Supporting Information

Clavariopsins C-I, antifungal cyclic depsipeptides from the aquatic hyphomycete *Clavariopsis aquatica*

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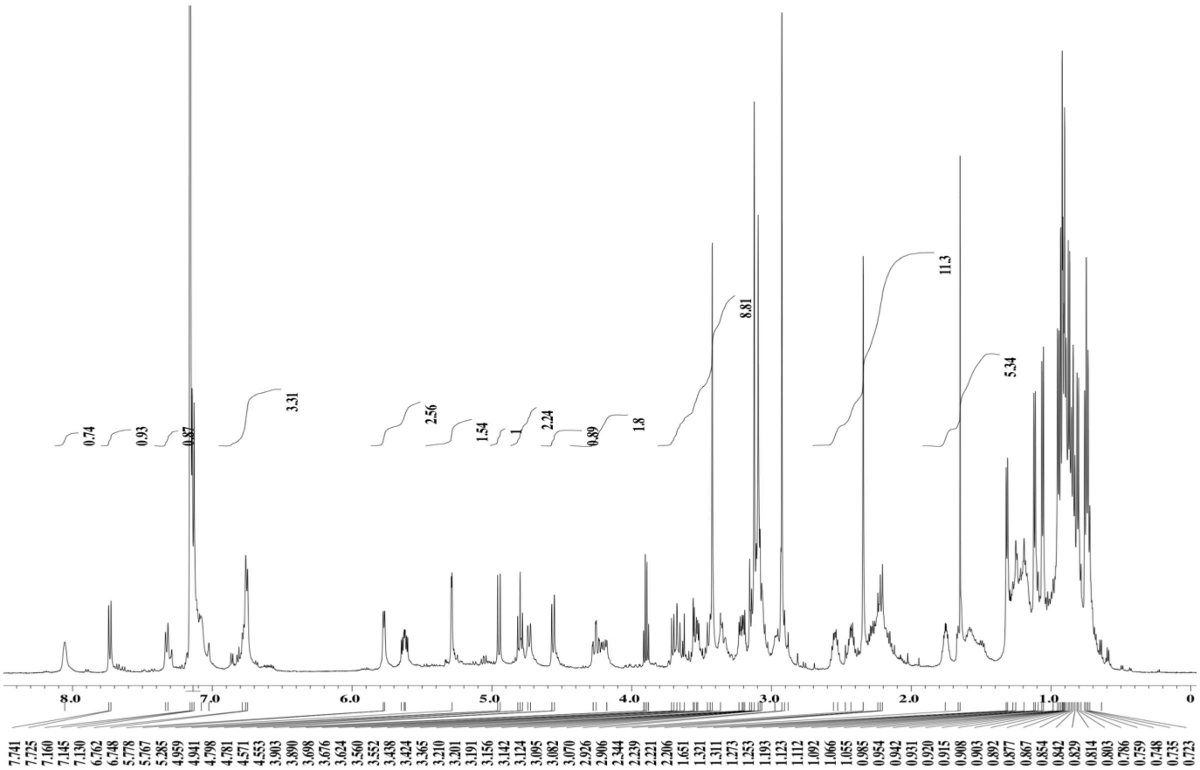


Figure S1. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **3**.

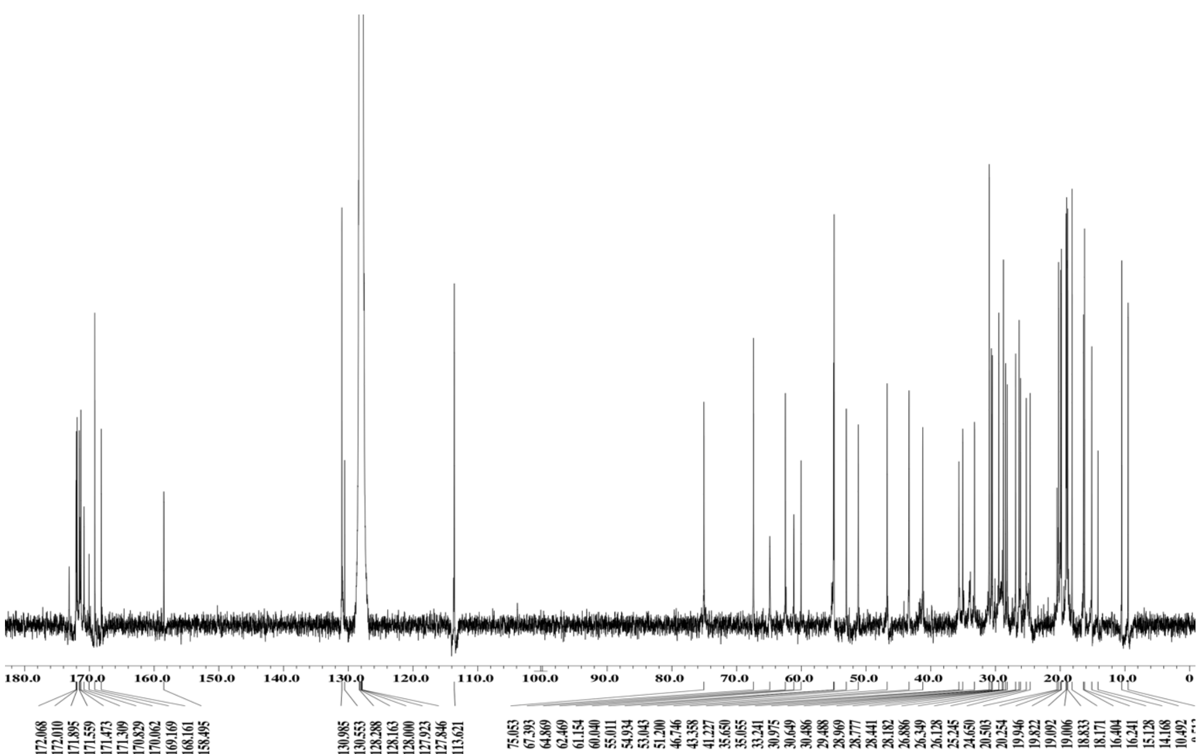


Figure S2. ^{13}C NMR (150 MHz, C_6D_6) spectrum of **3**.

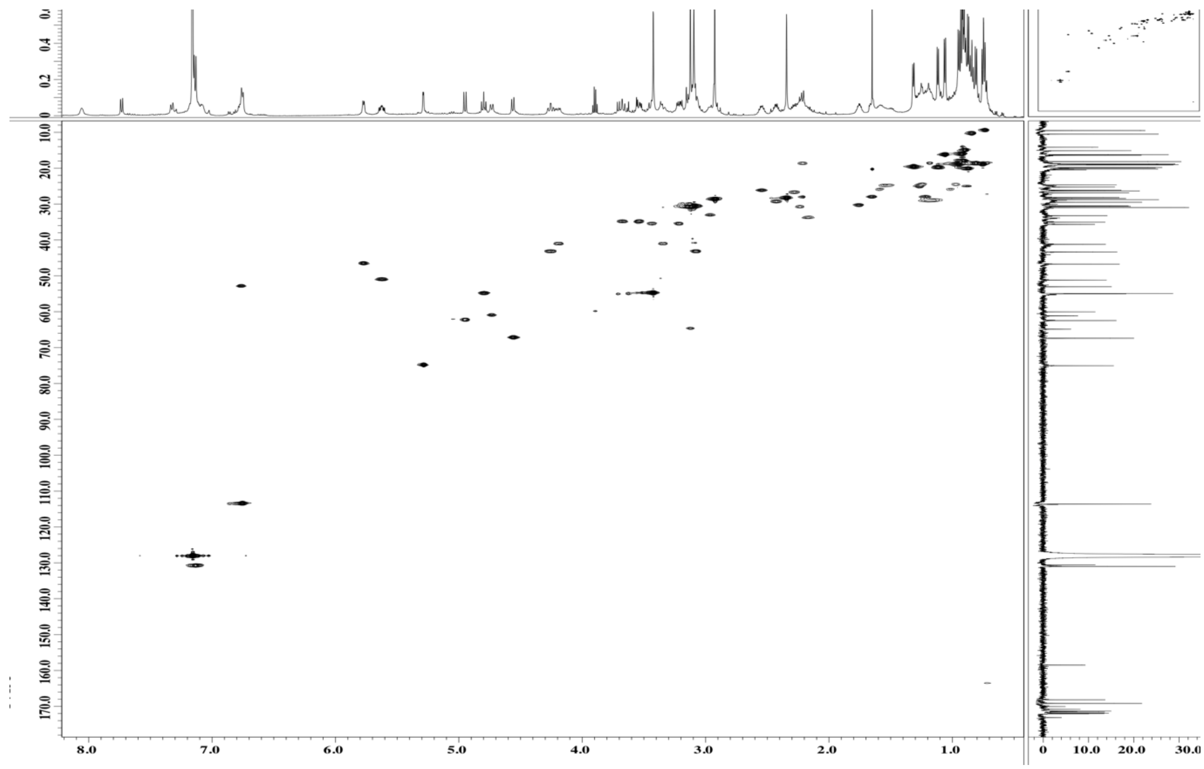


Figure S3. HSQC (600 MHz, C_6D_6) spectrum of **3**.

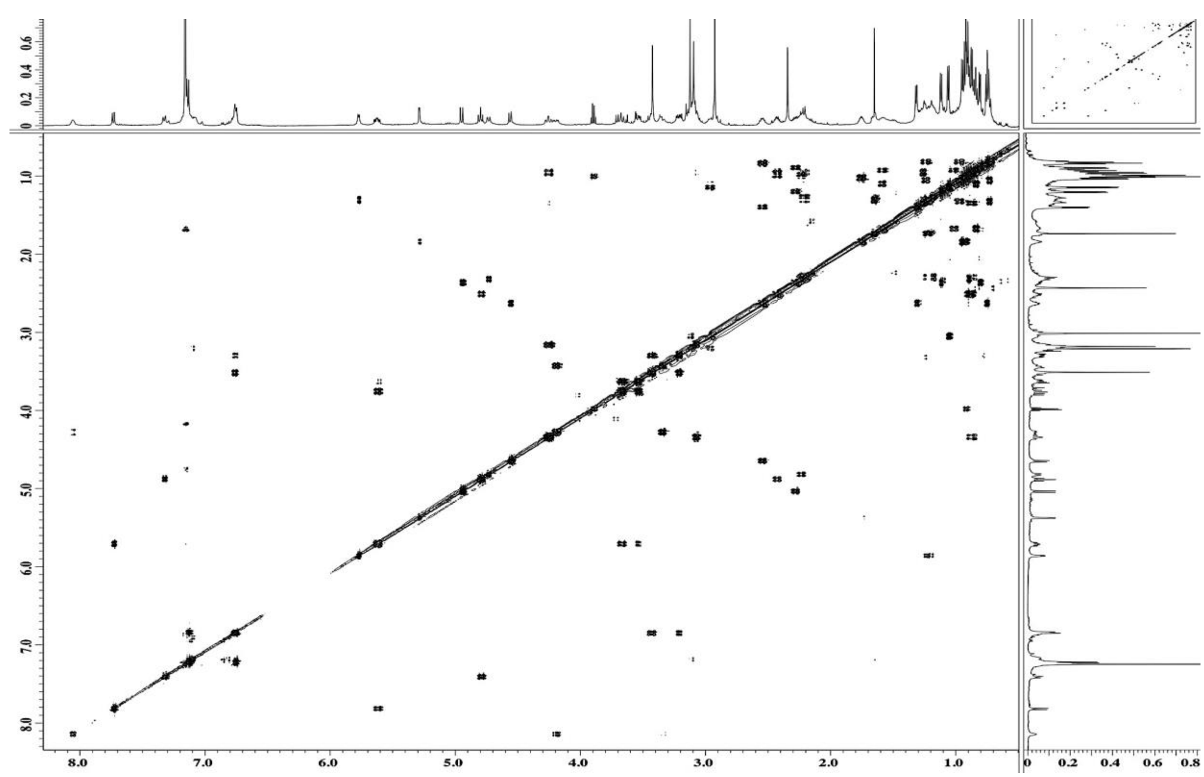


Figure S4. DQF-COSY (600 MHz, C_6D_6) spectrum of **3**.

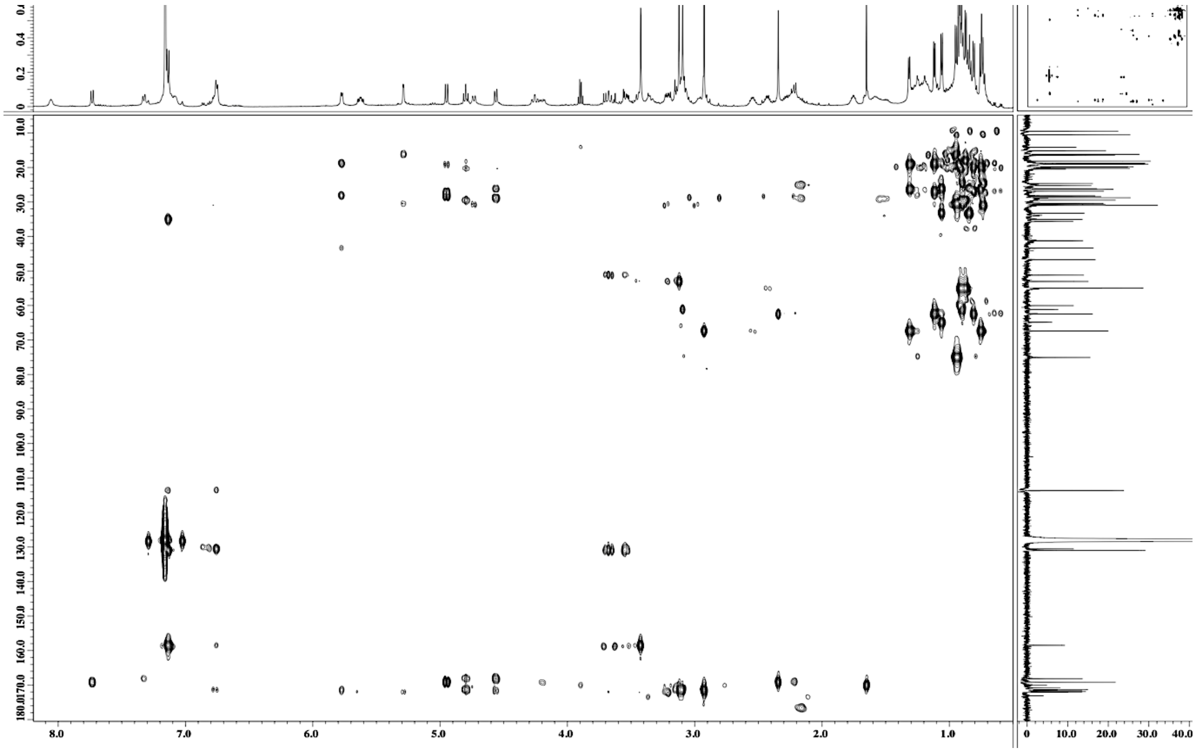


Figure S5. HMBC (600 MHz, C_6D_6) spectrum of **3**.

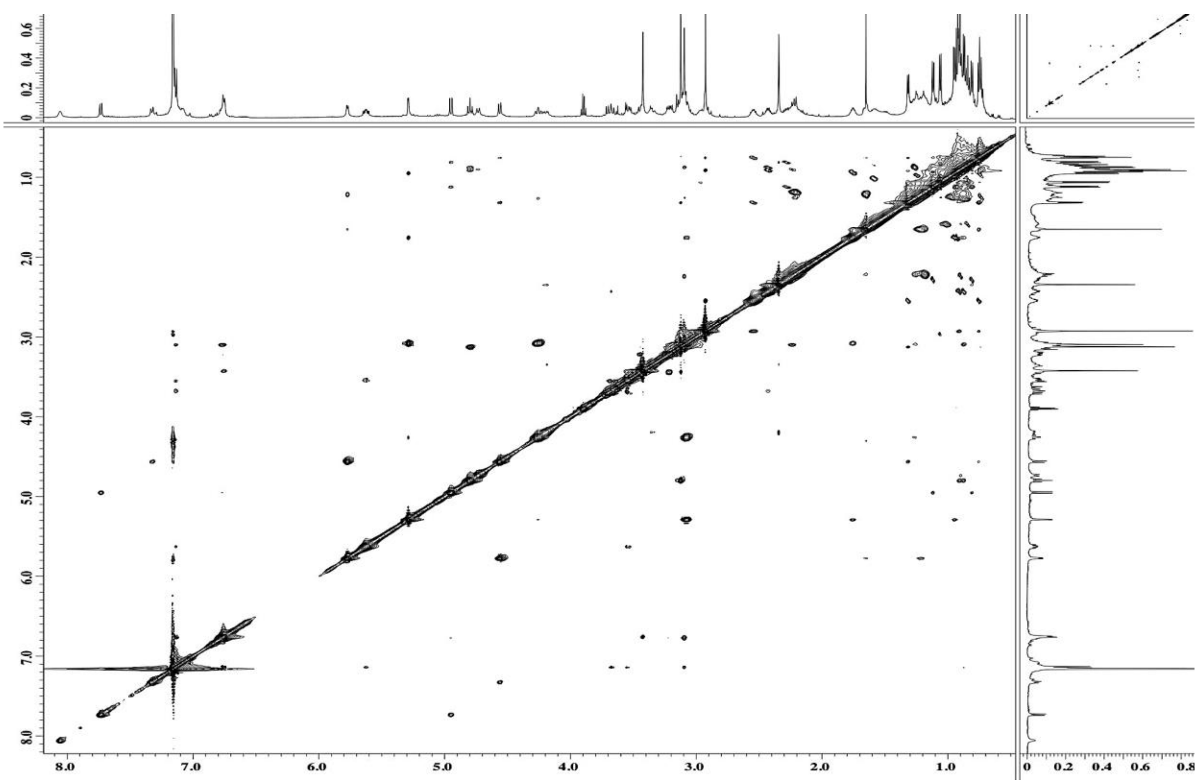


Figure S6. ROESY (600 MHz, C_6D_6) spectrum of **3**.

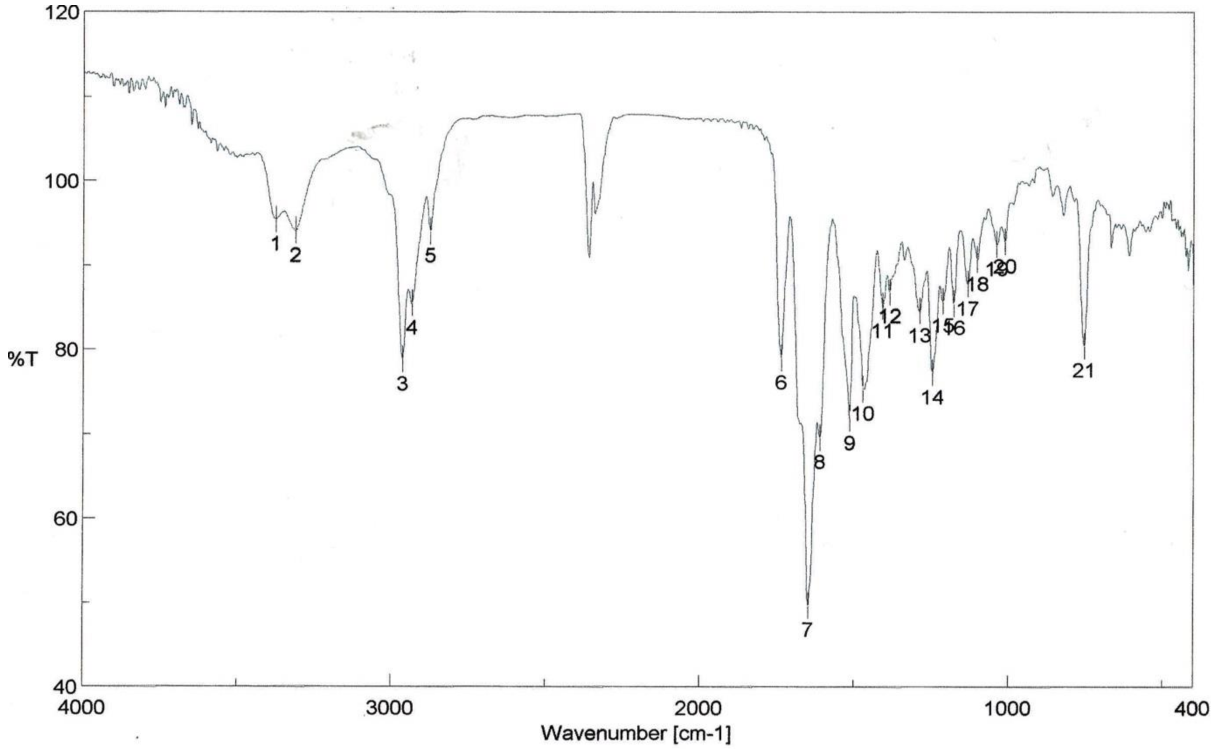


Figure S7. FT IR spectrum of **3** (film).

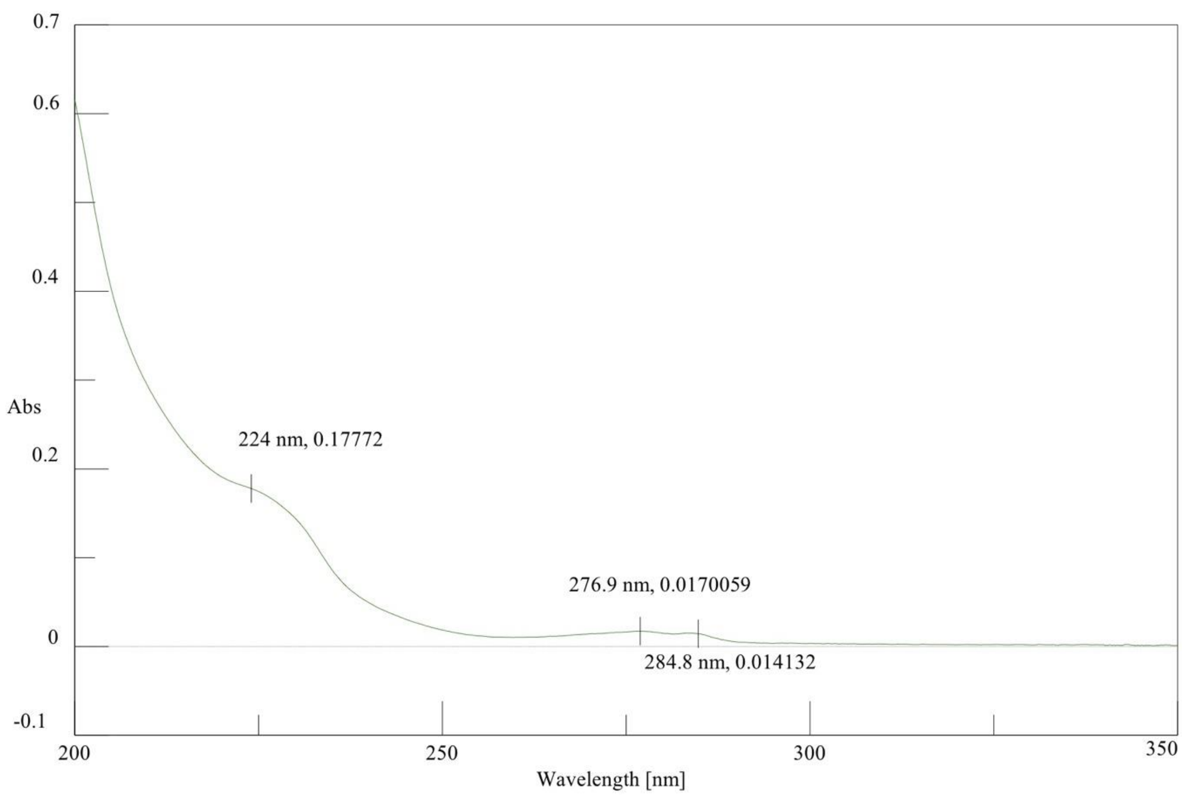


Figure S8. UV spectrum of **3** (10 μM in MeCN).

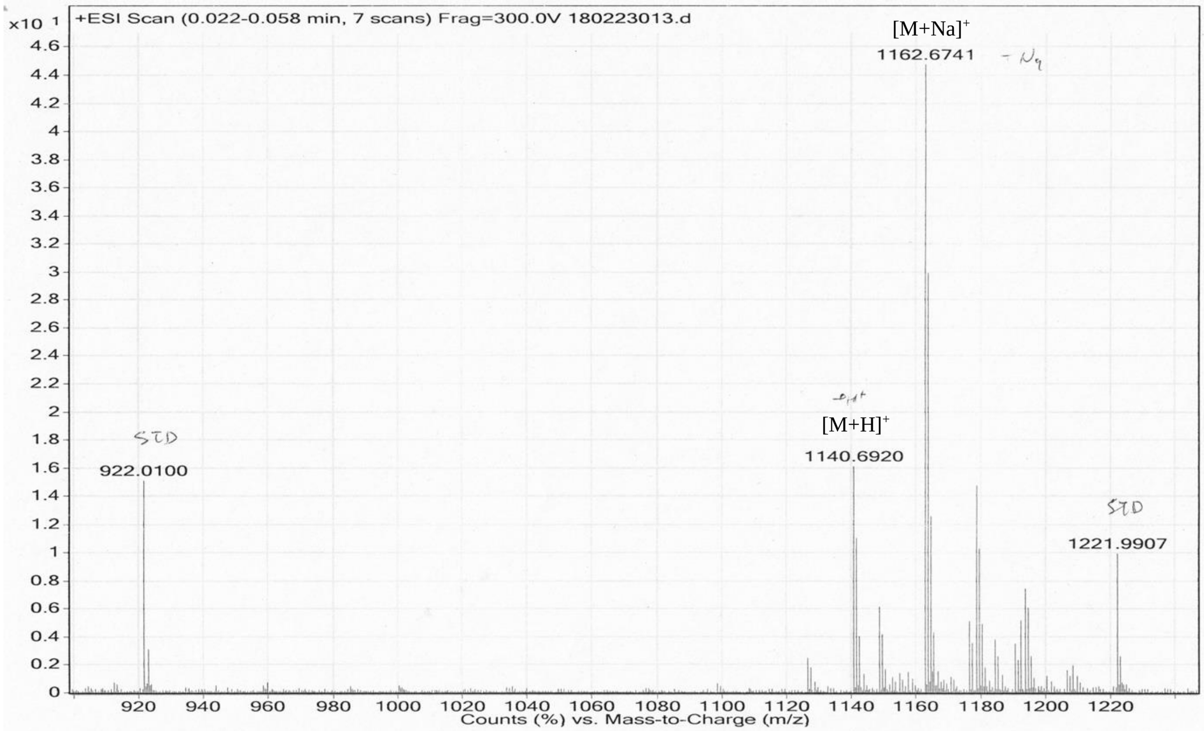


Figure S9. HRESIMS (+) of **3**.

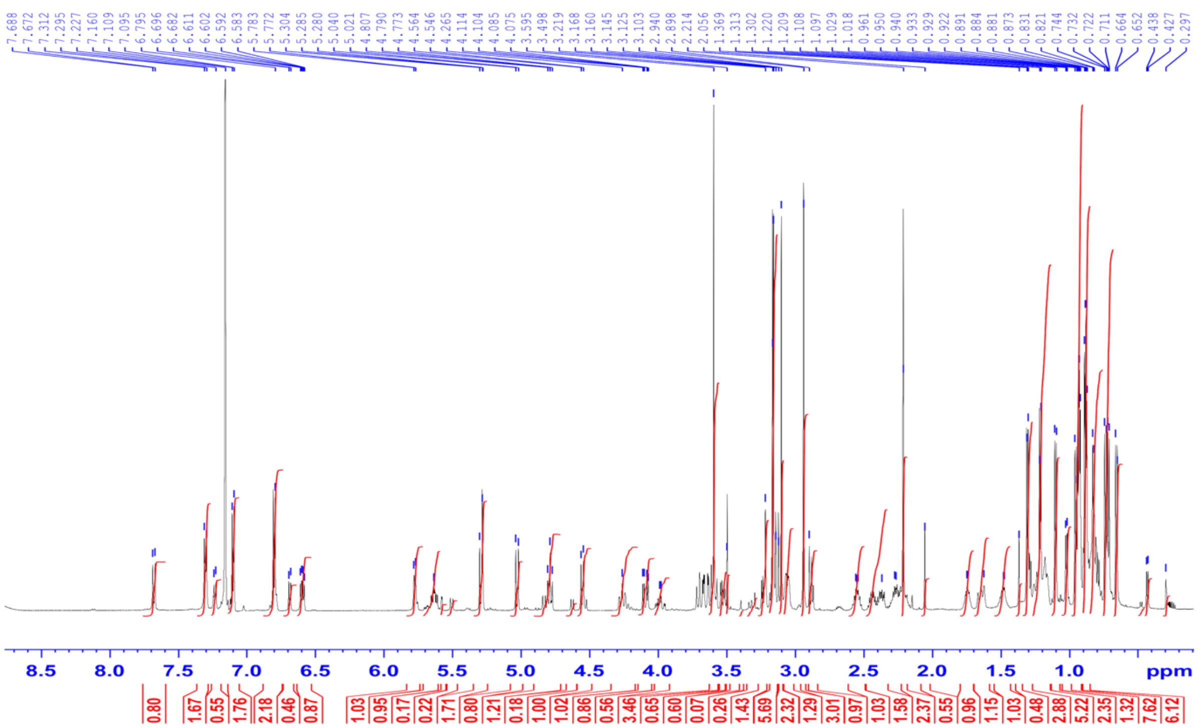
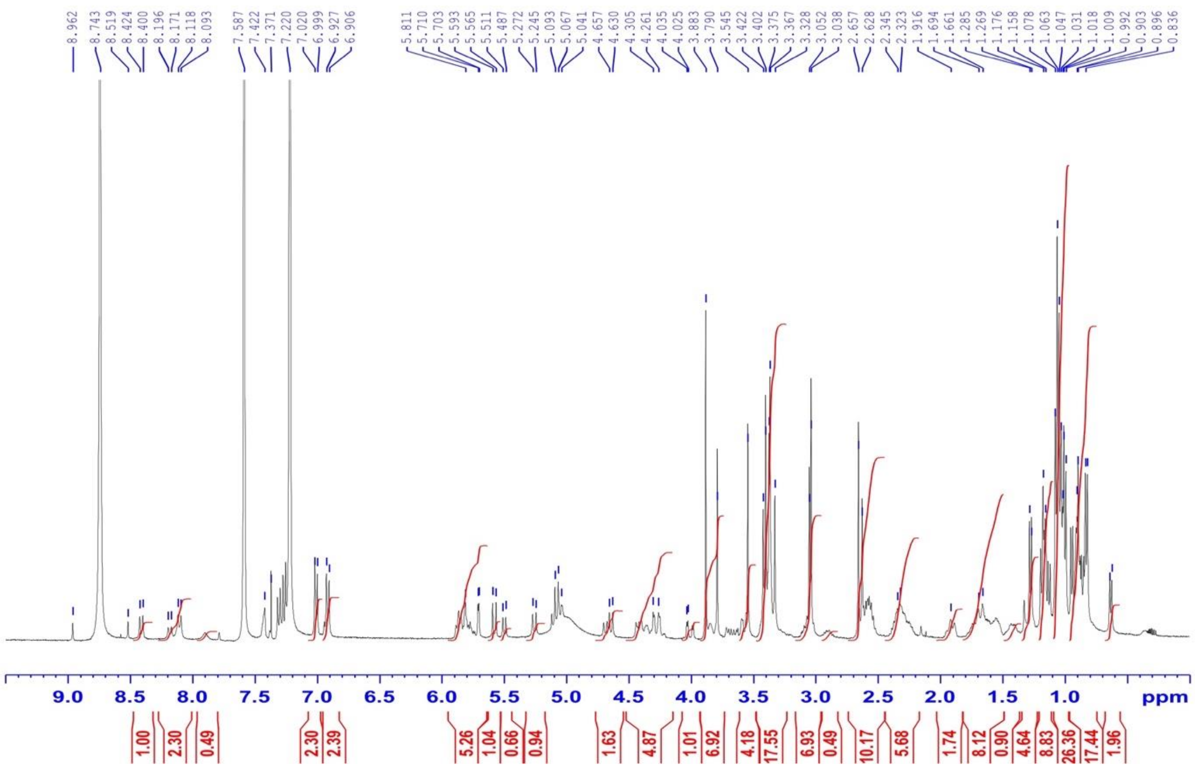


Figure S10. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **4**.



