Supporting Information

Bioactive Bianthraquinones and Meroterpenoids from a Marine Sponge-Derived *Stemphylium* sp. Fungus

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Ki-Bong Oh,[2,*] and Jongheon Shin[1,*]

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List of Supporting Information

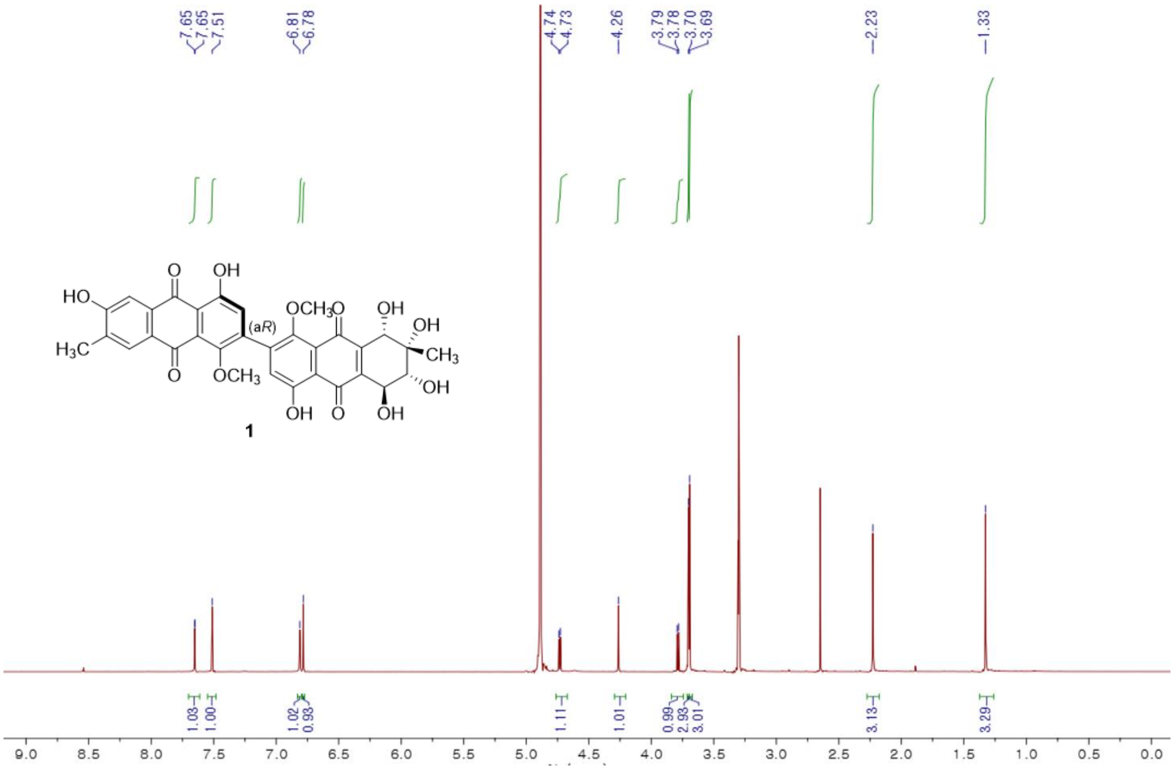


Figure S1. The ^{1}H NMR spectrum of Alterporriol Z1 (**1**) (600MHz, CD_3OD)

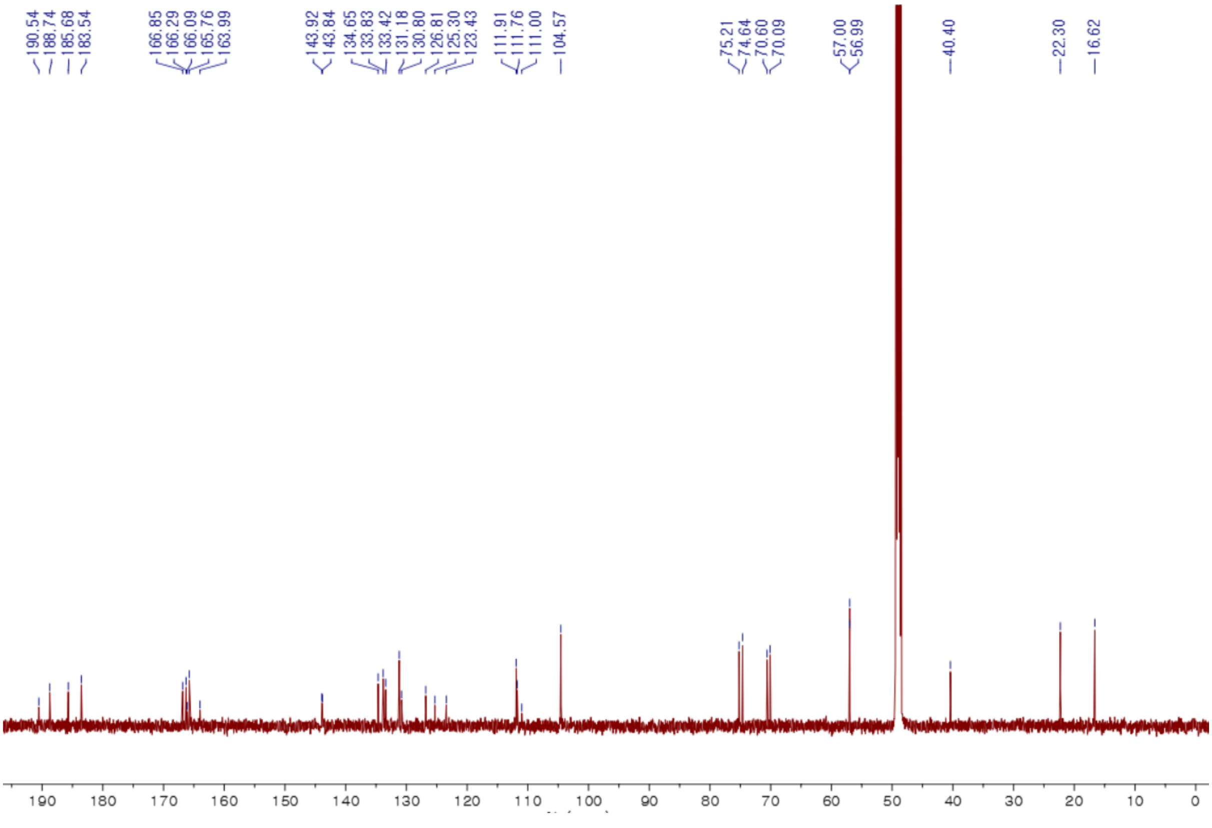


Figure S2. The ^{13}C NMR spectrum of Alterporriol Z1 (**1**) (150MHz, CD_3OD)

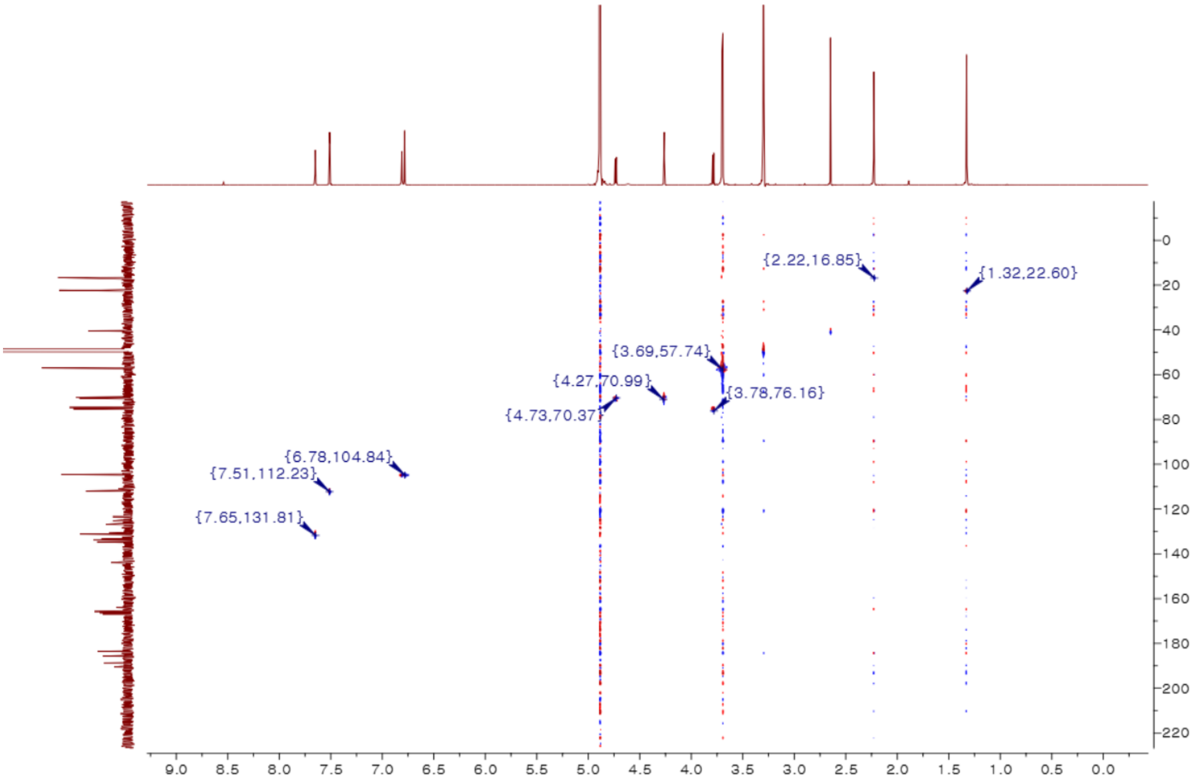


Figure S3. The HSQC spectrum of Alterporriol Z1 (**1**) (600MHz, CD_3OD)

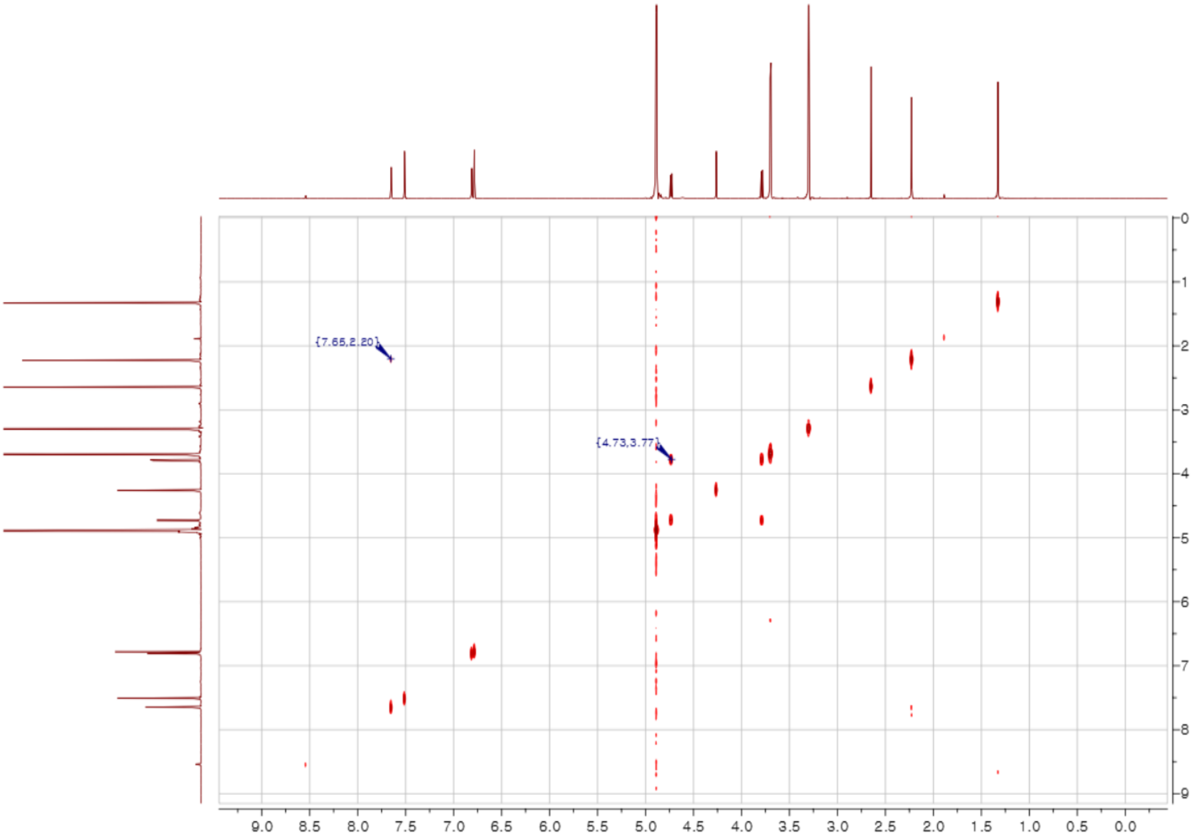


Figure S4. The COSY spectrum of Alterporriol Z1 (**1**) (600MHz, CD_3OD)

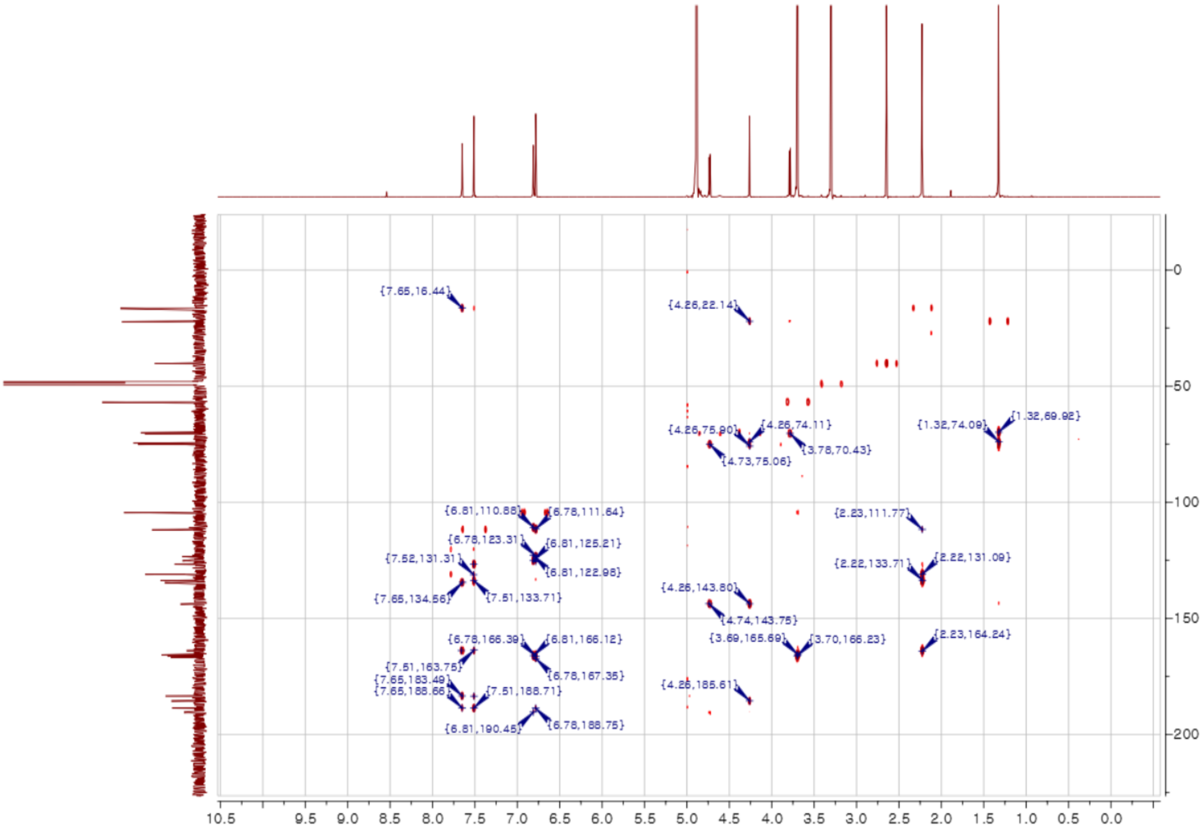


Figure S5. The HMBC spectrum of Alterporriol Z1 (**1**) (600MHz, CD_3OD)

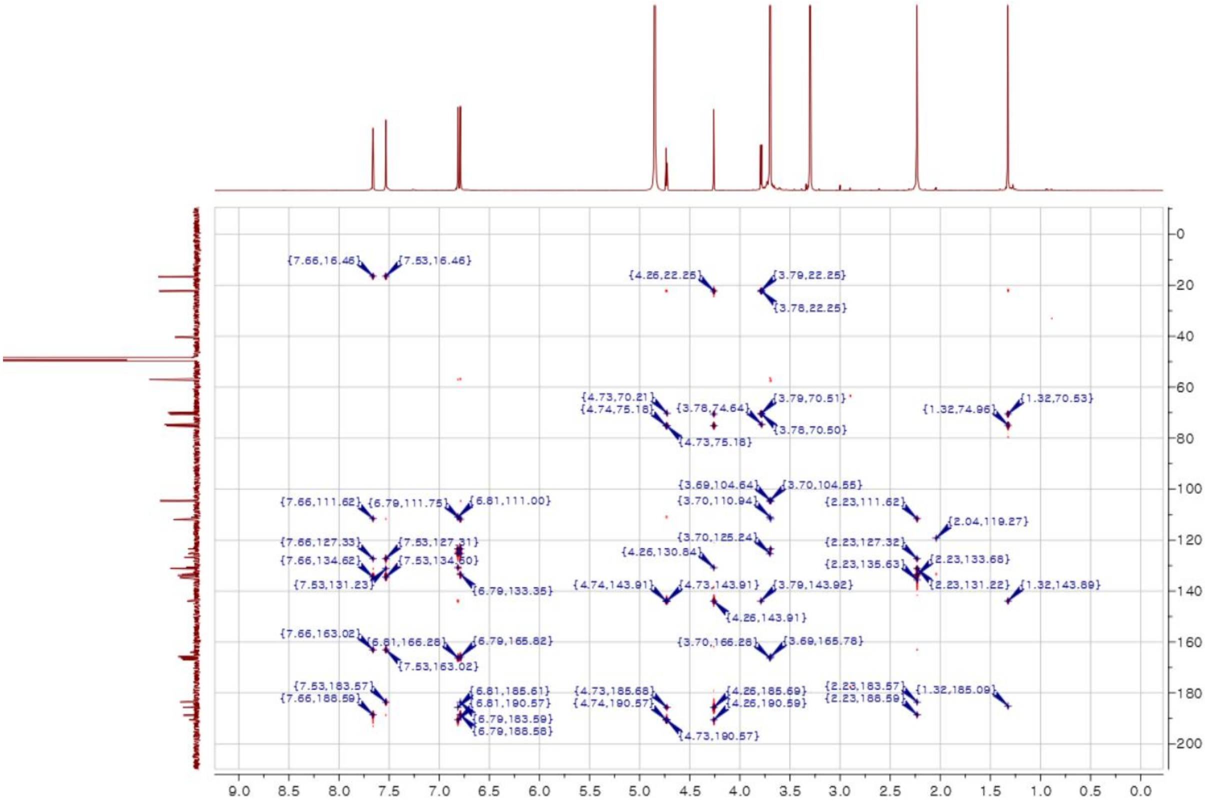


Figure S6. The LR-HSQMBC spectrum of Alterporriol Z1 (**1**) (800MHz, CD_3OD)

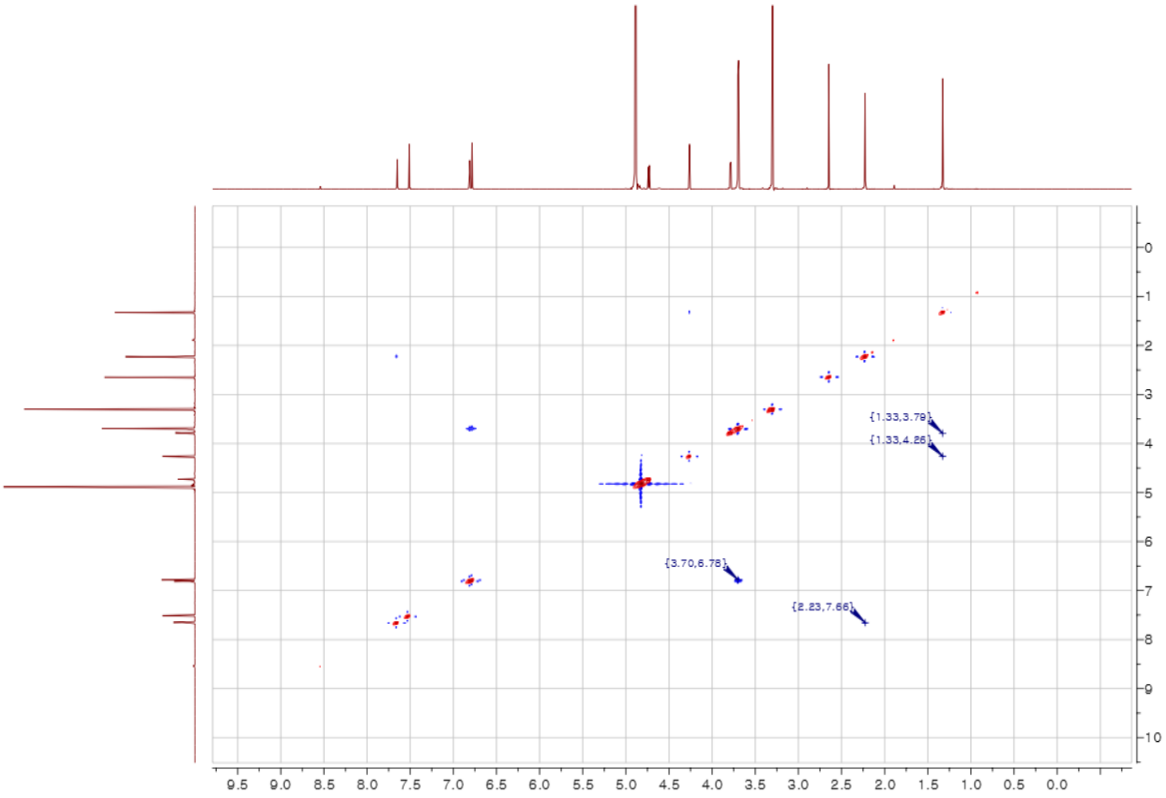


Figure S7. The NOESY spectrum of Alterporriol Z1 (**1**) (400MHz, CD_3OD)

