

Supporting Information for

Antimalarial Bromophycolides J-Q from the Fijian Red Alga *Callophycus serratus*

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Table S1: ^1H - ^1H COSY correlations for bromophycolides J-Q (1-8). For diastereotopic protons with dissimilar chemical shifts, the proton whose chemical shift is listed first in Table 1 of the main article is termed “a” and the other is “b”. “NA” (not applicable) indicates that no proton signal exists for that position.

^1H at position #:	COSY correlations observed between protons listed on far left and those below:							
	1	2	3	4	5	6	7	8
3	-	-	-	-	5a	-	16	-
5a	5b, 6	5b	5b	5b	3, 5b, 6	5b, 6	5b	5b
5b	5a	5a	5a	5a	5a, 6	5a	5a, 6	5a
6	5a	NA	NA	NA	5a, 5b, 20	5a	5b, 23b	NA
7	NA	8a, 8b	8a, 8b	NA	NA	NA	NA	NA
8a	8b, 9b	7, 8b	7, 8b, 9a	8b, 9b	8b, 9a, 9b	8b, 9a, 9b	8b, 9a, 9b	8b, 9a
8b	8a, 9a, 9b, 24	7, 8a, 9a, 9b	7, 8a, 9a	8a	8a, 9b	8a, 9a, 9b	8a, 9b	8a, 9a, 9b
9a	8b, 9b, 10	8b, 9b, 10	8a, 8b, 9b, 10	9b, 10	8a, 9b, 10	8a, 8b, 10	8a, 9b, 10	8a, 8b, 9b, 10
9b	8a, 8b, 9a, 10	9a, 8b	9a, 10	8a, 9a, 10	8a, 8b, 9a, 10	8a, 8b	8a, 8b, 9a, 10	8b, 9a, 10
10	9a, 9b	9a	9a, 9b	9a, 9b	9a, 9b	9a	9a, 9b	9a, 9b
12a	12b, 13a, 13b	12b, 13a, 13b	12b, 13a, 13b	12b, 13b	12b, 13a, 13b	12b, 13a, 13b	12b, 13a	13b
12b	12a, 13a, 13b	12a, 13a, 13b	12a, 13b	12a, 13b	12a, 13a	12a, 13a, 13b	12a, 13a	13a, 13b
13a	12a, 12b, 13b, 14	12a, 12b, 13b, 14	12a, 13b, 14	13b	12a, 12b, 13b, 14	12a, 12b, 13b, 14	12a, 12b, 13b	12b, 13b
13b	12a, 12b, 13a, 14	12a, 12b, 13a, 14	12a, 12b, 13a, 14	12a, 12b, 13a, 14	12a, 13a, 14	12a, 12b, 13a, 14	13a, 14	12a, 12b, 13a, 14
14	13a, 13b	13a, 13b	13a, 13b	13b, 26a, 26b	13a, 13b	13a, 13b	13b	13b
16	17	17	17	17	17	17	3, 17	17
17	16	16	16	16	16	16	16	16
20a	21a, 21b, 22	20b, 21a, 21b	20b	20b, 21a	6, 21a, 21b, 23	21, 23	20b, 21b	20b, 21a, 21b
20b	NA	20a, 21a, 21b	20a, 21	20a, 21b, 23	NA	NA	20a, 21a	20a, 21b
21a	20, 21b, 22	20a, 20b, 21b	20b, 24	20a, 21b, 22	20, 21b, 22	20, 22	20b, 21b, 22	20a, 21b, 22
21b	20, 21a, 22	20a, 20b, 21a, 24b	NA	20b, 21a, 22	20, 21a, 22	-	20a, 21a, 22	20a, 20b, 21a, 22
22	20, 21a, 21b	NA	NA	21a, 21b	21a, 21b	21	21a, 21b	21a, 21b
23a	-	-	-	20b	20	20	-	-
23b	NA	NA	NA	NA	NA	NA	6	NA
24a	8b	24b	21	-	-	-	-	-
24b	NA	24a, 21b	NA	NA	NA	NA	NA	NA
25	-	-	-	-	-	-	-	-
26a	-	-	26b, 27	14, 26b, 27	26b, 27	-	-	-
26b	NA	-	26a, 27	14, 26a, 27	26a, 27	NA	NA	NA
27	-	-	26a, 26b	26a, 26b	26a, 26b	-	-	-
28	-	NA	NA	NA	NA	NA	NA	NA

Table S2: HMBC correlations for bromophycolides J-Q (1-8). For diastereotopic protons with dissimilar chemical shifts, the proton whose chemical shift is listed first in Table 1 of the main article is termed “a” and the other is “b”. “NA” (not applicable) indicates that no proton signal exists for that position.

¹ H at position #:	HMBC correlations observed between protons listed on far left and carbons at positions listed below:							
	1	2	3	4	5	6	7	8
3	1, 5, 16, 18	1, 5, 16, 18	1, 16, 18	1, 5, 16, 18	1, 5, 16, 18	1, 5, 16, 18	1, 5, 16, 18	1, 5, 16, 18
5a	4, 7	7	6	3, 6, 7, 18, 19	3, 4, 6, 7, 19	4, 6	4, 6, 7, 18, 19	3, 4, 6, 18, 19
5b	3, 4, 6, 7, 18, 19	4	4, 6	3, 6, 7, 18, 19	3, 4, 6, 18, 19	-	3, 4, 6, 18, 19	3, 4
6	-	NA	NA	NA	-	19	4, 7, 19, 24	NA
7	NA	-	-	NA	NA	NA	NA	NA
8a	-	-	-	7, 22	-	-	-	9
8b	-	-	-	6	-	9	6	6, 7
9a	-	-	-	-	7	-	10	10
9b	-	-	-	-	-	-	-	-
10	11, 12	-	-	-	-	-	-	-
12a	-	-	-	-	-	10, 11	10, 11, 13	10, 11, 13
12b	-	-	-	10, 11, 13	-	13	10, 11, 13, 14	11, 13
13a	-	-	-	11	-	-	12, 14, 15	14
13b	-	-	-	-	-	-	-	14
14	1, 12	1	-	15	-	1	1, 12	1, 12
16	1, 3, 18	-	1, 3, 18	1, 3, 18	1, 3, 18	3, 18	1, 3, 18	3, 18
17	2, 4	2	2, 4	2, 4, 18	2, 4, 18	2, 4, 18	2, 4, 18	2, 4, 18
20a	-	-	-	-	-	-	-	-
20b	NA	-	-	22	NA	NA	-	-
21a	-	-	-	7, 19, 22	-	-	22	-
21b	-	-	NA	7	-	-	-	-
22	-	NA	NA	20	21, 24	6, 21, 24	24	-
23a	6, 19, 20	6, 19, 20	6, 19, 20	6, 19, 20	6, 19, 20	6, 19, 20	6, 20	6, 19, 20
23b	NA	NA	NA	NA	NA	NA	6, 20	NA
24a	6, 7, 8, 22	7, 21	7, 21, 22	6, 7, 8, 22	6, 7, 8, 22	6, 7, 8, 22	6, 7, 8, 22	6, 7, 8, 22
24b	NA	7, 21	NA	NA	NA	NA	NA	NA
25	10, 11, 12	10, 11, 12	10, 11, 12	10, 11, 12	10, 11, 12	10, 11, 12	10, 11, 12	10, 11, 12
26a	14, 15, 27	14, 15, 27	-	14, 27	14, 15, 27	14, 15, 27	14, 15, 27	14, 15, 27
26b	NA	NA	14	14, 15, 27	14, 27	NA	NA	NA
27	14, 15, 26	14, 15, 26	14, 15, 26	14, 15, 26	14, 15, 26	14, 15, 26	14, 15, 26	14, 15, 26
28	19	NA	NA	NA	NA	NA	NA	NA
OH (18)	-	17, 18	-	4, 17, 18	4, 18	4	-	-

Table S3: Observed NOEs from ROESY (1-7) or NOESY (8) NMR experiments, for bromophycolides J-Q (1-8). For diastereotopic protons with dissimilar chemical shifts, the proton whose chemical shift is listed first in Table 1 of the main article is termed “a” and the other is “b”. Only NOEs important to determinations of stereochemistry are listed.

¹ H at position #:	NOE observed between protons listed on far left and protons at positions listed below:							
	1	2	3	4	5	6	7	8
3	6	5a	5a, 5b		6, 10	6, 12b	6, 8a, 9b, 10, 27	
5a		3	3, 23	24	24	24	24	
5b	24		3, 23	24	23, 24		23b, 24	
6	3, 8a, 20, 28				3, 8a, 22, 23	3, 22	3, 22	
7			8b, 9a, 20b					
8a	6, 24				6		3	8b
8b	10, 24		7		21b	10	22	8a
9a	10	10, 24a	7		22			10
9b				22	22		3, 22	
10	8b, 9a, 25	9a, 25	25	25	3, 25	8b, 25	3, 25	9a
12a	14	14		14			25	13b
12b	14			14	14	3	13a, 25	
13a	14	14		14		14	12b, 14	
13b		14		14	14		14, 26	12a, 14
14	12a, 12b, 13a	12a, 13a, 13b	27	12a, 12b, 13a, 13b	12b, 13b, 27	13a	13a, 13b, 26, 27	13b
20a	6, 21b, 22, 28				21a, 21b, 23			21a
20b			7					
21a	23		24		20		24	20a, 22
21b	20, 22			22	8b, 20			
22	20, 21b			9b, 21b	6, 9a, 9b	6	6, 8b, 9b	21a
23a	21a, 24, 28		5a, 5b		5b, 6, 20		23b	
23b							5b, 23a	
24a	5b, 8a, 8b, 23	9a	21	5a, 5b	5a, 5b	5a	5a, 5b, 21a	
25	10	10	10	10	10	10	10, 12a, 12b	
26							13b, 14, 27	
27			14		14		3, 14, 26	
28	6, 20, 23							

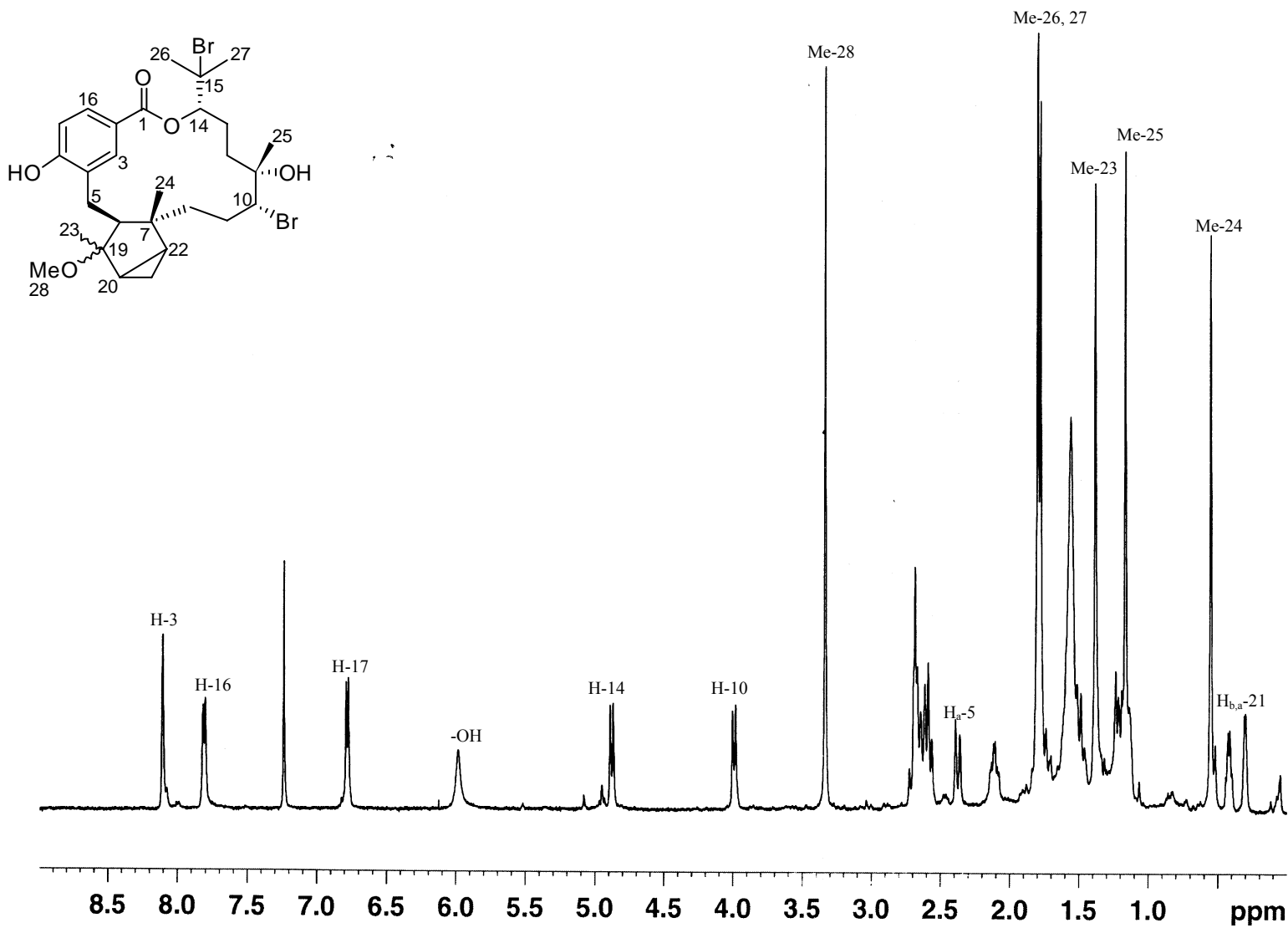


Figure S1. ¹H NMR spectrum of bromophycolide J (1) (500 MHz; CDCl₃)

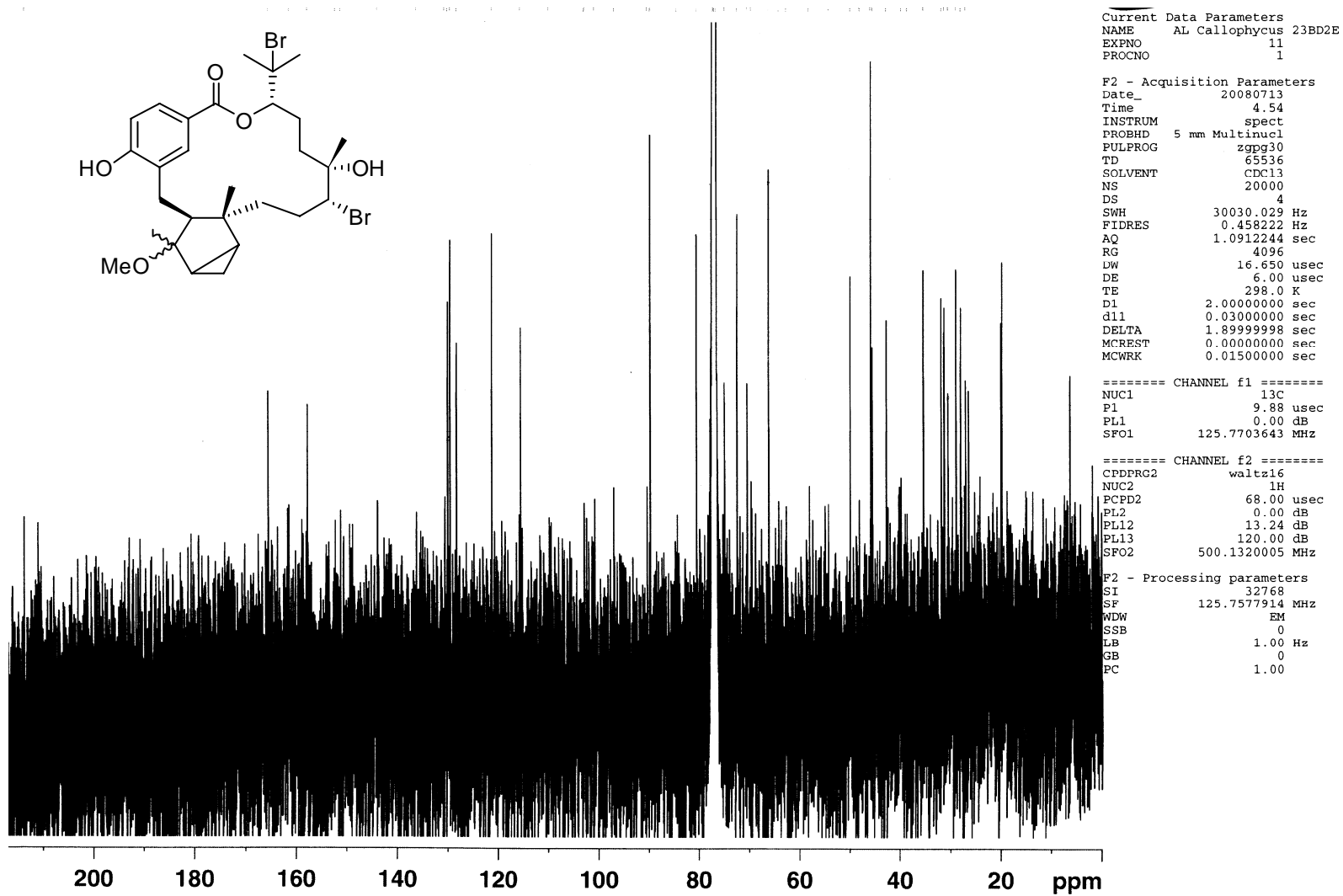


Figure S2. ¹³C NMR spectrum of bromophycolide J (1) (125 MHz; CDCl₃)