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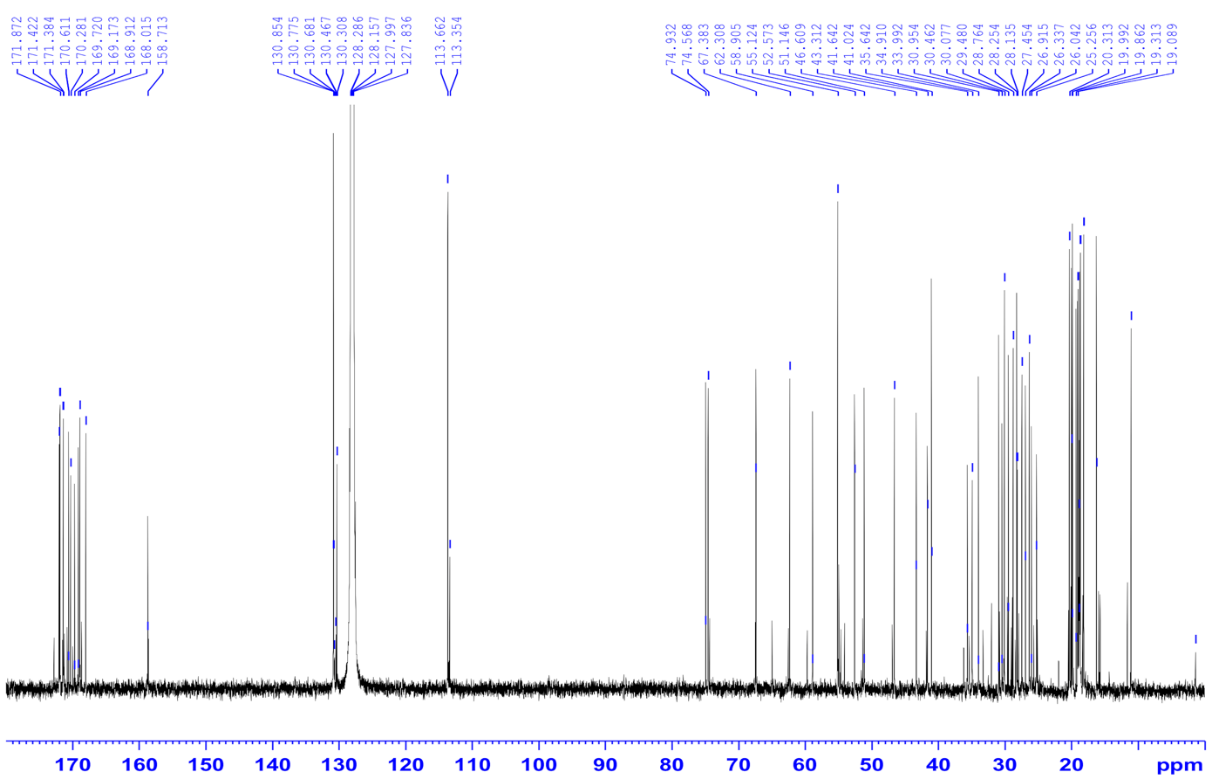
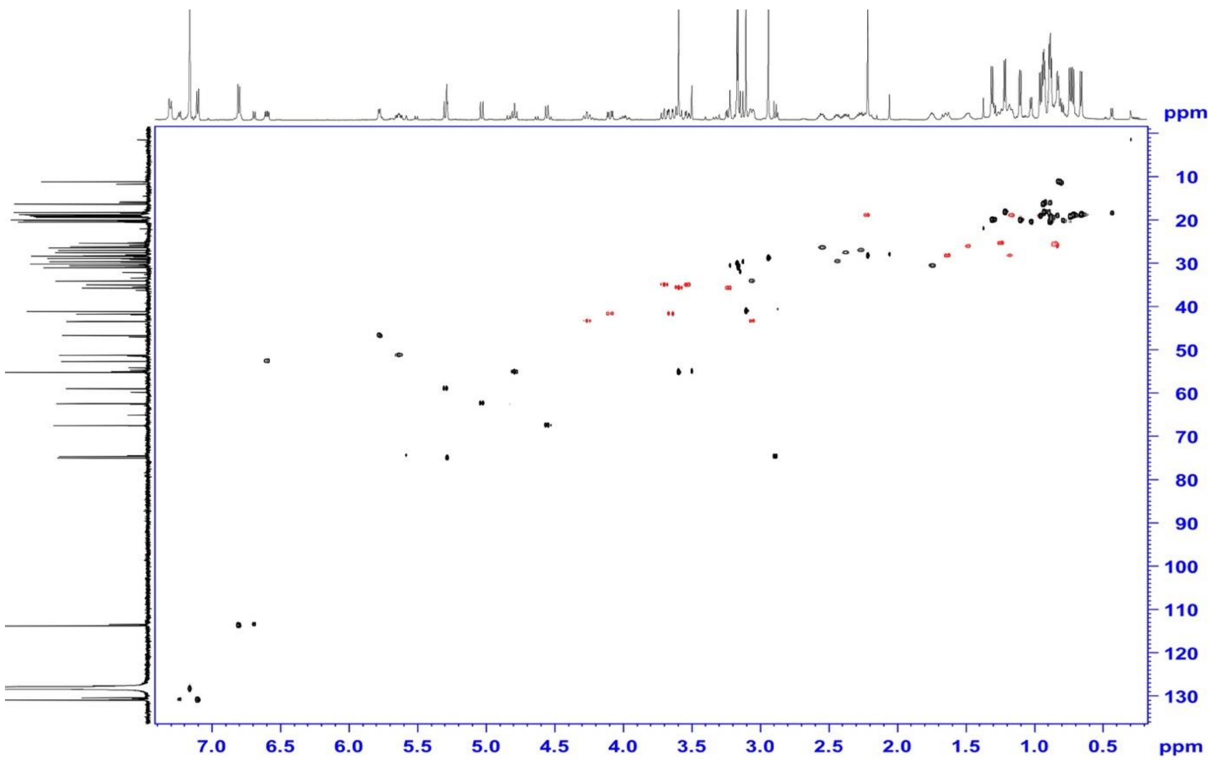


Figure S12. ^{13}C NMR (150 MHz, C_6D_6) spectrum of **4**.



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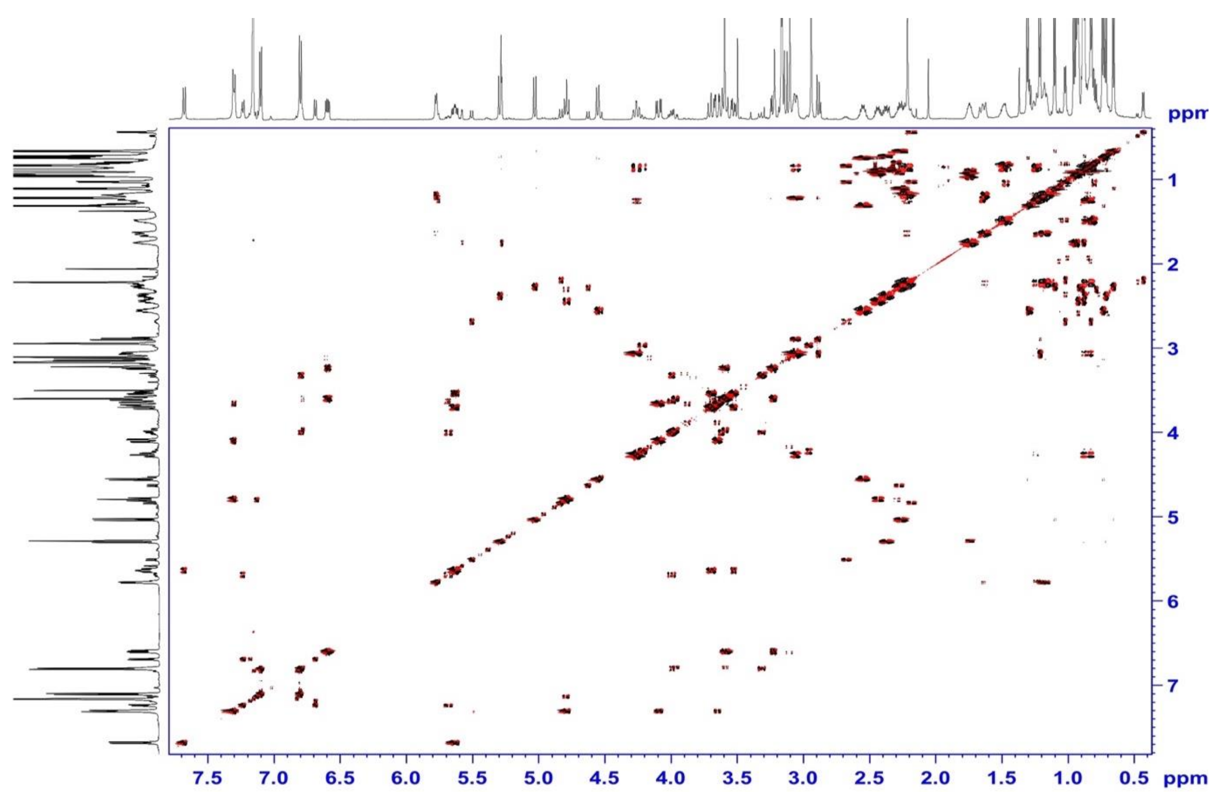


Figure S14. DQF-COSY (600 MHz, C_6D_6) spectrum of **4**.

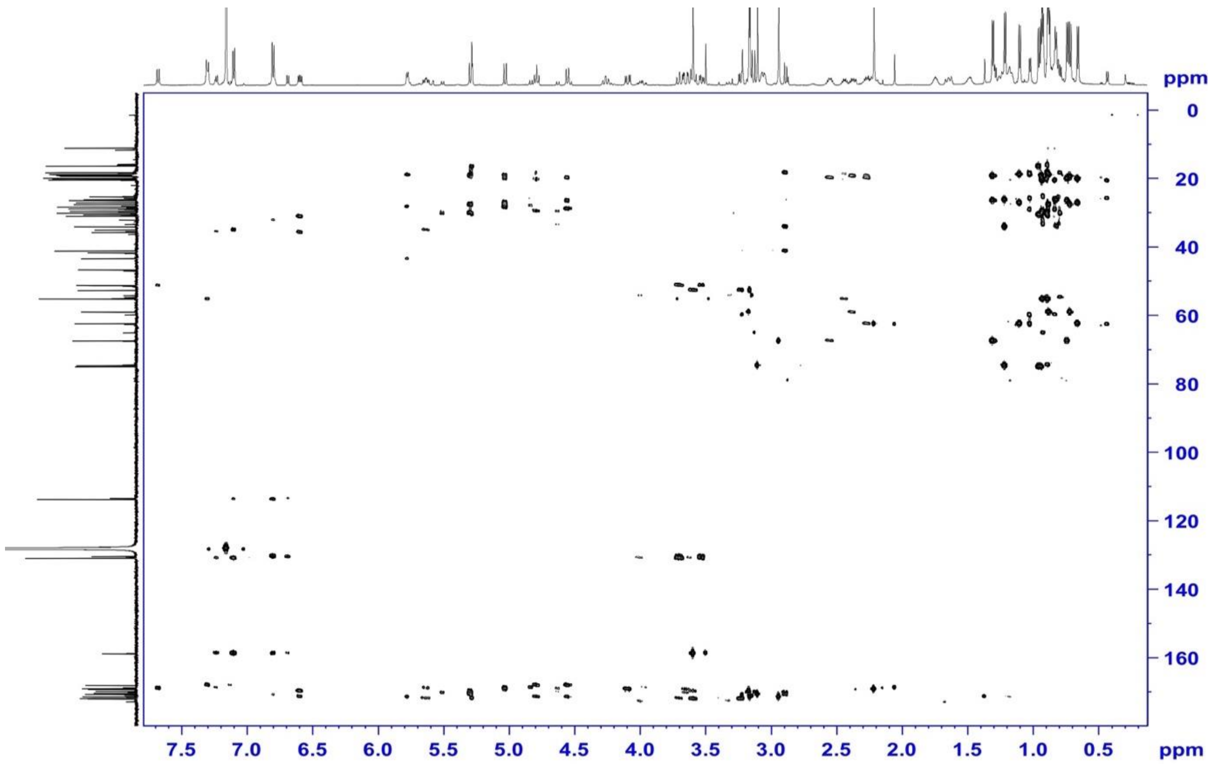


Figure S15. HMBC (600 MHz, C_6D_6) spectrum of **4**.

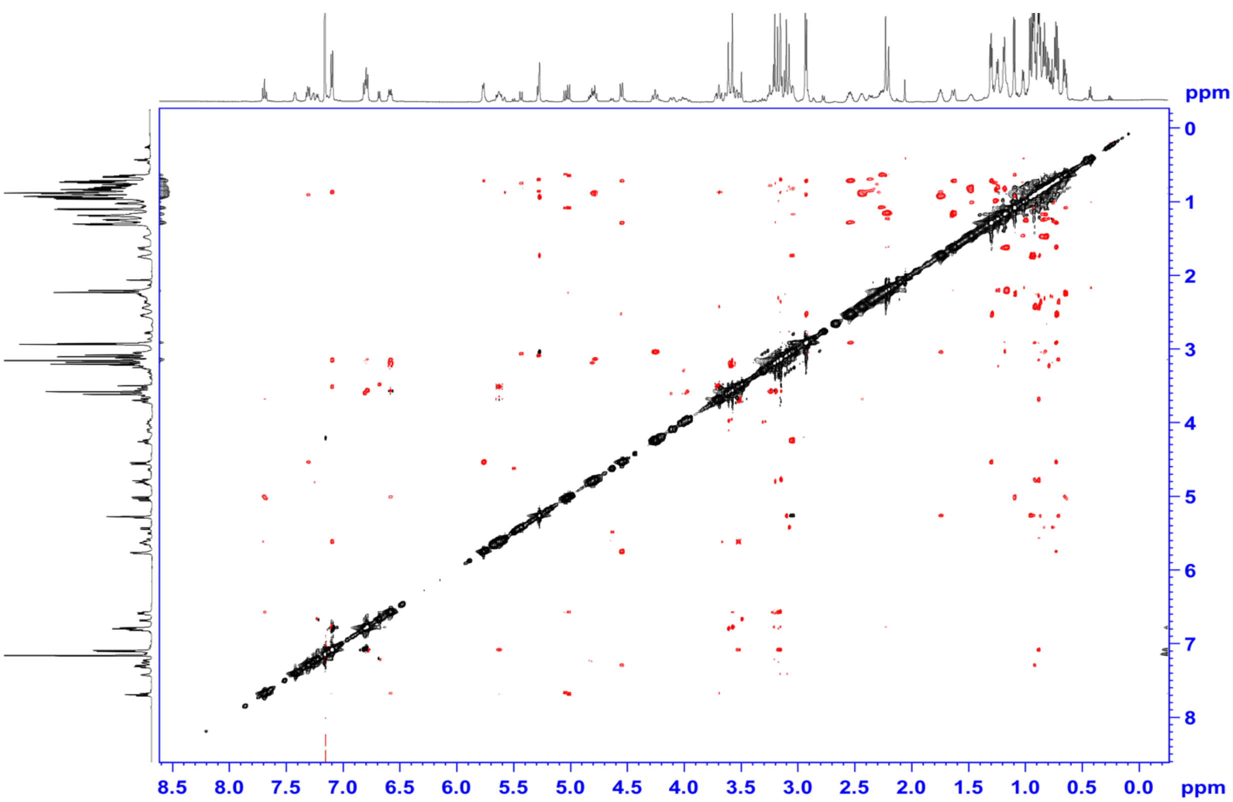


Figure S16. NOESY (600 MHz, C_6D_6) spectrum of **4**.

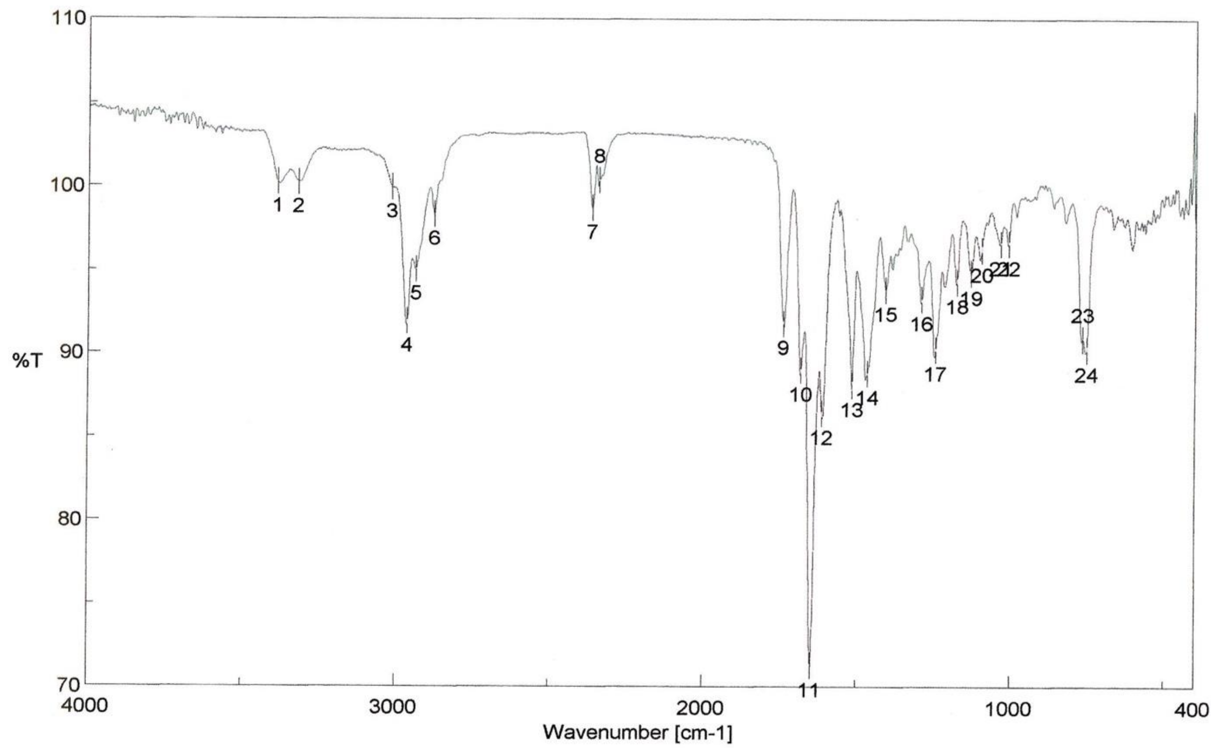


Figure S17. FT IR spectrum of **4** (film).

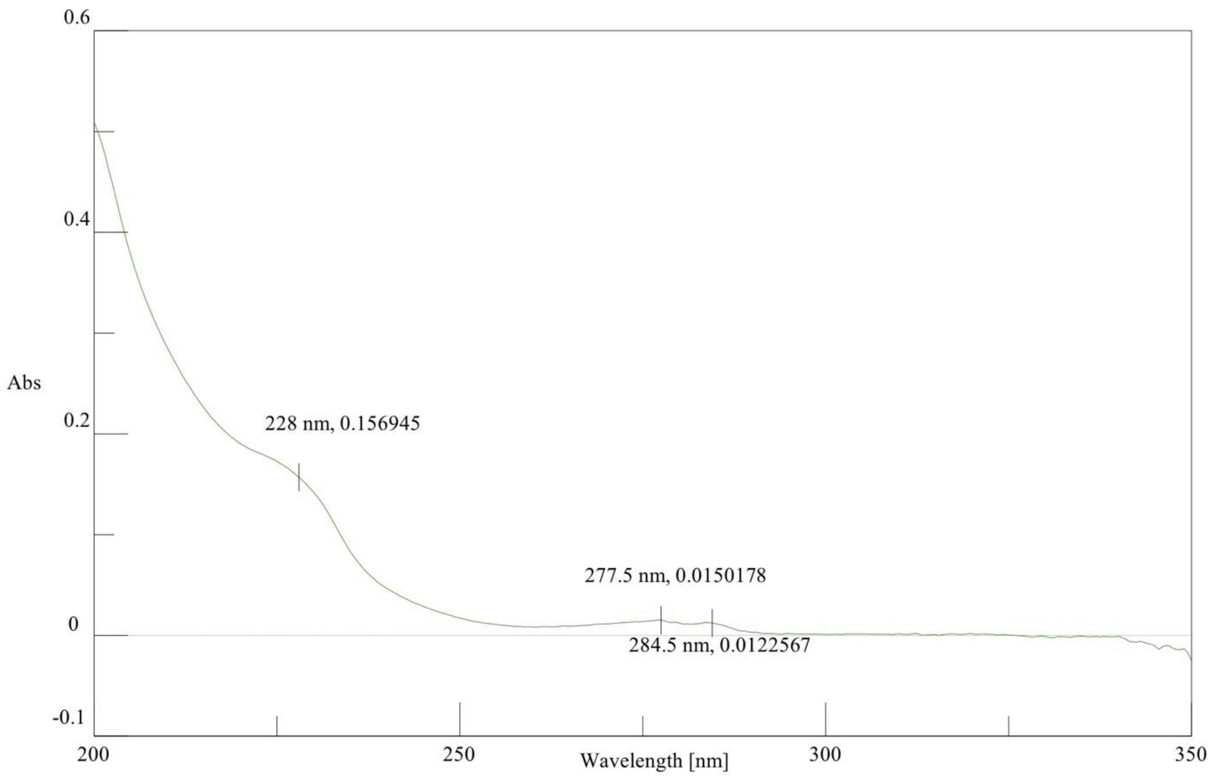


Figure S18. UV spectrum of **4** (10 μM in MeCN).

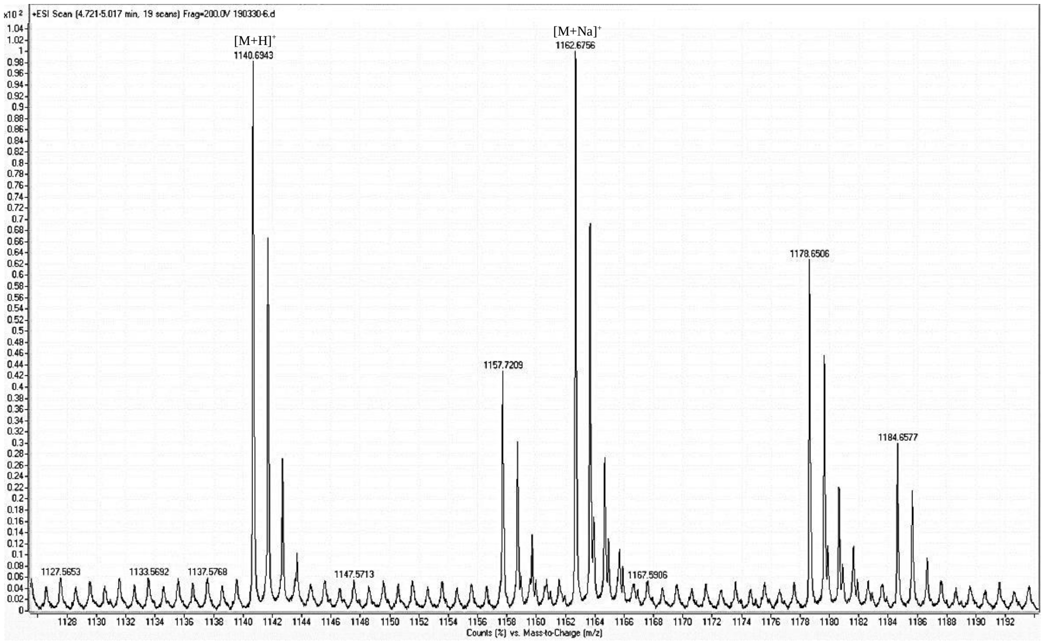


Figure S19. HRESITOFMS (+) of **4**.

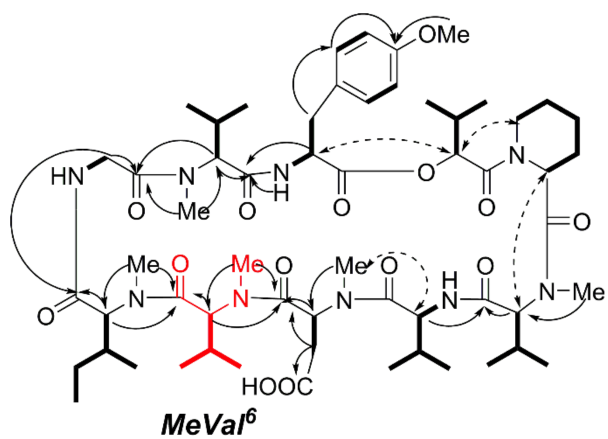


Figure S20. Key COSY (bold bonds), HMBC (arrows) and NOESY (dotted arrow) correlations of **4**.

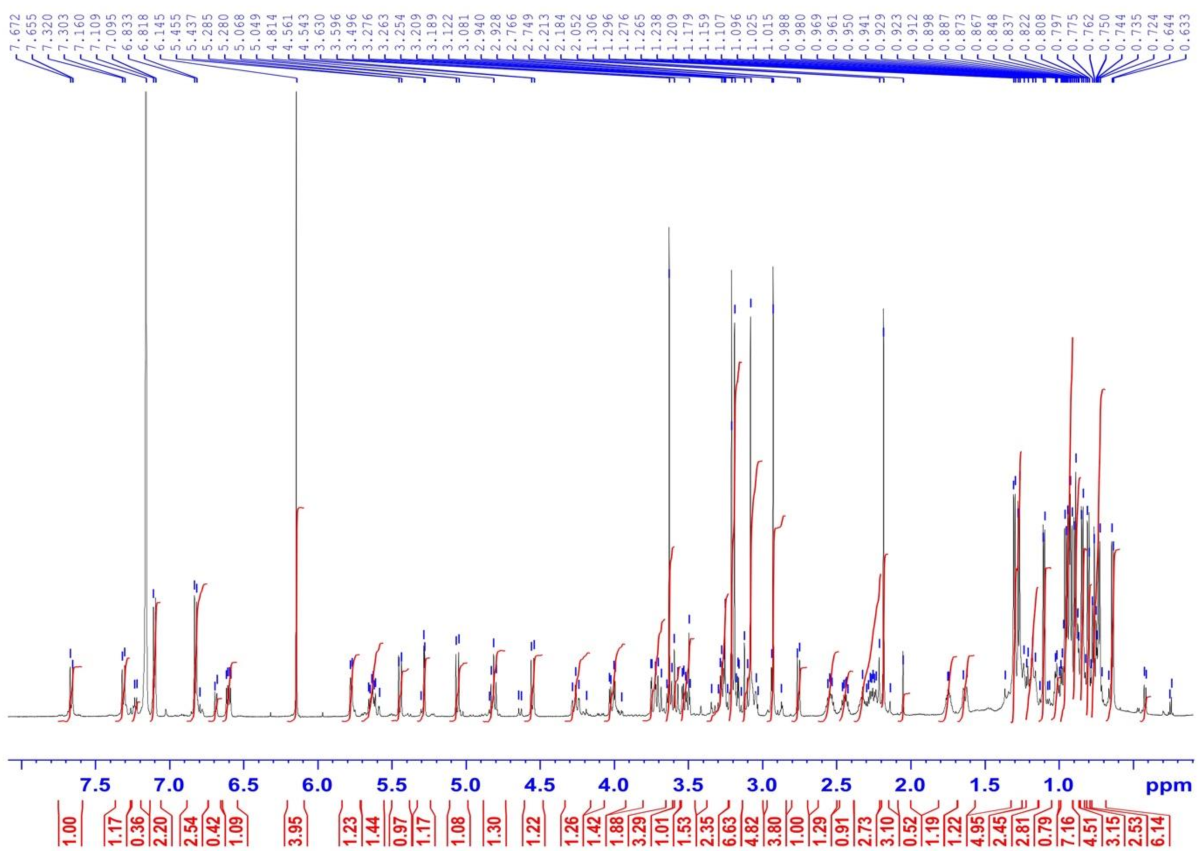


Figure S21. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **5**.

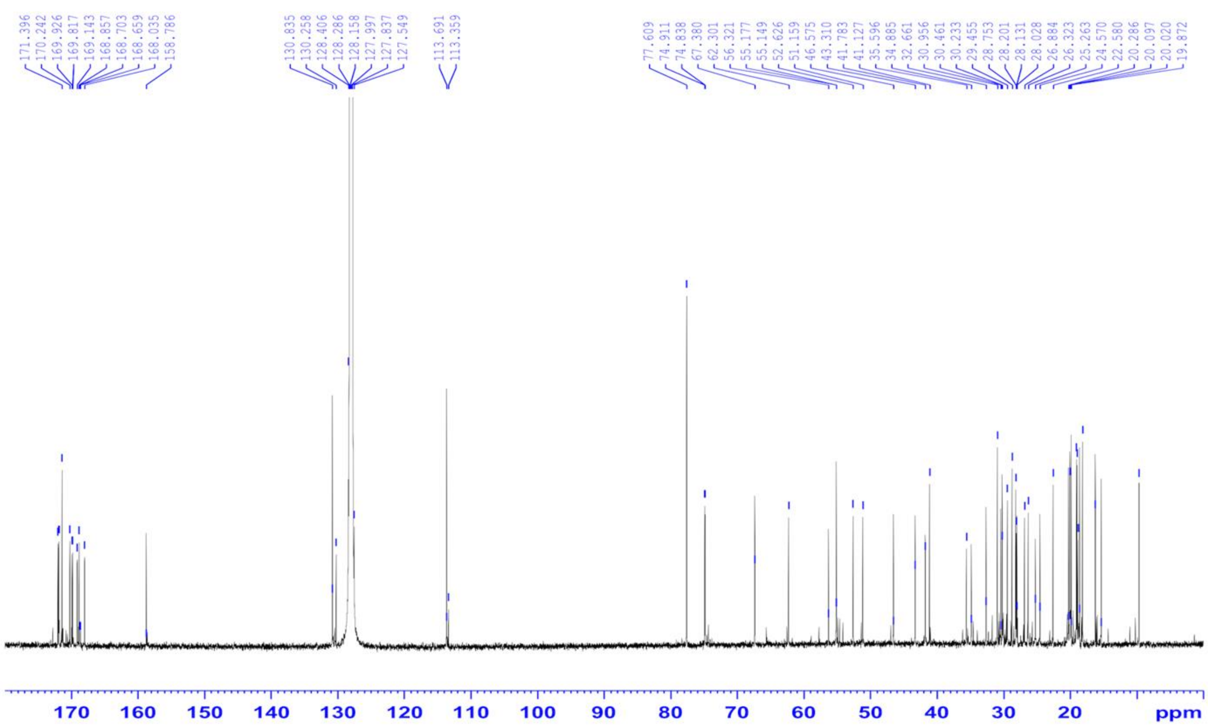
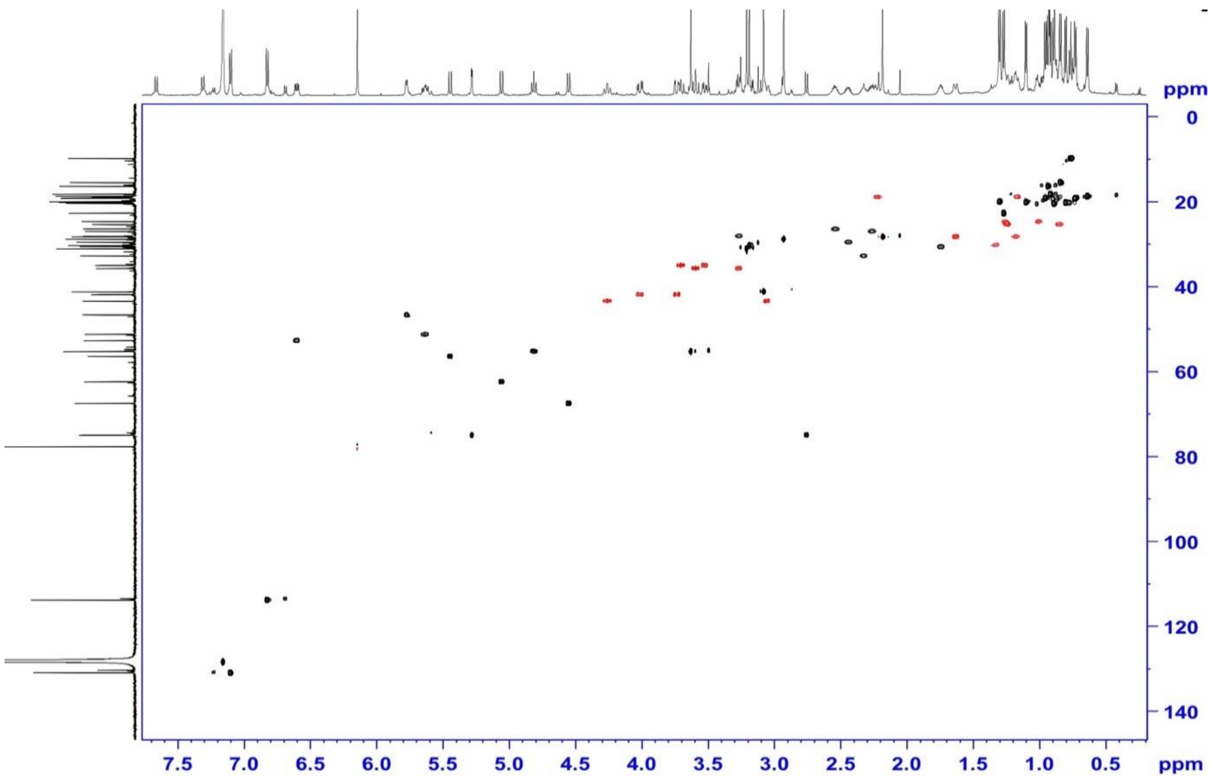


Figure S22. ^{13}C NMR (150 MHz, C_6D_6) spectrum of **5**.



