

Supplementary

Enhyprazinones A and B, Pyrazinone Natural Products from a Marine-derived Myxobacterium
Enhygromyxa sp.

Fan Zhang,¹ Doug R. Braun,¹ Scott R. Rajski,¹ Don DeMaria,² and Tim S. Bugni^{1,*}

¹Pharmaceutical Sciences Division, University of Wisconsin–Madison, Madison, Wisconsin
53705, United States

²Sea Samples, 369 Westshore Drive, Summerland Key, FL 33042, United States

* To whom correspondence should be addressed. Tel.: 1-608-263-2519. E-mail:

tim.bugni@wisc.edu.

Supporting Information Table of Contents

<u>Contents</u>	<u>Page</u>
1) Figure S1. ^1H NMR spectrum of enhyppyrizinone A (1 ; 600 MHz, $\text{DMSO-}d_6$).....	3
2) Figure S2. ^{13}C NMR spectrum of enhyppyrizinone A (1 ; 125 MHz, $\text{DMSO-}d_6$).....	4
3) Figure S3. gCOSY spectrum of enhyppyrizinone A (1 ; 600 MHz, $\text{DMSO-}d_6$).....	5
4) Figure S4. gHSQC spectrum of enhyppyrizinone A (1 ; 600 MHz, $\text{DMSO-}d_6$).....	6
5) Figure S5. gHMBC spectrum of enhyppyrizinone A (1 ; 600 MHz, $\text{DMSO-}d_6$).....	7
6) Figure S6. $^1\text{H-}^{15}\text{N}$ HMBC spectrum of enhyppyrizinone A (1 ; 600 MHz, $\text{DMSO-}d_6$).....	8
7) Figure S7. Positive ion HRESIMS of enhyppyrizinone A (1).....	9
8) Figure S8. ^1H NMR spectrum of enhyppyrizinone B (2 ; 500 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1)...	10
9) Figure S9. ^{13}C NMR spectrum of enhyppyrizinone B (2 ; 125 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1)...	11
10) Figure S10. gCOSY spectrum of enhyppyrizinone B (2 ; 500 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1)...	12
11) Figure S11. gHSQC spectrum of enhyppyrizinone B (2 ; 500 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1)...	13
12) Figure S12. gHMBC spectrum of enhyppyrizinone B (2 ; 500 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1)...	14
13) Figure S13. $^1\text{H-}^{15}\text{N}$ HMBC Spectrum of enhyppyrizinone B (2 ; 500 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1).....	15
14) Figure S14. ^1H NMR spectrum of enhyppyrizinone B (2 ; 500 MHz, $\text{DMSO-}d_6$).....	16
15) Figure S15. ^{13}C NMR spectrum of enhyppyrizinone B (2 ; 125 MHz, $\text{DMSO-}d_6$).....	17
16) Figure S16. gCOSY spectrum of enhyppyrizinone B (2 ; 500 MHz, $\text{DMSO-}d_6$).....	18
17) Figure S17. gHSQC spectrum of enhyppyrizinone B (2 ; 500 MHz, $\text{DMSO-}d_6$).....	19
18) Figure S18. gHMBC spectrum of enhyppyrizinone B (2 ; 500 MHz, $\text{DMSO-}d_6$).....	20
19) Figure S19. $^1\text{H-}^{15}\text{N}$ HMBC spectrum of enhyppyrizinone B (2 ; 500 MHz, $\text{DMSO-}d_6$).....	21
20) Figure S20. Positive ion HRESIMS of enhyppyrizinone B (2).....	22
21) Table S1. ^1H and ^{13}C NMR data for enhyppyrizinone B (2) (500 MHz for ^1H , 125 MHz for ^{13}C , $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1)	23

Figure S1. ^1H NMR spectrum of enhyprazinone A (**1**; 600 MHz, $\text{DMSO-}d_6$)

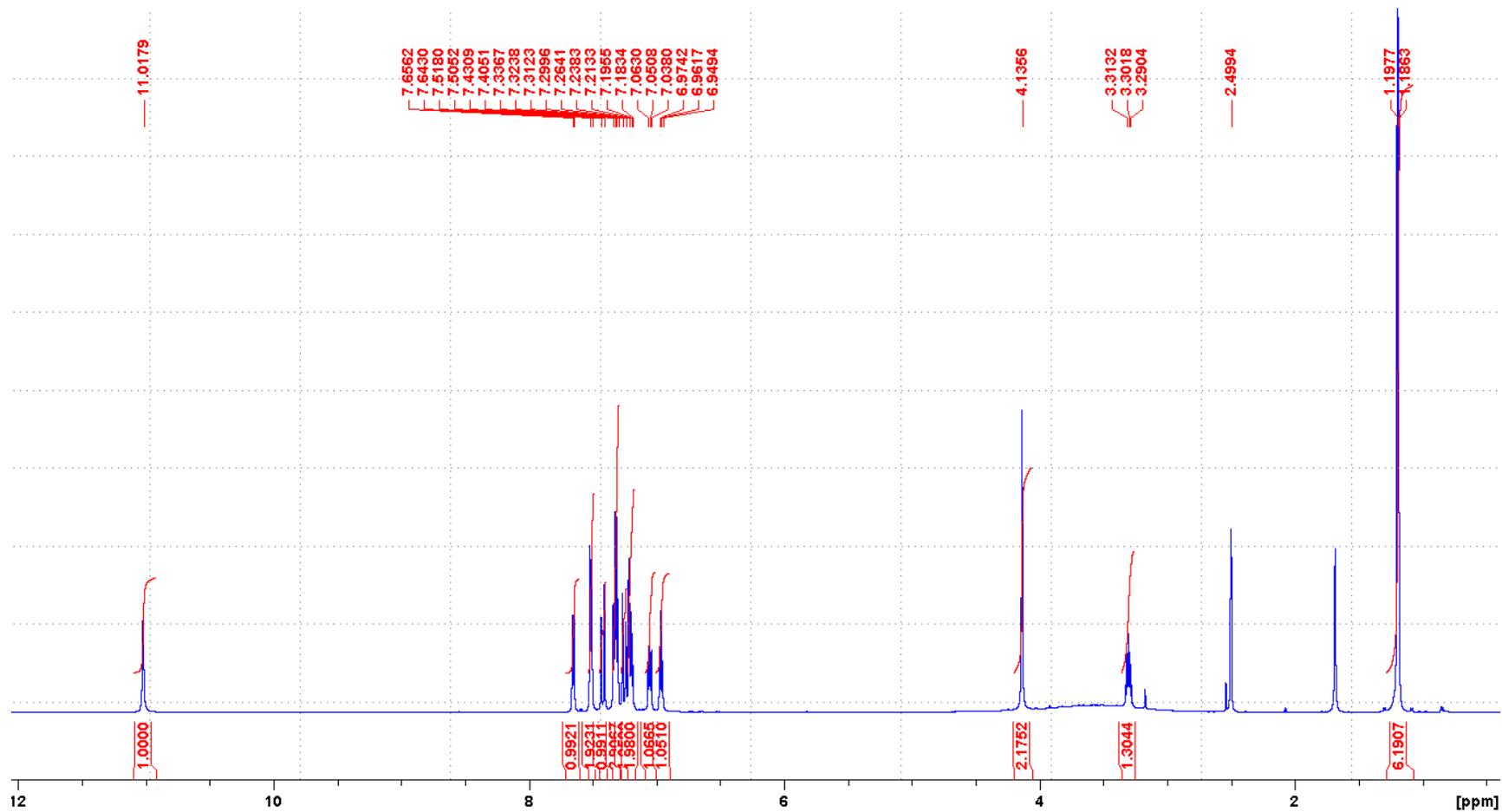


Figure S2. ^{13}C NMR spectrum of enhyppyrizinone A (**1**; 125 MHz, $\text{DMSO-}d_6$)

