

Supporting Information for

Marinisorolides, New Polyene-Polyol Macrolides from a Marine Actinomycete

of New Genus “*Marinispora*”

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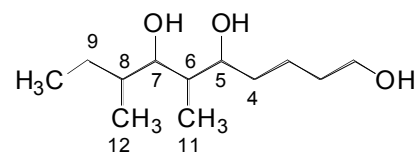
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General Experimental Procedures. ^1H NMR and 2D NMR spectra were obtained in $\text{DMSO-}d_6$, $\text{pyridine-}d_5$, or CD_3CN at 500 MHz. ^{13}C NMR spectra were obtained at 75 MHz or 125 MHz. HR-ESI-TOF MS data were obtained at the Scripps Research 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 detector. 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 analytical 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 ($\text{DMSO-}d_6$)^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 5 α -OH, 6 α -Me, 7 β -OH, 8 β -Me. ^c 5 α -OH, 6 α -Me, 7 α -OH, 8 α -Me. ^d 5 α -OH, 6 α -Me, 7 β -OH, 8 α -Me. ^e 5 α -OH, 6 α -Me, 7 α -OH, 8 β -Me. ^f 5 β -OH, 6 α -Me, 7 β -OH, 8 β -Me. ^g 5 β -OH, 6 α -Me, 7 α -OH, 8 α -Me. ^h 5 β -OH, 6 α -Me, 7 β -OH, 8 α -Me. ⁱ 5 β -OH, 6 α -Me, 7 α -OH, 8 β -Me.

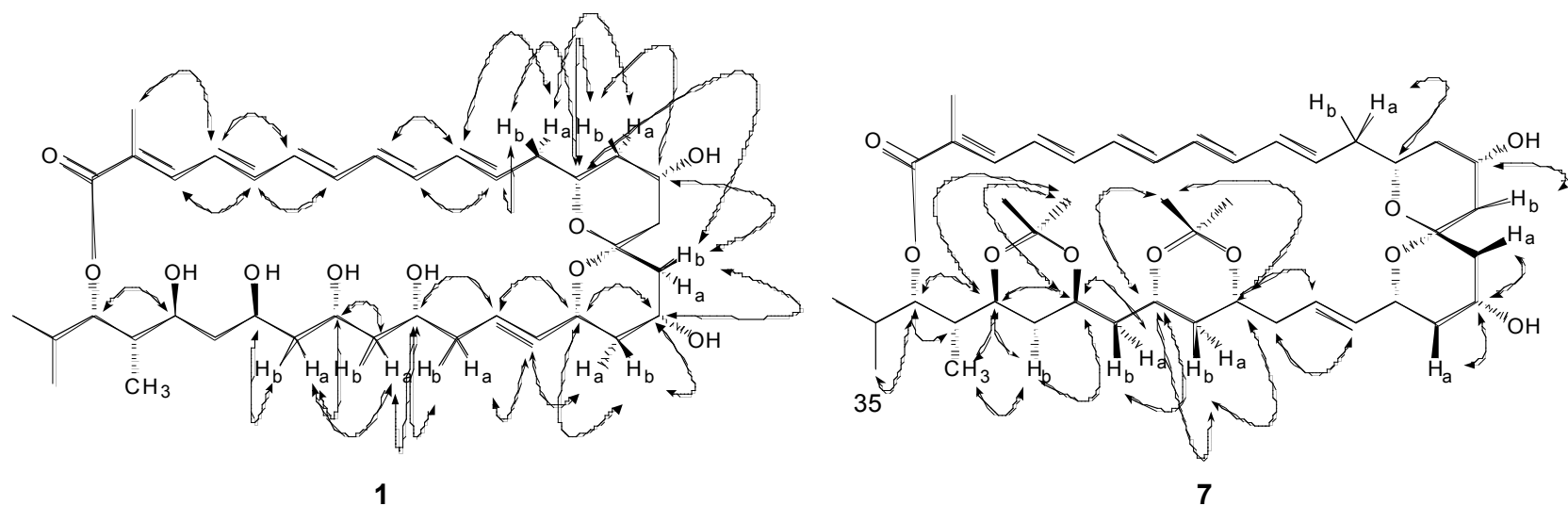


Figure S1. Key ROESY NMR correlation of compounds 1 and 7.

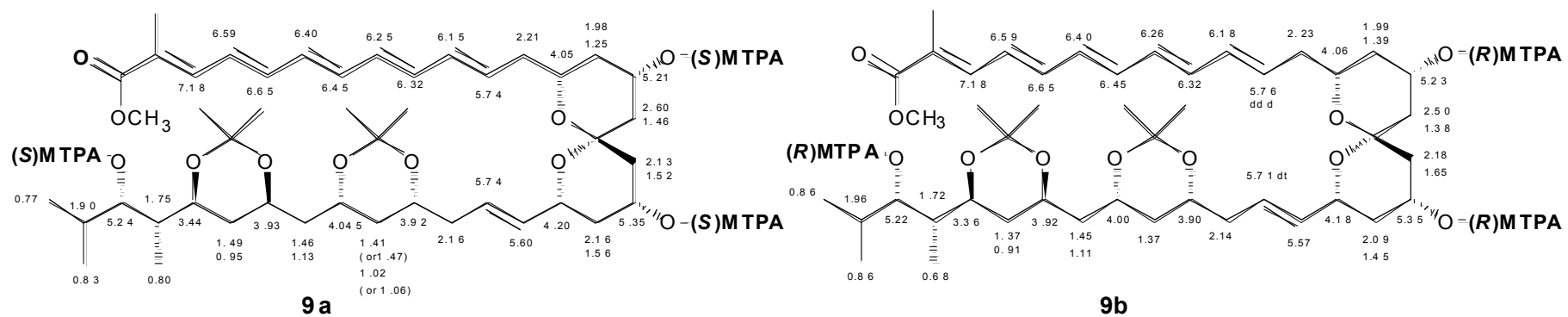


Figure S2. Proton chemical shifts in ¹H NMR spectra of 9a [(S)-Mosher ester of 8] and 9b [(R)-Mosher ester of 8].

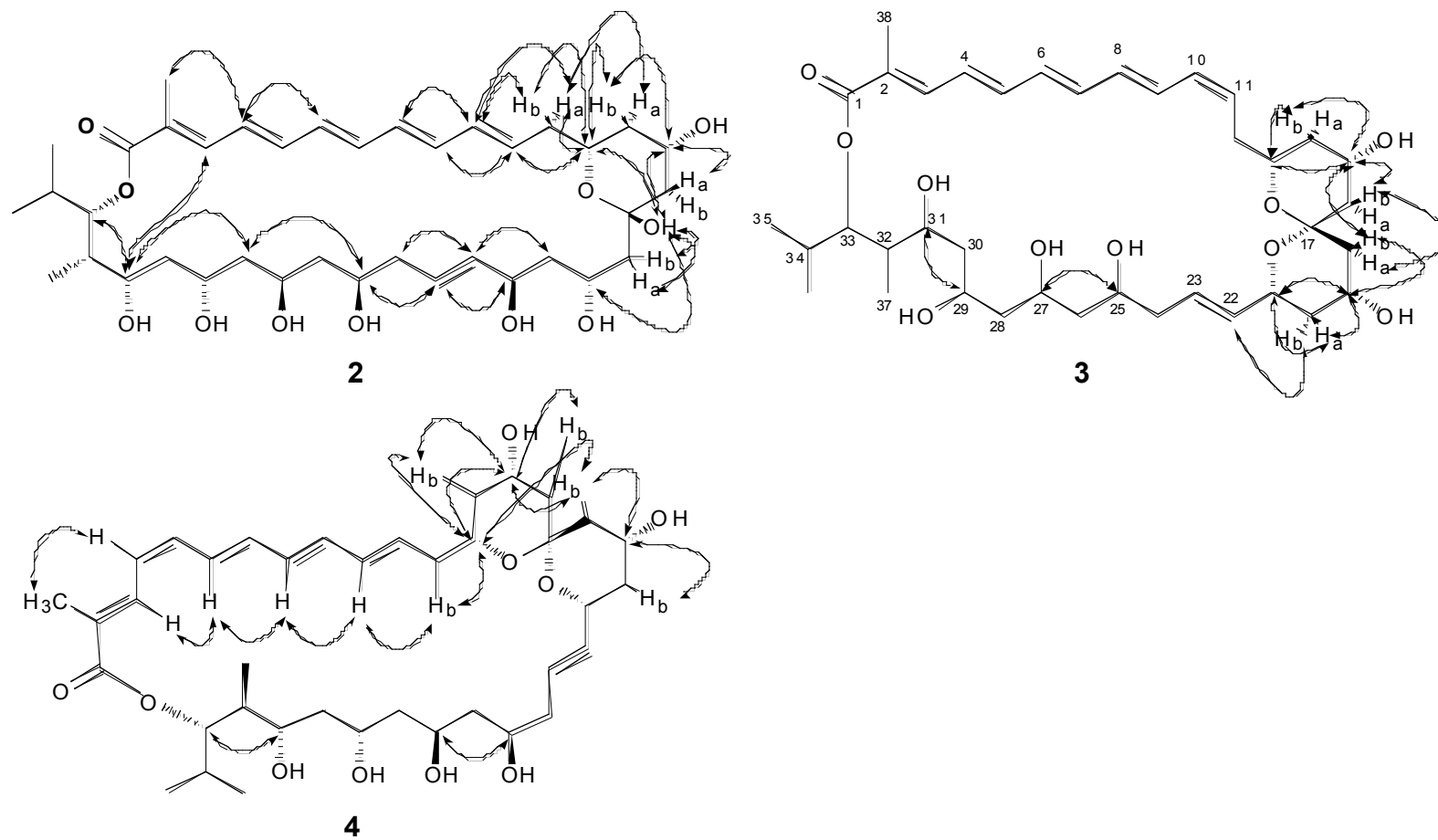


Figure S3. Key ROESY NMR correlation of compounds 2, 3 and 4.

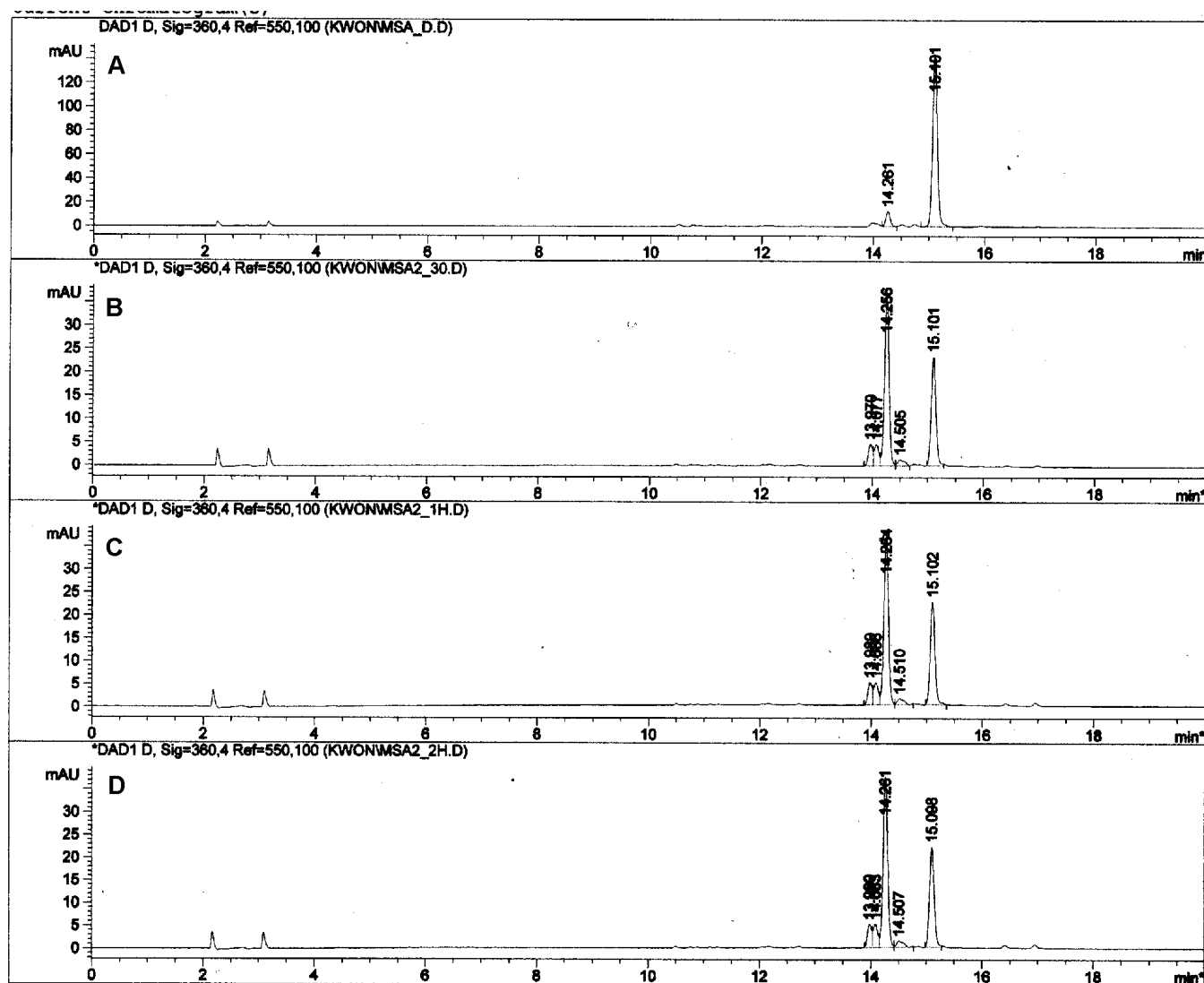


Figure S4. HPLC chromatogram of **1** and isomers of **1** derived from the photochemical conversion of **1** for one and two hours. UV detector 360 nm. Retention time 14.0 min – marinisporolide E (**5**); Rt 14.3 min – marinisporolide D (**4**); Rt 14.5 min – marinisporolide C (**3**); Rt 15.1 min –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

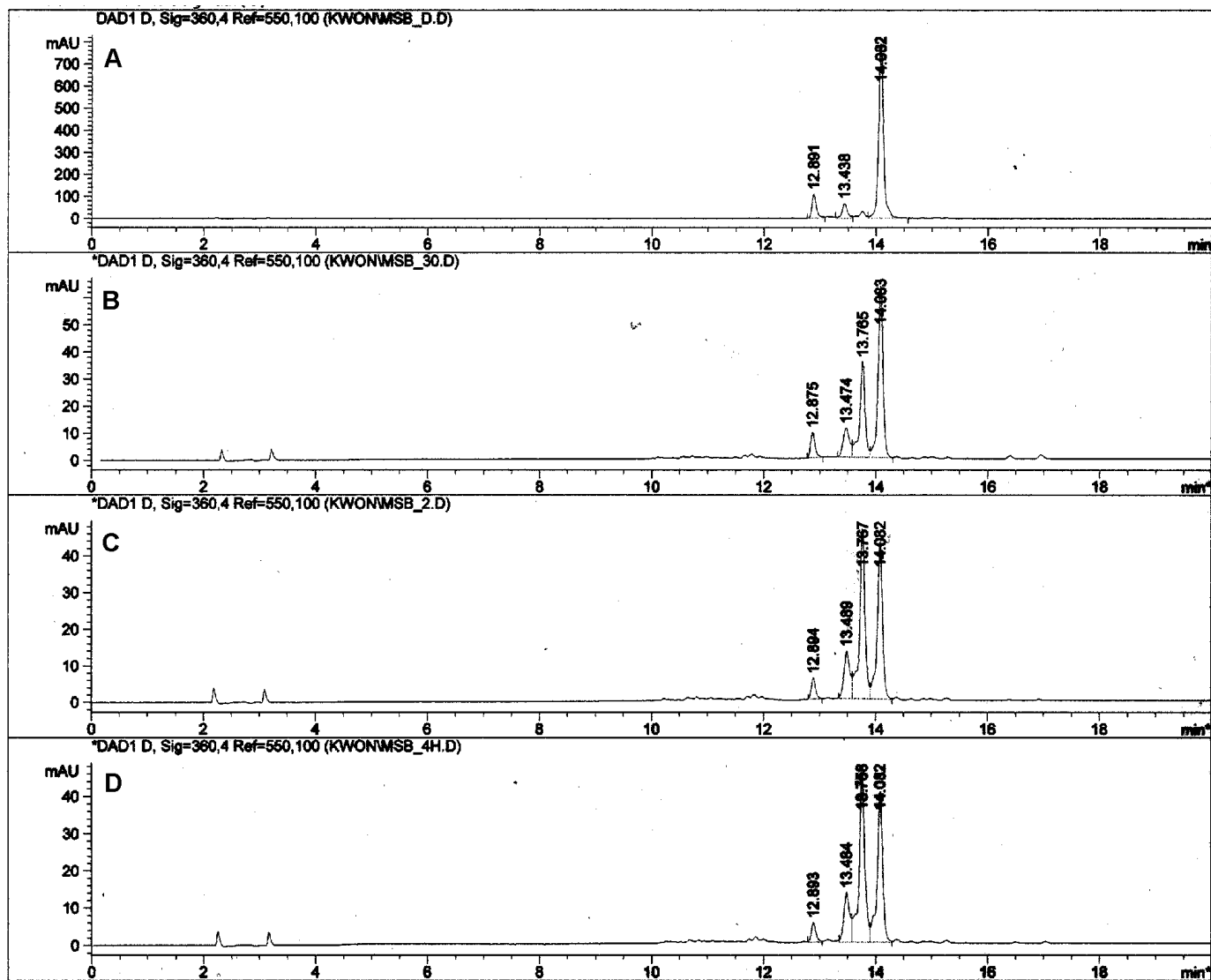


Figure S5. HPLC chromatogram of **2** and isomers of **2** derived from the photochemical conversion of **2** for one and two hours. (UV detector 360 nm). Retention time 14.1 min – marinisporolide B (**2**). (A) marinisporolide B (**2**) before exposure to light; (B) 30 min after exposure to light; (C)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

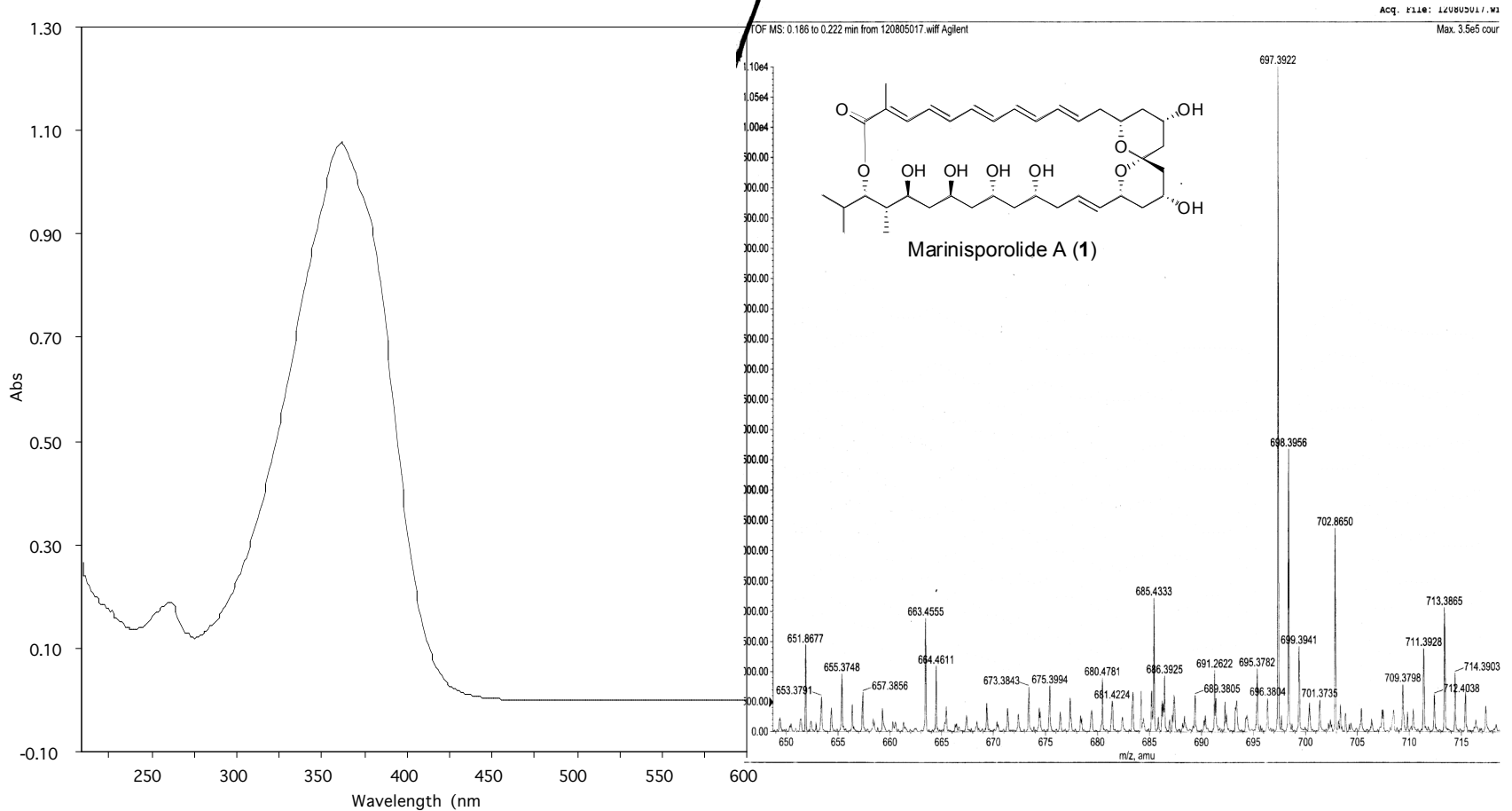


Figure S6. UV (MeOH) and HR-ESI-TOF MS spectra of marinisporolide A (1)

Q140_692_m2_B (500 MHz, DMSO-d6)

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_692_m2_B_25Jun2005

Pulse Sequence: s2pu1

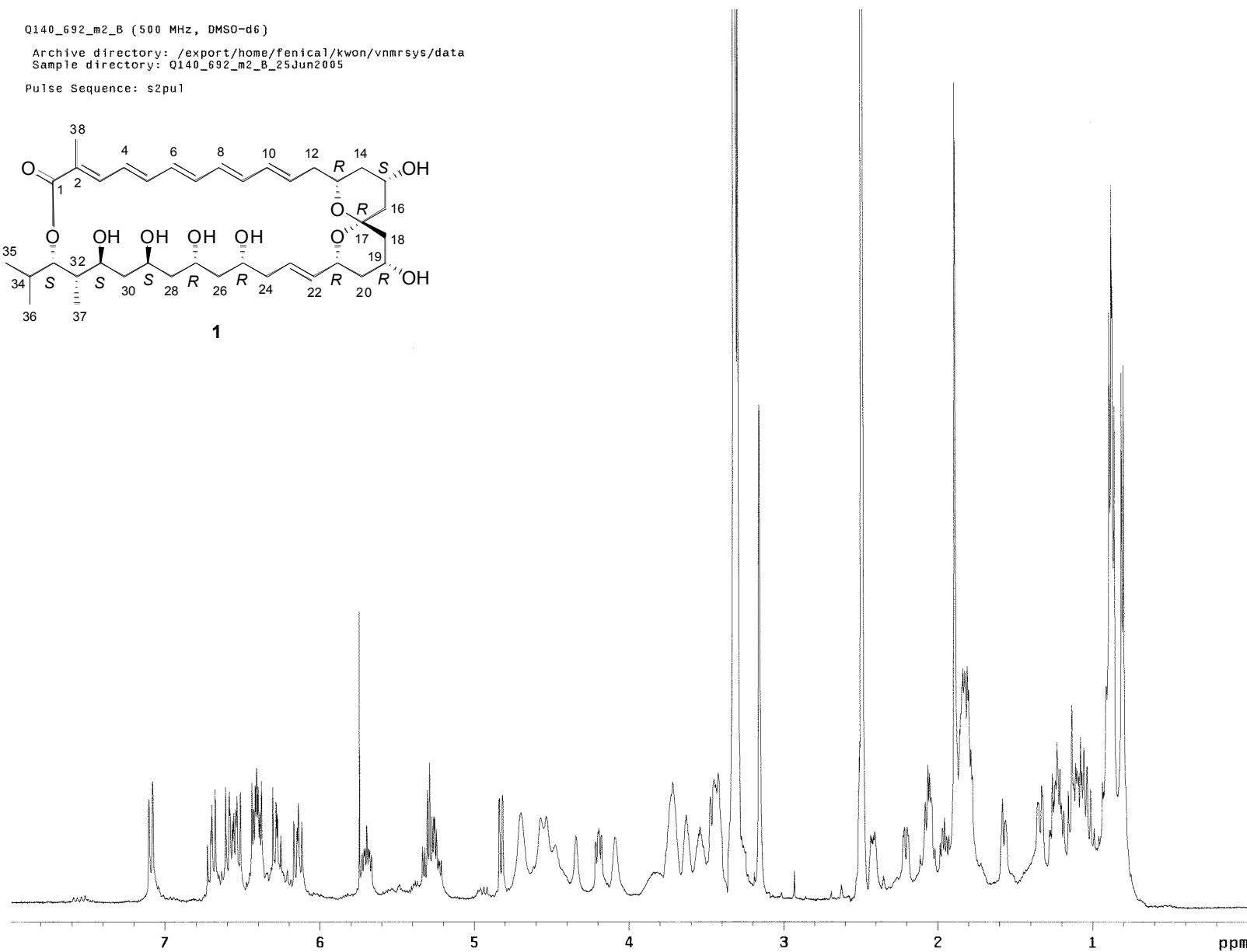
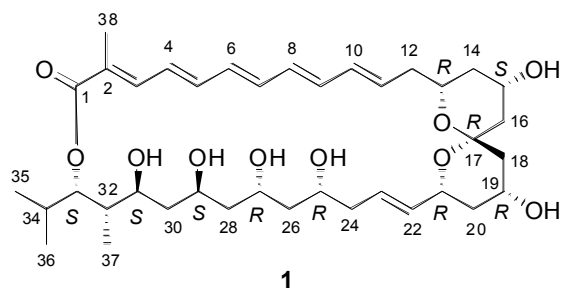


Figure S7. ^1H NMR spectrum of marinisporolide A (**1**) (500 MHz, $\text{DMSO-}d_6$)

Q140_692_m2_B_comp (75 MHz, DMSO-d6)

Pulse Sequence: s2pu1

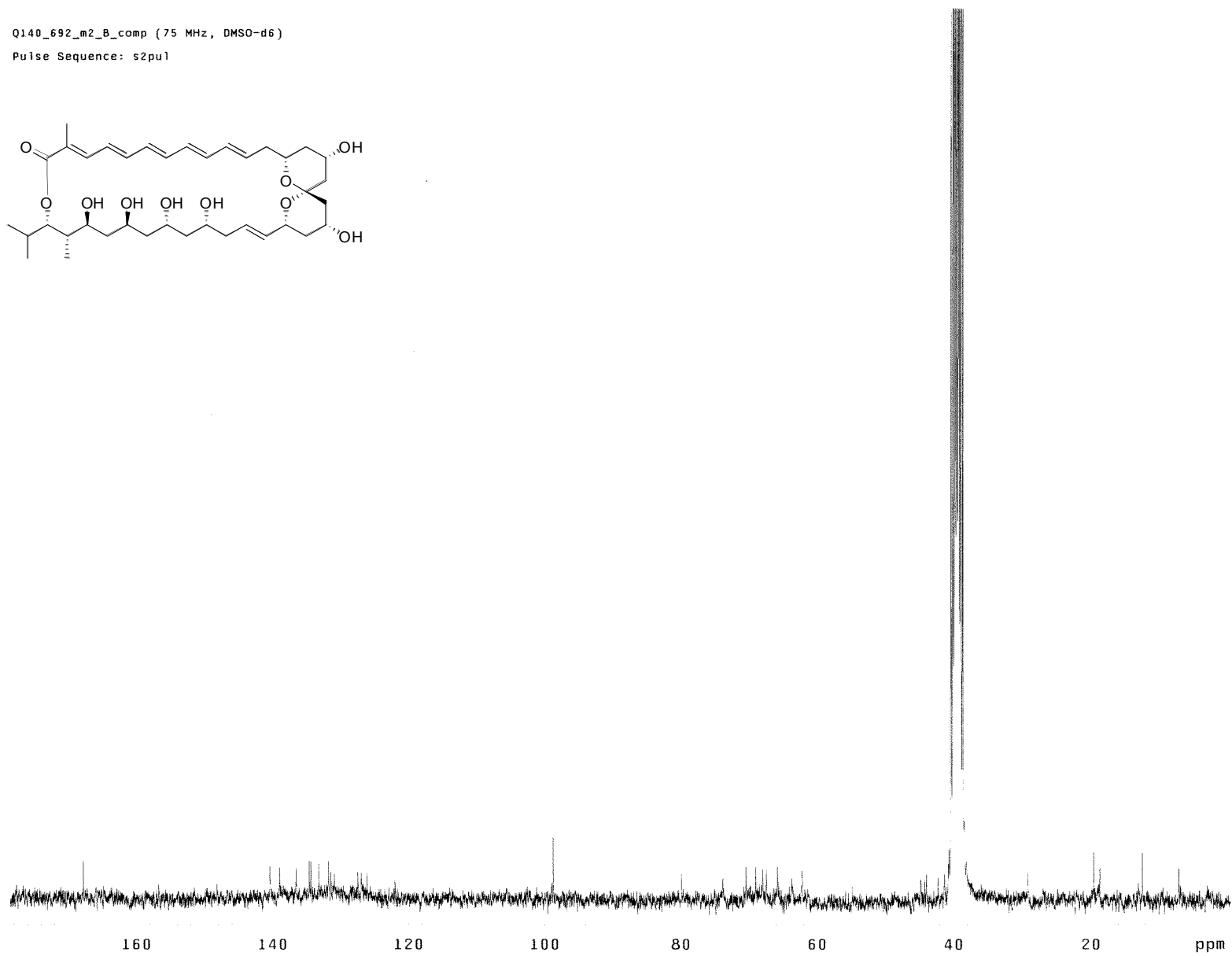
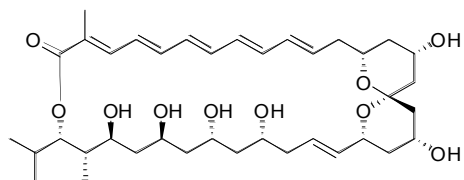


