

SUPPLEMENTARY MATERIAL

Piltunines A–F from the marine-derived fungus *Penicillium piltunense* KMM 4668

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Piltunines A–F from the marine-derived fungus *Penicillium piltunense* KMM 4668

Six new carotane sesquiterpenoids piltunines A–F (**1–6**) together with known compounds (**7–9**) were isolated from the marine-derived fungus *Penicillium piltunense* KMM 4668. Their structures were established using spectroscopic methods. The absolute configurations of **1–7** were determined based on CD and NOESY data as well as biogenetic considerations. The cytotoxic activity of some of the isolated compounds and their effects on regulation of ROS and NO production in lipopolysaccharide-stimulated macrophages were examined.

Keywords: *Penicillium piltunense*, secondary metabolites, carotane sesquiterpenoids, cytotoxic activity

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Experimental Section

Table S1. NMR Data for compounds **1a** and **7**

Position	1a^a			7^b		
	¹³ C (δC)	¹ H (δH, J in Hz)	HMBC	¹³ C (δc)	¹ H (δH, J in Hz)	HMBC
1	36.1 CH ₂	α: 2.06 d (13.5) β: 2.20 dd (6.9, 12.5)	3, 6, 7, 13 2, 3, 6, 7, 8, 12	37.6 CH ₂	α: 2.03 d (13.2) β: 2.25 dd (8.1, 13.2)	2, 3, 6, 7, 13 2, 3, 6, 7, 8
2	84.7 CH	4.18 d (9.1)	3, 4, 7, 13	82.6 CH	4.25 m	3, 4, 7, 13
3	78.4 C			77.6 C		
4	33.2 CH ₂	α: 1.49 m β: 2.37 m	3, 5, 12 2, 3, 5, 6, 12	33.7 CH ₂	α: 1.41 td (1.0, 13.1) β: 2.41 dd (7.5, 14.3)	3, 5, 6, 12 2, 3, 5, 6
5	23.1 CH ₂	α: 2.44 d (7.6) β: 1.80 m	4, 6, 7, 10 3, 4, 6, 7	18.1 CH ₂	α: 1.50 m β: 1.81 m	4, 6, 7, 10 3
6	55.8 CH	2.35 d (7.5)	1, 4, 5, 8, 13	56.8 CH	1.71 m	4, 5, 9, 10, 13
7	52.5 C			51.1 C		
8	34.2 CH ₂	α: 1.71 dd (8.1, 12.5) β: 1.52 t (5.1)	1, 7, 9 6, 7, 9, 10, 13	32.0 CH ₂	α: 1.85 dd (3.5, 10.5) β: 1.68 m	1, 6, 7, 13 1, 6, 7, 9, 13
9	31.3 CH ₂	α: 2.47 d (7.8) β: 2.12 m	7, 10	38.5 CH ₂	α: 2.12 m β: 1.65 m	6, 7, 8, 10, 11 6, 7, 8, 11
10	140.0 C			84.5 C		
11	127.9 C			148.8 C		
12	175.9 C			176.7 C		
13	75.9 CH ₂	a: 3.38 dd (1.4, 8.5) b: 3.77 d (8)	3, 6, 7, 8 1, 2, 6, 7	75.0 CH ₂	a: 3.41 d (8.0) b: 4.67 d (8.1)	6, 7, 8 1, 6, 7, 8
14	66.1 CH ₂	a: 4.00 d (11.1) b: 4.09 d (11.0)	10, 11, 14	18.9 CH ₃	1.78s	10, 11, 15
15	16.6 CH ₃	1.84 brs	10, 11, 15	109.3 CH ₂	a: 4.87 t (1.5) b: 5.01 brs	10, 11, 14
16	52.5 CH ₃	3.79 s	12	37.6 CH ₂		

^aChemical shifts were measured at 500.13 Hz and 125.77 Hz in CD₃OD. ^bChemical shifts were measured at 500.13 Hz and 125.77 Hz in mixture CD₃OD+CDCl₃.

Table S2. NMR data for piltunines A–C (1–3) ^a.

Position	1				2				3			
	¹³ C (δC)	¹ H (δH, J in Hz)	HMBC	NOESY	¹³ C (δC)	¹ H (δH, J in Hz)	HMBC	NOESY	¹³ C (δC)	¹ H (δH, J in Hz)	HMBC	NOESY
1	37.4 CH ₂	α: 2.05 d (13.1) β: 2.19 dd (8.6, 13.3)	2, 6, 7, 13 2, 3, 6, 7, 8, 12	6 2, 8β, 13a	37.3 CH ₂	α: 2.05 d (14.1) β: 2.19 d (8.2)	3, 6, 7, 13 2, 3, 6, 7, 8	4α, 6, 8α 2, 8β, 13a	34.3 CH ₂	α: 1.89 d (13.0) β: 2.28 dd (8.7, 13.0)	3, 6, 7, 13 2, 3, 7, 8	4α, 6, 8α 2, 8β
2	85.5 CH	4.32 d (8.5)	1, 3, 4, 12, 13	1β	85.5 CH	4.32 d (8.1)	3, 4, 7, 13	1β	84.1 CH	4.40 d (8.5)	3, 4, 7, 13	1β
3	80.0 C				79.9 C				78.9 C			
4	35.7 CH ₂	α: 1.43 t (12.0) β: 2.44 m	3, 5, 6 2, 3, 5, 6, 12	6	35.6 CH ₂	α: 1.43 t (11.0) β: 2.44 m	2, 5, 6, 7	1α, 6 15	35.6 CH	α: 1.42 t (12.3) β: 2.43 m	3, 6 2, 3, 6	1α, 6 15
5	25.0 CH ₂	2.44 m	3, 4, 6, 7 3, 7	15 13b	25.0 CH ₂	α: 2.43 m β: 1.73 m	3, 6, 7 7	15 13b	25.3 CH ₂	α: 2.40 m β: 1.71 dd (14.0, 12.6)	3, 4 3, 7	13 15
6	57.6 CH	2.37 brd (11.6)	5, 9	1α, 4α, 8α, 15	57.7 CH	2.39 d (12.0)		1α, 4α, 8α, 15	58.1 CH	2.31 d (14.0)		4
7	54.4 C				54.5 C				58.5 C			
8	35.9 CH ₂	α: 1.71 m β: 1.53 dd (7.2, 12.1)	1, 6, 7, 9, 13 5, 6, 7, 9, 10, 13		35.7 CH ₂	α: 1.74 m β: 1.54 dd (8.1, 12.0)	7, 9 6, 7, 9, 10, 13	4, 6, 13	31.9 CH ₂	α: 1.46 dd (3.1, 12.2) β: 1.94 dd (7.1, 12.2)	1, 7, 9, 13 6, 10, 13	1α, 6 1β
9	32.6 CH ₂	α: 2.47 m β: 2.11 m	6, 7, 8, 10, 11	14a,b	32.8 CH ₂	α: 2.49 dd (9.1, 17.2) β: 2.17 m	6, 7, 8 7, 10	14a,b 13b, 14a,b	32.6 CH ₂	α: 2.24 m β: 2.21 m		14 13, 14
10	141.3 C				144.5 C				137.4 C			
11	129.7 C				125.2 C				124.8 C			
12	178.4 C				178.4 C				178.4 C			
13	77.0 CH ₂	a: 3.37 dd (1.4, 8.3) b: 3.73 d (8.1)	6, 7, 8 1, 2, 6, 7	1β, 8β, 9β 5β, 9β	77.0 CH ₂	a: 3.38 dd (1.0, 8.1) b: 3.71 d (8.1)	6, 8 1, 2, 6, 7	1β, 8β 5β, 9β	101.1 CH	4.74 s	1, 2, 6, 7	5β, 9β
14	66.5 CH ₂	a: 3.92 d (11.8) b: 4.01 d (11.8)	10, 11, 15 10, 11, 15	9α 9α	69.4 CH ₂	a: 4.48 d (12.0) b: 4.52 d (12.1)	10, 11, 15, 16 10, 11, 15, 16	9α,β, 15 9α,β, 15	24.3 CH ₃	1.62 s	10, 11, 15	9α,β, 15
15	17.3 CH ₃	1.81 brs	10, 11, 14	5α, 6	17.5 CH ₃	1.78 drs	10, 11, 14	4β, 5α, 6	21.4 CH ₃	1.74 brs	10, 11, 14	4β, 5α, 6, 14
16					173.6 C							
17					21.4 CH ₃	2.03 s	14, 16	9β, 15				

^a Chemical shifts were measured at 700.13 Hz and 176.04 Hz in CD₃OD.

Table S3. NMR data for piltunines D–F (4–6) ^a

Position	4				5				6			
	¹³ C (δC)	¹ H (δH, J in Hz)	HMBC	NOESY	¹³ C (δC)	¹ H (δH, J in Hz)	HMBC	NOESY	¹³ C (δC)	¹ H (δH, J in Hz)	HMBC	NOESY
1	36.9 CH ₂	α: 2.16 d (13.1) β: 2.21 dd (8.1, 13.0)	6, 7, 13 2, 3, 6, 7, 8	4α, 6 2, 8β	36.3 CH ₂	α: 2.19 d (13.5) β: 2.24 d (8.8)	2, 3, 6, 7, 13 2, 3, 6, 7, 13	13a 4α, 6, 8α	39.1 CH ₂	α: 2.32 d (13.4) β: 2.07 dd (8.3, 13.4)	3, 6, 7, 13 3, 3, 6, 7, 8	4α 8α, 13a
2	85.6 CH	4.33 d (8.5)	1, 3, 7	1β	85.7 CH	4.36 d (8.4)	1, 3, 4, 7, 12, 13	1α,β	85.0 CH	4.42 d (8.4)	4, 7, 12, 13	1α,β
3	80.0 C				80.0 C				78.6 C			
4	36.7 CH ₂	α: 1.37 m β: 2.46 m	6 2, 3, 12	6	36.4 CH ₂	α: 1.39 t (14.0) β: 2.48 dd (8.0, 14.0)	3, 5, 6, 12 2, 3, 5, 6, 12	1α	32.6 CH ₂	α: 1.46 ddd (14.7, 10.4, 1.5) β: 2.26 dd (10.3, 14.6)	2, 3, 5, 6 3, 5, 6, 12	1α 13b
5	23.5 CH ₂	α: 2.37 dd (7.9, 14.5) β: 1.88 q (14.5)	3	14,15 13b	21.8 CH ₂	α: 2.61 m β: 1.64 q (13.0)	6, 7, 10 3, 4, 6, 7	13b	23.3 CH ₂	α: 3.12 ddd (15.6, 9.8, 1.6) β: 2.74 ddd (15.9, 10.4, 1.7)	3, 6 3	13b
6	60.4 CH	2.59 d (12.0)		1α, 4α, 14, 15	58.7 CH	2.70 d (13.0)	1, 7, 9	1α, 8α	162.7 C			
7	56.0 C				55.5 C				60.5 C			
8	40.4 CH ₂	α: 2.48 m β: 2.06 dd (2.8, 15.6)	1, 10 6, 7, 9, 10, 13	1α 1β, 13a	40.9 CH ₂	α: 2.26 dd (2.6, 14.0) β: 2.62 m	1, 6, 7, 9, 10, 13 1, 6, 7, 9, 10, 11, 13	1α	33.4 CH ₂	α: 1.96 m β: 1.89 m	1, 6, 7, 9, 10, 13 1, 6, 7, 9, 10, 13	1β 13a
9	129.7 CH	5.68 dd (2.8, 5.0)	6, 7, 10, 11	14, 15, 16	147.8 CH	6.90 q (2.6)	6, 7, 8, 10, 11	14	33.7 CH ₂	2.67 m	6, 10	14
10	152.0 C				149.0				135.4 C			
11	77.7 C				200.8 C				202.5 C			
12	178.6 C				178.5 C				178.3 C			
13	78.5 CH ₂	a: 3.38 d (8.5) b: 3.98 d (8.4)	6, 7, 8 1, 2, 6, 7	1β, 8β 5β	77.6 CH ₂	a: 3.38 d (8.7) b: 3.91 d (8.4)	6, 7, 8 1, 2, 6, 7	1β 5β	79.7 CH ₂	a: 3.74 d(8.8) b: 3.84 d (8.4)	1, 2, 6, 7 6, 7, 8	1β, 8β 4β, 5β
14	27.4 CH ₃	1.30 s	10, 11,15	5α, 6, 9, 16	27.9 CH ₃	2.26 s	9, 10, 11	9	31.0 CH ₃	2.24 s	9,10, 11	9
15	26.6 CH ₃	1.31 s	10, 11, 14	5α, 9, 16								
16	51.8 CH ₃	3.12 s	11	5α, 6, 9, 13b, 14, 15								

^a Chemical shifts were measured at 700.13 Hz and 176.04 Hz in CD₃OD.

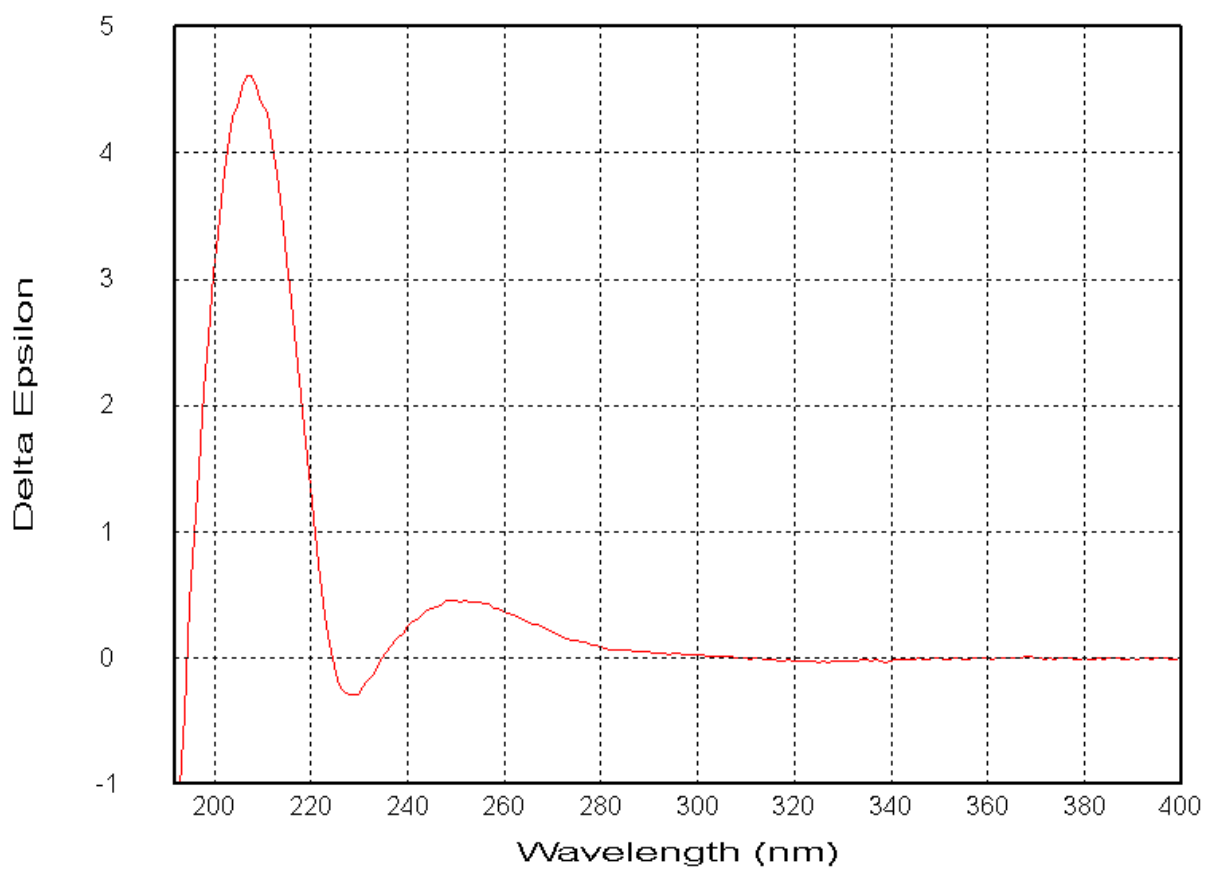


Figure S1. CD spectrum of **1**

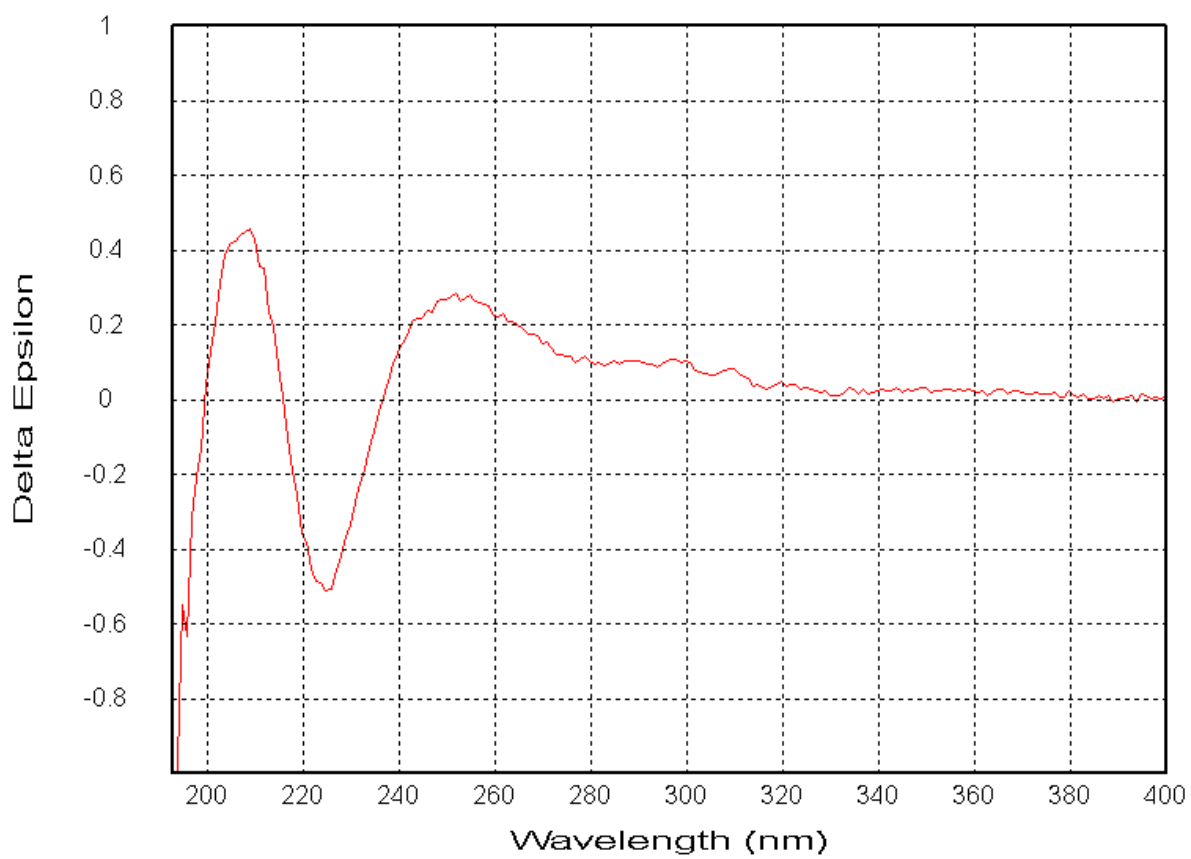


Figure S2. CD spectrum of **2**

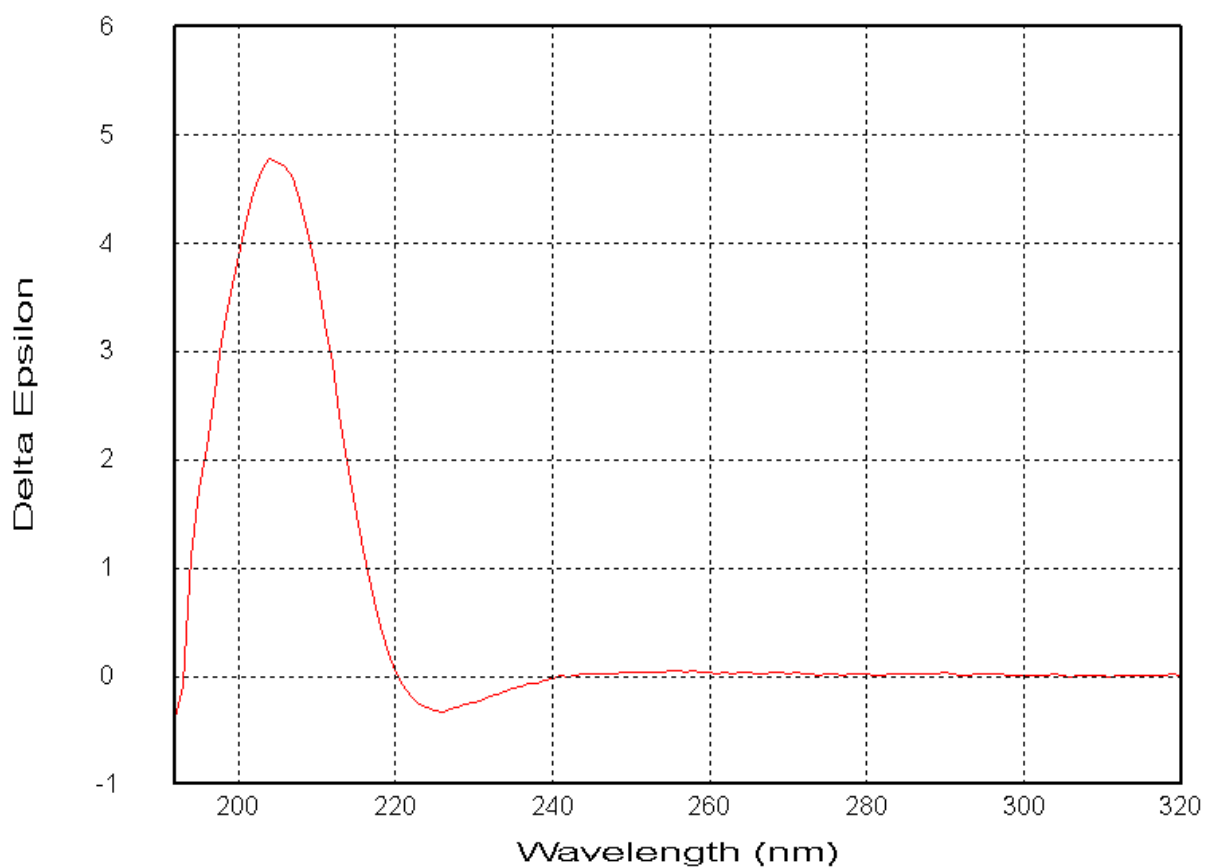


Figure S3. CD spectrum of **3**

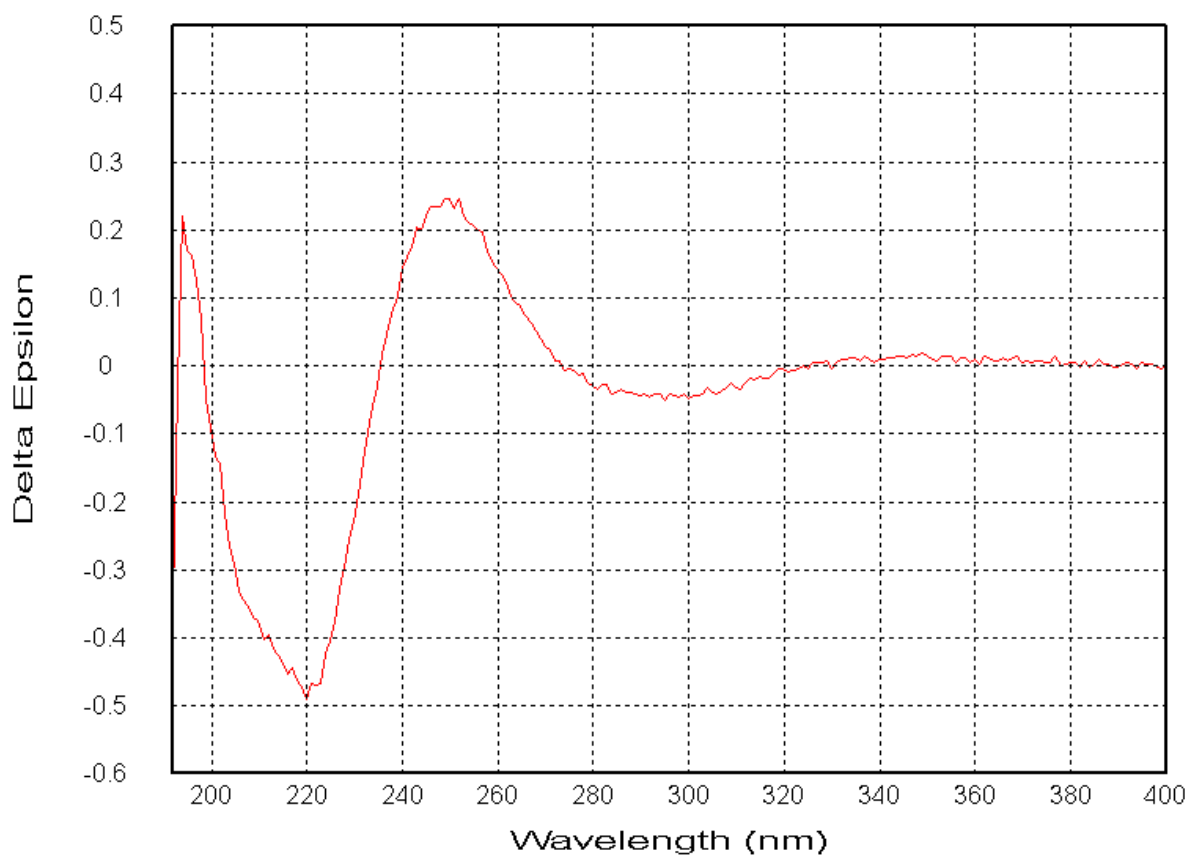


Figure S4. CD spectrum of **4**

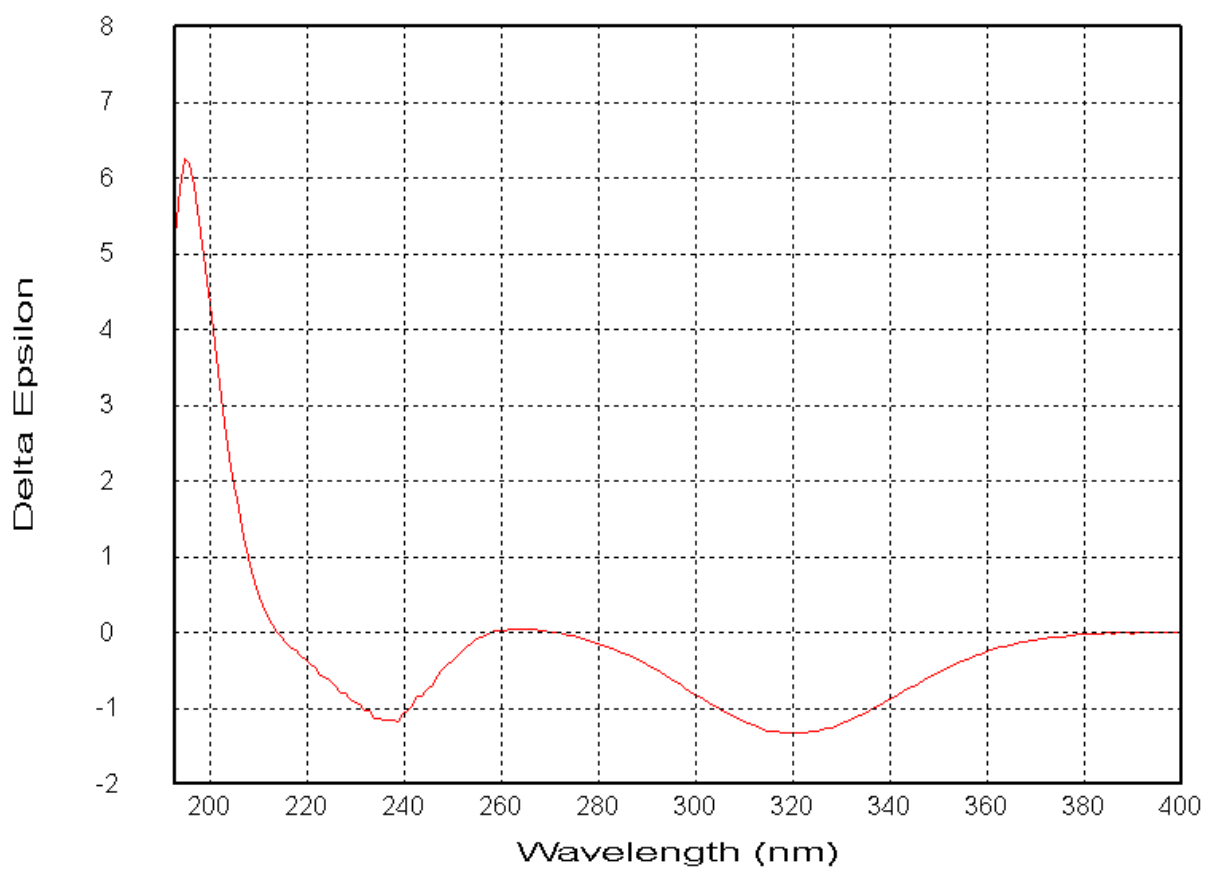


Figure S5. CD spectrum of **5**

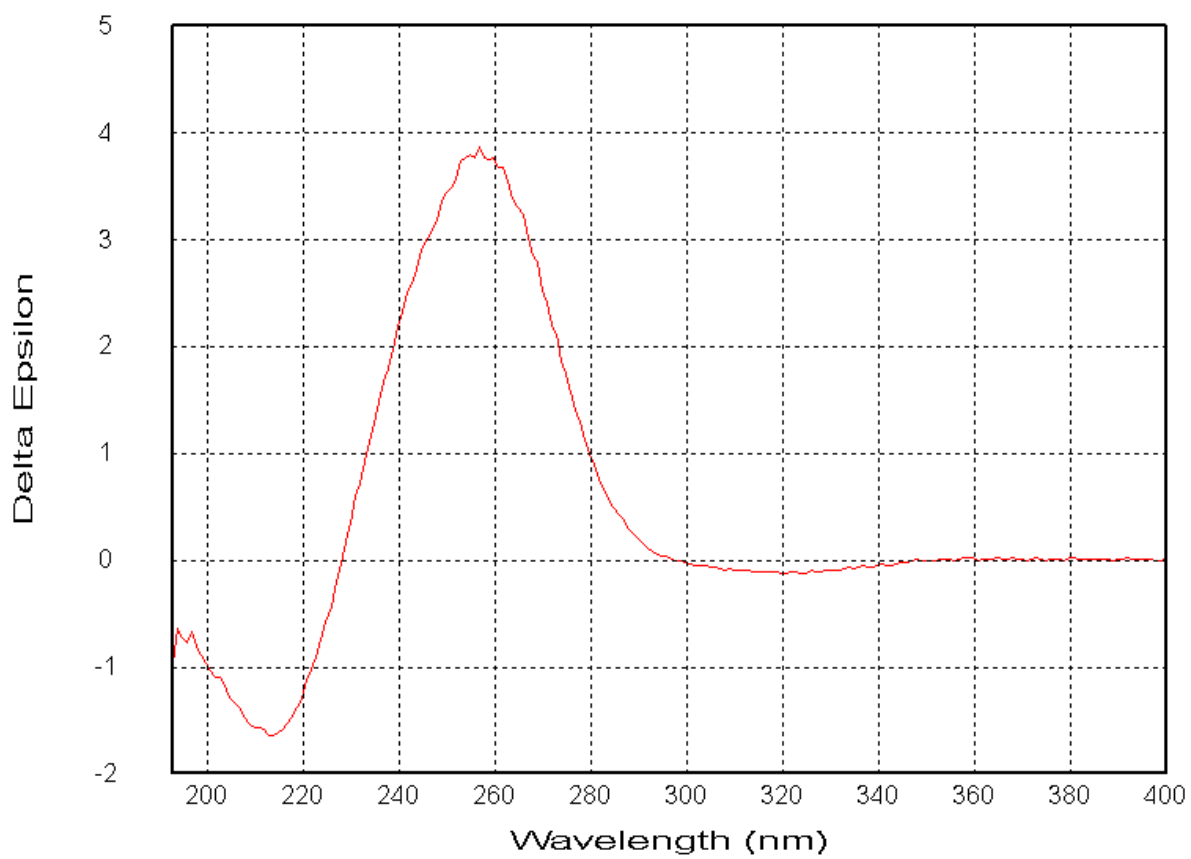


Figure S6. CD spectrum of **6**

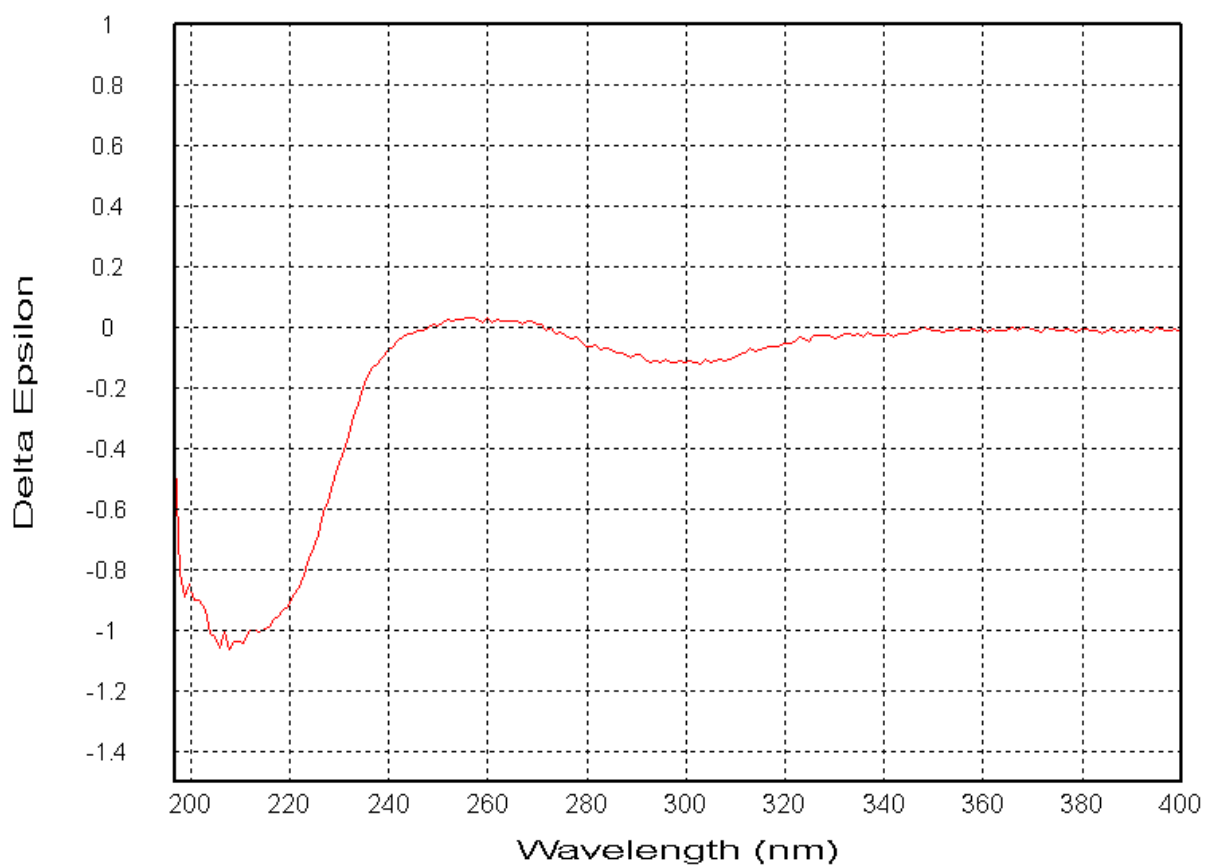


Figure S7. CD spectrum of **7**

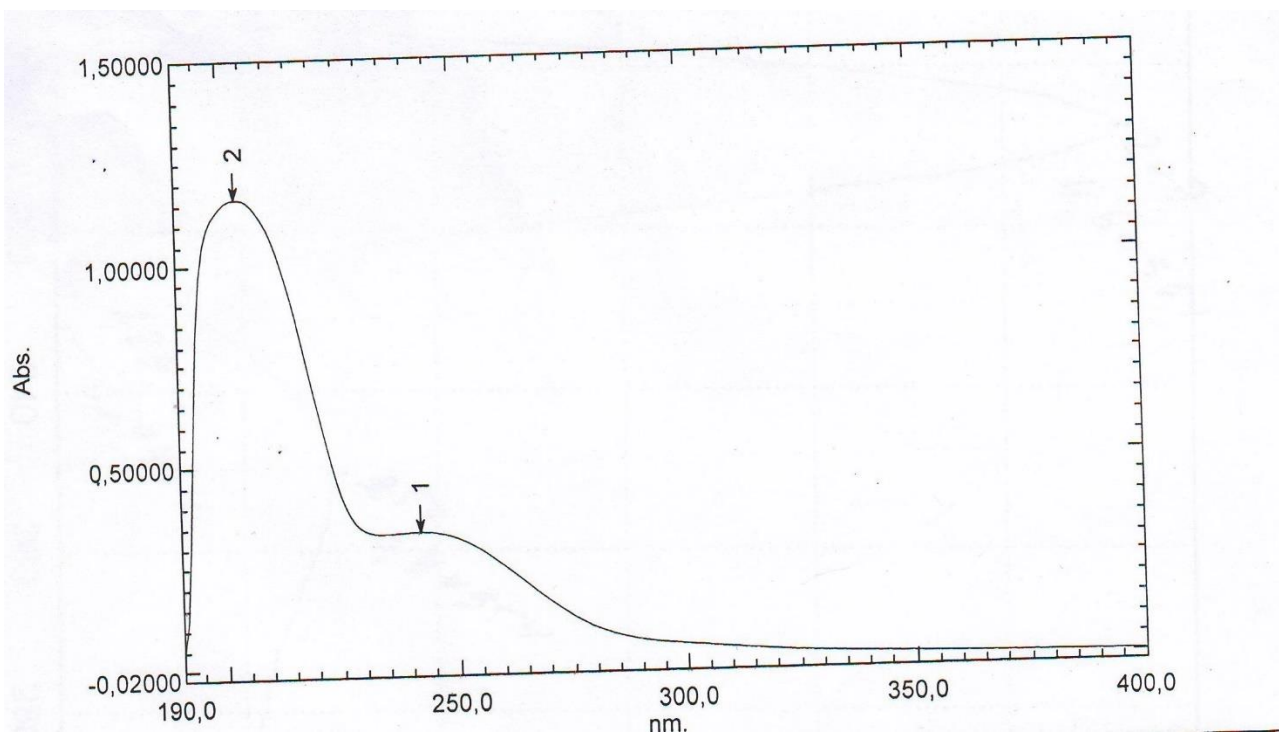


Figure S8. UV spectrum of **1**

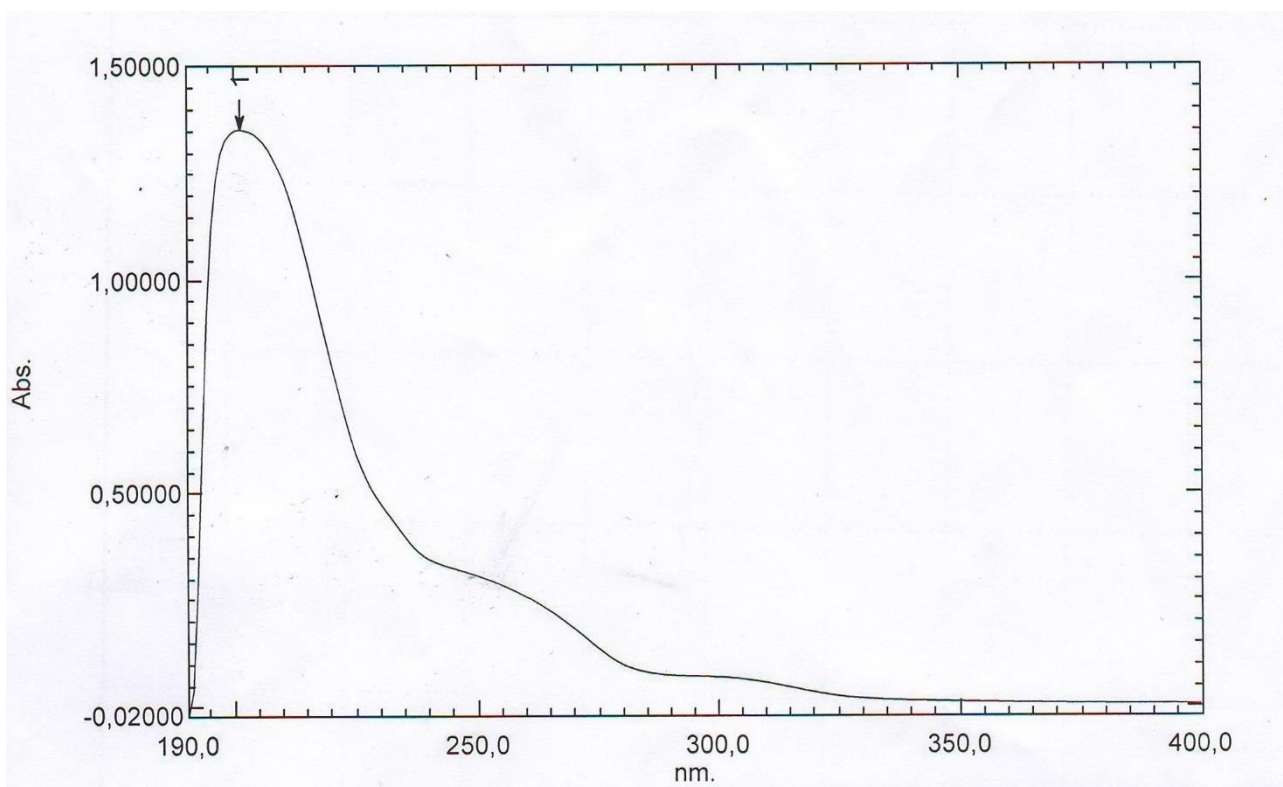


Figure S9. UV spectrum of **2**.

