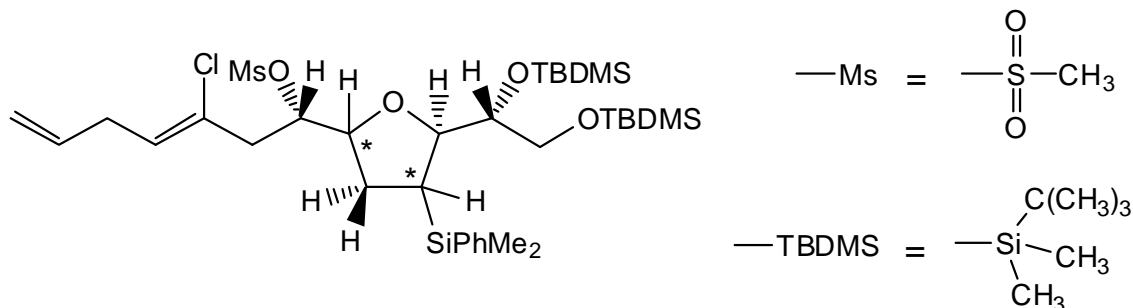


Problem Set 3
Multi-Pulse NMR
Due: Wednesday, October 10

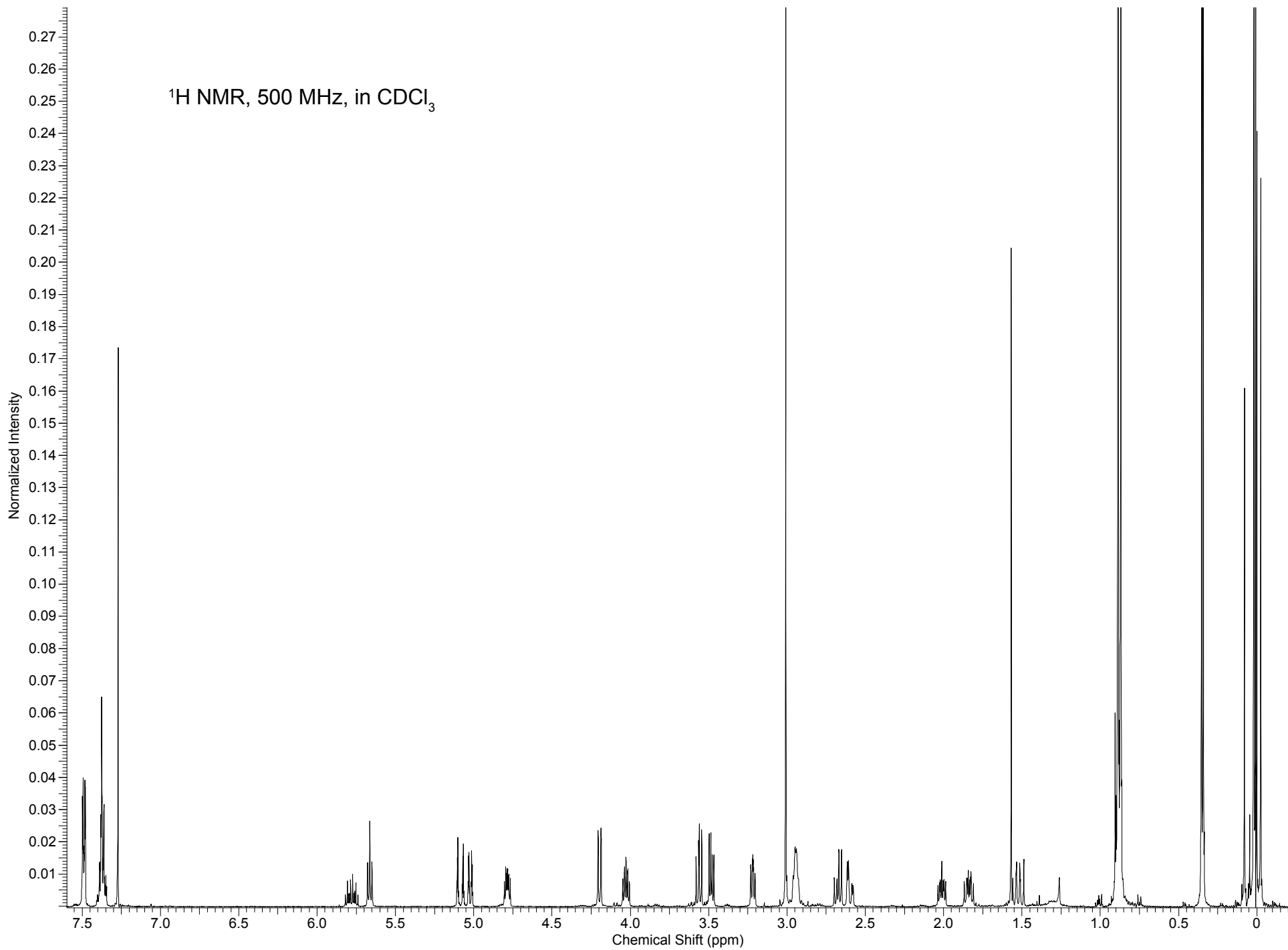
1. Individual nuclear Overhauser effect (NOE) experiments were performed to help assign relative stereochemistry to the molecule below:



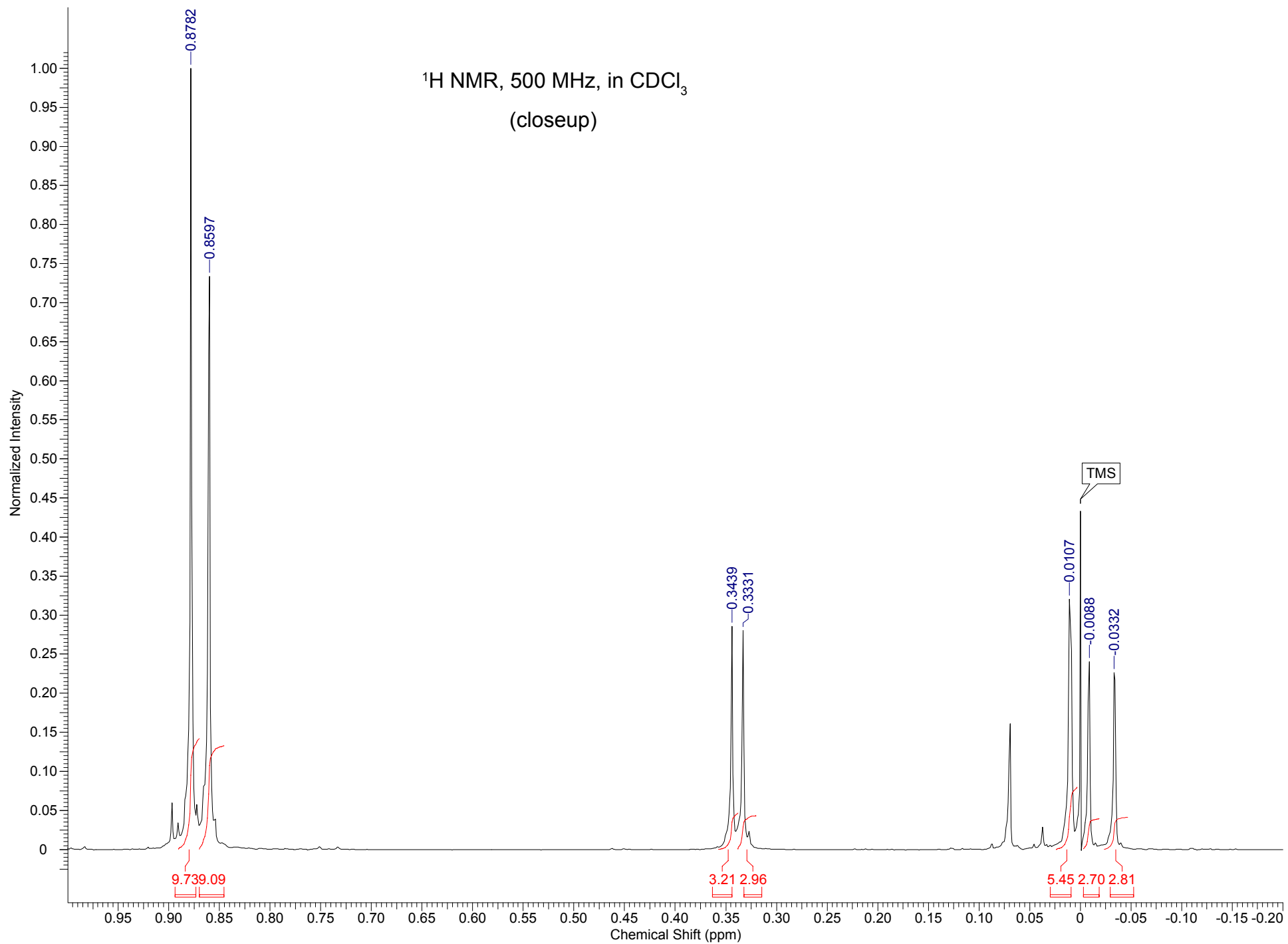
The asterisks denote chiral centers with unknown stereochemistry. Using the ^1H NMR spectrum (500 MHz, in CDCl_3) and 1D NOE spectra (irradiated at 4.20, 4.03, and 1.83 ppm) on the following pages, assign stereochemistry at these two positions.