Figure S8. ¹³C NMR spectrum of **1** (75 MHz, DMSO-*d*₆)

Q140-962-m2-B-homo2dj (500 MHz, DMSO-d₆)
Pulse Sequence: homo2dj

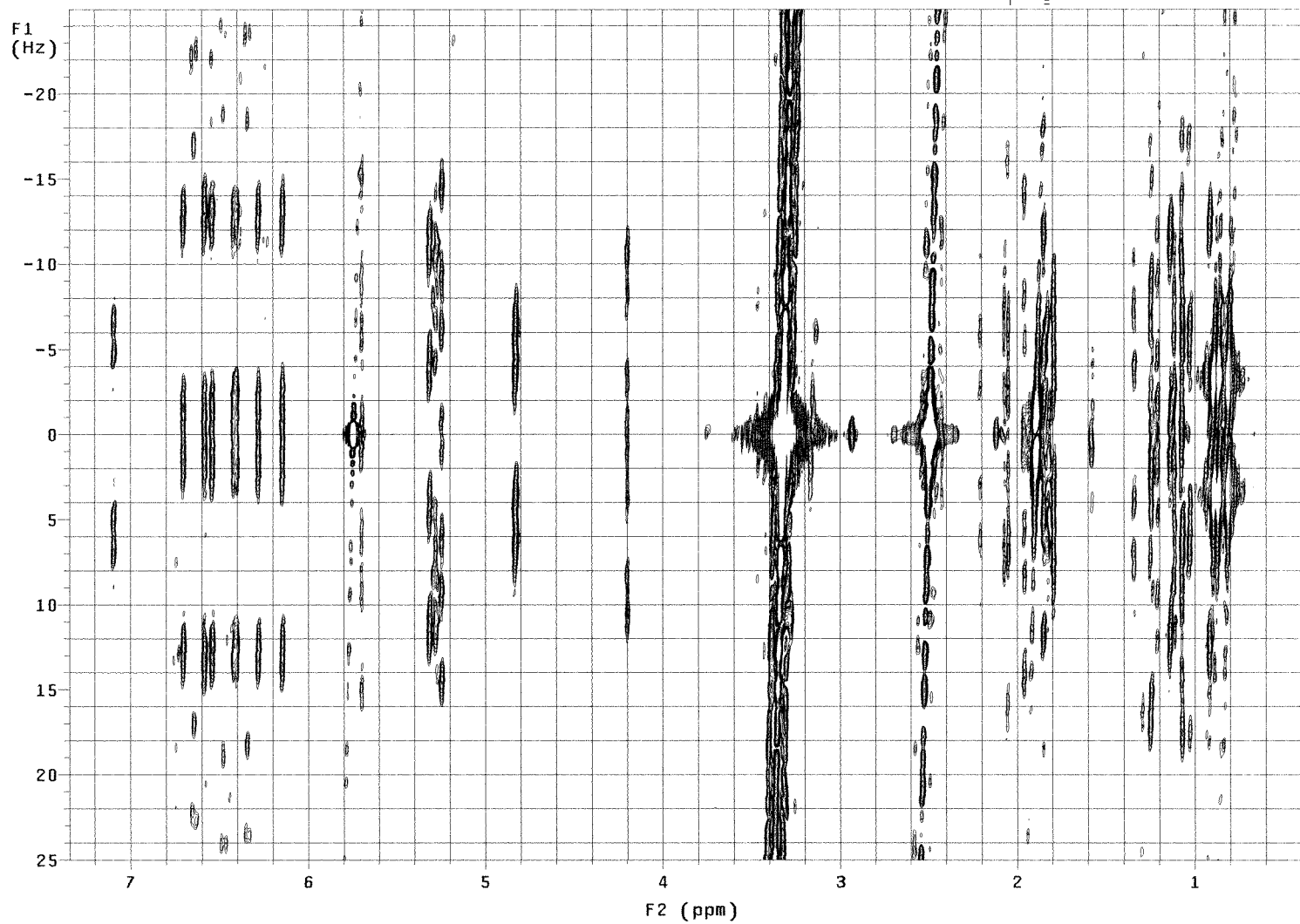
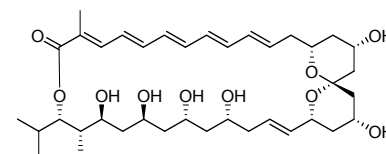


Figure S9. Homo 2D *J*-resolved ¹H NMR spectrum of **1** (500 MHz, DMSO-*d*₆)

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

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_692_m2_B_25Jun2005

Pulse Sequence: gCOSY

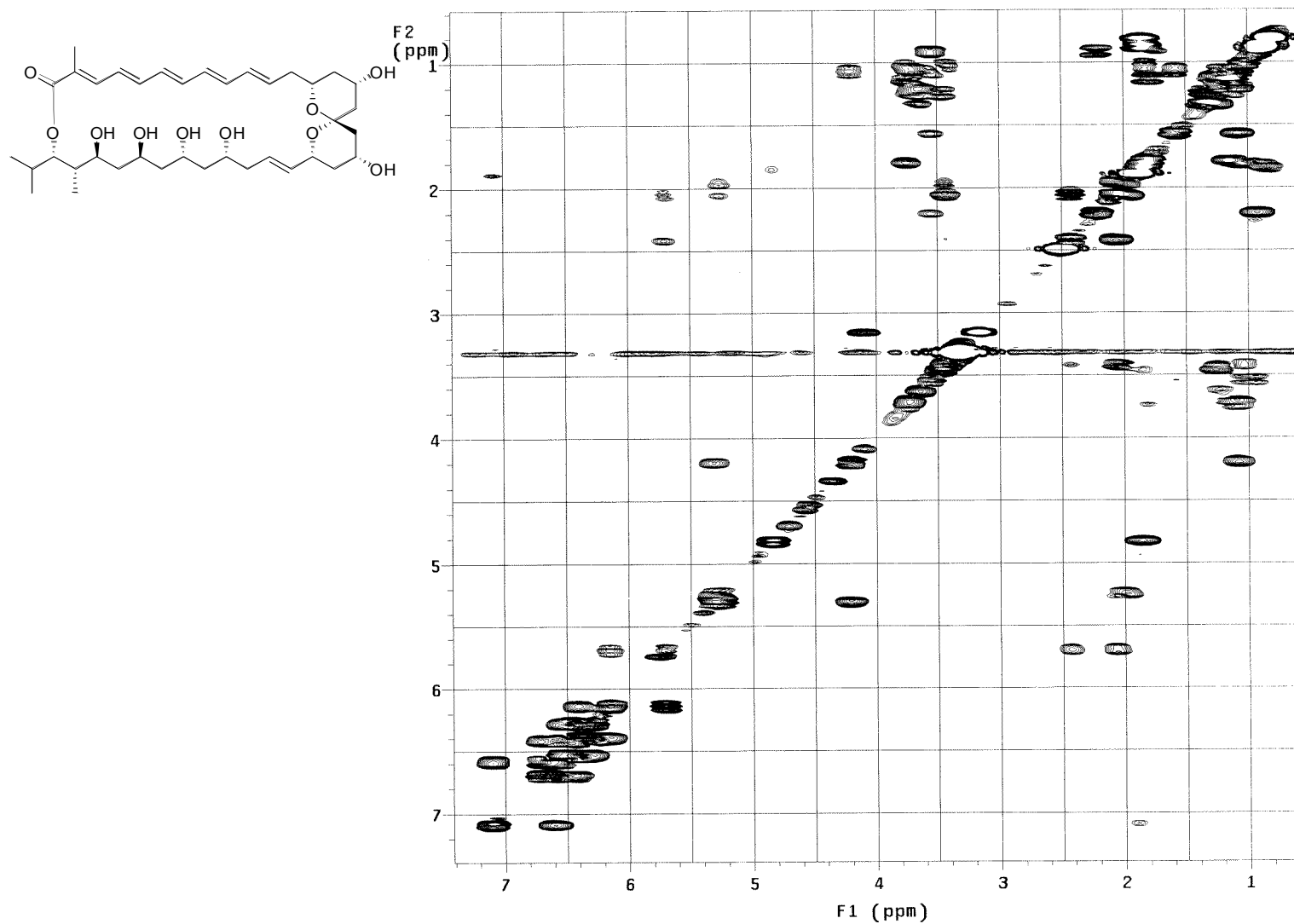


Figure S10. ¹H-¹H COSY spectrum of **1** (500 MHz, DMSO-*d*₆)

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

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_692_m2_B_1H_HMQC_25Jun2005
File: gHMQC

Pulse Sequence: gHMQC

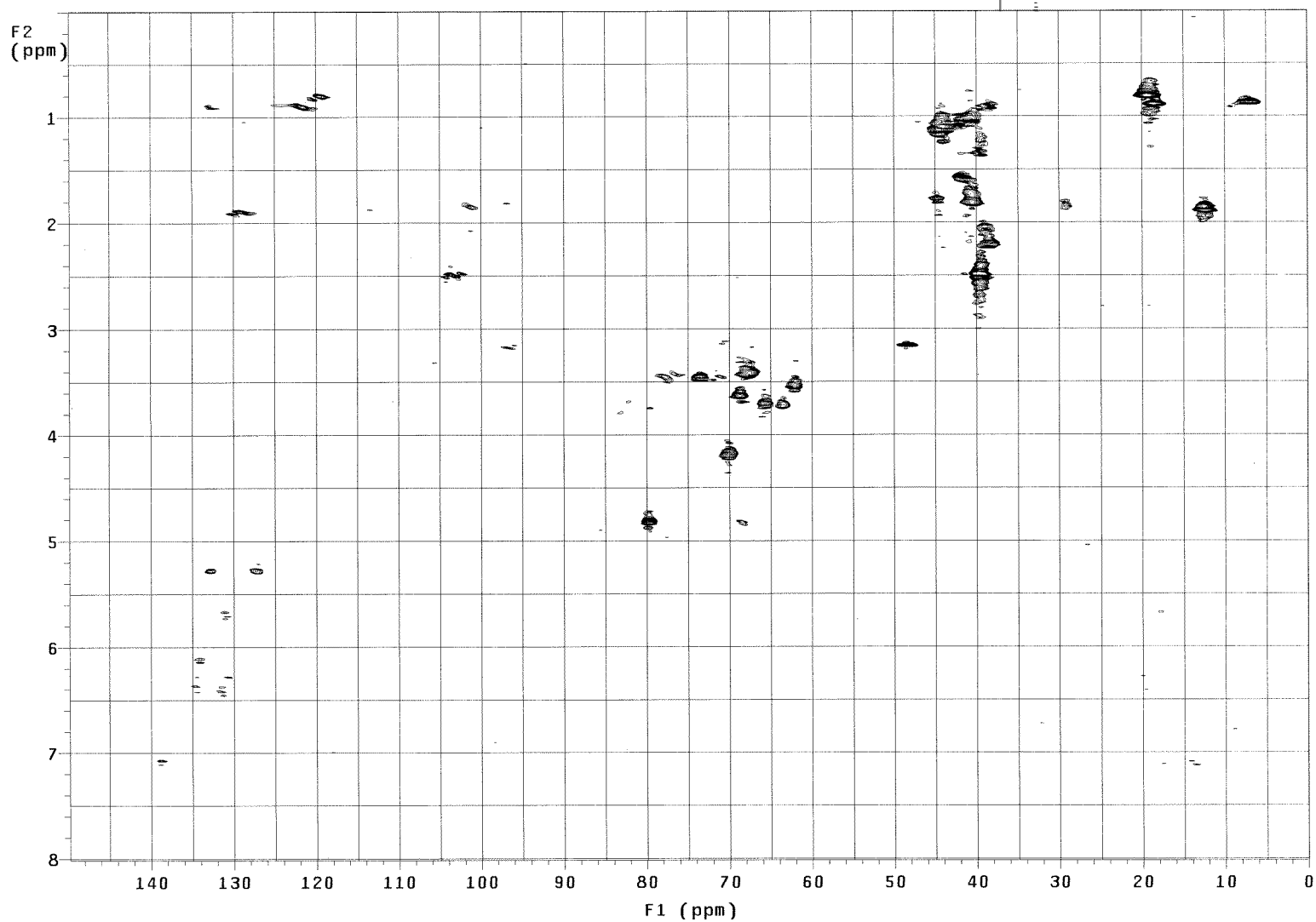
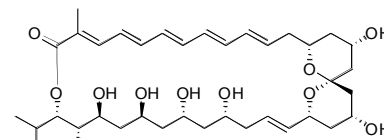


Figure S11. gHMQC spectrum of **1** (500 MHz, DMSO- d_6)

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

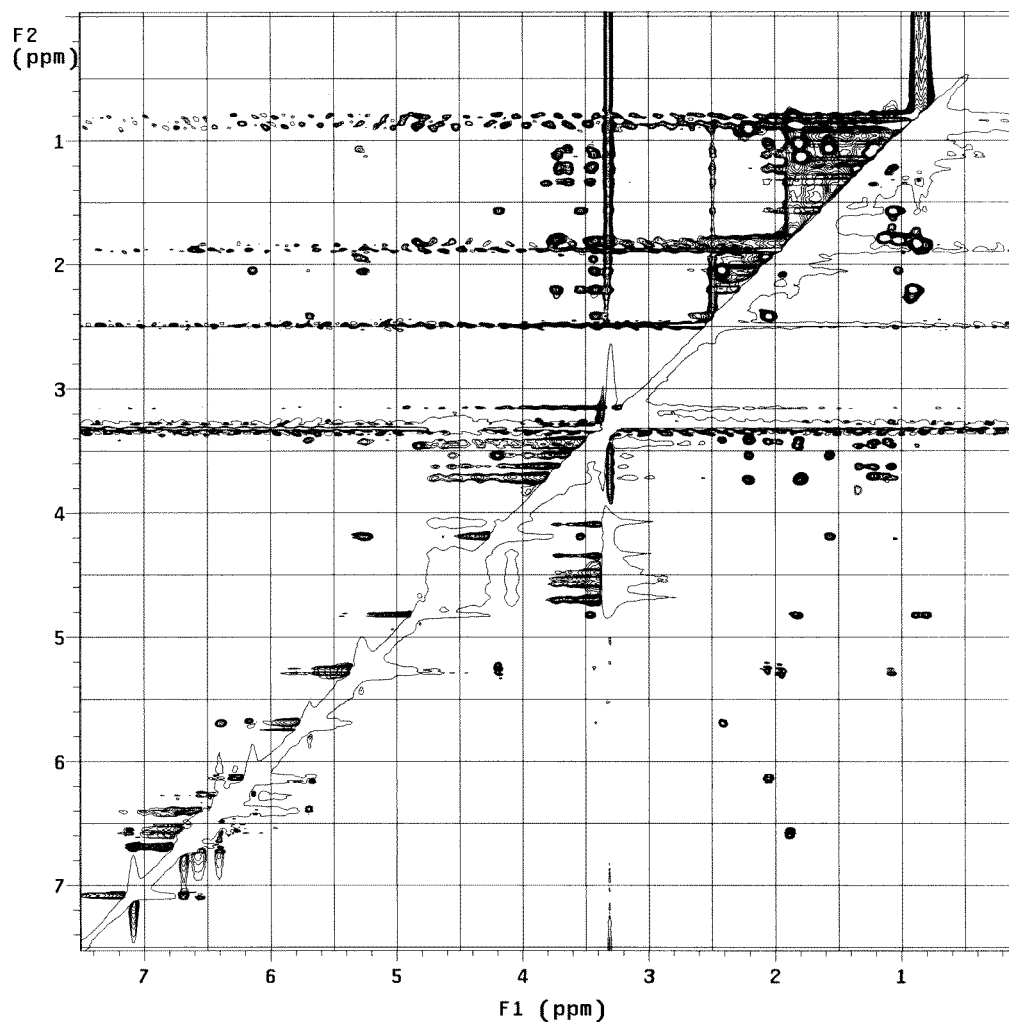
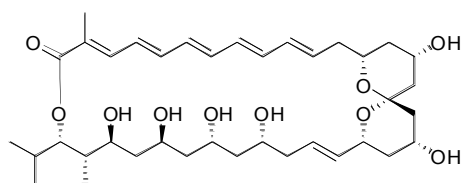
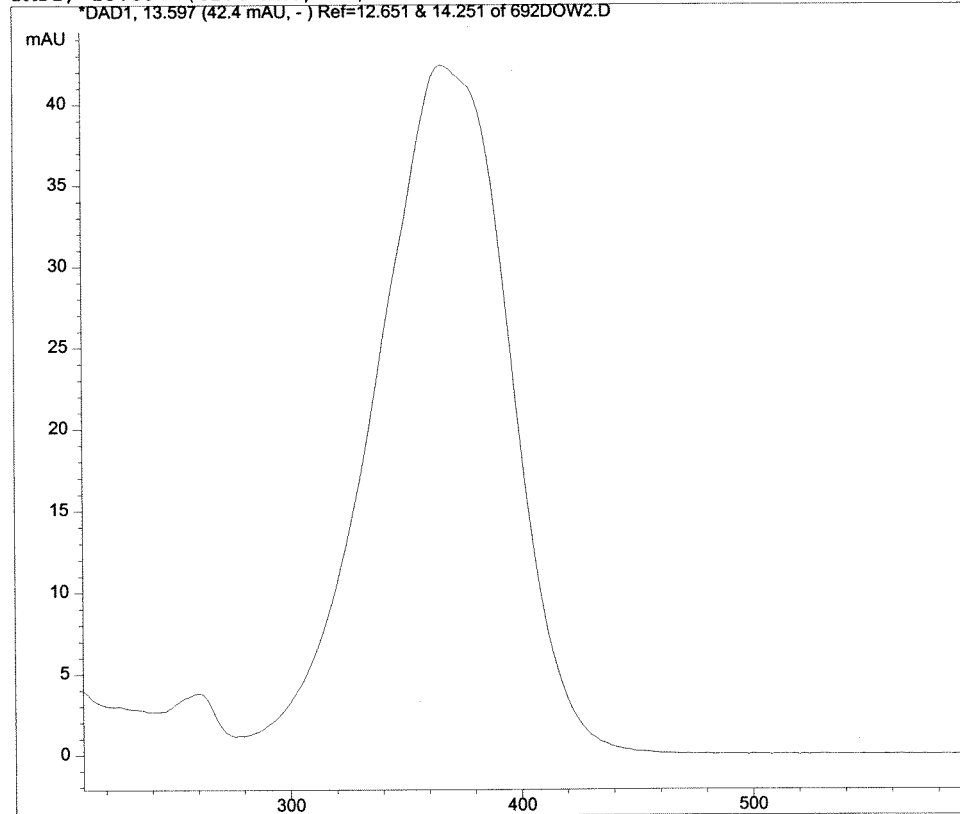


Figure S13. ROESY spectrum of 1 (500 MHz, DMSO-*d*₆)

DAD1, 13.597 (42.4 mAU, -) Ref=12.651 & 14.251 of 692DOW2.D



MS Spectrum

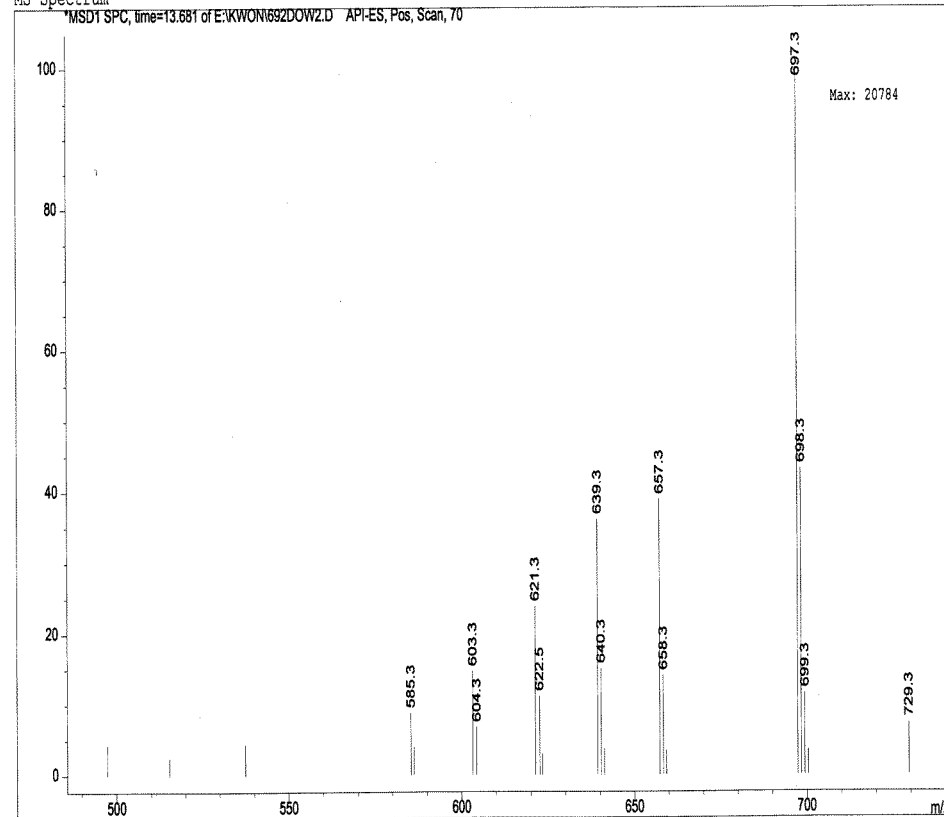


Figure S14. UV and ESI-MS spectra derived from HPLC-DAD-MSD (MeCN-H₂O) of compound 1.

Q140_692A_Dowex_m2b (500 MHz, DMSO-d6)

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

Sample directory:

File: PROTON

Pulse Sequence: s2pu1

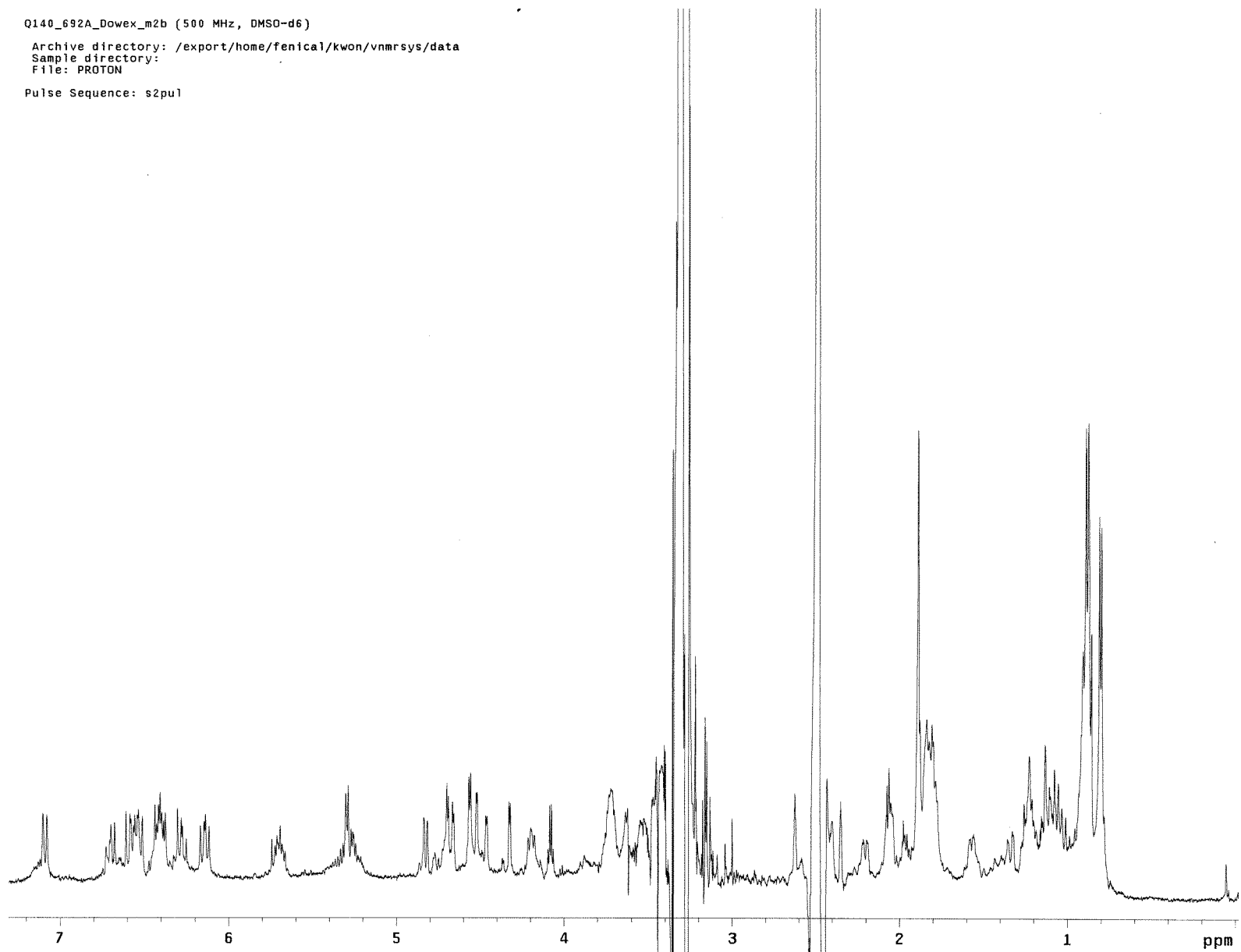


Figure S15. ¹H NMR spectrum of compound 1 (500 MHz, DMSO-*d*₆)

