Isolation, Structure Elucidation and Synthesis of Eudistomides A and B, Lipopeptides from a Fijian Ascidian *Eudistoma* sp.

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Supporting Info

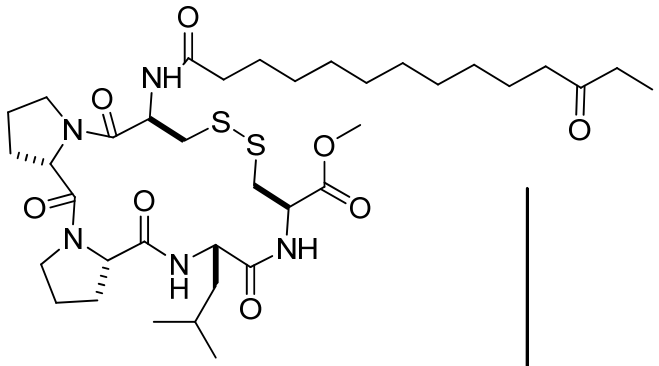
S2.

General Experimental Procedures. NMR data were collected using a 400 (^{1}H 400 MHz, ^{13}C 100 MHz) NMR spectrometer equipped with a 5 mm probe, a 500 (^{1}H 500 MHz, ^{13}C 125 MHz) NMR spectrometer with a 3 mm probe or a 600 (^{1}H 600 MHz, ^{13}C 150 MHz) NMR spectrometer equipped with a 5 mm ^{1}H [^{13}C,^{15}N] triple resonance cold probe with a z-axis gradient, all referenced to residual solvent. High-resolution ESIMS analyses were performed on either a LTQ-FT or a Q-tof micro. IR spectra were recorded on NaCl disks in a FT-IR spectrometer.

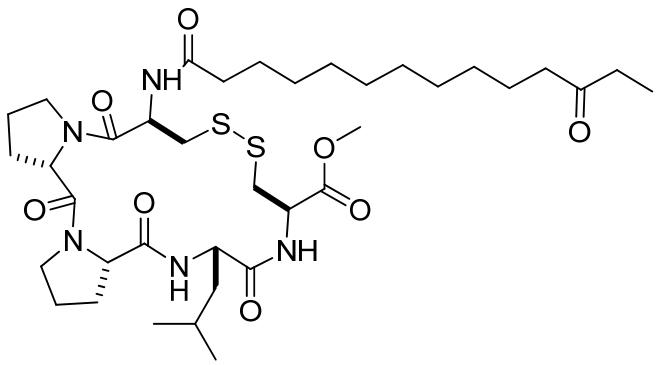
Eudistomide B Acetate Ester Epimers (13, 14). 50 μL of Ac_2O (0.53 mmol) was added to a solution of the eudistomide B alcohol epimers (**2**, **12**) (1.1 mg, 1.4 μmol) in 150 μL of dry pyridine (1.85 mmol). The reaction vial was flushed with argon, sealed, and allowed to stir overnight. CH_2Cl_2 was added to the reaction and subsequently dried under argon. Analysis of the ^{1}H NMR spectra and HSQC of the C-35 acetoxy epimers (**13**, **14**) indicated a quantitative yield for the reaction.

Enantionselective Lipase-Catalyzed Hydrolysis. The acetate ester epimers (**13**, **14**) (1.2 mg, 1.4 μmol) were dissolved in a minimal amount of isopropanol (25 μL). 120 μg of lipase B from *Candida antarctica* (~9 units/mg) dissolved in 100 μL of 1X PBS (pH = 7.4) was added to the epimer solution, and the solution was allowed to stir overnight at 37 °C. The solution was extracted with CH_2Cl_2, and dried under argon. The ^{1}H NMR and HSQC indicate the presence of one alcohol (**2**; 35*R*) and unreacted acetate esters (**13**, **14**).

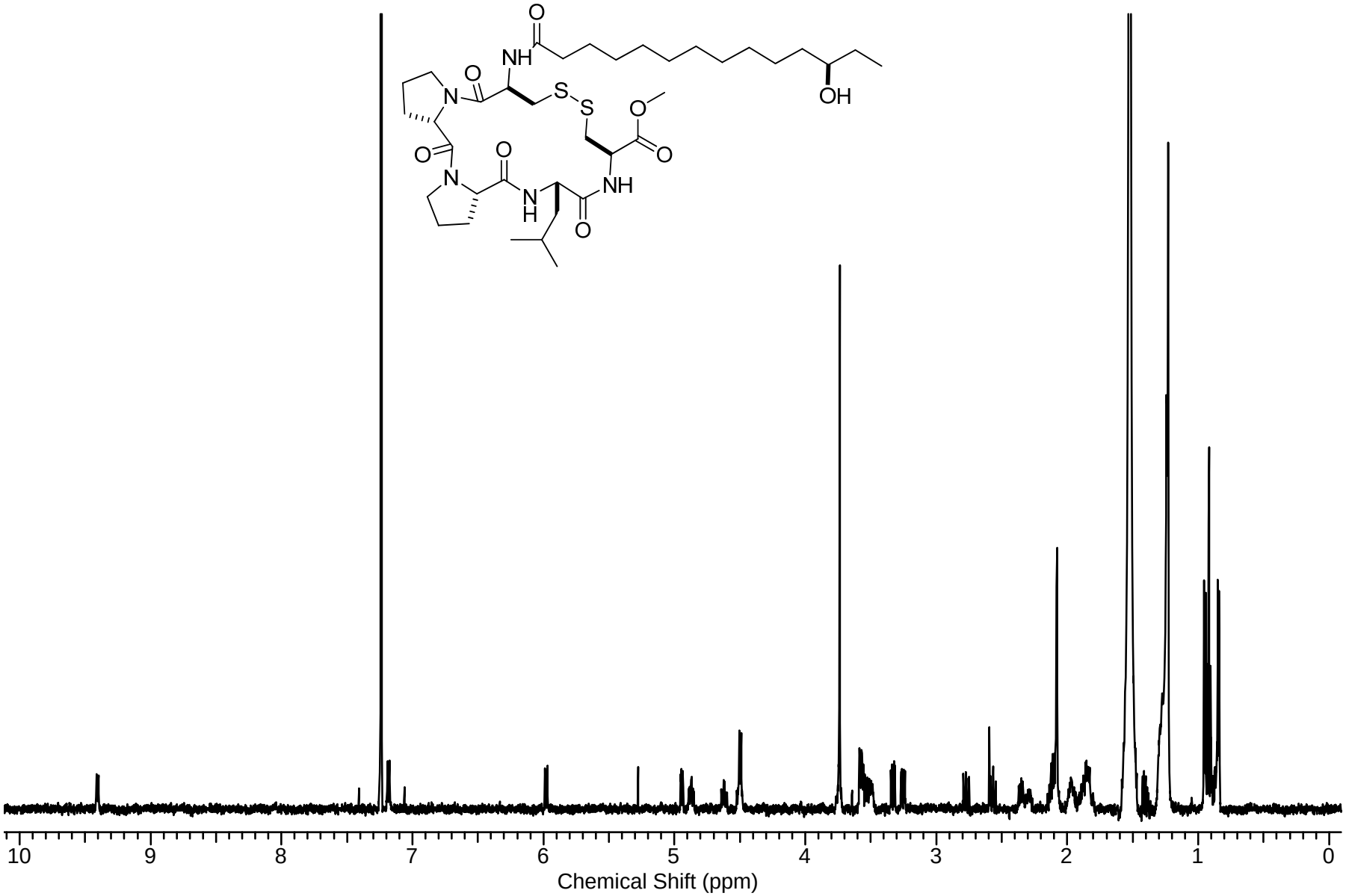
S3 ^{1}H NMR Spectrum of Eudistomide A (**1**) in $CDCl_3$