Hints:

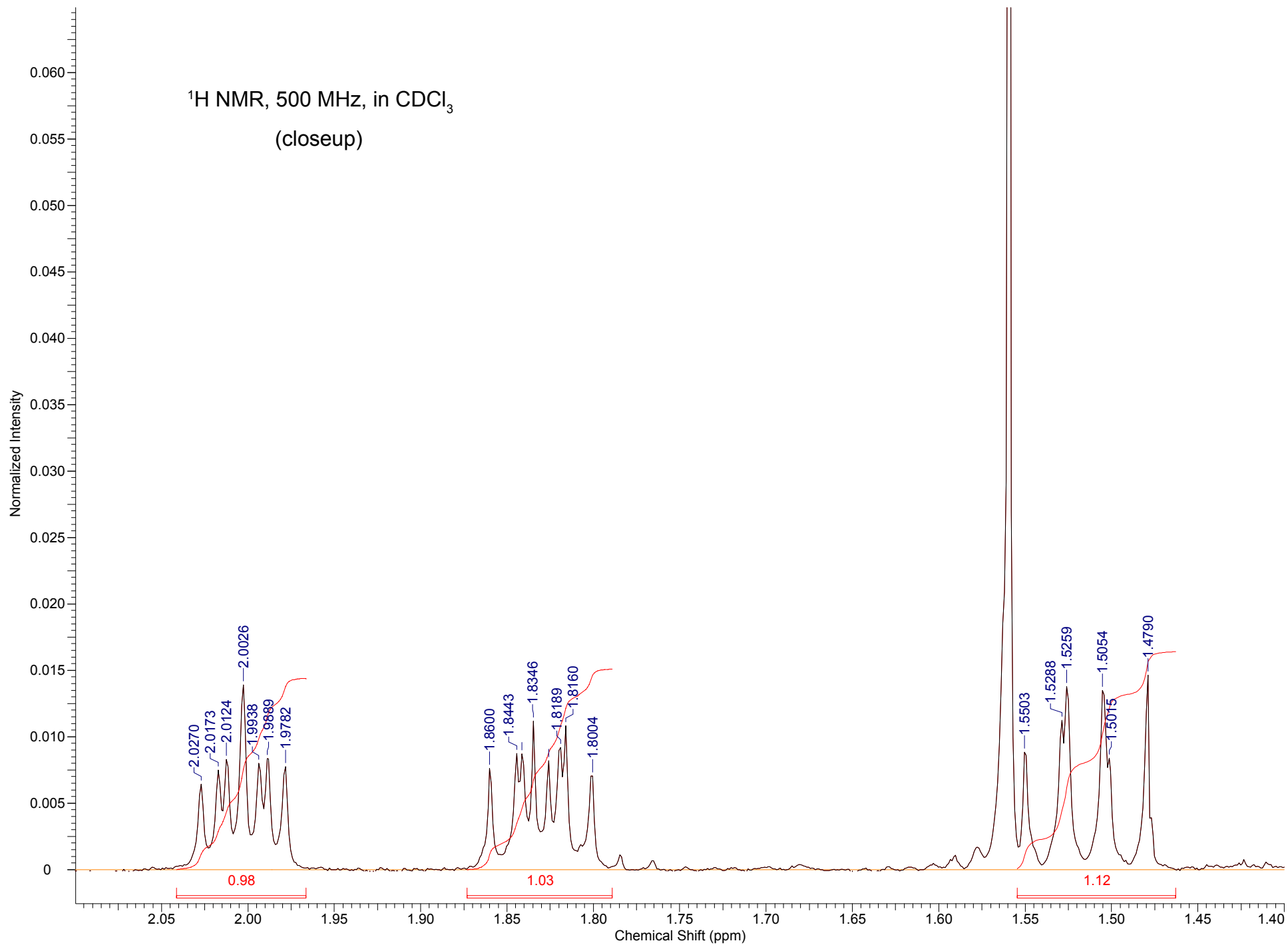
- You will need to assign most of the ^1H spectrum before interpreting the NOE spectra. It will probably be easiest to start with the three protons α to the OTBDMS groups; these appear in the $\delta = 3.2\text{--}3.6$ ppm region of the spectrum.
- Silicon is a very electropositive atom, and typically shifts nearby protons upfield. But the ---SiPhMe_2 group doesn't seem to have that much of an effect on its neighbors.
- I think the peak at $\delta = 1.56$ ppm is dissolved H_2O .