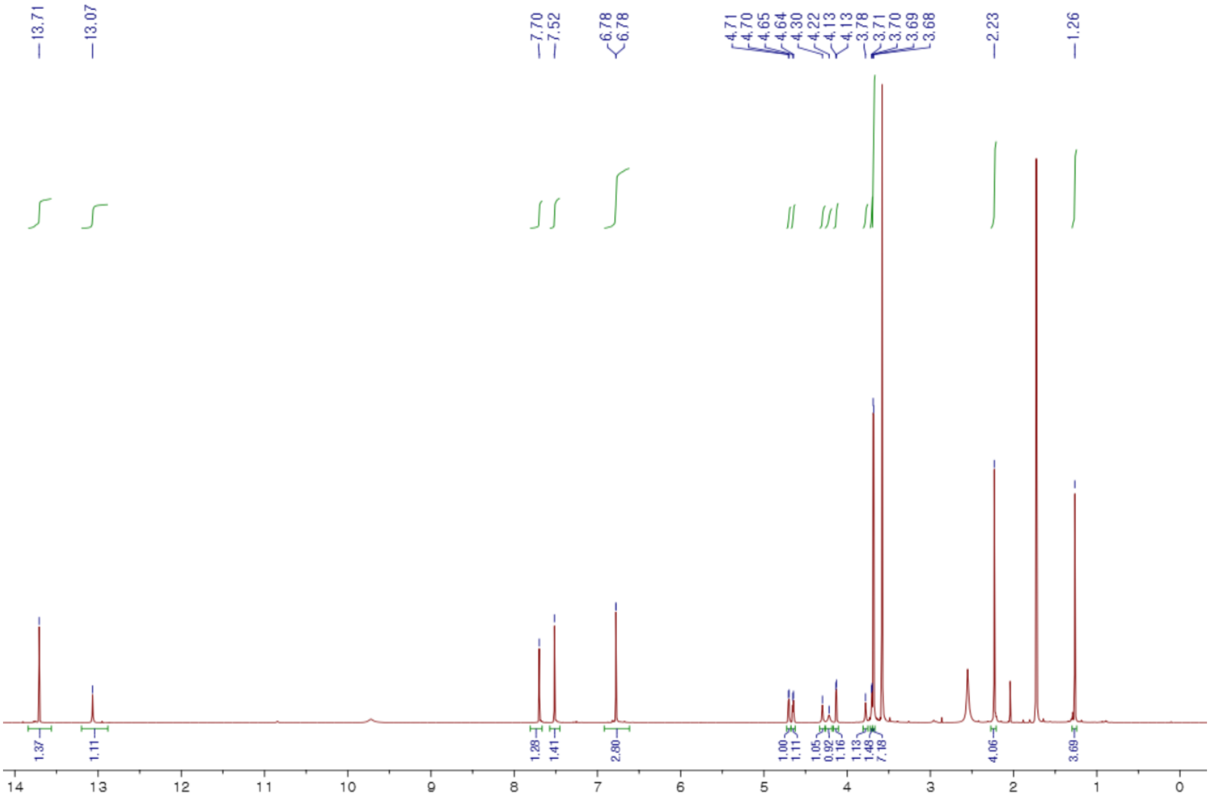


Figure S8. The ^{1}H NMR spectrum of Alterporriol Z1 (**1**) (800MHz, THF-d_8)

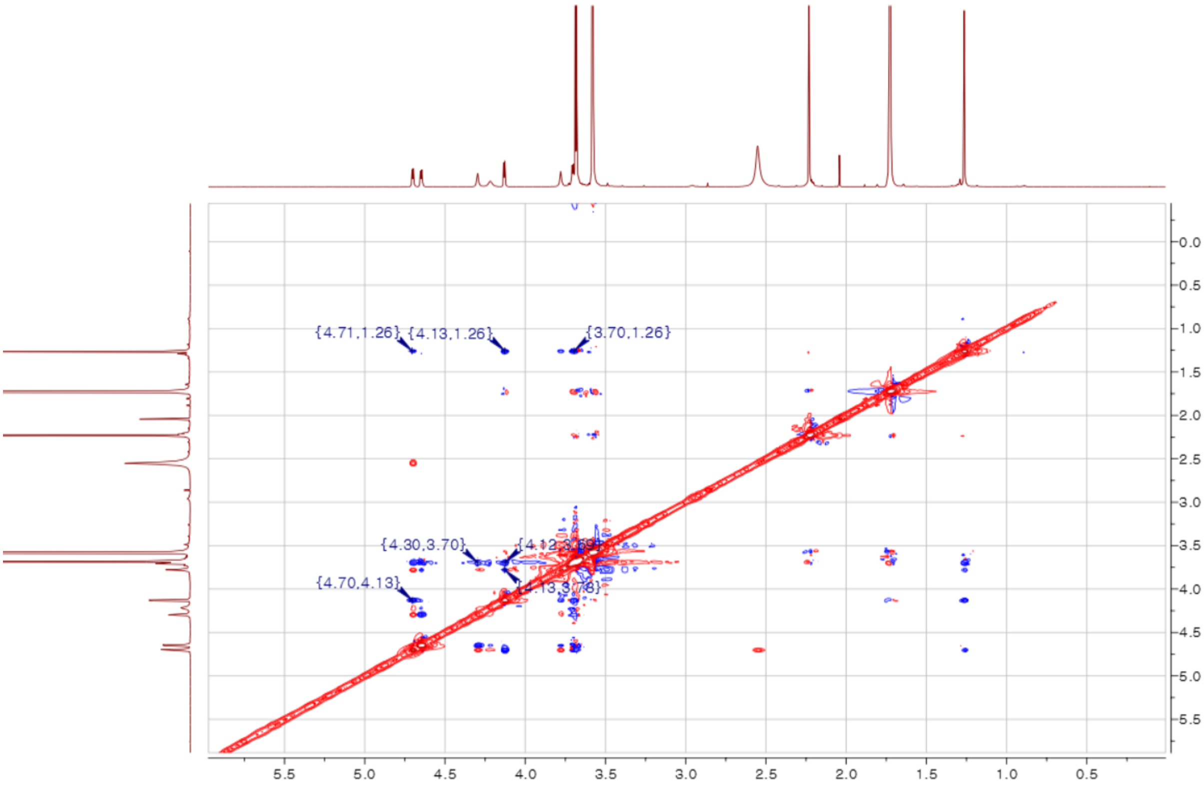
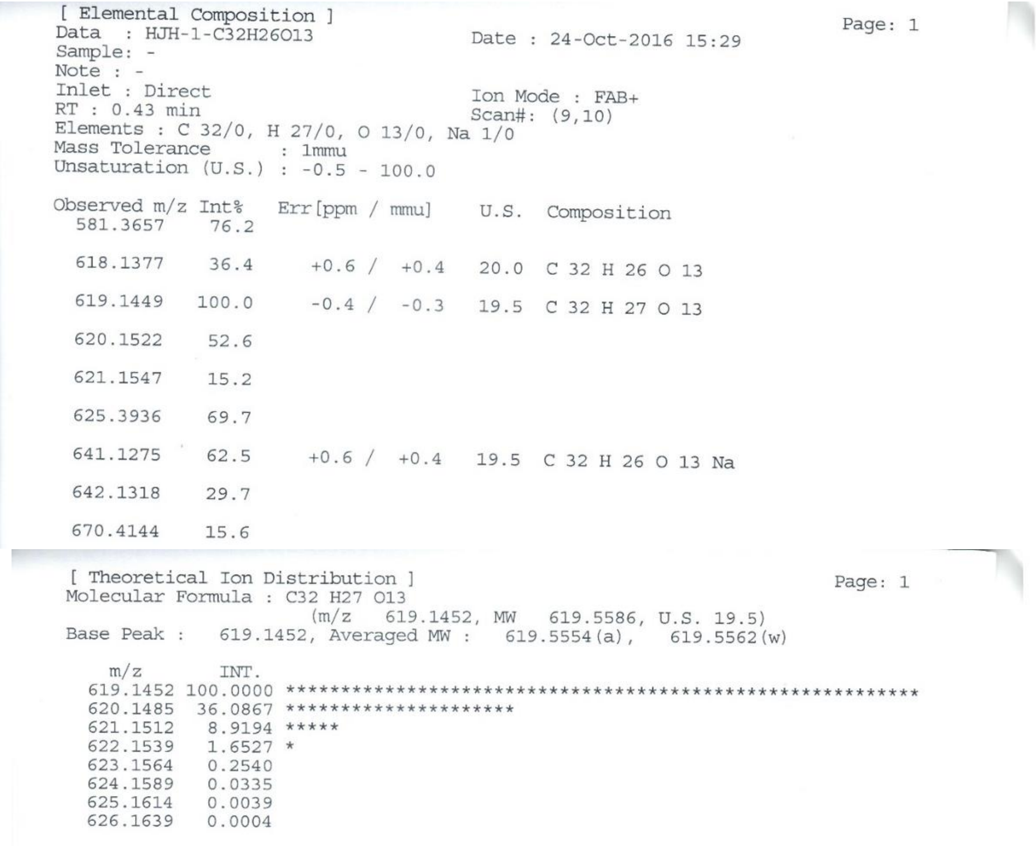


Figure S9. The NOESY spectrum of Alterporriol Z1 (**1**) (800MHz, THF-*d*8)



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Sample: -
Note : -
Inlet : Direct                          Ion Mode : FAB+
RT : 0.43 min                           Scan#: (9,10)
Elements : C 32/0, H 27/0, O 13/0, Na 1/0
Mass Tolerance        : 1mmu
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z  Int%   Err[ppm / mmu]    U.S.  Composition
  581.3657    76.2

  618.1377    36.4     +0.6 /  +0.4    20.0  C 32 H 26 O 13

  619.1449   100.0     -0.4 /  -0.3    19.5  C 32 H 27 O 13

  620.1522    52.6

  621.1547    15.2

  625.3936    69.7

  641.1275    62.5     +0.6 /  +0.4    19.5  C 32 H 26 O 13 Na

  642.1318    29.7

  670.4144    15.6
```

```
[ Theoretical Ion Distribution ]                                Page: 1
Molecular Formula : C32 H27 O13
                     (m/z   619.1452, MW   619.5586, U.S. 19.5)
Base Peak :    619.1452, Averaged MW :    619.5554(a),    619.5562(w)

     m/z        INT.
  619.1452 100.0000 *************************************************************
  620.1485  36.0867 **********************
  621.1512   8.9194 *****
  622.1539   1.6527 *
  623.1564   0.2540
  624.1589   0.0335
  625.1614   0.0039
  626.1639   0.0004
```

Figure S10. The HRFABMS data of Alterporriol Z1 (**1**)

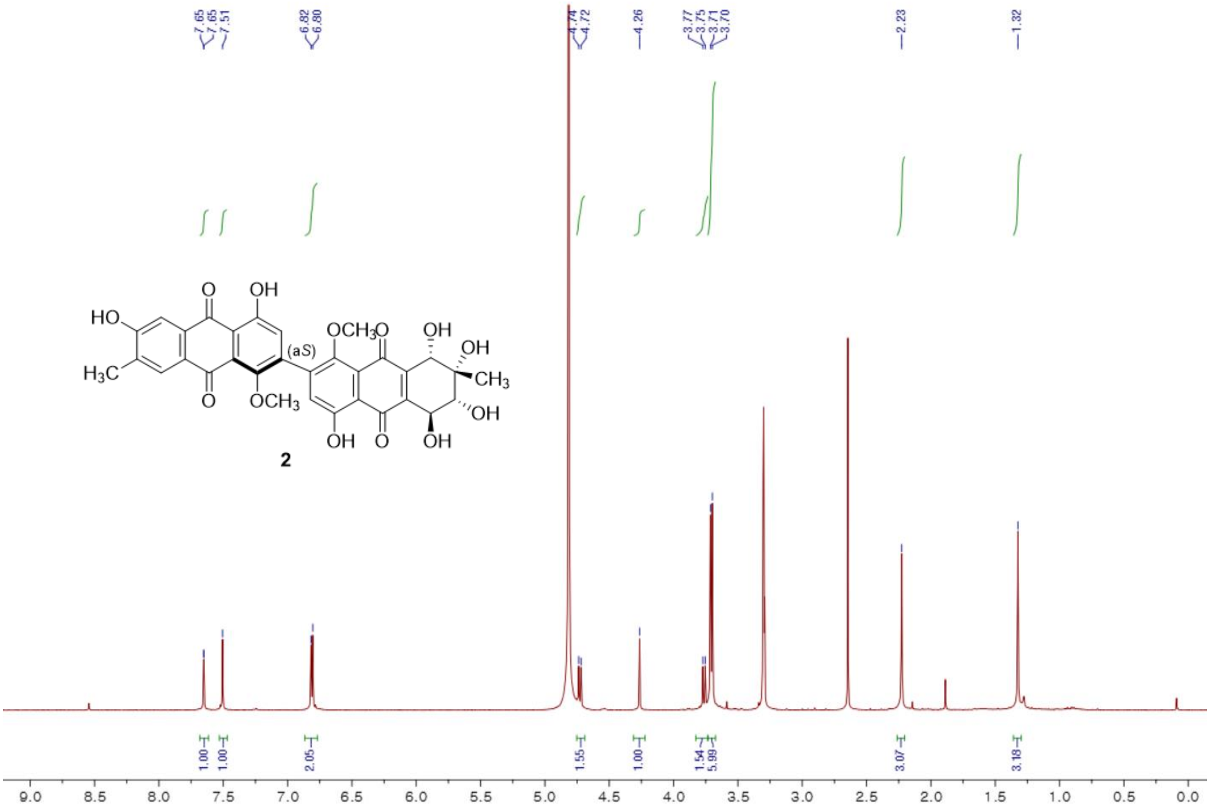


Figure S11. The ^{1}H NMR spectrum of Alterporriol Z2 (**2**) (400MHz, CD_3OD)

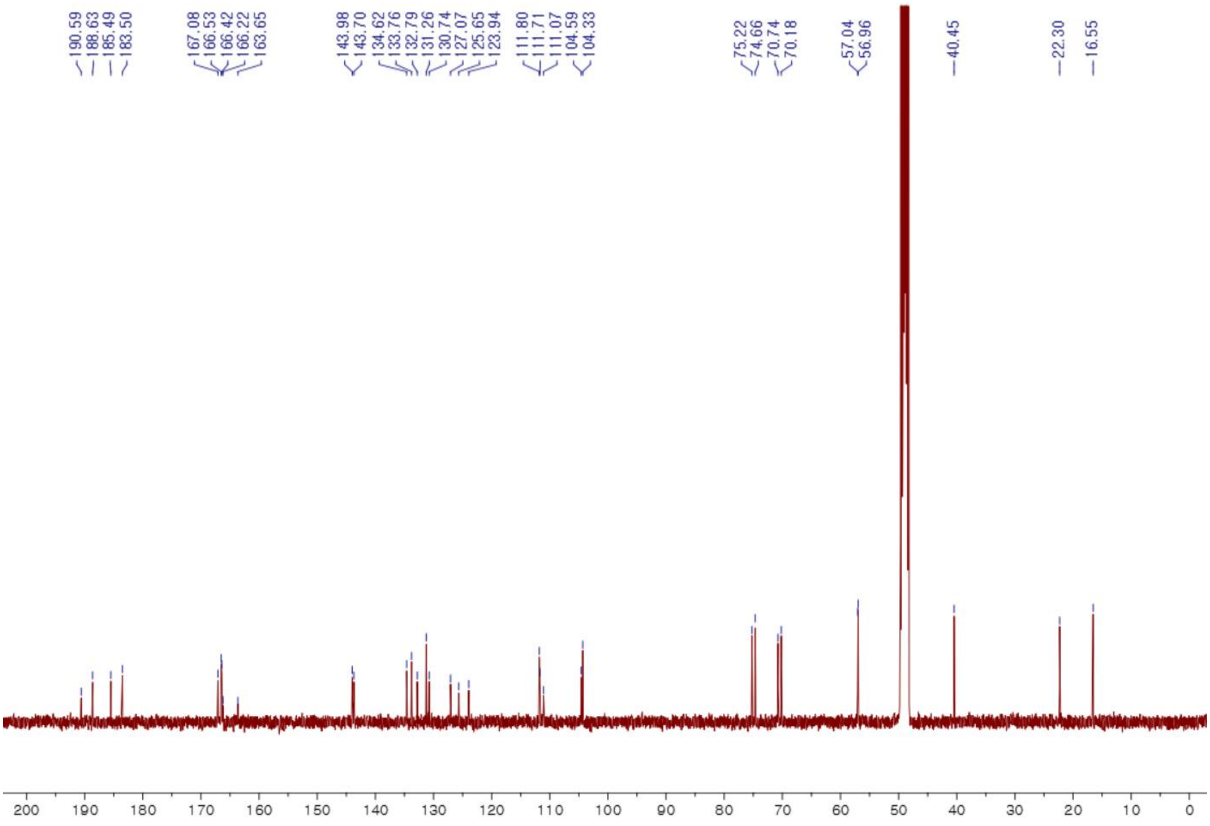


Figure S12. The ^{13}C NMR spectrum of Alterporriol Z2 (**2**) (100MHz, CD_3OD)

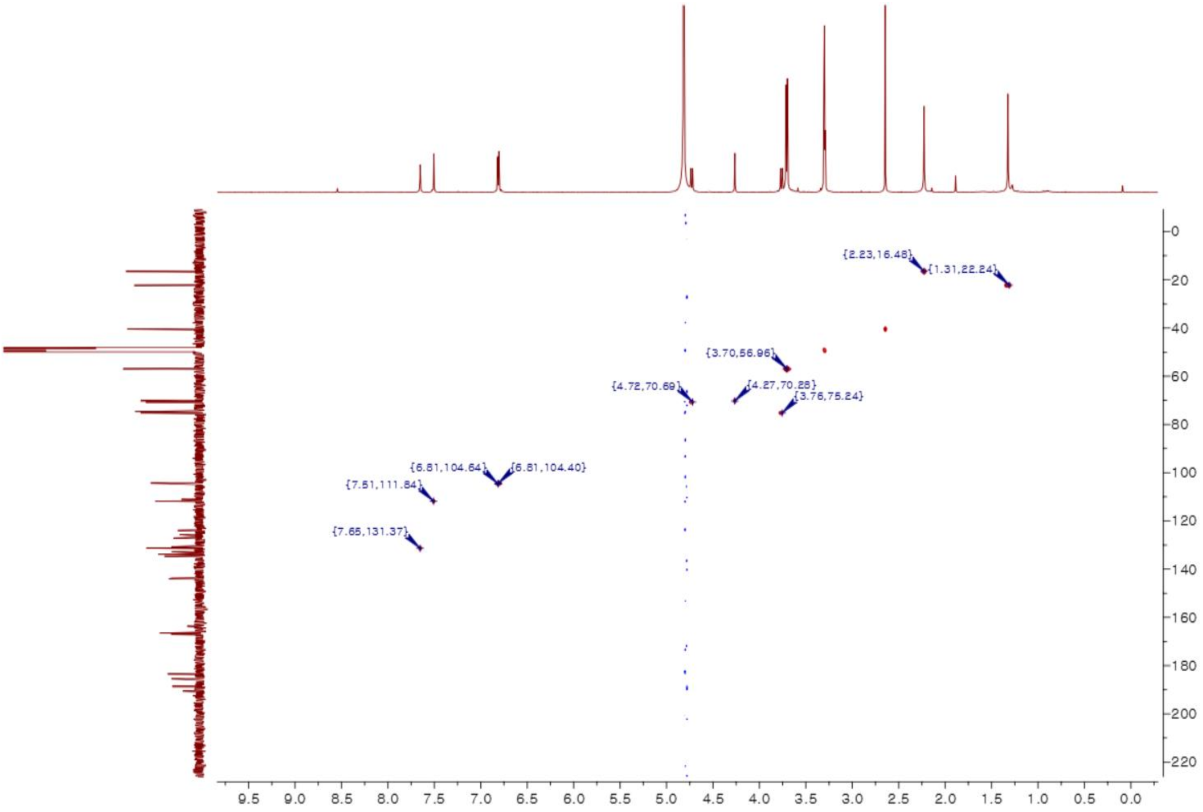


Figure S13. The HSQC spectrum of Alterporriol Z2 (**2**) (400MHz, CD_3OD)

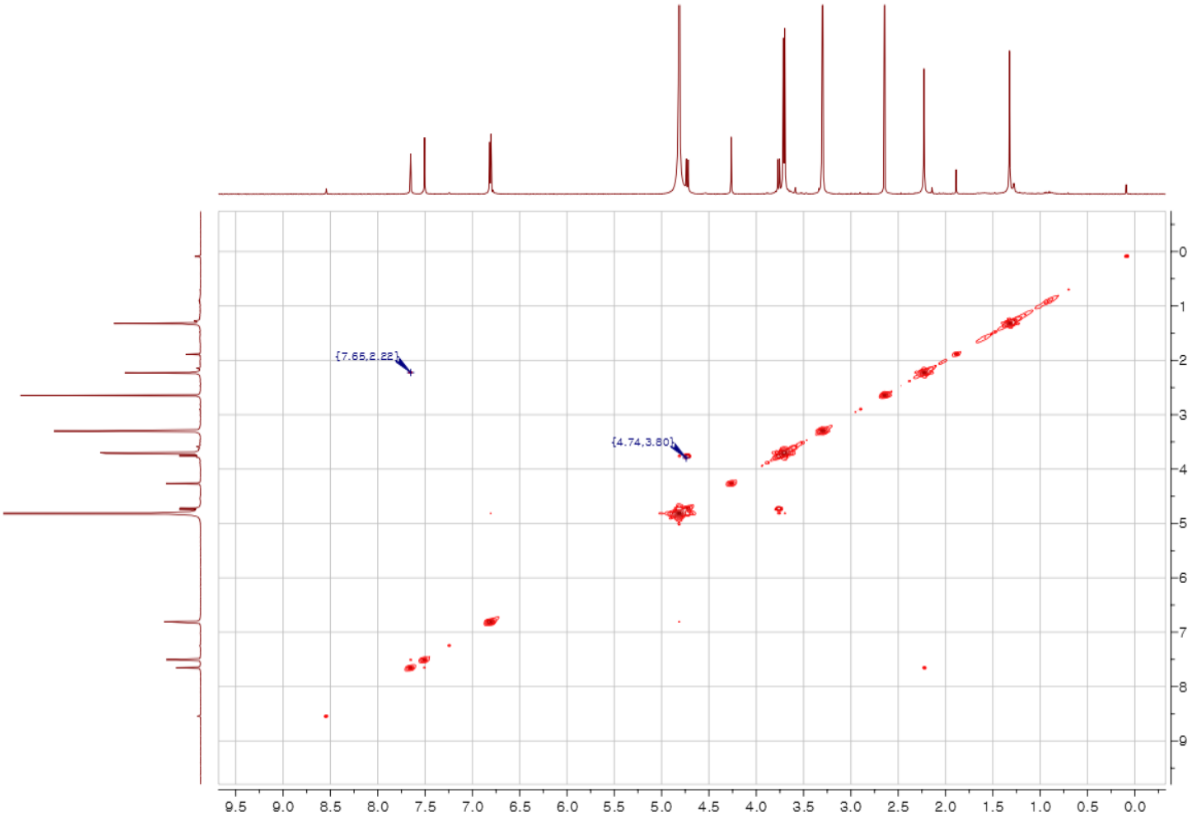


Figure S14. The COSY spectrum of Alterporriol Z2 (**2**) (400MHz, CD_3OD)

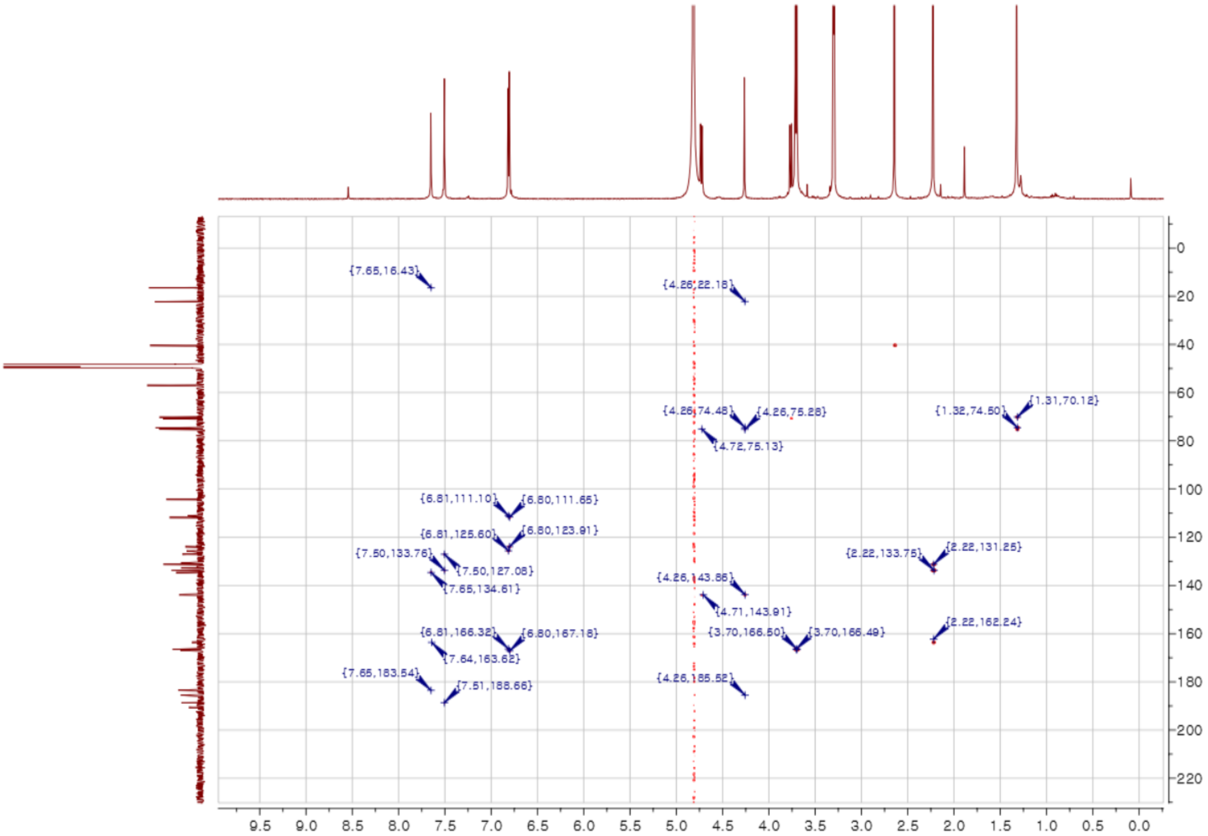


Figure S15. The HMBC spectrum of Alterporriol Z2 (**2**) (400MHz, CD_3OD)

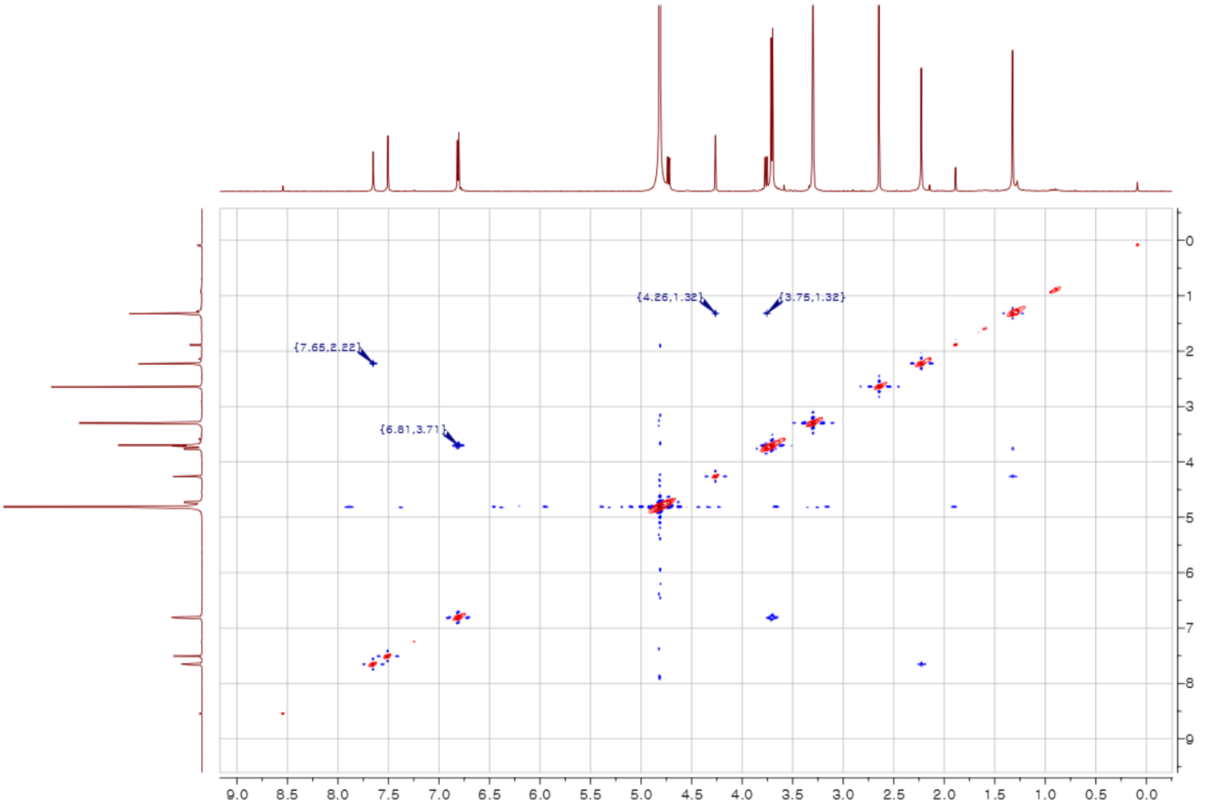
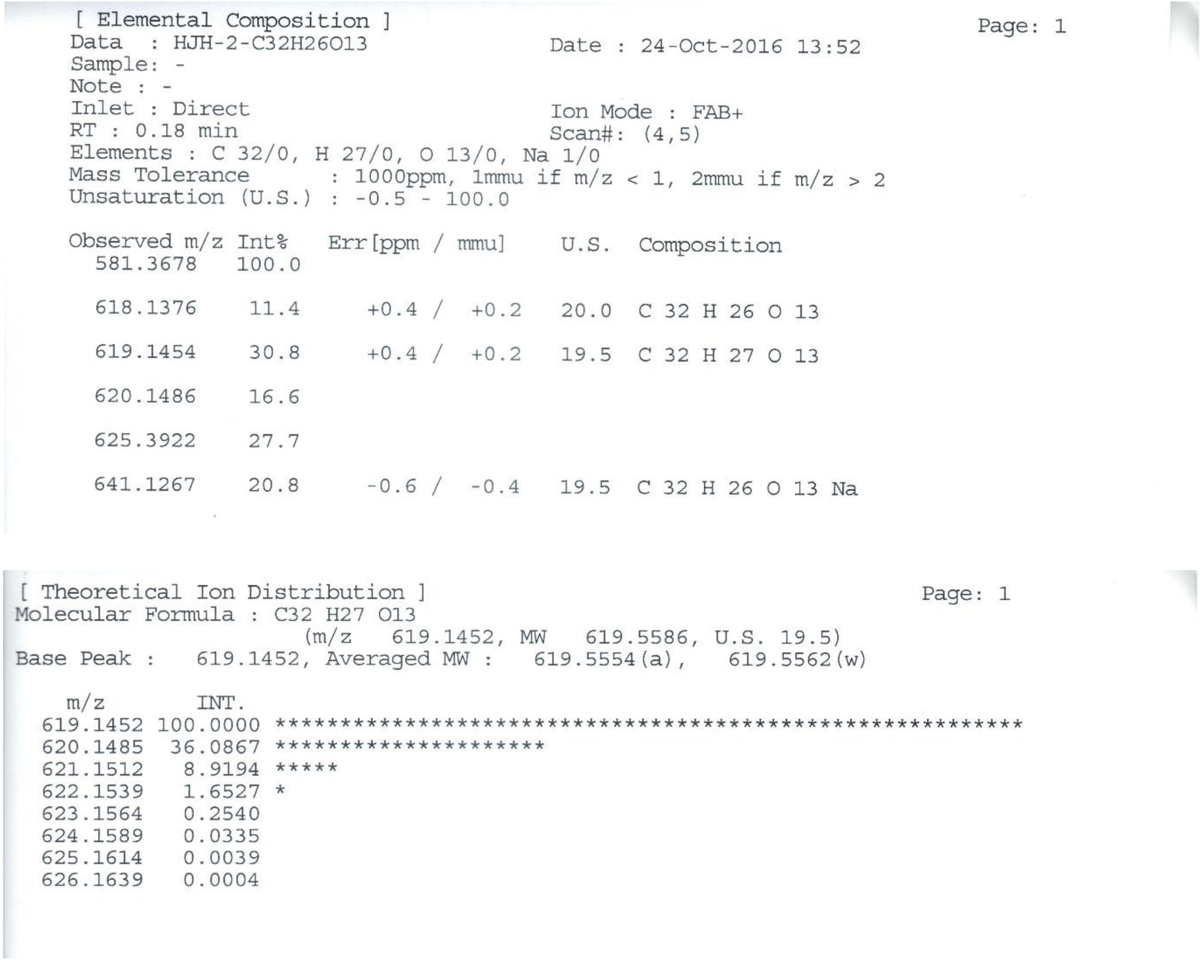


Figure S16. The NOESY spectrum of Alterporriol Z2 (**2**) (400MHz, CD_3OD)



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Data  : HJH-2-C32H26O13              Date : 24-Oct-2016 13:52
Sample: -
Note : -
Inlet : Direct                       Ion Mode : FAB+
RT : 0.18 min                        Scan#: (4,5)
Elements : C 32/0, H 27/0, O 13/0, Na 1/0
Mass Tolerance      : 1000ppm, 1mmu if m/z < 1, 2mmu if m/z > 2
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  581.3678   100.0

  618.1376    11.4     +0.4 /  +0.2   20.0  C 32 H 26 O 13

  619.1454    30.8     +0.4 /  +0.2   19.5  C 32 H 27 O 13

  620.1486    16.6

  625.3922    27.7

  641.1267    20.8     -0.6 /  -0.4   19.5  C 32 H 26 O 13 Na
```