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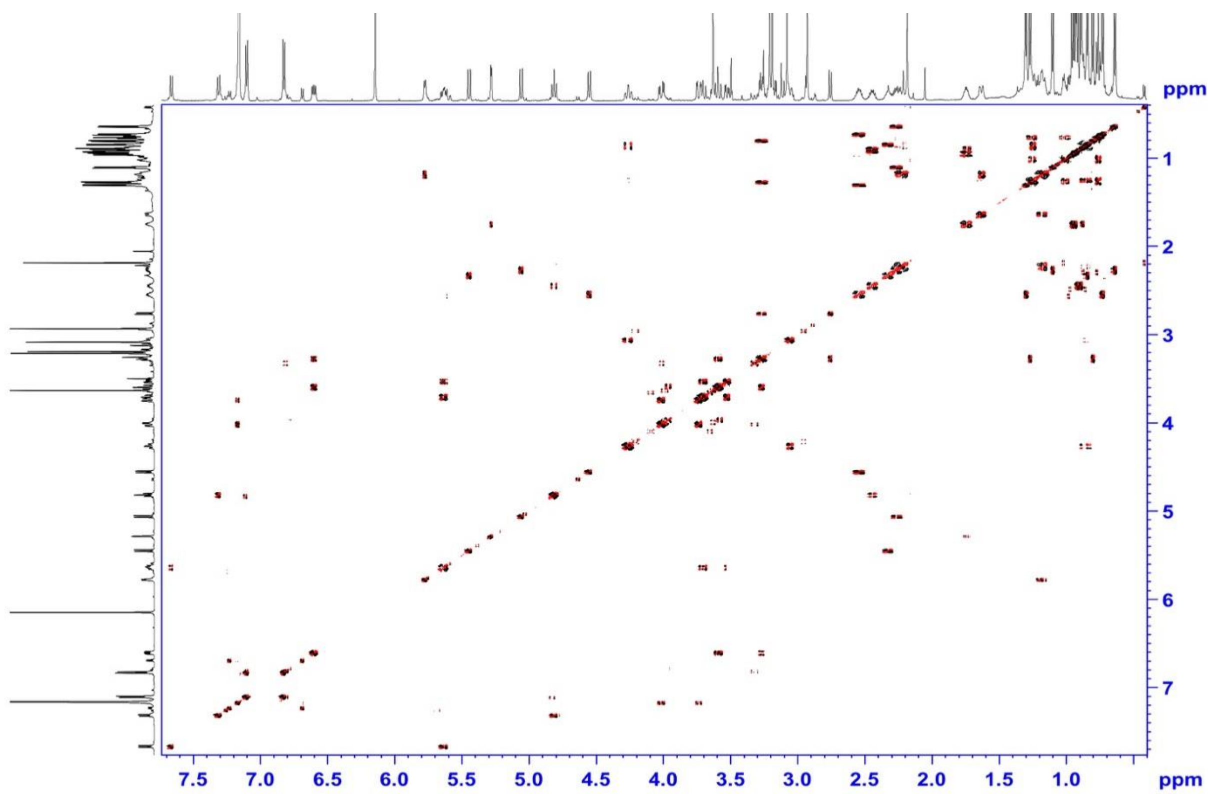


Figure S24. DQF-COSY (600 MHz, C_6D_6) spectrum of **5**.

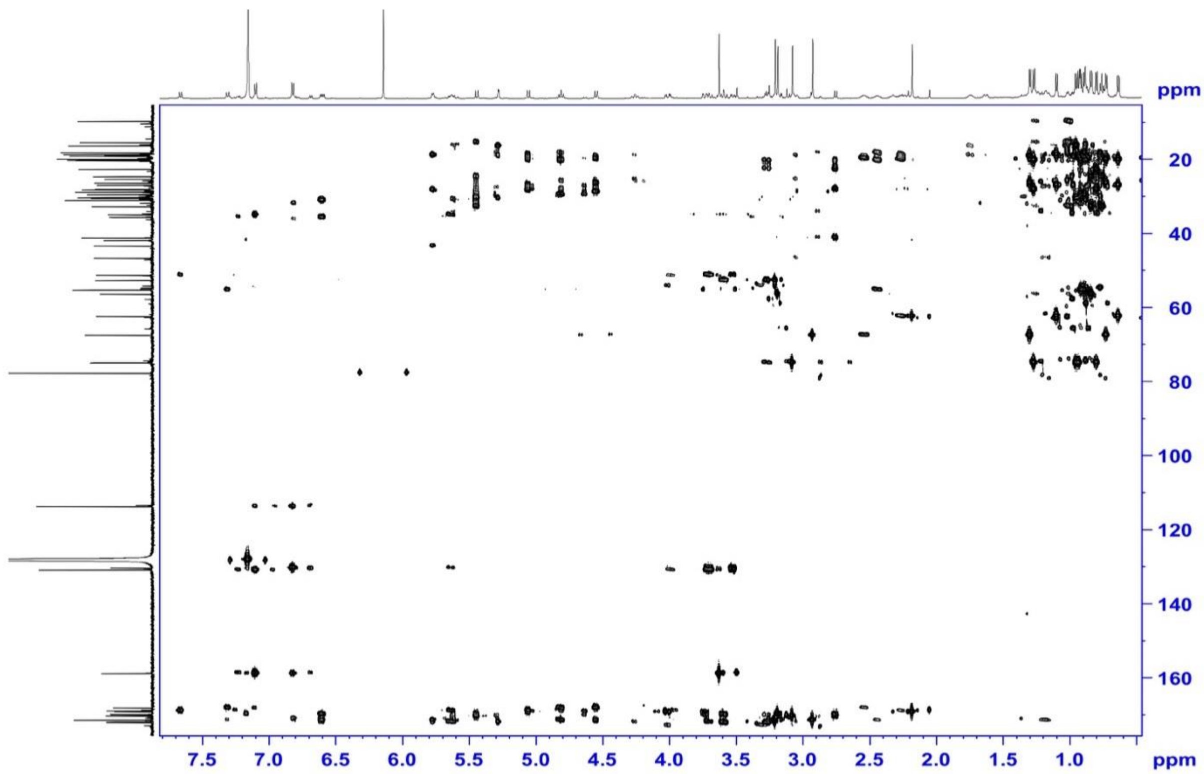
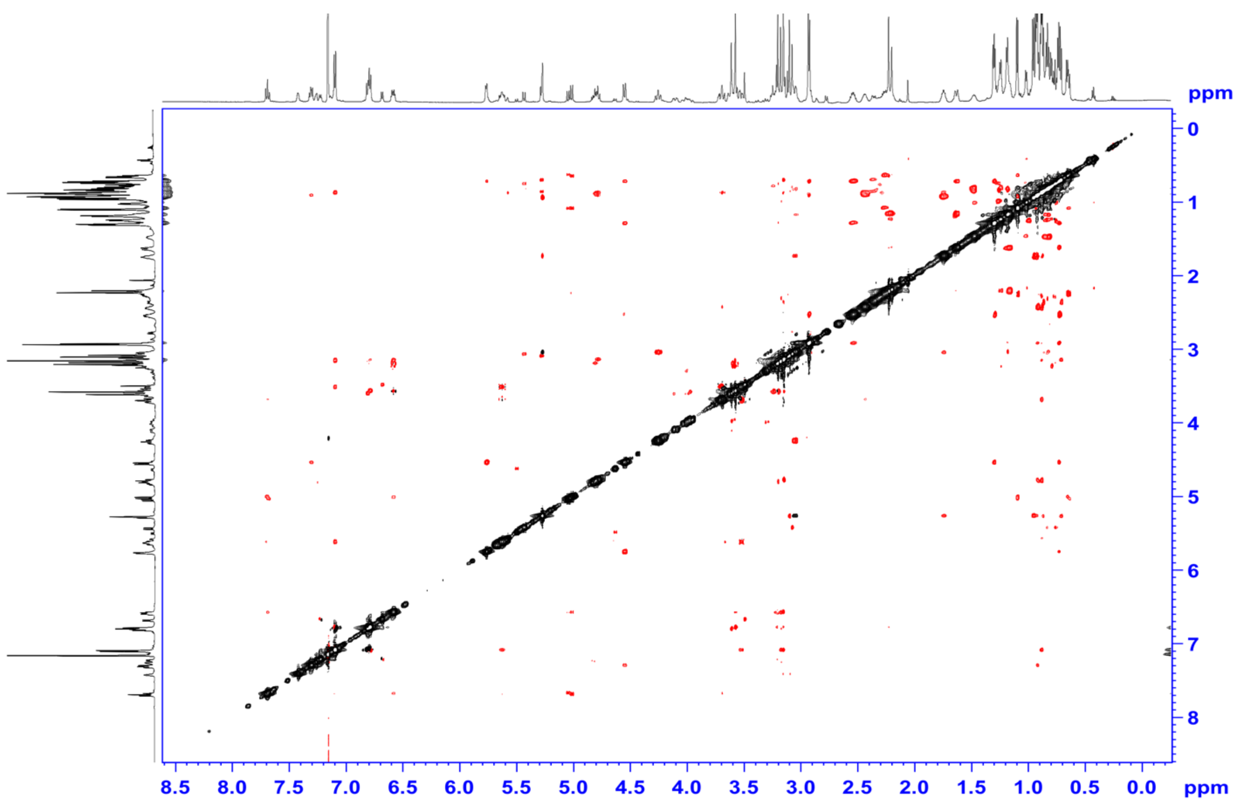


Figure S25. HMBC (600 MHz, C_6D_6) spectrum of **5**.



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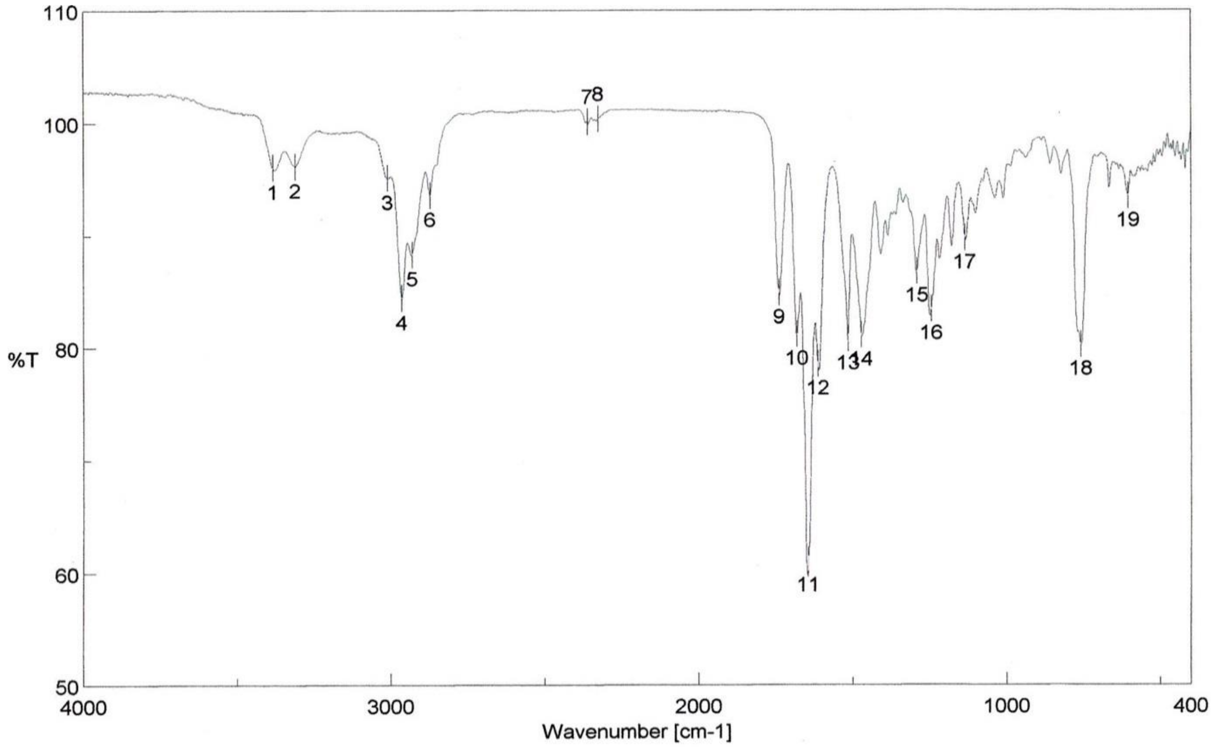


Figure S27. FT IR spectrum of **5** (film).

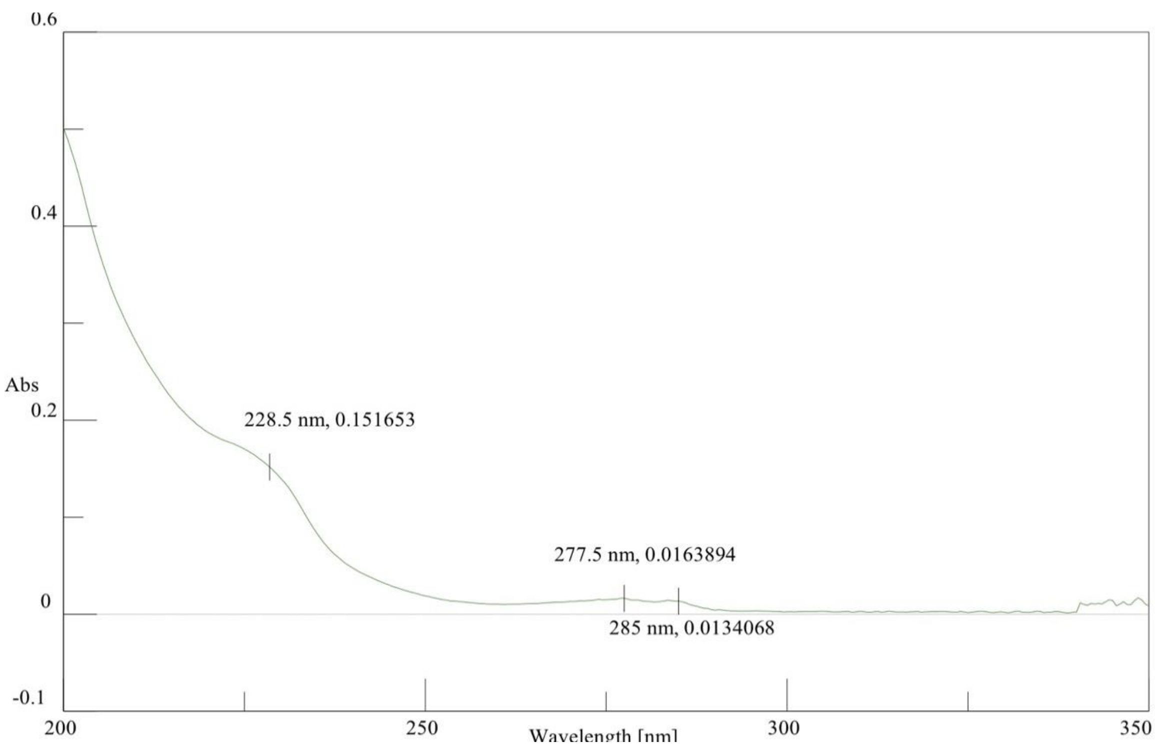
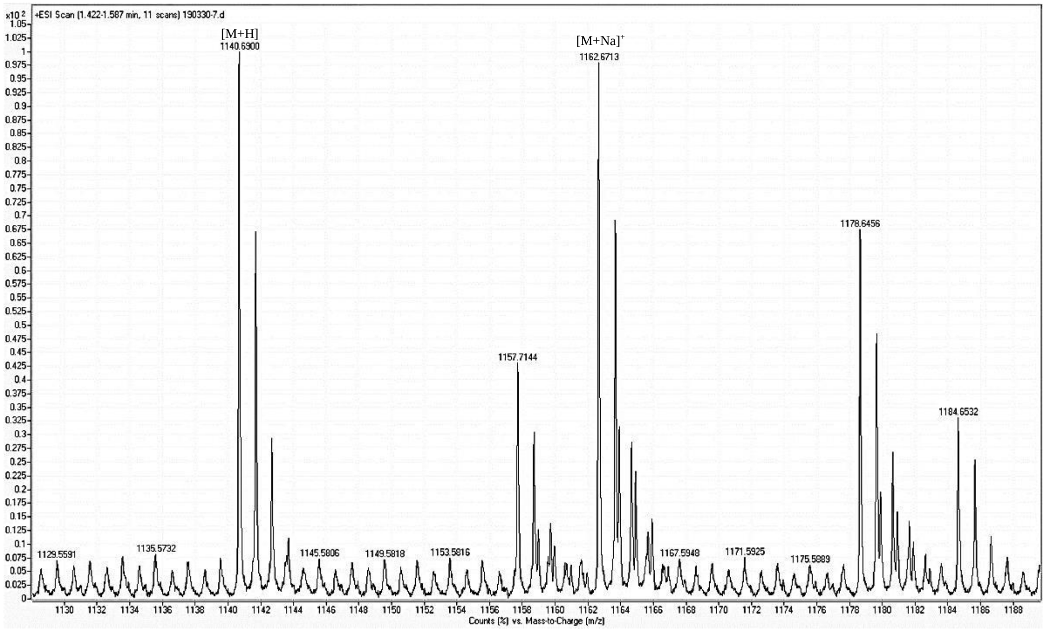


Figure S28. UV spectrum of **5** (10 μM in MeCN).



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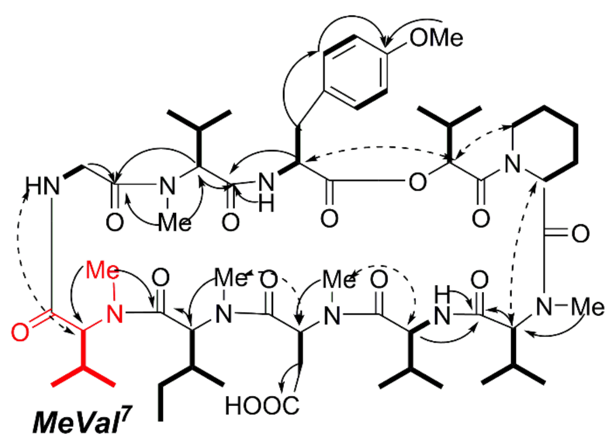


Figure S30. Key COSY (bold bonds), HMBC (arrows) and NOESY (dotted arrow) correlations of **5**.

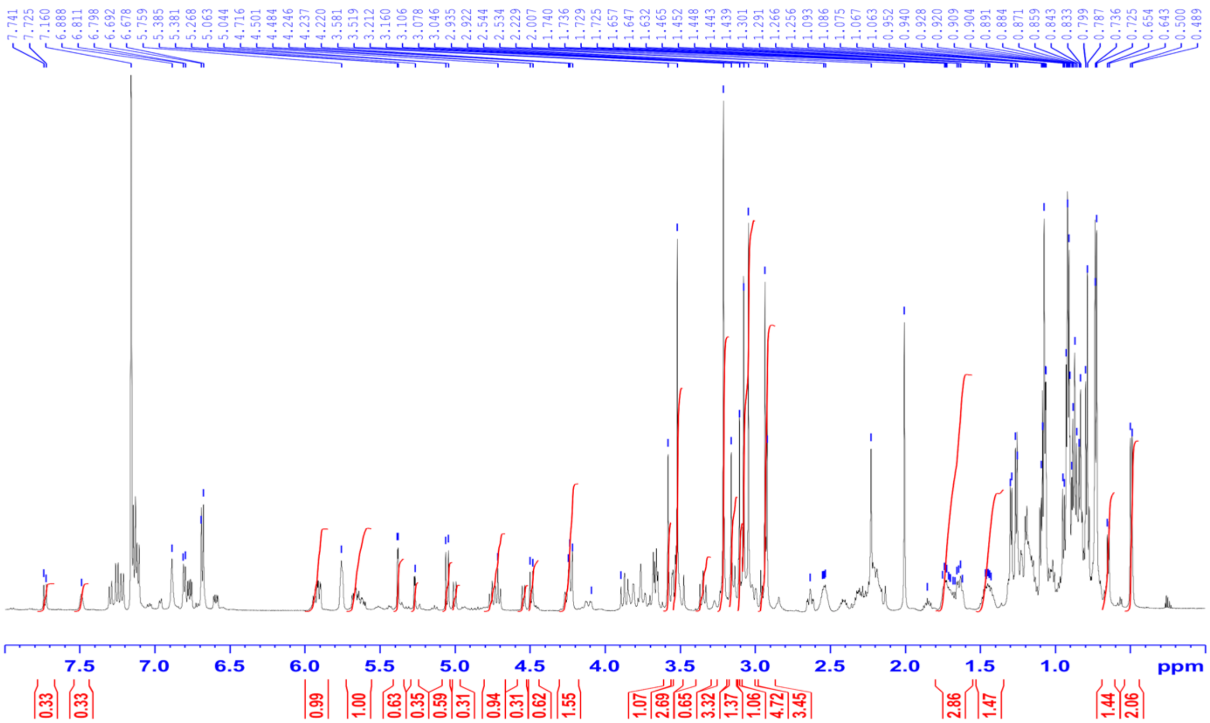


Figure S31. [1]H NMR (600 MHz, C_6D_6) spectrum of **6**.

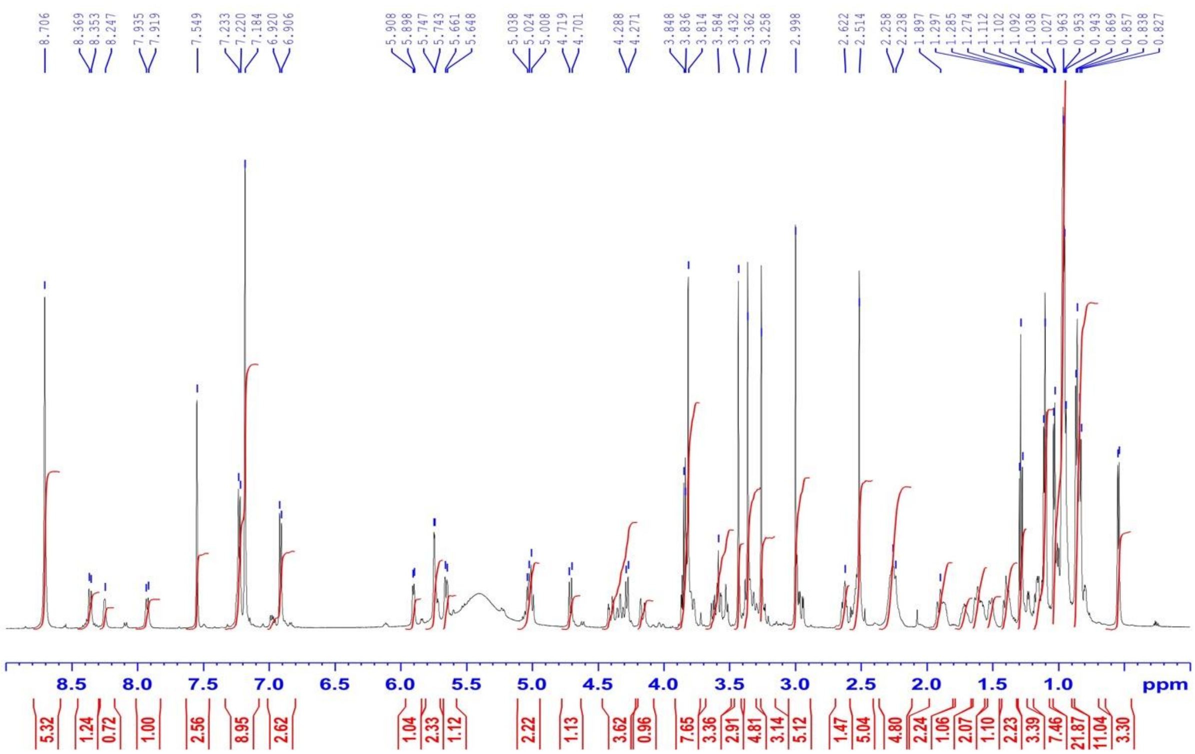


Figure S32. [1]H NMR (600 MHz, Pyridine-d_5) spectrum of **6**.

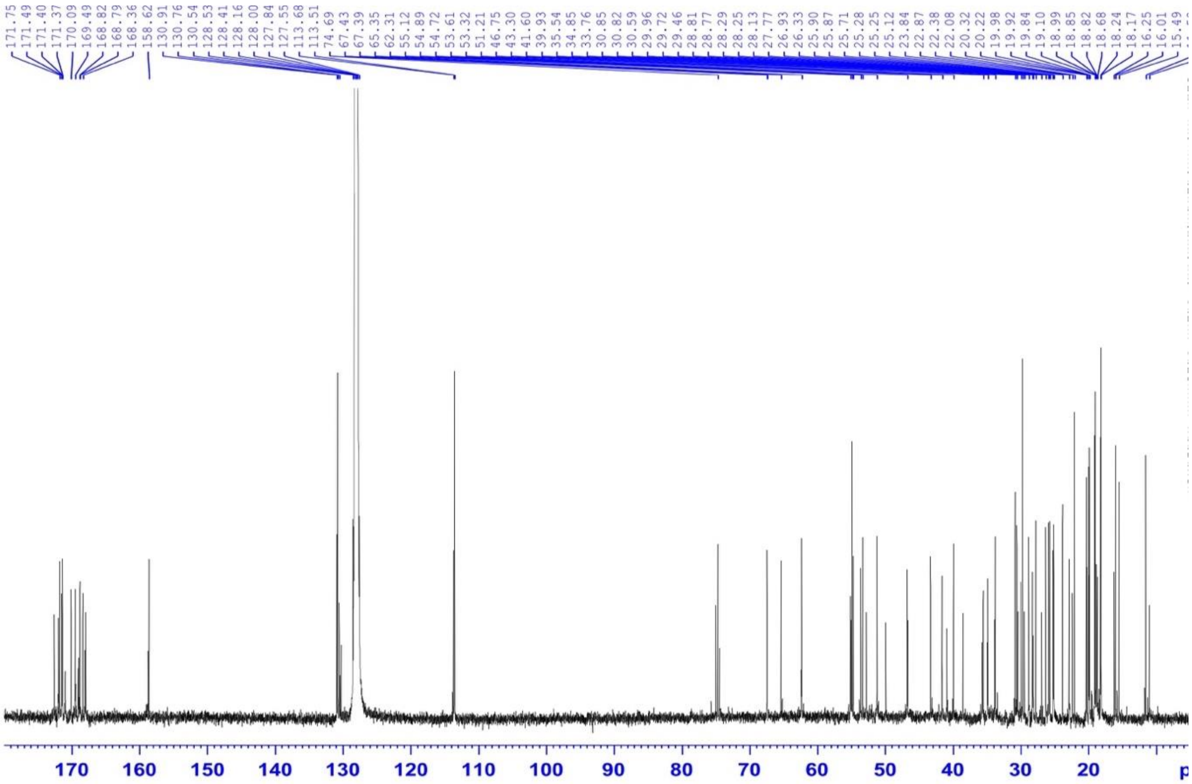
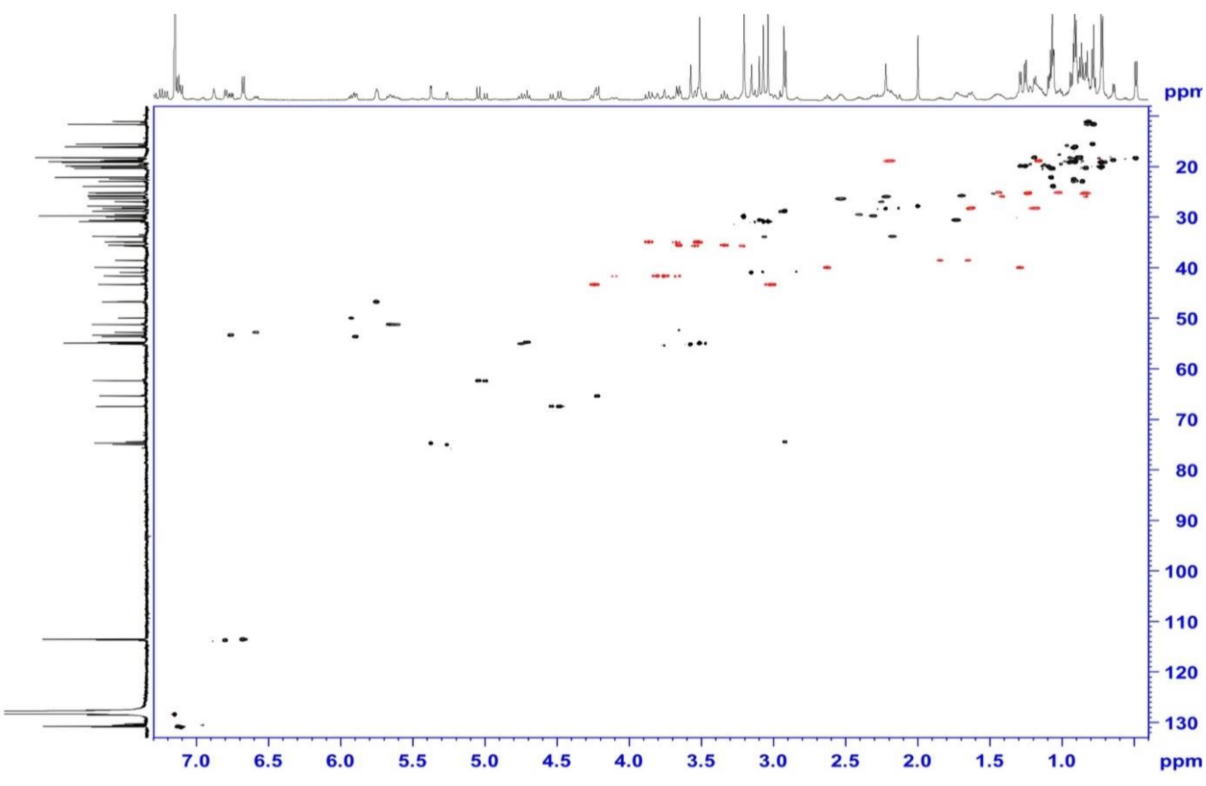


Figure S33. ^{13}C NMR (150 MHz, C_6D_6) spectrum of **6**.



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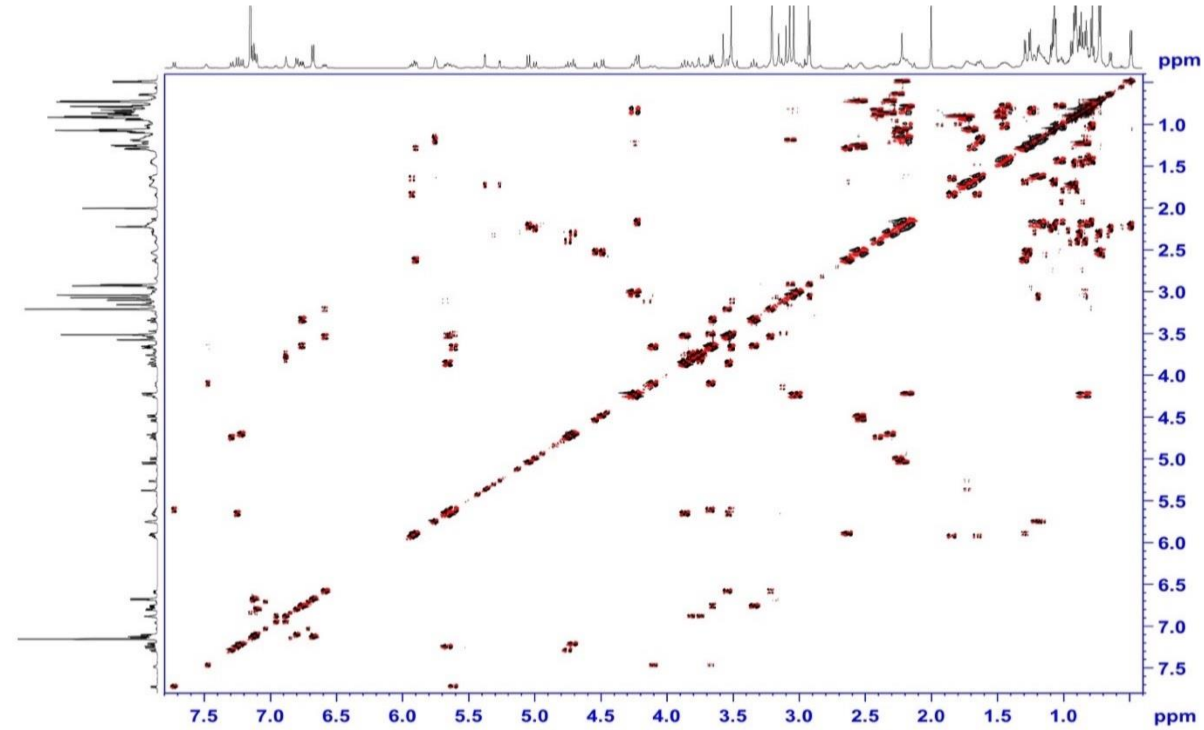


Figure S35. DQF-COSY (600 MHz, C_6D_6) spectrum of **6**.

