SUPPLEMENTARY MATERIAL

Exploration of the electrophilic reactivity of the cytotoxic marine alkaloid discorhabdin C and subsequent discovery of a new dimeric C-1/N-13-linked discorhabdin natural product

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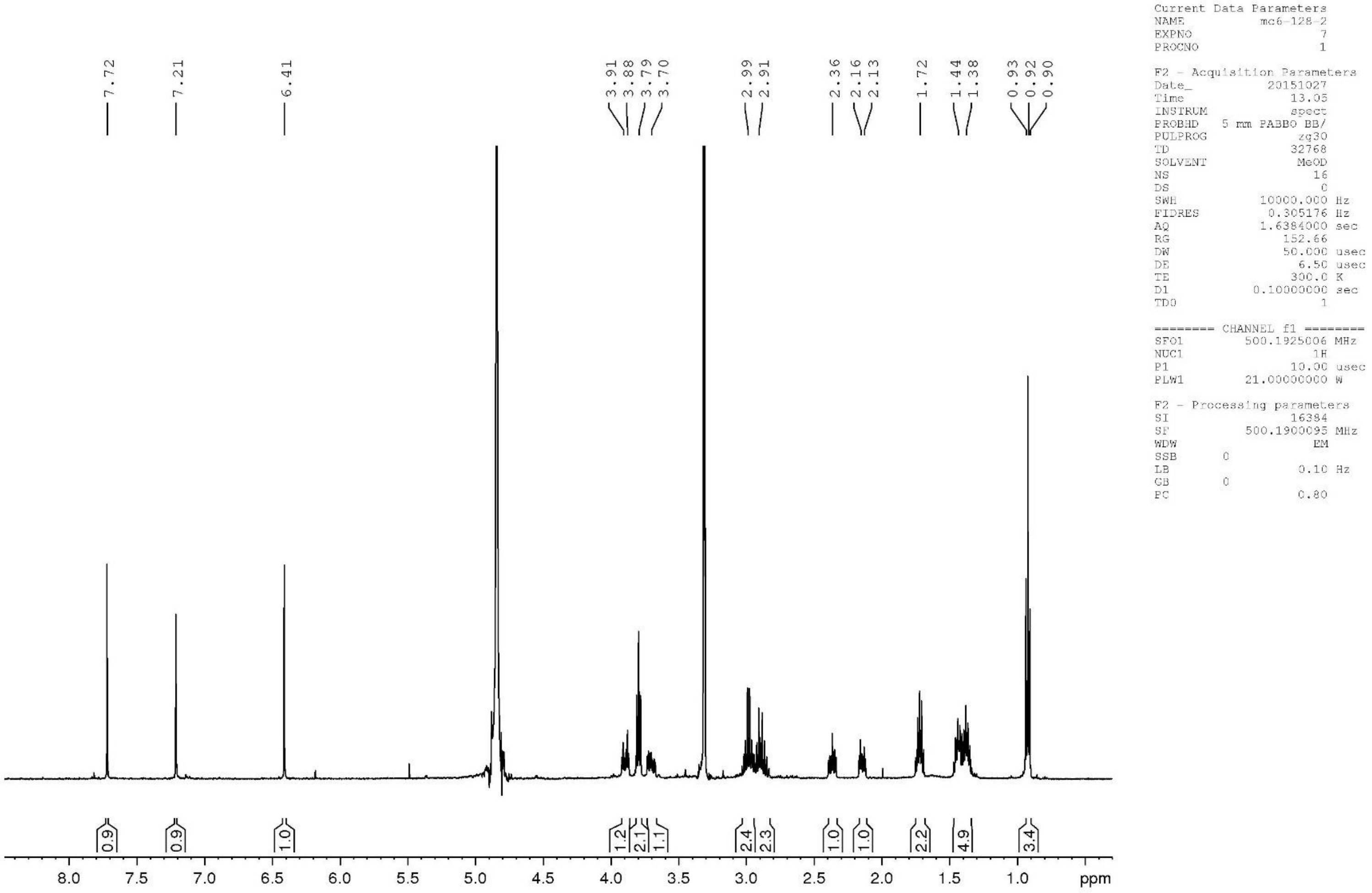

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NAME             mc6-128-2
EXPNO                    7
PROCNO                   1

F2 - Acquisition Parameters
Date_             20151027
Time                 13.05
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG               zg30
TD                   32768
SOLVENT               MeOD
NS                      16
DS                       0
SWH              10000.000 Hz
FIDRES            0.305176 Hz
AQ               1.6384000 sec
RG                  152.66
DW                  50.000 usec
DE                    6.50 usec
TE                   300.0 K
D1              0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           500.1925006 MHz
NUC1                    1H
P1                   10.00 usec
PLW1           21.00000000 W

F2 - Processing parameters
SI                   16384
SF             500.1900095 MHz
WDW                     EM
SSB      0
LB                    0.10 Hz
GB       0
PC                    0.80
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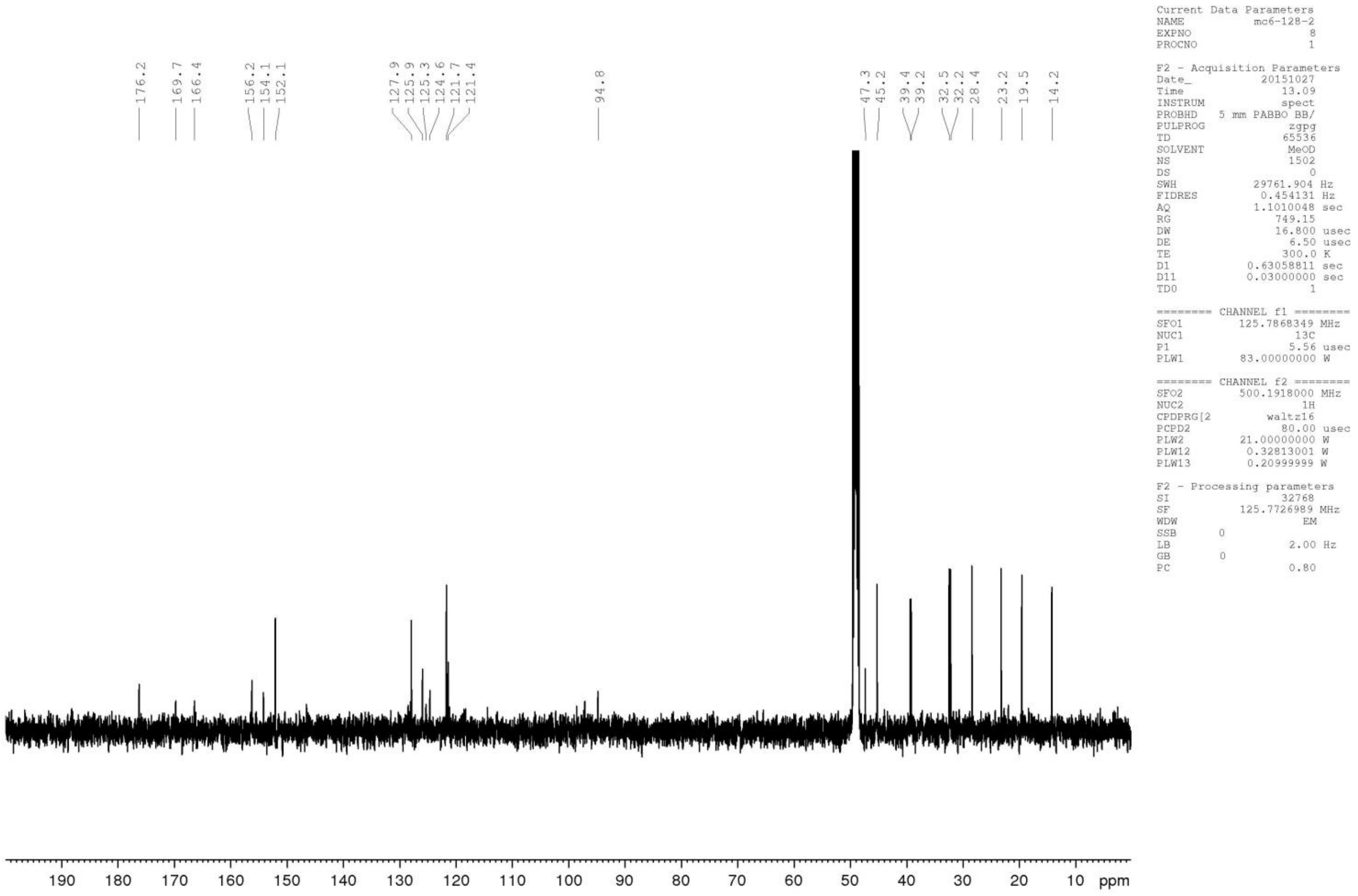
Figure S1. ^{1}H NMR spectrum of compound **4** (TFA salt, CD_3OD, 500 MHz).



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EXPNO                   8
PROCNO                  1

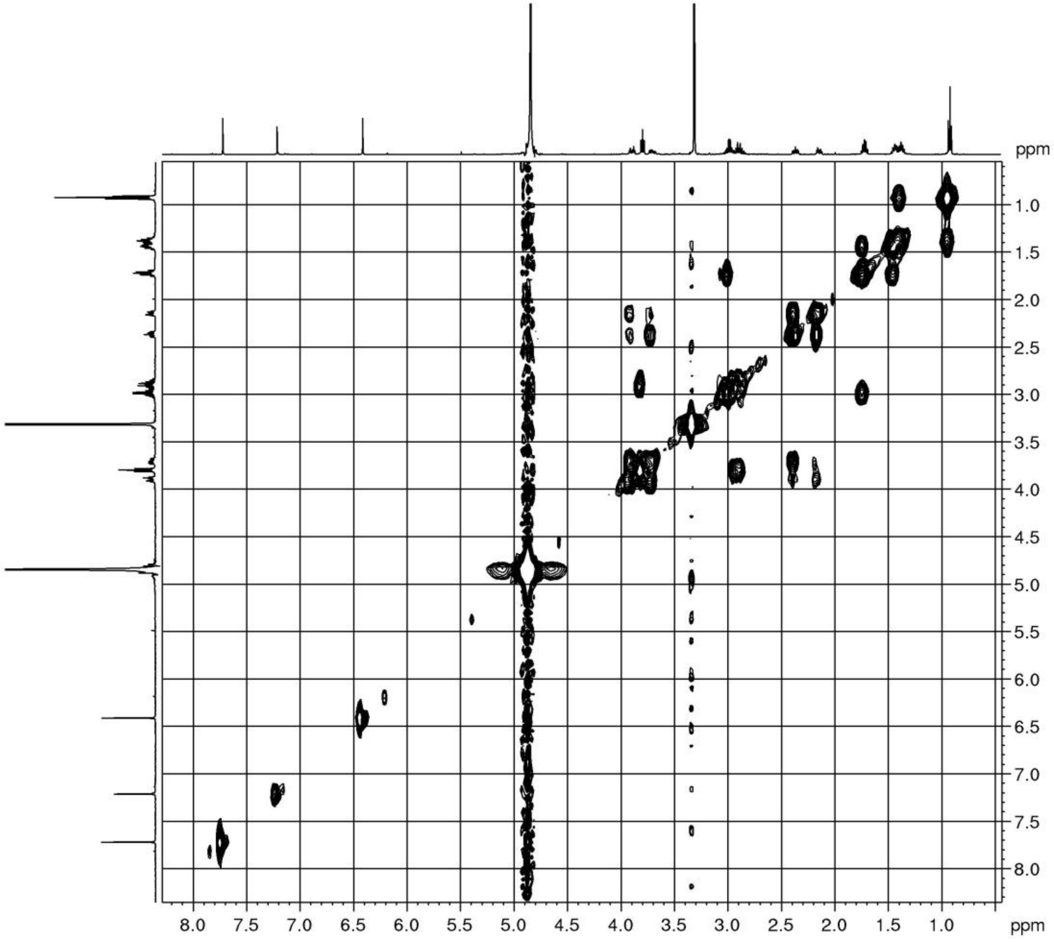
F2 - Acquisition Parameters
Date_            20151027
Time                13.09
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zgpg
TD                  65536
SOLVENT              MeOD
NS                   1502
DS                      0
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010048 sec
RG                 749.15
DW                 16.800 usec
DE                   6.50 usec
TE                  300.0 K
D1             0.63058811 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         125.7868349 MHz
NUC1                  13C
P1                   5.56 usec
PLW1          83.00000000 W

======== CHANNEL f2 ========
SFO2         500.1918000 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          21.00000000 W
PLW12          0.32813001 W
PLW13          0.20999999 W

F2 - Processing parameters
SI                  32768
SF           125.7726989 MHz
WDW                    EM
SSB      0
LB                   2.00 Hz
GB       0
PC                   0.80
```

Figure S2. ^{13}C NMR spectrum of compound **4** (TFA salt, CD_3OD, 125 MHz).



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Current Data Parameters
NAME             mc6-128-2
EXPNO                    9
PROCNO                   1

F2 - Acquisition Parameters
Date_             20151027
Time                 13.54
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG         cosygpppqf
TD                    2048
SOLVENT               MeOD
NS                       1
DS                       8
SWH              10000.000 Hz
FIDRES            4.882813 Hz
AQ               0.1024000 sec
RG                  312.43
DW                  50.000 usec
DE                    6.50 usec
TE                   300.0 K
D0              0.00000300 sec
D1              1.39999998 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00010000 sec

======== CHANNEL f1 ========
SFO1           500.1925006 MHz
NUC1                    1H
P0                   10.00 usec
P1                   10.00 usec
P17                2500.00 usec
PLW1           21.00000000 W
PLW10           3.10649991 W

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPZ1                 10.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                     256
SFO1              500.1925 MHz
FIDRES           78.125000 Hz
SW                  19.992 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF             500.1900000 MHz
WDW                   SINE
SSB       0
LB        0 Hz
GB        0
PC                    0.80

F1 - Processing parameters
SI                     256
MC2                     QF
SF             500.1900000 MHz
WDW                   SINE
SSB       0
LB        0 Hz
GB        0
```
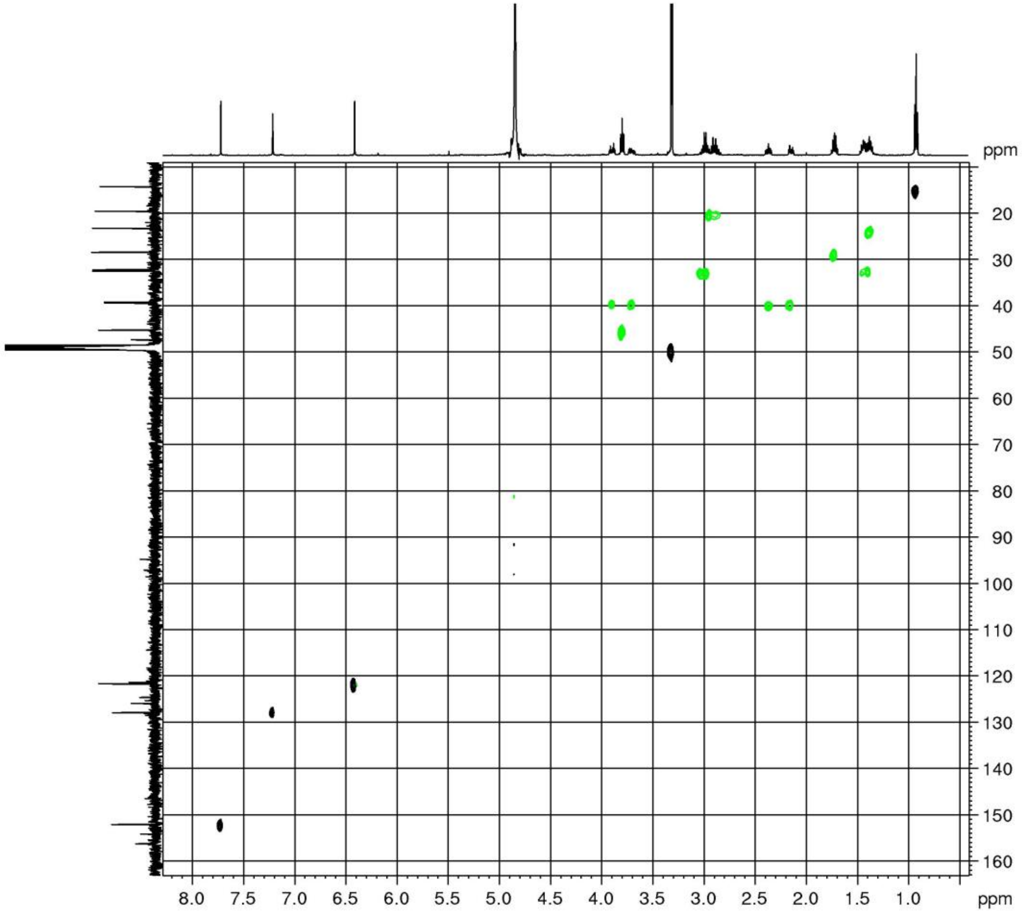

Figure S3. COSY spectrum of compound **4** (TFA salt, CD_3OD, 500 MHz).



