

# Zeamide, a glycosylinositol phosphorylceramide with the novel core Arap (1 $\beta$ →6)Ins motif from the marine sponge *Svenzea zeai*

Gerardo Della Sala,<sup>†</sup> Roberta Teta,<sup>†</sup> Germana Esposito,<sup>†</sup> Joseph R. Pawlik,<sup>‡</sup> Alfonso Mangoni,<sup>†</sup>  
Valeria Costantino<sup>†,\*</sup>

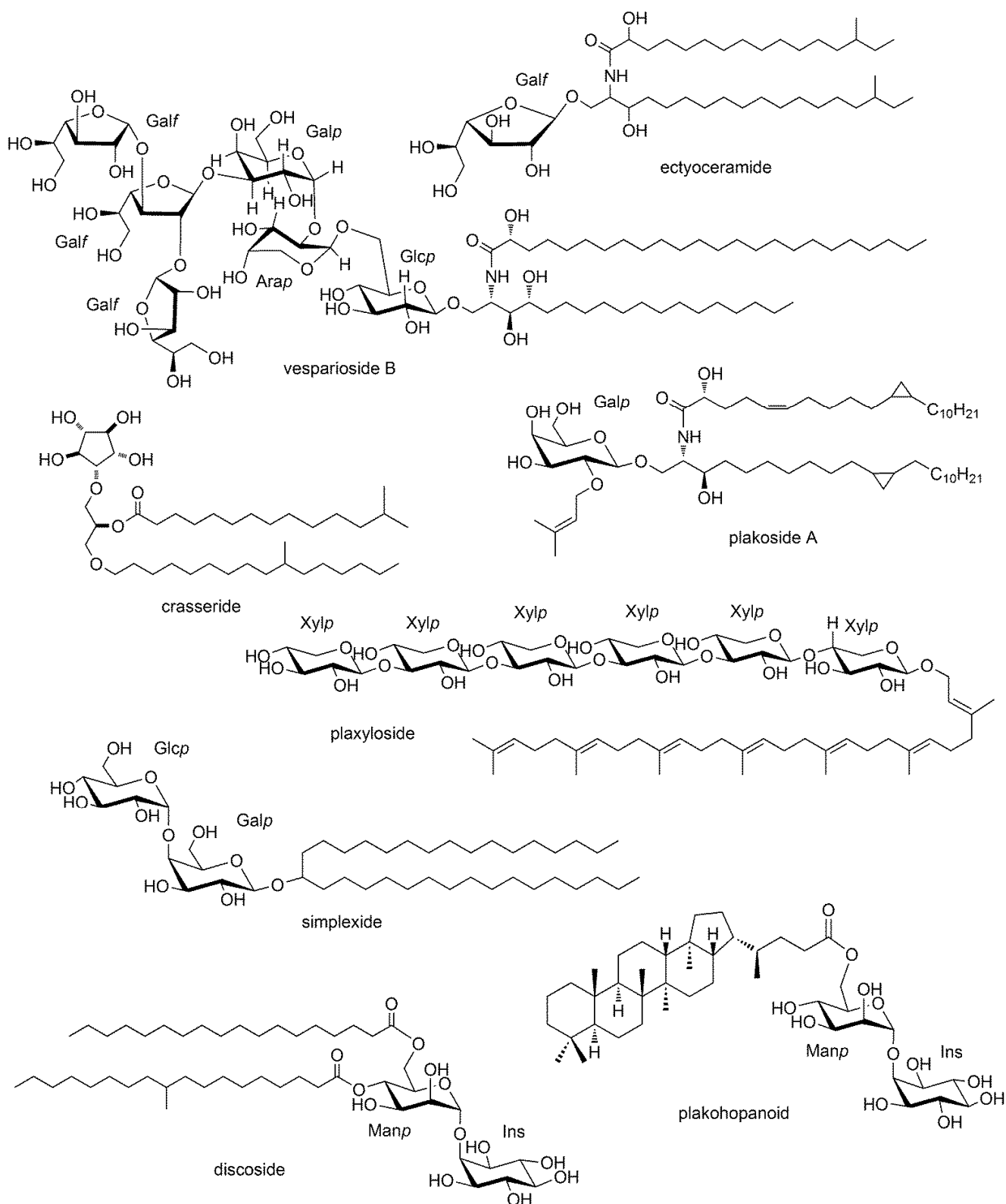
<sup>†</sup> *The NeaNat Group, Dipartimento di Farmacia, Università degli Studi di Napoli Federico II, via D.  
Montesano 49, 80131 Napoli, Italy*

<sup>‡</sup> *Department of Biology and Marine Biology, University of North Carolina Wilmington, Center for  
Marine Science, 5600 Marvin K Moss Lane, Wilmington, NC 28409, USA.*