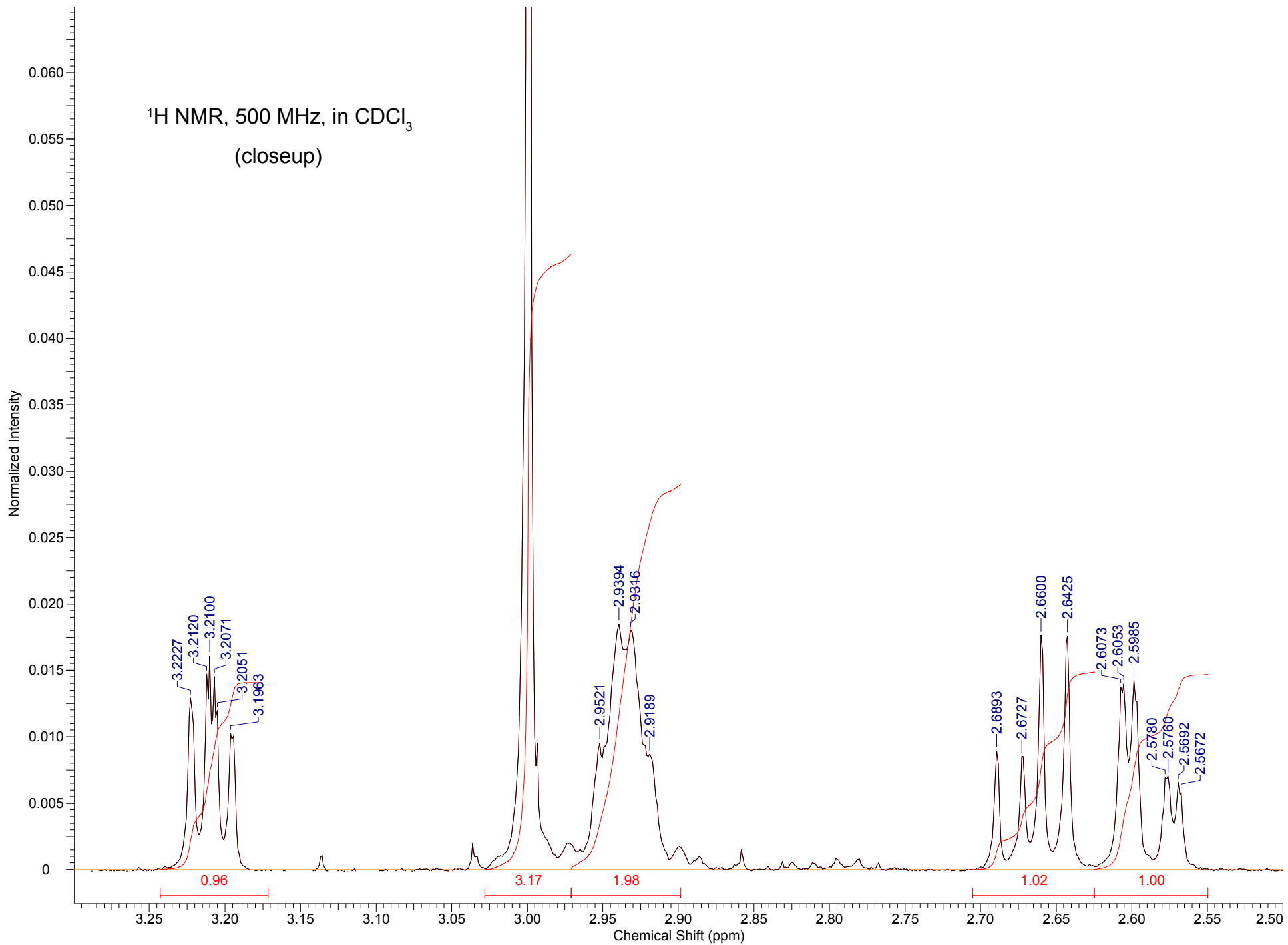


¹H NMR, 500 MHz, in CDCl₃
(closeup)

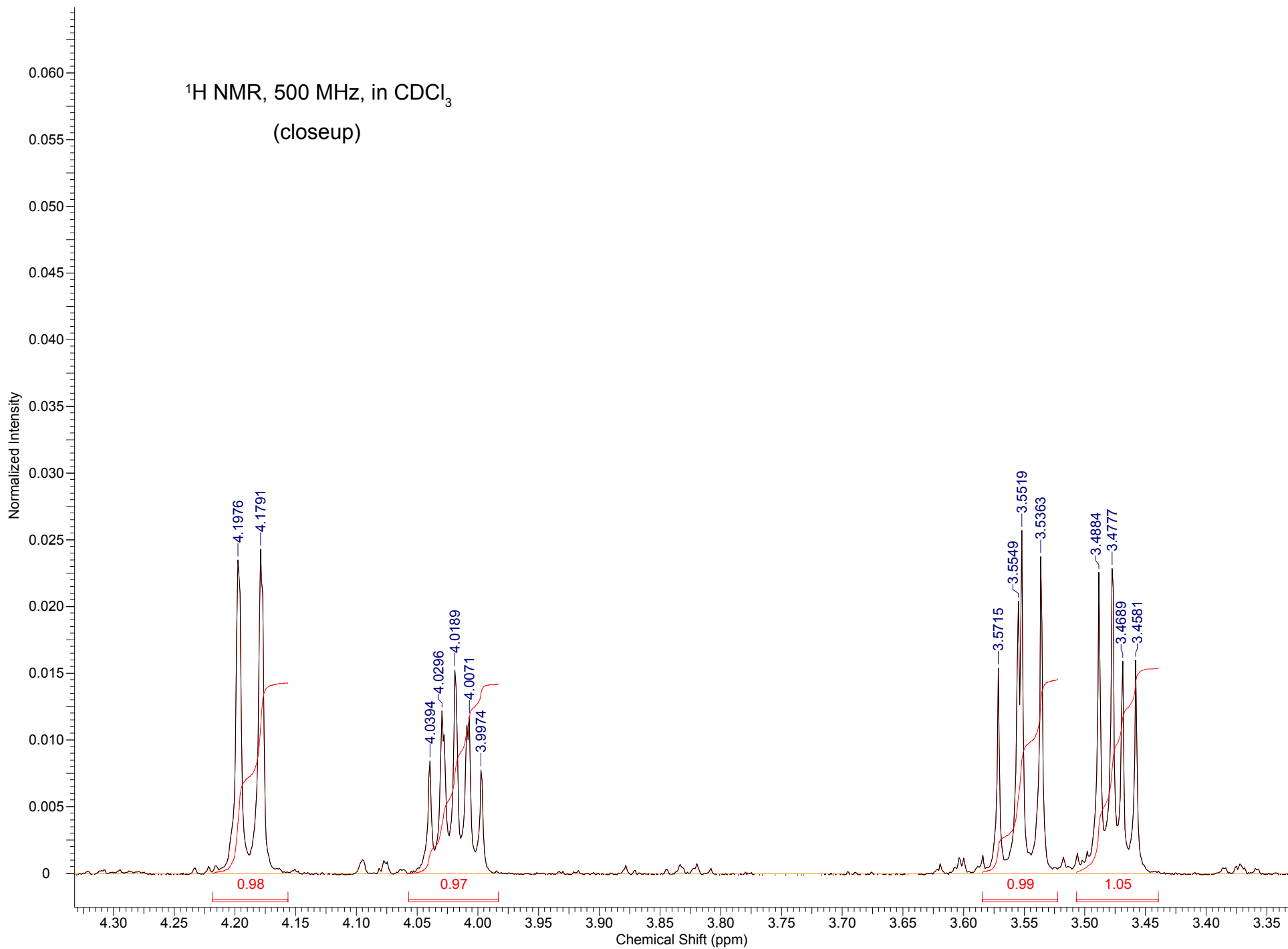


^1H NMR, 500 MHz, in CDCl_3
(closeup)

