

## *Supplementary Material*

# Structure elucidation of calyxoside B, a bipolar sphingolipid from a marine sponge *Cladocroce* sp. through the use of Beckmann rearrangement

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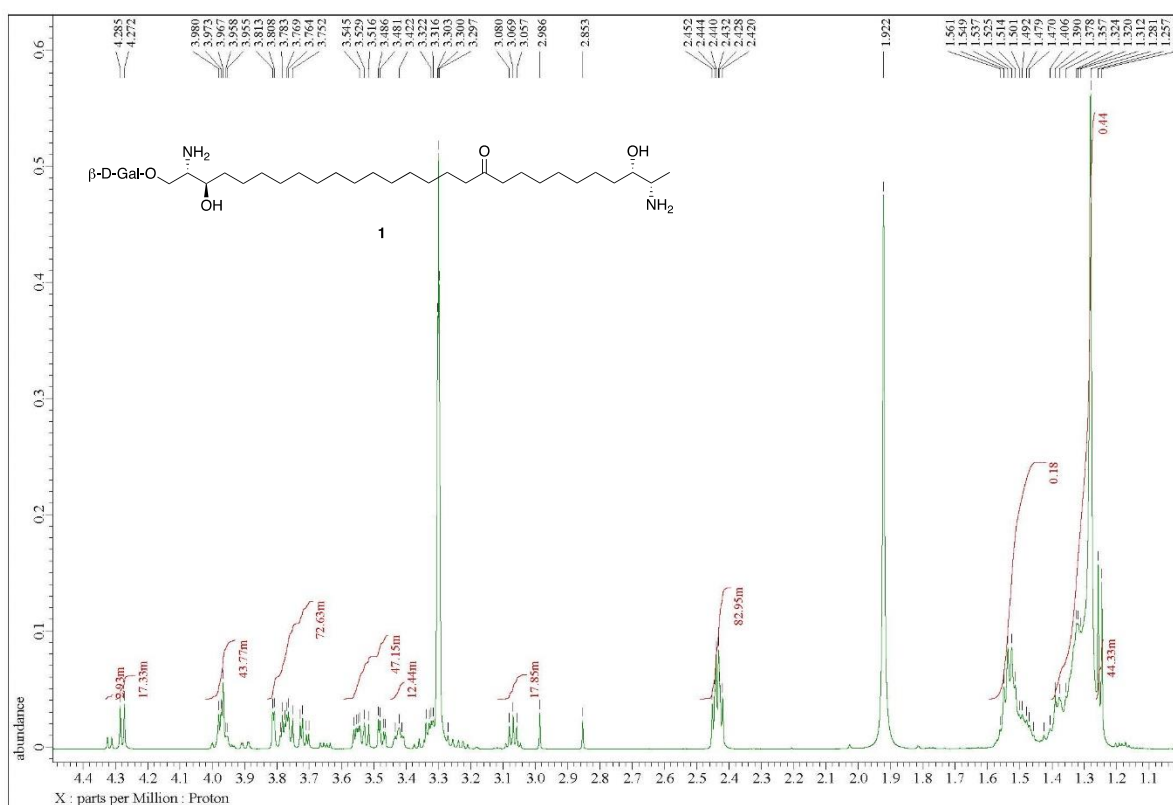
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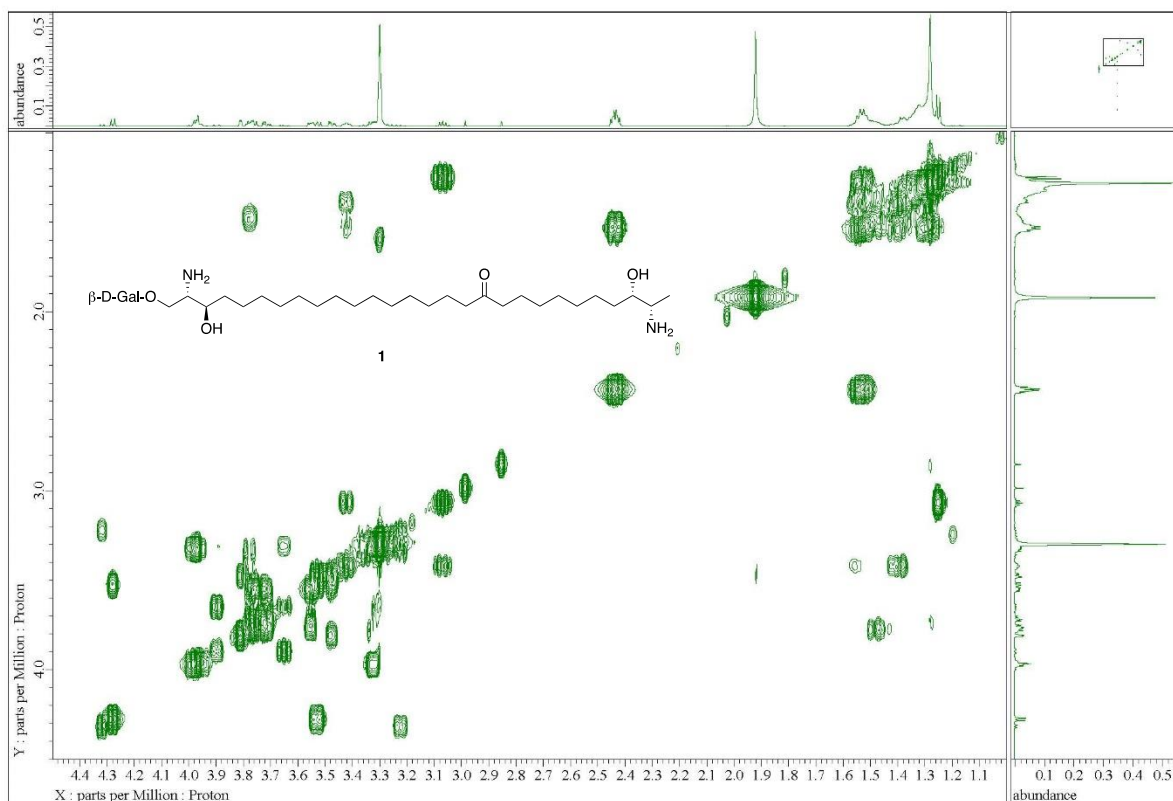
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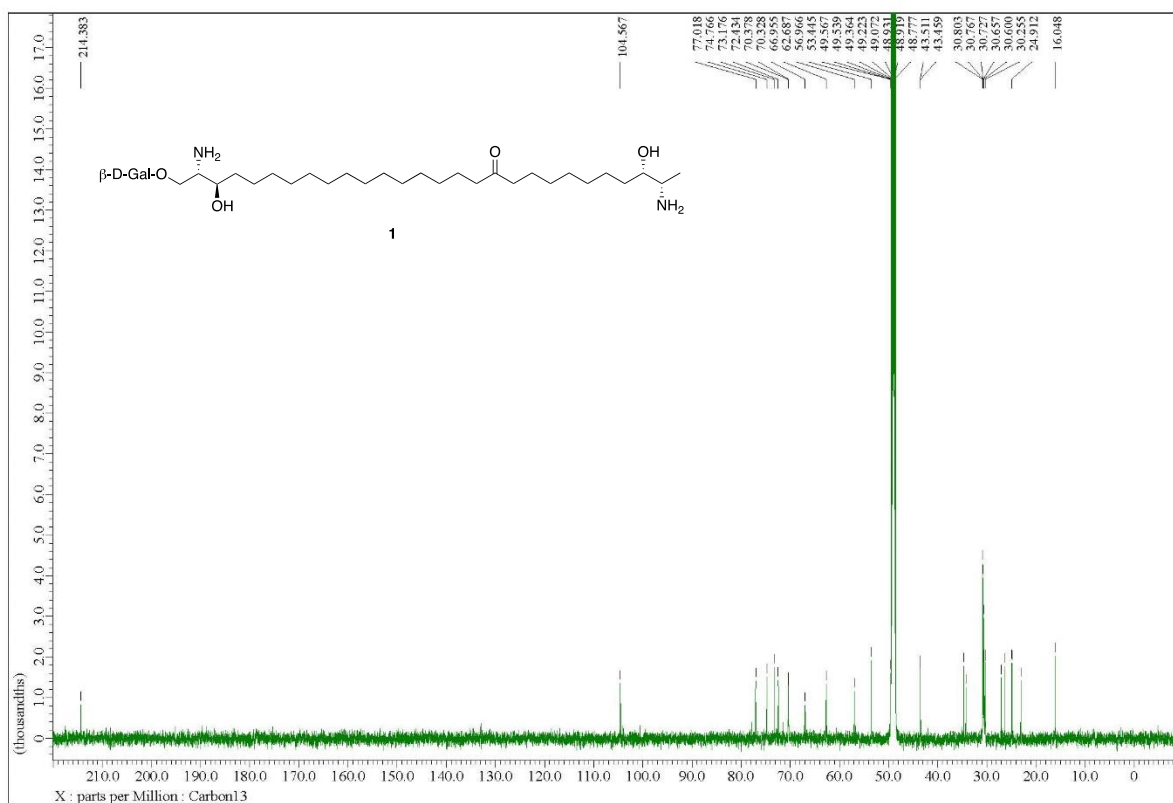
**Figure S1.** Photograph of a marine sponge *Cladocroce* sp.



