Supporting Information for

Marinisporolides, New Polyene-Polyol Macrolides from a Marine Actinomycete of New Genus "*Marinispora*"

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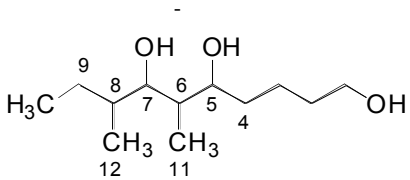
General Experimental Procedures. ^{1}H NMR and 2D NMR spectra were obtained in DMSO-d_6, pyridine-d_5, or CD_3CN at 500 MHz. ^{13}C NMR spectra were obtained at 75 MHz or 125 MHz. HR-ESI-TOF MS data were obtained at the Scripps Research Institute, La Jolla, CA. Semi preparative reversed-phase HPLC separations were performed using a Varian Dynamax® C-18 column (250 x 10 mm) and a Phenomenex Luna® 5u C-8(2) column (250 x 10 mm) at a flow rate of 2 mL/min using a Waters refractive index dectector. HPLC-MS data were obtained using a Agilent 1100 LC-MS system using a Phenomenex Luna® 5u C-18(2) analytical column (100 x 4.6 mm) and Agilent 1050 HPLC system with Kromasil 5u C-18 analyical column (150 x 4.6 mm) were used for the analysis of fractions and reaction mixtures.

Table S1. ^{13}C NMR data of diastereomers of 6-methyl-decane-1,5,7-triol (DMSO-d_6)[a]



	A ($\alpha\alpha\beta\beta$[b])	**B** ($\alpha\alpha\alpha\alpha$[c])	**C** ($\alpha\alpha\beta\alpha$[d])	**D** ($\alpha\alpha\alpha\beta$[e])	**E** ($\beta\alpha\beta\beta$[f])	**F** ($\beta\alpha\alpha\alpha$[g])	**G** ($\beta\alpha\beta\alpha$[h])	**H** ($\beta\alpha\alpha\beta$[i])
4	34.2	34.8	34.4	34.6	31.5	33.3	31.8	34.2
5	69.8	72.2	69.8	73.8	71.8	72.0	71.7	72.6
6	39.5	38.8	38.2	38.2	41.3	39.6	41.1	38.9
7	73.6	76.0	77.4	77.5	74.9	73.3	77.8	73.3
8	34.1	34.4	34.7	35.0	34.1	34.8	34.6	35.1
9	34.0	33.1	29.8	31.5	32.6	32.6	28.6	32.2
11	10.1	8.1	10.6	6.8	11.2	10.3	11.5	9.8
12	12.8	14.5	16.9	15.7	12.4	15.5	17.3	15.5

[a] Kobayashi, Y.; Tan, C.-H.; Kishi, Y. *J. Am. Chem. Soc.* **2001**, *123*, 2076-2078; Supporting information [b] 5α-OH, 6α-Me, 7β-OH, 8β-Me. [c] 5α-OH, 6α-Me, 7α-OH, 8α-Me. [d] 5α-OH, 6α-Me, 7β-OH, 8α-Me. [e] 5α-OH, 6α-Me, 7α-OH, 8β-Me. [f] 5β-OH, 6α-Me, 7β-OH, 8β-Me. [g] 5β-OH, 6α-Me, 7α-OH, 8α-Me. [h] 5β-OH, 6α-Me, 7β-OH, 8α-Me. [i] 5β-OH, 6α-Me, 7α-OH, 8β-Me.

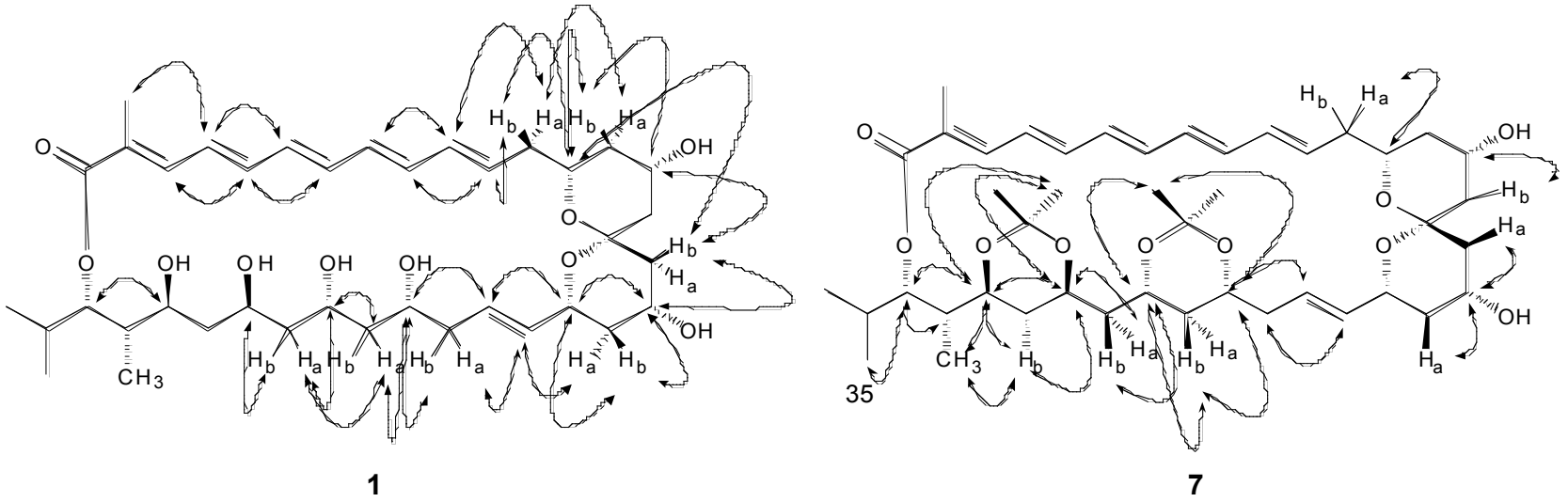


Figure S1. Key ROESY NMR correlation of compounds **1** and **7**.

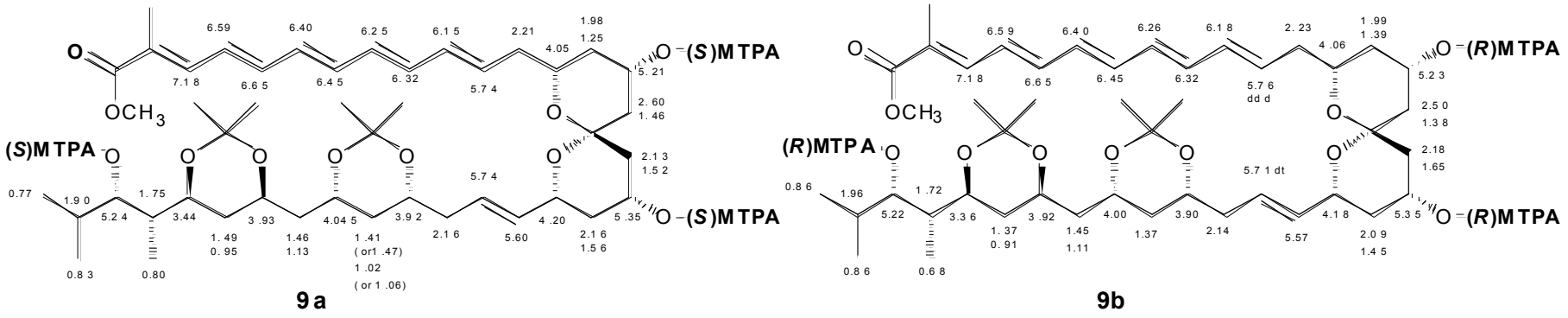


Figure S2. Proton chemical shifts in ^{1}H NMR spectra of **9a** [(*S*)-Mosher ester of **8**] and **9b** [(*R*)-Mosher ester of **8**].

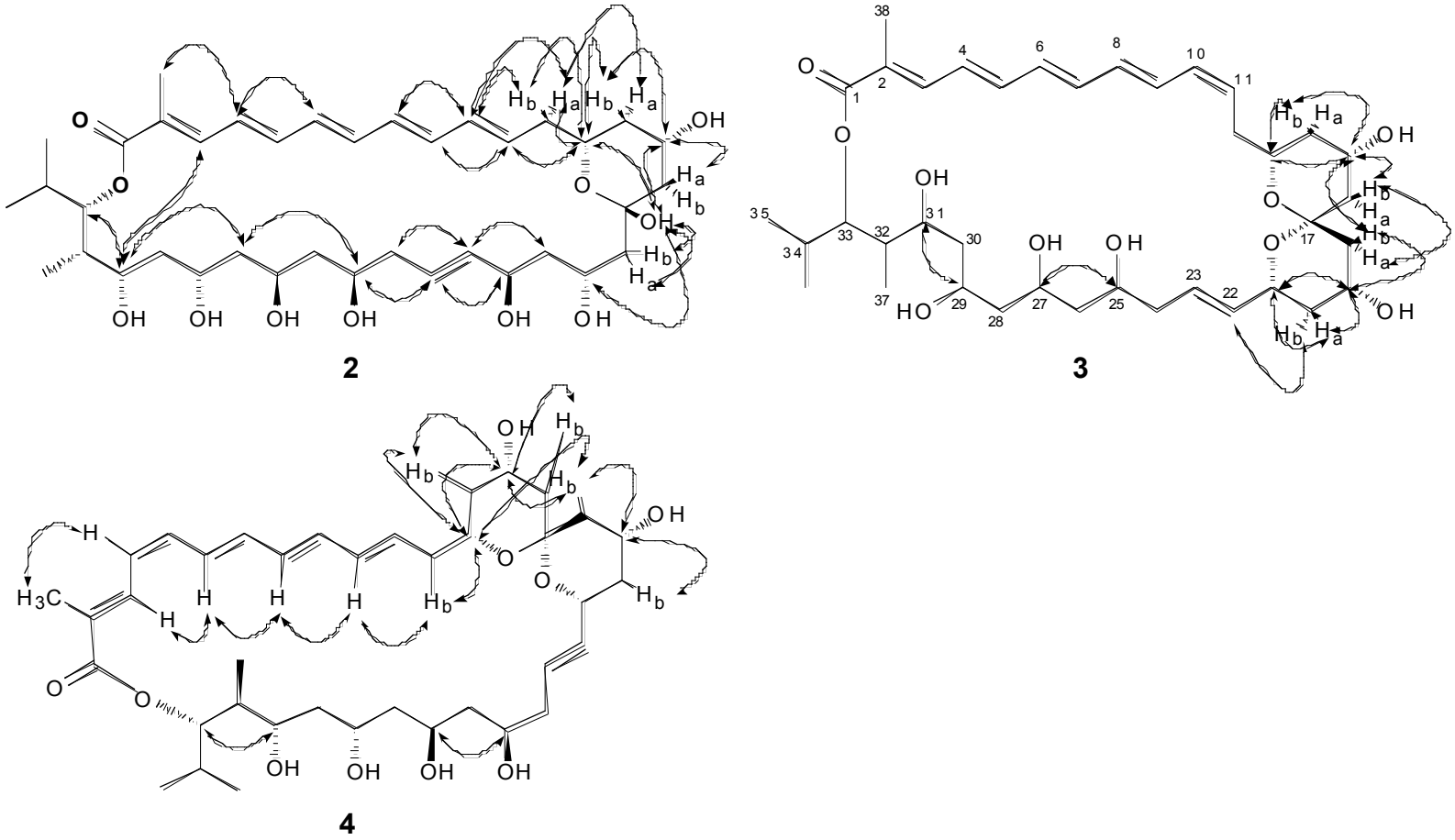


Figure S3. Key ROESY NMR correlation of compounds **2**, **3** and **4**.

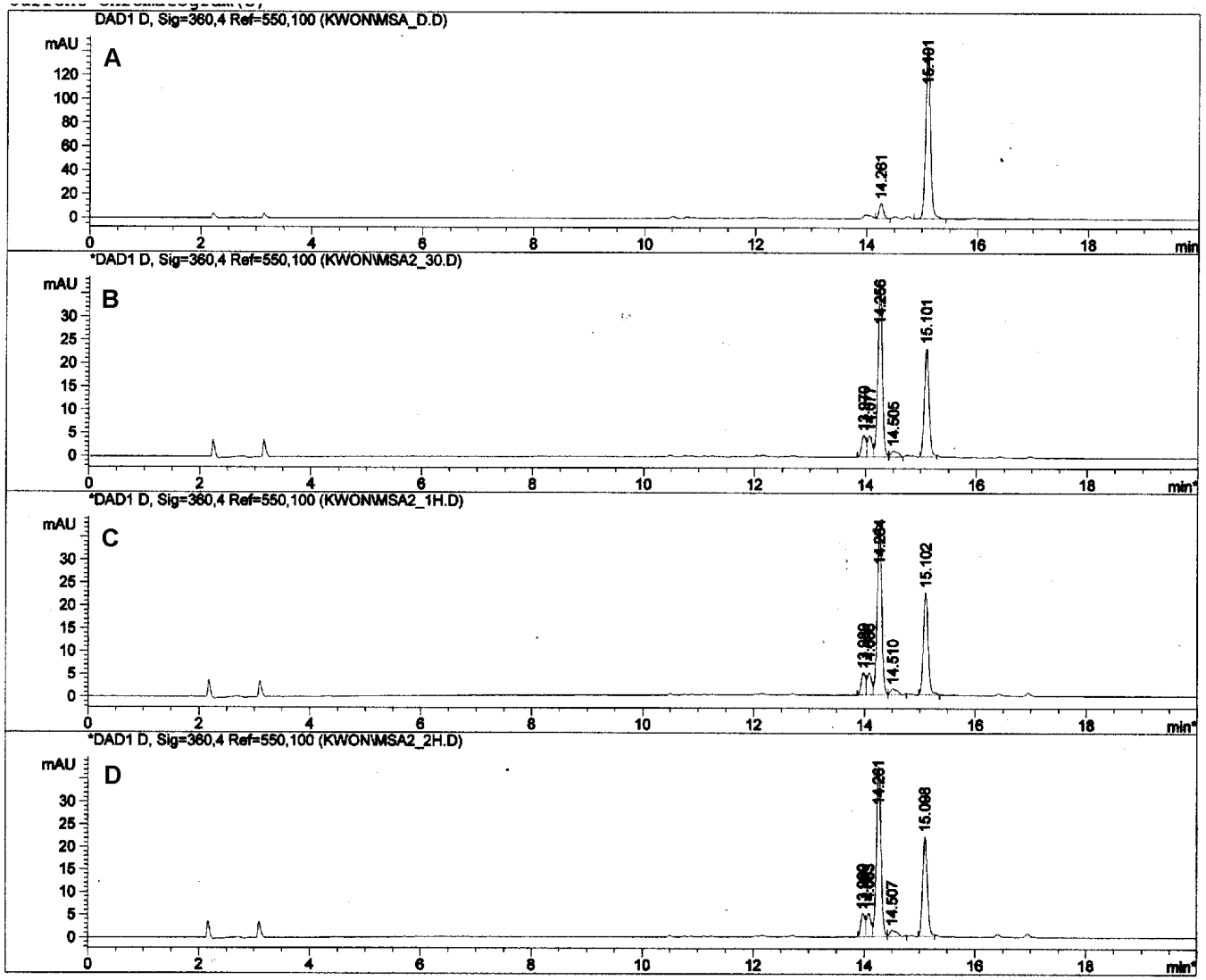


Figure S4. HPLC chromatogram of **1** and isomers of **1** derived from the photochemical conversion of **1** for one and two hours. UV detector 360 nm. Retention time 14.0 min – marinisporolide E (**5**); Rt 14.3 min – marinisporolide D (**4**); Rt 14.5 min – marinisporolide C (**3**); Rt 15.1 min – marinisporolide A (**1**). (A) marinisporolide A (**1**) before exposure to light; (B) 30 min after exposure to light; (C) 1 hours; (D) 2 hours.

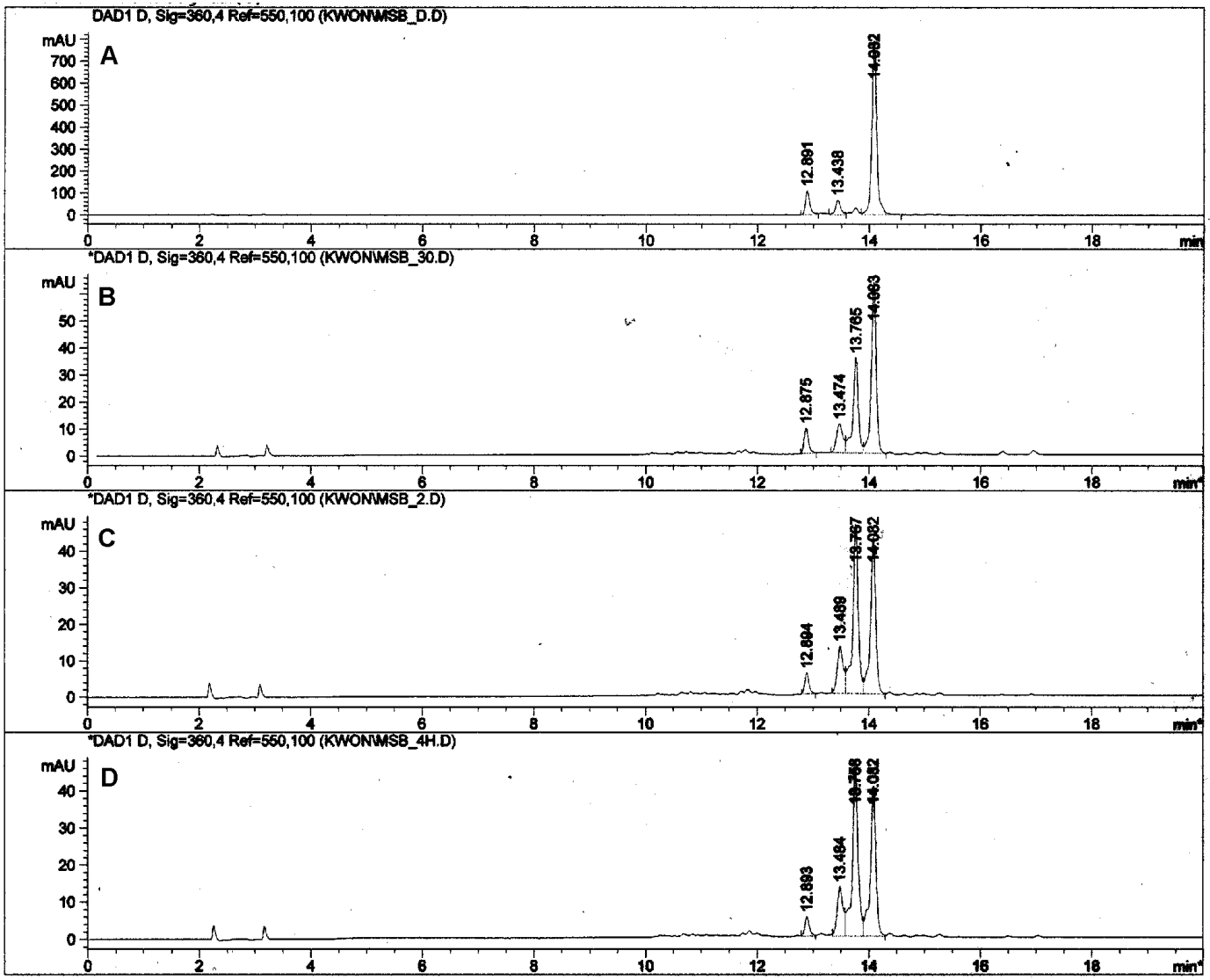


Figure S5. HPLC chromatogram of **2** and isomers of **2** derived from the photochemical conversion of **2** for one and two hours. (UV detector 360 nm). Retention time 14.1 min – marinisporolide B (**2**). (A) marinisporolide B (**2**) before exposure to light; (B) 30 min after exposure to light; (C) 2 hours; (D) 4 hours.

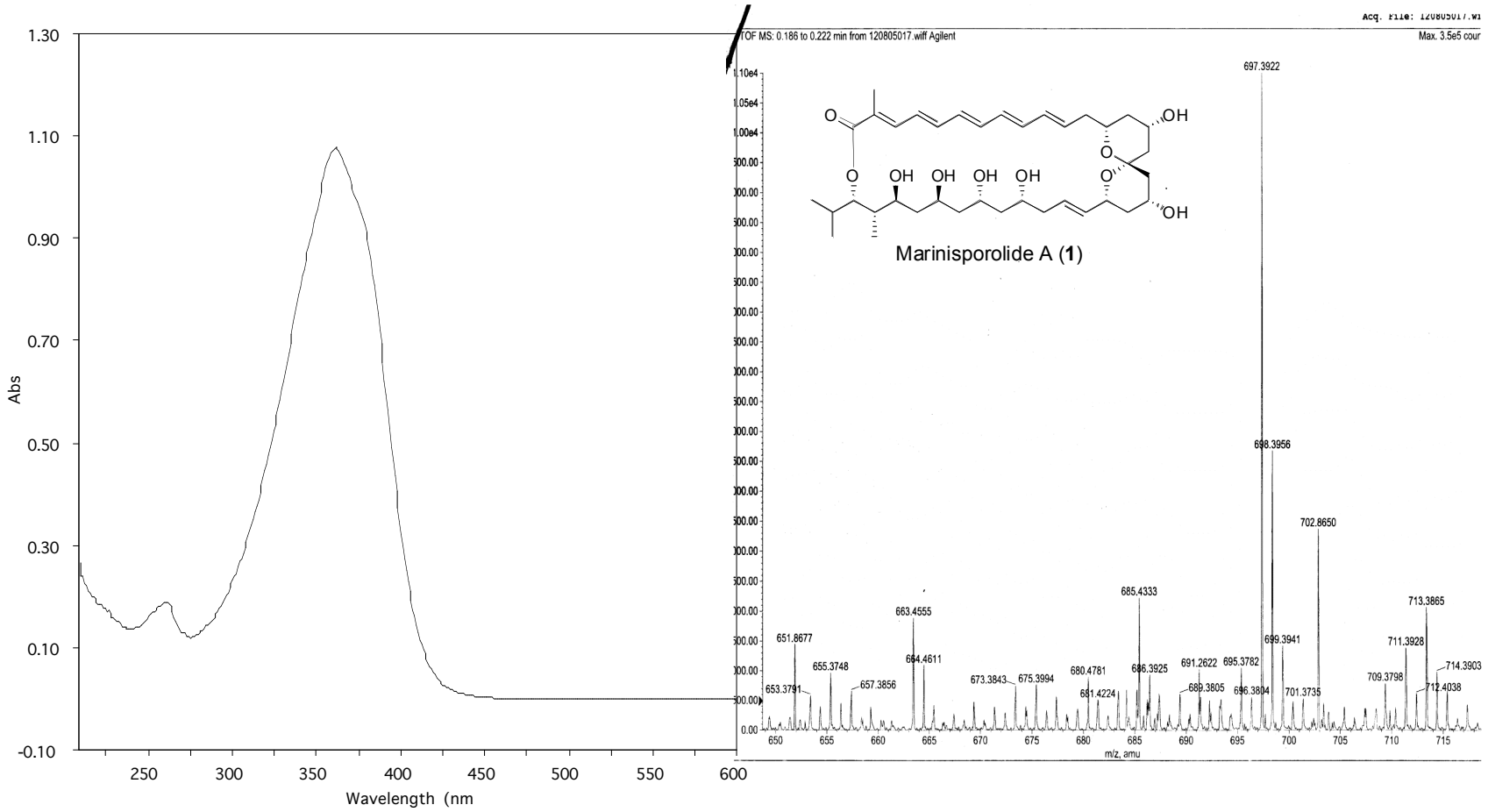


Figure S6. UV (MeOH) and HR-ESI-TOF MS spectra of marinisporolide A (**1**)

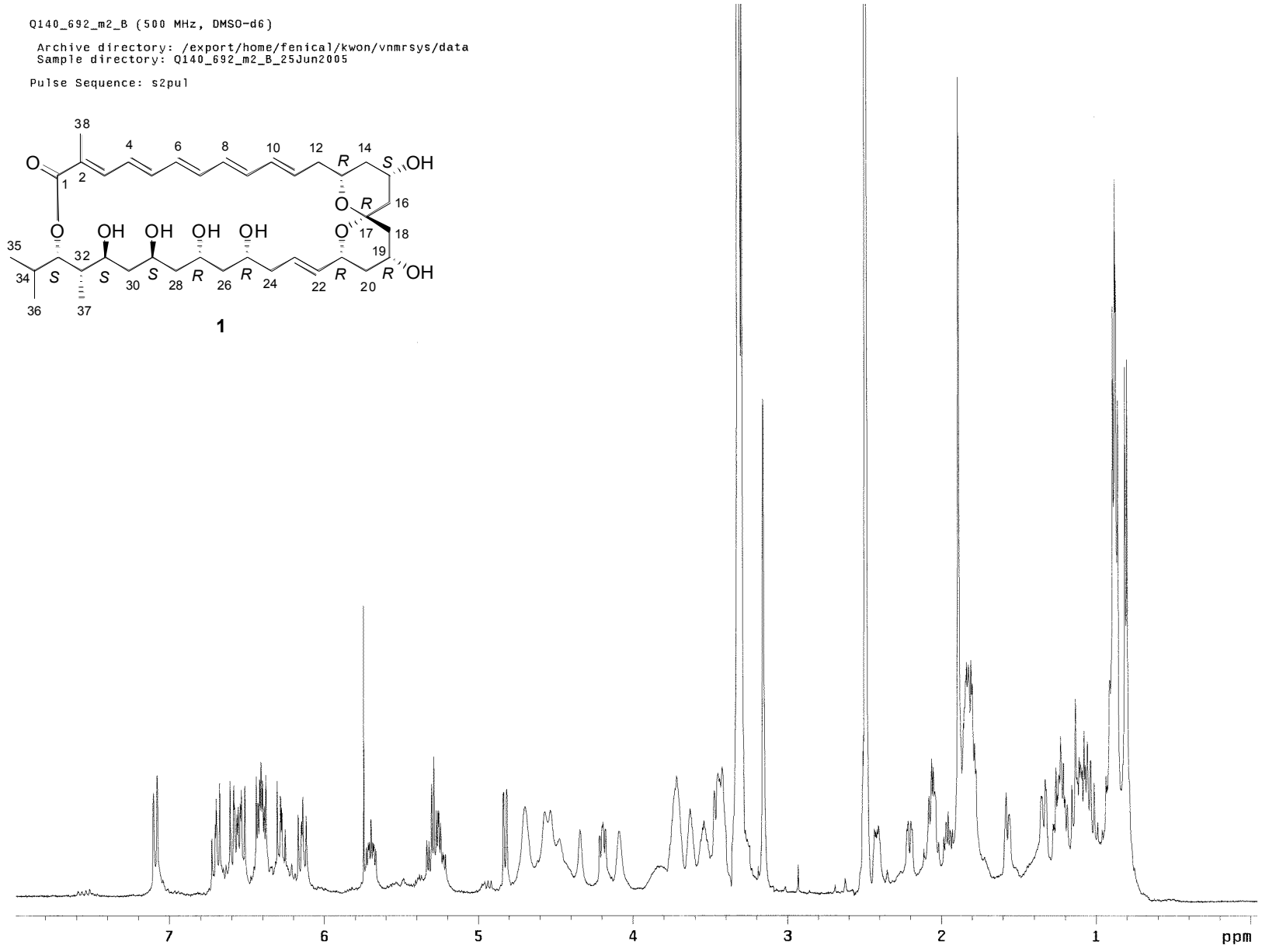


Figure S7. ^{1}H NMR spectrum of marinisporolide A (**1**) (500 MHz, DMSO-d_6)

