Supplementary Materials

Simultaneous Synthesis of Vitamins D_2, D_4, D_5, D_6, and D_7 from Commercially Available Phytosterol, β-Sitosterol, and Identification of Each Vitamin D by HSQC NMR

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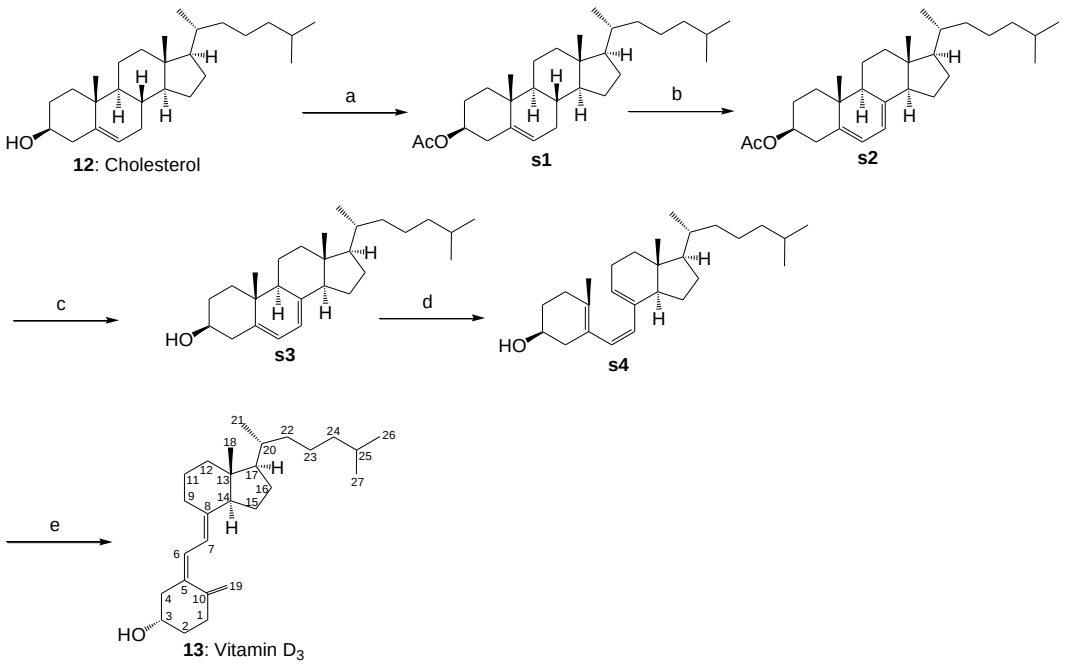
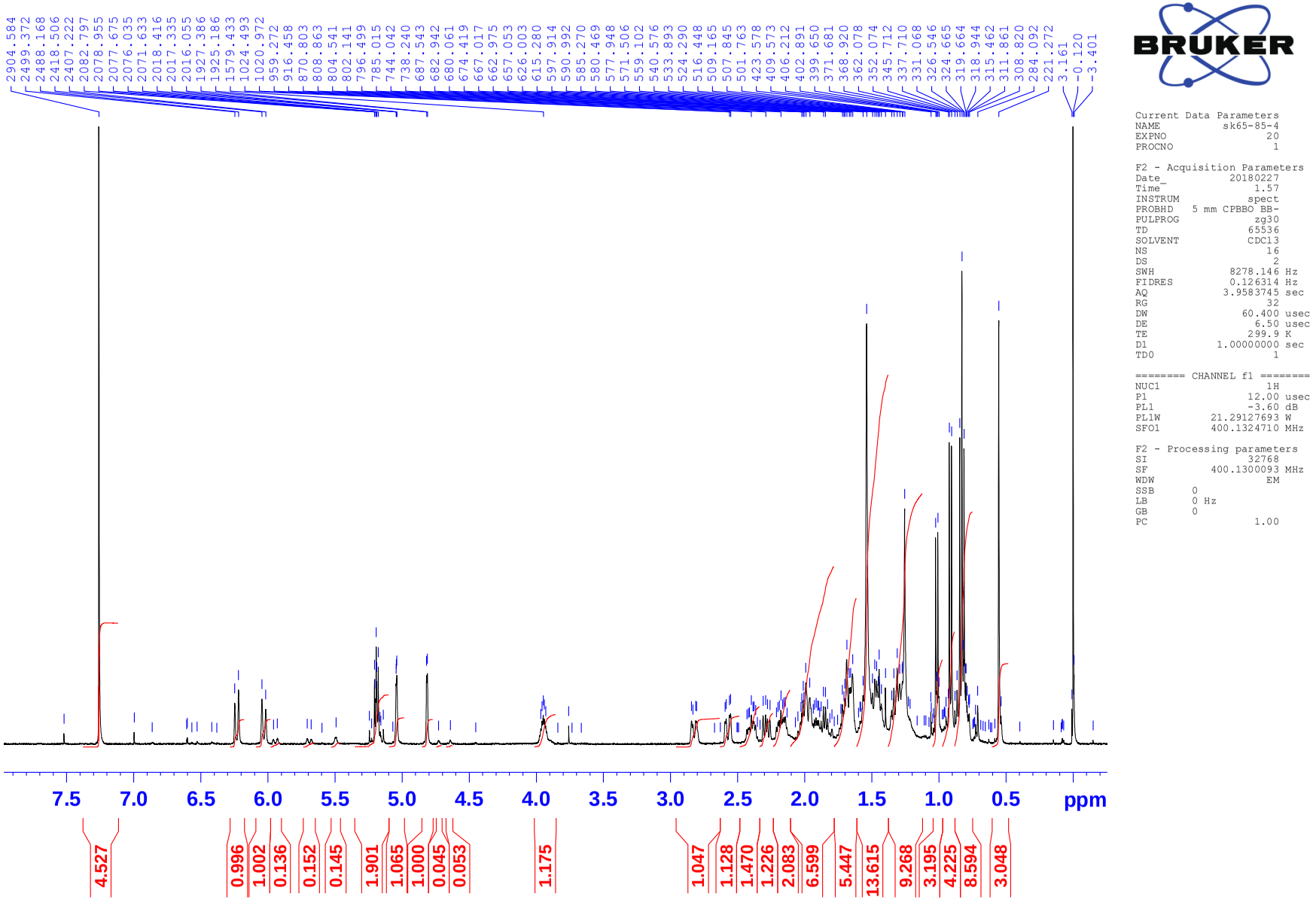


Figure S1. Synthesis of vitamin D_3. (a) Ac_2O, pyridine, 45 °C, 15 h, 98%. (b) 1) *N*-bromosuccinimide (NBS), cyclohexane, reflux, 1 h, 2) 1.0 M Bu_4NF/THF, room temperature, 12 h, 39%. (c) 28% NaOMe in MeOH, CH_2Cl_2/MeOH, room temp, 2 h, 62%. (d) 0.1% 3-*tert*-butyl-4-hydroxyanisole (BHA) in cyclohexane, 280 nm, 9.03 mW/cm^2, room temp, 1 h, 25%. (e) 0.1% BHA in cyclohexane, reflux, 1 h, 41%.

*The experimental details on the synthesis of vitamin D_3 (**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/cm^2) 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 D_3 (**13**: 2.08 mg, 41%). Vitamin D_3 (**13**); ^{1}H-NMR (400 MHz, $CDCl_3$), 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); ^{13}C-NMR (100 MHz, $CDCl_3$), 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).



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TD0 1

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Figure S2. ^{1}H NMR spectrum of vitamin D_2 (**9**).

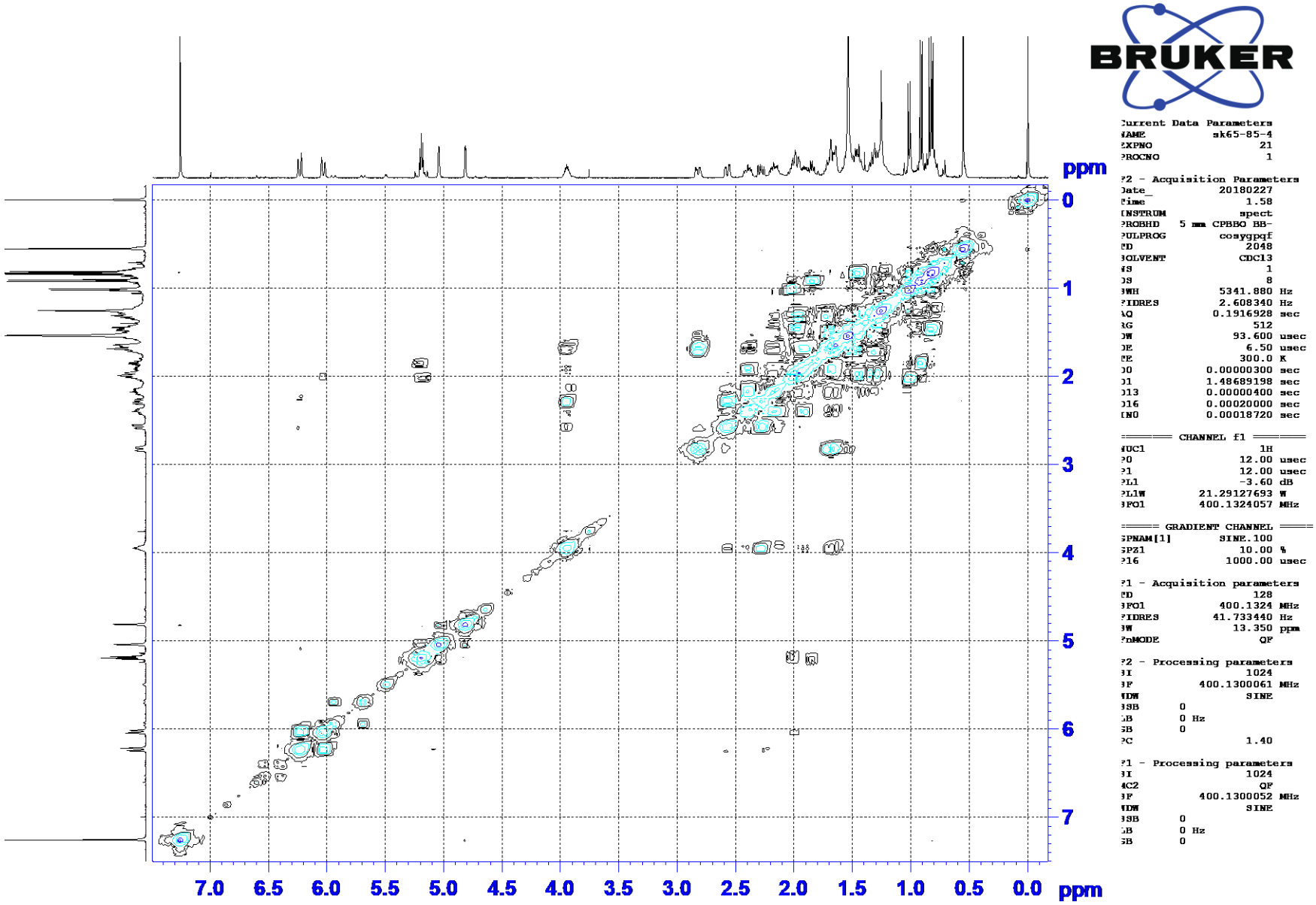


Figure S3. $^{1}H^{1}H$ COSY NMR spectrum of vitamin D_2 (**9**).