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Current Data Parameters
NAME           mc6-128-2
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20151027
Time               14.02
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG  hsqcedetgpsisp.2
TD                  2048
SOLVENT             MeOD
NS                     2
DS                    16
SWH            10000.000 Hz
FIDRES          4.882813 Hz
AQ             0.1024000 sec
RG                635.04
DW                50.000 usec
DE                  6.50 usec
TE                 300.2 K
CNST2        140.0000000
CNST17        -0.5000000
D0            0.00000300 sec
D1            1.00000000 sec
D4            0.00178571 sec
D11           0.03000000 sec
D16           0.00020000 sec
D21           0.00357143 sec
D24           0.00089286 sec
IN0           0.00001670 sec

======== CHANNEL f1 ========
SFO1         500.1925006 MHz
NUC1                  1H
P1                 10.00 usec
P2                 20.00 usec
P28              1000.00 usec
PLW1         21.00000000 W

======== CHANNEL f2 ========
SFO2         125.7868347 MHz
NUC2                 13C
CPDPRG[2            garp
P3                 10.00 usec
P14               500.00 usec
P24              2000.00 usec
PCPD2              70.00 usec
PLW0      0 W
PLW2         83.00000000 W
PLW12         1.69389999 W
SPNAM[3] Crp60,0.5,20.1
SPOAL3             0.500
SPOFFS3   0 Hz
SPW3         12.68099976 W
SPNAM[7]    Crp60comp.4
SPOAL7             0.500
SPOFFS7   0 Hz
SPW7         12.68099976 W

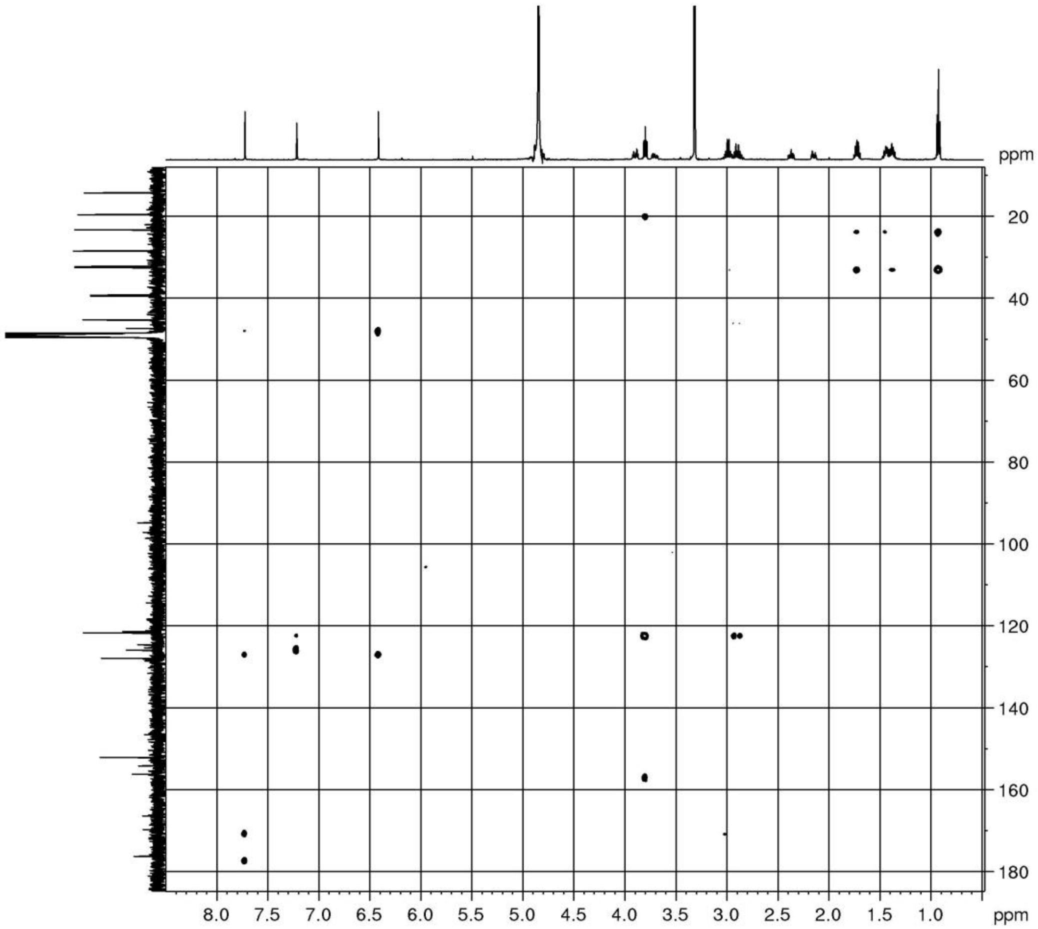
====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   256
SFO1            125.7868 MHz
FIDRES        233.907181 Hz
SW               238.023 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF           500.1900057 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
PC                  0.80

F1 - Processing parameters
SI                   256
MC2       echo-antiecho
SF           125.7726192 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
```

Figure S4. HSQC spectrum of compound **4** (TFA salt, CD_3OD, 500 MHz).



```
Current Data Parameters
NAME          mc6-128-2
EXPNO                12
PROCNO                1

F2 - Acquisition Parameters
Date_          20151027
Time              14.13
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG  impact-hmbc.ms
TD                 2048
SOLVENT            MeOD
NS                    8
DS                   64
SWH           10000.000 Hz
FIDRES         4.882813 Hz
AQ            0.1024000 sec
RG                 2050
DW               50.000 usec
DE                 6.50 usec
TE                300.0 K
CNST6       125.0000000
CNST7       165.0000000
CNST13        8.3299999
CNST30        0.5981119
D0           0.00000300 sec
D1           0.20000000 sec
D9           0.04000000 sec
D11          0.03000000 sec
D12          0.00002000 sec
D16          0.00020000 sec
D20          0.00214160 sec
IN0          0.00001670 sec
IN20         0.00001670 sec
L1                   14
P1                10.00 usec

======== CHANNEL f1 ========
SFO1        500.1925006 MHz
NUC1                 1H
P0                14.44 usec
P2                20.00 usec
P6                26.00 usec
PLW1        21.00000000 W
PLW10        3.10649991 W

======== CHANNEL f2 ========
SFO2        125.7868347 MHz
NUC2                13C
P3                10.00 usec
P24             2000.00 usec
PLW2        83.00000000 W
SPNAM[7]    Crp60comp.4
SPOAL7            0.500
SPOFFS7  0 Hz
SPW7        12.68099976 W

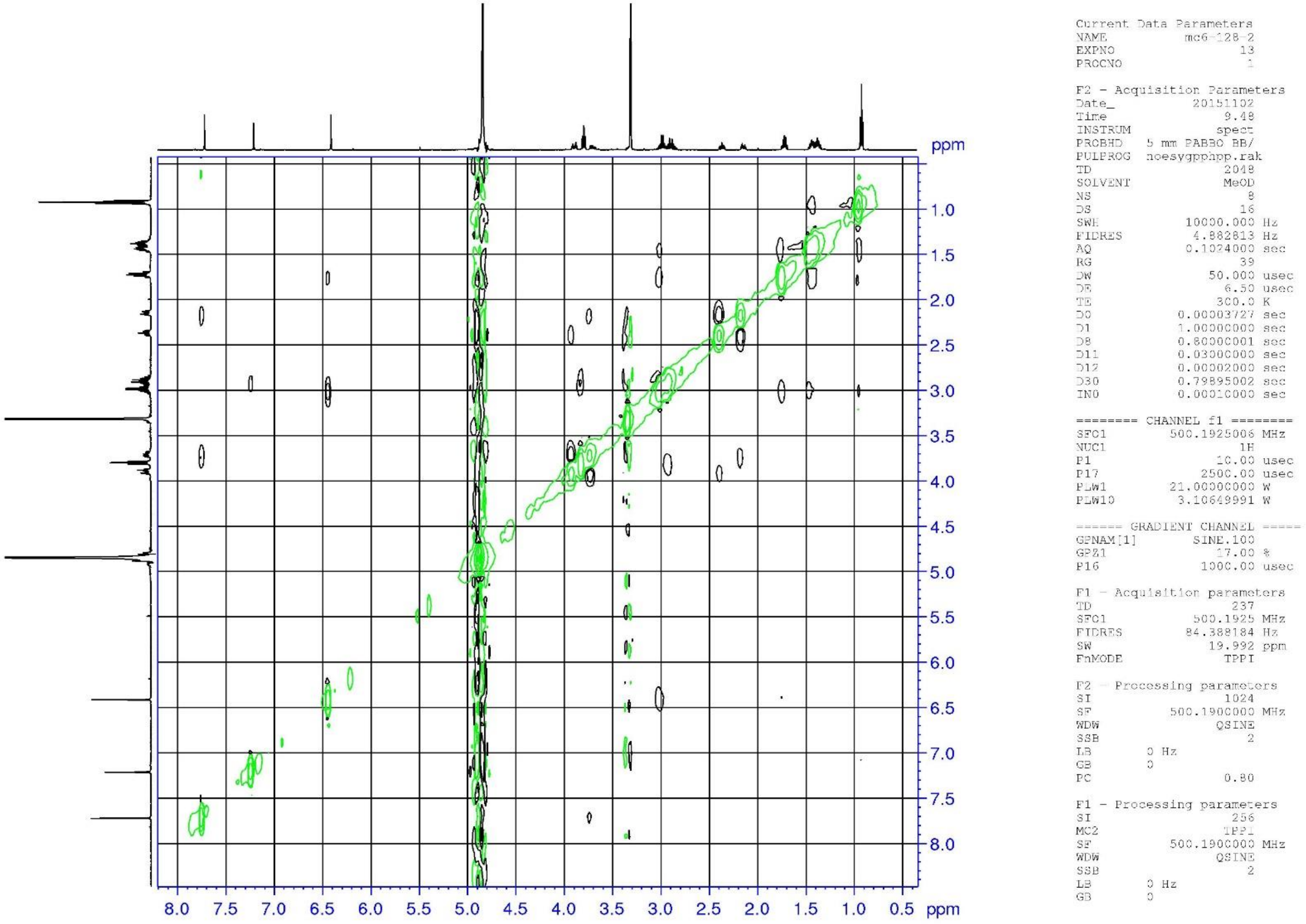
====== GRADIENT CHANNEL =====
GPNAM[1]       SINE.100
GPNAM[2]       SINE.100
GPNAM[3]       SINE.100
GPNAM[4]       SINE.100
GPNAM[5]       SINE.100
GPNAM[6]       SINE.100
GPZ1              80.00 %
GPZ2              37.00 %
GPZ3             -19.00 %
GPZ4             -11.00 %
GPZ5              -7.00 %
GPZ6             -17.00 %
P16             1000.00 usec

F1 - Acquisition parameters
TD                  256
SFO1           125.7868 MHz
FIDRES       233.907181 Hz
SW              238.023 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                 2048
SF          500.1900191 MHz
WDW               QSINE
SSB                   8
LB         0 Hz
GB         0
PC                 0.80

F1 - Processing parameters
SI                  256
MC2      echo-antiecho
SF          125.7726257 MHz
WDW               QSINE
SSB                   2
LB         0 Hz
GB         0
```

Figure S5. HMBC spectrum of compound **4** (TFA salt, CD_3OD, 500 MHz).



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Current Data Parameters
NAME            mc6-128-2
EXPNO                  13
PROCNO                  1

F2 - Acquisition Parameters
Date_            20151102
Time                 9.48
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG  noesygpphpp.rak
TD                   2048
SOLVENT              MeOD
NS                      8
DS                     16
SWH             10000.000 Hz
FIDRES           4.882813 Hz
AQ              0.1024000 sec
RG                     39
DW                 50.000 usec
DE                   6.50 usec
TE                  300.0 K
D0             0.00003727 sec
D1             1.00000000 sec
D8             0.80000001 sec
D11            0.03000000 sec
D12            0.00002000 sec
D30            0.79895002 sec
IN0            0.00010000 sec

======== CHANNEL f1 ========
SFO1          500.1925006 MHz
NUC1                   1H
P1                  10.00 usec
P17               2500.00 usec
PLW1          21.00000000 W
PLW10          3.10649991 W

====== GRADIENT CHANNEL =====
GPNAM[1]         SINE.100
GPZ1                17.00 %
P16               1000.00 usec

F1 - Acquisition parameters
TD                    237
SFO1             500.1925 MHz
FIDRES          84.388184 Hz
SW                 19.992 ppm
FnMODE               TPPI

F2 - Processing parameters
SI                   1024
SF            500.1900000 MHz
WDW                 QSINE
SSB                     2
LB          0 Hz
GB          0
PC                   0.80

F1 - Processing parameters
SI                    256
MC2                  TPPI
SF            500.1900000 MHz
WDW                 QSINE
SSB                     2
LB          0 Hz
GB          0
```

Figure S6. NOESY spectrum of compound **4** (600 ms mixing time, TFA salt, CD_3OD, 500 MHz).

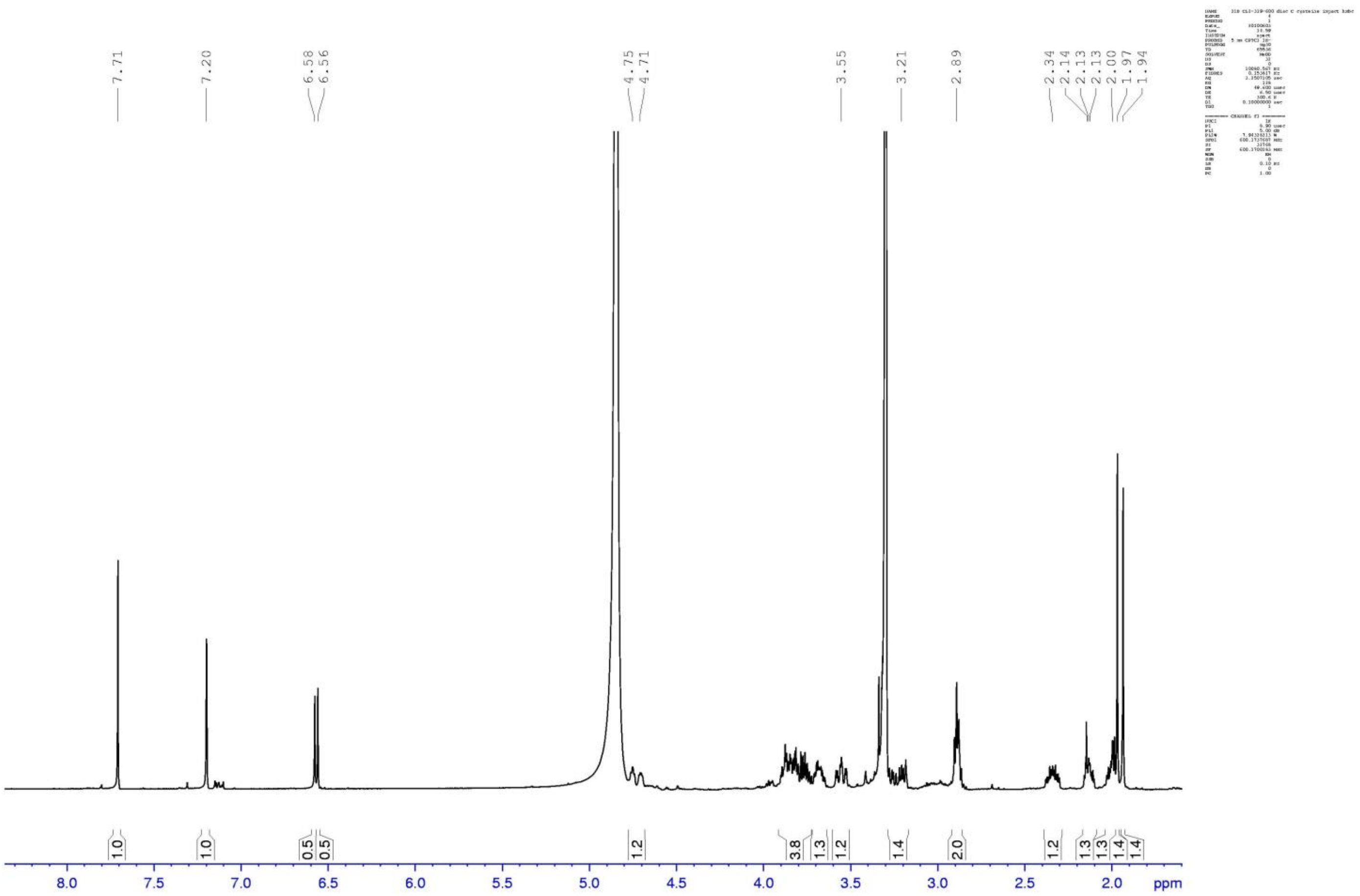


Figure S7. ^{1}H NMR spectrum of compound **5** (TFA salt, CD_3OD, 600 MHz).