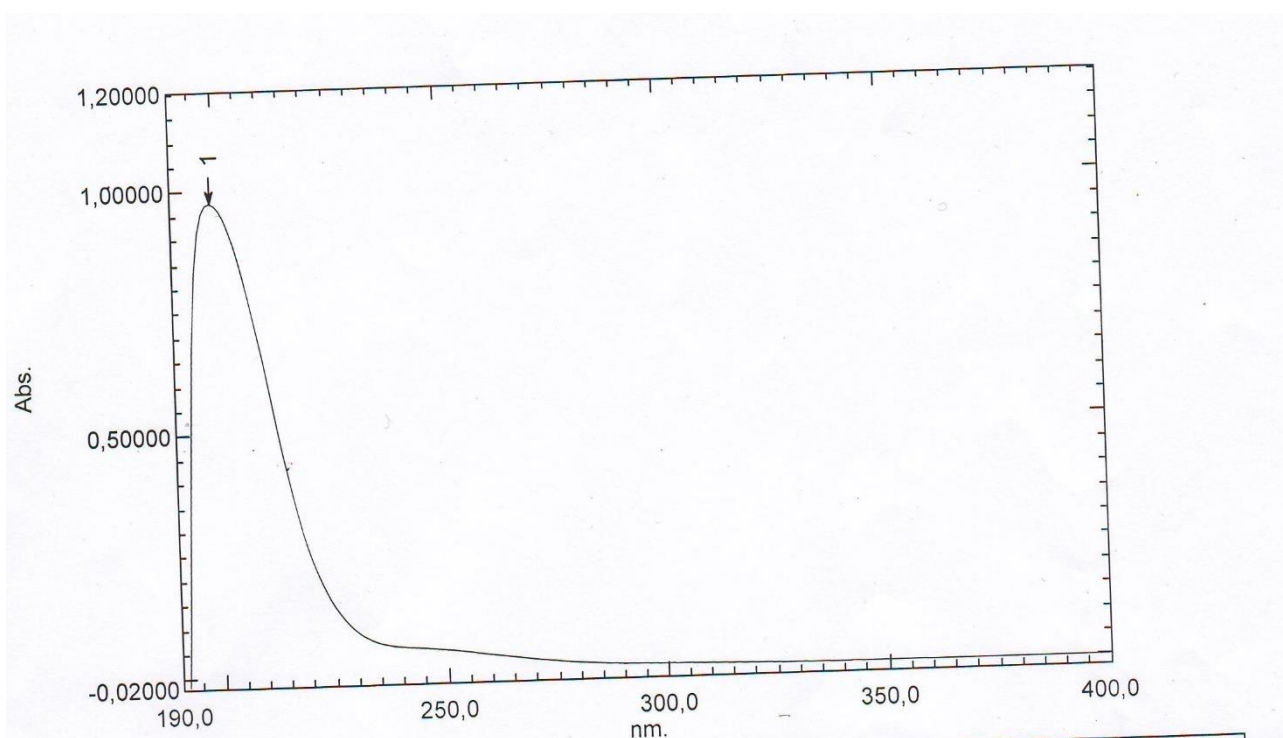


Figure S10. UV spectrum of **3**

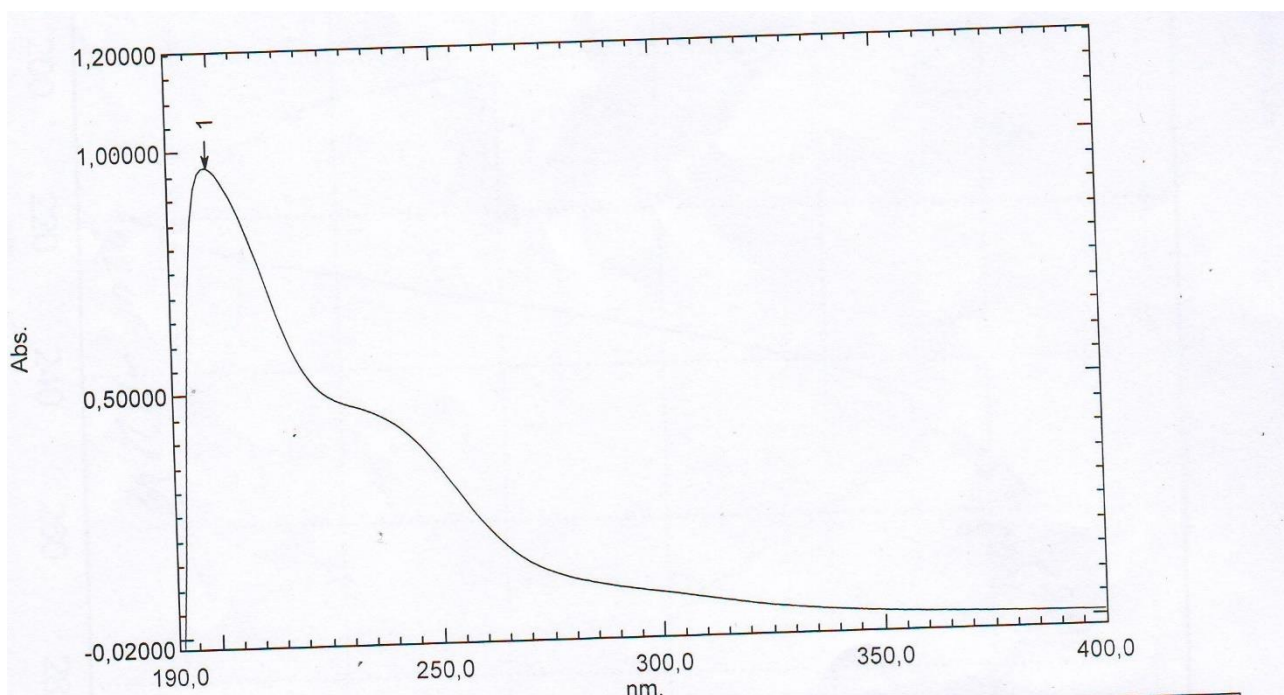


Figure S11. UV spectrum of **4**

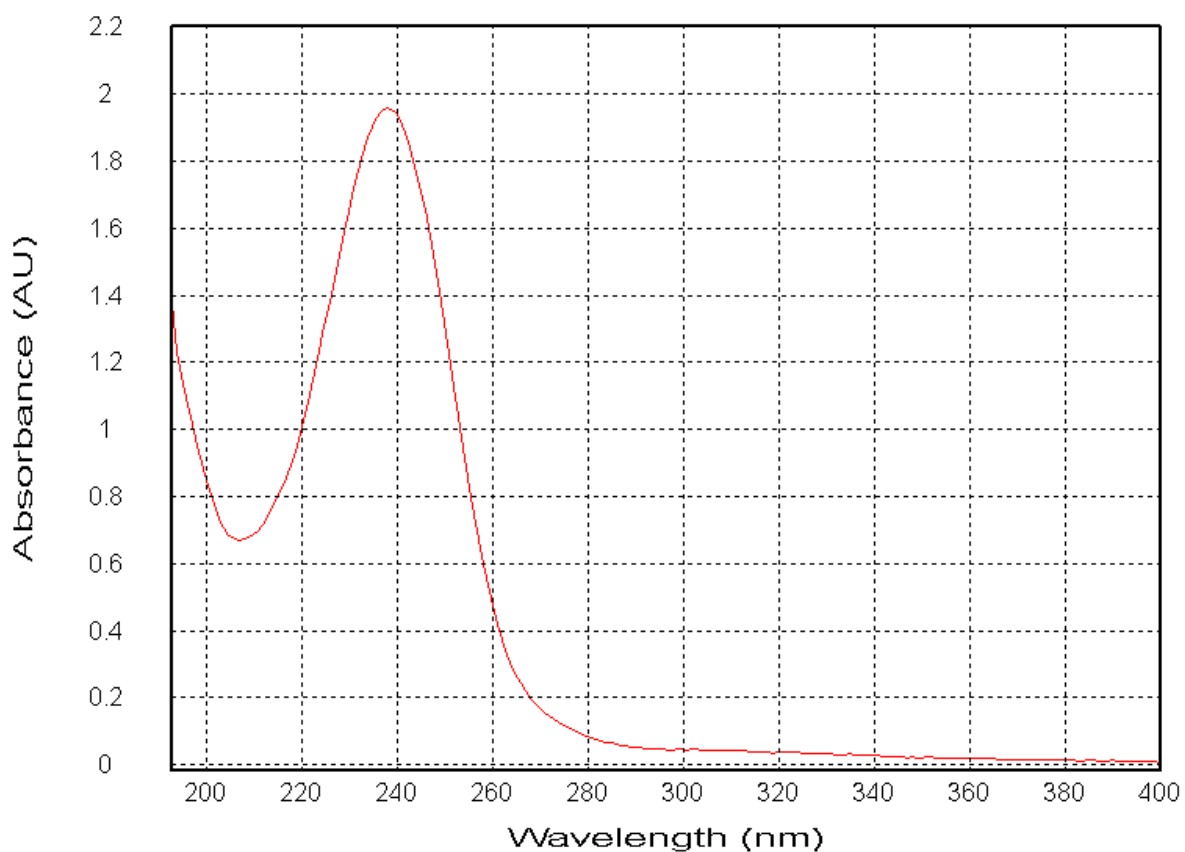


Figure S12. UV spectrum of **5**

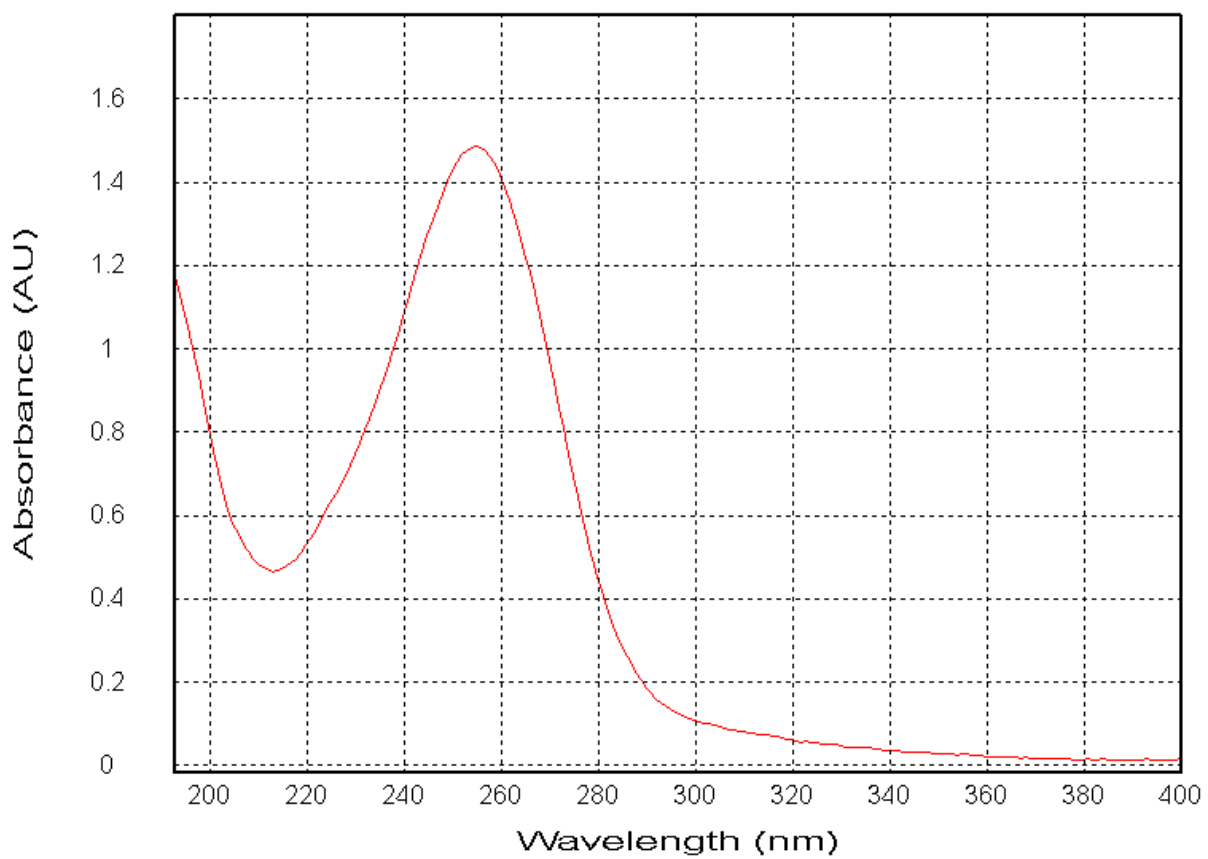


Figure S13. UV spectrum of **6**

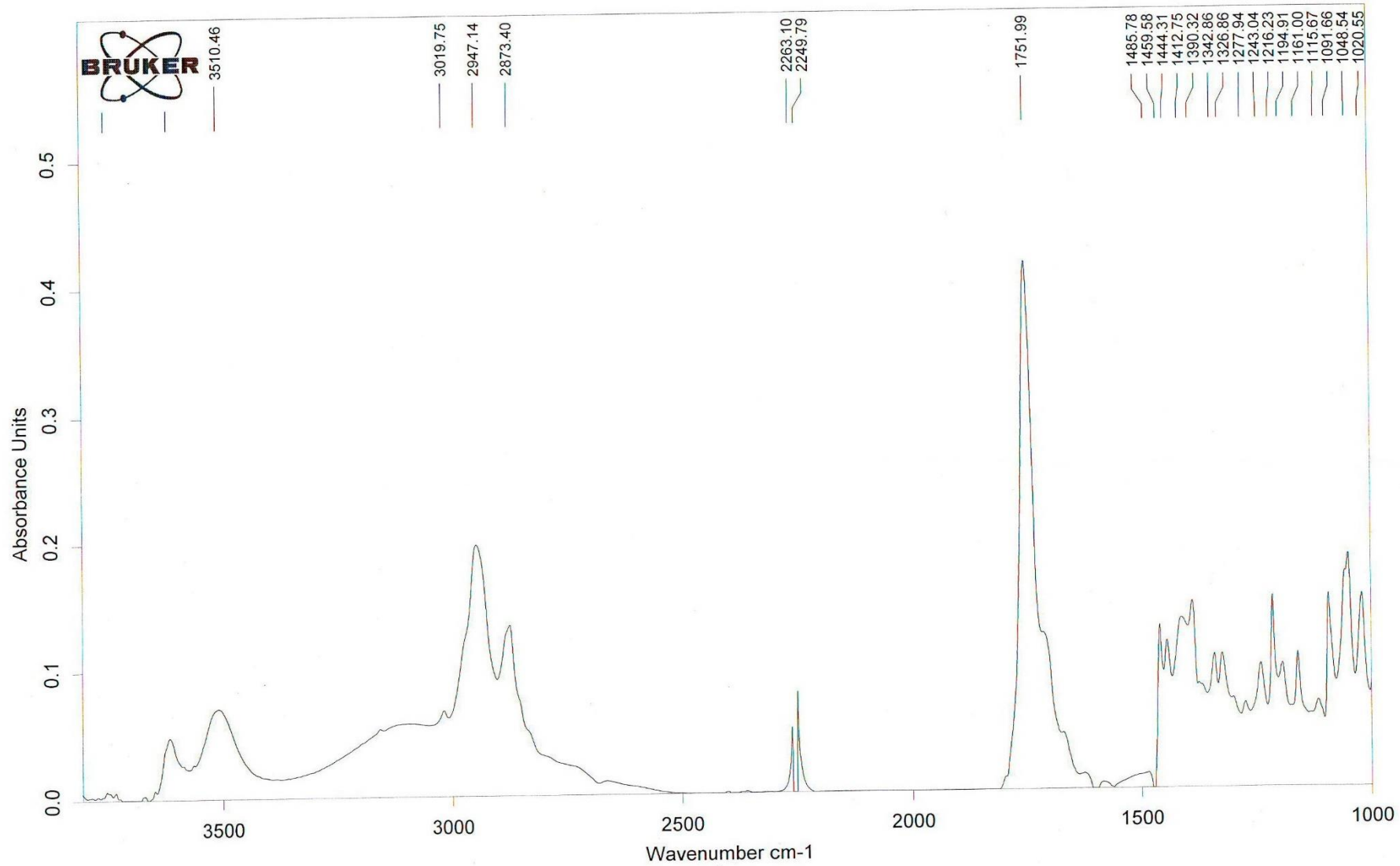


Figure S14. IR spectrum of **1** (3500 – 1000 cm⁻¹)

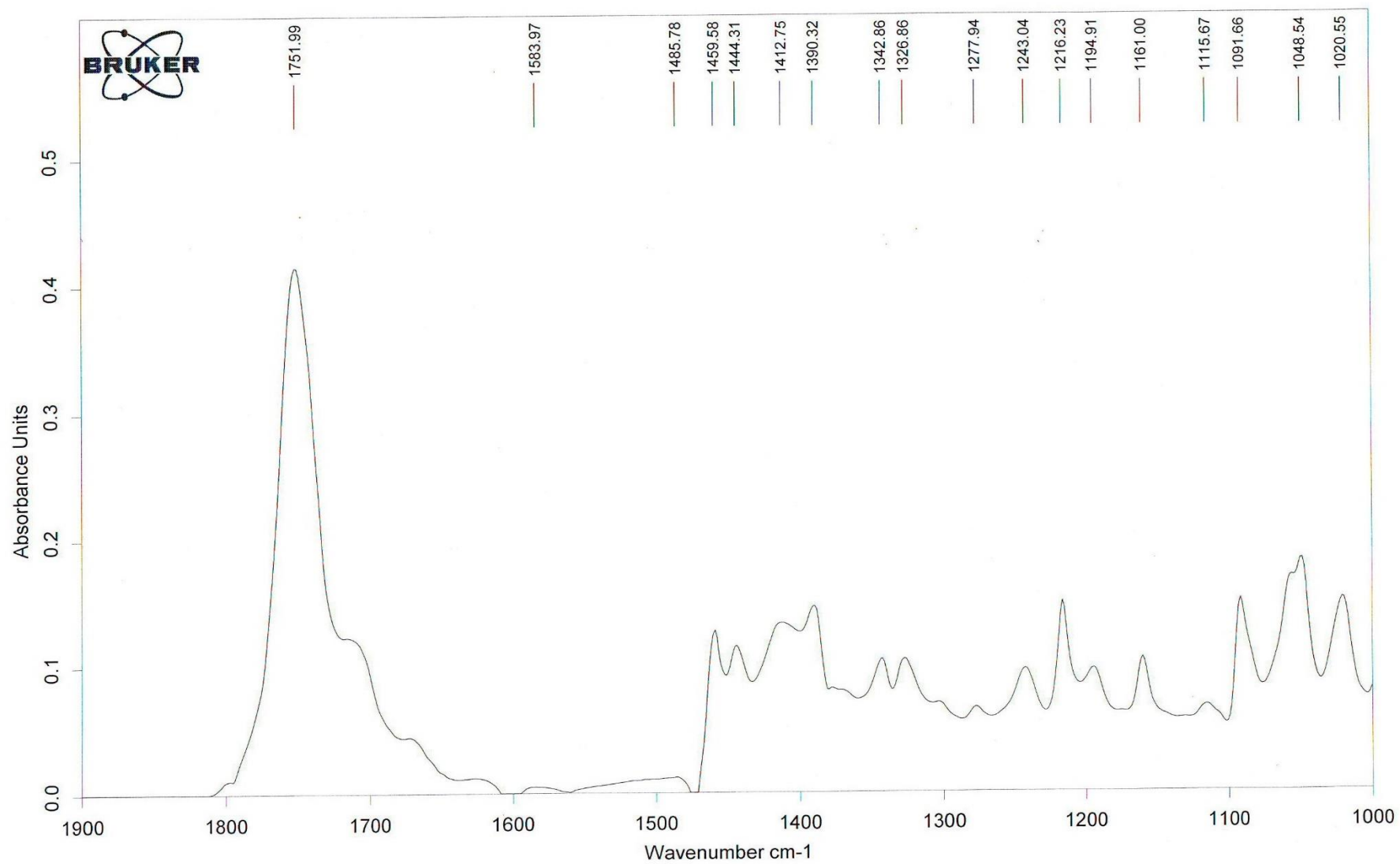


Figure S15. IR spectrum of **1** (1900 – 1000 cm⁻¹)

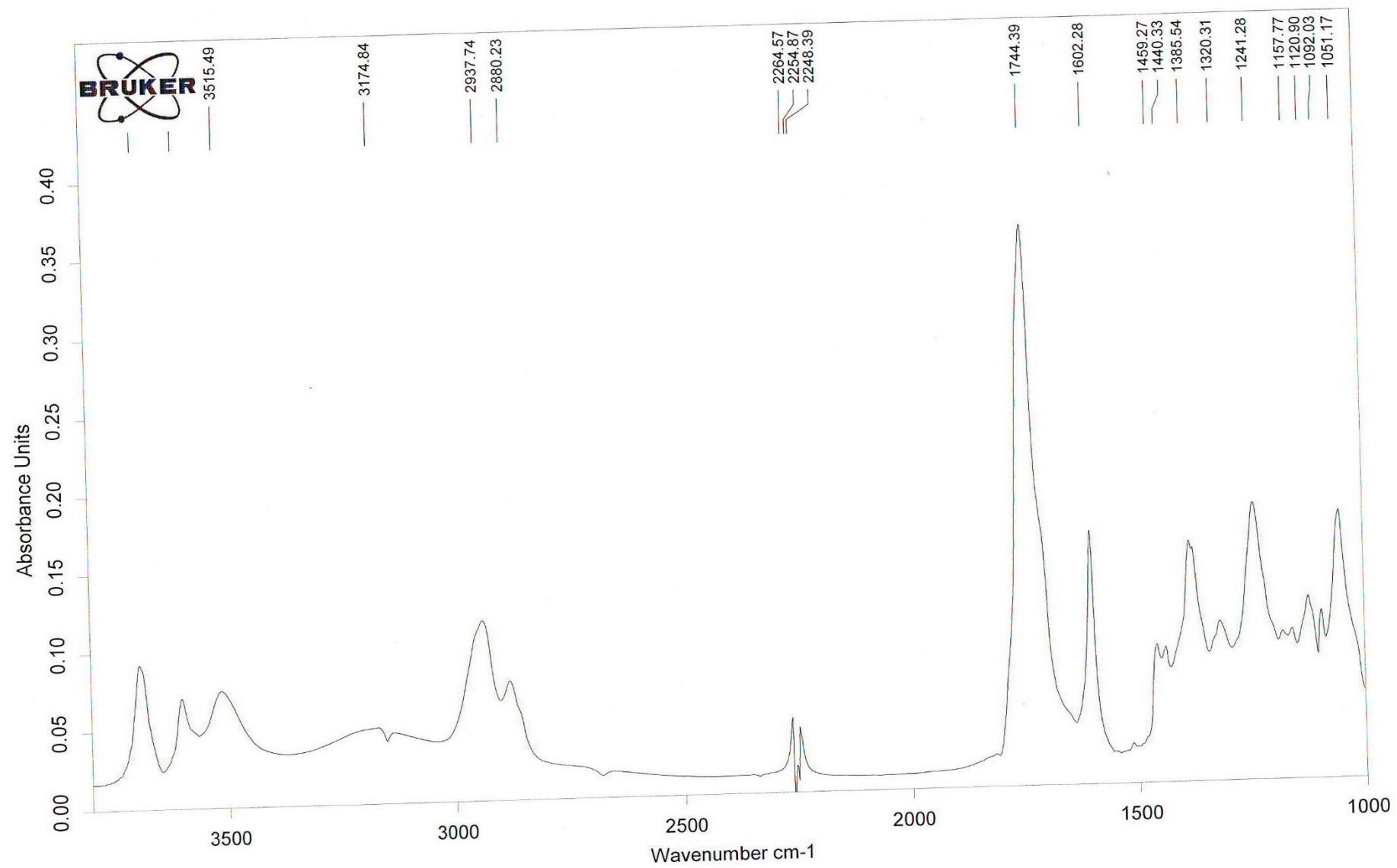


Figure S16. IR spectrum of **2** (3500 – 1000 cm⁻¹)

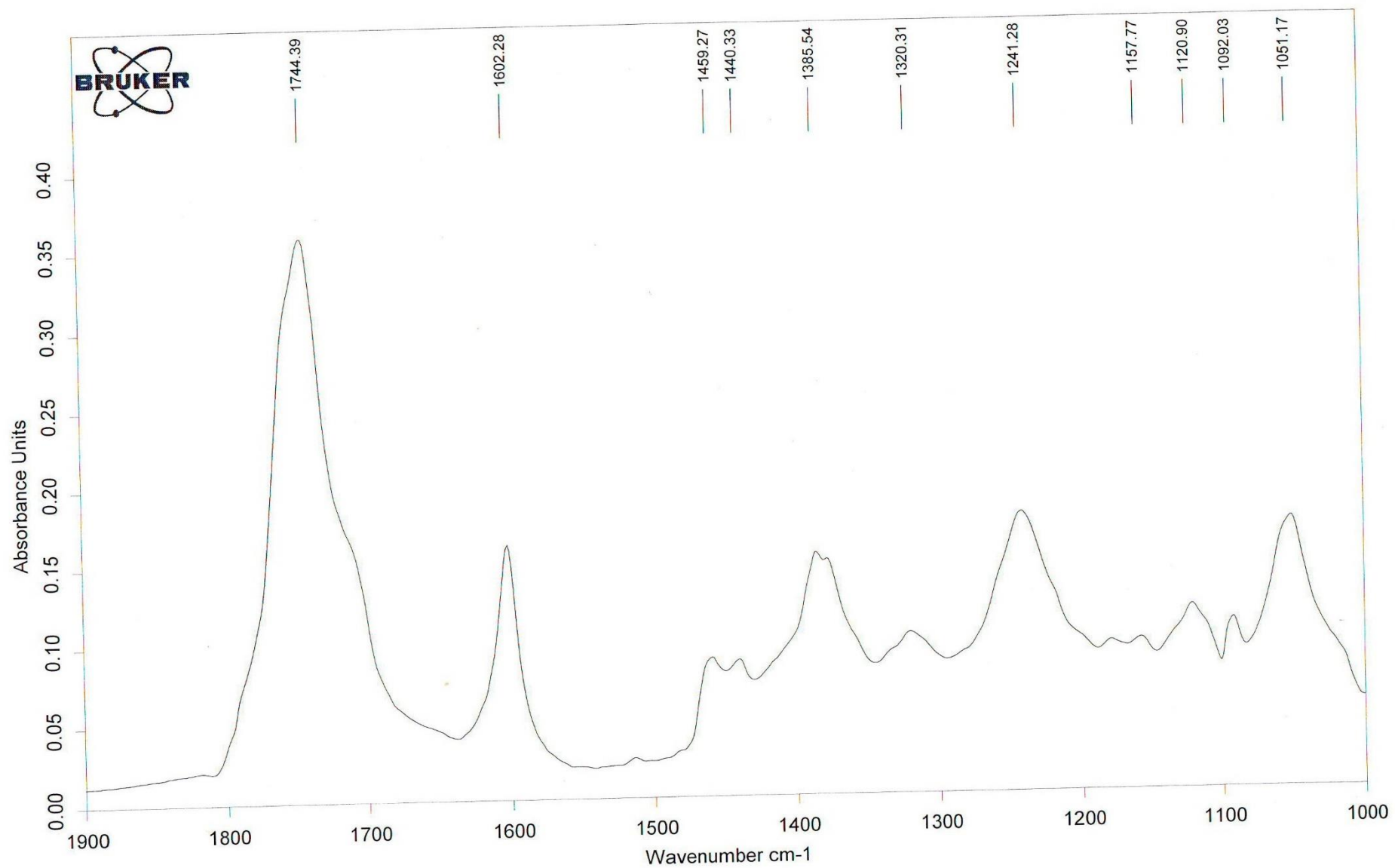


Figure S17. IR spectrum of **2** (1900 – 1000 cm⁻¹)

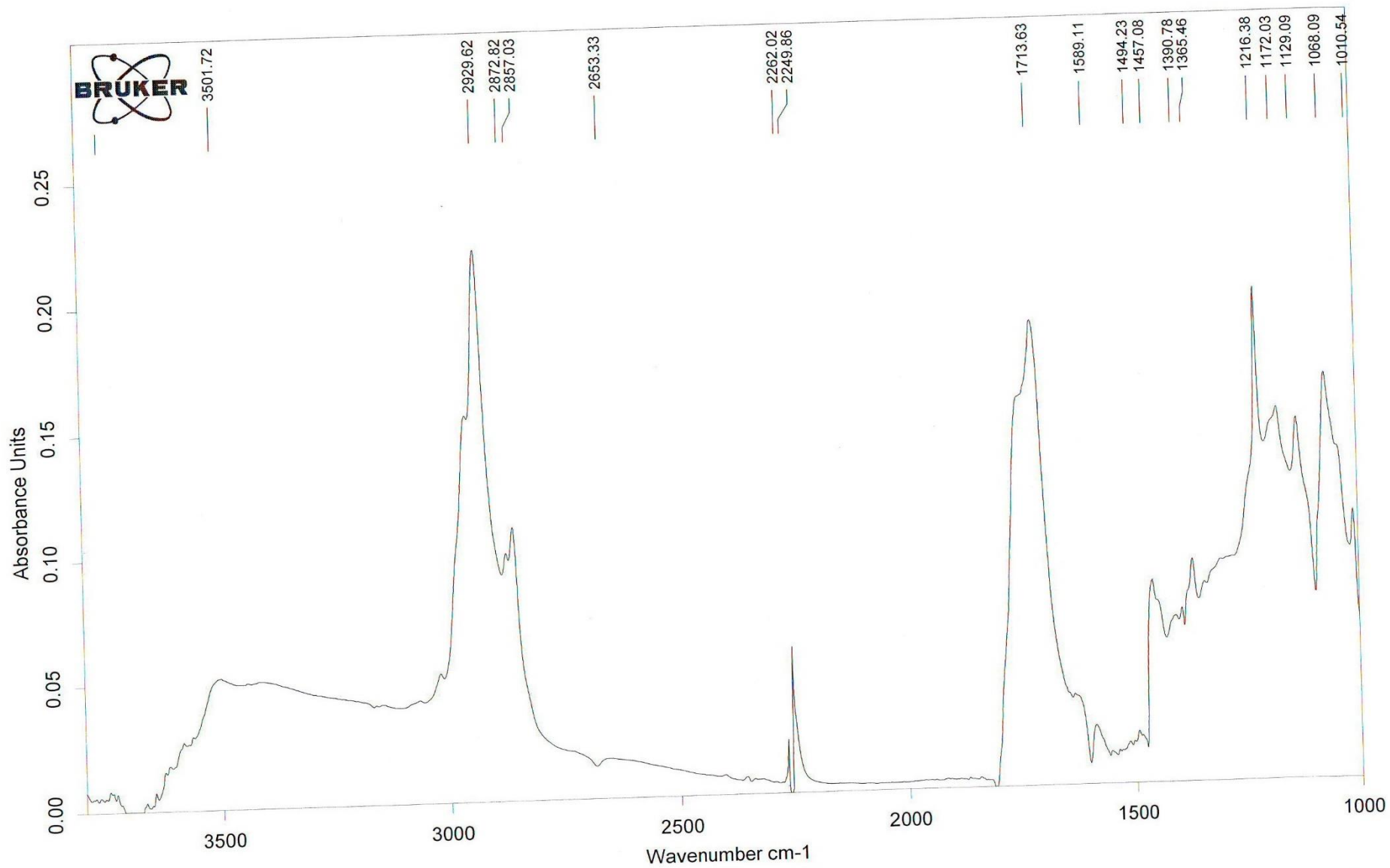


Figure S18. IR spectrum of **4** (3500 – 1000 cm⁻¹)

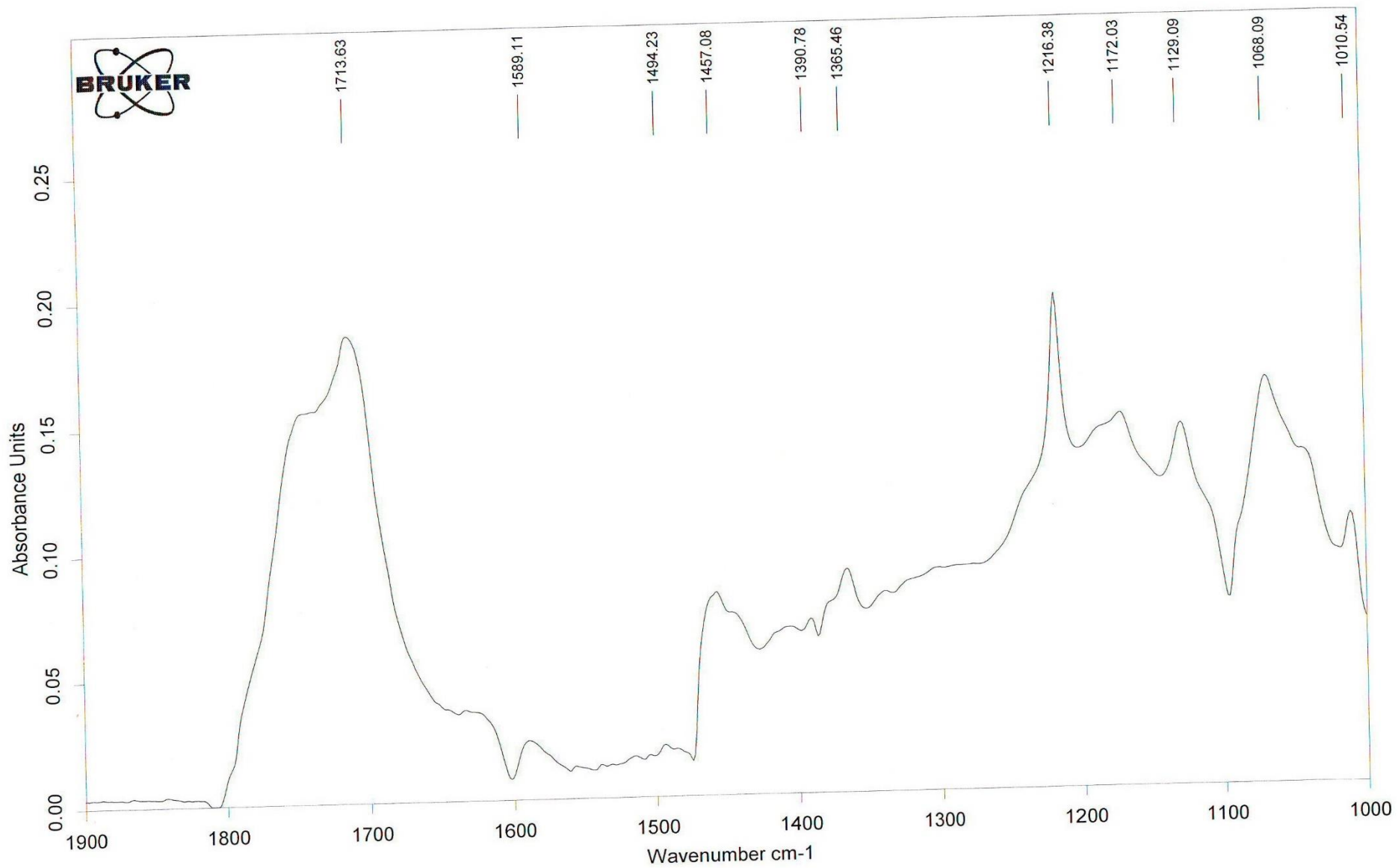


Figure S19. IR spectrum of **4** (1900 – 1000 cm⁻¹)

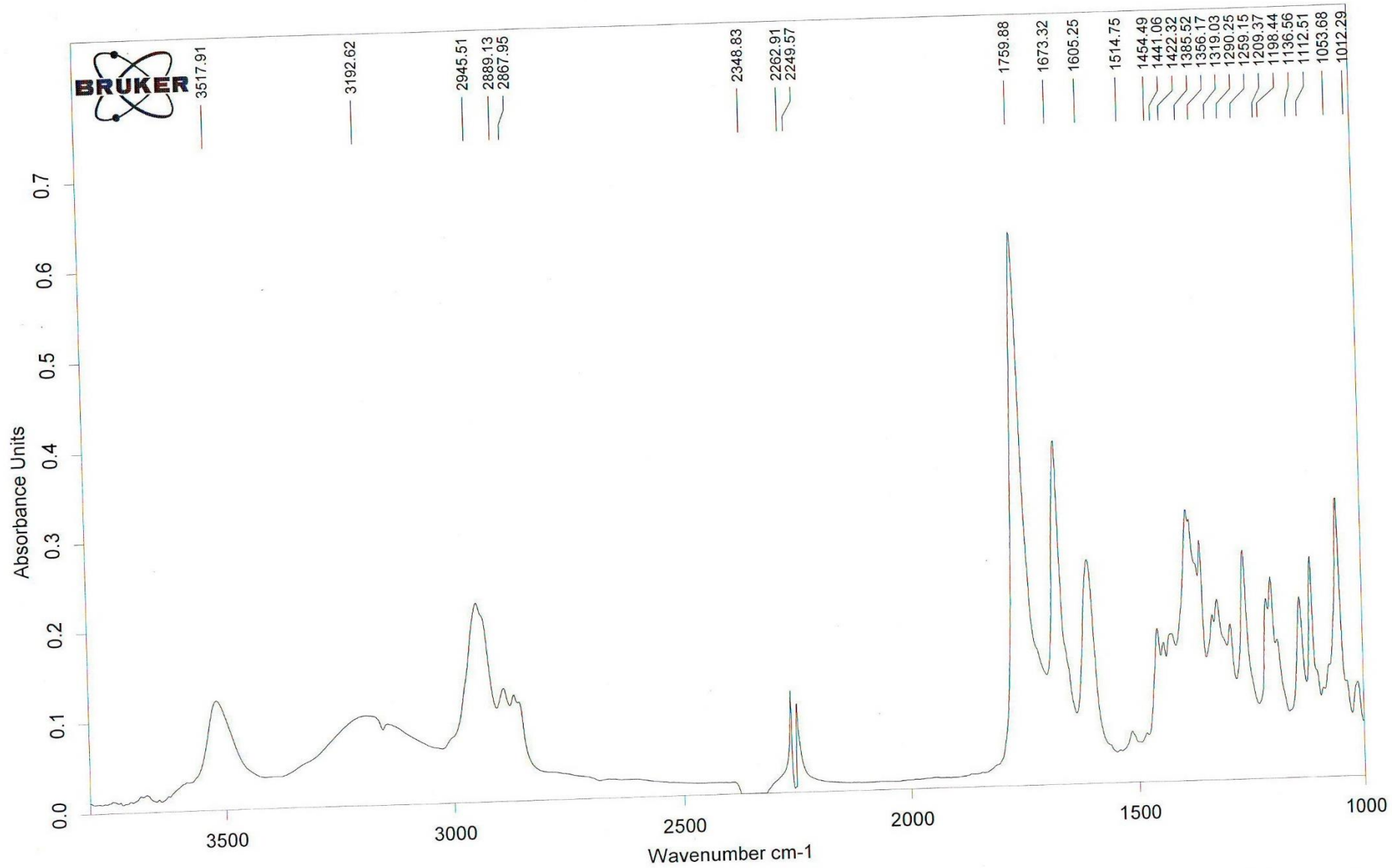


Figure S20. IR spectrum of **6** (3500 – 1000 cm⁻¹)

