

SUPPORTING INFORMATION

for

The Potential of Arctic *Pseudogymnoascus* Fungi in the Biosynthesis of Natural Products

Tatiana V. Antipova ^{1,*}, Kirill V. Zaitsev ^{2,*}, Valentina P. Zhelifonova ¹, Sergey V. Tarlachkov ¹, Yuri K. Grishin ², Galina A. Kochkina ¹ and Mikhail B. Vainshtein ¹

¹ G.K. Skryabin Institute of Biochemistry and Physiology of Microorganisms, FRC Pushchino Scientific Centre of Biological Research, Russian Academy of Sciences, 142290 Pushchino, Russia; zhelifonova@yandex.ru (V.P.Z.); sergey@tarlachkov.ru (S.V.T.); gaga56@mail.ru (G.A.K.); vain@ibpm.pushchino.ru (M.B.V.)

² Department of Chemistry, M.V. Lomonosov Moscow State University, 119991 Moscow, Russia; grishin@nmr.chem.msu.ru

* Correspondence: tatantip@rambler.ru (T.V.A.); zaitsev@org.chem.msu.ru (K.V.Z.)

Table of Contents

CI mass-spectra Data for the Compounds

Figure S1. (a) The positive ions CI mass spectrum of 1 ; (b) The positive ions CI mass spectrum of 2	S4
--	----

NMR Spectral Data for the Compounds

Table S1. Data of the NMR spectra for (+)-Macrosphelide A (1).....	S5
Figure S2. ¹ H NMR Spectrum of (+)-Macrosphelide A (1) (CDCl ₃ , RT).....	S6
Figure S3. ¹³ C NMR Spectrum of (+)-Macrosphelide A (1) (CDCl ₃ , RT).....	S7
Figure S4. ¹³ C APT NMR Spectrum of (+)-Macrosphelide A (1) (CDCl ₃ , RT).....	S8
Figure S5. ¹ H- ¹ H COSY NMR Spectrum of (+)-Macrosphelide A (1) (CDCl ₃ , RT).....	S9
Figure S6. HSQC NMR spectrum of (+)-Macrosphelide A (1) (CDCl ₃ , RT).....	S10
Figure S7. HMQC NMR Spectrum of (+)-Macrosphelide A (1) (CDCl ₃ , RT).....	S11
Figure S8. HMBC NMR spectrum of (+)-Macrosphelide A (1) (CDCl ₃ , RT).....	S12
Figure S9. NOESY NMR spectrum of (+)-Macrosphelide A (1) (CDCl ₃ , RT).....	S13

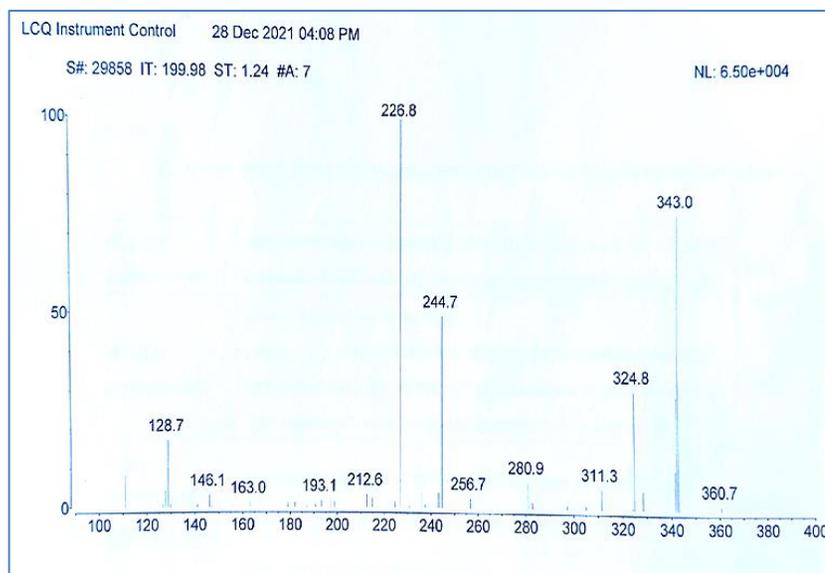
Table S2. Data of the NMR spectra for (+)-Macrosphelide B (2).....	S14
Figure S10. ¹ H NMR Spectrum of (+)-Macrosphelide B (2) (CDCl ₃ , RT).....	S15
Figure S11. ¹³ C NMR Spectrum of (+)-Macrosphelide B (2) (CDCl ₃ , RT).....	S16
Figure S12. ¹³ C APT NMR Spectrum of (+)-Macrosphelide B (2) (CDCl ₃ , RT).....	S17
Figure S13. HSQC NMR Spectrum of (+)-Macrosphelide B (2) (CDCl ₃ , RT).....	S18
Figure S14. HMBC NMR Spectrum of (+)-Macrosphelide B (2) (CDCl ₃ , RT).....	S19

Additional data on genome analysis

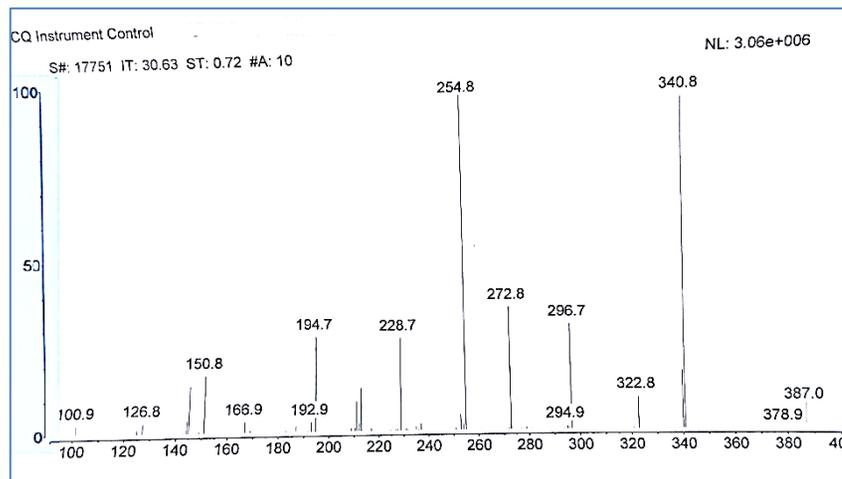
Figure S15. Identified secondary metabolites regions in the genome of the strain F-4518.....	S20
Figure S16. Identified secondary metabolites regions in the genome of the strain F-4519.....	S21

CI mass-spectra Data for the Compounds

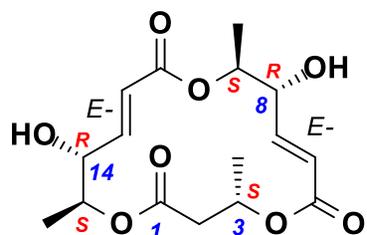
Figure S1. (a) The positive ions CI mass spectrum of **1**



(b) The positive ions CI mass spectrum of **2**



NMR Spectral Data for the Compounds



Chemical Formula: C₁₆H₂₂O₈
 Molecular Weight: 342,34
 (+)-Macrosphelide A (1)

Table S1. Data of the NMR spectra for (+)-Macrosphelide A (1).

