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†

Tadeusz F. Molinski,*,‡,§ Renata Biegelmeyer,⊥ E. Paige Stout,‡ Xiao Wang,‡

Mario L. C. Frota. Jr., and ‖Amelia T. Henriques⊥

‡*Department of Chemistry and Biochemistry, and* §*Skaggs School of Pharmacy and Pharmaceutical Sciences, University of California, San Diego, 9500 Gilman Dr., La Jolla, CA 92093-0358, USA.*

⊥*Pharmacognosy Laboratory and* ‖*Department of Biochemistry, Federal University of South Brazil, Porto Alegre, 90610-000, RS, Brazil.*

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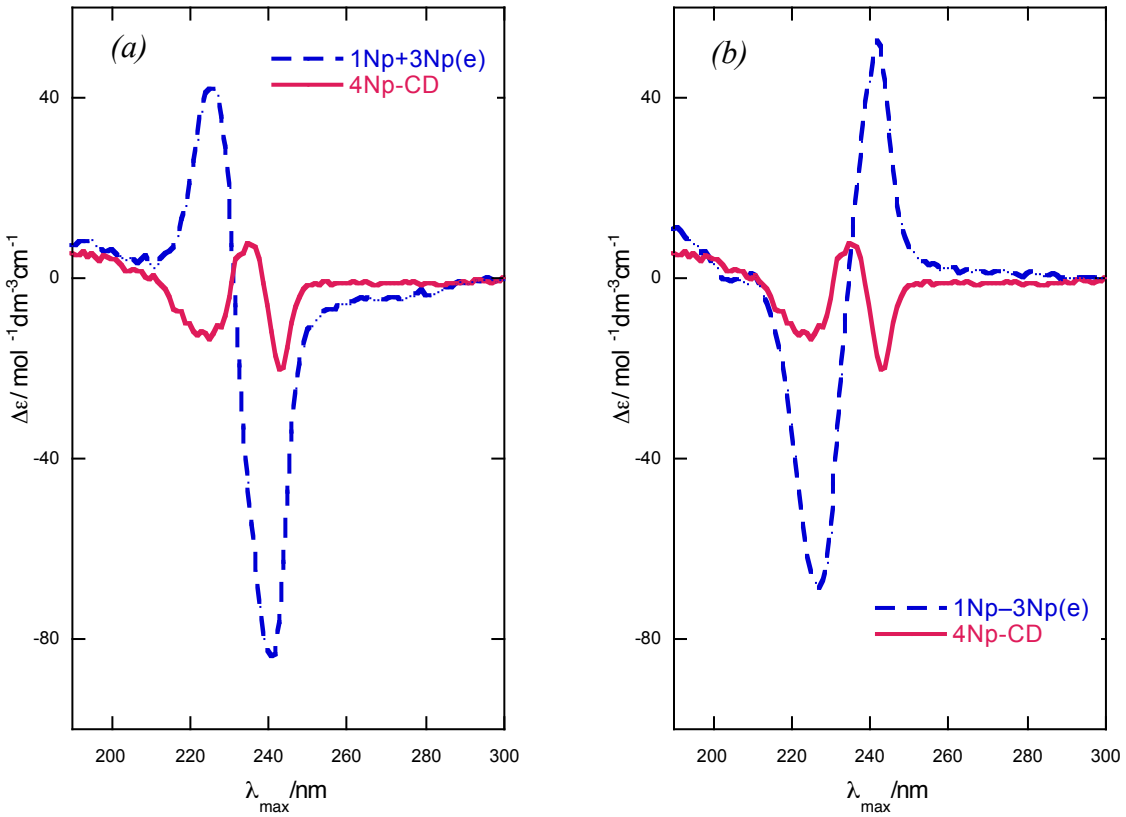
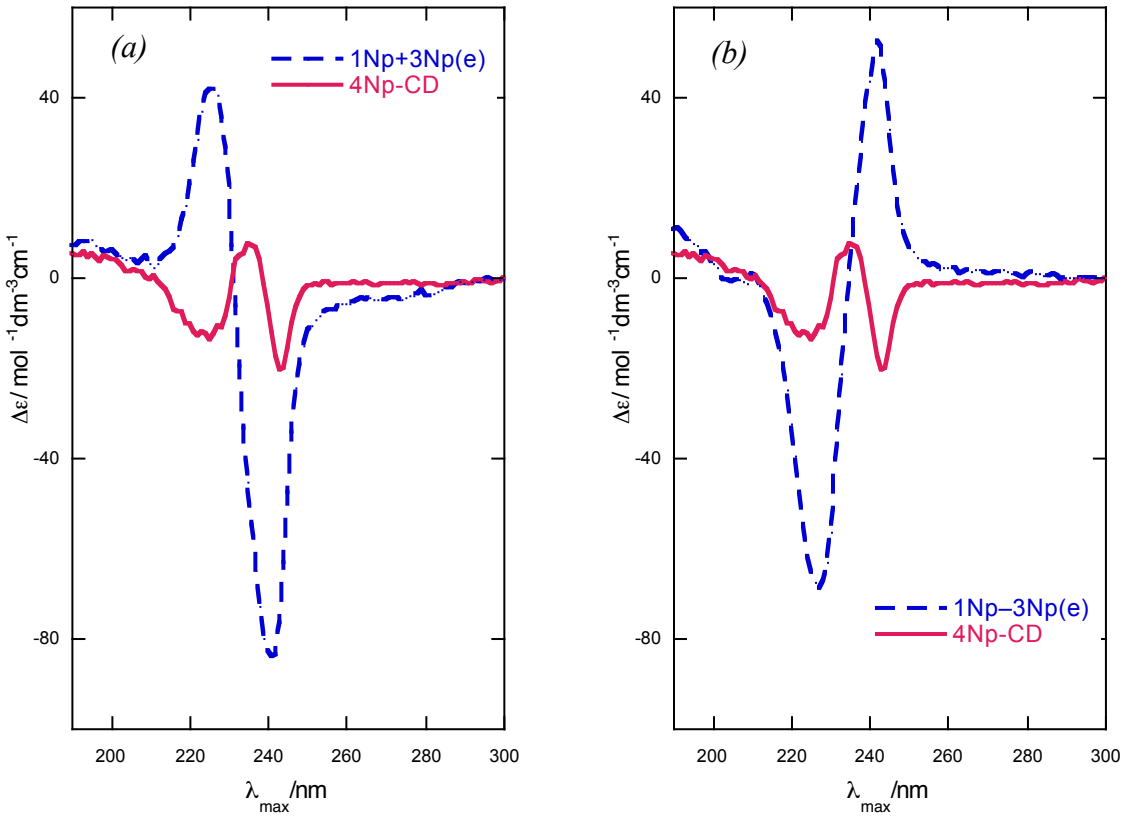


Figure S1. Measured CD spectra (CH_3CN, 24 ˚C) of *N*,*O*,*O*-tetranaphthoyl halisphingosine A (**5**, solid line) overlayed with hybrid spectra (dashed lines) generated from CD of **4** and *erythro*-**6b**. (a) CD = CD[**4**]+CD[**6b**]. (b) CD = CD[**4**]–CD[**6b**].

Table S1. Tabulated parameters [λ /nm (Δε /$mol^{-1}dm^3cm^{-1}$), and *A* values] for measured and hybrid CD spectra in **Fig. 4** and **Fig. S1**.[a]

CD /Hybrid CD	λ (Δε)	λ (Δε)	λ (Δε)	*A*
4[a]	190(+8)[b]	236(–21.9)	–	–
5[a]	224(–12.5)	235(+17.4)	243(–20.1)	32.5
6b[a]	226(+56)	242(+124)	–	124
7b[a]	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 (CH_3CN, 24 ˚C). *b*. truncated at end λ