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[ Theoretical Ion Distribution ]                                Page: 1
Molecular Formula : C32 H27 O13
                         (m/z   619.1452, MW   619.5586, U.S. 19.5)
Base Peak :    619.1452, Averaged MW :   619.5554(a),   619.5562(w)

   m/z       INT.
  619.1452 100.0000 ************************************************************
  620.1485  36.0867 **********************
  621.1512   8.9194 *****
  622.1539   1.6527 *
  623.1564   0.2540
  624.1589   0.0335
  625.1614   0.0039
  626.1639   0.0004
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Figure S17. The HRFABMS data of Alterporriol Z2 (**2**)

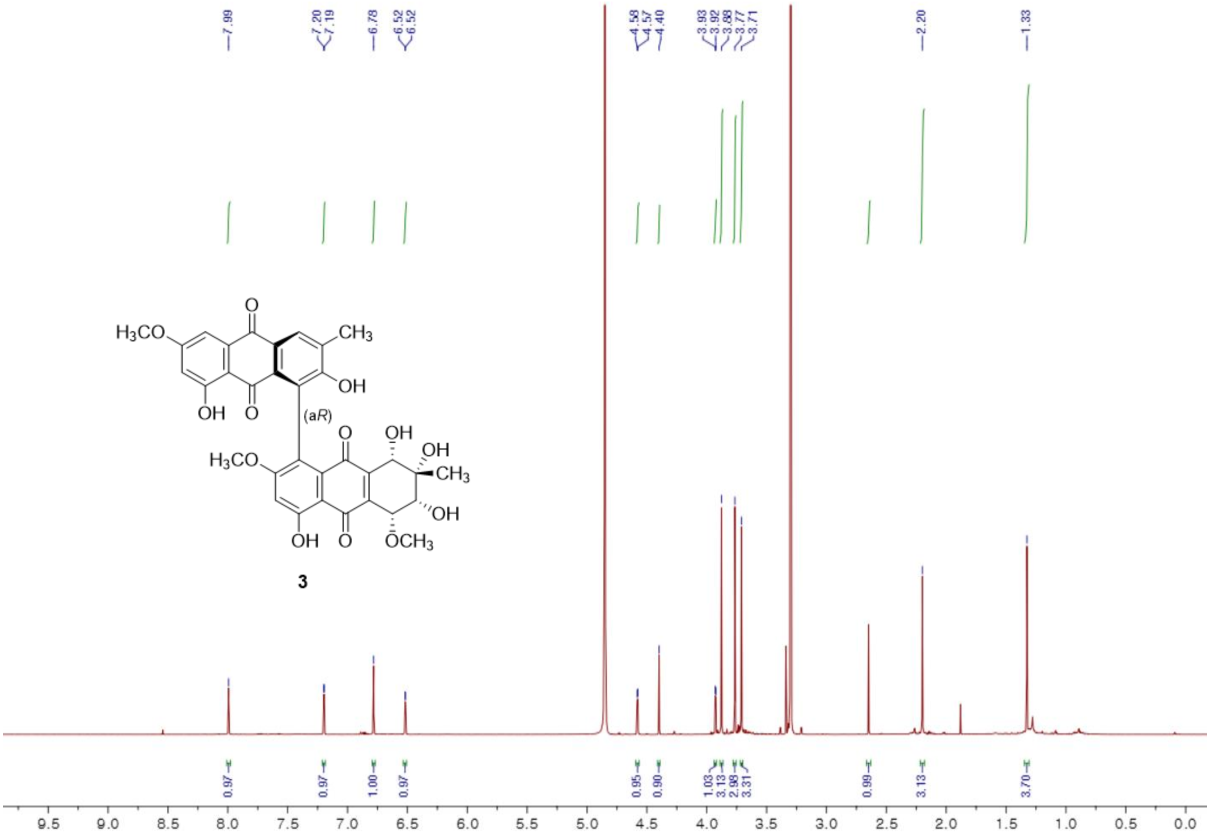


Figure S18. The ^{1}H NMR spectrum of Alterporriol Z3 (**3**) (800MHz, CD_3OD)

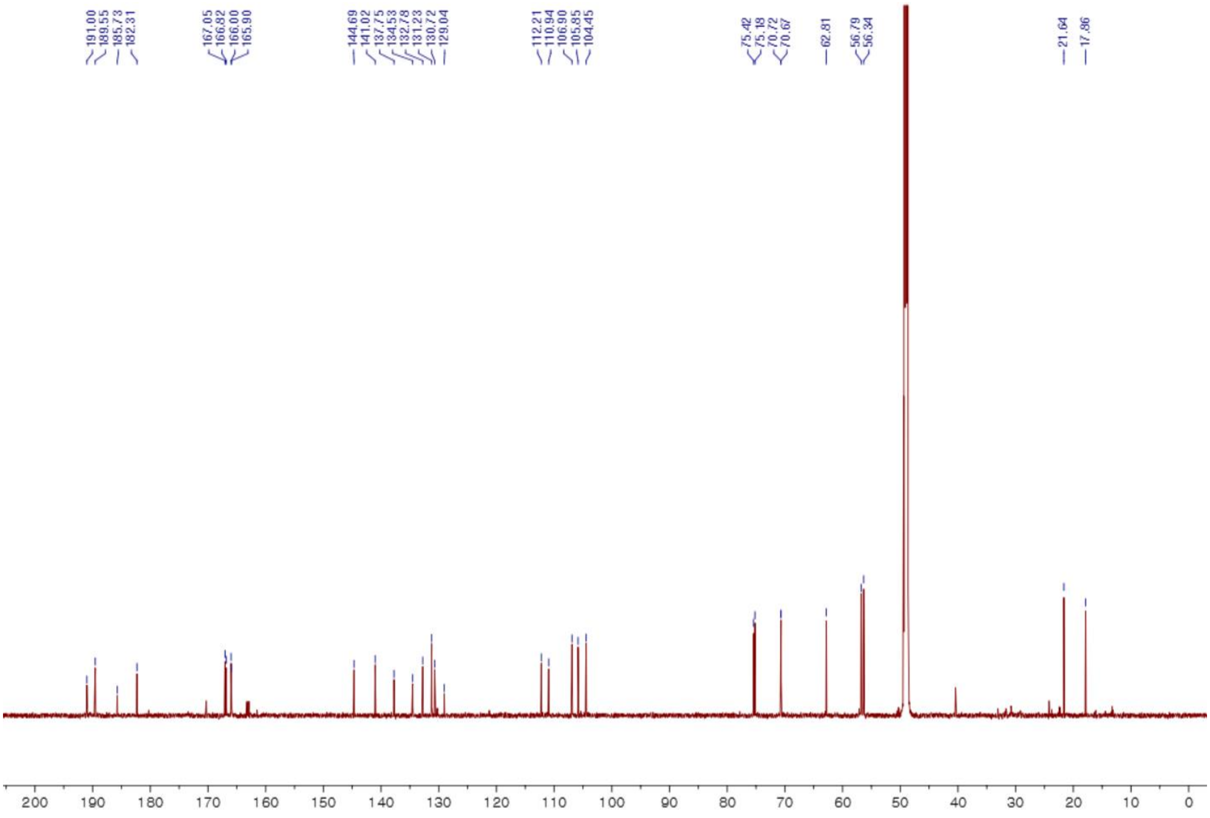


Figure S19. The ^{13}C NMR spectrum of Alterporriol Z3 (**3**) (200MHz, CD_3OD)

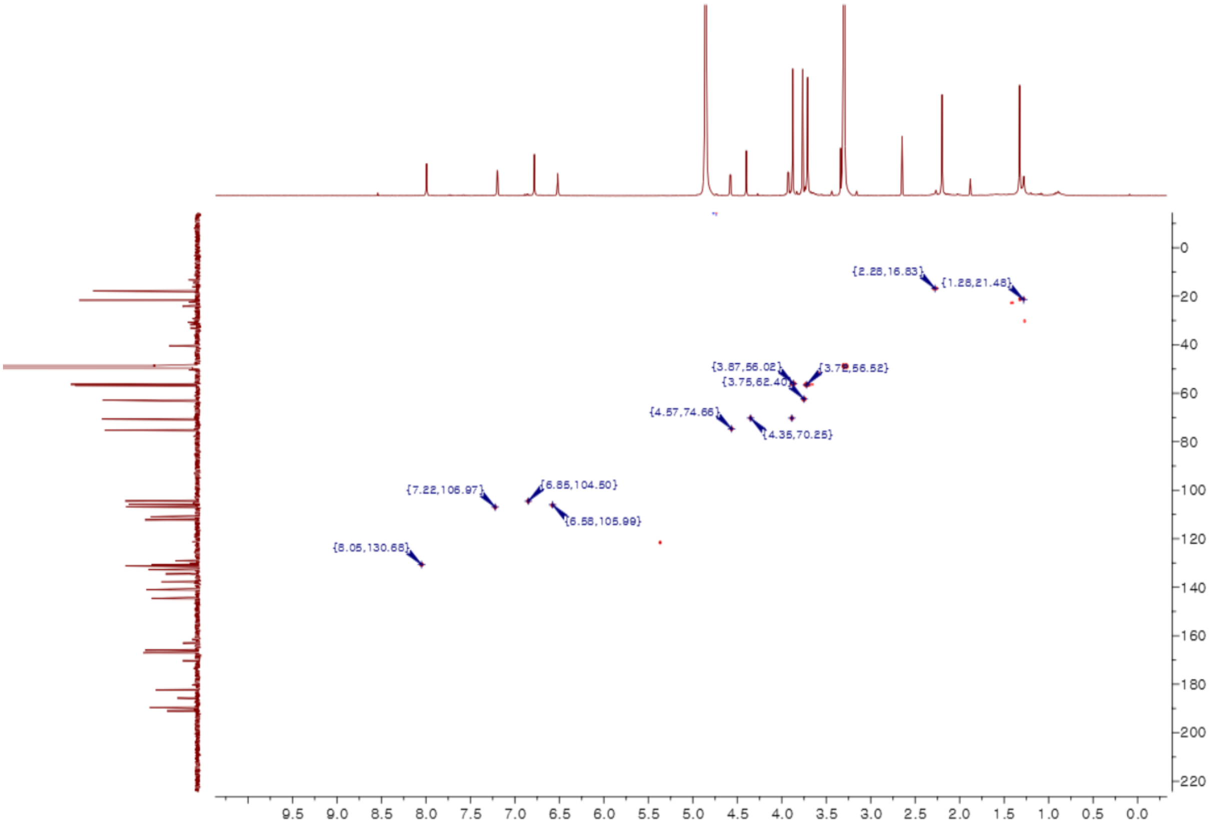


Figure S20. The HSQC spectrum of Alterporriol Z3 (**3**) (500MHz, CD_3OD)

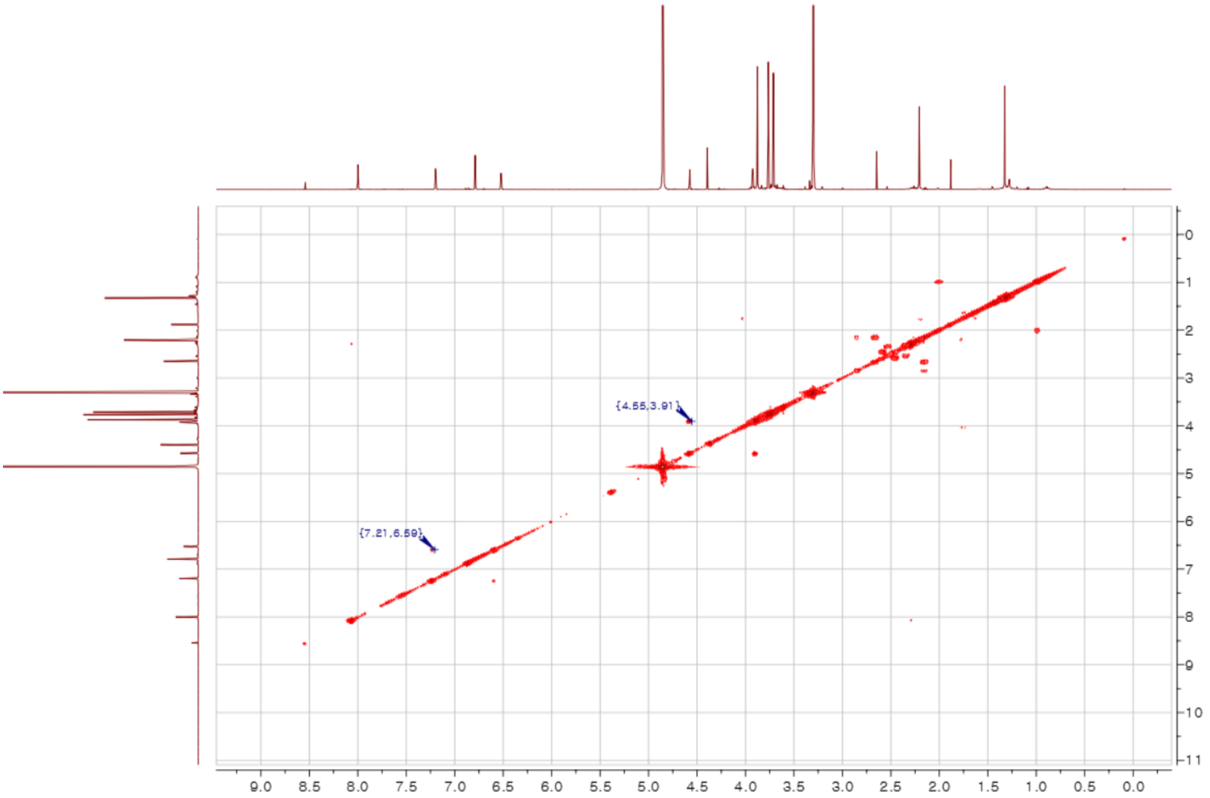


Figure S21. The COSY spectrum of Alterporriol Z3 (**3**) (500MHz, CD_3OD)

