

Supporting Information-II

Two-step, High-yielding Total Synthesis of Antibiotic Pyrones

Akram Hussain,^{[a]‡} Revoju Sravanthi,^{[a][b]‡} Sunitha Katta,^[b] and Dhevalapally B. Ramachary*^[a]

[a] Dr. Akram Hussain, Ms. Revoju Sravanthi, and Prof. Dr. Dhevalapally B. Ramachary
Catalysis Laboratory, School of Chemistry, University of Hyderabad, Hyderabad-500 046, India; E-mail: ramsc@uohyd.ac.in,
ramchary.db@gmail.com

[b] Dr. Sunitha Katta and Ms. Revoju Sravanthi, Pharmacognosy and Phytochemistry Division, Gitam Institute of Pharmacy, Gitam Deemed to
be University, Visakhapatnam, 530 045, Andhra Pradesh, India

‡These authors contributed equally.

CONTENTS

	Page No
1. Correlation NMR data of compound 7ab (Isogermicidin B)	S-3
2. Correlation NMR data of compound 7bb (Isogermicidin A)	S-4
3. Correlation NMR data of compound 7bc (Photopyrone A)	S-5
4. Correlation NMR data of compound 7cc (Pseudopyronine A)	S-6
5. Correlation NMR data of compound 7gc (Pseudopyronine B)	S-8
6. Correlation NMR data of compound 7jc (Pseudopyronine C)	S-9
7. Correlation NMR data of compound 7bd (Photopyrone B)	S-11
8. Correlation NMR data of compound 7bh (Germicidin I)	S-13
9. Correlation NMR data of compound 7ch (Violapyrone L)	S-14

10. Correlation NMR data of compound 7dh (Violapyrone J1)	S-15
11. Correlation NMR data of compound 7eh (Violapyrone J)	S-16
12. Correlation NMR data of compound 7fh (Violapyrone A)	S-18
13. Correlation NMR data of compound 7gh (Violapyrone I)	S-19
14. Correlation NMR data of compound 7hh (Violapyrone B)	S-20
15. Correlation NMR data of compound 7ih (Violapyrone H)	S-21
16. Correlation NMR data of compound (-)- 7lh [(-)-Violapyrone C]	S-23
17. Correlation NMR data of compound 11ch (Childinin G)	S-24
18. Correlation NMR data of compound 11fh (Violapyrone Q)	S-26
19. Correlation NMR data of compound 11gh (Violapyrone S)	S-27
20. Correlation NMR data of compound 11hh (Violapyrone R)	S-29
21. Correlation NMR data of compound 3d (Fistupyrene)	S-30
22. Correlation HRMS data of compound 7be (Photopyrone C), 7bf (Photopyrone E), 7bg (Photopyrone G)	S-31
23. References	S32-S33
24. Correlated ¹ H NMR and ¹³ C NMR Spectral data	S34-S73

Table S1. Correlation of Natural and Synthetic NMR Data of Compound **7ab** (Isogermicidin B):¹

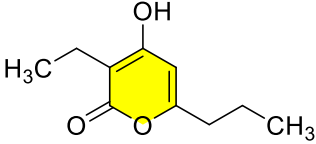
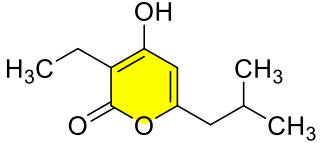
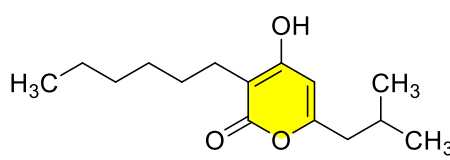
 <p>3-ethyl-4-hydroxy-6-propyl-2H-pyran-2-one (7ab) (Isogermicidin B)</p>		Isolated compound ¹³ C NMR (125 MHz, CD ₃ OD)	Present synthetic compound ¹³ C NMR (125 MHz, CD ₃ OD)
		168.9 (C)	168.8 (C)
		168.0 (C)	167.6 (C)
		165.0 (C)	165.0 (C)
		105.3 (C)	105.3 (C)
		101.6 (CH)	101.3 (CH)
Isolated compound ¹ H NMR (500 MHz, CD ₃ OD)	Present synthetic compound ¹ H NMR (500 MHz, CD ₃ OD)	36.3 (CH ₂)	36.3 (CH ₂)
5.98 (1H, s)	6.00 (1H, s)	21.4 (CH ₂)	21.3 (CH ₂)
2.44 (2H, t, <i>J</i> = 7.5 Hz)	2.46 (2H, t, <i>J</i> = 7.5 Hz)	17.4 (CH ₂)	17.3 (CH ₂)
2.39 (2H, q, <i>J</i> = 7.5 Hz)	2.41 (2H, q, <i>J</i> = 7.5 Hz)	13.8 (CH ₃)	13.7 (CH ₃)
1.67 (2H, m)	1.69 (2H, sext, <i>J</i> = 7.5 Hz)	12.9 (CH ₃)	12.9 (CH ₃)
1.03 (3H, t, <i>J</i> = 7.4 Hz)	1.05 (3H, t, <i>J</i> = 7.5 Hz)		
0.98 (3H, t, <i>J</i> = 7.4 Hz)	0.99 (3H, t, <i>J</i> = 7.5 Hz)		

Table S2. Correlation of Natural and Synthetic NMR Data of Compound **7bb** (Isogermicidin A):¹

 <p>3-ethyl-4-hydroxy-6-isobutyl-2H-pyran-2-one (7bb) (Isogermicidin A)</p>		Isolated compound ¹³ C NMR (125 MHz, CD ₃ OD)	Present synthetic compound ¹³ C NMR (125 MHz, CD ₃ OD)
		168.9 (C)	168.8 (C)
		167.9 (C)	167.5 (C)
		164.3 (C)	164.3 (C)
		105.3 (C)	105.3 (C)
		102.5 (CH)	102.2 (CH)
Isolated compound ¹ H NMR (500 MHz, CD ₃ OD)	Present synthetic compound ¹ H NMR (500 MHz, CD ₃ OD)	43.6 (CH ₂)	43.5 (CH ₂)
5.97 (1H, s)	5.99 (1H, s)	28.3 (CH)	28.1 (CH)
2.39 (2H, q, <i>J</i> = 7.4 Hz)	2.42 (2H, q, <i>J</i> = 7.5 Hz)	22.6 (2 x CH ₃)	22.5 (2 x CH ₃)
2.32 (2H, d, <i>J</i> = 7.2 Hz)	2.35 (2H, d, <i>J</i> = 7.0 Hz)	17.4 (CH ₂)	17.3 (CH ₂)
2.03 (1H, m)	2.05 (1H, nonet, <i>J</i> = 7.0 Hz)	12.9 (CH ₃)	12.9 (CH ₃)
1.04 (3H, t, <i>J</i> = 7.4 Hz)	1.05 (3H, t, <i>J</i> = 7.5 Hz)		
0.96 (3H, d, <i>J</i> = 6.7 Hz)	0.98 (6H, d, <i>J</i> = 6.5 Hz)		

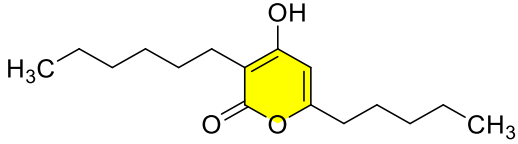
0.96 (3H, d, $J = 6.7$ Hz)		
----------------------------	--	--

Table S3. Correlation of Natural and Synthetic NMR Data of Compound **7bc** (Photopyrone A):²

 3-Hexyl-4-hydroxy-6-isobutyl-2H-pyran-2-one (7bc) (Photopyrone A)		Isolated compound ¹³ C NMR (125 MHz, CD ₃ OD)	Present synthetic compound ¹³ C NMR (125 MHz, CD ₃ OD)	
			174.1 (C)	168.3 (C)
			170.3 (C)	167.1 (C)
			164.0 (C)	163.7 (C)
			105.3 (CH)	103.5 (C)
			103.2 (C)	101.5 (CH)
Isolated compound ¹ H NMR (500 MHz, CD ₃ OD)	Present synthetic compound ¹ H NMR (500 MHz, CD ₃ OD)	43.1 (CH ₂)	42.9 (CH ₂)	
5.91 (1H, s)	5.94 (1H, s)	32.7 (CH ₂)	32.4 (CH ₂)	
2.34 (2H, dd, $J = 7.8, 7.2$ Hz)	2.34 (2H, t, $J = 7.5$ Hz)	30.0 (CH ₂)	29.7 (CH ₂)	
2.27 (2H, d, $J = 7.2$ Hz)	2.29 (2H, d, $J = 7.5$ Hz)	28.9 (CH ₂)	28.4 (CH ₂)	
2.01 (1H, sept, $J = 7.0$ Hz)	2.00 (1H, nonet, $J = 6.5$ Hz)	27.6 (CH)	27.6 (CH)	

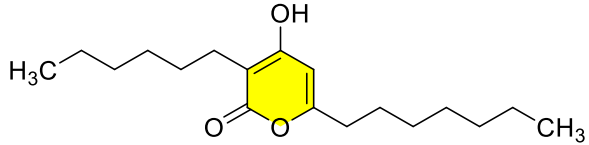
1.43 (2H, m)	1.42 (2H, quint, $J = 7.0$ Hz)	23.6 (CH ₂)	23.4 (CH ₂)
1.29 (2H, m)	1.32-1.24 (6H, m)	23.1 (CH ₂)	23.2 (CH ₂)
1.29 (2H, m)		22.1 (CH ₃)	21.9 (CH ₃)
1.29 (1H, m)		22.1 (CH ₃)	21.9 (CH ₃)
0.94 (3H, d, $J = 6.8$ Hz)	0.92 (3H, d, $J = 7.0$ Hz)	13.9 (CH ₃)	13.9 (CH ₃)
0.94 (3H, d, $J = 6.8$ Hz)	0.92 (3H, d, $J = 7.0$ Hz)		
0.88 (3H, d, $J = 6.8$ Hz)	0.86 (3H, t, $J = 6.0$ Hz)		

Table S4. Correlation of Natural and Synthetic NMR Data of Compound **7cc** (Pseudopyronine A):³

 3-Hexyl-4-hydroxy-6-pentyl-2H-pyran-2-one (7cc) (Pseudopyrinone A)	Isolated compound ¹³ C NMR (100 MHz, CD ₃ OD)	Present synthetic compound ¹³ C NMR (125 MHz, CD ₃ OD)	
		168.8 (C)	169.1 (C)
		167.7 (C)	168.0 (C)
		165.1 (C)	165.4 (C)
		103.9 (C)	104.2 (C)
		101.0 (CH)	101.3 (CH)

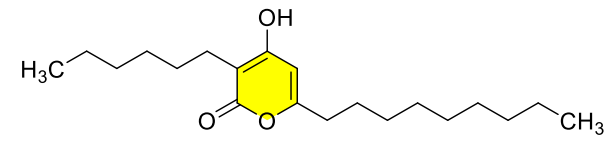
Isolated compound ¹ H NMR (400 MHz, CD ₃ OD)	Present synthetic compound ¹ H NMR (500 MHz, CD ₃ OD)		
		34.2 (CH ₂)	34.5 (CH ₂)
5.98 (1H, s)	6.02 (1H, s)	32.9 (CH ₂)	33.2 (CH ₂)
2.46 (2H, t, <i>J</i> = 7.6 Hz)	2.50 (2H, t, <i>J</i> = 7.5 Hz)	32.2 (CH ₂)	32.5 (CH ₂)
2.37 (2H, t, <i>J</i> = 7.5 Hz)	2.41 (2H, t, <i>J</i> = 8.0 Hz)	30.2 (CH ₂)	30.5 (CH ₂)
1.70-1.60 (2H, m)	1.69 (2H, quint, <i>J</i> = 7.5 Hz)	29.0 (CH ₂)	29.2 (CH ₂)
1.50-1.40 (2H, m)	1.49 (2H, quint, <i>J</i> = 7.5 Hz)	27.6 (CH ₂)	27.9 (CH ₂)
1.40-1.32 (10H, m)	1.44-1.33 (10H, m)	23.9 (CH ₂)	24.1 (CH ₂)
0.92 (3H, t, <i>J</i> = 7.0 Hz)	0.96 (3H, t, <i>J</i> = 7.5 Hz)	23.7 (CH ₂)	23.9 (CH ₂)
0.89 (3H, t, <i>J</i> = 7.0 Hz)	0.93 (3H, t, <i>J</i> = 6.5 Hz)	23.4 (CH ₂)	23.6 (CH ₂)
		14.4 (CH ₃)	14.7 (CH ₃)
		14.2 (CH ₃)	14.5 (CH ₃)

Table S5. Correlation of Natural and Synthetic NMR Data of Compound **7gc** (Pseudopyronine B):⁴

 <p>6-heptyl-3-hexyl-4-hydroxy-2<i>H</i>-pyran-2-one (7gc) (Pseudopyronine B)</p>		Isolated compound ¹³ C NMR (100 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹³ C NMR (125 MHz, DMSO- <i>d</i> ₆)
		165.0 (C)	164.8 (C)
		164.8 (C)	164.8 (C)
		162.6 (C)	162.7 (C)
		101.3 (C)	101.4 (C)
		99.2 (CH)	99.2 (CH)
Isolated compound ¹ H NMR (400 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)	32.6 (CH ₂)	32.6 (CH ₂)
	11.02 (1H, br s)	31.2 (CH ₂)	31.16 (CH ₂)
5.94 (1H, s)	5.96 (1H, s)	31.1 (CH ₂)	31.11 (CH ₂)
2.37 (2H, t, <i>J</i> = 8.0 Hz)	2.39 (2H, t, <i>J</i> = 7.5 Hz)	28.6 (CH ₂)	28.5 (CH ₂)
2.24 (2H, t, <i>J</i> = 8.0 Hz)	2.24 (2H, t, <i>J</i> = 7.5 Hz)	28.6 (CH ₂)	28.3 (CH ₂)
1.51 (2H, t, <i>J</i> = 8.0 Hz)	1.52 (2H, quint, <i>J</i> = 7.0 Hz)	28.2 (CH ₂)	28.2 (CH ₂)
1.35 (2H, t, <i>J</i> = 8.0 Hz)	1.35 (2H, quint, <i>J</i> = 7.0	27.5 (CH ₂)	27.5 (CH ₂)

	Hz)		
1.28 (2H, m)	1.31-1.17 (14H, m)	26.2 (CH ₂)	26.2 (CH ₂)
1.26 (2H, m)		22.7 (CH ₂)	22.6 (CH ₂)
1.26 (2H, m)		22.0 (CH ₂)	22.05 (CH ₂)
1.26 (2H, m)		22.0 (CH ₂)	22.02 (CH ₂)
1.26 (2H, m)		14.0 (CH ₃)	13.9 (CH ₃)
1.25 (2H, m)		13.8 (CH ₃)	13.9 (CH ₃)
1.25 (2H, m)			
0.84 (3H, m)		0.97-0.73 (6H, m)	
0.84 (3H, m)			

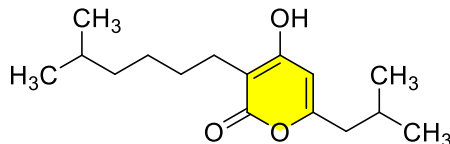
Table S6. Correlation of Natural and Synthetic NMR Data of Compound **7jc** (Pseudopyronine C):⁴

 <p>3-Hexyl-4-hydroxy-6-nonyl-2H-pyran-2-one (7jc) (Pseudopyrinone C)</p>	Isolated compound ¹³ C NMR (100 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹³ C NMR (100 MHz, DMSO- <i>d</i> ₆)
	166.9 (C)	164.7 (C)
	165.1 (C)	164.7 (C)

		162.0 (C)	162.7 (C)
		101.5 (C)	101.3 (C)
		100.4 (CH)	99.2 (CH)
Isolated compound ¹ H NMR (400 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)	32.6 (CH ₂)	32.5 (CH ₂)
	11.01 (1H, br s)	31.2 (CH ₂)	31.2 (CH ₂)
5.86 (1H, s)	5.98 (1H, s)	31.2 (CH ₂)	31.1 (CH ₂)
2.34 (2H, t, <i>J</i> = 8.0Hz)	2.41 (2H, t, <i>J</i> = 7.5 Hz)	28.8 (CH ₂)	28.8 (CH ₂)
2.22 (2H, t, <i>J</i> = 8.0 Hz)	2.26 (2H, t, <i>J</i> = 7.5 Hz)	28.6 (CH ₂)	28.62 (CH ₂)
1.50 (2H, t, <i>J</i> = 8.0 Hz)	1.54 (2H, quint, <i>J</i> = 6.5 Hz)	28.6 (CH ₂)	28.6 (CH ₂)
1.34 (2H, t, <i>J</i> = 8.0 Hz)	1.38 (2H, quint, <i>J</i> = 6.5 Hz)	28.6 (CH ₂)	28.5 (CH ₂)
1.28 (2H, m)		28.2 (CH ₂)	28.2 (CH ₂)

1.28 (2H, m)	1.28-1.23 (18H, m)	27.7 (CH ₂)	27.4 (CH ₂)
1.26 (2H, m)		26.2 (CH ₂)	26.2 (CH ₂)
1.26 (2H, m)		22.8 (CH ₂)	22.6 (CH ₂)
1.26 (2H, m)		22.1 (CH ₂)	22.05 (CH ₂)
1.26 (2H, m)		22.1 (CH ₂)	22.03 (CH ₂)
1.25 (2H, m)		13.9 (CH ₃)	13.9 (CH ₃)
1.24 (2H, m)		13.9 (CH ₃)	13.9 (CH ₃)
1.23 (2H, m)			
0.85 (3H, m)	0.96-0.78 (6H, m)		
0.85 (3H, m)			

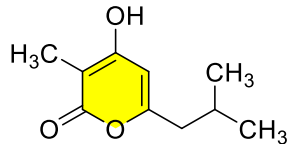
Table S7. Correlation of Natural and Synthetic NMR Data of Compound **7bd** (Photopyrone B):²

 4-Hydroxy-6-isobutyl-3-(5-methylhexyl)-2H-pyran-2-one (7bd) (Photopyrone B)	Isolated compound ¹³ C NMR (125 MHz, CD ₃ OD)	Present synthetic compound ¹³ C NMR (100 MHz, CD ₃ OD)	
		167.6 (C)	167.5 (C)
		166.9 (C)	166.3 (C)
		162.7 (C)	162.8 (C)

		102.4 (C)	102.5 (C)
		101.0 (CH)	100.6 (CH)
Isolated compound ¹ H NMR (500 MHz, CD ₃ OD)	Present synthetic compound ¹ H NMR (500 MHz, CD ₃ OD)	42.0 (CH ₂)	42.0 (CH ₂)
5.96 (1H, s)	5.97 (1H, s)	38.7 (CH ₂)	38.6 (CH ₂)
2.37 (2H, dd, <i>J</i> = 7.6, 7.3 Hz)	2.37 (2H, t, <i>J</i> = 8.0 Hz)	27.9 (CH ₂)	27.8 (CH ₂)
2.31 (2H, d, <i>J</i> = 7.0 Hz)	2.33 (2H, d, <i>J</i> = 7.5 Hz)	27.7 (CH)	27.7 (CH)
2.02 (1H, sept, <i>J</i> = 7.0 Hz)	2.03 (1H, nonet, <i>J</i> = 7.0 Hz)	26.9 (CH ₂)	26.9 (CH ₂)
1.52 (1H, sept, <i>J</i> = 6.7 Hz)	1.52 (1H, nonet, <i>J</i> = 6.5 Hz)	26.7 (CH)	26.7 (CH)
1.43 (2H, m)	1.44 (2H, quint, <i>J</i> = 7.5 Hz)	22.5 (CH ₂)	22.5 (CH ₂)
1.31 (2H, m)	1.36-1.28 (2H, m)	21.6 (CH ₃)	21.6 (CH ₃)
1.19 (2H, m)	1.20 (2H, q, <i>J</i> = 6.5 Hz)	21.6 (CH ₃)	21.6 (CH ₃)
0.94 (3H, d, <i>J</i> = 6.7 Hz)	0.95 (6H, d, <i>J</i> = 7.0 Hz)	21.0 (CH ₃)	21.1 (CH ₃)
0.94 (3H, d, <i>J</i> = 6.7 Hz)		21.0 (CH ₃)	21.1 (CH ₃)

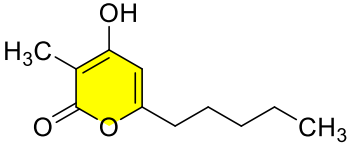
0.86 (3H, d, $J = 6.7$ Hz)	0.87 (6H, d, $J = 6.5$ Hz)		
0.86 (3H, d, $J = 6.7$ Hz)			

Table S8. Correlation of Natural and Synthetic NMR Data of Compound **7bh** (Germicidin I):⁵

 4-Hydroxy-6-isobutyl-3-methyl-2H-pyran-2-one (7bh) (Germicidin I)		Isolated compound ¹³ C NMR (125 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹³ C NMR (100 MHz, DMSO- <i>d</i> ₆)
		168.0 (C)	165.1 (C)
		165.4 (C)	164.7 (C)
		160.3 (C)	161.6 (C)
		101.9 (CH)	100.2 (CH)
		94.7 (C)	96.6 (C)
Isolated compound ¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)	41.6 (CH ₂)	41.6 (CH ₂)
	11.12 (1H, br s, OH)	26.0 (CH)	26.4 (CH)
5.86 (1H, s)	5.97 (1H, s)	21.7 (CH ₃)	21.9 (CH ₃)
2.21 (2H, d, $J = 6.5$ Hz)	2.28 (2H, d, $J = 7.0$ Hz)	21.7 (CH ₃)	21.9 (CH ₃)
1.89 (1H, m)	1.91 (1H, nonet, $J = 7.0$)	8.4 (CH ₃)	8.4 (CH ₃)

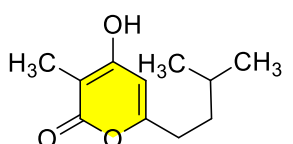
	Hz)		
1.69 (3H, s)	1.74 (3H, s)		
0.88 (3H, d, $J = 6.5$ Hz)	0.88 (6H, d, $J = 6.5$ Hz)		
0.88 (3H, d, $J = 6.5$ Hz)			

Table S9. Correlation of Natural and Synthetic NMR Data of Compound **7ch** (Violapyrone L):⁶

 <p>4-Hydroxy-3-methyl-6-pentyl-2H-pyran-2-one (7ch) (Violapyrone L)</p>	Isolated compound ¹³ C NMR (125 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹³ C NMR (125 MHz, DMSO- <i>d</i> ₆)	
	165.2 (C)	167.7 (C)	
	165.0 (C)	167.1 (C)	
	163.2 (C)	164.2 (C)	
	99.6 (CH)	100.6 (CH)	
	96.3 (C)	97.7 (C)	
Isolated compound ¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)		
5.98 (1H, s)	5.98 (1H, s)	32.9 (CH ₂)	33.1 (CH ₂)
2.40 (2H, t, $J = 7.5$ Hz)	2.36 (2H, t, $J = 7.5$ Hz)	30.8 (CH ₂)	30.9 (CH ₂)
		26.3 (CH ₂)	26.5 (CH ₂)

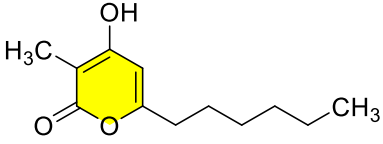
1.74 (3H, s)	1.70 (3H, s)	22.1 (CH ₂)	22.3 (CH ₂)
1.53 (2H, quintet, <i>J</i> = 7.5 Hz)	1.48 (2H, quintet, <i>J</i> = 7.5 Hz)	14.1 (CH ₃)	14.3 (CH ₃)
1.29 (2H, m)	1.25-1.14 (4H, m)	8.7 (CH ₃)	8.7 (CH ₃)
1.27 (2H, m)			
0.88 (3H, t, <i>J</i> = 7.1 Hz)	0.78 (3H, t, <i>J</i> = 7.0 Hz)		

Table S10. Correlation of Natural and Synthetic NMR Data of Compound **7dh** (Violapyrone J1):⁷

 <p>4-Hydroxy-6-isopentyl-3-methyl-2H-pyran-2-one (7dh) (Violapyrone J1)</p>	Isolated compound ¹³ C NMR (150 MHz, CD ₃ OD)	Present synthetic compound ¹³ C NMR (100 MHz, CD ₃ OD)
	169.3 (C)	169.4 (C)
	168.4 (C)	168.2 (C)
	165.1 (C)	165.4 (C)
	101.1 (CH)	101.1 (CH)
	98.8 (C)	99.2 (C)
Isolated compound ¹ H NMR	Present synthetic compound ¹ H NMR	
	37.1 (CH ₂)	37.3 (CH ₂)

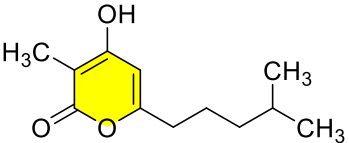
(600 MHz, CD ₃ OD)	(500 MHz, CD ₃ OD)		
5.98 (1H, s)	5.90 (1H, s)	32.2 (CH ₂)	32.6 (CH ₂)
2.47 (2H, t, <i>J</i> = 7.8 Hz)	2.39 (2H, t, <i>J</i> = 8.0 Hz)	28.3 (CH)	28.9 (CH)
1.83 (3H, s)	1.75 (3H, s)	22.3 (2 x CH ₃)	22.9 (2 x CH ₃)
1.58 (1H, m)	1.50 (1H, nonet, <i>J</i> = 6.5 Hz)	8.3 (CH ₃)	8.5 (CH ₃)
1.53 (2H, m)	1.46-1.40 (2H, m)		
0.95 (6H, d, <i>J</i> = 6.6 Hz)	0.84 (6H, d, <i>J</i> = 6.5 Hz)		

Table S11. Correlation of Natural and Synthetic NMR Data of Compound **7eh** (Violapyrone J):⁸