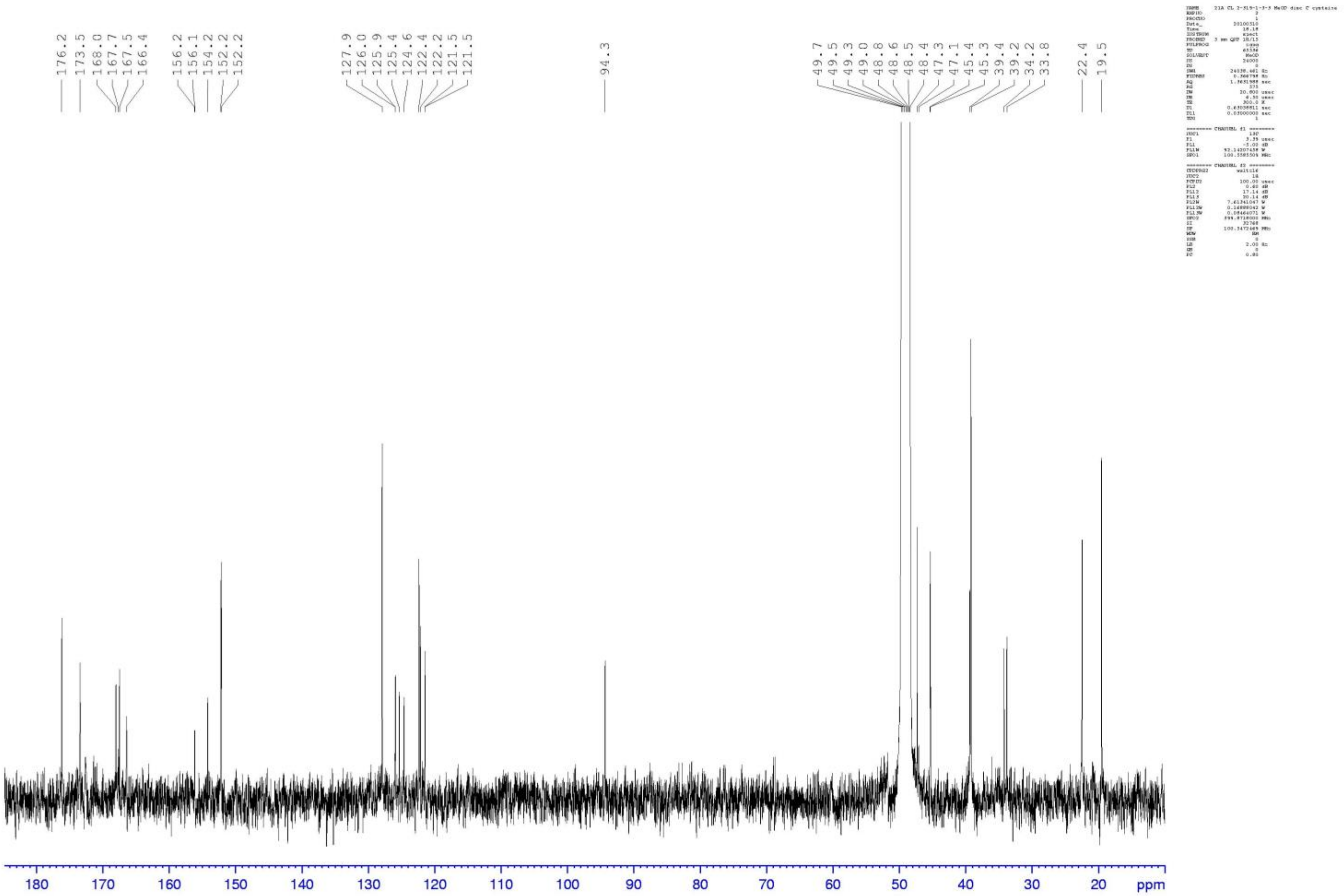
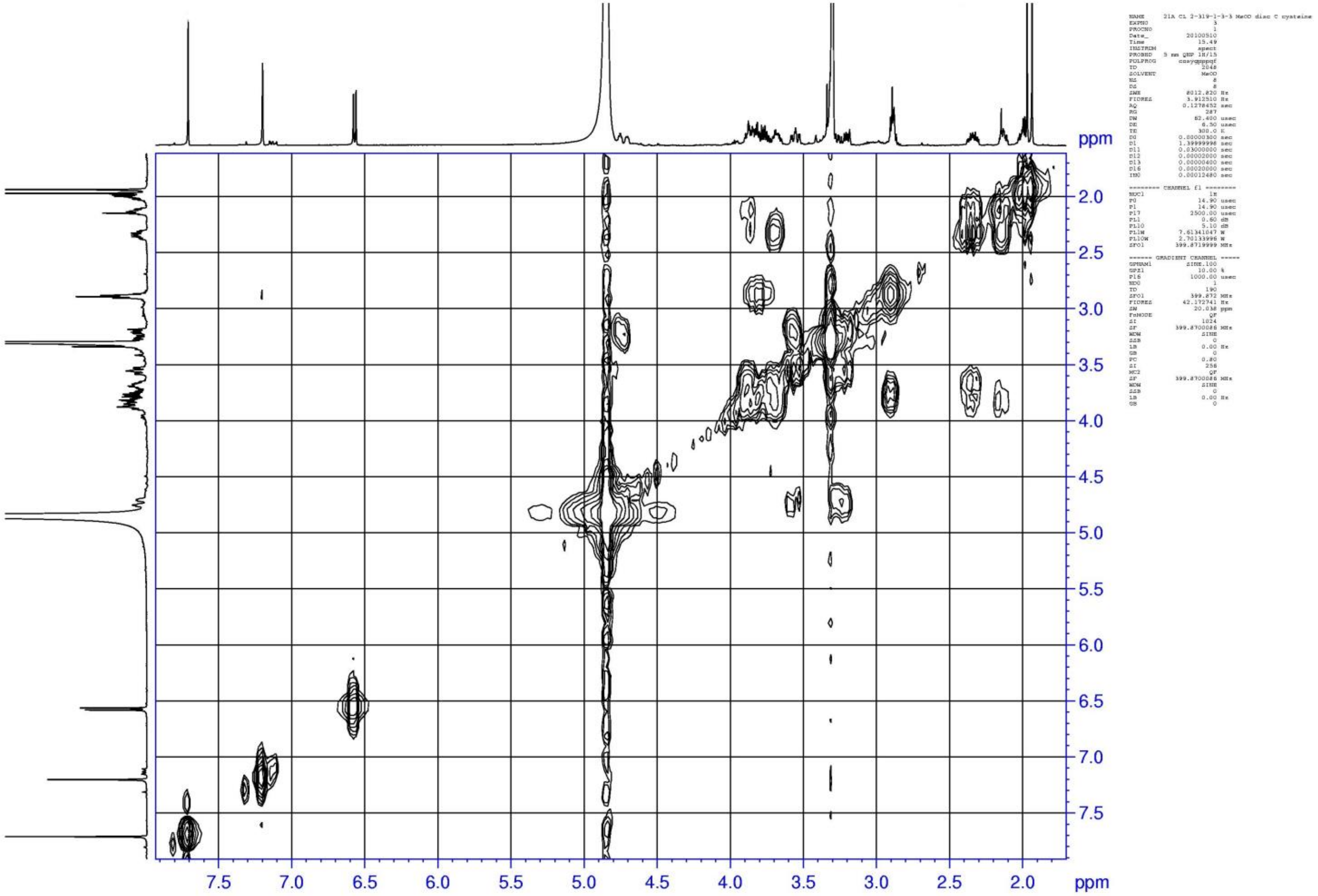


Figure S8. ^{13}C NMR spectrum of compound **5** (TFA salt, CD_3OD, 100 MHz).



```
NAME       21A CL 2-319-1-3-3 MeOD disc C cysteine
EXPNO                    3
PROCNO                   1
Date_             20100510
Time                 15.49
INSTRUM              spect
PROBHD   5 mm QNP 1H/15
PULPROG         cosygpppqf
TD                    2048
SOLVENT               MeOD
NS                       8
DS                       8
SWH               8012.820 Hz
FIDRES            3.912510 Hz
AQ               0.1278452 sec
RG                     287
DW                  62.400 usec
DE                    6.50 usec
TE                   300.0 K
D0              0.00000300 sec
D1              1.39999998 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00012480 sec

======== CHANNEL f1 ========
NUC1                    1H
P0                   14.90 usec
P1                   14.90 usec
P17                2500.00 usec
PL1                   0.60 dB
PL10                  5.10 dB
PL1W            7.61341047 W
PL10W           2.70133996 W
SFO1           399.8719999 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPZ1                 10.00 %
P16                1000.00 usec
ND0                      1
TD                     190
SFO1               399.872 MHz
FIDRES           42.172741 Hz
SW                  20.038 ppm
FnMODE                  QF
SI                    1024
SF             399.8700086 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    0.80
SI                     256
MC2                     QF
SF             399.8700086 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
```

Figure S9. COSY spectrum of compound **5** (TFA salt, CD_3OD, 400 MHz).

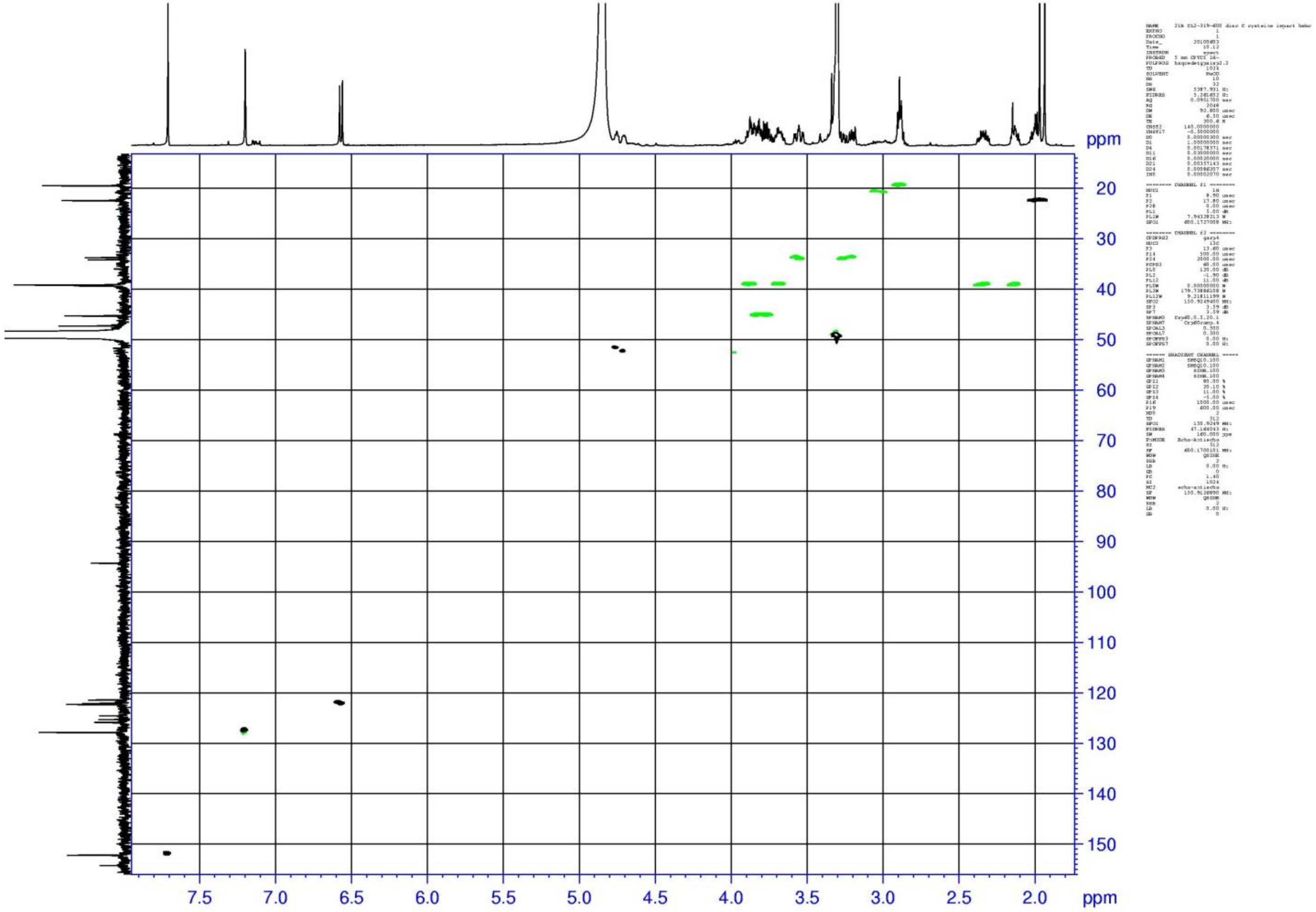
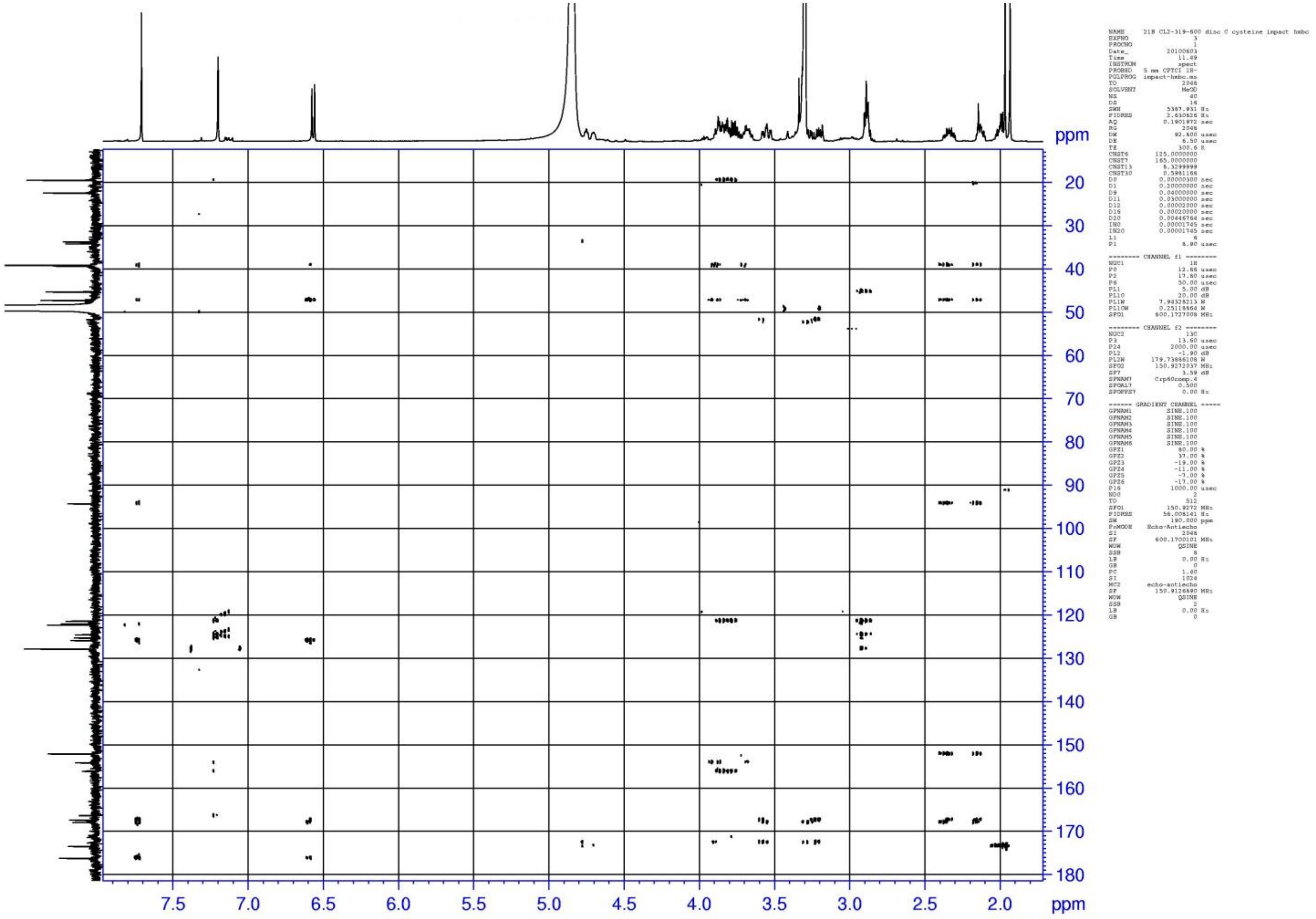
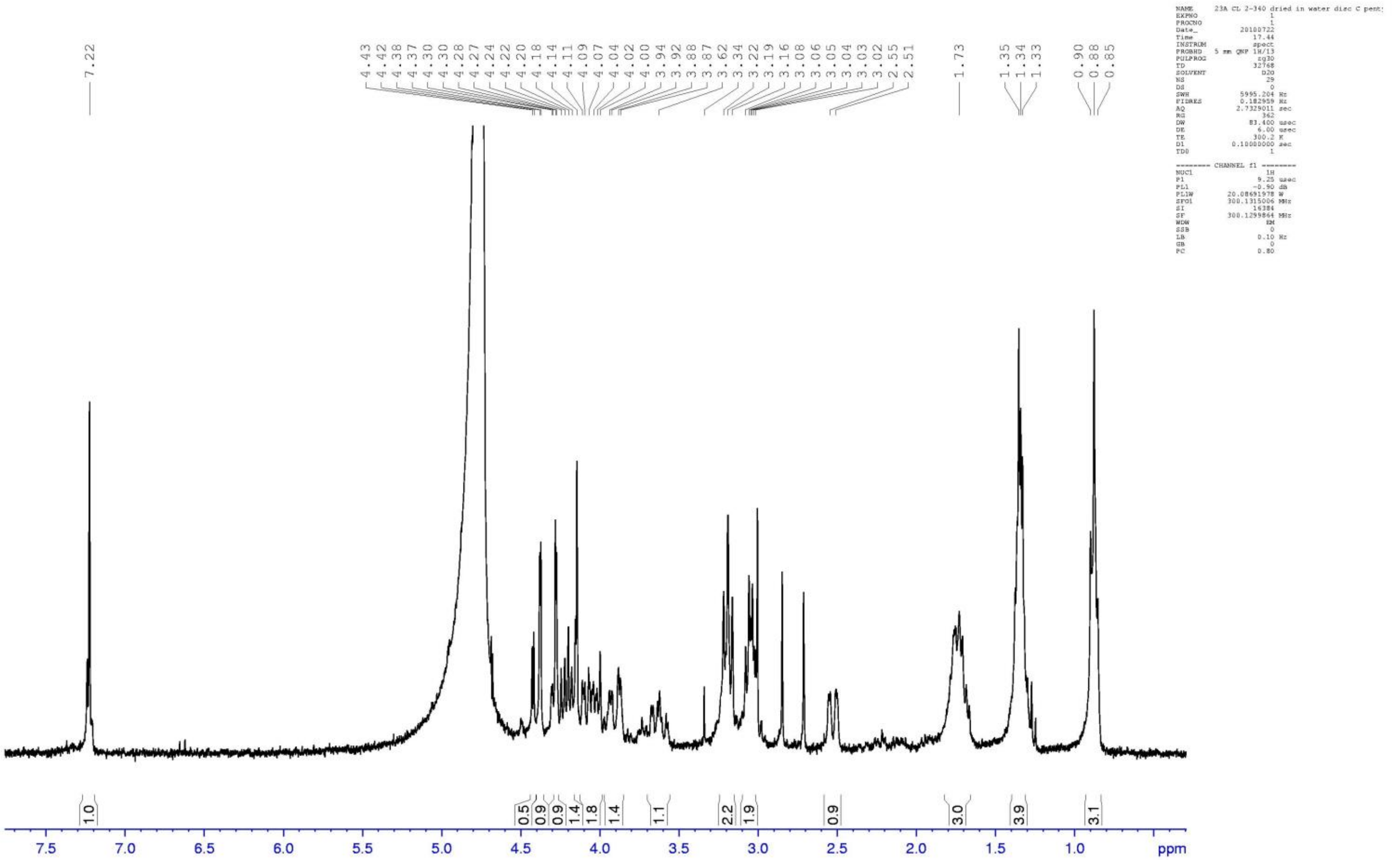


