

## Ligations of O-acyl threonine units to give native peptides *via* 5-, 8-, 9- and 10-membered cyclic transition states

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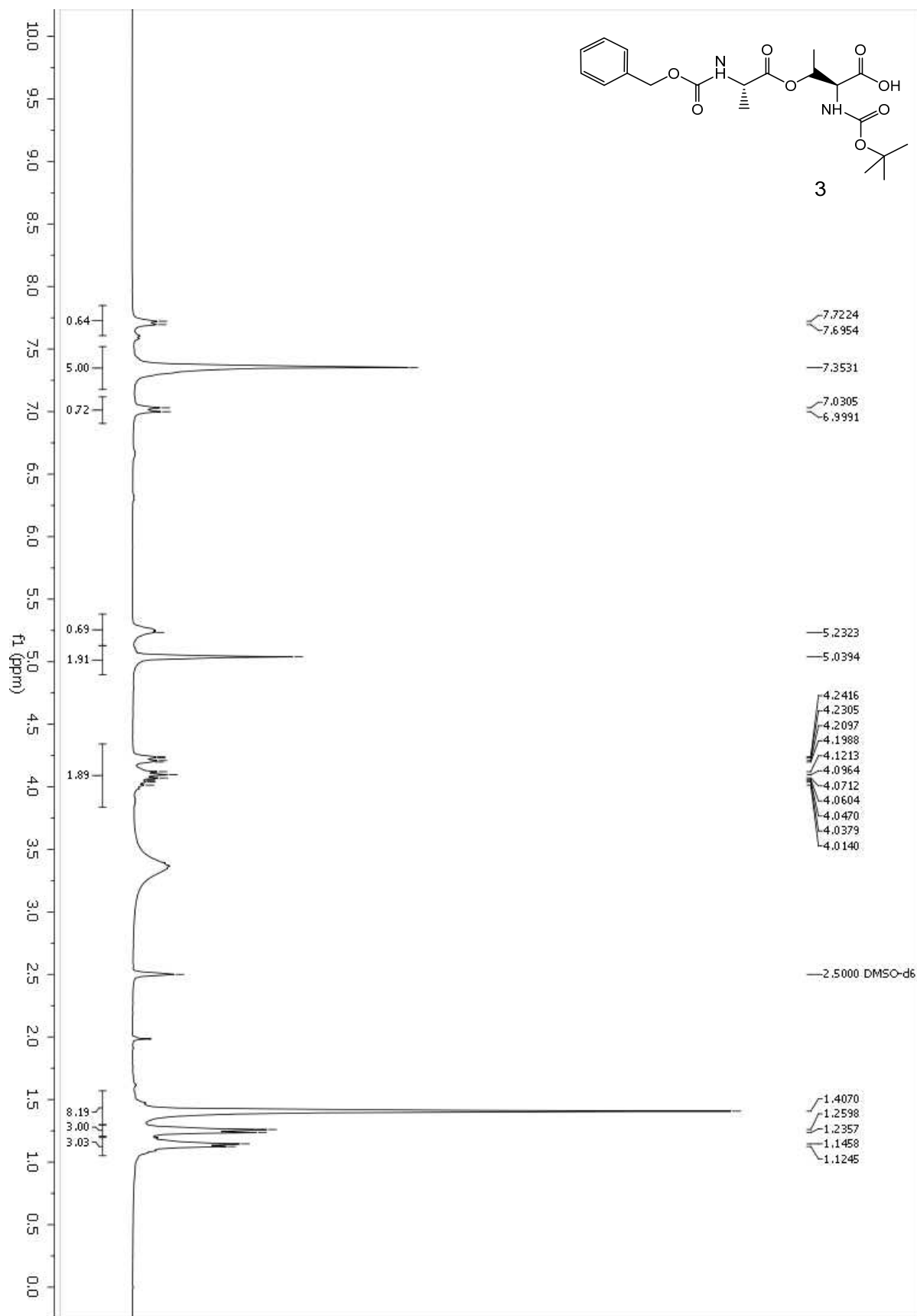
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