

Supporting Information for
**“Novel Iodinated Diterpenes from a Marine
Cyanobacterium and Red Alga Assemblage”**

Philip G. Williams, Wesley Y. Yoshida, Richard E. Moore, Valerie J. Paul

Extraction and Isolation of VP643 – Lipophilic Extract. The freeze-dried cyanobacterium (300 g) was thrice extracted with a 4:1 mixture of CH_3CN - CH_2Cl_2 to provide a total of 2.67 g of lipophilic extract. After partitioning between hexane and 80 % aqueous methanol the aqueous residue was loaded on to a Si flash column and was eluted with increasing amounts of MeOH in CH_2Cl_2 . The 5 % fraction from was loaded onto a Sephadex LH-20 column (50 x 2.5 cm) and eluted with 4:1 CH_2Cl_2 :MeOH. The samples eluting between 120 and 180 mL were again separated by Sephadex LH-20 using 5 % MeOH in CH_2Cl_2 . The fraction eluting between 180 and 240 mL was concentrated and separated by repeated RP-HPLC [1. Ultracarb ODS 30, 250 x 10 mm, 60 % aqueous CH_3CN , flow rate 3 mL/min, t_R 34.2 min; 2. Ultracarb ODS 30, 70 % aqueous MeOH, flow rate 3 mL/min, t_R 27.0 min; 3. Ultracarb ODS 30, 85 % aqueous MeOH, flow rate 3 mL/min, t_R 12.0 min; 4. Ultracarb ODS 30, 70 % aqueous CH_3CN , flow rate 3 mL/min, t_R 19.6 min] to yield tasihalide A (**1**, 0.9 mg).

Extraction and Isolation of VP643 – Aqueous Extract. The cyanobacterium (300 g), which had already been extracted with 4:1 CH_3CN : CH_2Cl_2 , was exhaustively extracted with 30 % aqueous EtOH to give 2 g of extract. After partitioning between *n*-BuOH and water, the dry organic residue was loaded onto a Sephadex LH-20 column (50 x 2.5 cm) and eluted with 5 % MeOH in CHCl_3 (400 mL), 15 % MeOH (700 mL), and pure MeOH (500 mL). The 5 % MeOH Sephadex fractions eluting between 80 and 140 mL were combined, loaded on a C_{18} column, and eluted with increasing amounts of aqueous MeCN. The 50 % and 60 % fractions were combined and subjected to reversed-phase HPLC [Ultracarb ODS 30, 250 x 10 mm, 45 % MeCN in H_2O , flow rate 3 mL/min, detection 220 nm] to give tasihalide B (**1.16**) (t_R 48 min). Tasihalide B (**2**) was purified by repeated HPLC [1. Ultracarb ODS 30, 250 x 10 mm, 60:40 CH_3CN : 0.0025M Na_2SO_4 , flow rate 3 mL/min, detection at 220 nm, t_R 25 min; 2. YMC-AQ ODS, 250 x 10 mm, 80 % aqueous MeCN, flow rate 2.0 mL/min, detection at 220 nm, t_R 10.5 min; 3. Ultracarb ODS 30, 250 x 10 mm, 80 % aqueous MeOH, flow rate 3 mL/min, detection at 220 nm, t_R 14.2 min] to yield 0.8 mg.

Table S1. NMR Spectral Data for Tasihalide B (**2**) in CDCl₃

C/H no.	$\delta_{\text{H}}^{\text{a}}$ (<i>J</i> in Hz)	$\delta_{\text{C}}^{\text{b,c}}$	^1H - ^1H COSY	HMBC ^{d,e}	ROSEY
1	2.40, m	33.1, d			
2	5.06, br s	73.8, d	3	18	3, 18, 20, 21
3ax	2.59, m	39.0, t	2, 3eq		2
3eq	2.40, m		2, 3ax		2
4	5.10, dd (7.3, 5.1)	52.8, d		21	9, 28
5		45.9, s		21	
6	5.53, d (2.8)	73.9, d	7	21	7, 21, 26
7	5.13, dd (2.8, 1.3)	69.6, d	6, 8		6, 8, 24
8	1.85, dd (11.1, 1.3)	45.5, d	9		7, 10, 13ax, 24
9	2.91, dd (11.1, 10.5)	31.1, d	8, 10		4, 17
10	2.39, d (10.5)	50.3, d	9	18, 21	8
11	2.96, d (4.8)	37.0, d	12	16a, 17	12, 17
12	5.33, dd (8.5, 4.8)	68.6, d	11, 13	11, 13ax	11, 13eq, 16a
13	2.33, dd (-15.5, 8.5)	45.4, t	12, 13ax		12, 16a
	1.47, d (-15.5)		12, 13eq		8, 24
14		72.7, s		24	
15		76.4, s		16a, 17	
16	3.25, dd (-10.2, 1.0)	15.3, t	16b	17	12, 13eq
	3.09, d (-10.2)		16a		17
17	1.70, br s	26.3, q			9, 11, 16b, 20, 28
18	1.17, d (7.1)	17.8, q			2, 9
19		171.2, s		20	
20	2.25, s	22.24, q			2, 17, 21
21	1.09, s	18.5, q			3, 6, 9, 20
22		168.7, s		23	
23	2.10, s	21.0, q			
24	1.03, s	22.16, q			7, 8, 13ax
25		169.8, s		26	
26	2.13, s	21.7, q			6
27		169.2, s		28	
28	2.17, s	21.4, q			4, 17

^a Recorded at 500 MHz. ^b Recorded at 125 MHz. ^c Multiplicity deduced by HSQC. ^d Protons showing long range correlation with indicated carbon. ^e Correlations were observed for $^nJ_{\text{CH}} = 7$ Hz