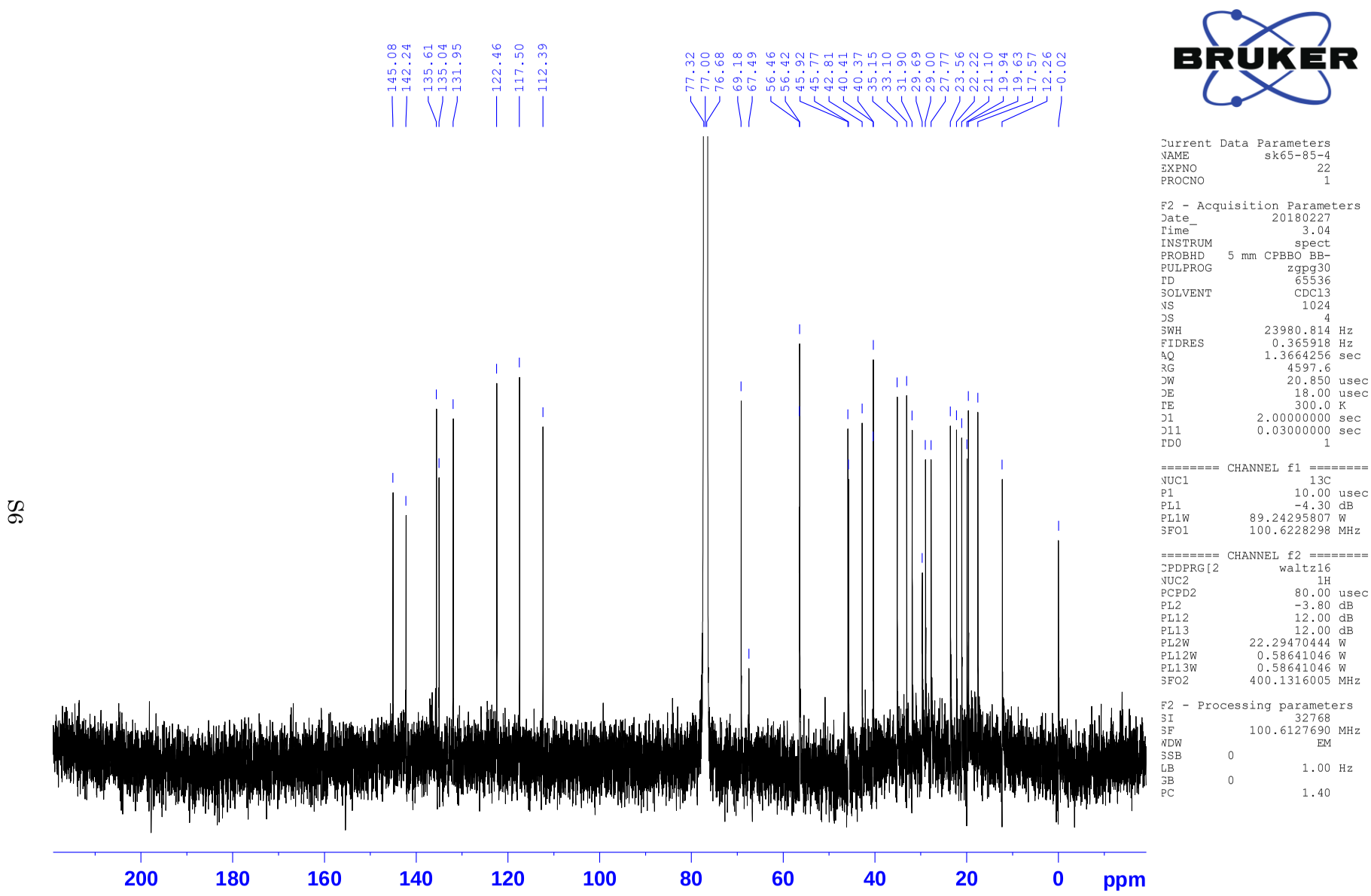
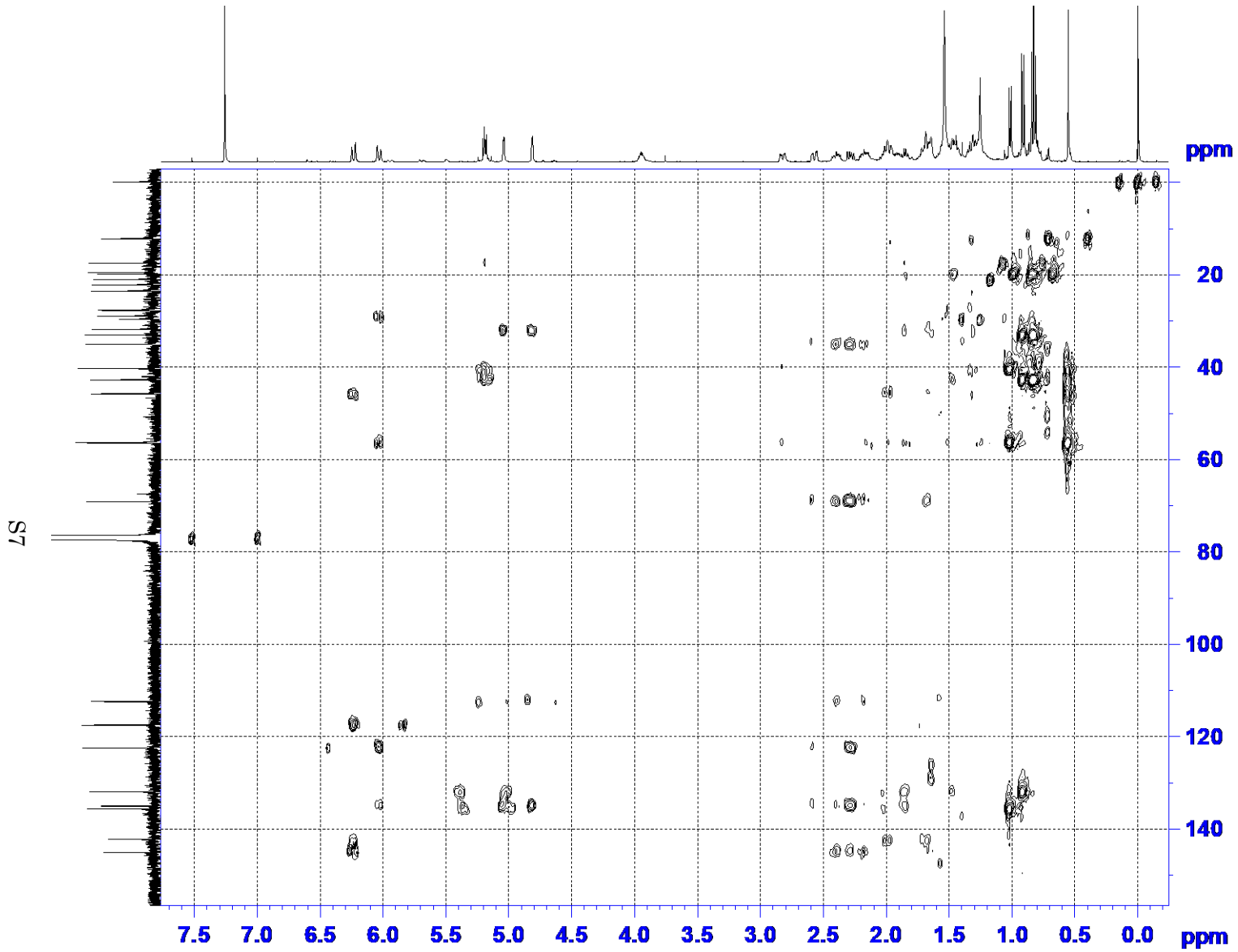


Figure S4. ^{13}C NMR spectrum of vitamin D$_2$ (**9**).

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DS                           16
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FIDRES               1.304170 Hz
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RG                       46341
DW                     93.600 usec
DE                      6.50 usec
TE                     300.0 K
CNST13               8.0000000
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D1                   1.50000000 sec
D6                   0.06250000 sec
D16                  0.00020000 sec
IN0                  0.00002235 sec

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P1                       12.00 usec
P2                       24.00 usec
PL1                      -3.60 dB
PL1W                21.29127693 W
SFO1               400.1324057 MHz

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GPZ3                     40.10 %
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SW                    222.095 ppm
FnMODE                       QF

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WDW                        SINE
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GB                    0
PC                         1.40

F1 - Processing parameters
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WDW                        SINE
SSB                   0
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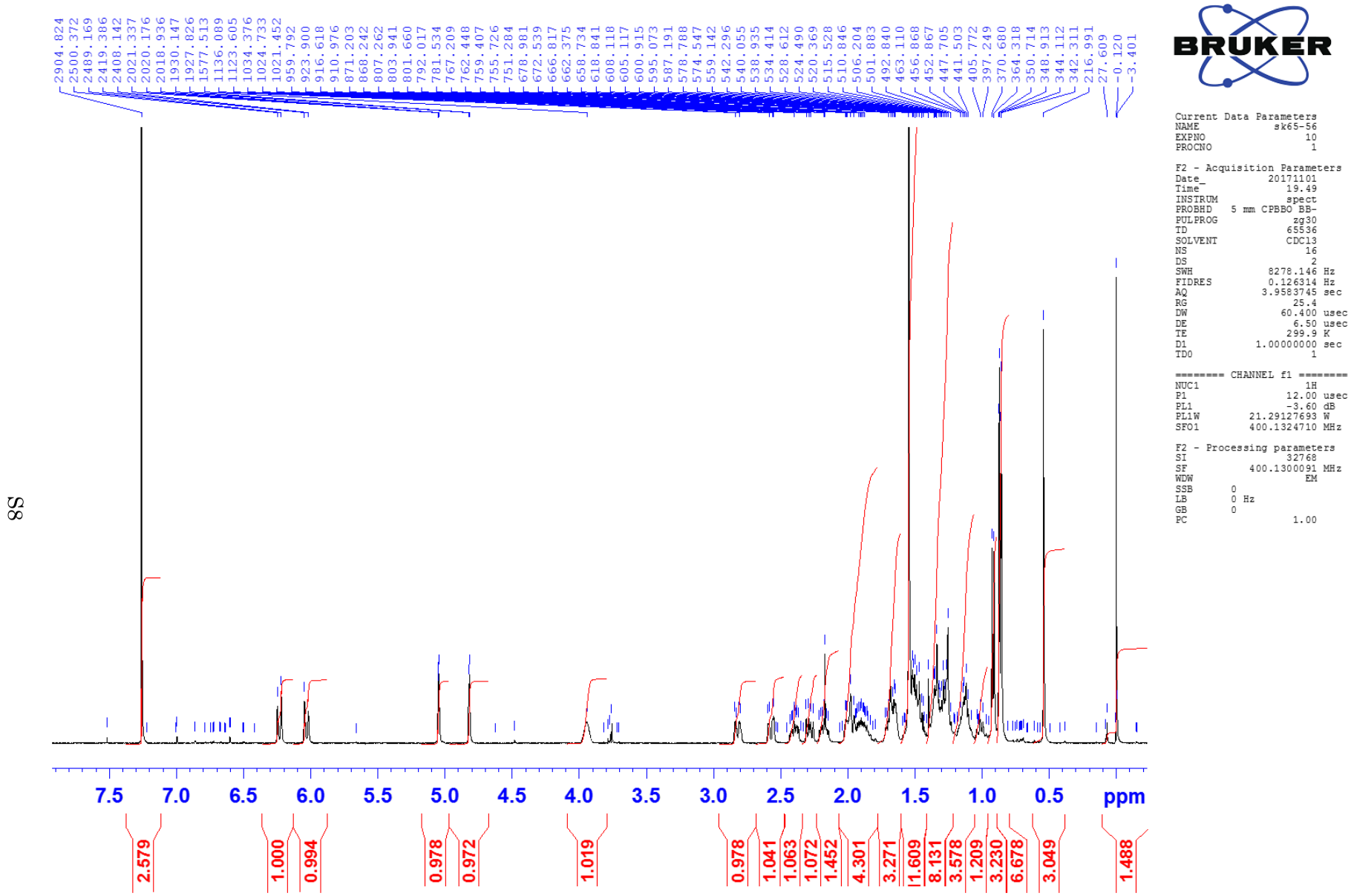
Figure S5. HMBC NMR spectrum of vitamin D_2 (**9**).



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FIDRES 0.126314 Hz
AQ 3.9583745 sec
RG 25.4
DW 60.400 usec
DE 6.50 usec
TE 299.9 K
D1 1.00000000 sec
TD0 1

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SFO1 400.1324710 MHz

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GB 0
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Figure S6. ^{1}H NMR spectrum of vitamin D$_3$ (**13**).