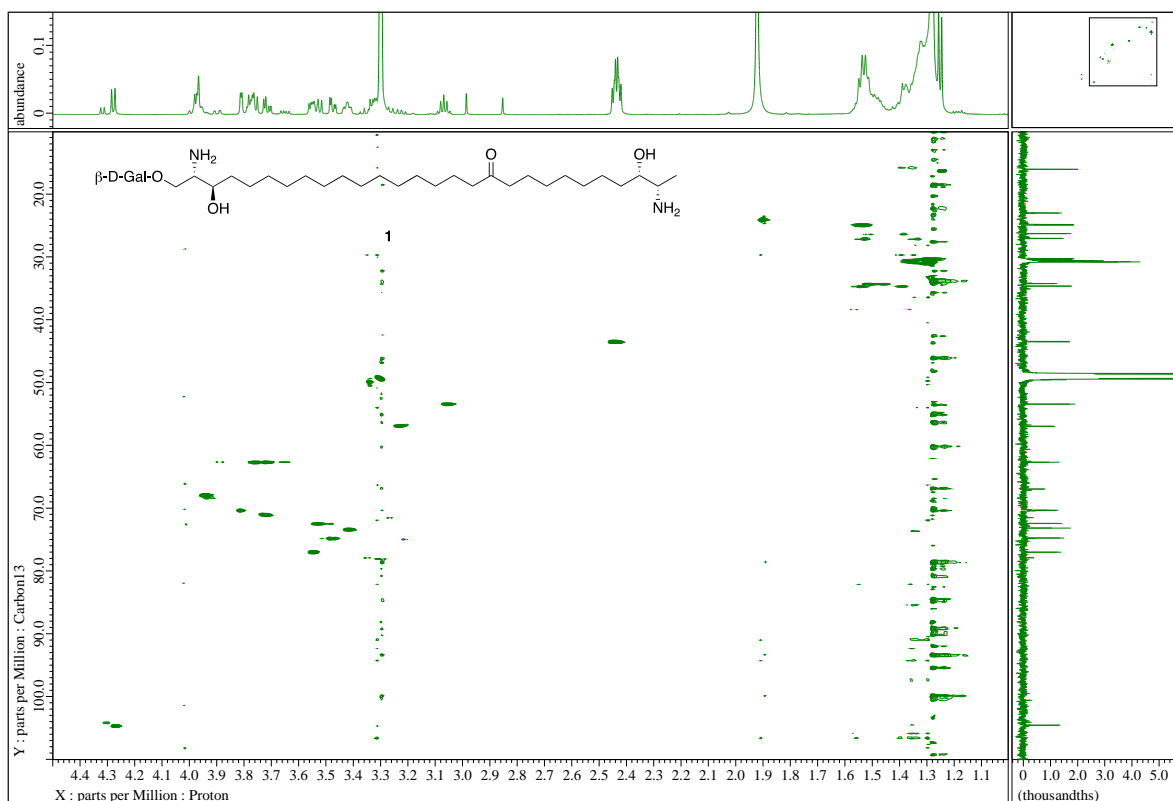
**Figure S2.** <sup>1</sup>H NMR spectrum (600 MHz) of calyxoside B (1) in CD<sub>3</sub>OD



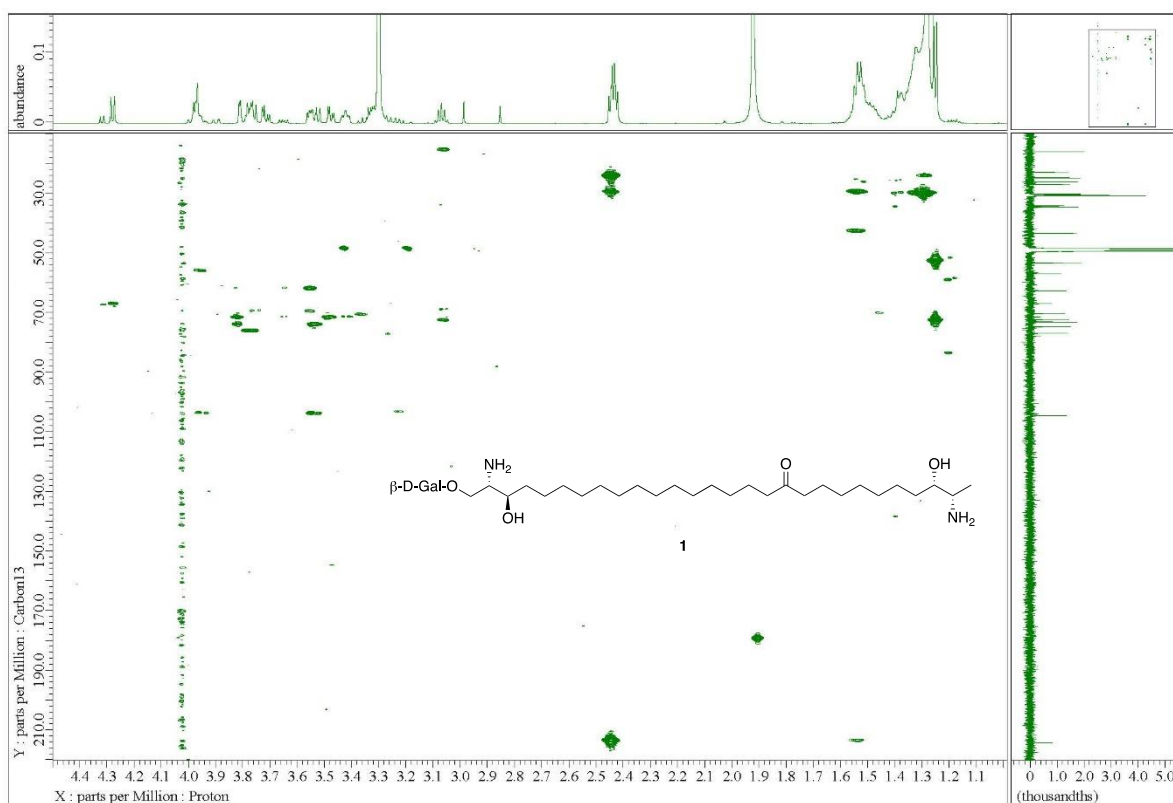
**Figure S3.** COSY spectrum (600 MHz) of calyxoside B (1) in CD<sub>3</sub>OD



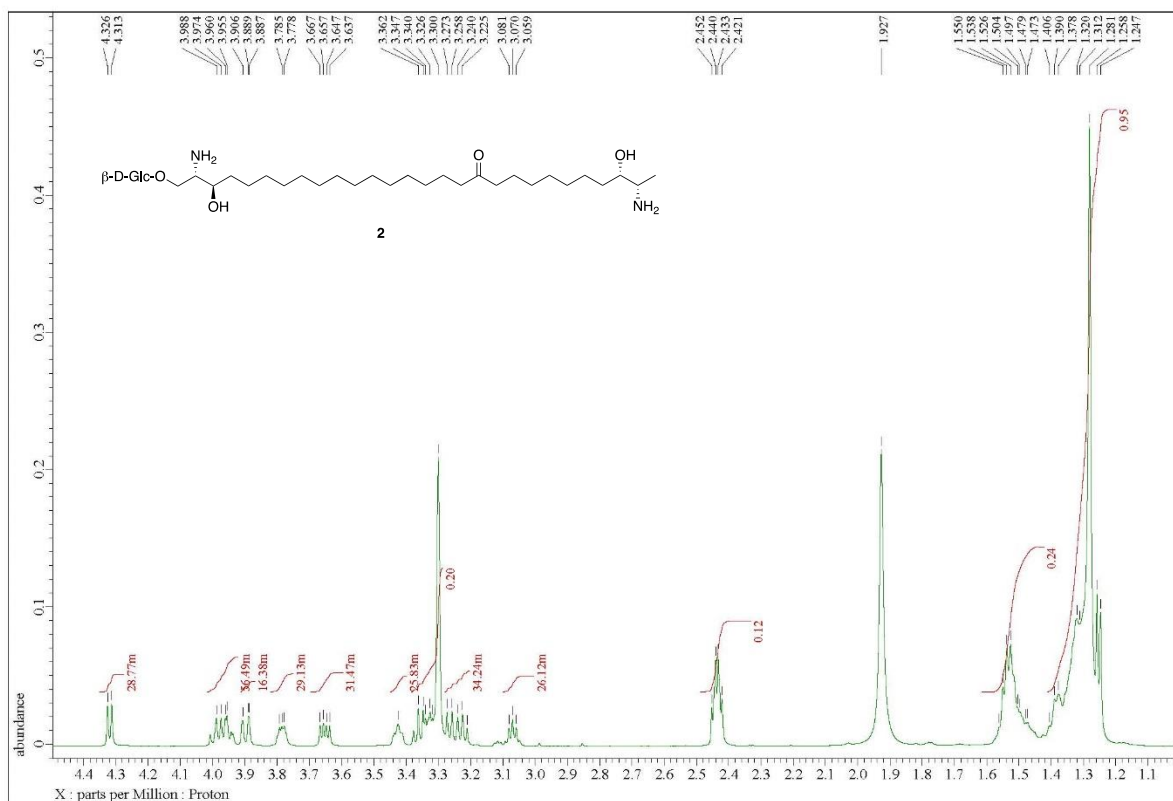
**Figure S4.** <sup>13</sup>C NMR spectrum (150 MHz) of calyxoside B (1) in CD<sub>3</sub>OD