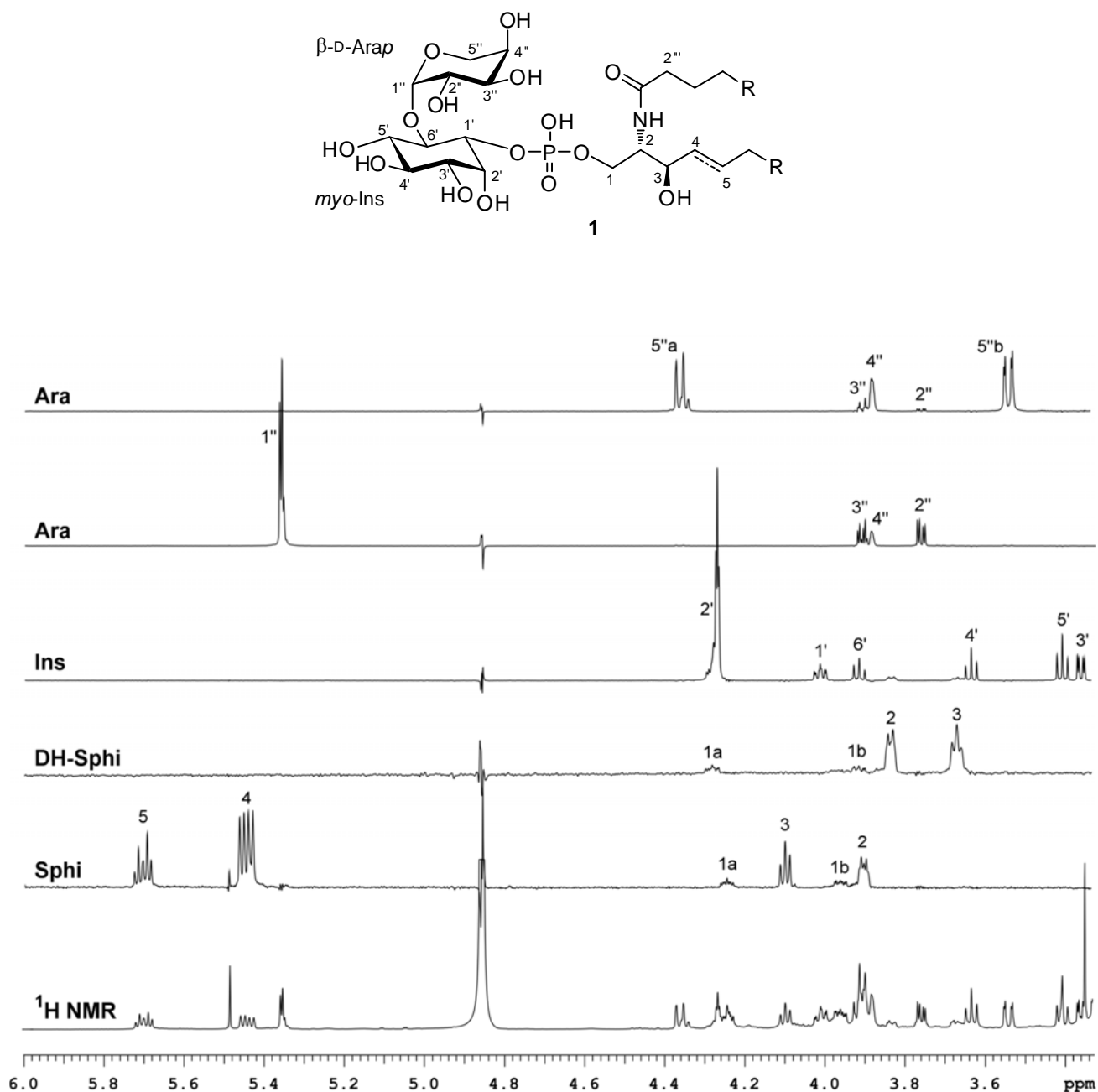
## Supporting Information

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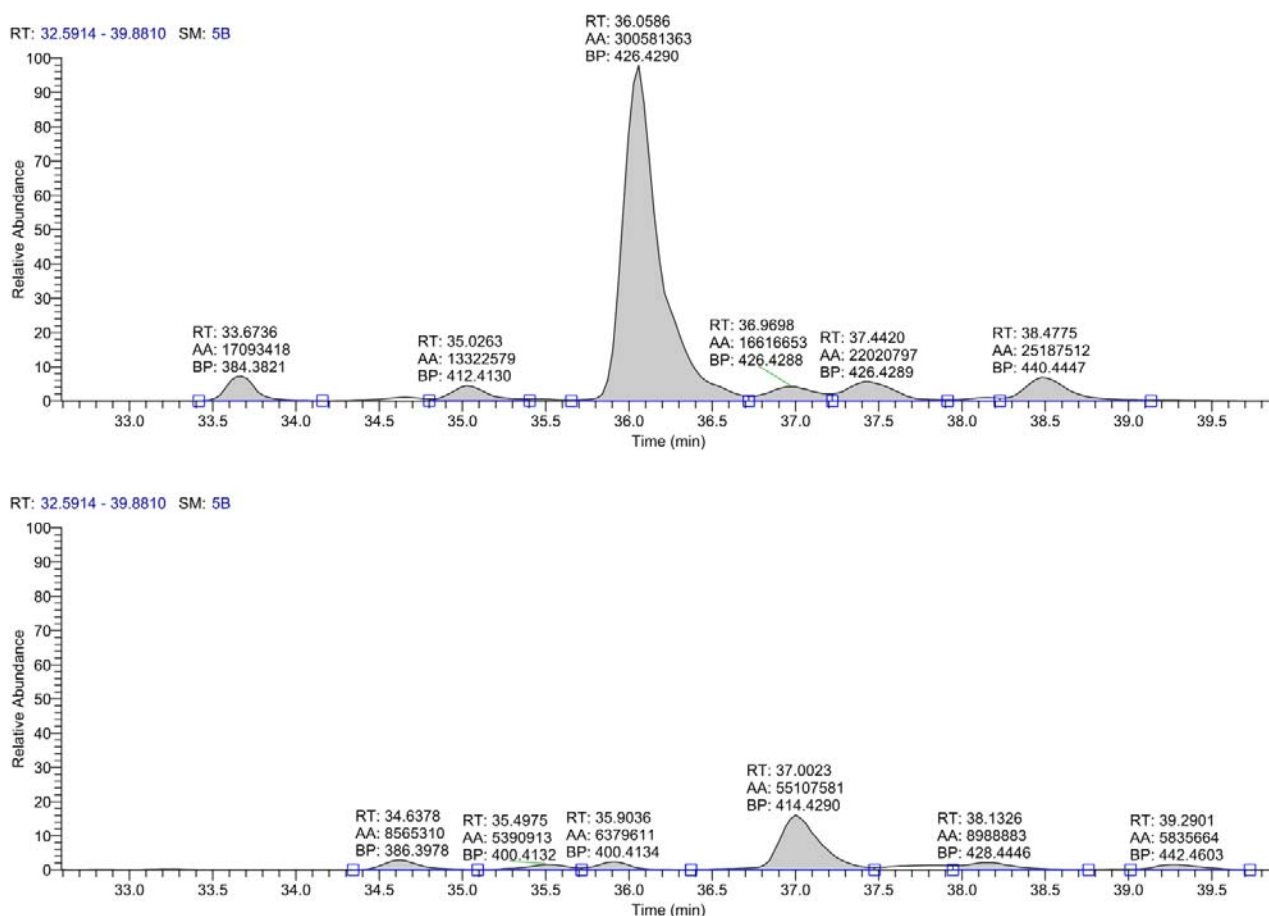