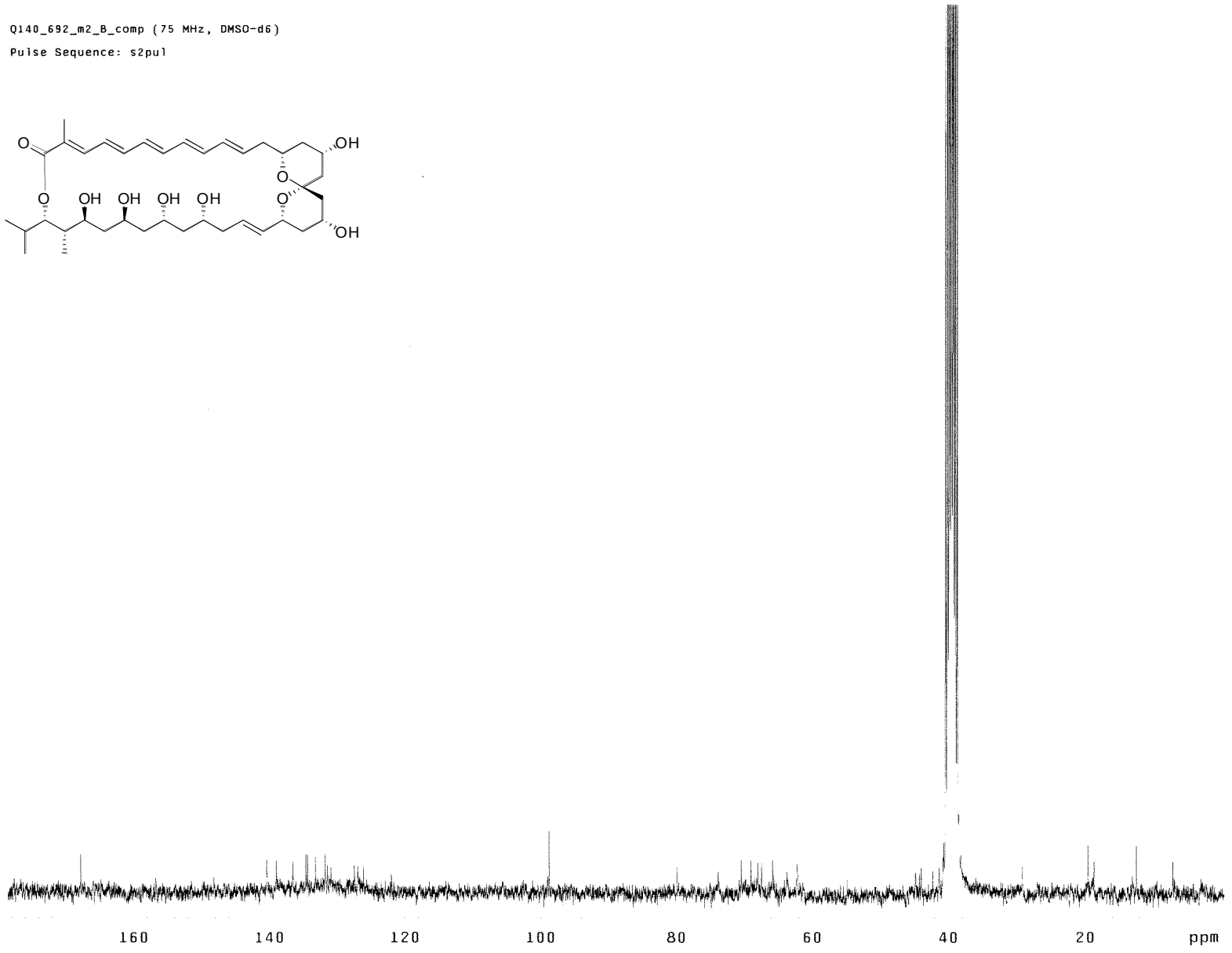


Figure S8. ^{13}C NMR spectrum of **1** (75 MHz, DMSO-d_6)

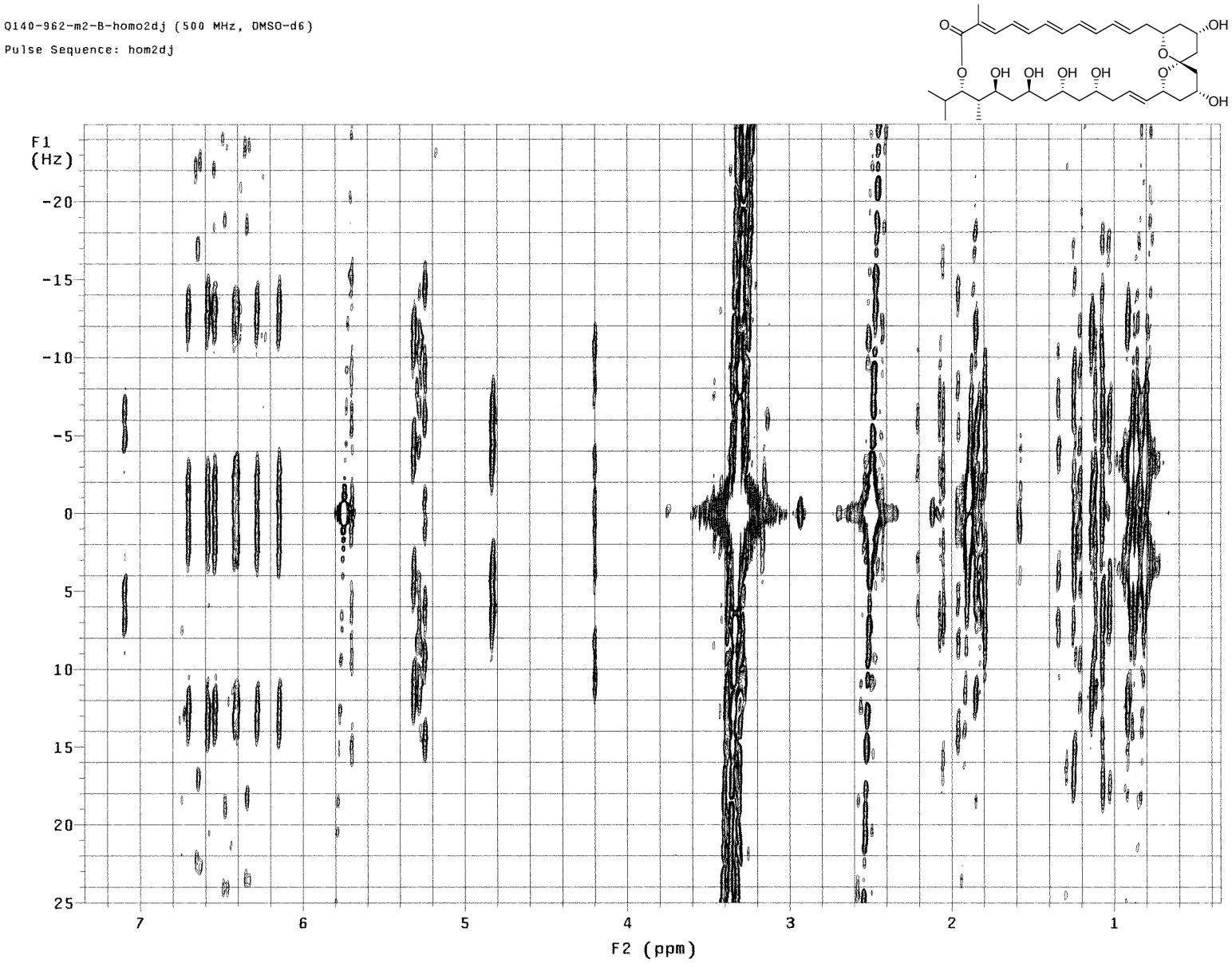


Figure S9. Homo 2D *J*-resolved ^{1}H NMR spectrum of **1** (500 MHz, DMSO-d_6)

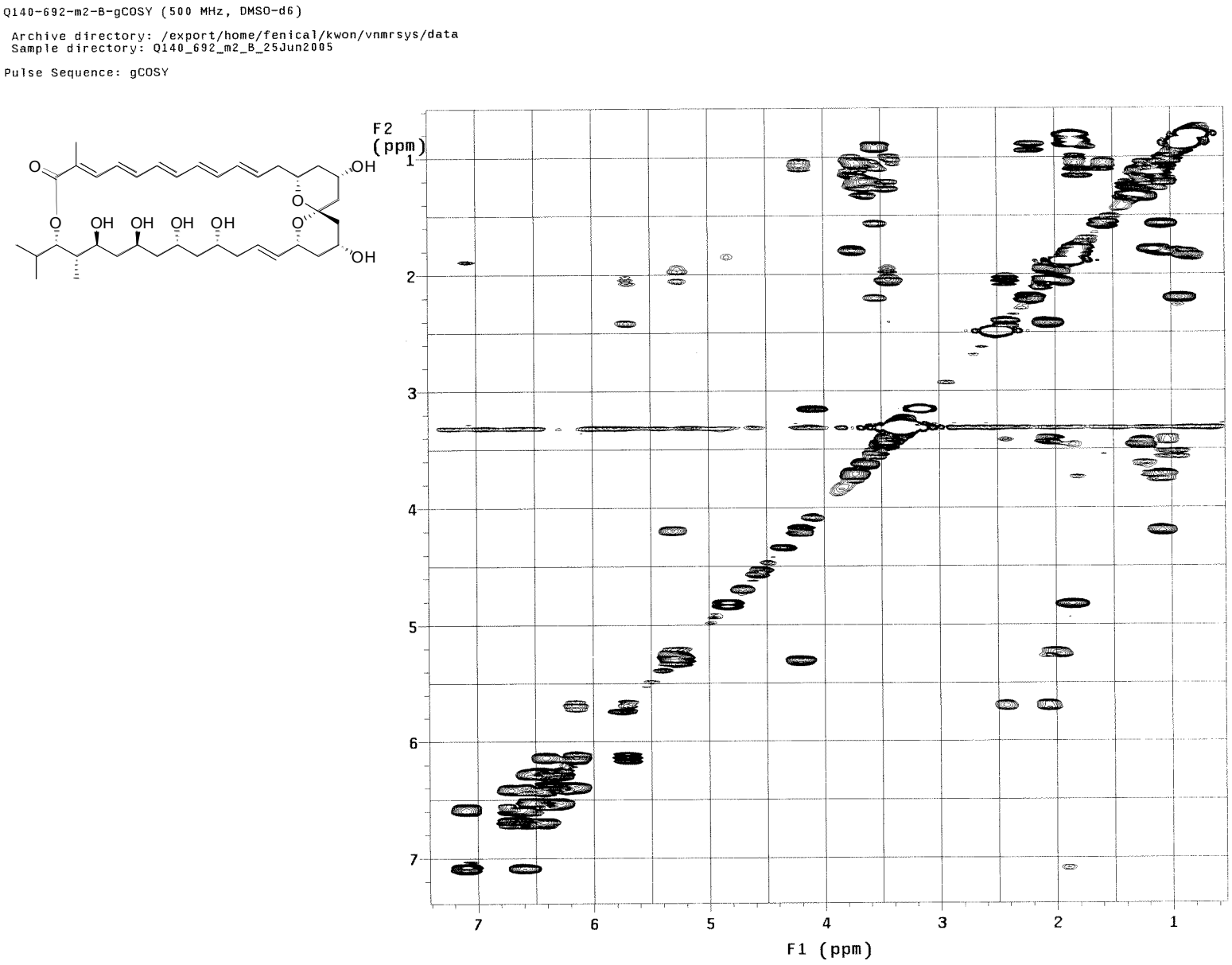


Figure S10. ^{1}H-^{1}H COSY spectrum of **1** (500 MHz, DMSO-d_6)

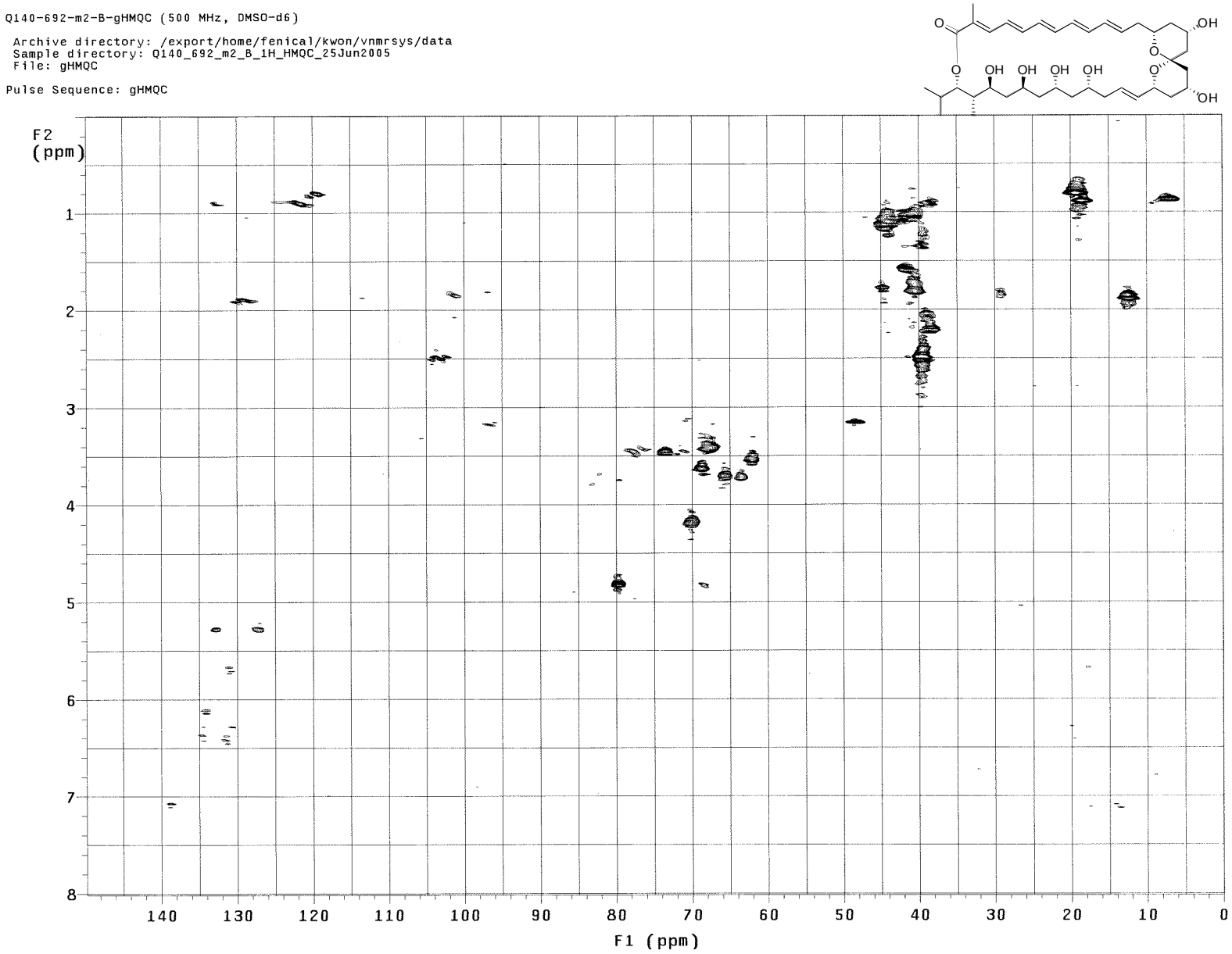


Figure S11. gHMQC spectrum of **1** (500 MHz, DMSO-d_6)

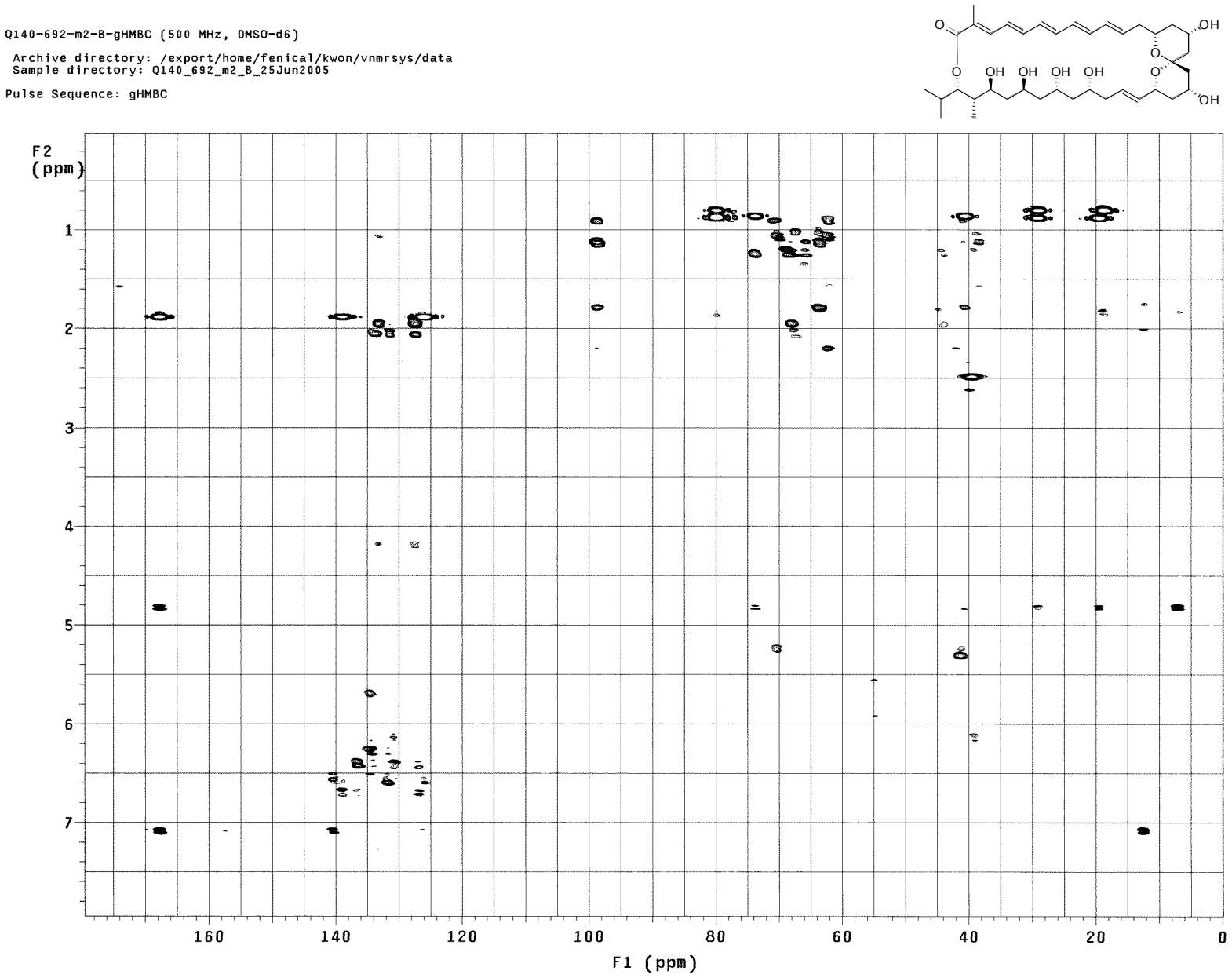


Figure S12. gHMBC spectrum of **1** (500 MHz, DMSO-d_6)

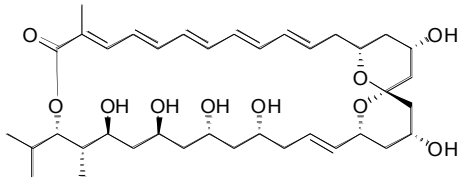
Q140-692-m2-B-ROESY (500 MHz, DMSO-d6)

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_692_m2_B_1H_ROESY_25Jun2005

Pulse Sequence: ROESY

Solvent: DMSO
Temp. 25.0 C / 298.1 K
File: Q140_692_m2_B_ROESY_500_DMSO
INOVA-500 "nightmare500"

Relax. delay 2.000 sec
Mixing 0.200 sec
Acq. time 0.171 sec
Width 5995.2 Hz
2D Width 5995.2 Hz
16 repetitions
2 x 256 increments
OBSERVE H1, 499.5905057 MHz
DATA PROCESSING
Gauss apodization 0.079 sec
F1 DATA PROCESSING
Gauss apodization 0.023 sec
FT size 2048 x 2048
Total time 5 hr, 31 min, 11 sec



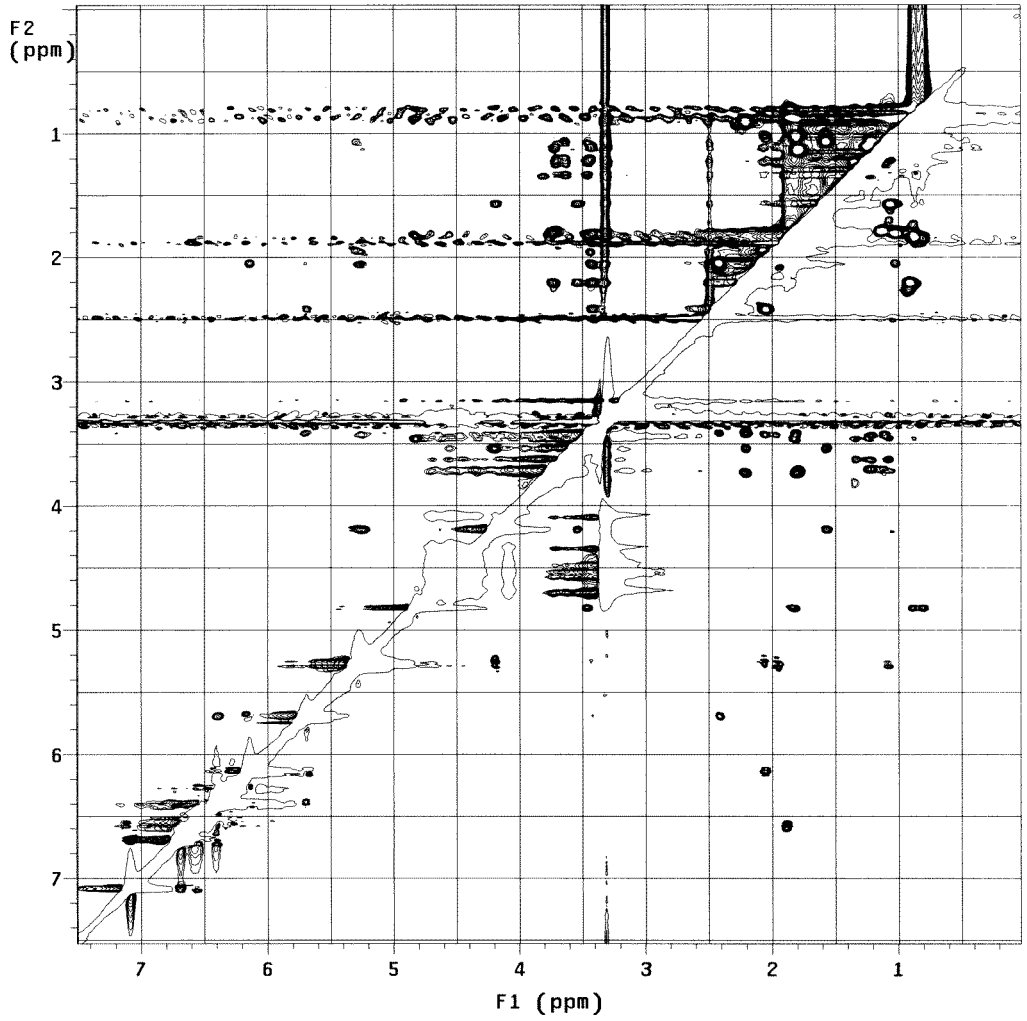


Figure S13. ROESY spectrum of **1** (500 MHz, DMSO-d_6)

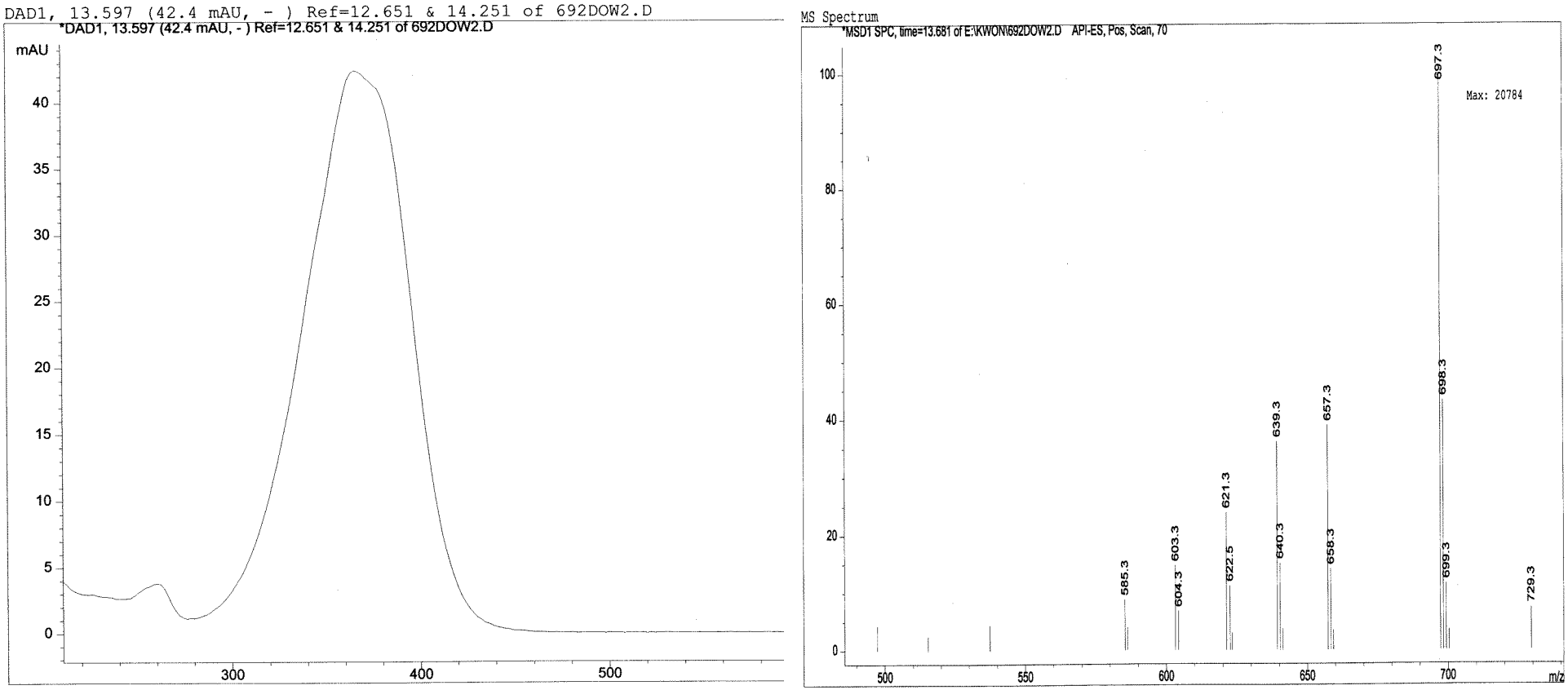


Figure S14. UV and ESI-MS spectra derived from HPLC-DAD-MSD (MeCN-H_2O) of compound **1**.