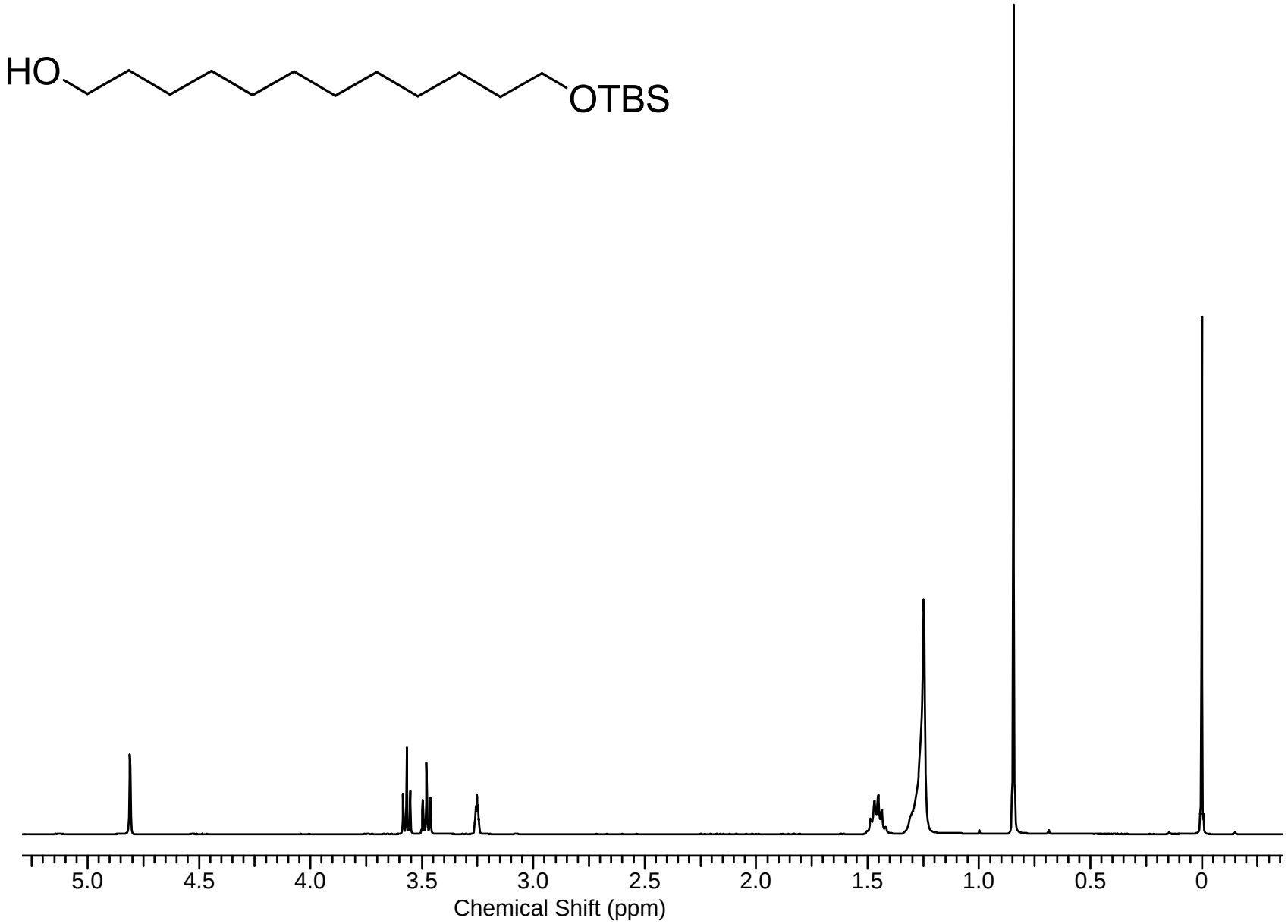
S4 ^{13}C NMR Spectrum of Eudistomide A (**1**) in $CDCl_3$



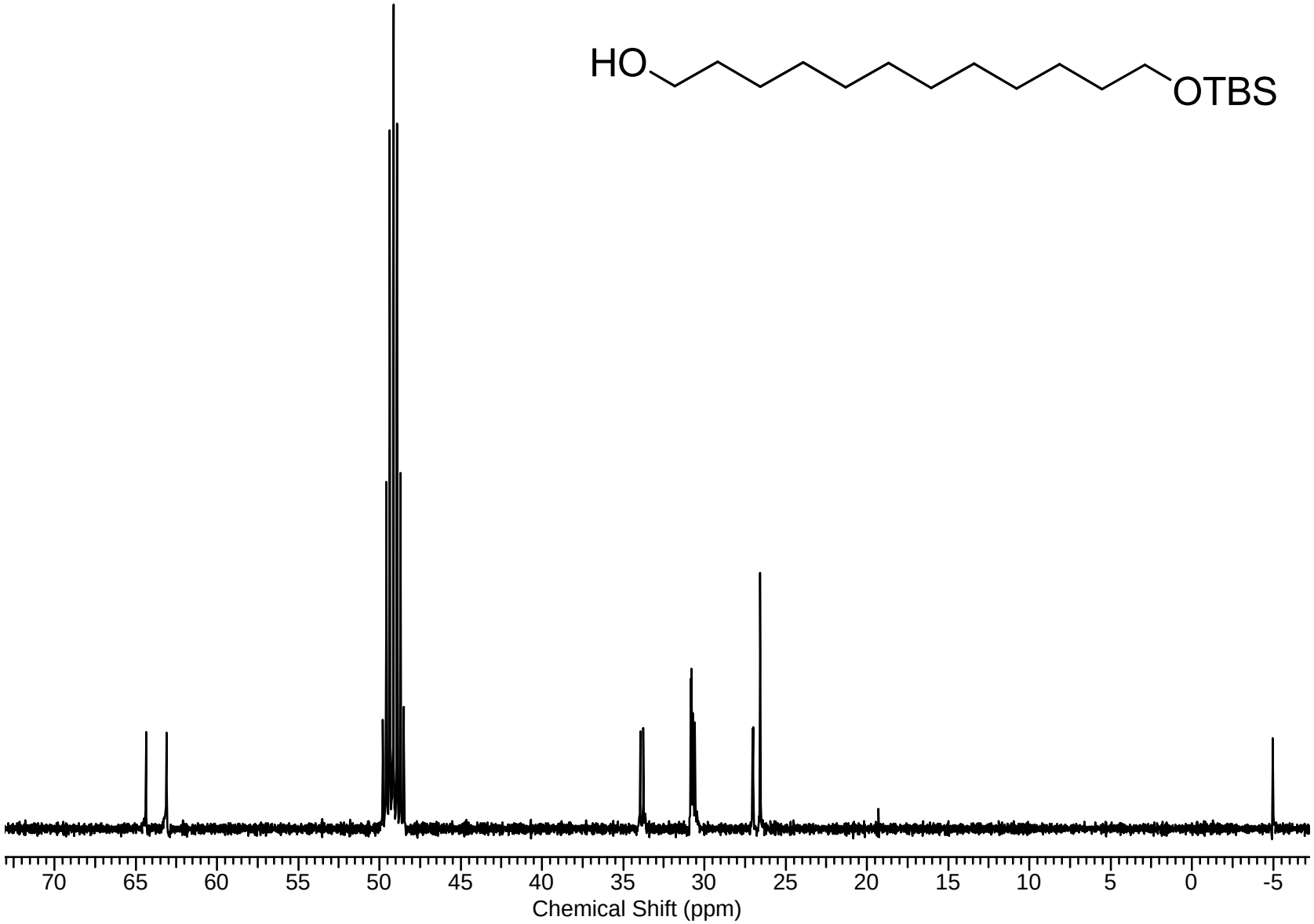
S5 ^{1}H NMR Spectrum of Eudistomide B (**2**) in $CDCl_3$



