

Supporting Information

Chemical Constituents of the Deep-Sea-Derived *Penicillium citreonigrum* MCCC 3A00169 and Their Antiproliferative Effects

Zheng-Biao Zou ^{1,2,†}, Gang Zhang ^{3,†}, Yu-Qi Zhou ^{4,†}, Chun-Lan Xie ², Ming-Min Xie ², Lin Xu ², You-Jia Hao ², Lian-Zhong Luo ³, Xiao-Kun Zhang ^{4,*}, Xian-Wen Yang ^{2,*}, and Jun-Song Wang ^{1,*}

¹ Center for Molecular Metabolism, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, 200 Xiaolingwei Street, Nanjing 210094, China

² Key Laboratory of Marine Genetic Resources, Third Institute of Oceanography, Ministry of Natural Resources, 184 Daxue Road, Xiamen 361005, China

³ Xiamen Key Laboratory of Marine Medicinal Natural Products Resources; Fujian Province Universities and Colleges Engineering Research Center for Marine Biomedical Resource Utilization; Xiamen Medical College, 1999 Guankouzhong Road, Xiamen 361023, China

⁴ School of Pharmaceutical Sciences, Xiamen University, South Xiang'an Road, Xiamen, 361102, China

* Correspondence: wang.junsong@gmail.com (J.-S.W.); xkzhang@xmu.edu.cn (X.-K.Z.); yangxianwen@tio.org.cn (X.-W.Y.); Tel.: +86-25- 8431-5512 (J.-S.W.); +86-592-2181851 (X.-K.Z.); +86-592-2195319 (X.-W.Y.)

† These authors contributed equally to this work.

Content

Figure S1. Chemical structures of compounds 7–28.

Figure S2. HR-ESI-MS of citreoviridin J (1).

Figure S3. ¹H NMR spectrum (400 MHz, CD₃OD) of citreoviridin J (1).

Figure S4. ¹³C NMR and DEPT spectra (100 MHz, CD₃OD) of citreoviridin J (1).

Figure S5. HMQC spectrum (400 MHz, CD₃OD) of citreoviridin J (1).

Figure S6. ¹H-¹H COSY spectrum (400 MHz, CD₃OD) of citreoviridin J (1).

Figure S7. HMBC spectrum (400 MHz, CD₃OD) of citreoviridin J (1).

Figure S8. NOESY spectrum of (400 MHz, CD₃OD) citreoviridin J (1).

Figure S9. HR-ESI-MS of citreoviridin K (2).

Figure S10. ¹H NMR spectrum (400 MHz, CD₃OD) of citreoviridin K (2).

Figure S11. ¹³C NMR and DEPT (100 MHz, CD₃OD) of citreoviridin K (2).

Figure S12. HMQC spectrum (400 MHz, CD₃OD) of citreoviridin K (2).

Figure S13. ¹H-¹H COSY spectrum (400 MHz, CD₃OD) of citreoviridin K (2).

Figure S14. HMBC spectrum (400 MHz, CD₃OD) of citreoviridin K (2).

Figure S15. NOESY spectrum (400 MHz, CD₃OD) of citreoviridin K (2).

Figure S16. HR-ESI-MS of citreoviridin L (3).

Figure S17. ¹H NMR spectrum (400 MHz, CD₃OD) of citreoviridin L (3).

Figure S18. ¹³C NMR and DEPT (100 MHz, CD₃OD) of citreoviridin L (3).

Figure S19. HMQC spectrum (400 MHz, CD₃OD) of citreoviridin L (3).

Figure S20. ¹H-¹H COSY spectrum (400 MHz, CD₃OD) of citreoviridin L (3).

Figure S21. HMBC spectrum (400 MHz, CD₃OD) of citreoviridin L (**3**).

Figure S22. NOESY spectrum (400 MHz, CD₃OD) of citreoviridin L (**3**).

Figure S23. HR-ESI-MS of citreoviridin M (**4**).

Figure S24. ¹H NMR spectrum (400 MHz, CD₃OD) of citreoviridin M (**4**).

Figure S25. ¹³C NMR and DEPT (100 MHz, CD₃OD) of citreoviridin M (**4**).

Figure S26. HMQC spectrum (400 MHz, CD₃OD) of citreoviridin M (**4**).

Figure S27. ¹H-¹H COSY spectrum (400 MHz, CD₃OD) of citreoviridin M (**4**).

Figure S28. HMBC spectrum (400 MHz, CD₃OD) of citreoviridin M (**4**).

Figure S29. NOESY spectrum (400 MHz, CD₃OD) of citreoviridin M (**4**).

Figure S30. ¹H NMR spectrum (400 MHz, CD₃OD) of citreoviridins N and O (**5** and **6**).

Figure S31. Amplified ¹H NMR spectrum (400 MHz, CD₃OD) of citreoviridins N and O (**5** and **6**).

Figure S32. ¹³C NMR and DEPT (100 MHz, CD₃OD) of citreoviridins N and O (**5** and **6**).

Figure S33. Amplified ¹³C NMR spectrum (100 MHz, CD₃OD) of citreoviridins N and O (**5** and **6**).

Figure S34. HMQC spectrum (400 MHz, CD₃OD) of citreoviridins N and O (**5** and **6**).

Figure S35. ¹H-¹H COSY spectrum (400 MHz, CD₃OD) of citreoviridins N and O (**5** and **6**).

Figure S36. HMBC spectrum (400 MHz, CD₃OD) of citreoviridins N and O (**5** and **6**).

Figure S37. NOESY spectrum (400 MHz, CD₃OD) of citreoviridins N and O (**5** and **6**).

Figure S38. HR-ESI-MS of citreoviridin N (**5**).

Figure S39. ¹H NMR spectrum (400 MHz, CD₃OD) of citreoviridin N (**5**).

Figure S40. ¹H-¹H COSY spectrum (400 MHz, CD₃OD) of citreoviridin N (**5**).

Figure S41. NOESY spectrum (400 MHz, CD₃OD) of citreoviridin N (**5**).

Figure S42. HR-ESI-MS of citreoviridin O (**6**).

Figure S43. ¹H NMR spectrum (400 MHz, CD₃OD) of citreoviridin O (**6**).

Figure S44. ¹H-¹H COSY spectrum (400 MHz, CD₃OD) of citreoviridin O (**6**).

Figure S45. NOESY spectrum (400 MHz, CD₃OD) of citreoviridin O (**6**).

Figure S46. HR-ESI-MS of pyrenocine A (**7**).

Figure S47. ¹H NMR spectrum (400 MHz, CD₃OD) of pyrenocine A (**7**).

Figure S48. ¹³C NMR spectrum (100 MHz, CD₃OD) of pyrenocine A (**7**).

Figure S49. HR-ESI-MS of terrein (**14**).

Figure S50. ¹H NMR spectrum (400 MHz, CD₃OD) of terrein (**14**).

Figure S51. ¹³C NMR spectrum (100 MHz, CD₃OD) of terrein (**14**).

Figure S52. HR-ESI-MS of citreoviridin (**20**).

Figure S53. ¹H NMR spectrum (400 MHz, CD₃OD) of citreoviridin (**20**).

Figure S54. ¹³C NMR spectrum (100 MHz, CD₃OD) of citreoviridin (**20**).

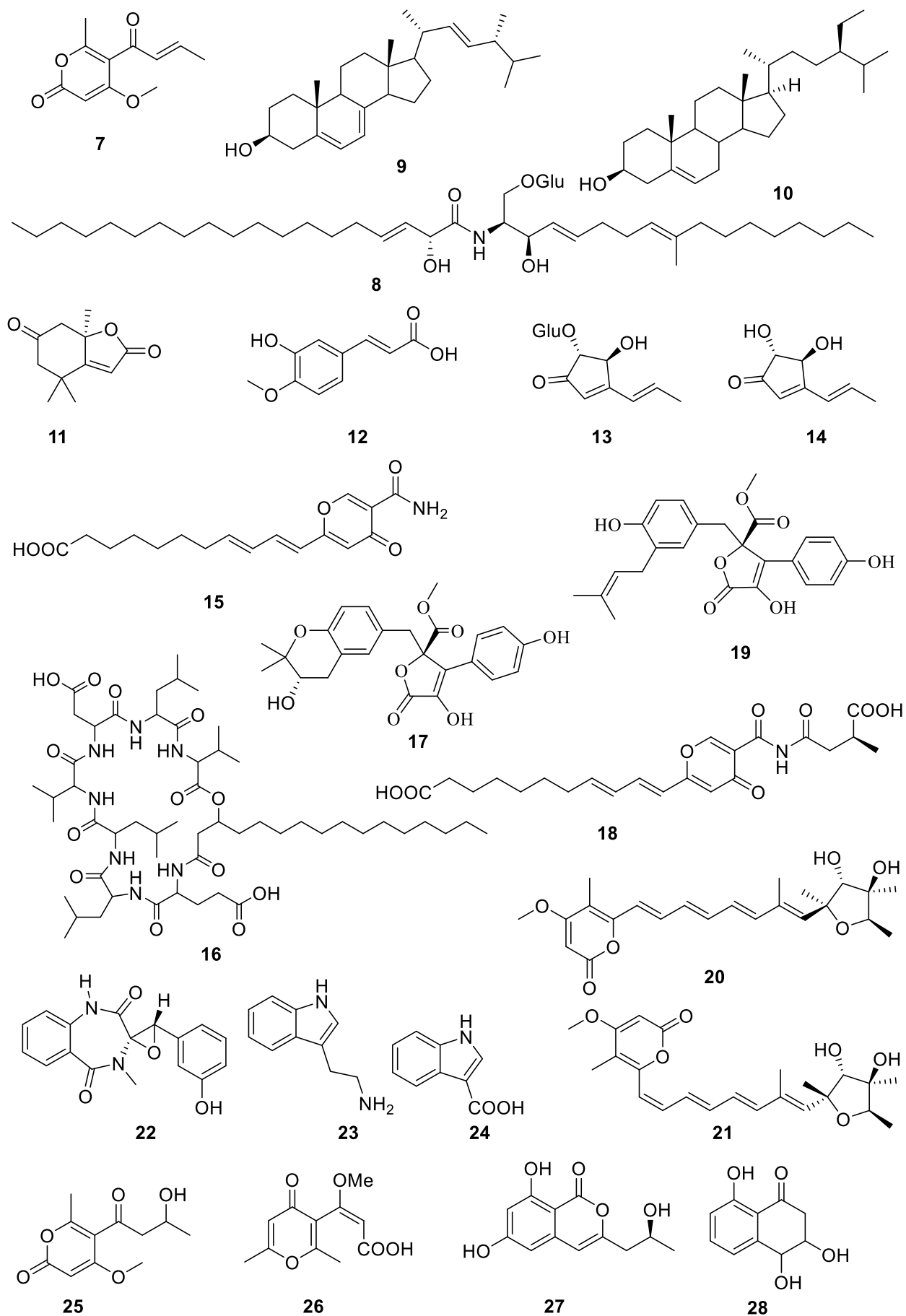


Figure S1 Chemical structures of compounds 7–28.

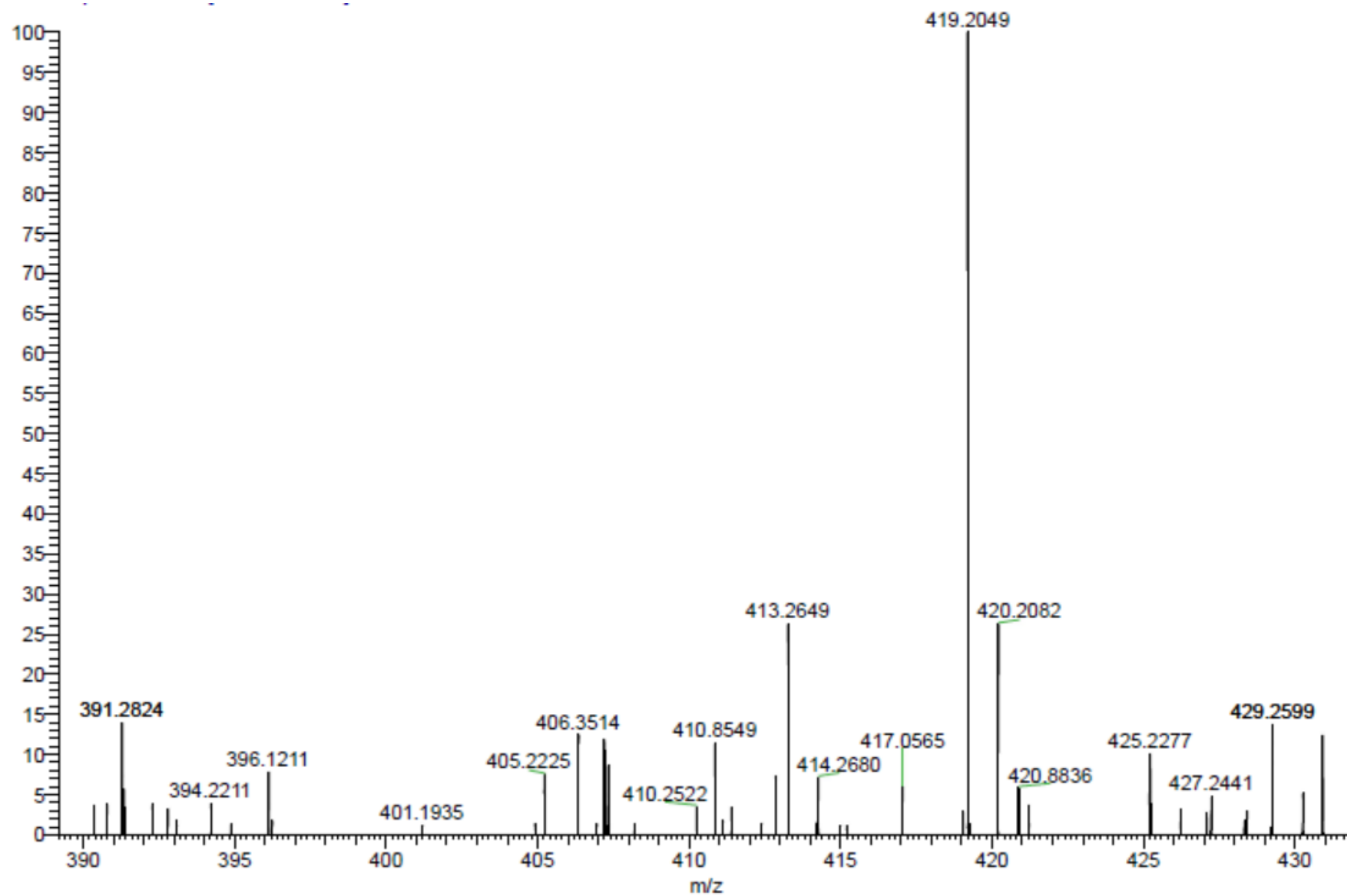


Figure S2. HR-ESI-MS of citreoviridin J (1)

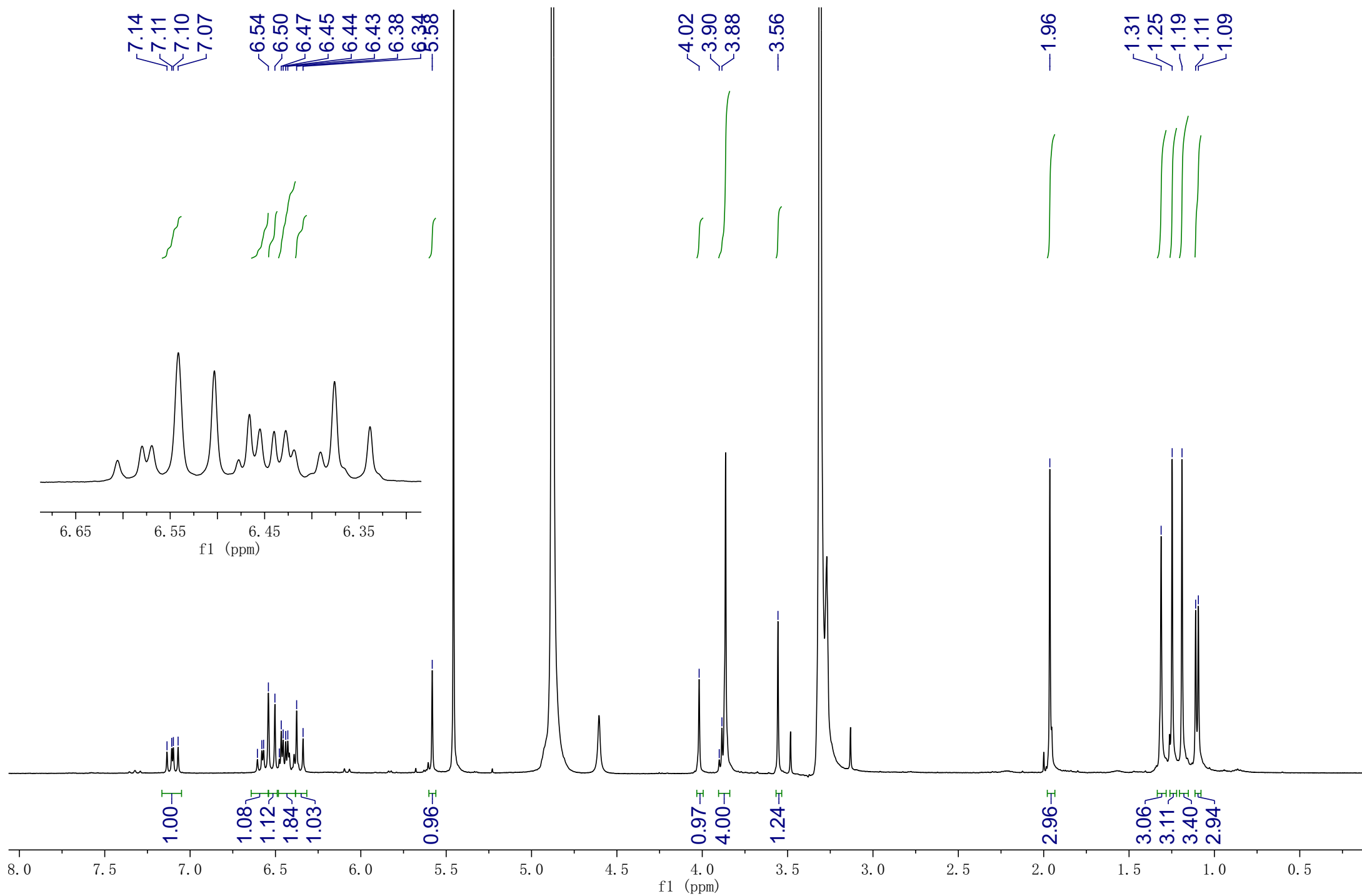


Figure S3. ^1H NMR spectrum (400 MHz, CD_3OD) of citreoviridin J (**1**)

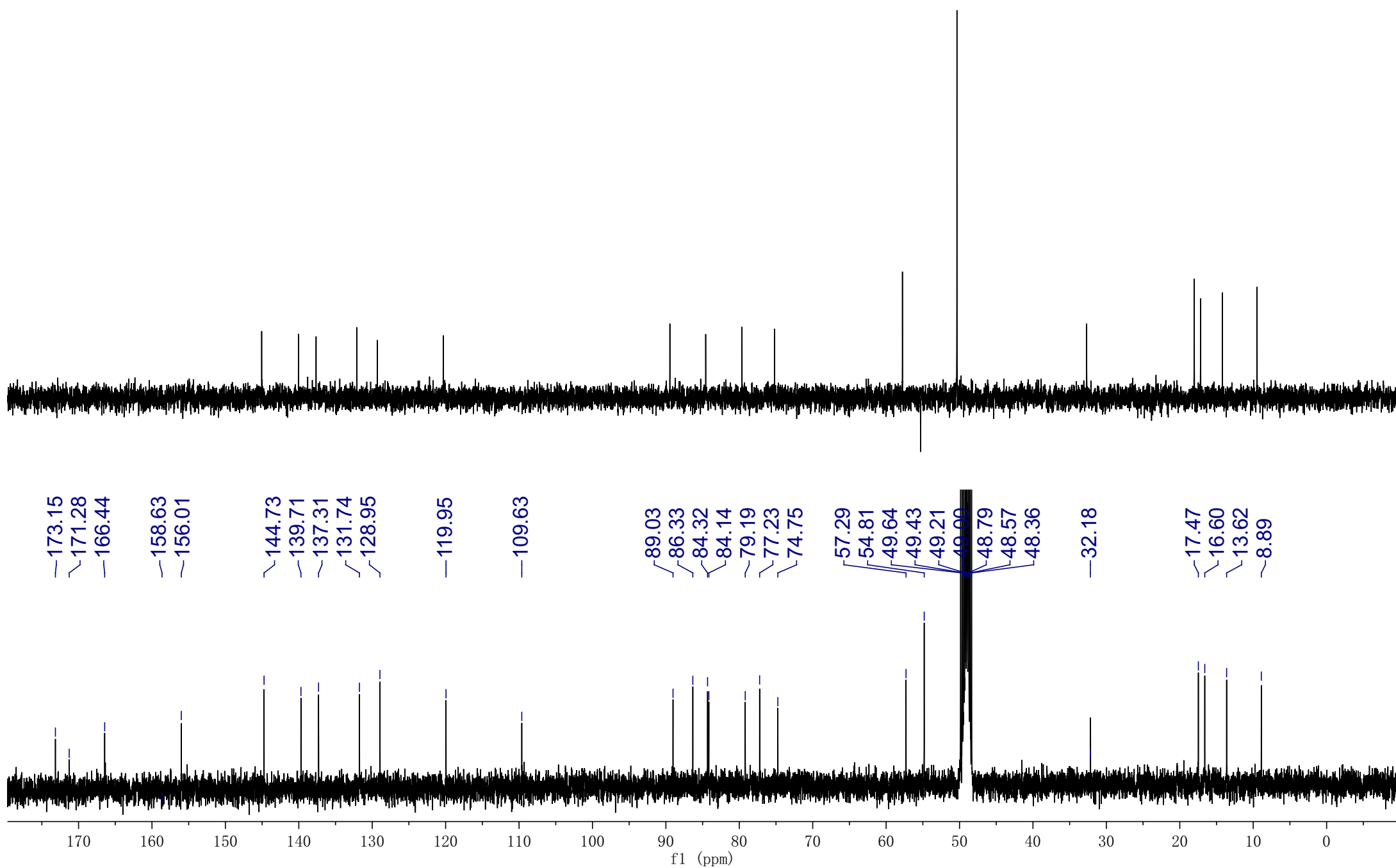


Figure S4. ¹³C NMR and DEPT spectra (100 MHz, CD₃OD) of citreoviridin J (**1**)

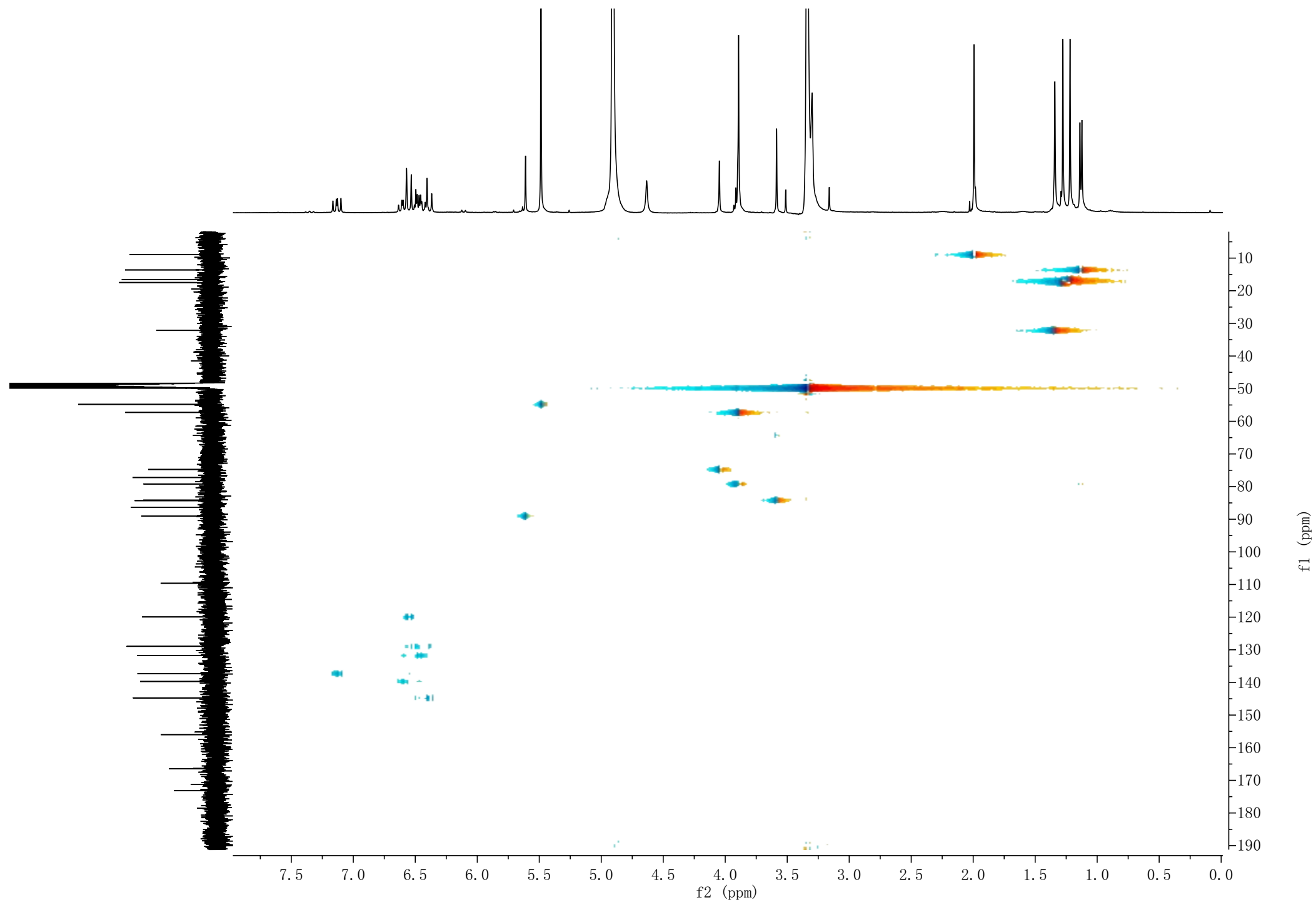


Figure S5. HMQC spectrum (400 MHz, CD₃OD) of citreoviridin J (**1**)

