

Supporting Information

Fischernolides A–D, Four Novel Diterpene-Based Meroterpenoid Scaffolds with Antitumor Activities from *Euphorbia fischeriana*

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List of Supporting Information

Contents	Page
Table S1. NMR Data of fischernolide A (1) and fischernolide B (2)	1
Table S2. NMR Data of fischernolide C (3) and fischernolide D (4)	2
Table S3. The 3D conformers of (5 <i>R</i> ,8 <i>S</i> ,9 <i>S</i> ,10 <i>R</i> ,14 <i>R</i>)- 2 with Boltzmann distribution over 1%.	3
Table S4. The 3D conformers of (5 <i>R</i> ,8 <i>R</i> ,9 <i>S</i> ,10 <i>R</i>)- 4 with Boltzmann distribution over 1%.	4
Spectra of Fischernolides A–D (1–4)	
Figure S3. UV spectrum of fischernolide A (1) in MeOH	5
Figure S4. IR spectrum of fischernolide A (1)	6
Figure S5. HRESIMS spectrum of fischernolide A (1)	7
Figure S6. ¹ H NMR spectrum of fischernolide A (1) in DMSO- <i>d</i> ₆ (400 MHz)	8
Figure S7. ¹³ C NMR spectrum of fischernolide A (1) in DMSO- <i>d</i> ₆ (100 MHz)	9
Figure S8. DEPT-135 spectrum of fischernolide A (1) in DMSO- <i>d</i> ₆ (100 MHz)	10
Figure S9. HSQC spectrum of fischernolide A (1) in DMSO- <i>d</i> ₆	11
Figure S10. HMBC spectrum of fischernolide A (1) in DMSO- <i>d</i> ₆	12
Figure S11. Enlarged HMBC spectrum of fischernolide A (1) in DMSO- <i>d</i> ₆	13
Figure S12. NOESY spectrum of fischernolide A (1) in DMSO- <i>d</i> ₆ (400 MHz)	14
Figure S13. UV spectrum of fischernolide B (2) in MeOH	15
Figure S14. IR spectrum of fischernolide B (2)	16
Figure S15. HRESIMS spectrum of fischernolide B (2)	17
Figure S16. ¹ H NMR spectrum of fischernolide B (2) in DMSO- <i>d</i> ₆ (600 MHz)	18
Figure S17. ¹³ C NMR spectrum of fischernolide B (2) in DMSO- <i>d</i> ₆ (150 MHz)	19
Figure S18. DEPT-135 spectrum of fischernolide B (2) in DMSO- <i>d</i> ₆ (150 MHz)	20
Figure S19. HSQC spectrum of fischernolide B (2) in DMSO- <i>d</i> ₆	21
Figure S20. HMBC spectrum of fischernolide B (2) in DMSO- <i>d</i> ₆	22
Figure S21. Enlarged HMBC spectrum of fischernolide B (2) in DMSO- <i>d</i> ₆	23
Figure S22. NOESY spectrum of fischernolide B (2) in DMSO- <i>d</i> ₆ (600 MHz)	24
Figure S23. ¹ H NMR spectrum of fischernolide B (2) in pyridine- <i>d</i> ₅ (400 MHz)	25
Figure S24. ¹³ C NMR spectrum of fischernolide B (2) in pyridine- <i>d</i> ₅ (100 MHz)	26
Figure S25. NOESY spectrum of fischernolide B (2) in pyridine- <i>d</i> ₅ (400 MHz)	27
Figure S26. ECD spectrum of fischernolide B (2) in MeOH	28
Figure S27. UV spectrum of fischernolide C (3) in MeOH	29
Figure S28. IR spectrum of fischernolide C (3)	30
Figure S29. HRESIMS spectrum of fischernolide C (3)	31
Figure S30. ¹ H NMR spectrum of fischernolide C (3) in DMSO- <i>d</i> ₆ (600 MHz)	32
Figure S31. ¹³ C NMR spectrum of fischernolide C (3) in DMSO- <i>d</i> ₆ (150 MHz)	33
Figure S32. DEPT-135 spectrum of fischernolide C (3) in DMSO- <i>d</i> ₆ (150 MHz)	34

Figure S33. HSQC spectrum of fischernolide C (3) in DMSO- <i>d</i> ₆	35
Figure S34. HMBC spectrum of fischernolide C (3) in DMSO- <i>d</i> ₆	36
Figure S35. Enlarged HMBC spectrum of fischernolide C (3) in DMSO- <i>d</i> ₆	37
Figure S36. NOESY spectrum of fischernolide C (3) in DMSO- <i>d</i> ₆ (600 MHz)	38
Figure S37. ECD spectrum of fischernolide C (3) in MeOH	39
Figure S38. UV spectrum of fischernolide D (4) in MeOH	40
Figure S39. IR spectrum of fischernolide D (4)	41
Figure S40. HRESIMS spectrum of fischernolide D (4)	42
Figure S41. ¹ H NMR spectrum of fischernolide D (4) in DMSO- <i>d</i> ₆ (600 MHz)	43
Figure S42. ¹³ C NMR spectrum of fischernolide D (4) in DMSO- <i>d</i> ₆ (150 MHz)	44
Figure S43. DEPT-135 spectrum of fischernolide D (4) in DMSO- <i>d</i> ₆ (150 MHz)	45
Figure S44. HSQC spectrum of fischernolide D (4) in DMSO- <i>d</i> ₆	46
Figure S45. HMBC spectrum of fischernolide D (4) in DMSO- <i>d</i> ₆	47
Figure S46. Enlarged HMBC spectrum of fischernolide D (4) in DMSO- <i>d</i> ₆	48
Figure S47. Enlarged HMBC spectrum of fischernolide D (4) in DMSO- <i>d</i> ₆	49
Figure S48. NOESY spectrum of fischernolide D (4) in DMSO- <i>d</i> ₆ (600 MHz)	50
Figure S49. Enlarged NOESY spectrum of fischernolide D (4) in DMSO- <i>d</i> ₆ (600 MHz)	51
Figure S50. ECD spectrum-1 of fischernolide D (4) in MeOH	52
Figure S51. ECD spectrum-2 of fischernolide D (4) in MeOH	53

Table S1. NMR Data of fischernolide A (1) and fischernolide B (2) (*J* in Hz)

no.	1^a		2^b		2^c	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}
1	1.51, 2H, overlapped	40.0	1.38, overlapped 1.18, m	41.2	1.30, m 1.12, overlapped	41.3
2	1.38, m 1.15, overlapped	17.9	1.51, m 1.40, overlapped	18.0	1.64, m 1.46, m	19.3
3	1.35, overlapped 1.16, overlapped	41.1	1.46, m	39.9	1.29, m 1.10, m	42.3
4		33.1		33.5		33.9
5	0.95, m	54.2	0.97, d (12.1)	54.3	1.12, overlapped	55.7
6	1.51, overlapped 1.15, overlapped	18.8	1.63, m 1.33, m	19.4	1.62, m 1.46, m	20.7
7	2.25, d (12.9) 1.35, overlapped	36.7	2.31, m 1.13, m	36.4	2.92, d (12.3) 1.60, m	38.4
8		73.2		74.4		76.1
9	2.15, s	68.0	2.23, s	67.3	2.96, s	68.8
10		38.6		38.8		40.3
11		194.0		195.4		197.2
12		143.3		146.1		148.9
13		123.4		122.5		120.8
14	5.46, s	76.8	5.04, t (8.5)	66.6	6.07, s	68.7
15		121.3		118.5		124.6
16		170.6		161.9		164.0
17	7.54, s	127.8	8.05, s	138.1	8.75, s	139.9
18	0.90, s	33.3	0.90, s	33.1	0.83, s	34.2
19	0.80, s	21.4	0.83, s	21.6	0.74, s	22.3
20	1.00, s	15.4	0.91, s	15.7	1.34, s	17.1
21		103.5		102.8		104.7
22		166.0		158.7		164.6
23		106.2		107.6		108.2
24		164.3		163.9		160.2
25	6.10, s	90.2	6.72, s	91.1	6.33, s	91.4
26		164.3		158.3		160.2
27		202.6		204.3		205.0
28	2.55, s	32.7	2.65, s	33.1	2.55, s	33.5
-OCH ₃	3.87, s	55.9	3.98, s	57.0	3.76, s	56.8
8-OH	5.03, s		4.38, s			
12-OH			8.68, s			
14-OH			5.01, t (8.5)			
22-OH	15.00, s		14.54, brs			

^a 400 MHz in DMSO-*d*₆; ^b 600 MHz in DMSO-*d*₆; ^c 400 MHz in pyridine-*d*₅.

Table S2. NMR Data of fischernolide C (3) and fischernolide D (4) (600 MHz in DMSO-*d*₆, *J* in Hz)

no.	3^a		4^a	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}
1	1.38, m 1.19, m	41.3	1.38, m 1.18, m	41.0
2	1.53, m 1.41, overlapped	18.1	1.53, overlapped 1.41, m	17.7
3	1.44, 2H, m	39.9	1.44, m 1.26, m	38.9
4		33.1		32.8
5	1.00, d (12.0)	54.6	1.00, d (11.4)	53.5
6	1.69, d (13.2) 1.42, overlapped	19.5	1.67, m 1.32, m	19.2
7	2.21, d (13.8) 1.26, m	37.3	2.18, m 1.53, overlapped	40.8
8		75.3		69.0
9	2.15, s	67.7	2.52, overlapped	70.5
10		38.9		38.9
11		195.2		196.1
12		146.3		179.1
13		121.0		138.4
14	4.71, s	78.2	7.54, s	155.8
15		117.5		115.0
16		162.2		165.0
17	7.99, s	138.5	8.10, s	138.9
18	0.90, s	33.5	0.89, s	33.5
19	0.83, s	21.6	0.75, s	21.6
20	0.95, s	15.7	0.87, s	20.3
21		103.0		104.4
22		158.8		158.9
23		108.2		110.3
24		164.0		164.2
25	6.67, s	90.9	6.38, s	87.6
26		158.8		159.1
27		204.3		202.9
28	2.62, s	33.2	2.54, overlapped	33.0
24-OCH ₃	3.97, s	57.0	3.89, s	56.4
14-OCH ₃	3.36, s	61.7		
8-OH	4.47, s			

Table S3. The 3D conformers of (5*R*,8*S*,9*S*,10*R*,14*R*)-**2** with Boltzmann distribution over 1%.

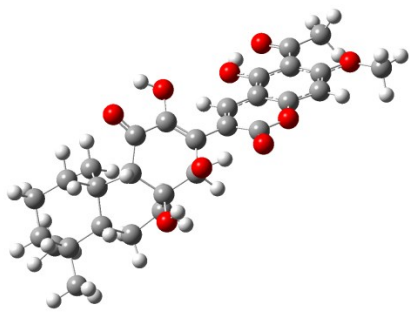
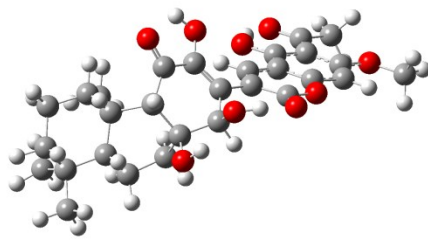
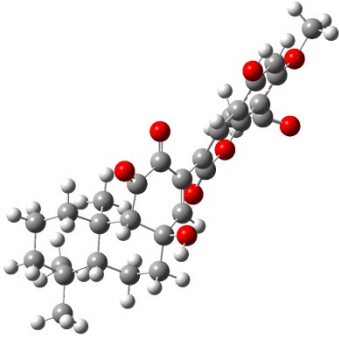
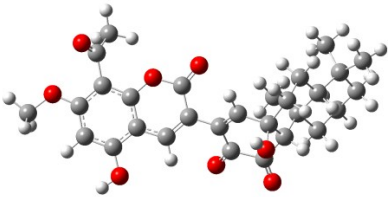
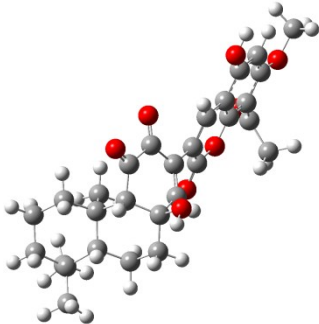
No.	Conformers	E (kcal/mol)	Population (%)
1		-1131182.79	50.00
2		-1131182.79	50.00

Table S4. The 3D conformers of (5*R*,8*R*,9*S*,10*R*)-**4** with Boltzmann distribution over 1%.

No.	Conformers	E (kcal/mol)	Population (%)
1		-1083206.47	26.00
2		-1083206.82	47.39
3		-1083206.46	25.65

Spectra of Fischernolides A–D (1–4)

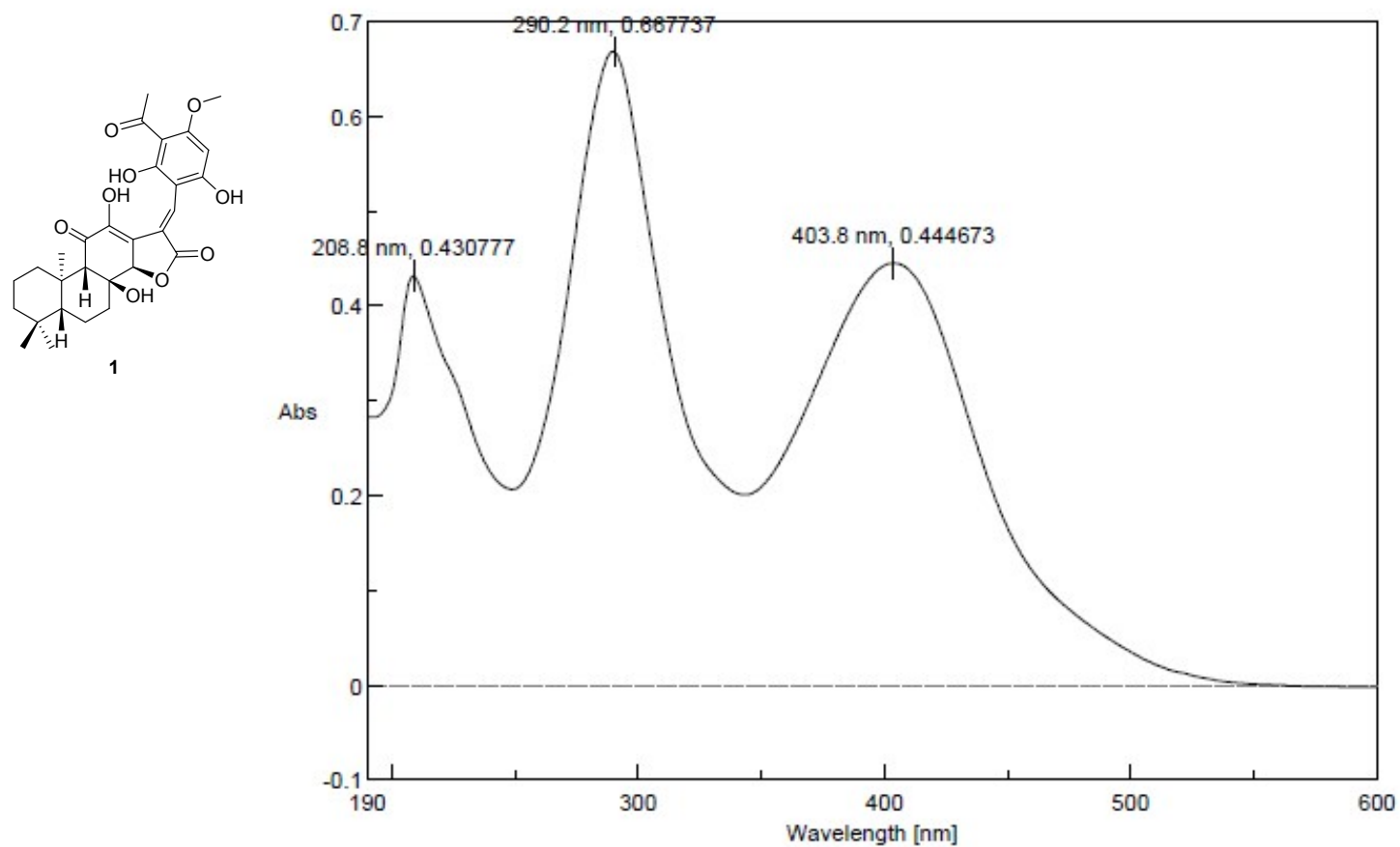


Figure S3. UV spectrum of fischernolide A (1) in MeOH

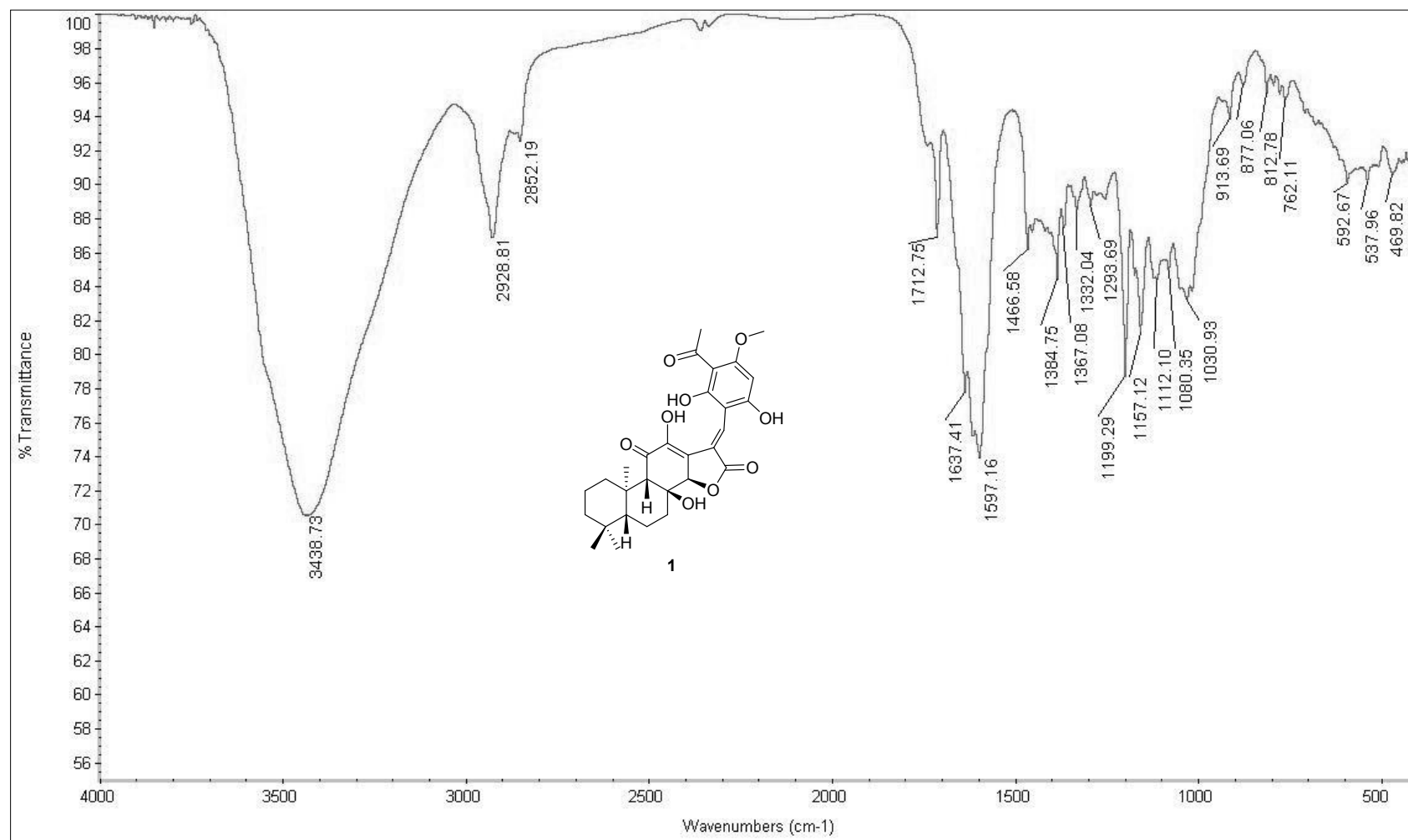


Figure S4. IR spectrum of fischernolide A (**1**)

AP-4 #19-25 RT: 0.18-0.24 AV: 4 NL: 3.15E8
T: FTMS + p ESI Full ms [100.0000-1000.0000]

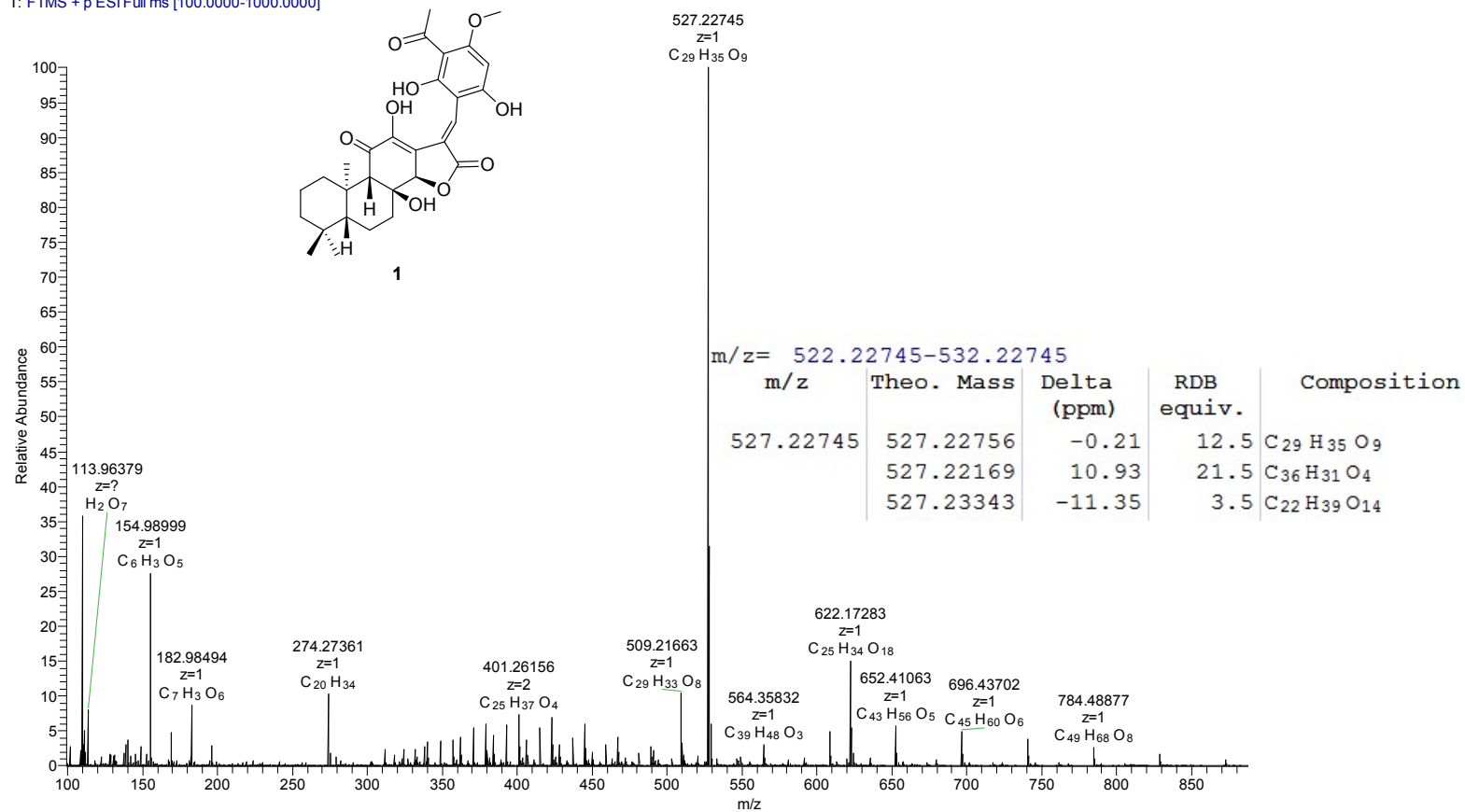


Figure S5. HRESIMS spectrum of fischernolide A (1)