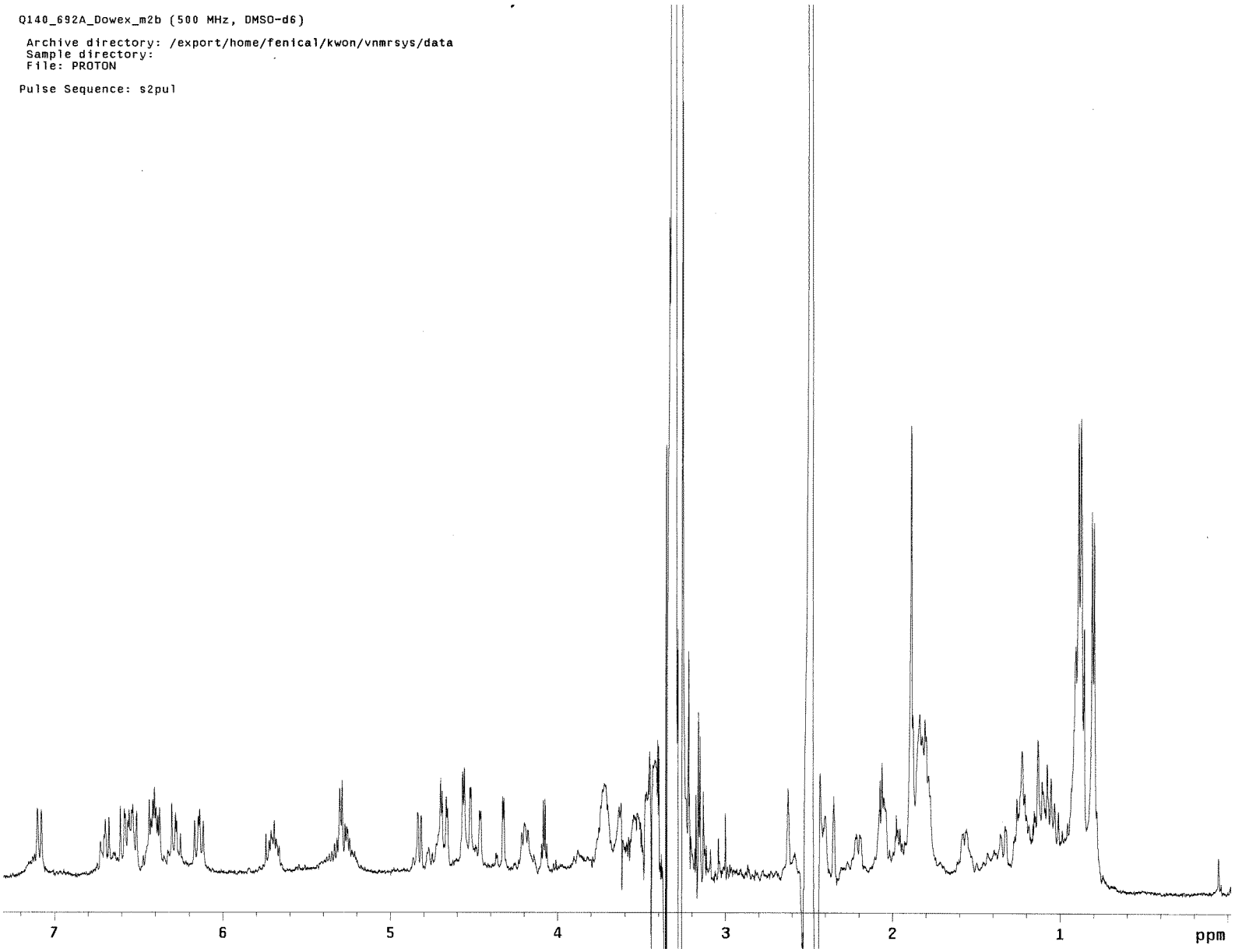


Figure S15. ^{1}H NMR spectrum of compound **1** (500 MHz, DMSO-d_6)

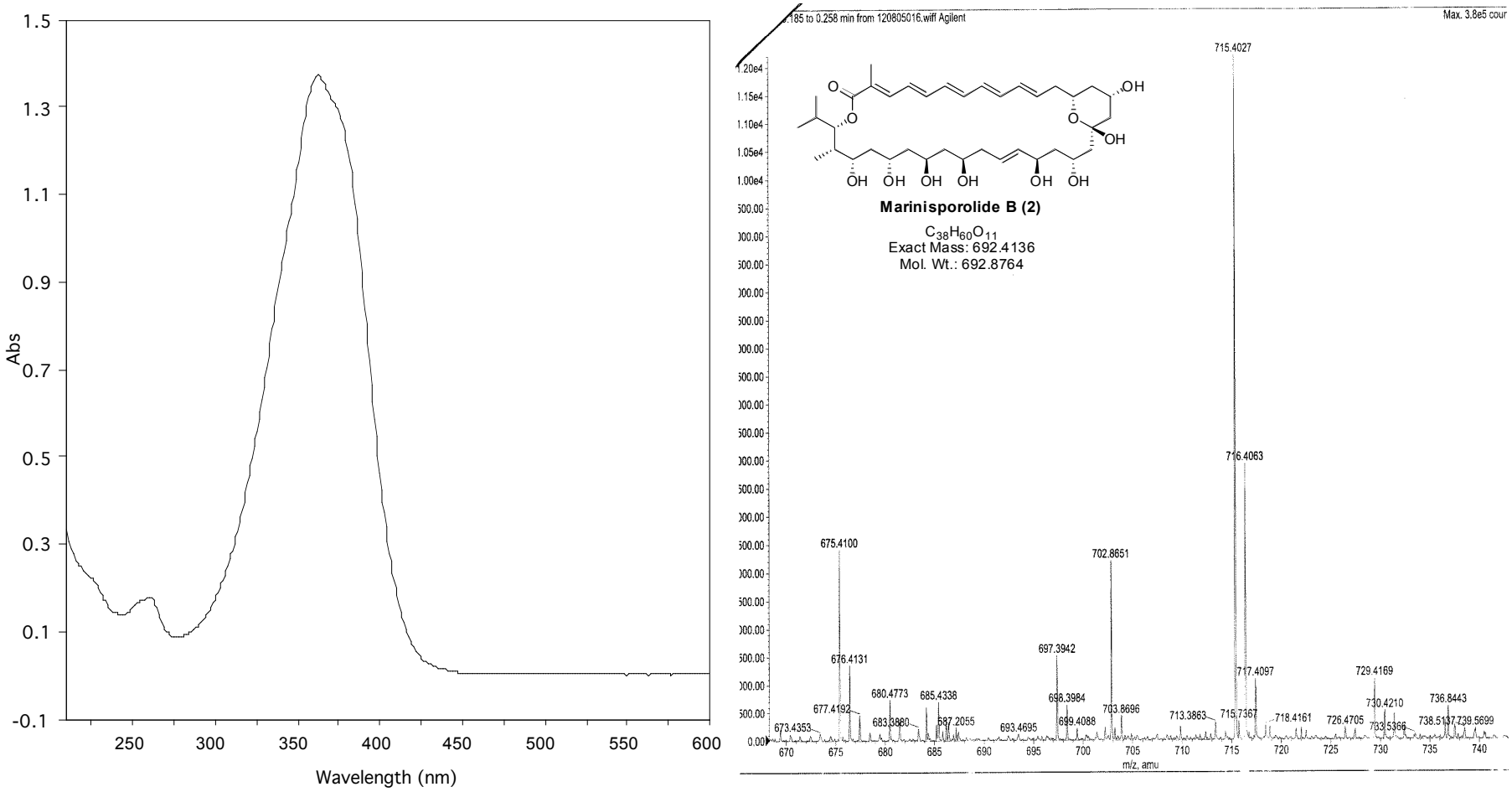


Figure S16. UV (MeOH) and HR-ESI-TOF MS spectra of marinisporolide B (**2**)

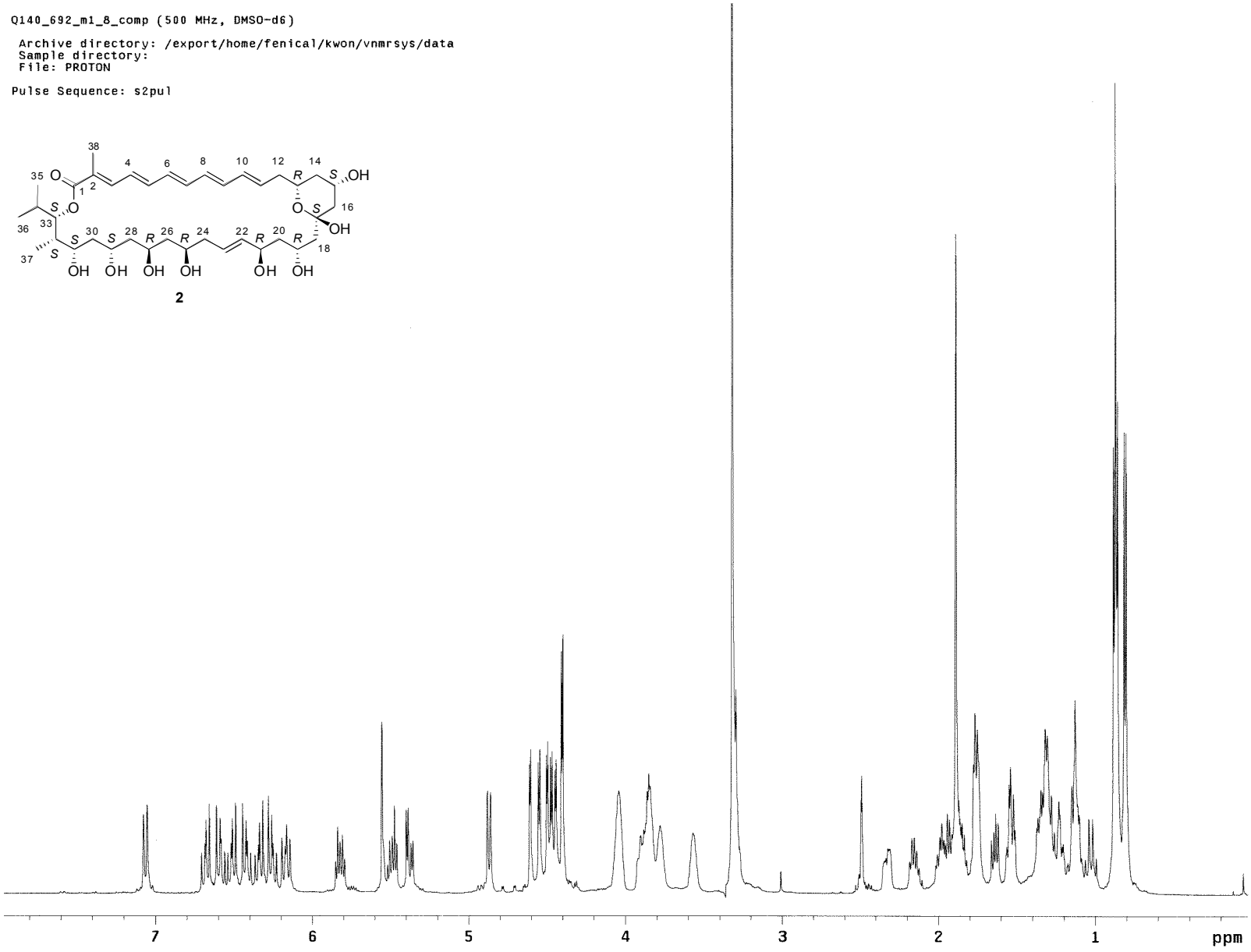


Figure S17. ^{1}H NMR spectrum of marinisporolide B (**2**) (500 MHz, DMSO-d_6)

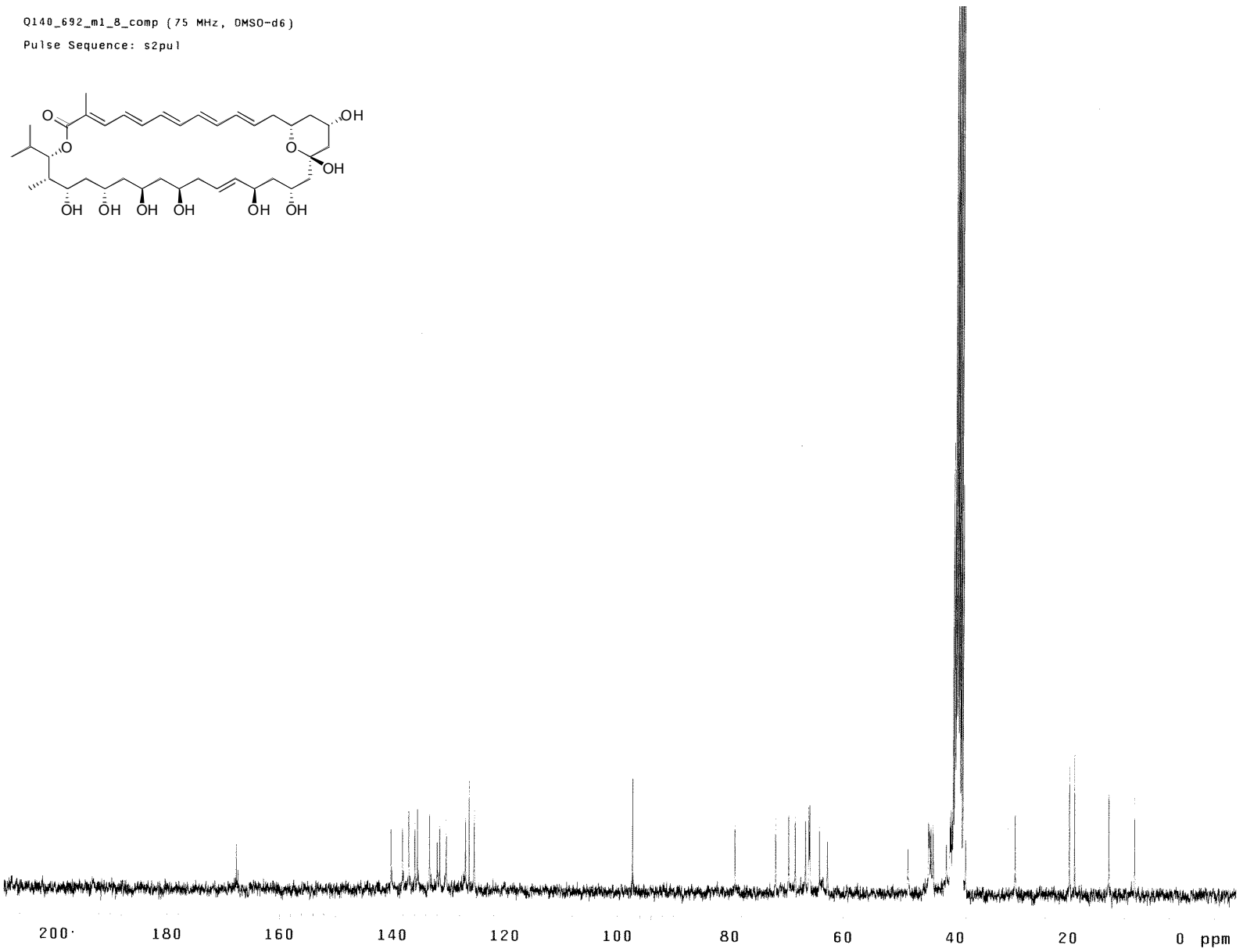


Figure S18. ^{13}C NMR spectrum of **2** (75 MHz, DMSO-d_6).

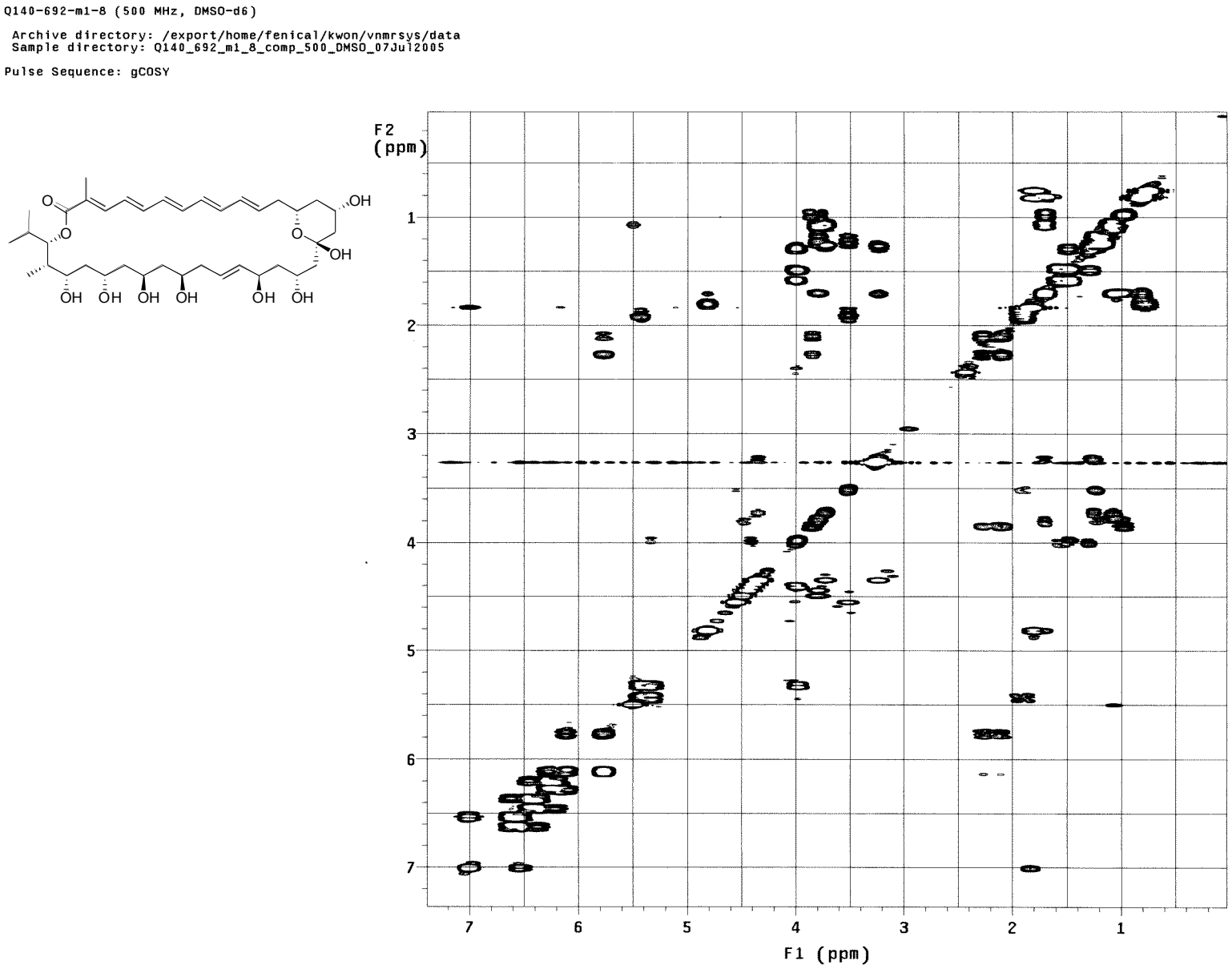


Figure S19. ^{1}H-^{1}H COSY spectrum of **2** (500 MHz, DMSO-d_6)

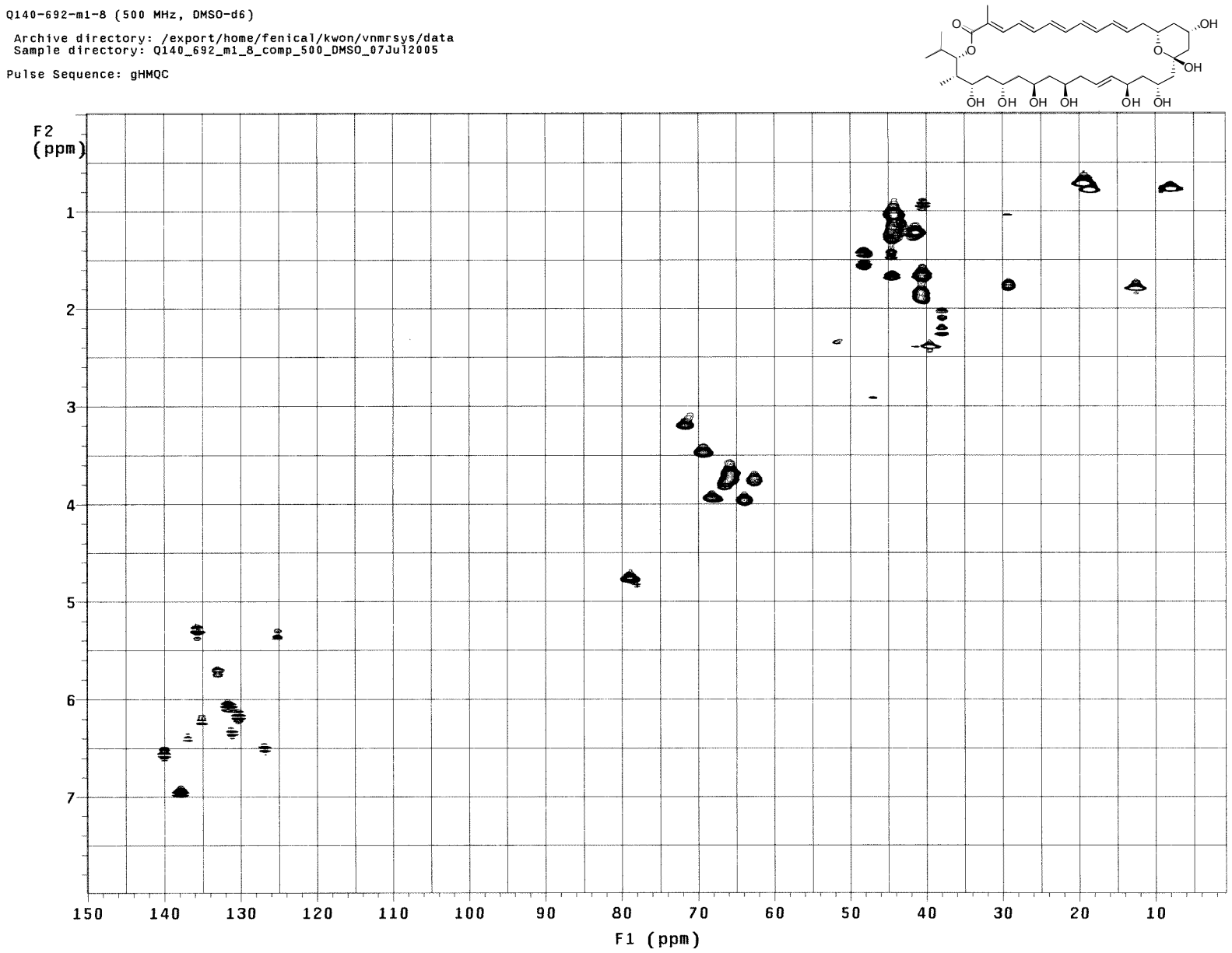


Figure S20. gHMQC spectrum of **2** (500 MHz, DMSO-d_6)

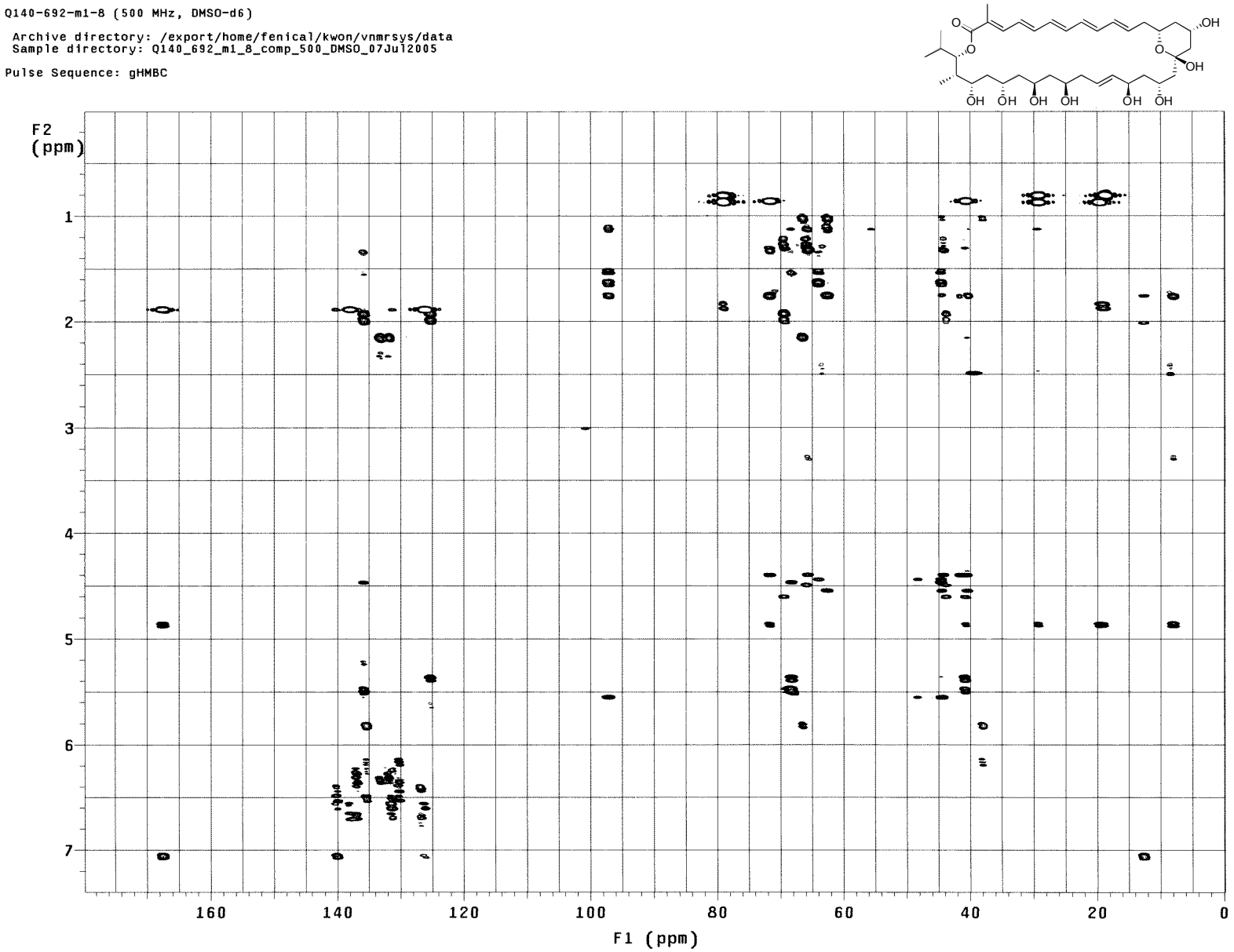


Figure S21. gHMBC spectrum of **2** (500 MHz, DMSO-d_6)

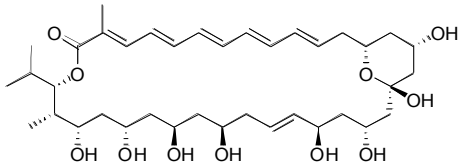
Q140-692-m1-8 (500 MHz, DMSO-d6)

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_692_m1_8_comp_500_DMSO_07Jul2005

Pulse Sequence: ROESY

Solvent: DMSO
Temp. 25.0 C / 298.1 K
File: Q140_692_m1_8_ROESY
INOVA-500 "nightmare500"

Relax. delay 3.000 sec
Mixing 0.200 sec
Acq. time 0.205 sec
Width 4995.9 Hz
2D Width 4995.9 Hz
16 repetitions
2 x 200 increments
OBSERVE H1, 499.5905054 MHz
DATA PROCESSING
Gauss apodization 0.095 sec
F1 DATA PROCESSING
Gauss apodization 0.015 sec
FT size 2048 x 2048
Total time 6 hr, 10 min, 33 sec



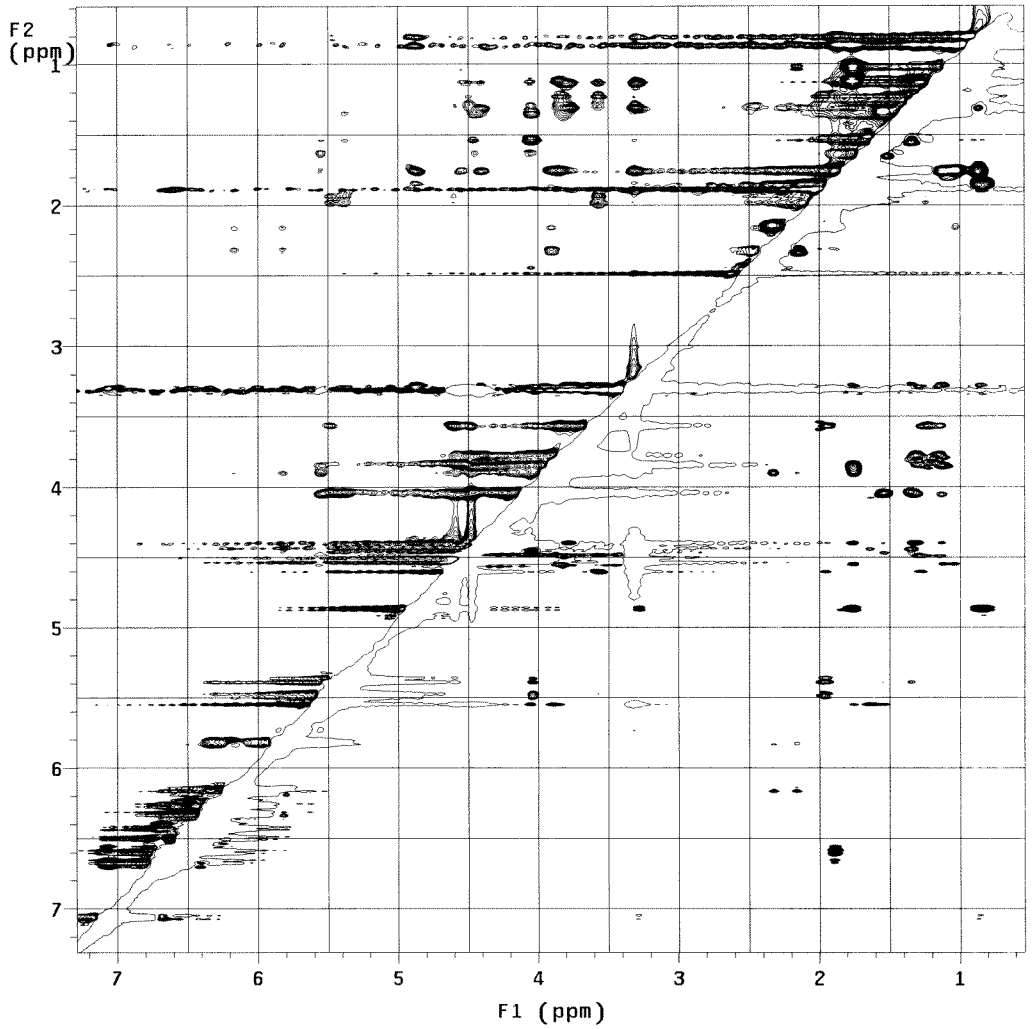


Figure S22. ROESY spectrum of **2** (500 MHz, DMSO-d_6)