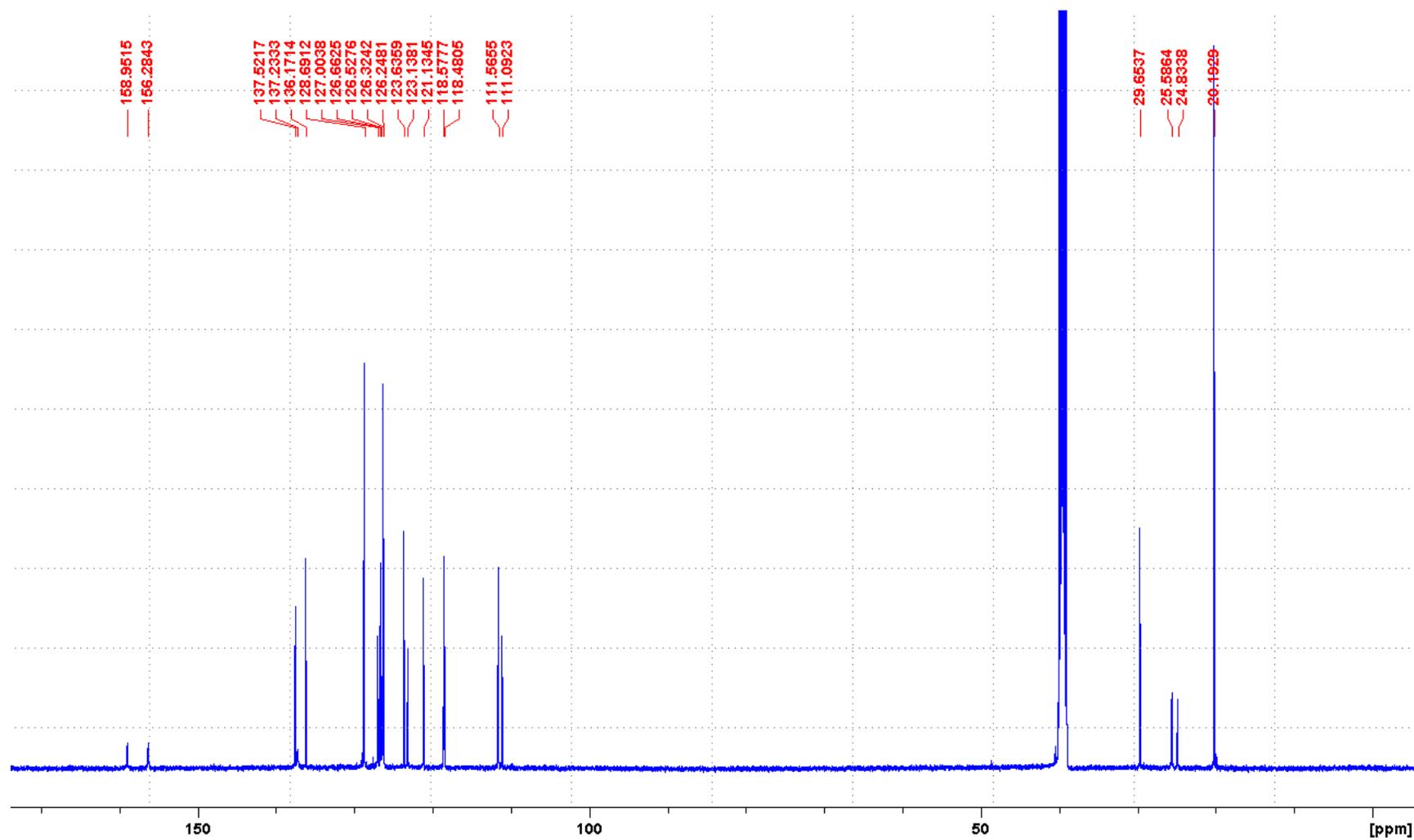


Figure S3. gCOSY spectrum of enhyprazinone A (**1**; 600 MHz, DMSO-*d*₆)

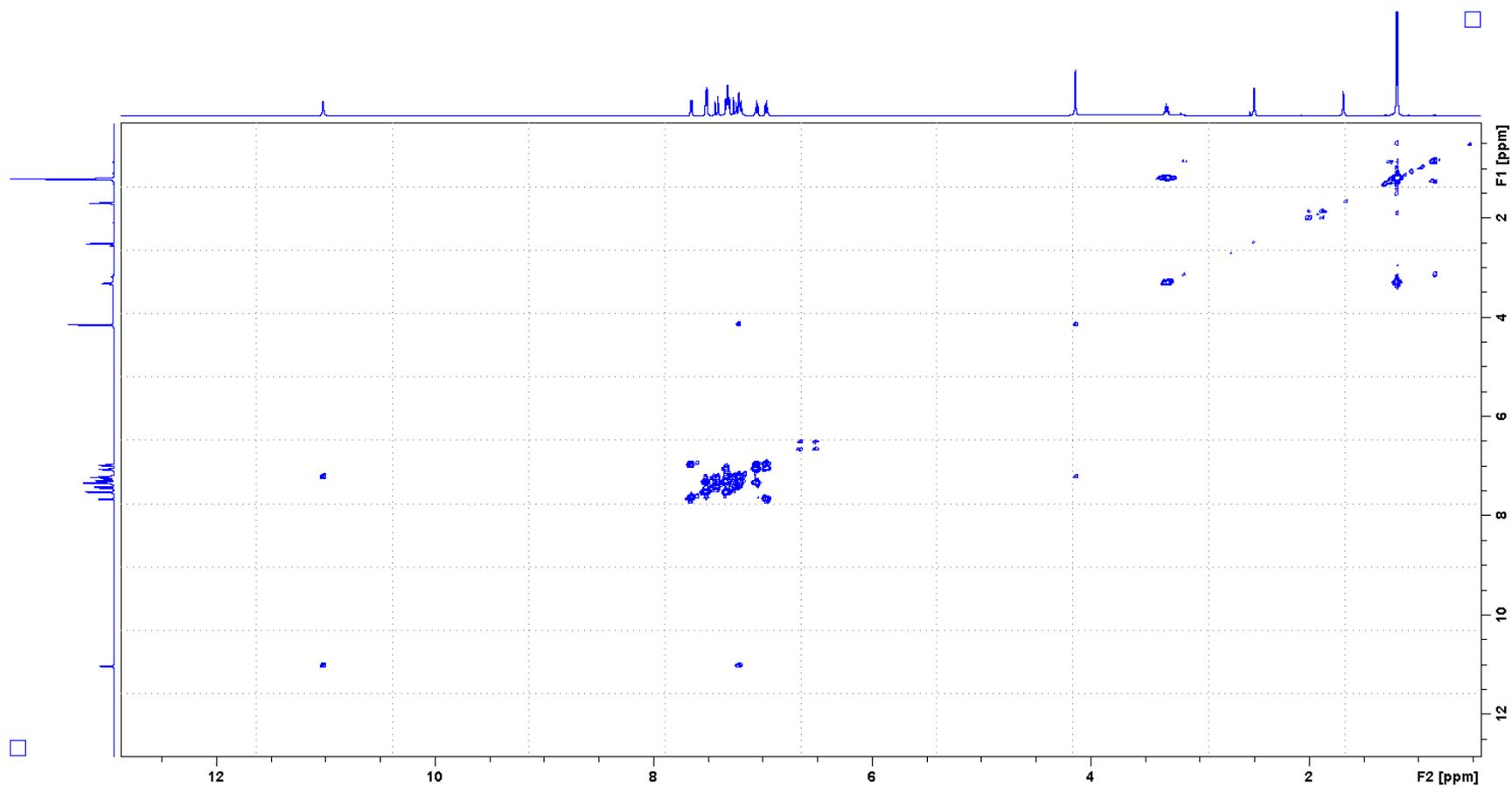


Figure S4. gHSQC spectrum of enhyprazinone A (**1**; 600 MHz, DMSO- d_6)

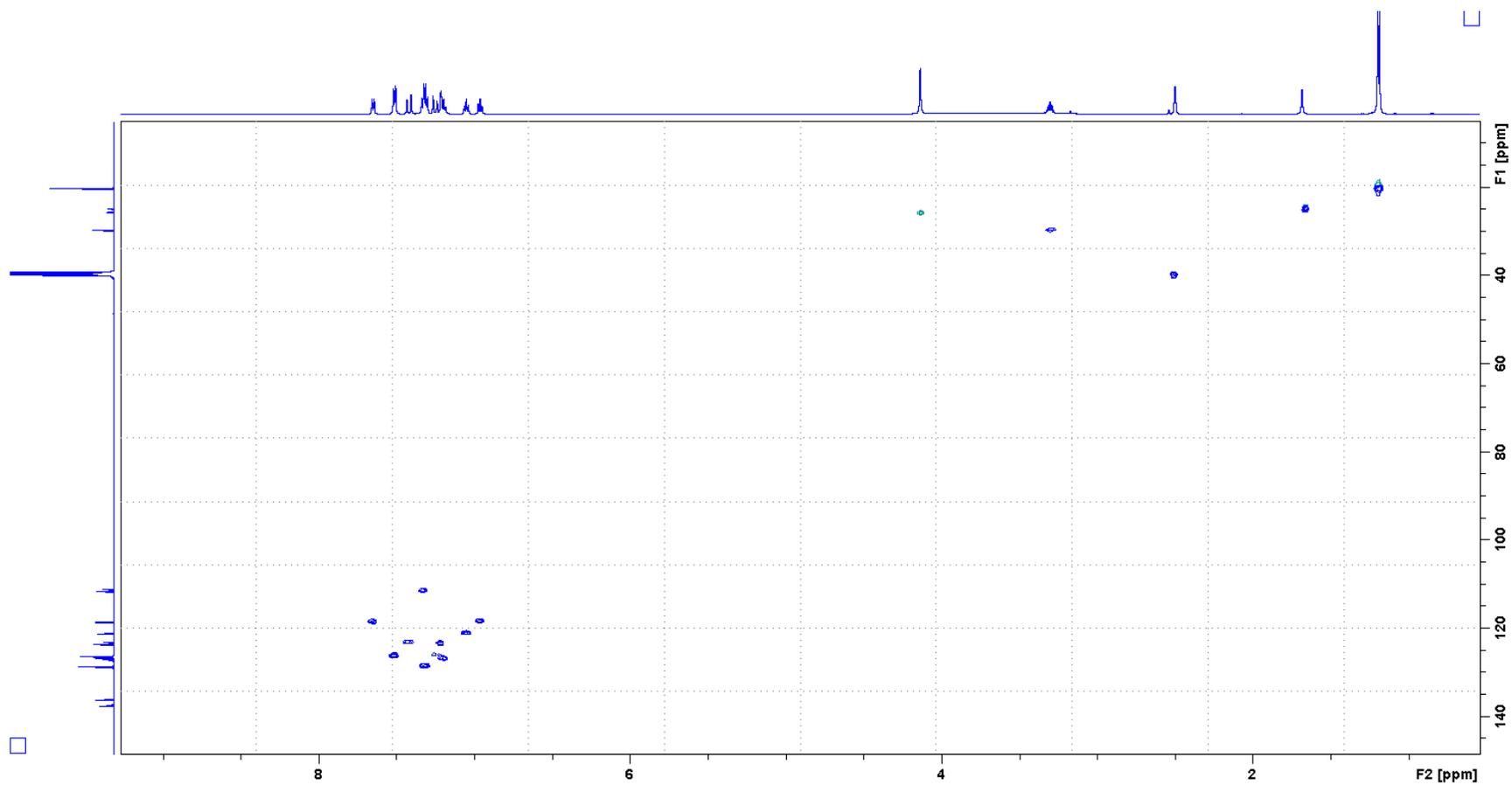


Figure S5. gHMBC spectrum of enhyprazinone A (**1**; 600 MHz, DMSO-*d*₆)

