

Supporting Information

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Secondary Metabolites Isolated from the Marine Fungal Strain *Aspergillus* sp. AF119

*S Liu, C Lu, J Huang, Y Shen**

School of Life Sciences, Xiamen University Xiamen, Fujian 361005 China

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General Experimental Procedures. Column chromatography (CC): silica gel (SiO₂; 200-300 and 80-100 mesh; Qingdao Marine Chemical Factory), silica gel GF₂₅₄ (Merck), RP-18 gel (40-63 μm Merck), or Sephadex LH-20 gel (Amersham Biosciences). TLC: precoated silica-gel GF₂₅₄ plates(0.20-0.25 mm, Qingdao Marine Chemical Factory, Qingdao, P.R.China). UV Spectra: GenesysTM 2Thermospectronic, λ_{max} (ε); in nm. IR Spectra: Thermo Nicolet 380 FT-IR spectrophotometer, with KBr cells; in cm⁻¹. NMR Spectra: BrukerArx 600 spectrometer operating, at 600/150 MHz, δ in in ppm rel. to Me₄Si; *J* in Hz. HR-Q-TOF-MS: Bio TOFTM-Q mass spectrometer (Bruker); in m/z. Optical rotations: AUTOPOL[®] IV automatic polarimeter.

Fermentation & Isolation. The fermentation was cultured in *petri dishes* laid with ca. 20 ml half sea water PDA medium for 15 d at 28°C. The culture material (total 7 L) was extracted with EtOAc thrice. The solvent was evaporated under reduced pressure to afford 7.2 g of crude extract. The crude extract was subjected to MPLC over RP-18 (170 g) using a stepwise gradient of 30, 50, 70, and 100% (v/v) acetone in H₂O to afford Fr.1 (750 mg), Fr.2 (1.08 g), Fr.3 (320 mg) and Fr.4 (220 mg), obtained from 30% acetone, and Fr.5 (490 mg) and Fr.6 (65 mg), from 50% acetone. Fr.1 was subjected to *Sephadex LH-20* column twice, and eluted with MeOH and acetone, respectively, and then it was fractionated on silica gel CC (CHCl₃/MeOH) to yield **1** (5 mg). Fr.3 was dissolved in MeOH and filtered. Filtrate was subjected to *Sephadex LH-20* eluted with MeOH to afford Fr.3.1 (26 mg) and Fr.3.2 (56 mg). Fr.3.1 was subjected to *Sephadex LH-20* eluted with acetone, then purified by CC (silica gel, CHCl₃/MeOH) to yield **2** (10 mg). Fr.5 was subjected to *Sephadex LH-20* eluted with MeOH to afford Fr.5.1 (50 mg) and Fr.5.2 (53 mg). Fr.5.1 was subjected to *Sephadex LH-20* eluted with acetone, then purified by CC (silica gel, petroleum ether/EtOAc) to yield **4** (3 mg). Fr.6 was subjected to *Sephadex LH-20* column twice, and eluted with MeOH and acetone, respectively, and then it was fractionated on silica gel CC (petroleum ether /AcOEt) to yield **3** (3 mg).

Barceloneic lactone B (1). White amorphous powder; $[\alpha]_D^{20} = 0$ (c = 0.5, MeOH); UV (MeOH): 230.0 nm ($\epsilon = 3.52$), 281.0 nm ($\epsilon = 3.34$); IR (KBr): 3341, 2923, 1731, 1602, 1582, 1478 cm^{-1} ; ^1H - and ^{13}C -NMR: Table S4. HR-ESI-Q-TOF MS: 325.0704 $[\text{M} + \text{Na}]^+$.

Barceloneic acids C (2). White amorphous powder; $[\alpha]_D^{20} = 0$ (c = 0.5, MeOH); UV (MeOH): 230.0 nm ($\epsilon = 3.71$), 281.0 nm ($\epsilon = 3.14$); IR (KBr): 3341, 2925, 1692, 1604, 1467, 1082 cm^{-1} ; ^1H - and ^{13}C -NMR: Table S5. HR-ESI-Q-TOF MS: 325.0780 $[\text{M} + \text{Na}]^+$.

5'-hydroxychlorflavonin (3). Yellow amorphous powder; $[\alpha]_D^{20} = 0$ (c = 0.2, MeOH); UV (MeOH): 230.0 nm ($\epsilon = 2.91$), 280.0 nm ($\epsilon = 2.02$); IR (KBr): 3340, 2929, 1693, 1600, 1452, 1205 cm^{-1} ; ^1H - and ^{13}C -NMR: Table S6. HR-ESI-Q-TOF MS: 395.0948 $[\text{M} + \text{H}]^+$.

Table S1. NMR Spectral Data for barceloneic lactone B (1) and barceloneic acids C (2)^a

Position	9				10			
	¹ H (mult. <i>J</i> in Hz)	¹³ C (mult)	HMBC (H→C)	COSY (H→H)	¹ H (mult. <i>J</i> in Hz)	¹³ C (mult)	HMBC (H→C)	COSY (H→H)
1		166.8 (s)				166.3 (s)		
2		115.6 (s)				114.1 (s)		
3		157.2 (s)				156.5 (s)		
4	7.09 (d, 8.3)	110.0 (d)	C-6, C-2, C-3	H-5	6.77 (d, 8.4)	105.4 (d)	C-6, C-2	H-5
5	7.57 (t, 8.3)	134.3 (d)	C-7, C-3	H-6, H-4	7.22 (t, 8.4)	130.4 (d)	C-7, C-3	H-6, H-4
6	6.79 (d, 8.3)	114.7 (d)	C-4, C-2, C-7	H-5	6.09 (d, 8.4)	106.5 (d)	C-4, C-2	H-5
7		152.8 (s)				155.3 (s)		
8		142.8 (s)				141.9 (s)		
9		149.1 (s)				150.5 (s)		
10	6.92 (s)	116.2 (d)	C-15, C-12, C-8, C-9		7.12 (s)	123.8 (d)	C-15, C-12, C-10	
11		139.7 (s)				136.2 (s)		
12	6.56 (s)	117.8 (d)	C-15, C-14, C-10, C-8		7.09 (s)	117.8 (d)	C-15, C-10, C-8, C-14	
13		127.7 (s)				129.4 (s)		
14	5.05 (s, 2H)	68.9 (t)	C-12, C-13, C-8, C-1		10.11 (s)	189.4 (d)	C-12, C-13	
15	4.35 (d, 5.7, 2H)	62.6 (t)	C-10, C-12, C-11	HO-15	2.31 (s, 3H)	20.5 (q)	C-12, C-10, C-11	
3a	3.86 (s, 3H)	56.7 (q)	C-3		3.81 (s, 3H)	56.0 (q)	C-3	
HO-9	9.71 (br s)		C-10, C-8, C-9					
HO-15	5.15 (t, 5.7)		C-15, C-11	H-15				

^a Spectra were acquired at 600 MHz (¹H) or 150MHz (¹³C) at 25 °C in DMSO. Chemical shifts (δ) were referenced to TMS in ppm.