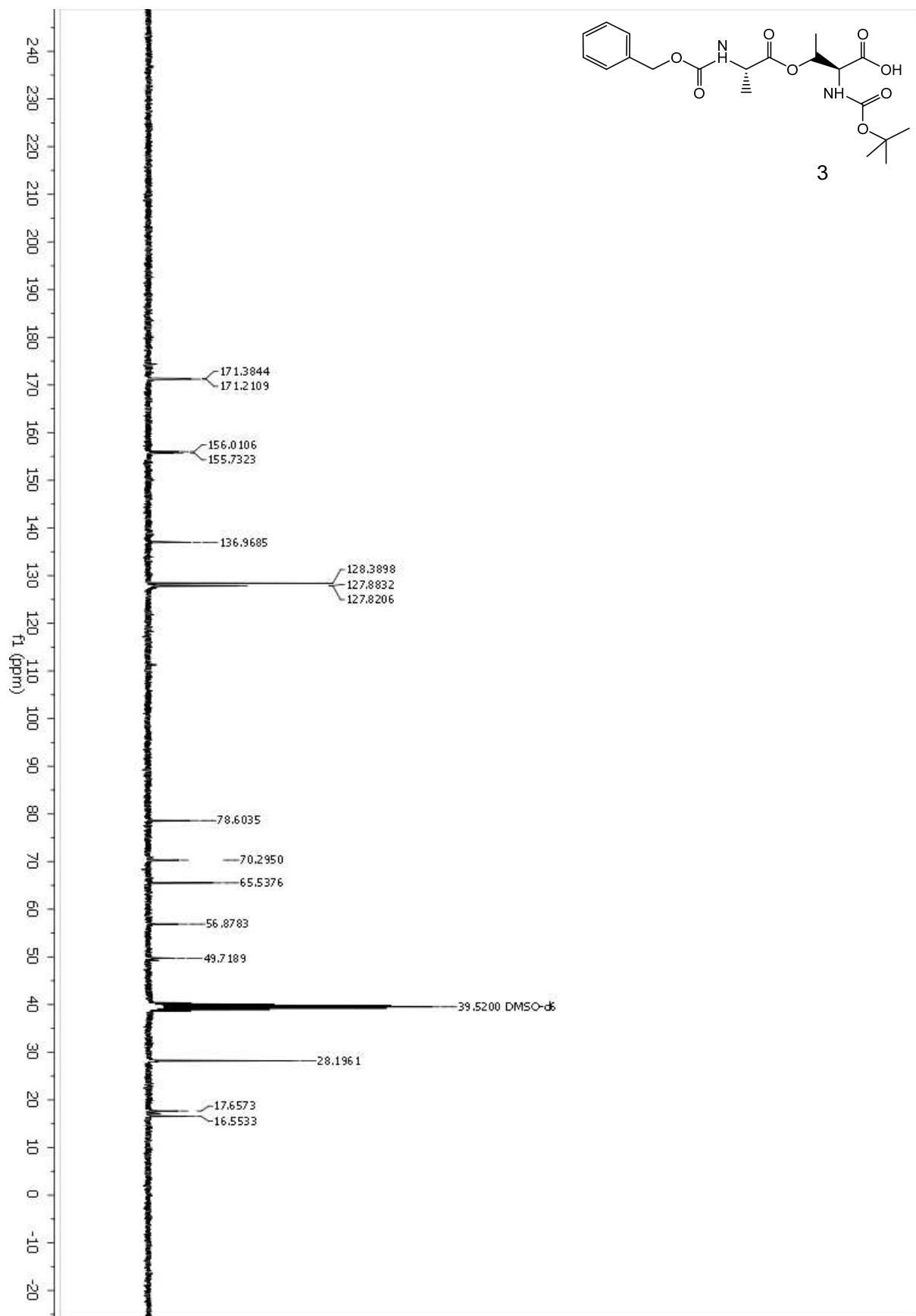
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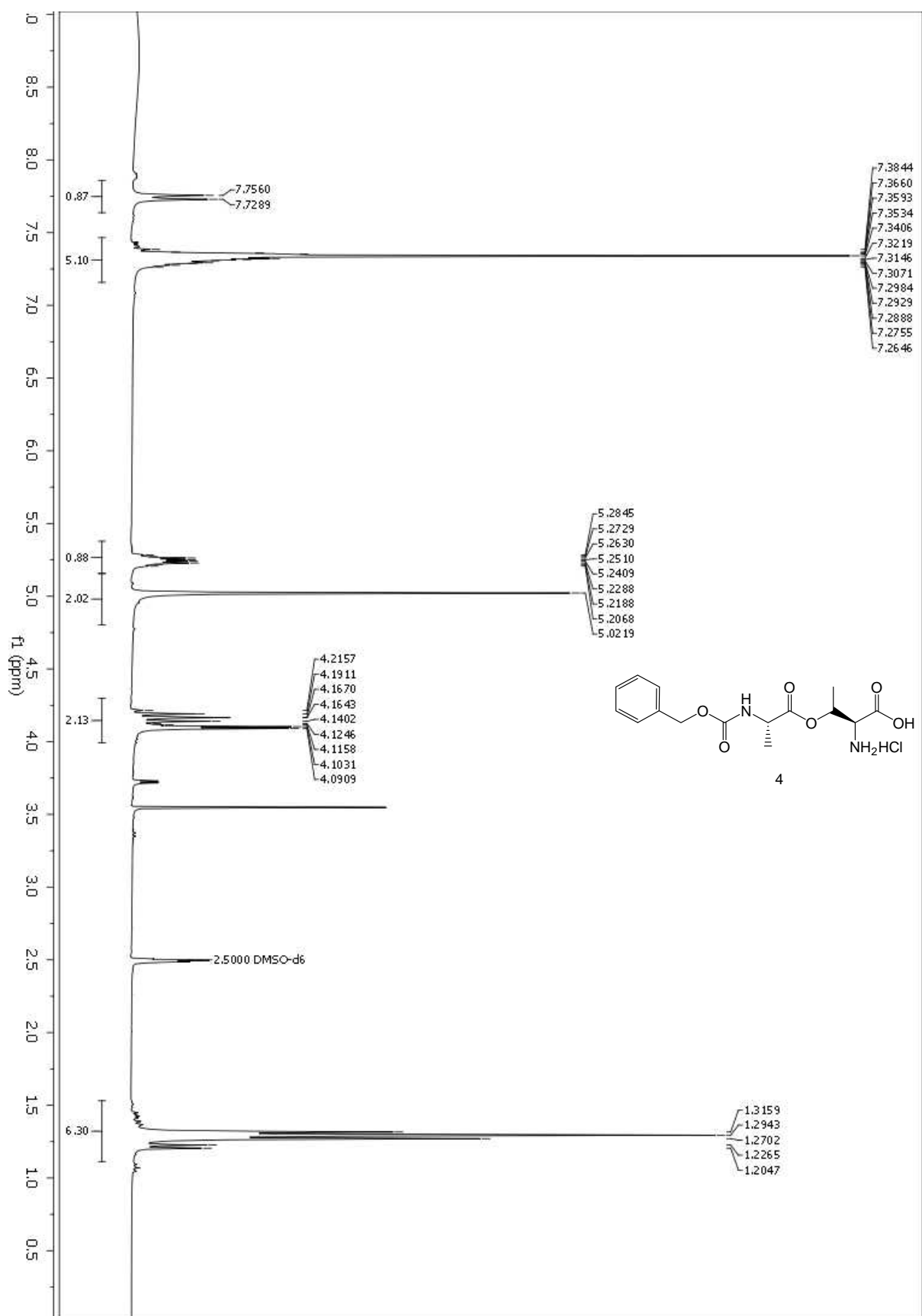
