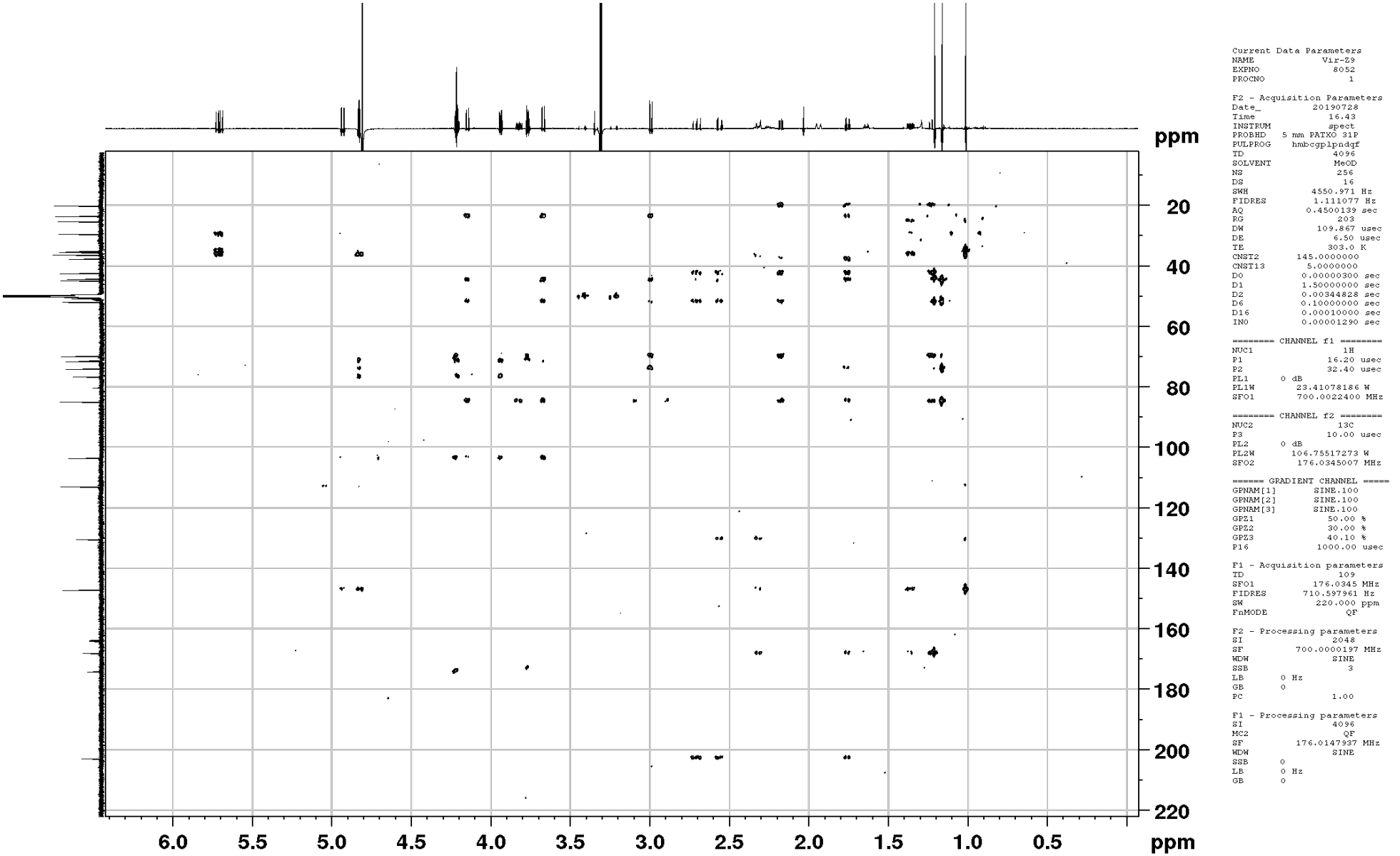


Figure S16. HSQC spectrum (700 MHz, CD_3OD) of **3**




```
Current Data Parameters
NAME                  Vir-Z9
EXPNO                   8052
PROCNO                     1

F2 - Acquisition Parameters
Date_               20190728
Time                   16.43
INSTRUM                spect
PROBHD     5 mm PATXO 31P
PULPROG     hmbcgplpndqf
TD                      4096
SOLVENT                 MeOD
NS                       256
DS                        16
SWH                4550.971 Hz
FIDRES              1.111077 Hz
AQ                 0.4500139 sec
RG                       203
DW                 109.867 usec
DE                   6.50 usec
TE                   303.0 K
CNST2              145.0000000
CNST13               5.0000000
D0                 0.00000300 sec
D1                 1.50000000 sec
D2                 0.00344828 sec
D6                 0.10000000 sec
D16                0.00010000 sec
IN0                0.00001290 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      16.20 usec
P2                      32.40 usec
PL1             0 dB
PL1W              23.41078186 W
SFO1              700.0022400 MHz

======== CHANNEL f2 ========
NUC2                      13C
P3                      10.00 usec
PL2             0 dB
PL2W             106.75517273 W
SFO2              176.0345007 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]             SINE.100
GPNAM[2]             SINE.100
GPNAM[3]             SINE.100
GPZ1                    50.00 %
GPZ2                    30.00 %
GPZ3                    40.10 %
P16                   1000.00 usec

F1 - Acquisition parameters
TD                         109
SFO1                176.0345 MHz
FIDRES              710.597961 Hz
SW                    220.000 ppm
FnMODE                     QF

F2 - Processing parameters
SI                        2048
SF                700.0000197 MHz
WDW                       SINE
SSB                          3
LB              0 Hz
GB              0
PC                        1.00

F1 - Processing parameters
SI                        4096
MC2                        QF
SF                176.0147937 MHz
WDW                       SINE
SSB             0
LB              0 Hz
GB              0
```

Figure S17. HMBC spectrum (700 MHz, CD_3OD) of **3**

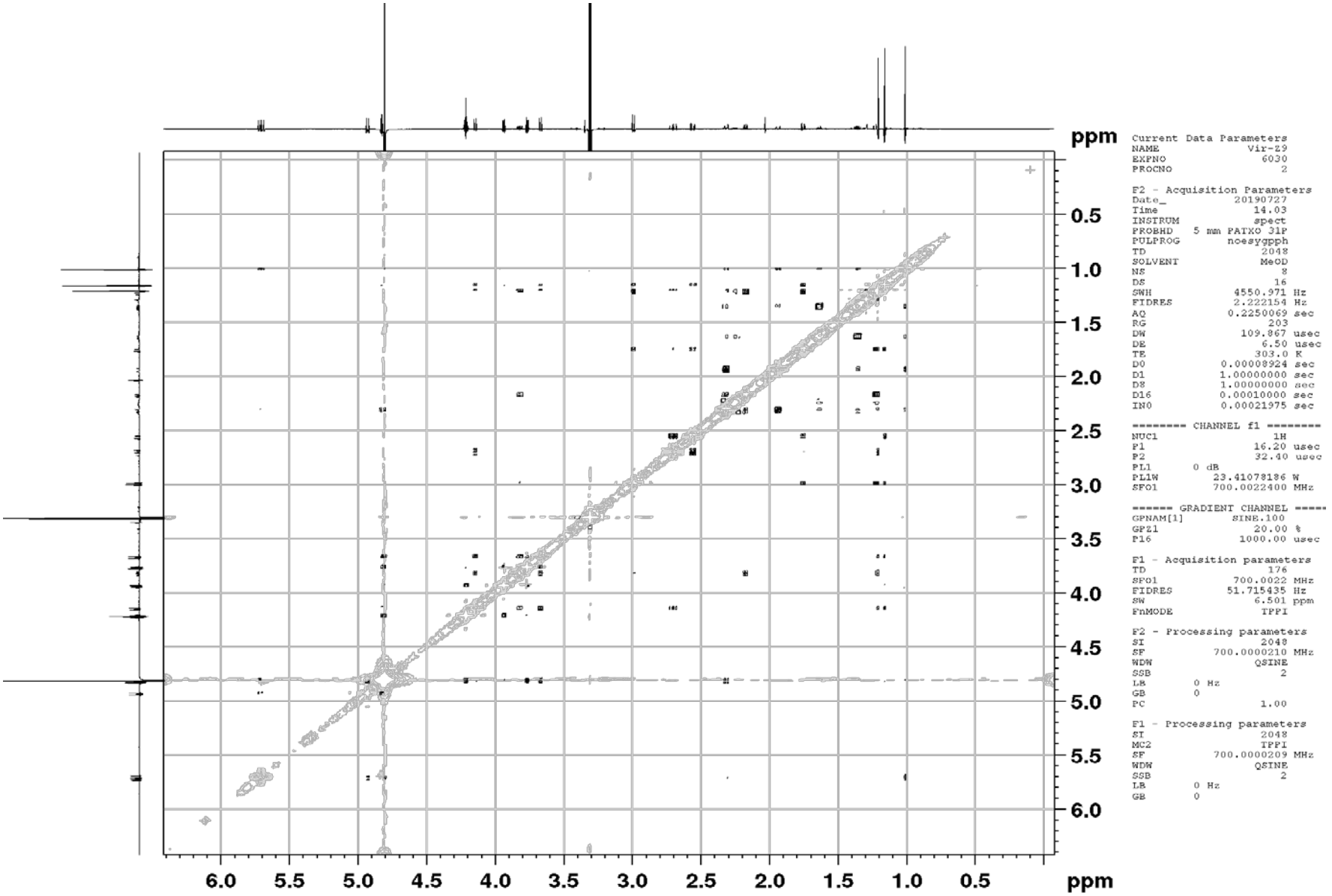


Figure S18. NOESY spectrum (700 MHz, CD_3OD) of **3**

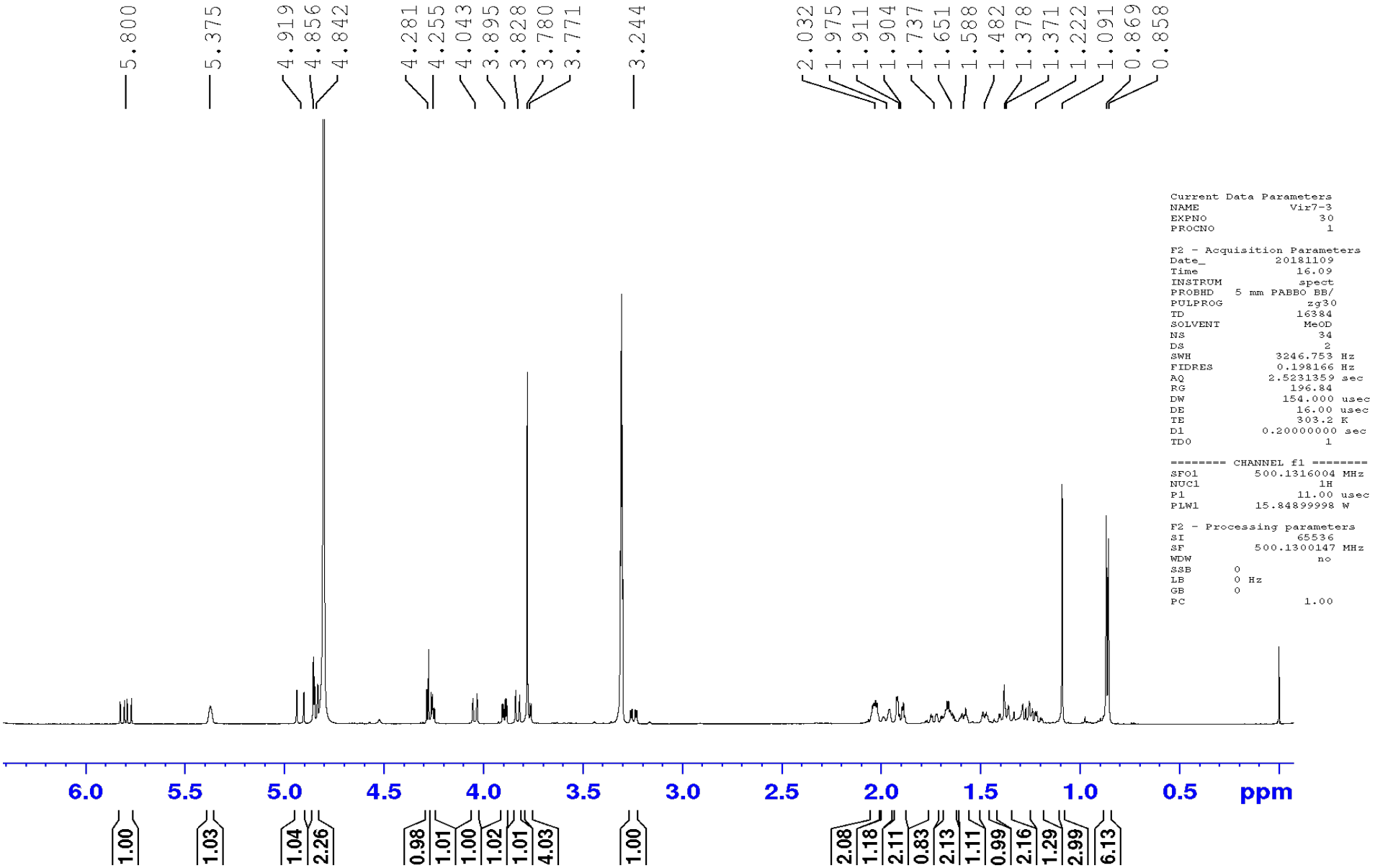


Figure S19. ^{1}H NMR spectrum (500 MHz, CD_3OD) of **4**

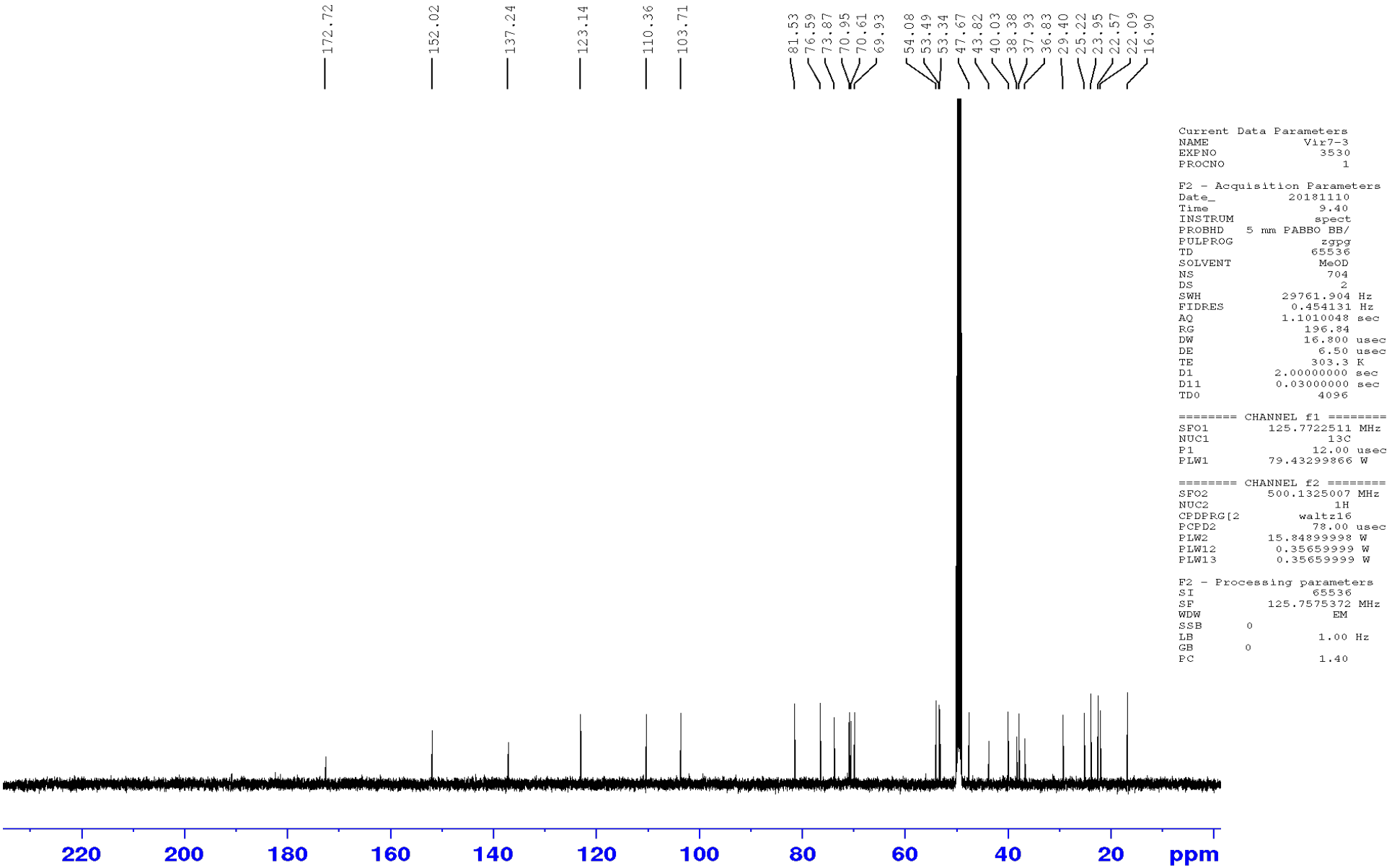


Figure S20. ^{13}C NMR spectrum (125 MHz, CD_3OD) of **4**

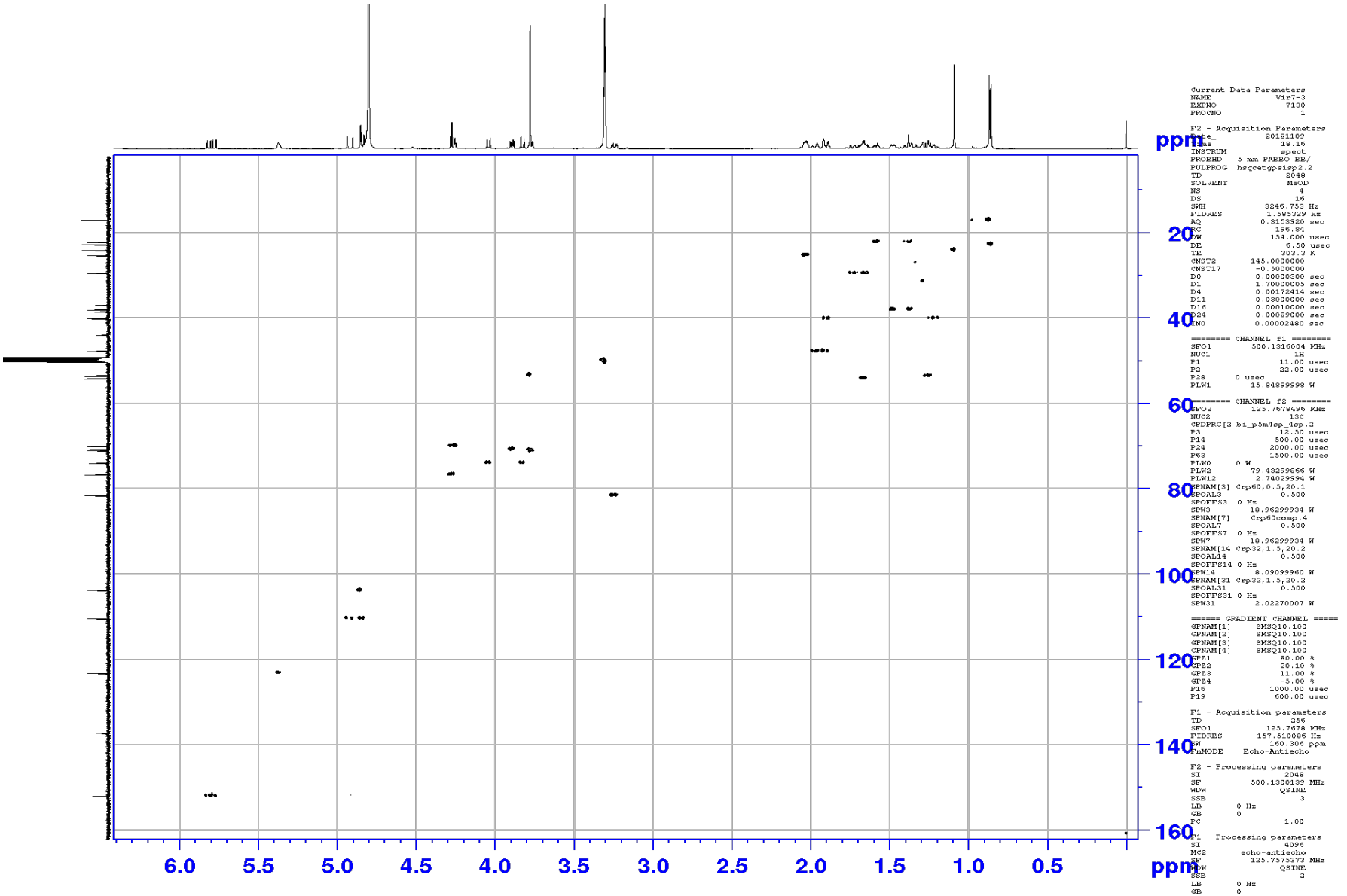


Figure S21. HSQC spectrum (500 MHz, CD_3OD) of **4**

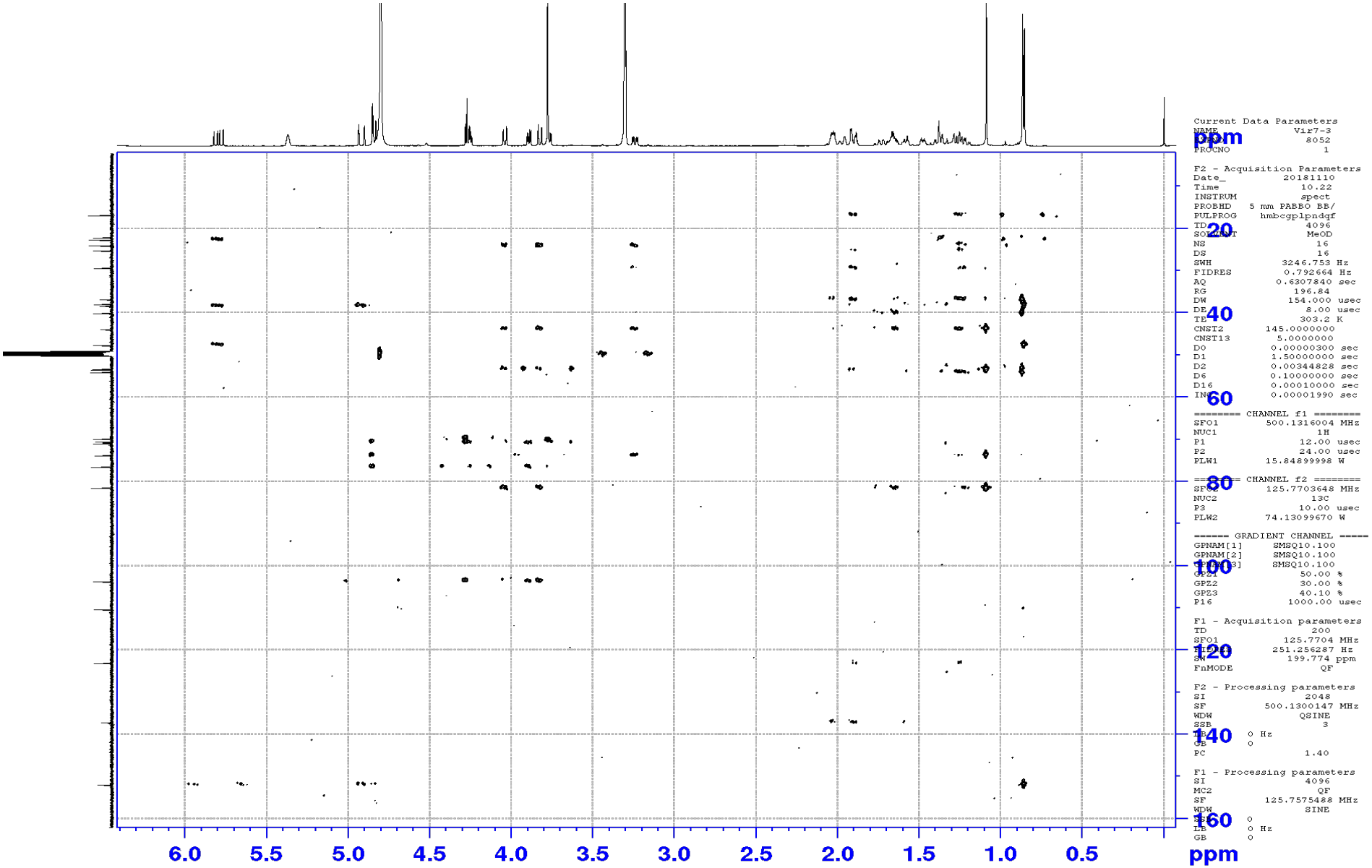


Figure S22. HMBC spectrum (500 MHz, CD_3OD) of **4**

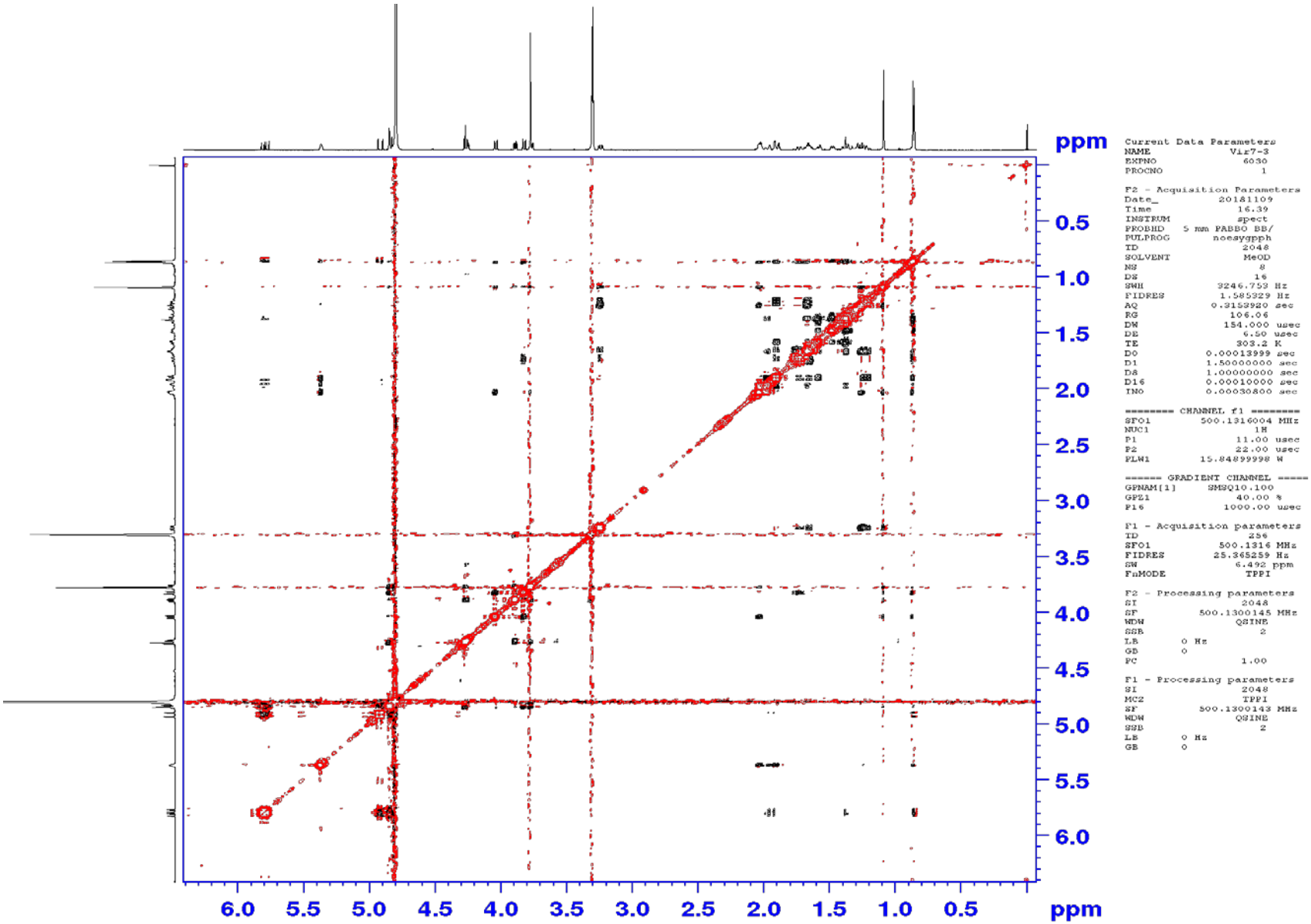
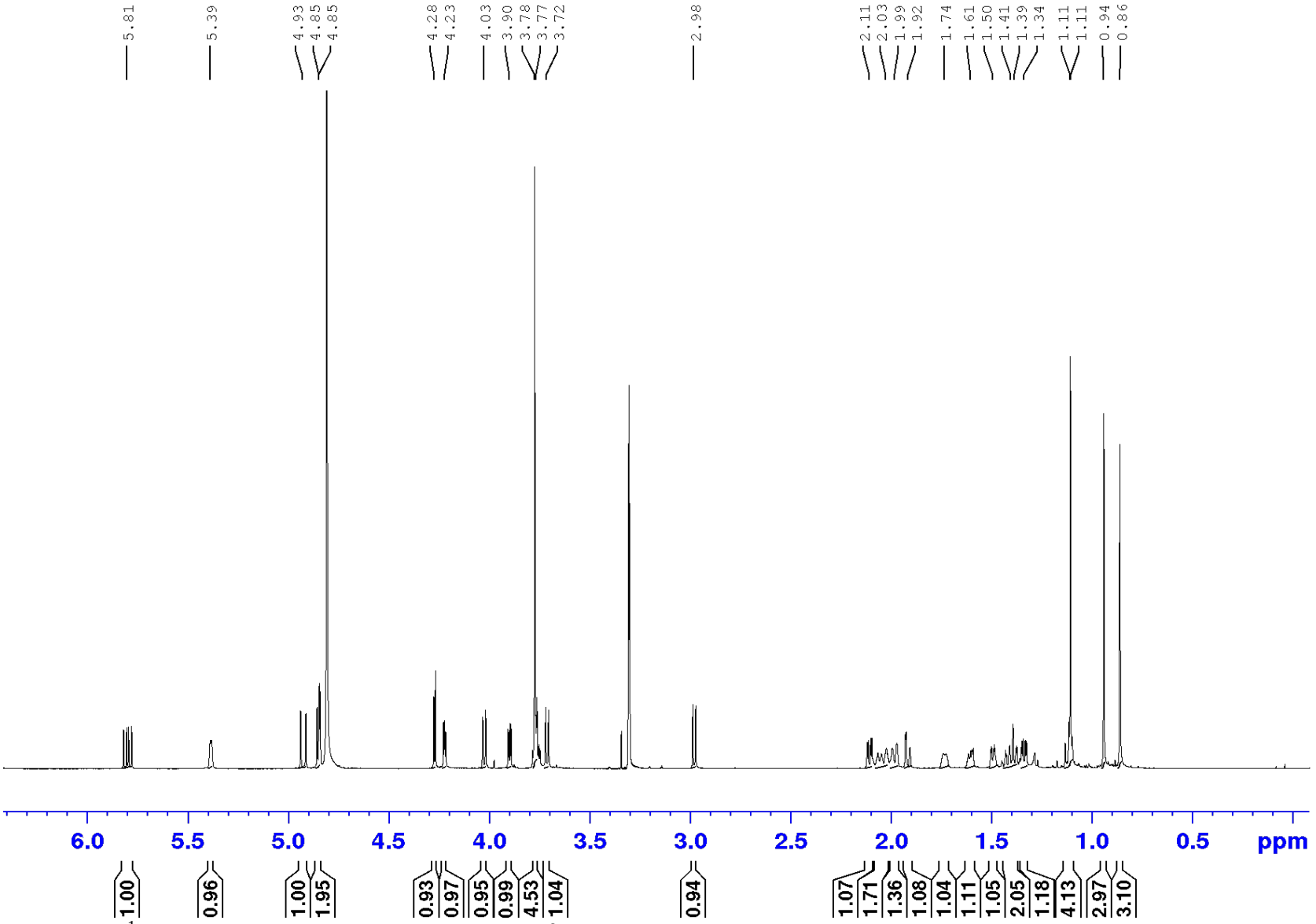
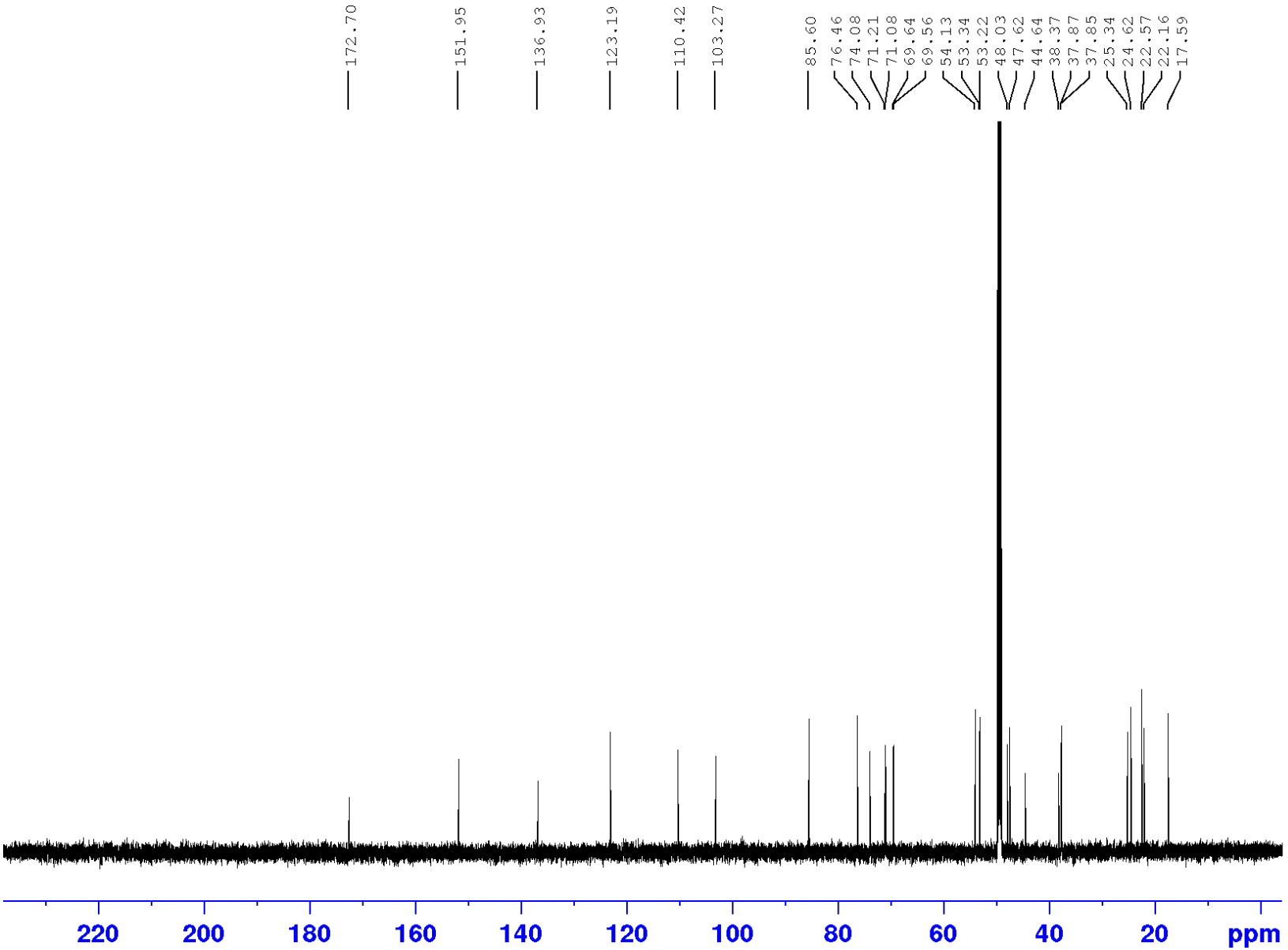


