

## Supporting Information

### A Clickable and Photocleavable Lipid Analog for Cell Membrane Delivery and Release

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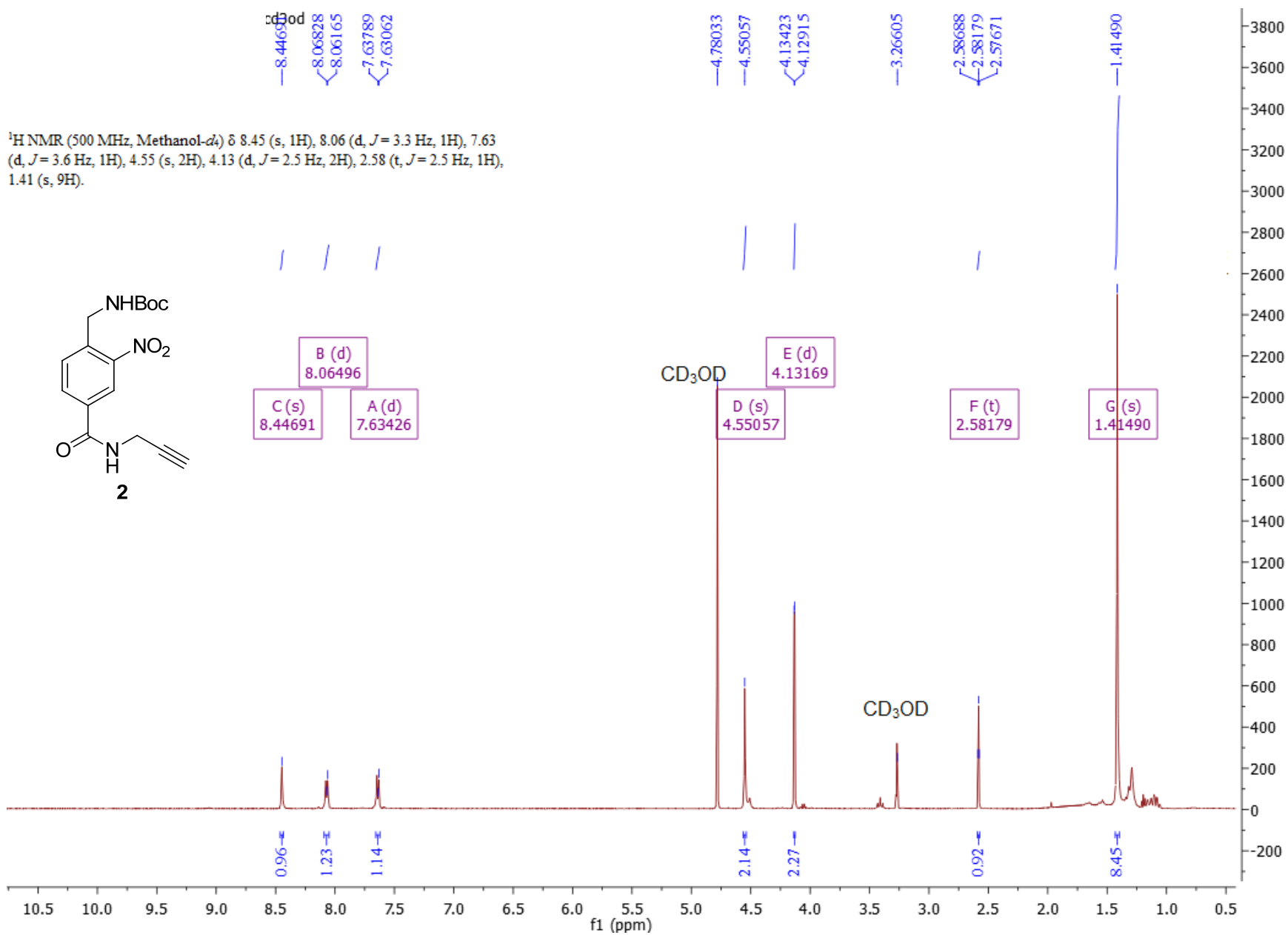
<sup>2</sup>Department of Biochemistry and Cellular and Molecular Biology, University of Tennessee, Knoxville, TN 37996, U.S.A.

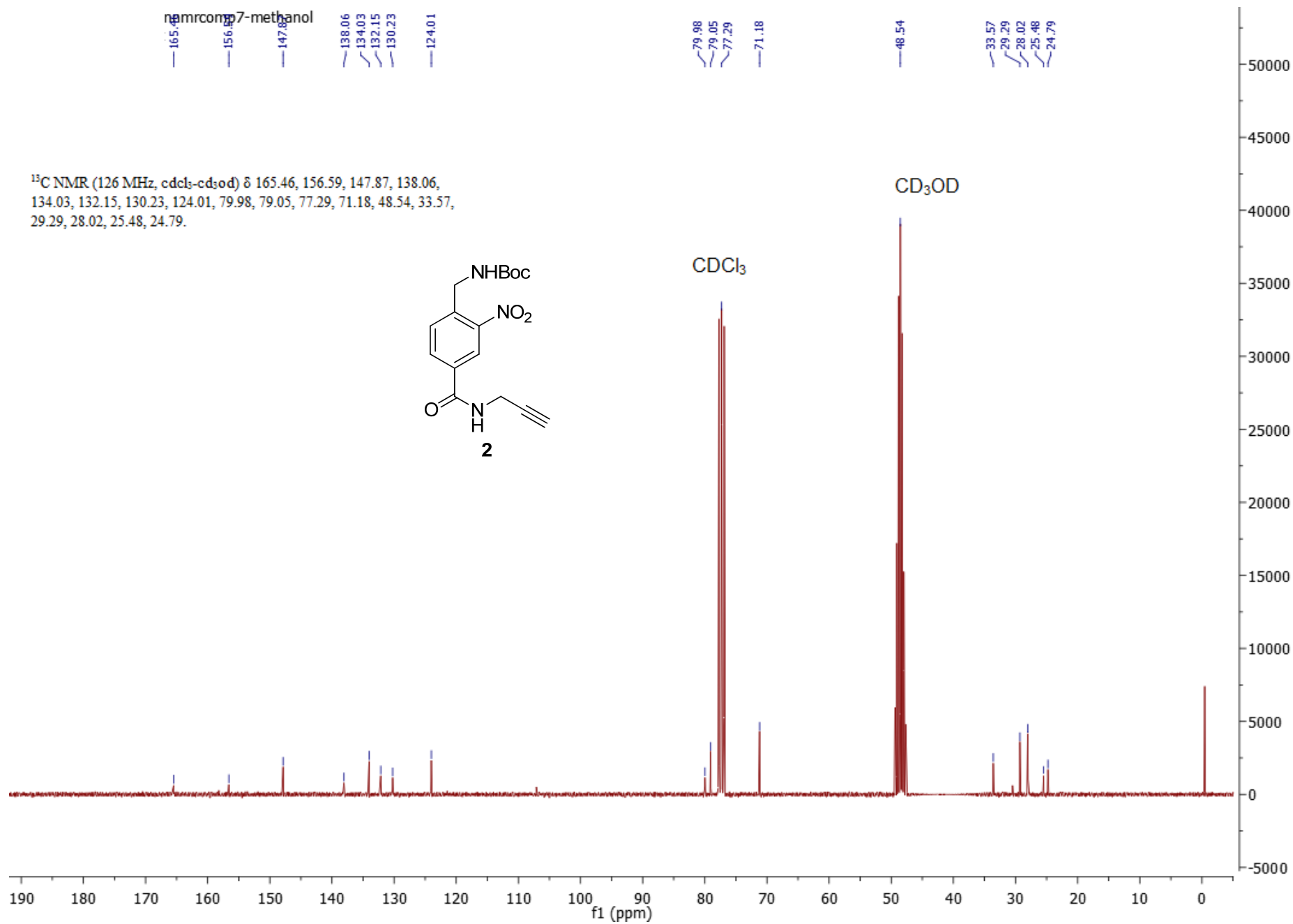
<sup>3</sup>Department of Chemistry, The University of Georgia, Athens, GA, 30602, U.S.A.  
e-mail: [mdbest@utk.edu](mailto:mdbest@utk.edu)