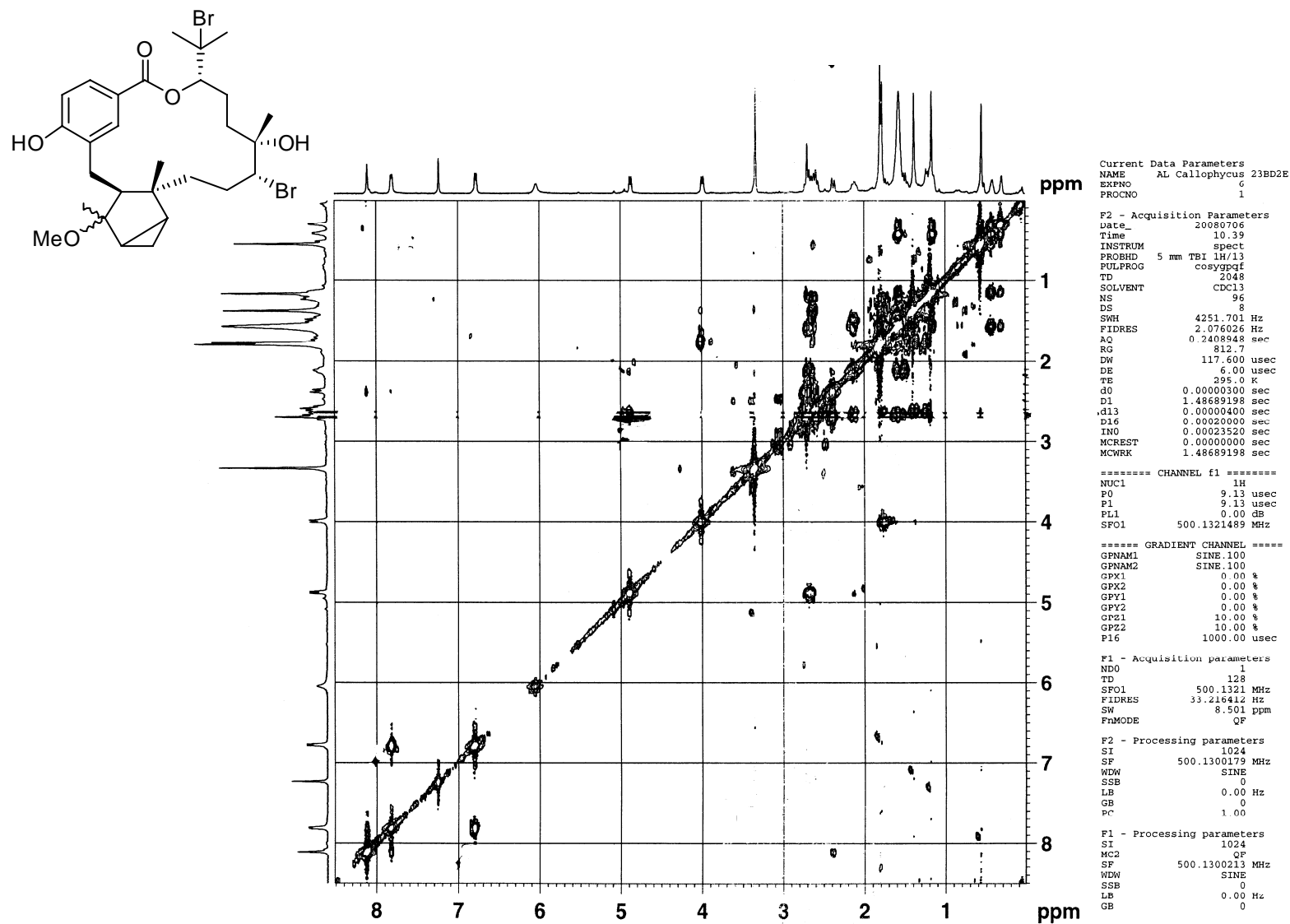


Figure S3. ^1H - ^1H COSY spectrum of bromophycolide J (1) (500 MHz; CDCl_3)

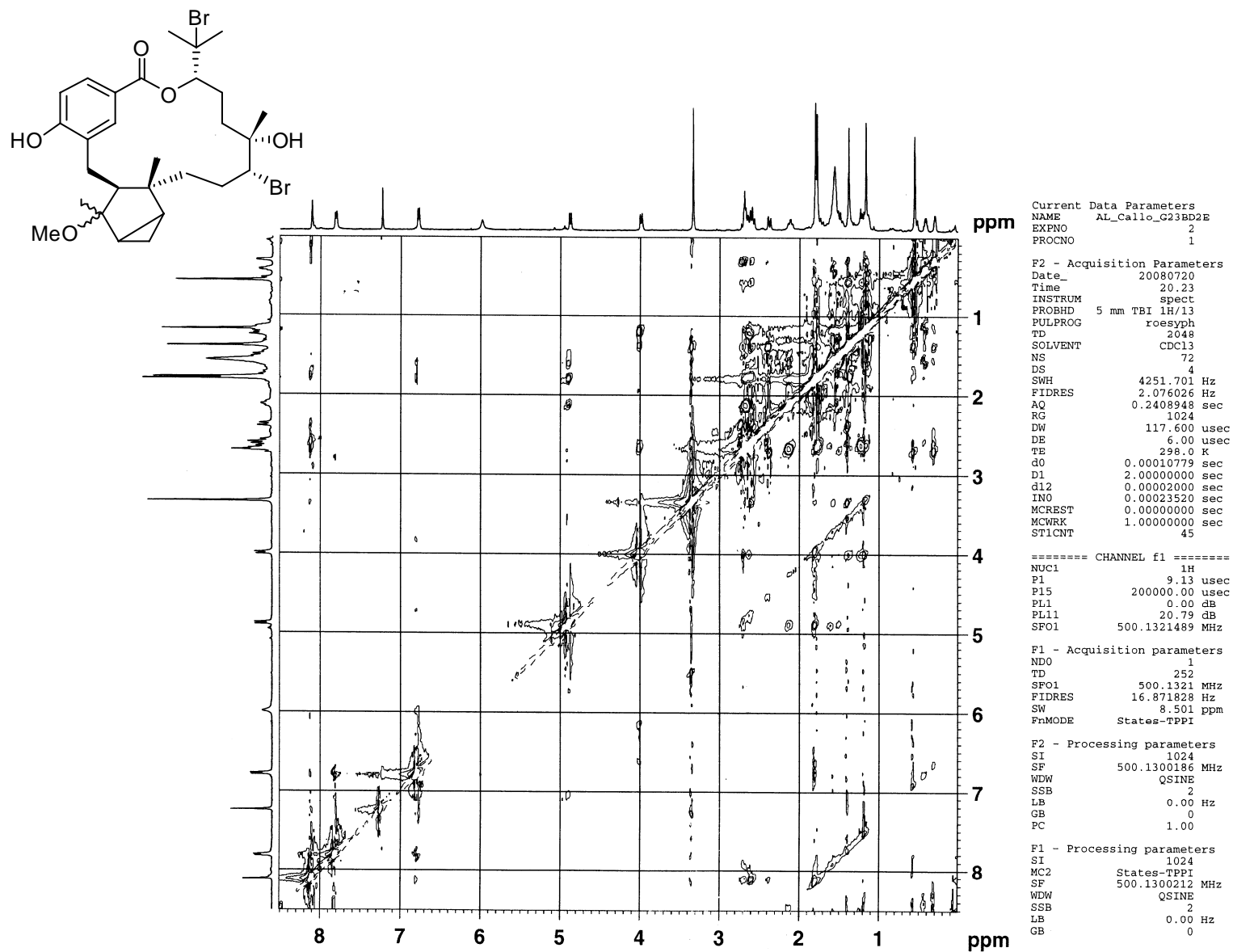


Figure S4. ROESY spectrum of bromophycolide J (**1**) (500 MHz; CDCl₃)

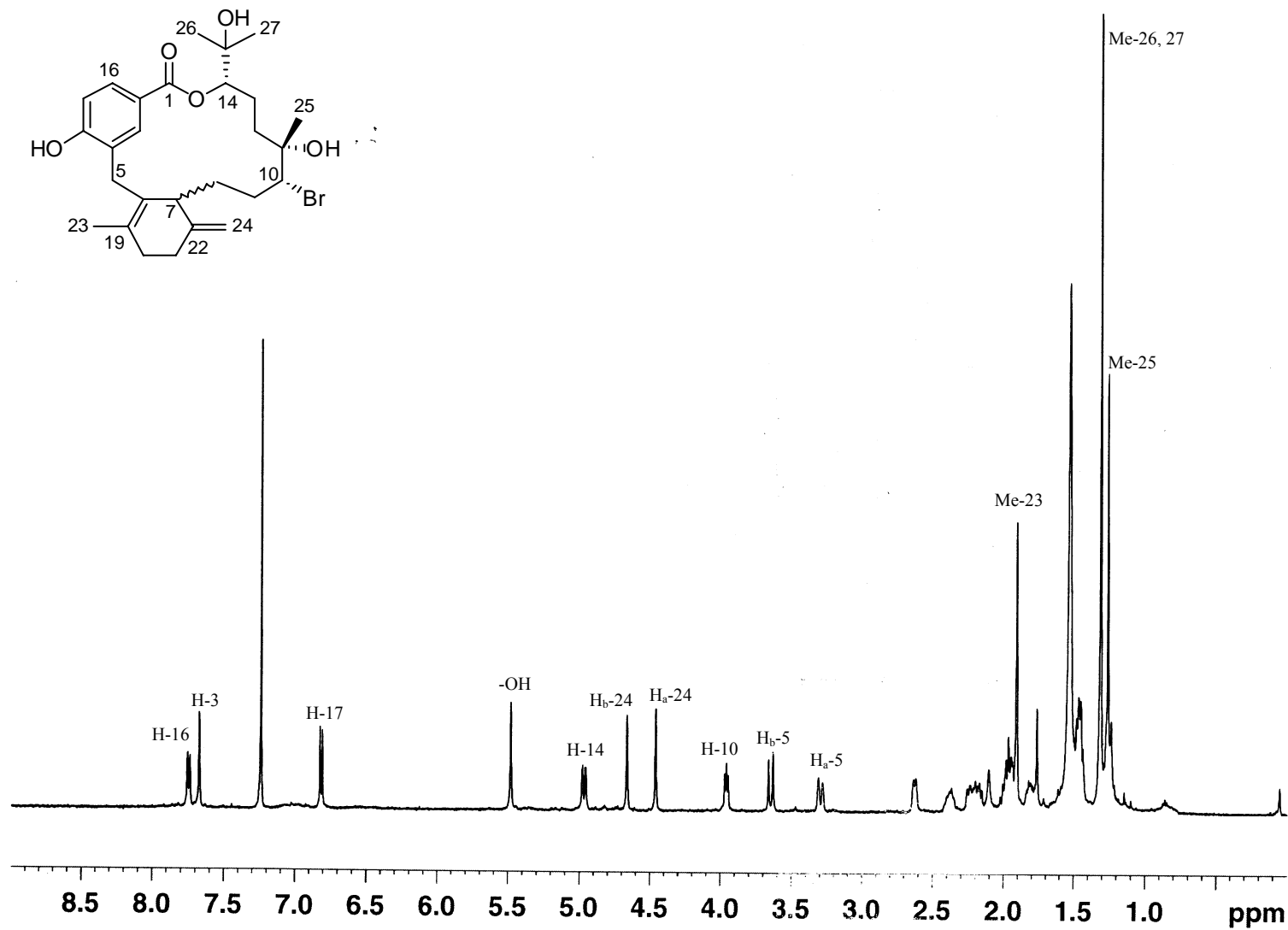


Figure S5. ¹H NMR spectrum of bromophycolide K (2) (500 MHz; CDCl₃)

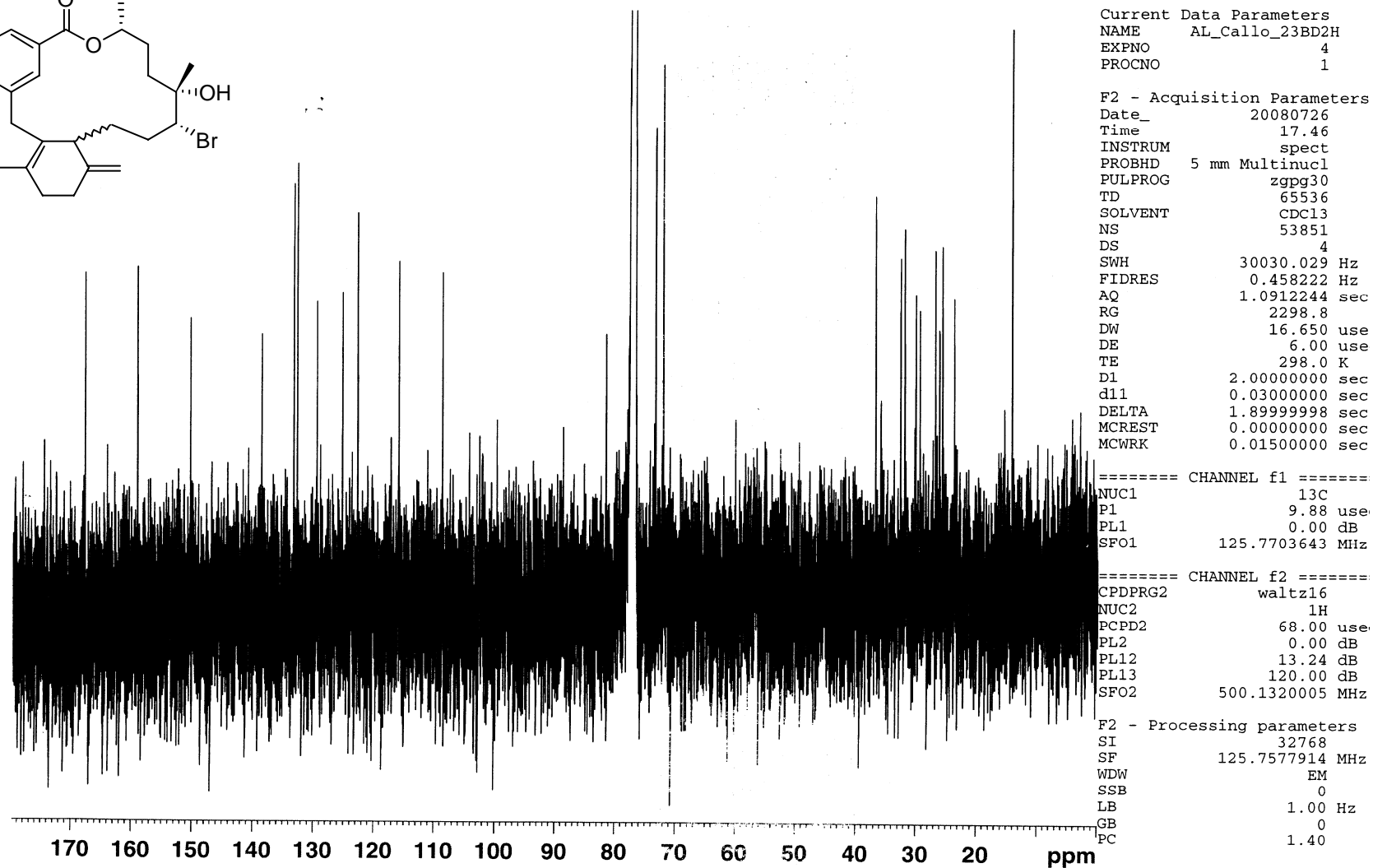
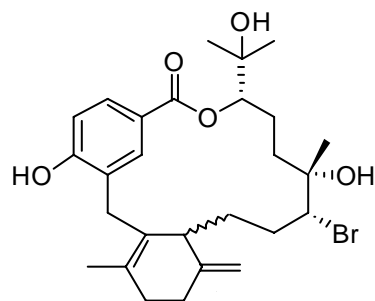


Figure S6. ^{13}C NMR spectrum of bromophycolide K (2) (125 MHz; CDCl_3)