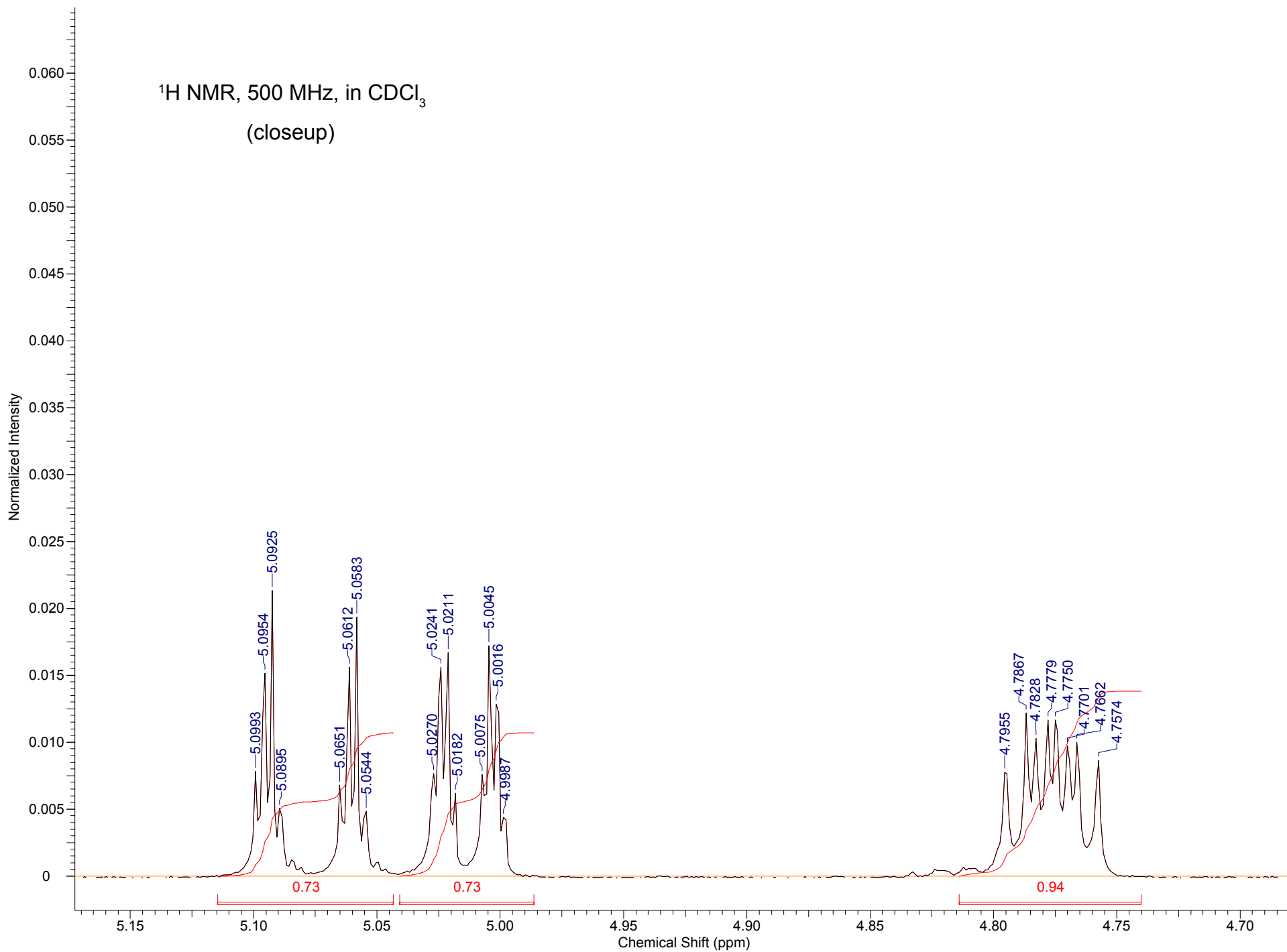




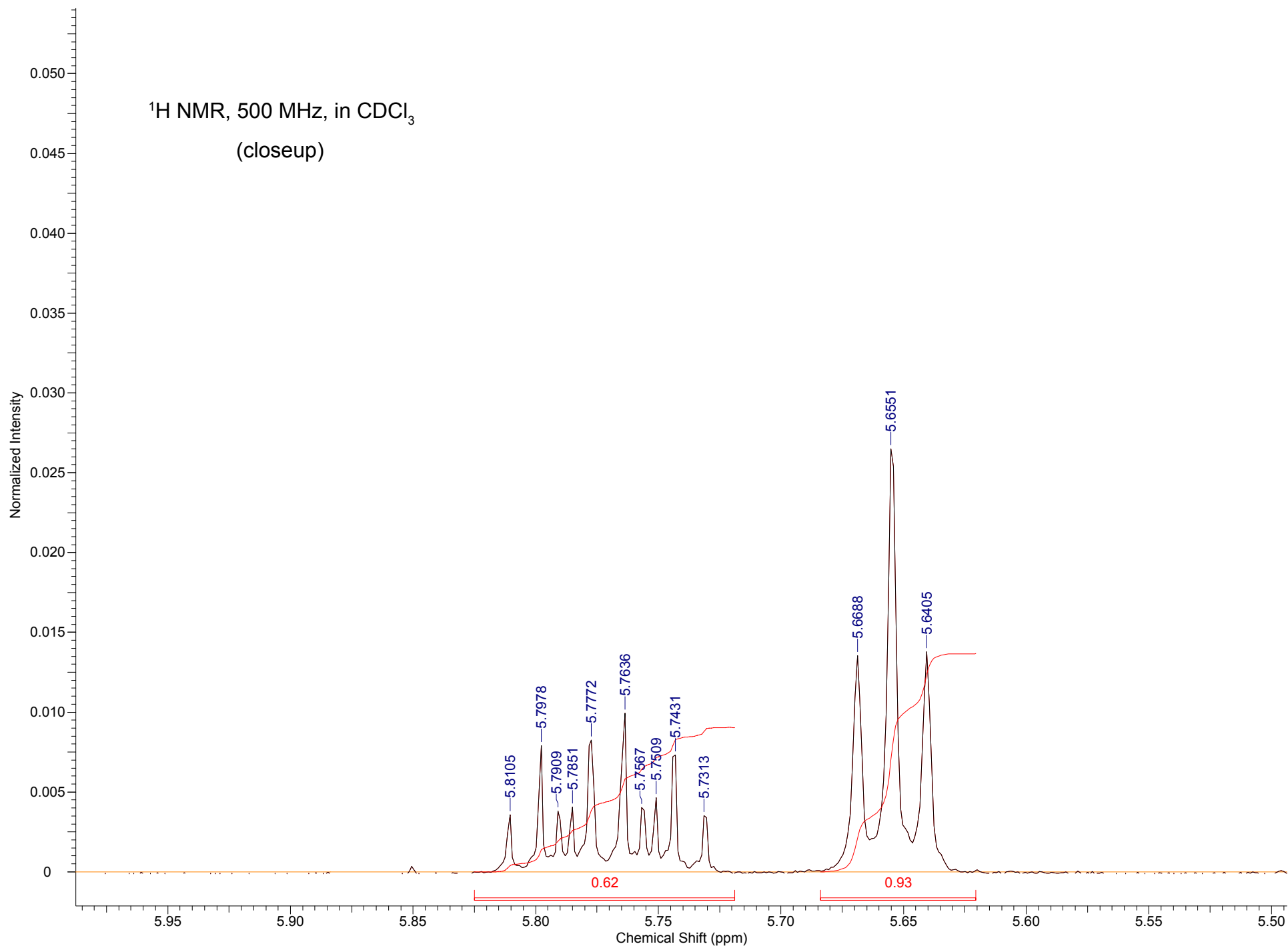
^1H NMR, 500 MHz, in CDCl_3
(closeup)