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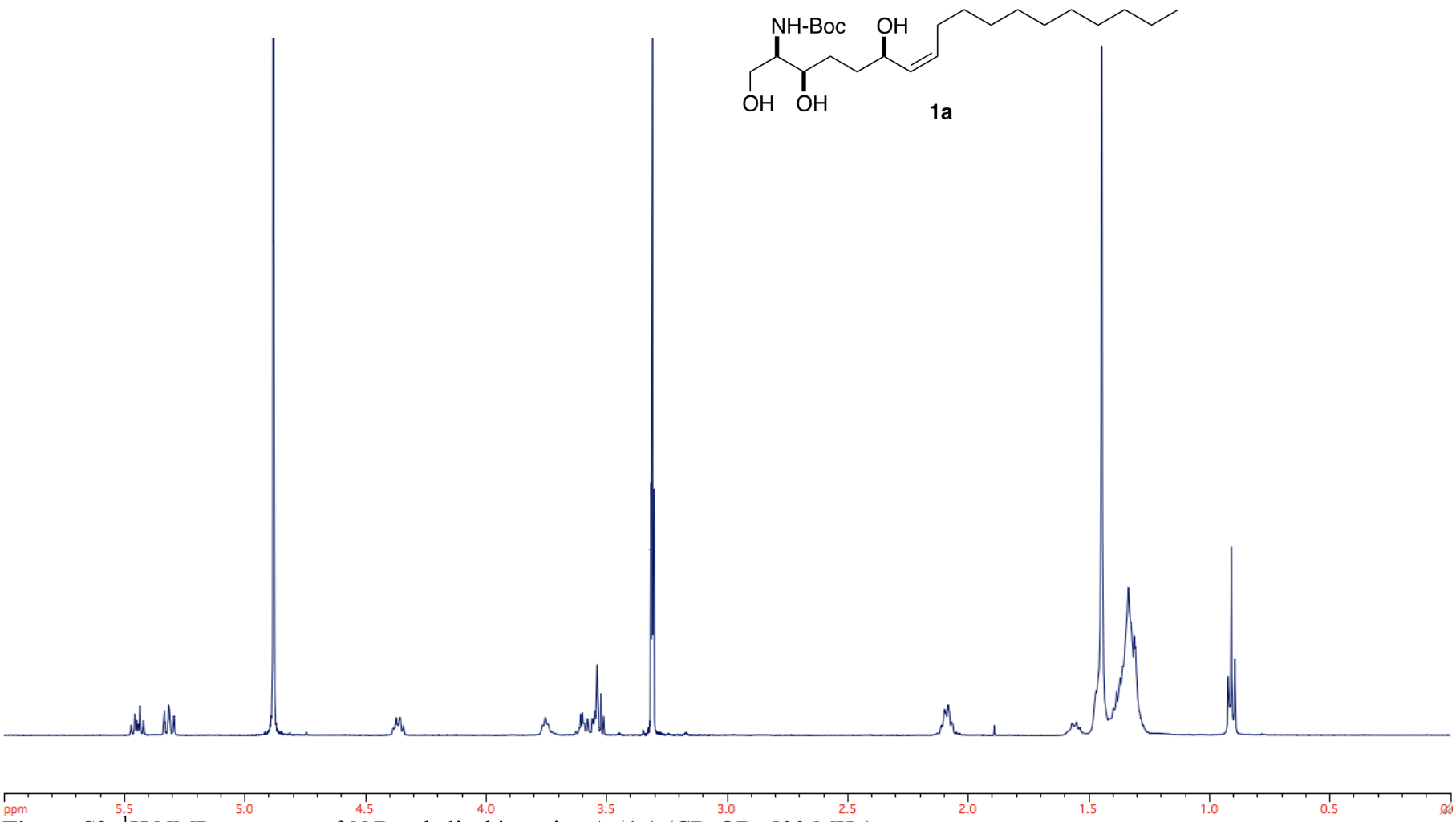


Figure S2. ^{1}H NMR spectrum of *N*-Boc-halisphingosine A (**1a**) (CD_3OD, 500 MHz).

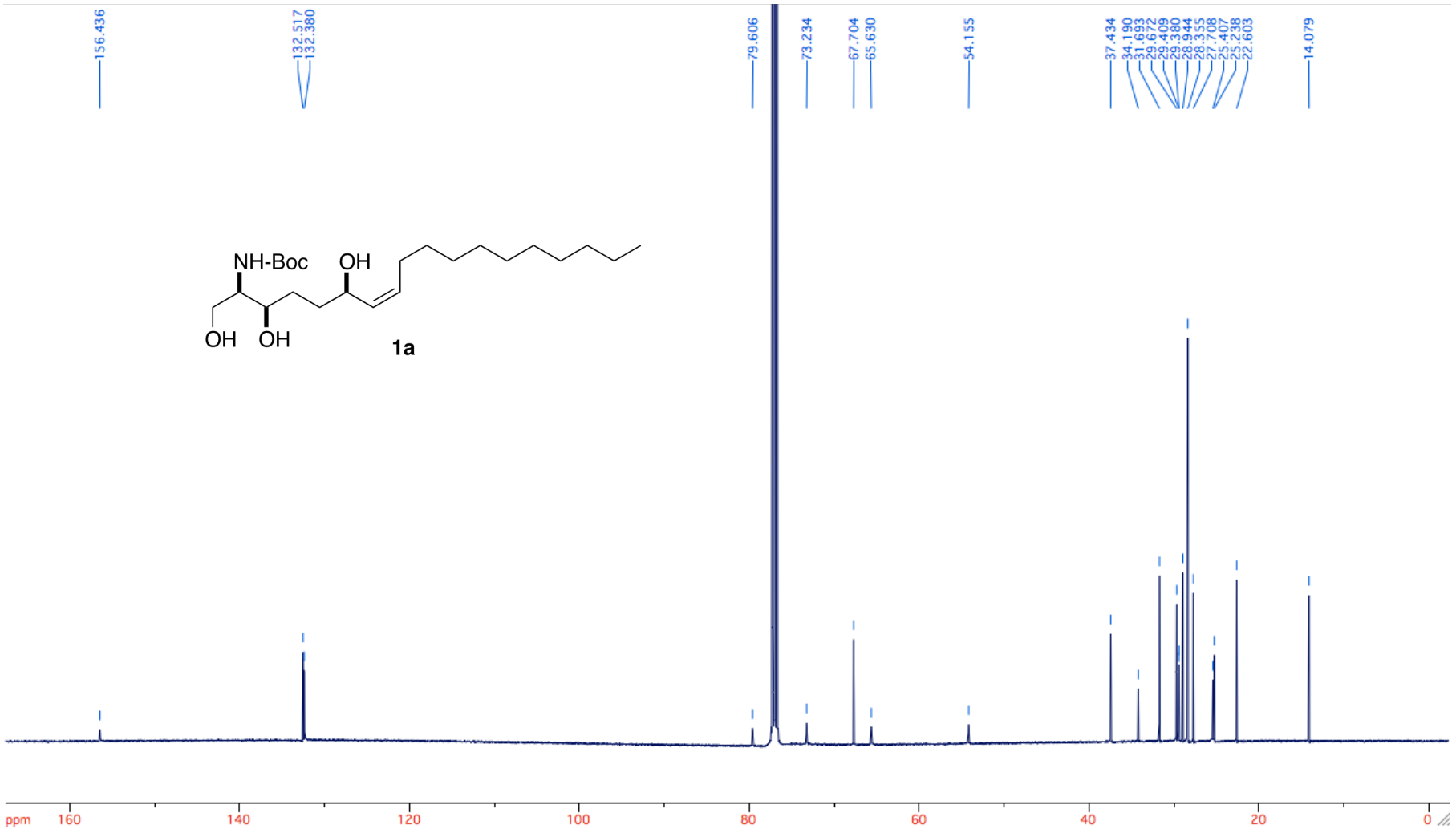


Figure S3. ^{13}C NMR spectrum of *N*-Boc-halisphingosine A (**1a**) ($CDCl_3$, 125 MHz).