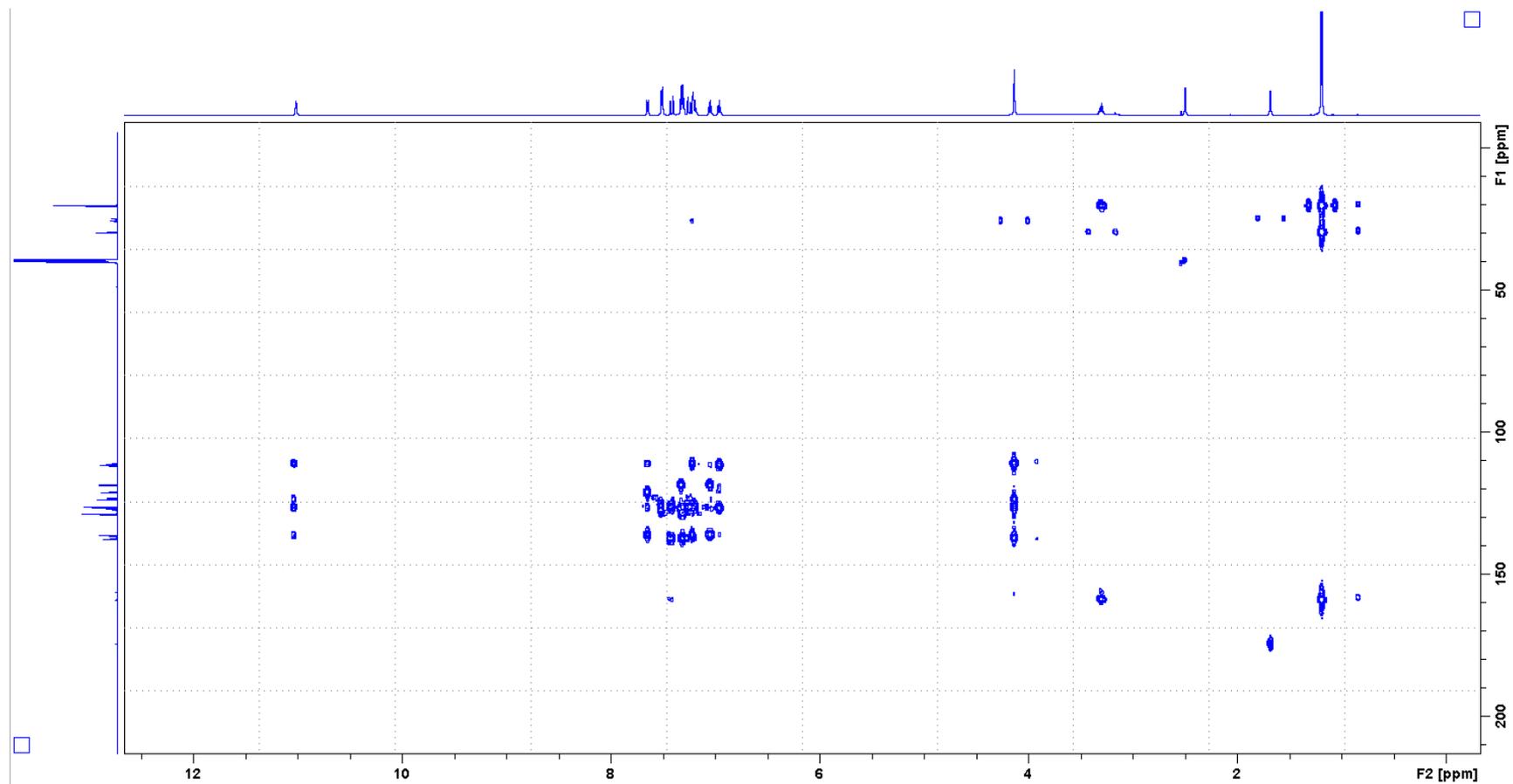


Figure S6. ^1H - ^{15}N HMBC spectrum of enhyprazinone A (**1**; 600 MHz, $\text{DMSO-}d_6$)

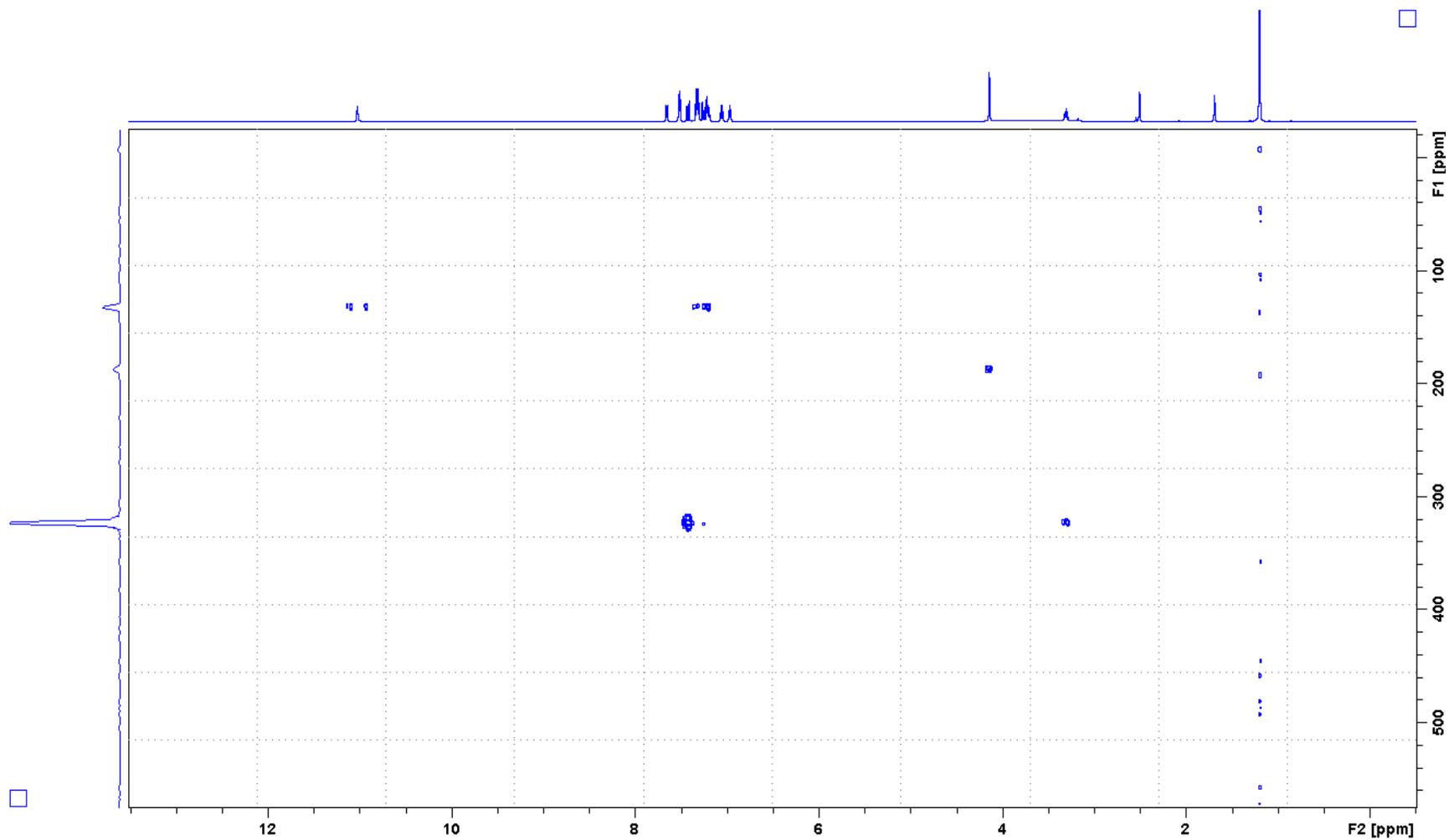


Figure S7. Positive ion HRESIMS of enhyprazinone A (1)

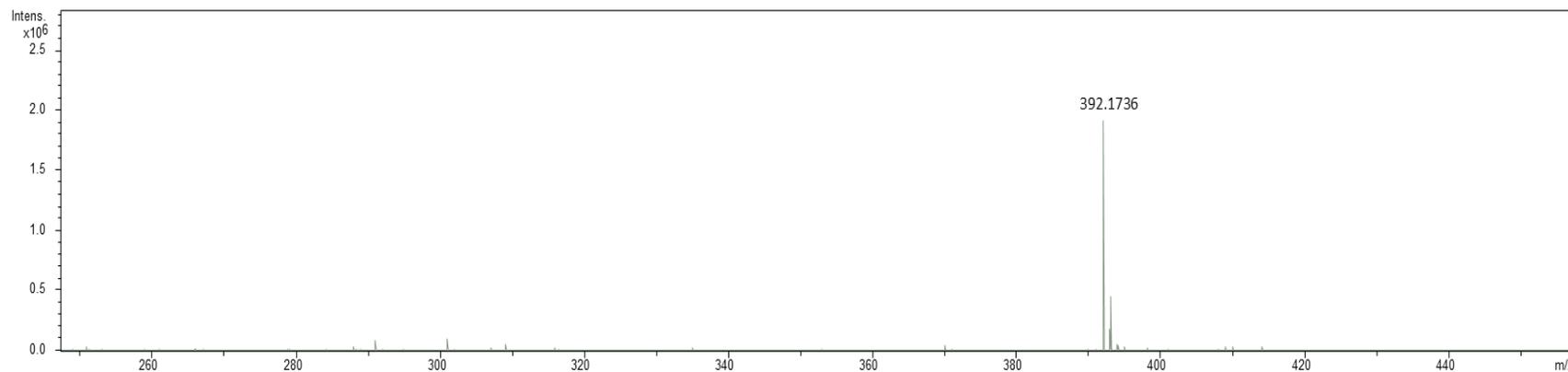


Figure S8. ^1H NMR spectrum of enhyprazinone B (**2**; 500 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1)

