

SUPPLEMENTARY MATERIAL

A new diketopiperazine from the gorgonian coral *Menella kanisa*

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Chemical investigation on the gorgonian *Menella kanisa* collected from Beibu Gulf led to the isolation of a new diketopiperazine, named menazepine A (**1**), as well as three known diketopiperazines, namely cyclo(4-hydroxyprolylleucyl) (**2**), cyclo(Pro-Leu) (**3**) and cyclo(4-hydroxyprolylphenylalanyl) (**4**). The structure of the new diketopiperazine was elucidated on the basis of extensive spectroscopic analysis and by comparison of the data with those of related metabolites. Compounds **1–4** were also evaluated for the brine shrimp lethality.

Keywords: *Menella kanisa*; diketopiperazine; menazepine A; brine shrimp lethality

Table S1: Toxicity towards brine shrimp larvae of compounds **1–4**.

Compounds	LD ₅₀ (μg/ml)
1	20.6
2	245.1
3	0.8
4	72.5

Figure S2: Key ¹H-¹H COSY, HMBC and NOESY for **1**.

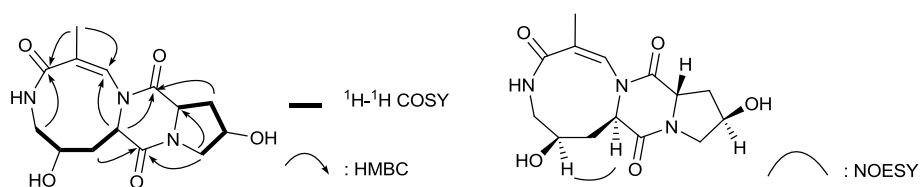
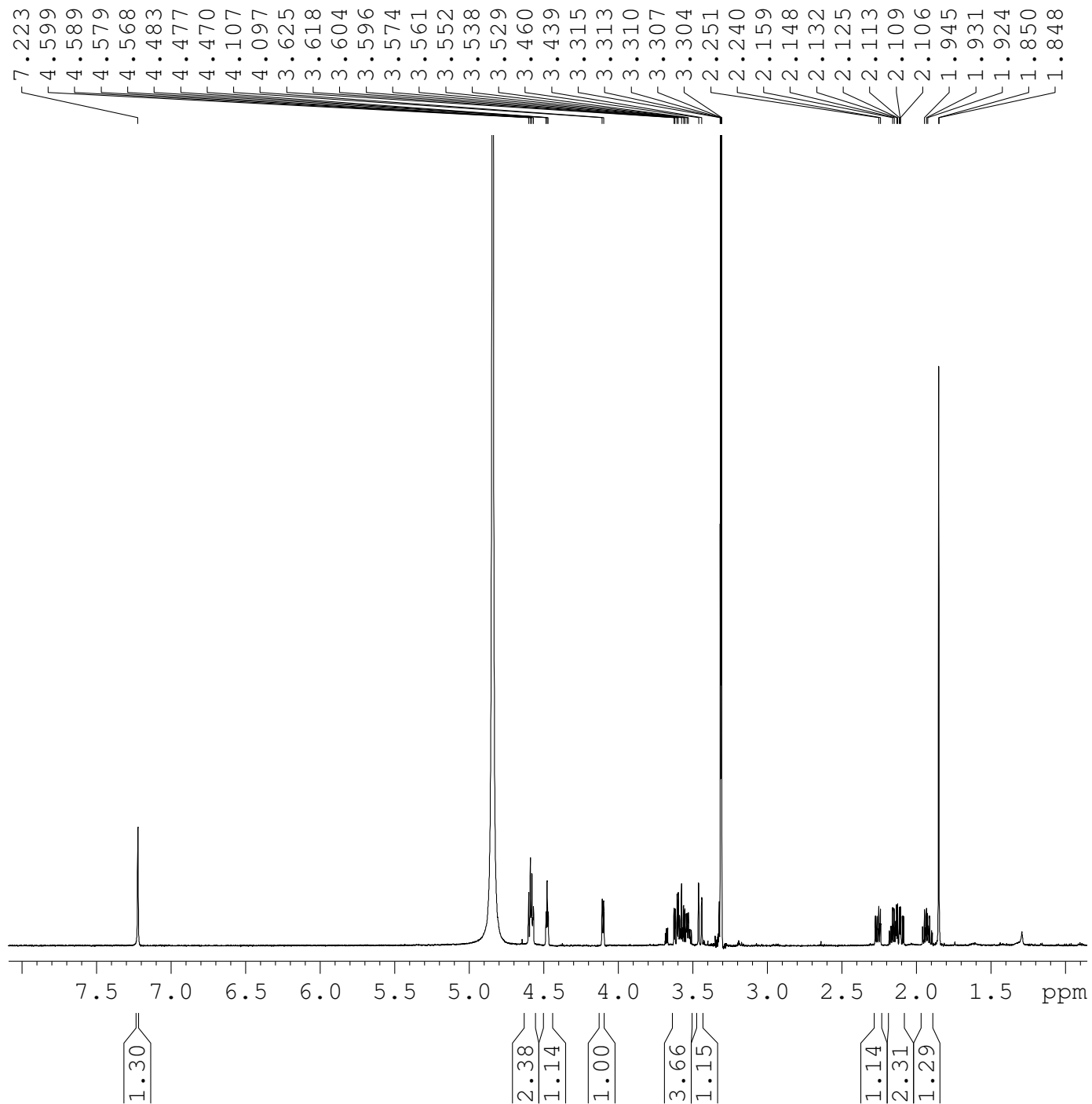