Carbon number	¹ H NMR, δ, ppm	¹³ C NMR, δ, ppm
1	-	170.10
2	2.56 (br s, 1H) 2.55 (br s, 1H)	40.86
3	5.35-5.25 (m, 1H)	67.75
5	-	165.05
6	5.95 (dd, ³ J _{H-H} 15.7, ⁴ J _{H-H} 1.4 Hz, 1H)	122.43
7	6.84 (dd, ³ J _{H-H} 15.7, 9.5 Hz, 1H)	145.87
8	4.16-4.12 (m, 1H)	74.09
9	4.94-4.85 (m, 1H)	74.35
11	-	165.74
12	5.98 (dd, ³ J _{H-H} 15.6, ⁴ J _{H-H} 1.4 Hz, 1H)	121.99
13	6.82 (dd, ³ J _{H-H} 15.6, 9.2 Hz, 1H)	146.54
14	4.08-4.03 (m, 1H)	72.72
15	4.84-4.76 (m, 1H)	73.43
Me-3	1.28 (d, ³ J _{H-H} 6.5 Hz, 3H)	19.52
Me-9	1.38 (d, ³ J _{H-H} 6.5 Hz, 3H)	17.75
Me-15	1.31 (d, ³ J _{H-H} 6.5 Hz, 3H)	17.60
OH	3.80 (br s, 1H)	
OH	3.94 (br s, 1H)	

NMR Spectral Data for the Compounds

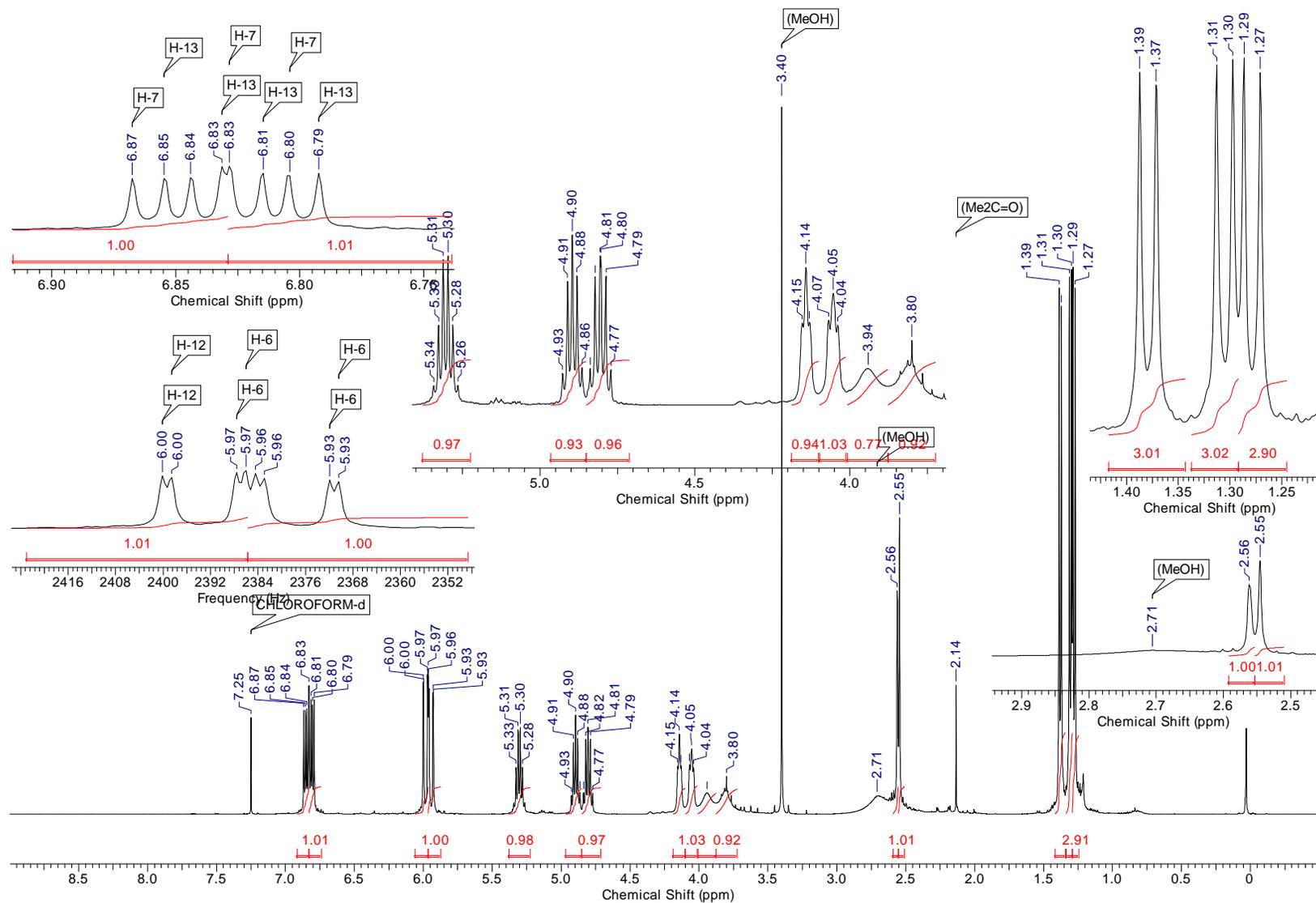


Figure S2. ^1H NMR Spectrum of (+)-Macrosphelide A (1) (CDCl_3 , RT).