Figure S23. NOESY spectrum (500 MHz, CD_3OD) of **4**




```
Current Data Parameters
NAME                  Vir2-F1
EXPNO                      31
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180903
Time                   15.38
INSTRUM                spect
PROBHD    5 mm PATXO 31P
PULPROG                zg30
TD                    16384
SOLVENT                MeOD
NS                       49
DS                        0
SWH                4550.971 Hz
FIDRES             0.277769 Hz
AQ                 1.8000555 sec
RG                       203
DW                 109.867 use
DE                   6.50 use
TE                   303.0 K
D1          0 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     16.20 use
PL1         0 dB
PL1W          23.41078186 W
SFO1          700.0022400 MHz

F2 - Processing parameters
SI                      32768
SF            700.0000215 MHz
WDW                        no
SSB         0
LB          0 Hz
GB          0
PC                      1.00
```

Figure S24. ^{1}H NMR spectrum (700 MHz, CD_3OD) of **5**




```
Current Data Parameters
NAME                  Vir2-F1
EXPNO                    3730
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180903
Time                   16.11
INSTRUM                spect
PROBHD    5 mm PATXO 31P
PULPROG                zgpg
TD                    65536
SOLVENT                MeOD
NS                      128
DS                        2
SWH                42613.637 Hz
FIDRES              0.650232 Hz
AQ                  0.7689557 sec
RG                      203
DW                   11.733 usec
DE                    6.50 usec
TE                   303.7 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                    4096

======== CHANNEL f1 ========
NUC1                    13C
P1                   10.40 usec
PL1       0 dB
PL1W        106.75517273 W
SFO1         176.0353807 MHz

======== CHANNEL f2 ========
CPDPRG[2             waltz16
NUC2                    1H
PCPD2                71.90 usec
PL2       0 dB
PL12                 12.53 dB
PL13                 17.00 dB
PL2W           23.41078186 W
PL12W           1.30742240 W
PL13W           0.46710649 W
SFO2          700.0028000 MHz

F2 - Processing parameters
SI                    65536
SF               176.0147895 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

Figure S25. ^{13}C NMR spectrum (176 MHz, CD_3OD) of **5**

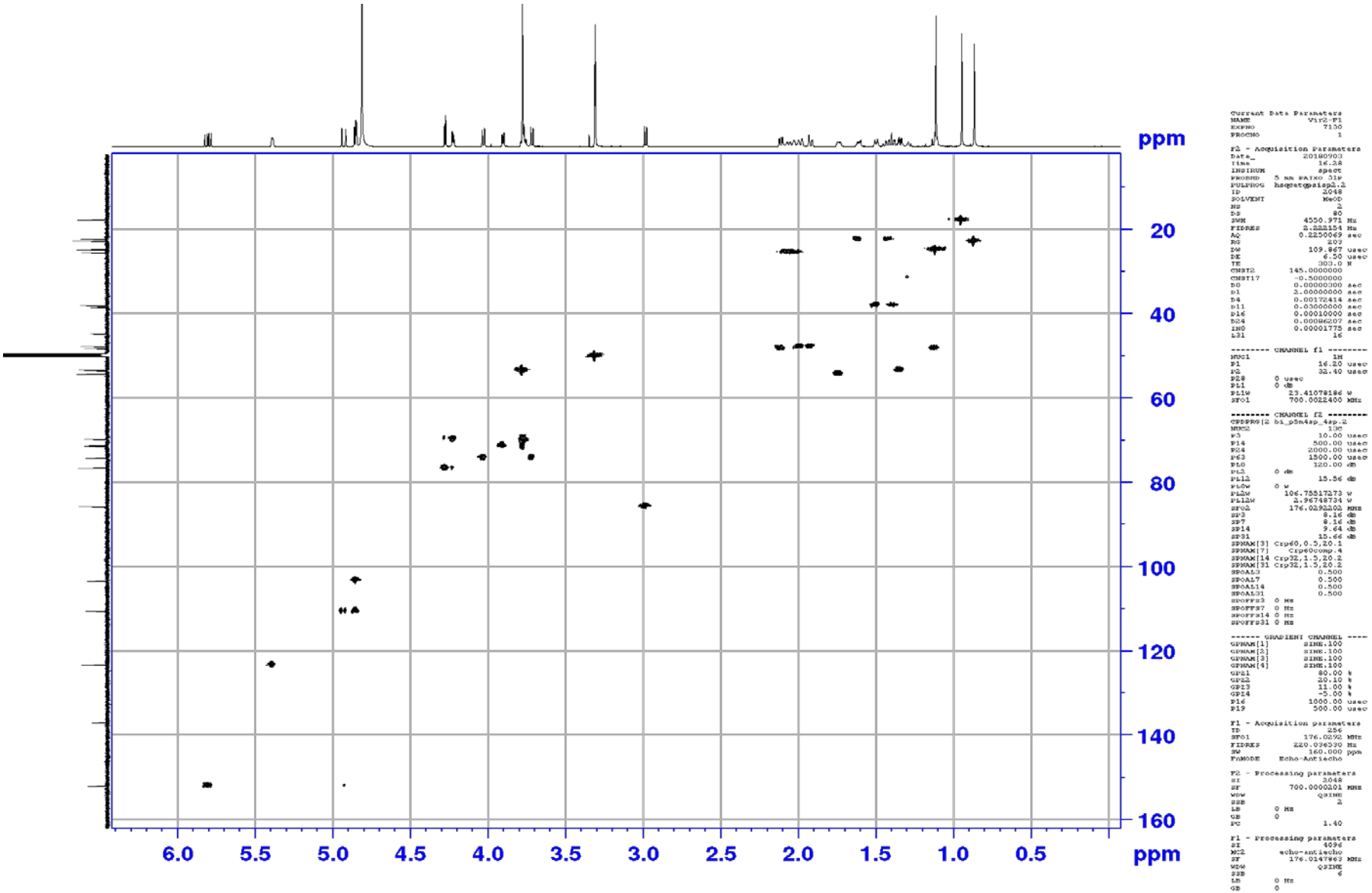
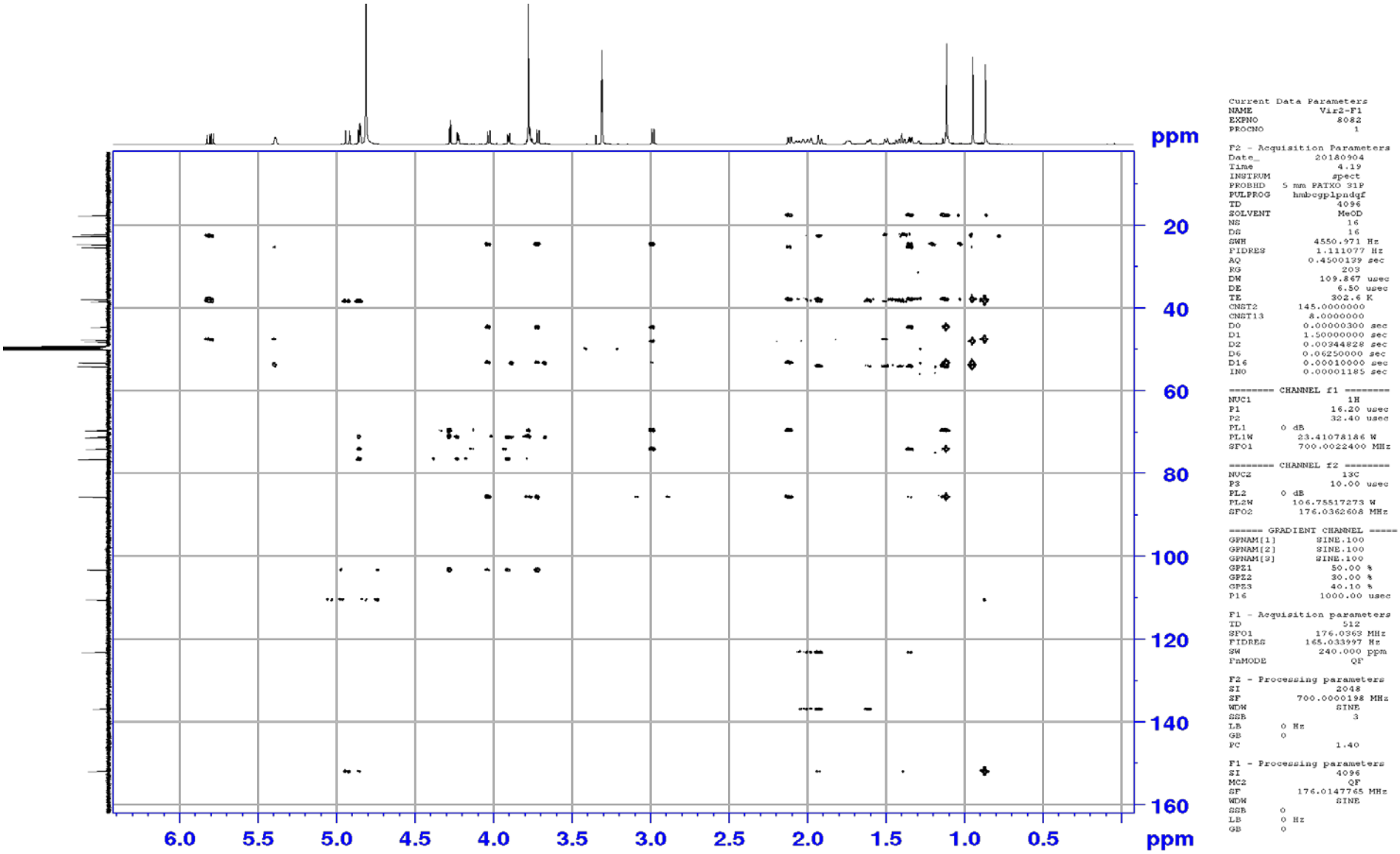
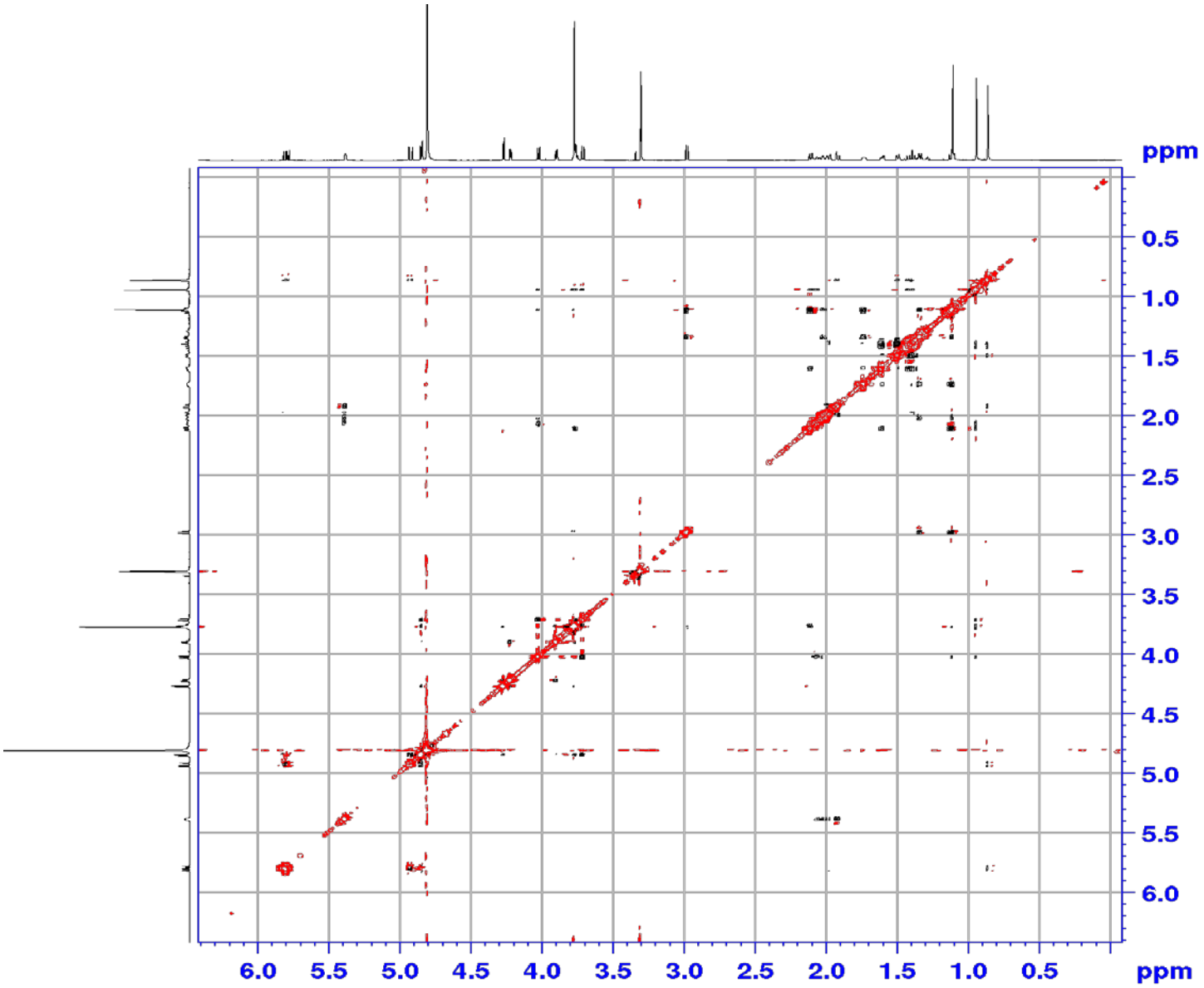


Figure S26. HSQC spectrum (700 MHz, CD_3OD) of **5**




```
Current Data Parameters
NAME                  Vir2-F1
EXPNO                    8082
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180904
Time                    4.19
INSTRUM                spect
PROBHD     5 mm PATXO 31P
PULPROG     hmbcgplpndqf
TD                      4096
SOLVENT                 MeOD
NS                        16
DS                        16
SWH                 4550.971 Hz
FIDRES              1.111077 Hz
AQ                  0.4500139 sec
RG                        203
DW                  109.867 usec
DE                      6.50 usec
TE                     302.6 K
CNST2               145.0000000
CNST13                8.0000000
D0                  0.00000300 sec
D1                  1.50000000 sec
D2                  0.00344828 sec
D6                  0.06250000 sec
D16                 0.00010000 sec
IN0                 0.00001185 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      16.20 usec
P2                      32.40 usec
PL1          0 dB
PL1W          23.41078186 W
SFO1           700.0022400 MHz

======== CHANNEL f2 ========
NUC2                      13C
P3                      10.00 usec
PL2          0 dB
PL2W         106.75517273 W
SFO2          176.0362608 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]             SINE.100
GPNAM[2]             SINE.100
GPNAM[3]             SINE.100
GPZ1                    50.00 %
GPZ2                    30.00 %
GPZ3                    40.10 %
P16                   1000.00 usec

F1 - Acquisition parameters
TD                         512
SFO1                176.0363 MHz
FIDRES              165.033997 Hz
SW                     240.000 ppm
FnMODE                      QF

F2 - Processing parameters
SI                         2048
SF                  700.0000198 MHz
WDW                        SINE
SSB                           3
LB           0 Hz
GB           0
PC                        1.40

F1 - Processing parameters
SI                         4096
MC2                         QF
SF                  176.0147765 MHz
WDW                        SINE
SSB          0
LB           0 Hz
GB           0
```

Figure S27. HMBC spectrum (700 MHz, CD_3OD) of **5**




```
Current Data Parameters
NAME                  Vir2-F1
EXPNO                    6030
PROCNO                      1

F2 - Acquisition Parameters
Date_               20180903
Time                   15.49
INSTRUM                spect
PROBHD    5 mm PATXO 31P
PULPROG          noesygpph
TD                       2048
SOLVENT                  MeOD
NS                          4
DS                         16
SWH                4550.971 Hz
FIDRES             2.222154 Hz
AQ                 0.2250069 sec
RG                       203
DW                 109.867 usec
DE                   6.50 usec
TE                   303.0 K
D0                 0.00008924 sec
D1                 1.00000000 sec
D8                 1.00000000 sec
D16                0.00010000 sec
IN0                0.00021975 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      16.20 usec
P2                      32.40 usec
PL1             0 dB
PL1W           23.41078186 W
SFO1          700.0022400 MHz

======= GRADIENT CHANNEL =====
GPNAM[1]           SINE.100
GPZ1                  20.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                       121
SFO1              700.0022 MHz
FIDRES           75.222450 Hz
SW                    6.501 ppm
FnMODE                 TPPI

F2 - Processing parameters
SI                       2048
SF              700.0000210 MHz
WDW                    QSINE
SSB                         2
LB              0 Hz
GB              0
PC                      1.00

F1 - Processing parameters
SI                       2048
MC2                    TPPI
SF              700.0000210 MHz
WDW                    QSINE
SSB                         2
LB              0 Hz
GB              0
```

Figure S28. NOESY spectrum (700 MHz, CD_3OD) of **5**

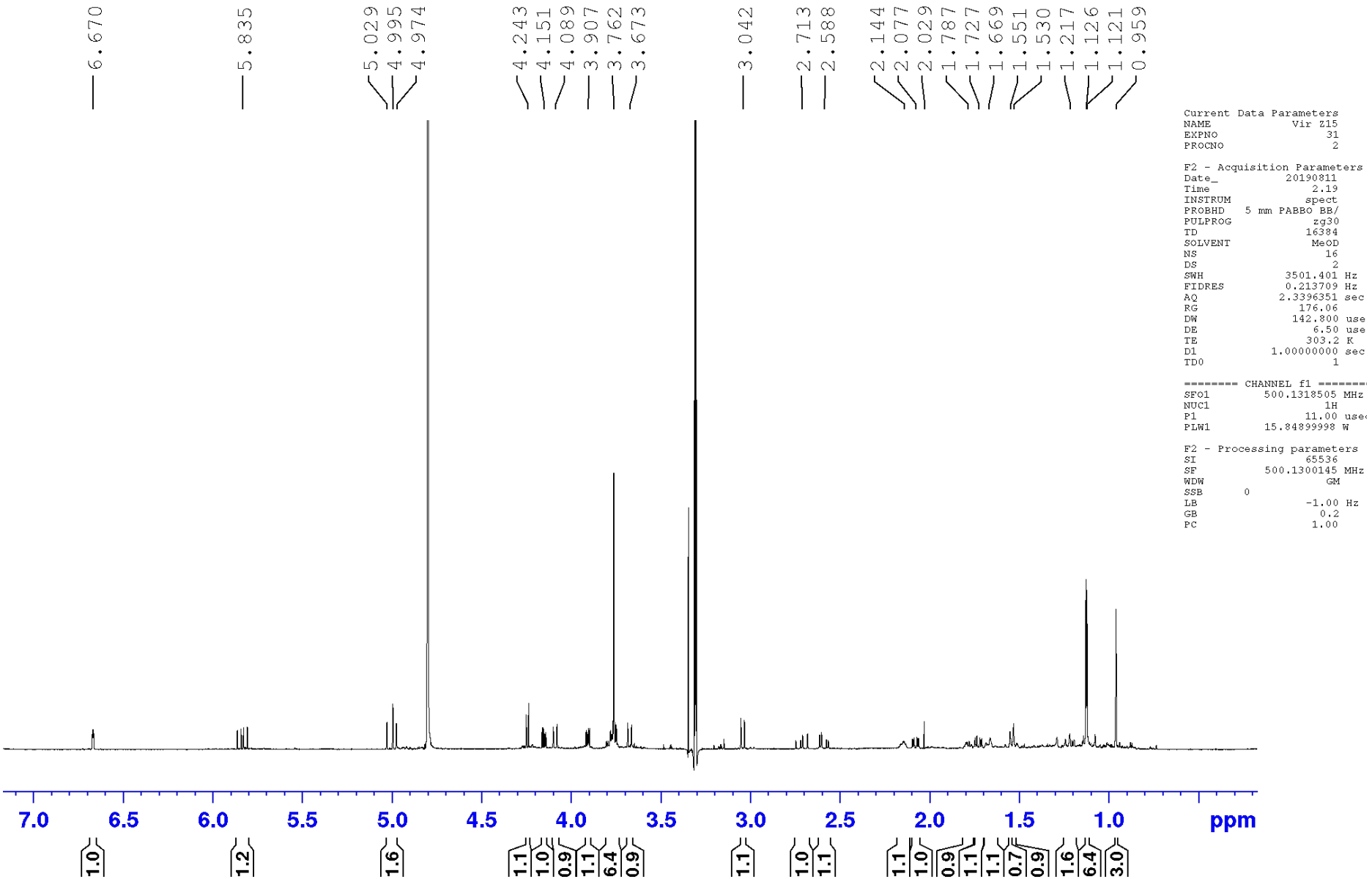


Figure S29. ^{1}H NMR spectrum (500 MHz, CD_3OD) of **6**

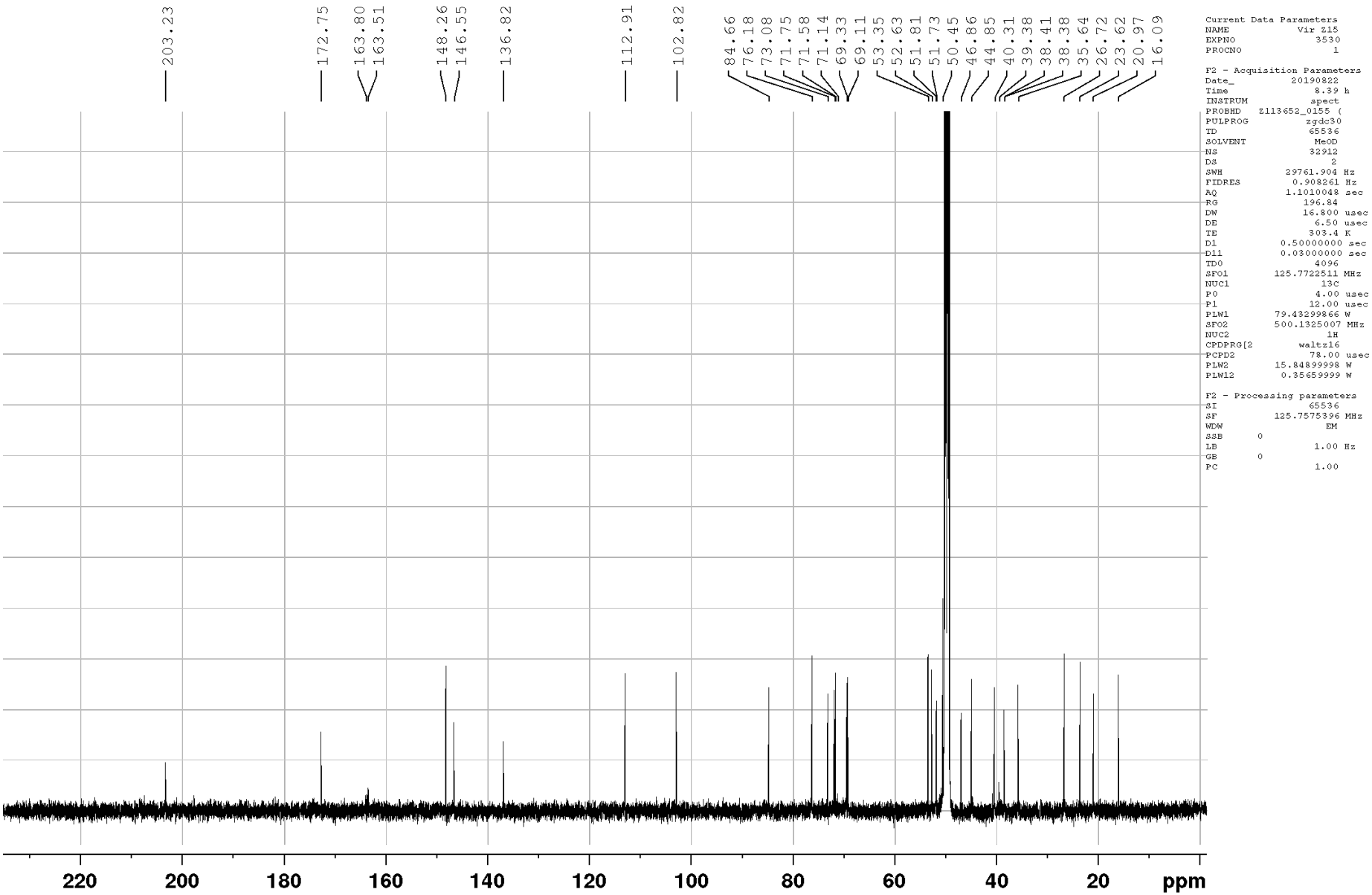
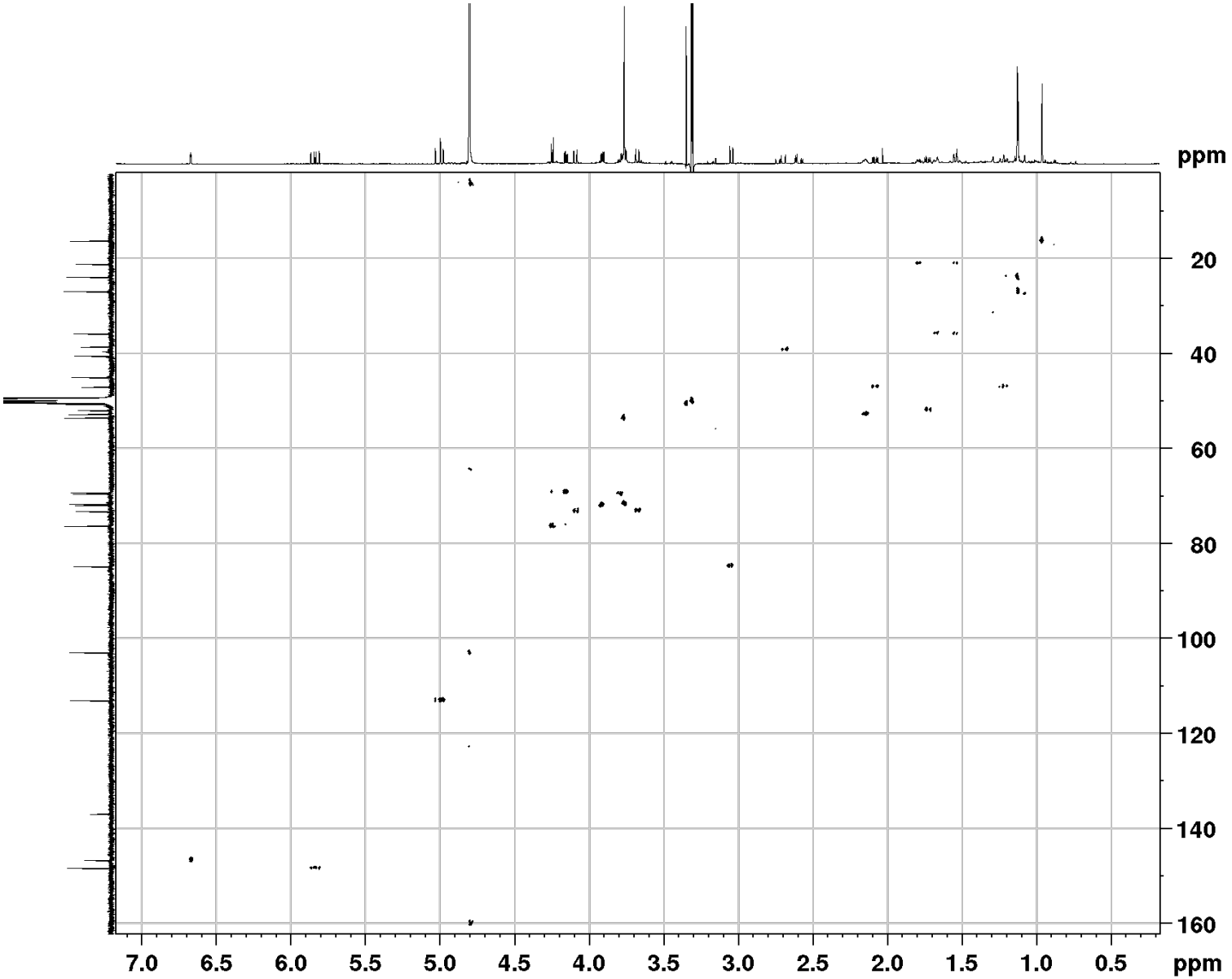


Figure S30. ^{13}C NMR spectrum (125 MHz, CD_3OD) of **6**