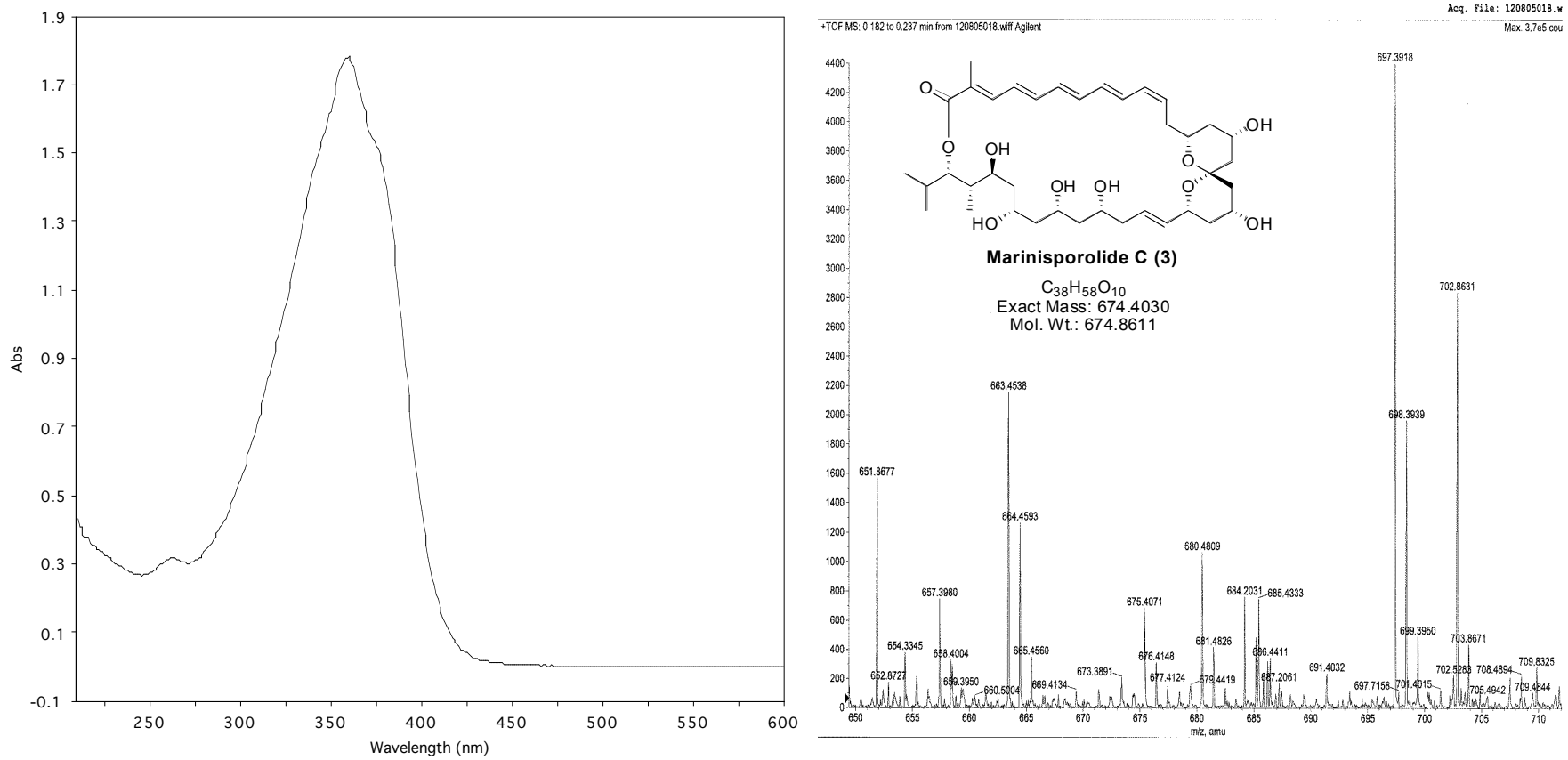


Figure S23. UV (MeOH) and HR-ESI-TOF MS spectra of marinisporolide C (**3**).

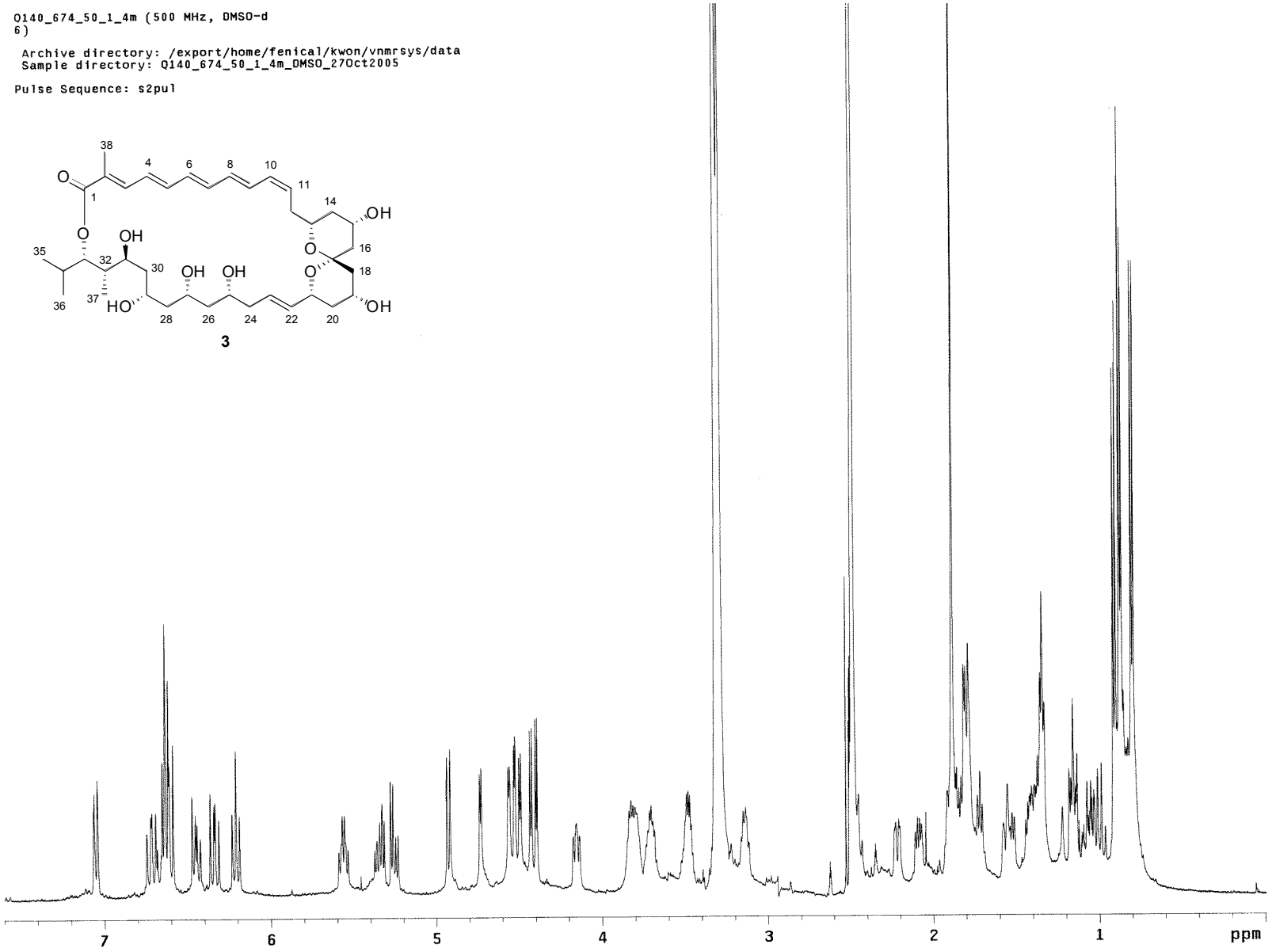


Figure S24. ^{1}H NMR spectrum of marinisporolide C (**3**) (500 MHz, DMSO-d_6).

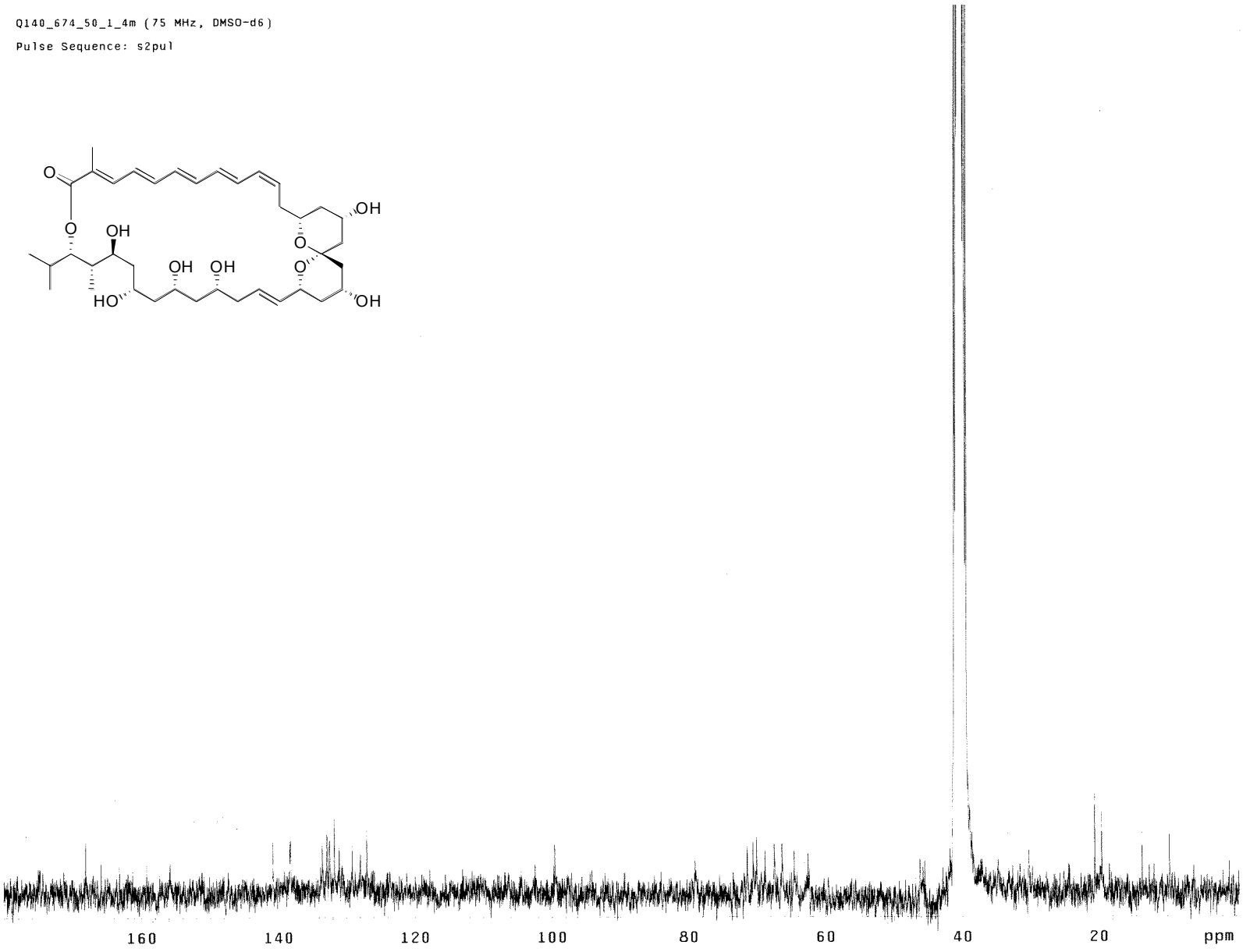


Figure S25. ^{13}C NMR spectrum of **3** (75 MHz, DMSO-d_6)

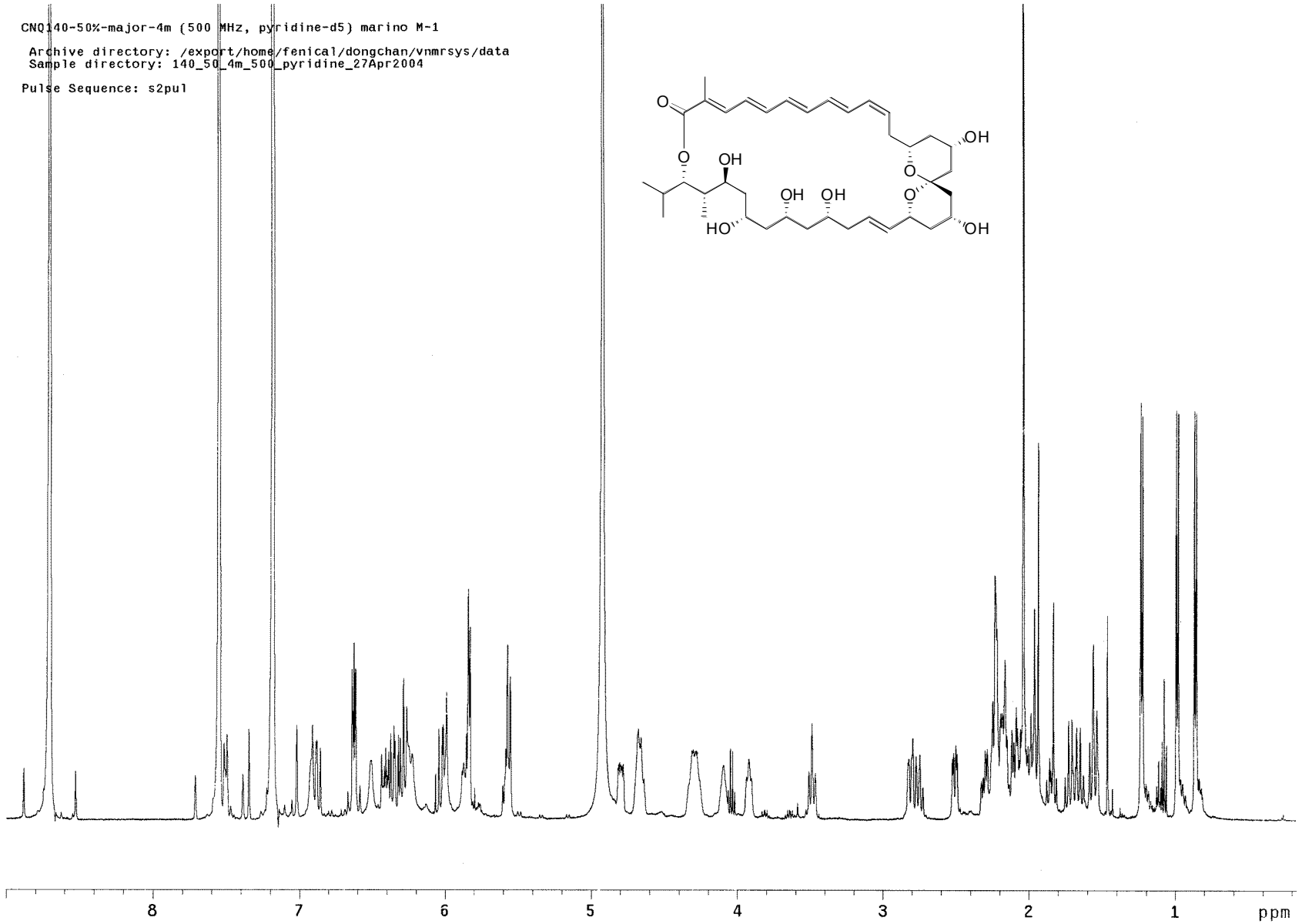


Figure S26. ^{1}H NMR spectrum of **3** (500 MHz, pyridine-d_5).

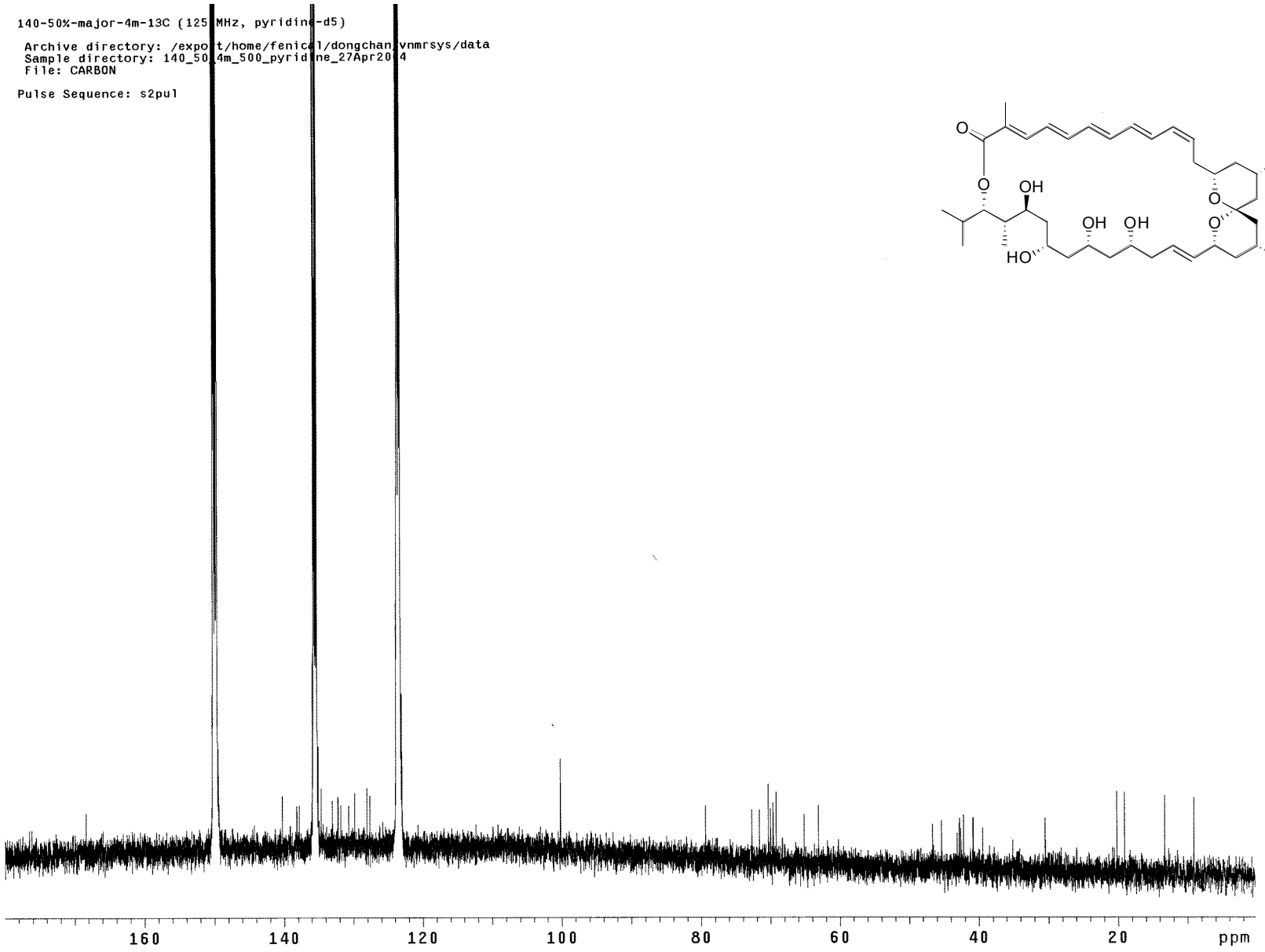


Figure S27. ^{13}C NMR spectrum of **3** (125 MHz, pyridine-d_5).

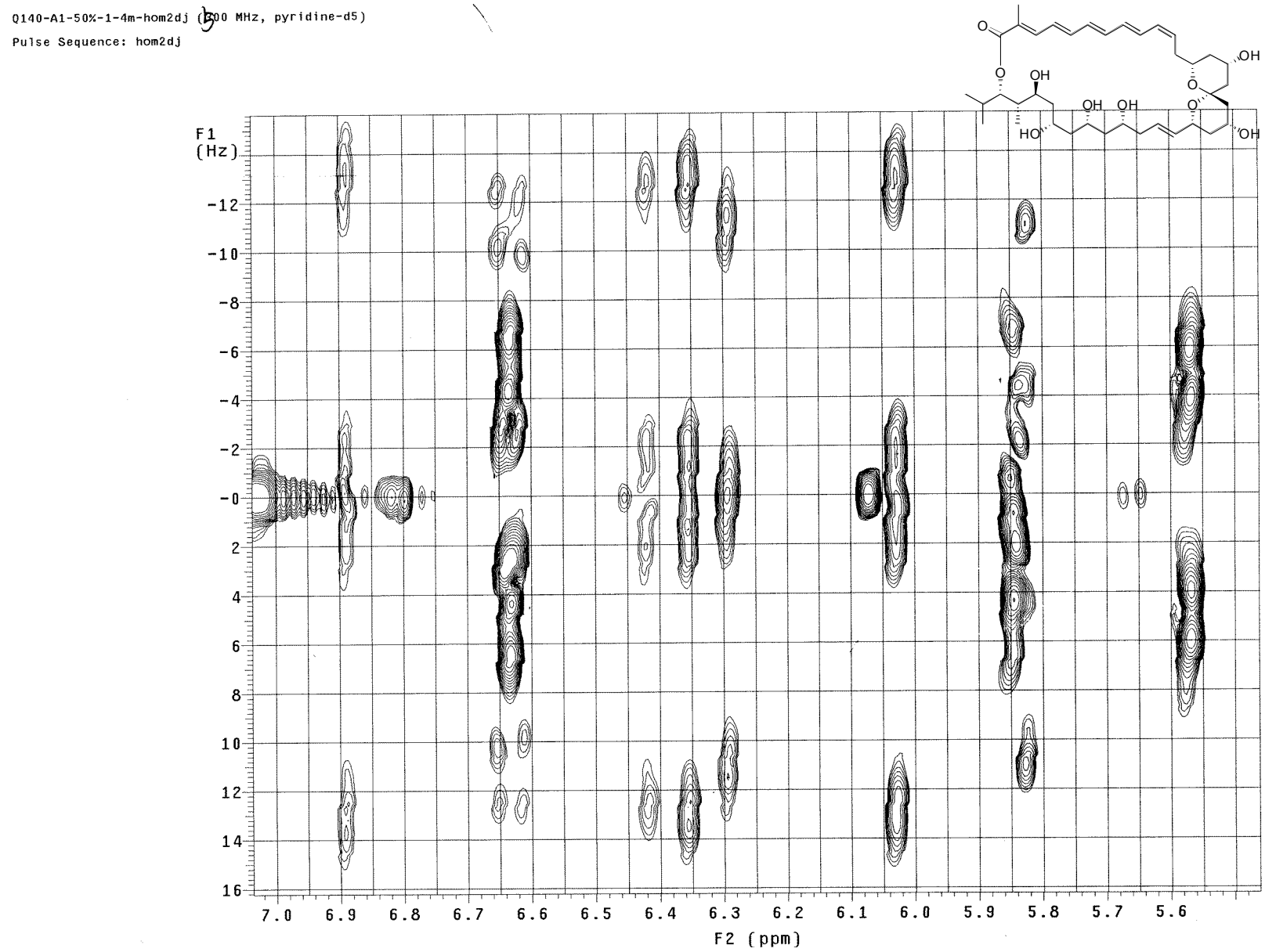


Figure S28. Expanded homo 2D *J*-resolved ^{1}H NMR spectrum of **3** (500 MHz, pyridine-d_5).