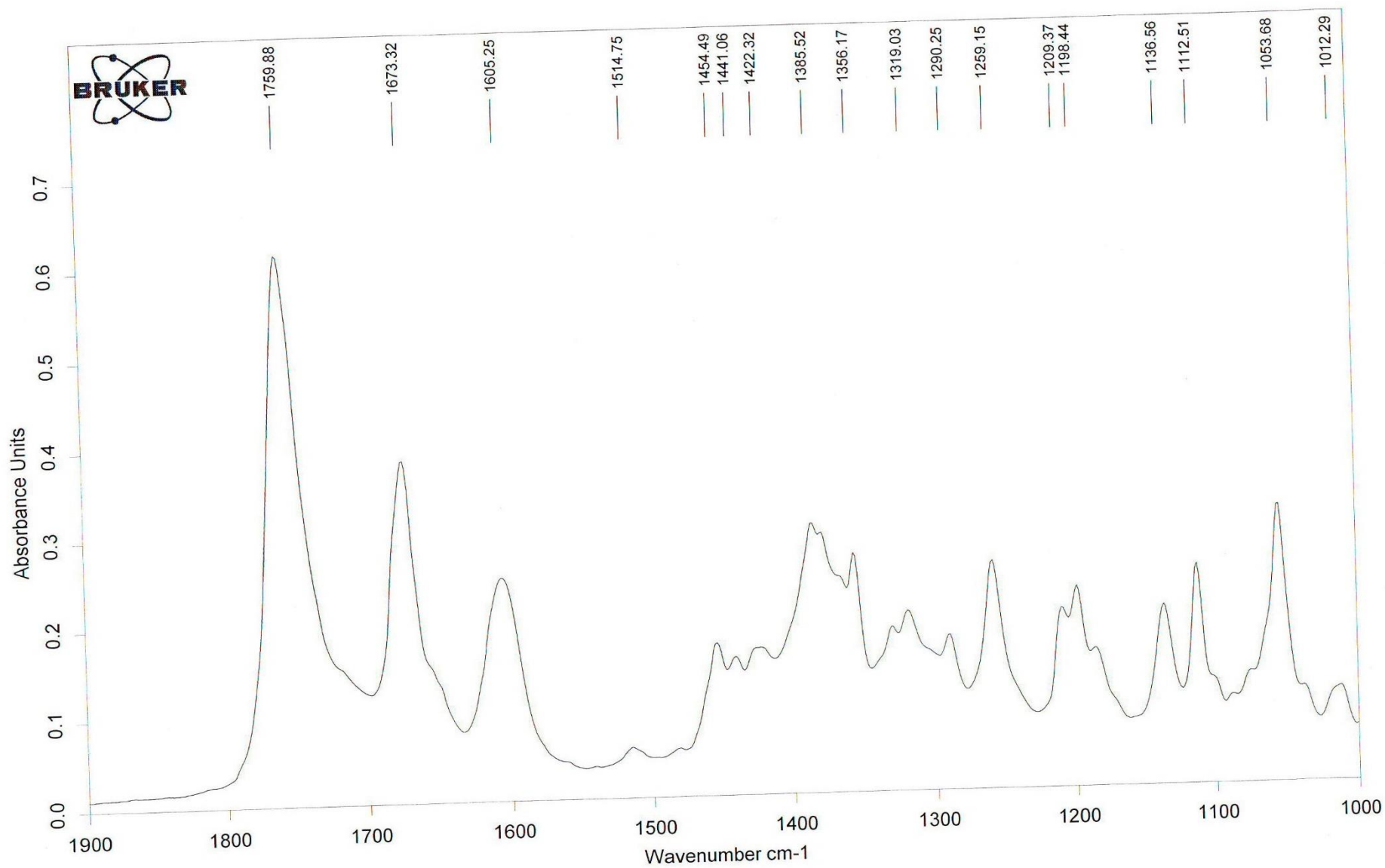


Figure S21. IR spectrum of **6** (1900 – 1000 cm⁻¹)

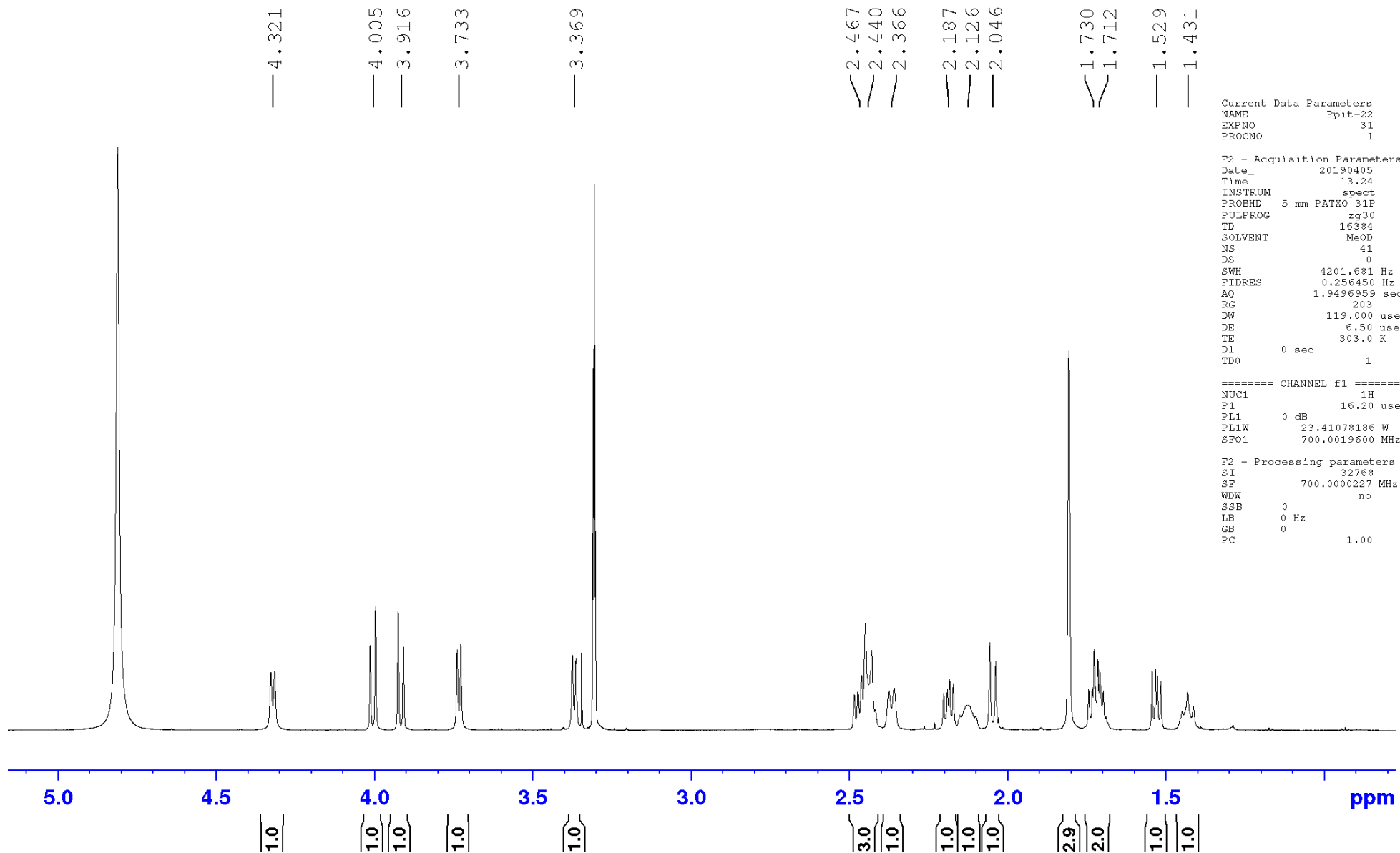
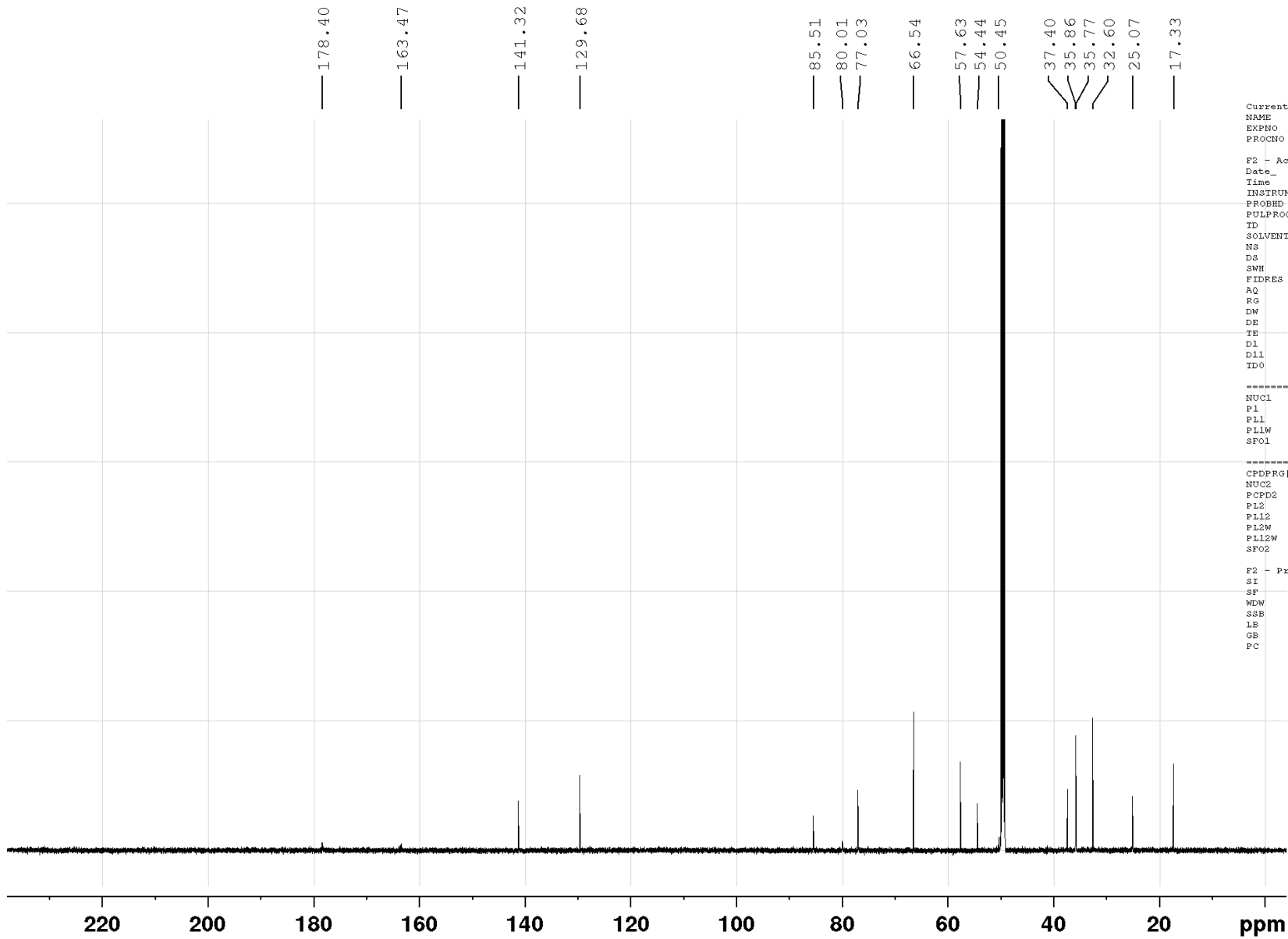


Figure S22. ¹H NMR spectrum (700 MHz, CD₃OD) of **1**



```

Current Data Parameters
NAME      Ppit-22
EXPNO    3730
PROCNO   1

F2 - Acquisition Parameters
Date_    20190405
Time     13.27
INSTRUM  spect
PROBHD   5 mm PATXO 31P
PULPROG  zgpg30
TD       65536
SOLVENT  MeOD
NS       5072
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       303.2 K
D1       0.50000000 sec
D11      0.03000000 sec
TD0      4096

----- CHANNEL f1 -----
NUC1     13C
P1       10.40 usec
PL1      0 dB
PL1W     106.75517273 W
SF01     176.0353807 MHz

----- CHANNEL f2 -----
CPDPRG[2] waltz16
NUC2     1H
PCPD2    71.90 usec
PL2      0 dB
PL12     12.68 dB
PL12W    23.41078186 W
PL12W    1.26303649 W
SF02     700.0021000 MHz

F2 - Processing parameters
SI       65536
SF       176.0147885 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.00

```

Figure S23. ¹³C NMR spectrum (176 MHz, CD₃OD) of **1**

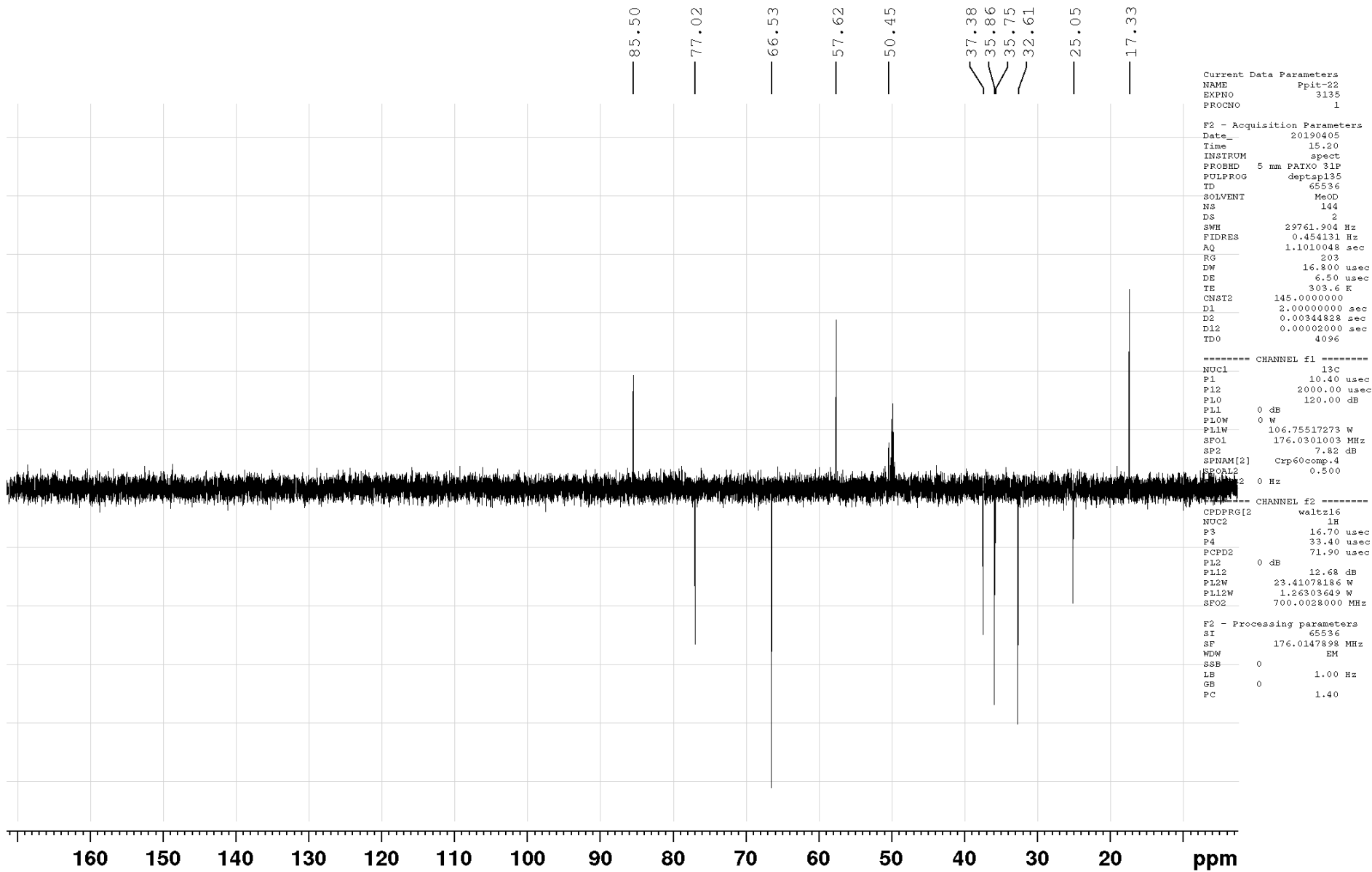


Figure S24. DEPT-135 NMR spectrum (176 MHz, CD₃OD) of **1**

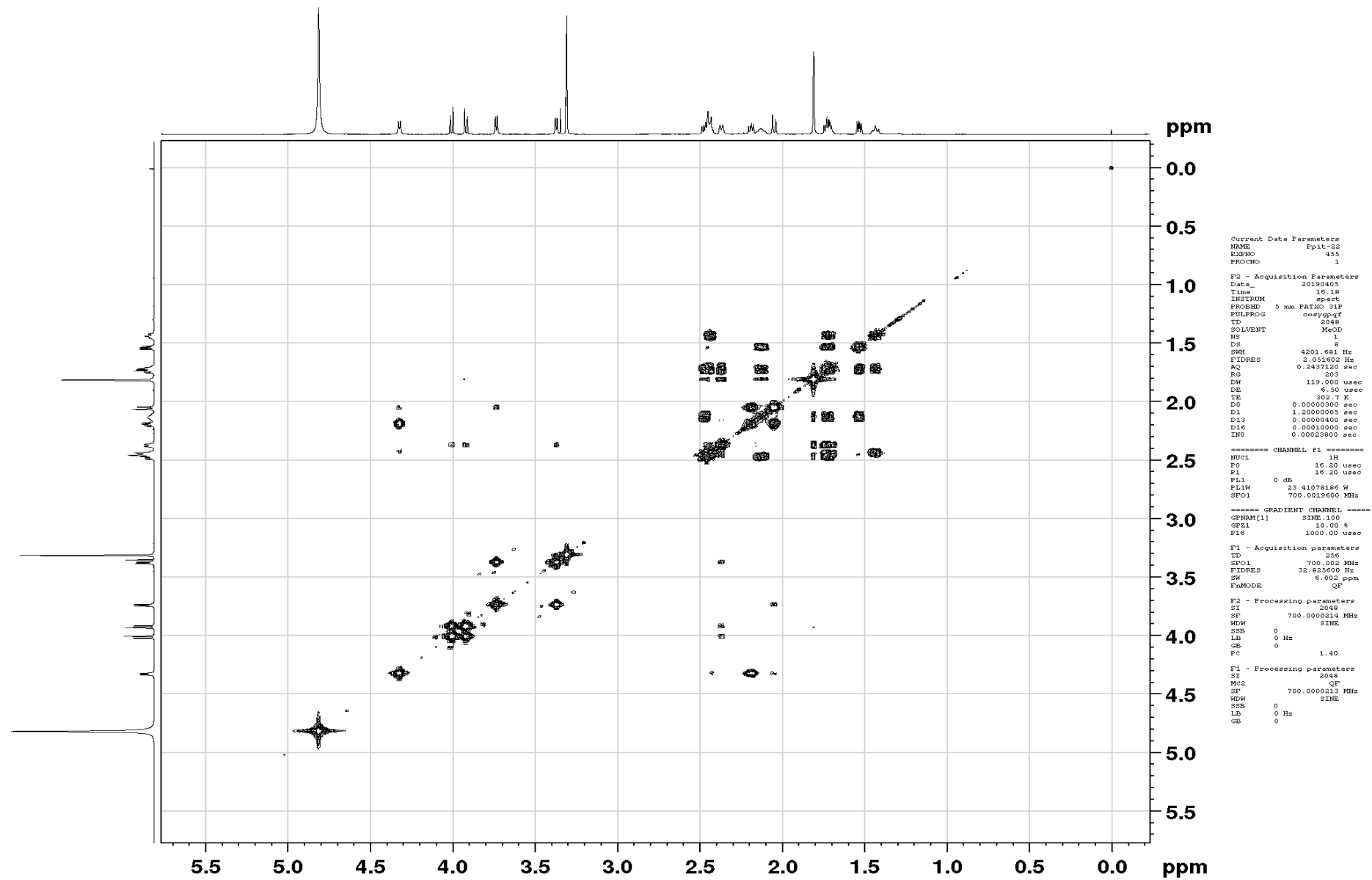
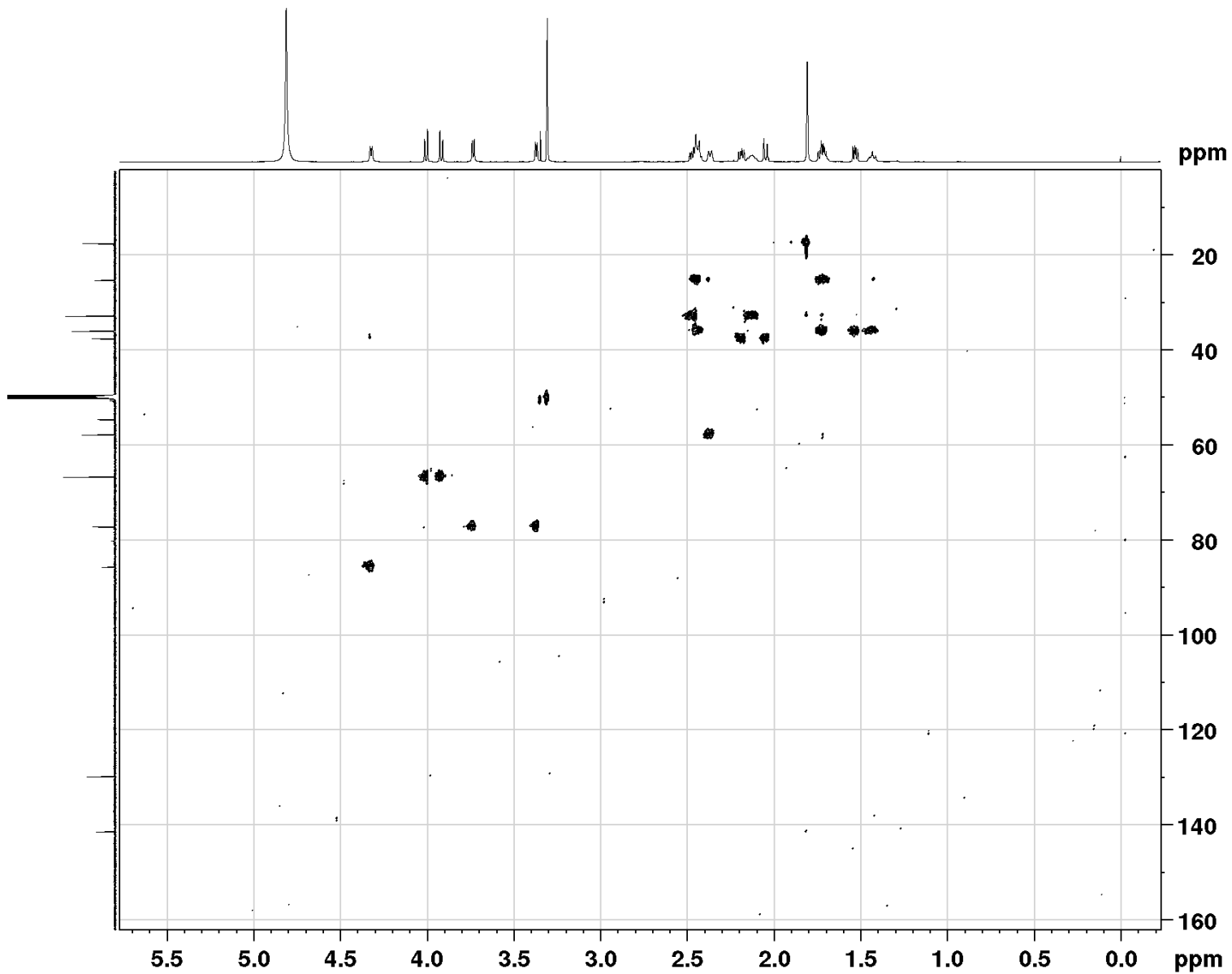


Figure S25. COSY-45 spectrum (700 MHz, CD₃OD) of **1**



```

Current Data Parameters
NAME      Ppit-22
EXPNO     7130
PROCNO    1

F2 - Acquisition Parameters
Date_     20190405
Time      15:37
INSTRUM   spect
PROBHD    5 mm PATCO 31P
PULPROG   hsqcetgpsig2
TD         2048
SOLVENT   MeOH
NS         4
DS         48
SWH        4201.684 Hz
FIDRES     2.031603 Hz
AQ         0.2437120 sec
RG         203
DQ         119.000 usec
DE         6.50 usec
TE         303.2 K
CNS12     145.0000000
CNS17     -0.5000000
D0         0.0000000 sec
D1         2.00000000 sec
D4         0.00172414 sec
D11        0.03000000 sec
D16        0.00010000 sec
D24        0.00082207 sec
IND0       0.00001775 sec
L31        16

----- CHANNEL f1 -----
NUC1       1H
P1         16.20 usec
P2         32.40 usec
P3         0 usec
P4         0 dB
P5         23.41078184 W
SFO1       700.0015600 MHz

----- CHANNEL f2 -----
CPDPRG2   b1_p5M4sp_4sp.2
NUC2       13C
P3         10.00 usec
P14        500.00 usec
P24        2000.00 usec
P3         1500.00 usec
P10        100.00 dB
P12        0 dB
P122       15.56 dB
P124       0 W
P1242     106.73517273 W
P12422    2.76748734 W
SFO2       176.0292000 MHz
SP3        8.16 dB
SP7        8.16 dB
SP14       9.64 dB
SP31       15.66 dB
SFO1A1[3]  cnp60,0.5,20.1
SFO1A1[7]  cnp60comp.4
SFO1A1[14] cnp32,1.5,20.2
SFO1A1[31] cnp32,1.5,20.2
SFO1A12    0.500
SFO1A17    0.500
SFO1A114   0.500
SFO1A131   0.500
SFO1F22    0 Hz
SFO1F27    0 Hz
SFO1F214   0 Hz
SFO1F231   0 Hz

----- GRADIENT CHANNEL -----
GFO1A1[1]  SINE,100
GFO1A1[2]  SINE,100
GFO1A1[3]  SINE,100
GFO1A1[4]  SINE,100
GFO1E1     80.00 %
GFO1E2     20.10 %
GFO1E3     11.00 %
GFO1E4     -5.00 %
P16        1000.00 usec
P19        500.00 usec

F1 - Acquisition parameters
TD         256
SFO1       176.0292 MHz
FIDRES     220.006500 Hz
SW         160.000 ppm
FMODE      Echo-Antiecho

F2 - Processing parameters
SI         2048
SF         700.0000002 MHz
WDW        QSHINE
SSB        2
LB         0 Hz
GB         0
PC         1.40

F1 - Processing parameters
SI         4096
MC2        echo-antiecho
SF         176.0147846 MHz
WDW        QSHINE
SSB        8
LB         0 Hz
GB         0