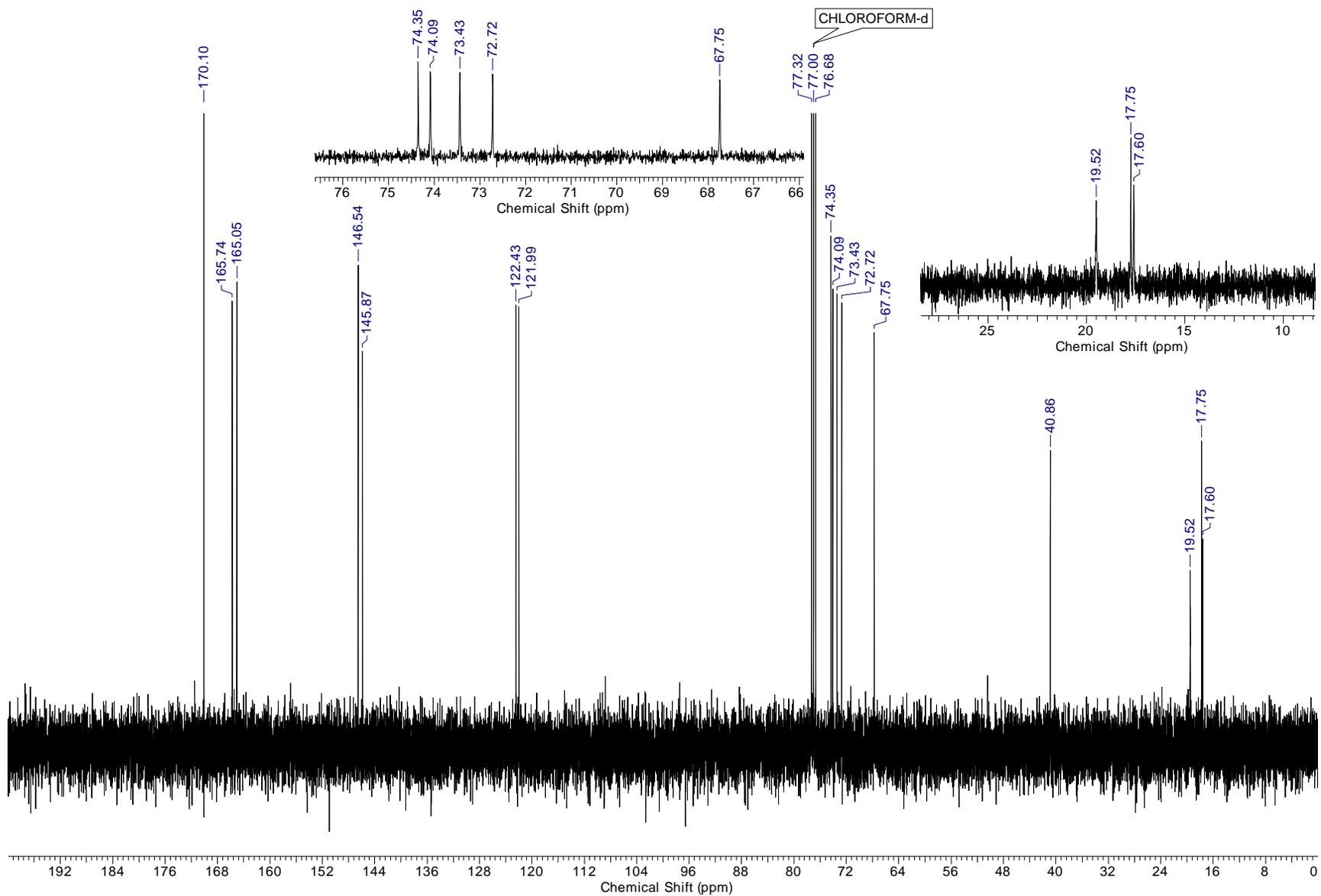


Figure S3. ^{13}C NMR Spectrum of (+)-Macrosphelide A (1) (CDCl_3 , RT).

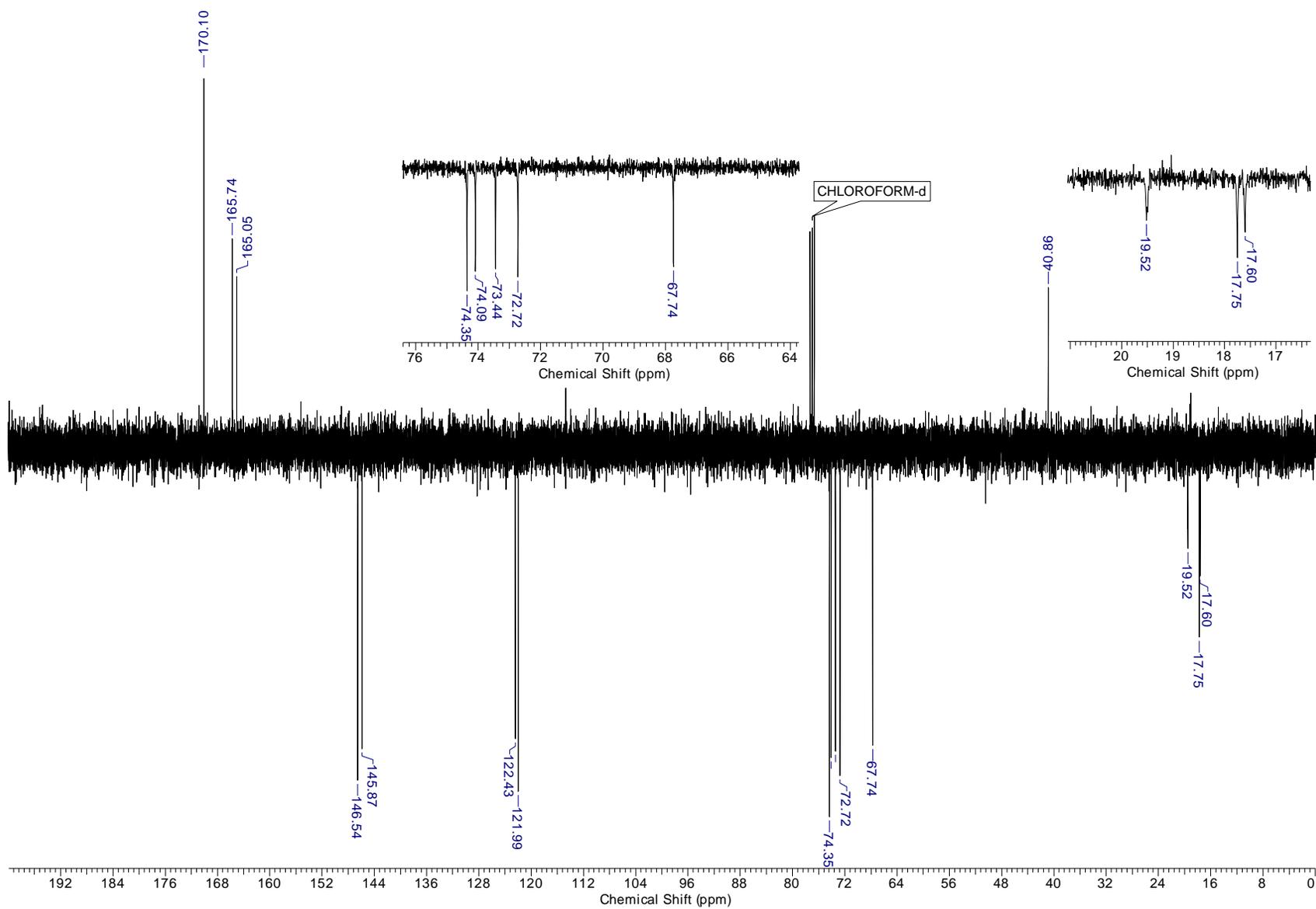


Figure S4. ^{13}C APT NMR Spectrum of (+)-Macrosphelide A (**1**) (CDCl_3 , RT).



Figure S5. ^1H - ^1H COSY NMR Spectrum of (+)-Macrosphelide A (**1**) (CDCl_3 , RT).