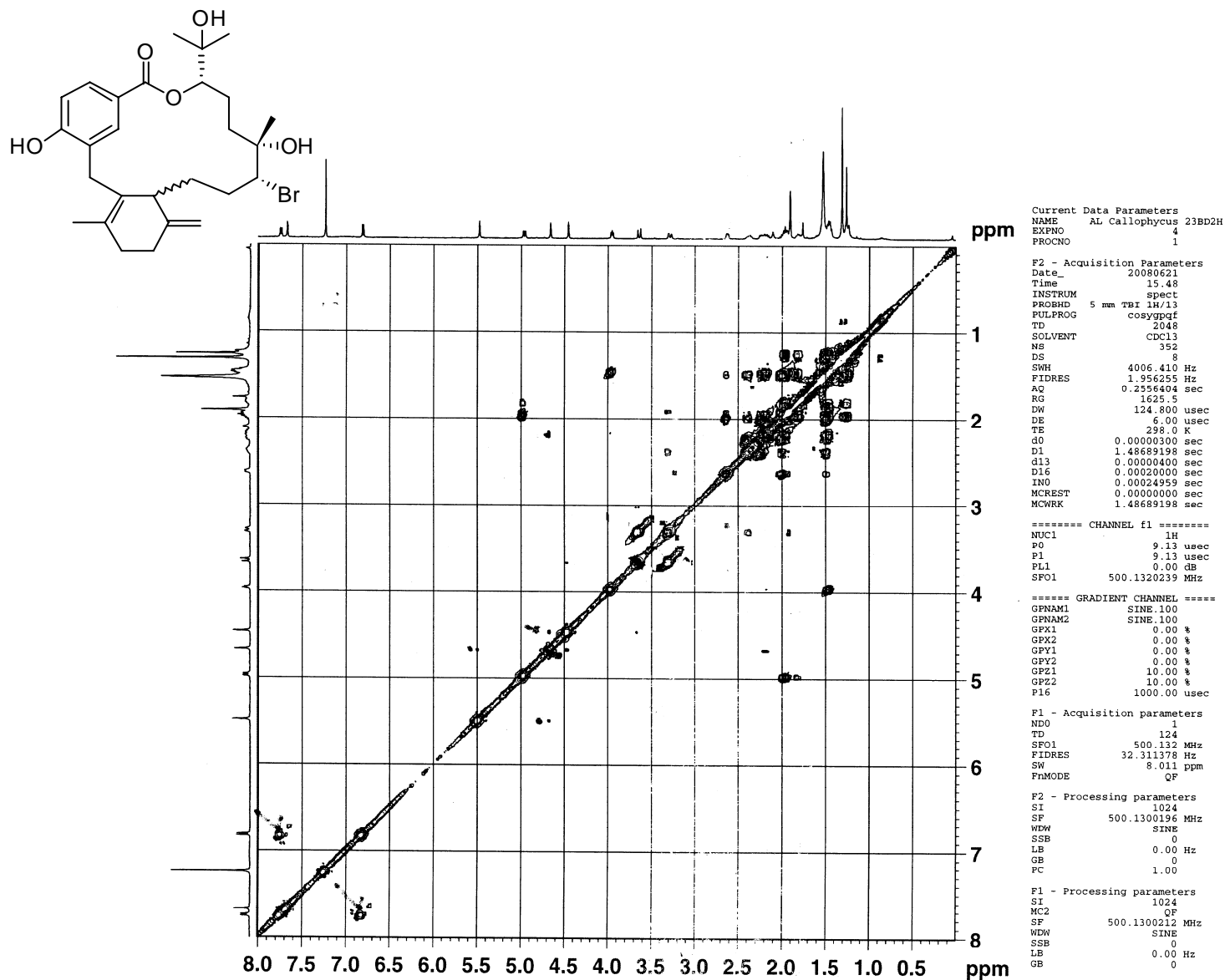


Figure S7. ^1H - ^1H COSY spectrum of bromophycolide K (2) (500 MHz; CDCl_3)

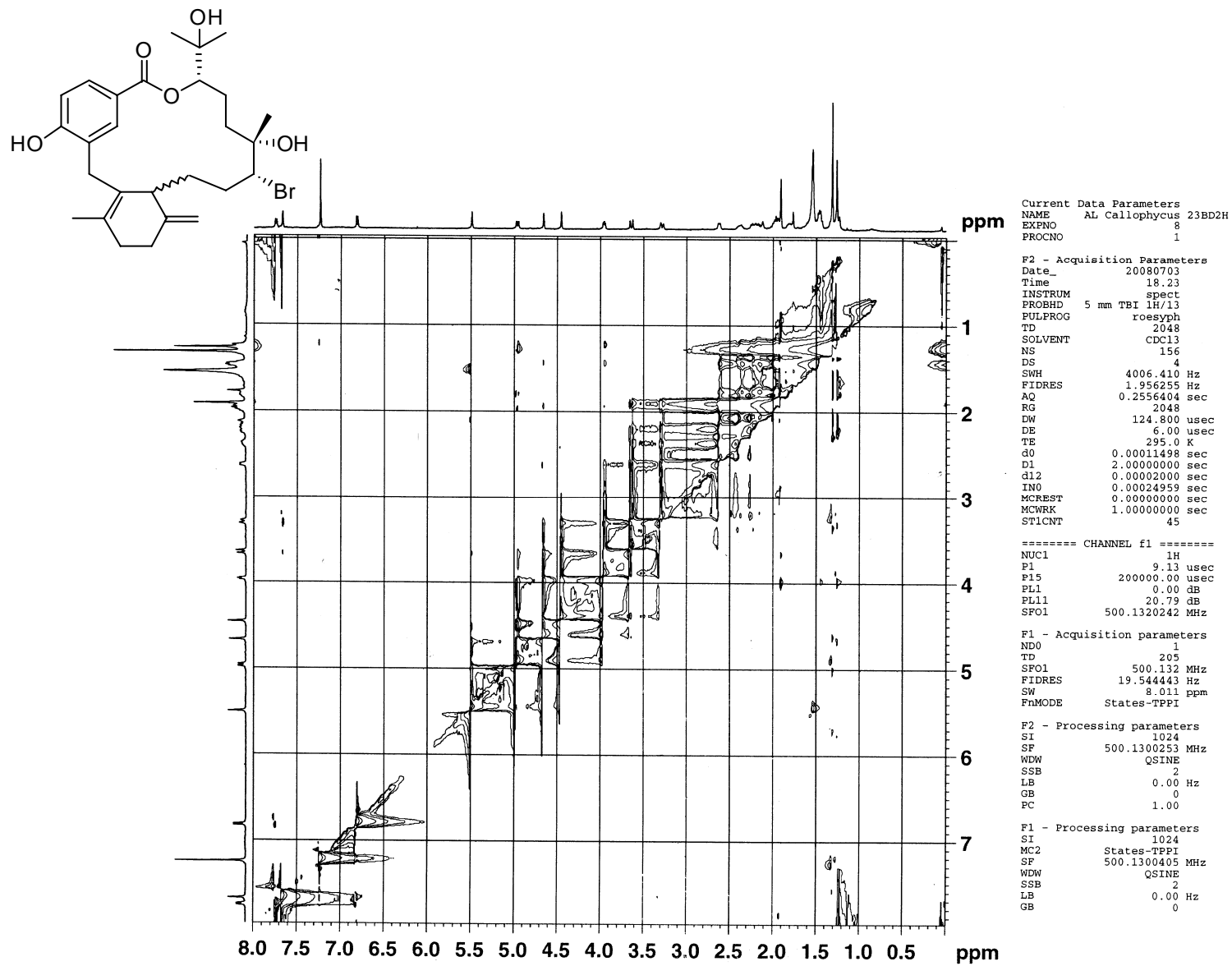


Figure S8. ROESY spectrum of bromophycolide K (2) (500 MHz; CDCl₃)

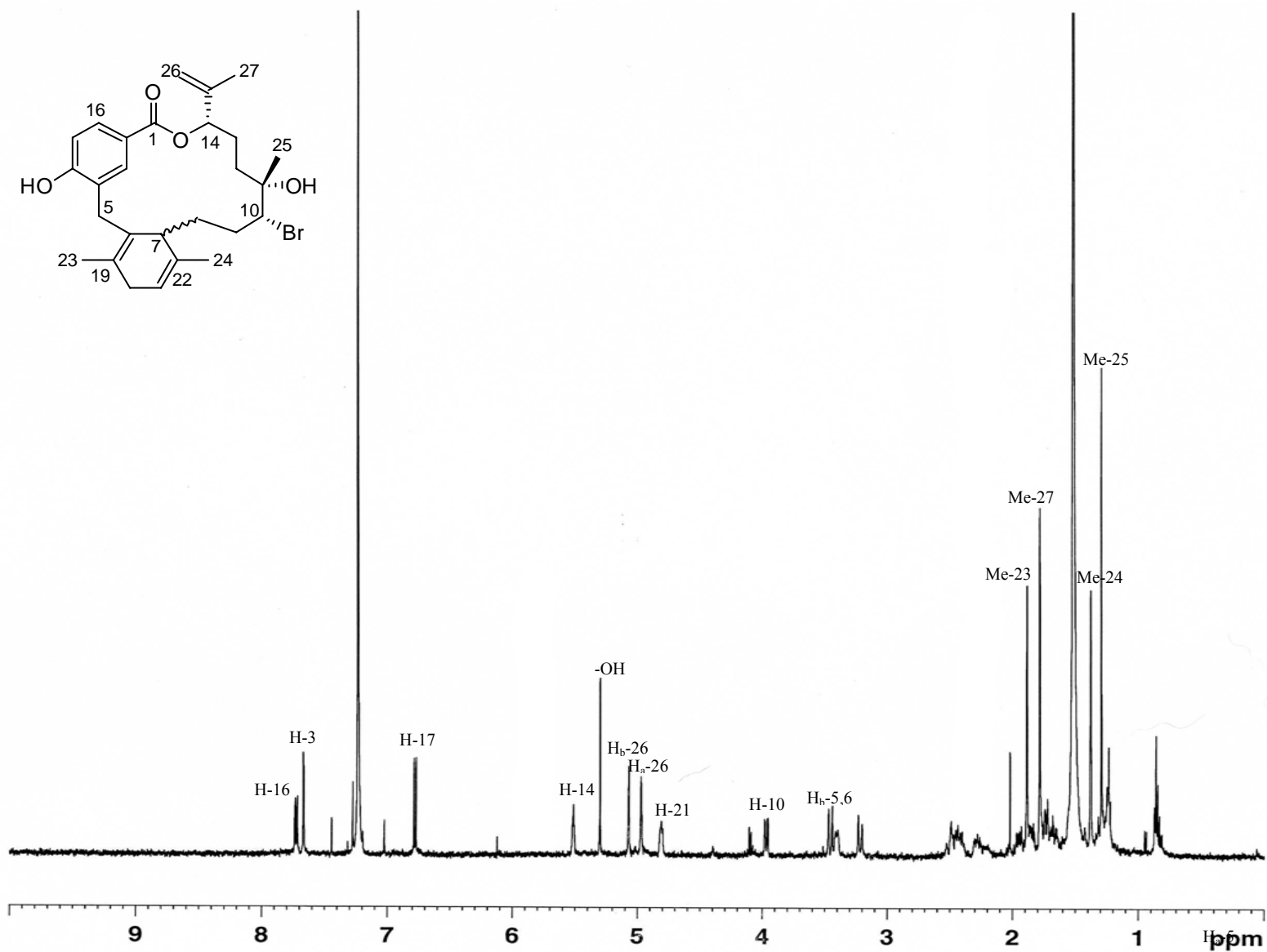
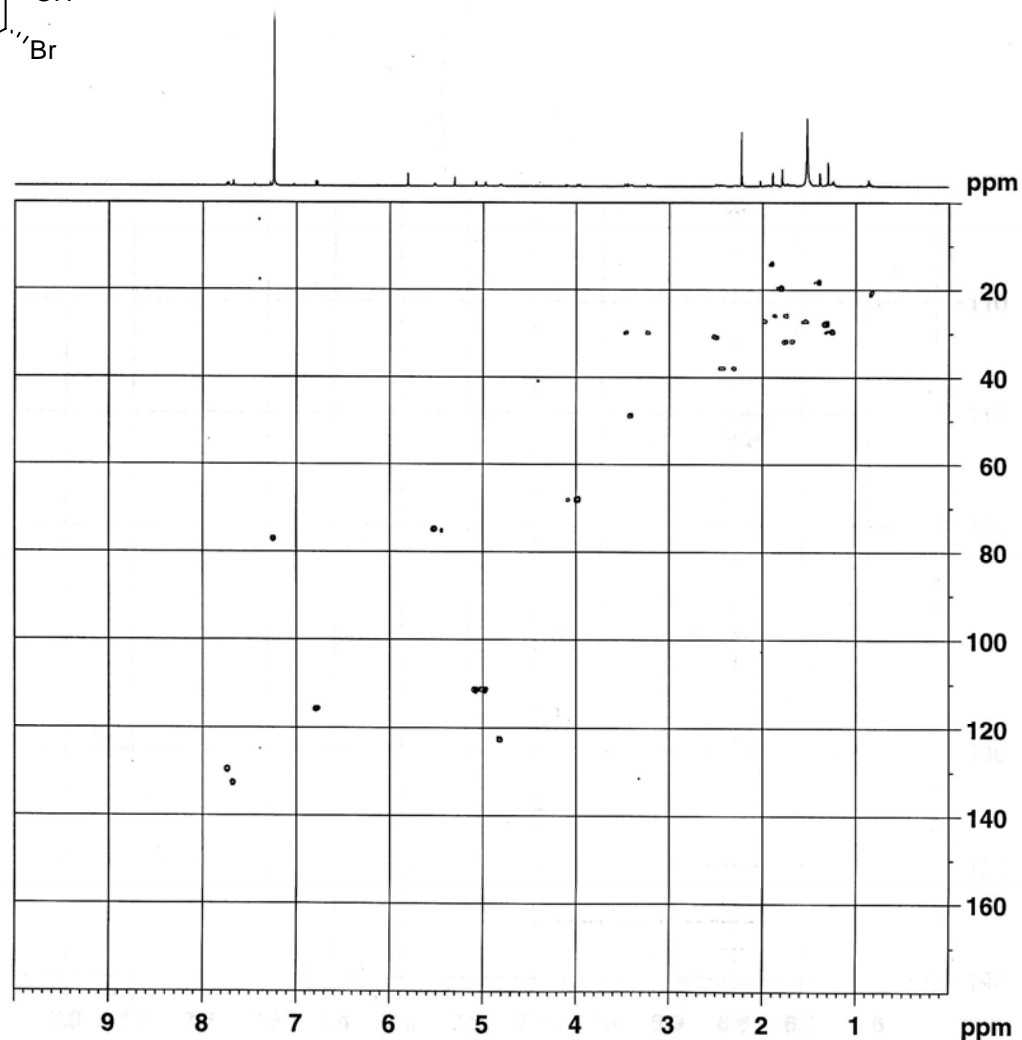
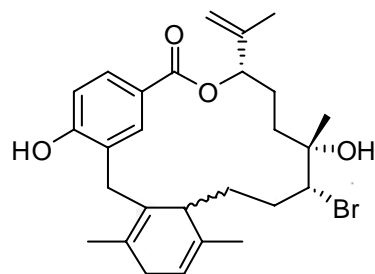


Figure S9. ¹H NMR spectrum of bromophycolide L (**3**) (500 MHz; CDCl₃)



```

Current Data Parameters
NAME      23B011a
EXPNO    3
PROCNO   1

F2 - Acquisition Parameters
Date_    20081019
Time     12.34
INSTRUM  spect
PROBHD   5 mm TRX 13C/B
PULPROG  hsgpgpg12
TD       1024
SOLVENT  CDCl3
NS       104
DS       16
SWH      5000.000 Hz
FIDRES   4.882812 Hz
AQ       0.1224500 sec
RG       18390.4
RW       100.000 usec
DE       6.00 usec
TE       298.0 K
CNS2     145.000000
d0       0.0000000 sec
d1       1.5000000 sec
d4       0.0017244 sec
d11      0.0100000 sec
d13      0.0000400 sec
d16      0.0002000 sec
d24      0.0008207 sec
DELTA    0.0017424 sec
DELTA1   0.0012000 sec
DELTA2   0.0009207 sec
DELTA3   0.0002414 sec
IND      0.0000210 sec
SFLCNT   128
ZGPGPNS

***** CHANNEL f1 *****
NUC1     1H
P1       9.13 usec
P2       18.26 usec
P28      1000.00 usec
PL1      0.00 dB
SFO1     500.1325230 MHz

***** CHANNEL f2 *****
CPDPRG2  gbrp
NUC2     13C
P3       16.00 usec
P4       32.00 usec
PCPD2    61.71 usec
PL2      -4.00 dB
PL12     179.72 dB
SFO2     125.7693972 MHz

***** GRADIENT CHANNEL *****
GPMAM1   SINE 100
GPMAM2   SINE 100
GPMAM3   SINE 100
GPMAM4   SINE 100
GPF1     0.00 %
GPF2     0.00 %
GPF3     0.00 %
GPF4     0.00 %
GPF1     0.00 %
GPF2     0.00 %
GPF3     0.00 %
GPF4     0.00 %
GPF1     80.00 %
GPF2     20.10 %
GPF3     11.00 %
GPF4     -5.00 %
P16      1000.00 usec
P19      600.00 usec

F1 - Acquisition parameters
NUC0     13C
TD       256
SFO1     125.7691 MHz
FIDRES   88.374594 Hz
SM       179.889 ppm
PULPROG  Echo-Antiecho

F2 - Processing parameters
SI       1024
SF       500.1300205 MHz
WDW      GEMIN
SSB      0
LB       0.00 Hz
GB       0
PC       1.00

F1 - Processing parameters
SI       1024
MC2     echo-antiecho
SF       125.7578075 MHz
WDW      GEMIN
SSB      0
LB       0.00 Hz
GB       0
  
```

Figure S10. HSQC spectrum of bromophycolide L (**3**) (500 MHz; CDCl₃)