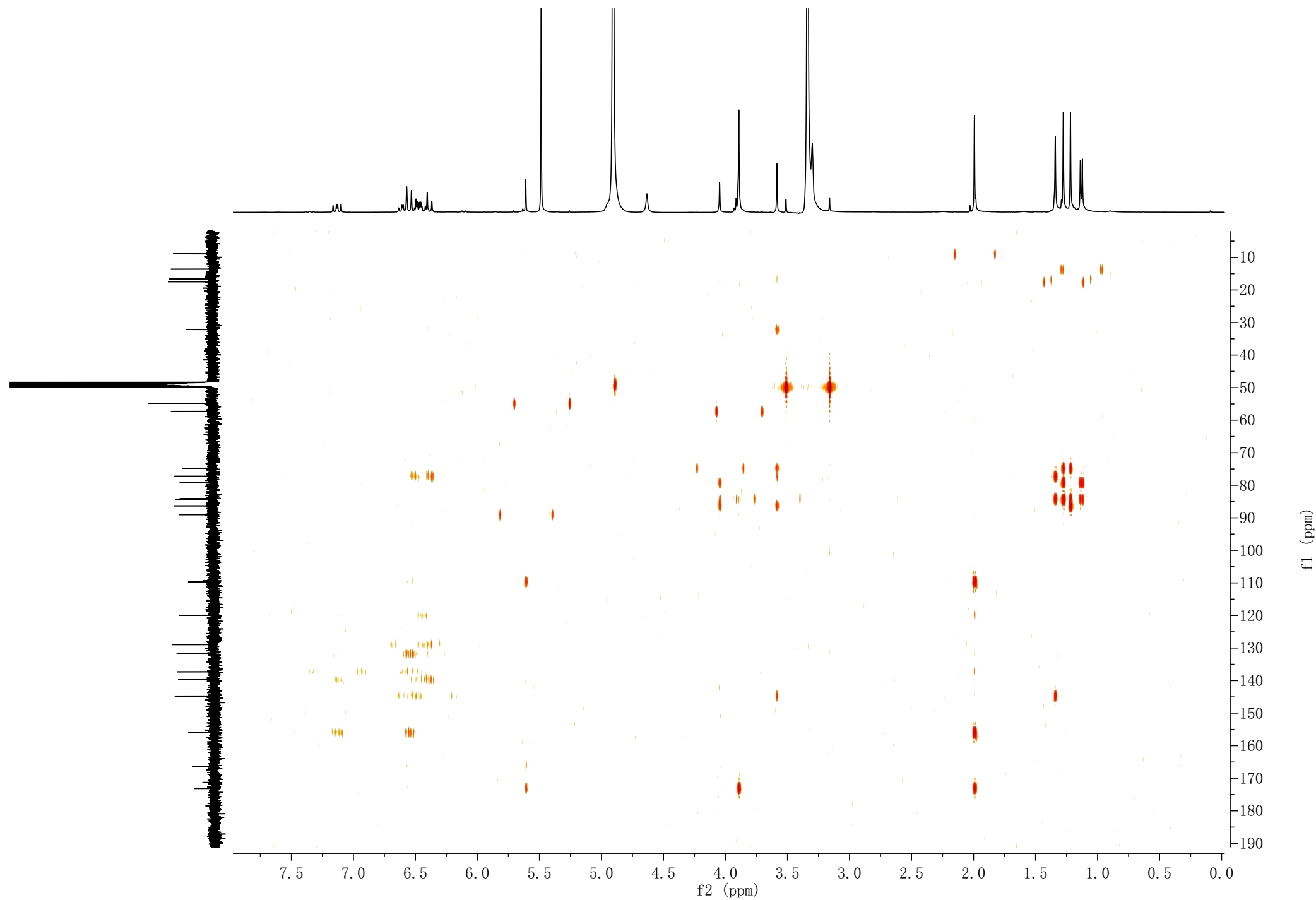


Figure S7. HMBC spectrum (400 MHz, CD₃OD) of citreoviridin J (**1**)

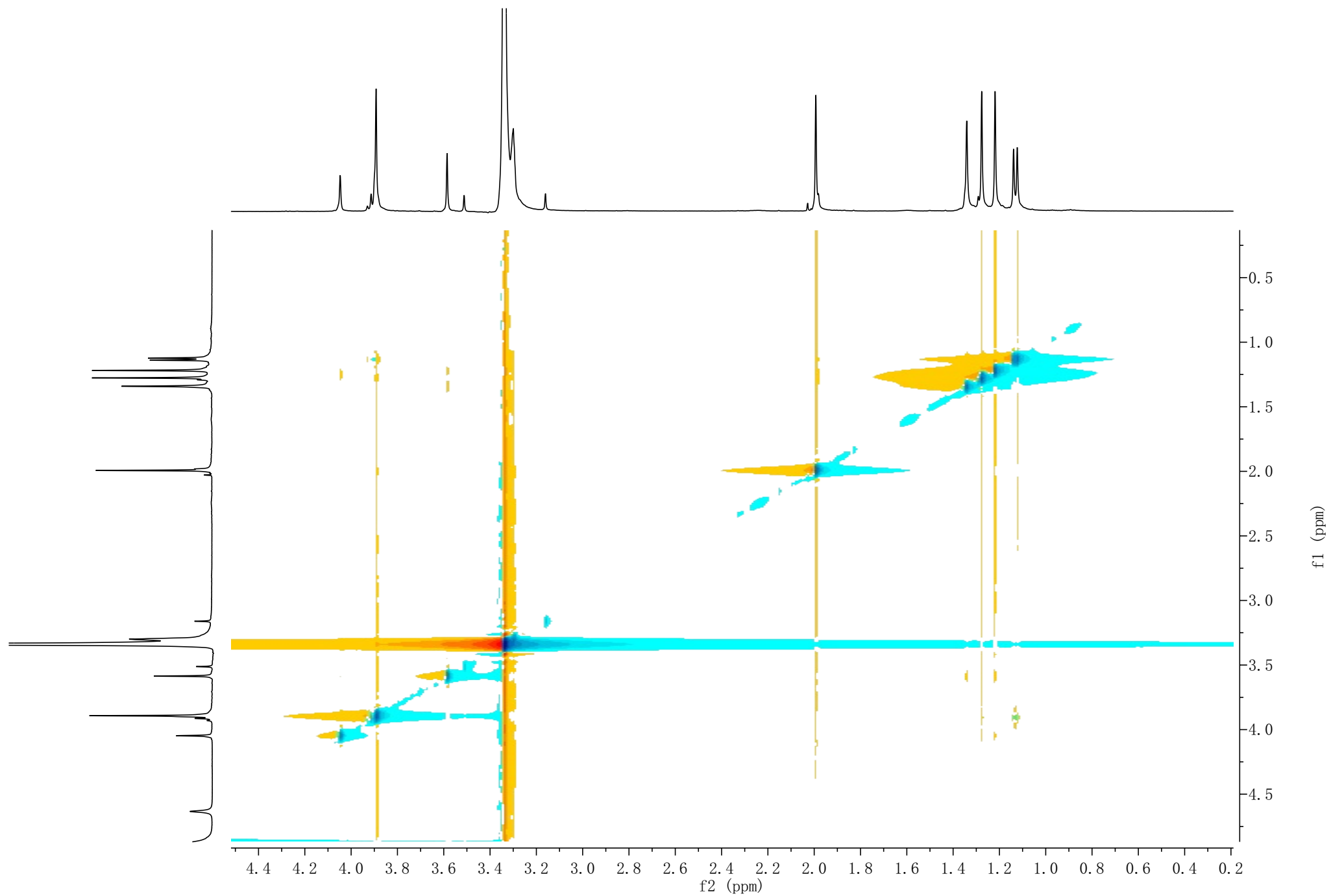


Figure S8. NOESY spectrum of (400 MHz, CD₃OD) citreoviridin J (**1**)

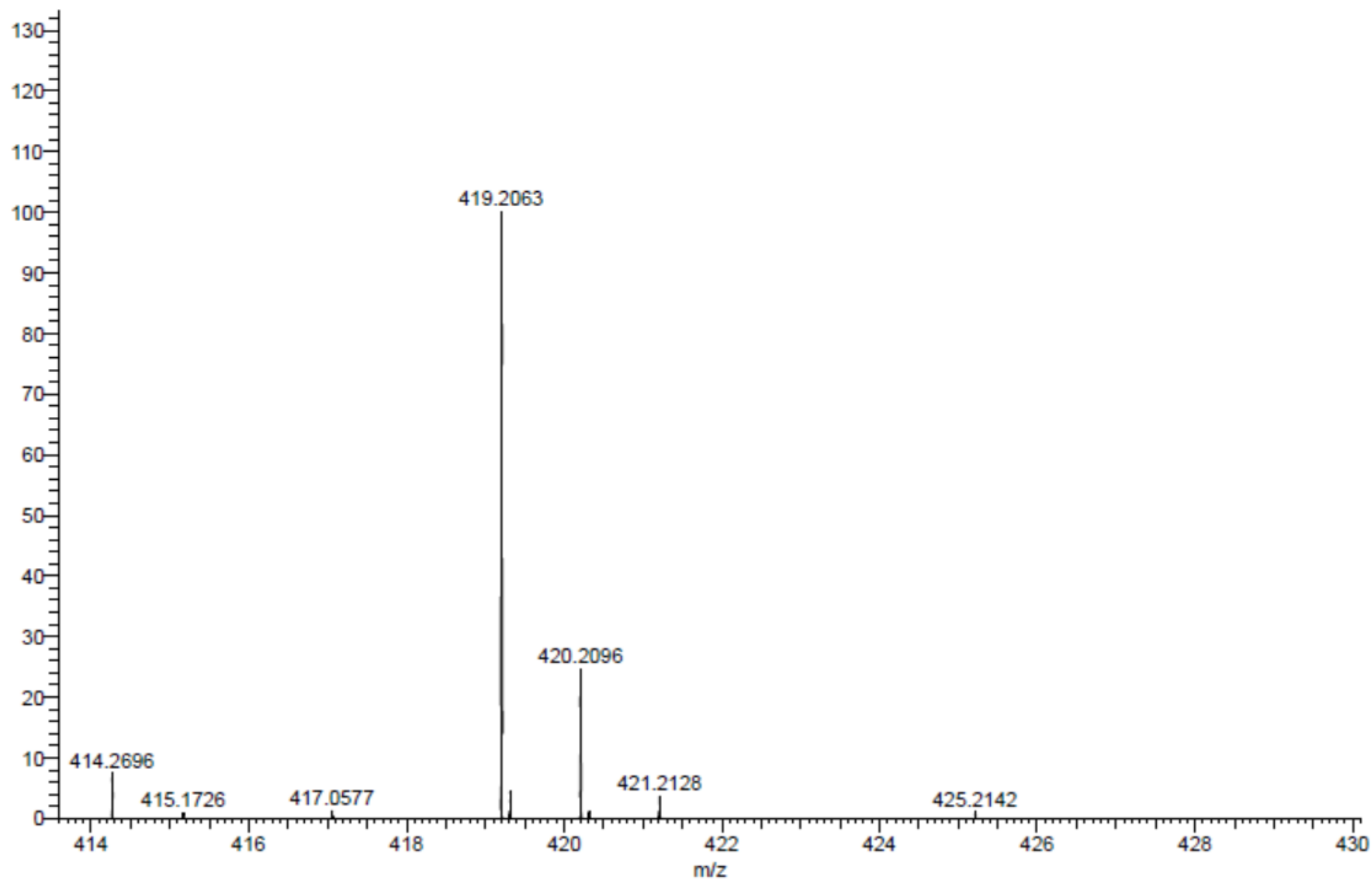


Figure S9. HR-ESI-MS of citreoviridin K (2)

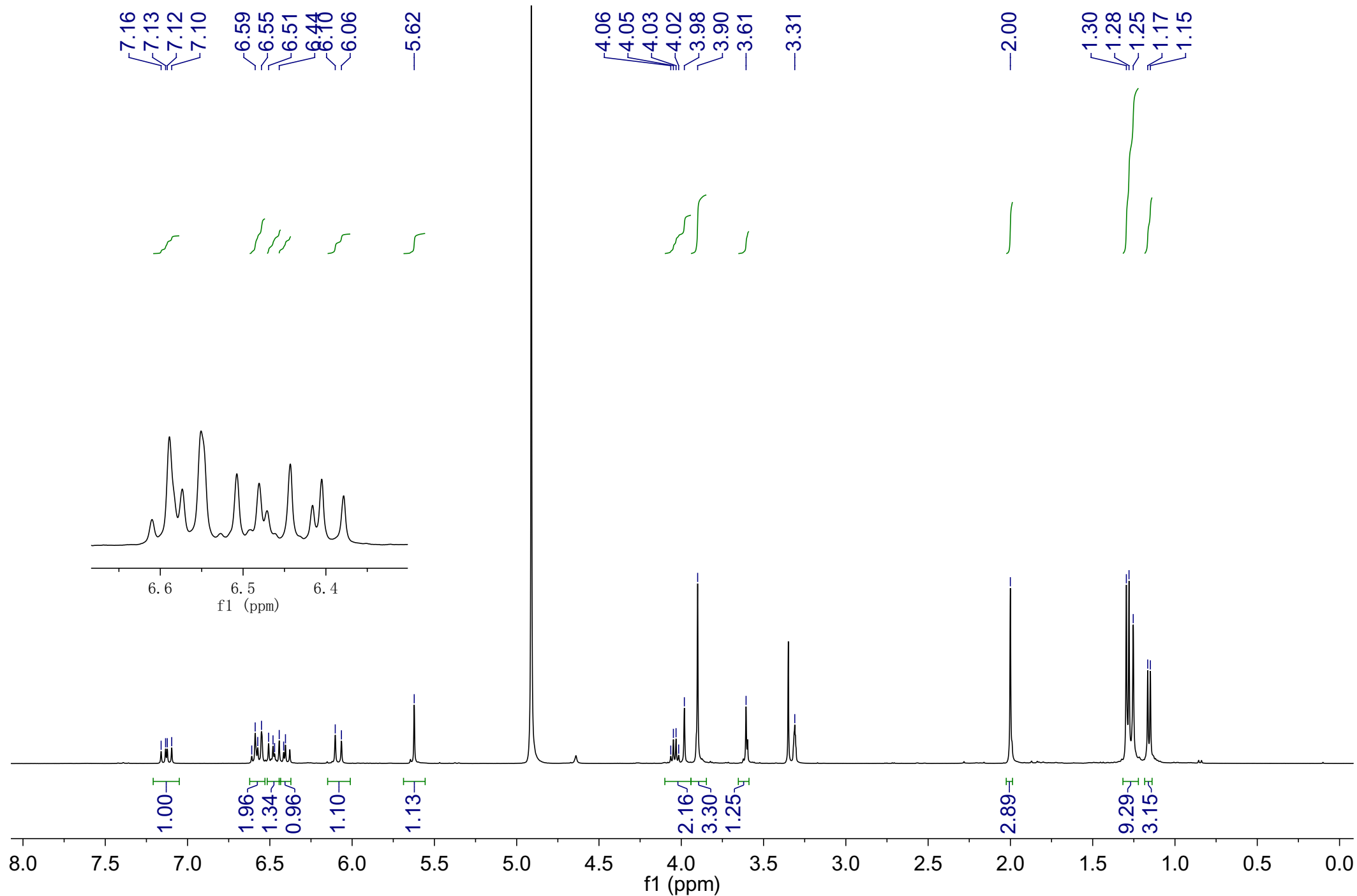


Figure S10. ^1H NMR spectrum (400 MHz, CD_3OD) of citreoviridin K (2)

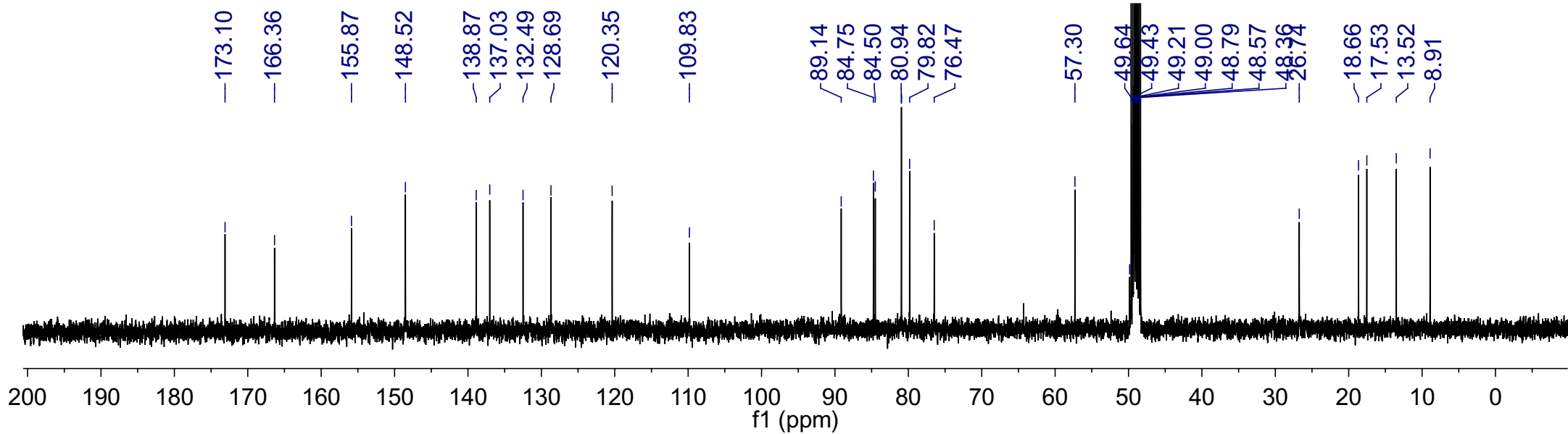
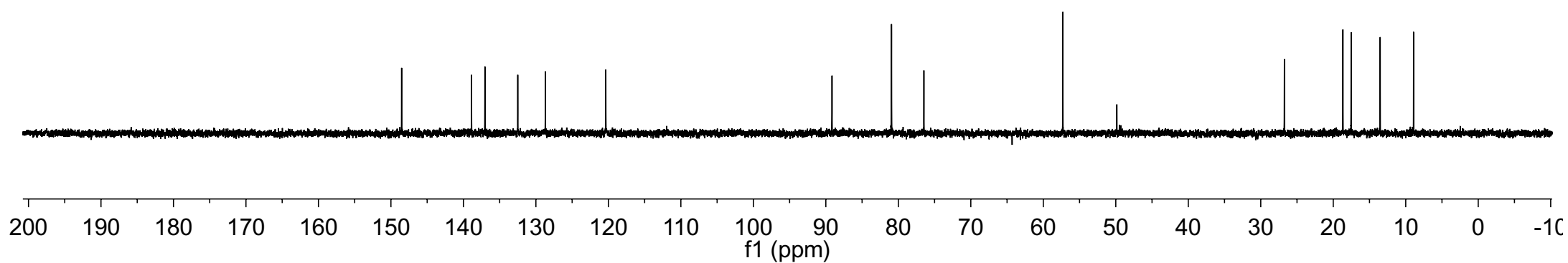


Figure S11. ¹³C NMR and DEPT (100 MHz, CD₃OD) of citreoviridin K (2)

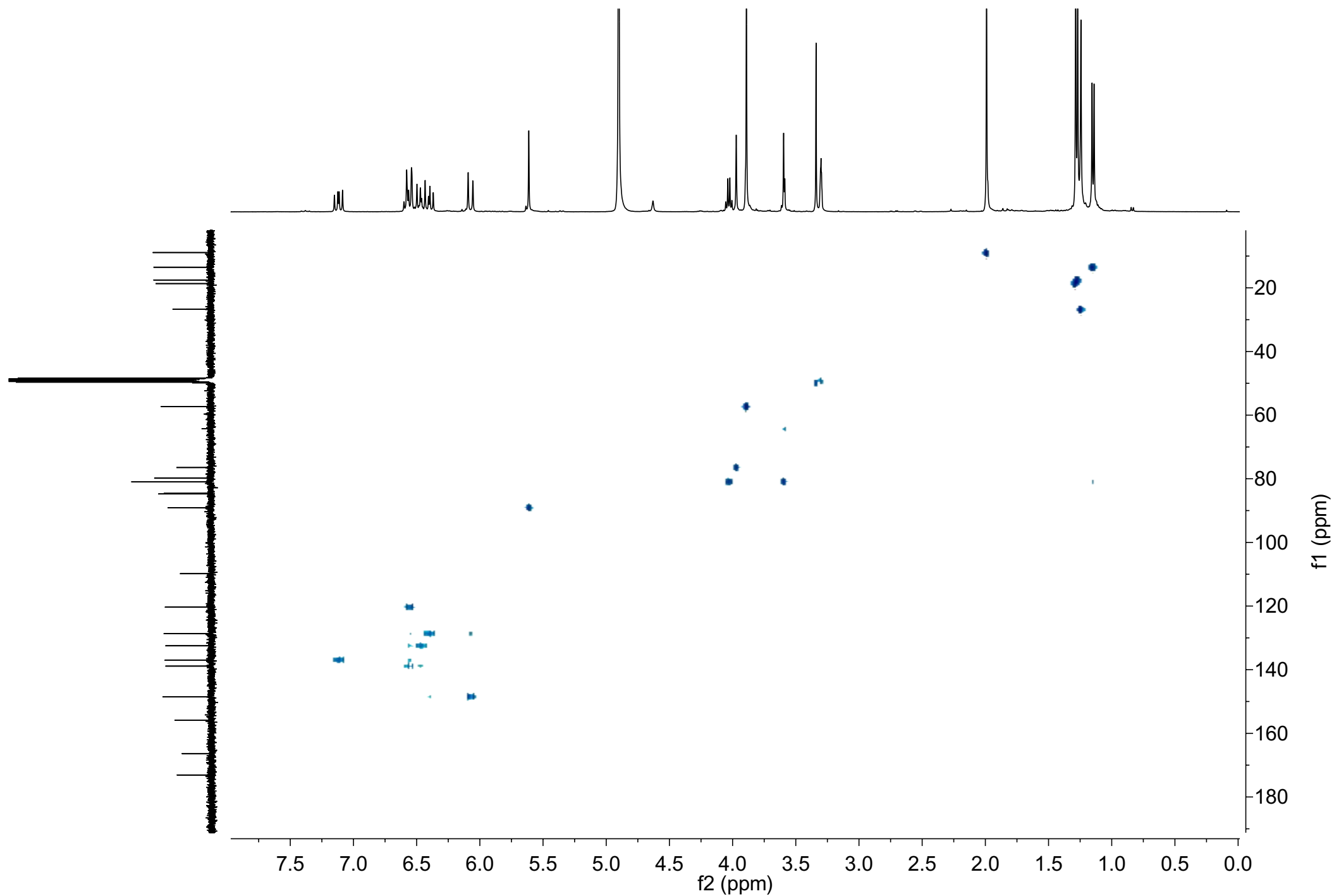


Figure S12. HMQC spectrum (400 MHz, CD₃OD) of citreoviridin K (**2**)

