

Supporting Information:

Landomycins P-W, Cytotoxic Angucyclines from *Streptomyces cyanogenus* S-136

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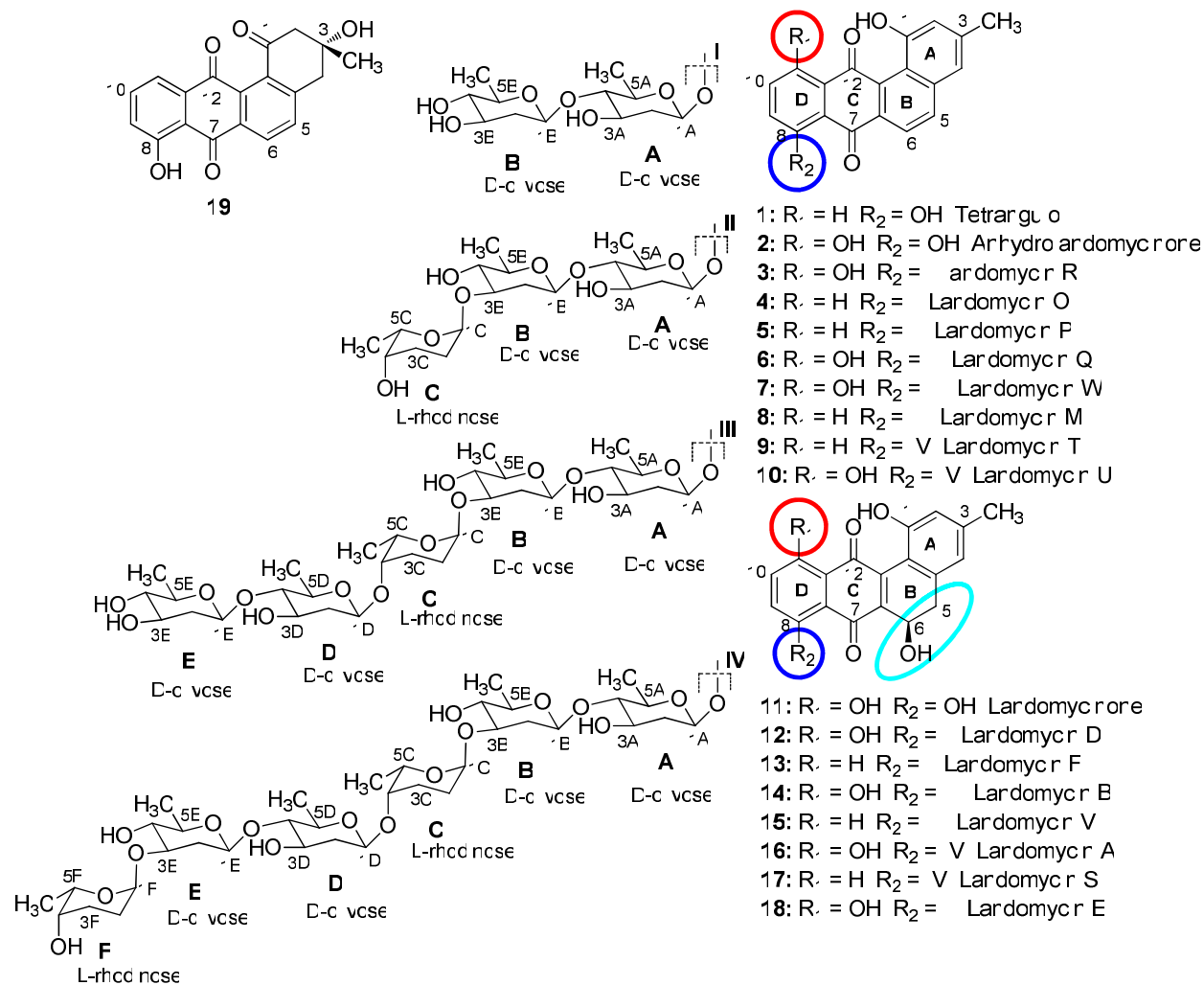
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Supporting Information

HPLC analysis of the crude extract obtained from the *Streptomyces cyanogenus* S-136 strain; work-up procedure scheme; ^1H and ^{13}C NMR spectra of isolated angucyclin(on)es (**1-17, 19**) and data of their cytotoxicity.



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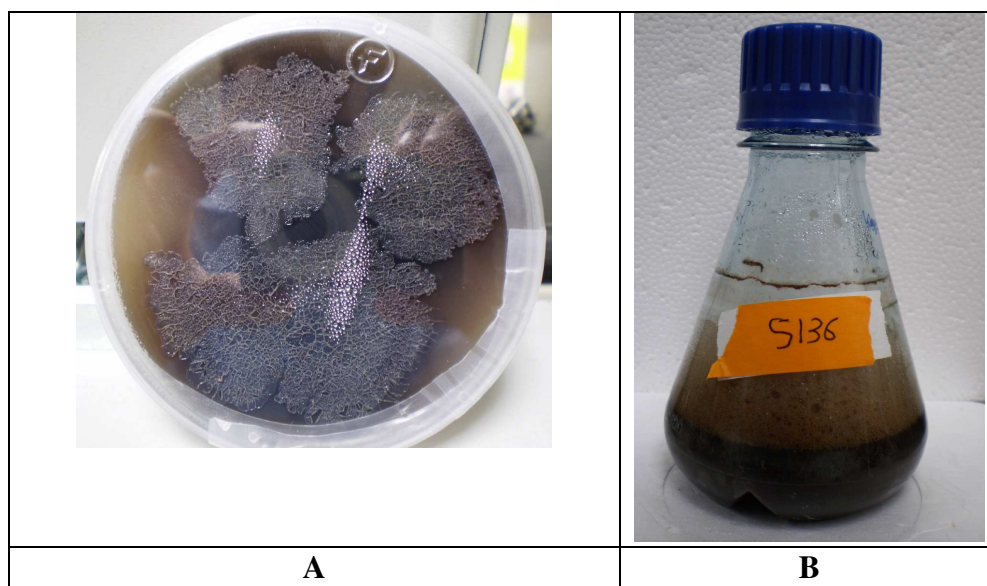


Figure S1: **A)** The *Streptomyces cyanogenus* S-136 was cultivated on M₂-agar plates at 28 °C for 2 days; **B)** A 100 ml of the reddish brown culture broth from *Streptomyces cyanogenus* S-136 after inoculation and cultivation at 28 °C (250 rpm) for 48 hrs on SG-medium.

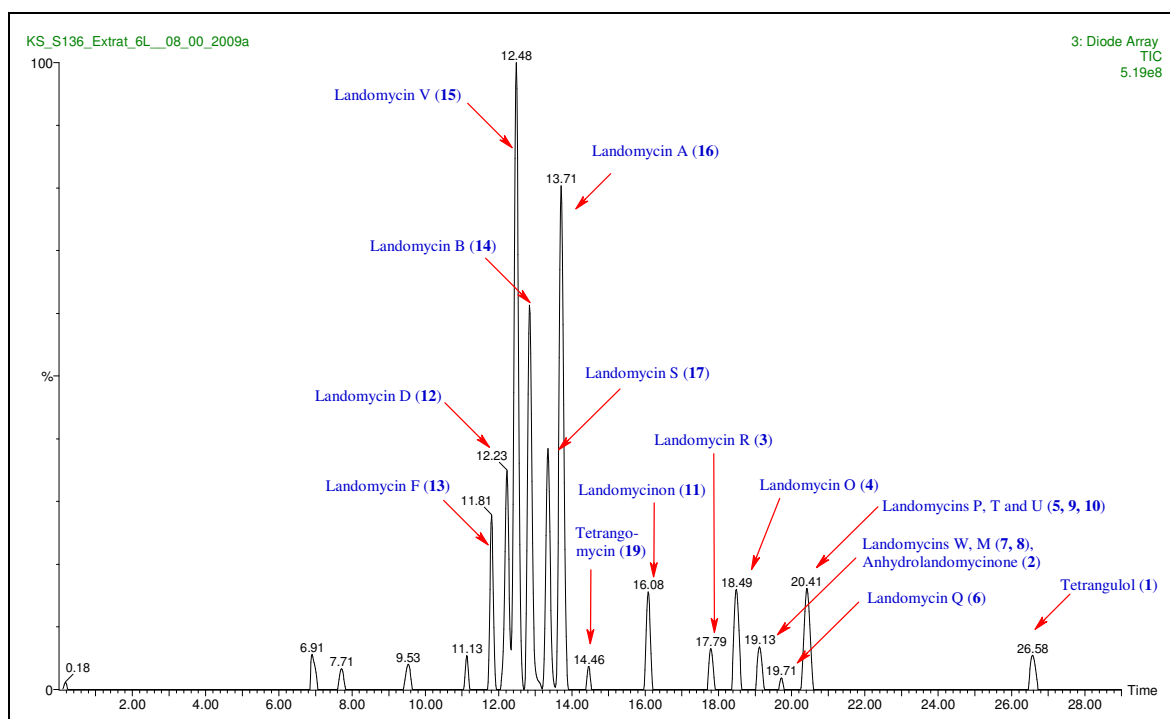


Figure S2: HPLC analysis of the crude extract obtained from the *Streptomyces cyanogenus* S-136 strain, the detection wavelength was 254 nm. Solvent A: H₂O, solvent B: acetonitrile; flow

rate: 0.5 mLmin⁻¹; 0–15 min, 75-0% A (linear gradient), 15–24 min 0% A and 100 % B, 24–26 min 0-75% A (linear gradient), 26–29 min 75% A.

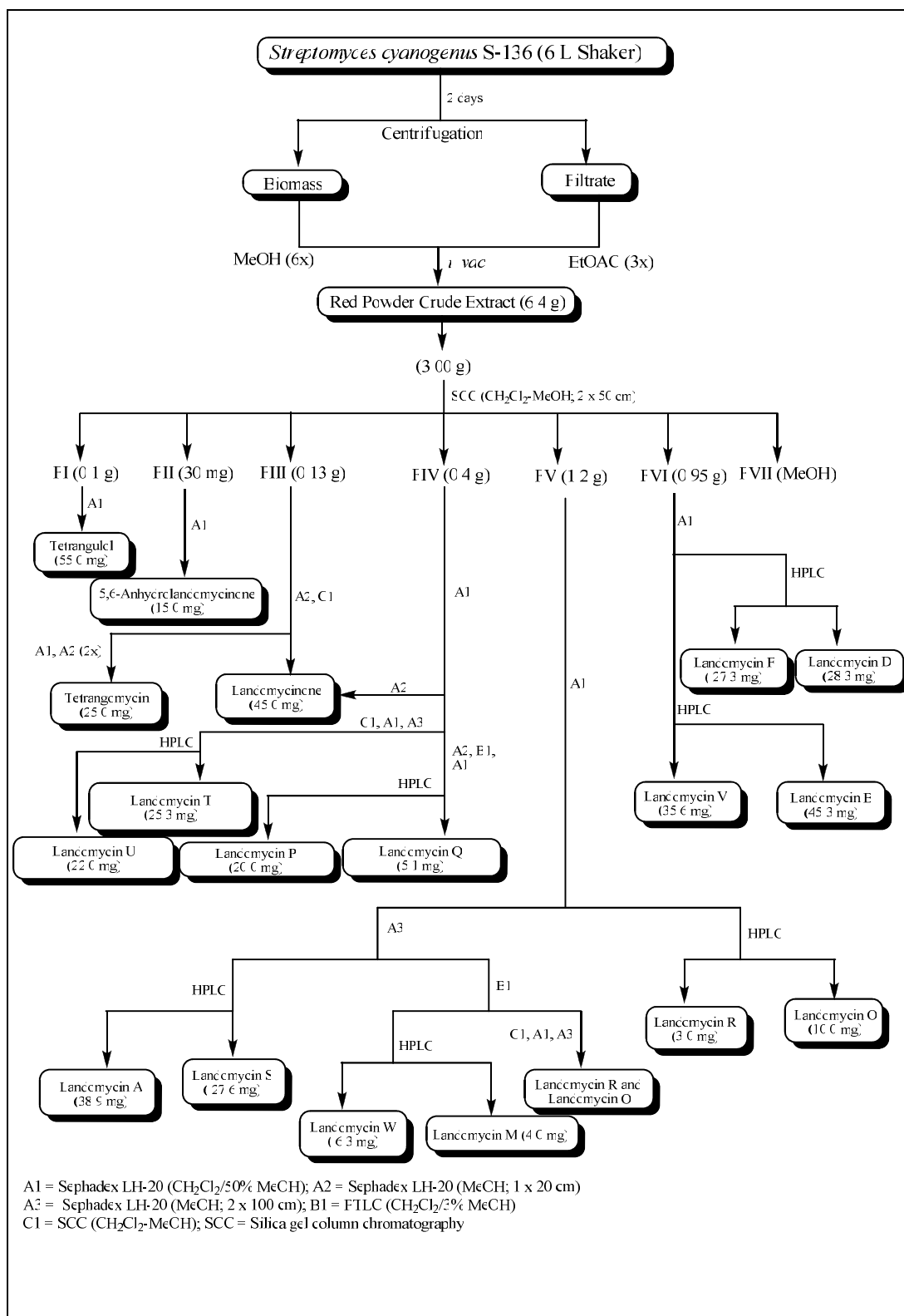


Figure S3: Work-up procedure of extracts from the *Streptomyces cyanogenus* S-136

The antitumor potency of the angucycline molecules differed according to their substitution pattern (Supporting Information, Table S1).

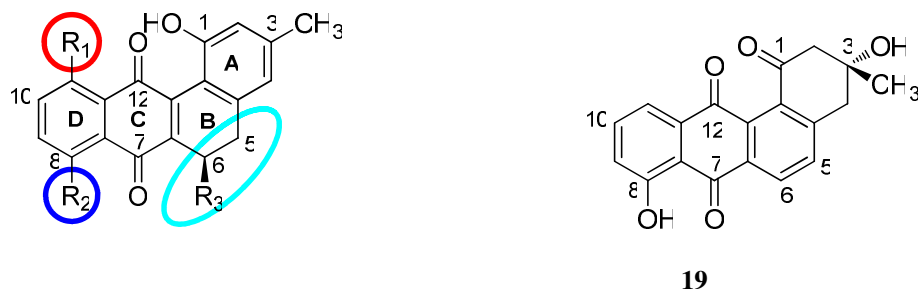


Table S1: Cytotoxic activity of angucyclin(on)es **1-17** and **19** against an estrogen receptor (ER) positive (MCF-7) and an ER-refractory human cancer cell line (MDA-231)

No.	Name	Structure	Activites (mean IC ₅₀ , μ M)	
			MCF-7	MDA-231
1	Tetrangulol	R ₁ = H, R ₂ = OH, R ₃ = H, $\Delta^{5,6}$	NP*	1.5
2	Anhydrolandomycinone	R ₁ = OH, R ₂ = OH, R ₃ = H, $\Delta^{5,6}$	1.8	2
3	landomycin R	R ₁ = OH, R ₂ = disaccharide (I), R ₃ = H, $\Delta^{5,6}$	NP*	1.7
4	Landomycin O	R ₁ = H, R ₂ = disaccharide (I), R ₃ = H, $\Delta^{5,6}$	NP*	3.55
5	Landomycin P	R ₁ = H, R ₂ = trisaccharide (II), R ₃ = H, $\Delta^{5,6}$	NP*	3.55
6	Landomycin Q	R ₁ = OH, R ₂ = trisaccharide (II), R ₃ = H, $\Delta^{5,6}$	NP*	3.85
7	Landomycin W	R ₁ = OH, R ₂ = pentasaccharide (III), R ₃ = H, $\Delta^{5,6}$	6.9	2.65
8	Landomycin M	R ₁ = H, R ₂ = pentasaccharide (III), R ₃ = H, $\Delta^{5,6}$	7.1	1.9
9	Landomycin T	R ₁ = H, R ₂ = hexasaccharide (IV), R ₃ = H, $\Delta^{5,6}$	NP*	1.85
10	Landomycin U	R ₁ = OH, R ₂ = hexasaccharide (IV), R ₃ = H, $\Delta^{5,6}$	2.1	7.3
11	Landomycinone	R ₁ = OH, R ₂ = OH, R ₃ = OH	2.1	1.4
12	Landomycin D	R ₁ = OH, R ₂ = disaccharide (I), R ₃ = OH	7.6	1.75
13	Landomycin F	R ₁ = H, R ₂ = disaccharide (I), R ₃ = OH	NP*	1.8
14	Landomycin B	R ₁ = OH, R ₂ = pentasaccharide (III), R ₃ = OH	4.25	1.8
15	Landomycin V	R ₁ = H, R ₂ = pentasaccharide (III), R ₃ = OH	6.1	1.5
16	Landomycin A	R ₁ = OH, R ₂ = hexasaccharide (IV), R ₃ = OH	2.5	1.4
17	Landomycin S	R ₁ = H, R ₂ = hexasaccharide (IV), R ₃ = OH	6.7	1.5
19	Tetrangomycin	Structure 19	NP*	1.55

NP* = not potent

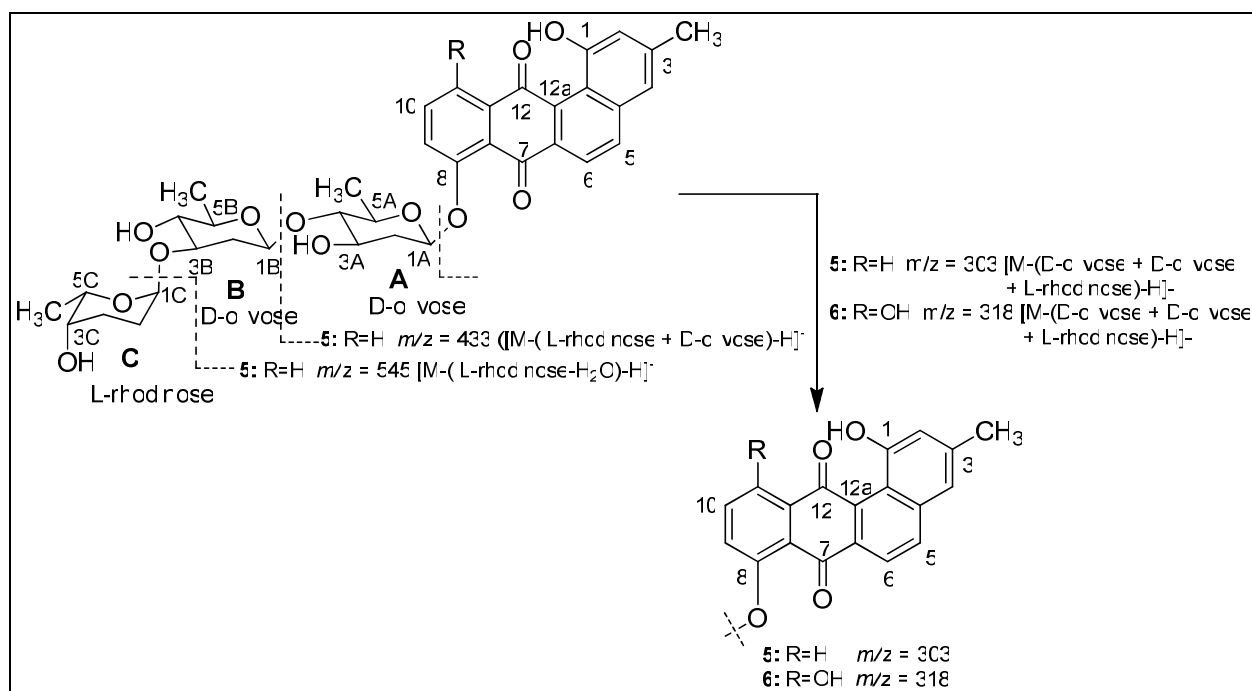


Figure S4: (-) ESI-MS/MS Fragmentations pattern scheme in Landomycins P (**5**) and Q (**6**)

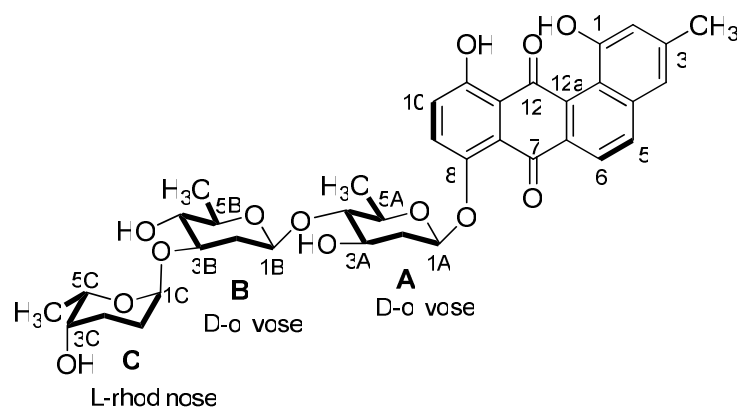


Figure S5: 1H - 1H COSY (bold lines) couplings in Landomycin Q (**6**)

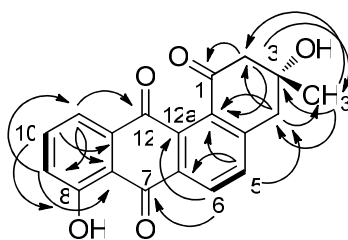


Figure S6: Selected HMBC ($\rightarrow$) couplings in Tetrangomycin (**19**)

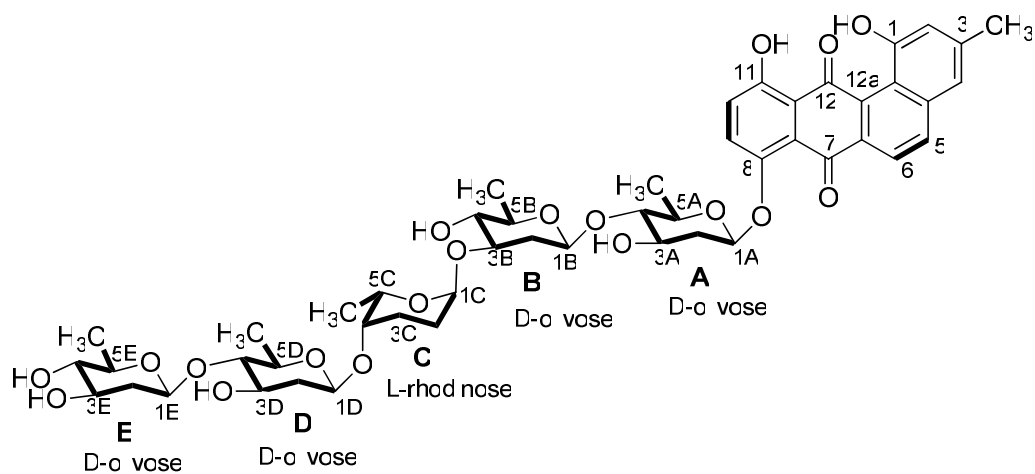


Figure S7: ^1H - ^1H COSY (bold lines) couplings in Landomycin W (**7**)

