

## *Supporting Information*

# **Halisphingosines A and B, Modified Sphingoid Bases from *Haliclona tubifera*. Assignment of Configuration by Circular Dichroism and van't Hoff's Principle of Optical Superposition<sup>†</sup>**

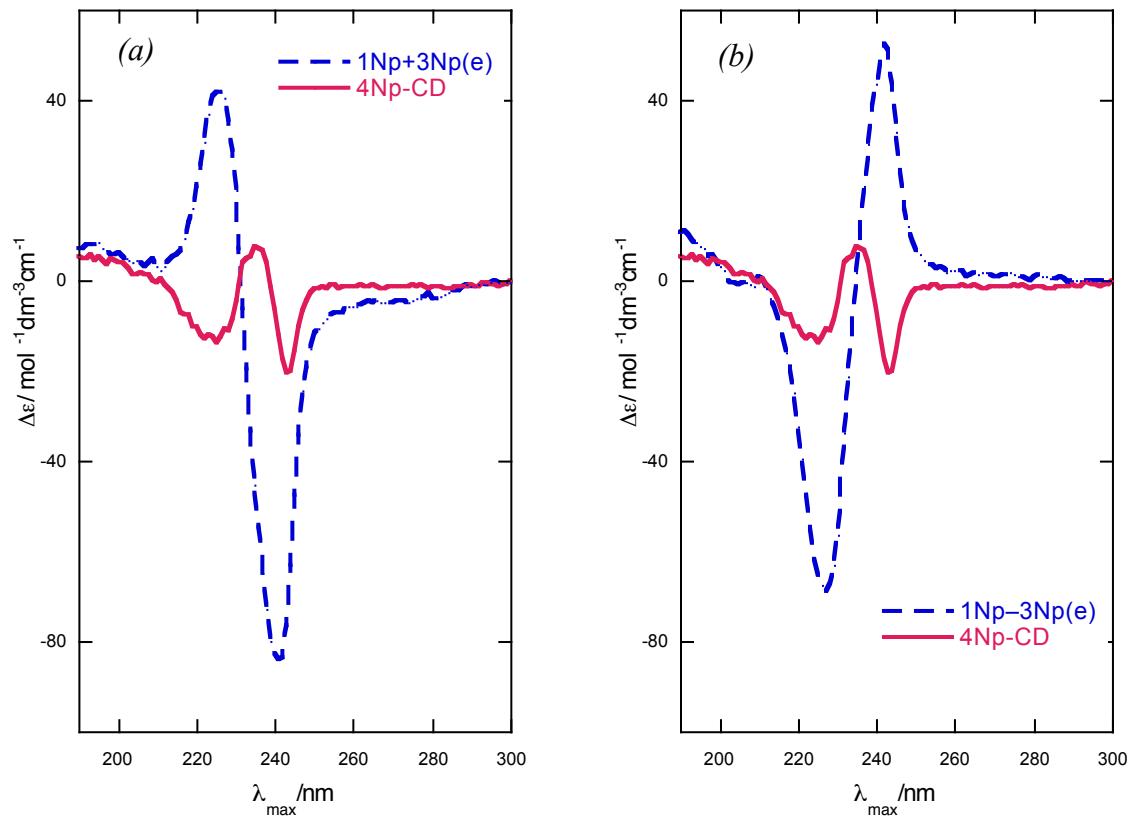
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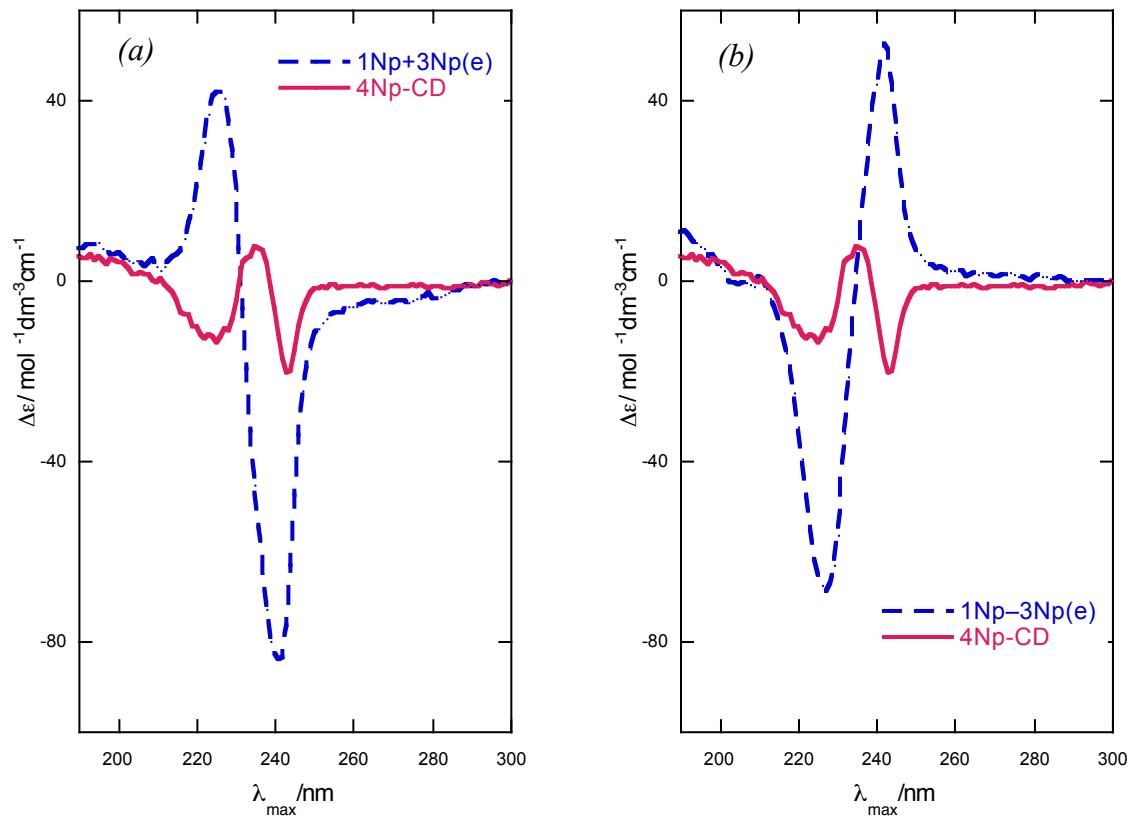


**Figure S1.** Measured CD spectra ( $\text{CH}_3\text{CN}$ ,  $24^\circ\text{C}$ ) of *N,O,O*-tetranaphthoyl halisphingosine A (**5**, solid line) overlayed with hybrid spectra (dashed lines) generated from CD of **4** and *erythro*-**6b**. (a)  $\text{CD} = \text{CD}[4] + \text{CD}[6b]$ . (b)  $\text{CD} = \text{CD}[4] - \text{CD}[6b]$ .

**Table S1.** Tabulated parameters [ $\lambda$  /nm ( $\Delta\epsilon$  /mol $^{-1}\text{dm}^3\text{cm}^{-1}$ ), and  $A$  values] for measured and hybrid CD spectra in **Fig. 4** and **Fig. S1**.<sup>a</sup>

CD / Hybrid CD	$\lambda$ ( $\Delta\epsilon$ )	$\lambda$ ( $\Delta\epsilon$ )	$\lambda$ ( $\Delta\epsilon$ )	$A$
<b>4</b> <sup>a</sup>	190(+8) <sup>b</sup>	236(-21.9)	–	–
<b>5</b> <sup>a</sup>	224(-12.5)	235(+17.4)	243(-20.1)	32.5
<b>6b</b> <sup>a</sup>	226(+56)	242(+124)	–	124
<b>7b</b> <sup>a</sup>	221(+7.2)	237(-19.3)	–	26.5
CD[4]+CD[7b]	–	237(-40.9)	–	–
CD[4]-CD[7b]	227(-18.5)	237(-2.5)	243(-12.4)	–
CD[4]+CD[6b]	226(+42)	241(-84)	–	126
CD[4]-CD[6b]	227(-69)	242 (+53)	–	122

*a*, all measured CD spectra under the same conditions ( $\text{CH}_3\text{CN}$ ,  $24^\circ\text{C}$ ). *b*, truncated at end  $\lambda$