 <p>6-Hexyl-4-hydroxy-3-methyl-2<i>H</i>-pyran-2-one (7eh) (Violapyrone J)</p>	Isolated compound ¹³ C NMR (125 MHz, DMSO- <i>d</i> ₆) ⁷	Present synthetic compound ¹³ C NMR (125 MHz, DMSO- <i>d</i> ₆)
	166.7 (C)	165.1 (C)
	165.2 (C)	164.8 (C)
	161.9 (C)	162.5 (C)
	100.2 (CH)	99.2 (CH)

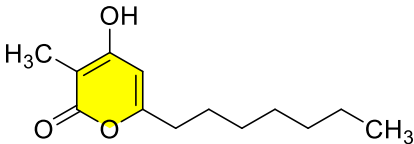
		95.5 (C)	96.5 (C)
Isolated compound ¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)	32.6 (CH ₂)	32.6 (CH ₂)
	11.09 (1H, br s)	30.9 (CH ₂)	30.9 (CH ₂)
5.91 (1H, br s)	5.97 (1H, s)	27.6 (CH ₂)	27.9 (CH ₂)
2.37 (2H, t, <i>J</i> = 7.5 Hz)	2.39 (2H, t, <i>J</i> = 7.5 Hz)	26.1 (CH ₂)	26.2 (CH ₂)
1.71 (3H, s)	1.73 (3H, s)	21.7 (CH ₂)	21.9 (CH ₂)
1.51(2H, m)	1.51 (2H, quint, <i>J</i> = 7.5 Hz)	13.7 (CH ₃)	13.8 (CH ₃)
1.27 (2H, m)	1.32-1.19 (6H, m)	8.3 (CH ₃)	8.3 (CH ₃)
1.26 (2H, m)			
1.26 (2H, m)			
0.85 (3H, t, <i>J</i> = 6.5 Hz)	0.84 (3H, t, <i>J</i> = 7.0 Hz)		

Table S12. Correlation of Natural and Synthetic NMR Data of Compound **7fh** (Violapyrone A):⁹

 <p>4-Hydroxy-3-methyl-6-(4-methylpentyl)- 2<i>H</i>-pyran-2-one (7fh) (Violapyrone A)</p>		Isolated compound ¹³ C NMR (150 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹³ C NMR (125 MHz, DMSO- <i>d</i> ₆)
		165.6 (C)	165.1 (C)
		165.5 (C)	164.8 (C)
		162.9 (C)	162.5 (C)
		99.8 (CH)	99.2 (CH)
		96.9 (C)	96.5 (C)
Isolated compound ¹ H NMR (600 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)	38.0 (CH ₂)	37.5 (CH ₂)
5.96 (1H, s)	5.95 (1H, s)	33.2 (CH ₂)	32.8 (CH ₂)
2.37 (2H, t, <i>J</i> = 7.3 Hz)	2.36 (2H, t, <i>J</i> = 7.5 Hz)	27.7 (CH)	27.2 (CH)
1.72 (3H, s)	1.71 (3H, s)	24.6 (CH ₂)	24.2 (CH ₂)
1.51 (2H, m)	1.54-1.45 (3H, m)	22.8 (2 x CH ₃)	22.4 (2 x CH ₃)
1.50 (1H, m)		8.8 (CH ₃)	8.3 (CH ₃)
1.15 (2H, q, <i>J</i> = 6.9 Hz)	1.14 (2H, q, <i>J</i> = 7.0 Hz)		

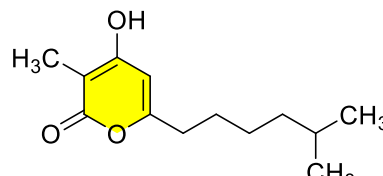
0.84 (6H, d, $J = 6.6$ Hz)	0.83 (6H, d, $J = 6.5$ Hz)		
----------------------------	----------------------------	--	--

Table S13. Correlation of Natural and Synthetic NMR Data of Compound **7gh** (Violapyrone I):¹¹

 <p>6-Heptyl-4-hydroxy-3-methyl-2H-pyran-2-one (7gh) (Violapyrone I)</p>		Isolated compound ¹³ C NMR (125 MHz, CD ₃ OD)	Present synthetic compound ¹³ C NMR (100 MHz, CD ₃ OD)	
			169.2 (C)	169.2 (C)
			168.0 (C)	167.9 (C)
			165.0 (C)	165.0 (C)
			101.1 (CH)	101.1 (CH)
			99.0 (C)	99.1 (C)
Isolated compound ¹ H NMR (500 MHz, CD ₃ OD)	Present synthetic compound ¹ H NMR (500 MHz, CD ₃ OD)			
5.99 (1H, s)	5.99 (1H, s)	34.4 (CH ₂)	34.4 (CH ₂)	
2.48-2.45 (2H, t, $J = 8.1$ Hz)	2.47 (2H, t, $J = 7.5$ Hz)	33.0 (CH ₂)	32.9 (CH ₂)	
1.85 (3H, s)	1.85 (3H, s)	30.2 (CH ₂)	30.2 (CH ₂)	
1.65-1.62 (2H, m)	1.69-1.59 (2H, m)	30.1 (CH ₂)	30.1 (CH ₂)	
		28.1 (CH ₂)	28.1 (CH ₂)	

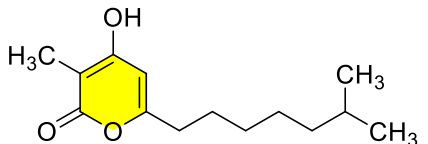
1.35-1.30 (8H, m)	1.38-1.27 (8H, m)	23.8 (CH ₂)	23.8 (CH ₂)
0.91-0.89 (3H, t, <i>J</i> = 6.9 Hz)	0.90 (3H, t, <i>J</i> = 7.0 Hz)	14.6 (CH ₃)	14.5 (CH ₃)
		8.4 (CH ₃)	8.4 (CH ₃)

Table S14. Correlation of Natural and Synthetic NMR Data of Compound **7hh** (Violapyrone B):⁹

 <p>4-hydroxy-3-methyl-6-(5-methylhexyl)- 2<i>H</i>-pyran-2-one (7hh) (Violapyrone B)</p>	Isolated compound ¹³ C NMR (125 MHz, DMSO- <i>d</i> ₆) ⁷	Present synthetic compound ¹³ C NMR (125 MHz, DMSO- <i>d</i> ₆)	
	165.2 (C)	165.1 (C)	
	164.9 (C)	164.9 (C)	
	162.6 (C)	162.5 (C)	
	99.2 (CH)	99.2 (CH)	
	96.6 (C)	96.5 (C)	
Isolated compound ¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)	Present synthetic compound ¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)		
11.1 (1H, br s)	11.1 (1H, br s)		
		38.1 (CH ₂)	38.0 (CH ₂)
		32.6 (CH ₂)	32.6 (CH ₂)

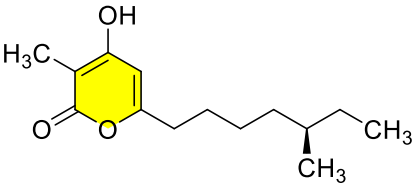
5.98 (1H, br s)	5.98 (1H, s)	27.4 (CH)	27.3 (CH)
2.41 (2H, t, $J = 7.3$ Hz)	2.41 (2H, t, $J = 7.5$ Hz)	26.6 (CH ₂)	26.5 (CH ₂)
1.74 (3H, s)	1.74 (3H, s)	26.1 (CH ₂)	26.0 (CH ₂)
1.50 (2H, m)	1.50 (3H, quint, $J = 7.5$ Hz)	22.5 (2 x CH ₃)	22.5 (2 x CH ₃)
1.49 (1H, m)		8.4 (CH ₃)	8.4 (CH ₃)
1.27 (2H, m)	1.28 (2H, quint, $J = 7.0$ Hz)		
1.16 (2H, m)	1.16 (2H, q, $J = 8.0$ Hz)		
0.85 (6H, d, $J = 6.6$ Hz)	0.84 (6H, d, $J = 6.5$ Hz)		

Table S15. Correlation of Natural and Synthetic NMR Data of Compound **7ih** (Violapyrone H):¹⁰

 4-hydroxy-3-methyl-6-(6-methylheptyl)-2H-pyran-2-one (7ih) (Violapyrone H)	Isolated compound ¹³ C NMR (100 MHz, CD ₃ OD)	Present synthetic compound ¹³ C NMR (125 MHz, CD ₃ OD)	
		169.9 (C)	169.1 (C)
		169.5 (C)	167.9 (C)
		164.8 (C)	164.9 (C)

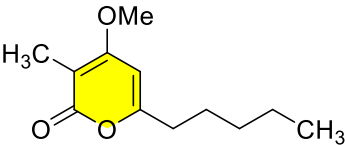
		102.0 (CH)	101.0 (CH)
		98.7 (C)	98.9 (C)
Isolated compound ¹ H NMR (400 MHz, CD ₃ OD)	Present synthetic compound ¹ H NMR (500 MHz, CD ₃ OD)	40.1 (CH ₂)	40.0 (CH ₂)
5.96 (1H, s)	6.01 (1H, s)	34.4 (CH ₂)	34.2 (CH ₂)
2.46 (2H, t, <i>J</i> = 7.5 Hz)	2.49 (2H, t, <i>J</i> = 7.5 Hz)	30.4 (CH ₂)	30.2 (CH ₂)
1.84 (3H, s)	1.87 (3H, s)	29.7 (CH)	29.1 (CH)
1.64 (2H, m)	1.66 (2H, quint, <i>J</i> = 7.5 Hz)	28.3 (CH ₂)	28.2 (CH ₂)
1.53 (1H, m)	1.55 (1H, septet, <i>J</i> = 6.5 Hz)	28.1 (CH ₂)	28.0 (CH ₂)
1.34 (2H, m)	1.36 (4H, quint, <i>J</i> = 3.5 Hz)	23.1 (2 x CH ₃)	23.0 (2 x CH ₃)
1.34 (2H, m)		8.4 (CH ₃)	8.2 (CH ₃)
1.19 (2H, m)	1.21 (2H, m)		
0.88 (6H, d, <i>J</i> = 6.5 Hz)	0.90 (6H, d, <i>J</i> = 7.0 Hz)		

Table S16. Correlation of Natural and Synthetic NMR Data of Compound (-)-**71h** [(-)-Violapyrone C]:¹¹

 <p>(<i>R</i>)-4-hydroxy-3-methyl-6-(5-methylheptyl)- 2<i>H</i>-pyran-2-one ((-)-71h) (Violapyrone C)</p>		Isolated compound ¹³ C NMR (125 MHz, CD ₃ OD)	Present synthetic compound ¹³ C NMR (125 MHz, CD ₃ OD)
		169.3 (C)	169.2 (C)
		168.2 (C)	168.0 (C)
		165.0 (C)	165.0 (C)
		101.3 (CH)	101.1 (CH)
		99.0 (C)	99.0 (C)
Isolated compound ¹ H NMR (500 MHz, CD ₃ OD)	Present synthetic compound ¹ H NMR (500 MHz, CD ₃ OD)	37.5 (CH ₂)	37.4 (CH ₂)
5.99 (1H, s)	6.01 (1H, s)	35.7 (CH)	35.6 (CH)
2.47 (2H, t, <i>J</i> = 7.5 Hz)	2.49 (2H, t, <i>J</i> = 7.5 Hz)	34.4 (CH ₂)	34.3 (CH ₂)
1.85 (3H, s)	1.87 (3H, s)	30.7 (CH ₂)	30.6 (CH ₂)
1.62 (2H, m)	1.70-1.58 (2H, m)	28.4 (CH ₂)	28.3 (CH ₂)
1.36 (2H, m)	1.45-1.30 (5H, m)	27.6 (CH ₂)	27.5 (CH ₂)
1.33 (2H, m)		19.7 (CH ₃)	19.6 (CH ₃)

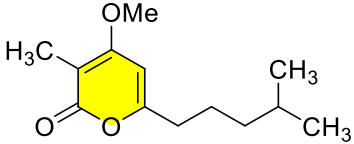
1.32 (1H, m)		11.9 (CH ₃)	11.8 (CH ₃)
1.15 (2H, m)	1.22-1.11 (2H, m)	8.4 (CH ₃)	8.3 (CH ₃)
0.87 (3H, t, <i>J</i> = 7.0 Hz)	0.93-0.85 (6H, m)		
0.86 (3H, d, <i>J</i> = 6.5 Hz)			

Table S17. Correlation of Natural and Synthetic NMR Data of Compound **11ch** (Childinin G):^{12,13}

 <p>4-Methoxy-3-methyl-6-pentyl-2<i>H</i>-pyran-2-one (11ch) (Childinin G)</p>	Isolated compound ¹³ C NMR (150 MHz, CDCl ₃)	Present synthetic compound ¹³ C NMR (125 MHz, CDCl ₃)	
	166.2 (C)	165.9 (C)	
	166.0 (C)	165.8 (C)	
	164.6 (C)	164.4 (C)	
	94.3 (C)	100.8 (C)	
94.3 (CH)	94.1 (CH)		
Isolated compound ¹ H NMR (600 MHz, CDCl ₃)	Present synthetic compound ¹ H NMR (500 MHz, CDCl ₃)	56.3 (CH ₃)	56.1 (CH ₃)

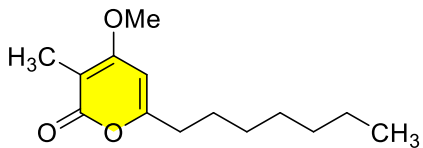
5.99 (1H, s)	5.99 (1H, s)	34.3 (CH ₂)	34.1 (CH ₂)
3.87 (3H, s)	3.87 (3H, s)	31.3 (CH ₂)	31.1 (CH ₂)
2.47 (2H, t, $J = 7.9$ Hz)	2.48 (2H, t, $J = 8.0$ Hz)	26.9 (CH ₂)	26.7 (CH ₂)
1.90 (3H, s)	1.90 (3H, s)	22.5 (CH ₂)	22.2 (CH ₂)
1.66 (2H, m)	1.67 (2H, quint, $J = 7.5$ Hz)	14.1 (CH ₃)	13.8 (CH ₃)
1.32 (4H, m)	1.37-1.29 (4H, m)	8.6 (CH ₃)	8.3 (CH ₃)
0.89 (3H, t, $J = 7.1$ Hz)	0.90 (3H, t, $J = 7.0$ Hz)		

Table S18. Correlation of Natural and Synthetic NMR Data of Compound **11fh** (Violapyrone Q):¹³

 <p>4-Methoxy-3-methyl-6-(4-methylpentyl)-2H-pyran-2-one (11fh) (Violapyrone Q)</p>		Isolated compound ¹³ C NMR (125 MHz, DMSO- d ₆)	Present synthetic compound ¹³ C NMR (125 MHz, DMSO-d ₆)
		166.6 (C)	166.6 (C)
		165.4 (C)	164.9 (C)
		164.4 (C)	164.5 (C)
		95.5 (C)	99.1 (C)
		95.1 (CH)	95.3 (CH)
Isolated compound ¹ H NMR (500 MHz, DMSO-d ₆)	Present synthetic compound ¹ H NMR (500 MHz, DMSO-d ₆)	56.0 (CH ₃)	57.2 (CH ₃)
6.48 (1H, s)	6.48 (1H, s)	38.0 (CH ₂)	38.1 (CH ₂)
3.95 (3H, s)	3.88 (3H, s)	33.6 (CH ₂)	33.8 (CH ₂)
2.44 (2H, t, <i>J</i> = 7.5 Hz)	2.48 (2H, t, <i>J</i> = 7.5 Hz)	27.6 (CH)	27.6 (CH)
1.73 (3H, s)	1.76 (3H, s)	24.6 (CH ₂)	24.8 (CH ₂)
1.59 (2H, m)	1.62-1.53 (3H, m)	22.8 (CH ₃)	22.8 (CH ₃)
1.53 (1H, m)		22.8 (CH ₃)	22.8 (CH ₃)
1.16 (2H, m)	1.19 (2H, q, <i>J</i> = 7.0 Hz)	9.0 (CH ₃)	8.8 (CH ₃)

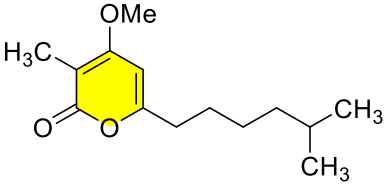
0.86 (3H, d, $J = 6.5$ Hz)	0.87 (3H, d, $J = 7.0$ Hz)		
0.86 (3H, d, $J = 6.5$ Hz)	0.87 (3H, d, $J = 7.0$ Hz)		

Table S19. Correlation of Natural and Synthetic NMR Data of Compound **11gh** (Violapyrone S):¹³

 <p>6-Heptyl-4-methoxy-3-methyl-2H-pyran-2-one (11gh) (Violapyrone S)</p>		Isolated compound ¹³ C NMR (125 MHz, DMSO- d ₆)	Present synthetic compound ¹³ C NMR (125 MHz, DMSO-d ₆)
		166.3 (C)	166.2 (C)
		164.7 (C)	164.5 (C)
		164.2 (C)	164.1 (C)
		98.8 (C)	98.6 (C)
		94.9 (CH)	94.9 (CH)
Isolated compound ¹ H NMR (500 MHz, DMSO-d ₆)	Present synthetic compound ¹ H NMR (500 MHz, DMSO-d ₆)	56.8 (CH ₃)	56.7 (CH ₃)
6.47 (1H, s)	6.43 (1H, s)	33.2 (CH ₂)	33.1 (CH ₂)
3.85 (3H, s)	3.85 (3H, s)	31.3 (CH ₂)	31.1 (CH ₂)
2.46 (2H, t, $J = 7.5$ Hz)	2.48-2.43 (2H, m)	28.5 (CH ₂)	28.3 (CH ₂)

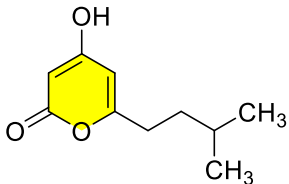
1.75 (3H, s)	1.73 (3H, s)	28.4 (CH ₂)	28.3 (CH ₂)
1.58 (2H, m)	1.55 (2H, quint, $J = 7.0$ Hz)	26.5 (CH ₂)	26.5 (CH ₂)
1.29 (2H, m)	1.28-1.21 (8H, m)	22.4 (CH ₂)	22.0 (CH ₂)
1.28 (2H, m)		14.2 (CH ₃)	13.9 (CH ₃)
1.26 (2H, m)		8.6 (CH ₃)	8.3 (CH ₃)
1.22 (2H, m)			
0.83 (3H, d, $J = 6.7$ Hz)	0.83 (3H, t, $J = 7.0$ Hz)		

Table S20. Correlation of Natural and Synthetic NMR Data of Compound **11hh** (Violapyrone R):^{13,14}

 <p>4-Methoxy-3-methyl-6-(5-methylhexyl)-2H-pyran-2-one (11hh) (Violapyrone R)</p>		Isolated compound ¹³ C NMR (125 MHz, DMSO- _d ₆)	Present synthetic compound ¹³ C NMR (125 MHz, DMSO- _d ₆)
		166.2 (C)	166.3 (C)
		164.5 (C)	164.6 (C)
		164.2 (C)	164.2 (C)
		98.6 (C)	98.7 (C)
		95.0 (CH)	95.0 (CH)
Isolated compound ¹ H NMR (500 MHz, DMSO- _d ₆)	Present synthetic compound ¹ H NMR (500 MHz, DMSO- _d ₆)	56.9 (CH ₃)	56.8 (CH ₃)
6.48 (1H, s)	6.48 (1H, s)	38.1 (CH ₂)	38.1 (CH ₂)
3.87 (3H, s)	3.87 (3H, s)	33.3 (CH ₂)	33.2 (CH ₂)
2.50 (2H, t, <i>J</i> = 7.5 Hz)	2.49 (2H, t, <i>J</i> = 7.5 Hz)	27.4 (CH)	27.4 (CH)
1.75 (3H, s)	1.75 (3H, s)	26.8 (CH ₂)	26.8 (CH ₂)
1.53 (2H, m)	1.60 - 1.47 (3H, m)	26.1 (CH ₂)	26.2 (CH ₂)
1.47 (1H, m)		22.6 (CH ₃)	22.5 (CH ₃)

1.29 (2H, m)	1.30 (2H, m)	22.6 (CH ₃)	22.5 (CH ₃)
1.18 (2H, m)	1.18 (2H, m)	8.7 (CH ₃)	8.5 (CH ₃)
0.86 (3H, dd, $J = 15.6$, 7.0 Hz)	0.85 (3H, d, $J = 6.5$ Hz)		
0.86 (3H, dd, $J = 15.6$, 7.0 Hz)	0.85 (3H, d, $J = 6.5$ Hz)		

Table S21. Correlation of Natural and Synthetic NMR Data of Compound **3d** (Fistupyron):¹⁴

 <p>4-Hydroxy-6-isopentyl-2H-pyran-2-one (3d) (Fistupyron)</p>	Isolated compound ¹³ C NMR (100 MHz, CDCl ₃)	Present synthetic compound ¹³ C NMR (100 MHz, CDCl ₃)	
	172.7 (C)	172.6 (C)	
	168.4 (C)	168.3 (C)	
	167.6 (C)	167.5 (C)	
	101.2 (CH)	101.1 (CH)	
	89.7 (CH)	89.6 (CH)	
Isolated compound ¹ H NMR (400 MHz, CDCl ₃)	Present synthetic compound ¹ H NMR (500 MHz, CDCl ₃)	35.5 (CH ₂)	35.5 (CH ₂)

6.01 (1H, s)	5.99 (1H, s)	31.6 (CH ₂)	31.5 (CH ₂)
5.58 (1H, s)	5.58 (1H, d, <i>J</i> = 1.5 Hz)	27.5 (CH)	27.4 (CH)
2.49 (2H, t, <i>J</i> = 7.8 Hz)	2.48 (2H, t, <i>J</i> = 7.5 Hz)	22.2 (2 x CH ₃)	22.1 (2 x CH ₃)
1.57 (1H, m)	1.59 (1H, nonet, <i>J</i> = 6.5 Hz)		
1.53 (2H, m)	1.52 (2H, q, <i>J</i> = 8.0 Hz)		
0.91 (6H, d, <i>J</i> = 6.4 Hz)	0.91 (6H, d, <i>J</i> = 6.5 Hz)		

Table S22: Correlation of Natural and Synthetic HRMS values for Photopyrone C, E, G.²

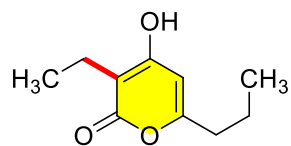
Photopyrone	Product Number	Molecular formula	Calcd. [M+H] (m/z)	Isolated compound HR ESI MS (m/z)	Present synthetic compound HR ESI MS (m/z)
C	7be	C ₁₇ H ₂₈ O ₃	281.211121	281.2115	281.2117
E	7bf	C ₁₉ H ₃₂ O ₃	309.242421	309.2428	309.2430
G	7bg	C ₂₁ H ₃₆ O ₃	337.273721	337.2741	337.2743

23. References:

1. Zhang, X. M.; Peng, A. H.; Xie, W. D.; Wang, M.; Zheng, D.; Feng, M. K.; Hexokinase II Inhibitory Effect of Secondary Metabolites Derived from a *Streptomyces* sp. Associated with Mud Dauber Wasp. *Chem. Biodiverse.*, **2020**, *17*, e2000140.
2. Brachmann, A. O.; Brameyer, S.; Kresovic, D.; Hitkova, I.; Kopp, Y.; Manske, C.; Schubert, K.; Bode, H. B.; Heermann, R. Pyrones as bacterial signaling molecules. *Nat. Chem. Bio.* **2013**, *9*, 573-578.
3. Chaladaj, W.; Corbet, M.; Fürstner, A. Total synthesis of neurymenolide A based on a gold-catalyzed synthesis of 4-hydroxy-2-pyrones. *Angew. Chem. Int. Ed.* **2012**, *51*, 6929-6933.
4. Kresovic, D.; Schempp, F.; Cheikh-Ali, Z.; Bode, H. B. A novel and widespread class of ketosynthase is responsible for the head-to-head condensation of two acyl moieties in bacterial pyrone biosynthesis. *Beilstein J. Org. Chem.* **2015**, *11*, 1412-1417.
5. Hou, L.; Huang, H.; Li, H.; Wang, S.; Ju, J.; Li, W. Overexpression of a type III PKS gene affording novel violapyrones with enhanced anti-influenza A virus activity. *Microb. Cell Factories* **2018**, *17*, 61.
6. Georgousaki, K.; González-Menéndez, V.; Tormo, J. R.; Tsafantakis, N.; Mackenzie, T. A.; Martín, J.; Gumeni, S.; Trougakos, I. P.; Reyes, F.; Fokialakis, N.; Genilloud, O. Comoclatrin, a novel potent skin-whitening agent produced by endophytic *Comoclatris* strains associated with Andalusia desert plants. *Scientific Reports* **2022**, *12*, 1649.
7. Yang, R.-M.; Zhang, X.-L.; Wang, Li.; Huang, J.-P.; Yang, J.; Yan, Y.-J.; Luo, J.-Y.; Wang, X.-T.; Huang, S.-X. α -Pyrone derivatives from a *Streptomyces* strain resensitize tamoxifen resistance in breast cancer cells. *Nat. Prod. Bioprospect.* **2017**, *7*, 329-334.
8. Huang, H.; Hou, L.; Li, H.; Qiu, Y.; Ju, J.; Li, W. Activation of a plasmid-situated type III PKS gene cluster by deletion of a *wbl* gene in deepsea-derived *Streptomyces somaliensis* SCSIO ZH66. *Microb. Cell Factories* **2016**, *15*, 116.
9. Zhang, J.; Jiang, Y.; Cao, Y.; Liu, J.; Zheng, D.; Chen, X.; Han, Li.; Jiang, C.; Huang, X. Violapyrones A–G, α -Pyrone derivatives from *Streptomyces violascens* isolated from *Hylobates hoolock* feces. *J. Nat. Prod.* **2013**, *76*, 2126-2130.
10. Shin, H. J.; Lee, H. S.; Lee, J. S.; Shin, J.; Lee, M. A.; Lee, Y. J.; Yun, J.; Kang, J. S. Violapyrones H and I, New Cytotoxic Compounds Isolated from *Streptomyces* sp Associated with the Marine Starfish *Acanthaster planci*. *Mar. Drugs* **2014**, *12*, 3283-3291, DOI: 10.3390/md12063283.
11. Lee, J. S.; Shin, J.; Shin, H. J.; Lee, H.-S.; Lee, Y.-J.; Lee, H.-S.; Won, H. Total synthesis and configurational validation of (+)-violapyrone C. *Eur. J. Org. Chem.* **2014**, *2014*, 4472-4476.
12. Zhao, Z.-Z.; Chen, H.-P.; Huang, Y.; Zhang, S.-B.; Li, Z.-H.; Feng, T.; Liu, J.-K. Bioactive polyketides and 8,14-*seco*-ergosterol from fruiting bodies of the ascomycete *Daldinia childiae*. *Phytochem.* **2017**, *142*, 68-75.