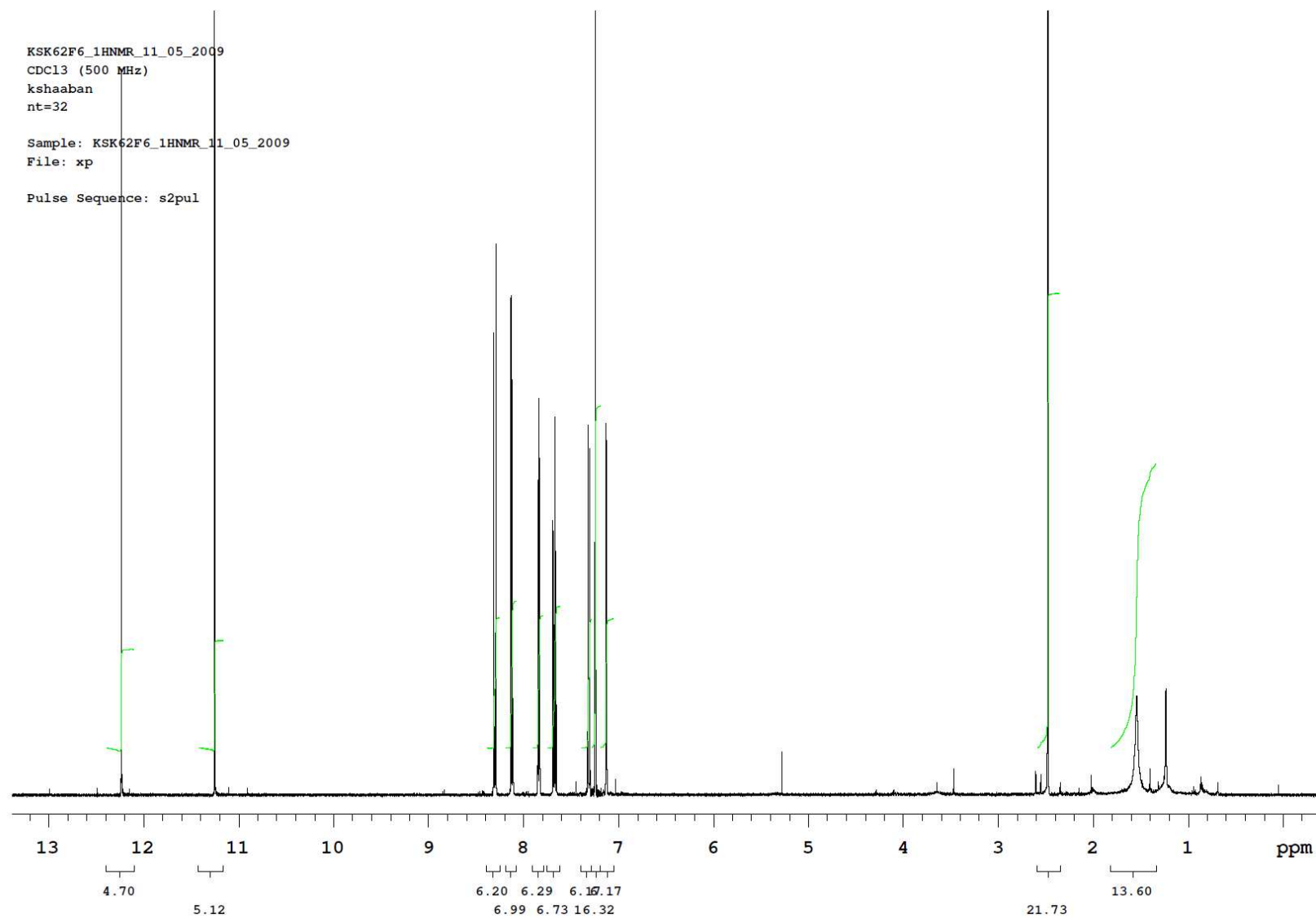


Figure S8: ¹H NMR spectrum (CDCl₃, 500 MHz) of Tetrangulol (**1**)
S10

KSS136F1_13C_08_18_2009
 13C NMR (125 MHz)
 KShaaban
 15 h

exp3 Carbon

SAMPLE SPECIAL
 date Aug 17 2009 temp not used
 solvent cdcl3 gain 30
 file /home/khaled/~ spin 20
 vnmrsys/data/KSS13~ hst 0.008
 6F1_13C_08_18_2009~ pw90 11.900
 .fid alfa 10.000

ACQUISITION FLAGS
 sw 30487.8 il n
 at 1.300 in n
 np 79298 dp y
 fb 17000 hs nn
 bs 64
 dl 1.000 lb 0.50
 nt 20000 fn not used
 ct 20000 DISPLAY

TRANSMITTER sp -935.4
 tn C13 wp 27811.9
 sfrq 125.657 rfl 11724.1
 tof 1285.0 rfp 9703.4
 tpwr 59 rp 59.6
 pw 5.950 lp -136.3

DECOUPLER PLOT
 dn H1 wc 250
 dof 0 sc 0
 dm yyy vs 878557
 dnm w th 7
 dpwr 32 ai cdc ph
 dmf 11912

INDEX	FREQUENCY	PPM	HEIGHT
1	23846.2	189.793	7.8
2	23623.4	188.019	9.1
3	20335.3	161.849	13.0
4	19536.5	155.492	11.7
5	17865.0	142.188	12.4
6	17502.2	139.300	13.8
7	17319.3	137.845	31.1
8	17218.9	137.045	13.9
9	16962.1	135.002	18.2
10	15695.3	124.919	11.2
11	15333.8	122.043	25.0
12	15263.1	121.480	10.0
13	15257.5	121.435	20.8
14	15120.3	120.343	12.0
15	15104.0	120.213	8.8
16	14428.1	114.834	6.6
17	9735.1	77.482	116.8
18	9703.4	77.230	120.9
19	9671.3	76.975	119.8
20	2697.9	21.473	8.6
21	2693.2	21.436	6.6

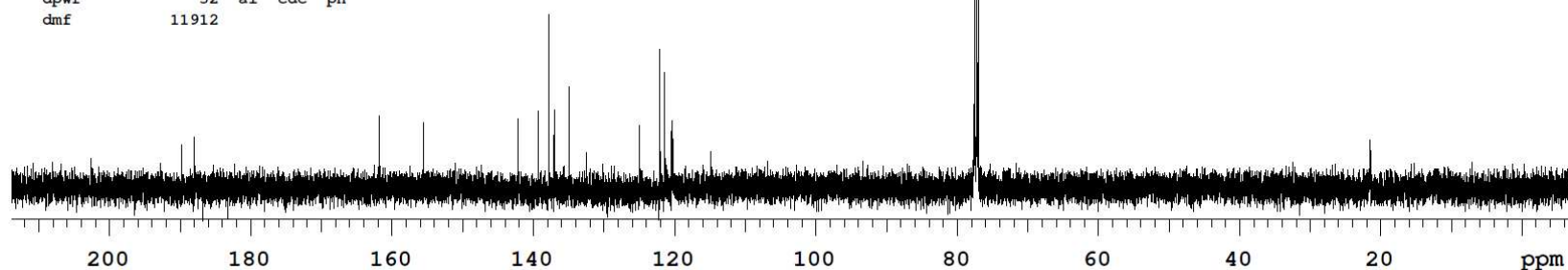


Figure S9: ^{13}C NMR spectrum (CDCl_3 , 150 MHz) of Tetrangulol (1)

KSS136F3B1_1H_08_24_2009
1H NMR (500 MHz)
KShaaban
nt=32
CDCl3

Sample: KSS136F3B1_1H_08_24_2009
File: xp
Pulse Sequence: s2pul

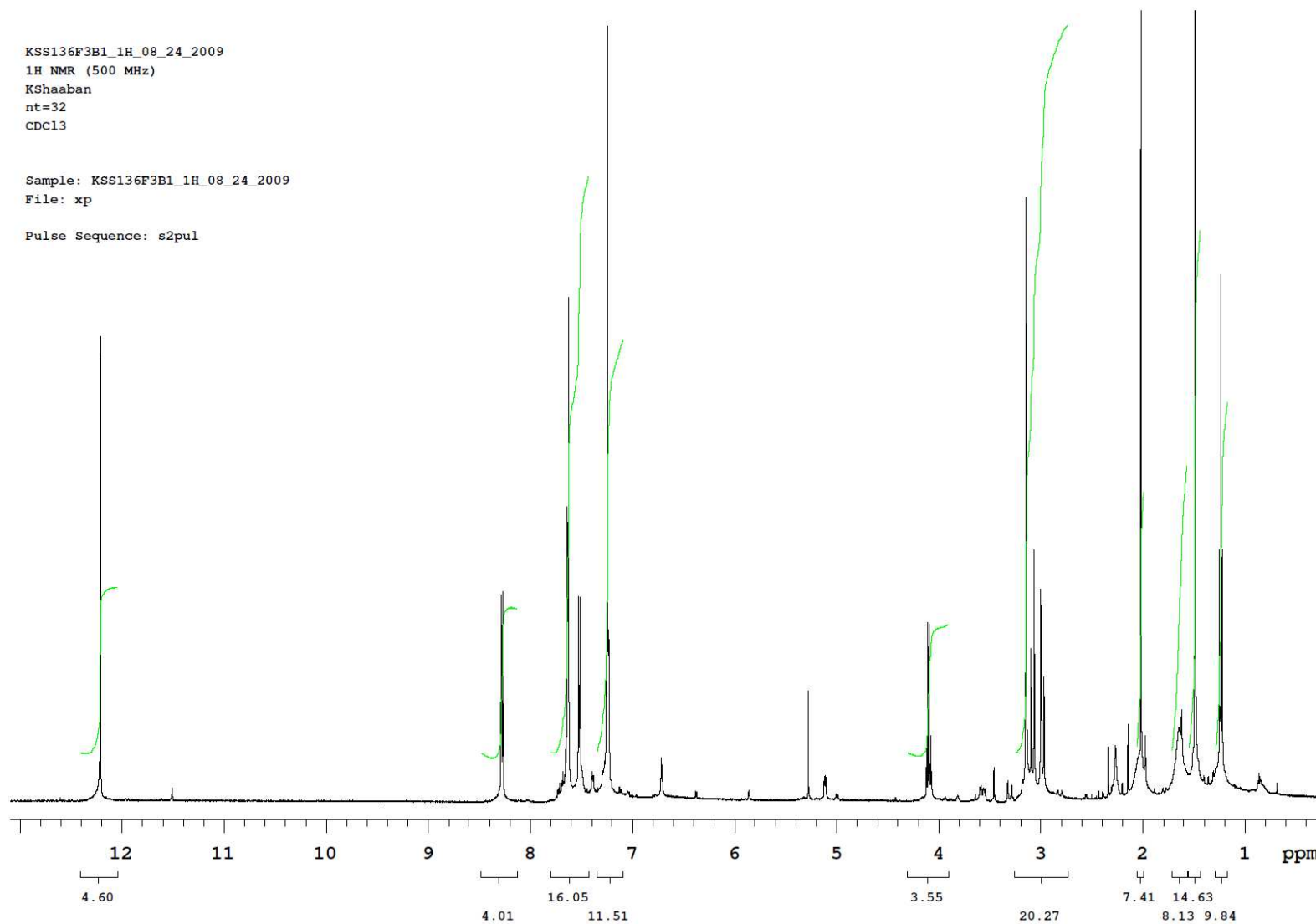


Figure S10: ^1H NMR spectrum (CDCl_3 , 500 MHz) of Tetrangomycin (19)

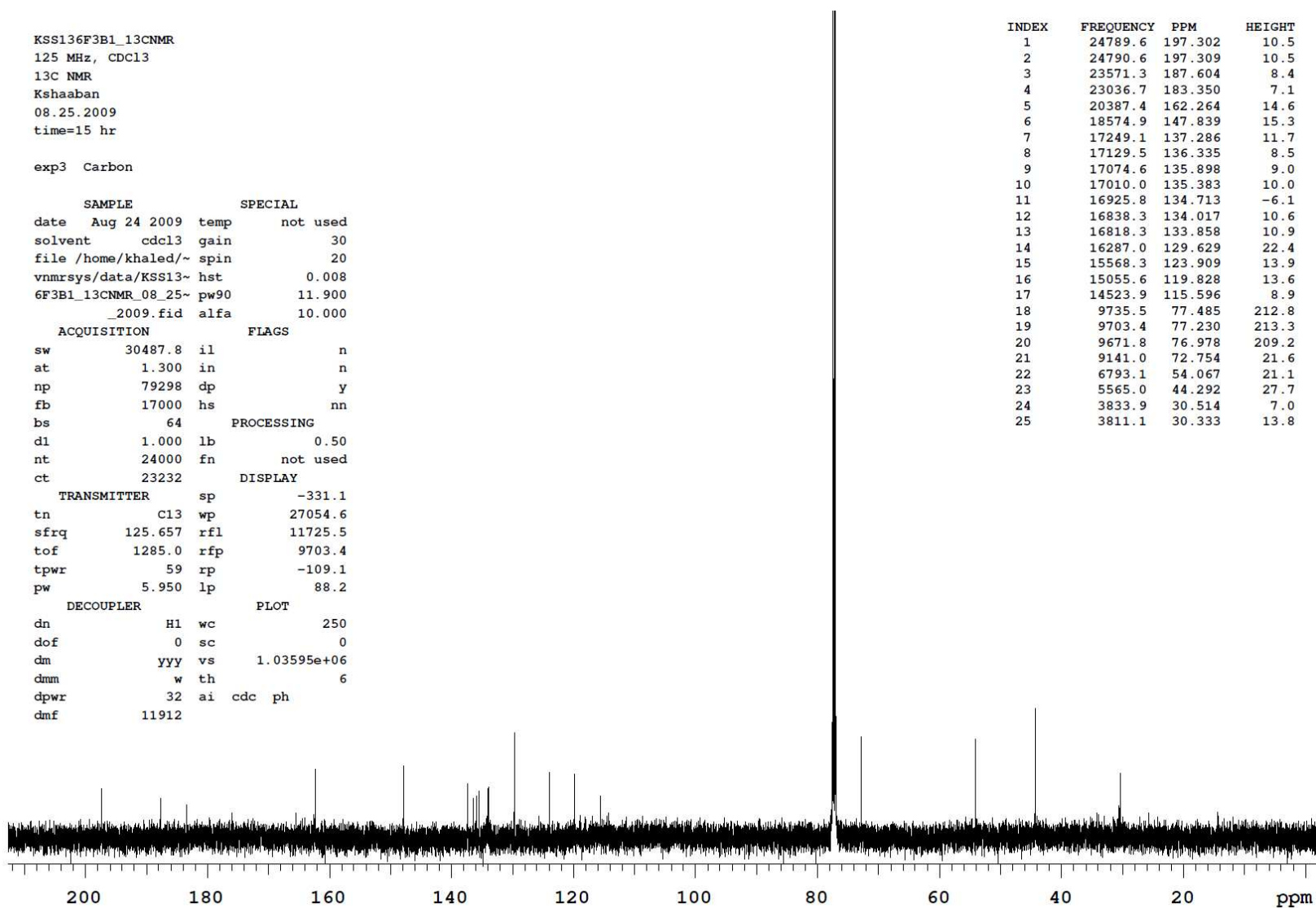


Figure S11: ^{13}C NMR spectrum (CDCl_3 , 150 MHz) of Tetrangomycin (**19**)

KSS136F4C_1H_08_19_2009
1H NMR (500 MHz)
KShaaban
nt=32
CDCl3

Sample: KSS136F4C_1H_08_19_2009
File: xp
Pulse Sequence: s2pul

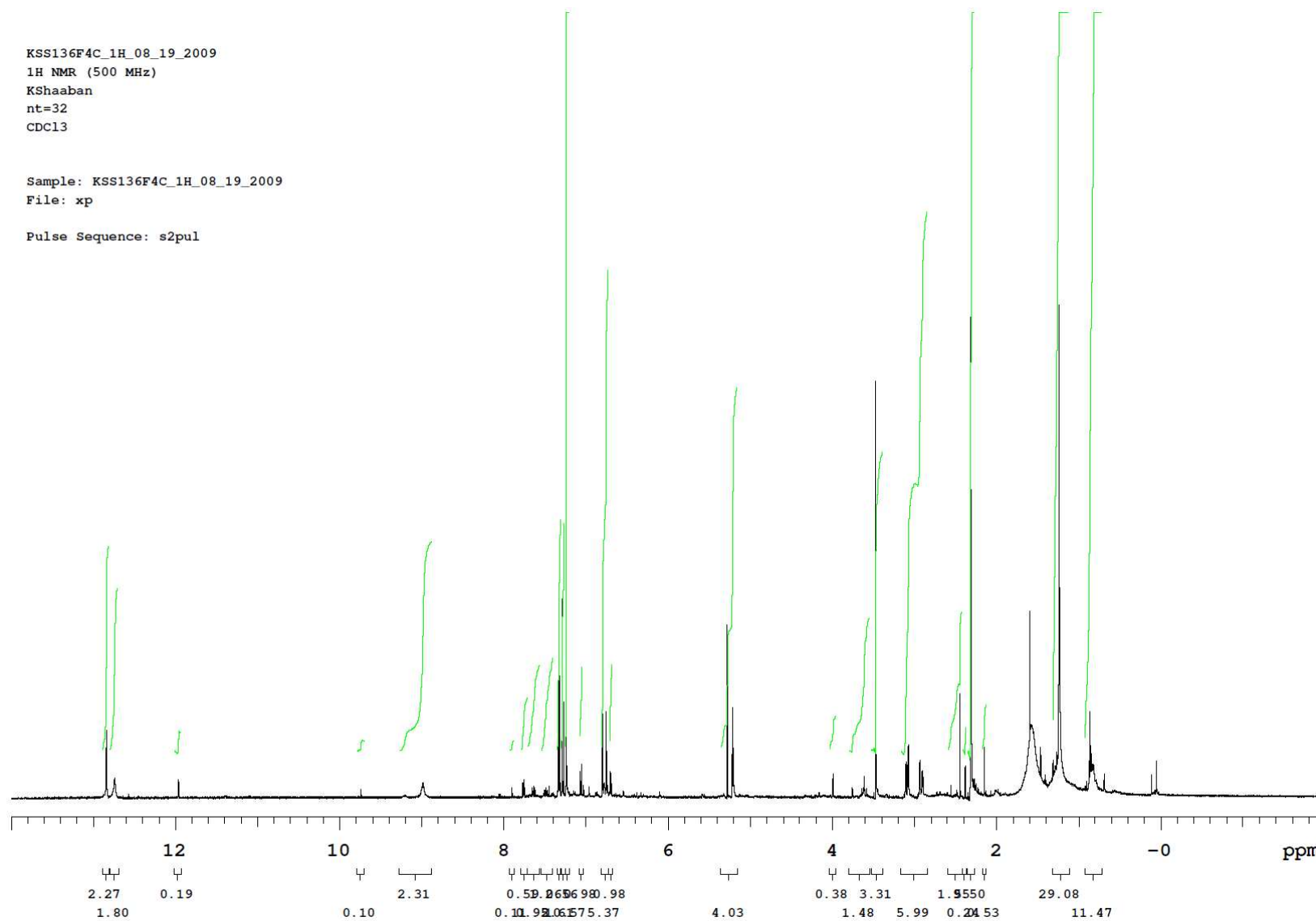


Figure S12: ^1H NMR spectrum (CDCl_3 , 500 MHz) of Landomycinone (**11**)
S14

KSS136F4B1_1H NMR
500 MHz, CDCl₃
1H NMR
Kshaaban
08.26.2009
nt=32

Sample: KSS136F4B1_1HNMR_08_31_2009
File: xp

Pulse Sequence: s2pul

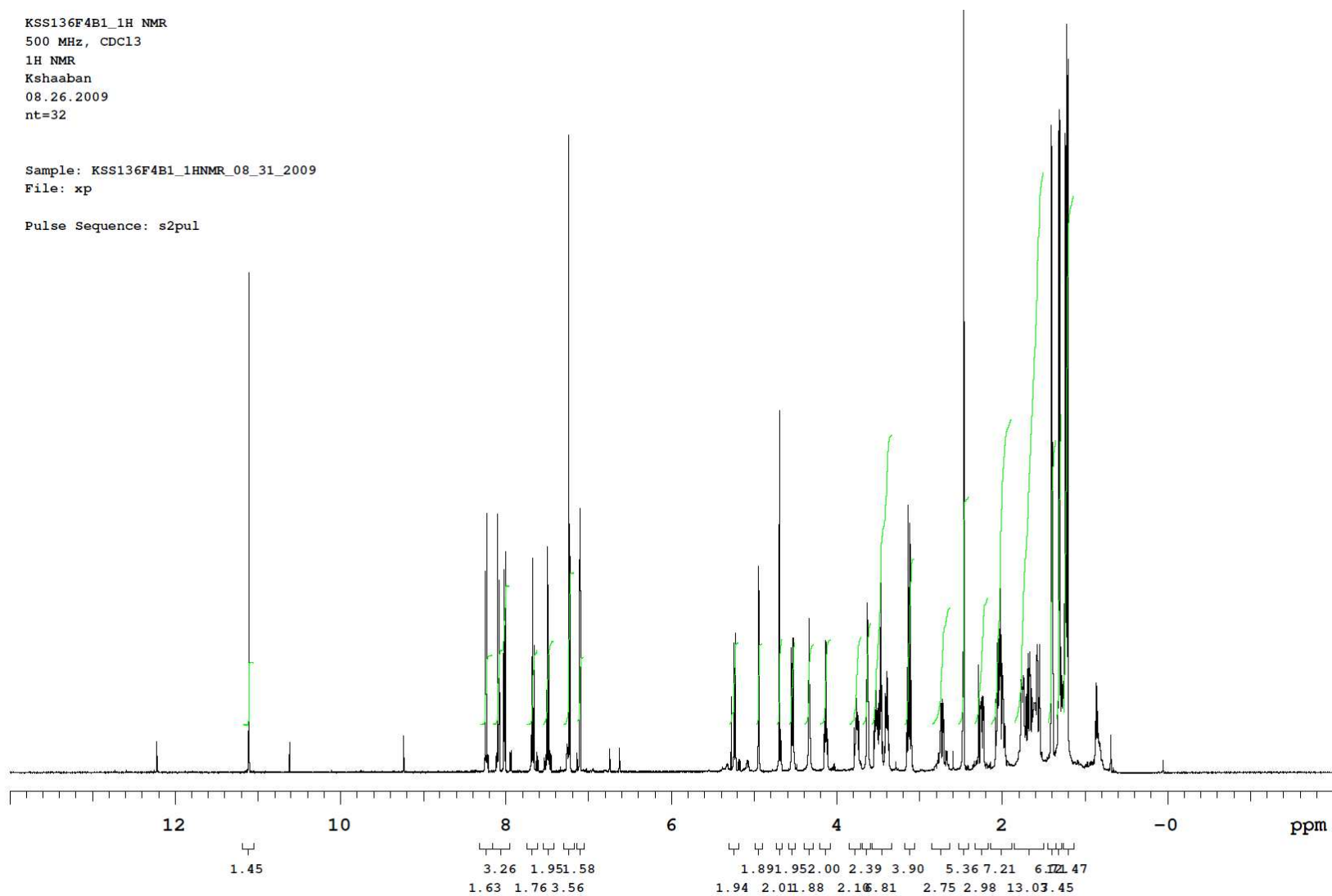


Figure S13: ¹H NMR spectrum (CDCl₃, 500 MHz) of Landomycin P (**5**)