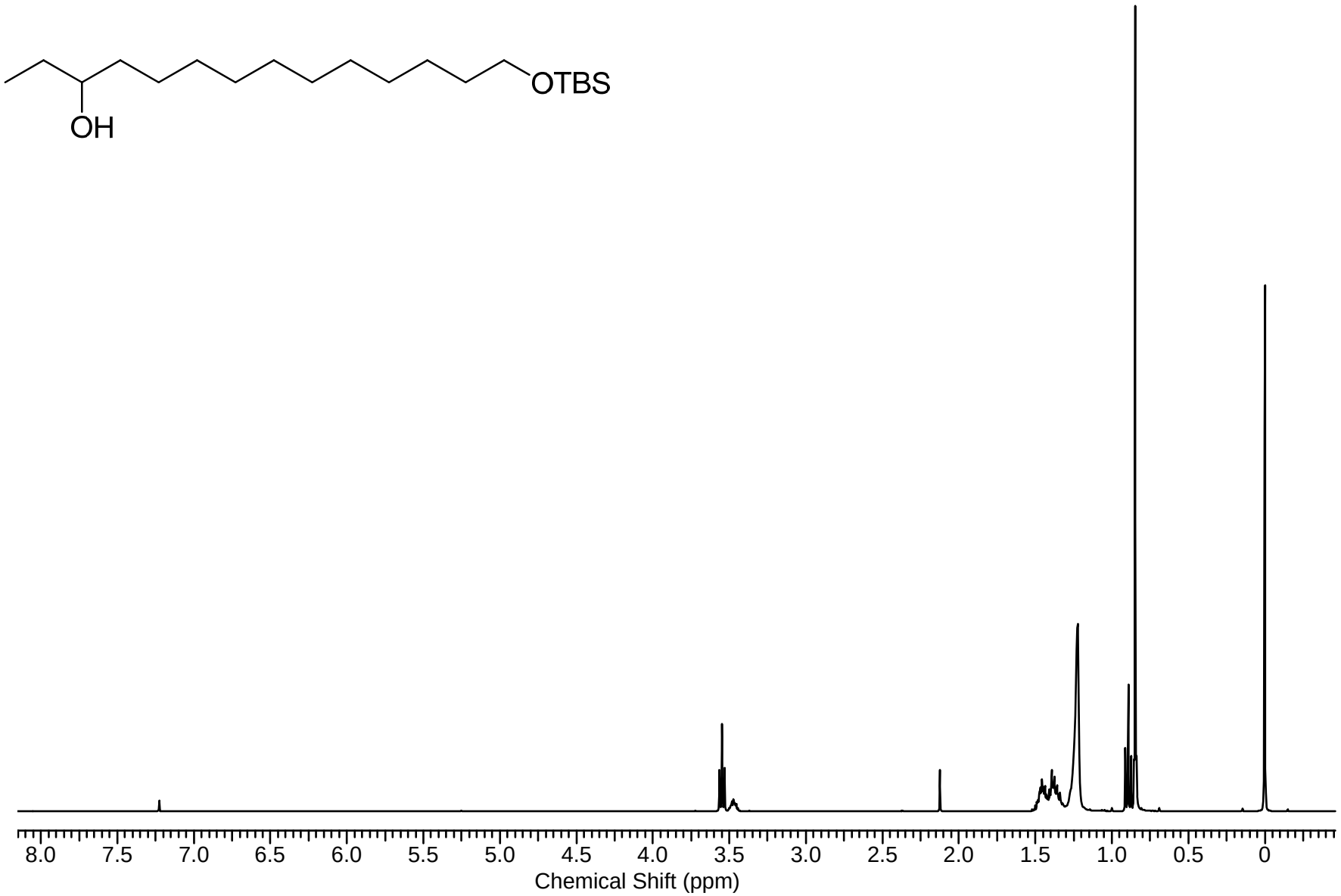
S6 ^{1}H NMR Spectrum of 12-(*tert*-butyldimethylsilyloxy)dodecan-1-ol (**5**) in CD_3OD