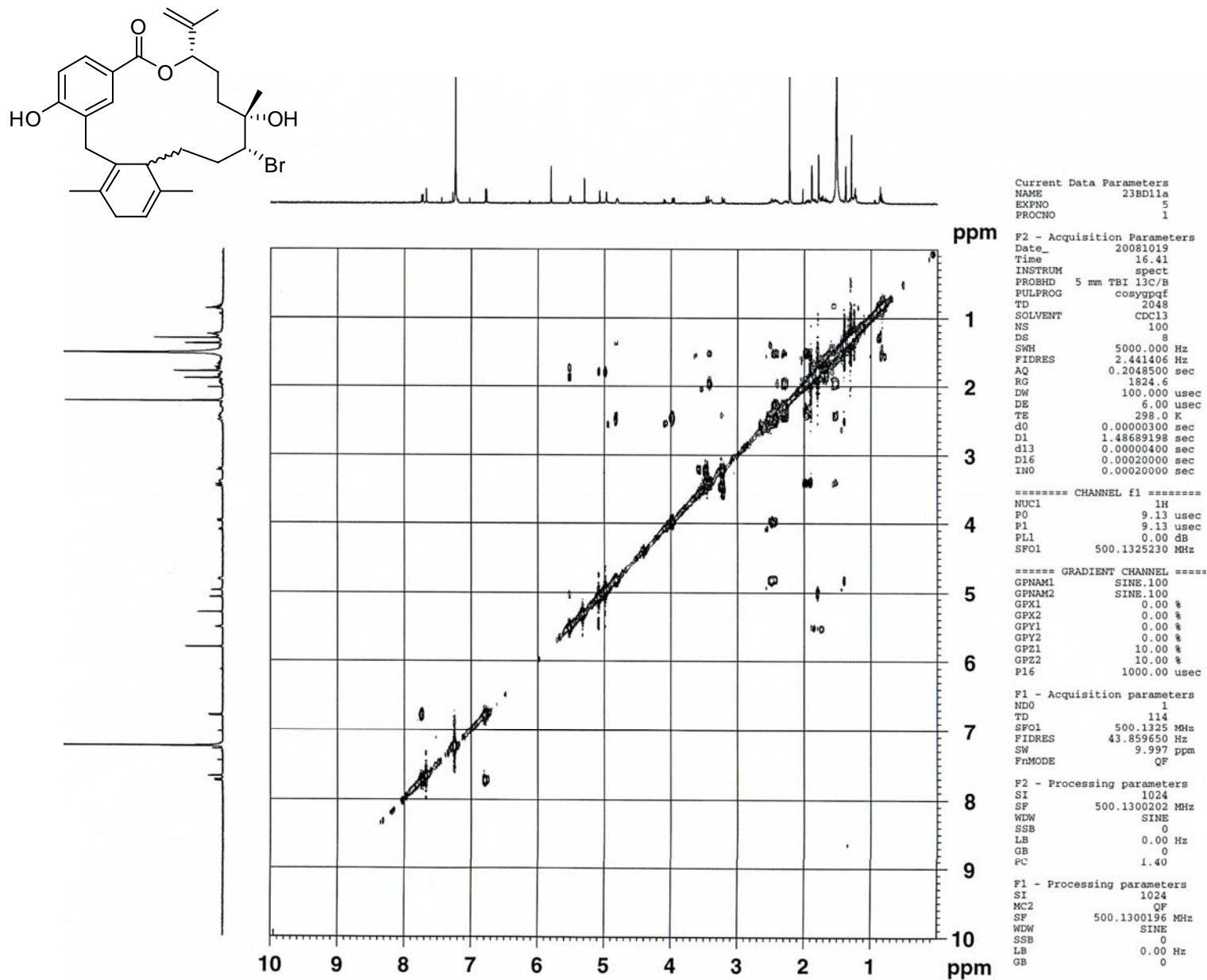


Figure S11. ^1H - ^1H COSY spectrum of bromophycolide L (**3**) (500 MHz; CDCl_3)

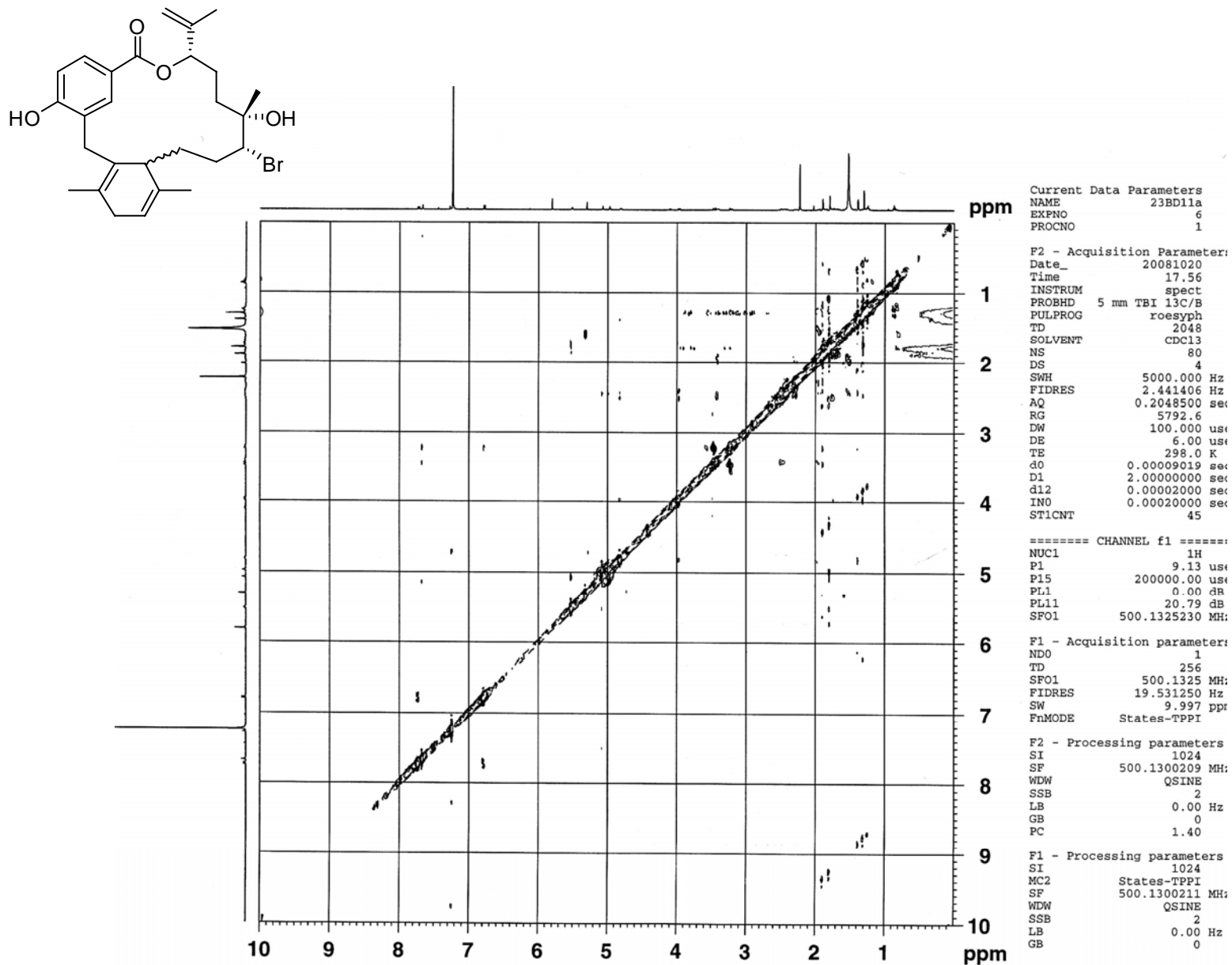


Figure S12. ROESY spectrum of bromophycolide L (**3**) (500 MHz; CDCl₃)

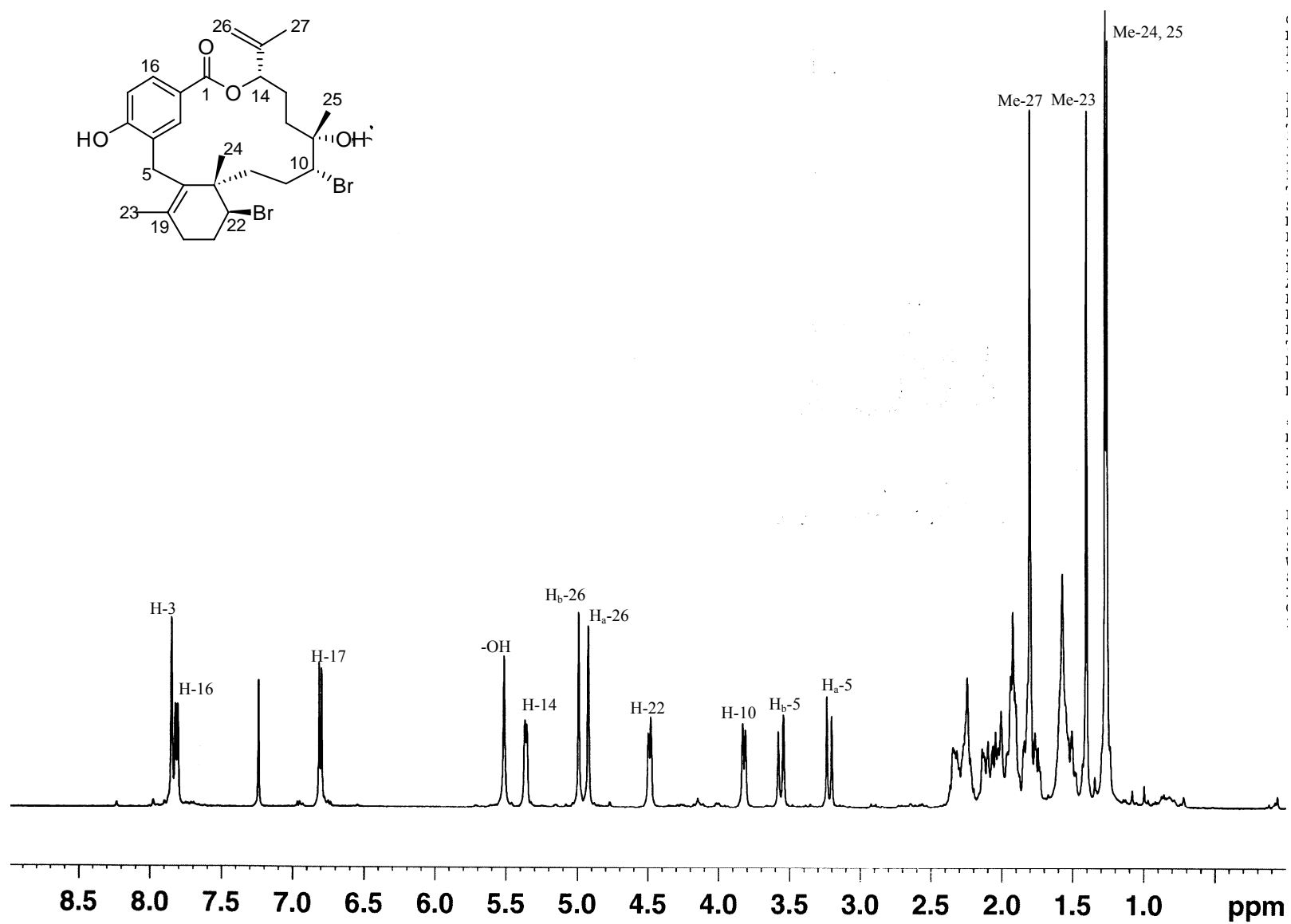


Figure S13. ¹H NMR spectrum of bromophycolide M (4) (500 MHz; CDCl₃)

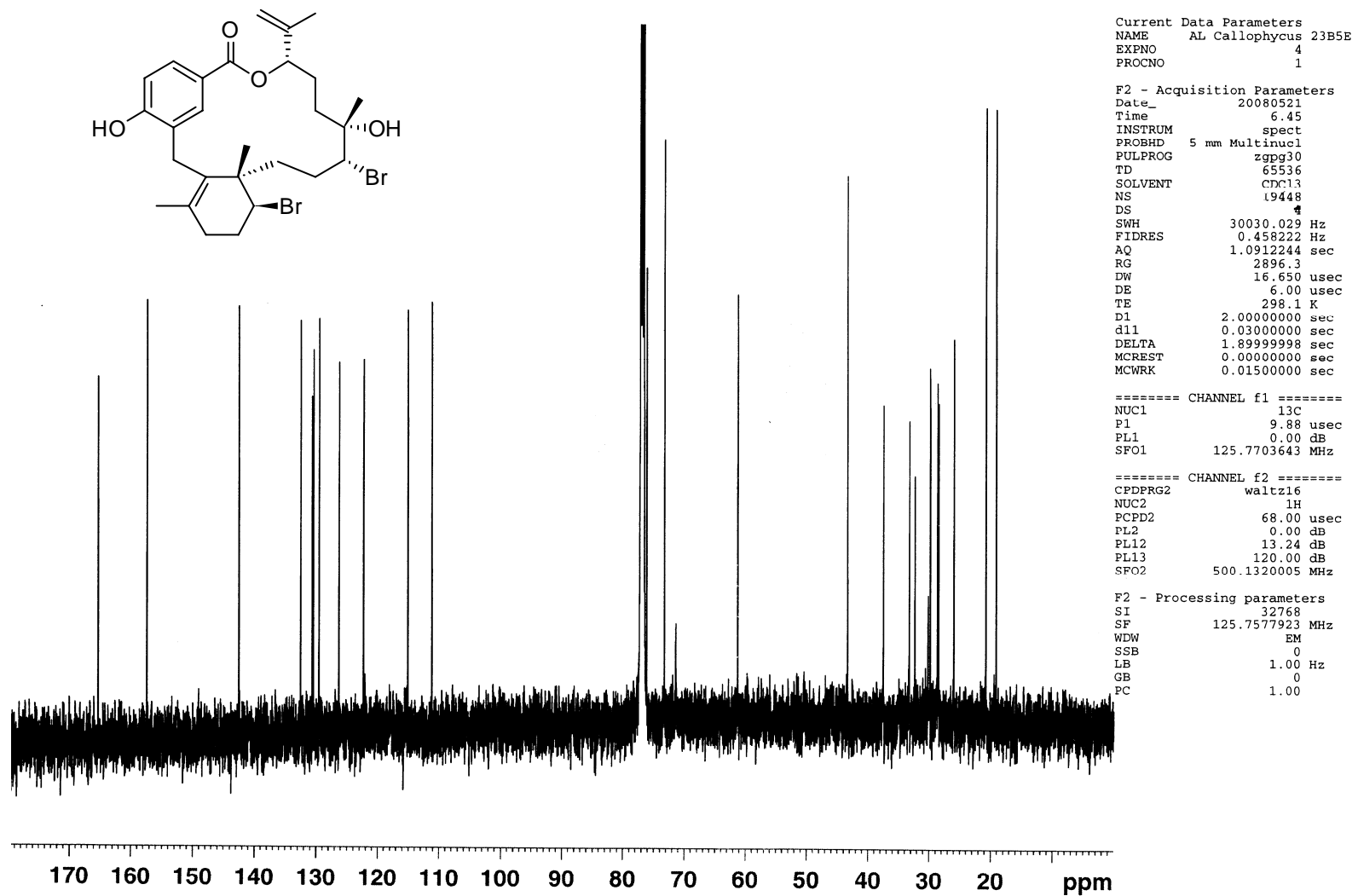


Figure S14. ¹³C NMR spectrum of bromophycolide M (4) (125 MHz; CDCl₃)

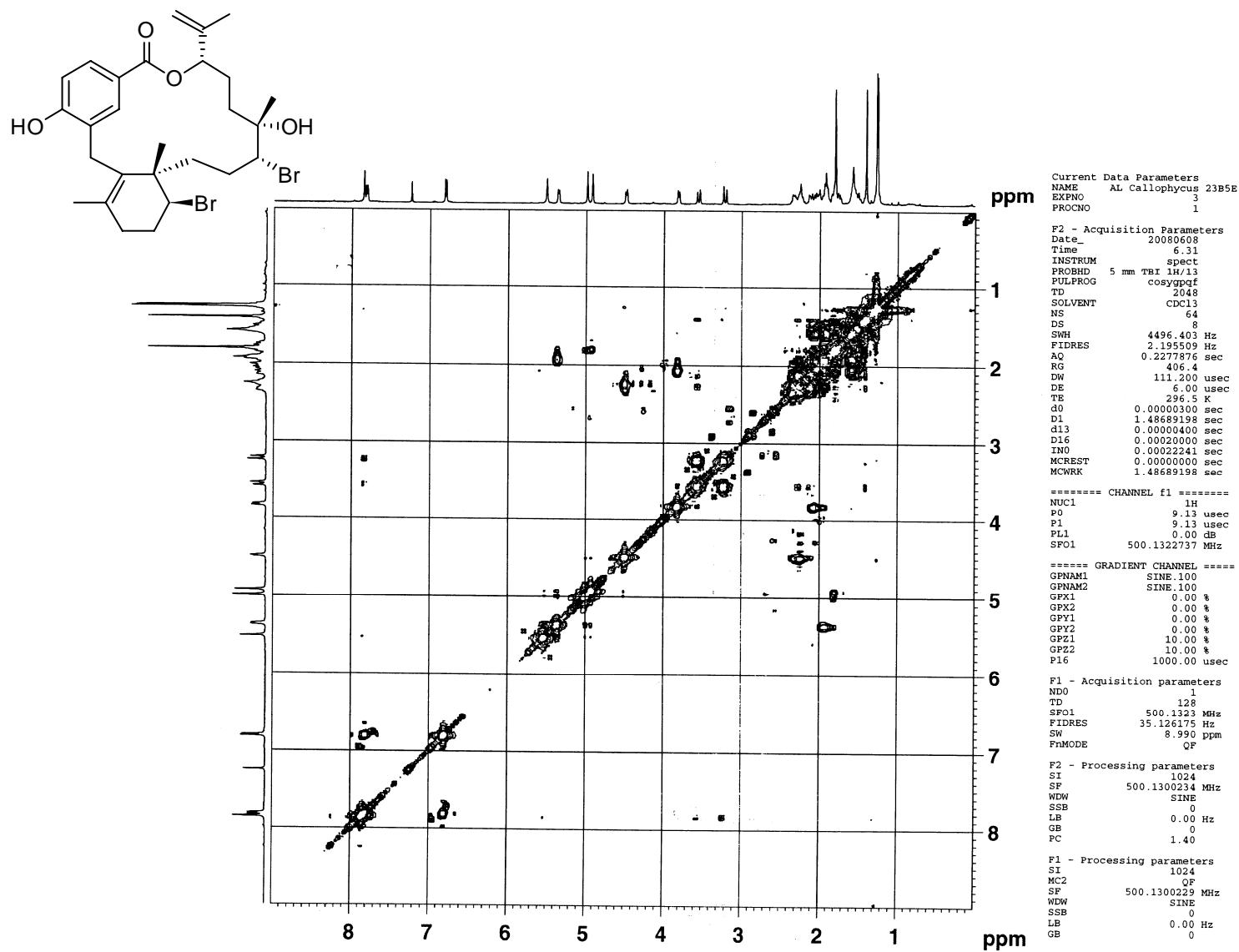


Figure S15. ^1H - ^1H COSY spectrum of bromophycolide M (**4**) (500 MHz; CDCl_3)