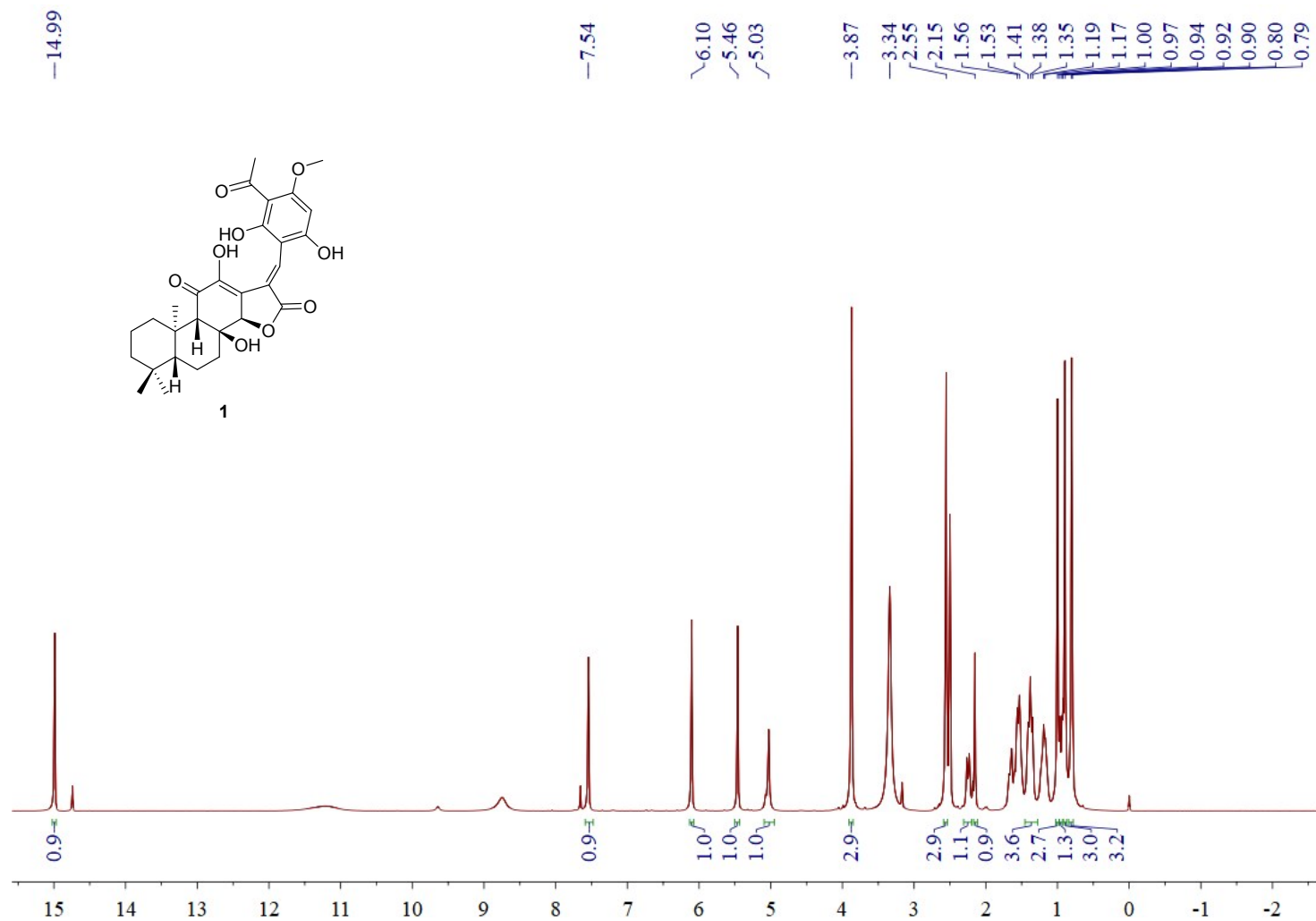


Figure S6. ^1H NMR spectrum of fischernolide A (**1**) in $\text{DMSO}-d_6$ (400 MHz)

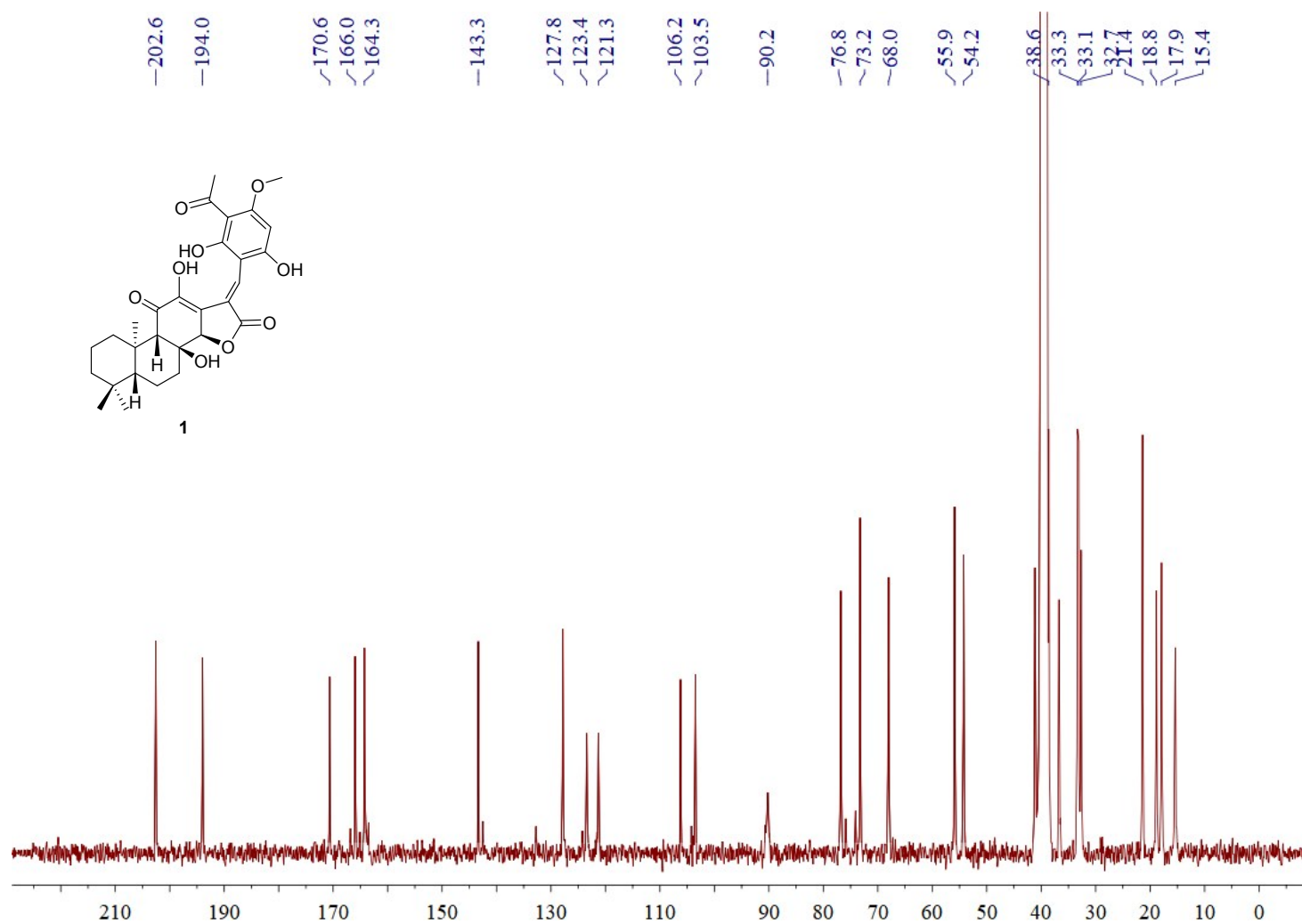


Figure S7. ^{13}C NMR spectrum of fischernolide A (**1**) in $\text{DMSO}-d_6$ (100 MHz)

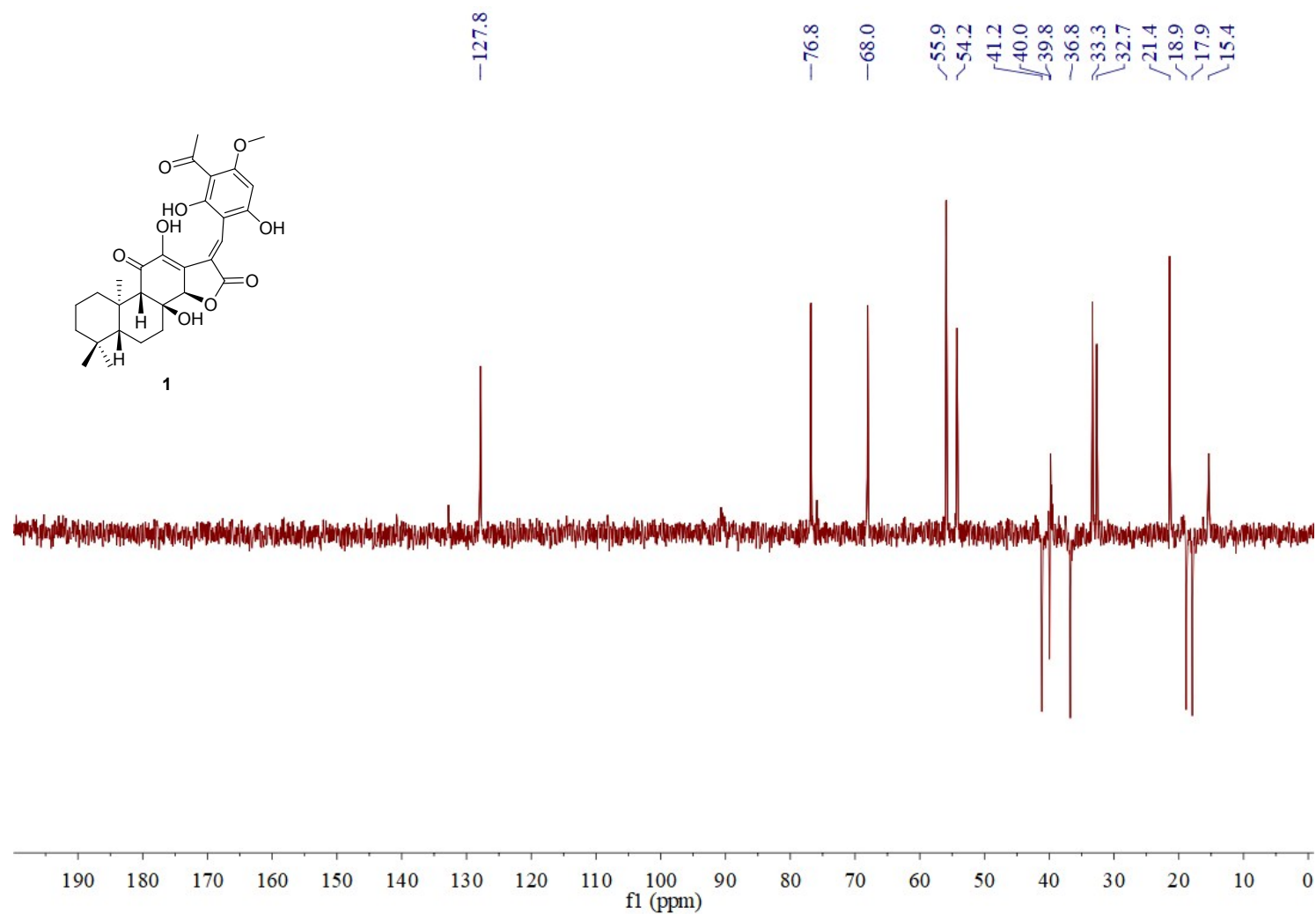


Figure S8. DEPT-135 spectrum of fischerinolide A (**1**) in DMSO- d_6 (100 MHz)

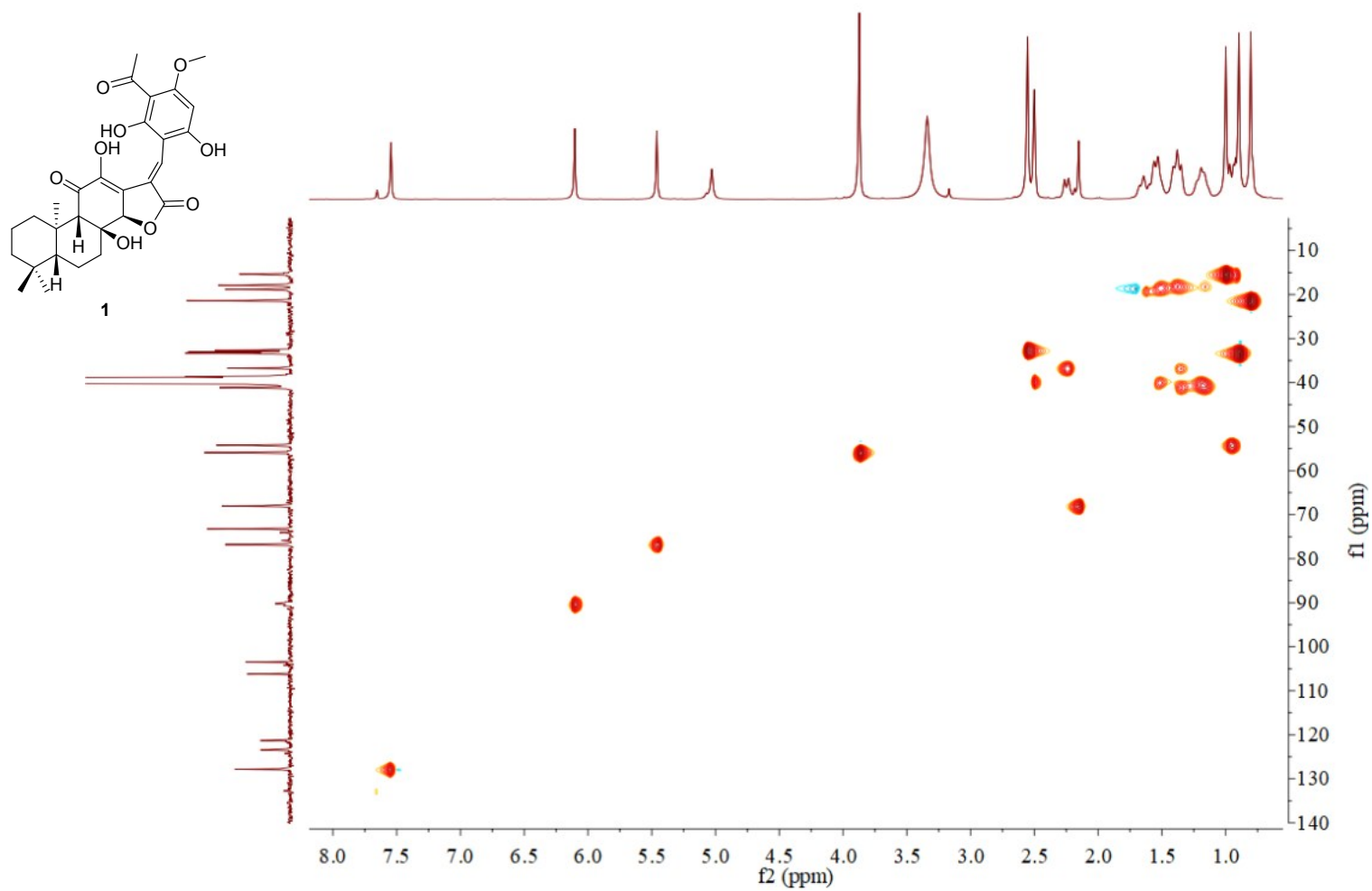


Figure S9. HSQC spectrum of fischernolide A (**1**) in DMSO- d_6

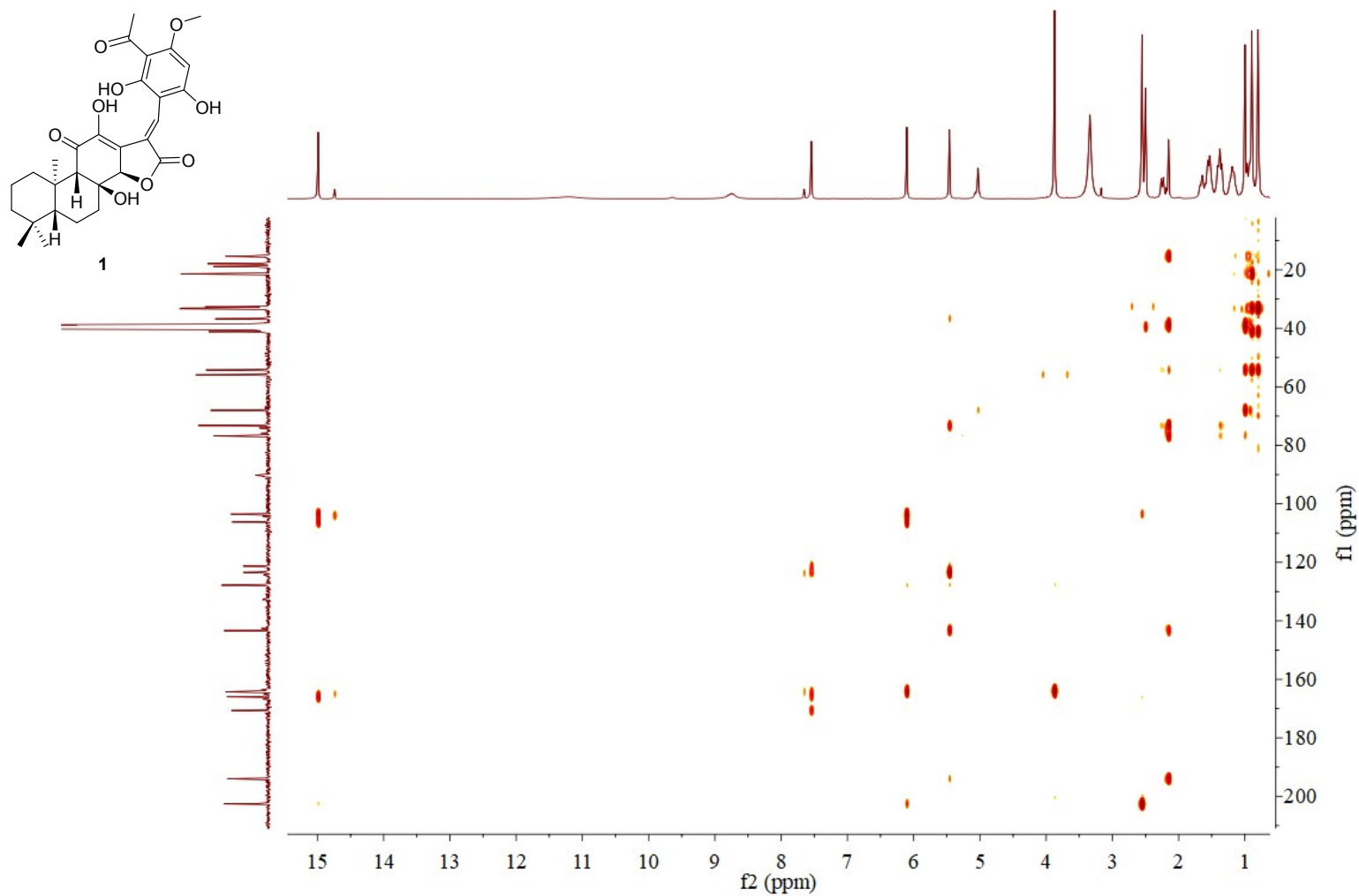


Figure S10. HMBC spectrum of fischerinolide A (1) in DMSO- d_6

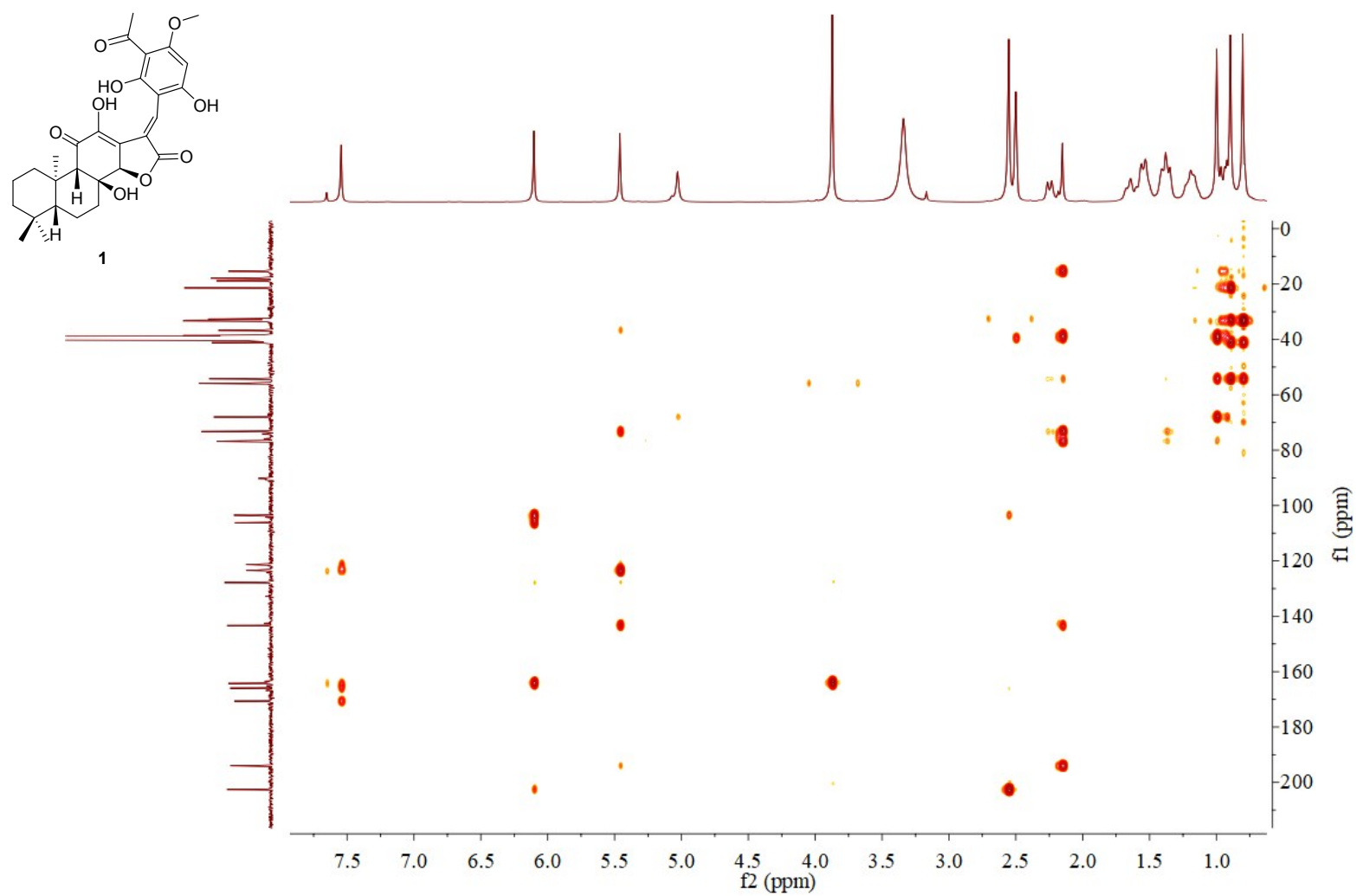


Figure S11. Enlarged HMBC spectrum of fischerinolide A (**1**) in DMSO- d_6

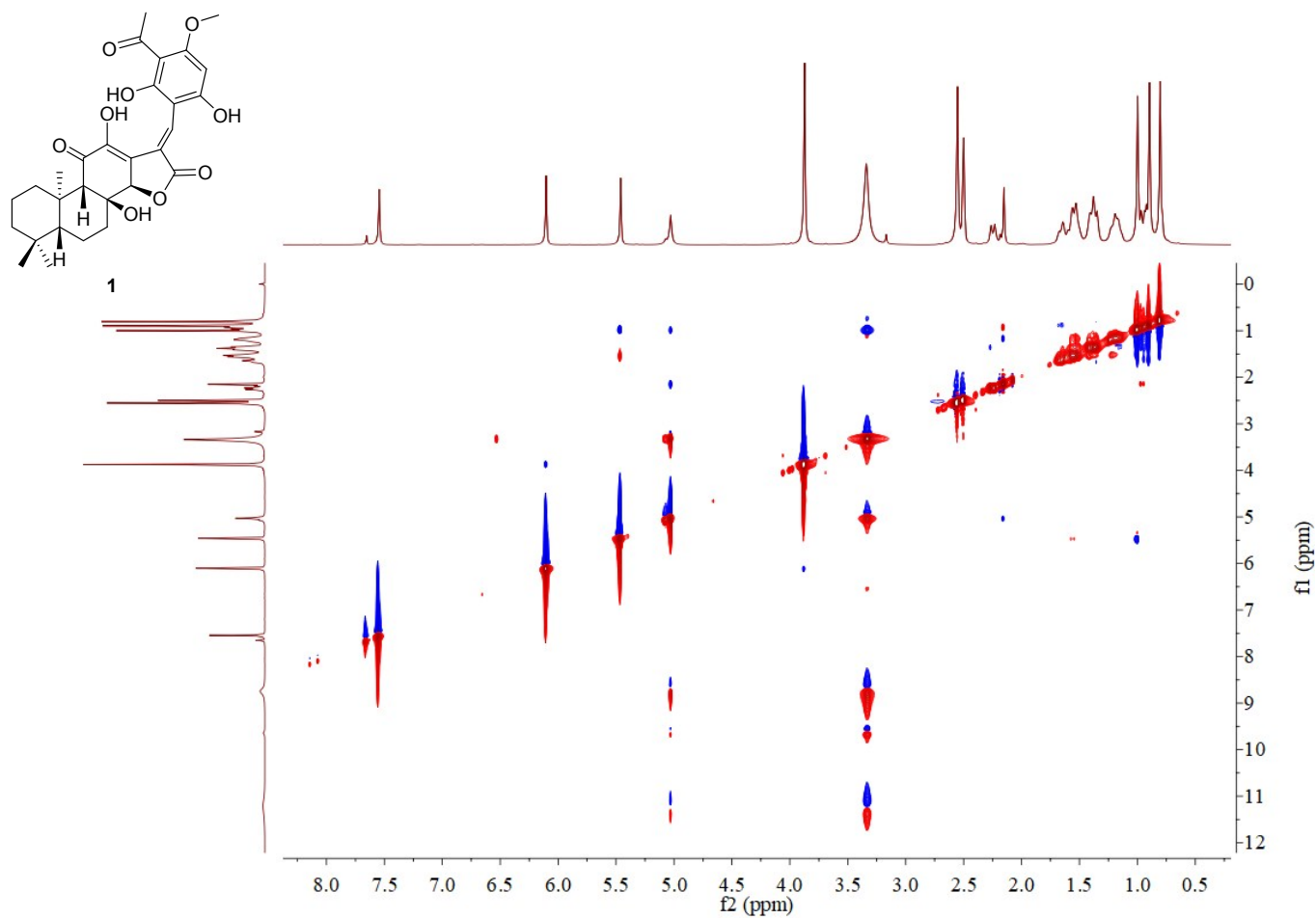


Figure S12. NOESY spectrum of fischernolide A (**1**) in DMSO-*d*₆ (400 MHz)