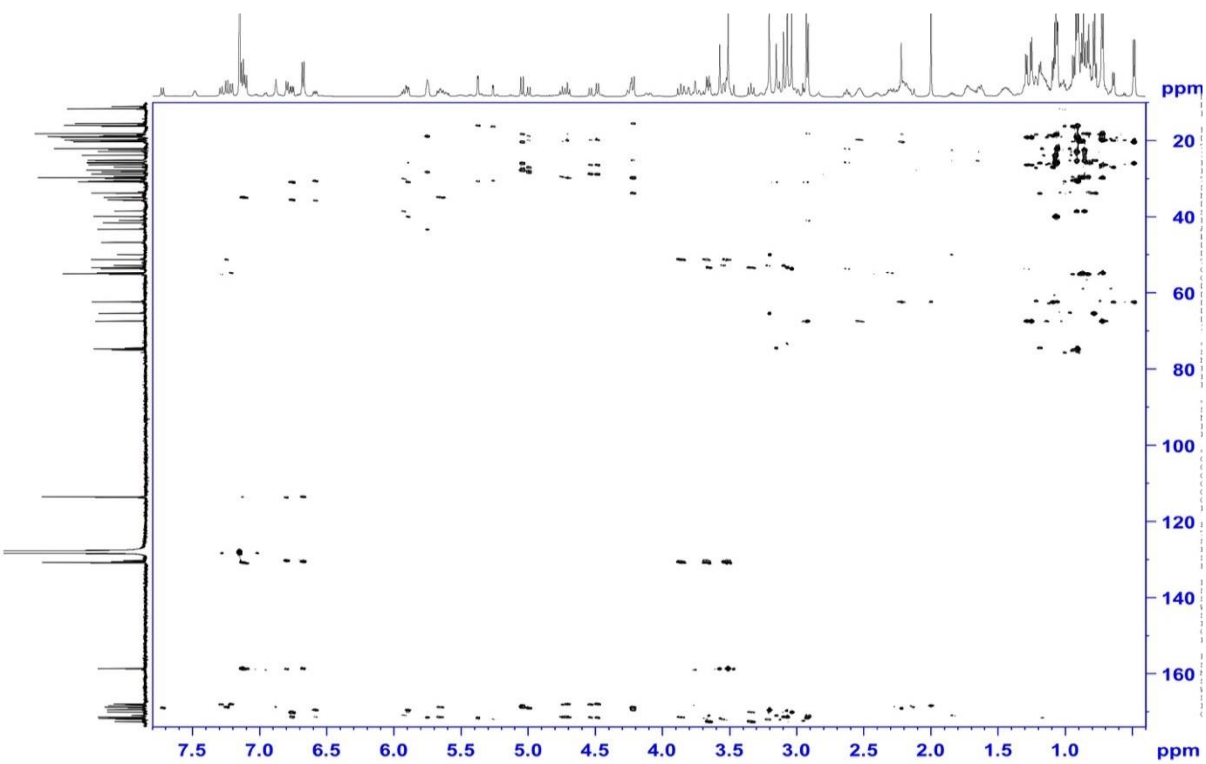
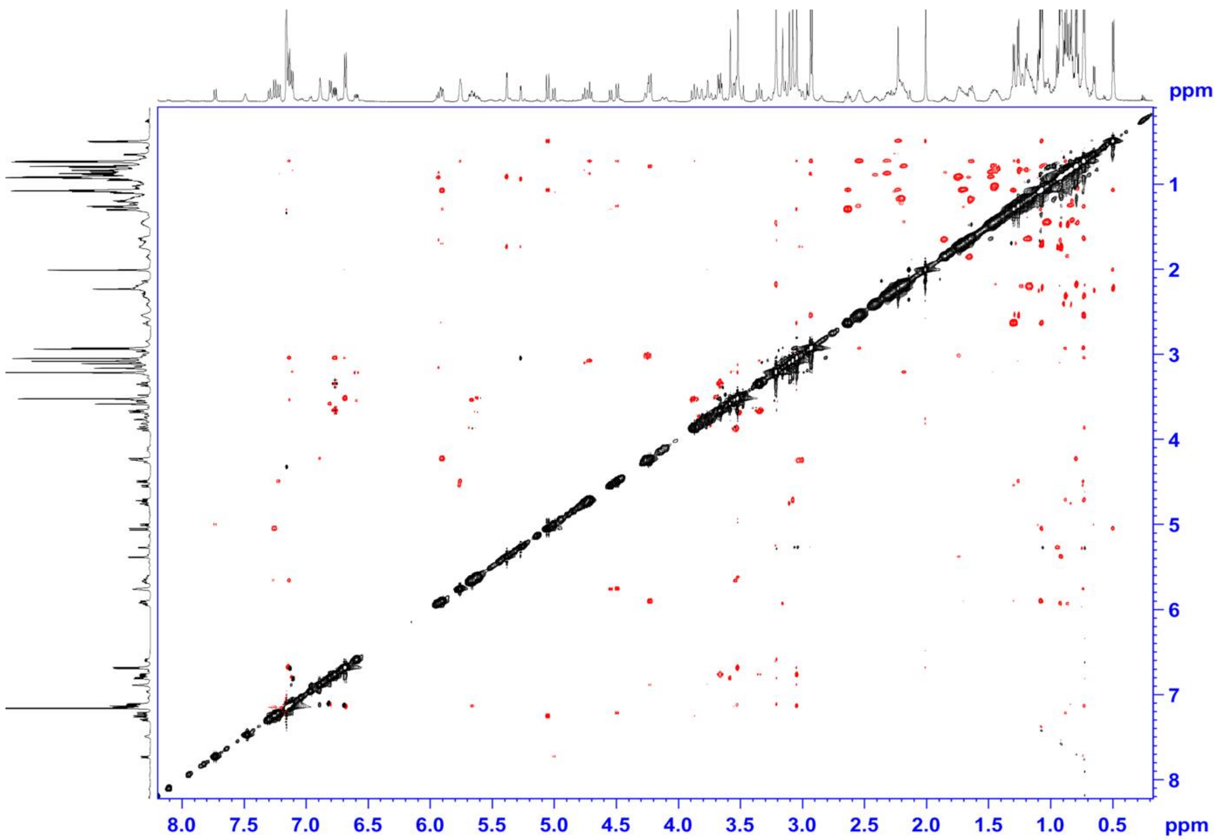


Figure S36. HMBC (600 MHz, C_6D_6) spectrum of **6**.



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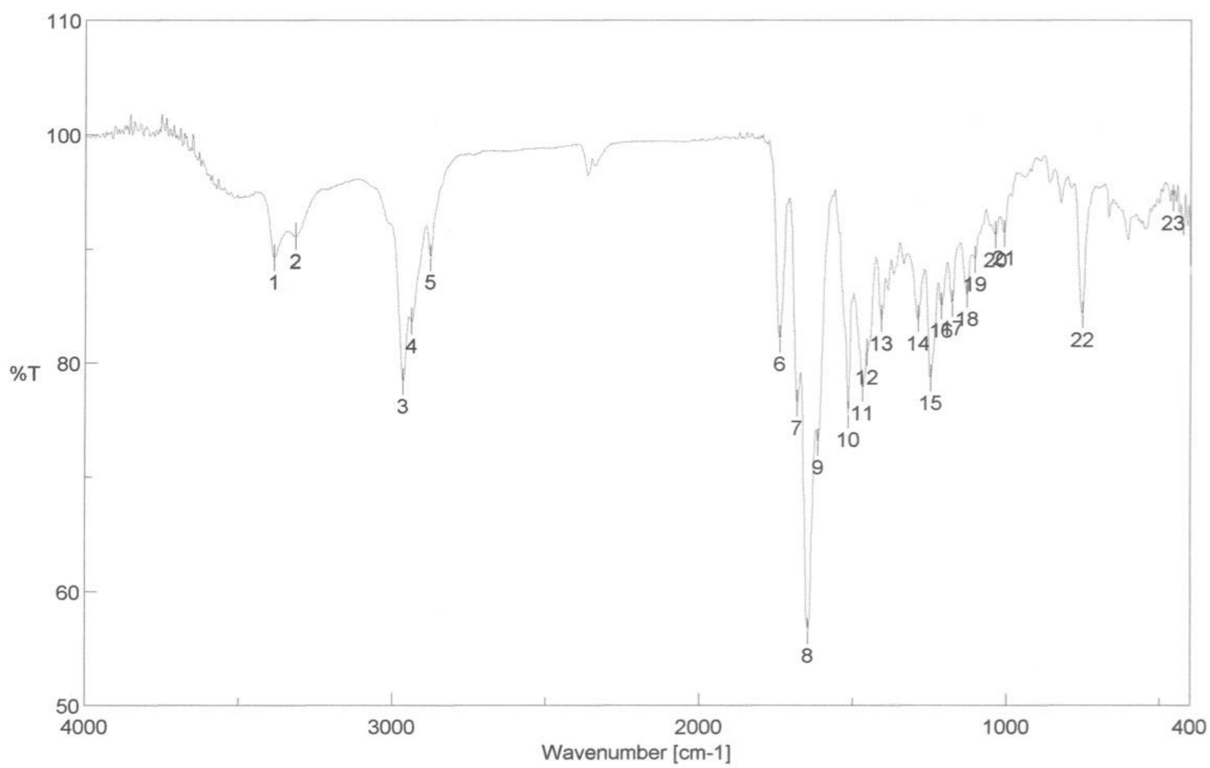


Figure S38. FT IR spectrum of **6** (film).

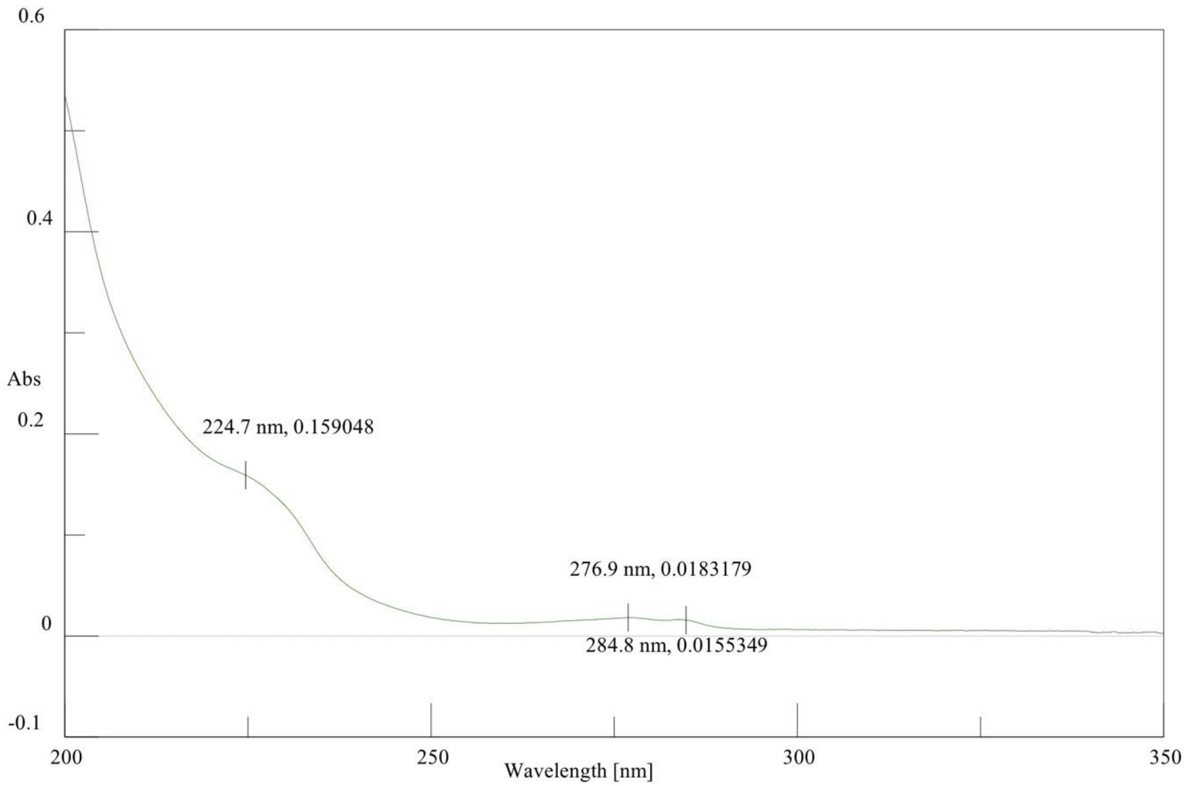


Figure S39. UV spectrum of **6** (10 μM in MeCN).

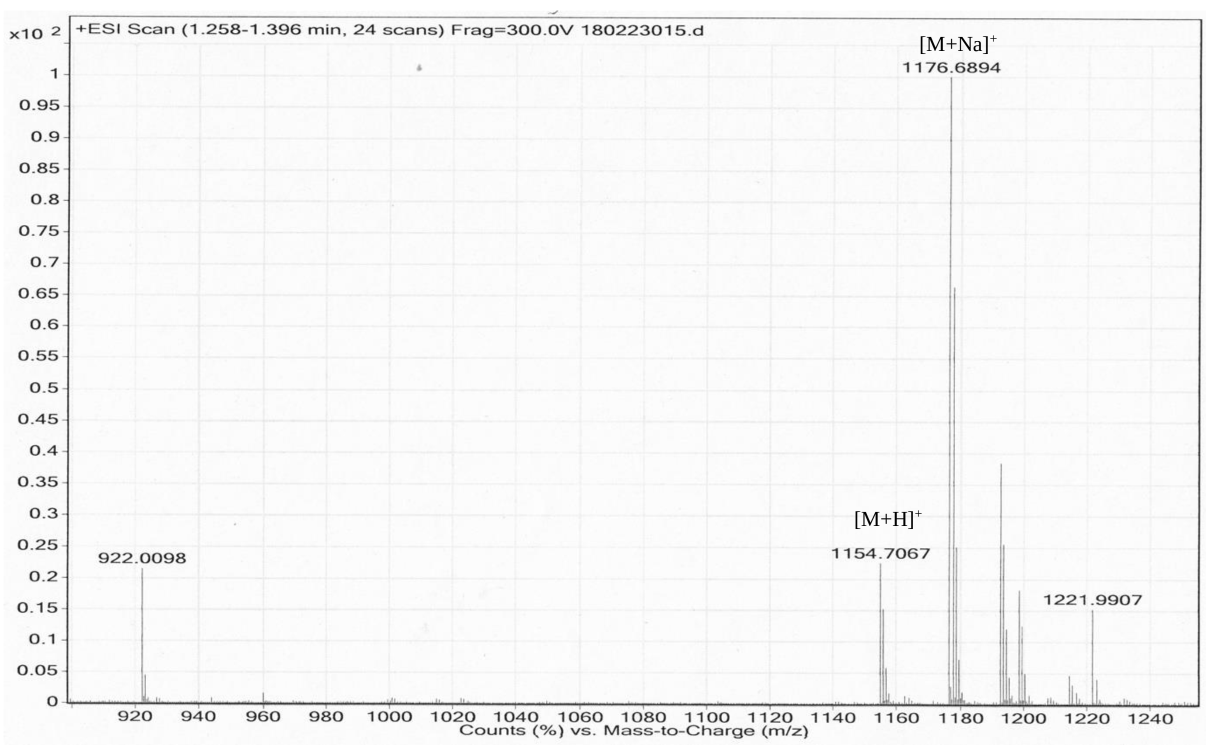


Figure S40. HRESIMS (+) of **6**.

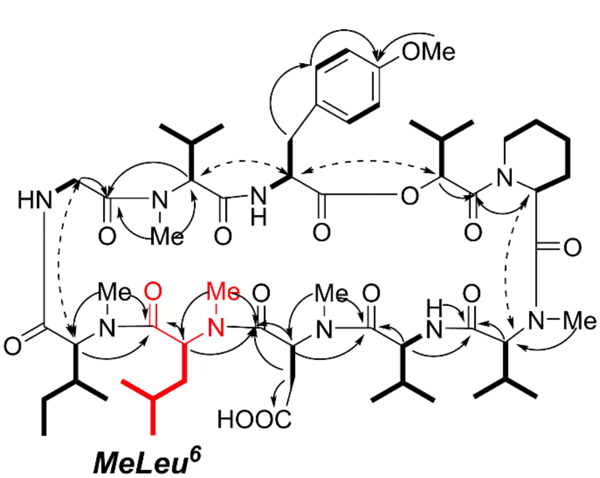


Figure S41. Key COSY (bold bonds), HMBC (arrows) and NOESY (dotted arrow) correlations of **6**.

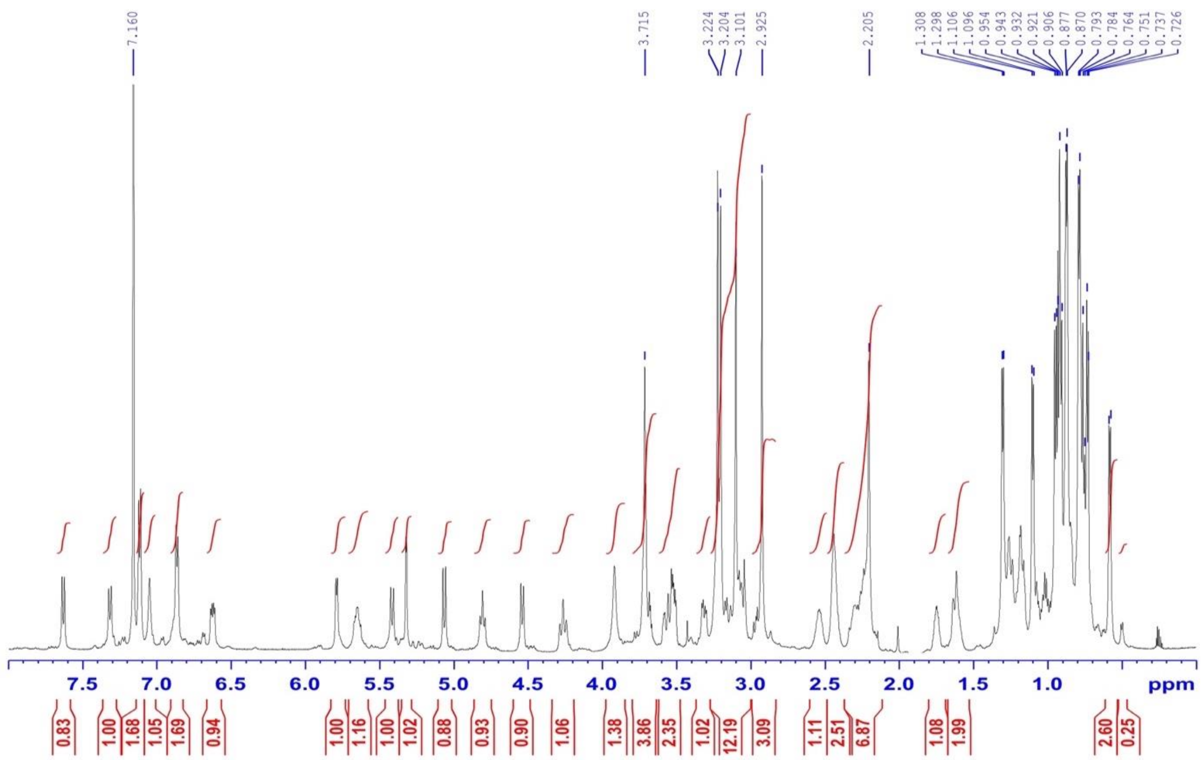


Figure S42. ^1H NMR (600 MHz, C_6D_6) spectrum of **7**.

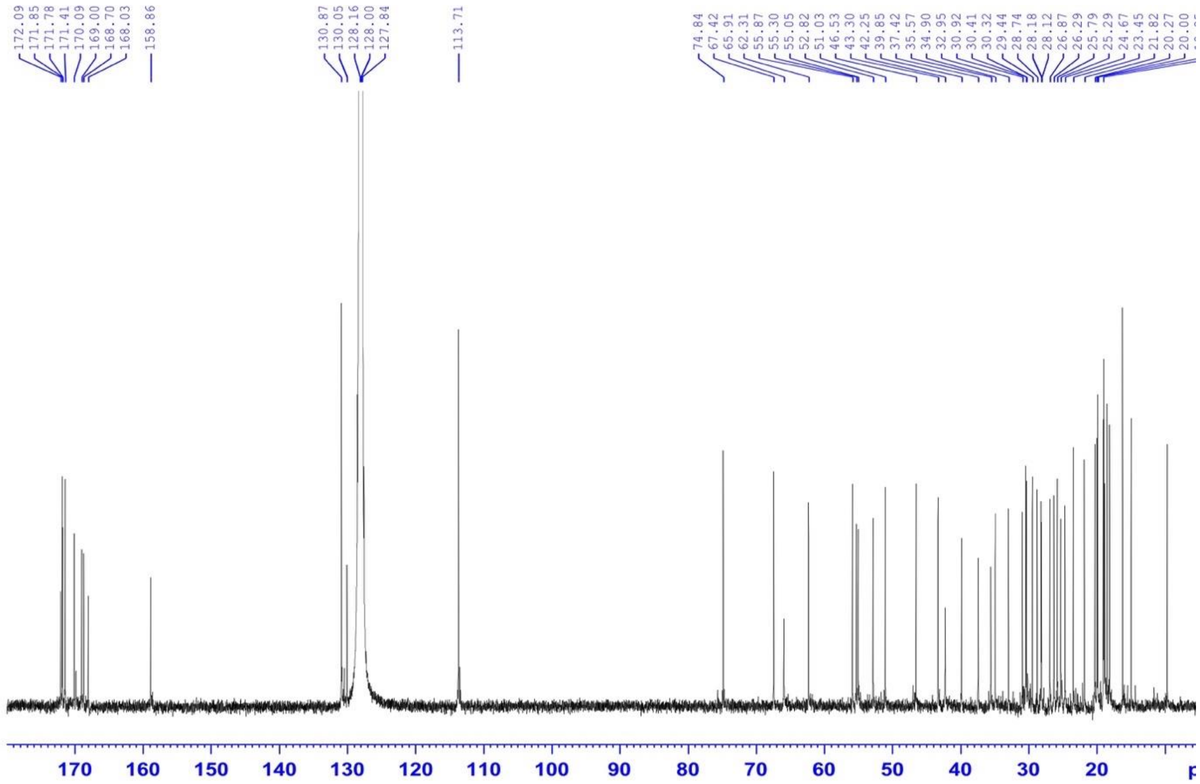


Figure S43. ^{13}C NMR (150 MHz, C_6D_6) spectrum of **7**.

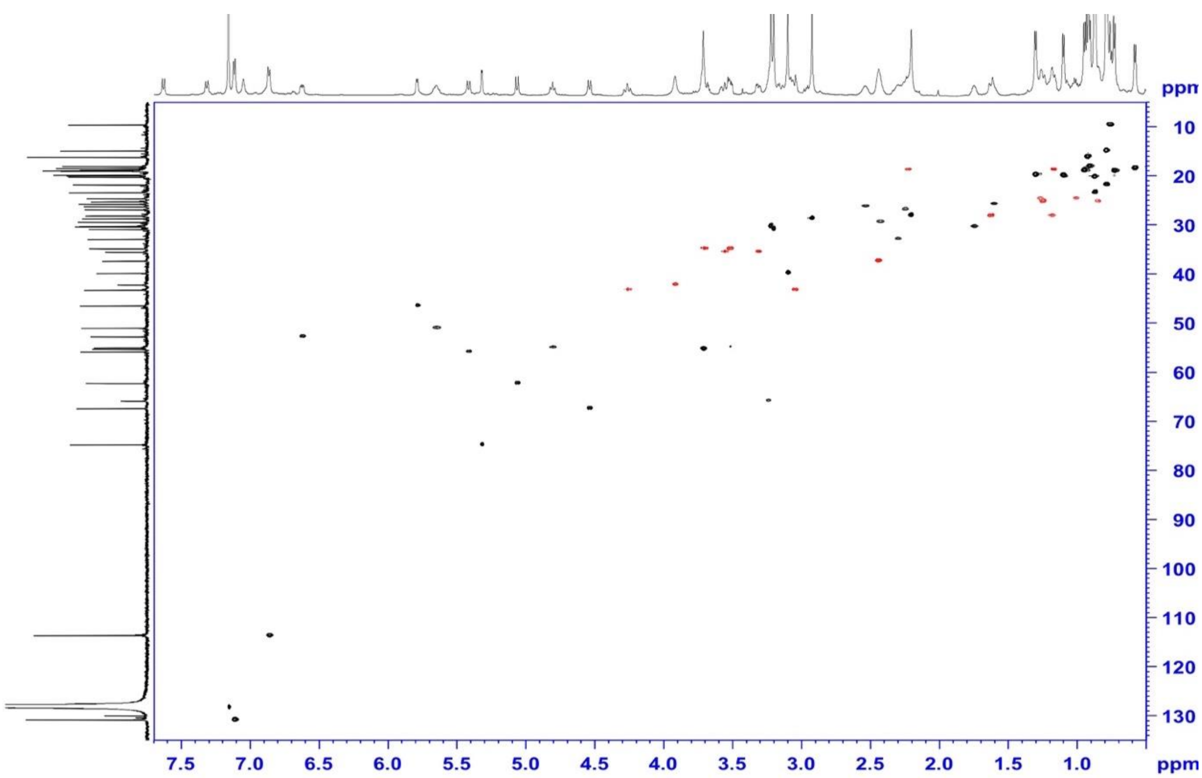


Figure S44. HSQC (600 MHz, C_6D_6) spectrum of **7**.

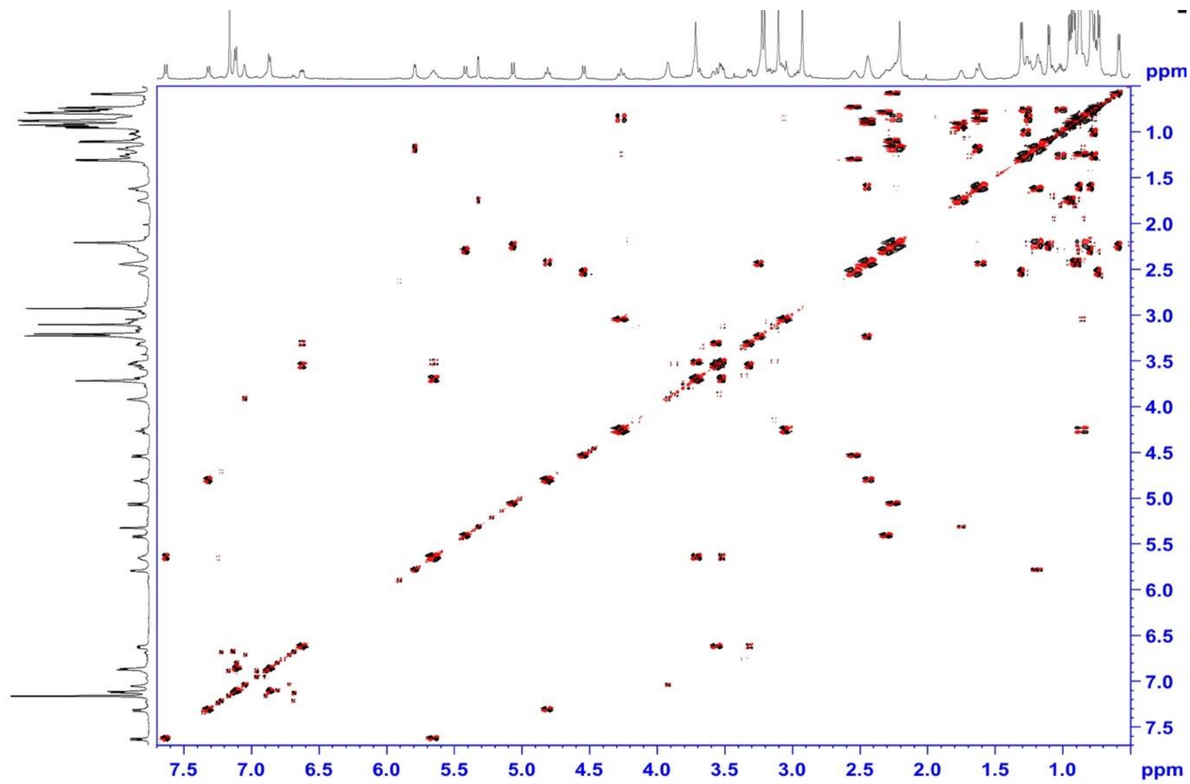


Figure S45. DQF-COSY (600 MHz, C_6D_6) spectrum of **7**.

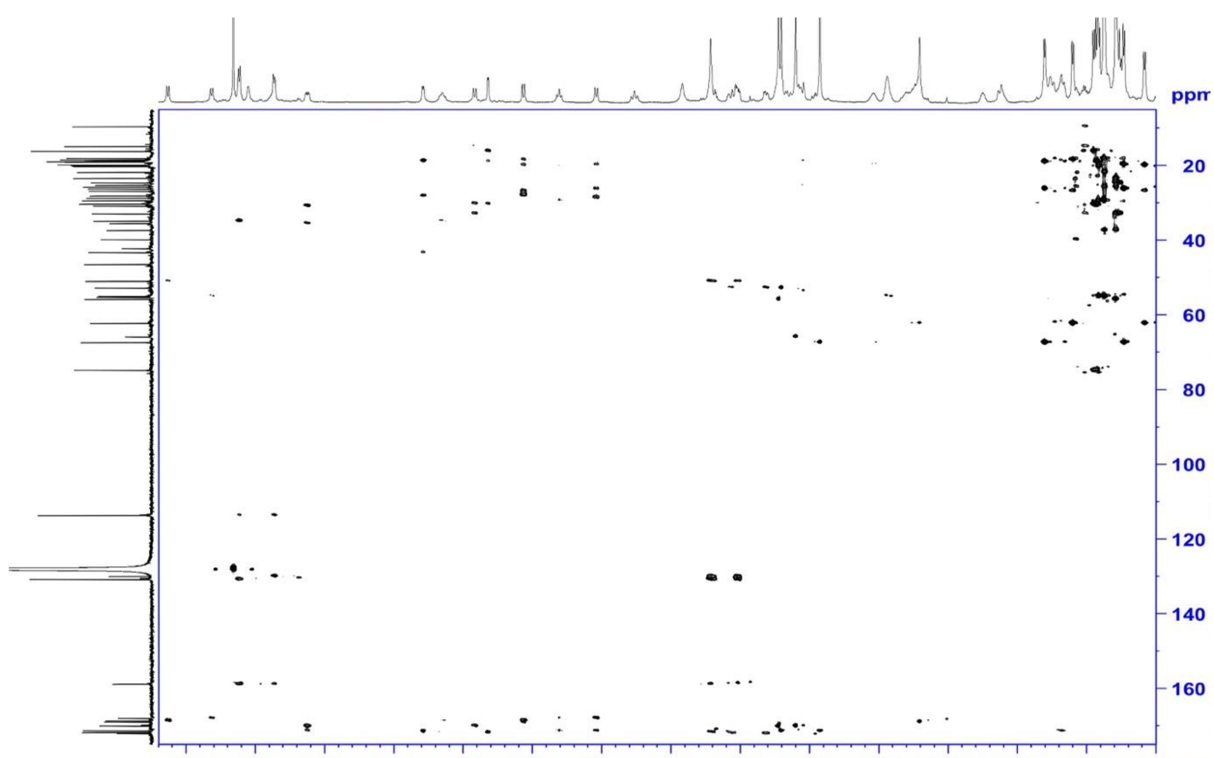


Figure S46. HMBC (600 MHz, C_6D_6) spectrum of **7**.

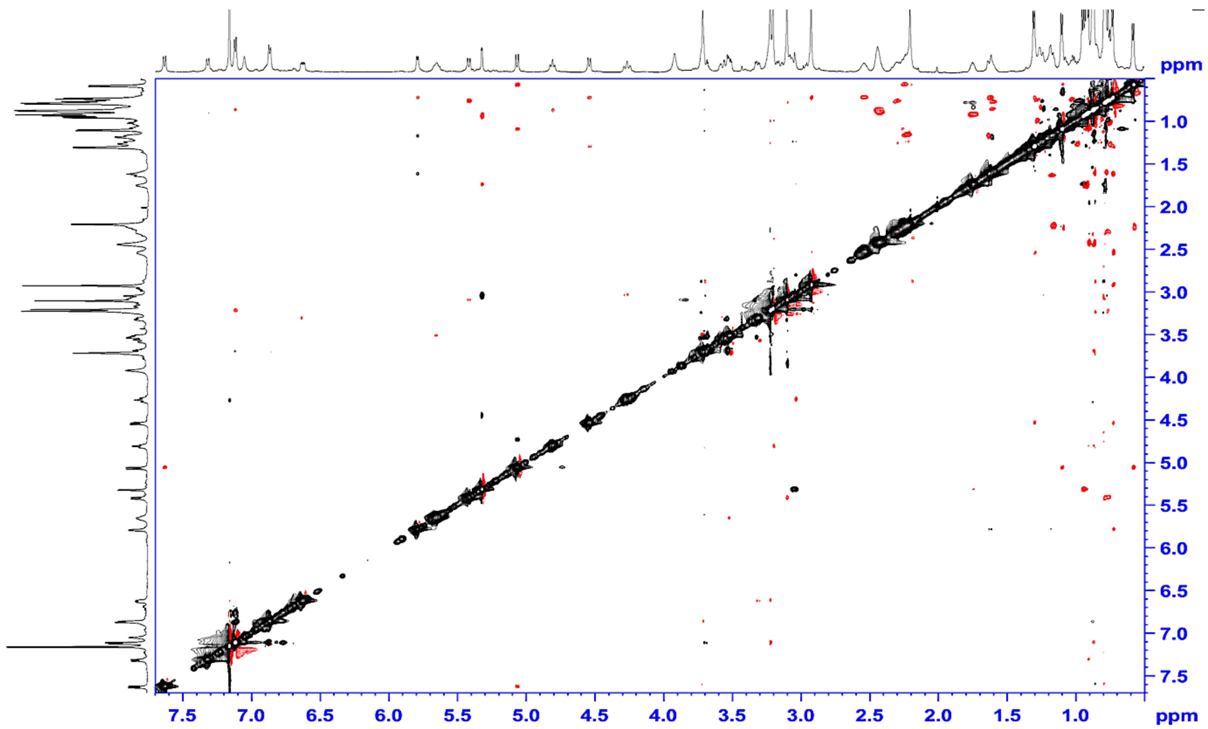


Figure S47. NOESY (600 MHz, C_6D_6) spectrum of **7**.