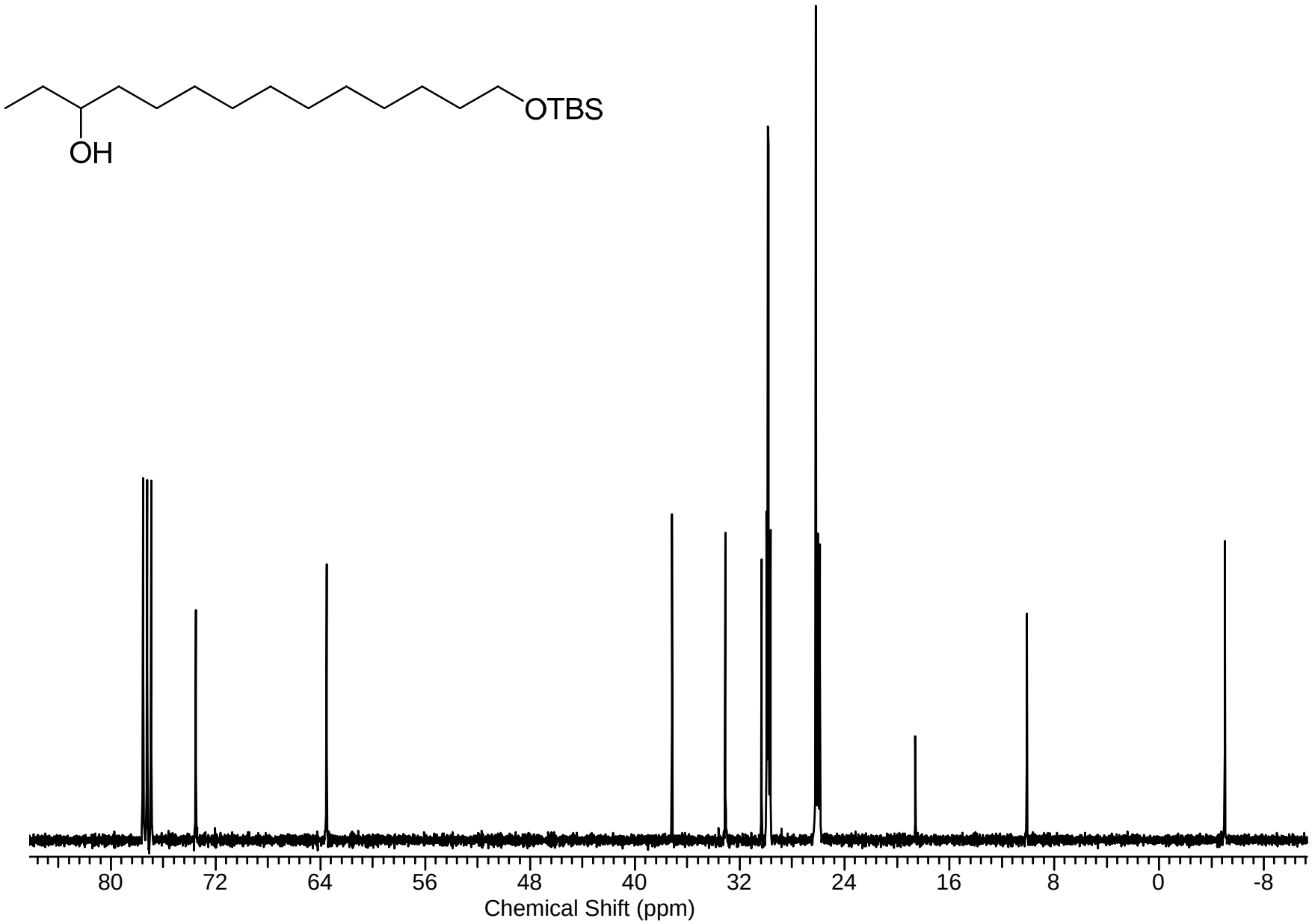
S7 ^{13}C NMR Spectrum of 12-(*tert*-butyldimethylsilyloxy)dodecan-1-ol (**5**) in CD_3OD



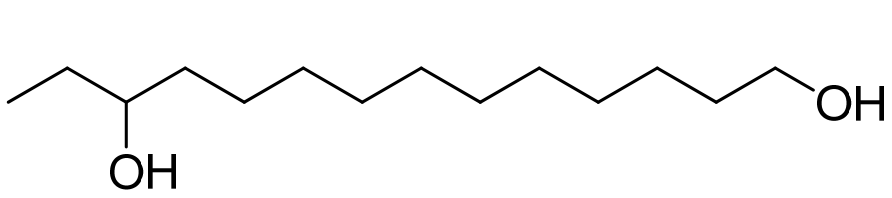
S8 ^{1}H NMR Spectrum of 14-(*tert*-butyldimethylsilyloxy)tetradecan-3-ol (**6**) in CDCl3



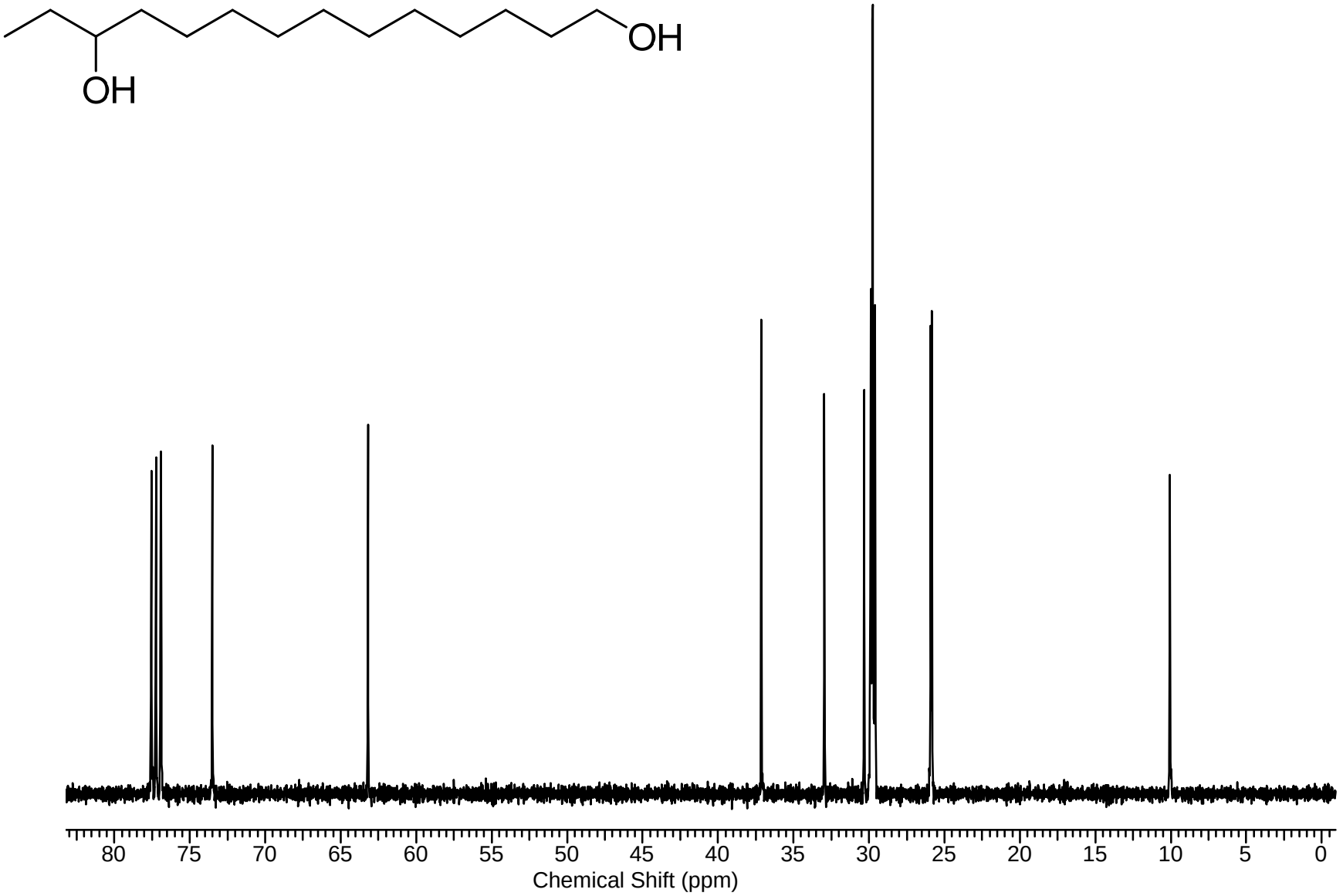
S9 ^{13}C NMR Spectrum of 14-(*tert*-butyldimethylsilyloxy)tetradecan-3-ol (**6**) in CDCl3