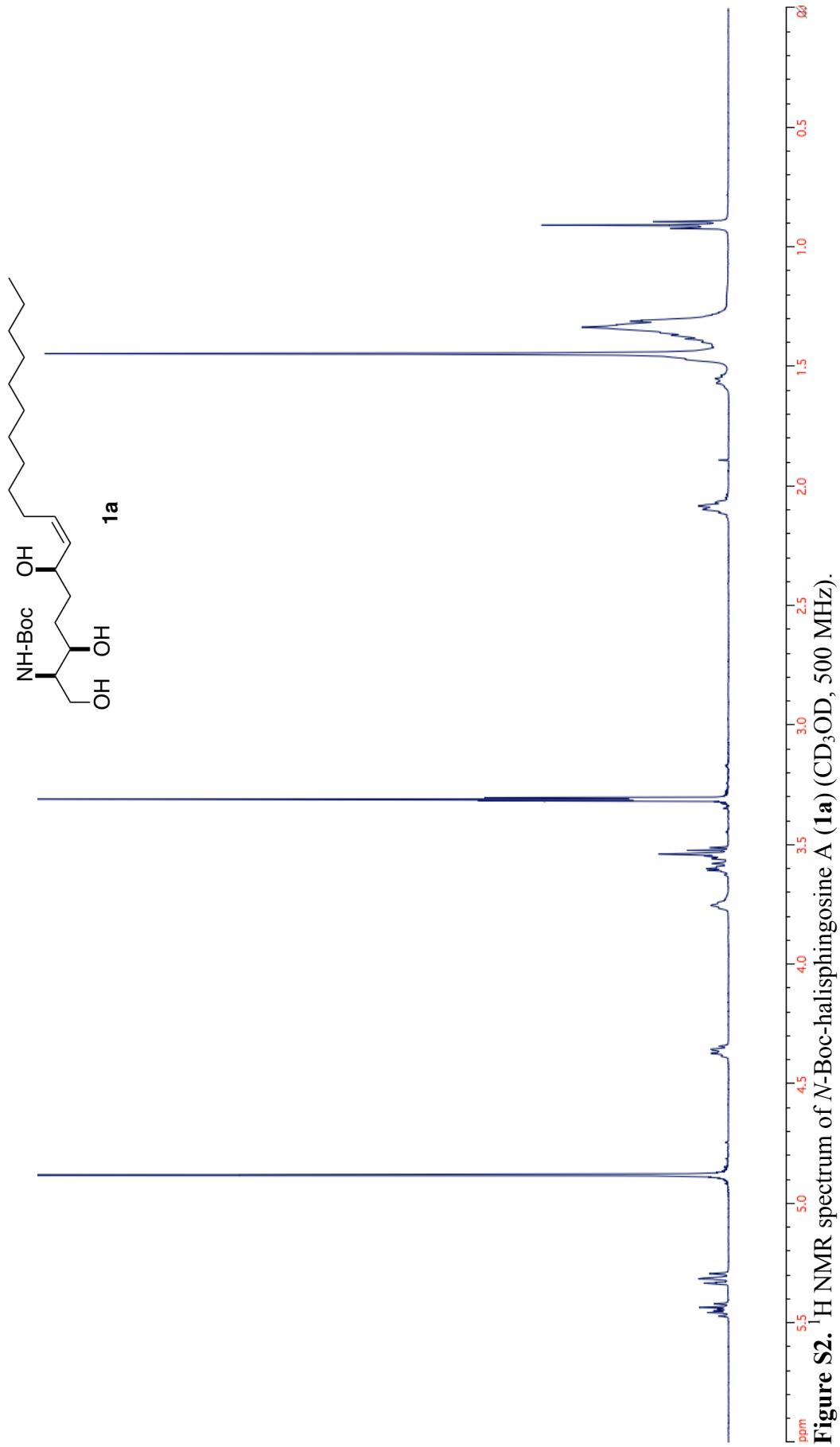


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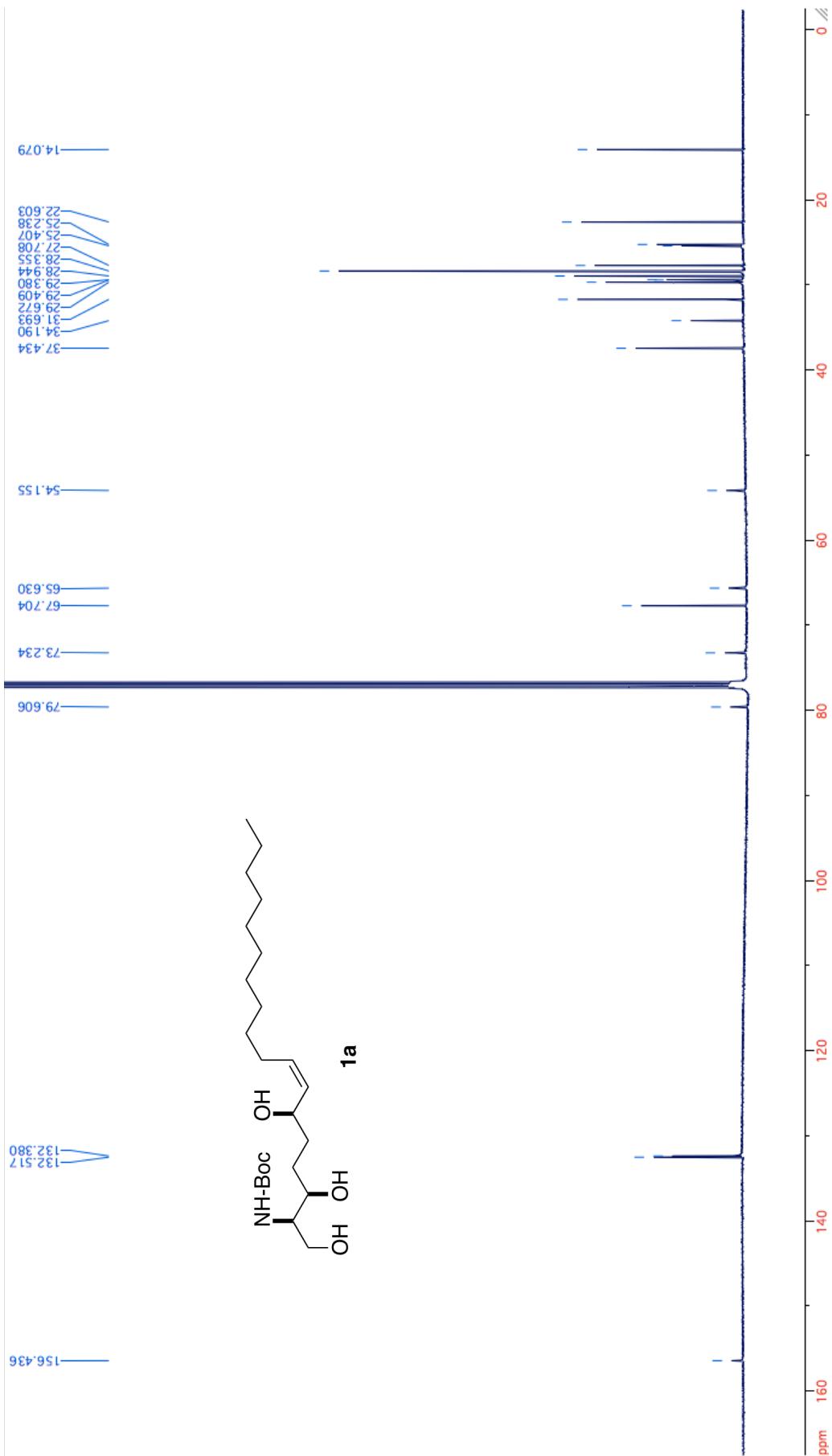
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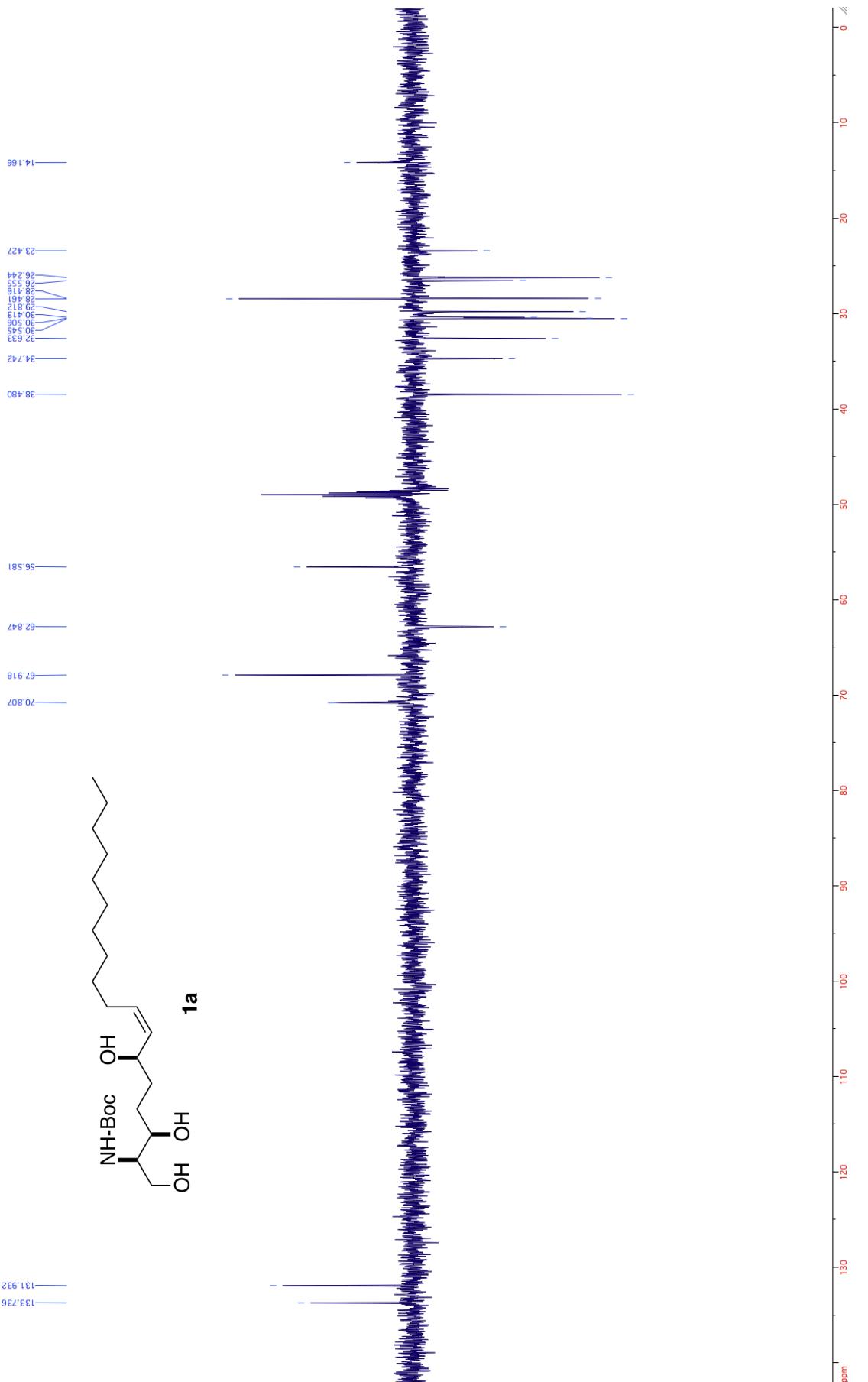
*a*, all measured CD spectra under the same conditions ( $\text{CH}_3\text{CN}$ ,  $24^\circ\text{C}$ ). *b*, truncated at end  $\lambda$