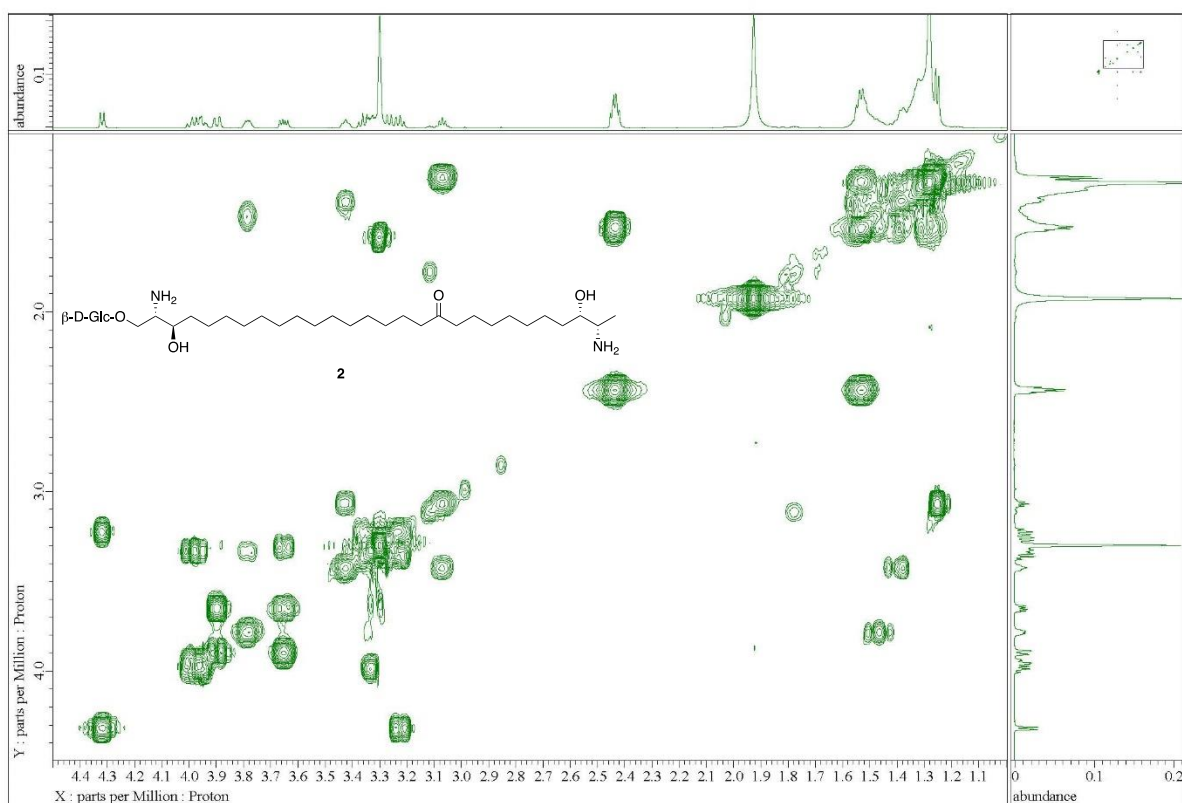
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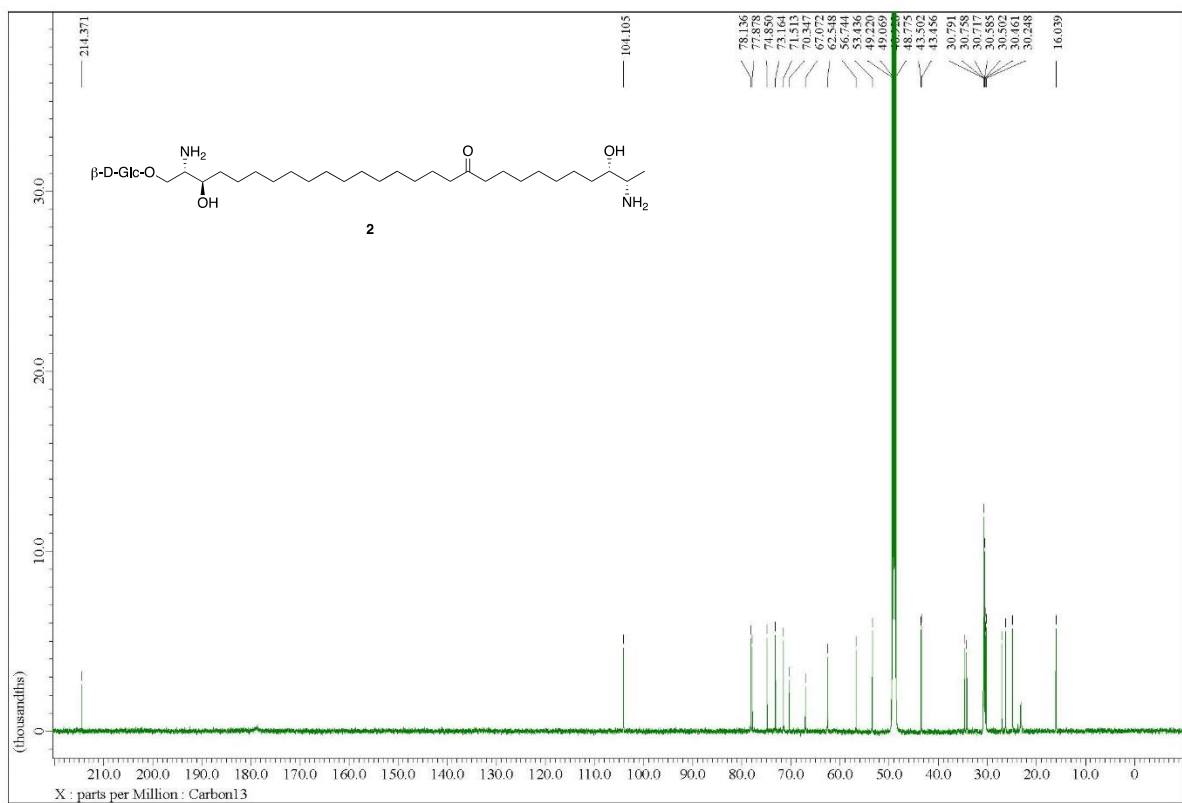
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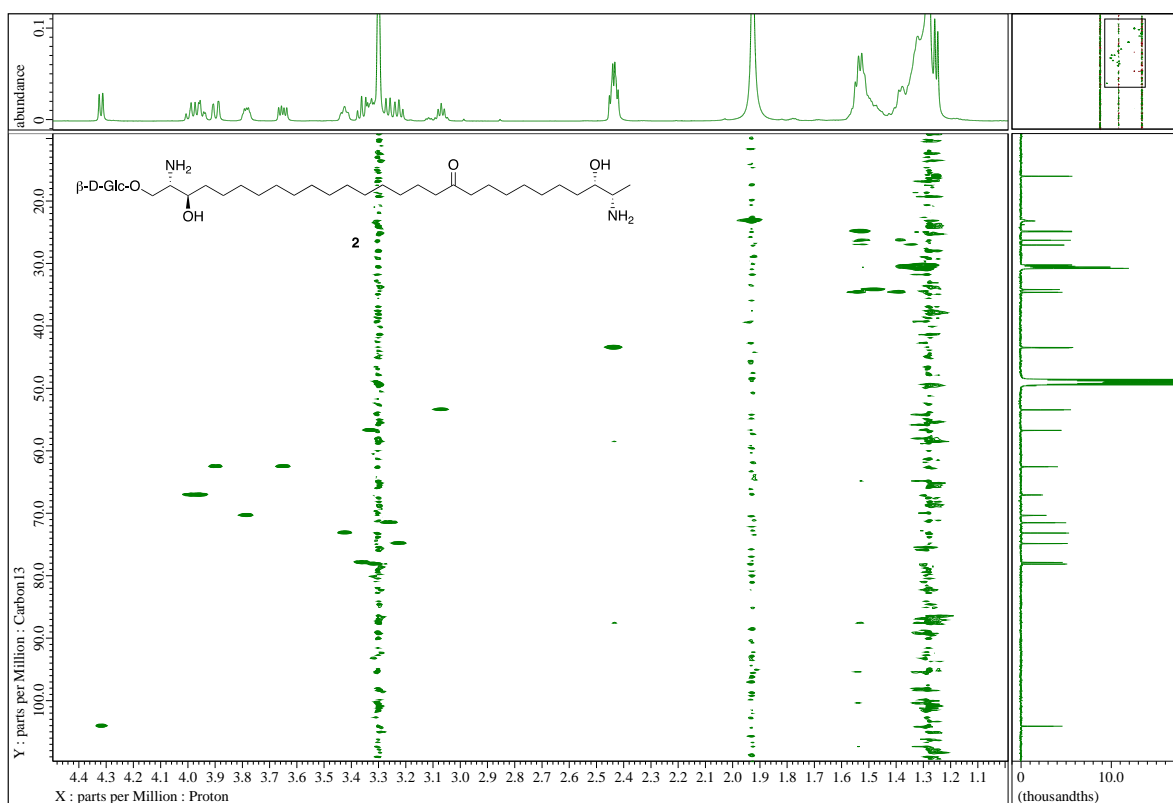