Figure S1. 500 MHz ^1H NMR Spectrum of Tasihalide A (**1**) in CDCl_3

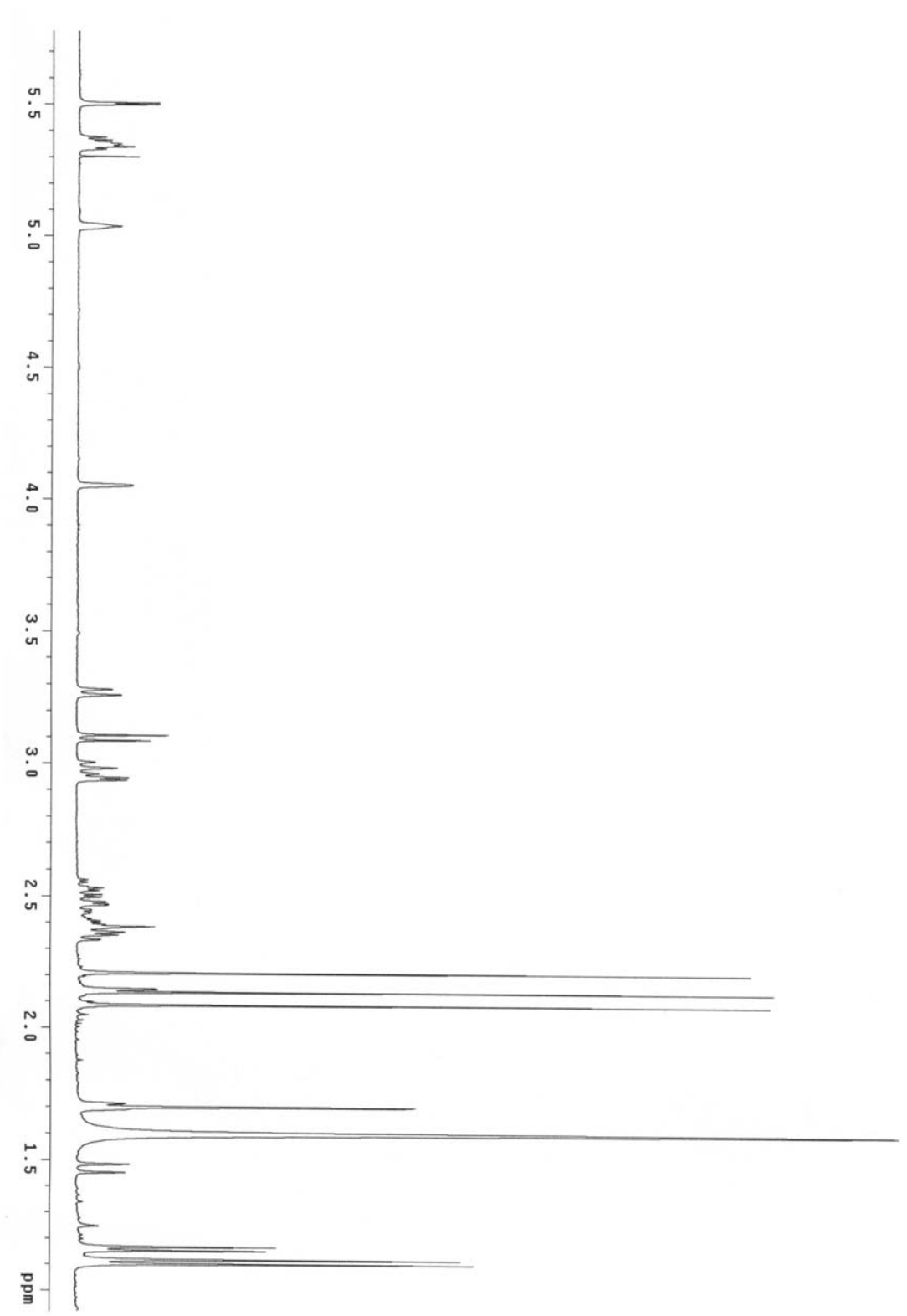


Figure S2. 125 MHz ^{13}C NMR of Tasihalide A (**1**) in CDCl_3

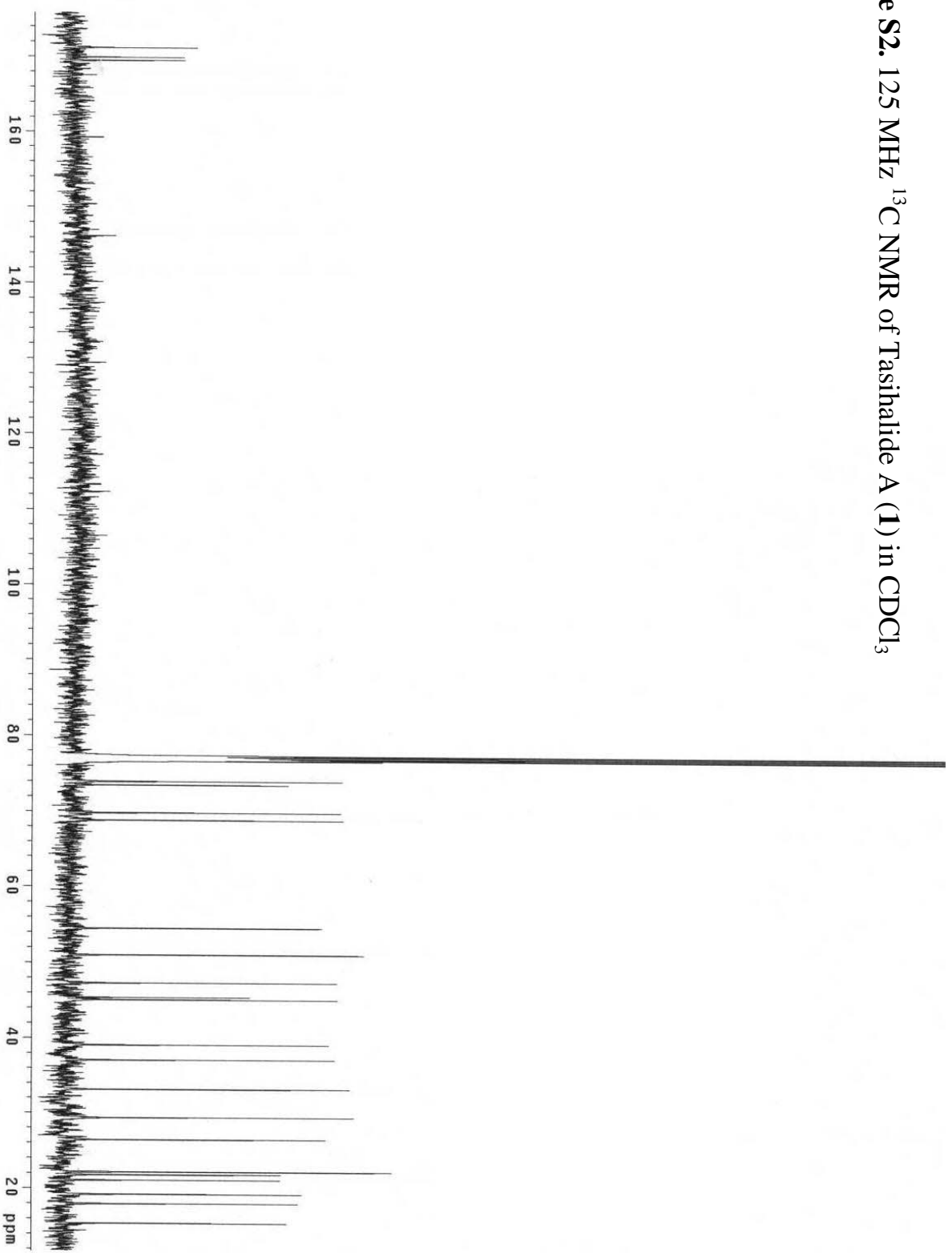