**Figure S1.** Structures of some unusual glycolipids from sponges cited in the main text. Many of these compounds have been isolated as mixture of homologues; one representative homologue is presented here.

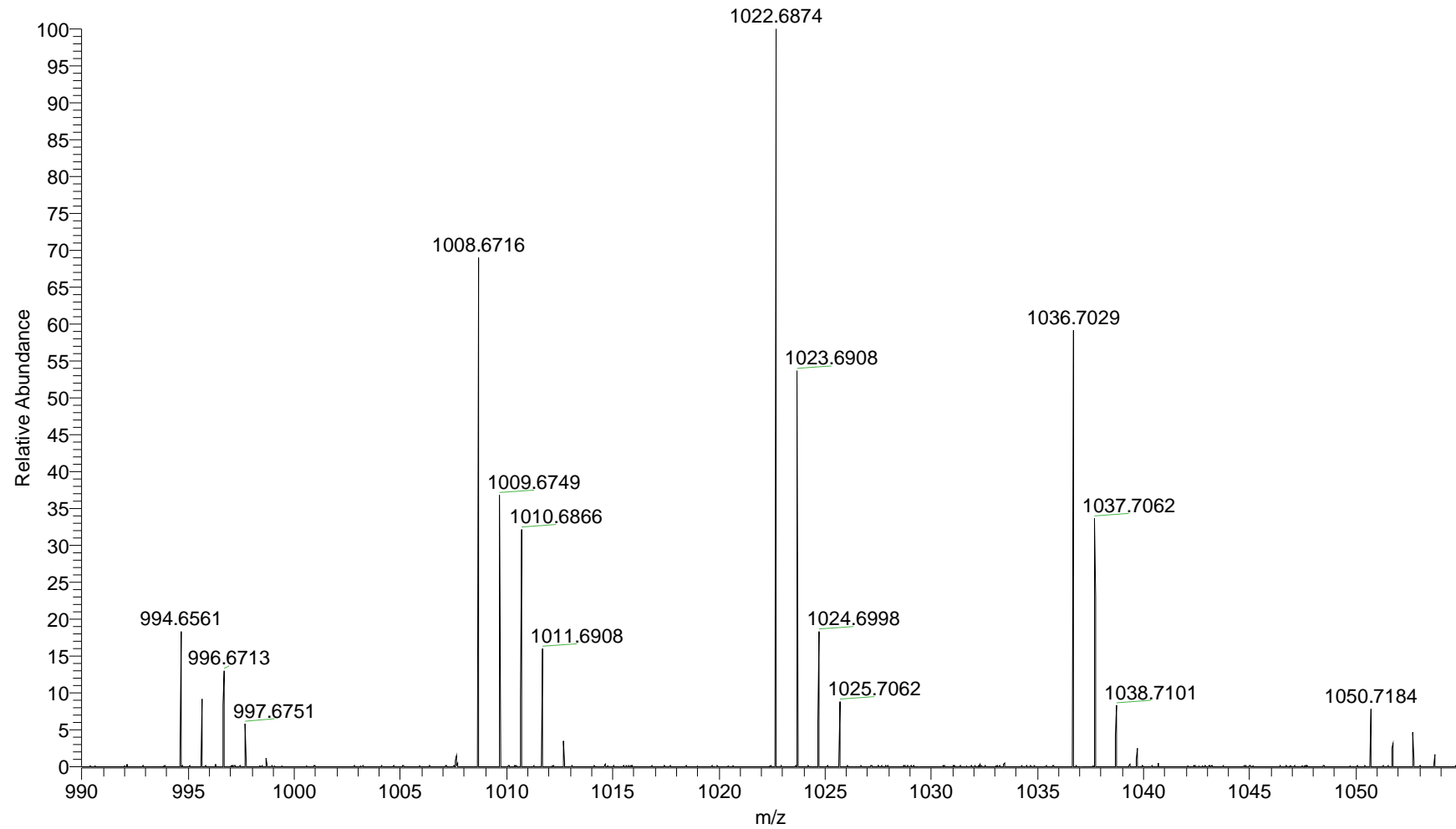


**Figure S2.** Sections of the 2D  $z$ -TOCSY spectrum (700 MHz, CD<sub>3</sub>OD, mixing time 100 ms) of zeamide (**1**), showing partial or complete subspectra of the spin-systems of the molecule.