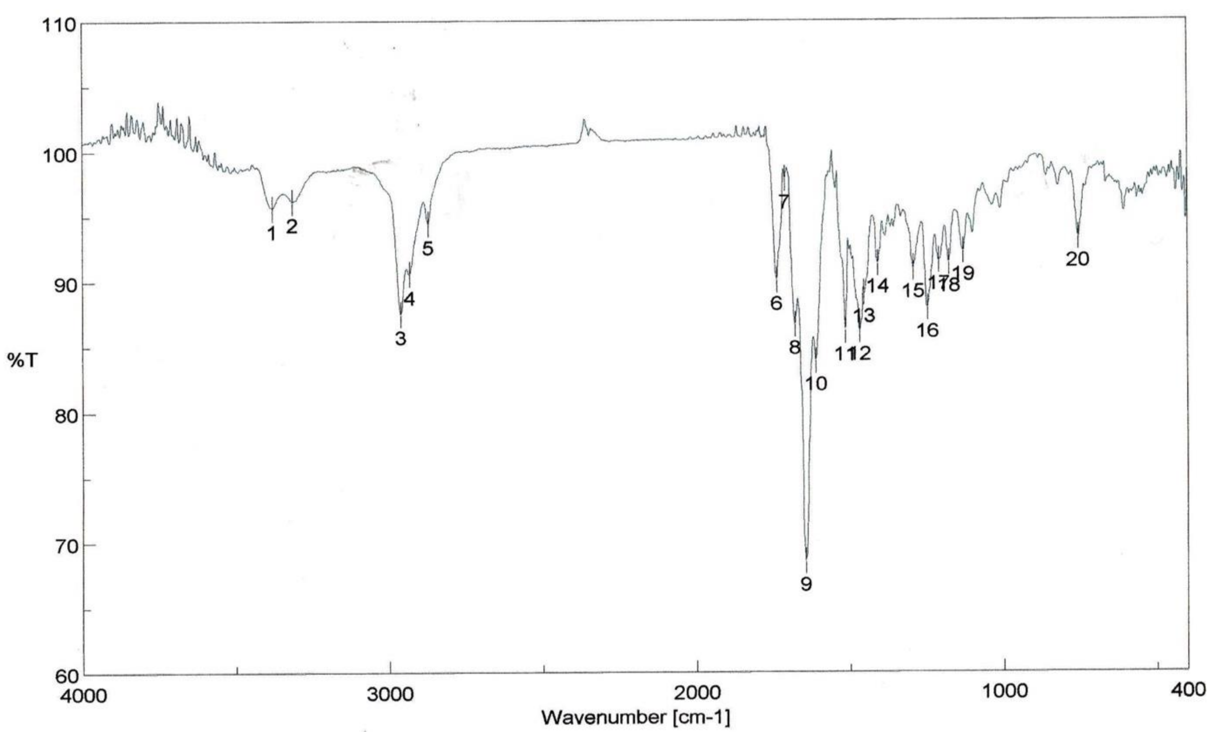


Figure S48. FT IR spectrum of **7** (film).

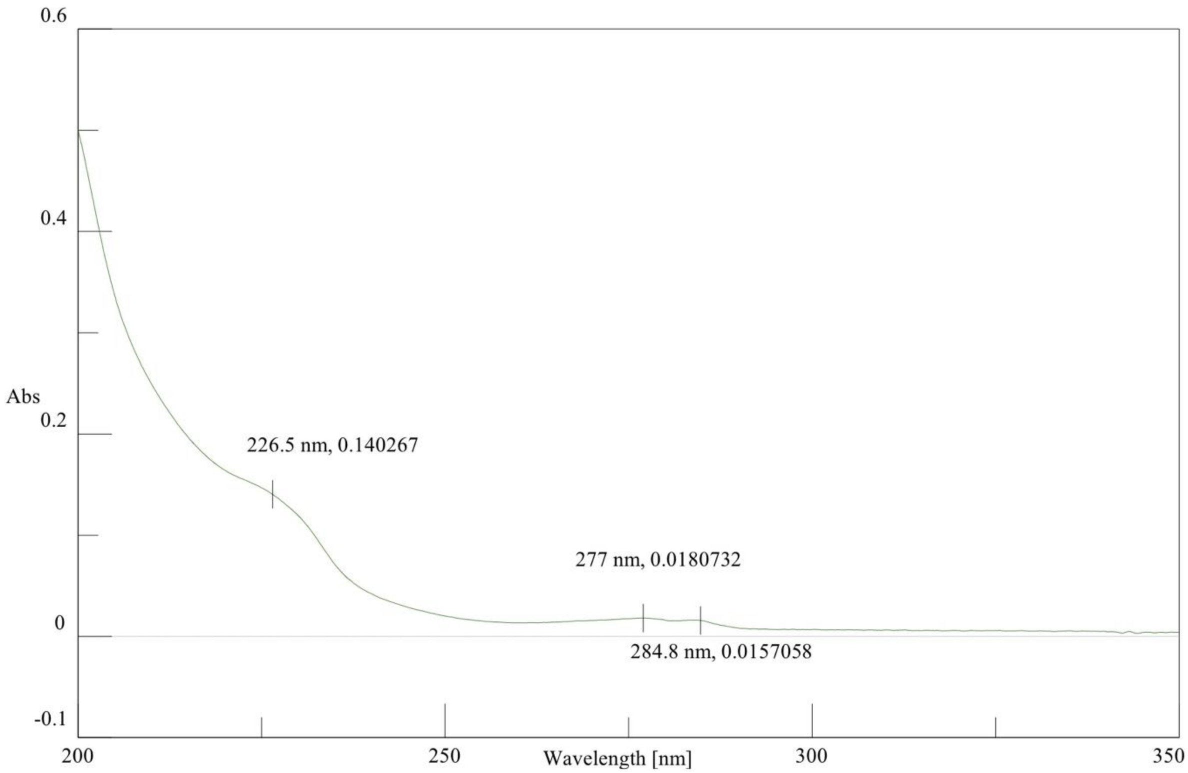


Figure S49. UV spectrum of **7** (10 μM in MeCN).

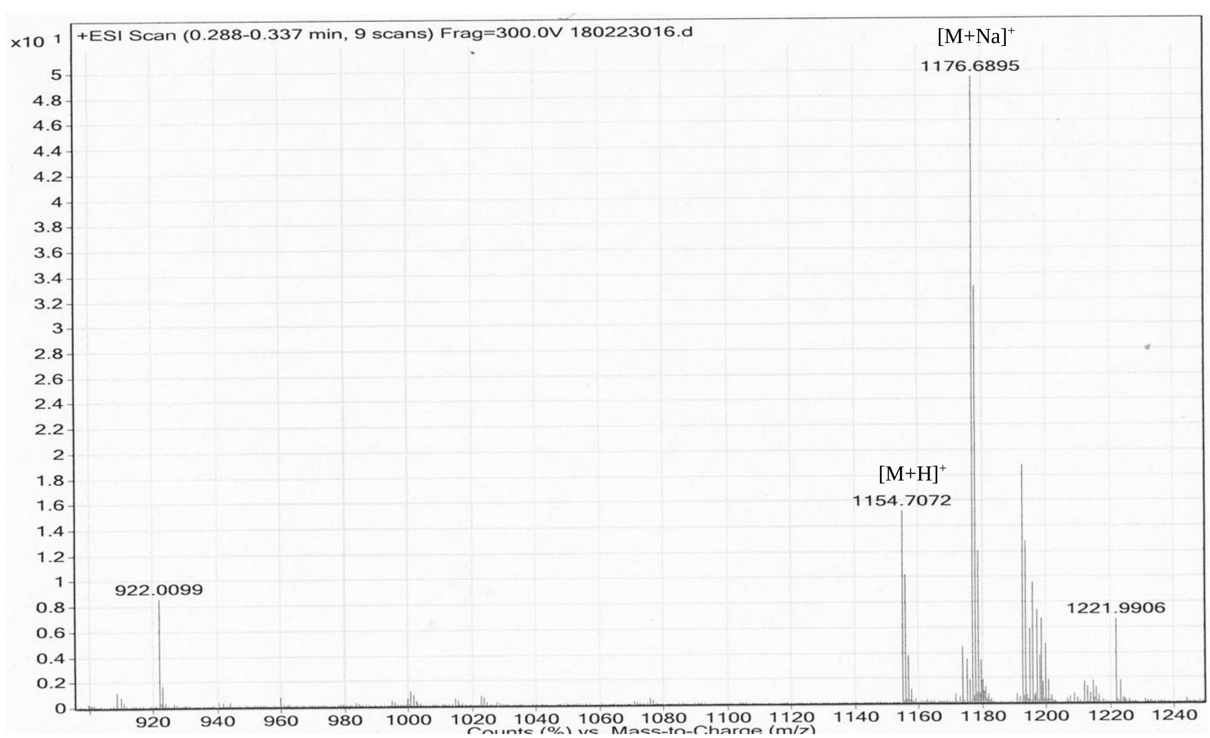


Figure S50. HRESIMS (+) of **7**.

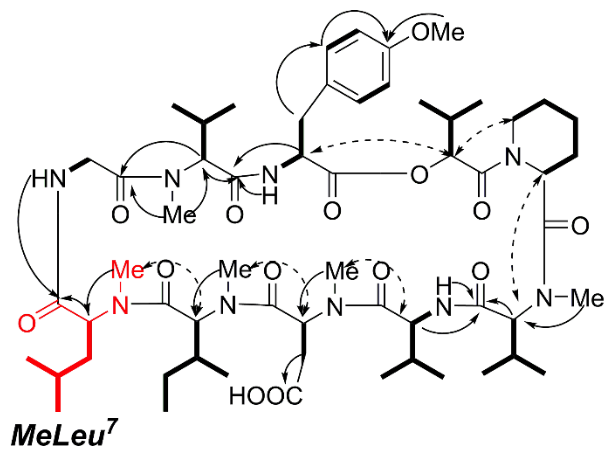


Figure S51. Key COSY (bold bonds), HMBC (arrows) and NOESY (dotted arrow) correlations of **7**.

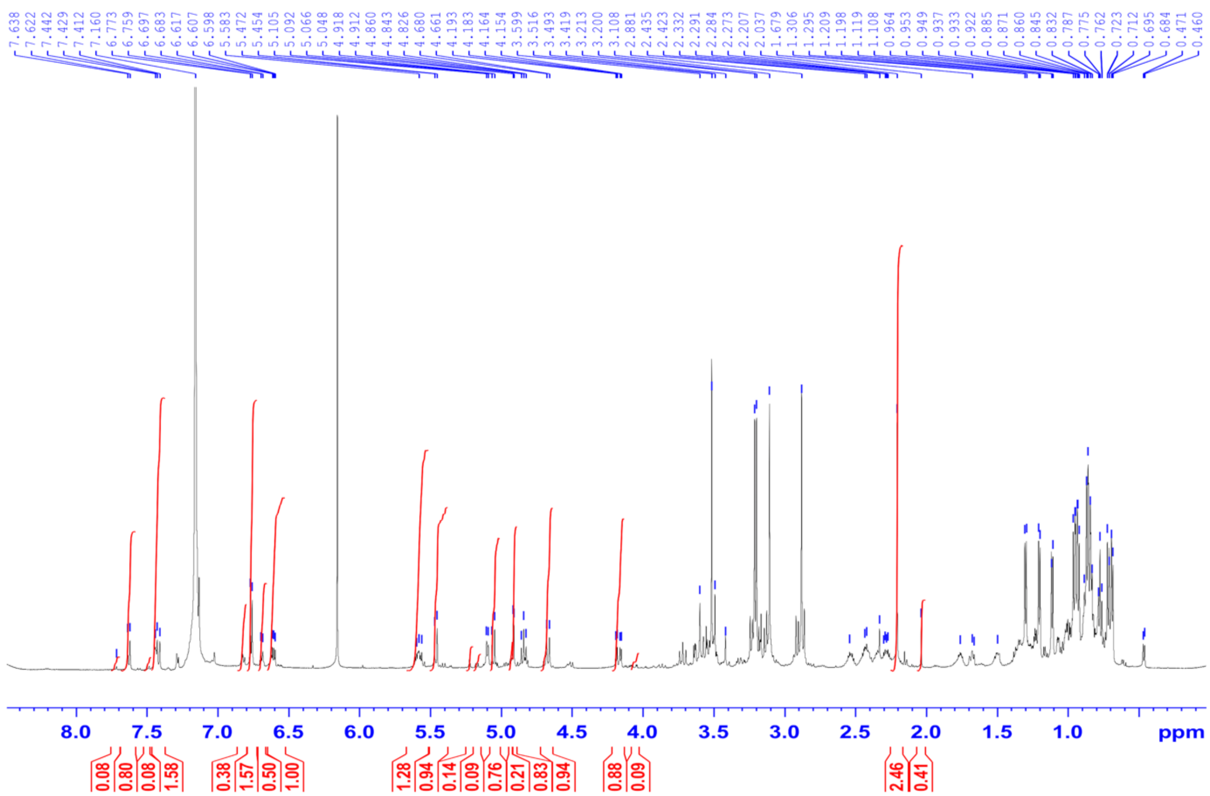


Figure S52. ^{1}H NMR (600 MHz, C6D6) spectrum of **8**.

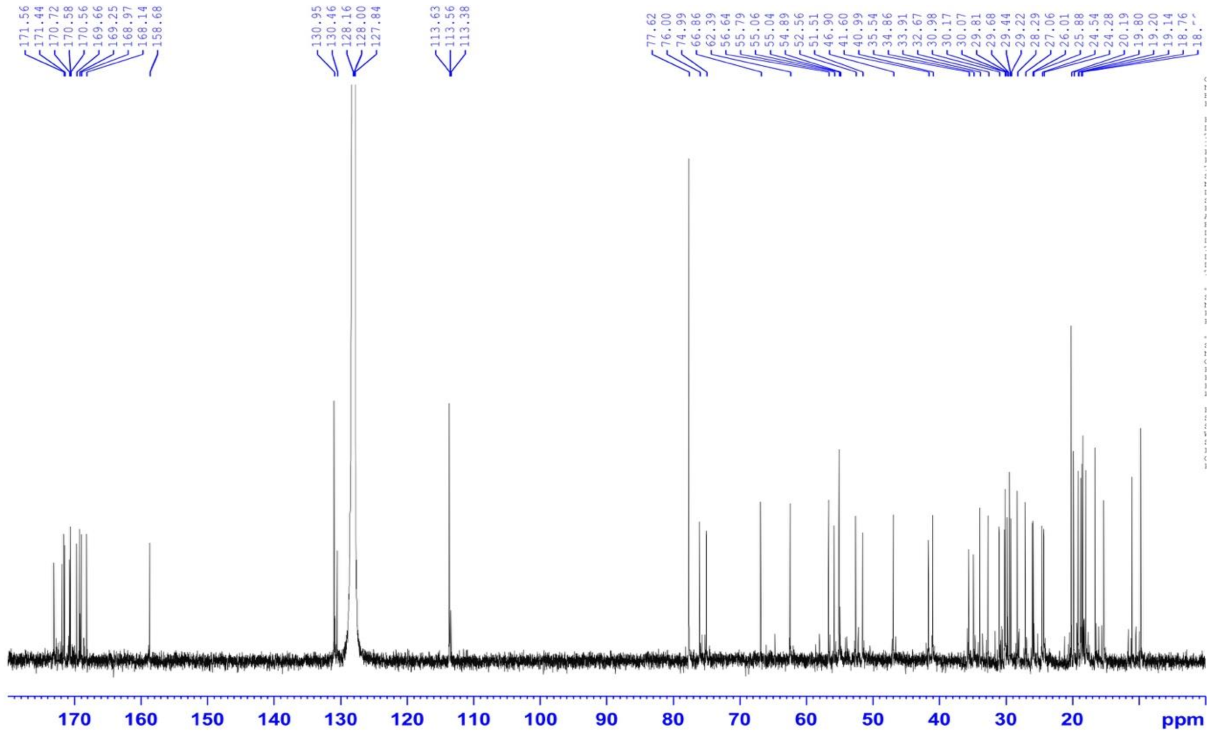


Figure S53. ^{13}C NMR (150 MHz, C_6D_6) spectrum of **8**.

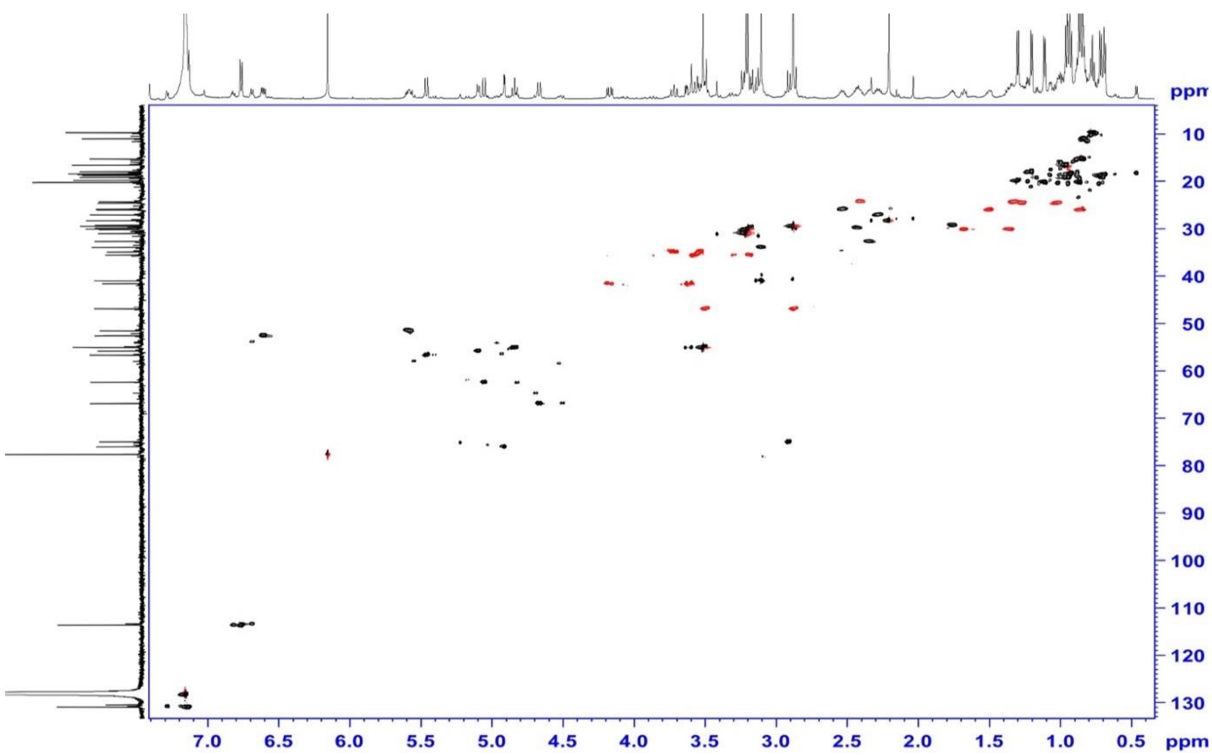


Figure S54. HSQC (600 MHz, C_6D_6) spectrum of **8**.

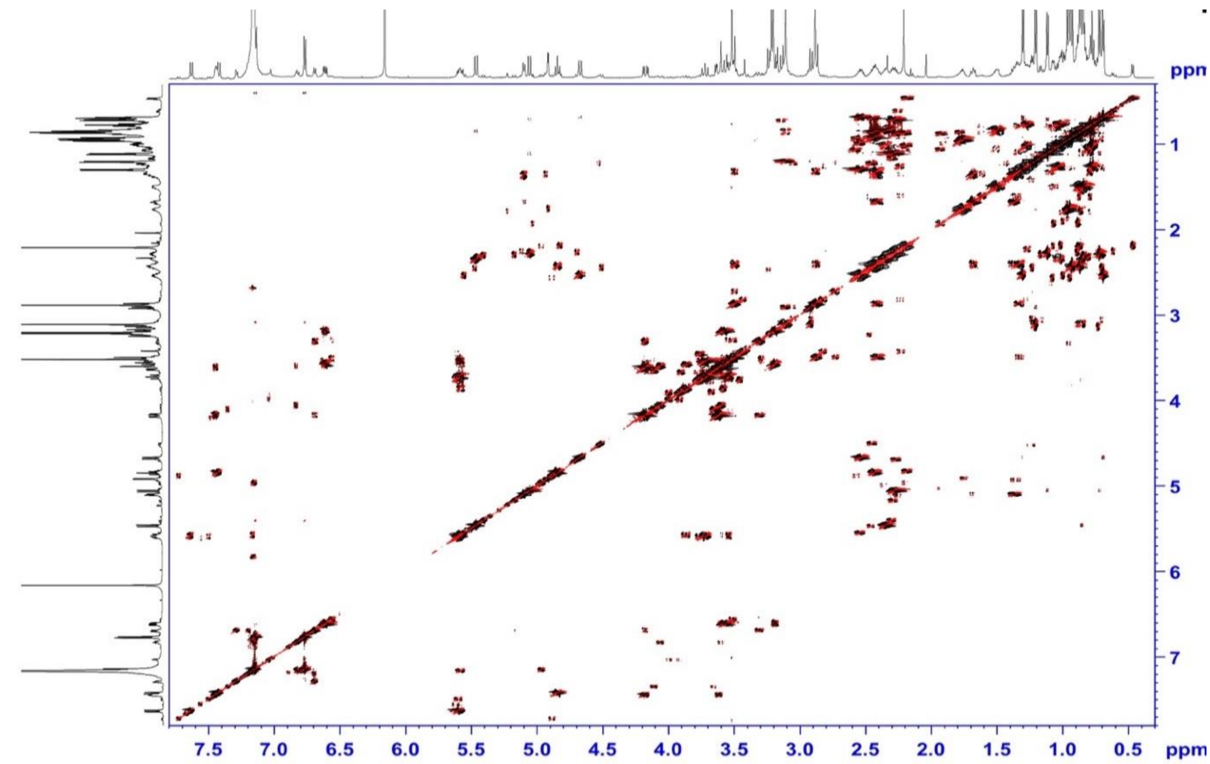


Figure S55. DQF-COSY (600 MHz, C_6D_6) spectrum of **8**.

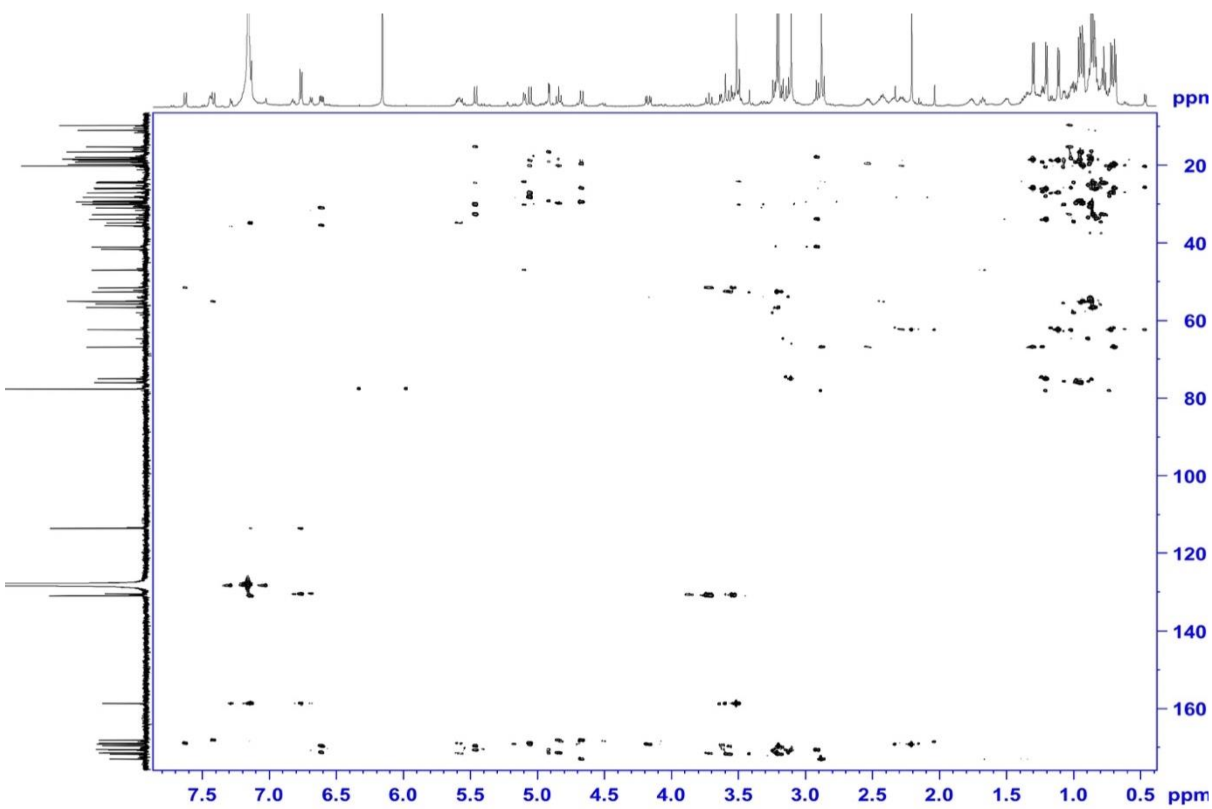


Figure S56. HMBC (600 MHz, C_6D_6) spectrum of **8**.

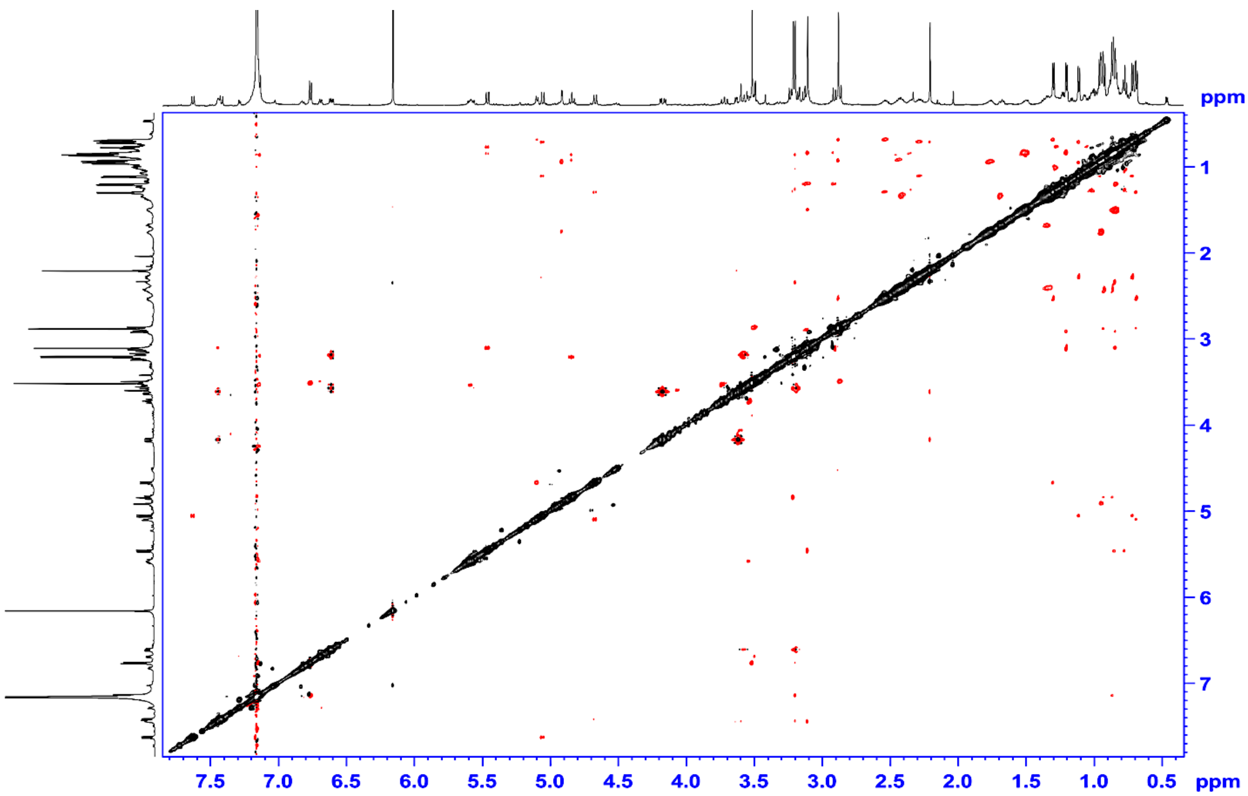


Figure S57. NOESY (600 MHz, C_6D_6) spectrum of **8**.

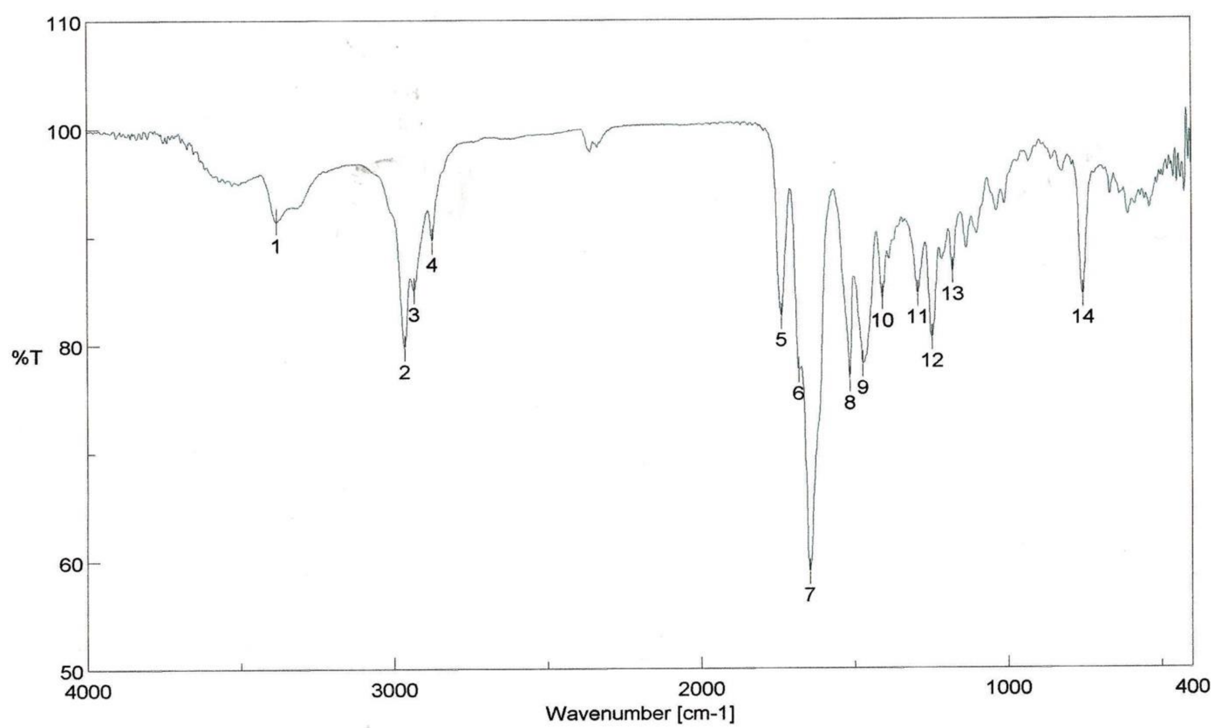


Figure S58. FT IR spectrum of **8** (film).

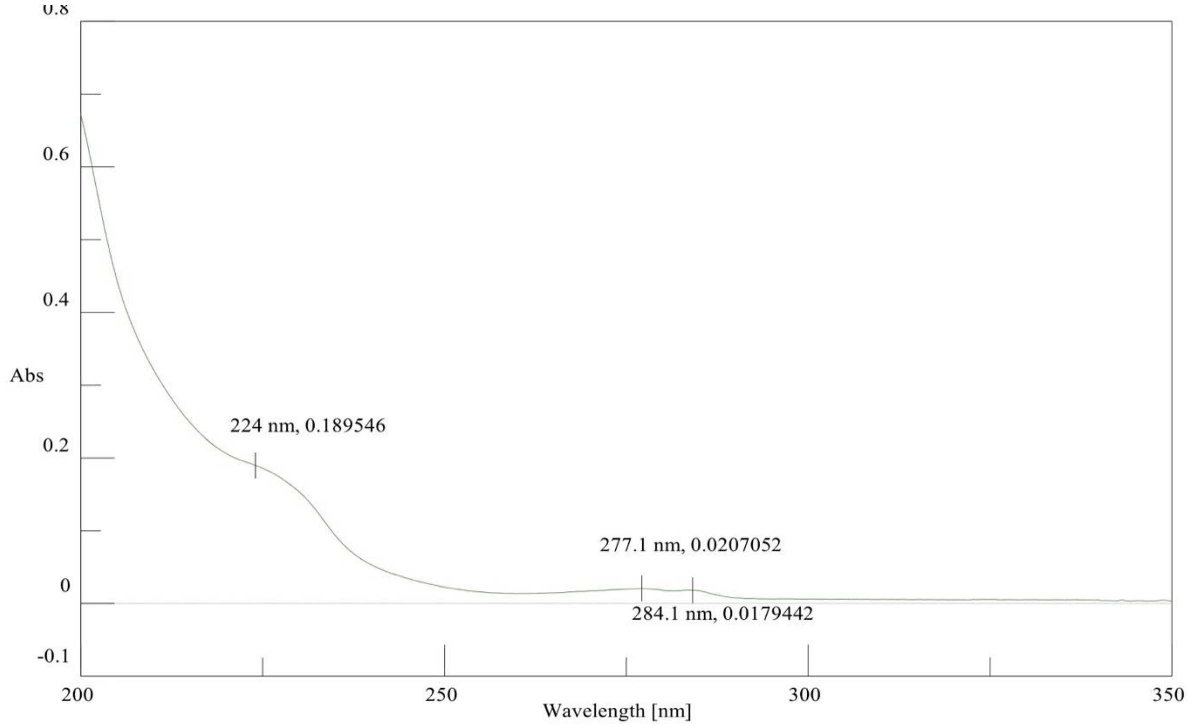


Figure S59. UV spectrum of **8** (10 µM in MeCN).