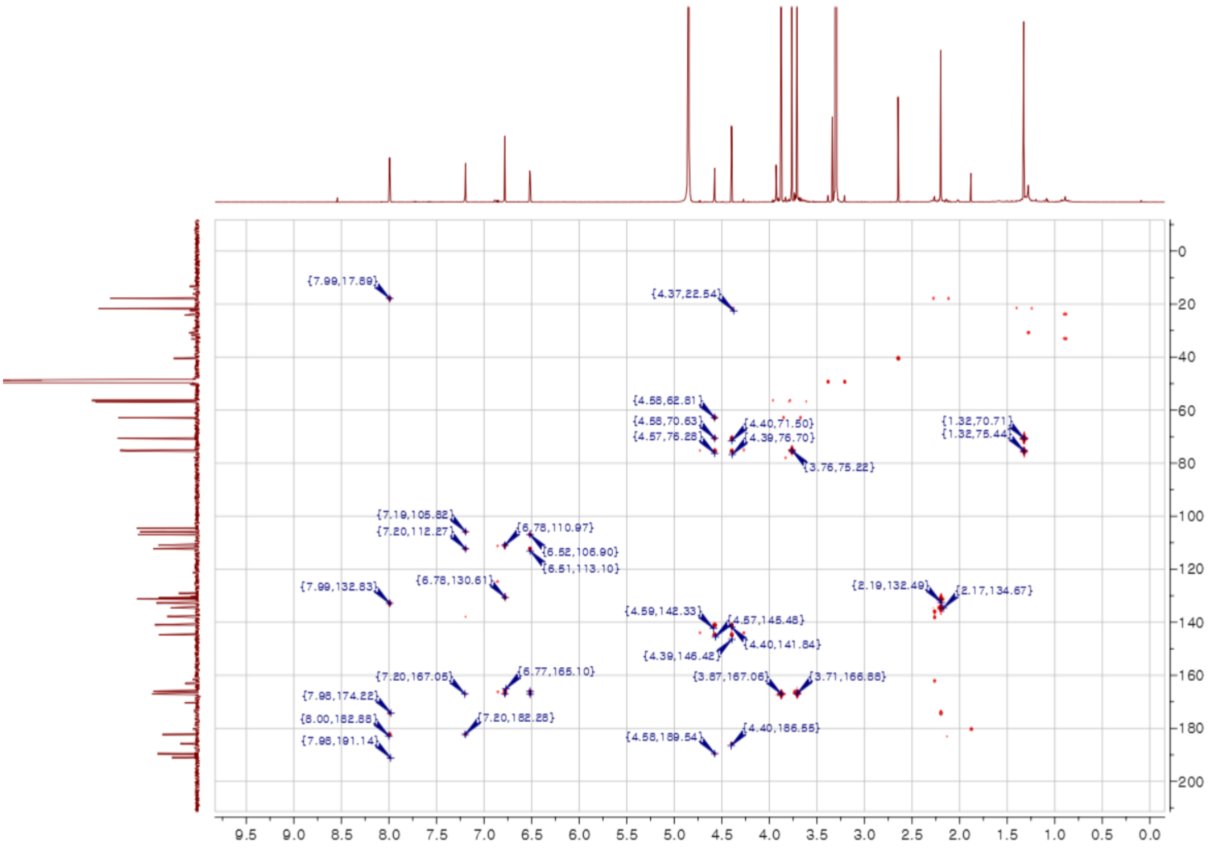


Figure S22. The HMBC spectrum of Alterporriol Z3 (**3**) (800MHz, CD_3OD)

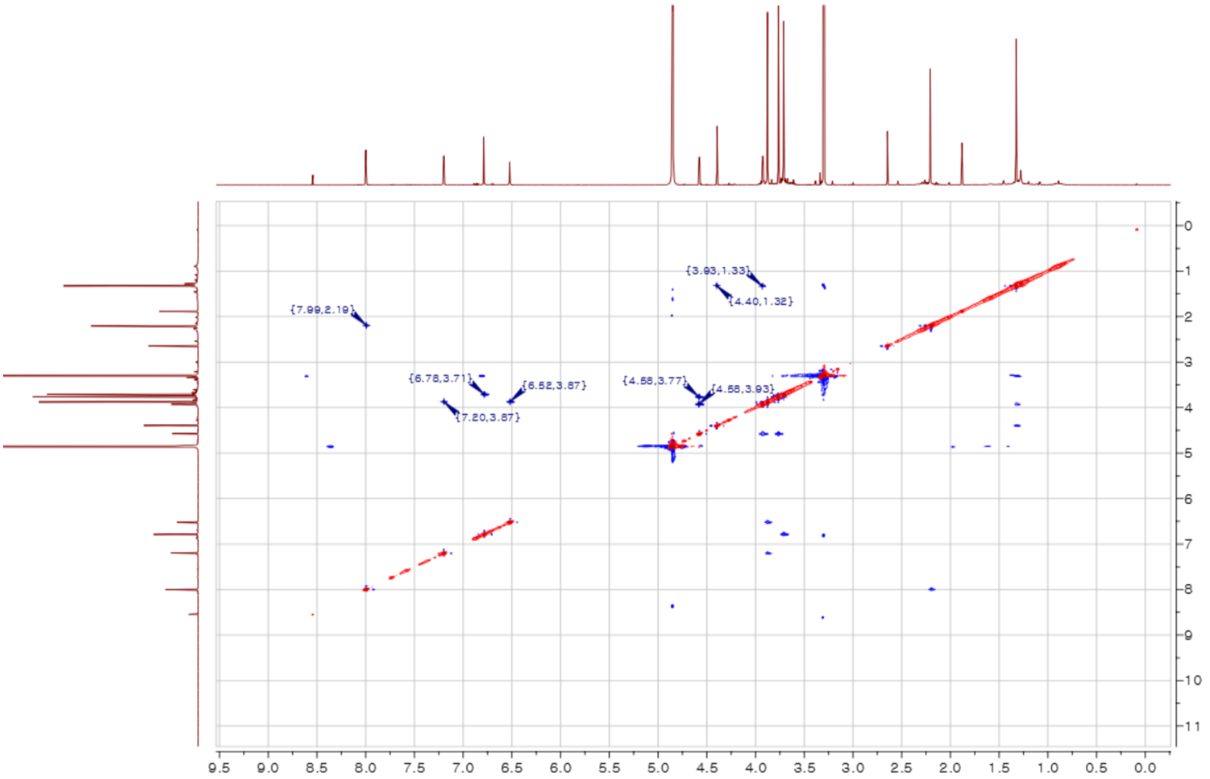
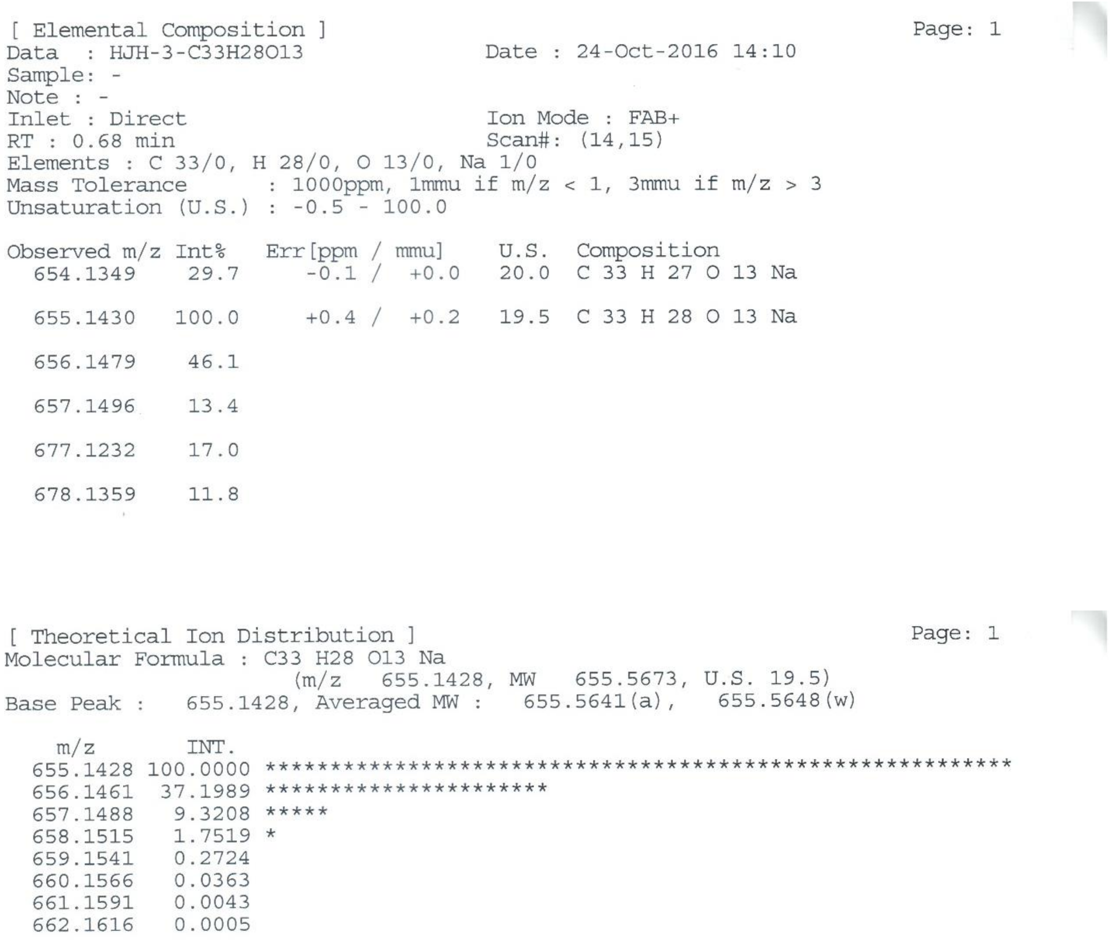


Figure S23. The NOESY spectrum of Alterporriol Z3 (**3**) (500MHz, CD_3OD)



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Sample: -
Note : -
Inlet : Direct                      Ion Mode : FAB+
RT : 0.68 min                       Scan#: (14,15)
Elements : C 33/0, H 28/0, O 13/0, Na 1/0
Mass Tolerance      : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  654.1349   29.7     -0.1 /  +0.0    20.0  C 33 H 27 O 13 Na

  655.1430  100.0     +0.4 /  +0.2    19.5  C 33 H 28 O 13 Na

  656.1479   46.1

  657.1496   13.4

  677.1232   17.0

  678.1359   11.8
```

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[ Theoretical Ion Distribution ]                             Page: 1
Molecular Formula : C33 H28 O13 Na
                       (m/z   655.1428, MW   655.5673, U.S. 19.5)
Base Peak :   655.1428, Averaged MW :   655.5641(a),   655.5648(w)

   m/z       INT.
  655.1428 100.0000 ************************************************************
  656.1461  37.1989 **********************
  657.1488   9.3208 *****
  658.1515   1.7519 *
  659.1541   0.2724
  660.1566   0.0363
  661.1591   0.0043
  662.1616   0.0005
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Figure S24. The HRFABMS data of Alterporriol Z3 (**3**)

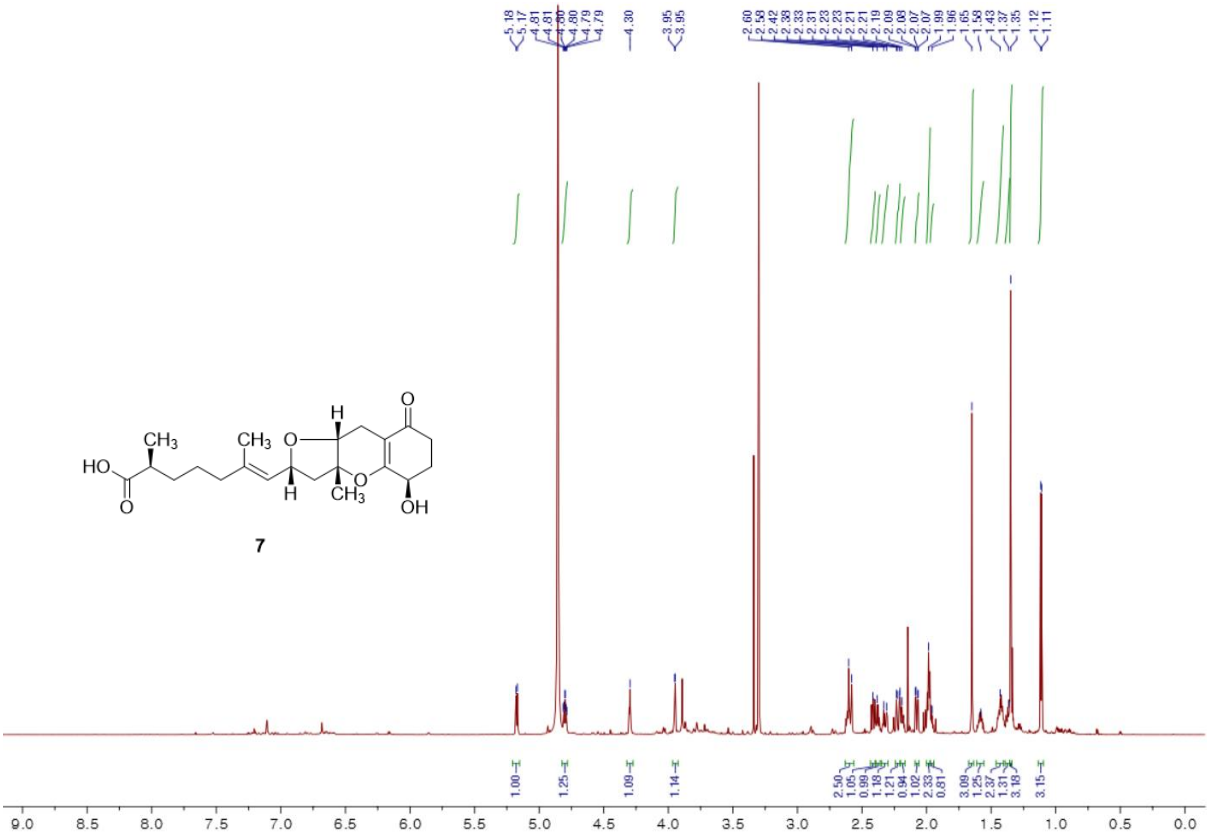


Figure S25. The ^{1}H NMR spectrum of Tricycloalterfurene E (**7**) (800MHz, CD_3OD)

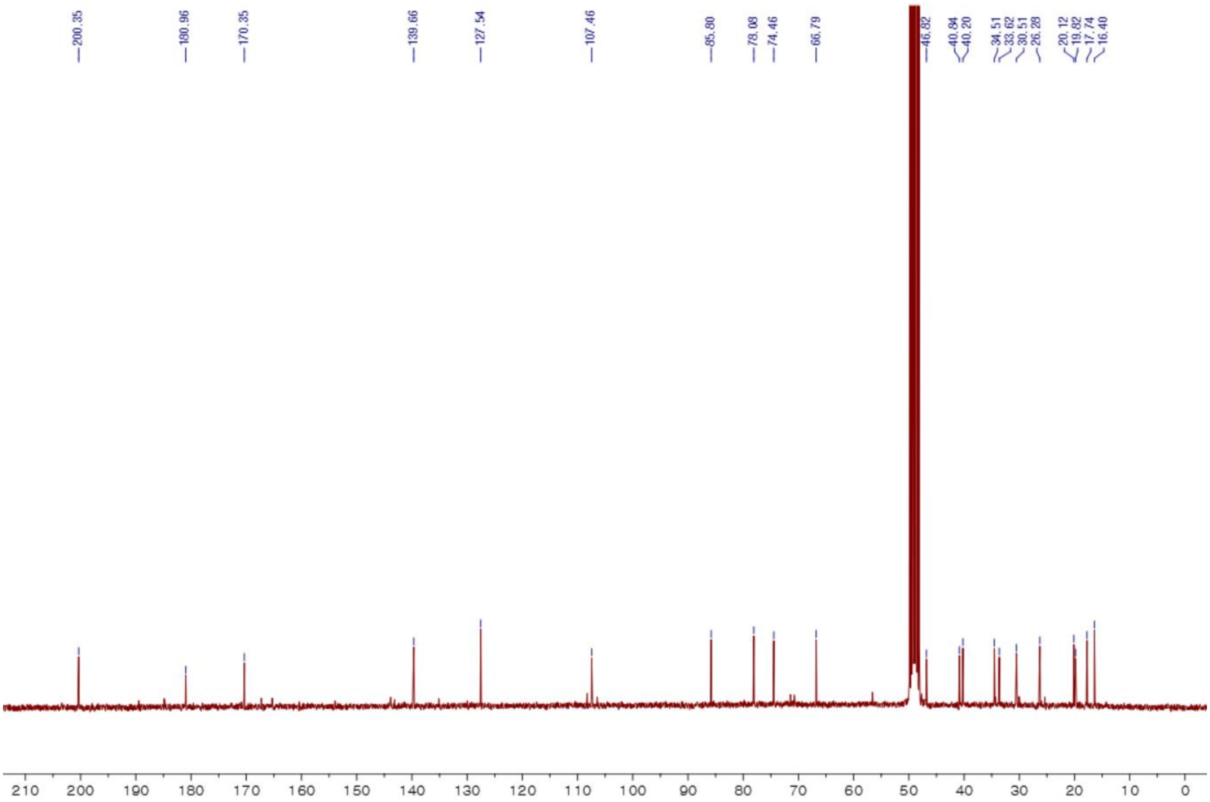


Figure S26. The ^{13}C NMR spectrum of Tricycloalterfurene E (**7**) (100MHz, CD_3OD)

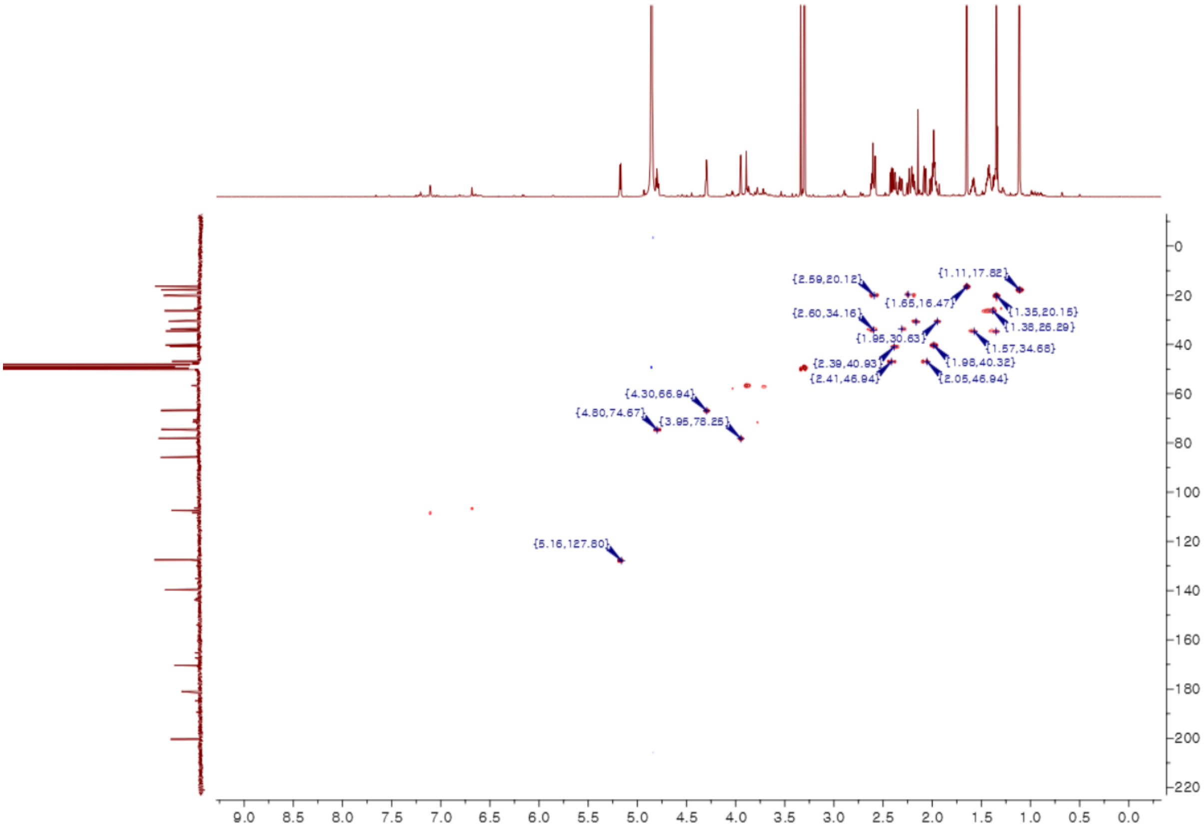


Figure S27. The HSQC spectrum of Tricycloalterfurene E (**7**) (400MHz, CD_3OD)

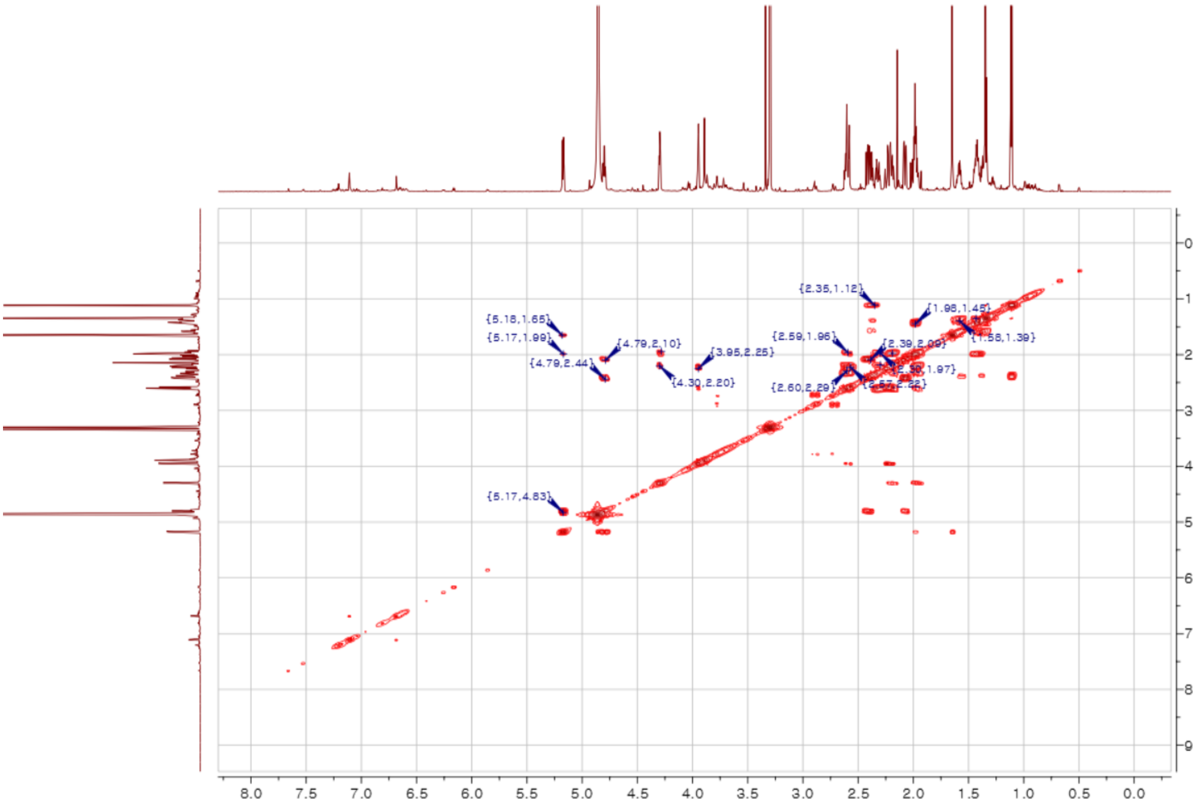


Figure S28. The COSY spectrum of Tricycloalterfurene E (**7**) (400MHz, CD_3OD)

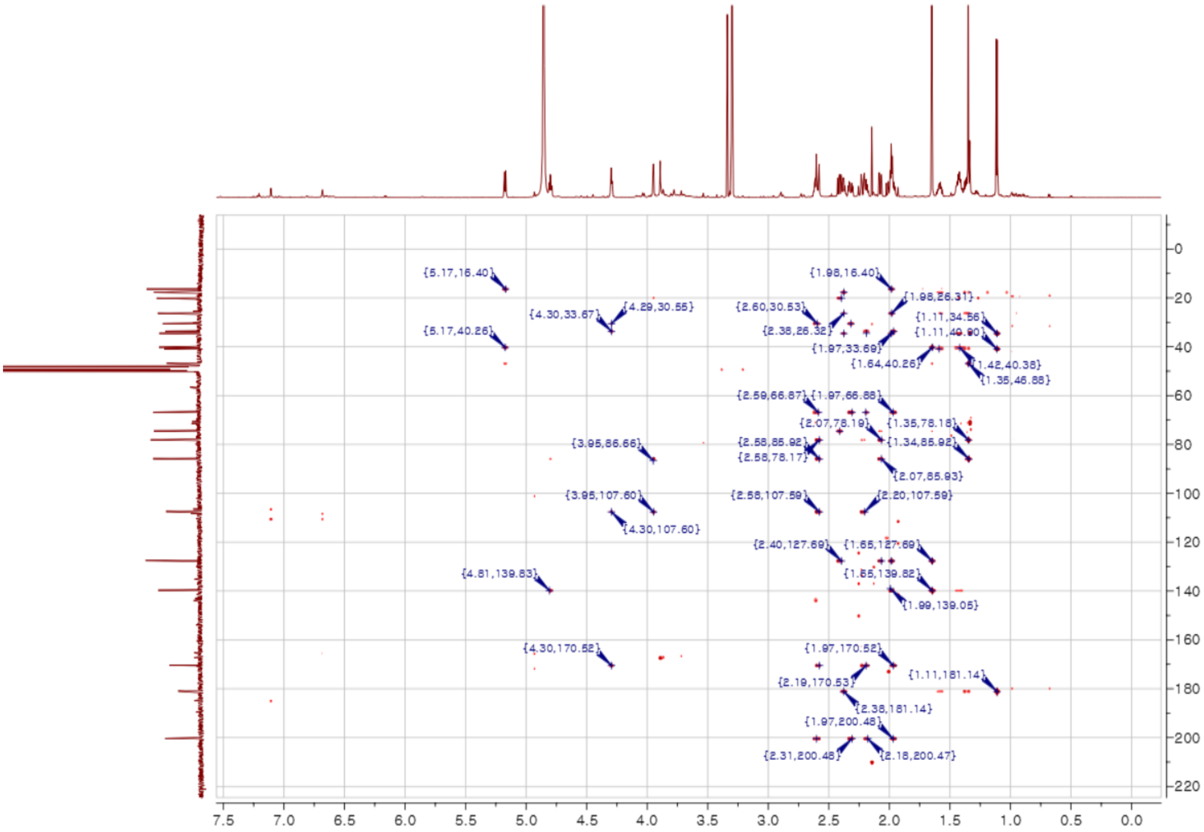


Figure S29. The HMBC spectrum of Tricycloalterfurene E (**7**) (800MHz, CD_3OD)

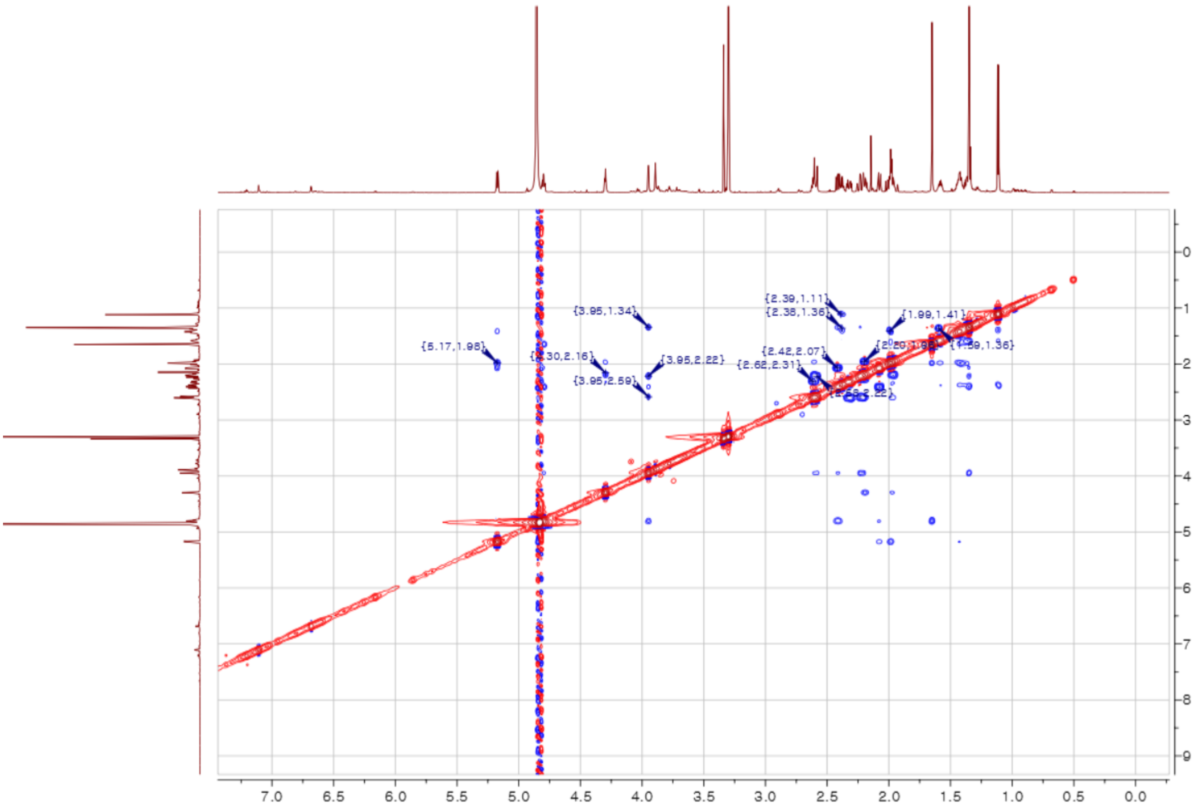
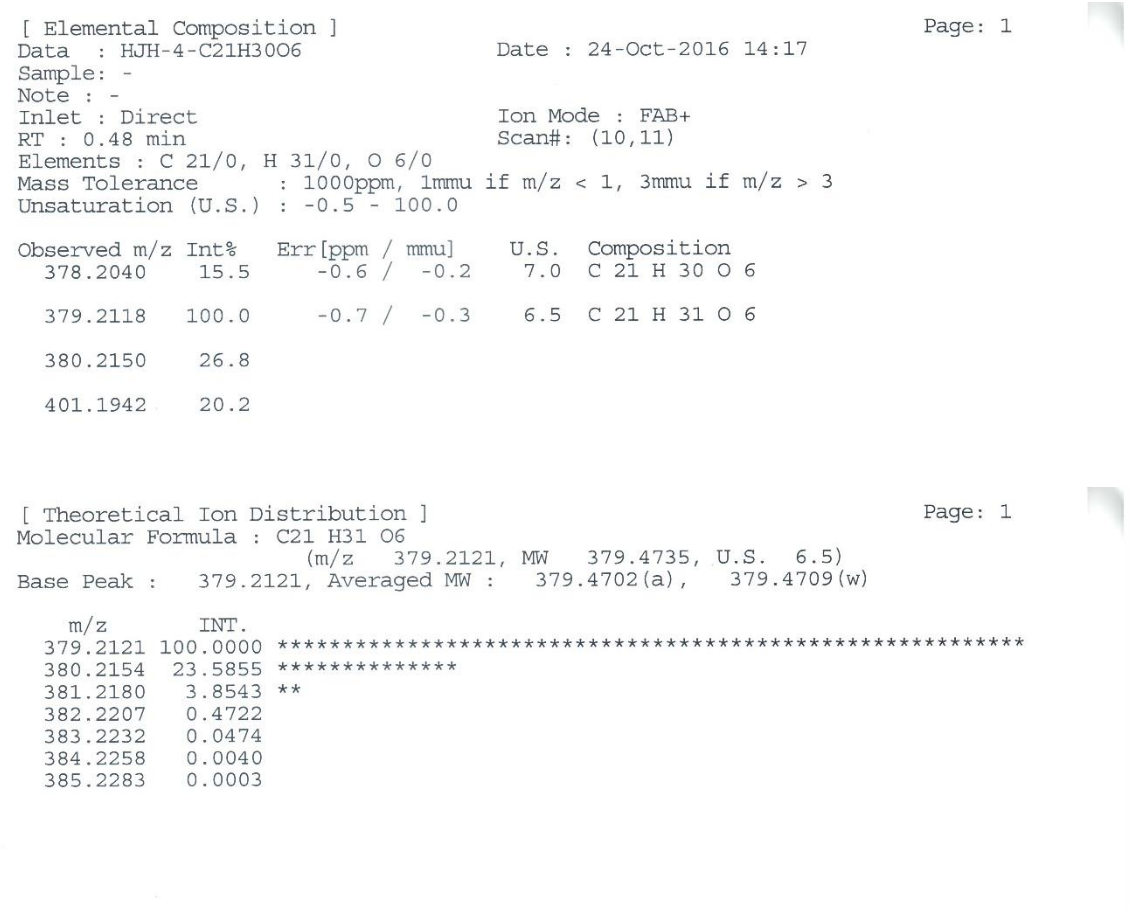


Figure S30. The NOESY spectrum of Tricycloalterfurene E (**7**) (600MHz, CD_3OD)



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Sample: -
Note : -
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RT : 0.48 min                       Scan#: (10,11)
Elements : C 21/0, H 31/0, O 6/0
Mass Tolerance      : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  378.2040    15.5     -0.6 /  -0.2    7.0  C 21 H 30 O 6

  379.2118   100.0     -0.7 /  -0.3    6.5  C 21 H 31 O 6

  380.2150    26.8

  401.1942    20.2
```