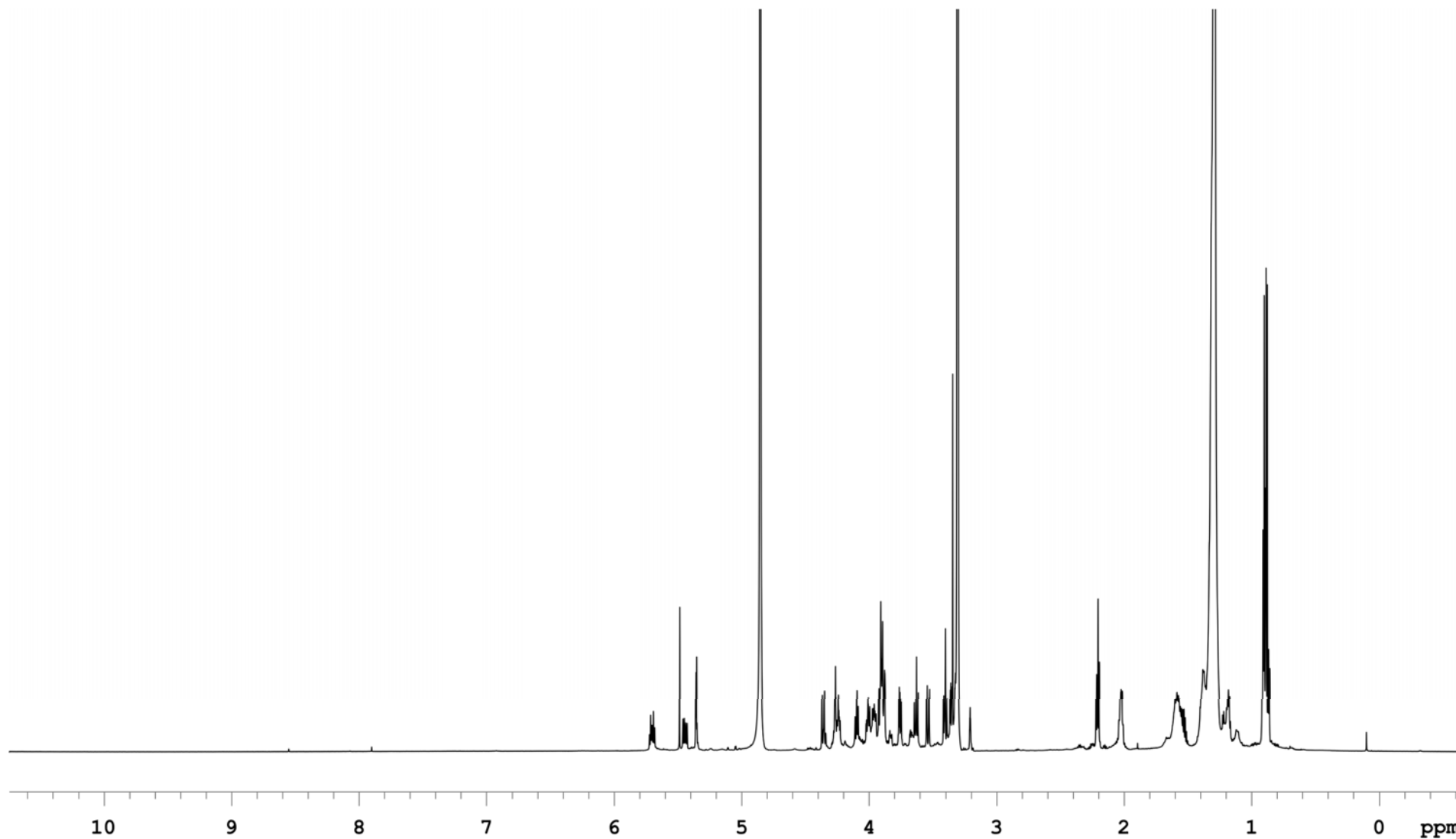
From the bottom up: <sup>1</sup>H NMR spectrum; section at  $\delta$  5.45 (H-4), sphingosine protons; section at  $\delta$  1.56 (H-4b), dihydrosphingosine protons; section at  $\delta$  4.27 (H-2'), inositol protons; section at  $\delta$  5.36 (H-1''), arabinose protons; section at  $\delta$  3.54 (H-5''b), arabinose protons.