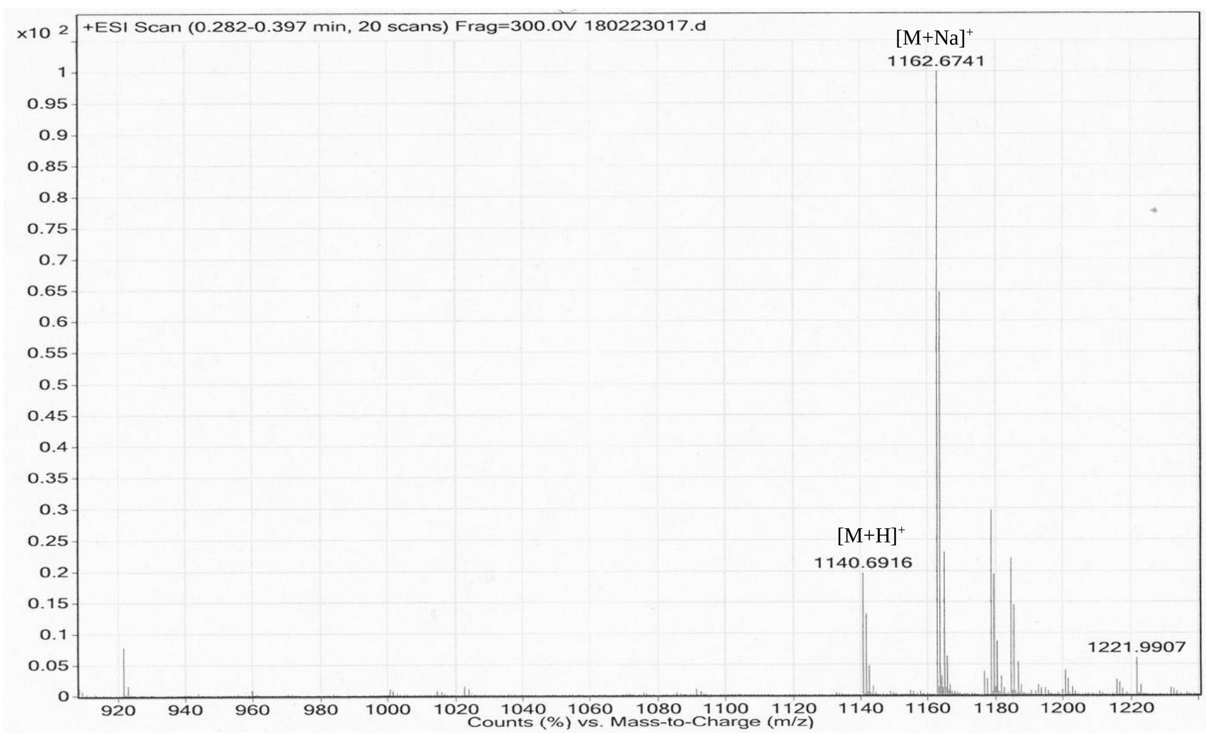


Figure S60. HRESIMS (+) of **8**.

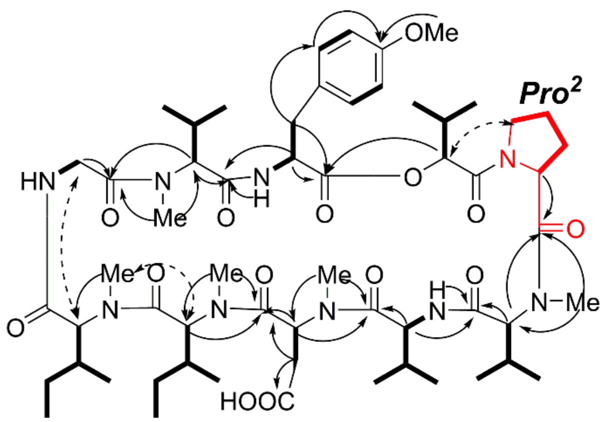


Figure S61. Key COSY (bold bonds), HMBC (arrows) and NOESY (dotted arrow) correlations of **8**.

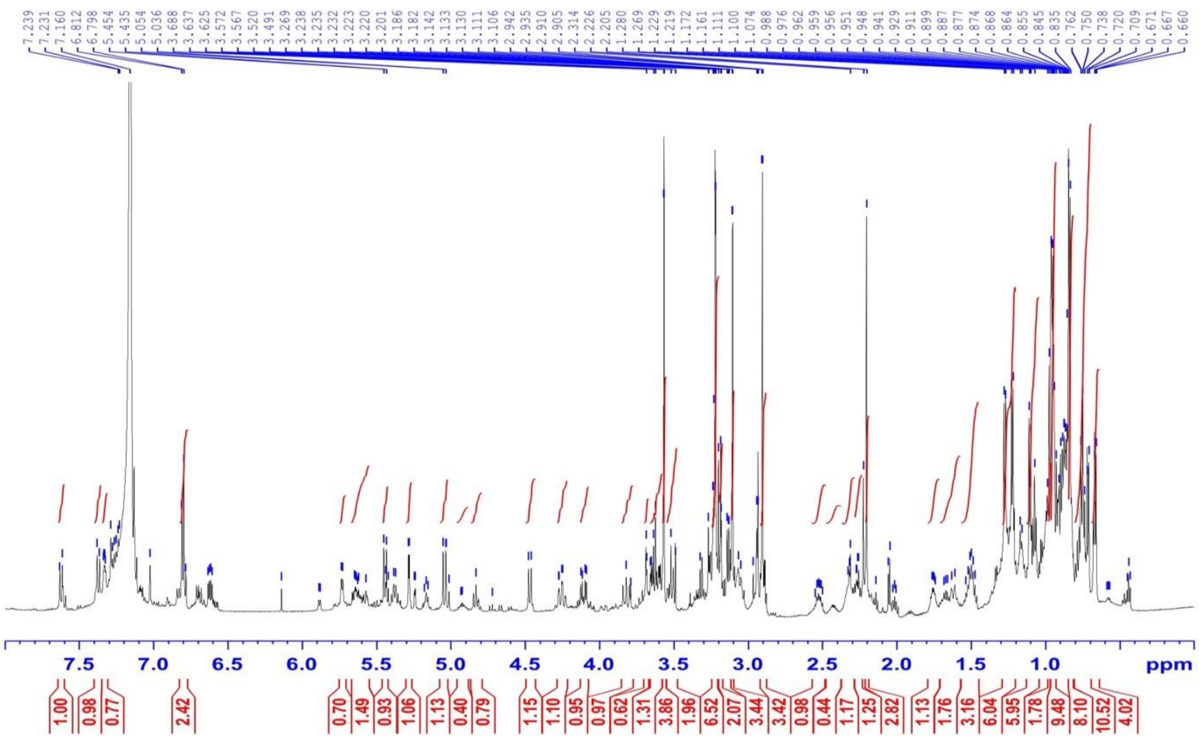


Figure S62. ^{1}H NMR (600 MHz, C_6D_6) spectrum of **9**.

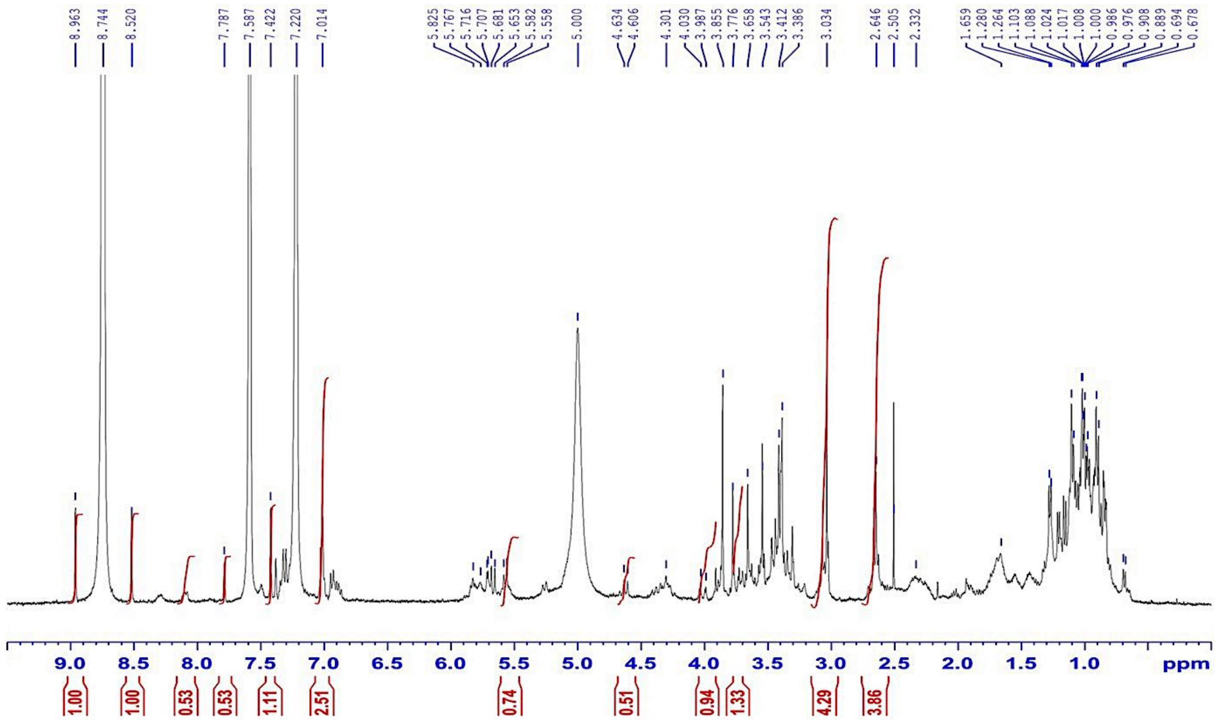


Figure S63. ^{1}H NMR (400 MHz, Pyridine-d_5) spectrum of **9**.

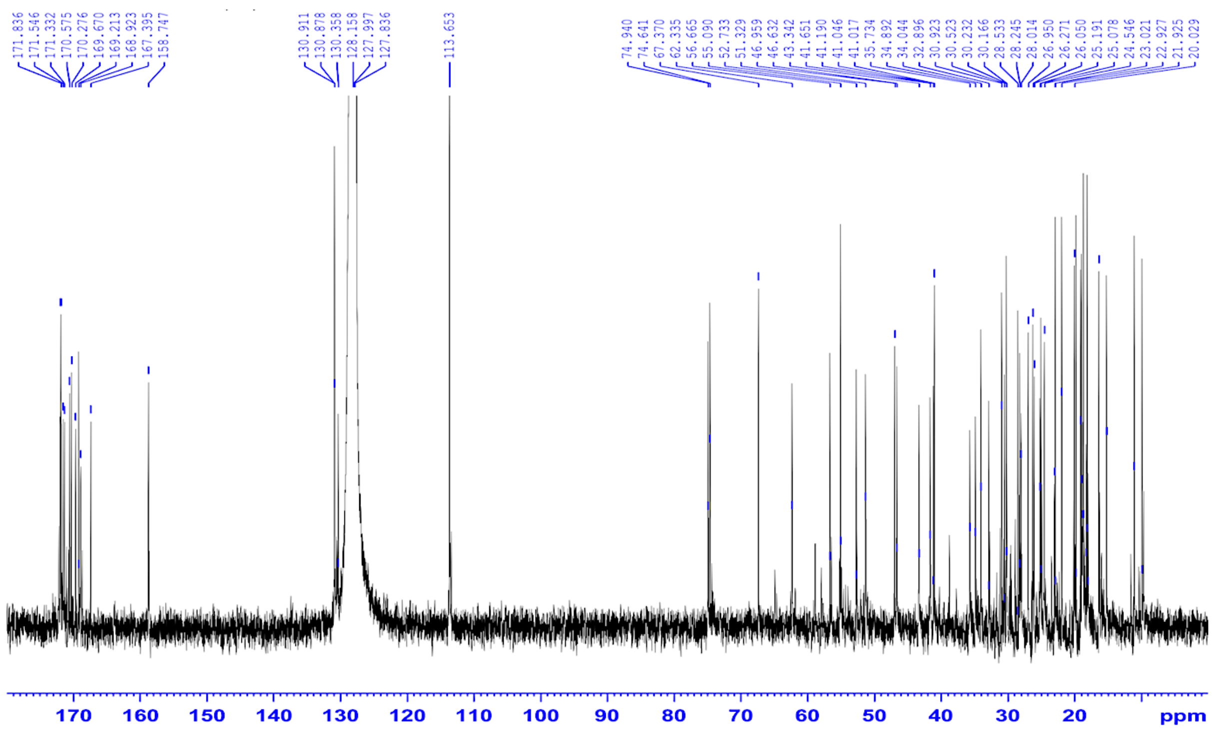


Figure S64. ^{13}C NMR (150 MHz, C_6D_6) spectrum of **9**.

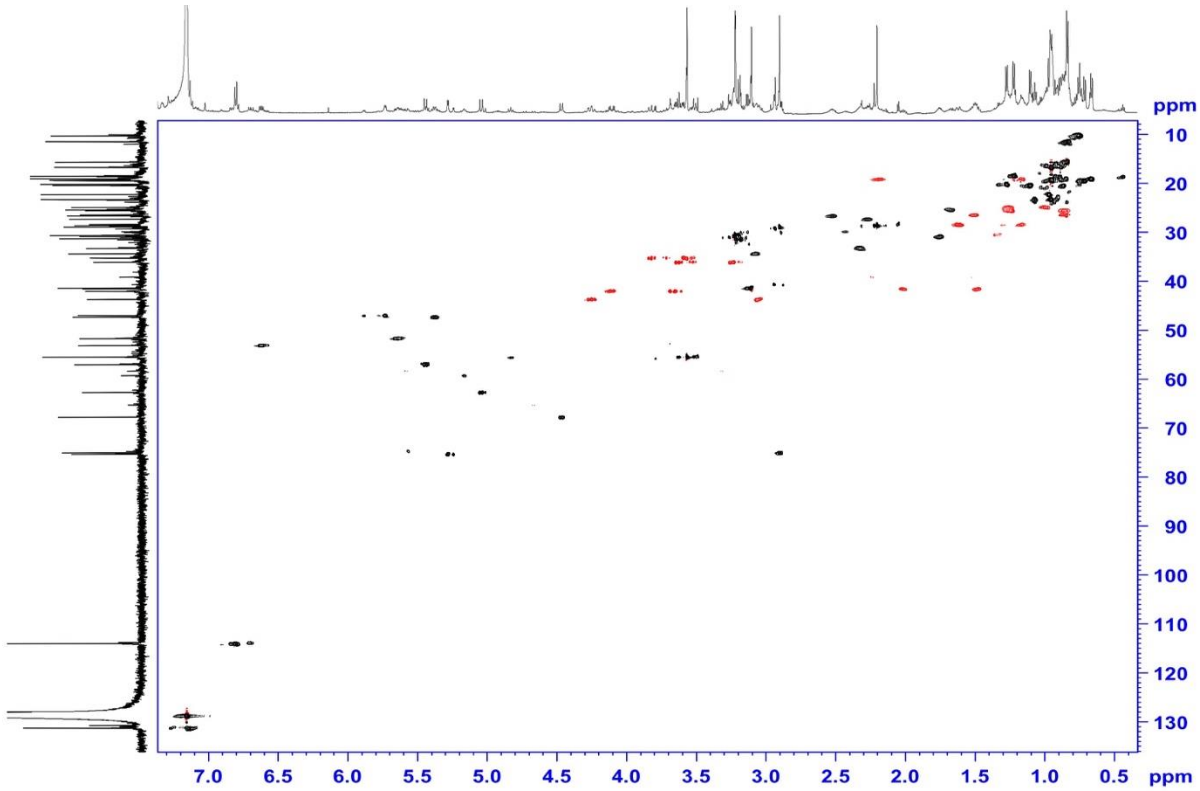


Figure S65. HSQC (600 MHz, C_6D_6) spectrum of **9**.

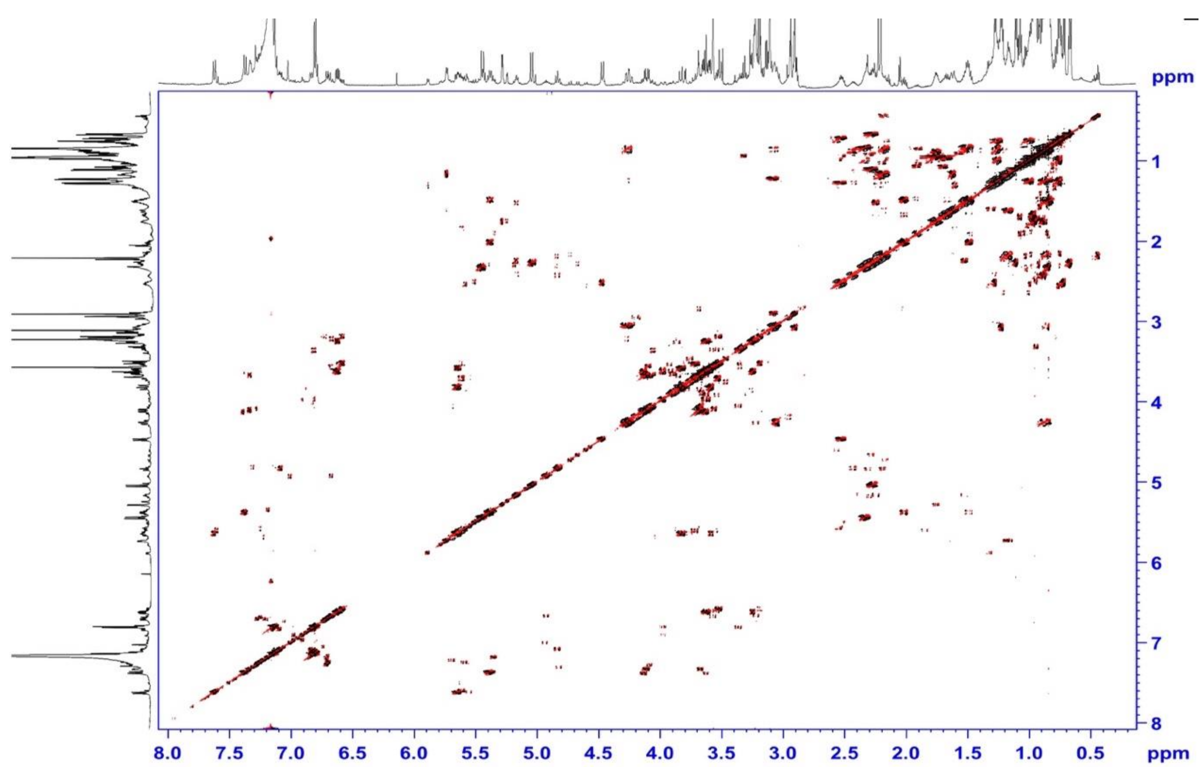


Figure S66. DQF-COSY (600 MHz, C_6D_6). spectrum of **9**.

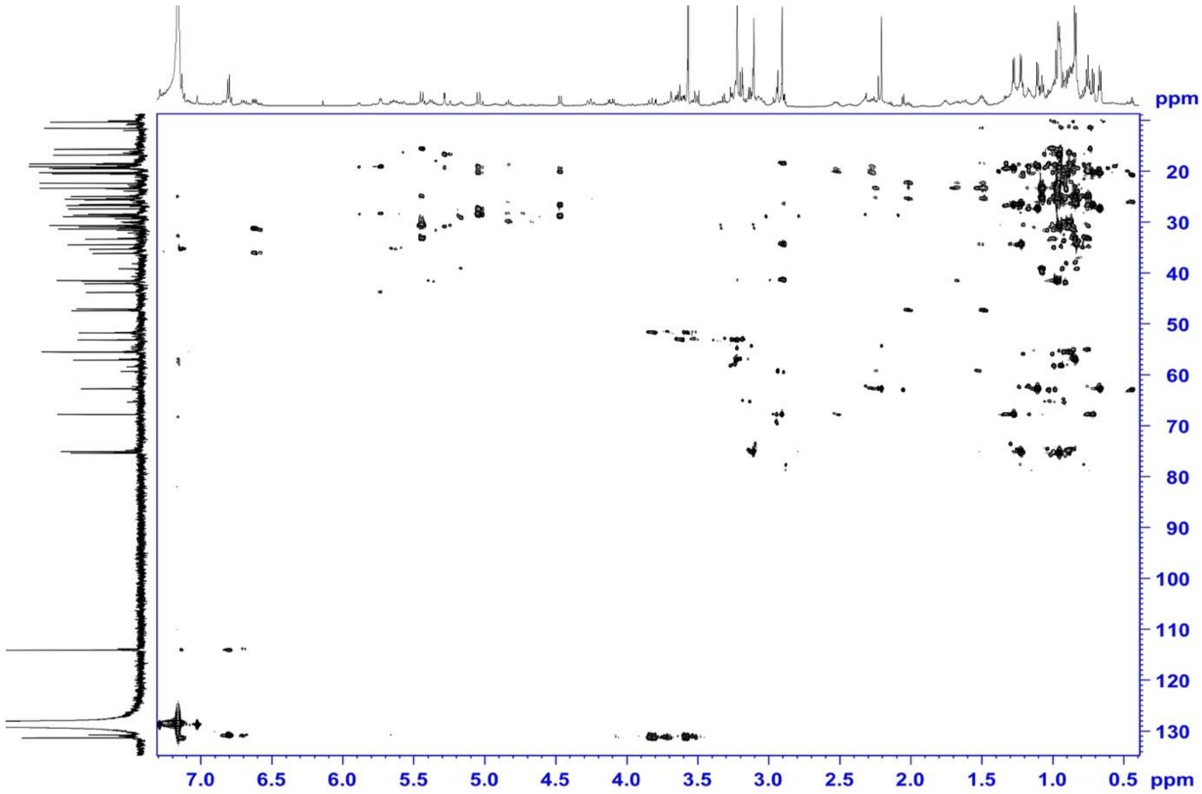


Figure S67. HMBC (600 MHz, C_6D_6) spectrum of **9**.

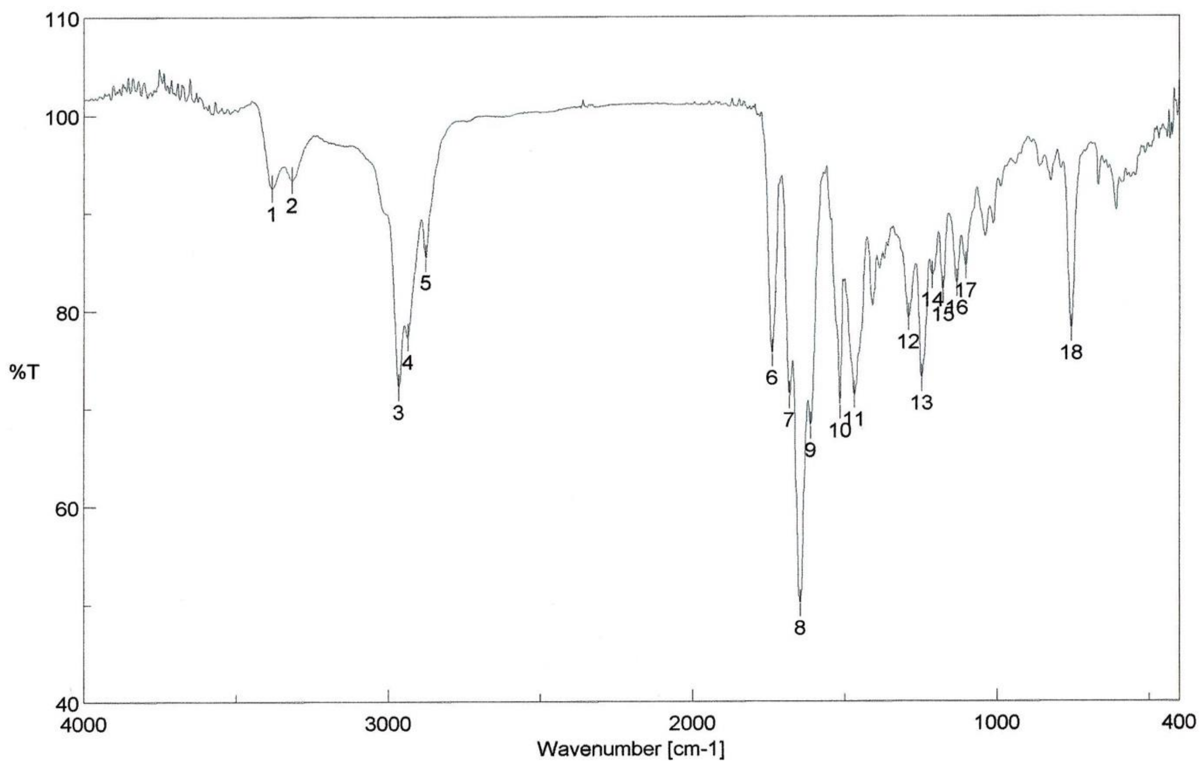


Figure S68. FT IR spectrum of **9** (film).

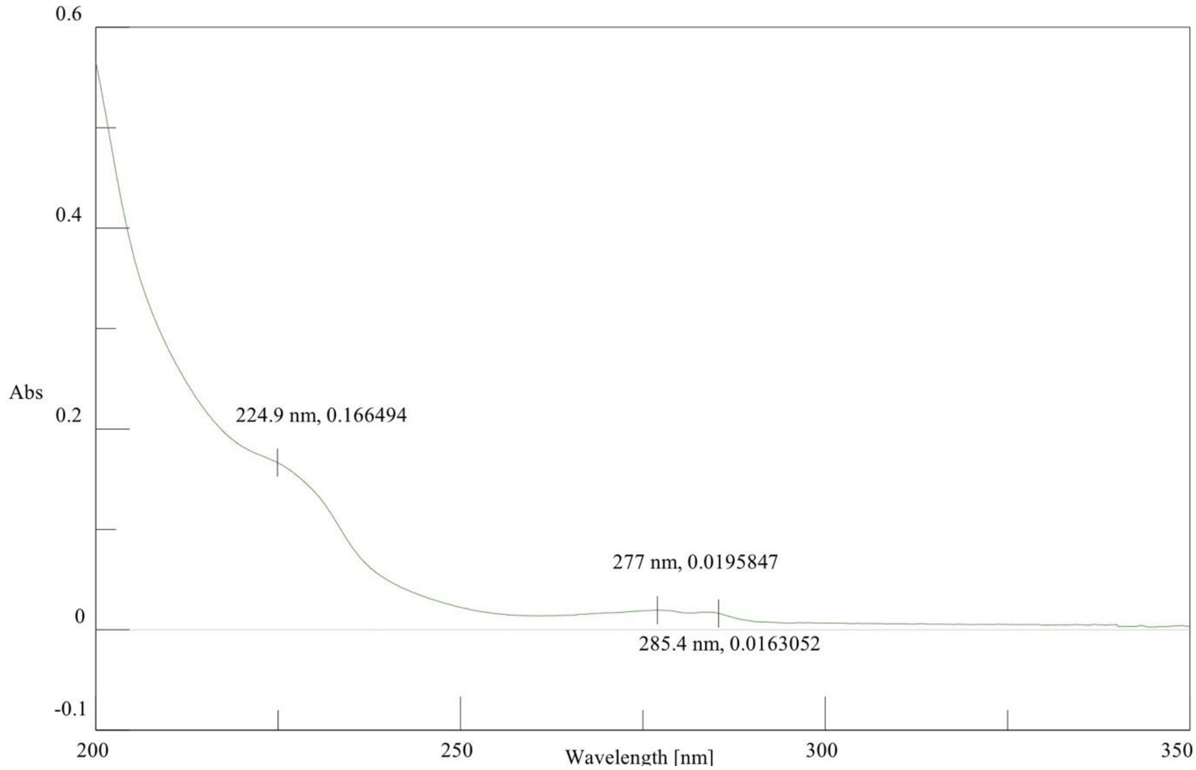


Figure S69. UV spectrum of **9** (10 μM in MeCN).

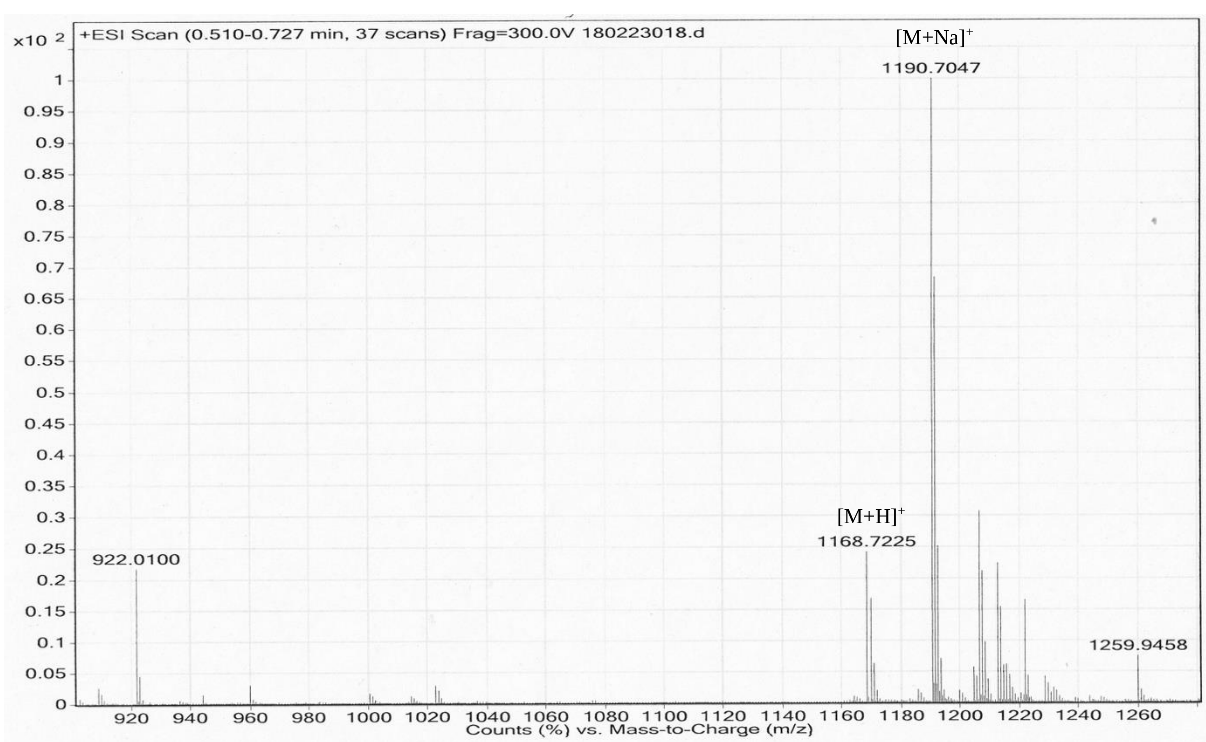


Figure S70. HRESIMS (+) of **9**.

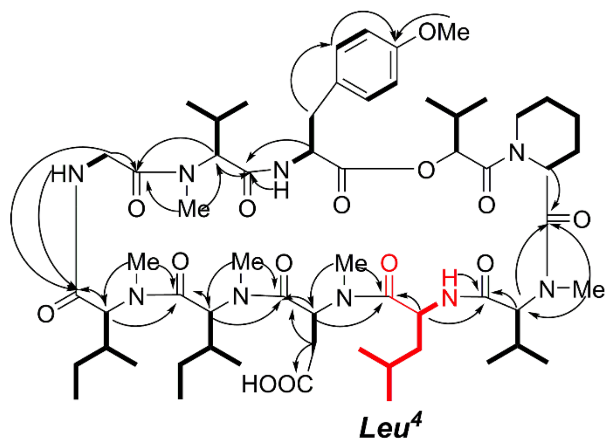


Figure S71. Key COSY (bold bonds) and HMBC (arrows) correlations of **9**.

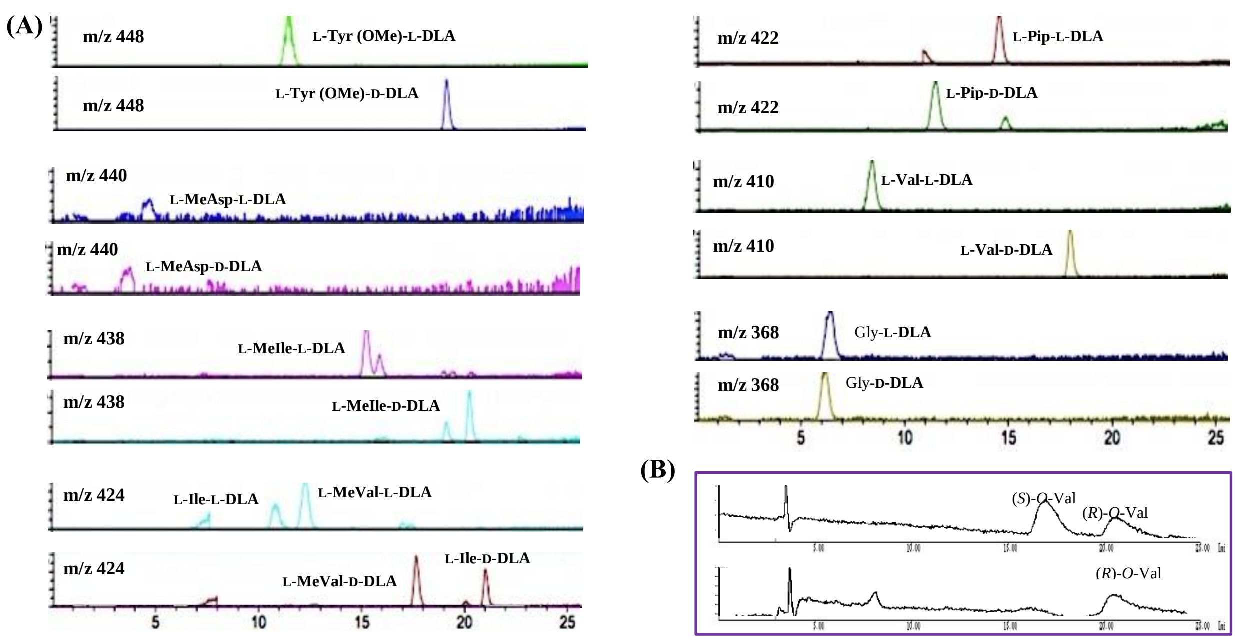


Figure S72. Elucidation of absolute configuration of amino acids and hydroxy acid of **3**.
(A) Mass chromatograms of L- and D-DLA derivatives of acid hydrolysate; (B) Chiral HPLC of *O*-Val of standard (upper) and acid hydrolysate (lower).