**Figure S8.** COSY spectrum (600 MHz) of calyxoside (**2**) in CD<sub>3</sub>OD

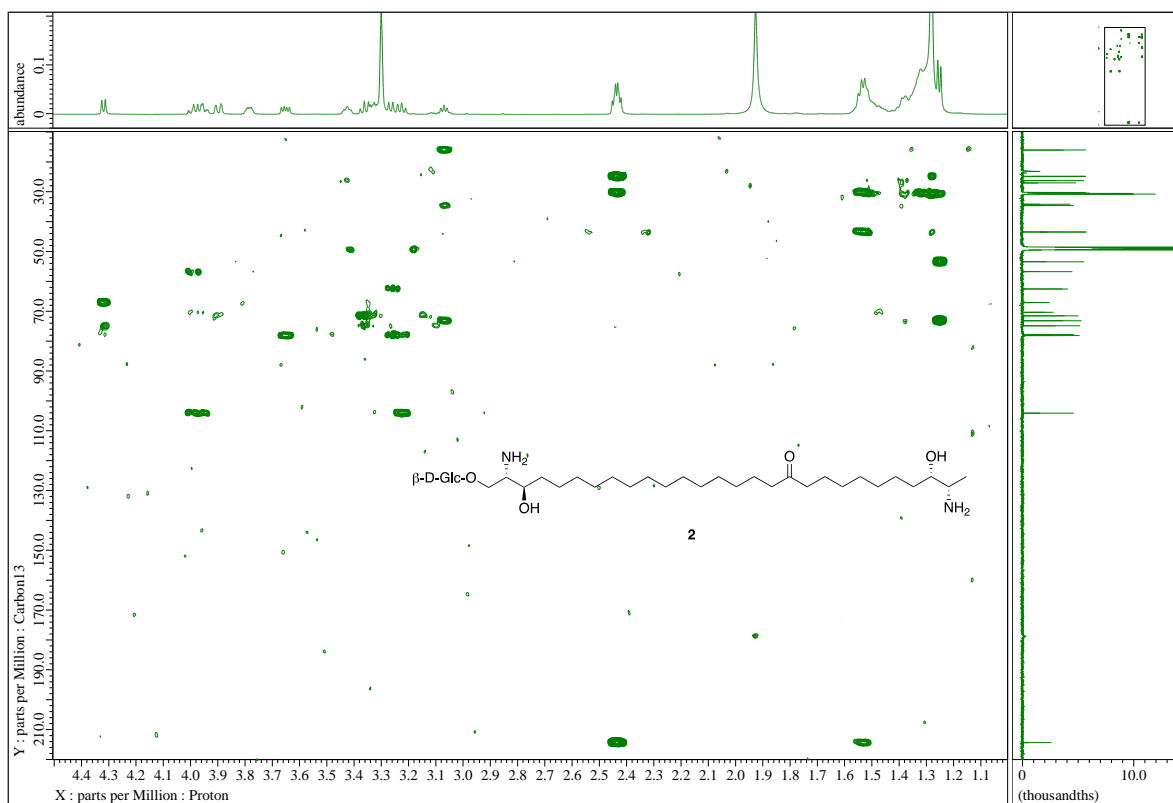


**Figure S9.** <sup>13</sup>C NMR spectrum (150 MHz) of calyxoside (**2**) in CD<sub>3</sub>OD



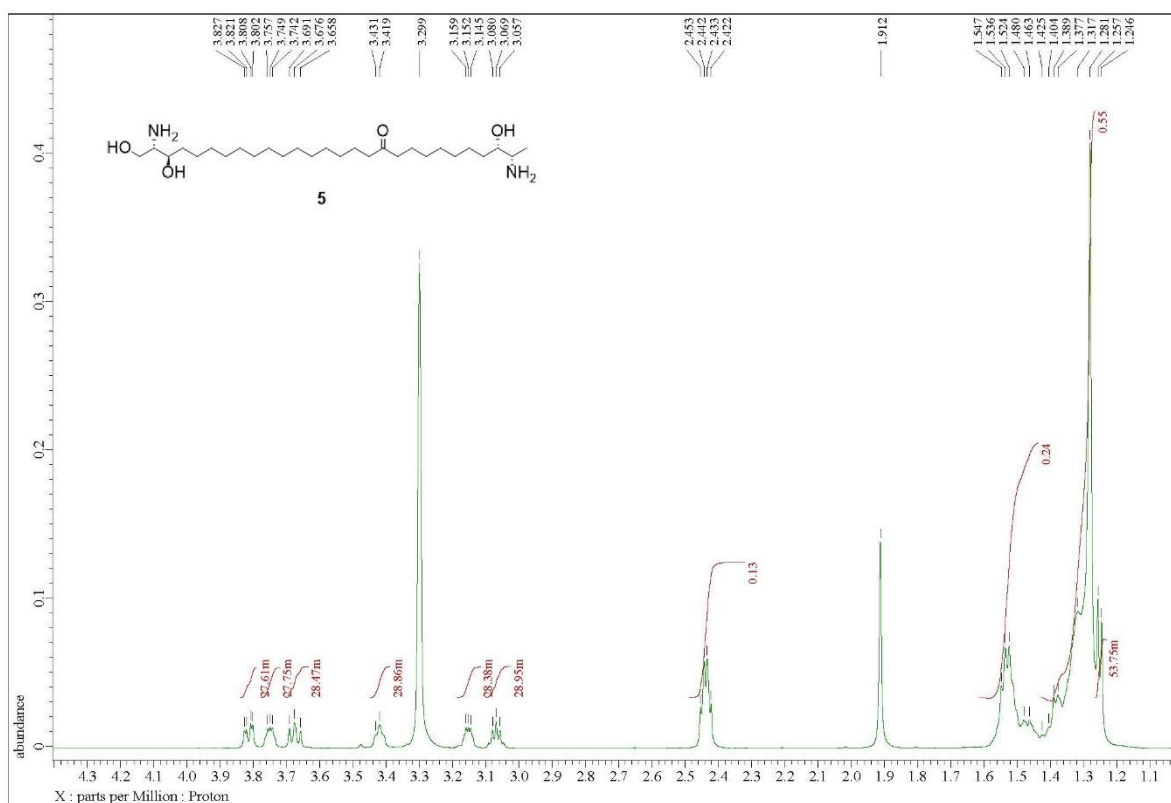


**Figure S10.** HSQC spectrum (600 MHz) of calyxoside (**2**) in CD<sub>3</sub>OD

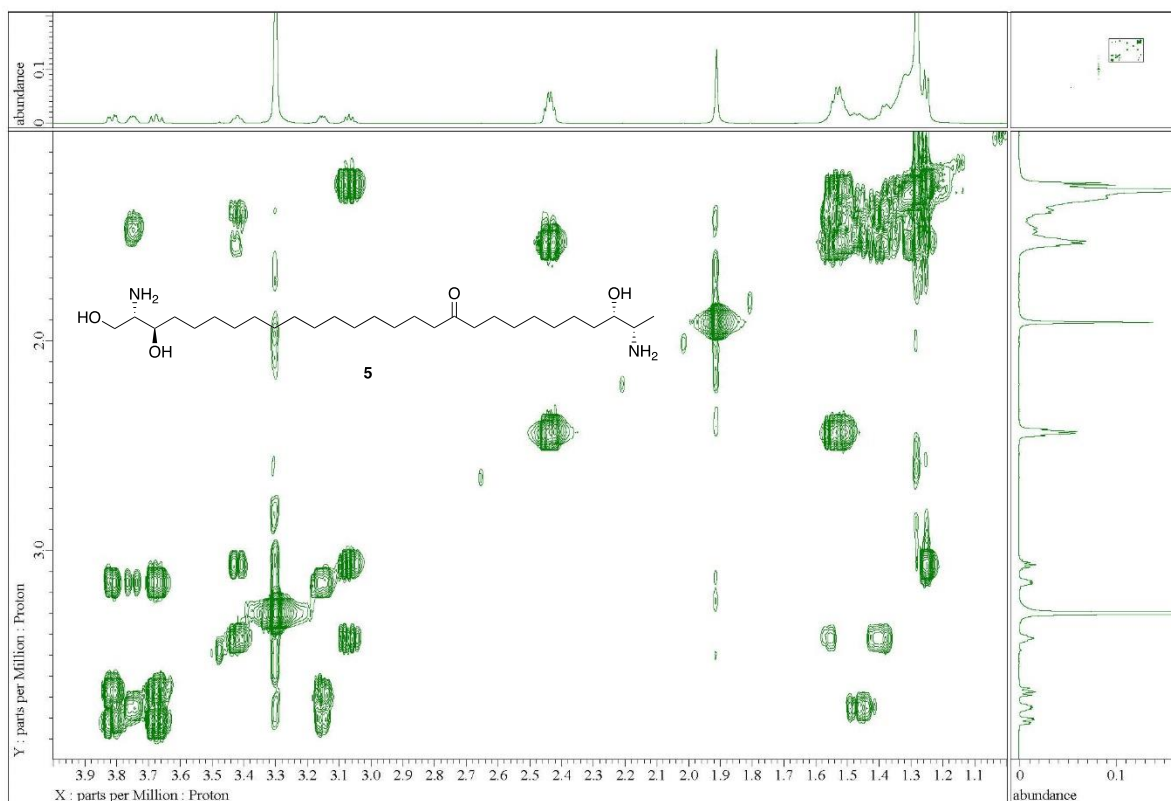


**Figure S11.** HMBC spectrum (600 MHz) of calyxoside (**2**) in CD<sub>3</sub>OD

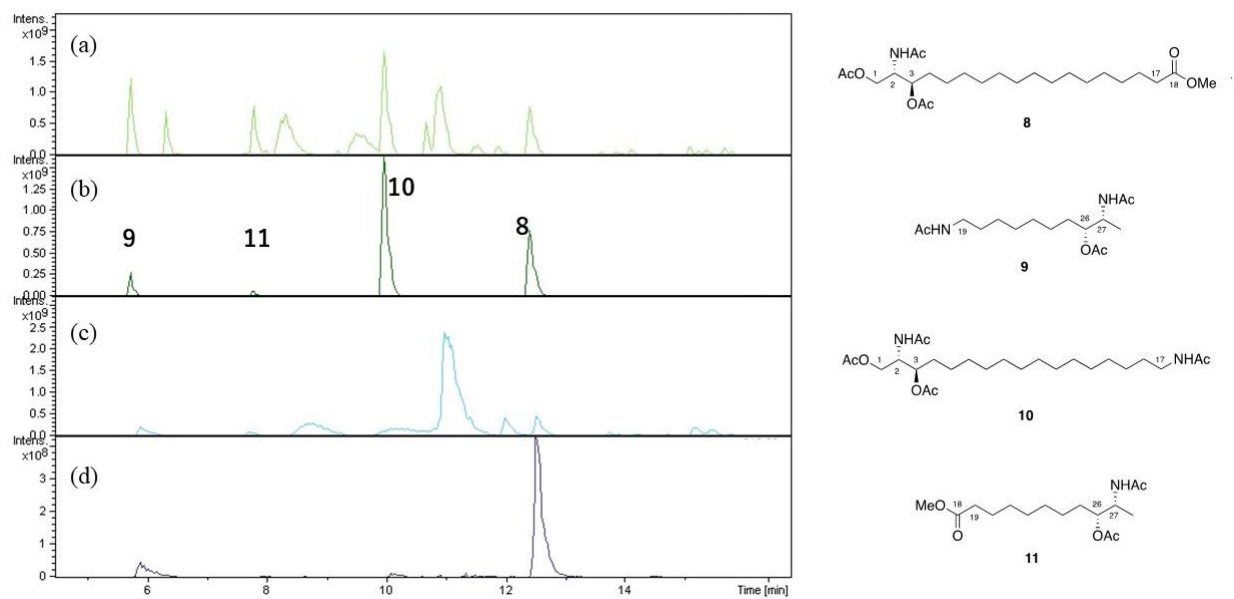