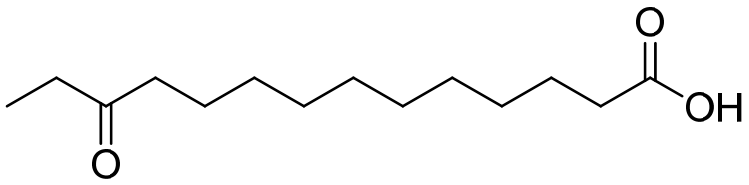
S10 ^{1}H NMR Spectrum of tetradecane-1,12-diol (**7**) in $CDCl_3$



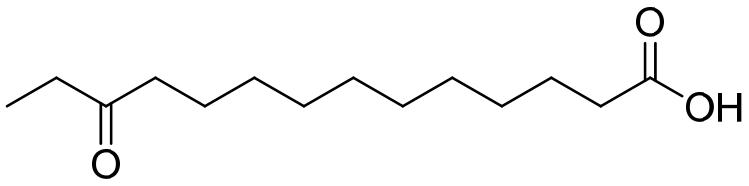
S11 ^{13}C NMR Spectrum of tetradecane-1,12-diol (**7**) in $CDCl_3$



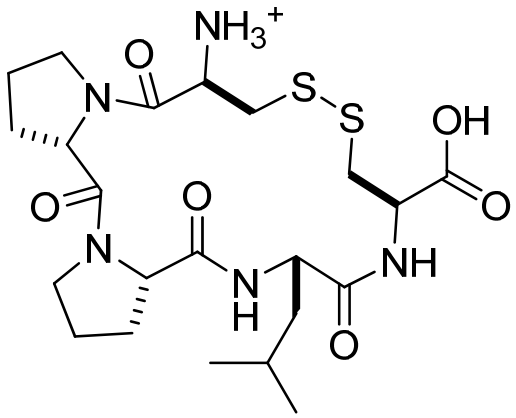
S12 ^{1}H NMR Spectrum of 12-oxo-tetradecanoic acid (**8**) in $CDCl_3$



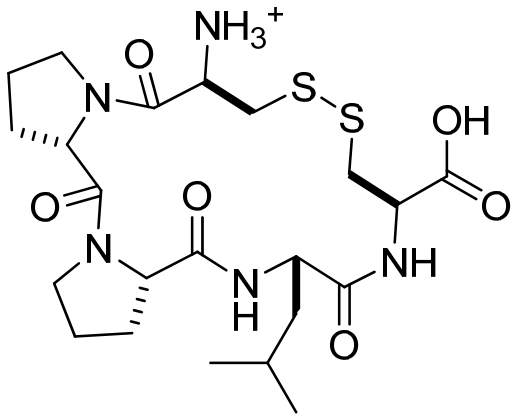
S13 ^{13}C NMR Spectrum of 12-oxo-tetradecanoic acid (**8**) in $CDCl_3$