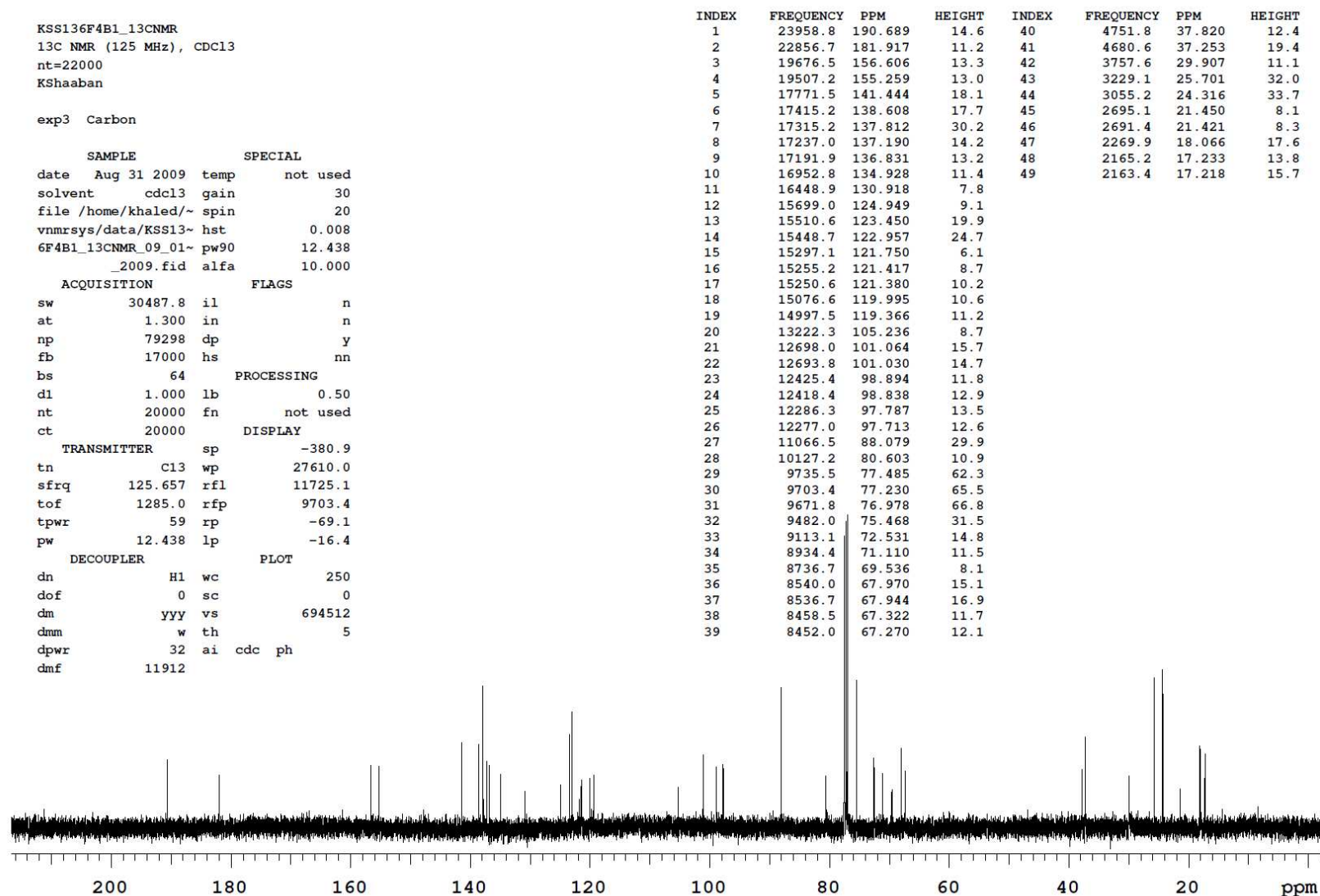


Figure S14: ^{13}C NMR spectrum (CDCl_3 , 150 MHz) of Landomycin P (5)

09-0605 #87-97 RT: 2.47-2.75 AV: 11 NL: 2.21E5
T: - p Full ms2 677.30@31.00 [185.00-1000.00]

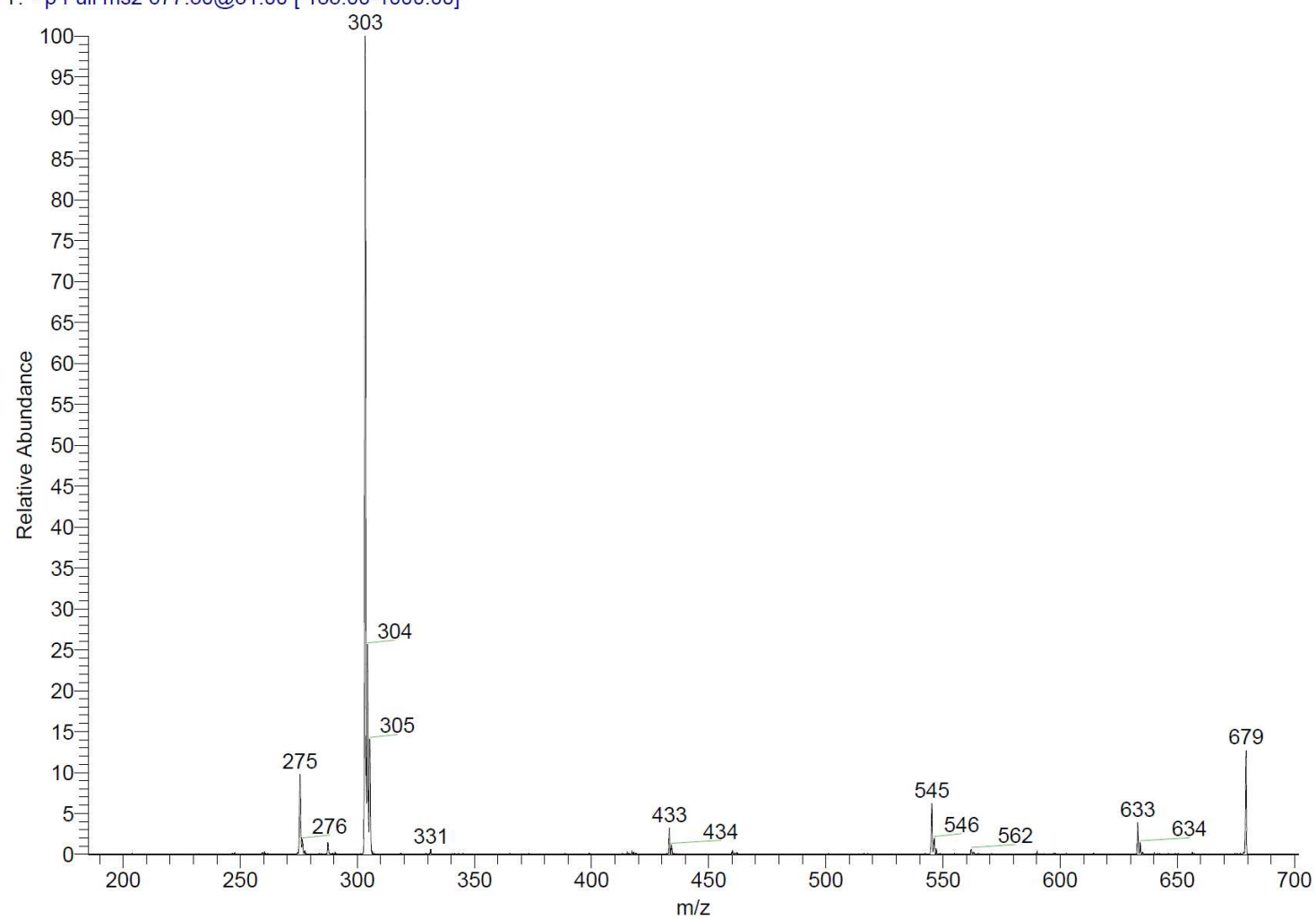


Figure S15: (-) ESI-MS/MS Fragmentation pattern of Landomycin P (5)

KSS136F4B2A_1HNMR_09_05_2009
500 MHz
CDCl₃
KShaaban

Sample: KSS136F4B2A_1HNMR_09_05_2009
File: xp

Pulse Sequence: s2pul

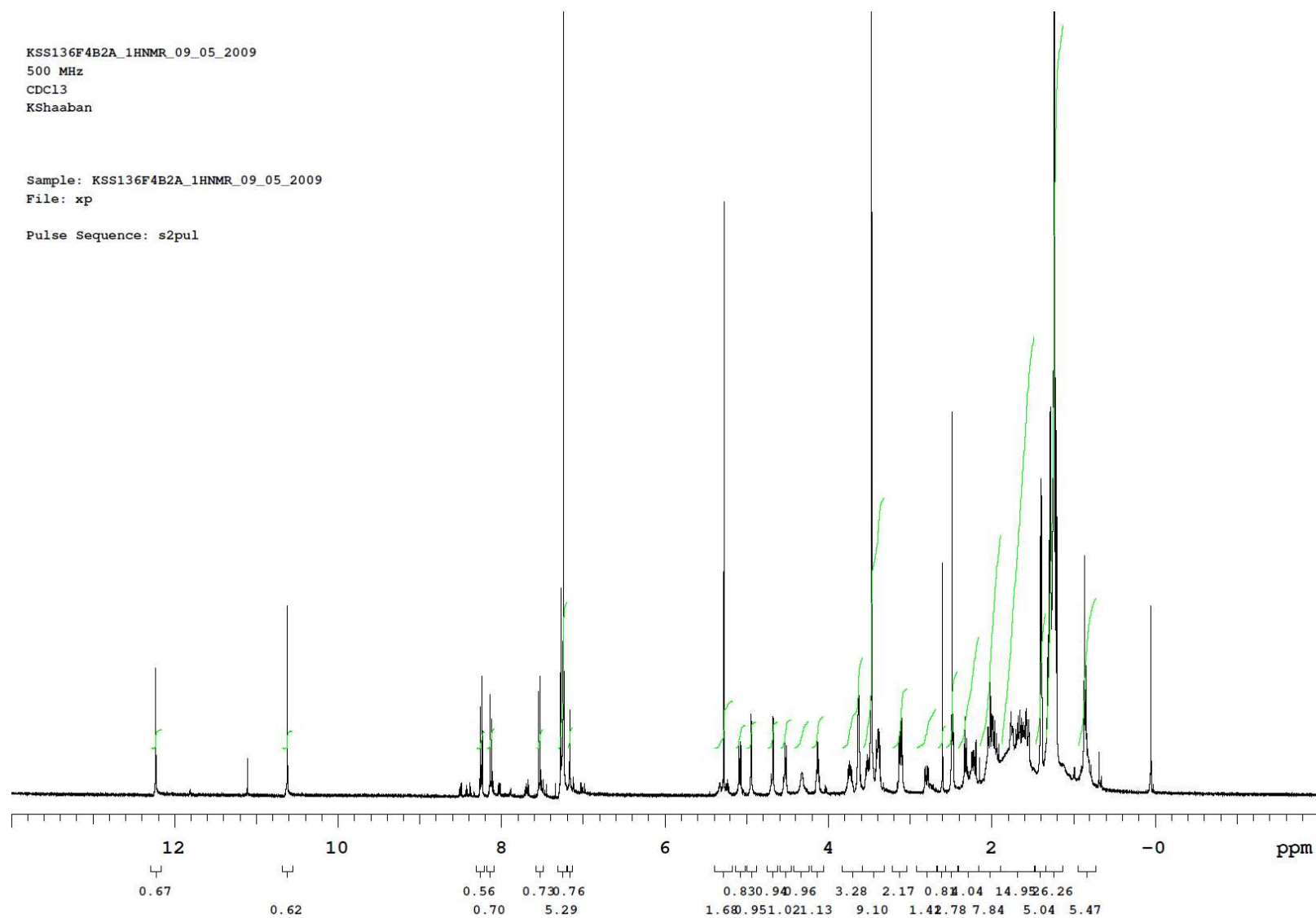


Figure S16: ¹H NMR spectrum (CDCl₃, 500 MHz) of Landomycin Q (6)

09-0604 #13-19 RT: 0.33-0.49 AV: 7 NL: 2.95E5
T: - p Full ms2 693.30@29.00 [190.00-1000.00]

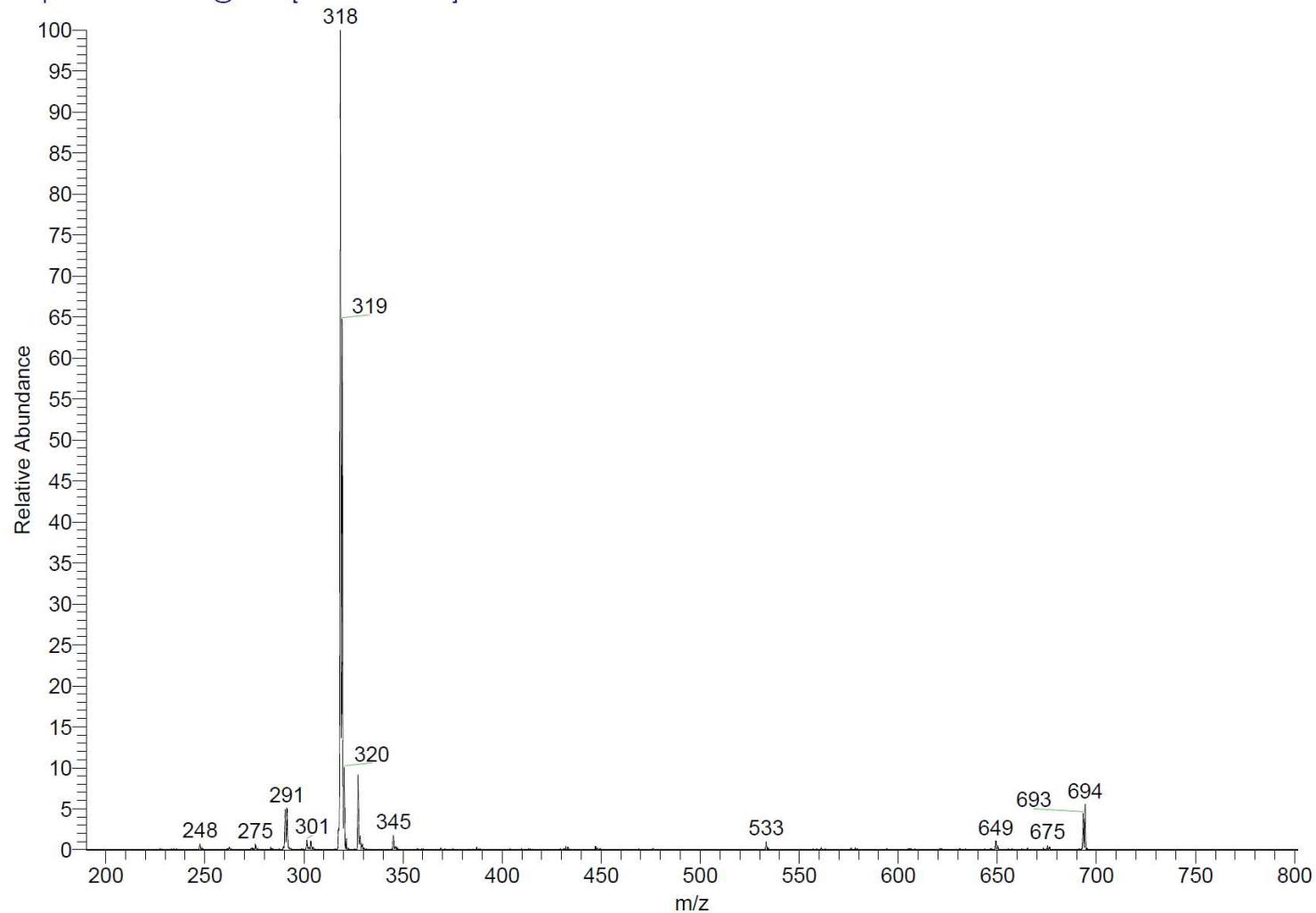


Figure S17: (-) ESI-MS/MS Fragmentation pattern of Landomycin Q (5)

KSS136F5B1_1HNMR_09_21_2009

DMSO-d6 (500 MHz)

nt=32

kshaaban

Sample: KSS136F5B1_1HNMR_09_21_2009

File: xp

Pulse Sequence: s2pul

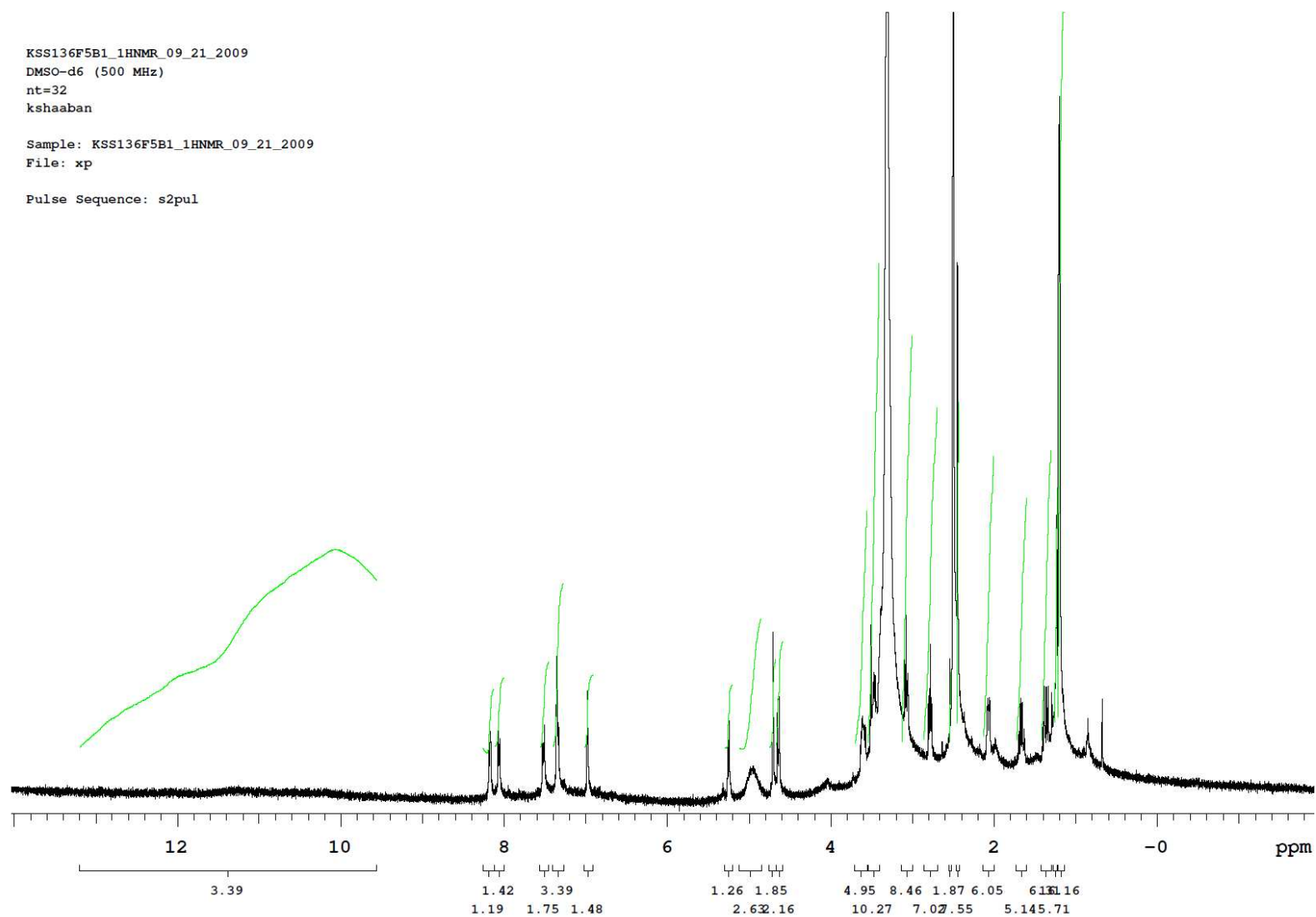


Figure S18: ^1H NMR spectrum (DMSO- d_6 , 500 MHz) of Landomycin R (**3**)

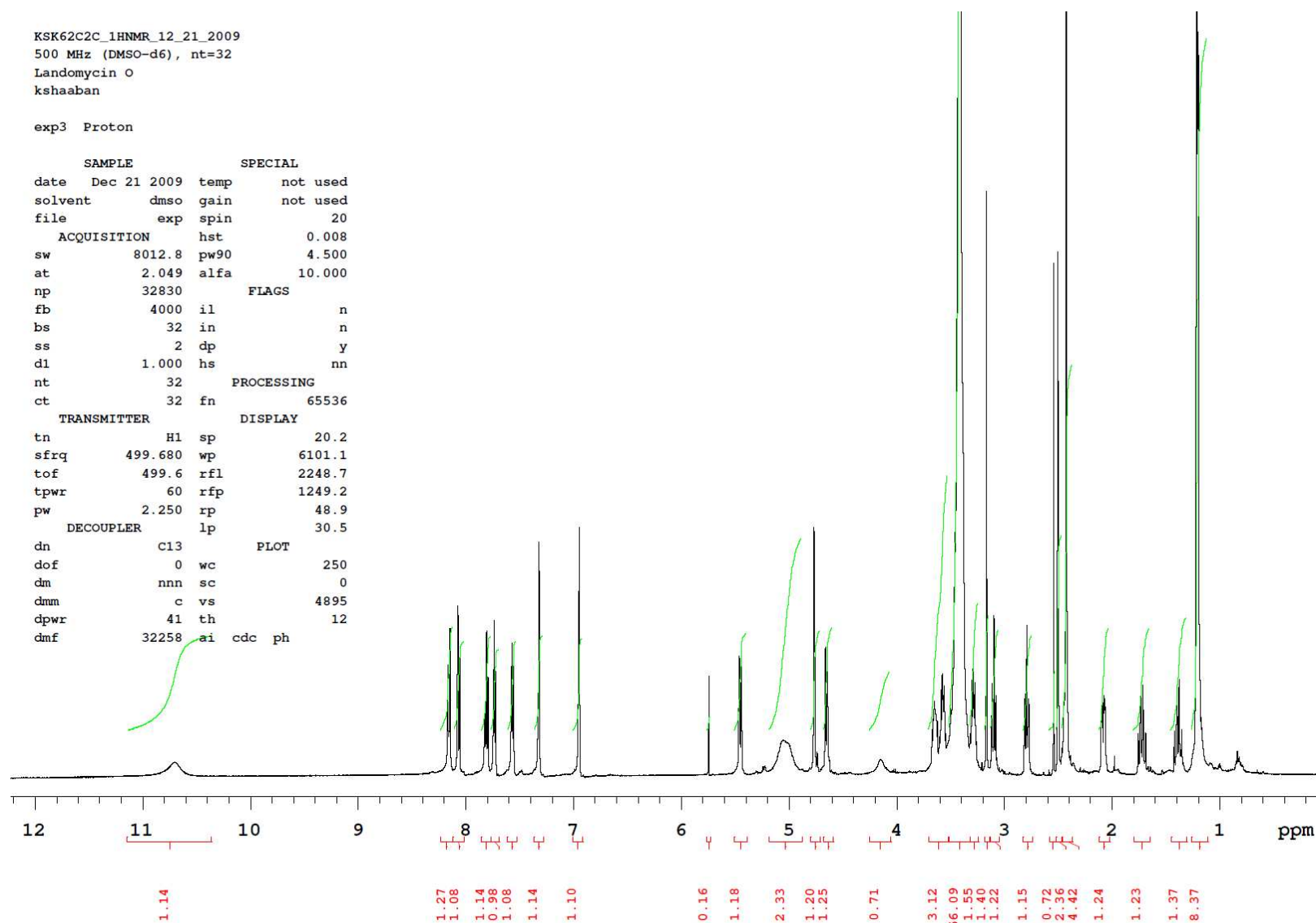


Figure S19: ¹H NMR spectrum (DMSO-d₆, 500 MHz) of Landomycin O (**4**)