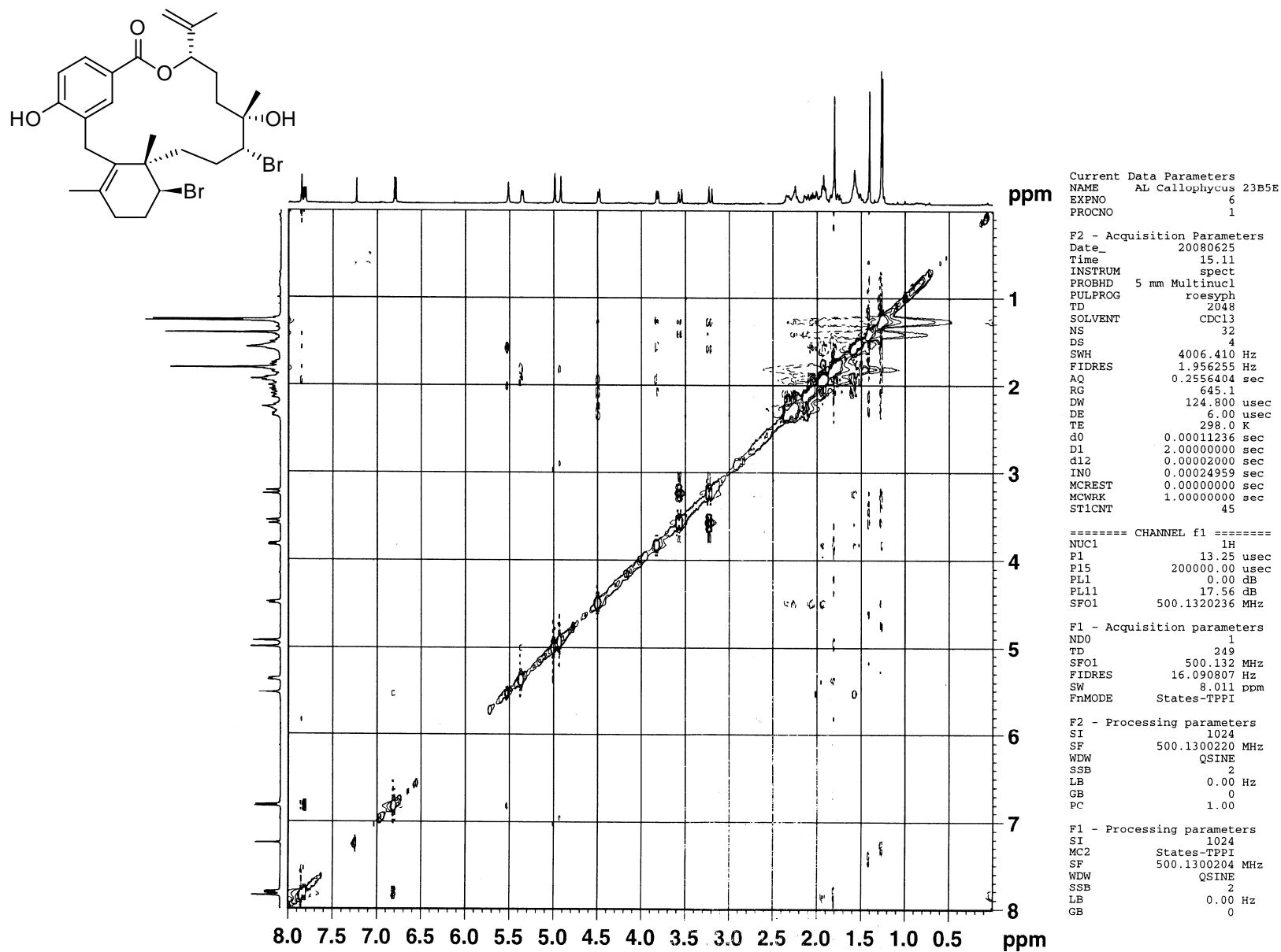


Figure S16. ROESY spectrum of bromophylolide M (4) (500 MHz; CDCl₃)

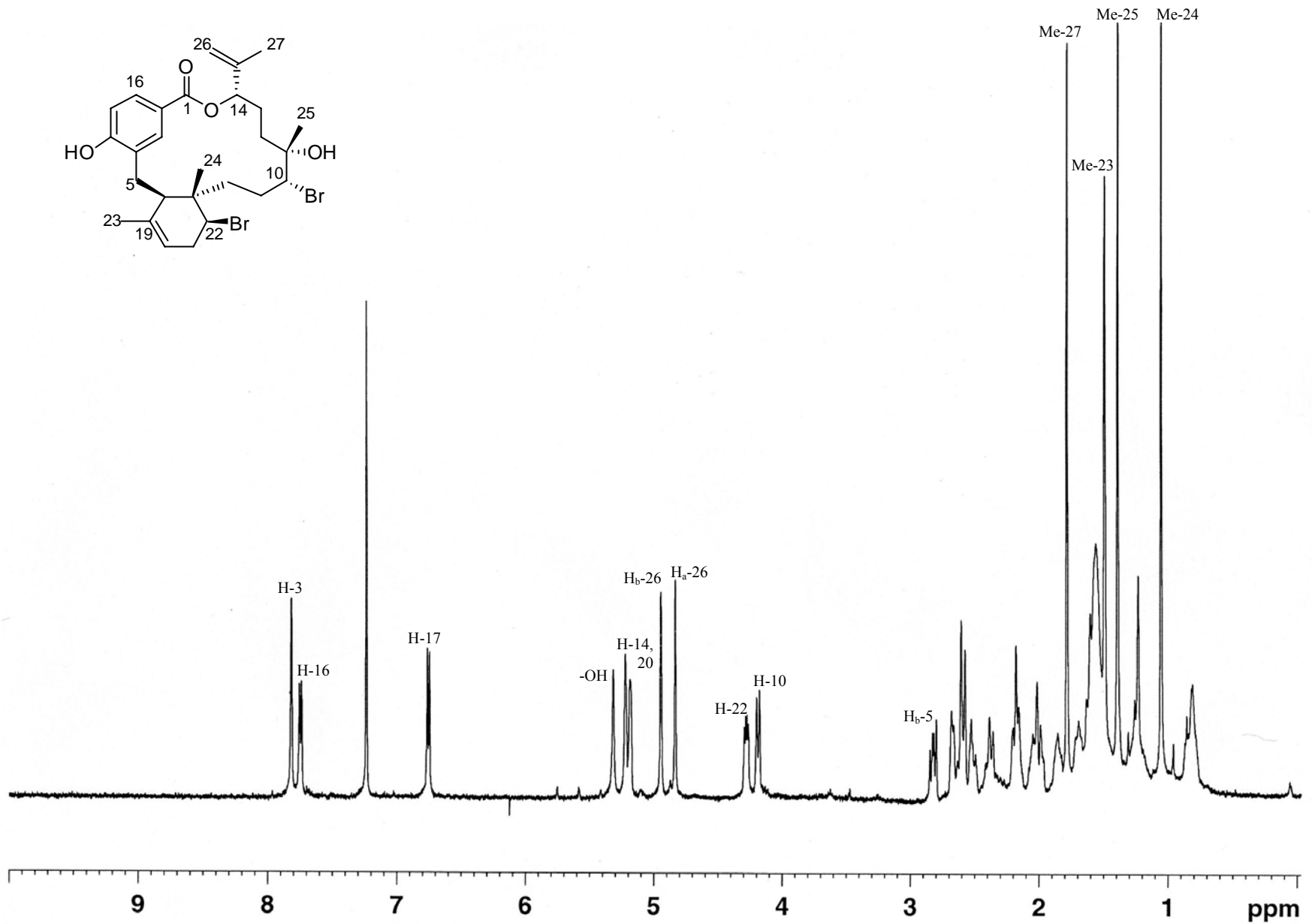
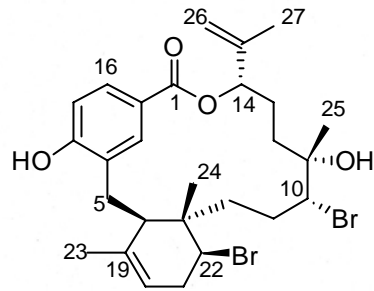


Figure S17. ^1H NMR spectrum of bromophycolide N (**5**) (500 MHz; CDCl_3)

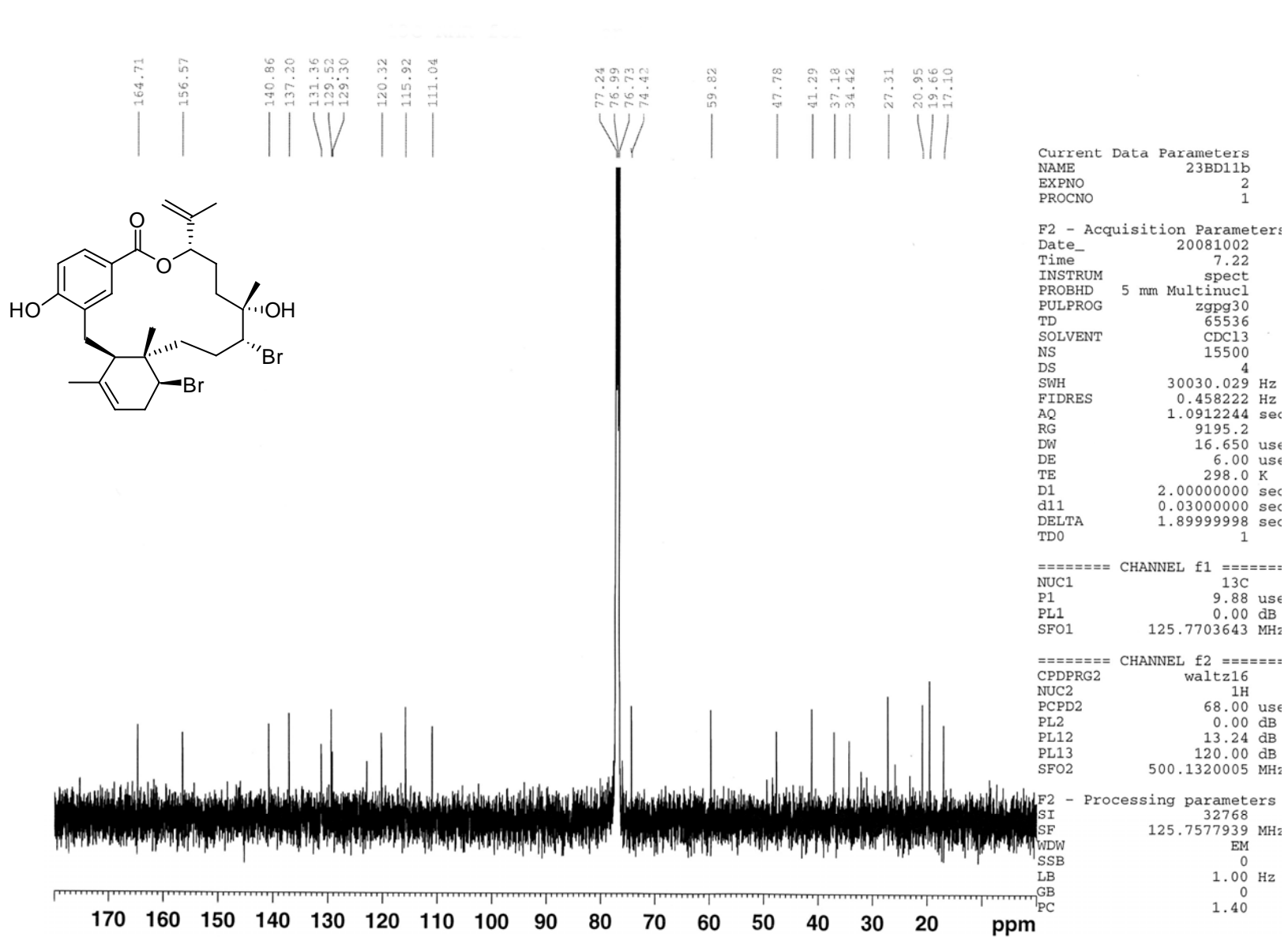


Figure S18. ¹³C NMR spectrum of bromophycolide N (5) (125 MHz; CDCl₃)

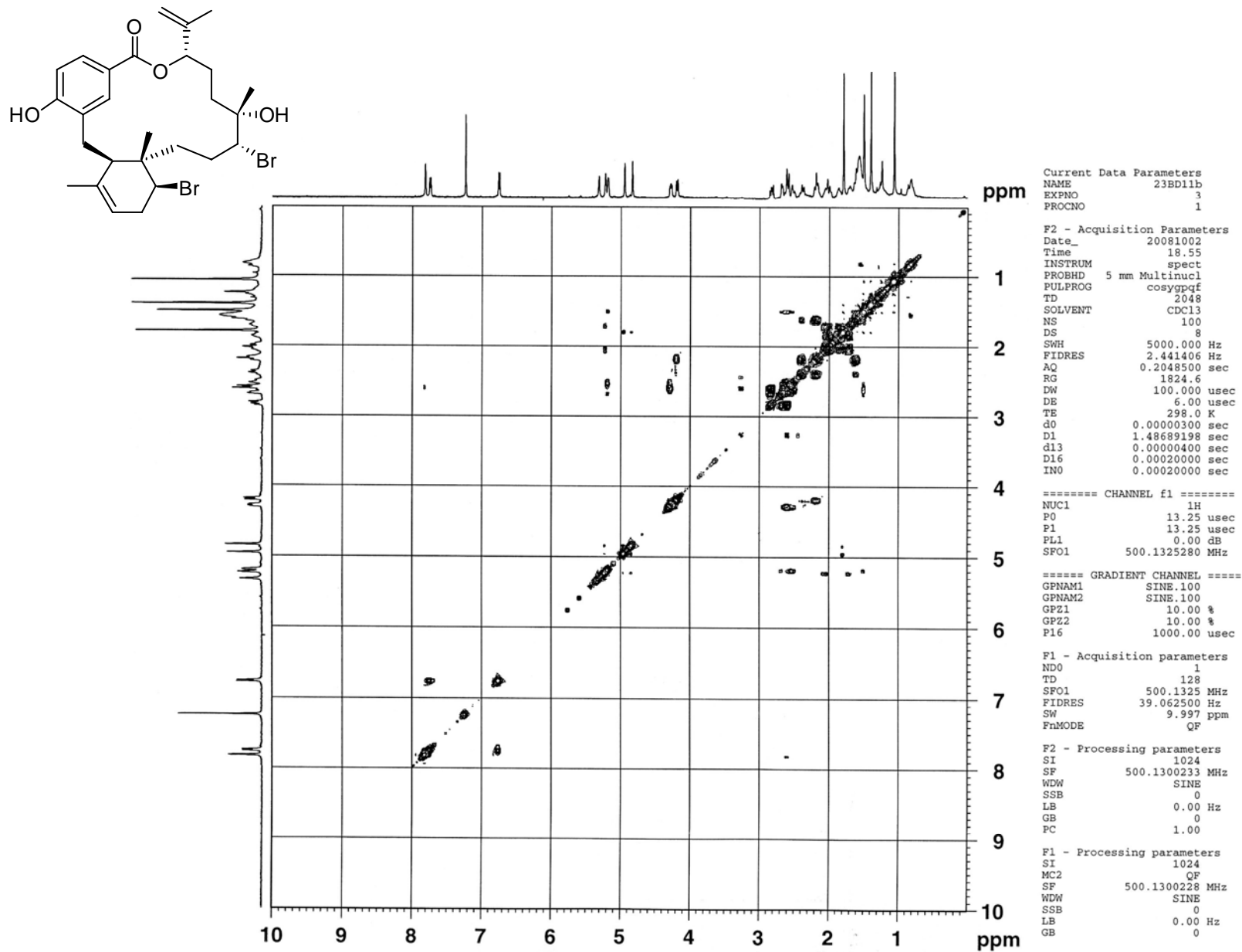


Figure S19. ^1H - ^1H COSY spectrum of bromophycolide N (**5**) (500 MHz; CDCl_3)