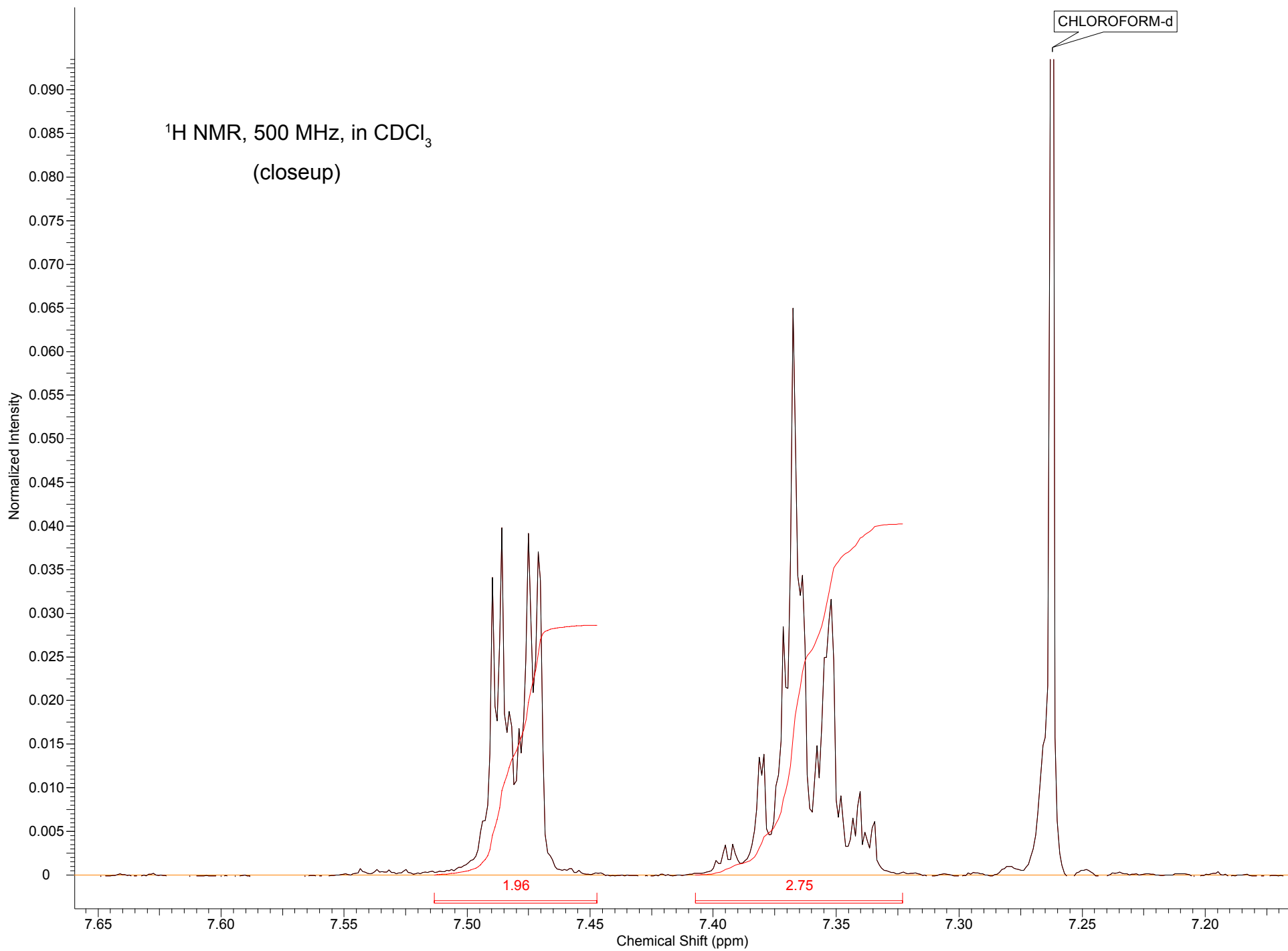


^1H NMR, 500 MHz, in CDCl_3
(closeup)