Figure S3. 500 MHz HSQC Spectrum of Tashalide A (**1**) in CDCl₃

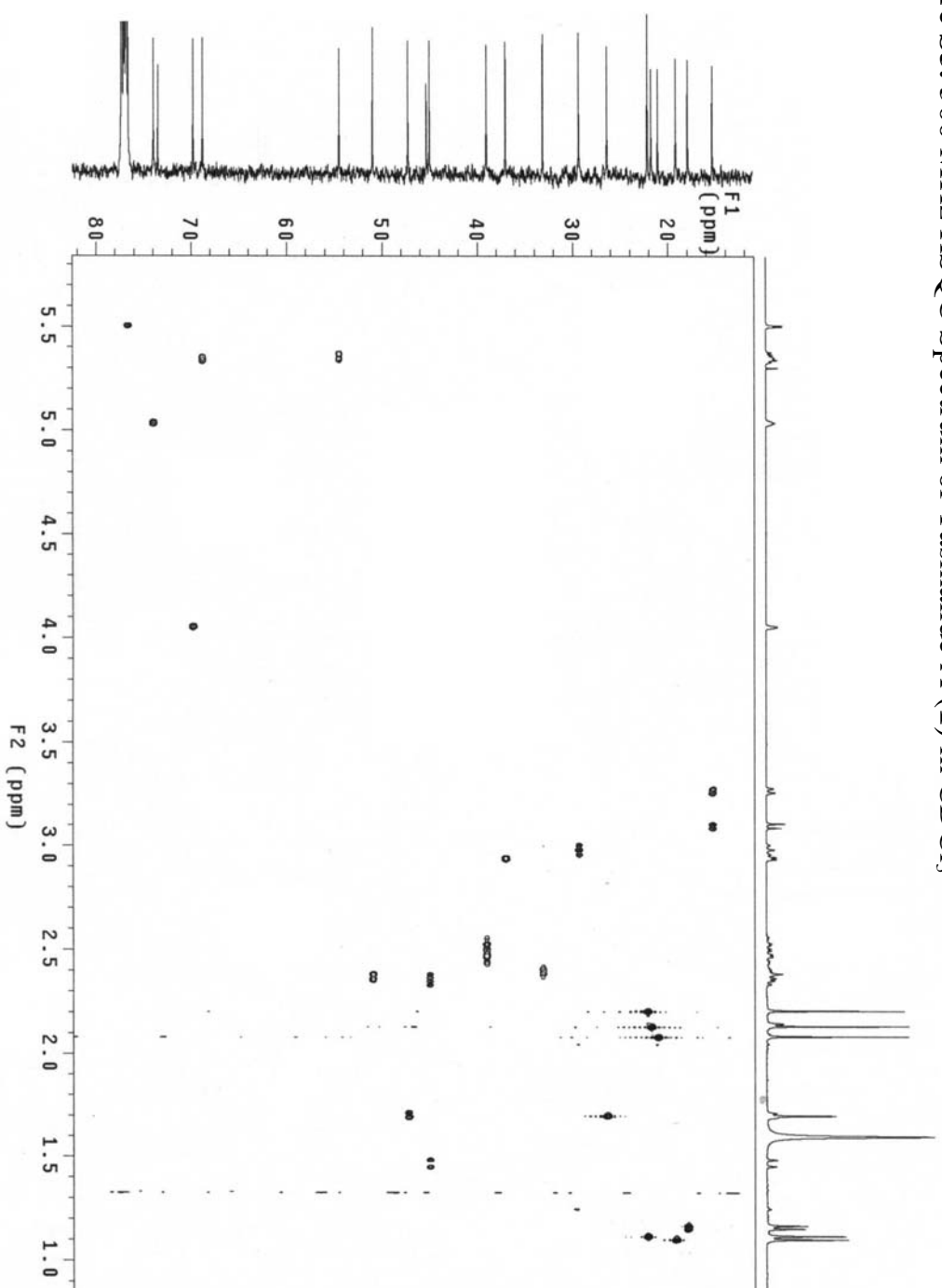


Figure S4. 500 MHz COSY Spectrum of Tashalide A (**1**) in CDCl_3

