

Supplementary Materials

Simultaneous Synthesis of Vitamins D₂, D₄, D₅, D₆, and D₇ from Commercially Available Phytosterol, β -Sitosterol, and Identification of Each Vitamin D by HSQC NMR

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Figure S1. Synthesis of vitamin D₃. S2

The experimental details on the synthesis of vitamin D₃ (**13**).

S2–S3

NMR spectra of vitamin D₂ (**9**) S4–S7

NMR spectra of vitamin D₃ (**13**) S8–S11

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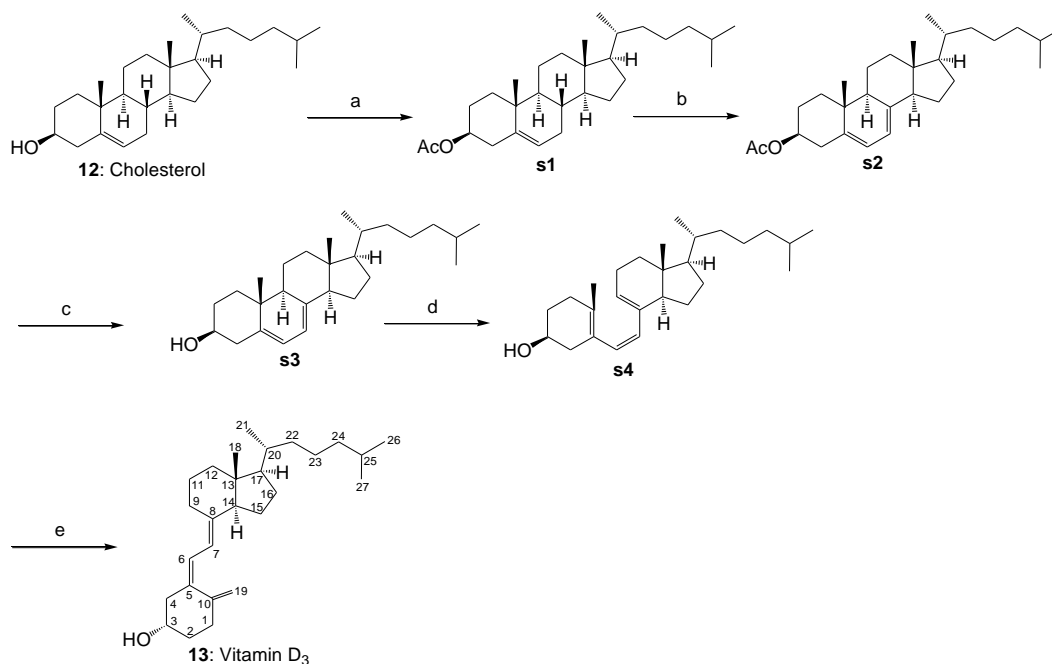


Figure S1. Synthesis of vitamin D₃. (a) Ac₂O, pyridine, 45 °C, 15 h, 98%. (b) 1) *N*-bromosuccinimide (NBS), cyclohexane, reflux, 1 h, 2) 1.0 M Bu₄NF/THF, room temperature, 12 h, 39%. (c) 28% NaOMe in MeOH, CH₂Cl₂/MeOH, room temp, 2 h, 62%. (d) 0.1% 3-*tert*-butyl-4-hydroxyanisole (BHA) in cyclohexane, 280 nm, 9.03 mW/cm², room temp, 1 h, 25%. (e) 0.1% BHA in cyclohexane, reflux, 1 h, 41%.

The experimental details on the synthesis of vitamin D₃ (13).

Cholesterol **12** (3.0 g, 7.76 mmol) was dissolved in pyridine (20 mL), acetic anhydride (5.0 mL, 52.9 mmol) was added, and the mixture was stirred at 45 °C for 15 h. After ice was added, the mixture was stirred for 1 h, extracted with chloroform, washed with 2N aq. HCl, concentrated, and then the product was crystallized with ethanol to obtain compound **s1** (3.25 g, 98%). Compound **s1** (3.0 g, 7.00 mmol) was dissolved in cyclohexane (80 mL) at 65 °C, *N*-bromosuccinimide (NBS; 1.868 g, 10.49 mmol) was added and then stirred under reflux conditions (90 °C) for 1 h. After cooling the reaction to room temperature, water (100 mL) was added and then stirred for 1 h. The mixture was extracted with *n*-hexane, washed with water, concentrated and dried in vacuo. To the resulting mixture, a 1.0 M solution of tetrabutylammonium fluoride in THF (10.5 mL) was added and stirred at room temperature for 12 h. The reaction product was extracted using *n*-hexane, washed with water, concentrated, and then the main product was separated with silica-gel column chromatography (ethyl acetate/*n*-hexane 1:10) to obtain compound **s2** (1.17 g, 39%). Compound **s2** (1.12 g, 2.62 mmol)

was dissolved in dichloromethane (8 mL) and methanol (30 mL), 28% NaOMe in MeOH was added until pH 10 and then stirred for 2 h. After the reaction mixture was concentrated, the main product was separated with silica-gel column chromatography (ethyl acetate/*n*-hexane 1:4) to obtain compound **s3** (0.625 g, 62%). Compound **s3** (20 mg, 0.052 mmol) was dissolved in 0.1% 3-*tert*-butyl-4-hydroxyanisole (BHA) in cyclohexane (2 mL) and transferred to a petri dish. While stirring the mixture in a petri dish covered with a polyvinylidene chloride food wrap, the mixture was irradiated with UV at 280 nm (9.03 mW/cm²) for 1 h. After the reaction mixture was concentrated, the main product was separated using silica-gel column chromatography (ethyl acetate/*n*-hexane 1:4) to obtain compound **s4** (5.02 mg, 25%). Compound **s4** (5.02 mg, 0.013 mmol) was dissolved in 0.1% BHA in cyclohexane (2 mL) and the mixture was stirred under reflux conditions (100 °C) for 1 h. After the reaction mixture was concentrated, the main product was separated using silica-gel column chromatography (ethyl acetate/*n*-hexane 1:4) to obtain the vitamin D₃ (**13**: 2.08 mg, 41%). Vitamin D₃ (**13**); ¹H-NMR (400 MHz, CDCl₃), δ = 0.54 (s, 3H, Me-18), 0.86 (d, 3H, *J* = 6.6 Hz, Me-26 or Me-27), 0.87 (d, 3H, *J* = 6.6 Hz, Me-26 or Me-27), 0.92 (d, 3H, *J* = 6.4 Hz, Me-21), 1.01 (m, 1H, H-22a), 1.08 – 1.18 (m, 3H, H-23a, H-24a, H-24b), 1.23 – 1.41 (m, 6H, H-12a, H-16a, H-17, H-20, H-22b, H-23b), 1.43 – 1.58 (m, 4H, H-11a, H-15a, H-15b, H-25), 1.63 – 1.73 (m, 3H, H-2a, H-9a, H-11b), 1.81 – 2.03 (m, 4H, H-2b, H-12b, H-14, H-16b), 2.18 (m, 1H, H-1a), 2.28 (dd, 1H, *J* = 12.9, 7.3 Hz, H-4a), 2.40 (m, 1H, H-1b), 2.57 (dd, 1H, *J* = 12.9, 3.2 Hz, H-4b), 2.82 (m, 1H, H-9b), 3.95 (m, 1H, H-3), 4.82 (broad d, 1H, H-19a), 5.05 (m, 1H, H-19b), 6.03 (d, 1H, *J* = 11.2 Hz, H-7), 6.23 (d, 1H, *J* = 11.2 Hz, H-6); ¹³C-NMR (100 MHz, CDCl₃), δ = 12.0 (C-18), 18.8 (C-21), 22.3 (C-15), 22.5 (C-26 or C-27), 22.8 (C-26 or C-27), 23.6 (C-11), 23.9 (C-23), 27.6 (C-16), 28.0 (C-25), 29.0 (C-9), 31.9 (C-1), 35.2 (C-2), 36.1 (C-20 and C-22), 39.5 (C-24), 40.5 (C-12), 45.86 (C-4 or C-13), 45.93 (C-4 or C-13), 56.4 (C-14), 56.6 (C-17), 69.2 (C-3), 112.4 (C-19), 117.5 (C-7), 122.5 (C-6), 135.0 (C-5), 142.4 (C-8), 145.1 (C-10).



```

Current Data Parameters
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PROCNO       1

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Date_         20180227
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PULPROG      zg30
TD           65536
SOLVENT      CDCl3
DS           1
NS           2
SWH          8278.146 Hz
FIDRES      0.126314 Hz
AQ          3.9583745 sec
RG          32
DW          60.400 usec
DE          296.9
TE          29.9
D1          1.00000000 sec
TD0         1

===== CHANNEL f1 =====
NUC1         1H
P1          12.00 usec
PL1         0 dB
PL12        21.29127693 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
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SF          400.1300093 MHz
WDW         EM
SSB         0 Hz
LB          0
GB          0
PC          1.00
  
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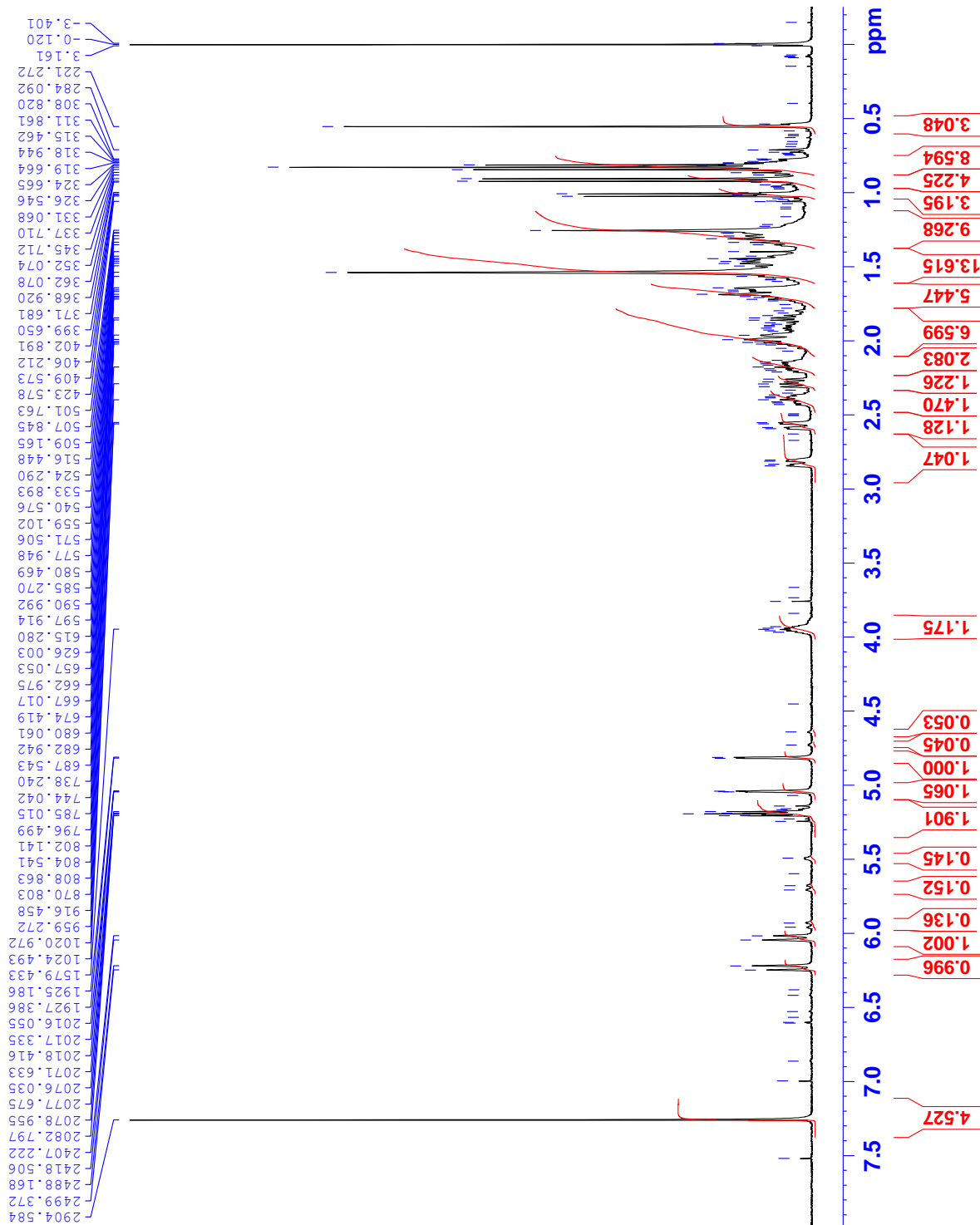


Figure S2. ¹H NMR spectrum of vitamin D₂ (9).



Current Data Parameters
 NAME: sK65-85-4
 EXPNO: 21
 PROCNO: 1

?2 - Acquisition Parameters
 Date_ 20180227
 Time 1:58

INSTRUM spect
 PROBHD 5 mm CPBBO BB-
 PULPROG cosygpcf
 ZUGS 2048
 SOLVENT CDCl3
 NS 8
 DS 8
 SWH 5341.880 Hz
 FIDRES 2.608340 Hz
 AQ 0.1916928 sec
 RG 512
 JW 93.600 usec
 FE 6.50 usec
 DE 300.0 K
 TO 0.00000300 sec
 TI 1.48689198 sec
 S13 0.00000400 sec
 T16 0.00020000 sec
 LNO 0.00018720 sec

CHANNEL f1
 NUCL 1H
 P0 12.00 usec
 P1 12.00 usec
 PL1 -3.60 dB
 PL2W 21.29127693 W
 P0L 400.1324057 MHz

GRADIENT CHANNEL
 SPWAM[1] SINE.100
 PZ1 10.00 %
 P16 1000.00 usec

?1 - Acquisition parameters
 CH 128
 F0L 400.1324 MHz
 FIDRES 41.733540 Hz
 W 13.350 PPM
 FMODE QF

?2 - Processing parameters
 SI 1024
 SF 400.1300061 MHz
 SINE
 VDW 0
 SSB 0 Hz
 GB 0 Hz
 GC 1.40

?1 - Processing parameters
 SI 1024
 QF
 SF 400.1300052 MHz
 SINE
 VDW 0 Hz
 SSB 0 Hz

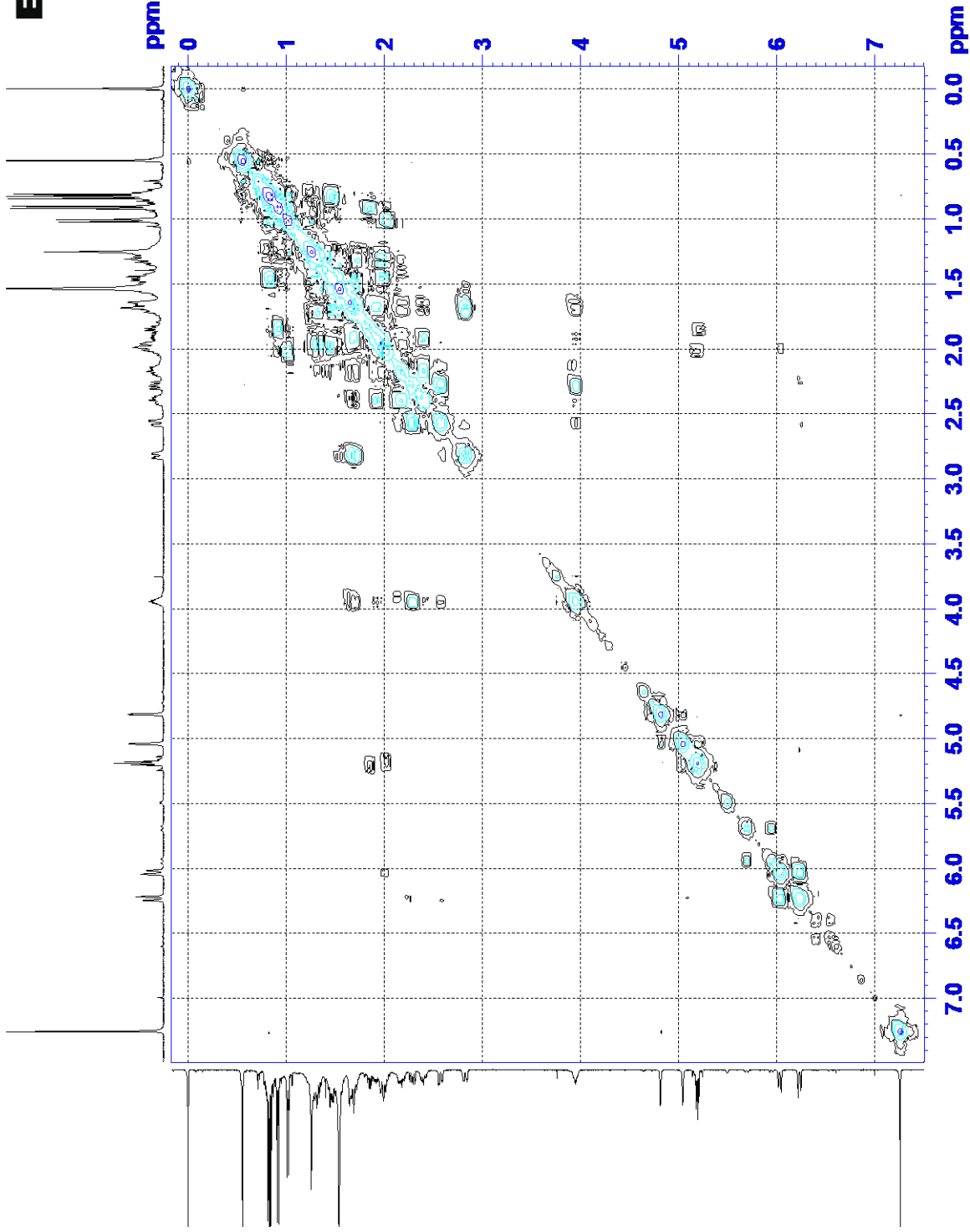


Figure S3. ¹H¹H COSY NMR spectrum of vitamin D₂(9).