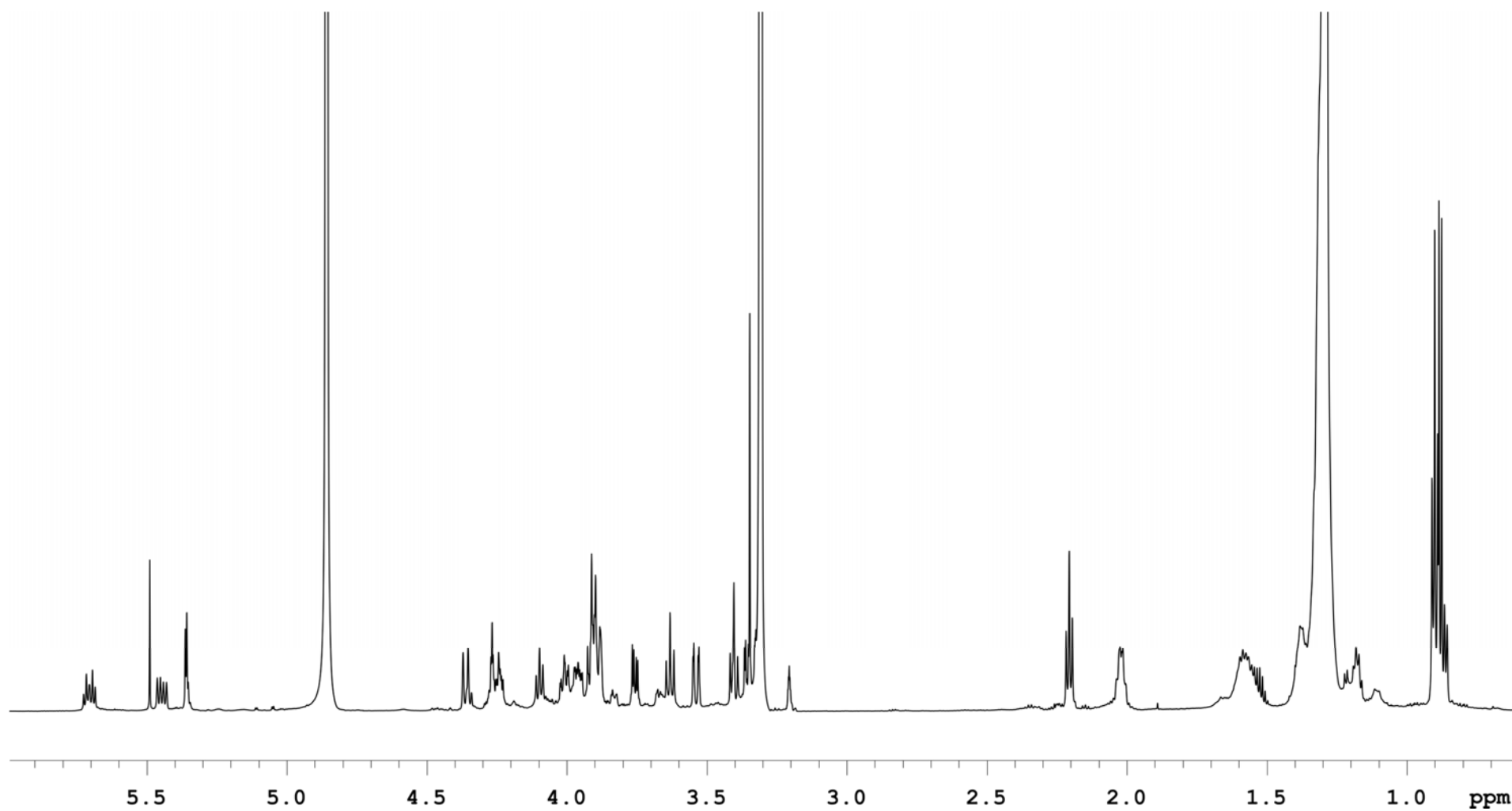
**Figure S3.** LC-HRMS analysis for sphingosines of the basic hydrolysis product of zeamide (**1**). Upper chromatogram: extracted-ion chromatogram at  $m/z$  384.3834, 398.3990, 412.4146, 426.4302, 440.4458 ( $C_{24}$ - $C_{28}$  sphingosines). Lower chromatogram: extracted-ion chromatogram at  $m/z$  386.3990, 400.4146, 414.4302, 428.4458, 442.4614 ( $C_{24}$ - $C_{28}$  dihydrosphingosines). Each chromatographic peak is labeled with retention time, area, and exact mass. The two chromatograms have the same vertical scale.



High-resolution ESI mass spectrum of zeamide (1)