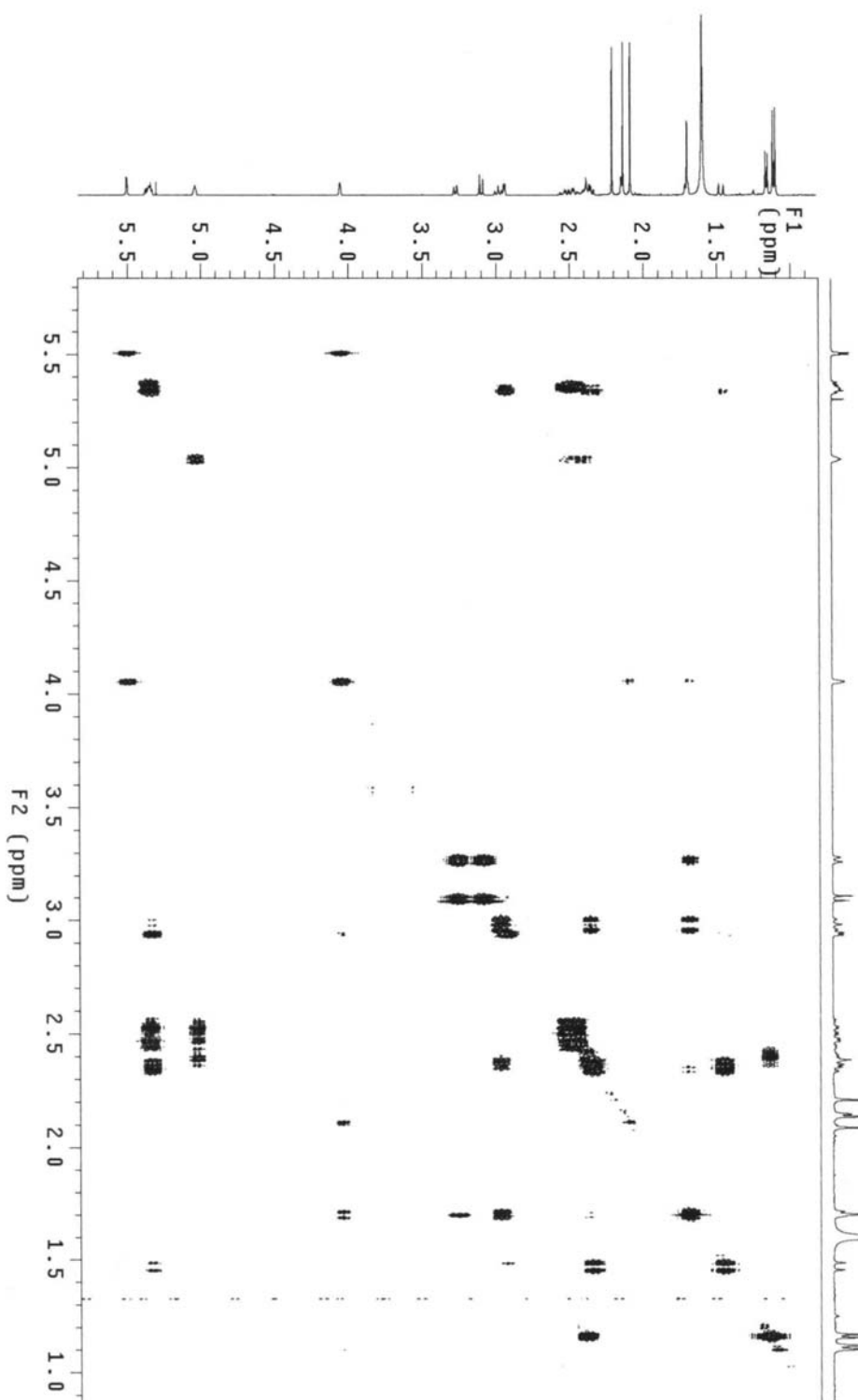


Figure S5. 500 MHz HMBC Spectrum of Tasihalide A (**1**) in CDCl₃

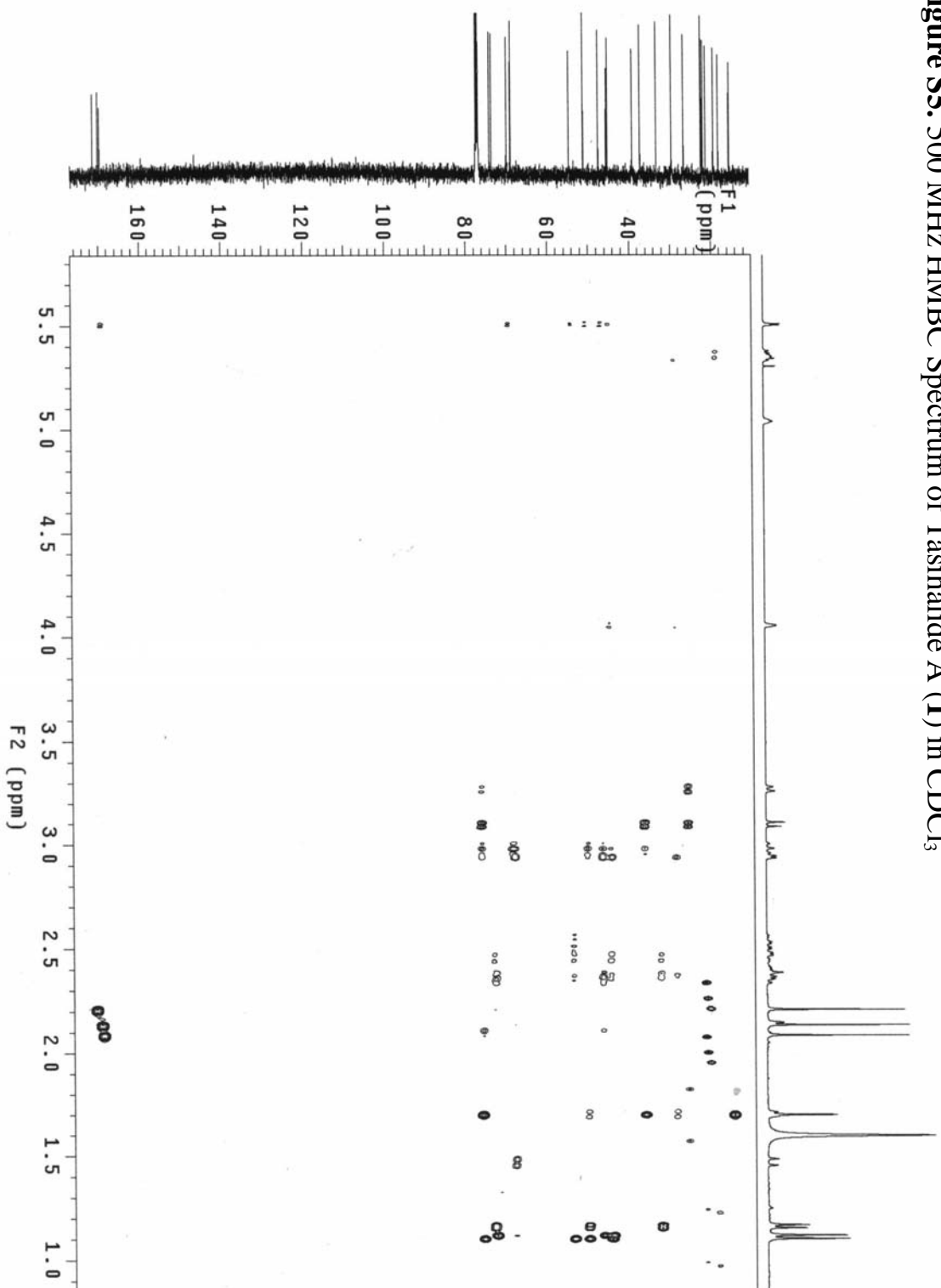


Figure S6. Expansion of 500 MHz HMBC Spectrum of Tasihalide A (**1**) in CDCl₃