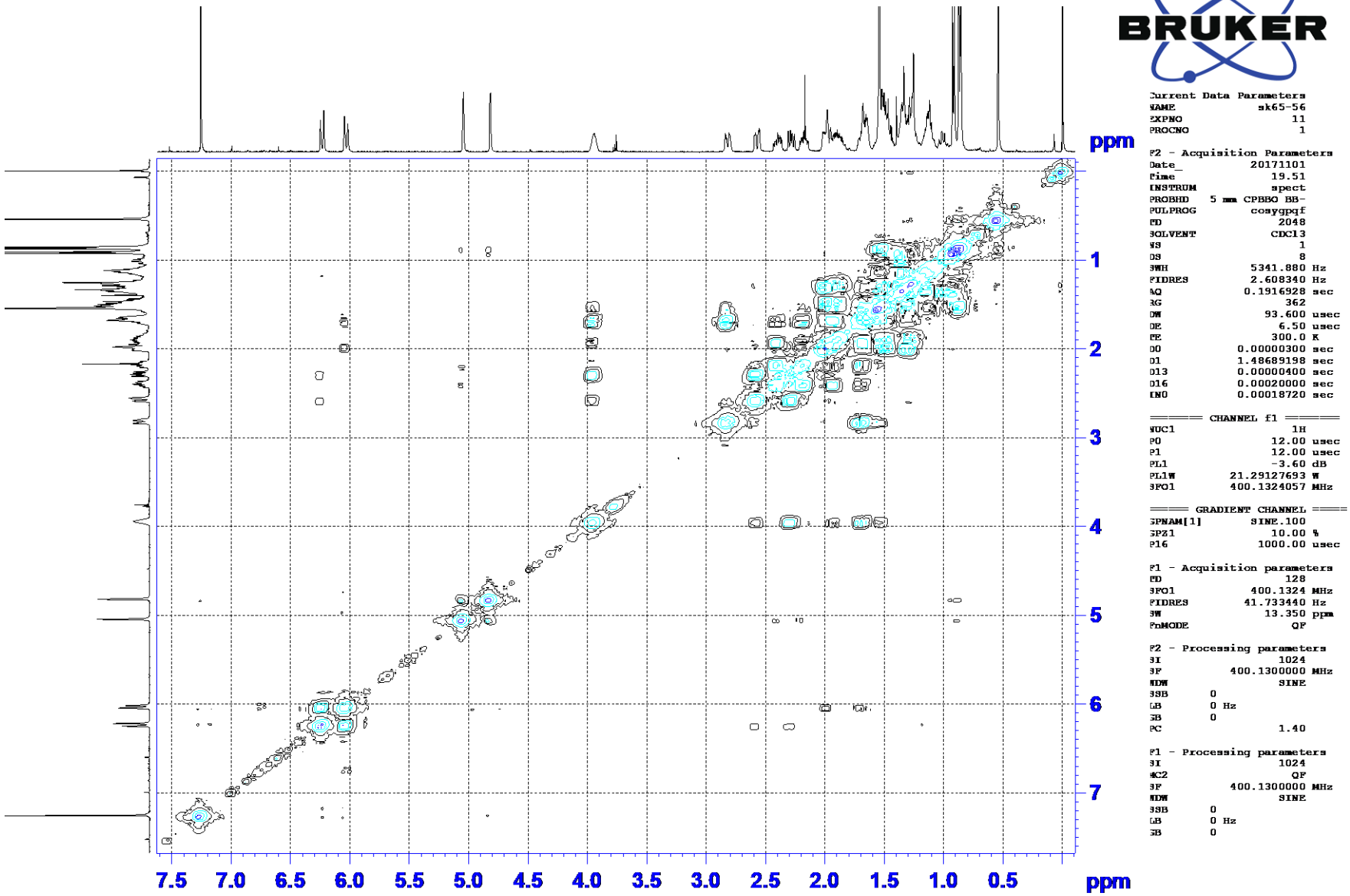
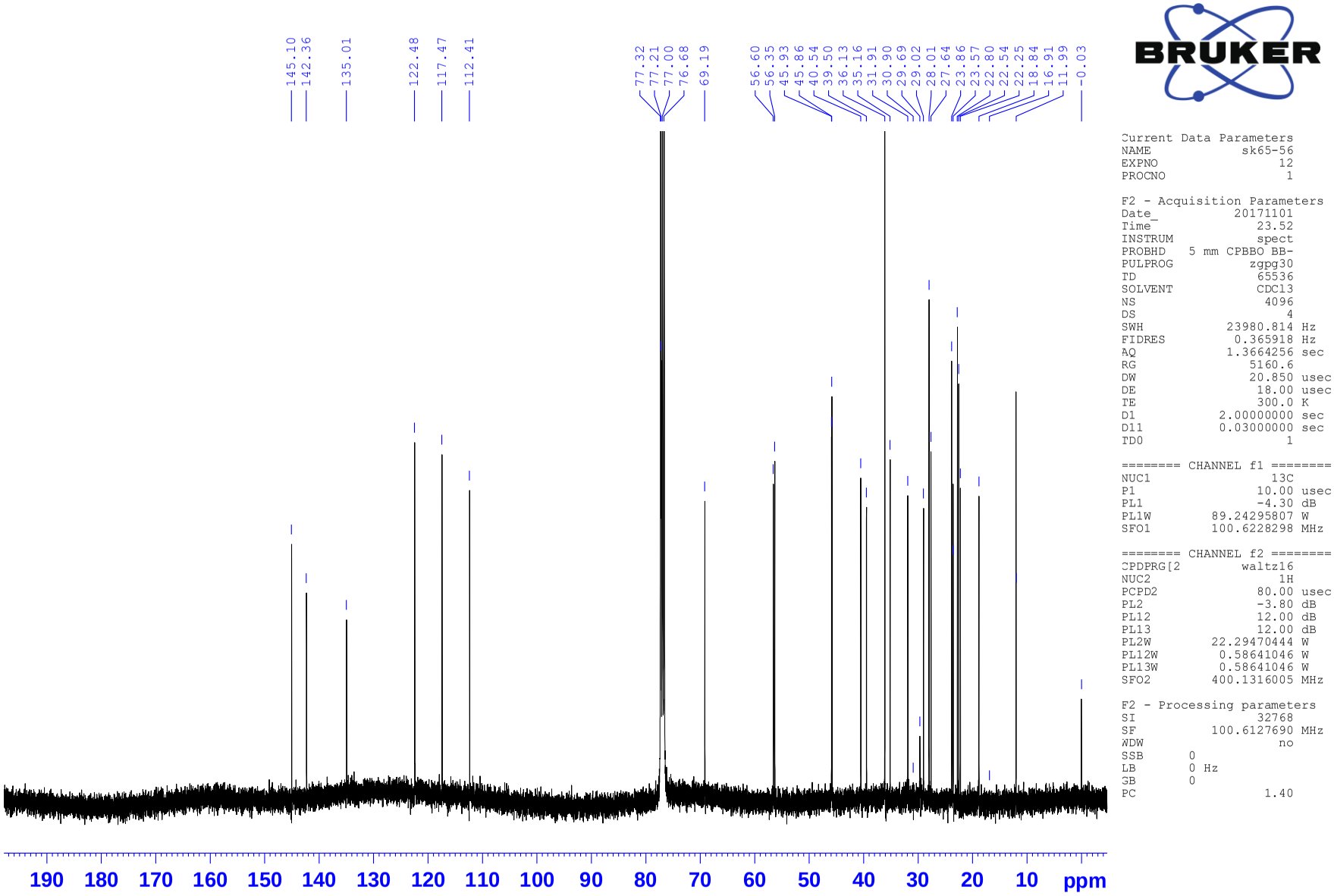


Figure S7. $^{1}H^{1}H$ COSY NMR spectrum of vitamin D_3 (**13**).

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TE                  300.0 K
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D11             0.03000000 sec
TD0                      1

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P1                   10.00 usec
PL1                  -4.30 dB
PL1W          89.24295807 W
SFO1          100.6228298 MHz

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PL12                 12.00 dB
PL13                 12.00 dB
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PL12W          0.58641046 W
PL13W          0.58641046 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                    32768
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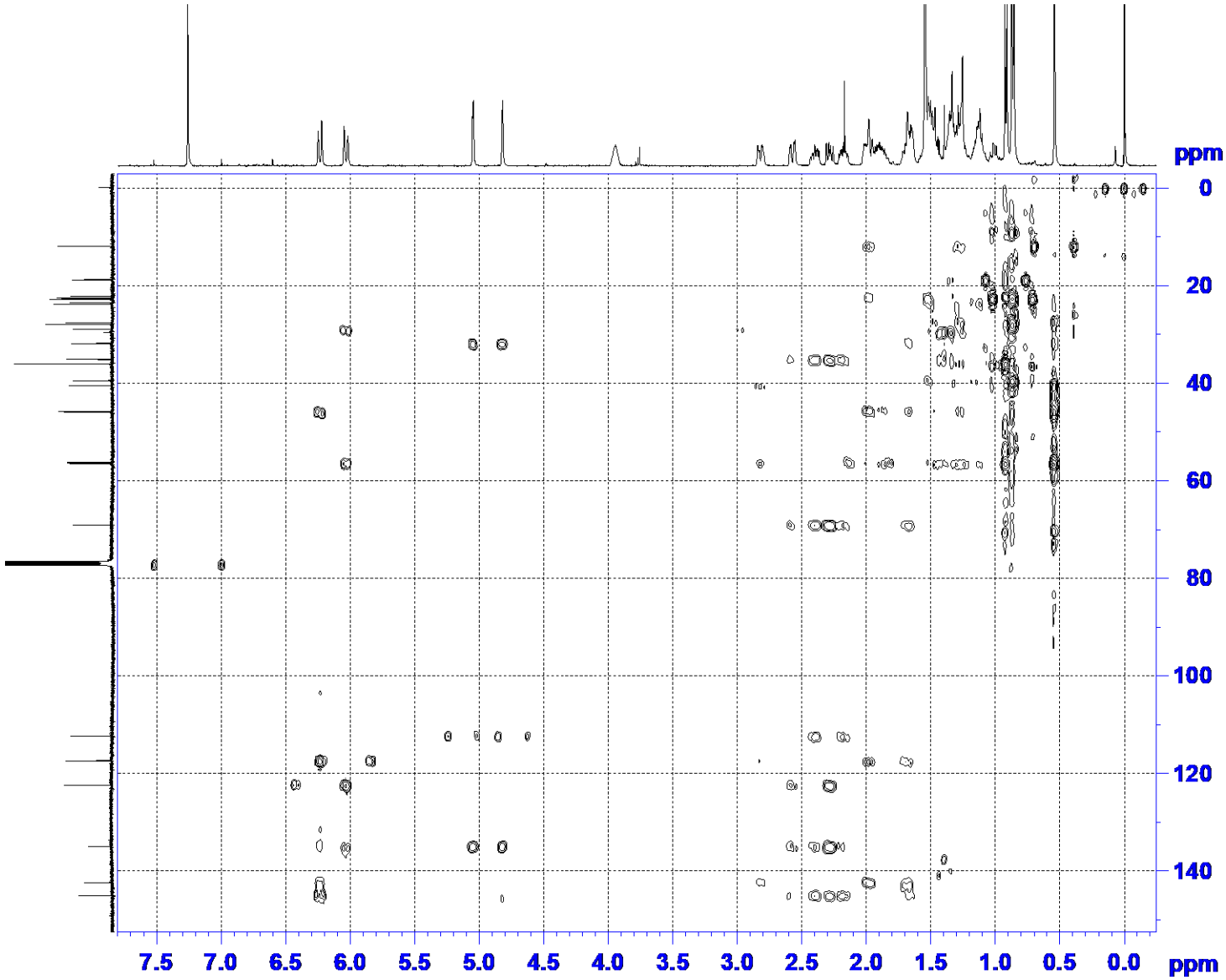
Figure S8. ^{13}C NMR spectrum of vitamin D_3 (**13**).

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PROCNO                      1

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TD                      4096
SOLVENT                CDCl3
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DS                        16
SWH                5341.880 Hz
FIDRES             1.304170 Hz
AQ                 0.3833856 sec
RG                     46341
DW                    93.600 usec
DE                     6.50 usec
TE                    300.0 K
CNST13             8.0000000
D0                 0.00000300 sec
D1                 1.50000000 sec
D6                 0.06250000 sec
D16                0.00020000 sec
IN0                0.00002235 sec

======= CHANNEL f1 =======
NUC1                      1H
P1                     12.00 usec
P2                     24.00 usec
PL1                    -3.60 dB
PL1W           21.29127693 W
SFO1           400.1324057 MHz

======= CHANNEL f2 =======
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PL2                    -4.30 dB
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SFO2           100.6228138 MHz

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SW                222.095 ppm
FnMODE                    QF

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LB           0 Hz
GB           0
PC                       1.40

F1 - Processing parameters
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Figure S9. HMBC NMR spectrum of vitamin D_3 (**13**).

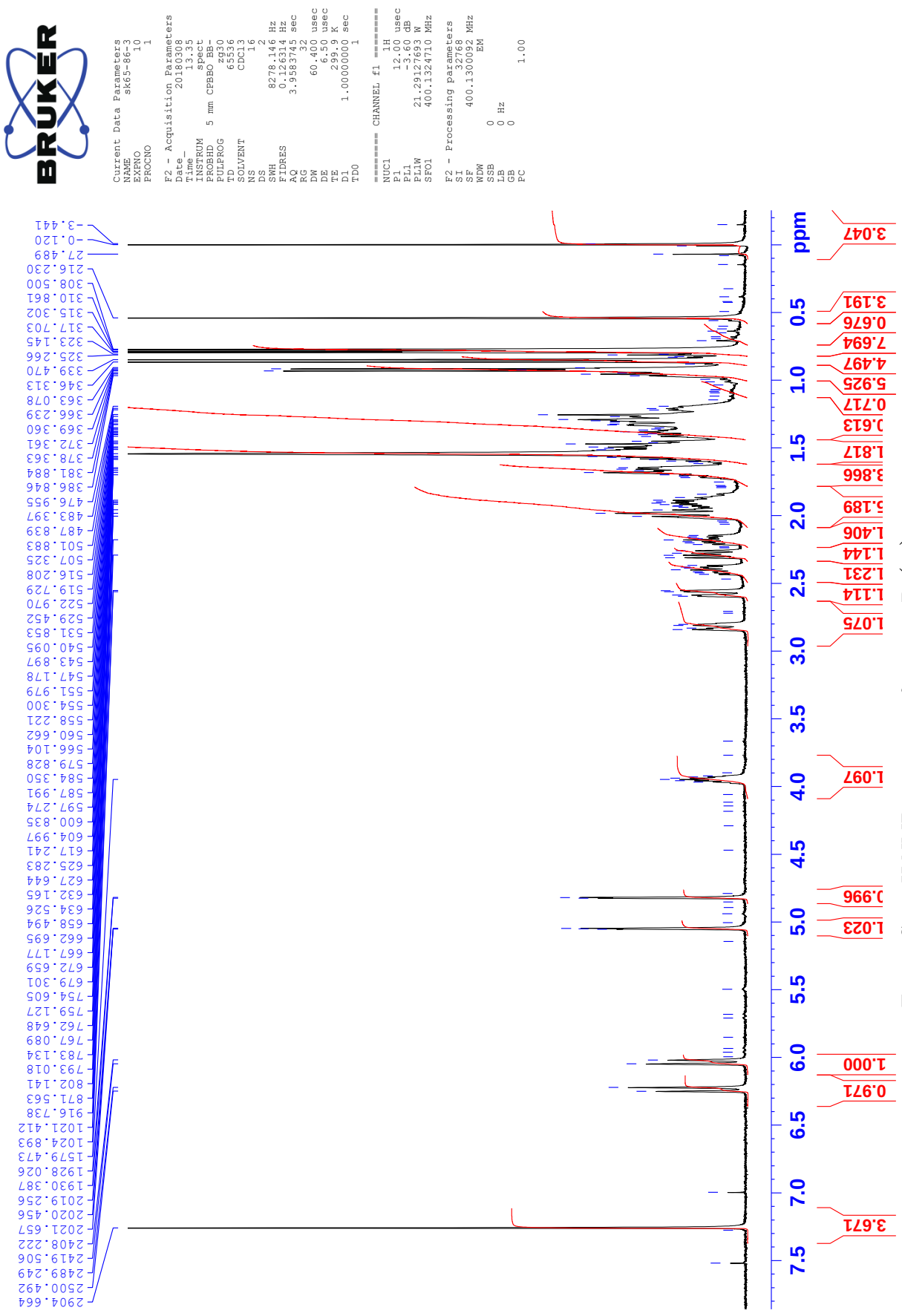


Figure S10. ^{1}H NMR spectrum of vitamin D_4 (10).