**Figure S2.**  $^1\text{H}$  NMR spectrum of *N*-Boc-halisphingosine A (**1a**) ( $\text{CD}_3\text{OD}$ , 500 MHz).



**Figure S3.**  $^{13}\text{C}$  NMR spectrum of *N*-Boc-haliphosphingosine A (**1a**) ( $\text{CDCl}_3$ , 125 MHz).



**Figure S4.** DEPT135 NMR spectrum of *N*-Boc-halissphingosine A (**1a**) ( $\text{CD}_3\text{OD}$ , 125 MHz).

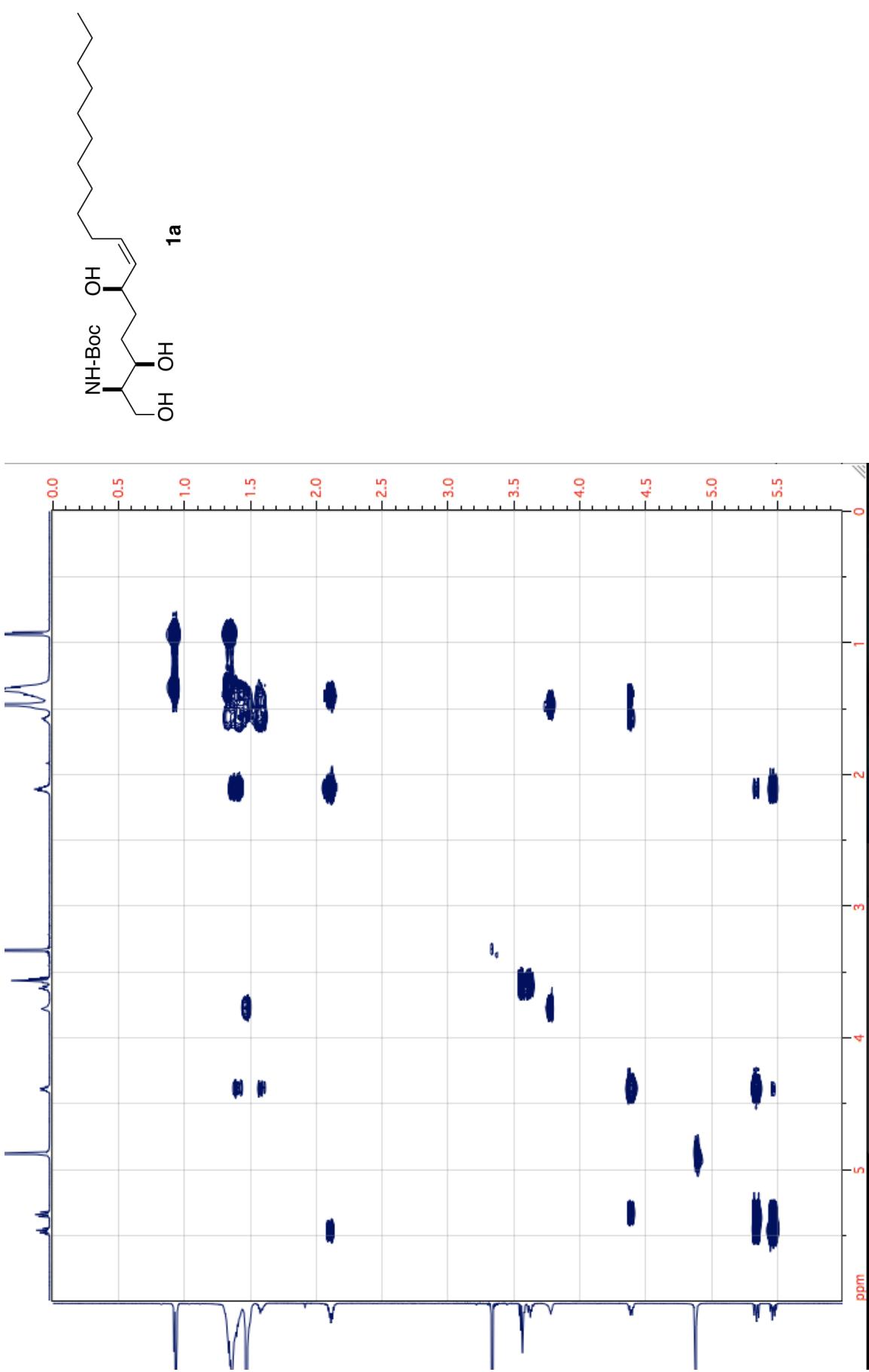
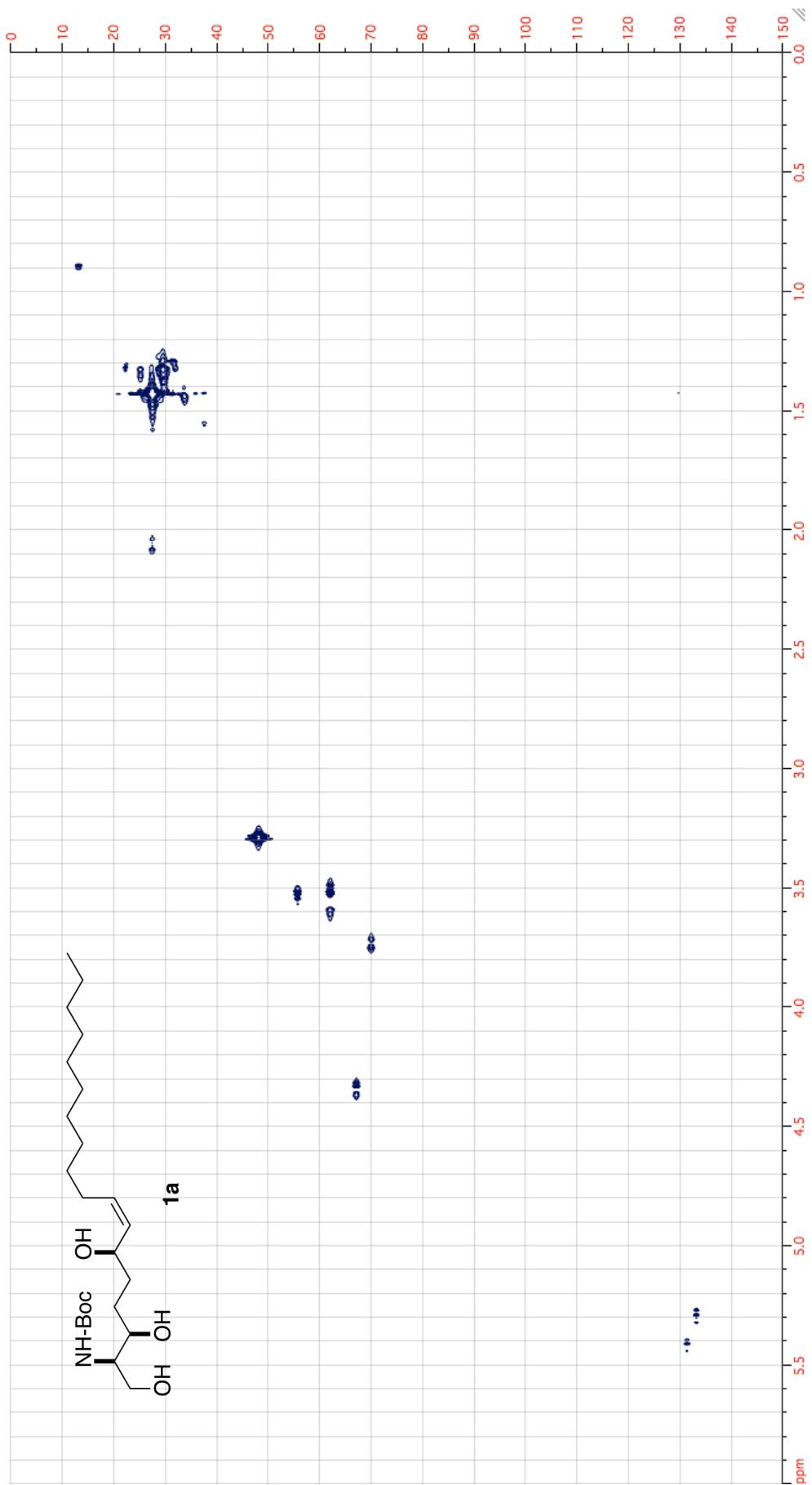
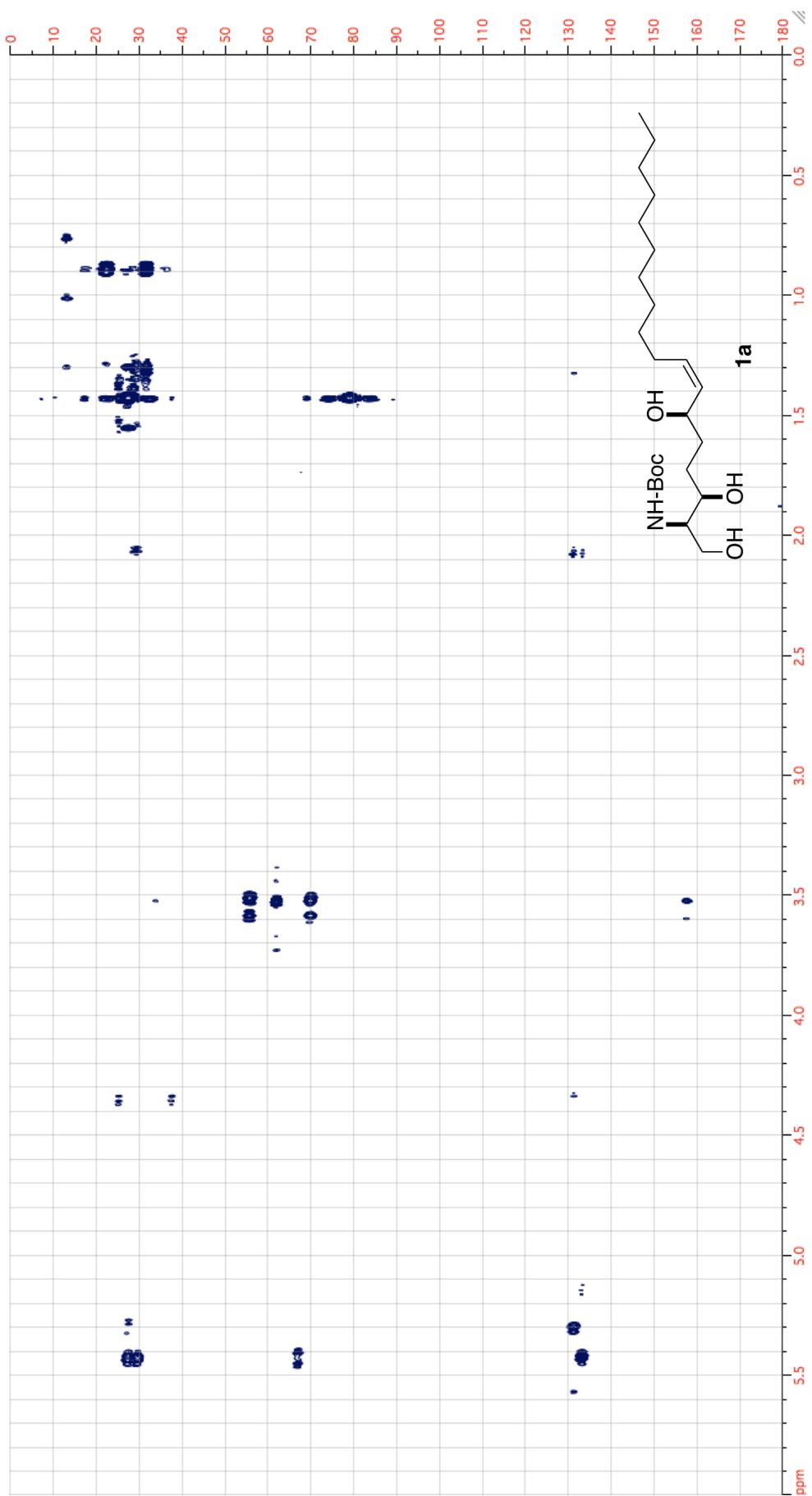


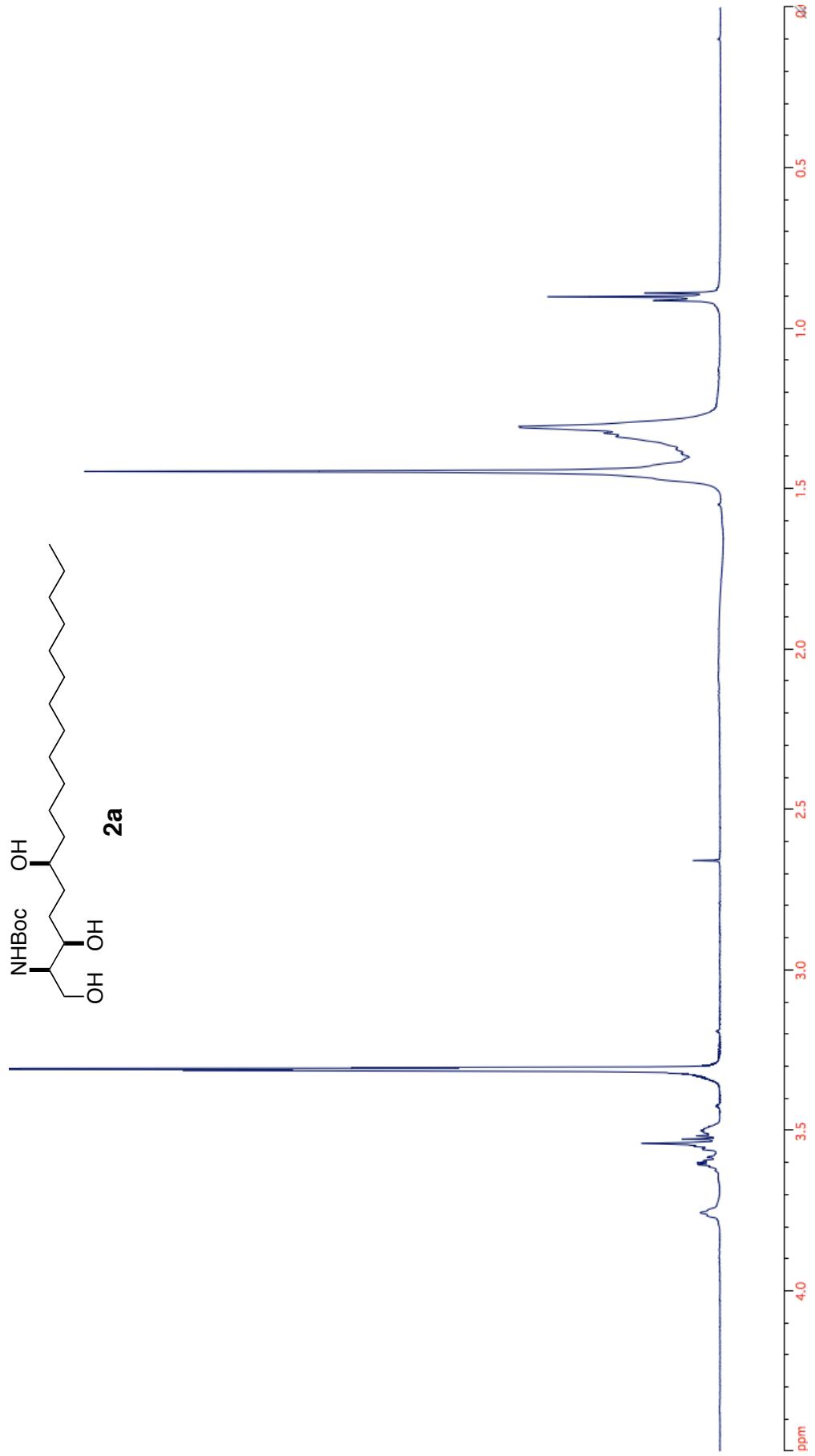
Figure S5.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of *N*-Boc-halisphingosine A (1a) ( $\text{CD}_3\text{OD}$ , 600 MHz).