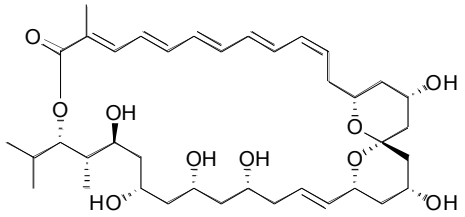
Q140_50_1_4m_ROESY (500 MHz, pyri
dine-d5)

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_50_1_4m_ROESY_12Jun2005

Pulse Sequence: ROESY

Solvent: pyridine
Temp. 25.0 C / 298.1 K
File: ROESY
INOVA-500 "nightmare500"

Relax. delay 3.000 sec
Mixing 0.200 sec
Acq. time 0.128 sec
Width 7993.6 Hz
2D Width 7993.6 Hz
16 repetitions
2 x 256 increments
OBSERVE H1, 499.5881356 MHz
DATA PROCESSING
Gauss apodization 0.070 sec
F1 DATA PROCESSING
Gauss apodization 0.016 sec
FT size 2048 x 2048
Total time 7 hr, 42 min, 11 sec



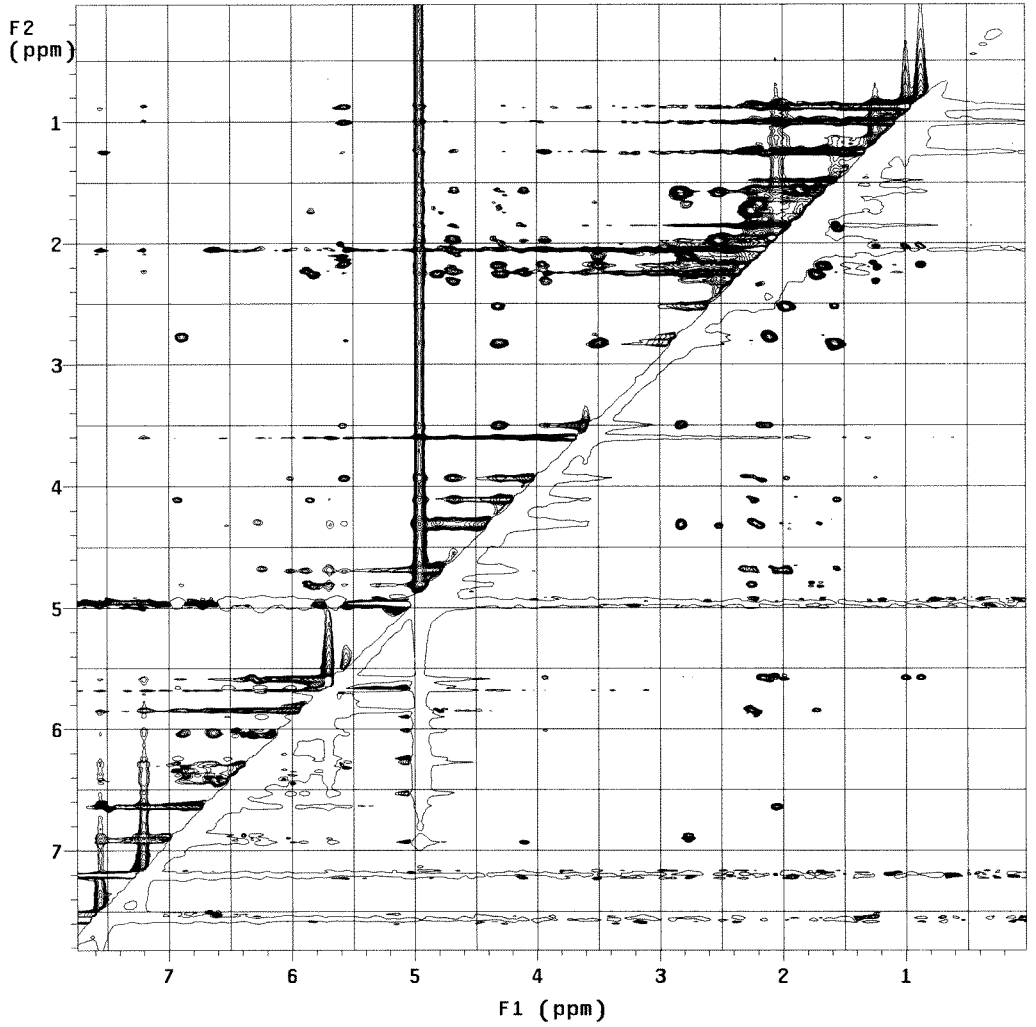


Figure S29. ROESY spectrum of **3** (500 MHz, pyridine-d_5)

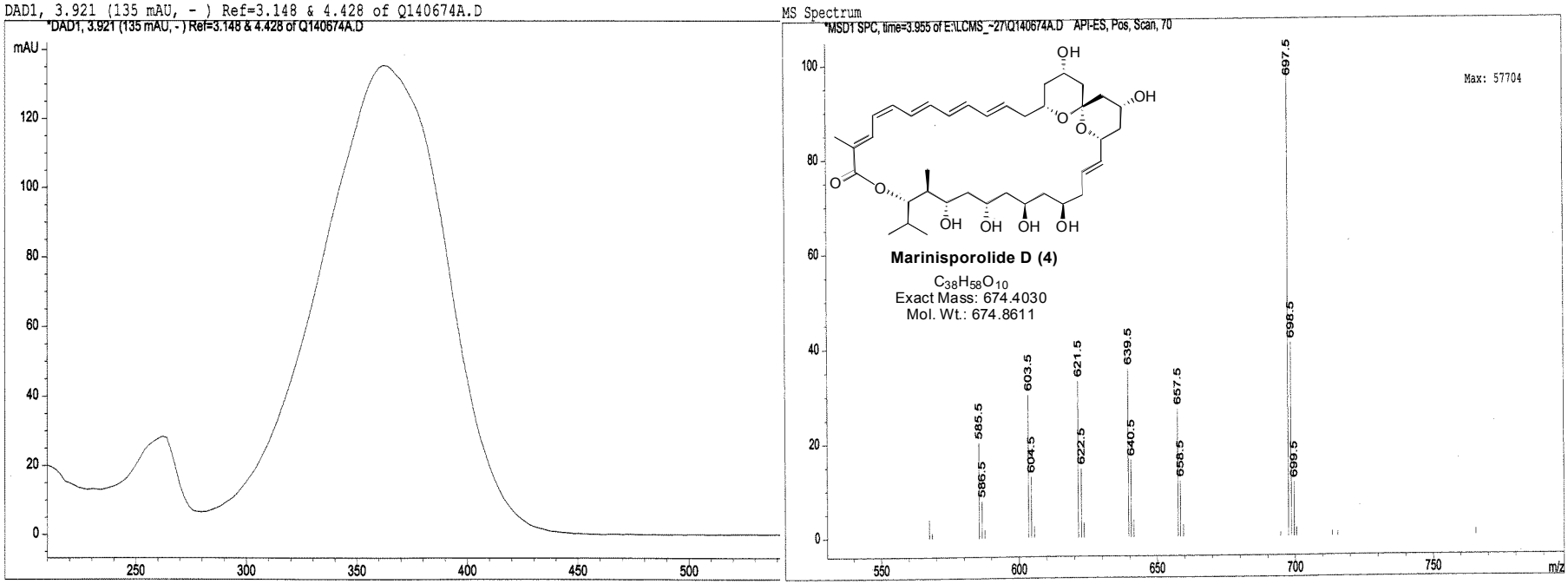


Figure S30. UV and ESI-MS spectra derived from HPLC-DAD-MSD (MeCN-H_2O) of marinisporolide D (**4**)

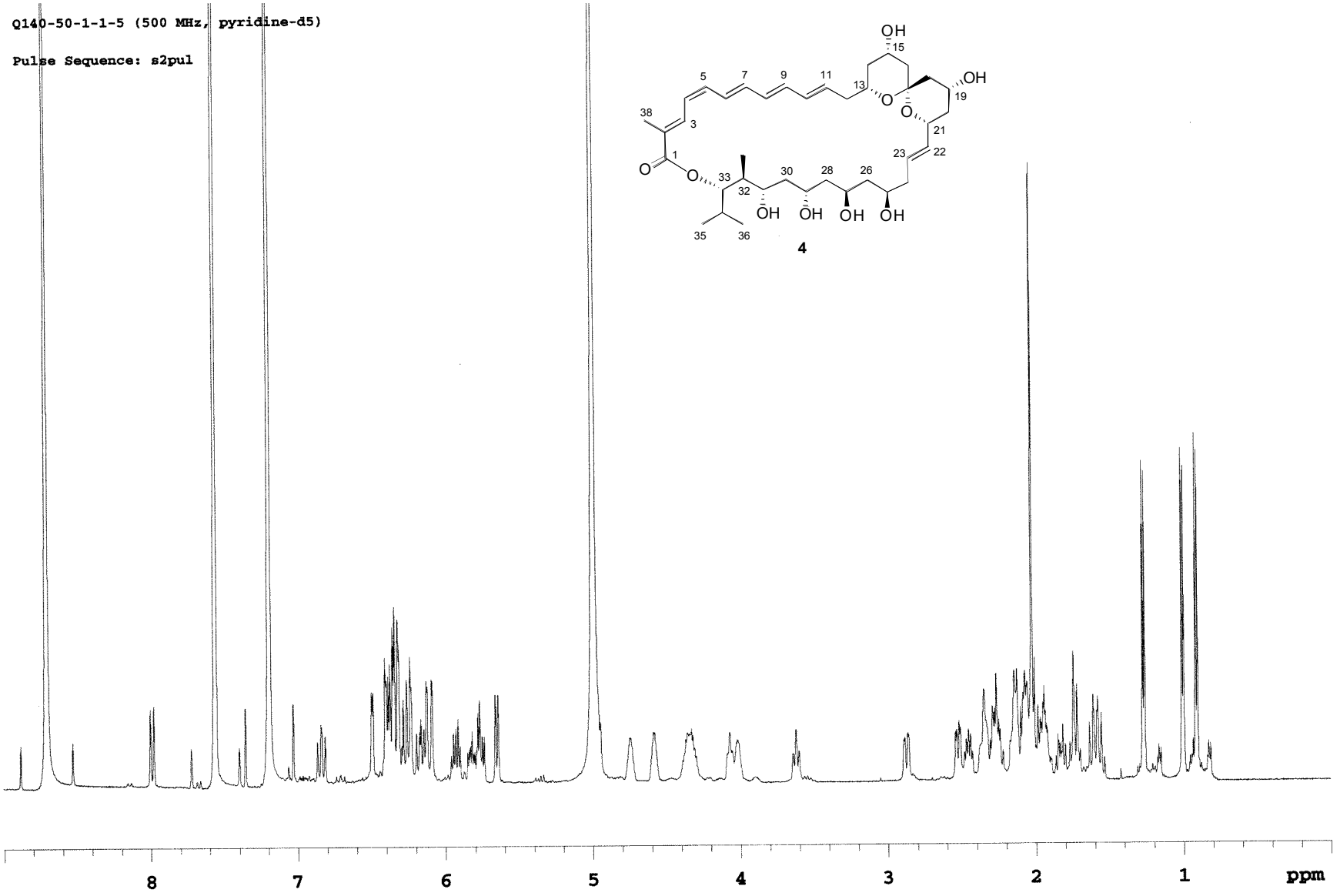


Figure S31. ^{1}H NMR spectrum of marinisporolide D (**4**) (500 MHz, pyridine-d_5)

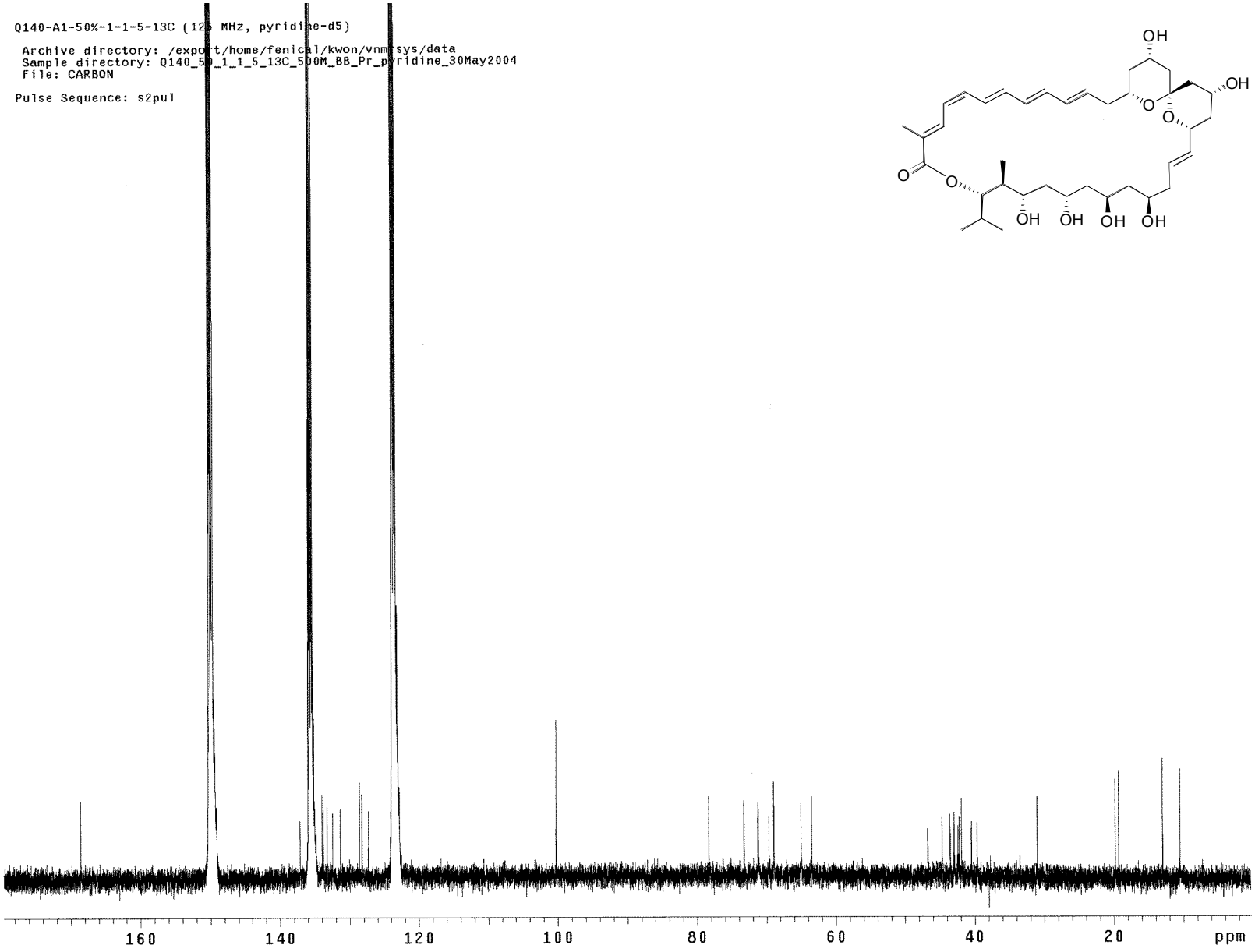


Figure S32. ^{13}C NMR spectrum of **4** (125 MHz, pyridine-d_5)

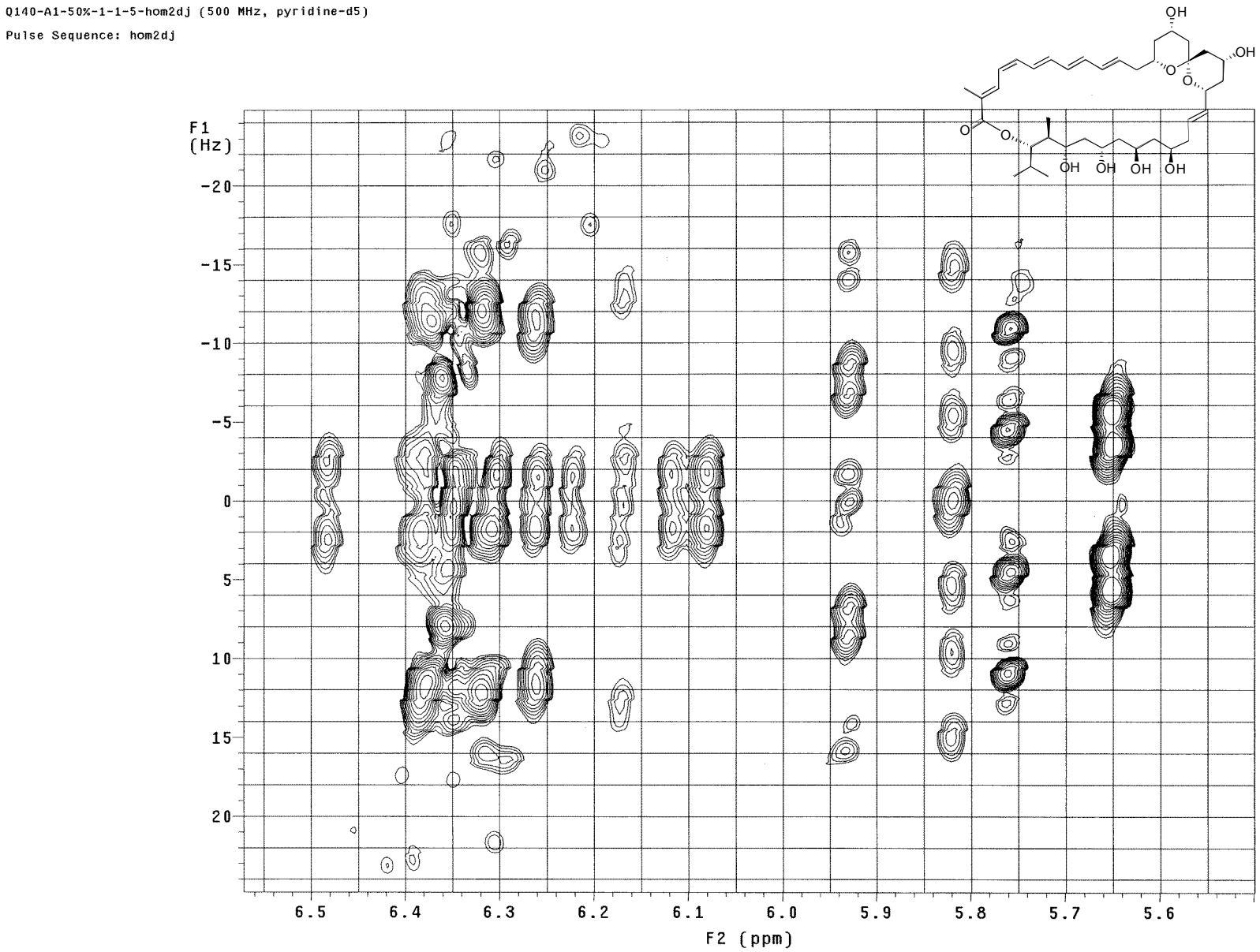
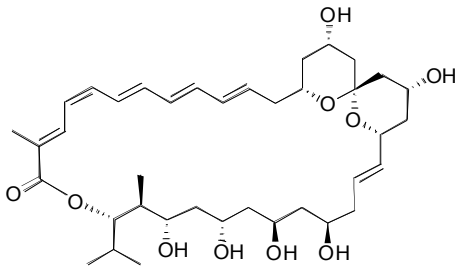


Figure S33. Homo 2D *J*-resolved ^{1}H NMR spectrum of **4** (500 MHz, pyridine-d_5).

Q140-A1-50-1-1-5 (500 MHz, pyridine-d5) 2

Pulse Sequence: ROESY



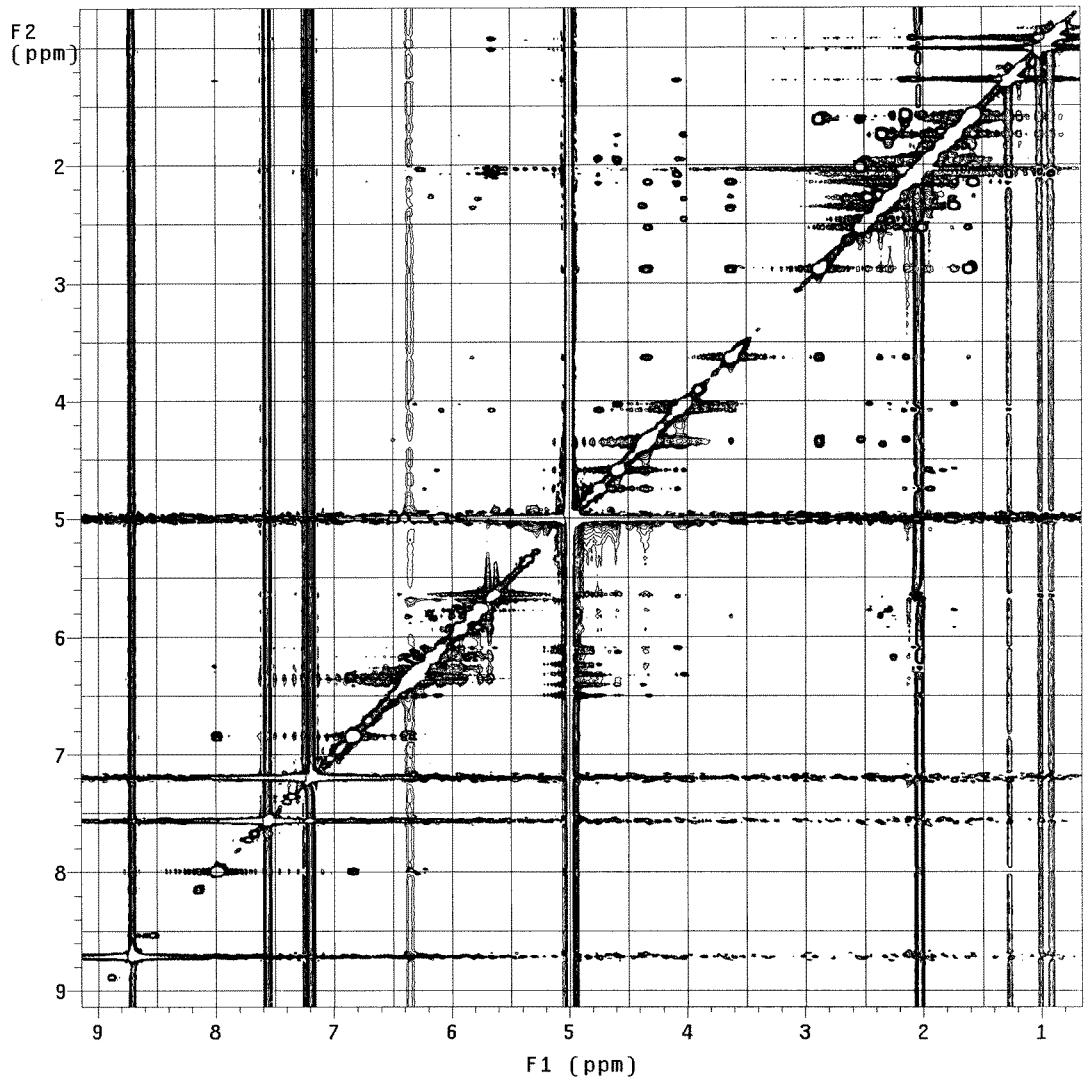


Figure S34. ROESY spectrum of **4** (500 MHz, pyridine-d_5)

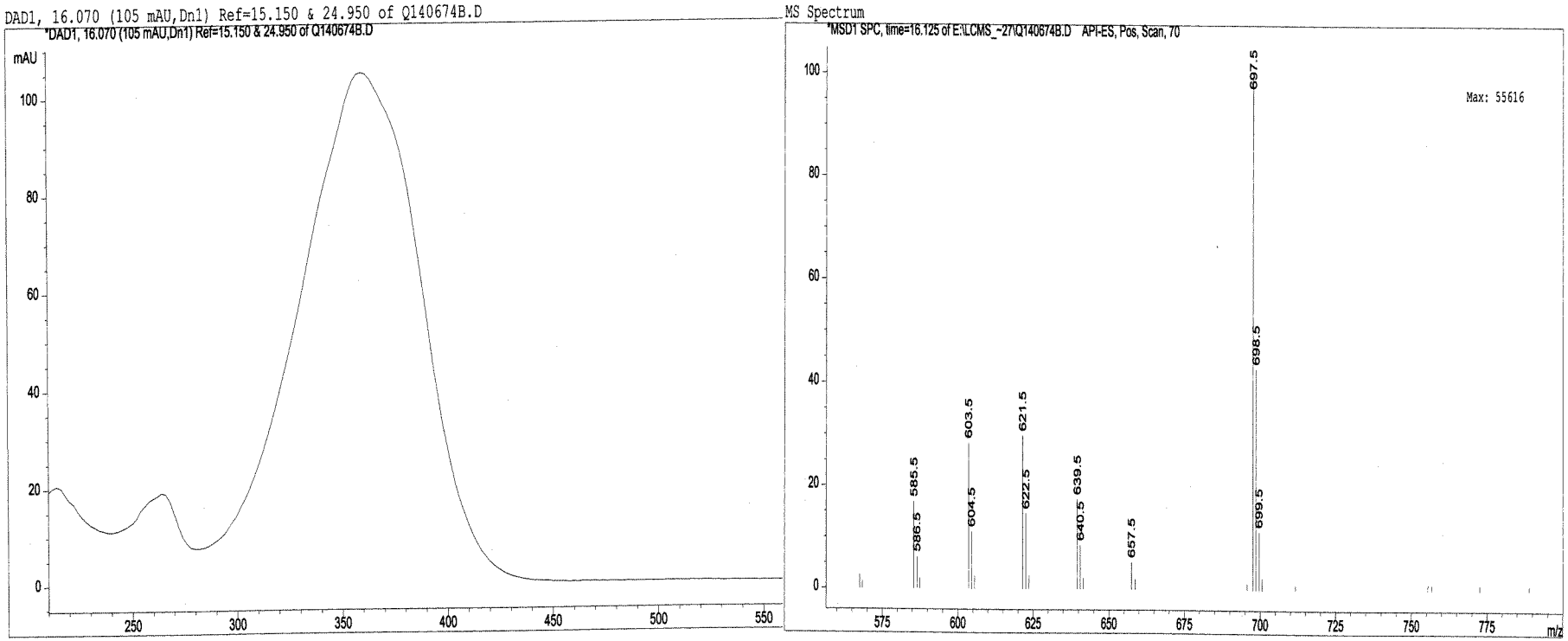


Figure S35. UV and ESI-MS spectra derived from HPLC-DAD-MSD (MeCN-H_2O) of marinisporolide E (**5**)

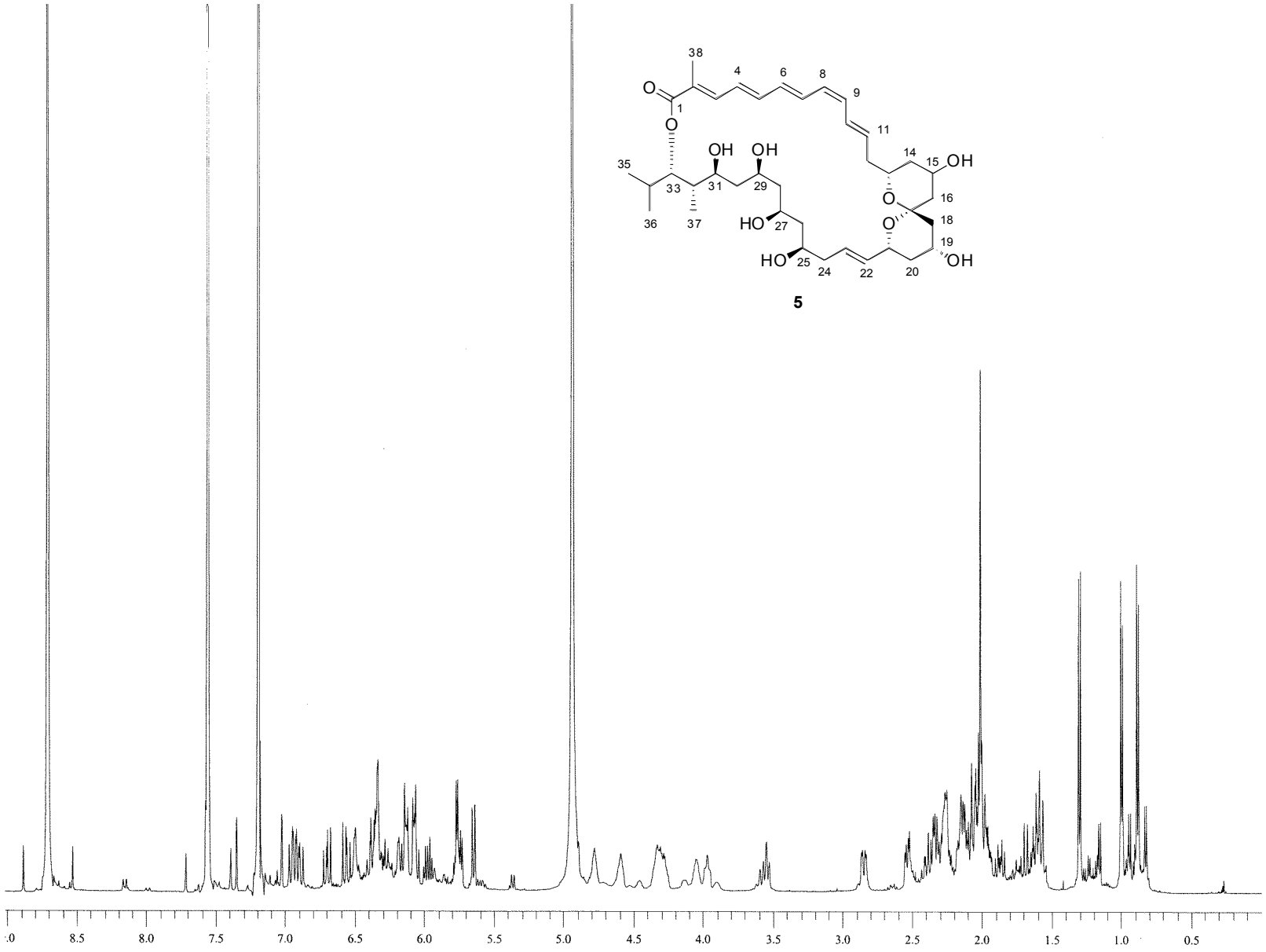


Figure S36. ^{1}H NMR spectrum of marinisporolide E (**5**) (500 MHz, pyridine-d_5).