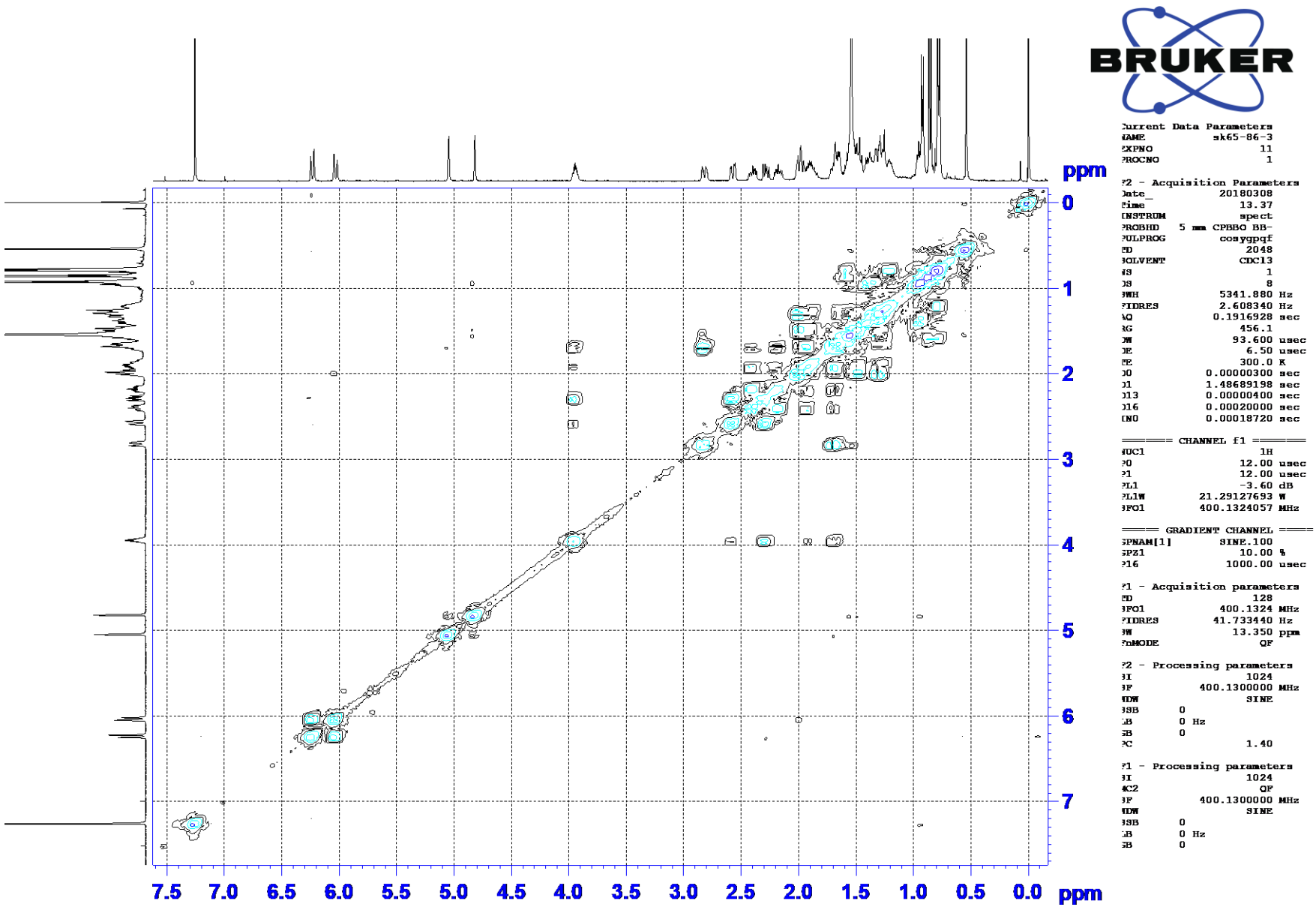
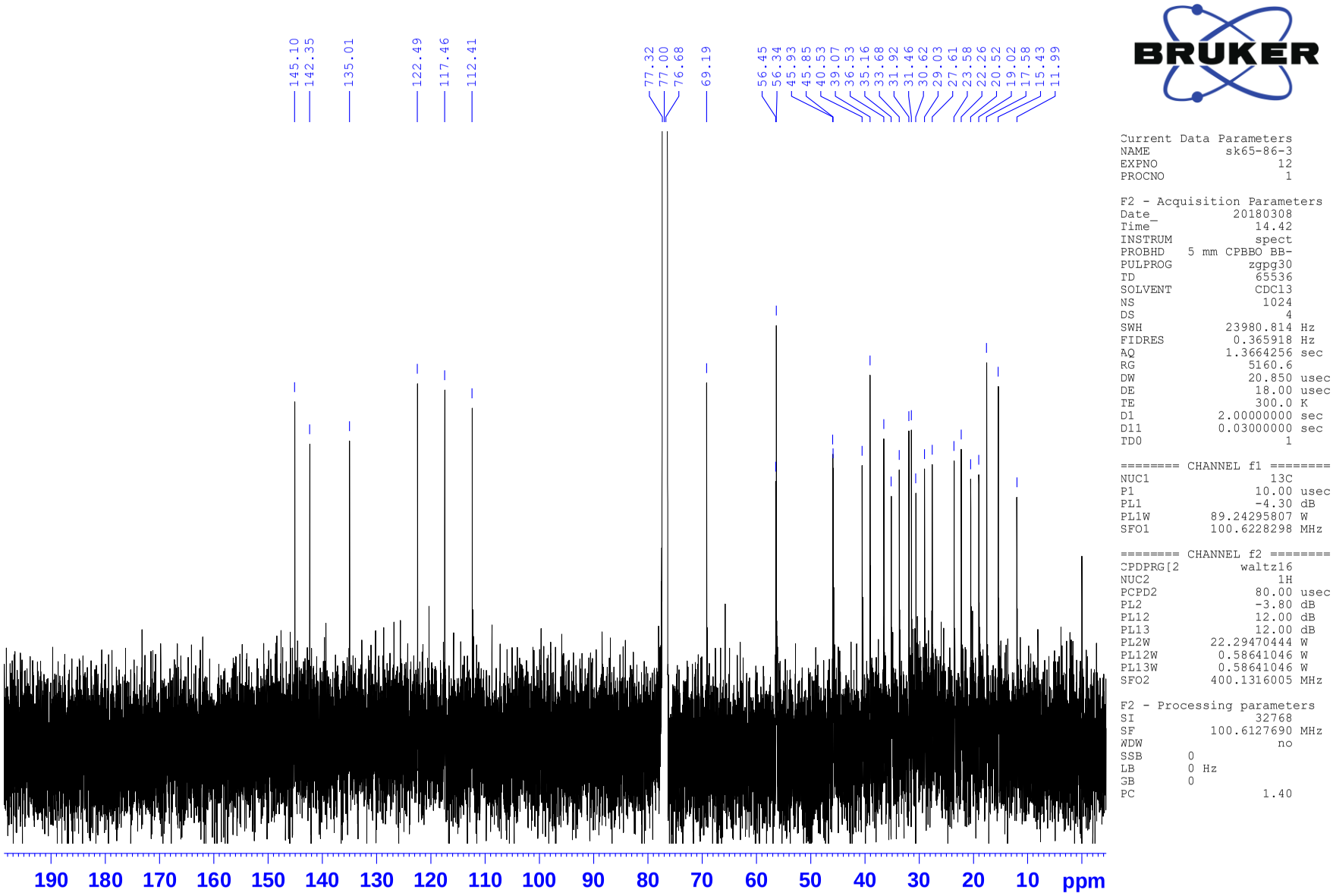


Figure S11. $^{1}H^{1}H$ COSY NMR spectrum of vitamin D_4 (**10**).

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FIDRES               0.365918 Hz
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RG                      5160.6
DW                      20.850 usec
DE                      18.00 usec
TE                      300.0 K
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D11                0.03000000 sec
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PL1                      -4.30 dB
PL1W               89.24295807 W
SFO1              100.6228298 MHz

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NUC2                        1H
PCPD2                    80.00 usec
PL2                      -3.80 dB
PL12                     12.00 dB
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PL2W               22.29470444 W
PL12W               0.58641046 W
PL13W               0.58641046 W
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                       32768
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SSB          0
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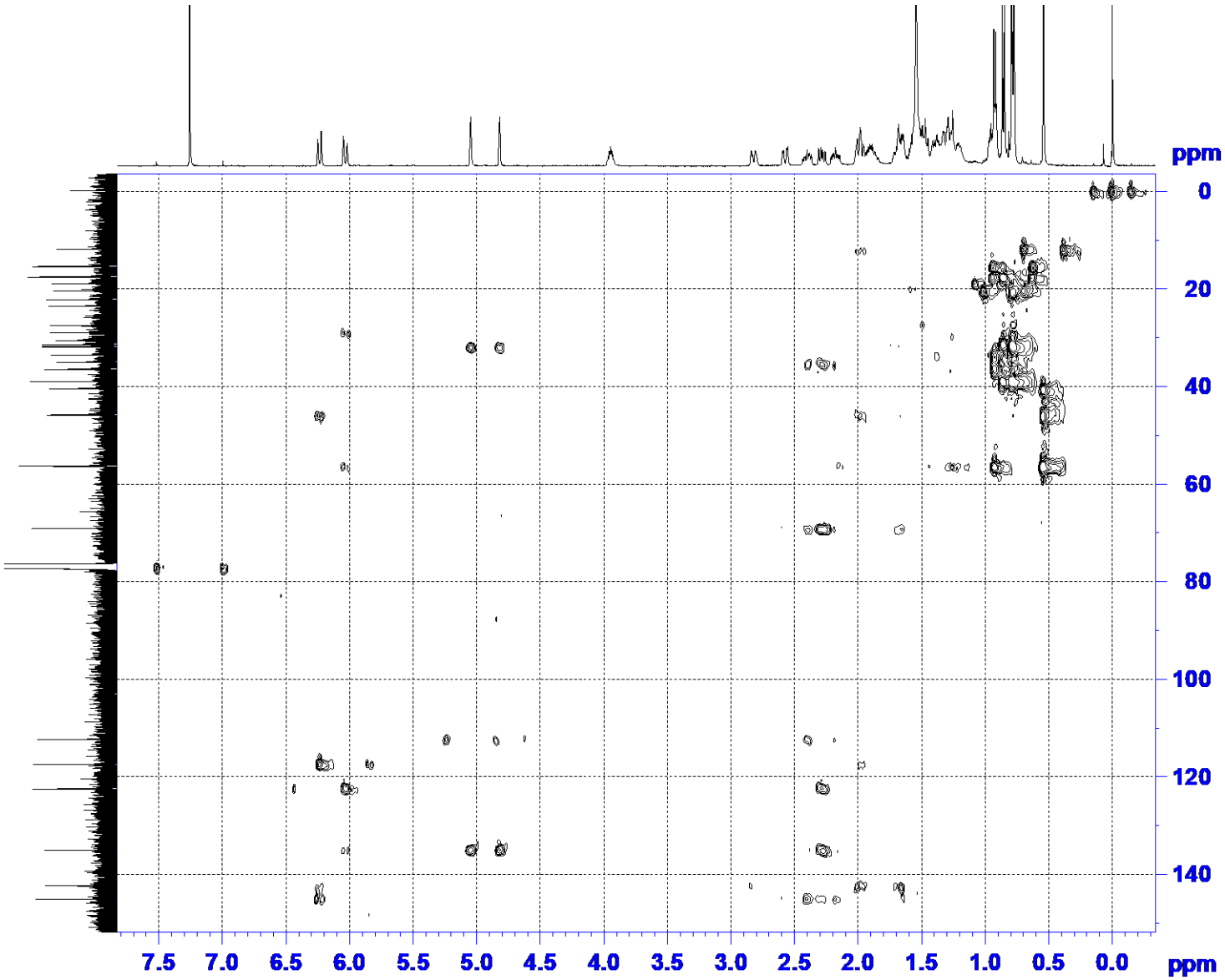
Figure S12. ^{13}C NMR spectrum of vitamin D_4 (**10**).