Table S2. NMR Spectral Data for 5'-hydroxychlorflavonin (3)^a and chlorflavonin (4)

Position	4				3			
	¹ H (mult. <i>J</i> in Hz)	¹³ C (mult)	HMBC (H→C)	COSY (H→H)	¹ H (mult. <i>J</i> in Hz)	¹³ C (mult)	HMBC (H→C)	COSY (H→H)
2		156.1 (s)				155.4 (s)		
3		139.9 (s)				139.3 (s)		
4		179.1 (s)				178.9 (s)		
5		157.0 (s)				157.4 (s)		
6	6.64 (s)	96.3 (d)	C-10, C-8, C-5, C-7		6.54 (s)	95.6 (d)	C-10, C-8, C-5, C-7	
7		158.7 (s)				158.9 (s)		
8		128.9 (s)				129.0 (s)		
9		149.2 (s)				149.2 (s)		
10		105.7 (s)				105.4 (s)		
1'		120.3 (s)				122.4 (s)		
2'		151.4 (s)				144.1 (s)		
3'		122.1 (s)				120.4 (s)		
4'	7.59 (d, 8.0)	119.2 (d)	C-3', C-6', C-2'	H-5'	7.11 (d, 2.8)	119.2 (d)	C-6', C-3', C-2', C-5'	H-6'
5'	7.02 (t, 8.0)	120.7 (d)	C-1', C-3'	H-6', H-4'		150.5 (s)		
6'	7.42 (d, 8.0)	130.0 (d)	C-4', C-2, C-2'	H-5'	7.05 (d, 2.8)	115.6 (d)	C-4', C-2, C-2'	H-4'
3a	3.71 (s, 3H)	57.1 (q)	C-3		3.84 (s, 3H)	60.3 (q)	C-3	
7a	3.92 (s, 3H)	60.6 (q)	C-7		3.98 (s, 3H)	56.0 (q)	C-7	
8a	3.70 (s, 3H)	61.4 (q)	C-8		3.78 (s, 3H)	60.7 (q)	C-8	
HO-5	12.42 (br s)		C-6, C-10, C-5		12.43 (br s)		C-6, C-10, C-5	
HO-2'	10.08 (br s)		C-3', C-1', C-2'		8.19 (br s)		C-3', C-1', C-2'	
HO-5'					8.63 (br s)		C-5', C-4', C-5'	

^a Spectra were acquired at 600 MHz (¹H) or 150MHz (¹³C) at 25 °C in DMSO (**11**) and in (CD₃)₂CO (**12**). Chemical shifts (δ) were referenced to TMS in ppm.

Figure S1 ¹H NMR (600 MHz, DMSO) spectrum for barceloneic lactone B (1)