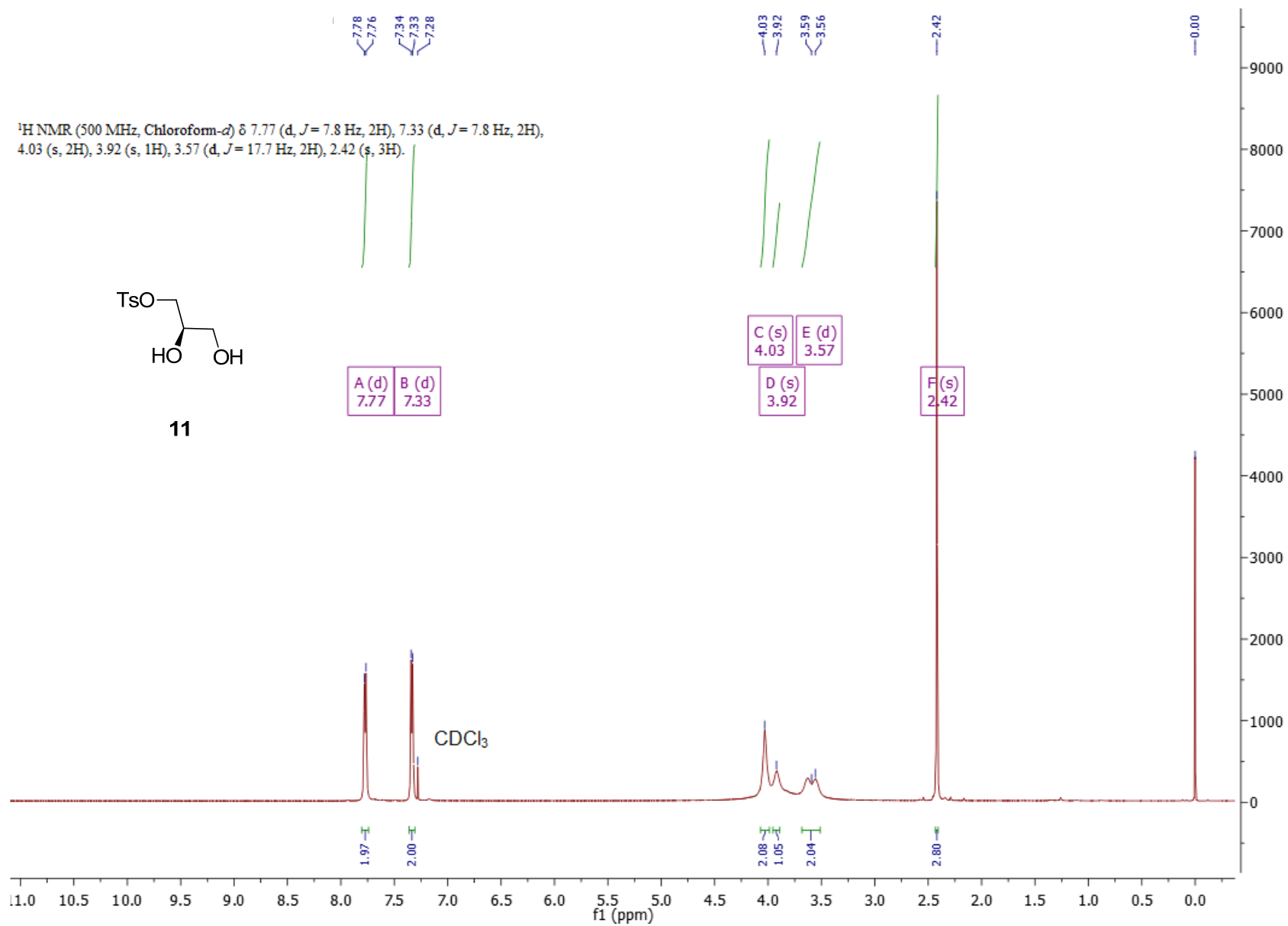
#### Index Contents:

**S2 – S11: NMR Spectra for Synthetic Compounds**

**S12 – S15 : Mass Spectra of Clicked Conjugate and Released Products**







5-22-14-tosylateddiol-cdcl3

145.22

132.21

130.02

127.95

77.10

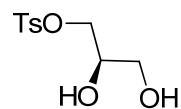
70.94

69.68

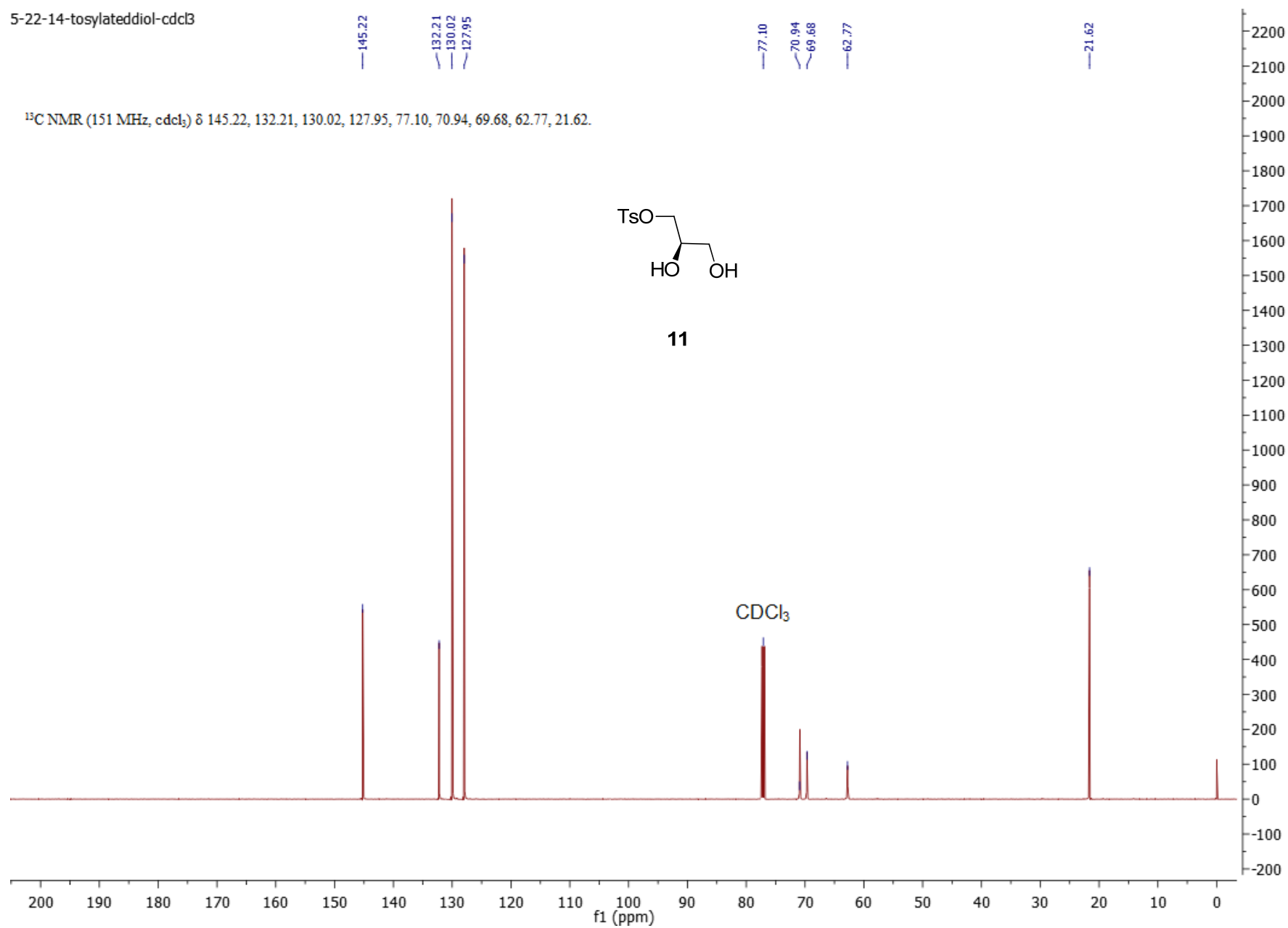
62.77

21.62

$^{13}\text{C}$  NMR (151 MHz,  $\text{cdcl}_3$ )  $\delta$  145.22, 132.21, 130.02, 127.95, 77.10, 70.94, 69.68, 62.77, 21.62.