KSK62F5_1HNMR_11_05_2009
DMSO-d6 (500 MHz)
kshaaban
nt=32

Sample: KSK62F5_1HNMR_11_05_2009
File: xp

Pulse Sequence: s2pul

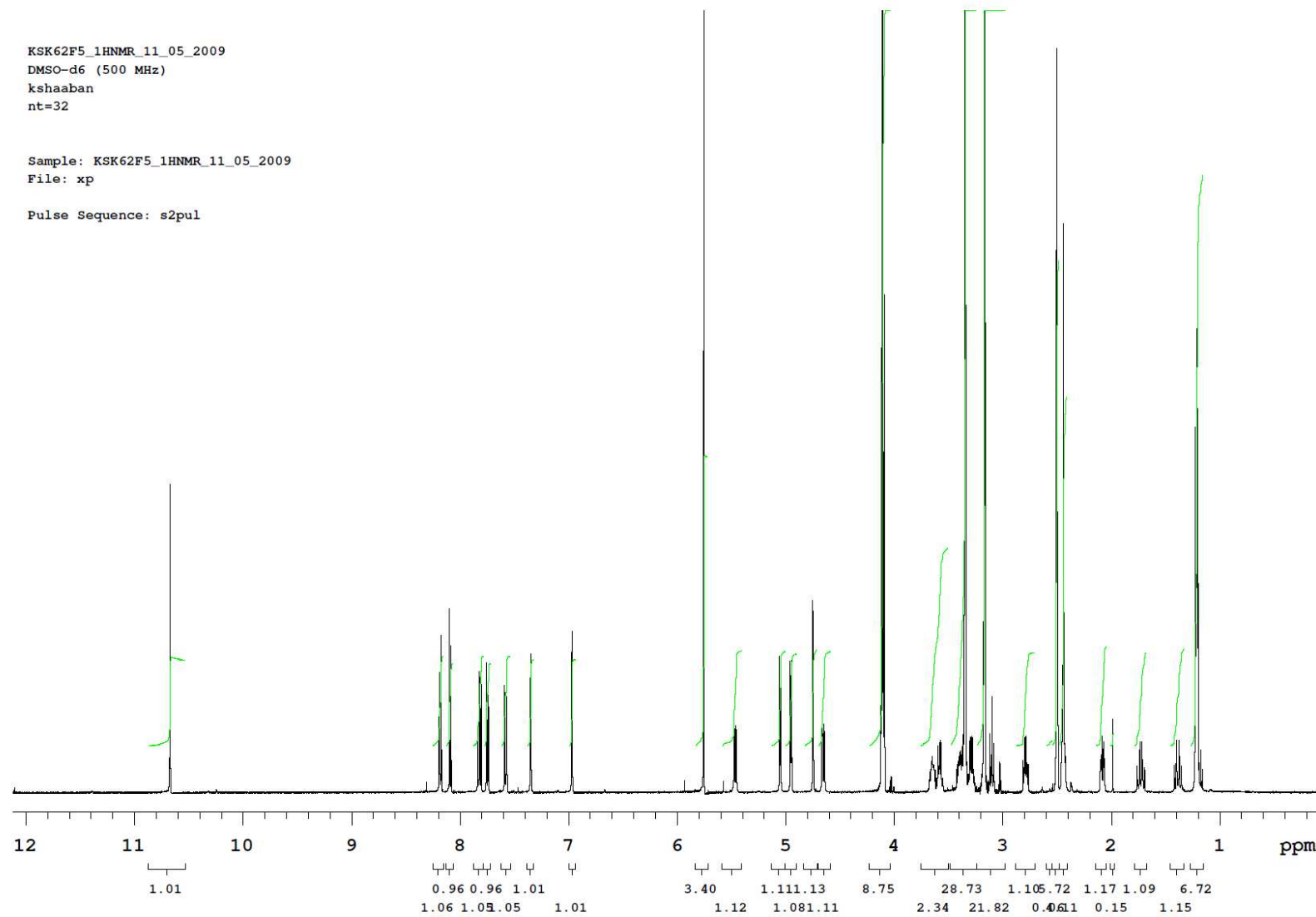


Figure S20: ^1H NMR spectrum (DMSO- d_6 , 500 MHz) of Landomycin O (4)
S22

exp3 Carbon

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	23515.3	187.158	26.1	40	4796.3	38.173	23.5
2	22719.7	180.826	24.9	41	2661.9	21.186	17.0
3	19597.3	155.975	27.6	42	2247.9	17.891	41.3
4	19447.9	154.786	31.2	43	2219.0	17.661	41.0
5	17669.0	140.627	27.6				
6	17296.4	137.662	26.8				
7	17282.4	137.551	27.6				
8	17004.2	135.336	17.2				
9	16951.2	134.914	24.4				
10	16889.3	134.422	23.9				
11	16707.4	132.974	18.0				
12	15484.4	123.240	-9.9				
13	15378.3	122.396	12.0				
14	15338.8	122.081	-9.4				
15	15319.2	121.926	16.5				
16	15169.0	120.730	10.8				
17	15120.1	120.341	22.4				
18	15019.2	119.538	11.4				
19	14808.0	117.857	20.1				
20	14658.2	116.664	23.0				
21	12594.5	100.240	21.0				
22	12590.3	100.206	24.5				
23	12157.2	96.759	21.2				
24	12154.4	96.737	24.3				
25	10872.8	86.536	37.9				
26	9605.6	76.451	36.0				
27	9051.0	72.037	39.6				
28	8828.2	70.264	20.1				
29	8808.2	70.104	31.9				
30	8592.8	68.390	22.2				
31	6117.4	48.689	9.6				
32	5027.0	40.010	67.9				
33	5006.1	39.843	211.7				
34	4985.1	39.677	423.1				
35	4974.0	39.588	58.1				
36	4964.2	39.510	495.4				
37	4943.3	39.343	422.3				
38	4921.9	39.173	214.8				
39	4900.9	39.006	69.8				

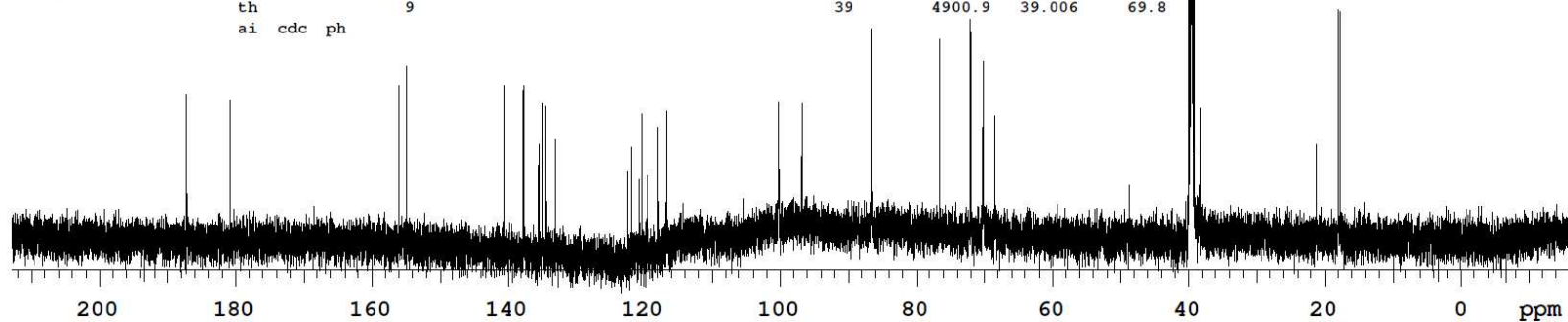


Figure S21: ^{13}C NMR spectrum (DMSO- d_6 , 125 MHz) of Landomycin O (**4**)

KSK62F1_1HNMR_11_06_2009
DMSO-d6 (500 MHz)
kshaaban
nt=32

Sample: KSK62F1_1HNMR_11_06_2009
File: xp

Pulse Sequence: s2pul

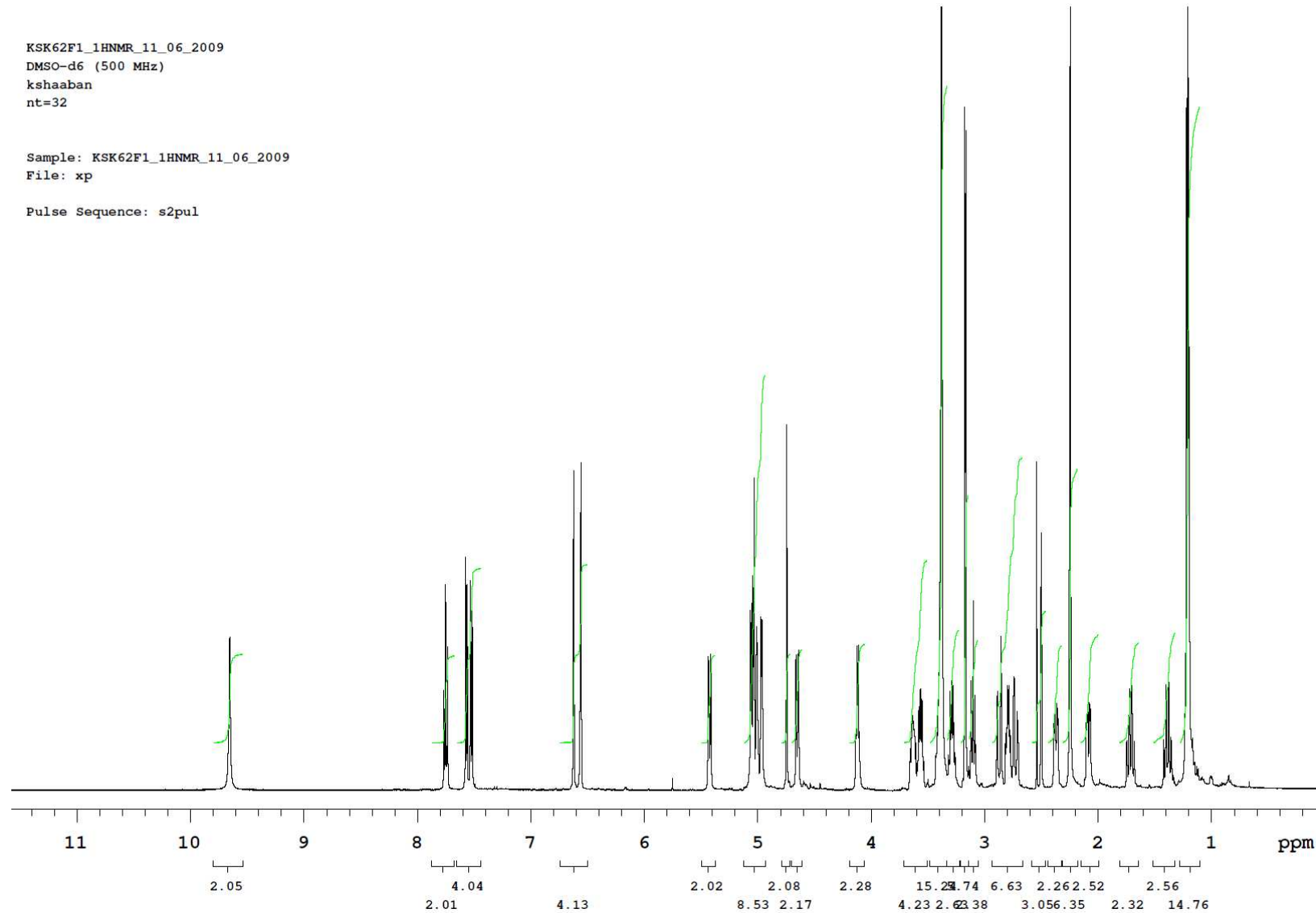


Figure S22: ^1H NMR spectrum (DMSO- d_6 , 500 MHz) of Landomycin F (13)

KSK62F1_13CNMR_12_22_2009
DMSO-d6 (125 MHz), time=2 hrs
Landomycin F
KShaaban

exp3 Carbon

SAMPLE		SPECIAL	
date	Dec 22 2009	temp	not used
solvent	dms	gain	30
file	exp	spin	20
ACQUISITION		hst	0.008
sw	30487.8	pw90	11.900
at	1.300	alfa	10.000
np	79298	FLAGS	
fb	17000	il	n
bs	64	in	n
dl	1.000	dp	y
nt	32000	hs	nn
ct	3328	PROCESSING	
TRANSMITTER		lb	0.50
tn	C13	fn	not used
sfrq	125.657	DISPLAY	
tof	1285.0	sp	-2100.0
tpwr	59	wp	28998.2
pw	5.950	rfl	7064.6
DECOUPLER		rfl	4964.2
dn	H1	rp	15.3
dof	0	lp	10.8
dm	YYY	PLOT	
dmm	w	wc	250
dpwr	32	sc	0
dmf	11912	vs	420452
		th	10
		ai	cdc ph

INDEX	FREQUENCY	PPM	HEIGHT
1	23157.5	184.310	41.0
2	22774.6	181.263	44.3
3	19550.8	155.604	43.5
4	19523.8	155.390	51.0
5	17769.0	141.424	37.0
6	17740.6	141.198	36.2
7	17617.4	140.216	39.4
8	17362.9	138.191	34.7
9	17087.5	135.999	34.9
10	16910.2	134.589	21.4
11	15316.4	121.904	14.2
12	15199.7	120.974	17.7
13	15070.8	119.949	45.2
14	15032.7	119.645	16.2
15	14485.6	115.291	15.0
16	14303.2	113.839	42.5
17	12591.3	100.214	22.1
18	12122.8	96.485	22.8
19	10870.5	86.518	37.7
20	9605.1	76.447	40.9
21	9047.8	72.011	41.0
22	8820.3	70.201	28.5
23	8808.7	70.108	37.8
24	8588.2	68.353	24.5
25	7168.3	57.053	14.4
26	5027.0	40.010	60.9
27	5006.1	39.843	182.1
28	4985.1	39.677	361.7
29	4964.2	39.510	427.7
30	4943.3	39.343	363.8
31	4922.3	39.177	180.2
32	4900.9	39.006	59.4
33	4791.1	38.133	23.5
34	4612.5	36.711	19.9
35	2661.0	21.179	28.2
36	2245.1	17.868	69.0
37	2217.1	17.646	61.8

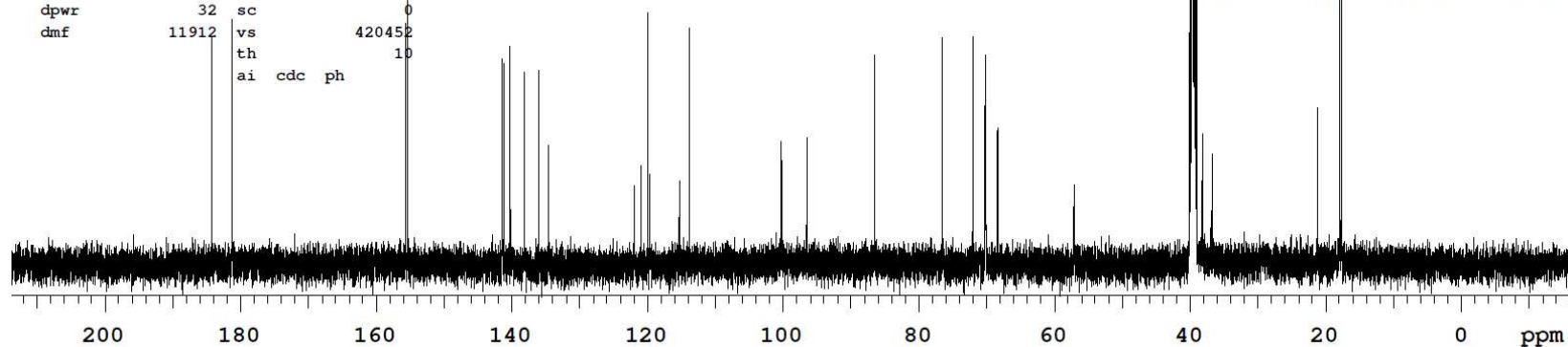


Figure S23: ^{13}C NMR spectrum (DMSO- d_6 , 125 MHz) of Landomycin F (13)

09-0583 #30-34 RT: 1.29-1.44 AV: 5 NL: 2.59E5
T: - p Full ms2 581.30@29.00 [160.00-2000.00]

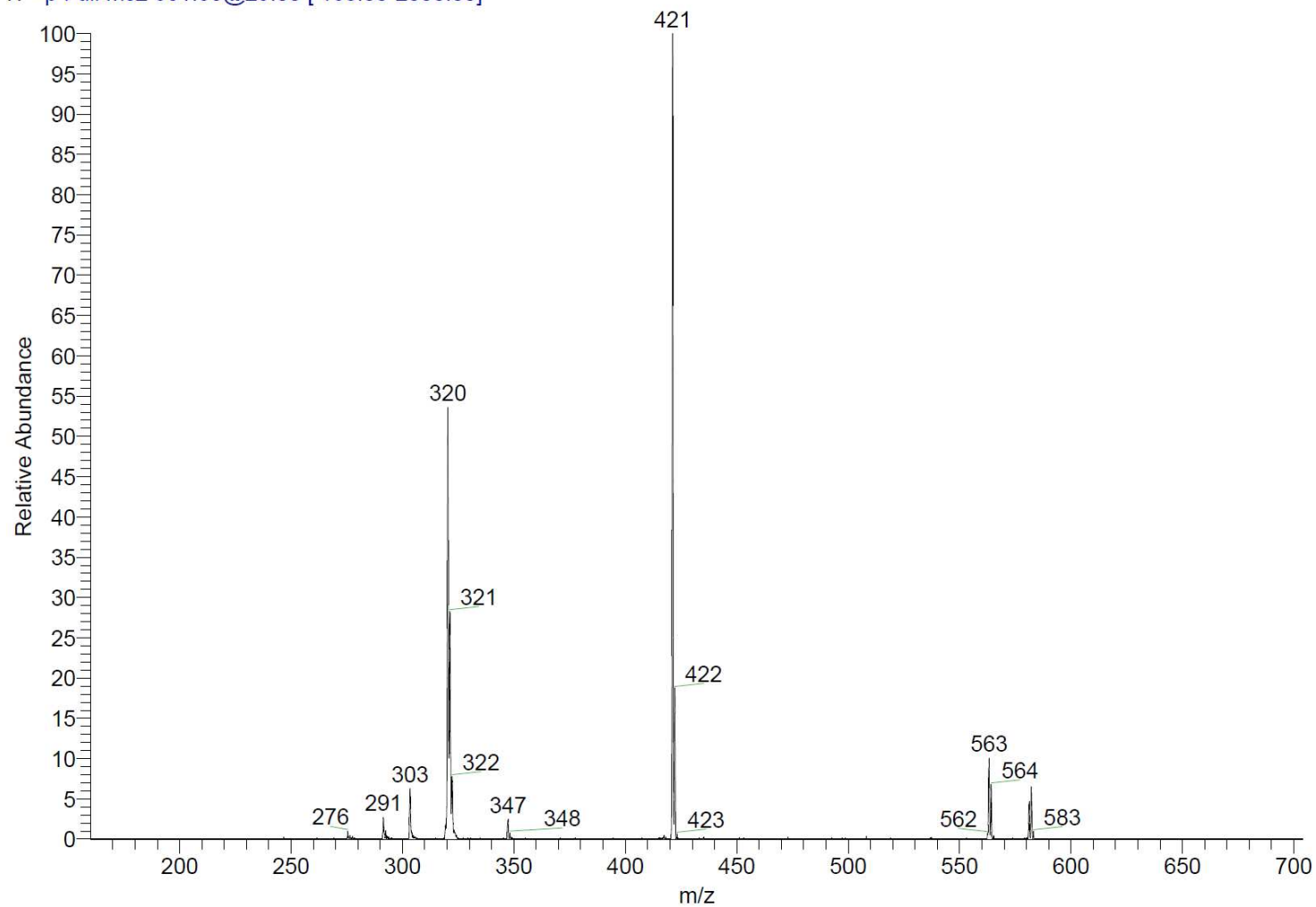


Figure S24: (-) ESI-MS/MS Fragmentation pattern of Landomycin F (**13**)

KSS136F6B2_1HNMR_10_12_2009_DMSO
nt=64 (500 MHz)
KShaaban

Sample: KSS136F6B2_1HNMR_10_12_2009_DMSO
File: xp

Pulse Sequence: s2pul

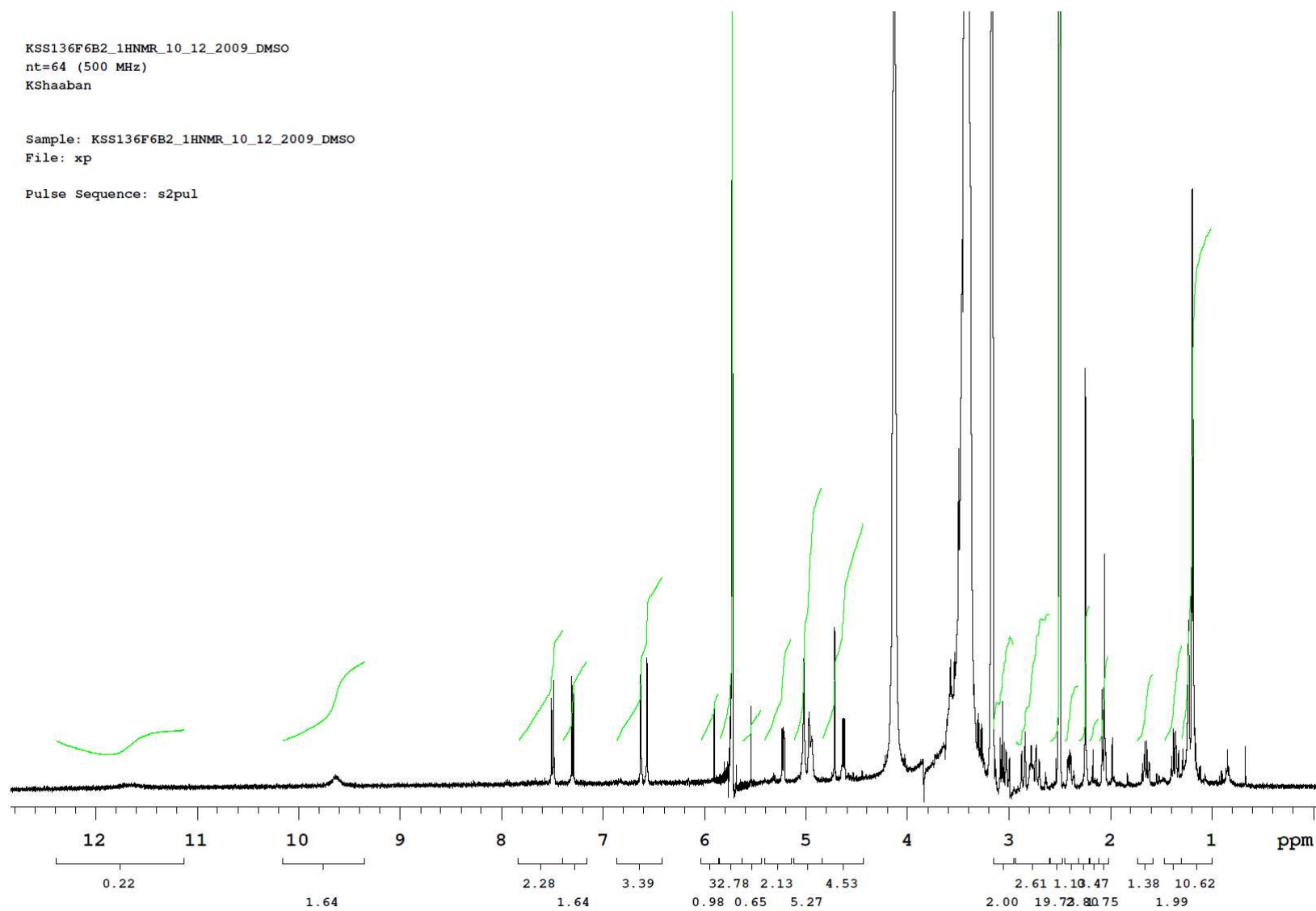


Figure S25: ^1H NMR spectrum ($\text{DMSO}-d_6$, 500 MHz) of Landomycin D (12)

09-0584 #35-39 RT: 1.52-1.66 AV: 5 NL: 4.01E5
T: - p Full ms2 597.30@29.00 [160.00-2000.00]