Figure S10. HSQC spectrum of compound **5** (TFA salt, CD_3OD, 600 MHz).



```
NAME      21B CL2-319-600 disc C cysteine impact hmbc
EXPNO                    3
PROCNO                   1
Date_             20100603
Time                 11.49
INSTRUM              spect
PROBHD    5 mm CPTCI 1H-
PULPROG   impact-hmbc.ms
TD                    2048
SOLVENT               MeOD
NS                      40
DS                      16
SWH               5387.931 Hz
FIDRES            2.630826 Hz
AQ               0.1901972 sec
RG                    2048
DW                  92.800 usec
DE                    6.50 usec
TE                   300.6 K
CNST6          125.0000000
CNST7          165.0000000
CNST13           8.3299999
CNST30           0.5981168
D0              0.00000300 sec
D1              0.20000000 sec
D9              0.04000000 sec
D11             0.03000000 sec
D12             0.00002000 sec
D16             0.00020000 sec
D20             0.00446764 sec
IN0             0.00001745 sec
IN20            0.00001745 sec
L1                       6
P1                    8.90 usec

======== CHANNEL f1 ========
NUC1                    1H
P0                   12.66 usec
P2                   17.80 usec
P6                   50.00 usec
PL1                   5.00 dB
PL10                 20.00 dB
PL1W            7.94328213 W
PL10W           0.25118864 W
SFO1           600.1727008 MHz

======== CHANNEL f2 ========
NUC2                   13C
P3                   13.60 usec
P24                2000.00 usec
PL2                  -1.90 dB
PL2W          179.73886108 W
SFO2           150.9272037 MHz
SP7                   3.59 dB
SPNAM7         Crp60comp.4
SPOAL7               0.500
SPOFFS7               0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPNAM3            SINE.100
GPNAM4            SINE.100
GPNAM5            SINE.100
GPNAM6            SINE.100
GPZ1                 80.00 %
GPZ2                 37.00 %
GPZ3                -19.00 %
GPZ4                -11.00 %
GPZ5                 -7.00 %
GPZ6                -17.00 %
P16                1000.00 usec
ND0                      2
TD                     512
SFO1              150.9272 MHz
FIDRES           56.008141 Hz
SW                 190.000 ppm
FnMODE        Echo-Antiecho
SI                    2048
SF             600.1700101 MHz
WDW                  QSINE
SSB                      8
LB                    0.00 Hz
GB                       0
PC                    1.40
SI                    1024
MC2          echo-antiecho
SF             150.9126690 MHz
WDW                  QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
```

Figure S11. HMBC spectrum of compound **5** (TFA salt, CD_3OD, 600 MHz).



```
NAME      23A CL 2-340 dried in water disc C pent:
EXPNO                  1
PROCNO                 1
Date_           20100722
Time               17.44
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 32768
SOLVENT              D2O
NS                    29
DS                     0
SWH             5995.204 Hz
FIDRES          0.182959 Hz
AQ             2.7329011 sec
RG                   362
DW                83.400 usec
DE                  6.00 usec
TE                 300.2 K
D1            0.10000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.25 usec
PL1                -0.90 dB
PL1W         20.08691978 W
SFO1         300.1315006 MHz
SI                 16384
SF           300.1299864 MHz
WDW                   EM
SSB                    0
LB                  0.10 Hz
GB                     0
PC                  0.80
```

Figure S12. ^{1}H NMR spectrum of compound **6** (TFA salt, D_2O, 400 MHz).

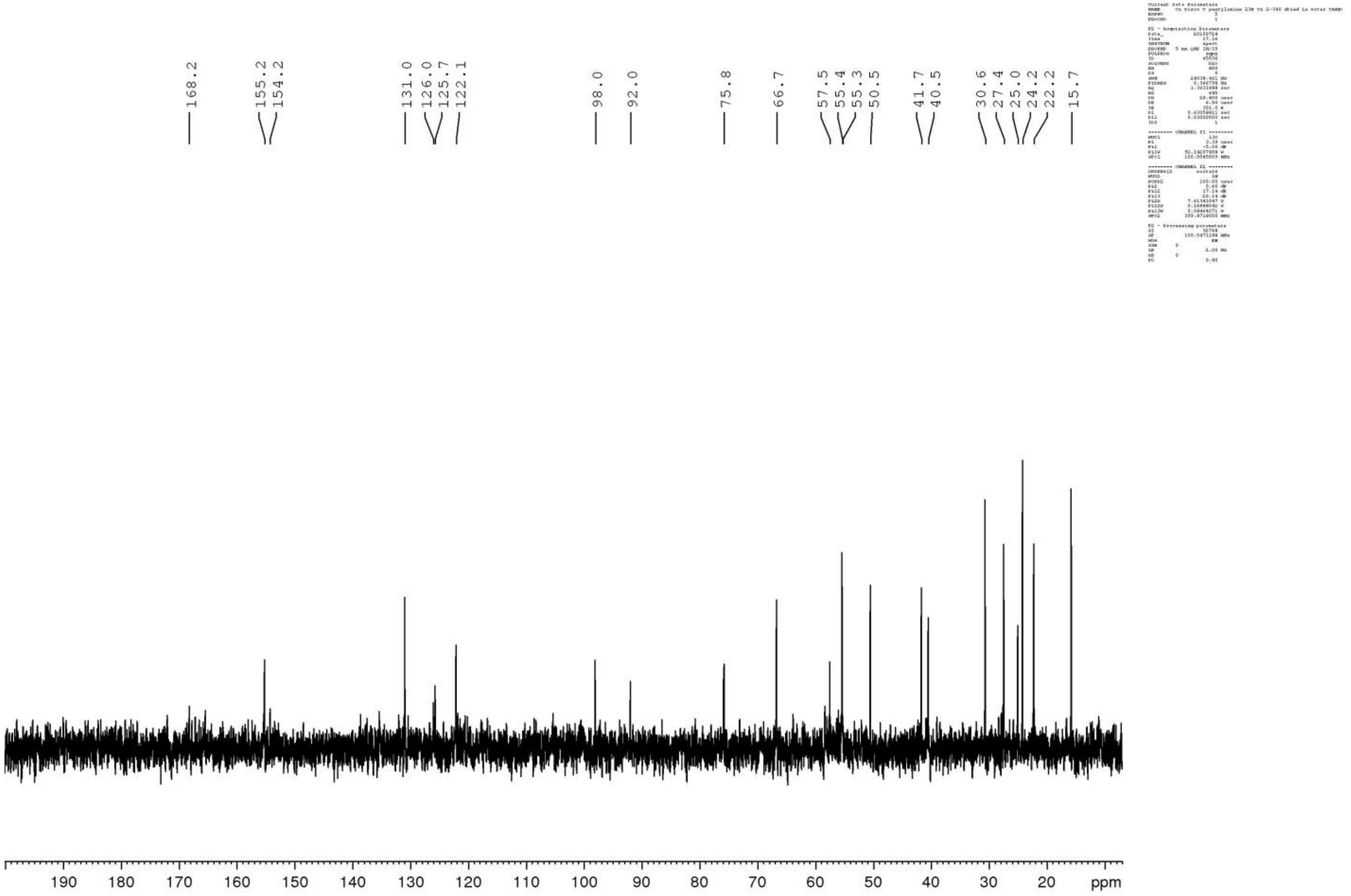
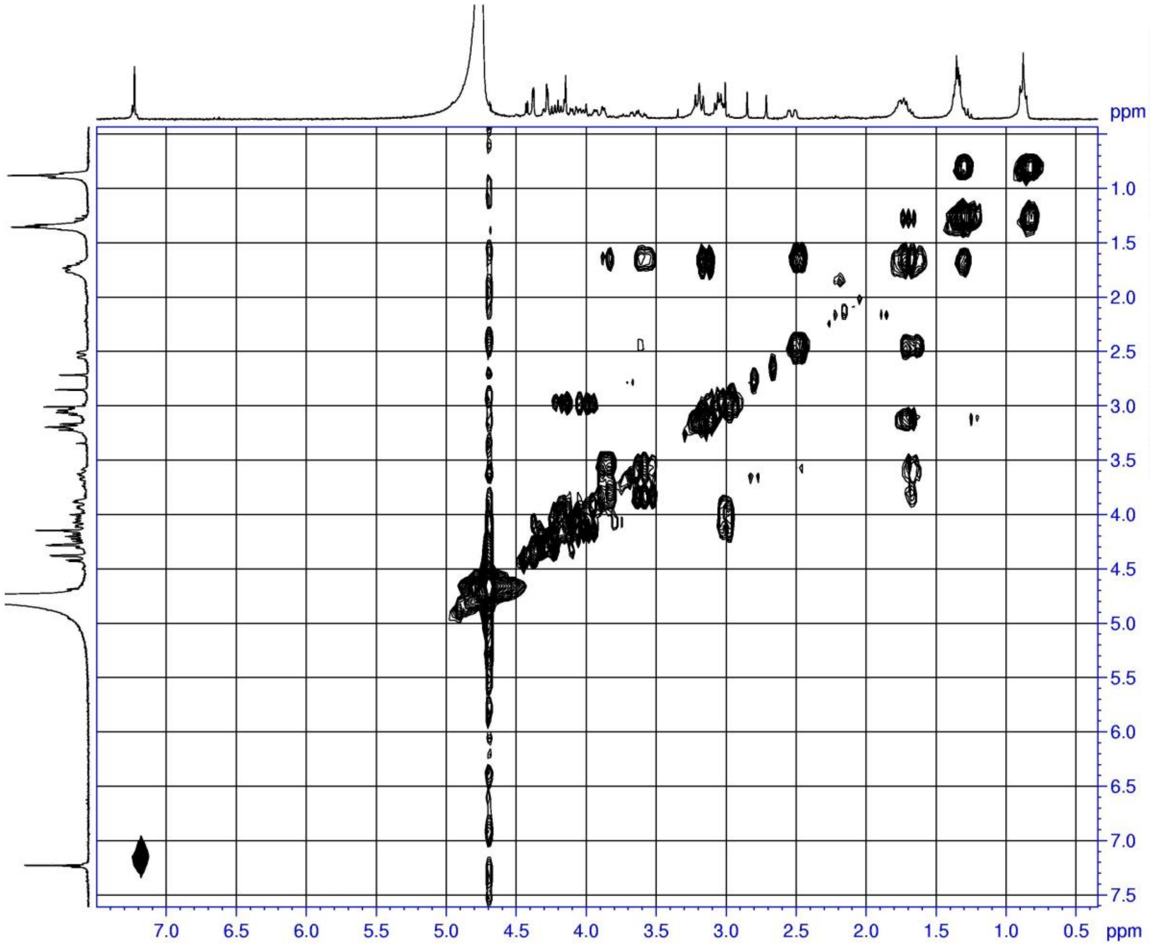


Figure S13. ^{13}C NMR spectrum of compound **6** (TFA salt, D_2O, 100 MHz).



```
NAME      23A CL 2-340 dried in water disc C pentyl
EXPNO                  3
PROCNO                 1
Date_           20100722
Time               18.36
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG        cosygpppqf
TD                  2048
SOLVENT              D2O
NS                     6
DS                     8
SWH             5995.204 Hz
FIDRES          2.927346 Hz
AQ             0.1708532 sec
RG                  1024
DW                83.400 usec
DE                  6.00 usec
TE                 300.2 K
D0            0.00000300 sec
D1            1.00000000 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00010000 sec
IN0           0.00016720 sec

======== CHANNEL f1 ========
NUC1                  1H
P0                  9.25 usec
P1                  9.25 usec
P17              2500.00 usec
PL1                -0.90 dB
PL10                9.03 dB
PL1W         20.08691978 W
PL10W         2.04133081 W
SFO1         300.1315007 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPZ1               10.00 %
P16              1000.00 usec
ND0                    1
TD                   256
SFO1            300.1315 MHz
FIDRES         23.362740 Hz
SW                19.927 ppm
FnMODE                QF
SI                  1024
SF           300.1300000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  0.80
SI                   256
MC2                   QF
SF           300.1300000 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
```

Figure S14. COSY spectrum of compound **6** (TFA salt, D_2O, 400 MHz).

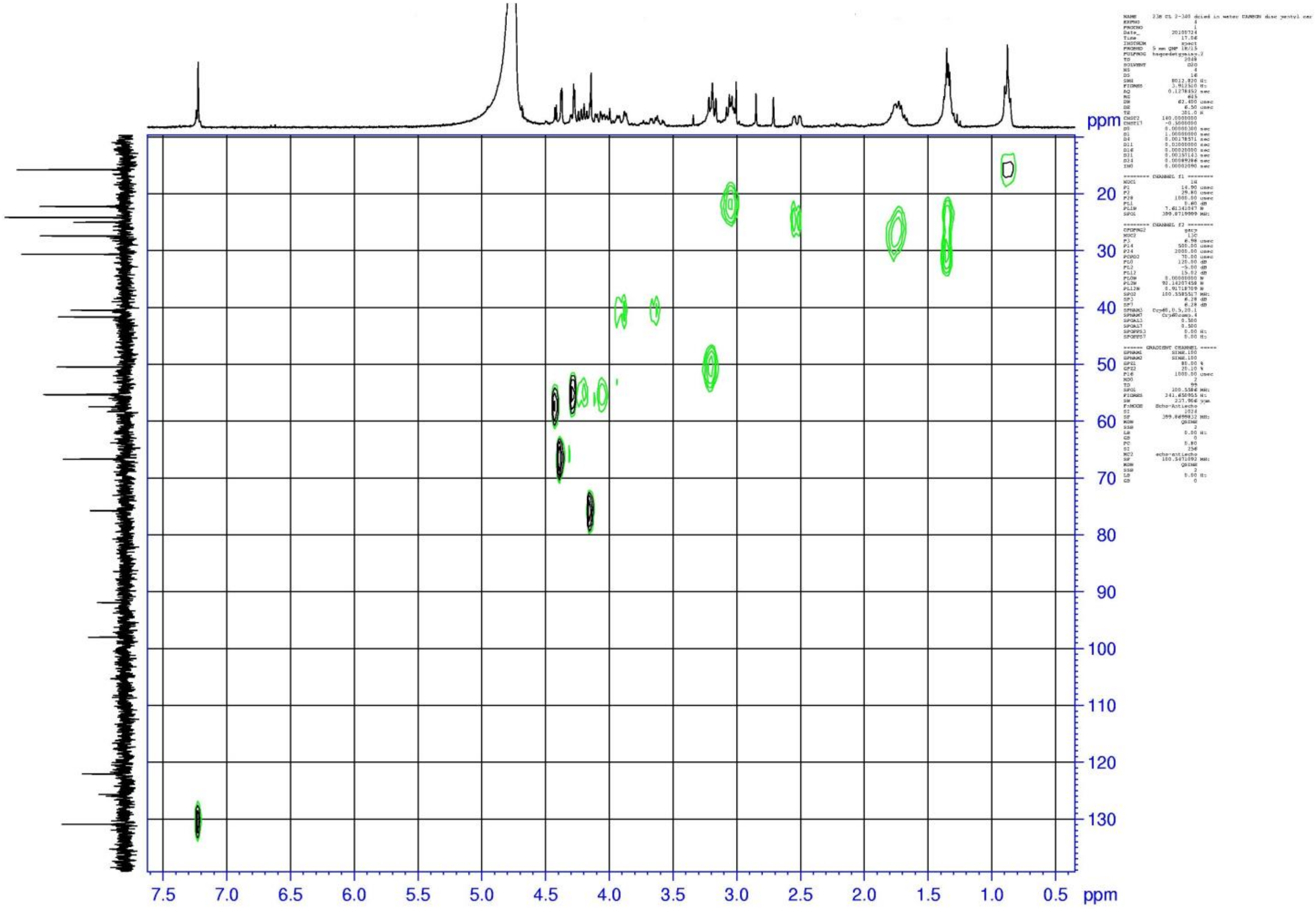


Figure S15. HSQC spectrum of compound **6** (TFA salt, D_2O, 400 MHz).