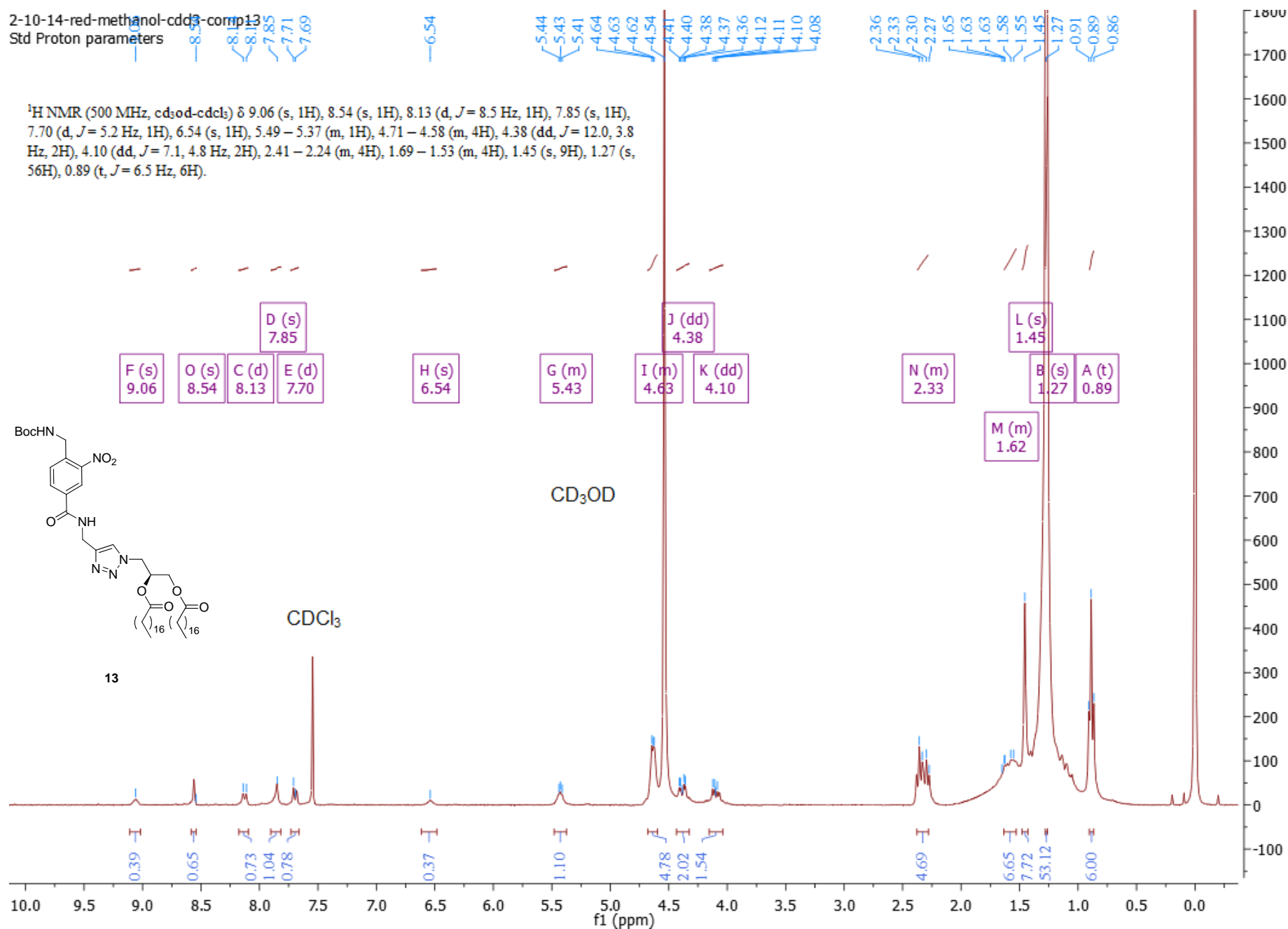


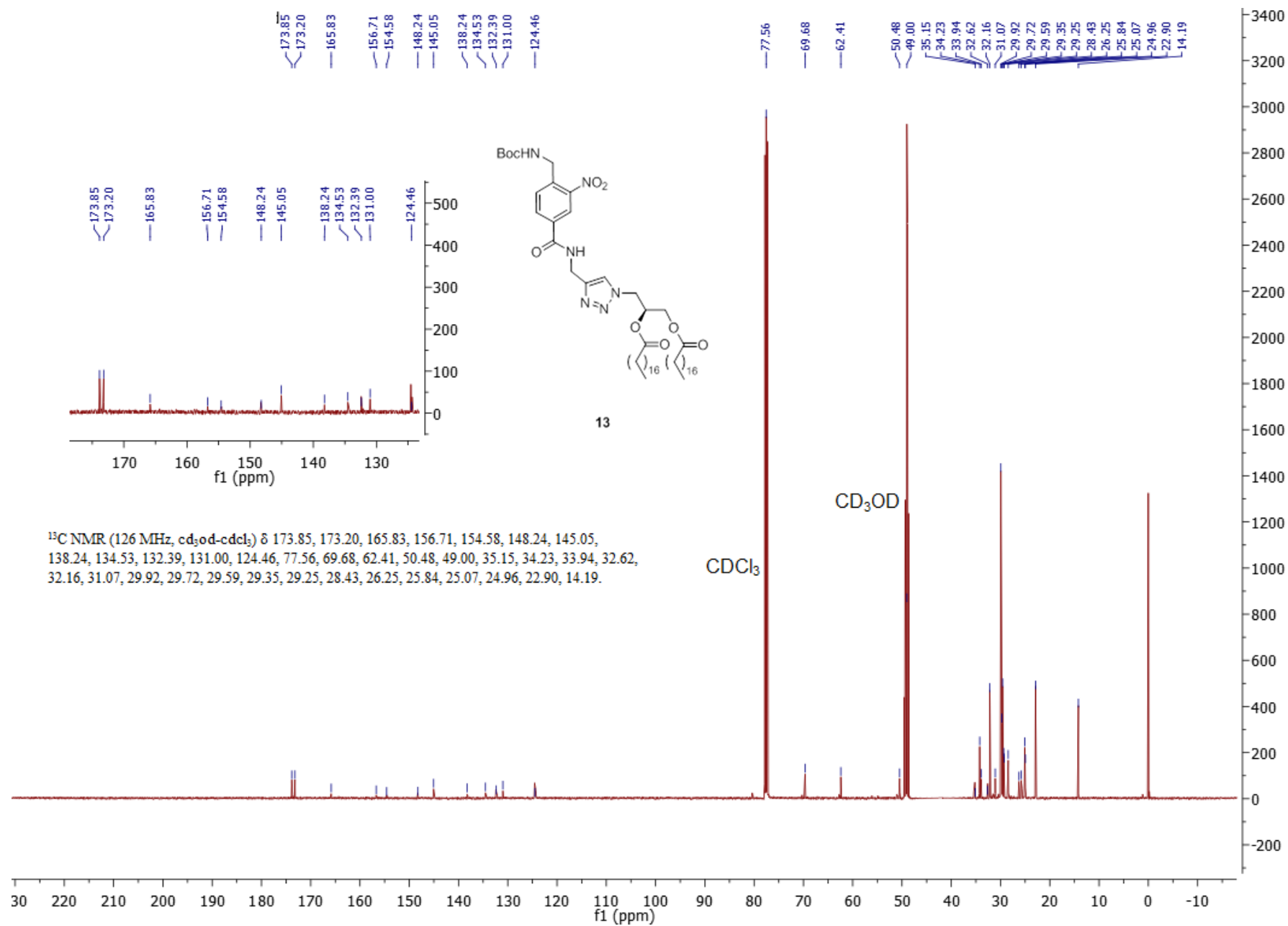
11



2-10-14-red-methanol-cdcl3-comp13  
 Std Proton parameters

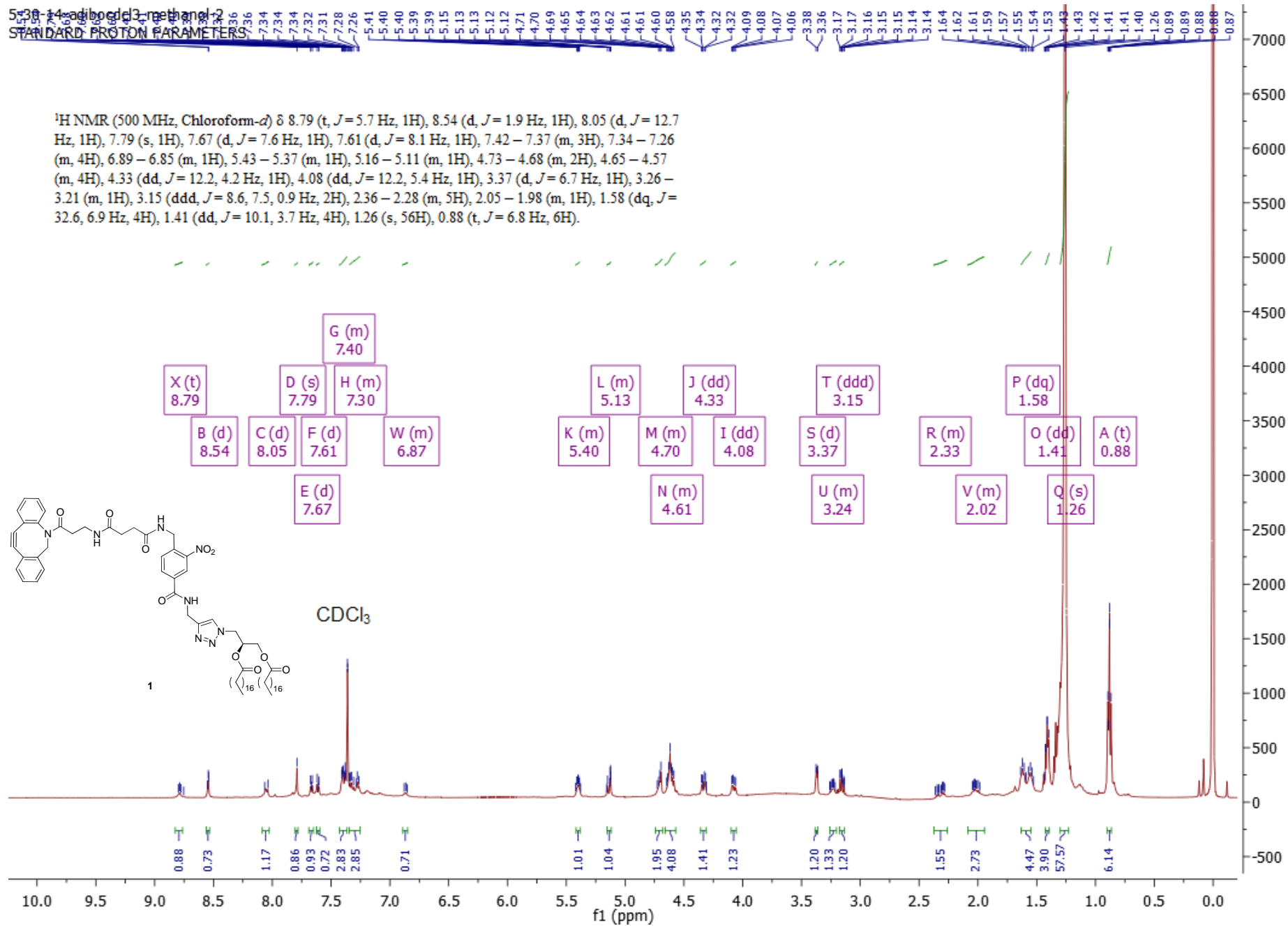
$^1\text{H NMR}$  (500 MHz,  $\text{cd}_3\text{od-cdcl}_3$ )  $\delta$  9.06 (s, 1H), 8.54 (s, 1H), 8.13 (d,  $J = 8.5$  Hz, 1H), 7.85 (s, 1H), 7.70 (d,  $J = 5.2$  Hz, 1H), 6.54 (s, 1H), 5.49–5.37 (m, 1H), 4.71–4.58 (m, 4H), 4.38 (dd,  $J = 12.0, 3.8$  Hz, 2H), 4.10 (dd,  $J = 7.1, 4.8$  Hz, 2H), 2.41–2.24 (m, 4H), 1.69–1.53 (m, 4H), 1.45 (s, 9H), 1.27 (s, 56H), 0.89 (t,  $J = 6.5$  Hz, 6H).