<sup>†</sup>*Deceased on February 10, 2014*

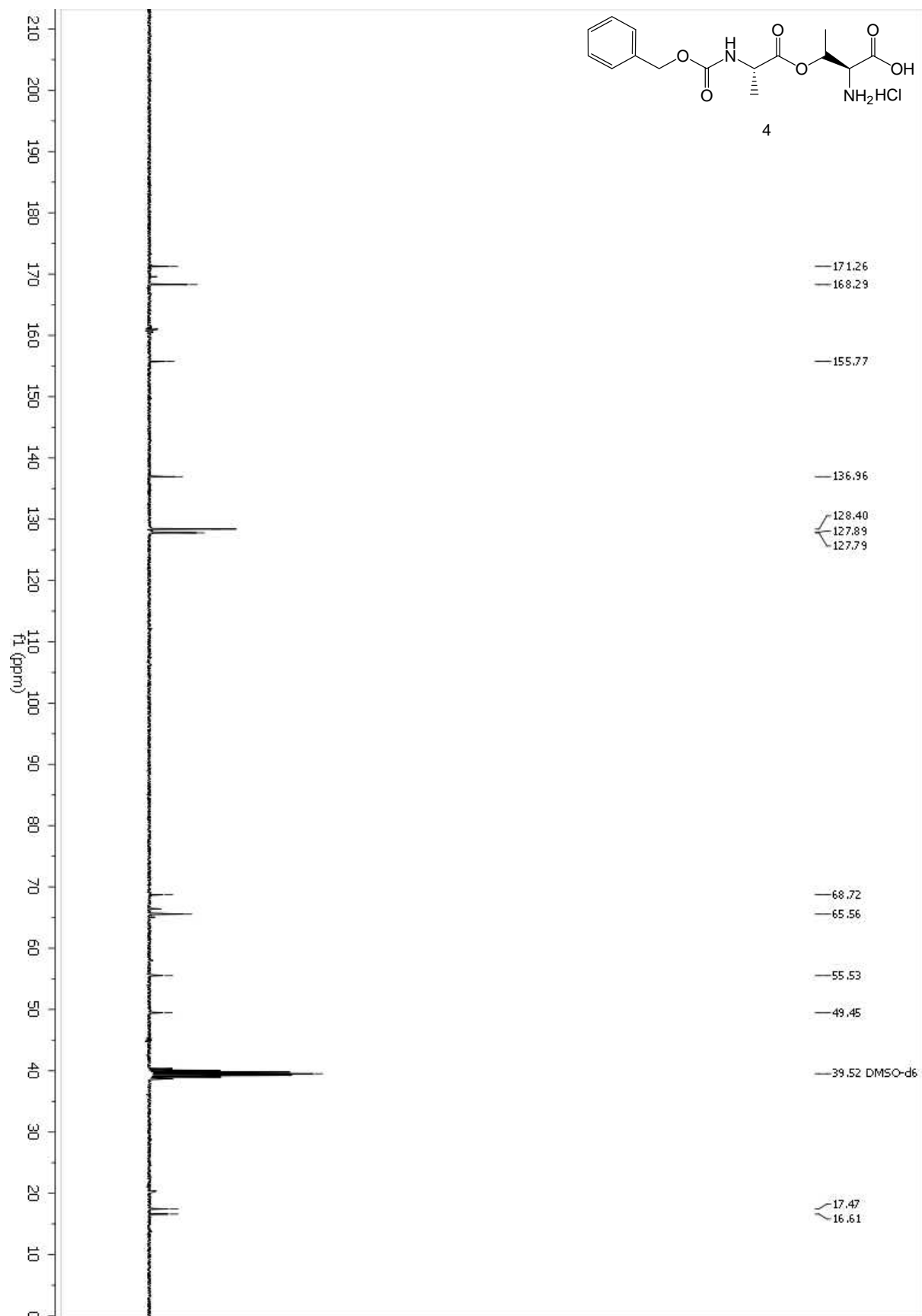
### SUPPORTING INFORMATION