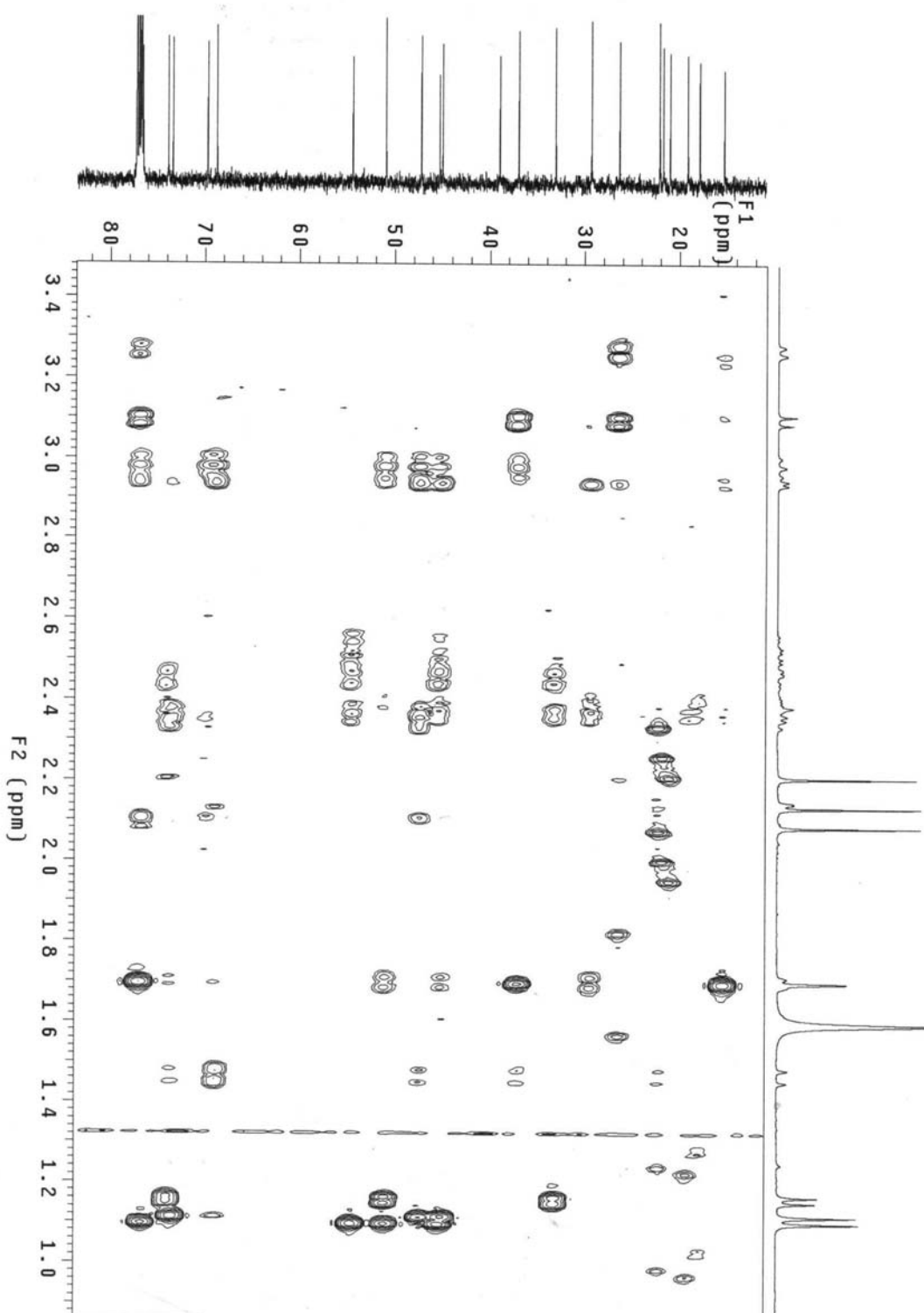


Figure S7. 500 MHz ROESY Spectrum of Tasihalide A (**1**) in CDCl₃

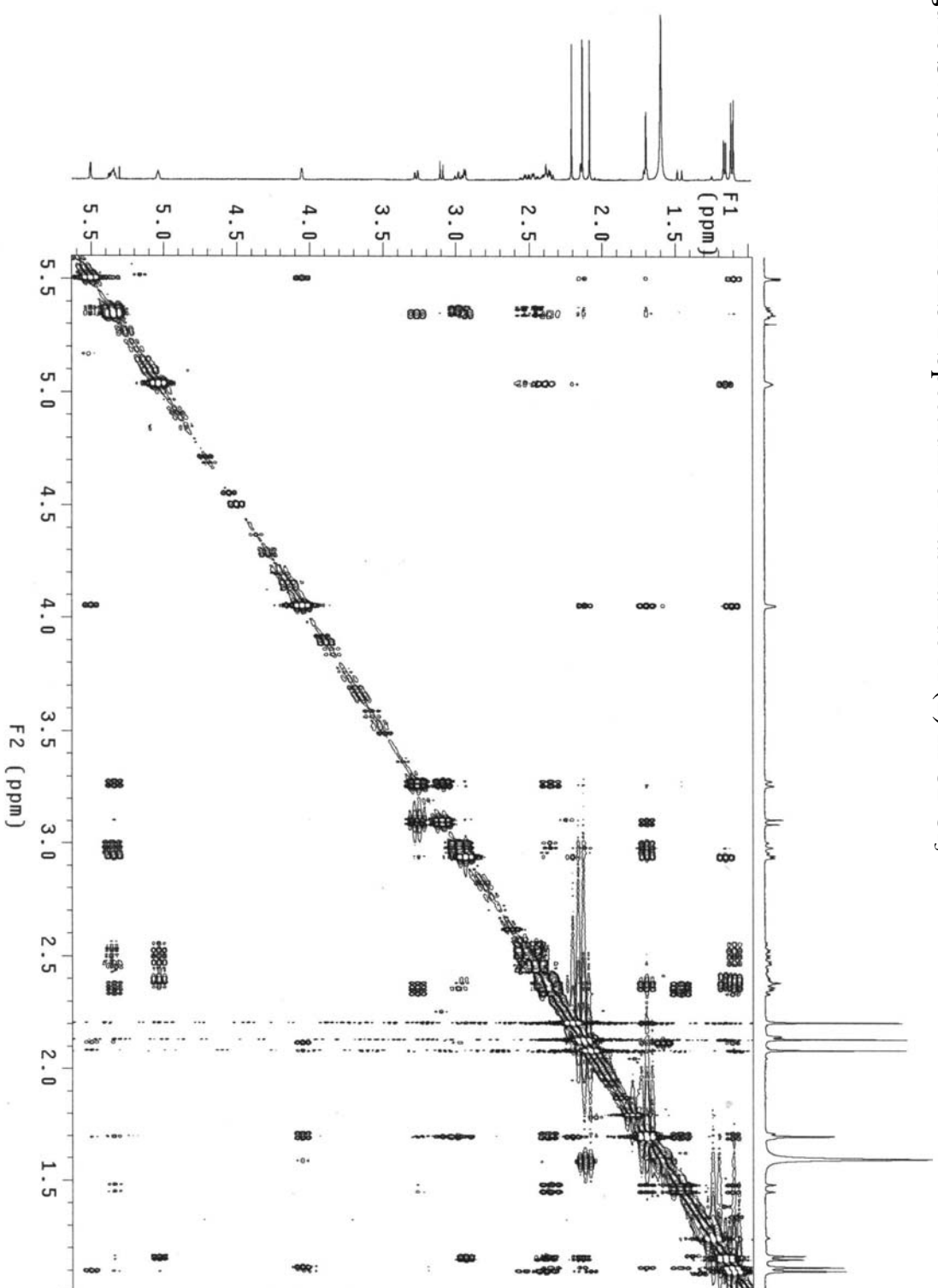