```

Current Data Parameters
NAME      sk65-85-4
EXPNO    22
PROCNO   1

F2 - Acquisition Parameters
Date_    20180227
Time     3.04
INSTRUM spect
PROBHD   5 mm CPBEO BB-
PULPROG zgpg30
TD       65536
SOLVENT  CDCl3
NS       1024
DS       4
SWH      23980.814 Hz
FIDRES   0.365918 Hz
AQ       1.3664256 sec
RG       4597.6
RW       20.850 usec
RE       16.00 usec
IE       300.0 K
C1       2.00000000 sec
C11      0.03000000 sec
TD0      1

===== CHANNEL f1 =====
NUC1     13C
P1       10.00 usec
PL1      -4.30 dB
PL1W     89.24295807 W
SFO1     100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG12 waltz16
NUC2     1H
PCPD2    80.00 usec
PL2      -3.80 dB
PL12     12.00 dB
PL13     12.00 dB
PL2W     22.29470444 W
PL12W    0.58641046 W
PL13W    0.58641046 W
SFO2     400.1316005 MHz

F2 - Processing parameters
SI       32768
SF       100.6127690 MHz
AQDW     EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40
  
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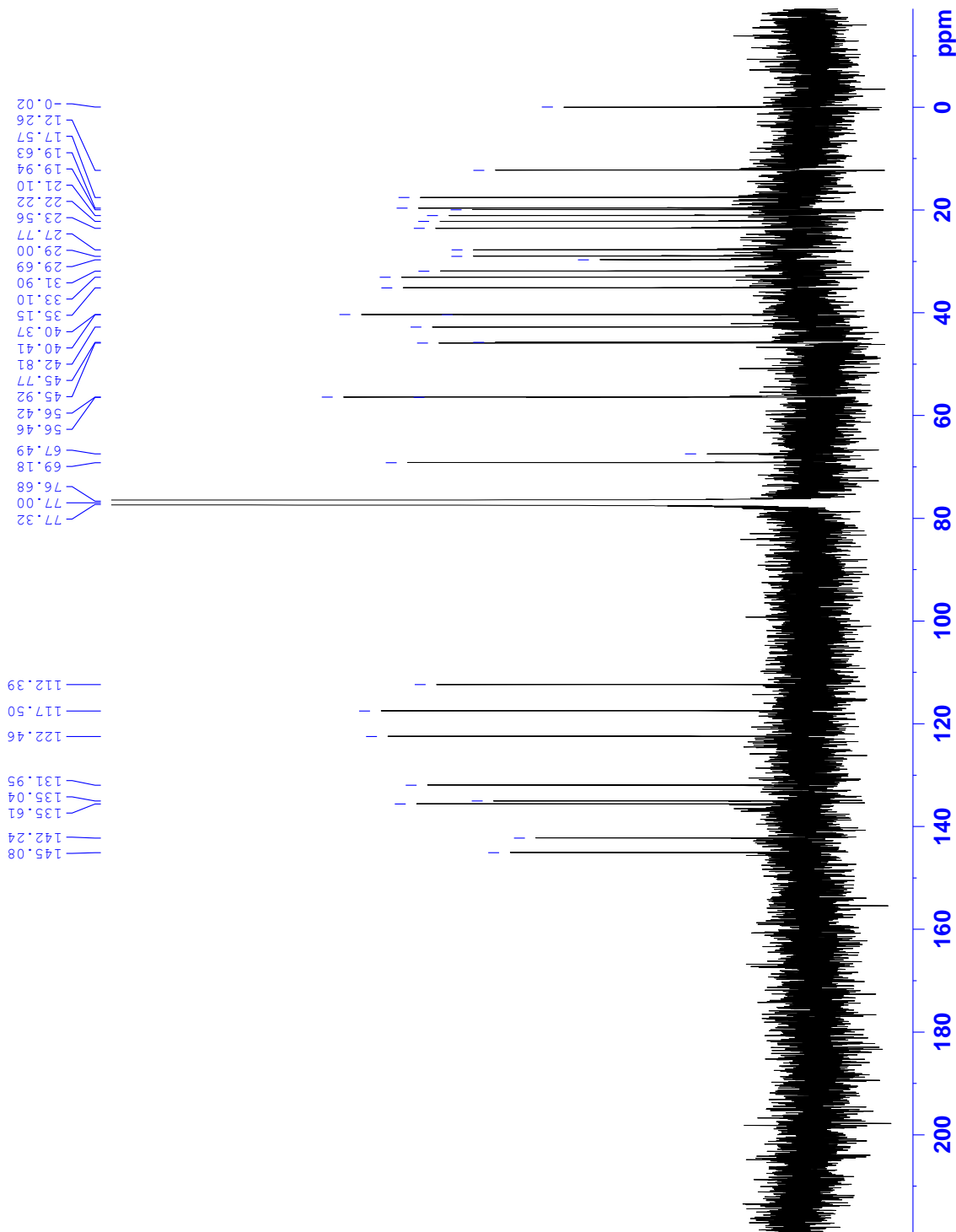


Figure S4. ¹³C NMR spectrum of vitamin D₂ (9).



Current Data Parameters
 NAME 3165-95-4
 EXPNO 24
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20180227
 Time 3:23
 INSTRUM spect
 PROBRD 5 mm CPBBO BB-
 PULPROG zgpg30
 TD 4096
 SOLVENT CDCl3
 NS 8
 DS 16
 SWH 5341.800 Hz
 FIDRES 0.1833856 Hz
 AQ 4.6341
 RG 93.600 usec
 DE 6.50 usec
 TE 300.0 K
 CREST13 8.0000000
 DD 0.0000300 sec
 DA 0.0625000 sec
 DI6 0.0002000 sec
 INO 0.00002335 sec

==== CHANNEL F1 =====

NUC1 1H
 P1 12.00 usec
 PL1 2.00 dB
 FL1 -3.50 dB
 ELW 21.29127693 W
 SF01 400.1324057 MHz

==== CHANNEL F2 =====

NUC2 13C
 P2 10.00 usec
 PL2 0.00 dB
 ELW 89.24295807 W
 SF02 100.6238138 MHz

==== GRADIENT CHANNEL =====

GENAM(1) SINE.100
 GENAM(2) SINE.100
 GENAM(3) SINE.100
 GR21 30.00 %
 GR22 30.00 %
 GR23 40.10 %
 PL6 1000.00 usec

F1 - Acquisition parameters

TD 128
 SFO1 400.1324057 MHz
 SF02 100.6238138 MHz
 SW 222.085 Ppm
 PRMODE OP

F2 - Processing parameters

SI 1024
 SF 400.1300038 MHz
 NWDW 0
 NGB 0 Hz
 GB 0
 PC 1.40

F1 - Processing parameters

SI 1024
 SF 100.6178949 MHz
 NWDW 0
 NGB 0 Hz
 GB 0

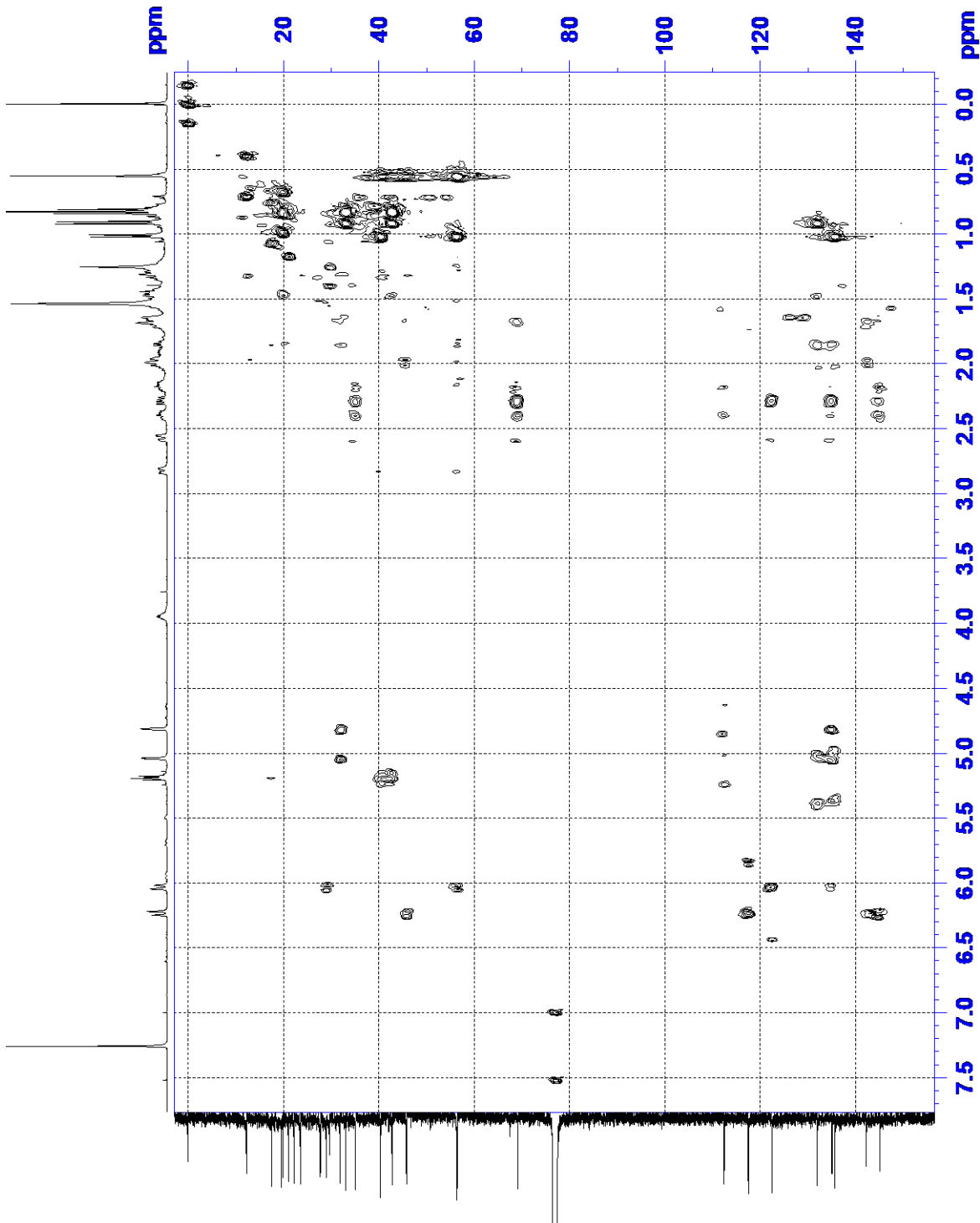


Figure S5. HMBC NMR spectrum of vitamin D₂ (9).



```

Current Data Parameters
NAME          ssk65-56
EXPNO         10
PROCNO        1
F2 - Acquisition Parameters
Date_         20110919
Time          19:09
INSTRUM       spect
PROBHD        5 mm CPBBO BB-
PULPROG       zg30
ID            65536
SOLVENT       CDCl3
NS            16
DS            1
SWH           8278.146 Hz
FIDRES       0.156314 Hz
AQ           3.9583745 sec
RG           25.4
DW           60.400 usec
DE           6.50 usec
TE           299.9 K
TD           1.000000001 sec
===== CHANNEL f1 =====
NUC1          1H
P1            12.00 usec
PL1          -3.60 dB
ELW          21.29127653 W
SFO1         400.1324710 MHz
F2 - Processing parameters
SI           32768
SF           400.1300091 MHz
WDW          EM
SSB          0
LB           0 Hz
GB           0
PC           1.00
  
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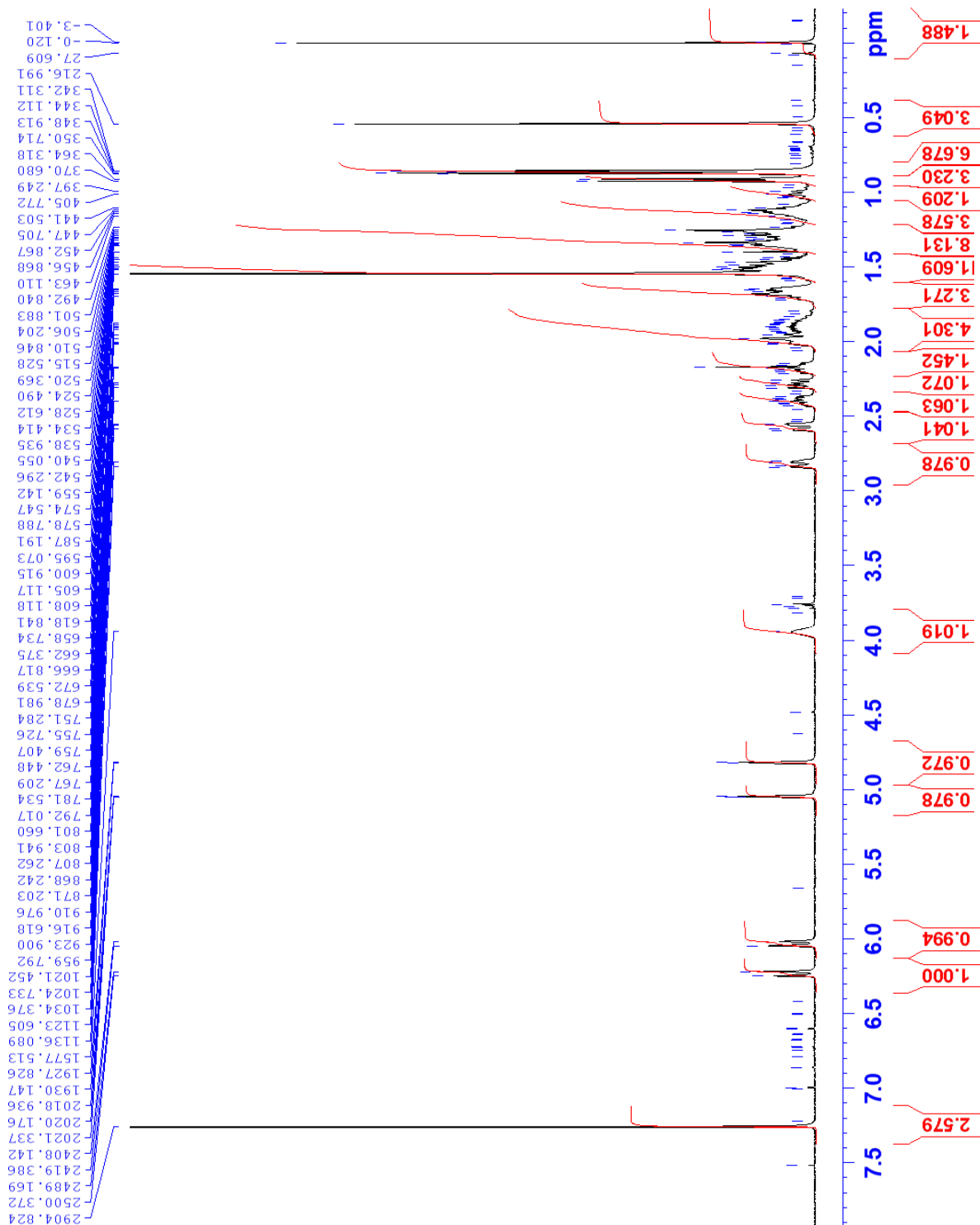


Figure S6. ¹H NMR spectrum of vitamin D₃ (13).