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[ Theoretical Ion Distribution ]                                Page: 1
Molecular Formula : C21 H31 O6
                      (m/z   379.2121, MW   379.4735, U.S.  6.5)
Base Peak :   379.2121, Averaged MW :   379.4702(a),   379.4709(w)

   m/z       INT.
  379.2121 100.0000 ***********************************************************
  380.2154  23.5855 **************
  381.2180   3.8543 **
  382.2207   0.4722
  383.2232   0.0474
  384.2258   0.0040
  385.2283   0.0003
```

Figure S31. The HRFABMS data of Tricycloalterfurene E (**7**)

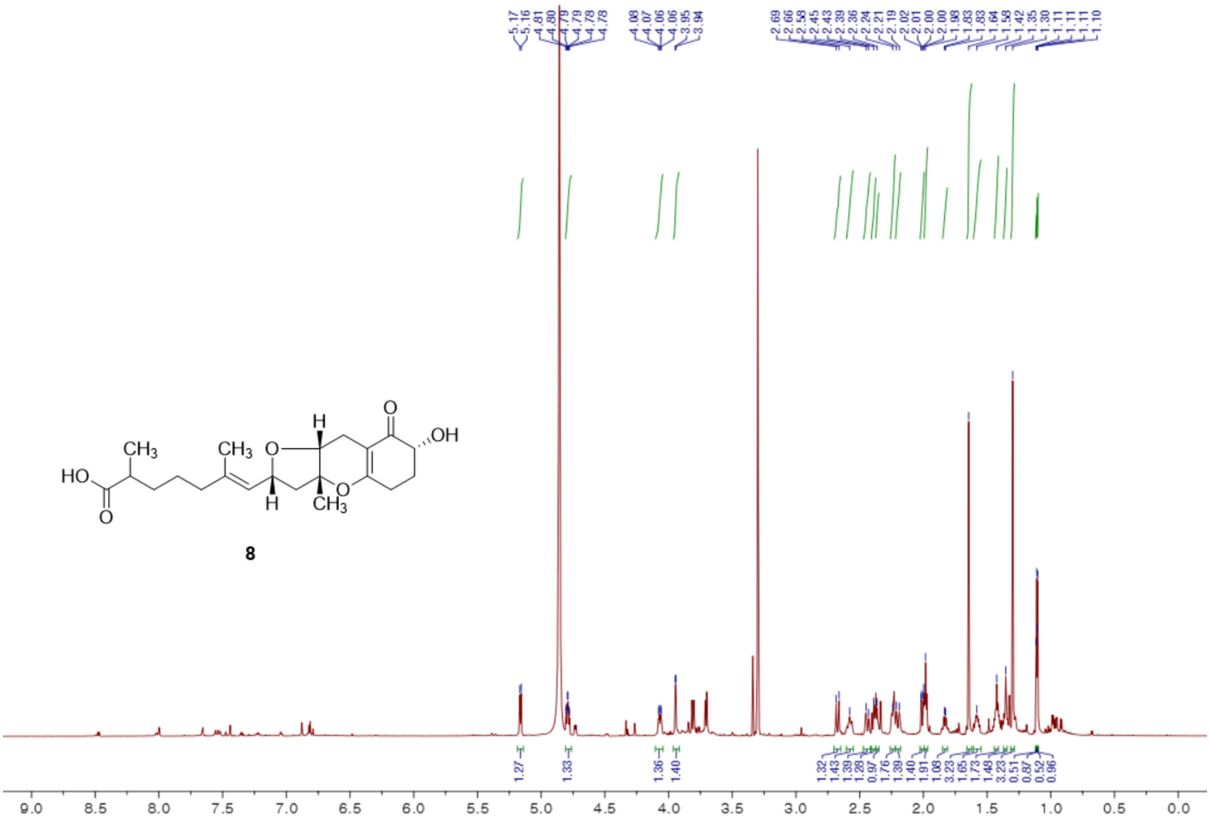


Figure S32. The ^{1}H NMR spectrum of Tricycloalterfurene F (**8**) (800MHz, CD_3OD)

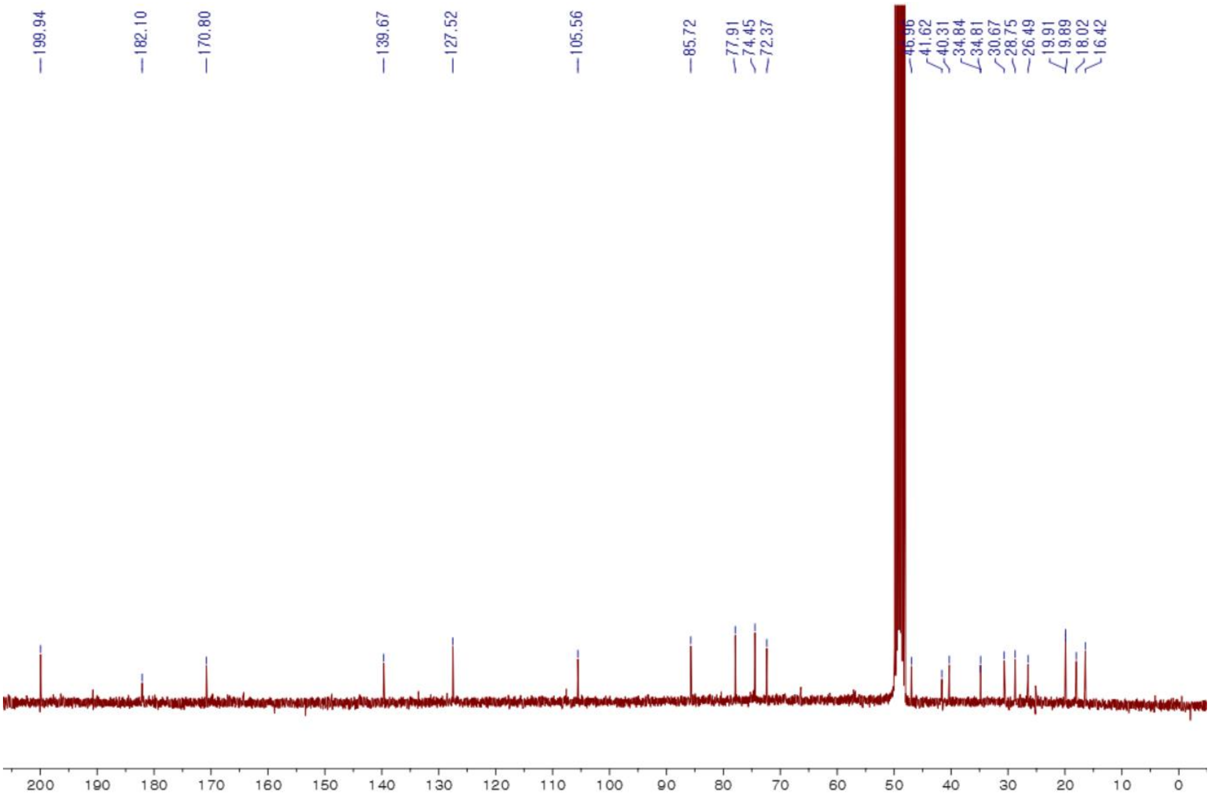


Figure S33. The ^{13}C NMR spectrum of Tricycloalterfurene F (**8**) (100MHz, CD_3OD)

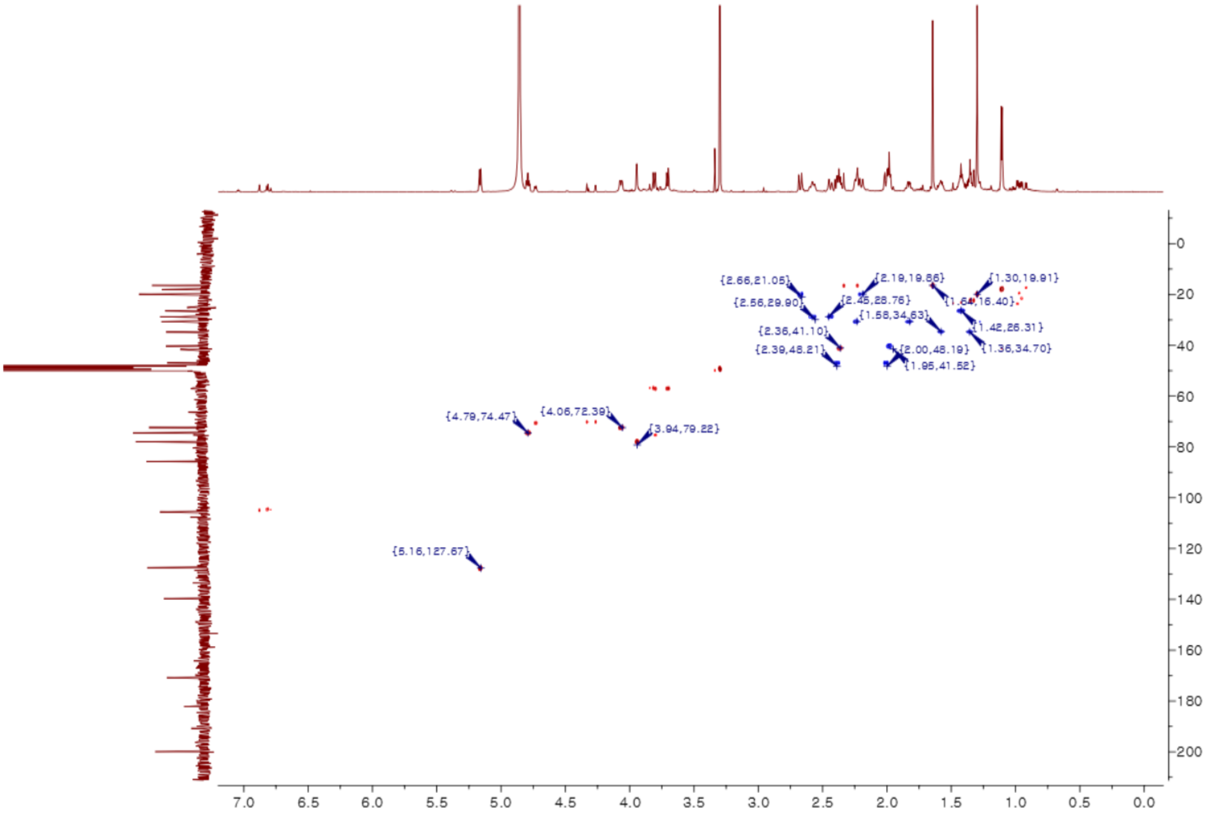


Figure S34. The HSQC spectrum of Tricycloalterfurene F (**8**) (800MHz, CD_3OD)

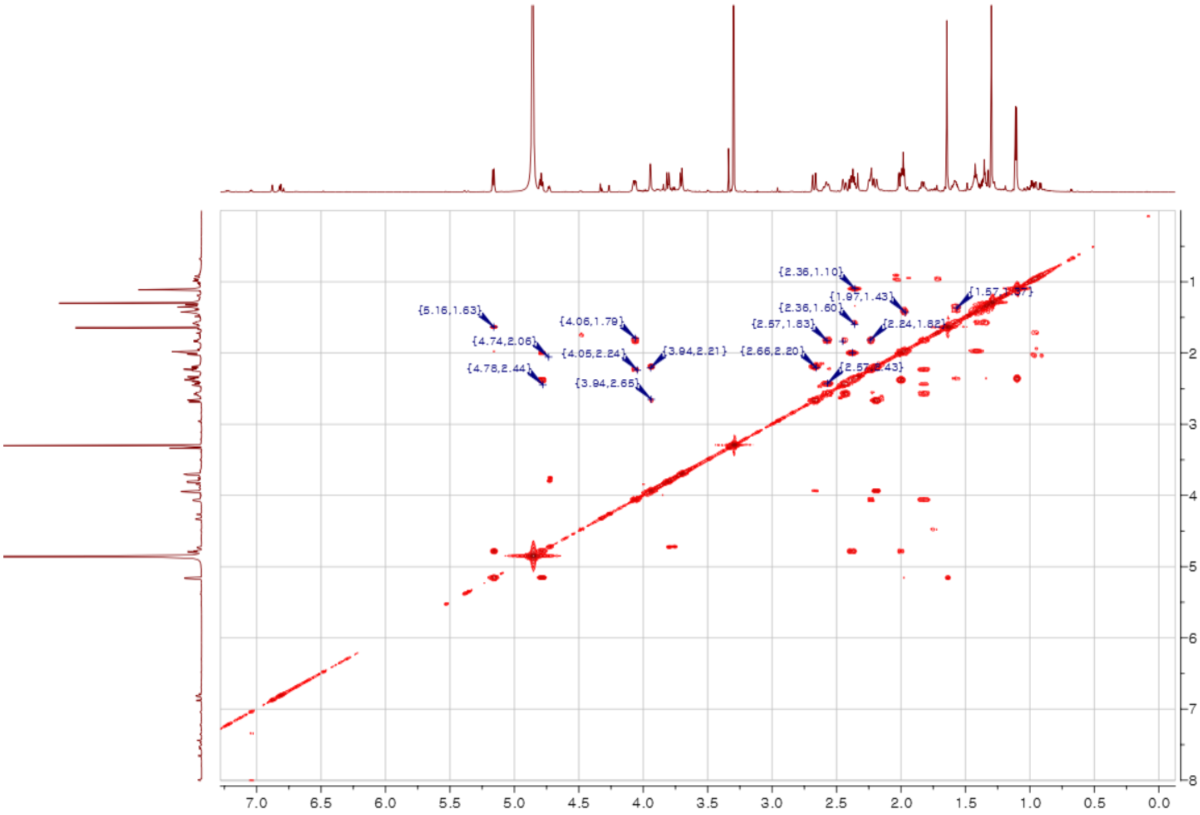


Figure S35. The COSY spectrum of Tricycloalterfurene F (**8**) (800MHz, CD_3OD)

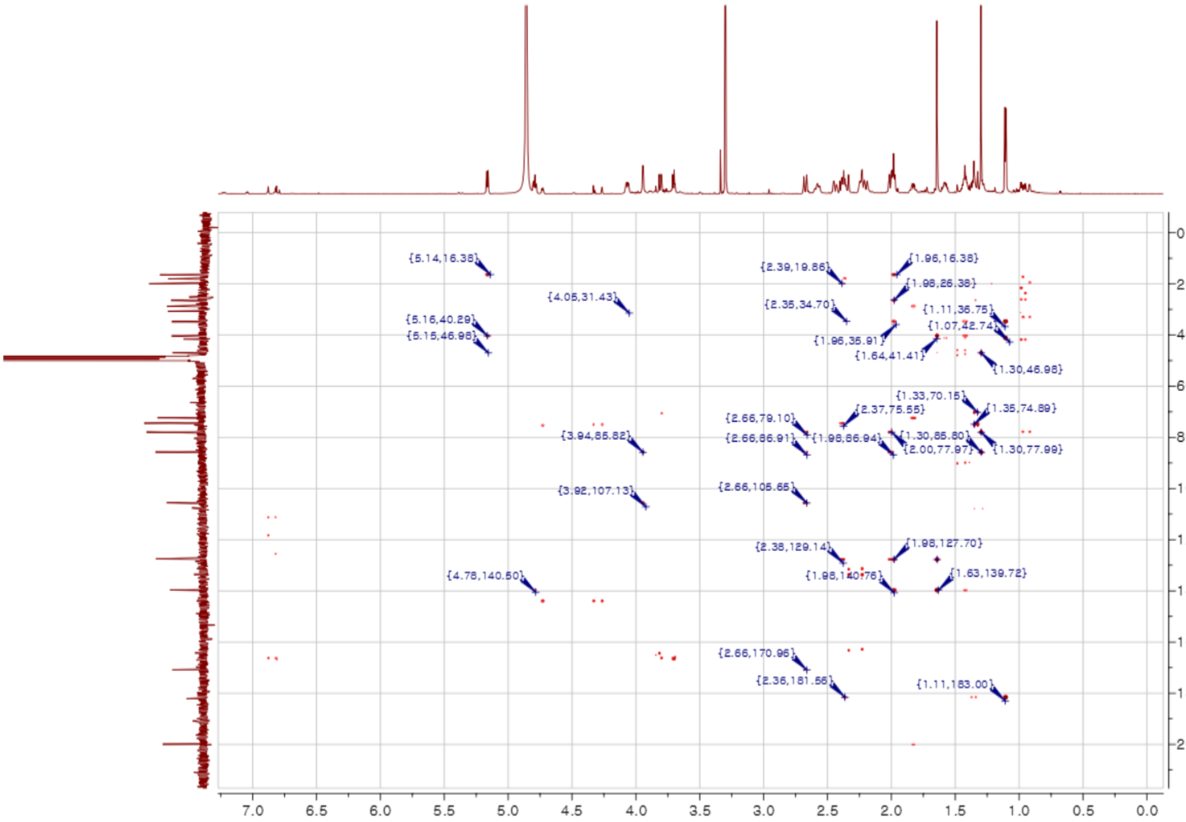


Figure S36. The HMBC spectrum of Tricycloalterfurene F (**8**) (800MHz, CD_3OD)

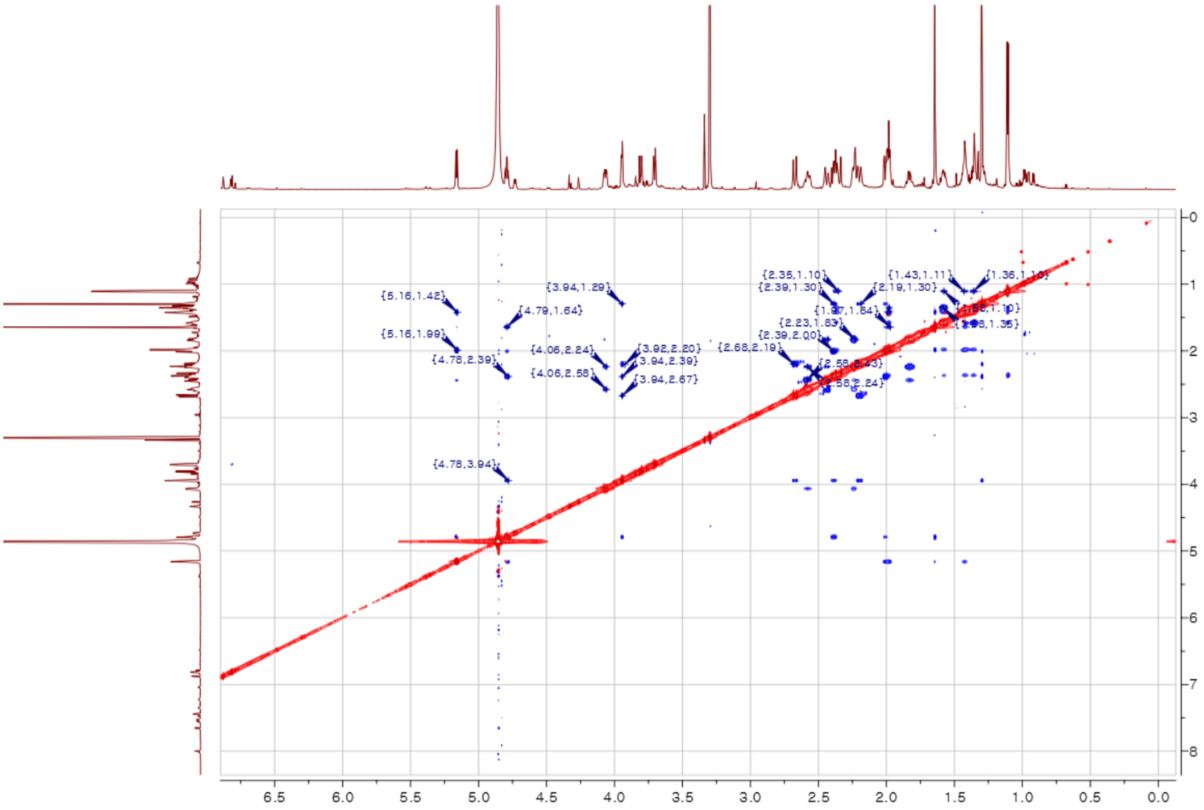
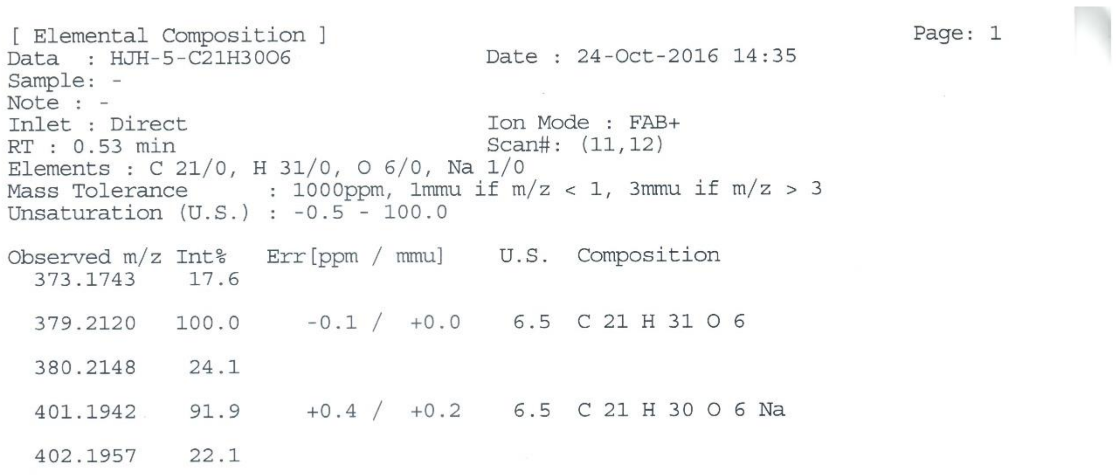


Figure S37. The NOESY spectrum of Tricycloalterfurene F (**8**) (800MHz, CD_3OD)



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Sample: -
Note : -
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RT : 0.53 min                        Scan#: (11,12)
Elements : C 21/0, H 31/0, O 6/0, Na 1/0
Mass Tolerance      : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3
Unsaturation (U.S.) : -0.5 - 100.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  373.1743    17.6

  379.2120   100.0     -0.1 /  +0.0    6.5  C 21 H 31 O 6

  380.2148    24.1

  401.1942    91.9     +0.4 /  +0.2    6.5  C 21 H 30 O 6 Na

  402.1957    22.1
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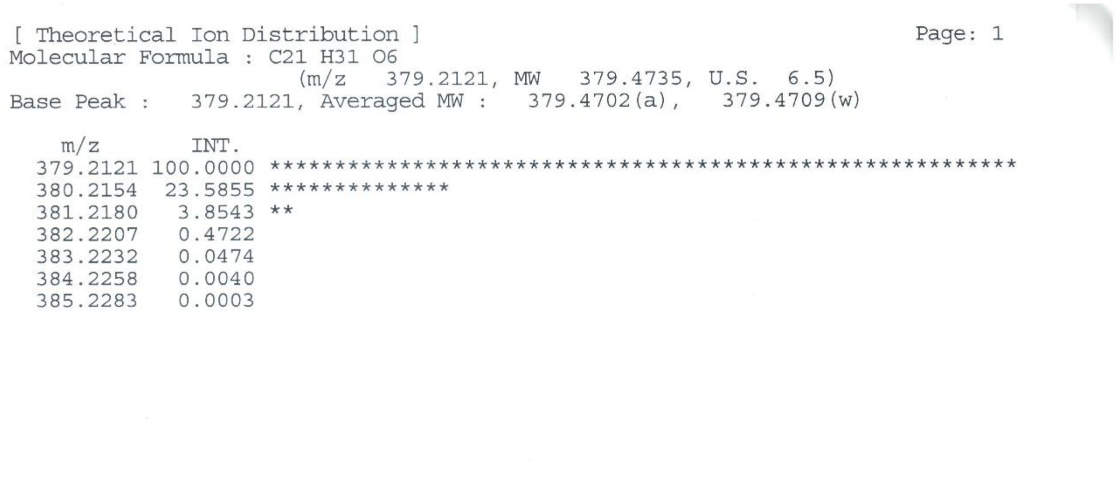

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Molecular Formula : C21 H31 O6
                     (m/z   379.2121, MW   379.4735, U.S.  6.5)
Base Peak :   379.2121, Averaged MW :   379.4702(a),   379.4709(w)

   m/z       INT.
  379.2121 100.0000 ************************************************************
  380.2154  23.5855 **************
  381.2180   3.8543 **
  382.2207   0.4722
  383.2232   0.0474
  384.2258   0.0040
  385.2283   0.0003
```