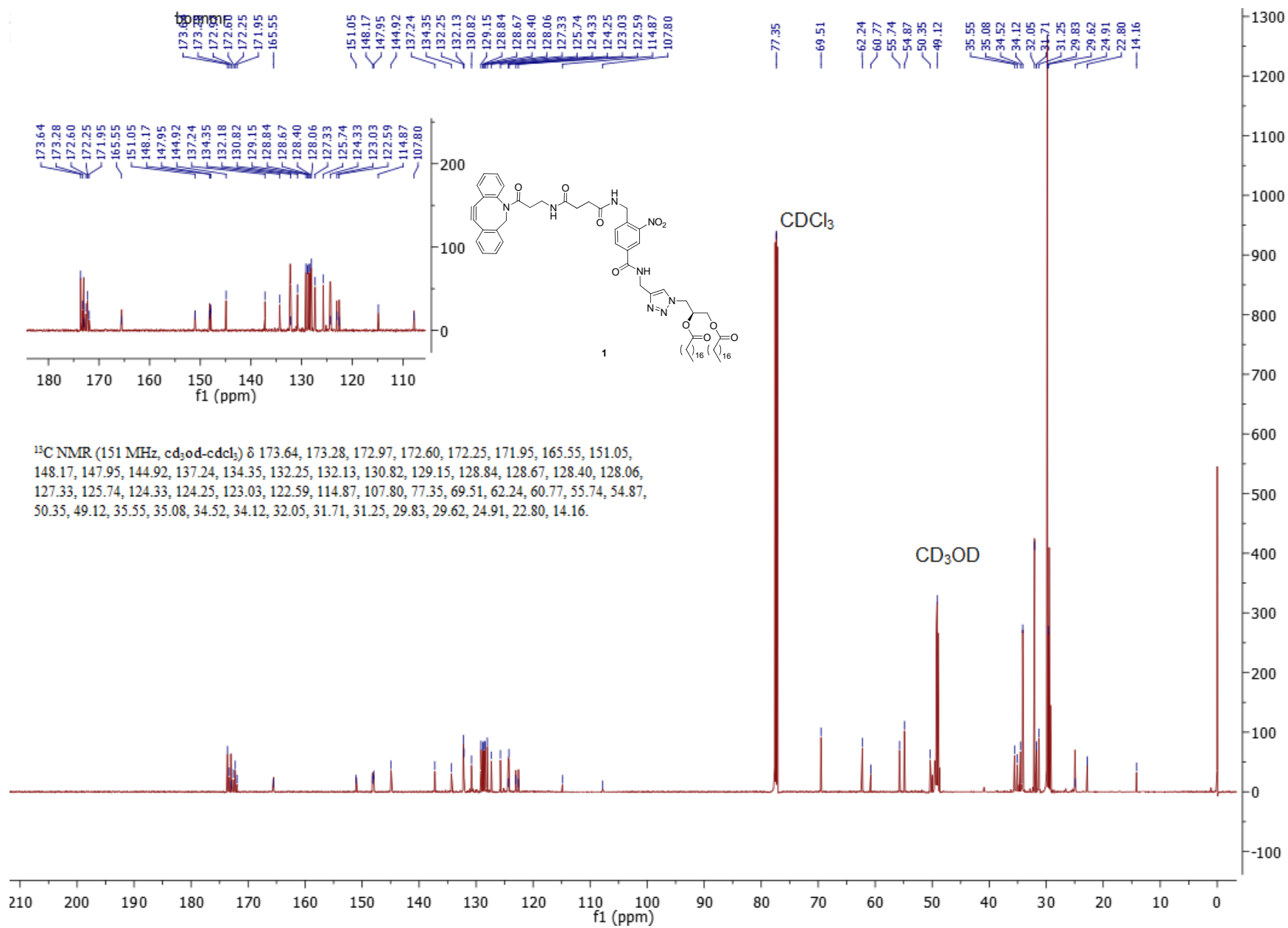


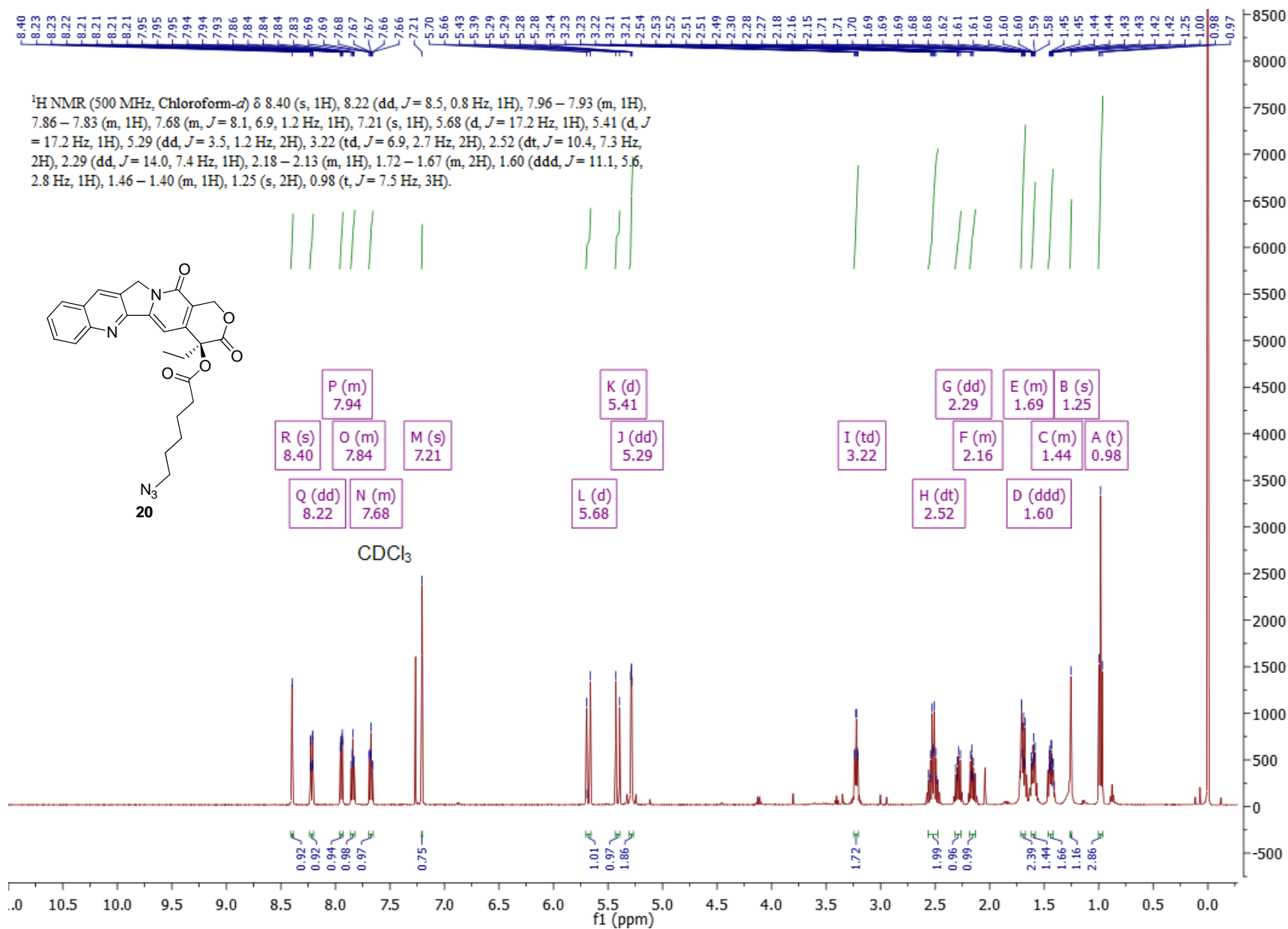
5-30-14-adibocd3-methanol-2  
STANDARD PROTON PARAMETERS