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FIDRES             1.304170 Hz
AQ                 0.3833856 sec
RG                       46341
DW                    93.600 usec
DE                     6.50 usec
TE                    299.9 K
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D1                 1.50000000 sec
D6                 0.06250000 sec
D16                0.00020000 sec
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======= CHANNEL f1 =======
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P2                      24.00 usec
PL1                     -3.60 dB
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SFO1           400.1324057 MHz

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PL2                     -4.30 dB
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SFO2           100.6228138 MHz

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GPZ3                 40.10 %
P16                1000.00 usec

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FIDRES          174.592422 Hz
SW                222.095 ppm
FnMODE                    QF

F2 - Processing parameters
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SF              400.1300062 MHz
WDW                      SINE
SSB          0
LB           0 Hz
GB           0
PC                       1.40

F1 - Processing parameters
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Figure S13. HMBC NMR spectrum of vitamin D_4 (**10**).

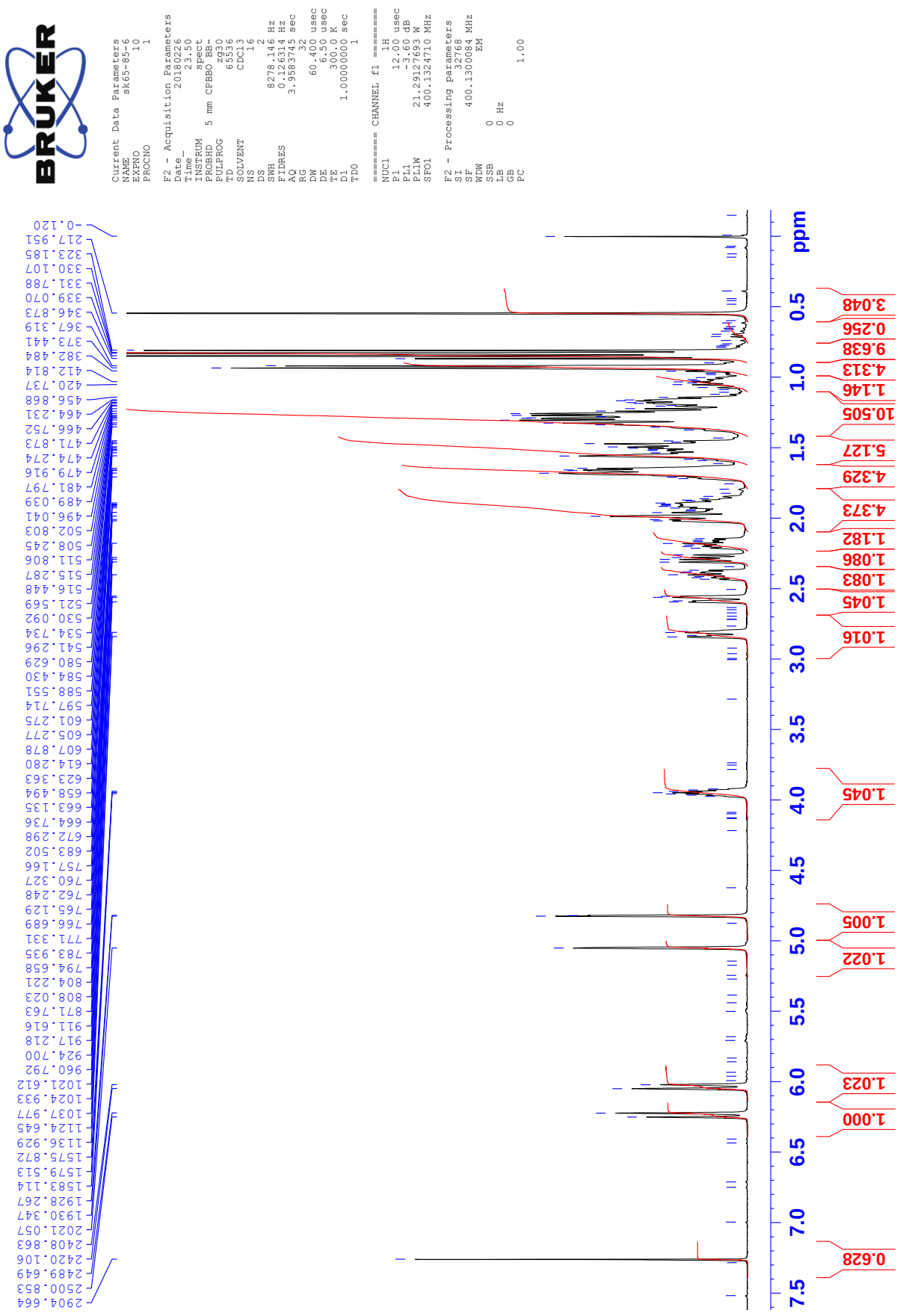


Figure S14. ^{1}H NMR spectrum of vitamin D_5 (**6**).

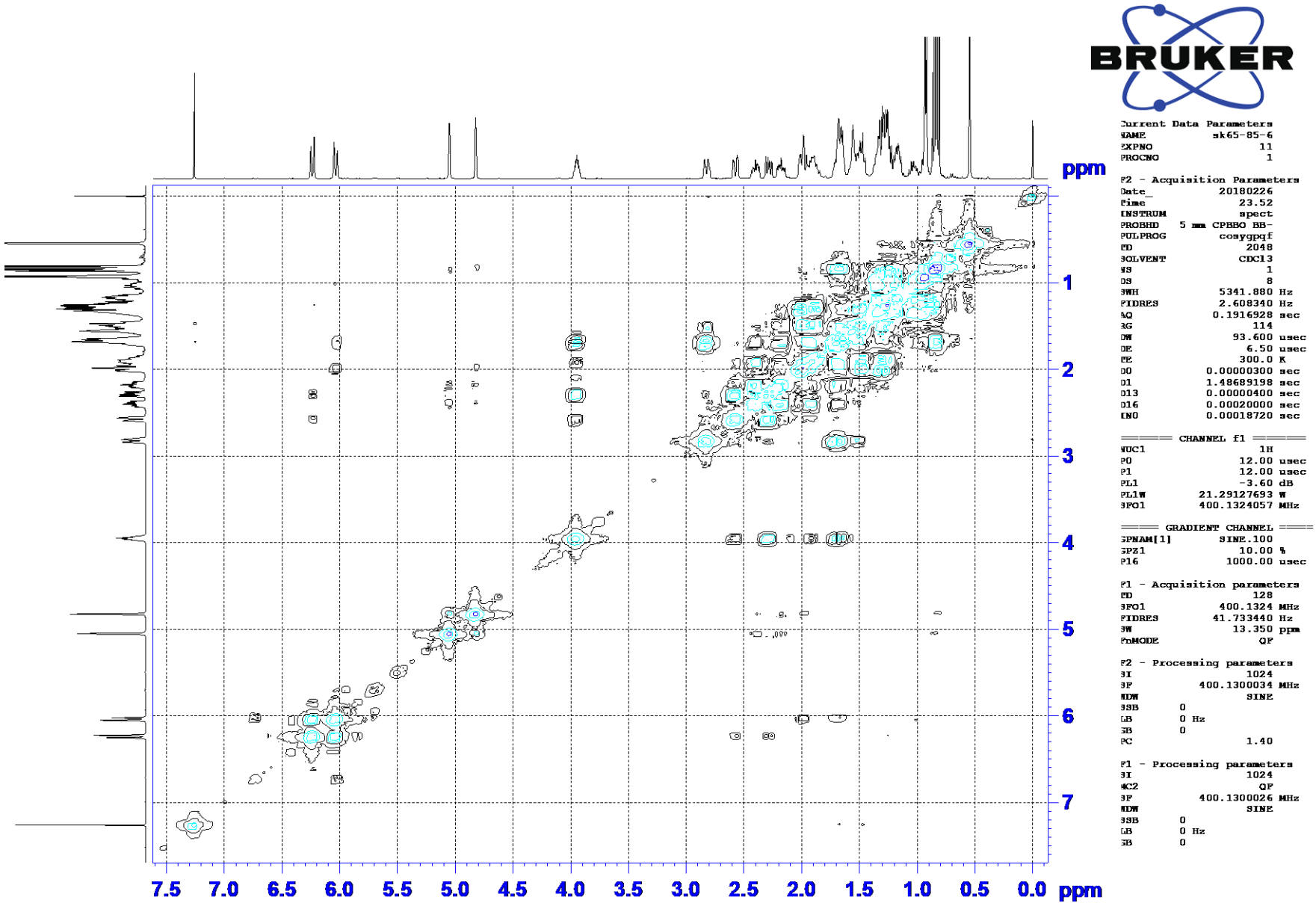


Figure S15. $^{1}H^{1}H$ COSY NMR spectrum of vitamin D_5 (**6**).

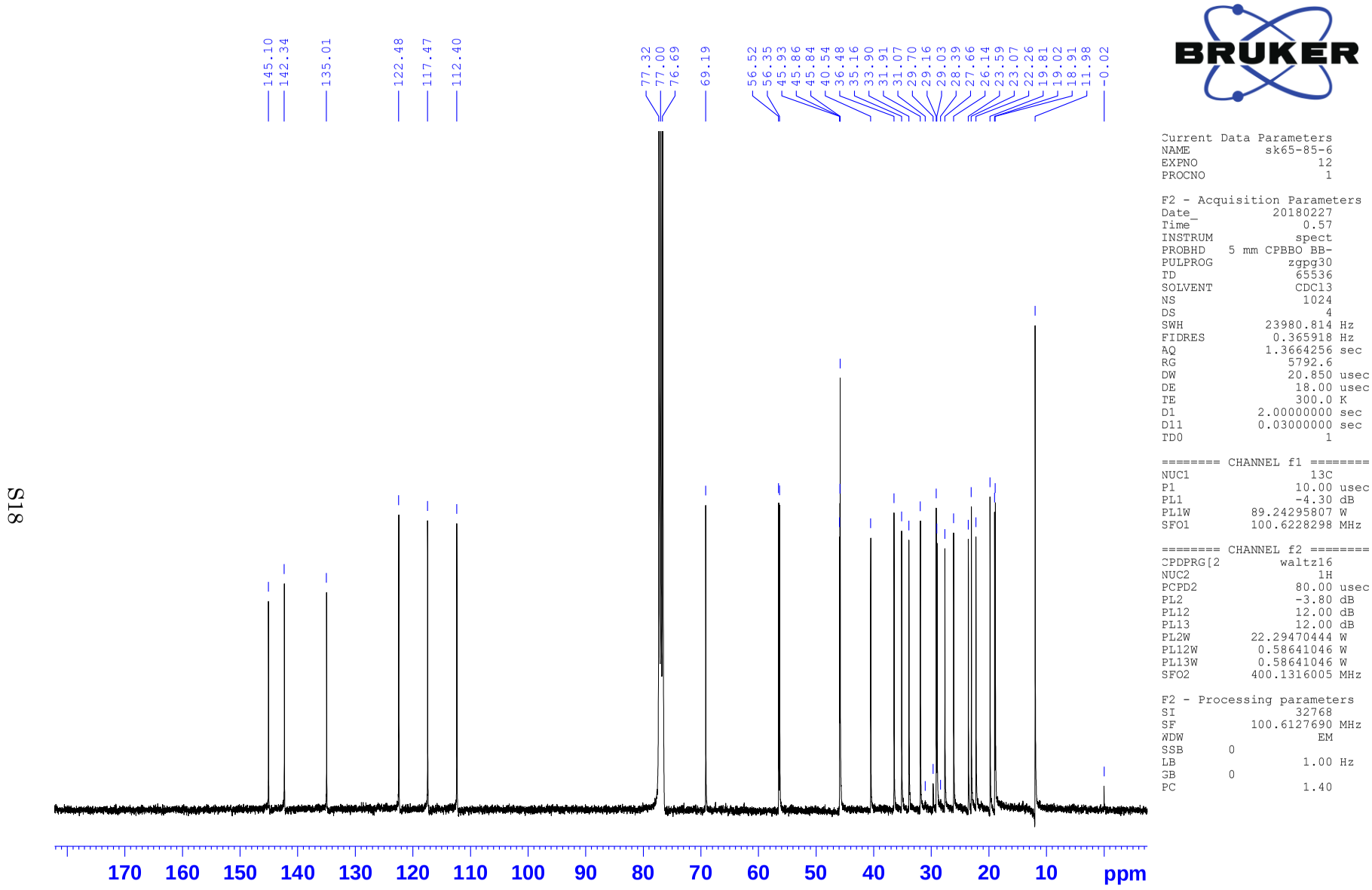
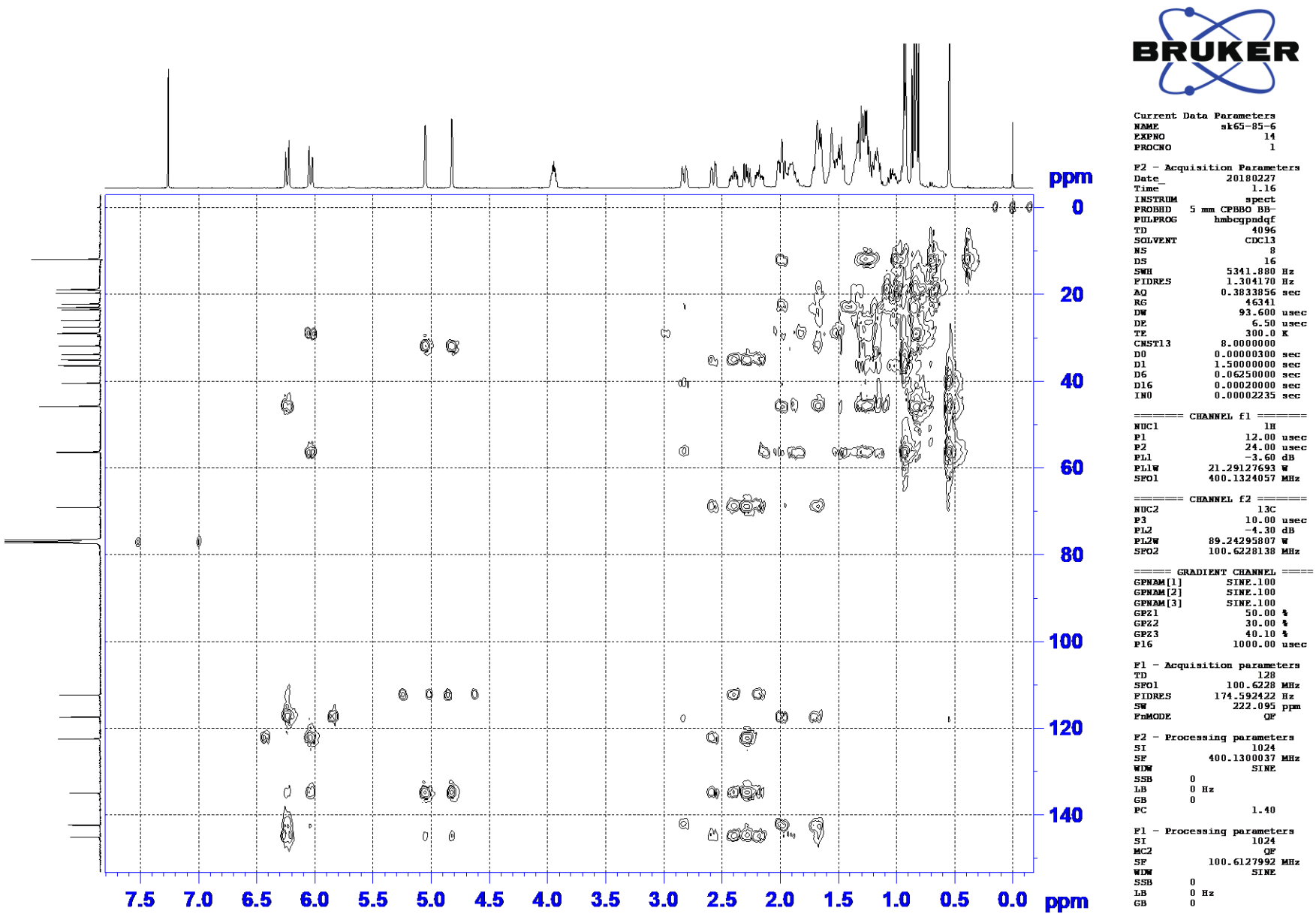