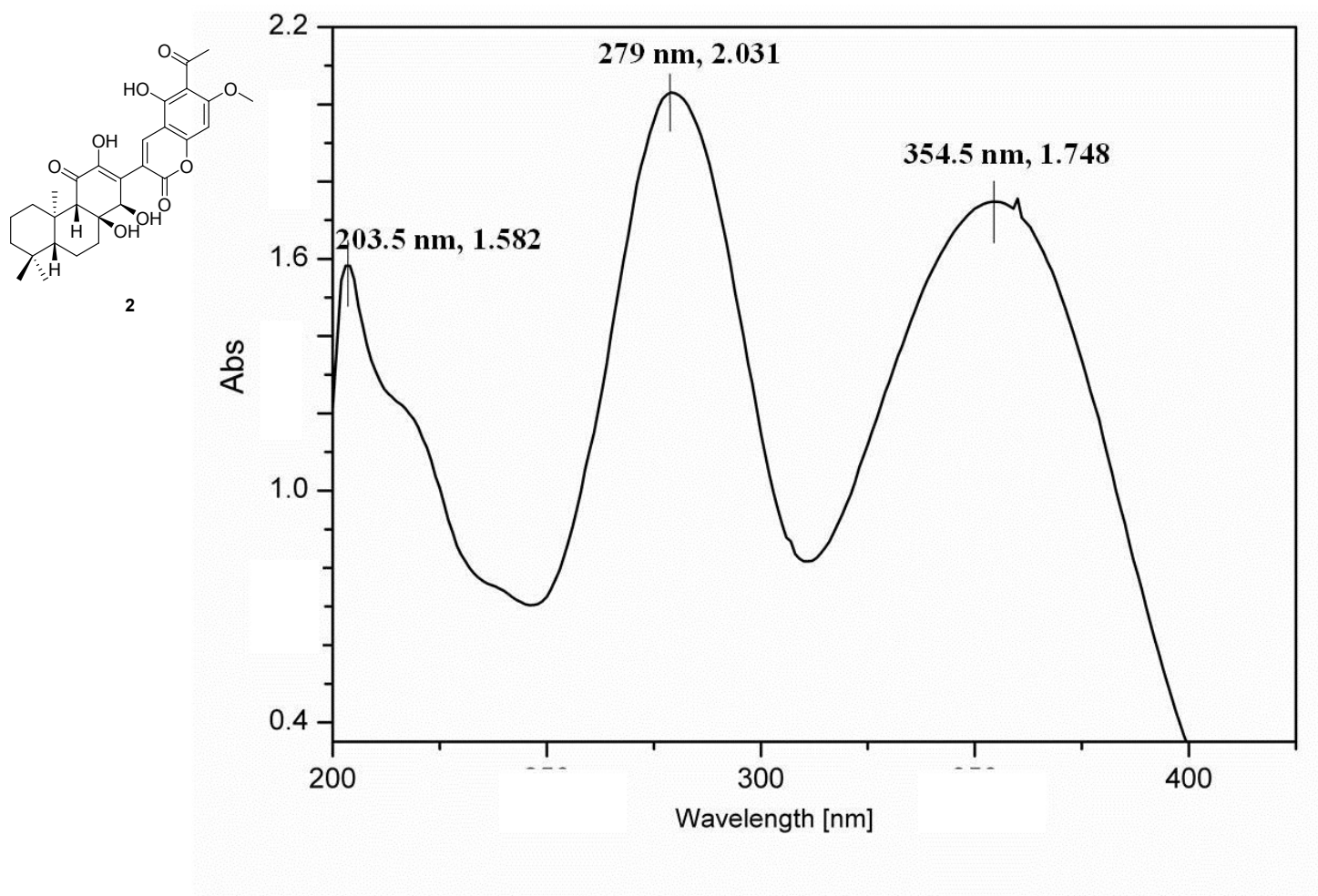


Figure S13. UV spectrum of fischernolide B (**2**) in MeOH

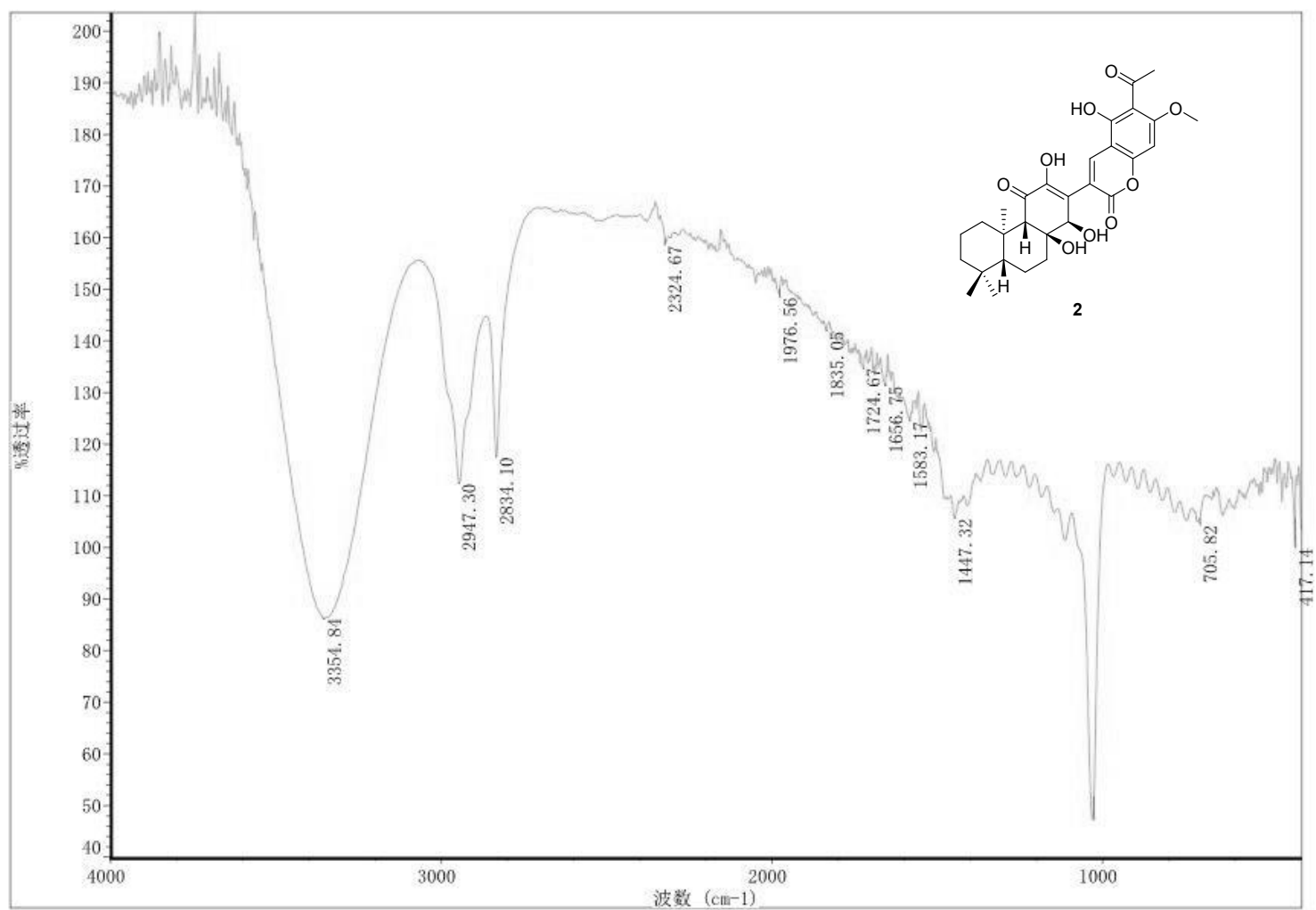


Figure S14. IR spectrum of fischernolide B (2)

AP-1 #1750 RT: 10.25 AV: 1 NL: 7.93E8
T: FTMS +p ESI Full ms [200.0000-600.0000]

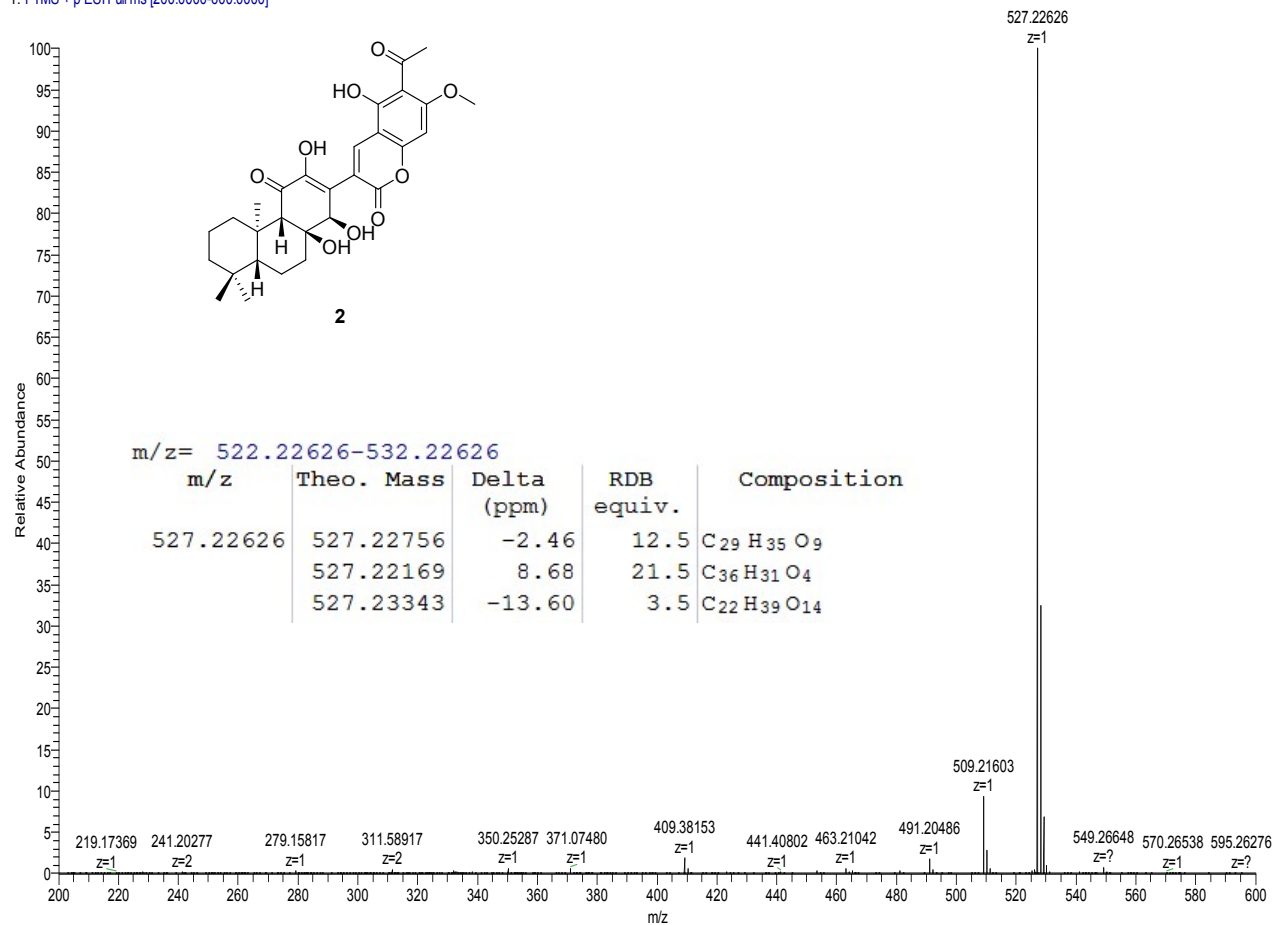


Figure S15. HRESIMS spectrum of fischernolide B (2)

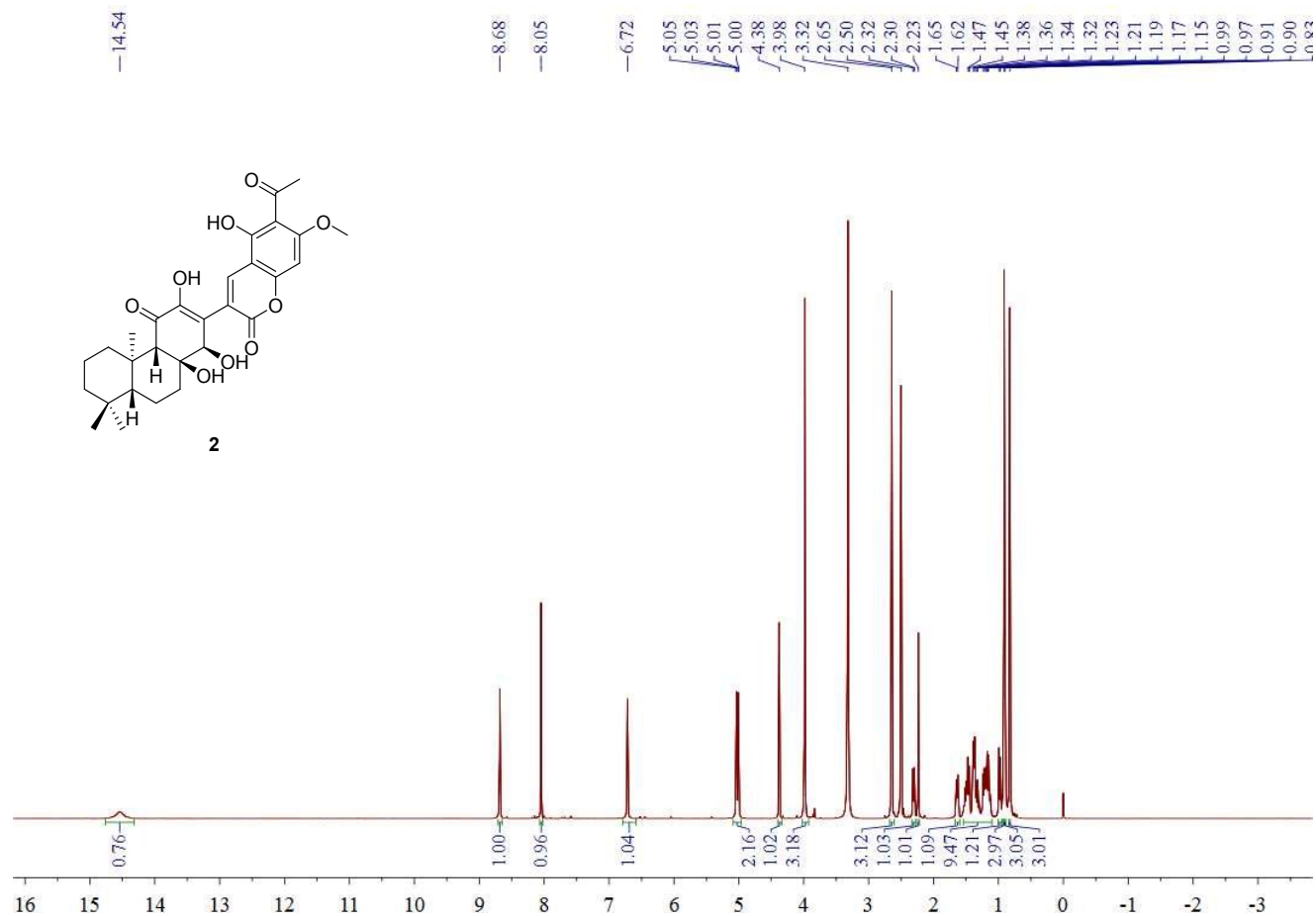


Figure S16. ^1H NMR spectrum of fischernolide B (2) in $\text{DMSO}-d_6$ (600 MHz)

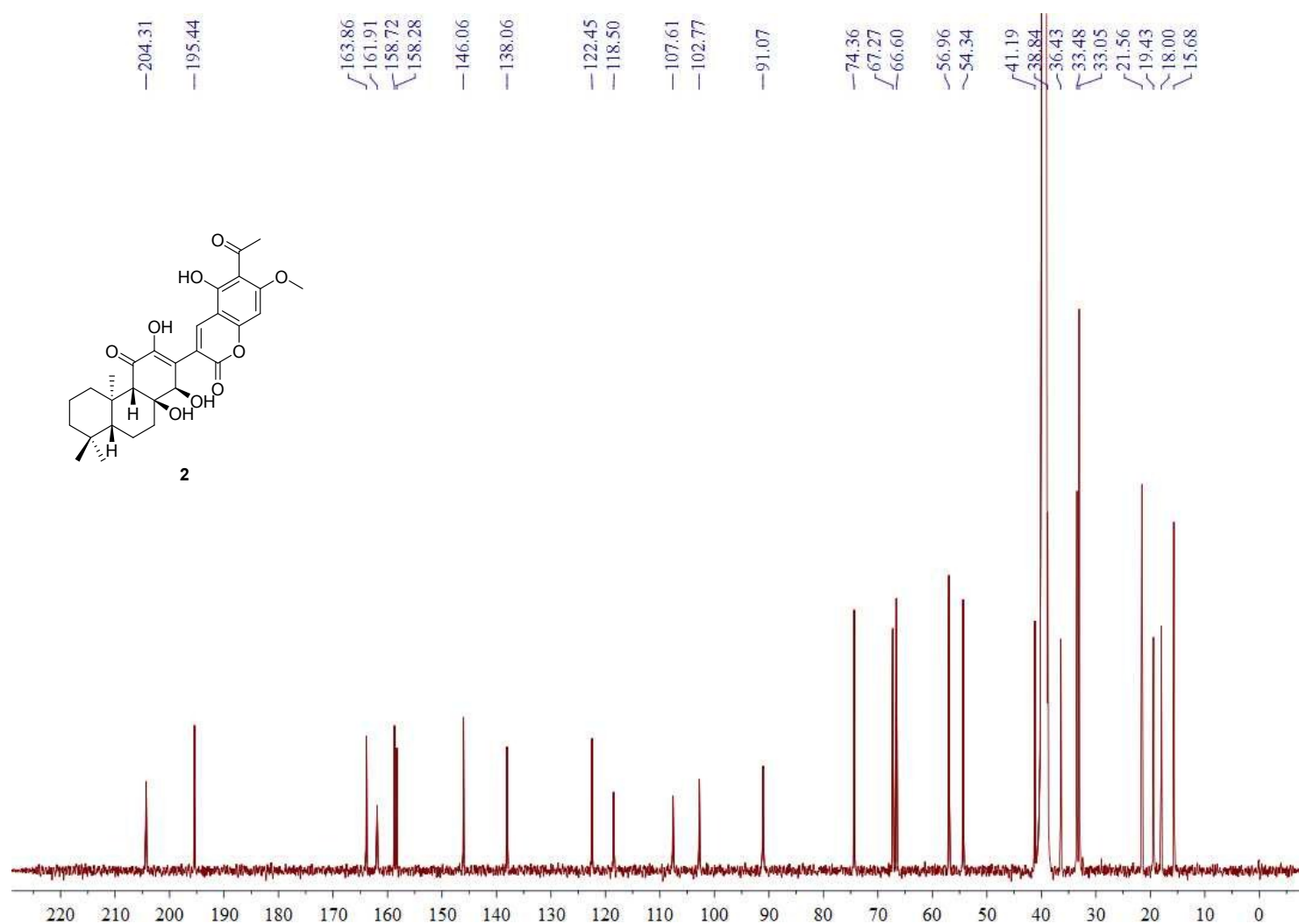


Figure S17. ^{13}C NMR spectrum of fischernolide B (**2**) in $\text{DMSO-}d_6$ (150 MHz)

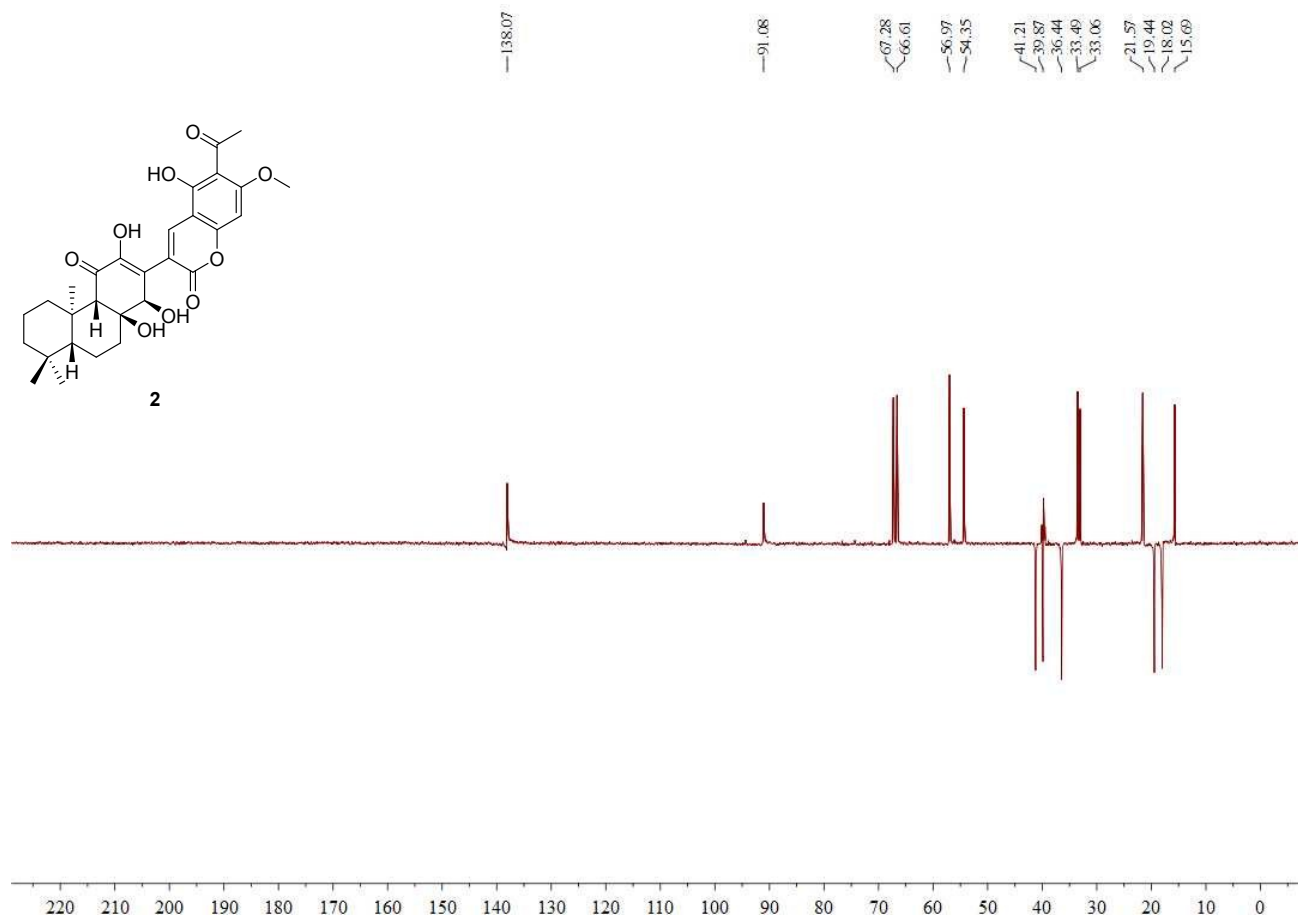


Figure S18. DEPT-135 spectrum of fischernolide B (**2**) in DMSO-*d*₆ (150 MHz)