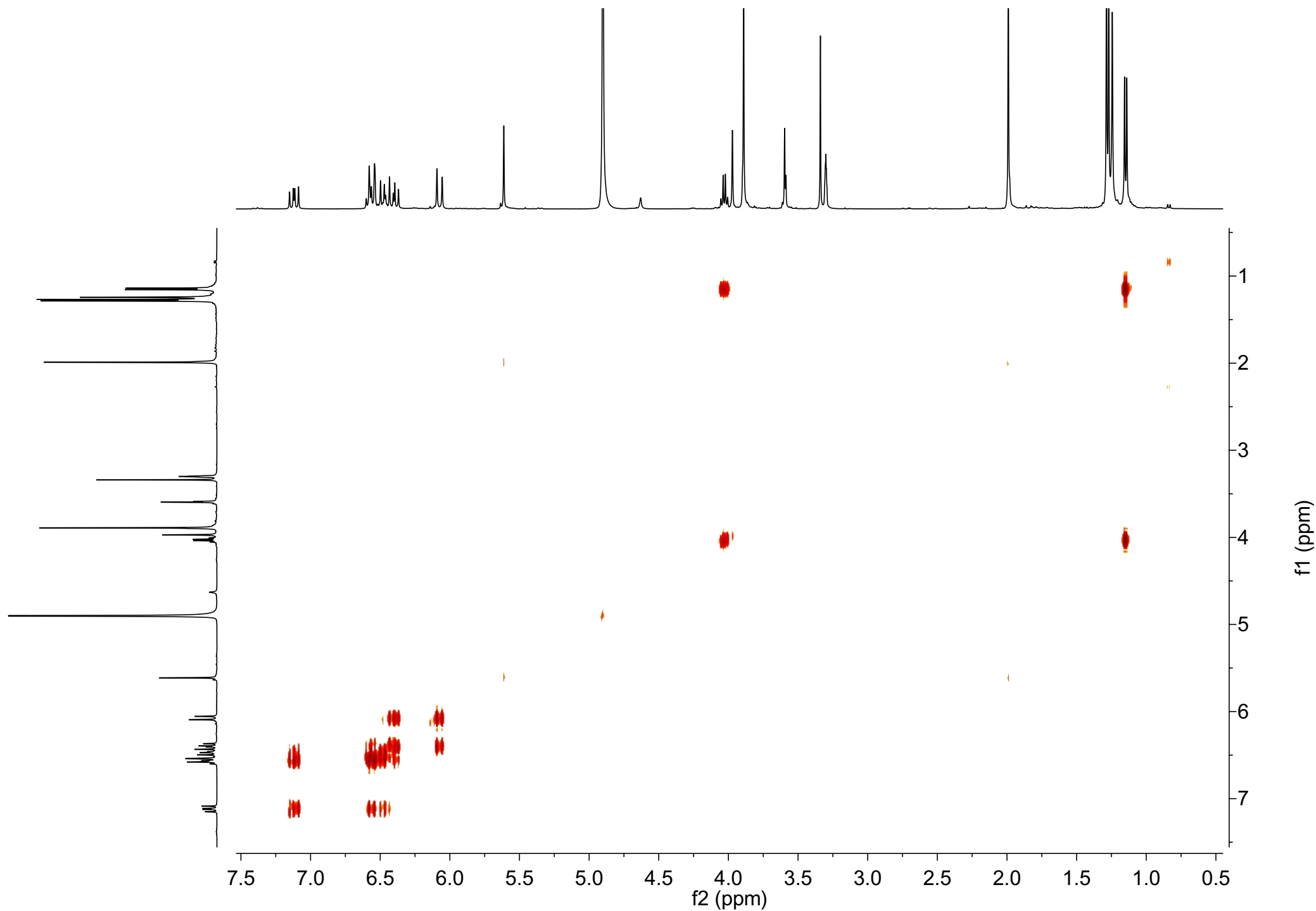


Figure S13. ^1H - ^1H COSY spectrum (400 MHz, CD_3OD) of citreoviridin K (**2**)

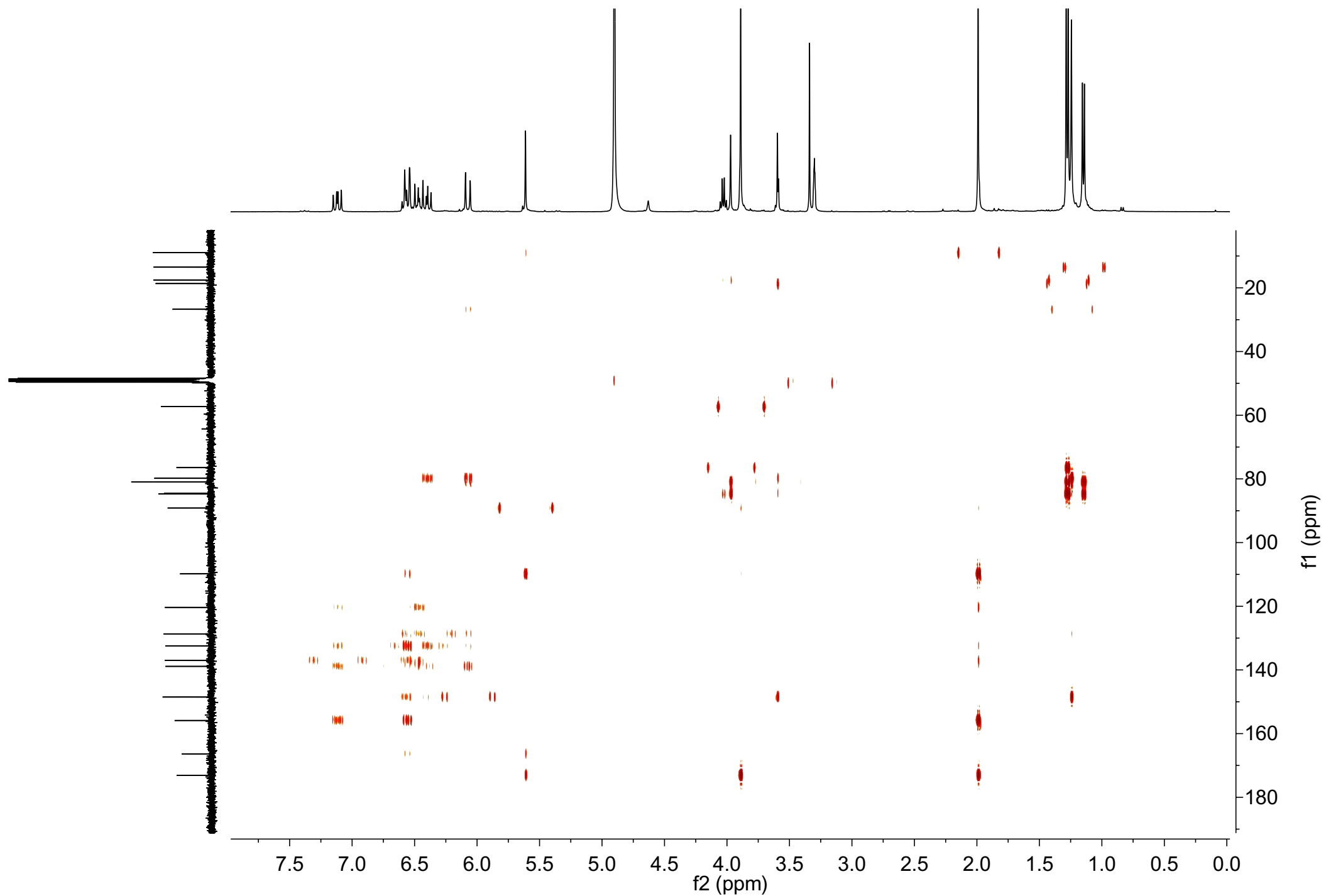


Figure S14. HMBC spectrum (400 MHz, CD₃OD) of citreoviridin K (**2**)

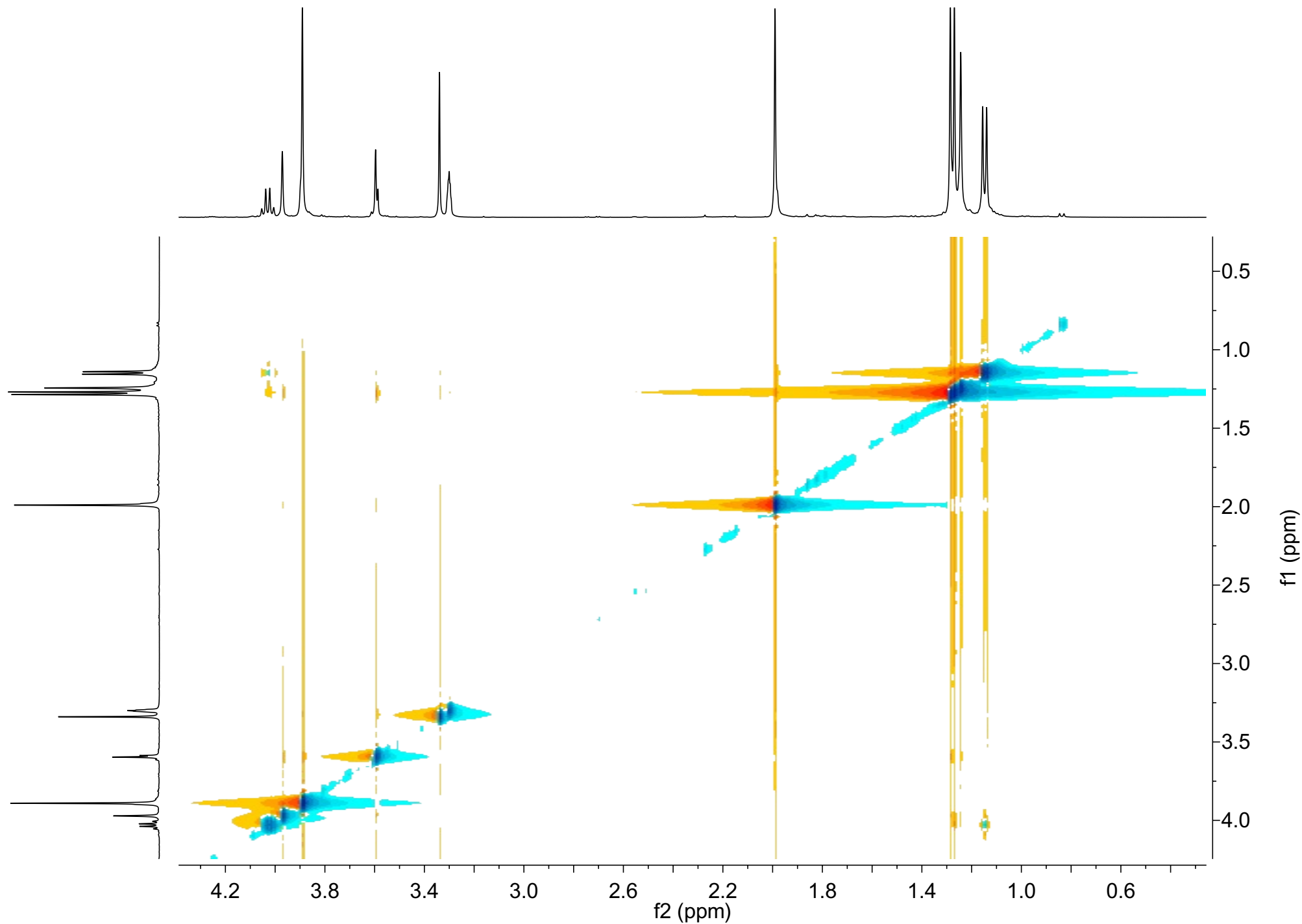


Figure S15. NOESY spectrum (400 MHz, CD₃OD) of citreoviridin K (2)

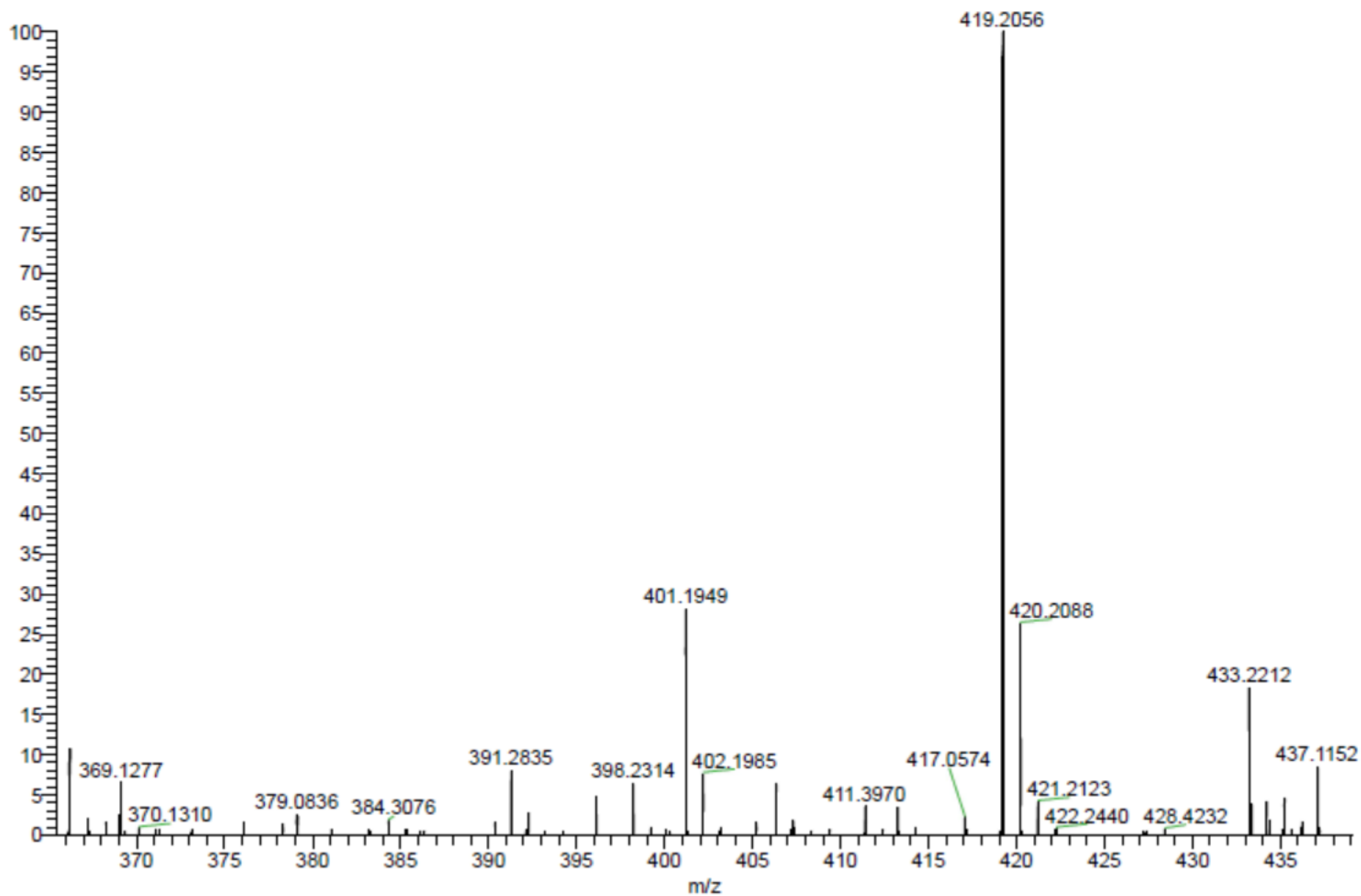


Figure S16. HR-ESI-MS of citreoviridin L (3)

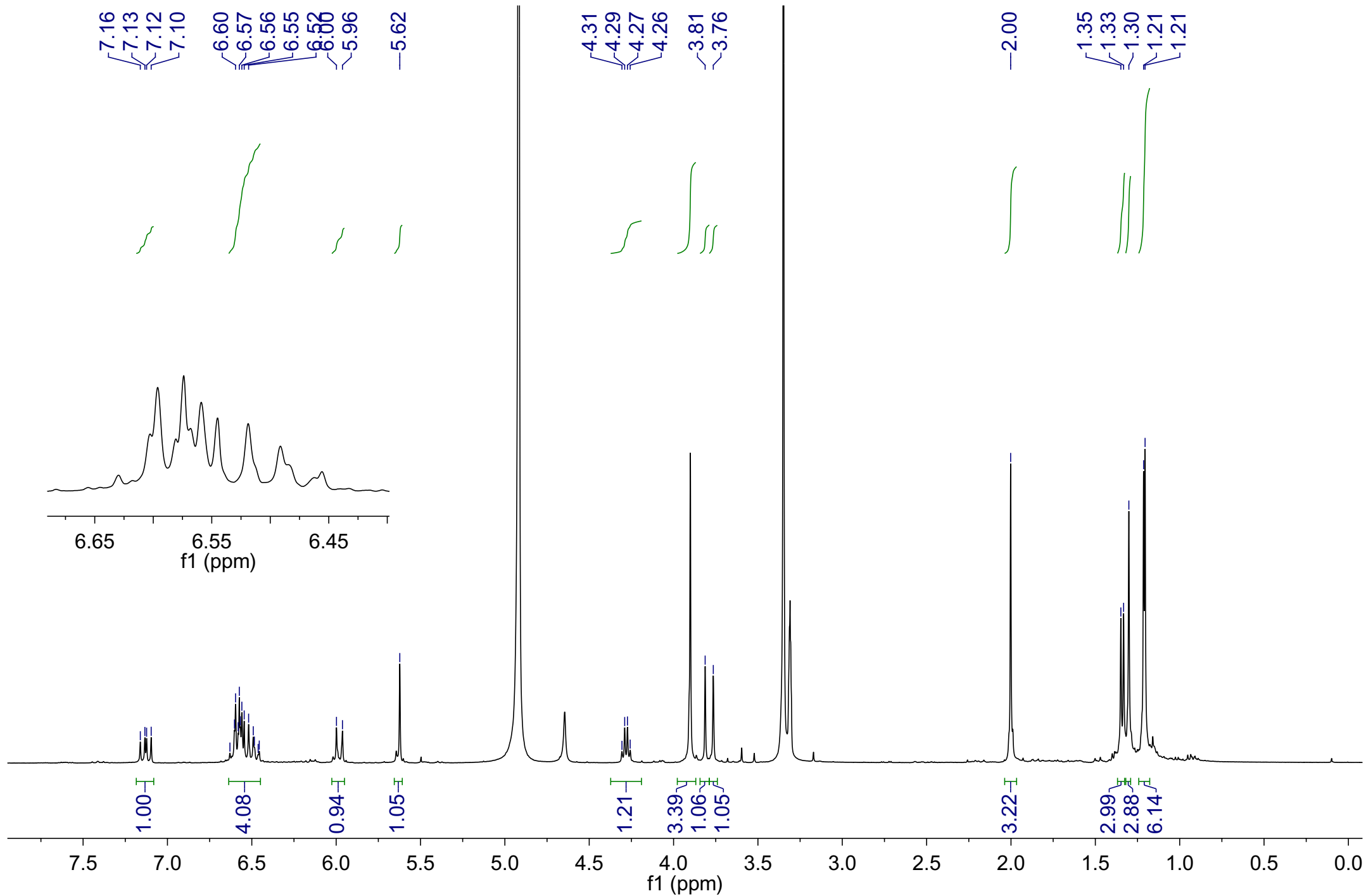


Figure S17. ^1H NMR spectrum (400 MHz, CD_3OD) of citreoviridin L (**3**)

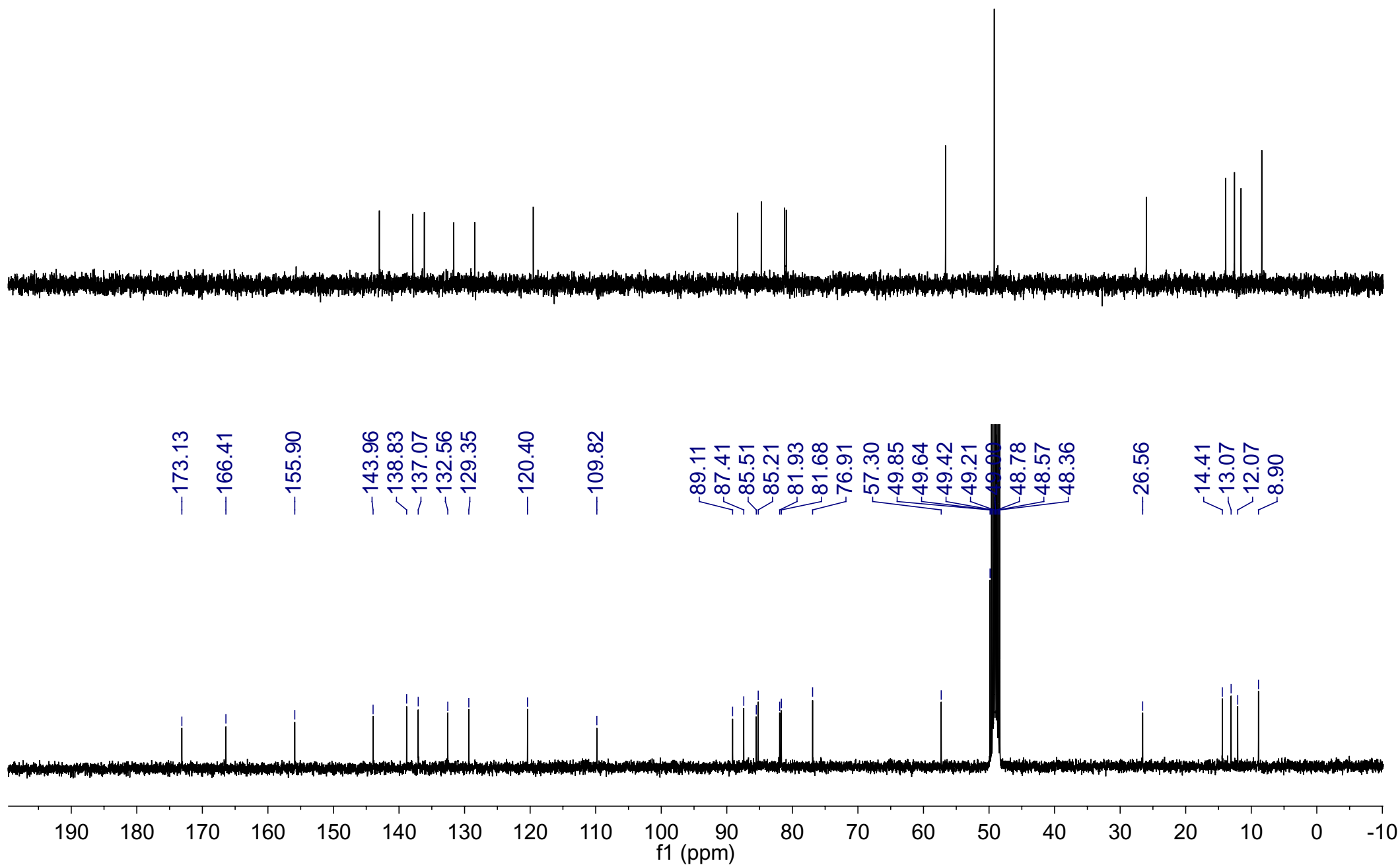


Figure S18. ¹³C NMR and DEPT (100 MHz, CD₃OD) of citreoviridin L (3)

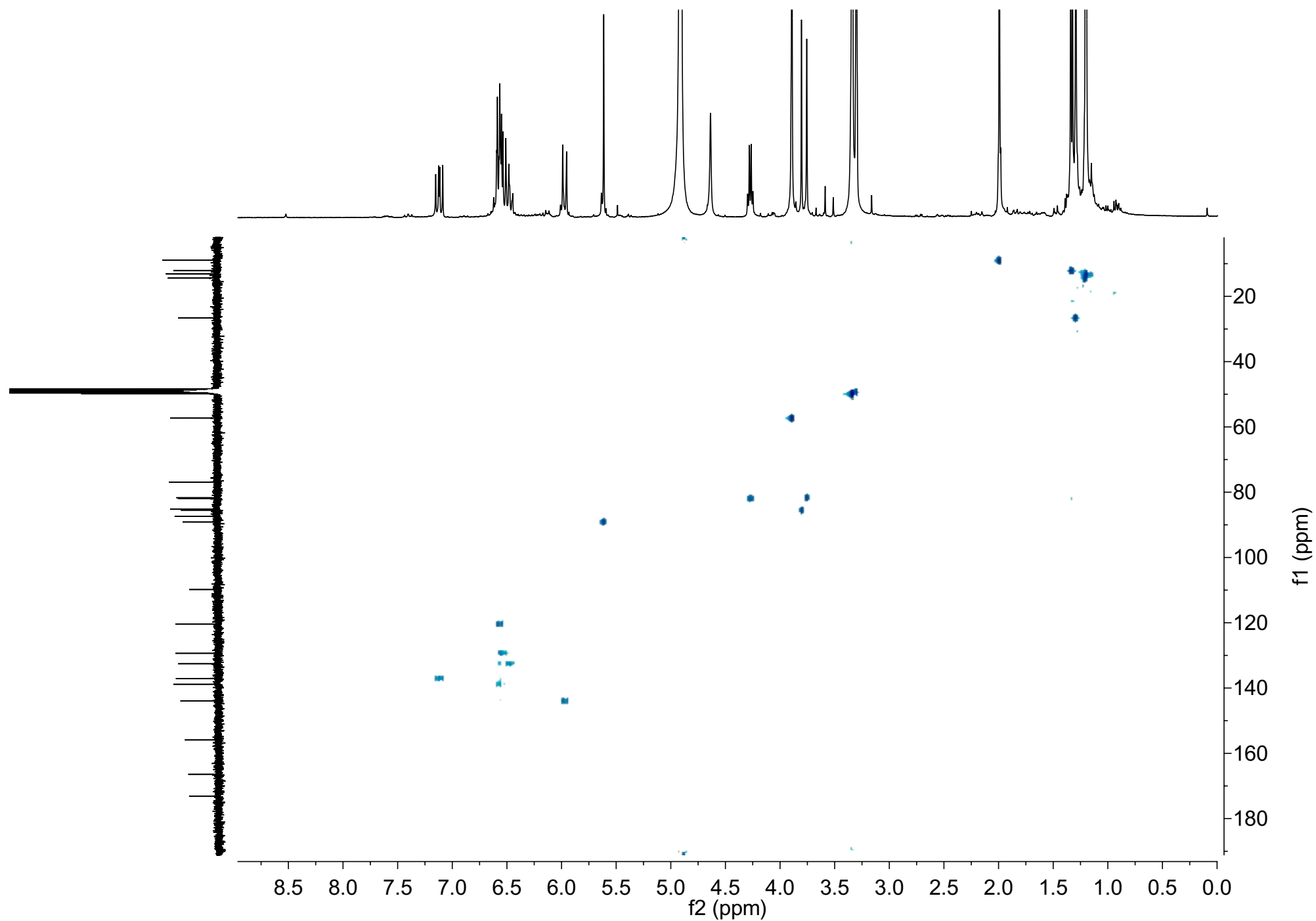


Figure S19. HMQC spectrum (400 MHz, CD₃OD) of citreoviridin L (3)