```

Figure S26. HSQC spectrum (700 MHz, CD₃OD) of 1

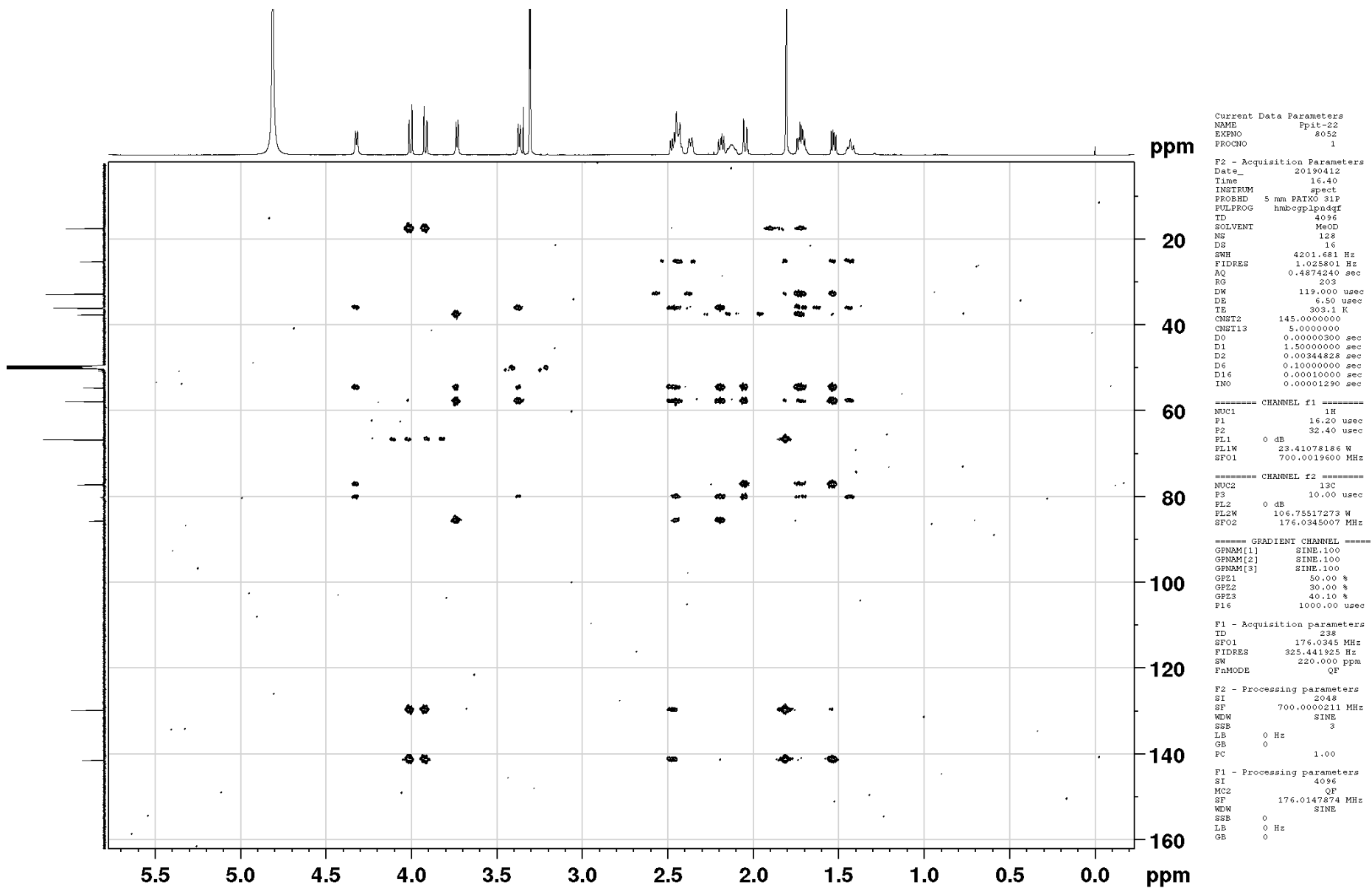


Figure S27. HMBC spectrum (700 MHz, CD₃OD) of **1**

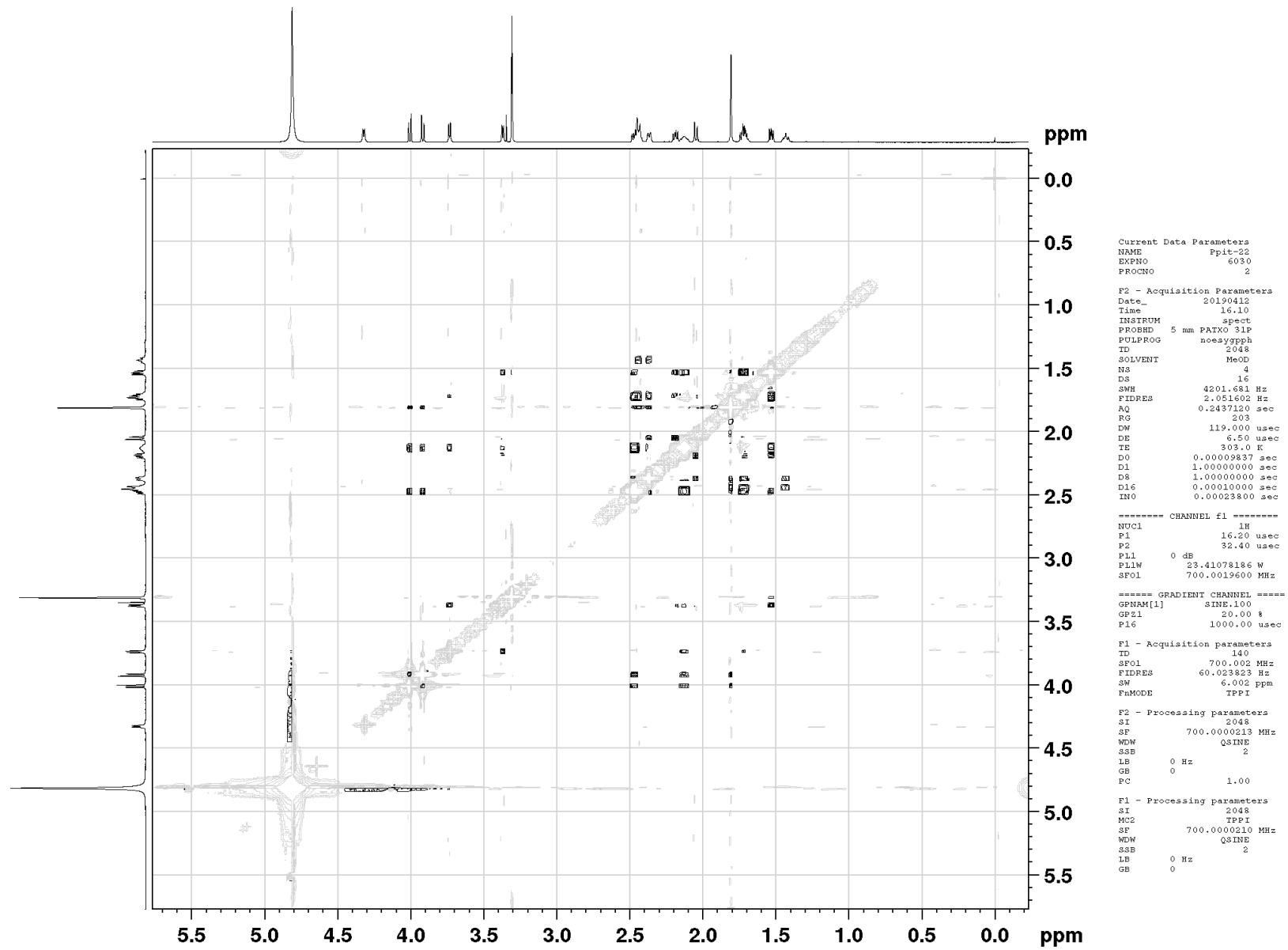


Figure S28. NOESY spectrum (700 MHz, CD₃OD) of **1**

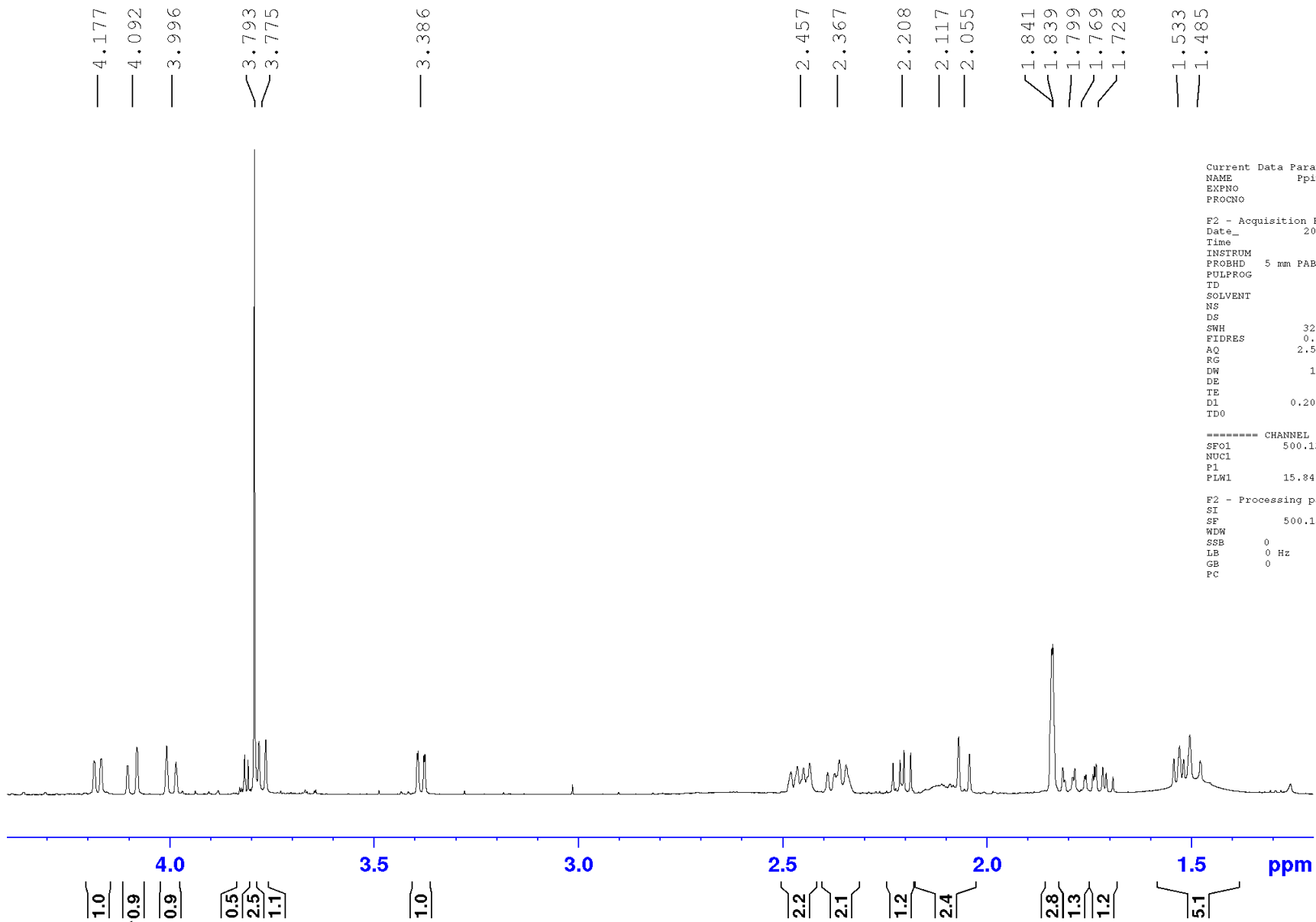


Figure S29. ¹H NMR spectrum (500 MHz, CD₃OD) of **1a**

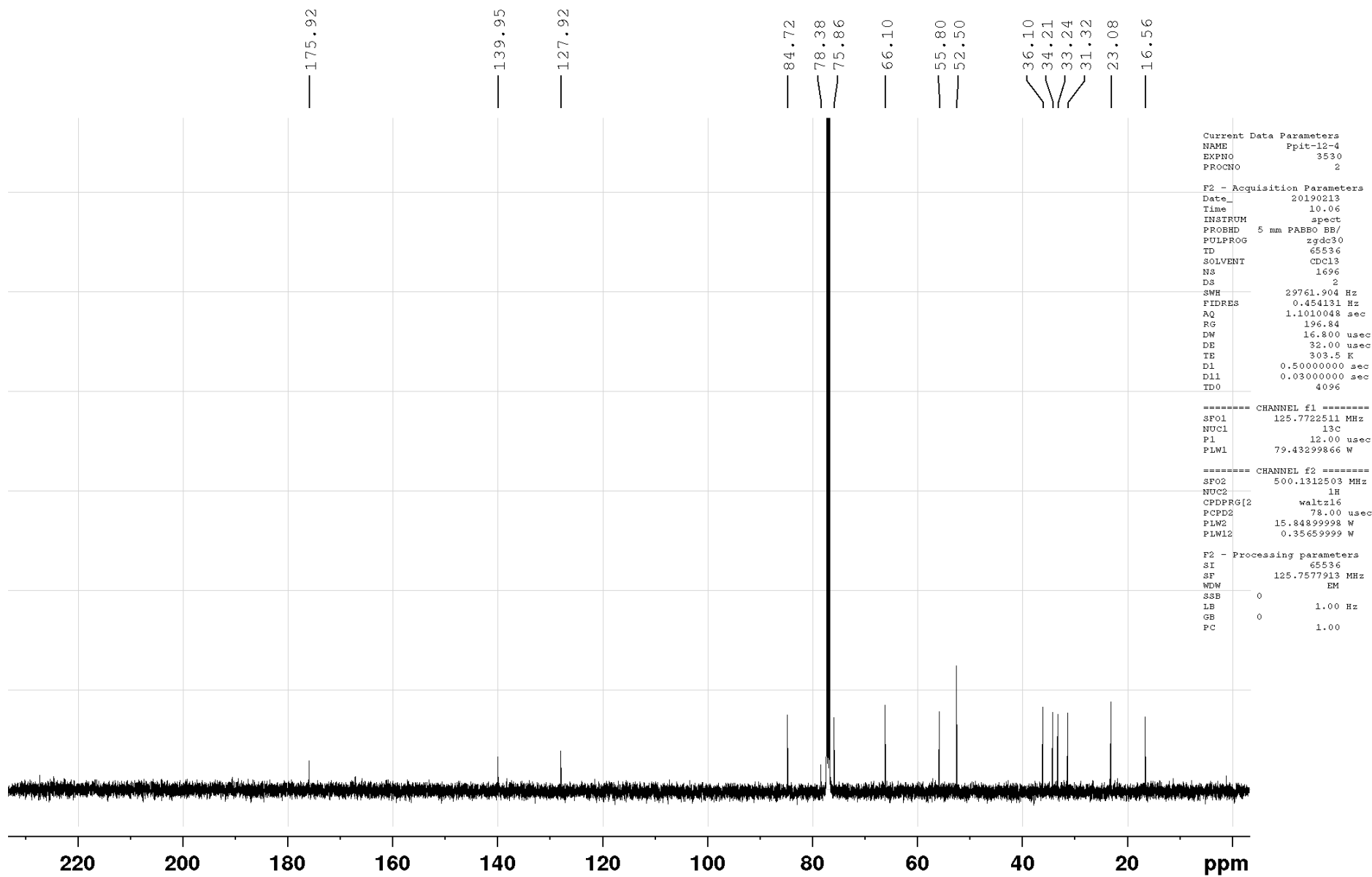
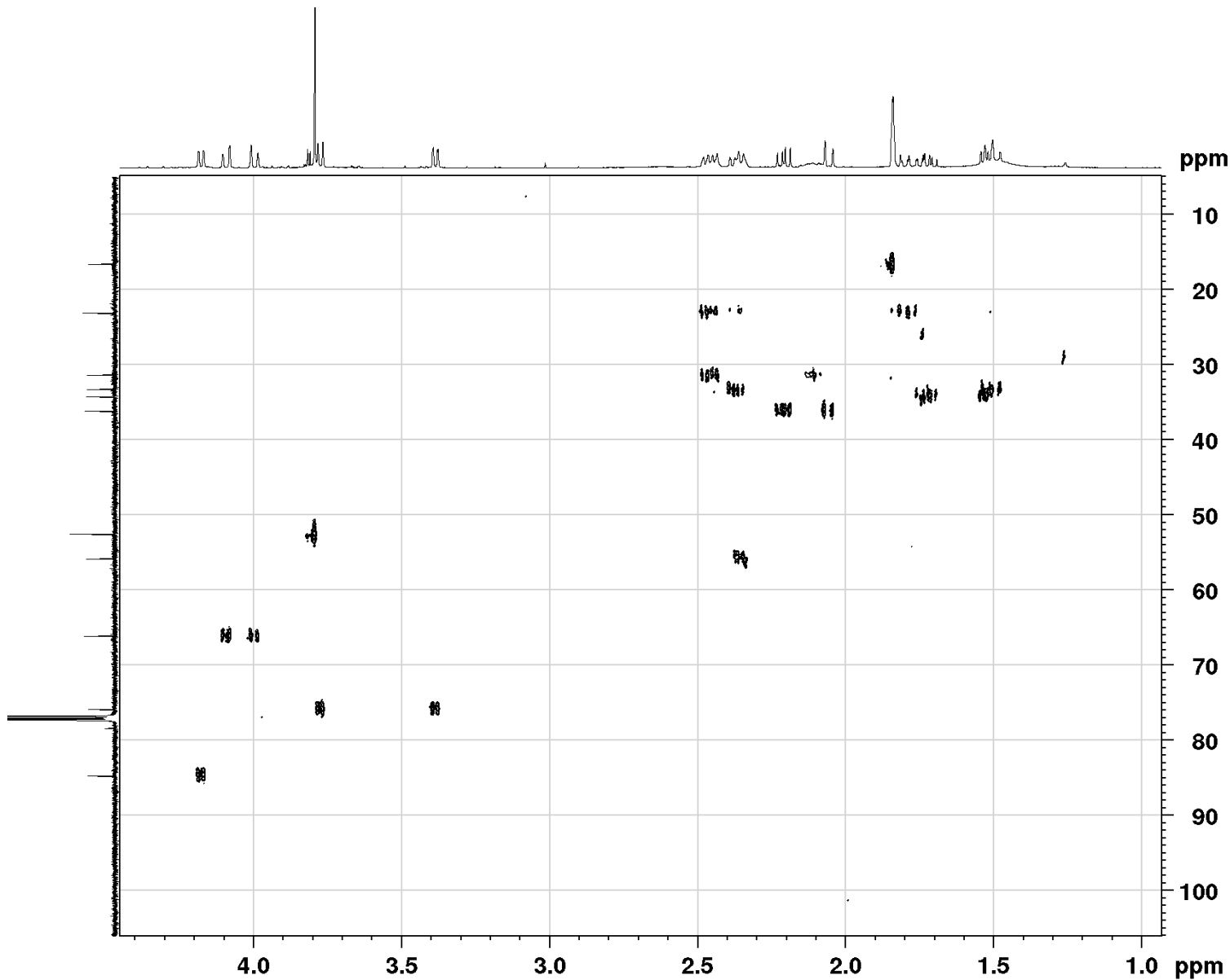


Figure S30. ¹³C NMR spectrum (125 MHz, CD₃OD) of **1a**



```

Current Data Parameters
NAME      Ppat-12-4
EXPNO    7130
PROCNO   2

F2 - Acquisition Parameters
Date_    20190213
Time     9:39
INSTRUM  spect
PROBHD   5 mm F4BBO BB/
PULPROG  zgpg30
TD       2048
SOLVENT  CDCl3
NS       8
DS       16
SWH      3001.200 Hz
FIDRES   1.445430 Hz
AQ       0.3411968 sec
RG       150.84
DW       188.600 usec
DE       6.50 usec
TE       303.4 K
CNS12    145.0000000
CNS17    -0.5000000
D0       0.0000300 sec
D1       1.200000000 sec
D4       0.00172414 sec
D11      0.05000000 sec
D16      0.00010000 sec
D24      0.00089000 sec
IN0      0.00002480 sec

===== CHANNEL f1 =====
SFO1     500.1314004 MHz
NUC1     1H
P1       11.00 usec
P2       22.00 usec
PR2      0 usec
PLW1     13.84899998 W

===== CHANNEL f2 =====
SFO2     125.7678496 MHz
NUC2     13C
CPDPRG2  bs_p5m4p_4p.2
P3       12.50 usec
P14      500.00 usec
P24      200.00 usec
P63      1500.00 usec
PLW0     0 W
PLW2     79.43299866 W
PLW12    2.74029994 W
SENAM[3] Crp60,0.5,20.1
SFOAL3   0.500
SFOFFS3  0 Hz
SEW6     18.96299994 W
SENAM[7] Crp60comp.4
SFOAL7   0.500
SFOFFS7  0 Hz
SEW7     18.96299994 W
SENAM[14] Crp32,1.5,20.2
SFOAL14  0.500
SFOFFS14 0 Hz
SEW14    8.09099960 W
SENAM[31] Crp32,1.5,20.2
SFOAL31  0.500
SFOFFS31 0 Hz
SEW31    2.02270007 W

===== GRADIENT CHANNEL =====
GENAM[1] SMSQ10.100
GENAM[2] SMSQ10.100
GENAM[3] SMSQ10.100
GENAM[4] SMSQ10.100
GPE1     80.00 %
GPE2     20.10 %
GPE3     11.00 %
GPE4     -5.00 %
P16      1000.00 usec
P19      600.00 usec

F1 - Acquisition parameters
TD       120
SFO1     125.7678 MHz
FIDRES   336.021515 Hz
SW       160.306 ppm
P1MODE   Echo-Antiecho

F2 - Processing parameters
SI       2048
SF       500.1300202 MHz
WDW      QSINE
SFB      3
LB       0 Hz
GB       0
PC       1.00

F1 - Processing parameters
SI       8096
MC2      echo-antiecho
SF       125.7577939 MHz
WDW      QSINE
SFB      6
LB       0 Hz
GB       0

```

Figure S31. HSQC spectrum (500 MHz, CD₃OD) of 1a

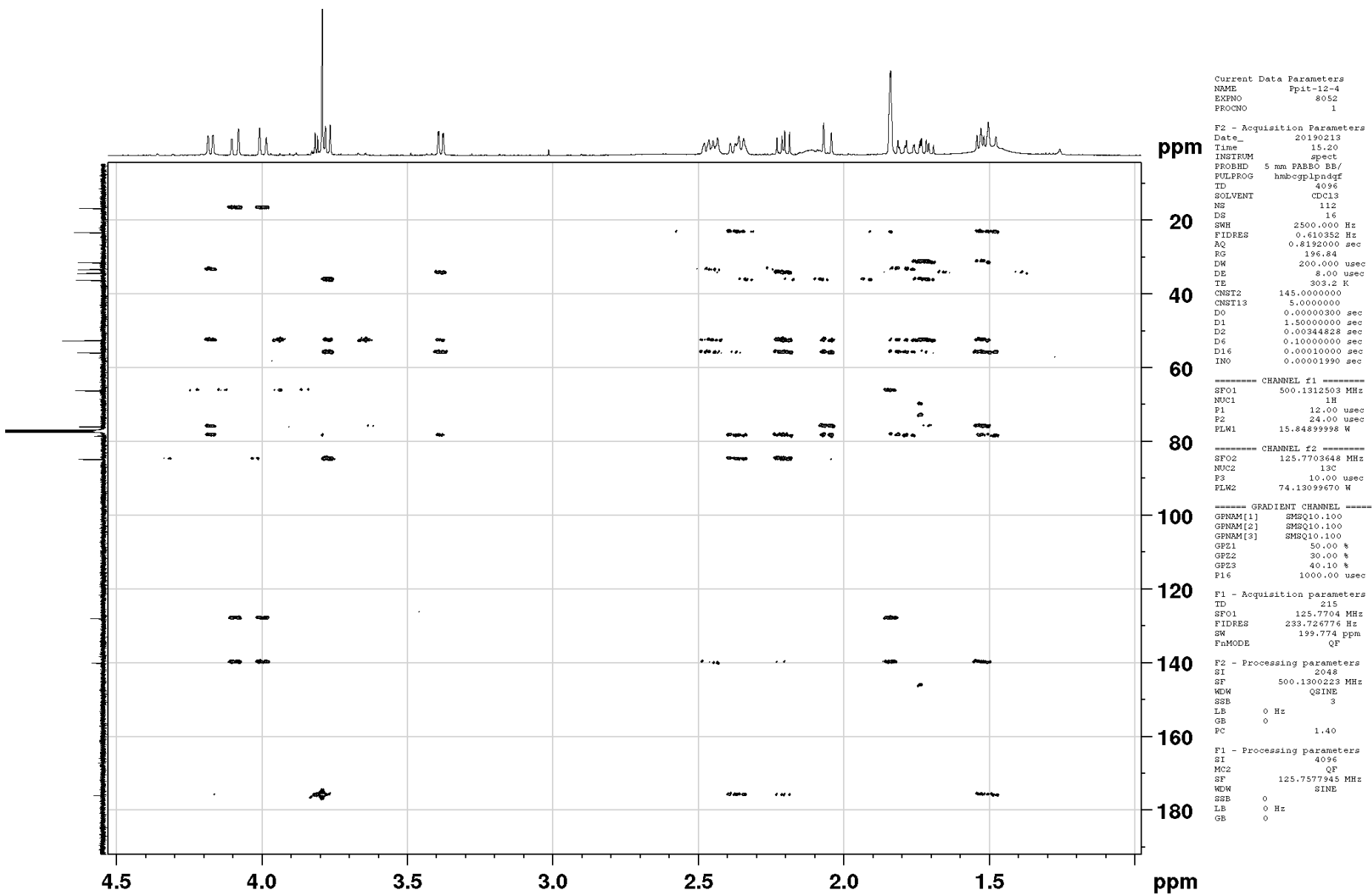


Figure S32. HMBC spectrum (500 MHz, CD₃OD) of **1a**

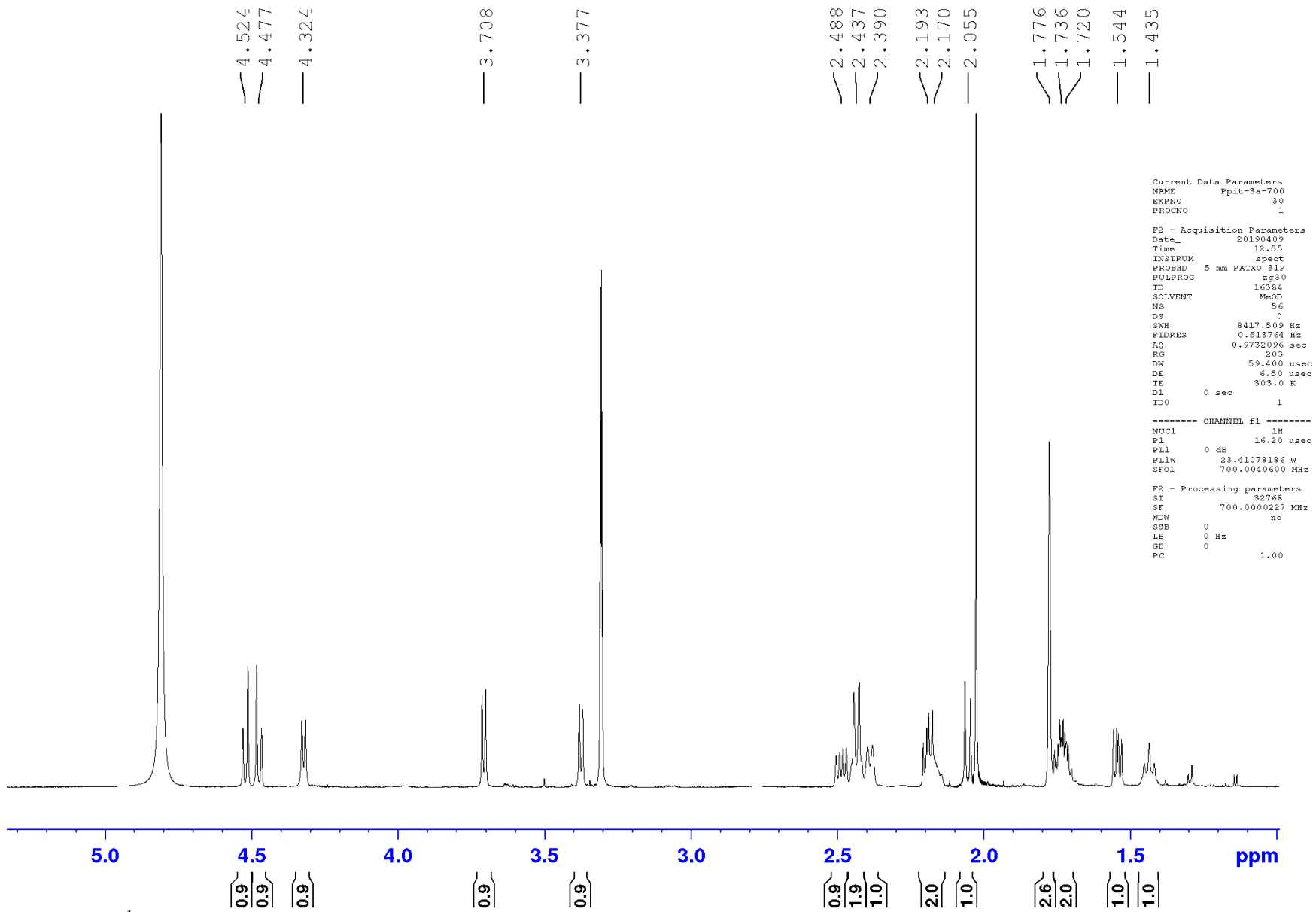


Figure S33. ^1H NMR spectrum (700 MHz, CD_3OD) of **2**

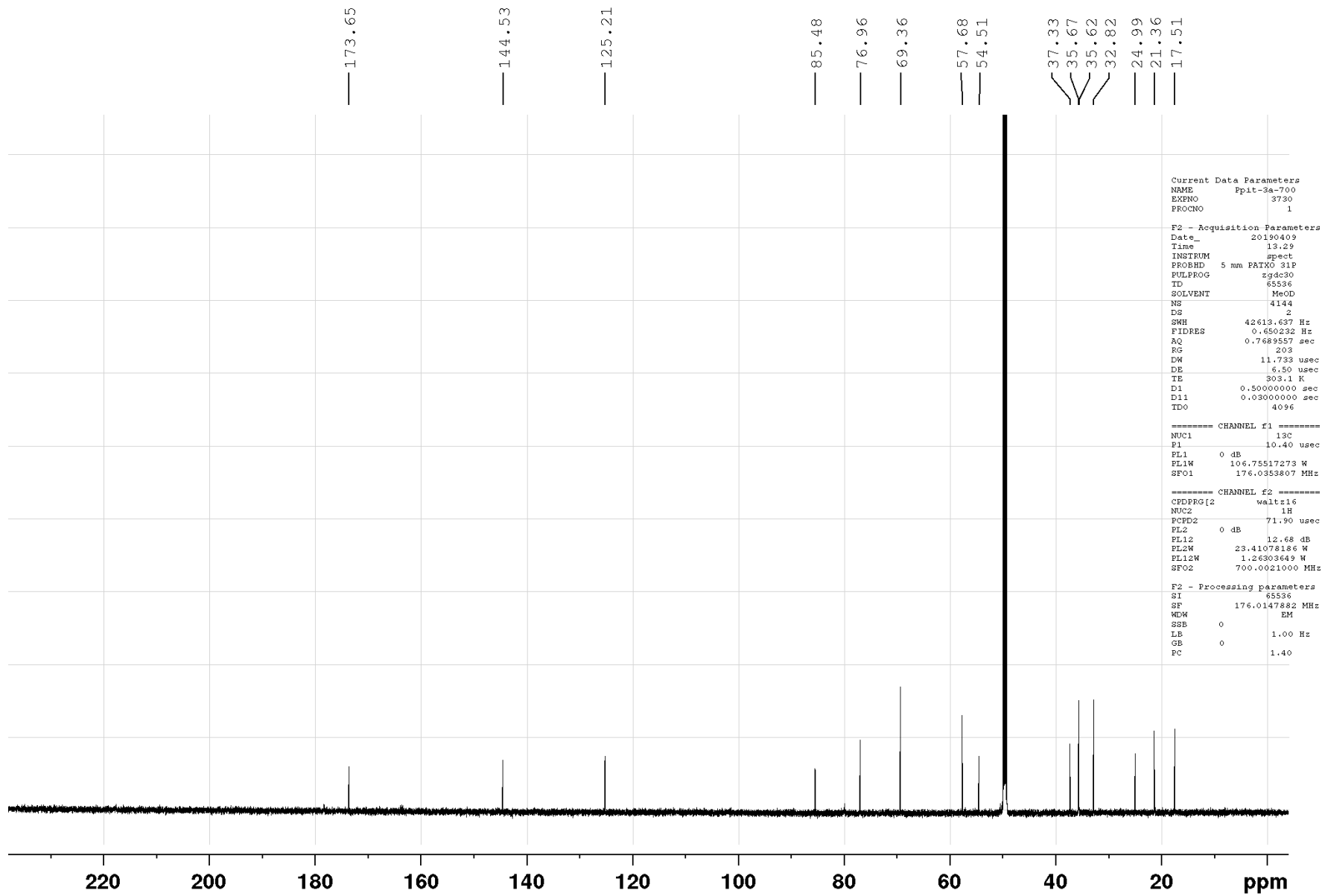


Figure S34. ¹³C NMR spectrum (176 MHz, CD₃OD) of 2

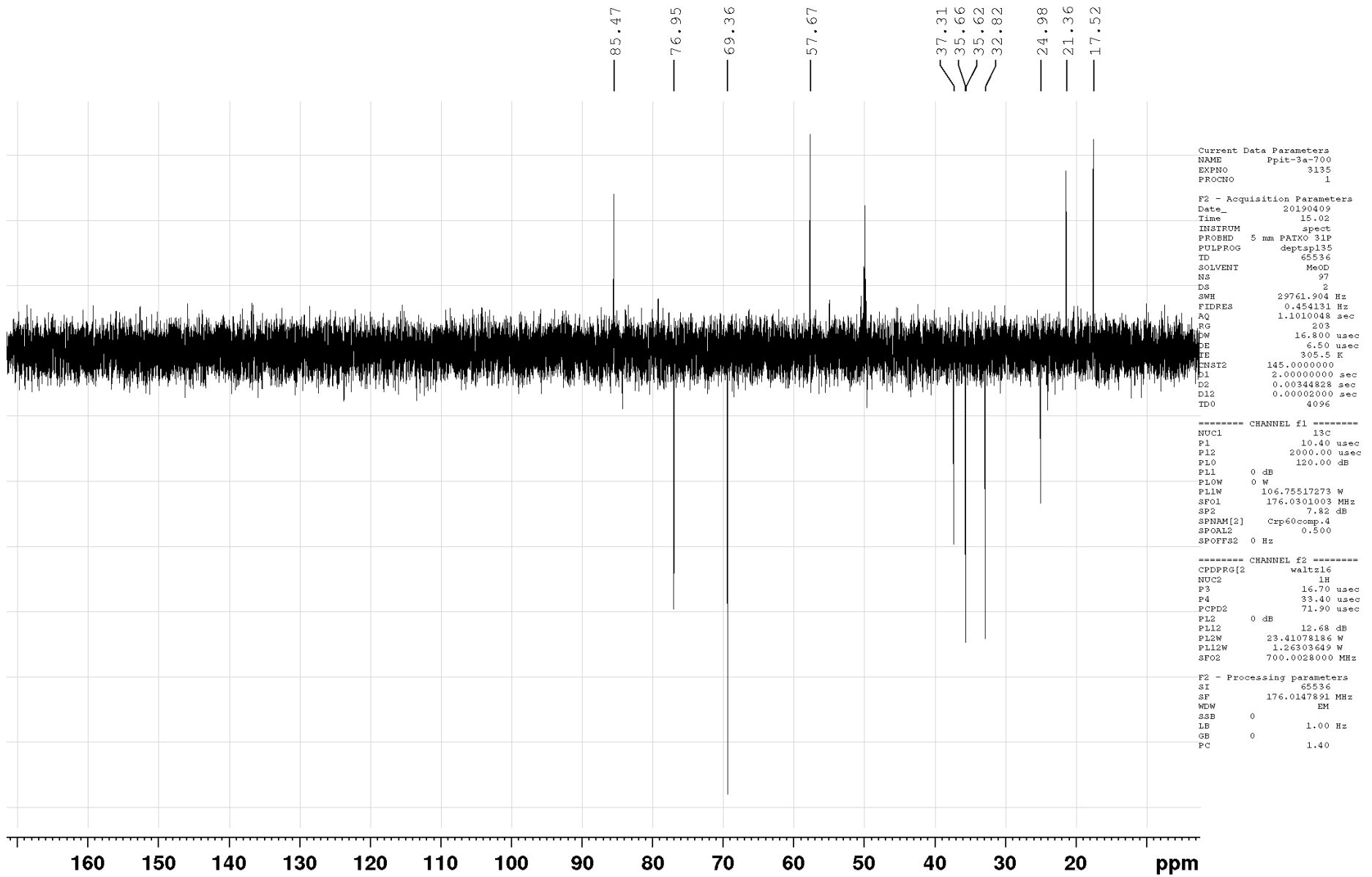
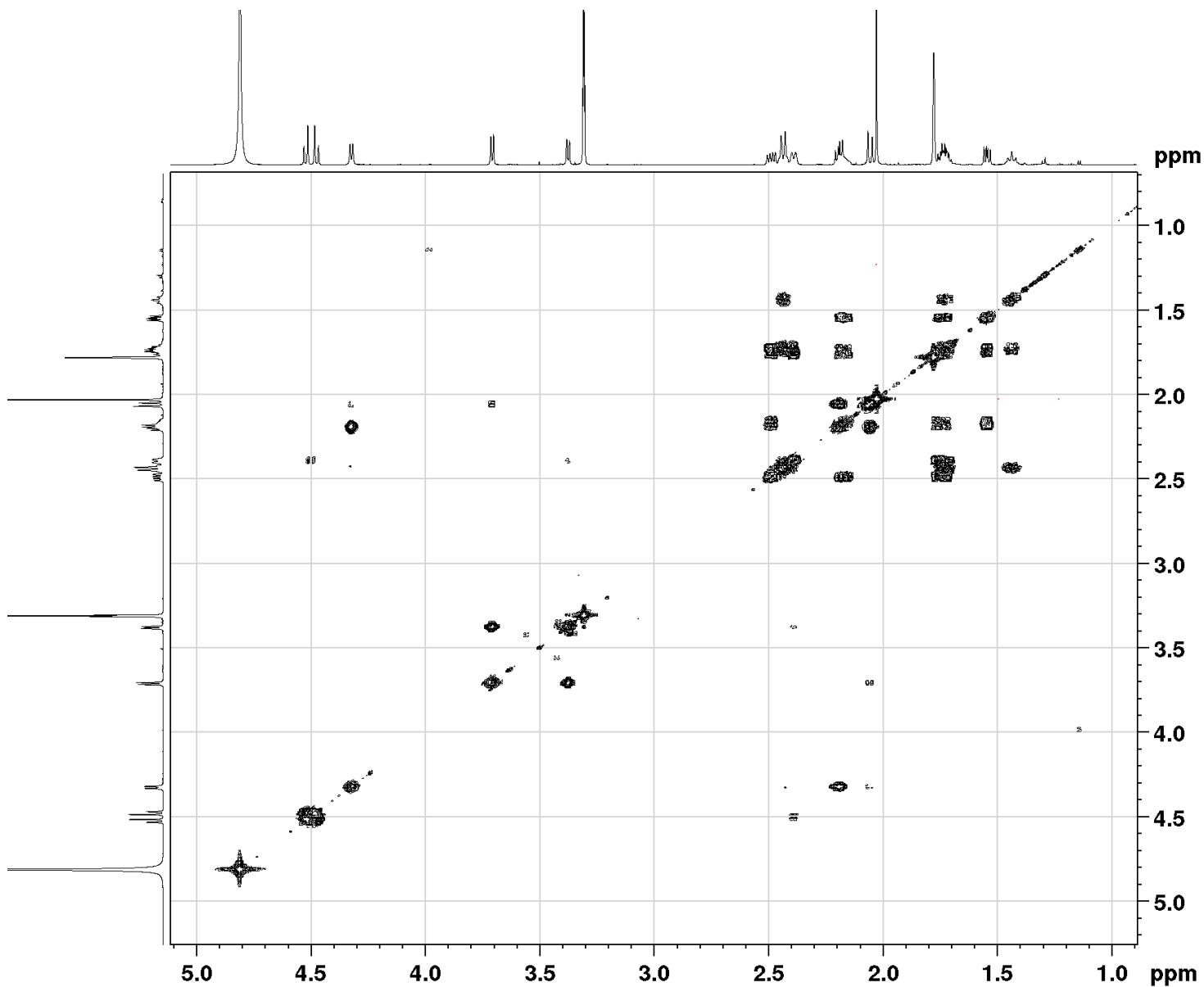


Figure S35. DEPT-135 NMR spectrum (176 MHz, CD₃OD) of 2



```

Current Data Parameters
NAME      Ppit-3a-700
EXPNO    455
PROCNO   1

F2 - Acquisition Parameters
Date_    20190409
Time     13.00
INSTRUM  spect
PROBHD   5 mm PATKO 31P
PULPROG  cosygpgf
TD       2048
SOLVENT  MeOD
NS       1
DS       8
SWH      4201.681 Hz
FIDRES   2.051602 Hz
AQ       0.2437120 sec
RG       203
DW       119.000 usec
DE       6.50 usec
TE       303.0 K
DO       0.00000300 sec
DL       1.20000005 sec
DL3      0.00000400 sec
DL6      0.00010000 sec
IN0      0.00023800 sec

----- CHANNEL f1 -----
NUC1     1H
PQ       16.20 usec
PI       16.20 usec
PL1      0 dB
PL1W     23.41078186 W
SF01     700.0019600 MHz

----- GRADIENT CHANNEL -----
GPNAM[1] SINE.100
GP21     10.00 s
P16      1000.00 usec

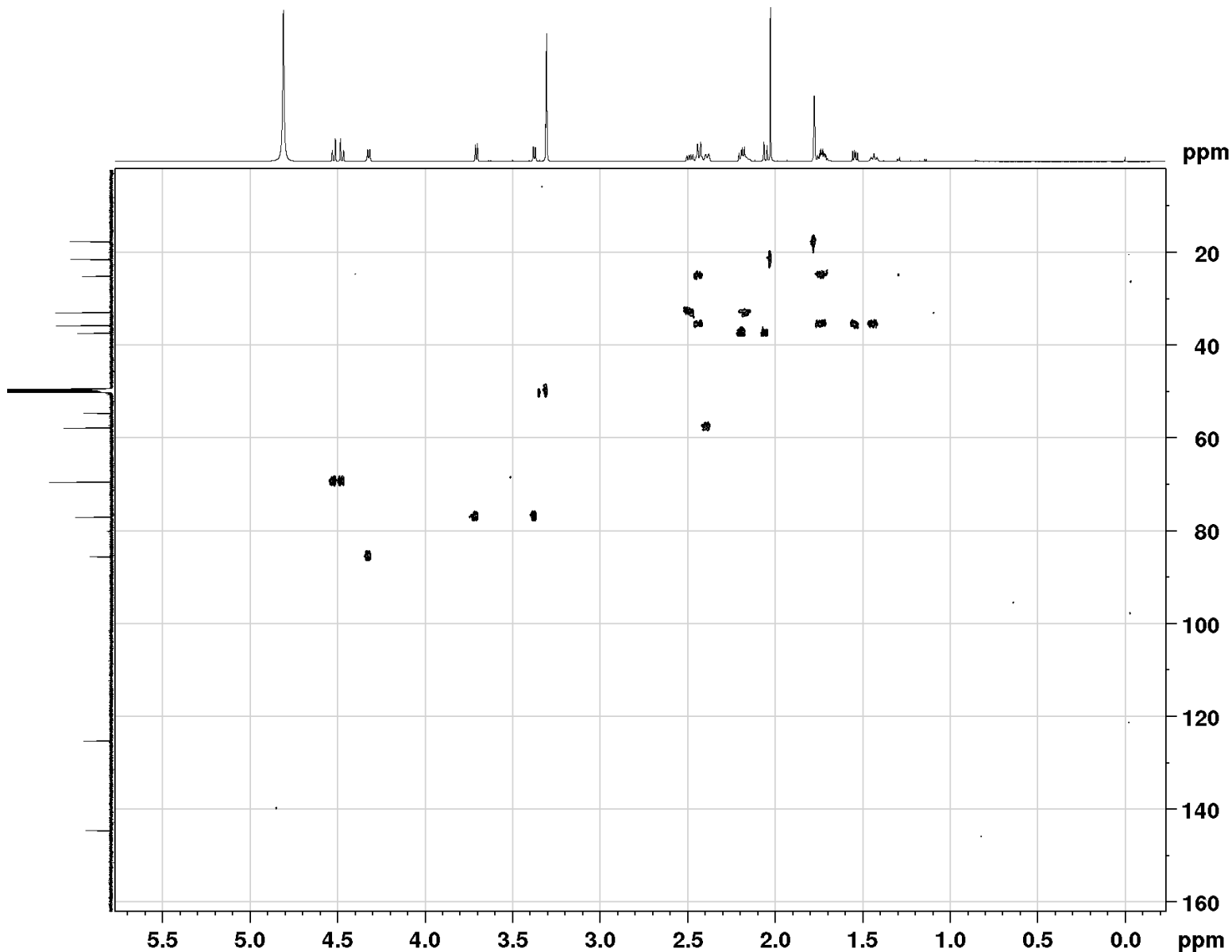
F1 - Acquisition parameters
TD       256
SF01     700.002 MHz
FIDRES   32.825600 Hz
SW       6.002 ppm
FhMODE   QF

F2 - Processing parameters
SI       2048
SF       700.000219 MHz
WDW      SINE
SSB      0
LB       0 Hz
GB       0
PC       1.00

F1 - Processing parameters
SI       2048
MC2      QF
SF       700.000220 MHz
WDW      SINE
SSB      0
LB       0 Hz
GB       0

```

Figure S36. COSY-45 spectrum (700 MHz, CD₃OD) of 2



```

Current Data Parameters
NAME      Epit-3a-700
EXPNO    7130
PROCNO    1

F2 - Acquisition Parameters
Date_    20190409
Time     13.14
INSTRUM  spect
PROBHD   5 mm PABBO 31P
PULPROG  hsqcetgpsisp2.2
TD        2048
SOLVENT  MeOD
NS        2
DS        16
SWH       4201.681 Hz
FIDRES    2.051602 Hz
AQ        0.2437120 sec
RG        203
DM        119.000 usec
DE        6.50 usec
TE        303.2 K
CHST2    145.0000000
CHST17   -0.5000000
D0        0.0000000 sec
D1        2.0000000 sec
D4        0.00172414 sec
D11       0.0300000 sec
D16       0.0001000 sec
D24       0.00086207 sec
IND0     0.00001775 sec
L31      16

----- CHANNEL f1 -----
NUC1      1H
P1        16.20 usec
P2        32.40 usec
P28       0 usec
PL1       0 db
PL19      23.41078186 W
SFO1      700.0019600 MHz

----- CHANNEL f2 -----
CPDPRG2  [2 bi_p5m4sp_4sp_2
NUC2      13C
P3        10.00 usec
P14       500.00 usec
P24       2000.00 usec
P63       1500.00 usec
P10       120.00 db
P12       0 db
P109      0 W
P129      106.75517273 W
P129W     2.76748734 W
SFO2      176.0262502 MHz
SF3       8.16 db
SF7       8.16 db
SF14      9.64 db
SF31      15.66 db
SFOAM[3]  crp60,0.5,20.1
SFOAM[7]  crp60comp,4
SFOAM[14] crp32,1.5,20.2
SFOAM[31] crp32,1.5,20.2
SFOAL3    0.500
SFOAL7    0.500
SFOAL14   0.500
SFOAL31   0.500
SFOFF3    0 Hz
SFOFF7    0 Hz
SFOFF14   0 Hz
SFOFF31   0 Hz

----- GRADIENT CHANNEL -----
GFOAM[1]  SINE,100
GFOAM[2]  SINE,100
GFOAM[3]  SINE,100
GFOAM[4]  SINE,100
GPE2     80.00 %
GPE3     20.10 %
GPE3     11.00 %
GPE4     -5.00 %
P16      1000.00 usec
P19      500.00 usec

F1 - Acquisition parameters
ID        163
SFO1      176.0252 MHz
FIDRES    345.578827 Hz
SM        160.000 ppm
FQMODE    Echo-Antiecho

F2 - Processing parameters
SI        2048
SF        700.0000205 MHz
WDW       QSHINE
SSB       2
LB        0 Hz
GB        0
PC        1.00

F1 - Processing parameters
SI        4096
MC2       echo-antiecho
SF        176.0147857 MHz
WDW       QSHINE
SSB       6
LB        0 Hz
GB        0