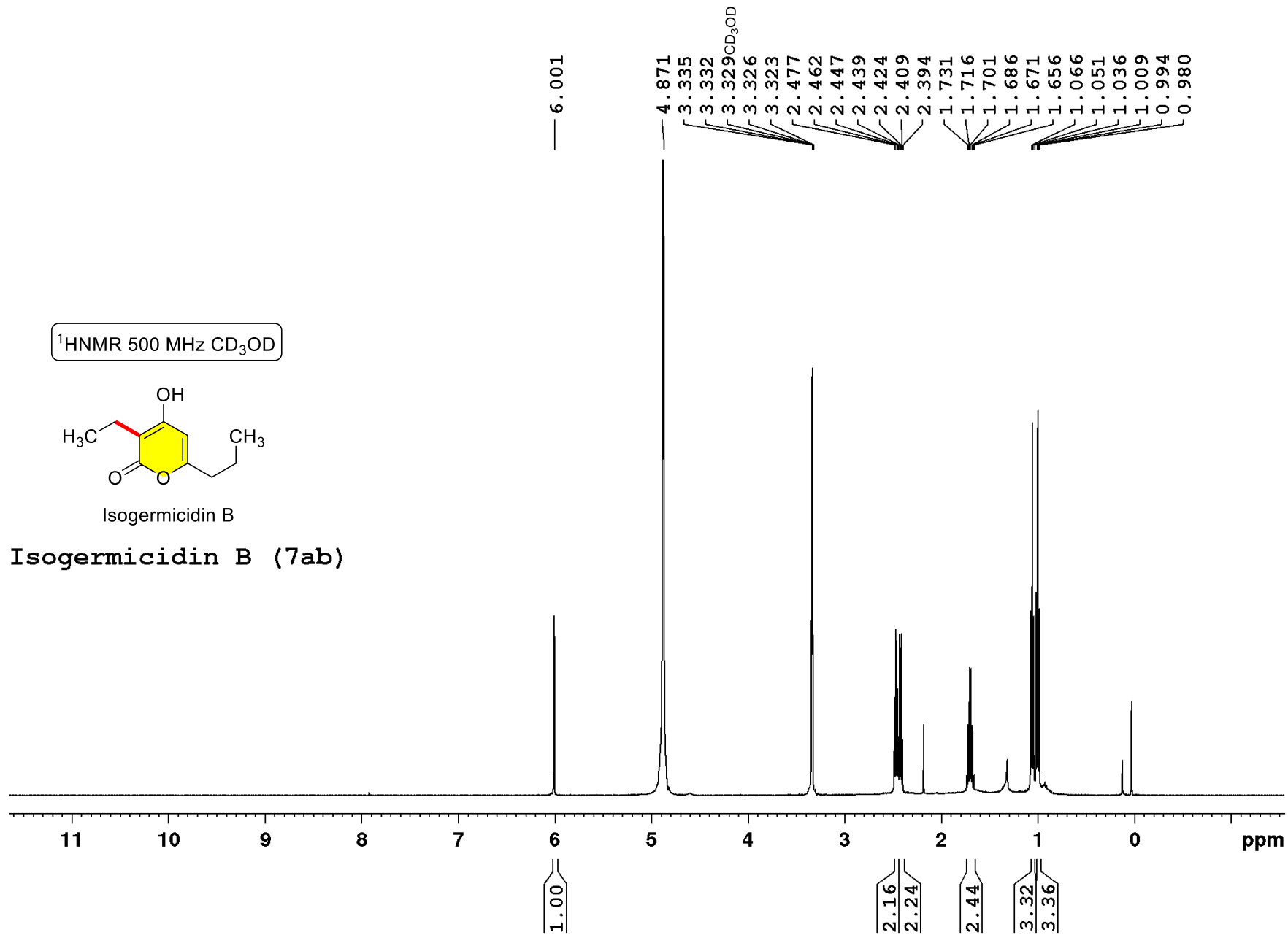
13. Hou, L.; Wang, S.; Huang, H.; Li, H.; Wang, W.; Li, W. Generation of methylated violapyrones with improved anti-influenza A virus activity by heterologous expression of a type III PKS gene in a marine *Streptomyces* strain. *Bioorganic Med. Chem. Lett.* **2018**, *28*, 2865-2868.
14. Igarashi, Y.; Ogawa, M.; Sat, Y.; Saito, N.; Yoshida, R.; Kunoh, H.; Onaka, H.; Furumai, T. Fistupyronone, a novel inhibitor of the infection of chinese cabbage by *Alternaria brassicicola*, from *Streptomyces* sp. TP-A0569. *J. Antibiot.* **2000**, *53*, 1117-1122.

¹HNMR 500 MHz CD₃OD

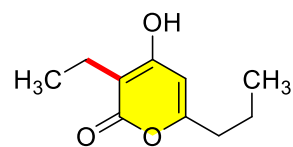


Isogermicidin B

Isogermicidin B (7ab)

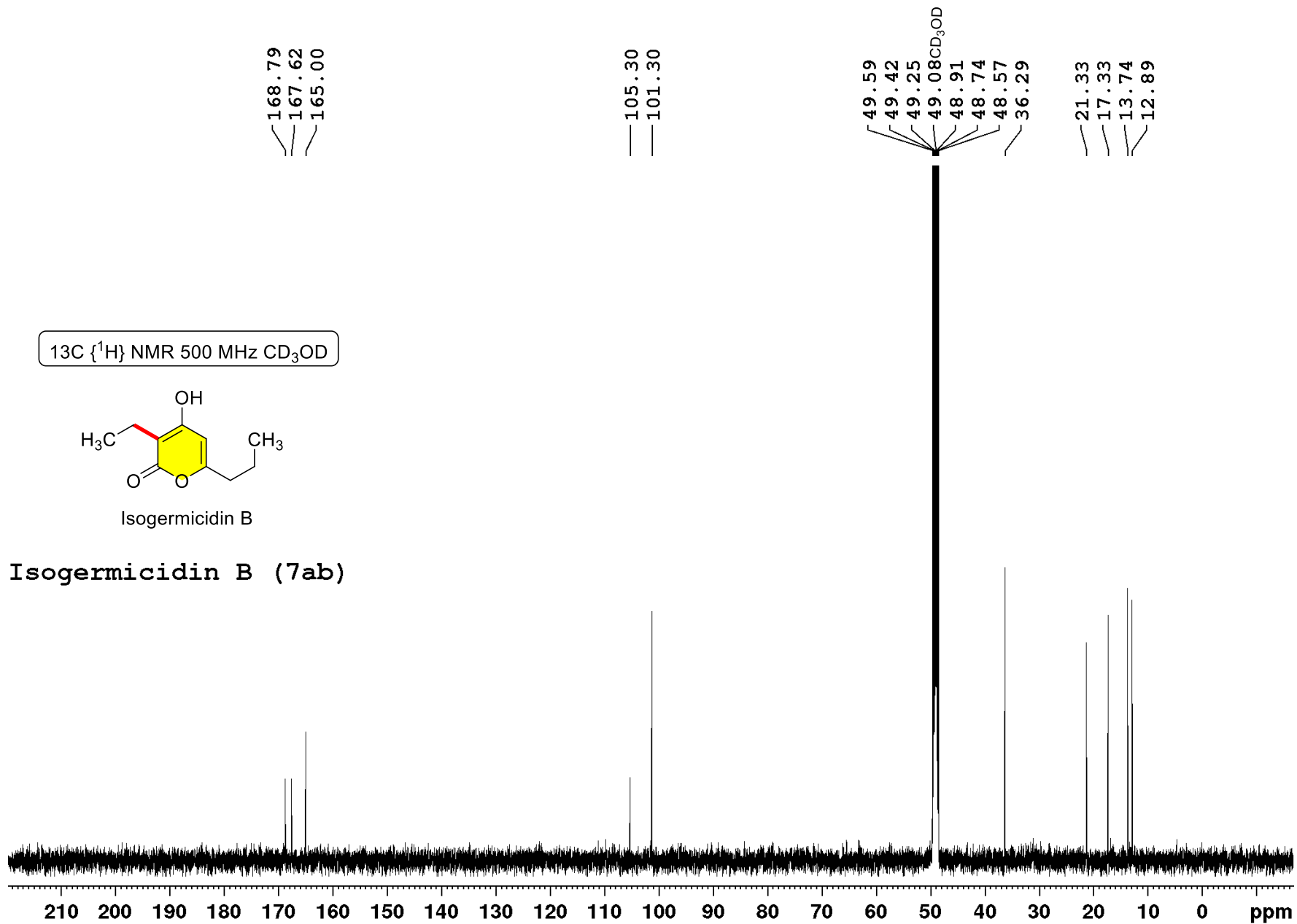


13C {1H} NMR 500 MHz CD₃OD

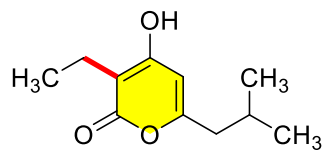


Isogermicidin B

Isogermicidin B (7ab)

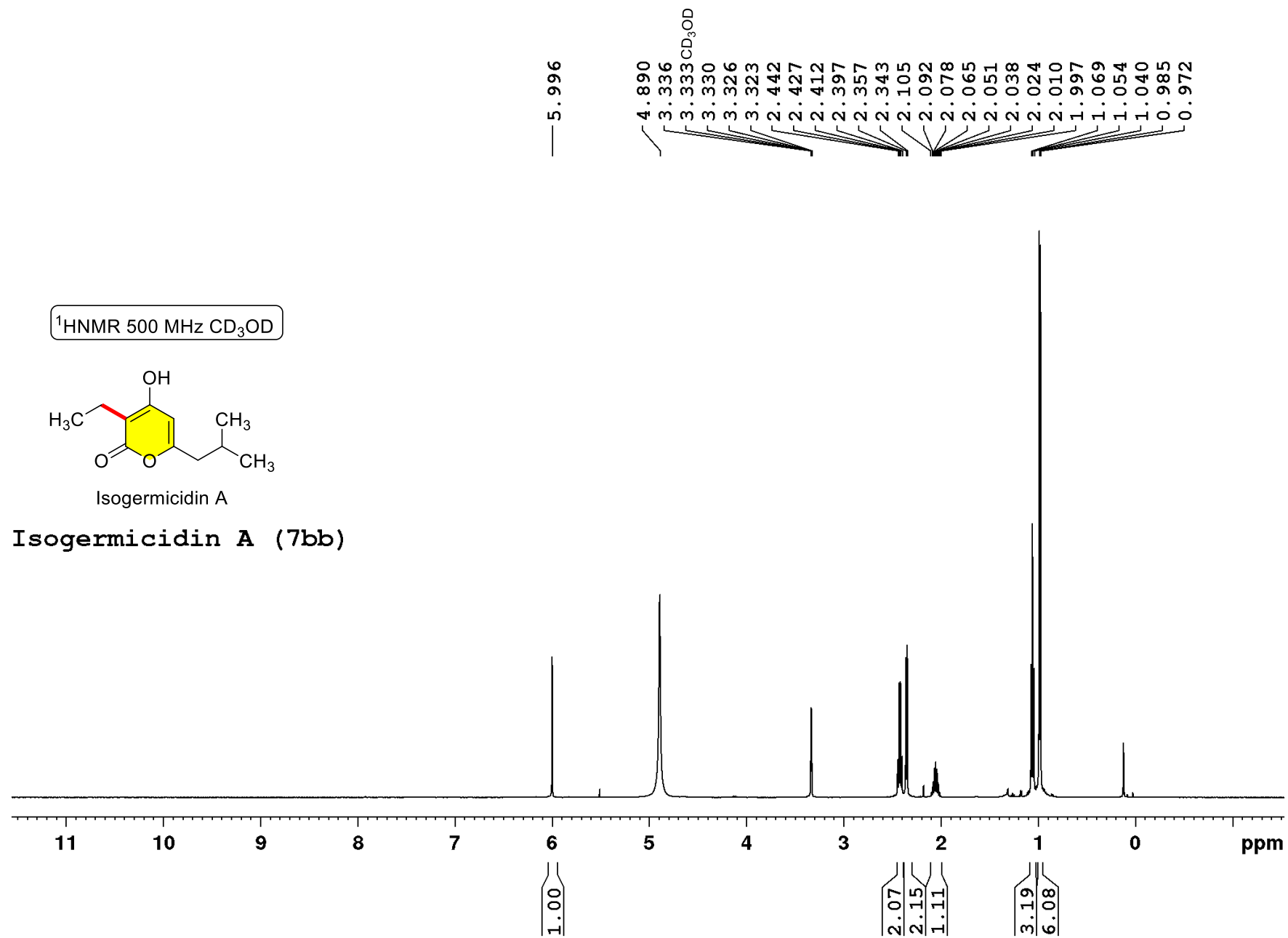


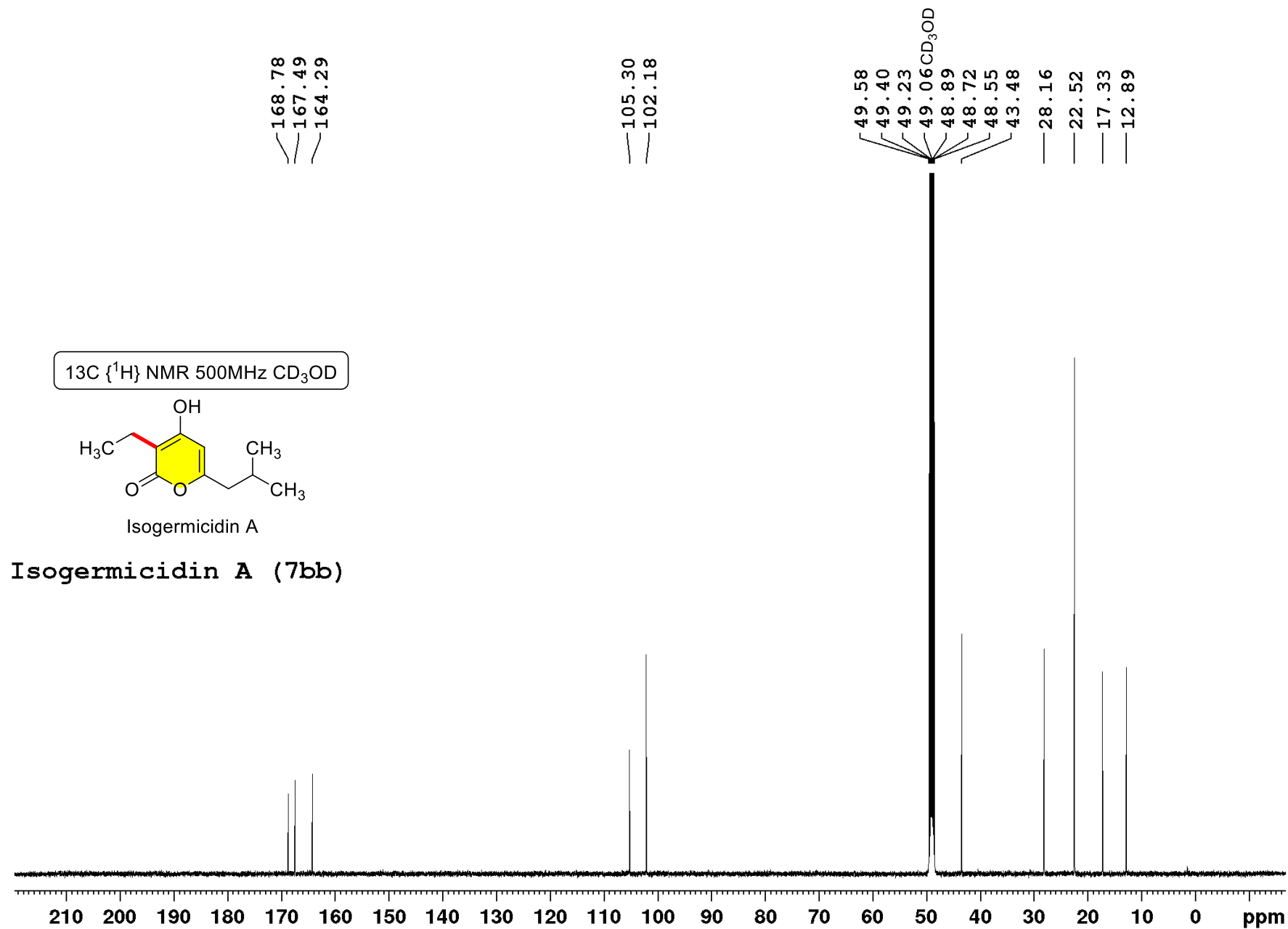
¹HNMR 500 MHz CD₃OD



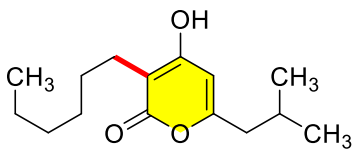
Isogermicidin A

Isogermicidin A (7bb)



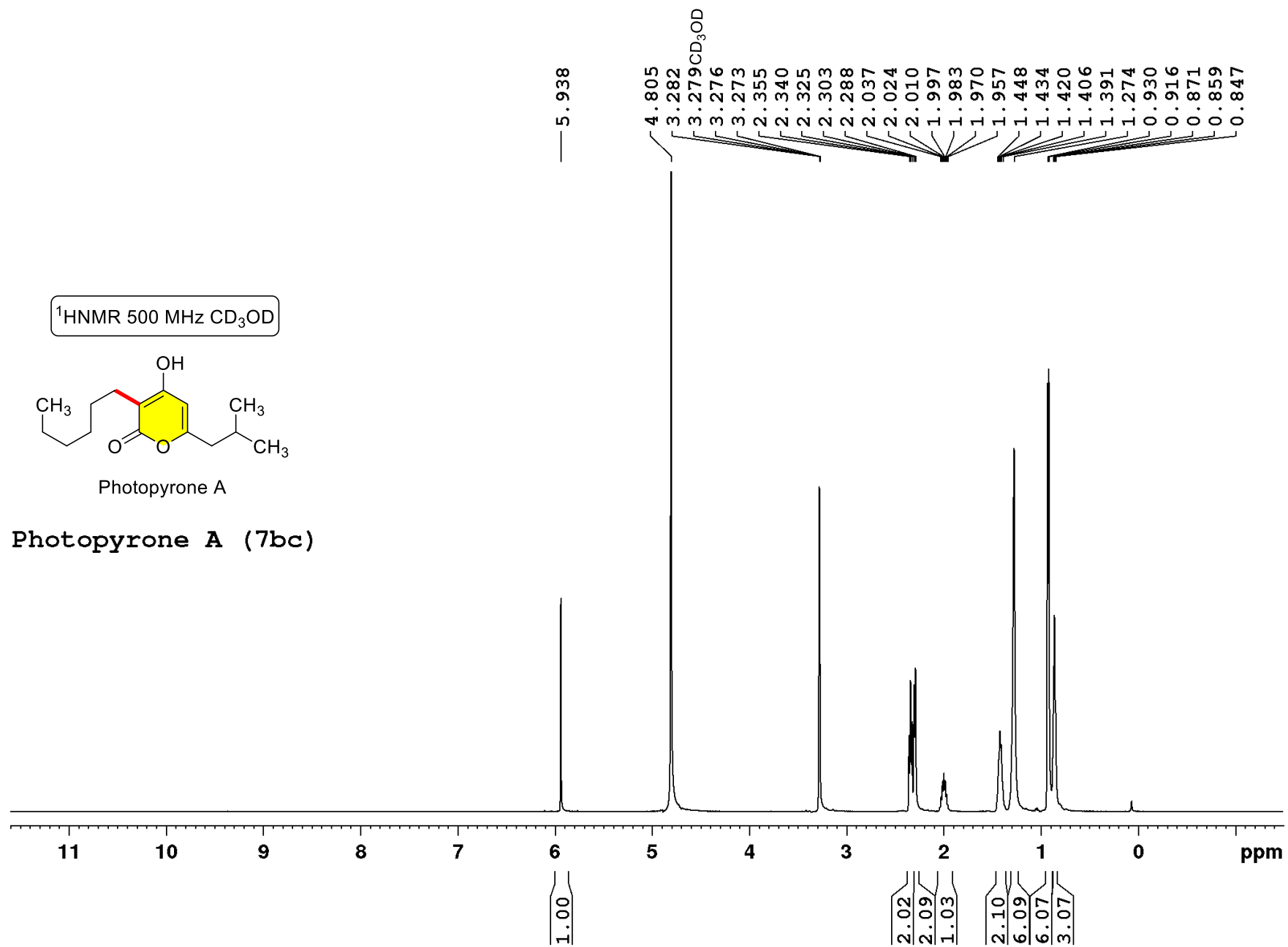


¹HNMR 500 MHz CD₃OD

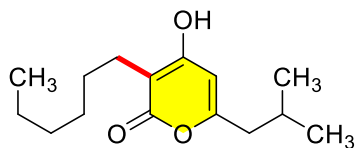


Photopyrone A

Photopyrone A (7bc)

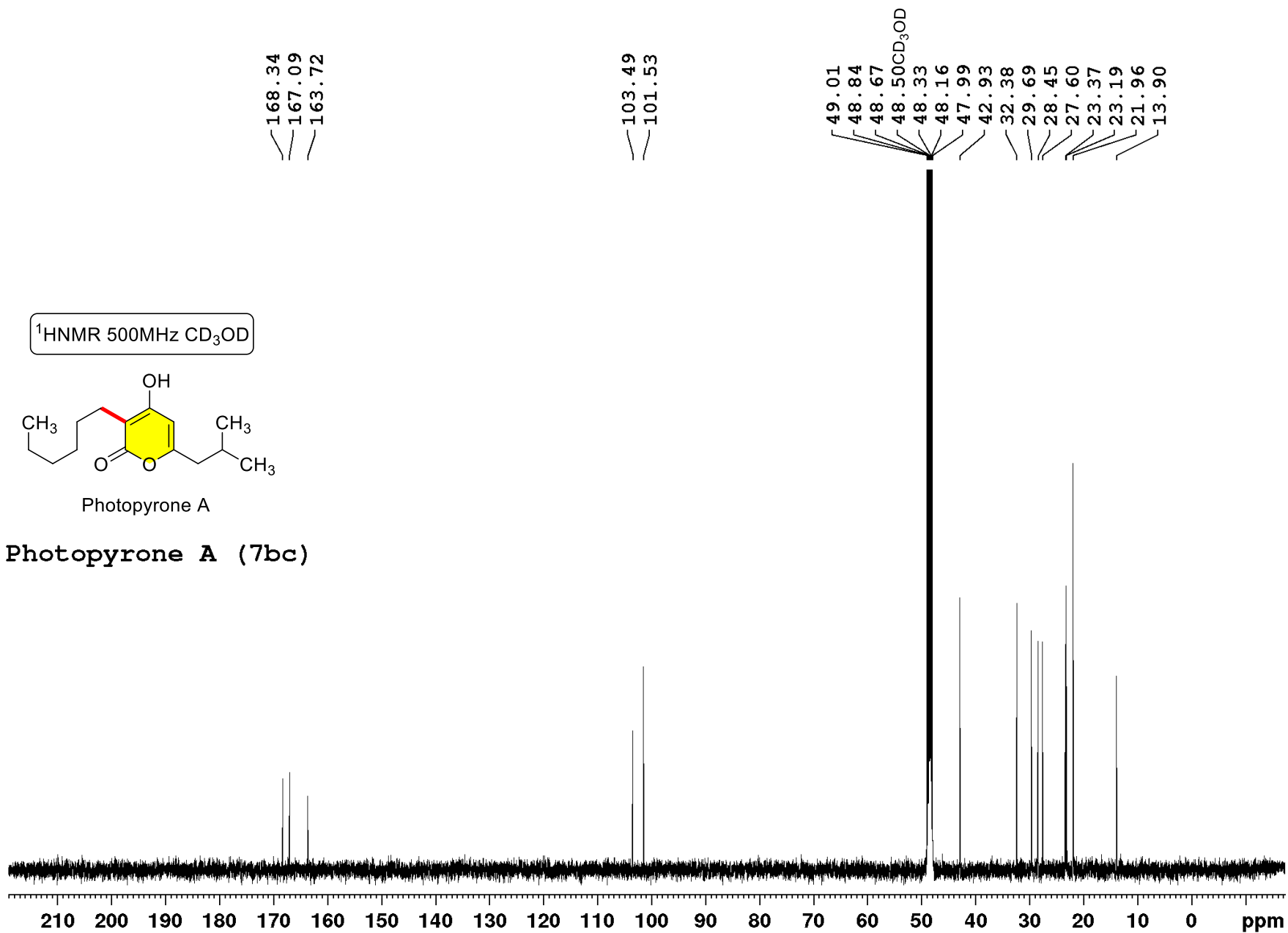


¹HNMR 500MHz CD₃OD

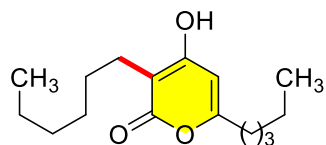


Photopyrone A

Photopyrone A (7bc)