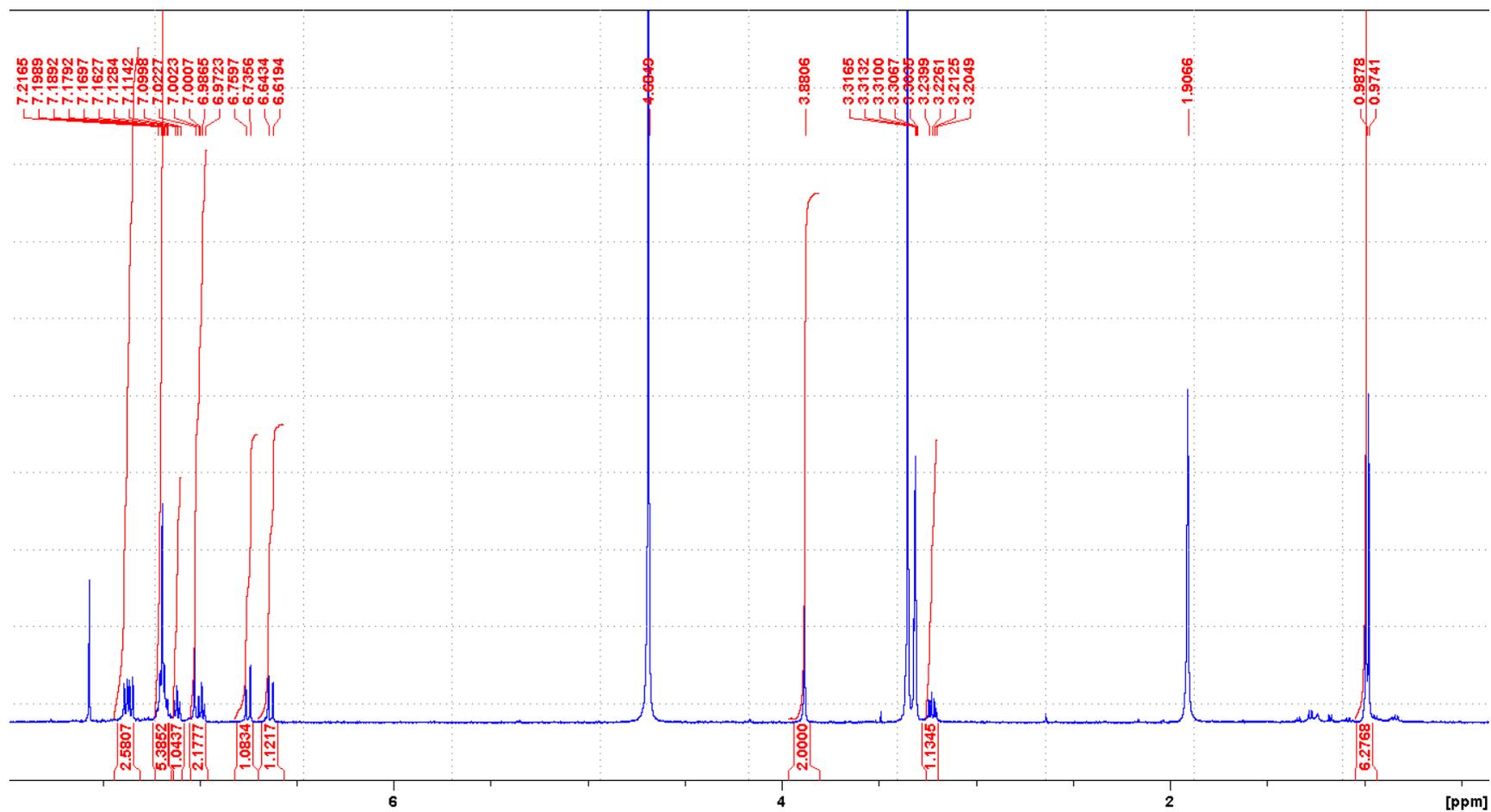


Figure S9. ^{13}C NMR spectrum of enhyppyrizinone B (**2**; 125 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1)

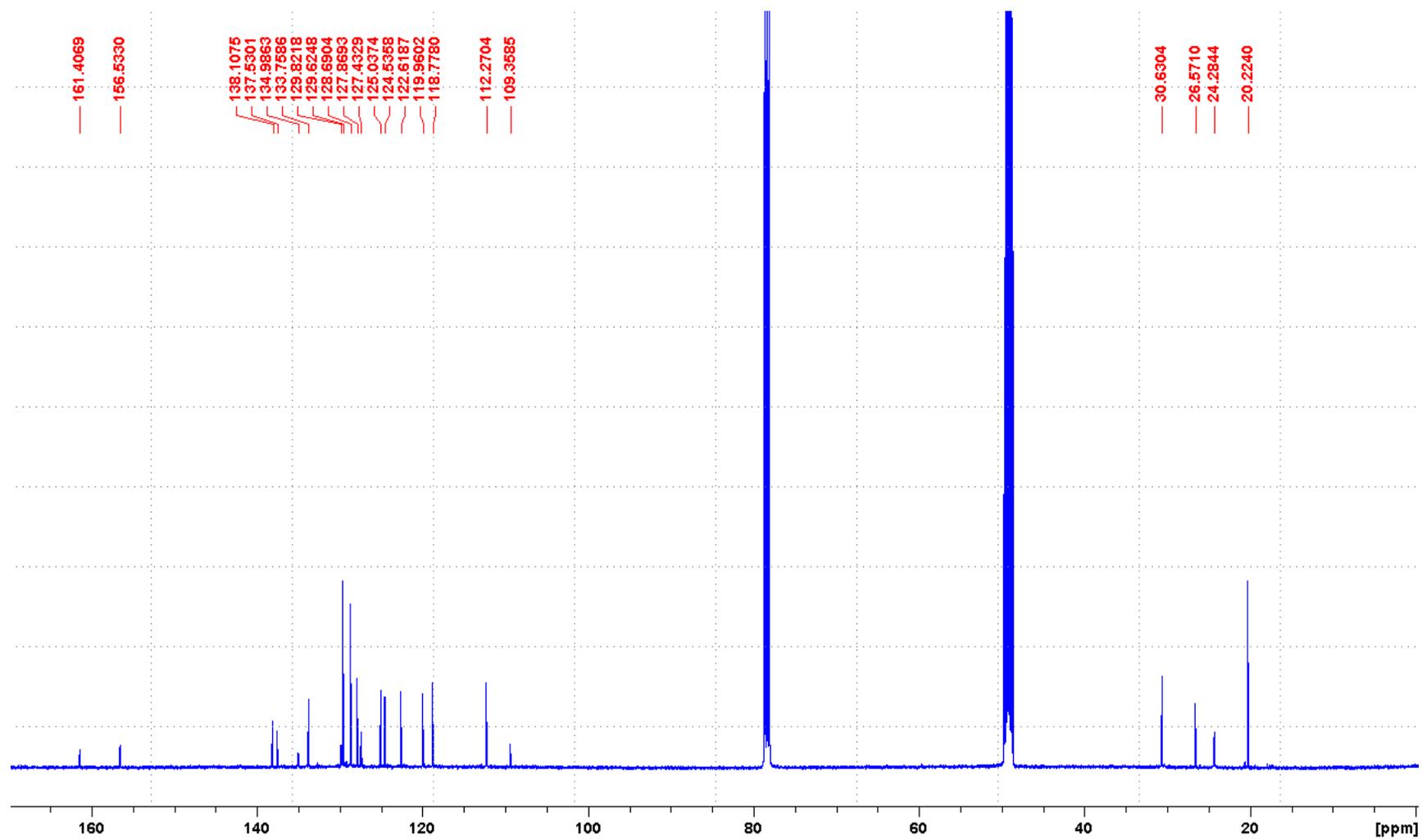


Figure S10. gCOSY spectrum of enhyprazinone B (**2**; 500 MHz, CDCl₃/CD₃OD 1:1)

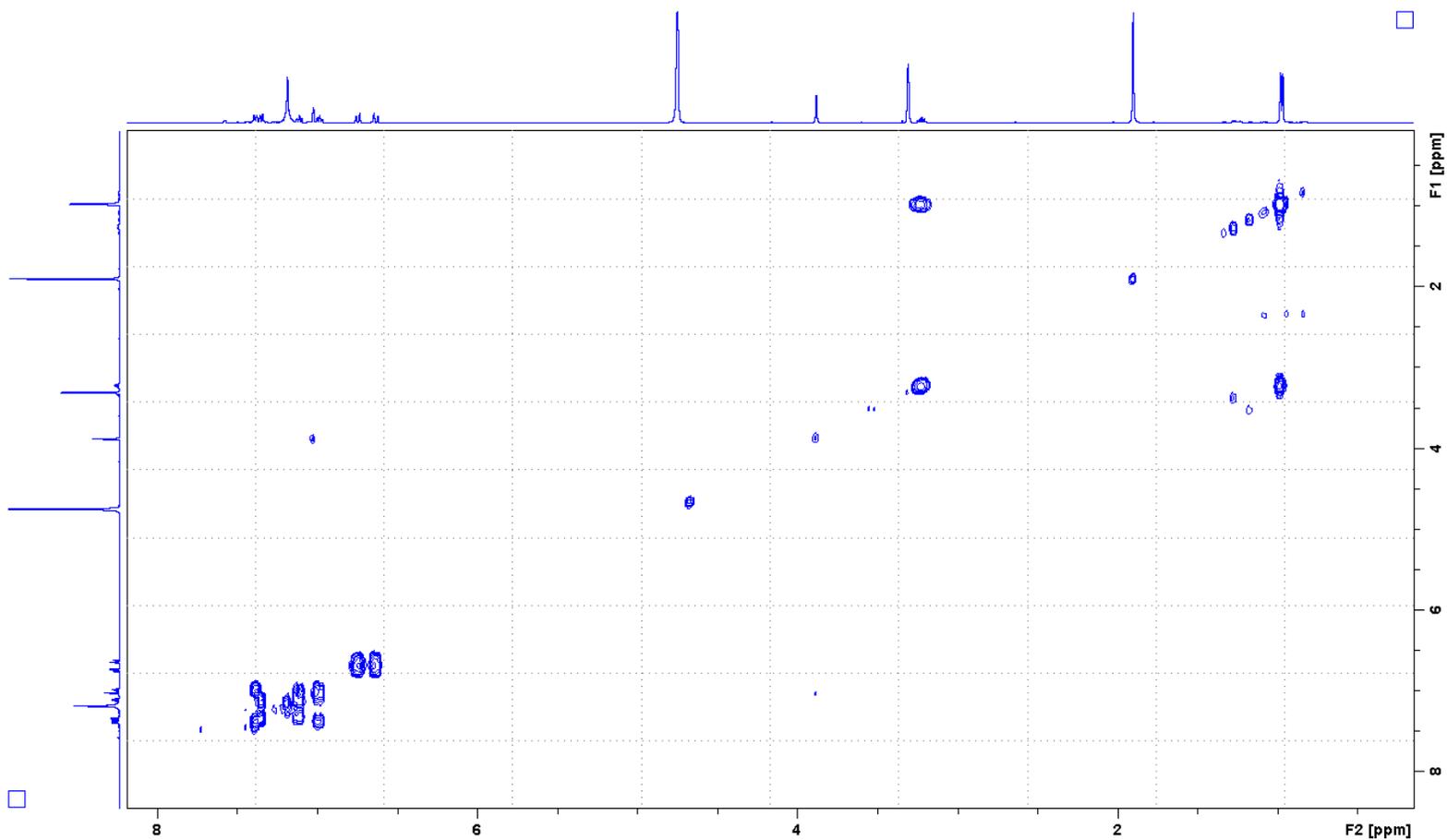


Figure S11. gHSQC spectrum of enhyprazinone B (**2**; 500 MHz, CDCl₃/CD₃OD 1:1)