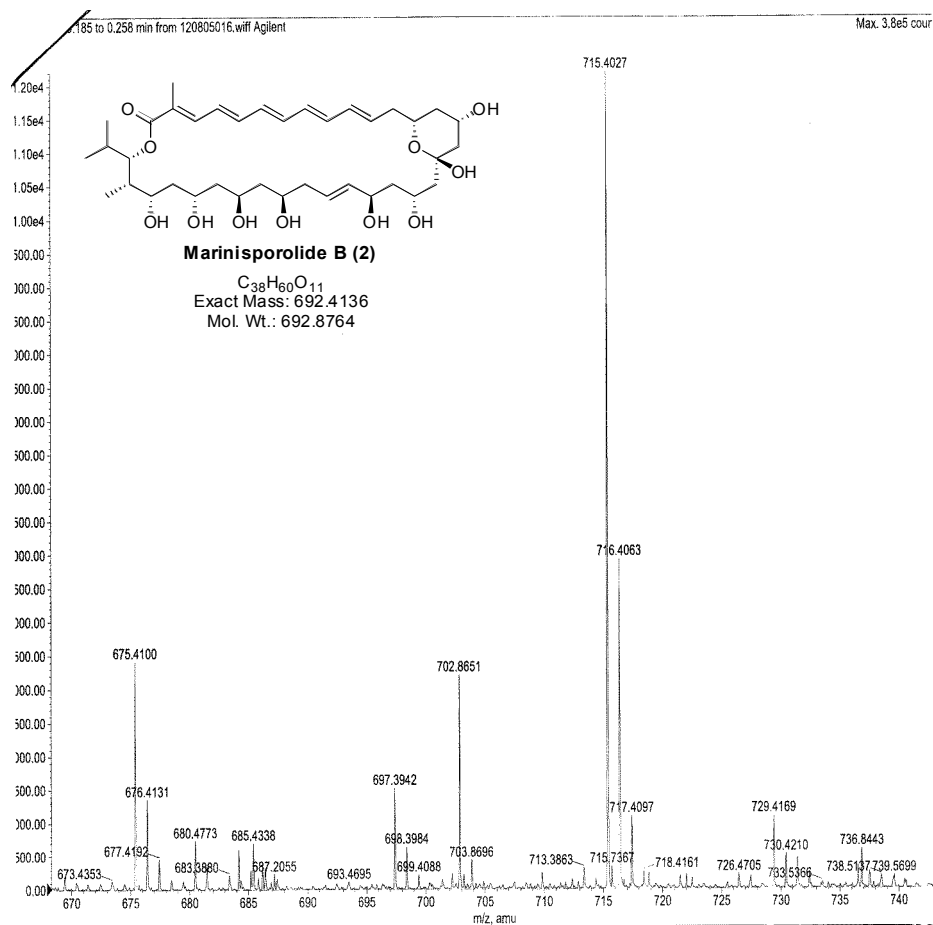
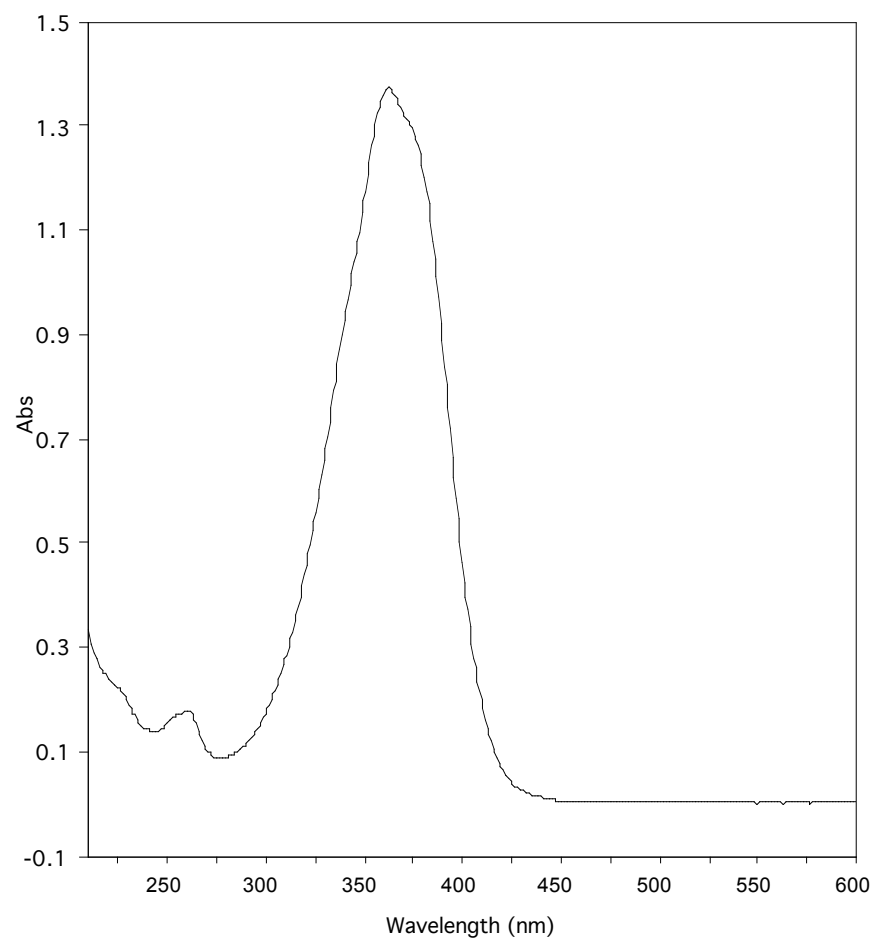


Figure S16. UV (MeOH) and HR-ESI-TOF MS spectra of marinisporolide B (2)

Q140_692_m1_8_comp (500 MHz, DMSO-d6)
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Sample directory:
File: PROTON
Pulse Sequence: s2pu1

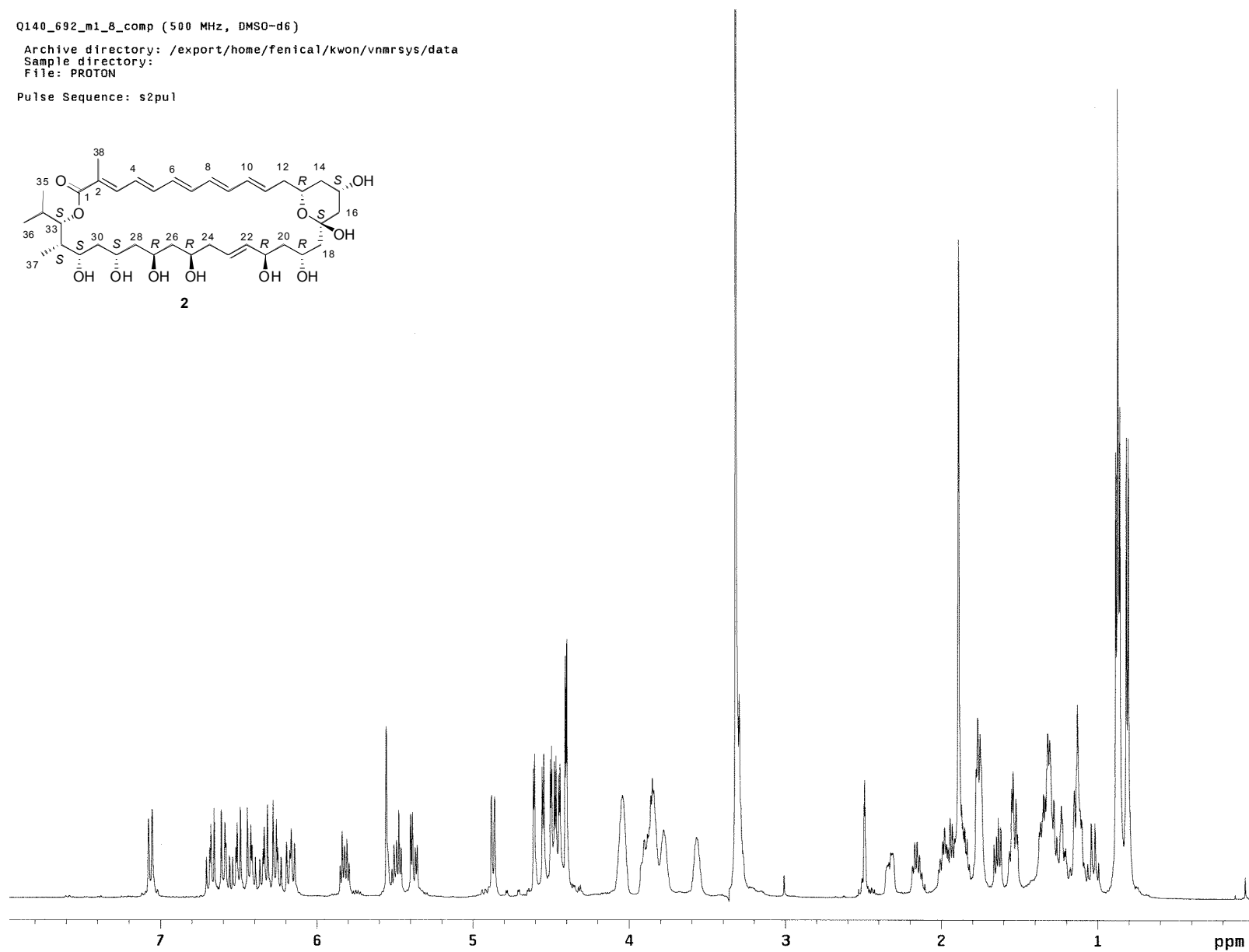
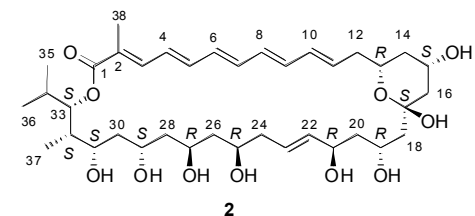


Figure S17. ^1H NMR spectrum of marinisporolide B (**2**) (500 MHz, DMSO- d_6)

Q140_692_m1_8_comp (75 MHz, DMSO-d₆)

Pulse Sequence: s2pu1

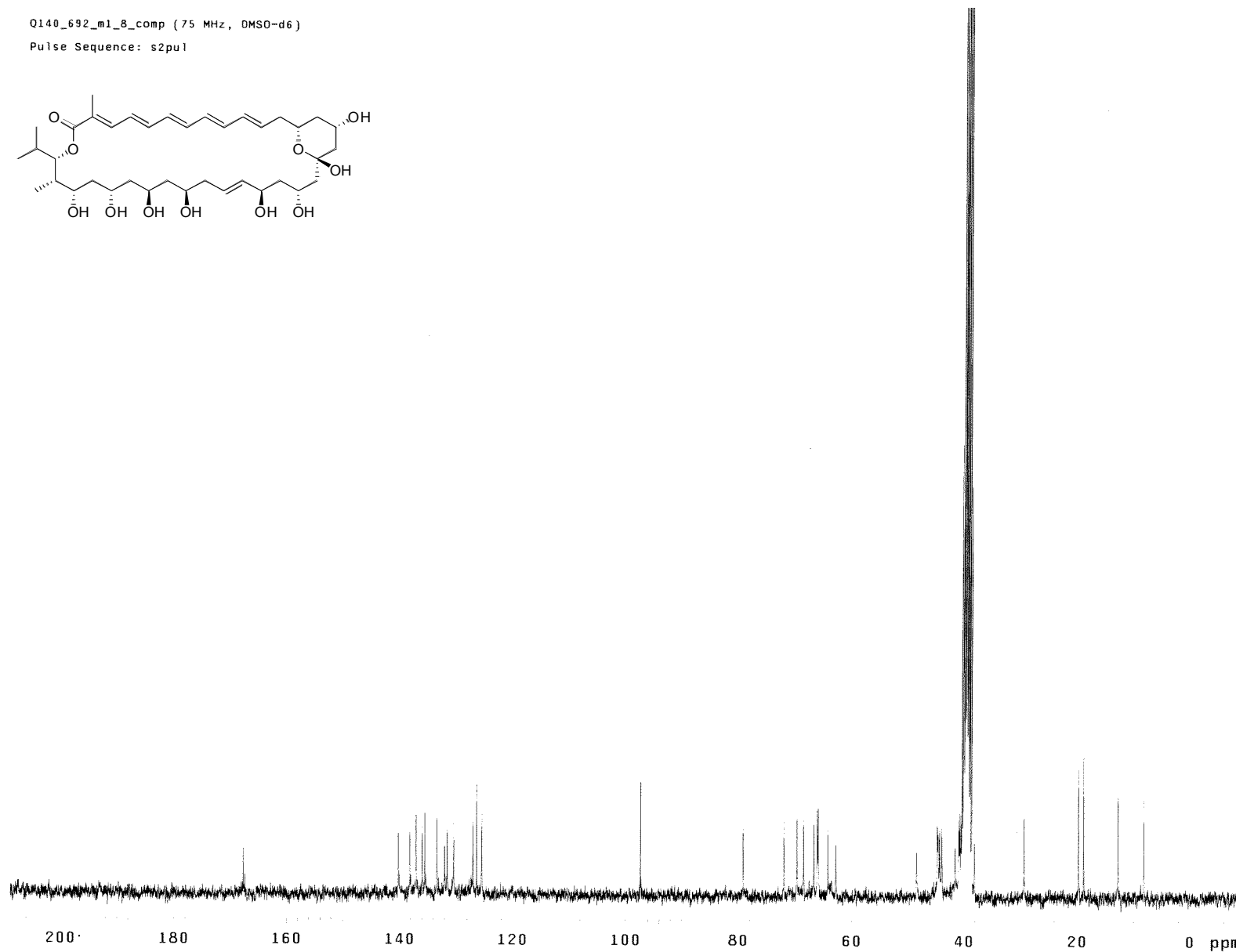
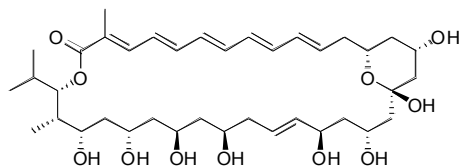


Figure S18. ¹³C NMR spectrum of **2** (75 MHz, DMSO-*d*₆).

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: gCOSY

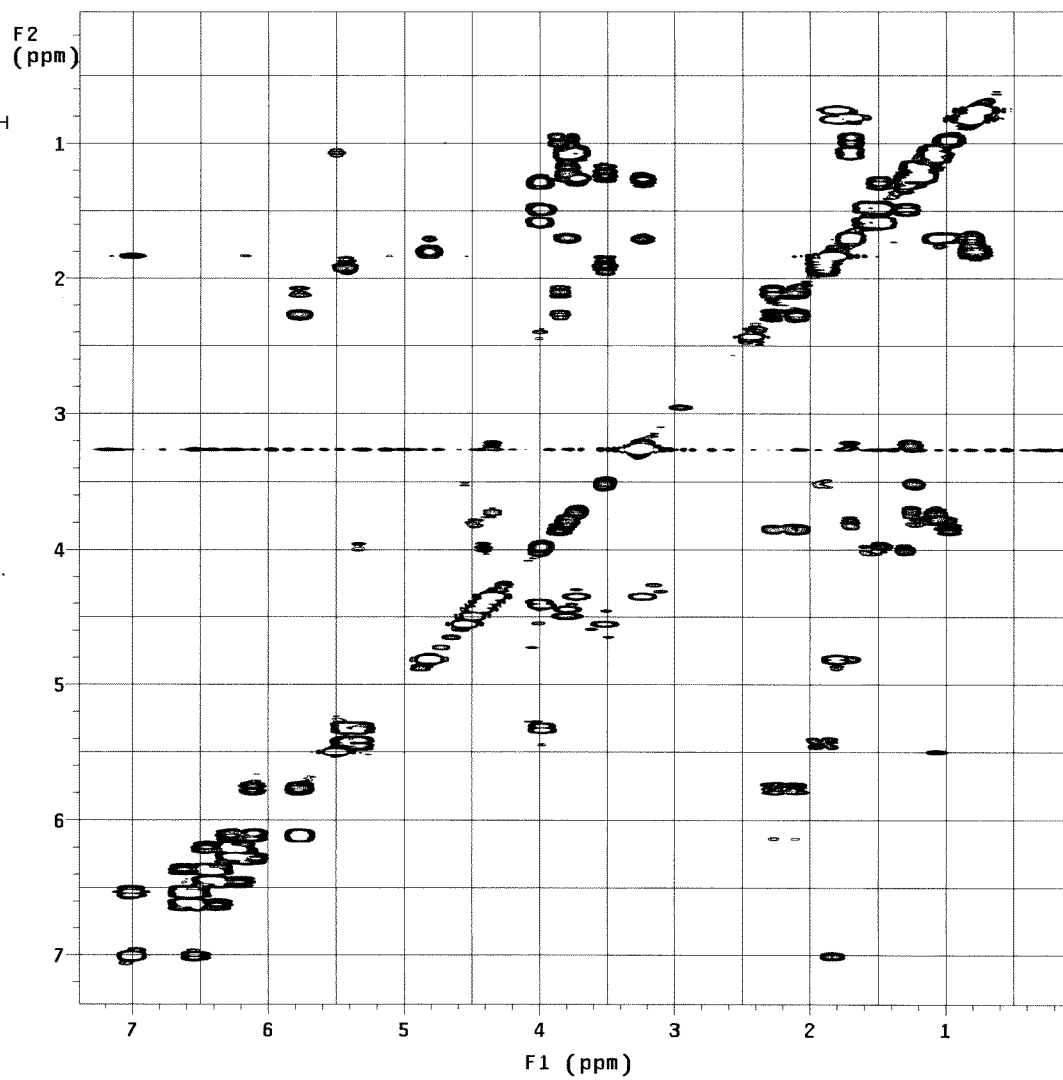
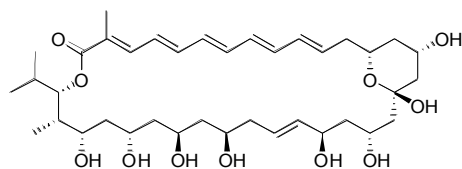


Figure S19. ^1H - ^1H COSY spectrum of **2** (500 MHz, DMSO- d_6)

Q140-692-m1-8 (500 MHz, DMSO-d₆)

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Sample directory: Q140_692_m1_8_comp_500_DMSO_07Jul2005

Pulse Sequence: gHMQC

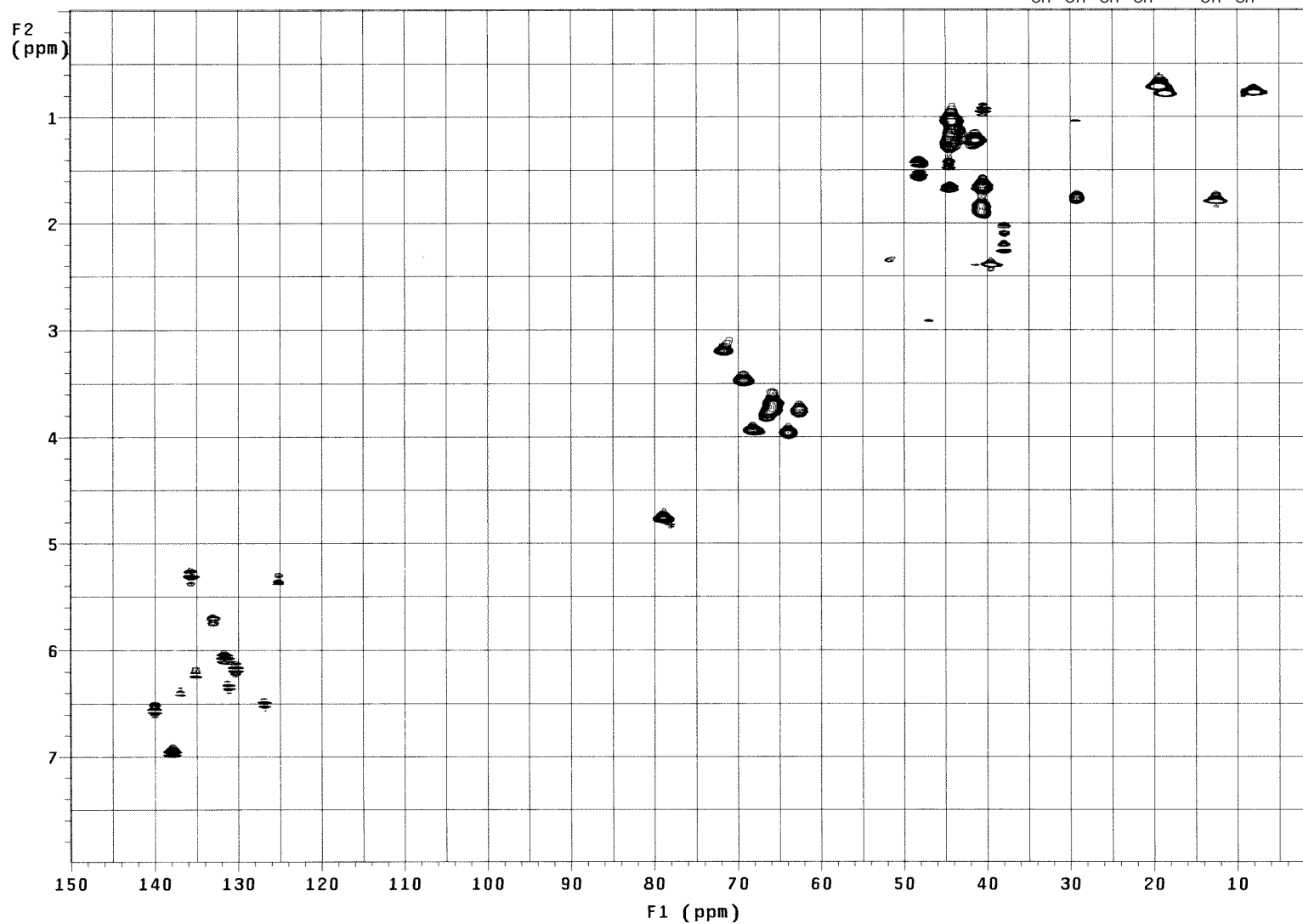
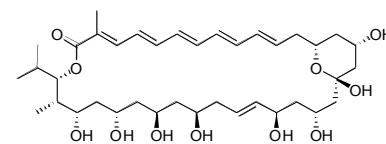


Figure S20. gHMQC spectrum of **2** (500 MHz, DMSO-*d*₆)

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
INNOVA-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

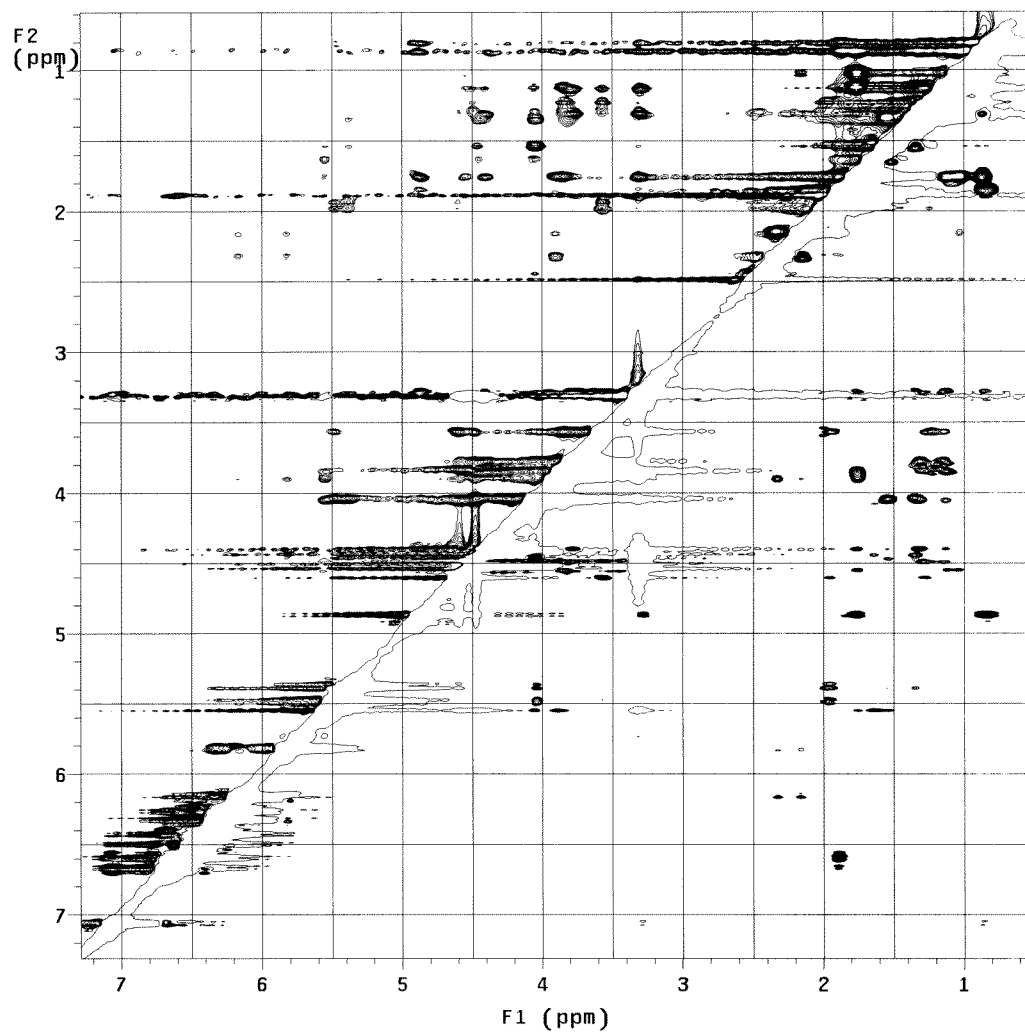
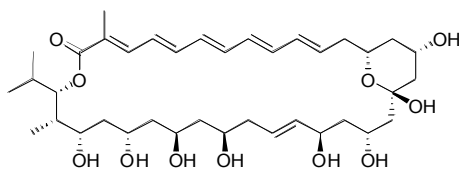


Figure S22. ROESY spectrum of **2** (500 MHz, DMSO-*d*₆)

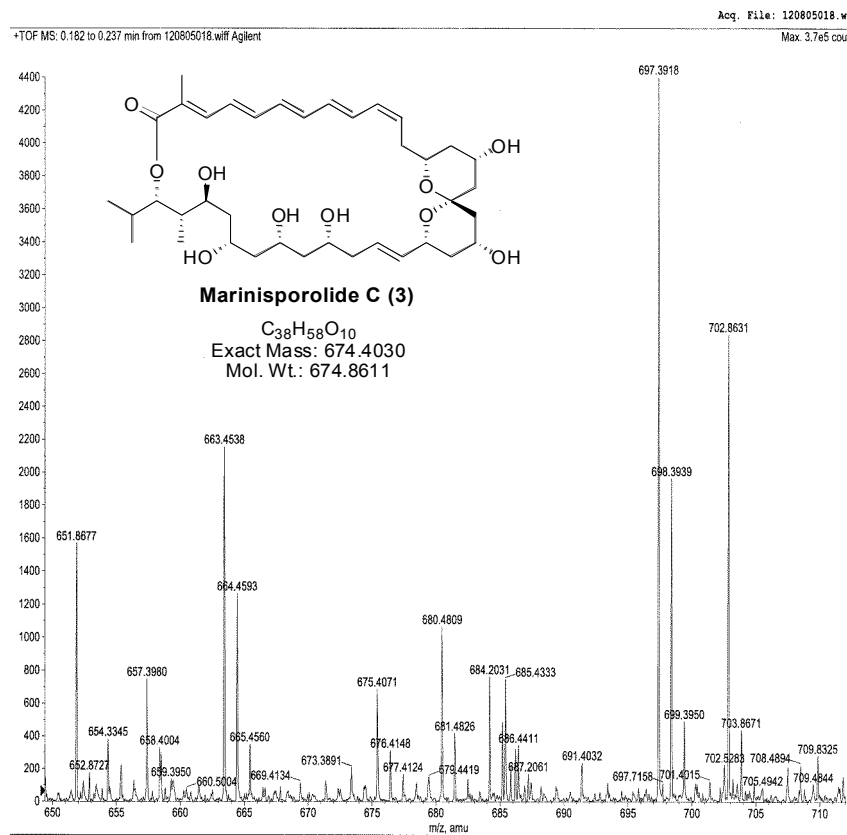
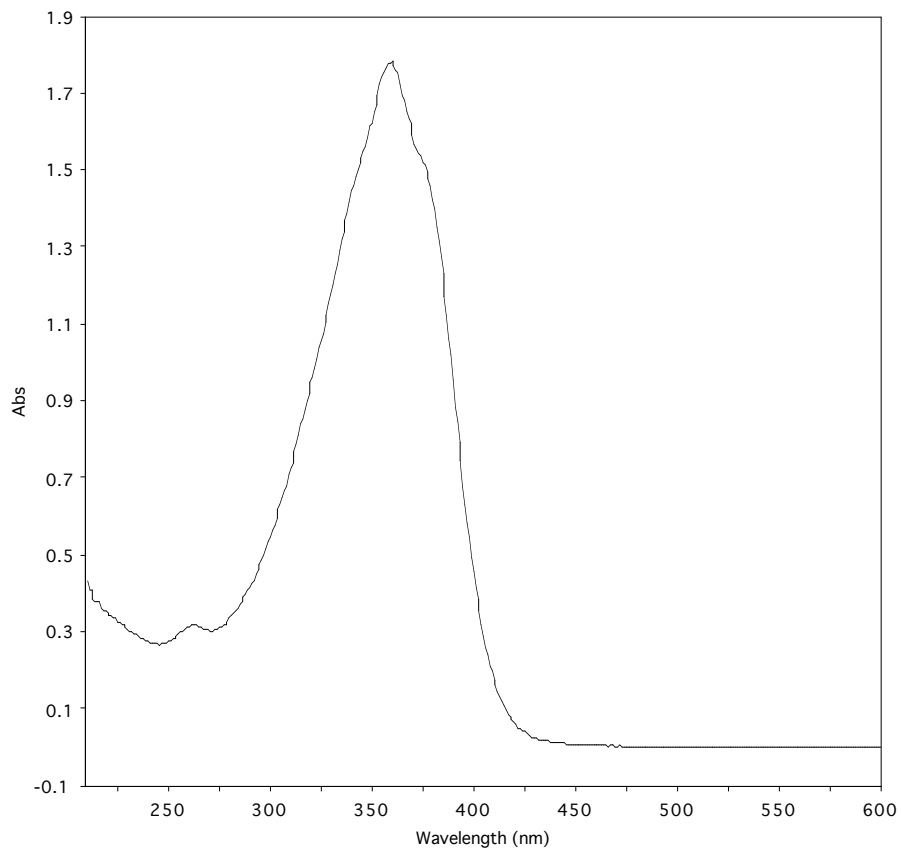


Figure S23. UV (MeOH) and HR-ESI-TOF MS spectra of marinisporolide C (3).