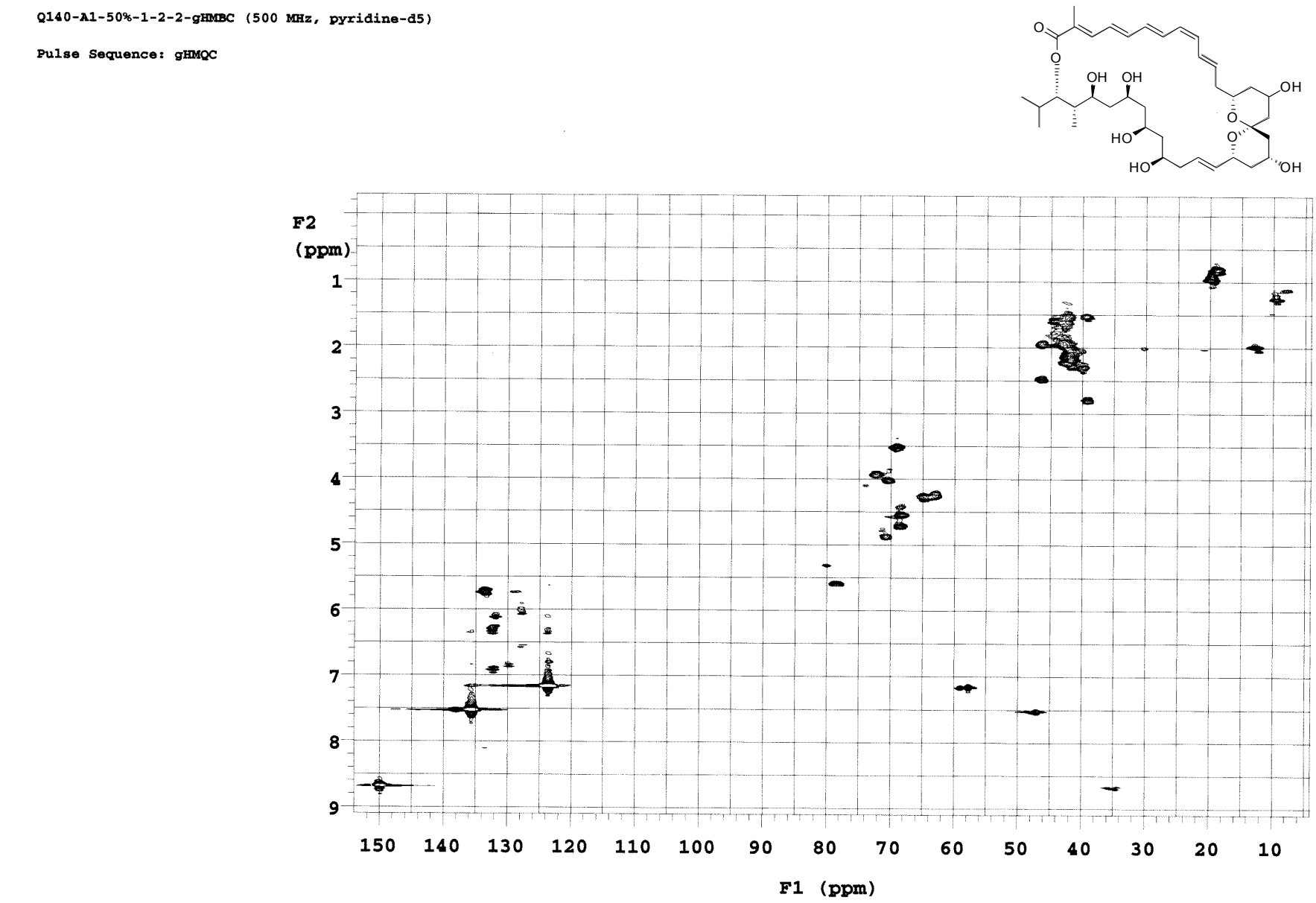


Figure S37. gHMQC spectrum of **5** (500 MHz, pyridine-d_5).

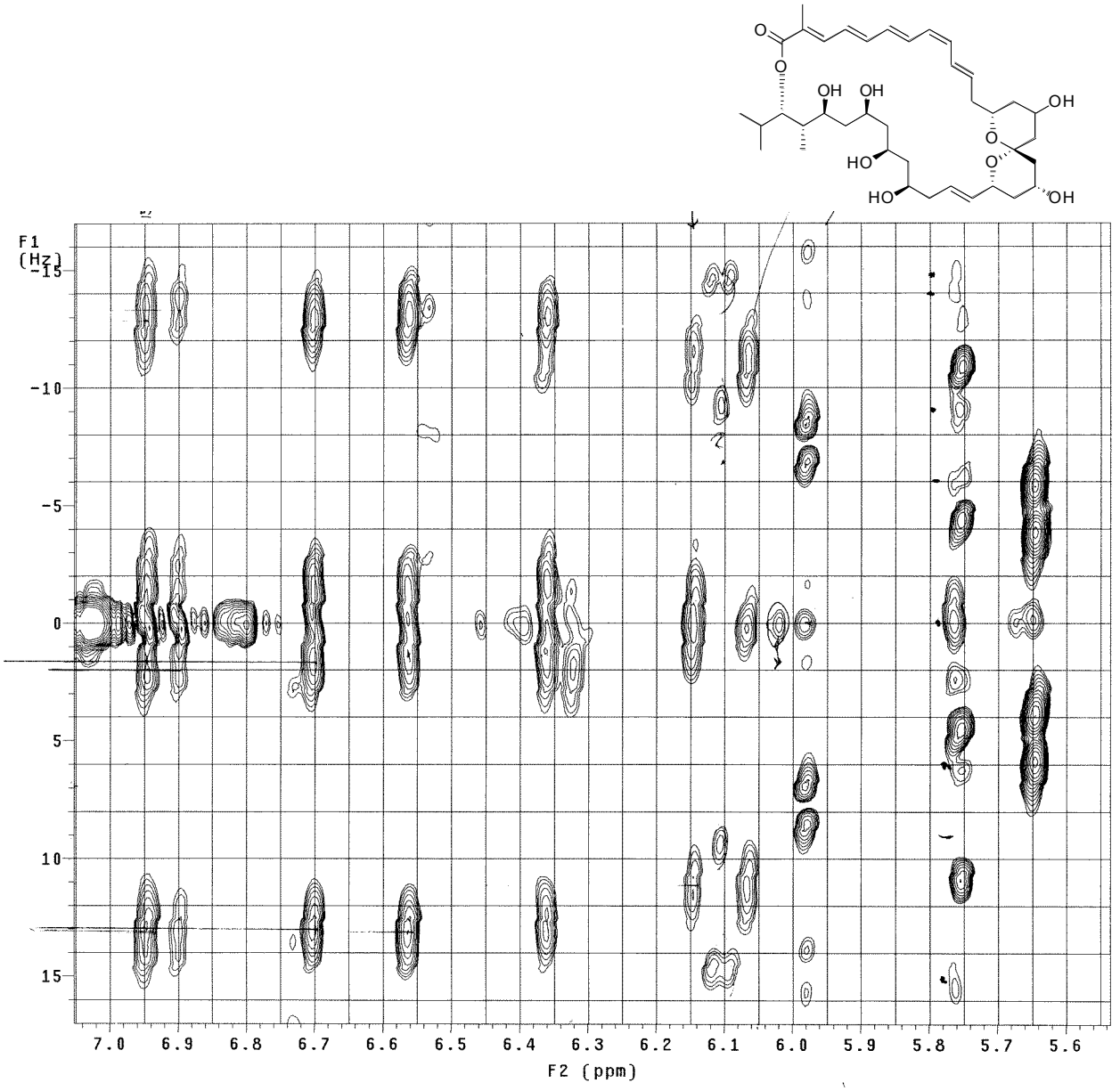


Figure S38. Expanded homo 2D *J*-resolved ^{1}H NMR spectrum of **5** (500 MHz, pyridine-d_5).

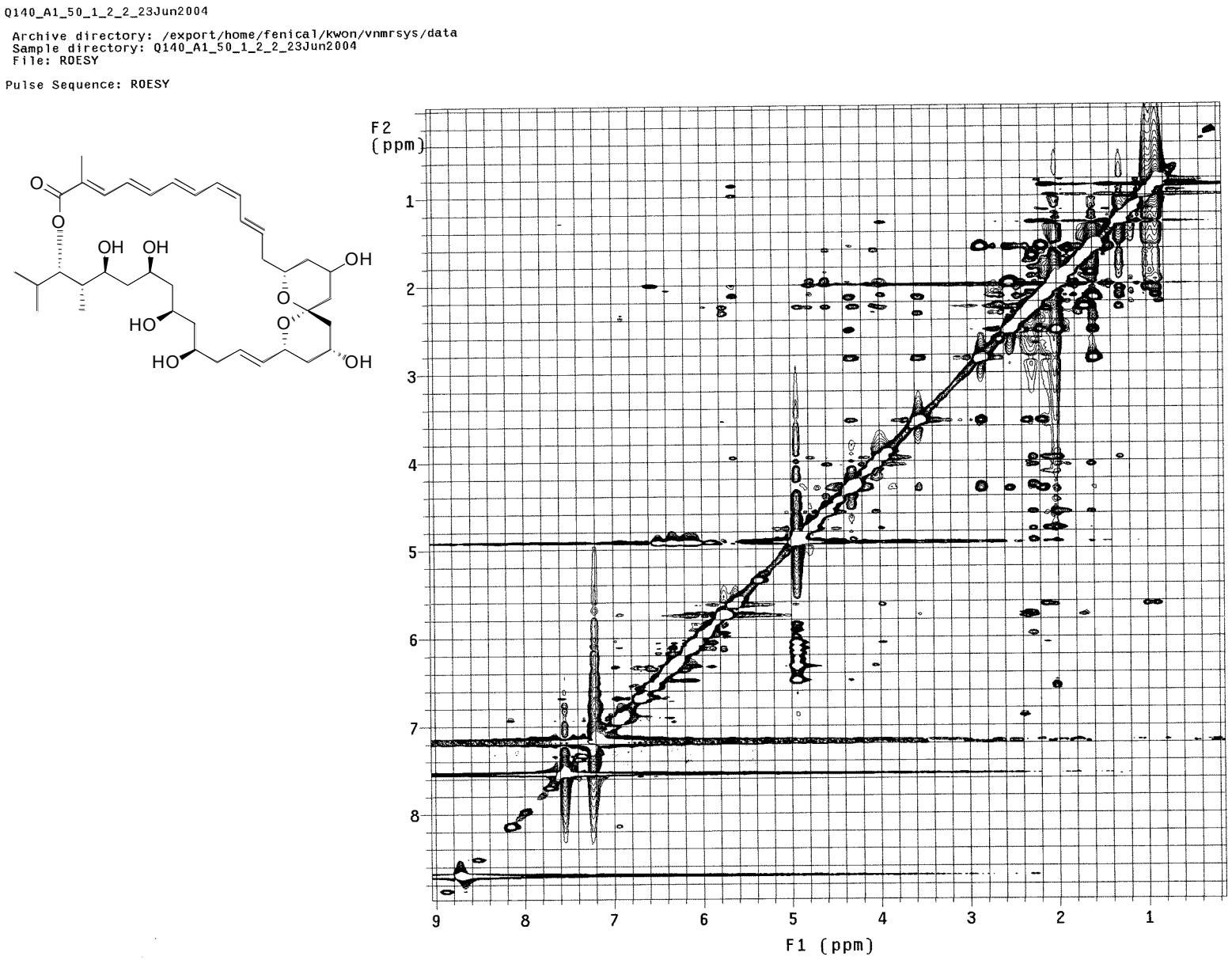


Figure S39. ROESY spectrum of **5** (500 MHz, pyridine-d_5).

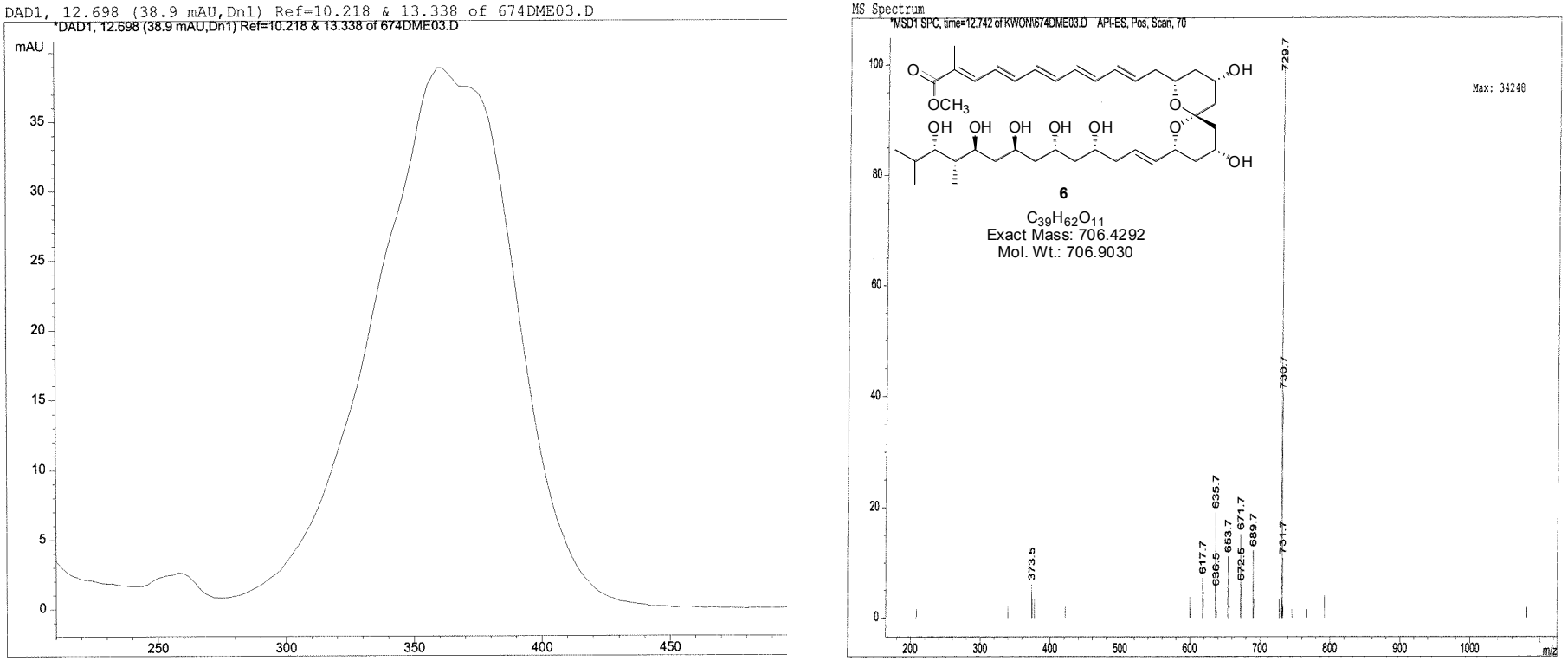


Figure S40. UV and ESI-MS spectra derived from HPLC-DAD-MSD of compound **6**.

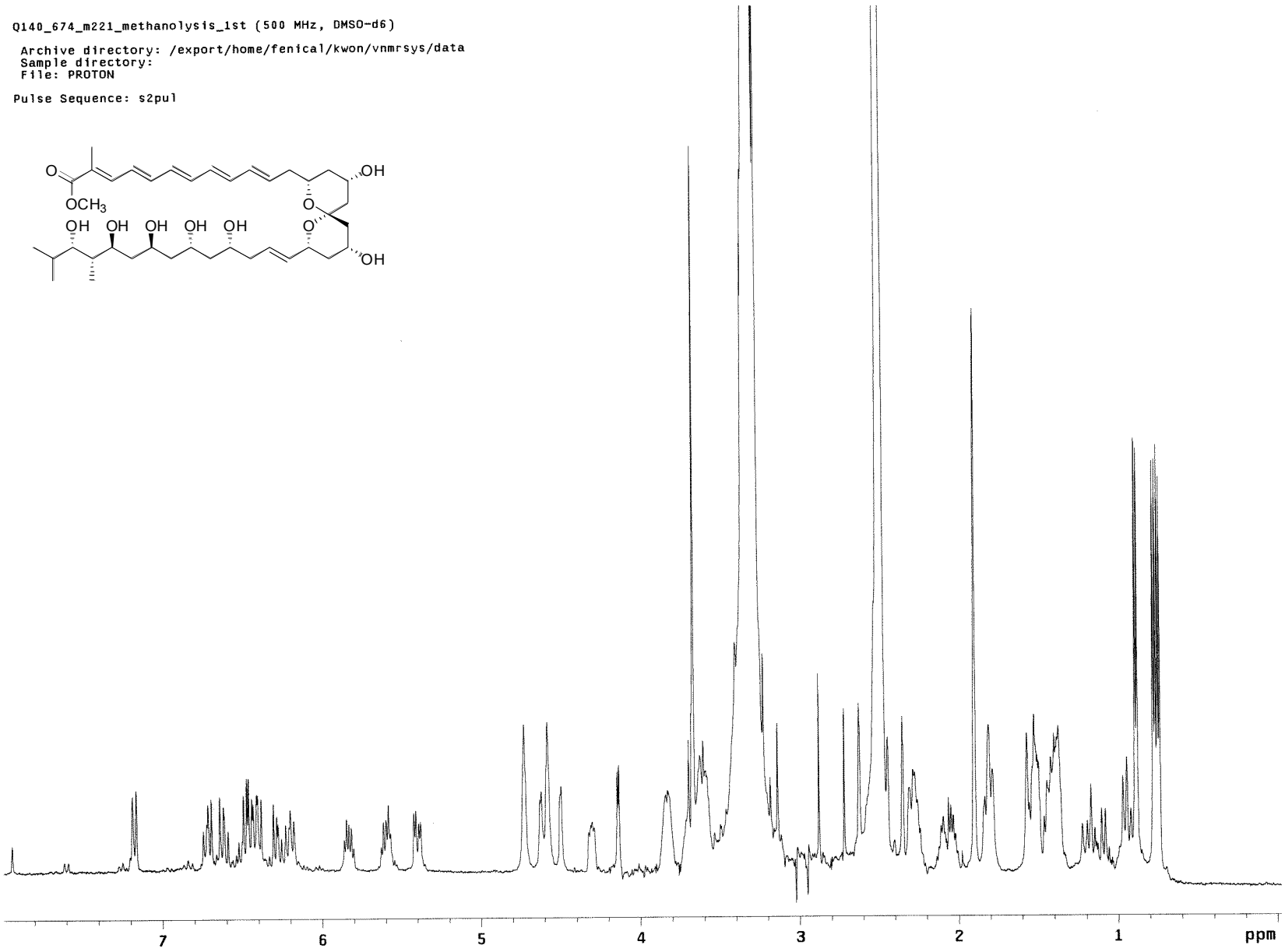


Figure S41. ^{1}H NMR spectrum of **6** (500 MHz, DMSO-d_6)

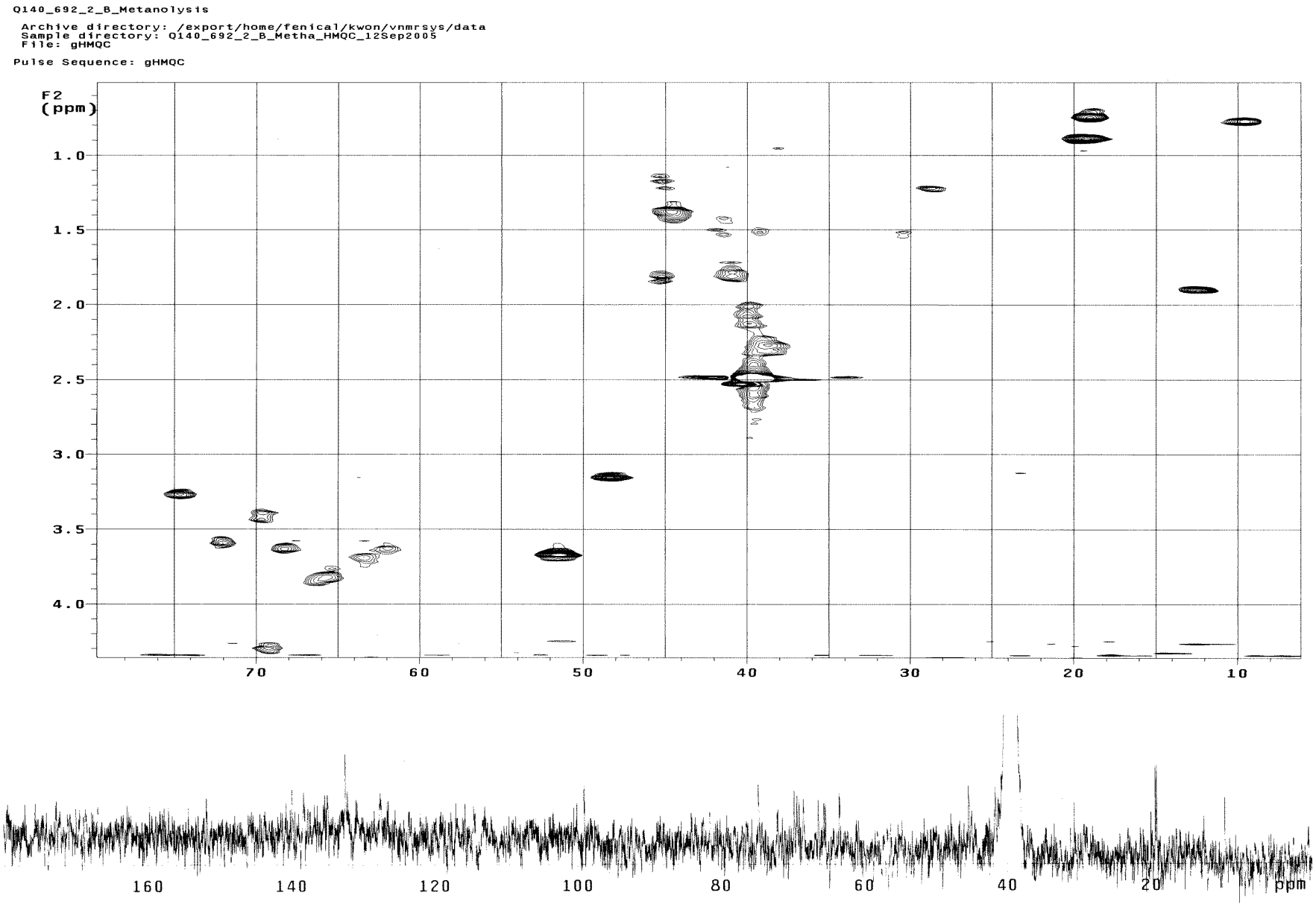


Figure S42. Expanded gHMQC spectrum (500 MHz, DMSO-d_6) and ^{13}C NMR spectrum (75 MHz, DMSO-d_6) of **6**.

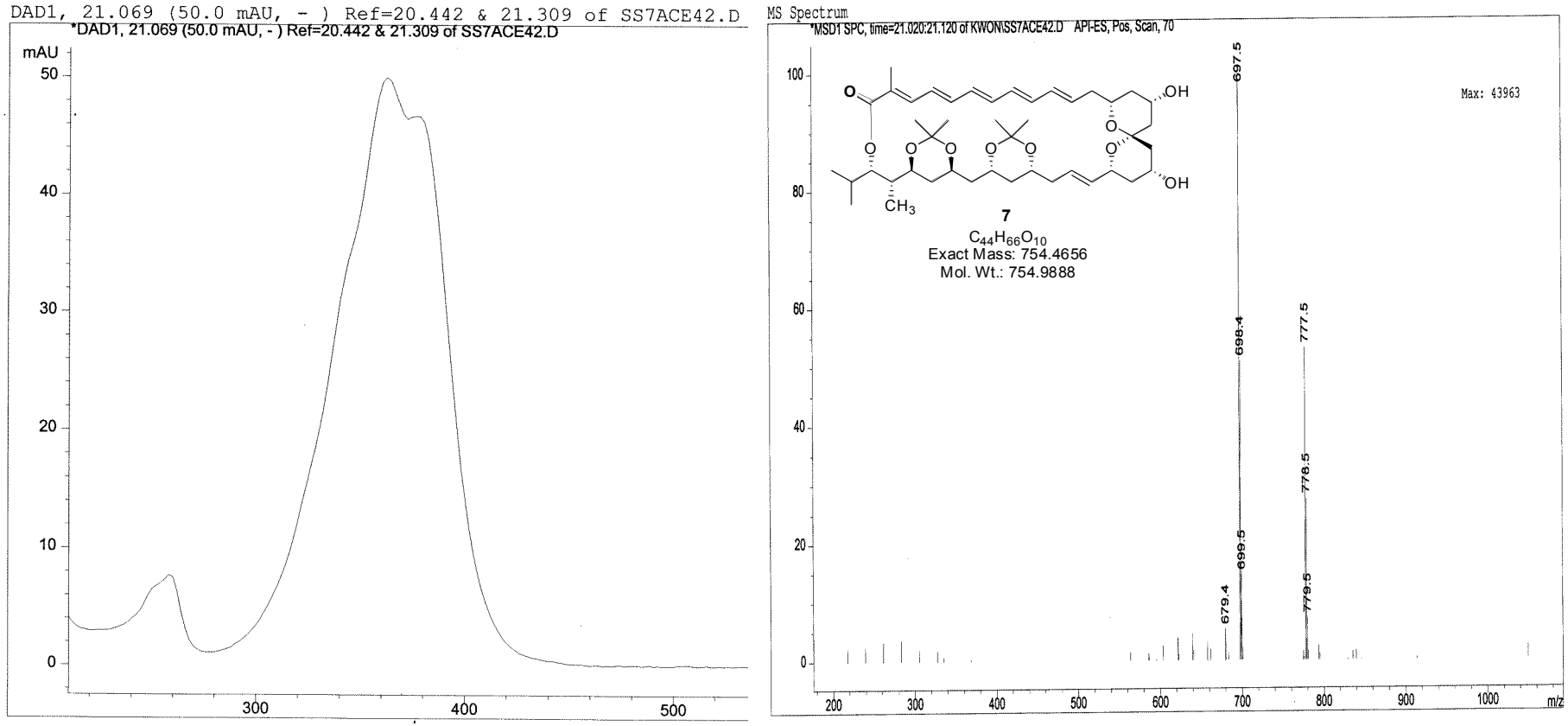


Figure S43. UV and ESI-MS spectra derived from HPLC-DAD-MSD of compound **7**.

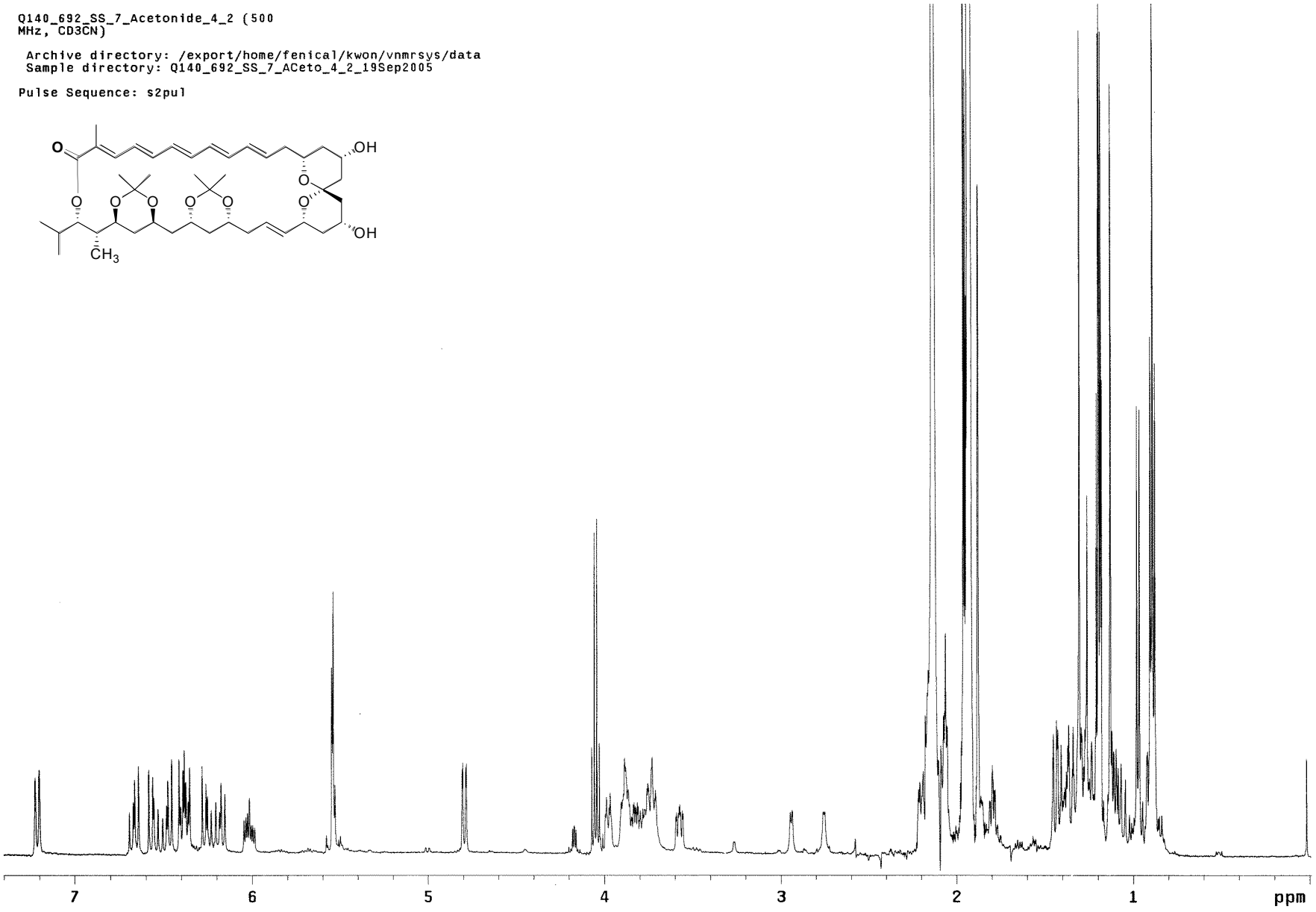


Figure S44. ^{1}H NMR spectrum of **7** (500 MHz, CD_3CN).