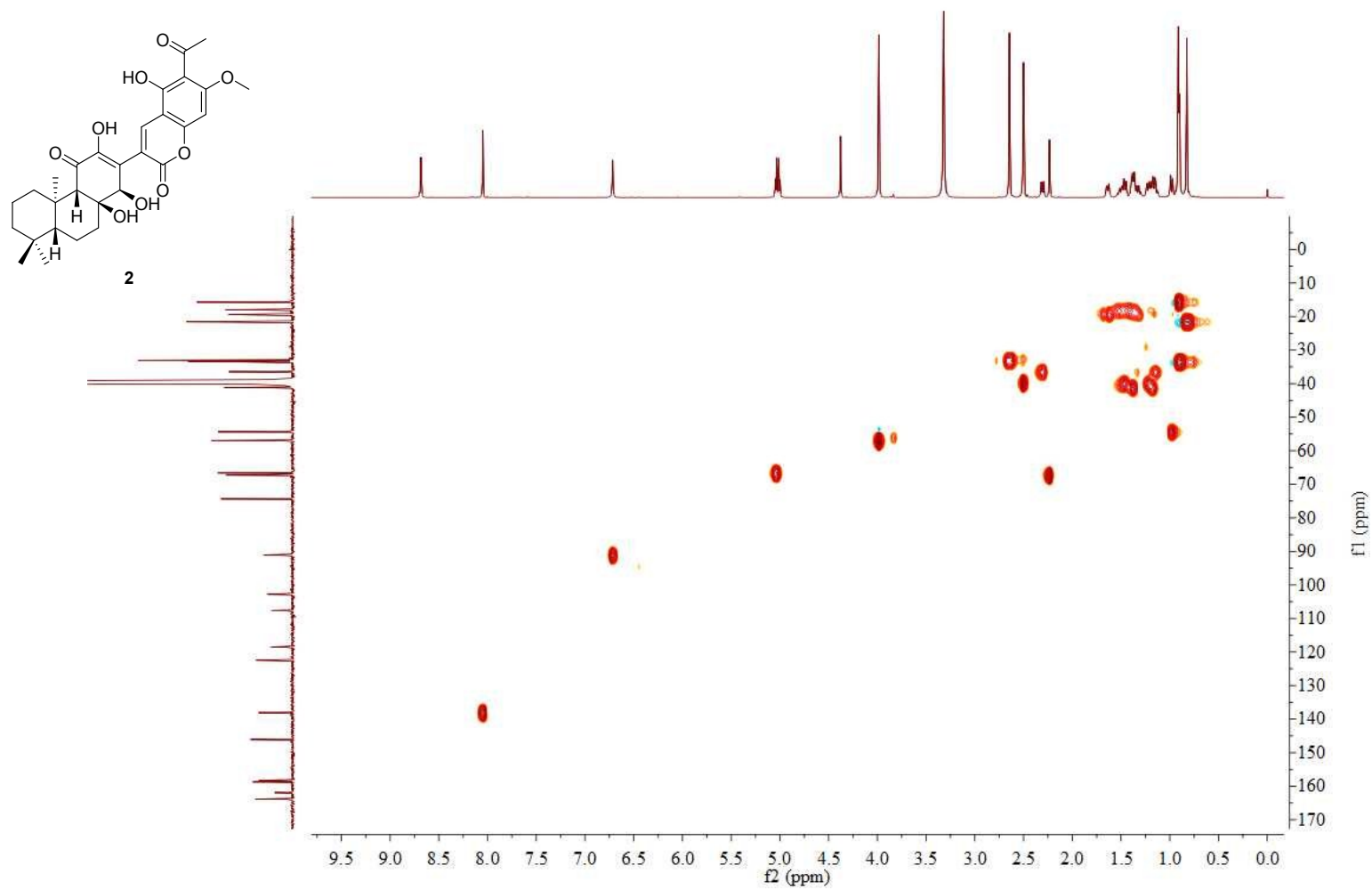


Figure S19. HSQC spectrum of fischernolide B (**2**) in $\text{DMSO}-d_6$

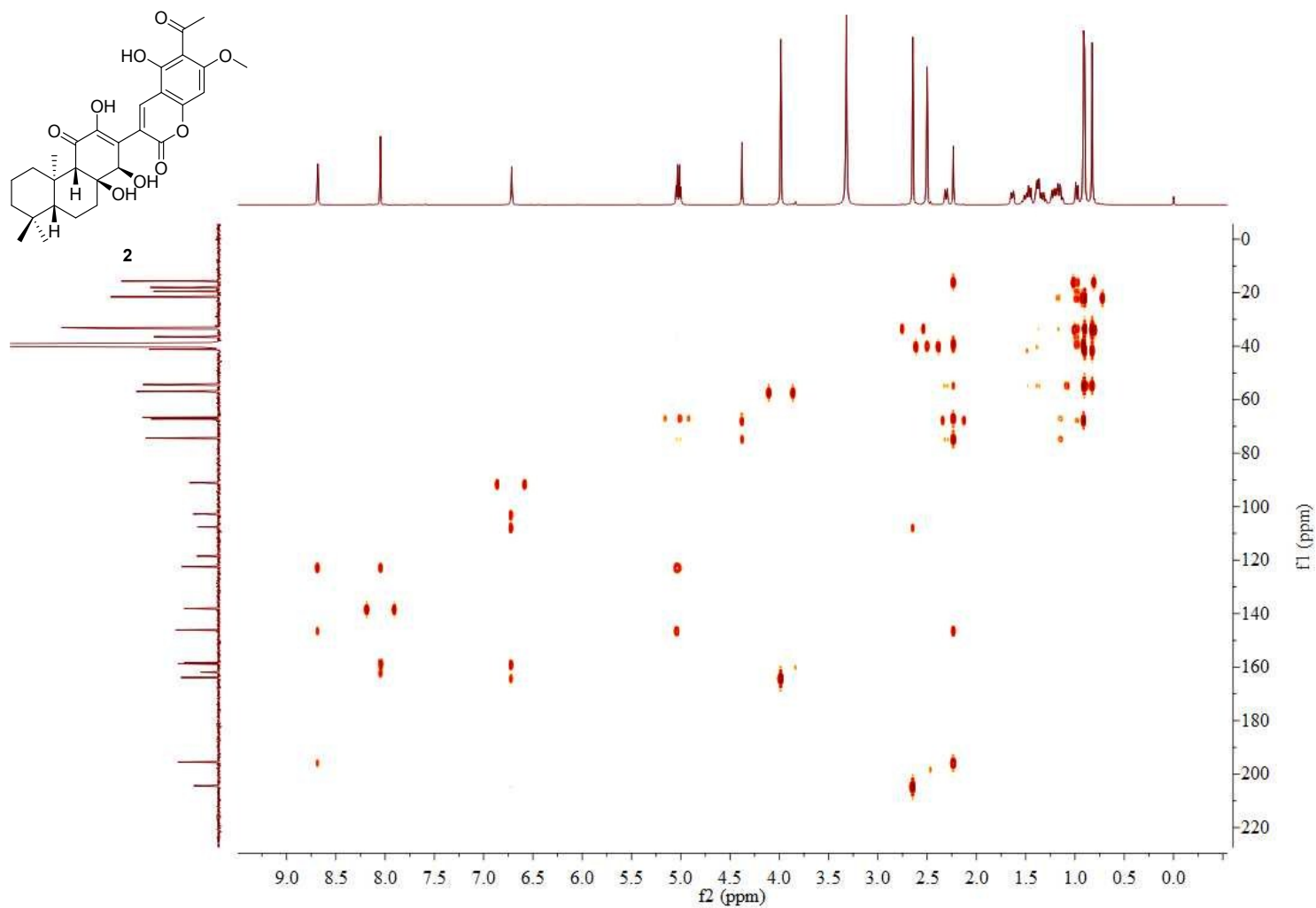


Figure S20. HMBC spectrum of fischerolide B (**2**) in DMSO- d_6

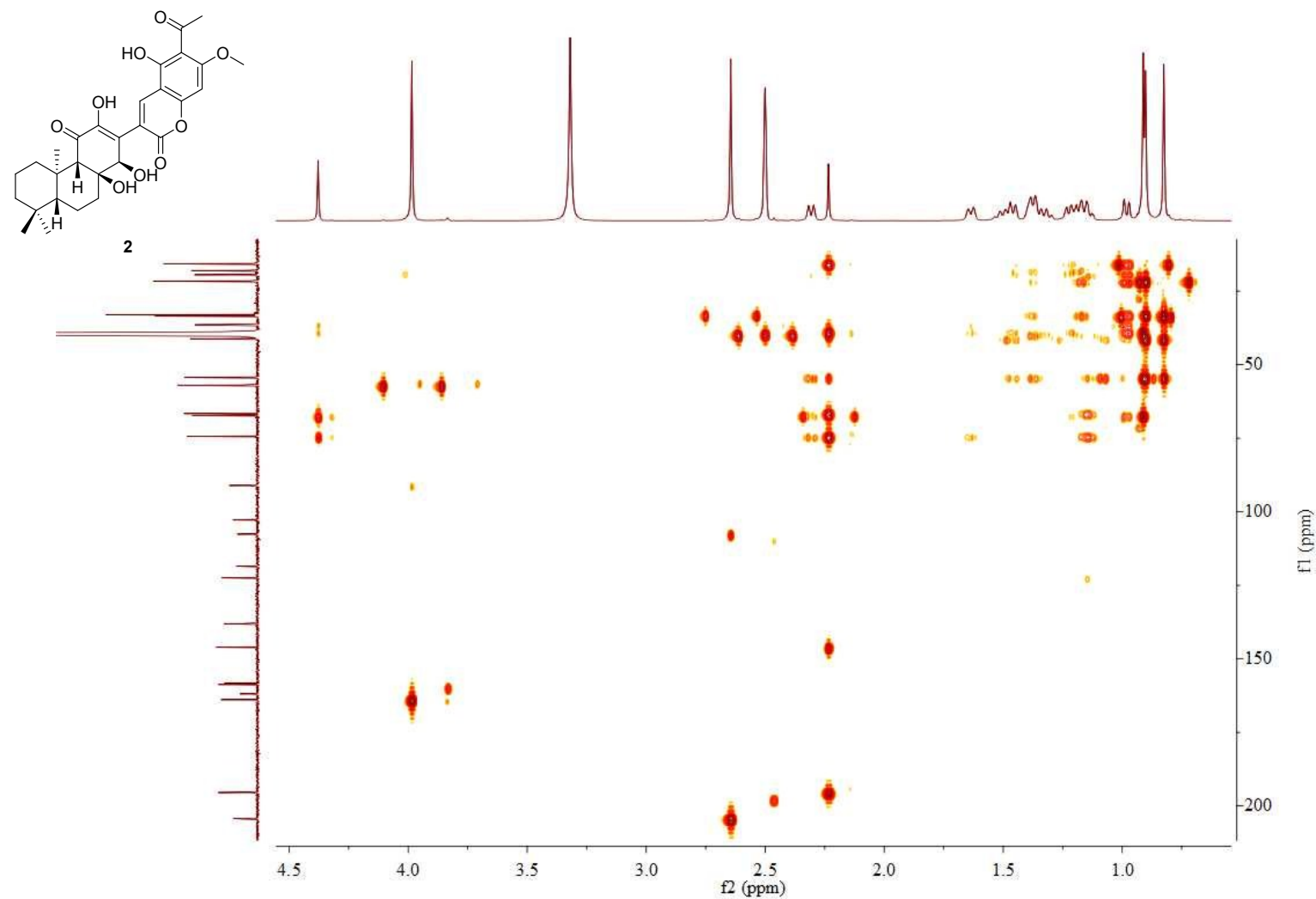


Figure S21. Enlarged HMBC spectrum of fischernolide B (**2**) in DMSO- d_6

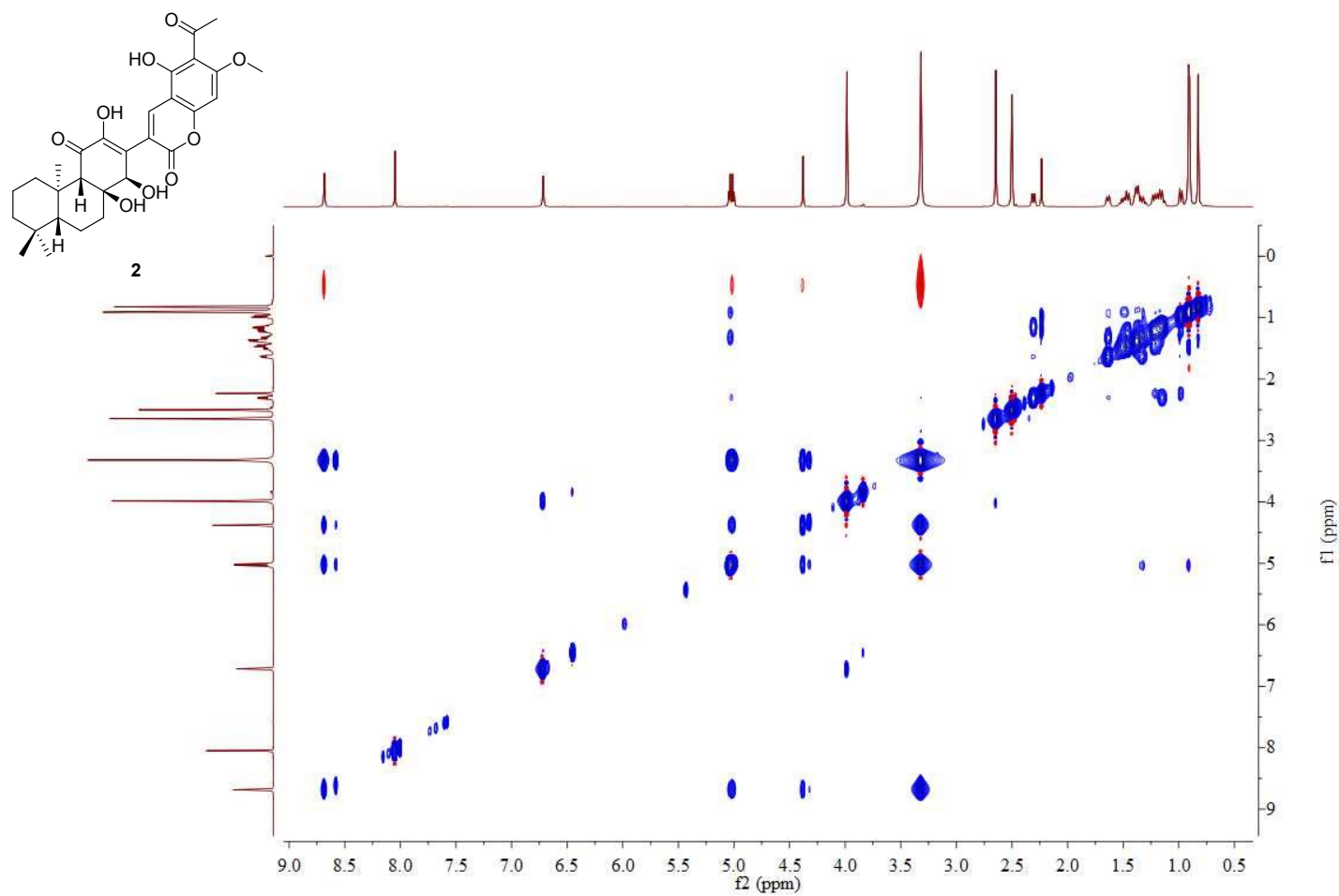


Figure S22. NOESY spectrum of fischernolide B (**2**) in DMSO- d_6 (600 MHz)

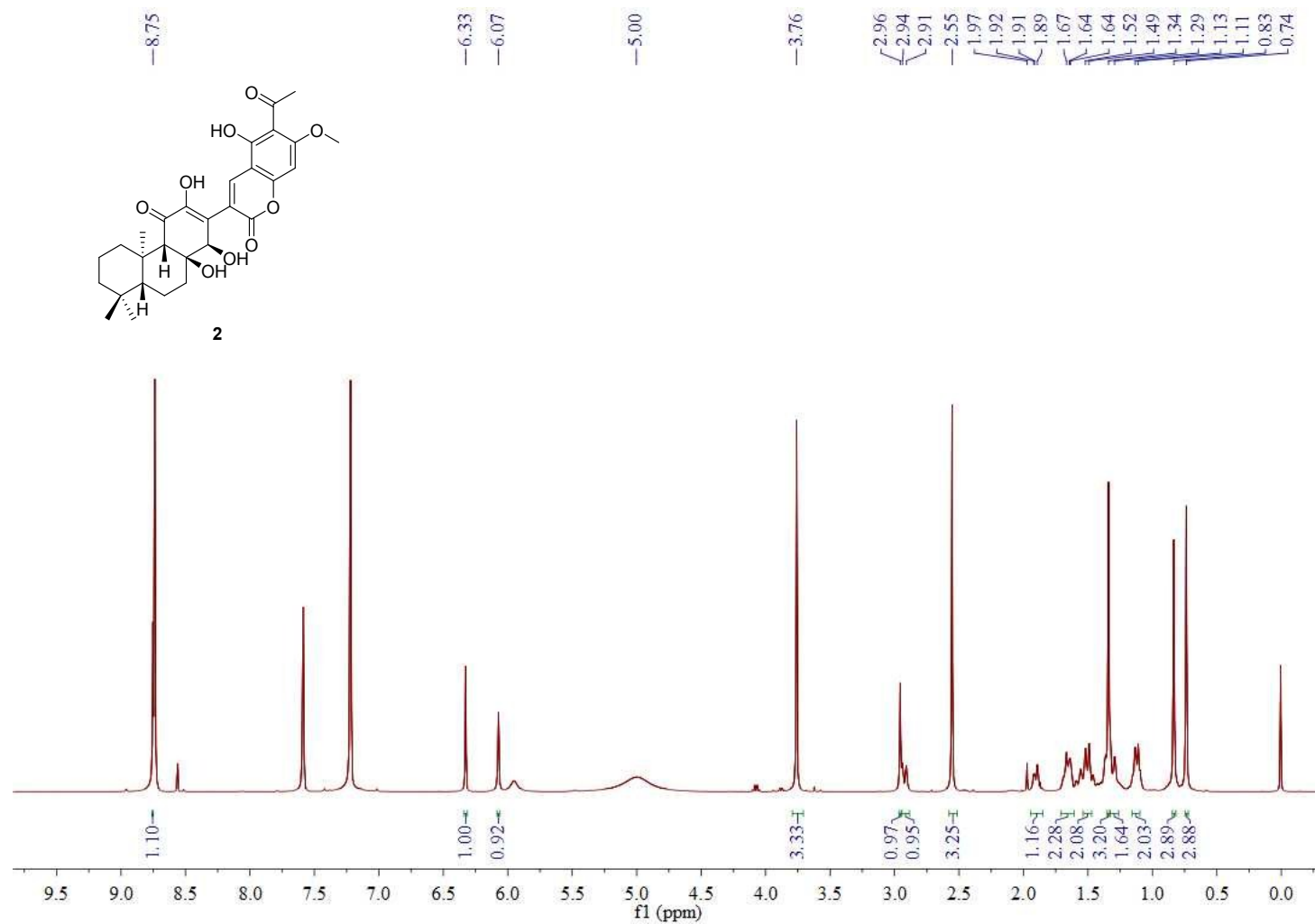


Figure S23. ¹H NMR spectrum of fischernolide B (2) in pyridine-*d*₅ (400 MHz)

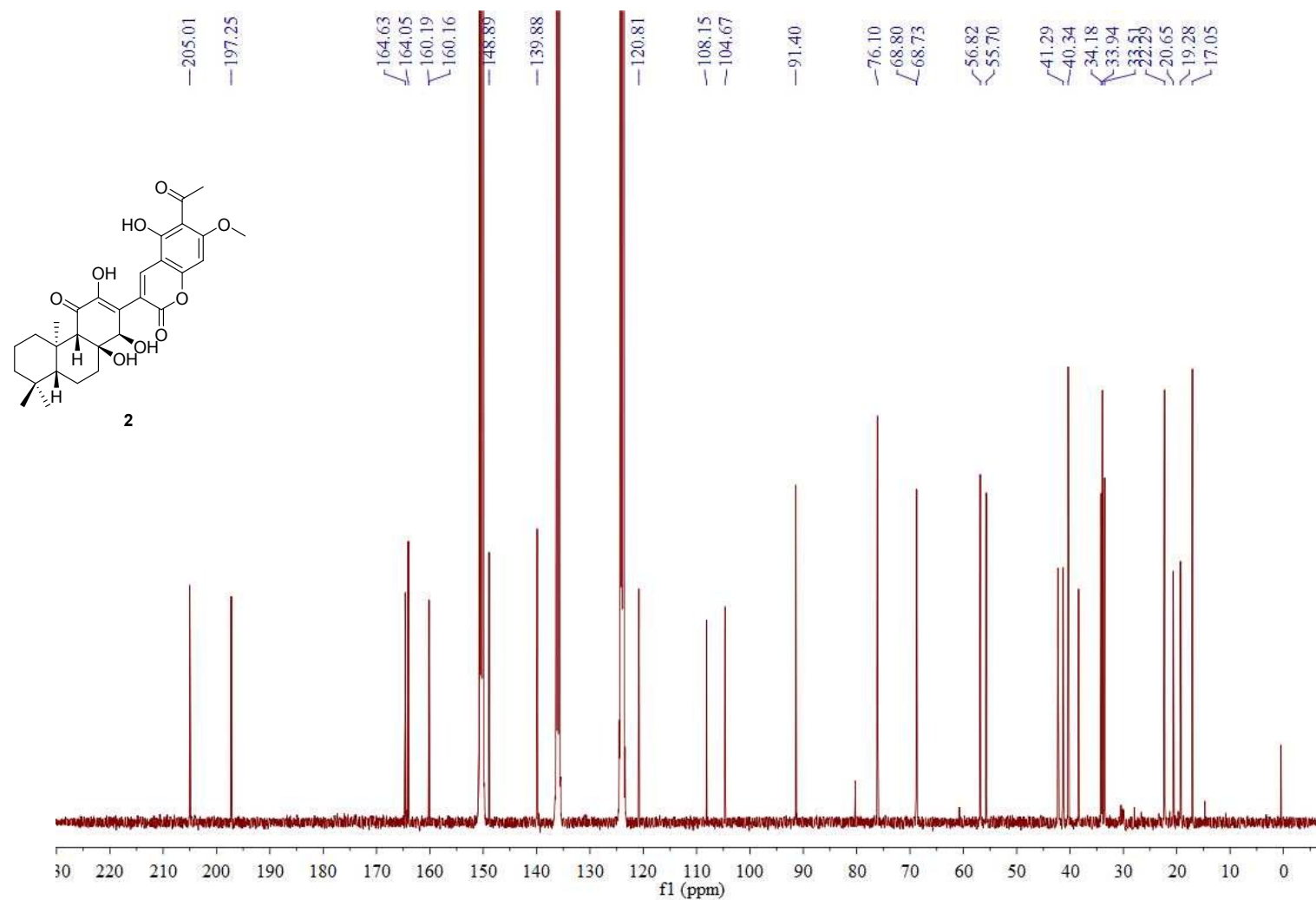


Figure S24. ¹³C NMR spectrum of fischernolide B (**2**) in pyridine-*d*₅ (100 MHz)

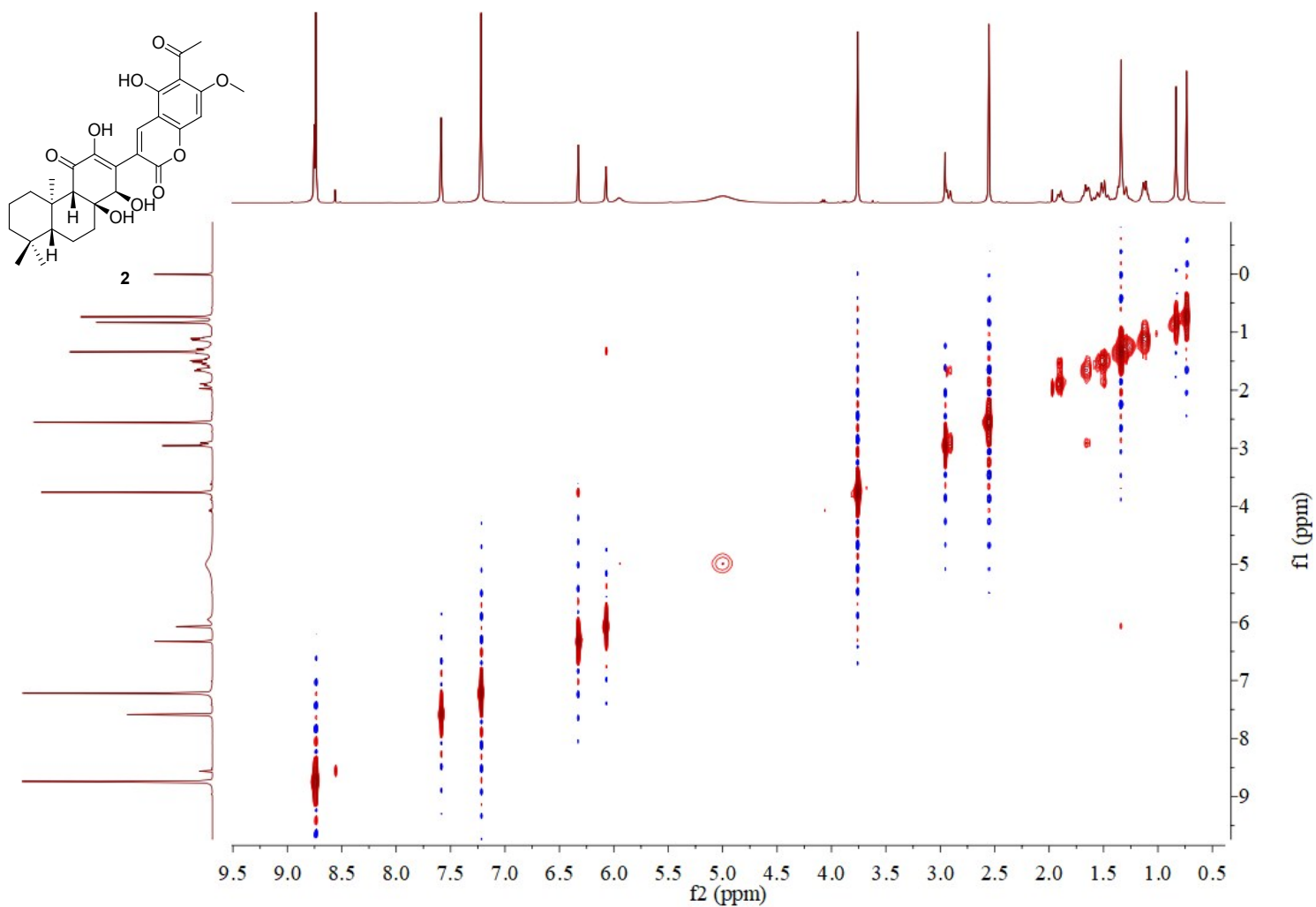


Figure S25. NOESY spectrum of fischernolide B (**2**) in pyridine- d_5 (400 MHz)