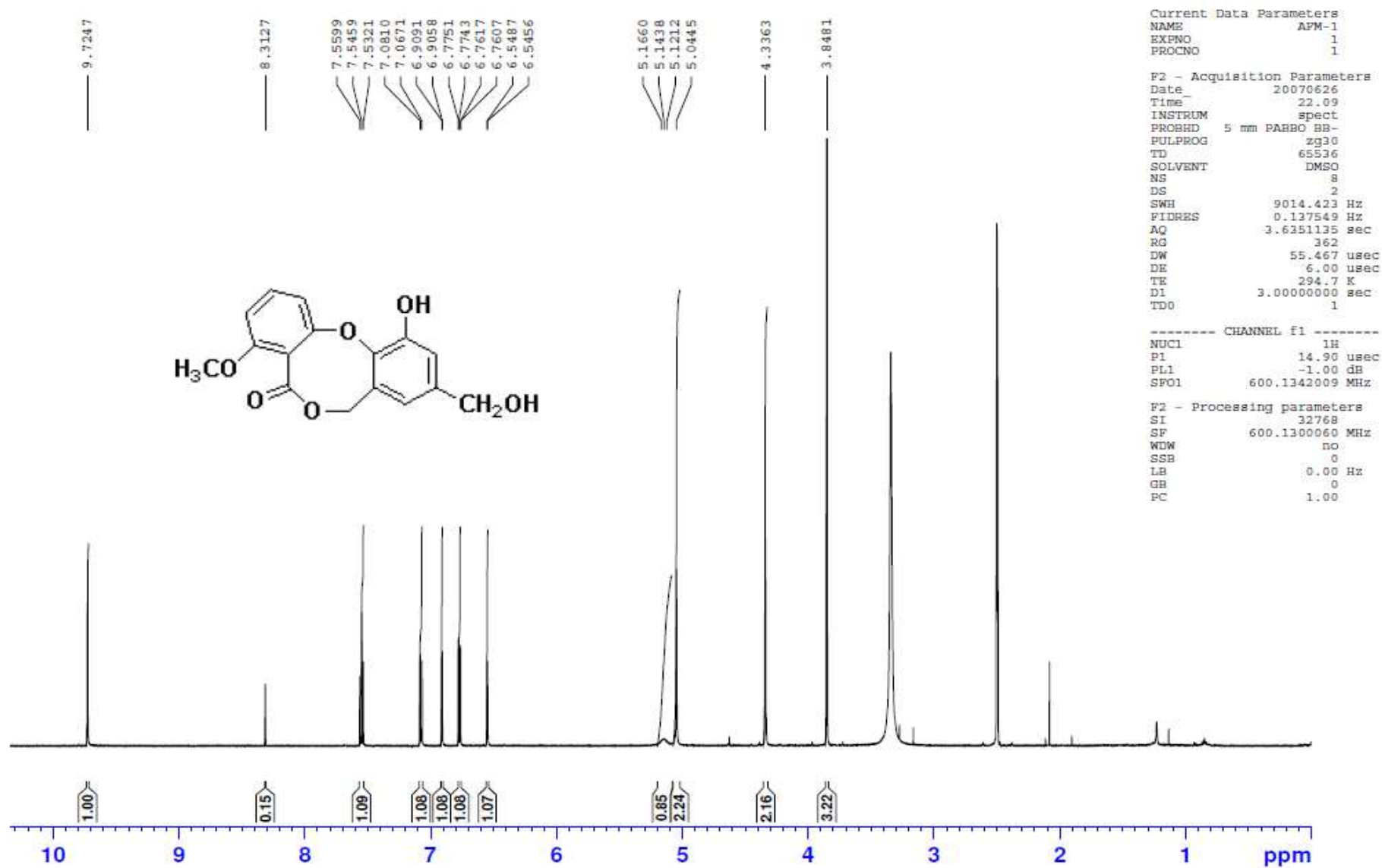


Figure S2 ^{13}C NMR (150 MHz, DMSO) spectrum for barceloneic lactone B (1)

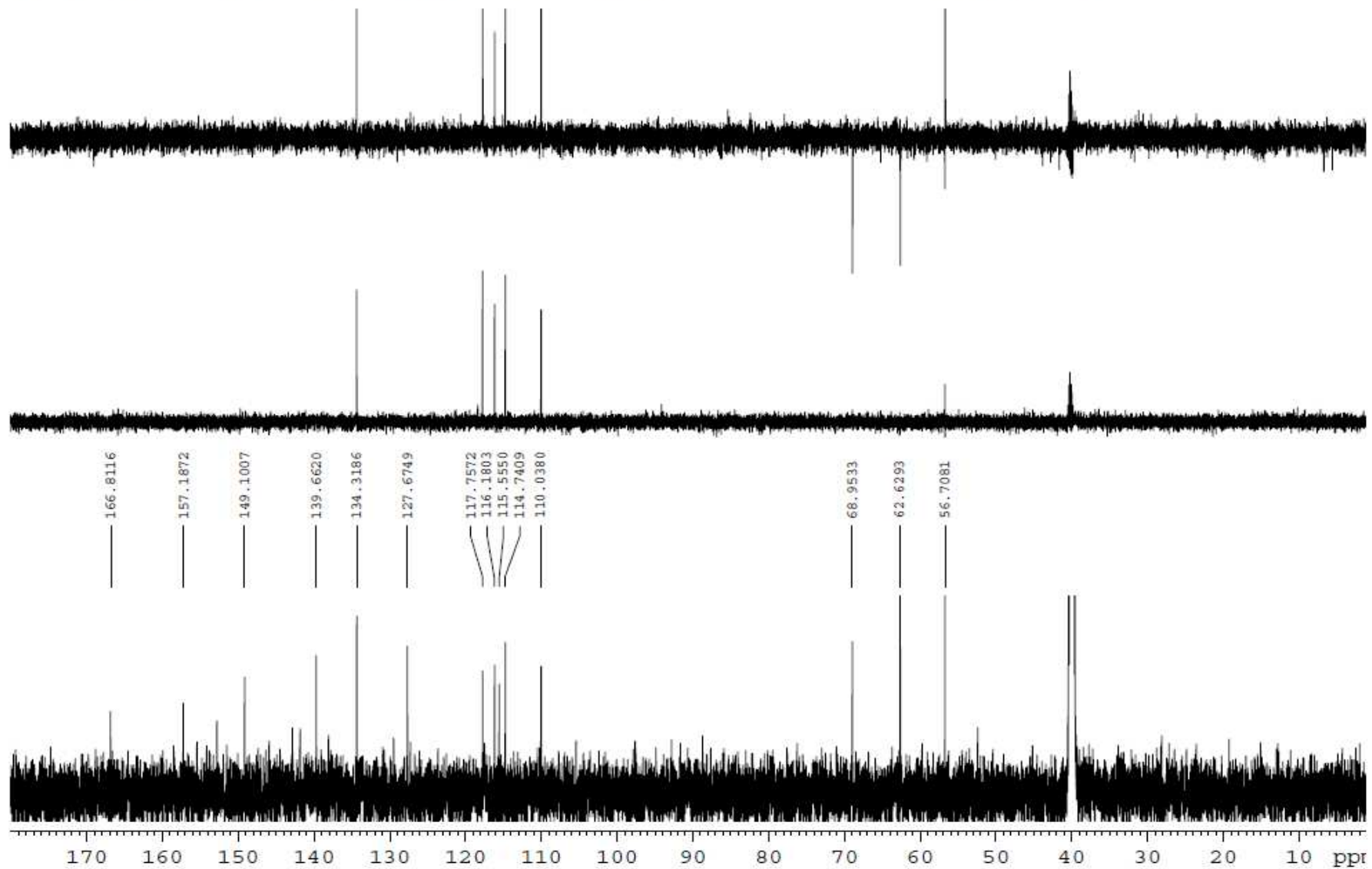


Figure S3 ¹H NMR (600 MHz, DMSO) spectrum for barceloneic acids C (2)