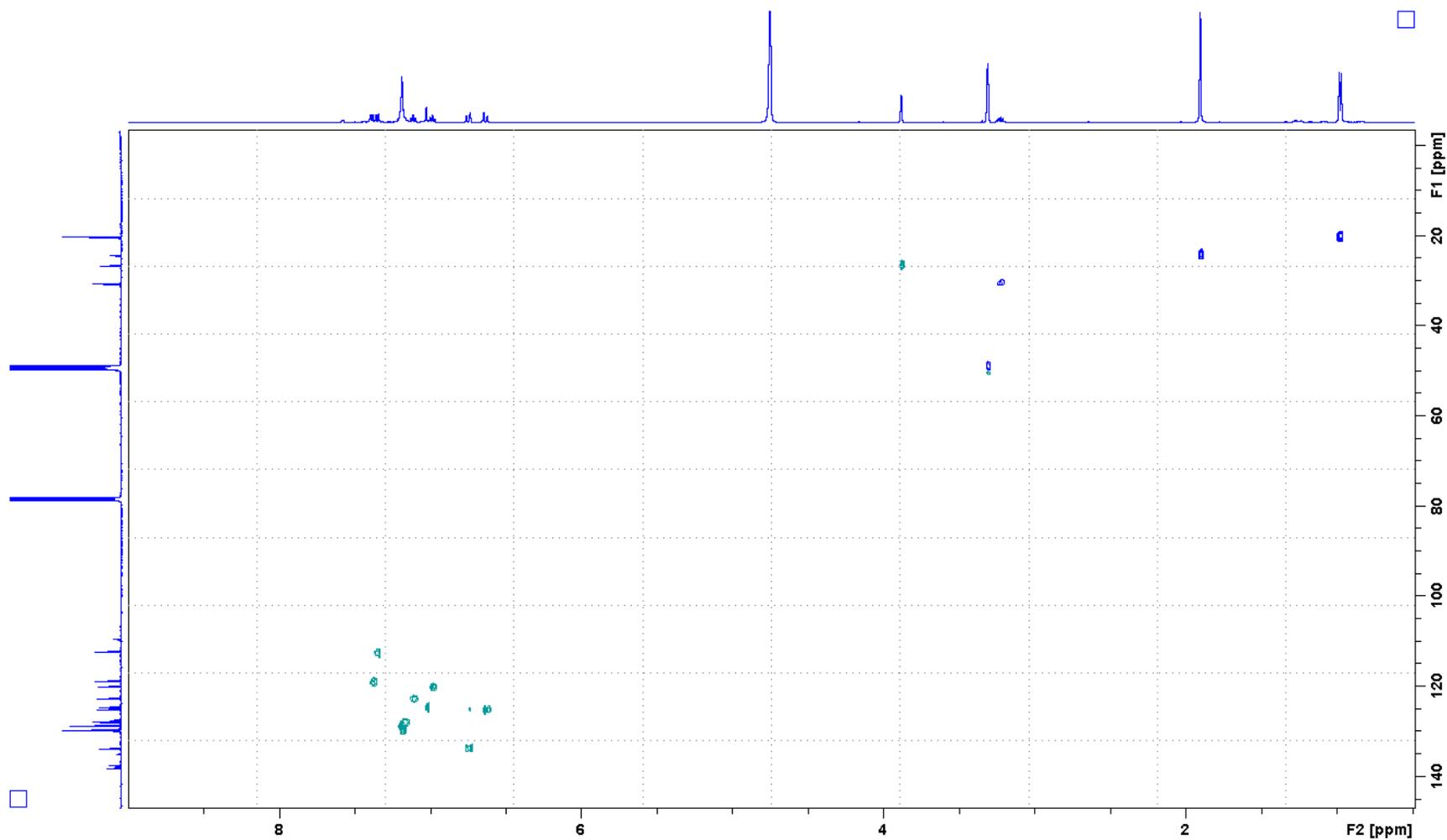


Figure S12. gHMBC spectrum of enhyprazinone B (**2**; 500 MHz, CDCl₃/CD₃OD 1:1)

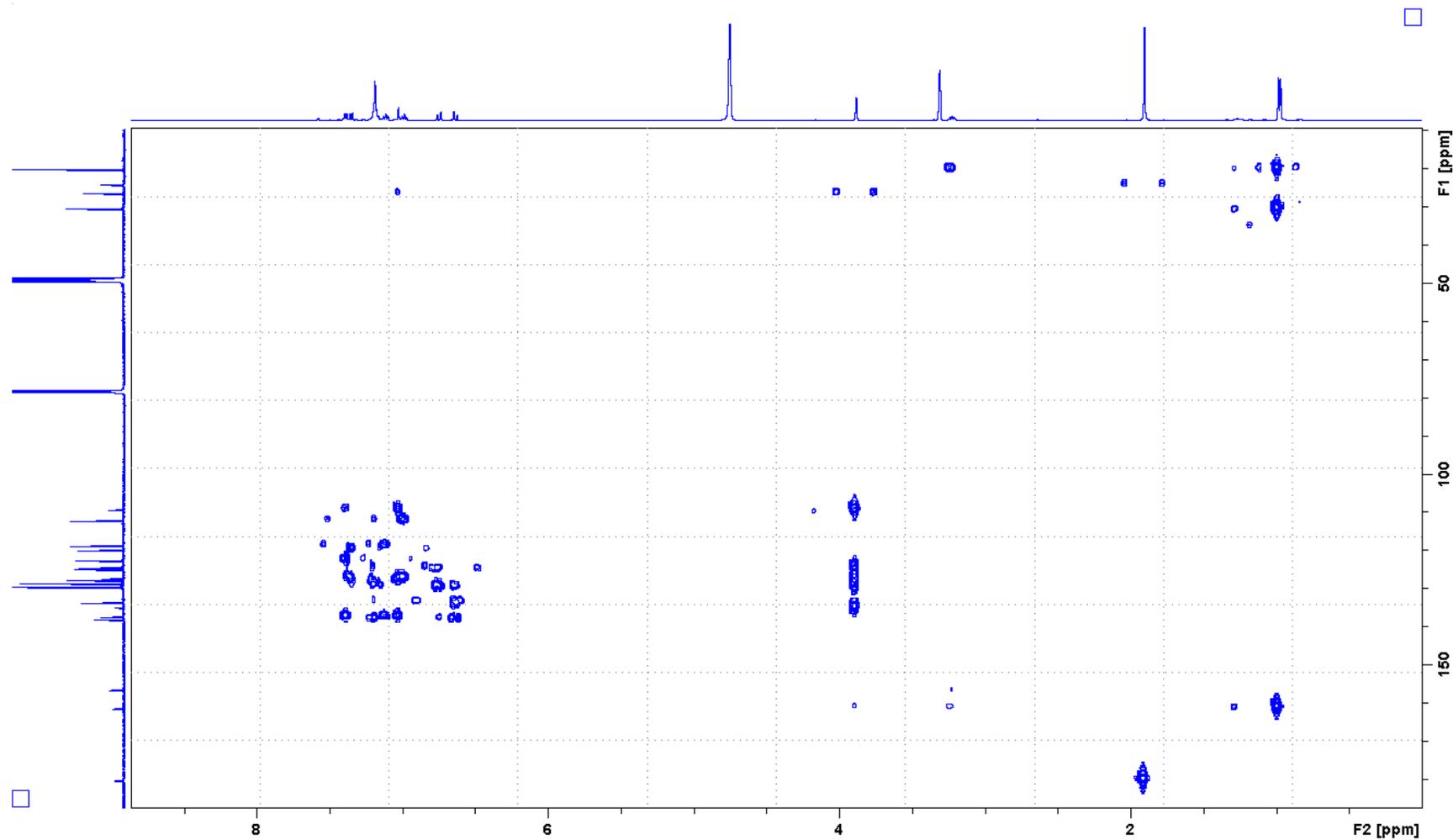


Figure S13. ^1H - ^{15}N HMBC Spectrum of enhyprazinone B (**2**; 500 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1)