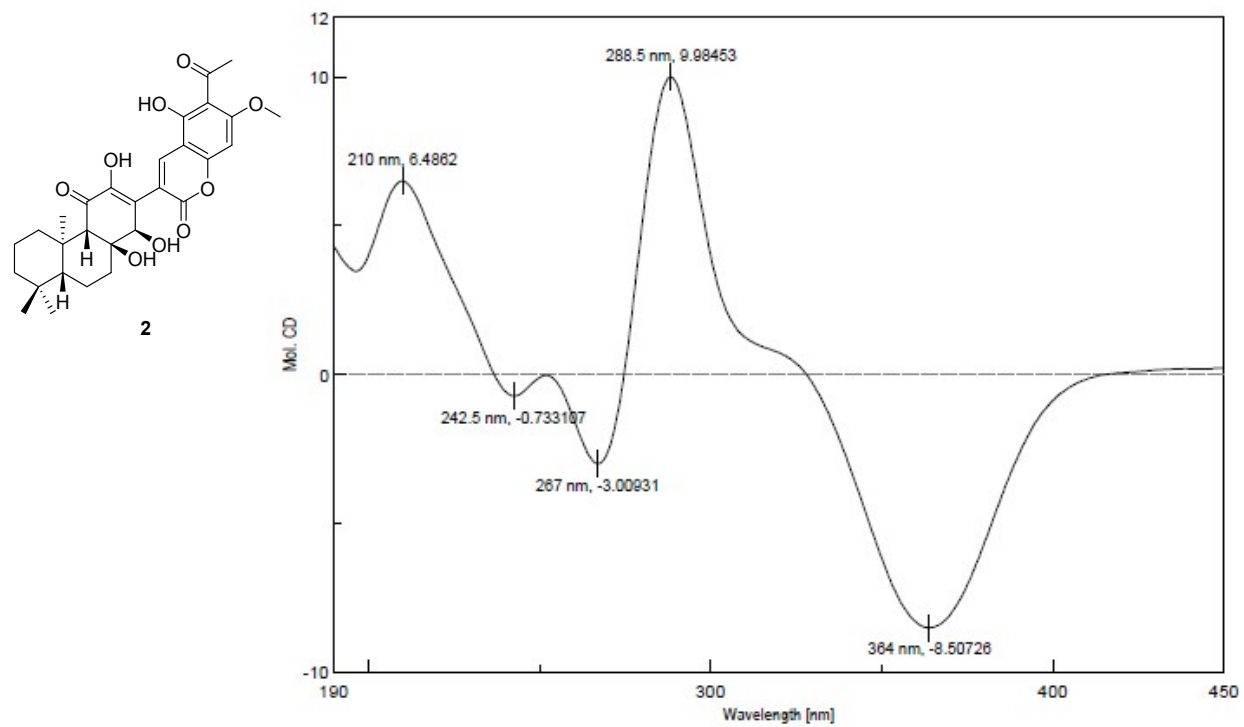


Figure S26. ECD spectrum of fischernolide B (**2**) in MeOH

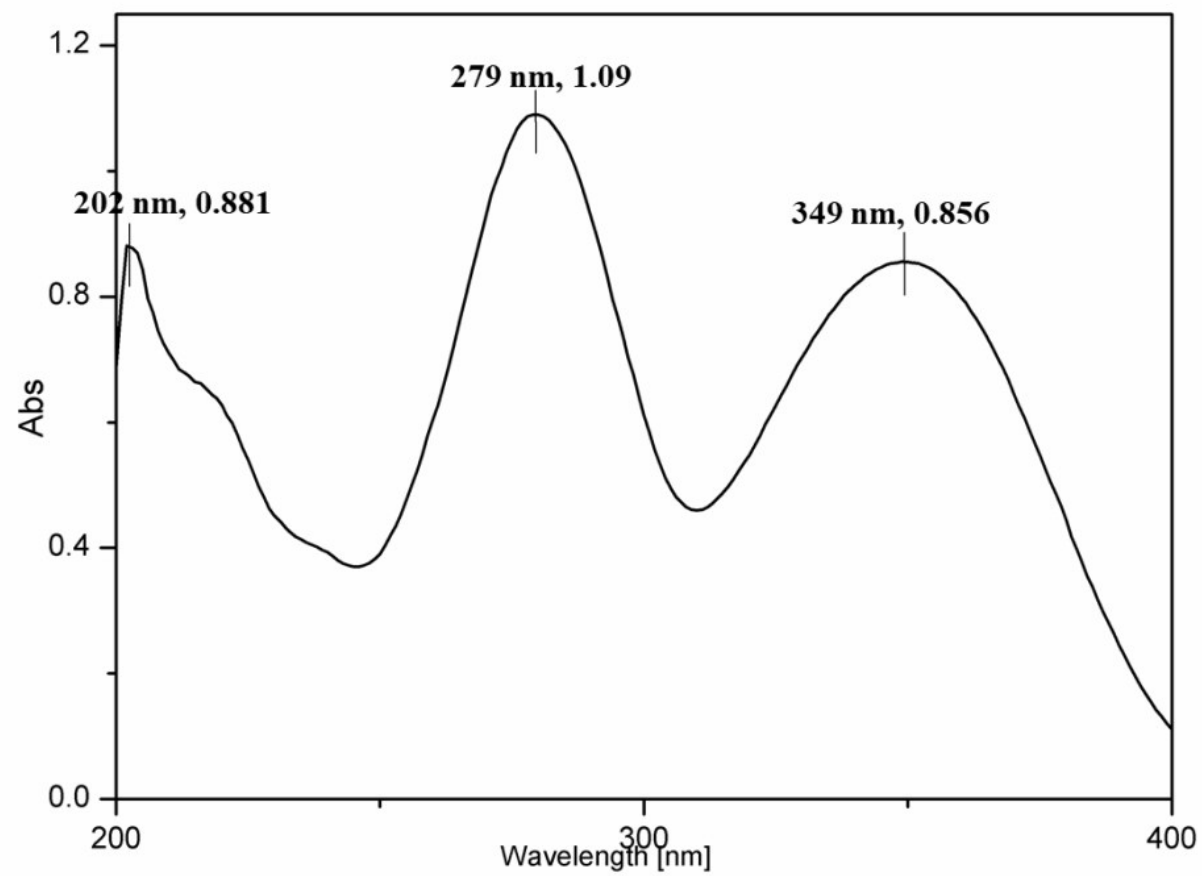
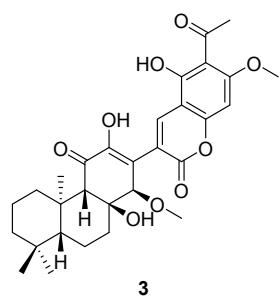


Figure S27. UV spectrum of fischernolide C (**3**) in MeOH

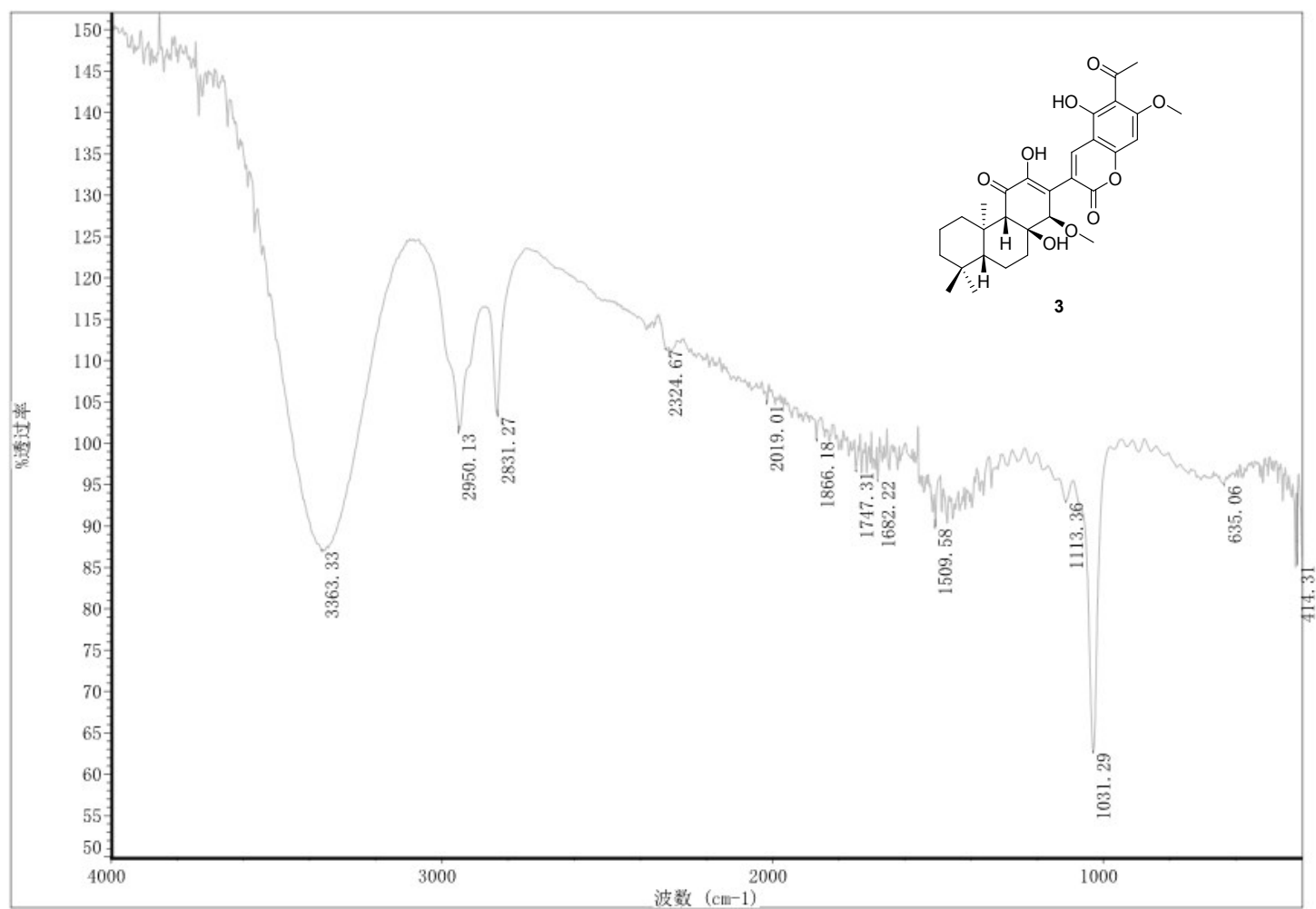


Figure S28. IR spectrum of fischernolide C (**3**)

AP-2_171013145306 #1434 RT: 11.28 AV: 1 NL: 2.01E8
T: FTMS - p ESI Full ms [200.0000-600.0000]

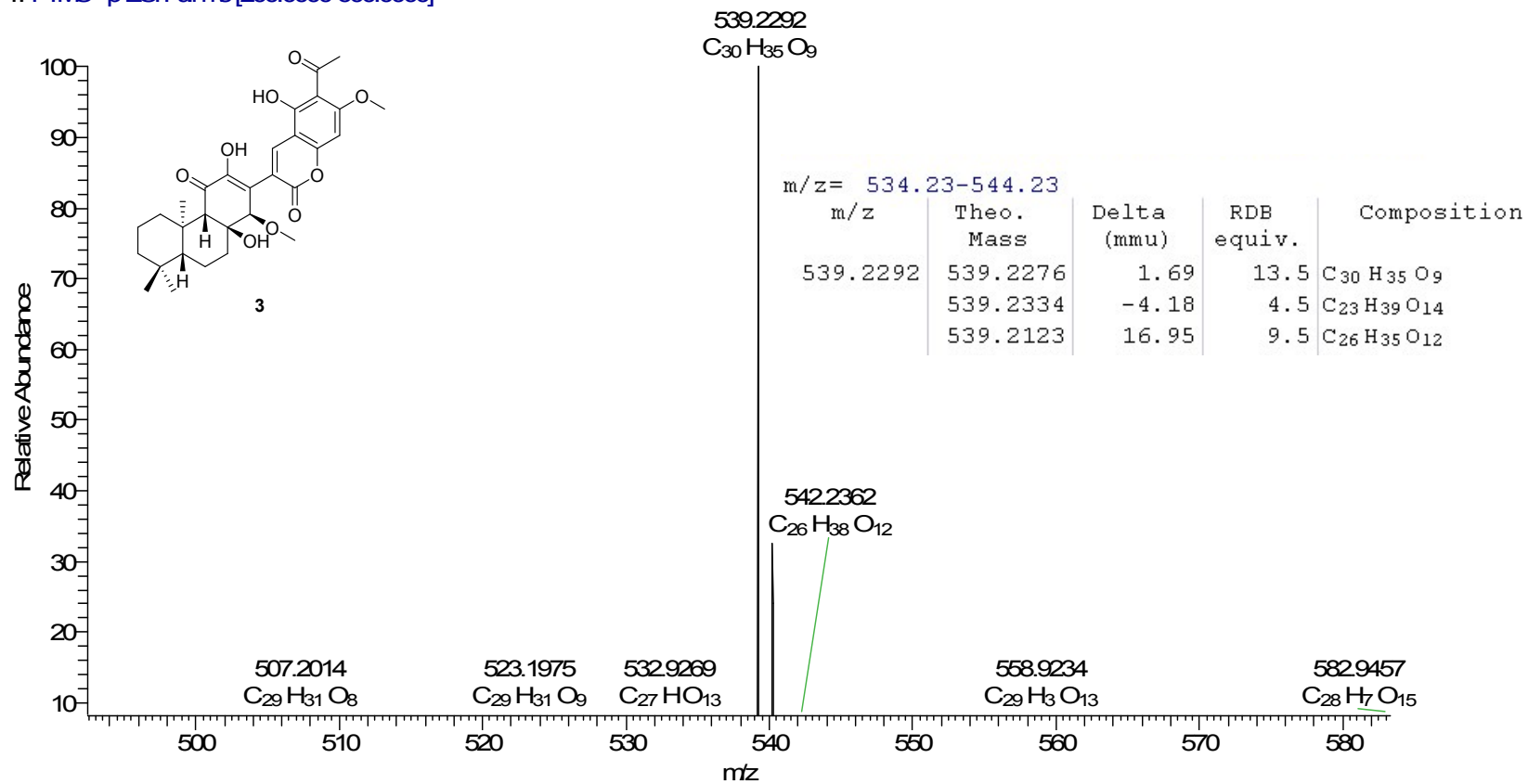


Figure S29. HRESIMS spectrum of fischerinolide C (3)

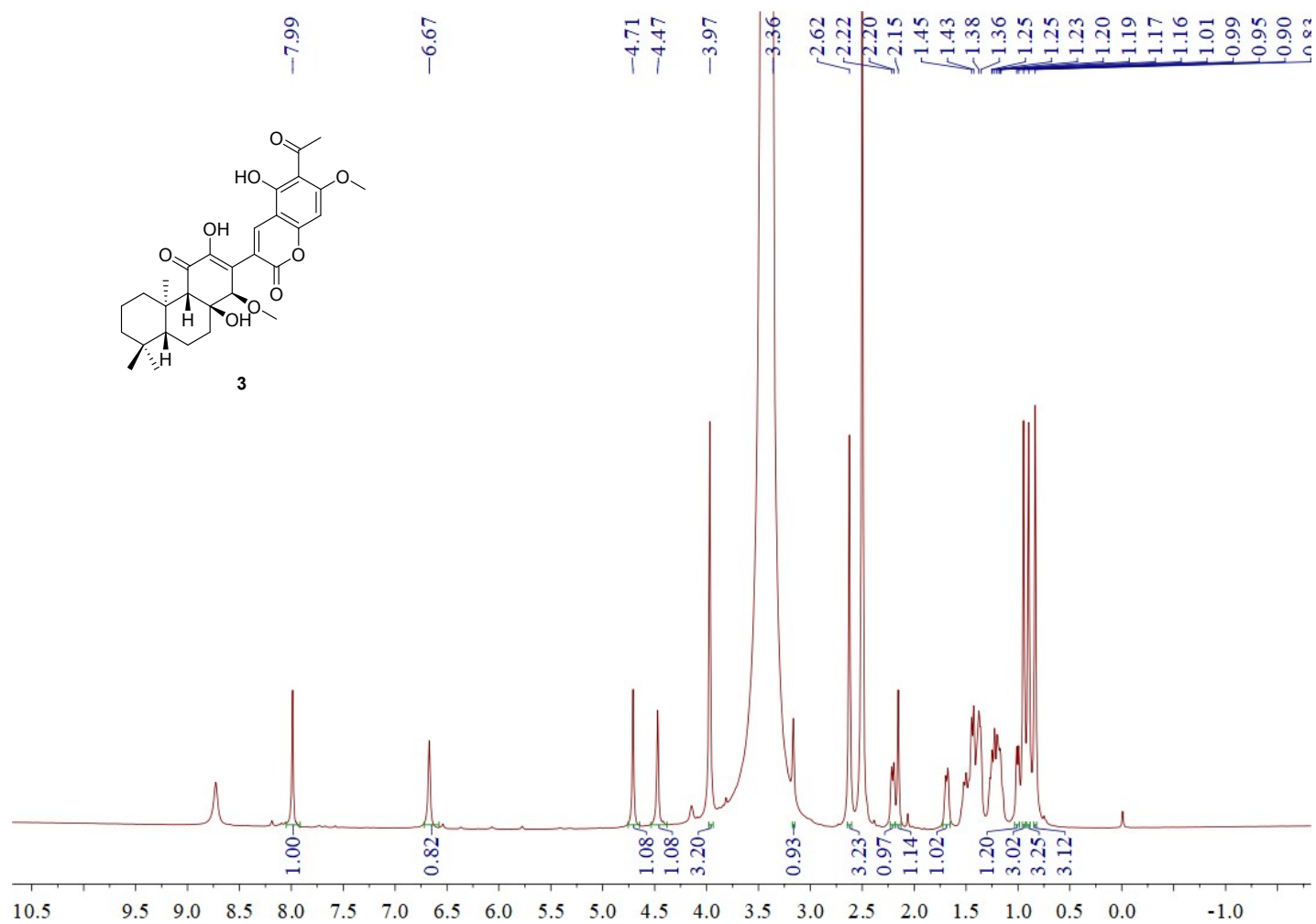


Figure S30. ¹H NMR spectrum of fischerolide C (**3**) in DMSO-*d*₆ (600 MHz)

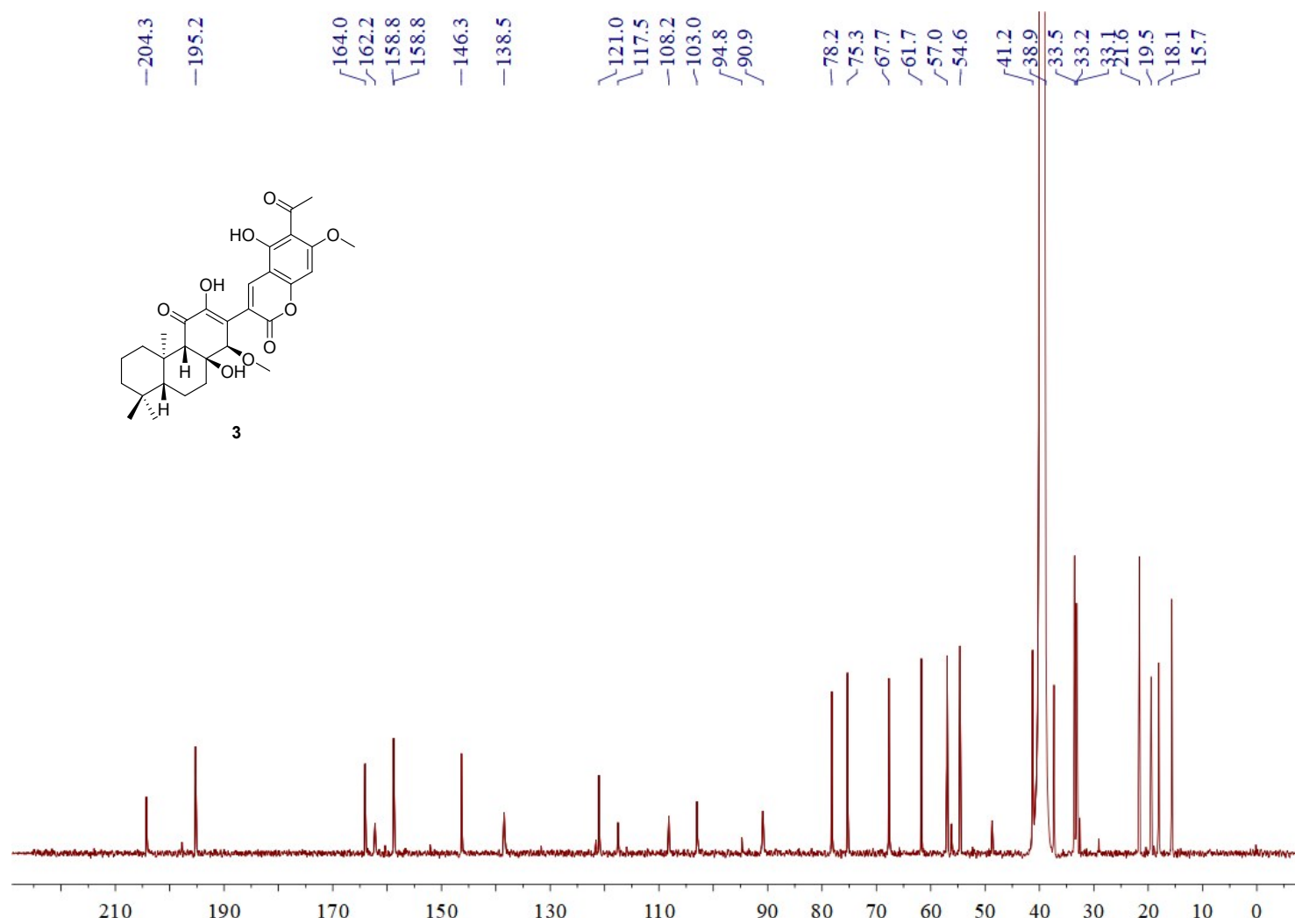


Figure S31. ^{13}C NMR spectrum of fischernolide C (**3**) in $\text{DMSO}-d_6$ (150 MHz)

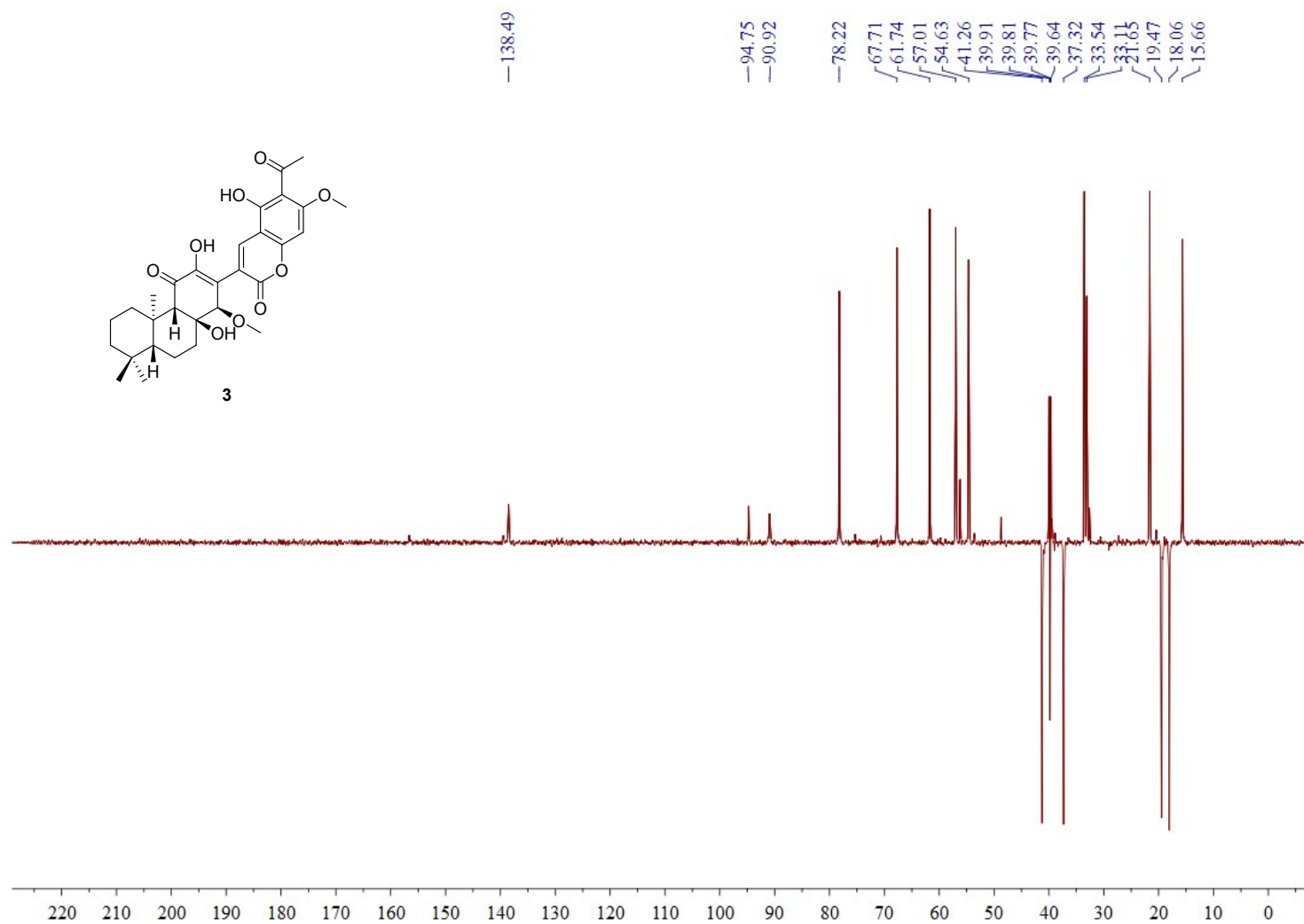


Figure S32. DEPT-135 spectrum of fischernolide C (**3**) in DMSO-*d*₆ (150 MHz)