```

Current Data Parameters
NAME          SK65-56
EXPNO         11
PROCNO        1

P2 - Acquisition Parameters
Date_         20171101
Time          15:31
INSTRUM       spect
PROBHD        5 mm CPBBO BB-
PULPROG       cmgprf
PD            2048
SOLVENT       CDCl3
NS            1
DS            8
SWH           5341.880 Hz
FIDRES        2.608340 Hz
AQ            0.1916928 sec
RG            362
DM            93.600 usec
DE            6.50 usec
FE            300.0 K
DD            0.0000300 sec
D1            1.4685198 sec
D13           0.0000400 sec
D16           0.0026000 sec
RG0           0.00016720 sec

===== CHANNEL f1 =====
NUC1           1H
P0            12.00 usec
P1            12.00 usec
PL1           -3.60 dB
PL1W          21.29127693 W
SFO1           400.1324057 MHz

===== GRADIENT CHANNEL =====
SFO1M1         SINE.100
SFO1           10.00 %
P16           1000.00 usec

P1 - Acquisition parameters
PD            128
SFO1           400.1324 MHz
FIDRES        41.73350 Hz
PACMODE       13.350 Ppm
PACMODE       QF

P2 - Processing parameters
SI            1024
SF            400.1300000 MHz
WDW           SINE
SSB           0
GB            0
EB            0
PC            1.40

F1 - Processing parameters
SI            1024
AQ            0.1916928 sec
SF            400.1300000 MHz
WDW           SINE
SSB           0
GB            0
EB            0
PC            1.40

```

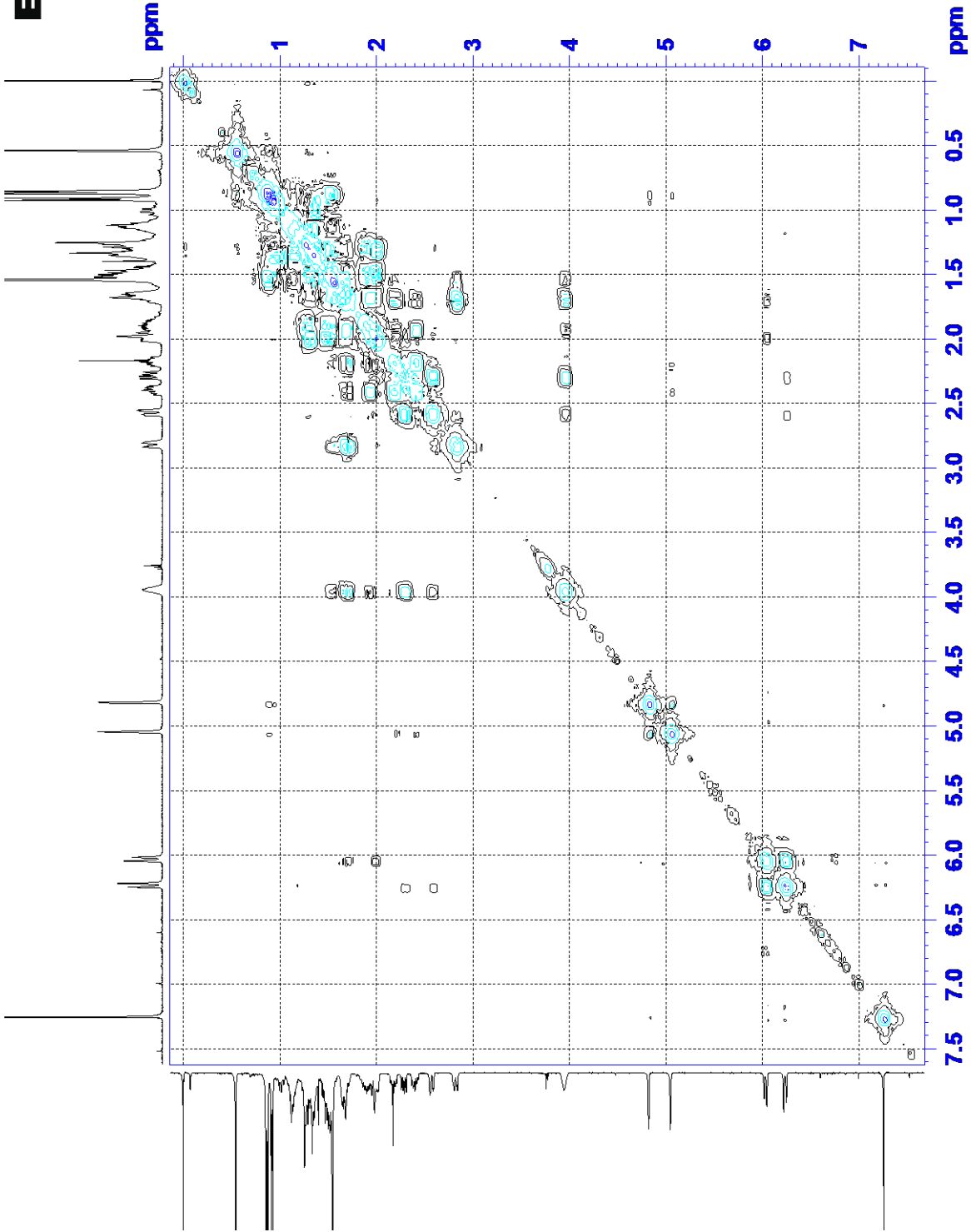


Figure S7. ^1H COSY NMR spectrum of vitamin D₃ (13).

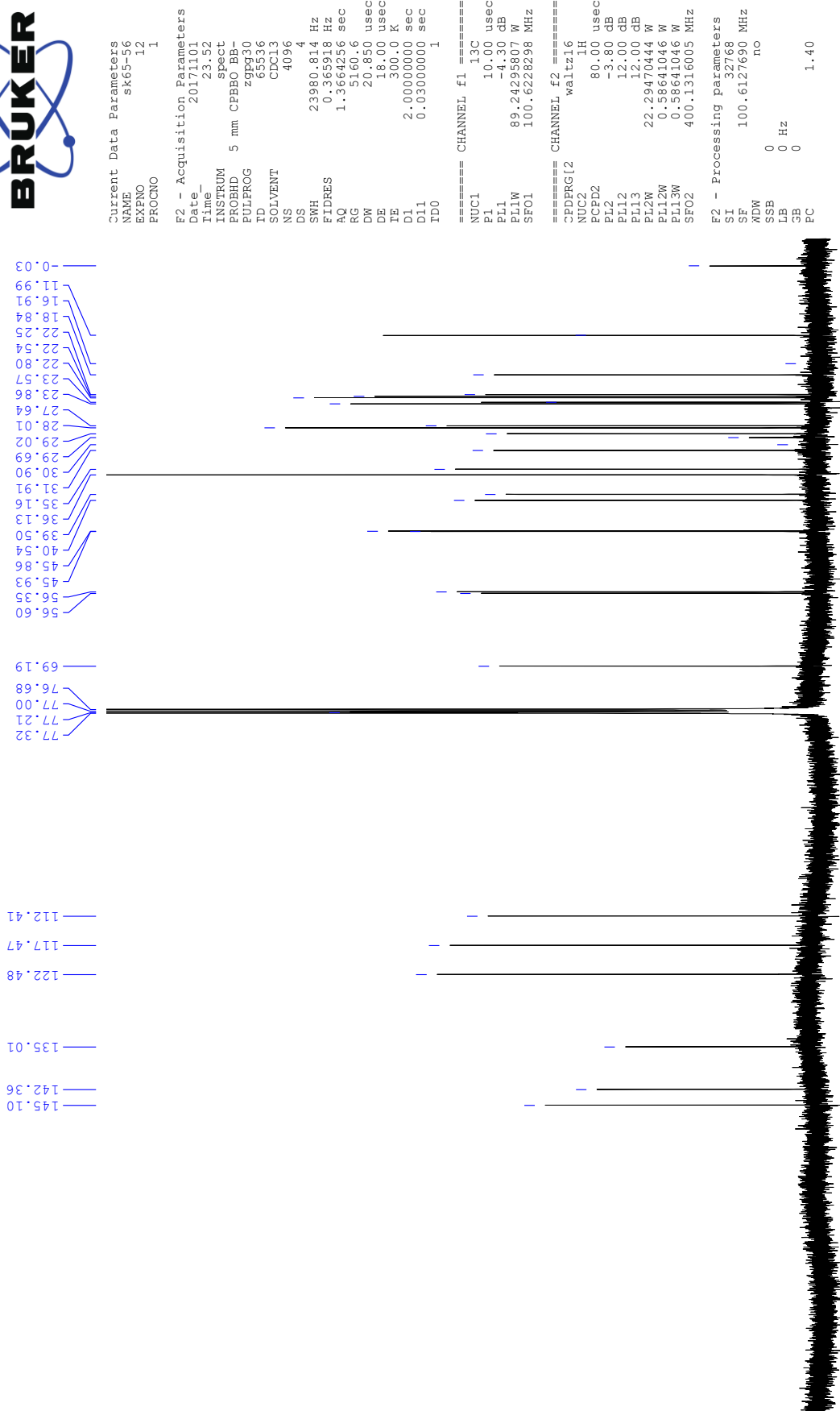


Figure S8. ¹³C NMR spectrum of vitamin D₃ (13).



```

Current Data Parameters
NAME          sk65-56
EXPNO         14
PROCNO        1
=====
F2 - Acquisition Parameters
Date_         20171102
Time          0.53
=====
INSTRUM       spect
PROBHD        5 mm CPBBO BB-
PULPROG       hmcgpcpqr4f
PC            1016
SOLVENT       CDCl3
NS            32
DS            16
SWH           5341.880 Hz
AQ            1.304170 Hz
RG            0.3833956 sec
RG2           96441
RG3           5650
RG4           5650
TE            300.0 K
=====
CST13         8.0000000
D0            0.00000300 sec
D1            1.50000000 sec
D6            0.06230000 sec
D16           0.00020000 sec
IN0           0.0006233 sec
=====
===== CHANNEL F1 =====
NUC1          1H
P1            12.00 usec
P2            24.00 usec
PL1           3.60 dB
PL2           21.2937657 dB
PL16          400.1344057 MHz
=====
===== CHANNEL F2 =====
NUC2          13C
P3            10.00 usec
P4            4.30 dB
PL3           89.2235907 MHz
PL4           100.6226130 MHz
=====
===== GRADIENT CHANNEL =====
GPRAM[1]     SINE.100
GPRAM[2]     SINE.100
GPRAM[3]     SINE.100
GRZ1         50.00 %
GRZ2         40.00 %
GRZ3         40.00 %
PL6          1000.00 usec
=====
F1 - Acquisition parameters
TD            128
SF01          100.6228 MHz
FIDRES       174.592422 Hz
SFO1          222.093 ppm
=====
F2 - Processing parameters
SI            1024
SF            400.1300045 MHz
WDW           0
SSB           0 Hz
GB            0
PC            1.40
=====
F1 - Processing parameters
SI            1024
MC2           0F
SF            100.6127995 MHz
WDW           0
SSB           0 Hz
GB            0

```

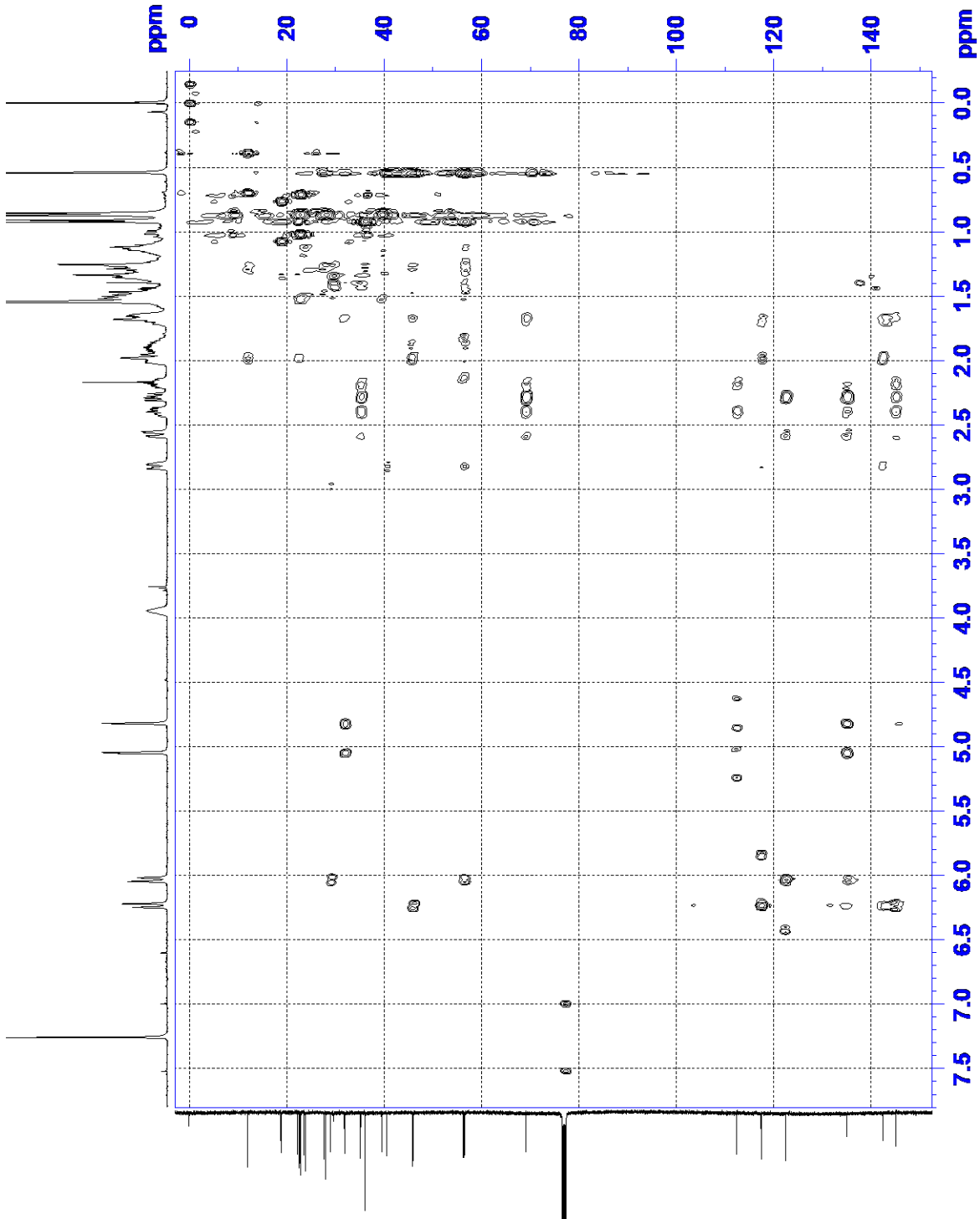


Figure S9. HMBC NMR spectrum of vitamin D₃ (13).