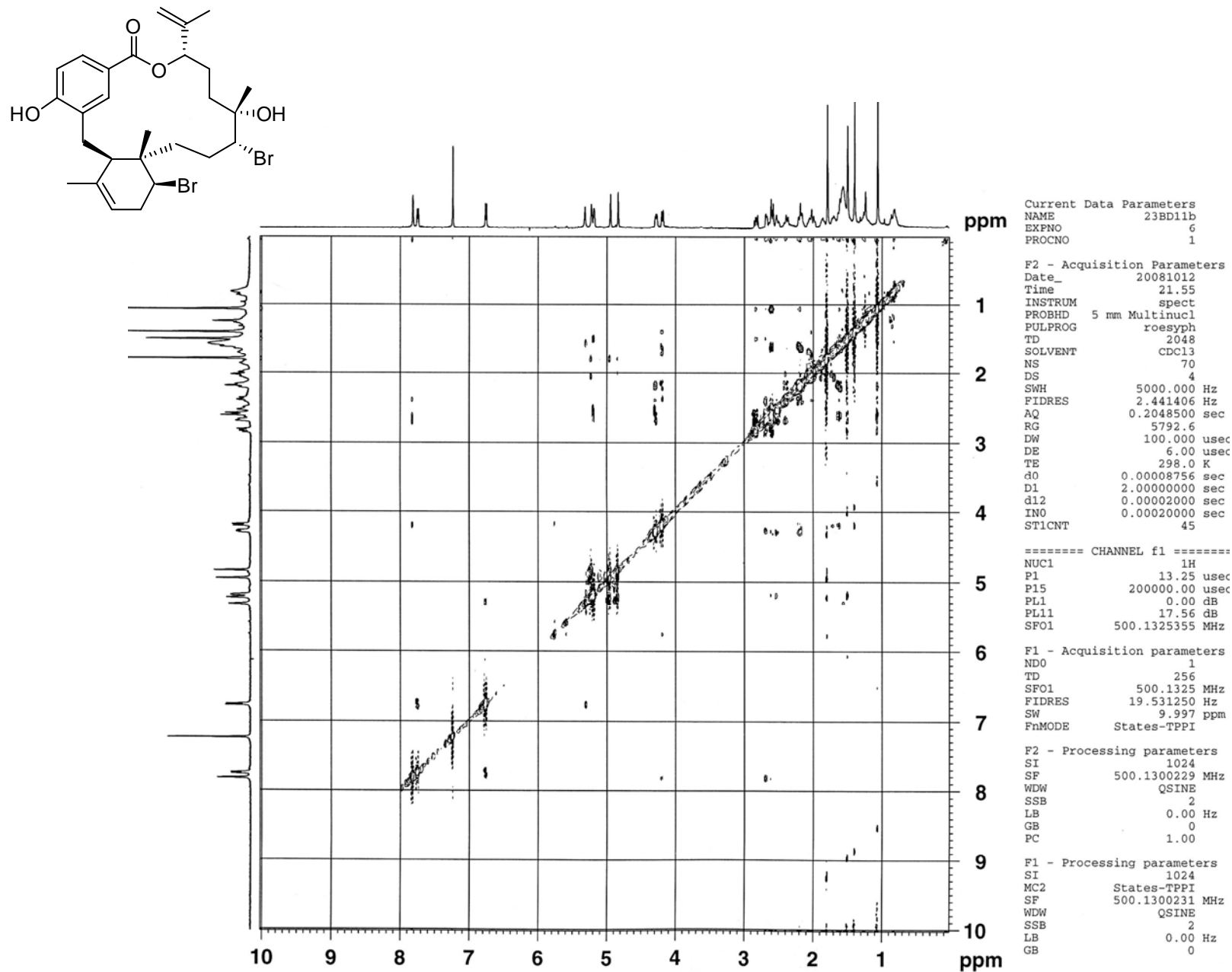


Figure S20. ROESY spectrum of bromophycolide N (5) (500 MHz; CDCl₃)

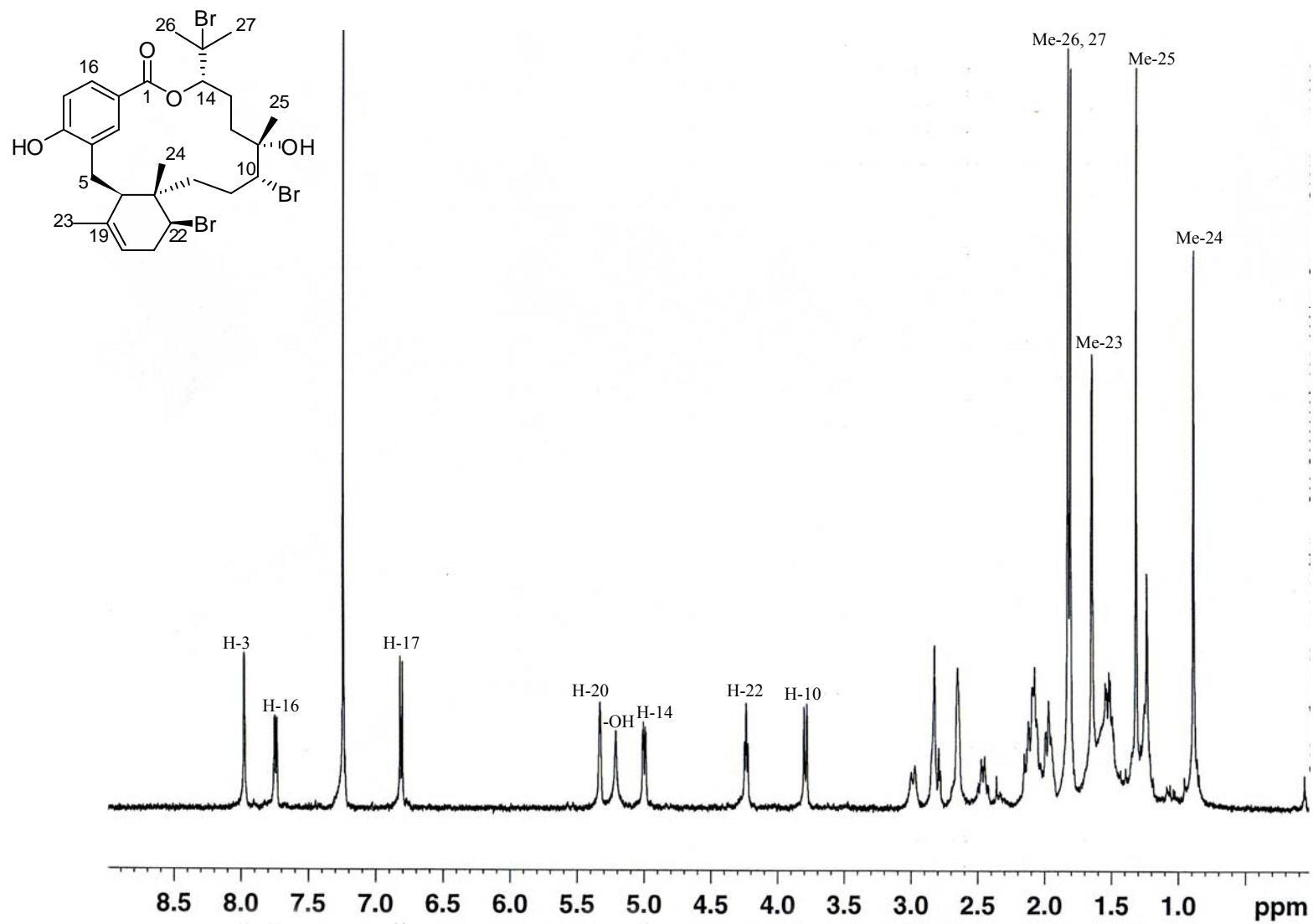


Figure S21. ¹H NMR spectrum of bromophycolide O (**6**) (500 MHz; CDCl₃)

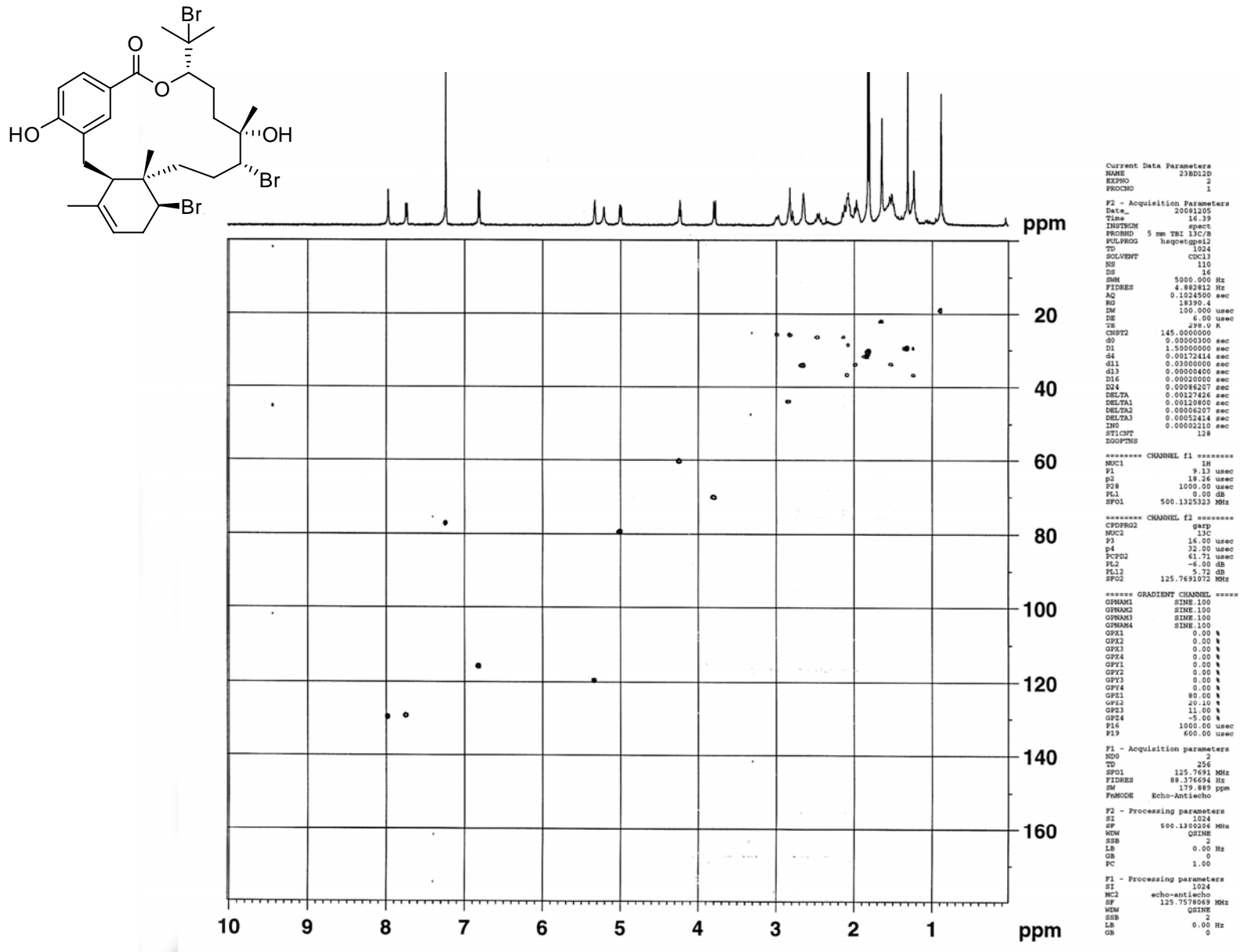


Figure S22. HSQC spectrum of bromophycolide O (6) (500 MHz; CDCl₃)

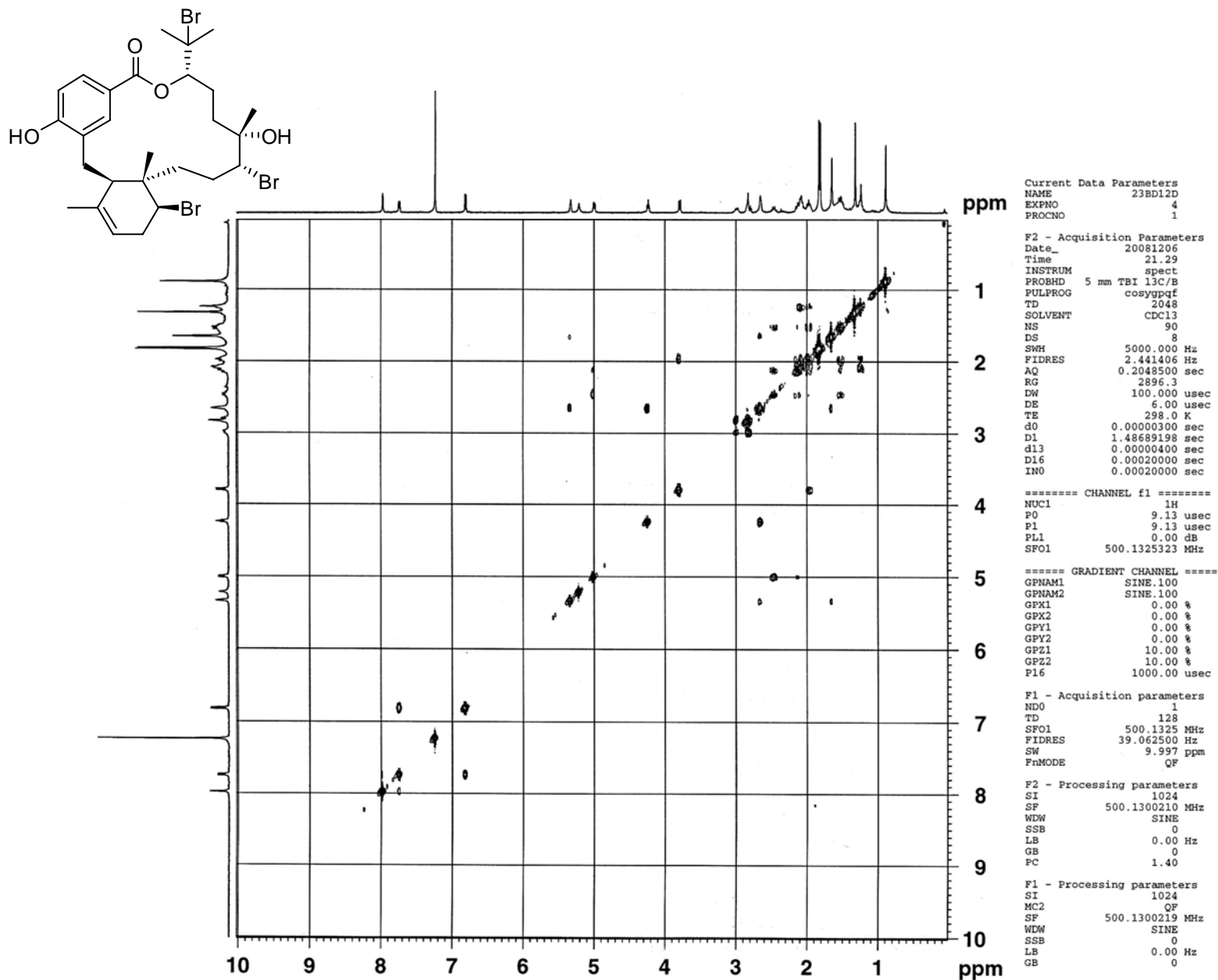


Figure S23. ^1H - ^1H COSY spectrum of bromophycolide O (**6**) (500 MHz; CDCl_3)

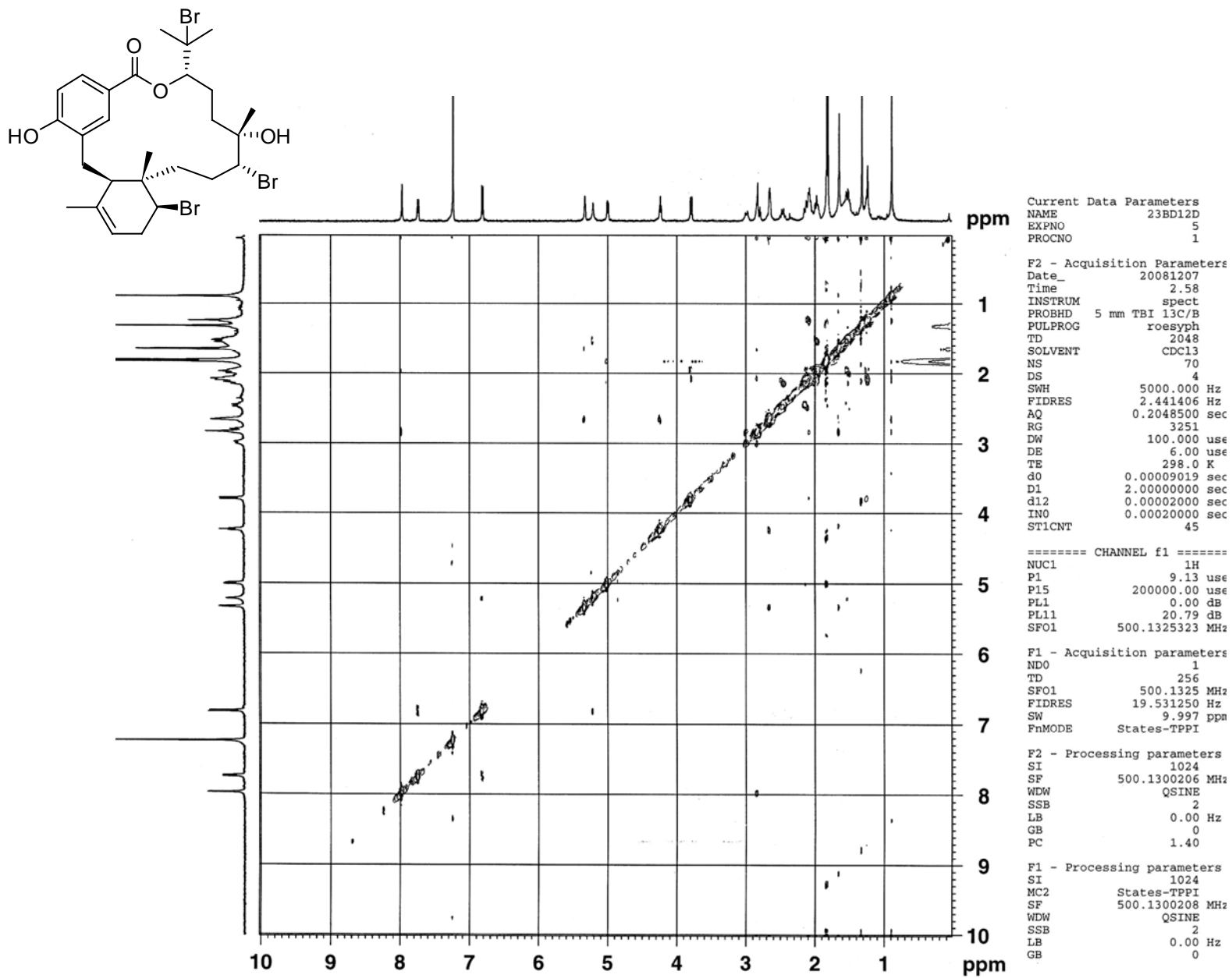


Figure S24. ROESY spectrum of bromophycolide O (**6**) (500 MHz; CDCl_3)