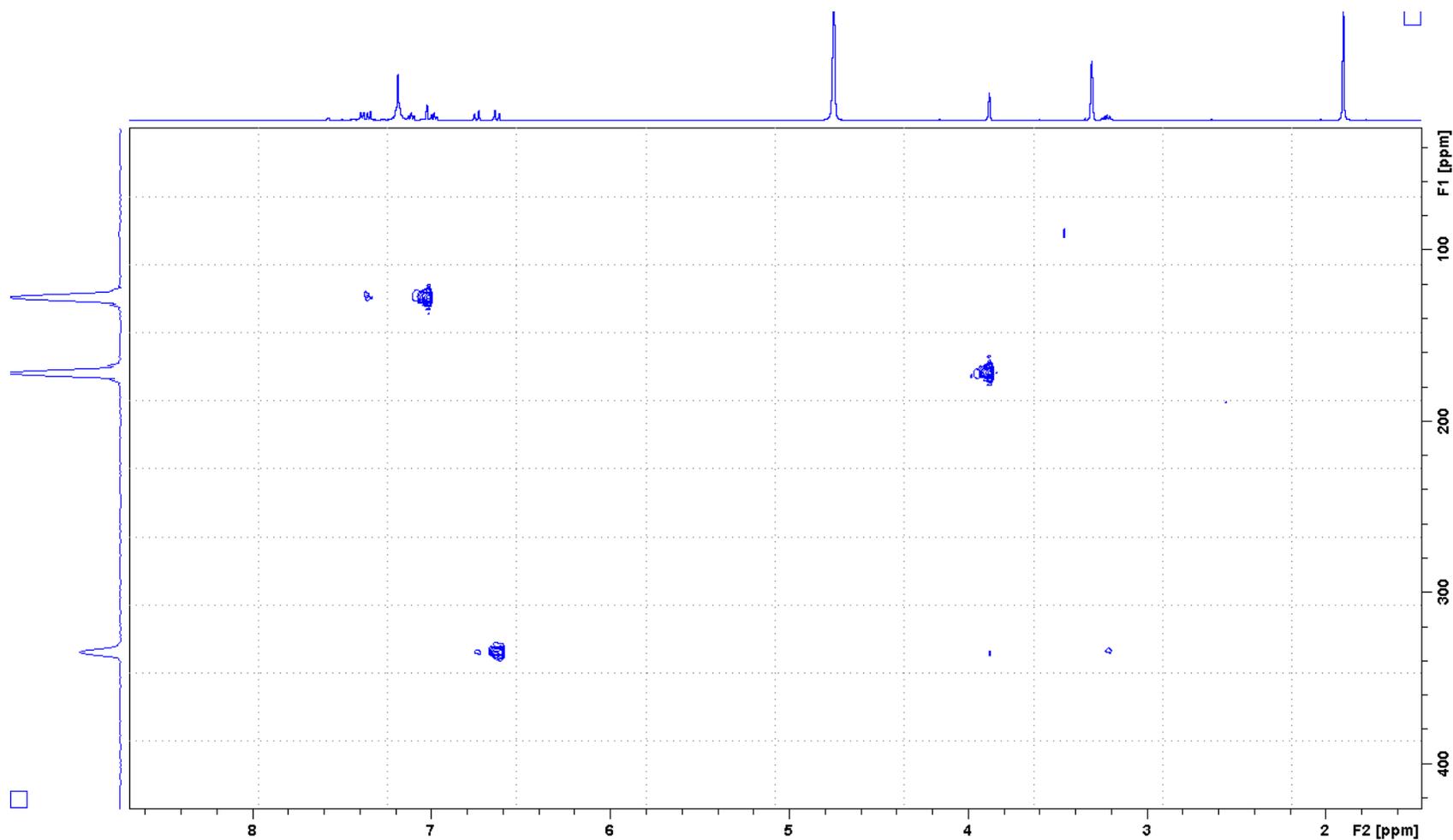


Figure S14. ^1H NMR spectrum of enhyprazinone B (**2**; 500 MHz, $\text{DMSO-}d_6$)

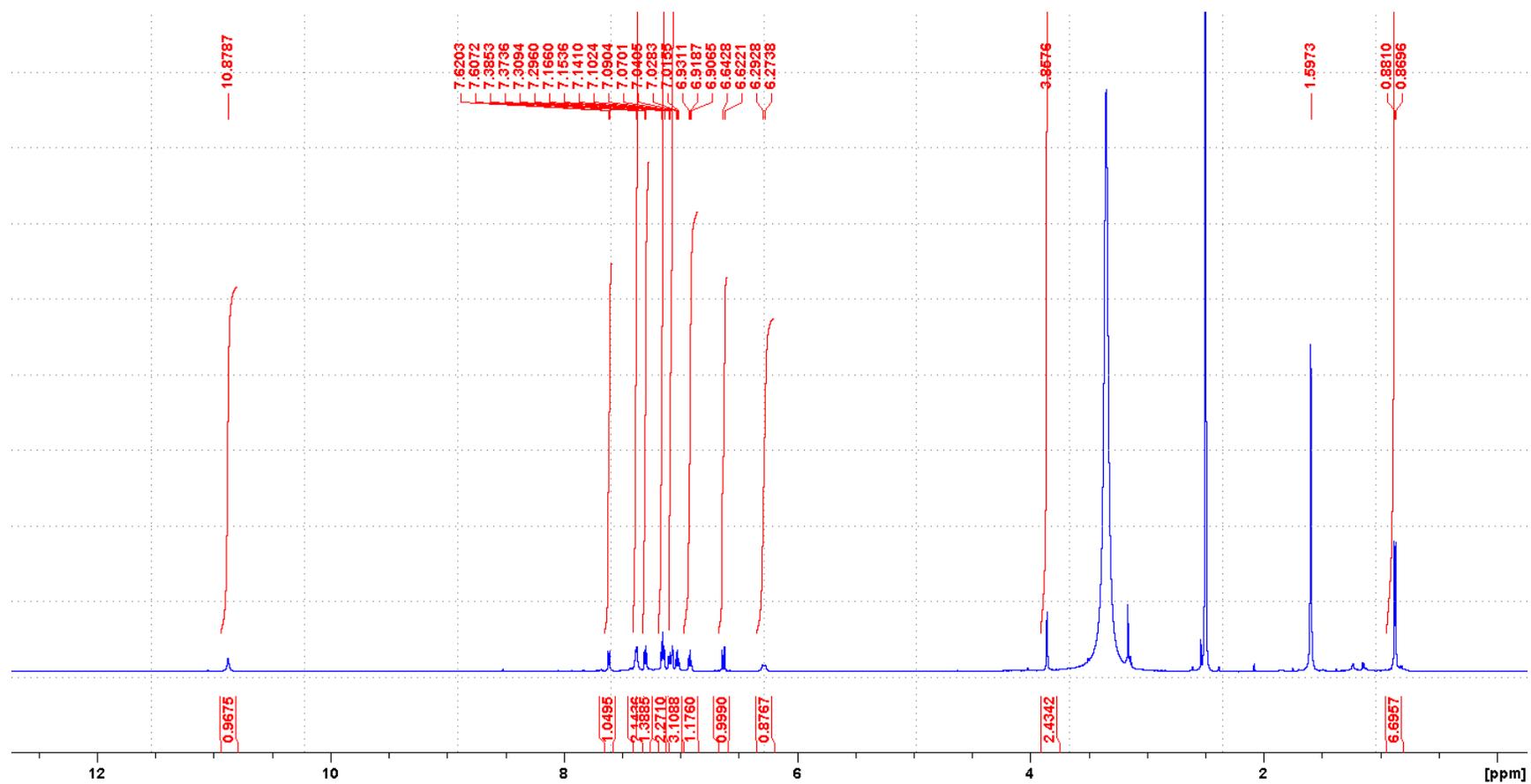


Figure S15. ^{13}C NMR spectrum of enhyprazinone B (**2**; 125 MHz, $\text{DMSO-}d_6$)

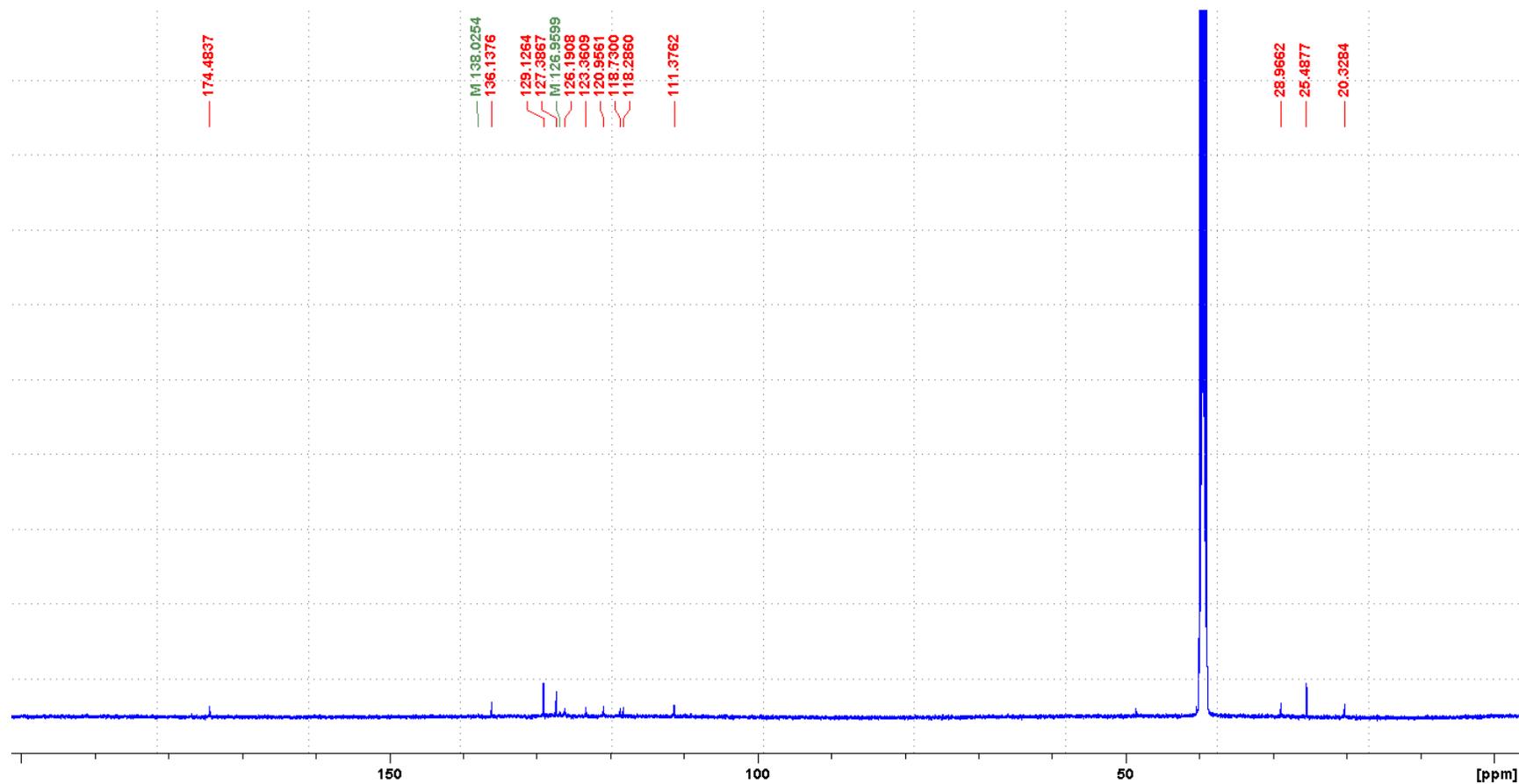


Figure S16. gCOSY spectrum of enhyprazinone B (**2**; 500 MHz, DMSO- d_6)