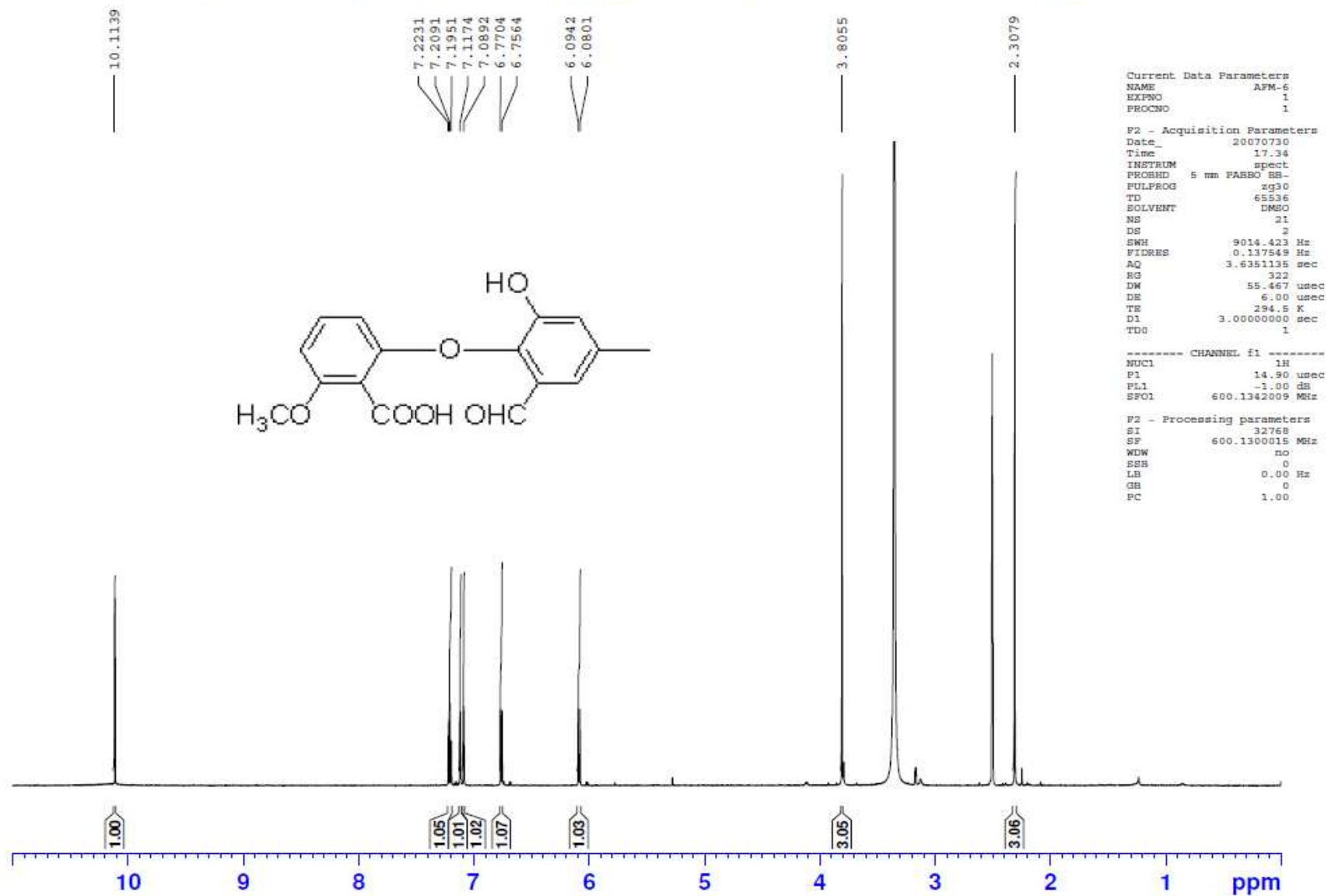


Figure S4 ^{13}C NMR (150 MHz, DMSO) spectrum for barceloneic acids C (2)

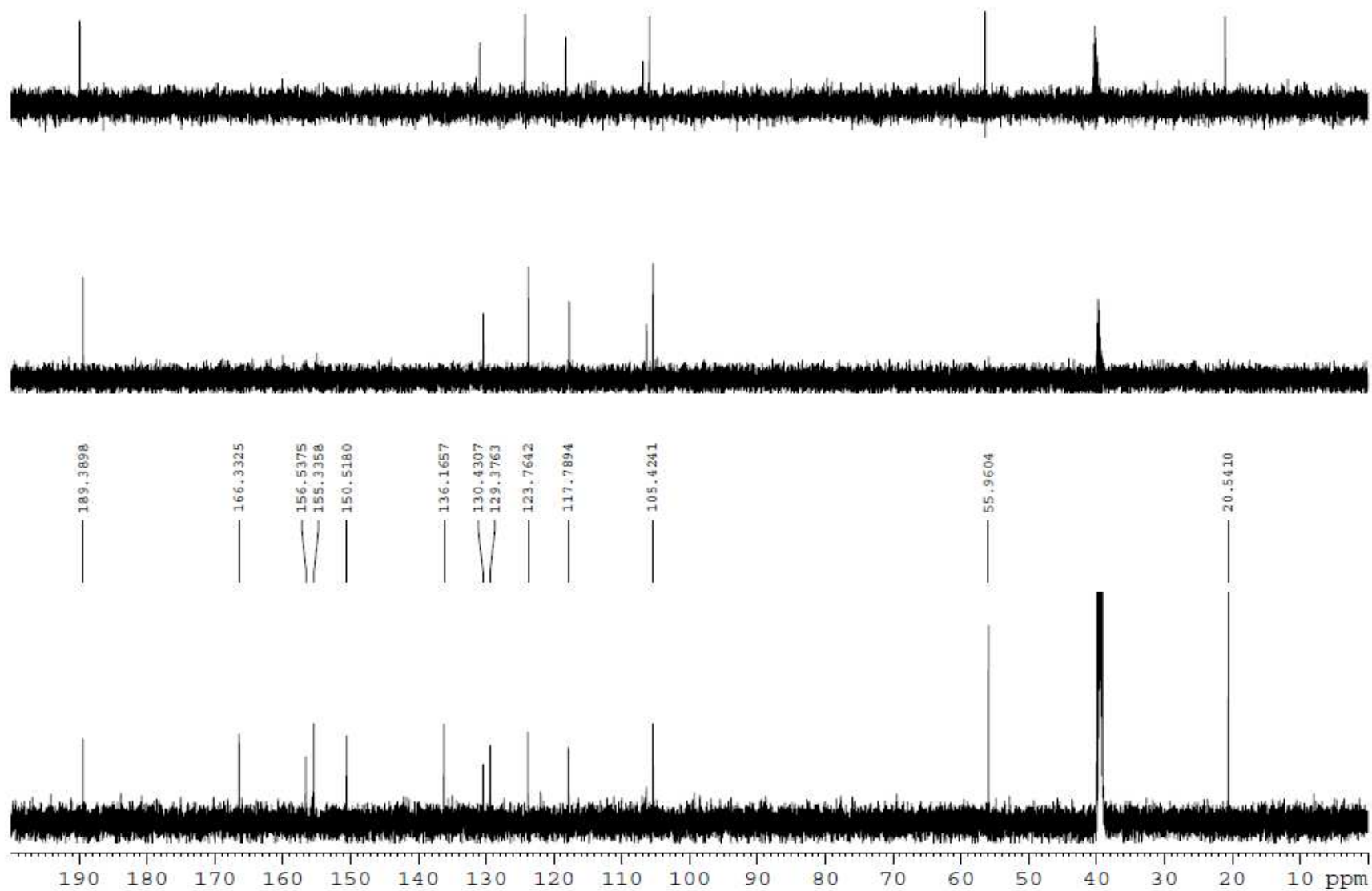


Figure S5 ¹H NMR (600 MHz, (CD₃)₂CO) spectrum for 5'-hydroxychlorflavonin (3)