Figure S3. ¹H-NMR spectrum of 1.



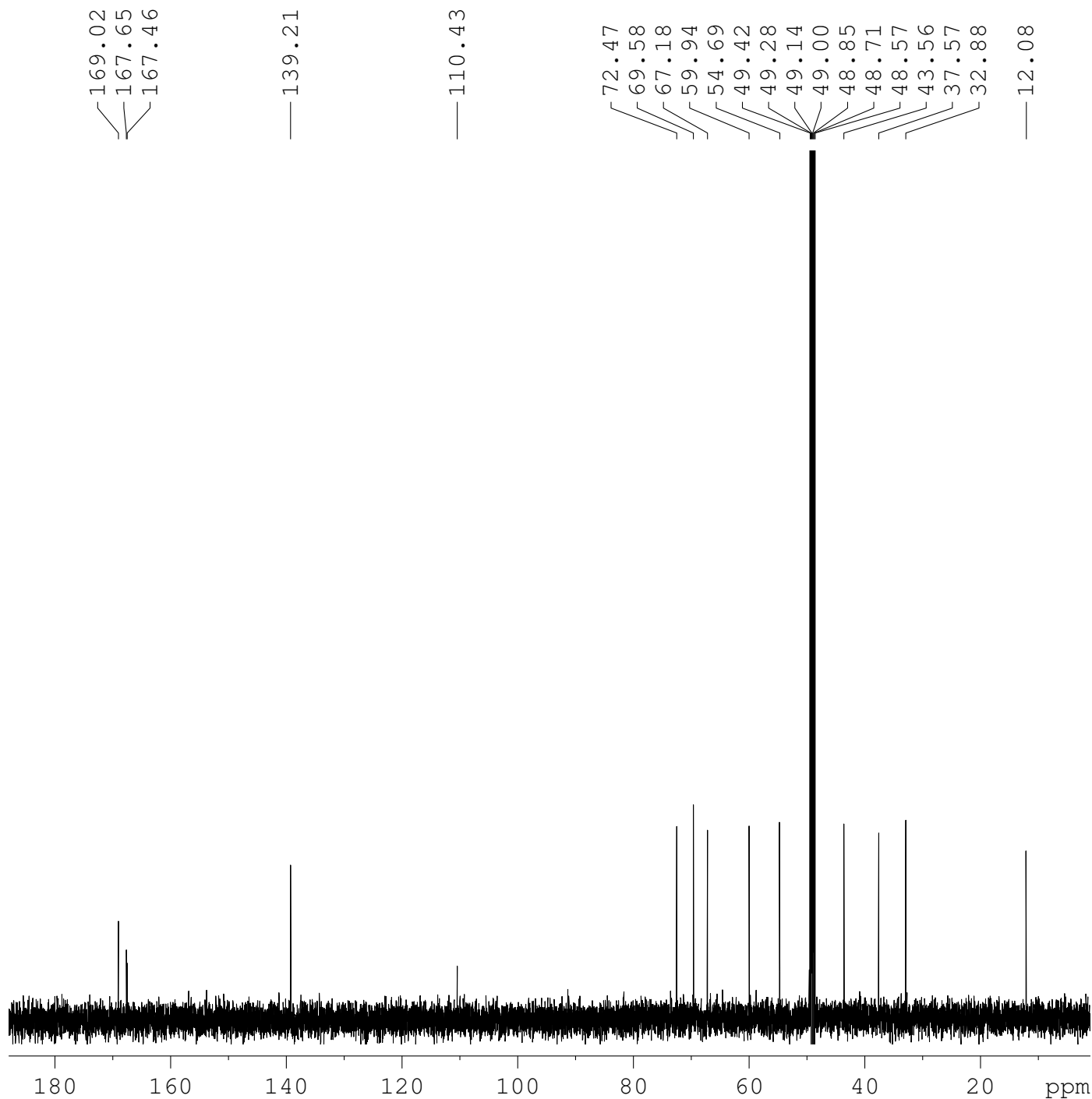
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NAME      120709  YZ-2
EXPNO      1
PROCNO     1
Date_      20120709
Time       15.40
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    zg30
TD         32768
SOLVENT    MeOD
NS         8
DS         2
SWH        12315.271 Hz
FIDRES     0.375832 Hz
AQ         1.3304307 sec
RG         203
DW         40.600 usec
DE         6.50 usec
TE         299.2 K
D1         2.00000000 sec
TD0        1
    