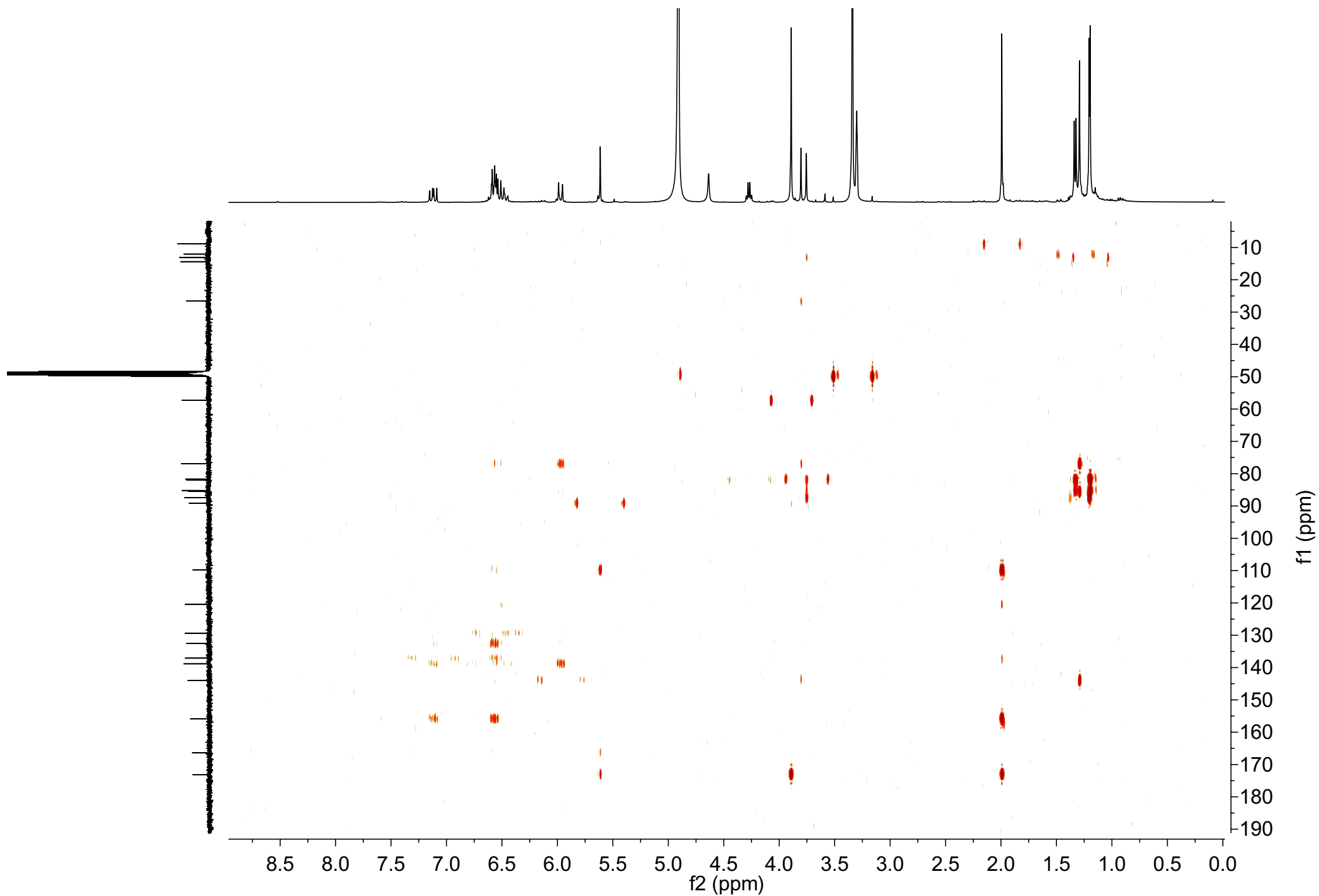


Figure S21. HMBC spectrum (400 MHz, CD_3OD) of citreoviridin L (**3**)

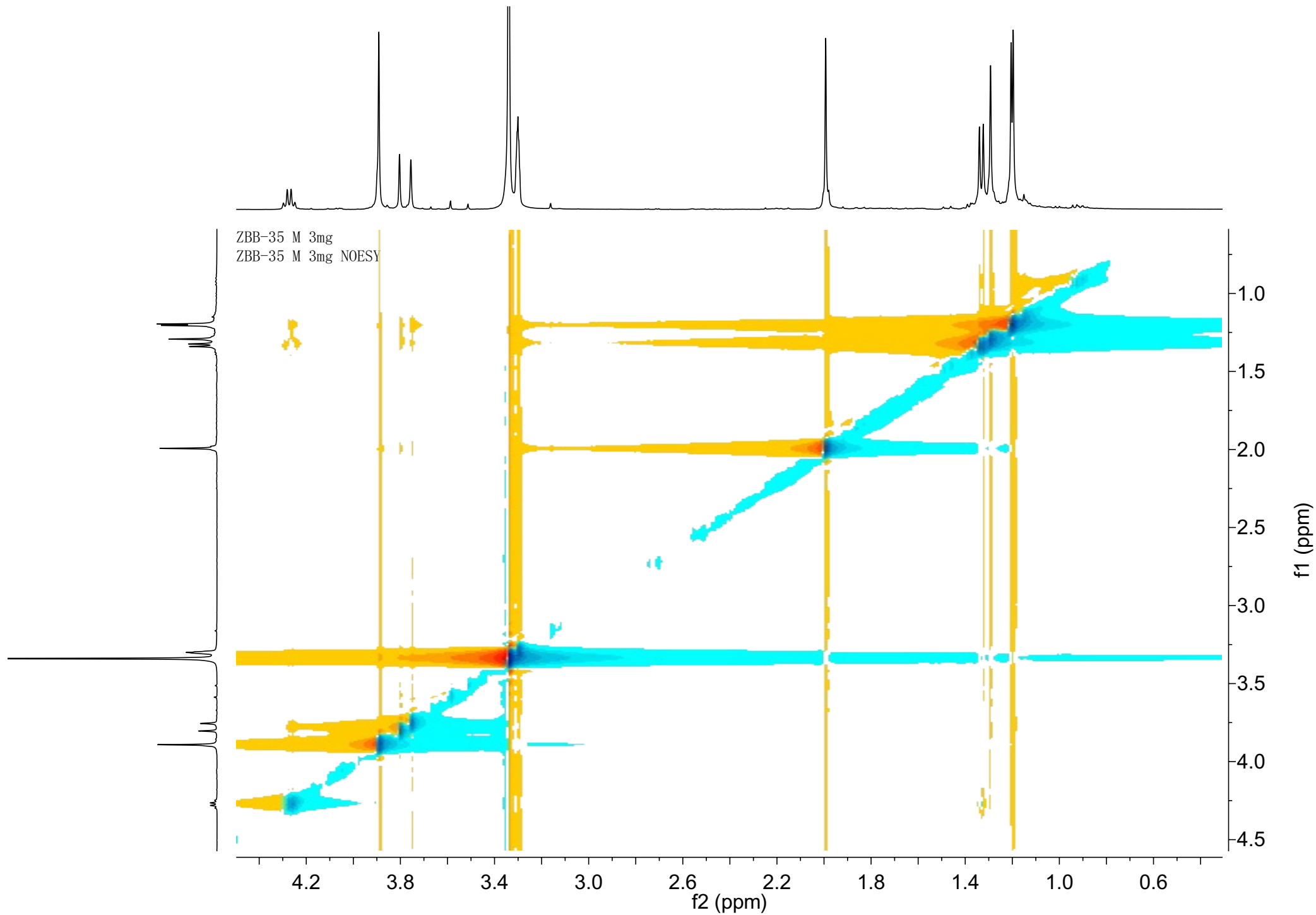


Figure S22. NOESY spectrum (400 MHz, CD₃OD) of citreoviridin L (3)

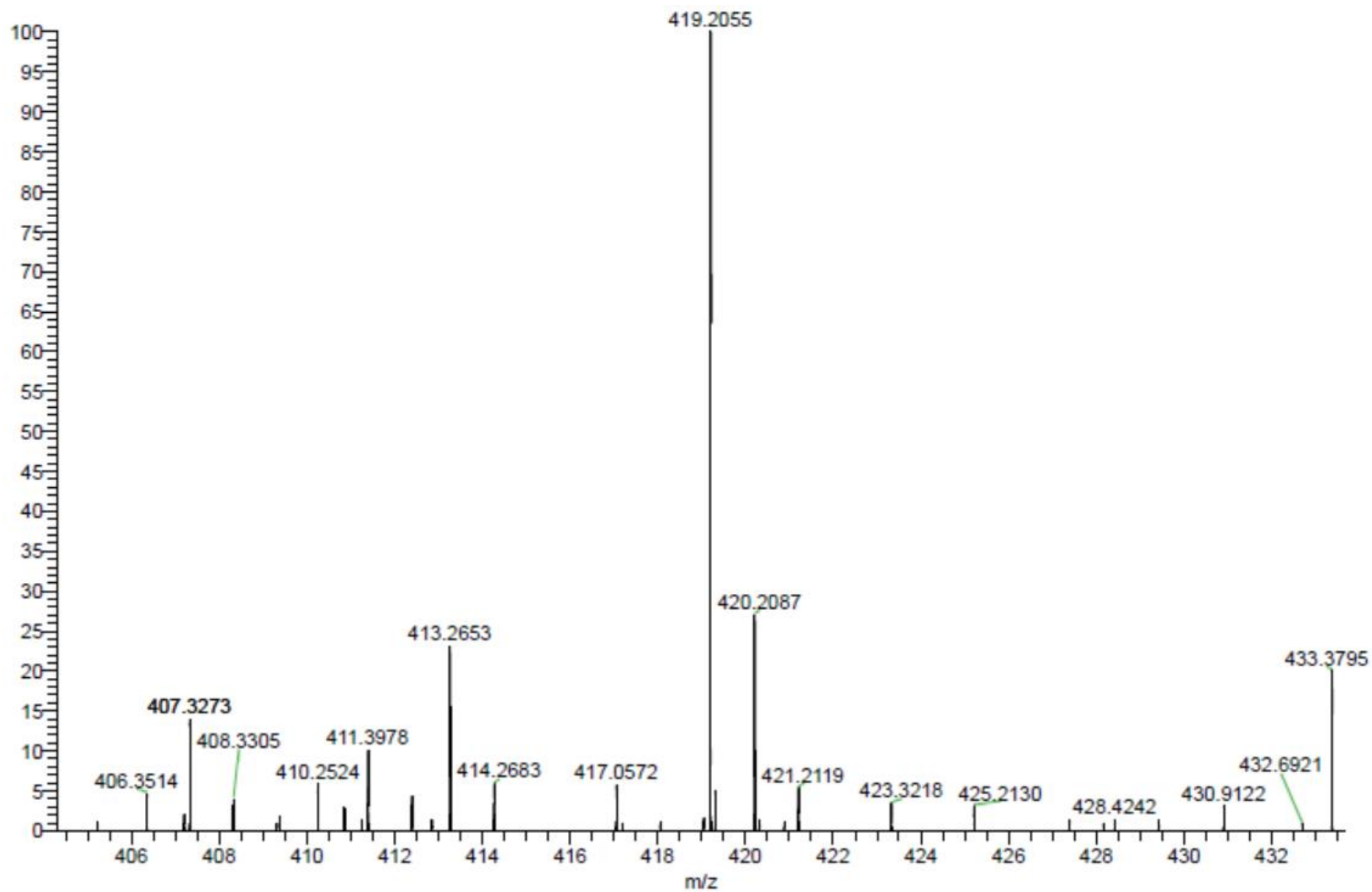


Figure S23. HR-ESI-MS of citreoviridin M (4)

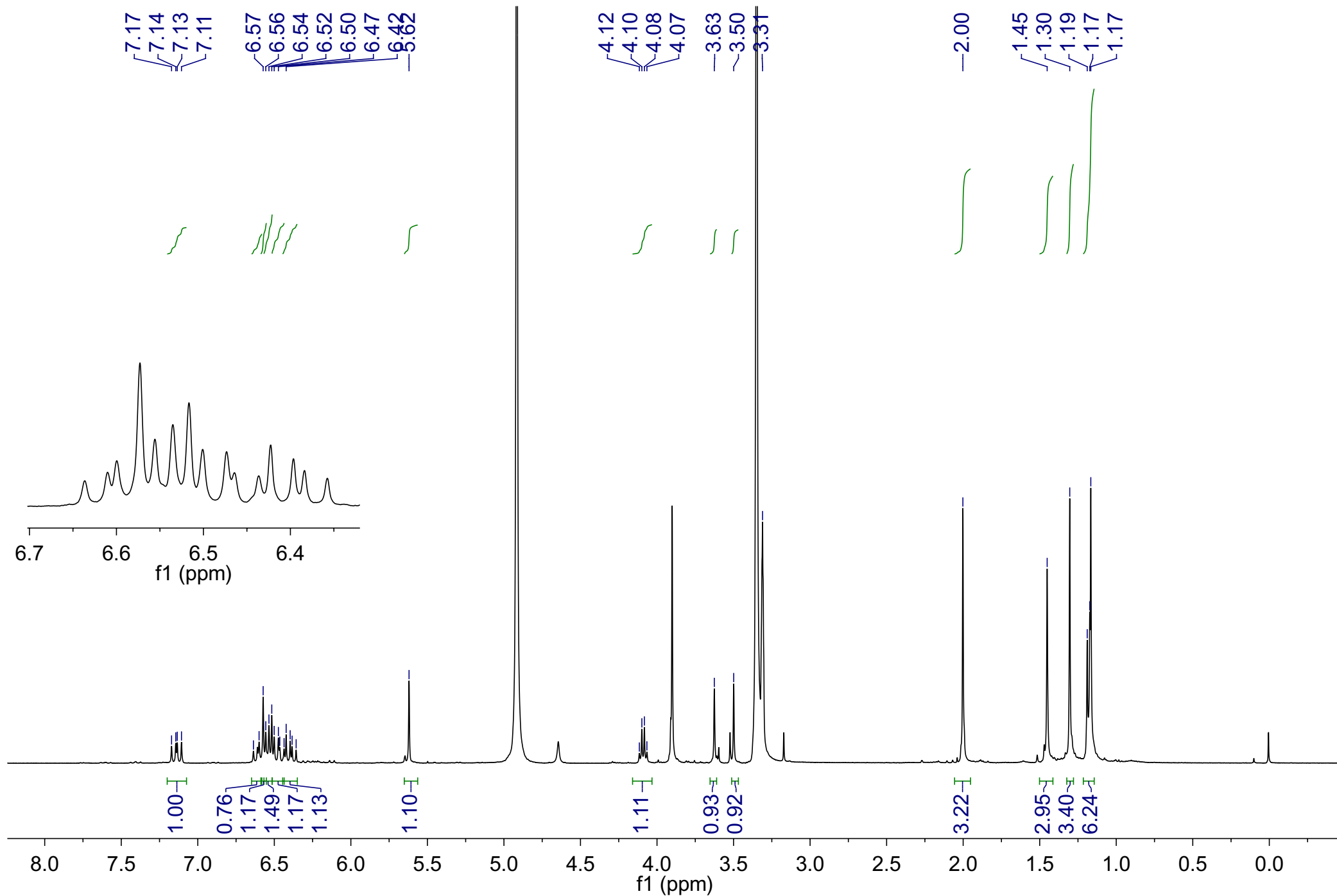


Figure S24. ^1H NMR spectrum (400 MHz, CD_3OD) of citreoviridin M (**4**)

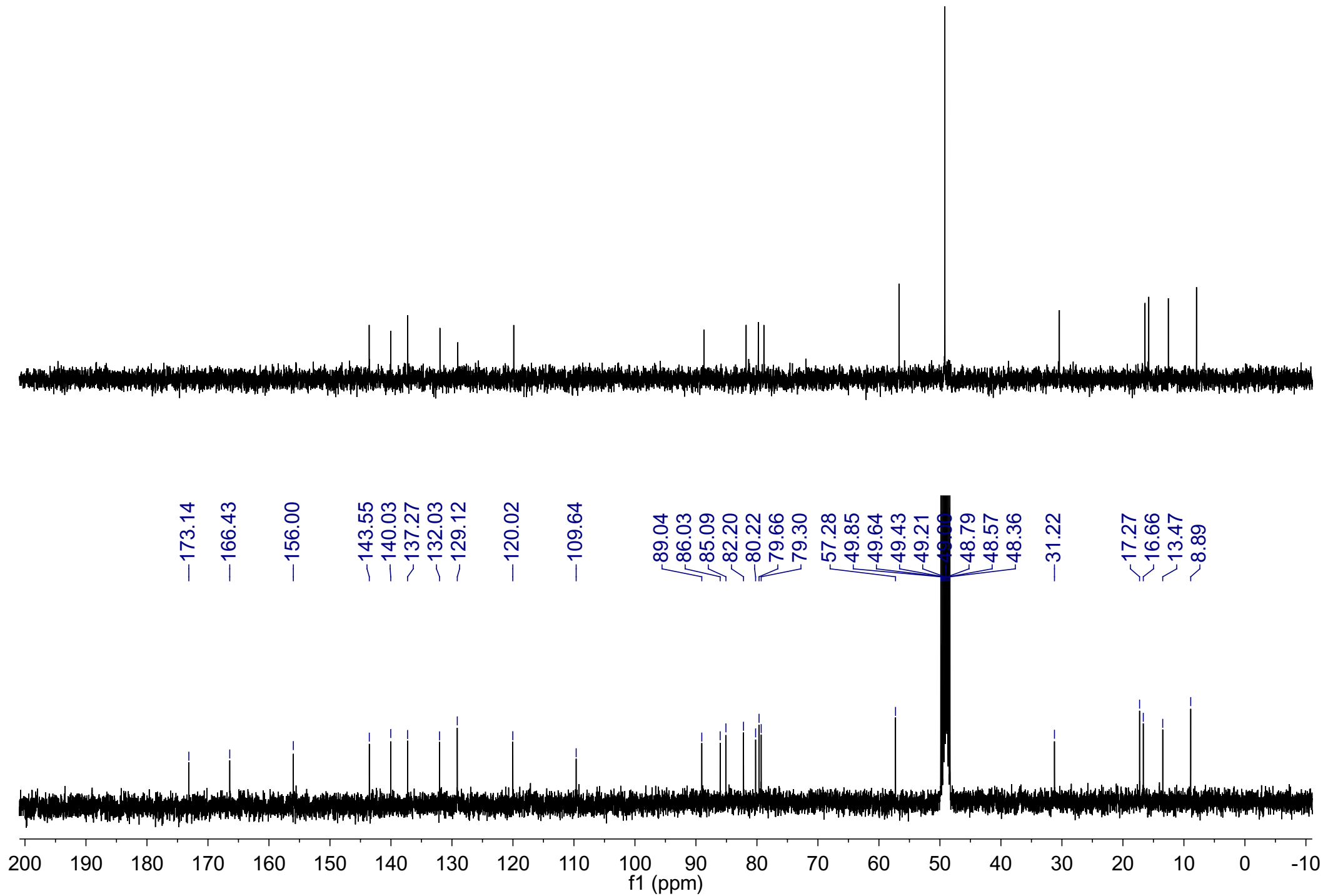


Figure S25. ¹³C NMR and DEPT (100 MHz, CD₃OD) of citreoviridin M (4)

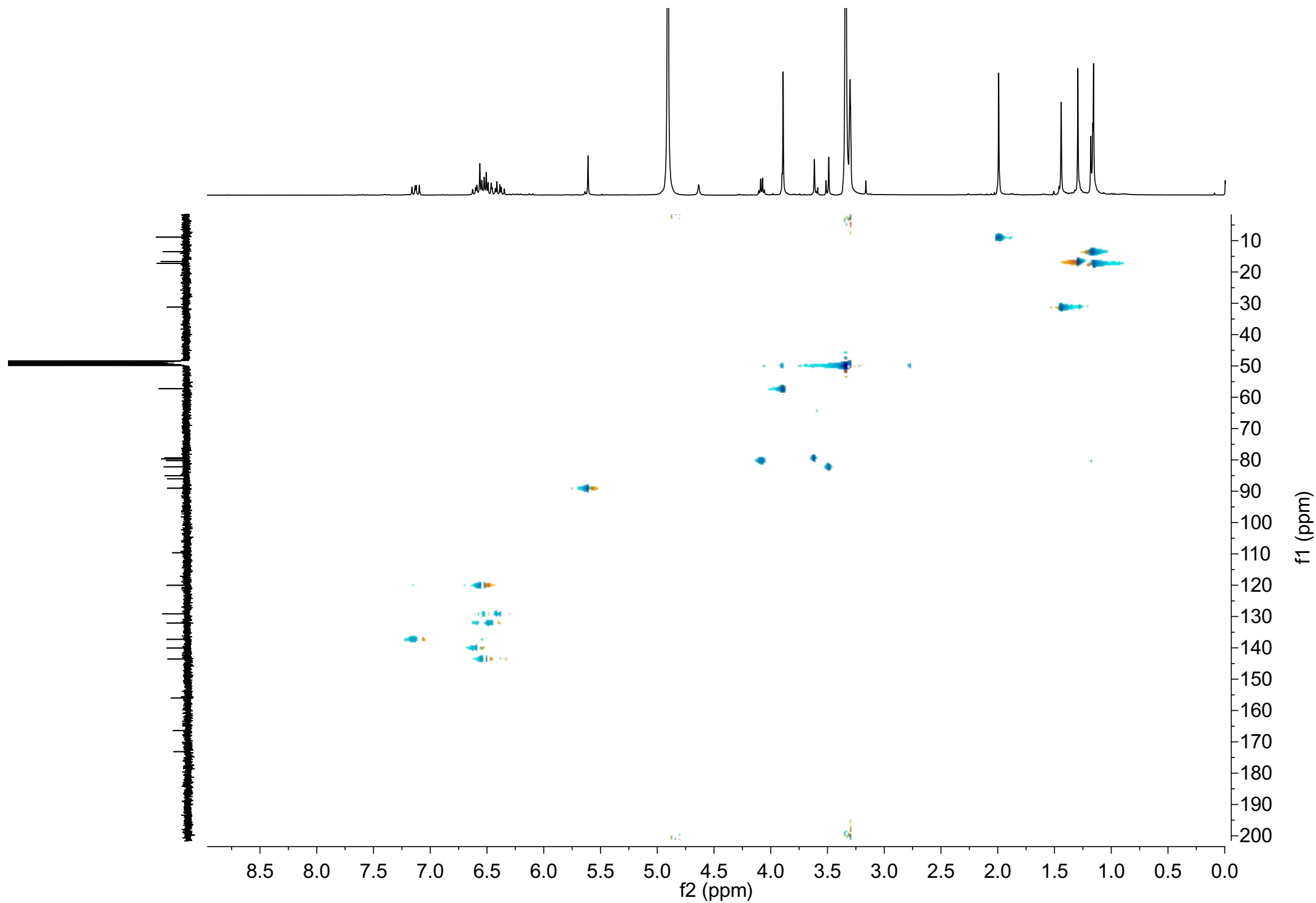


Figure S26. HMQC spectrum (400 MHz, CD₃OD) of citreoviridin M (4)