Figure S16. ^{13}C NMR spectrum of vitamin D_5 (**6**).

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SWH                  5341.880 Hz
FIDRES               1.304170 Hz
AQ                   0.3833856 sec
RG                         46341
DW                    93.600 usec
DE                     6.50 usec
TE                     300.0 K
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P1                        12.00 usec
P2                        24.00 usec
PL1                       -3.60 dB
PL1W              21.29127693 W
SFO1              400.1324057 MHz

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P3                        10.00 usec
PL2                       -4.30 dB
PL2W              89.24295807 W
SFO2              100.6228138 MHz

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GPZ2                     30.00 %
GPZ3                     40.10 %
P16                    1000.00 usec

F1 - Acquisition parameters
TD                          128
SFO1              100.6228 MHz
FIDRES            174.592422 Hz
SW                   222.095 ppm
FnMODE                       QF

F2 - Processing parameters
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SF                400.1300037 MHz
WDW                        SINE
SSB           0
LB            0 Hz
GB            0
PC                         1.40

F1 - Processing parameters
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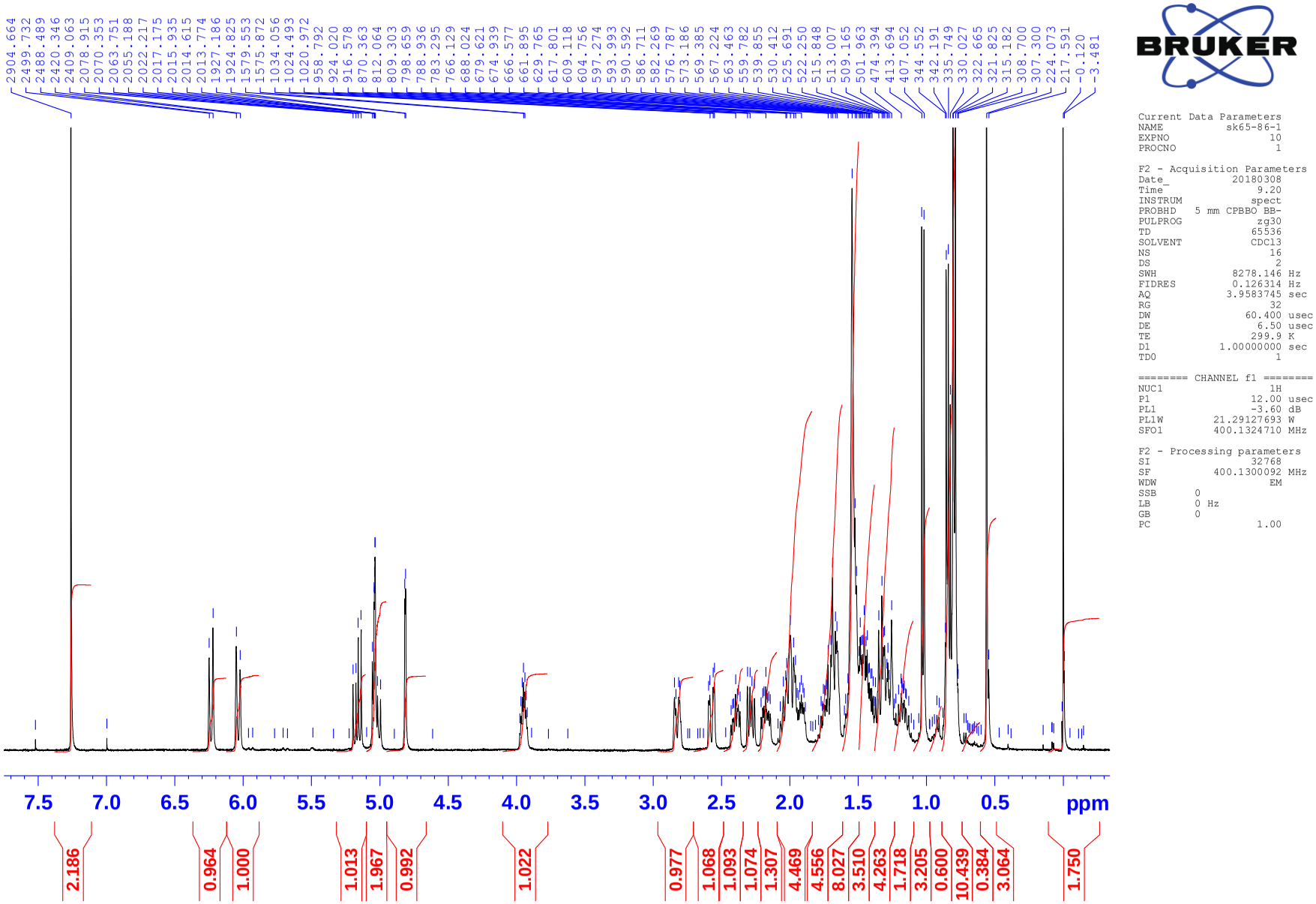
MC2                          QF
SF                100.6127992 MHz
WDW                        SINE
SSB           0
LB            0 Hz
GB            0
```

Figure S17. HMBC NMR spectrum of vitamin D_5 (**6**).




```
Current Data Parameters
NAME                  sk65-86-1
EXPNO                        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                          16
DS                           2
SWH                   8278.146 Hz
FIDRES                0.126314 Hz
AQ                    3.9583745 sec
RG                          32
DW                      60.400 usec
DE                       6.50 usec
TE                      299.9 K
D1                 1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       12.00 usec
PL1                      -3.60 dB
PL1W                21.29127693 W
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. ^{1}H NMR spectrum of vitamin D$_6$ (**8**).

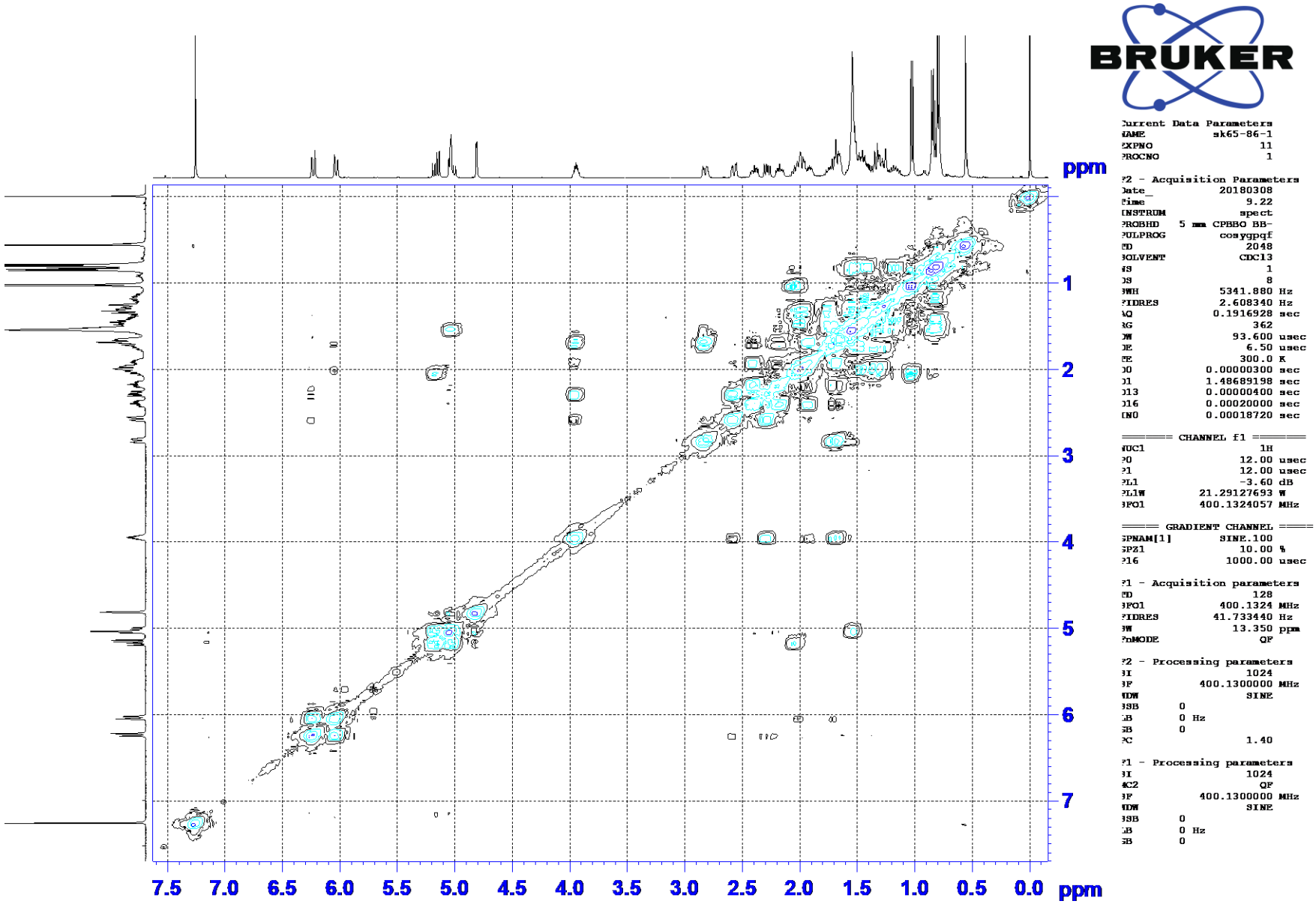


Figure S19. $^{1}H^{1}H$ COSY NMR spectrum of vitamin D_6 (**8**).