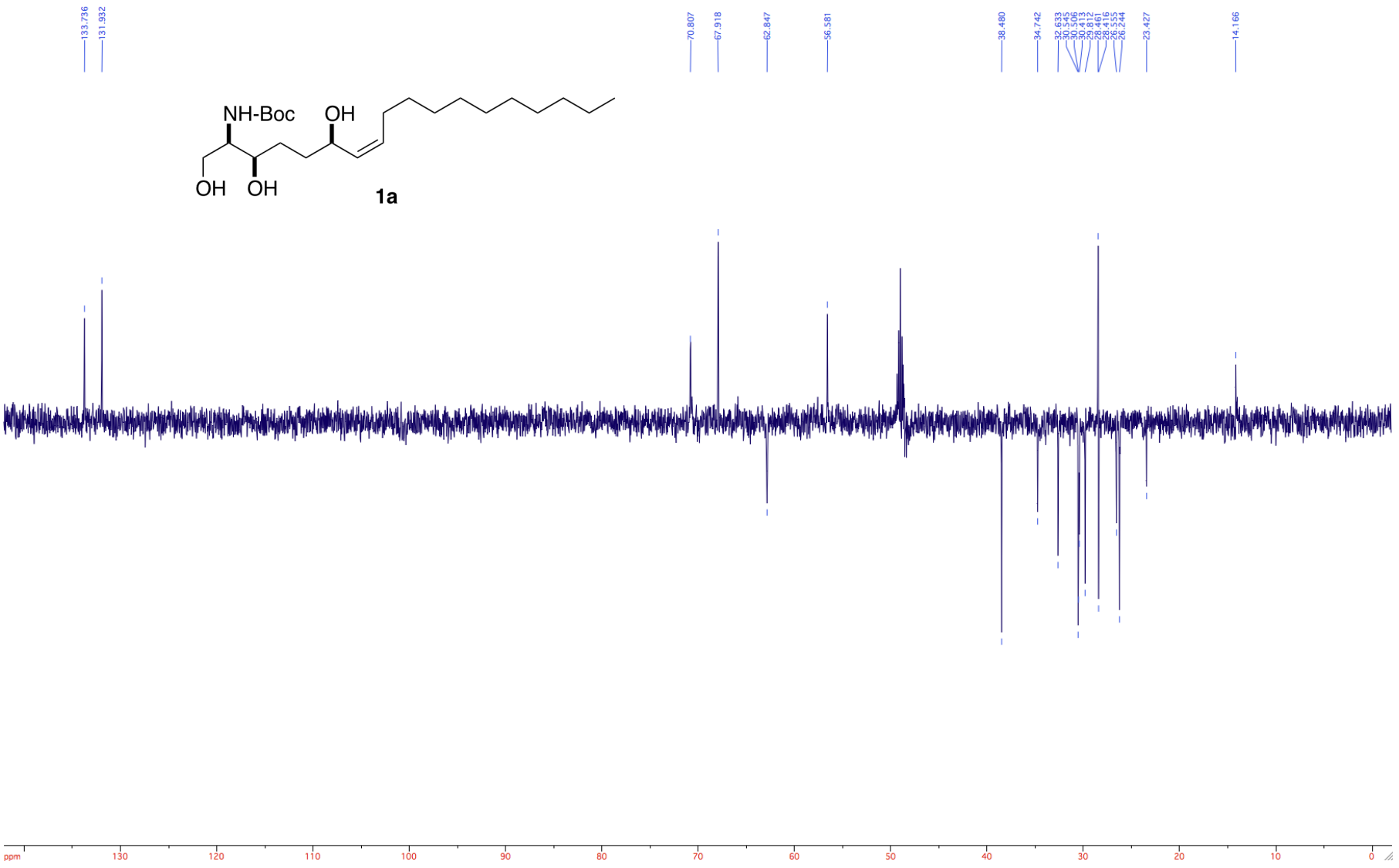
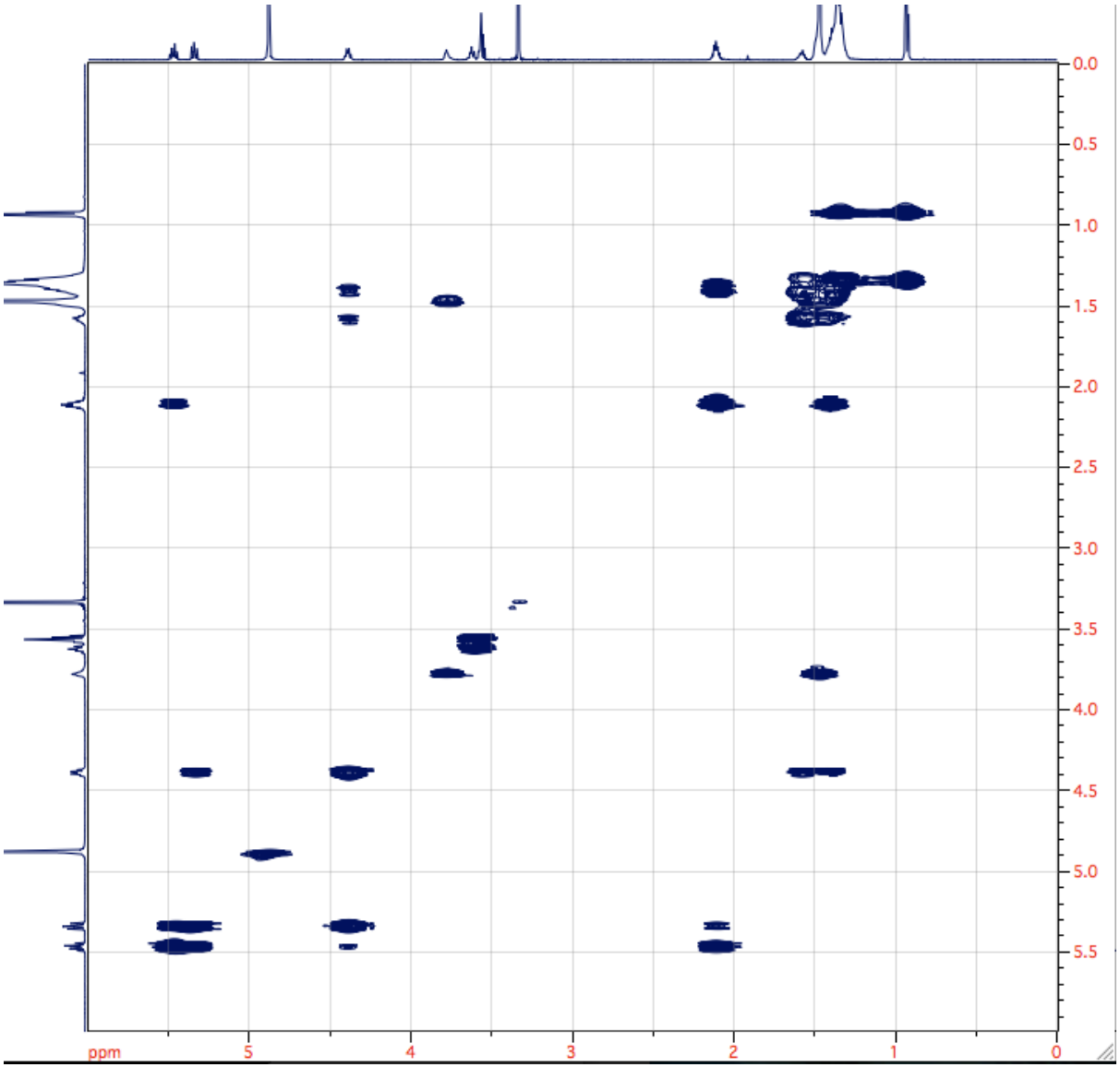
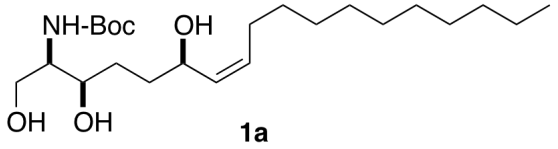


Figure S4. DEPT135 NMR spectrum of *N*-Boc-halisphingosine A (**1a**) (CD_3OD, 125 MHz).





1a

Figure S5. ^{1}H–^{1}H COSY spectrum of *N*-Boc-halisphingosine A (**1a**) (CD_3OD, 600 MHz).