```

Current Data Parameters
NAME      sk65-86-3
EXPNO    10
PROCNO   1

F2 - Acquisition Parameters
Date_    20180308
Time_    13.35
INSTRUM  spect
PROBHD   5 mm CPBBO BB-
PULPROG  zg30
TD        65536
SOLVENT  CDCl3
DS        2
SWH       8278.146 Hz
FIDRES    0.126314 Hz
AQ        3.9583745 sec
RG        32
DM        60.400 usec
DE        299.9 usec
TE        299.2 K
D1        1.00000000 sec
TDO       1

===== CHANNEL f1 =====
NUC1      1H
P1        12.00 usec
PL        0.00 dB
SFO1      400.1324710 MHz
SF01      400.1324710 MHz

F2 - Processing parameters
SI        32768
SF        400.1300092 MHz
WDW       EM
SSB       0 Hz
GB        0
PC        1.00
  
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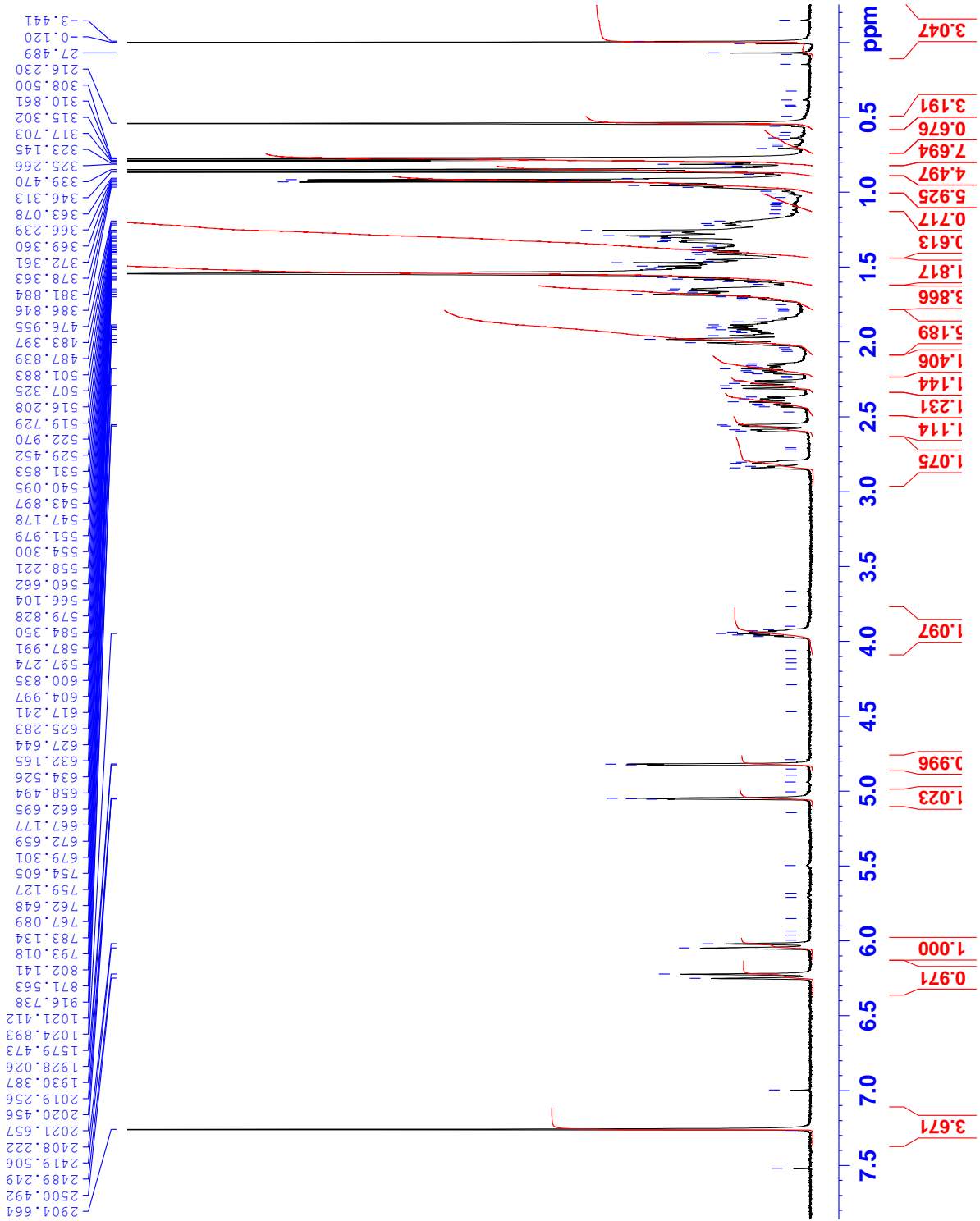


Figure S10. ¹H NMR spectrum of vitamin D₄(10).



```

Parent Data Parameters
NAME          SK63-06-3
EXPNO        11
PROCNO       1
=====
F2 - Acquisition Parameters
Date_         20180308
Time_        13.37
INSTRUM      spect
PROBHD       5 mm CPBBO BB-
PULPROG      convpqr4f
TD           2048
SOLVENT      CDCl3
NS           1
DS           1
SWH          5341.880 Hz
FIDRES      2.608340 Hz
AQ          0.1316528 sec
RG          436.1
WDW          93.600 usec
SSB          0.000000
GB          300.0 K
PC          0.00000000 sec
RL           1.48689198 sec
SI          313
SF           0.00000400 sec
D1          0.00020000 sec
D16         0.00018720 sec
DNO         0.00018720 sec
===== CHANNEL f1 =====
NUC1         1H
P0           12.00 usec
P1           12.00 usec
PL1         -3.60 dB
PL1W        21.29127693 W
PC1         400.1324057 MHz
===== GRADIENT CHANNEL =====
INVARM[1]   SINE,10.00 %
PC21        10.00
PC16        1000.00 usec
=====
F1 - Acquisition parameters
TD          128
FPO1       400.1324 MHz
FIDRES     41.733440 Hz
SW         13.350 ppm
PACODE     QF
=====
F2 - Processing parameters
SI          1024
SF         400.1300000 MHz
WDW        0 Hz
SSB        0 Hz
GB         0
PC         1.40
=====
F1 - Processing parameters
SI          1024
PC2        QF
SF         400.1300000 MHz
WDW        0 Hz
SSB        0 Hz
GB         0

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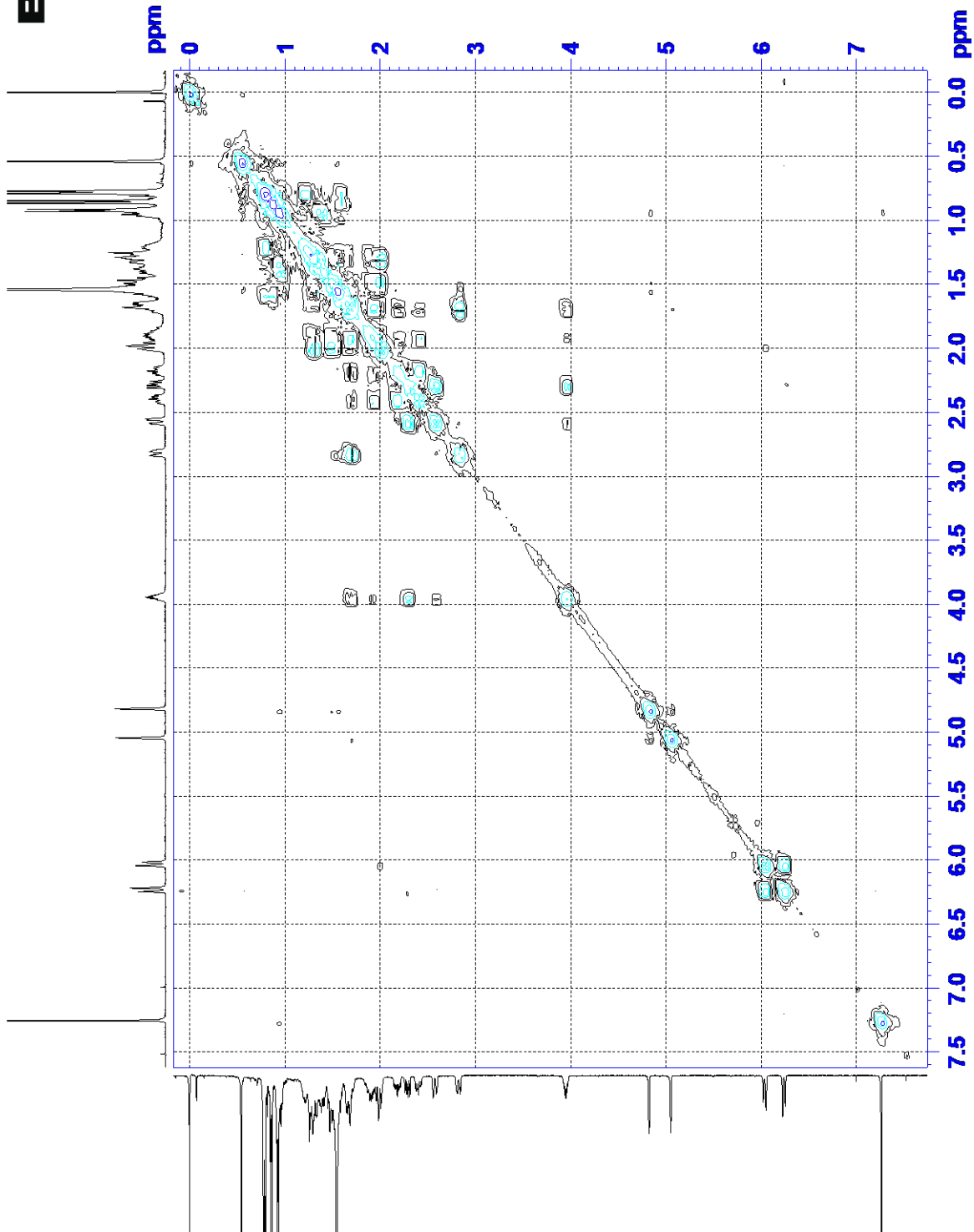


Figure S11. ¹H COSY NMR spectrum of vitamin D₄ (10).



```

Current Data Parameters
NAME      sk65-86-3
EXPNO    12
PROCNO   1

F2 - Acquisition Parameters
Date_    20180308
Time     14.42
INSTRUM spect
PROBHD   5 mm CPBBO BB-
PULPROG zgpg30
TD       65536
SOLVENT  CDCl3
NS       1024
DS       4
SMH      23980.814 Hz
FIDRES   0.365918 Hz
AQ       1.566256 sec
RG       5160.6
DW       20.850 usec
DE       18.00 usec
TE       300.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0      1

===== CHANNEL f1 =====
NUC1     13C
P1       10.00 usec
PL1      -4.30 dB
PL1W    89.24295807 W
SFO1    100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2     1H
PCPD2   80.00 usec
PL2      -3.80 dB
PL12    12.00 dB
PL13    12.00 dB
PL2W    22.29470444 W
PL12W   0.58641046 W
PL13W   0.58641046 W
SFO2    400.1316005 MHz

F2 - Processing parameters
SI       32768
SF       100.6127690 MHz
AQ       no
SSB      0
LB       0 Hz
GB       0
PC       1.40
  
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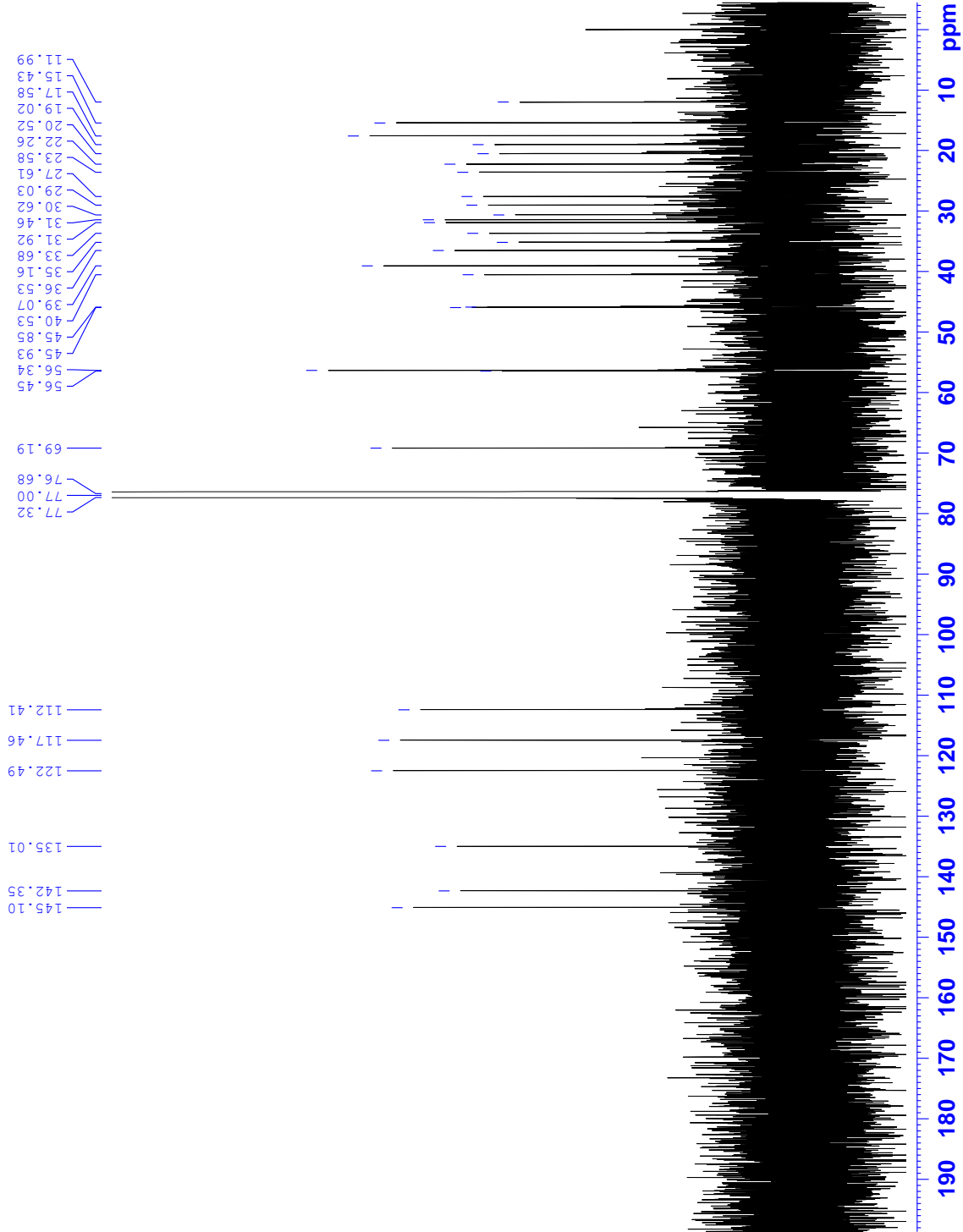


Figure S12. ¹³C NMR spectrum of vitamin D₄ (10).