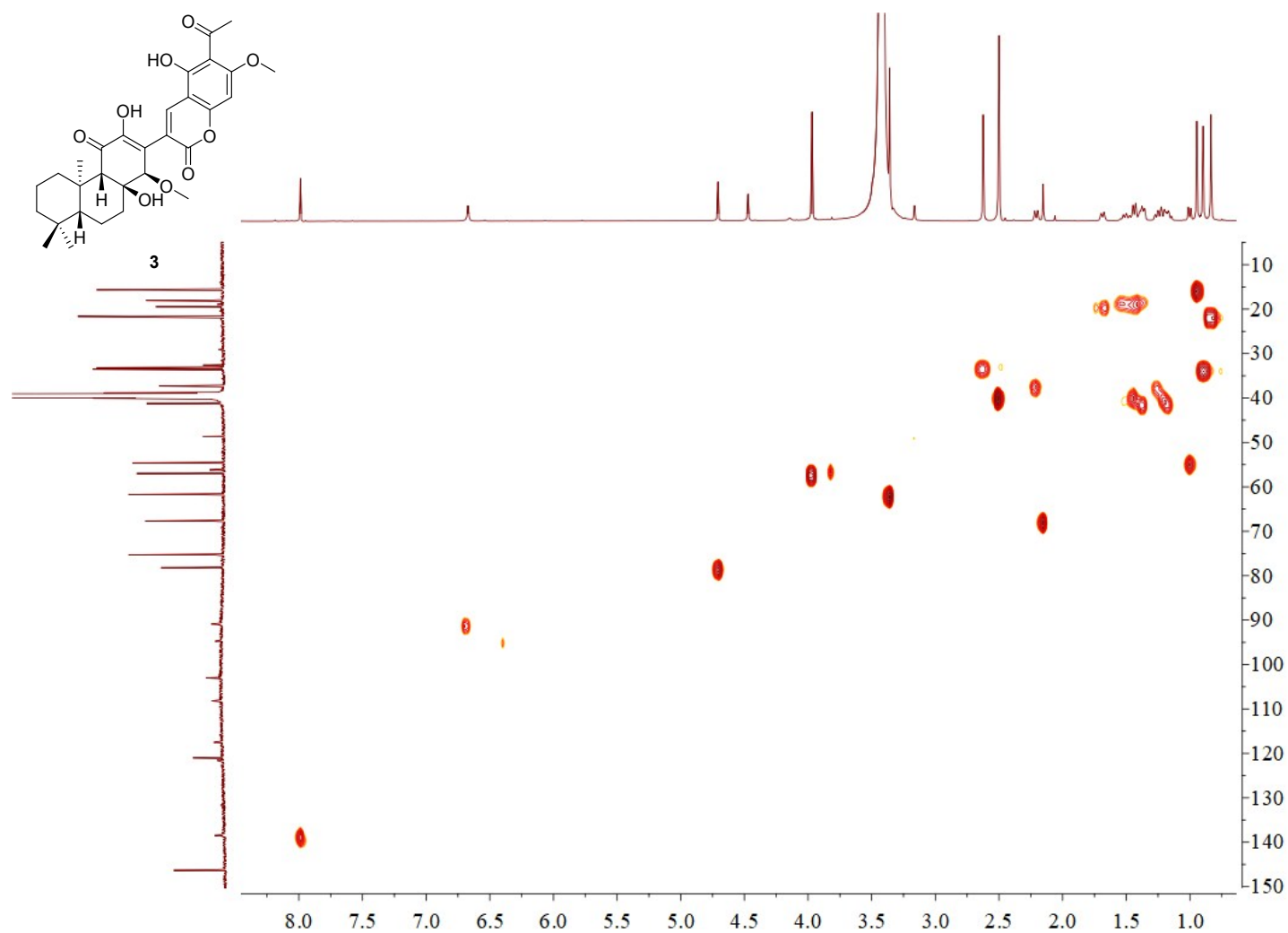


Figure S33. HSQC spectrum of fischernolide C (**3**) in DMSO- d_6

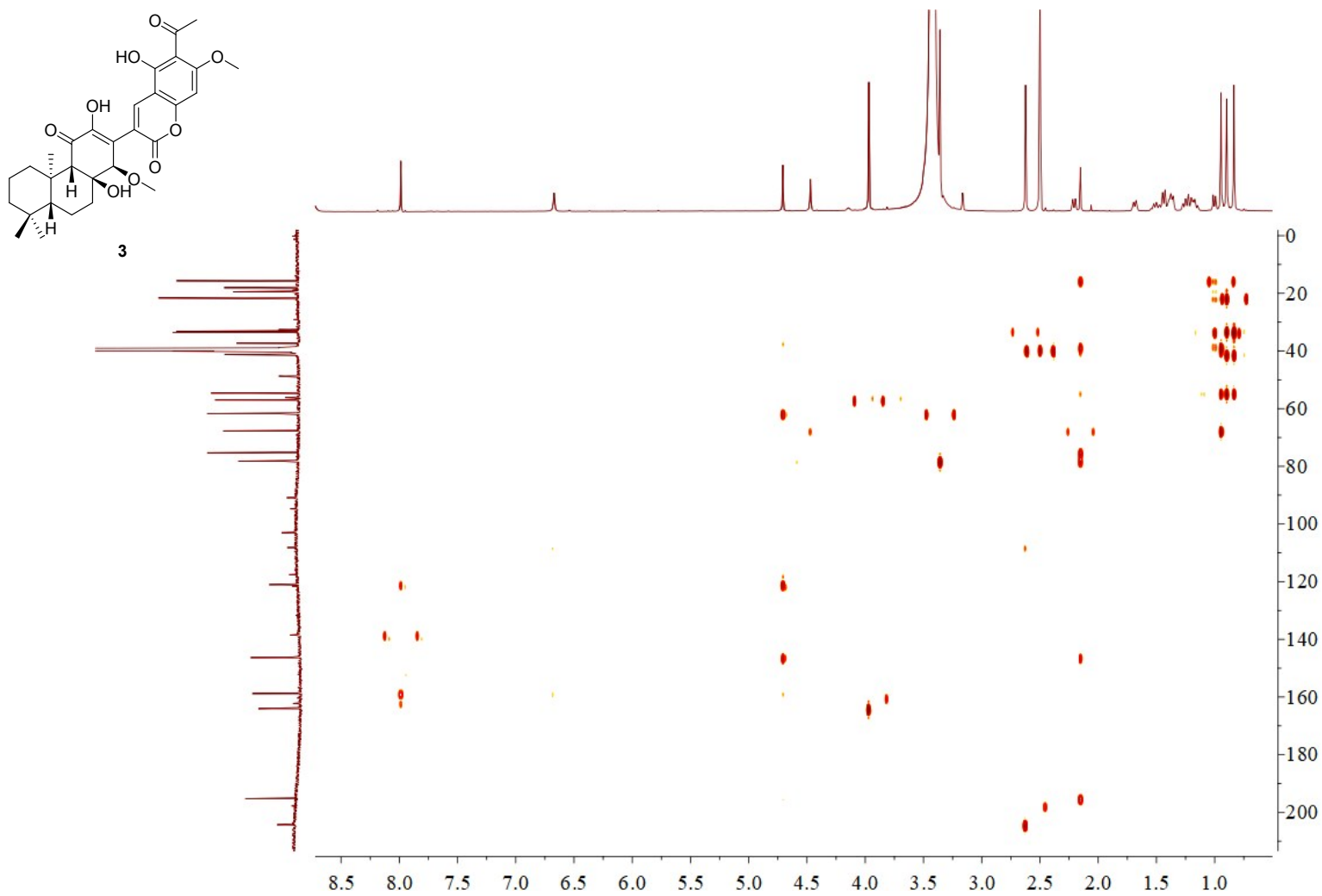


Figure S34. HMBC spectrum of fischernolide C (**3**) in DMSO-*d*₆

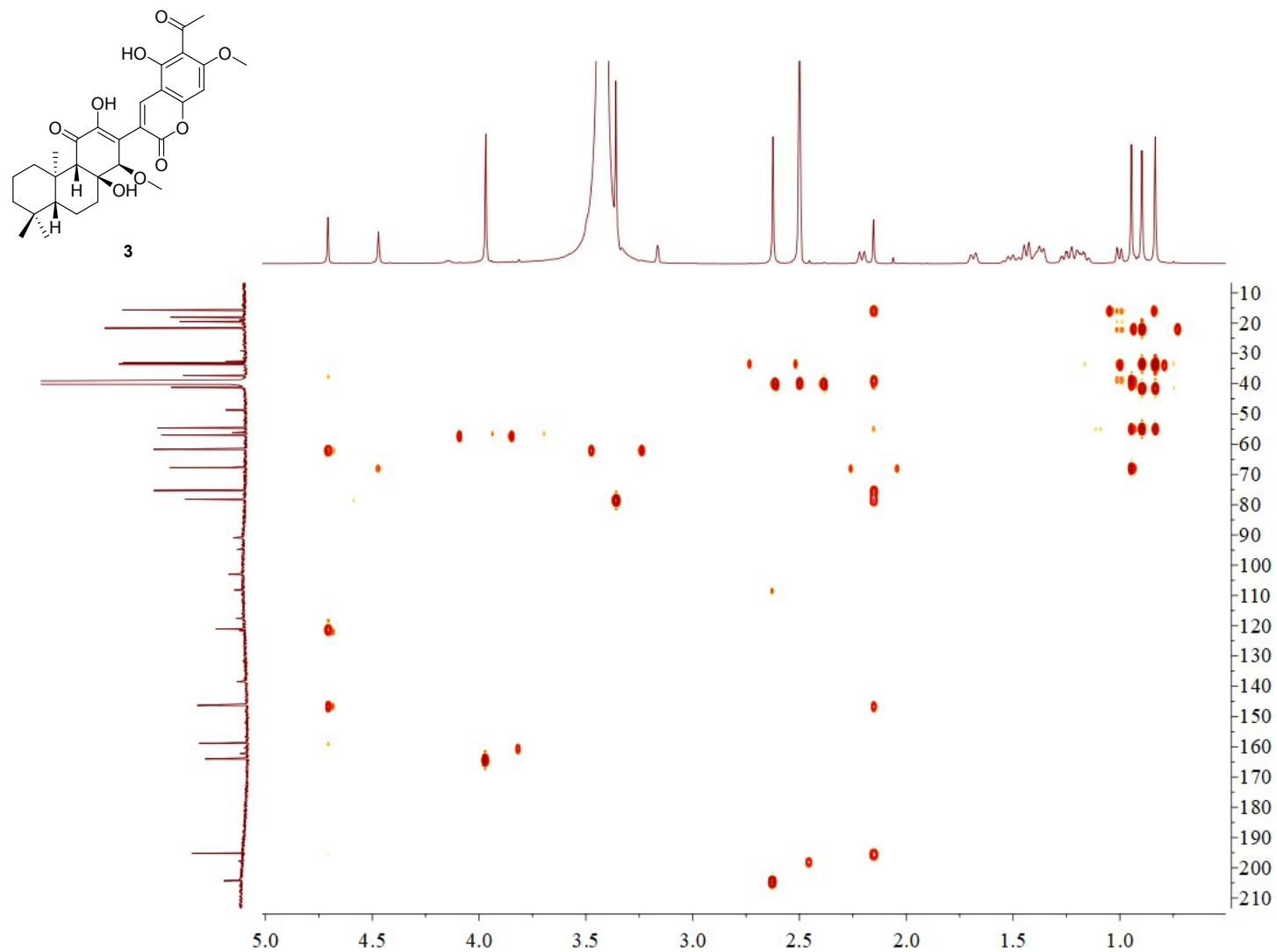


Figure S35. Enlarged HMBC spectrum of fischernolide C (**3**) in DMSO- d_6

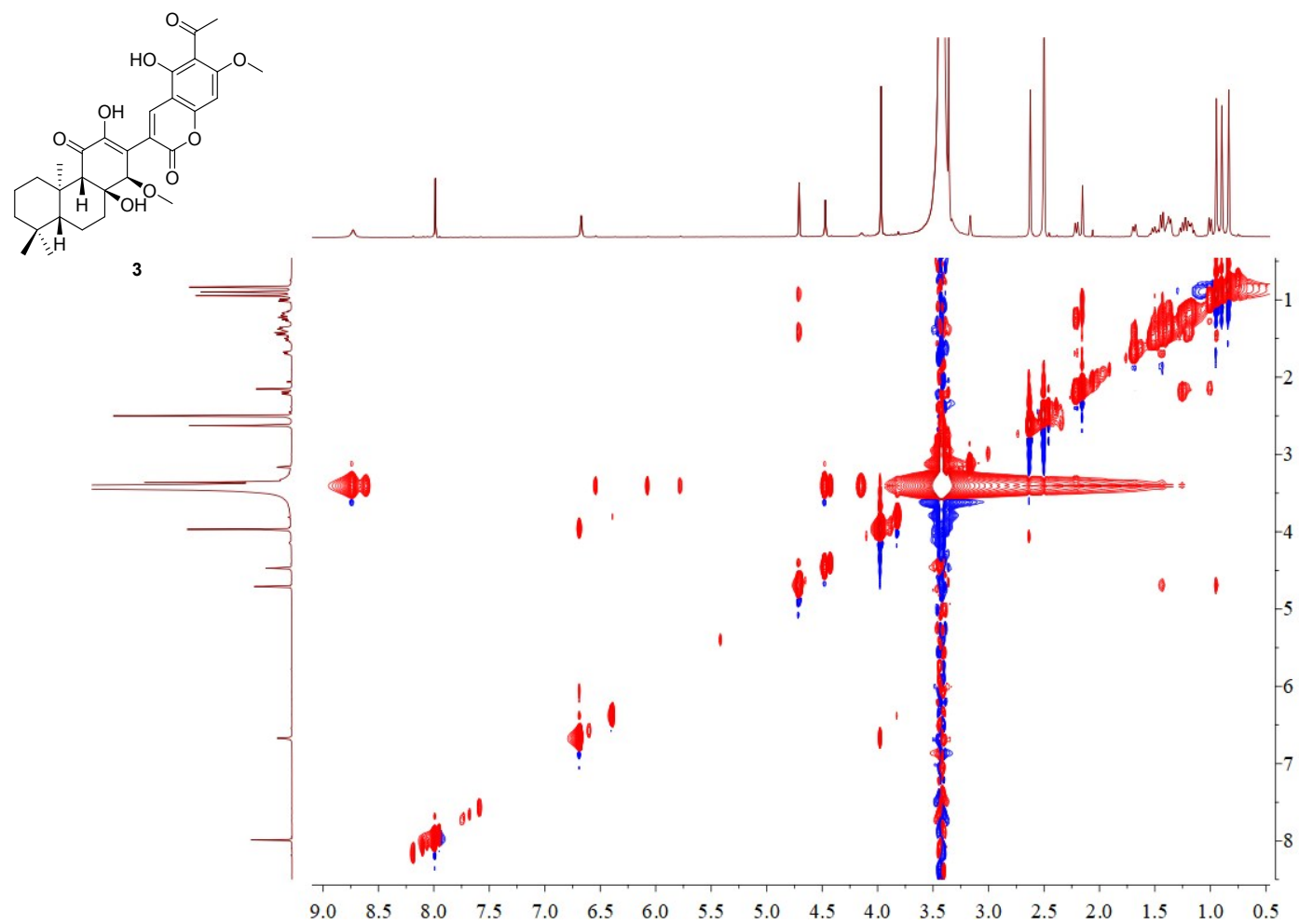


Figure S36. NOESY spectrum of fischernolide C (**3**) in DMSO-*d*₆ (600MHz)

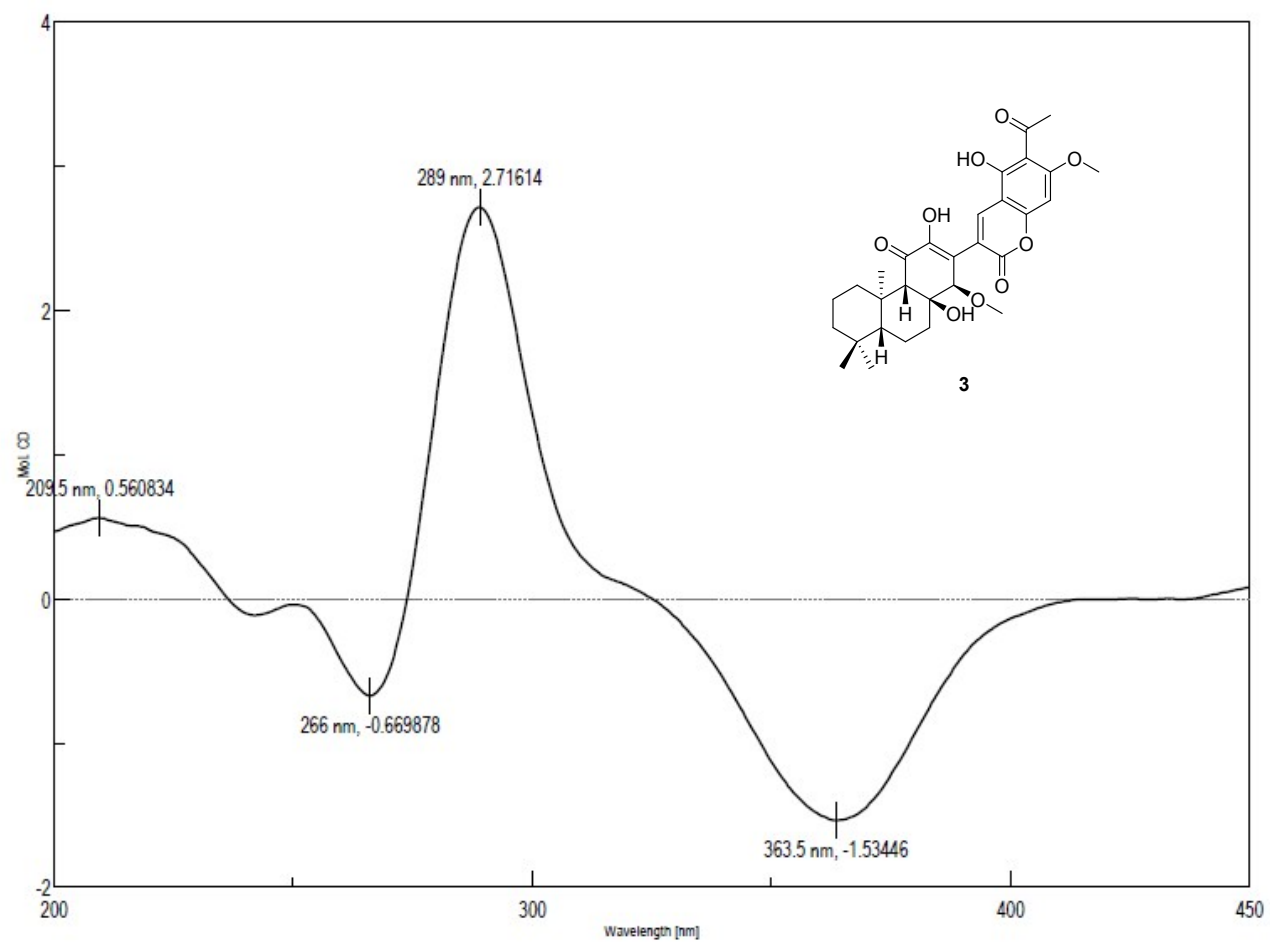


Figure S37. ECD spectrum of fischernolide C (**3**) in MeOH

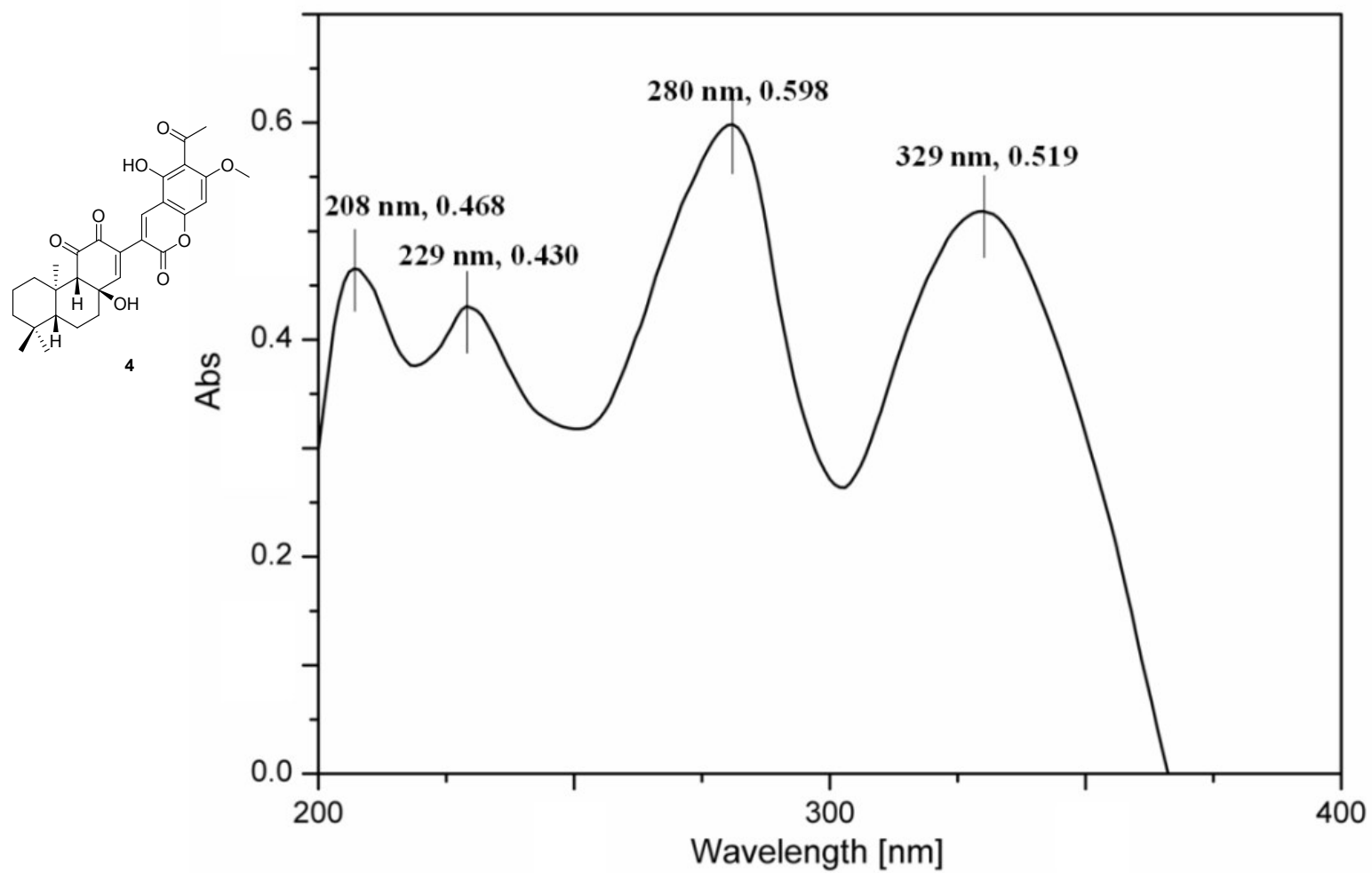


Figure S38. UV spectrum of fischernolide D (**4**) in MeOH

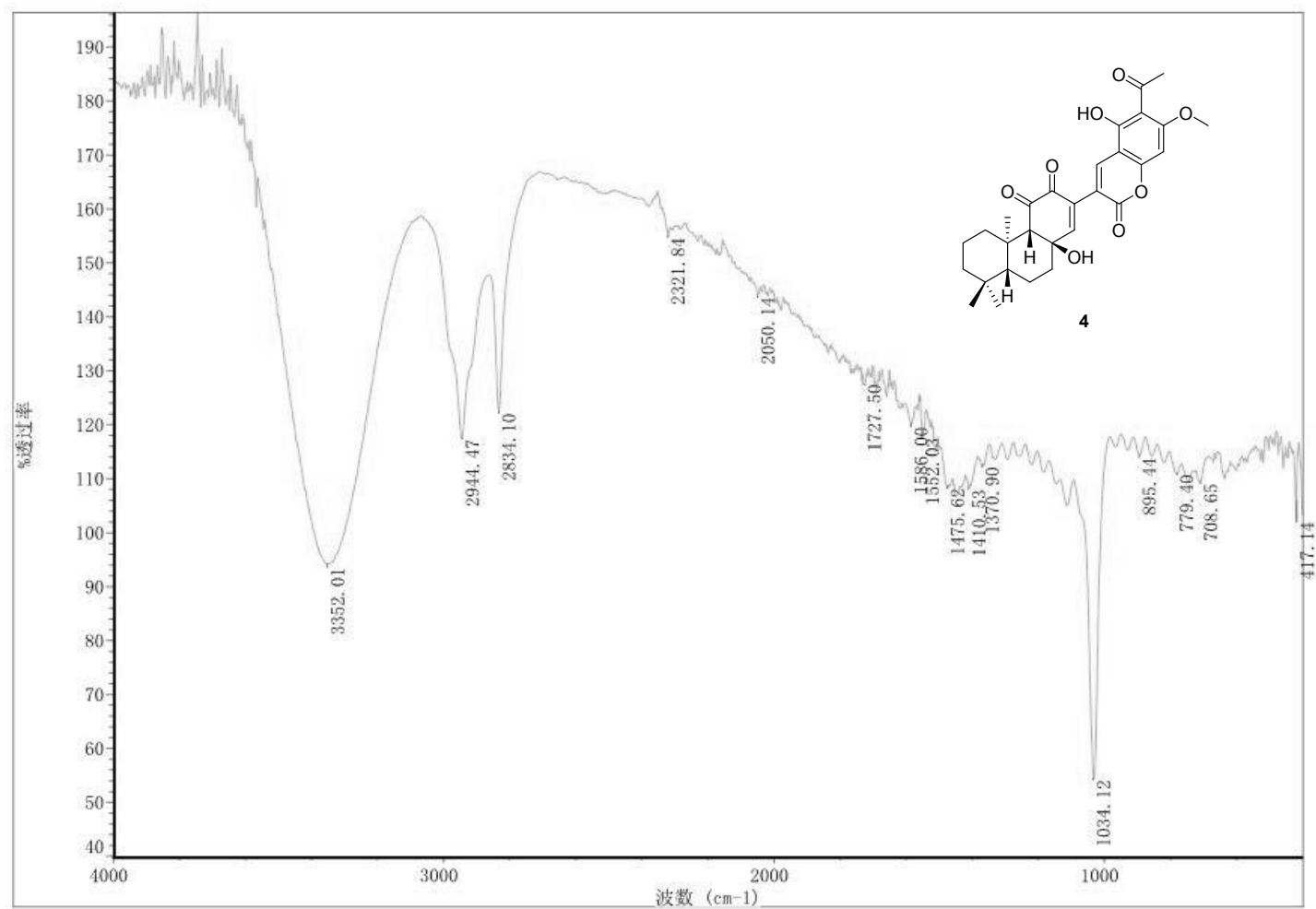


Figure S39. IR spectrum of fischernolide D (4)