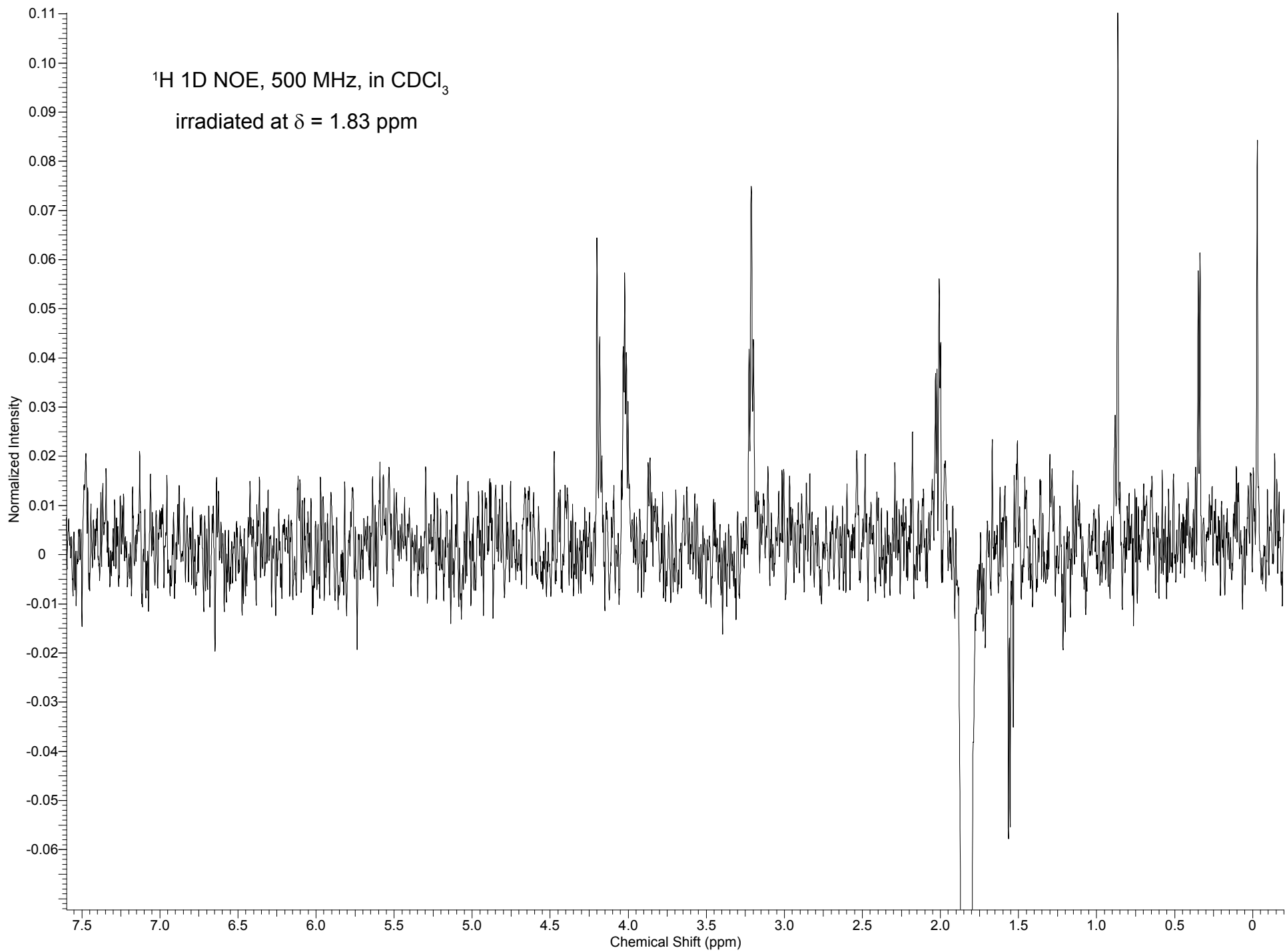


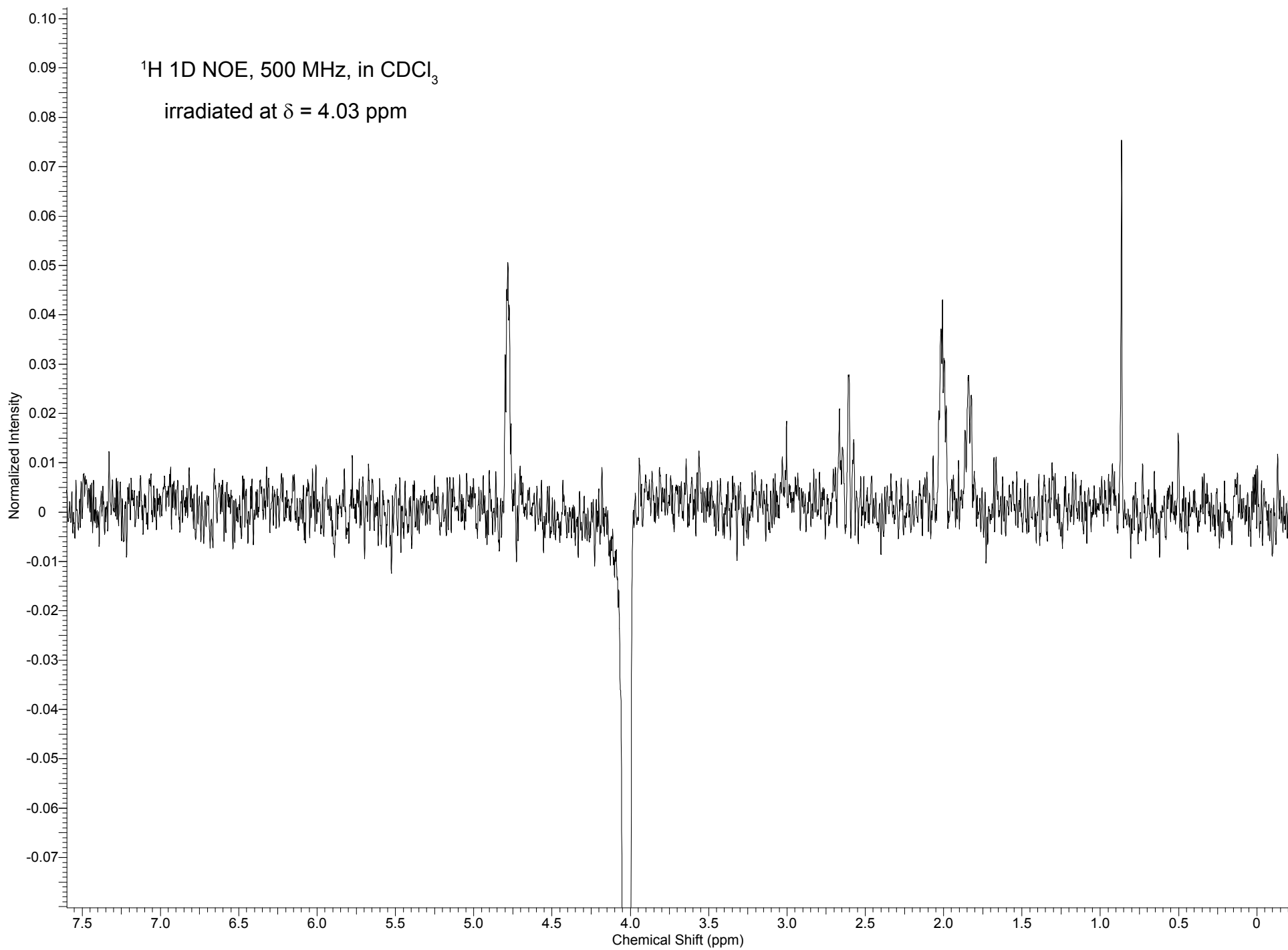
^1H NMR, 500 MHz, in CDCl_3
(closeup)

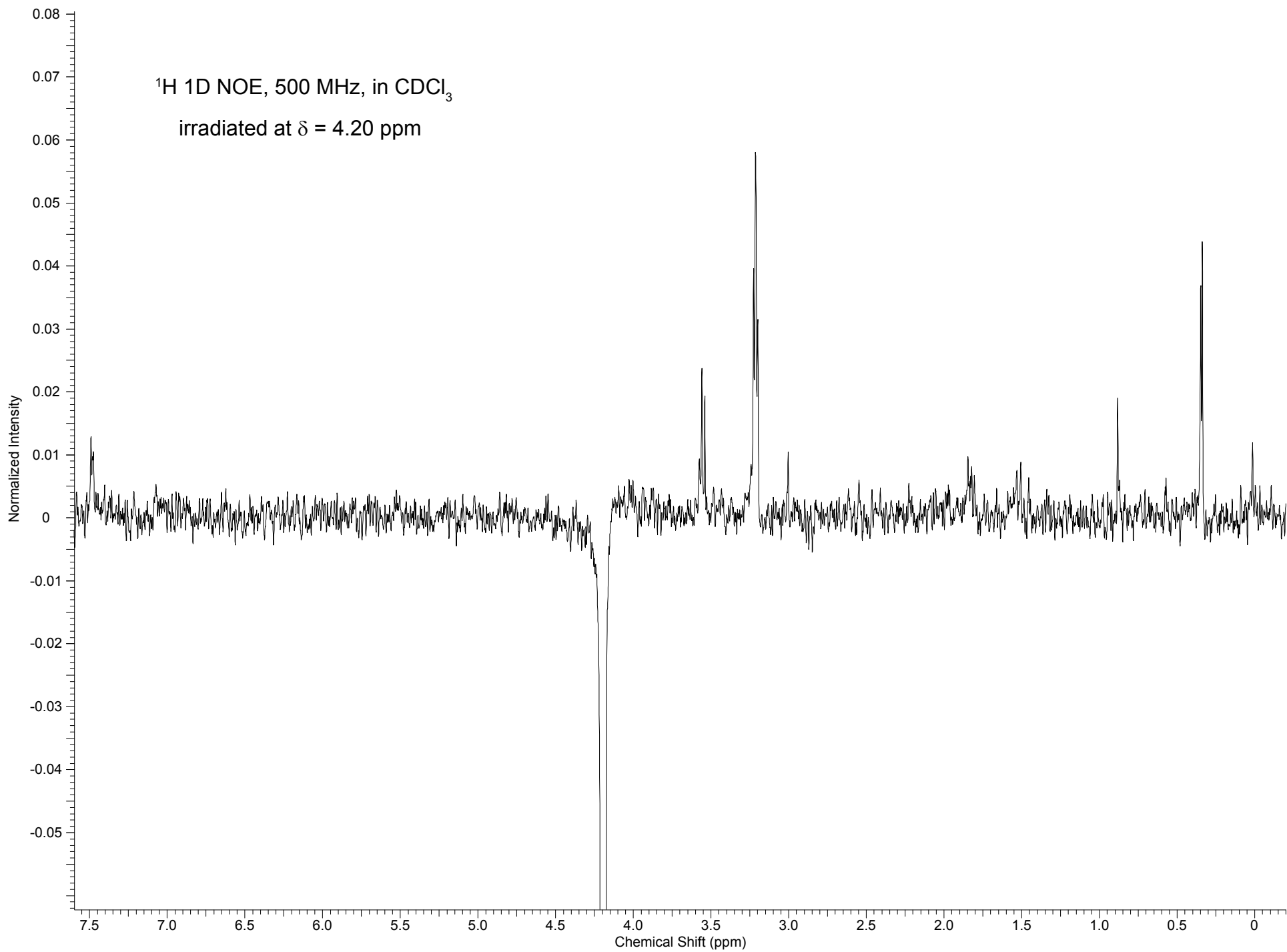




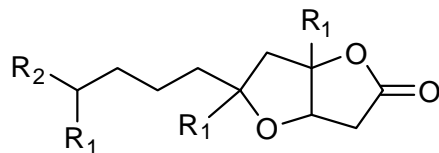
^1H 1D NOE, 500 MHz, in CDCl_3
irradiated at $\delta = 1.83$ ppm