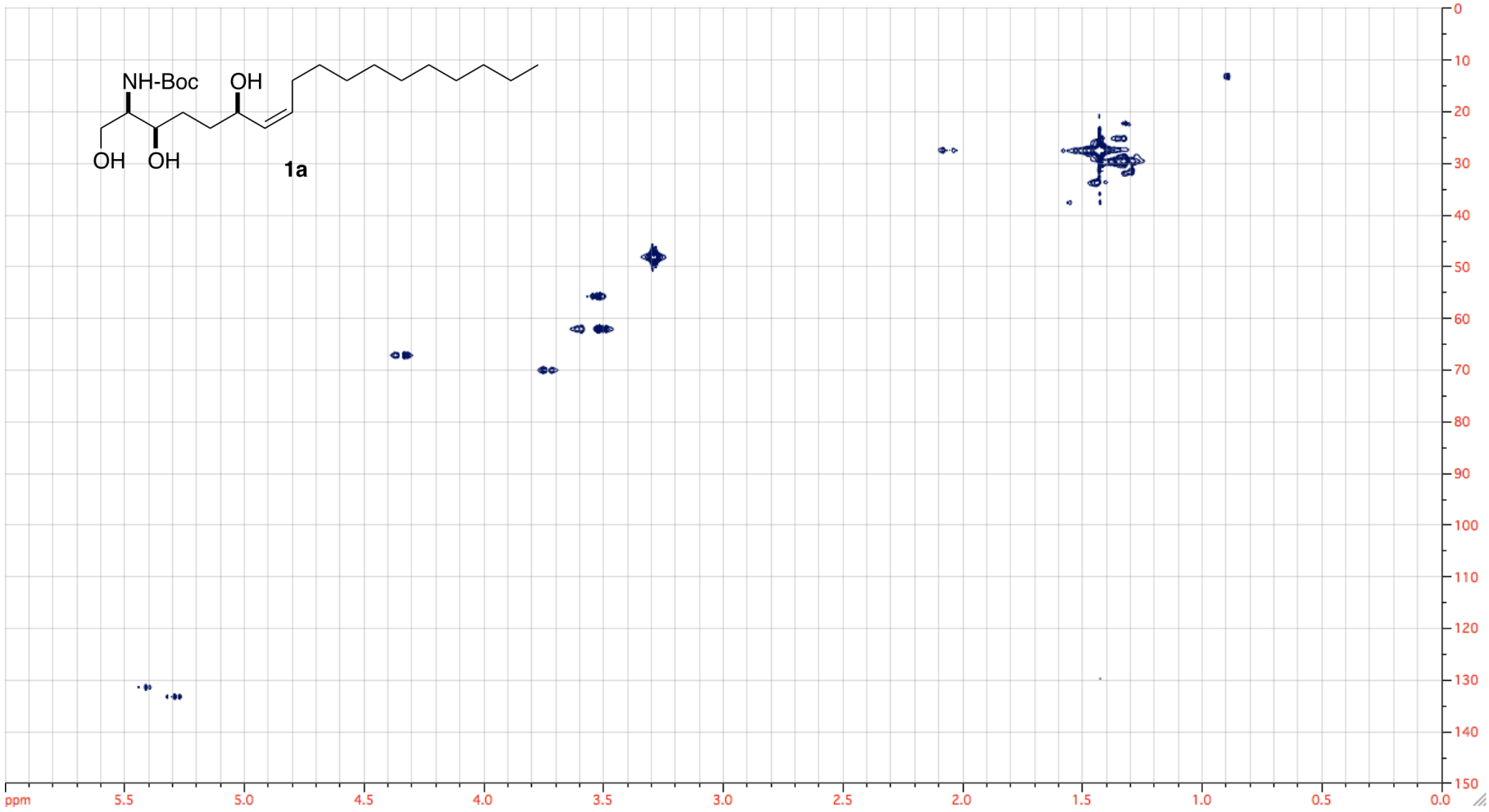


Figure S6. ^{1}H–^{13}C HSQC spectrum of *N*-Boc-halisphingosine A (**1a**) (CD_3OD, 500 MHz).

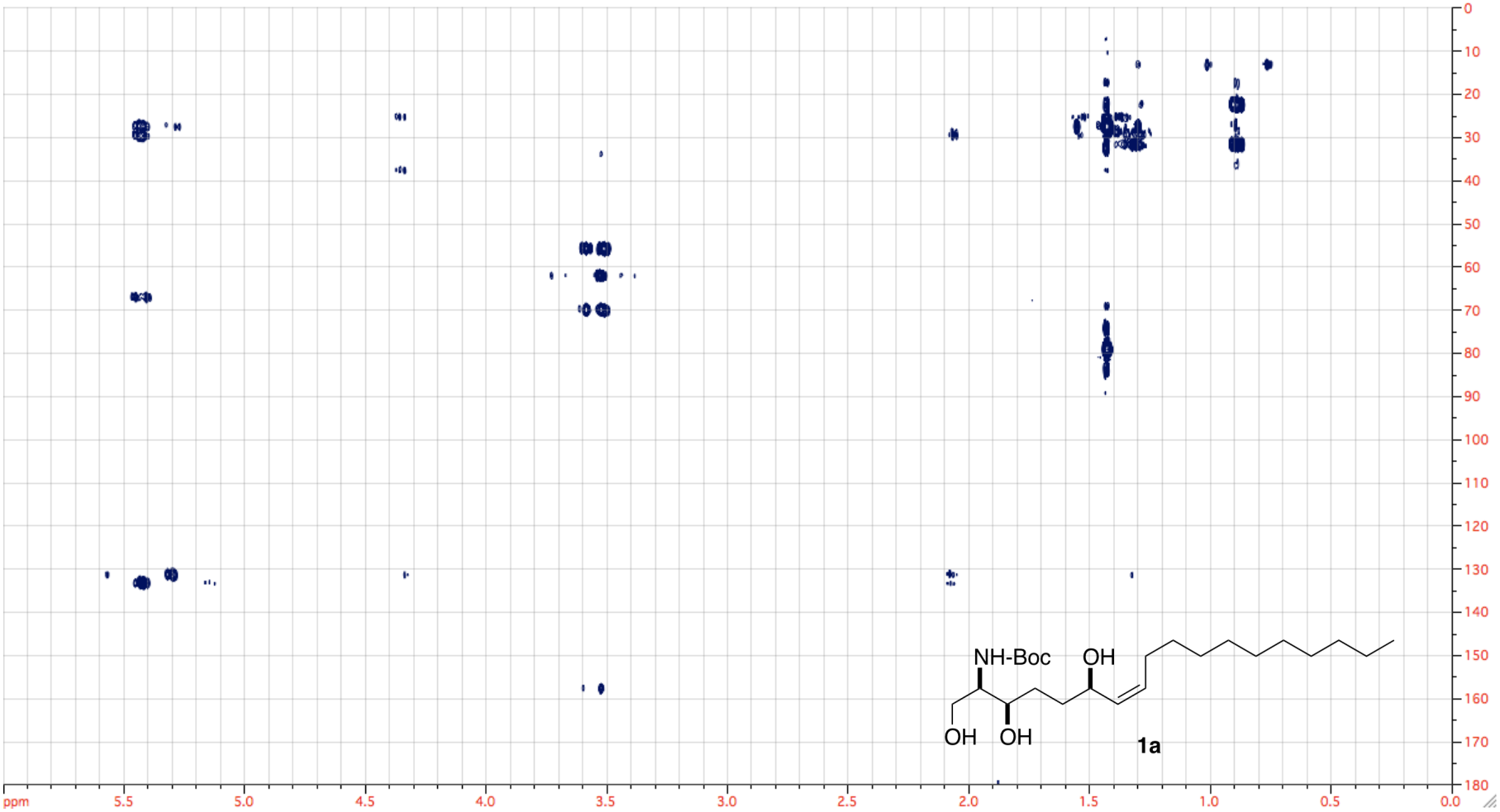


Figure S7. ^{1}H–^{13}C HMBC spectrum of *N*-Boc-halisphingosine A (**1a**) (CD_3OD, 500 MHz).