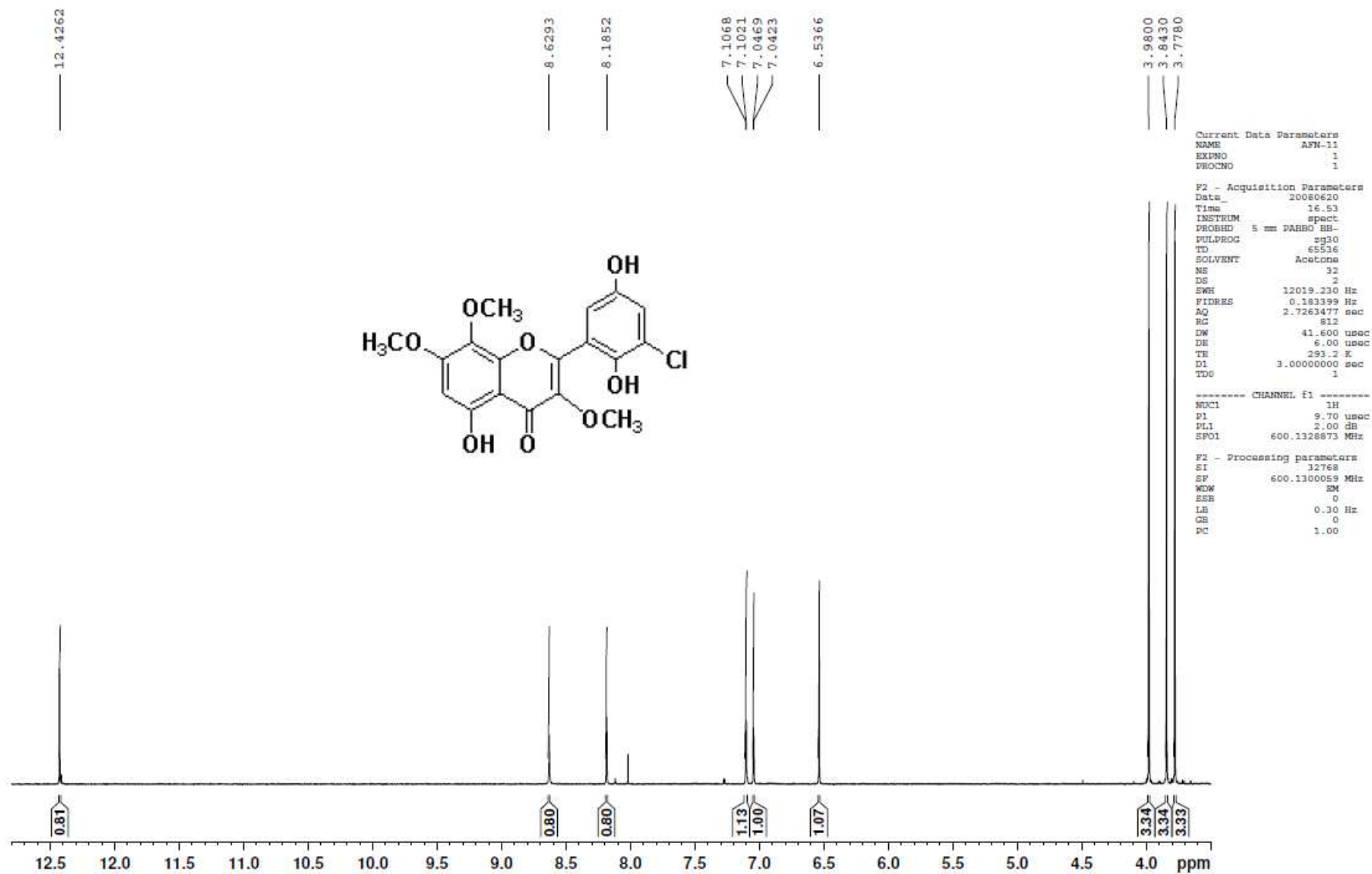


Figure S6 ¹³C NMR (150 MHz, (CD₃)₂CO) spectrum for 5'-hydroxychlorflavonin (3)