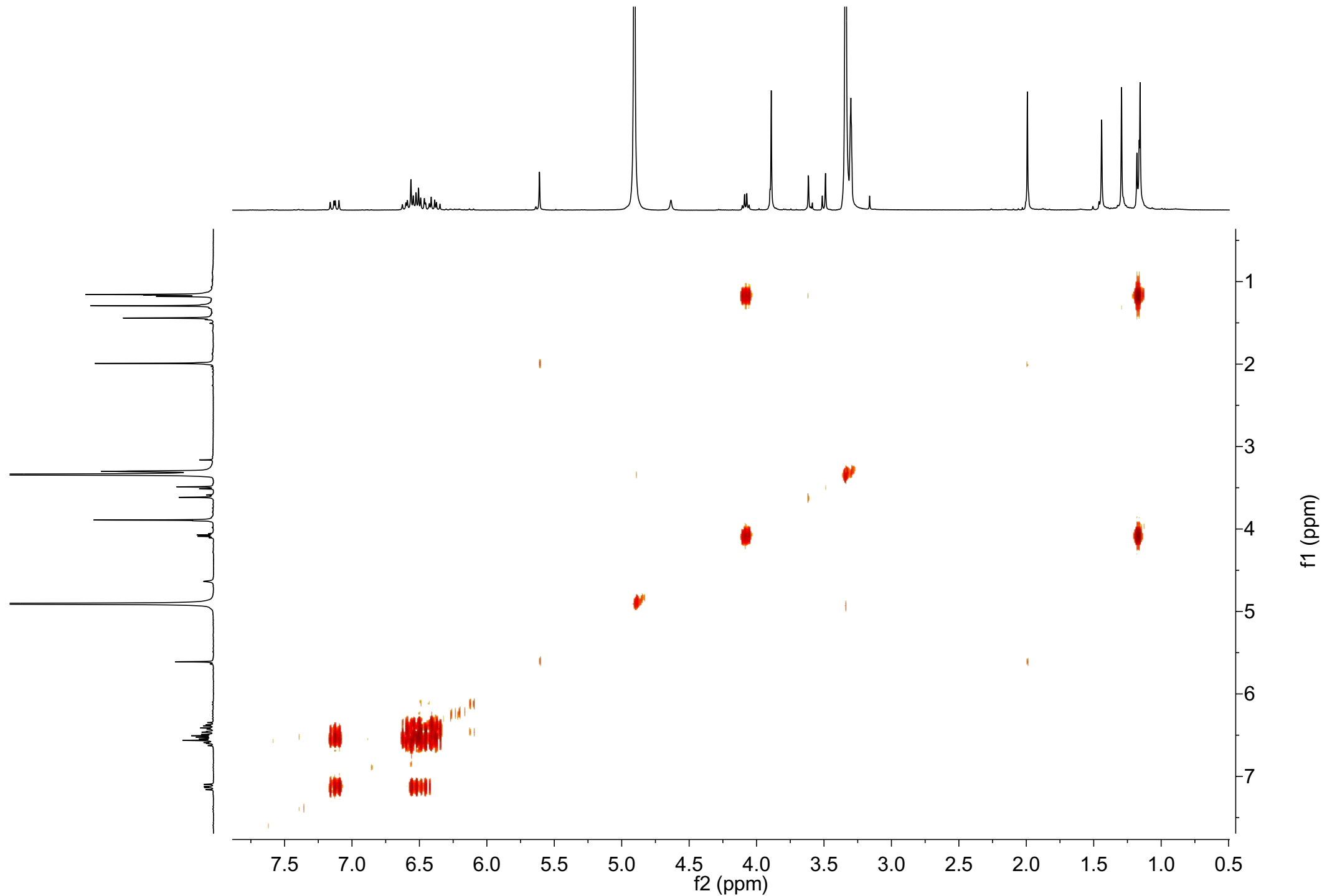


Figure S27. ^1H - ^1H COSY spectrum (400 MHz, CD_3OD) of citreoviridin M (4)

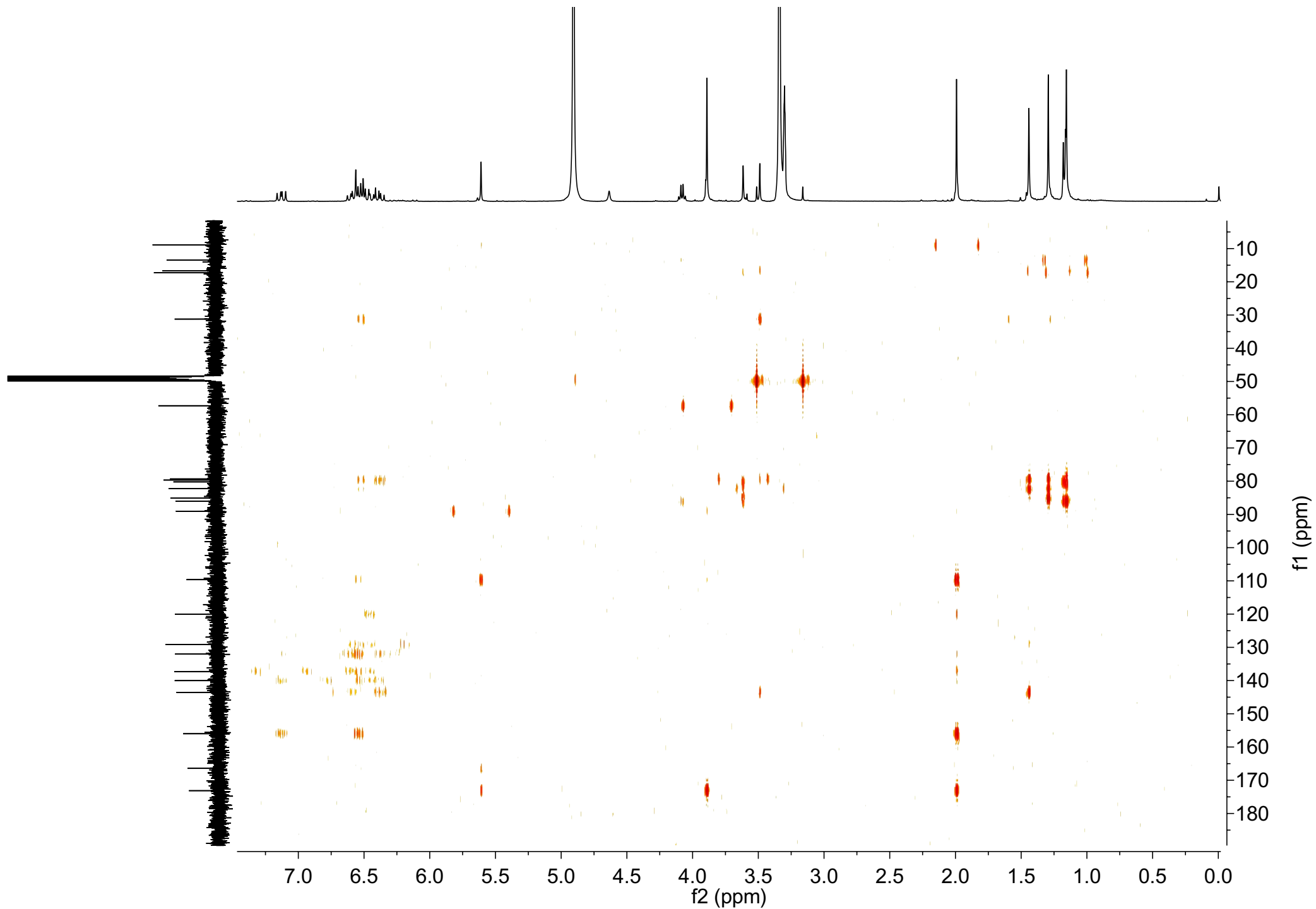


Figure S28. HMBC spectrum (400 MHz, CD_3OD) of citreoviridin M (4)

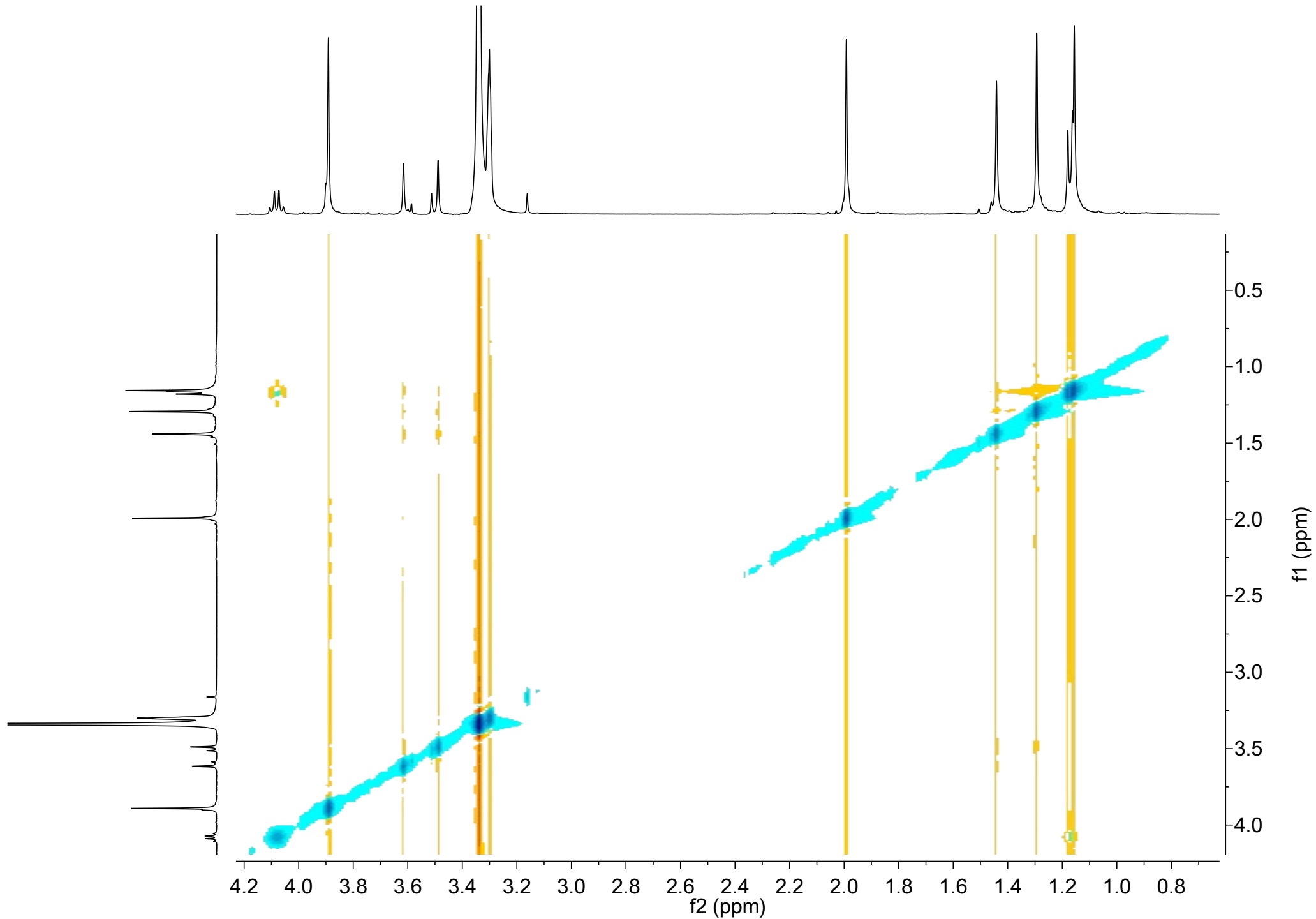


Figure S29. NOESY spectrum (400 MHz, CD₃OD) of citreoviridin M (4)

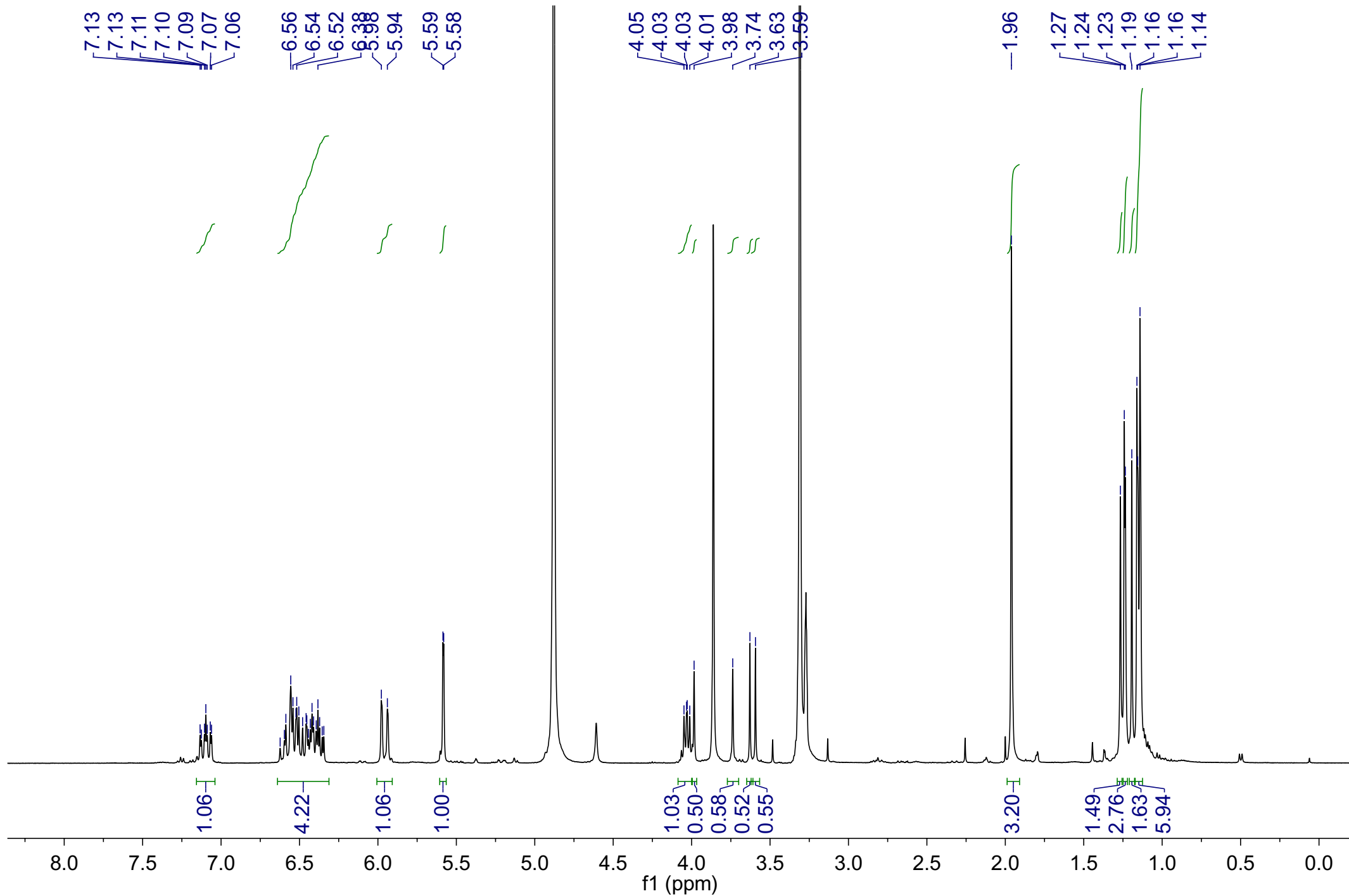


Figure S30. ¹H NMR spectrum (400 MHz, CD₃OD) of citreoviridins N and O (**5** and **6**)

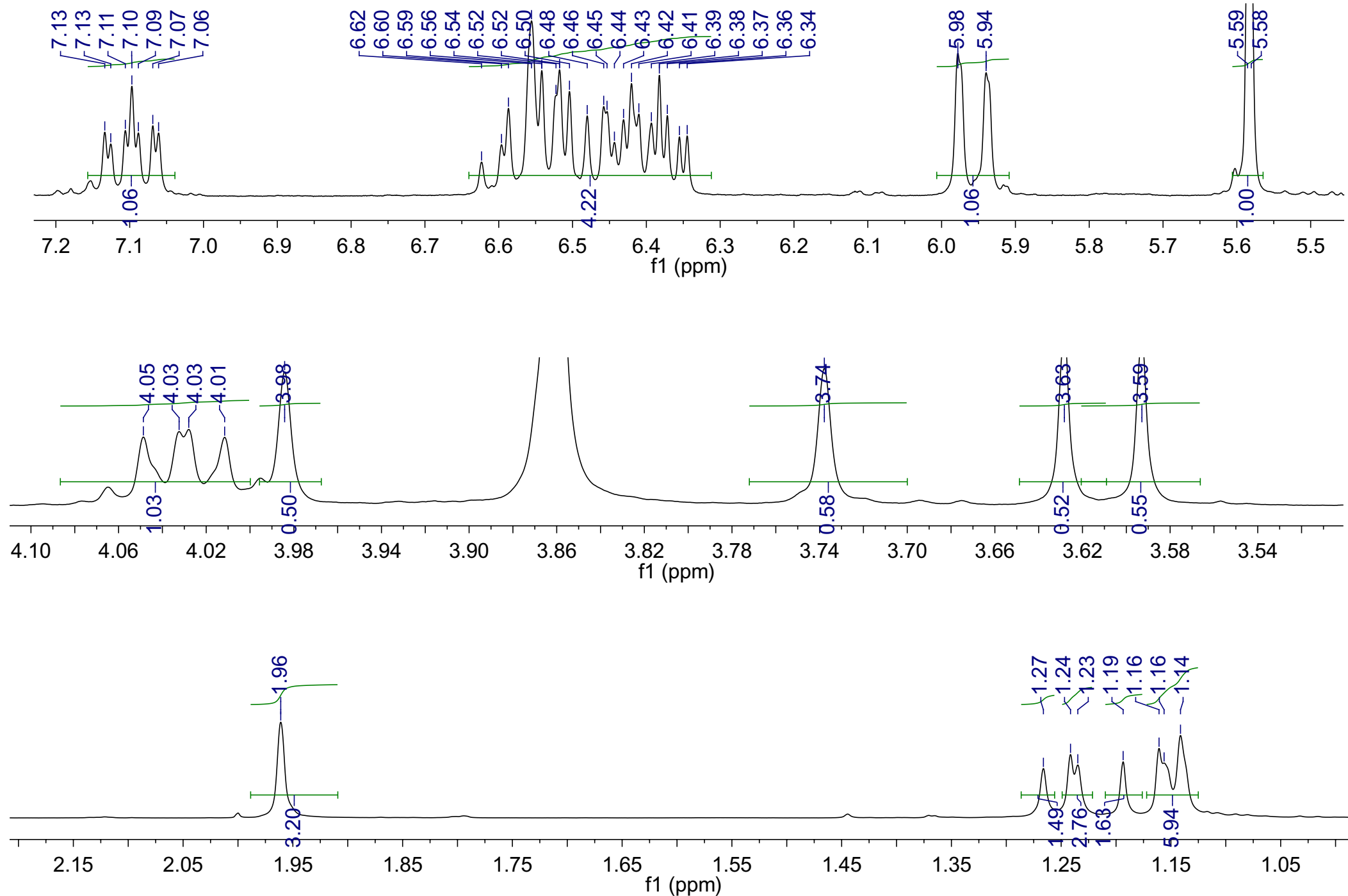


Figure S31. Amplified ^1H NMR spectrum (400 MHz, CD_3OD) of citreoviridins N and O (**5** and **6**)

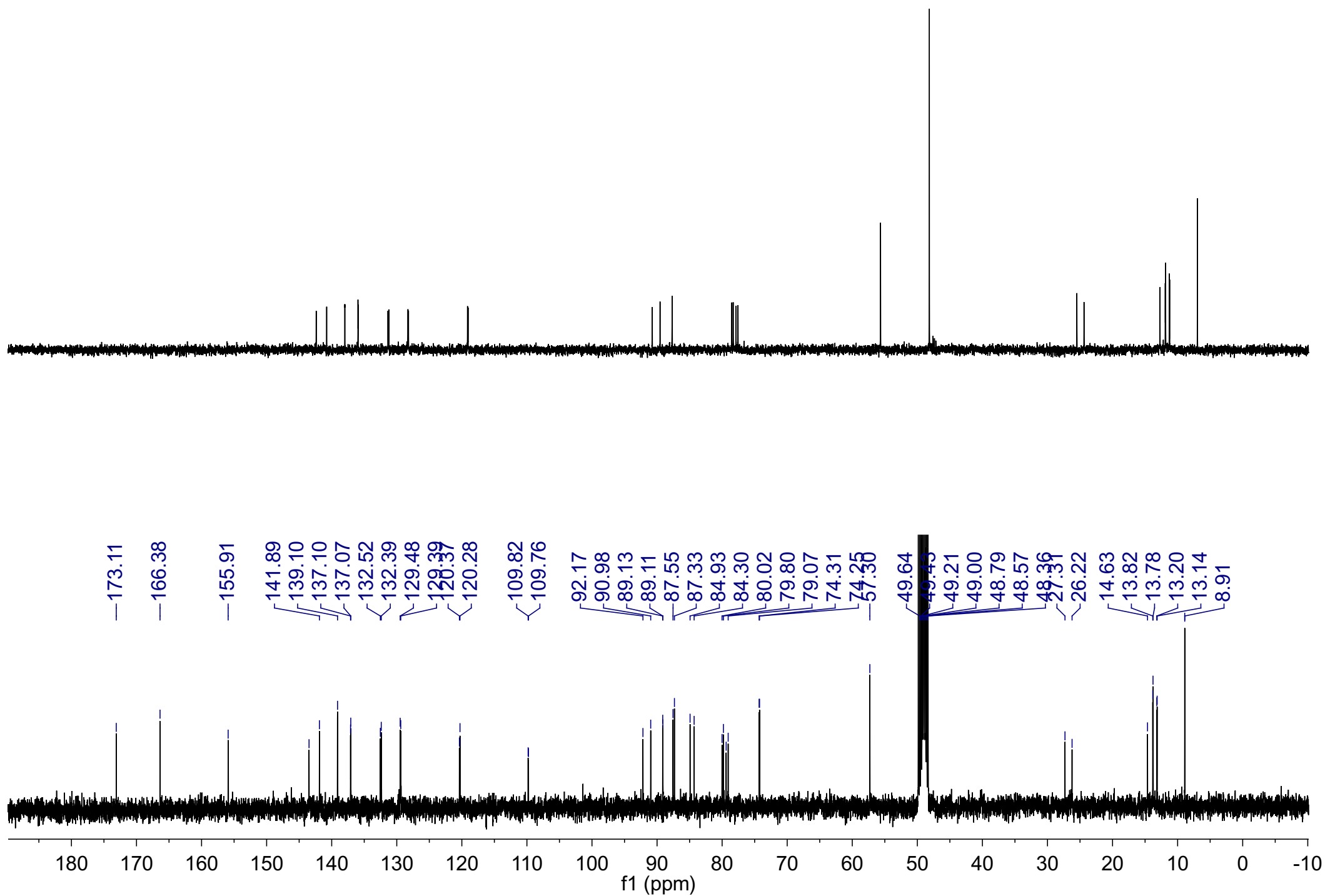


Figure S32. ^{13}C NMR and DEPT (100 MHz, CD_3OD) of citreoviridins N and O (5 and 6)

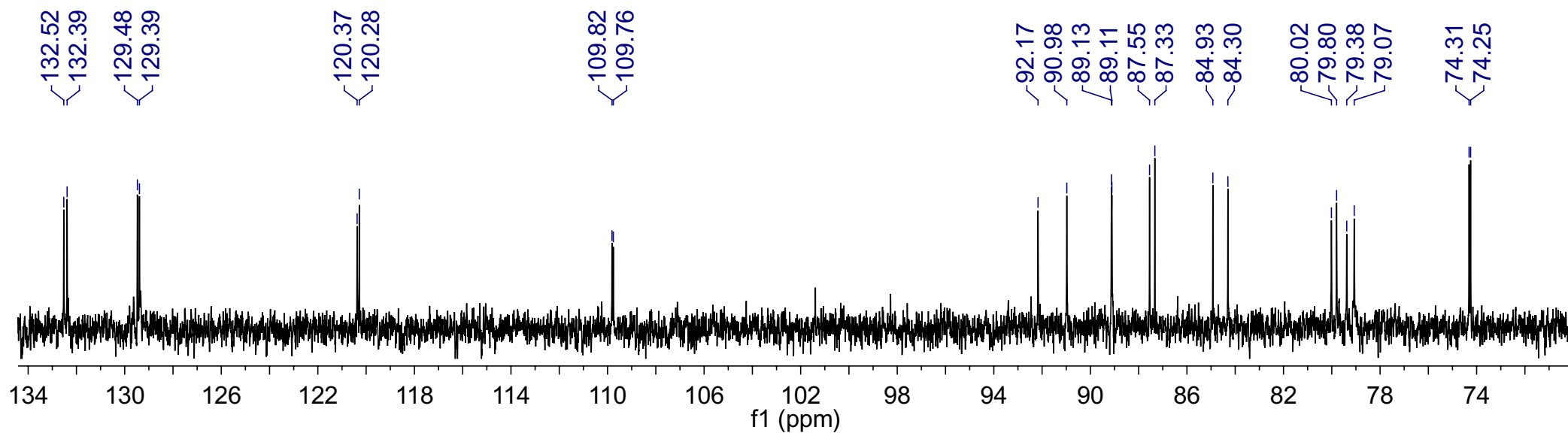
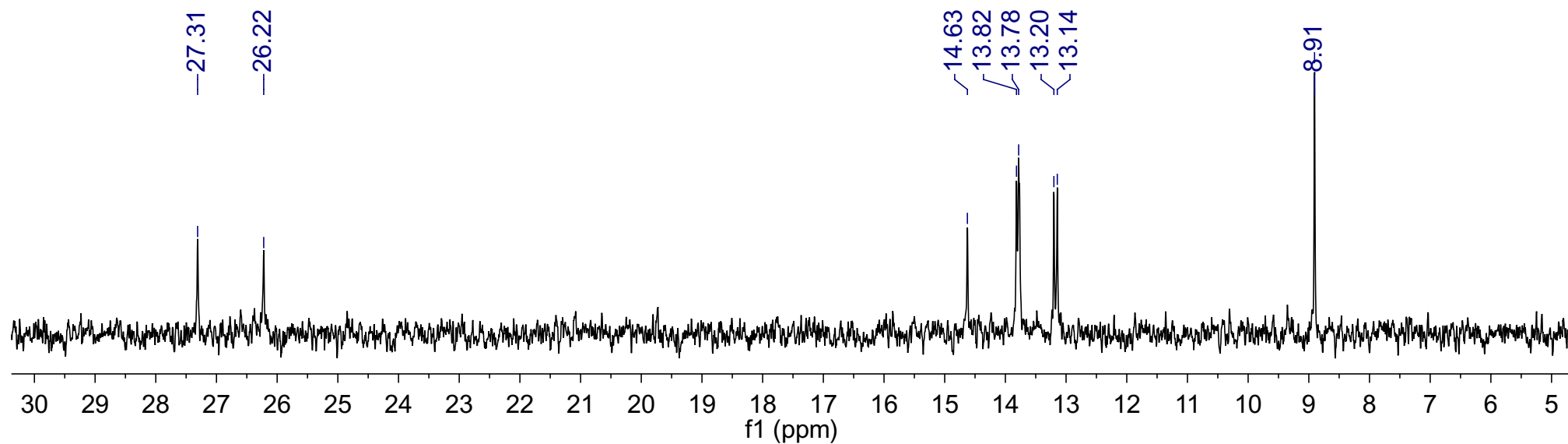