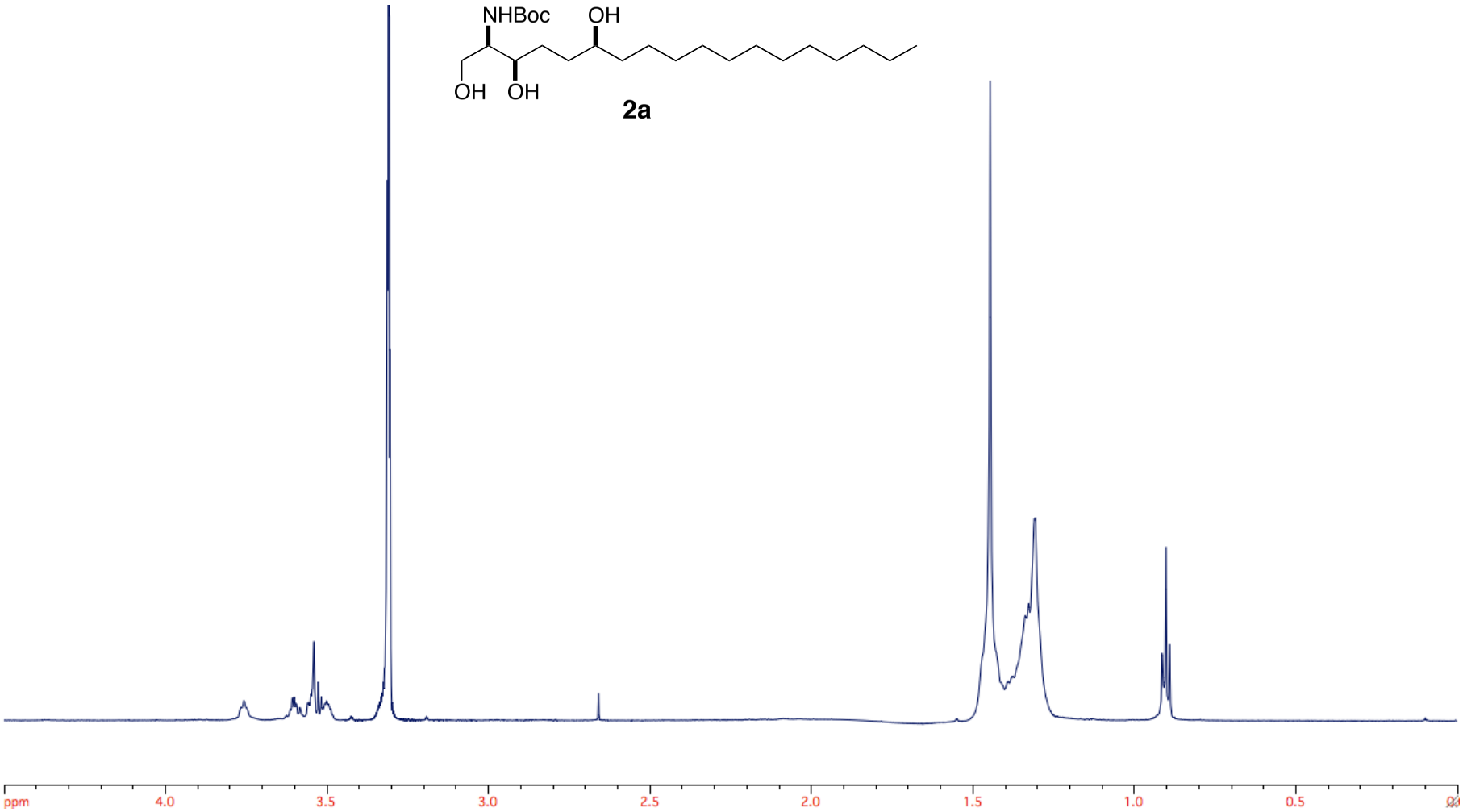
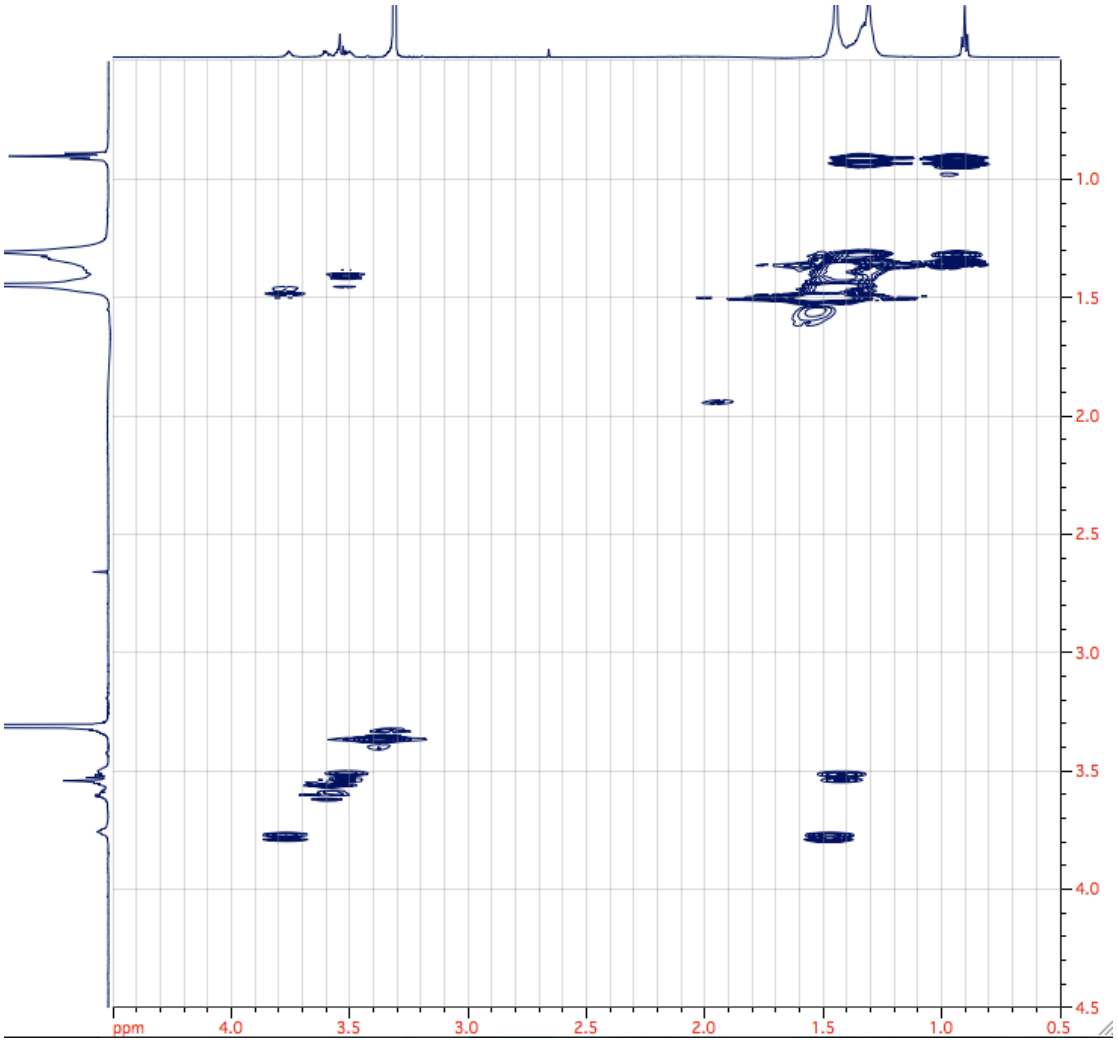
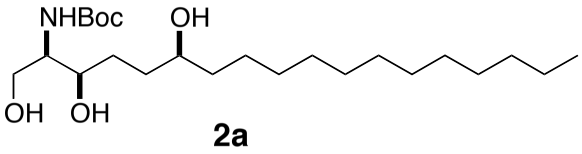


Figure S8. ^{1}H NMR spectrum of *N*-Boc-halisphingosine B (**2a**) (CD_3OD, 600 MHz).





2a

Figure S9. ^{1}H–^{1}H COSY spectrum of *N*-Boc-halisphingosine B (**2a**) (CD_3OD, 600 MHz).