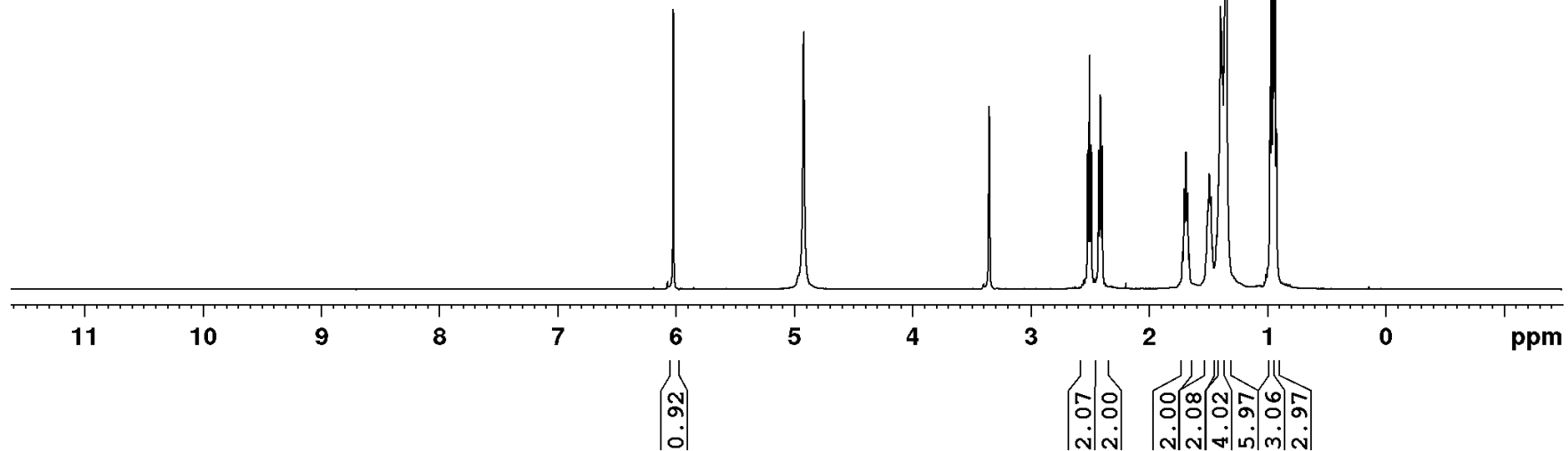


¹HNMR 500 MHz CD₃OD



Pseudopyronine A

Pseudopyronine A (7cc)



6.021

4.919

3.353

3.350 CD₃OD

3.347

2.517

2.502

2.487

2.425

2.410

2.394

1.716

1.701

1.687

1.672

1.658

1.502

1.490

1.476

1.461

1.426

1.413

1.400

1.396

1.389

1.381

1.375

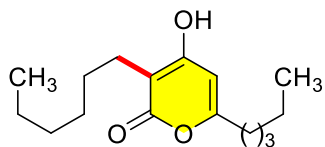
1.348

0.975

0.962

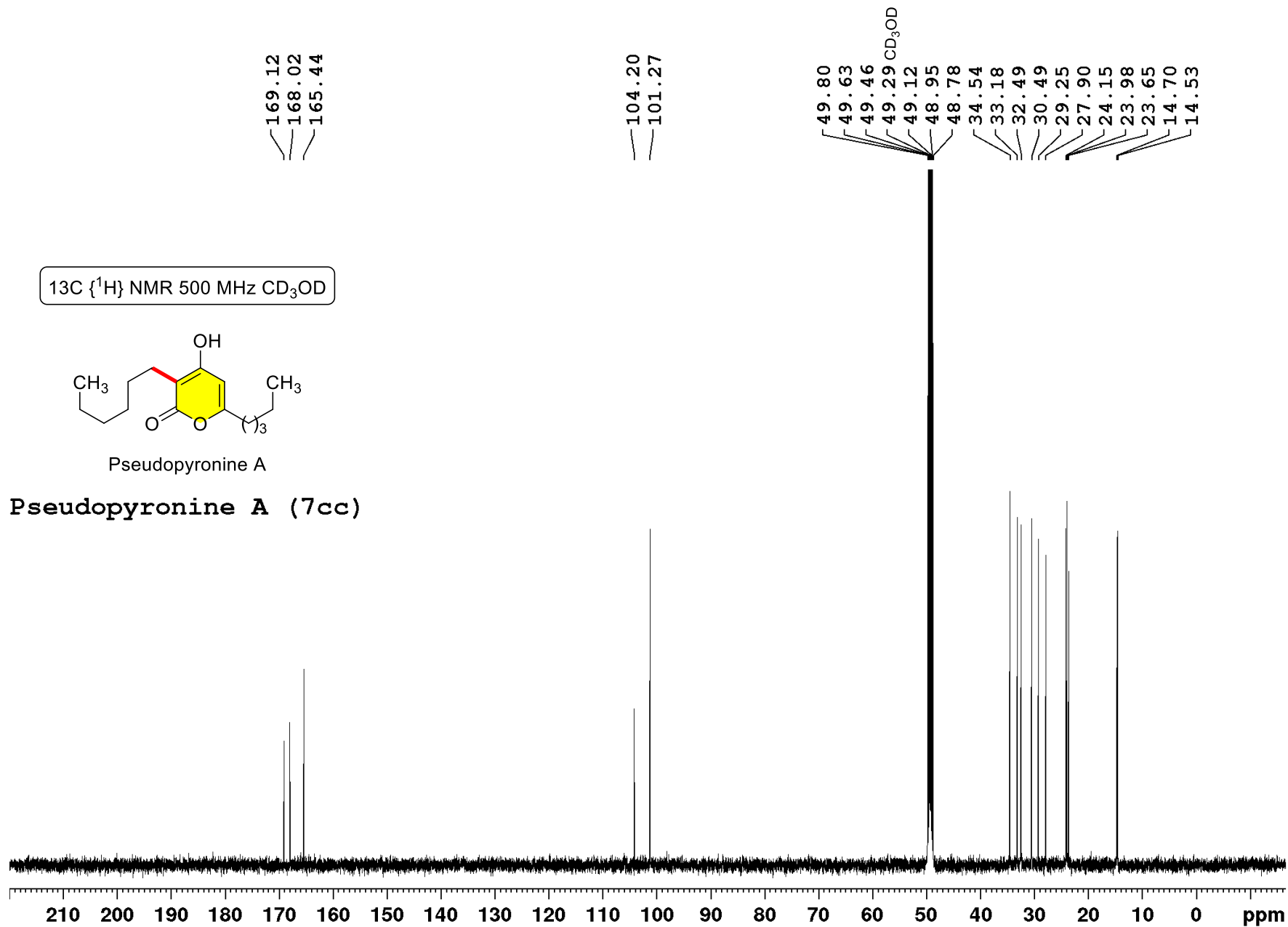
0.947

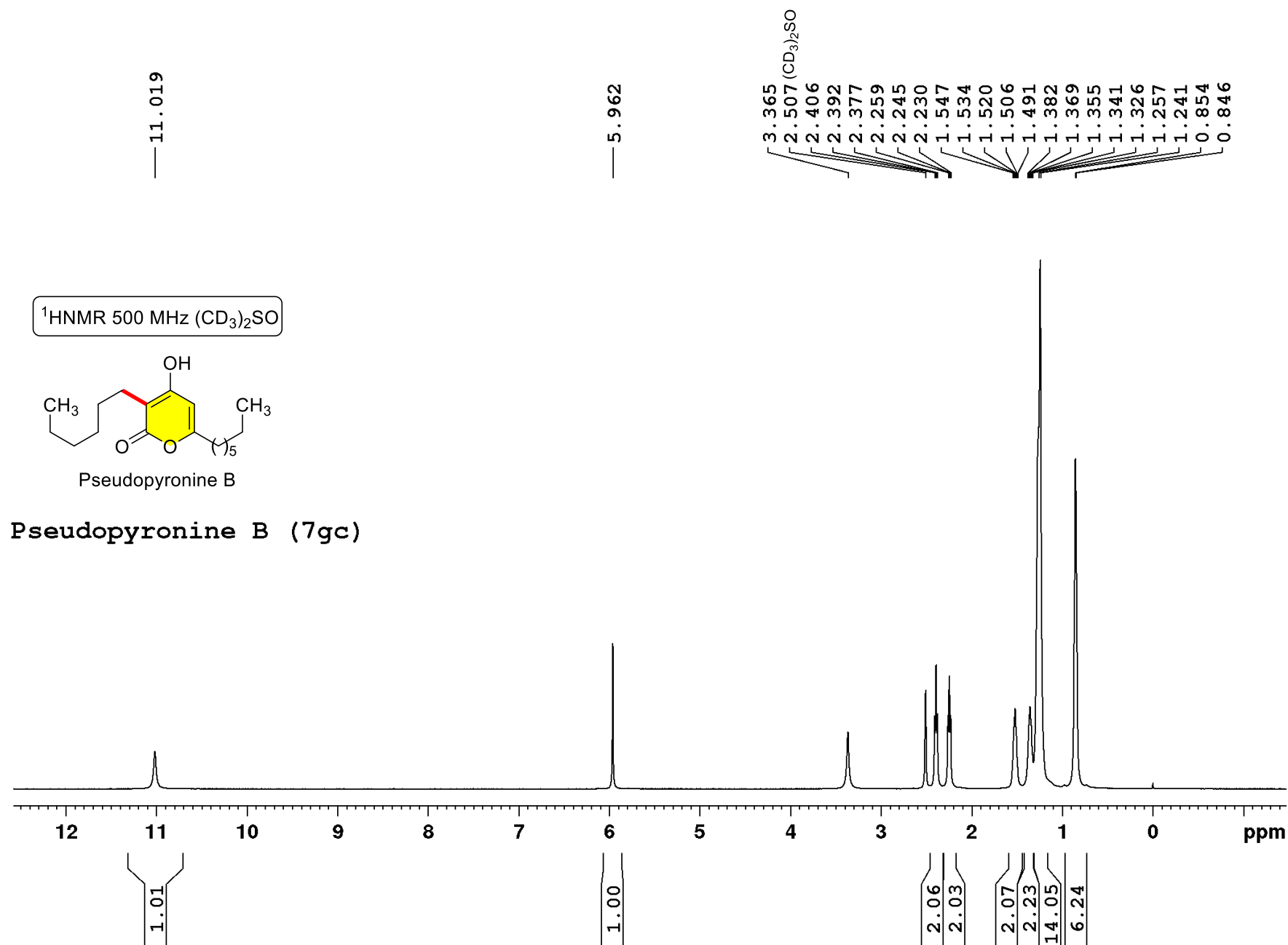
13C {1H} NMR 500 MHz CD3OD

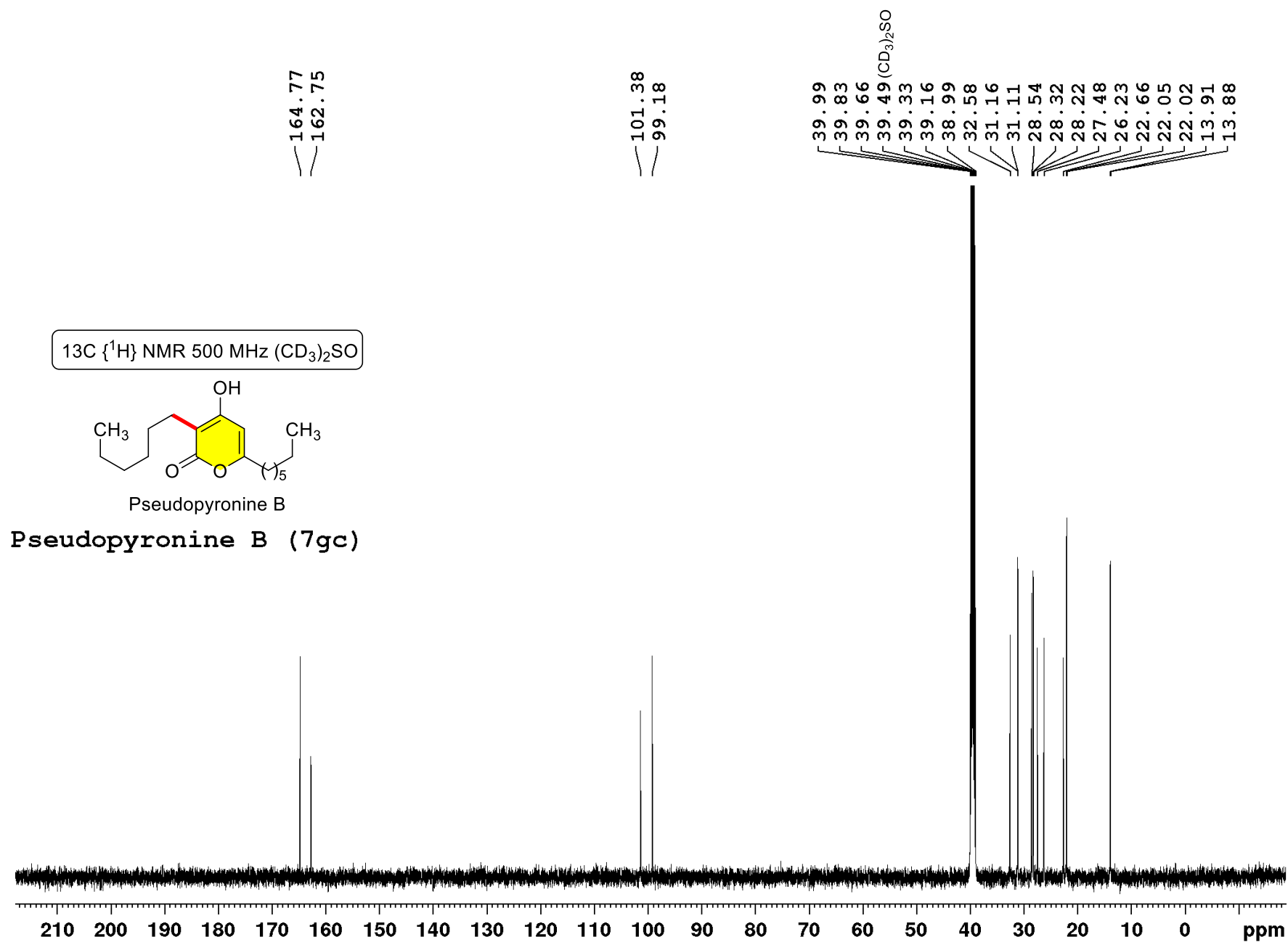


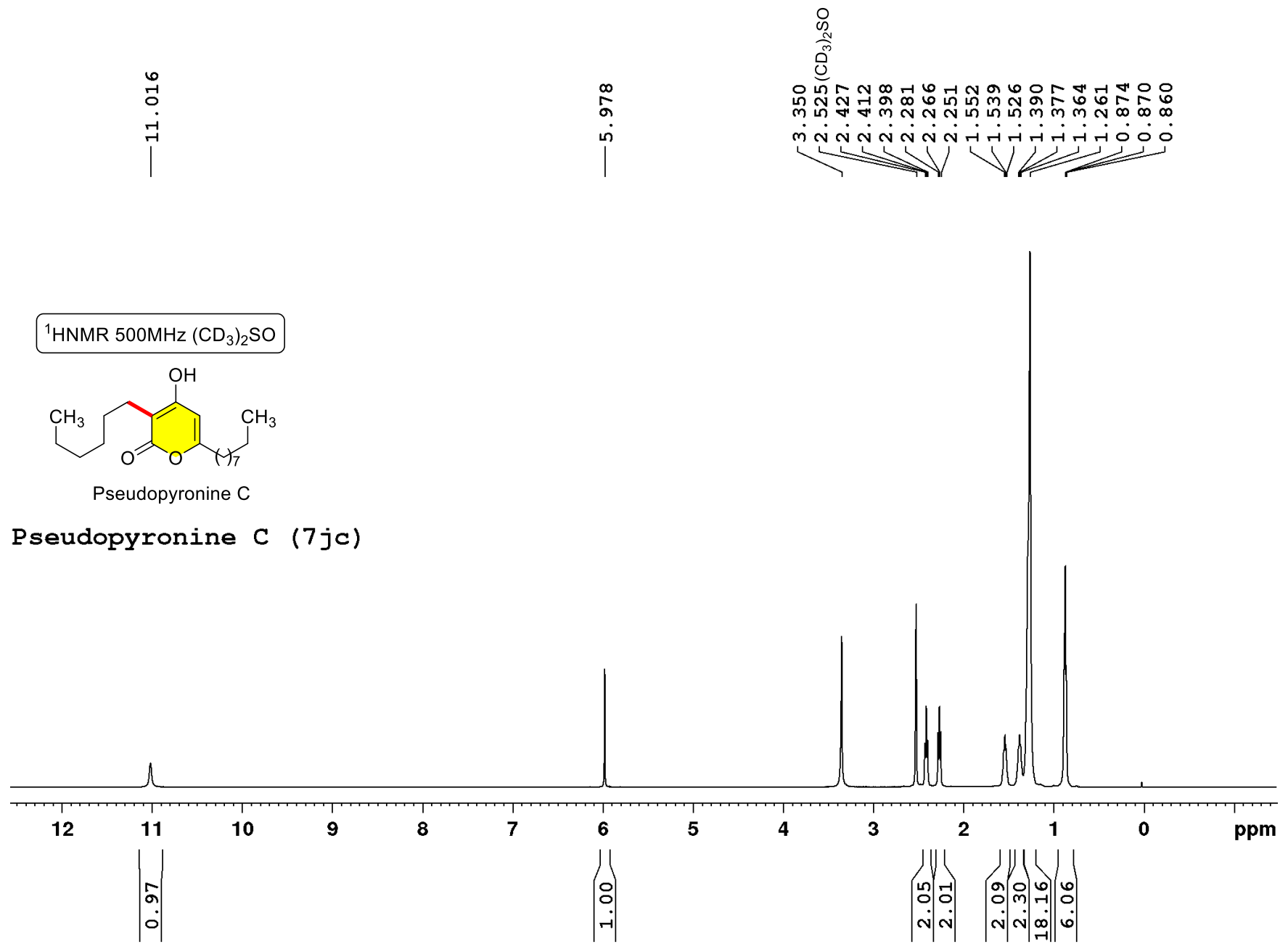
Pseudopyronine A

Pseudopyronine A (7cc)

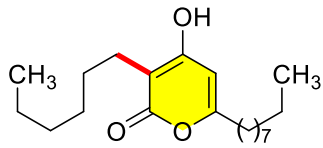






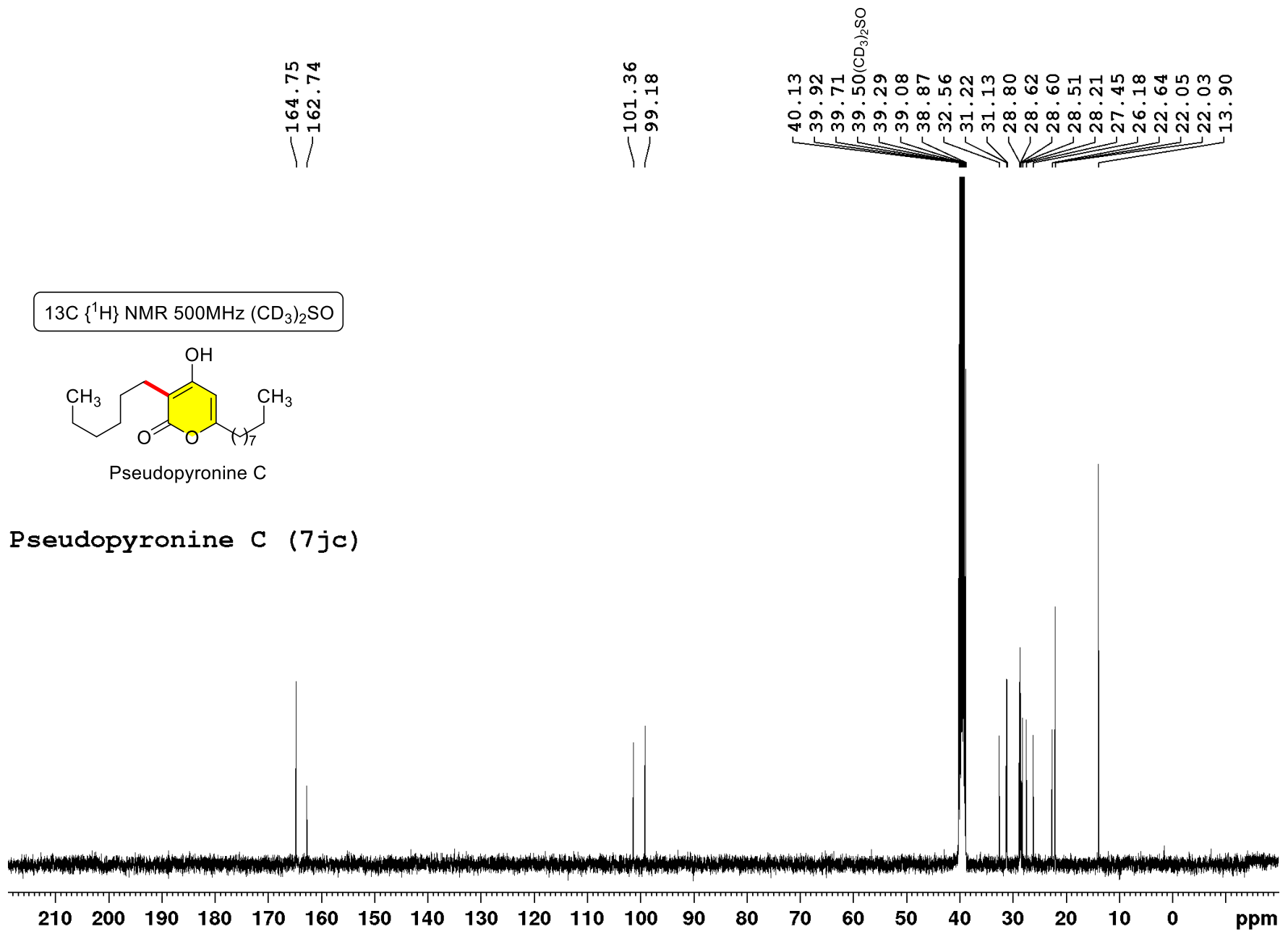


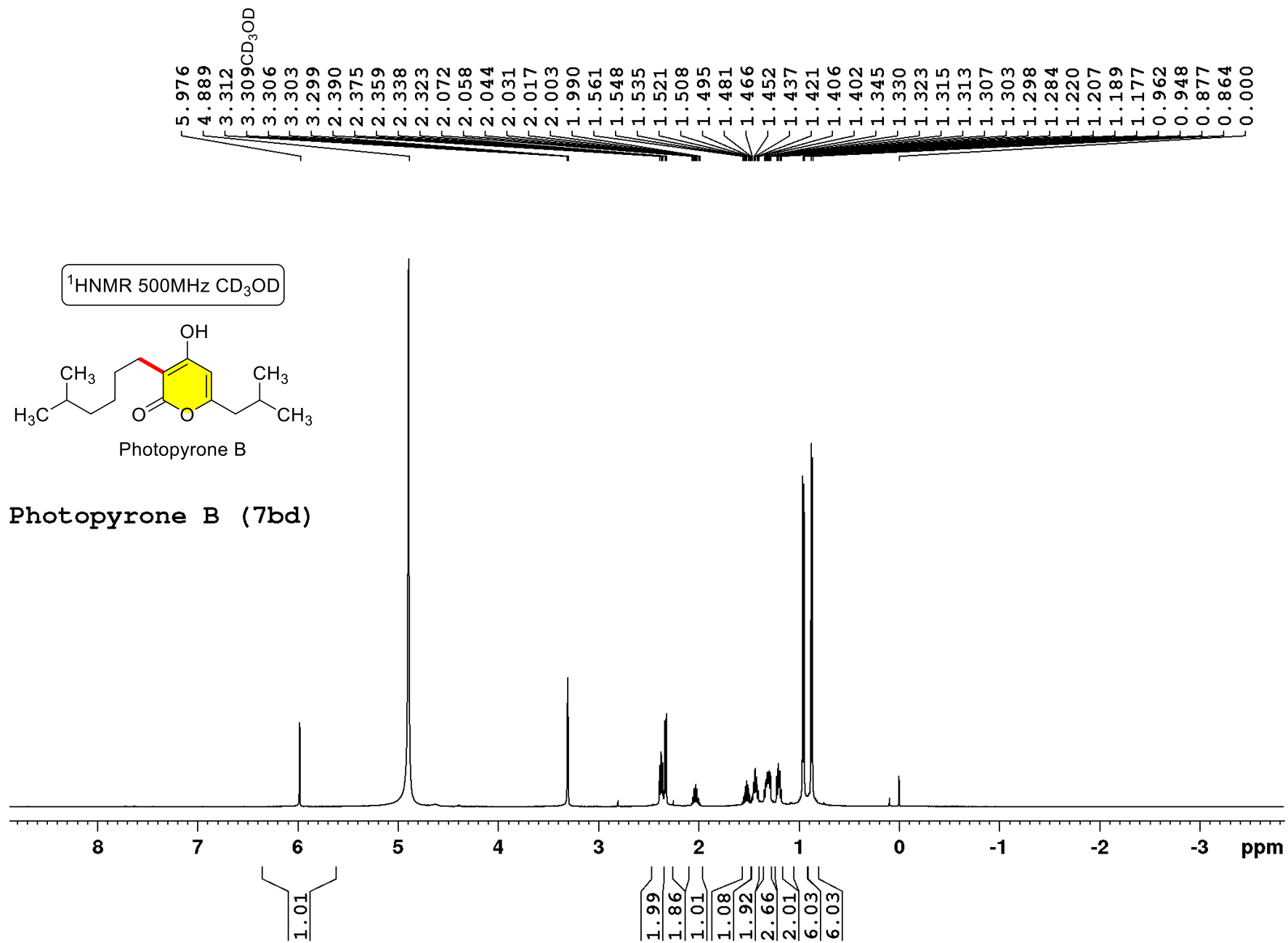
13C {1H} NMR 500MHz (CD3)2SO



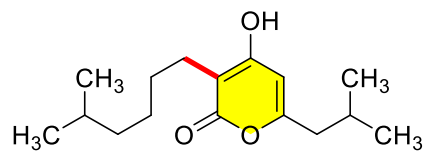
Pseudopyronine C

Pseudopyronine C (7jc)