Figure S33. Amplified ^{13}C NMR spectrum (100 MHz, CD_3OD) of citreoviridins N and O (**5** and **6**)

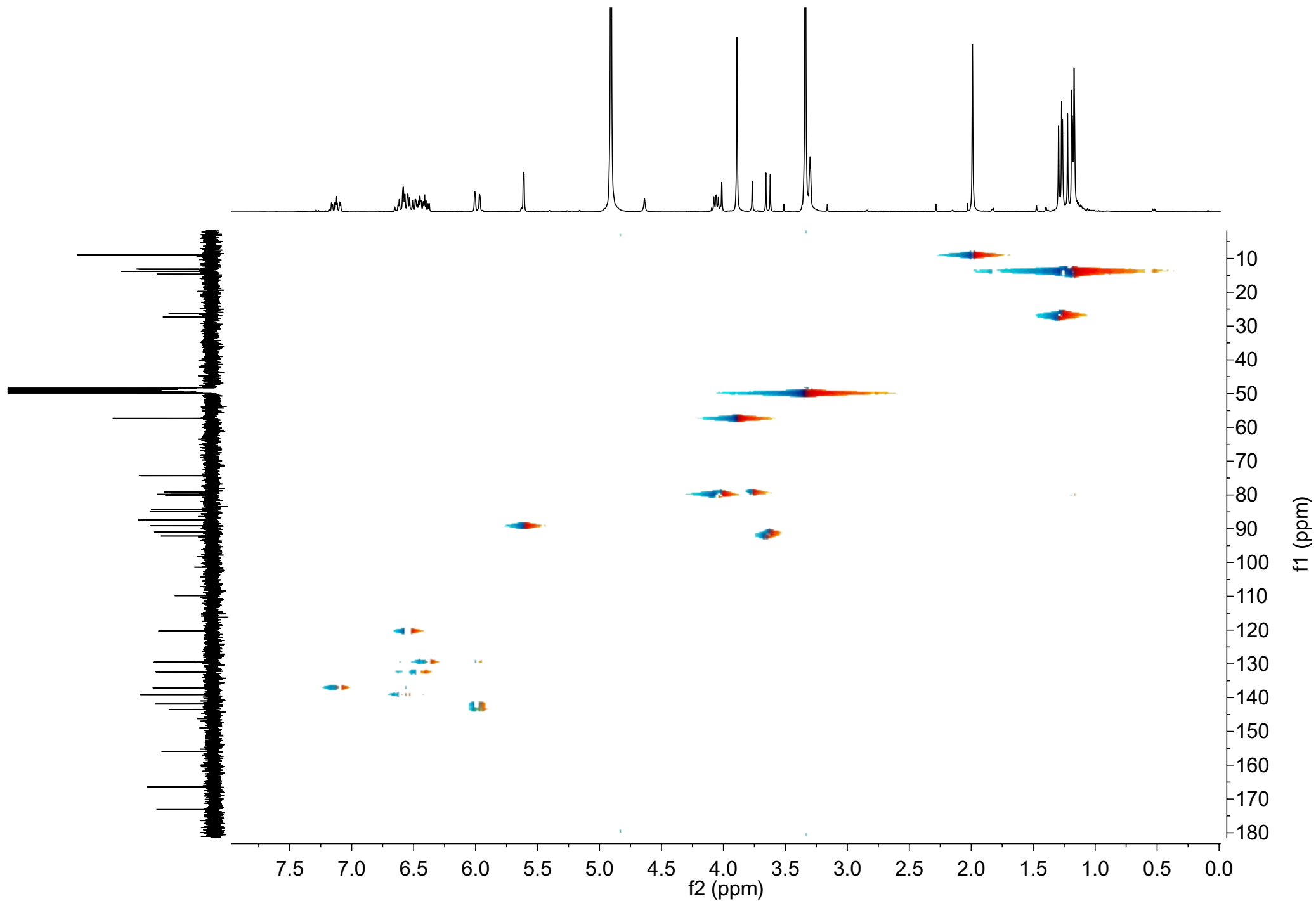


Figure S34. HMQC spectrum (400 MHz, CD_3OD) of citreoviridins N and O (**5** and **6**)

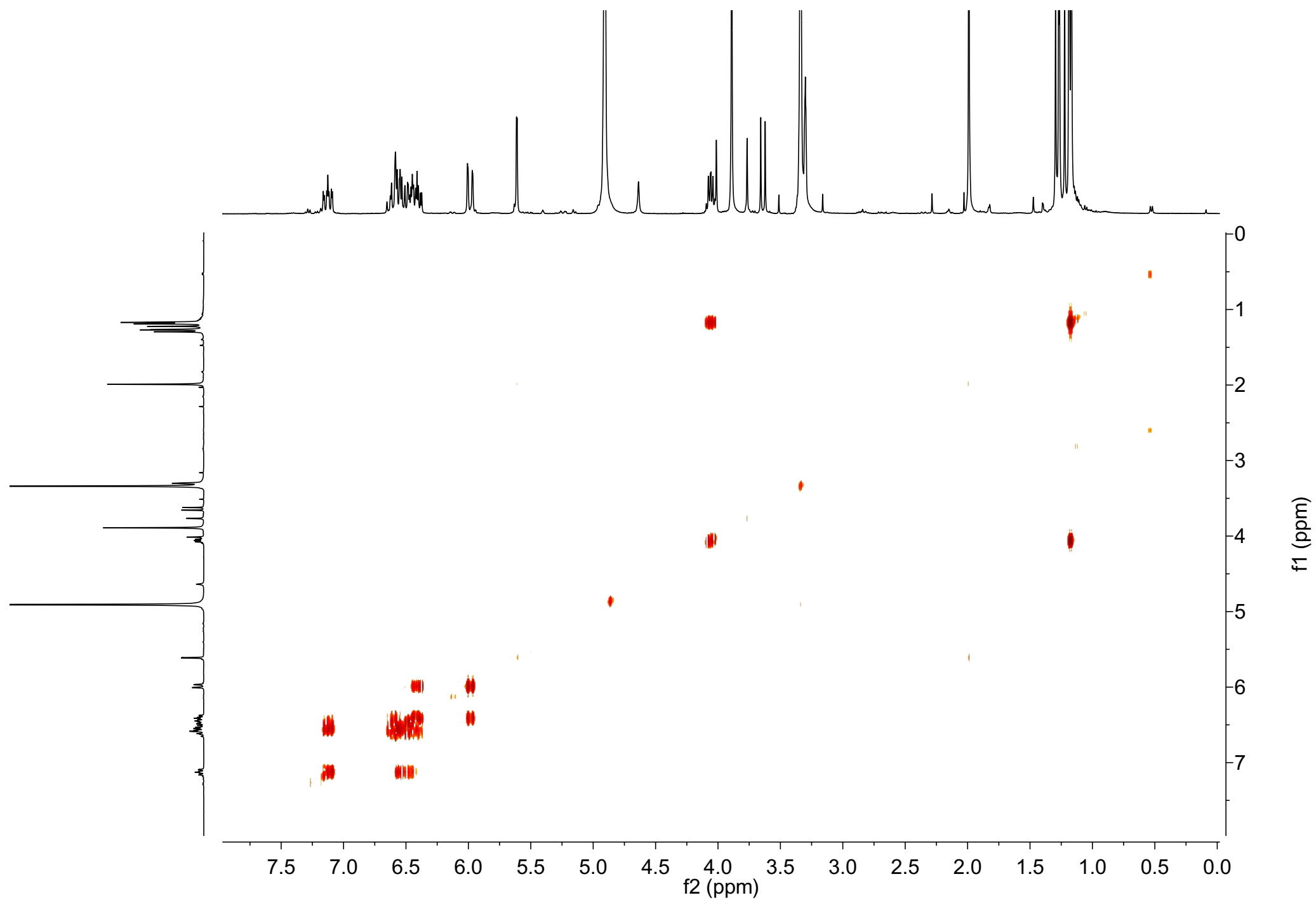


Figure S35. ^1H - ^1H COSY spectrum (400 MHz, CD_3OD) of citreoviridins N and O (**5** and **6**)

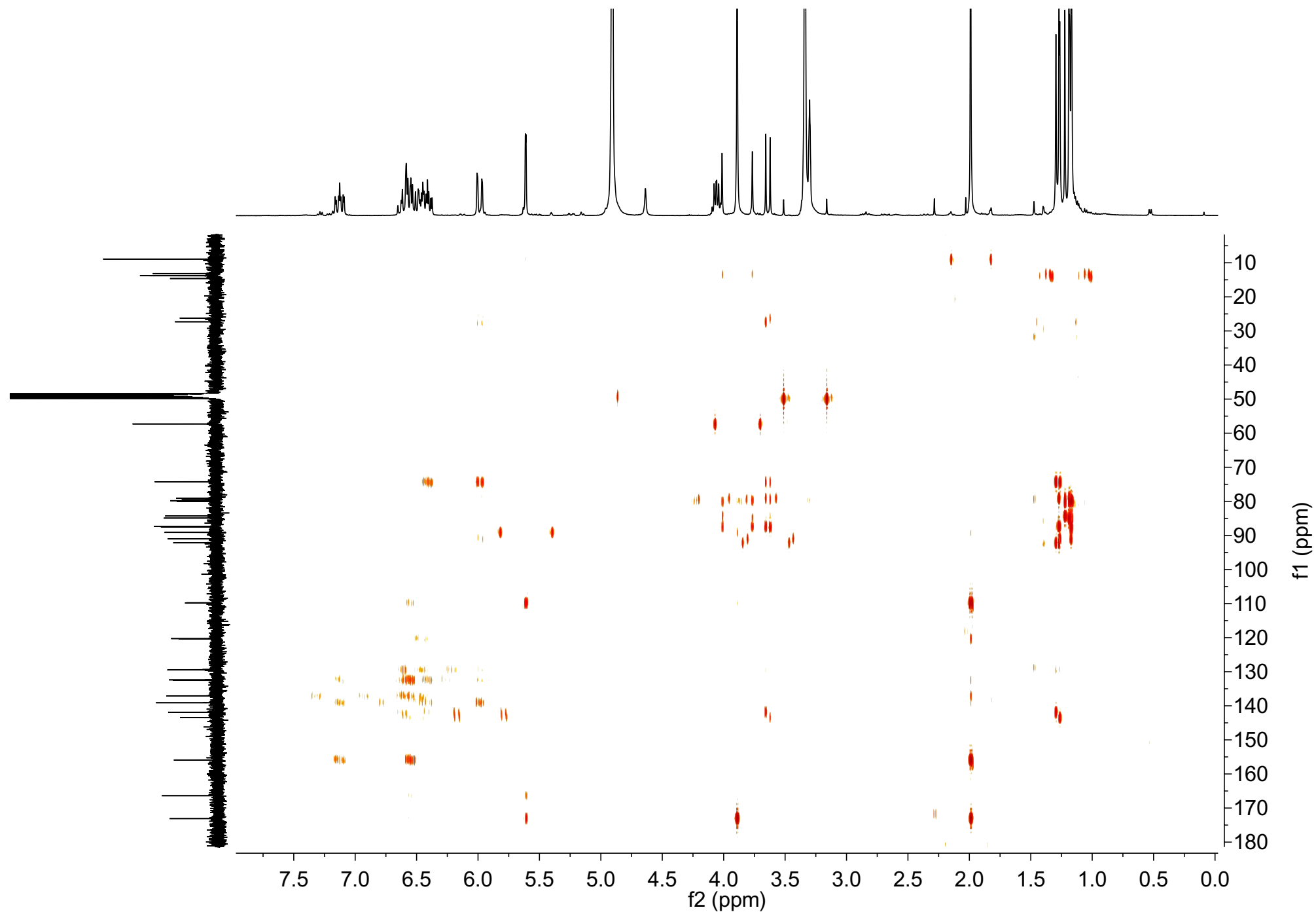


Figure S36. HMBC spectrum (400 MHz, CD₃OD) of citreoviridins N and O (**5** and **6**)

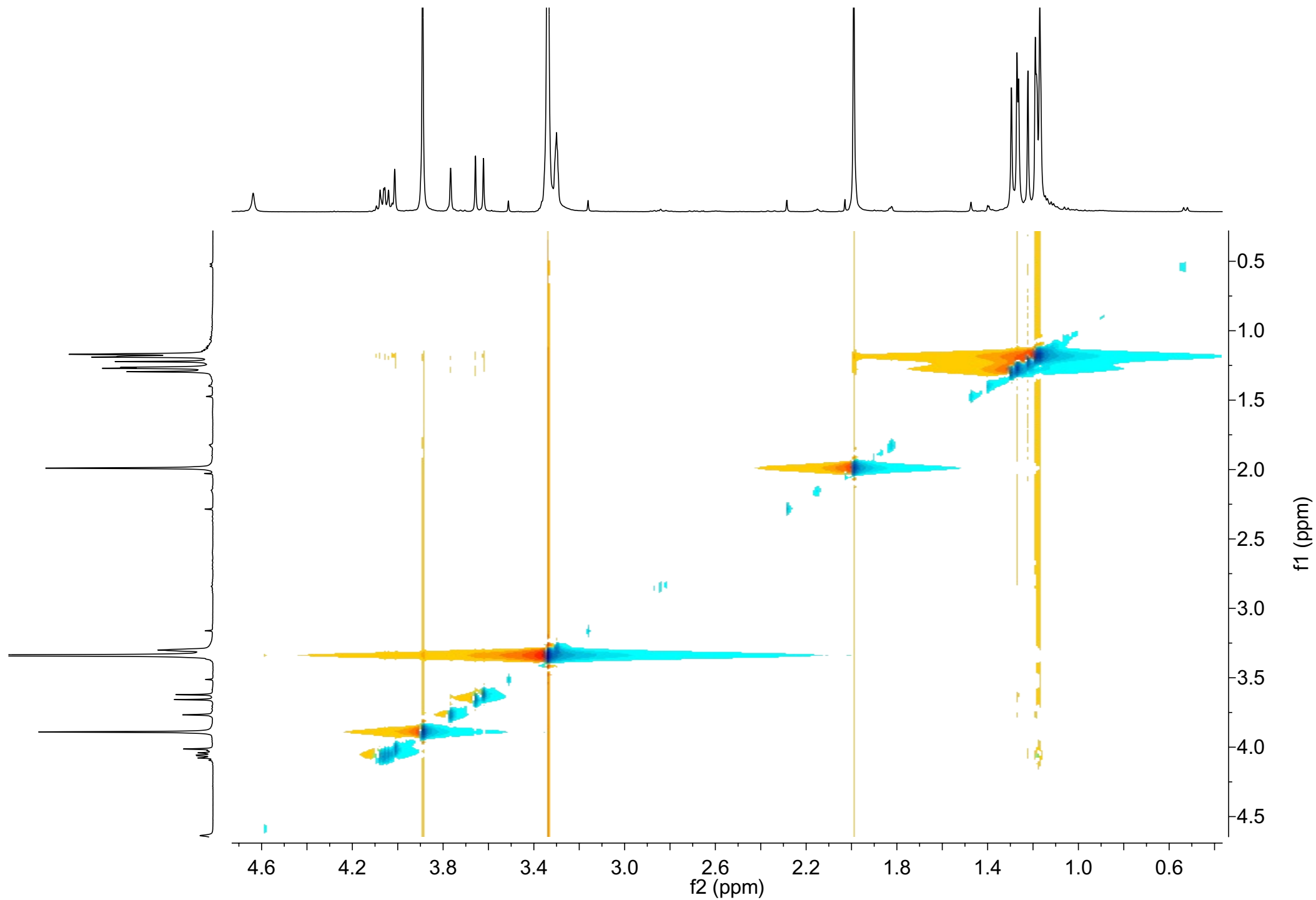


Figure S37. NOESY spectrum (400 MHz, CD₃OD) of citreoviridins N and O (**5** and **6**)

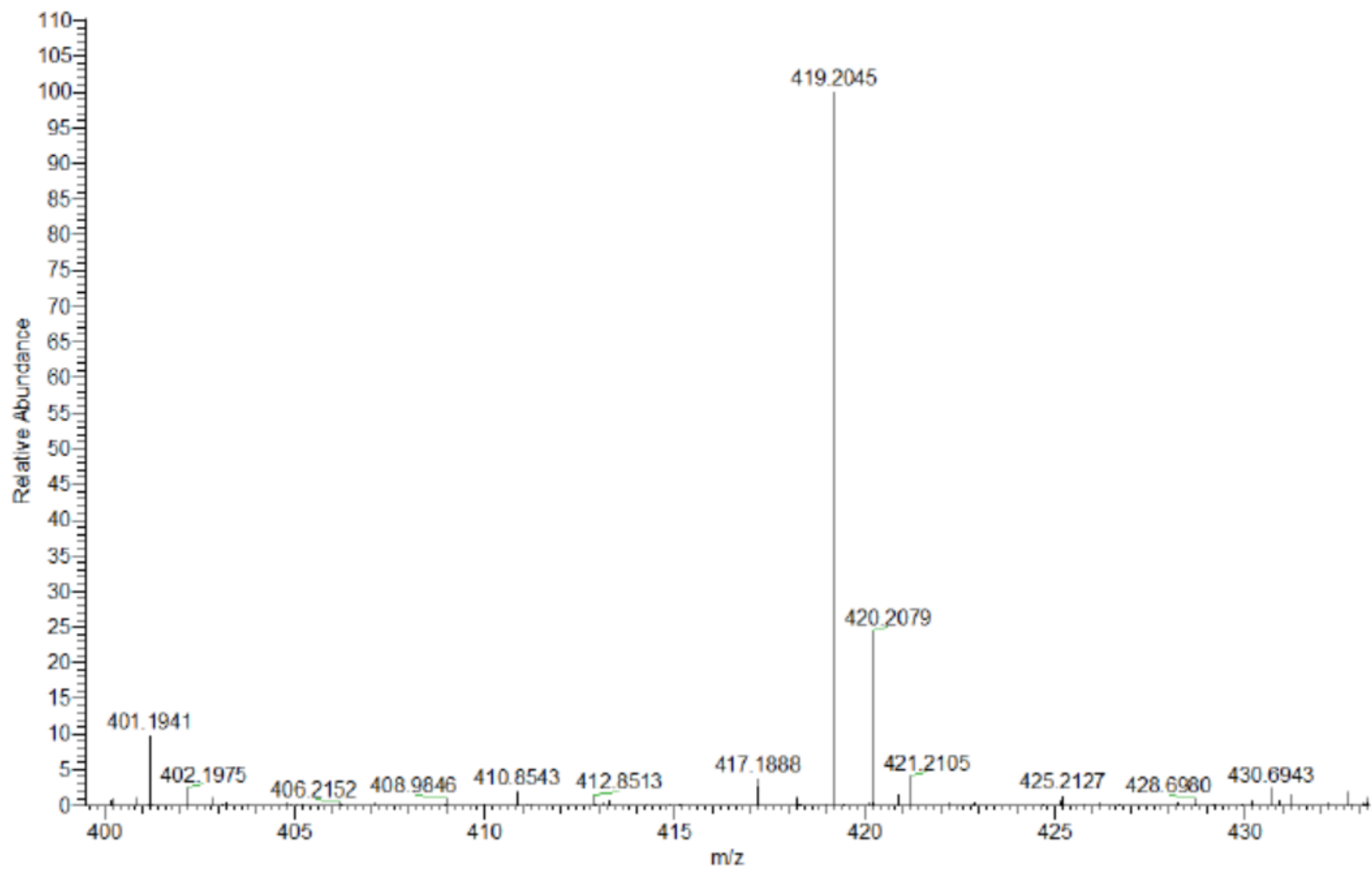


Figure S38. HR-ESI-MS of citreoviridin N (5)

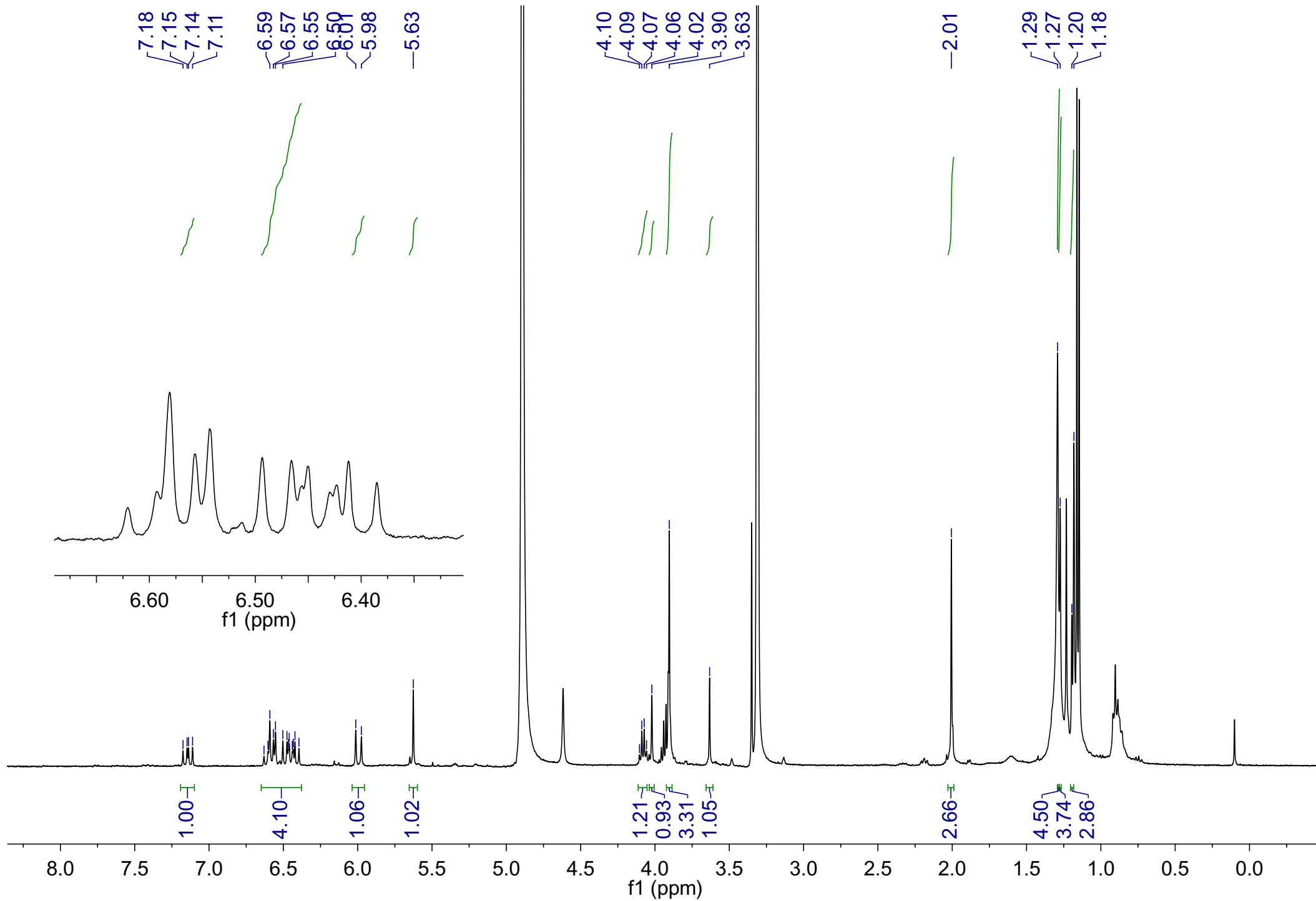


Figure S39. ^1H NMR spectrum (400 MHz, CD_3OD) of citreoviridin N (**5**)