Figure S8. 500 MHz ^1H NMR Spectrum of Tasihalide B (2) in CDCl_3

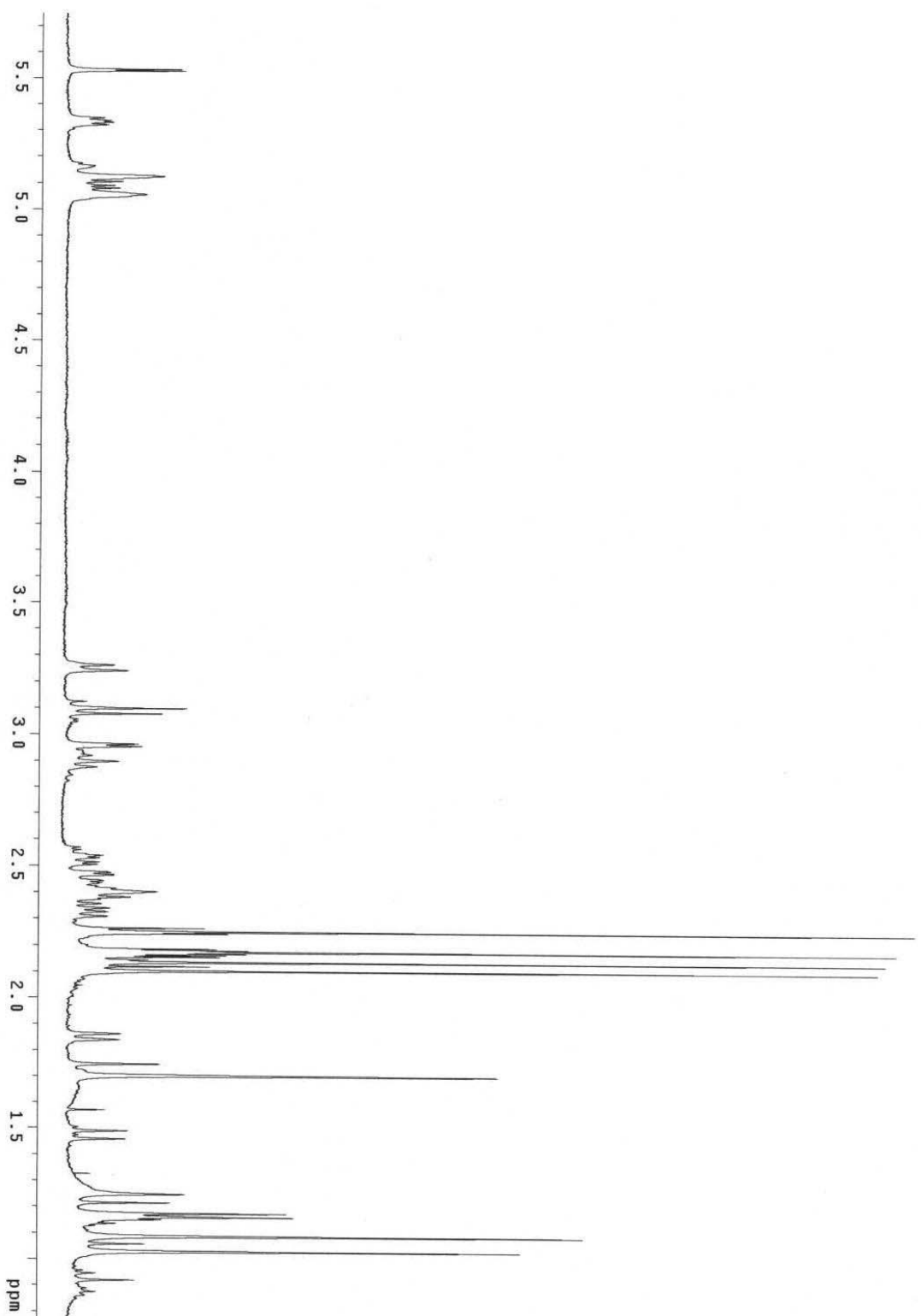


Figure S9. 125 MHz ^{13}C NMR Spectrum of Tasihalide B (**2**) in CDCl_3

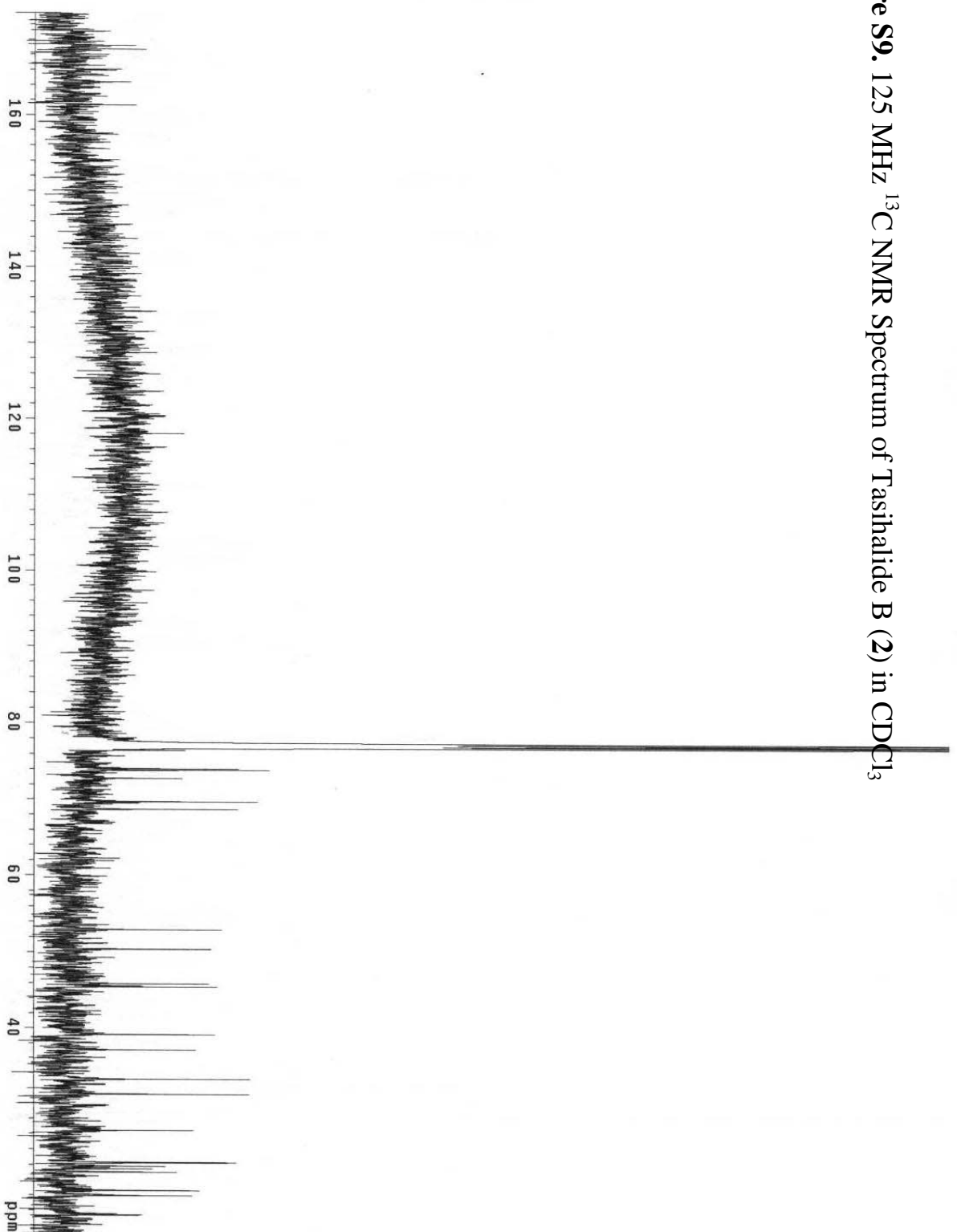