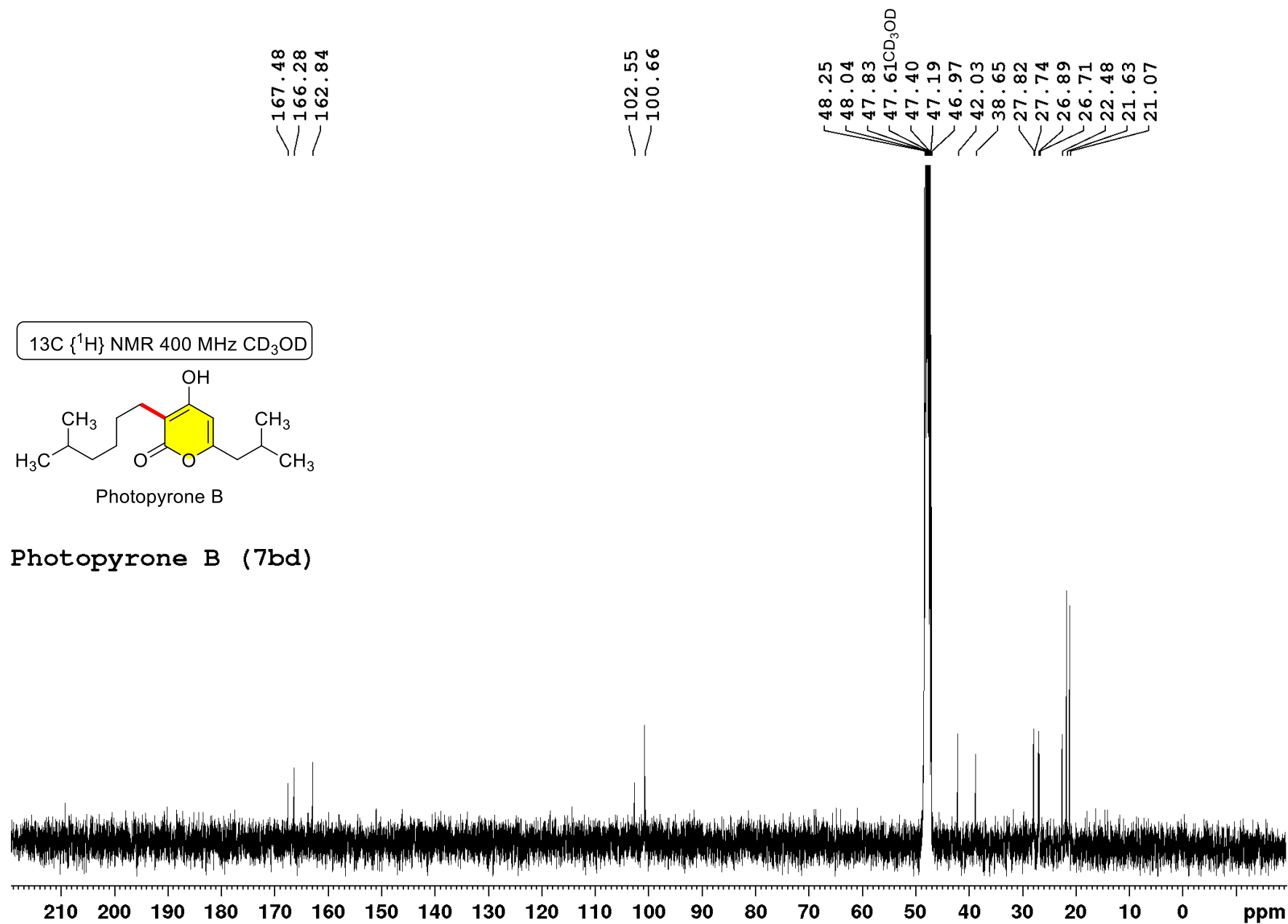


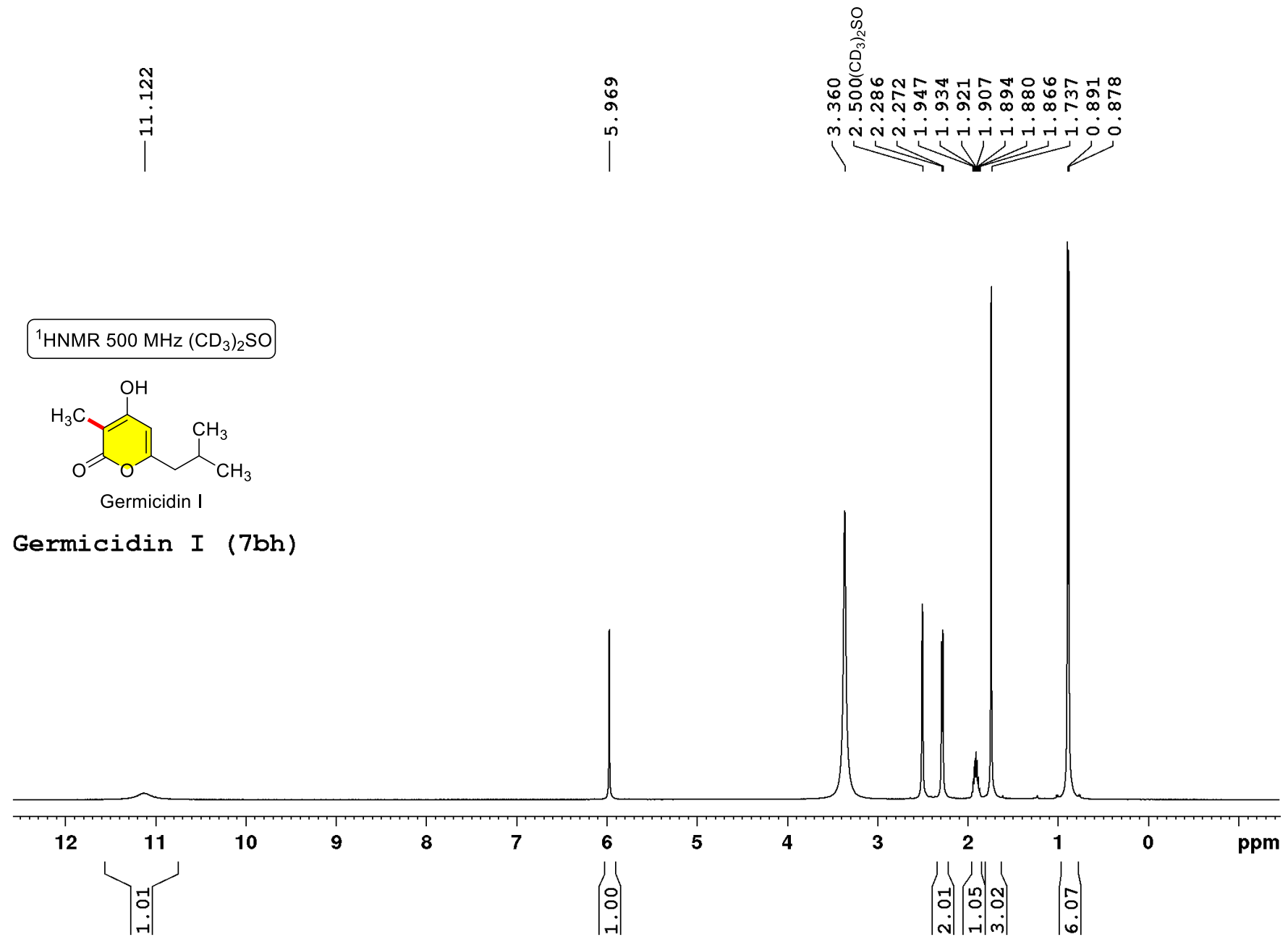
13C {1H} NMR 400 MHz CD₃OD



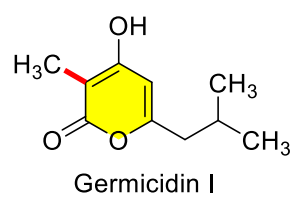
Photopyrone B

Photopyrone B (7bd)

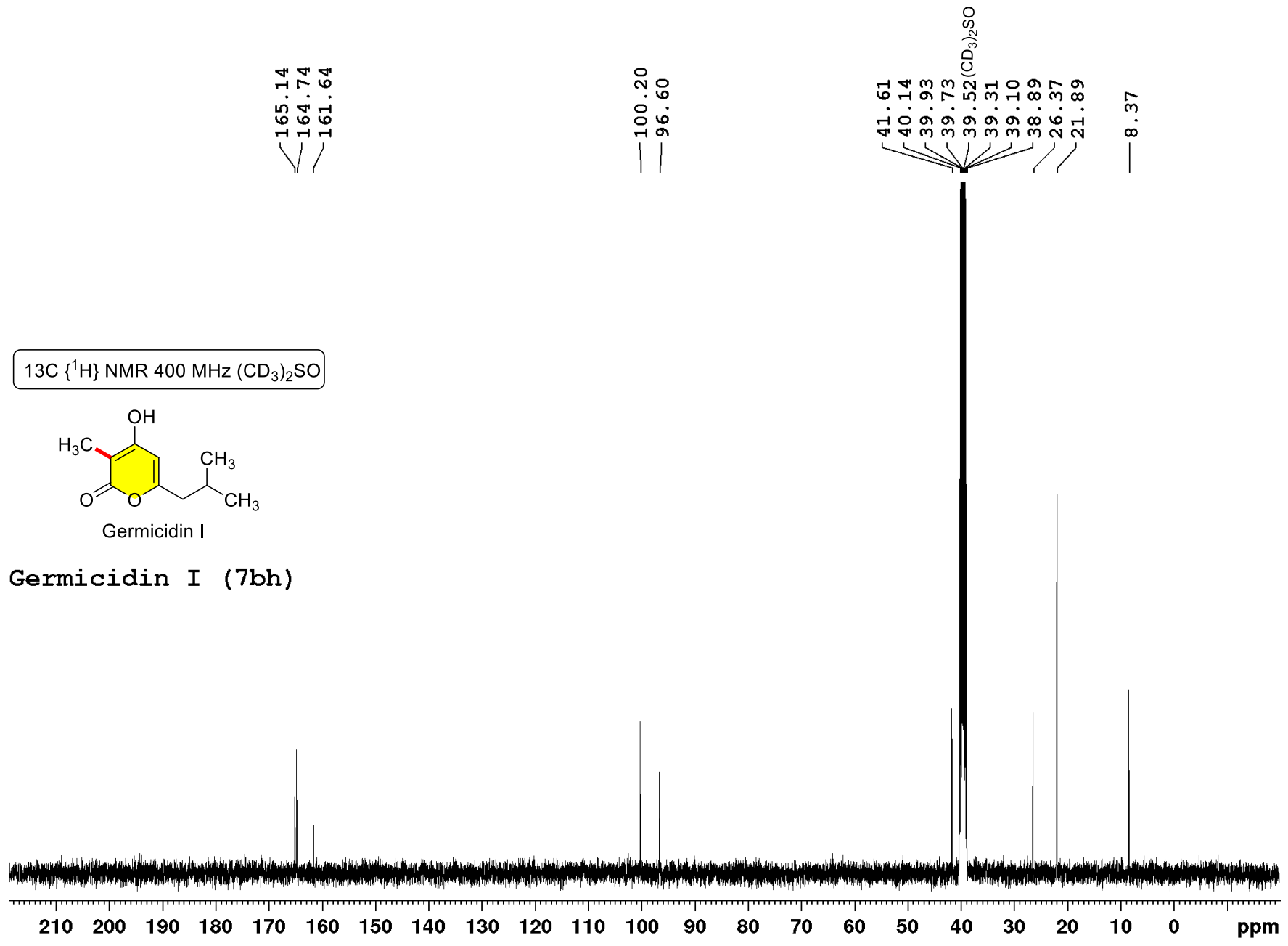


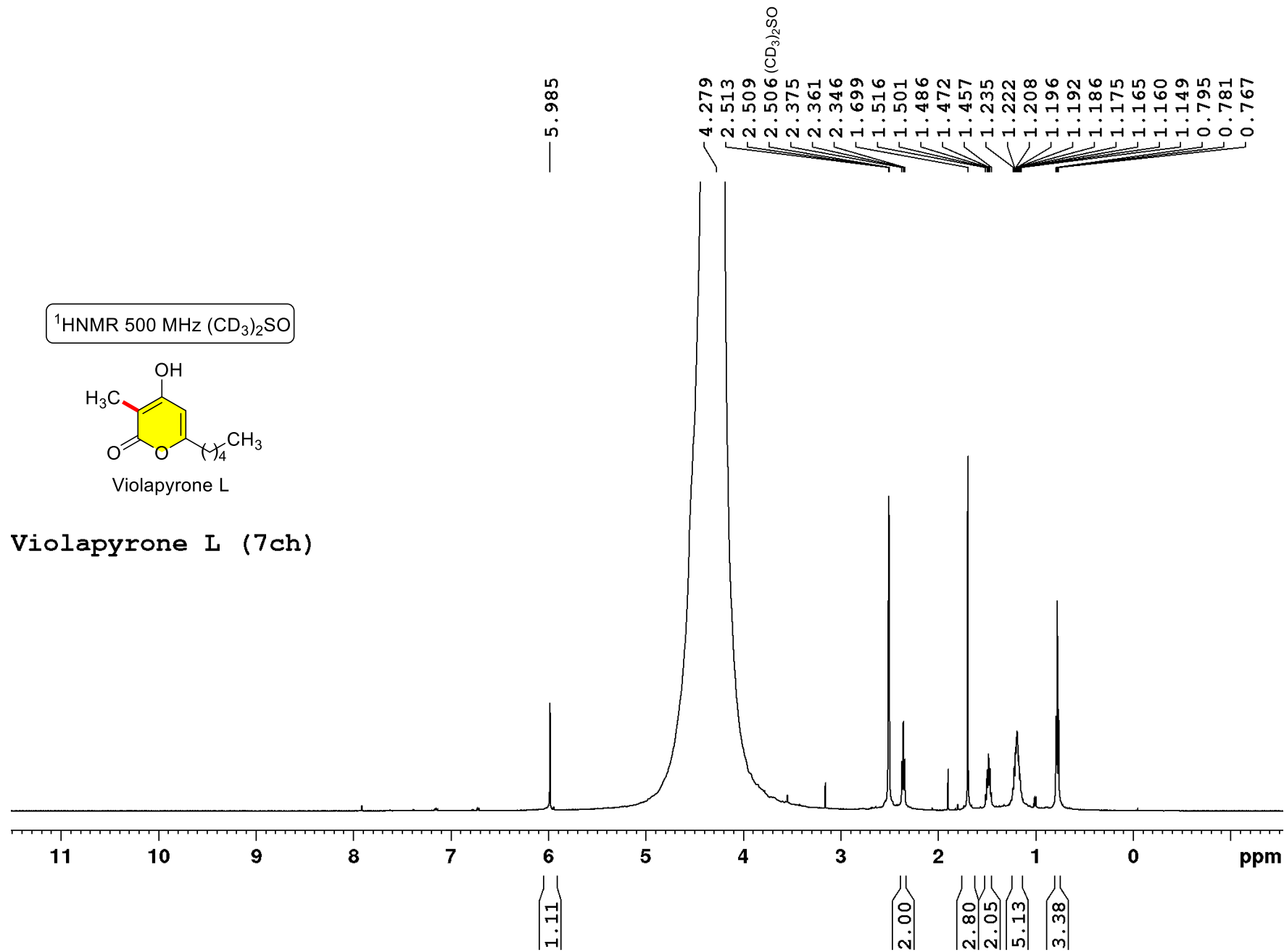


13C {1H} NMR 400 MHz (CD3)2SO

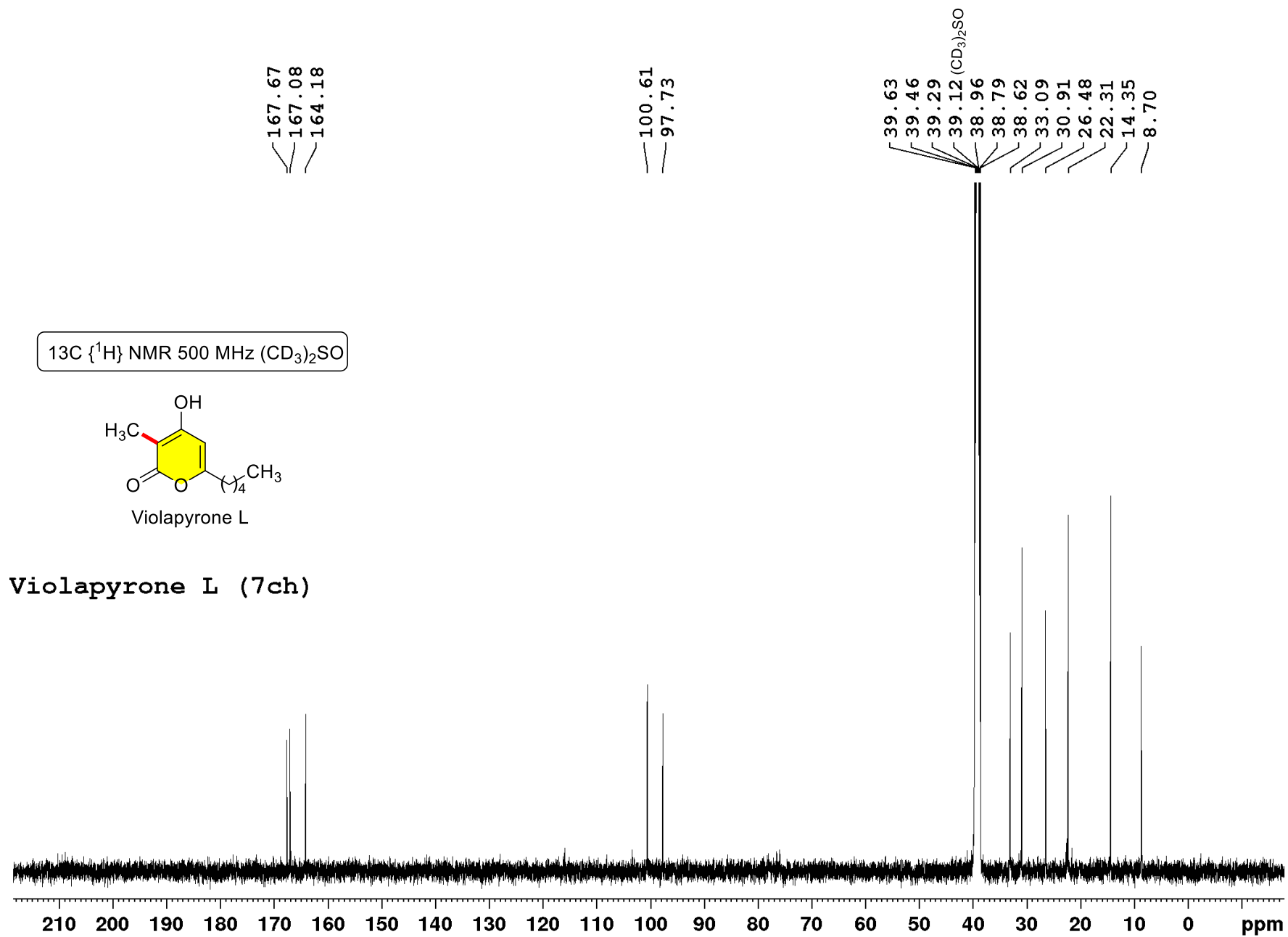
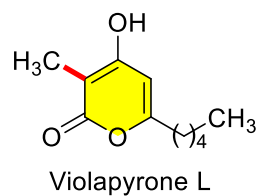


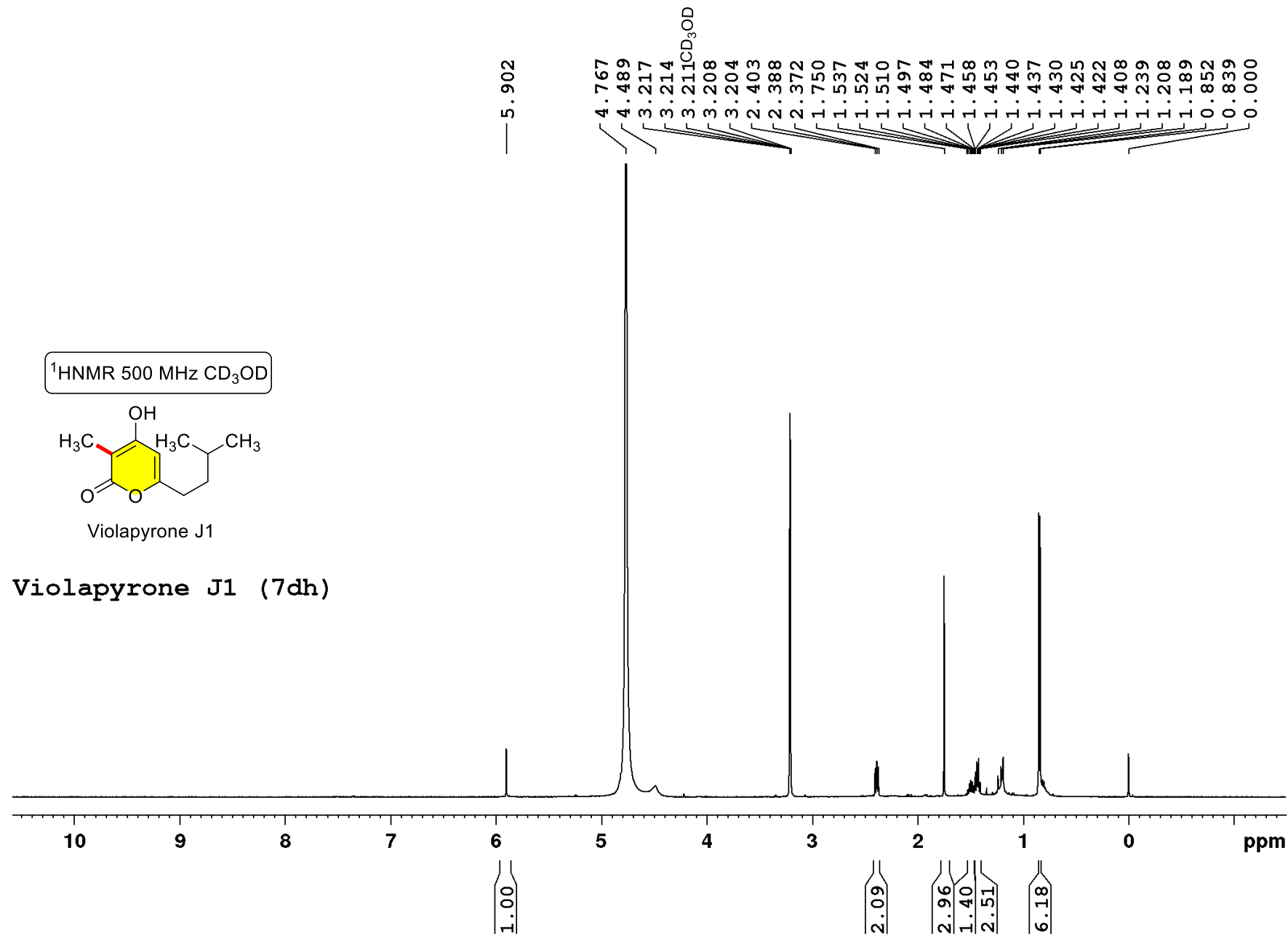
Germicidin I (7bh)