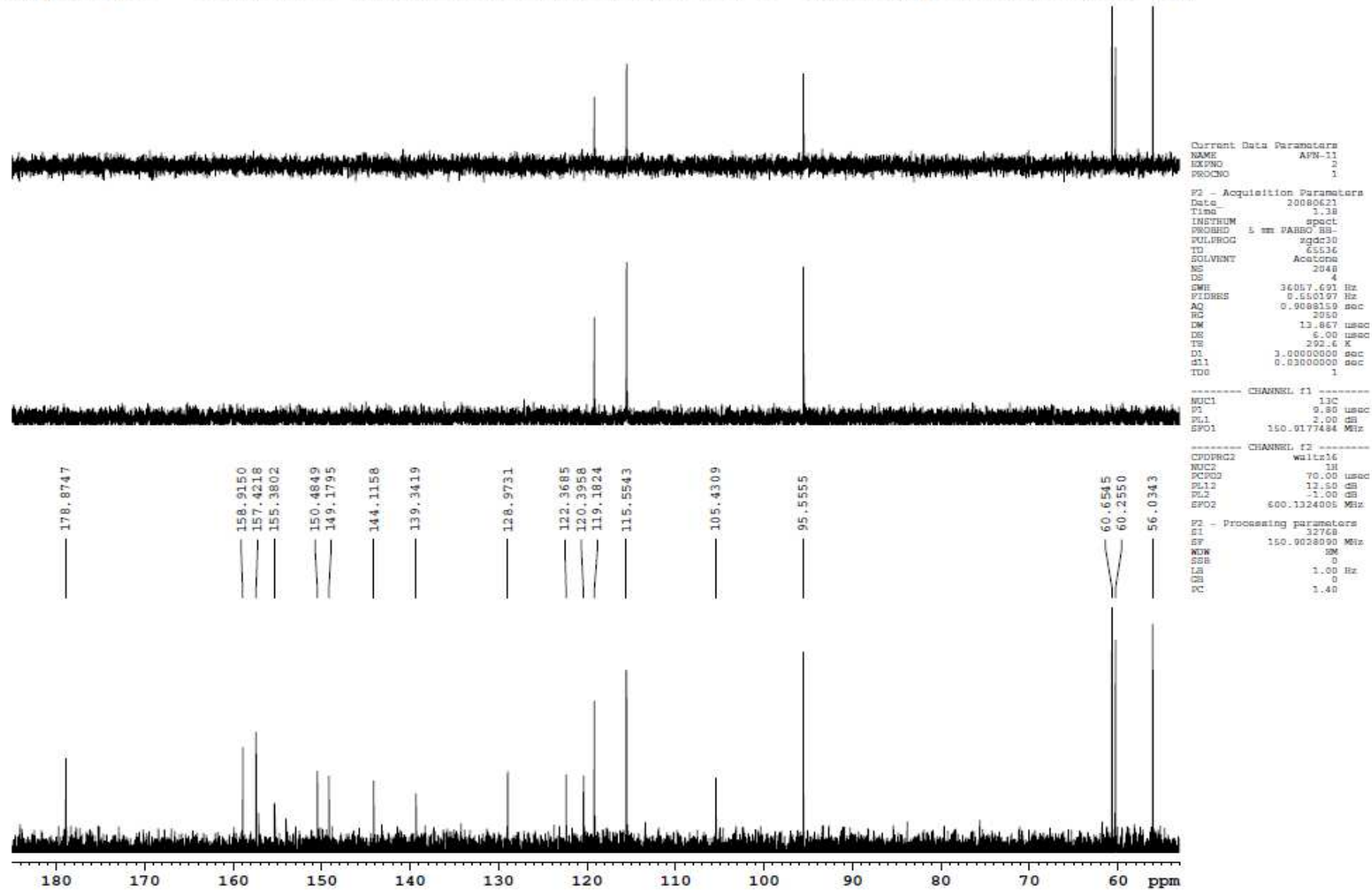


Figure S7 ¹H NMR (600 MHz, DMSO) spectrum for chlorflavonin (4)