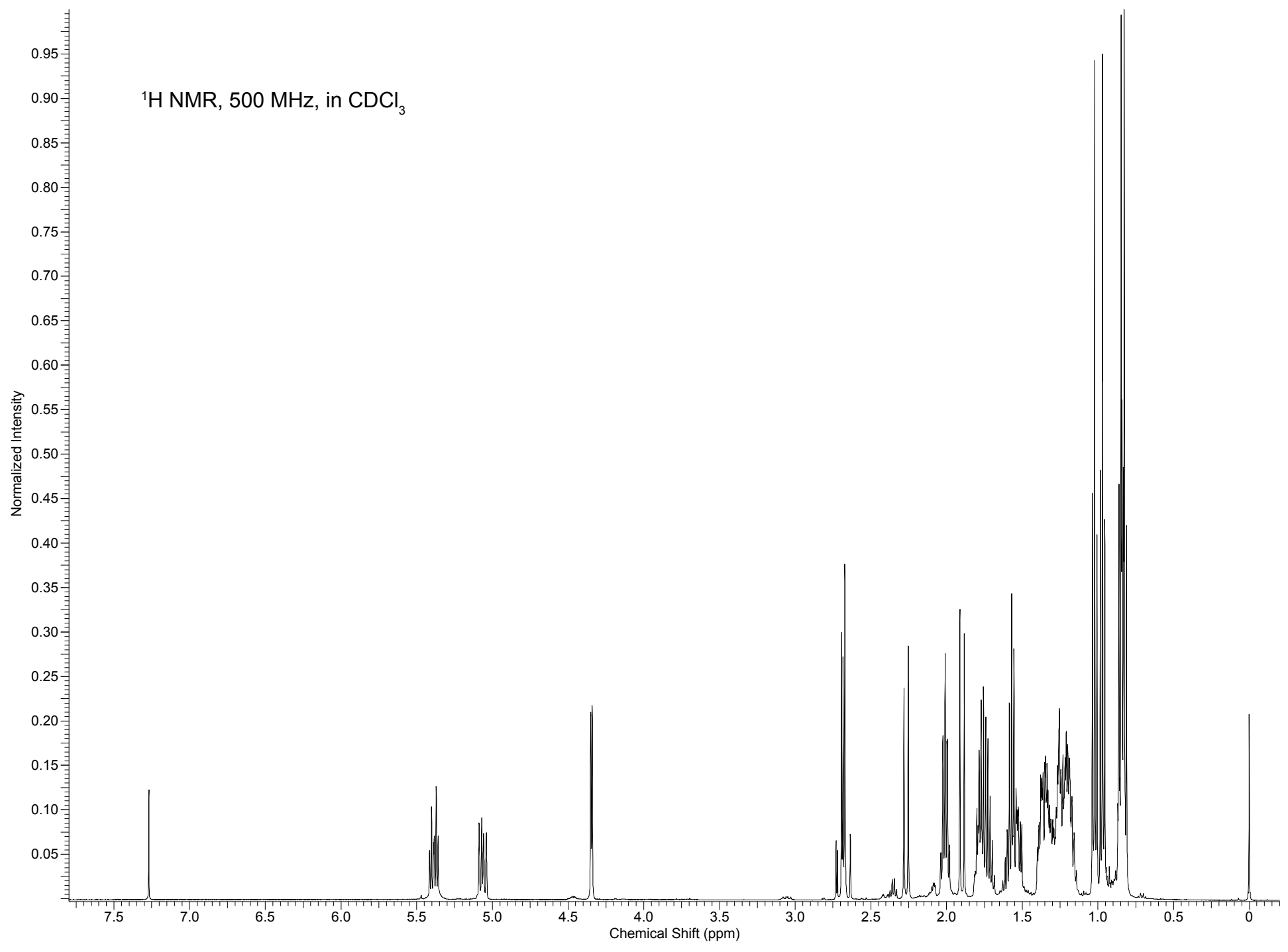




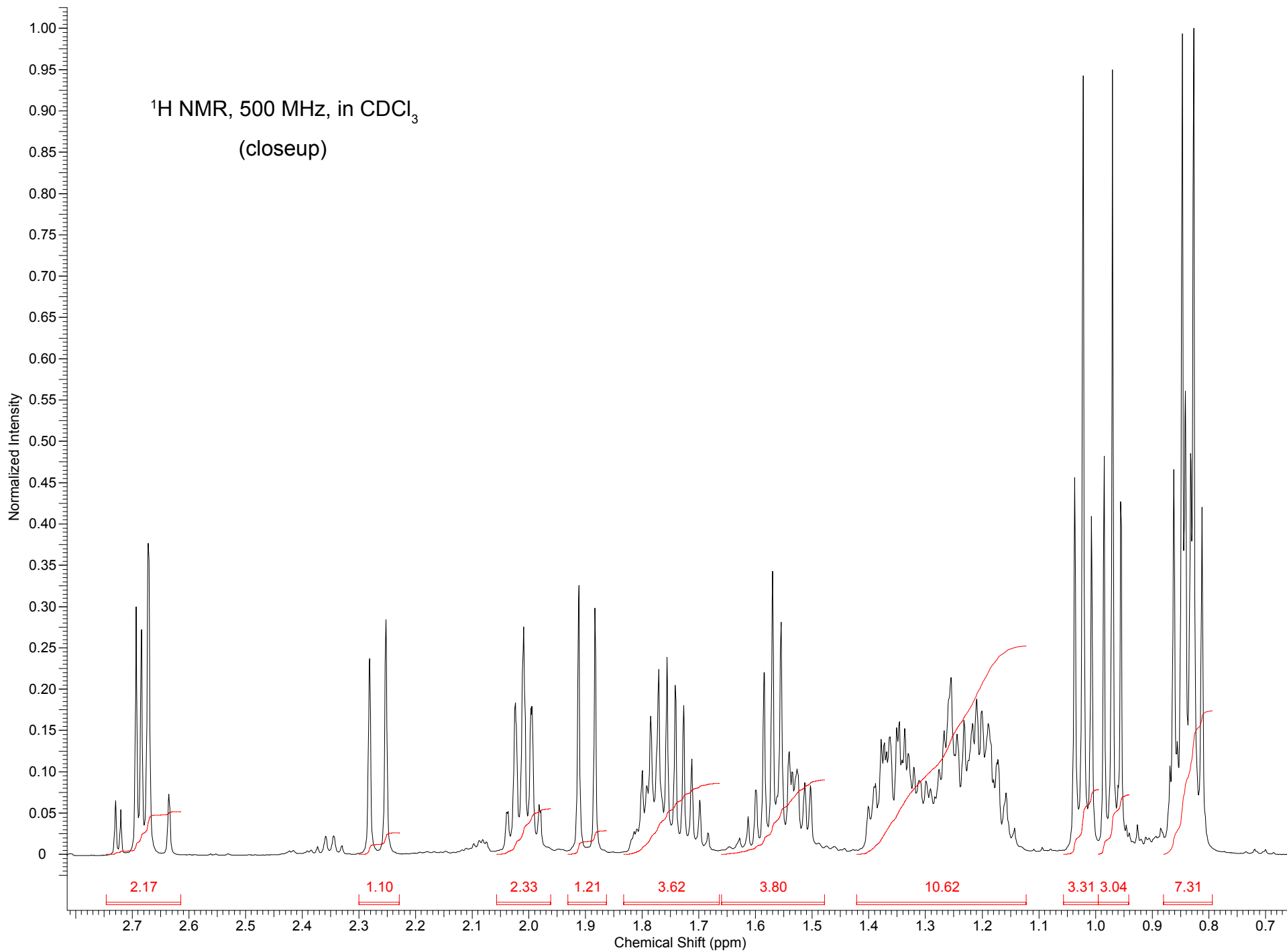
2. Seif Ayyad (Mansoura University, Egypt) isolated the compound below as one of a series of natural products from the marine sponge *Plakortis*. ^1H (500 MHz, in CDCl_3), ^{13}C (125 MHz, in CDCl_3) and DEPT spectra are shown on the following pages. Use these spectra to identify the substituents R_1 and R_2 .