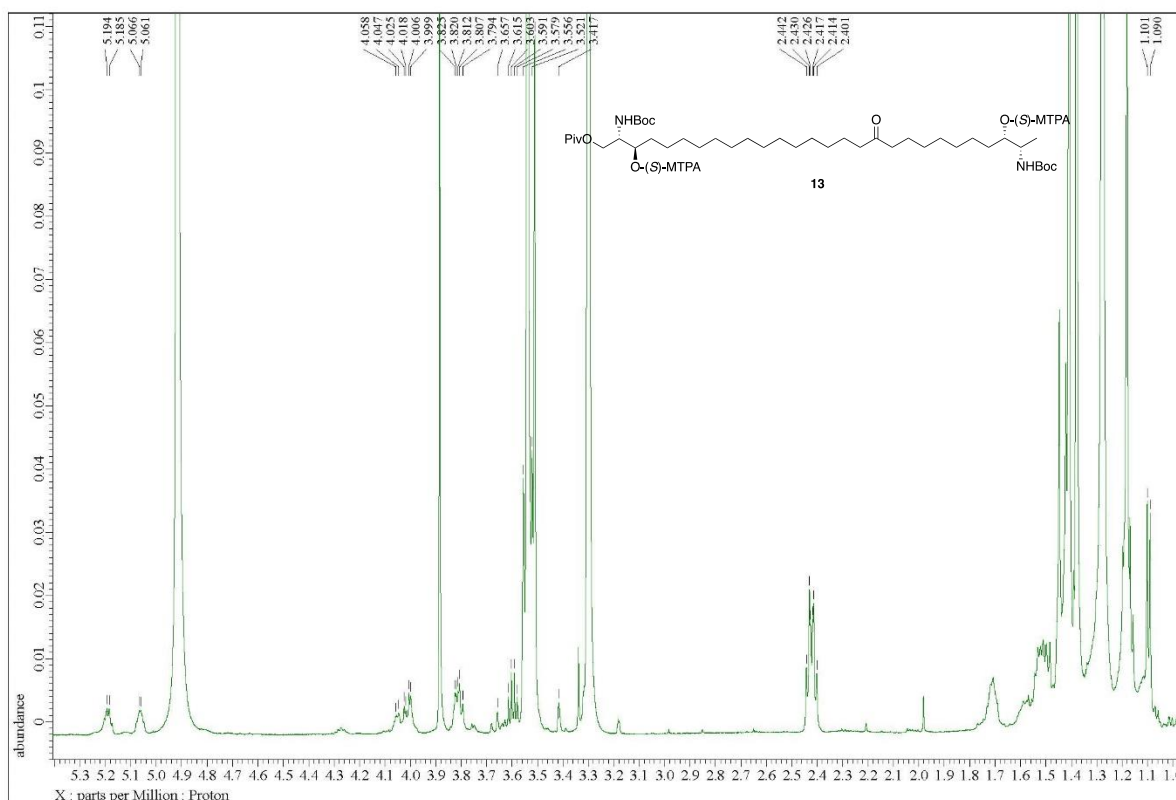
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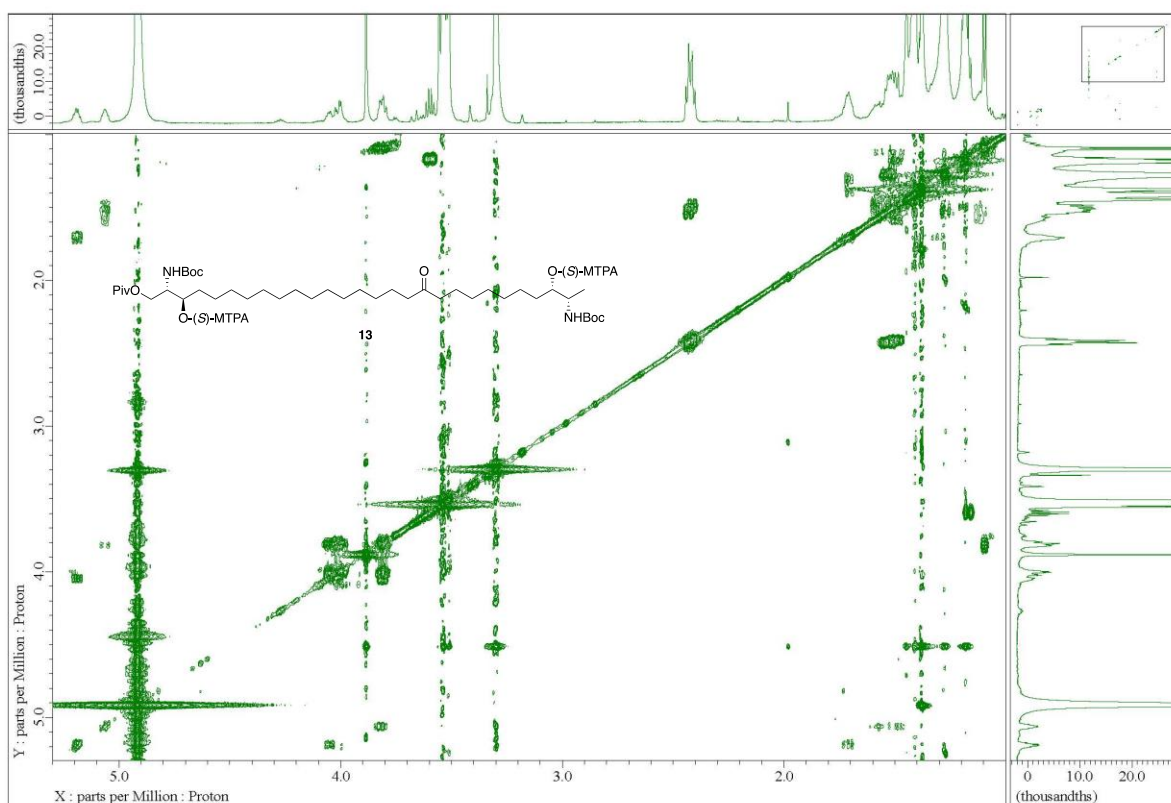
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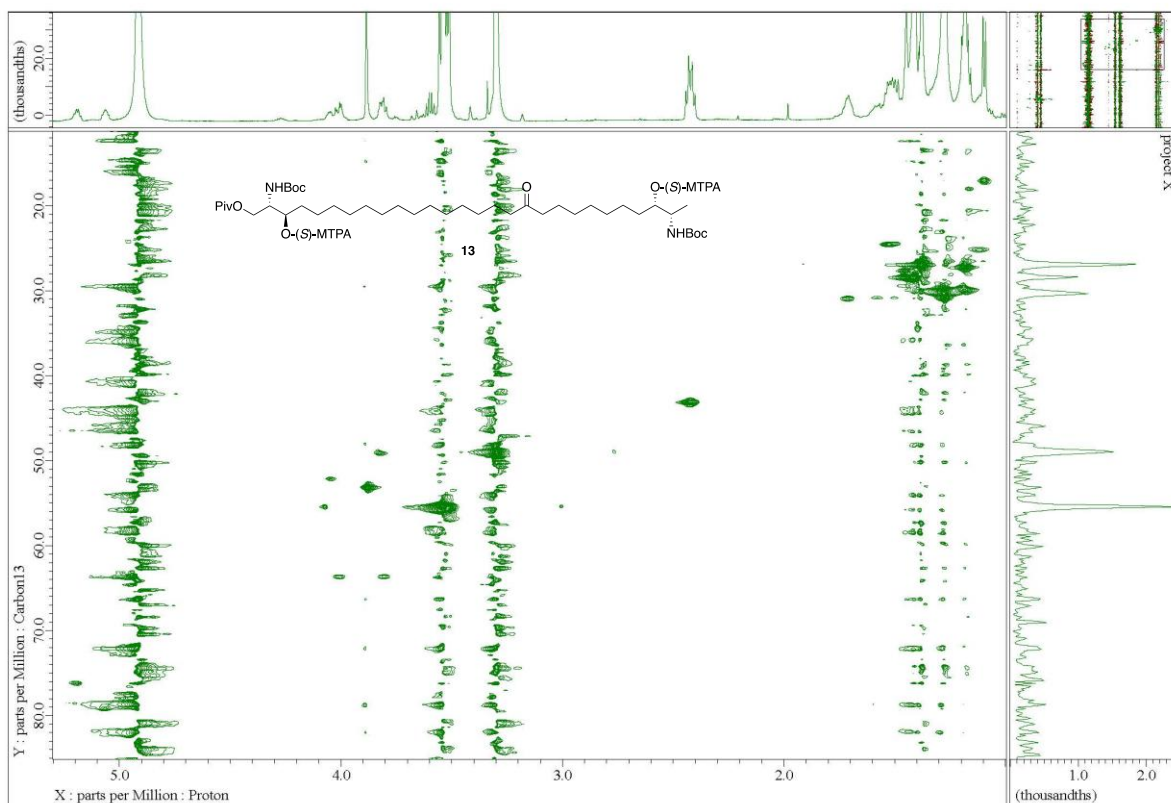
**Figure S14.** LC-MS chromatograms of derivatives of amide methanolysis products  
a: All ions from **6** and **7**, b: Ions at  $m/z$  472.3 (**8**), 315.2 (**9**), 471.3 (**10**) and 316.2 (**11**) from **6** and **7**,  
c: All ions from **6**, d: Ions at  $m/z$  472.3, 315.2, 471.3 and 316.2 from **6**