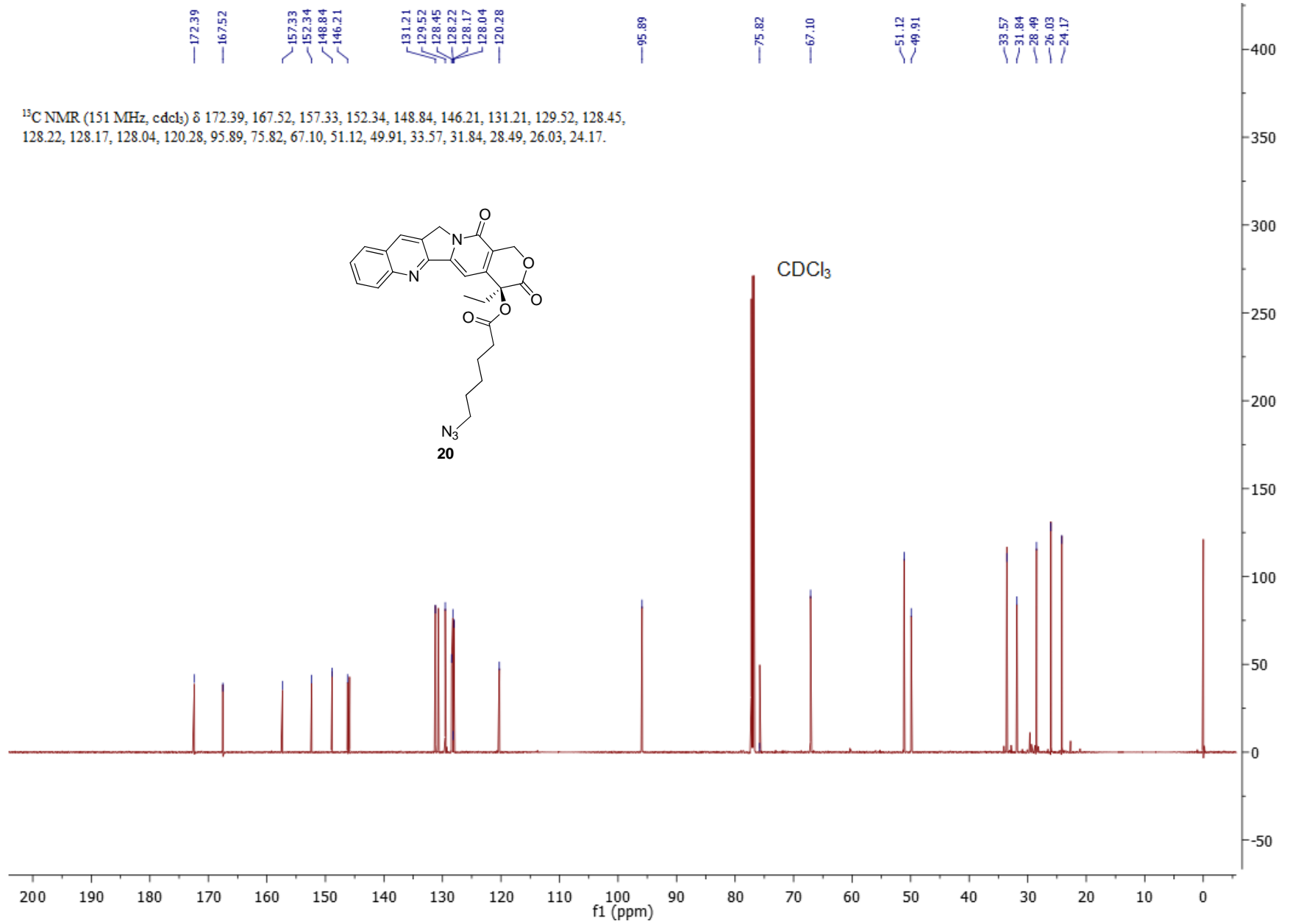
<sup>1</sup>H NMR (500 MHz, Chloroform-*d*) δ 8.79 (t, *J* = 5.7 Hz, 1H), 8.54 (d, *J* = 1.9 Hz, 1H), 8.05 (d, *J* = 12.7 Hz, 1H), 7.79 (s, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.34 – 7.26 (m, 4H), 6.89 – 6.85 (m, 1H), 5.43 – 5.37 (m, 1H), 5.16 – 5.11 (m, 1H), 4.73 – 4.68 (m, 2H), 4.65 – 4.57 (m, 4H), 4.33 (dd, *J* = 12.2, 4.2 Hz, 1H), 4.08 (dd, *J* = 12.2, 5.4 Hz, 1H), 3.37 (d, *J* = 6.7 Hz, 1H), 3.26 – 3.21 (m, 1H), 3.15 (ddd, *J* = 8.6, 7.5, 0.9 Hz, 2H), 2.36 – 2.28 (m, 5H), 2.05 – 1.98 (m, 1H), 1.58 (dq, *J* = 32.6, 6.9 Hz, 4H), 1.41 (dd, *J* = 10.1, 3.7 Hz, 4H), 1.26 (s, 56H), 0.88 (t, *J* = 6.8 Hz, 6H).