S14 ^{1}H NMR Spectrum of cyclic pentapeptide (**9**) in DMSO-d_6



S15 ^{13}C NMR Spectrum of cyclic pentapeptide (**9**) in DMSO-d_6

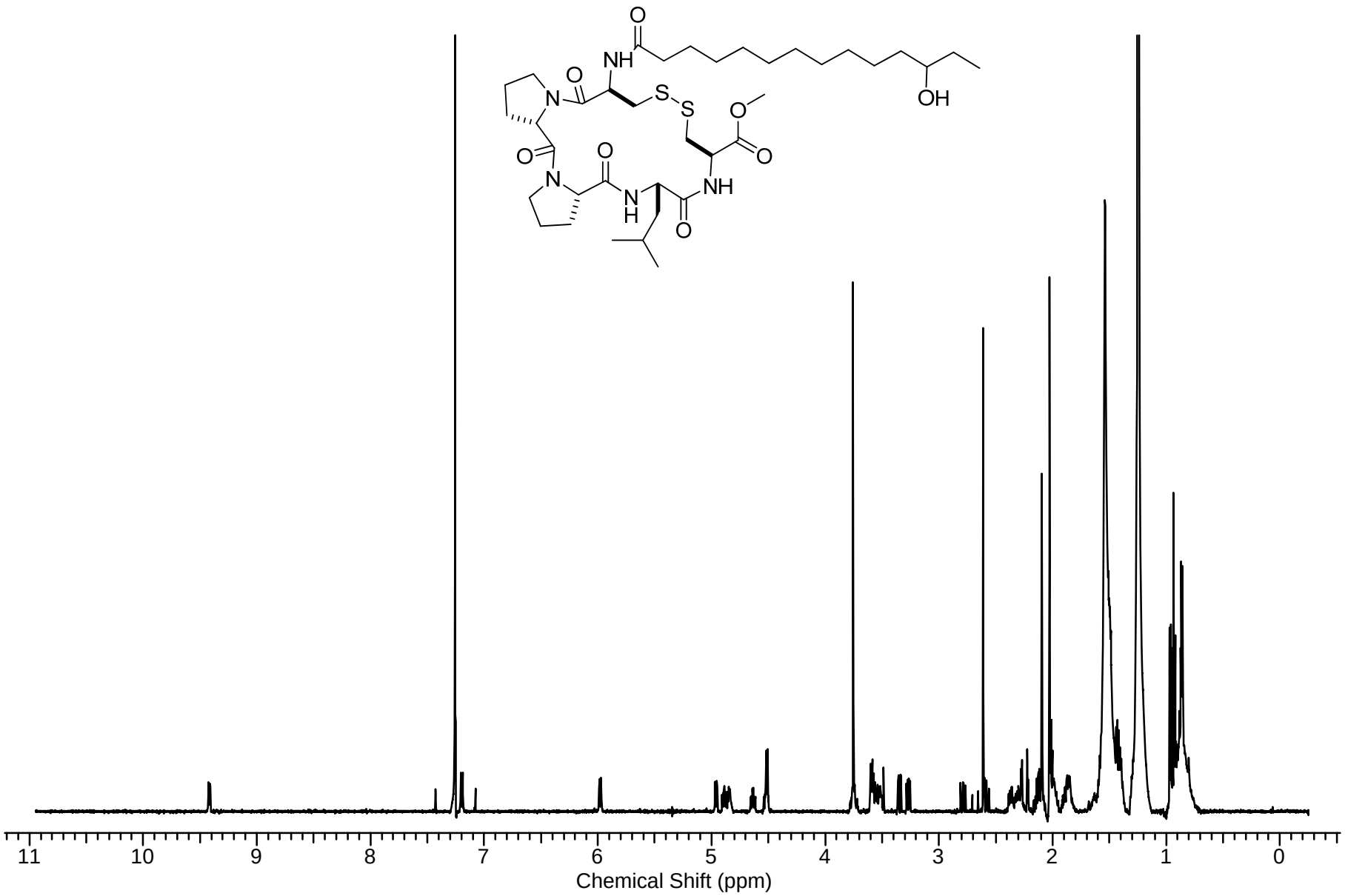


Supplemental Table 1. NMR data for the cyclic pentapeptide (**9**) (500 MHz, DMSO-d_6)

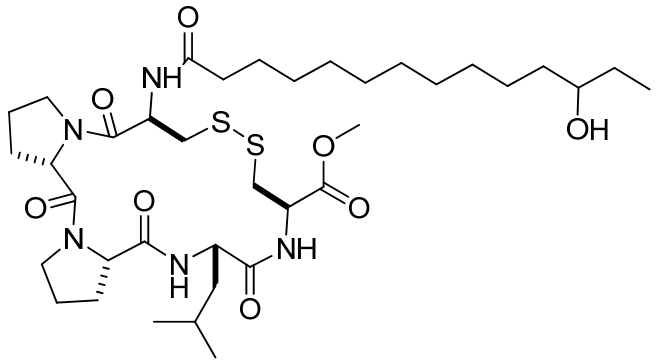
	Cyclic pentapeptide (**9**)		
	position	δ_H mult (*J*, Hz)	δ_C
Cys-1	1	—	171.9
	2	4.38, ddd (11.1, 7.5, 2.9)	51.9
	3	3.14, dd (13.8, 2.9)	41.9
		2.96, dd (13.8, 11.1)	
	NH	8.30, br d (7.5)	—
Leu	4	—	171.5
	5	4.02, m	52.0
	6	1.83,[a] m	37.3
		1.55,[a] m	
	7	1.48, m	24.3
	8	0.85, d (6.5)	21.3
	9	0.87, d (6.5)	23.0
	NH	8.61, br d (7.2)	—
Pro-1	10	—	171.0
	11	4.48,[a] m	59.5
	12	2.30, m	32.3
		2.10, m	
	13	1.83,[a] m	21.7
		1.57,[a] m	
	14	3.52,[a] m	47.0
		3.34,[a] m	
Pro-2	15	—	170.0
	16	4.46,[a] m	58.8
	17	2.38, m	30.5
		1.99, m	
	18	1.72, m	21.6
	19	3.49,[a] m	47.0
		3.37,[a] m	
Cys-2	20	—	166.4
	21	3.88, br t (5.7)	50.4
	22	3.24, dd (14.5, 5.7)	39.4
		2.91, dd (14.5, 5.7)	

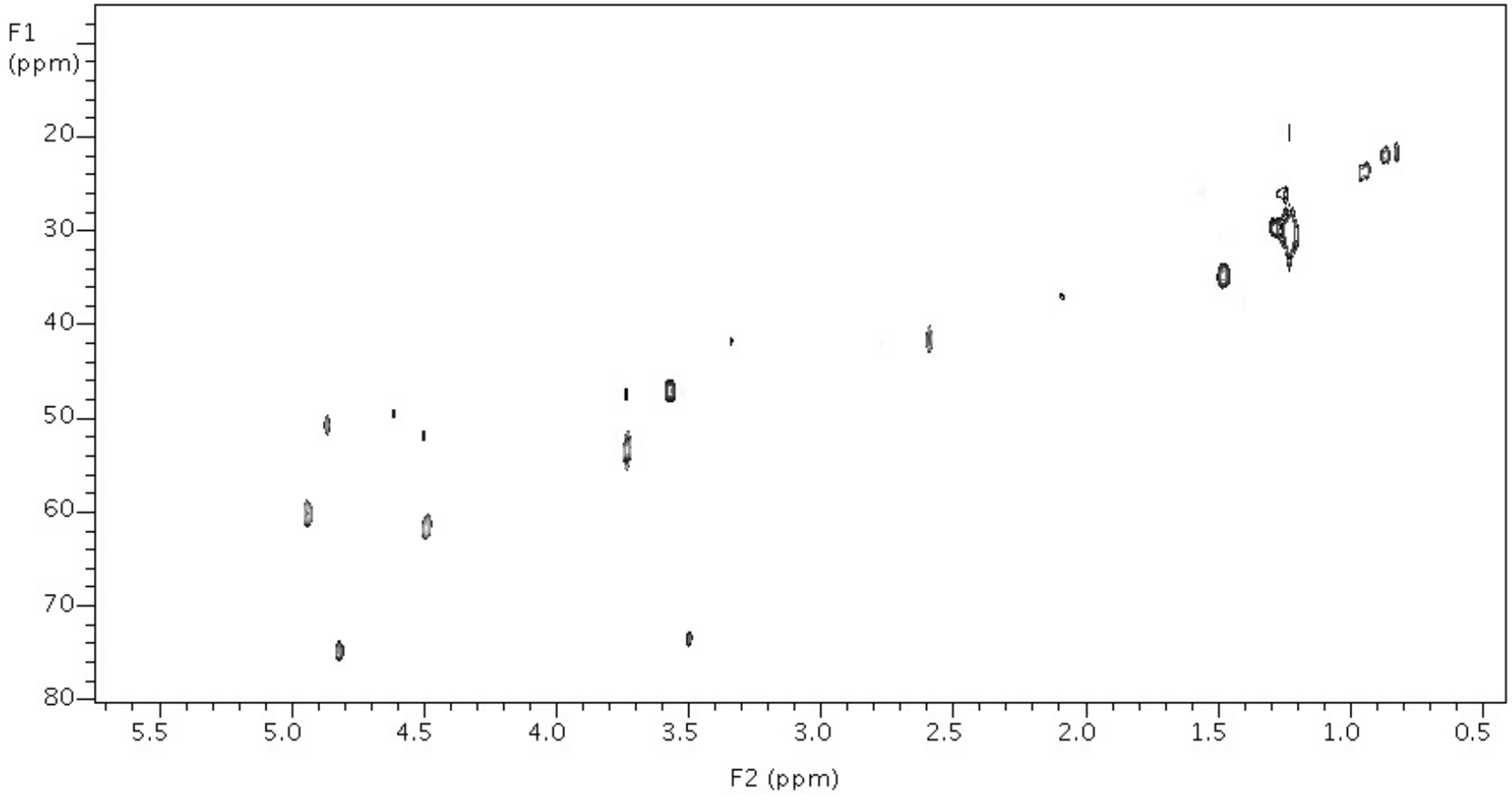
[a] Signals overlapped.