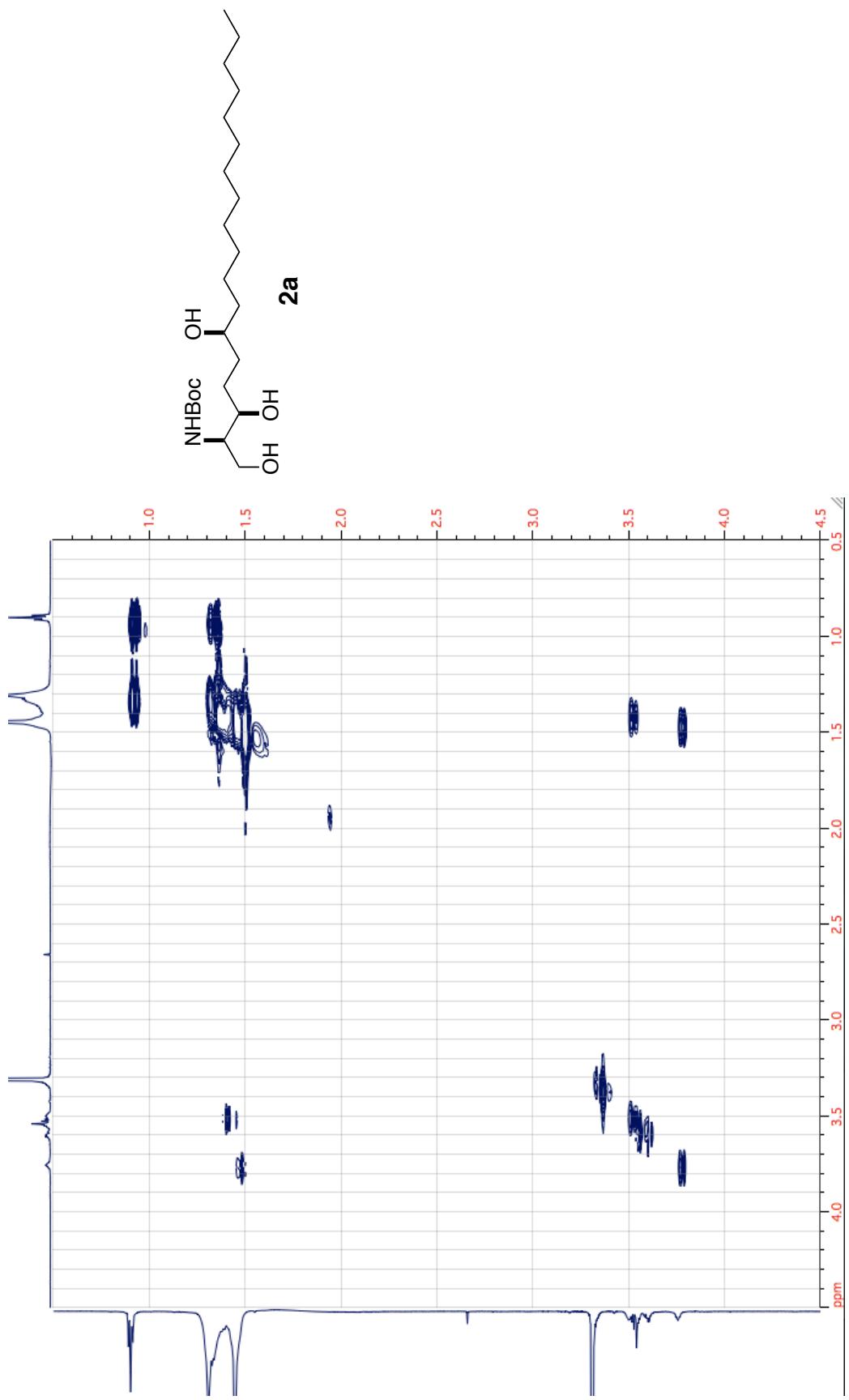
**Figure S6.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectrum of *N*-Boc-halisphingosine A (**1a**) ( $\text{CD}_3\text{OD}$ , 500 MHz).



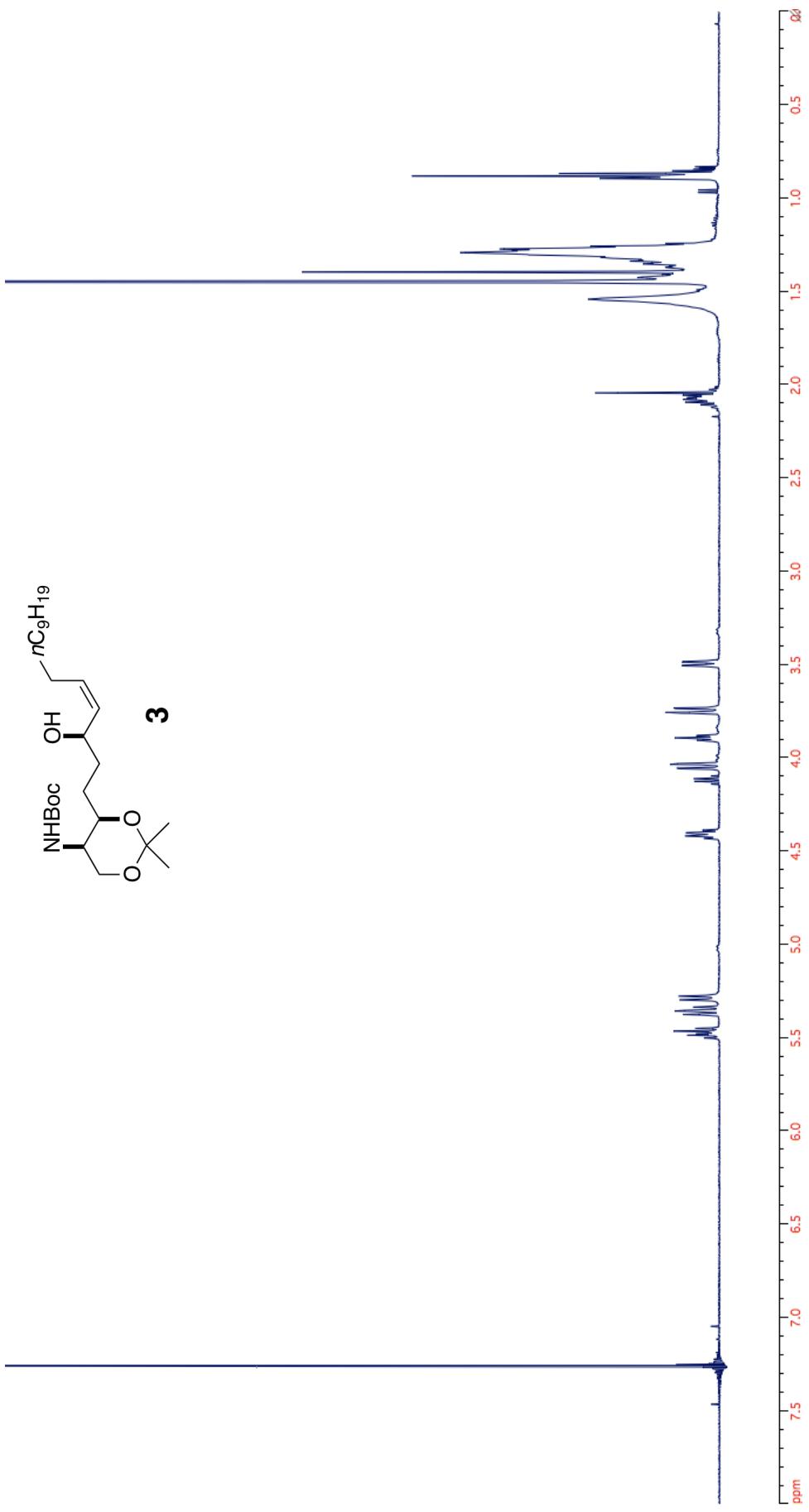
**Figure S7.**  $^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of *N*-Boc-haliphosphine A (**1a**) ( $\text{CD}_3\text{OD}$ , 500 MHz).