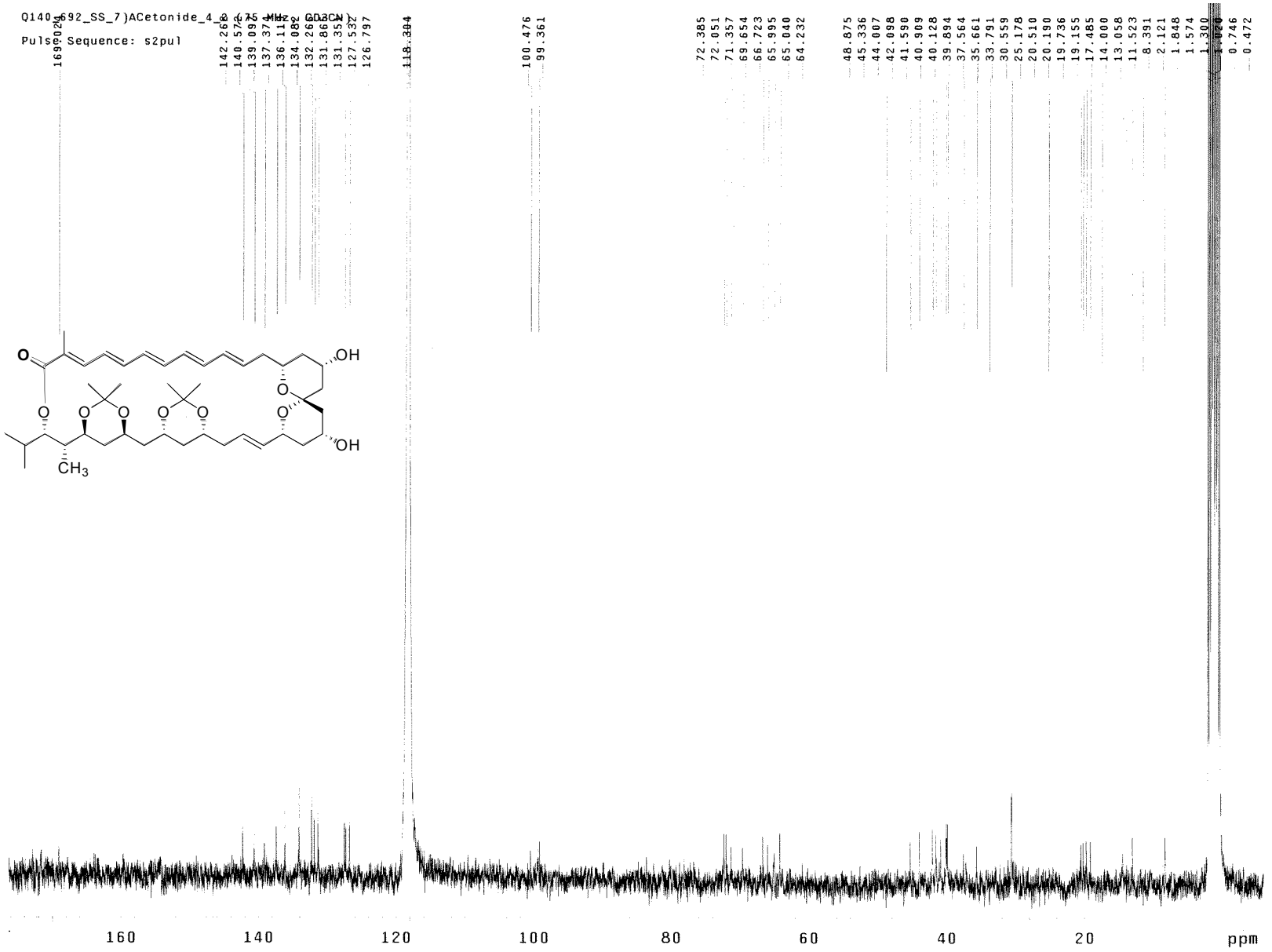


Figure S45. ^{13}C NMR spectrum of **7** (75 MHz, CD_3CN).

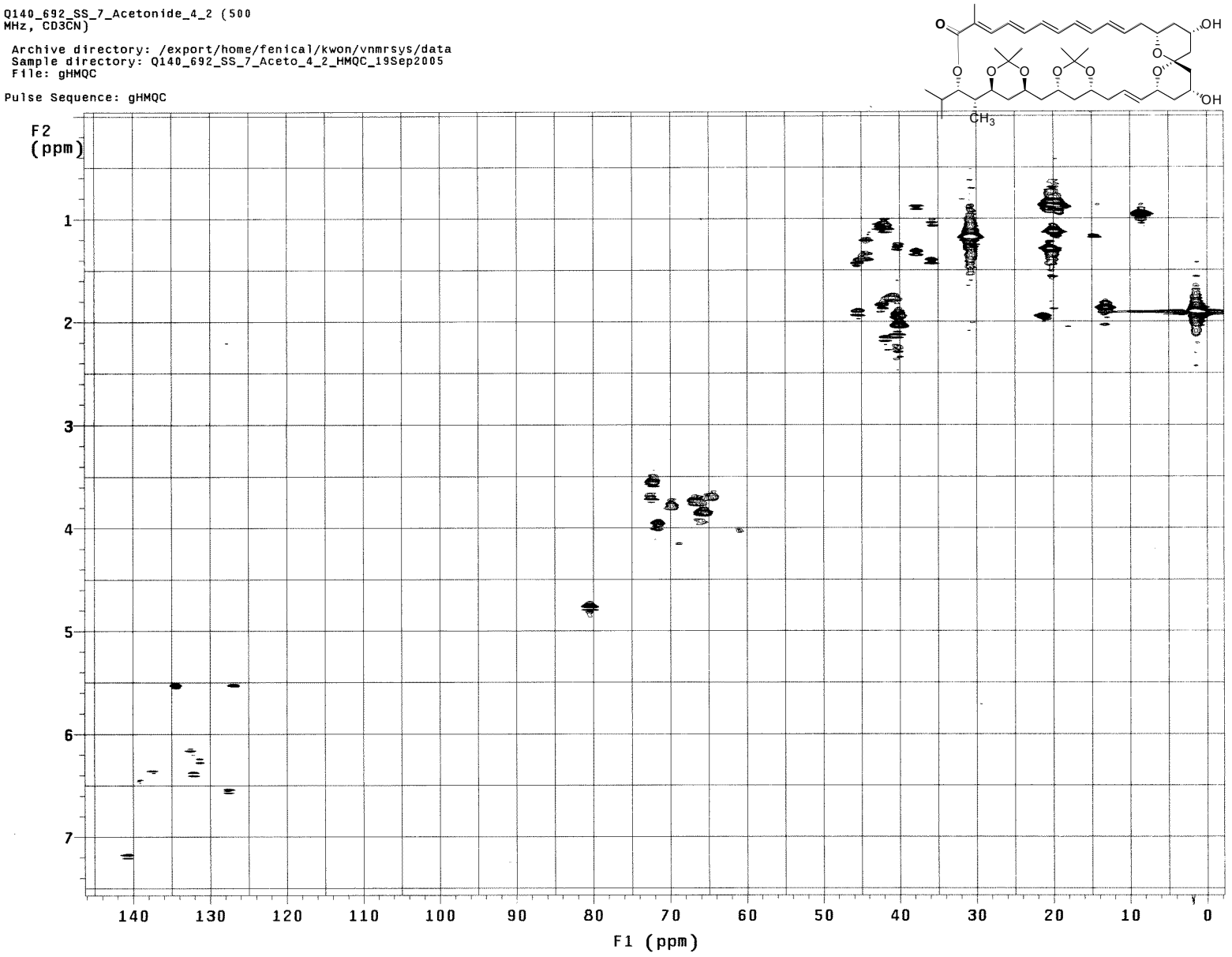


Figure S46. gHMQC spectrum of **7** (500 MHz, CD_3CN).

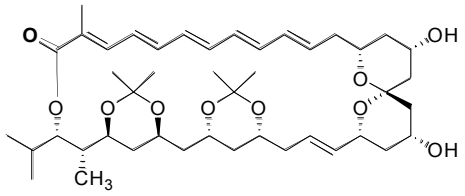
Q140_692_SS_7_Acetonide_4_2_ROESY
(500 MHz, CD3CN, 25C)

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_692_SS_7_Acetonide_ROESY_500_CD3CN_22Sep2005

Pulse Sequence: ROESY

Solvent: CD3CN
Temp. 25.0 C / 298.1 K
File: ROESY
INOVA-500 "nightmare500"

Relax. delay 3.000 sec
Mixing 0.200 sec
Acq. time 0.205 sec
Width 4995.9 Hz
2D Width 4995.9 Hz
32 repetitions
2 x 256 increments
OBSERVE H1, 499.5907954 MHz
DATA PROCESSING
Gauss apodization 0.095 sec
F1 DATA PROCESSING
Gauss apodization 0.022 sec
FT size 2048 x 2048
Total time 15 hr, 44 min, 29 sec



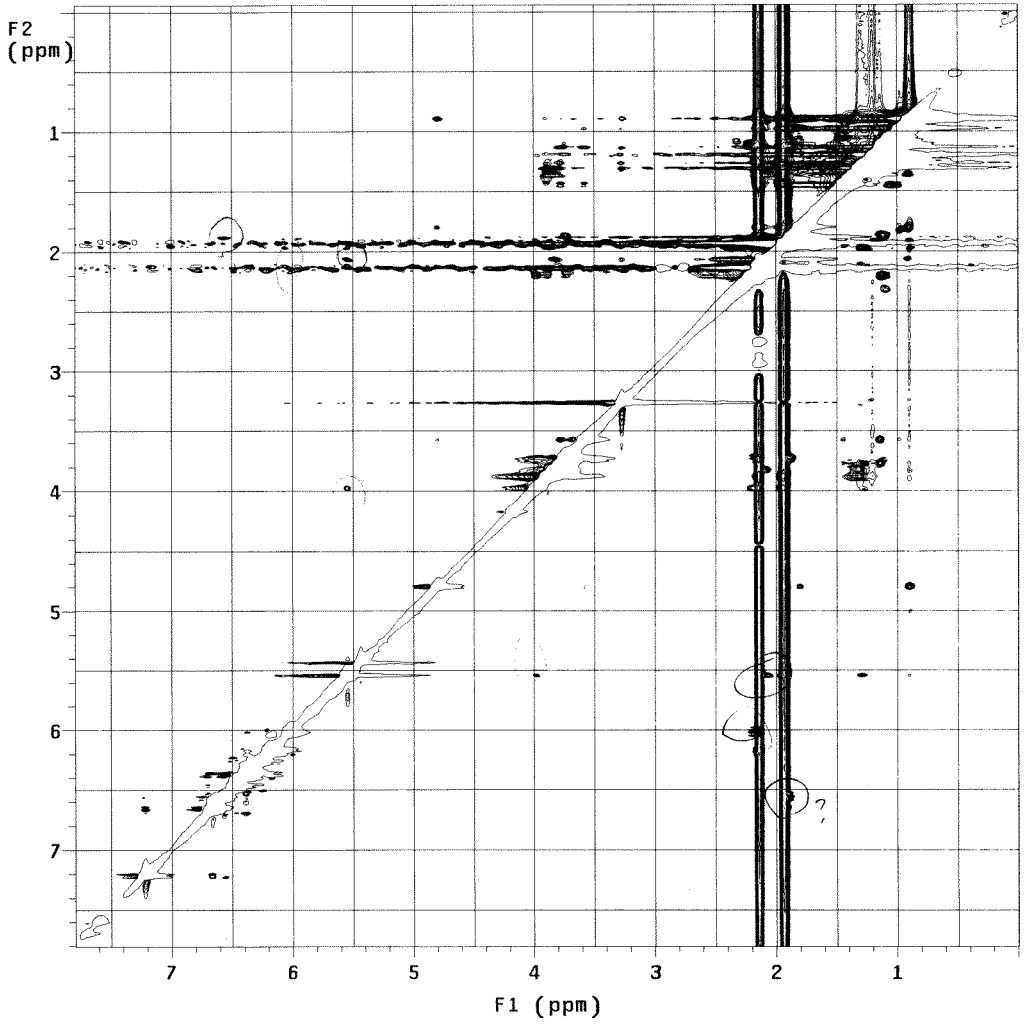


Figure S47. ROESY spectrum of **7** (500 MHz, CD_3CN).

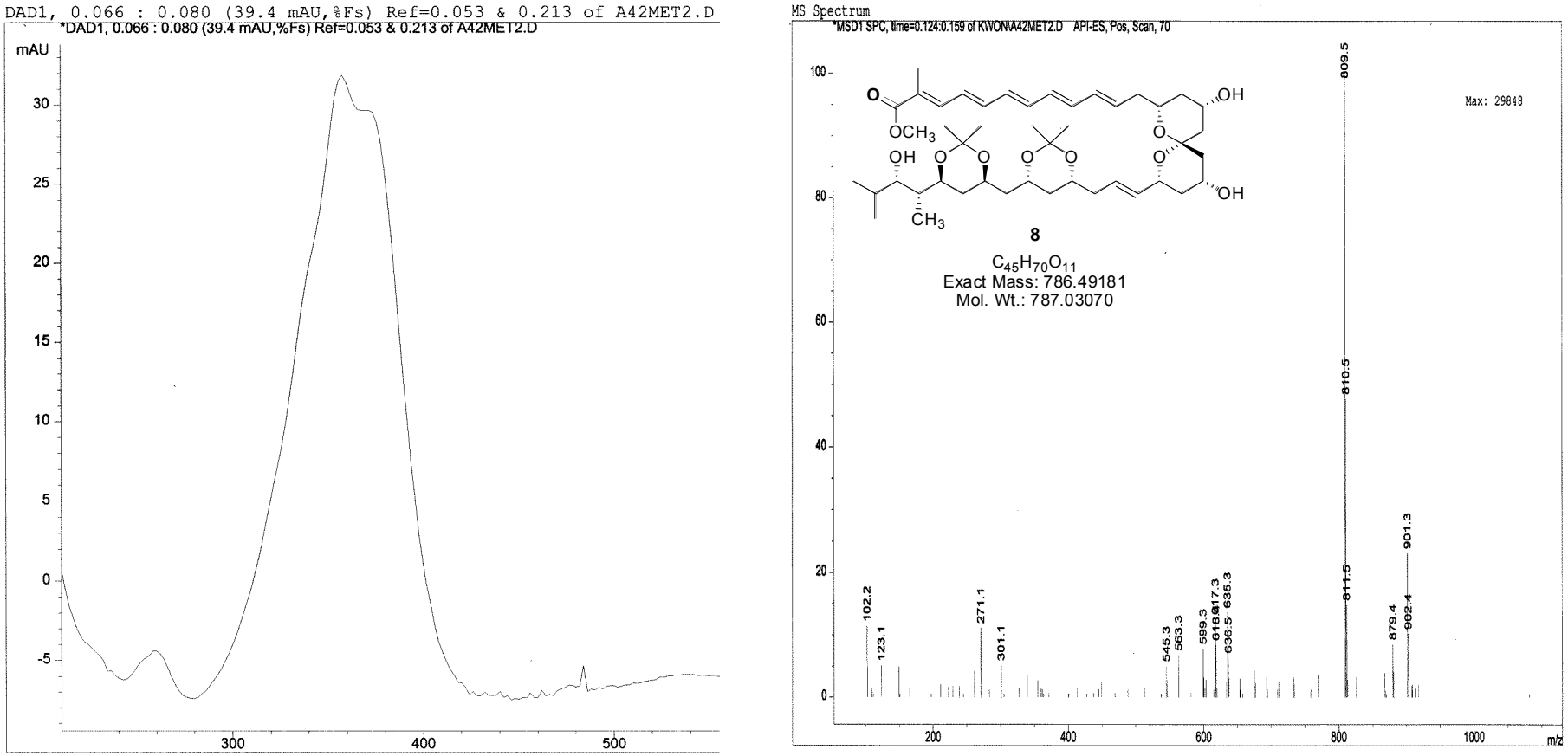


Figure S48. UV and ESI-MS spectra derived from HPLC-DAD-MSD of compound **8**.

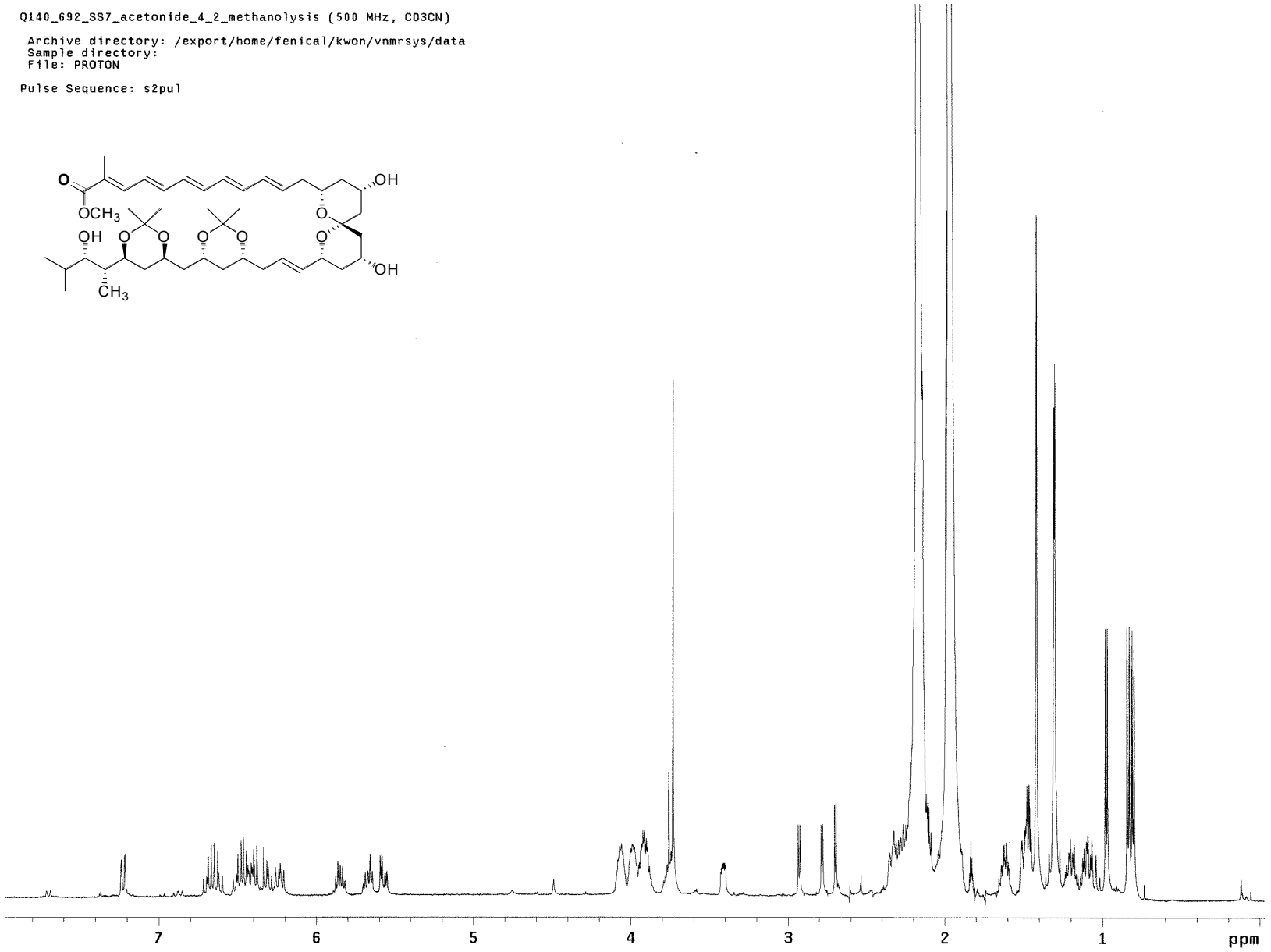


Figure S49. ^{1}H NMR spectrum of **8** (500 MHz, CD_3CN).

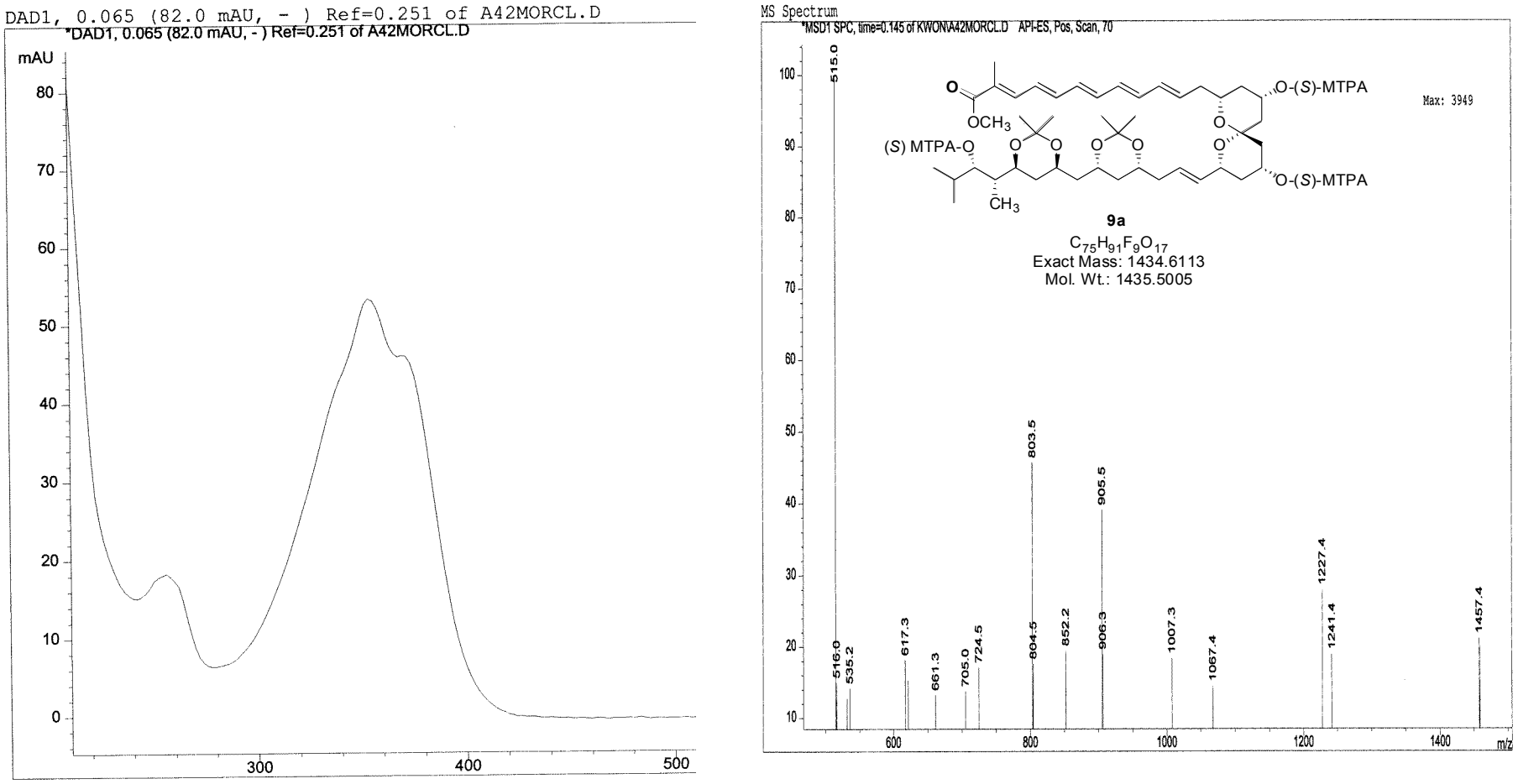


Figure S50. UV and ESI-MS spectra derived from HPLC-DAD-MSD of compound **9a**.

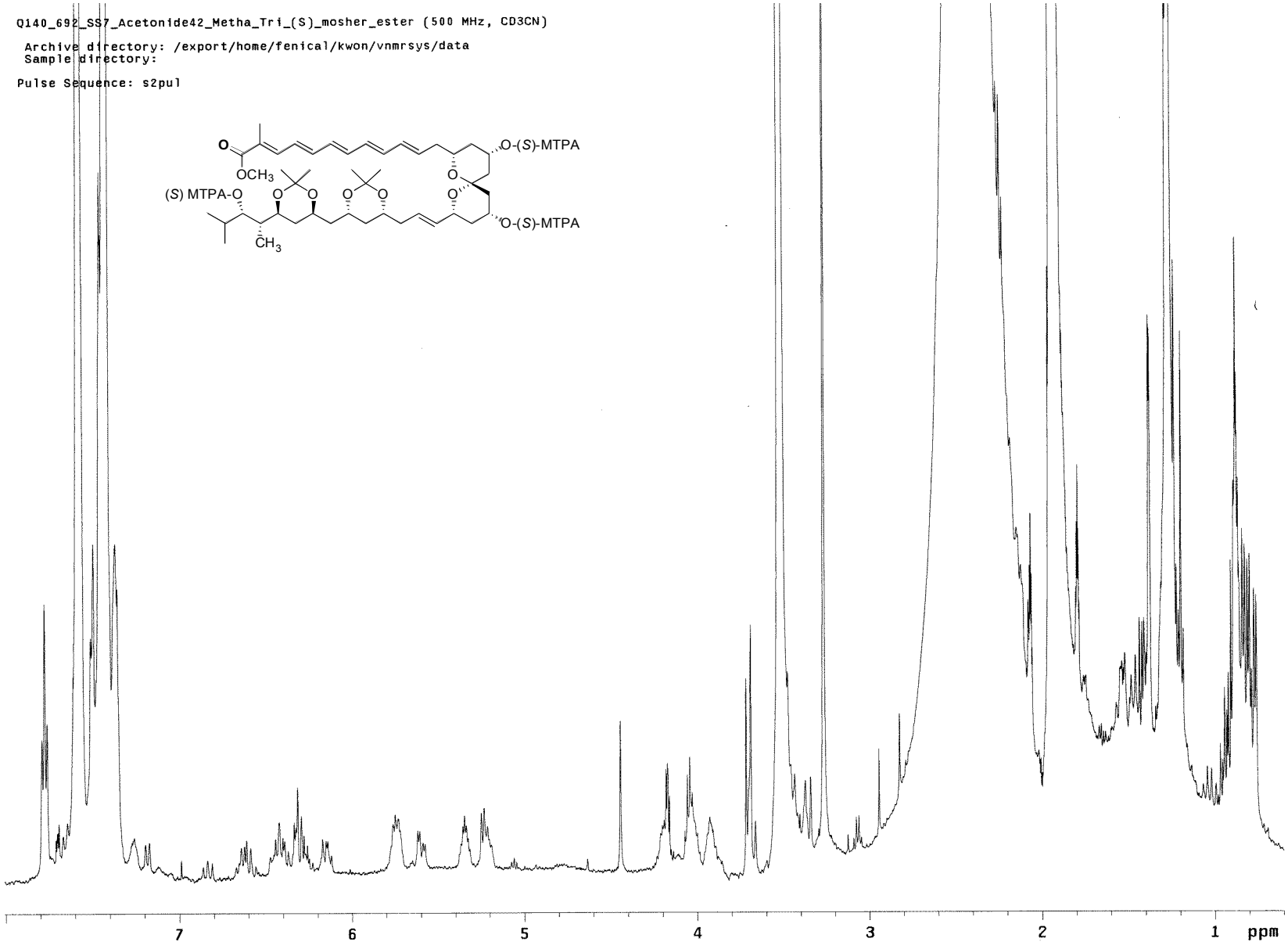


Figure S51. ^{1}H NMR spectrum of **9a** (500 MHz, CD_3CN).