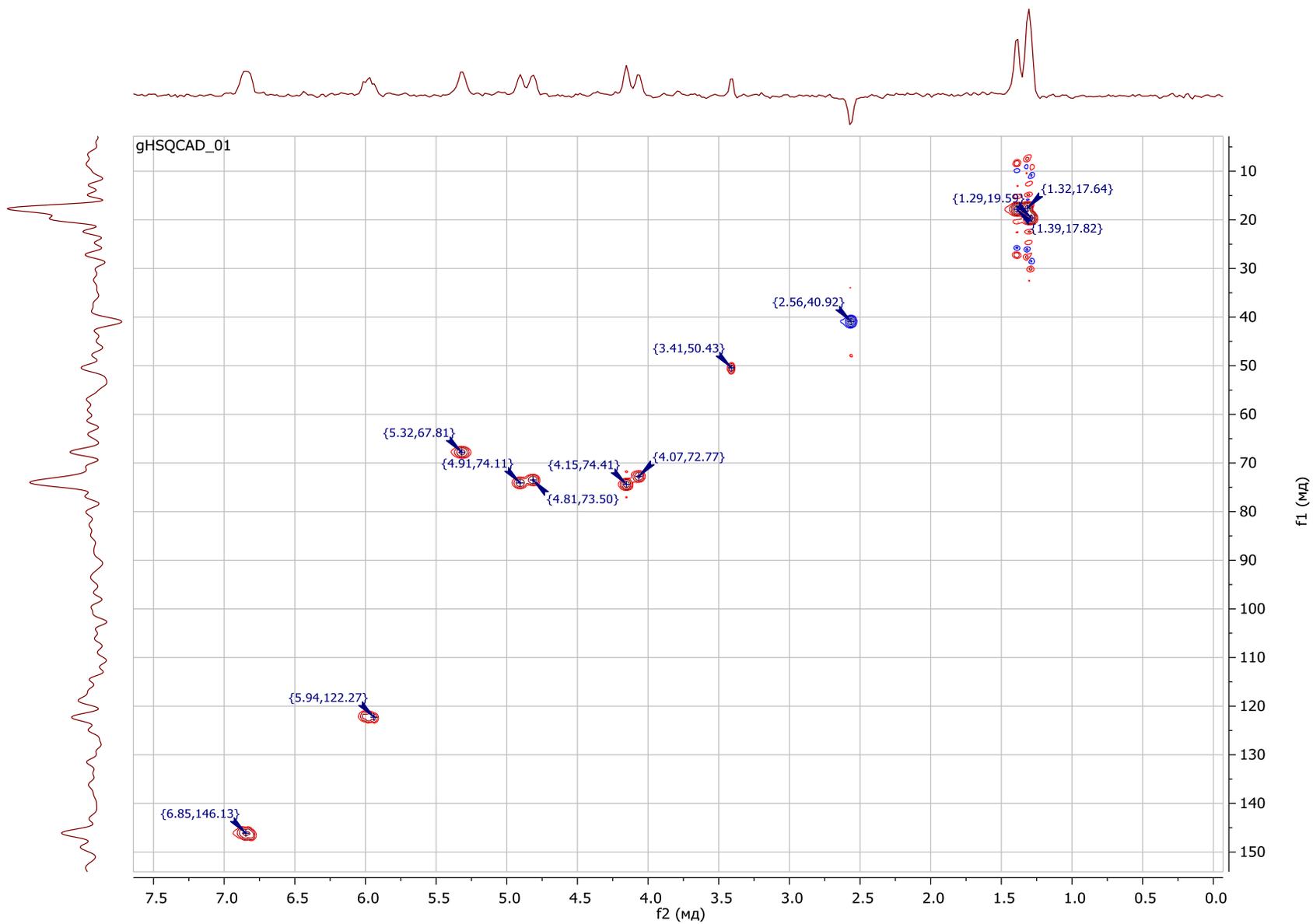


Figure S6. HSQC NMR spectrum of (+)-Macrosphelide A (**1**) (CDCl₃, RT).

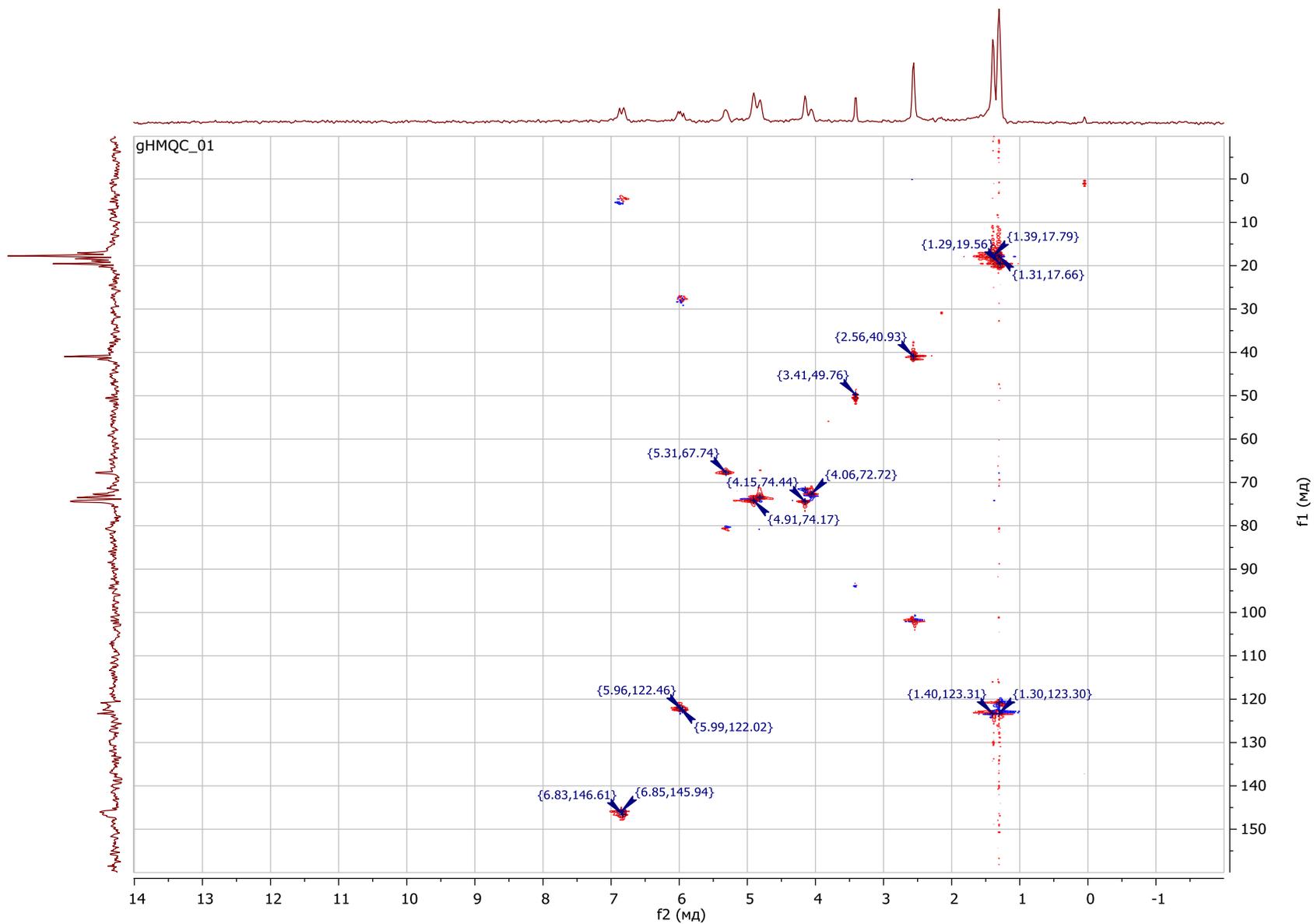


Figure S7. HMQC NMR Spectrum of (+)-Macrosphelide A (**1**) (CDCl₃, RT).