```

```

===== CHANNEL f1 =====
NUC1       1H
P1         14.25 usec
PL1        -1.00 dB
PL1W       18.87879753 W
SFO1       600.1754015 MHz
SI         32768
SF         600.1700127 MHz
WDW        no
SSB        0
LB         0.00 Hz
GB         0
PC         1.00
    
```

Figure S4. ¹³C-NMR spectrum of 1.



```

NAME      120709  YZ-2
EXPNO      2
PROCNO     1
Date_      20120716
Time       10.08
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    zgpg30
TD         32768
SOLVENT    MeOD
NS         557
DS         4
SWH        36057.691 Hz
FIDRES     1.100393 Hz
AQ         0.4544329 sec
RG         203
DW         13.867 usec
DE         6.50 usec
TE         302.1 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1
    
```

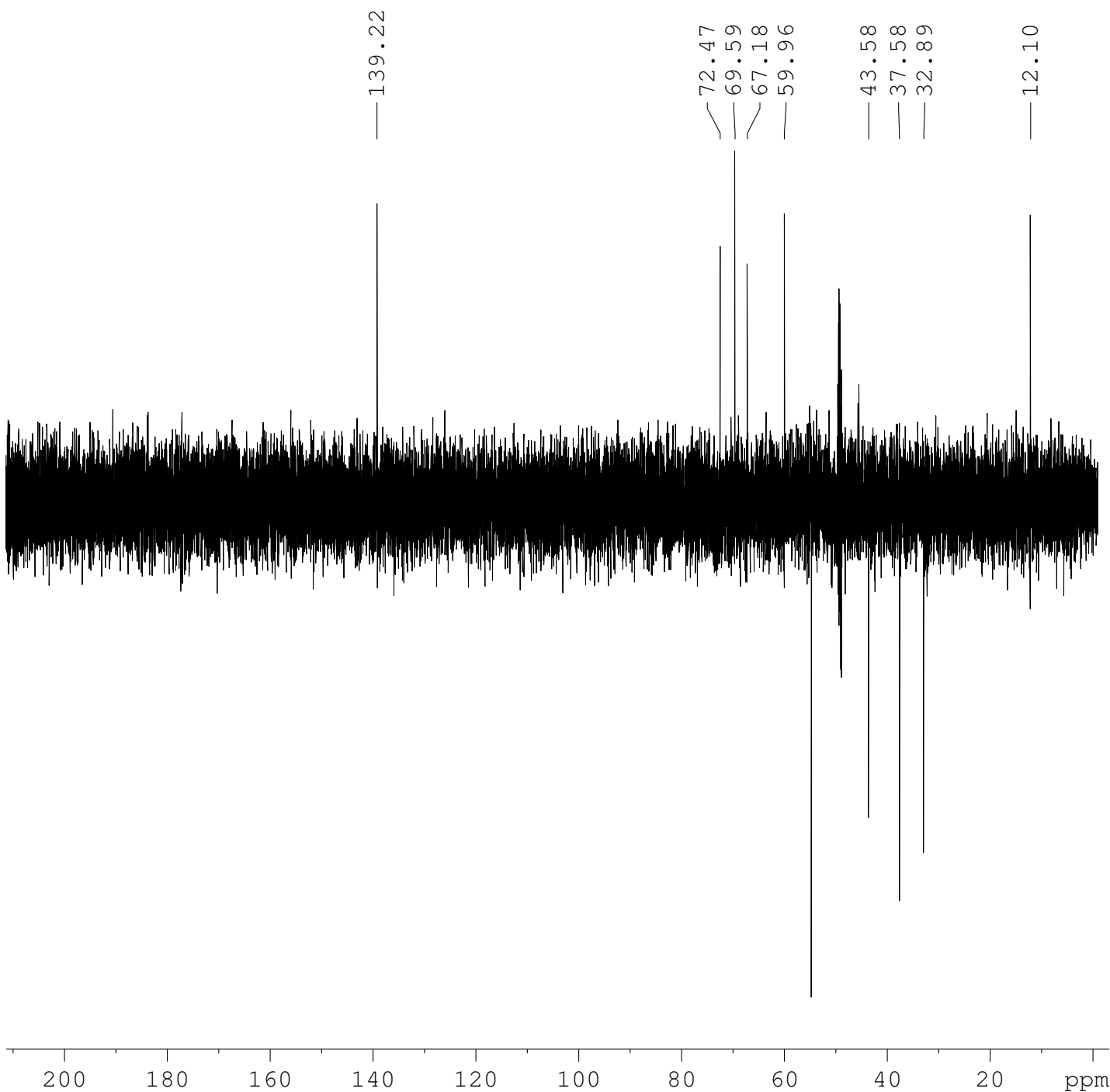
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===== CHANNEL f1 =====
NUC1       13C
P1         10.38 usec
PL1        1.50 dB
PL1W       69.70854950 W
SFO1       150.9305238 MHz
    
```

```

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      77.00 usec
PL2        -1.00 dB
PL12       14.00 dB
PL13       14.00 dB
PL2W       18.87879753 W
PL12W      0.59700000 W
PL13W      0.59700000 W
SFO2       600.1724007 MHz
SI         32768
SF         150.9126551 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

Figure S5. DEPT135 spectrum of 1.