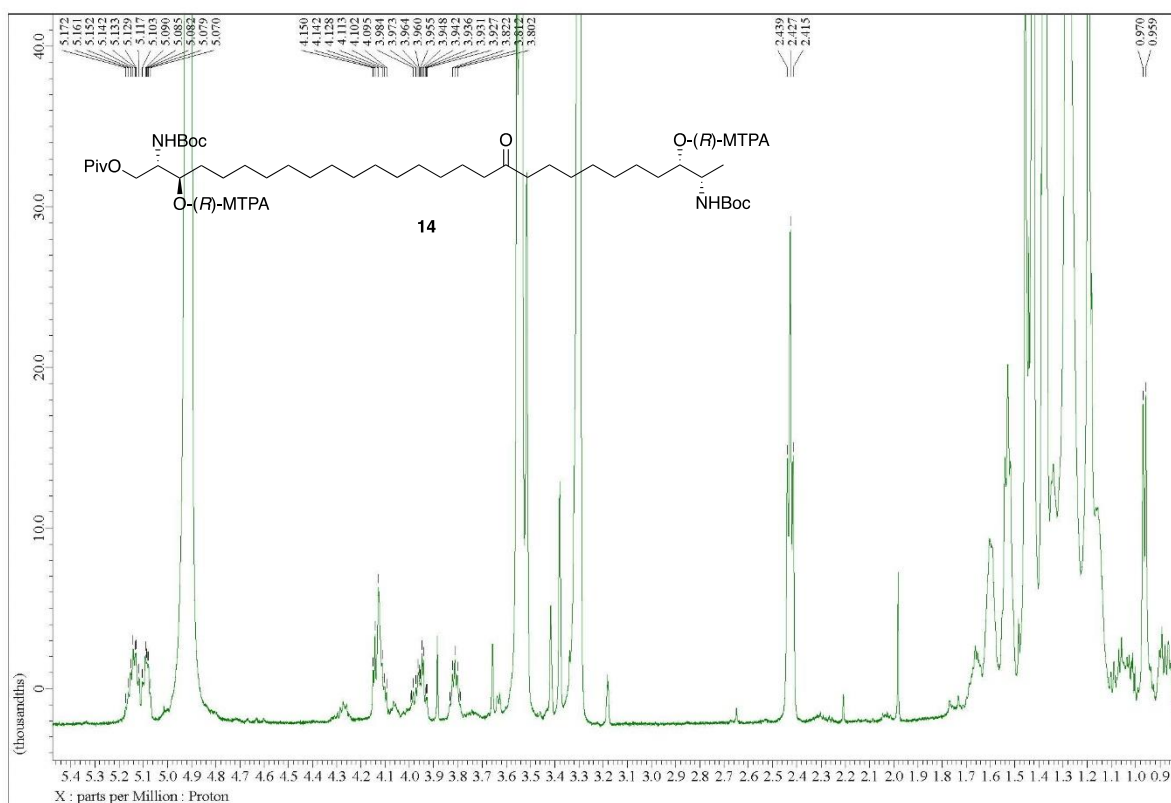
**Figure S15.**  $^1\text{H}$  NMR spectrum (600 MHz) of the (*S*)-MTPA ester (**13**) in  $\text{CD}_3\text{OD}$