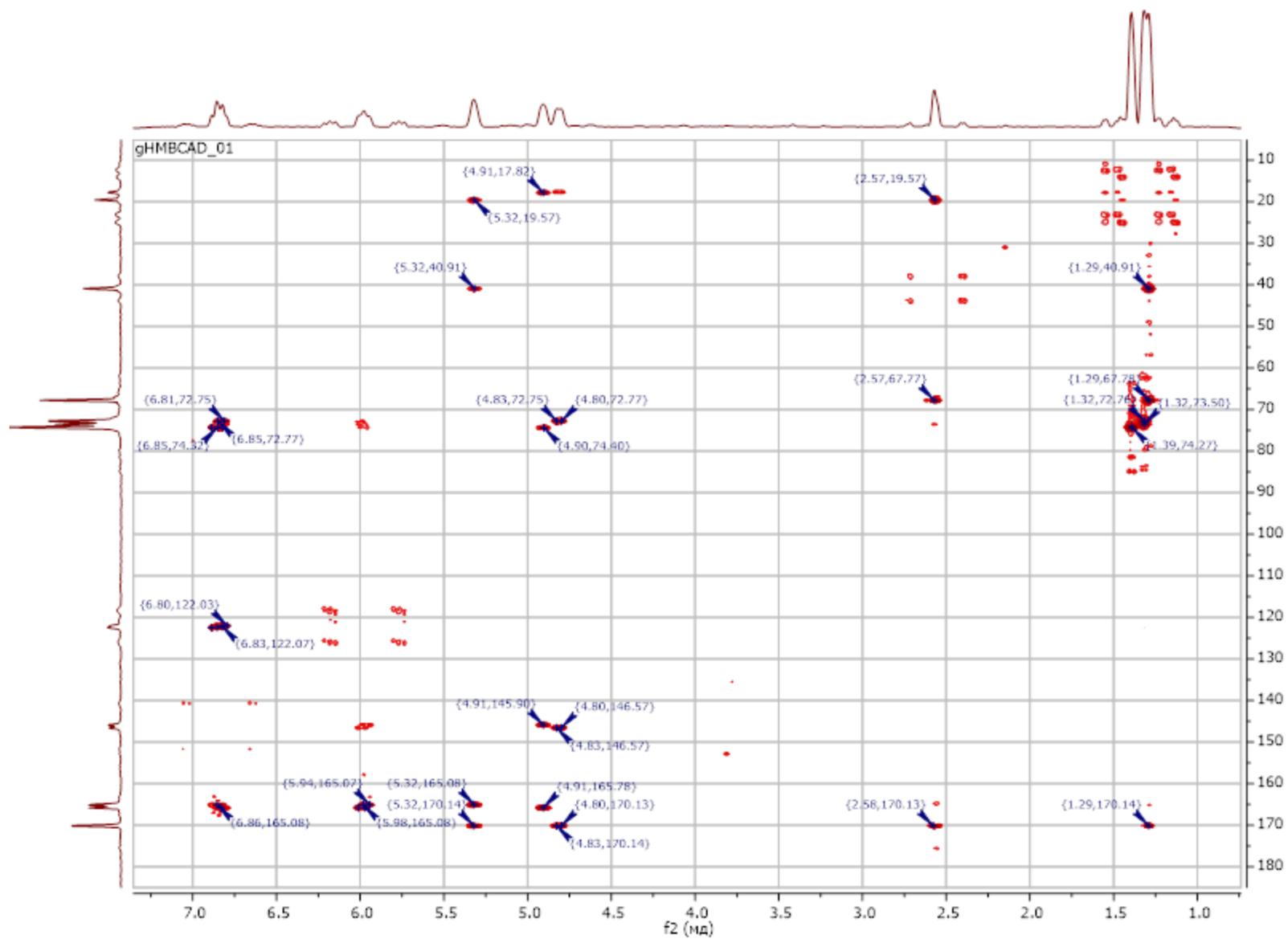


Figure S8. HMBC NMR spectrum of (+)-Macrosphelide A (**1**) (CDCl₃, RT).

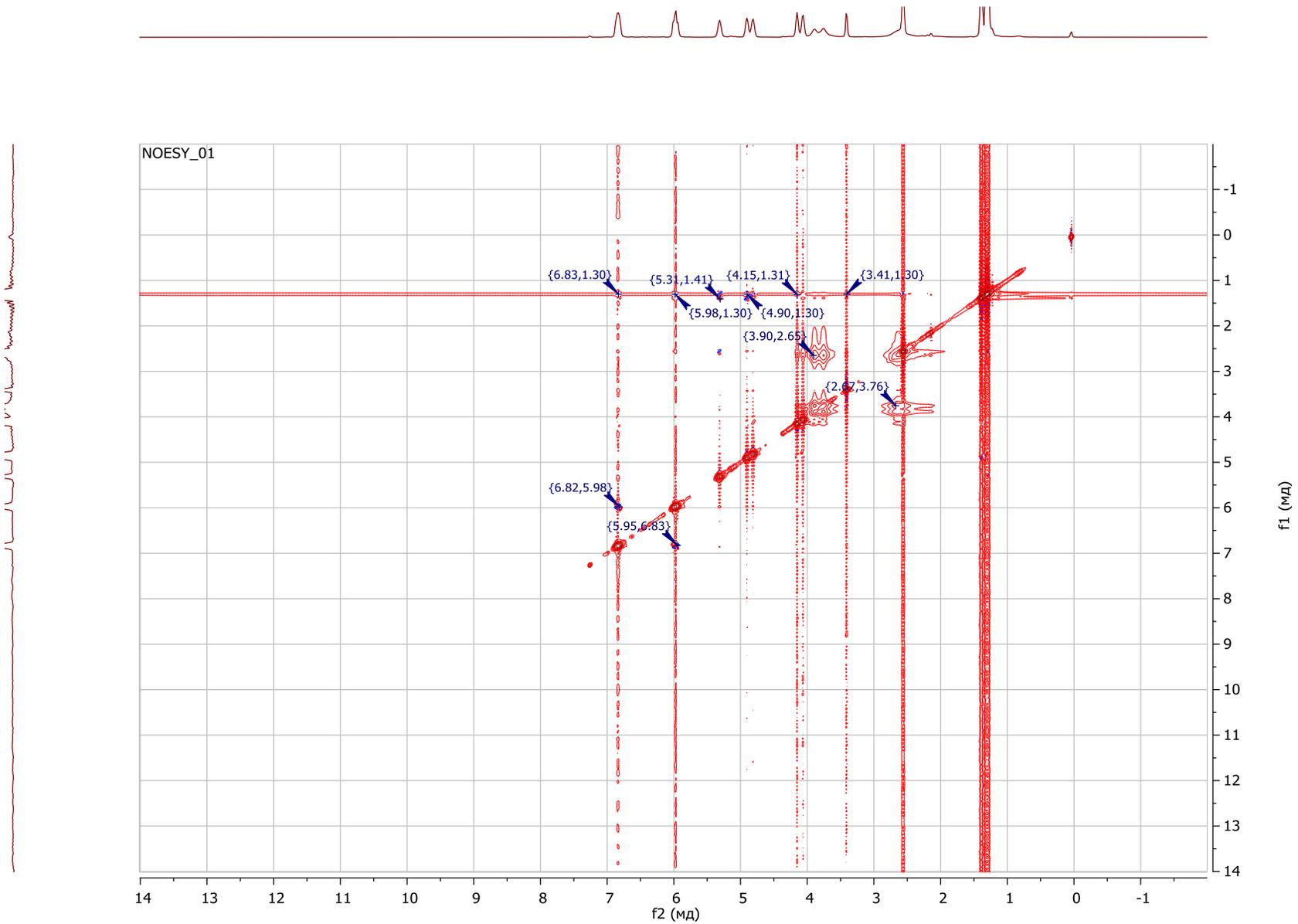
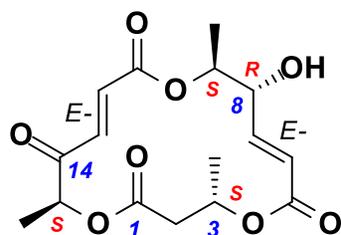


Figure S9. NOESY NMR spectrum of (+)-Macrosphelide A (**1**) (CDCl₃, RT).