**Figure S8.**  $^1\text{H}$  NMR spectrum of *N*-Boc-halisphingine B (**2a**) ( $\text{CD}_3\text{OD}$ , 600 MHz).



**Figure S9.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of *N*-Boc-halisphingosine B (**2a**) ( $\text{CD}_3\text{OD}$ , 600 MHz).



**Figure S10.**  $^1\text{H}$  NMR spectrum of *N*-Boc-halisphingosine A acetonide (**3**) ( $\text{CDCl}_3$ , 500 MHz).

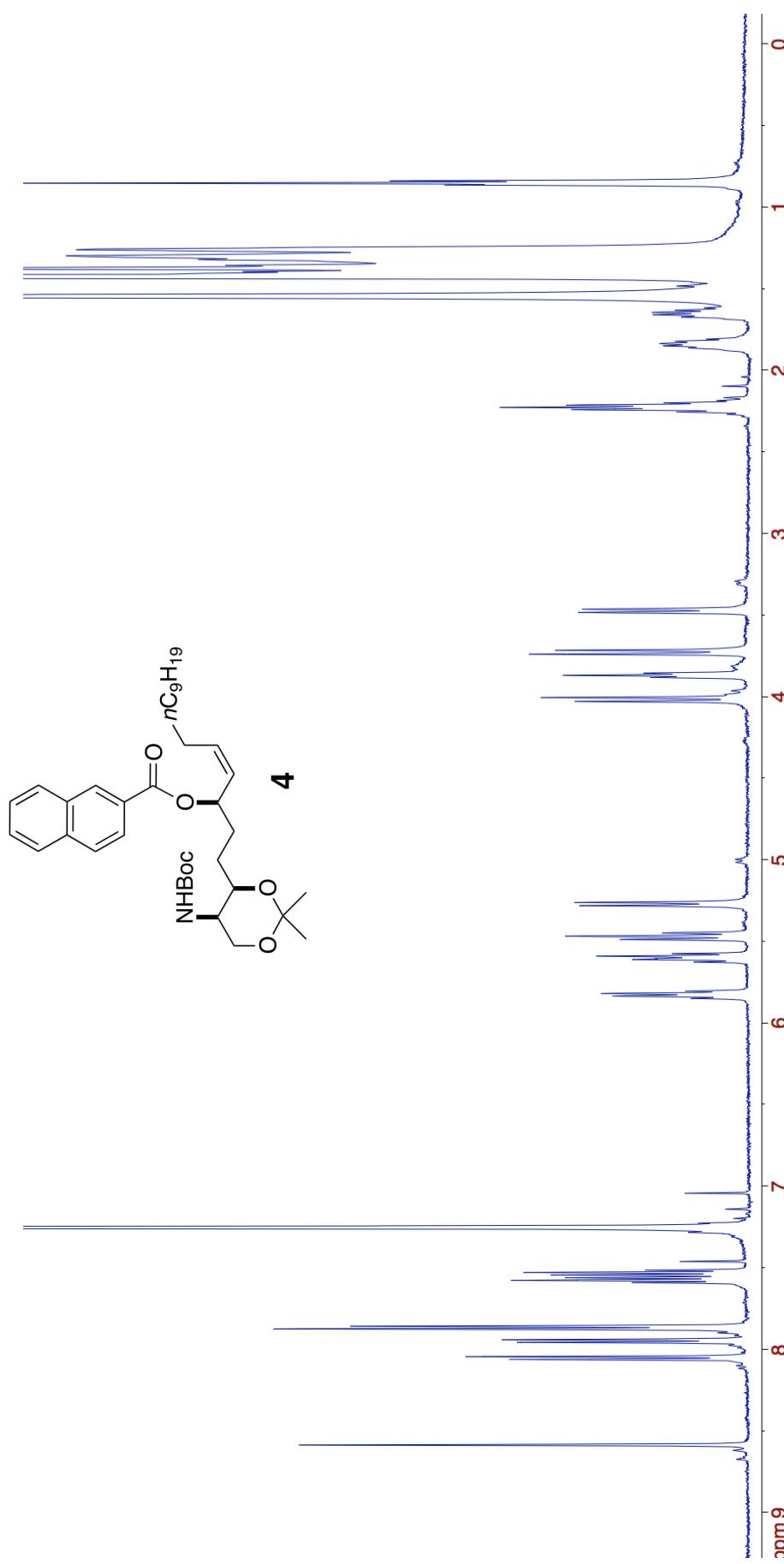


Figure S11.  $^1\text{H}$  NMR spectrum of *mono*-naphthoate (**4**) ( $\text{CDCl}_3$ , 500 MHz).