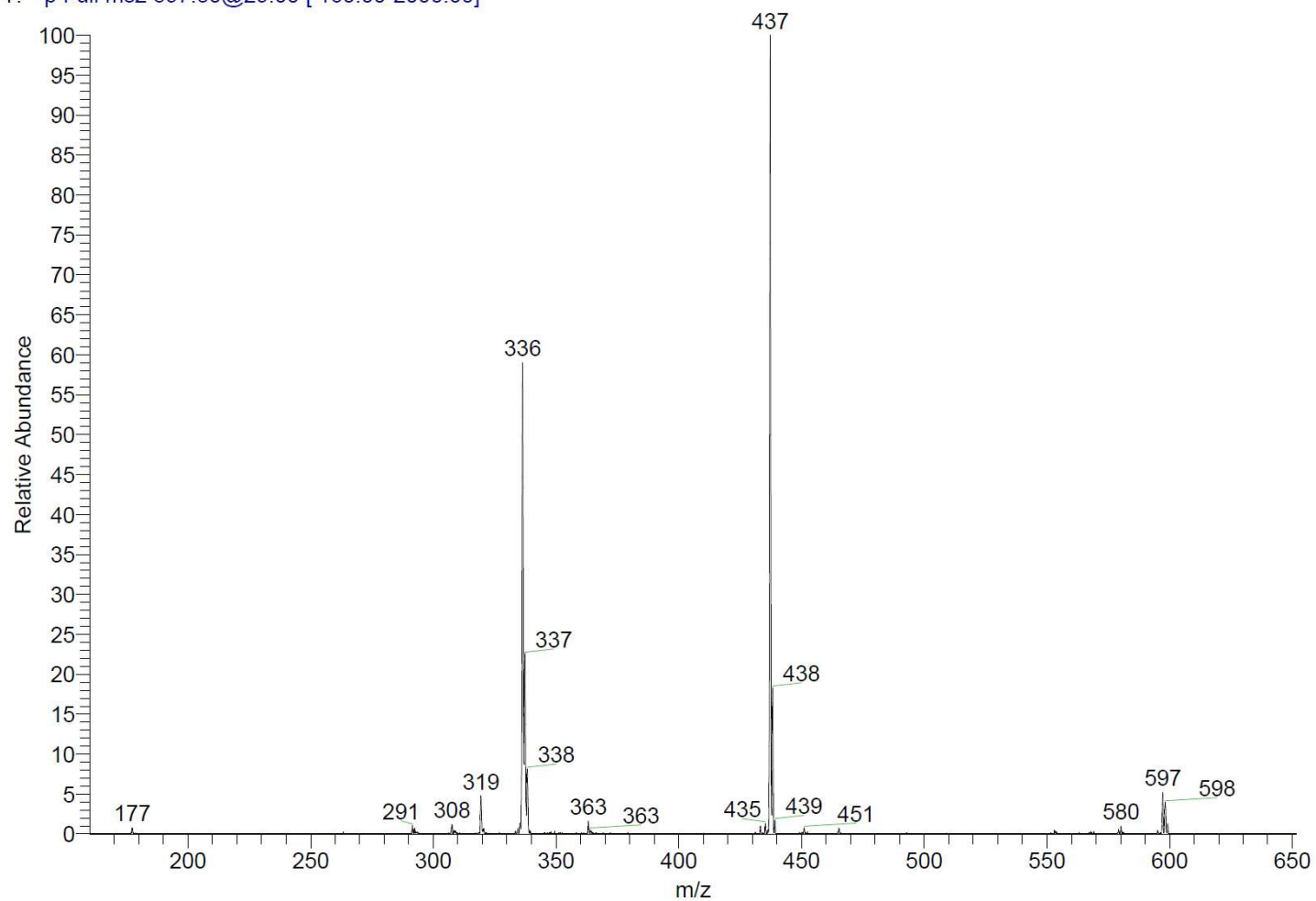


Figure S26: (-) ESI-MS/MS Fragmentation pattern of Landomycin D (**12**)

KSS136F6A2A2_1HNMR_10_22_2009

CDCl₃ (500 MHz)

nt=32

kshaaban

/home/khaled/vnmrsys/data/data/s2pul_001.fid/*

Sample: KSS136F6A2A2_1HNMR_10_22_2009

File: xp

Pulse Sequence: s2pul

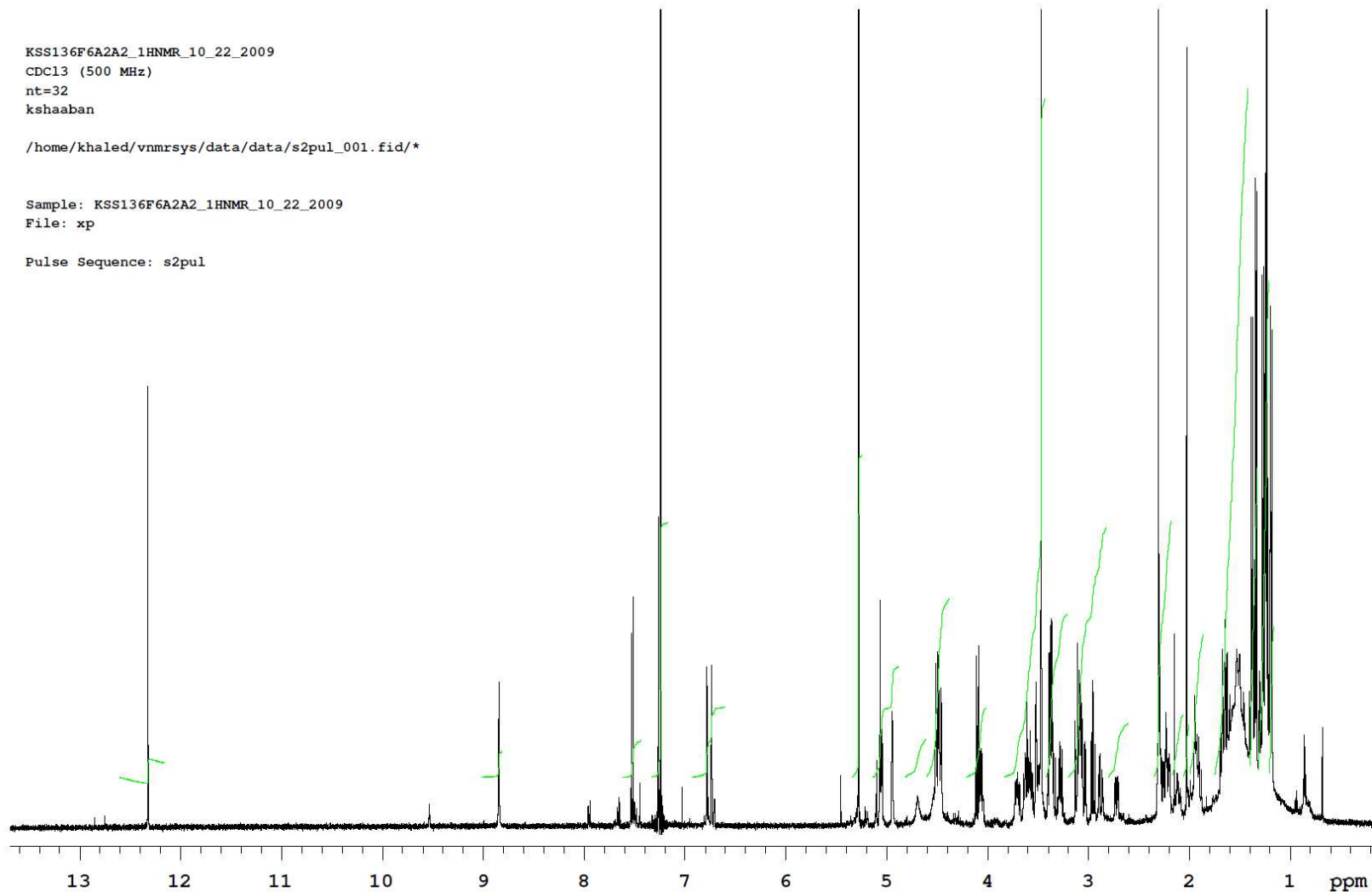


Figure S27: ¹H NMR spectrum (CDCl₃, 500 MHz) of Landomycin B (**14**)

09-0582 #44-52 RT: 1.84-2.10 AV: 9 NL: 9.46E5
T: - p Full ms2 971.40@29.00 [265.00-2000.00]

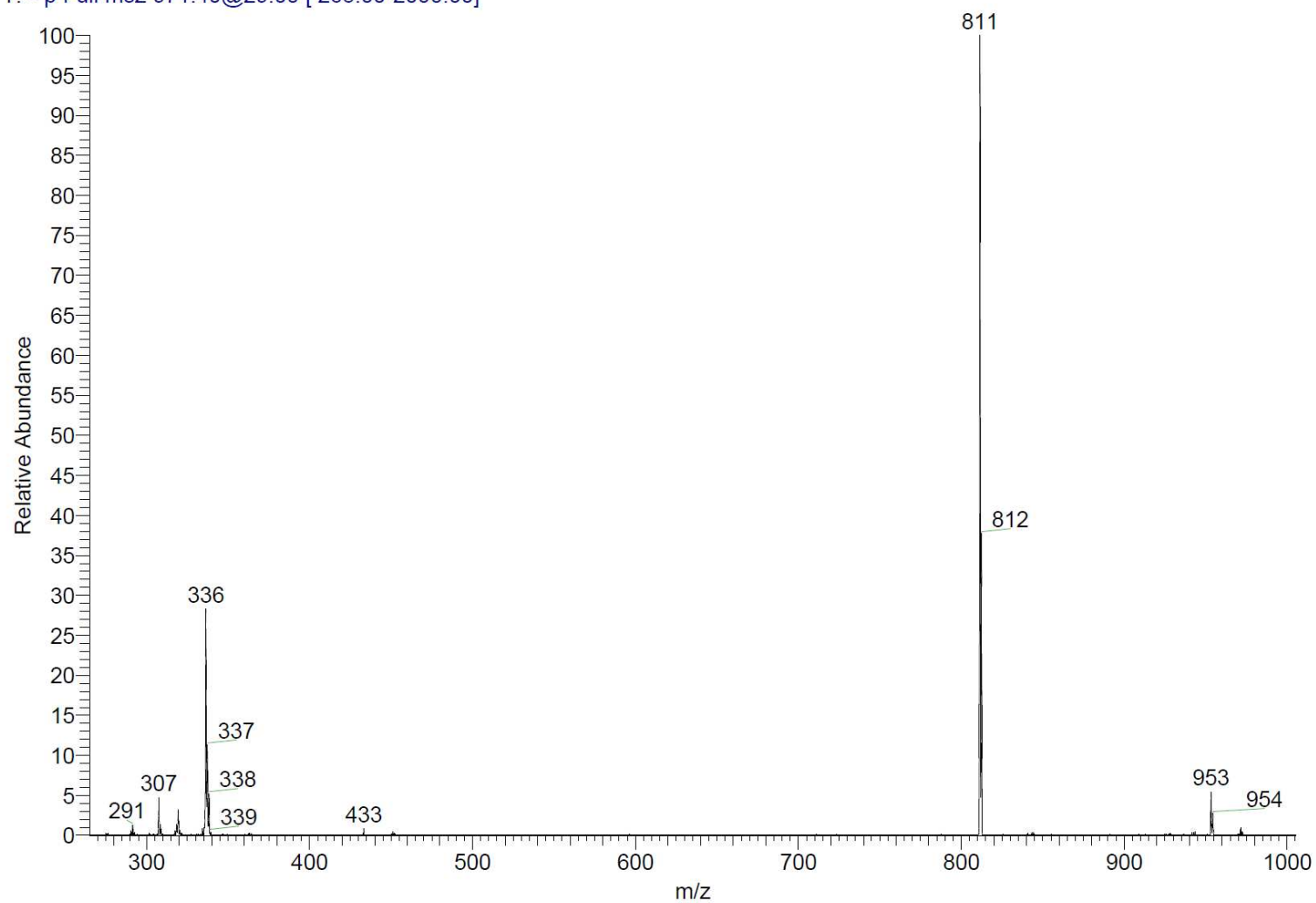


Figure S28: (-) ESI-MS/MS Fragmentation pattern of Landomycin B (**14**)
S30

KSK62F2_1HNMR_11_06_2009
CDCl₃ (500 MHz)
kshaaban
nt=32

Sample: KSK62F2_1HNMR_11_06_2009
File: xp

Pulse Sequence: s2pul

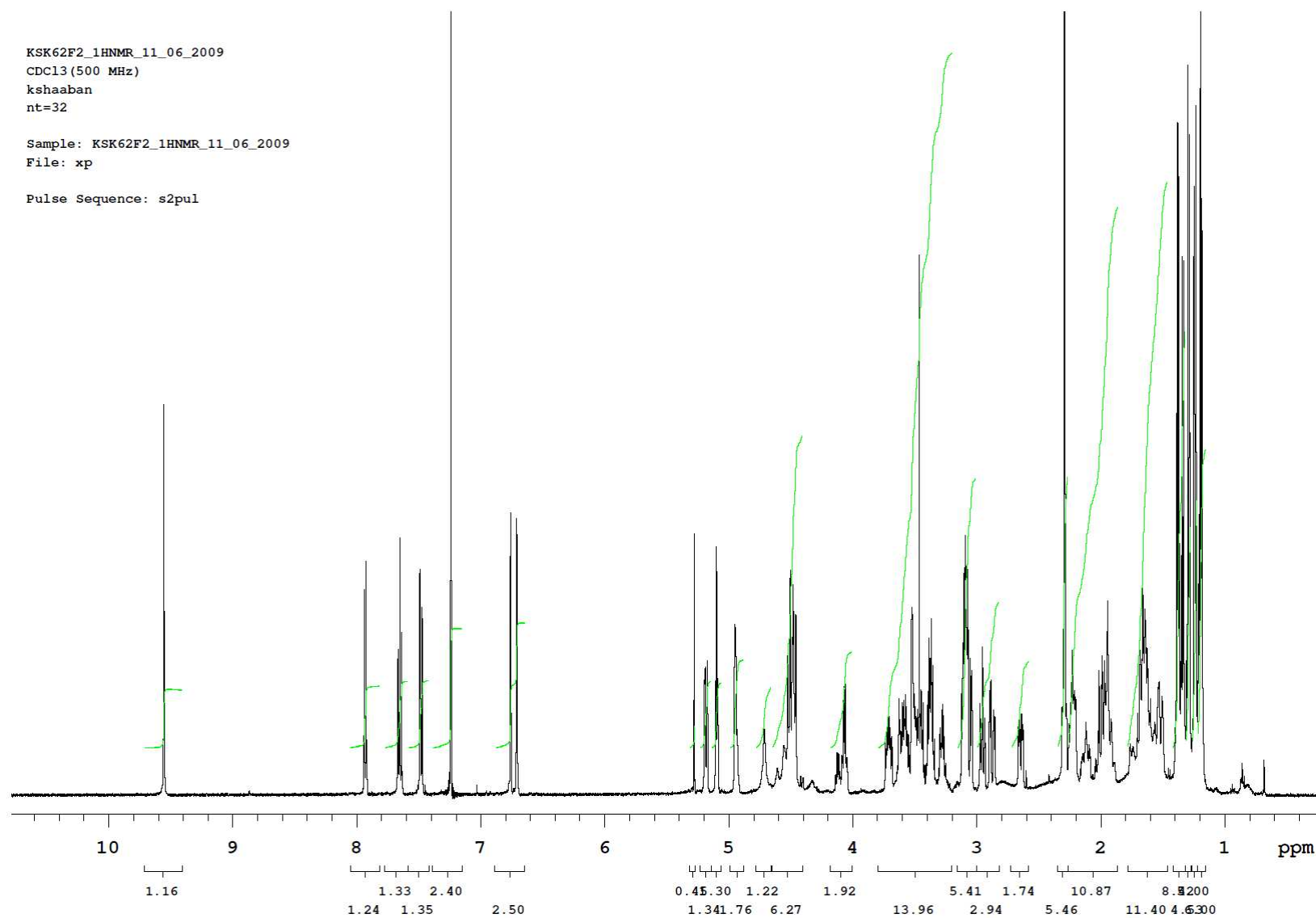


Figure S29: ¹H NMR spectrum (CDCl₃, 500 MHz) of Landomycin V (15)

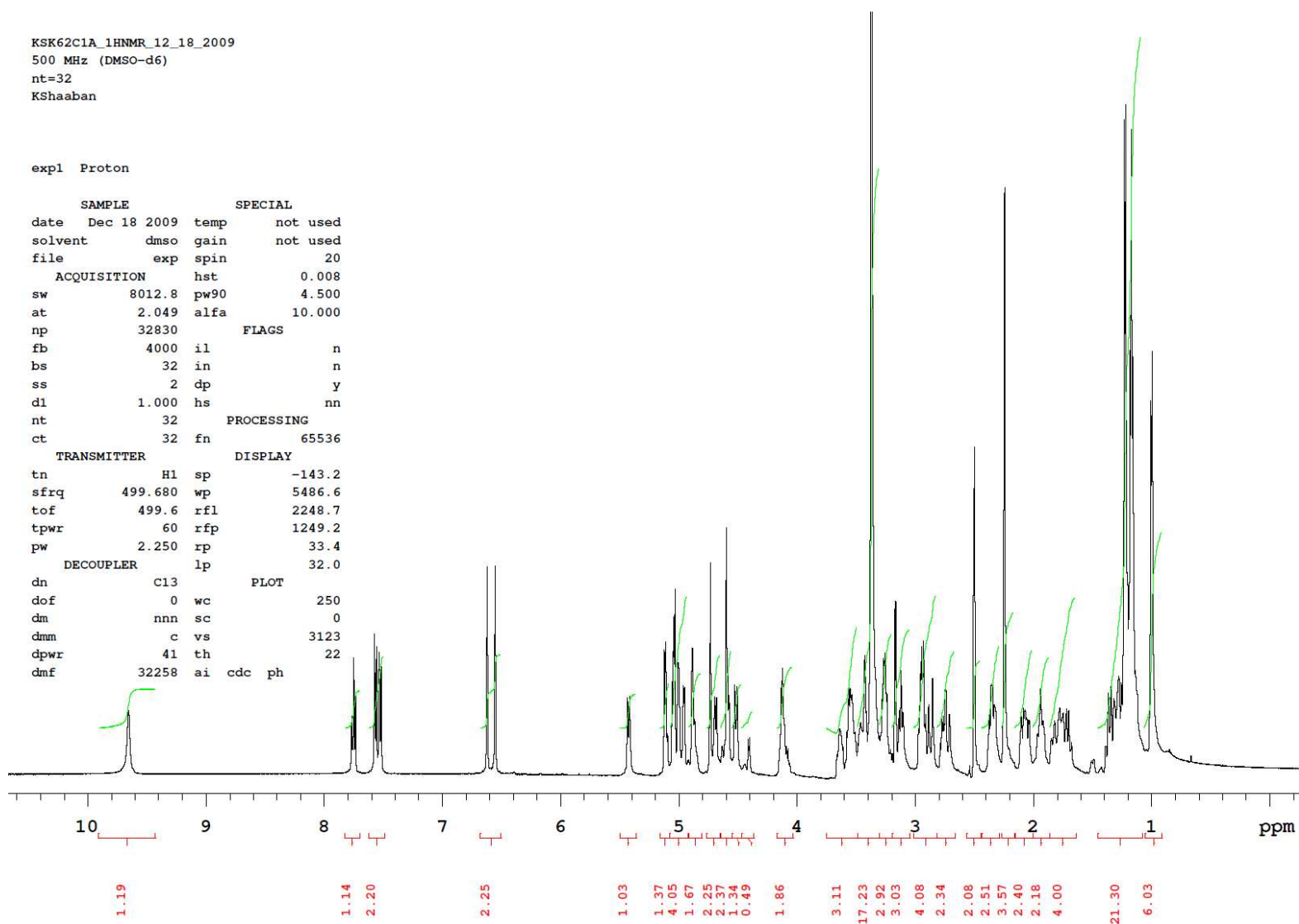


Figure S30: ^1H NMR spectrum (DMSO- d_6 , 500 MHz) of Landomycin V (**15**)

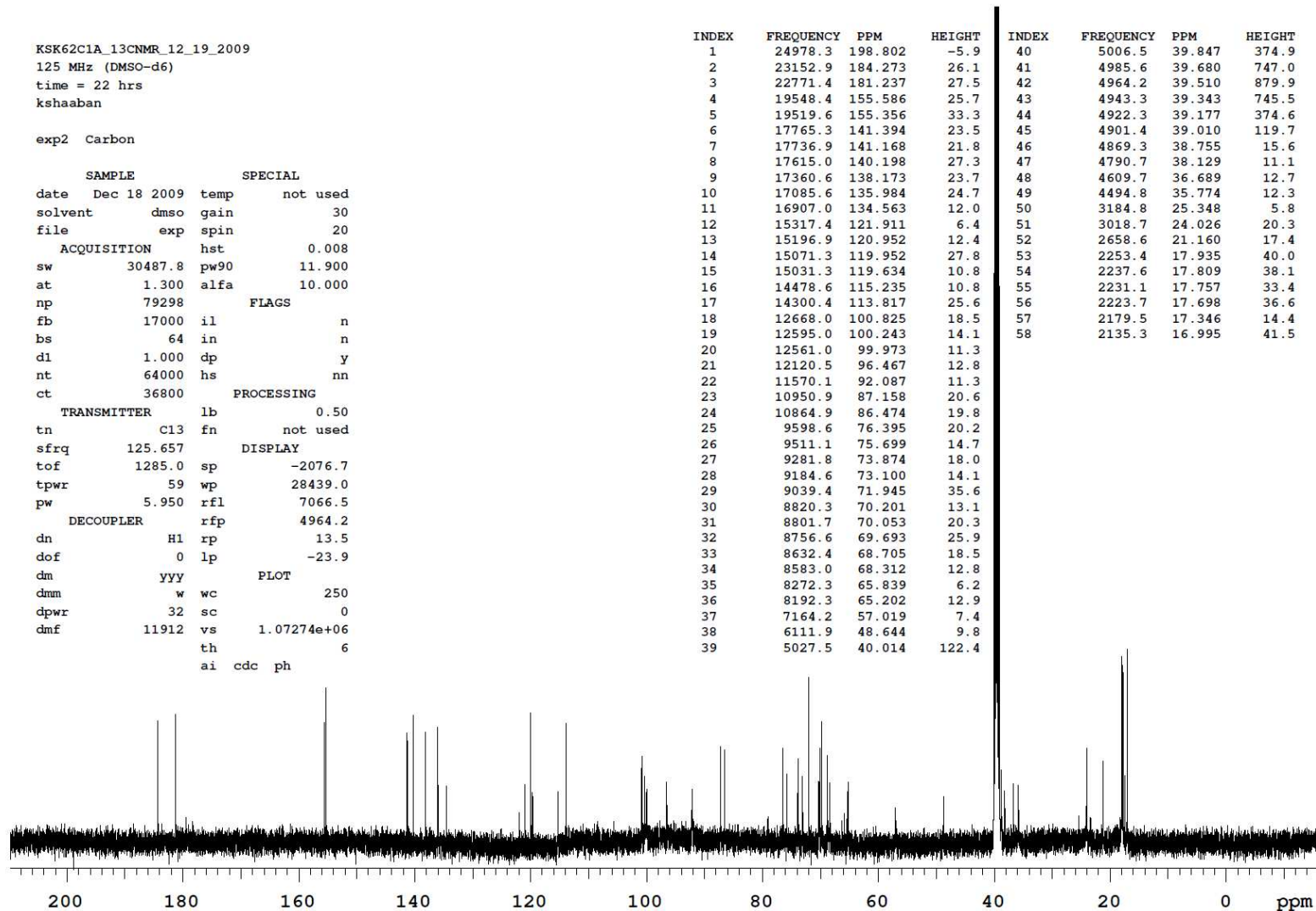
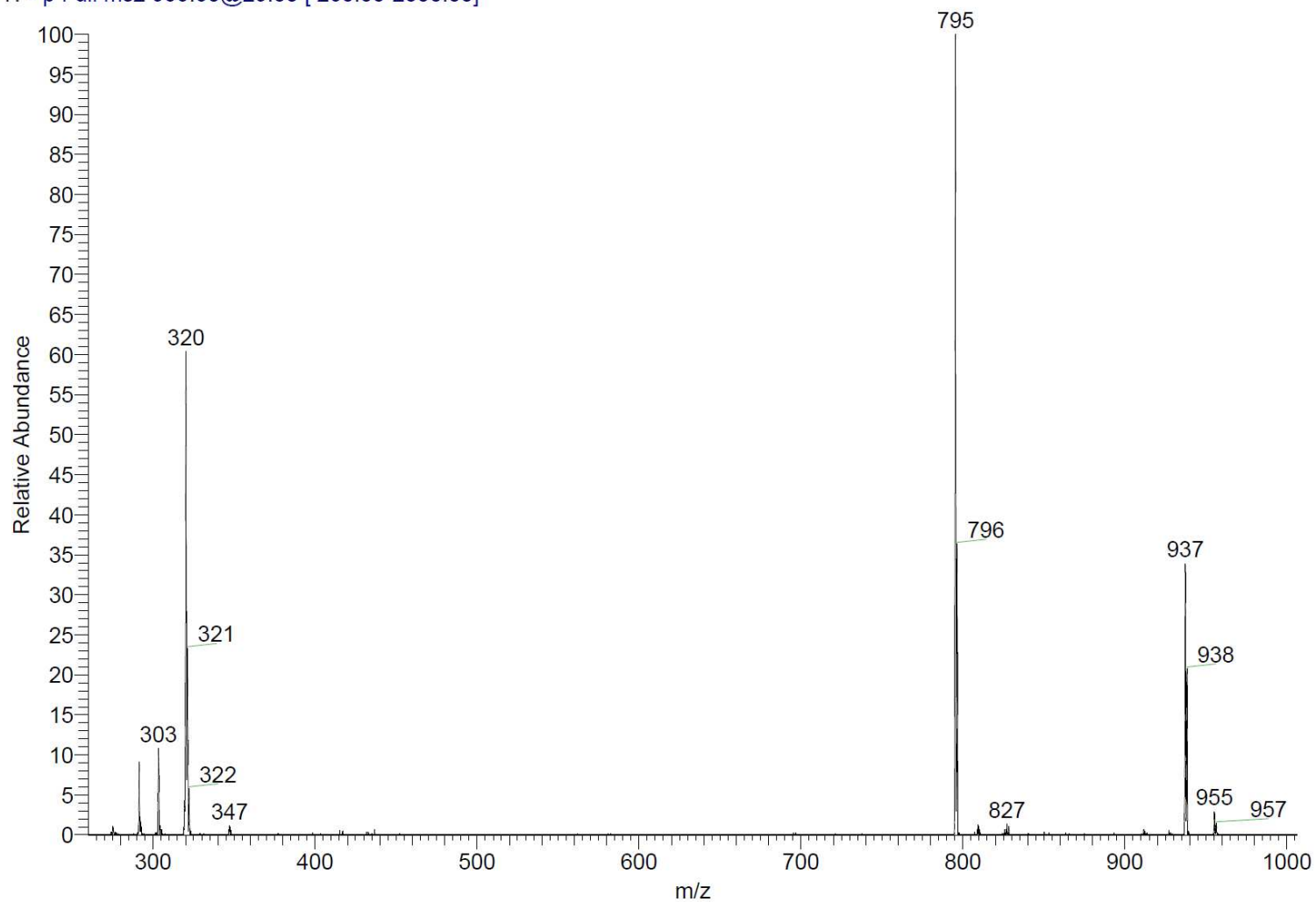