Chemical Formula: C₁₆H₂₀O₈
 Molecular Weight: 340,33
 (+)-Macrosphelide B (2)

Table S2. Data of the NMR spectra for (+)-Macrosphelide B (2).

Carbon number	¹ H NMR, δ, ppm	¹³ C NMR, δ, ppm
1	-	170.33
2	2.81 (dd, ² J _{H-H} 16.2, ³ J _{H-H} 11.2 Hz, 1H) 2.61 (dd, ² J _{H-H} 16.2, ² J _{H-H} 2.3 Hz, 1H)	40.59
3	5.47-5.40 (m, 1H)	67.70
5	-	164.23
6	6.07 (dd, ³ J _{H-H} 15.8, ⁴ J _{H-H} 2.0 Hz, 1H)	122.50
7	6.90 (dd, ³ J _{H-H} 15.8, 3.8 Hz, 1H)	144.37
8	4.32-4.28 (m, 1H)	74.73
9	5.08-5.01 (m, 2H) *	75.75
11	-	165.30
12	7.01 (d, ³ J _{H-H} 15.7 Hz, 1H)	132.05
13	6.72 (d, ³ J _{H-H} 15.7 Hz, 1H)	132.54
14	-	196.19
15	5.08-5.01 (m, 2H) *	76.71
Me-3	1.34 (d, ³ J _{H-H} 6.4 Hz, 3H)	19.77
Me-9	1.48 (d, ³ J _{H-H} 6.8 Hz, 3H)	17.88
Me-15	1.42 (d, ³ J _{H-H} 7.8 Hz, 3H)	16.04
OH-3	1.23 (br s, 1H)	

* protons H-9 and H-15 are overlapped

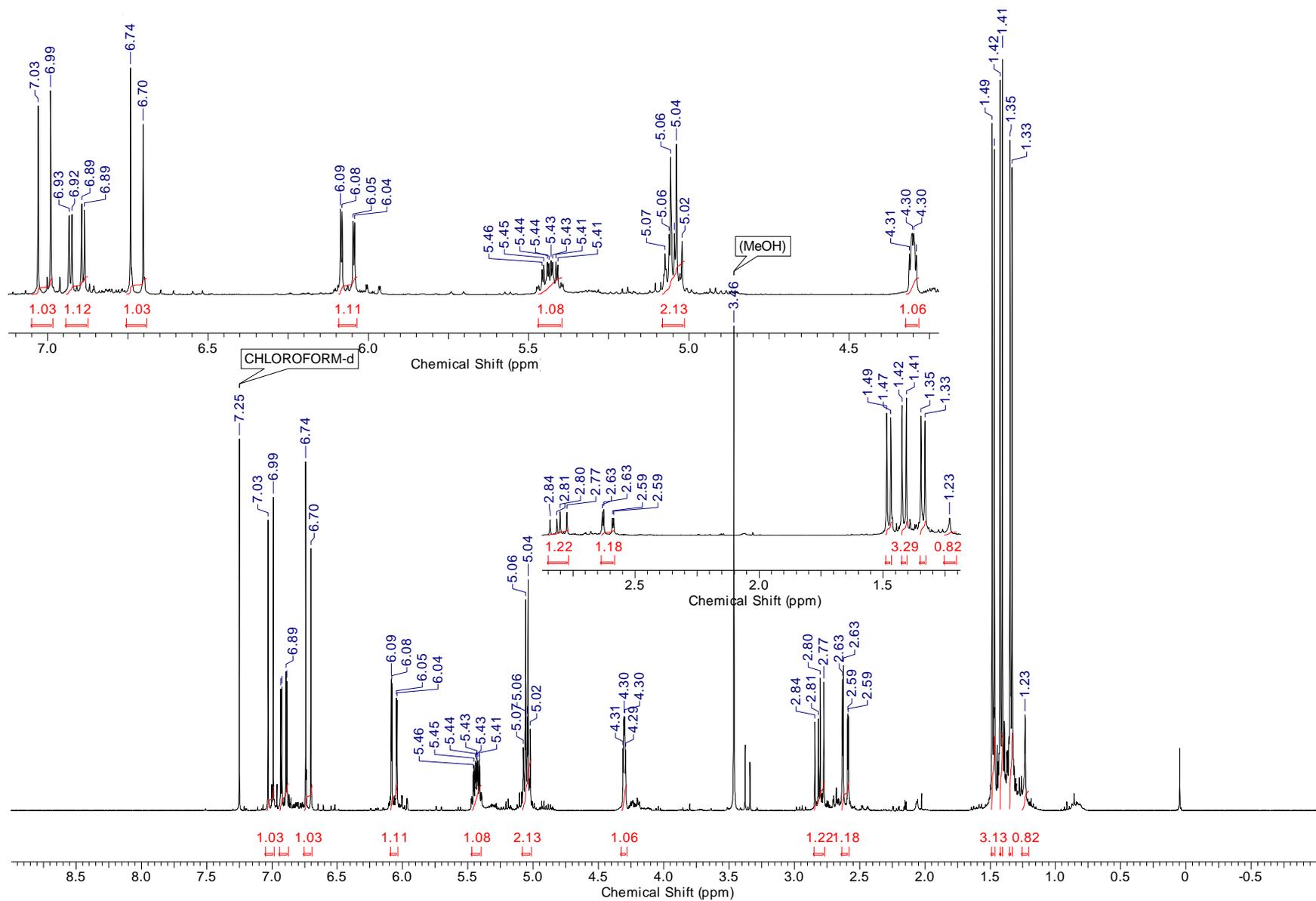


Figure S10. ^1H NMR Spectrum of (+)-Macrosphelide B (2) (CDCl_3 , RT).