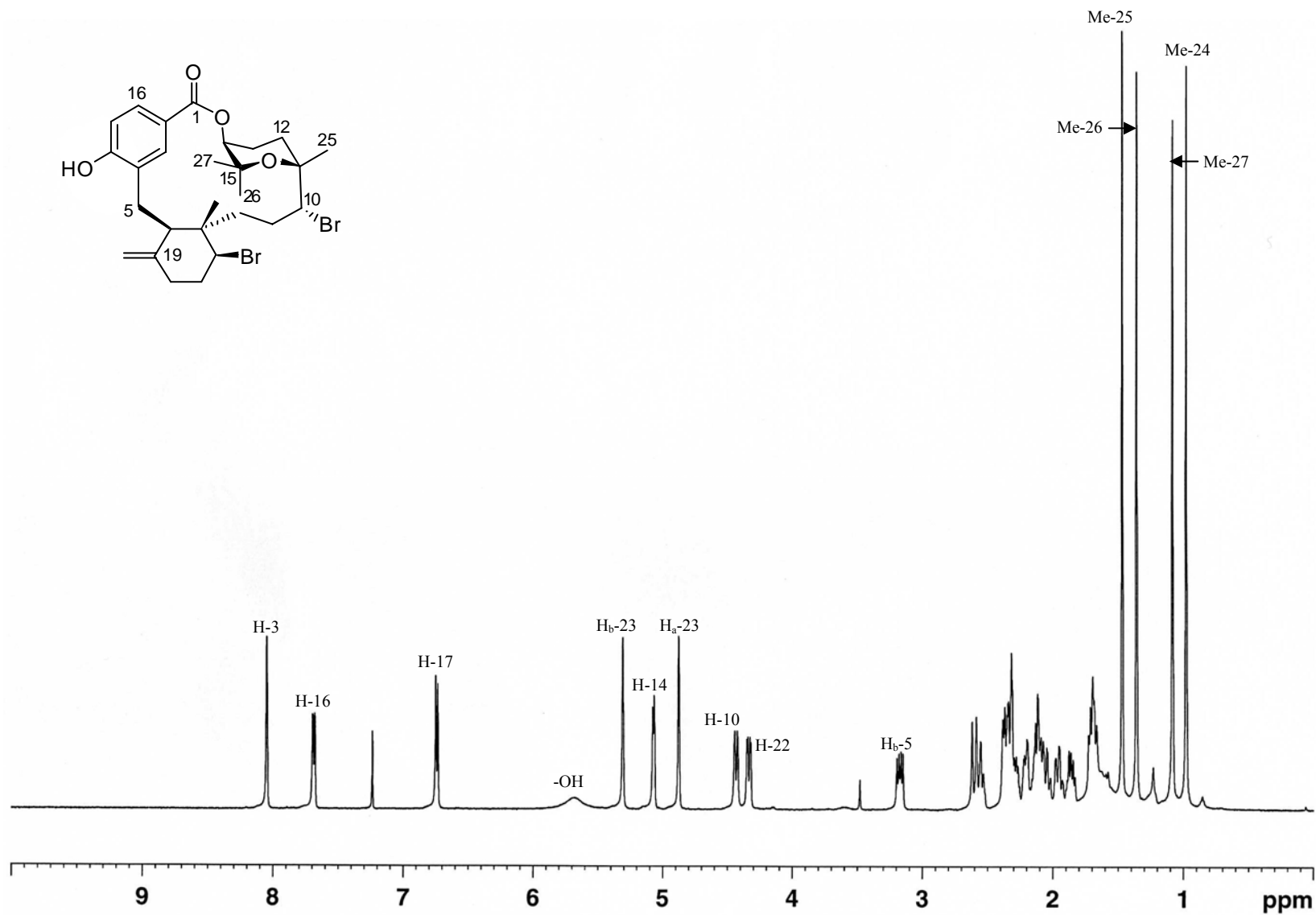


Figure S25. ¹H NMR spectrum of bromophycolide P (**7**) (500 MHz; CDCl₃)

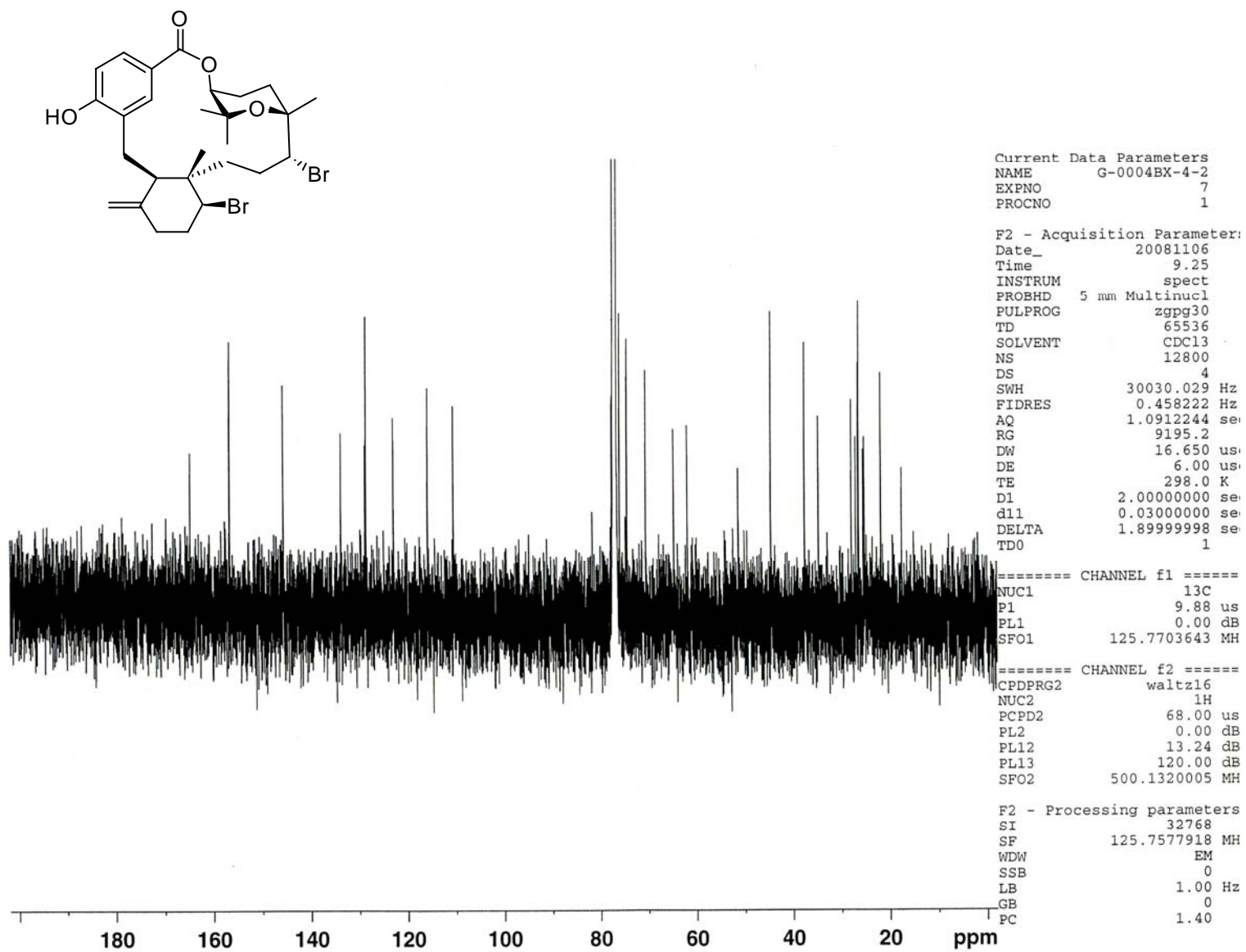
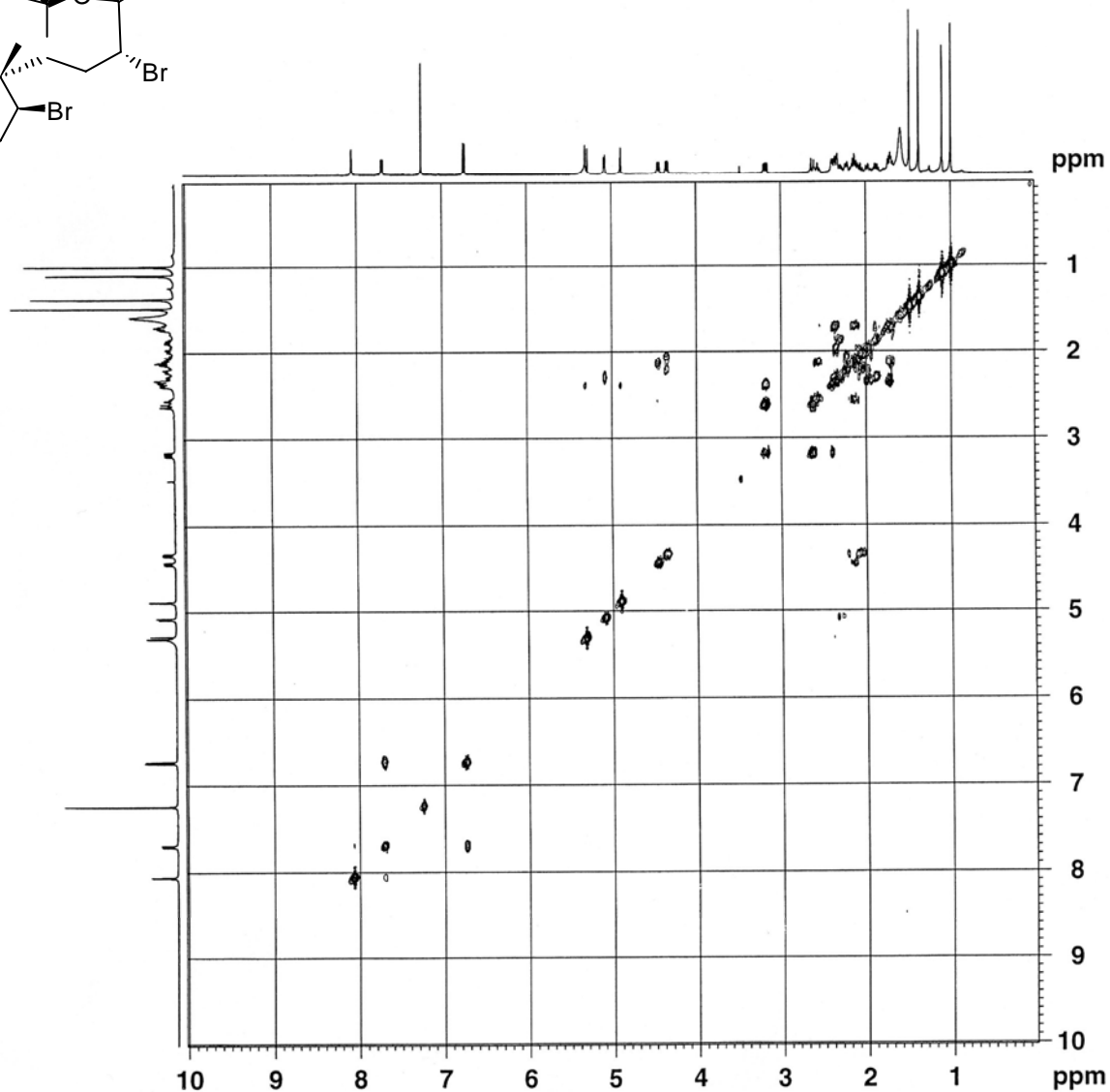
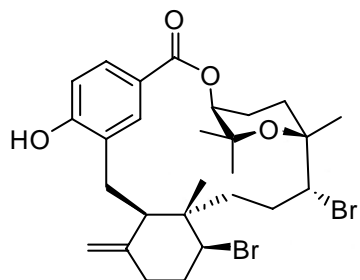


Figure S26. ¹³C NMR spectrum of bromophycolide P (**7**) (125 MHz; CDCl₃)



```

Current Data Parameters
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EXPNO    3
PROCNO   1

F2 - Acquisition Parameters
Date_    20081103
Time     16.52
INSTRUM  spect
PROBHD   5 mm TBI 13C/B
PULPROG  cosygpgpf
TD       2048
SOLVENT  CDCl3
NS       35
DS       8
SWH      5000.000 Hz
FIDRES   2.441406 Hz
AQ       0.2048500 sec
RG       1149.4
DW       100.000 usec
DE       6.00 usec
TE       298.1 K
d0       0.00000300 sec
d1       1.48689198 sec
d13      0.00000400 sec
d16      0.00020000 sec
IN0      0.00020000 sec

===== CHANNEL f1 =====
NUC1     1H
P0       9.13 usec
P1       9.13 usec
PL1      0.00 dB
SFO1     500.1325313 MHz

===== GRADIENT CHANNEL =====
GPNAM1   SINE.100
GPNAM2   SINE.100
GPX1     0.00 %
GPX2     0.00 %
GPY1     0.00 %
GPY2     0.00 %
GPZ1     10.00 %
GPZ2     10.00 %
P16      1000.00 usec

F1 - Acquisition parameters
ND0      1
TD       128
SFO1     500.1325 MHz
FIDRES   39.062500 Hz
SW       9.997 ppm
FnMODE   QF

F2 - Processing parameters
SI       1024
SF       500.1300196 MHz
WDW      SINE
SSB      0
LB       0.00 Hz
GB       0
PC       1.00

F1 - Processing parameters
SI       1024
MC2      QF
SF       500.1300195 MHz
WDW      SINE
SSB      0
LB       0.00 Hz
GB       0
  
```

Figure S27. ^1H - ^1H COSY spectrum of bromophycolide P (7) (500 MHz; CDCl_3)

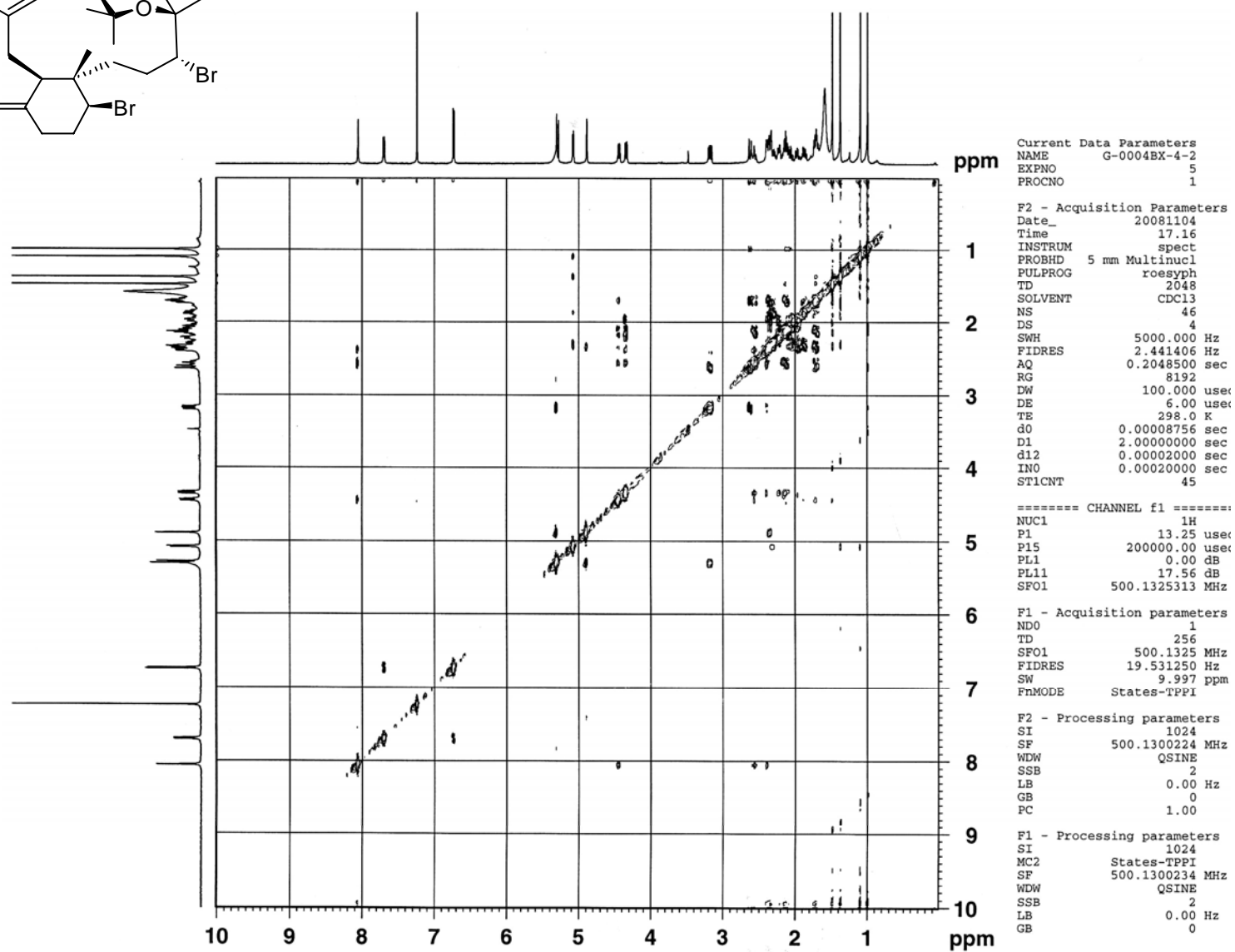
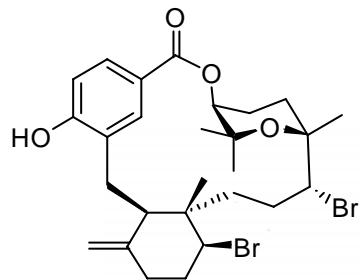