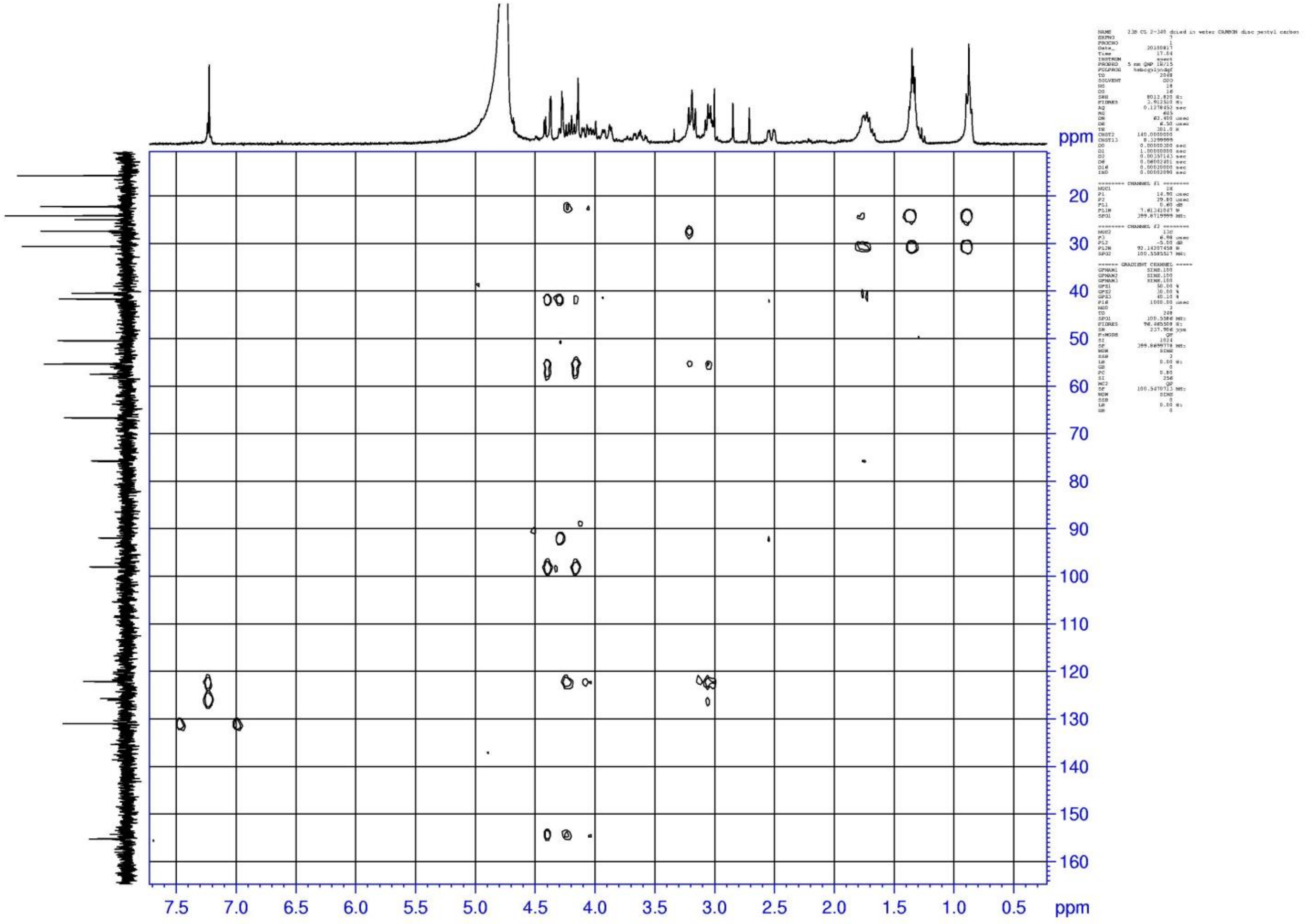
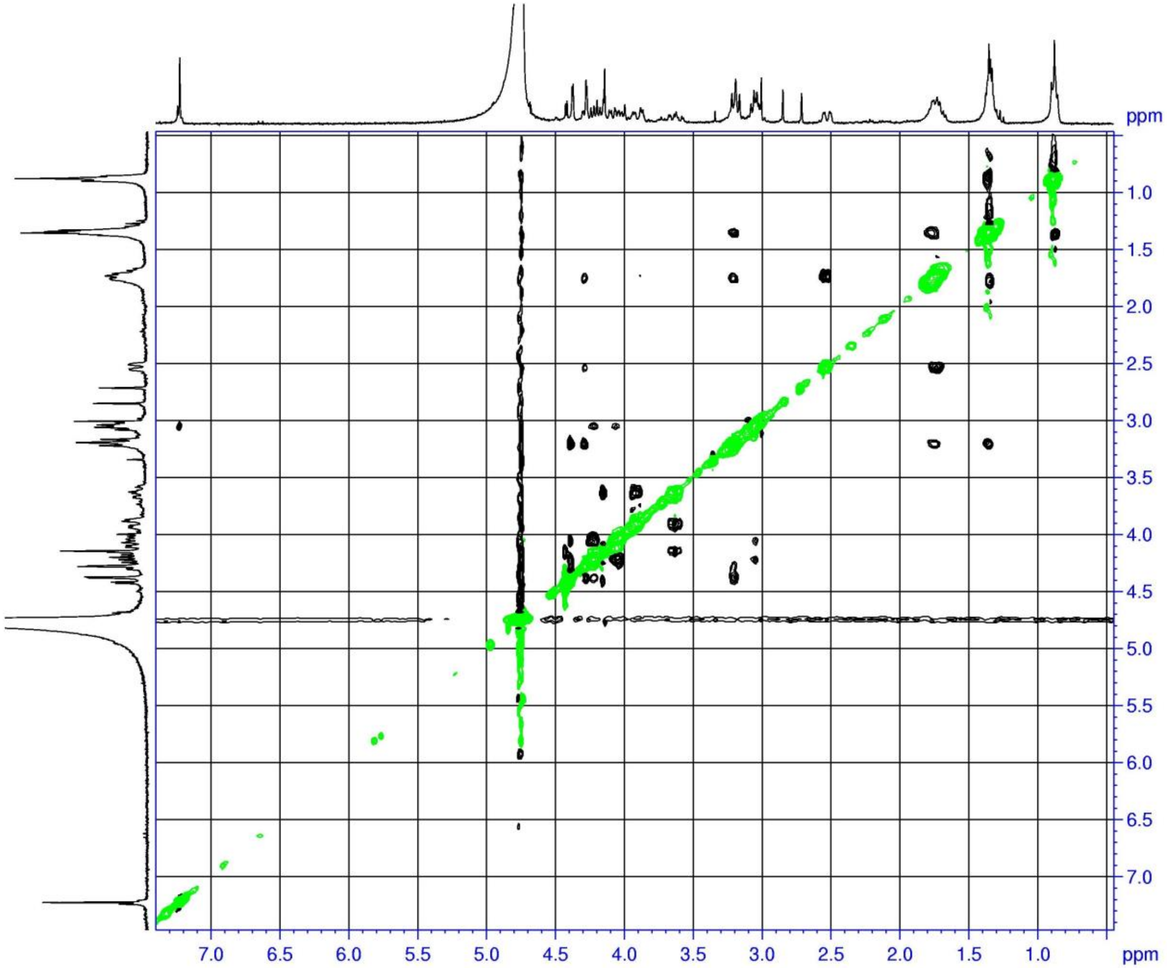
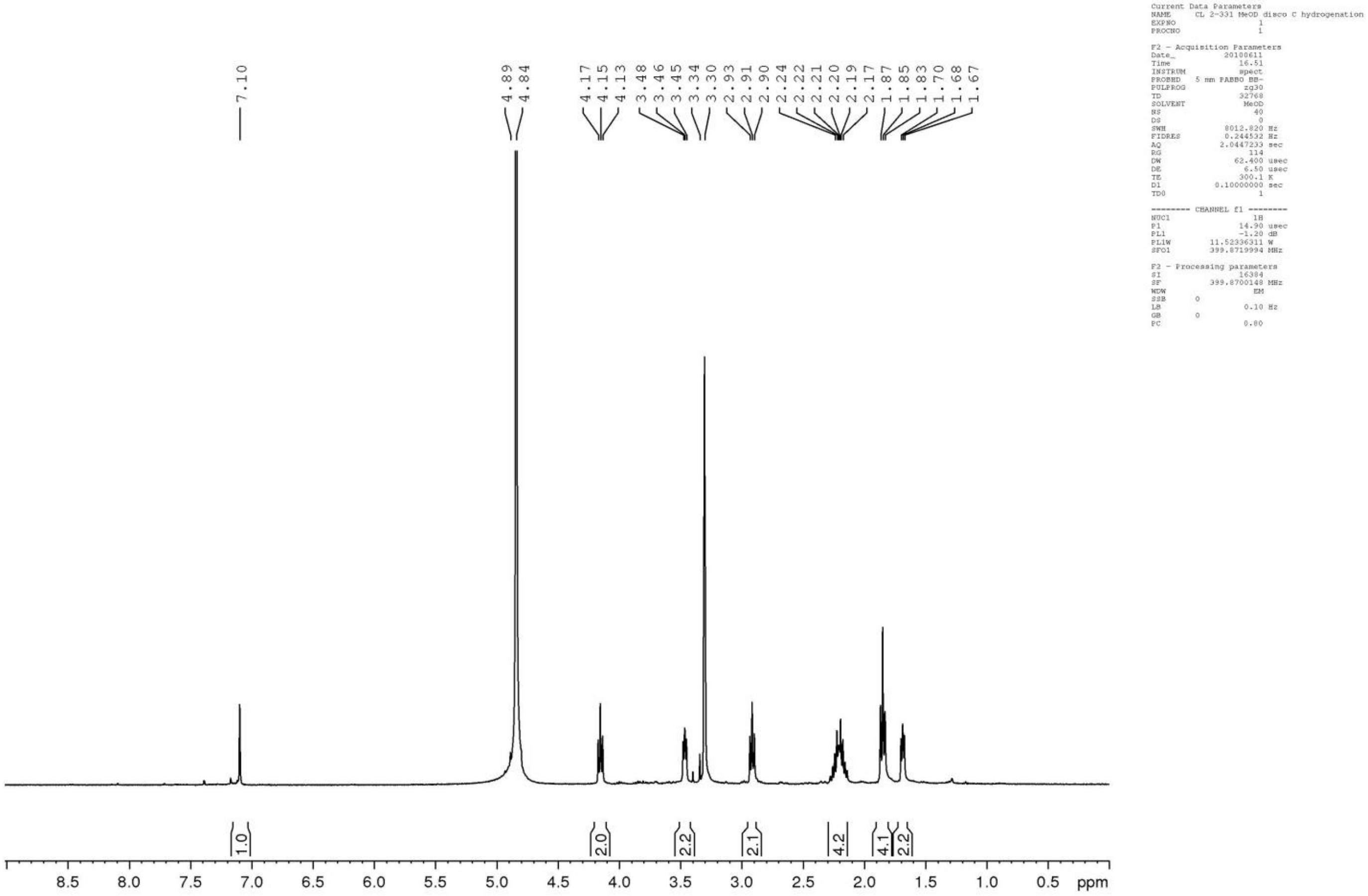


Figure S16. HMBC spectrum of compound **6** (TFA salt, D_2O, 400 MHz).



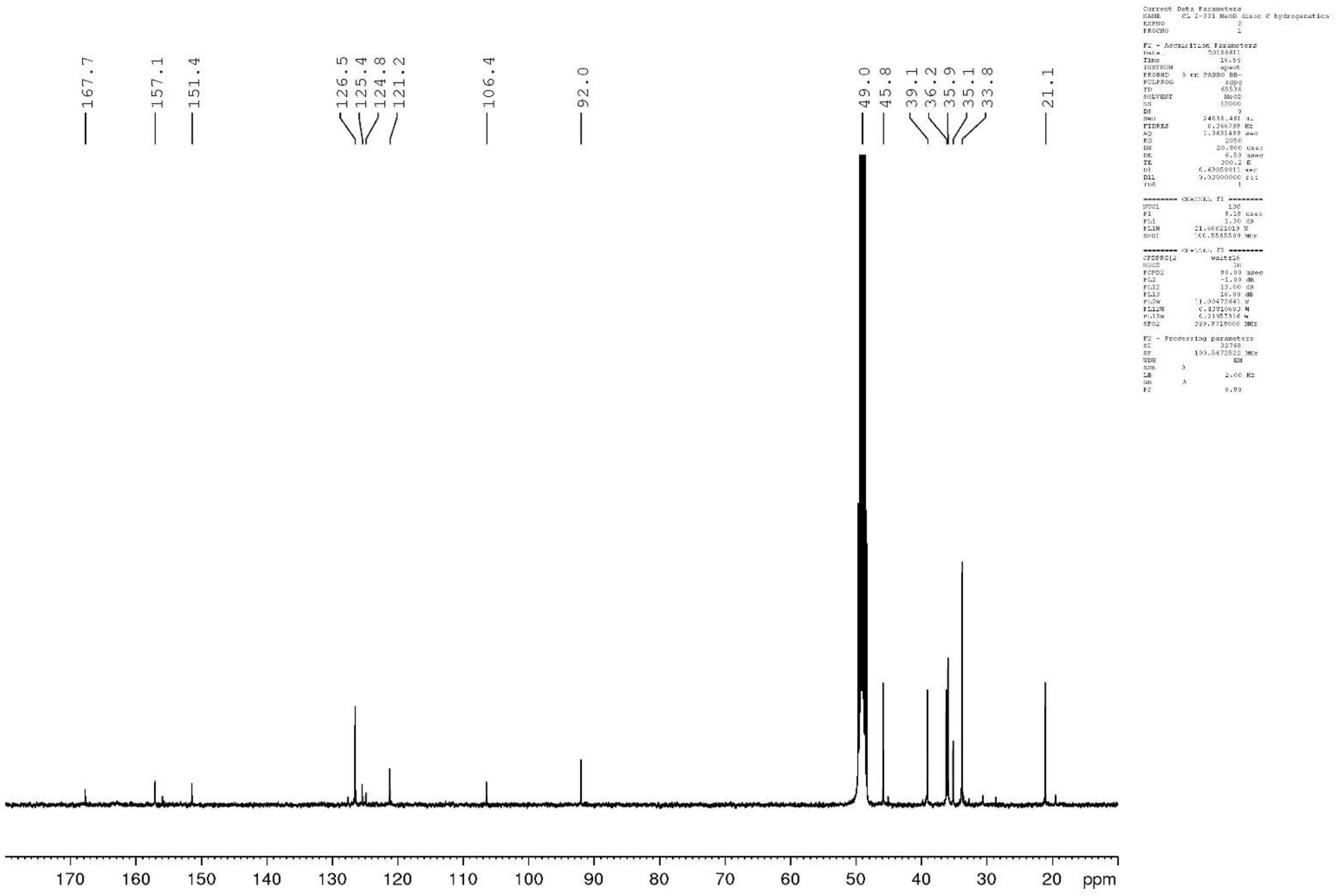
```
NAME     23B CL 2-340 dried in water CARBON disc pentyl c
EXPNO                   6
PROCNO                  1
Date_            20100725
Time                12.08
INSTRUM             spect
PROBHD   5 mm QNP 1H/15
PULPROG  noesygpphpp.rak
TD                   2048
SOLVENT               D2O
NS                     10
DS                     16
SWH              8012.820 Hz
FIDRES           3.912510 Hz
AQ              0.1278452 sec
RG                     57
DW                 62.400 usec
DE                   6.50 usec
TE                  301.0 K
D0             0.00004343 sec
D1             1.00000000 sec
D8             0.80000001 sec
D11            0.03000000 sec
D12            0.00002000 sec
D30            0.79895002 sec
IN0            0.00012480 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.90 usec
P17               2500.00 usec
PL1                  0.60 dB
PL10                 5.10 dB
PL1W           7.61341047 W
PL10W          2.70133996 W
SFO1          399.8719999 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPZ1                17.00 %
P16               1000.00 usec
ND0                     1
TD                    256
SFO1              399.872 MHz
FIDRES          31.300078 Hz
SW                 20.038 ppm
FnMODE               TPPI
SI                   1024
SF            399.8699829 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
PC                   0.80
SI                   1024
MC2                  TPPI
SF            399.8699835 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
```

Figure S17. NOESY spectrum of compound **6** (600 ms mixing time, TFA salt, D_2O, 400 MHz).