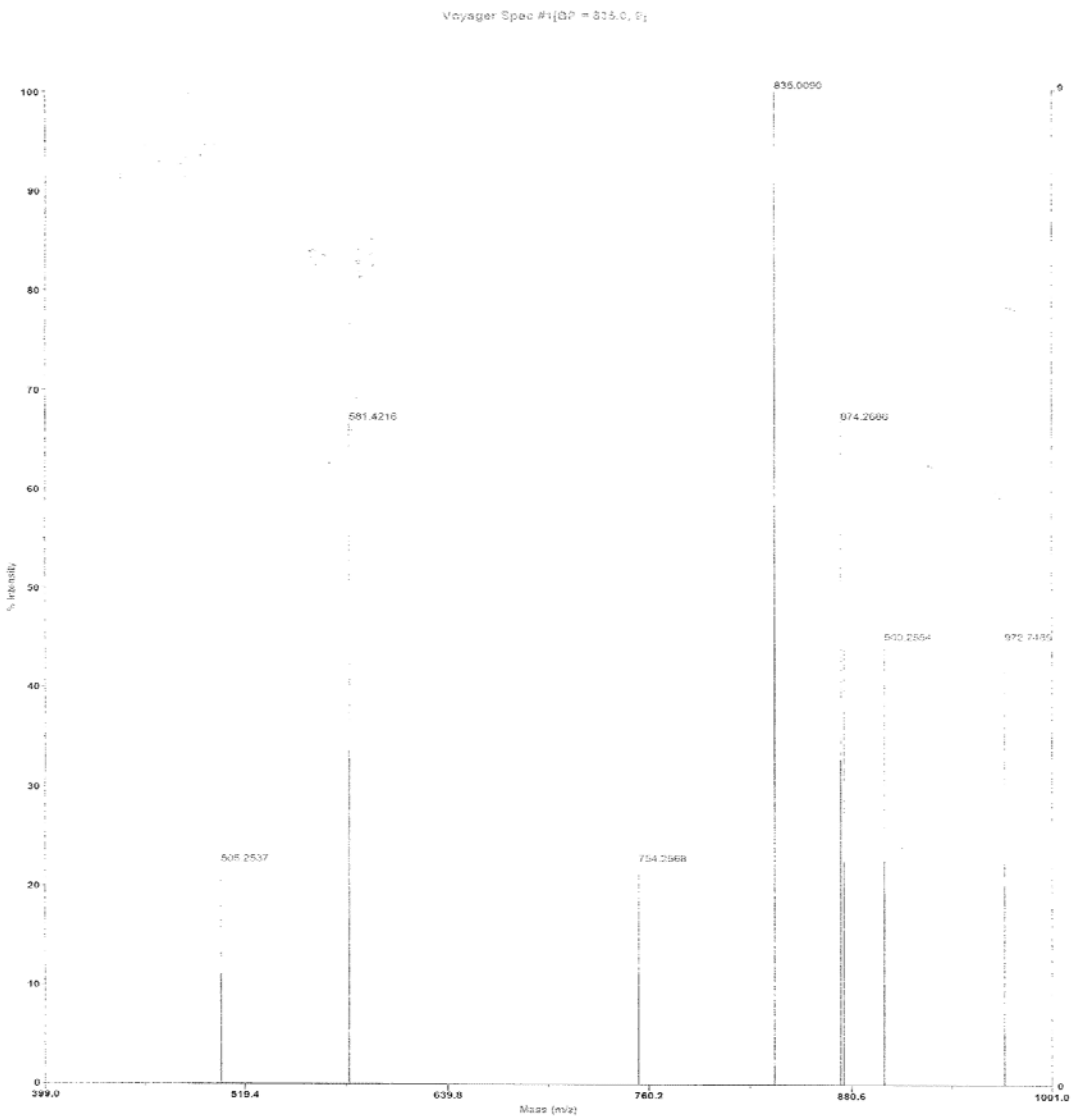




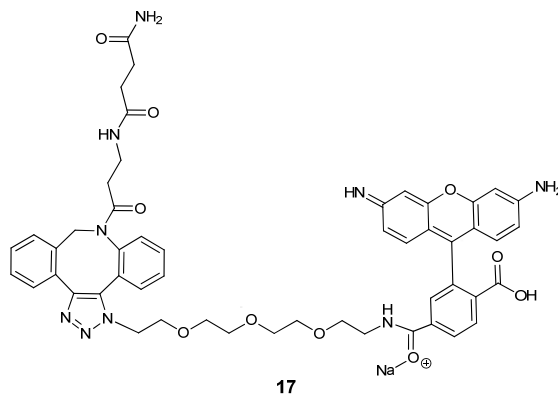




Mass spectrum of released fluorophore **17** following treatment of *S. Cerevisiae* cells with lipid **1**, fluorophore **14** and photocleavage.