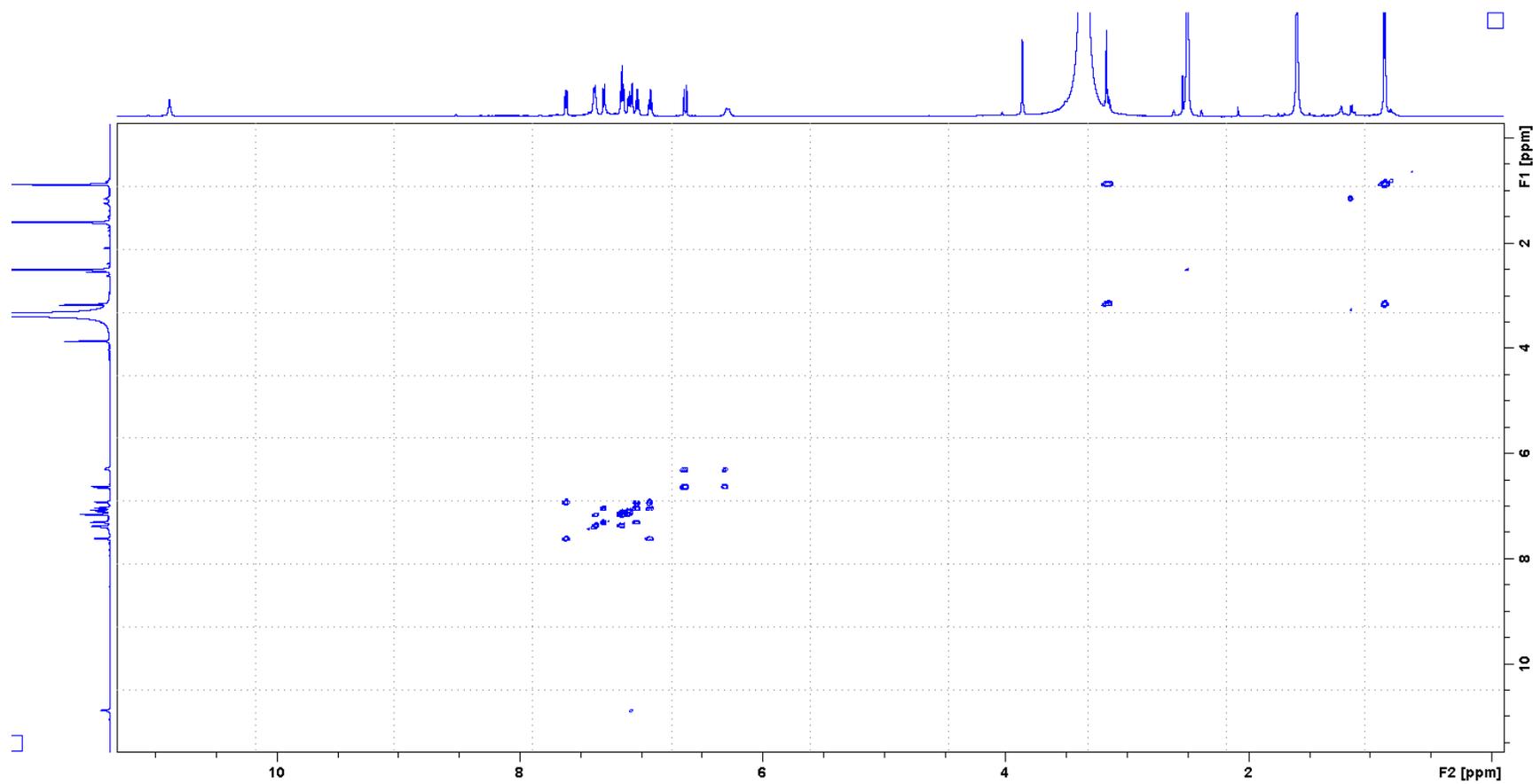


Figure S17. gHSQC spectrum of enhyprazinone B (**2**; 500 MHz, DMSO-*d*₆)

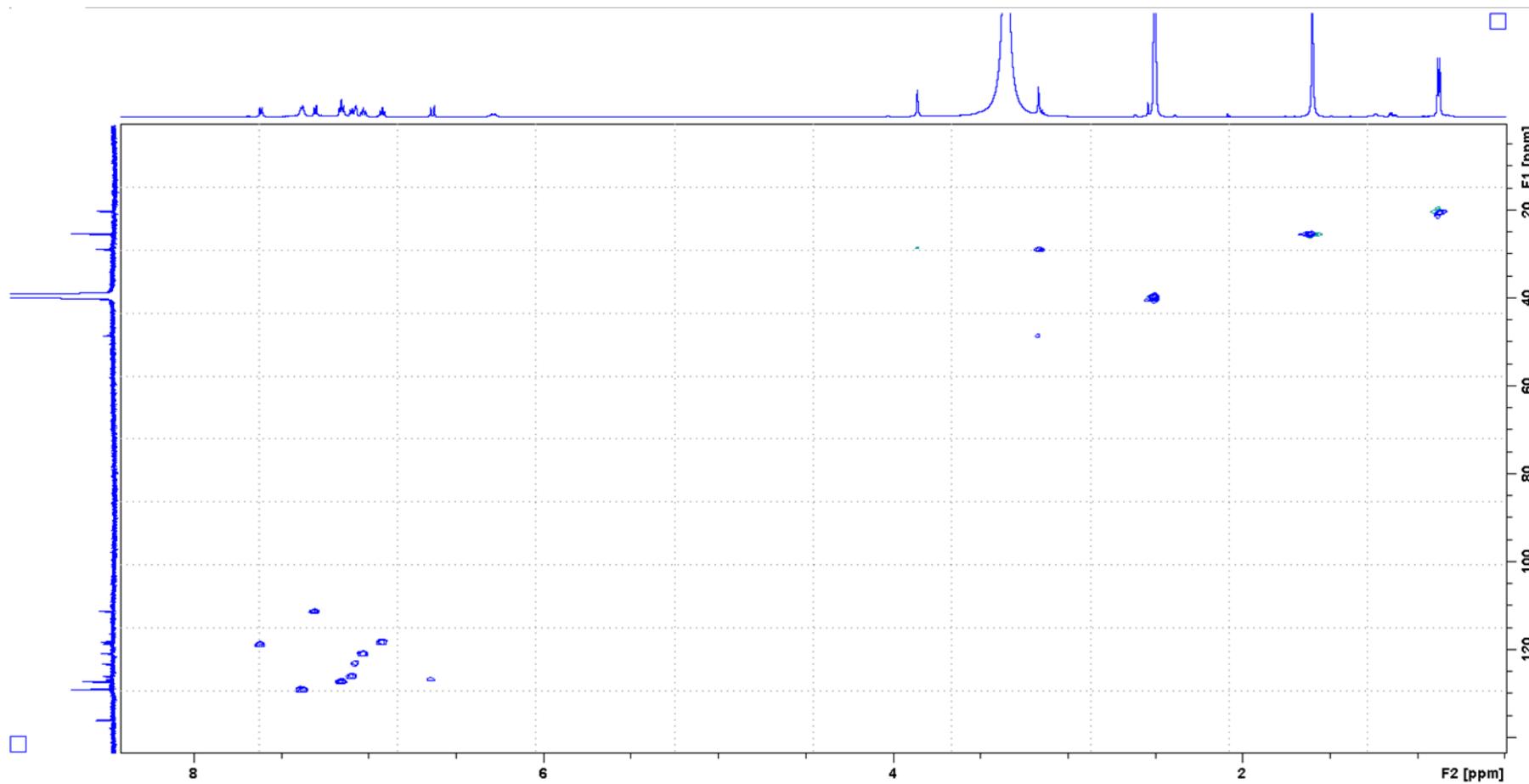


Figure S18. gHMBC spectrum of enhyprazinone B (**2**; 500 MHz, DMSO-*d*₆)