S17 ^{1}H NMR Spectrum of Eudistomide B epimers (**2**, **12**) in $CDCl_3$

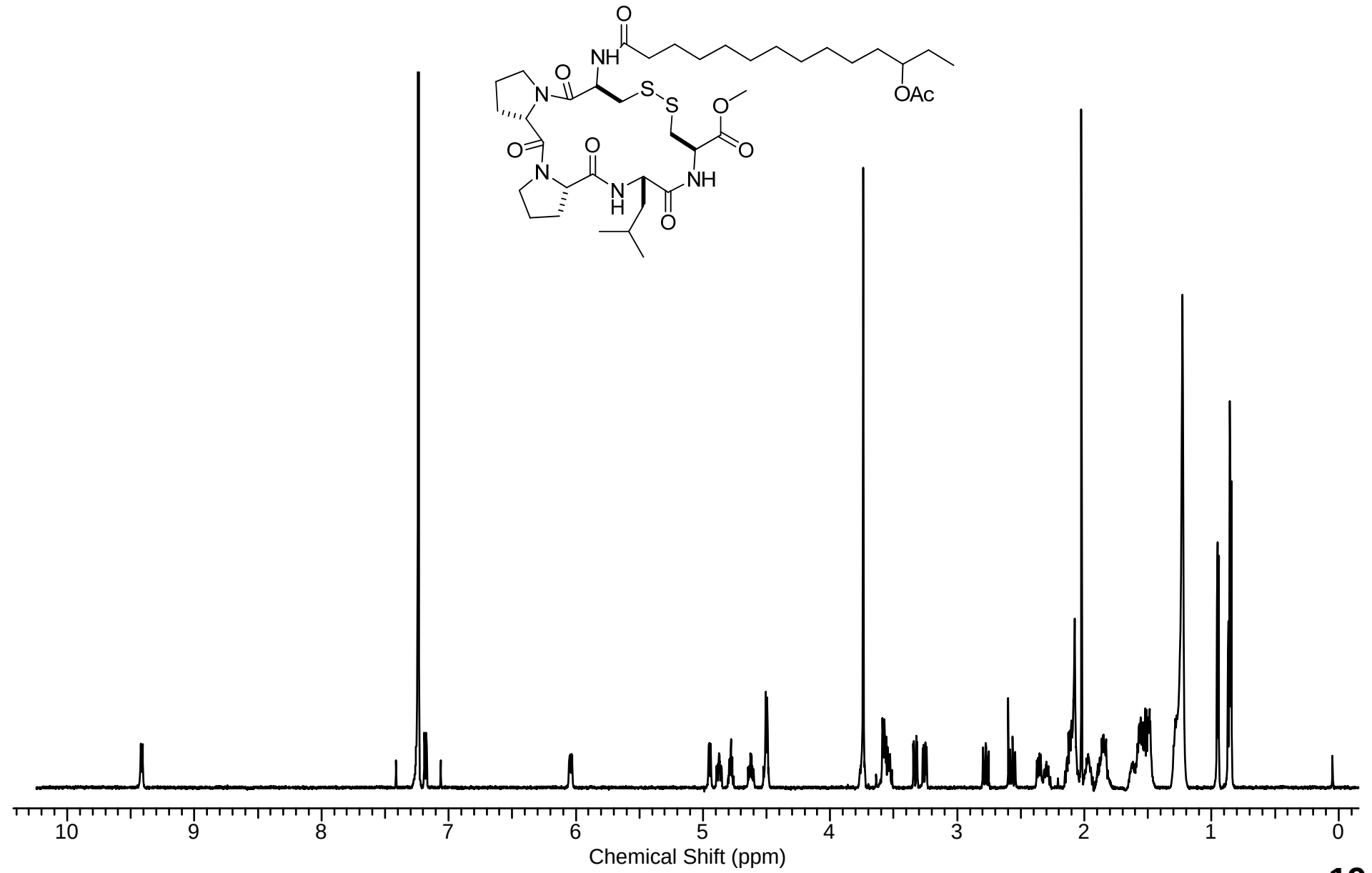


S18 HSQC Spectrum of Eudistomide B epimers (**2**, **12**) in $CDCl_3$

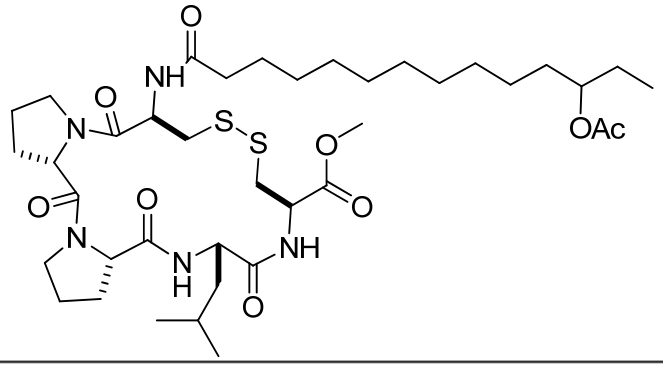


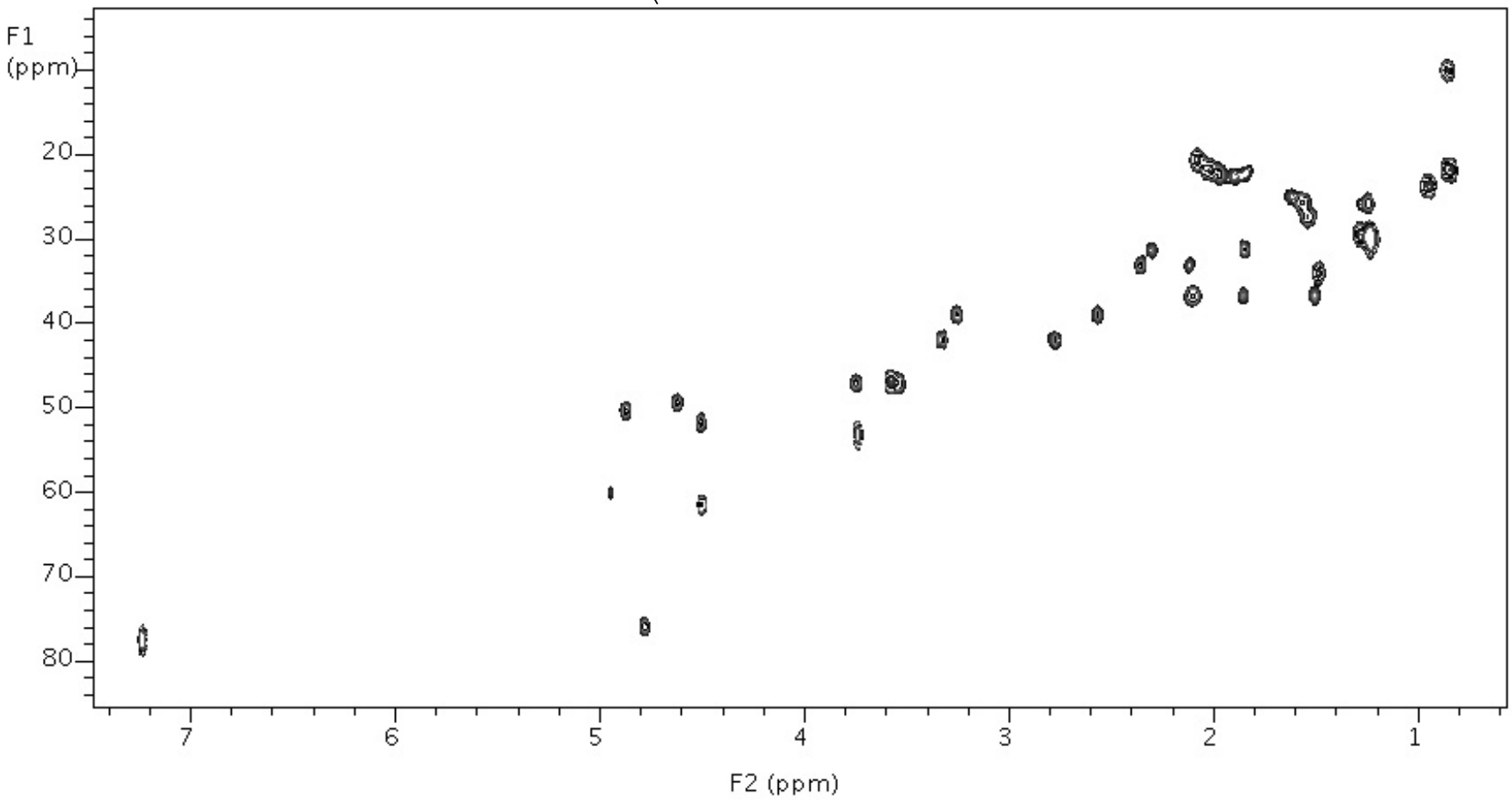


S19 ^{1}H NMR Spectrum of Eudistomide B acetate ester epimers (**13**, **14**) in $CDCl_3$