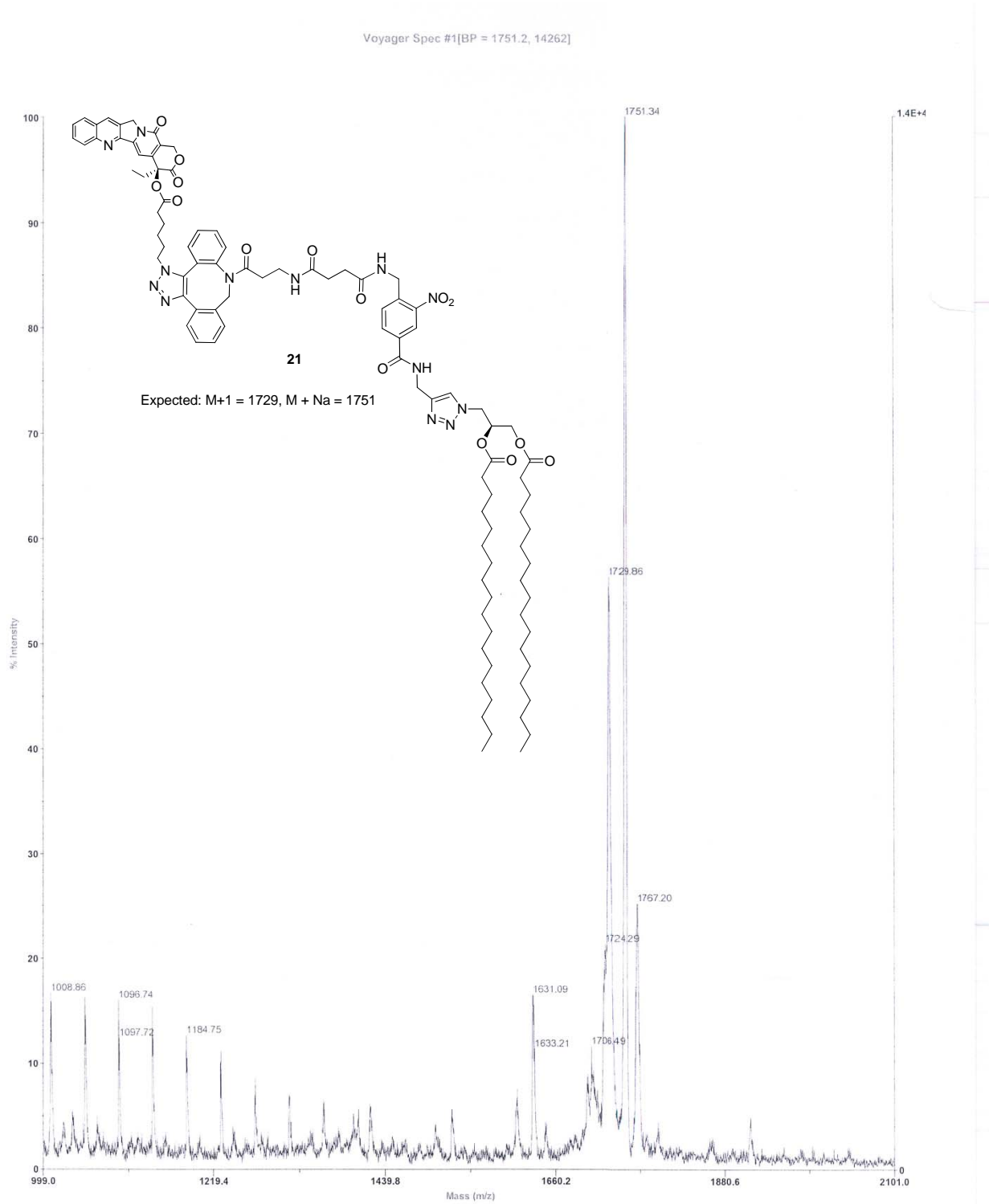


D:\...best-shahrina-sample3-wash\_0001.dat  
Acquired: 11.12.00, March 14, 2015



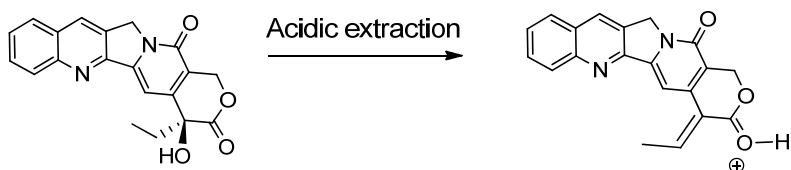
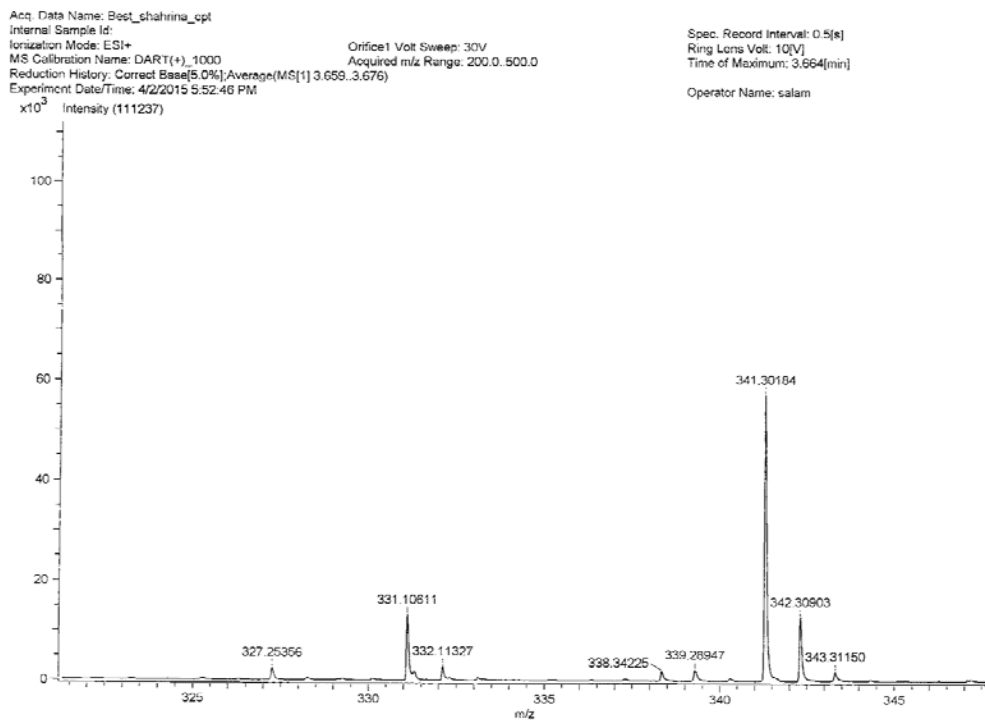
Expected Mass for M + Na: 973

# Mass Spectrum of Camptothecin-Lipid Conjugate



D:\...best-shahrina-B-linear-4th\_0002.dat  
Acquired: 14:44:00, August 14, 2014

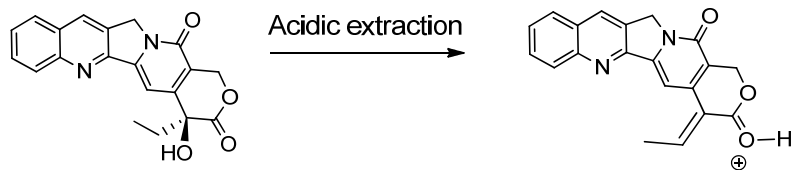
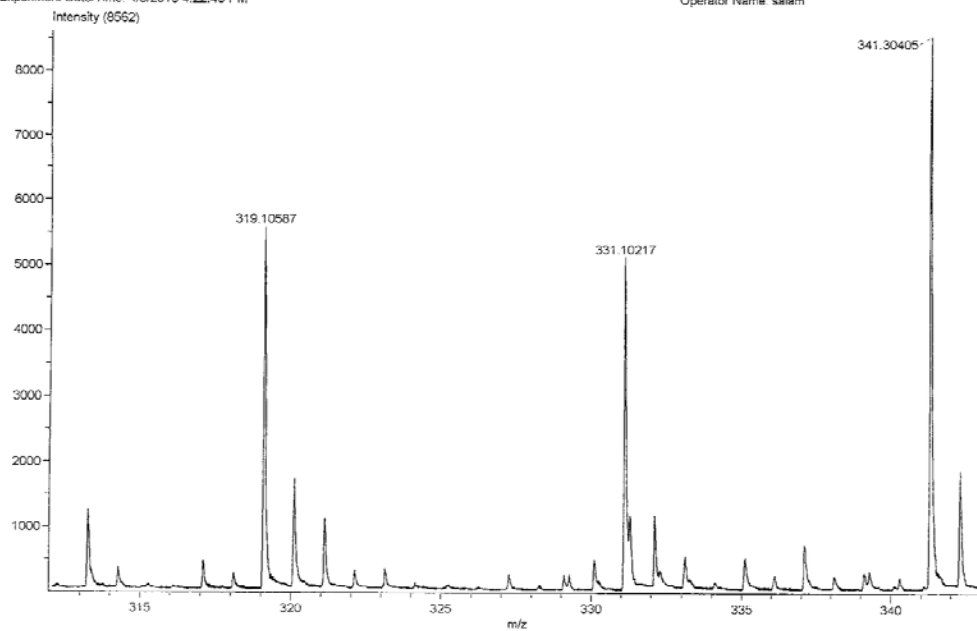
Mass spectrum of released camptothecin obtained following acidic extraction of HeLa cells that were treated with camptothecin-lipid conjugate **21**.



Expected Mass:  $M - H_2O + 1 = 331$

Mass spectrum obtained from a standard solution of camptothecin subjected to acidic extraction

Acq. Data Name: Best\_shahinna\_optinhd  
Internal Sample Id:  
Ionization Mode: ESI+ Orifice1 Volt Sweep: 30V Spec. Record Interval: 0.5[s]  
MS Calibration Name: DART(+), 1000 Acquired m/z Range: 200.0..500.0 Ring Lens Volt: 10[V]  
Reduction History: Correct Base[5.0%], Average[MS[1] 1.086..1.093] Time of Maximum: 1.090[min]  
Experiment Date/Time: 4/3/2015 4:22:45 PM Operator Name: salam



Expected Mass:  $M - H_2O + 1 = 331$