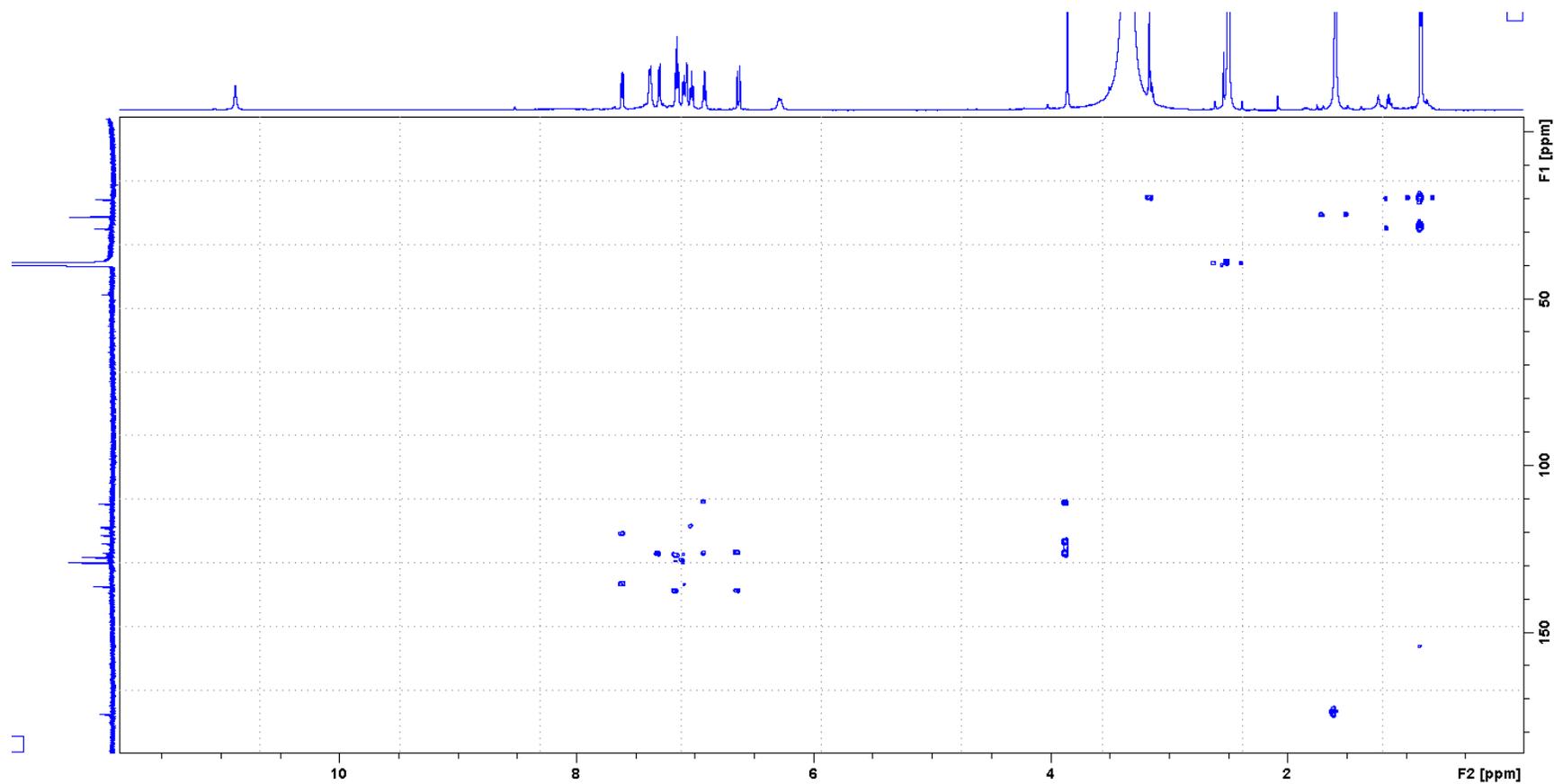


Figure S19. ^1H - ^{15}N HMBC spectrum of enhyprazinone B (**2**; 500 MHz, $\text{DMSO-}d_6$)

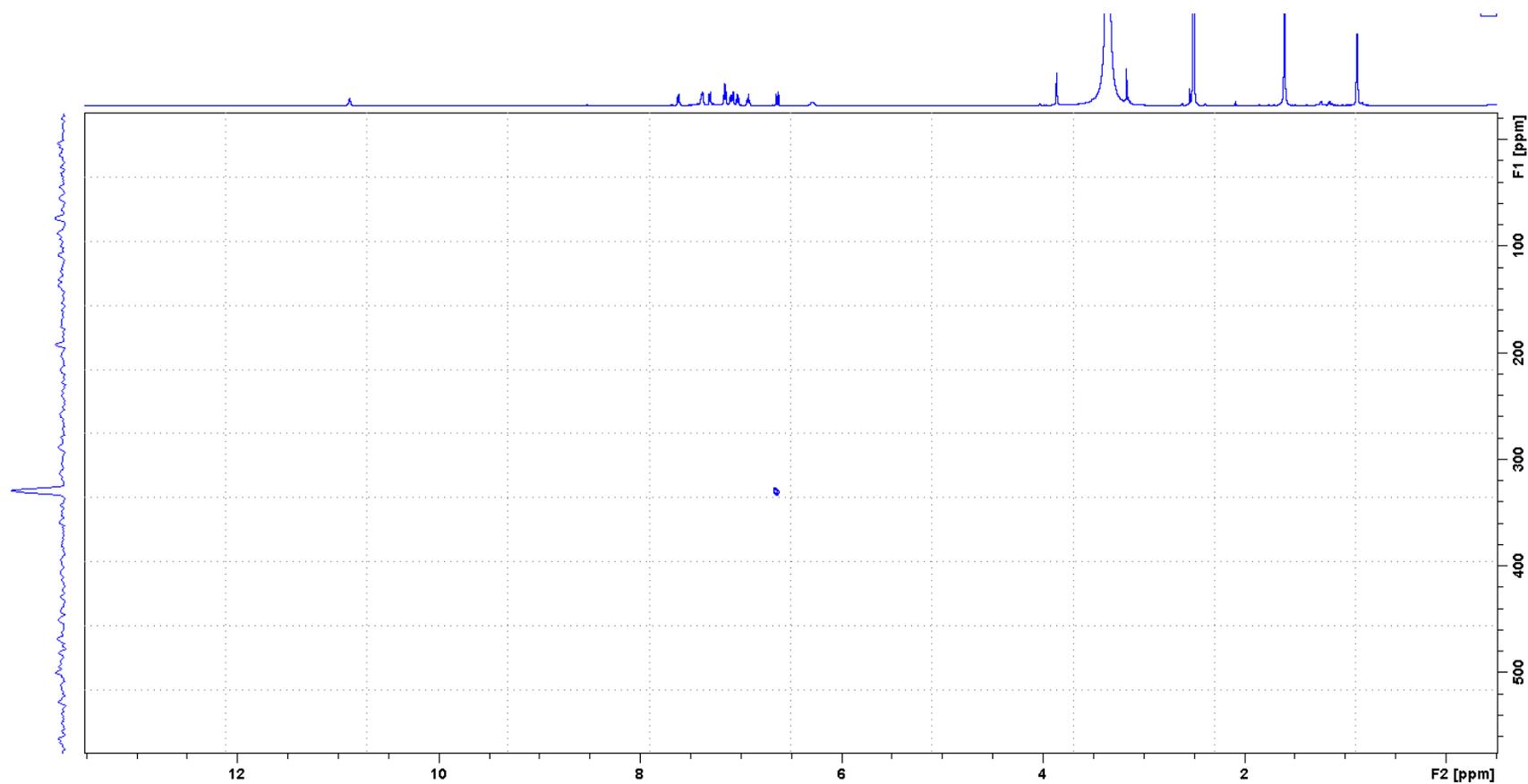
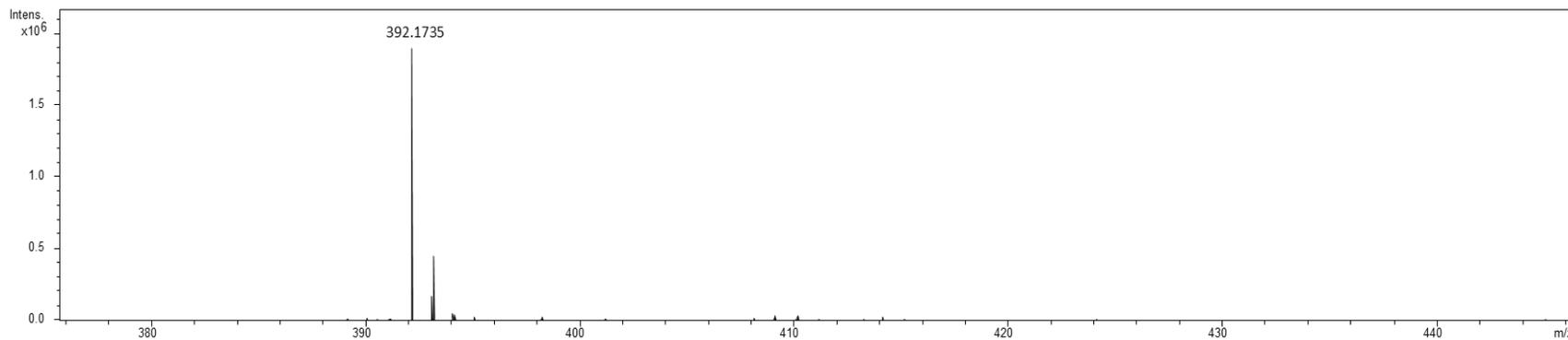


Figure S20. Positive ion HRESIMS of enhyprazinone B (2)



Supporting Information: Enhyppyrizinones A and B, Pyrazinone Natural Products from a Marine-derived Myxobacterium *Enhygromyxa* sp.

Table 1. ^1H and ^{13}C NMR data for enhyppyrizinone B (**2**) (500 MHz for ^1H , 125 MHz for ^{13}C , $\text{CDCl}_3/\text{CD}_3\text{OD}$ 1:1).

Position	δ_{C} , mult.	δ_{H} (J in Hz)	^1H - ^1H COSY	^1H - ^{13}C HMBC ^a	$\delta_{\text{N}}^{\text{b}}$	^1H - ^{15}N HMBC ^c
1	156.5, qC					
2					172.1	
3	135.0, qC					
4	129.8, qC					
5					335.1	
6	161.4, qC					
7	26.6, CH ₂	3.88, s	9	3, 4, 8, 9, 16		2
8	109.4, qC					
9	124.5, CH	7.03, s	7	8, 11, 16		10
10					127.7	
11	137.5, qC					
12	112.3, CH	7.35, d (8.0)	13	14, 16		10 (weak)
13	122.6, CH	7.11, t (8.0)		11, 15		
14	120.0, CH	6.99, t (8.0)	15	12, 15		
15	118.8, CH	7.39, d (8.0)	14	8, 11, 13		
16	127.4, qC					
17	125.0, CH	6.64, d (12.0)	18	3, 4, 18, 19		5
18	133.8, CH	6.75, d (12.0)	17	4, 17, 19		
19	138.1, qC					
20	129.6, CH	7.19, m		18, 19, 21		
21	128.7, CH	7.22, m		22		
22	127.9, CH	7.16, m		20, 24		
23	128.7, CH	7.22, m		24		
24	129.6, CH	7.19, m		18, 19, 23		
25	30.6, CH	3.22, m	26, 27	6, 26, 27		5 (weak)
26	20.2, CH ₃	0.98, d (6.8)	25	6, 25, 27		
27	20.2, CH ₃	0.98, d (6.8)	25	6, 25, 26		

^aHMBC correlations are from proton(s) to the indicated carbon.

^bThe chemical shifts of ^{15}N were determined by ^1H - ^{15}N -HMBC.

^cHMBC correlations are from proton(s) to the indicated nitrogen