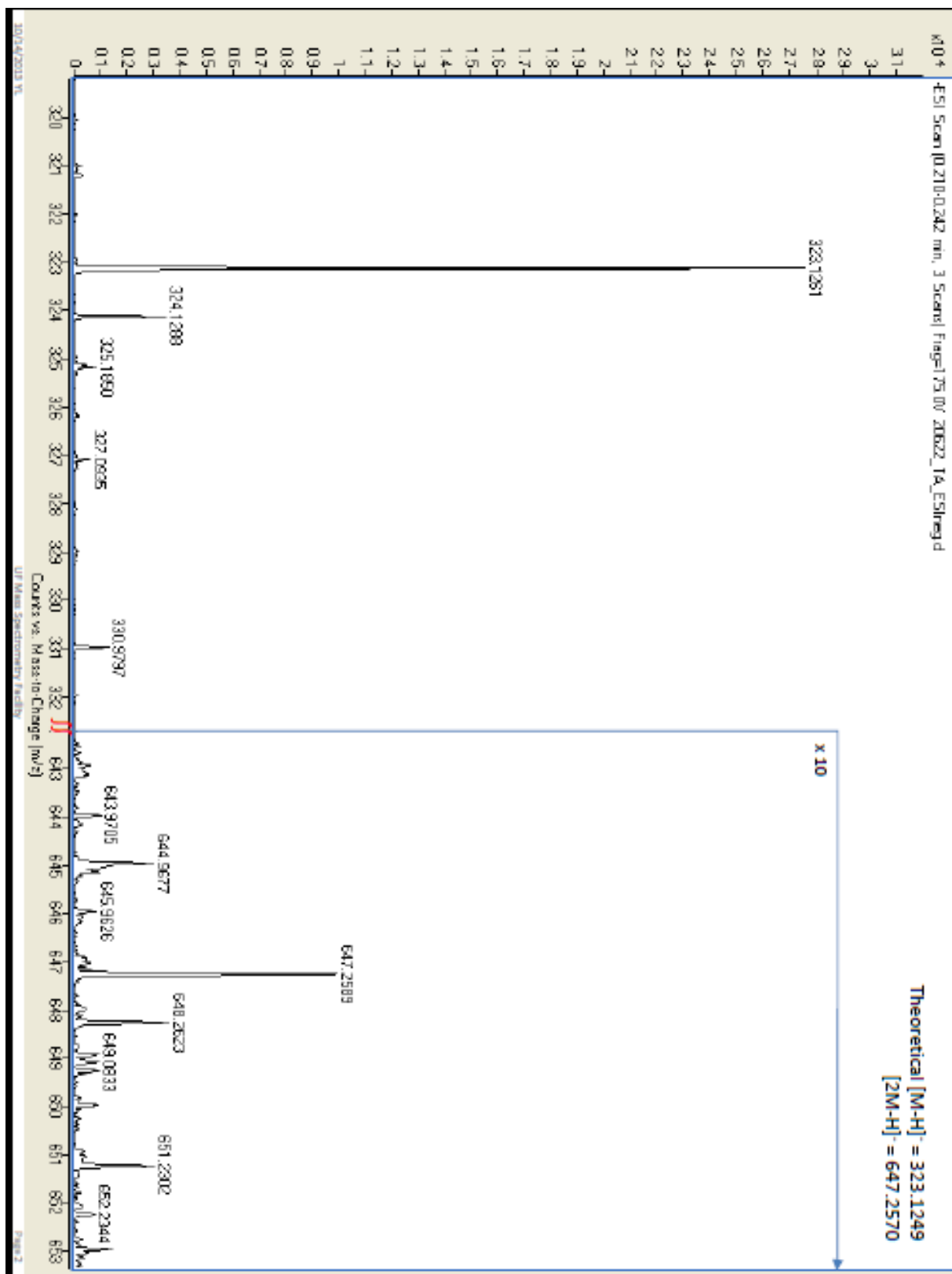
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|---|-----|
| 1. Copy of <sup>1</sup> H, <sup>13</sup> C NMR and CHN/HRMS spectra for compounds <b>3</b> , <b>4</b> , <b>8a-c</b> , and <b>9a-c</b> | S2  |
| 2. HPLC-MS spectra for compounds <b>4-6</b> , <b>9b</b> , <b>10b</b> and <b>11b</b>   | S25 |

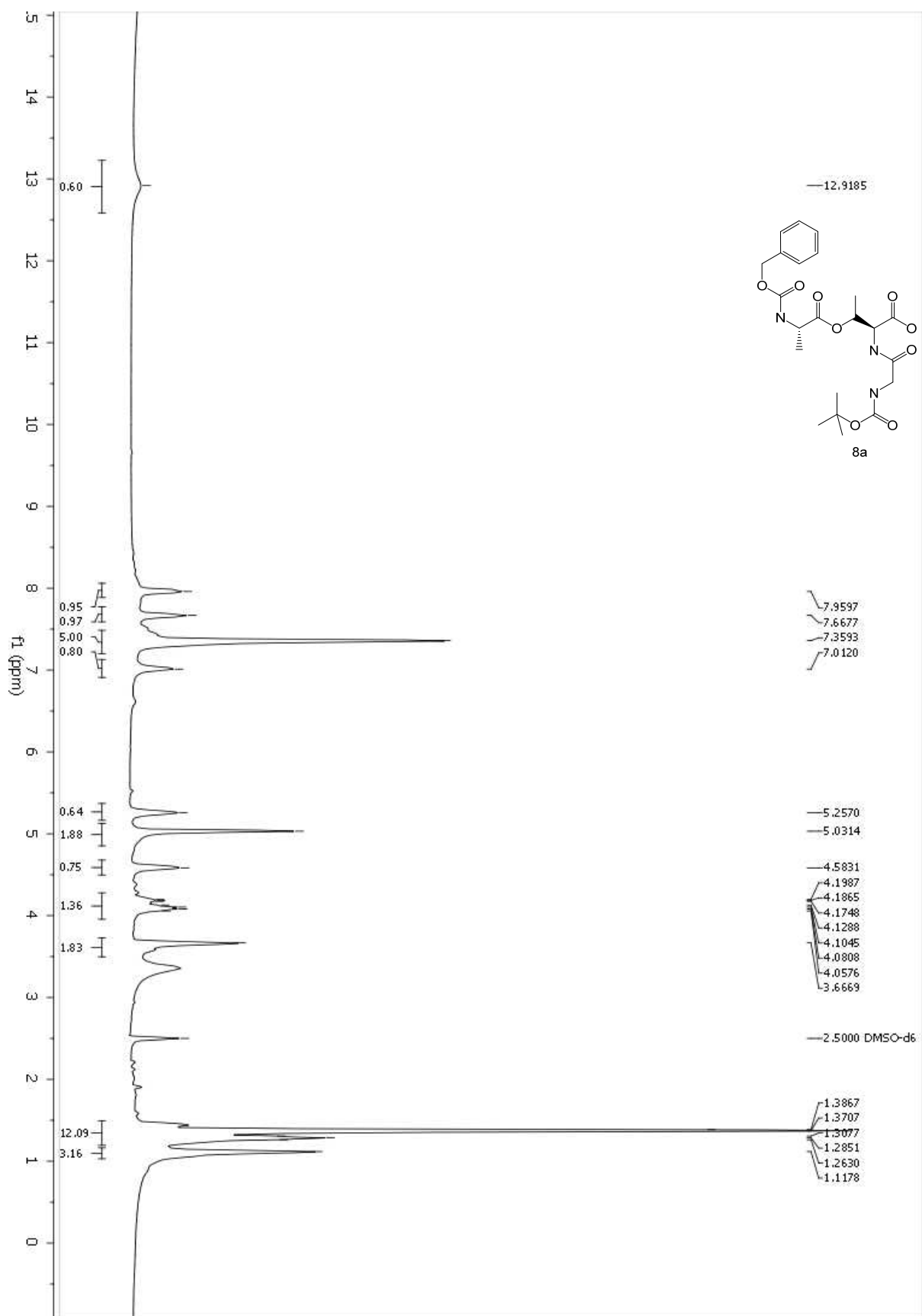