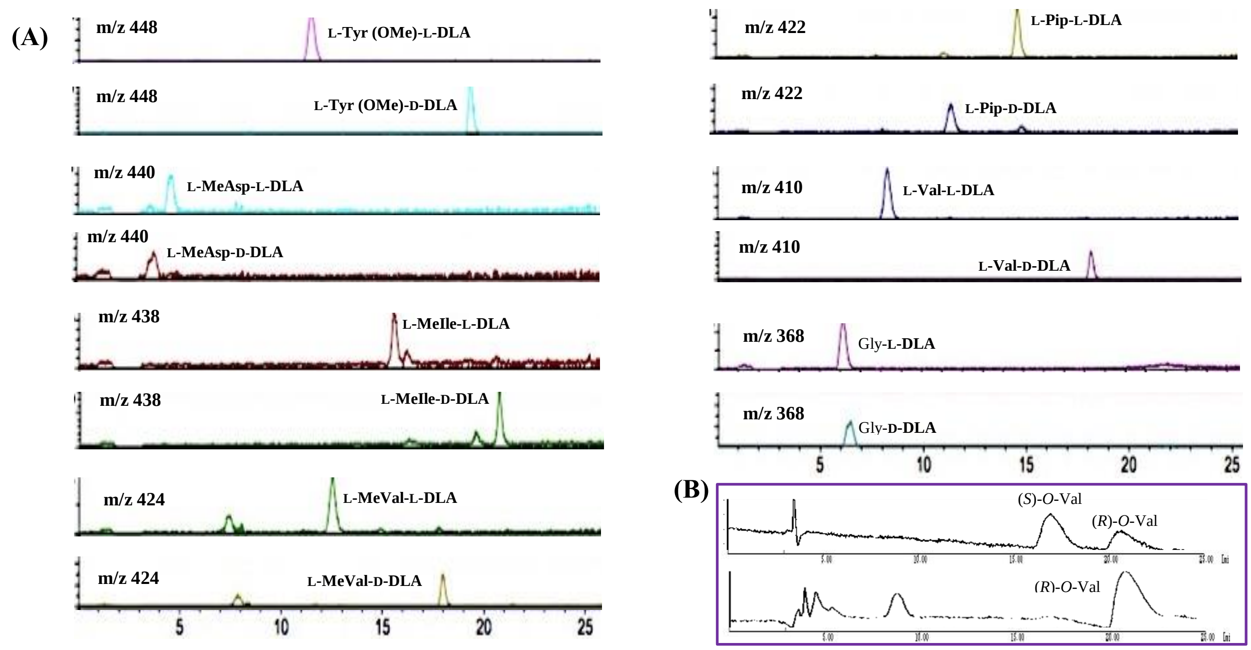


Figure S73. Elucidation of absolute configuration of amino acids and hydroxy acid of a mixture of **4** and **5**.
(A) Mass chromatograms of L- and D-DLA derivatives of acid hydrolysate; (B) Chiral HPLC of *O*-Val of standard (upper) and acid hydrolysate (lower).

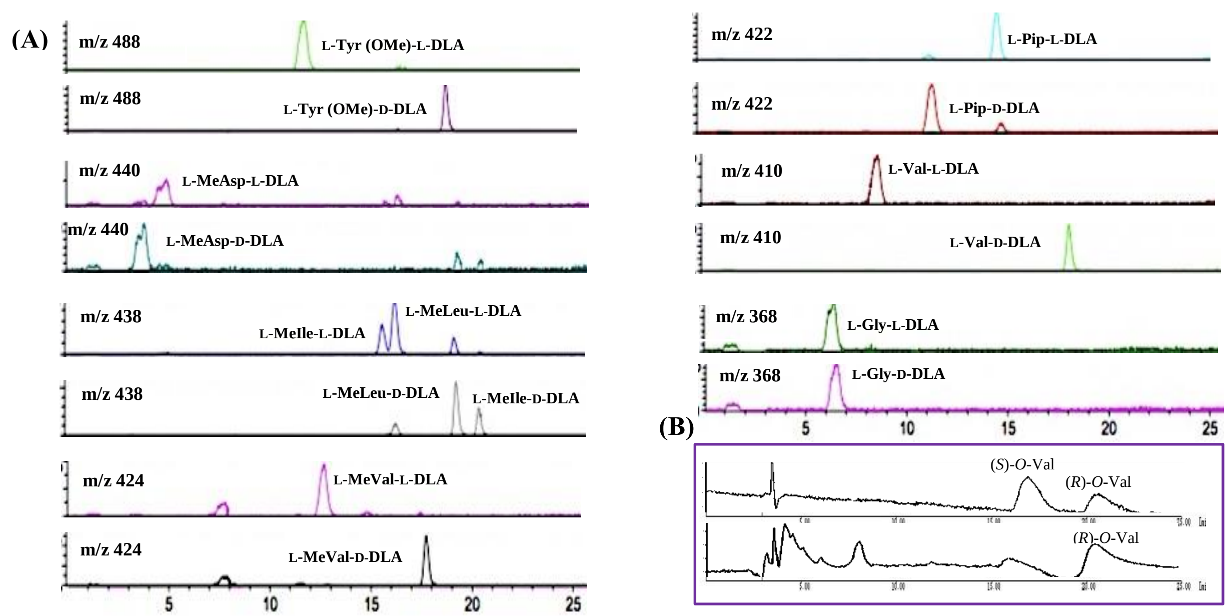


Figure S74. Elucidation of absolute configuration of amino acids and hydroxy acid of **6**.
(A) Mass chromatograms of L- and D-DLA derivatives of acid hydrolysate; (B) Chiral HPLC of *O*-Val of standard (upper) and acid hydrolysate (lower).

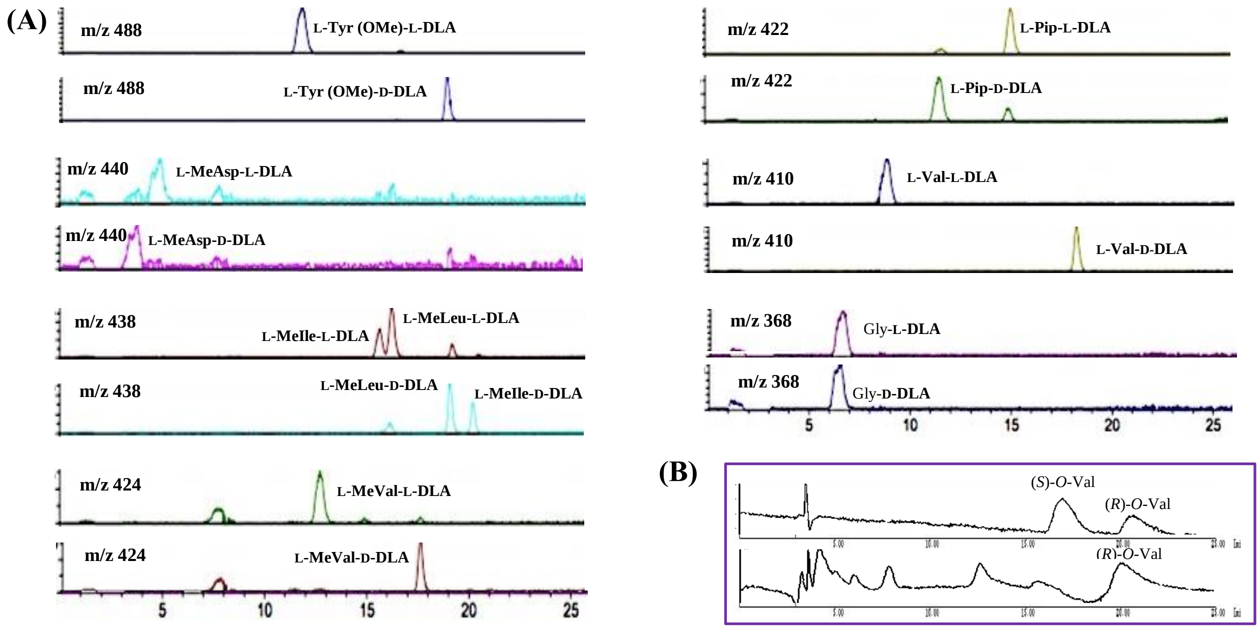


Figure S75. Elucidation of absolute configuration of amino acids and hydroxy acid of **7**.
(A) Mass chromatograms of L- and D-DLA derivatives of acid hydrolysate; (B) Chiral HPLC of *O*-Val of standard (upper) and acid hydrolysate (lower).

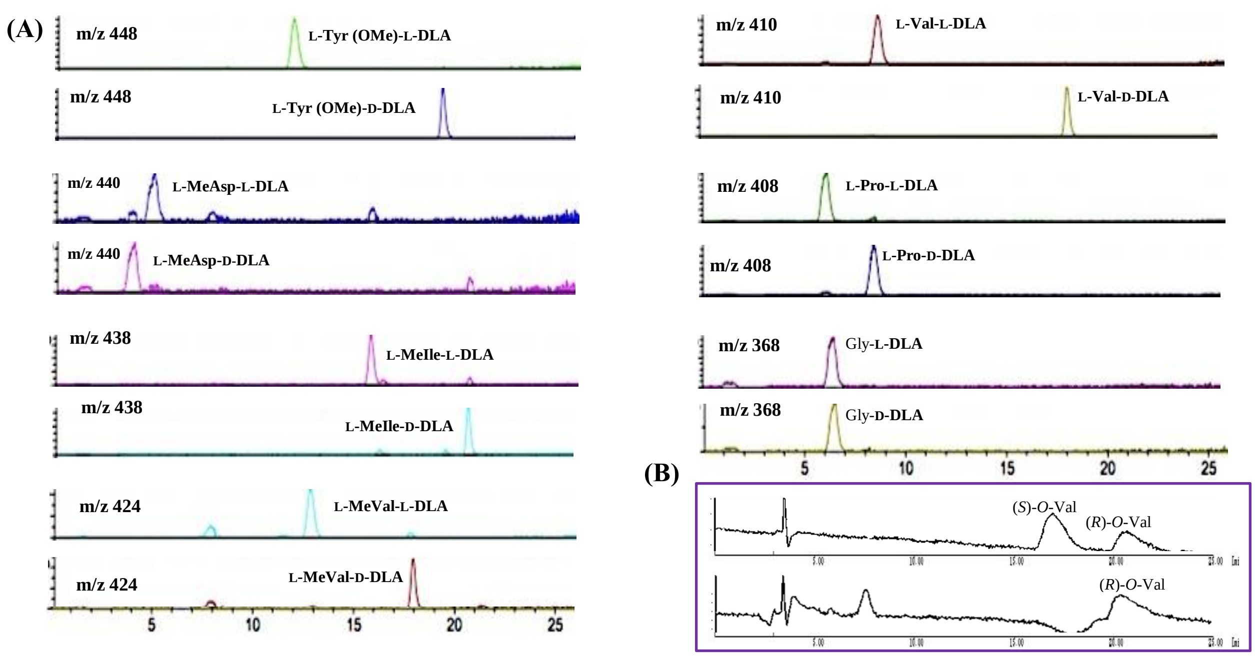


Figure S76. Elucidation of absolute configuration of amino acids and hydroxy acid of **8**.
(A) Mass chromatograms of L- and D-DLA derivatives of acid hydrolysate; (B) Chiral HPLC of *O*-Val of standard (upper) and acid hydrolysate (lower).

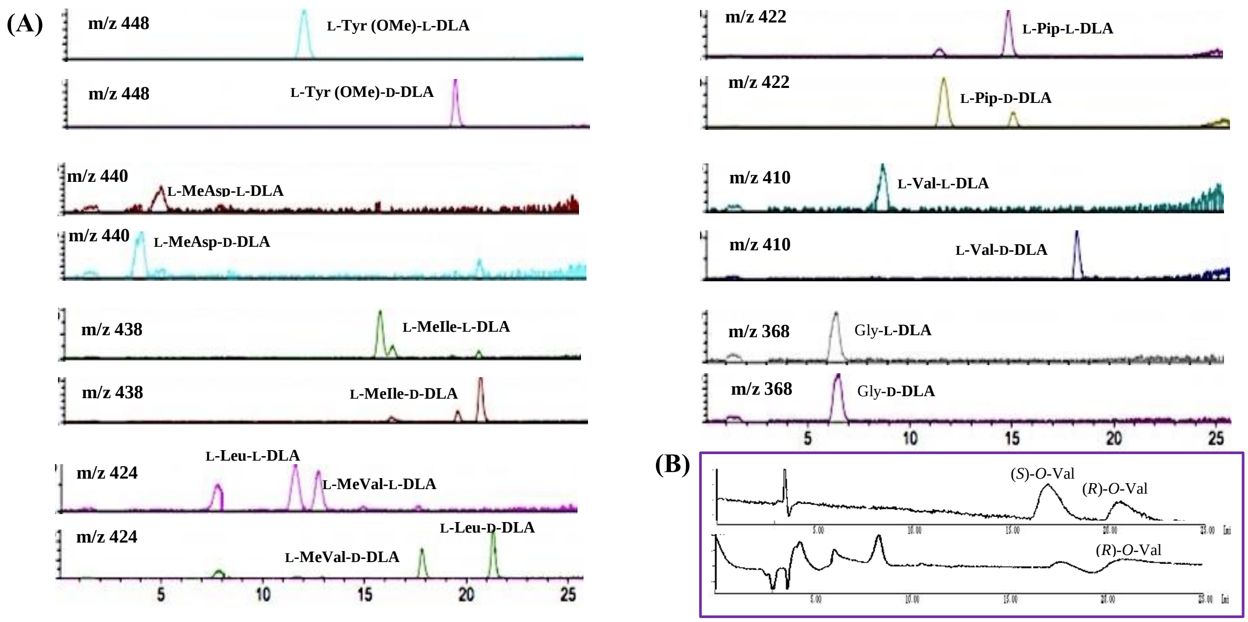


Figure S77. Elucidation of absolute configuration of amino acids and hydroxy acid of **9**.
(A) Mass chromatograms of L- and D-DLA derivatives of acid hydrolysate; (B) Chiral HPLC of *O*-Val of standard (upper) and acid hydrolysate (lower).

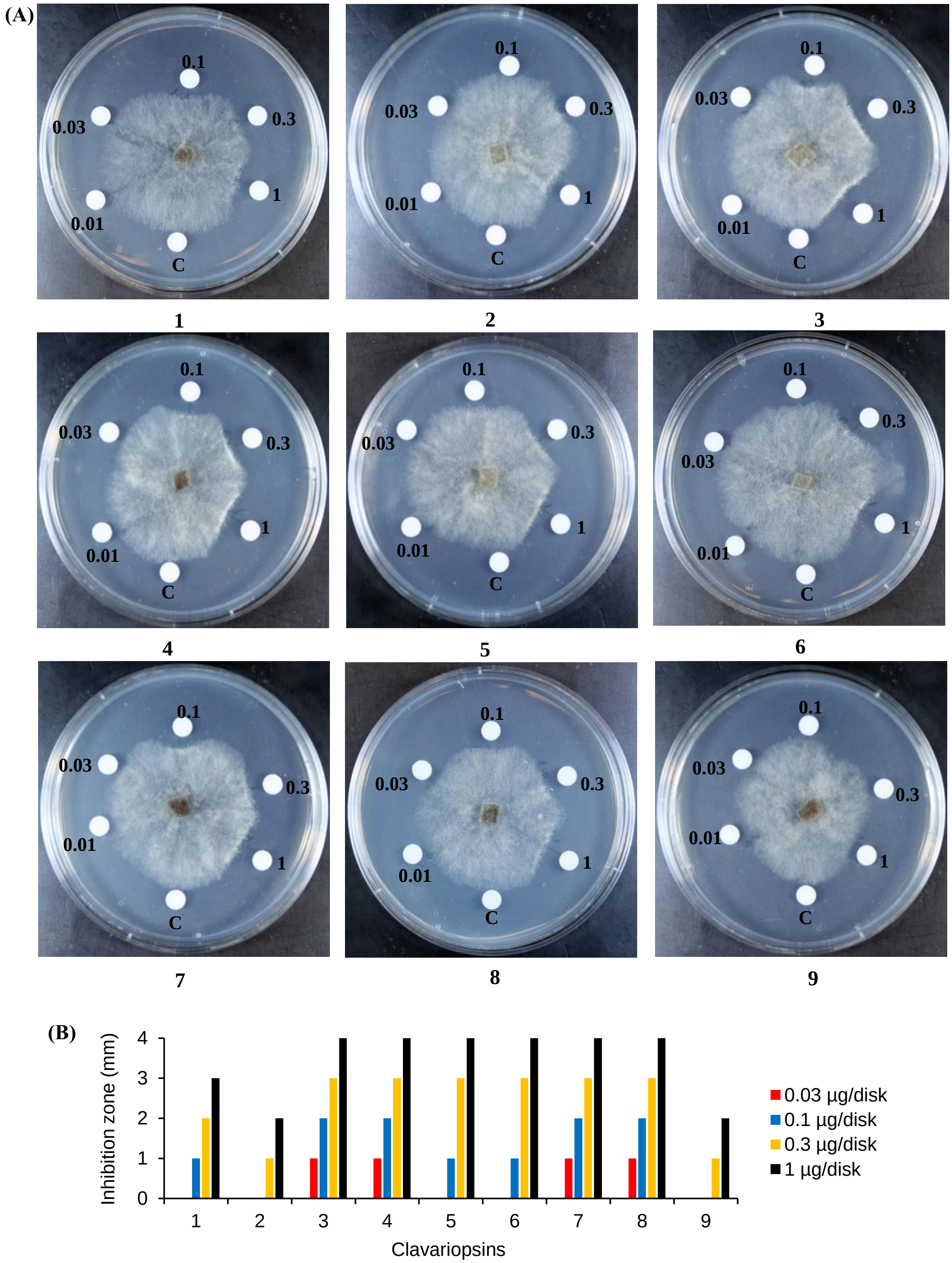


Figure S78. Growth inhibition of *B. cinerea* by clavariopsins **1**–**9**.
(A) Photographs of a paper disk diffusion assay. Doses are in µg/disk. DMSO was used as solvent and control; (B) Bar graphs of inhibition zone (mm).

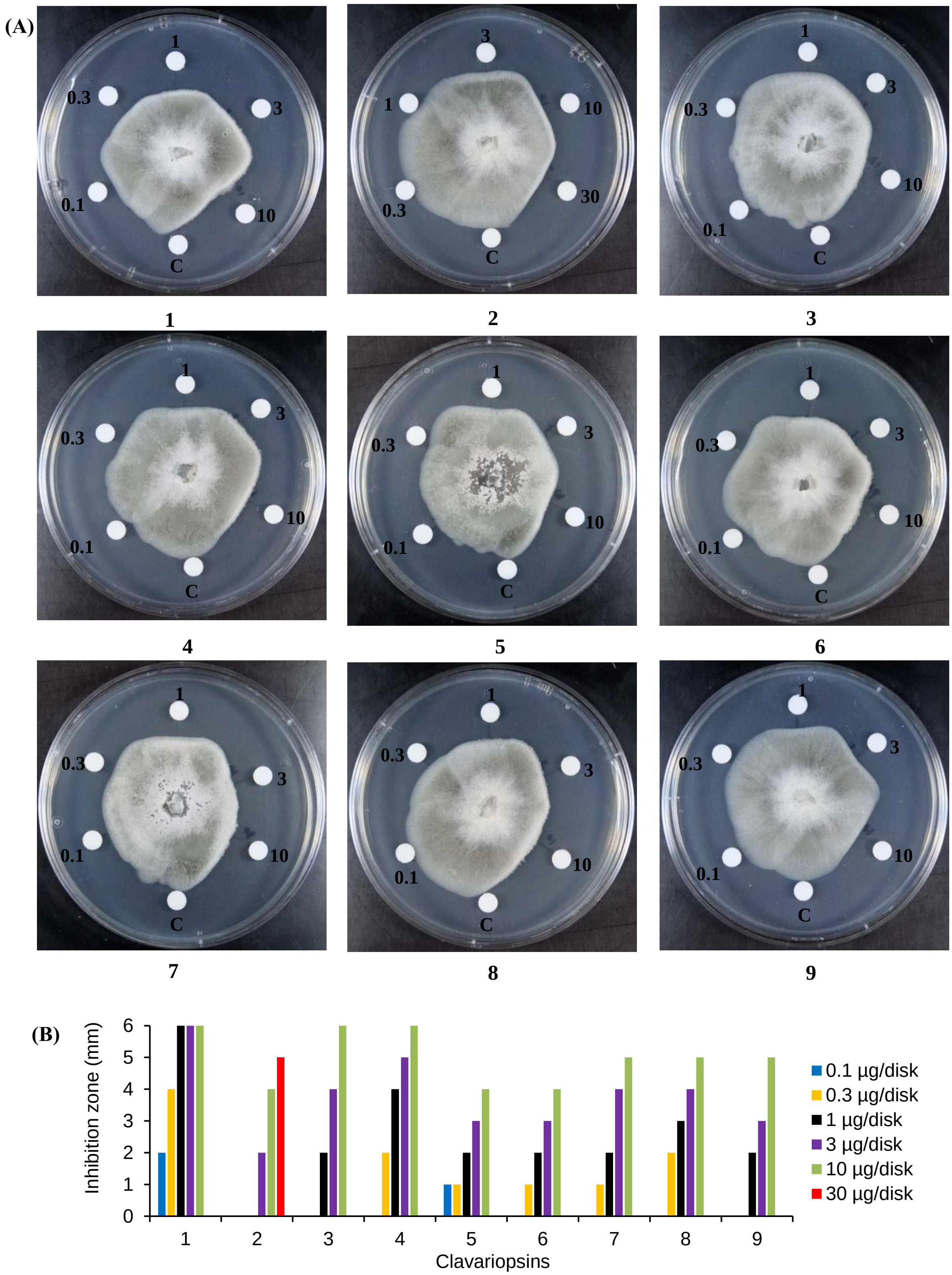


Figure S79. Growth inhibition of *M. oryzae* by clavariopsins **1**–**9**.
(A) Photographs of a paper disk diffusion assay. Doses are in μg/disk. DMSO was used as solvent and control; (B) Bar graphs of inhibition zone (mm).

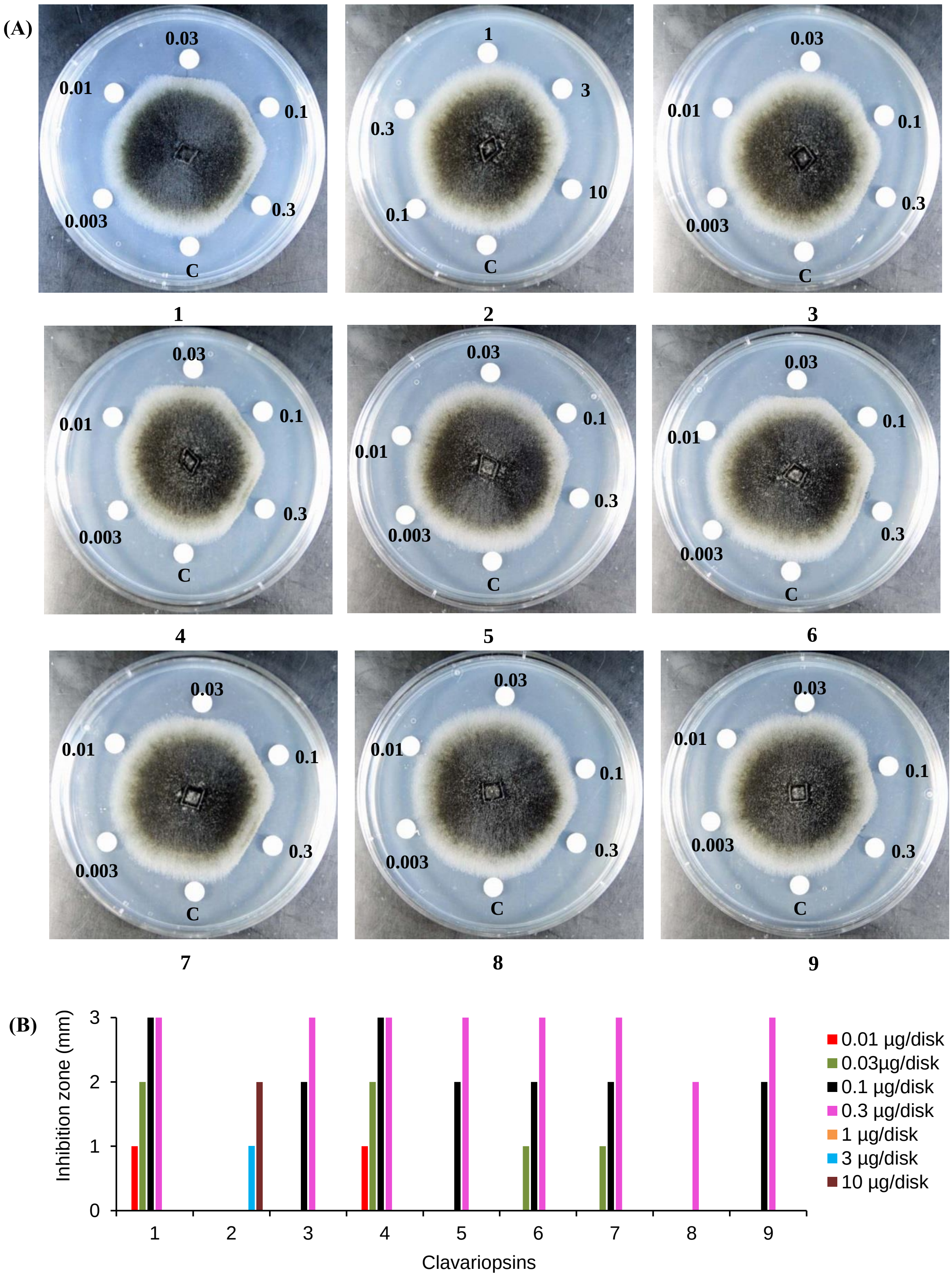


Figure S80. Growth inhibition of *C. orbiculare* by clavariopsins **1**–**9**.
(A) Photographs of a paper disk diffusion assay. Doses are in µg/disk. DMSO was used as solvent and control; (B). Bar graphs of inhibition zone (mm).

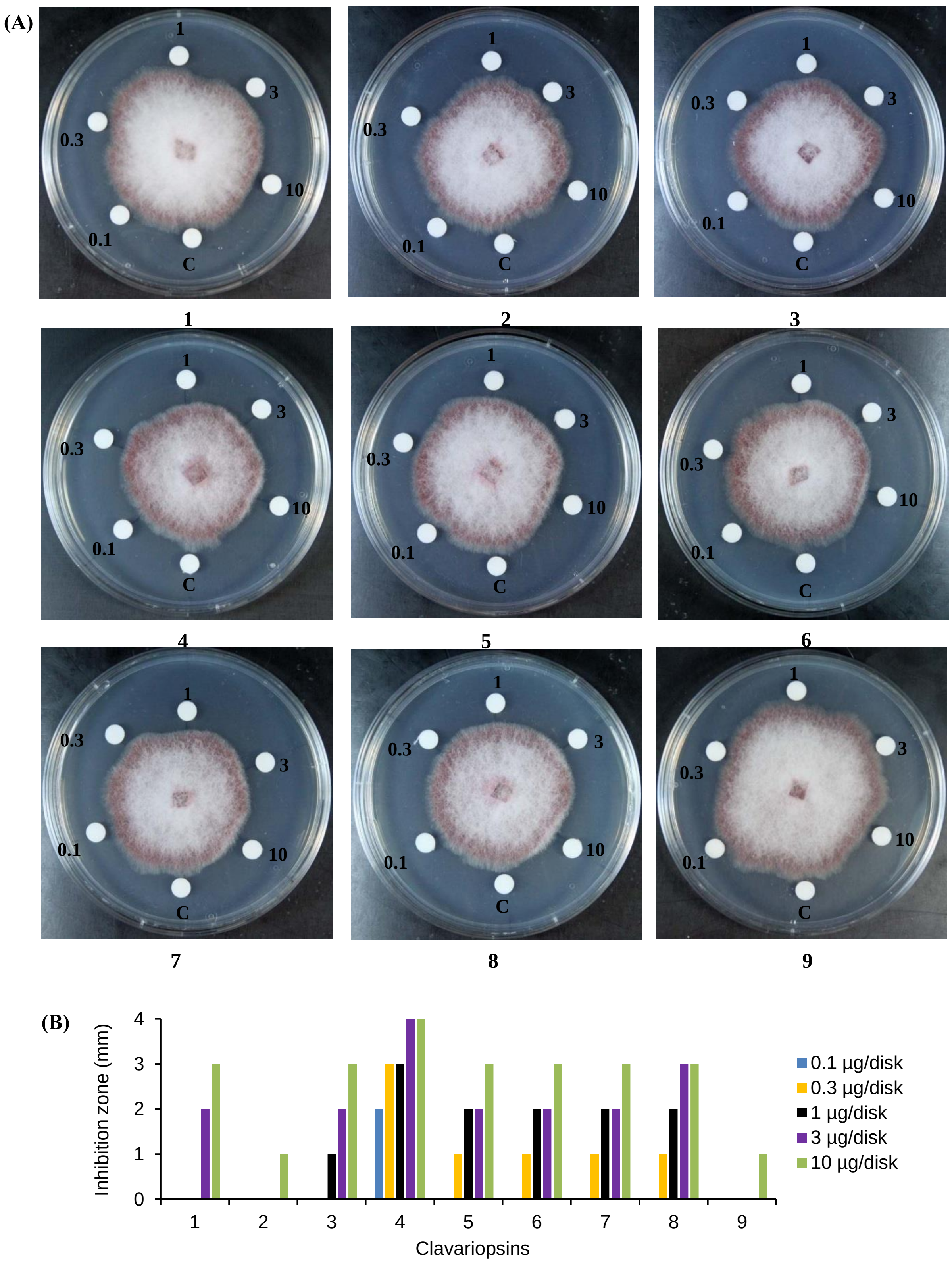
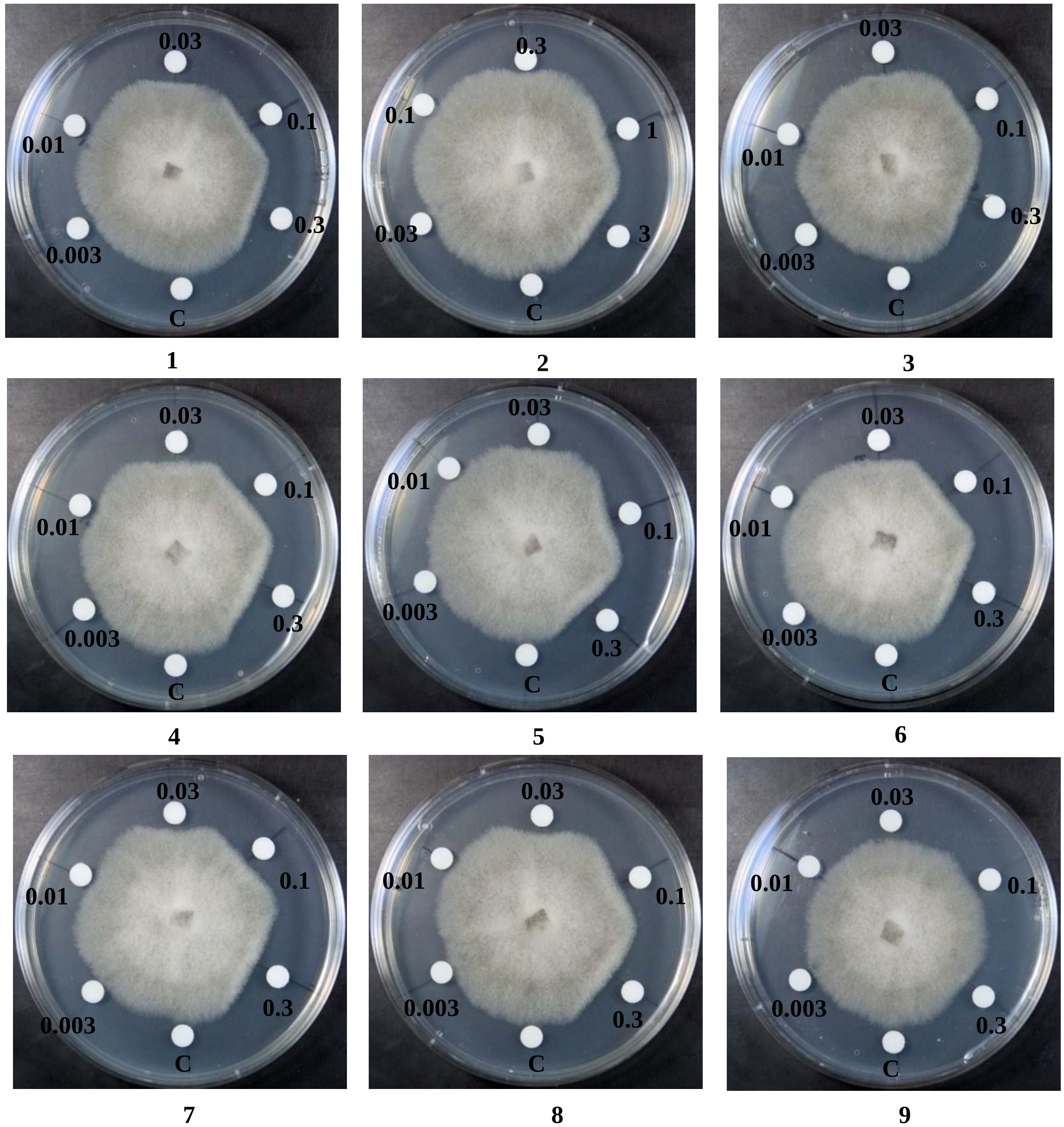


Figure S81. Growth inhibition of *F. oxysporum* by clavariopsins **1**–**9**.
(A) Photographs of a paper disk diffusion assay. Doses are in µg/disk. DMSO was used as solvent and control; (B) Bar graphs of inhibition zone (mm).