Q140_674_50_1_4m (500 MHz, DMSO-d
6)

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_674_50_1_4m_DMSO_27Oct2005

Pulse Sequence: s2pul

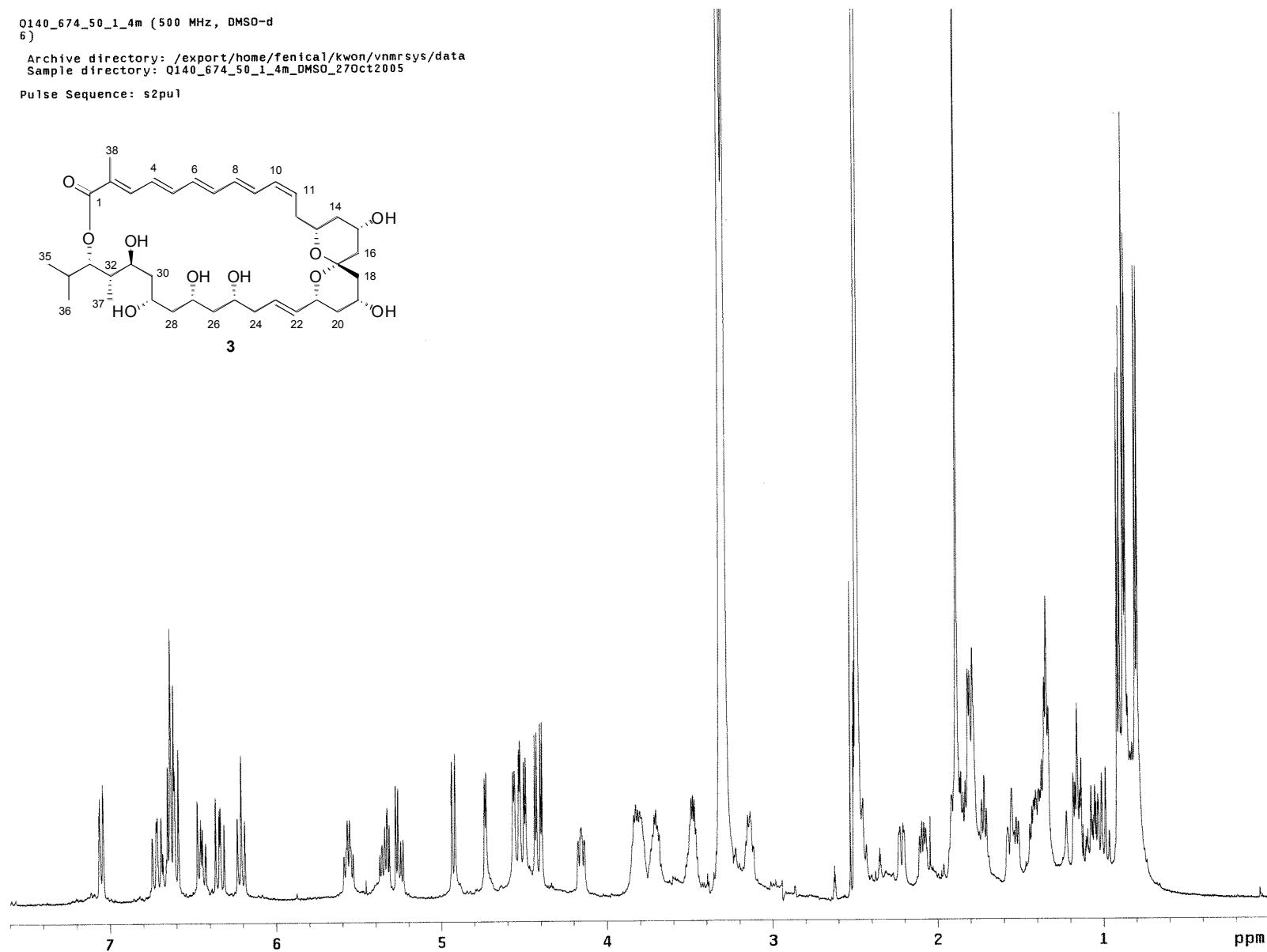
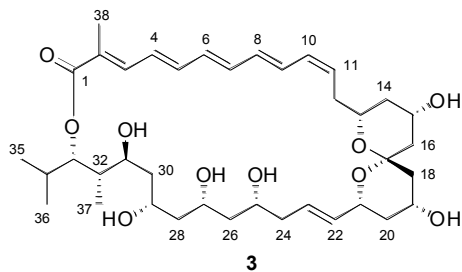


Figure S24. ^1H NMR spectrum of marinisporolide C (**3**) (500 MHz, $\text{DMSO-}d_6$).

Q140_674_50_1_4m (75 MHz, DMSO-d6)

Pulse Sequence: s2pul

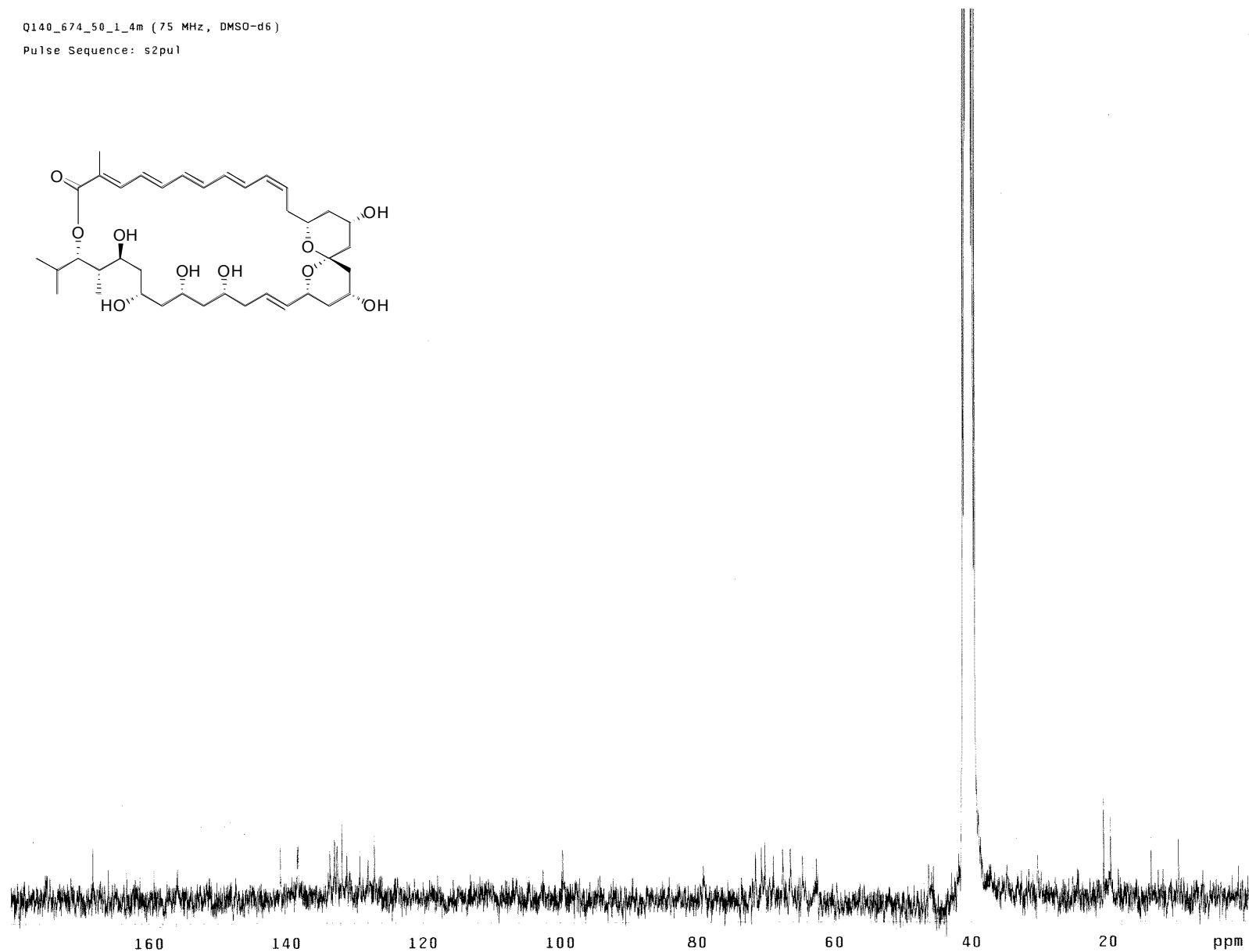
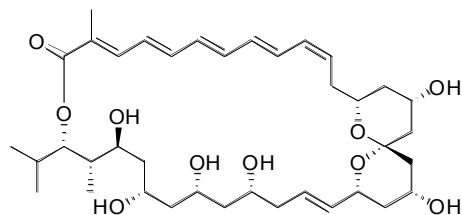


Figure S25. ^{13}C NMR spectrum of **3** (75 MHz, DMSO- d_6)

CN0140-50%-major-4m (500 MHz, pyridine-d5) marino M-1
Archive directory: /export/home/fenical/dongchan/vnmrsys/data
Sample directory: 140_50_4m_500_pyridine_27Apr2004
Pulse Sequence: s2pu1

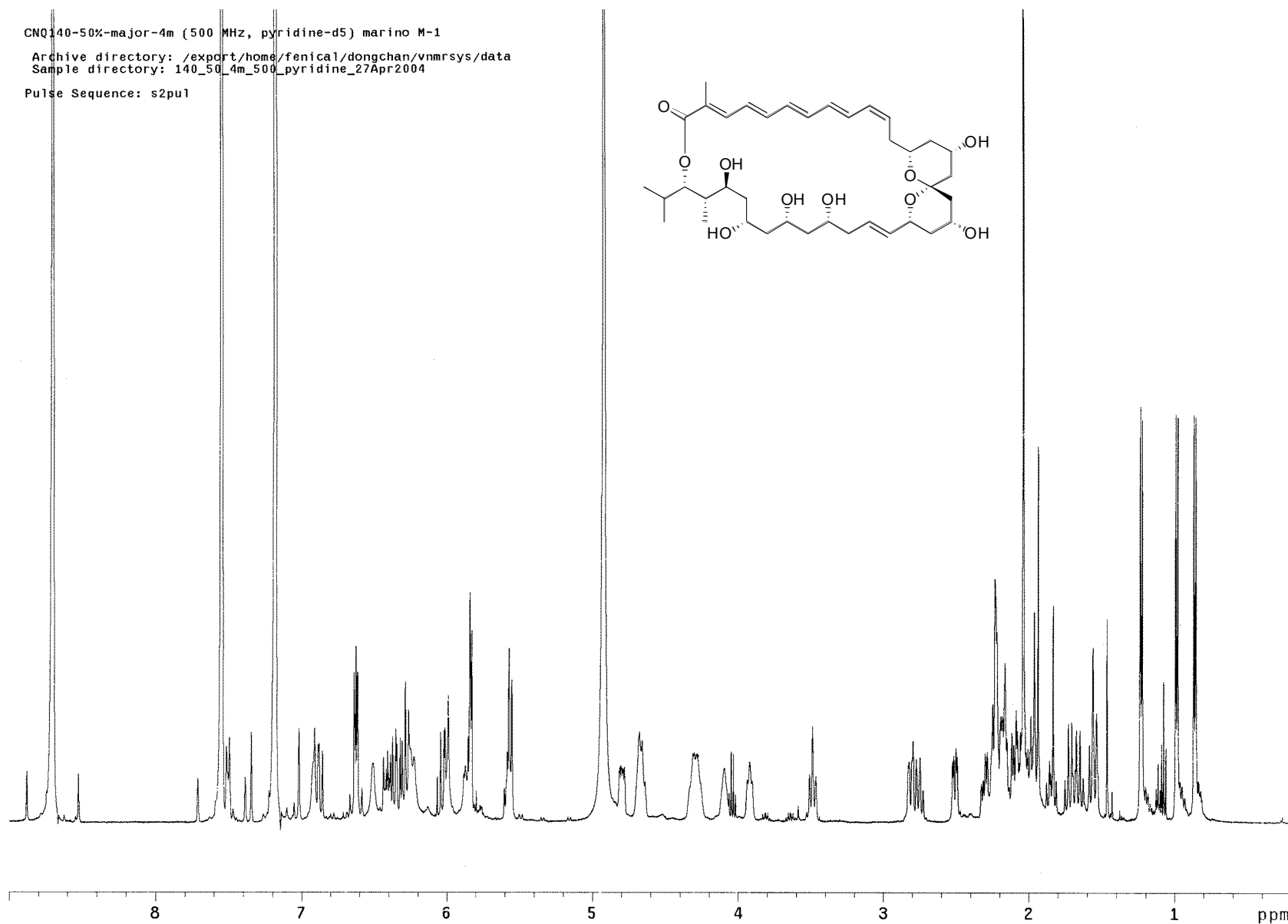
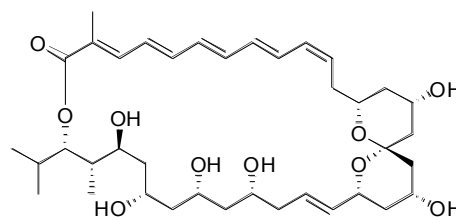


Figure S26. ¹H NMR spectrum of **3** (500 MHz, pyridine-*d*₅).

140-50%-major-4m-13C (125 MHz, pyridine-d5)
Archive directory: /export/home/fenice1/dongchan/vnmrsys/data
Sample directory: 140_50_4m_500_pyridine_27Apr2014
File: CARBON
Pulse Sequence: s2pu1

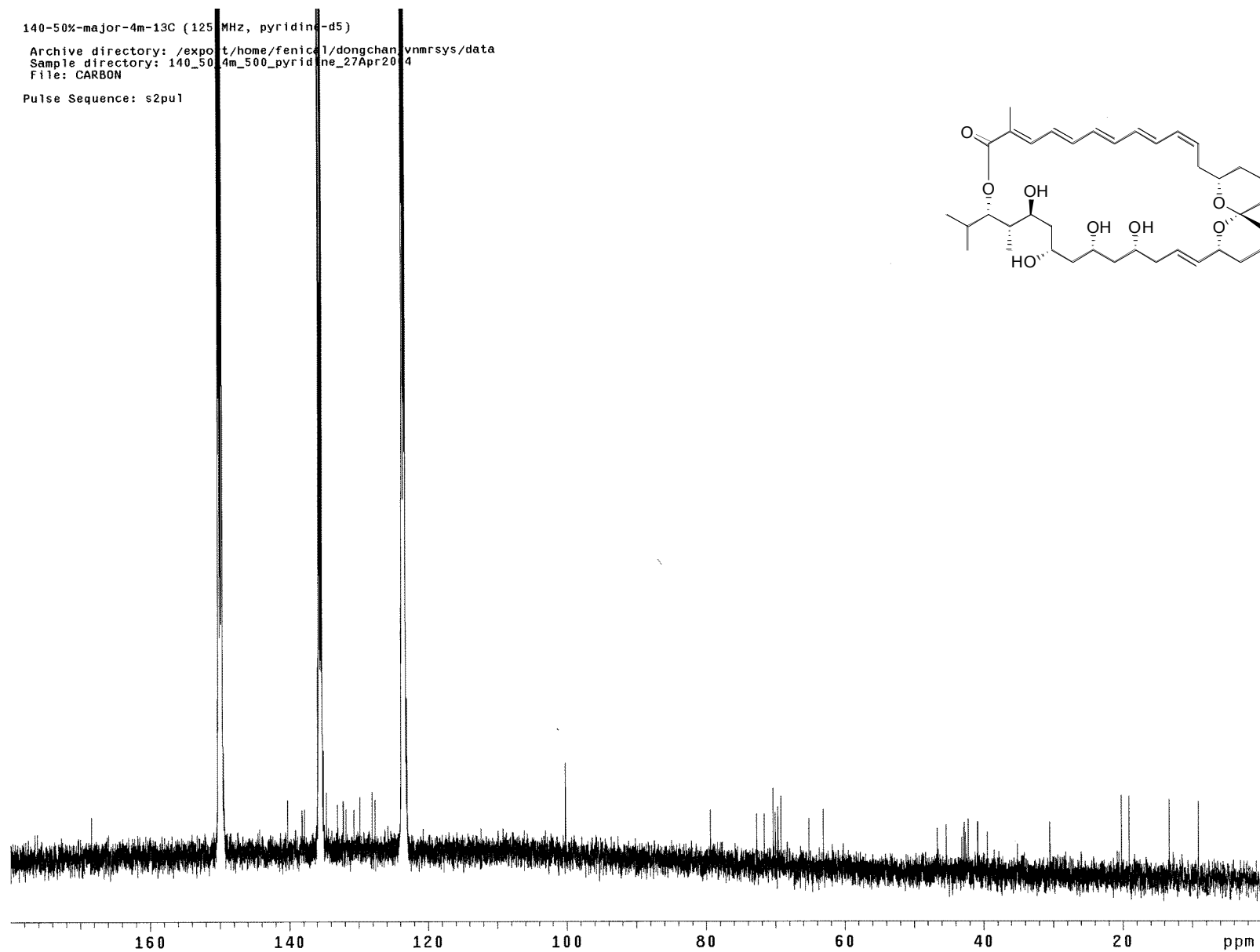


Figure S27. ¹³C NMR spectrum of 3 (125 MHz, pyridine-*d*₅).

Q140-A1-50%-1-4m-hom2dj (500 MHz, pyridine-d₅)
Pulse Sequence: hom2dj

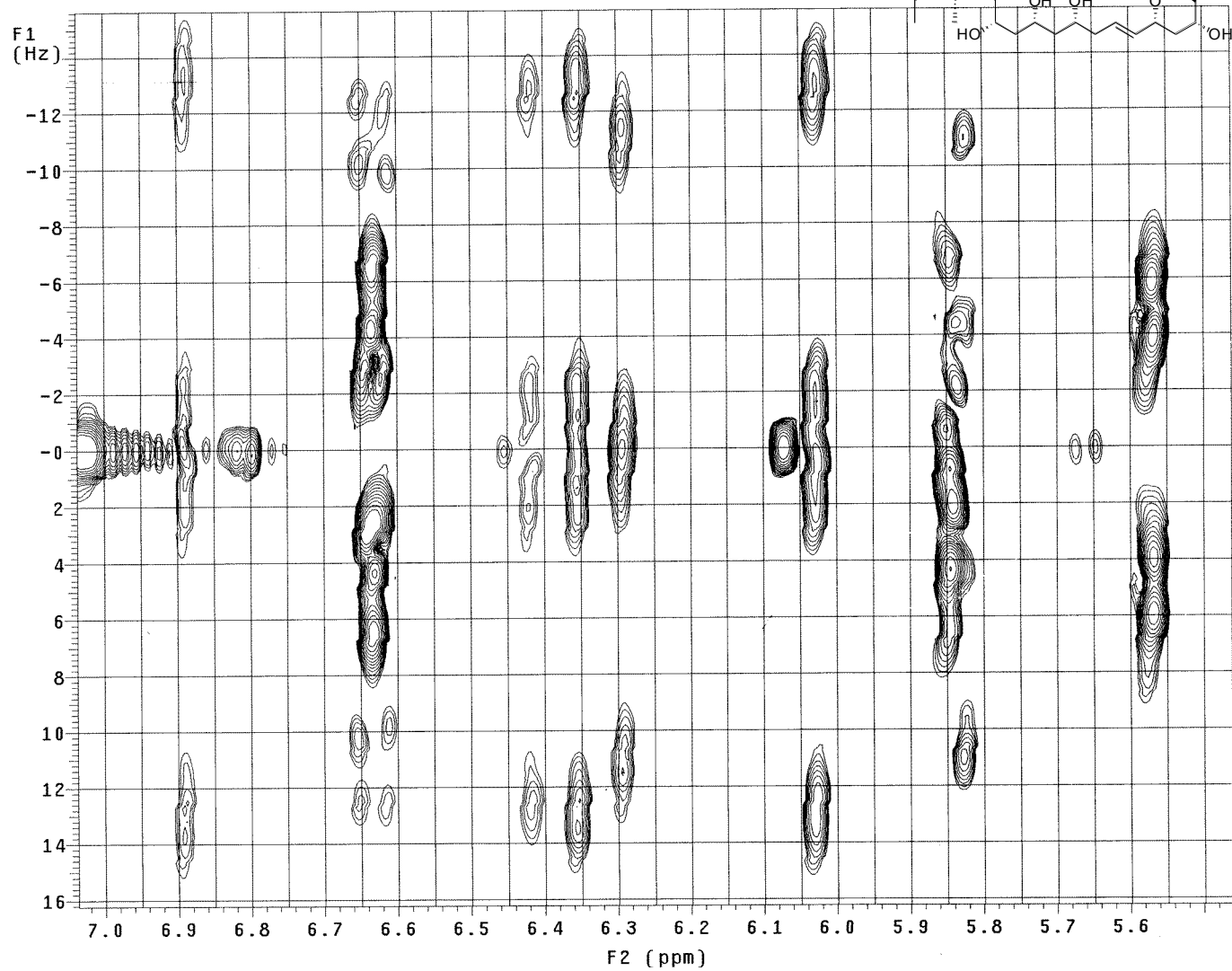


Figure S28. Expanded homo 2D J -resolved ^1H NMR spectrum of **3** (500 MHz, pyridine- d_5).

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

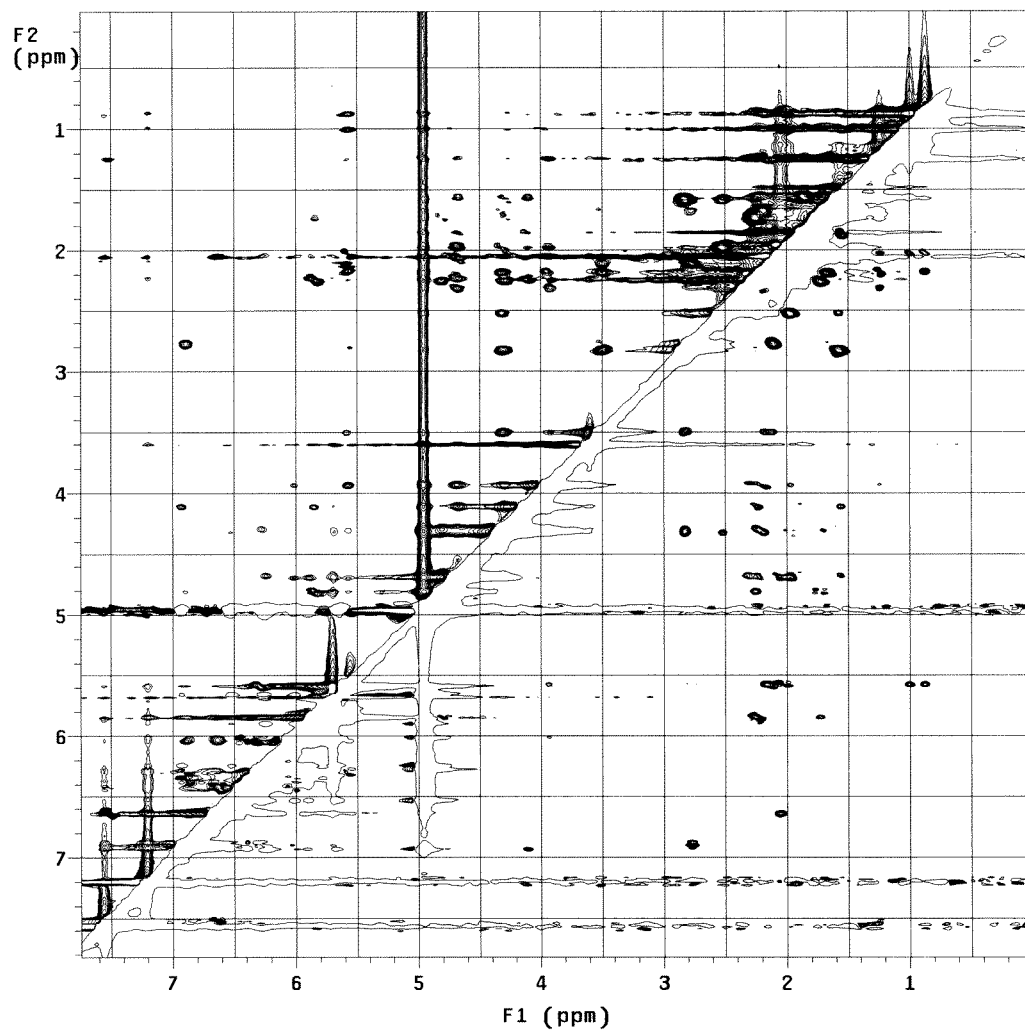
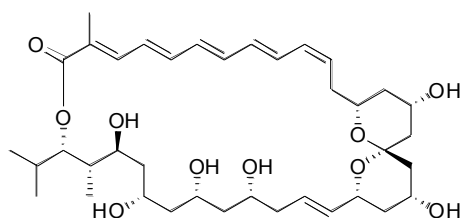


Figure S29. ROESY spectrum of 3 (500 MHz, pyridine- d_5)

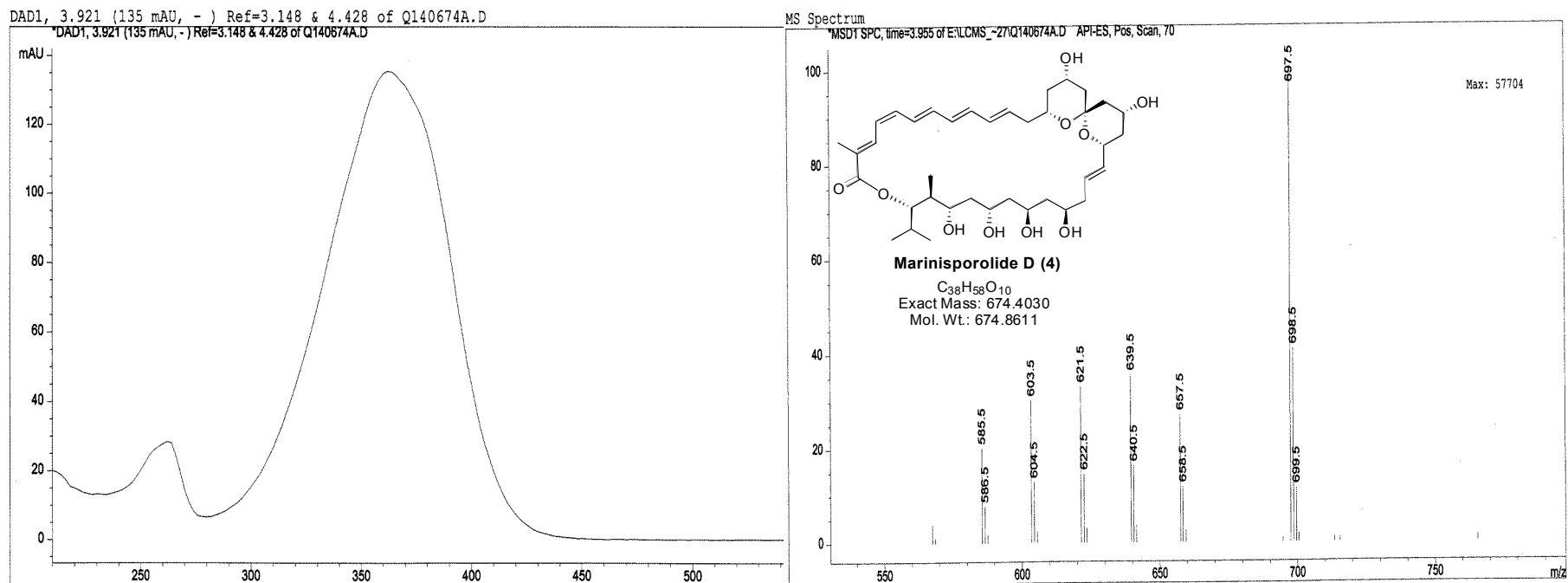


Figure S30. UV and ESI-MS spectra derived from HPLC-DAD-MSD (MeCN-H₂O) of marinisporolide D (4)

Q140-50-1-1-5 (500 MHz, pyridine-d₅)