```

Figure S37. HSQC spectrum (700 MHz, CD₃OD) of 2

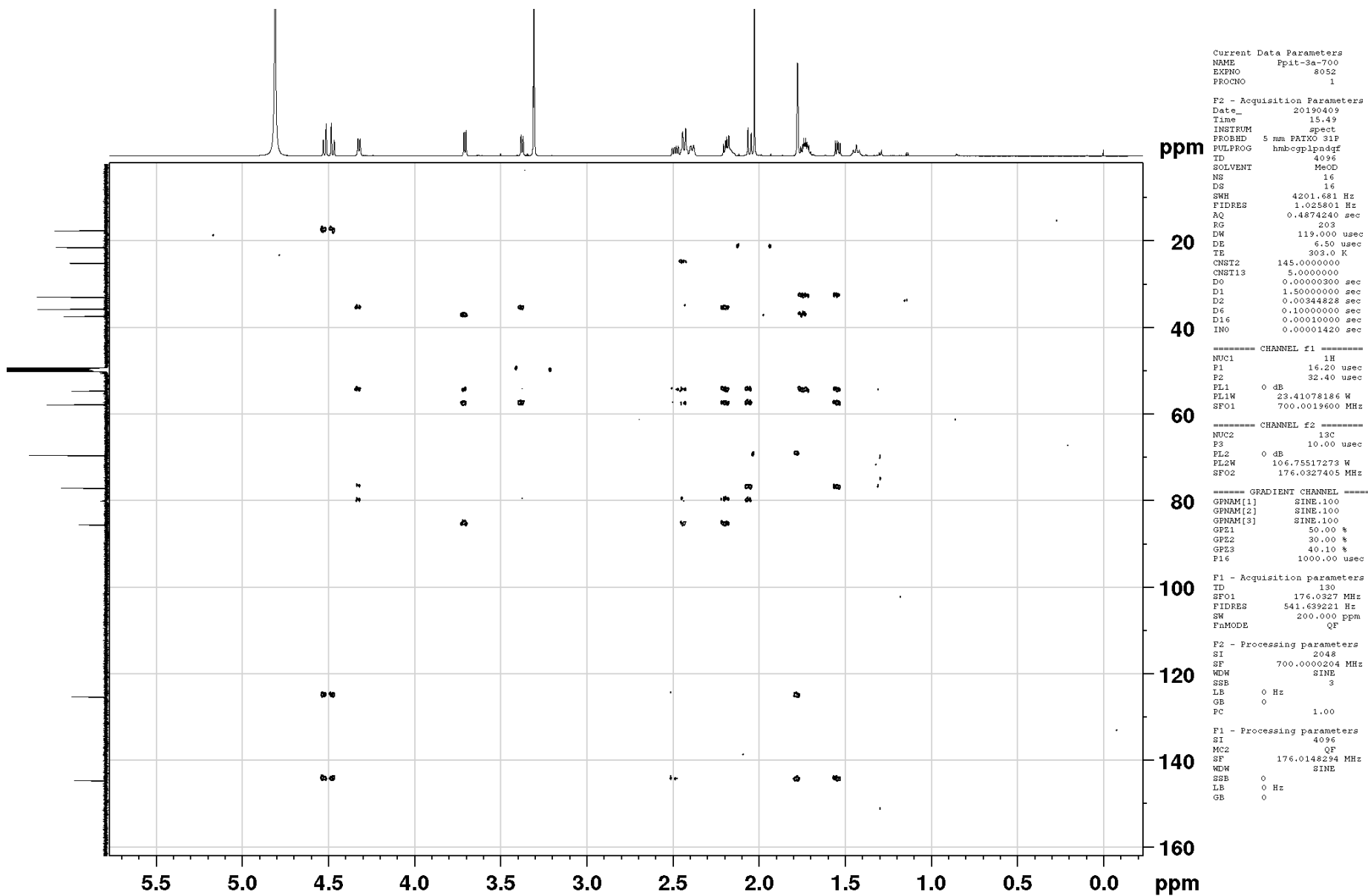


Figure S38. HMBC spectrum (700 MHz, CD₃OD) of 2

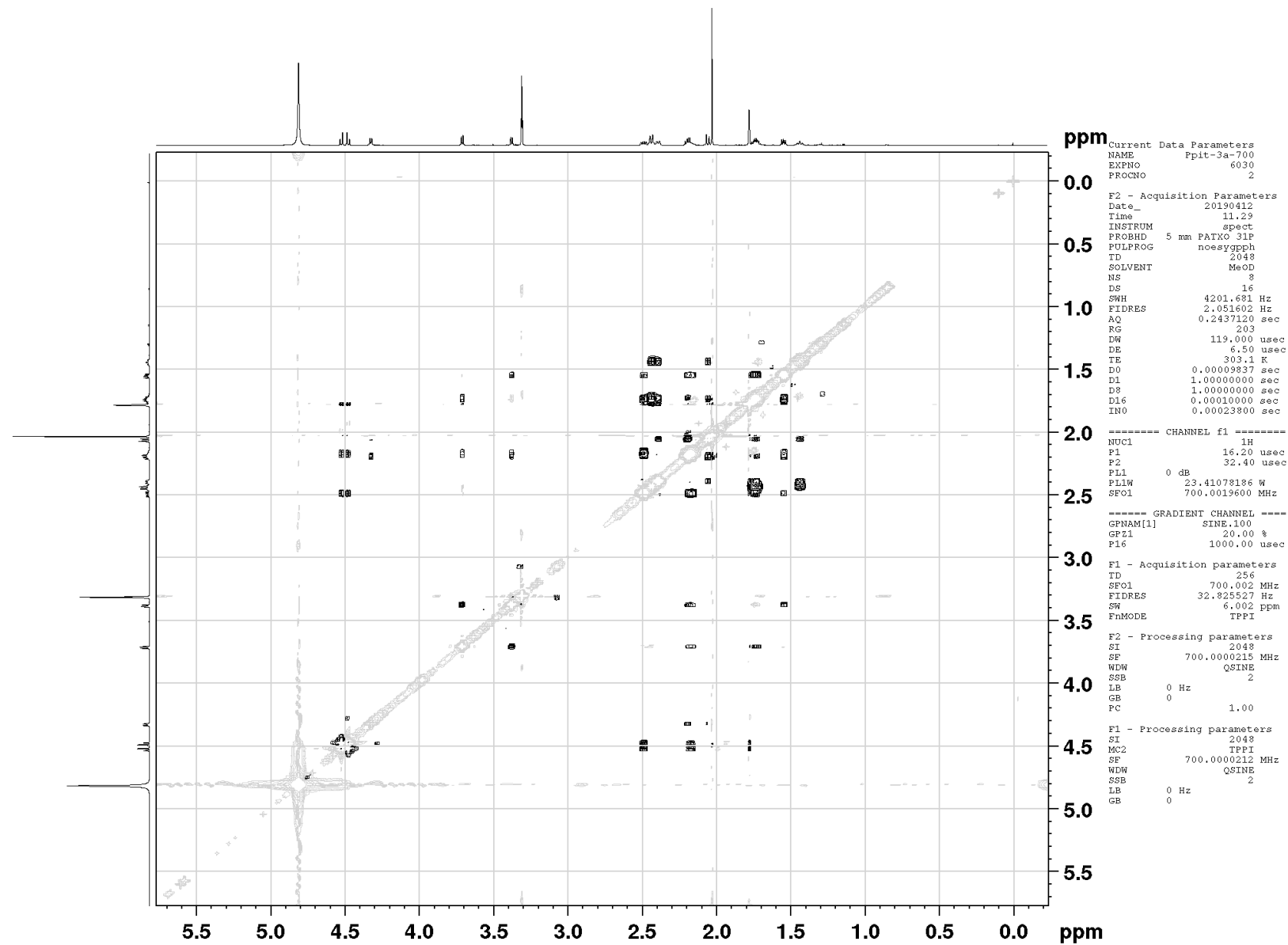


Figure S39. NOESY spectrum (700 MHz, CD₃OD) of 2

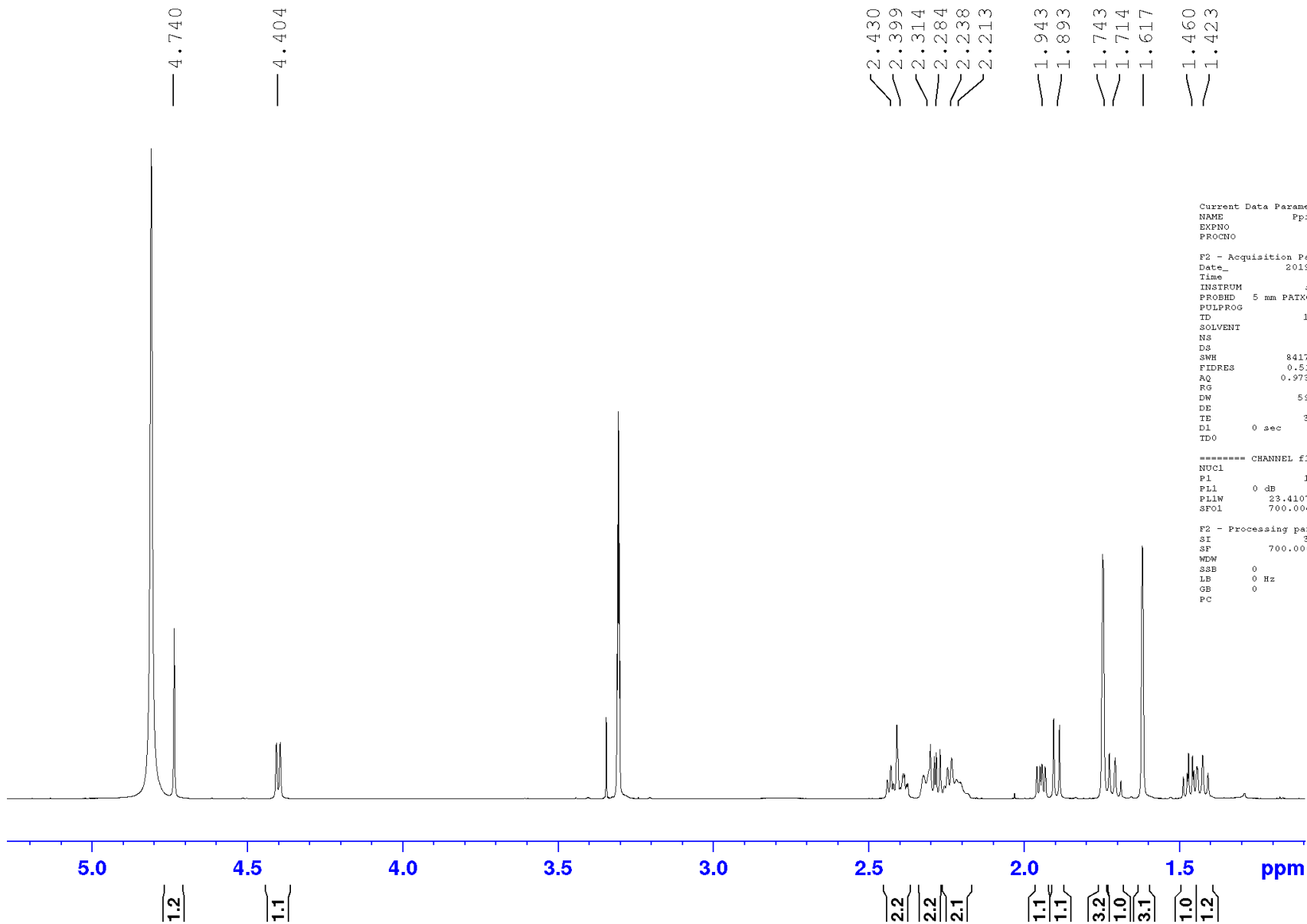


Figure S40. ¹H NMR spectrum (700 MHz, CD₃OD) of 3

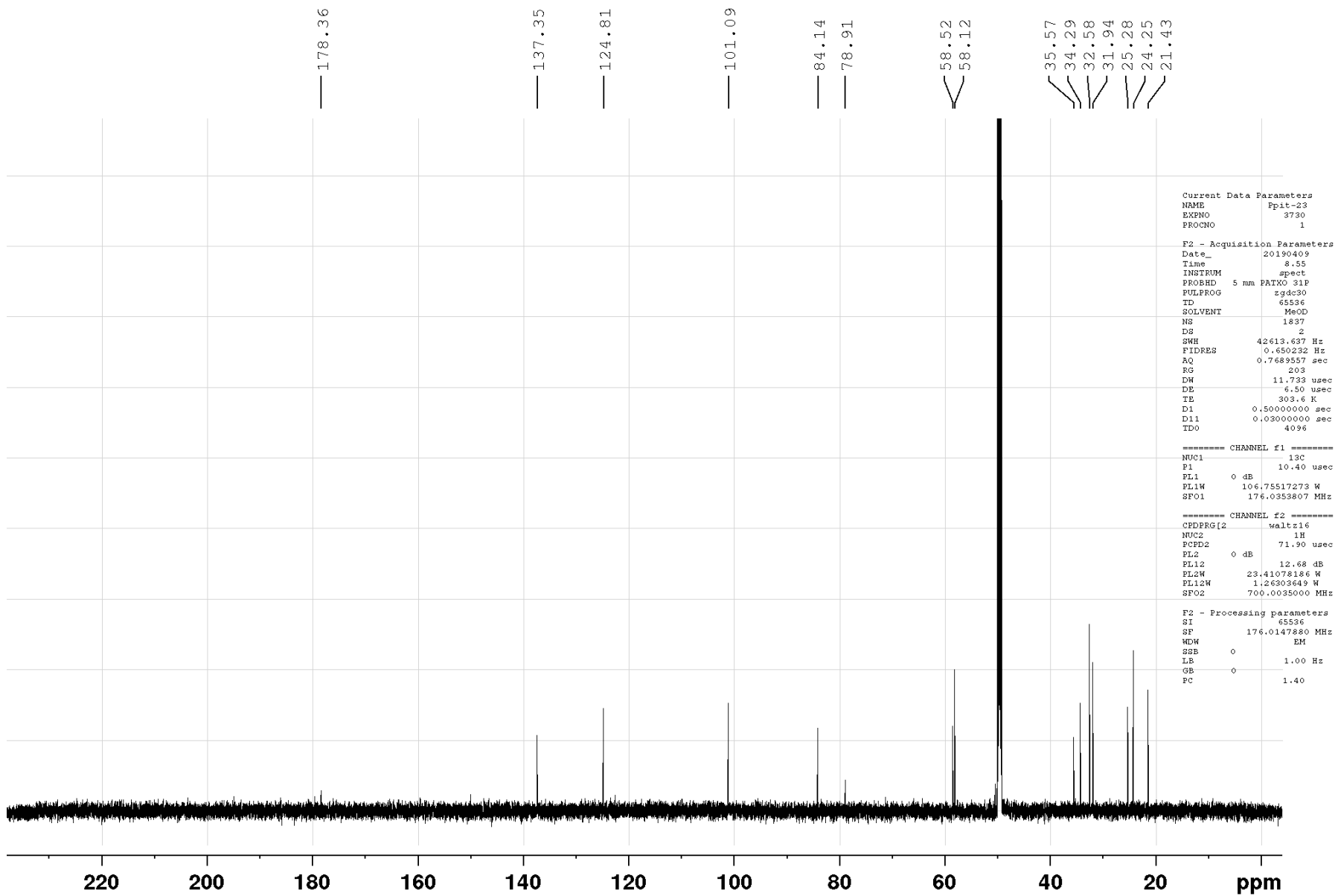


Figure S41. ¹³C NMR spectrum (176 MHz, CD₃OD) of 3

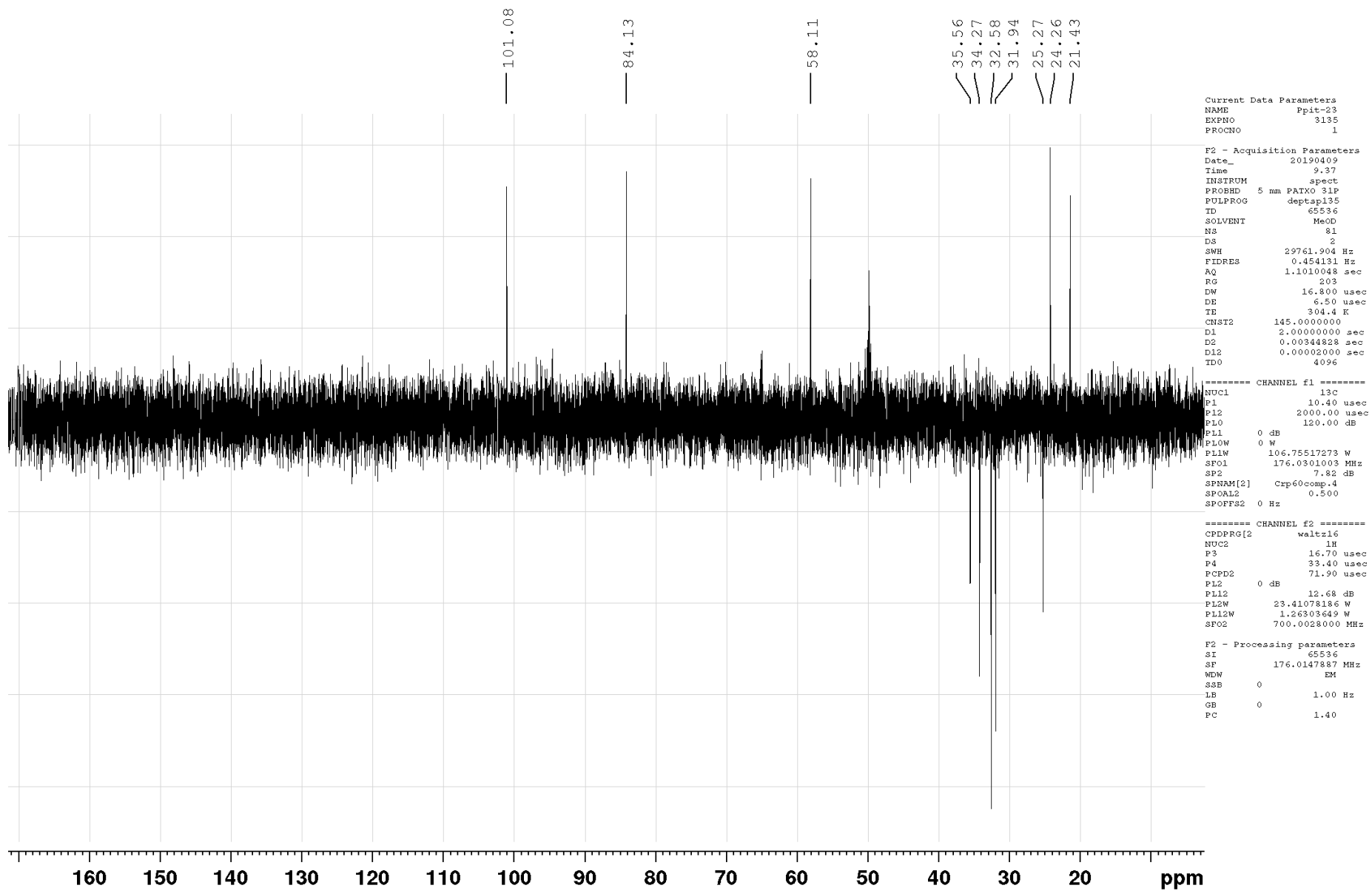


Figure S42. DEPT-135 NMR spectrum (176 MHz, CD₃OD) of 3

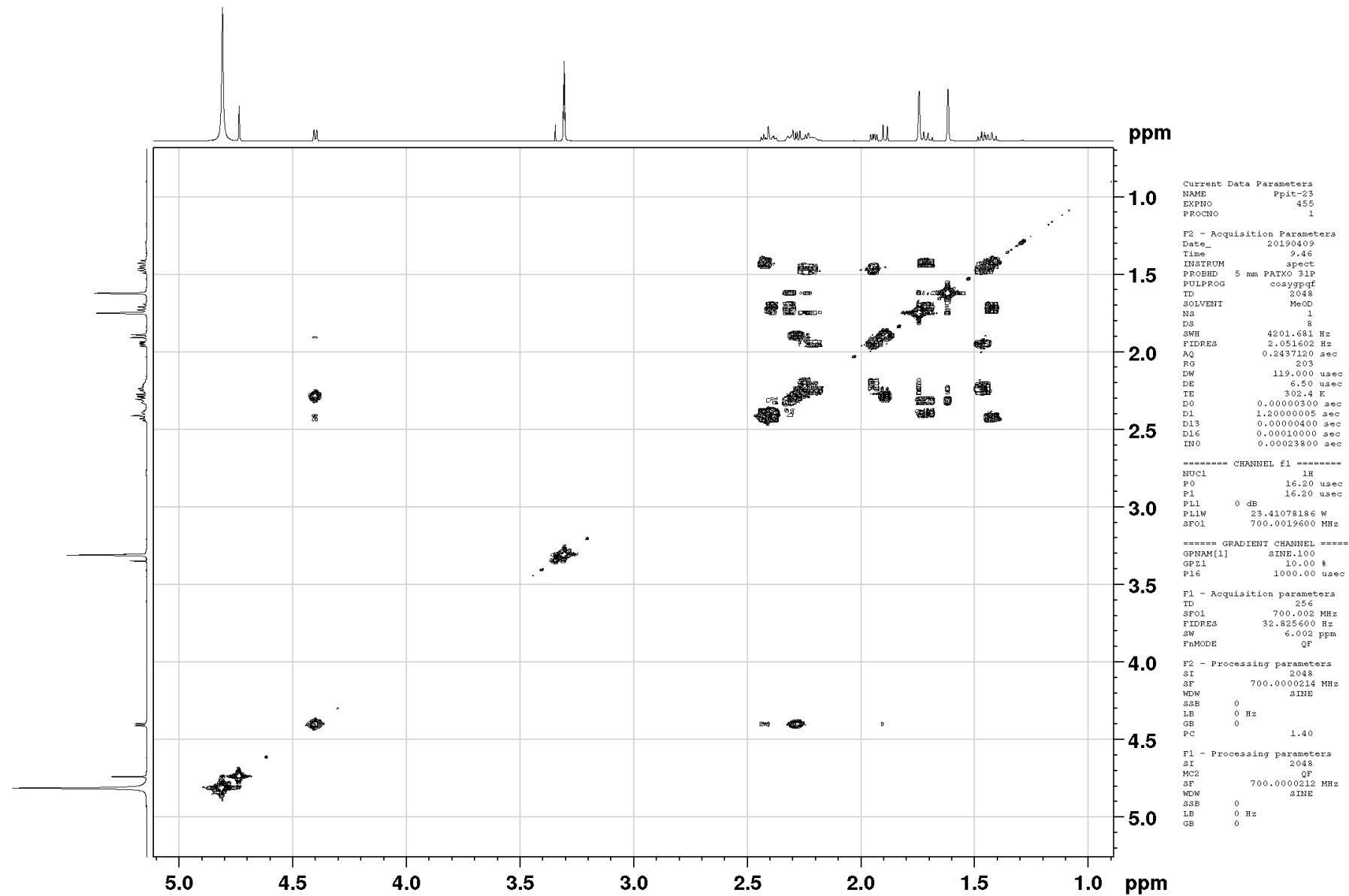
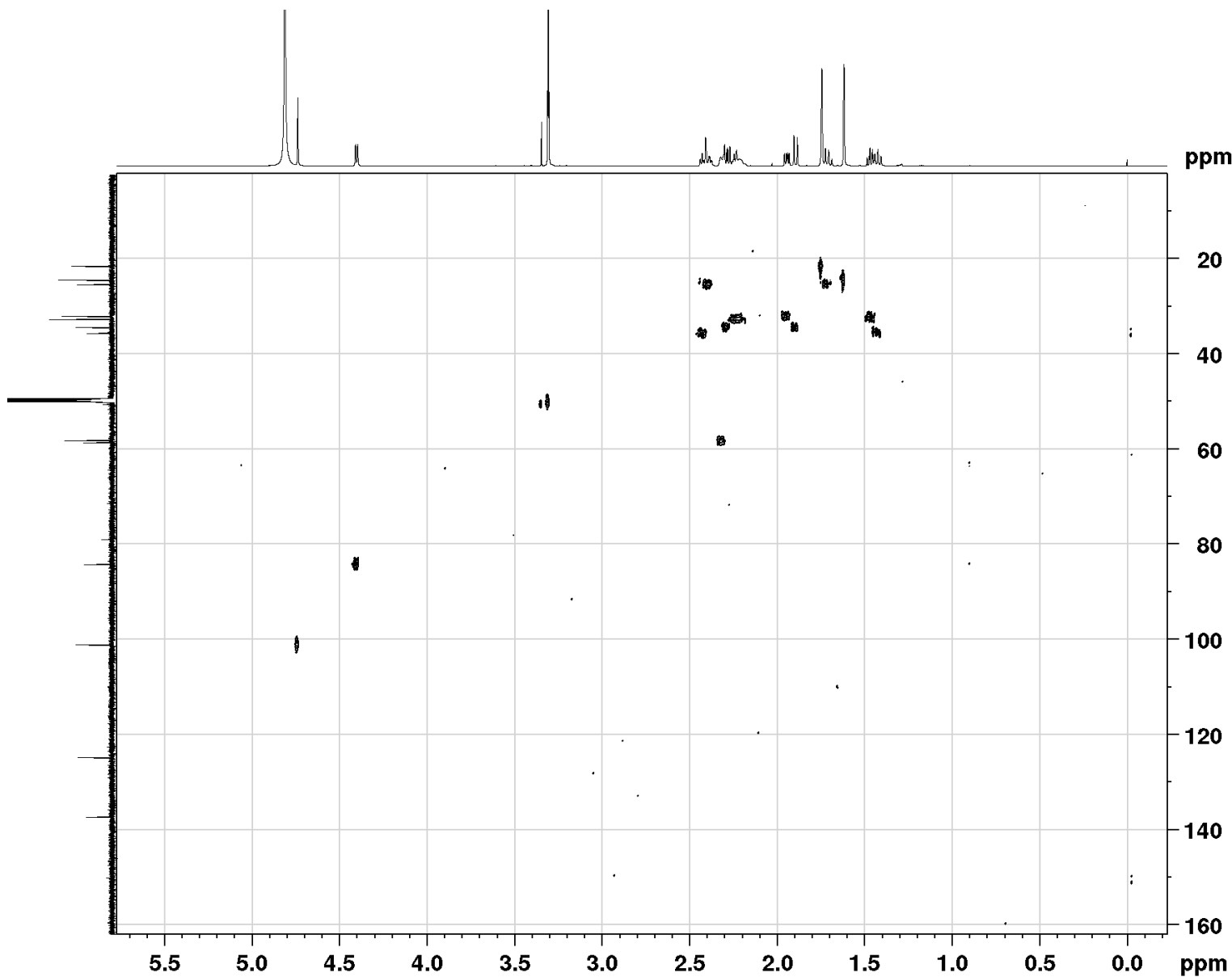


Figure S43. COSY-45 spectrum (700 MHz, CD₃OD) of **3**



```

Current Data Parameters
NAME      Ppit-23
EXPNO    7100
PROCNO    1

F2 - Acquisition Parameters
Date_     20190409
Time      9.57
INSTRUM   spect
PROBHD    5 mm PAKO 31P
PULPROG   hsqcetqs1cp2.2
TD        2048
SOLVENT   MeOD
NS        2
DS        48
SWH        4201.682 Hz
FIDRES    2.051602 Hz
AQ        0.2437120 sec
RG        203
DW        119.000 usec
DE        6.50 usec
TE        303.7 K
CNS12     145.0000000
CNS17     -0.5000000
D0        0.0000000 sec
D1        2.0000000 sec
D4        0.00124244 sec
D11       0.0300000 sec
D16       0.0001000 sec
D24       0.0006207 sec
IND       0.0001775 sec
LS1       16

----- CHANNEL f1 -----
NUC1      1H
P1        16.20 usec
P2        32.40 usec
PGR       0 usec
PL1       0 db
PL12      23.4107818c w
SFO1      700.0019600 MHz

----- CHANNEL f2 -----
CPDPRG2   bl_p5msep_4sp-2
NUC2      13C
P3        10.00 usec
P14       500.00 usec
P24       2000.00 usec
P23       1200.00 usec
P10       120.00 dB
P12       0 db
P112      15.56 db
P10W      0 w
P16W      10c.75517273 w
PL12W     2.96748734 w
SFO2      176.0292202 MHz
SF3        8.16 db
SF7        8.16 db
SF14       9.64 db
SF31       15.66 db
SPNAM[3]   crp60,0.5,20.1
SPNAM[7]   crp00comp,4
SPNAM[14]  crp32,1.5,20.2
SPNAM[31]  crp32,1.5,20.2
SFOAL3     0.500
SFOAL7     0.500
SFOAL14    0.500
SFOAL31    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
ID         126
SFO1      176.0292 MHz
FIDRES    447.038300 Hz
SM        160.000 ppm
FmMODE    Echo-AntiEcho

F2 - Processing parameters
SI         2048
SF         700.000201 MHz
WDW        QSINE
SSB        2
LB         0 Hz
GB         0
PC         1.40

F1 - Processing parameters
SI         4096
MC2        echo-antiEcho
SF         176.0147678 MHz
WDW        QSINE
SSB        8
LB         0 Hz
GB         0