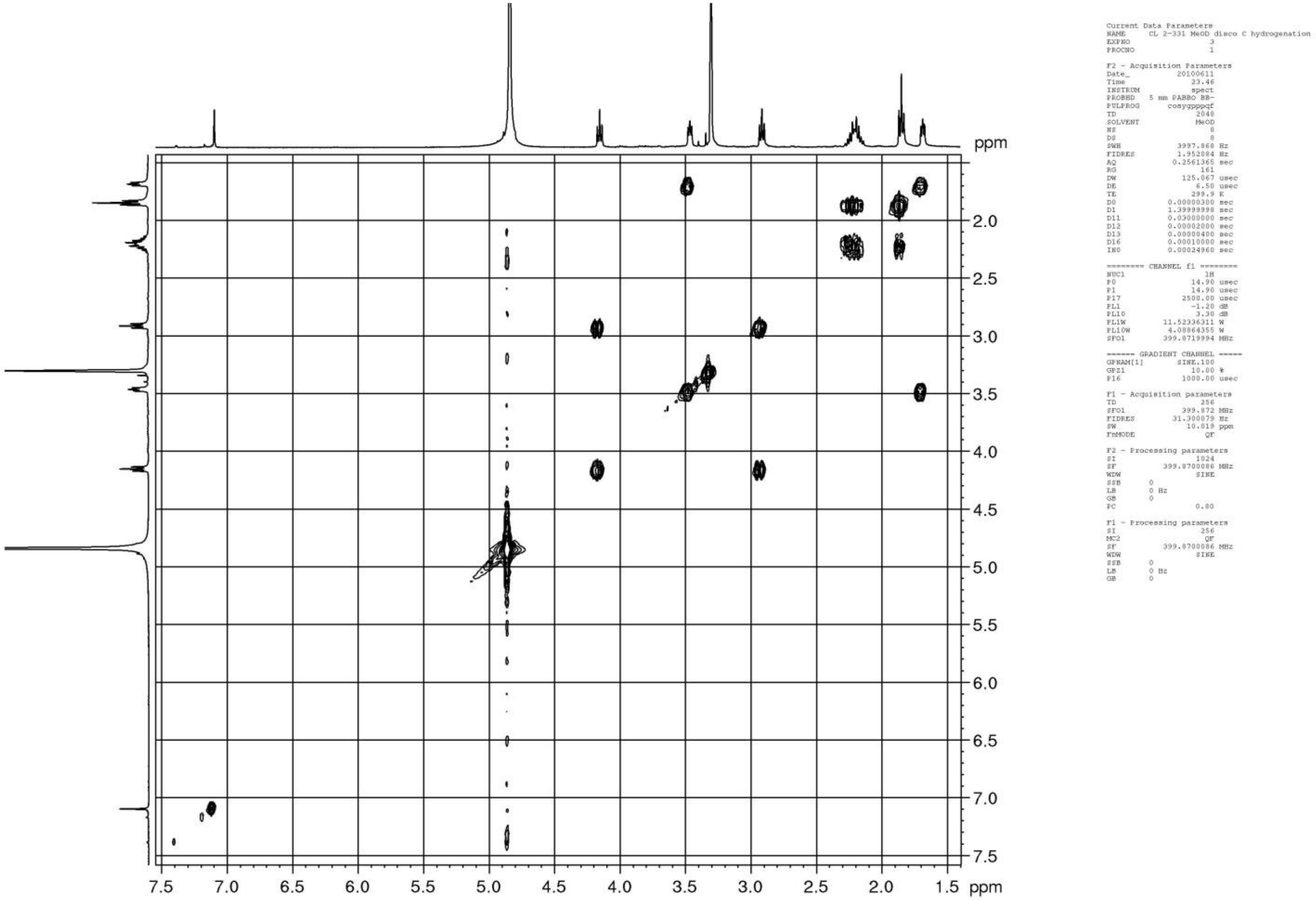
```
Current Data Parameters
NAME      CL 2-331 MeOD disco C hydrogenation
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20100611
Time                 16.51
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT               MeOD
NS                      40
DS                       0
SWH               8012.820 Hz
FIDRES            0.244532 Hz
AQ               2.0447233 sec
RG                     114
DW                  62.400 usec
DE                    6.50 usec
TE                   300.1 K
D1              0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.90 usec
PL1                  -1.20 dB
PL1W           11.52336311 W
SFO1           399.8719994 MHz

F2 - Processing parameters
SI                   16384
SF             399.8700148 MHz
WDW                     EM
SSB      0
LB                    0.10 Hz
GB       0
PC                    0.80
```

Figure S18. ^{1}H NMR spectrum of compound **7** (TFA salt, CD_3OD, 400 MHz).



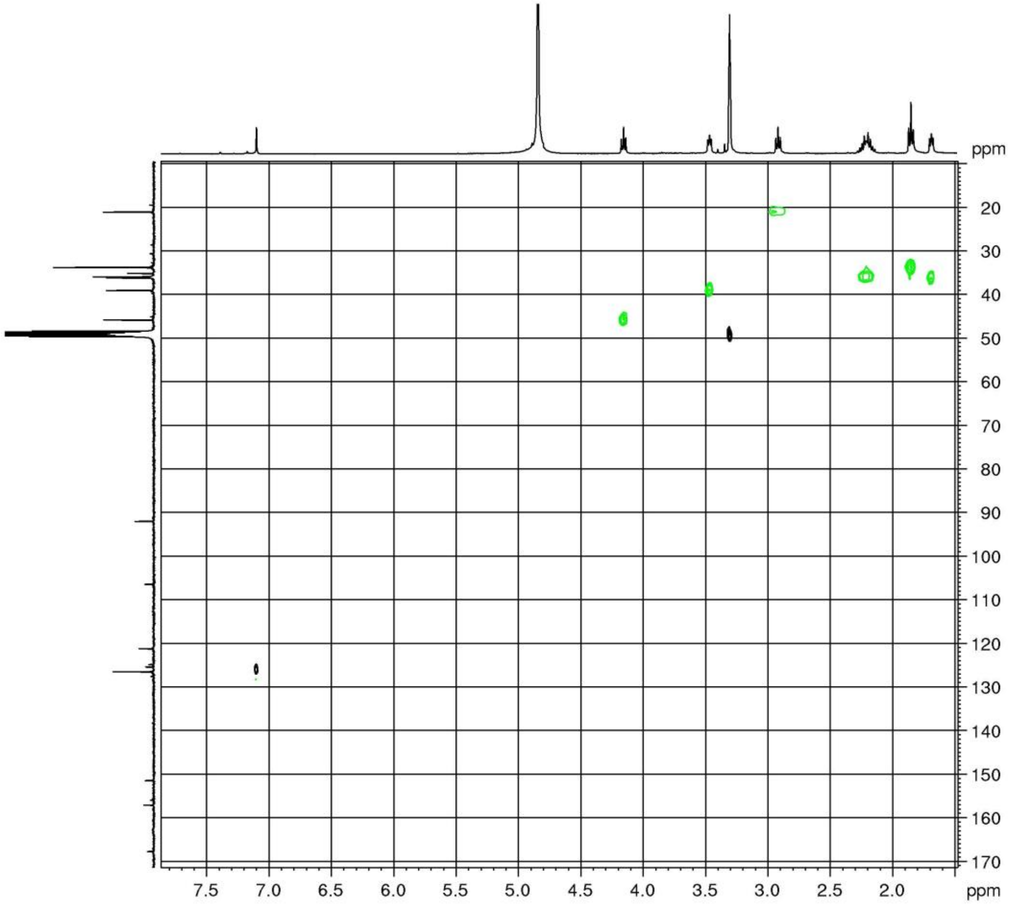
```
Current Data Parameters
NAME      CL 2-331 MeOD disc C hydrogenation
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100811
Time               16.54
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg
TD                 65536
SOLVENT             MeOD
NS                 12000
DS                     0
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                  2050
DW                20.800 usec
DE                  6.50 usec
TE                 300.2 K
D1            0.63058811 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.18 usec
PL1                 1.30 dB
PL1W         21.60021019 W
SFO1         100.5585509 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -1.00 dB
PL12               13.00 dB
PL13               16.00 dB
PL2W         11.00472641 W
PL12W         0.43910602 W
PL13W         0.21957316 W
SFO2         399.8718000 MHz

F2 - Processing parameters
SI                 32768
SF           100.5472522 MHz
WDW                   EM
SSB      0
LB                  2.00 Hz
GB       0
PC                  0.00
```

Figure S19. ^{13}C NMR spectrum of compound **7** (TFA salt, CD_3OD, 100 MHz).



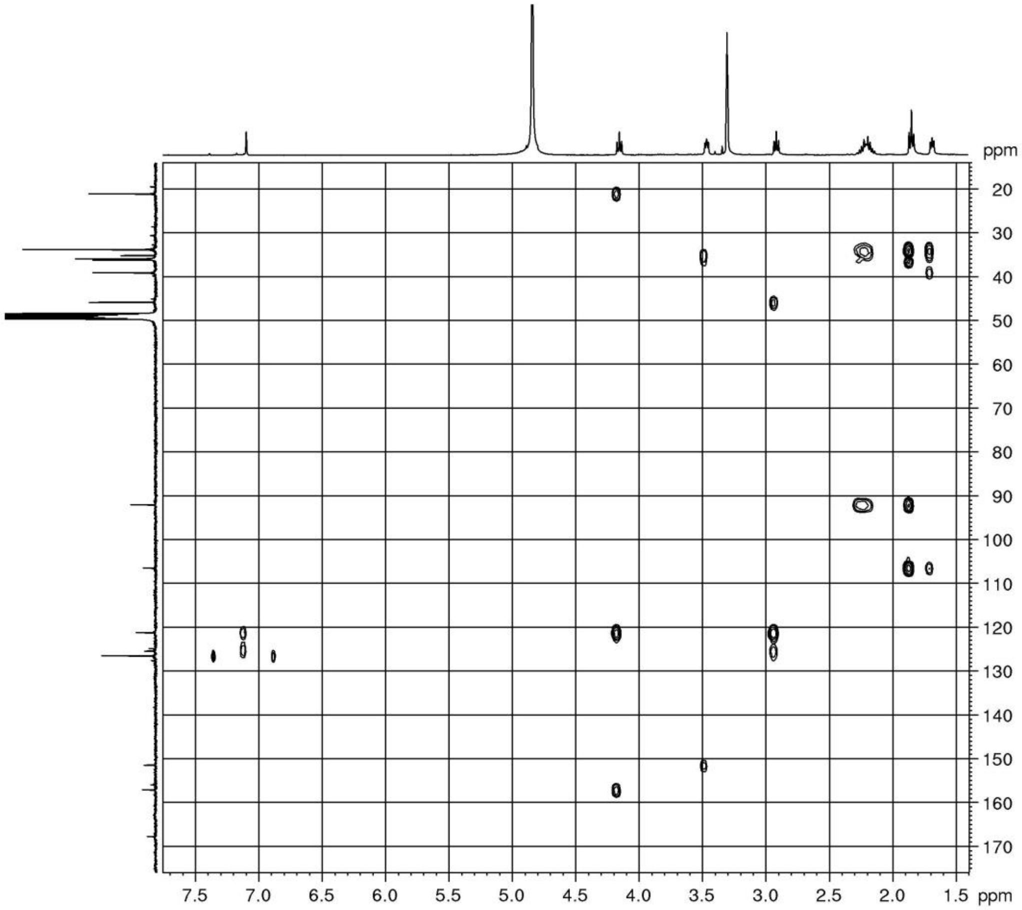
```
Current Data Parameters
NAME      CL 2-331 MeOD disco C hydrogenation
EXPNO                    3
PROCNO                   1

F2 - Acquisition Parameters
Date_             20100611
Time                 23.46
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG         cosygpppqf
TD                    2048
SOLVENT               MeOD
NS                       8
DS                       8
SWH               3997.868 Hz
FIDRES            1.952084 Hz
AQ               0.2561365 sec
RG                     161
DW                 125.067 usec
DE                    6.50 usec
TE                   299.9 K
D0              0.00000300 sec
D1              1.39999998 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00010000 sec
IN0             0.00024960 sec

======== CHANNEL f1 ========
NUC1                    1H
P0                   14.90 usec
P1                   14.90 usec
P17                2500.00 usec
PL1                  -1.20 dB
PL10                  3.30 dB
PL1W           11.52336311 W
PL10W           4.08864355 W
SFO1           399.8719994 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]          SINE.100
GPZ1                 10.00 %
P16                1000.00 usec

F1 - Acquisition parameters
TD                     256
SFO1               399.872 MHz
FIDRES           31.300079 Hz
SW                  10.019 ppm
FnMODE                  QF

F2 - Processing parameters
SI                    1024
SF             399.8700086 MHz
WDW                   SINE
SSB       0
LB        0 Hz
GB        0
PC                    0.80

F1 - Processing parameters
SI                     256
MC2                     QF
SF             399.8700086 MHz
WDW                   SINE
SSB       0
LB        0 Hz
GB        0
```

Figure S20. COSY spectrum of compound **7** (TFA salt, CD_3OD, 400 MHz).



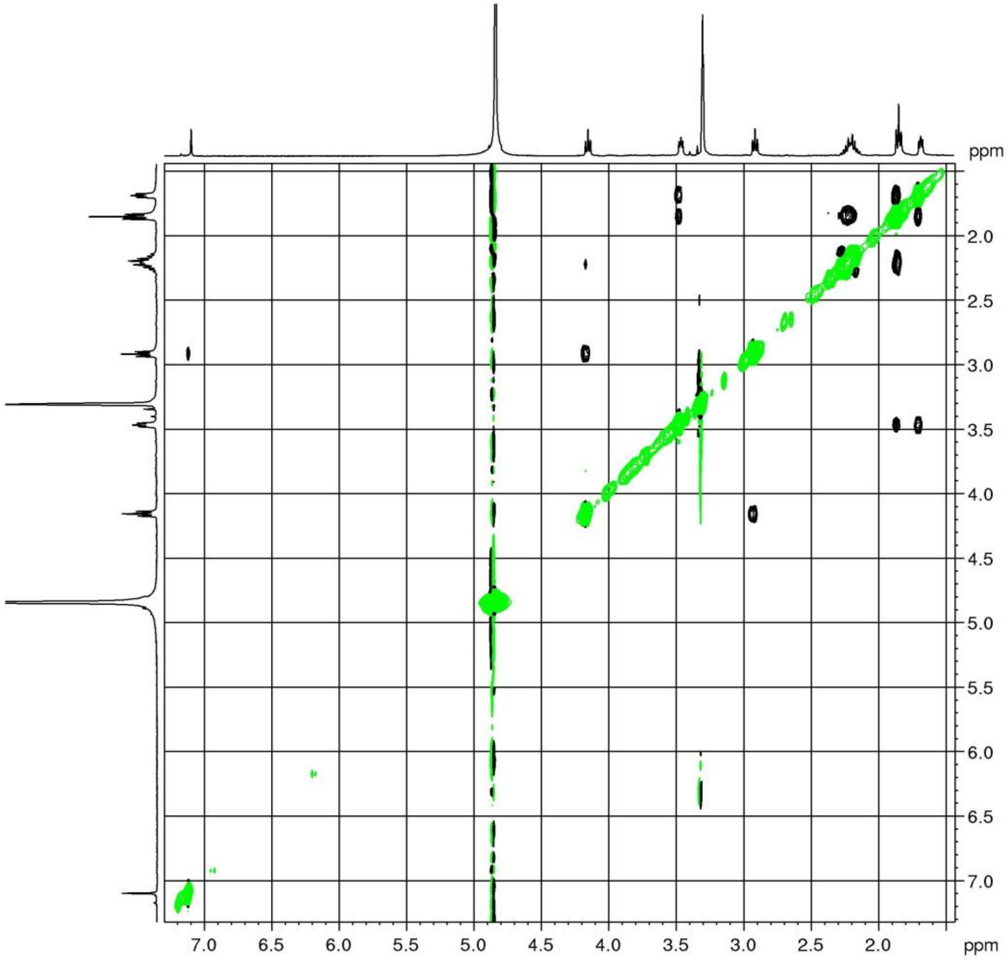
```
Current Data Parameters
NAME      CL 2-331 MeOD disco C hydrogenation
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180612
Time                0.47
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG  hsqcedetgpsisp.2
TD                  2048
SOLVENT             MeOD
NS                    10
DS                    16
SWH             3997.868 Hz
FIDRES          1.952084 Hz
AQ             0.2561365 sec
RG                   645
DW               125.067 usec
DE                  6.50 usec
TE                 300.1 K
CNST2        140.0000000
CNST17        -0.5000000
D0            0.00000300 sec
D1            1.00000000 sec
D4            0.00178571 sec
D11           0.03000000 sec
D16           0.00010000 sec
D21           0.00357143 sec
D24           0.00089286 sec
IN0           0.00002160 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.90 usec
P2                 29.80 usec
P28              2000.00 usec
PL1                -1.20 dB
PL1W         11.52336311 W
SFO1         399.8719994 MHz

======== CHANNEL f2 ========
CPDPRG[2            garp
NUC2                 13C
P3                  9.80 usec
P14               500.00 usec
P24              2000.00 usec
PCPD2              70.00 usec
PL0               120.00 dB
PL2                -2.00 dB
PL12               15.00 dB
PLOW      0 W
PL2W         46.18043137 W
PL12W         0.92142075 W
SFO2         100.5589539 MHz
SP3                 6.33 dB
SP7                 6.33 dB
SPNAM[3] Crp60,0.5,20.1
SPNAM[7]     Crp60comp.4
SPOAL3             0.500
SPOAL7             0.500
SPOFFS3  0 Hz
SPOFFS7  0 Hz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPNAM[2]        SINE.100
GPZ1               80.00 %
GPZ2               20.10 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   256
SFO1             100.559 MHz
FIDRES        180.844910 Hz
SW               230.195 ppm
FnMODE    Echo-Antiecho

F2 - Processing parameters
SI                  1024
SF           399.8700143 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
PC                  0.80

F1 - Processing parameters
SI                   256
MC2        echo-antiecho
SF           100.5472150 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
```