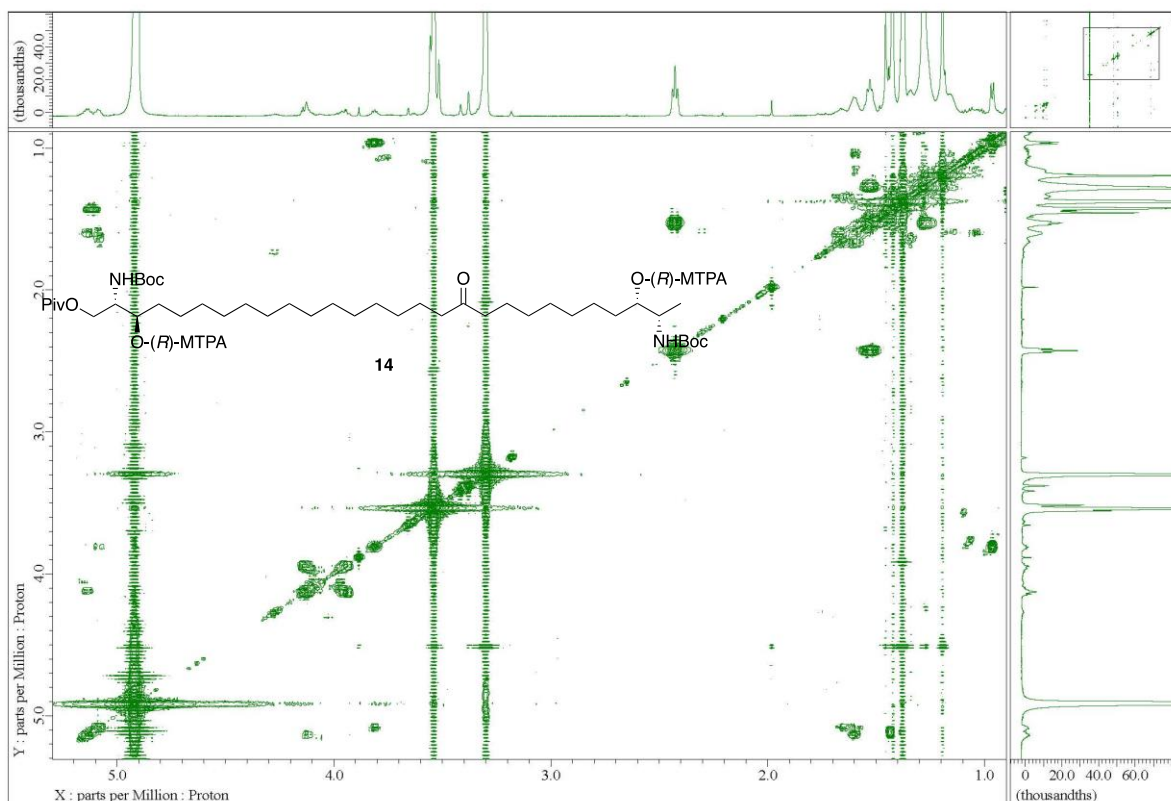
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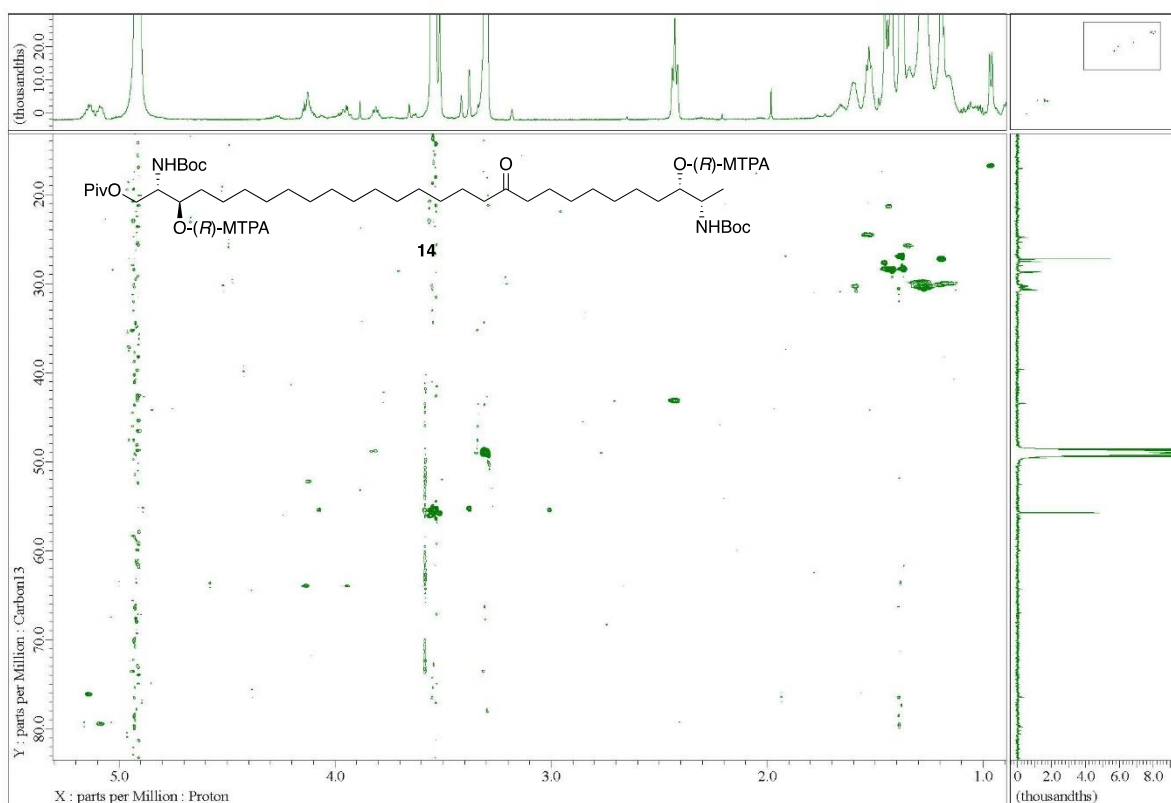
**Figure S17.** HSQC spectrum (600 MHz) of the (*S*)-MTPA ester (**13**) in CD<sub>3</sub>OD



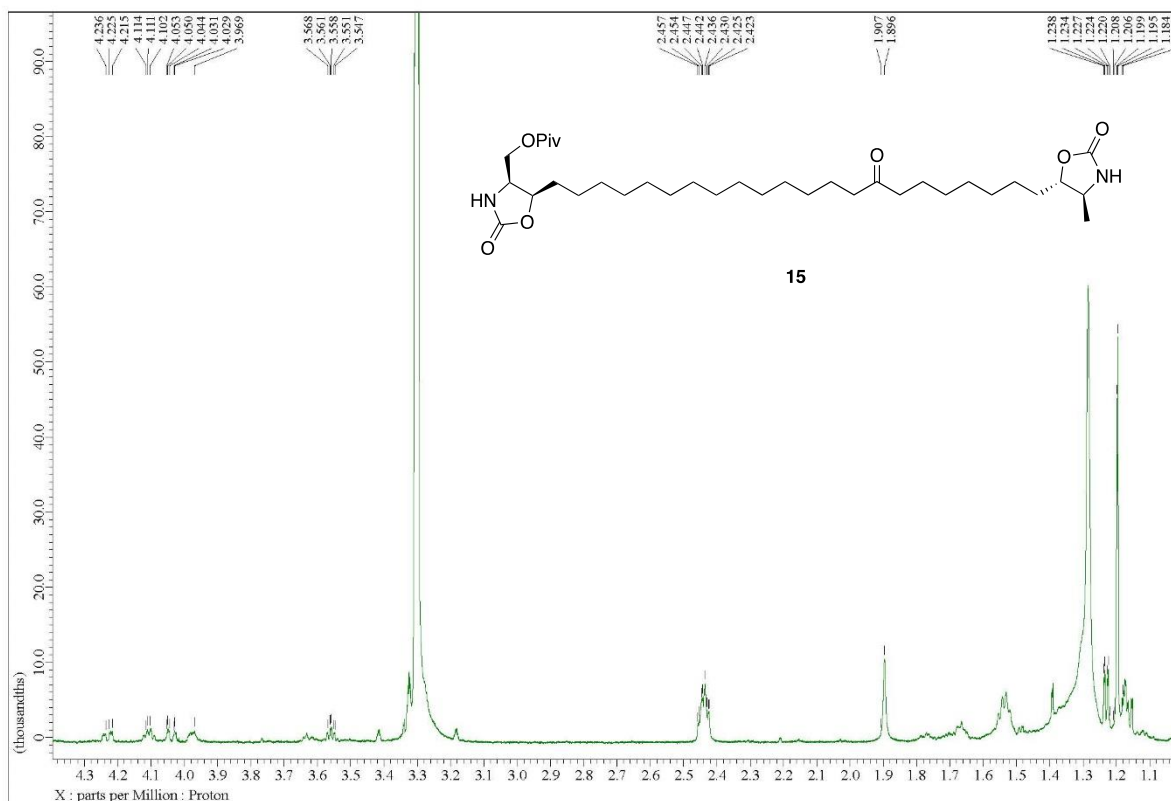
**Figure S18.**  $^1\text{H}$  NMR spectrum (600 MHz) of the (*R*)-MTPA ester (**14**) in  $\text{CD}_3\text{OD}$