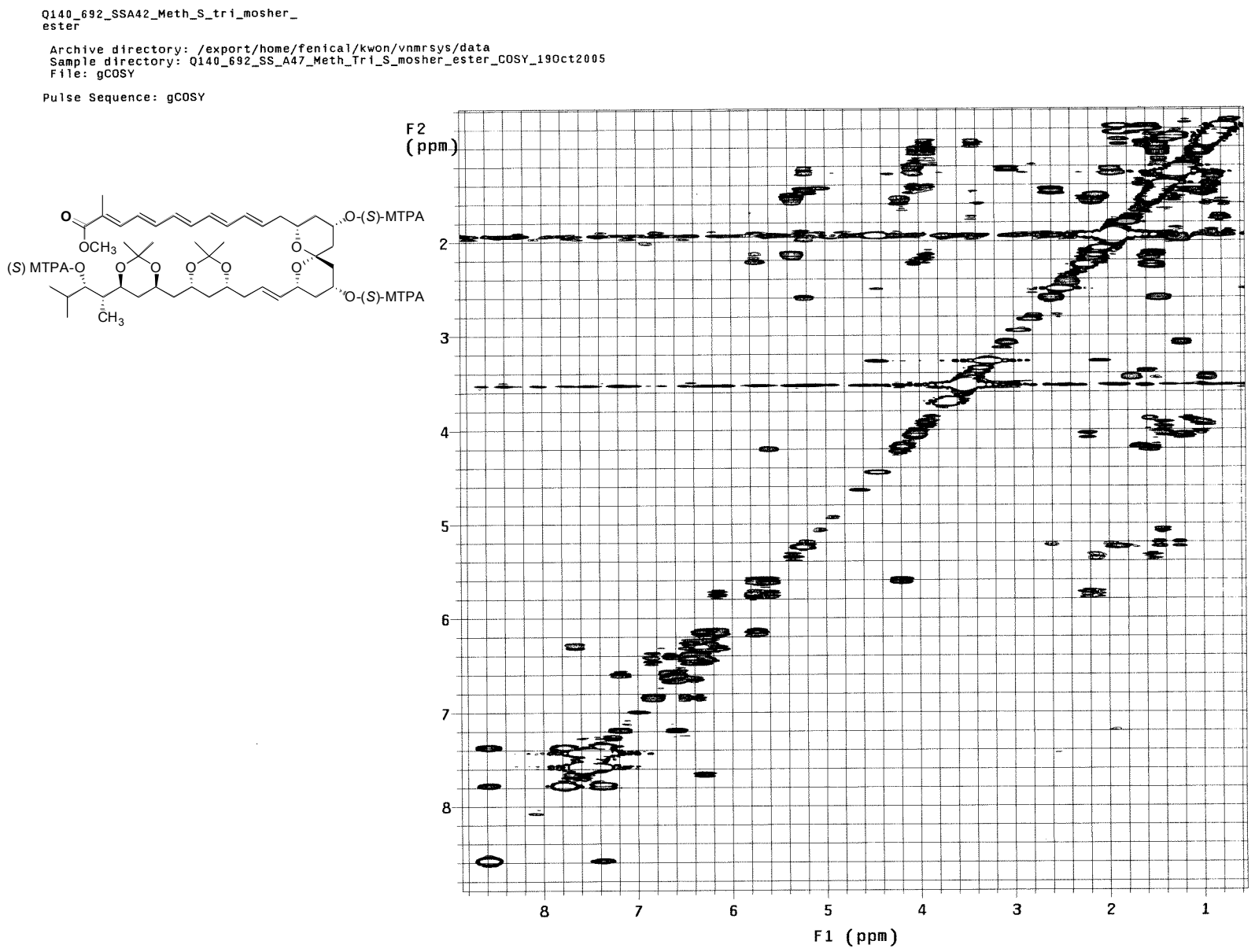


Figure S52. ^{1}H-^{1}H COSY spectrum of **9a** (500 MHz, CD_3CN).

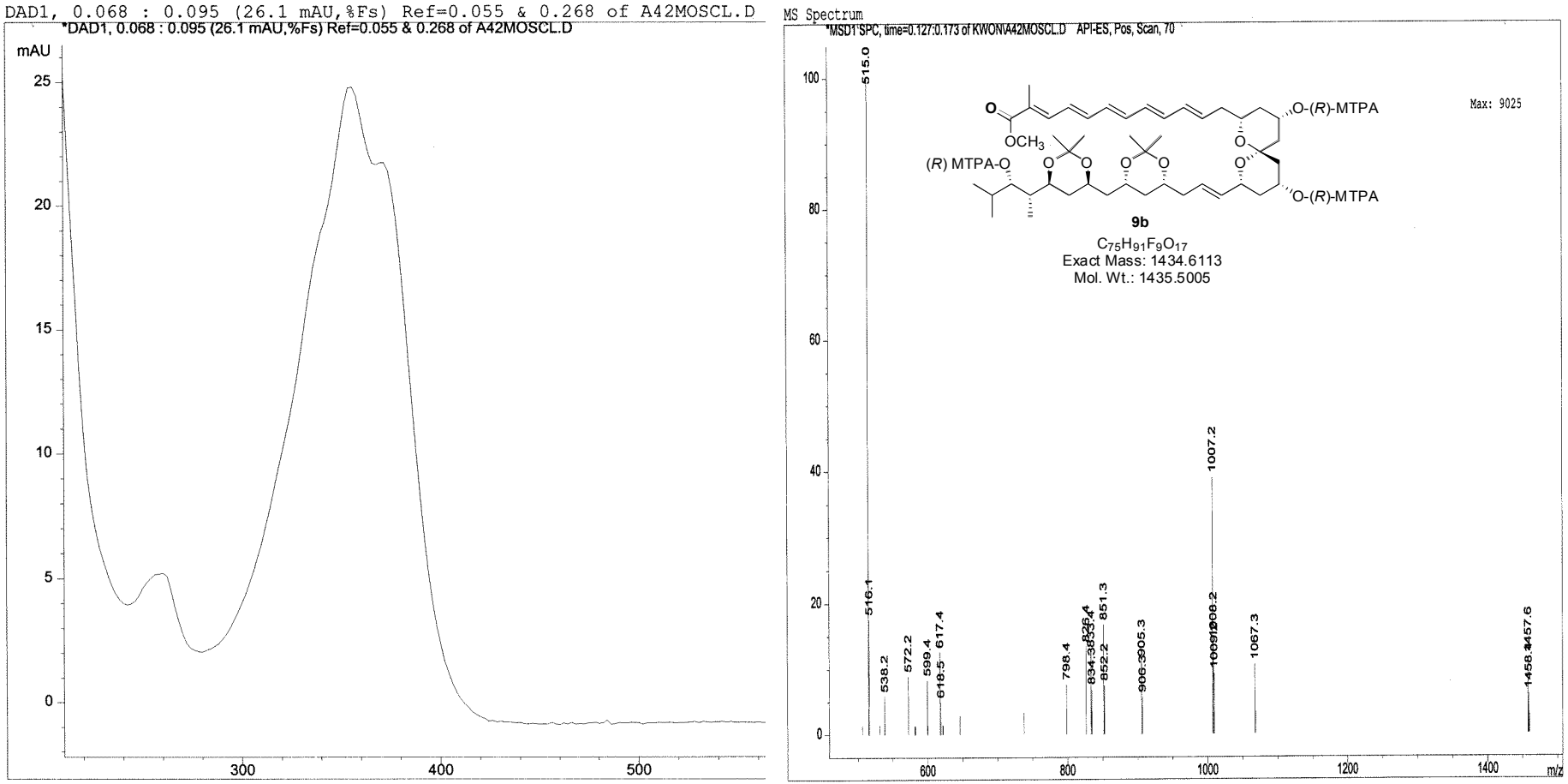


Figure S53. UV and ESI-MS spectra derived from HPLC-DAD-MSD (MeCN-H_2O) of compound **9b.**

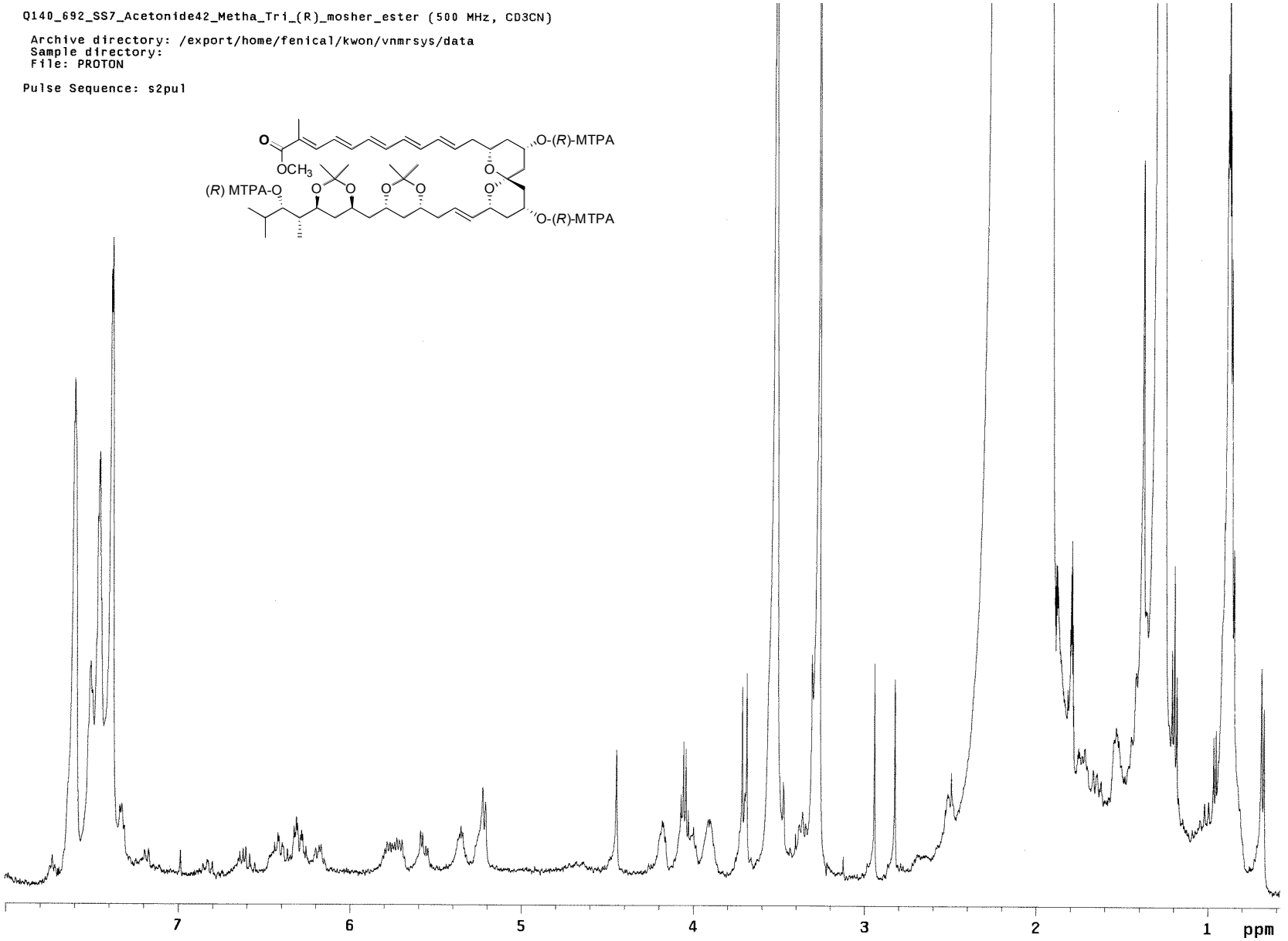


Figure S54. ^{1}H NMR spectrum of **9b** (500 MHz, CD_3CN).

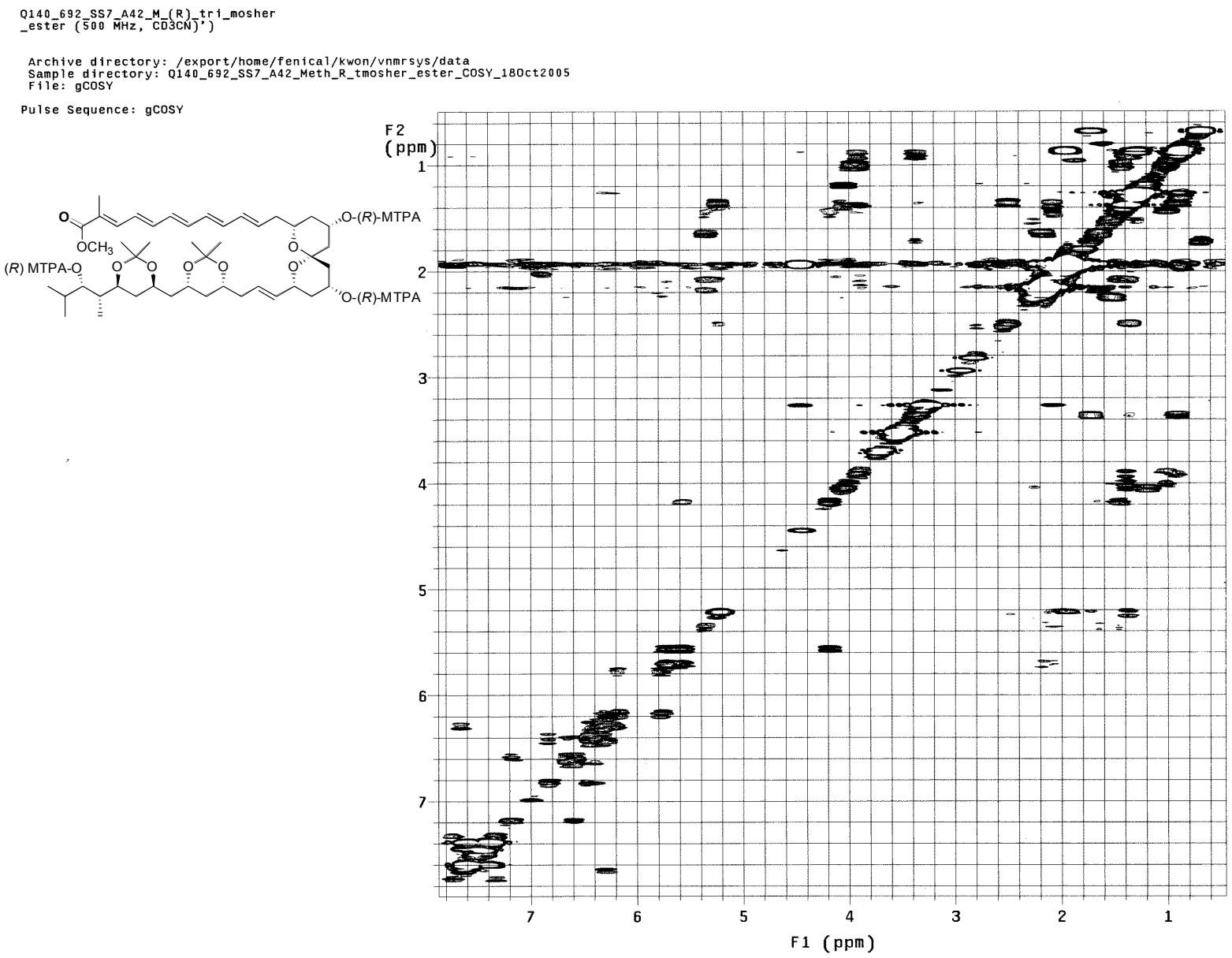


Figure S55. ^{1}H-^{1}H COSY spectrum of **9b** (500 MHz, CD_3CN).

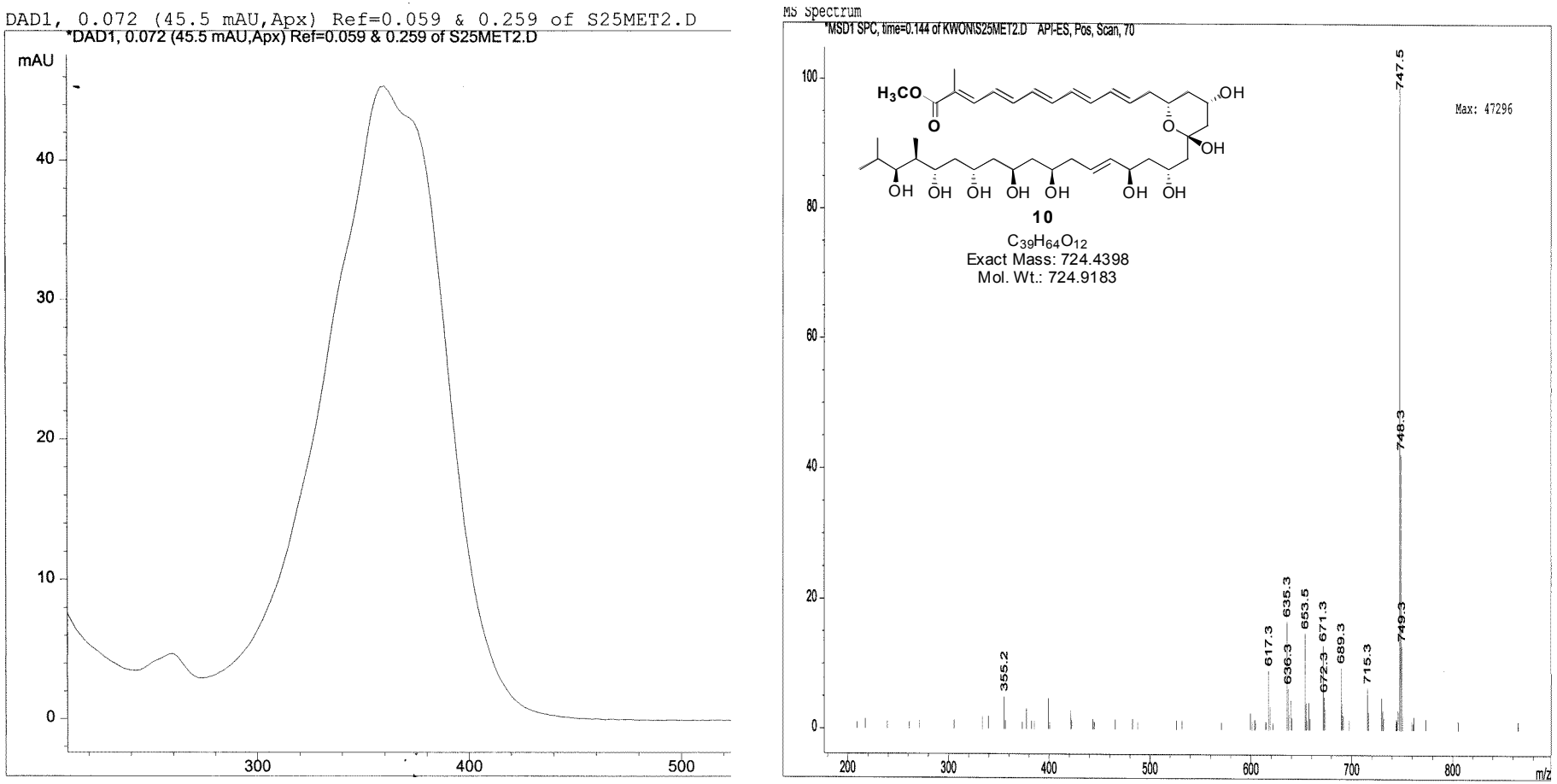


Figure S56. UV and ESI-MS spectra derived from HPLC-DAD-MSD (MeCN-H_2O) of compound **10**.

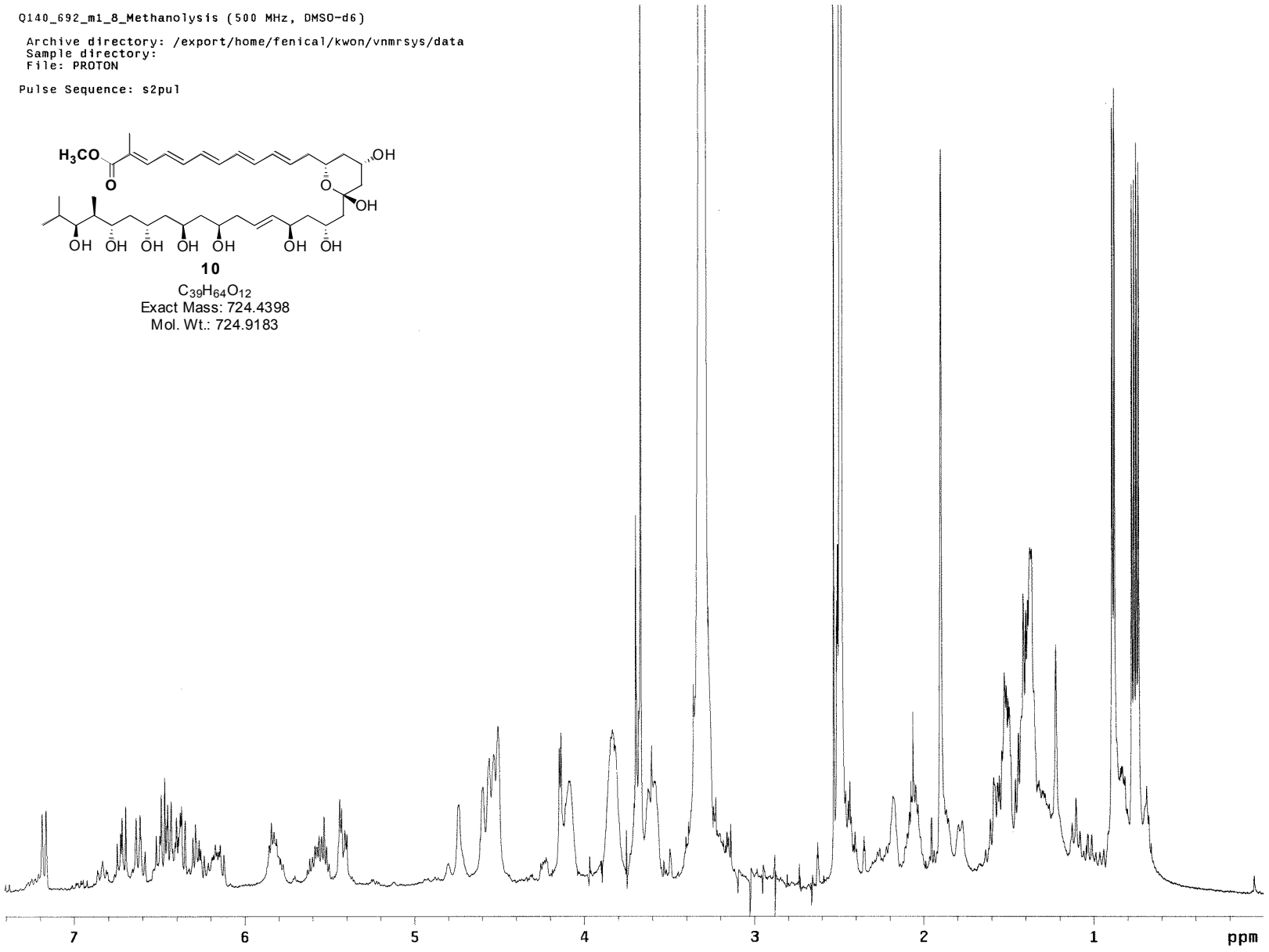


Figure S57. ^{1}H NMR spectrum of compound **10** (500 MHz, DMSO-d_6).

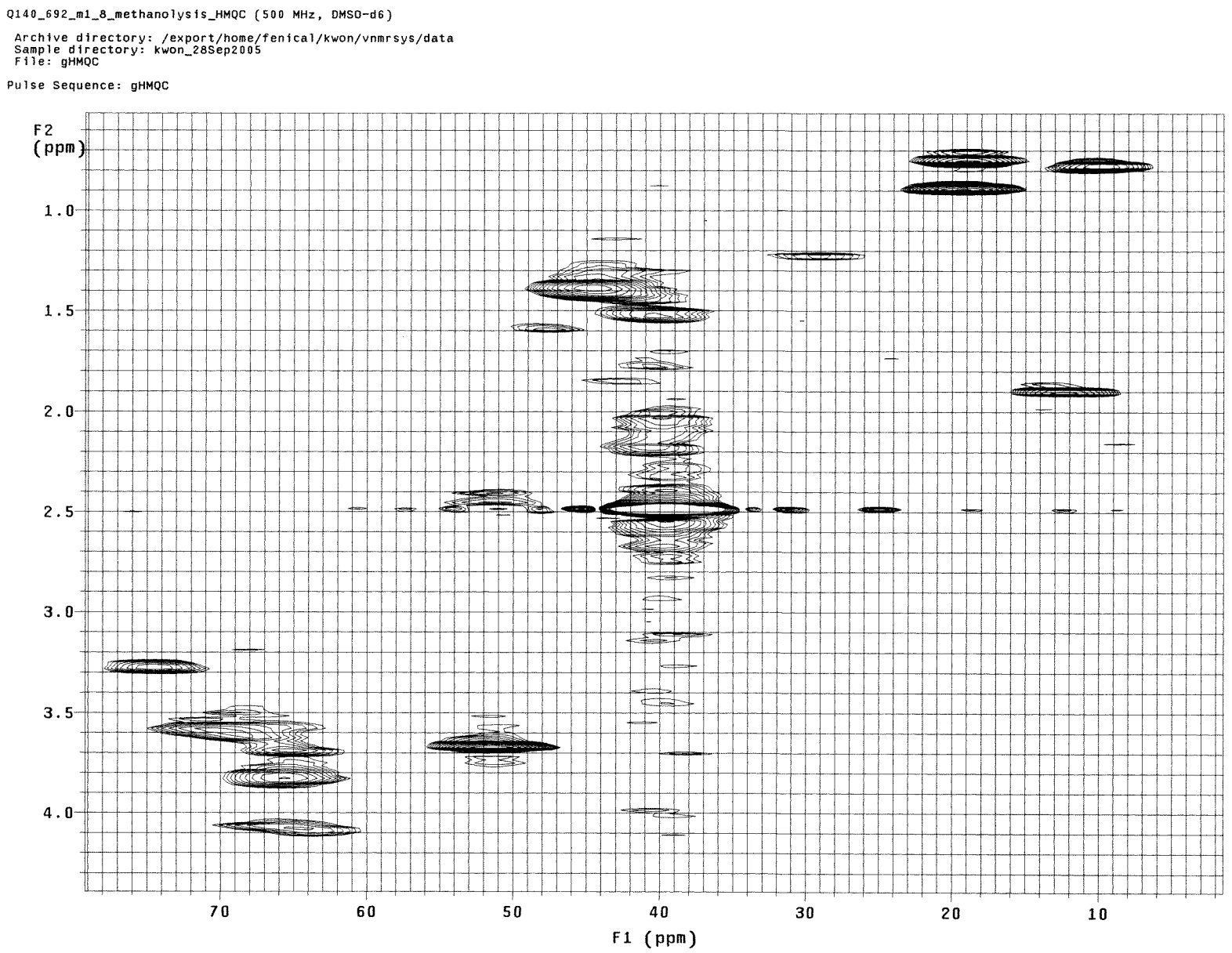


Figure S58. Expanded gHMQC spectrum of **10** (500 MHz, DMSO-d_6).

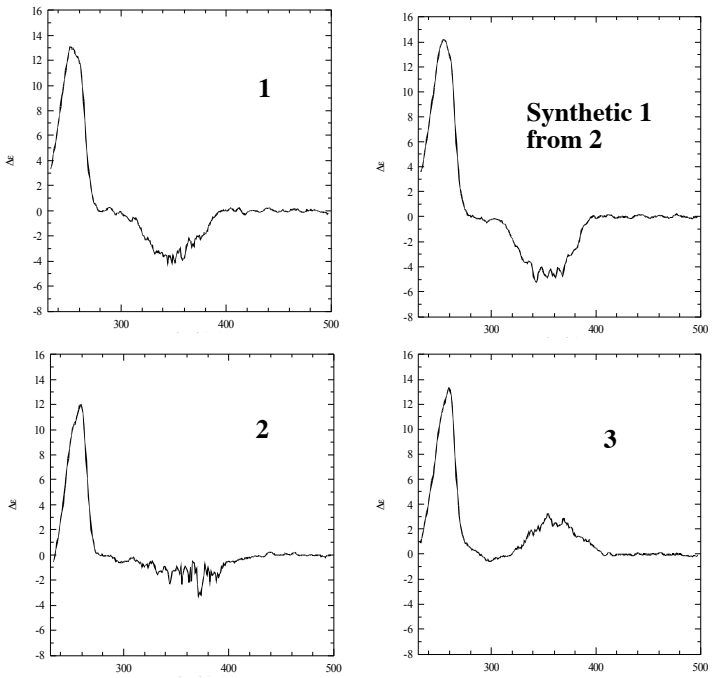


Figure S59. CD spectra of **1**, synthetic **1**, **2**, and **3** in methanol.