Figure S21. HSQC spectrum of compound **7** (TFA salt, CD_3OD, 400 MHz).



```
Current Data Parameters
NAME     CL 2-331 MeOD disco C hydrogenation
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_          20180612
Time               1.46
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG    hmbcgplpndqf
TD                 2048
SOLVENT            MeOD
NS                  110
DS                   16
SWH            3997.868 Hz
FIDRES         1.952084 Hz
AQ            0.2561365 sec
RG                  645
DW              125.067 usec
DE                 6.50 usec
TE                300.0 K
CNST2       140.0000000
CNST13        8.3299999
D0           0.00000300 sec
D1           1.00000000 sec
D2           0.00357143 sec
D6           0.06002401 sec
D16          0.00010000 sec
IN0          0.00002160 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                14.90 usec
P2                29.80 usec
PL1               -1.20 dB
PL1W        11.52336311 W
SFO1        399.8719994 MHz

======== CHANNEL f2 ========
NUC2                13C
P3                 9.80 usec
PL2               -2.00 dB
PL2W        46.18043137 W
SFO2        100.5589539 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                  177
SFO1            100.559 MHz
FIDRES       261.561005 Hz
SW              230.195 ppm
FnMODE               QF

F2 - Processing parameters
SI                 1024
SF          399.8700086 MHz
WDW                SINE
SSB                   2
LB       0 Hz
GB       0
PC                 0.80

F1 - Processing parameters
SI                  256
MC2                  QF
SF          100.5472137 MHz
WDW                SINE
SSB      0
LB       0 Hz
GB       0
```

Figure S22. HMBC spectrum of compound **7** (TFA salt, CD_3OD, 400 MHz).



```
Current Data Parameters
NAME      CL 2-331 MeOD disco C hydrogenation
EXPNO                    8
PROCNO                   1

F2 - Acquisition Parameters
Date_           20100620
Time               17.18
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG  noesygpphpp.rak
TD                  2048
SOLVENT             MeOD
NS                    90
DS                    16
SWH             3997.868 Hz
FIDRES          1.952084 Hz
AQ             0.2561365 sec
RG                    57
DW               125.067 usec
DE                  6.50 usec
TE                 300.0 K
D0            0.00010583 sec
D1            1.00000000 sec
D8            0.80000001 sec
D11           0.03000000 sec
D12           0.00002000 sec
D30           0.79895002 sec
IN0           0.00024960 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.90 usec
P17              2500.00 usec
PL1                -1.20 dB
PL10                3.30 dB
PL1W         11.52336311 W
PL10W         4.08864355 W
SFO1         399.8719994 MHz

====== GRADIENT CHANNEL =====
GPNAM[1]        SINE.100
GPZ1               17.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   256
SFO1             399.872 MHz
FIDRES         31.300079 Hz
SW                10.019 ppm
FnMODE              TPPI

F2 - Processing parameters
SI                  1024
SF           399.8700086 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
PC                  0.80

F1 - Processing parameters
SI                   256
MC2                 TPPI
SF           399.8700086 MHz
WDW                QSINE
SSB                    2
LB        0 Hz
GB        0
```

Figure S23. NOESY spectrum of compound **7** (600 ms mixing time, TFA salt, CD_3OD, 400 MHz).

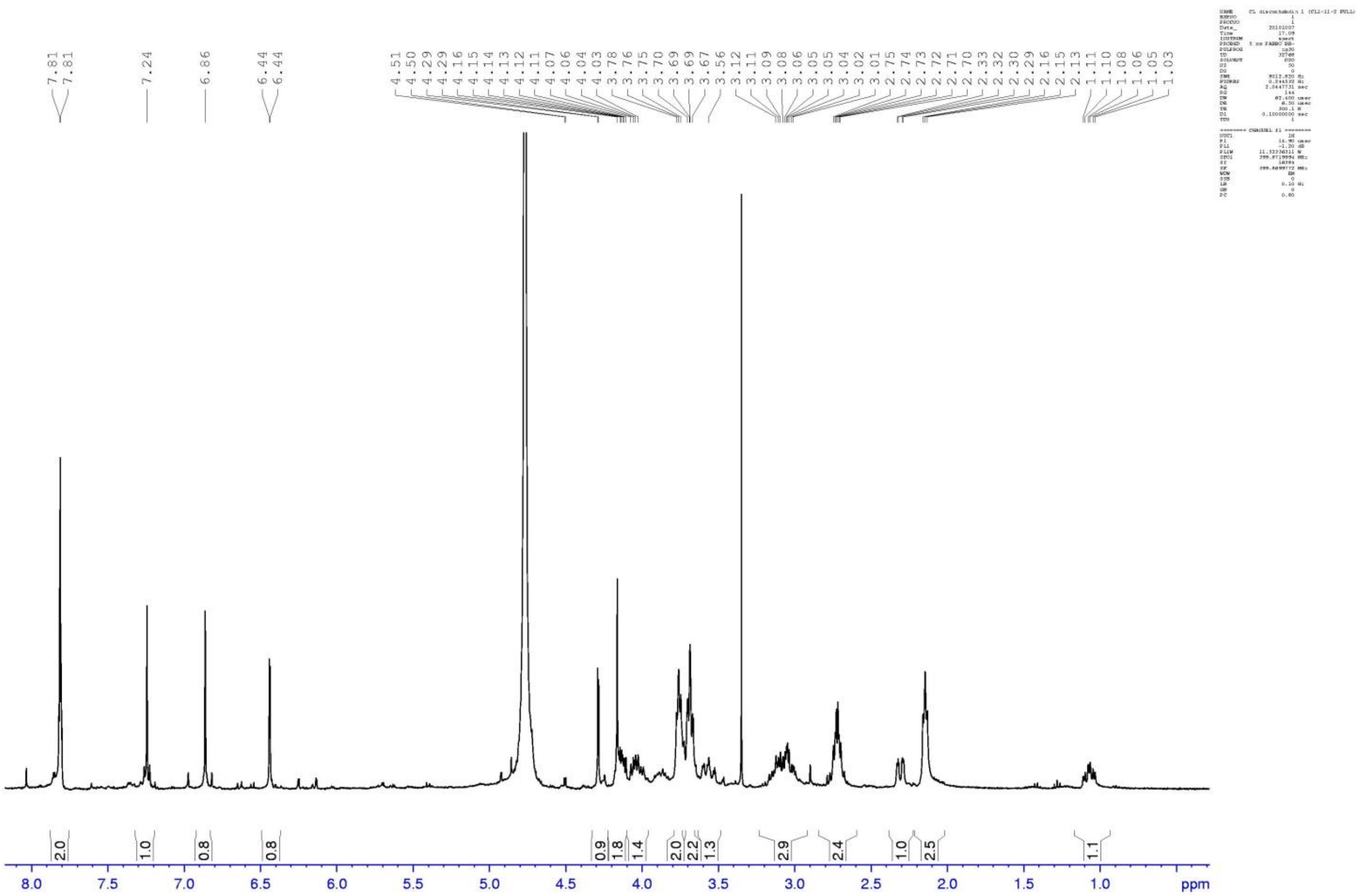
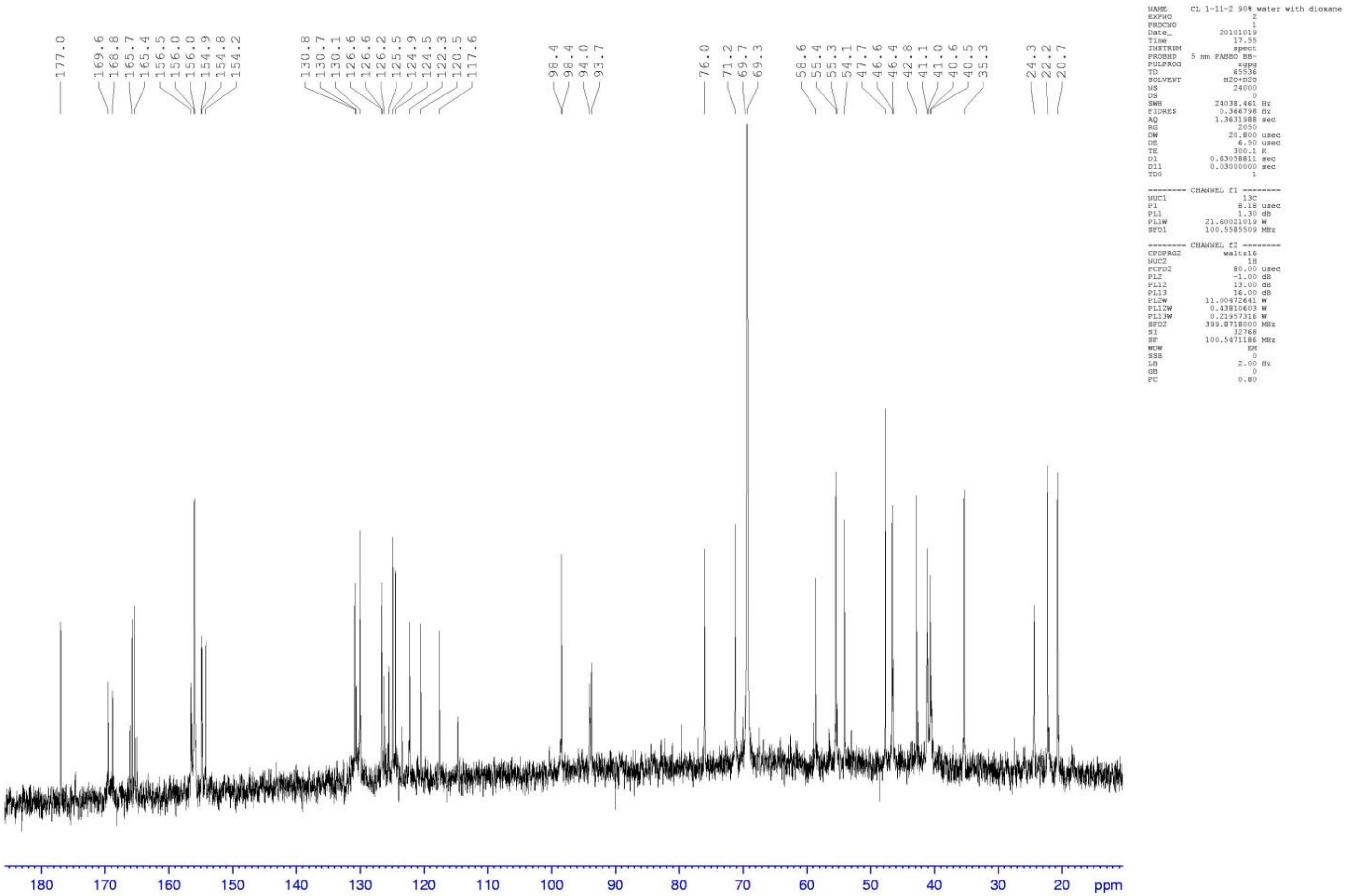
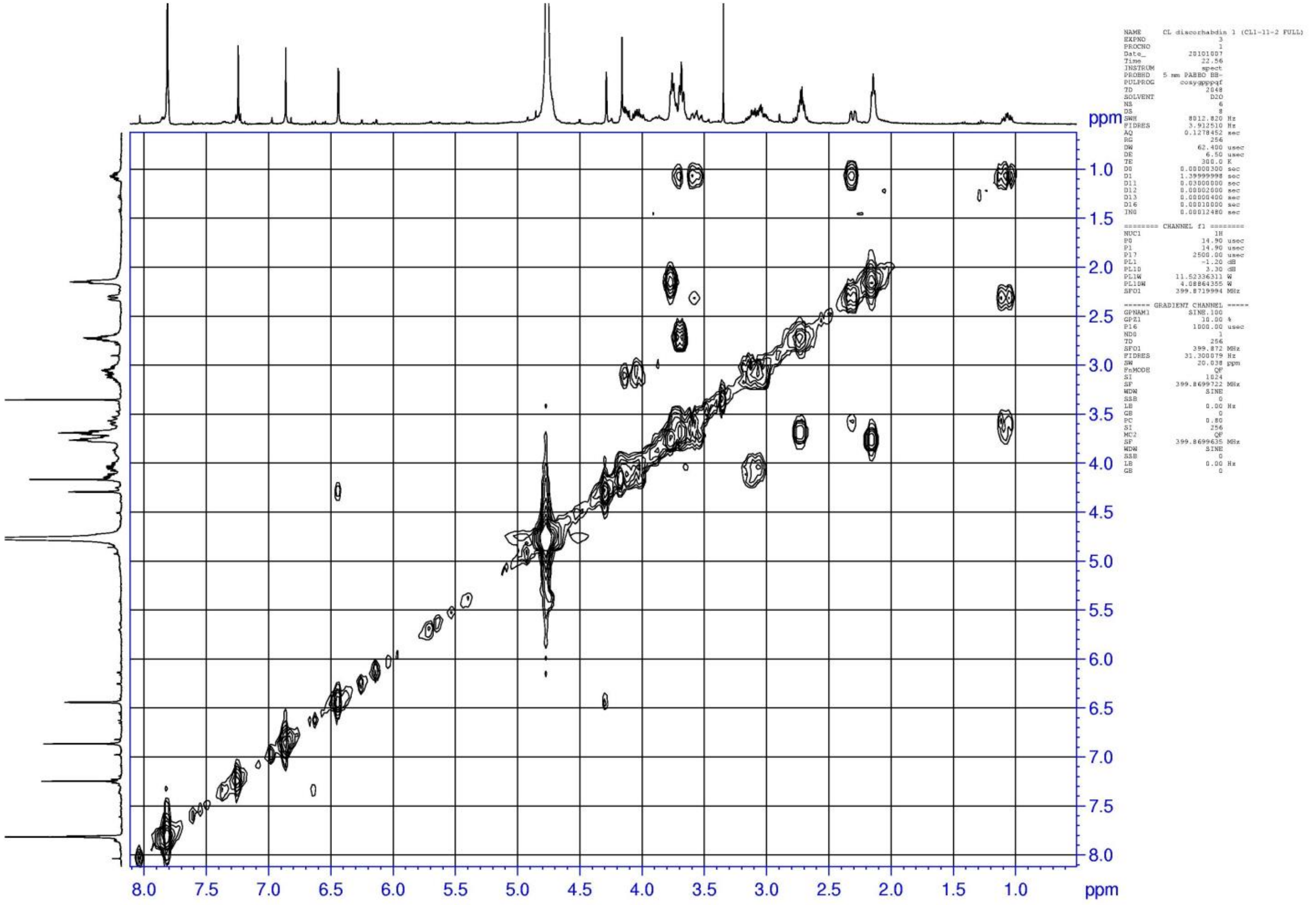


Figure S24. ^{1}H NMR spectrum of compound **8** (TFA salt, D_2O, 400 MHz).