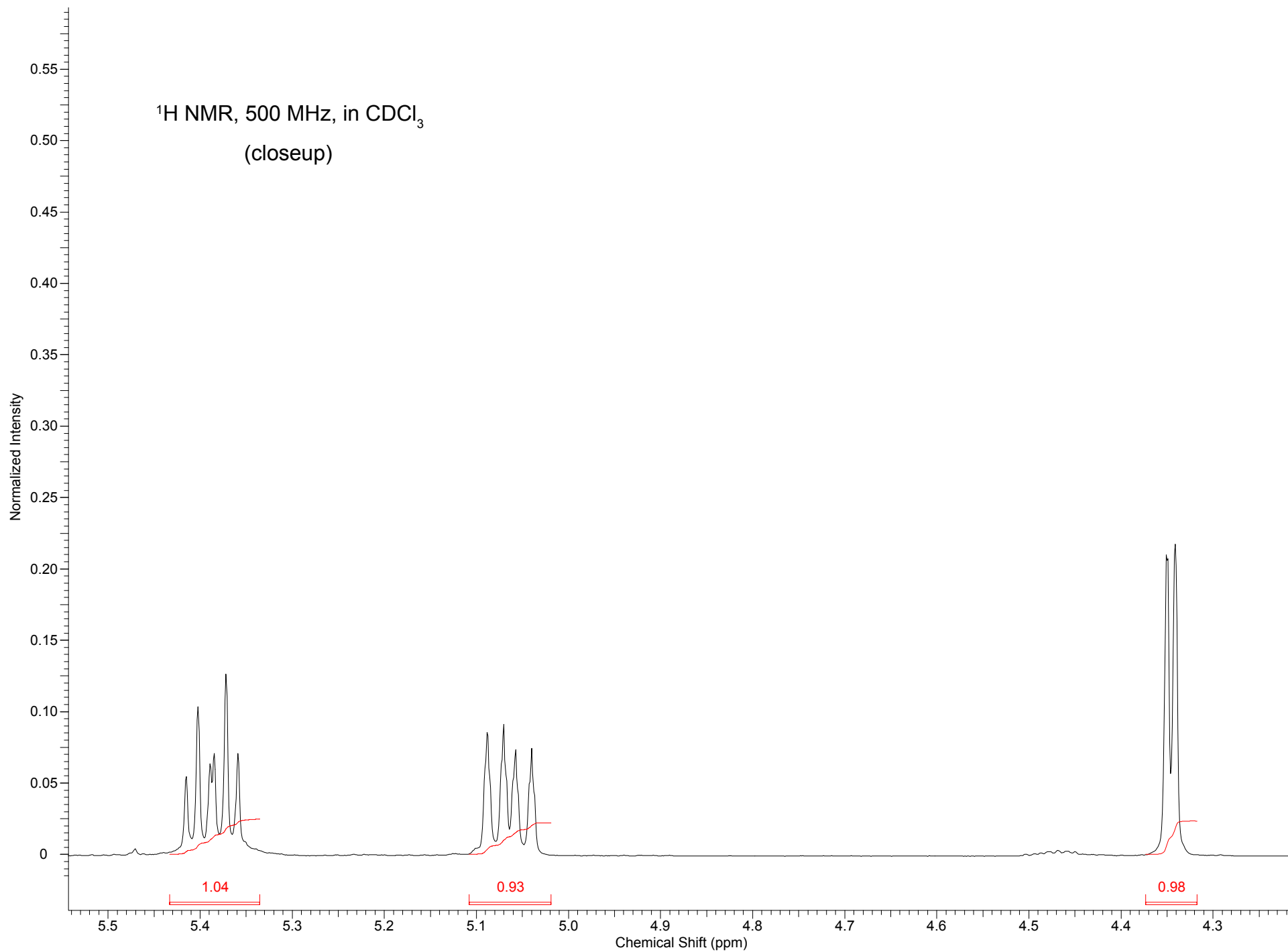
^1H NMR, 500 MHz, in CDCl_3



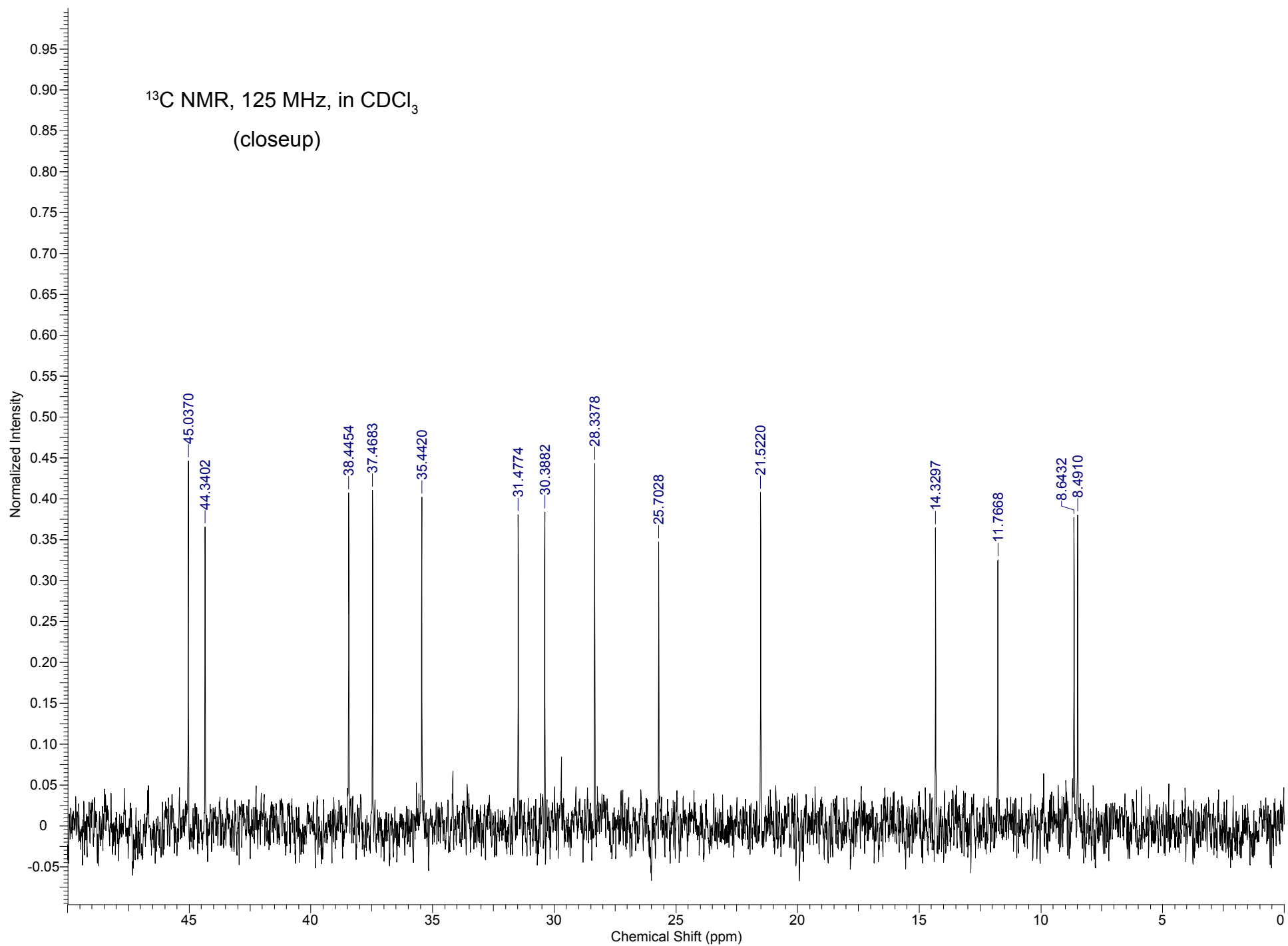
^1H NMR, 500 MHz, in CDCl_3
(closeup)



^1H NMR, 500 MHz, in CDCl_3
(closeup)



^{13}C NMR, 125 MHz, in CDCl_3
(closeup)



^{13}C NMR, 125 MHz, in CDCl_3
(closeup)