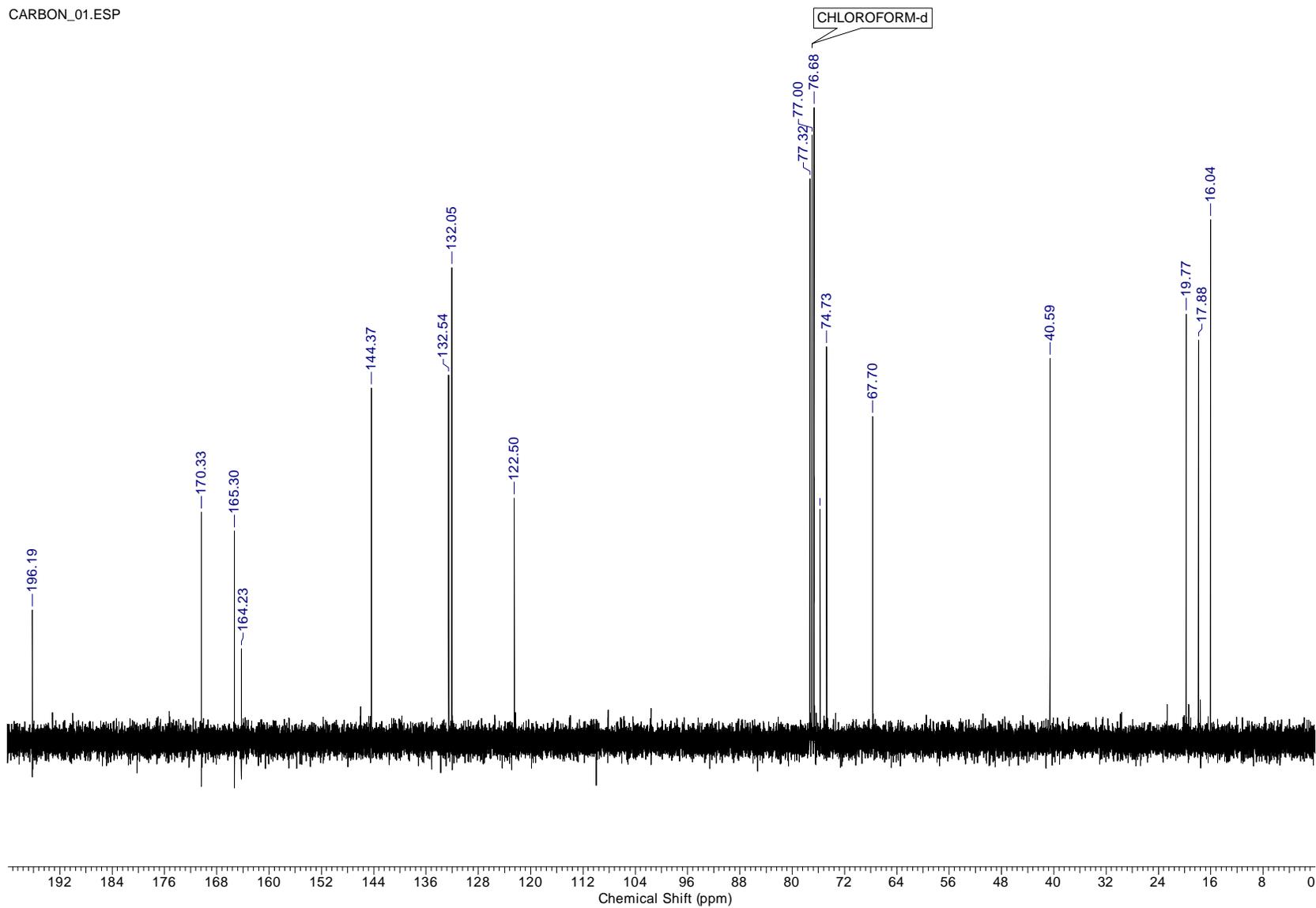


Figure S11. ^{13}C NMR Spectrum of (+)-Macrosphelide B (**2**) (CDCl_3 , RT).

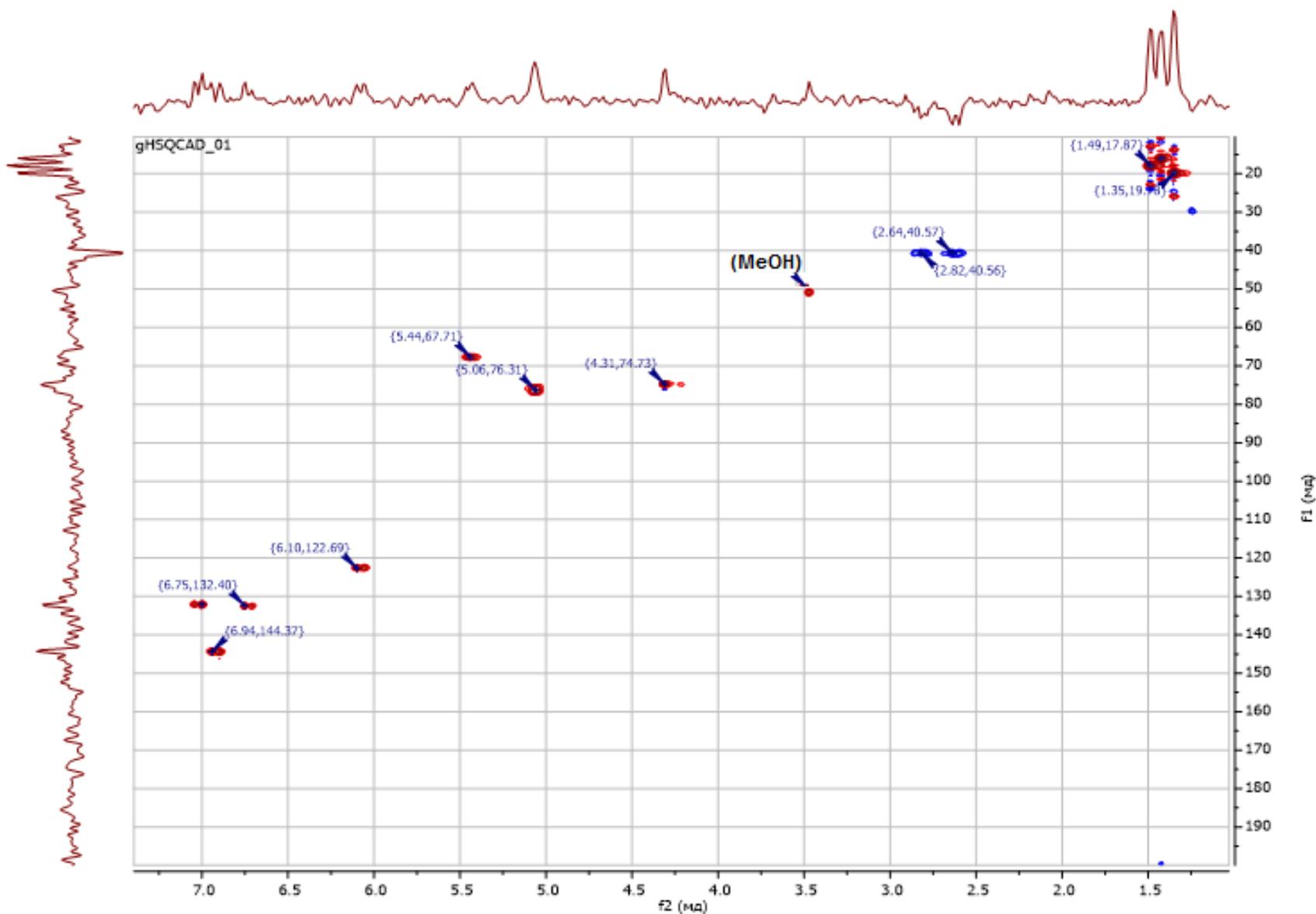


Figure S13. HSQC NMR Spectrum of (+)-Macrosphelide B (**2**) (CDCl₃, RT).