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single\_pulse

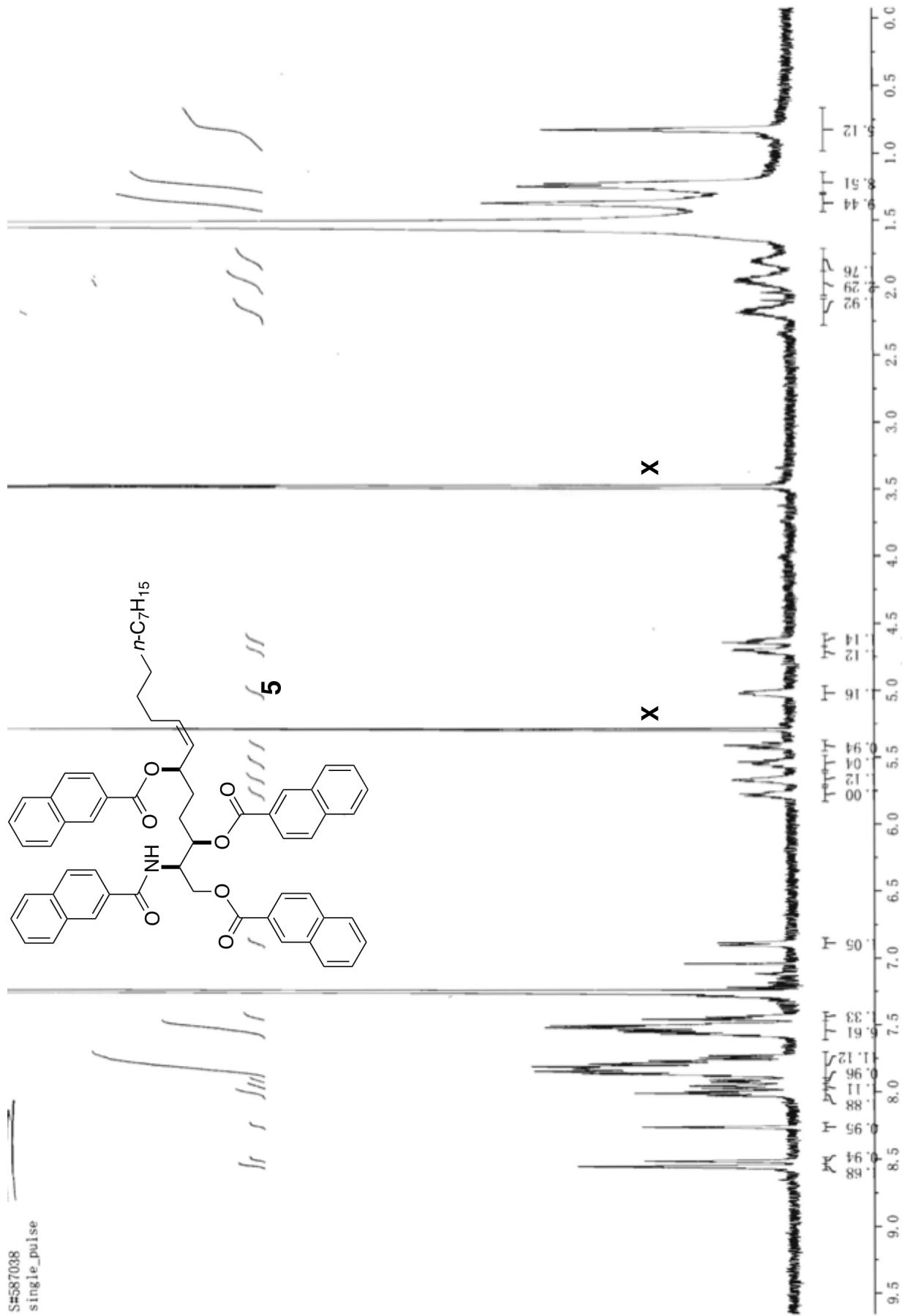
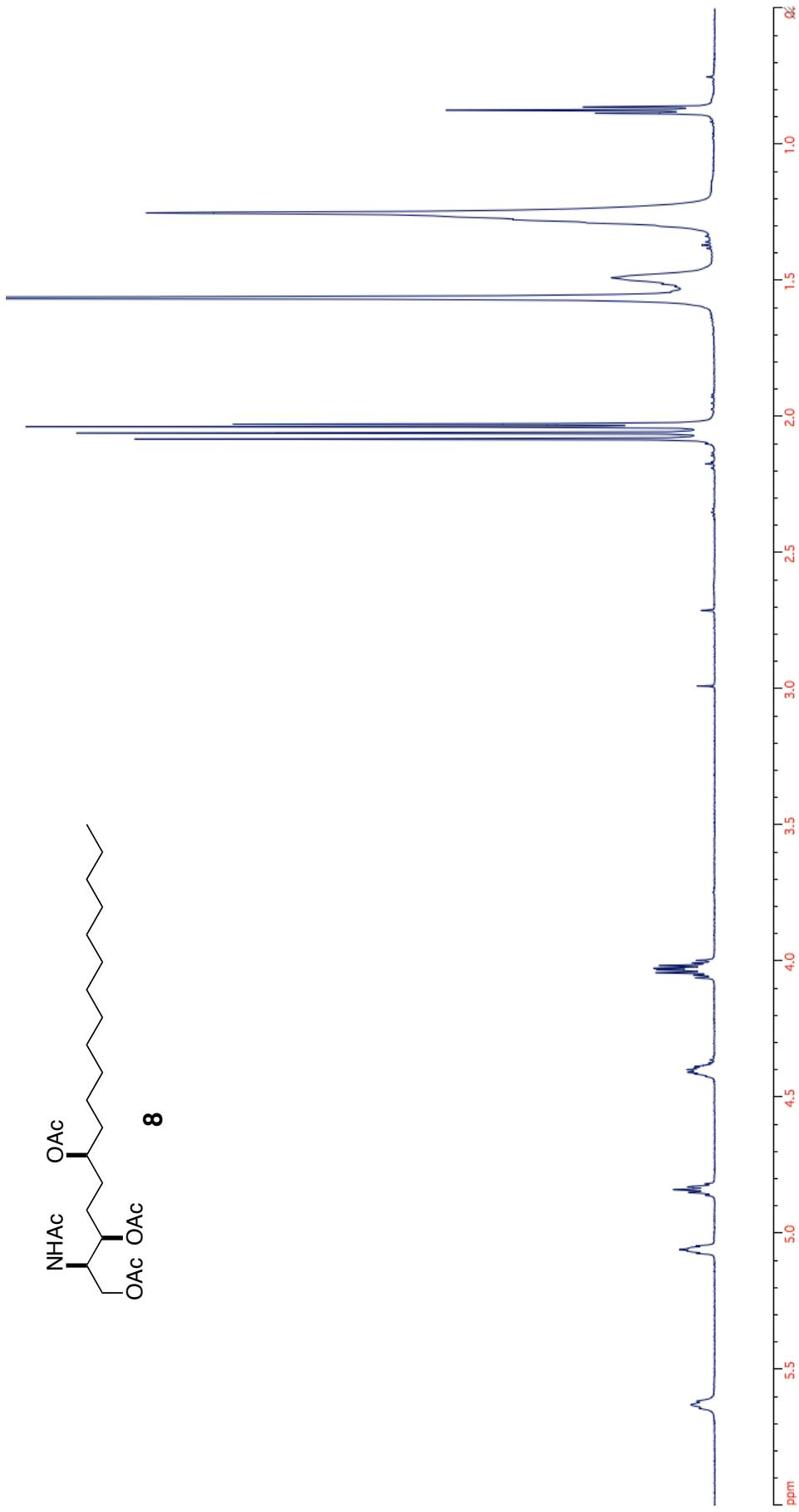
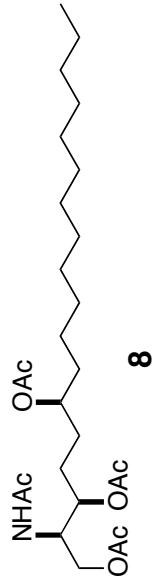


Figure S12. <sup>1</sup>H NMR spectrum of tetranaphthoyl-haliphosphingosine (**5**) (CDCl<sub>3</sub>, 500 MHz).



**Figure S13.**  $^1\text{H}$  NMR spectrum of per-acetyl-halsphingosine B (**8**) ( $\text{CDCl}_3$ , 600 MHz).

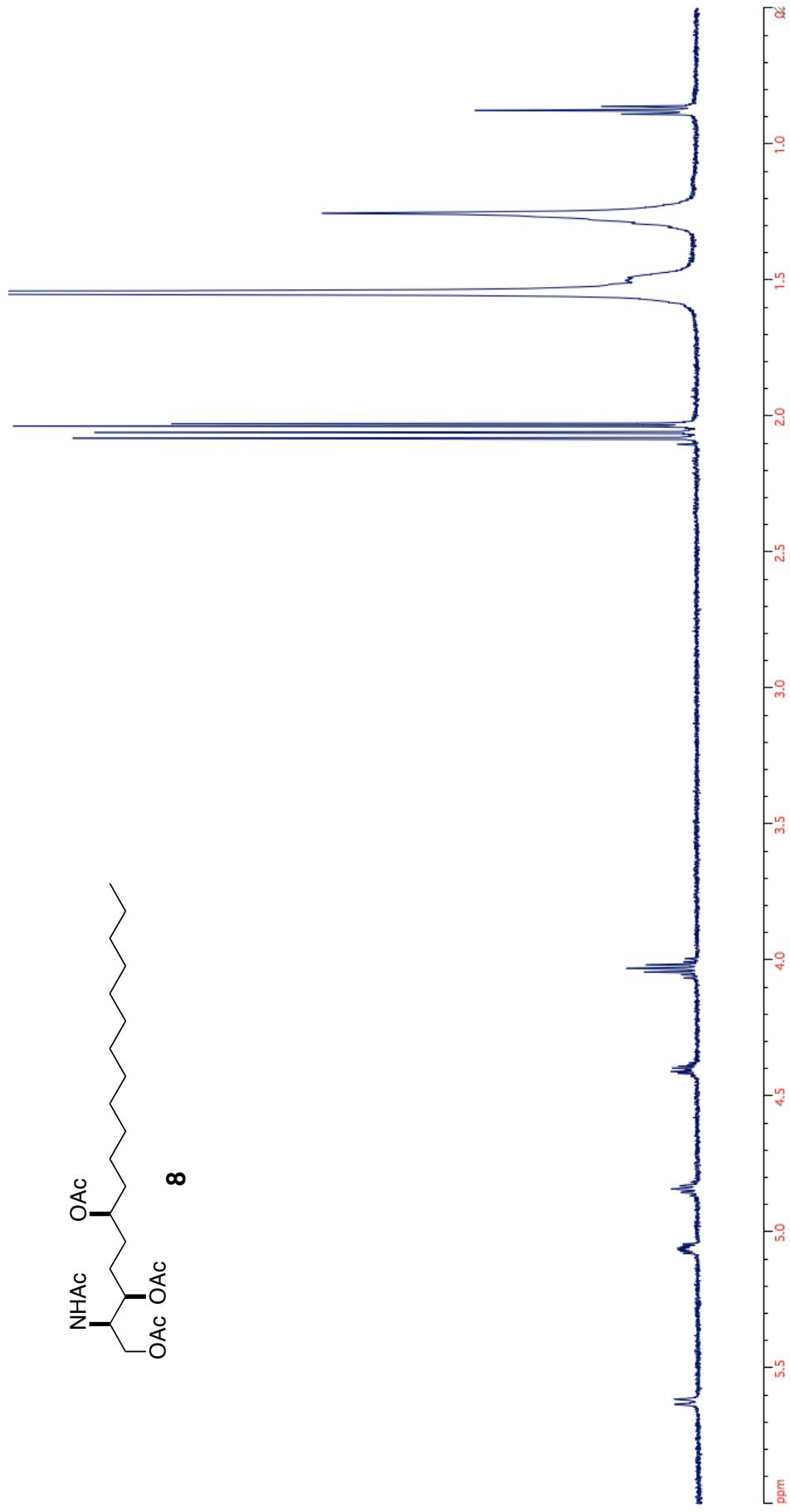


Figure S14. <sup>1</sup>H NMR spectrum of 7,8-dihydro-per-acetyl-haliphingosine A (**8**) (CDCl<sub>3</sub>, 500 MHz).