AP-3_170831121015 #1436 RT: 11.07 AV: 1 NL: 1.50E8
T: FTMS - p ESI Full ms [200.0000-600.0000]

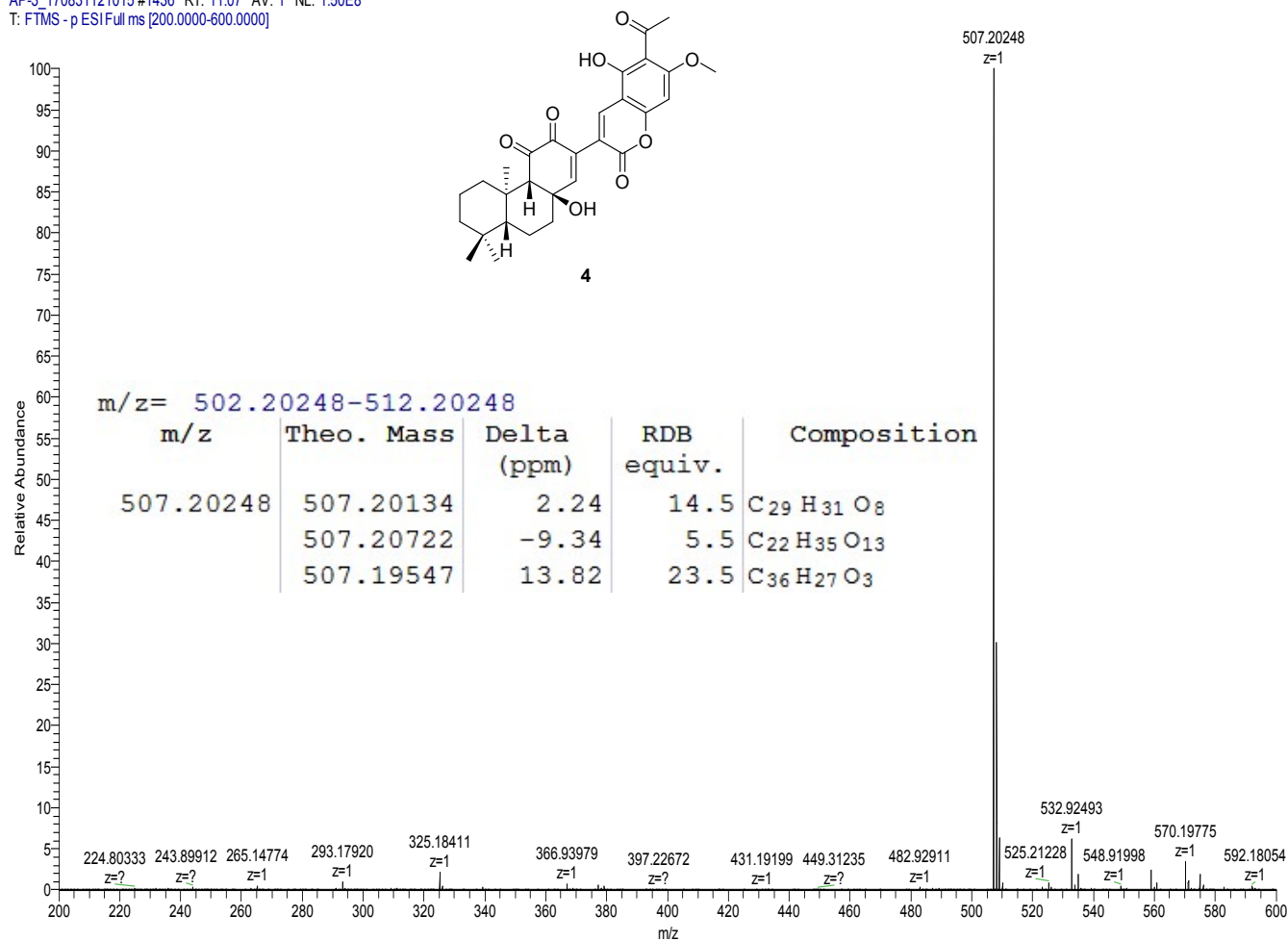


Figure S40. HRESIMS spectrum of fischernolide D (**4**)

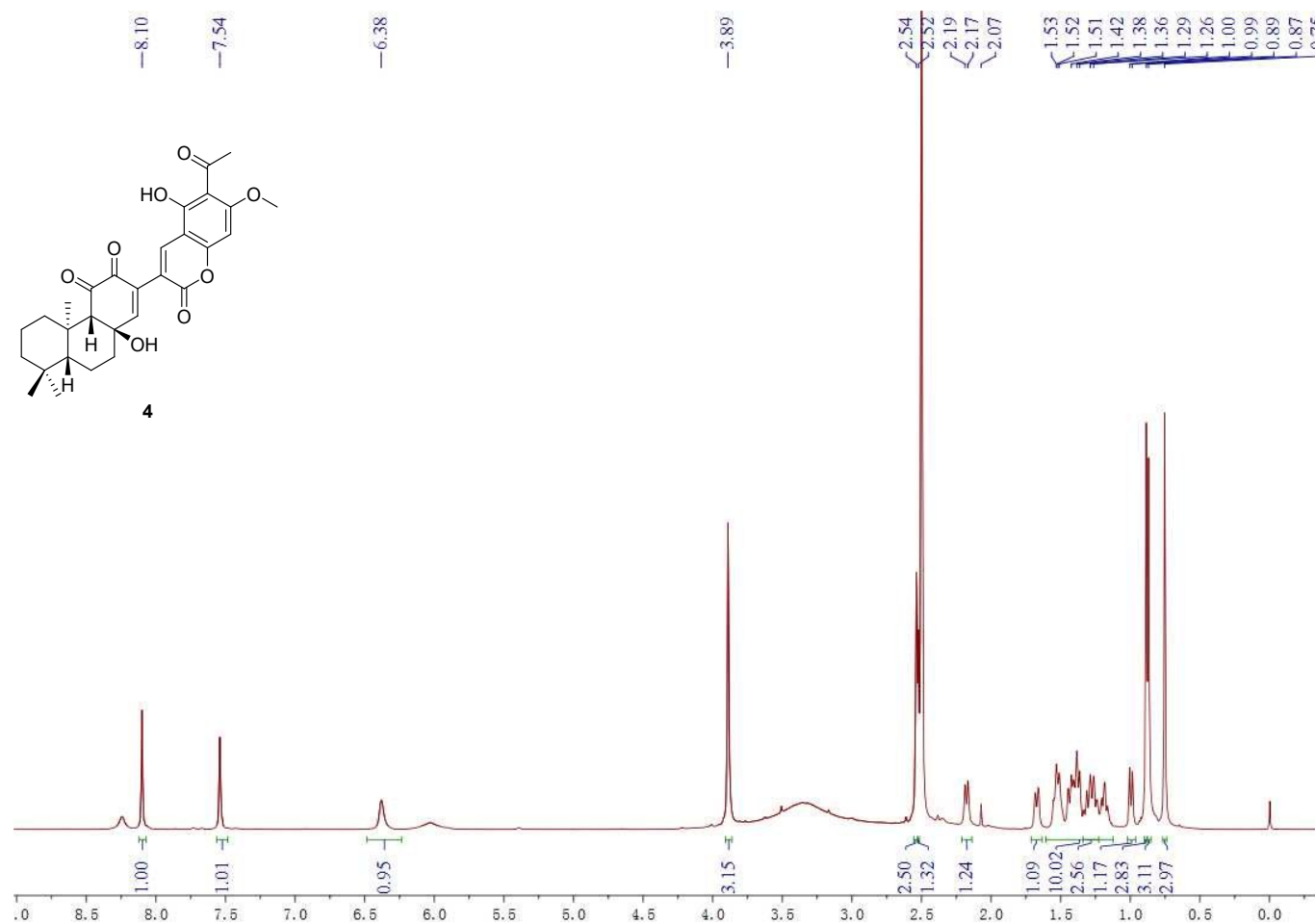


Figure S41. ^1H NMR spectrum of fischernolide D (**4**) in $\text{DMSO}-d_6$ (600 MHz)

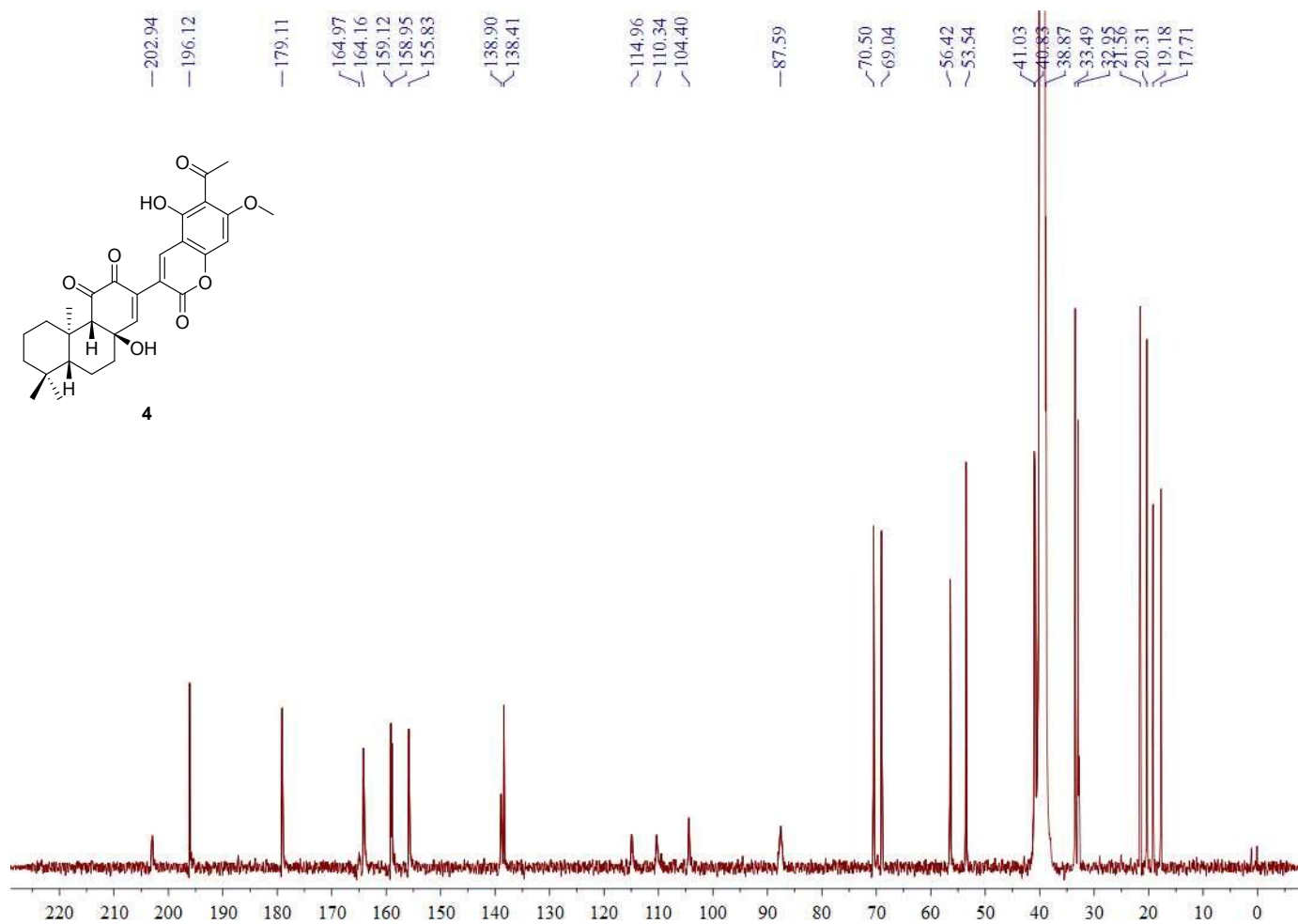


Figure S42. ^{13}C NMR spectrum of fischernolide D (**4**) in $\text{DMSO}-d_6$ (150 MHz)

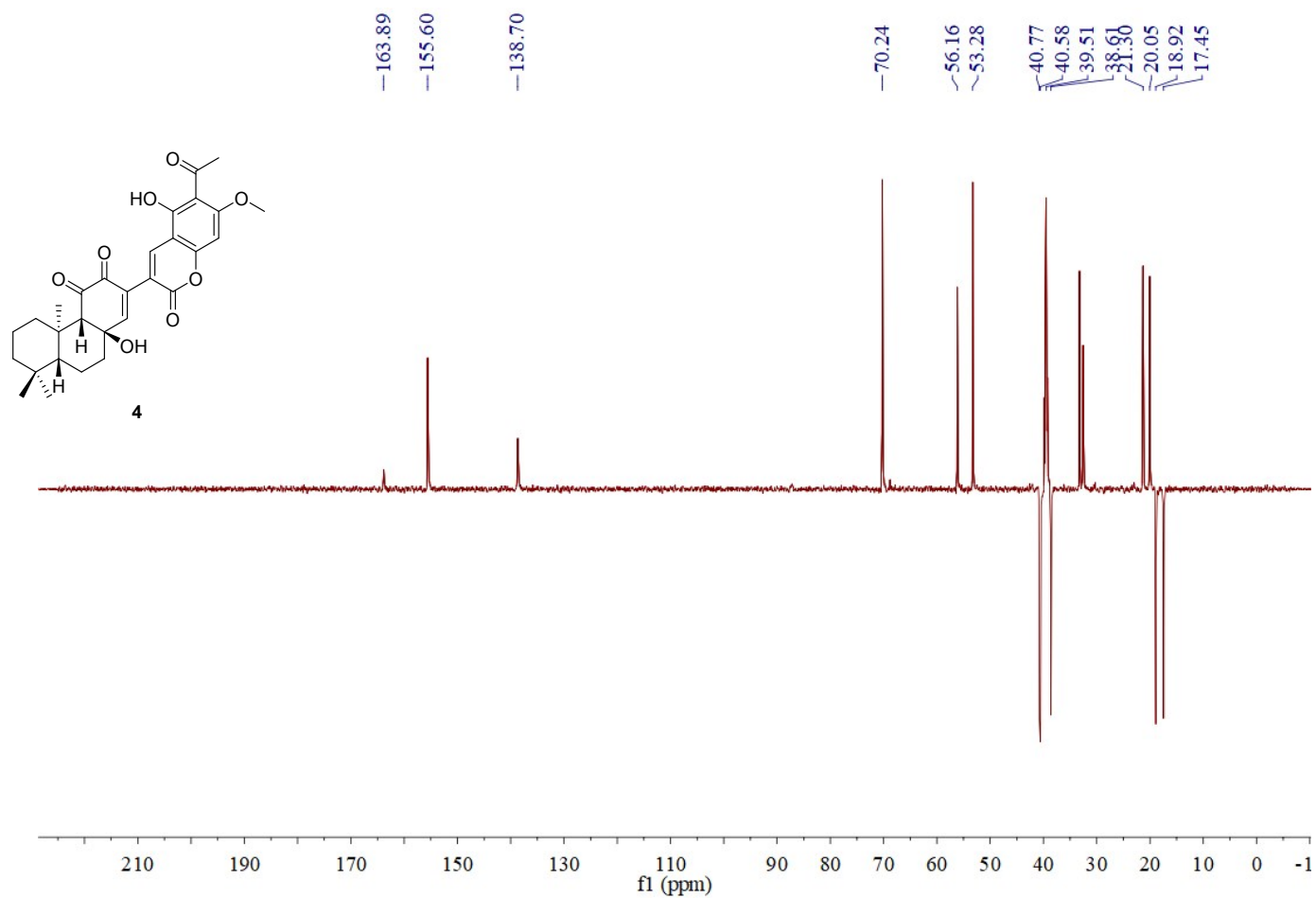


Figure S43. DEPT-135 spectrum of fischerinolide D (4) in DMSO- d_6 (150 MHz)