Current Data Parameters
 NAME 3465-86-3
 EXPNO 14
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20180309
 Time 13:02
 PROBHD 5 mm CPBBO BB-
 PULPROG zgpg30
 TD 4096
 SOLVENT CDCl3
 NS 8
 DS 16
 SWH 5341.090 Hz
 FWHZ 304.490 Hz
 AQ 0.3833656 sec
 RG 46341
 INW 93.600 usec
 DE 6.50 usec
 TE 299.9 K
 CEST13 8.0000000
 D0 0.0000000 sec
 D1 0.5000000 sec
 D5 0.06250000 sec
 D16 0.00020000 sec
 INU 0.00002235 sec

==== CHANNEL F1 =====

NUC1 1H
 P1 12.00 usec
 PL1 2.00 dB
 PL2 -3.60 dB
 PL1W 21.29127693 W
 SFO1 400.1324057 MHz

==== CHANNEL F2 =====

NUC2 13C
 P2 10.00 usec
 PL2 0.00 dB
 PL2W 89.24295802 W
 SFO2 100.6228138 MHz

==== GRADIENT CHANNEL =====

GENAM[1] SINE.100
 GENAM[2] SINE.100
 GENAM[3] SINE.100
 GR21 50.00 %
 GR22 30.00 %
 GR23 40.10 %
 PL6 1000.00 usec

F1 - Acquisition parameters

TD 100.228
 SFO1 400.1324057 MHz
 FWHZ 304.490 Hz
 SW 222.095 Ppm
 EQMODE OP

F2 - Processing parameters

SI 1024
 SF 400.1300062 MHz
 SINE
 NS 0
 DS 0
 GB 0
 PC 1.40

F1 - Processing parameters

SI 1024
 SF 100.6127487 MHz
 SINE
 NS 0
 DS 0
 GB 0

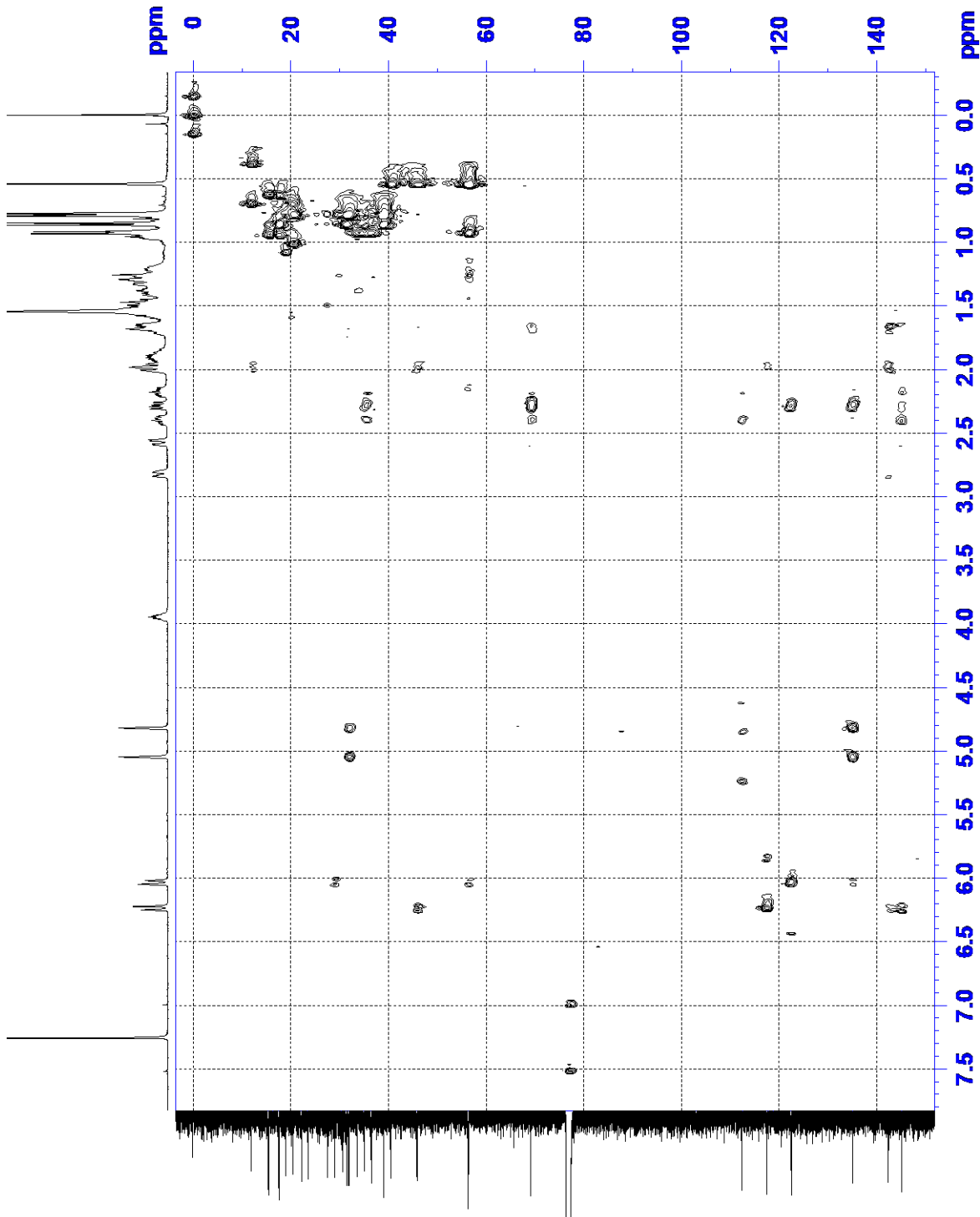


Figure S13. HMBC NMR spectrum of vitamin D₄ (10).



Current Data Parameters
NAME SK65-85-6
PROCNO 1
PROCNO 1
F2 - Acquisition Parameters
Date 20180226
Time 23.50
INSTRUM spect
PROBHD 5 mm CPBBO BB-
TDLPFG 6536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9983745 sec
RG 640
WDW 60.400 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TDO 1
===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -3.60 dB
PLW 21.29127693 W
SF01 400.1324710 MHz
F2 - Processing Parameters
SI 32788
WDW EM
SSB 0 Hz
LB 0
GB 0
PC 1.00

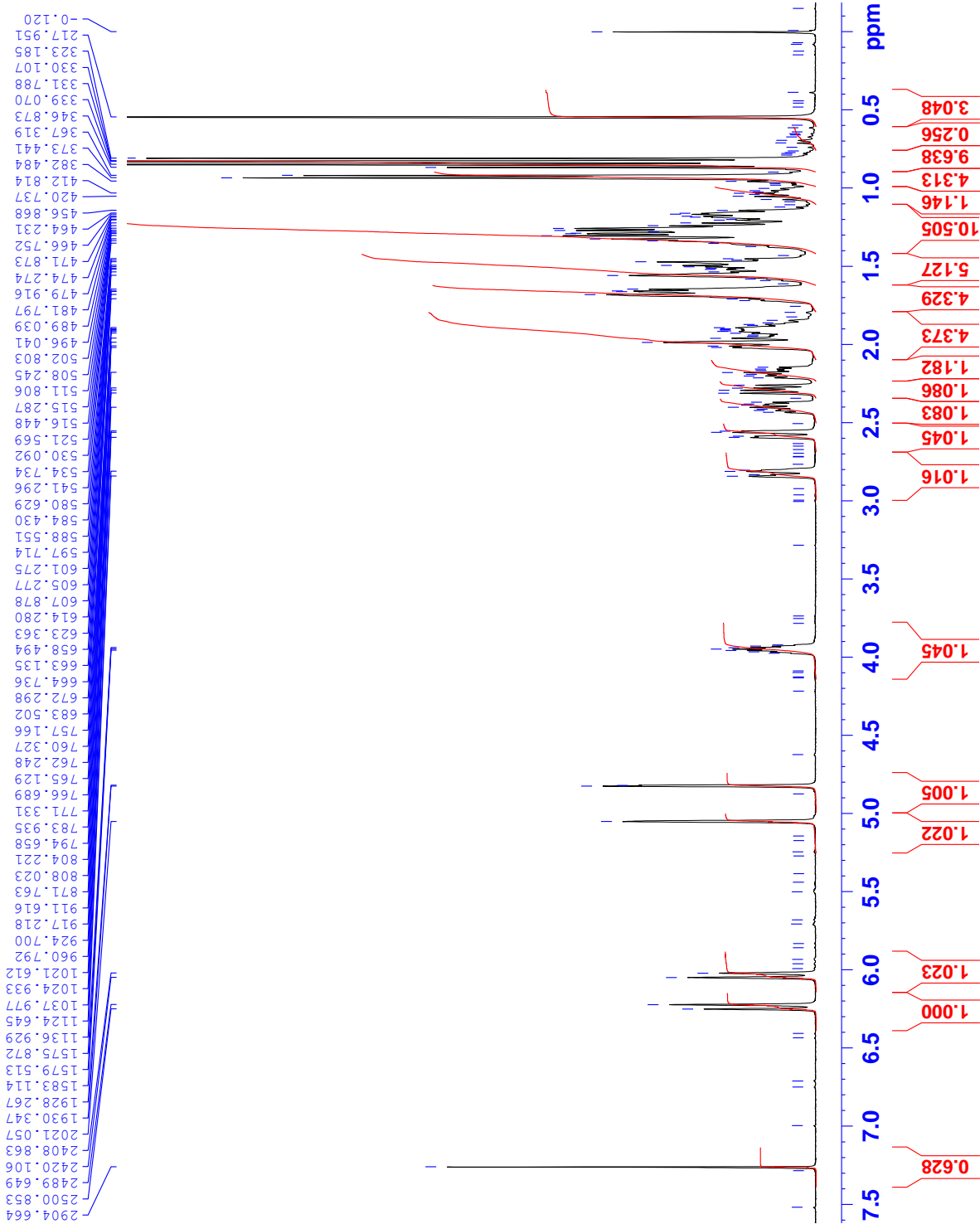


Figure S14. ¹H NMR spectrum of vitamin D₅ (6).



Current Data Parameters
 NAME ak65-85-6
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20180226
 Time 23.52

INSTRUM spect
 PROBHD 5 mm CPBBO BB
 PULPROG zgpg30
 FIDRES 0.1916928 sec
 AQ 0.1916928 sec
 RG 114
 DW 93.600 usec
 DE 6.50 usec
 FE 300.0 K
 DD 0.00000300 sec
 D1 1.4868198 sec
 D13 0.0000400 sec
 D16 0.0002000 sec
 LMO 0.00016720 sec

CHANNEL f1
 NUCL1 1H
 P0 12.00 usec
 P1 12.00 usec
 PL1 -3.60 dB
 PL1W 21.29127693 W
 SF01 400.1324057 MHz

GRADIENT CHANNEL
 SPNAM11 SINE.100
 SP21 10.00 %
 P16 1000.00 usec

F1 - Acquisition parameters
 FID 128
 SF01 400.1324 MHz
 FIDRES 41.733940 Hz
 SW 13.350 PPM
 FREQ02 QF

F2 - Processing parameters
 SI 1024
 SF 400.1300034 MHz
 SINE SINE
 NSB 0
 LB 0 Hz
 SB 0
 PC 1.40

F1 - Processing parameters
 SI 1024
 SC2 QF
 SF 400.1300026 MHz
 SINE SINE
 NSB 0 Hz
 LB 0
 SB 0

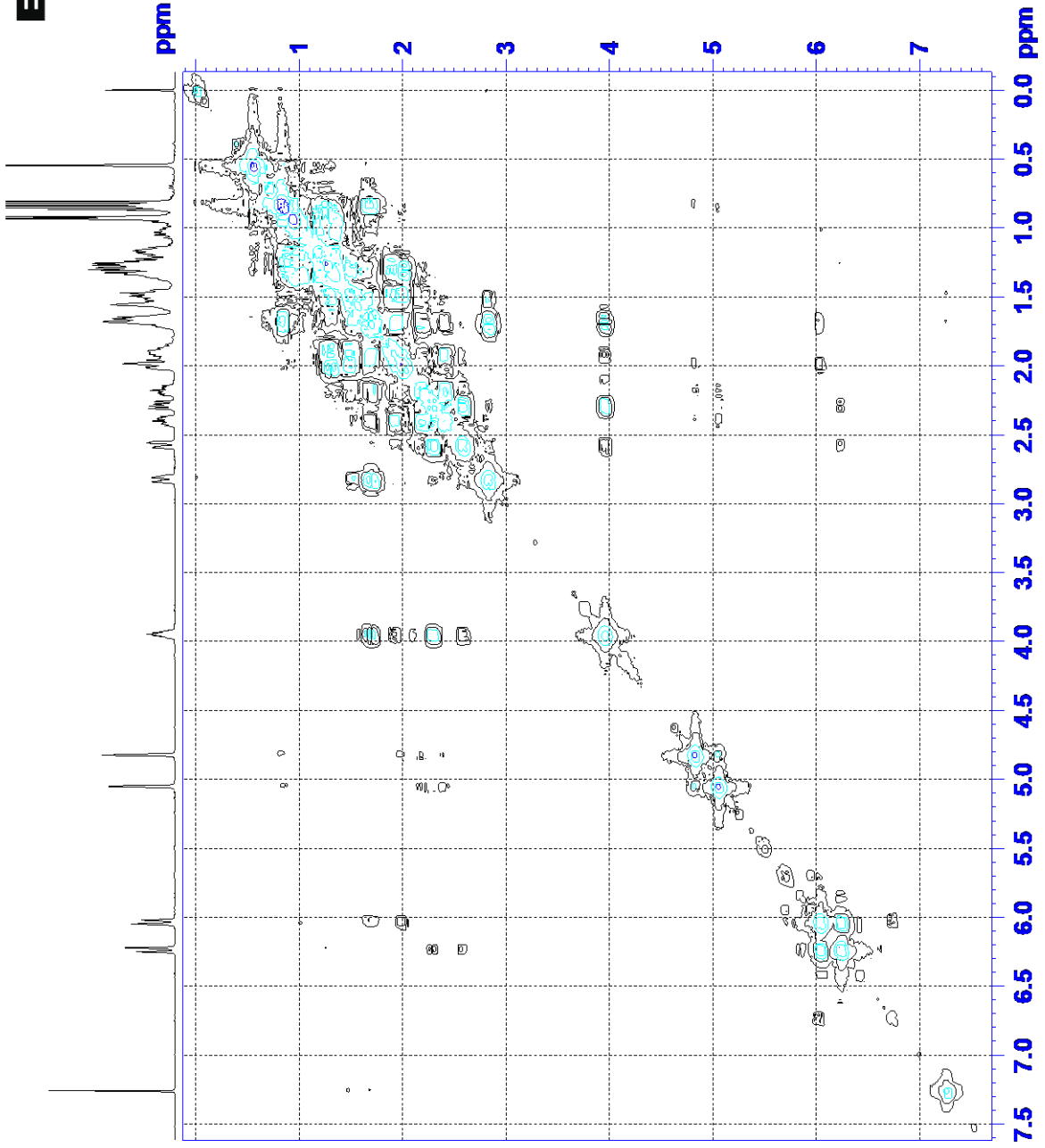


Figure S15. ¹H-¹H COSY NMR spectrum of vitamin D₅ (6).