```

NAME      120709  YZ-2
EXPNO     4
PROCNO    1
Date_     20121012
Time      16.00
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   dept135
TD        32768
SOLVENT   MeOD
NS        88
DS        8
SWH       36057.691 Hz
FIDRES    1.100393 Hz
AQ        0.4544329 sec
RG        203
DW        13.867 usec
DE        6.50 usec
TE        300.0 K
CNST2     145.0000000
D1        2.0000000 sec
D2        0.00344828 sec
D12       0.00002000 sec
TD0       1
    
```

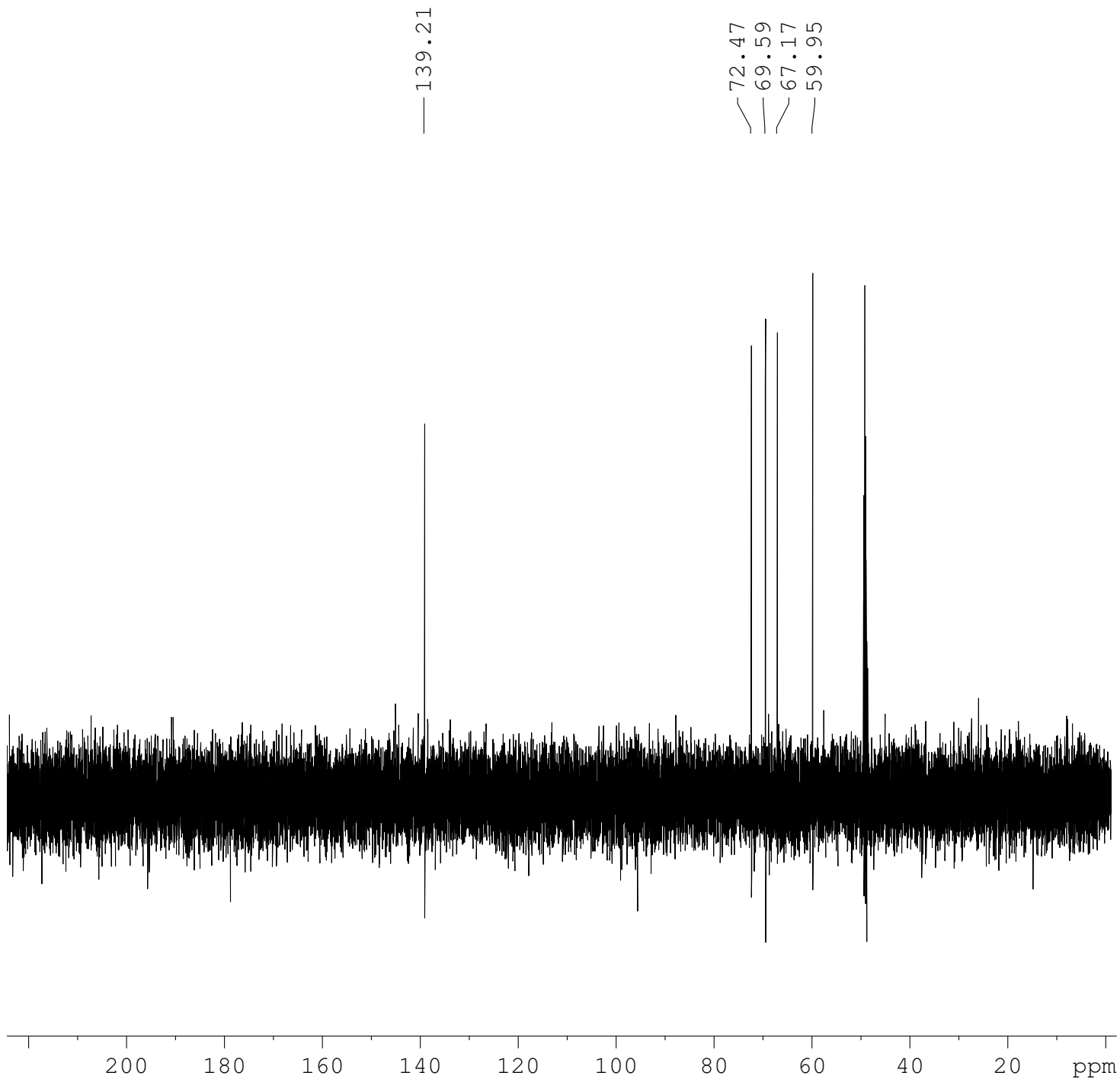
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===== CHANNEL f1 =====
NUC1      13C
P1        9.23 usec
P2        18.46 usec
PL1       1.00 dB
PL1W      78.21427917 W
SFO1     150.9305238 MHz
    
```

```

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
P3        13.82 usec
P4        27.64 usec
PCPD2     100.00 usec
PL2       -2.50 dB
PL12      14.69 dB
PL2W      26.66701126 W
PL12W     0.50930083 W
SFO2     600.1724007 MHz
SI        32768
SF        150.9126524 MHz
WDW       no
SSB       0
LB        0.00 Hz
GB        0
PC        1.40
    
```