Figure S31: ^{13}C NMR spectrum (DMSO- d_6 , 125 MHz) of Landomycin V (**15**)

09-0581 #36-40 RT: 1.43-1.56 AV: 5 NL: 1.01E6

T: - p Full ms2 955.50@29.00 [260.00-2000.00]

**Figure S32:** (-) ESI-MS/MS Fragmentation pattern of Landomycin V (**15**)

KSS136F5A2B2A2_1HNMR_10_02_2009
CDCl₃
nt=32
kshaaban

Sample: KSS136F5A2B2A2_1HNMR_10_02_2009_CDC13

File: xp

Pulse Sequence: s2pul

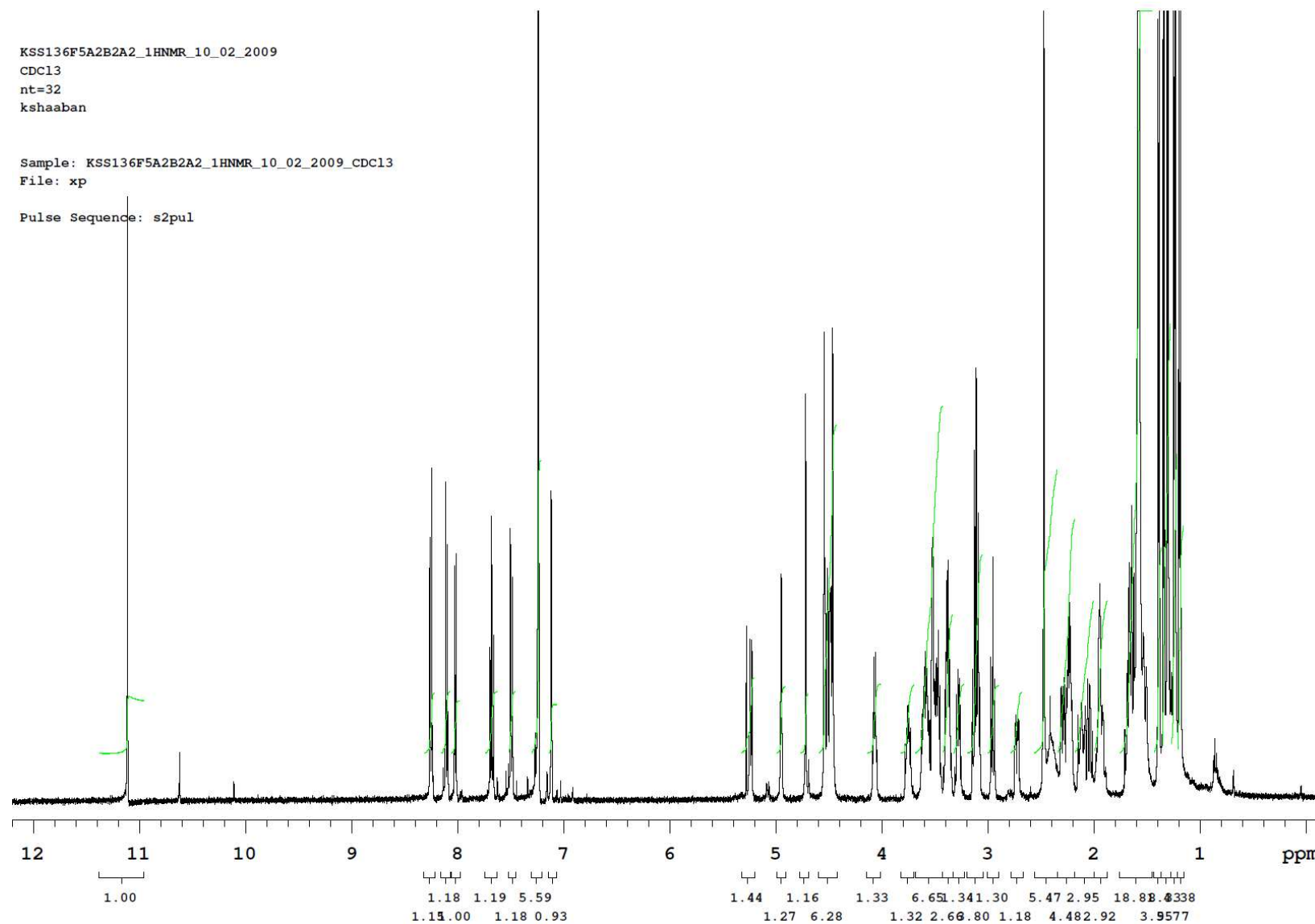


Figure S33: ¹H NMR spectrum (CDCl₃, 500 MHz) of Landomycin M (**8**)

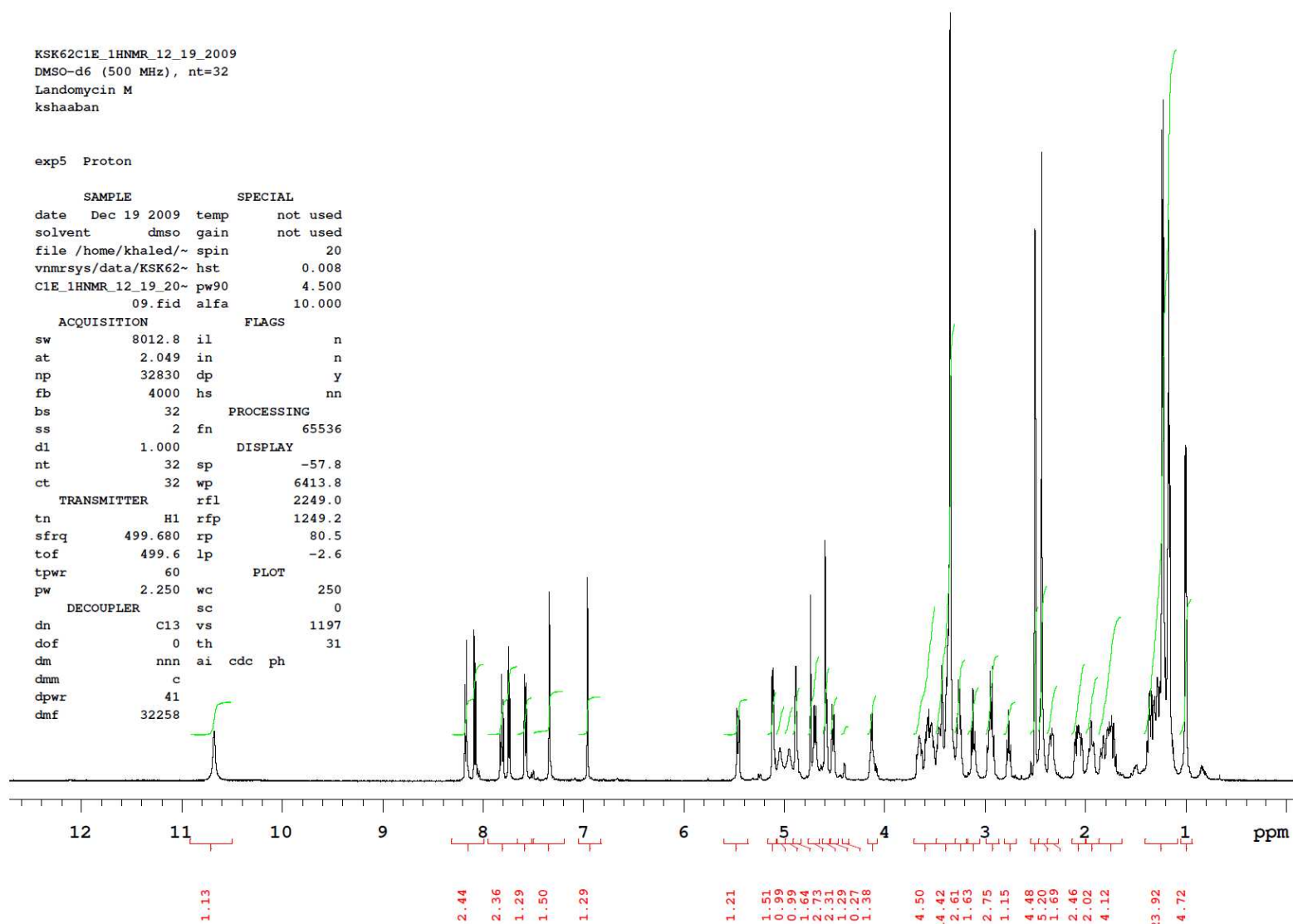


Figure S34: ^1H NMR spectrum (DMSO- d_6 , 500 MHz) of Landomycin M (**8**)

KSK62C1E_13CNMR_12_20_2009
DMSO-d6 (125 MHz), Time= 14 hrs
Landomycin M
kshaaban

exp4 Carbon

SAMPLE		SPECIAL	
date	Dec 19 2009	temp	not used
solvent	dms0	gain	30
file	/home/khaled/~	spin	20
vnmr	sys/data/KSK62~	hst	0.008
C1E_13CNMR_12_20_2~		pw90	11.900
	009.fid	alfa	10.000

ACQUISITION		FLAGS	
sw	30487.8	il	n
at	1.300	in	n
np	79298	dp	y
fb	17000	hs	nn

PROCESSING	
bs	64
dl	1.000 lb 0.50
nt	32000 fn not used
ct	27328

TRANSMITTER		DISPLAY	
tn	C13	wp	28868.4
sfrq	125.657	rfl	7069.3
tof	1285.0	rfl	4964.2
tpwr	59	rp	-363.0
pw	5.950	lp	93.2

DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	1.86409e+06
dmm	w	th	9
dpwr	32	ai	cdc ph
dmf	11912		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	23505.5	187.080	19.9	40	8629.6	68.683	15.9
2	23332.4	185.703	-9.2	41	8580.7	68.294	11.6
3	22710.4	180.752	20.3	42	8190.4	65.187	10.7
4	19591.2	155.927	21.6	43	5027.0	40.010	179.7
5	19442.4	154.742	25.7	44	5006.1	39.843	543.9
6	17657.8	140.539	16.7	45	4985.1	39.677	1083.4
7	17289.4	137.606	17.7	46	4964.2	39.510	1278.9
8	17277.8	137.514	19.7	47	4943.3	39.343	1069.2
9	16994.9	135.262	9.2	48	4922.3	39.177	530.9
10	16940.9	134.833	14.3	49	4900.9	39.006	167.5
11	16883.7	134.377	18.9	50	4866.5	38.732	13.9
12	16704.2	132.948	21.7	51	4792.5	38.144	9.4
13	15376.0	122.377	11.1	52	4492.0	35.752	13.6
14	15313.7	121.881	11.7	53	3016.4	24.007	17.6
15	15116.4	120.311	26.1	54	2906.1	23.130	-9.1
16	15006.6	119.438	10.2	55	2654.9	21.130	17.2
17	14802.4	117.812	21.3	56	2251.1	17.917	21.0
18	14649.8	116.598	15.2	57	2235.3	17.791	29.6
19	13804.1	109.866	9.5	58	2228.8	17.739	27.5
20	13382.1	106.508	9.6	59	2220.9	17.676	30.2
21	12667.1	100.817	20.0	60	2132.9	16.976	32.5
22	12594.5	100.240	15.1				
23	12562.4	99.984	13.7				
24	12386.6	98.585	9.7				
25	12152.1	96.719	16.4				
26	12033.0	95.771	9.4				
27	11567.8	92.068	12.5				
28	10947.2	87.129	17.7				
29	10865.3	86.477	21.3				
30	10403.9	82.804	9.7				
31	9864.7	78.513	9.3				
32	9595.3	76.369	16.7				
33	9507.9	75.673	12.7				
34	9279.5	73.855	12.5				
35	9179.9	73.063	13.0				
36	9037.1	71.926	32.7				
37	8819.8	70.197	13.6				
38	8798.9	70.030	16.1				
39	8753.3	69.668	20.9				

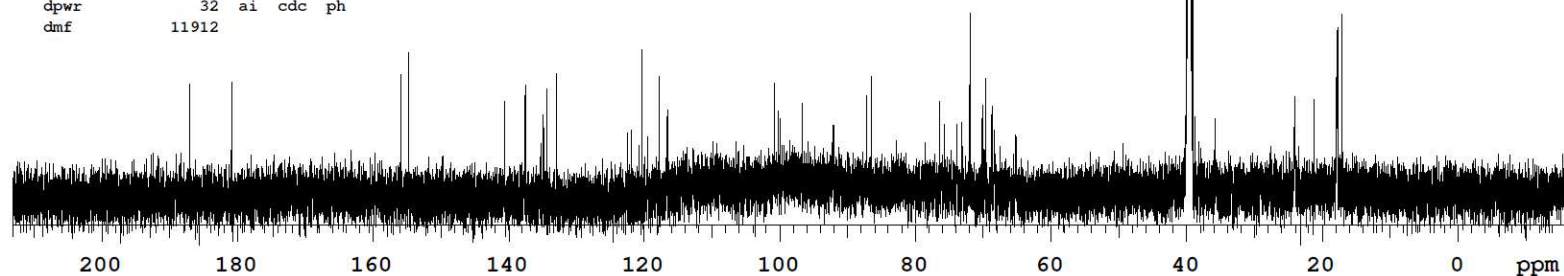


Figure S35: ^{13}C NMR spectrum (DMSO- d_6 , 125 MHz) of Landomycin M (8)

KSS136F5A2B2A1_1HNMR_10_05_2009_CDCL3
CDCL3 (500 MHz)
KShaaban
nt=32

Sample: KSS136F5A2B2A1_1HNMR_10_05_2009_CDCL3
File: xp

Pulse Sequence: s2pul

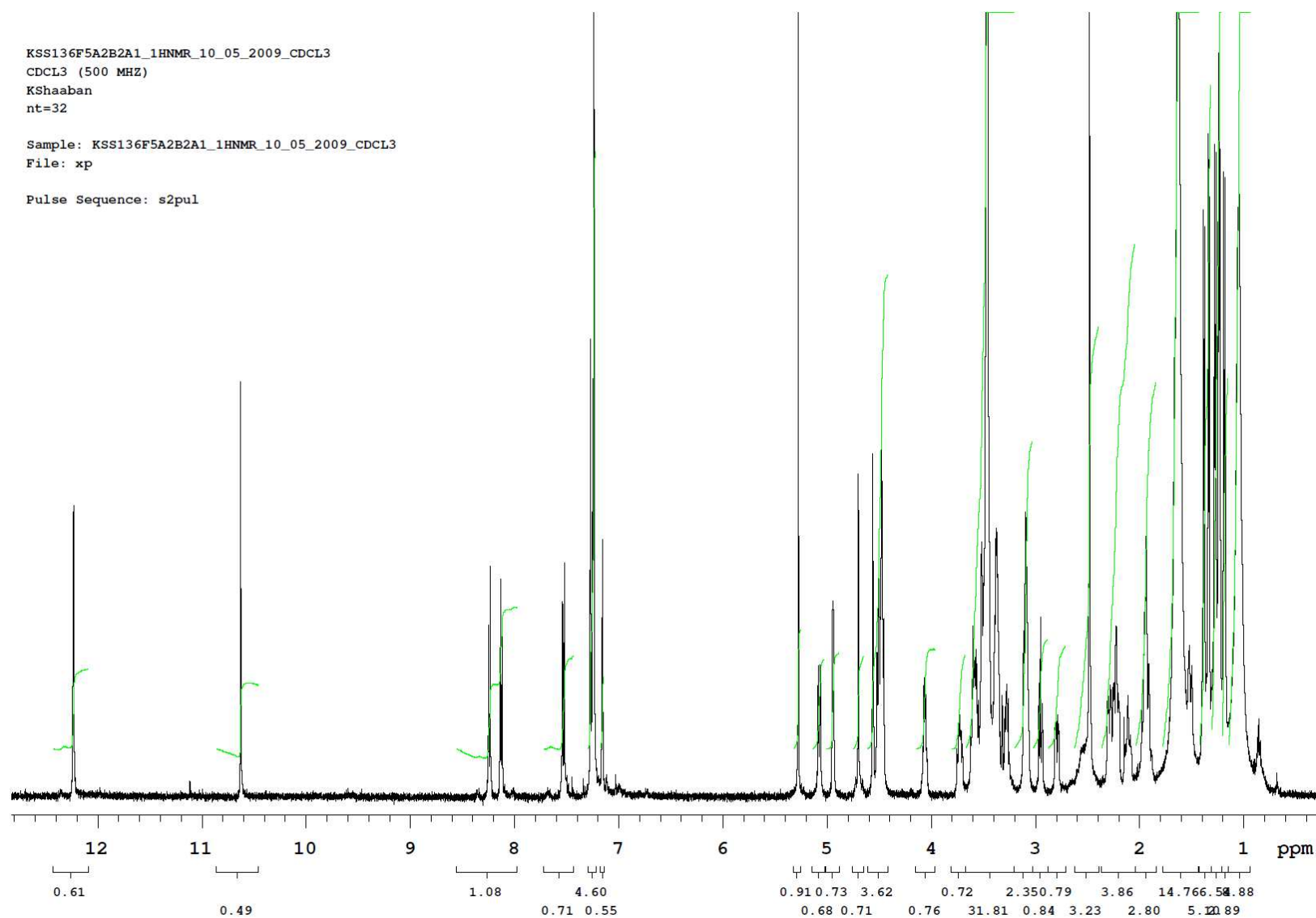


Figure S36: ^1H NMR spectrum (CDCl_3 , 500 MHz) of Landomycin W (7)

KSS136F5A2B2A1_1HNMR_10_02_2009
DMSO-d6
nt=32
kshaaban

Sample: KSS136F5A2B2A1_1HNMR_10_02_2009
File: xp
Pulse Sequence: s2pul

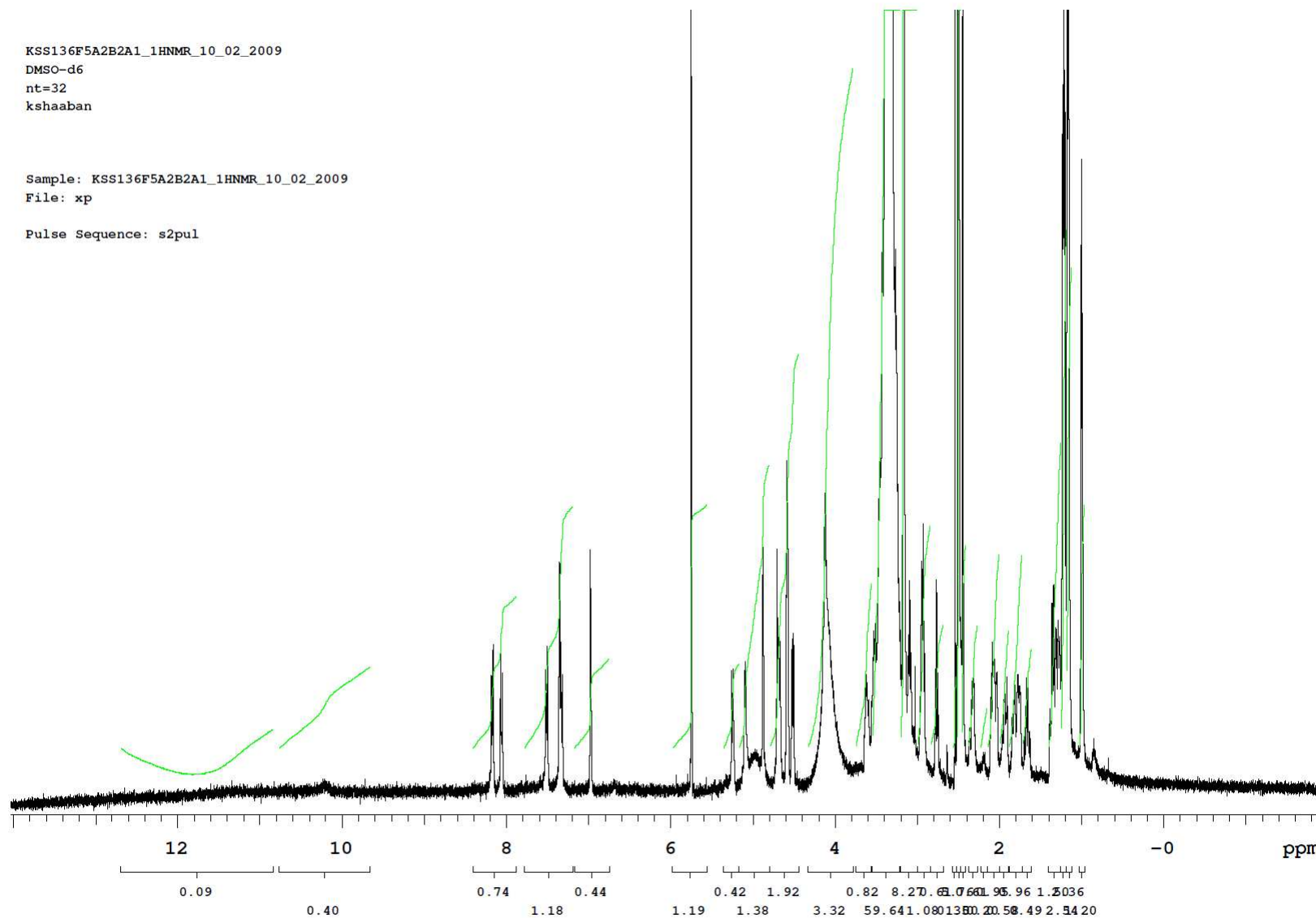


Figure S37: ^1H NMR spectrum ($\text{DMSO}-d_6$, 500 MHz) of Landomycin W (7)