```
Current Data Parameters
NAME                  Vir Z15
EXPNO                    7130
PROCNO                      1

F2 - Acquisition Parameters
Date_              20190822
Time                   9.41 h
INSTRUM                spect
PROBHD    Z113652_0155 (
PULPROG   hsqcetgpsisp2.2
TD                       2048
SOLVENT                  MeOD
NS                         16
DS                         16
SWH                3501.401 Hz
FIDRES                3.419337 Hz
AQ                 0.2924544 sec
RG                       196.84
DW                       142.800 usec
DE                         6.50 usec
TE                       303.1 K
CNST2             145.0000000
CNST17             -0.5000000
D0                 0.00000300 sec
D1                 1.50000000 sec
D4                 0.00172414 sec
D11                0.03000000 sec
D16                0.00020000 sec
D24                0.00089000 sec
IN0                0.00002480 sec
SPARSELI                    0
TDsv                        1
SFO1               500.1318505 MHz
NUC1                       1H
P1                        11.00 usec
P2                        22.00 usec
P28                     1000.00 usec
PLW1              15.84899998 W
SFO2              125.7678496 MHz
NUC2                       13C
CPDPRG[2 bi_p5m4sp_4sp.2
P3                        12.50 usec
P14                      500.00 usec
P24                     2000.00 usec
P63                     1500.00 usec
PLW0      0 W
PLW2              79.43299866 W
PLW12              2.03999996 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3                    0.500
SPOFFS3   0 Hz
SPW3              18.96299934 W
SPNAM[7]     Crp60comp.4
SPOAL7                    0.500
SPOFFS7   0 Hz
SPW7              18.96299934 W
SPNAM[14 Crp32,1.5,20.2
SPOAL14                   0.500
SPOFFS14 0 Hz
SPW14              8.09099960 W
SPNAM[31 Crp32,1.5,20.2
SPOAL31                   0.500
SPOFFS31 0 Hz
SPW31              2.02270007 W
GPNAM[1]     SMSQ10.100
GPZ1                     80.00 %
GPNAM[2]     SMSQ10.100
GPZ2                     20.10 %
GPNAM[3]     SMSQ10.100
GPZ3                     11.00 %
GPNAM[4]     SMSQ10.100
GPZ4                     -5.00 %
P16                     1000.00 usec
P19                      600.00 usec

F1 - Acquisition parameters
TD                         64
SFO1              125.7678 MHz
FIDRES            630.040344 Hz
SW                   160.306 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                       2048
SF                500.1300138 MHz
WDW                      QSINE
SSB                         3
LB        0 Hz
GB        0
PC                        1.40

F1 - Processing parameters
SI                       4096
MC2          echo-antiecho
SF                125.7575372 MHz
WDW                      QSINE
SSB                         6
LB        0 Hz
GB        0
```

Figure S31. HSQC spectrum (500 MHz, CD_3OD) of **6**

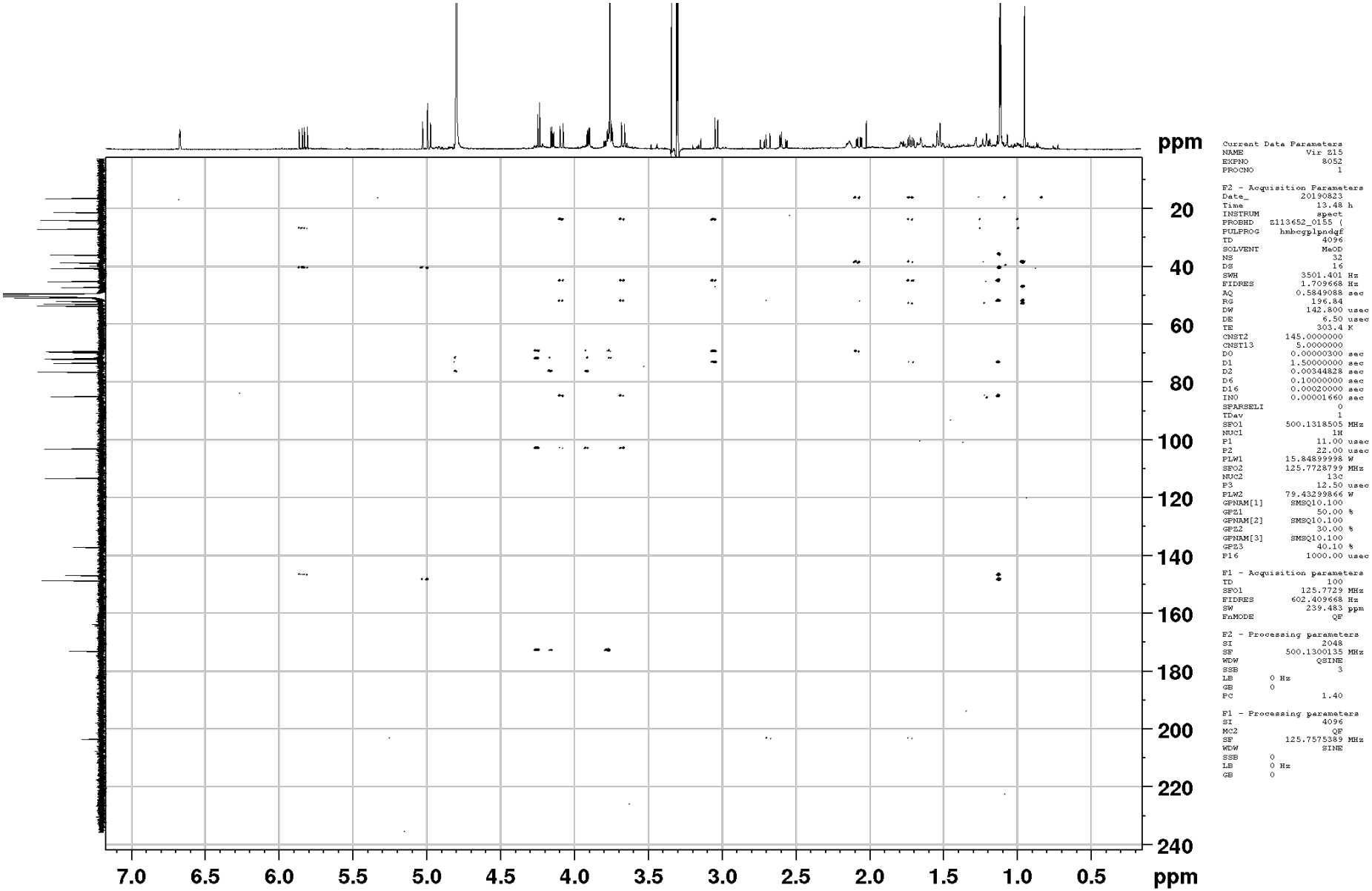
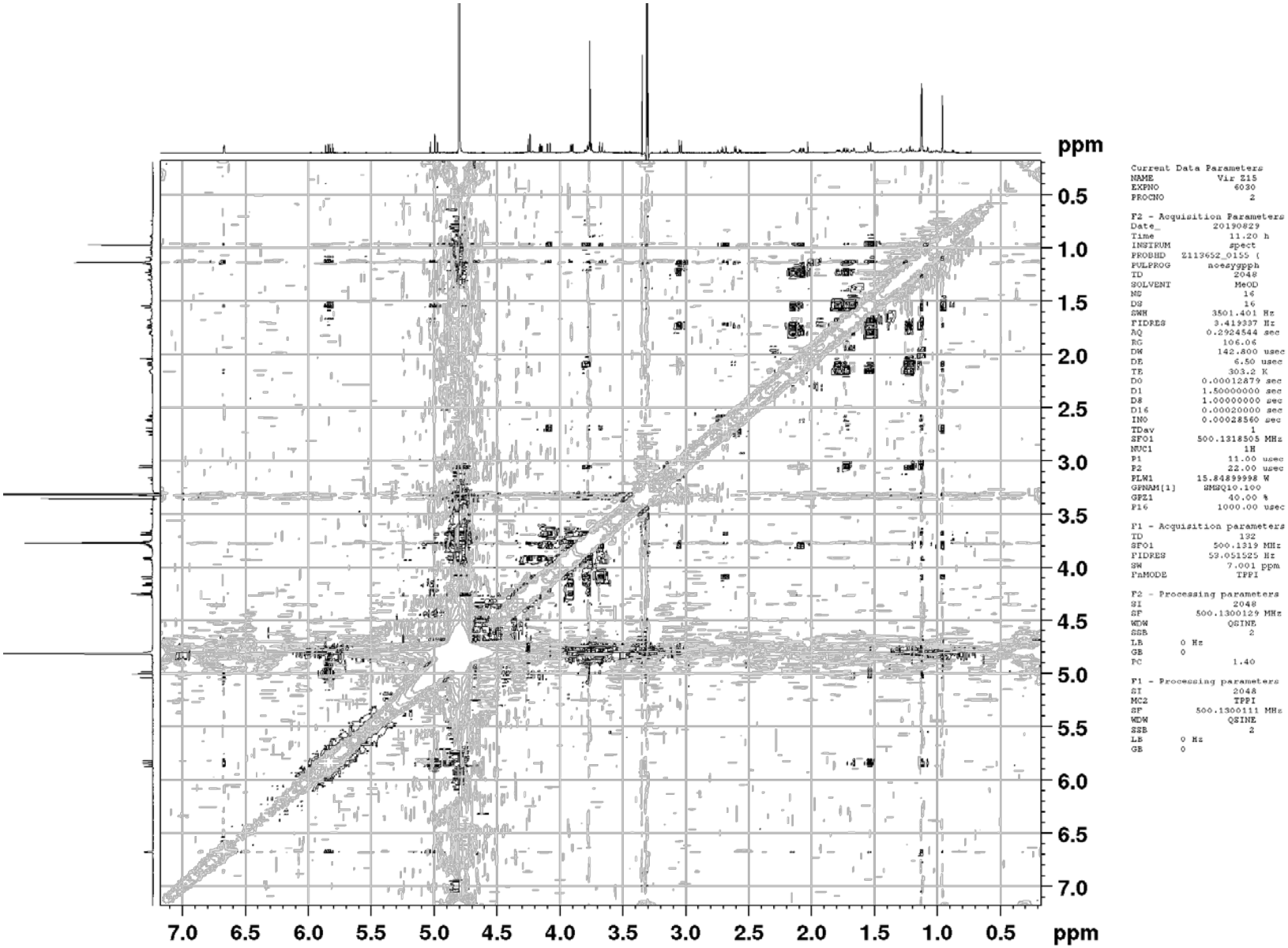


Figure S32. HMBC spectrum (500 MHz, CD_3OD) of **6**




```
Current Data Parameters
NAME                  Vir Z15
EXPNO                    6030
PROCNO                      2

F2 - Acquisition Parameters
Date_               20190829
Time                   11.20 h
INSTRUM                spect
PROBHD     Z113652_0155 (
PULPROG             noesygpph
TD                       2048
SOLVENT                  MeOD
NS                         16
DS                         16
SWH                  3501.401 Hz
FIDRES               3.419337 Hz
AQ                   0.2924544 sec
RG                      106.06
DW                     142.800 usec
DE                       6.50 usec
TE                      303.2 K
D0                   0.00012879 sec
D1                   1.50000000 sec
D8                   1.00000000 sec
D16                  0.00020000 sec
IN0                  0.00028560 sec
TDav                        1
SFO1                500.1318505 MHz
NUC1                       1H
P1                      11.00 usec
P2                      22.00 usec
PLW1                15.84899998 W
GPNAM[1]          SMSQ10.100
GPZ1                    40.00 %
P16                   1000.00 usec

F1 - Acquisition parameters
TD                         192
SFO1                500.1319 MHz
FIDRES              53.051525 Hz
SW                      7.001 ppm
FnMODE                   TPPI

F2 - Processing parameters
SI                       2048
SF                  500.1300129 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
PC                      1.40

F1 - Processing parameters
SI                       2048
MC2                      TPPI
SF                  500.1300111 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
```

Figure S33. NOESY spectrum (500 MHz, CD_3OD) of **6**

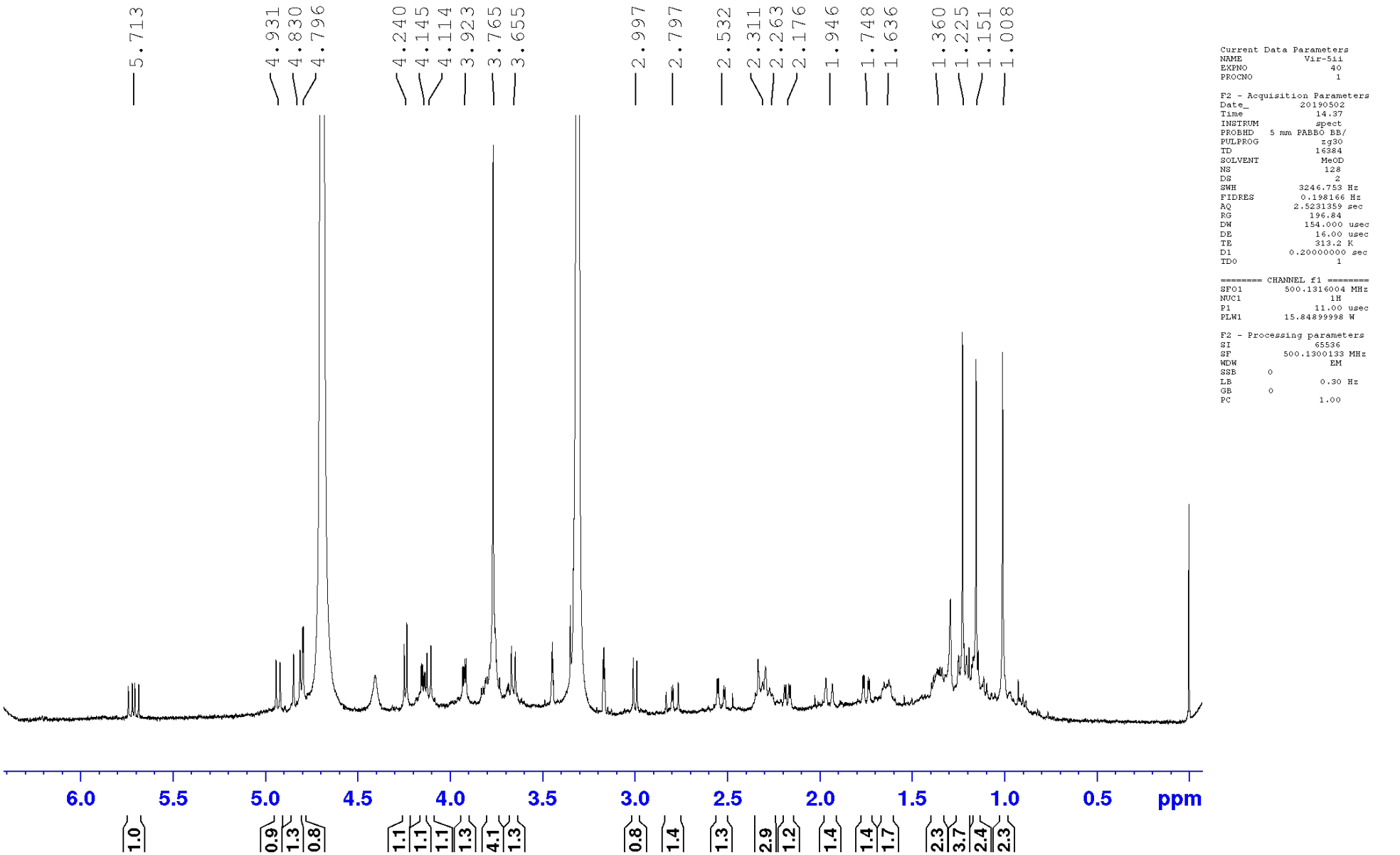


Figure S34. ^{1}H NMR spectrum (700 MHz, CD_3OD) of **7**

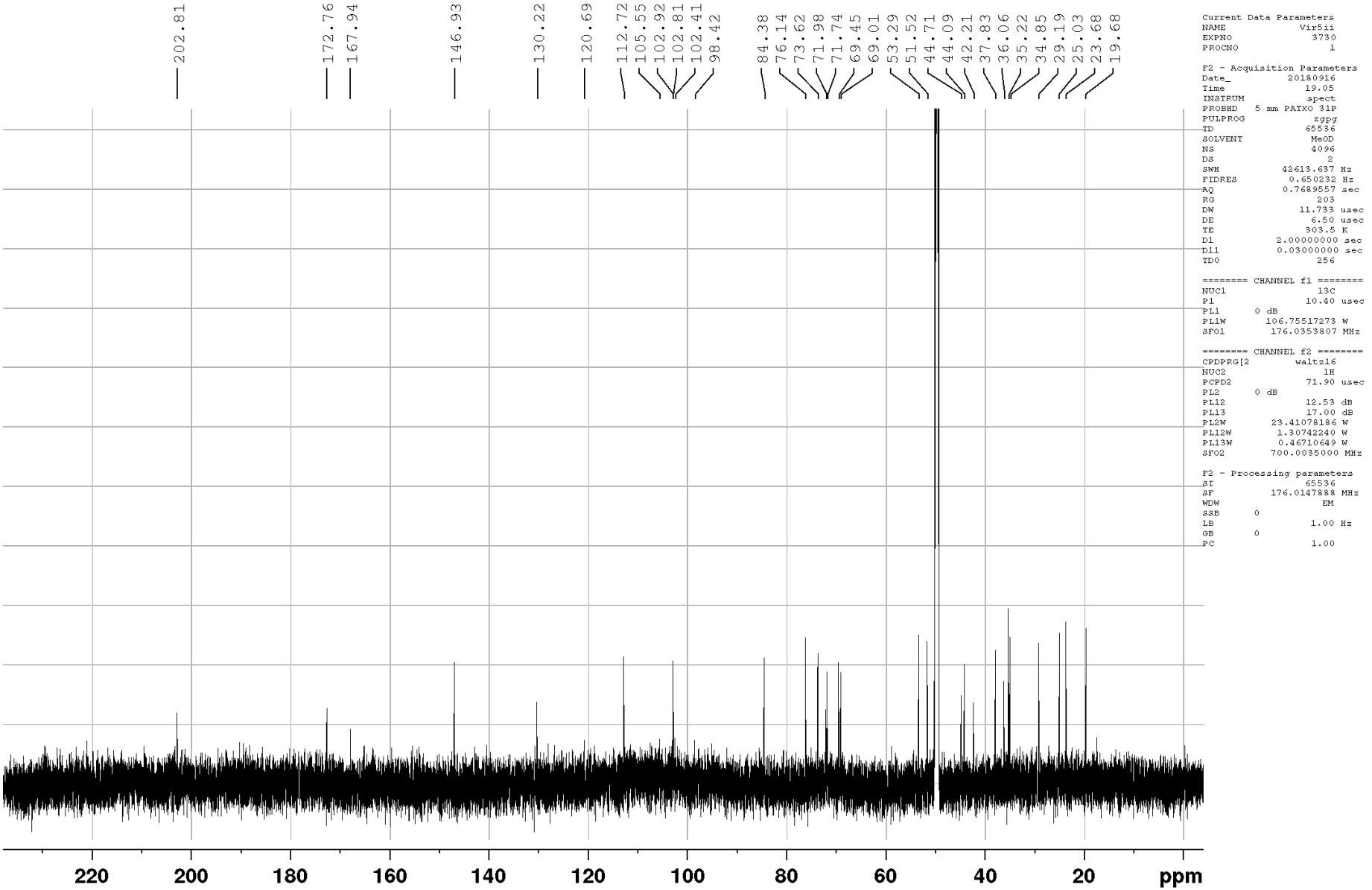
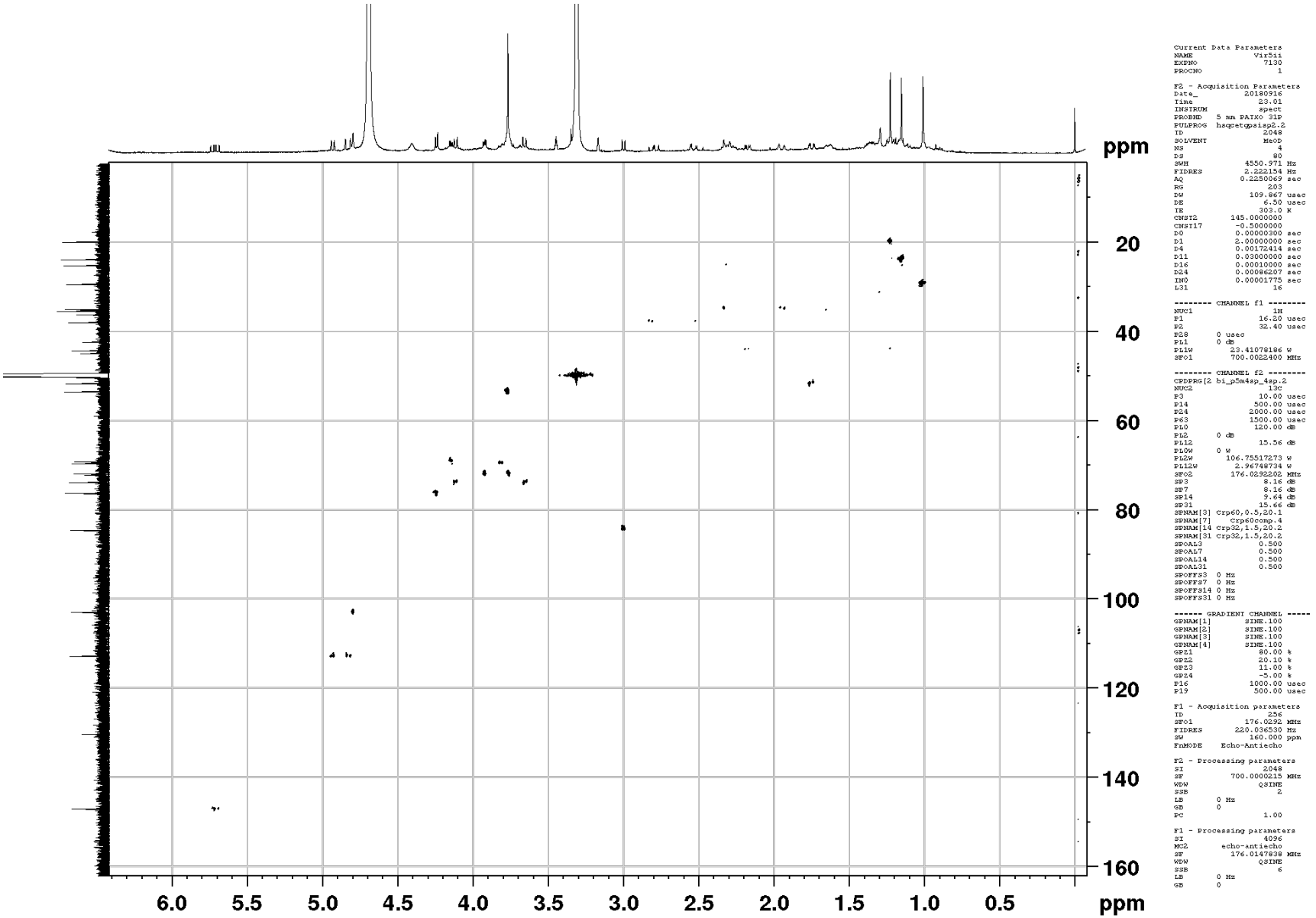
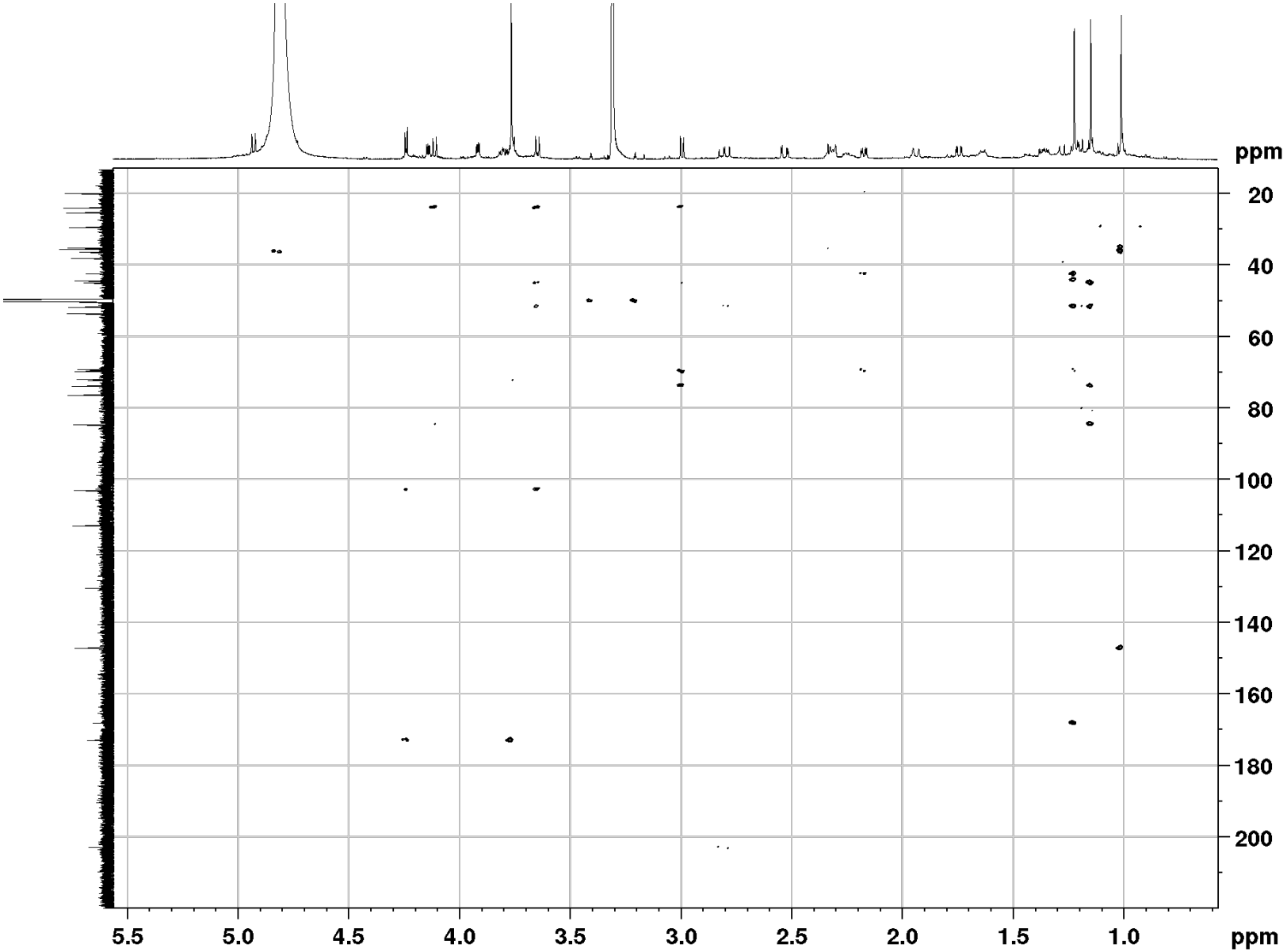


Figure S35. ^{13}C NMR spectrum (176 MHz, CD_3OD) of **7**



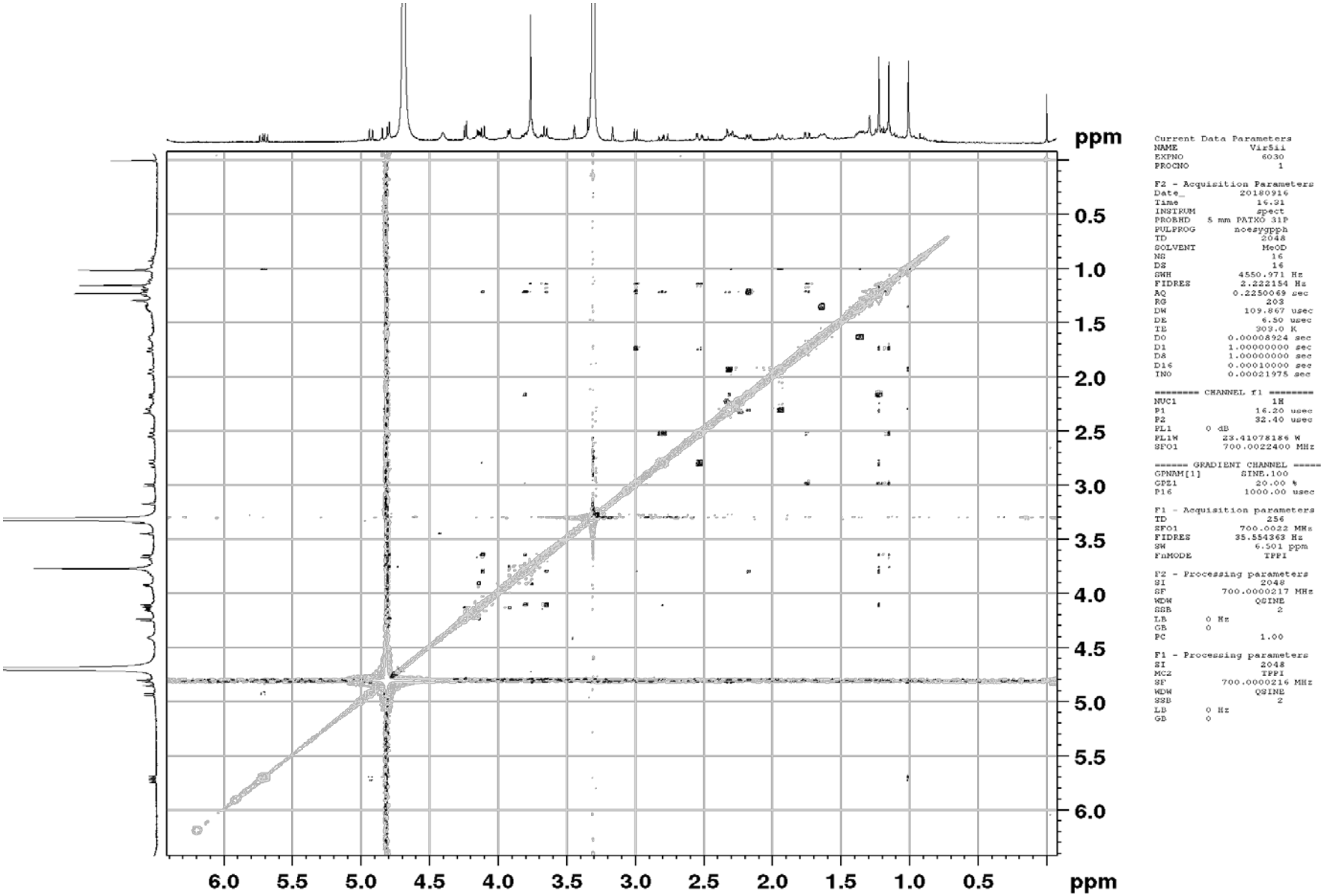