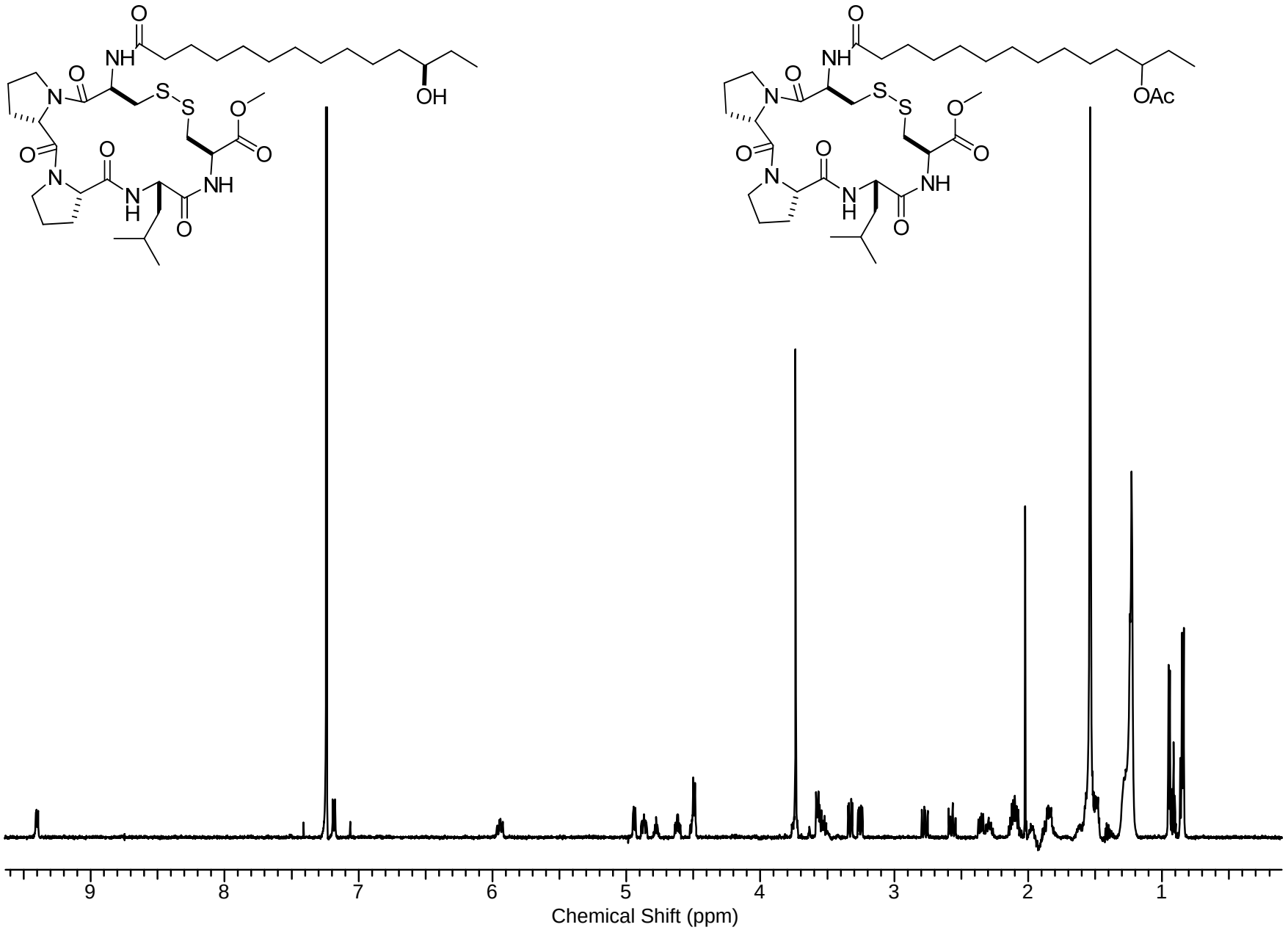


S20 HSQC Spectrum of Eudistomide B acetate ester epimers (**13**, **14**) in $CDCl_3$





S21 ^{1}H NMR Spectrum of the lipase reaction products (**2**, **13**, **14**) in $CDCl_3$



S22 HSQC Spectrum of the lipase reaction products (**2**, **13**, **14**) in $CDCl_3$