Figure S38. The HRFABMS data of Tricycloalterfurene F (**8**)

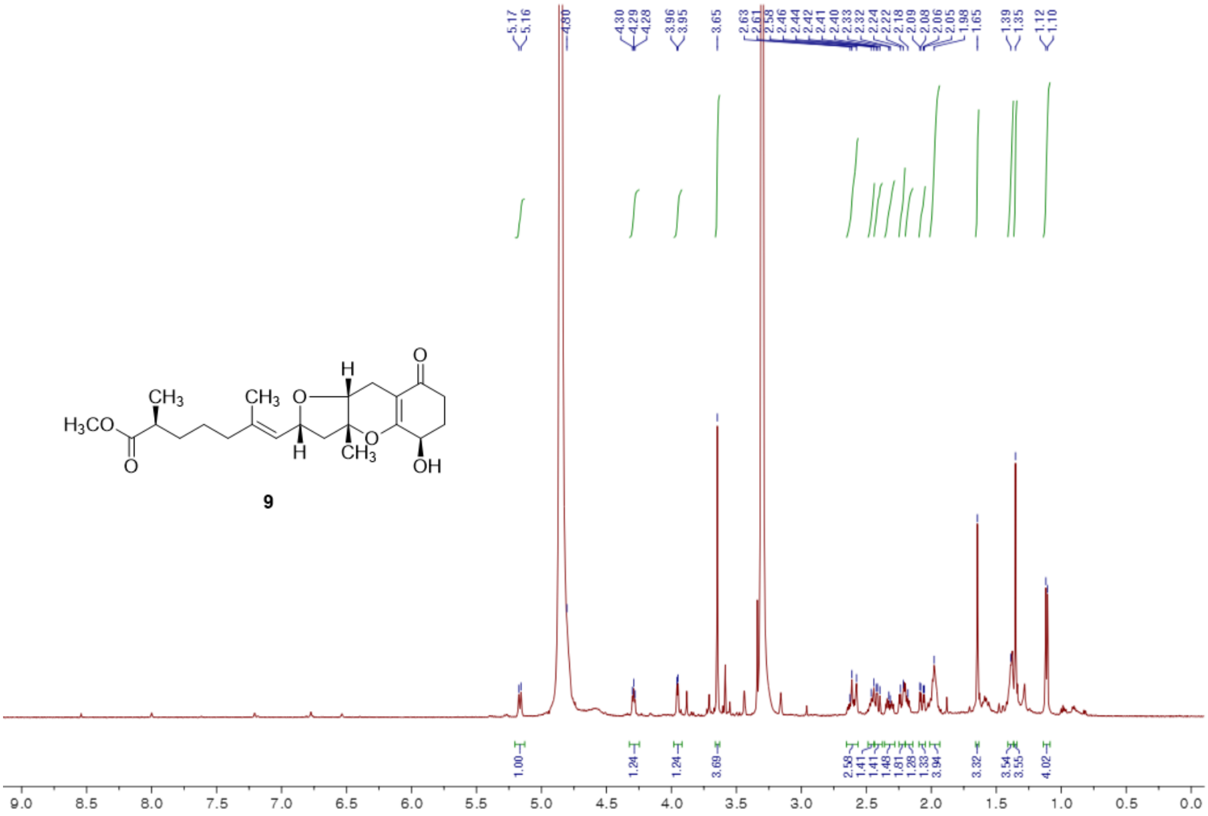


Figure S39. The ^{1}H NMR spectrum of Tricycloalterfurene G (**9**) (500MHz, CD_3OD)

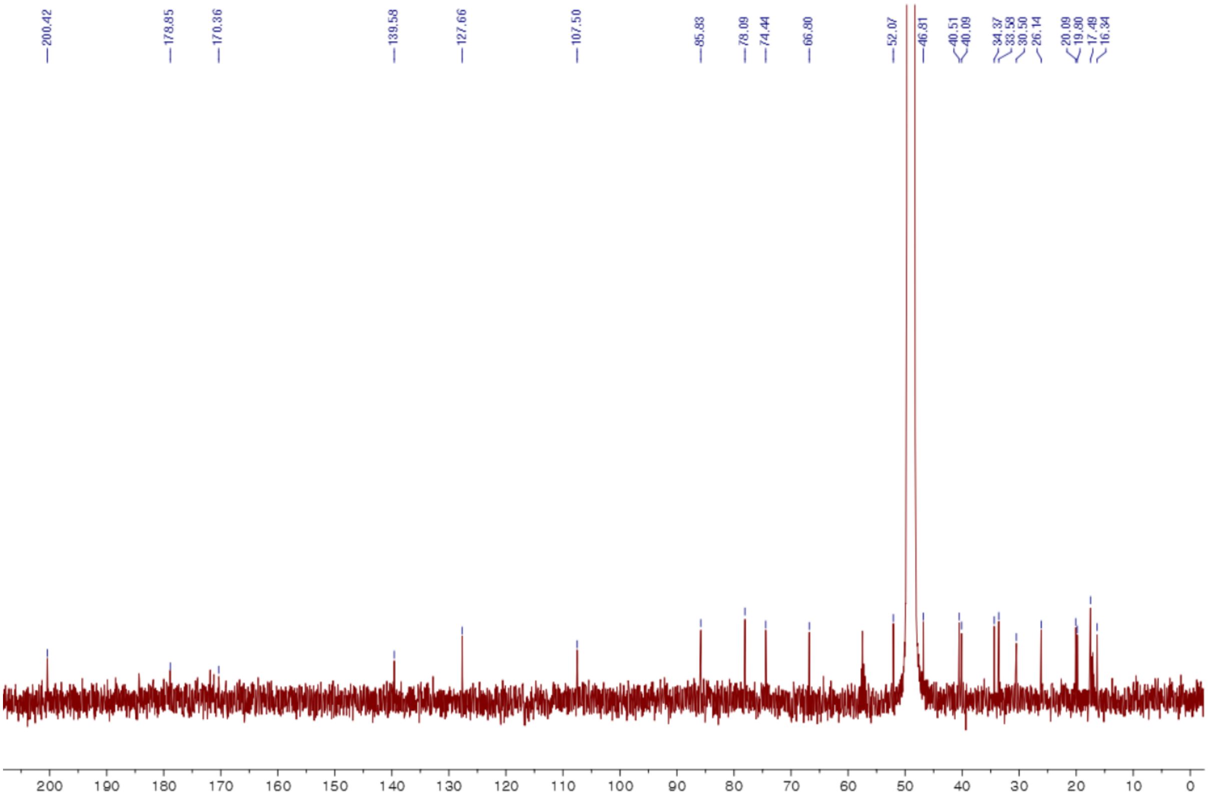


Figure S40. The ^{13}C NMR spectrum of Tricycloalterfurene G (**9**) (100MHz, CD_3OD)

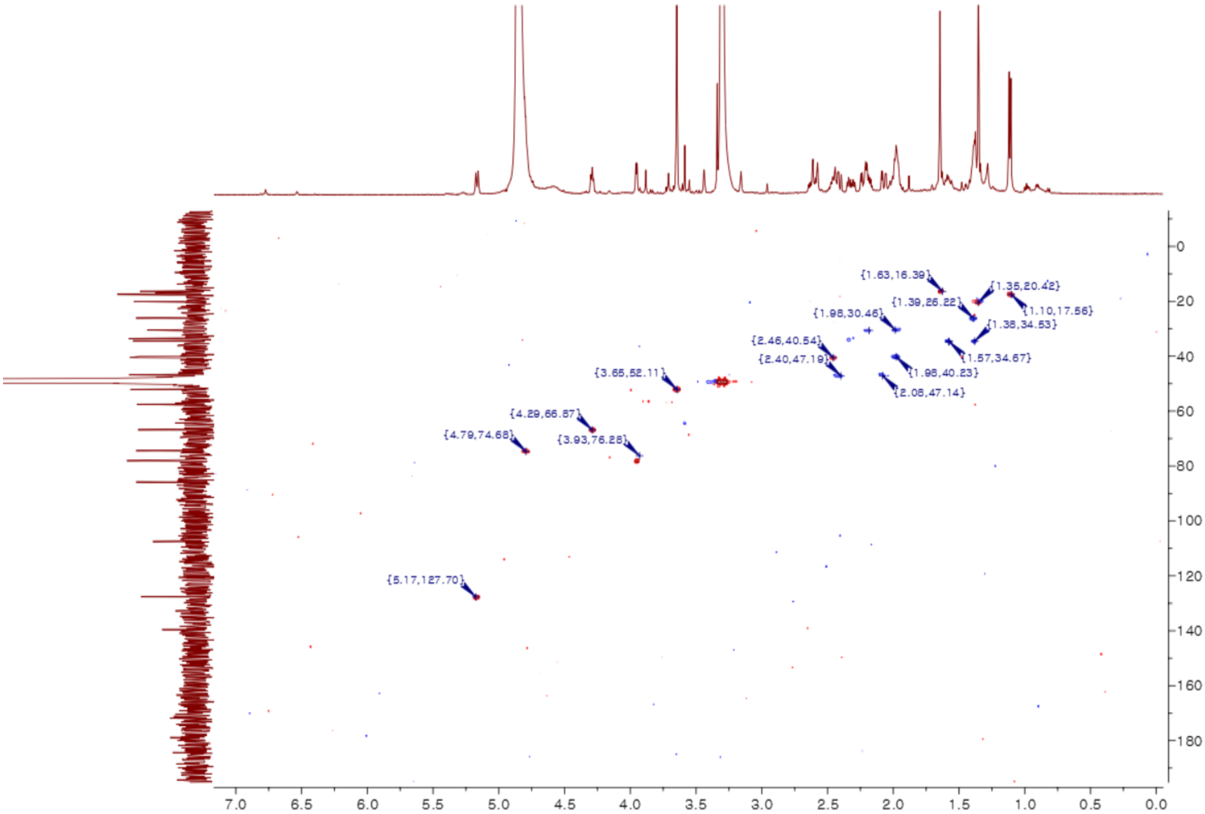


Figure S41. The HSQC spectrum of Tricycloalterfurene G (**9**) (500MHz, CD_3OD)

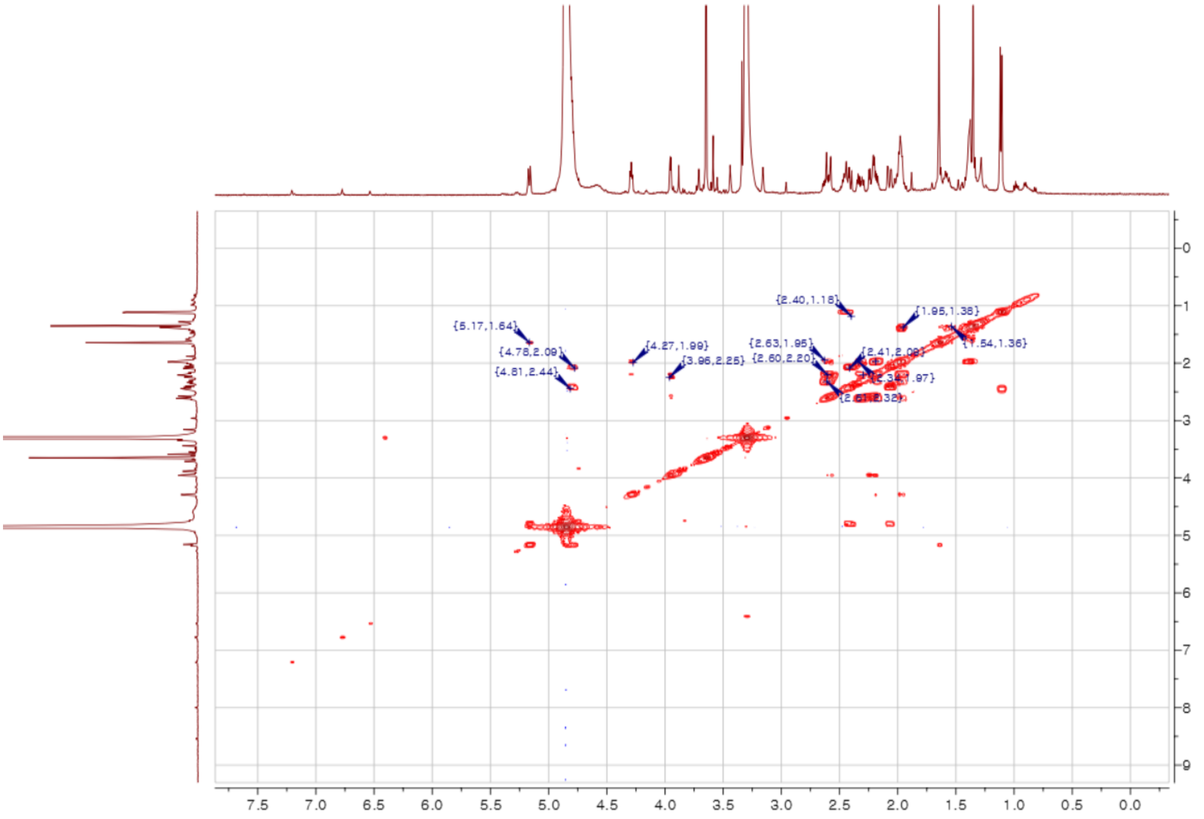


Figure S42. The COSY spectrum of Tricycloalterfurene G (**9**) (400MHz, CD_3OD)