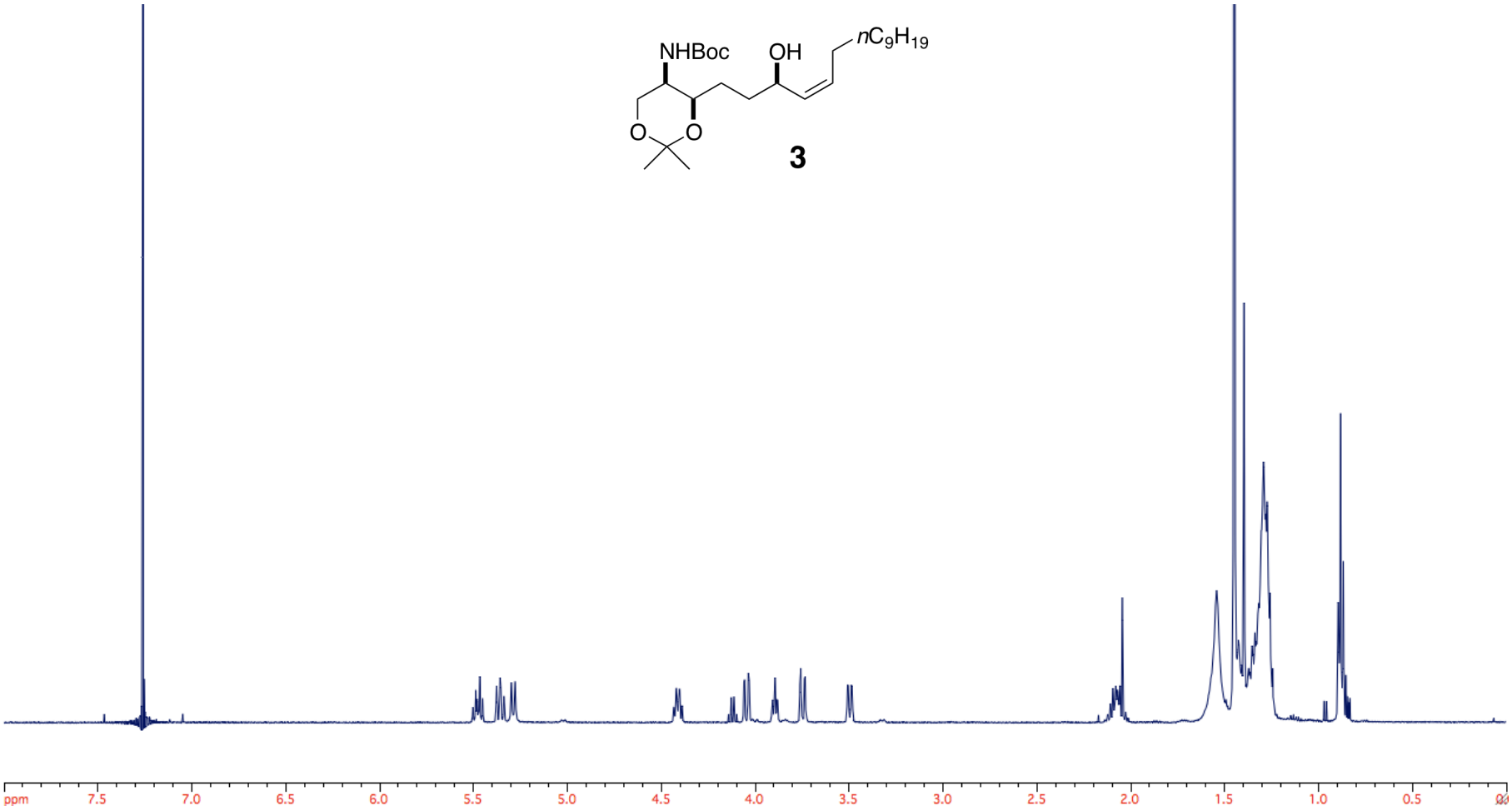


Figure S10. ^{1}H NMR spectrum of *N*-Boc-halisphingosine A acetonide (**3**) ($CDCl_3$, 500 MHz).

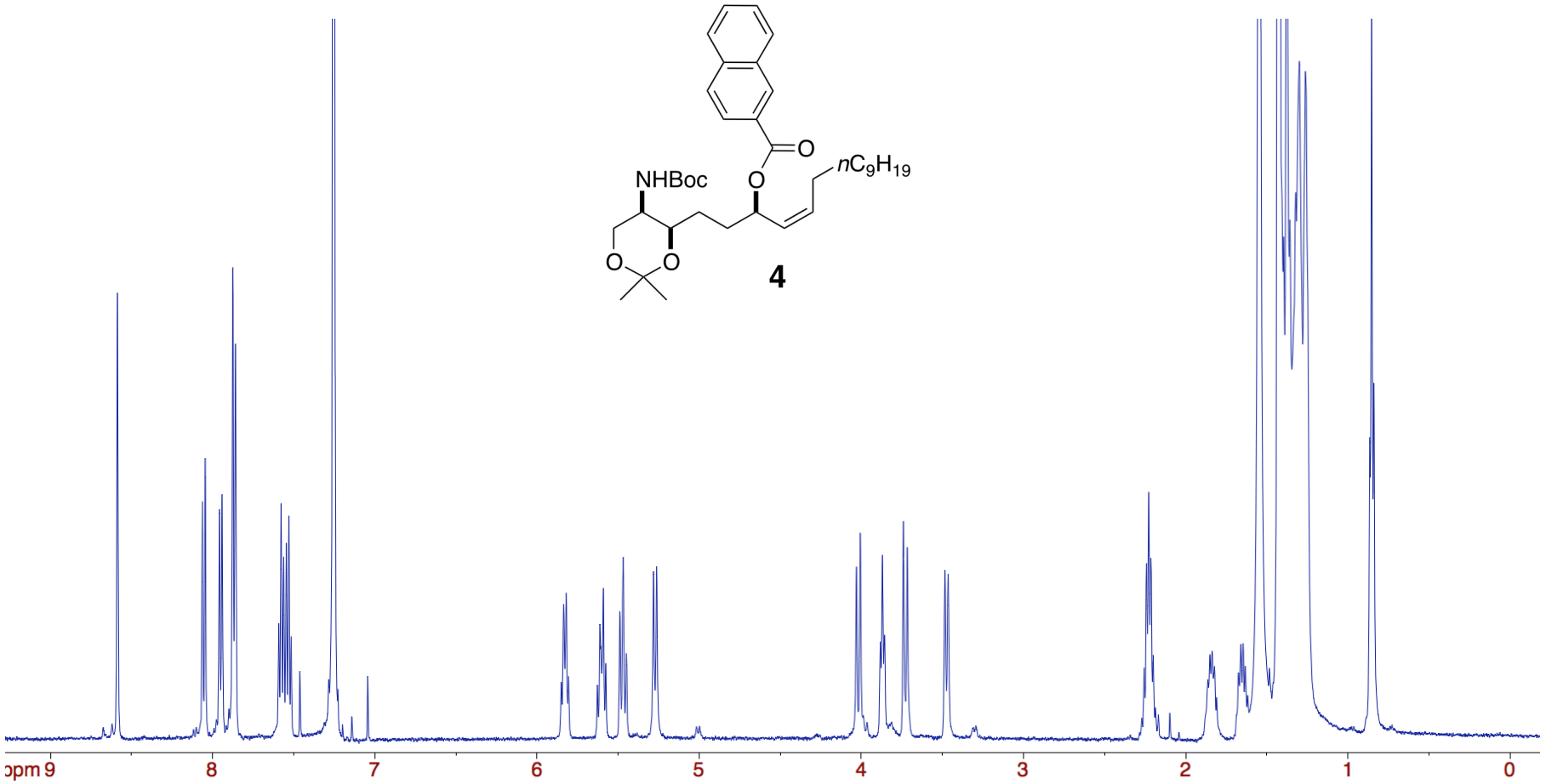


Figure S11. ^{1}H NMR spectrum of *mono*-naphthoate (**4**) ($CDCl_3$, 500 MHz).

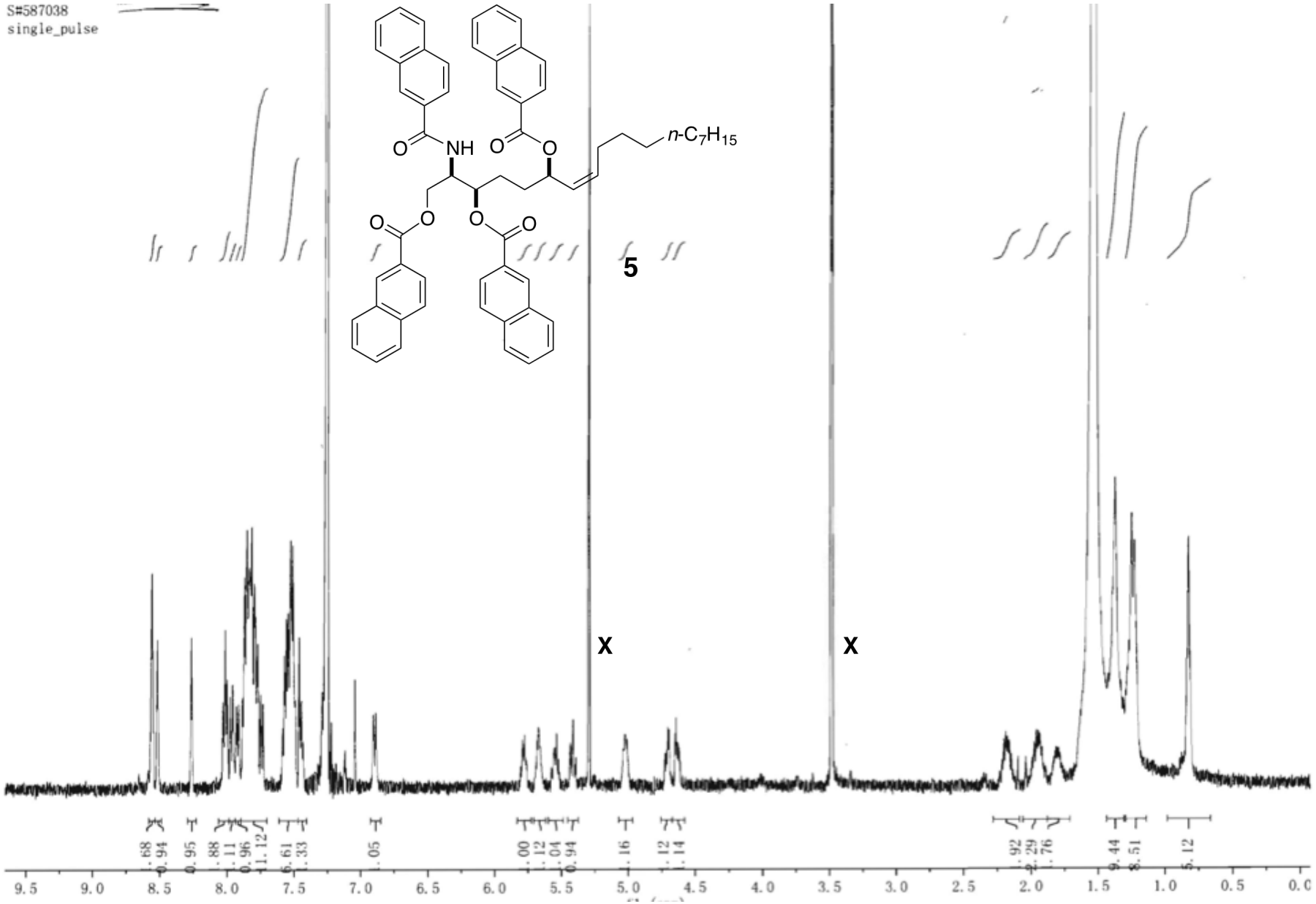


Figure S12. ^{1}H NMR spectrum of tetranaphthoyl-halisphingosine (**5**) ($CDCl_3$, 500 MHz).