Pulse Sequence: s2pul

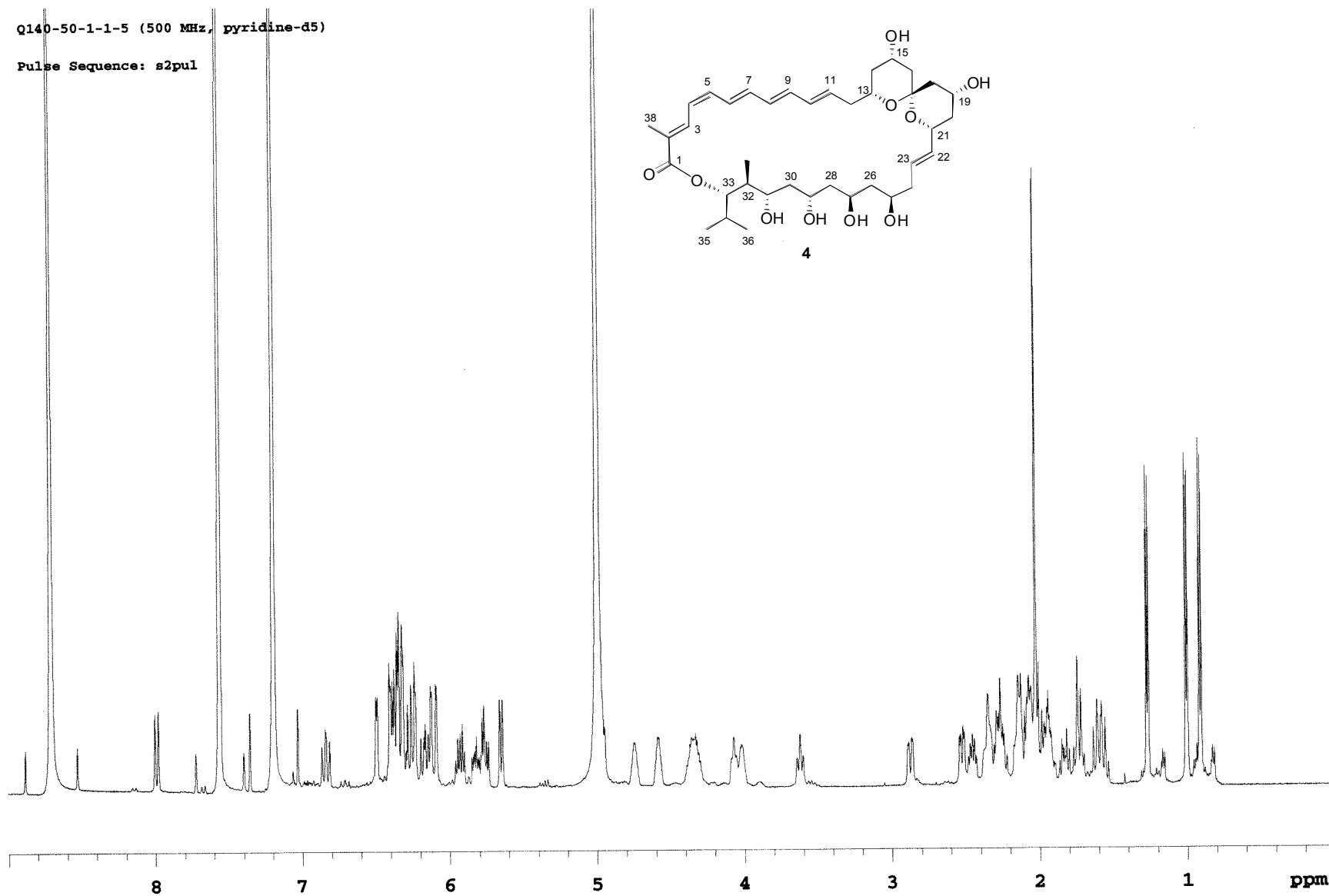
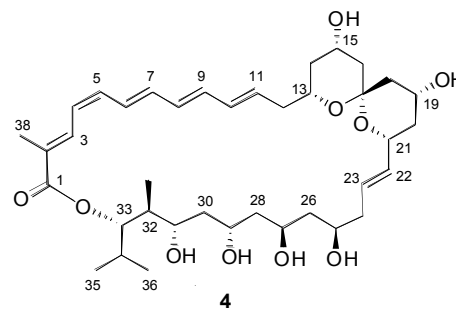


Figure S31. ¹H NMR spectrum of marinisporolide D (4) (500 MHz, pyridine-*d*₅)

Q140-A1-50%-1-1-5-13C (125 MHz, pyridine-*d*₅)
Archive directory: /export/home/fenical/kwon/vnmr/sys/data
Sample directory: Q140_50_1_1_5_13C_500M_BB_Pr_pyridine_30May2004
File: CARBON
Pulse Sequence: s2pu1

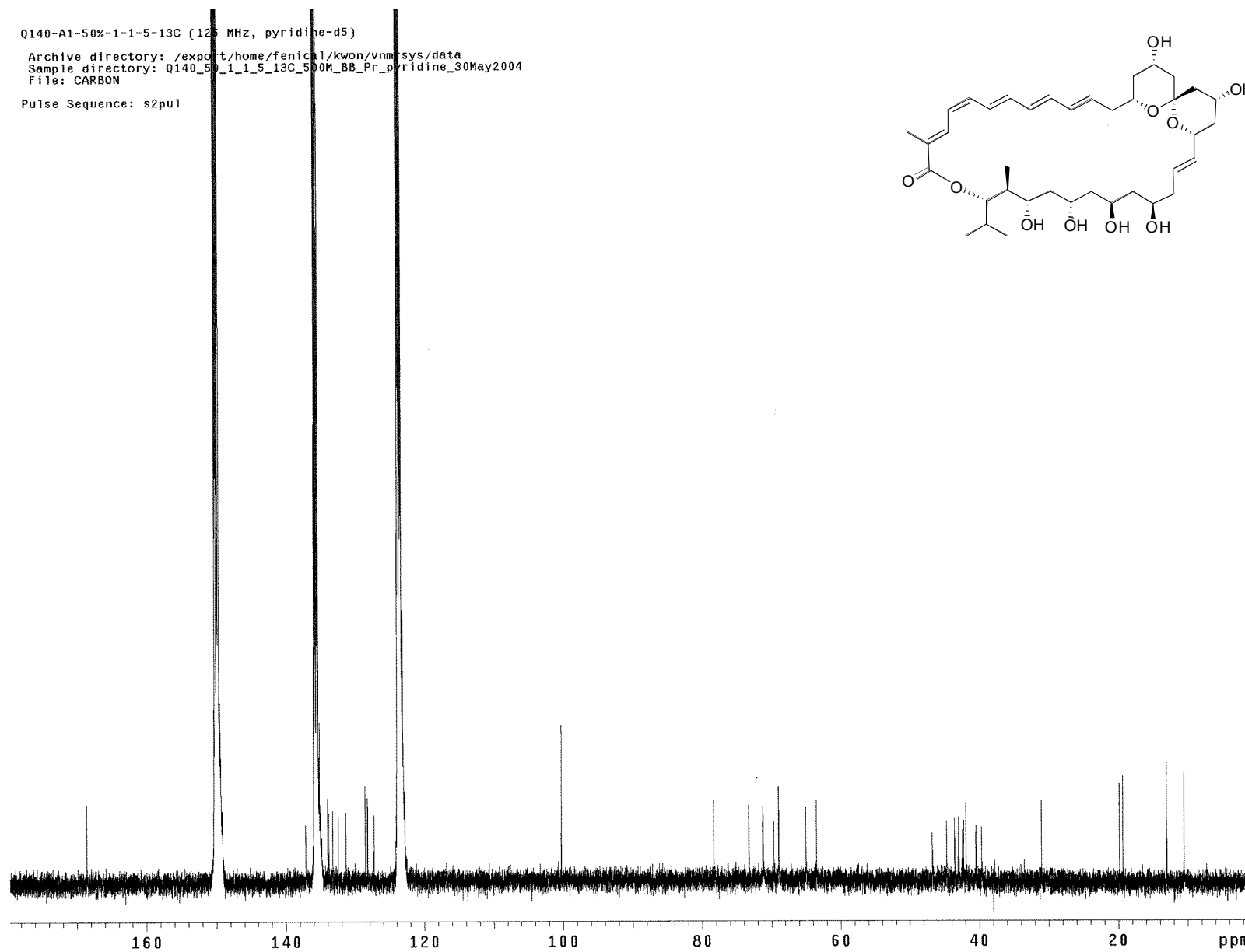
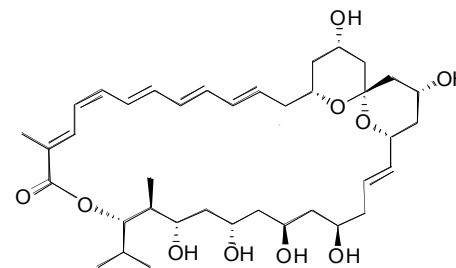


Figure S32. ¹³C NMR spectrum of **4** (125 MHz, pyridine-*d*₅)

Q140-A1-50%-1-1-5-hom2dj (500 MHz, pyridine-d5)

Pulse Sequence: hom2dj

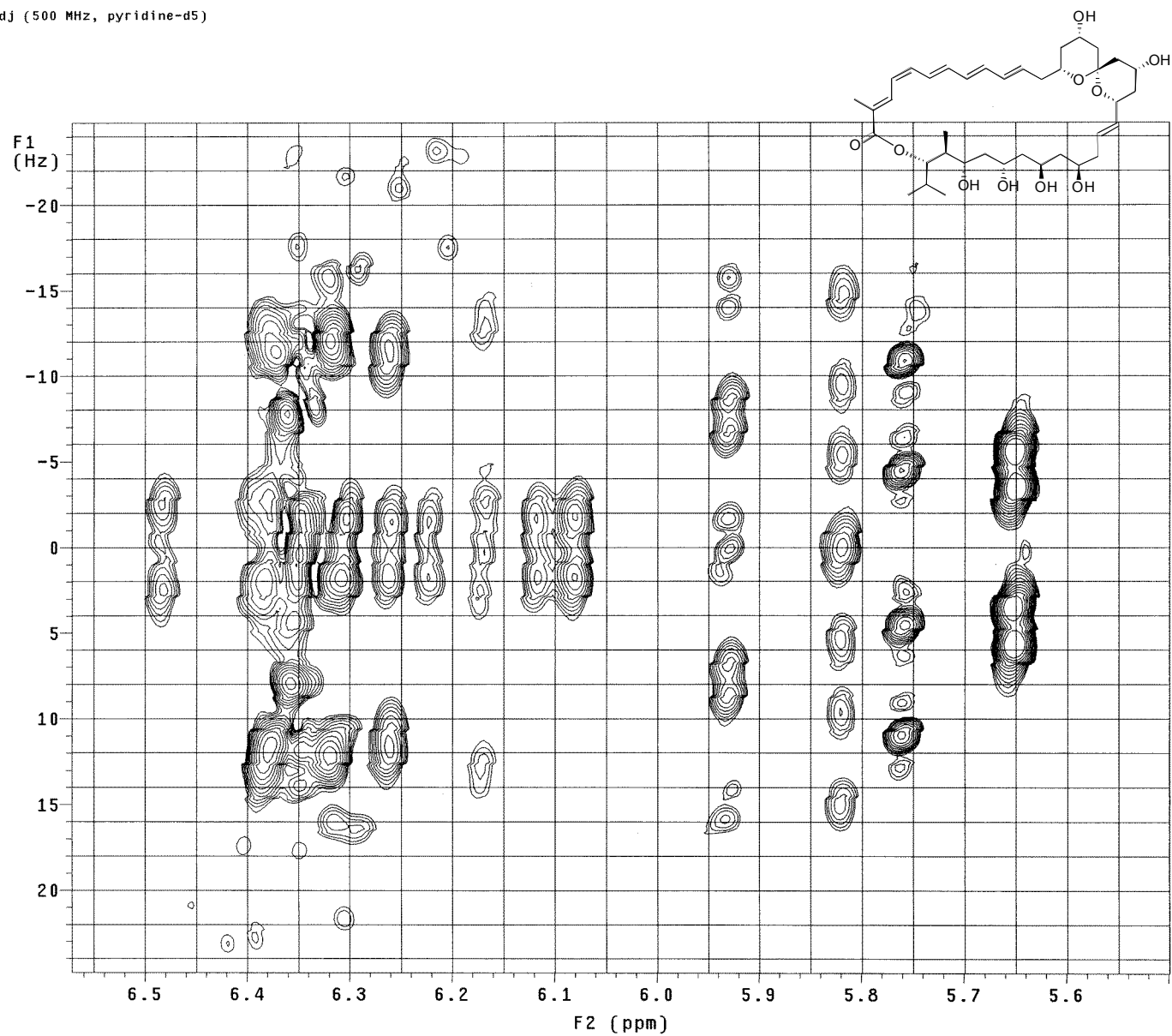


Figure S33. Homo 2D *J*-resolved ¹H NMR spectrum of 4 (500 MHz, pyridine-d₅).

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

Pulse Sequence: ROESY

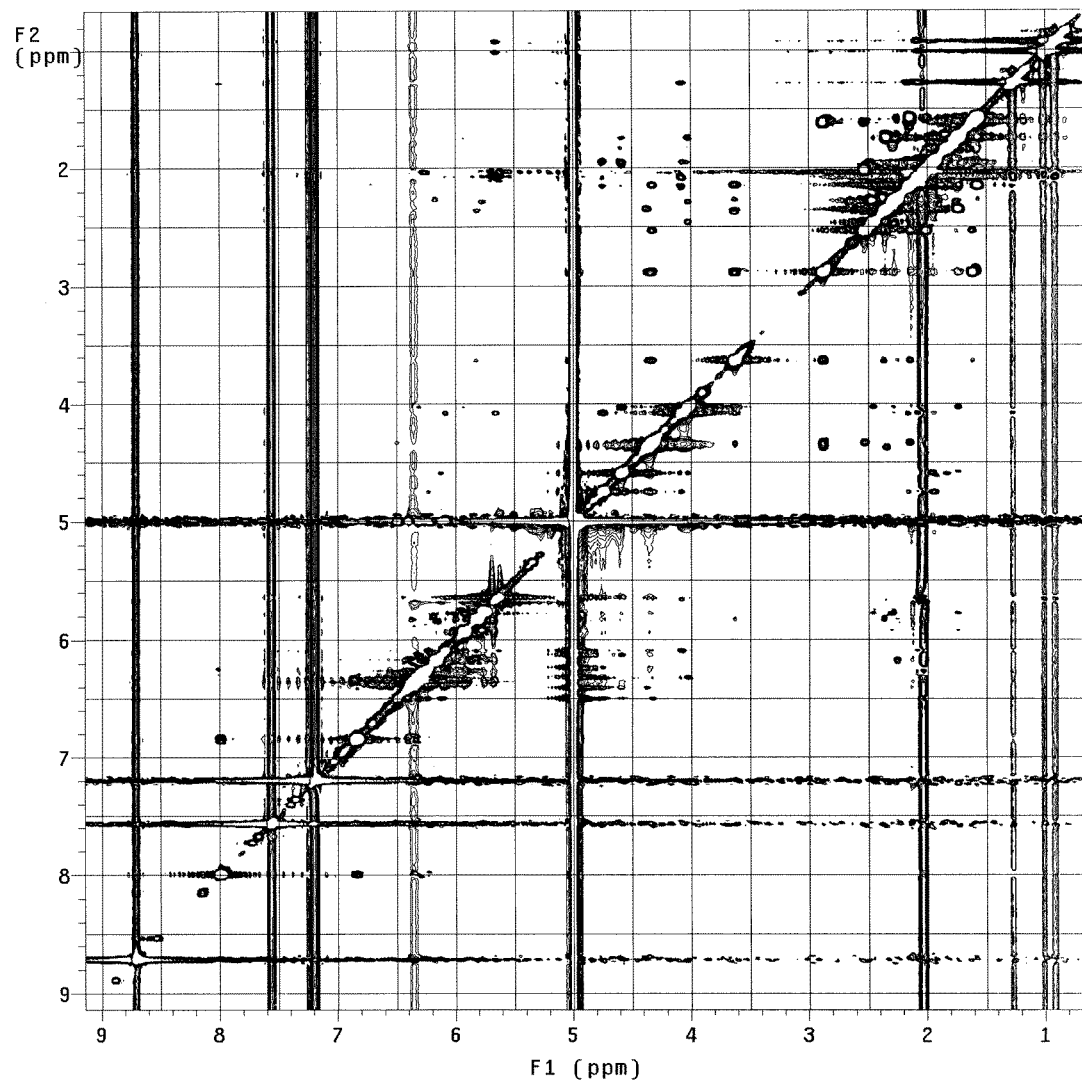
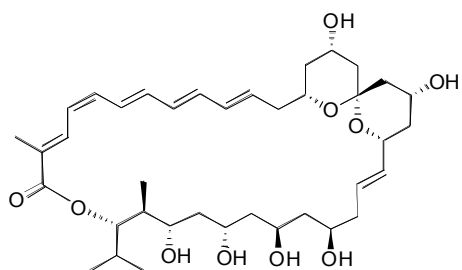


Figure S34. ROESY spectrum of 4 (500 MHz, pyridine-*d*₅)

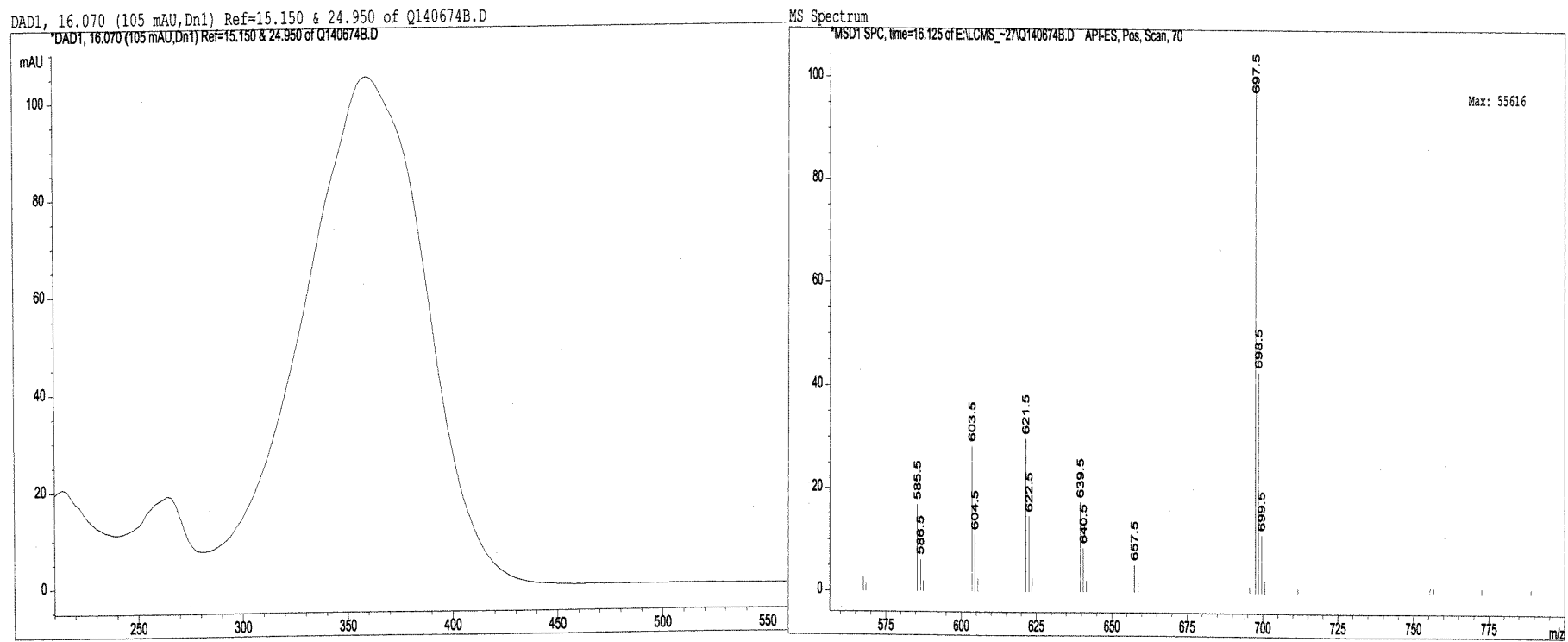


Figure S35. UV and ESI-MS spectra derived from HPLC-DAD-MSD (MeCN-H₂O) of marinisporolide E (**5**)

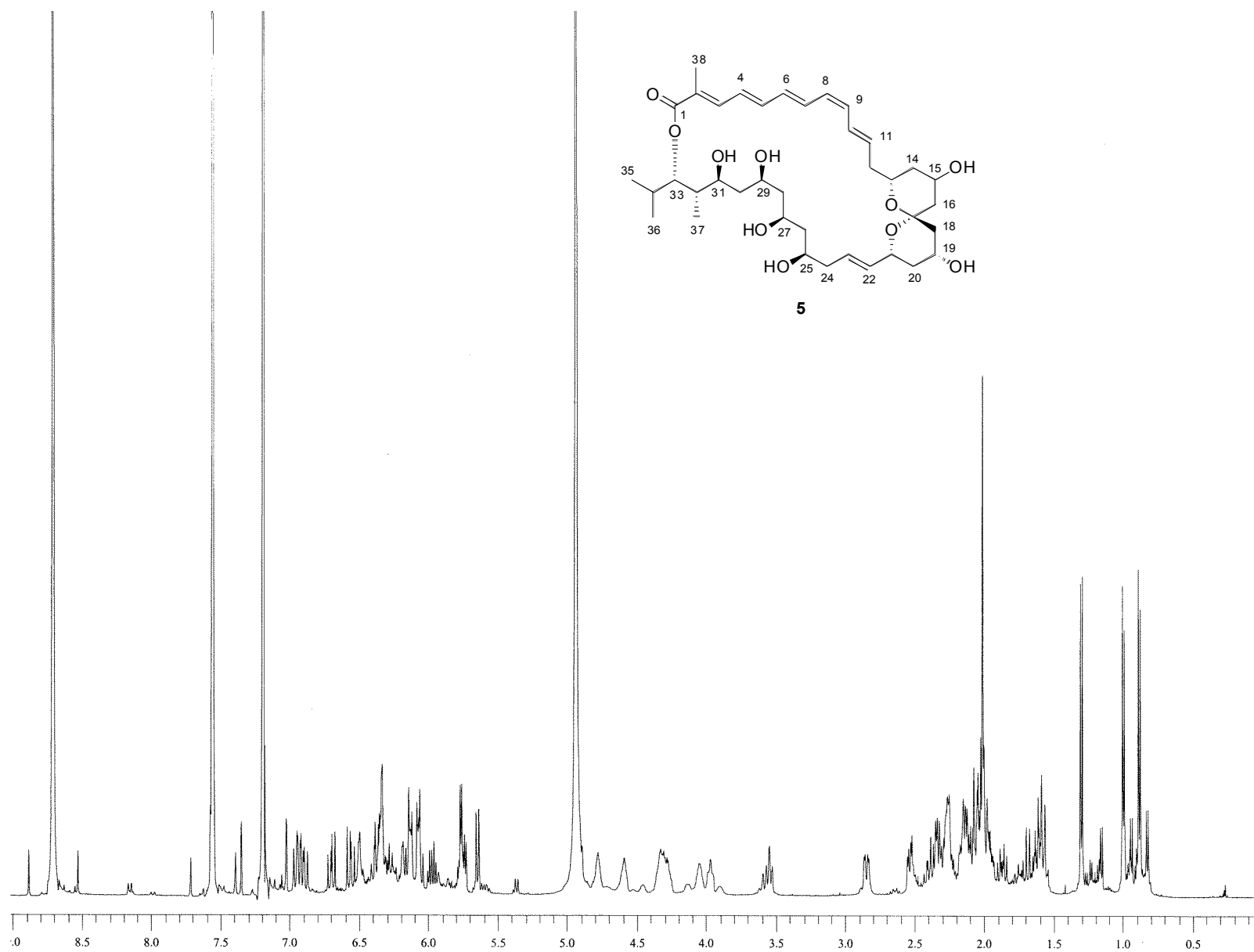


Figure S36. ¹H NMR spectrum of marinisporolide E (**5**) (500 MHz, pyridine-*d*₅).

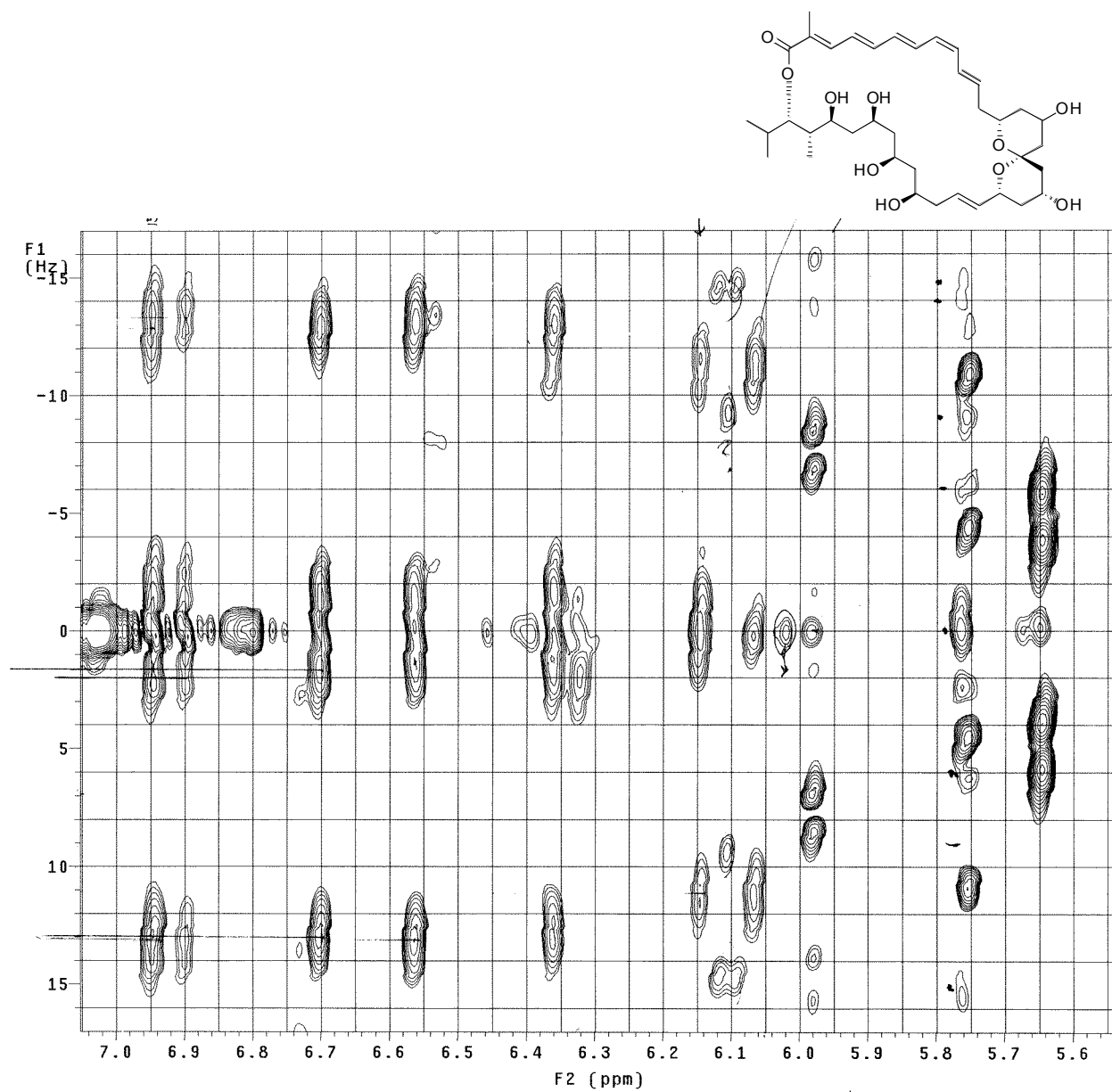


Figure S38. Expanded homo 2D J -resolved ^1H NMR spectrum of **5** (500 MHz, pyridine- d_5).

Q140_A1_50_1_2_2_23Jun2004

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_A1_50_1_2_2_23Jun2004
File: ROESY

Pulse Sequence: ROESY

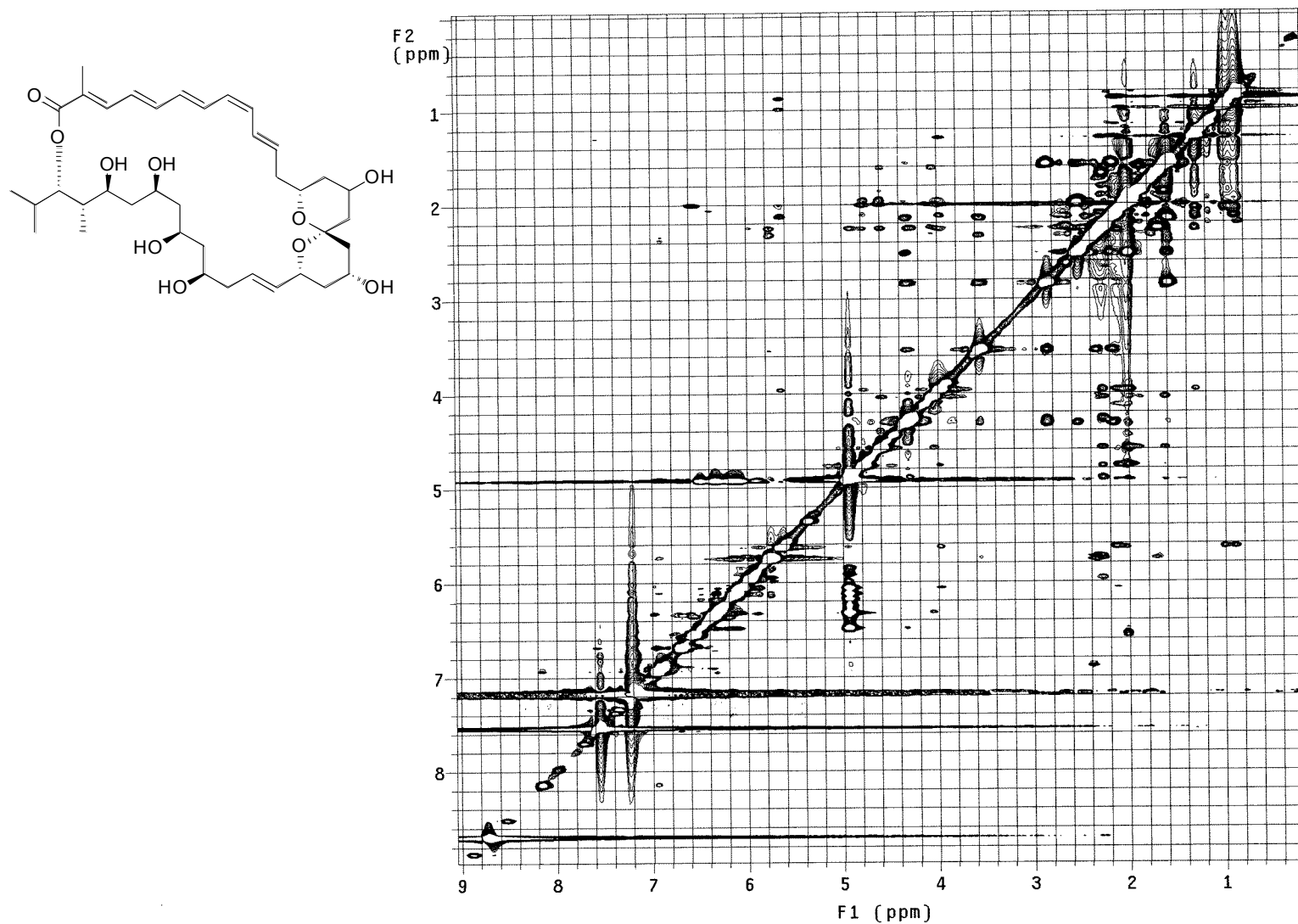


Figure S39. ROESY spectrum of **5** (500 MHz, pyridine-*d*₅).