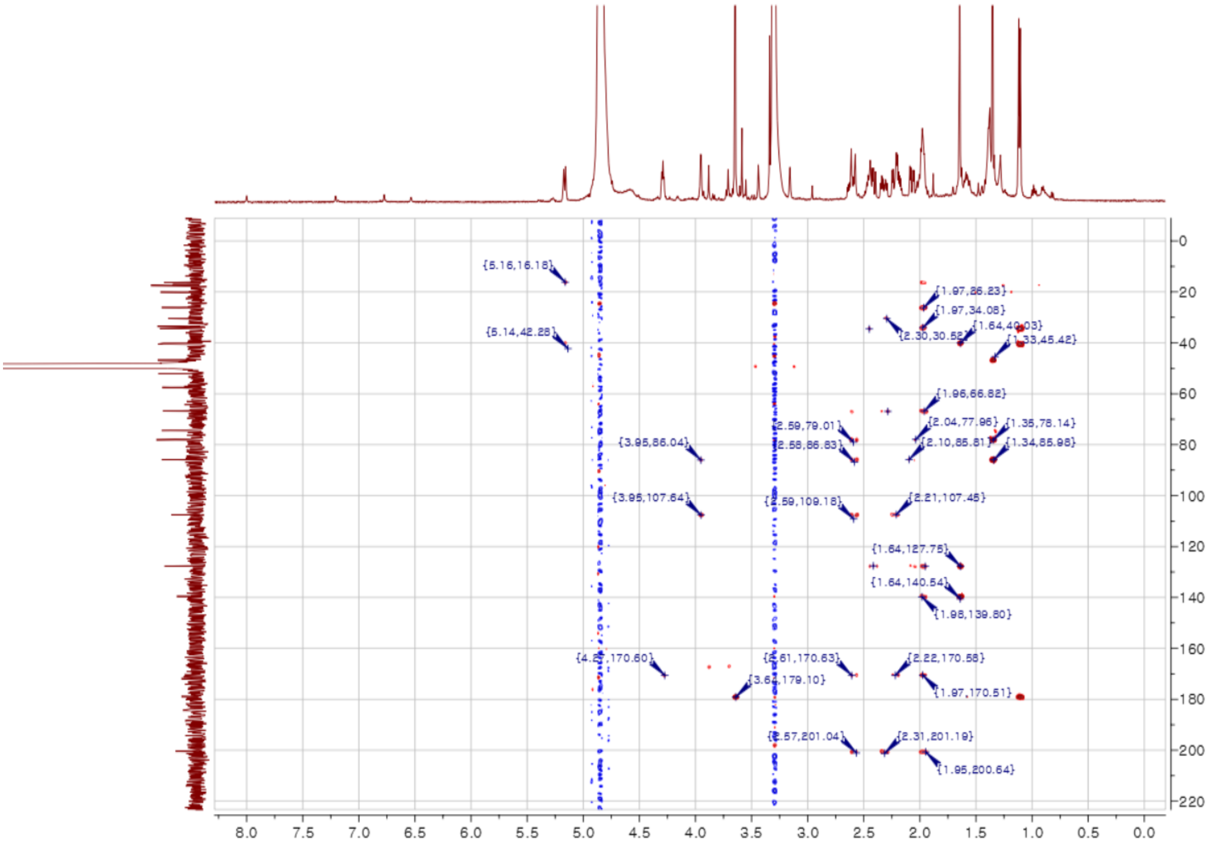


Figure S43. The HMBC spectrum of Tricycloalterfurene G (**9**) (400MHz, CD_3OD)

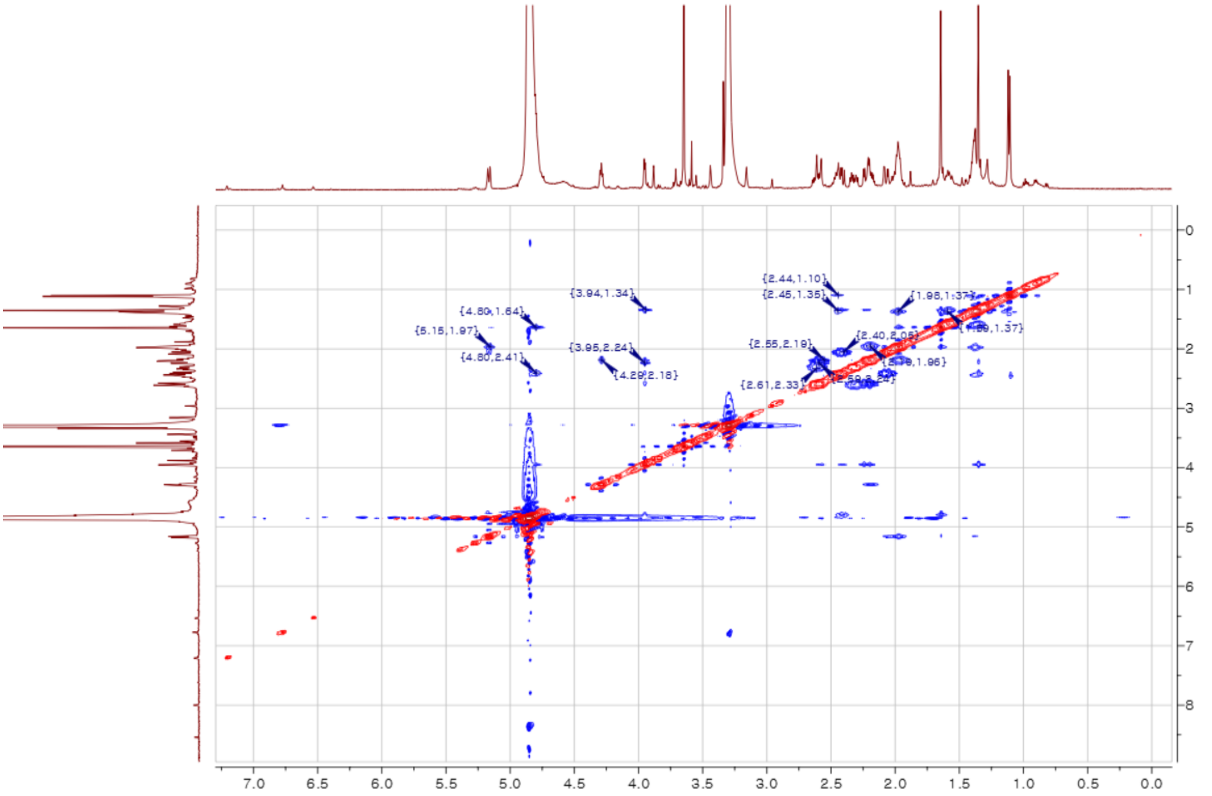
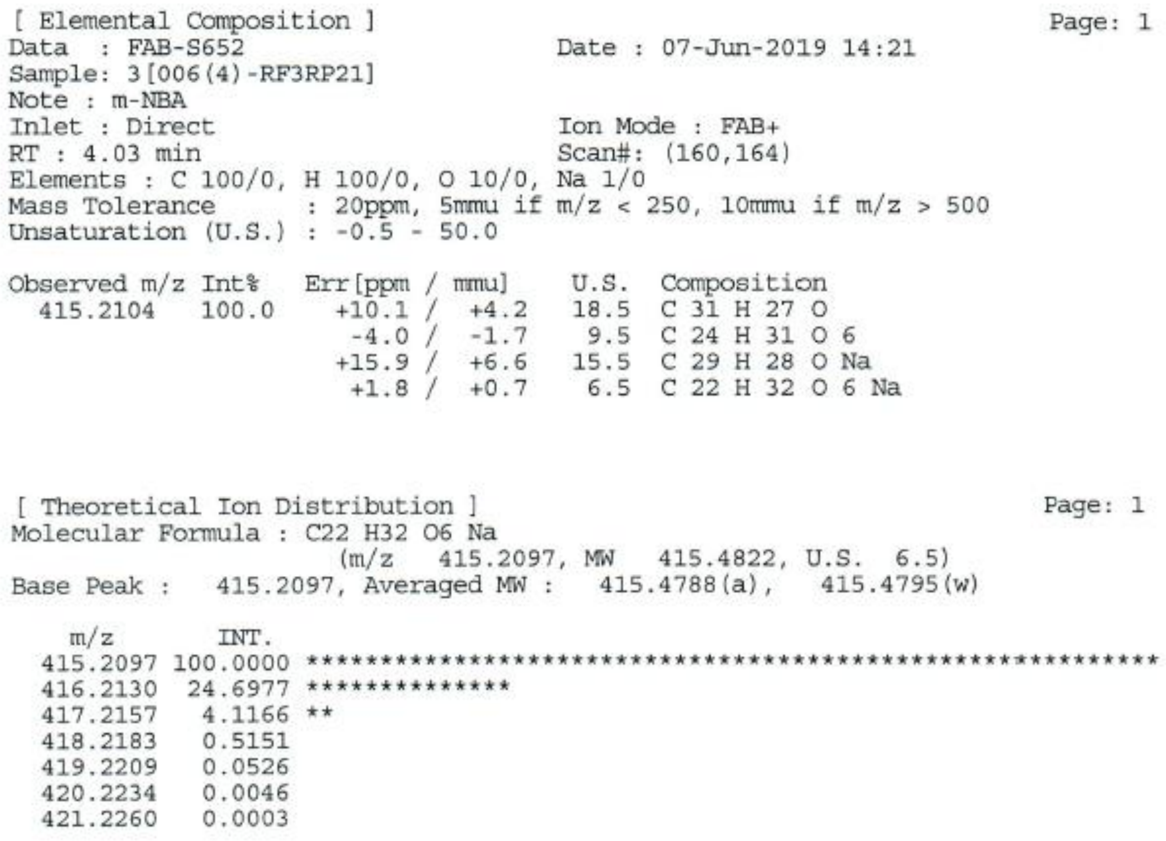


Figure S44. The NOESY spectrum of Tricycloalterfurene G (**9**) (400MHz, CD_3OD)



```
[ Elemental Composition ]                                         Page: 1
Data   : FAB-S652                  Date : 07-Jun-2019 14:21
Sample: 3[006(4)-RF3RP21]
Note : m-NBA
Inlet : Direct                     Ion Mode : FAB+
RT : 4.03 min                      Scan#: (160,164)
Elements : C 100/0, H 100/0, O 10/0, Na 1/0
Mass Tolerance        : 20ppm, 5mmu if m/z < 250, 10mmu if m/z > 500
Unsaturation (U.S.) : -0.5 - 50.0

Observed m/z Int%   Err[ppm / mmu]    U.S.  Composition
  415.2104   100.0    +10.1 /  +4.2   18.5  C 31 H 27 O
                       -4.0 /  -1.7    9.5  C 24 H 31 O 6
                      +15.9 /  +6.6   15.5  C 29 H 28 O Na
                       +1.8 /  +0.7    6.5  C 22 H 32 O 6 Na


[ Theoretical Ion Distribution ]                                  Page: 1
Molecular Formula : C22 H32 O6 Na
                       (m/z   415.2097, MW   415.4822, U.S.  6.5)
Base Peak :   415.2097, Averaged MW :   415.4788(a),   415.4795(w)

   m/z        INT.
  415.2097 100.0000 **********************************************************
  416.2130  24.6977 **************
  417.2157   4.1166 **
  418.2183   0.5151
  419.2209   0.0526
  420.2234   0.0046
  421.2260   0.0003
```

Figure S45. The HRFABMS data of Tricycloalterfurene G (**9**)

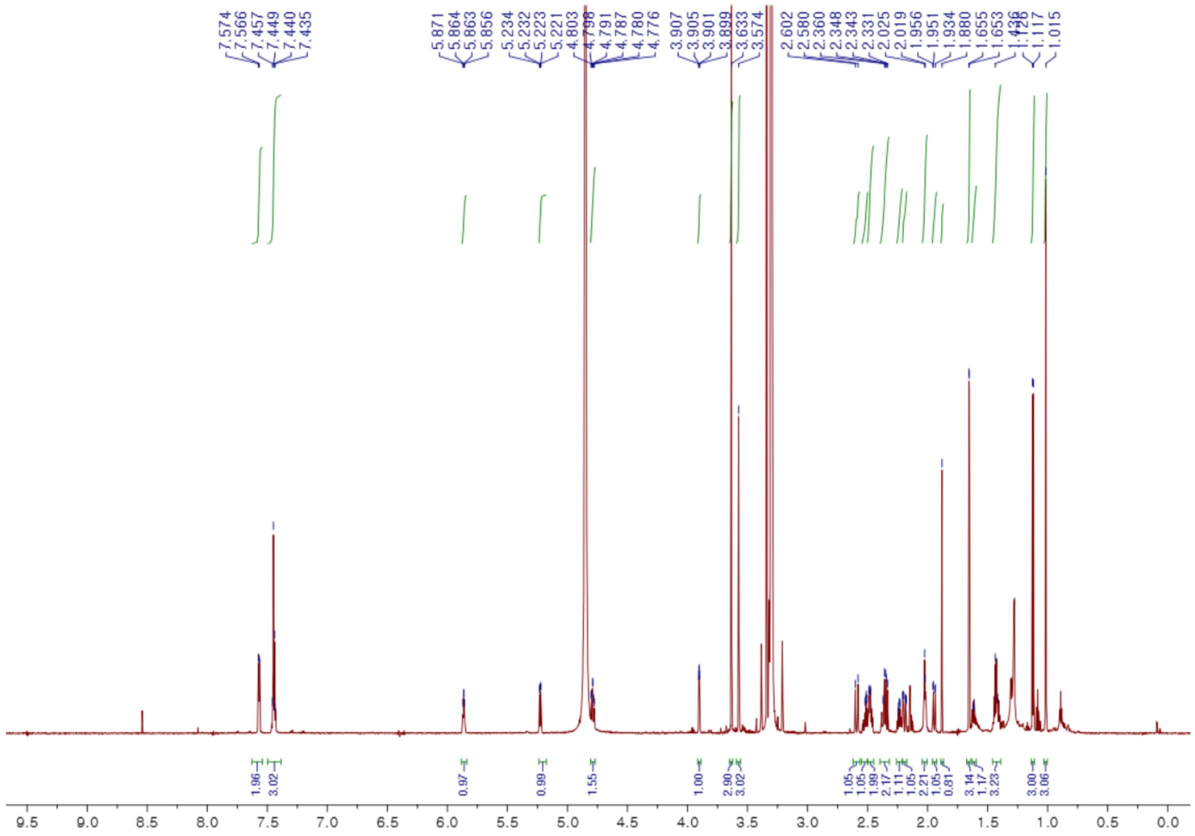


Figure S46. The ^{1}H NMR spectrum of (*S*)-MTPA Ester of **7** (800MHz, CD_3OD)

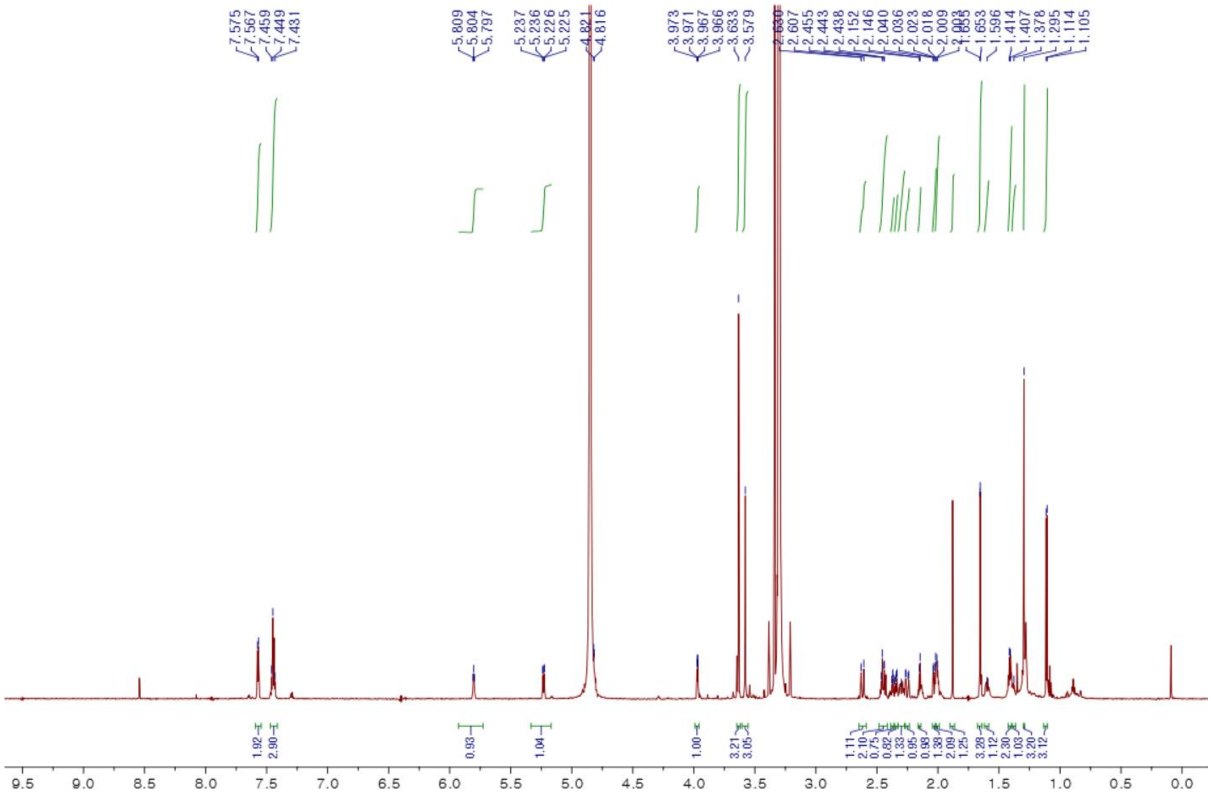


Figure S47. The ^{1}H NMR spectrum of (*R*)-MTPA Ester of **7** (800MHz, CD_3OD)

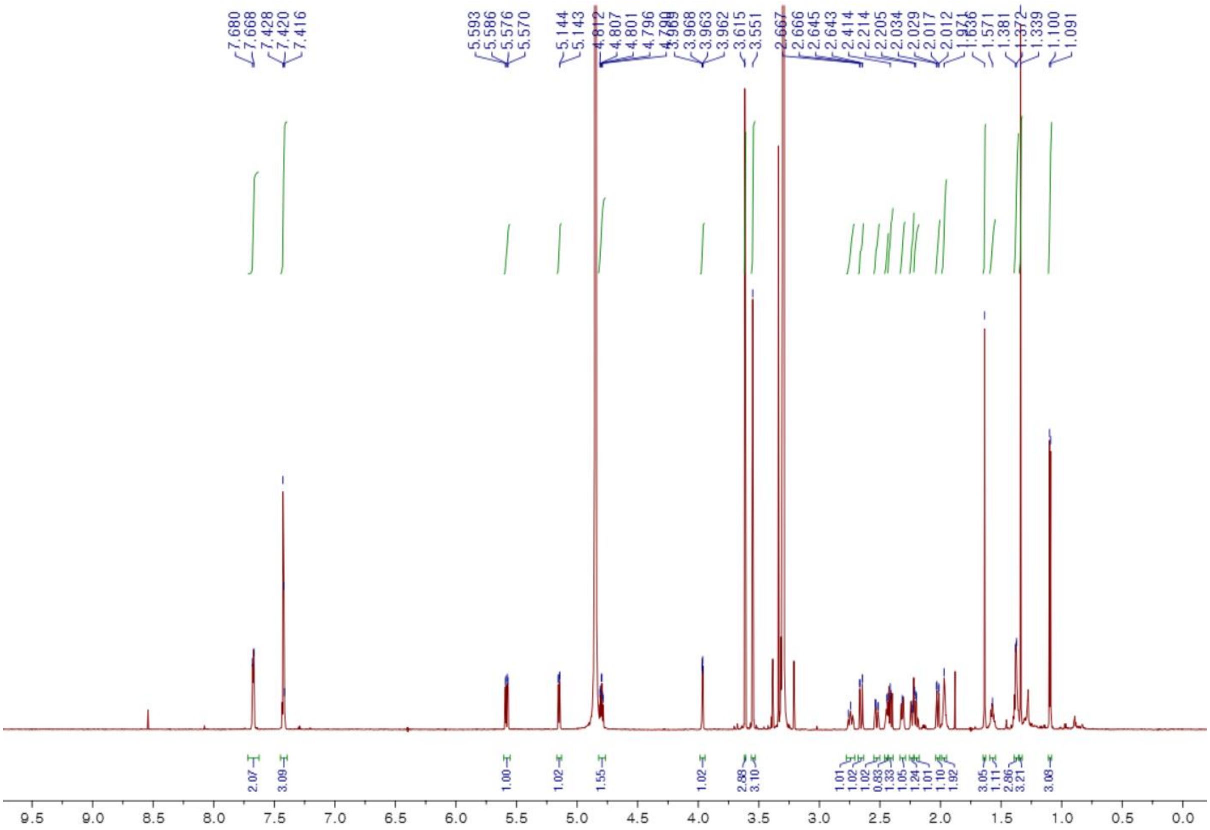


Figure S48. The ^{1}H NMR spectrum of (*S*)-MTPA Ester of **8** (800MHz, CD_3OD)

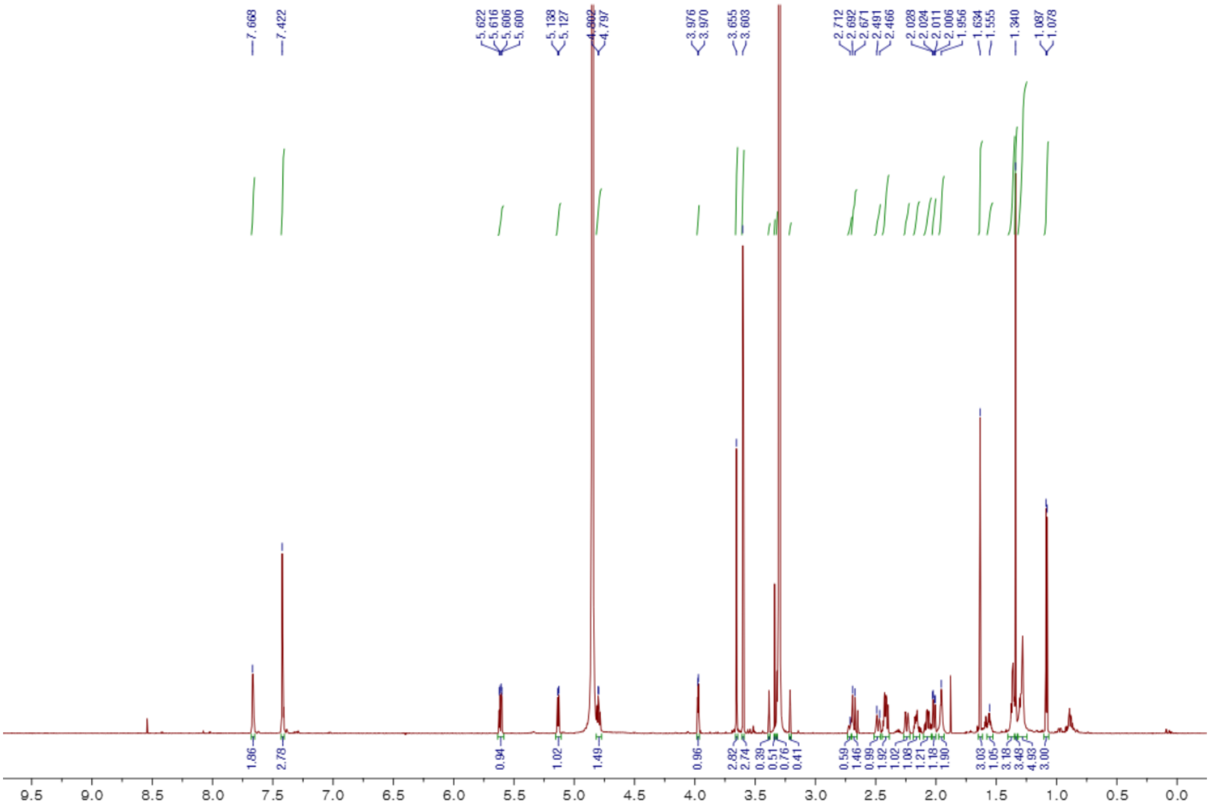


Figure S49. The ^{1}H NMR spectrum of (*R*)-MTPA Ester of **8** (800MHz, CD_3OD)