```
Current Data Parameters
NAME                  Vir5ii
EXPNO                   7130
PROCNO                     1

F2 - Acquisition Parameters
Date_              20180916
Time                  23.01
INSTRUM               spect
PROBHD    5 mm PATXO 31P
PULPROG  hsqcetgpsisp2.2
TD                     2048
SOLVENT                MeOD
NS                        4
DS                       80
SWH                4550.971 Hz
FIDRES             2.222154 Hz
AQ                 0.2250069 sec
RG                      203
DW                   109.867 usec
DE                     6.50 usec
TE                    303.0 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                    16.20 usec
P2                    32.40 usec
PL1         0 usec
PL1         0 dB
PL1W           23.41078186 W
SFO1          700.0022400 MHz

-------- CHANNEL f2 --------
CPDPRG[2 bi_p5m4sp_4sp.2
NUC2                    13C
P3                   10.00 usec
P14                 500.00 usec
P24                2000.00 usec
P63                1500.00 usec
PL0                 120.00 dB
PL2         0 dB
PL12                  15.56 dB
PL0W        0 W
PL2W          106.75517273 W
PL12W           2.96748734 W
SFO2          176.0292202 MHz
SP3                    8.16 dB
SP7                    8.16 dB
SP14                   9.64 dB
SP31                  15.66 dB
SPNAM[3] Crp60,0.5,20.1
SPNAM[7]      Crp60comp.4
SPNAM[14 Crp32,1.5,20.2
SPNAM[31 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 -----
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPNAM[3]          SINE.100
GPNAM[4]          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             176.0292 MHz
FIDRES         220.036530 Hz
SW                 160.000 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                     2048
SF            700.0000215 MHz
WDW                   QSINE
SSB                       2
LB          0 Hz
GB          0
PC                     1.00

F1 - Processing parameters
SI                     4096
MC2         echo-antiecho
SF            176.0147838 MHz
WDW                   QSINE
SSB                       6
LB          0 Hz
GB          0
```

Figure S36. HSQC spectrum (700 MHz, CD_3OD) of **7**




```
Current Data Parameters
NAME                 Vir5ii
EXPNO                  8052
PROCNO                    1

F2 - Acquisition Parameters
Date_              20180916
Time                  23.43
INSTRUM               spect
PROBHD    5 mm PATXO 31P
PULPROG     hmbcgplpndqf
TD                     4096
SOLVENT                MeOD
NS                       96
DS                       16
SWH               11160.714 Hz
FIDRES             2.724784 Hz
AQ                 0.1835008 sec
RG                       203
DW                  44.800 usec
DE                   6.50 usec
TE                  302.9 K
CNST2             145.0000000
CNST13              5.0000000
D0                 0.00000300 sec
D1                 1.50000000 sec
D2                 0.00344828 sec
D6                 0.10000000 sec
D16                0.00010000 sec
IN0                0.00001185 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     16.20 usec
P2                     32.40 usec
PL1       0 dB
PL1W            23.41078186 W
SFO1             700.0022400 MHz

======== CHANNEL f2 ========
NUC2                     13C
P3                     10.00 usec
PL2       0 dB
PL2W           106.75517273 W
SFO2             176.0362608 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPNAM[3]          SINE.100
GPZ1                 50.00 %
GPZ2                 30.00 %
GPZ3                 40.10 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                      194
SFO1              176.0363 MHz
FIDRES          435.553650 Hz
SW                240.000 ppm
FnMODE                    QF

F2 - Processing parameters
SI                     2048
SF             700.0000185 MHz
WDW                    SINE
SSB                       3
LB        0 Hz
GB        0
PC                     1.00

F1 - Processing parameters
SI                     4096
MC2                       QF
SF             176.0147745 MHz
WDW                    SINE
SSB       0
LB        0 Hz
GB        0
```

Figure S37. HMBC spectrum (700 MHz, CD_3OD) of **7**




```
Current Data Parameters
NAME                  Vir5ii
EXPNO                   6030
PROCNO                     1

F2 - Acquisition Parameters
Date_               20180916
Time                   14.21
INSTRUM                spect
PROBHD    5 mm PATXO 31P
PULPROG          noesygpph
TD                      2048
SOLVENT                 MeOD
NS                        16
DS                        16
SWH                 4550.971 Hz
FIDRES              2.222154 Hz
AQ                  0.2250069 sec
RG                        203
DW                  109.867 usec
DE                    6.50 usec
TE                    303.0 K
D0                  0.00008924 sec
D1                  1.00000000 sec
D8                  1.00000000 sec
D16                 0.00010000 sec
IN0                 0.00021975 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     16.20 usec
P2                     32.40 usec
PL1         0 dB
PL1W          23.41078186 W
SFO1          700.0022400 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]           SINE.100
GPZ1                  20.00 %
P16                 1000.00 usec

F1 - Acquisition parameters
TD                       256
SFO1              700.0022 MHz
FIDRES            35.554363 Hz
SW                    6.501 ppm
FnMODE                 TPPI

F2 - Processing parameters
SI                      2048
SF              700.0000217 MHz
WDW                    QSINE
SSB                        2
LB          0 Hz
GB          0
PC                      1.00

F1 - Processing parameters
SI                      2048
MC2                     TPPI
SF              700.0000216 MHz
WDW                    QSINE
SSB                        2
LB          0 Hz
GB          0
```

Figure S38. NOESY spectrum (700 MHz, CD_3OD) of **7**

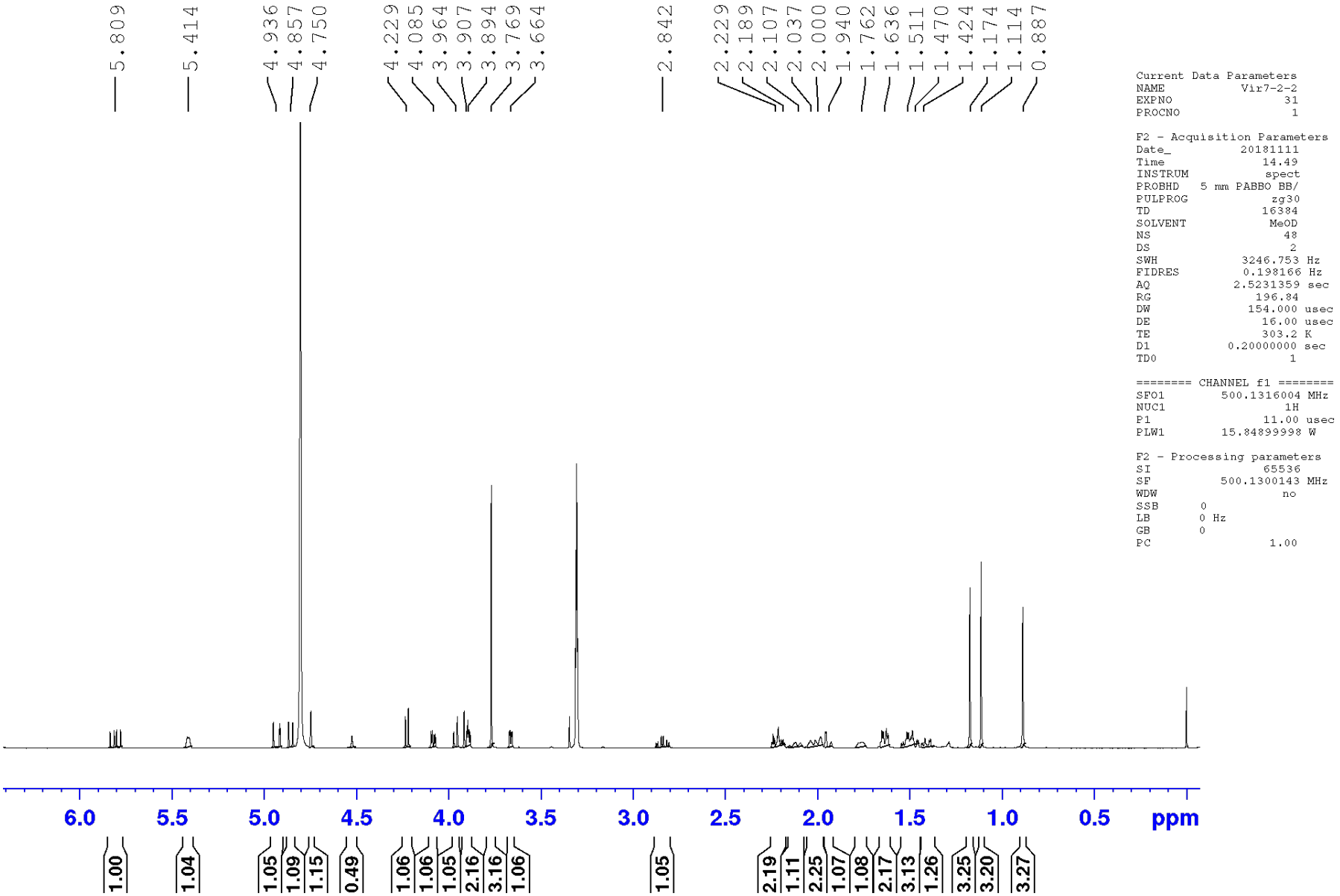
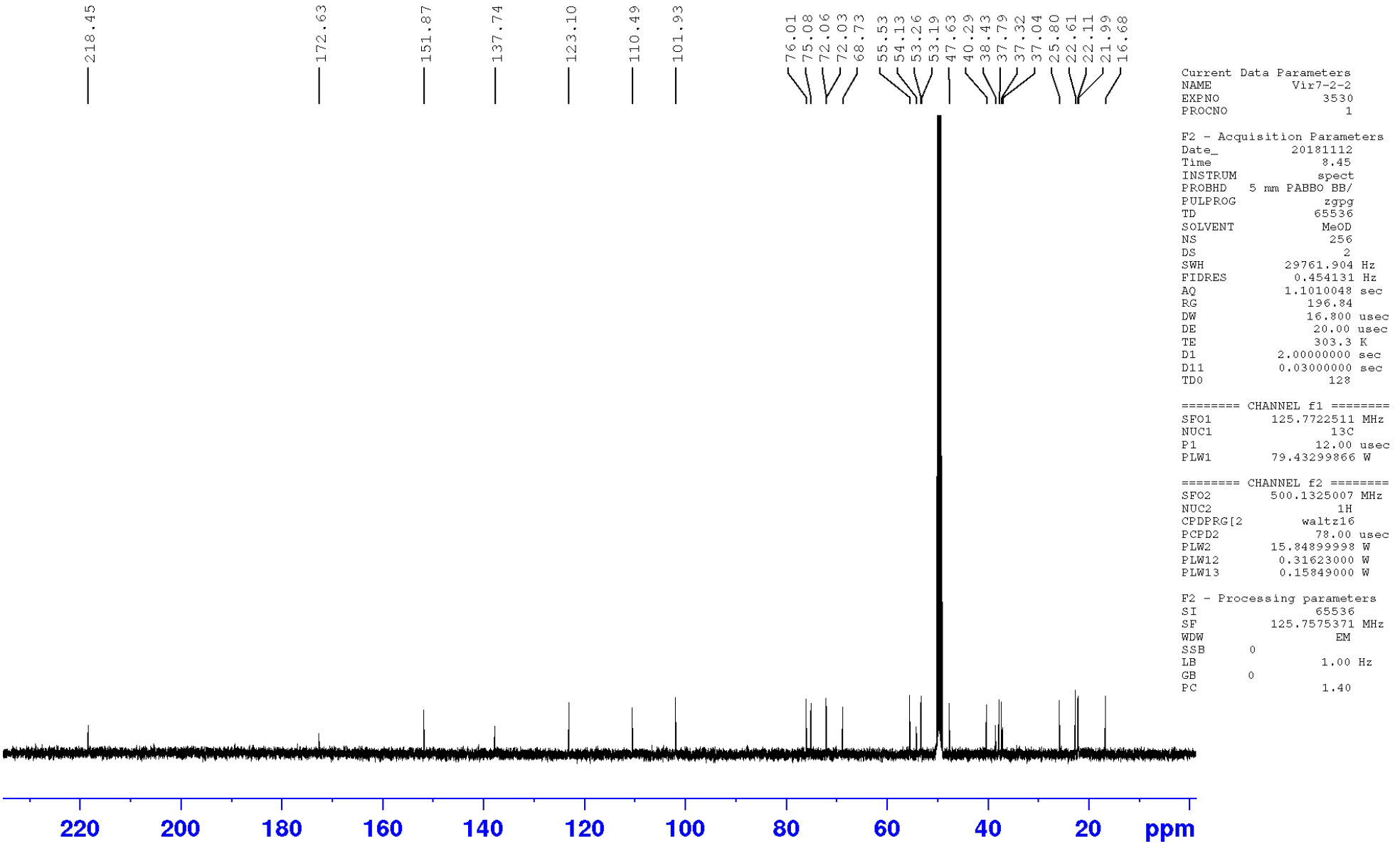


Figure S39. ^{1}H NMR spectrum (500 MHz, CD_3OD) of **8**




```
Current Data Parameters
NAME                  Vir7-2-2
EXPNO                     3530
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20181112
Time                      8.45
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                  zgpg
TD                      65536
SOLVENT                  MeOD
NS                        256
DS                          2
SWH                 29761.904 Hz
FIDRES               0.454131 Hz
AQ                   1.1010048 sec
RG                      196.84
DW                     16.800 usec
DE                     20.00 usec
TE                      303.3 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        128

======== CHANNEL f1 ========
SFO1               125.7722511 MHz
NUC1                       13C
P1                      12.00 usec
PLW1               79.43299866 W

======== CHANNEL f2 ========
SFO2               500.1325007 MHz
NUC2                       1H
CPDPRG[2               waltz16
PCPD2                   78.00 usec
PLW2               15.84899998 W
PLW12               0.31623000 W
PLW13               0.15849000 W

F2 - Processing parameters
SI                        65536
SF                 125.7575371 MHz
WDW                          EM
SSB           0
LB                       1.00 Hz
GB            0
PC                       1.40
```

Figure S40. ^{13}C NMR spectrum (125 MHz, CD_3OD) of **8**

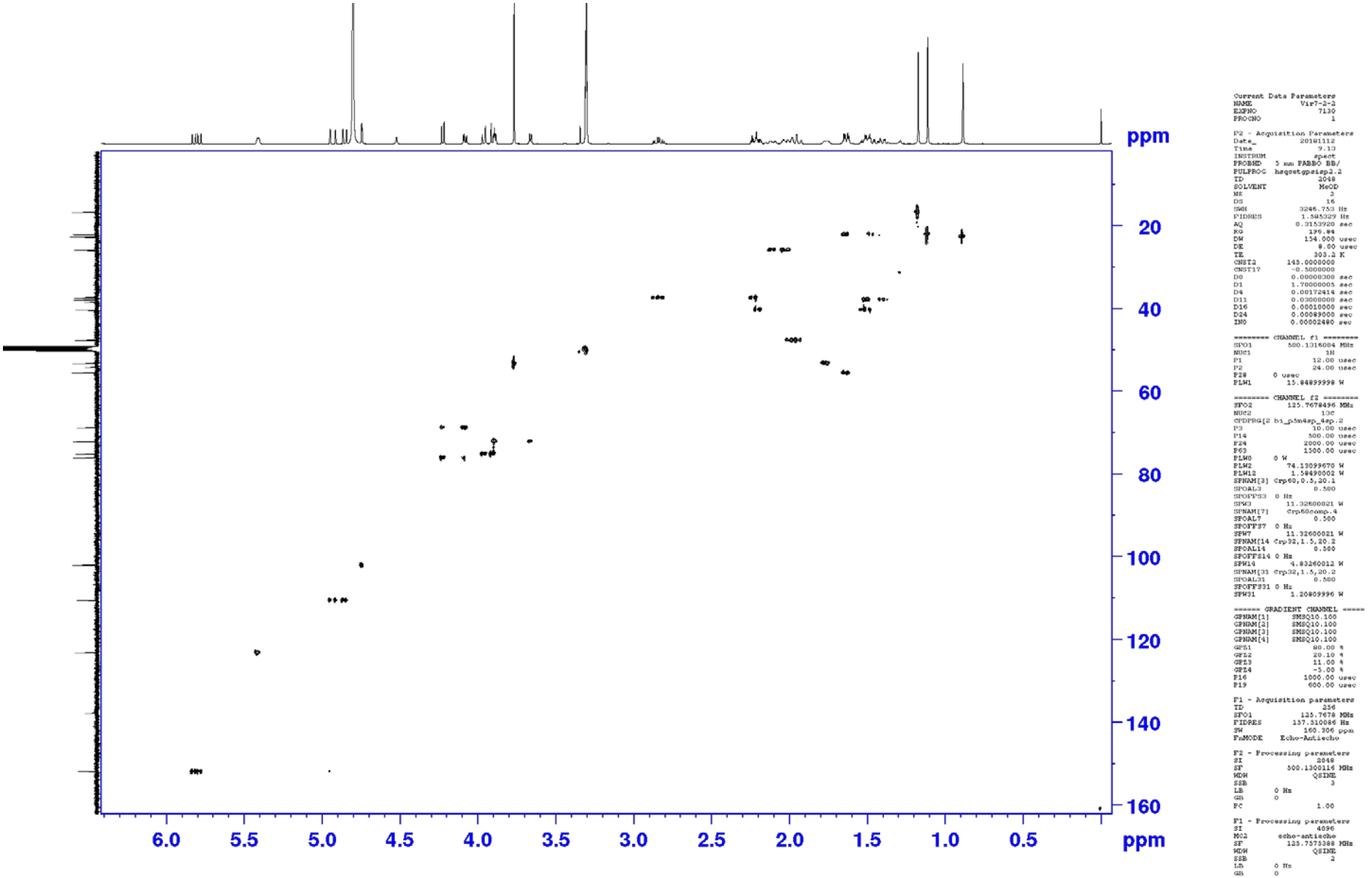
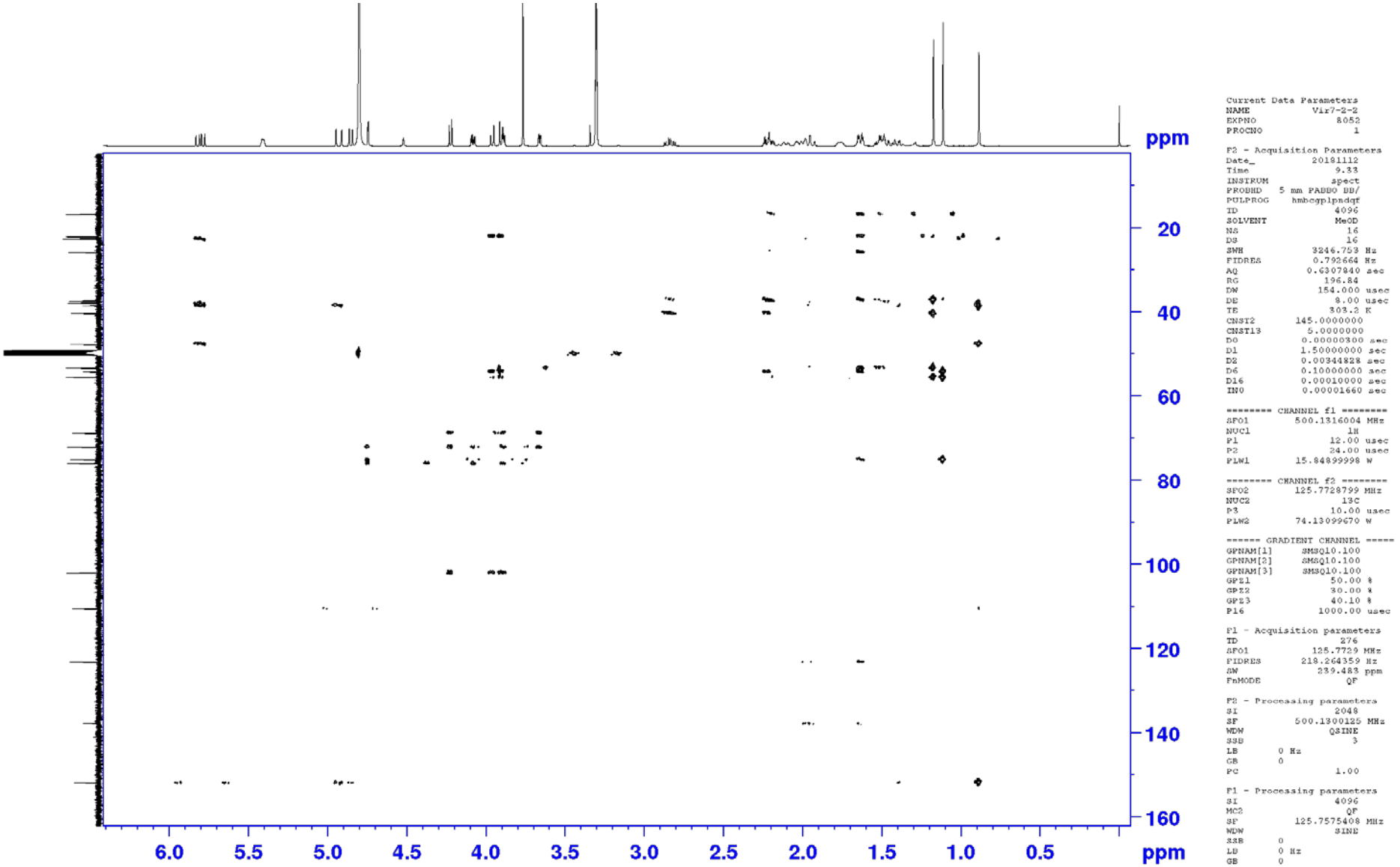
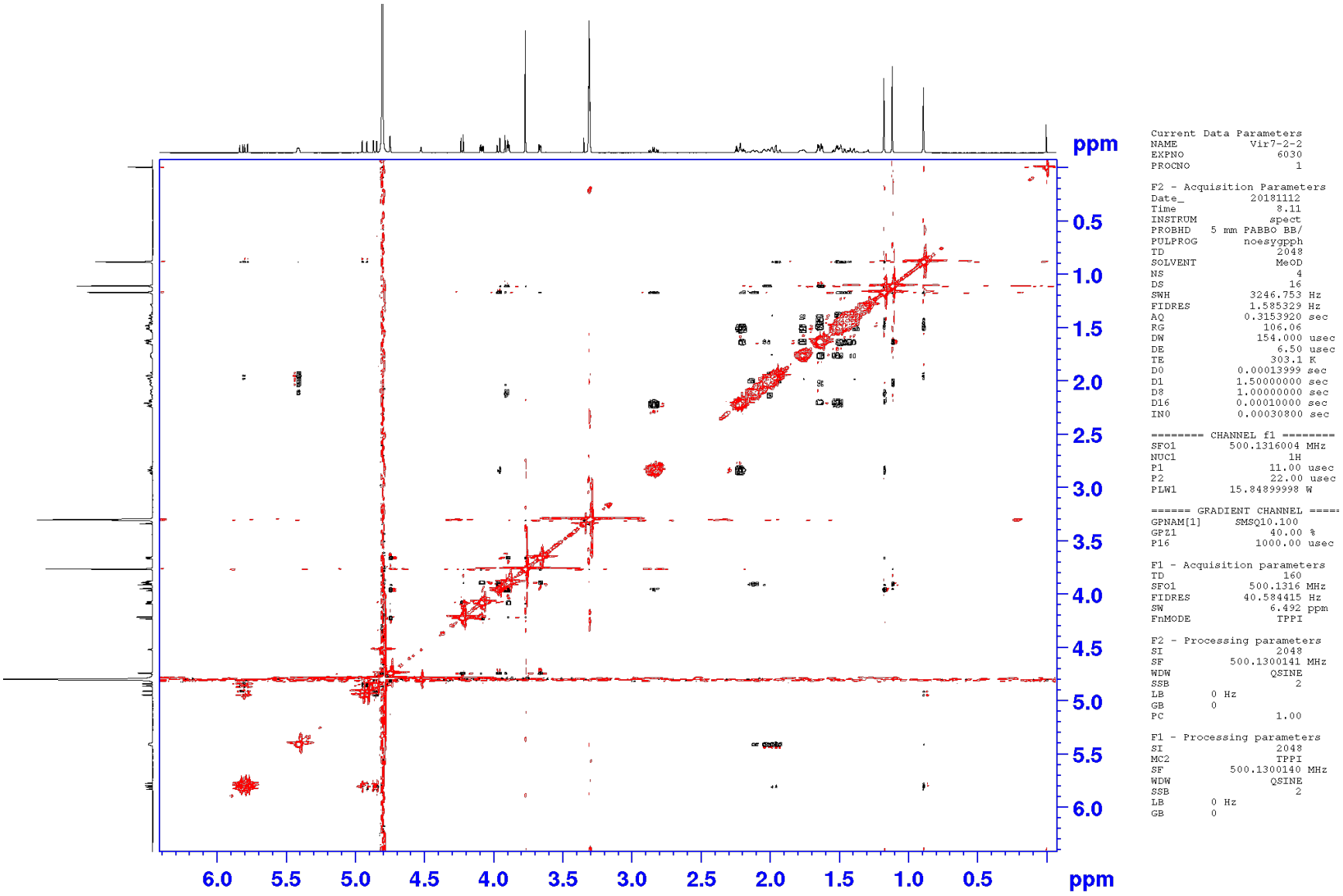


Figure S41. HSQC spectrum (500 MHz, CD_3OD) of **8**




```
Current Data Parameters
NAME                  Vir7-2-2
EXPNO                     8052
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20181112
Time                      9.33
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG     hmbcgplpndqf
TD                        4096
SOLVENT                   MeOD
NS                          16
DS                          16
SWH                 3246.753 Hz
FIDRES              0.792664 Hz
AQ                  0.6307840 sec
RG                      196.84
DW                     154.000 usec
DE                       8.00 usec
TE                      303.2 K
CNST2               145.0000000
CNST13                5.0000000
D0                  0.00000300 sec
D1                  1.50000000 sec
D2                  0.00344828 sec
D6                  0.10000000 sec
D16                 0.00010000 sec
IN0                 0.00001660 sec

======== CHANNEL f1 ========
SFO1                500.1316004 MHz
NUC1                        1H
P1                       12.00 usec
P2                       24.00 usec
PLW1                15.84899998 W

======== CHANNEL f2 ========
SFO2                125.7728799 MHz
NUC2                        13C
P3                       10.00 usec
PLW2                74.13099670 W

====== GRADIENT CHANNEL =====
GPNAM[1]              SMSQ10.100
GPNAM[2]              SMSQ10.100
GPNAM[3]              SMSQ10.100
GPZ1                     50.00 %
GPZ2                     30.00 %
GPZ3                     40.10 %
P16                    1000.00 usec

F1 - Acquisition parameters
TD                          276
SFO1                125.7729 MHz
FIDRES              218.264359 Hz
SW                      239.483 ppm
FnMODE                       QF

F2 - Processing parameters
SI                          2048
SF                  500.1300125 MHz
WDW                       QSINE
SSB                           3
LB          0 Hz
GB          0
PC                         1.00

F1 - Processing parameters
SI                          4096
MC2                          QF
SF                  125.7575408 MHz
WDW                       SINE
SSB         0
LB          0 Hz
GB          0
```

Figure S42. HMBC spectrum (500 MHz, CD_3OD) of **8**




```
Current Data Parameters
NAME                 Vir7-2-2
EXPNO                    6030
PROCNO                      1

F2 - Acquisition Parameters
Date_                20181112
Time                     8.11
INSTRUM                 spect
PROBHD    5 mm PABBO BB/
PULPROG             noesygpph
TD                       2048
SOLVENT                  MeOD
NS                          4
DS                         16
SWH                3246.753 Hz
FIDRES             1.585329 Hz
AQ                 0.3153920 sec
RG                    106.06
DW                   154.000 usec
DE                     6.50 usec
TE                    303.1 K
D0                 0.00013999 sec
D1                 1.50000000 sec
D8                 1.00000000 sec
D16                0.00010000 sec
IN0                0.00030800 sec

======== CHANNEL f1 ========
SFO1          500.1316004 MHz
NUC1                     1H
P1                    11.00 usec
P2                    22.00 usec
PLW1          15.84899998 W

====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPZ1                 40.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                       160
SFO1              500.1316 MHz
FIDRES           40.584415 Hz
SW                    6.492 ppm
FnMODE                TPPI

F2 - Processing parameters
SI                       2048
SF              500.1300141 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
PC                       1.00