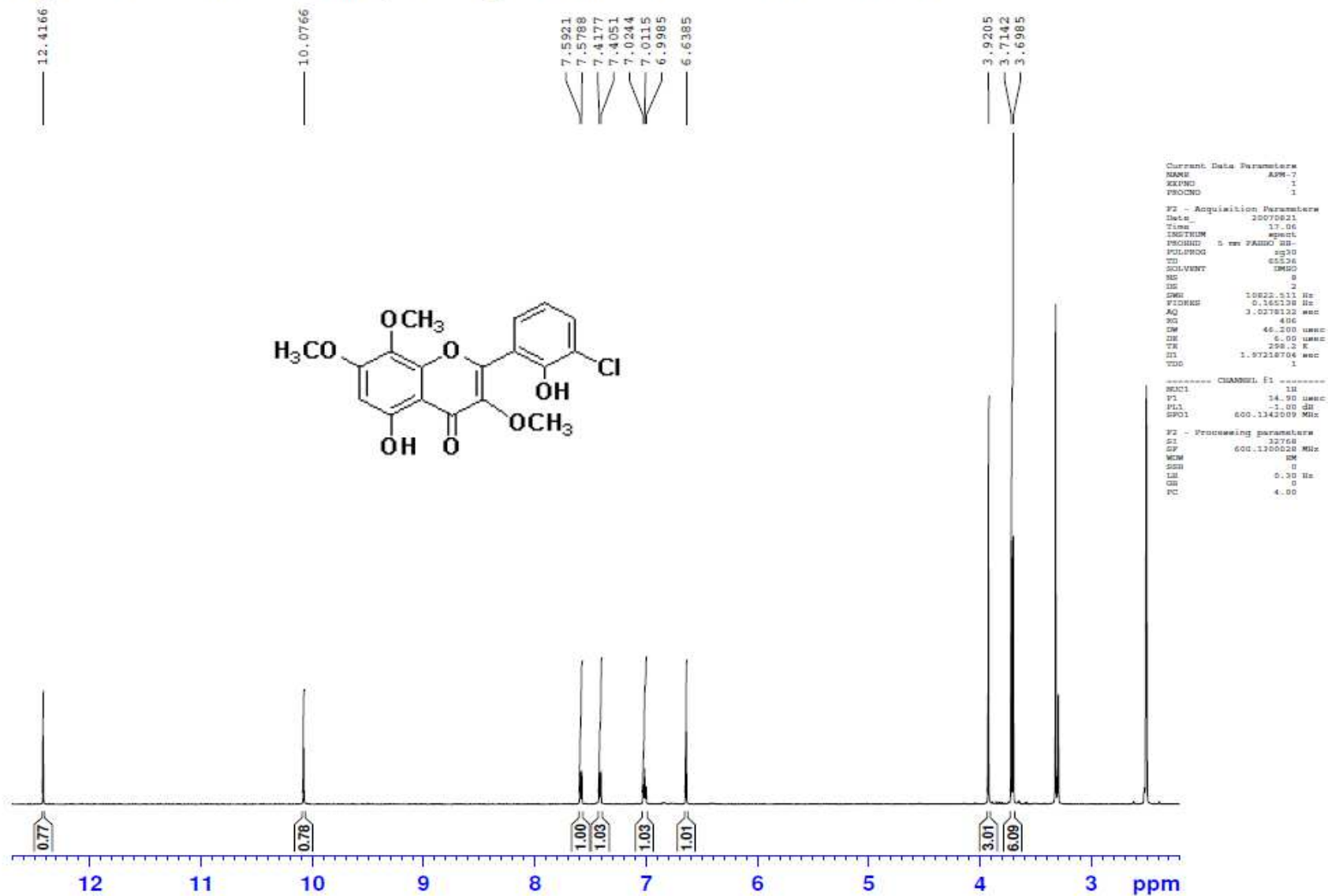
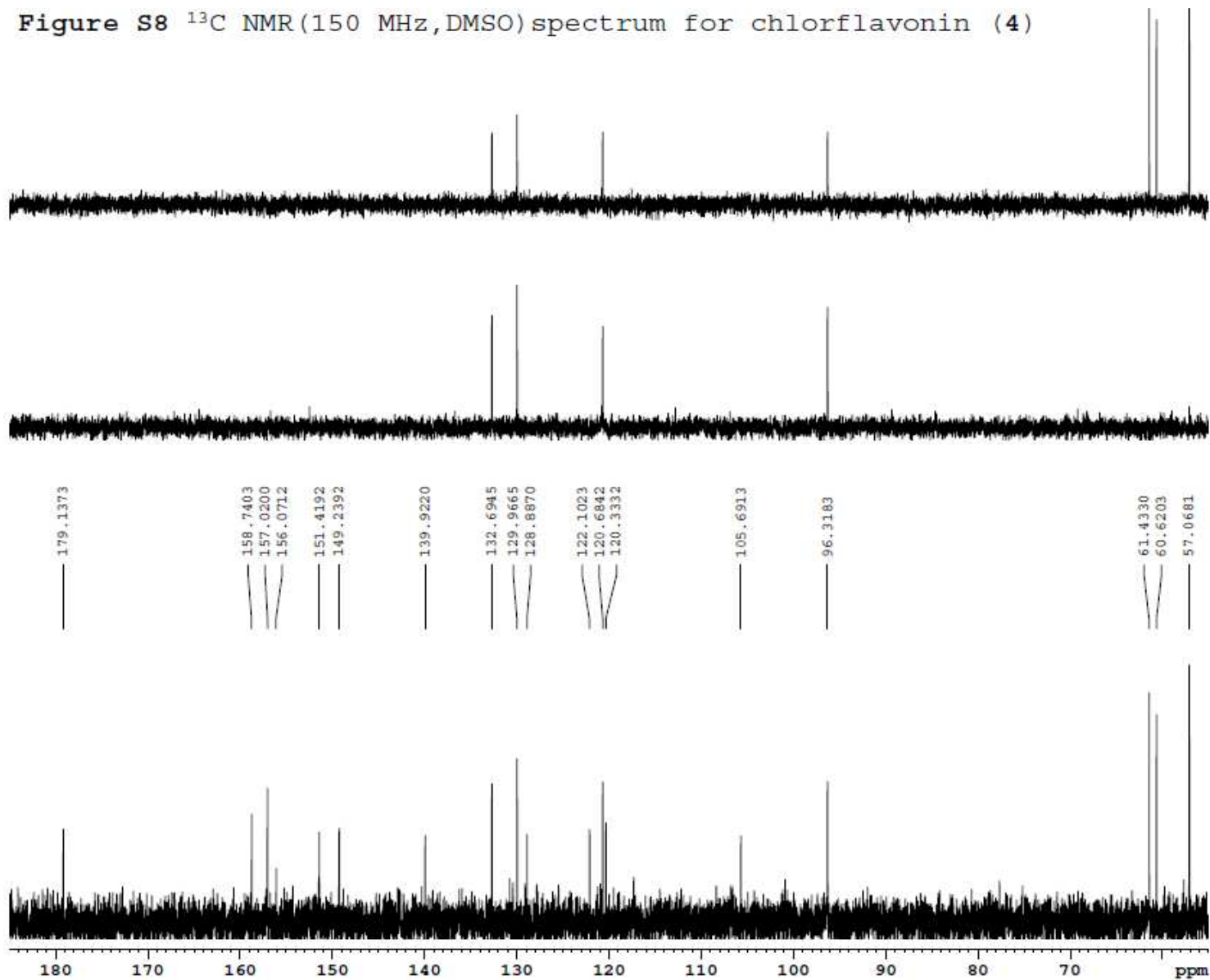


Figure S8 ¹³C NMR (150 MHz, DMSO) spectrum for chlorflavonin (4)



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Figure S9 MS spectrum for 5'-hydroxychlorflavonin (**3**)