```

Figure S44. HSQC spectrum (700 MHz, CD₃OD) of 3

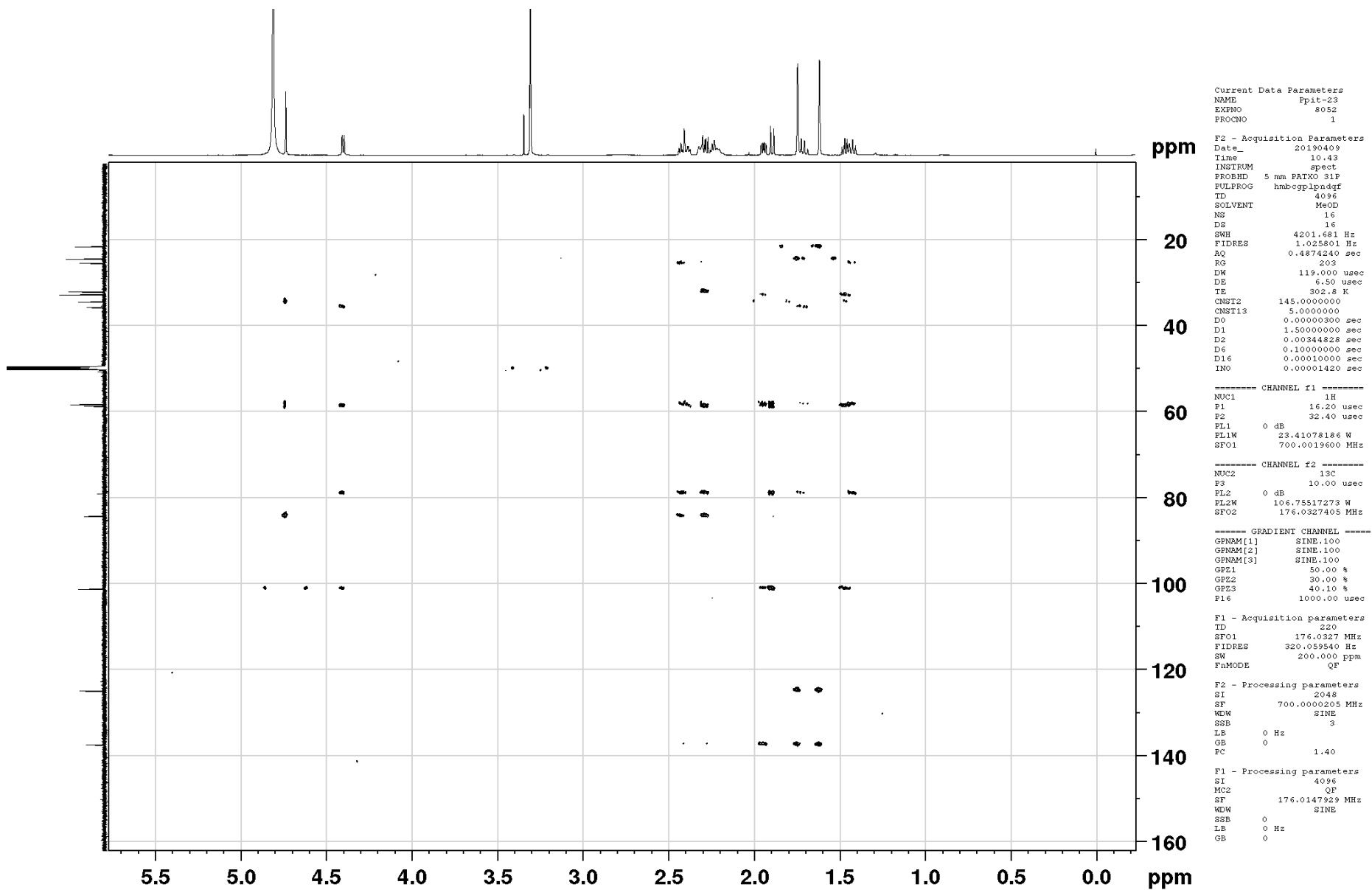


Figure S45. HMBC spectrum (700 MHz, CD₃OD) of 3

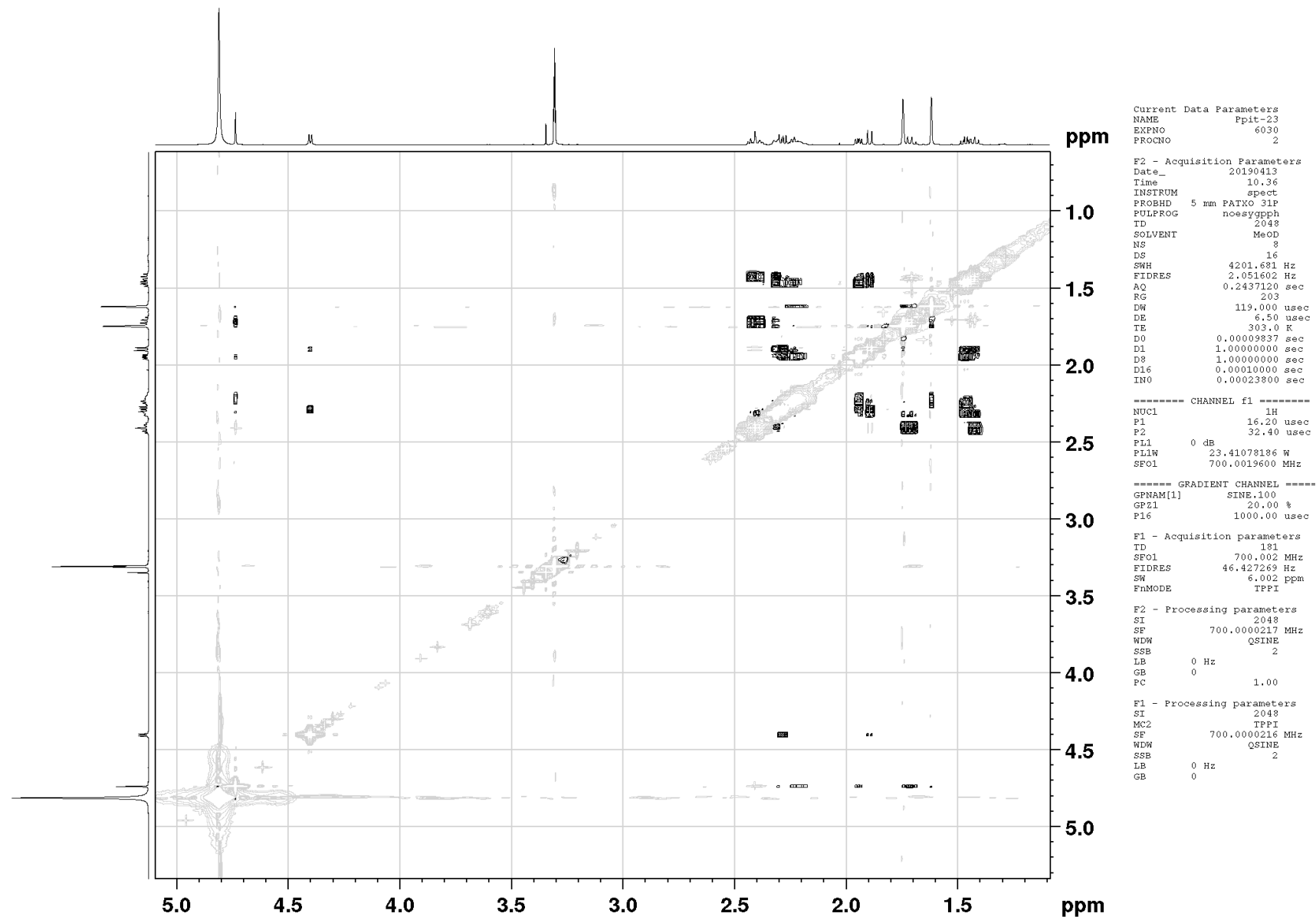


Figure S46. NOESY spectrum (700 MHz, CD₃OD) of 3

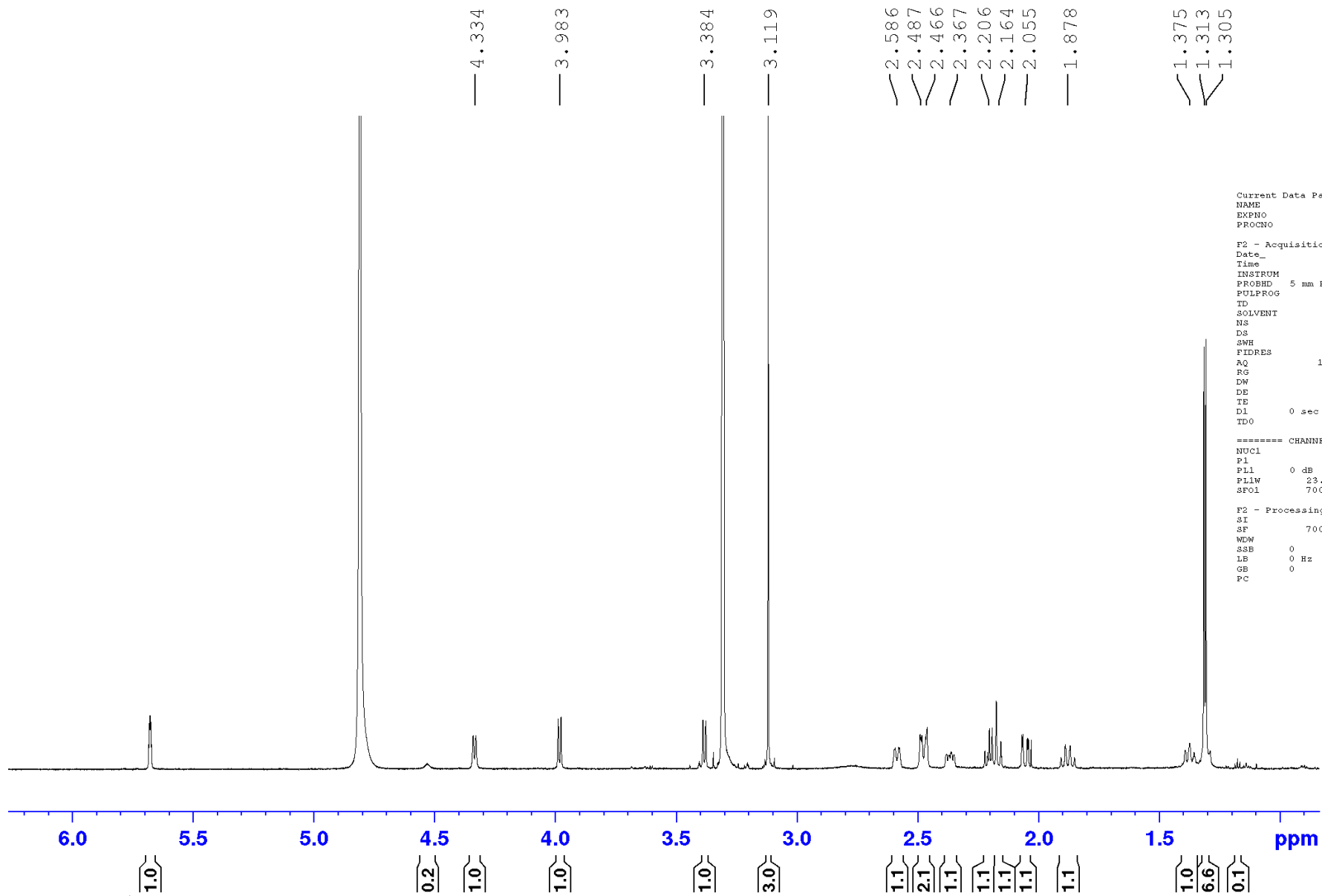


Figure S47. ¹H NMR spectrum (700 MHz, CD₃OD) of **4**

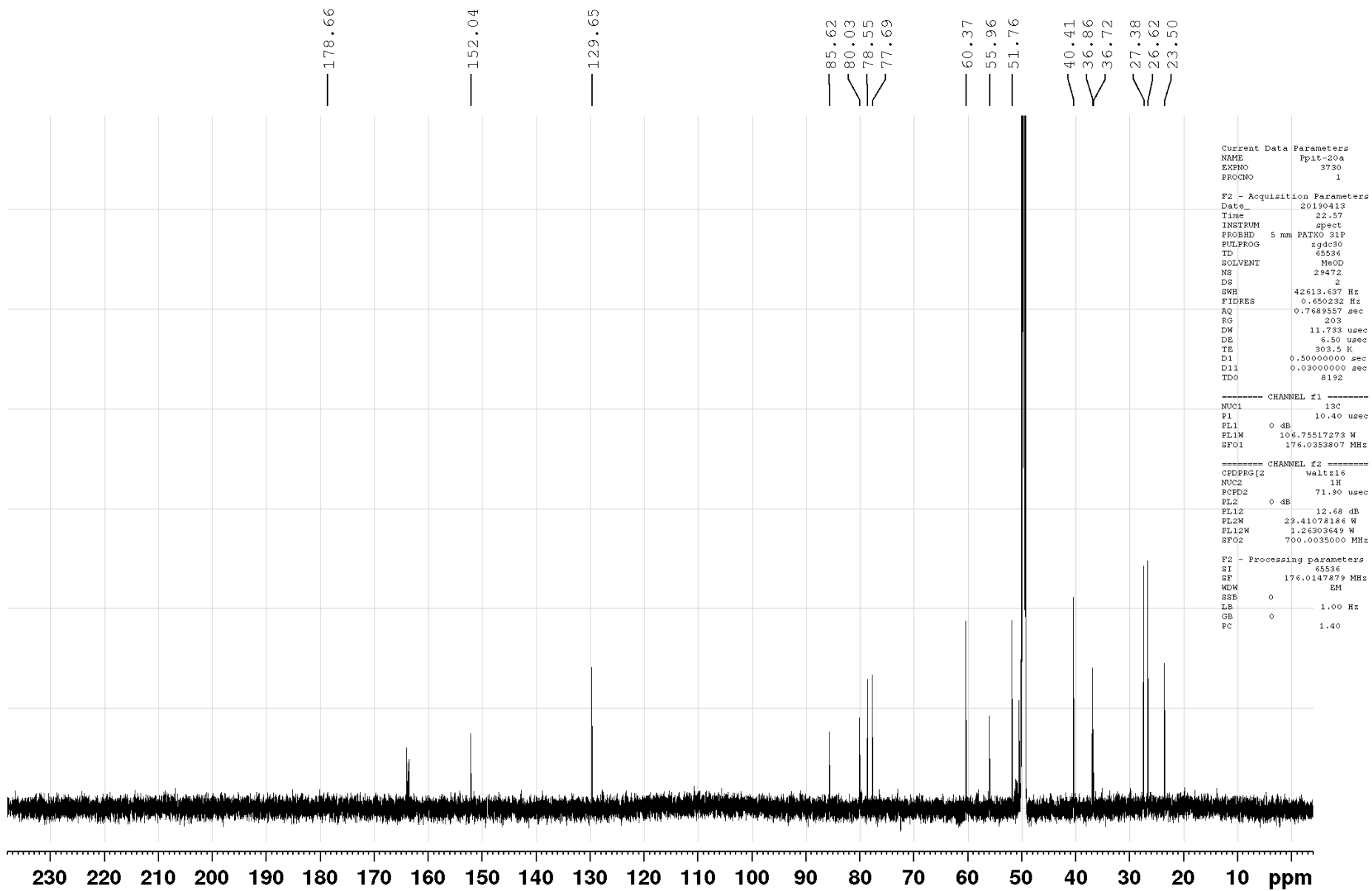


Figure S48. ¹³C NMR spectrum (176 MHz, CD₃OD) of 4

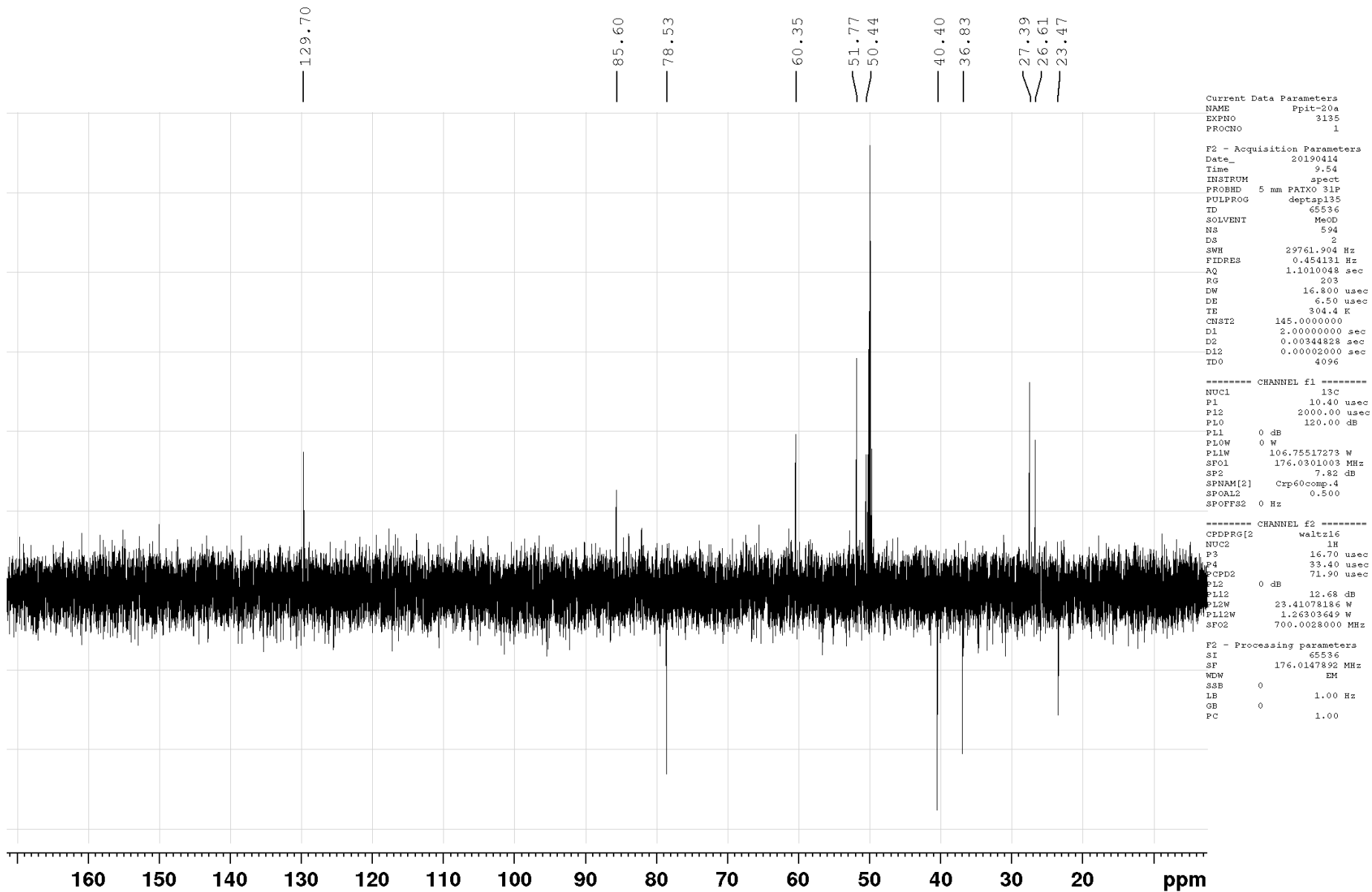


Figure S49. DEPT-135 NMR spectrum (176 MHz, CD₃OD) of 4

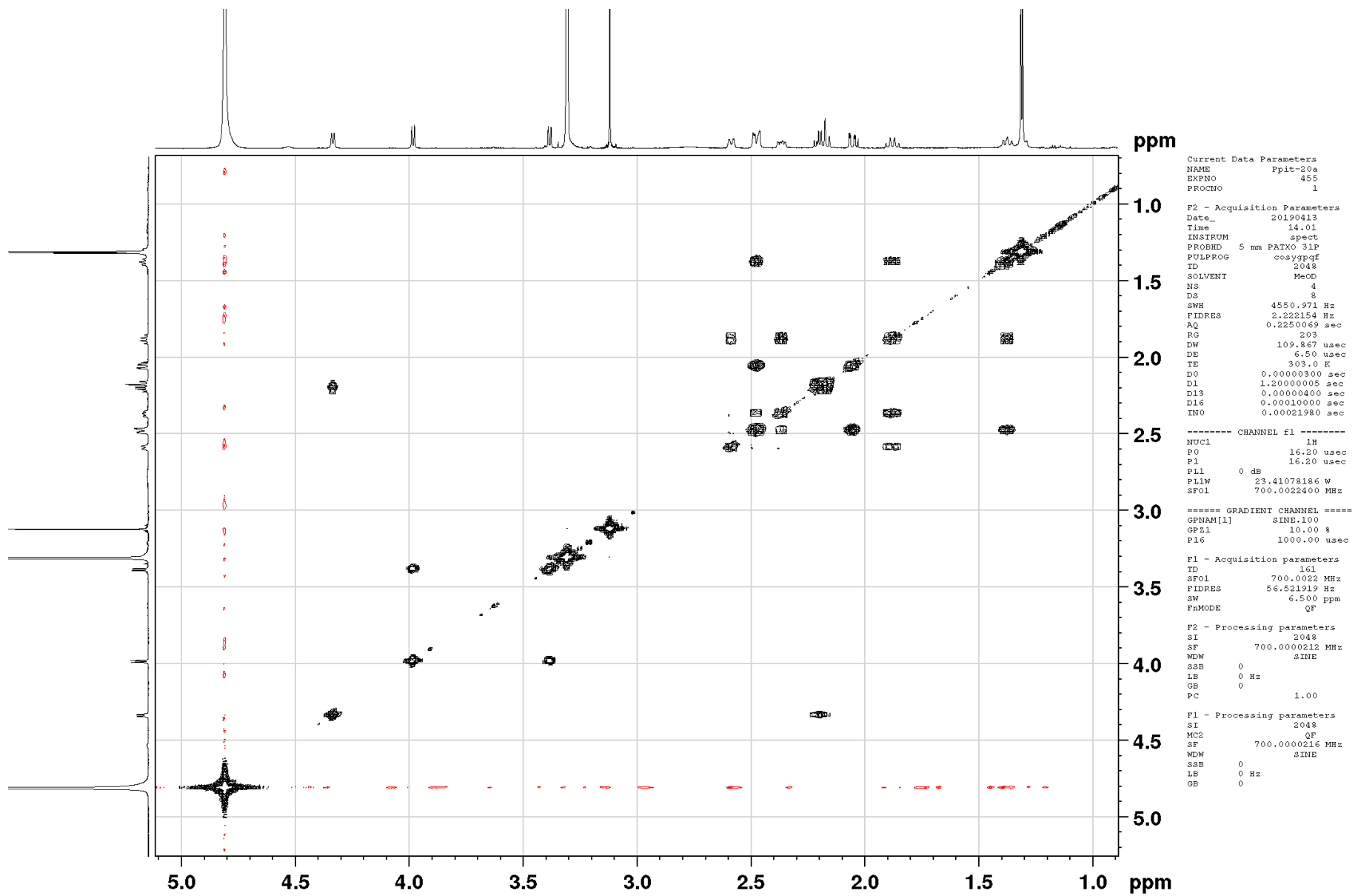


Figure S50. COSY-45 spectrum (700 MHz, CD₃OD) of 4

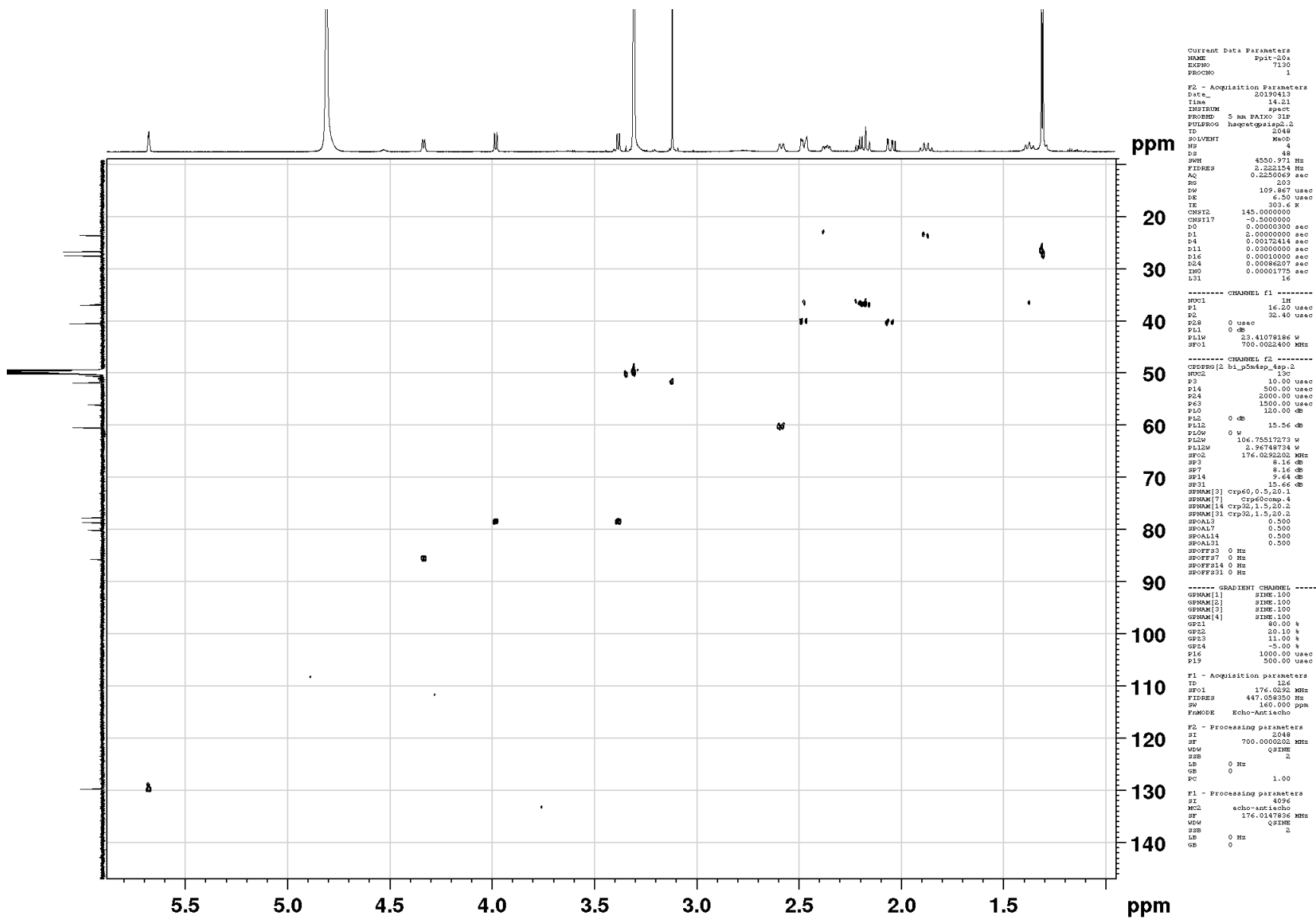


Figure S51. HSQC spectrum (700 MHz, CD₃OD) of 4

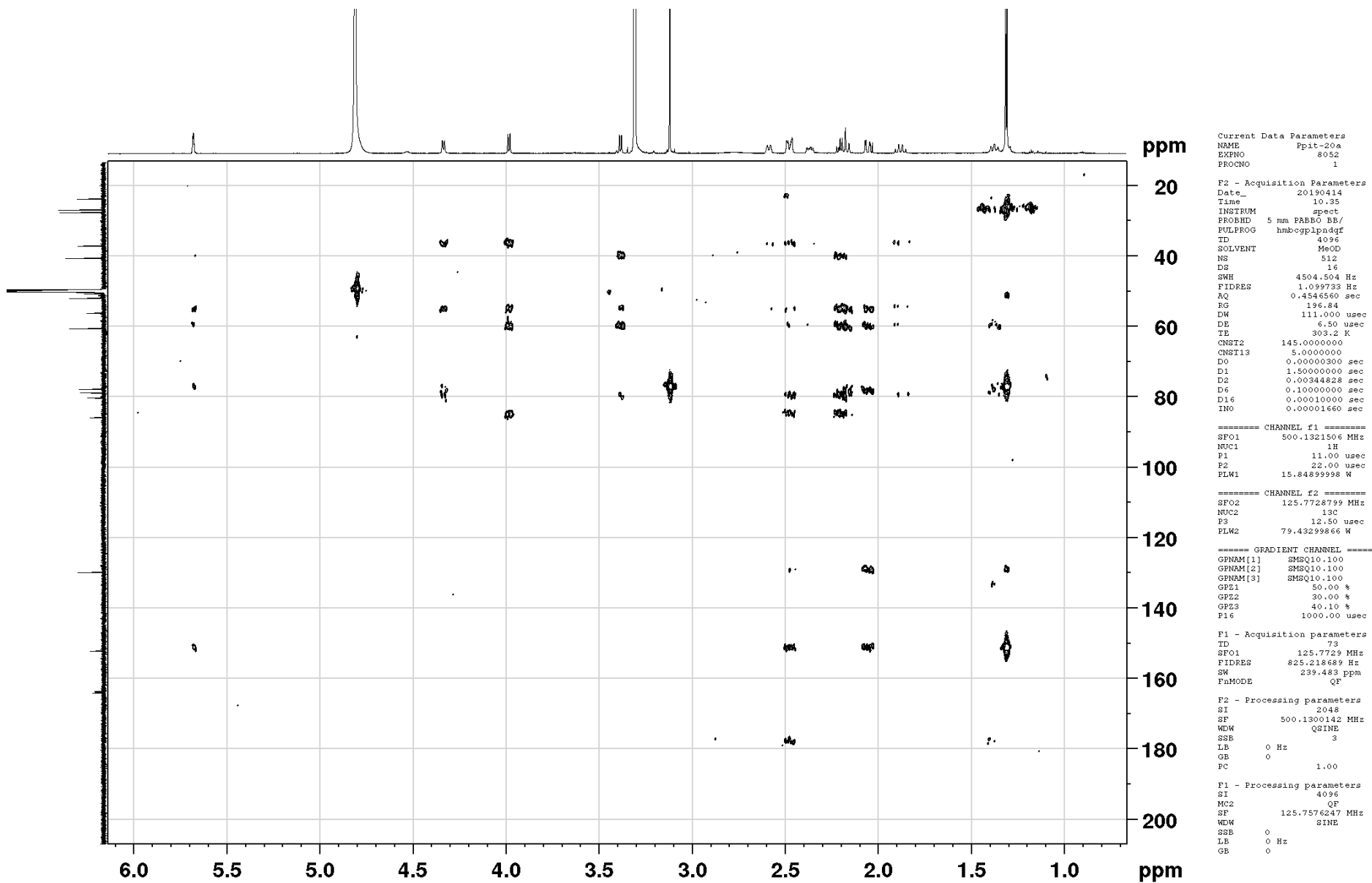


Figure S52. HMBC spectrum (500 MHz, CD₃OD) of 4

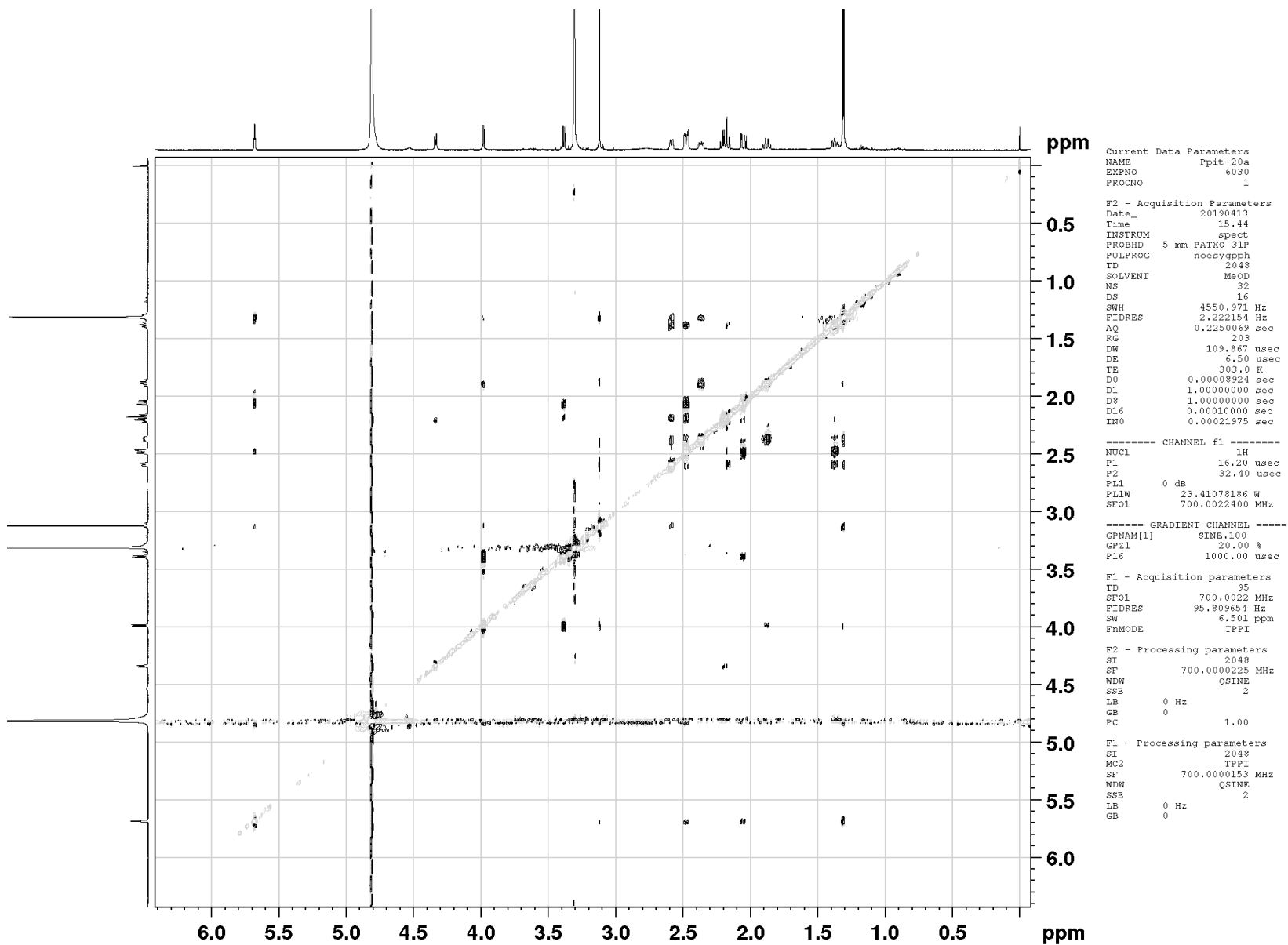


Figure S53. NOESY spectrum (700 MHz, CD₃OD) of 4

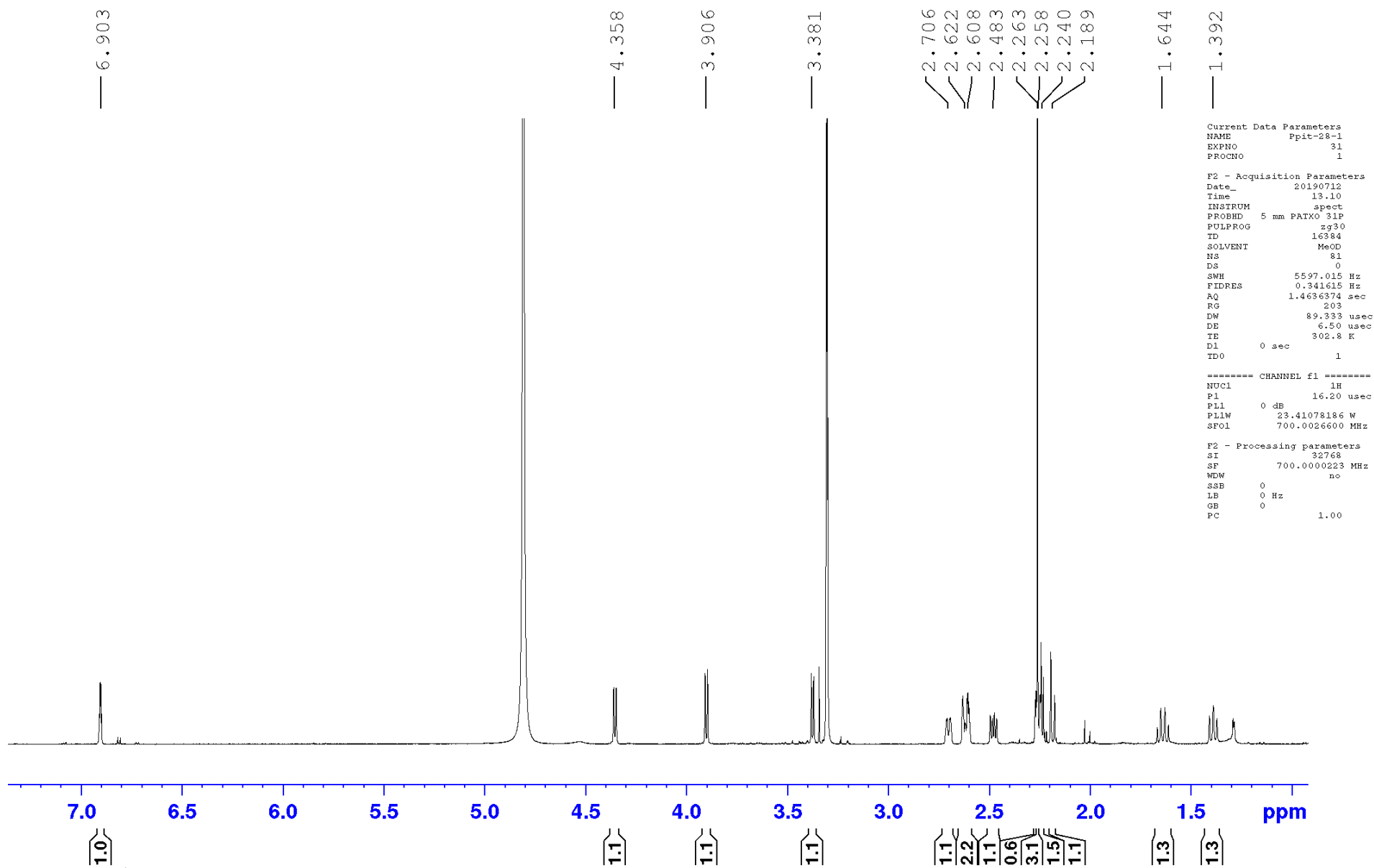


Figure S54. ^1H NMR spectrum (700 MHz, CD_3OD) of **5**

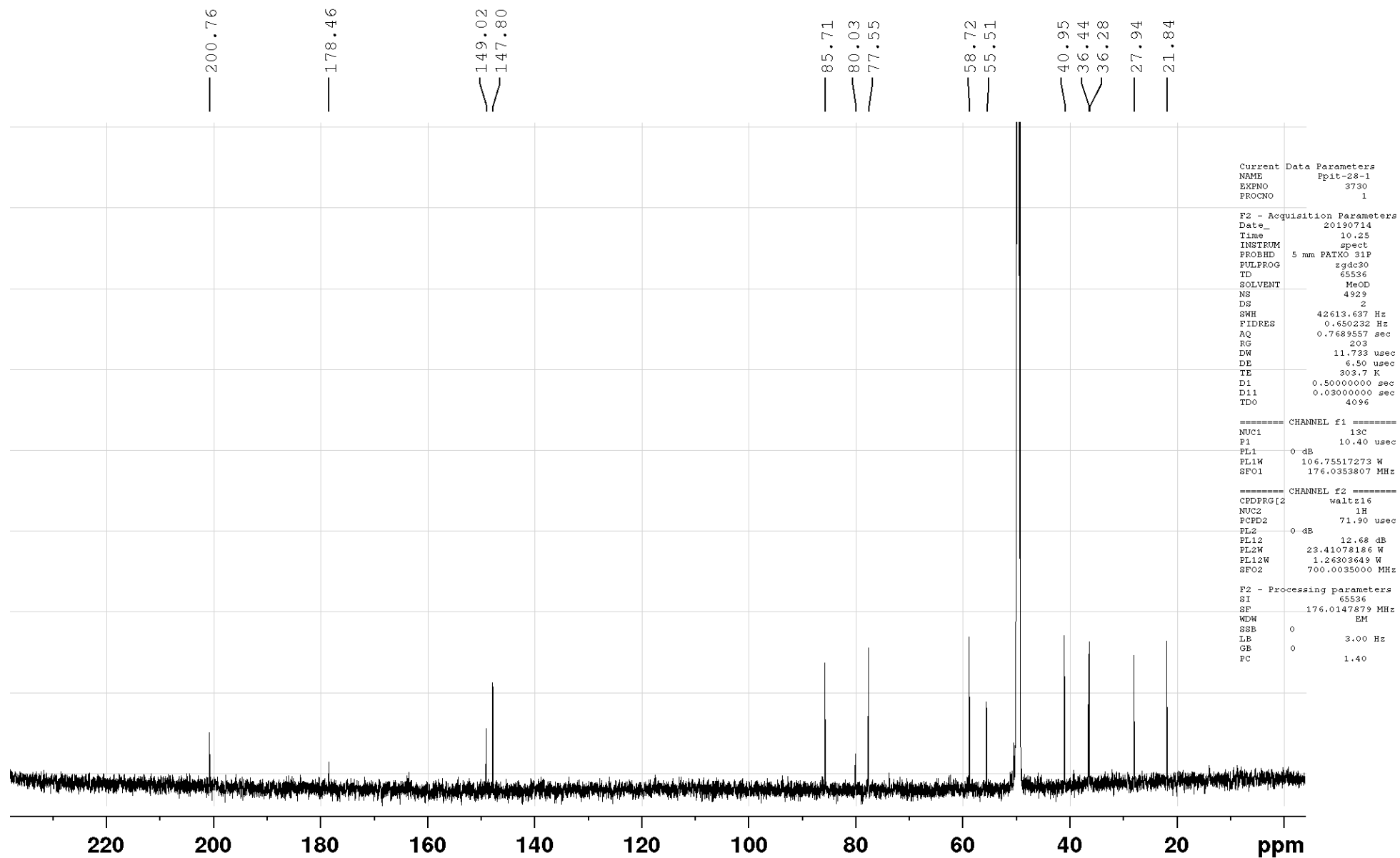


Figure S55. ^{13}C NMR spectrum (176 MHz, CD_3OD) of **5**

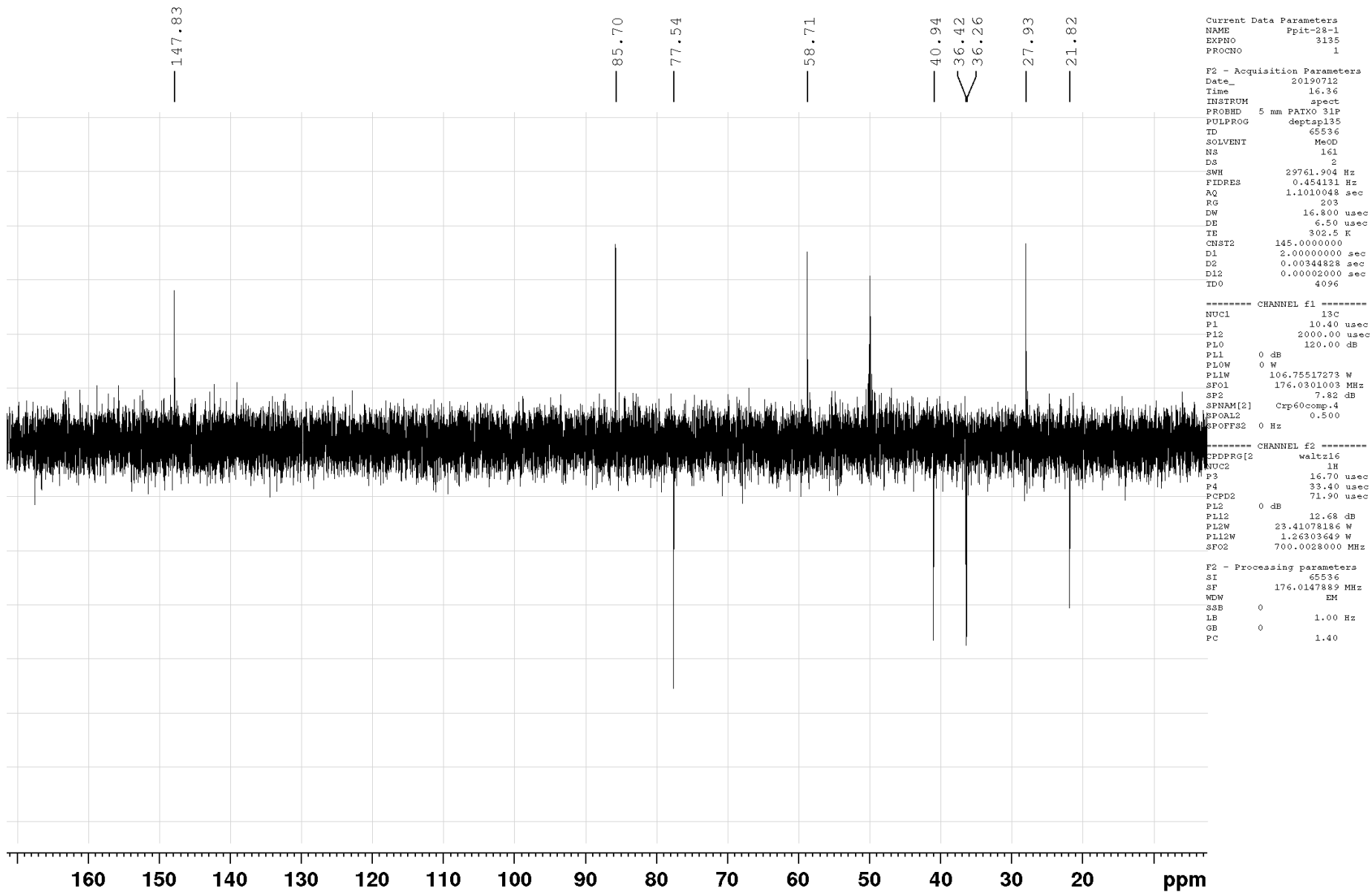


Figure S56. DEPT-135 NMR spectrum (176 MHz, CD₃OD) of 5

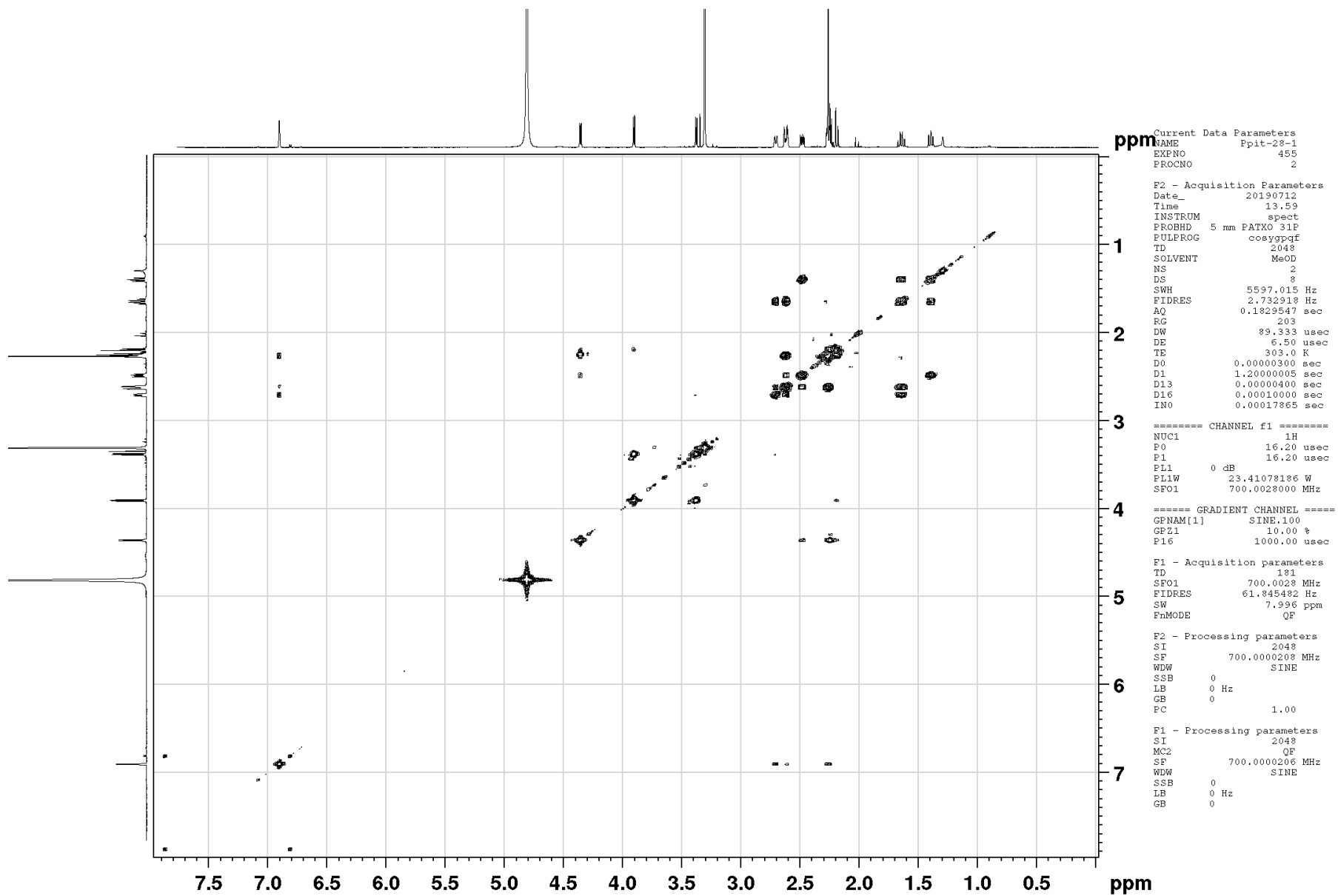
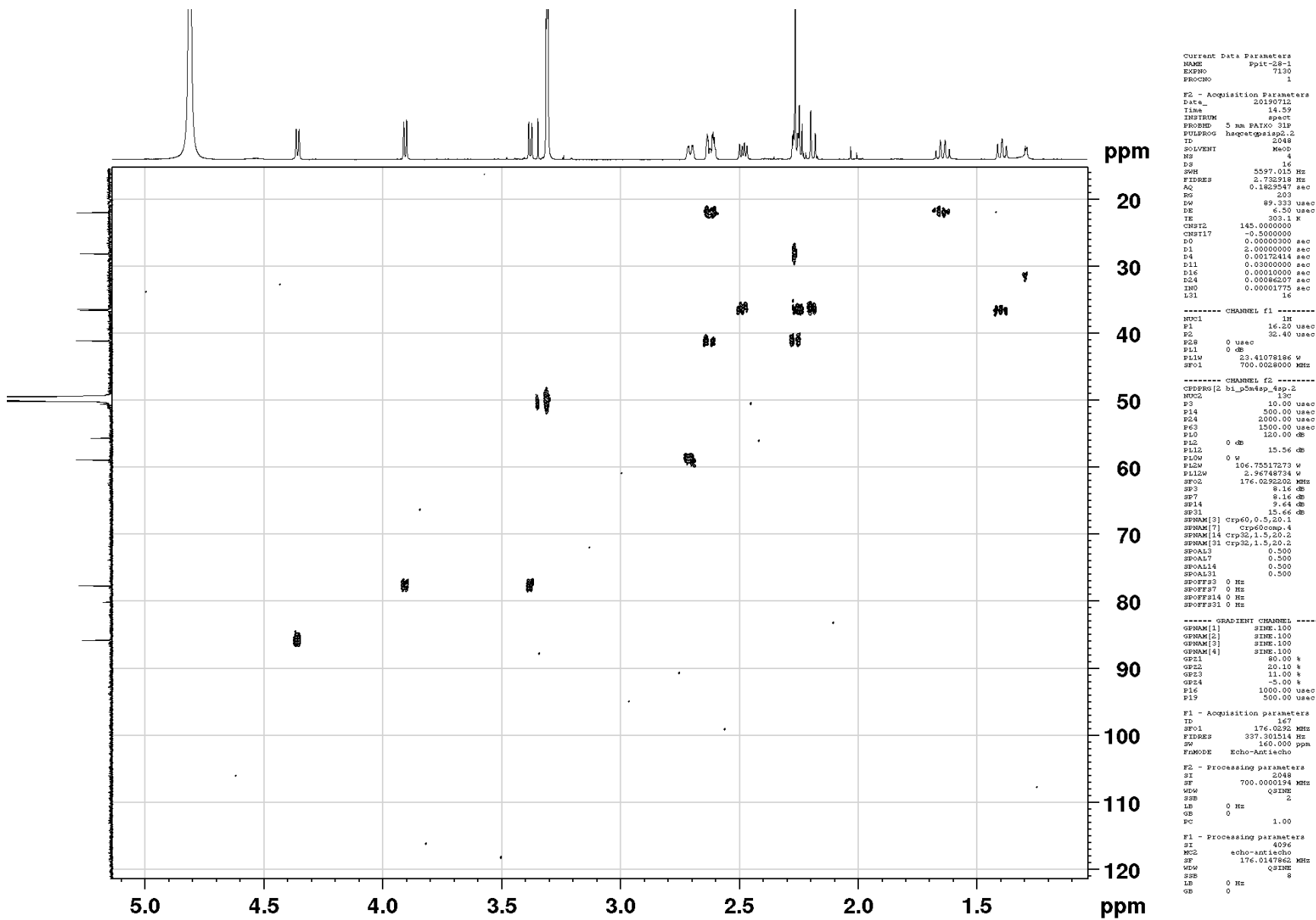