Figure S10. 500 MHz HSQC Spectrum of Tashalide B (2) in CDCl₃

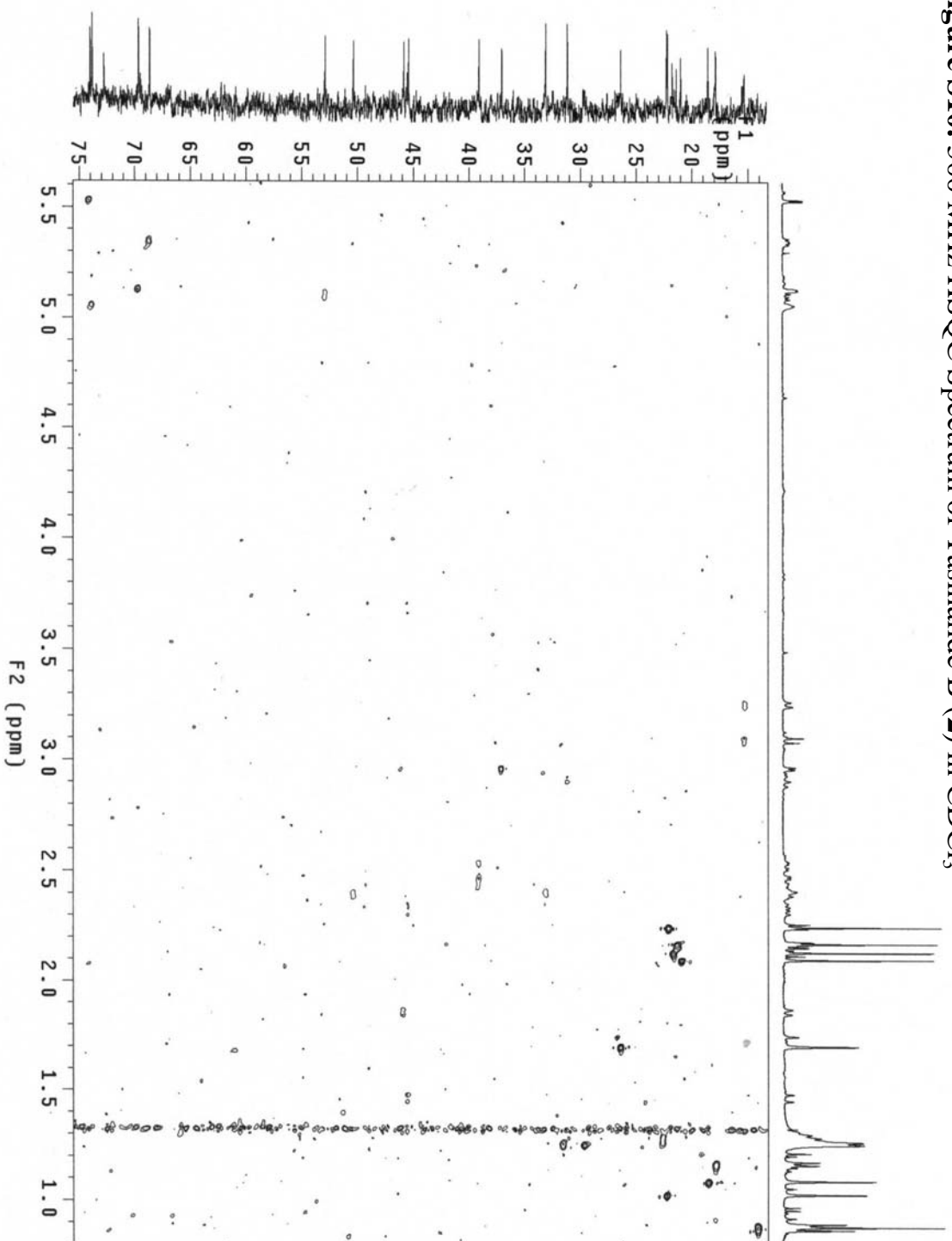


Figure S11. 500 MHz COSY Spectrum of Tashalide B (2) in CDCl₃

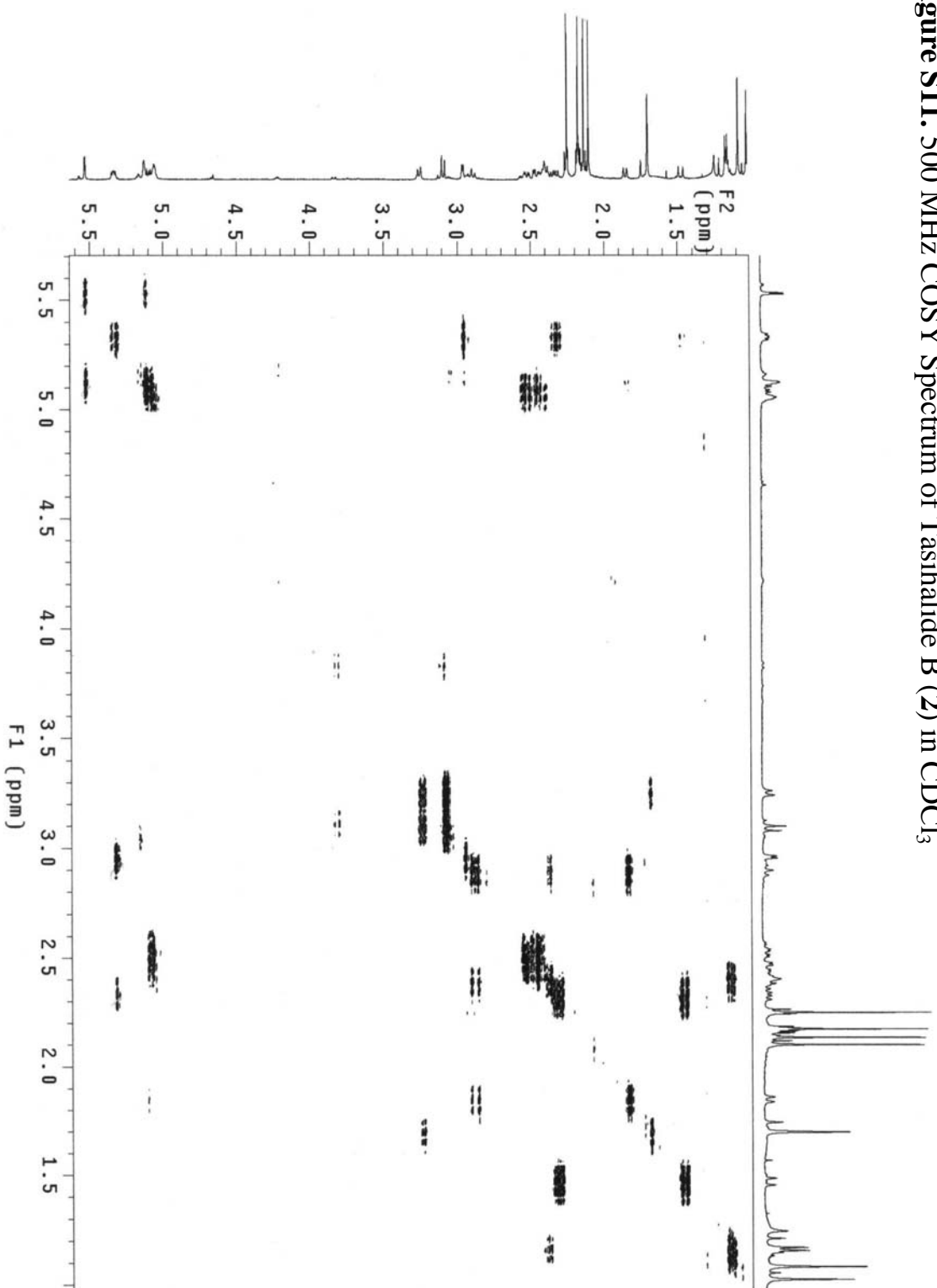