F1 - Processing parameters
SI                       2048
MC2                      TPPI
SF              500.1300140 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
```

Figure S43. NOESY spectrum (500 MHz, CD_3OD) of **8**

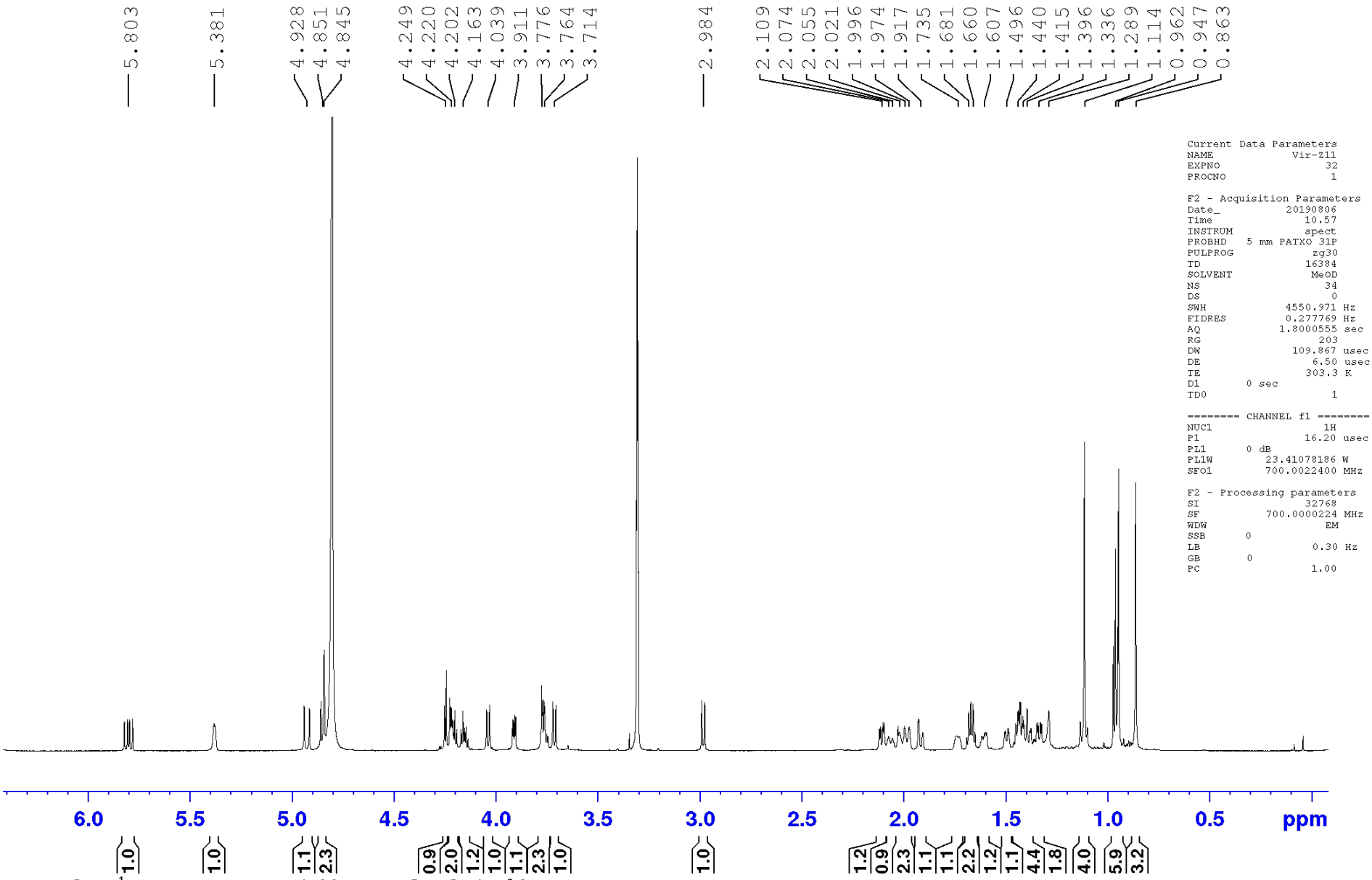


Figure S44. ^{1}H NMR spectrum (700 MHz, CD_3OD) of **9**

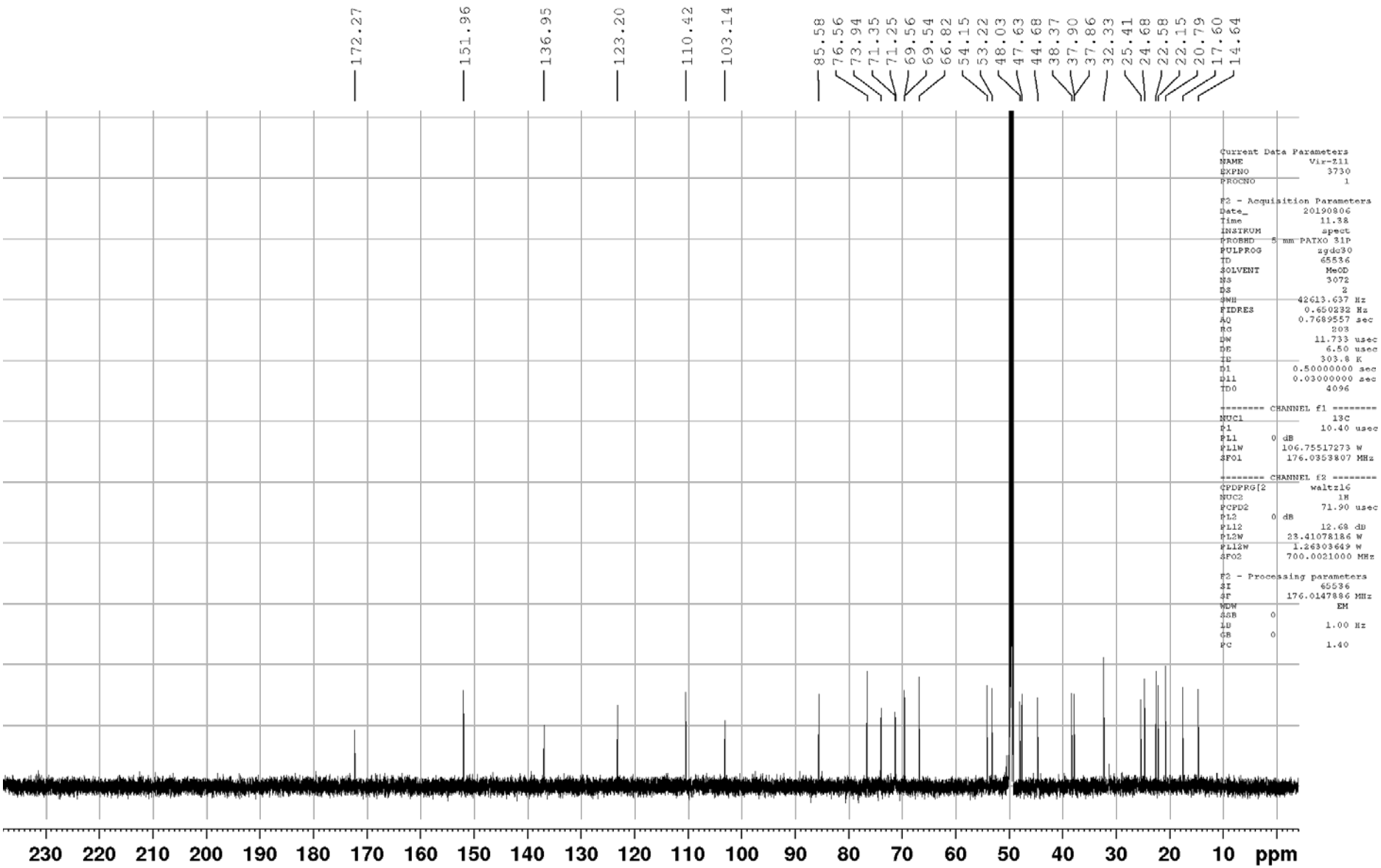


Figure S45. ^{13}C NMR spectrum (176 MHz, CD_3OD) of **9**

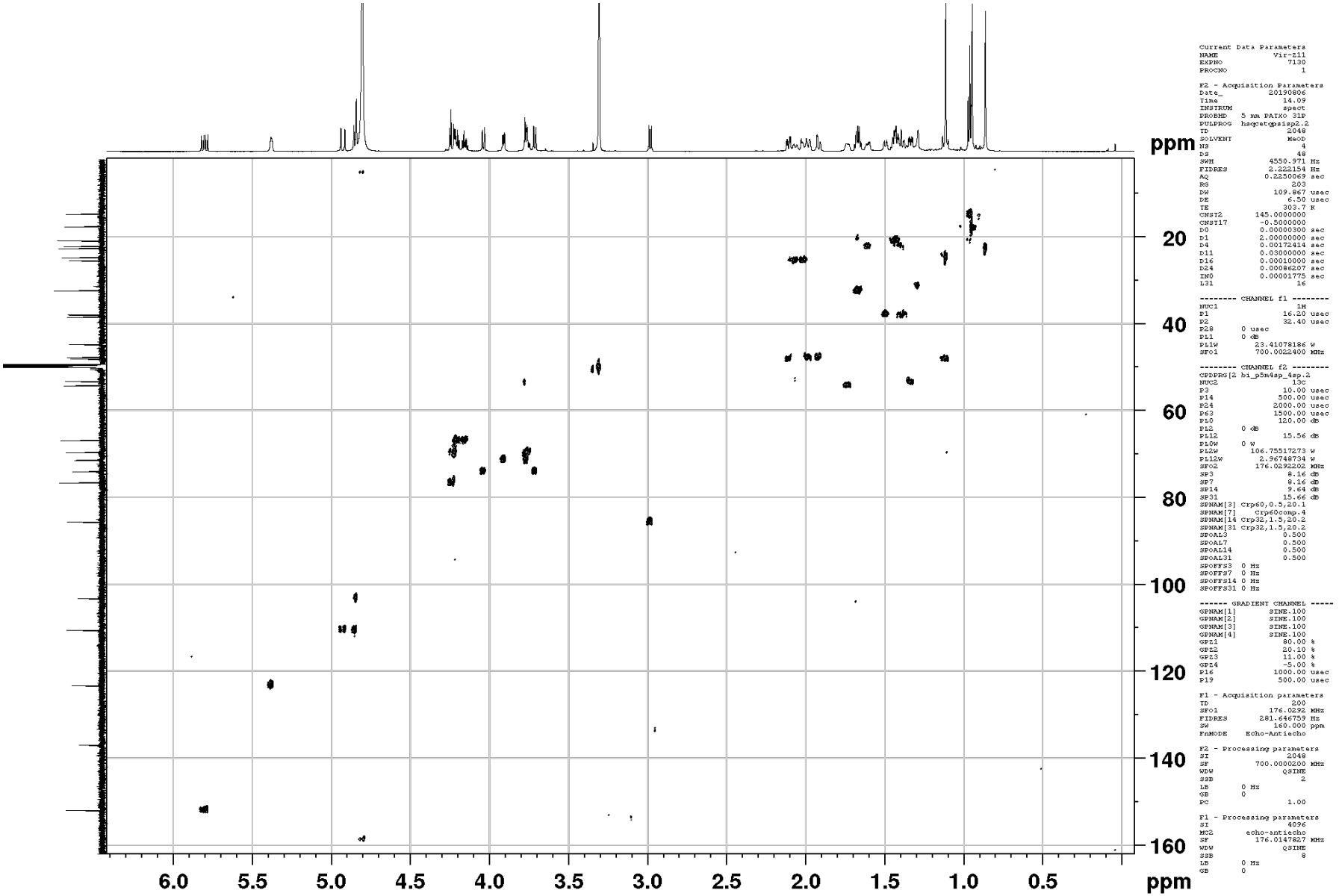


Figure S46. HSQC spectrum (700 MHz, CD_3OD) of **9**

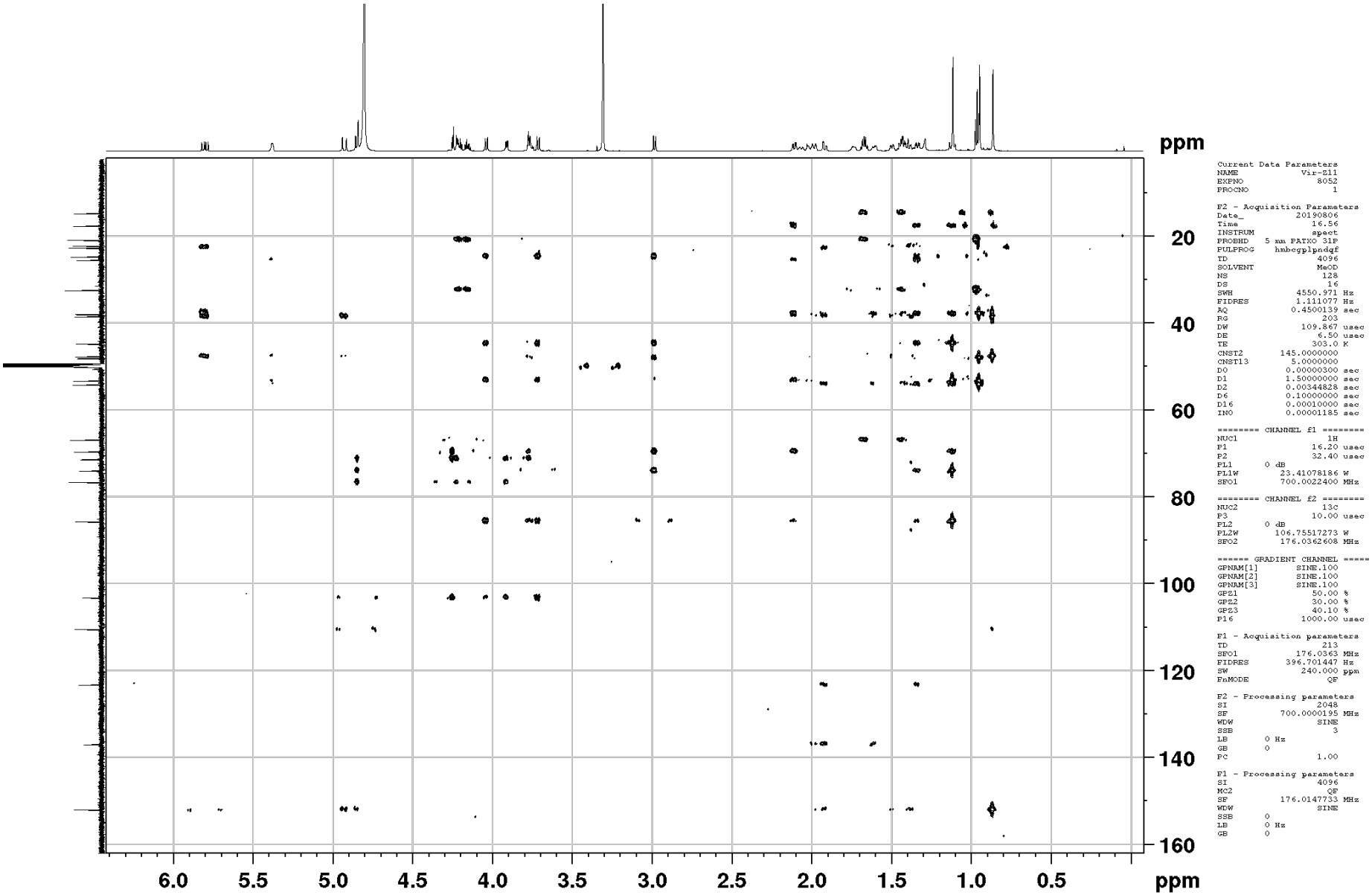
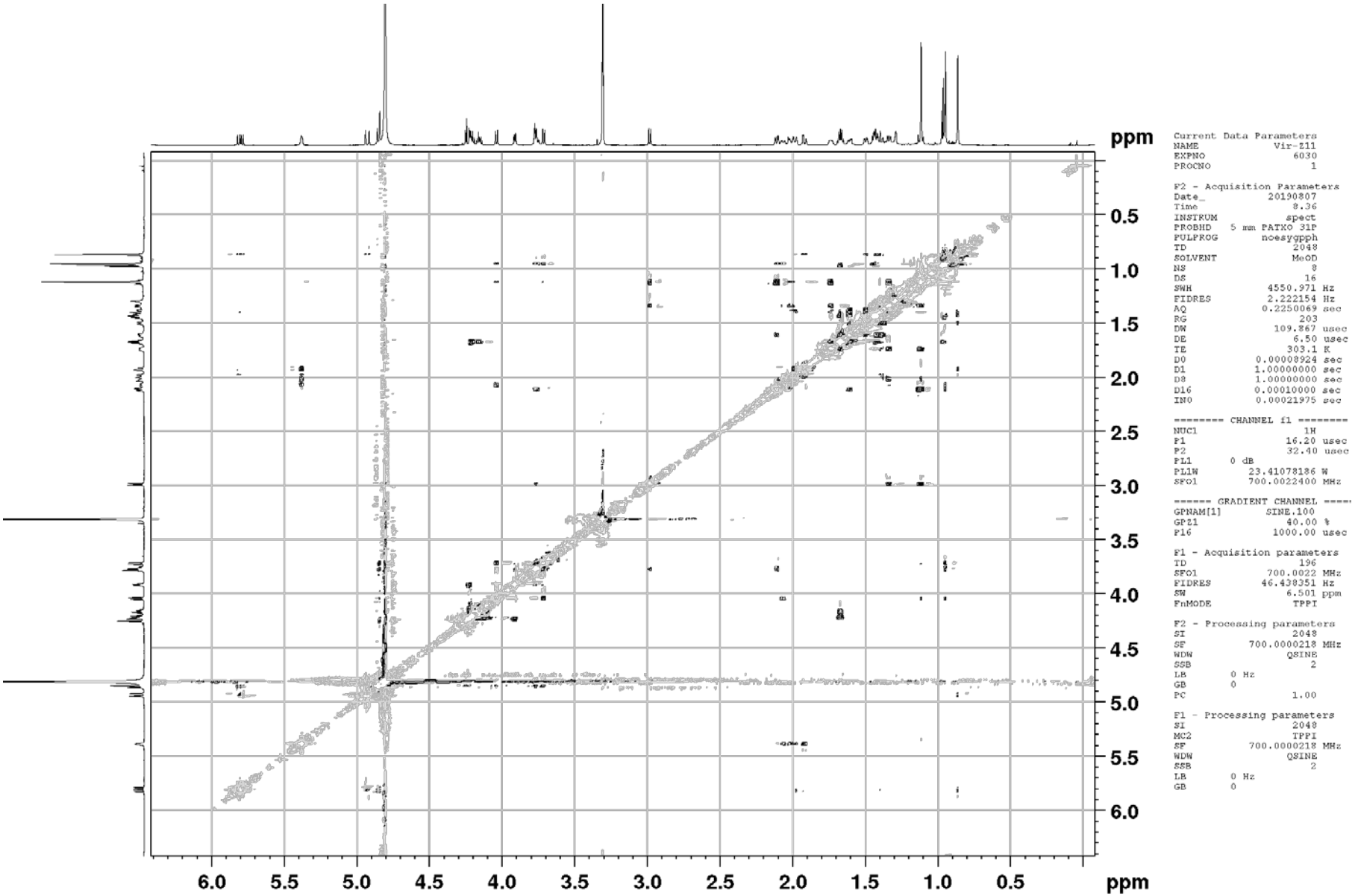


Figure S47. HMBC spectrum (700 MHz, CD_3OD) of **9**




```
Current Data Parameters
NAME                  Vir-Z11
EXPNO                    6030
PROCNO                      1

F2 - Acquisition Parameters
Date_              20190807
Time                    8.36
INSTRUM                spect
PROBHD    5 mm PATXO 31P
PULPROG           noesygpph
TD                       2048
SOLVENT                  MeOD
NS                          8
DS                         16
SWH                  4550.971 Hz
FIDRES               2.222154 Hz
AQ                   0.2250069 sec
RG                         203
DW                     109.867 usec
DE                        6.50 usec
TE                       303.1 K
D0                 0.00008924 sec
D1                 1.00000000 sec
D8                 1.00000000 sec
D16                0.00010000 sec
IN0                0.00021975 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      16.20 usec
P2                      32.40 usec
PL1          0 dB
PL1W            23.41078186 W
SFO1           700.0022400 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPZ1                 40.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                       196
SFO1               700.0022 MHz
FIDRES            46.438351 Hz
SW                    6.501 ppm
FnMODE                 TPPI

F2 - Processing parameters
SI                       2048
SF                700.0000218 MHz
WDW                     QSINE
SSB                          2
LB           0 Hz
GB           0
PC                        1.00

F1 - Processing parameters
SI                       2048
MC2                      TPPI
SF                700.0000218 MHz
WDW                     QSINE
SSB                          2
LB           0 Hz
GB           0
```

Figure S48. NOESY spectrum (700 MHz, CD_3OD) of **9**

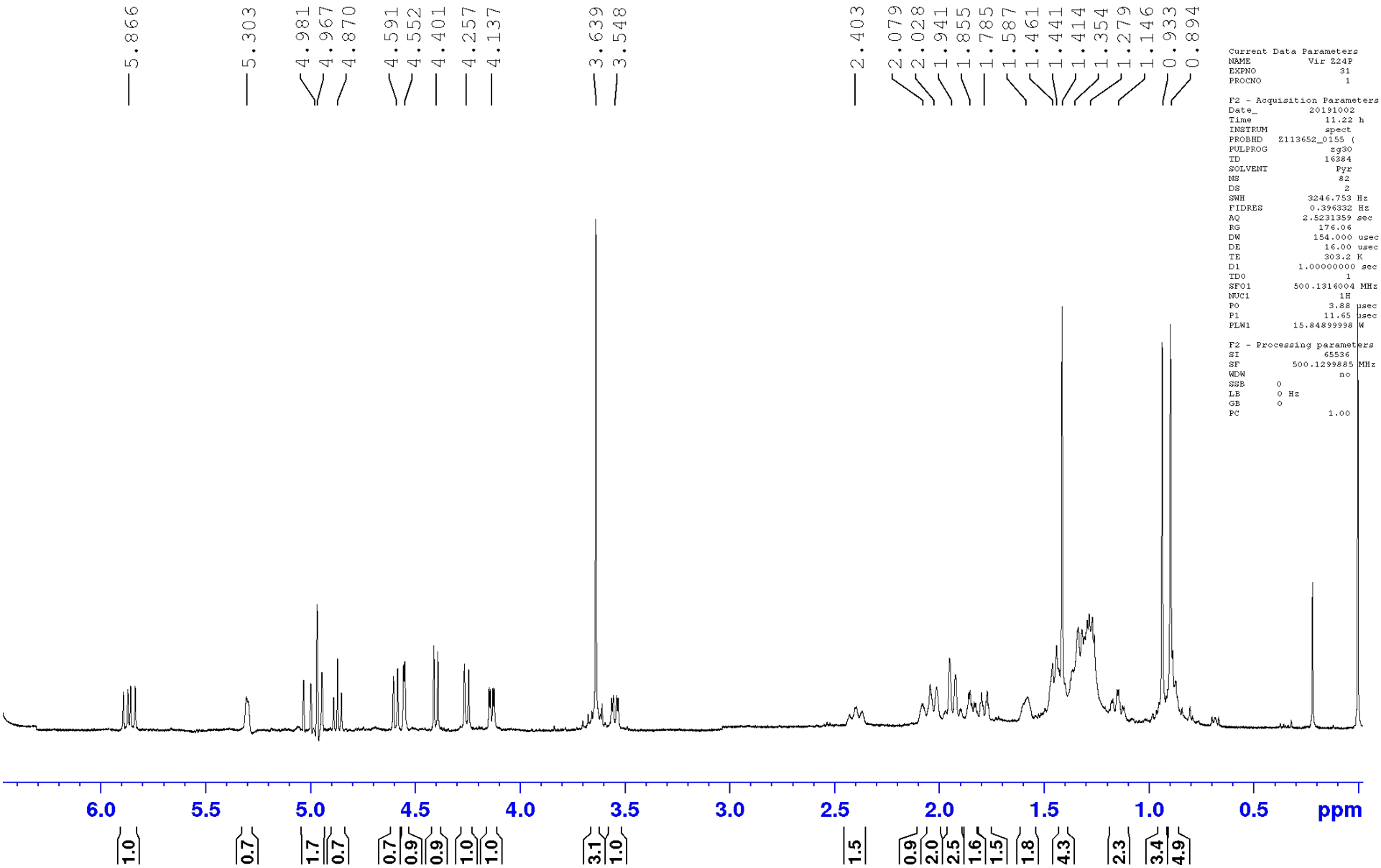


Figure S49. ^{1}H NMR spectrum (500 MHz, Pyr-d_5) of **10**

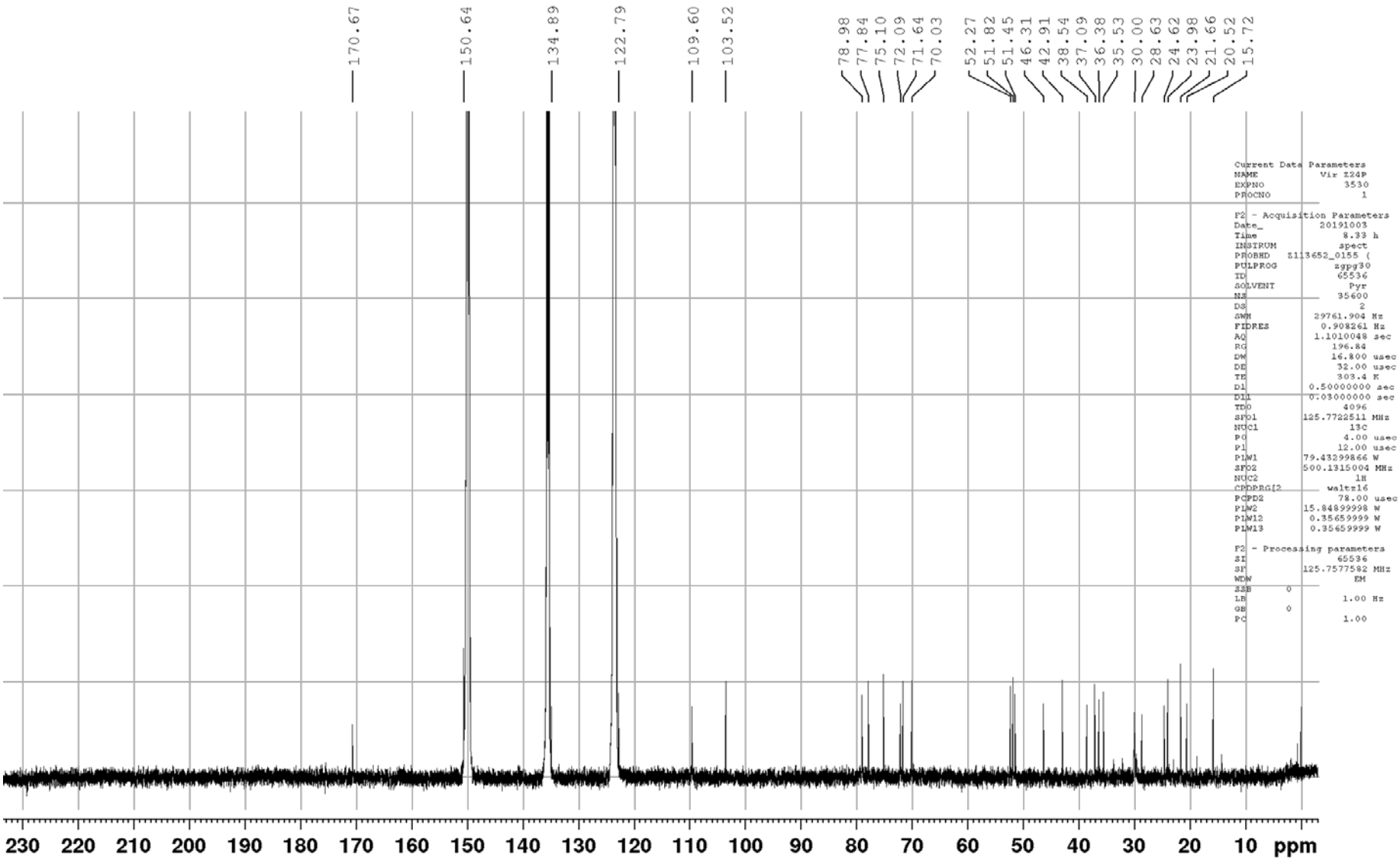
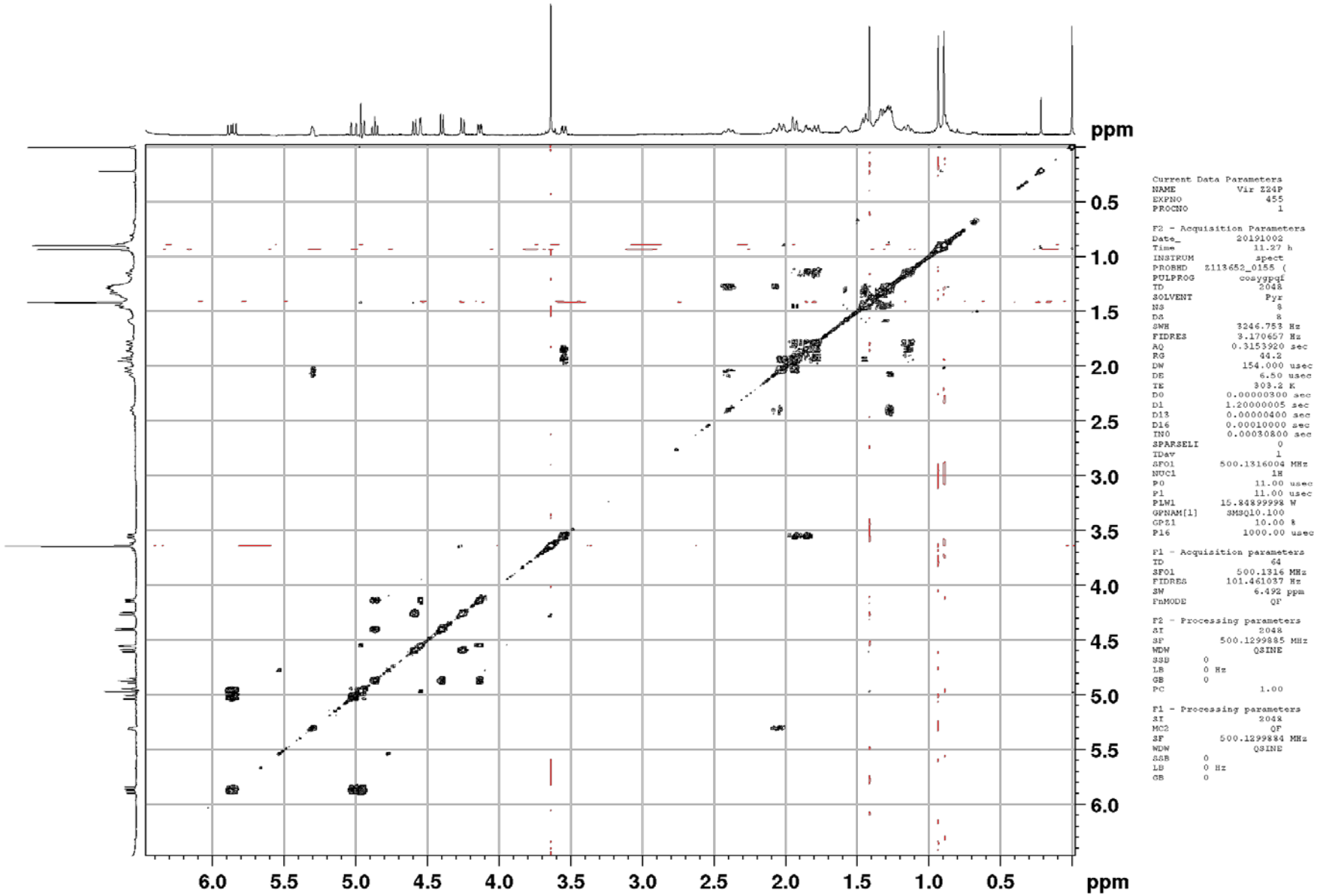


Figure S50. ^{13}C NMR spectrum (125 MHz, Pyr-d_5) of **10**




```
Current Data Parameters
NAME                  Vir Z24P
EXPNO                      455
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20191002
Time                     11.27 h
INSTRUM                   spect
PROBHD    Z113652_0155 (
PULPROG                cosygpqf
TD                         2048
SOLVENT                     Pyr
NS                            8
DS                            8
SWH                    3246.753 Hz
FIDRES                 3.170657 Hz
AQ                     0.3153920 sec
RG                          44.2
DW                      154.000 usec
DE                        6.50 usec
TE                       303.2 K
D0                    0.00000300 sec
D1                    1.20000005 sec
D13                   0.00000400 sec
D16                   0.00010000 sec
IN0                   0.00030800 sec
SPARSELI                      0
TDav                          1
SFO1                500.1316004 MHz
NUC1                        1H
P0                       11.00 usec
P1                       11.00 usec
PLW1                15.84899998 W
GPNAM[1]             SMSQ10.100
GPZ1                     10.00 %
P16                    1000.00 usec

F1 - Acquisition parameters
TD                           64
SFO1                500.1316 MHz
FIDRES               101.461037 Hz
SW                         6.492 ppm
FnMODE                        QF

F2 - Processing parameters
SI                         2048
SF                  500.1299885 MHz
WDW                       QSINE
SSB                0
LB                 0 Hz
GB                 0
PC                         1.00