KSS136F5A2A2_1HNMR_10_09_2009
500 MHz (CDCl₃)
nt=32
Landomycin A
kshaaban

Sample: KSS136F5A2A2_1HNMR_10_09_2009
File: xp

Pulse Sequence: s2pul

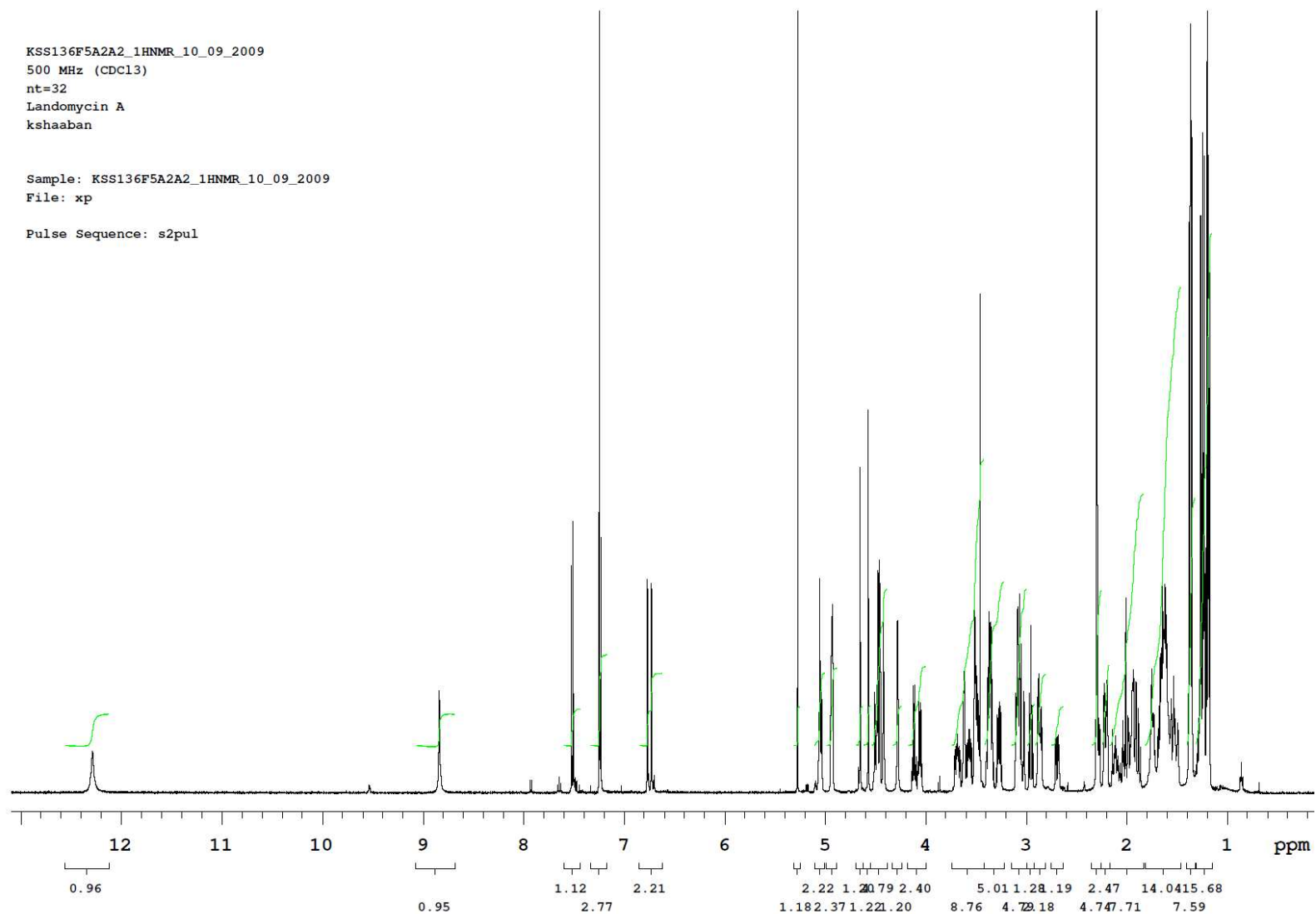


Figure S38: ¹H NMR spectrum (CDCl₃, 500 MHz) of Landomycin A (16)

09-0580 #35 RT: 1.53 AV: 1 NL: 1.08E5
T: - p Full ms2 1085.50@29.00 [295.00-2000.00]

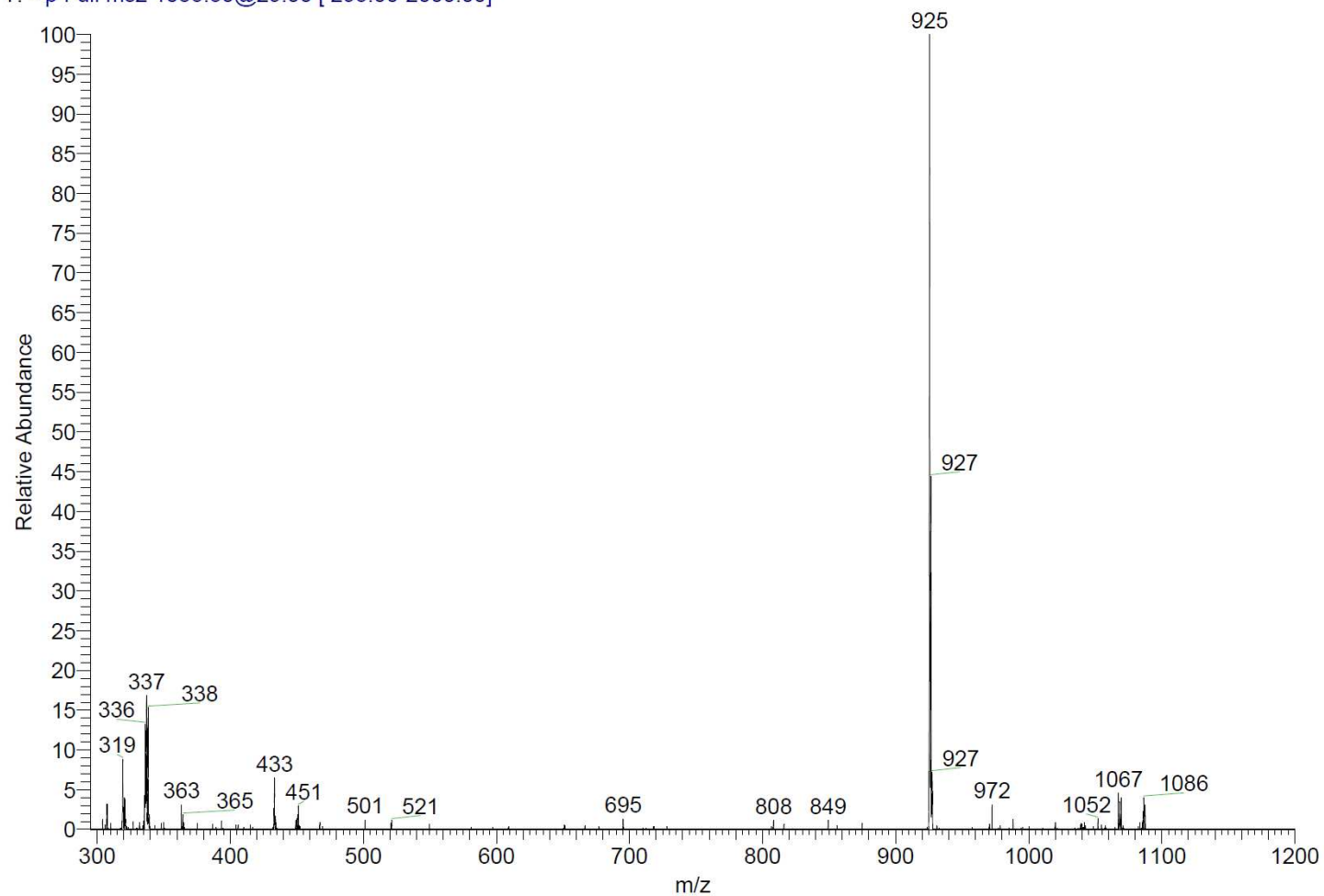


Figure S39: (-) ESI-MS/MS Fragmentation pattern of Landomycin A (**16**)

KSK62F3_1HNMR_11_05_2009
CDCl₃ (500 MHz)
kshaaban
nt=32

Sample: KSK62F3_1HNMR_11_05_2009
File: xp

Pulse Sequence: s2pul

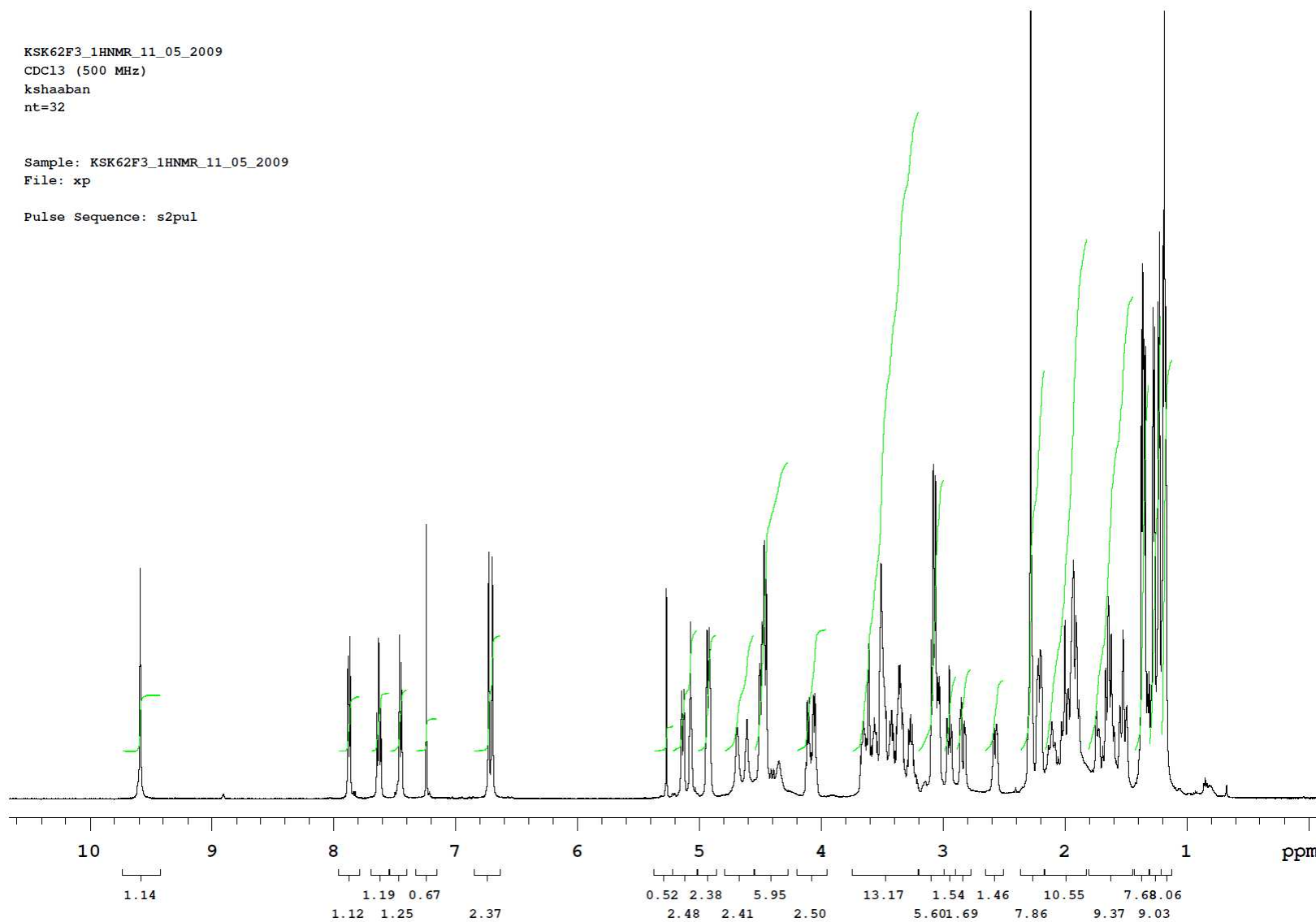


Figure S40: ¹H NMR spectrum (CDCl₃, 500 MHz) of Landomycin S (**17**)

KSS136F5A2A1_13CNMR_10_12_2009

CDCl₃, 125 MHz

KShaaban

nt=30000 (time = 20hrs)

exp4 Carbon

SAMPLE		SPECIAL	
date	Oct 11 2009	temp	not used
solvent	cdcl3	gain	30
file	/home/khaled/~	spin	20
vnmsys/data/KSS13~		hst	0.008
6F5A2A1_13CNMR_10_~		pw90	11.900
12_2009.fid	alfa		10.000

ACQUISITION		FLAGS	
sw	30487.8	il	n
at	1.300	in	n
np	79298	dp	y
fb	17000	hs	nn
bs	64	PROCESSING	
dl	1.000	lb	0.50
nt	30000	fn	not used
ct	30000	DISPLAY	

TRANSMITTER		sp	
tn	C13	wp	29351.3
sfrq	125.657	rfl	11725.5
tof	1285.0	rfp	9703.4
tpwr	59	rp	-170.2
pw	5.950	lp	-8.8

DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	1.48247e+06
dmm	w	th	8
dpwr	32	ai	cdc ph
dmf	11912		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	23830.4	189.667	29.4	40	8731.6	69.495	9.7
2	23088.8	183.765	27.2	41	8539.0	67.962	30.3
3	19651.0	156.403	27.1	42	8530.6	67.896	28.3
4	19582.1	155.855	35.5	43	8457.1	67.311	24.3
5	18328.4	145.876	23.5	44	8445.5	67.218	22.2
6	18071.6	143.832	24.7	45	7798.4	62.068	10.4
7	17427.7	138.708	23.5	46	7782.6	61.942	13.5
8	17209.5	136.971	23.4	47	4836.9	38.497	15.5
9	16932.3	134.765	26.7	48	4732.7	37.668	9.8
10	15543.2	123.709	16.7	49	4689.4	37.323	16.0
11	15454.3	123.002	9.3	50	4677.3	37.227	17.8
12	15160.8	120.665	22.4	51	4590.8	36.538	13.1
13	15092.4	120.121	21.5	52	3227.8	25.690	34.2
14	14242.5	113.356	28.7	53	3175.7	25.275	18.6
15	12774.3	101.671	22.3	54	3098.4	24.660	17.8
16	12705.0	101.119	23.2	55	3053.3	24.301	32.0
17	12400.7	98.698	15.5	56	2686.7	21.384	12.8
18	12384.4	98.568	12.6	57	2679.3	21.324	11.1
19	12312.3	97.994	13.4	58	2269.9	18.066	36.7
20	12294.2	97.850	13.8	59	2264.3	18.022	48.1
21	12278.4	97.724	24.6	60	2163.8	17.222	23.4
22	12260.2	97.579	23.0	61	2157.8	17.174	22.2
23	11143.3	88.690	12.0	62	2149.4	17.107	17.2
24	11051.1	87.956	16.3				
25	10137.0	80.681	10.1				
26	10106.8	80.440	9.7				
27	9735.5	77.485	317.8				
28	9722.5	77.382	10.7				
29	9703.4	77.230	327.4				
30	9671.3	76.975	314.9				
31	9549.0	76.001	17.0				
32	9539.2	75.923	13.0				
33	9481.1	75.460	29.0				
34	9477.8	75.434	26.9				
35	9117.7	72.568	15.7				
36	9106.1	72.476	15.2				
37	8936.3	71.124	10.0				
38	8865.1	70.558	24.2				
39	8782.3	69.899	8.6				

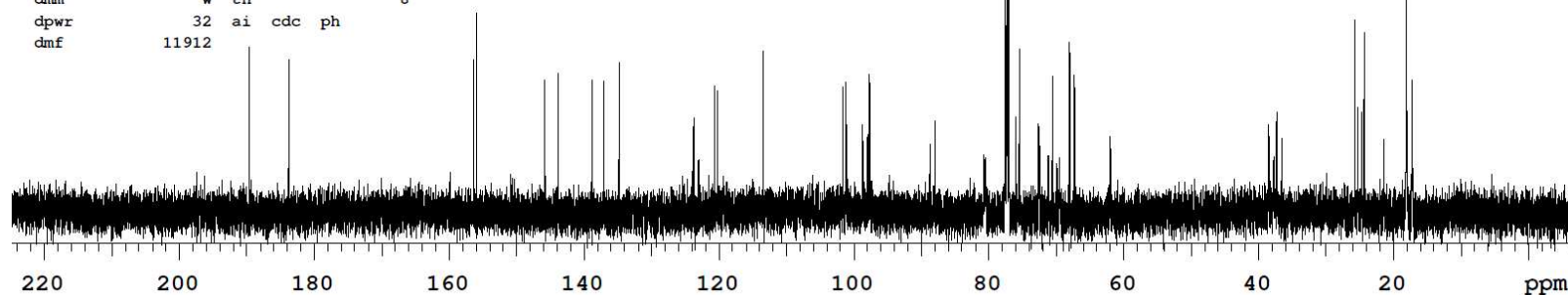


Figure S41: ¹³C NMR spectrum (CDCl₃, 125 MHz) of Landomycin S (**17**)

09-0579 #36-42 RT: 1.56-1.76 AV: 7 NL: 1.89E5
T: - p Full ms2 1069.50@29.00 [290.00-2000.00]

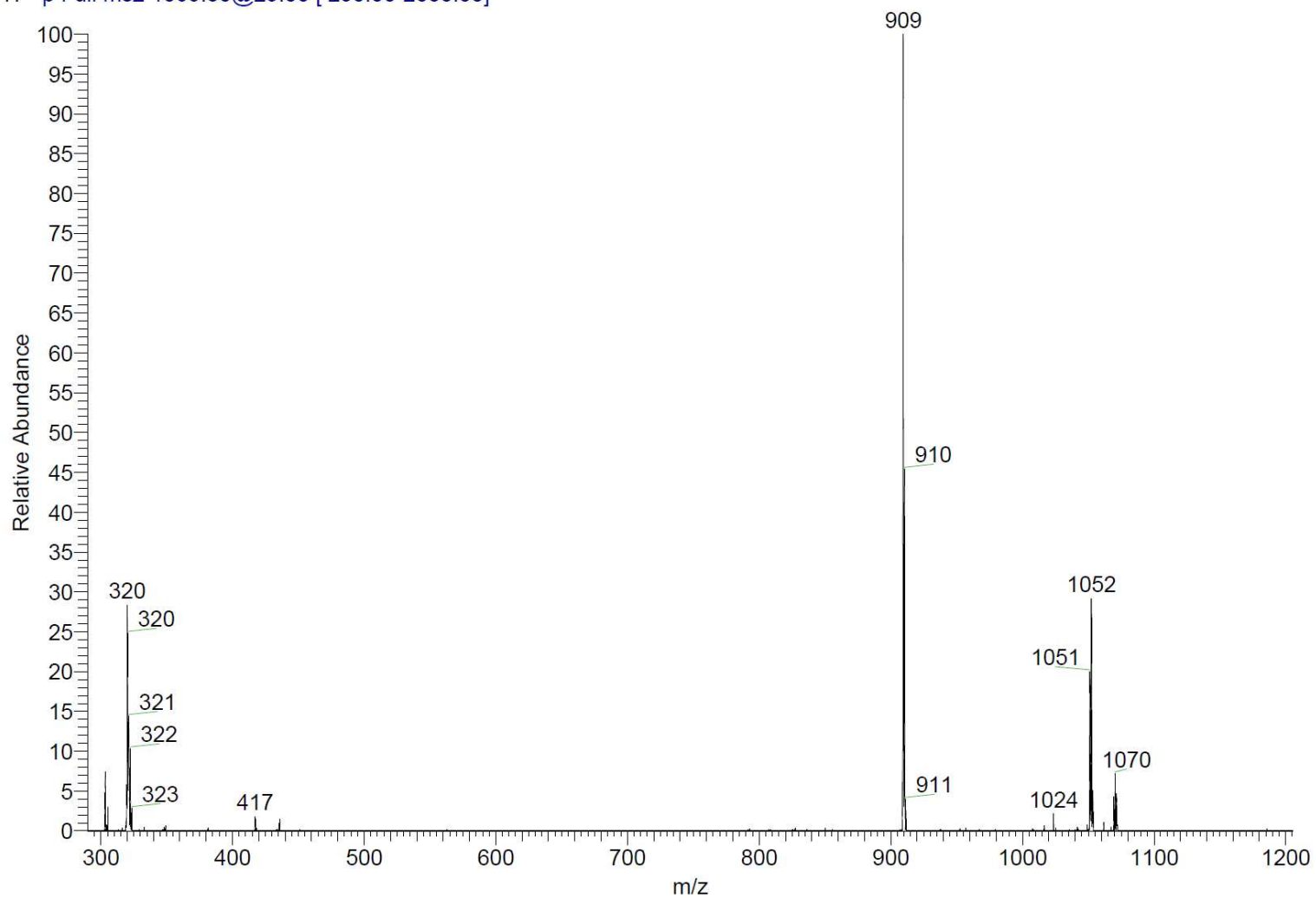


Figure S42: (-) ESI-MS/MS Fragmentation pattern of Landomycin S (**17**)
S44

KSK62C1F_1HNMR_12_04_2009
 CDC13 (500 MHz), nt=32
 KShaaban

exp4 Proton

SAMPLE		SPECIAL	
date	Dec 4 2009	temp	not used
solvent	cdc13	gain	not used
file	/home/khaled/~	spin	20
vnmrsys/data/KSK62~		hst	0.008
C1F_1HNMR_12_04_20~		pw90	4.500
09.fid	alfa		10.000
ACQUISITION		FLAGS	
sw	8012.8	il	n
at	2.049	in	n
np	32830	dp	y
fb	4000	hs	nn
bs	32	PROCESSING	
ss	2	fn	65536
dl	1.000	DISPLAY	
nt	32	sp	-29.5
ct	32	wp	6413.8
TRANSMITTER		rfl	4635.6
tn	H1	rfl	3617.6
sfrq	499.678	rp	-0.1
tof	499.7	lp	4.7
tpwr	60	PLOT	
pw	2.250	wc	250
DECOUPLER		sc	0
dn	C13	vs	2176
dof	0	th	50
dm	nnn	ai	cdc ph
dmm	c		
dpwr	41		
dmf	32258		