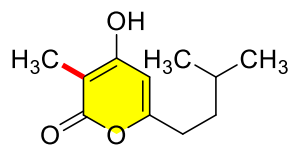


13C {1H} NMR 500 MHz (CD3)2SO



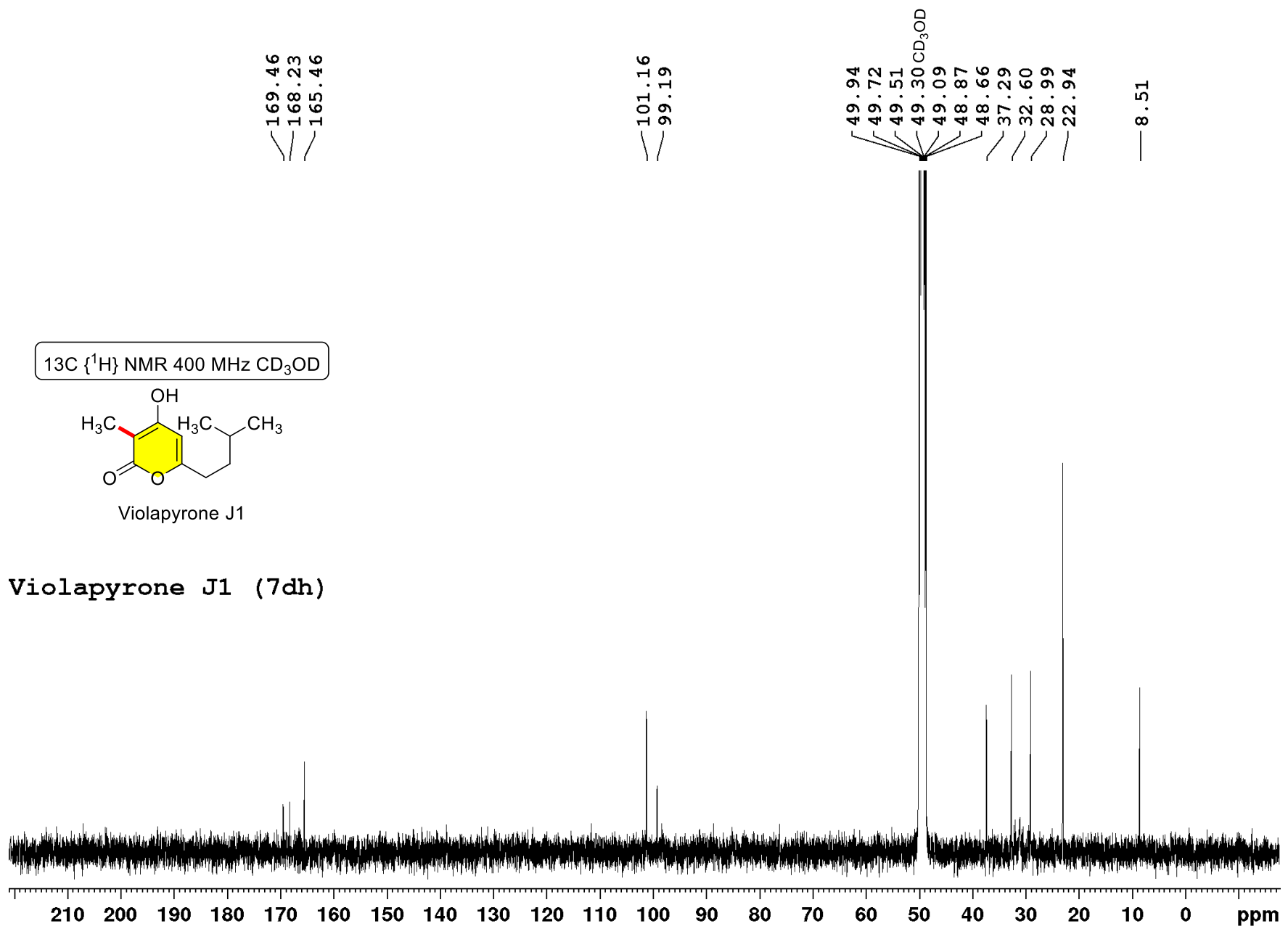


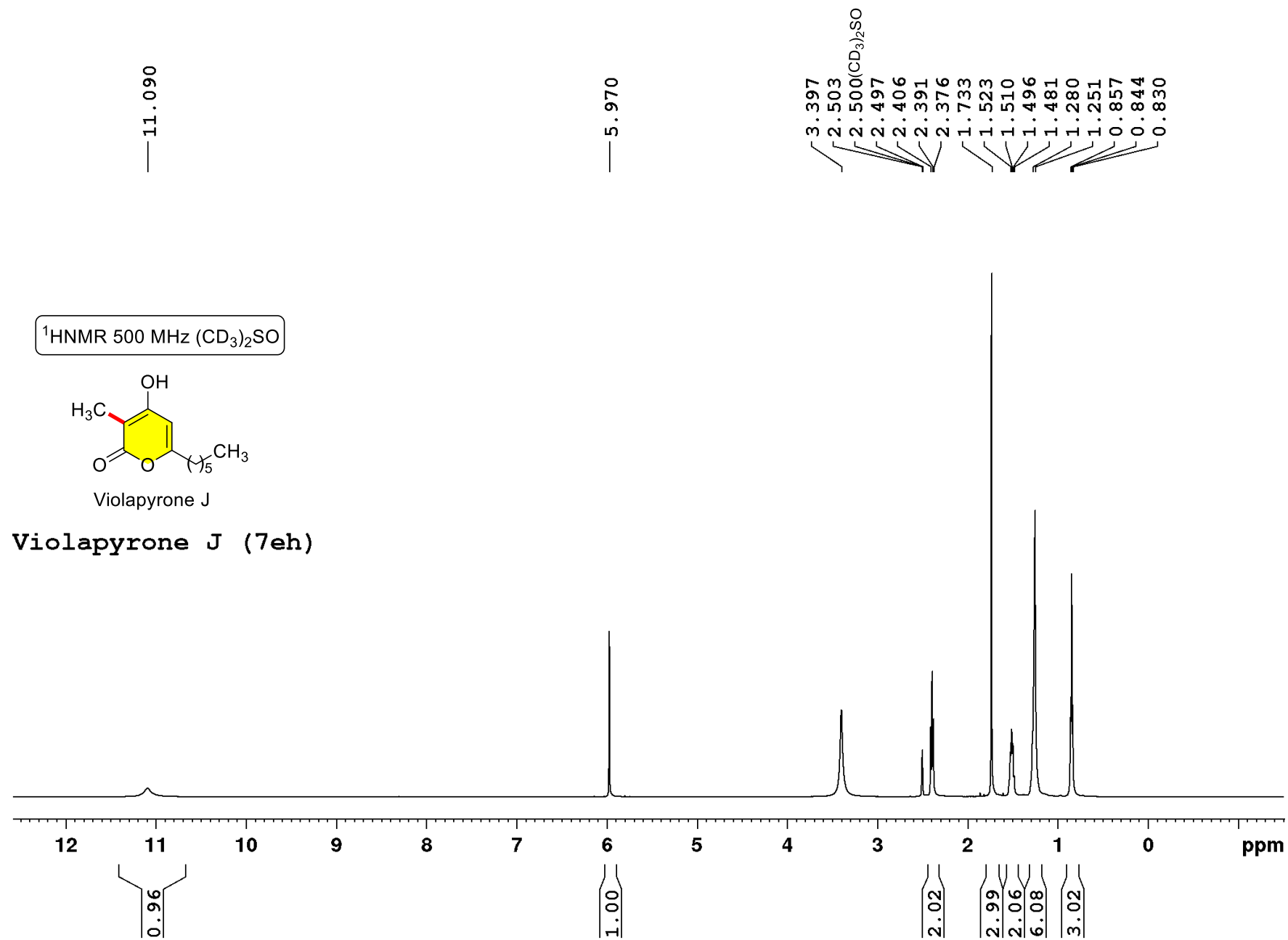
13C {1H} NMR 400 MHz CD3OD



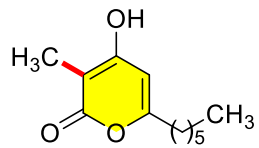
Violapyrone J1

Violapyrone J1 (7dh)



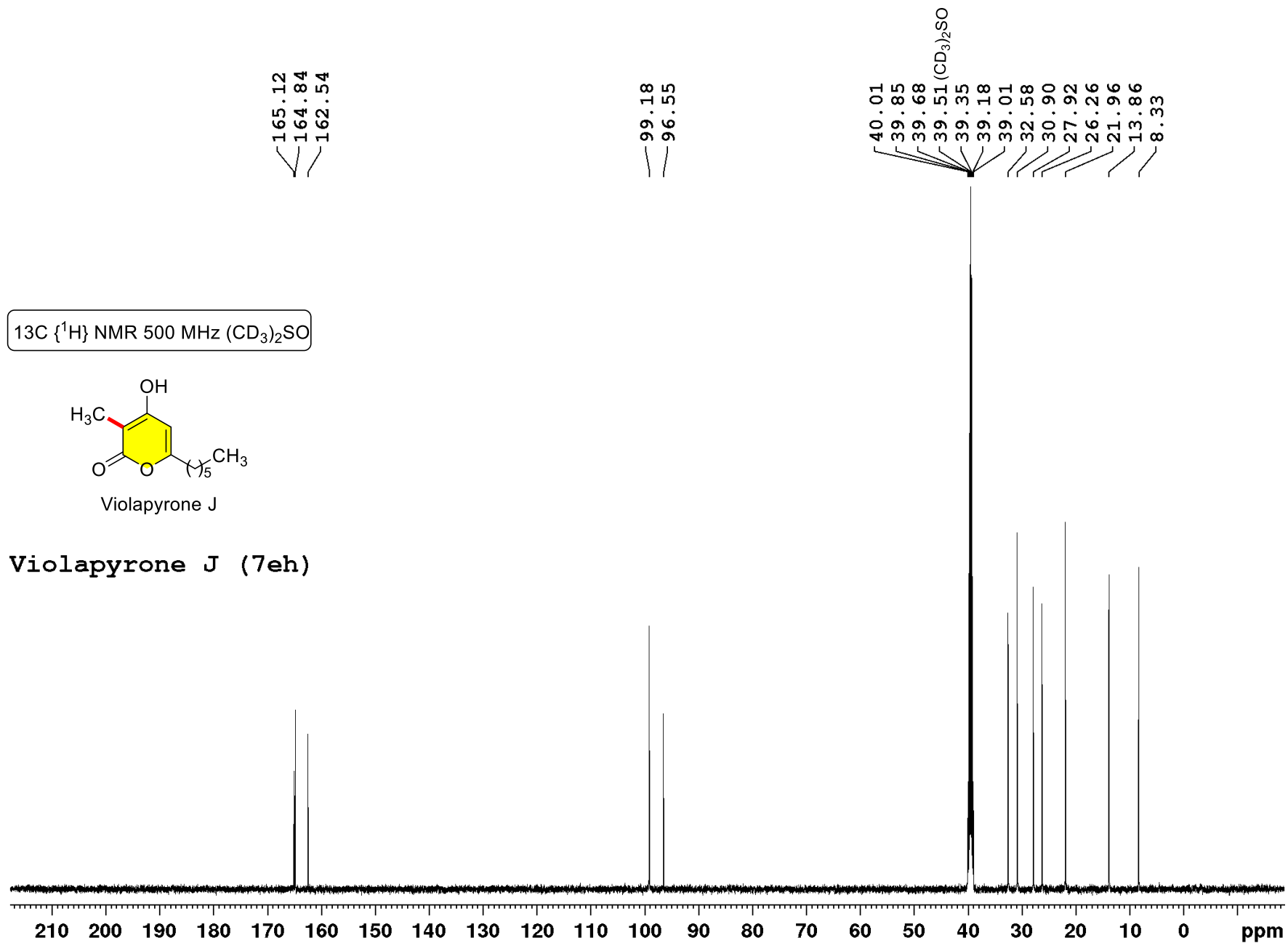


$^{13}\text{C} \{^1\text{H}\}$ NMR 500 MHz $(\text{CD}_3)_2\text{SO}$

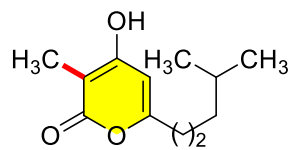


Violapyrone J

Violapyrone J (7eh)

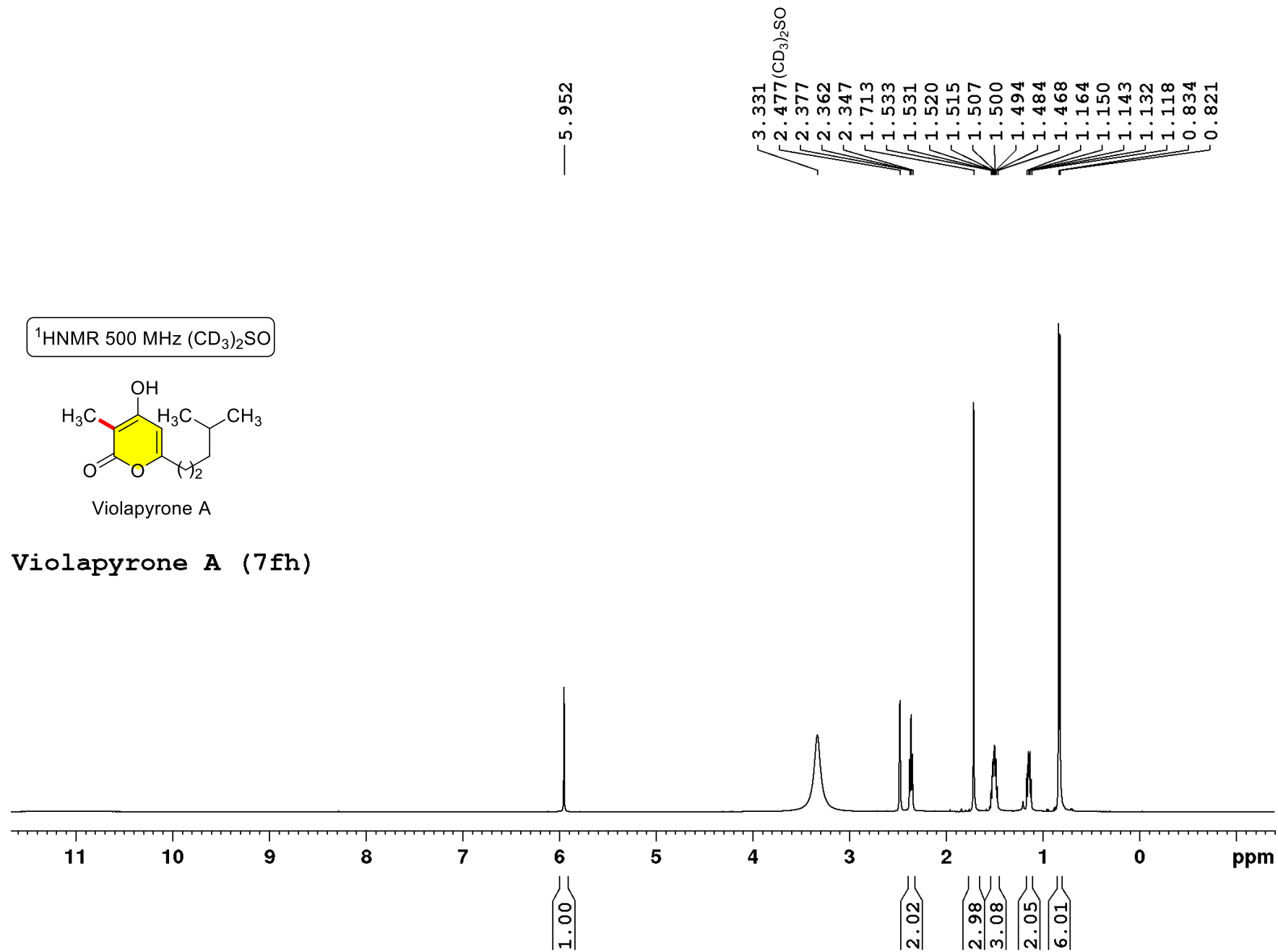


¹HNMR 500 MHz (CD₃)₂SO

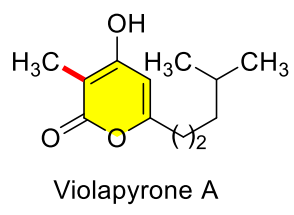


Violapyrone A

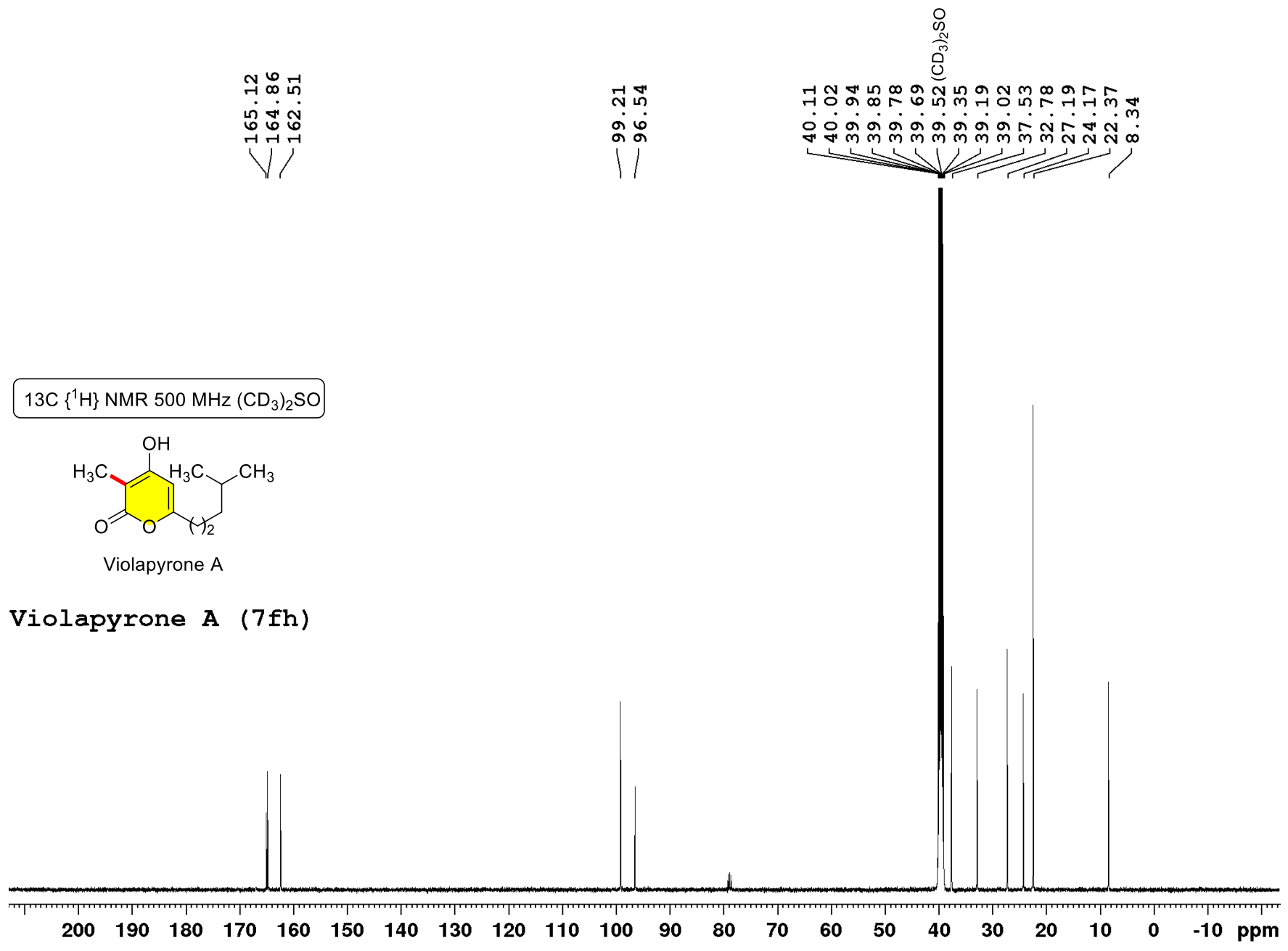
Violapyrone A (7fh)



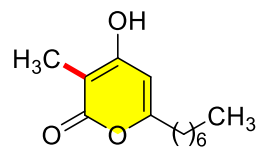
13C {1H} NMR 500 MHz (CD3)2SO



Violapyrone A (7fh)

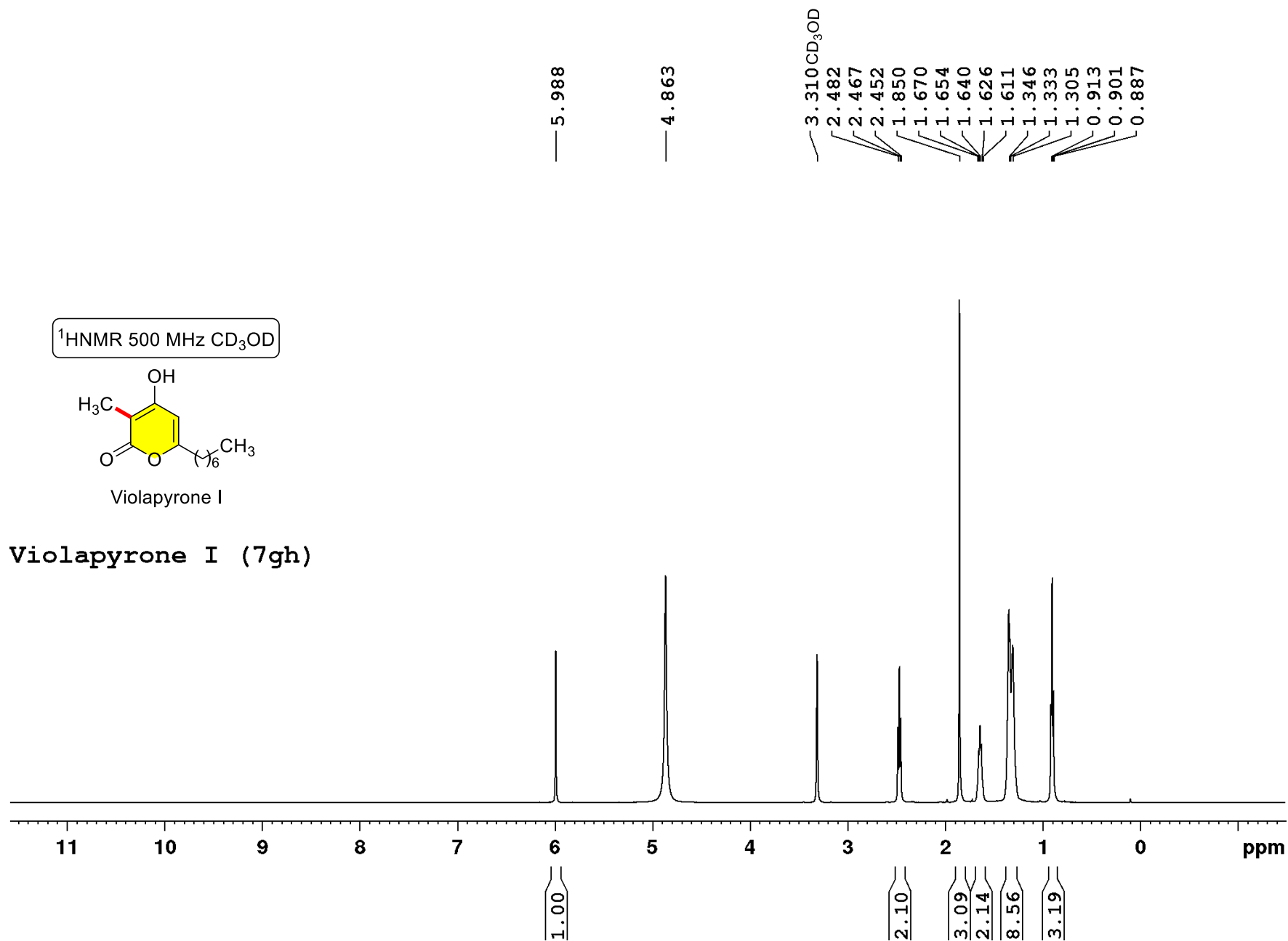


¹HNMR 500 MHz CD₃OD

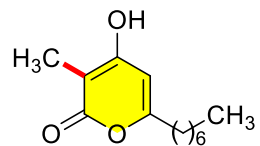


Violapyrone I

Violapyrone I (7gh)

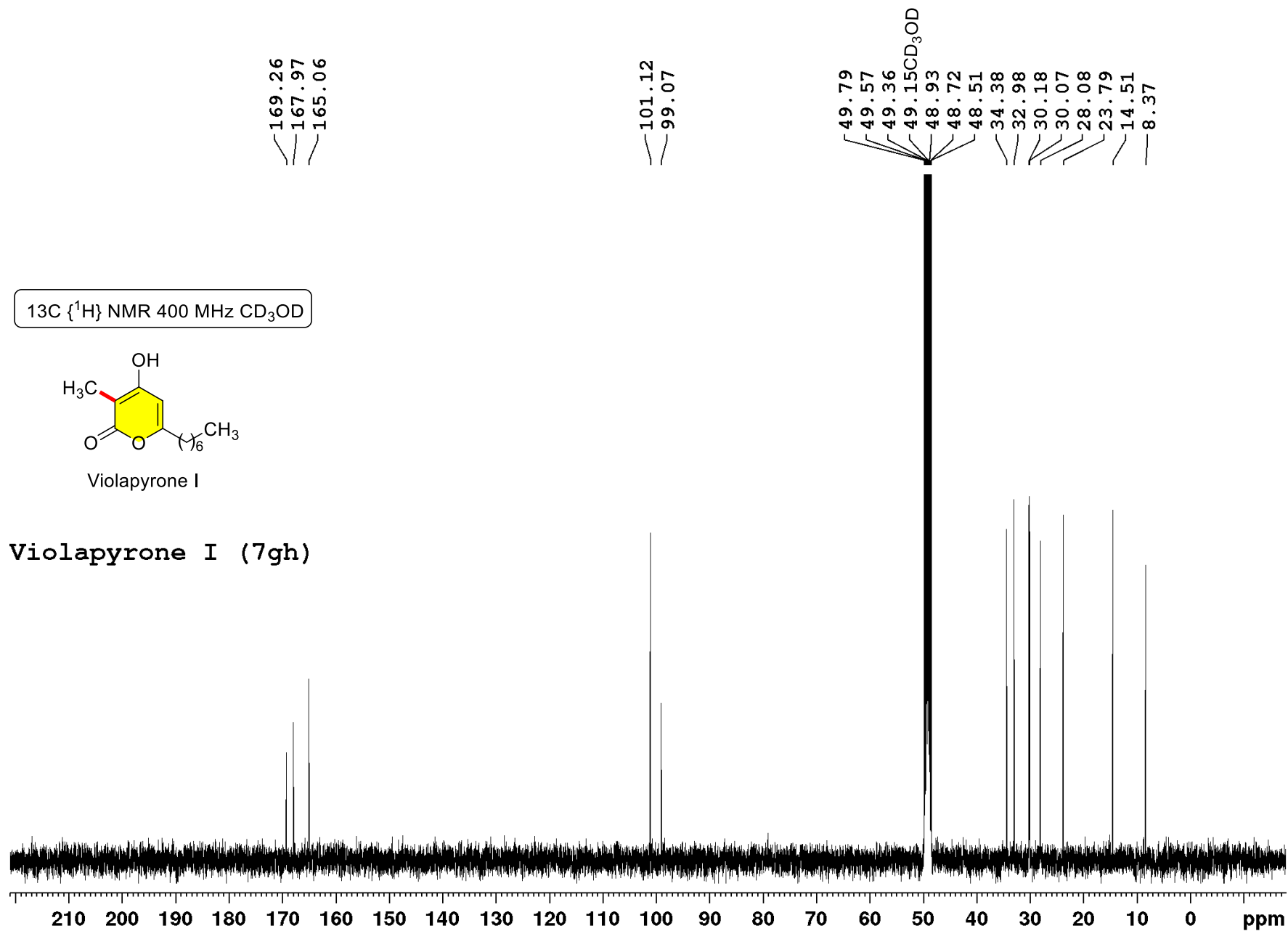


13C {1H} NMR 400 MHz CD₃OD

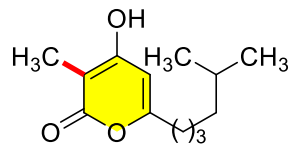


Violapyrone I

Violapyrone I (7gh)