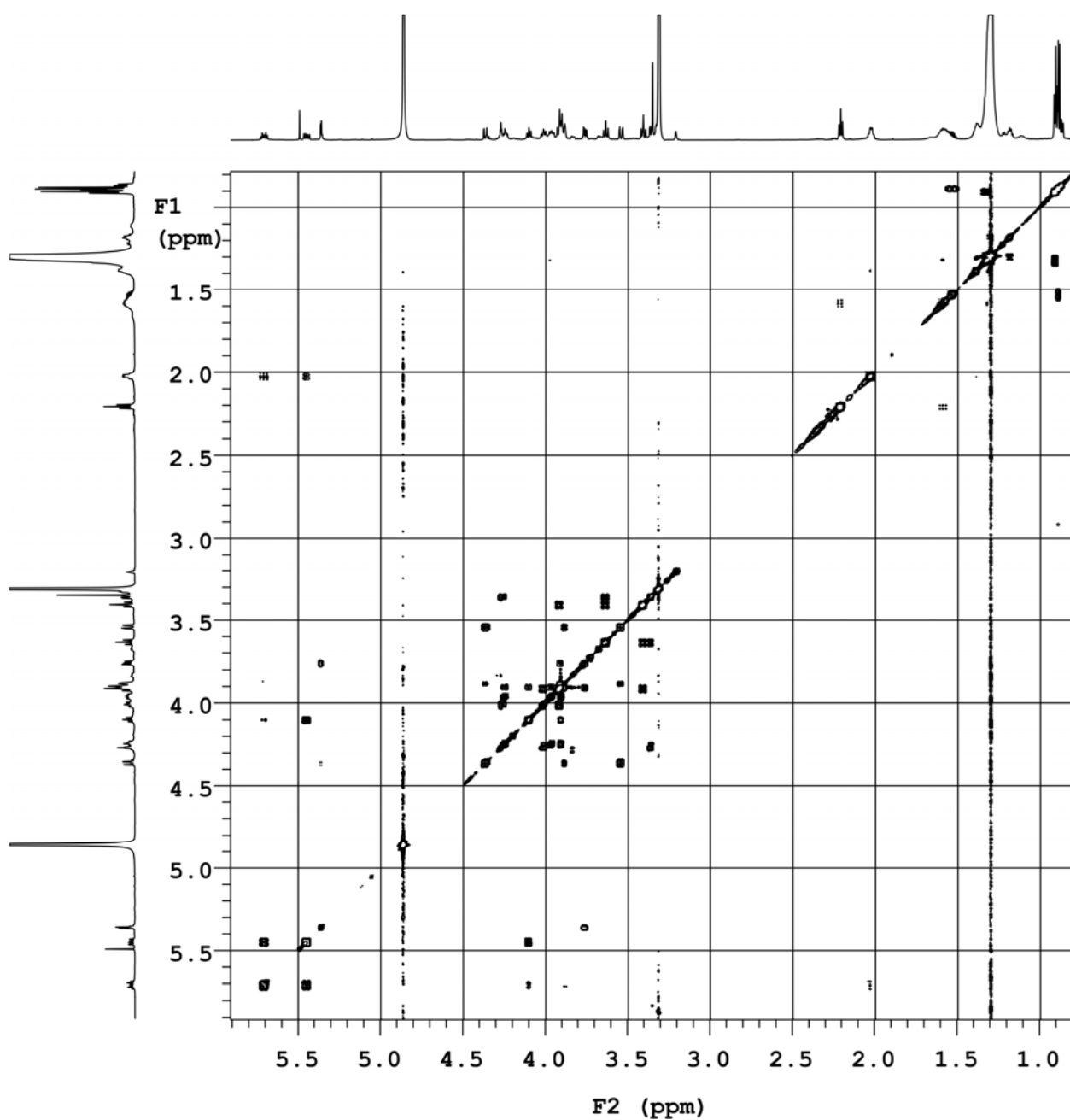


$^1\text{H-NMR}$  spectrum of zeamide (**1**) (700 MHz,  $\text{CD}_3\text{OD}$ ) – full spectral window



$^1\text{H}$ -NMR spectrum of zeamide (**1**) (700 MHz,  $\text{CD}_3\text{OD}$ ) – expansion