Figure S6. DEPT90 spectrum of 1.



```
NAME      120709  YZ-2
EXPNO      3
PROCNO     1
Date_      20121012
Time       15.52
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    dept90
TD         32768
SOLVENT    MeOD
NS         152
DS         8
SWH        36057.691 Hz
FIDRES     1.100393 Hz
AQ         0.4544329 sec
RG         203
DW         13.867 usec
DE         6.50 usec
TE         299.8 K
CNST2     145.0000000
D1         2.00000000 sec
D2         0.00344828 sec
D12        0.00002000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         9.23 usec
P2         18.46 usec
PL1        1.00 dB
PL1W       78.21427917 W
SFO1       150.9305238 MHz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
P3         13.82 usec
P4         27.64 usec
PCPD2      100.00 usec
PL2        -2.50 dB
PL12       14.69 dB
PL2W       26.66701126 W
PL12W      0.50930083 W
SFO2       600.1724007 MHz
SI         32768
SF         150.9126759 MHz
WDW        no
SSB        0
LB         0.00 Hz
GB         0
PC         1.40
```

Figure S7. HMBC spectrum of 1.

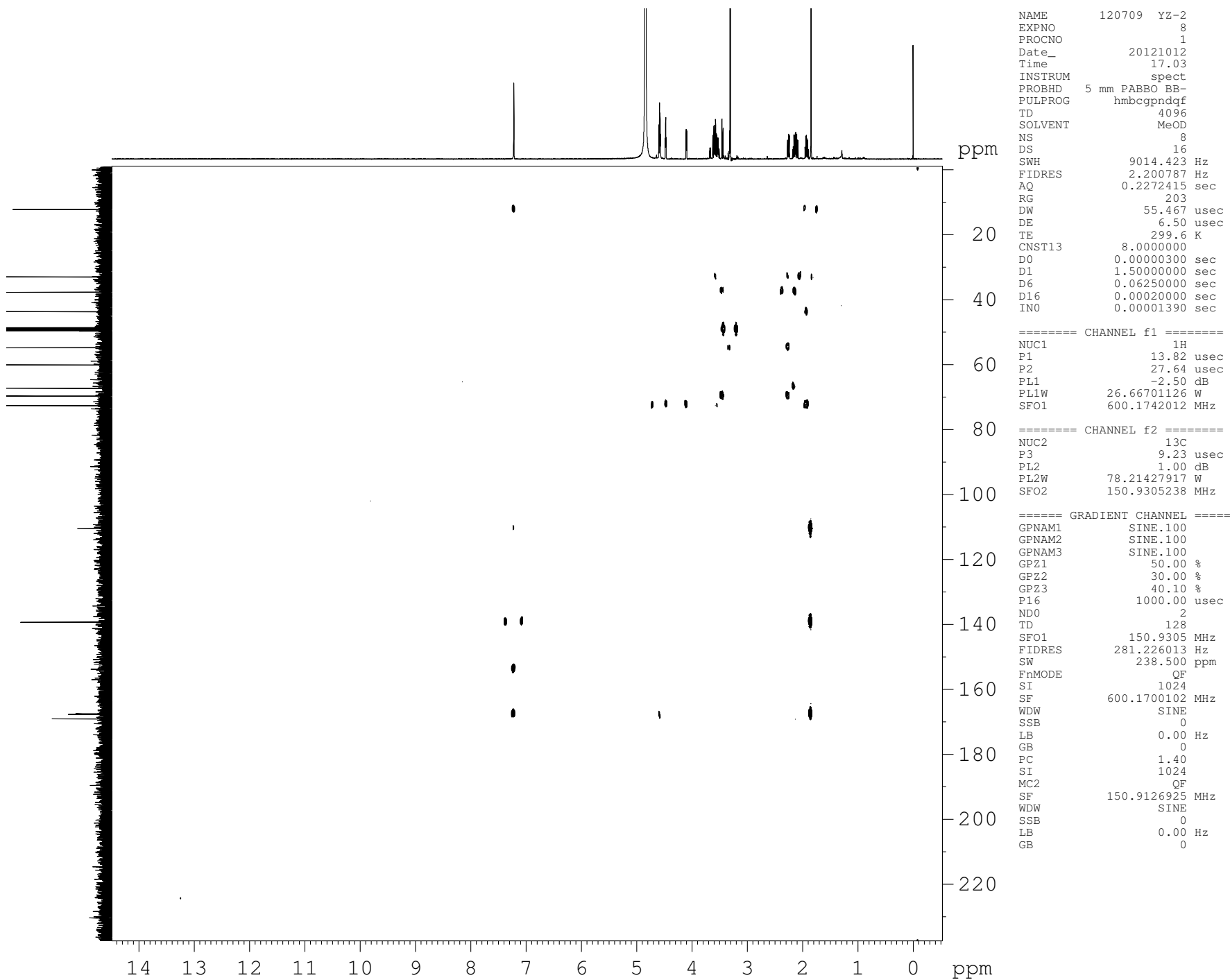
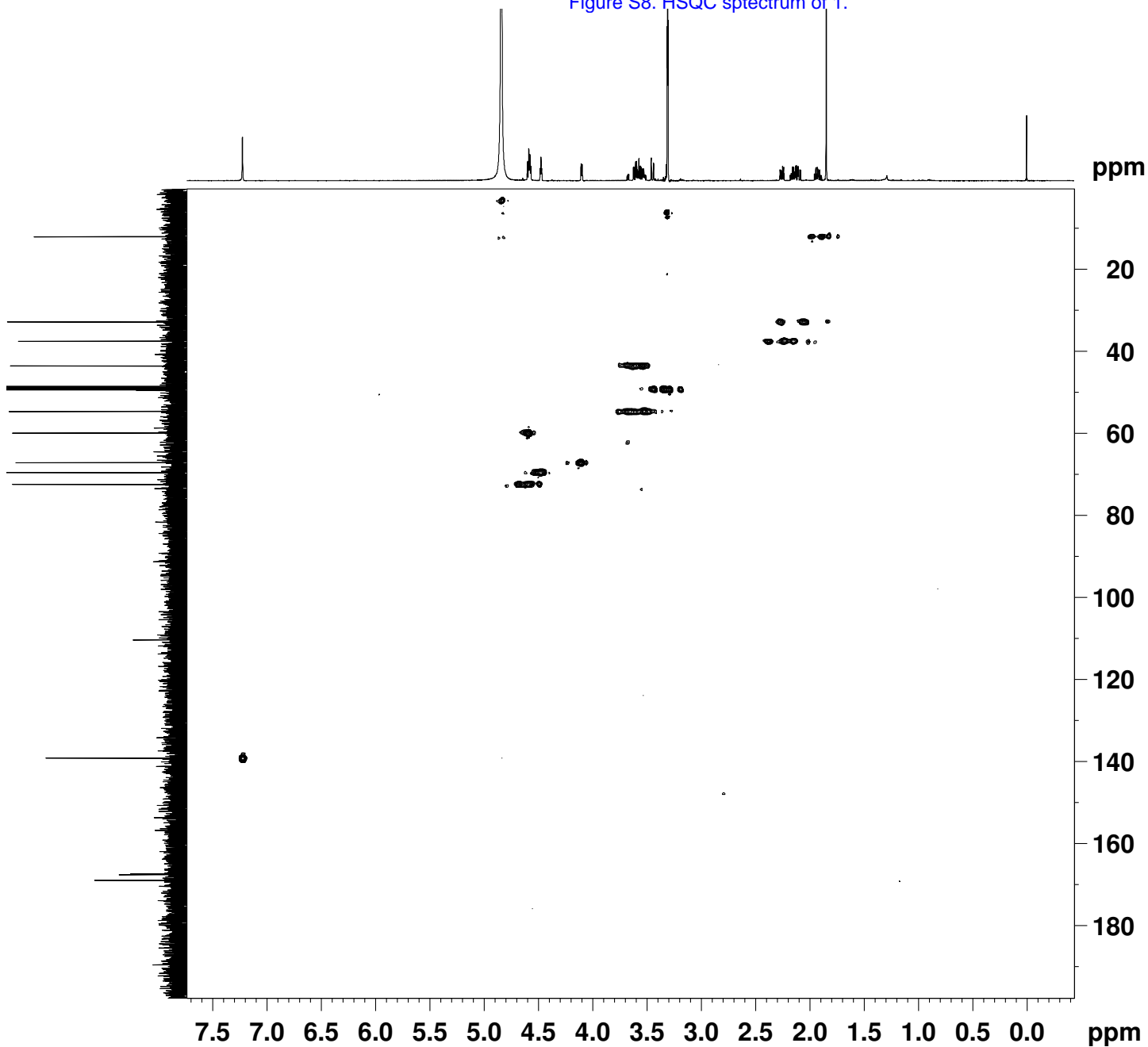