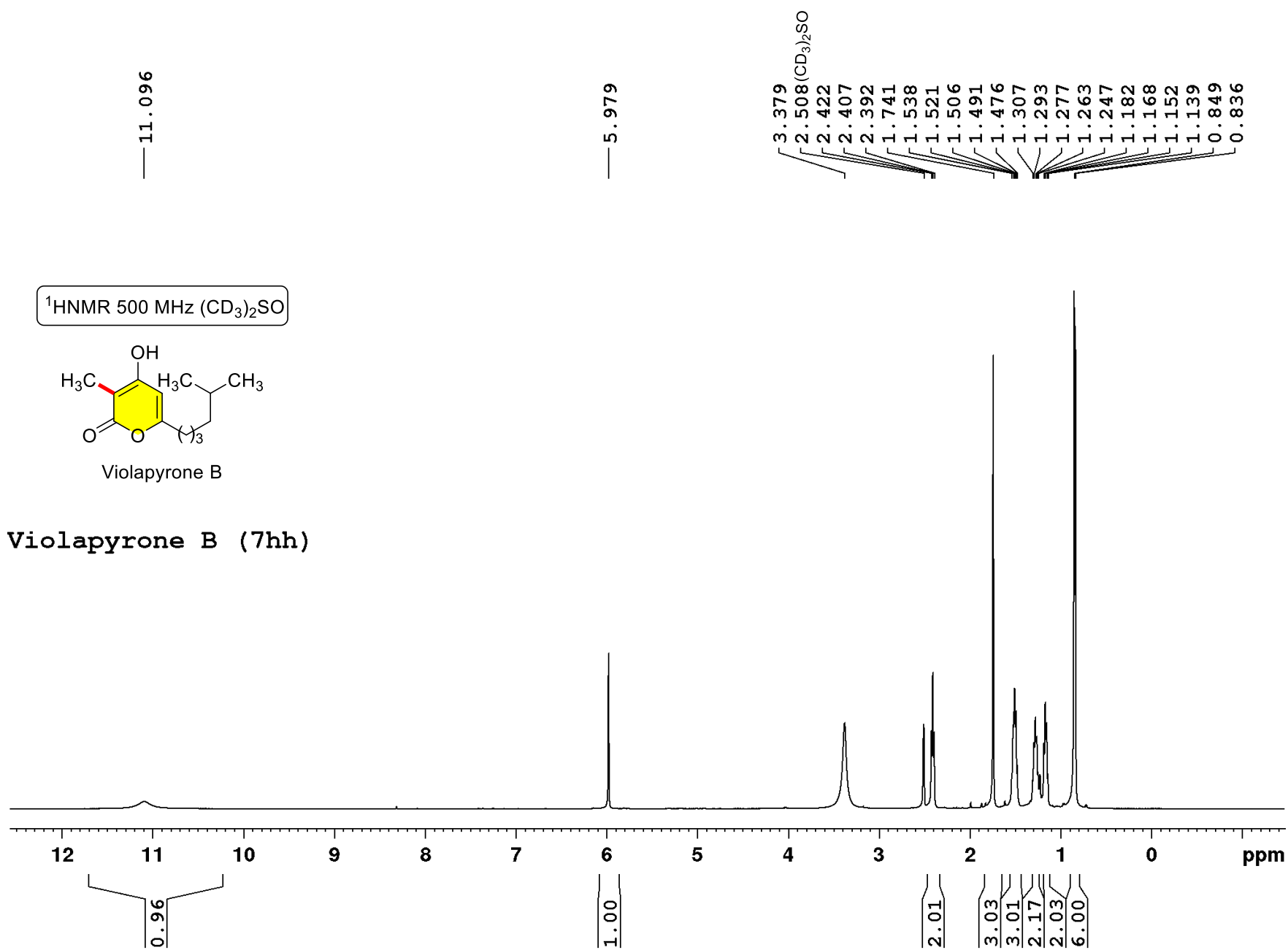


¹HNMR 500 MHz (CD₃)₂SO

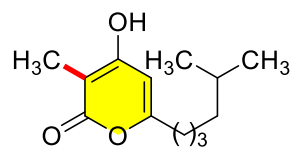


Violapyrone B

Violapyrone B (7hh)

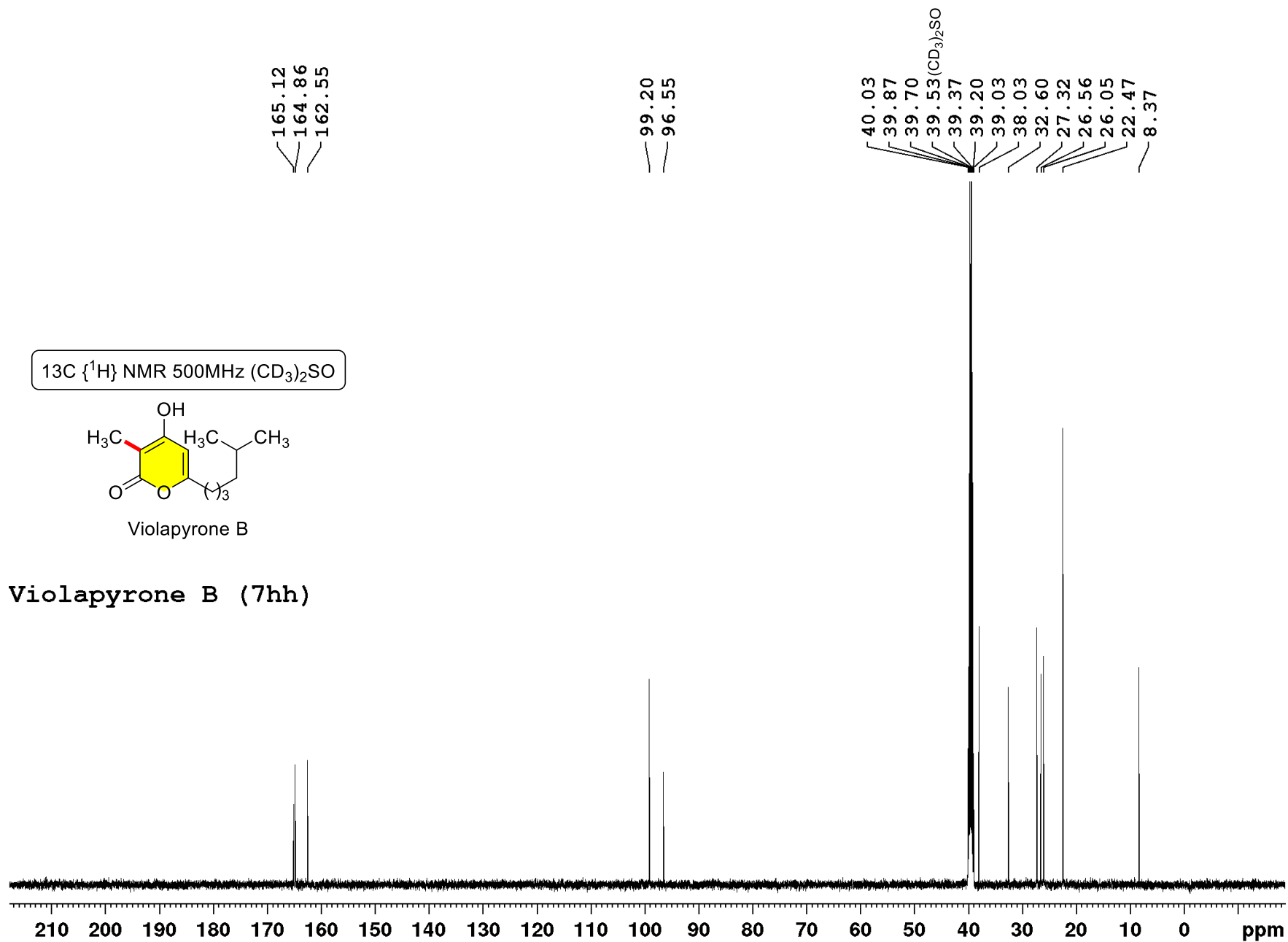


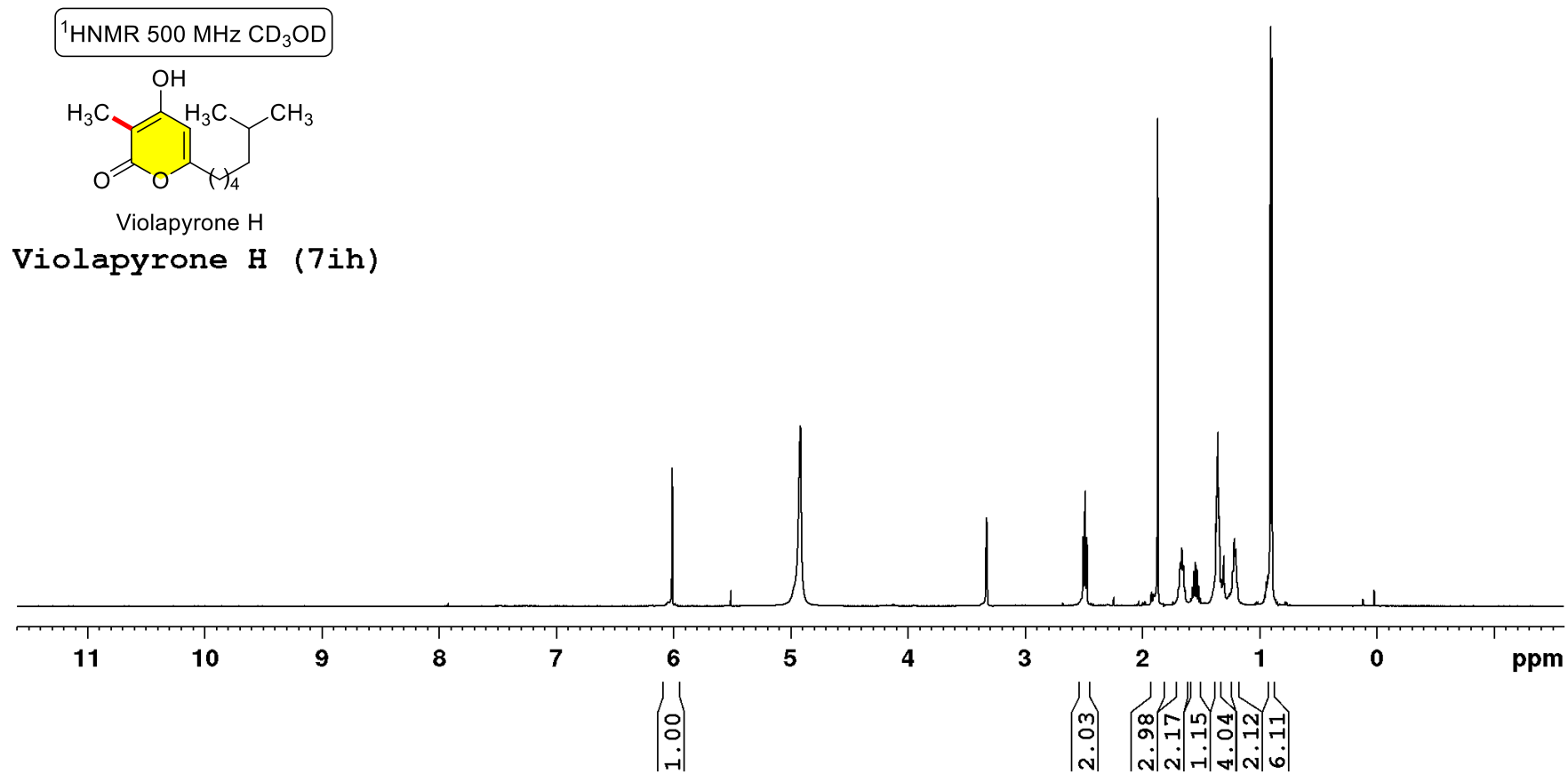
13C {1H} NMR 500MHz (CD3)2SO



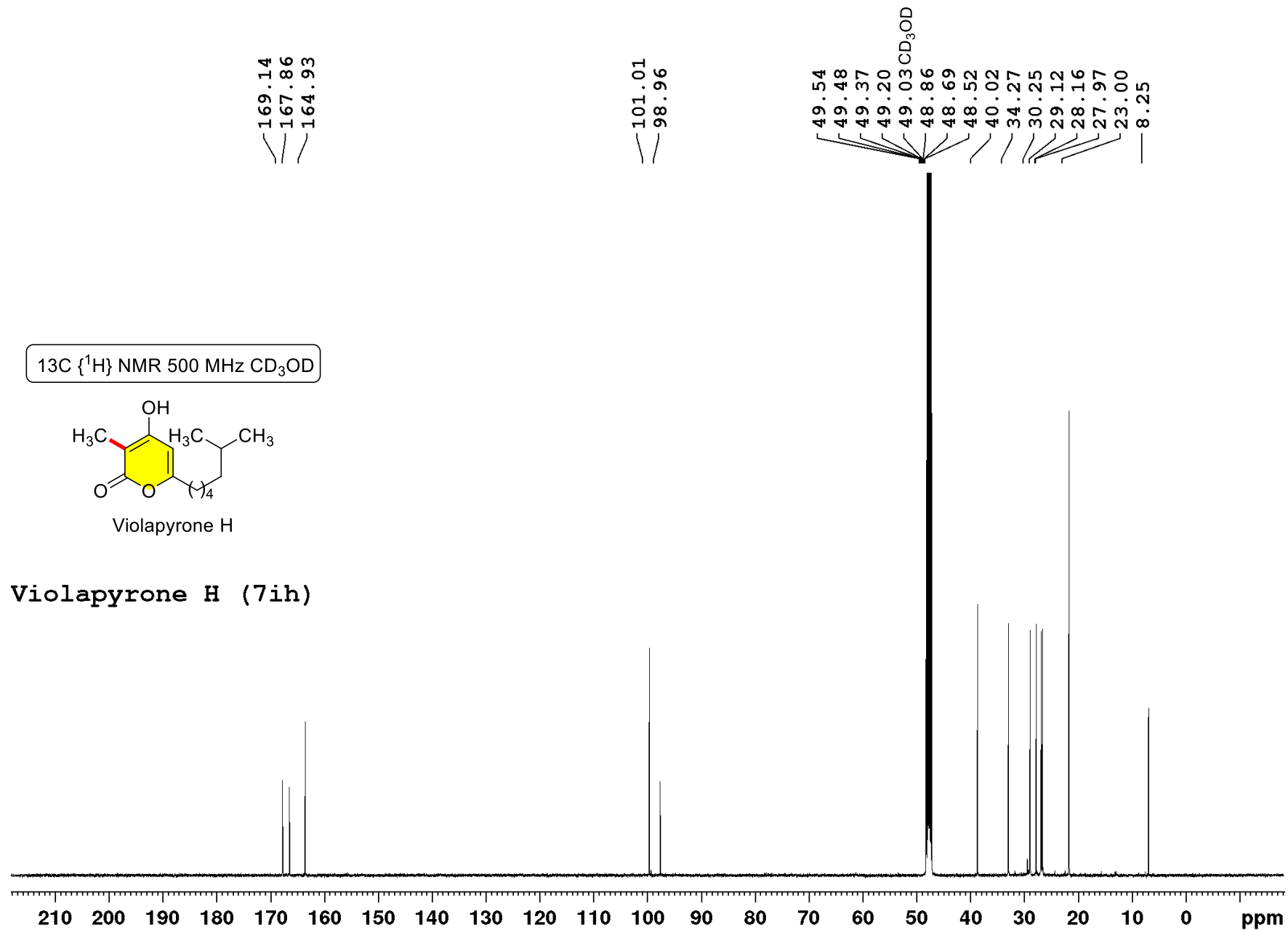
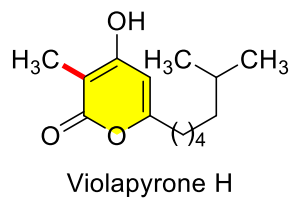
Violapyrone B

Violapyrone B (7hh)





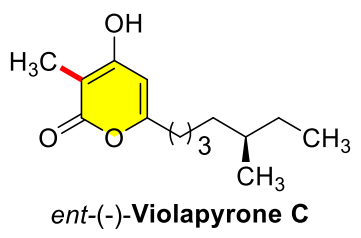
13C {1H} NMR 500 MHz CD3OD



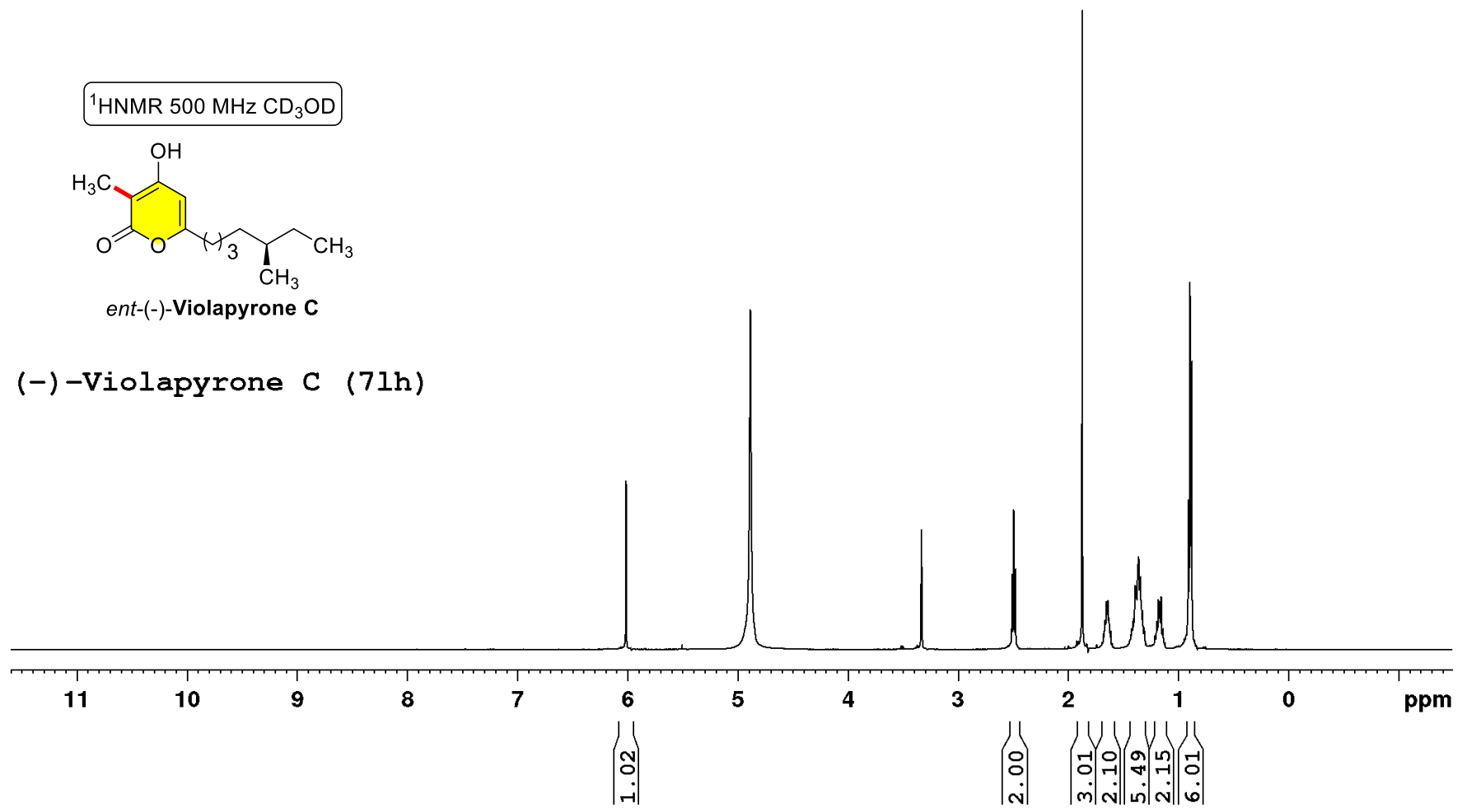
Violapyrone H (7ih)

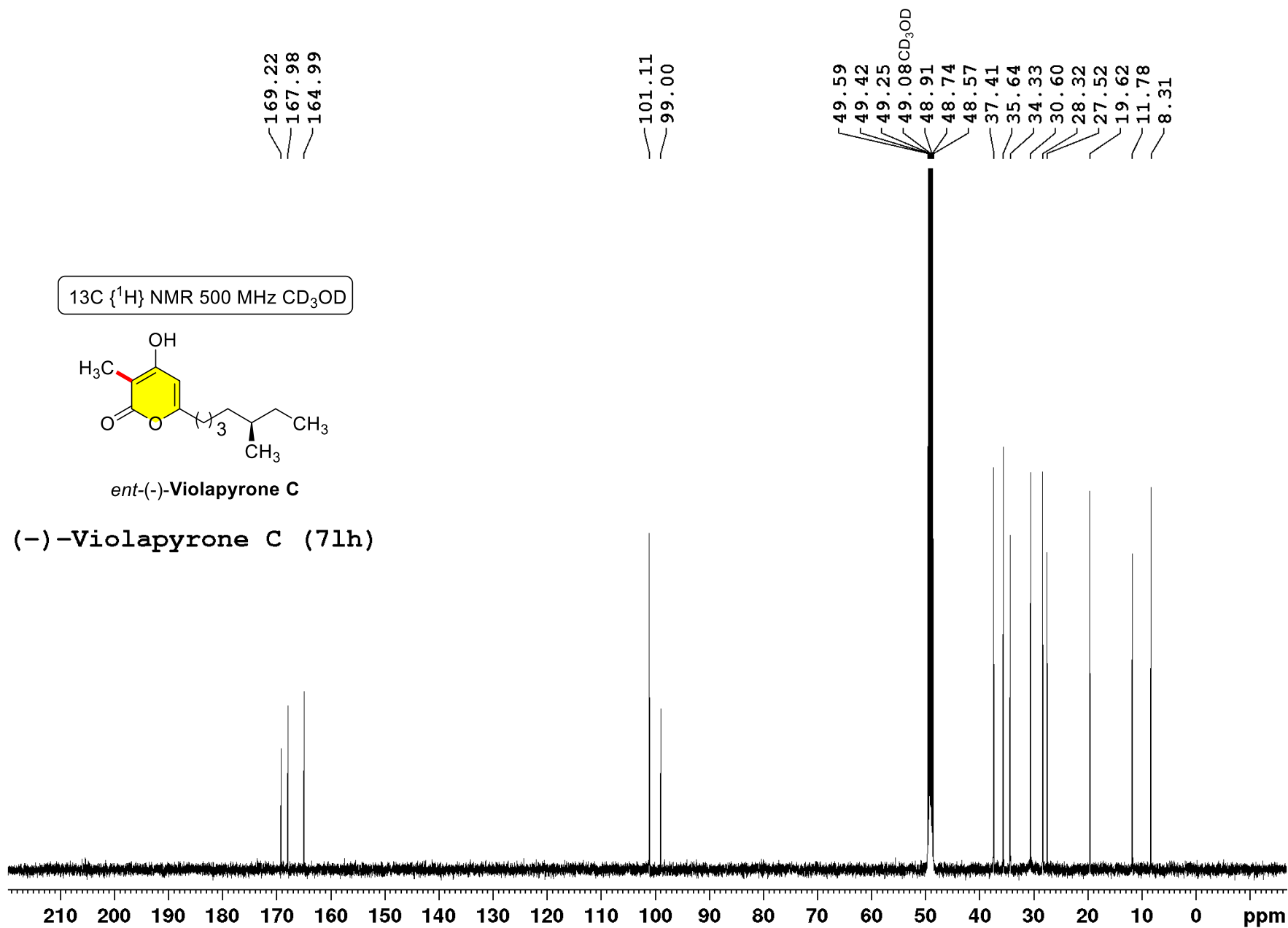
6.011
 4.883
 3.335
 3.332
 3.329 CD₃OD
 3.326
 3.322
 2.507
 2.492
 2.477
 1.870
 1.678
 1.670
 1.665
 1.661
 1.651
 1.637
 1.626
 1.623
 1.618
 1.611
 1.427
 1.421
 1.417
 1.409
 1.402
 1.390
 1.384
 1.380
 1.377
 1.372
 1.368
 1.363
 1.358
 1.351
 1.344
 1.336
 1.334
 1.322
 1.309
 1.304
 1.210
 1.208
 1.196
 1.193
 1.179
 1.173
 1.166
 1.164
 1.159
 1.153
 1.139
 1.138
 0.908
 0.893
 0.889
 0.878
 0.876

¹HNMR 500 MHz CD₃OD

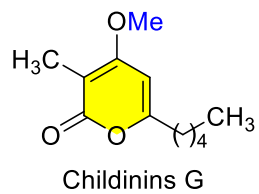


(-)-Violapyrone C (71h)