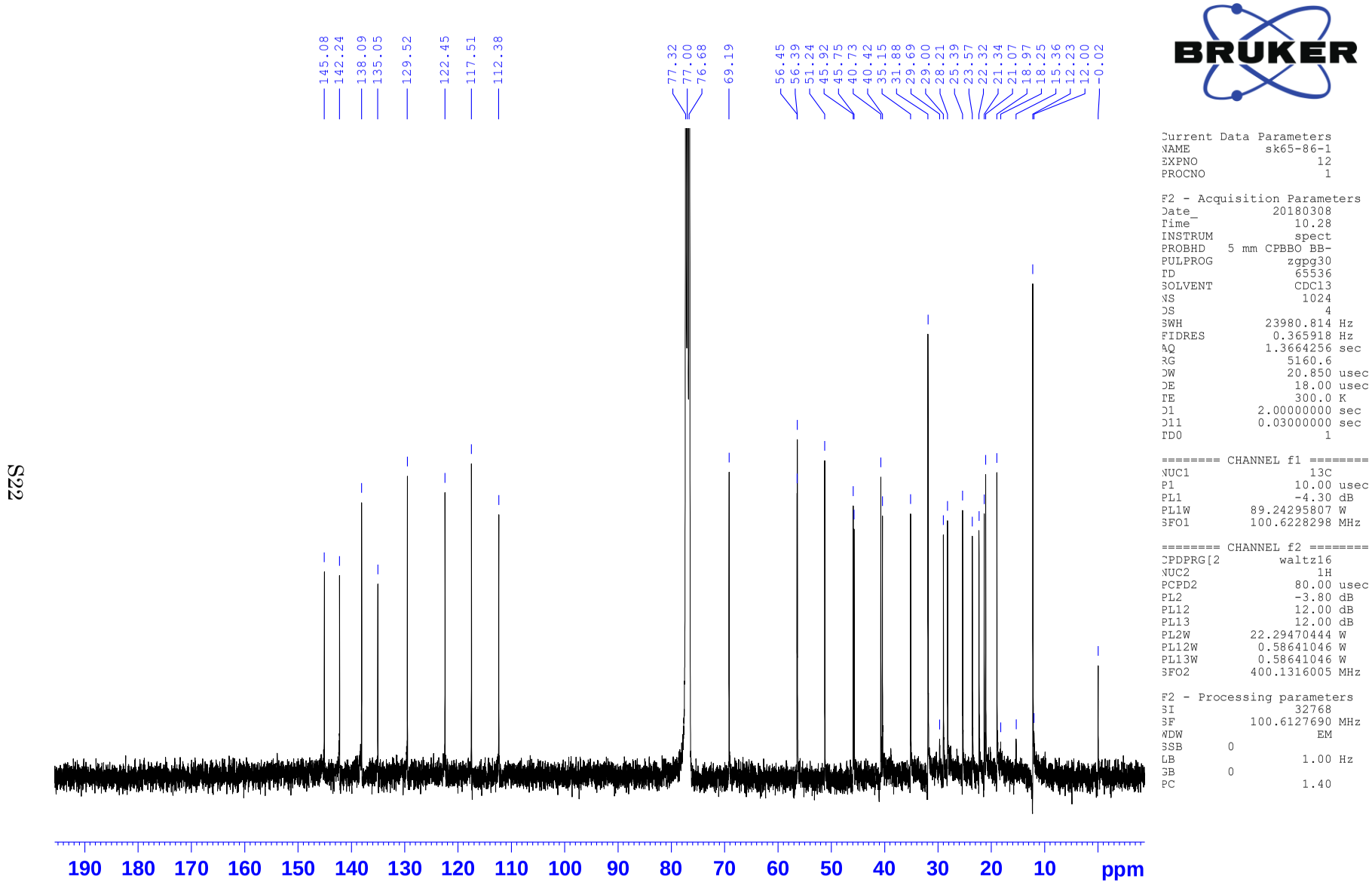
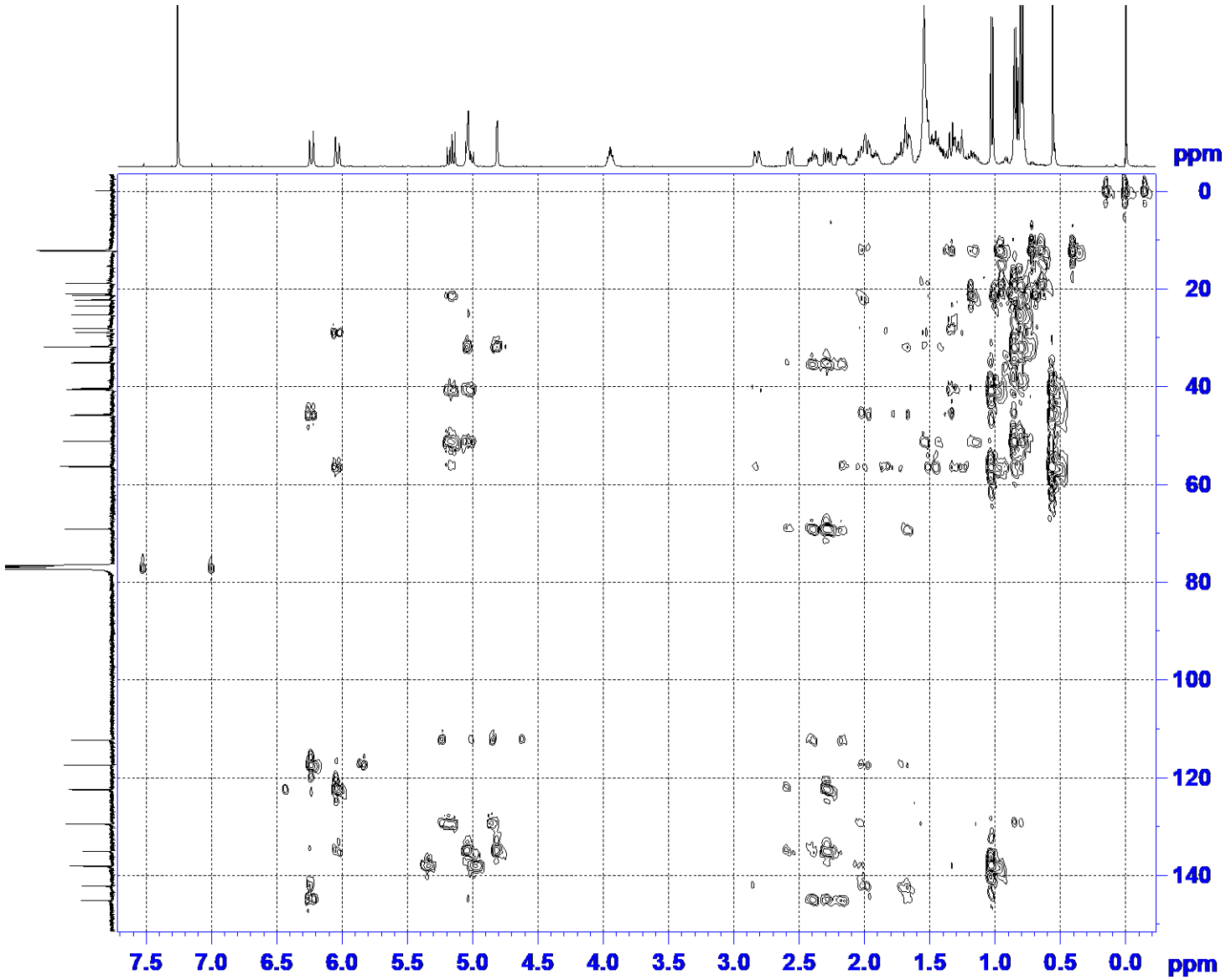


Figure S20. ^{13}C NMR spectrum of vitamin D_6 (**8**).




```
Current Data Parameters
NAME                  sk65-86-1
EXPNO                        14
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20180308
Time                      10.47
INSTRUM                   spect
PROBHD     5 mm CPBBO BB-
PULPROG           hmbcgpndqf
TD                        4096
SOLVENT                 CDCl3
NS                            8
DS                           16
SWH                5341.880 Hz
FIDRES             1.304170 Hz
AQ                 0.3833856 sec
RG                       46341
DW                    93.600 usec
DE                     6.50 usec
TE                    299.9 K
CNST13             8.0000000
D0                 0.00000300 sec
D1                 1.50000000 sec
D6                 0.06250000 sec
D16                0.00020000 sec
IN0                0.00002235 sec

====== CHANNEL f1 ======
NUC1                      1H
P1                     12.00 usec
P2                     24.00 usec
PL1                    -3.60 dB
PL1W            21.29127693 W
SFO1           400.1324057 MHz

====== CHANNEL f2 ======
NUC2                     13C
P3                     10.00 usec
PL2                    -4.30 dB
PL2W            89.24295807 W
SFO2           100.6228138 MHz

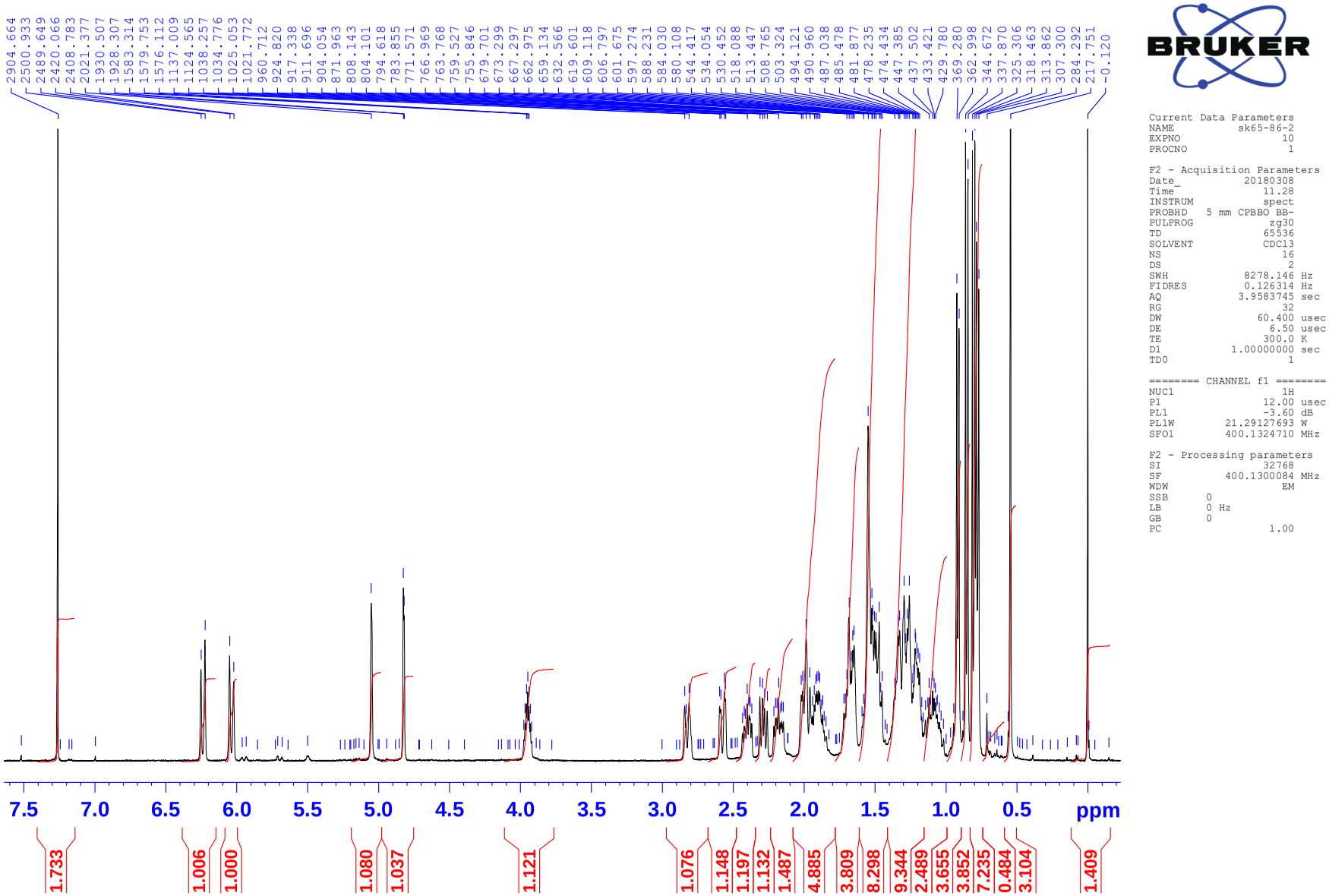
==== GRADIENT CHANNEL ====
GPNAM[1]            SINE.100
GPNAM[2]            SINE.100
GPNAM[3]            SINE.100
GPZ1                   50.00 %
GPZ2                   30.00 %
GPZ3                   40.10 %
P16                  1000.00 usec

F1 - Acquisition parameters
TD                         128
SFO1              100.6228 MHz
FIDRES           174.592422 Hz
SW                  222.095 ppm
FnMODE                     QF

F2 - Processing parameters
SI                        1024
SF             400.1300033 MHz
WDW                       SINE
SSB          0
LB           0 Hz
GB           0
PC                        1.40

F1 - Processing parameters
SI                        1024
MC2                        QF
SF             100.6127717 MHz
WDW                       SINE
SSB          0
LB           0 Hz
GB           0
```

Figure S21. HMBC NMR spectrum of vitamin D_6 (**8**).




```
Current Data Parameters
NAME                  sk65-86-2
EXPNO                        10
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20180308
Time                      11.28
INSTRUM                   spect
PROBHD    5 mm CPBBO BB-
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          16
DS                           2
SWH                   8278.146 Hz
FIDRES                0.126314 Hz
AQ                    3.9583745 sec
RG                          32
DW                       60.400 usec
DE                        6.50 usec
TE                       300.0 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                       12.00 usec
PL1                      -3.60 dB
PL1W                21.29127693 W
SFO1                400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF                  400.1300084 MHz
WDW                         EM
SSB          0
LB           0 Hz
GB           0
PC                        1.00
```

Figure S22. ^{1}H NMR spectrum of vitamin D$_7$ (**7**).