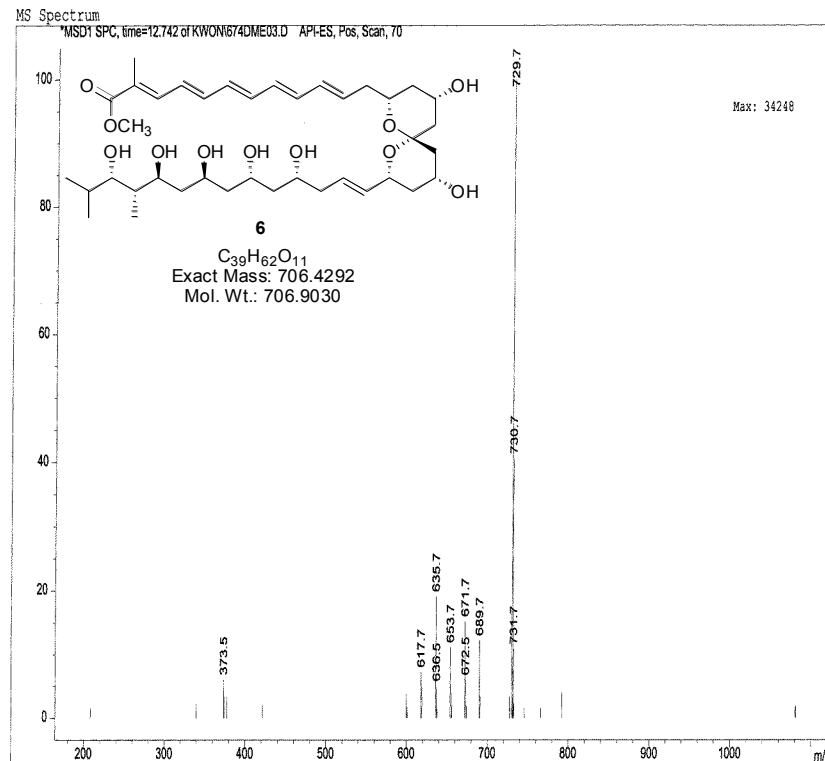
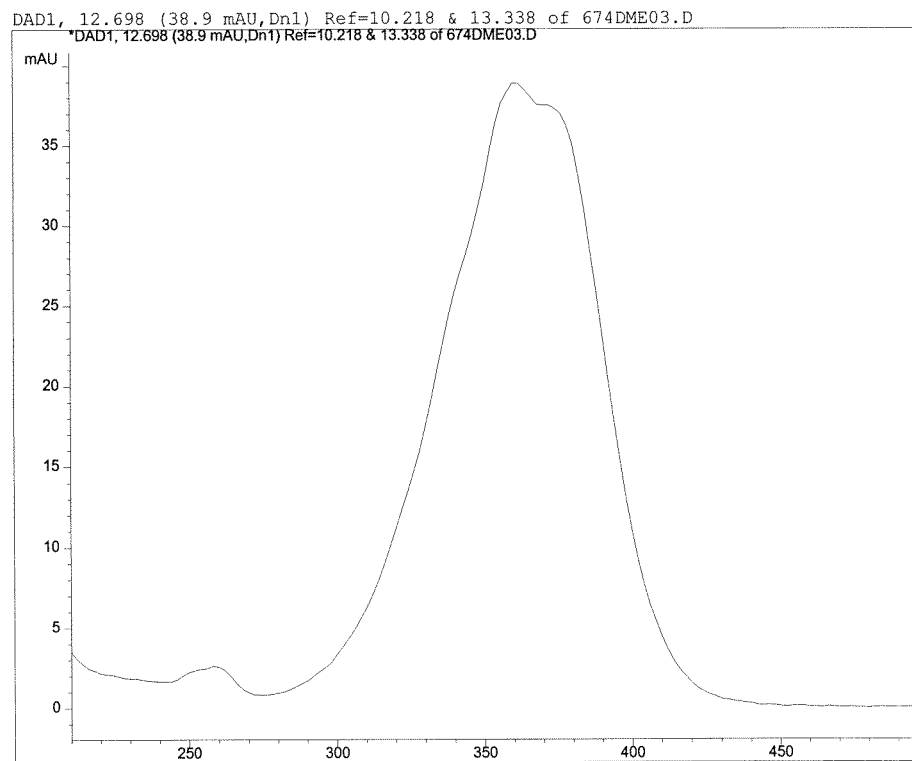


Figure S40. UV and ESI-MS spectra derived from HPLC-DAD-MSD of compound 6.

Q140_674_m221_methanolysis_1st (500 MHz, DMSO-d6)

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

Sample directory:

File: PROTON

Pulse Sequence: s2pu1

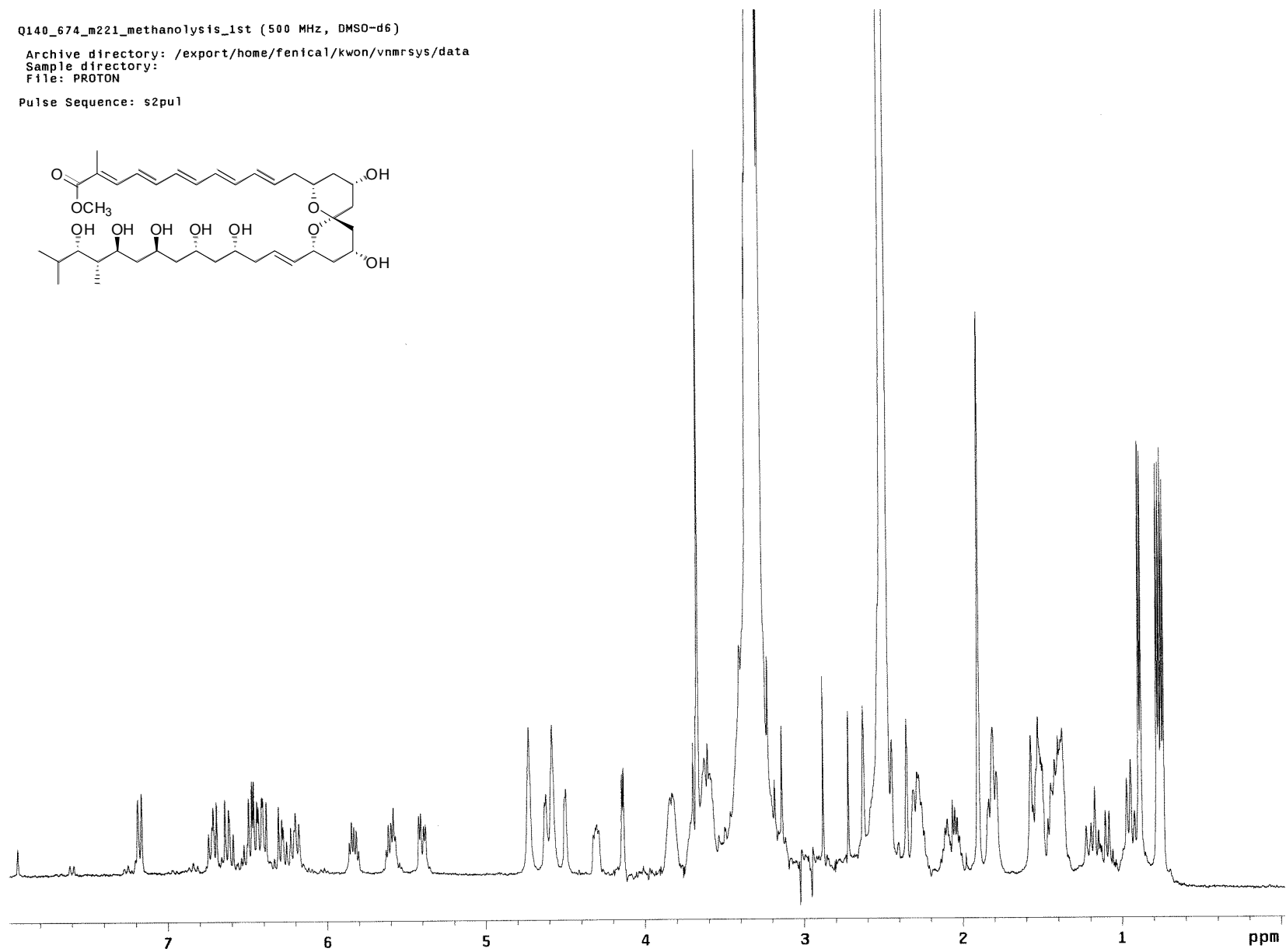
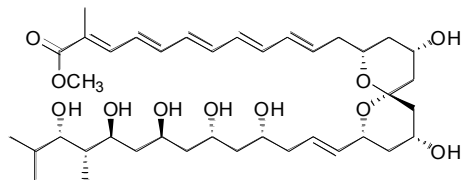


Figure S41. ¹H NMR spectrum of **6** (500 MHz, DMSO-*d*₆)

Q140_692_2_B_Metanalysis

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_692_2_B_Metha_HMQC_12Sep2005
File: gHMQC

Pulse Sequence: gHMQC

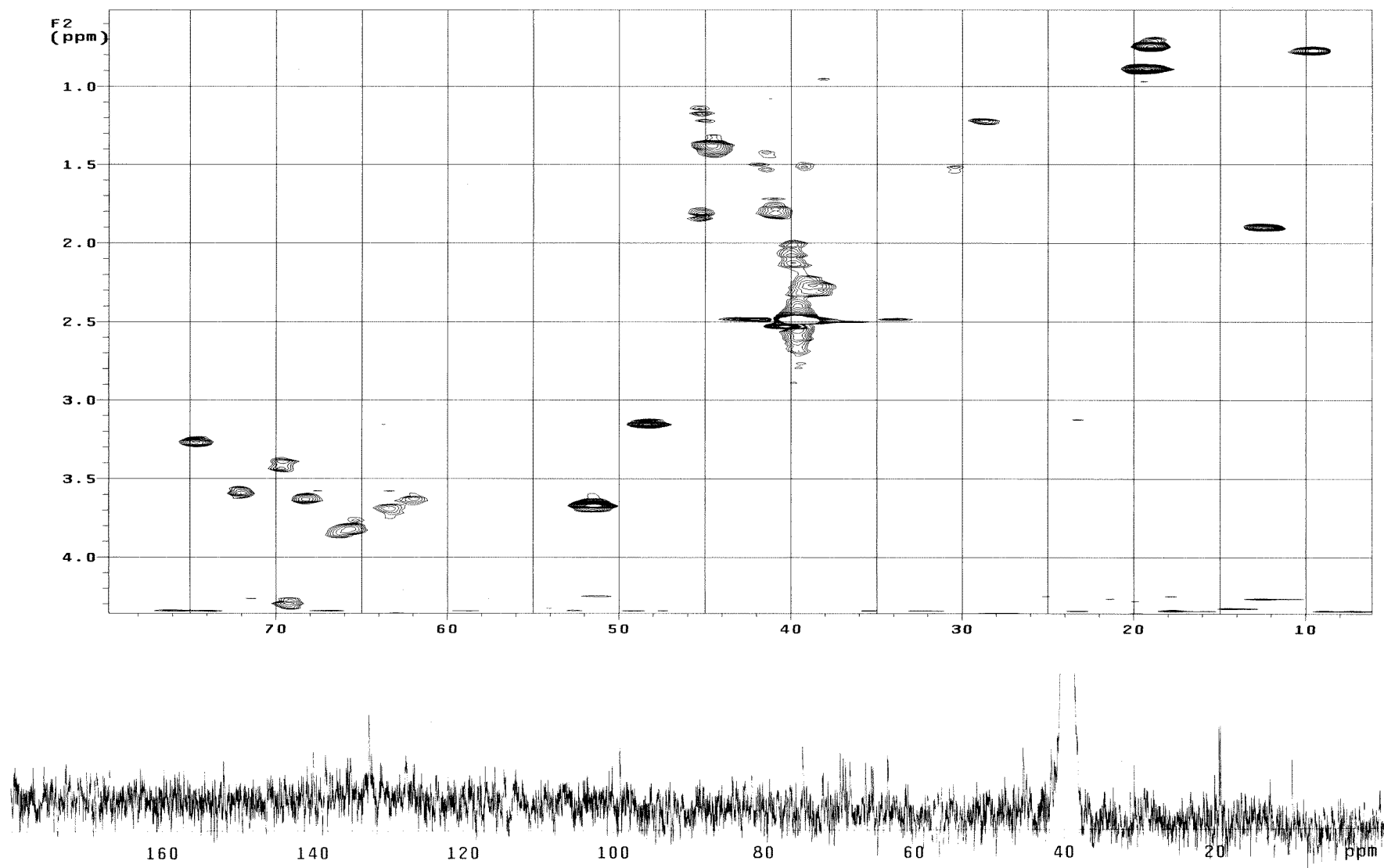
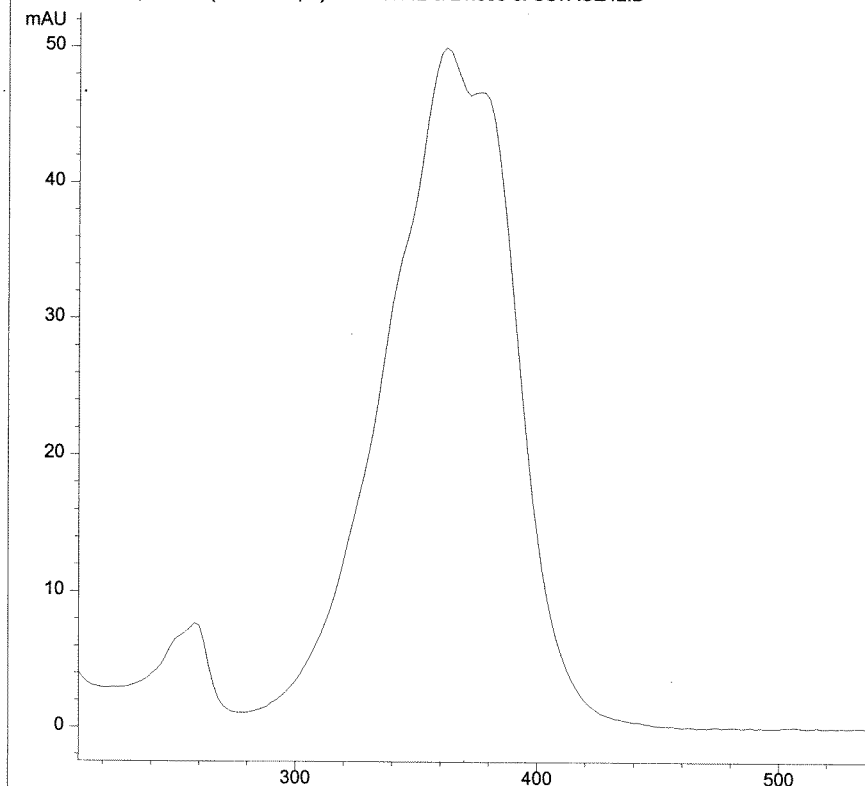


Figure S42. Expanded gHMQC spectrum (500 MHz, DMSO- d_6) and ^{13}C NMR spectrum (75 MHz, DMSO- d_6) of **6**.

DAD1, 21.069 (50.0 mAU, -) Ref=20.442 & 21.309 of SS7ACE42.D
*DAD1, 21.069 (50.0 mAU, -) Ref=20.442 & 21.309 of SS7ACE42.D



MS Spectrum

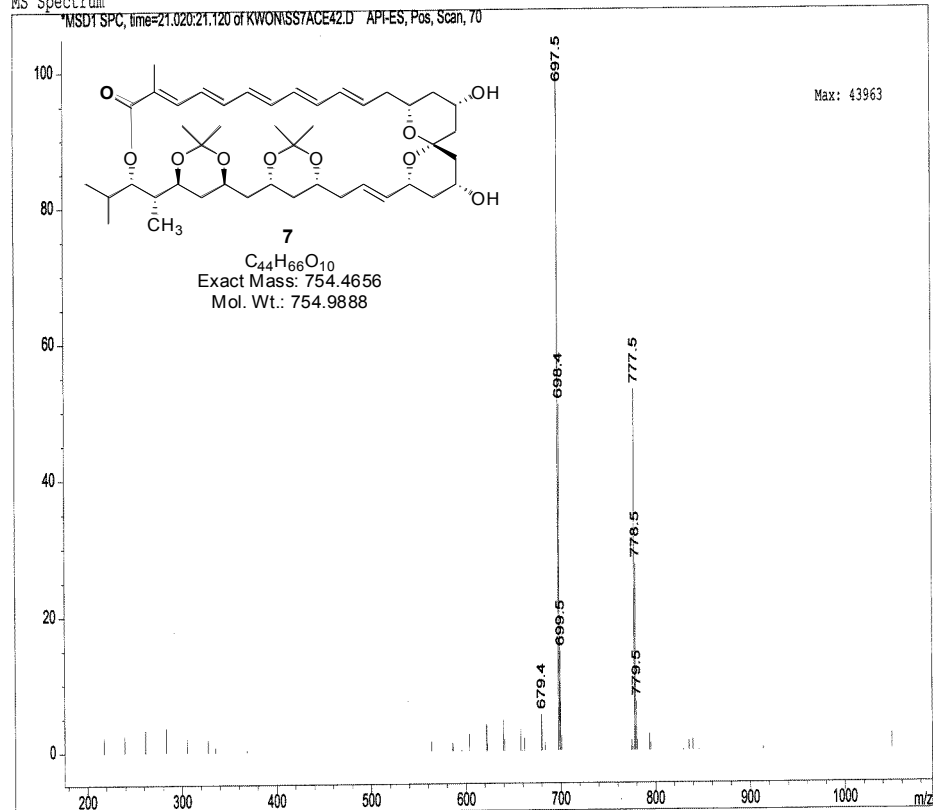


Figure S43. UV and ESI-MS spectra derived from HPLC-DAD-MSD of compound 7.

Q140_692_SS_7_Acetonide_4_2 (500
MHz, CD₃CN)

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_692_SS_7_ACeto_4_2_19Sep2005

Pulse Sequence: s2pu1

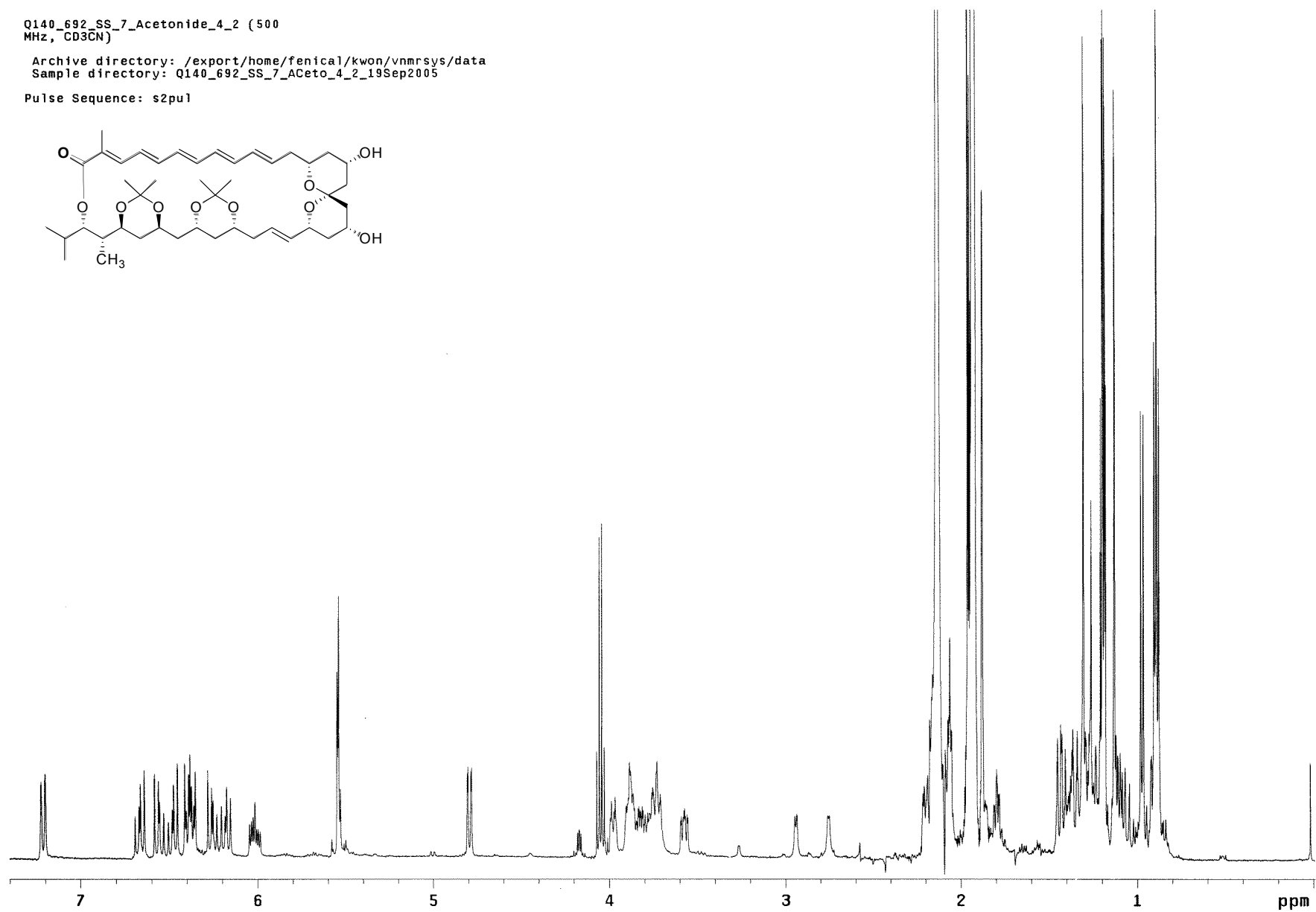
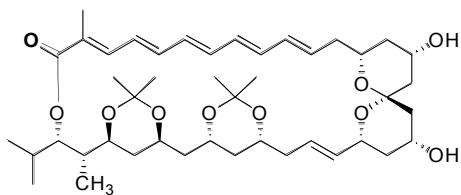


Figure S44. ¹H NMR spectrum of 7 (500 MHz, CD₃CN).

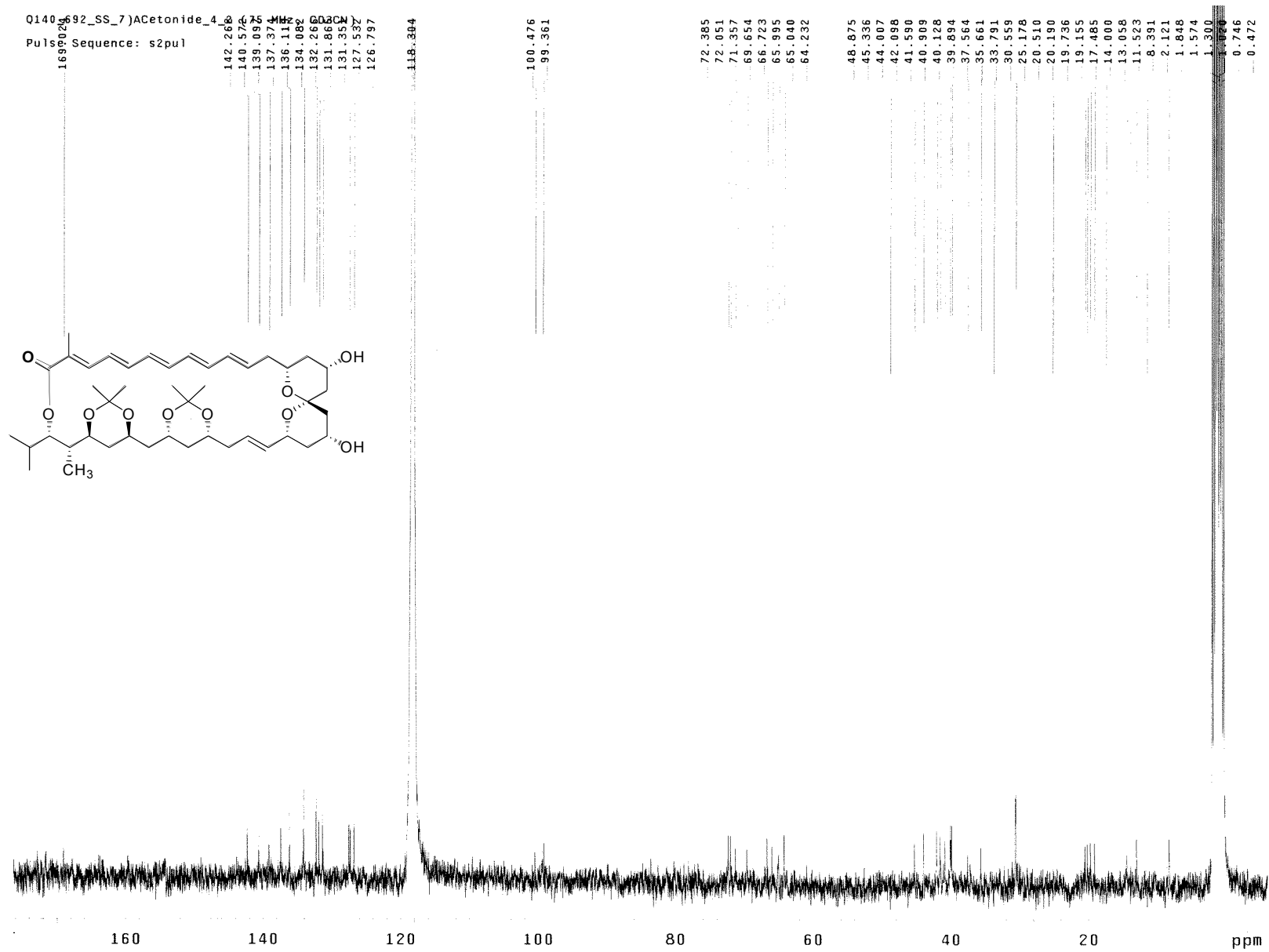


Figure S45. ^{13}C NMR spectrum of **7** (75 MHz, CD_3CN).

Q140_692_SS_7_Acetonide_4_2 (500
MHz, CD₃CN)

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_692_SS_7_Aceto_4_2_HMQC_19Sep2005
File: gHMQC

Pulse Sequence: gHMQC

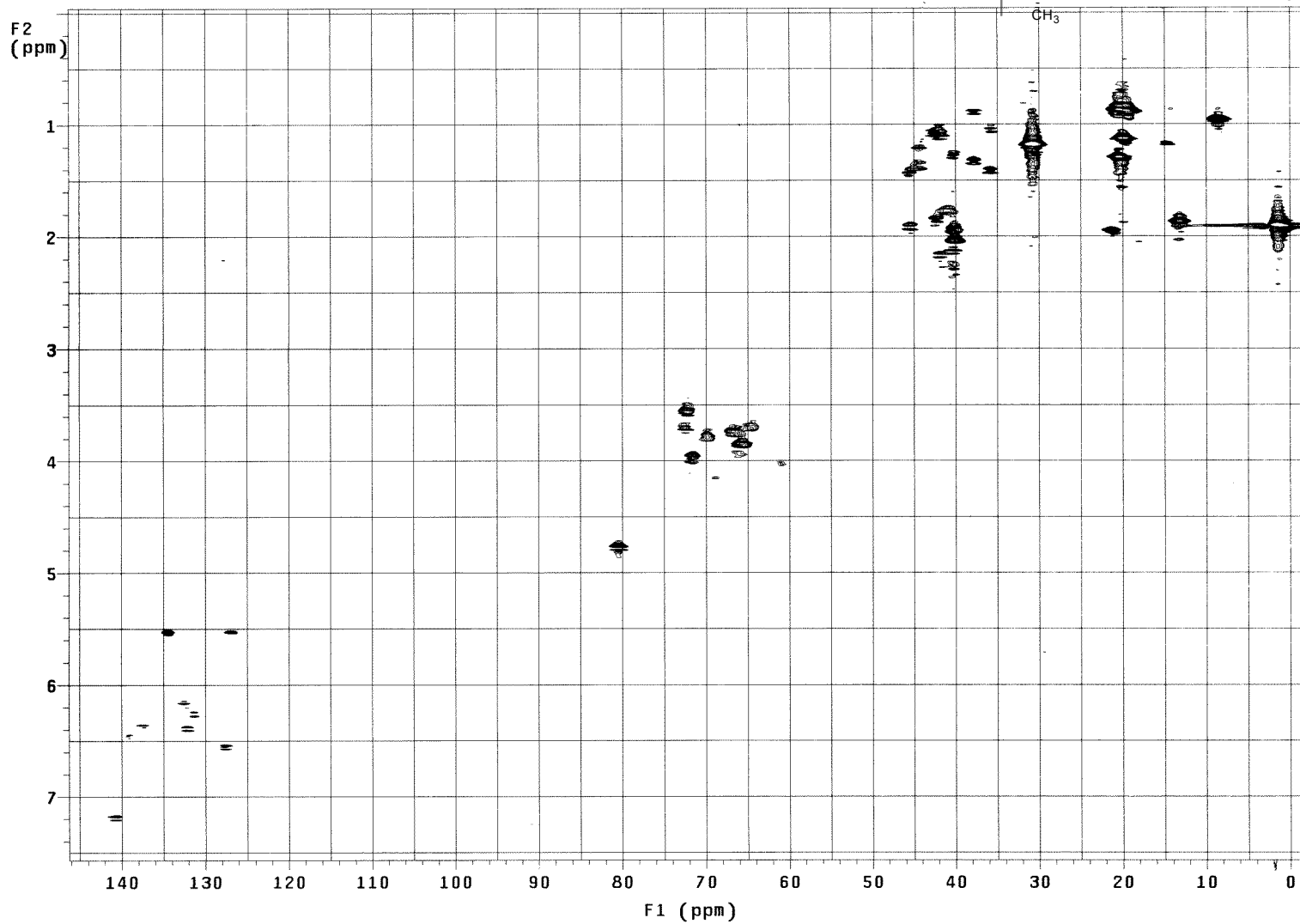


Figure S46. gHMQC spectrum of 7 (500 MHz, CD₃CN).