Figure S12. 500 MHz HMBC Spectrum of Tasihalide B (**2**) in CDCl_3

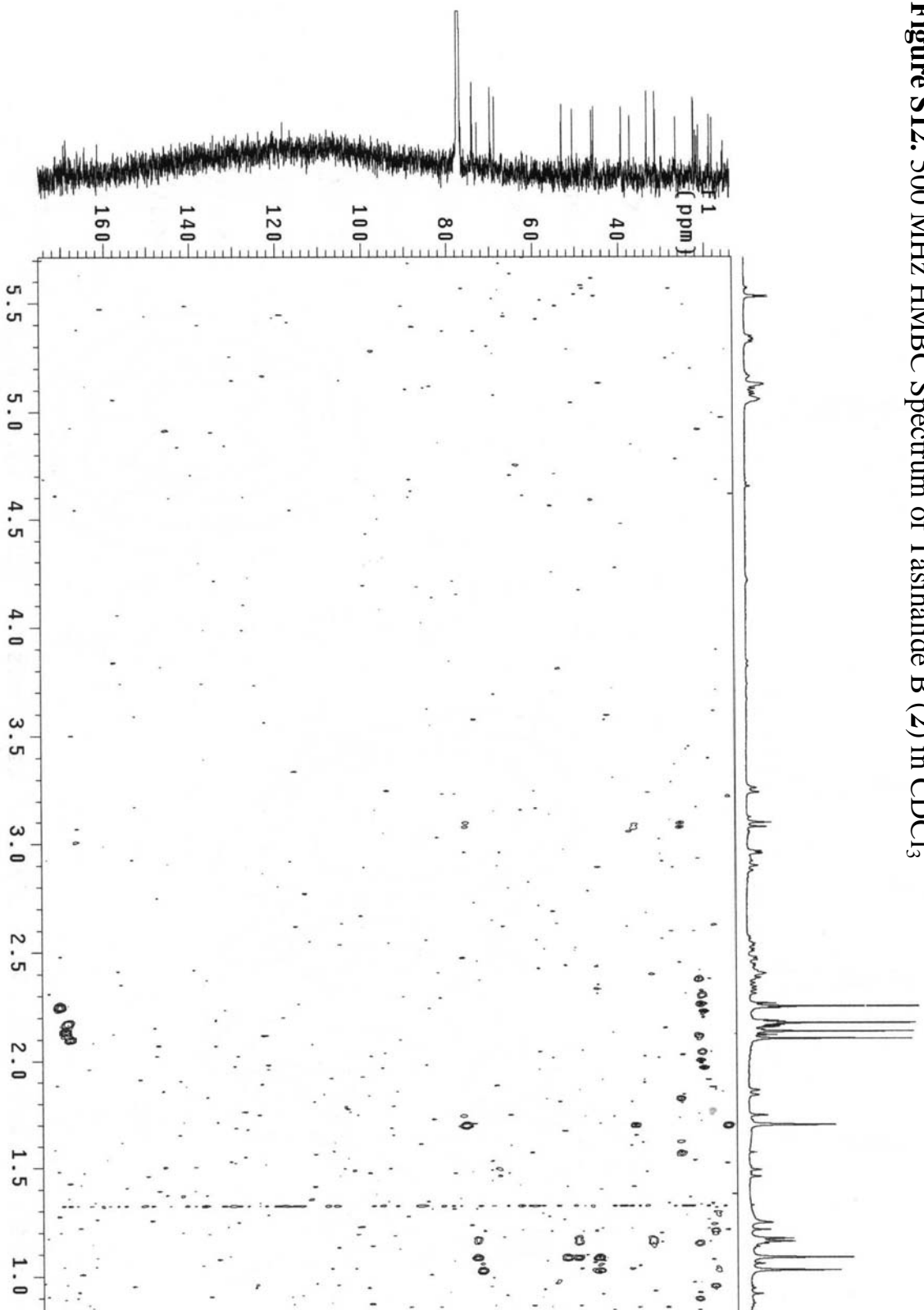


Figure S13. 500 MHz ROESY Spectrum of Tasihalide B (**2**) in CDCl₃