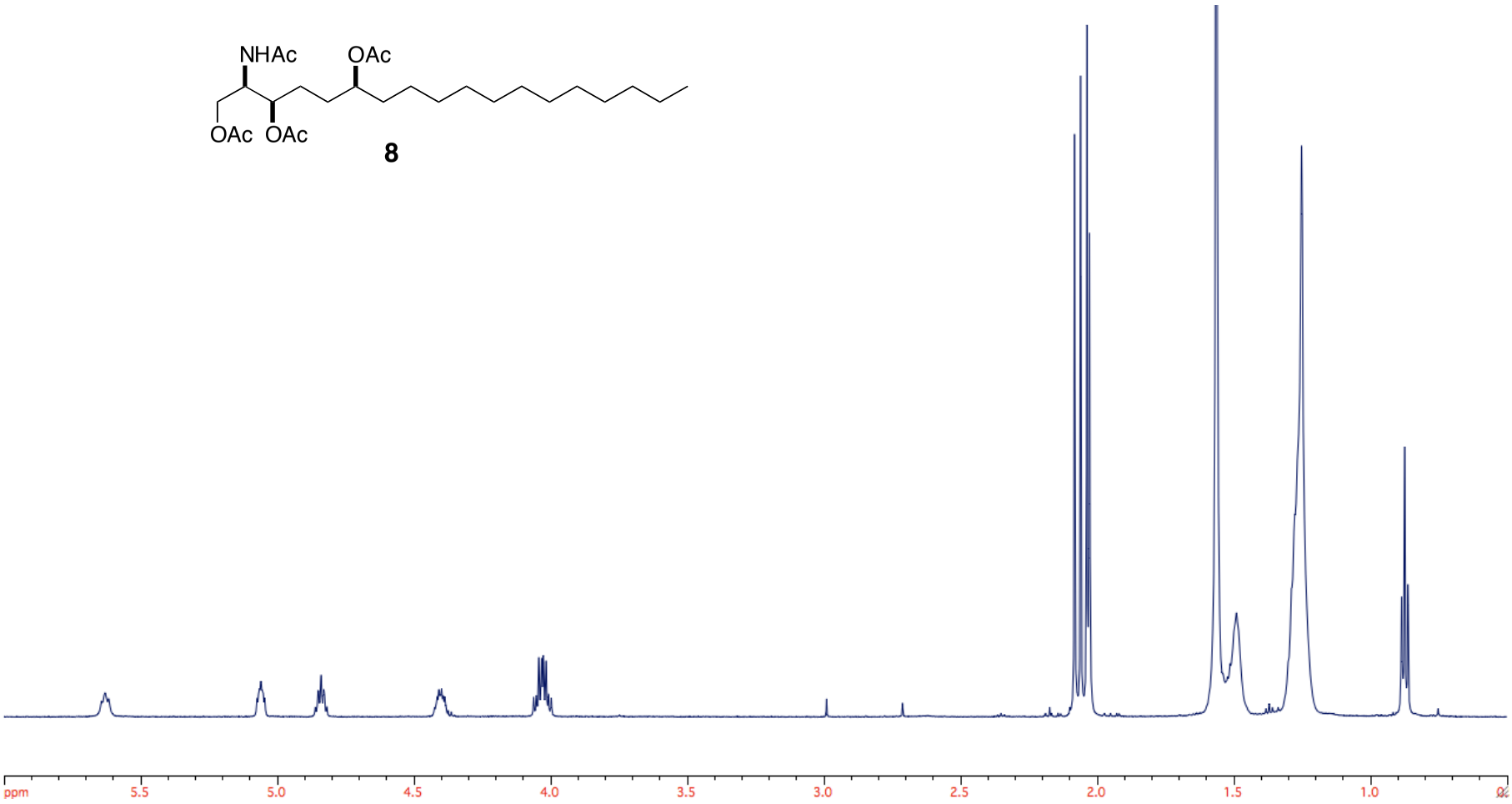


Figure S13. ^{1}H NMR spectrum of per-acetyl-halisphingosine B (**8**) ($CDCl_3$, 600 MHz).