**Figure S19.** COSY spectrum (600 MHz) of the (*R*)-MTPA ester (**14**) in  $\text{CD}_3\text{OD}$

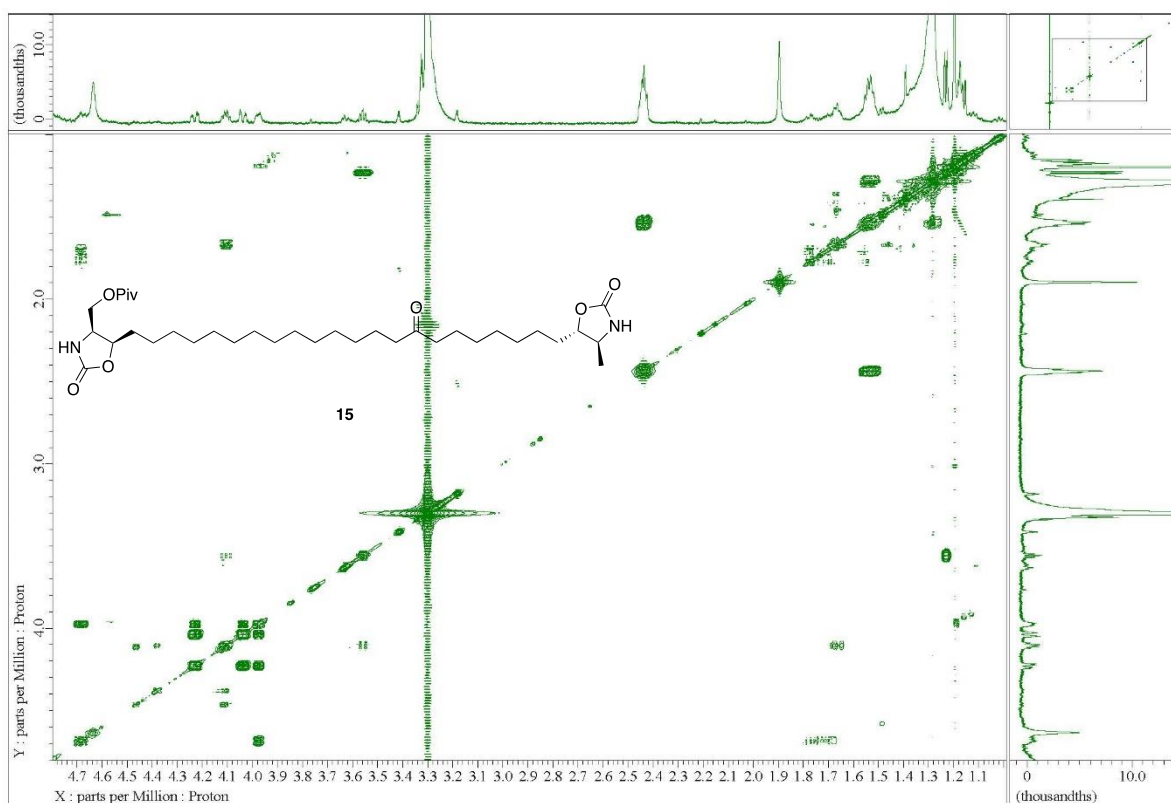


**Figure S20.** HSQC spectrum (600 MHz) of the (*R*)-MTPA ester (**14**) in CD<sub>3</sub>OD

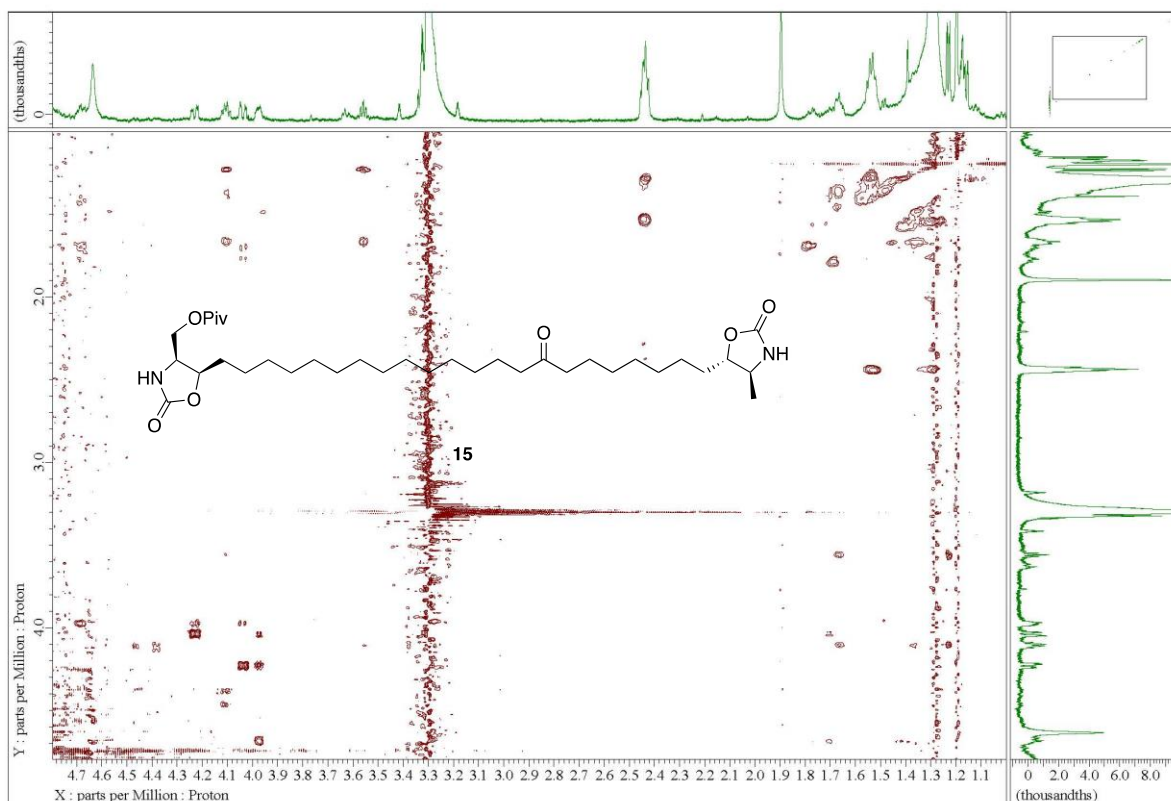


**Figure S21.** <sup>1</sup>H NMR spectrum (600 MHz) of the bis-oxazolidinone (**15**) in CD<sub>3</sub>OD

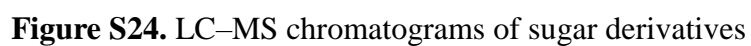




**Figure S22.** COSY spectrum (600 MHz) of the bis-oxazolidinone (15) in CD<sub>3</sub>OD



**Figure S23.** NOESY spectrum (600 MHz) of the bis-oxazolidinone (15) in CD<sub>3</sub>OD



**Graph#1**

y axis

x axis

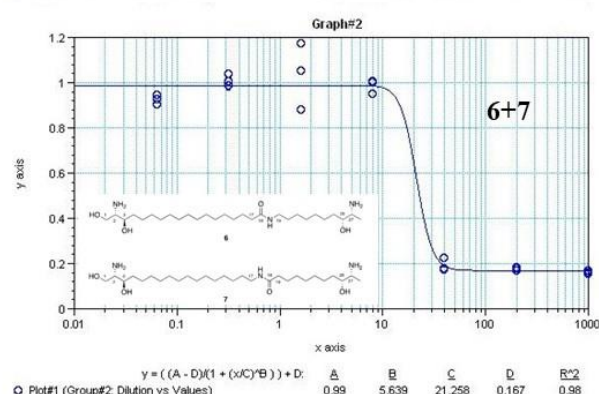
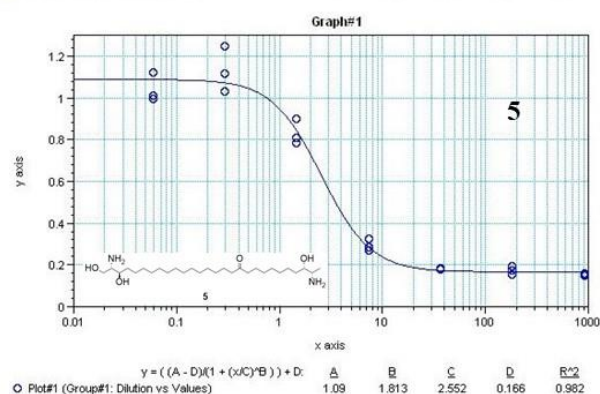
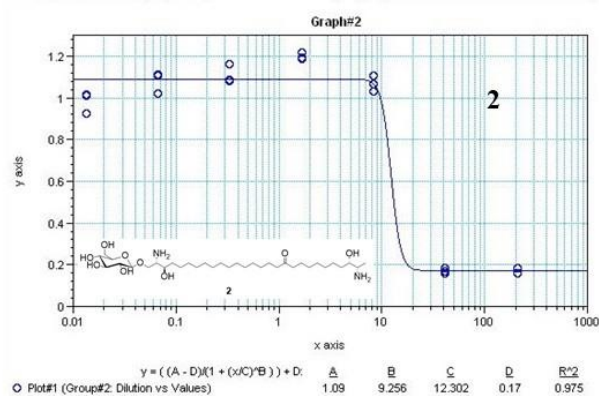
1

OCC(O)C(=O)NCCCCCCCCCCCNC(=O)CCCCCO

1

$y = ((A - D)/(1 + (x/C)^B)) + D$

	A	B	C	D	R <sup>2</sup>
○ Plot#1 (Group#1: Dilution vs Values)	1.164	19.057	31.035	0.161	0.949



**Figure S25.** Graphs of MTT assay of **1**, **2**, **5** and the mixture of **6** and **7** against HeLa cells