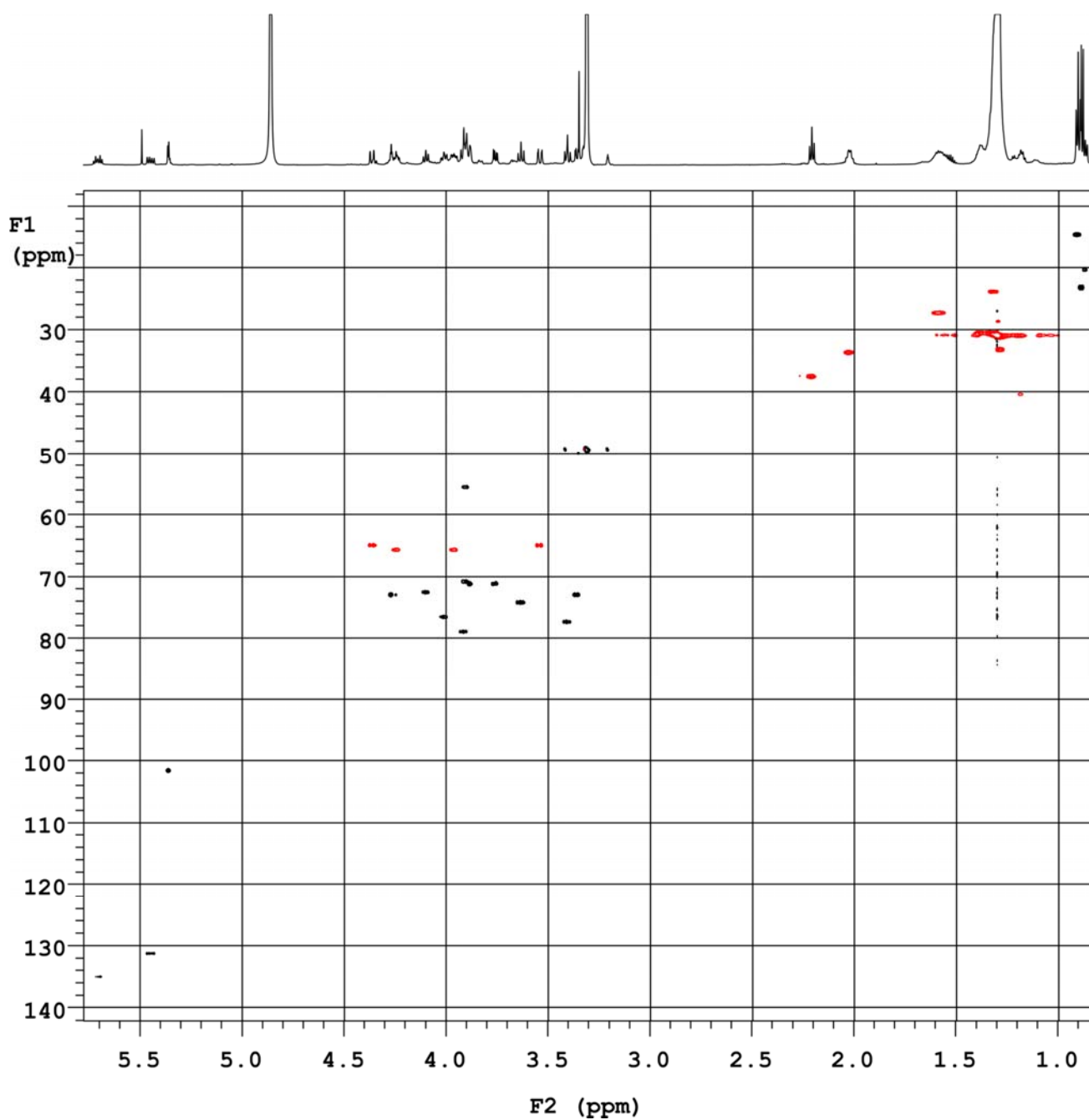
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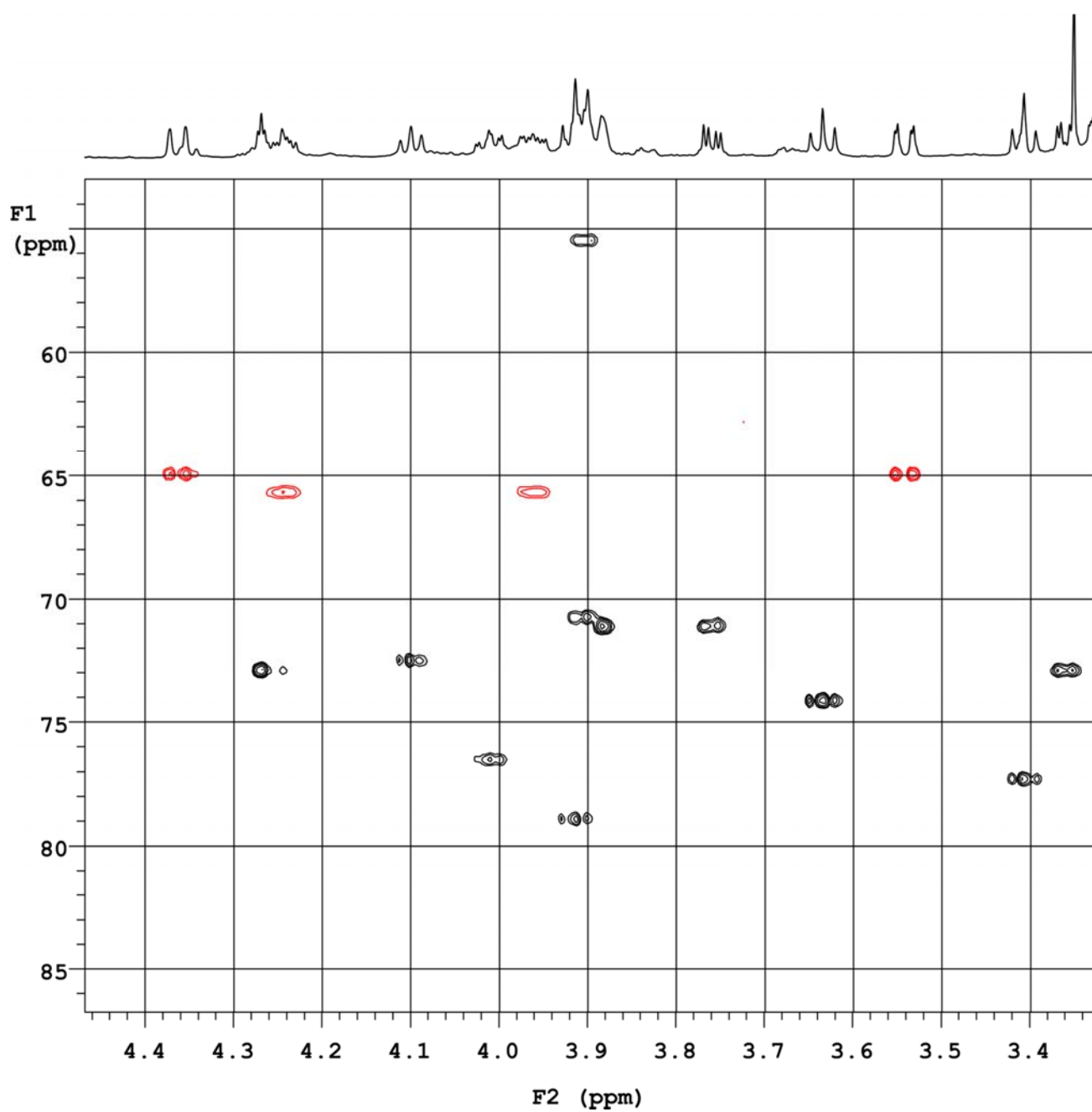
COSY spectrum of zeamide (1) (700 MHz, CD<sub>3</sub>OD)