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

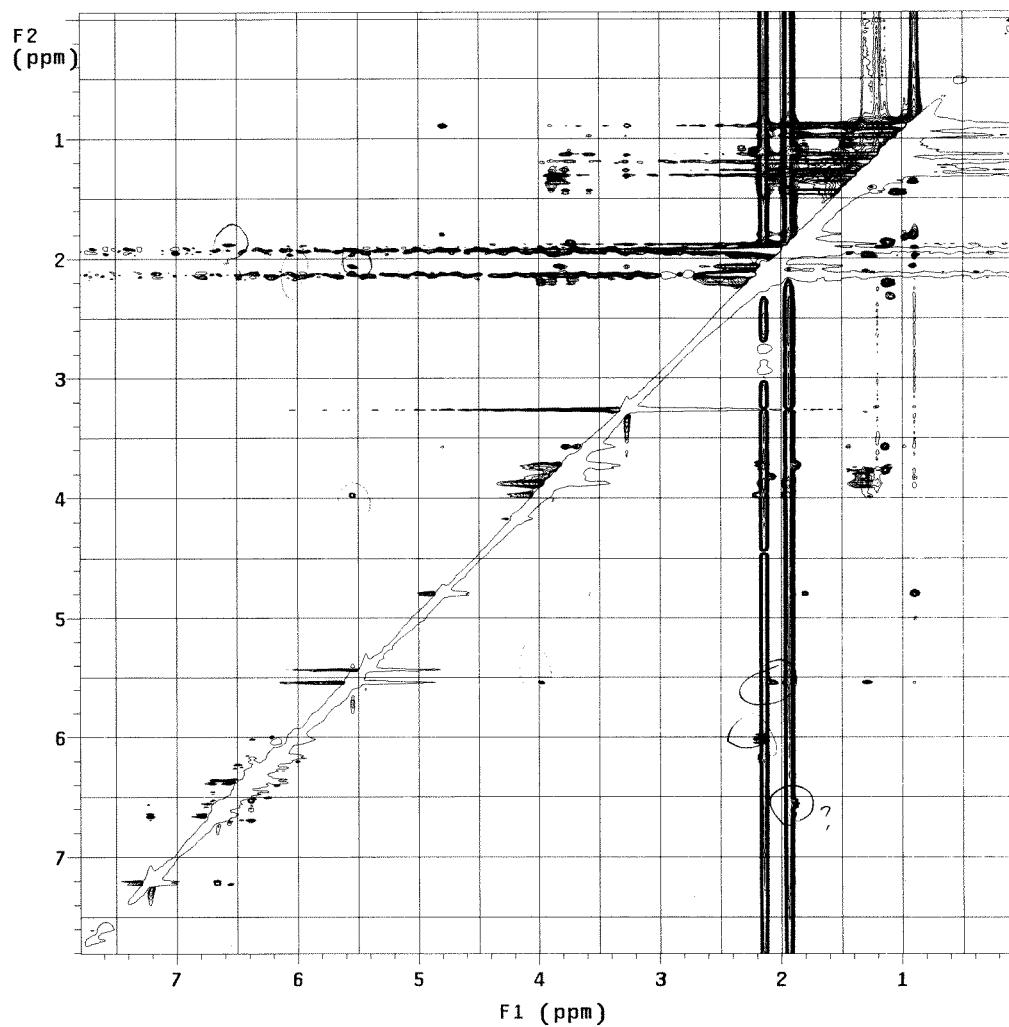
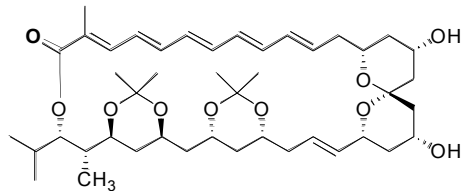


Figure S47. ROESY spectrum of **7** (500 MHz, CD₃CN).

DAD1, 0.066 : 0.080 (39.4 mAU,%Fs) Ref=0.053 & 0.213 of A42MET2.D
DAD1, 0.066 : 0.080 (39.4 mAU,%Fs) Ref=0.053 & 0.213 of A42MET2.D

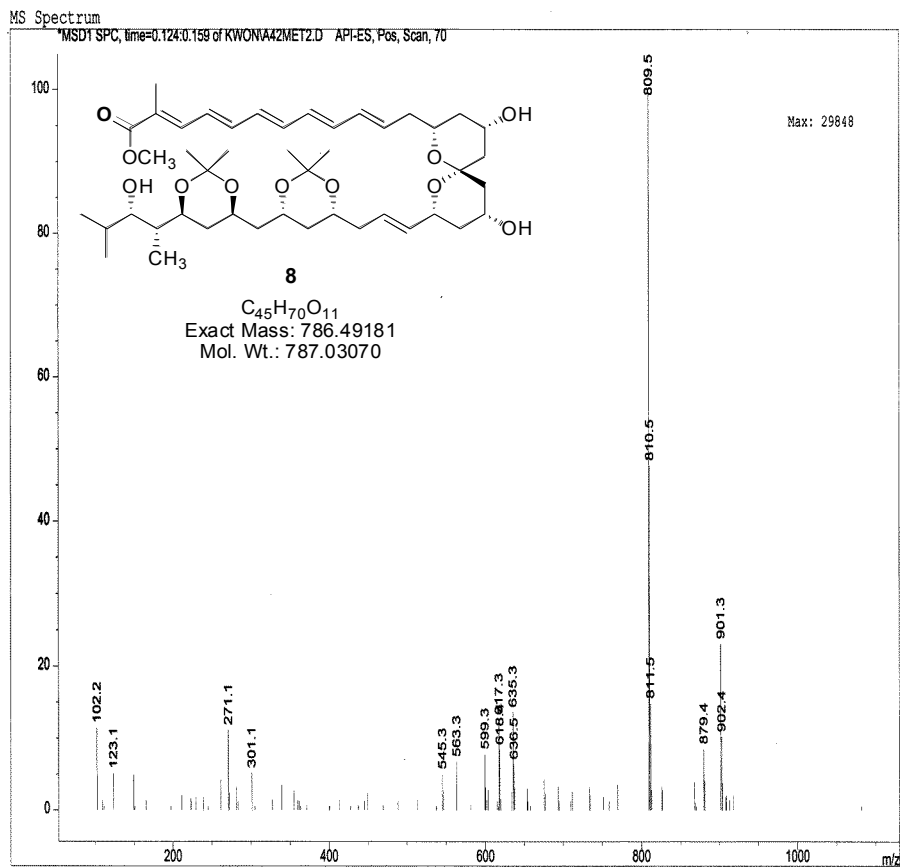
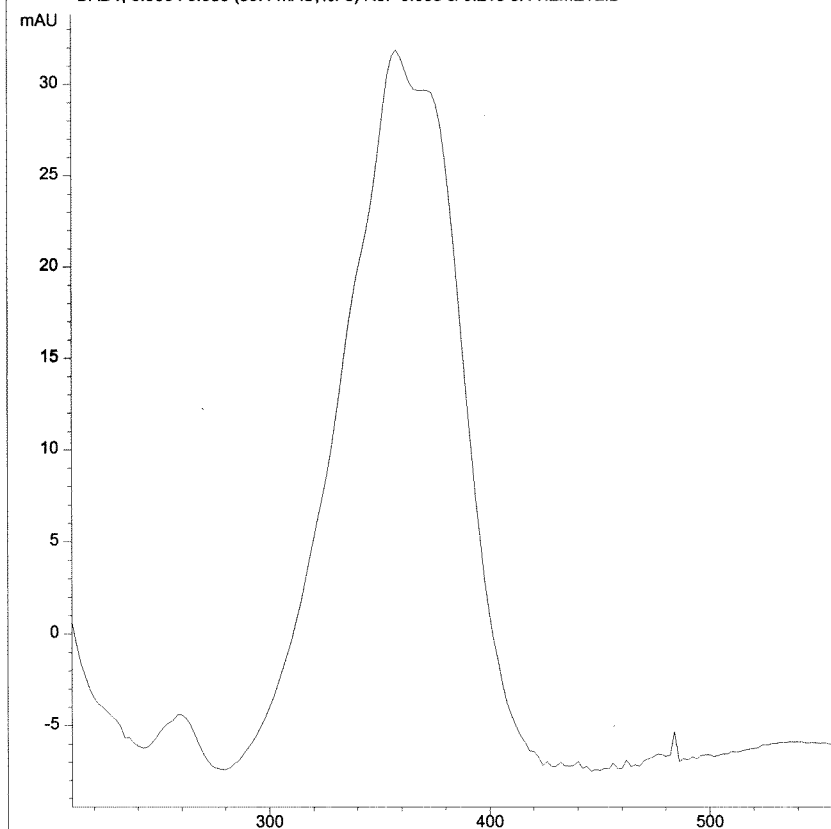


Figure S48. UV and ESI-MS spectra derived from HPLC-DAD-MSD of compound 8.

Q140_692_SS7_acetonide_4_2_methanolysis (500 MHz, CD₃CN)

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory:
File: PROTON

Pulse Sequence: s2pu1

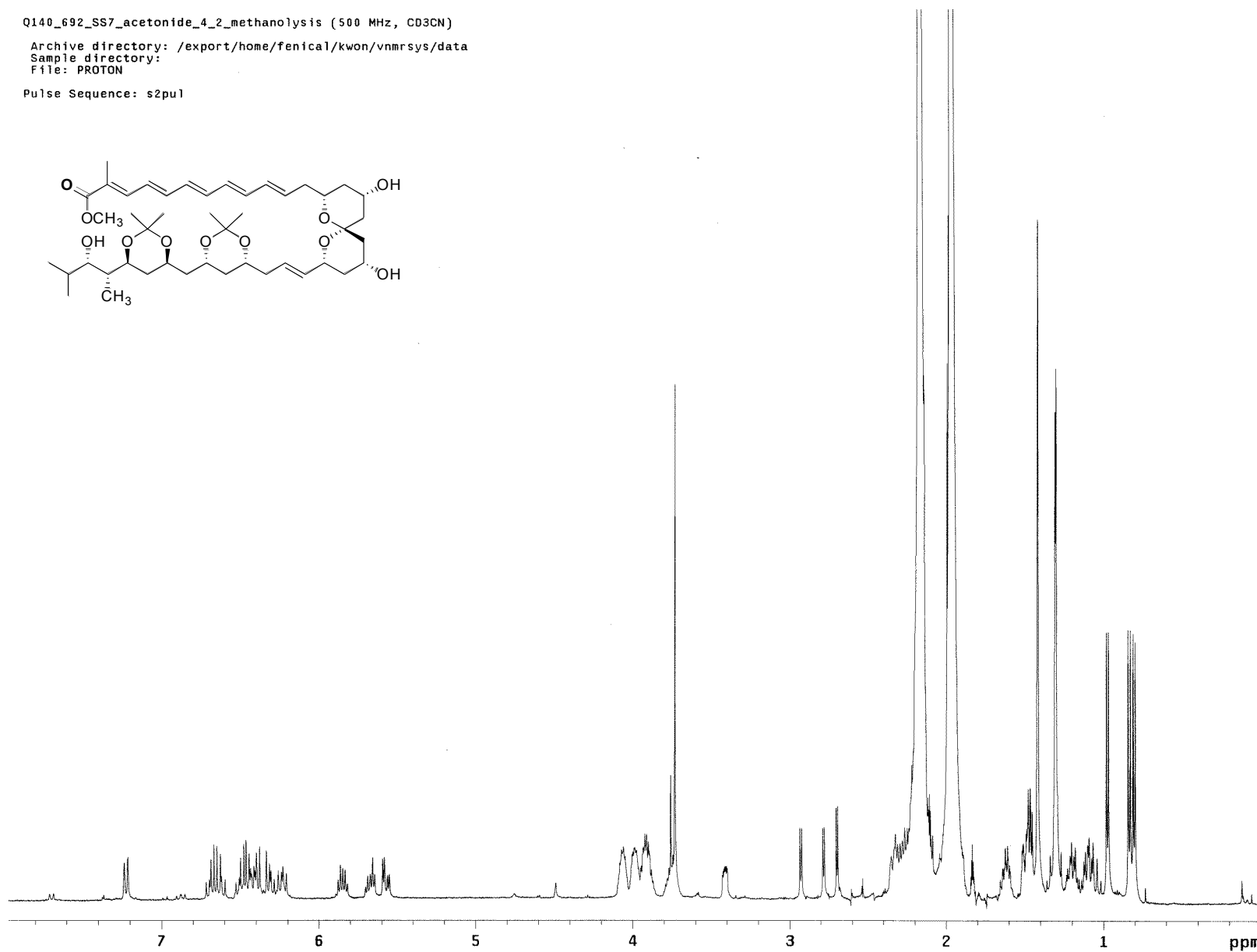
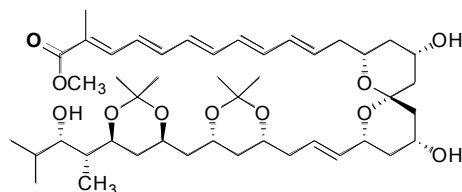


Figure S49. ¹H NMR spectrum of **8** (500 MHz, CD₃CN).

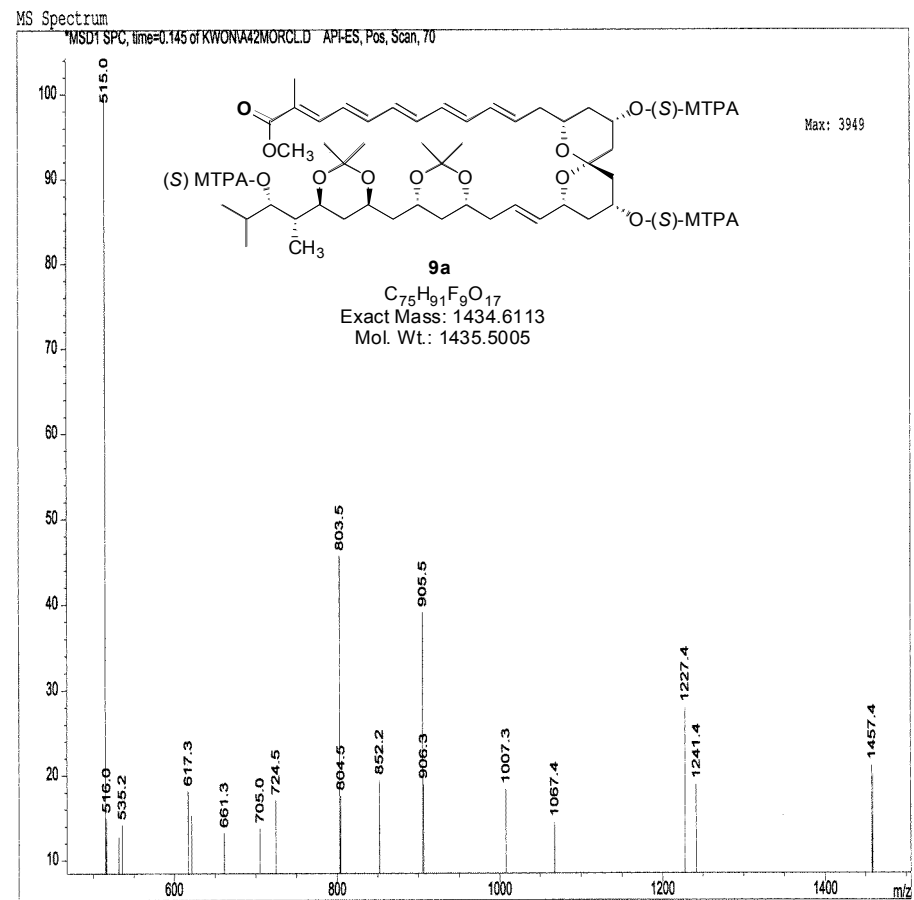
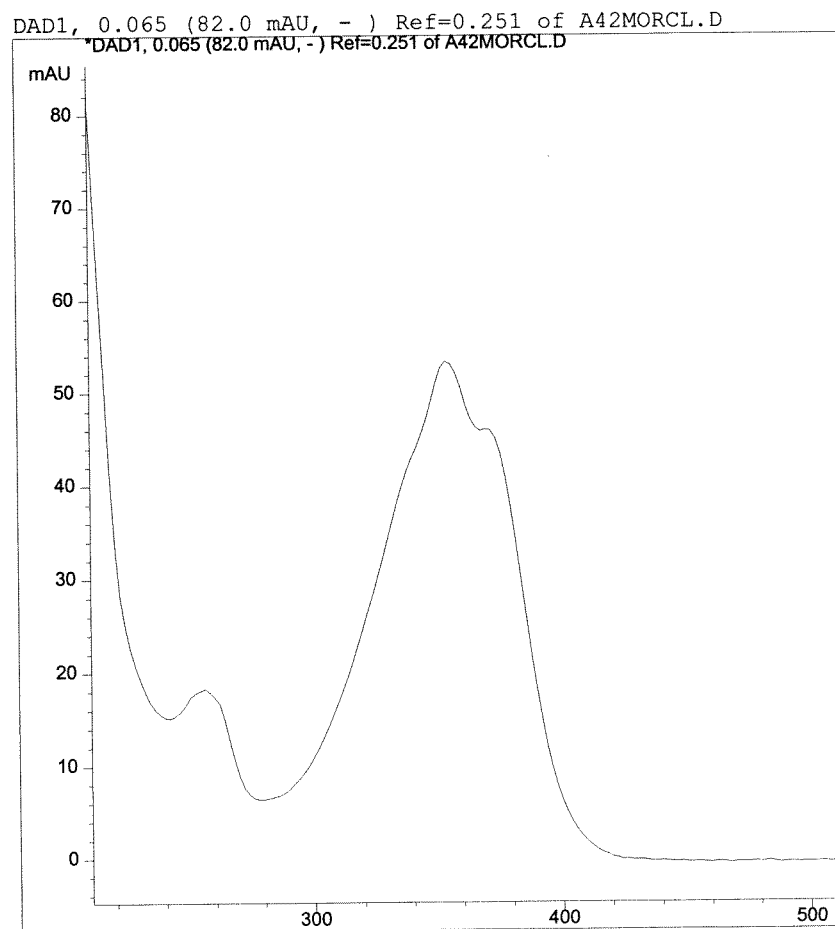


Figure S50. UV and ESI-MS spectra derived from HPLC-DAD-MSD of compound **9a**.

Q140_692_SS7_Acetonide42_Metha_Tri_(S)_mosher_ester (500 MHz, CD₃CN)

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

Pulse Sequence: s2pu1

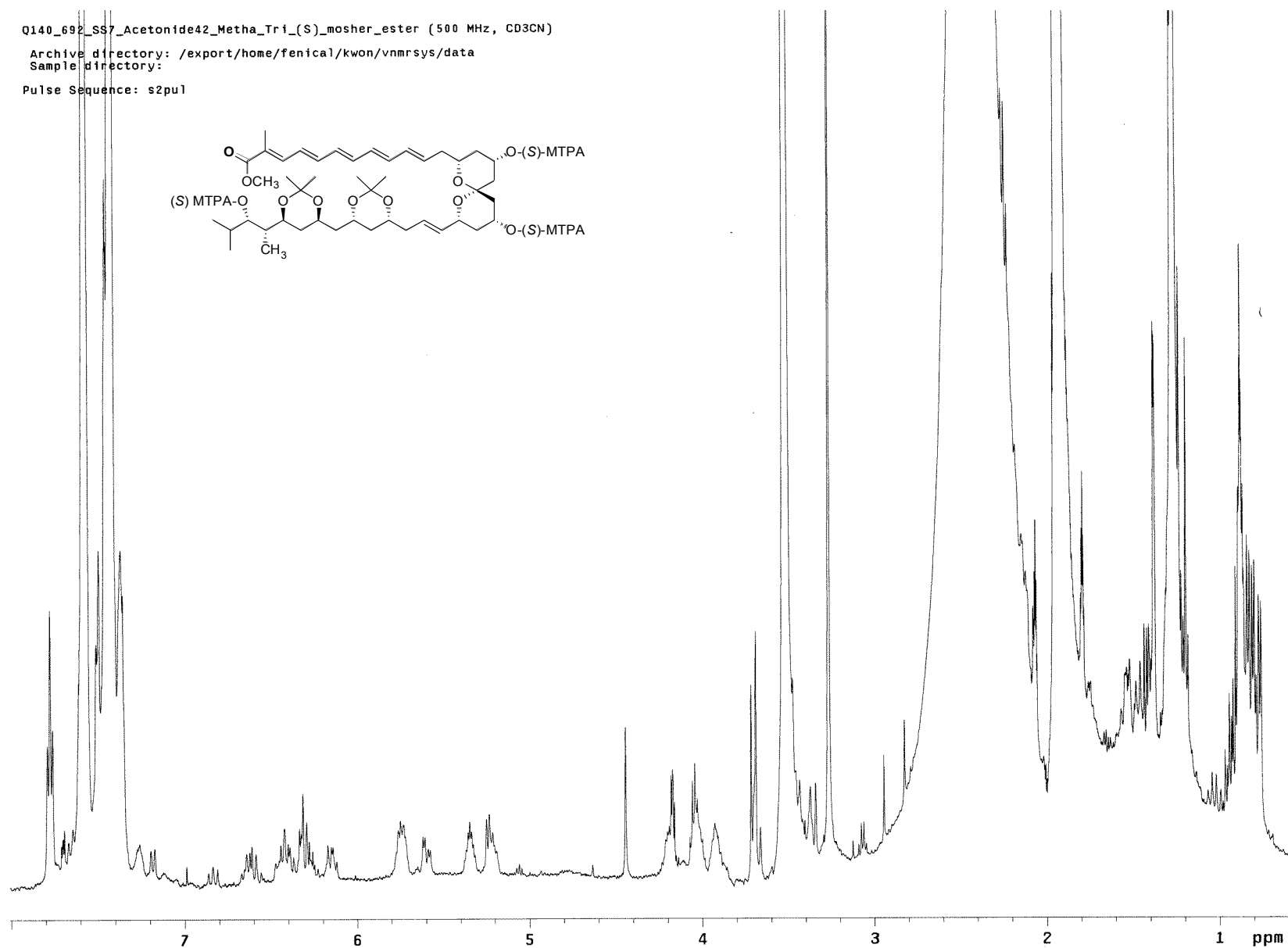
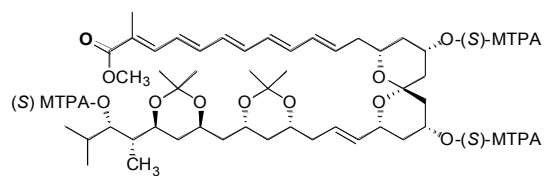


Figure S51. ¹H NMR spectrum of **9a** (500 MHz, CD₃CN).

Q140_692_SSA42_Meth_S_tri_mosher_ester

Archive directory: /export/home/fenical/kwon/vnmrsys/data
Sample directory: Q140_692_SS_A47_Meth_Tri_S_mosher_ester_COSY_19oct2005
File: gCOSY

Pulse Sequence: gCOSY

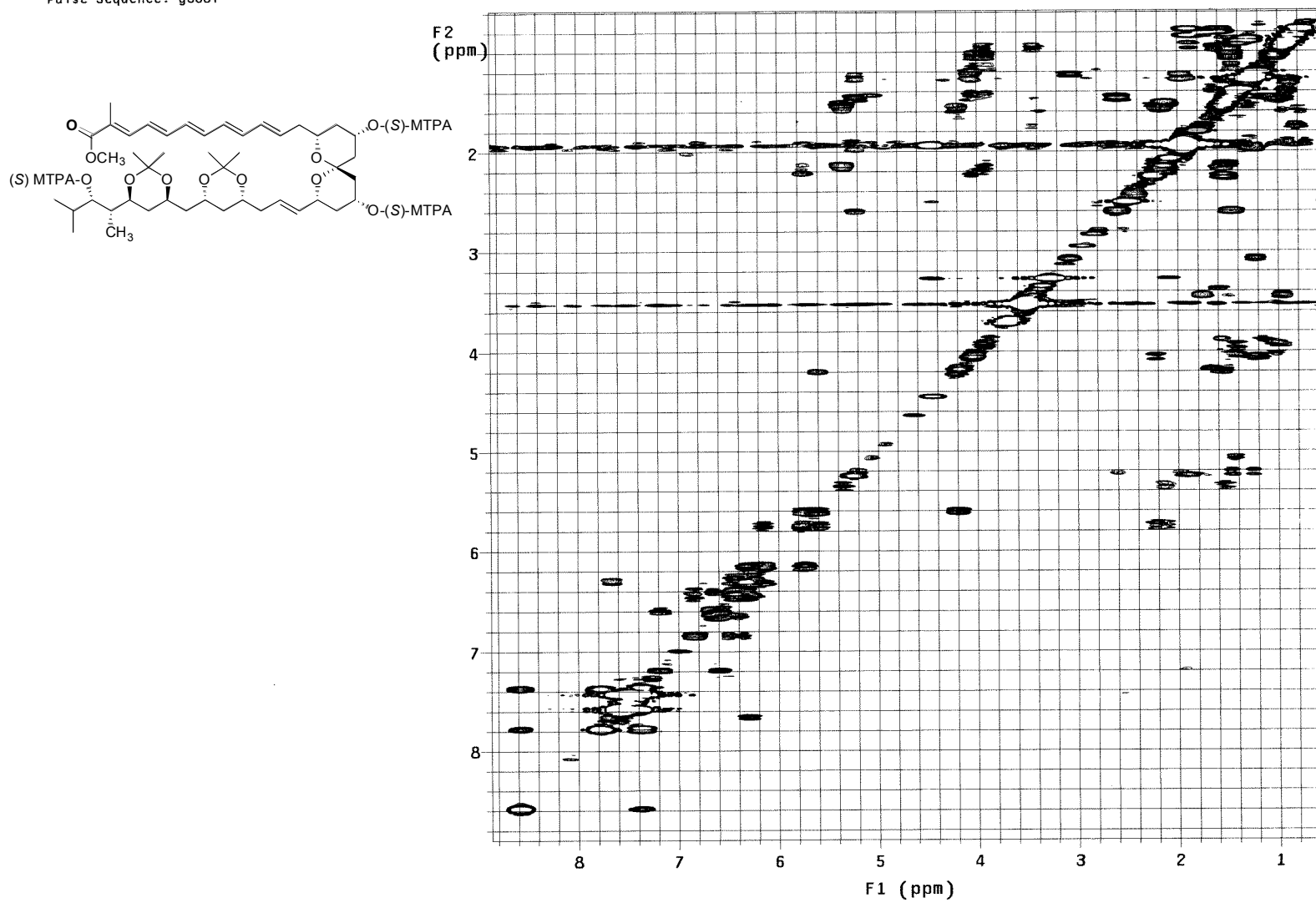
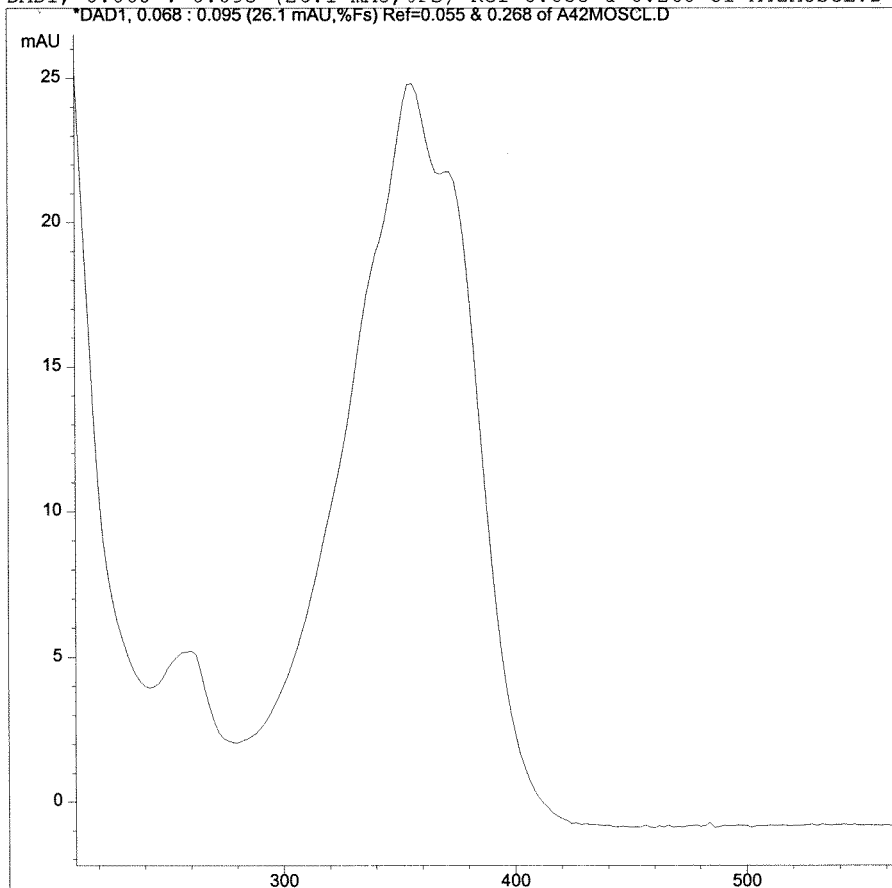


Figure S52. ^1H - ^1H COSY spectrum of **9a** (500 MHz, CD_3CN).