Current Data Parameters
NAME sk65-85-6
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180227
Time_ 0.57
INSTRUM spect
PROBHD 5 mm CPBBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SFOH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.5668256 sec
RG 5792.6
DW 20.850 usec
DE 18.00 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

=====
CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 -4.30 dB
PL1W 89.24295807 W
SFO1 100.6228298 MHz

=====
CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -3.80 dB
PL12 12.00 dB
PL13 12.00 dB
PL2W 22.2947044 W
PL12W 0.58641046 W
PL13W 0.58641046 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
ADW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

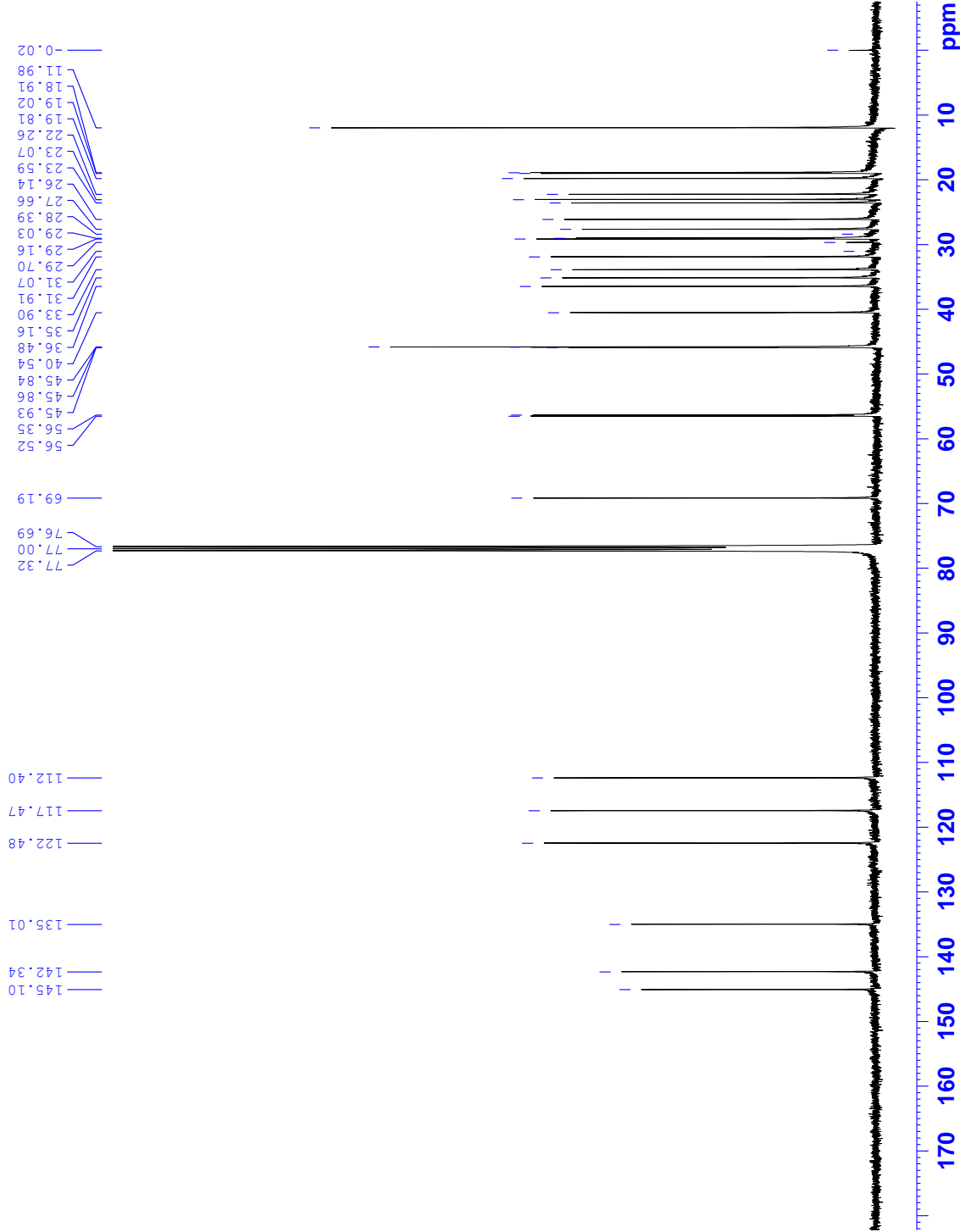


Figure S16. ¹³C NMR spectrum of vitamin D₅ (6).



```

Current Data Parameters
NAME          sk65-85-6
EXPNO         14
PROCNO        1
F2 - Acquisition Parameters
Date_         20180227
Time          1.16
INSTRUM       spect
PROBHD        5 mm CPBBO BB-
PULPROG       hmcpspqc4f
SOLVENT       DMS
SOLVENT       CDCl3
NS            8
DS            16
SWH           5341.880 Hz
FIDRES        1.304170 Hz
AQ            0.381356 sec
RG            4624
DE            93.600 usec
TE            300.0 K
CNST13        8.0000000
D0            0.0000300 sec
D1            1.5000000 sec
D6            0.0625000 sec
D16           0.0000000 sec
D18           0.0002235 sec
===== CHANNEL f1 =====
NUC1           1H
P1            12.00 usec
P2            24.00 usec
PL1           3.60 dB
PL2           3.60 dB
SFO1          400.1324057 MHz
===== CHANNEL f2 =====
NUC2           13C
P3            10.00 usec
PL3           -4.30 dB
PL12         99.2425507 W
SFO2          100.626150 MHz
===== GRADIENT CHANNEL =====
GENDAM[1]     SINE.100
GENDAM[2]     SINE.100
GENDAM[3]     SINE.100
GRZ1          50.00 %
GRZ2          40.10 %
GRZ3          40.10 %
P16           1000.00 usec
F1 - Acquisition parameters
TD            128
SFO1          100.6228 MHz
FIDRES        174.552422 Hz
AQ            222.000000 sec
PAMODE        CP
F2 - Processing parameters
SI            1024
SF            400.1300037 MHz
WDW           SINE
SSB           0 Hz
GB            0
PC            1.40
F1 - Processing parameters
SI            1024
MC2           CP
SFO2          100.617692 MHz
WDW           SINE
SSB           0
LB            0 Hz
GB            0
  
```

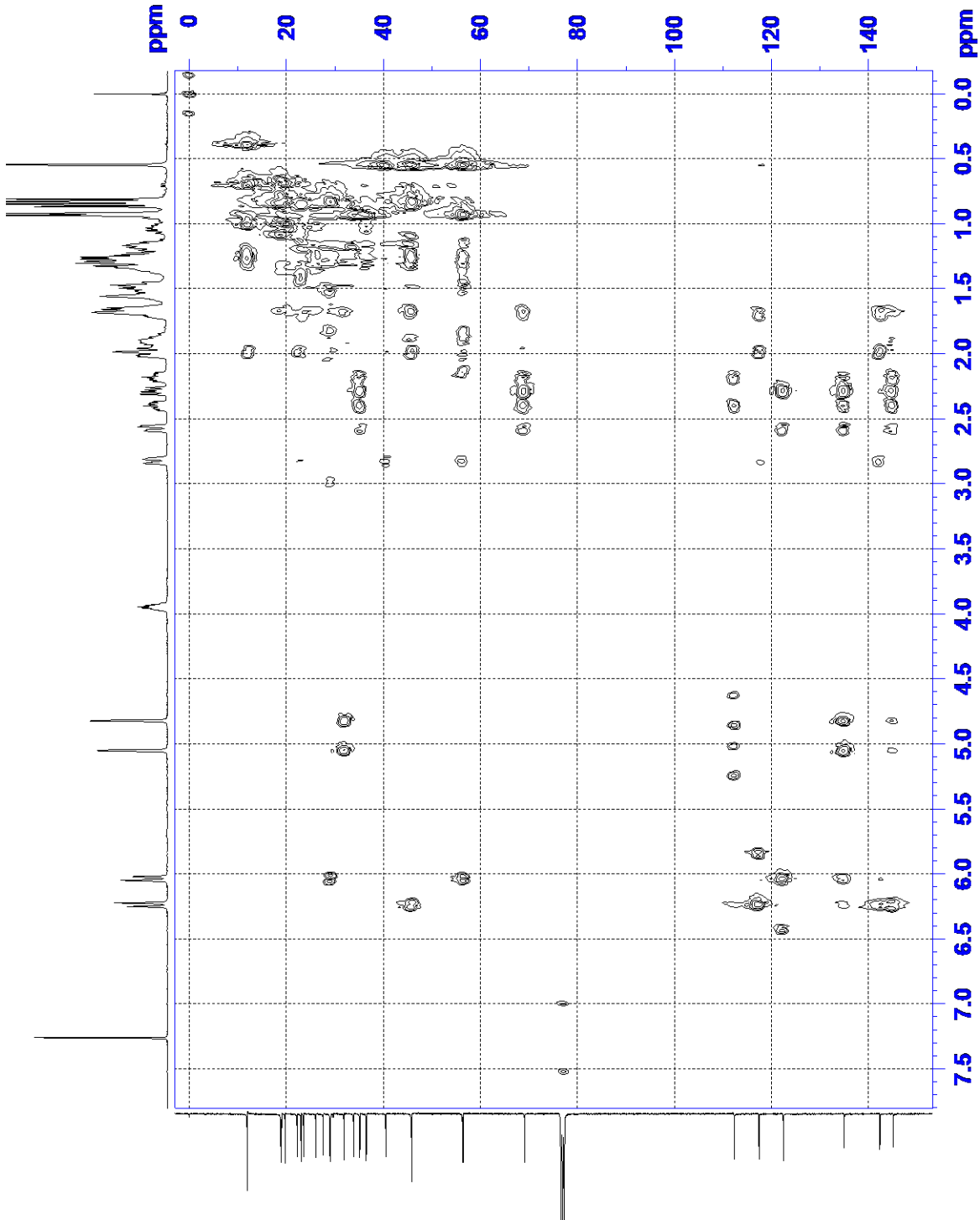


Figure S17. HMBC NMR spectrum of vitamin D₅ (6).



Current Data Parameters
NAME sk65-86-1
EXENO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180308
Time_ 9:20
INSTRUM spect
PROBHD 5 mm CPBBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 12
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 32
DM 60.400 usec
DE 6.50 usec
TE 300.00 K
D1 1.00000000 sec
TDO 1

==== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 0.00 dB
PL2 21.20173.60 dB
PL3 0.00 dB
PL4 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300092 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00

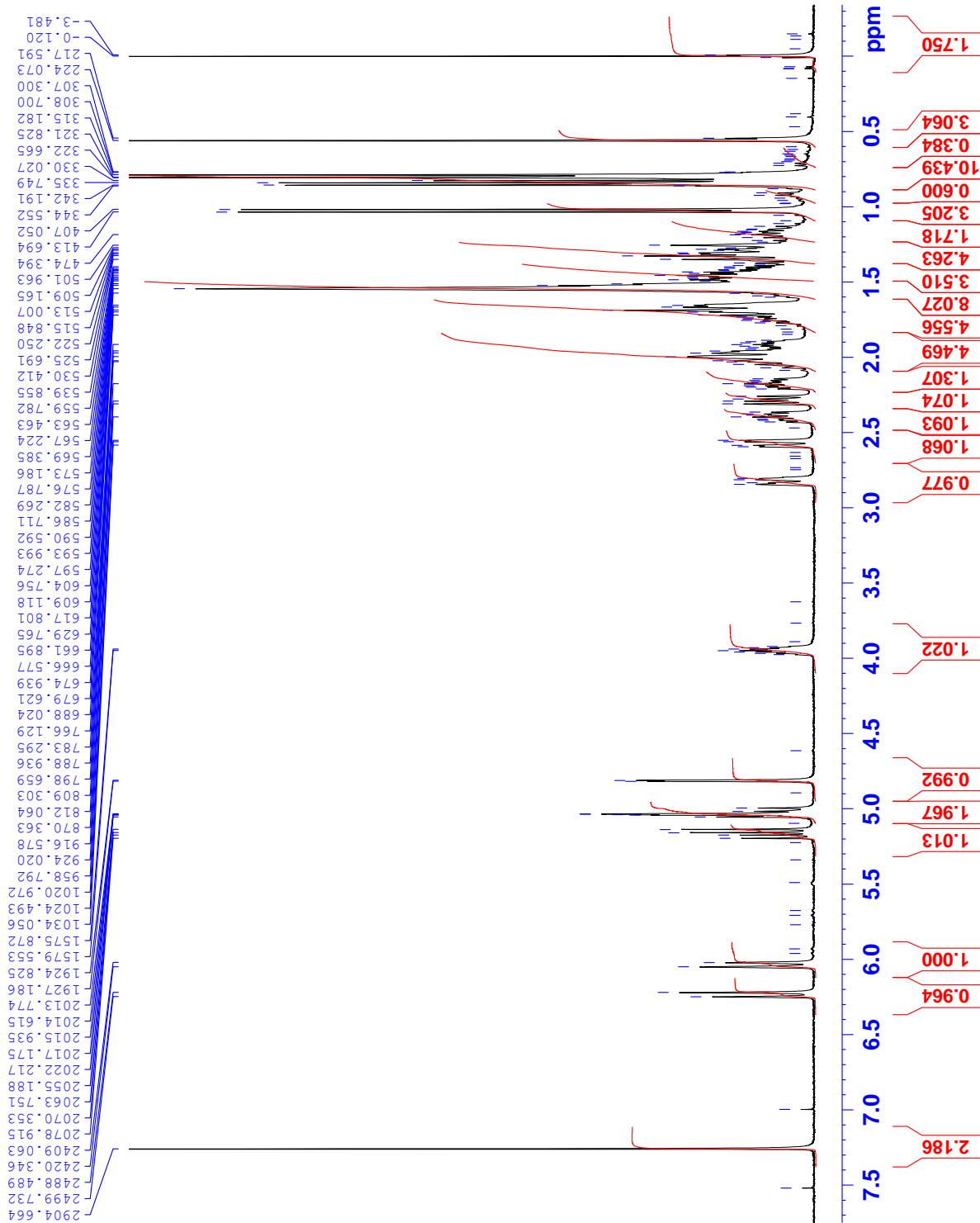


Figure S18. ¹H NMR spectrum of vitamin D₆ (8).



Current Data Parameters
 NAME: SKE3-06-11
 EXPNO: 11
 PROCNO: 1

F2 - Acquisition Parameters

Date: 20180308
 Time: 9.22
 INSTRUM: spect
 PROBHD: 5 mm CPBBO BB-
 PULPROG: coasyphf
 ED: 2048
 SOLVENT: CDCl3
 NS: 1
 DS: 8
 SWH: 5341.880 Hz
 FIDRES: 2.608340 Hz
 AQ: 0.1316328 sec
 RG: 93.362 usec
 RW: 6.500 usec
 RE: 6.500 usec
 KE: 300.0 K
 JO: 0.0000300 sec
 SI: 1.48689198 sec
 S1: 0.0000400 sec
 S16: 0.0002000 sec
 ENO: 0.00018720 sec

==== CHANNEL F1 =====
 FOC1: 1H
 P0: 12.00 usec
 P1: 12.00 usec
 PL1: -3.60 dB
 PL1W: 21.29127693 W
 FFO1: 400.1324057 MHz

==== GRADIENT CHANNEL =====
 SPAM[1]: SINK_100
 SPZ1: 10.00 %
 SP16: 1000.00 usec

F1 - Acquisition parameters
 ED: 128
 FFO1: 400.1324 MHz
 FIDRES: 41.733440 Hz
 SW: 13.350 ppm
 P1: 1.40

F2 - Processing parameters
 SI: 1024
 SF: 400.1300000 MHz
 SINE
 TDW: 0 Hz
 SB: 0 Hz
 SC: 0 Hz

F1 - Processing parameters
 SI: 1024
 CP: 0
 SF: 400.1300000 MHz
 SINE
 TDW: 0 Hz
 SB: 0 Hz

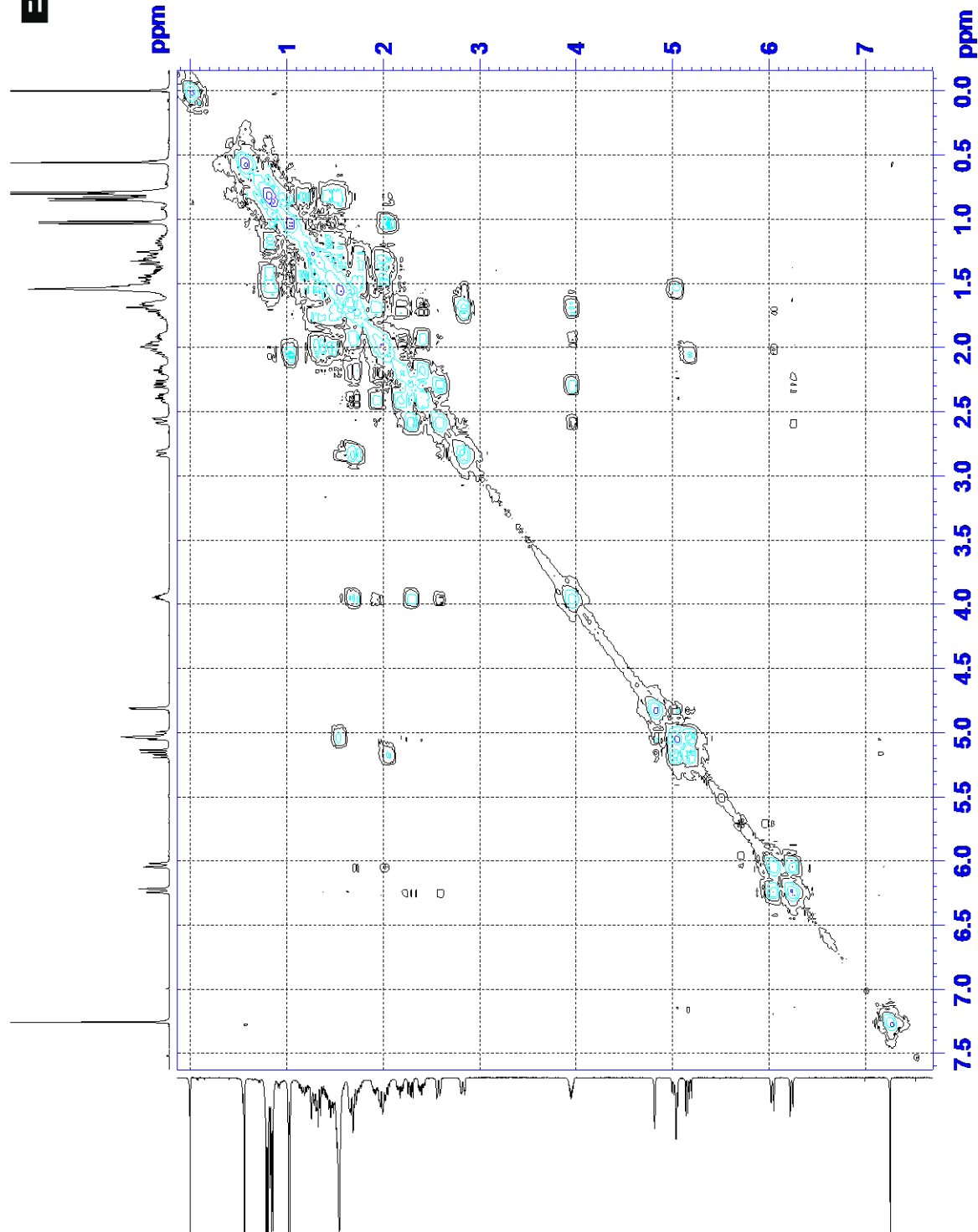


Figure S19. ¹H¹H COSY NMR spectrum of vitamin D₆ (8).