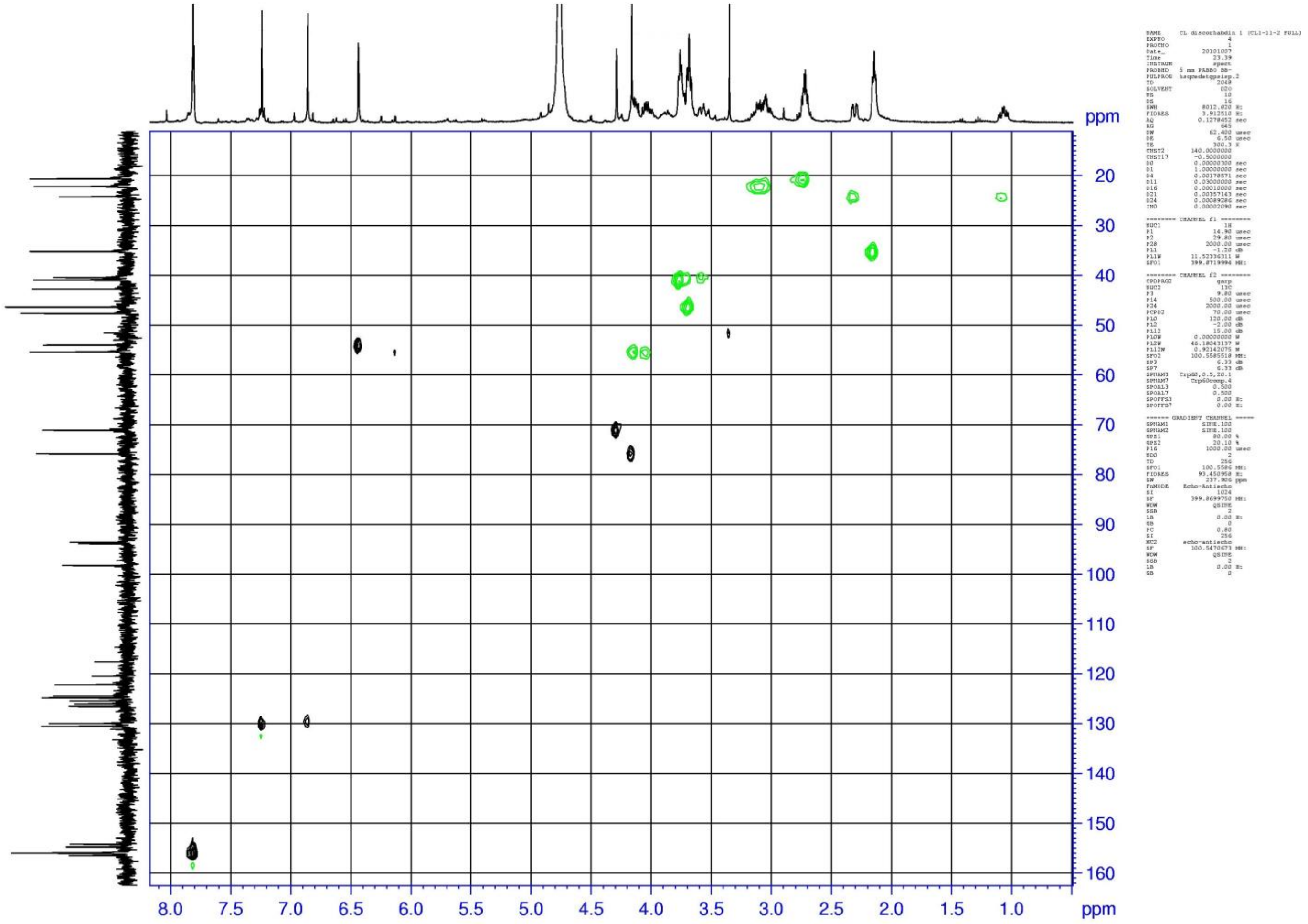
```
NAME      CL 1-11-2 90% water with dioxane
EXPNO                    2
PROCNO                   1
Date_             20101019
Time                 17.55
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zgpg
TD                   65536
SOLVENT            H2O+D2O
NS                   24000
DS                       0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                    2050
DW                  20.800 usec
DE                    6.50 usec
TE                   300.1 K
D1              0.63058811 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    8.18 usec
PL1                   1.30 dB
PL1W           21.60021019 W
SFO1           100.5585509 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -1.00 dB
PL12                 13.00 dB
PL13                 16.00 dB
PL2W           11.00472641 W
PL12W           0.43810603 W
PL13W           0.21957316 W
SFO2           399.8718000 MHz
SI                   32768
SF             100.5471186 MHz
WDW                     EM
SSB                      0
LB                    2.00 Hz
GB                       0
PC                    0.80
```

Figure S25. ^{13}C NMR spectrum of compound **8** (TFA salt, 90% H_2O : 10% D_2O, 100 MHz).



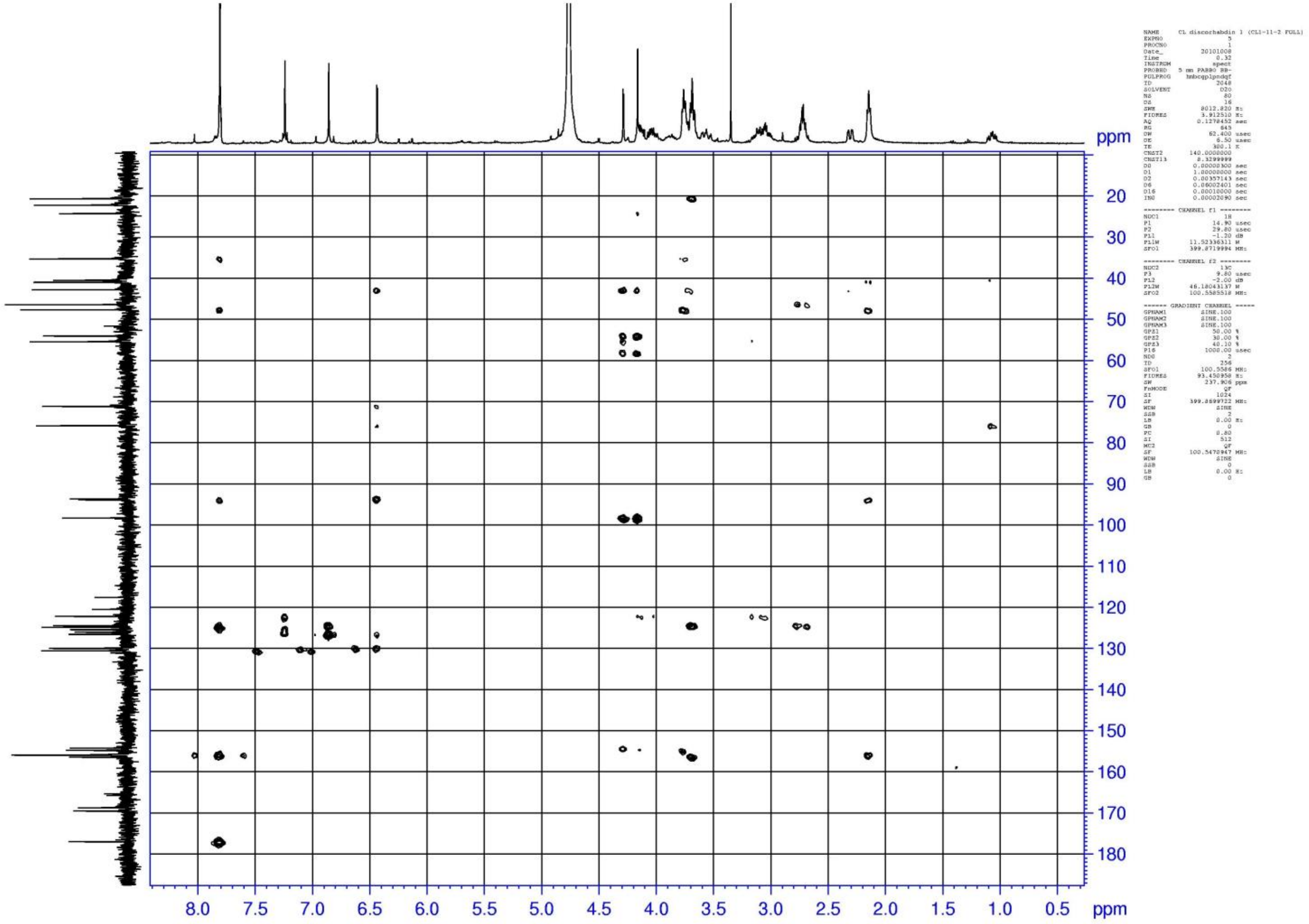
```
NAME      CL discorhabdin 1 (CL1-11-2 FULL)
EXPNO                 3
PROCNO                1
Date_          20101007
Time              22.56
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG      cosygpppqf
TD                 2048
SOLVENT             D2O
NS                    6
DS                    8
SWH            8012.820 Hz
FIDRES         3.912510 Hz
AQ            0.1278452 sec
RG                  256
DW               62.400 usec
DE                 6.50 usec
TE                300.0 K
D0           0.00000300 sec
D1           1.39999998 sec
D11          0.03000000 sec
D12          0.00002000 sec
D13          0.00000400 sec
D16          0.00010000 sec
IN0          0.00012480 sec

======== CHANNEL f1 ========
NUC1                 1H
P0                14.90 usec
P1                14.90 usec
P17             2500.00 usec
PL1               -1.20 dB
PL10               3.30 dB
PL1W        11.52336311 W
PL10W        4.08864355 W
SFO1        399.8719994 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPZ1              10.00 %
P16             1000.00 usec
ND0                   1
TD                  256
SFO1            399.872 MHz
FIDRES        31.300079 Hz
SW               20.038 ppm
FnMODE               QF
SI                 1024
SF          399.8699722 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 0.80
SI                  256
MC2                  QF
SF          399.8699635 MHz
WDW                SINE
SSB                   0
LB                 0.00 Hz
GB                    0
```

Figure S26. COSY spectrum of compound **8** (TFA salt, D_2O, 400 MHz).



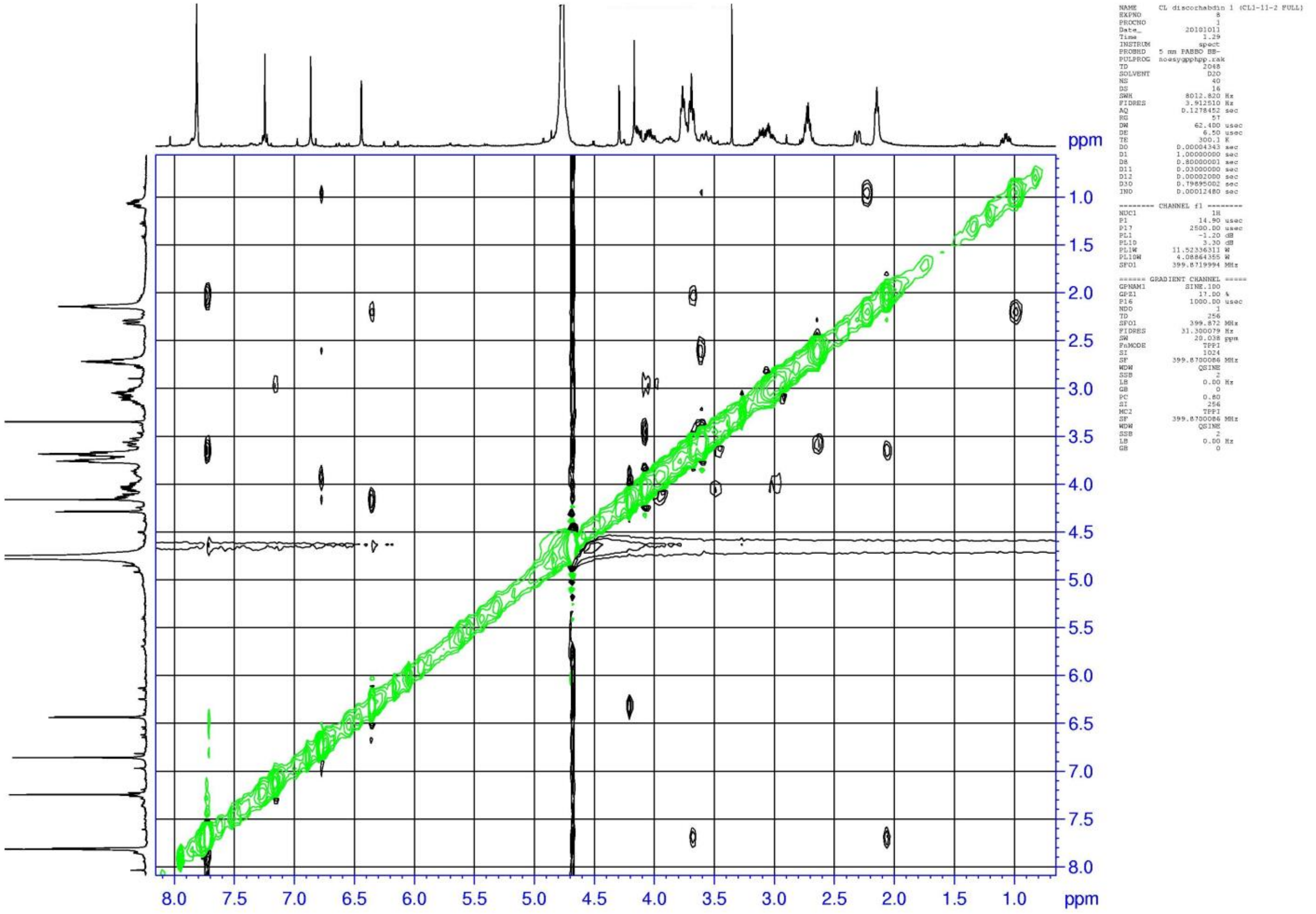
```
NAME       CL discorhabdin 1 (CL1-11-2 FULL)
EXPNO                   4
PROCNO                  1
Date_            20101007
Time                23.39
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG   hsqcedetgpsisp.2
TD                   2048
SOLVENT               D2O
NS                     10
DS                     16
SWH              8012.820 Hz
FIDRES           3.912510 Hz
AQ              0.1278452 sec
RG                    645
DW                 62.400 usec
DE                   6.50 usec
TE                  300.3 K
CNST2         140.0000000
CNST17         -0.5000000
D0             0.00000300 sec
D1             1.00000000 sec
D4             0.00178571 sec
D11            0.03000000 sec
D16            0.00010000 sec
D21            0.00357143 sec
D24            0.00089286 sec
IN0            0.00002090 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.90 usec
P2                  29.80 usec
P28               2000.00 usec
PL1                 -1.20 dB
PL1W          11.52336311 W
SFO1          399.8719994 MHz

======== CHANNEL f2 ========
CPDPRG2              garp
NUC2                  13C
P3                   9.80 usec
P14                500.00 usec
P24               2000.00 usec
PCPD2               70.00 usec
PL0                120.00 dB
PL2                 -2.00 dB
PL12                15.00 dB
PL0W           0.00000000 W
PL2W          46.18043137 W
PL12W          0.92142075 W
SFO2          100.5585518 MHz
SP3                  6.33 dB
SP7                  6.33 dB
SPNAM3    Crp60,0.5,20.1
SPNAM7      Crp60comp.4
SPOAL3              0.500
SPOAL7              0.500
SPOFFS3              0.00 Hz
SPOFFS7              0.00 Hz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPZ1                80.00 %
GPZ2                20.10 %
P16               1000.00 usec
ND0                     2
TD                    256
SFO1             100.5586 MHz
FIDRES          93.450958 Hz
SW                237.906 ppm
FnMODE       Echo-Antiecho
SI                   1024
SF            399.8699750 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
PC                   0.80
SI                    256
MC2          echo-antiecho
SF            100.5470673 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
```

Figure S27. HSQC spectrum of compound **8** (TFA salt, D_2O, 400 MHz).



```
NAME       CL discorhabdin 1 (CL1-11-2 FULL)
EXPNO                    5
PROCNO                   1
Date_             20101008
Time                  0.32
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG      hmbcgplpndqf
TD                    2048
SOLVENT                D2O
NS                      80
DS                      16
SWH               8012.820 Hz
FIDRES            3.912510 Hz
AQ               0.1278452 sec
RG                     645
DW                  62.400 usec
DE                    6.50 usec
TE                   300.1 K
CNST2          140.0000000
CNST13           8.3299999
D0              0.00000300 sec
D1              1.00000000 sec
D2              0.00357143 sec
D6              0.06002401 sec
D16             0.00010000 sec
IN0             0.00002090 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.90 usec
P2                   29.80 usec
PL1                  -1.20 dB
PL1W           11.52336311 W
SFO1           399.8719994 MHz

======== CHANNEL f2 ========
NUC2                   13C
P3                    9.80 usec
PL2                  -2.00 dB
PL2W           46.18043137 W
SFO2           100.5585518 MHz

====== GRADIENT CHANNEL =====
GPNAM1            SINE.100
GPNAM2            SINE.100
GPNAM3            SINE.100
GPZ1                 50.00 %
GPZ2                 30.00 %
GPZ3                 40.10 %
P16                1000.00 usec
ND0                      2
TD                     256
SFO1              100.5586 MHz
FIDRES           93.450958 Hz
SW                 237.906 ppm
FnMODE                  QF
SI                    1024
SF             399.8699722 MHz
WDW                   SINE
SSB                      2
LB                    0.00 Hz
GB                       0
PC                    0.80
SI                     512
MC2                     QF
SF             100.5470947 MHz
WDW                   SINE
SSB                      0
LB                    0.00 Hz
GB                       0
```

Figure S28. HMBC spectrum of compound **8** (TFA salt, D_2O, 400 MHz).



```
NAME      CL discorhabdin 1 (CL1-11-2 FULL)
EXPNO                  8
PROCNO                 1
Date_           20101011
Time                1.29
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG   noesygpphpp.rak
TD                  2048
SOLVENT              D2O
NS                    40
DS                    16
SWH             8012.820 Hz
FIDRES          3.912510 Hz
AQ             0.1278452 sec
RG                    57
DW                62.400 usec
DE                  6.50 usec
TE                 300.1 K
D0            0.00004343 sec
D1            1.00000000 sec
D8            0.80000001 sec
D11           0.03000000 sec
D12           0.00002000 sec
D30           0.79895002 sec
IN0           0.00012480 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.90 usec
P17              2500.00 usec
PL1                -1.20 dB
PL10                3.30 dB
PL1W         11.52336311 W
PL10W         4.08864355 W
SFO1         399.8719994 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPZ1               17.00 %
P16              1000.00 usec
ND0                    1
TD                   256
SFO1             399.872 MHz
FIDRES         31.300079 Hz
SW                20.038 ppm
FnMODE              TPPI
SI                  1024
SF           399.8700086 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
PC                  0.80
SI                   256
MC2                 TPPI
SF           399.8700086 MHz
WDW                QSINE
SSB                    2
LB                  0.00 Hz
GB                     0
```

Figure S29. NOESY spectrum of compound **8** (600 ms mixing time, TFA salt, D_2O, 400 MHz).