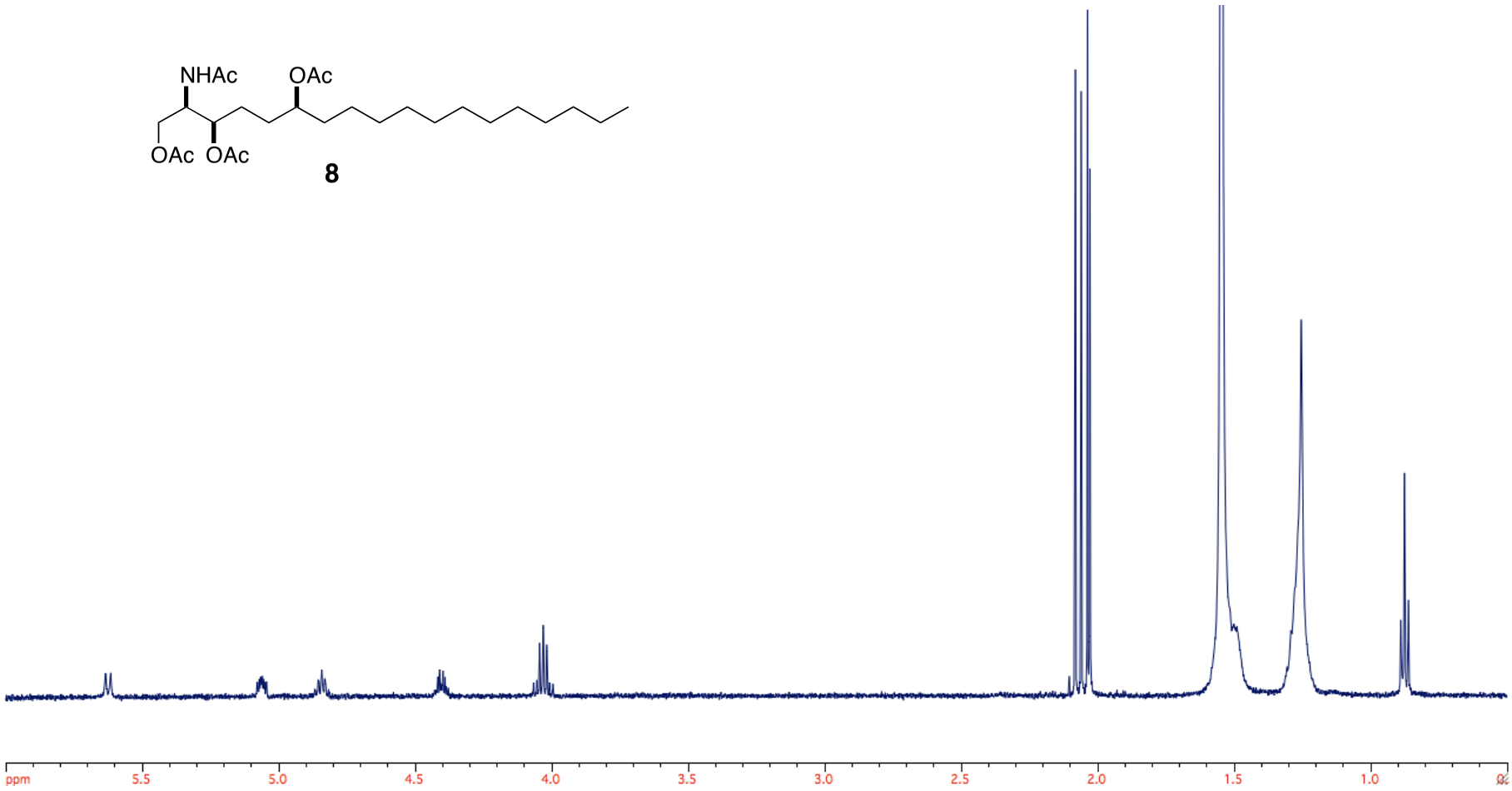
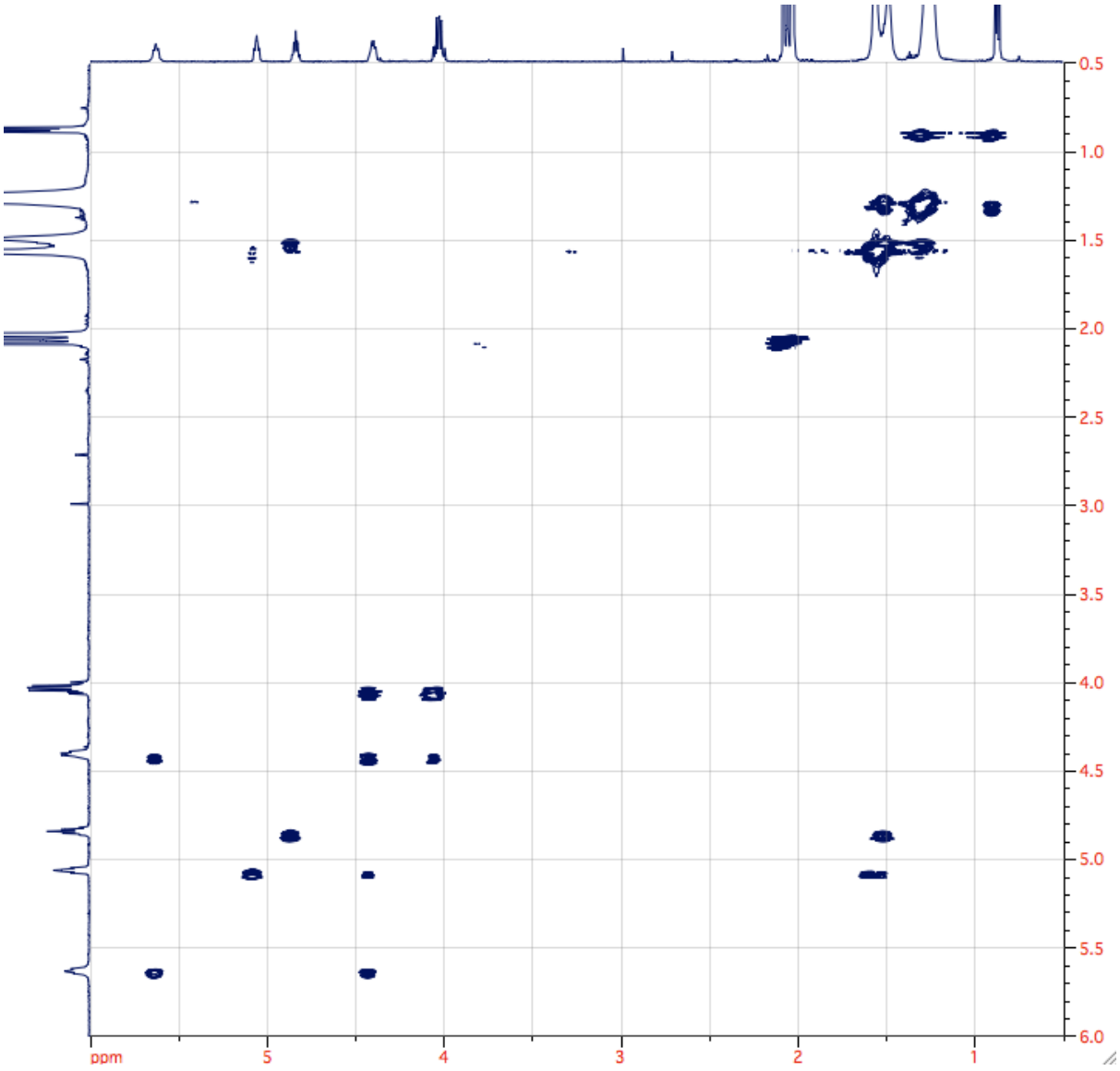


Figure S14. ^{1}H NMR spectrum of 7,8-dihydro-per-acetyl-halisphingosine A (**8**) ($CDCl_3$, 500 MHz).



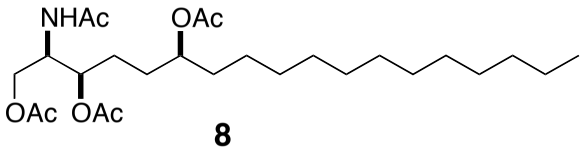


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Figure S15. ^{1}H–^{1}H COSY spectrum of per-acetyl-halisphingosine B (**8**) ($CDCl_3$, 600 MHz).

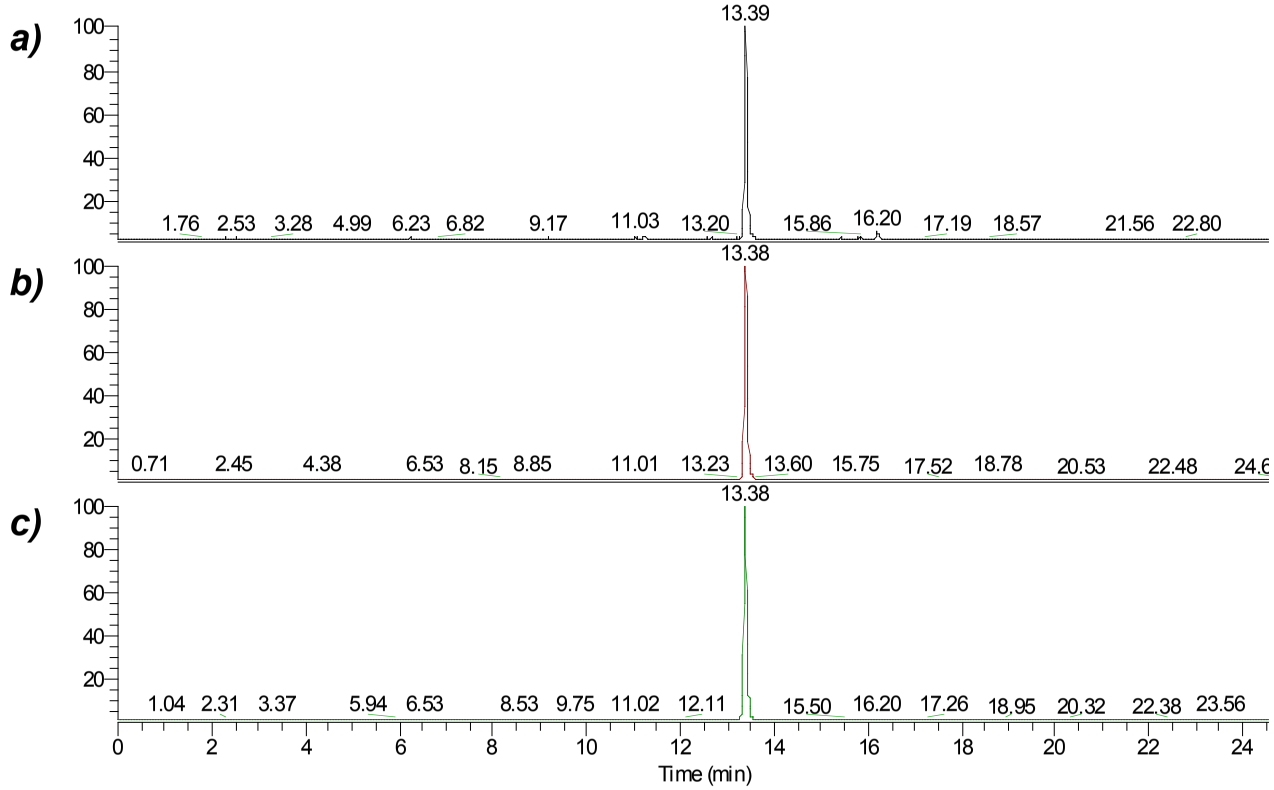

Figure S16. LCMS total ion count (TIC) for ***a)*** 7,8-dihydro-per-acetyl-halisphingosine A (**8**), ***b)*** per-acetyl-halisphingosine B (**8**), and ***c)*** co-injection. LCMS conditions: Phenomenex Kinetex C_{18} column (4.6 x 150 mm, 2.6 µm); linear gradient 60% CH_3CN to 100% CH_3CN, 0.1% formic acid, over 15 minutes, 0.7 $mLmin^{-1}$, APCI probe.