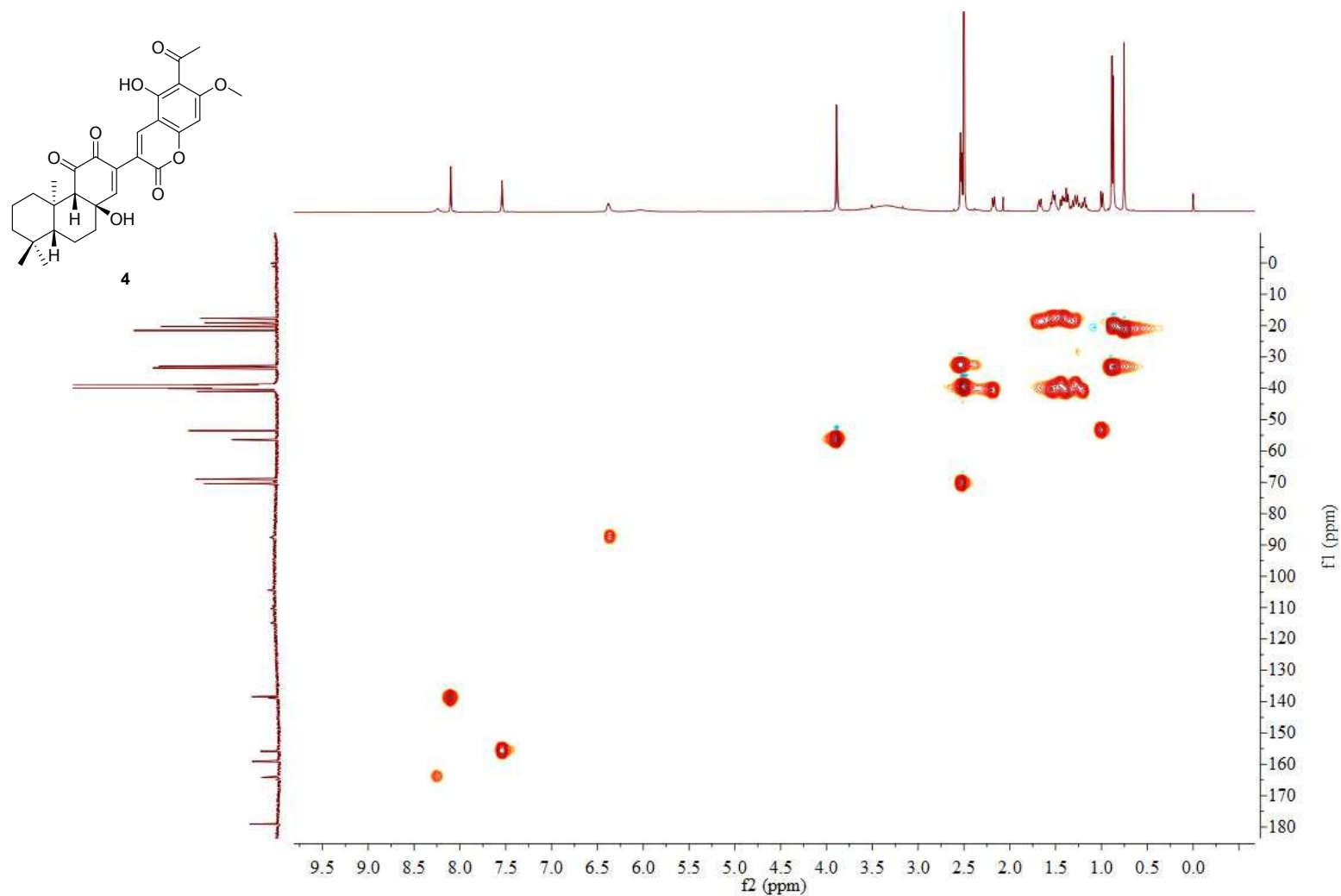


Figure S44. HSQC spectrum of fischernolide D (4) in $\text{DMSO-}d_6$

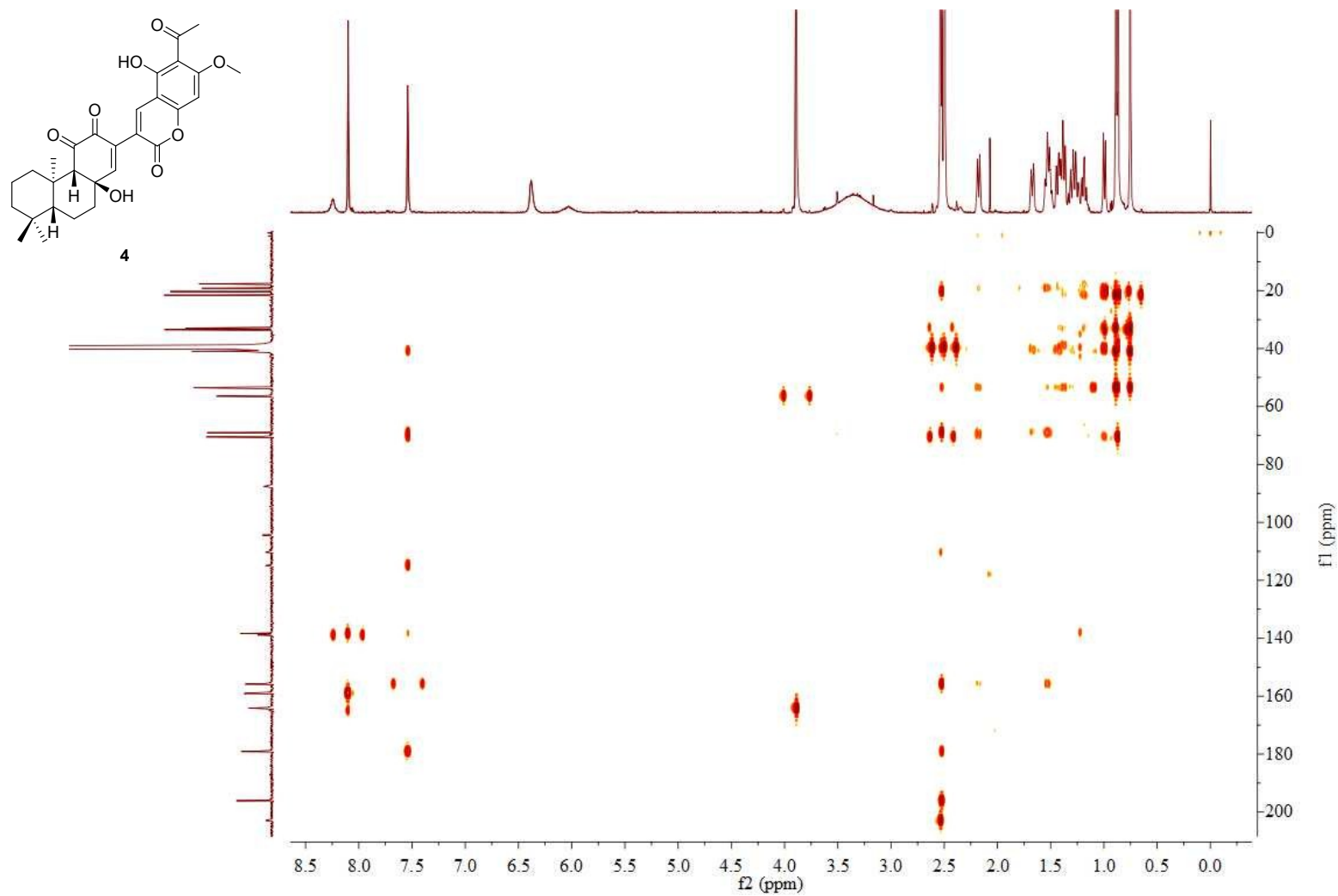


Figure S45. HMBC spectrum of fischernolide D (**4**) in DMSO-*d*₆

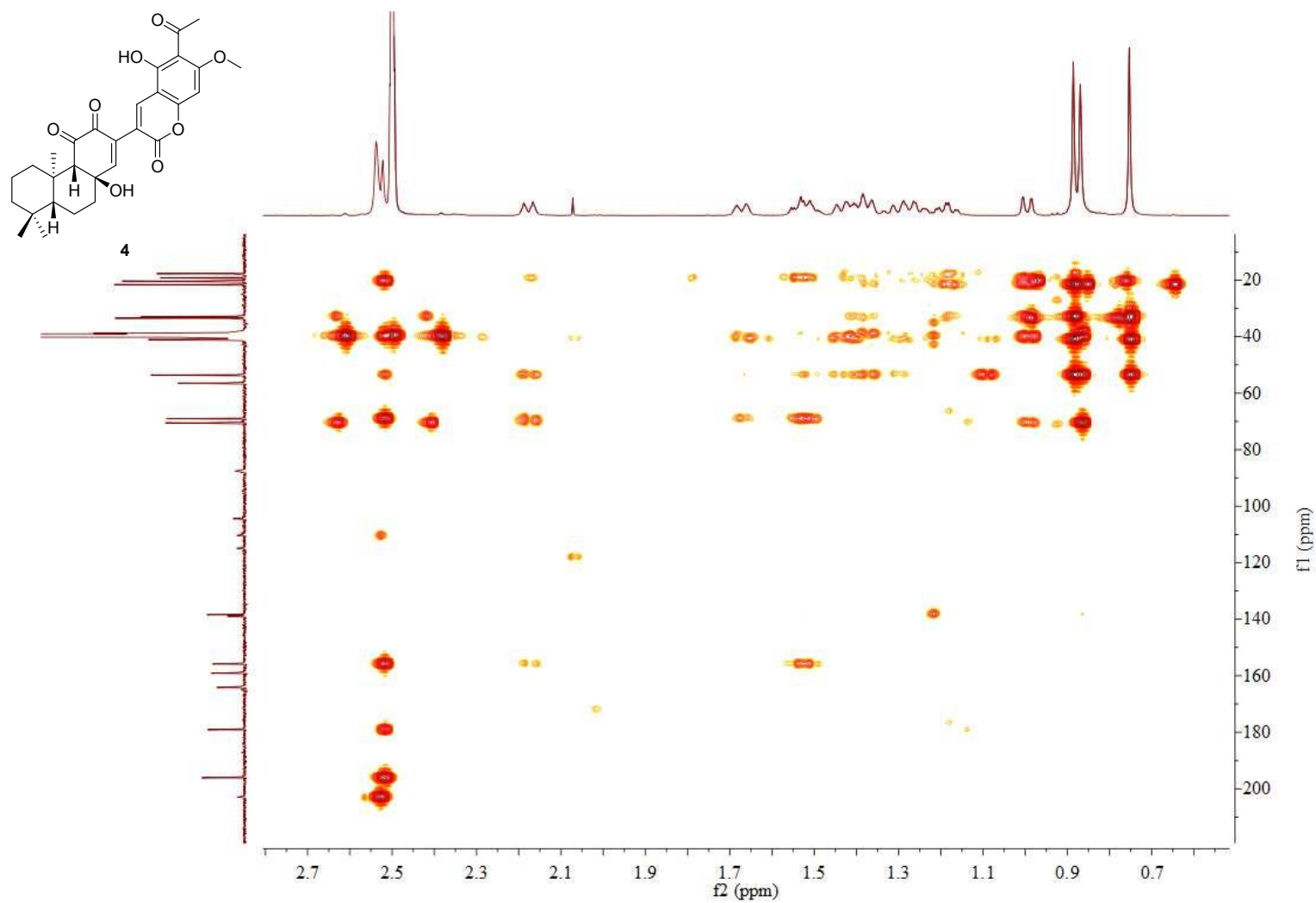


Figure S46. Enlarged HMBC spectrum of fischernolide D (**4**) in DMSO- d_6

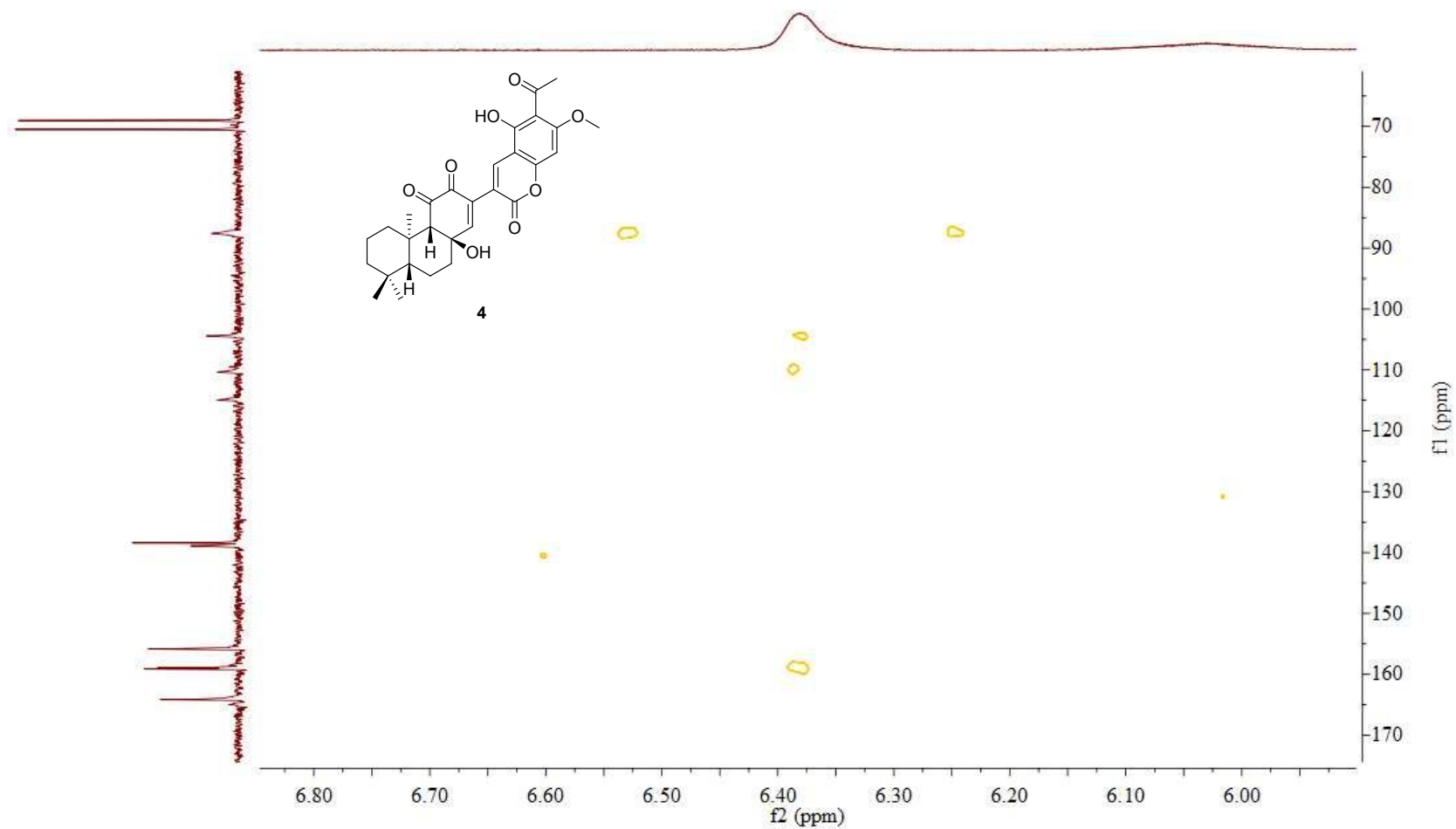


Figure S47. Enlarged HMBC spectrum of fischernolide D (4) in $\text{DMSO}-d_6$

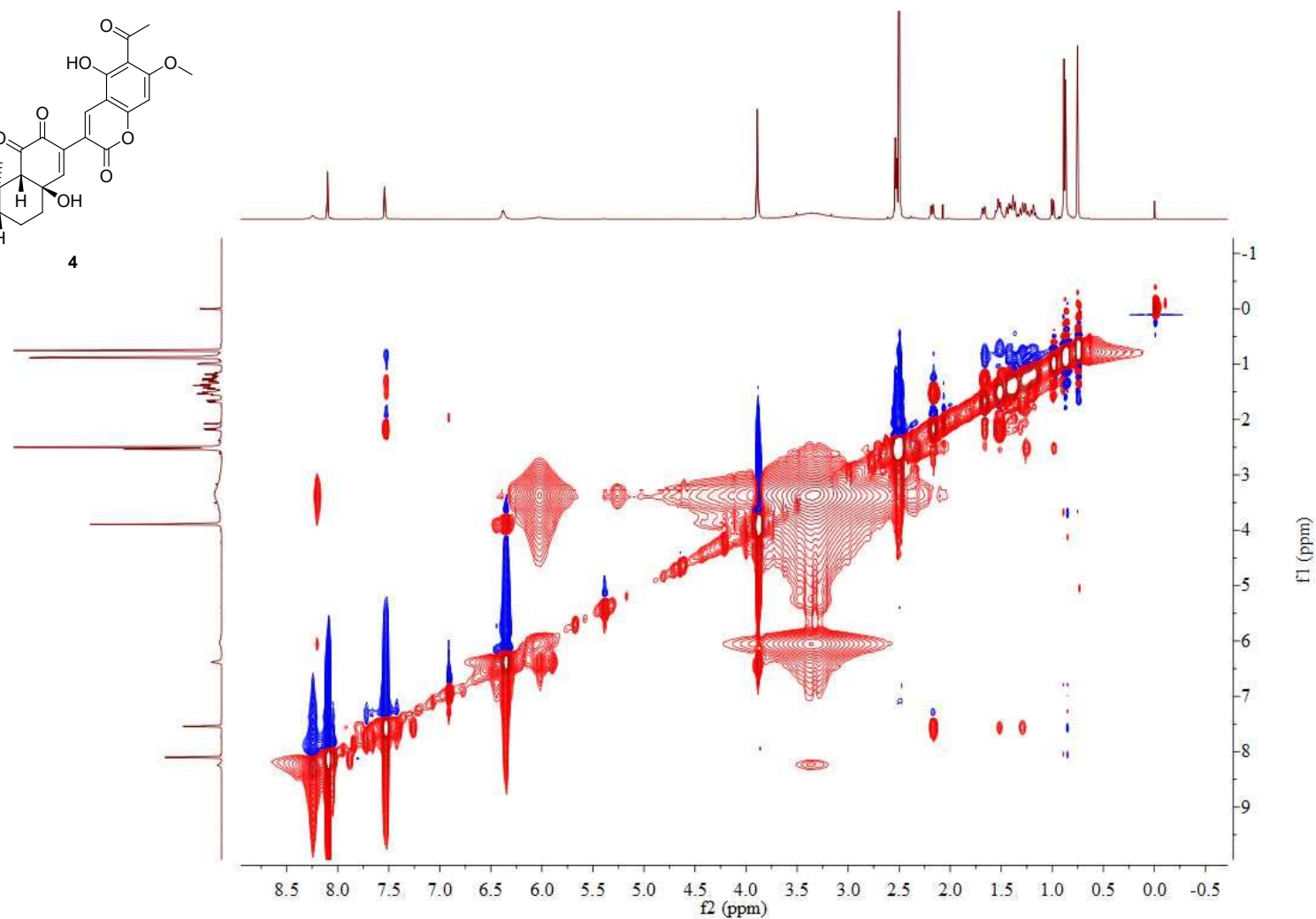
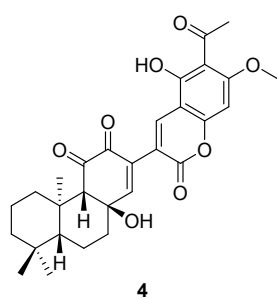


Figure S48. NOESY spectrum of fischernolide D (**4**) in DMSO- d_6 (600MHz)

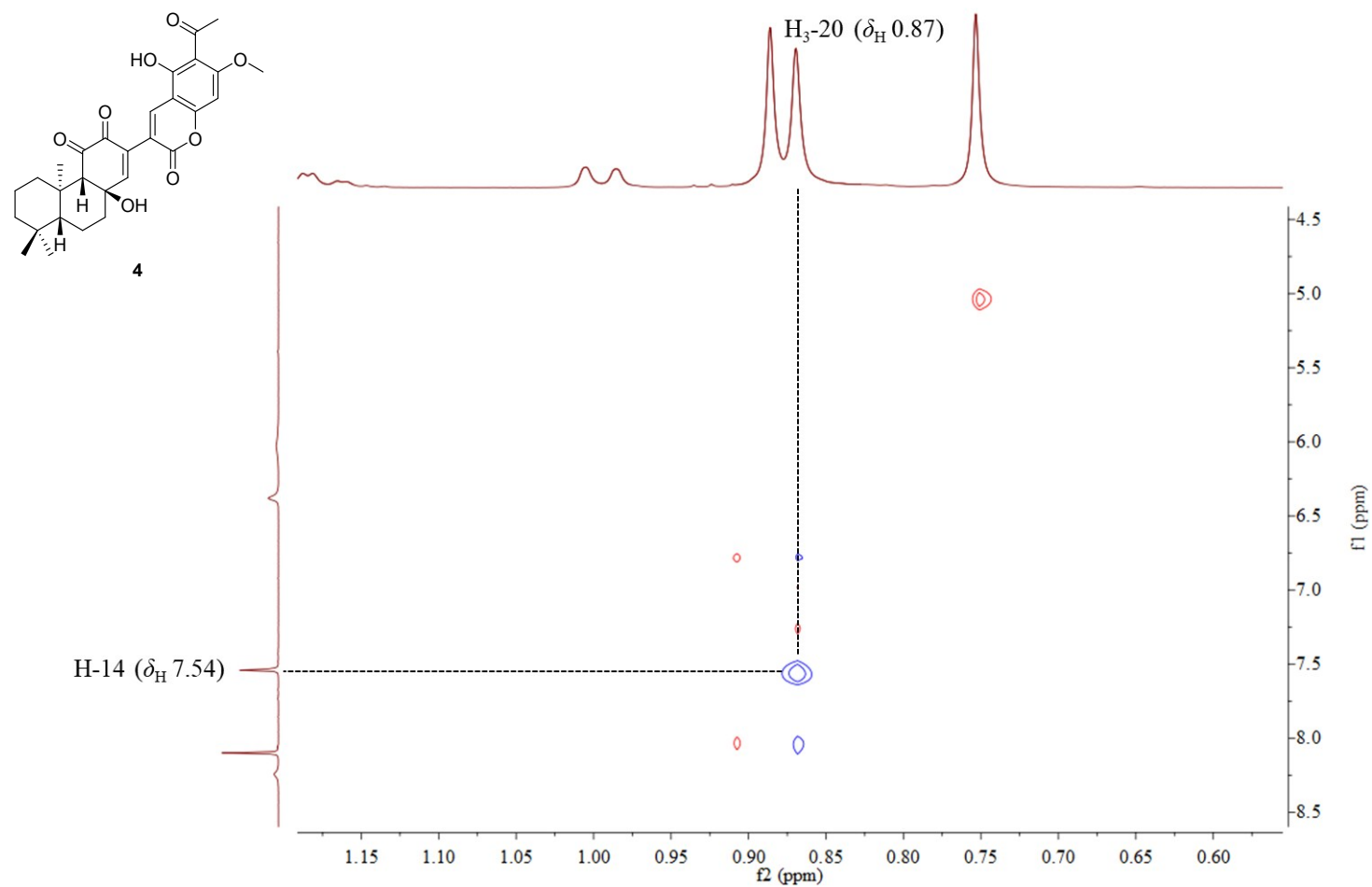


Figure S49. Enlarged NOESY spectrum of fischerinide D (4) in $\text{DMSO-}d_6$ (600MHz)

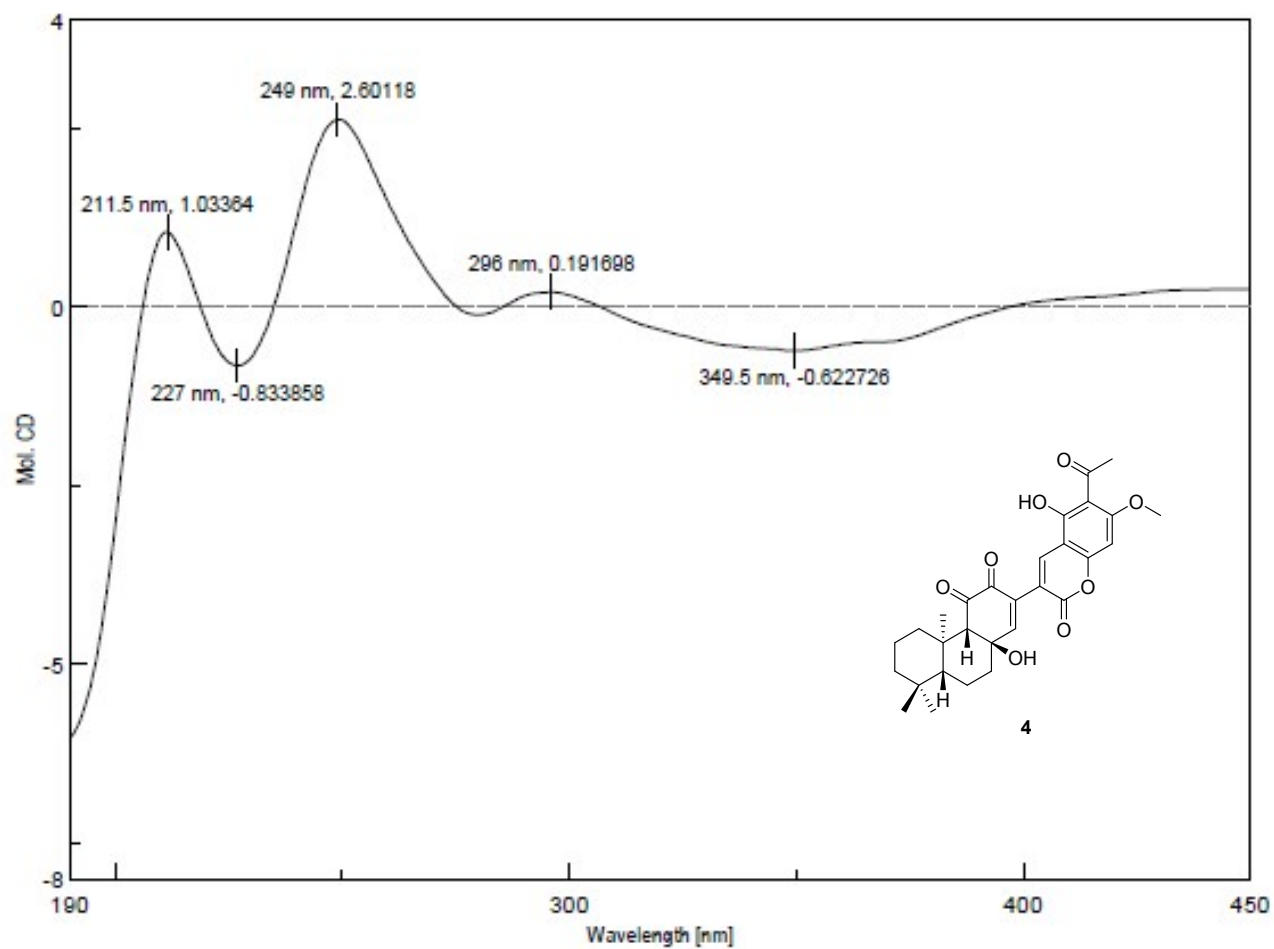


Figure S50. ECD spectrum-1 of fischernolide D (**4**) in MeOH

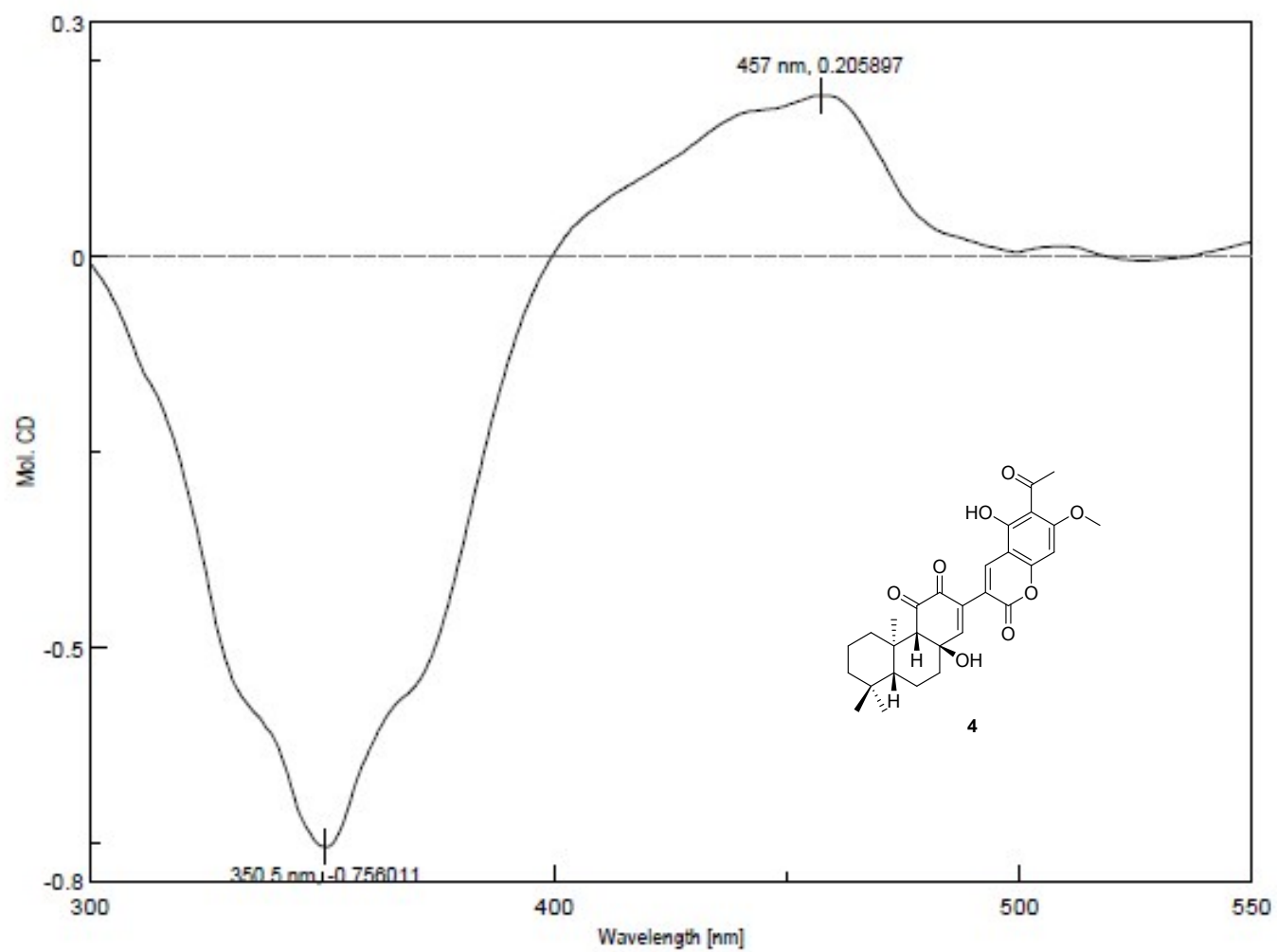


Figure S51. ECD spectrum-2 of fischernolide D (**4**) in MeOH