F1 - Processing parameters
SI                         2048
MC2                           QF
SF                  500.1299884 MHz
WDW                       QSINE
SSB                0
LB                 0 Hz
GB                 0
```

Figure S51. COSY-45 spectrum (500 MHz, Pyr-d_5) of **10**

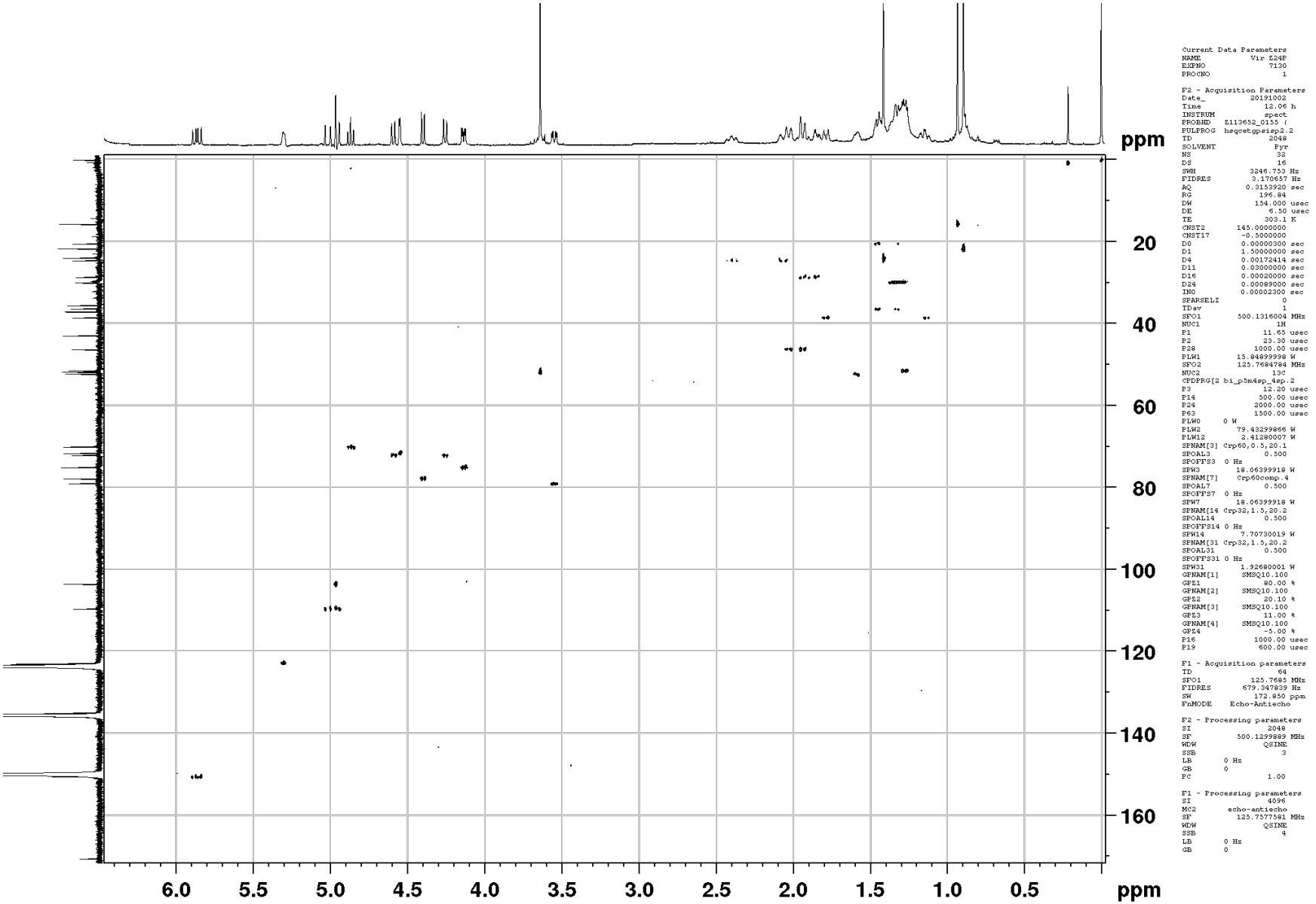


Figure S52. HSQC spectrum (500 MHz, Pyr-d_5) of **10**

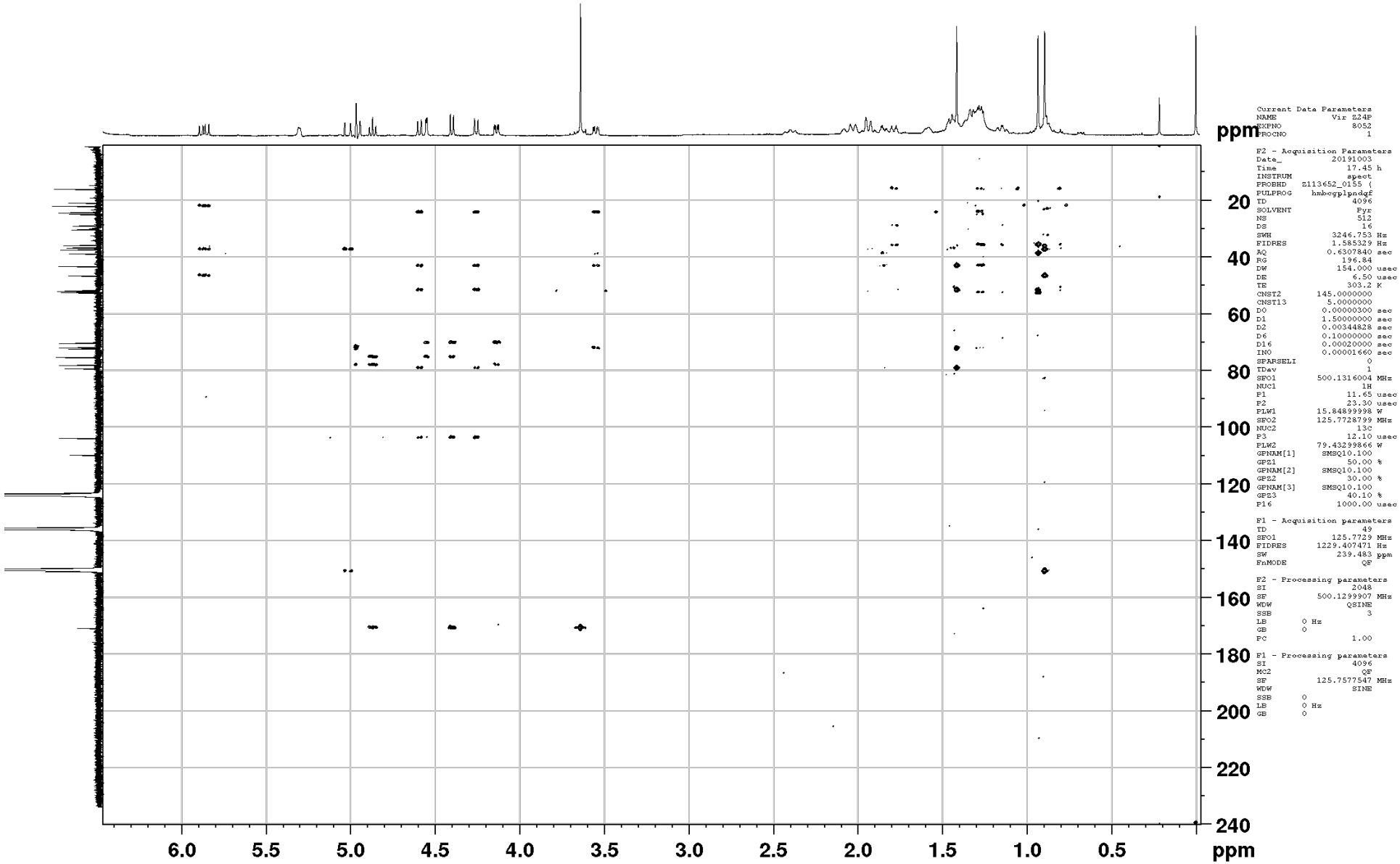


Figure S53. HMBC spectrum (500 MHz, Pyr-d_5) of **10**

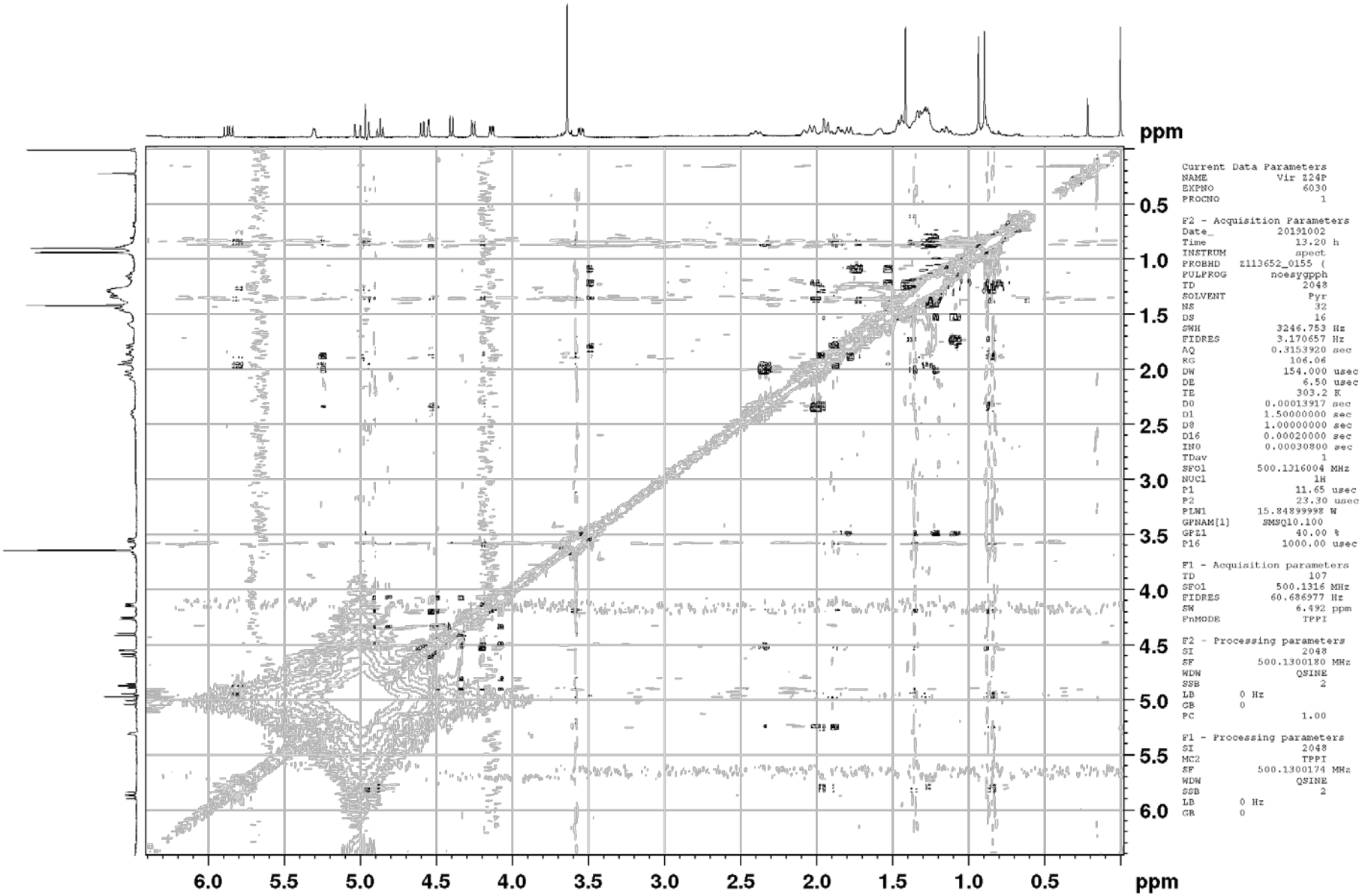


Figure S54. NOESY spectrum (500 MHz, Pyr-d_5) of **10**

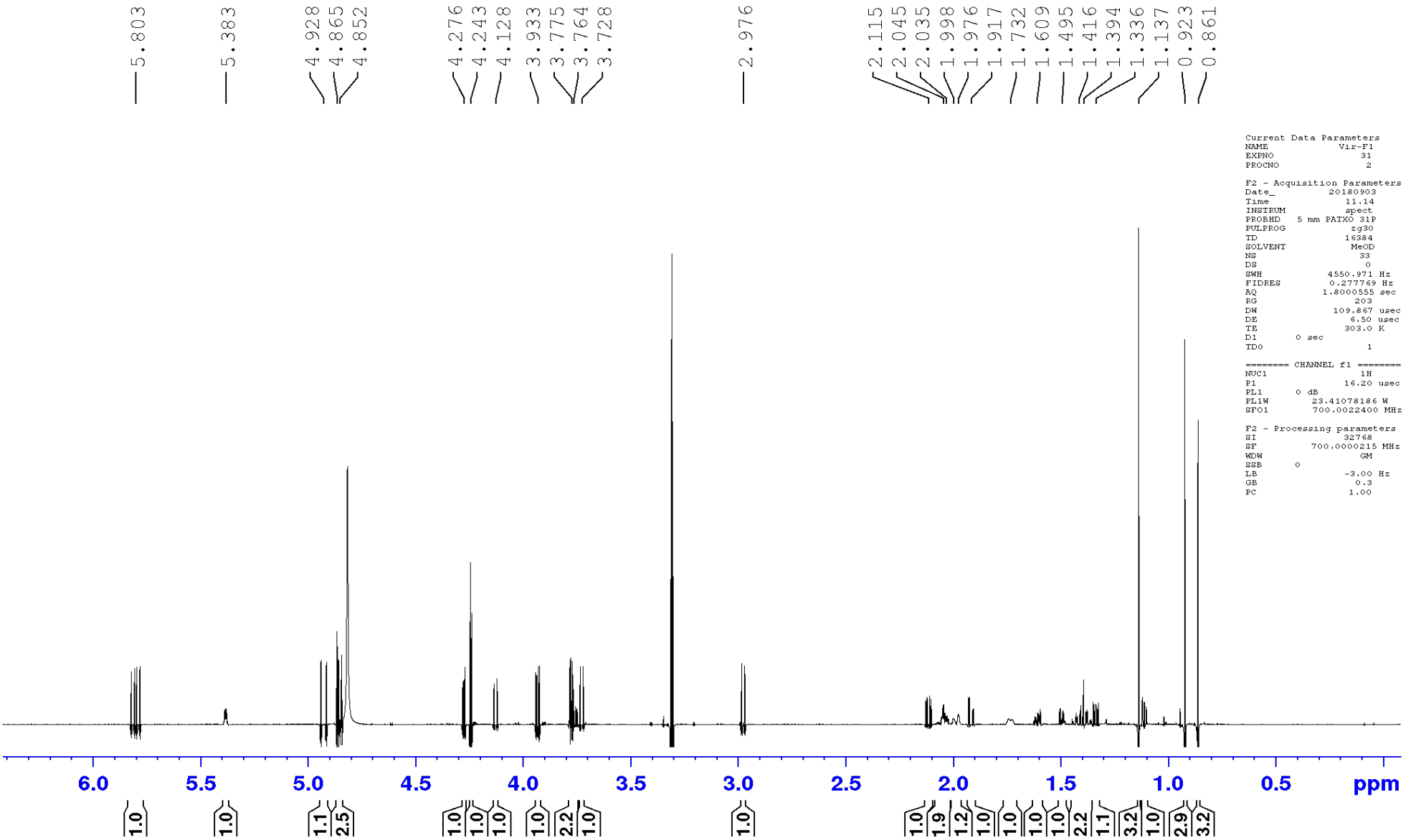


Figure S55. ^{1}H NMR spectrum (700 MHz, CD_3OD) of **11**

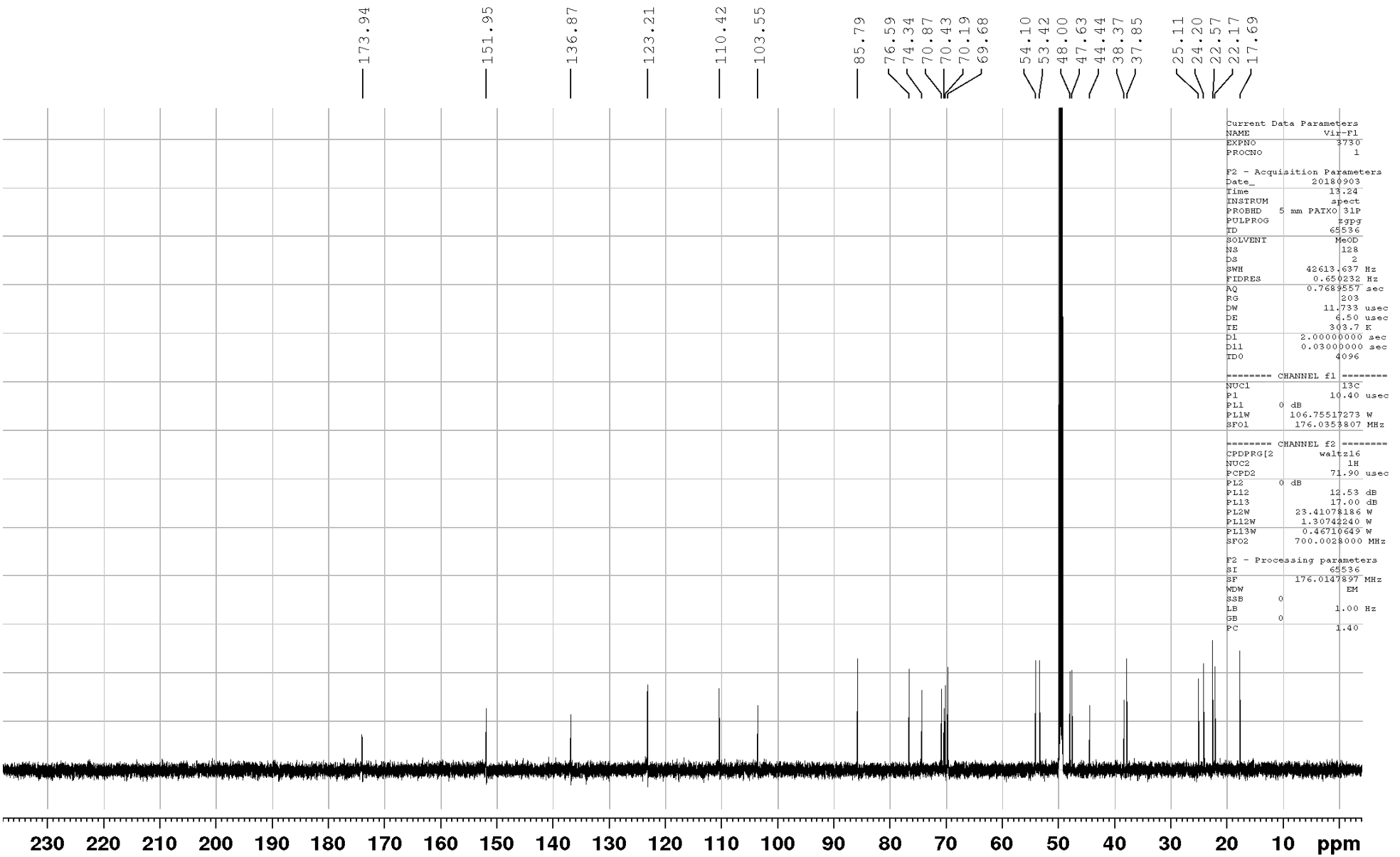


Figure S56. ^{13}C NMR spectrum (176 MHz, CD_3OD) of **11**

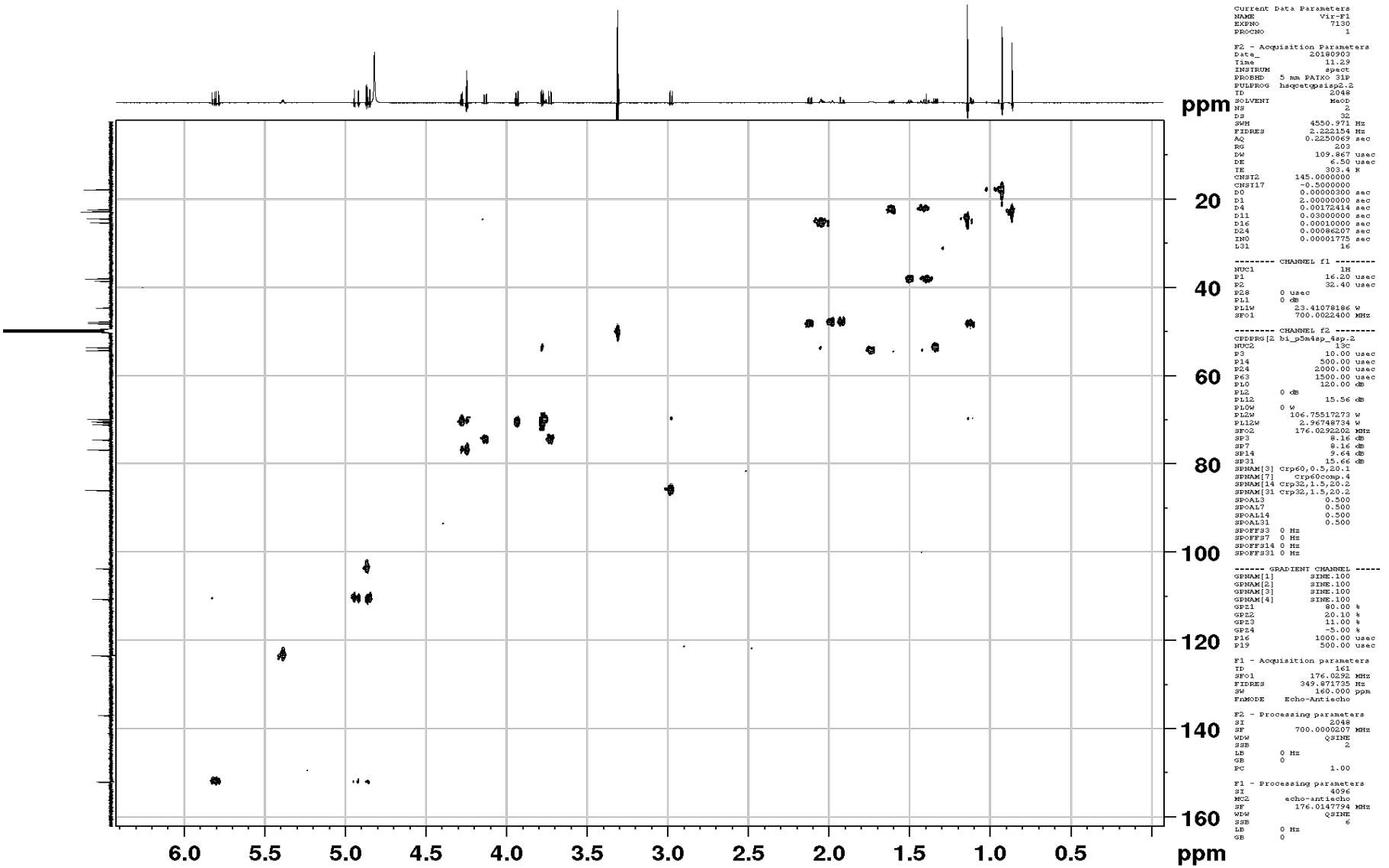


Figure S57. HSQC spectrum (700 MHz, CD_3OD) of **11**

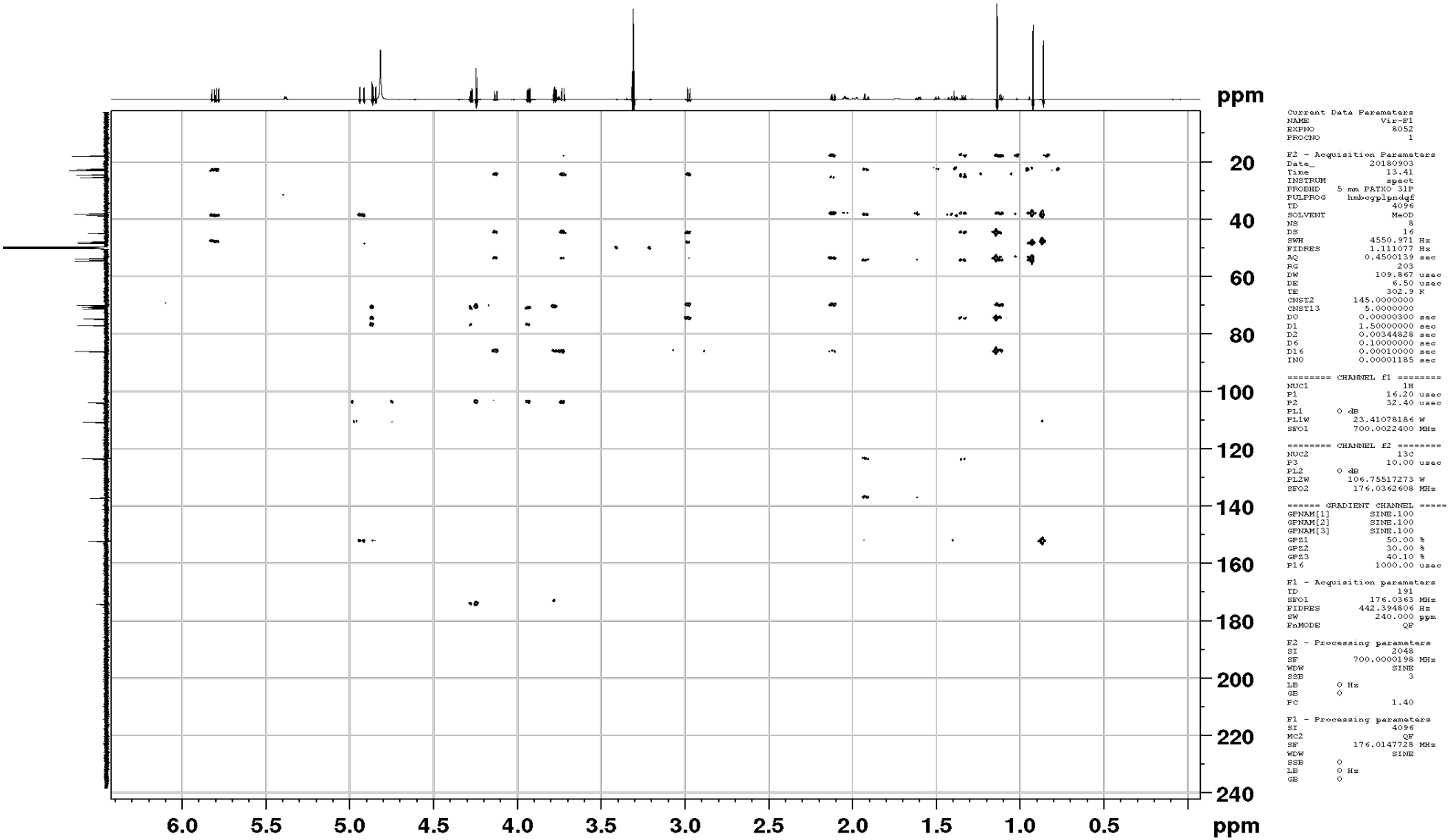


Figure S58. HMBC spectrum (700 MHz, CD_3OD) of **11**

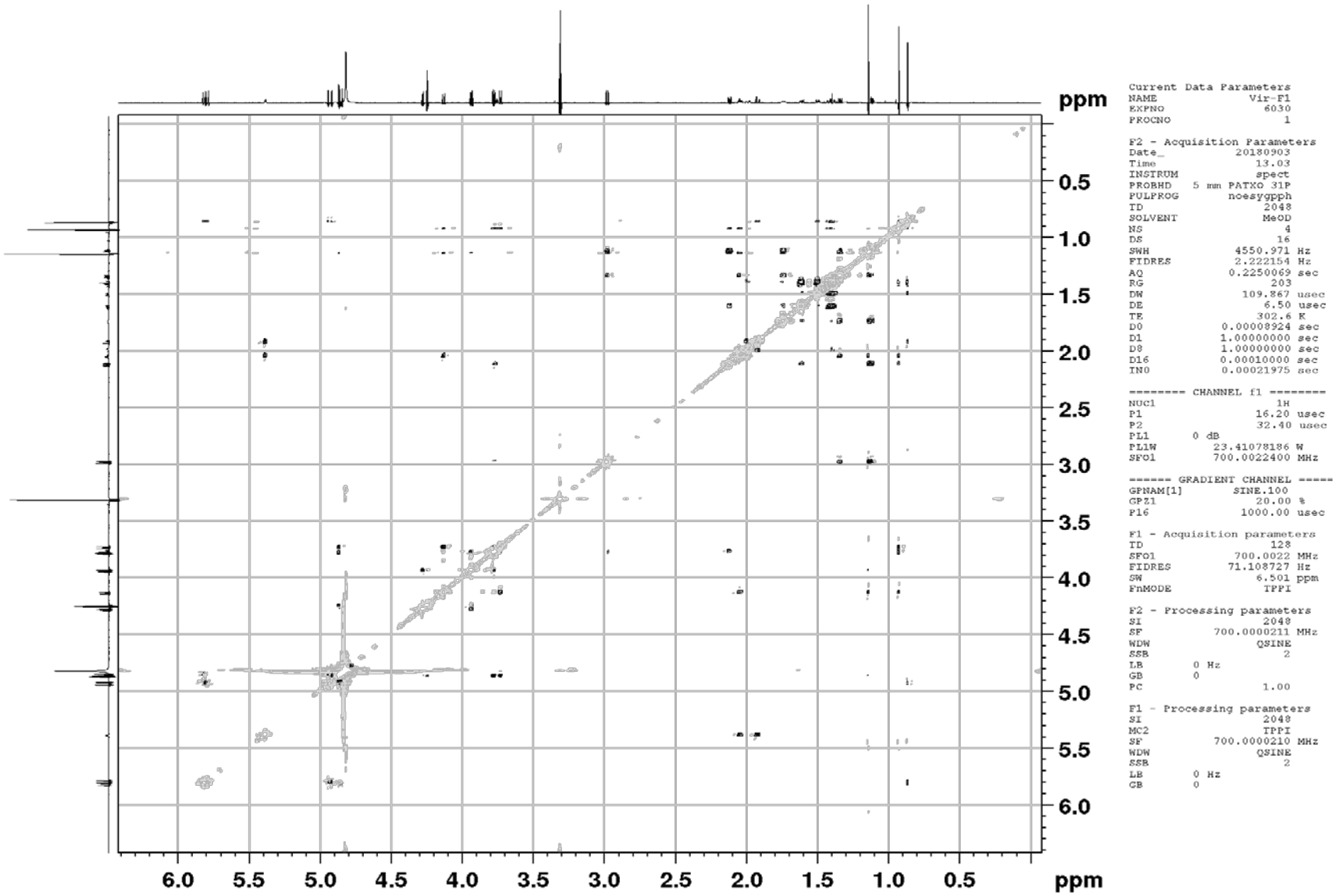


Figure S59. NOESY spectrum (700 MHz, CD_3OD) of **11**

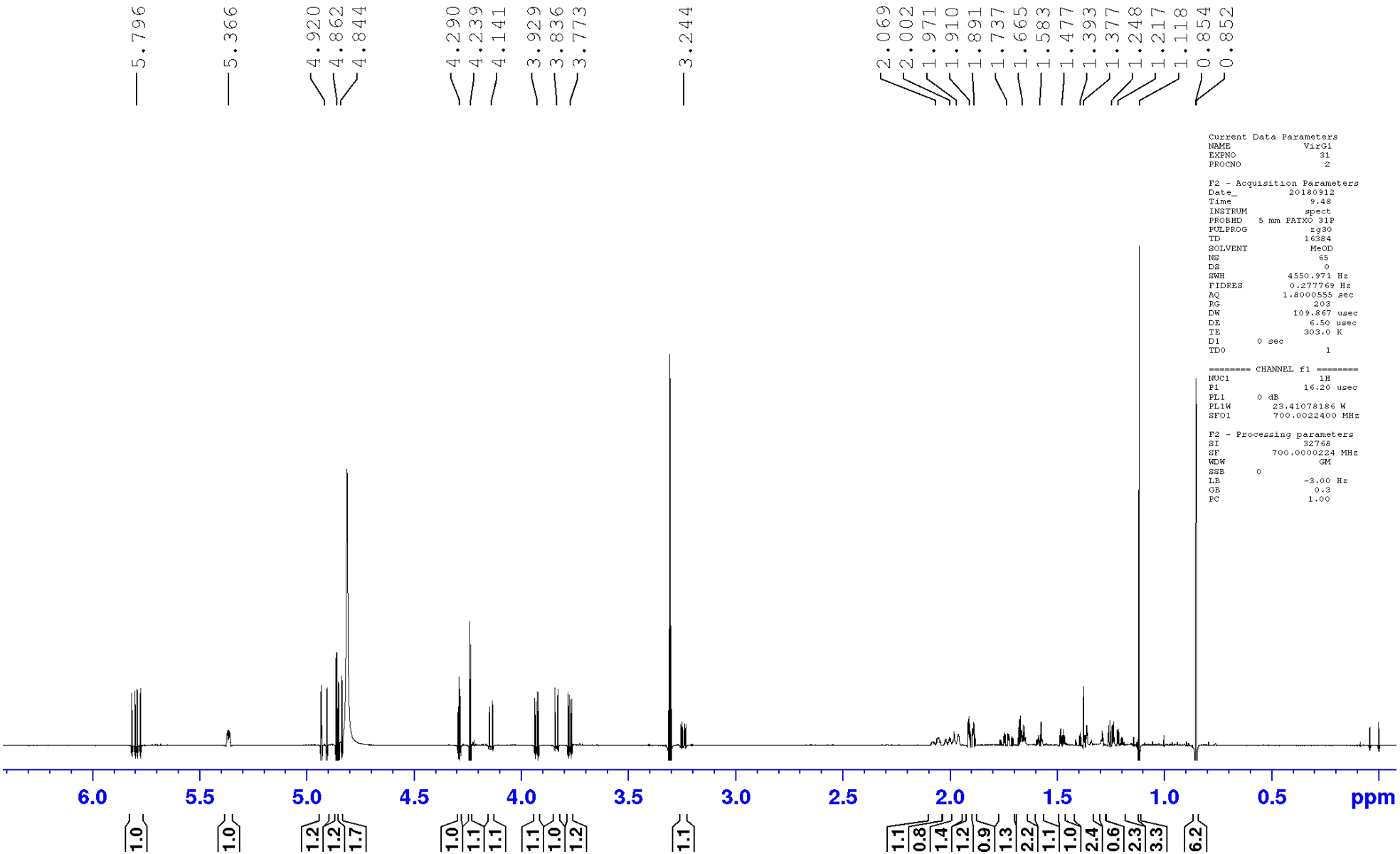


Figure S60. ^{1}H NMR spectrum (700 MHz, CD_3OD) of **12**

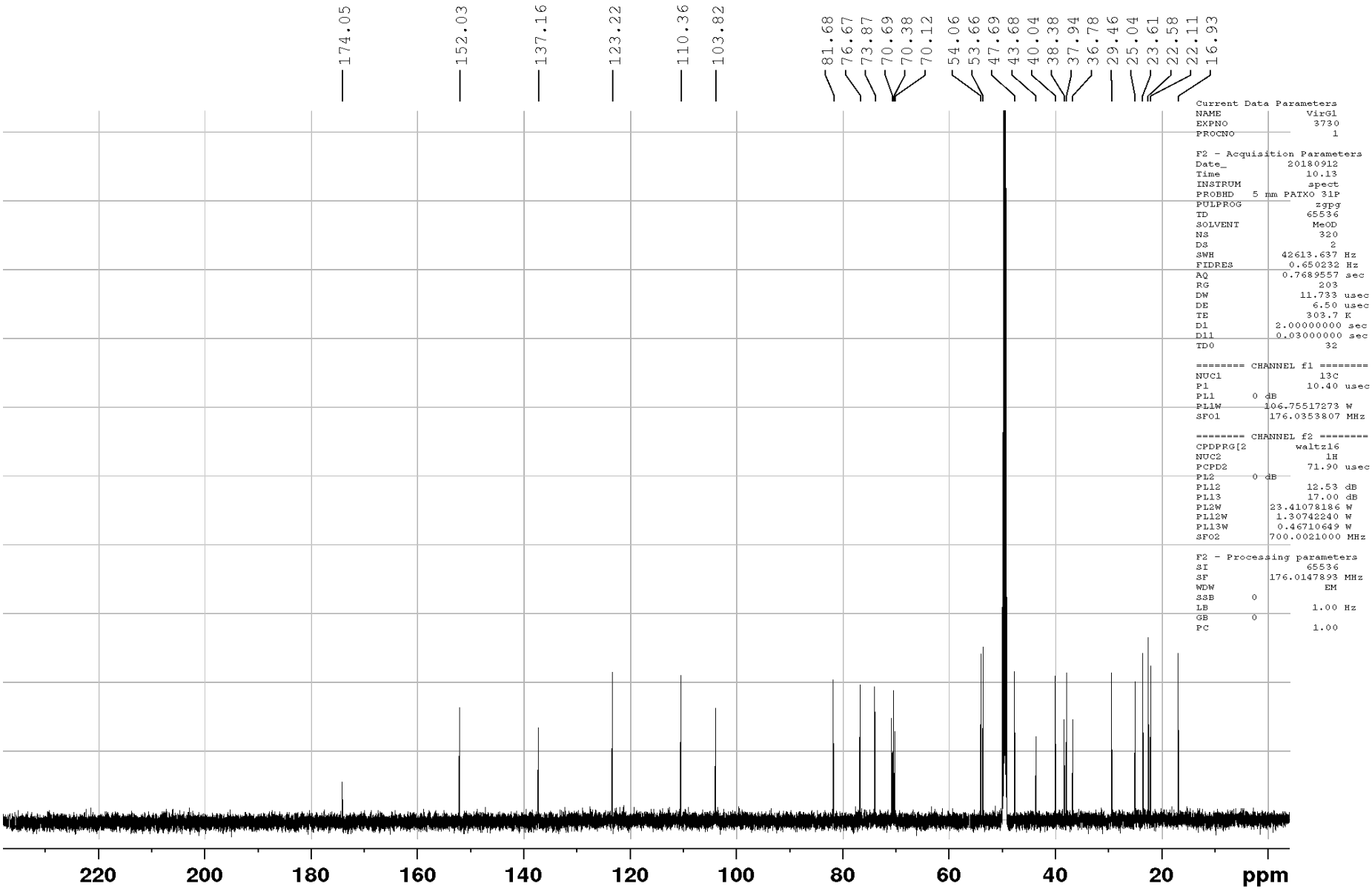


Figure S61. ^{13}C NMR spectrum (176 MHz, CD_3OD) of **12**

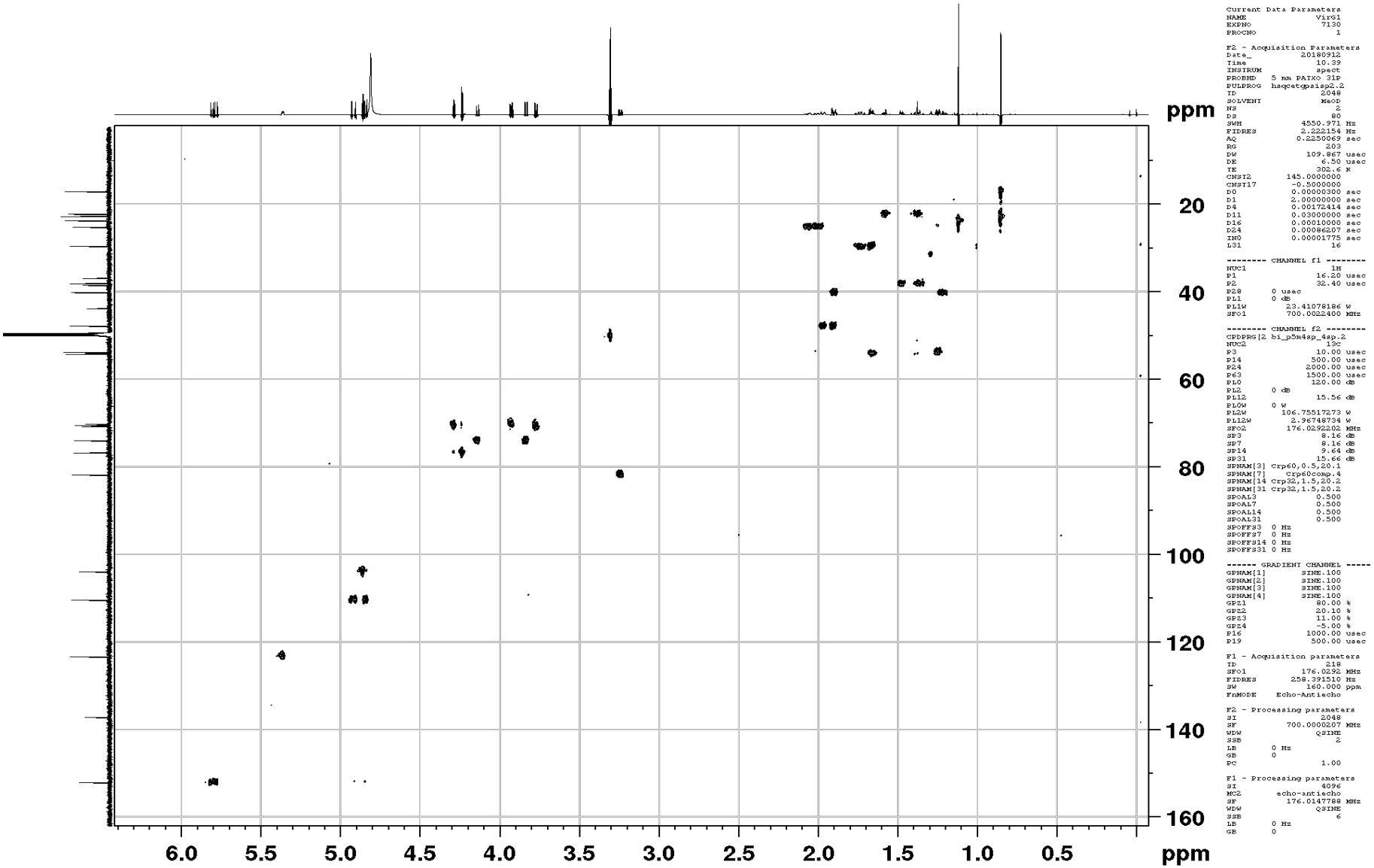


Figure S62. HSQC spectrum (700 MHz, CD_3OD) of **12**

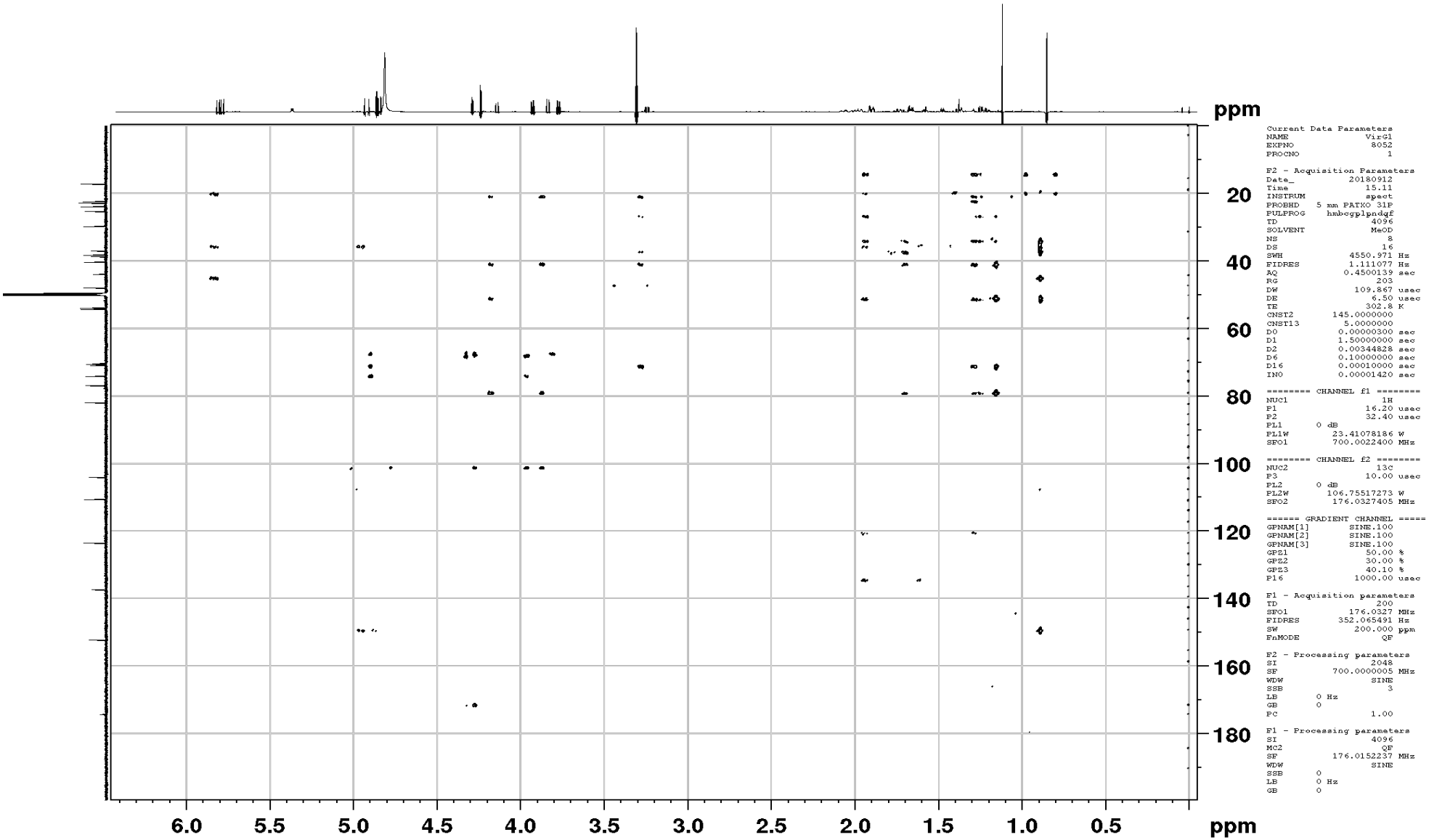


Figure S63. HMBC spectrum (700 MHz, CD_3OD) of **12**

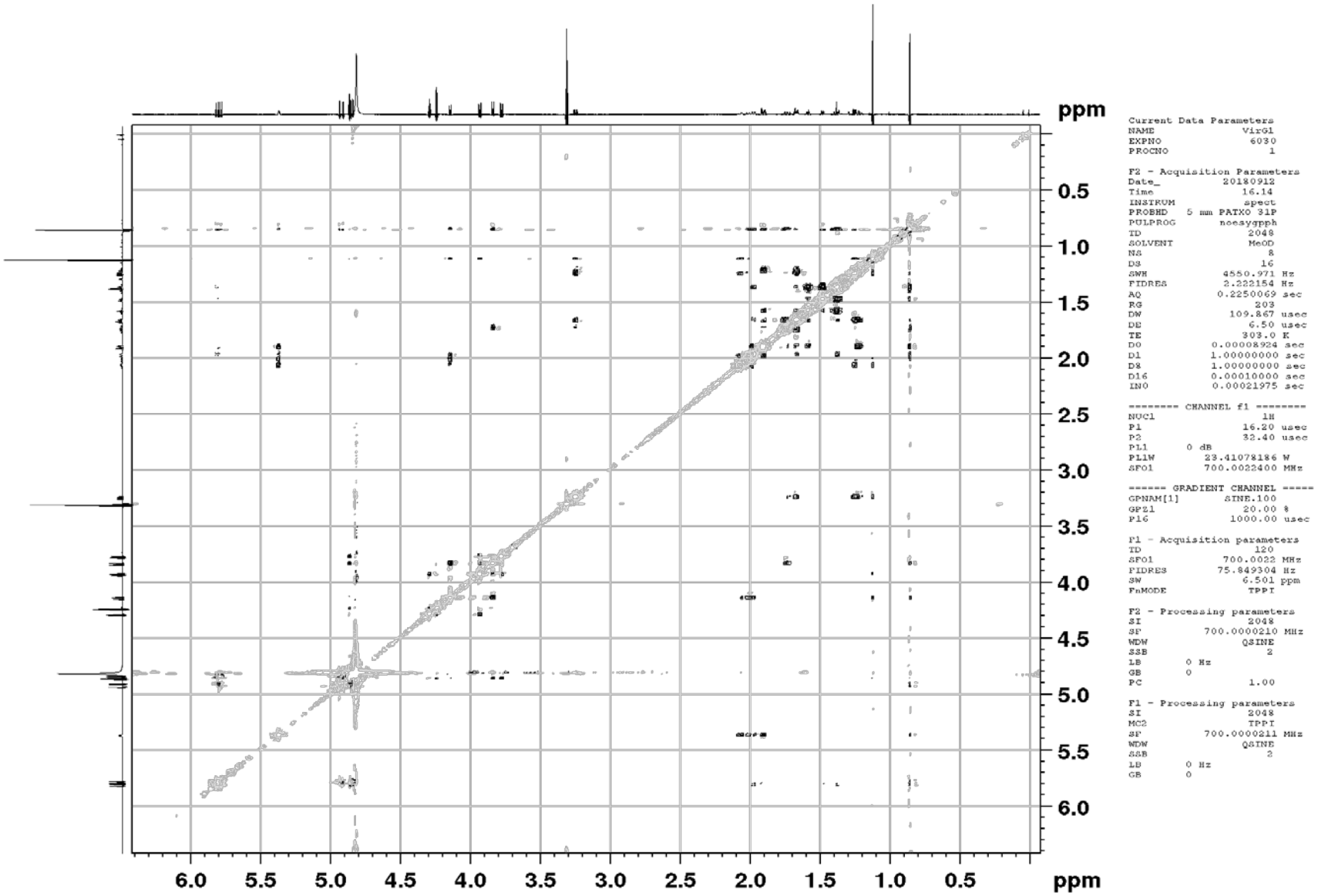
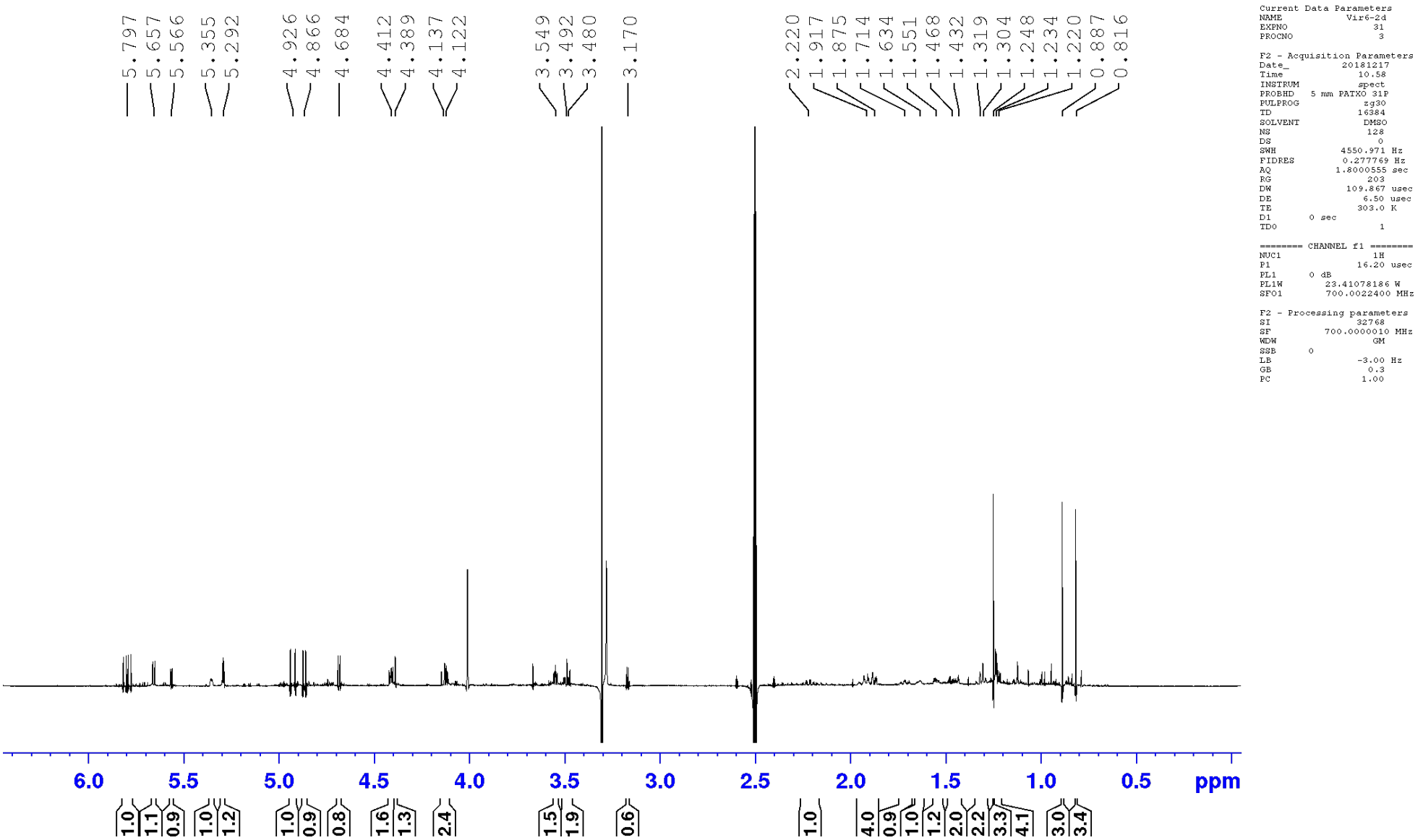


Figure S64. NOESY spectrum (700 MHz, CD_3OD) of **12**