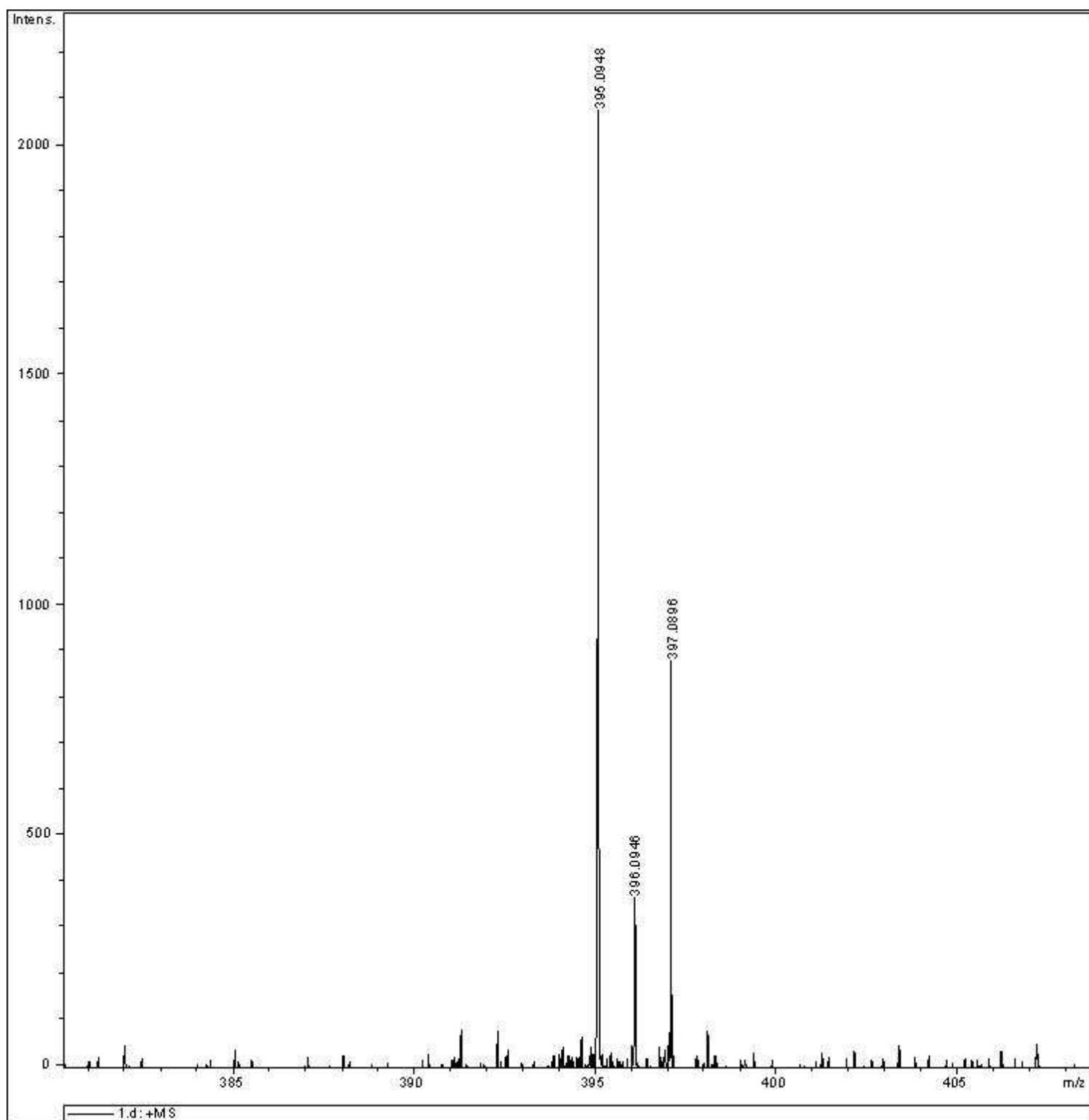


Figure S10 MS spectrum for chlorflavonin (4)

Display Report

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Acquisition Parameter

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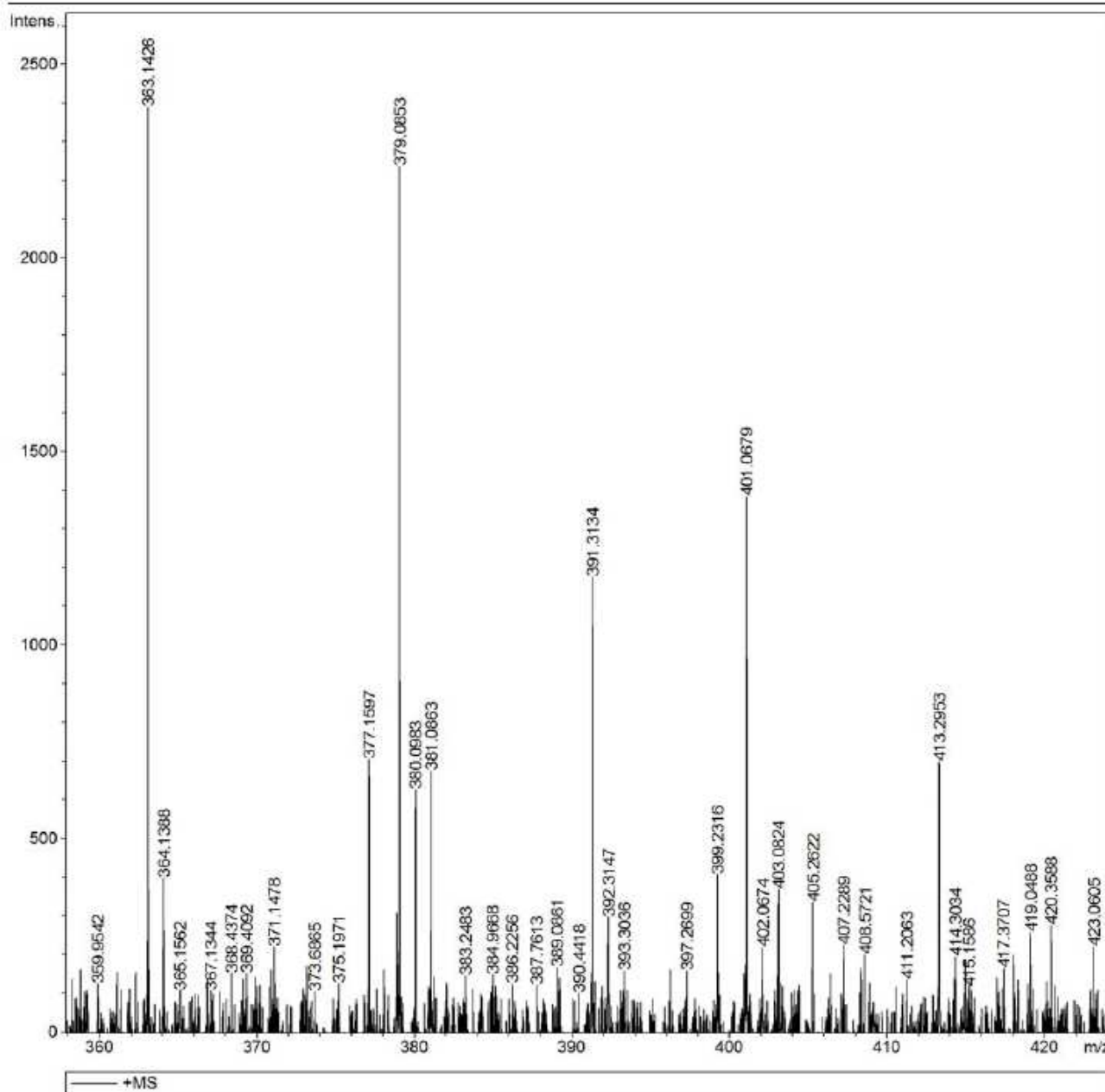


Figure S11 Structure of secondary metabolites from the strain AF119