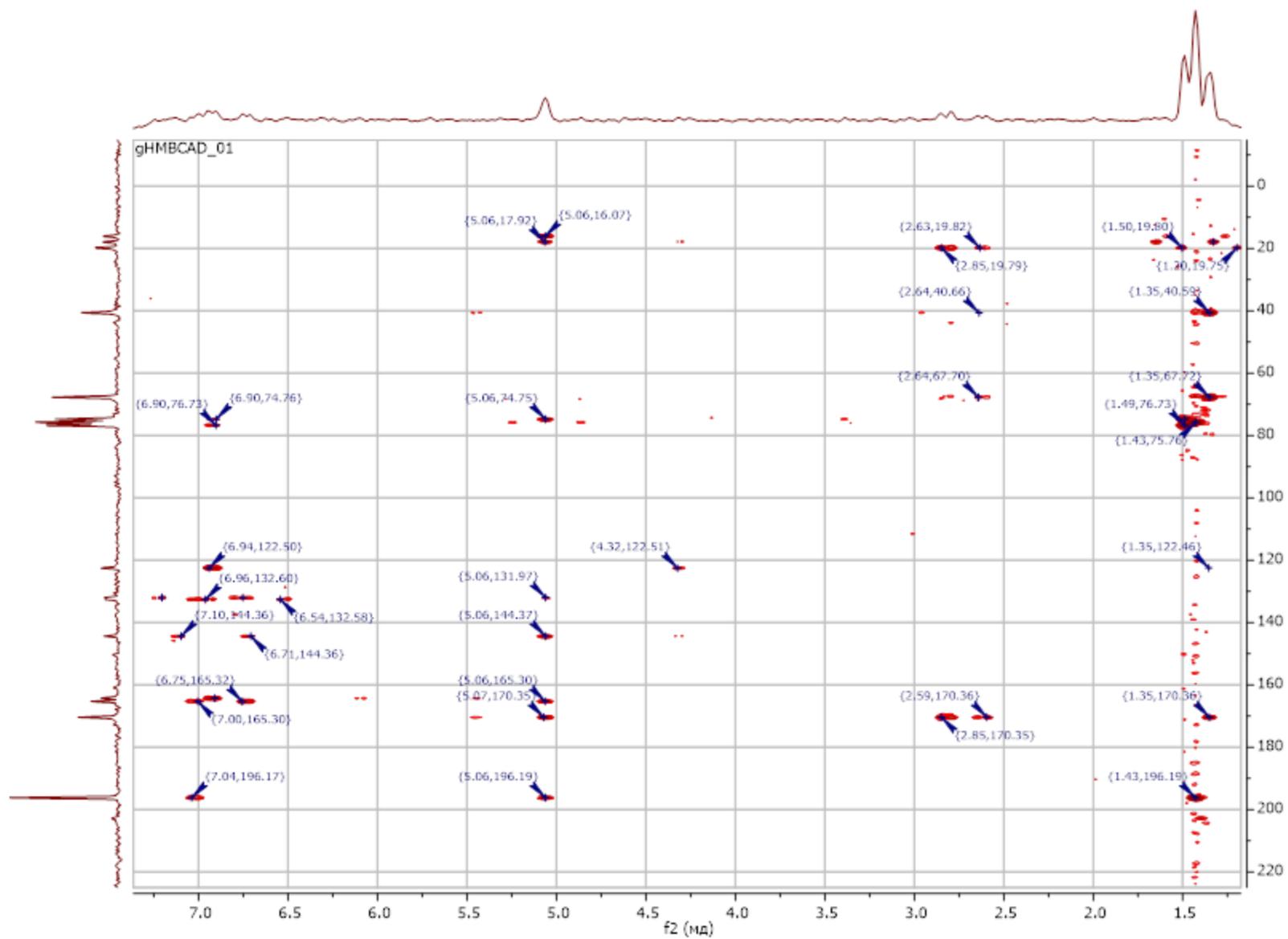


Figure S14. HMBC NMR Spectrum of (+)-Macrosphelide B (**2**) (CDCl₃, RT).

Additional data on genome analysis

Region	Type	From	To	Most similar known cluster		Similarity
Region 1.1	T1PKS	1	15,076	ustilaginoïdin N/ustilaginoïdin O/ustilaginoïdin M/ustilaginoïdin A/ustilaginoïdin F/ustilaginoïdin E/ustilaginoïdin D/ustilaginoïdin G	Polyketide	23%
Region 31.1	T3PKS	1	10,927			
Region 32.1	fungal-RIPP-like terpene	15,383	64,173			
Region 40.1	fungal-RIPP-like	1	13,166			
Region 53.1	T1PKS	6,889	32,830	secalonic acids	Polyketide	12%
Region 213.1	NRPS	1	39,657			
Region 230.1	NRPS	1	20,339			
Region 234.1	T1PKS	1	2,705			
Region 250.1	fungal-RIPP-like	1	9,011			
Region 254.1	terpene	1	7,416			
Region 270.1	fungal-RIPP-like	1	9,834			
Region 271.1	fungal-RIPP-like	1	35,154			
Region 327.1	fungal-RIPP-like	1	12,140			
Region 342.1	T1PKS	1	21,697			
Region 343.1	NRPS	1	24,150			
Region 349.1	NRPS	1	17,423			
Region 399.1	T1PKS	1	39,308			
Region 401.1	fungal-RIPP-like	1	47,258			
Region 410.1	T1PKS	1	16,082			
Region 416.1	NRPS	1	31,458			
Region 443.1	NRPS	1	27,038			
Region 496.1	T1PKS	4,600	51,229	F9775A/F9775B/orsellinic acid	Polyketide:iterative type I polyketide	50%
Region 565.1	T1PKS NRPS	1	17,795			
Region 660.1	T1PKS	19,241	69,157			
Region 675.1	terpene	1	11,769			
Region 700.1	T1PKS	1	4,839			
Region 714.1	T1PKS	1	27,887	monacolin K	Polyketide	22%
Region 750.1	NRPS	1	33,830			
Region 935.1	terpene	22,244	43,568			
Region 940.1	T1PKS	1	25,739	1,3,6,8-tetrahydroxynaphthalene	Polyketide	100%
Region 959.1	NRPS-like	1	18,201			
Region 969.1	NRPS-like	6,042	35,863			

Figure S15. Identified secondary metabolites regions in the genome of the strain F-4518.

Region	Type	From	To	Most similar known cluster	Similarity
Region 95.1	NRPS	1	18,276		
Region 122.1	NRPS	15,703	49,305		
Region 183.1	T1PKS	1	43,063	azanigerone A/azanigerone B/azanigerone C/azanigerone D/azanigerone E/azanigerone F	Polyketide 20%
Region 224.1	T1PKS	1	19,551		
Region 295.1	NRPS	1	14,105		
Region 342.1	T1PKS	1	18,121	scytalone/T3HN	Polyketide 40%
Region 384.1	NRPS-like	35,666	61,986	choline	NRP 100%
Region 430.1	T1PKS	1	22,692		
Region 446.1	fungal-RIPP-like	1	22,491		
Region 587.1	NRPS	1	3,851		
Region 794.1	T1PKS	1	8,518		
Region 813.1	NRPS	1	29,183		
Region 850.1	T1PKS	1	20,490		
Region 892.1	fungal-RIPP-like	1	51,717		
Region 914.1	T1PKS , NRPS	1	32,243	phyllostictine A/phyllostictine B	NRP+Polyketide 20%
Region 960.1	NRPS , T1PKS	1	23,427	phomacin D/phomacin E	Polyketide+NRP 22%
Region 966.1	T1PKS	1	23,695		

Figure S16. Identified secondary metabolites regions in the genome of the strain F-4519.