```
Current Data Parameters
NAME                  Vir6-2d
EXPNO                      31
PROCNO                      3

F2 - Acquisition Parameters
Date_               20181217
Time                   10.58
INSTRUM                spect
PROBHD    5 mm PATXO 31P
PULPROG                zg30
TD                    16384
SOLVENT                DMSO
NS                       128
DS                         0
SWH                4550.971 Hz
FIDRES             0.277769 Hz
AQ                 1.8000555 sec
RG                       203
DW                 109.867 usec
DE                   6.50 usec
TE                   303.0 K
D1          0 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                   16.20 usec
PL1          0 dB
PL1W           23.41078186 W
SFO1           700.0022400 MHz

F2 - Processing parameters
SI                     32768
SF               700.0000010 MHz
WDW                       GM
SSB          0
LB                   -3.00 Hz
GB                       0.3
PC                      1.00
```

Figure S65. ^{1}H NMR spectrum (700 MHz, DMSO-d$_6$) of **13**

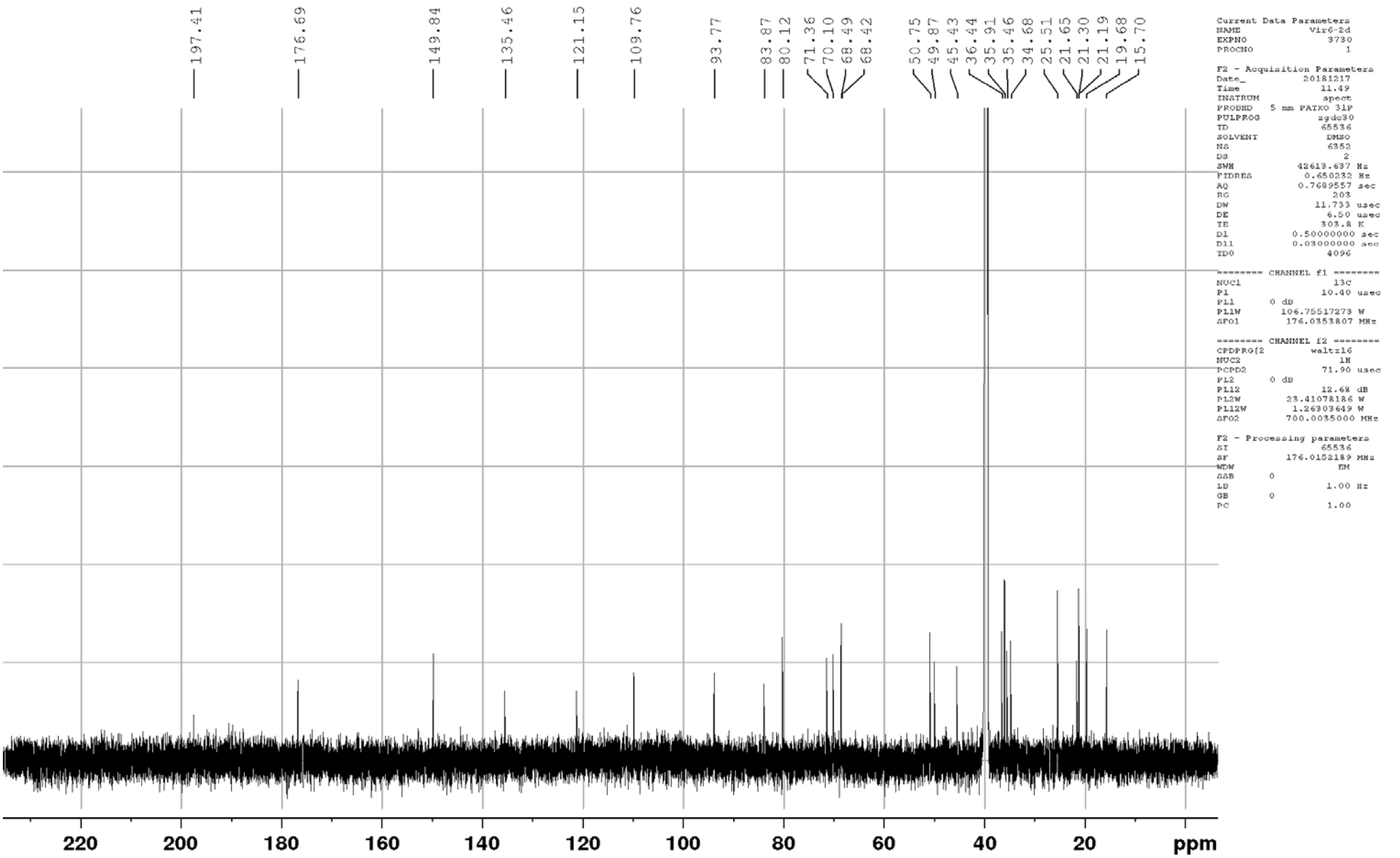
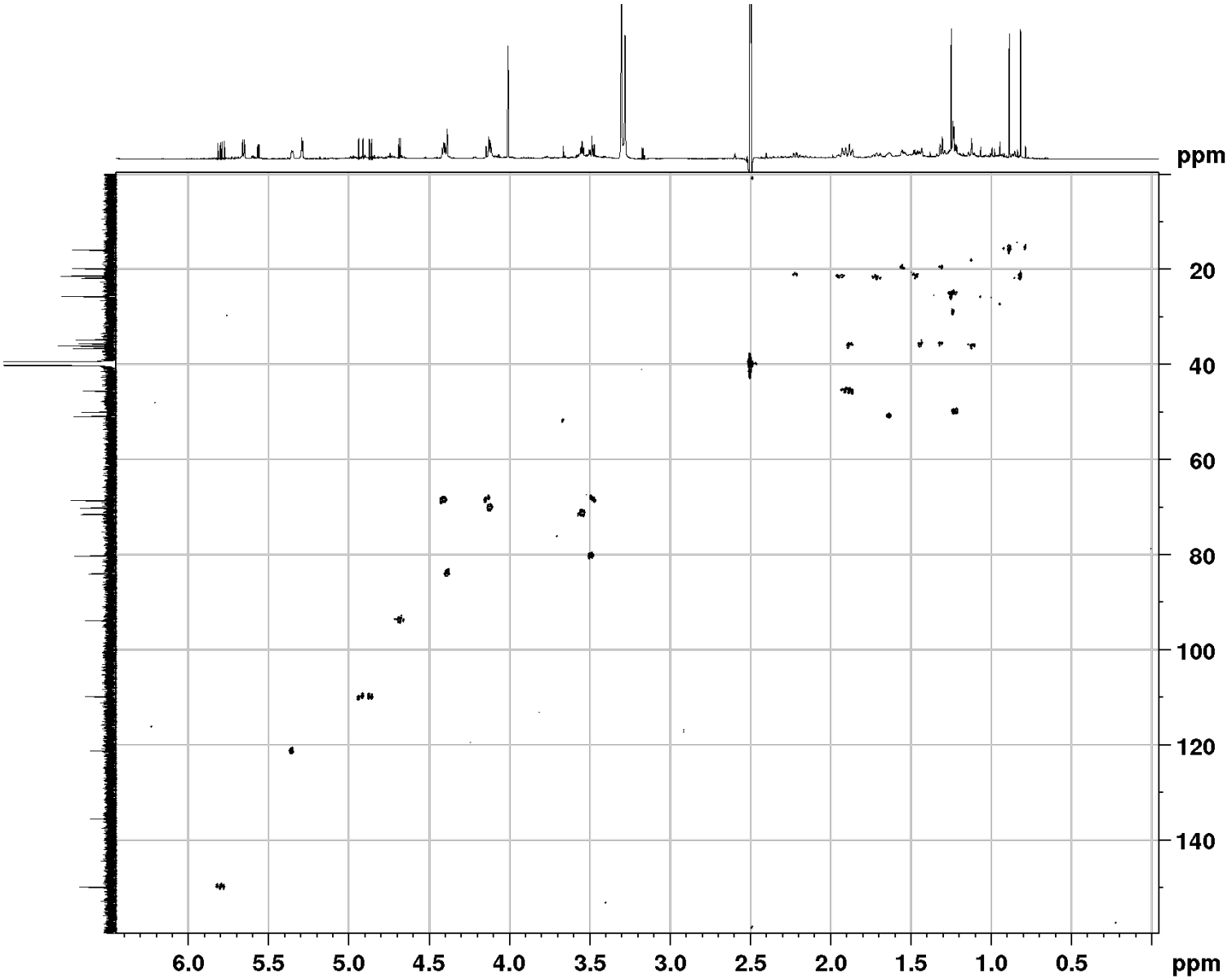


Figure S66. ^{13}C NMR spectrum (176 MHz, DMSO-d_6) of **13**




```
Current Data Parameters
NAME                 Vir6-2d
EXPNO                   7130
PROCNO                     2

F2 - Acquisition Parameters
Date_               20181218
Time                    8.52
INSTRUM                spect
PROBHD     5 mm PATxo 31P
PULPROG  hsqcetgpaisp2.2
TD                      2048
SOLVENT                 DMSO
NS                         8
DS                        32
SWH                4550.971 Hz
FIDRES             2.222154 Hz
AQ                 0.2250069 sec
RG                       203
DW                   109.867 usec
DE                      6.50 usec
TE                     302.9 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                      16.20 usec
P2                      32.40 usec
P28          0 usec
PL1          0 dB
PL1W          23.41078186 W
SFO1           700.0022400 MHz