Figure S28. ROESY spectrum of bromophycolide P (7) (500 MHz; CDCl₃)

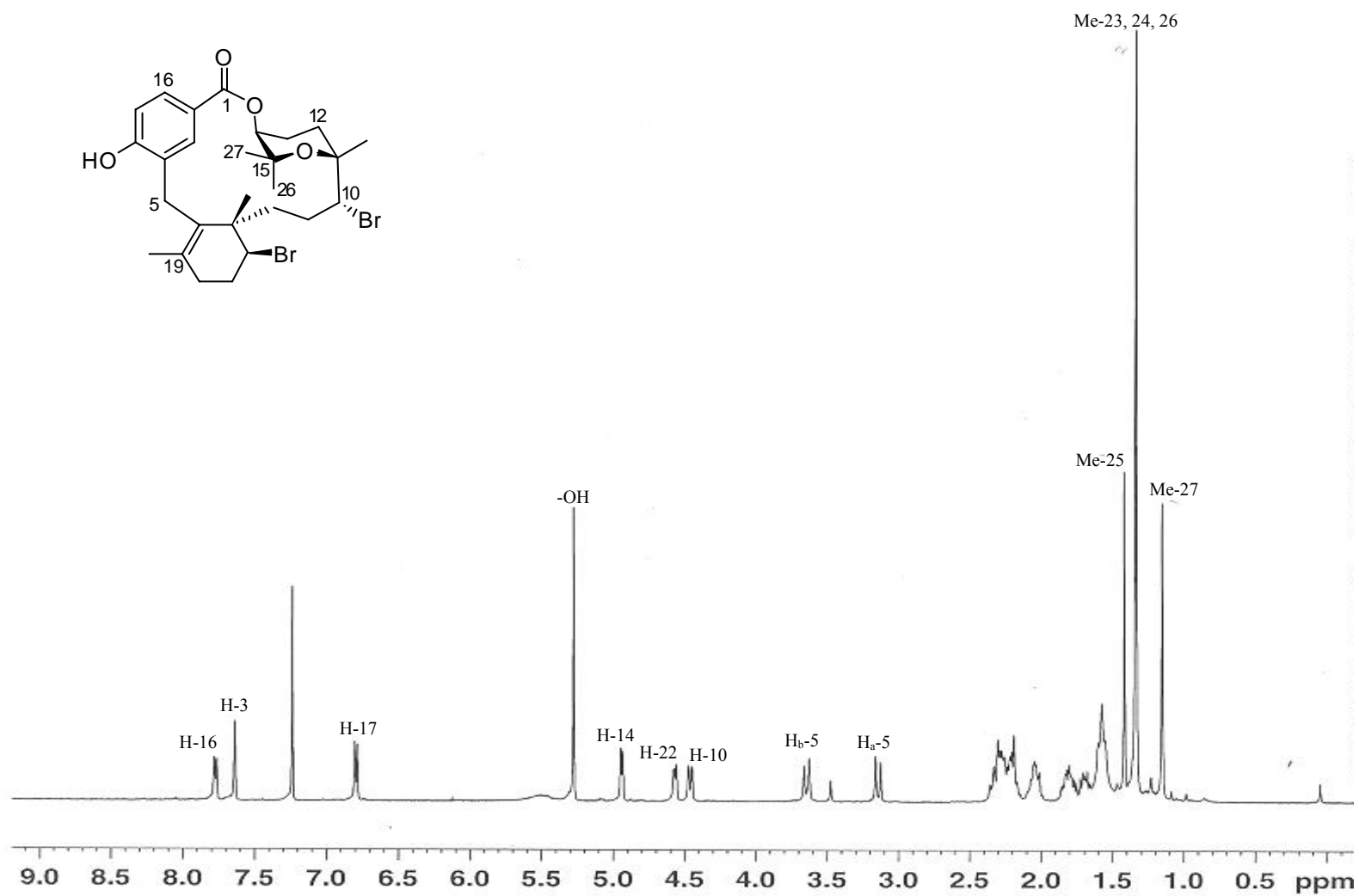


Figure S29. ¹H NMR spectrum of bromophycolide Q (**8**) (500 MHz; CDCl₃)

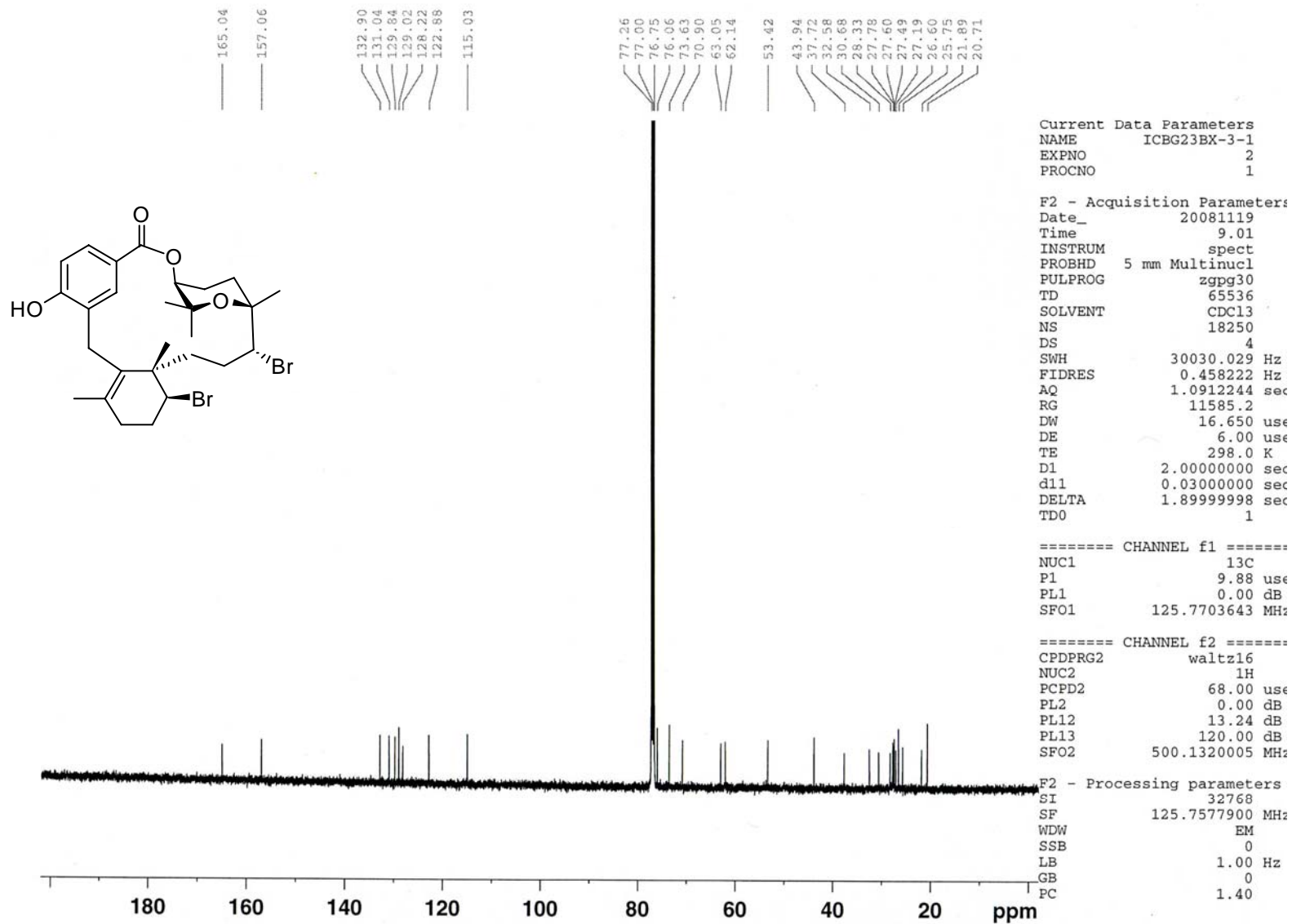


Figure S30. ¹³C NMR spectrum of bromophycolide Q (8) (125 MHz; CDCl₃)

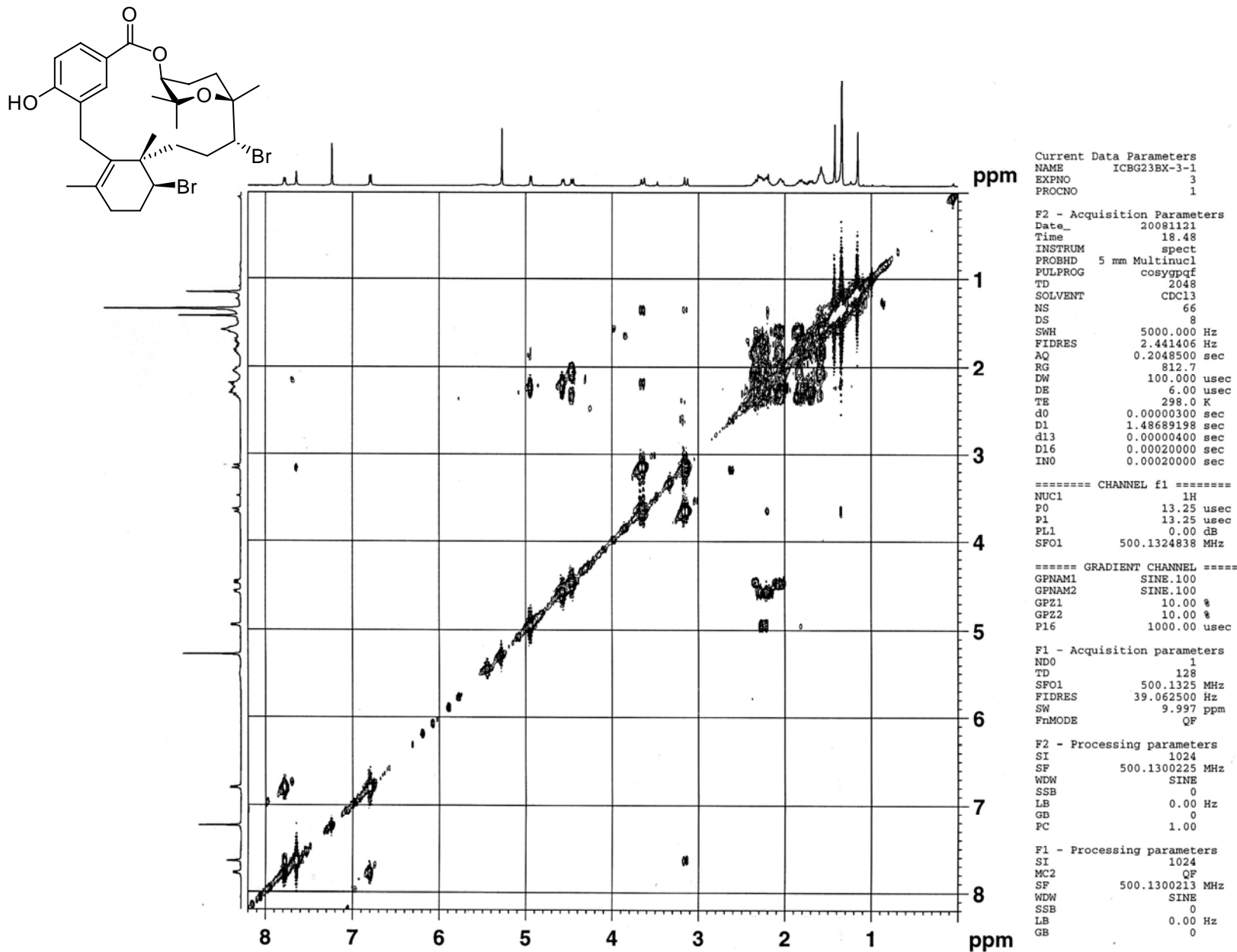


Figure S31. ^1H - ^1H COSY spectrum of bromophycolide Q (**8**) (500 MHz; CDCl_3)

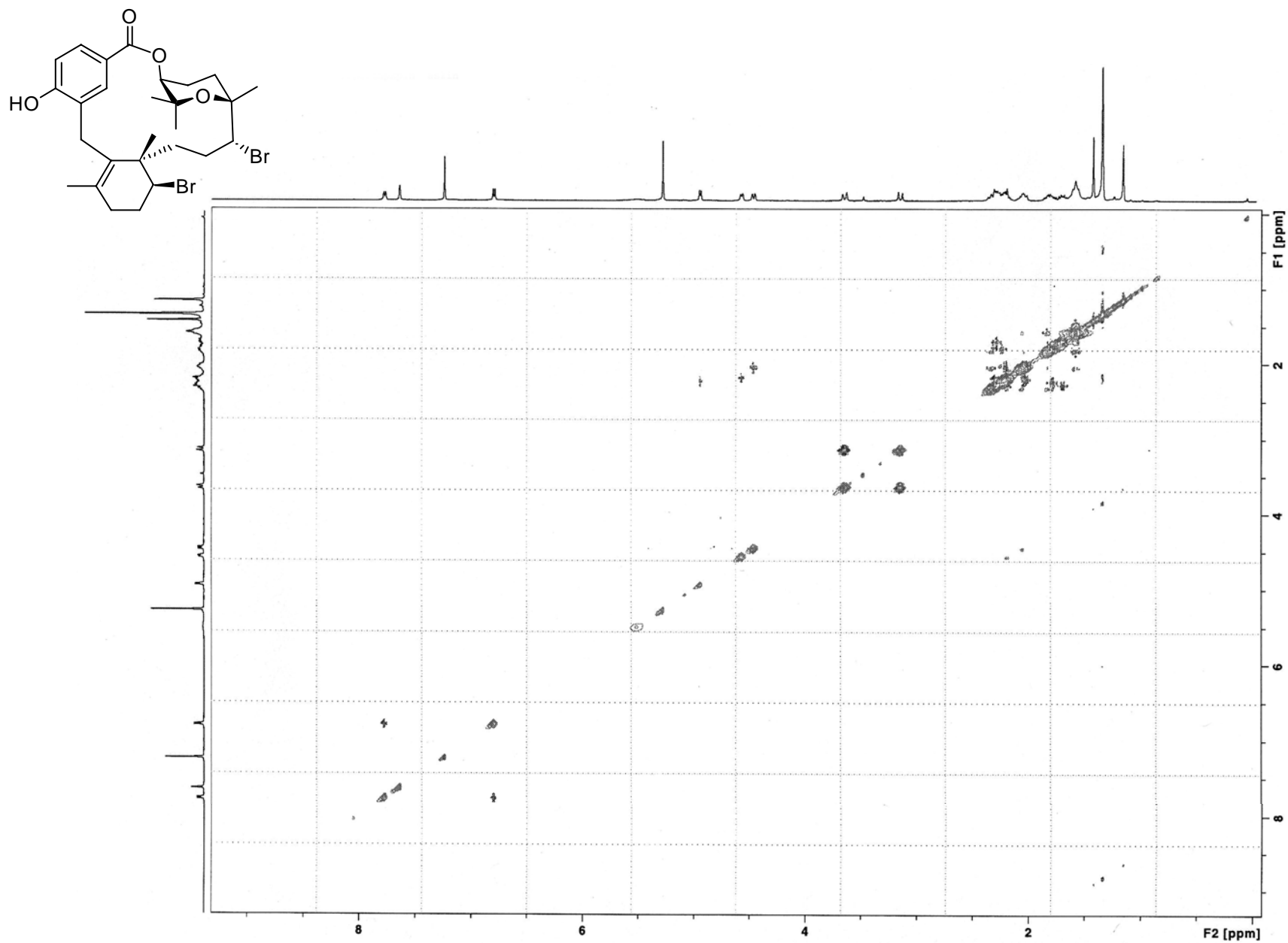


Figure S32. NOESY spectrum of bromophycolide Q (**8**) (500 MHz; CDCl₃)