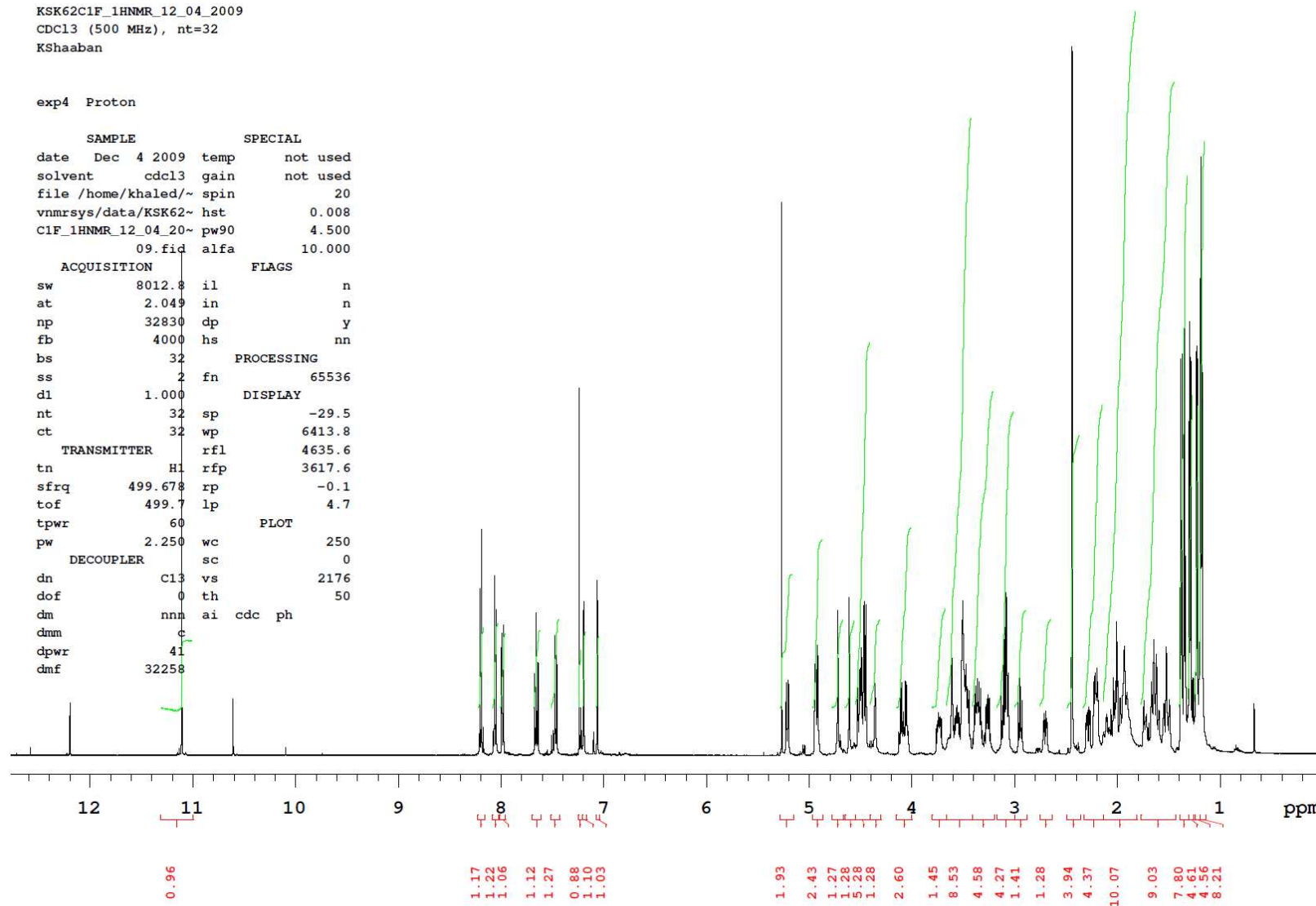


Figure S43: ^1H NMR spectrum (CDCl_3 , 500 MHz) of Landomycin T (**9**)

KSS136F4A1A2_1HNMR_09_28_2009
 DMSO-d6
 500 MHz
 nt=64
 kshaaban

Sample: KSS136F4A1A2_1HNMR_08_28_2009
 File: xp

Pulse Sequence: s2pul

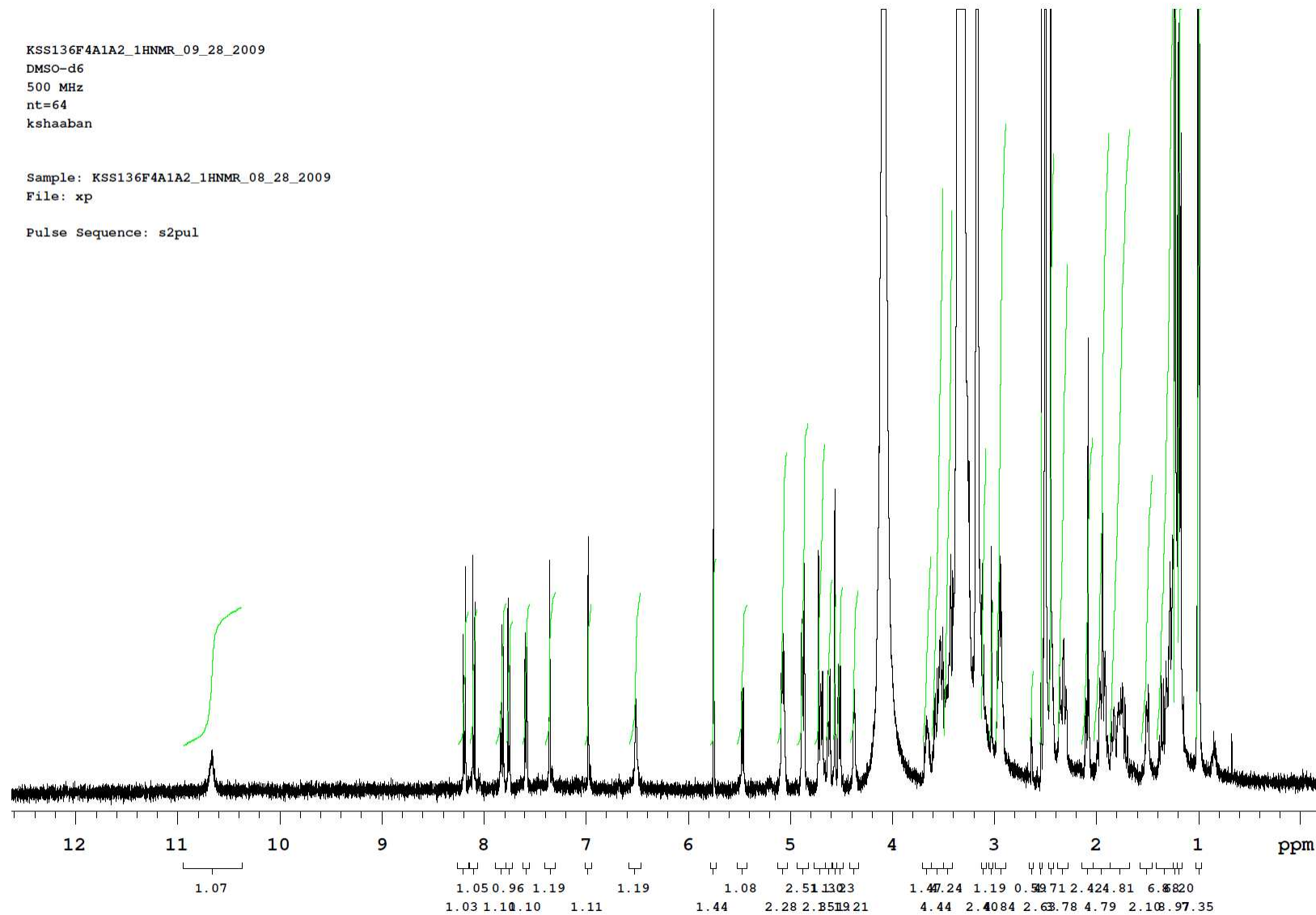


Figure S44: ¹H NMR spectrum (DMSO-*d*₆, 500 MHz) of Landomycin T (9)

KSK62C1F_13CNMR_12_10_2009
 CDC13 (125 MHz), time=15 hrs
 kshaaban

exp4 Carbon

SAMPLE		SPECIAL	
date	Dec 9 2009	temp	not used
solvent	cdcl3	gain	30
file	/home/khaled/~	spin	20
vnmsys/data/KSK62~		hst	0.008
CIF_13CNMR_12_10_2~		pw90	11.900
	009.fid	alfa	10.000

ACQUISITION		FLAGS	
sw	30487.8	il	n
at	1.300	in	n
np	79298	dp	y
fb	17000	hs	nn

PROCESSING	
dl	1.000 lb 0.50
nt	32000 fn not used
ct	23424 DISPLAY

TRANSMITTER		sp	
tn	C13	wp	-1957.9
sfrq	125.657	rfl	27485.4
tof	1285.0	rfp	11733.0
tpwr	59	rp	9703.4
pw	5.950	lp	0.2
			52.2

DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	964857
dmm	w	th	7
dpwr	32	ai	cdc ph
dmf	11912		

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	23945.3	190.581	33.6	40	9471.8	75.386	21.7
2	22846.0	181.832	28.4	41	9465.2	75.334	20.1
3	19664.4	156.510	28.8	42	9107.5	72.487	13.8
4	19488.6	155.110	41.4	43	9095.9	72.394	16.8
5	17761.3	141.363	26.9	44	8925.6	71.039	10.8
6	17400.8	138.493	33.0	45	8854.4	70.473	27.0
7	17308.6	137.760	26.8	46	8761.4	69.732	8.9
8	17219.8	137.053	35.2	47	8733.5	69.510	10.2
9	17176.1	136.705	33.3	48	8719.5	69.399	8.7
10	16954.6	134.942	9.2	49	8532.5	67.911	21.8
11	16430.8	130.773	30.4	50	8523.2	67.837	18.8
12	15680.4	124.801	7.5	51	8445.1	67.214	18.9
13	15500.8	123.372	14.3	52	8433.0	67.118	18.4
14	15439.0	122.879	24.3	53	4821.6	38.375	11.9
15	15272.0	121.550	25.0	54	4742.9	37.749	8.6
16	15254.8	121.413	12.2	55	4686.2	37.297	14.4
17	15242.7	121.317	12.6	56	4665.7	37.135	16.9
18	15069.1	119.936	11.1	57	3219.4	25.623	34.7
19	15059.4	119.858	9.2	58	3166.3	25.201	17.5
20	14981.7	119.240	26.5	59	3091.4	24.605	17.5
21	12769.1	101.630	21.2	60	3044.9	24.235	25.8
22	12697.0	101.056	25.2	61	2693.7	21.439	14.9
23	12686.3	100.971	15.1	62	2683.9	21.361	13.0
24	12409.5	98.768	15.5	63	2268.5	18.055	33.6
25	12395.1	98.653	13.3	64	2261.5	18.000	50.4
26	12316.0	98.024	16.0	65	2255.5	17.951	39.4
27	12296.5	97.868	14.3	66	2165.2	17.233	19.1
28	12278.8	97.728	19.7	67	2158.7	17.181	24.0
29	12259.7	97.576	17.4	68	2150.8	17.118	18.5
30	11133.5	88.612	11.4				
31	11051.6	87.960	18.3				
32	10141.7	80.718	9.6				
33	10111.0	80.473	9.7				
34	9735.5	77.485	280.6				
35	9720.6	77.367	10.1				
36	9703.4	77.230	294.1				
37	9671.3	76.975	287.3				
38	9549.0	76.001	12.5				
39	9538.8	75.919	13.7				

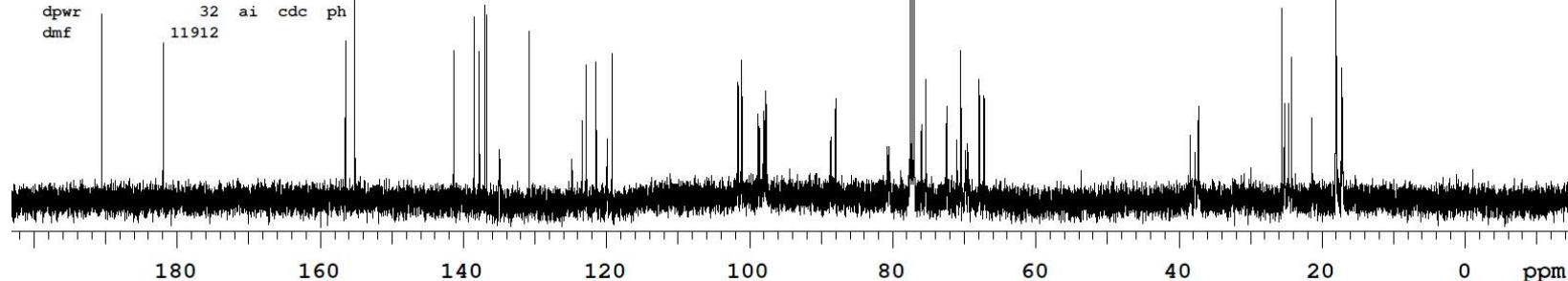


Figure S45: ^{13}C NMR spectrum (CDCl_3 , 125 MHz) of Landomycin T (9)

KSS136F4A1A1_1HNMR_10_05_2009_CDCL3
CDCL3 (500 MHz)
KShaaban
nt=32

Sample: KSS136F4A1A1_1HNMR_10_05_2009_CDCL3
File: xp

Pulse Sequence: s2pul

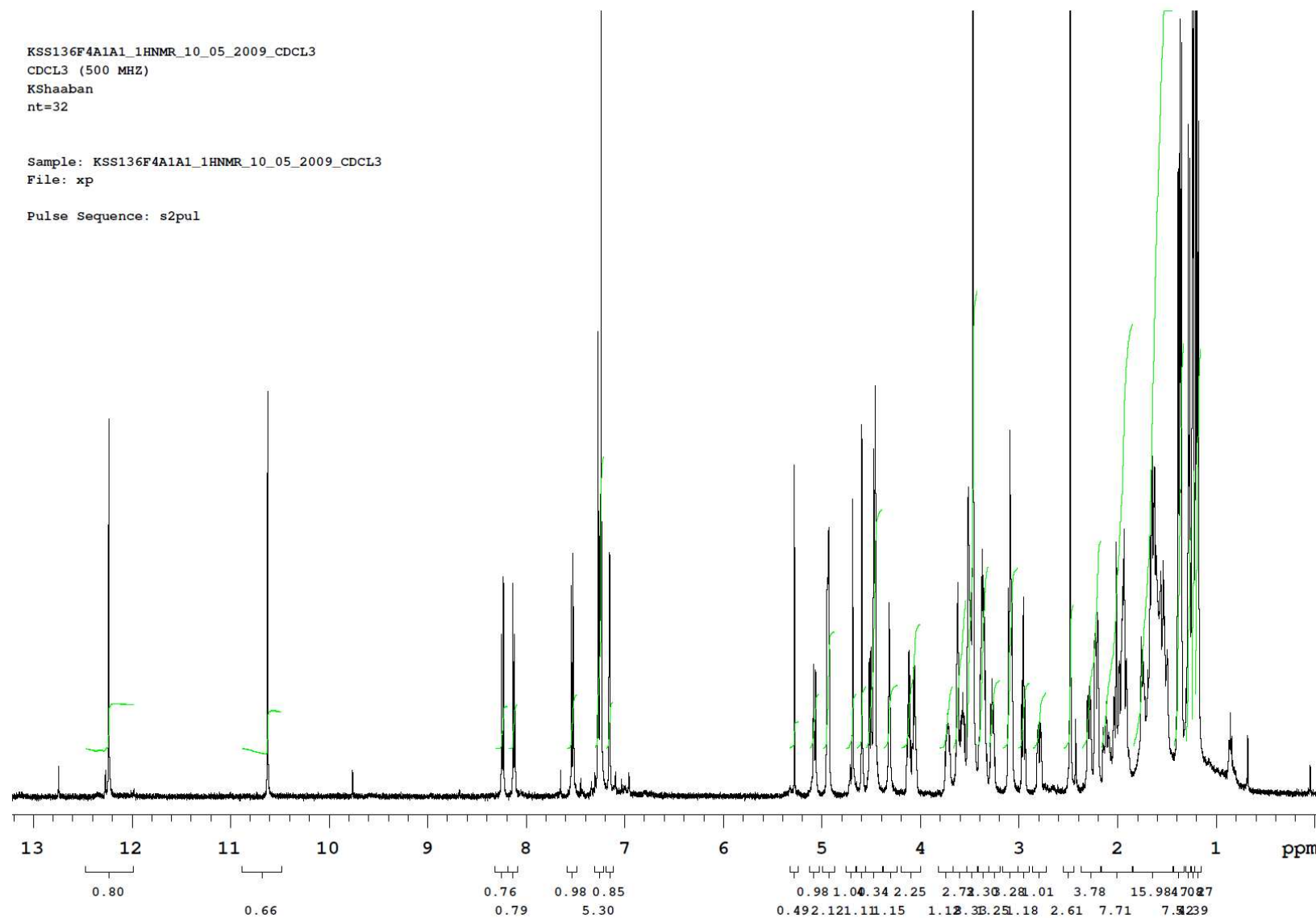


Figure S46: ^1H NMR spectrum (CDCl_3 , 500 MHz) of Landomycin U (10)

KSS136F4A1A1_1HNMR_08_28_2009
 DMSO-d6
 500 MHz
 nt=32
 kshaaban

Sample: KSS136F4A1A1_1HNMR_08_28_2009
 File: xp

Pulse Sequence: s2pul

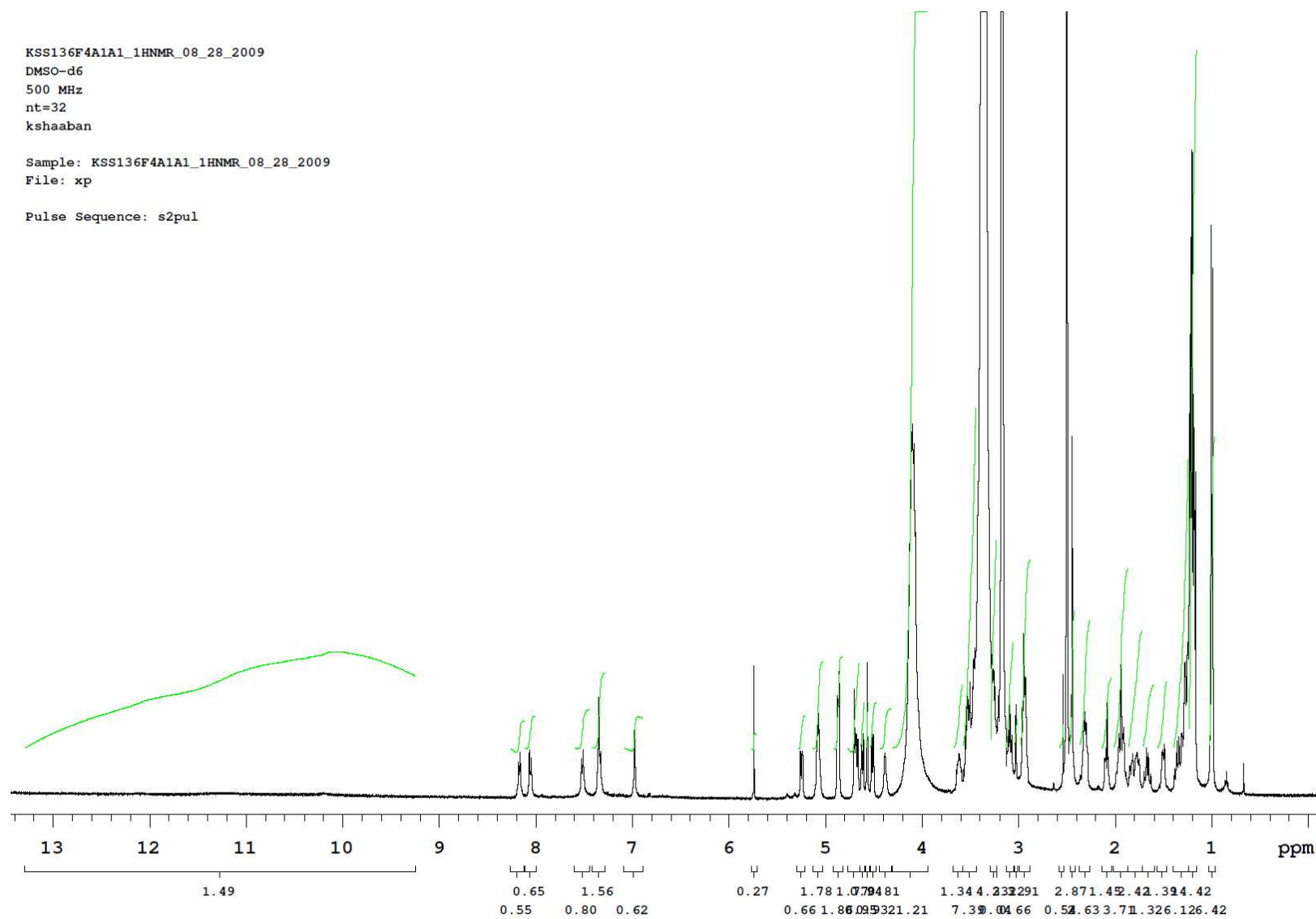


Figure S47: ^1H NMR spectrum (DMSO- d_6 , 500 MHz) of Landomycin U (10)

09-0641 #173-178 RT: 6.14-6.38 AV: 6 NL: 5.78E4
T: - p Full ms2 1067.40@28.00 [235.00-1500.00]

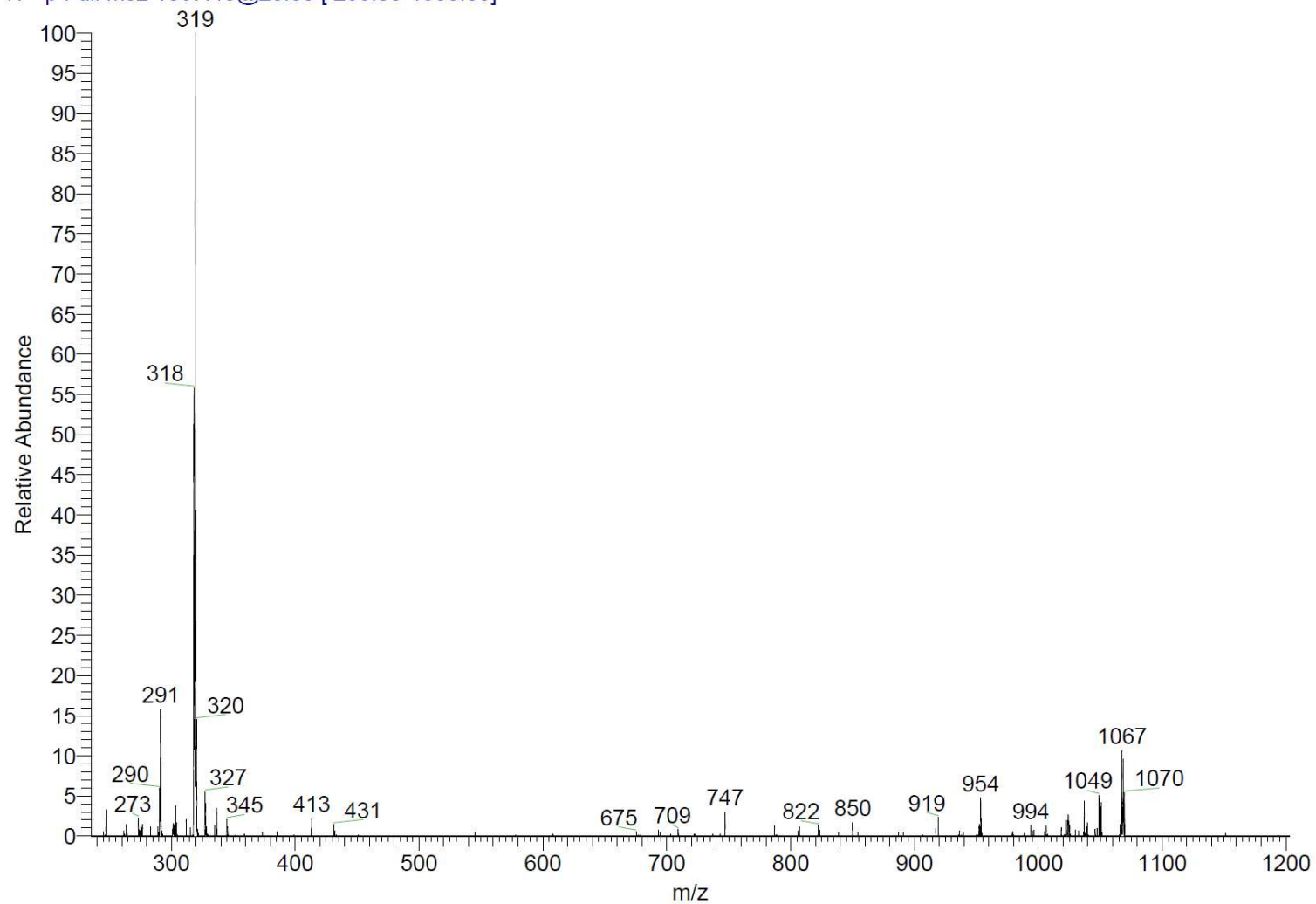


Figure S48: (-) ESI-MS/MS Fragmentation pattern of Landomycin U (**10**)
S50