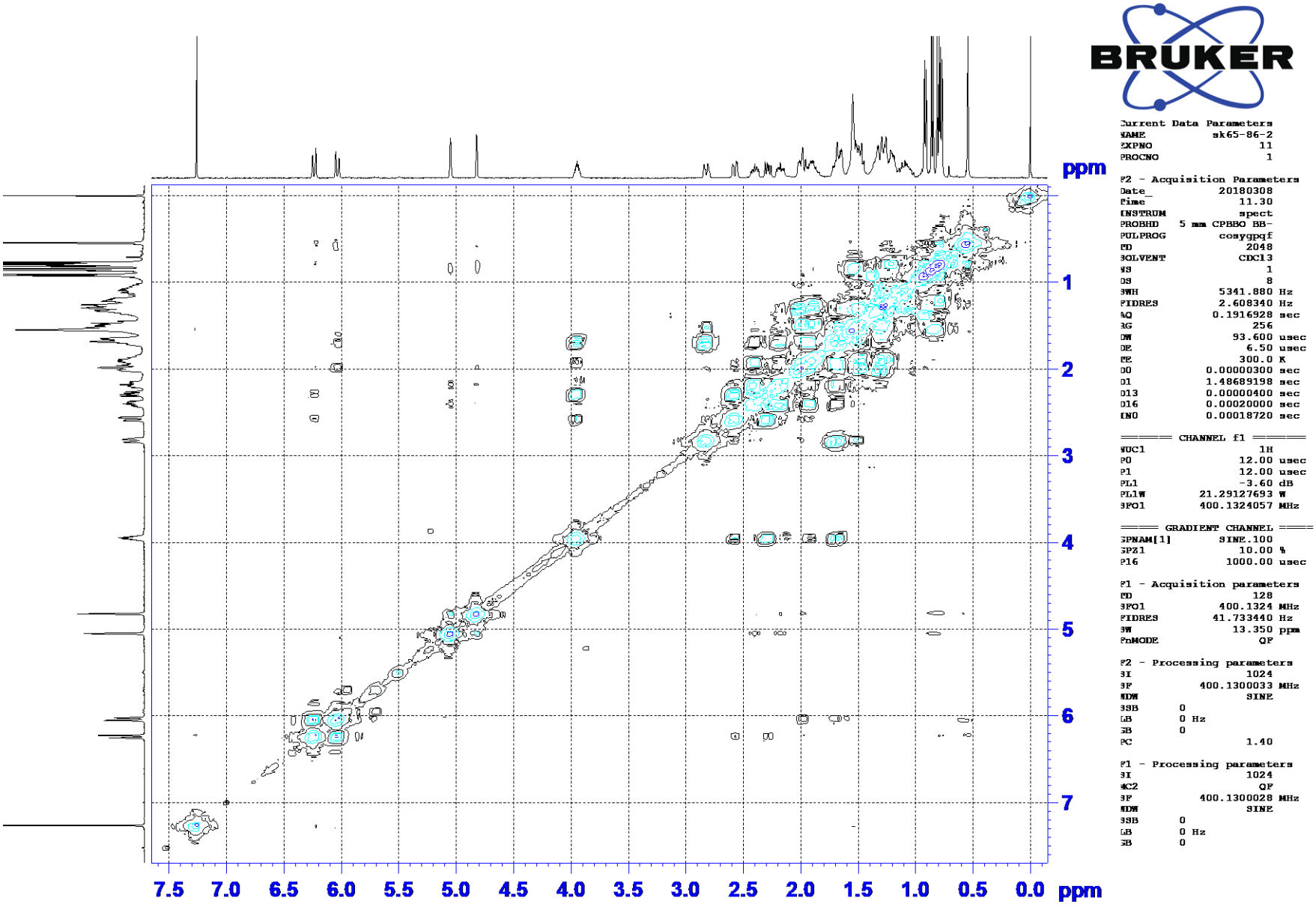
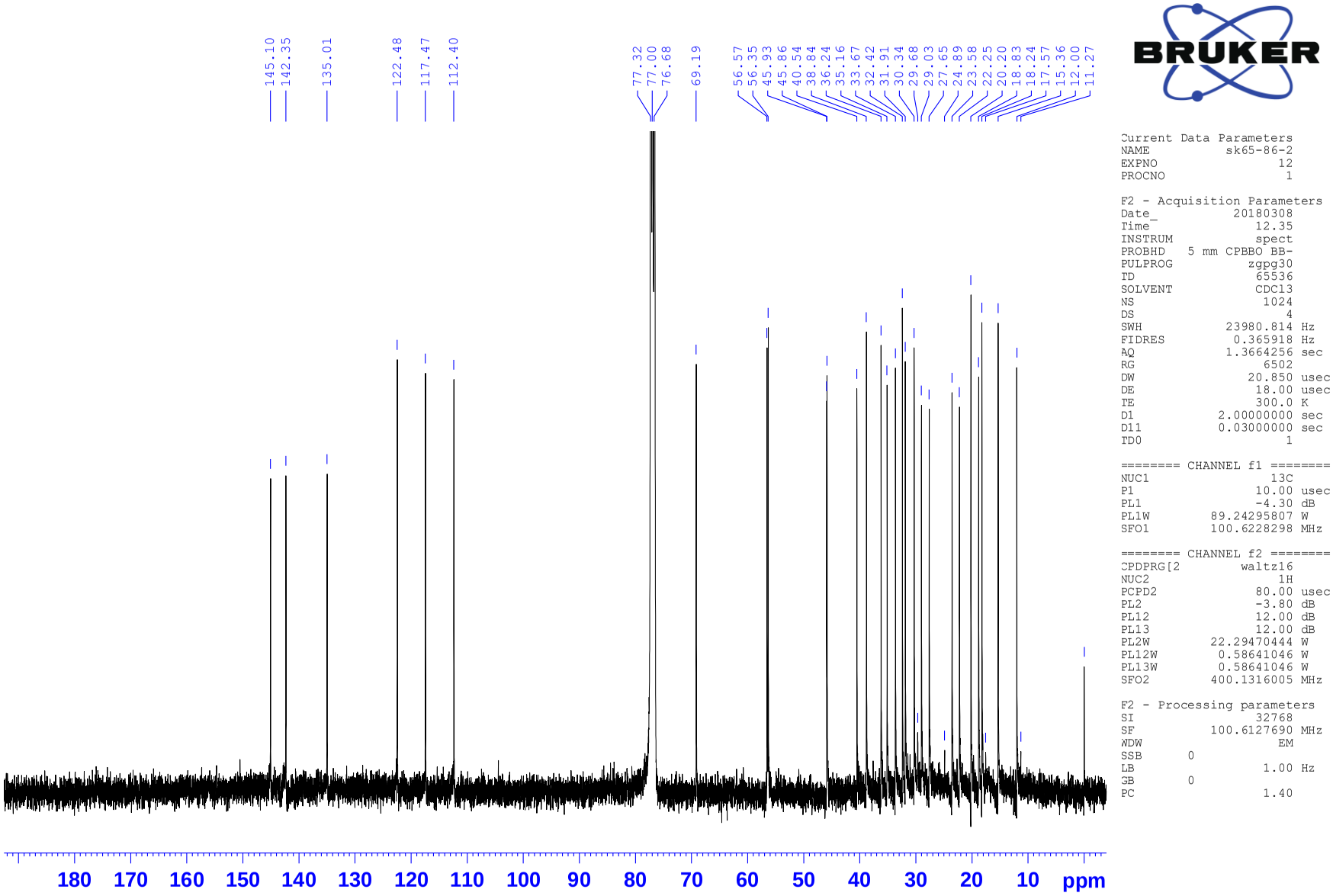


Figure S23. $^{1}H^{1}H$ COSY NMR spectrum of vitamin D_7 (**7**).




```
Current Data Parameters
NAME                 sk65-86-2
EXPNO                       12
PROCNO                       1

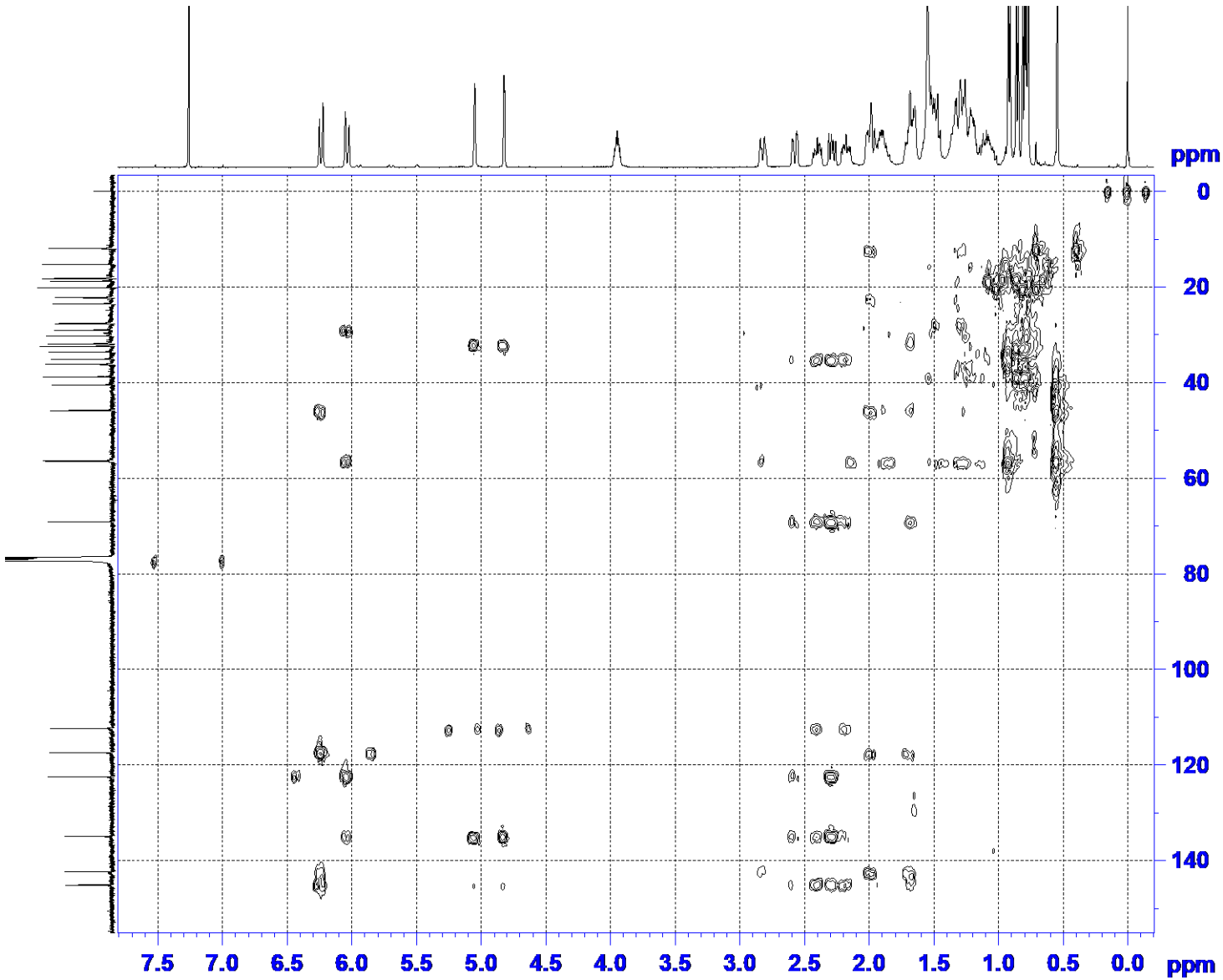
F2 - Acquisition Parameters
Date_               20180308
Time                    12.35
INSTRUM                 spect
PROBHD    5 mm CPBBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1024
DS                           4
SWH                  23980.814 Hz
FIDRES                0.365918 Hz
AQ                    1.3664256 sec
RG                        6502
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 ========
CPDPRG[2               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
WDW                         EM
SSB             0
LB                       1.00 Hz
GB              0
PC                       1.40
```

Figure S24. ^{13}C NMR spectrum of vitamin D_7 (**7**).




```
Current Data Parameters
NAME                  sk65-86-2
EXPNO                        14
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20180308
Time                      12.55
INSTRUM                   spect
PROBHD    5 mm CPBBO BB-
PULPROG            hmbcgpndqf
TD                        4096
SOLVENT                  CDCl3
NS                           8
DS                          16
SWH                 5341.880 Hz
FIDRES              1.304170 Hz
AQ                  0.3833856 sec
RG                        46341
DW                     93.600 usec
DE                      6.50 usec
TE                      300.0 K
CNST13               8.0000000
D0                  0.00000300 sec
D1                  1.50000000 sec
D6                  0.06250000 sec
D16                 0.00020000 sec
IN0                 0.00002235 sec

======== CHANNEL f1 =======
NUC1                        1H
P1                      12.00 usec
P2                      24.00 usec
PL1                     -3.60 dB
PL1W             21.29127693 W
SFO1             400.1324057 MHz

======== CHANNEL f2 =======
NUC2                       13C
P3                      10.00 usec
PL2                     -4.30 dB
PL2W             89.24295807 W
SFO2             100.6228138 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                         128
SFO1                100.6228 MHz
FIDRES              174.592422 Hz
SW                  222.095 ppm
FnMODE                     QF

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

F1 - Processing parameters
SI                        1024
MC2                         QF
SF                100.6127690 MHz
WDW                       SINE
SSB          0
LB           0 Hz
GB           0
```

Figure S25. HMBC NMR spectrum of vitamin D_7 (**7**).