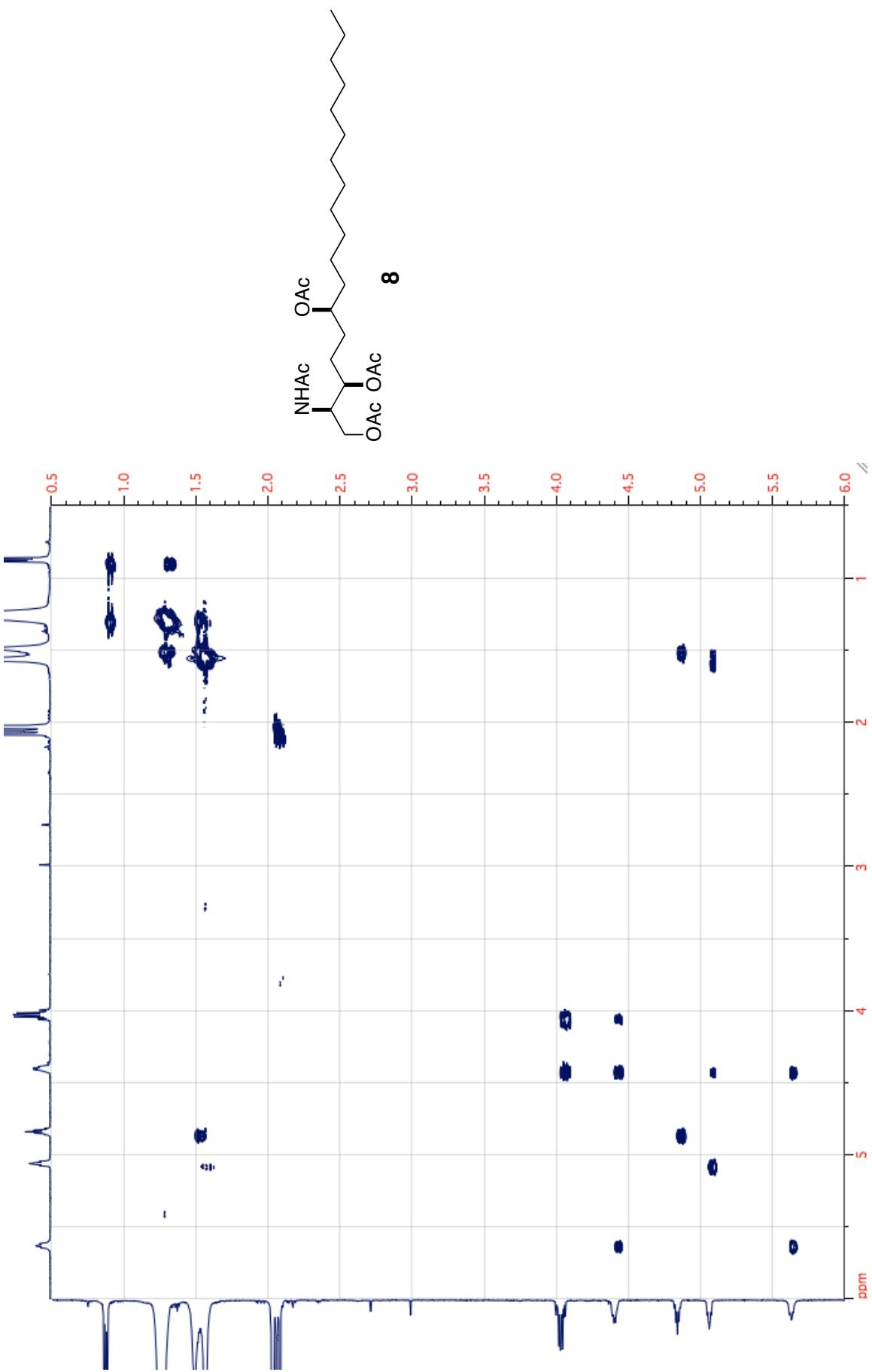
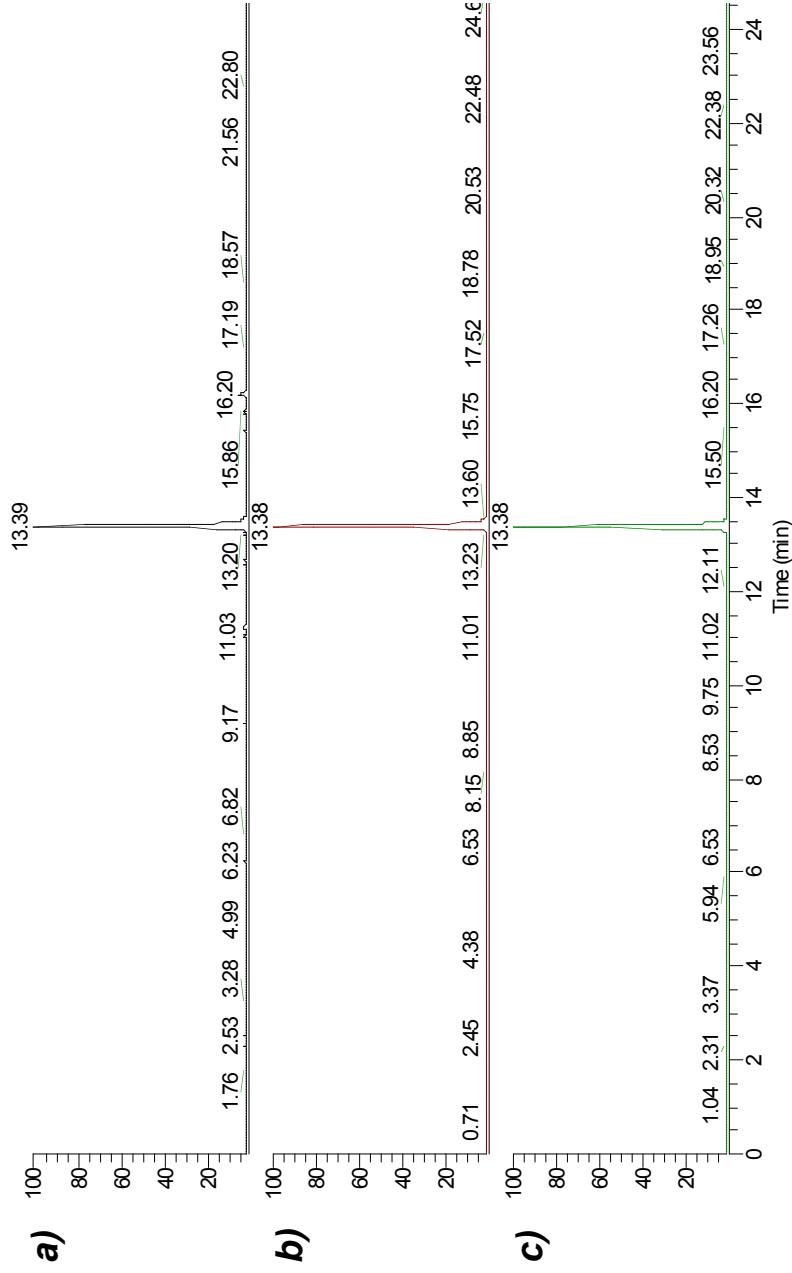


Figure S15.  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of per-acetyl-halissphingosine B (**8**) ( $\text{CDCl}_3$ , 600 MHz).



**Figure S16.** LCMS total ion count (TIC) for **a**) 7,8-dihydro-per-acetyl-halisphingosine A (**8**), **b**) per-acetyl-halisphingosine B (**8**), and **c**) co-injection. LCMS conditions: Phenomenex Kinetex C<sub>18</sub> column (4.6 x 150 mm, 2.6 μm); linear gradient 60% CH<sub>3</sub>CN to 100% CH<sub>3</sub>CN, 0.1% formic acid, over 15 minutes, 0.7 mL min<sup>-1</sup>, APCI probe.