Figure S8. HSQC spectrum of 1.



```

NAME      120709  YZ-2
EXPNO     7
PROCNO    1
Date_     20121012
Time      16.06
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   hsqcetgpsi2
TD         1024
SOLVENT   MeOD
NS         8
DS         16
SWH        9014.423 Hz
FIDRES     8.803147 Hz
AQ         0.0568479 sec
RG         203
DW         55.467 usec
DE         6.50 usec
TE         299.6 K
CNST2     145.0000000
D0         0.00000300 sec
D1         1.50000000 sec
D4         0.00172414 sec
D11        0.03000000 sec
D13        0.00000400 sec
D16        0.00020000 sec
D24        0.00086207 sec
IN0        0.00001390 sec
ZGOPTNS

===== CHANNEL f1 =====
NUC1       1H
P1         13.82 usec
P2         27.64 usec
P28        0.00 usec
PL1        -2.50 dB
PL1W       26.66701126 W
SFO1       600.1742012 MHz

===== CHANNEL f2 =====
CPDPRG2    garp
NUC2       13C
P3         9.23 usec
P4         18.46 usec
PCPD2      100.00 usec
PL2         1.00 dB
PL12       21.70 dB
PL2W       78.21427917 W
PL12W      0.66571140 W
SFO2       150.9305238 MHz

===== GRADIENT CHANNEL =====
GPNAM1     SINE.100
GPNAM2     SINE.100
GPNAM3     SINE.100
GPNAM4     SINE.100
GPZ1       80.00 %
GPZ2       20.10 %
GPZ3       11.00 %
GPZ4       -5.00 %
P16        1000.00 usec
P19        600.00 usec
ND0         2
TD          256
SFO1       150.9305 MHz
FIDRES     140.613007 Hz
SW         238.500 ppm
FnMODE     Echo-Antiecho
SI         1024
SF         600.1700109 MHz
WDW        QSINE
SSB         2
LB         0.00 Hz
GB         0
PC         1.40
SI         1024
MC2        echo-antiecho
SF         150.9126380 MHz
WDW        QSINE
SSB         2
LB         0.00 Hz
GB         0
    
```