Figure S57. COSY-45 spectrum (700 MHz, CD₃OD) of 5



```

Current Data Parameters
NAME      Fpic-28-1
EXPNO    7130
PROCNO    1

F2 - Acquisition Parameters
Date_    20190712
Time     14:59
INSTRUM  spect
PROBHD   5 mm PATAQ 51P
PULPROG  zgpg30
ID       2048
SOLVENT  MeOH
NS       4
DS       16
SWH      5597.015 Hz
FIDRES   2.732918 Hz
AQ       0.182947 sec
RG       203
LW       89.333 usec
DE       6.50 usec
TE       303.1 K
CNS12    145.000000
CNS17    -0.500000
EQ       0.000000000 sec
D1       2.0000000 sec
D4       0.00172414 sec
D11      0.0300000 sec
D16      0.0001000 sec
D24      0.0008207 sec
IND      0.00001775 sec
L31      16

----- CHANNEL f1 -----
NUC1     1H
P1       16.20 usec
P2       32.40 usec
RG1      0 usec
RG2      0 dB
PL1W    23.41078184 W
SFO1     700.0028000 MHz

----- CHANNEL f2 -----
CPEPRG2  zgpg30
NUC2     13C
P3       10.00 usec
P14      500.00 usec
P24      2000.00 usec
P63      1500.00 usec
P10      120.00 dB
P12      0 dB
P122     15.56 dB
P109     0 W
P12W    106.75517273 W
P12W    2.96748734 W
SFO2     176.0292202 MHz
SE3      8.16 dB
SE7      8.16 dB
SE14     9.64 dB
SE31     15.66 dB
SENAM[3] Crp60,0.5,20.1
SENAM[7] Crp60comp,4
SENAM[14] Crp32,1.5,20.2
SENAM[21] Crp32,1.5,20.2
SFOAL3   0.500
SFOAL7   0.500
SFOAL14  0.500
SFOAL31  0.500
SFOFF23  0 Hz
SFOFF37  0 Hz
SFOFF14  0 Hz
SFOFF31  0 Hz

----- GRADIENT CHANNEL -----
GENAM[1] SINE,100
GENAM[2] SINE,100
GENAM[3] SINE,100
GENAM[4] SINE,100
GE21     80.00 %
GE22     20.13 %
GE23     11.00 %
GE24     -5.00 %
P16      1000.00 usec
P19      500.00 usec

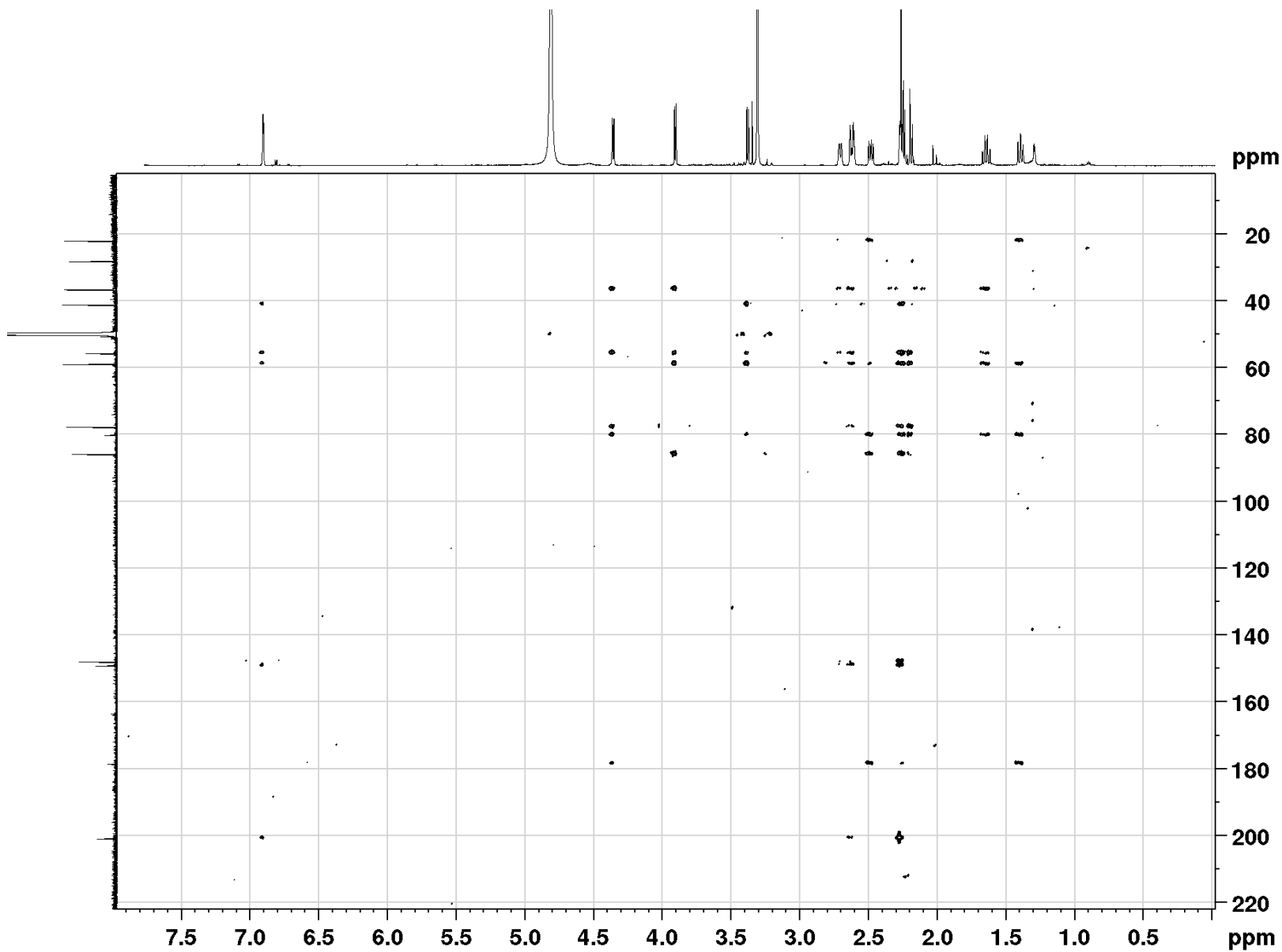
F1 - Acquisition parameters
ID       167
SFO1     176.0292 MHz
FIDRES   337.901514 Hz
SW       160.000 ppm
FAMODE   Echo-Antiecho

F2 - Processing parameters
SI       2048
SF       700.0000194 MHz
WDW      QSINE
SSB      2
LB       0 Hz
GB       0
PC       1.00

F1 - Processing parameters
SI       4096
MC2      echo-antiecho
SF       176.0147862 MHz
WDW      QSINE
SSB      8
LB       0 Hz
GB       0

```

Figure S58. HSQC spectrum (700 MHz, CD₃OD) of 5



```

Current Data Parameters
NAME      Ppit-28-1
EXPNO    8052
PROCNO   1

F2 - Acquisition Parameters
Date_    20190713
Time     15.19
INSTRUM  spect
PROBHD   5 mm PATKO 31P
PULPROG  hmbcgp1pndqf
TD        4096
SOLVENT  MeOD
NS        160
DS        16
SWH       5597.015 Hz
FIDRES    1.366459 Hz
AQ        0.3659093 sec
RG        203
DW        89.933 usec
DE        6.50 usec
TE        303.0 K
CNST2    145.0000000
CNST13    5.0000000
DO        0.00000300 sec
DL        1.50000000 sec
D2        0.00344828 sec
D6        0.10000000 sec
DL6       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
SF01      700.0028000 MHz

===== CHANNEL f2 =====
NUC2      13C
P3        10.00 usec
PL2       0 dB
PL2W      106.75517273 W
SF02      176.0345007 MHz

===== GRADIENT CHANNEL =====
GPNAM[1]  SINE.100
GPNAM[2]  SINE.100
GPNAM[3]  SINE.100
GP21      50.00 %
GP22      30.00 %
GP23      40.10 %
P16       1000.00 usec

F1 - Acquisition parameters
TD        217
SF01      176.0345 MHz
FIDRES    356.936310 Hz
SW        220.000 ppm
FnMODE    QF

F2 - Processing parameters
SI        2048
SF        700.0000189 MHz
WDW       SINE
SSB       3
LB        0 Hz
GB        0
PC        1.00

F1 - Processing parameters
SI        4096
MC2       QF
SF        176.0147996 MHz
WDW       SINE
SSB       0
LB        0 Hz
GB        0

```

Figure S59. HMBC spectrum (700 MHz, CD₃OD) of 5

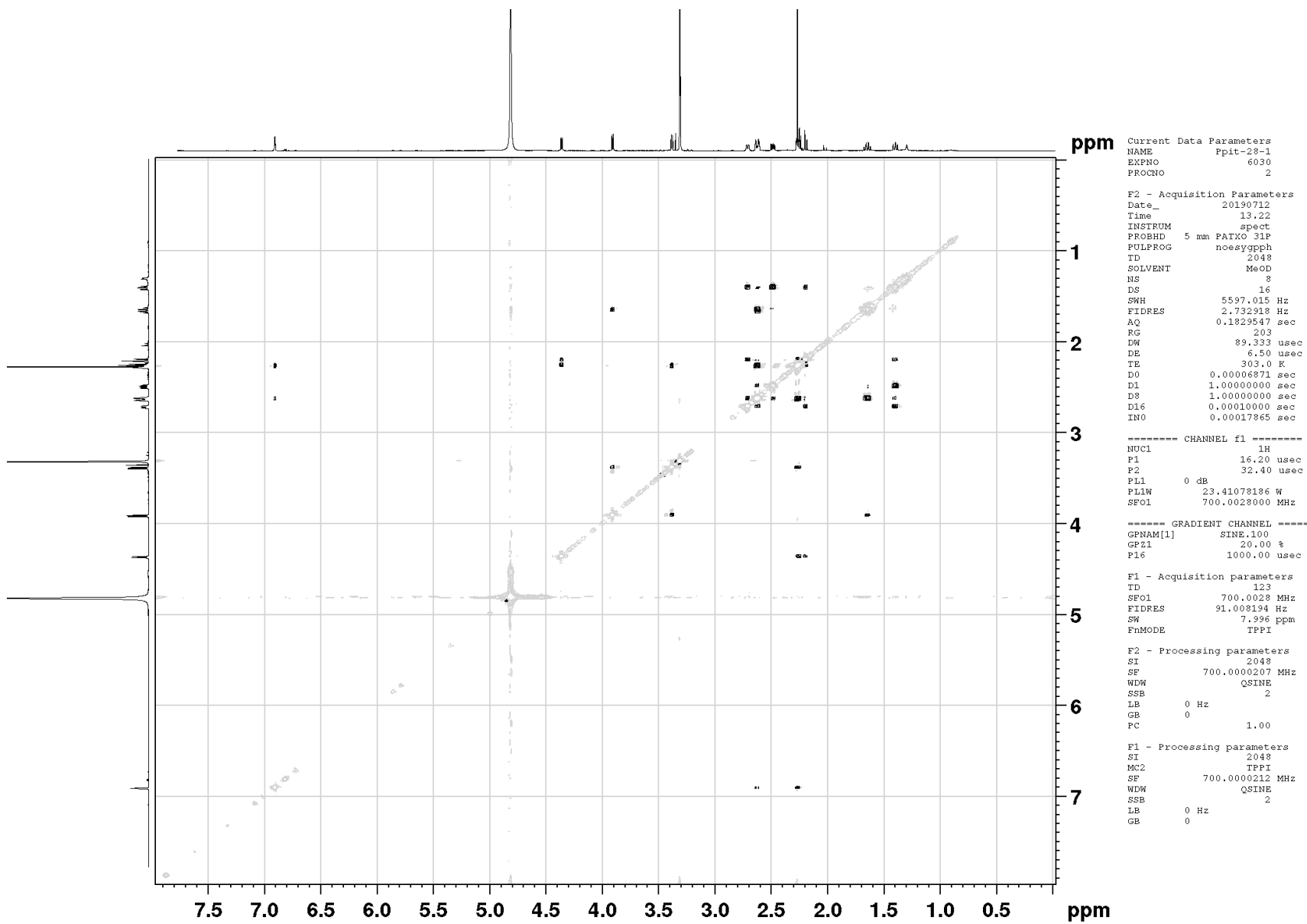


Figure S60. NOESY spectrum (700 MHz, CD₃OD) of 5

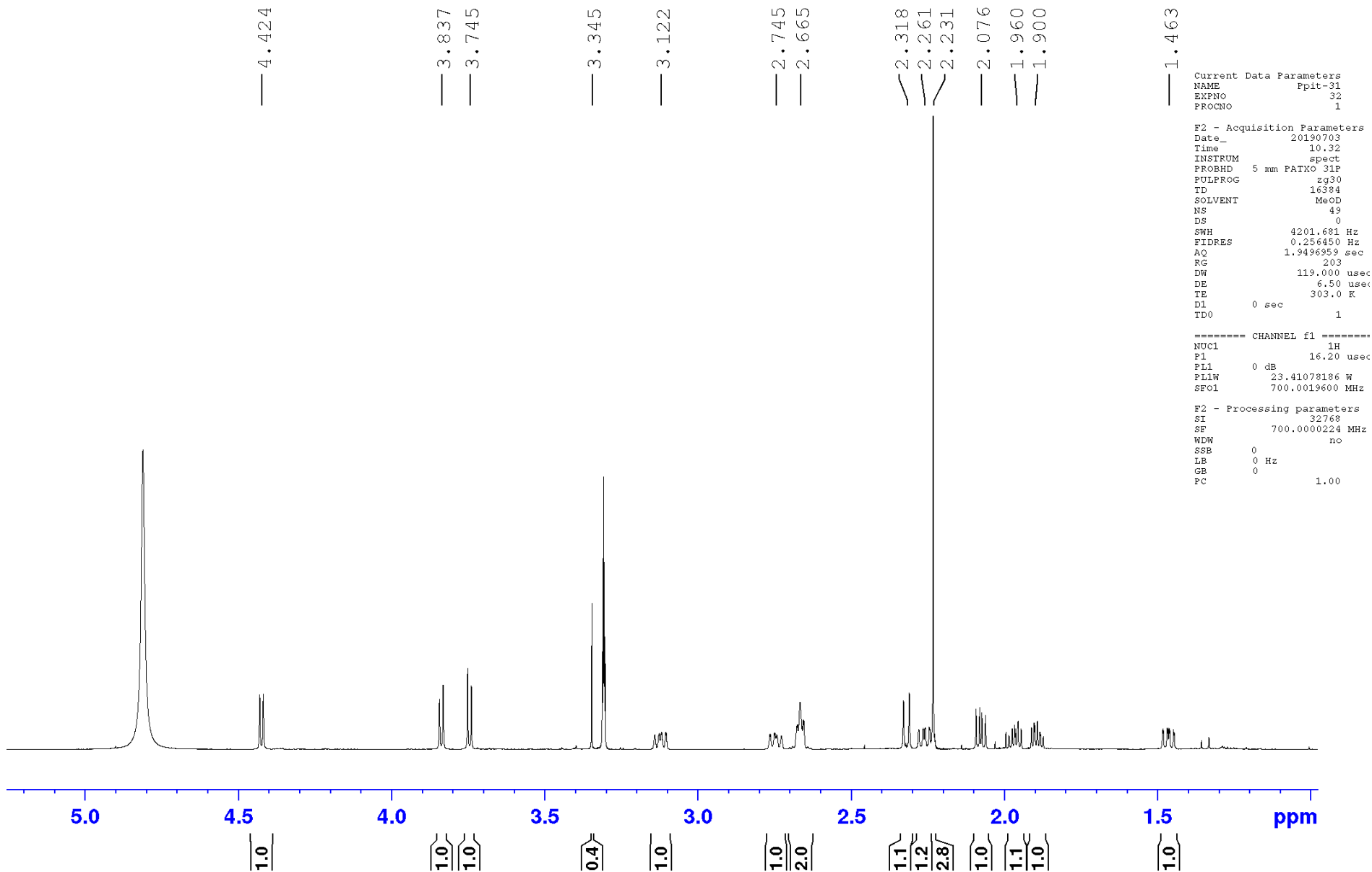


Figure S61. ¹H NMR spectrum (700 MHz, CD₃OD) of **6**

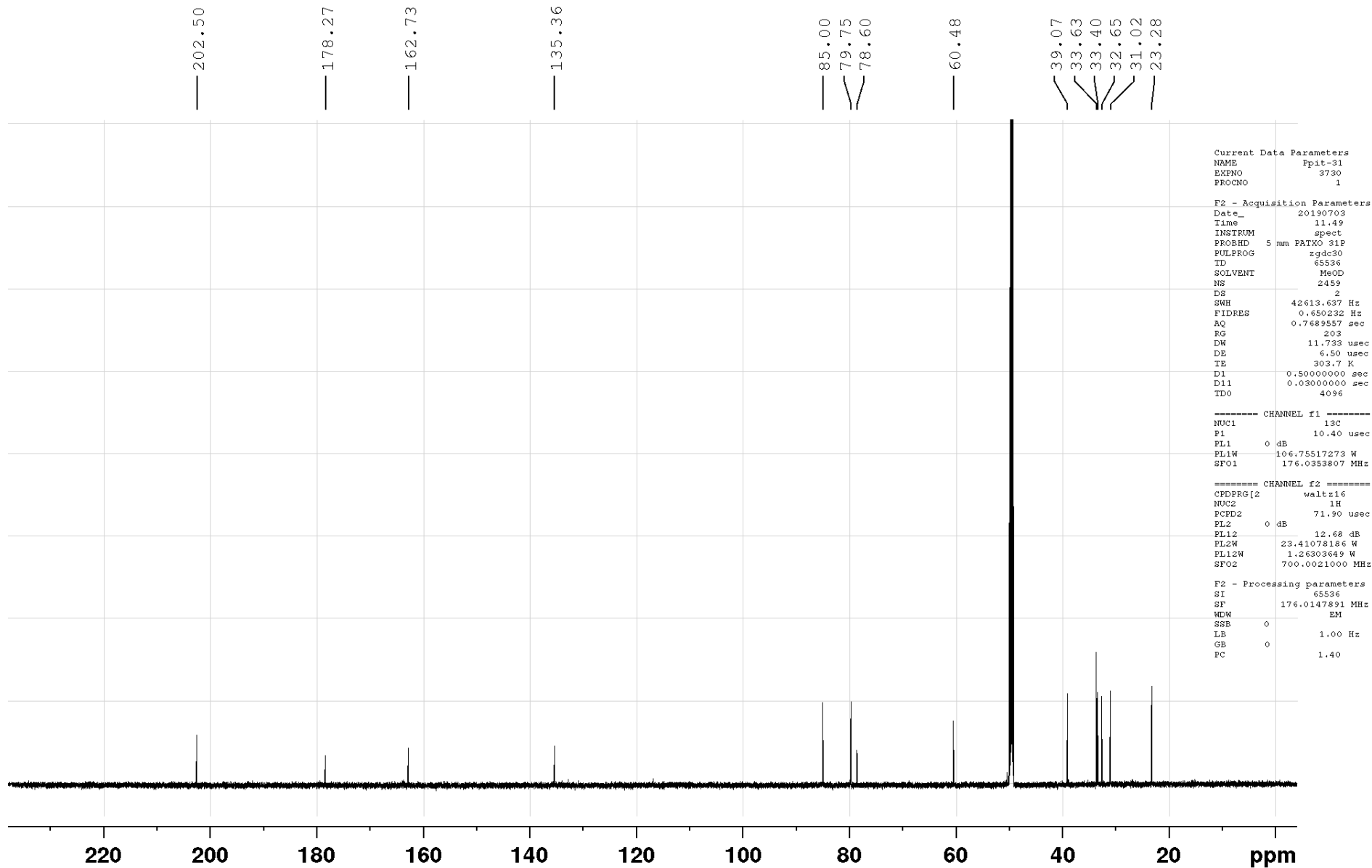


Figure S62. ¹³C NMR spectrum (176 MHz, CD₃OD) of **6**

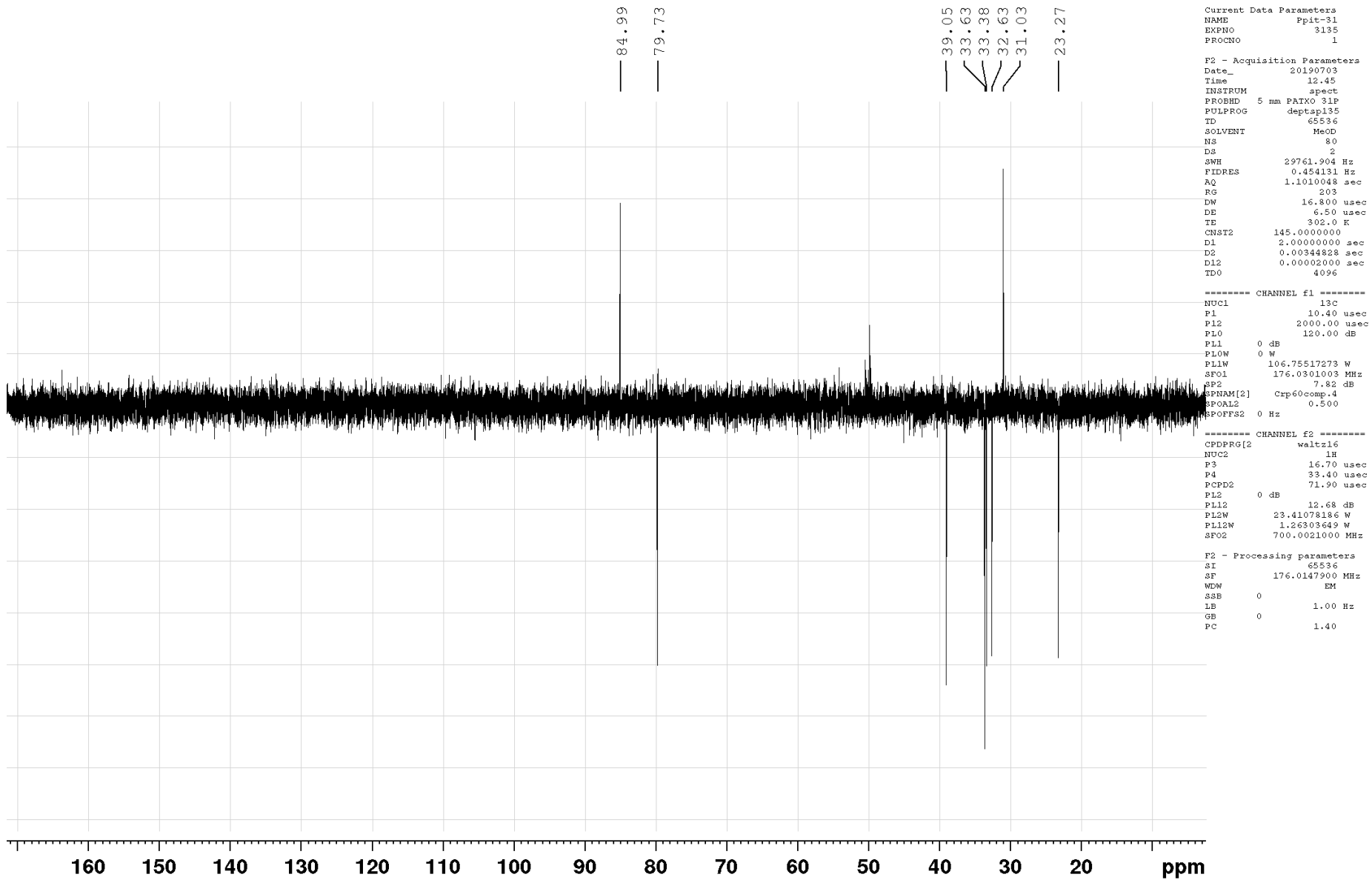
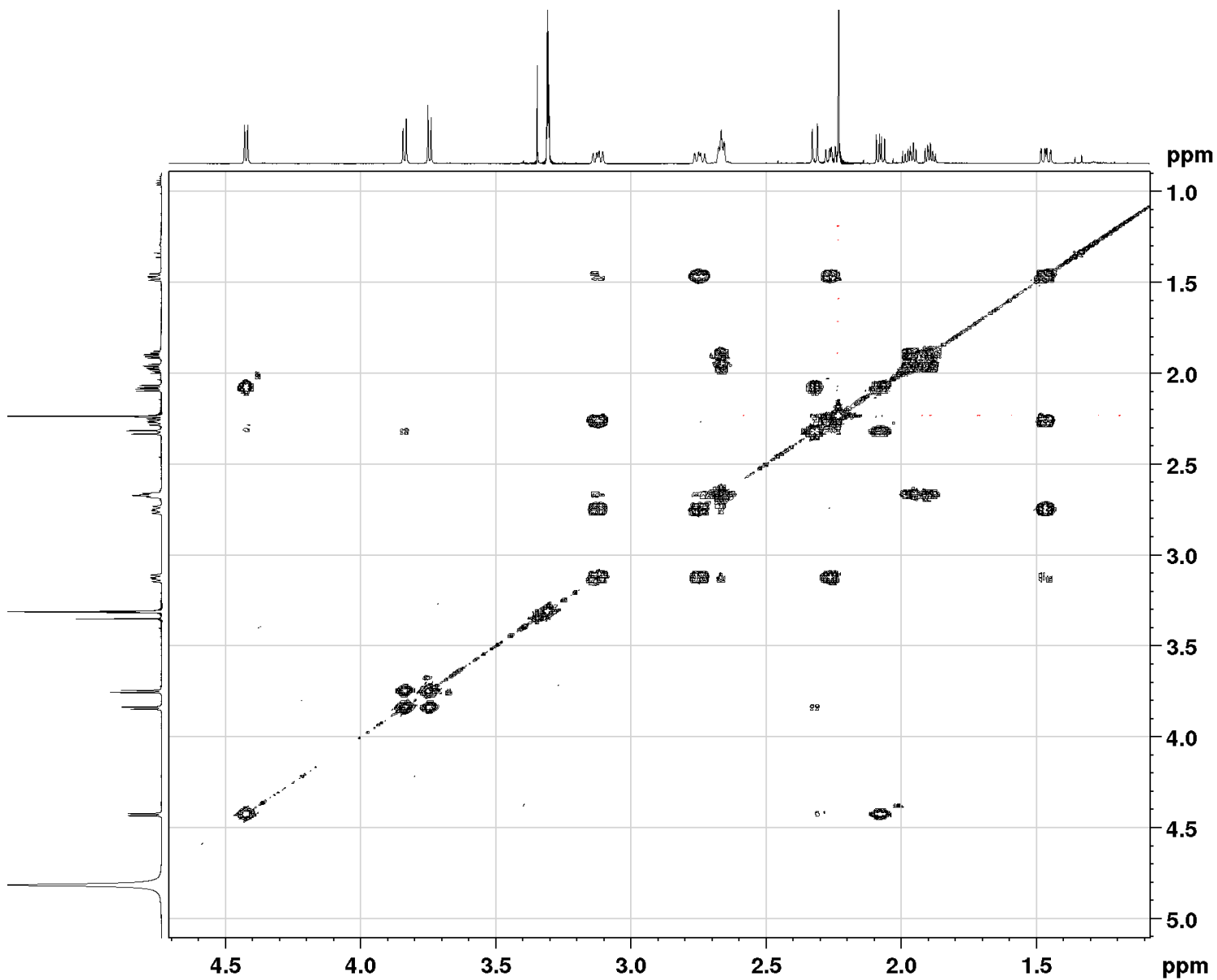


Figure S63. DEPT-135 NMR spectrum (176 MHz, CD₃OD) of 6



```

Current Data Parameters
NAME          Ppit-31
EXPNO        455
PROCNO       1

F2 - Acquisition Parameters
Date_        20190703
Time         10.33
INSTRUM      spect
PROBHD       5 mm PATKO 31P
PULPROG      cosygpcf
TD           2048
SOLVENT      MeOD
NS           1
DS           8
SWH          4201.681 Hz
FIDRES       2.051602 Hz
AQ           0.2437120 sec
RG           203
DW           119.000 usec
DE           6.50 usec
TE           303.0 K
D0           0.00000300 sec
D1           1.20000005 sec
D13          0.00000400 sec
D16          0.00010000 sec
IN0          0.00023800 sec

===== CHANNEL f1 =====
NUC1         1H
P0           16.20 usec
P1           16.20 usec
PL1          0 dB
PL1W        23.41078186 W
SF01         700.0021000 MHz

===== GRADIENT CHANNEL =====
GPNAM[1]     SINE.100
GP21         10.00 %
P16          1000.00 usec

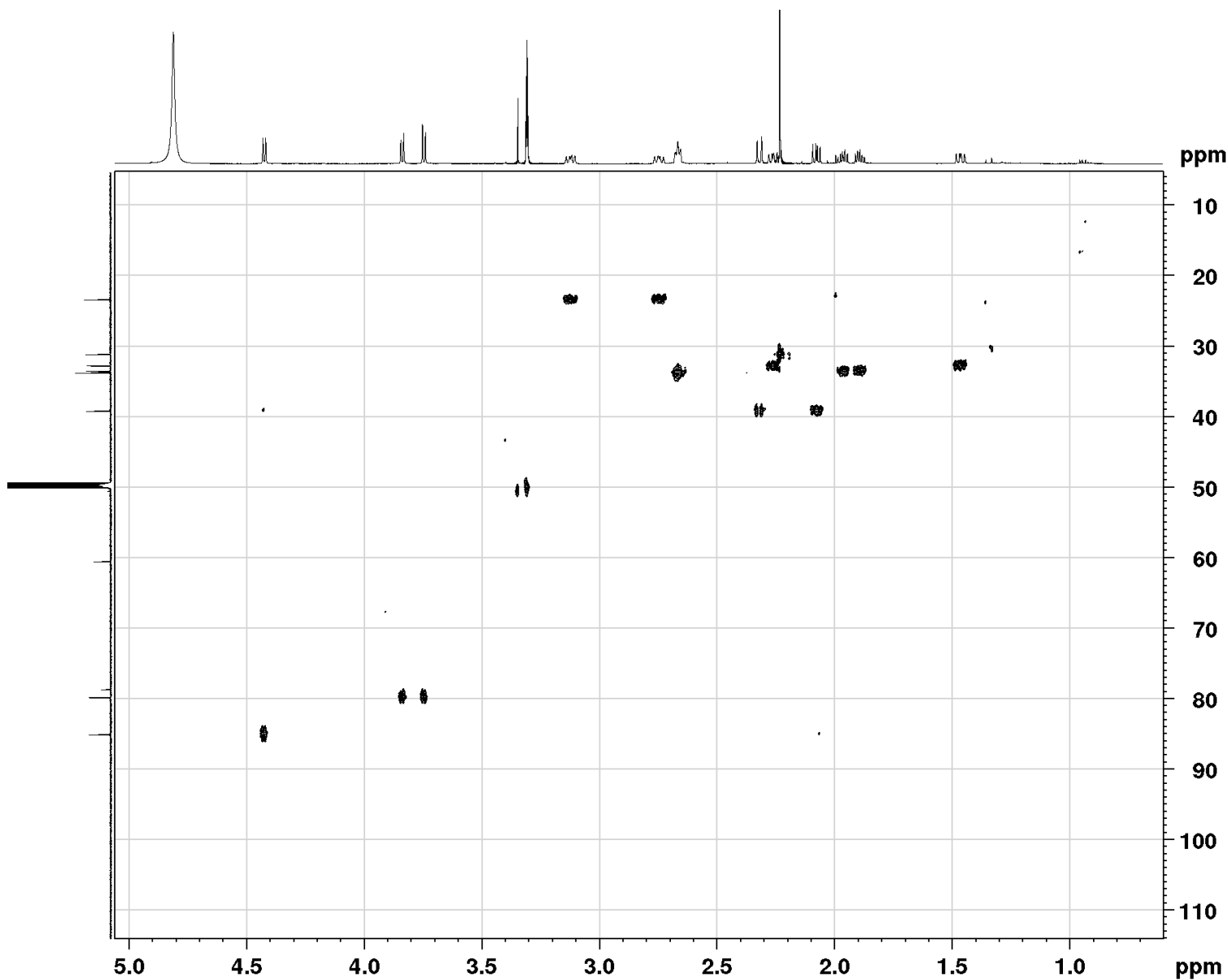
F1 - Acquisition parameters
TD           256
SF01         700.0021 MHz
FIDRES       32.825607 Hz
SW           6.002 ppm
FnmODE       QF

F2 - Processing parameters
SI           2048
SF           700.0000214 MHz
WDW          SINE
SSB          0
LB           0 Hz
GB           0
PC           1.00

F1 - Processing parameters
SI           2048
MC2          QF
SF           700.0000213 MHz
WDW          SINE
SSB          0
LB           0 Hz
GB           0

```

Figure S64. COSY-45 spectrum (700 MHz, CD₃OD) of **6**



```

Current Data Parameters
NAME          Pp11-11
EXPNO        7130
PROCNO       1

F2 - Acquisition Parameters
Date_        20190703
Time         11.19
INSTRUM      spect
PROBHD       5 mm PAKO 31P
PULPROG      zgpg30
TD           65536
SOLVENT      MeOD
NS           48
DS           4
SWH           4201.681 Hz
FIDRES       2.051602 Hz
AQ           0.2437120 sec
RG           203
DA           119.000 usec
DE           6.50 usec
TE           303.3 K
CH212       145.000000
CH217       -0.500000
DO           0.0000000 sec
D1           2.0000000 sec
D4           0.00176414 sec
D11          0.0300000 sec
D16          0.0001000 sec
D24          0.00086207 sec
IND          0.00001775 sec
L31          16

----- CHANNEL f1 -----
NUC1         1H
P1           16.20 usec
P2           32.40 usec
PC1          0 usec
PL1          0 dB
PL12         23.41078186 w
PL1W         700.0021000 MHz

----- CHANNEL f2 -----
CPDPRG2[2]  bt_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
PL1W         0 w
PL2W         106.75517273 w
PL12W        2.96748734 w
SFO2         176.0252200 MHz
SP3          8.16 dB
SP7          8.16 dB
SP14         7.64 dB
SP31         15.66 dB
SFMAM[3]    cpr60,0.5,20.1
SFMAM[7]    cpr60comp,4
SFMAM[14]   cpr52,1.5,20.2
SFMAM[31]   cpr52,1.5,20.2
SFOAL3      0.500
SFOAL7      0.500
SFOAL14     0.500
SFOFF3      0 Hz
SFOFF7      0 Hz
SFOFF14     0 Hz
SFOFF31     0 Hz

----- GRADIENT CHANNEL -----
GPMAM[1]    SINE,100
GPMAM[2]    SINE,100
GPMAM[3]    SINE,100
GPMAM[4]    SINE,100
GPE1        80.00 %
GPE2        20.10 %
GPE3        11.00 %
GPE4        -3.00 %
P16         1000.00 usec
P17         500.00 usec

F1 - Acquisition parameters
TD           256
SFO1         176.0252 MHz
FIDRES       220.036500 Hz
SV           140.000 ppm
FAMODE       Echo-Antiecho

F2 - Processing parameters
SI           700.0000159 MHz
SF           QSIMS
WDW          2
SSB          0
GB           0
PC           1.00

F1 - Processing parameters
SI           4096
MC2          echo-antiecho
SF           176.0147865 MHz
WDW          QSIMS
SSB          8
LB           0 Hz
GB           0

```

Figure S65. HSQC spectrum (700 MHz, CD₃OD) of **6**

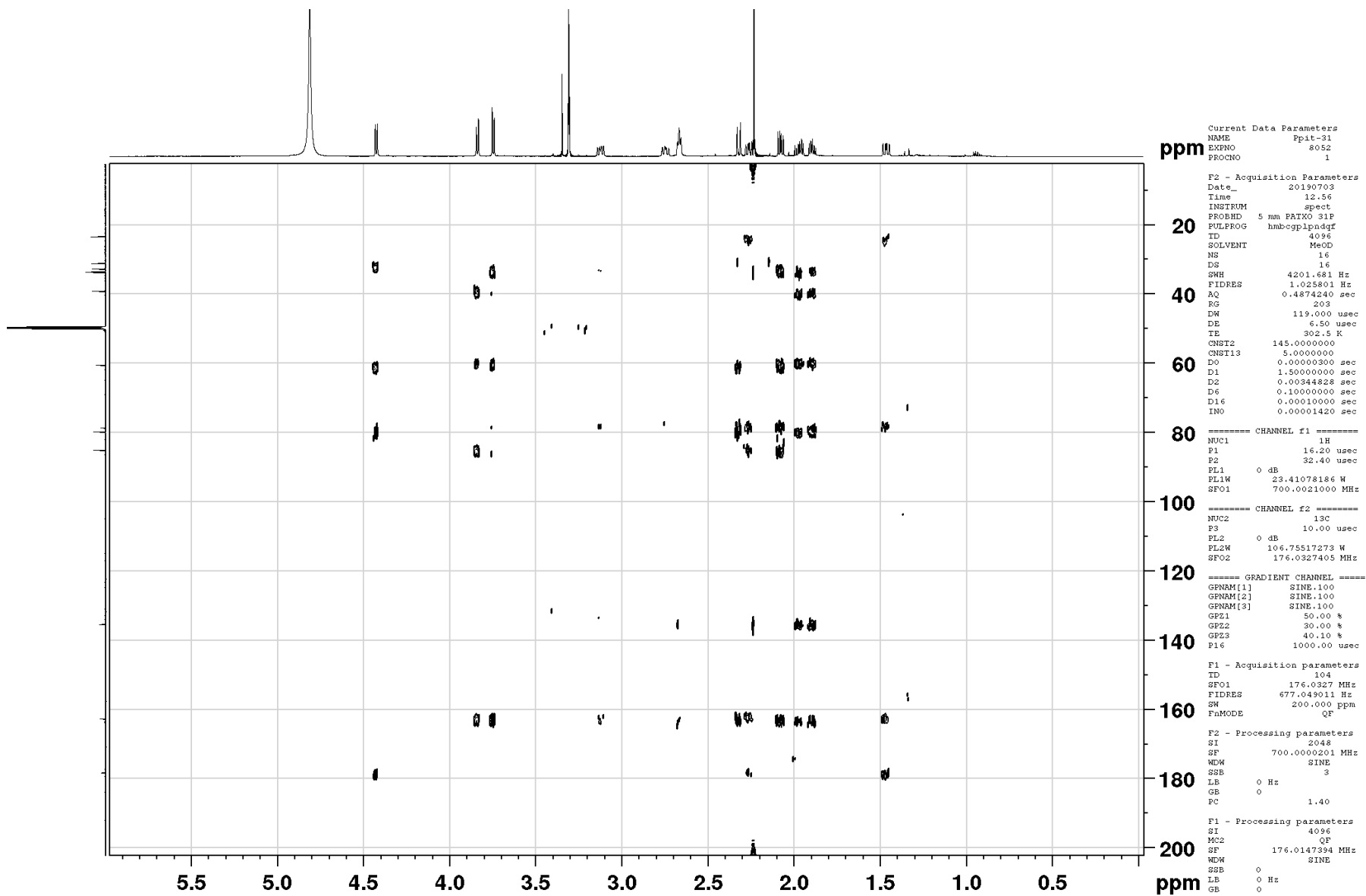


Figure S66. HMBC spectrum (700 MHz, CD₃OD) of 6

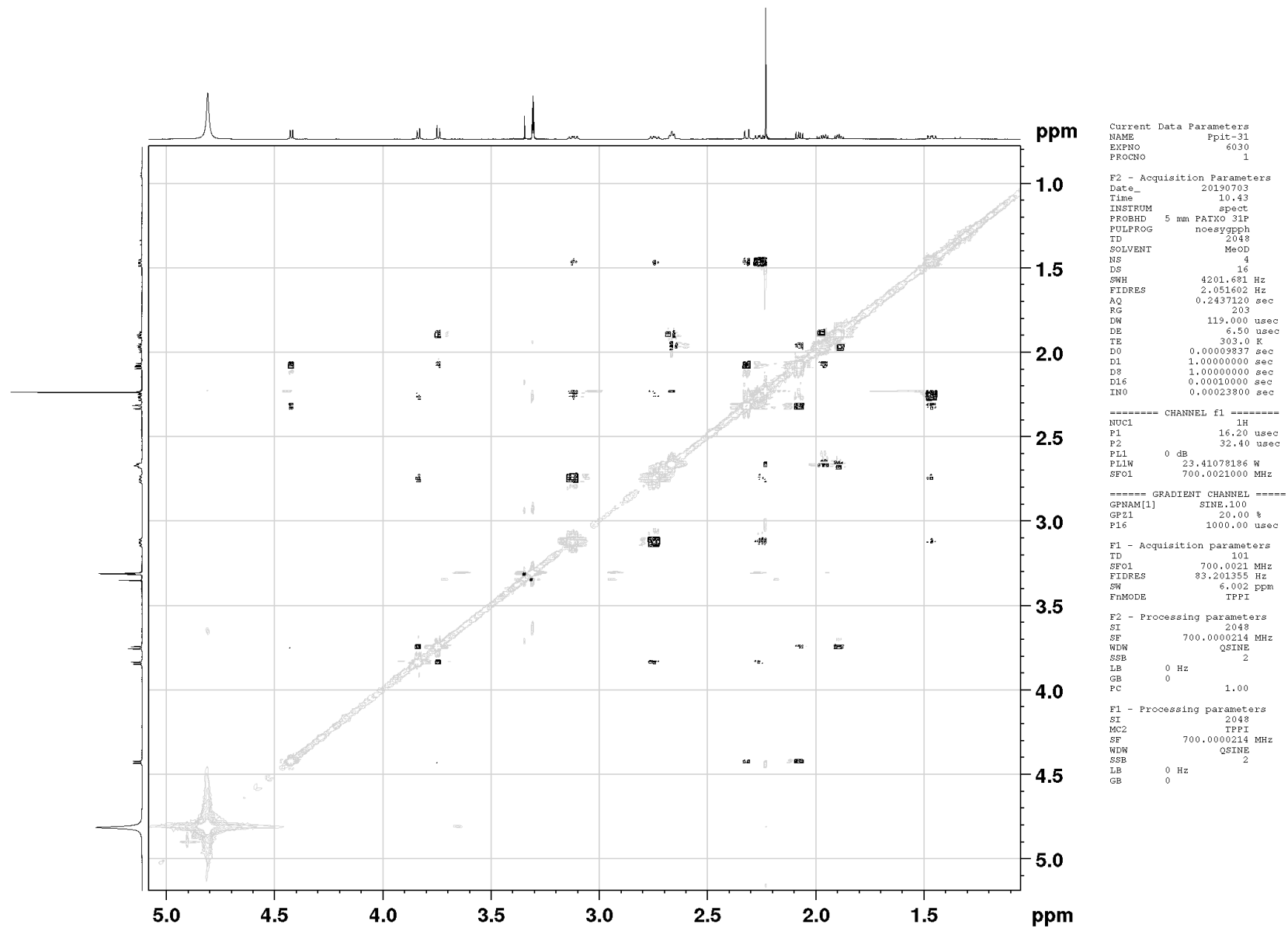
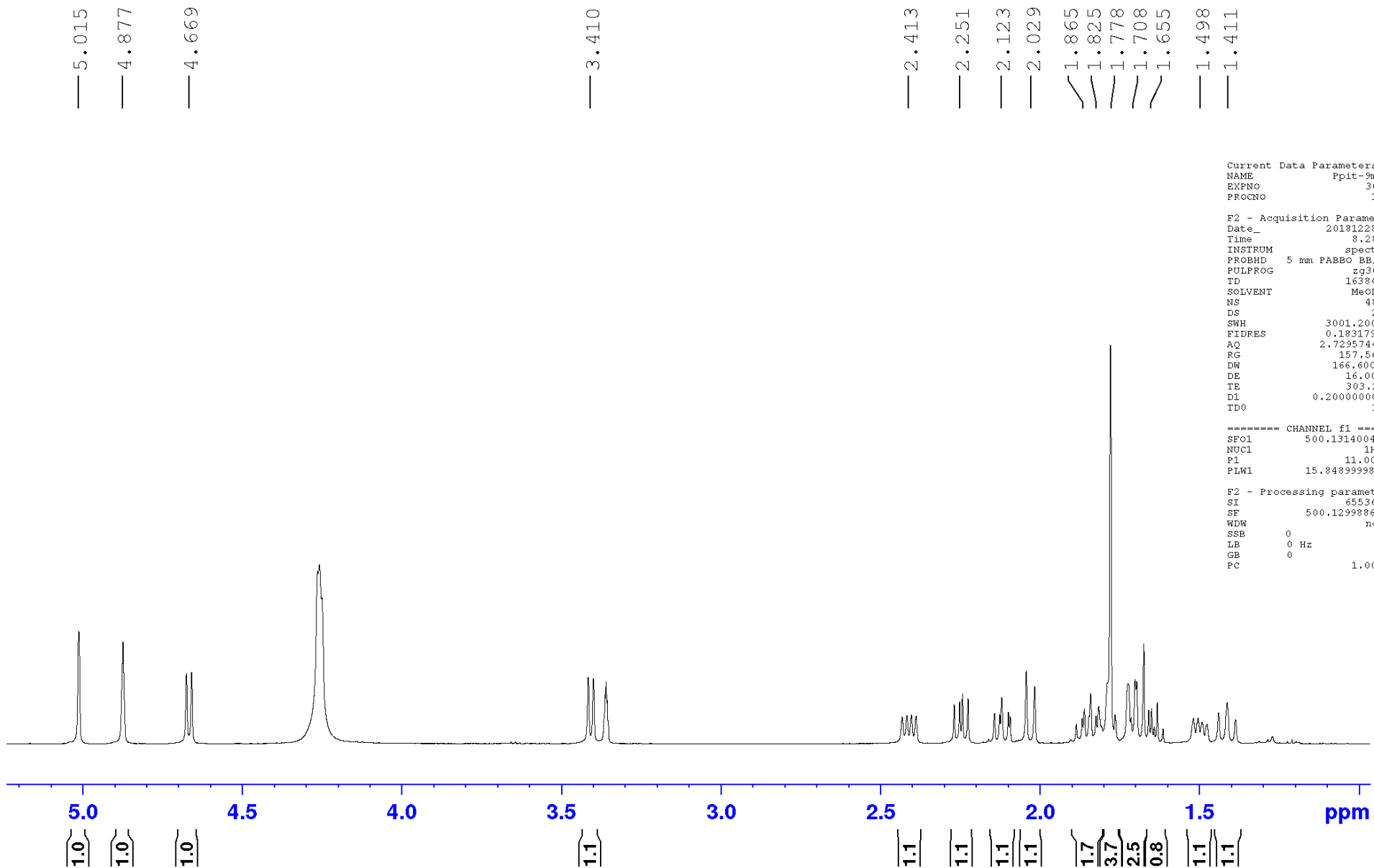