145.08
 142.24
 138.09
 135.05
 129.52
 122.45
 117.51
 112.38
 77.32
 77.00
 76.68
 69.19
 56.45
 56.39
 51.24
 45.92
 45.75
 40.73
 40.42
 35.15
 31.88
 29.69
 29.00
 25.39
 23.57
 22.32
 21.34
 21.07
 18.97
 18.25
 15.36
 12.23
 12.00
 0.02

```

Current Data Parameters
NAME      sk65-86-1
EXPNO    12
PROCNO   1

F2 - Acquisition Parameters
Date_    20180308
Time     10.28
INSTRUM  spect
PROBHD   5 mm CPBBO BB-
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        1024
DS         4
SWH       23980.814 Hz
FIDRES    0.365918 Hz
AQ         1.3664256 sec
RG         5160.6
WDW        20.850 usec
DE         18.00 usec
TE         300.0 K
D1         2.0000000 sec
d11        0.0300000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
PL1        -4.30 dB
PL1W       89.24295807 W
SFO1       100.6228298 MHz

===== CHANNEL f2 =====
2FDRPG12  waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        -3.80 dB
PL12       12.00 dB
PL13       12.00 dB
PL2W       22.29470444 W
PL12W      0.58641046 W
PL13W      0.58641046 W
SFO2       400.1316005 MHz

F2 - Processing parameters
SI         32768
SF         100.6127690 MHz
AQ         EM
WDW        0
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```

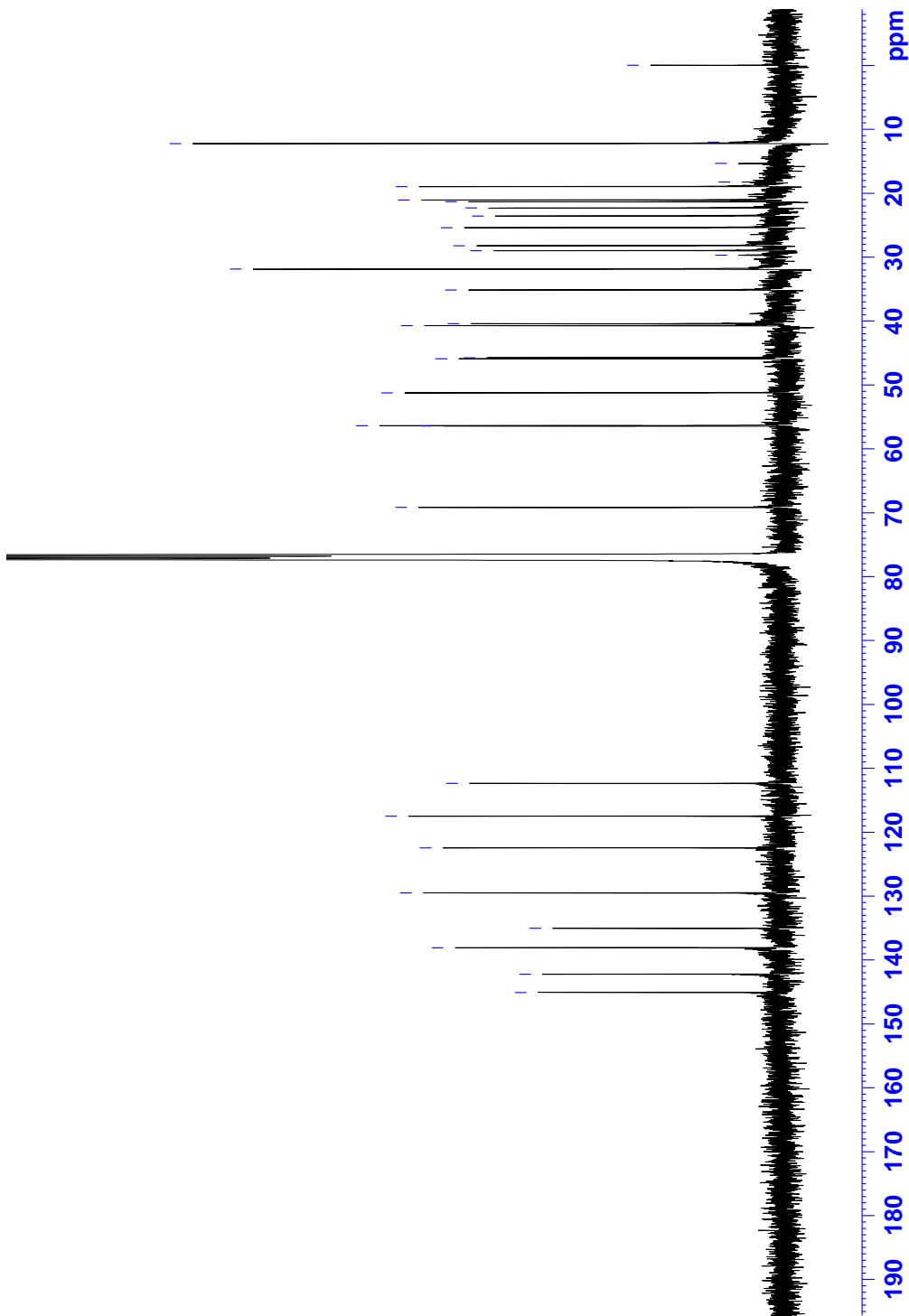


Figure S20. ¹³C NMR spectrum of vitamin D₆ (8).



```

Current Data Parameters
NAME          s163-867-1
PROCNO       1
PROBHD       1
PULPROG      zgpg30
PROCNO       1
F2 - Acquisition Parameters
Date_        20180308
Time         10.47
INSTRUM      spect
PROBHD       5 mm CPBBO
PULPROG      zgpg30
SOLVENT      DMSO-d6
TD           4096
AQ           0.395866 sec
RG           46341
WDW          EM
SSB          0
GB           0
PC           1.40
DE           6.50 usec
TE           299.9 K
===== CHANNEL F1 =====
NUC1         1H
P1           12.00 usec
PL1          -1.50 dB
PC1          0.00 usec
===== CHANNEL F2 =====
NUC2         13C
P2           10.00 usec
PL2          -1.50 dB
PC2          0.00 usec
===== GRADIENT CHANNEL =====
GPRAM[1]    SINE.100
GPRAM[2]    SINE.100
GPRAM[3]    SINE.100
GR21        30.00 %
GR22        40.10 %
GR23        40.10 %
GR24        1000.00 usec
===== Acquisition parameters =====
TD           128
SF01         100.628138 MHz
SF02         100.628138 MHz
===== Processing parameters =====
SI           1024
SF           100.628138 MHz
WDW          EM
SSB          0
GB           0
PC           1.40
===== Acquisition parameters =====
Date_        20180308
Time         10.47
INSTRUM      spect
PROBHD       5 mm CPBBO
PULPROG      zgpg30
SOLVENT      DMSO-d6
TD           4096
AQ           0.395866 sec
RG           46341
WDW          EM
SSB          0
GB           0
PC           1.40
===== Processing parameters =====
SI           1024
SF           100.628138 MHz
WDW          EM
SSB          0
GB           0

```

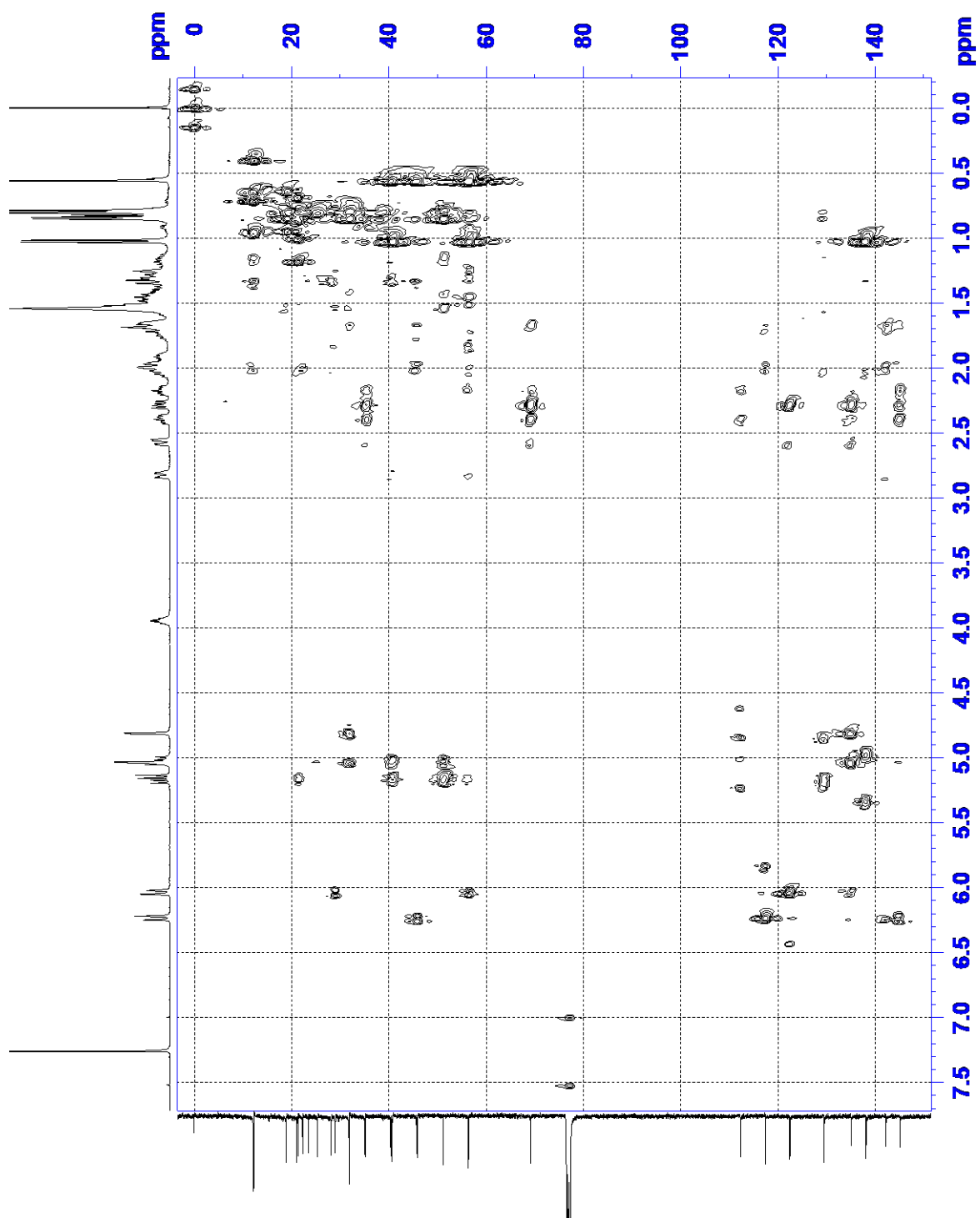


Figure S21. HMBC NMR spectrum of vitamin D₆(8).



```

Current Data Parameters
NAME      S163-01
EXPNO     10
PROCNO    1

F2 - Acquisition Parameters
Date_     20180308
Time     11.28
PROBHD   spect
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        16
DS        2
SWH       8278.146 Hz
AQ        0.167141 sec
RG        3.9593745
RG2       32
RG3       32
RG4       32
RG5       32
RG6       32
RG7       32
RG8       32
RG9       32
RG10      32
RG11      32
RG12      32
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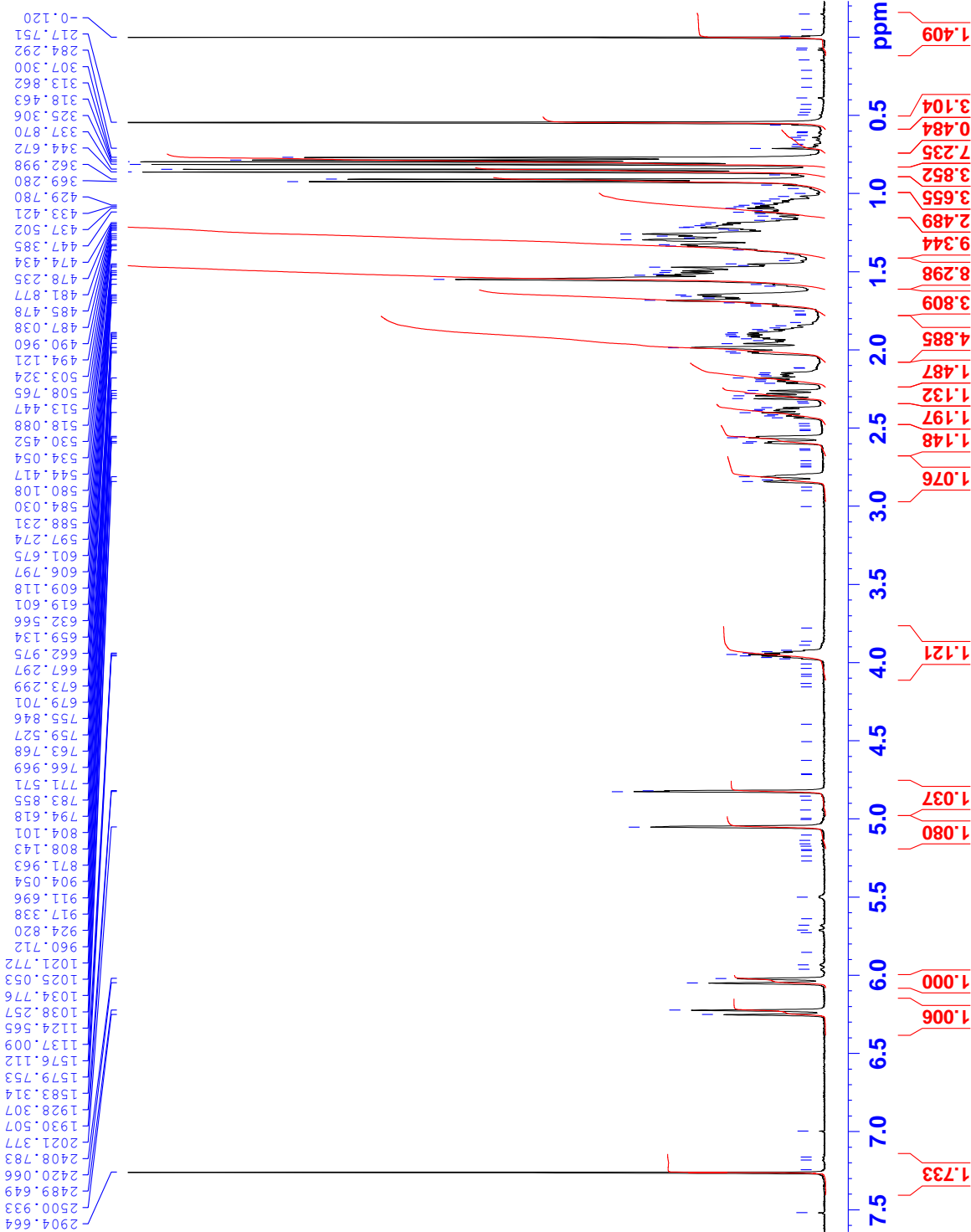


Figure S22. ¹H NMR spectrum of vitamin D₇ (7).