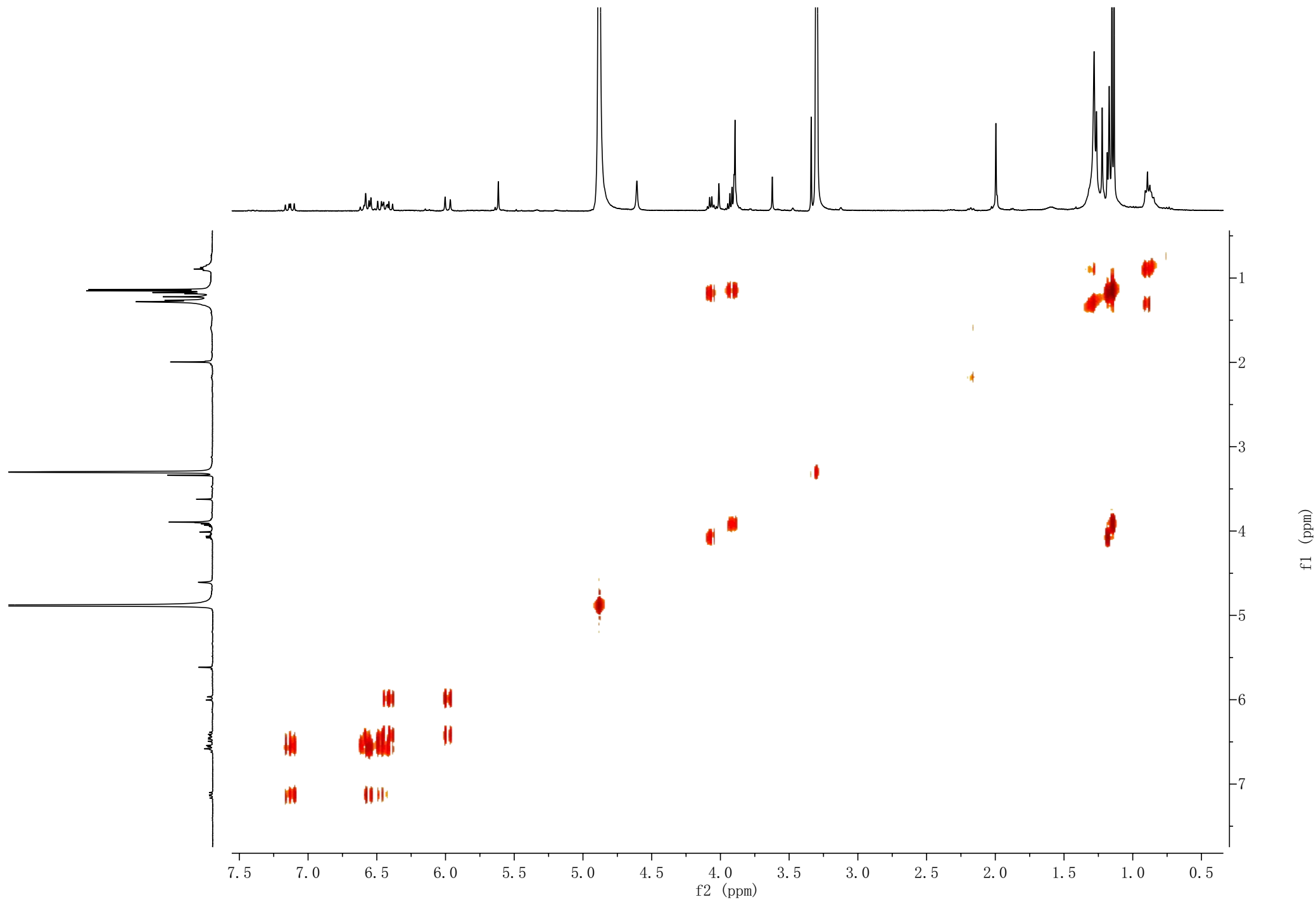


Figure S40. ^1H - ^1H COSY spectrum (400 MHz, CD_3OD) of citreoviridin N (**5**)

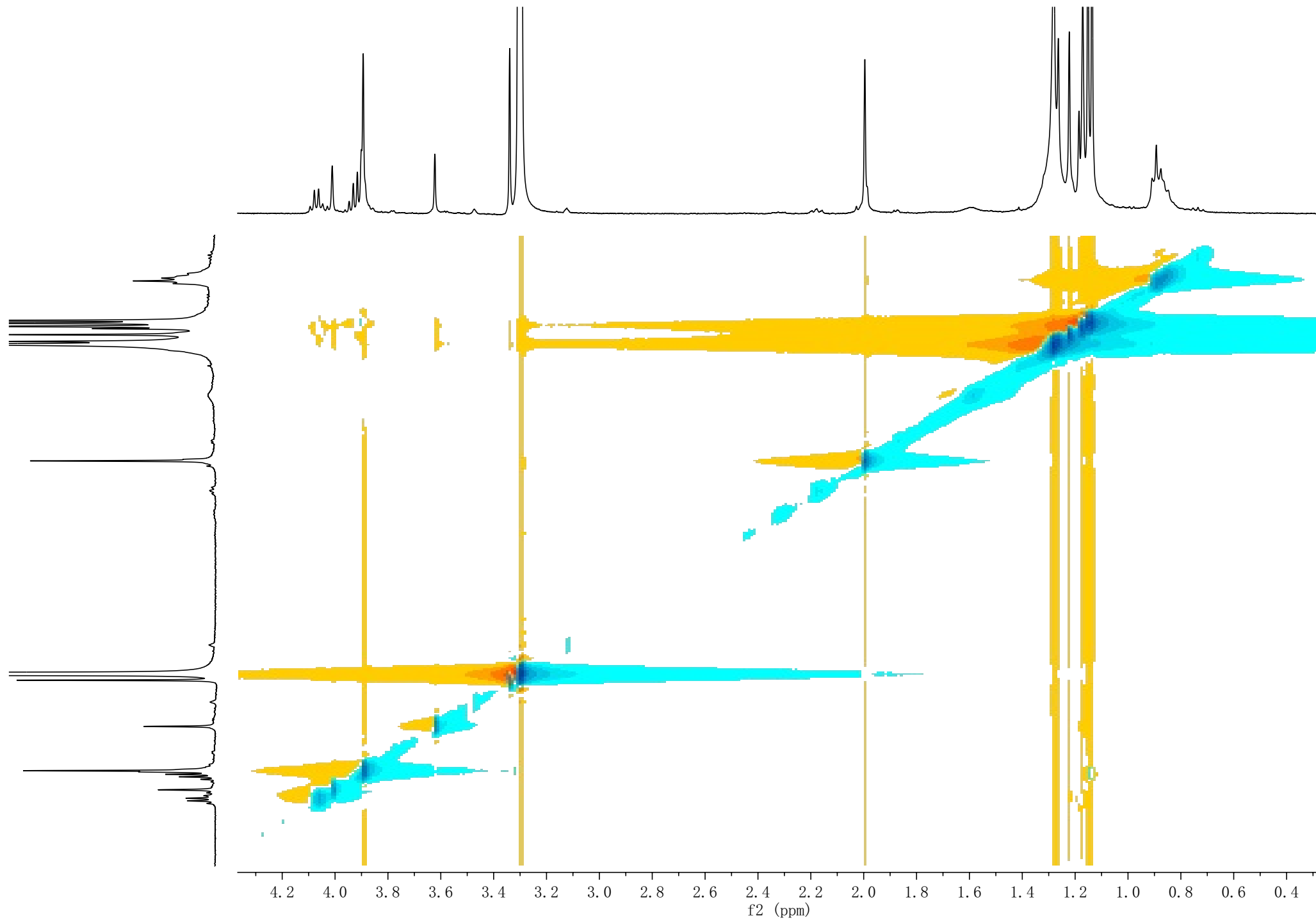


Figure S41. NOESY spectrum (400 MHz, CD₃OD) of citreoviridin N (**5**)

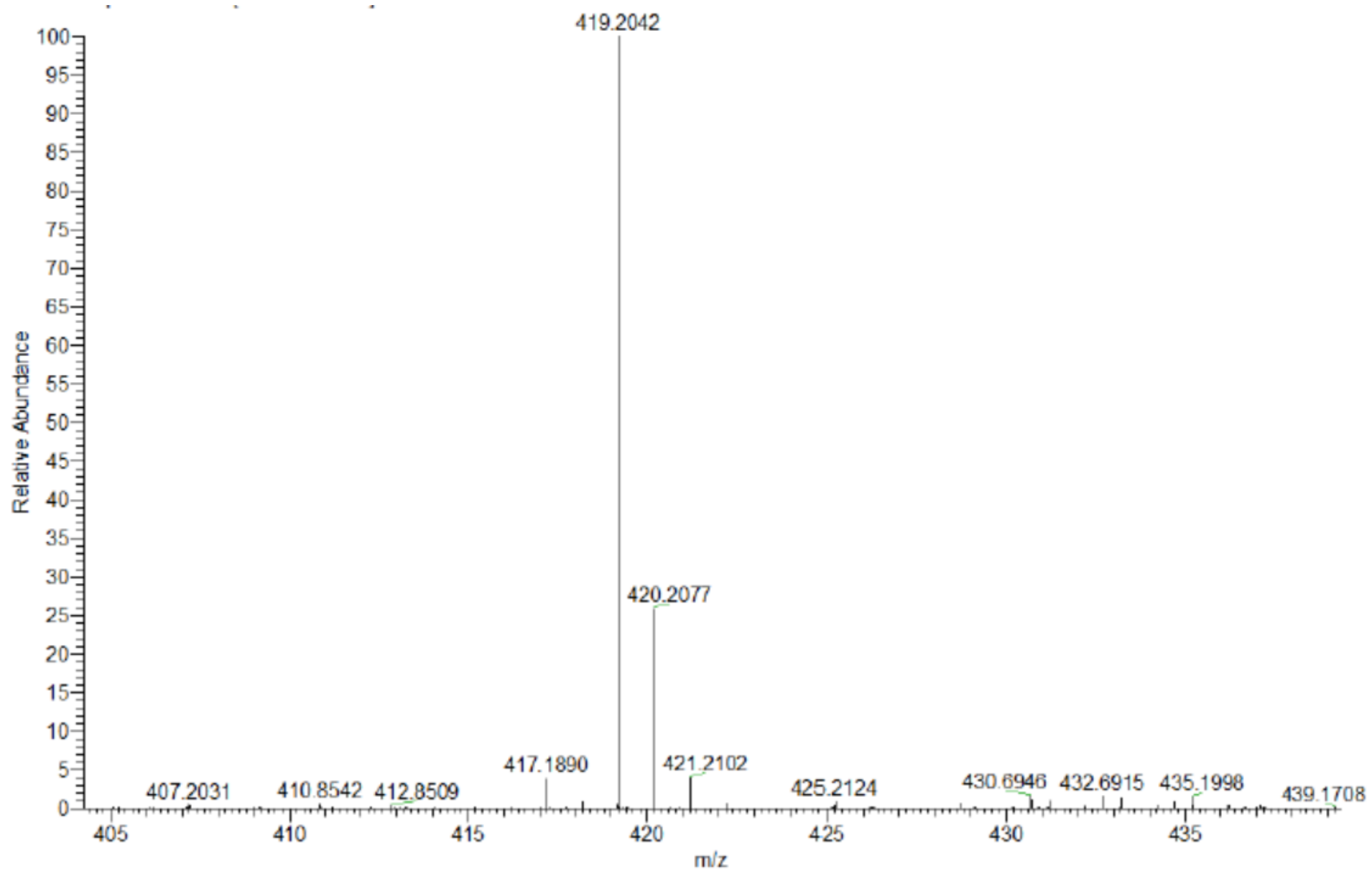


Figure S42. HR-ESI-MS of citreoviridin O (6)

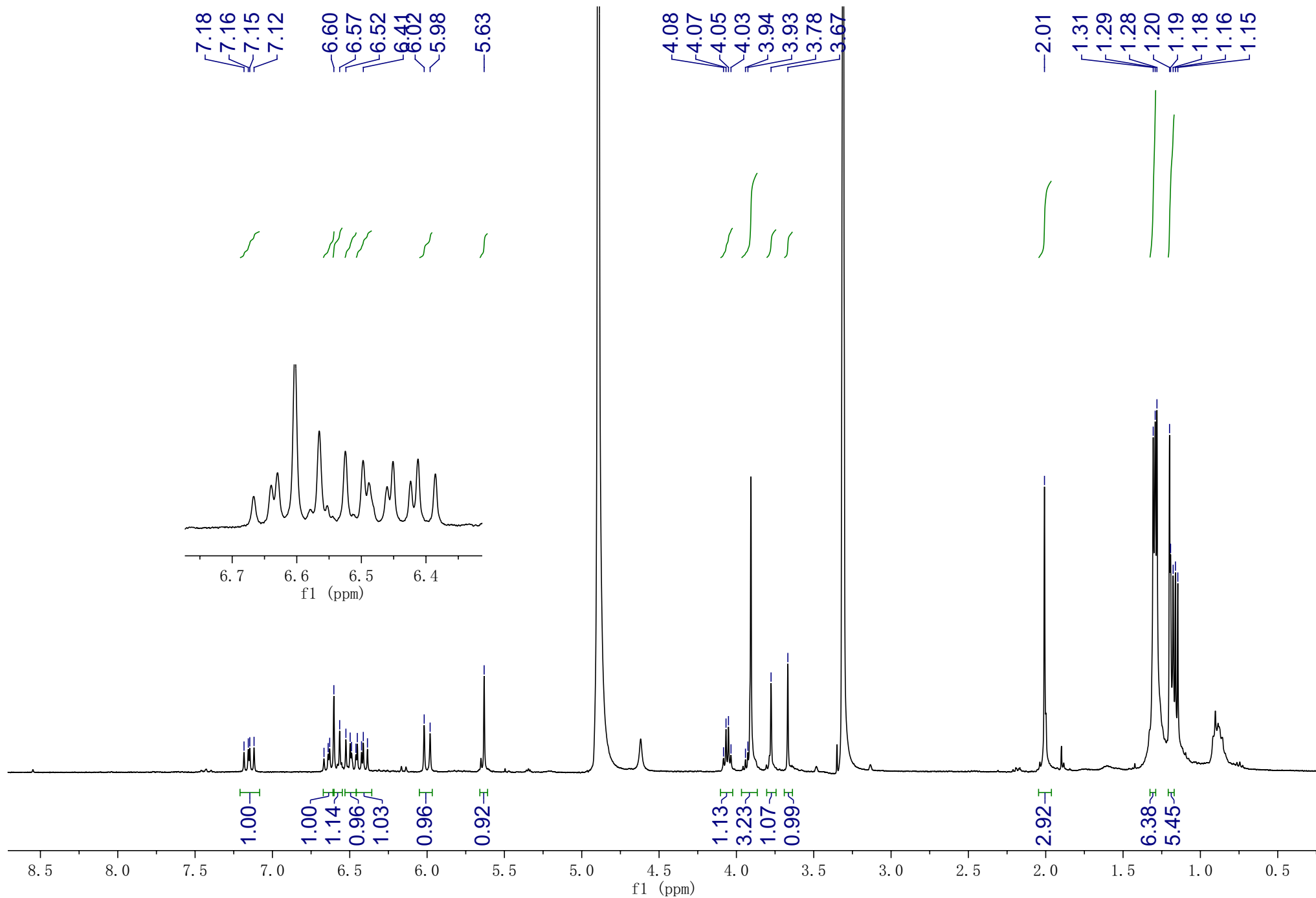


Figure S43. ^1H NMR spectrum (400 MHz, CD_3OD) of citreoviridin O (**6**)

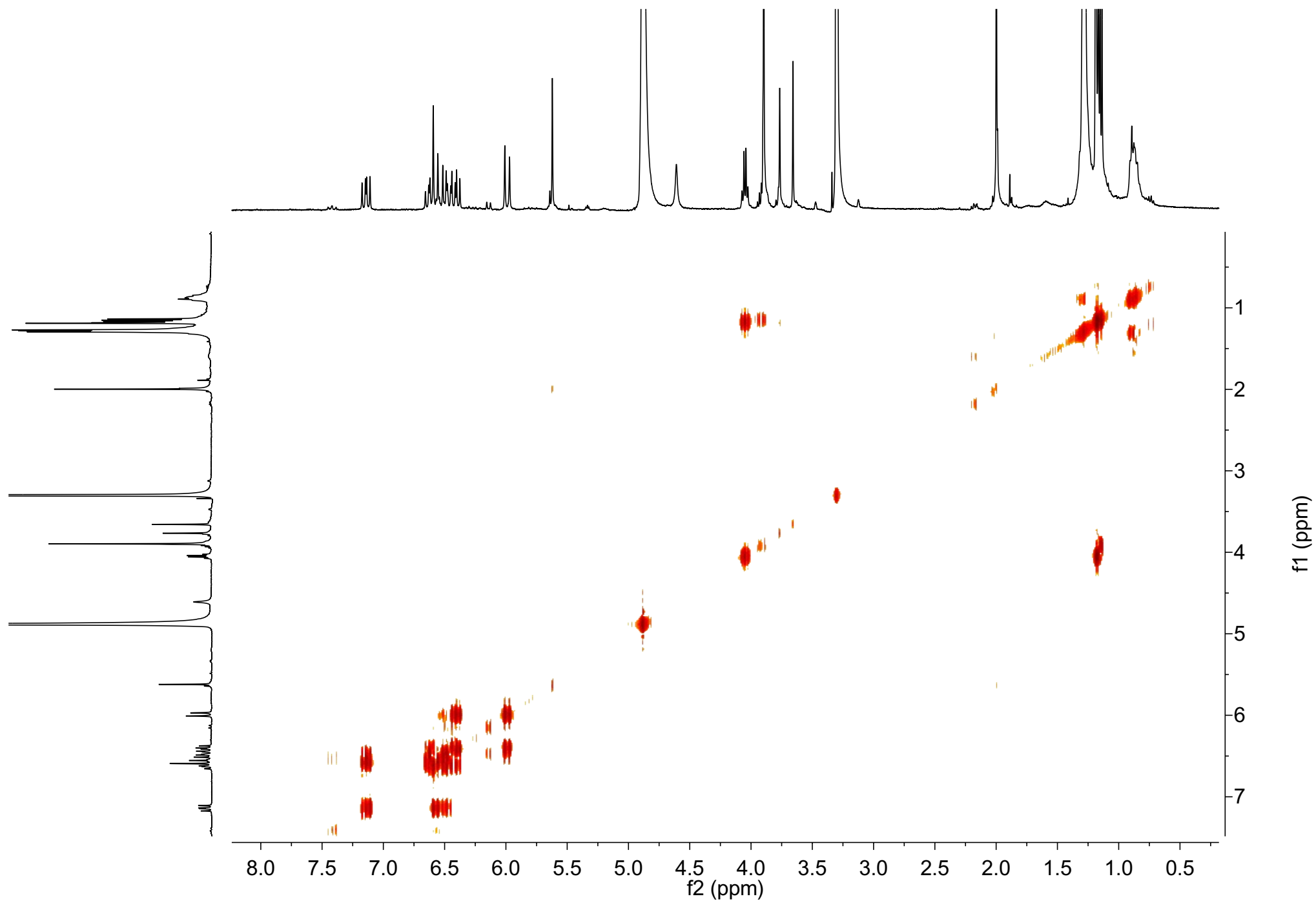


Figure S44. ^1H - ^1H COSY spectrum (400 MHz, CD_3OD) of citreoviridin O (**6**)

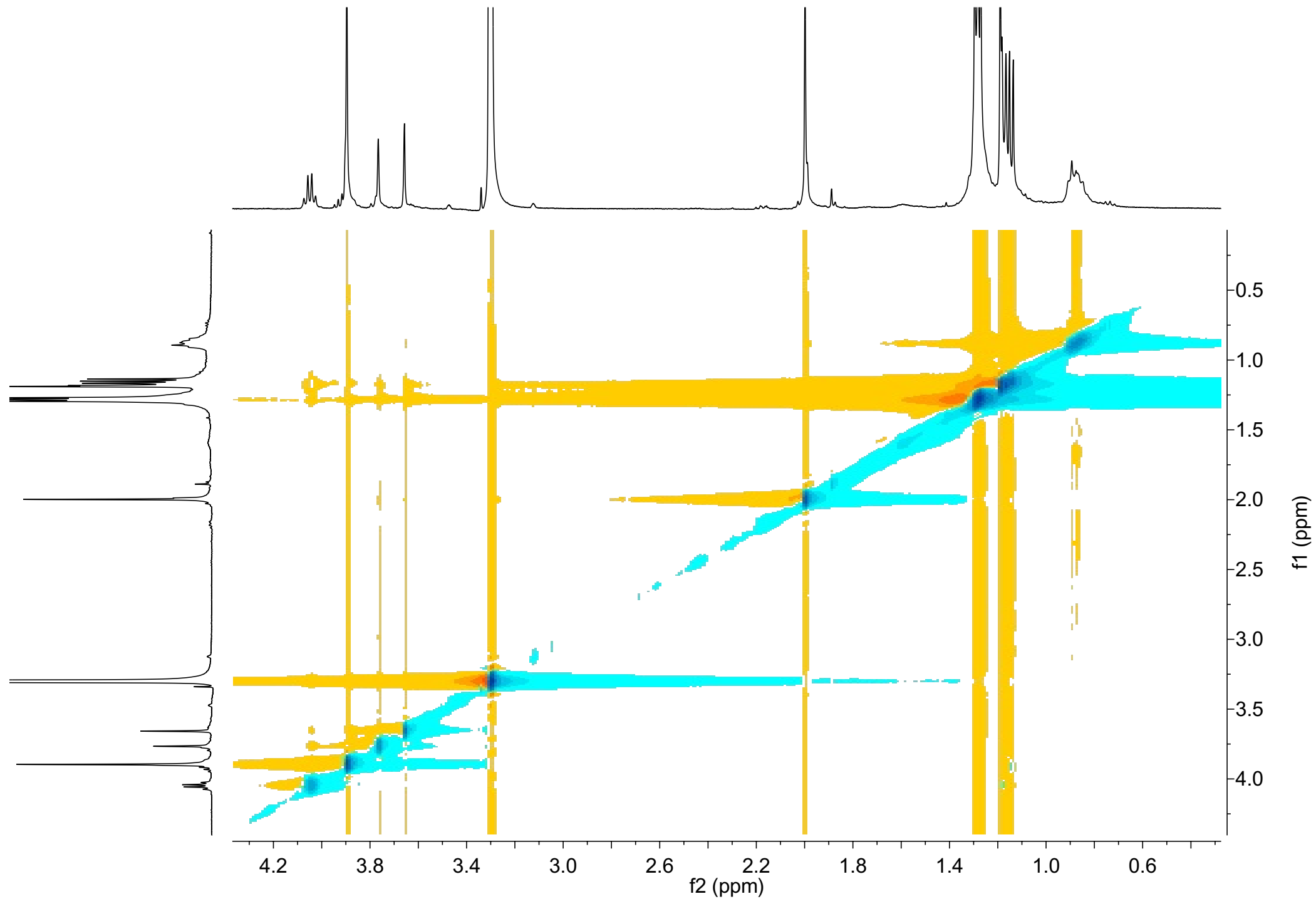


Figure S45. NOESY spectrum (400 MHz, CD₃OD) of citreoviridin O (6)

Single Mass Analysis

Tolerance = 10.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

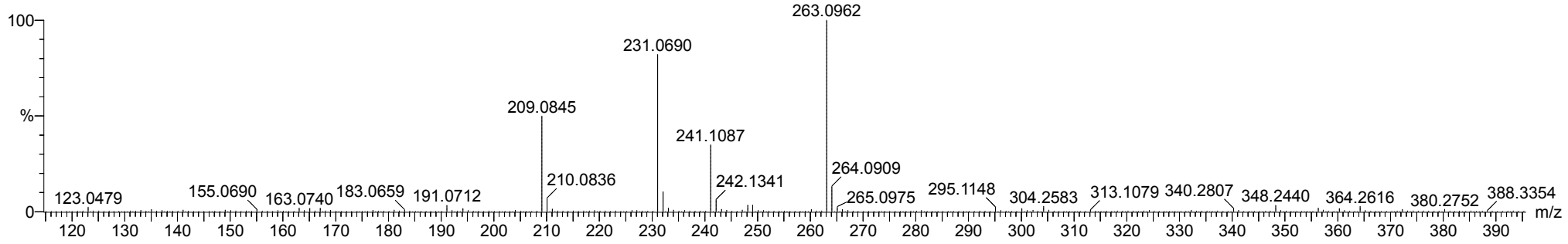
1 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 55-64 H: 0-200 N: 0-15 O: 0-20 Na: 0-1

ZBB-2-Dec 103 (0.408) Cm (97:104)

1: TOF MS ES+



Minimum: -1.5
Maximum: 10.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
0.0000	---							

Figure S46. HR-ESI-MS of pyrenocine A (7)