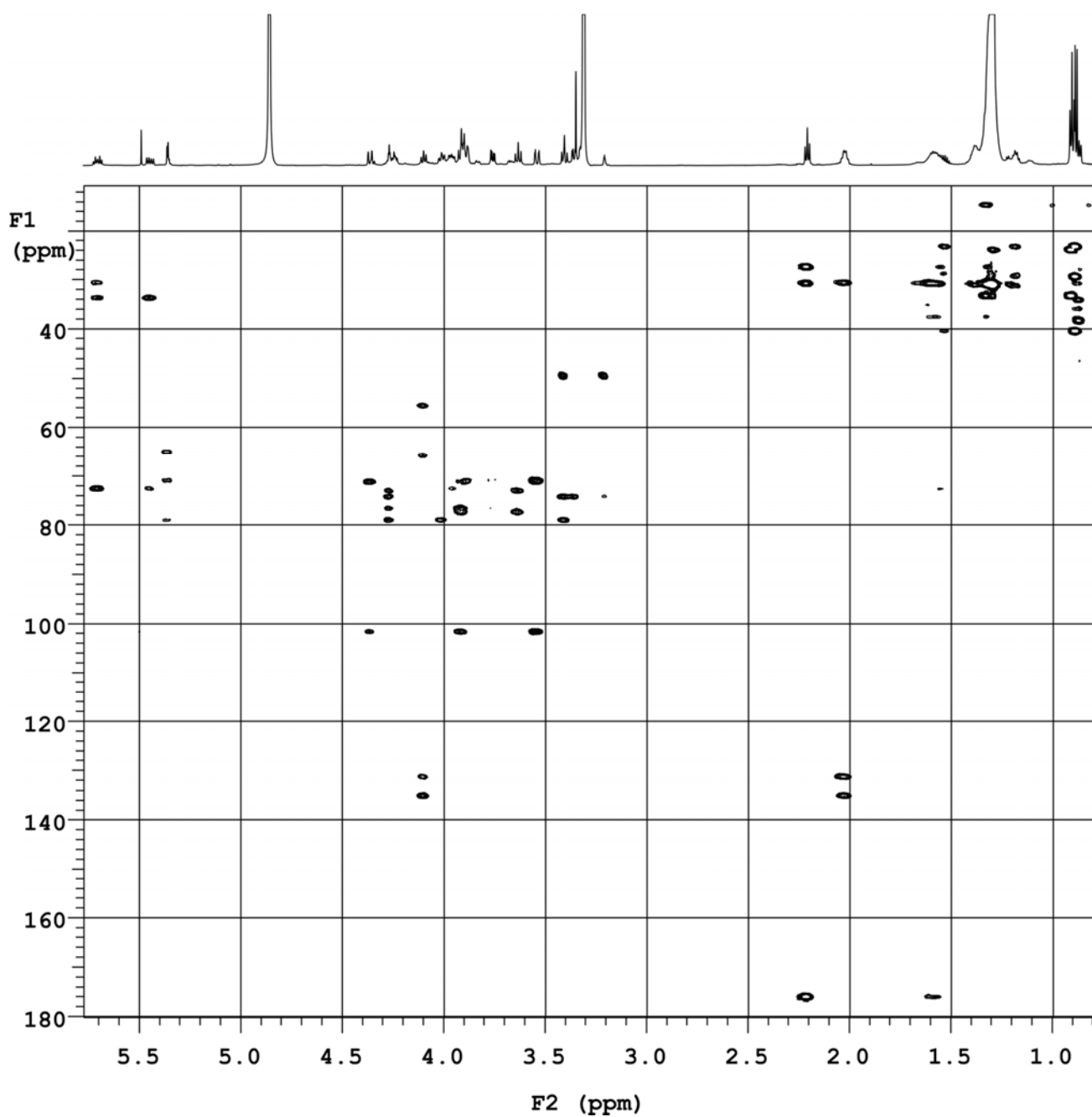




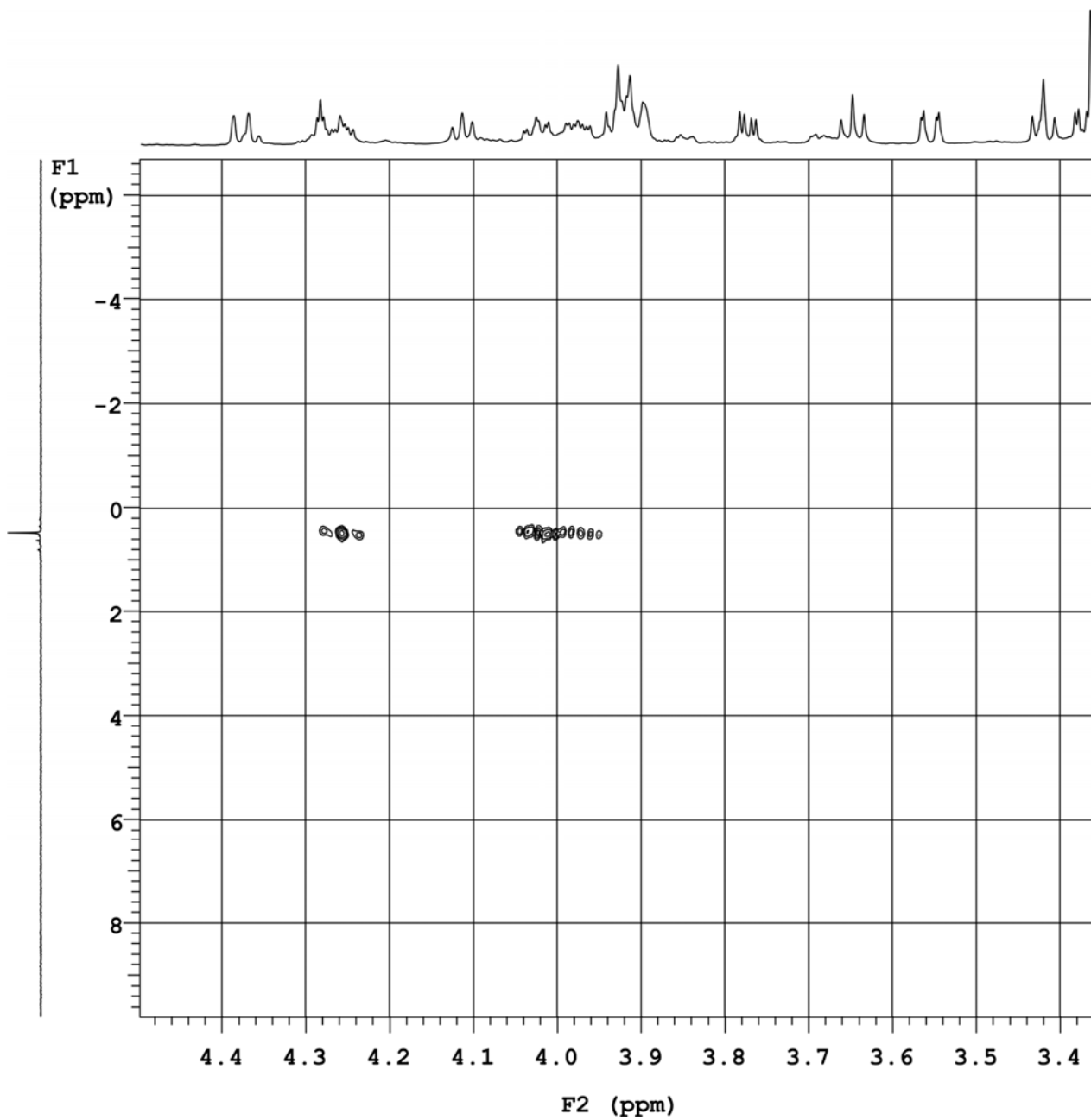
HSQC spectrum of zeamide (1) (700 MHz, CD<sub>3</sub>OD)



HSQC spectrum of zeamide (1) (700 MHz, CD<sub>3</sub>OD) – expansion



HMBC spectrum of zeamide (1) (700 MHz, CD<sub>3</sub>OD)



$^1\text{H}$ - $^{31}\text{P}$  HMBC spectrum of zeamide (**1**) (700 MHz,  $\text{CD}_3\text{OD}$ )