Current Data Parameters
 NAME ak65-86-2
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20180308
 Time 11:30

INSTRUM spect
 PROBRD 5 mm CPBBO BB-
 PULPROG cosygphf

TD 2048
 SOLVENT CDCl3
 NS 1
 DS 8

SWH 5341.880 Hz
 FIDRES 2.608340 Hz
 AQ 0.1916928 sec

RG 256
 DM 93.600 usec
 DE 6.50 usec

TE 300.0 K
 DT 0.0008199 sec
 D1 1.48689198 sec

D13 0.0000400 sec
 D16 0.0002000 sec
 ENO 0.00018720 sec

==== CHANNEL f1 =====
 NUCL1 1H
 P0 12.00 usec
 P1 12.00 usec

PL1 -3.60 dB
 PL1W 21.29127693 W
 SFO1 400.1324057 MHz

==== GRADIENT CHANNEL =====
 SPINAM11 SINE.100
 SFO21 10.00 %
 P16 1000.00 usec

F1 - Acquisition Parameters
 TD 1024
 SFO1 400.1324 MHz
 FIDRES 41.733440 Hz

SW 13.350 ppm
 F0CODE Qf

F2 - Processing parameters
 SI 1024
 SF 400.1300033 MHz
 SINE

SSB 0
 GB 0 Hz
 SB 0

PC 1.40

F1 - Processing parameters
 SI 1024
 SF 400.1300033 MHz
 SINE

SSB 0
 GB 0 Hz
 SB 0

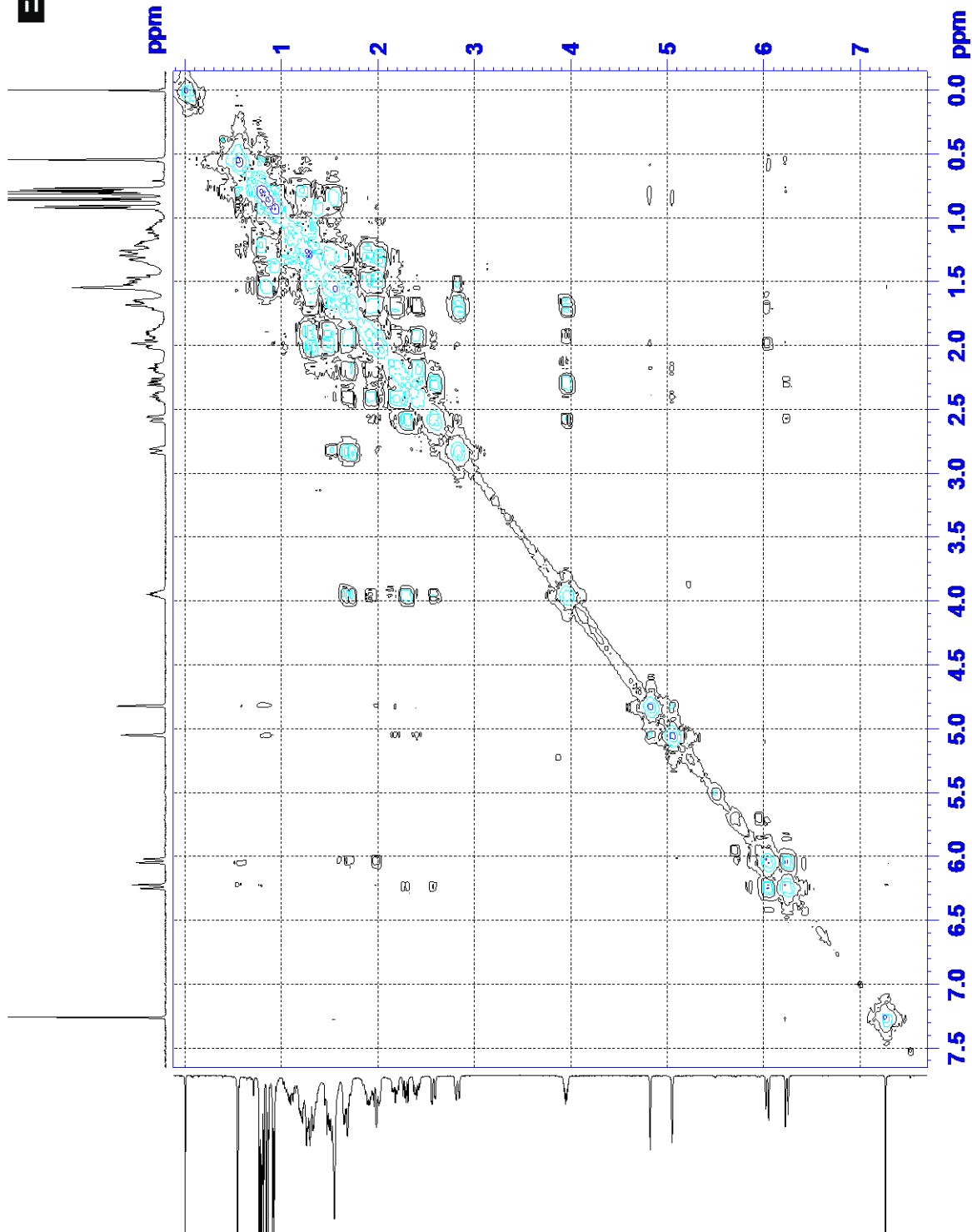


Figure S23. ¹H COSY NMR spectrum of vitamin D₇ (7).

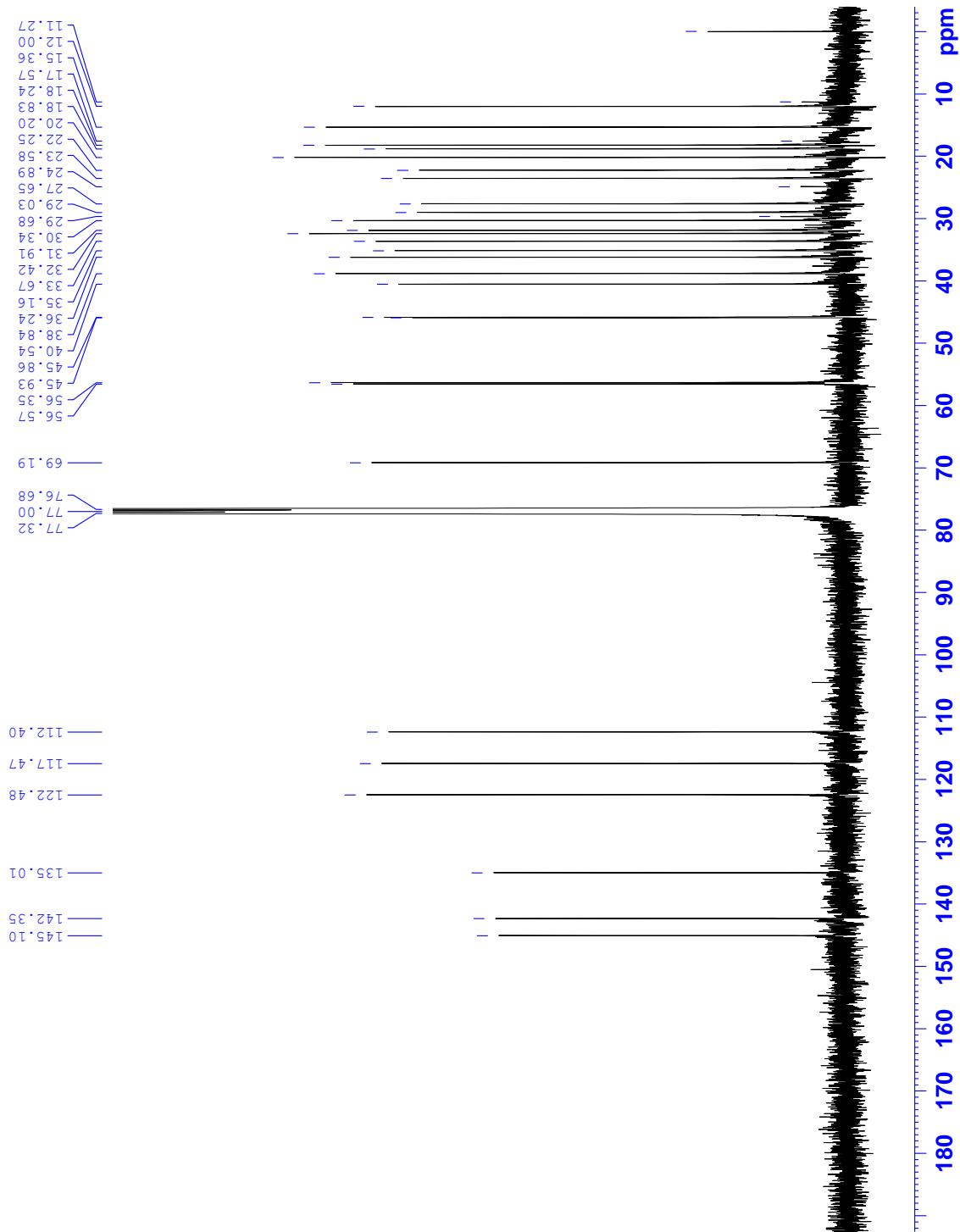


Figure S24. ¹³C NMR spectrum of vitamin D₇ (7).



Current Data Parameters
Date_ 20180308
Time_ 12.55

F2 - Acquisition Parameters
Date_ 20180308
Time_ 12.55

INSTRUM spect
PROBHD 5 mm CPBPRG
PULPROG zgpg30
TD 4096
SOLVENT CDCl3
NS 8
DS 16
SWH 5341.880 Hz
FIDRES 1.304170 Hz
RG 6534
AQ 0.394516 sec
RG 4634
DW 93.600 nsec
DE 6.50 nsec
TE 300.0 K
CST13 8.0000000
DD 0.0000300 sec
DL 1.5000000 sec
DLE 0.0000000 sec
D16 0.0002000 sec
180 0.00002233 sec

==== CHANNEL F1 =====
NUC1 1H
P1 12.00 usec
PC 12.00 usec
PL1 -3.50 dB
PL2 -3.50 dB
PL1W 21.29127693 W
SFO1 400.1324057 MHz

==== CHANNEL F2 =====
NUC2 13C
P3 10.00 usec
PC 10.00 usec
PL3 0.00 dB
PL4 0.00 dB
PL3W 89.24255003 W
SFO2 100.6288138 MHz

==== GRADIENT CHANNEL =====
GPM1(1) SINE.100
GPM1(2) SINE.100
GPM1(3) SINE.100
SP 30.00 %
SP2 30.00 %
SP3 30.00 %
GZ23 40.10 %
PL6 1000.00 nsec

F1 - Acquisition parameters
TD 128
SFO1 100.6228 MHz
SFO2 177.25242 Hz
SFO3 222.092 Ppm
PMODE OP

F2 - Processing parameters
SI 1024
SF 400.1300000 MHz
WDW 0
SSB 0
GB 0 Hz
PC 1.40

F1 - Processing parameters
SI 1024
SF 100.627690 MHz
WDW 0
SSB 0
GB 0 Hz

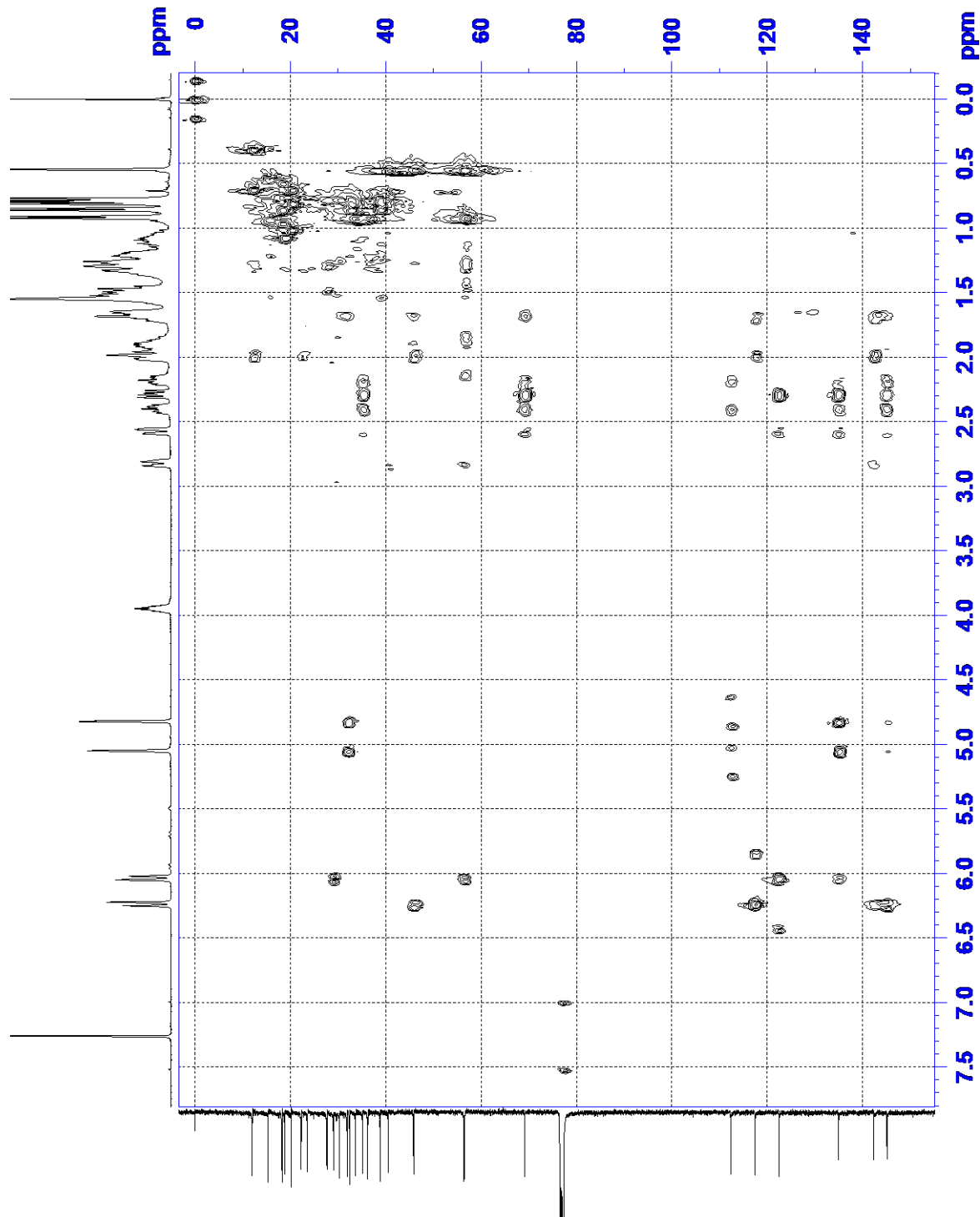


Figure S25. HMBC NMR spectrum of vitamin D₇ (7).