======== CHANNEL f2 ========
CPDPRG[2 bi_p5m4sp_4sp.2
NUC2                      13C
P3                     10.00 usec
P14                   500.00 usec
P24                  2000.00 usec
P63                  1500.00 usec
PL0                   120.00 dB
PL2          0 dB
PL12                   15.56 dB
PL0W         0 W
PL2W           106.75517273 W
PL12W            2.96748734 W
SFO2           176.0292202 MHz
SP3                     8.16 dB
SP7                     8.16 dB
SP14                    9.64 dB
SP31                   15.66 dB
SPNAM[3] Crp60,0.5,20.1
SPNAM[7]     crp60comp.4
SPNAM[14 Crp32,1.5,20.2
SPNAM[31 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 =====
GPNAM[1]          SINE.100
GPNAM[2]          SINE.100
GPNAM[3]          SINE.100
GPNAM[4]          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                       164
SFO1               176.0292 MHz
FIDRES           343.471649 Hz
SW                 160.000 ppm
FnMODE     Echo-Antiecho

F2 - Processing parameters
SI                       2048
SF             699.9999987 MHz
WDW                   QSINE
SSB                        2
LB           0 Hz
GB           0
PC                     1.40

F1 - Processing parameters
SI                       4096
MC2          echo-antiecho
SF               176.0152048 MHz
WDW                   QSINE
SSB                        8
LB           0 Hz
GB           0
```

Figure S67. HSQC spectrum (700 MHz, DMSO-d_6) of **13**

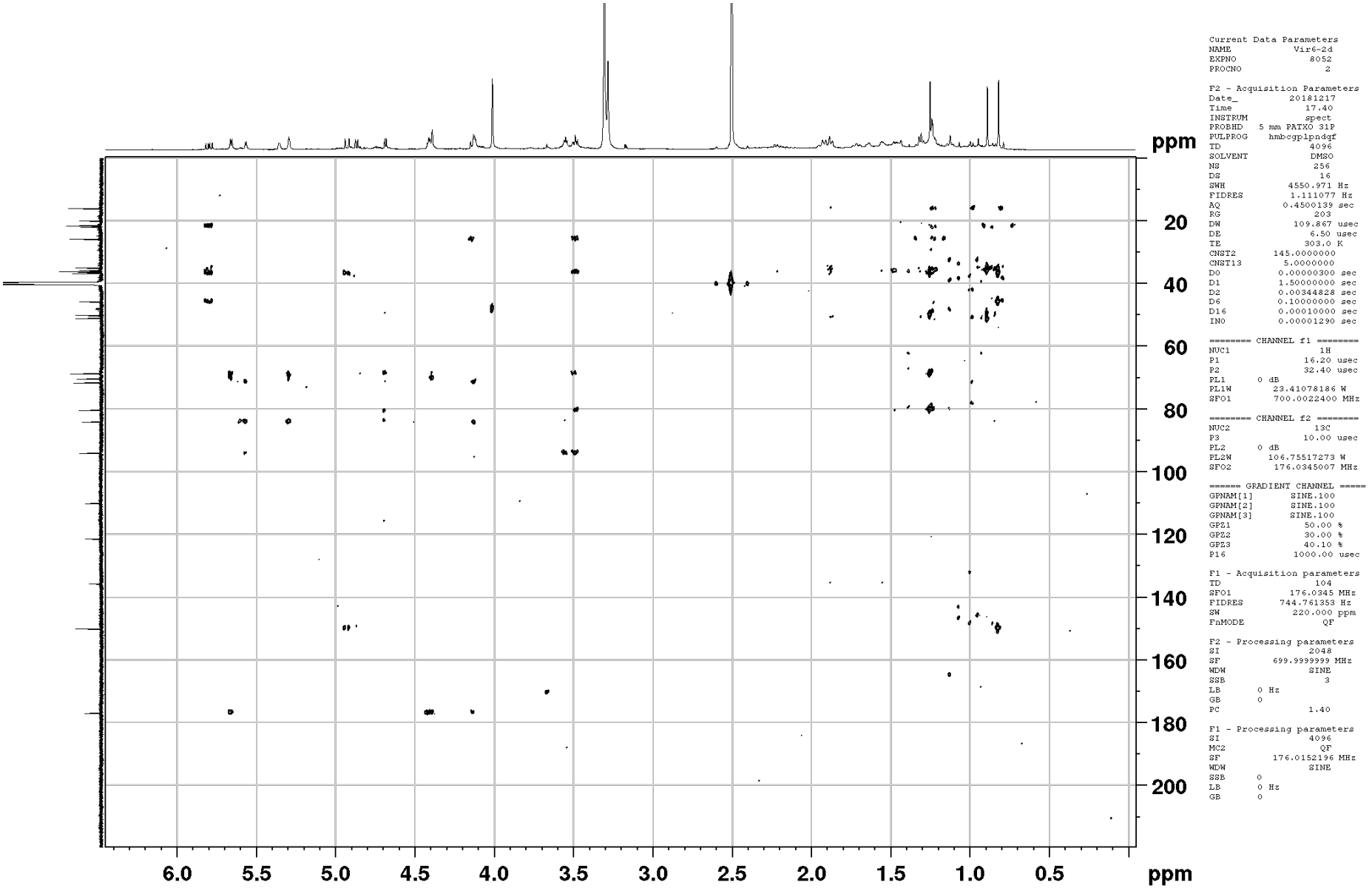


Figure S68. HMBC spectrum (700 MHz, DMSO-d_6) of **13**

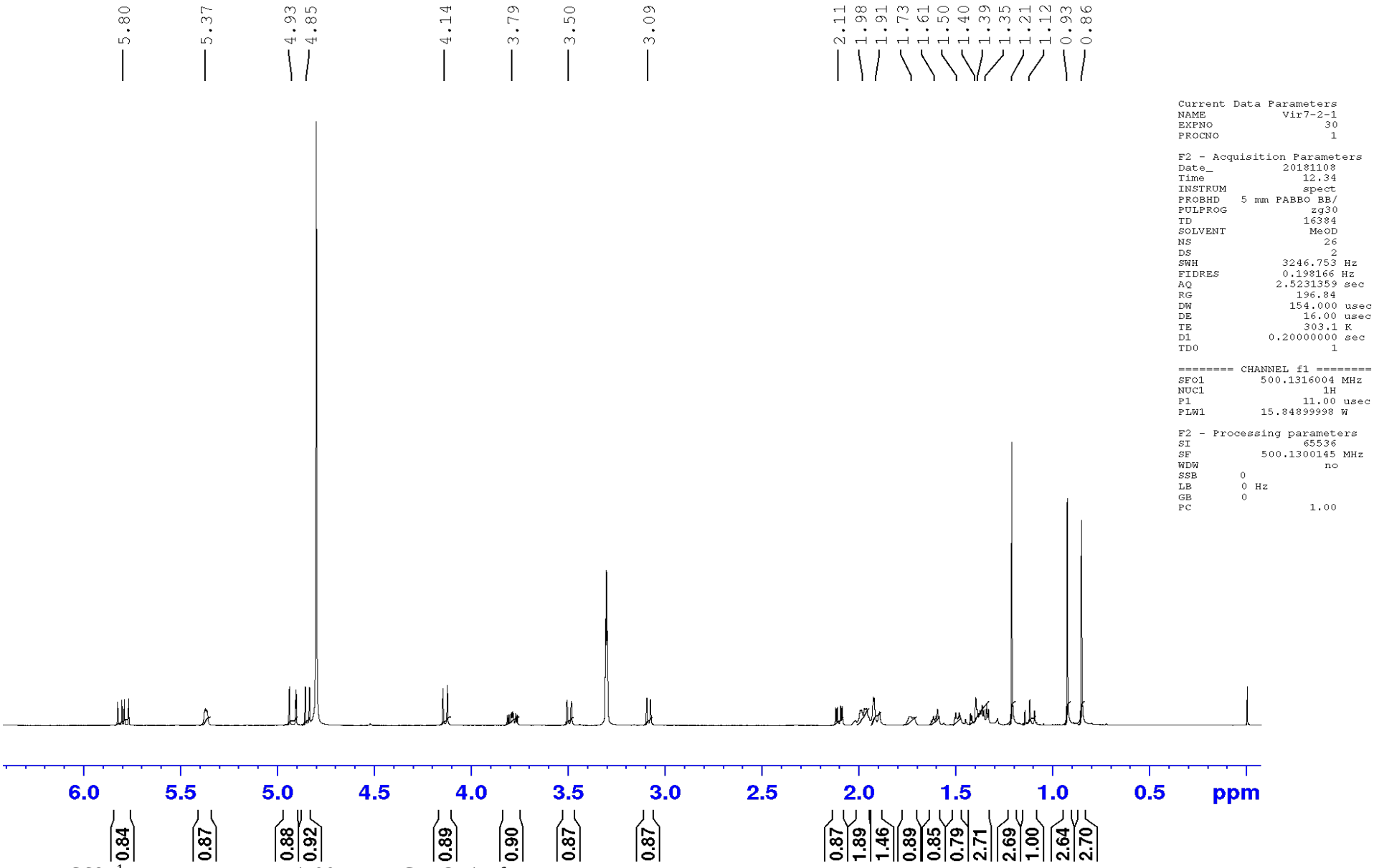
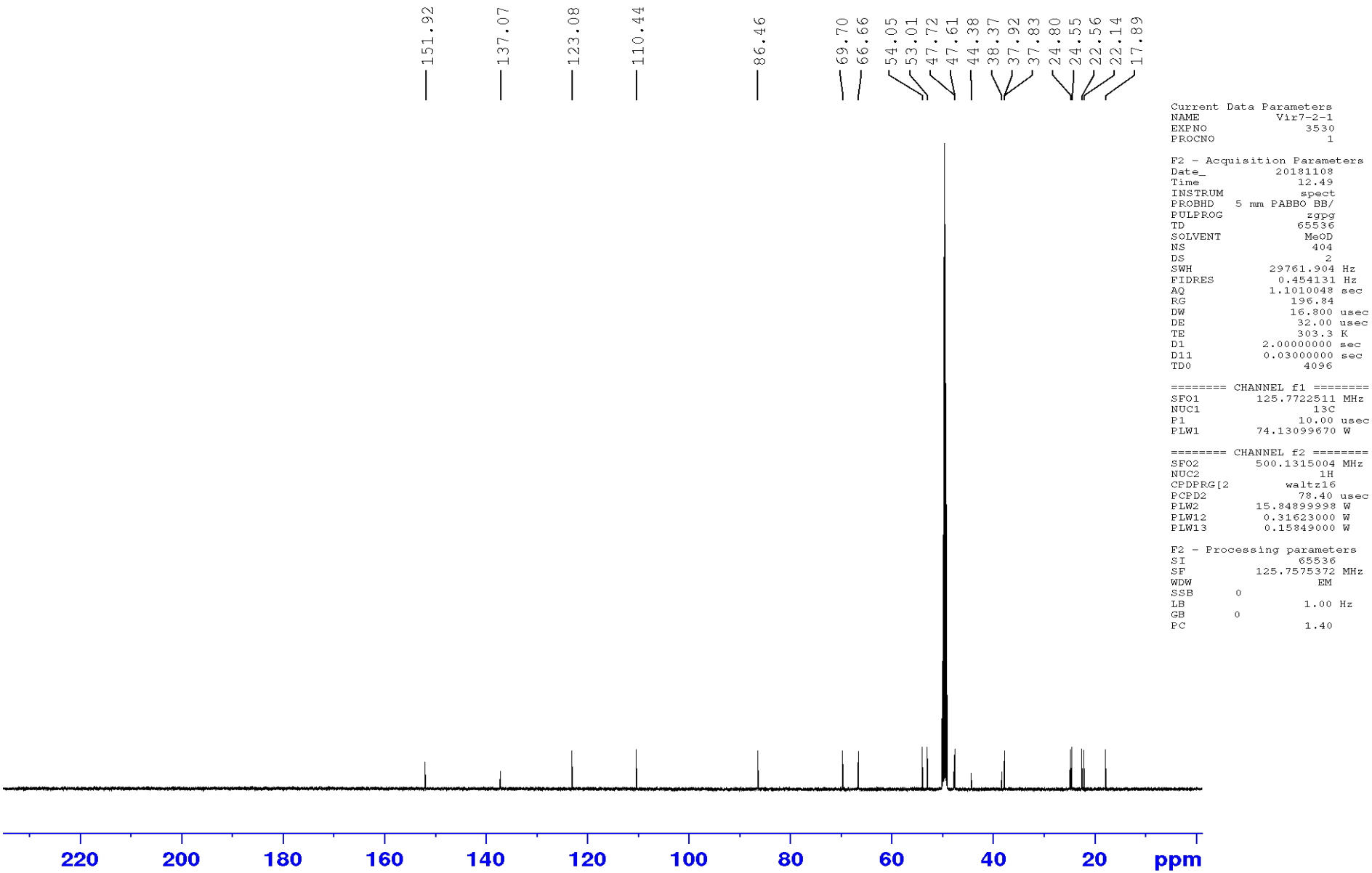
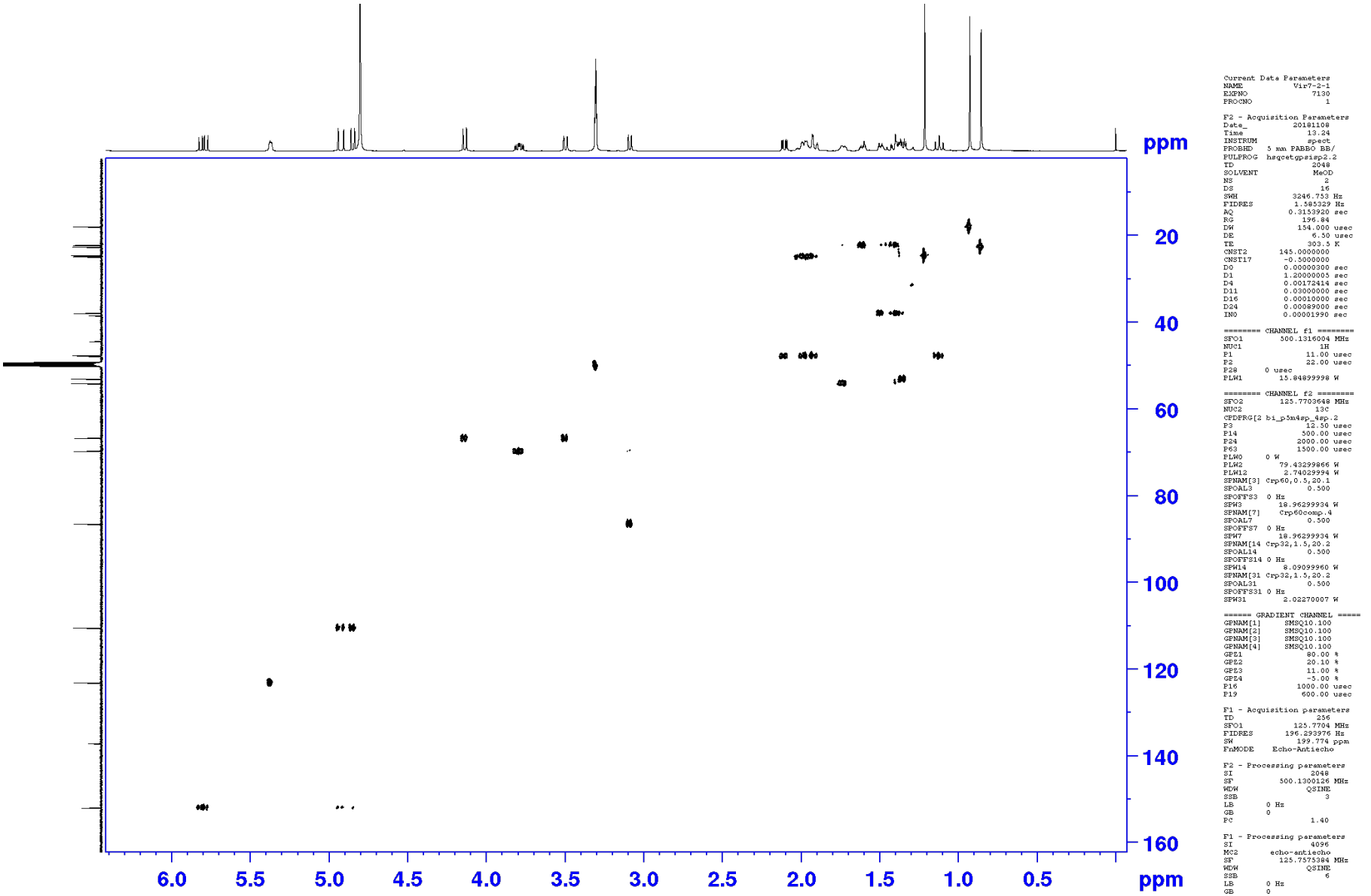


Figure S69. ^{1}H NMR spectrum (500 MHz, CD_3OD) of **14**




```
Current Data Parameters
NAME                  Vir7-2-1
EXPNO                     3530
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20181108
Time                     12.49
INSTRUM                  spect
PROBHD    5 mm PABBO BB/
PULPROG                  zgpg
TD                      65536
SOLVENT                  MeOD
NS                        404
DS                          2
SWH                 29761.904 Hz
FIDRES                0.454131 Hz
AQ                    1.1010048 sec
RG                       196.84
DW                       16.800 usec
DE                       32.00 usec
TE                       303.3 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                         4096

======== CHANNEL f1 ========
SFO1               125.7722511 MHz
NUC1                        13C
P1                       10.00 usec
PLW1               74.13099670 W

======== CHANNEL f2 ========
SFO2               500.1315004 MHz
NUC2                         1H
CPDPRG[2                waltz16
PCPD2                    78.40 usec
PLW2               15.84899998 W
PLW12               0.31623000 W
PLW13               0.15849000 W

F2 - Processing parameters
SI                      65536
SF                 125.7575372 MHz
WDW                        EM
SSB          0
LB                       1.00 Hz
GB           0
PC                       1.40
```

Figure S70. ^{13}C NMR spectrum (125 MHz, CD_3OD) of **14**



Current Data Parameters
NAME Vir7-2-1
EXPNO 7130
PROCNO 1

F2 - Acquisition Parameters
Date_ 20181108
Time 13.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG hsqcetgpsisp2.2
TD 2048
SOLVENT MeOD
NS 2
DS 16
SWH 3246.753 Hz
FIDRES 1.585329 Hz
AQ 0.3153920 sec
RG 196.84
DW 154.000 usec
DE 6.50 usec
TE 303.5 K
CNST2 145.0000000
CNST17 -0.5000000
D0 0.00000300 sec
D1 1.20000005 sec
D4 0.00172414 sec
D11 0.03000000 sec
D16 0.00010000 sec
D24 0.00089000 sec
IN0 0.00001990 sec

======== CHANNEL f1 ========
SFO1 500.1316004 MHz
NUC1 1H
P1 11.00 usec
P2 22.00 usec
P28 0 usec
PLW1 15.84899998 W

======== CHANNEL f2 ========
SFO2 125.7703648 MHz
NUC2 13C
CPDPRG[2 bi_p3m4sp_4sp.2
P3 12.50 usec
P14 500.00 usec
P24 2000.00 usec
P63 1500.00 usec
PLW0 0 W
PLW2 79.43299866 W
PLW12 2.74029994 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3 0.500
SPOFFS3 0 Hz
SPW3 18.96299934 W
SPNAM[7] Crp60comp.4
SPOAL7 0.500
SPOFFS7 0 Hz
SPW7 18.96299934 W
SPNAM[14 Crp32,1.5,20.2
SPOAL14 0.500
SPOFFS14 0 Hz
SPW14 8.09099960 W
SPNAM[31 Crp32,1.5,20.2
SPOAL31 0.500
SPOFFS31 0 Hz
SPW31 2.02270007 W

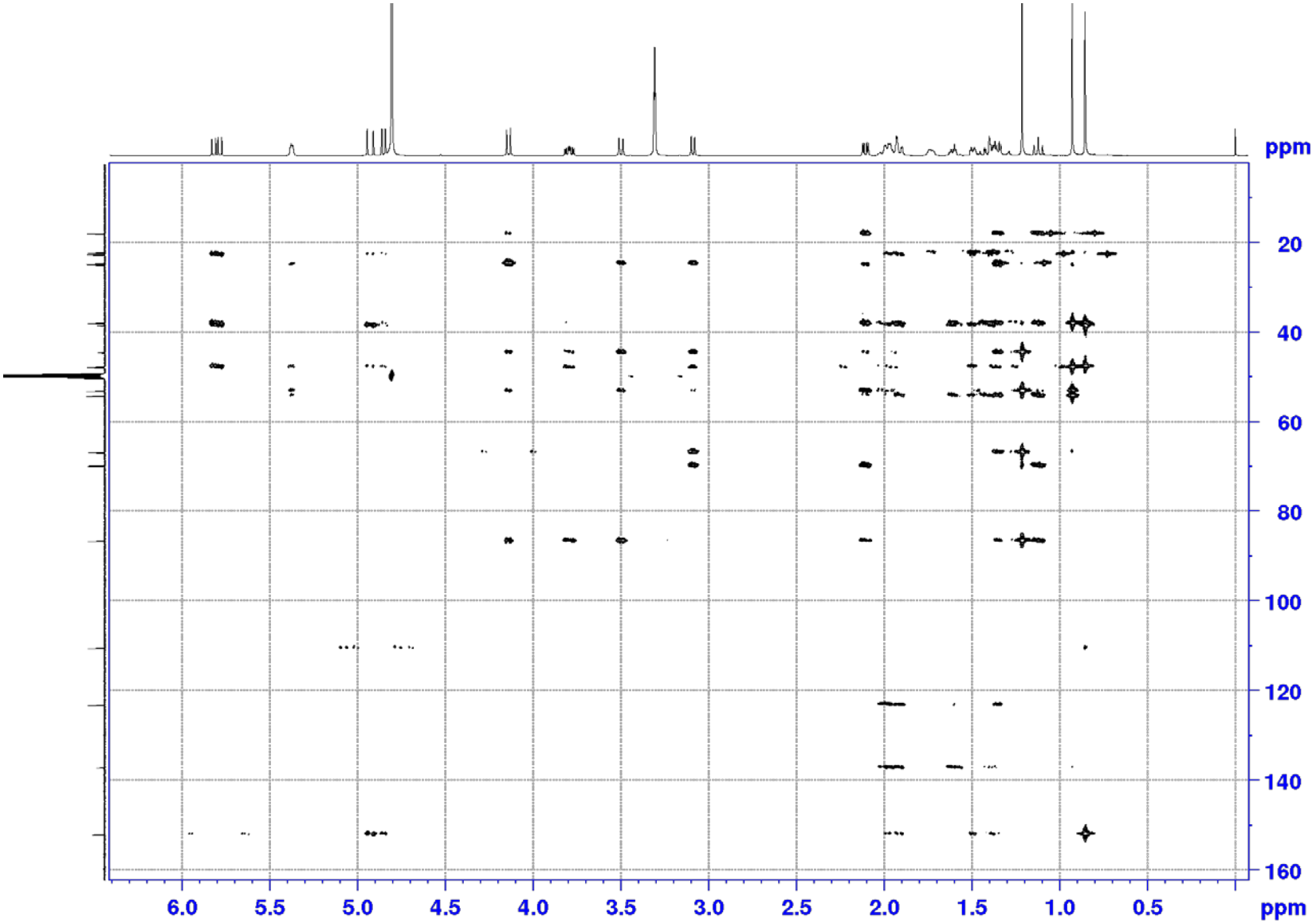
====== GRADIENT CHANNEL =====
GPNAM[1] SMSQ10.100
GPNAM[2] SMSQ10.100
GPNAM[3] SMSQ10.100
GPNAM[4] SMSQ10.100
GPZ1 80.00 %
GPZ2 20.10 %
GPZ3 11.00 %
GPZ4 -5.00 %
P16 1000.00 usec
P19 600.00 usec

F1 - Acquisition parameters
TD 256
SFO1 125.7704 MHz
FIDRES 196.293976 Hz
SW 199.774 ppm
FnMODE Echo-Antiecho

F2 - Processing parameters
SI 2048
SF 500.1300126 MHz
WDW QSINE
SSB 3
LB 0 Hz
GB 0
PC 1.40

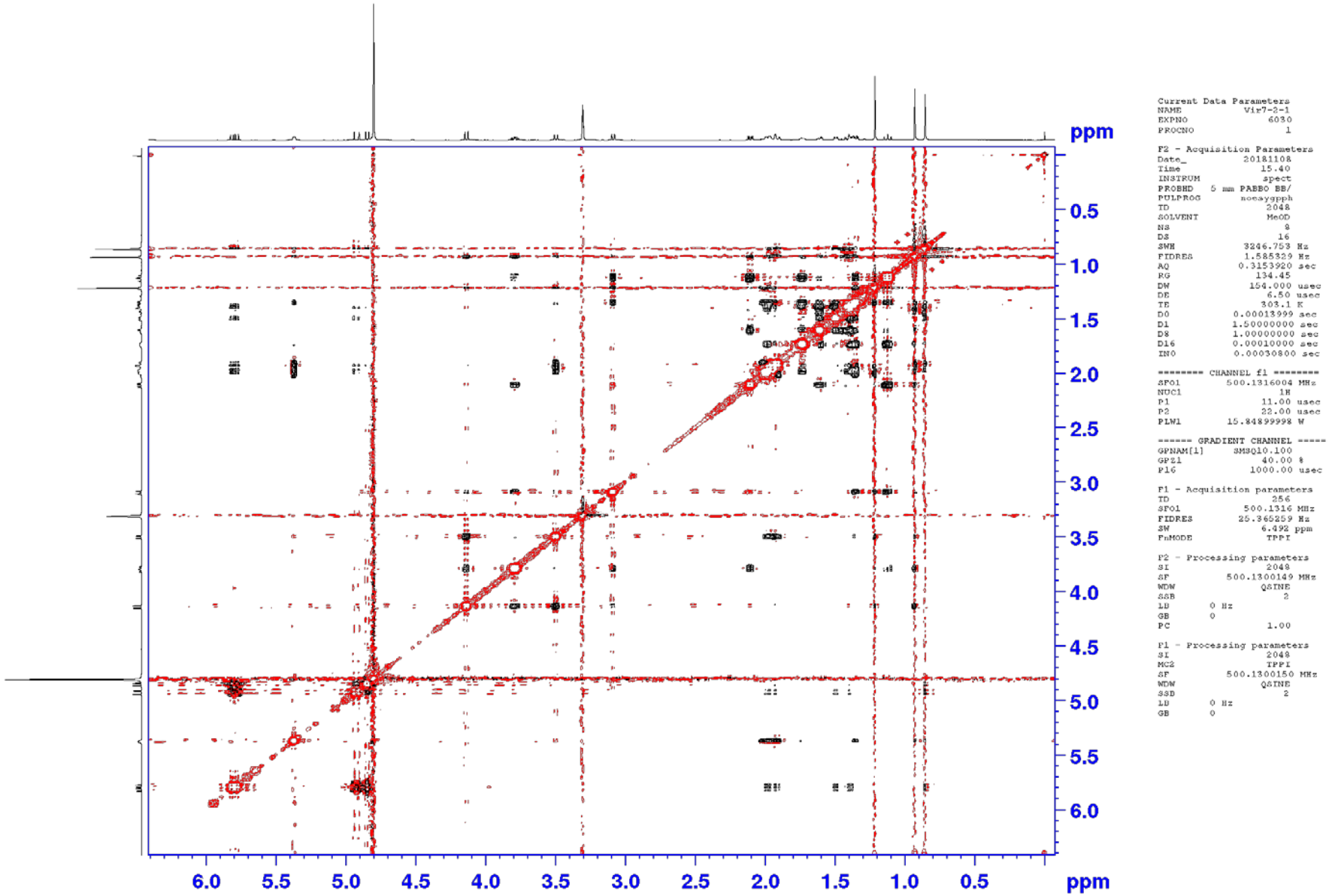
F1 - Processing parameters
SI 4096
MC2 echo-antiecho
SF 125.7575384 MHz
WDW QSINE
SSB 6
LB 0 Hz
GB 0

Figure S71. HSQC spectrum (500 MHz, CD_3OD) of **14**




```
Current Data Parameters
NAME                  Vir7-2-1
EXPNO                     8052
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20181108
Time                      17.20
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG     hmbcgplpndqf
TD                        4096
SOLVENT                   MeOD
NS                          64
DS                          16
SWH                 3246.753 Hz
FIDRES              0.792664 Hz
AQ                  0.6307840 sec
RG                      196.84
DW                     154.000 usec
DE                       6.50 usec
TE                      303.2 K
CNST2               145.0000000
CNST13                5.0000000
D0                  0.00000300 sec
D1                  1.50000000 sec
D2                  0.00344828 sec
D6                  0.10000000 sec
D16                 0.00010000 sec
IN0                 0.00001660 sec

======== CHANNEL f1 ========
SFO1                500.1316004 MHz
NUC1                        1H
P1                       11.00 usec
P2                       22.00 usec
PLW1                15.84899998 W

======== CHANNEL f2 ========
SFO2                125.7728799 MHz
NUC2                        13C
P3                       12.50 usec
PLW2                79.43299866 W

====== GRADIENT CHANNEL =====
GPNAM[1]             SMSQ10.100
GPNAM[2]             SMSQ10.100
GPNAM[3]             SMSQ10.100
GPZ1                     50.00 %
GPZ2                     30.00 %
GPZ3                     40.10 %
P16                    1000.00 usec

F1 - Acquisition parameters
TD                          371
SFO1                125.7729 MHz
FIDRES              162.374573 Hz
SW                      239.483 ppm
FnMODE                       QF

F2 - Processing parameters
SI                          2048
SF                  500.1300166 MHz
WDW                       QSINE
SSB                           3
LB                0 Hz
GB                0
PC                          1.00

F1 - Processing parameters
SI                          4096
MC2                          QF
SF                  125.7575373 MHz
WDW                        SINE
SSB               0
LB                0 Hz
GB                0
```

Figure S72. HMBC spectrum (500 MHz, CD_3OD) of **14**




```
Current Data Parameters
NAME                  Vir7-2-1
EXPNO                     6030
PROCNO                       1

F2 - Acquisition Parameters
Date_               20181108
Time                   15.40
INSTRUM                spect
PROBHD     5 mm PABBO BB/
PULPROG             noesygpph
TD                        2048
SOLVENT                   MeOD
NS                           8
DS                          16
SWH                 3246.753 Hz
FIDRES              1.585329 Hz
AQ                  0.3153920 sec
RG                     134.45
DW                    154.000 usec
DE                      6.50 usec
TE                     303.1 K
D0                  0.00013999 sec
D1                  1.50000000 sec
D8                  1.00000000 sec
D16                 0.00010000 sec
IN0                 0.00030800 sec

======== CHANNEL f1 ========
SFO1             500.1316004 MHz
NUC1                       1H
P1                      11.00 usec
P2                      22.00 usec
PLW1             15.84899998 W

====== GRADIENT CHANNEL =====
GPNAM[1]         SMSQ10.100
GPZ1                    40.00 %
P16                   1000.00 usec

F1 - Acquisition parameters
TD                         256
SFO1                500.1316 MHz
FIDRES              25.365259 Hz
SW                      6.492 ppm
FnMODE                   TPPI

F2 - Processing parameters
SI                        2048
SF                  500.1300149 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
PC                       1.00

F1 - Processing parameters
SI                        2048
MC2                      TPPI
SF                  500.1300150 MHz
WDW                     QSINE
SSB                         2
LB          0 Hz
GB          0
```

Figure S73. NOESY spectrum (500 MHz, CD_3OD) of **14**