Figure S67. NOESY spectrum (700 MHz, CD₃OD) of **6**



```

Current Data Parameters
NAME          Ppit-9m
EXPNO         30
PROCNO        1

F2 - Acquisition Parameters
Date_         20181228
Time          8.28
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zg30
TD            16384
SOLVENT       MeOD
NS            48
DS            2
SWH           3001.200 Hz
FIDRES        0.183179 Hz
AQ            2.7295744 sec
RG            157.56
DW            166.600 usec
DE            16.00 usec
TE            303.2 K
D1            0.20000000 sec
TD0           1

----- CHANNEL f1 -----
SFO1          500.1314004 MHz
NUC1           1H
P1            11.00 usec
PLW1          15.84899998 W

F2 - Processing parameters
SI            65536
SF            500.1299886 MHz
WDW           no
SSB           0
LB            0 Hz
GB            0
PC            1.00

```

Figure S68. ¹H NMR spectrum (500 MHz, CD₃OD+CDCl₃) of **7**

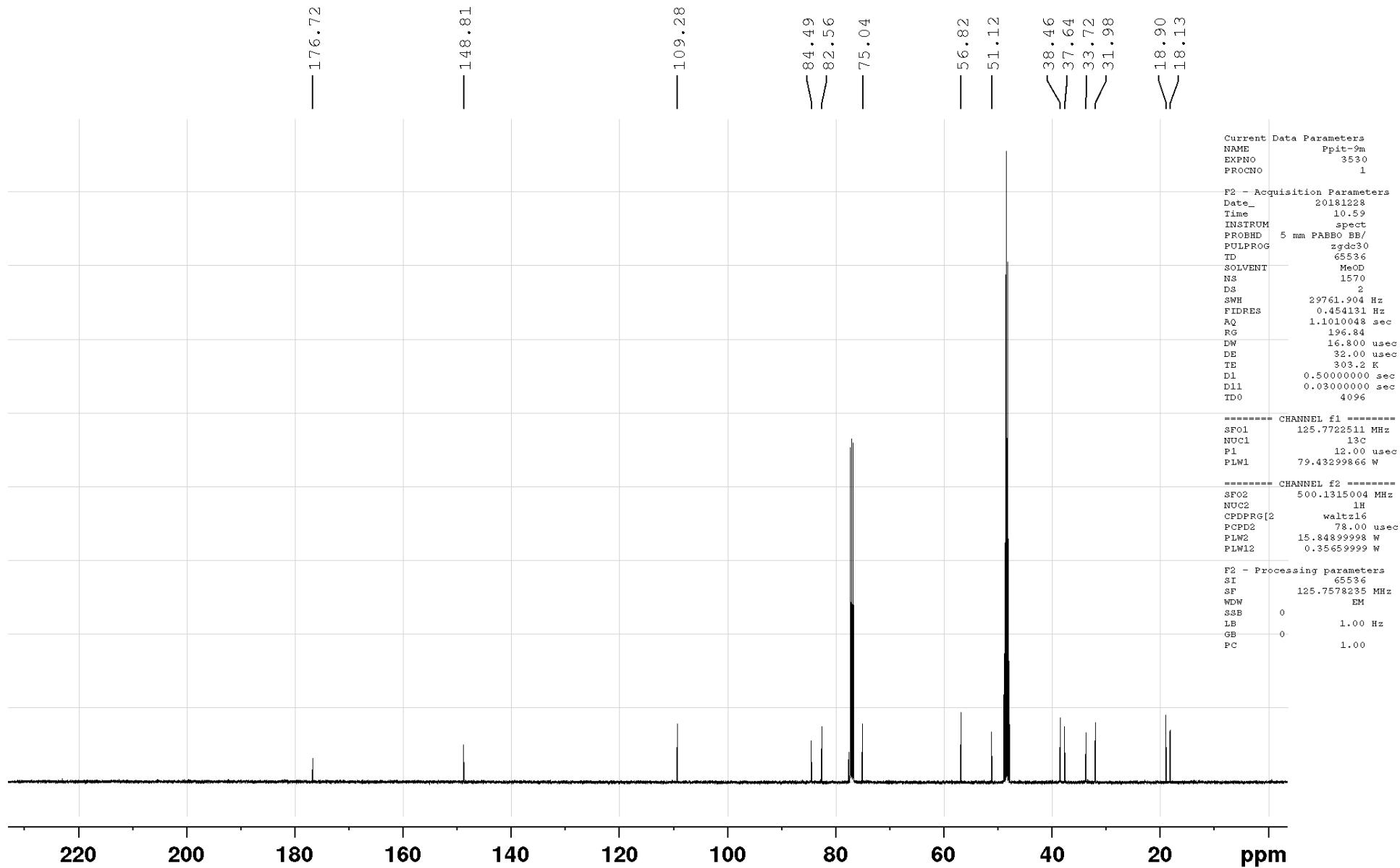


Figure S69. ¹³C NMR spectrum (125 MHz, CD₃OD+CDCl₃) of 7

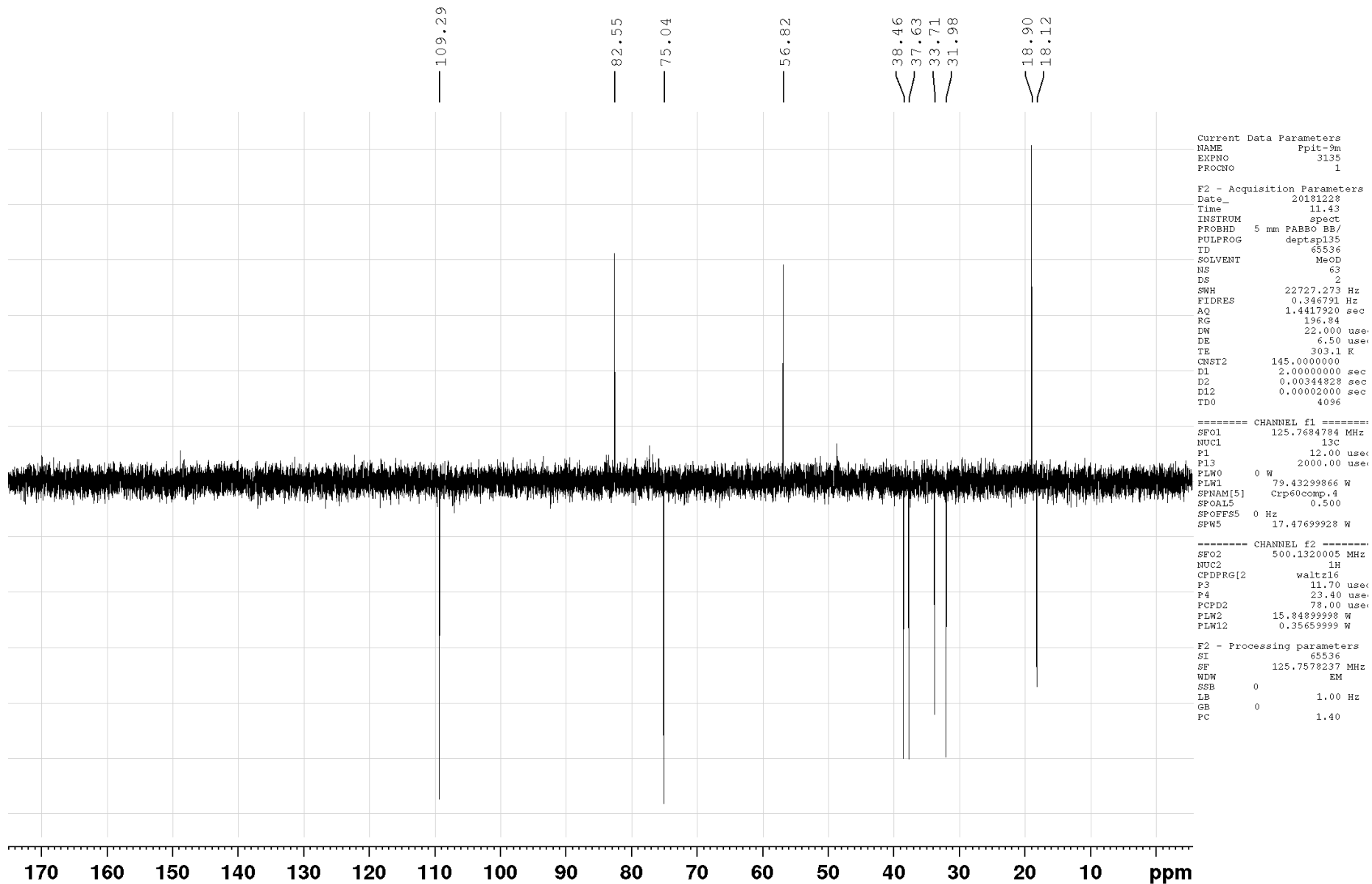


Figure S70. DEPT-135 NMR spectrum (125 MHz, CD₃OD+CDCl₃) of 7

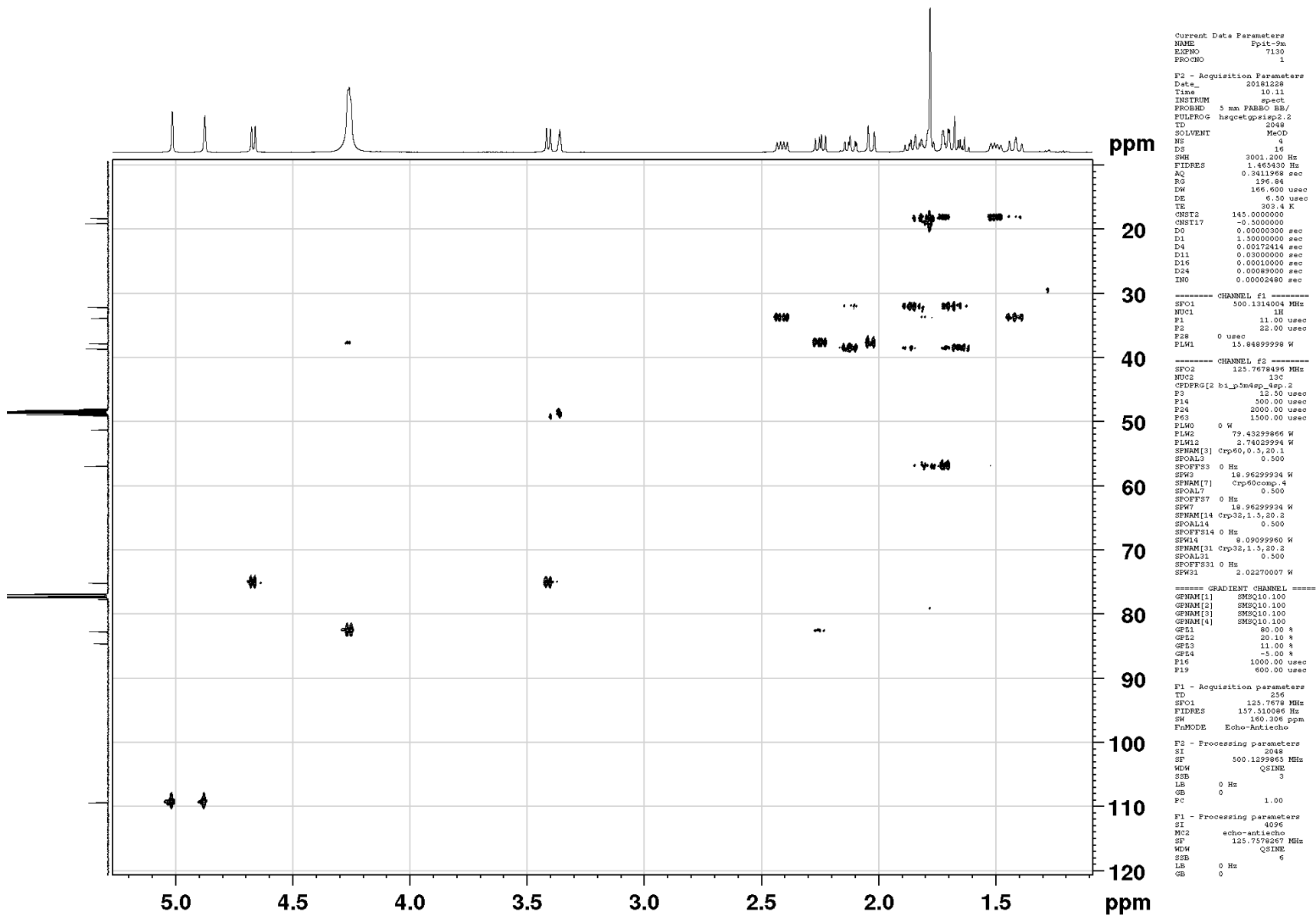


Figure S71. HSQC spectrum (500 MHz, CD₃OD+CDCl₃) of 7

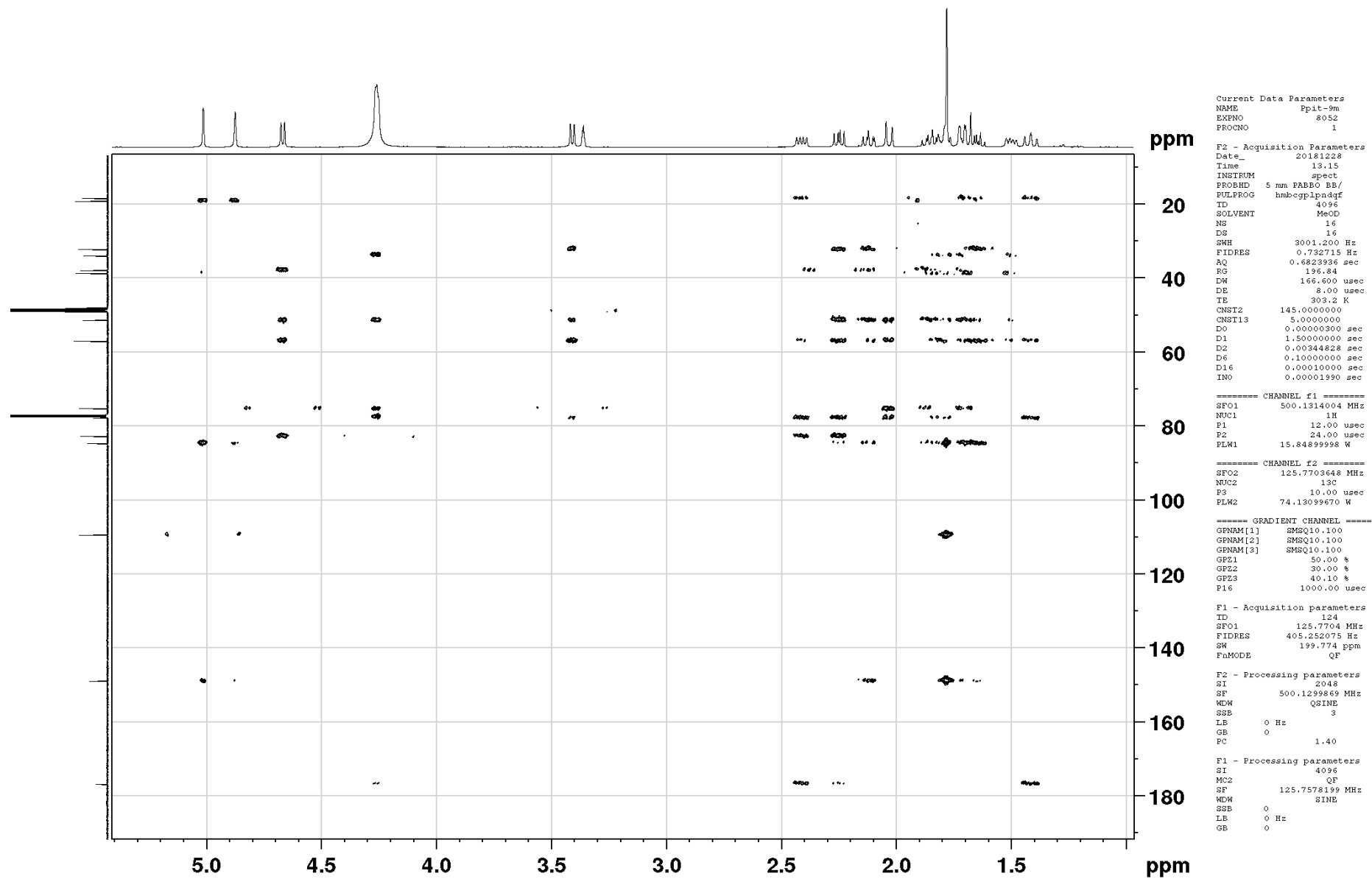


Figure S72. HMBC spectrum (500 MHz, CD₃OD+CDCl₃) of 7

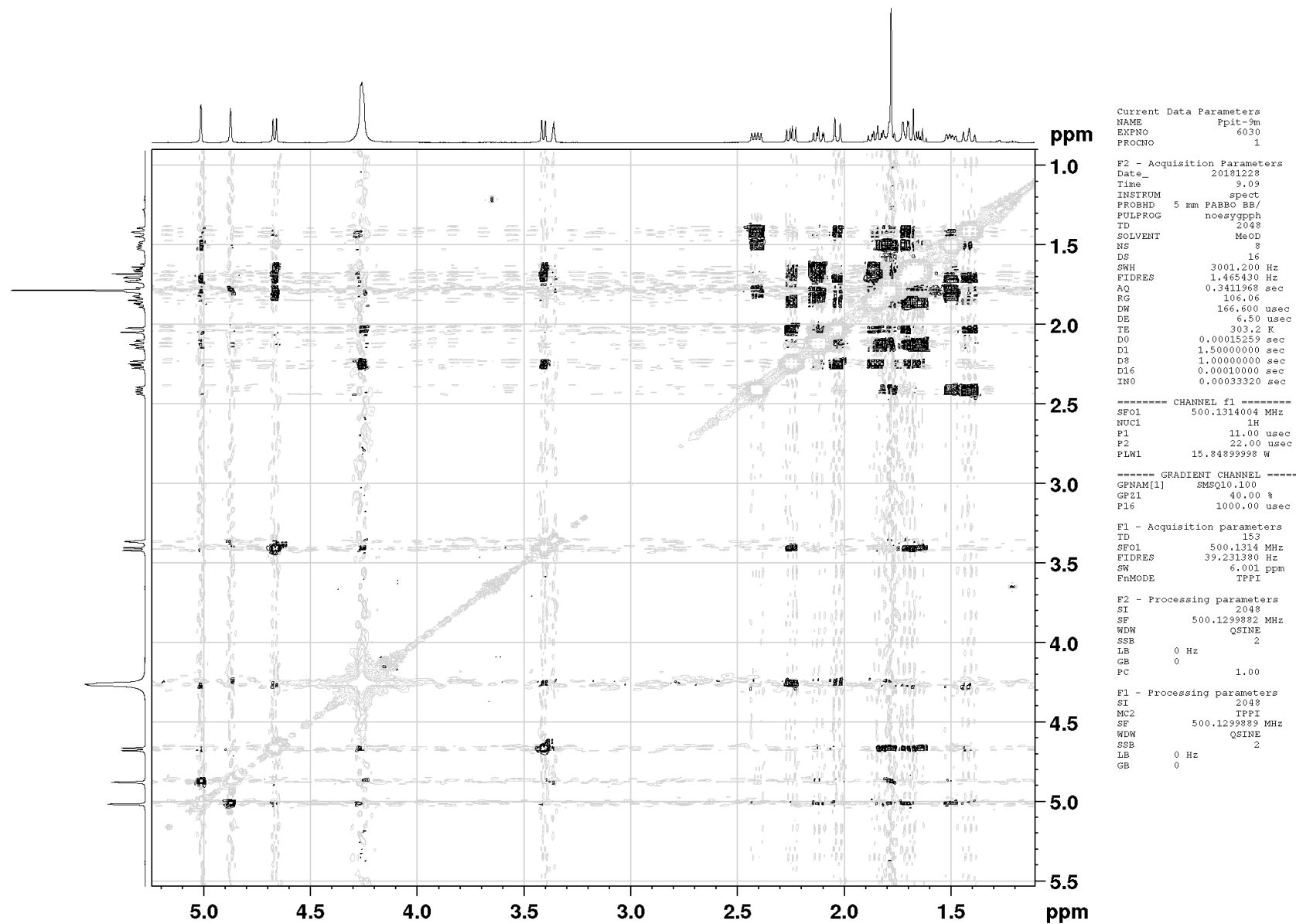


Figure S73. NOESY spectrum (500 MHz, CD₃OD+CDCl₃) of 7

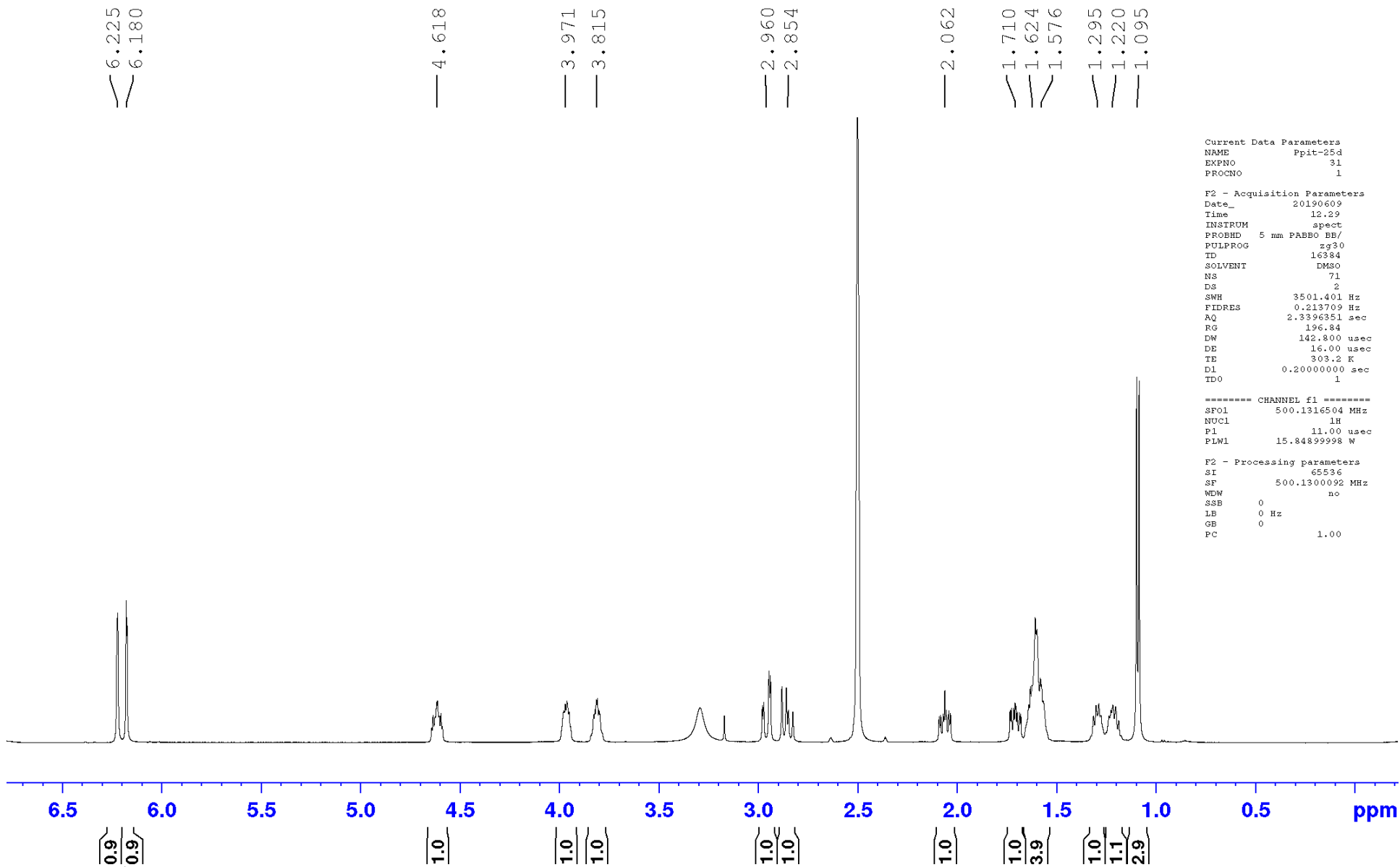


Figure S74. ¹H NMR spectrum (500 MHz, DMSO) of **8**

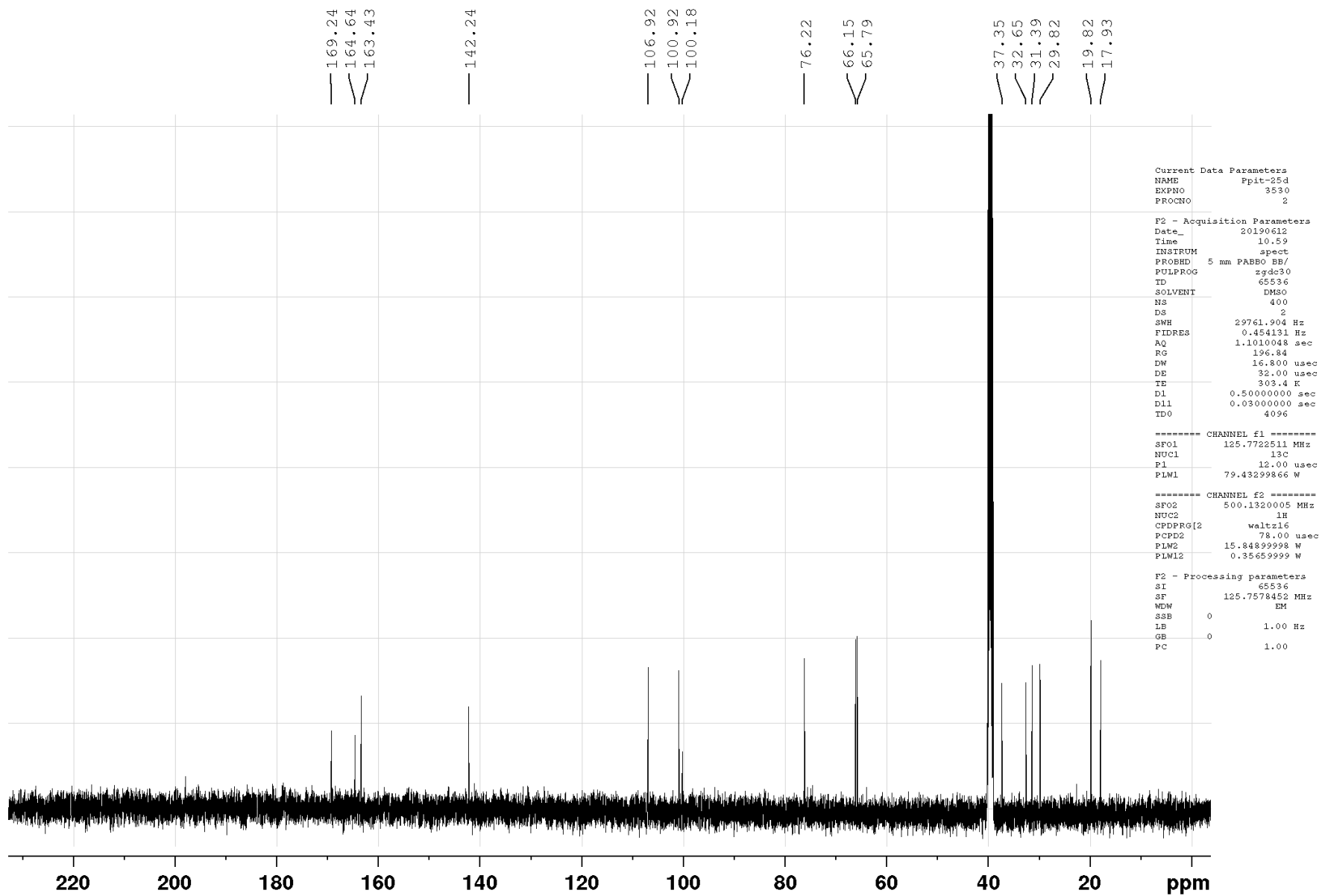
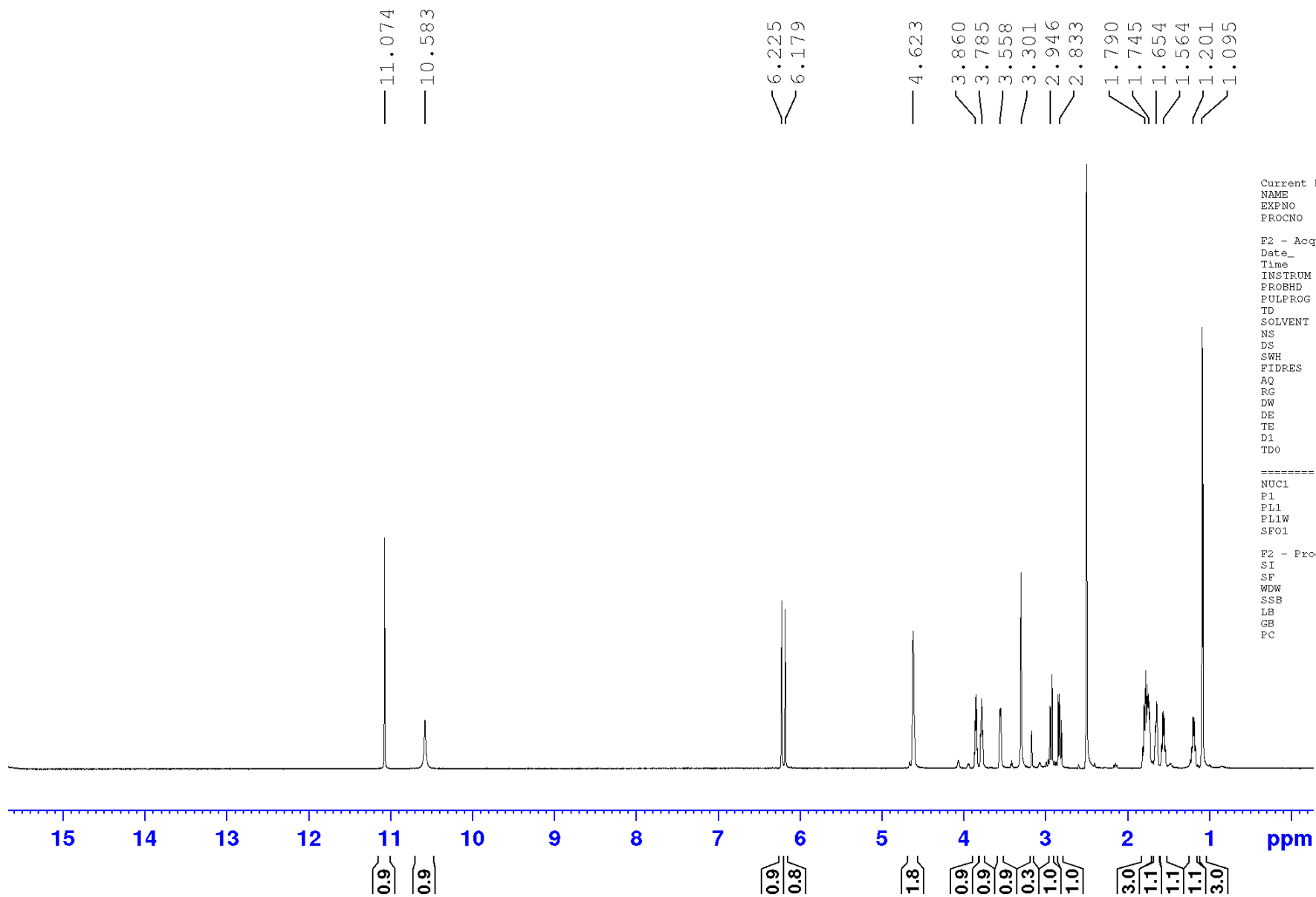


Figure S75. ^{13}C NMR spectrum (125 MHz, DMSO) of **8**



```

Current Data Parameters
NAME          Ppit-16d
EXPNO         30
PROCNO        2

F2 - Acquisition Parameters
Date_         20190318
Time          14.43
INSTRUM       spect
PROBHD        5 mm PATX0 31P
PULPROG       zg30
TD            16384
SOLVENT       DMSO
NS            203
DS            0
SWH           11160.714 Hz
FIDRES        0.681196 Hz
AQ            0.7340032 sec
RG            203
DW            44.800 usec
DE            6.50 usec
TE            303.2 K
D1            0 sec
TD0           1

===== CHANNEL f1 =====
NUC1           1H
P1            16.20 usec
PL1           0 dB
PL1W          23.41078186 W
SFO1          700.0053900 MHz

F2 - Processing parameters
SI            32768
SF            700.0000008 MHz
WDW           GM
SSB           0
LB            -3.00 Hz
GB            0.5
PC            1.00

```

Figure S76. ¹H NMR spectrum (700 MHz, DMSO) of **9**

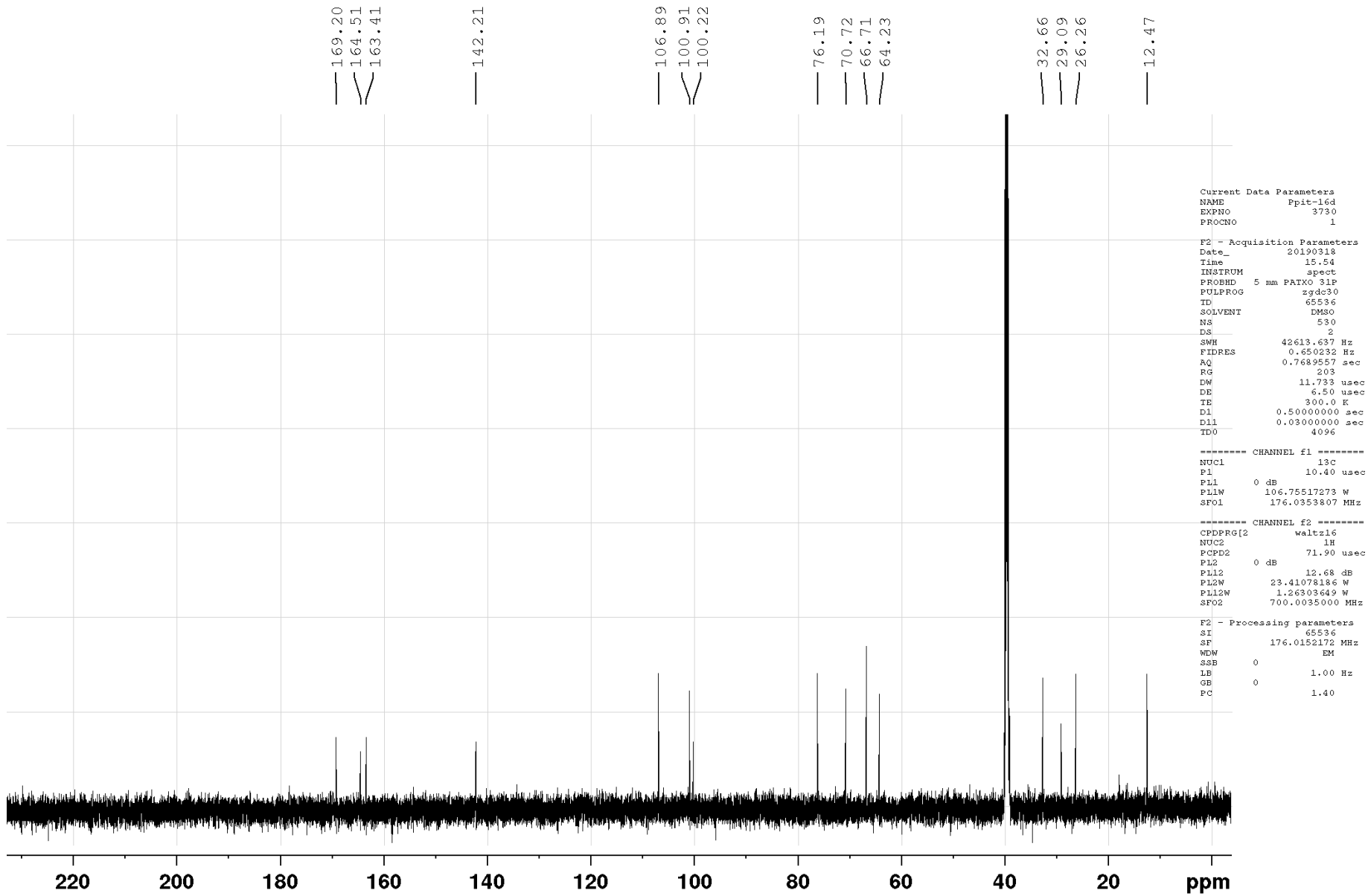


Figure S77. ¹³C NMR spectrum (176 MHz, DMSO) of **9**