DAD1, 0.068 : 0.095 (26.1 mAU,%Fs) Ref=0.055 & 0.268 of A42MOSCL.D
DAD1, 0.068 : 0.095 (26.1 mAU,%Fs) Ref=0.055 & 0.268 of A42MOSCL.D



MS Spectrum

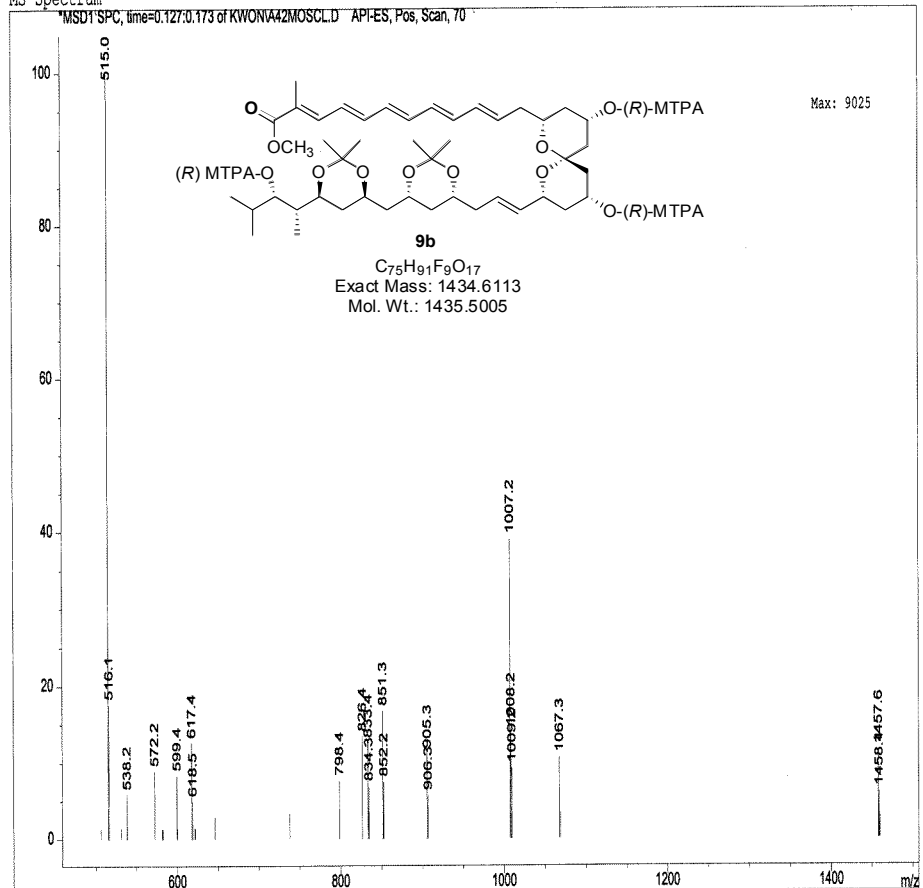


Figure S53. UV and ESI-MS spectra derived from HPLC-DAD-MSD (MeCN-H₂O) of compound 9b.

Q140_692_SS7_Acetonide42_Metha_Tri_(R)_mosher_ester (500 MHz, CD3CN)

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

Sample directory:

File: PROTON

Pulse Sequence: s2pu1

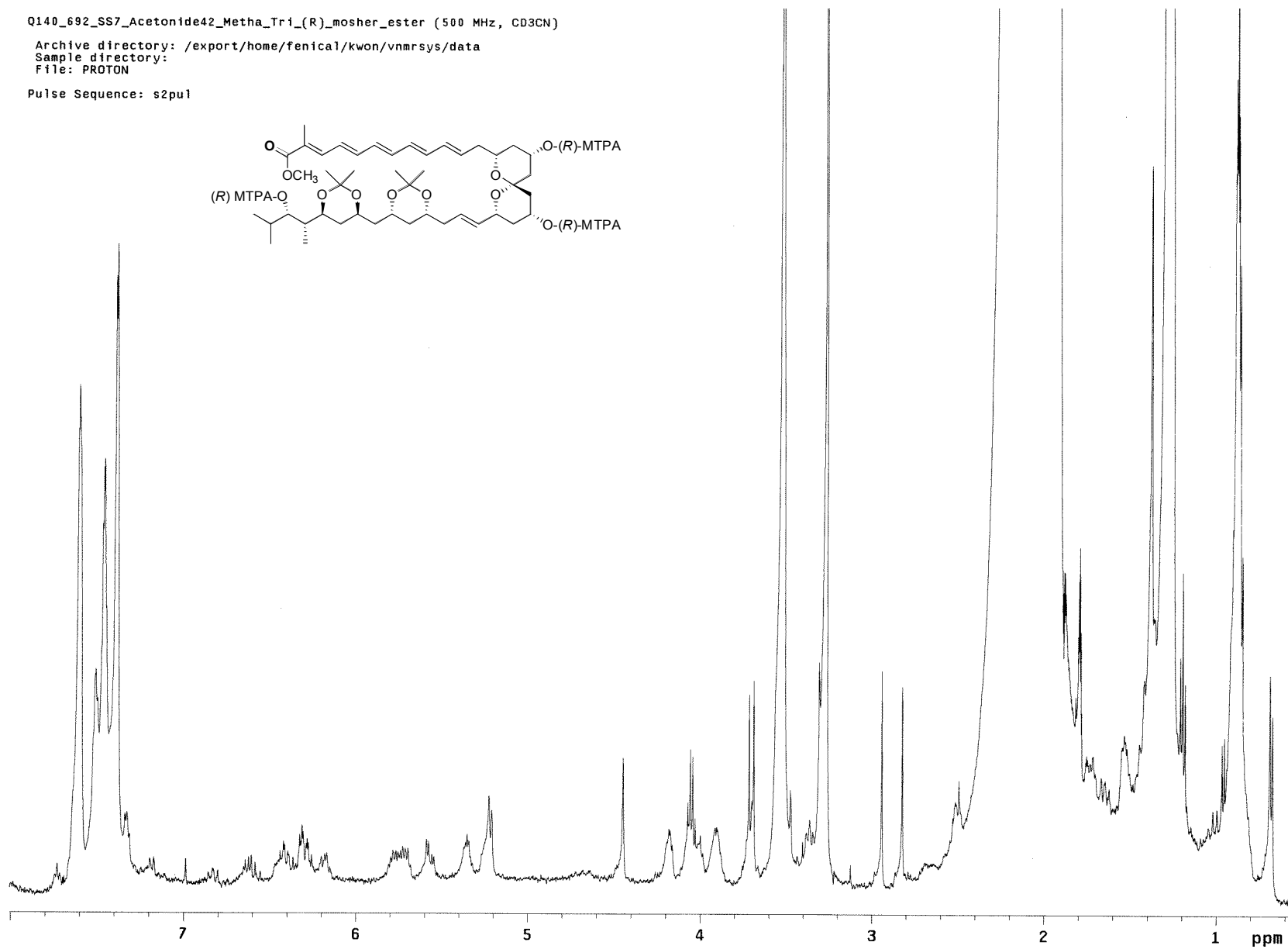
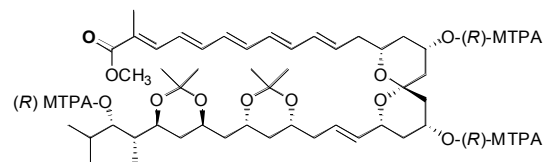


Figure S54. ¹H NMR spectrum of **9b** (500 MHz, CD₃CN).

Q140_692_SS7_A42_M_(R)_tri_mosher
_ester (500 MHz, CD₃CN)

Archive directory: /export/home/fenical/kwon/vnmrSYS/data
Sample directory: Q140_692_SS7_A42_Meth_R_tmosher_ester_COSY_18Oct2005
File: gCOSY

Pulse Sequence: gCOSY

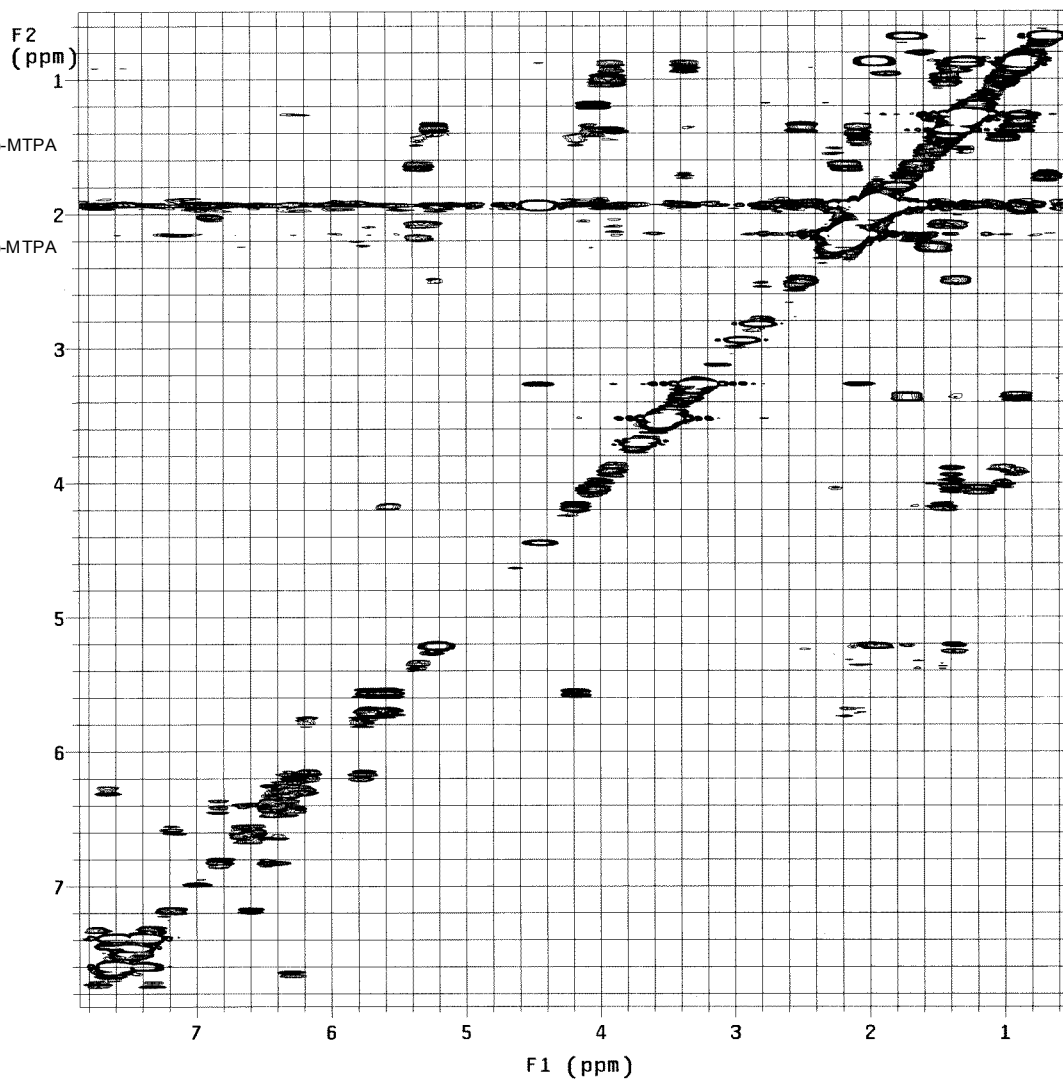
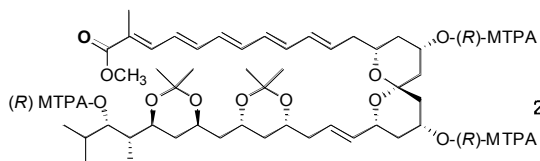


Figure S55. ¹H-¹H COSY spectrum of **9b** (500 MHz, CD₃CN).

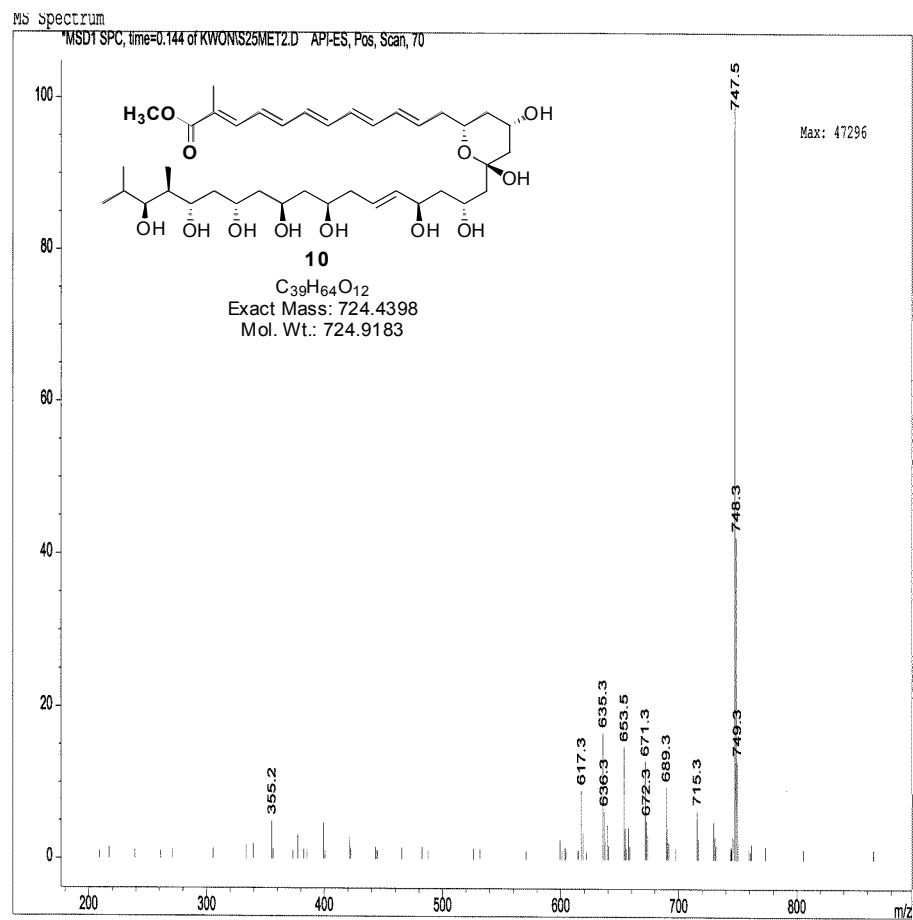
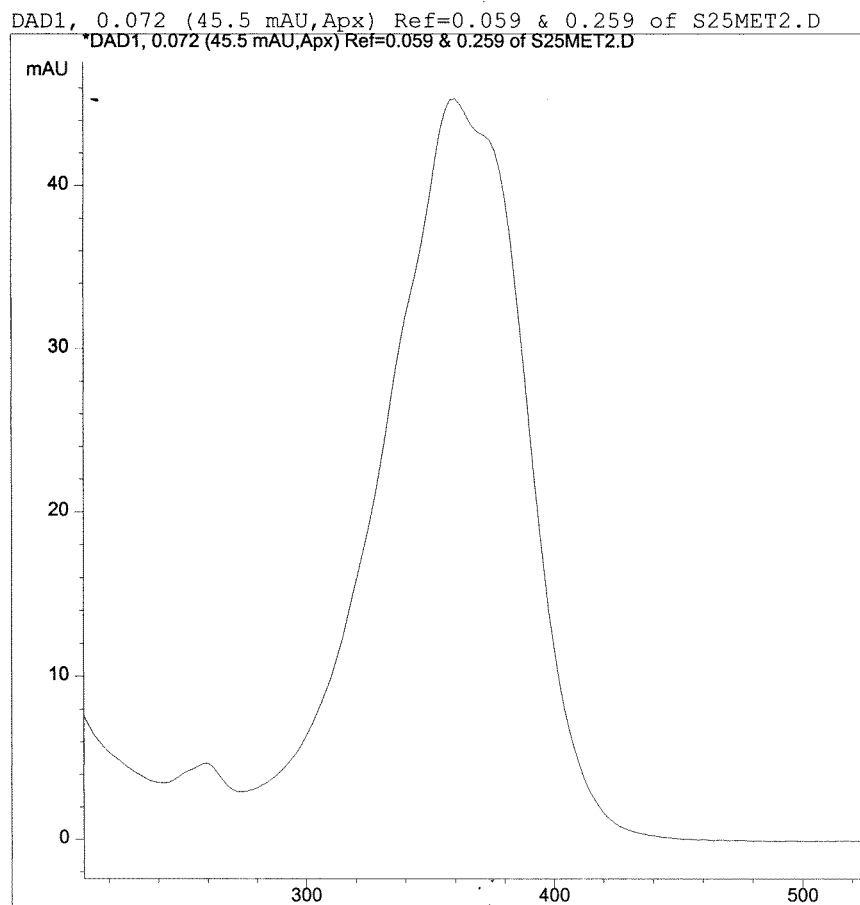


Figure S56. UV and ESI-MS spectra derived from HPLC-DAD-MSD (MeCN-H₂O) of compound **10**.

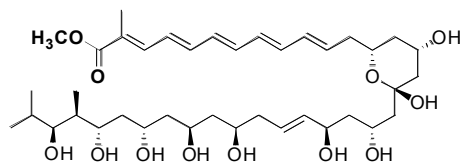
Q140_692_m1_8_Methanolysis (500 MHz, DMSO-d6)

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

Sample directory:

File: PROTON

Pulse Sequence: s2pu1



10

C₃₉H₆₄O₁₂

Exact Mass: 724.4398

Mol. Wt.: 724.9183

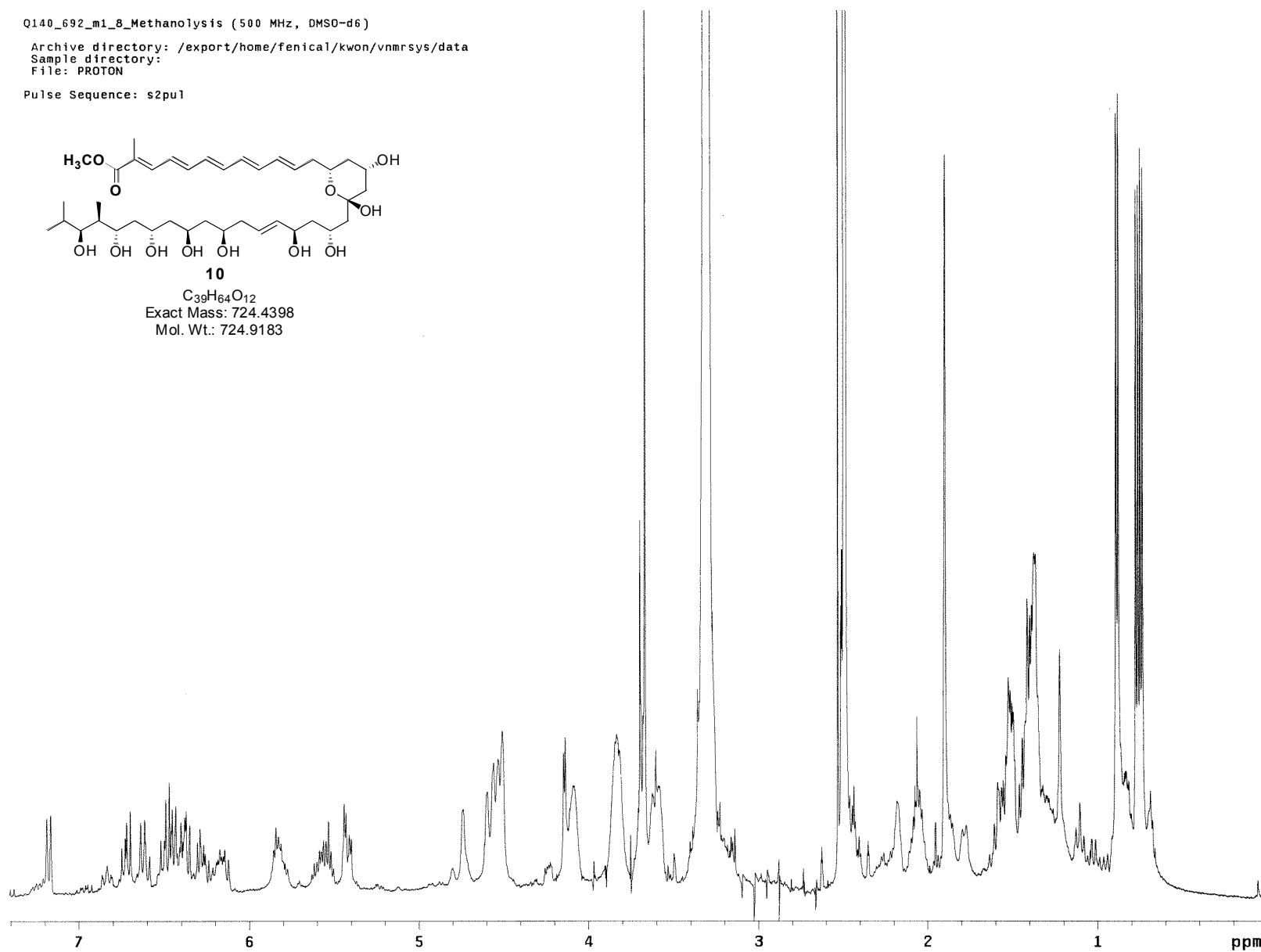


Figure S57. ¹H NMR spectrum of compound **10** (500 MHz, DMSO-*d*₆).

Q140_692_m1_8_methanolysis_HMQC (500 MHz, DMSO-d6)

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

Sample directory: kwon_28Sep2005

File: gHMQC

Pulse Sequence: gHMQC

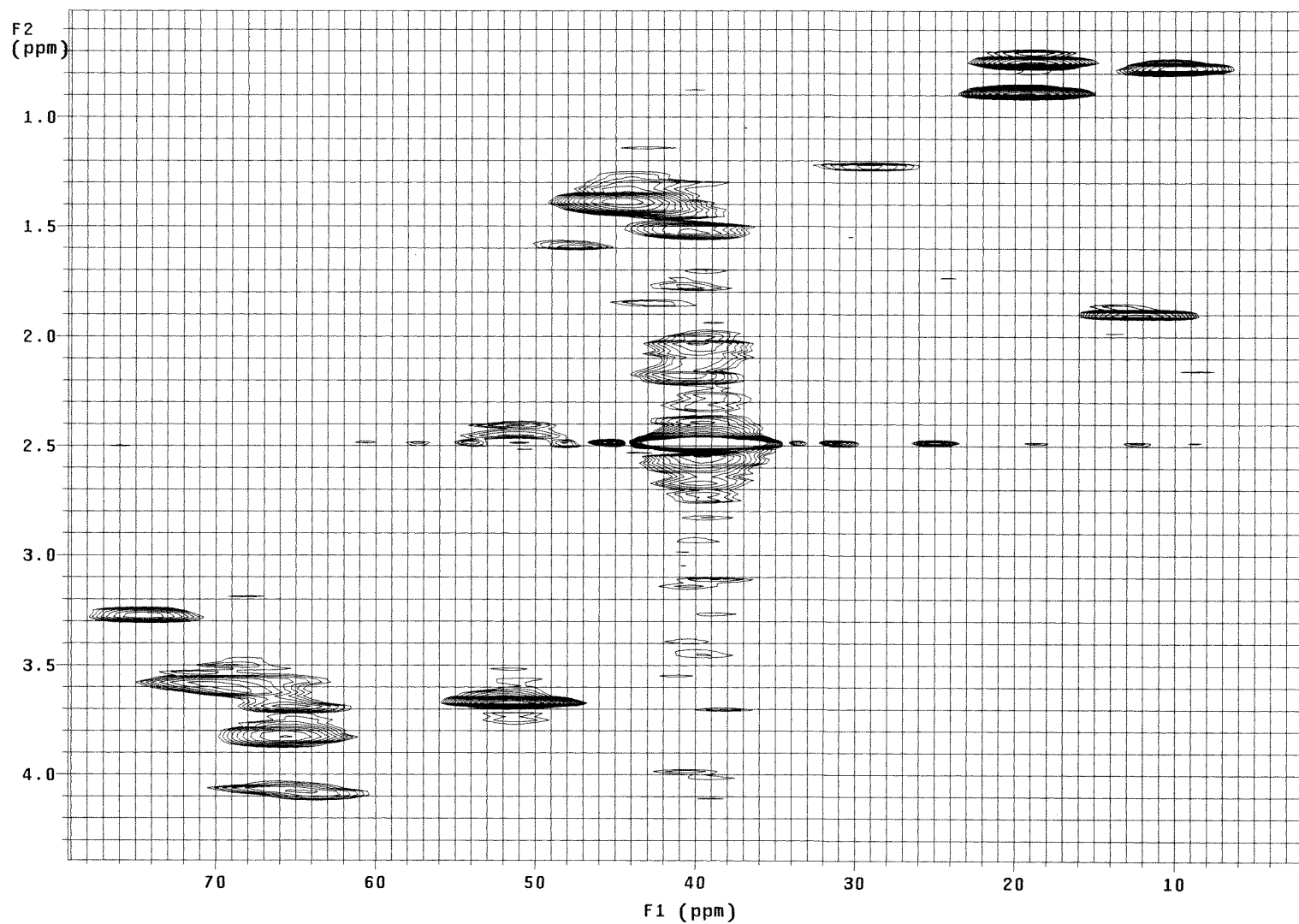


Figure S58. Expanded gHMQC spectrum of **10** (500 MHz, DMSO- d_6).

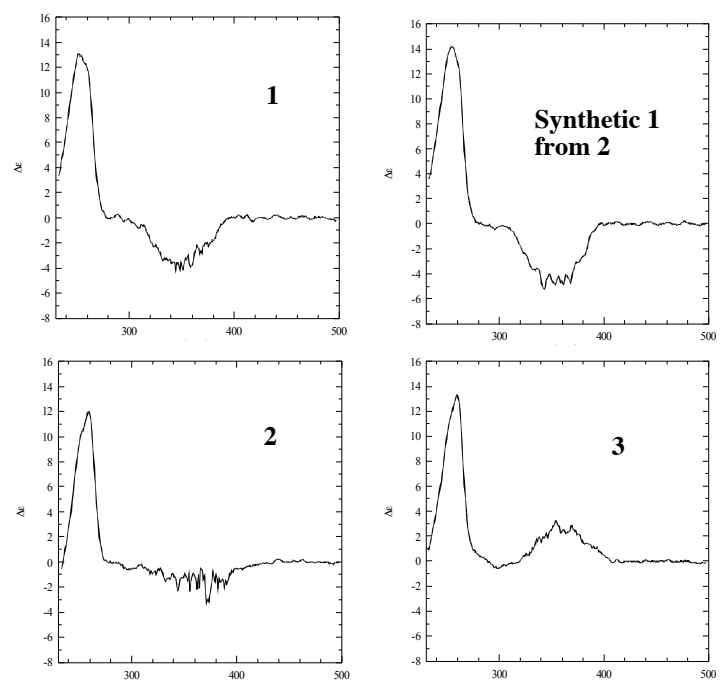


Figure S59. CD spectra of **1**, synthetic **1**, **2**, and **3** in methanol.