(A)



(B)

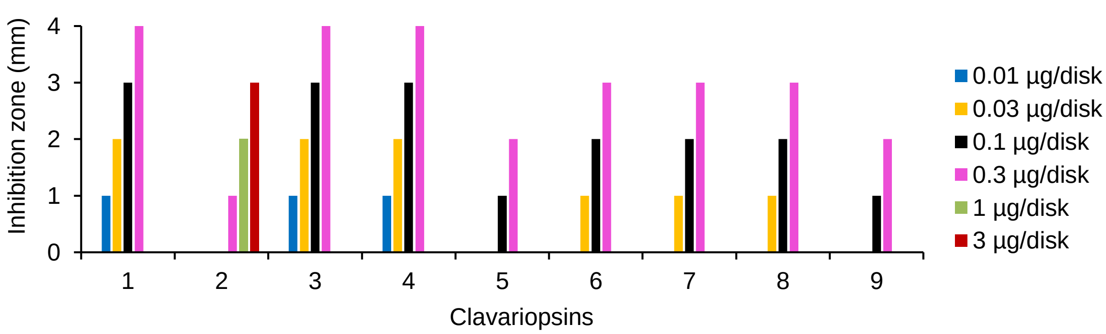


Figure S82. Growth inhibition of *A. alternata* by clavariopsins **1**–**9**.
(A) Photographs of a paper disk diffusion assay. Doses are in µg/disk. DMSO was used as solvent and control; (B) Bar graphs of inhibition zone (mm).

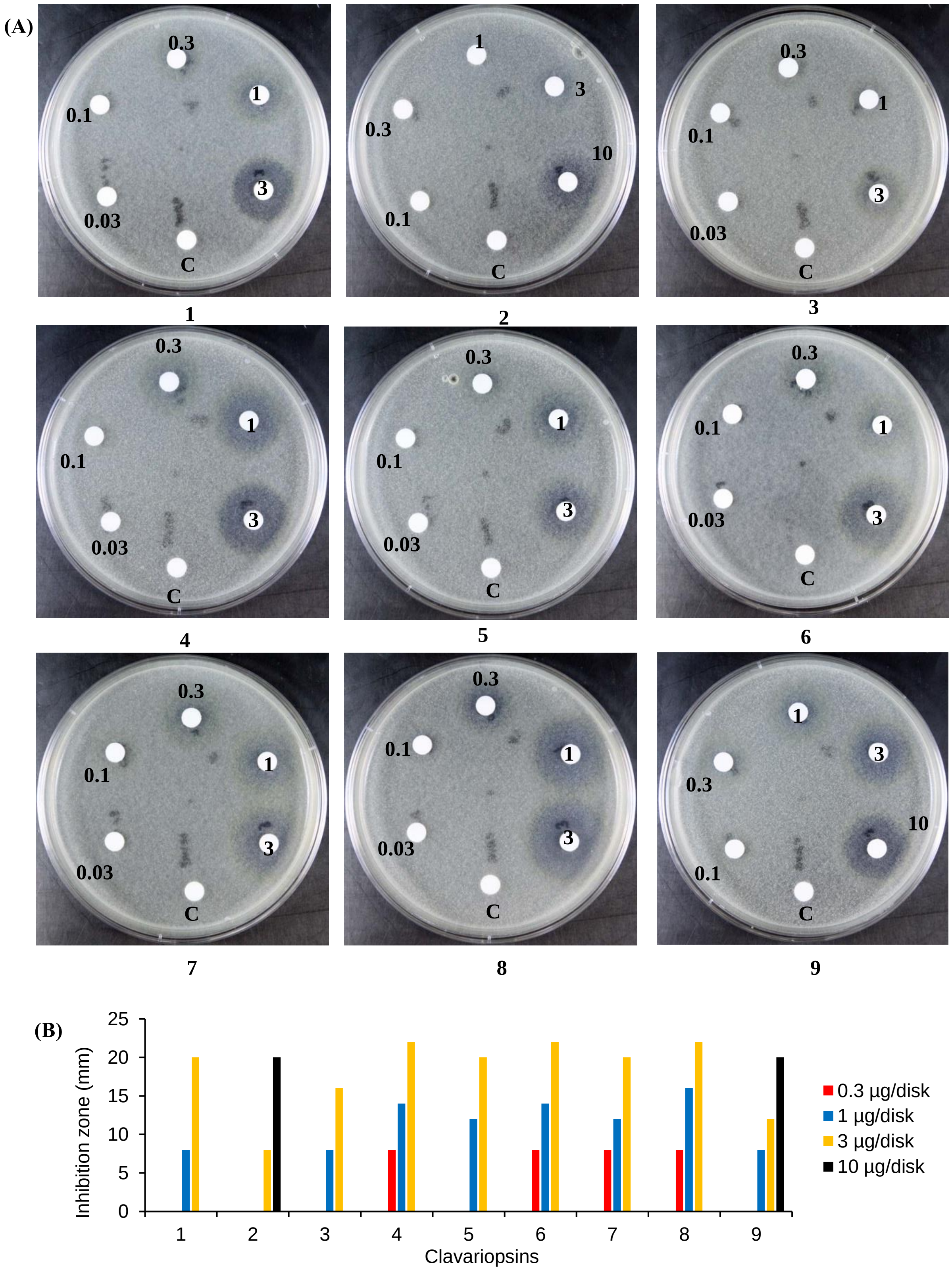
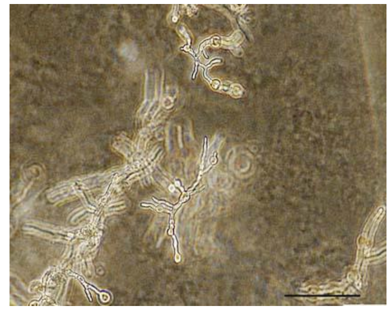


Figure S83. Growth inhibition of *A. niger* by clavariopsins **1**–**9**.
(A) Photographs of a paper disk diffusion assay. Doses are in µg/disk. DMSO was used as solvent and control; (B) Bar graphs of inhibition zone diameter (mm).

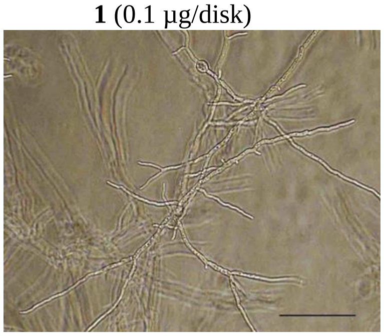
(A)

1 (0.1 μg/disk)

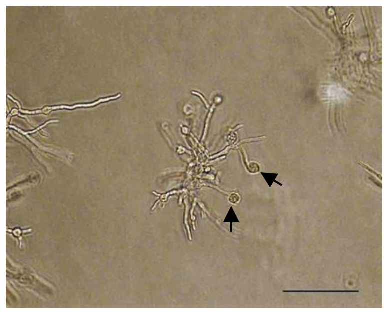
1 (0.3 μg/disk)



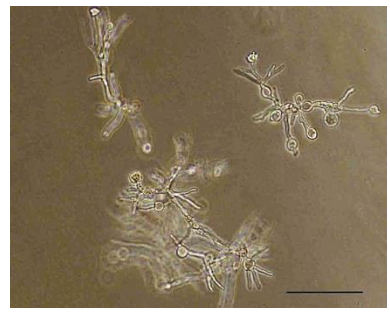
1 (1 μg/disk)



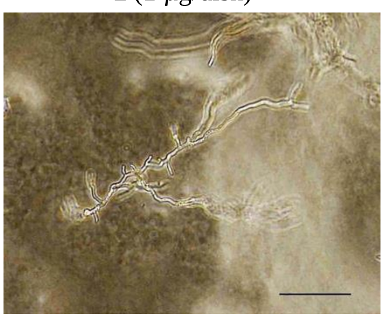
2 (1 μg/disk)



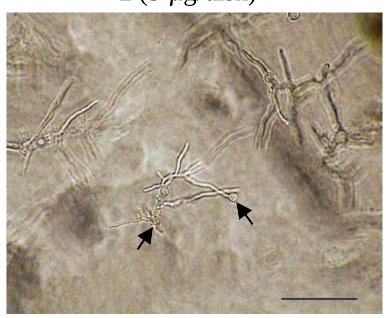
2 (3 μg/disk)



2 (10 μg/disk)

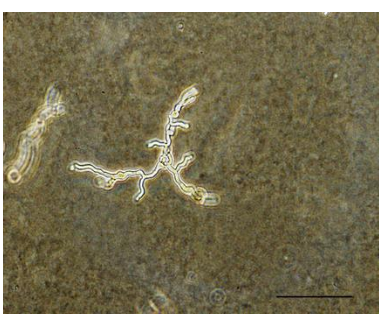


3 (0.1 μg/disk)

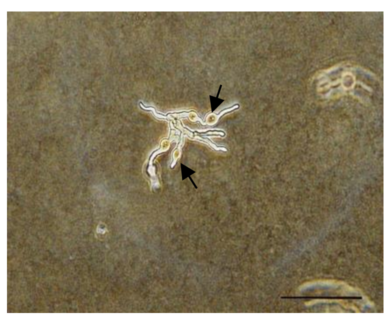


3 (0.3 μg/disk)

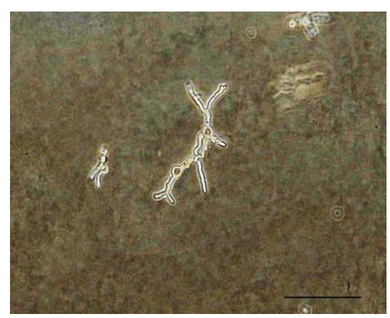
3 (1 μg/disk)



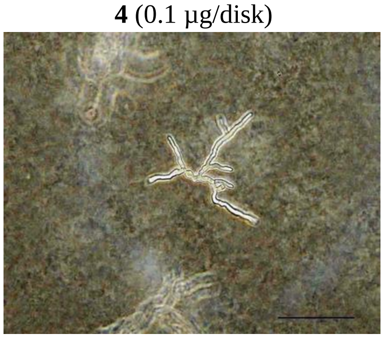
4 (0.1 μg/disk)



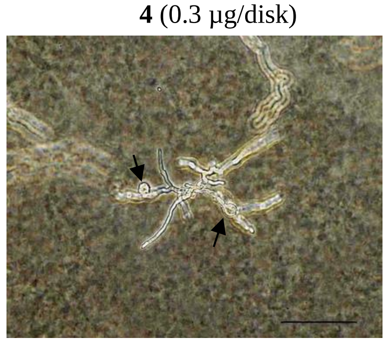
4 (0.3 μg/disk)



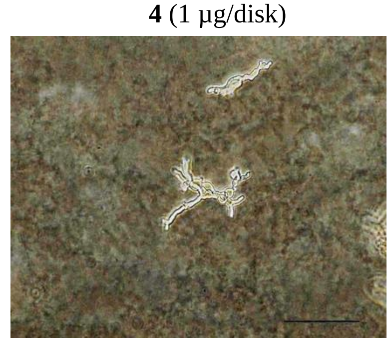
4 (1 μg/disk)



5 (0.1 μg/disk)

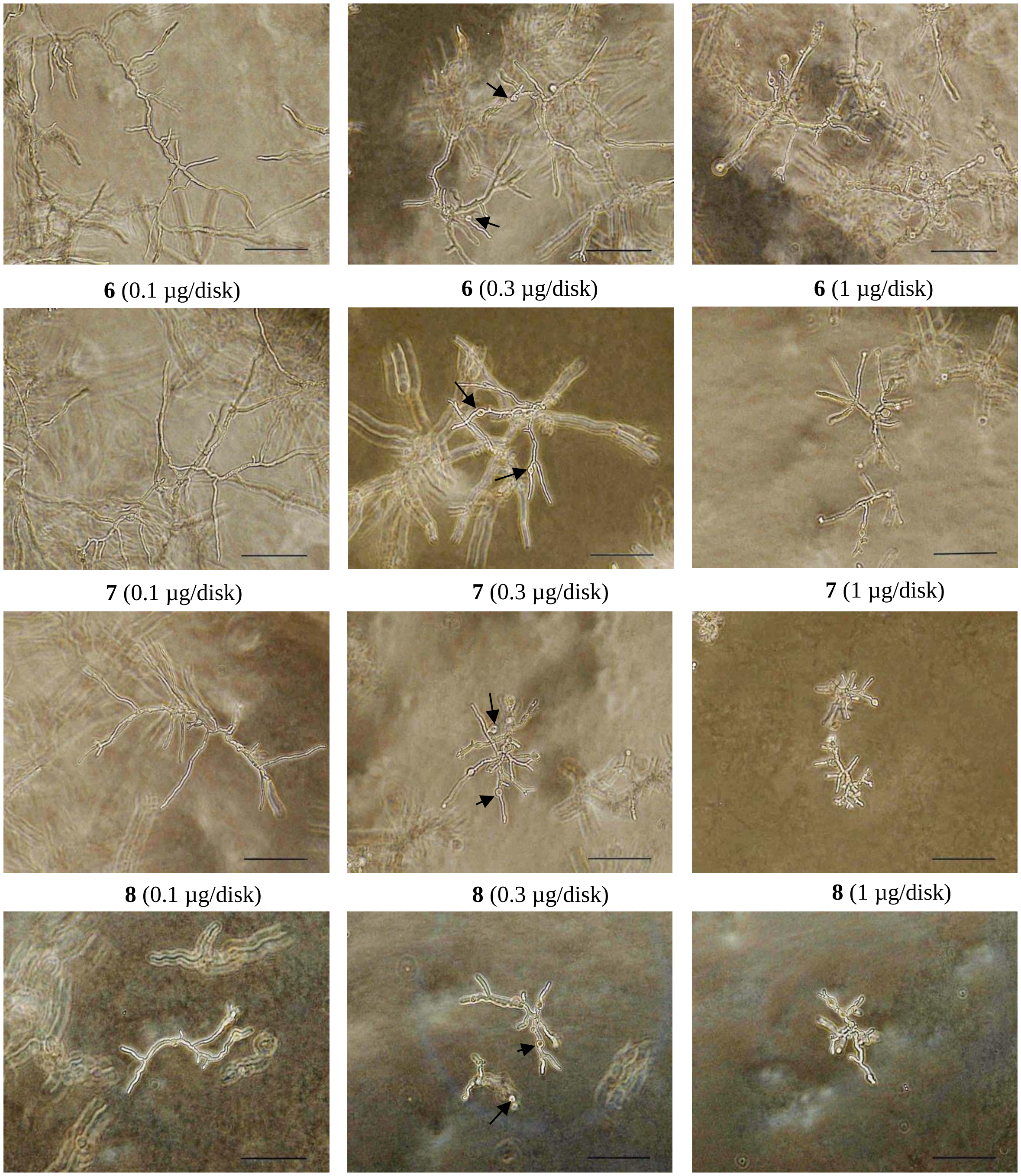


5 (0.3 μg/disk)



5 (1 μg/disk)

(B)



6 (0.1 µg/disk) **6** (0.3 µg/disk) **6** (1 µg/disk)

7 (0.1 µg/disk) **7** (0.3 µg/disk) **7** (1 µg/disk)

8 (0.1 µg/disk) **8** (0.3 µg/disk) **8** (1 µg/disk)

9 (1 µg/disk) **9** (3 µg/disk) **9** (10 µg/disk)

Figure S84. Hyphal morphology changes of *A. niger* treated with clavariopsins **1**–**9**. Conidia of *A. niger* were cultured in a potato-agar medium with a paper disk containing each compound at the dose of 0.1, 0.3, 1, 3, or 10 µg/disk. Germinated mycelia around the paper disk were observed after 16 h with a phase contrast microscope. The arrows show the swelling malformations. Scale bar represents 100 µm.

Table S1. NMR Data (^{1}H 600 MHz, ^{13}C 150 MHz, benzene-d_6) for Clavariopsins G–I (7–9)

	7		**8**		**9**[b]	
position[a]	δ_C, type	δ_H, mult. (*J* in Hz)	δ_C, type	δ_H, mult. (*J* in Hz)	δ_C, type	δ_H, mult. (*J* in Hz)
O-Hiv[1]						
CO	171.8, C		170.7[d], C		171.9[e], C	
α	74.8, CH	5.32, d (3.0)	76.0, CH	4.92, d (3.6)	74.9, CH	5.28, d (3.6)
β	30.4, CH	1.75, m	29.2, CH	1.76, m	30.5, CH	1.75, m
γ	19.0, CH_3	0.94, d (6.6)	19.1, CH_3	0.94, d (6.6)	19.4, CH_3	0.96, d (6.6)
γ	16.2, CH_3	0.92, d (6.6)	16.6, CH_3	0.96, d (6.6)	16.8, CH_3	0.96, d (6.6)
Pip[2]/Pro[2]						
CO	171.4, C		173.1, C		171.3, C	
α	46.5, CH	5.79, d (6.0)	55.8, CH	5.09, d (7.8)	46.6, CH	5.73, d (5.4)
β	28.2[c], CH_2	1.63, m; 1.19, m	30.2, CH_2	1.68, m; 1.36, m	28.3, CH_2	1.62, m; 1.17, m
γ	18.8, CH_2	2.23, m; 1.16, m	24.3, CH_2	2.42, m; 1.35, m	18.7, CH_2	2.17, m; 1.17, m
δ	25.3, CH_2	1.25, m; 0.86, m	46.9, CH_2	3.49, m; 2.87, m	25.2, CH_2	1.25, m; 0.86, m
ε	43.3, CH_2	4.27, m; 3.05, m			43.3, CH_2	4.25, ddd (13.8, 13.8, 3.0); 3.06, m
MeVal[3]						
CO	168.0, C		168.1, C		167.4, C	
α	67.4, CH	4.54, d (10.8)	66.9, CH	4.67, d (11.4)	67.4, CH	4.47, d (10.8)
β	26.3, CH	2.54, m	25.9, CH	2.53, m	26.3, CH	2.52, m
γ	19.9, CH_3	1.30, d (6.6)	19.8, CH_3	1.30, d (6.6)	19.8, CH_3	1.28, d (6.6)
γ	19.0, CH_3	0.73, d (6.6)	18.7, CH_3	0.69, d (6.6)	19.1, CH_3	0.72, d (6.6)
NMe	28.7, CH_3	2.93, s	29.4, CH_3	2.88, s	28.5, CH_3	2.91, s
Val[4]/Leu[4]						
CO	171.4, C		171.4, C		171.5, C	
α	55.1, CH	4.81, t (10.2)	55.0, CH	4.83, t (10.2)	47.0, CH	5.38, m
β	29.4, CH	2.44, m	29.8, CH	2.43, m	41.0, CH_2	2.02, m; 1.48, m
γ	18.1, CH_3	0.91, d (6.6)	18.4, CH_3	0.93, d (6.6)	25.1, CH	1.68, m
γ/δ	20.3, CH_3	0.87, d (6.6)	20.2, CH_3	0.87, d (6.6)	22.9, CH_3	0.96, d (6.6)
δ					21.9, CH_3	0.97, d (6.6)
NH		7.32, d (10.2)		7.42, d (10.2)		7.37, d (10.2)
MeAsp[5]						
CO	170.1, C		169.7, C		169.7, C	
α	52.8, CH	6.63, dd (11.4, 5.4)	52.6, CH	6.61, dd (11.4, 5.4)	52.7, CH	6.62, dd (11.4, 5.4)
β	35.6, CH_2	3.56, m; 3.31, m	35.5, CH_2	3.59, m; 3.18, m	35.7, CH_2	3.63, m; 3.25, m
COOH	172.1, C		171.8, C		172.0, C	
NMe	30.9, CH_3	3.20, s	30.9, CH_3	3.21, s	30.9, CH_3	3.22, s
MeIle[6]						
CO	170.1, C		170.6[d], C		170.7, C	
α	55.9, CH	5.42, d (10.8)	56.6, CH	5.46, d (10.8)	56.7, CH	5.44, d (11.4)
β	32.9, CH	2.30, m	32.7, CH	2.34, m	32.9, CH	2.32, m
γ	24.7, CH_2	1.26, m; 1.02, m	24.5, CH_2	1.26, m; 1.03, m	24.6, CH_2	1.27, m; 0.99, m
δ	14.9, CH_3	0.79, d (5.4)	15.3, CH_3	0.85, d (6.0)	15.3, CH_3	0.84, d (6.0)
δ	9.6, CH_3	0.76, m	9.7, CH_3	0.78, t (7.5)	9.9, CH_3	0.75, t (7.5)
NMe	30.3, CH_3	3.22, s	30.1, CH_3	3.20, s		30.2, CH_3
MeLeu[7]/MeIle[7]						
CO	169.8 (br), C		170.6[d], C		170.3, C	
α	65.9, CH	3.21, d (10.2)	74.9, CH	2.91, d (10.2)	74.6, CH	2.89, d (10.2)
β	37.4, CH_2	2.44, m	33.9, CH	3.11, m	34.0, CH	3.08, m
γ	25.8, CH	1.63, m	26.0, CH_2	1.49, m; 0.86, m	26.1, CH_2	1.51, m; 0.86, m

γ/δ	23.5, CH_3	0.79, d (5.4)	17.9, CH_3	1.20, d (6.0)	18.1, CH_3	1.22, d (6.0)
δ	21.8, CH_3	0.87, d (6.0)	11.0, CH_3	0.84, m	11.1, CH_3	0.84, m
NMe	39.8, CH_3	3.10, s	40.9, CH_3	3.11, s	41.0, CH_3	3.11, s
Gly[8]						
CO	169.0, C		169.3, C		169.2, C	
α	42.2, CH_2	3.92, br s	41.6, CH_2	4.17, dd (17.4, 6.0); 3.62, dd (17.4, 3.0)	41.7, CH_2	4.11, dd (17.4, 6.0); 3.67, dd (17.4, 3.0)
NH		7.05, br s		7.44, dd (6.0, 3.0)		7.33, dd (6.0, 3.0)
MeVal[9]						
CO	168.7, C		169.0, C		168.9, C	
α	62.3, CH	5.06, d (10.8)	62.4, CH	5.06, d (10.8)	62.3, CH	5.05, d (10.8)
β	26.9, CH	2.26, m	27.1, CH	2.28, m	27.0, CH	2.27, m
γ	20.0, CH_3	1.10, d (6.0)	20.2, CH_3	1.11, d (6.6)	19.8, CH_3	1.11, d (6.6)
γ	18.5, CH_3	0.58, d (6.6)	18.8, CH_3	0.72, d (6.6)	18.7, CH_3	0.67, d (6.6)
NMe	28.1[c], CH_3	2.21, s	28.3, CH_3	2.21, s	28.2, CH_3	2.21, s
Tyr(OMe)[10]						
CO	171.8, C		171.6, C		171.8[e], C	
α	51.0, CH	5.65, m	51.5, CH	5.58, ddd (12.6, 9.6, 4.8)	51.3, CH	5.64, ddd (12.6, 10.2, 4.8)
β	34.9, CH_2	3.71, m; 3.52, dd (13.8, 4.8)	34.9, CH_2	3.72, dd (13.8, 12.6); 3.54, dd (13.8, 4.8)	34.9, CH_2	3.81, m; 3.59, m
1'	130.1, C		130.5, C		130.4, C	
2', 6'	130.9, CH	7.12, d (7.8)	130.9, CH	7.14, d (8.4)	131.9, CH	7.14, d (8.4)
3', 5'	113.7, CH	6.87, d (7.8)	113.6, CH	6.77, d (8.4)	113.7, CH	6.81, d (8.4)
4'	158.9, C		158.7, C		158.7, C	
OMe	55.3, CH_3	3.72, s	55.0, CH_3	3.52, s	55.1, CH_3	3.57, s
NH		7.63, d (9.6)		7.63, d (9.6)		7.62, d (10.2)

[a]Hiv = 2-hydroxyisovaleric acid, Pip = pipecolic acid; [b]The data for the major conformer are listed. See Table S2 for the data for the minor conformer; [c–e]Interchangeable within the same letters.

Table S2. NMR Data (^{1}H 600 MHz, ^{13}C 150 MHz, benzene-d_6) for Minor Conformers of Clavariopsins D (4), F (6) and I (9)

	Conformer of **4**		Conformer of **6**		Conformer of **9**	
position[a]	δ_C, type	δ_H, mult. (J in Hz)	δ_C, type	δ_H, mult. (J in Hz)	δ_C, type	δ_H, mult. (J in Hz)
Hiv[1]						
CO	171.9, C		172.0, C		171.9[c], C	
α	74.4, CH	5.58, d (3.0)	75.0, CH	5.27, d (3.0)	74.8, CH	5.24, d (3.0)
β	30.5, CH	1.73, m	30.4, CH	1.85, m	30.5, CH	1.75, m
γ	19.2, CH_3	0.95, d (6.6)	19.0, CH_3	0.92, d (6.6)	20.1, CH_3	0.88, d (6.6)
γ	16.0, CH_3	0.94, d (6.6)	16.2, CH_3	0.91, d (6.6)	16.3, CH_3	0.89, d (6.6)
Pip[2]						
CO	171.4, C		171.5, C		171.1, C	
α	47.0, CH	5.76, d (6.0)	46.7, CH	5.75, m	46.6, CH	5.89, d (5.4)
β	28.2, CH_2	1.65, m; 1.19, m	28.3, CH_2	1.64, m; 1.19, m	28.3, CH_2	1.62, m; 1.17, m
γ	18.9, CH_2	2.26, m; 1.17, m	18.8, CH_2	2.18, m; 1.17, m	18.7, CH_2	2.21, m; 1.21, m
δ	25.3, CH_2	1.25, m; 0.86, m	25.3, CH_2	1.23, m; 0.86, m	25.2, CH_2	1.27, m; 0.88, m
ε	43.4, CH_2	4.21, m; 2.97, m	43.3, CH_2	4.22, m; 3.00, m	43.7, CH_2	4.25, ddd (13.8, 13.8, 3.0); 3.06, m
MeVal[3]						
CO	168.1, C		168.1, C		167.4, C	
α	67.5, CH	4.53, d (10.8)	67.4, CH	4.55, d (10.8)	67.4, CH	4.61, d (10.8)
β	26.4, CH	2.55, m	26.3, CH	2.53, m	26.3, CH	2.52, m
γ	20.0, CH_3	1.29, d (6.6)	19.8, CH_3	1.25, d (6.0)	19.8, CH_3	1.28, d (6.6)
γ	19.2, CH_3	0.74, d (6.6)	19.1, CH_3	0.73, d (6.6)	19.1, CH_3	0.72, d (6.6)
NMe	28.8, CH_3	2.94, s	28.8, CH_3	2.92, s	28.5, CH_3	2.94, s
Val[4]/Leu[4]						
CO	171.4, C		171.3[b], C		171.5, C	
α	55.2, CH	4.79, m	55.0, CH	4.76, t (10.2)	47.0, CH	5.35, m
β	29.7, CH	2.65, m	29.5, CH	2.41, m	41.1, CH_2	2.01, m; 1.50, m
γ	18.3, CH_3	1.02, d (6.6)	18.2, CH_3	0.84, d (6.6)	24.9, CH	1.68, m
γ/δ	20.2, CH_3	0.88, d (6.6)	20.2, CH_3	0.88, m	26.3, CH_3	0.96, d (6.6)
δ					21.9, CH_3	0.97, d (6.6)
NH		7.37, d (10.2)		7.30, d (10.2)		7.37, d (10.2)
MeAsp[5]						
CO	170.0, C		169.5, C		179.7, C	
α	54.1, CH	6.81, m	52.8, CH	6.60, dd (11.4, 5.4)	52.7, CH	6.62, dd (11.4, 5.4)
β	36.2, CH_2	4.01, m; 3.32, m	35.7, CH_2	3.53, m; 3.23, m	35.7, CH_2	3.78, m; 3.19, m
COOH	172.1, C		172.0, C		172.0, C	
NMe	32.1, CH_3	3.15, s	30.6, CH_3	3.11, s	31.2, CH_3	3.11, s
MeVal[6]/MeLeu[6]/MeIle[6]						
CO	171.5, C		171.0, C		170.7, C	
α	59.8, CH	5.51, d (10.8)	50.0, CH	5.94, m	56.5, CH	5.43, d (11.4)
β	29.1, CH	2.69, m	38.5, CH_2	1.85, m; 1.64, m	32.7, CH	2.32, m
γ	19.4, CH_3	1.02, d (6.0)	25.3, CH	1.46, m	24.5, CH_2	1.26, m; 1.00, m
γ/δ	18.8, CH_3	0.85, d (6.0)	22.4, CH_3	0.92, d (6.6)	15.2, CH_3	0.84, d (6.0)
δ			22.9, CH_3	0.86, d (6.6)	9.7, CH_3	0.75, t (7.5)
NMe	29.7, CH_3	3.17, s	29.7, CH_3	3.21, s	30.1, CH_3	3.21, s
MeIle[7]						
CO	170.8, C		171.4[b], C		170.4, C	
α	74.6, CH	2.88, d (10.2)	74.4, CH	2.96, d (10.2)	74.4, CH	2.91, m
β	33.3, CH	2.27, m	33.8, CH	3.06, m	34.0, CH	3.09, m

γ	26.1, CH_2	2.19, m; 0.86, m	25.9, CH_2	1.42, m; 0.84, m	26.1, CH_2	1.48, m; 0.86, m
γ	18.2, CH_3	1.22, d (6.0)	18.2, CH_3	1.14, d (6.6)	18.1, CH_3	0.90, d (6.0)
δ	11.7, CH_3	0.77, m	11.0, CH_3	0.84, m	11.1, CH_3	0.84, m
NMe	41.1, CH_3	3.10, s	41.0, CH_3	3.15, s	41.1, CH_3	3.15, s
Gly[8]						
CO	169.2, C		169.0, C		169.2, C	
α	41.9, CH_2	3.97, dd (17.4, 5.4); 3.60, m	41.6, CH_2	3.81, m; 3.66, m	41.4, CH_2	4.11, dd (17.4, 6.0); 3.67, dd (17.4, 3.0)
NH		7.30, d (10.2)		7.48, br s		7.33, dd (6.0, 3.0)
MeVal[9]						
CO	168.7, C		169.0, C		168.9, C	
α	62.6, CH	4.65, d (11.2)	62.4, CH	5.00, d (11.4)	62.3, CH	5.02, d (11.4)
β	27.0, CH	2.22, m	26.9, CH	2.24, m	27.0, CH	2.27, m
γ	20.5, CH_3	1.02, d (6.6)	20.0, CH_3	1.09, d (6.6)	19.8, CH_3	1.11, d (6.6)
γ	18.4, CH_3	0.43, d (6.6)	18.7, CH_3	0.65, d (6.6)	18.8, CH_3	0.67, d (6.6)
NMe	28.5, CH_3	2.06, s	28.3, CH_3	2.23, s	28.3, CH_3	2.22, s
Tyr(OMe)[10]						
CO	171.9, C		171.5, C		171.8[c], C	
α	51.4, CH	5.69, m	51.2, CH	5.62, m	51.2, CH	5.62, m
β	35.4, CH_2	4.10, m; 3.62, m	35.0, CH_2	3.66, m; 3.53, m	34.8, CH_2	3.72, m; 3.52, m
1'	130.5, C		130.3, C		130.4, C	
2', 6'	130.8, CH	7.24, d (8.4)	130.9, CH	7.11, d (8.4)	130.9, CH	7.12, d (8.4)
3', 5'	113.4, CH	6.69, d (8.4)	113.8, CH	6.77, d (8.4)	113.3, CH	6.71, d (8.4)
4'	158.7, C		158.8, C		158.7, C	
OMe	55.0, CH_3	3.50, s	55.1, CH_3	3.57, s	55.0, CH_3	3.93, s
NH		7.24, d (9.6)		7.73, d (9.6)		7.60, d (9.6)

[a]Hiv = 2-hydroxyisovaleric acid, Pip = pipecolic acid, [b,c]Interchangeable within the same marks

Table S3. Cytotoxicity of Clavariopsins against HeLa-S3 Cells

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	paclitaxel
IC_{50} (μM)	20	37	41	19	20	26	20	88[a]	14	0.007

[a]The data is an extrapolated value.