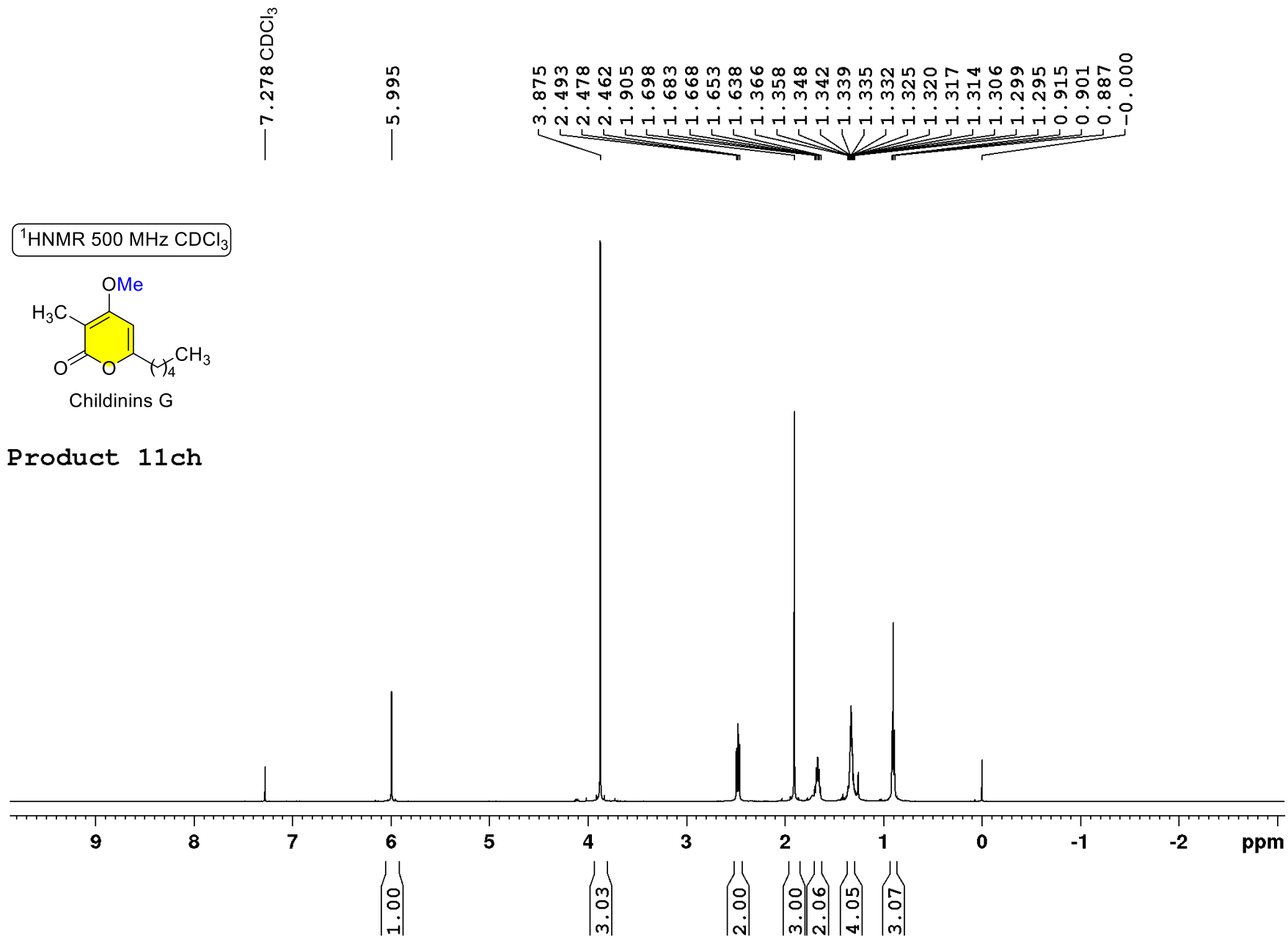




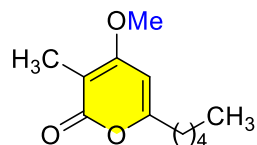
¹H NMR 500 MHz CDCl₃



Product 11ch

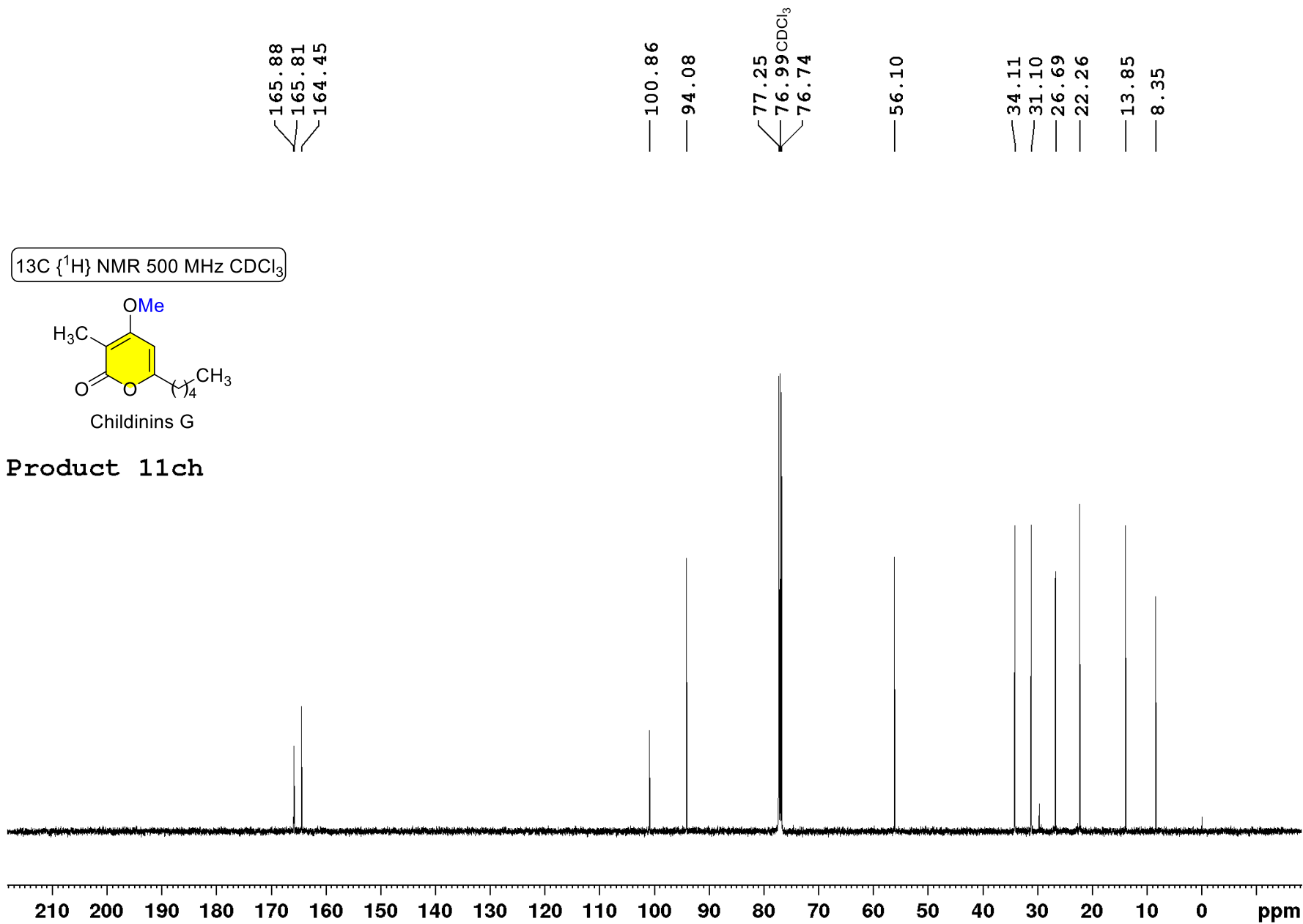


13C {1H} NMR 500 MHz CDCl3

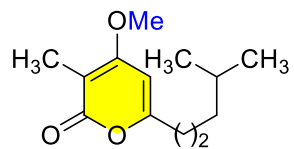


Childinins G

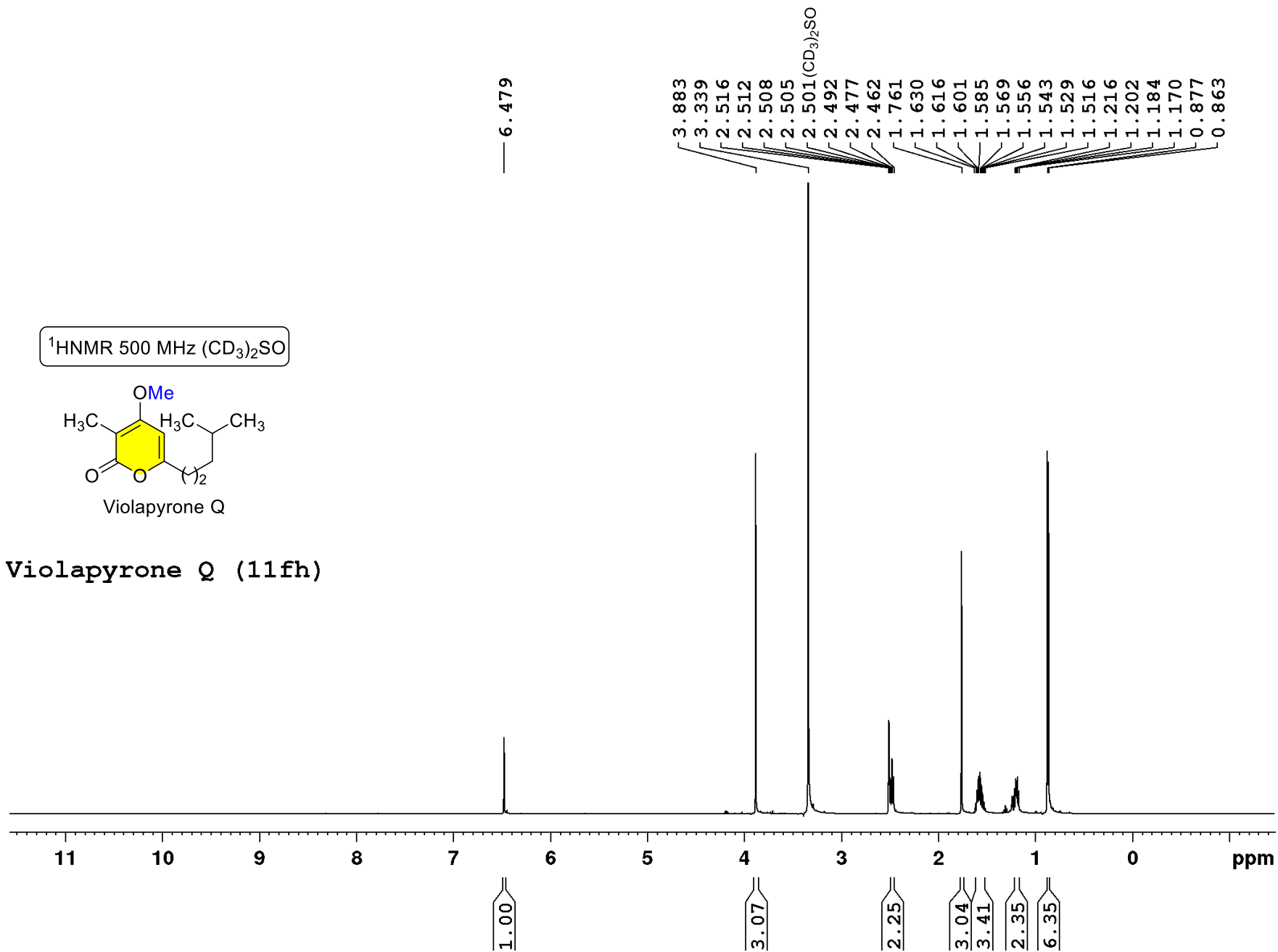
Product 11ch



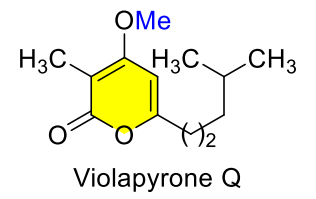
¹HNMR 500 MHz (CD₃)₂SO



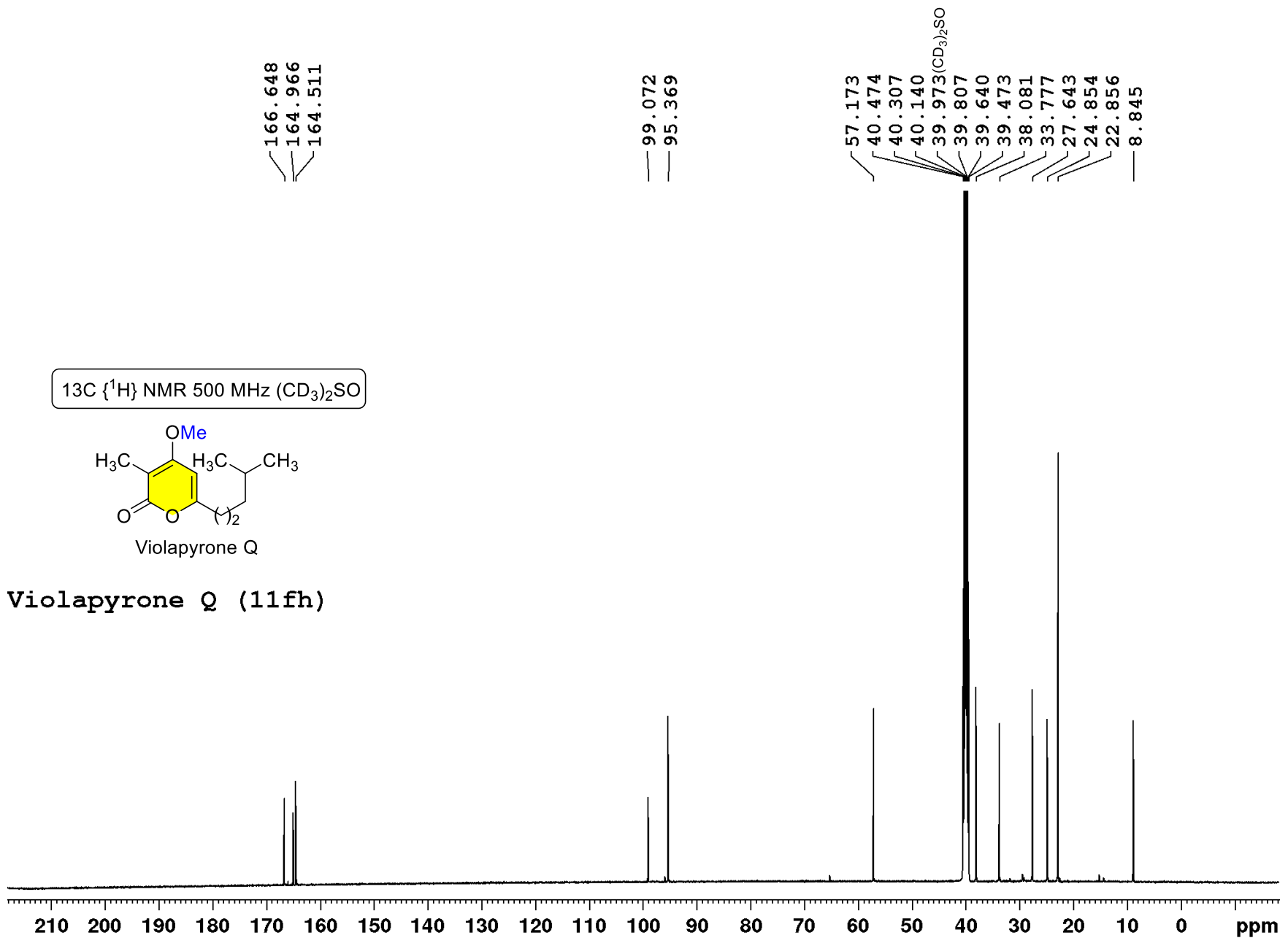
Violapyrone Q (11fh)



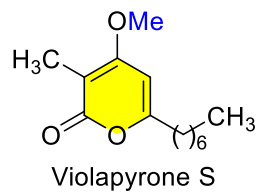
13C {1H} NMR 500 MHz (CD3)2SO



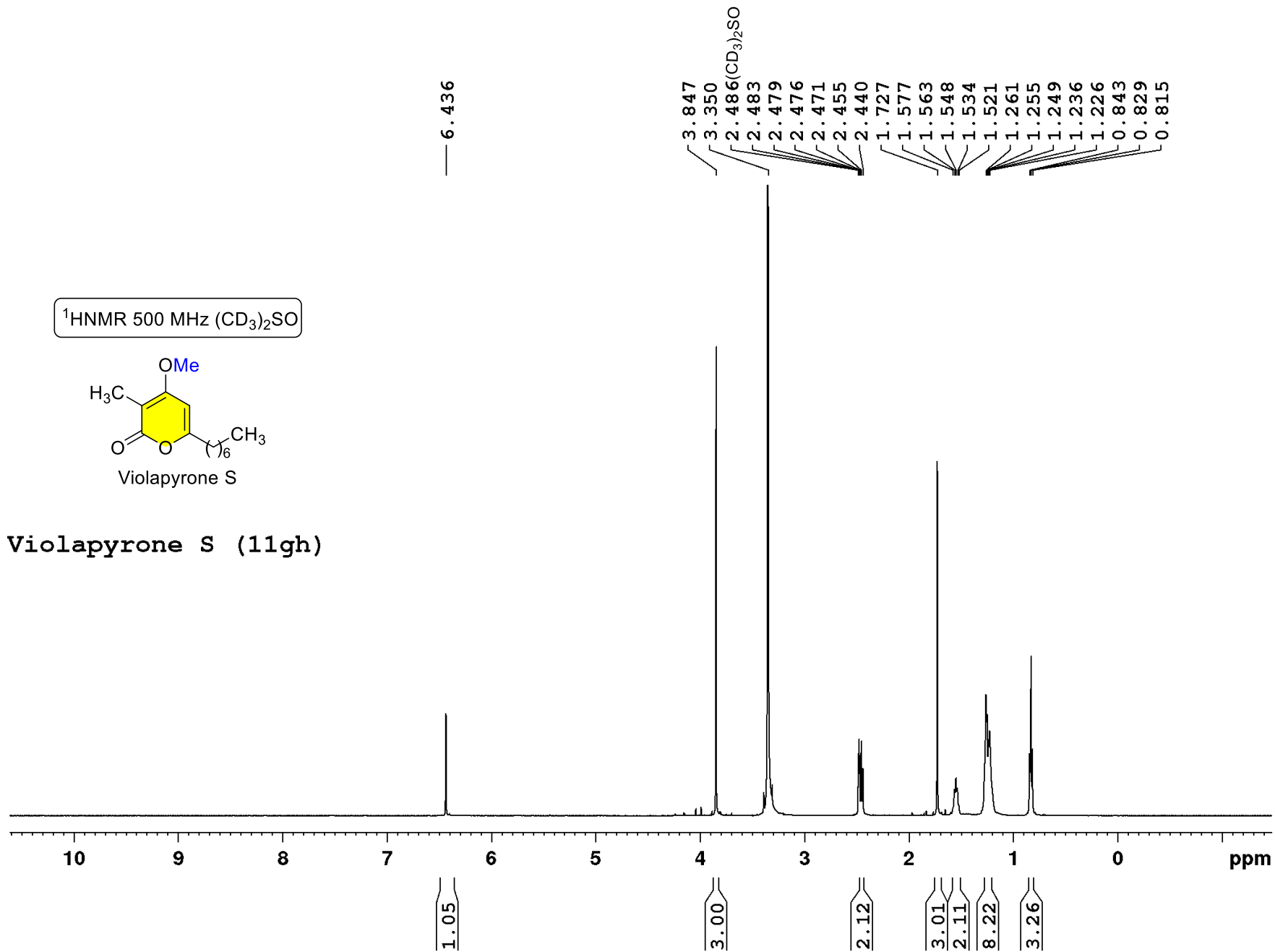
Violapyrone Q (11fh)



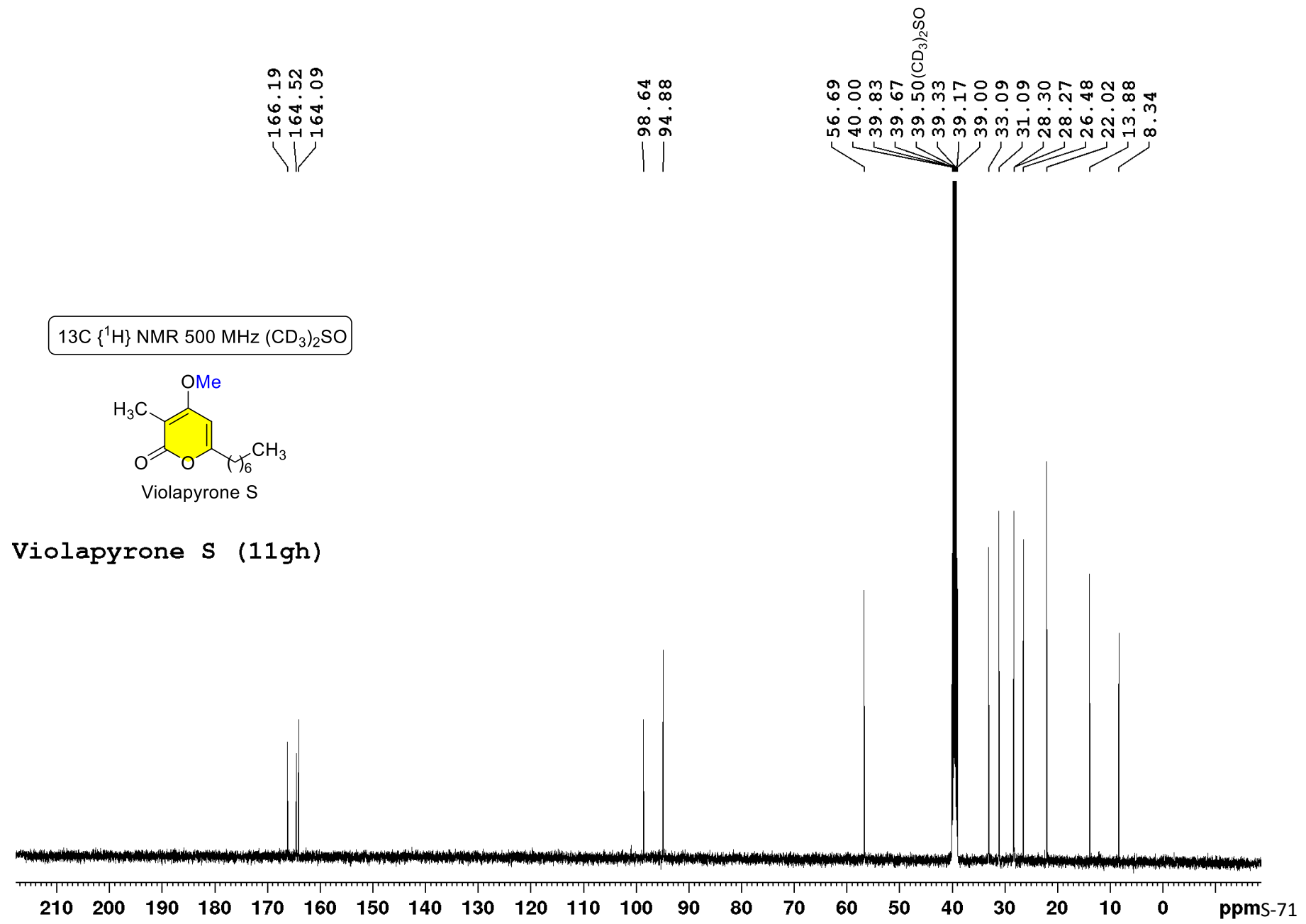
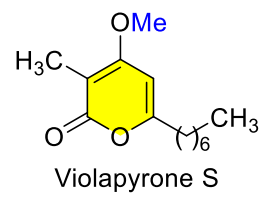
¹HNMR 500 MHz (CD₃)₂SO



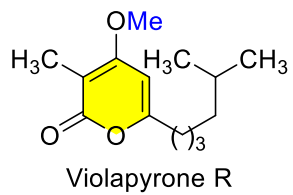
Violapyrone S (11gh)



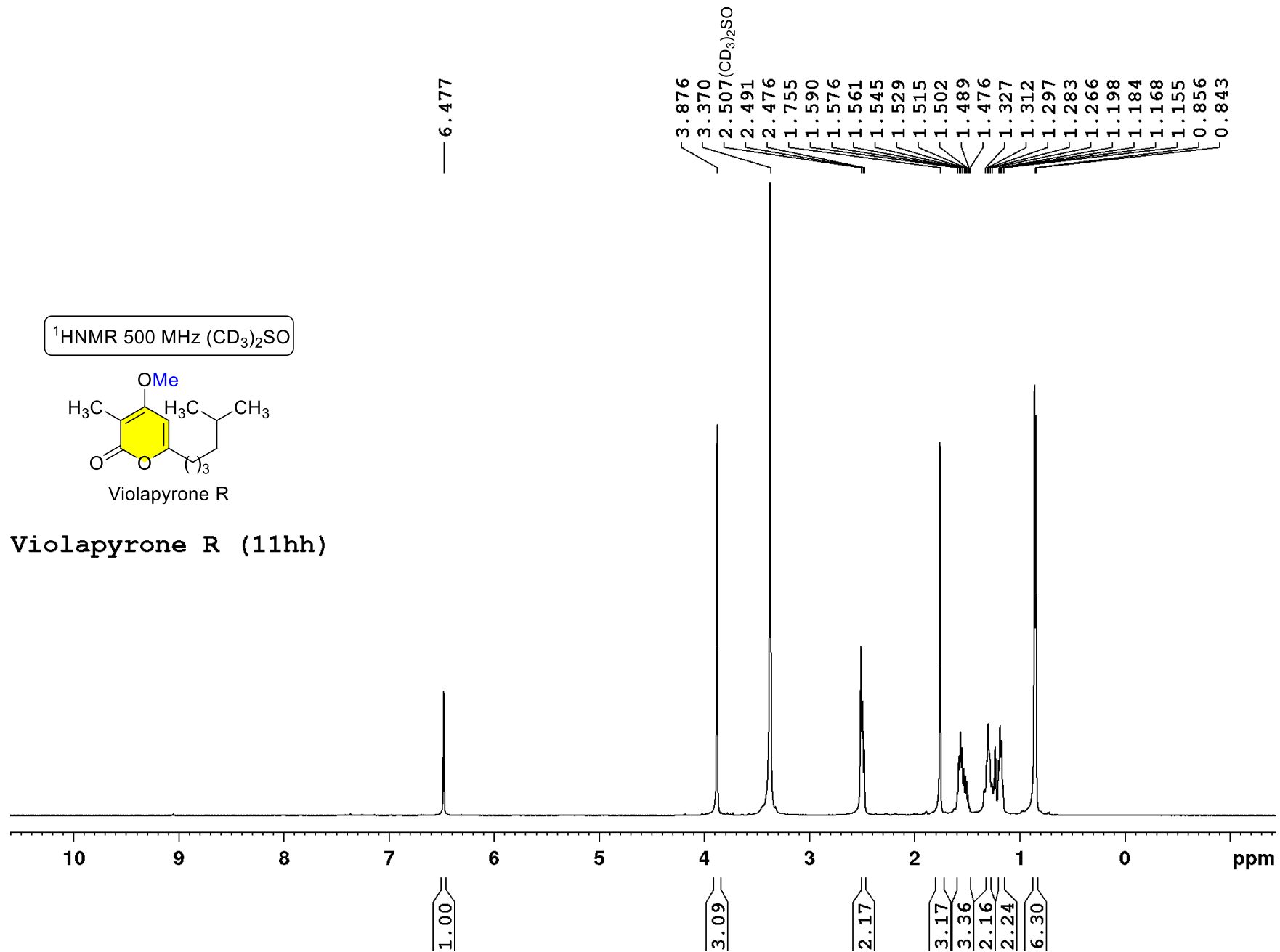
$^{13}\text{C} \{^1\text{H}\}$ NMR 500 MHz $(\text{CD}_3)_2\text{SO}$



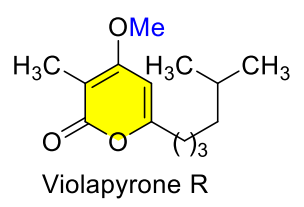
¹HNMR 500 MHz (CD₃)₂SO



Violapyrone R (11hh)



13C {1H} NMR 500 MHz (CD3)2SO



Violapyrone R (11hh)