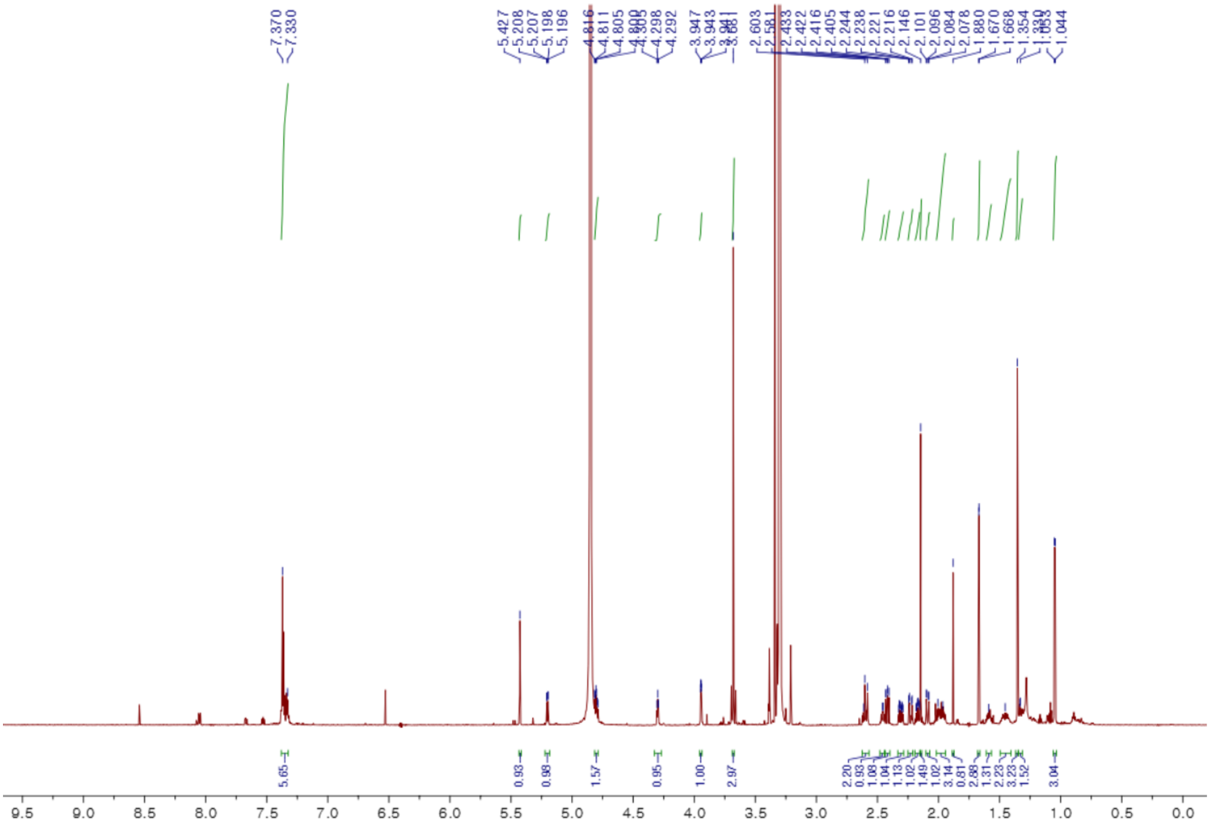


Figure S50. The ^{1}H NMR spectrum of (*S*)-PGME Amide of **7** (800MHz, CD_3OD)

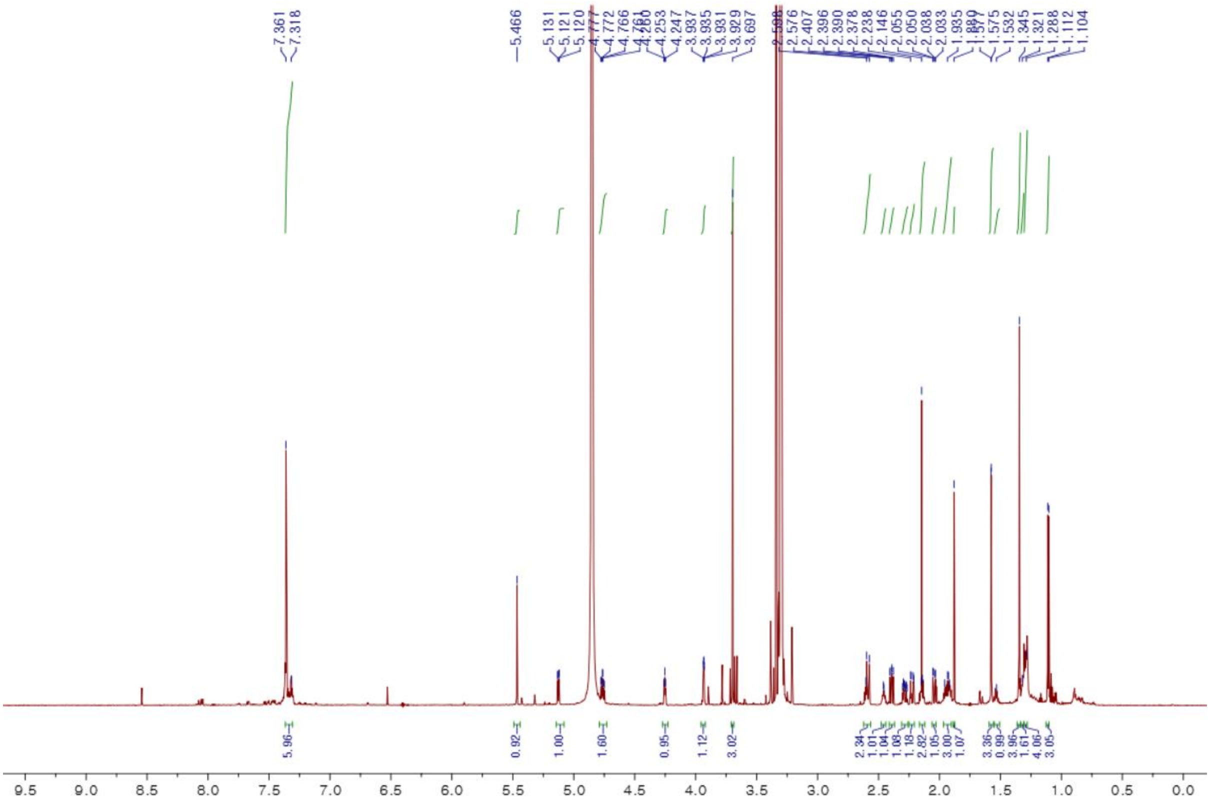


Figure S51. The ^{1}H NMR spectrum of (*R*)-PGME Amide of **7** (800MHz, CD_3OD)

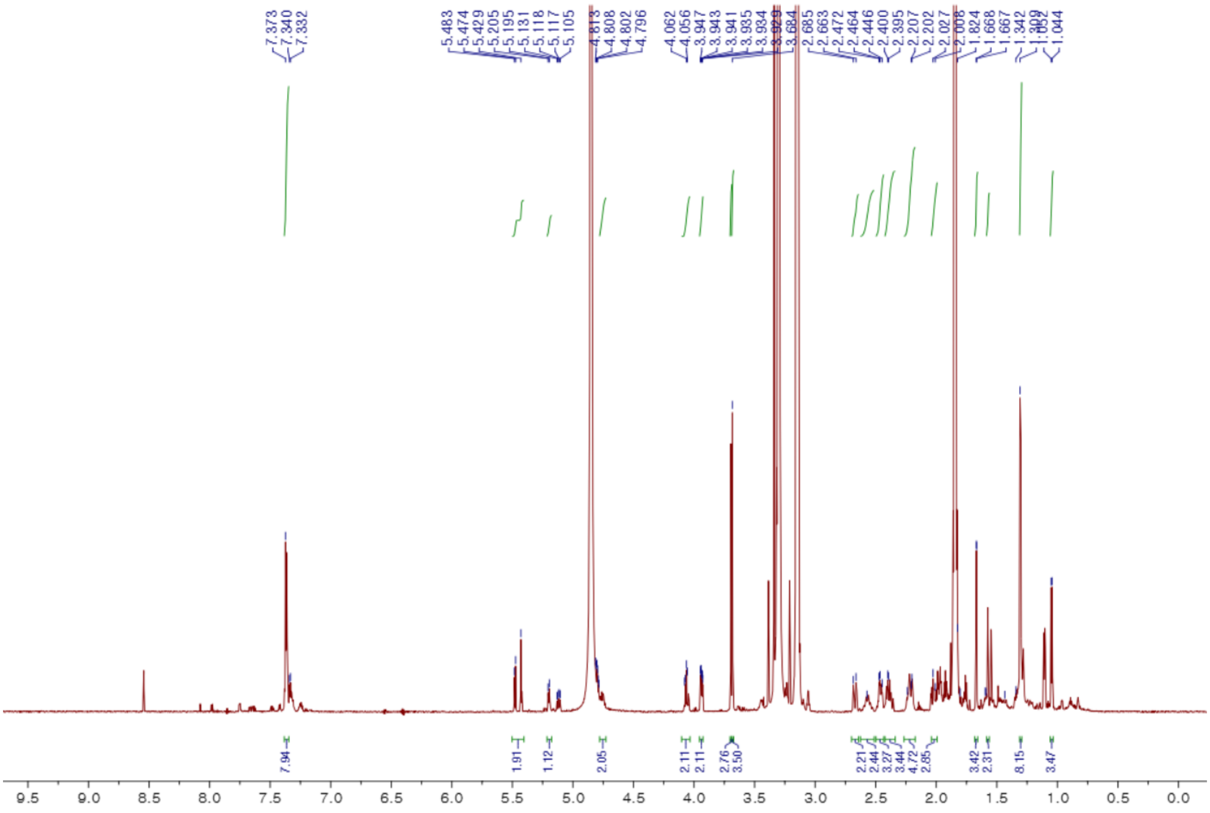


Figure S52. The ^{1}H NMR spectrum of (*S*)-PGME Amide of **8** (800MHz, CD_3OD)

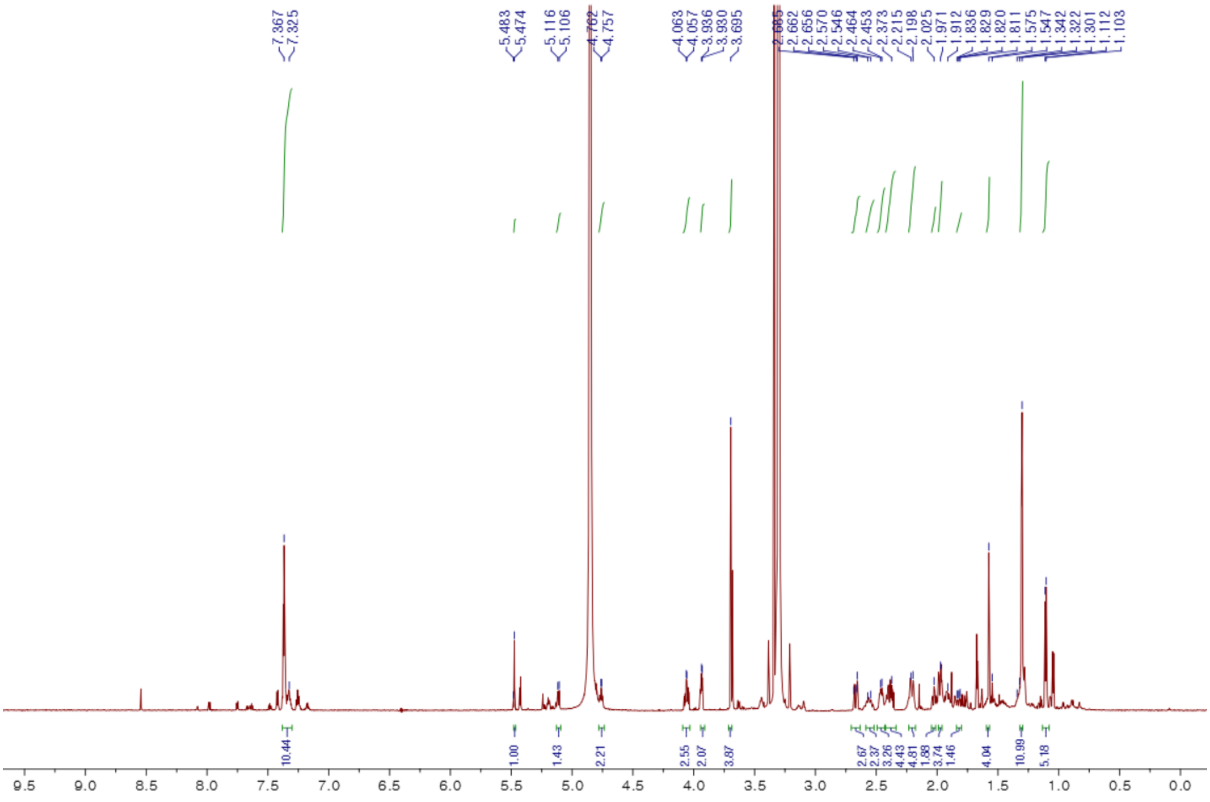
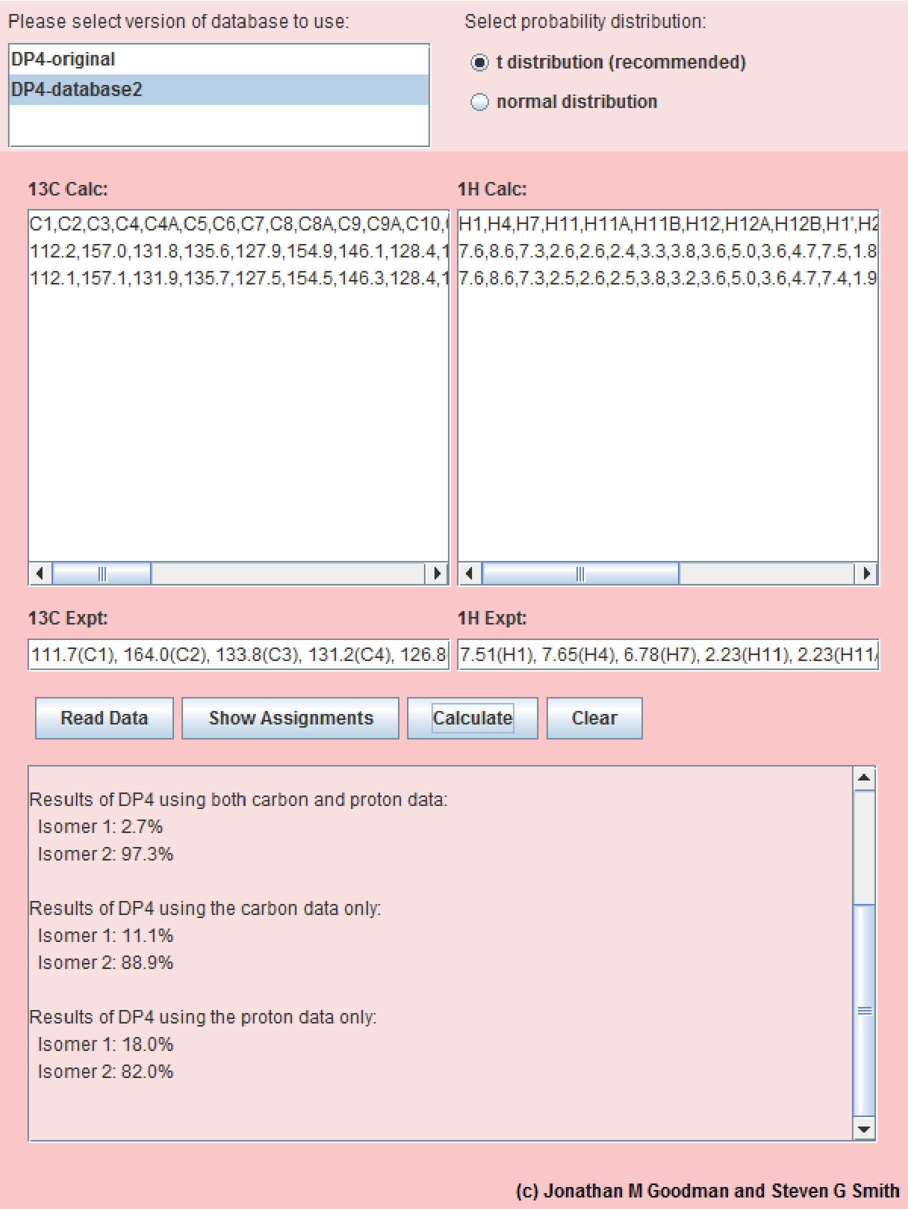


Figure S53. The ^{1}H NMR spectrum of (*R*)-PGME Amide of **8** (800MHz, CD_3OD)



Please select version of database to use:

DP4-original

DP4-database2

Select probability distribution:

● t distribution (recommended)

○ normal distribution

13C Calc:

```
C1,C2,C3,C4,C4A,C5,C6,C7,C8,C8A,C9,C9A,C10,
112.2,157.0,131.8,135.6,127.9,154.9,146.1,128.4,1
112.1,157.1,131.9,135.7,127.5,154.5,146.3,128.4,1
```

1H Calc:

```
H1,H4,H7,H11,H11A,H11B,H12,H12A,H12B,H1',H2
7.6,8.6,7.3,2.6,2.6,2.4,3.3,3.8,3.6,5.0,3.6,4.7,7.5,1.8
7.6,8.6,7.3,2.5,2.6,2.5,3.8,3.2,3.6,5.0,3.6,4.7,7.4,1.9
```

13C Expt:

```
111.7(C1), 164.0(C2), 133.8(C3), 131.2(C4), 126.8
```

1H Expt:

```
7.51(H1), 7.65(H4), 6.78(H7), 2.23(H11), 2.23(H11
```

```
Results of DP4 using both carbon and proton data:
 Isomer 1: 2.7%
 Isomer 2: 97.3%

Results of DP4 using the carbon data only:
 Isomer 1: 11.1%
 Isomer 2: 88.9%

Results of DP4 using the proton data only:
 Isomer 1: 18.0%
 Isomer 2: 82.0%
```

Figure S54. The results of DP4 analyses of Alterporriol Z1 (**1**)

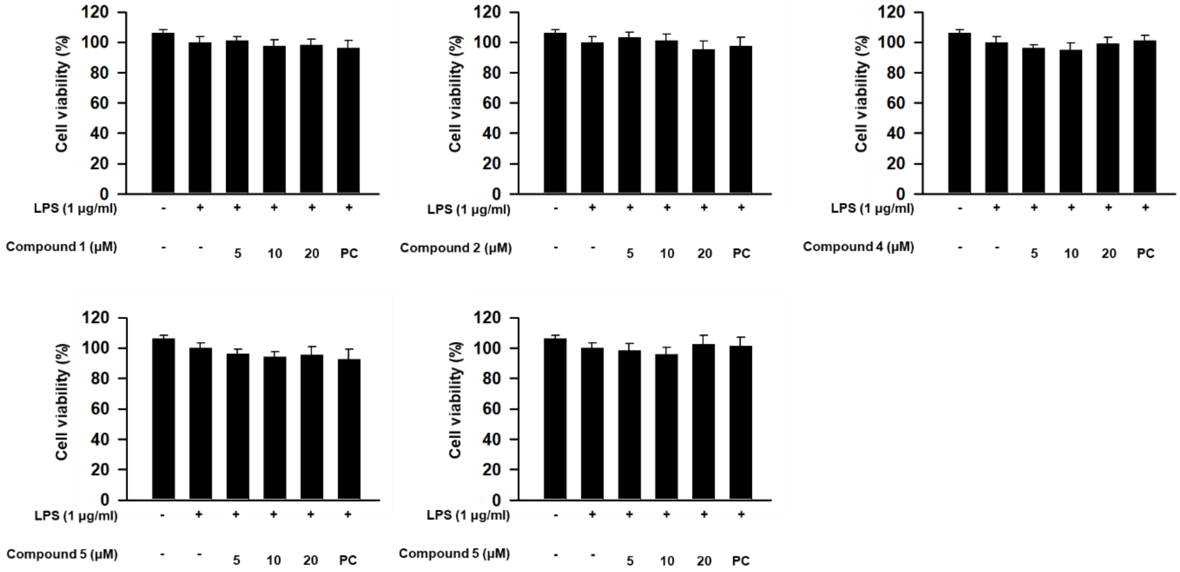
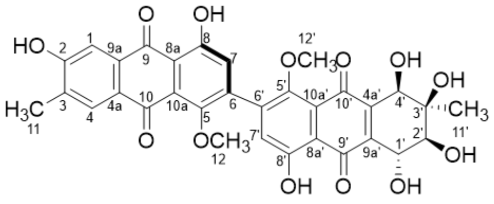
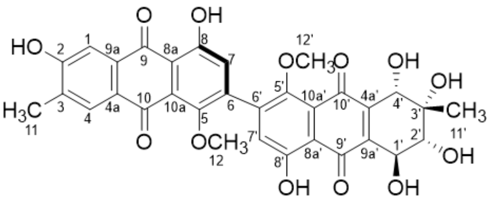


Figure S55. The viability of RAW 264.7 cells was measured using the MTT assay



aR,1'*R*,2'*S*,3'*R*,4'*R*

[Isomer 1]



aR,1'*S*,2'*R*,3'*S*,4'*S*

[Isomer 2]

No.	Aterporriol Z1	
1	111.7, CH	7.51, d (0.5)
2	164.0, C	
3	133.8, C	
4	131.2, CH	7.65, d (0.5)
4a	126.8, C	
5	165.8, C	
6	125.3, C	
7	104.6, CH	6.78, s
8	166.9, C	
8a	111.9, C	
9	188.7, C	
9a	134.7, C	
10	183.5, C	
10a	133.4, C	
11	16.6, CH_3	2.23, s
12	56.9, CH_3	3.69, s
1′	70.6, CH	4.73, d (7.5)
2′	75.2, CH	3.79, d (7.5)
3′	74.6, C	
4′	70.1, CH	4.26, s
4a′	143.8, C	
5′	166.3, C	
6′	123.4, C	
7′	104.6, CH	6.81, s
8′	166.1, C	
8a′	111.0, C	
9′	190.5, C	
9a′	143.9, C	
10′	185.7, C	
10a′	130.8, C	
11′	22.3, CH_3	1.33, s
12′	57.0, CH_3	3.70, s

No.	Isomer 1	
1	112.2	7.6
2	157.0	
3	131.8	
4	135.6	8.6
4a	127.9	
5	154.9	
6	146.1	
7	128.4	7.3
8	157.7	
8a	117.4	
9	187.1	
9a	132.0	
10	182.7	
10a	124.9	
11	20.6	2.6,2.6,2.4
12	61.7	3.3,3.8,3.6
1′	75.0	5.0
2′	84.6	3.6
3′	77.6	
4′	76.0	4.7
4a′	141.2	
5′	156.4	
6′	146.1	
7′	130.0	7.5
8′	156.8	
8a′	116.3	
9′	188.6	
9a′	143.4	
10′	187.8	
10a′	124.0	
11′	25.9	1.8,0.9,1.9
12′	61.4	3.5,4.0,3.4

No.	Isomer 2	
1	112.1	7.6
2	157.1	
3	131.9	
4	135.7	8.6
4a	127.5	
5	154.5	
6	146.3	
7	128.4	7.3
8	158.1	
8a	116.9	
9	187.2	
9a	131.9	
10	182.7	
10a	124.1	
11	20.6	2.5,2.6,2.5
12	61.8	3.8,3.2,3.6
1′	75.1	5.0
2′	82.6	3.6
3′	77.6	
4′	76.1	4.7
4a′	141.1	
5′	156.9	
6′	146.6	
7′	129.5	7.4
8′	157.1	
8a′	116.2	
9′	189.4	
9a′	143.4	
10′	187.8	
10a′	123.5	
11′	26.7	1.9,0.9,1.7
12′	61.1	4.0,3.6,3.4

Table S1. Experimental (Exp.) and calculated (Cal.) chemical shift values of enantiomers A and B on aliphatic ring part of Alterporriol Z1 (**1**)

No.	**1**[a]
	δ_H (*J* in Hz)
1	7.52, s
2	
3	
4	7.70, s
4a	
5	
6	
7	6.78, s
8	
8a	
9	
9a	
10	
10a	
11	2.23, s
12	3.68, s
1′	4.64, d (7.0)
2′	3.70, d (7.0)
3′	
4′	4.12, d (6.0)
4a′	
5′	
6′	
7′	6.78, s
8′	
8a′	
9′	
9a′	
10′	
10a′	
11′	1.26, s
12′	3.69, s
13′	
1′ OH	4.29, br. s
2′ OH	4.22, br. s
3′ OH	3.78, s
4′ OH	4.70, d (6.0)

[a] Measured at 800 MHz for ^{1}H NMR

Table S2. The ^{1}H NMR Data of Alterporriol Z1 (**1**) in THF-d_8