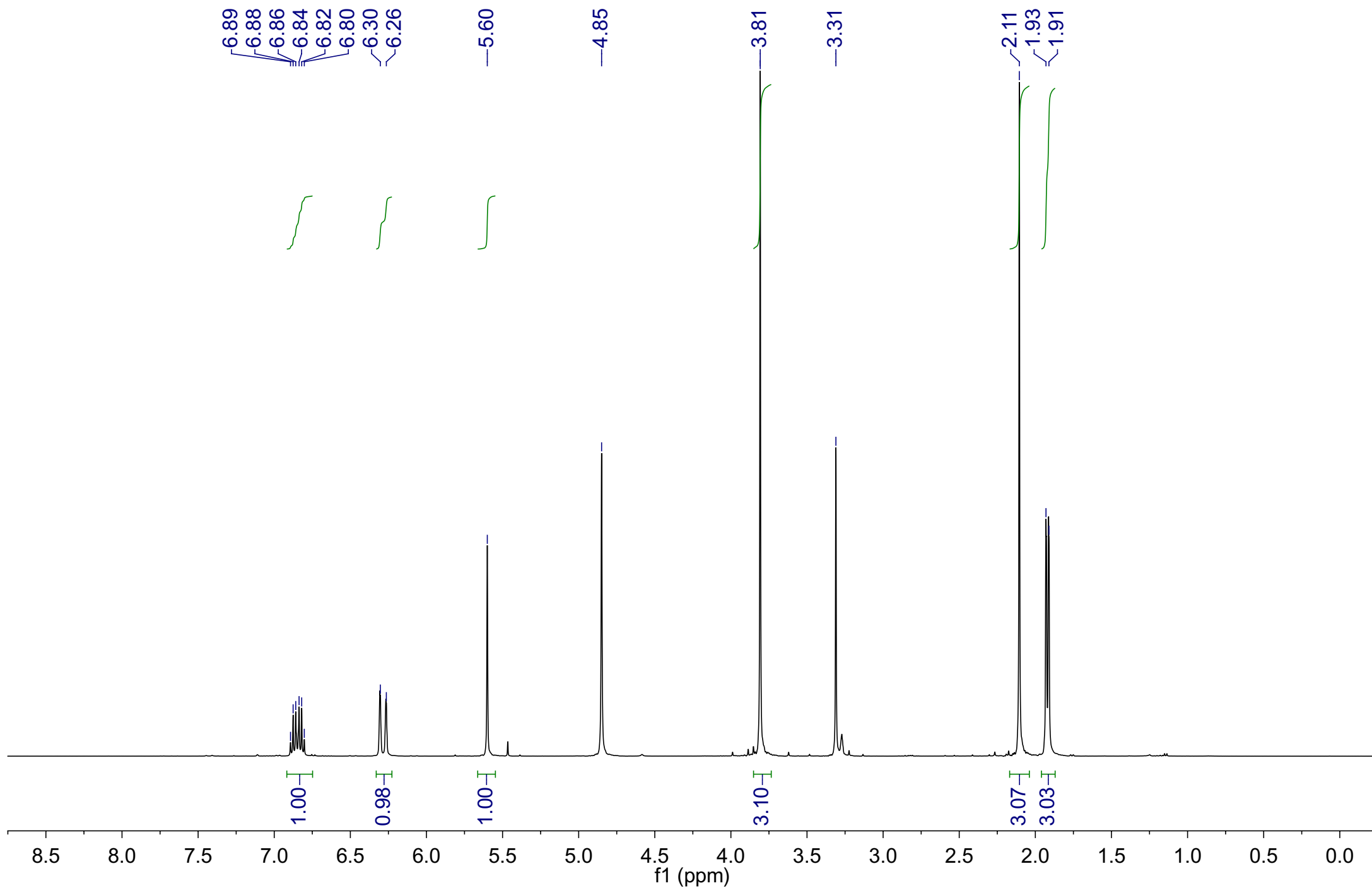


Figure S47. ¹H NMR spectrum (400 MHz, CD₃OD) of pyrenocine A (7)

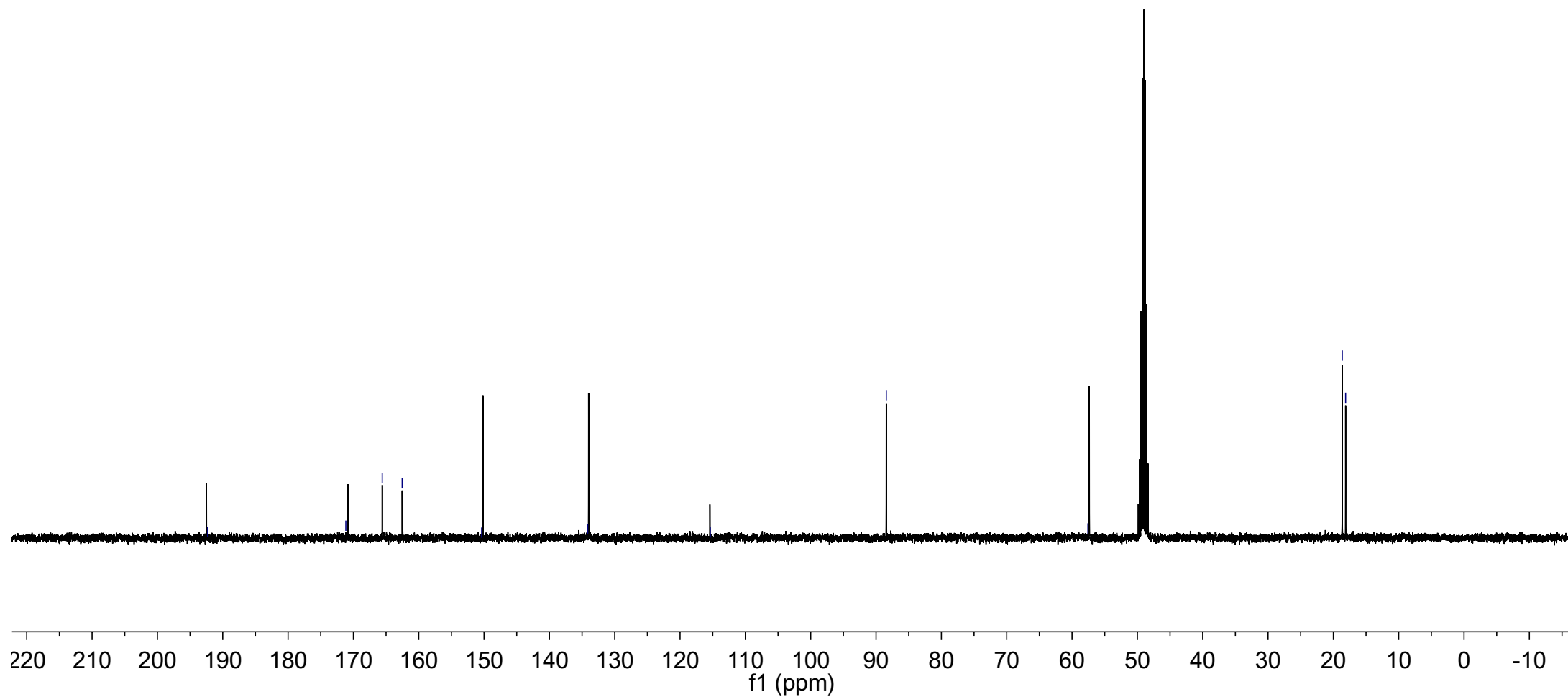


Figure S48. ¹³C NMR spectrum (100 MHz, CD₃OD) of pyrenocine A (7)

Single Mass Analysis

Tolerance = 10.0 mDa / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

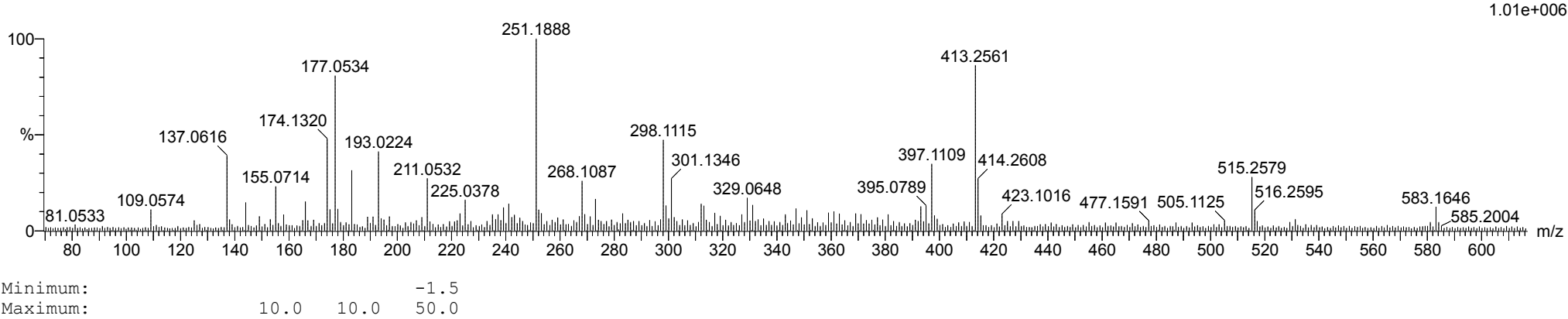
1 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 10-50 H: 0-200 N: 0-15 O: 0-20 Na: 0-1

ZBB-13-Dec 110 (0.433) Cm (105:112)

1: TOF MS ES+



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
0.0000	---							

Figure S49. HR-ESI-MS of terrein (14)

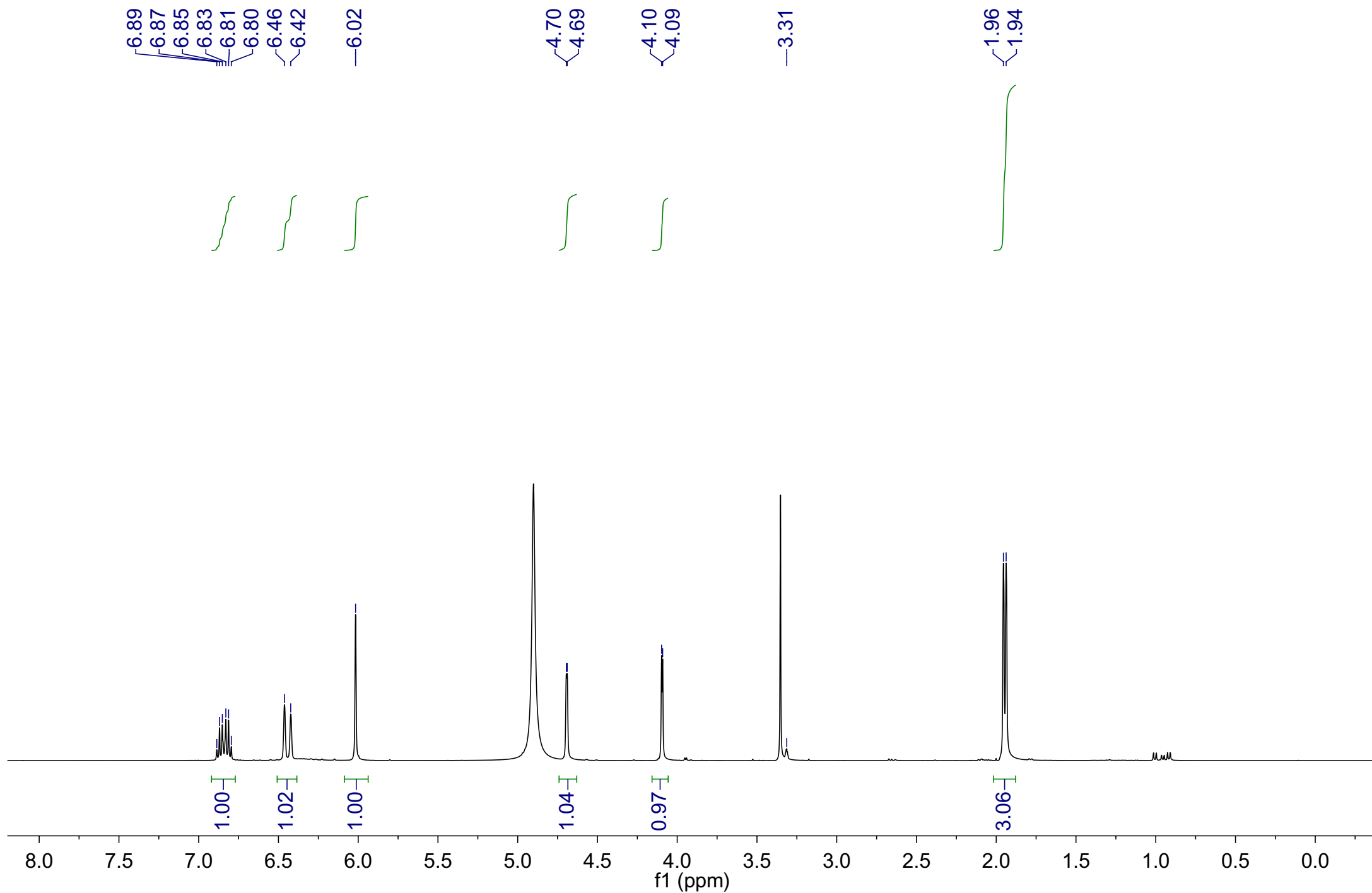


Figure S50. ¹H NMR spectrum (400 MHz, CD₃OD) of terrein (**14**)

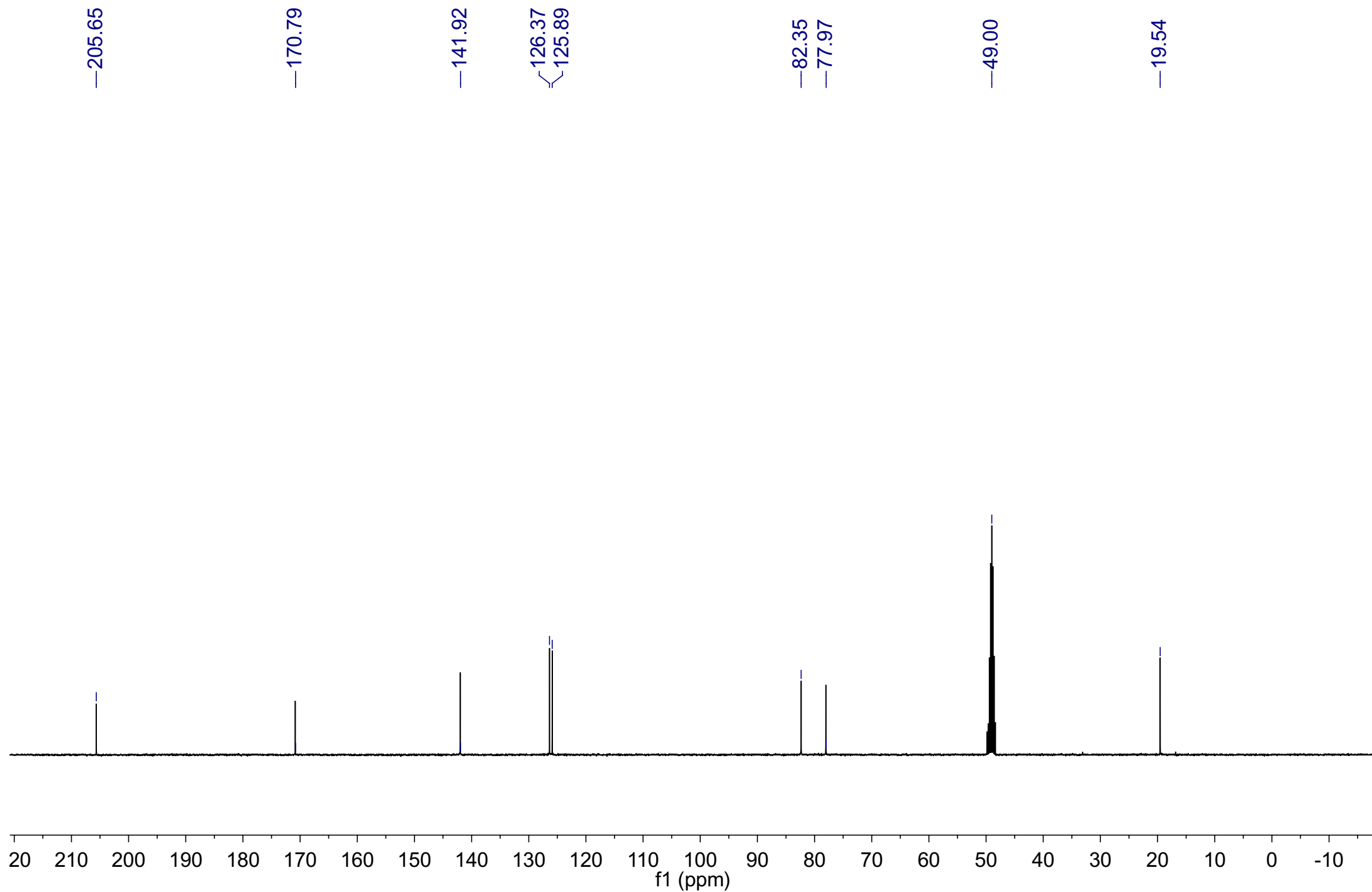


Figure S51. ¹³C NMR spectrum (100 MHz, CD₃OD) of terrein (14)

Single Mass Analysis

Tolerance = 10.0 mDa / DBE: min = -10.0, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

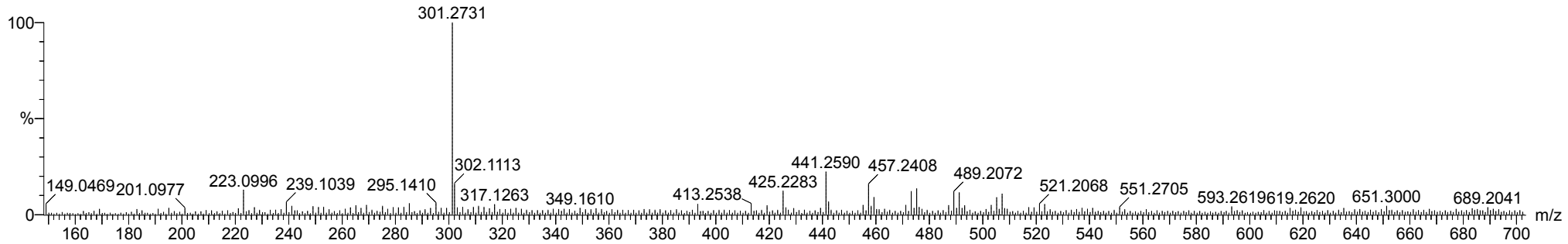
Monoisotopic Mass, Even Electron Ions

1 formula(e) evaluated with 0 results within limits (all results (up to 1000) for each mass)

Elements Used:

ZBB-23-Jan 101 (0.400) Cm (101:102)

1: TOF MS ES+



Minimum: -10.0
Maximum: 10.0 10.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
0.0000	---							

Figure S52. HR-ESI-MS of citreoviridin (20)

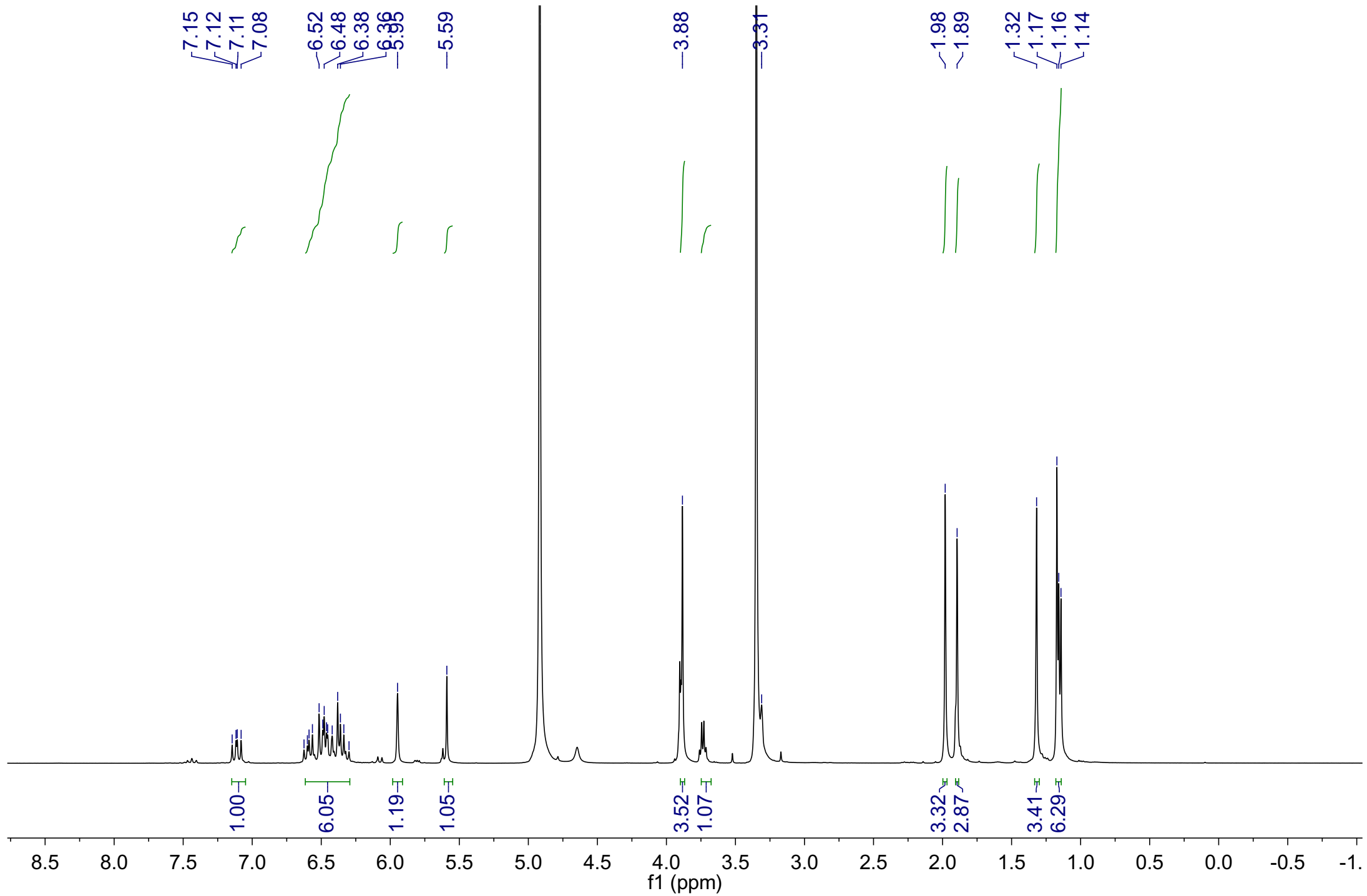


Figure S53. ¹H NMR spectrum (400 MHz, CD₃OD) of citreoviridin (**20**)

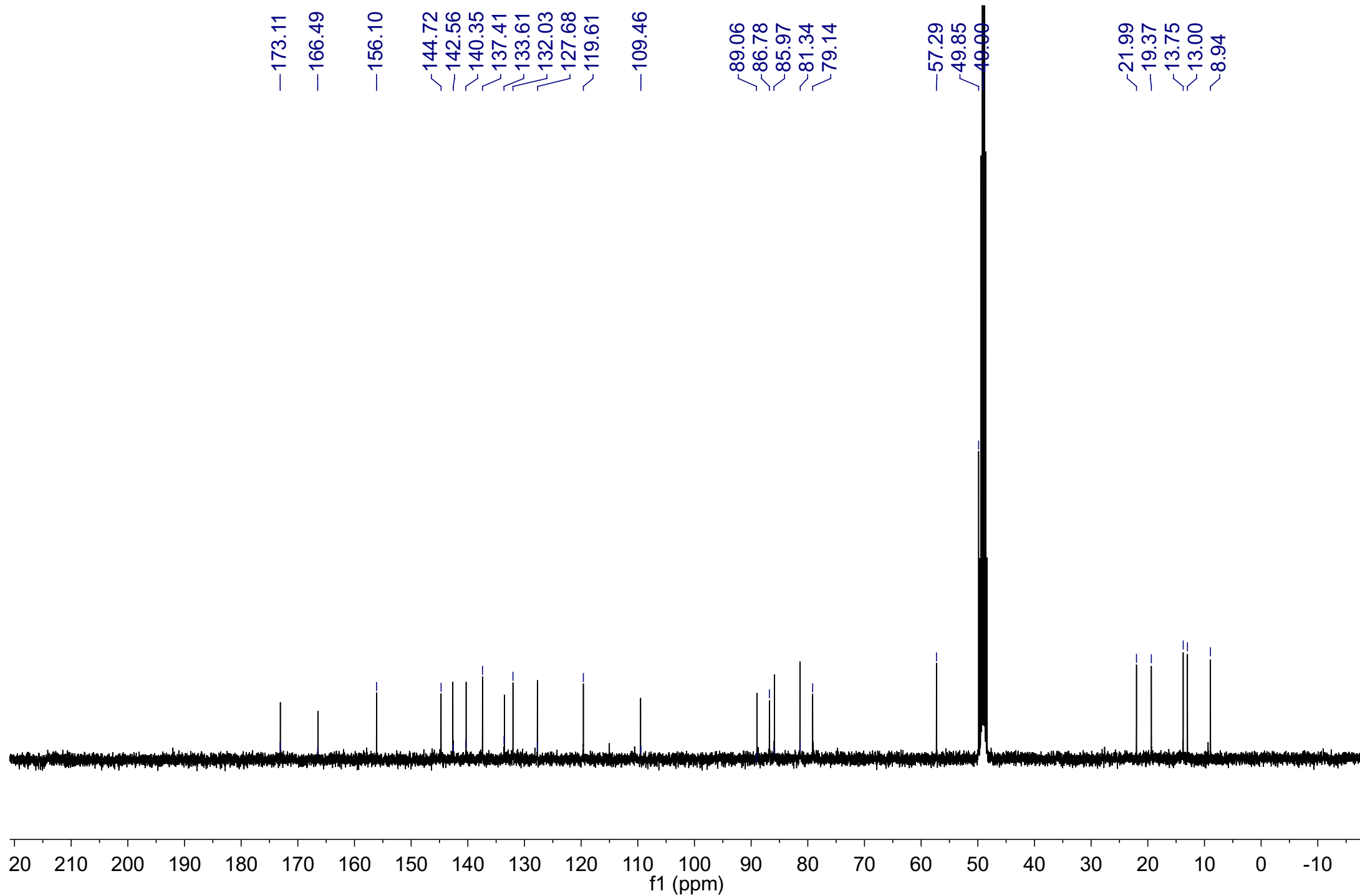


Figure S54. ¹³C NMR spectrum (100 MHz, CD₃OD) of citreoviridin (**20**)