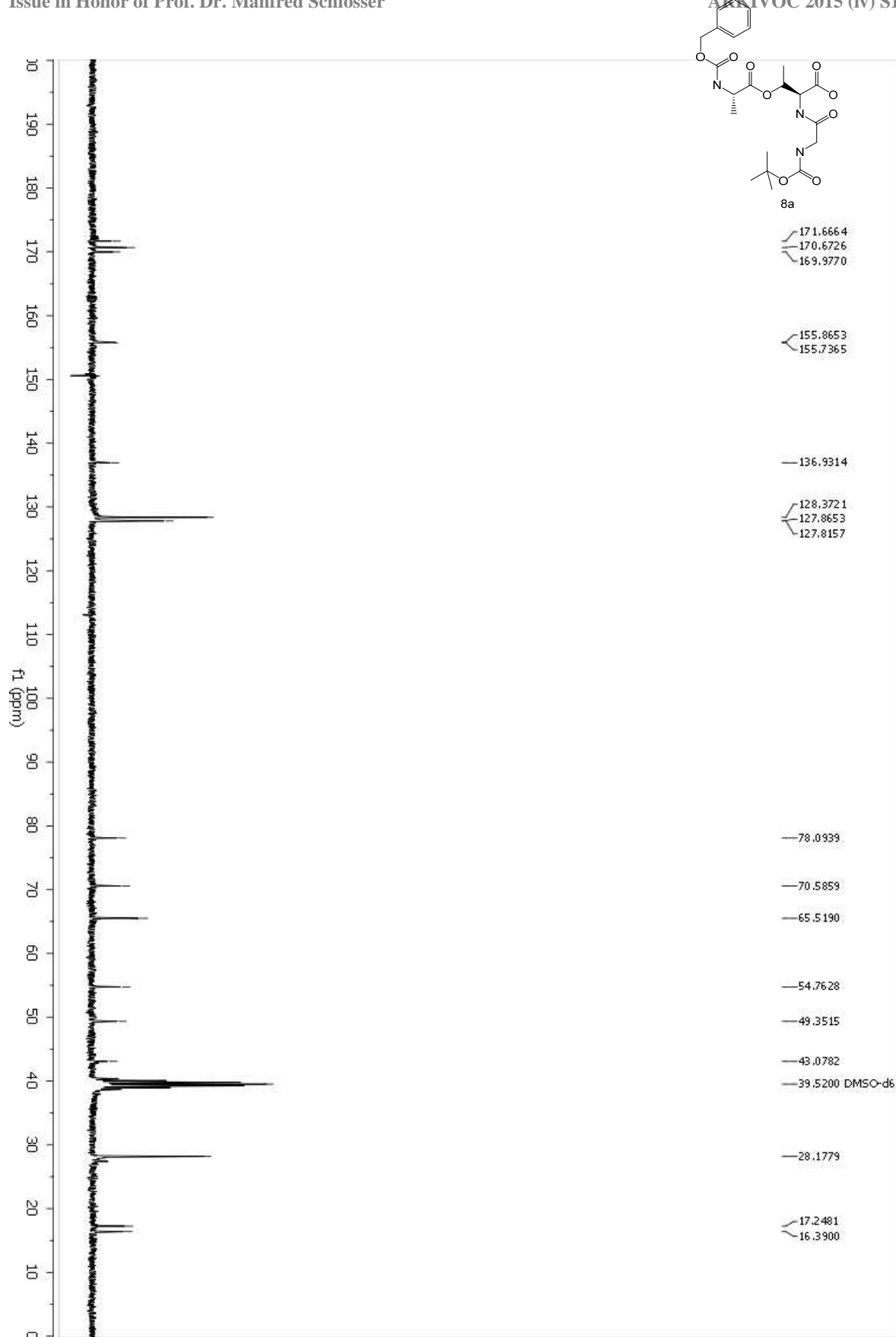




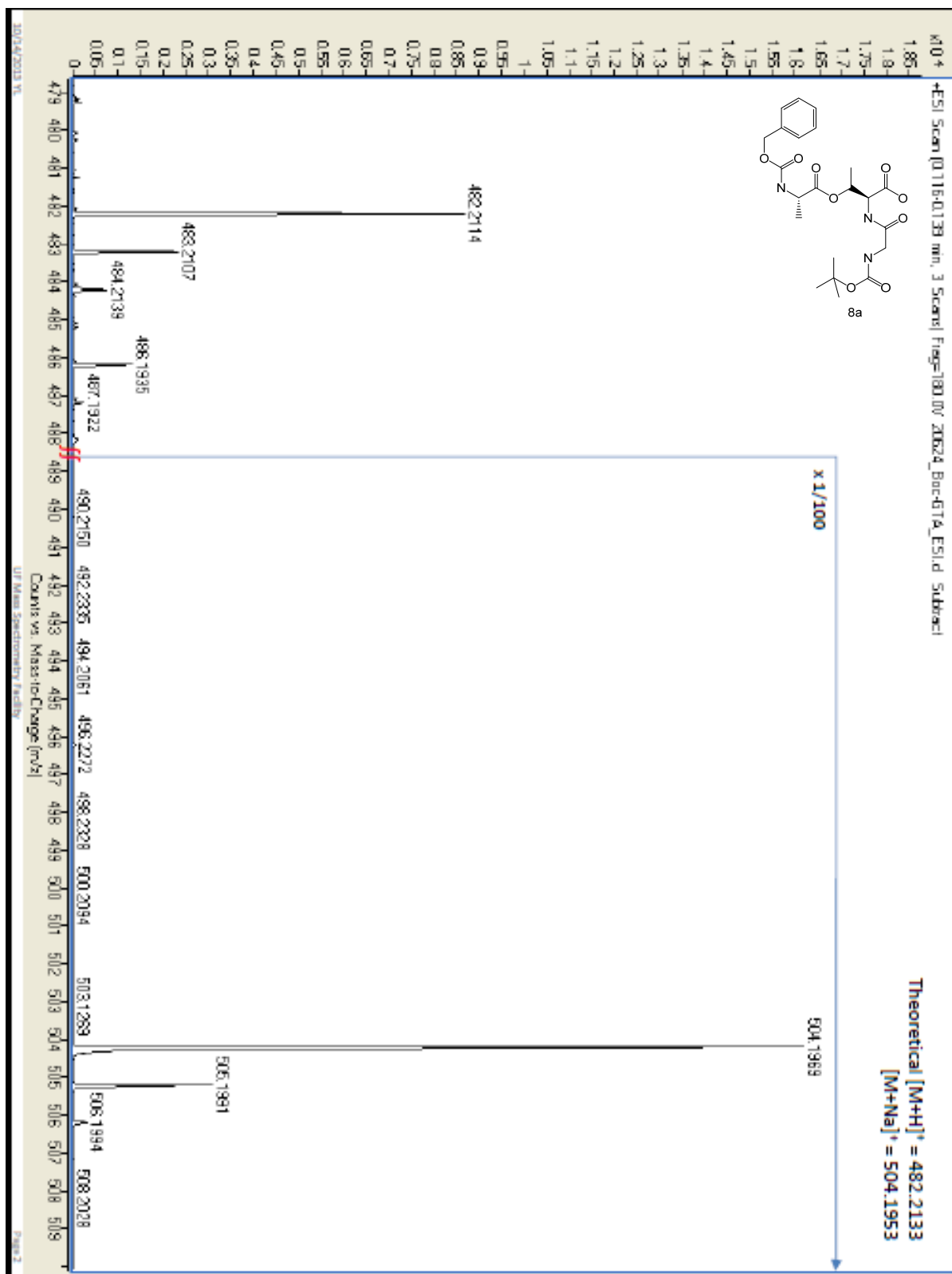


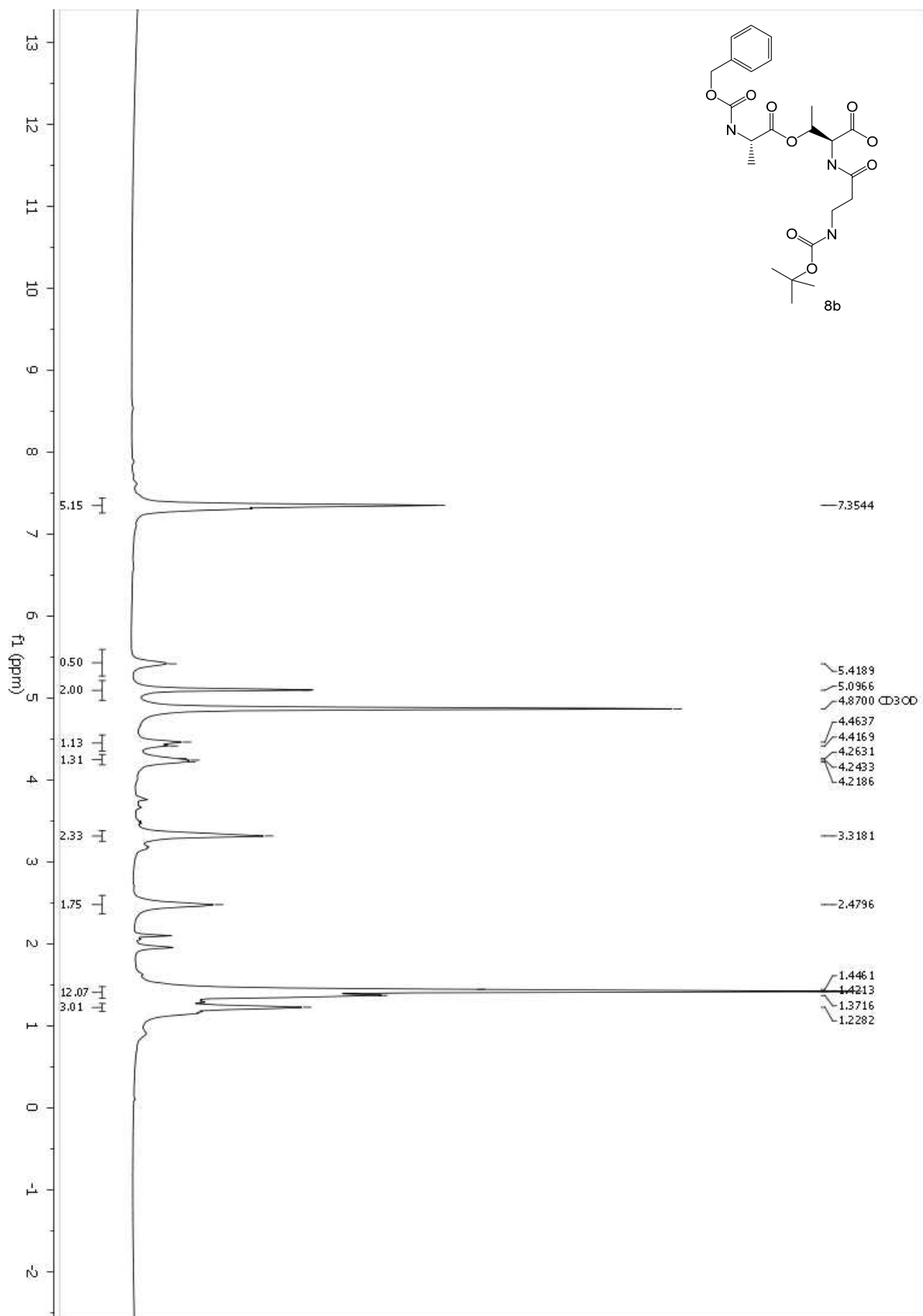


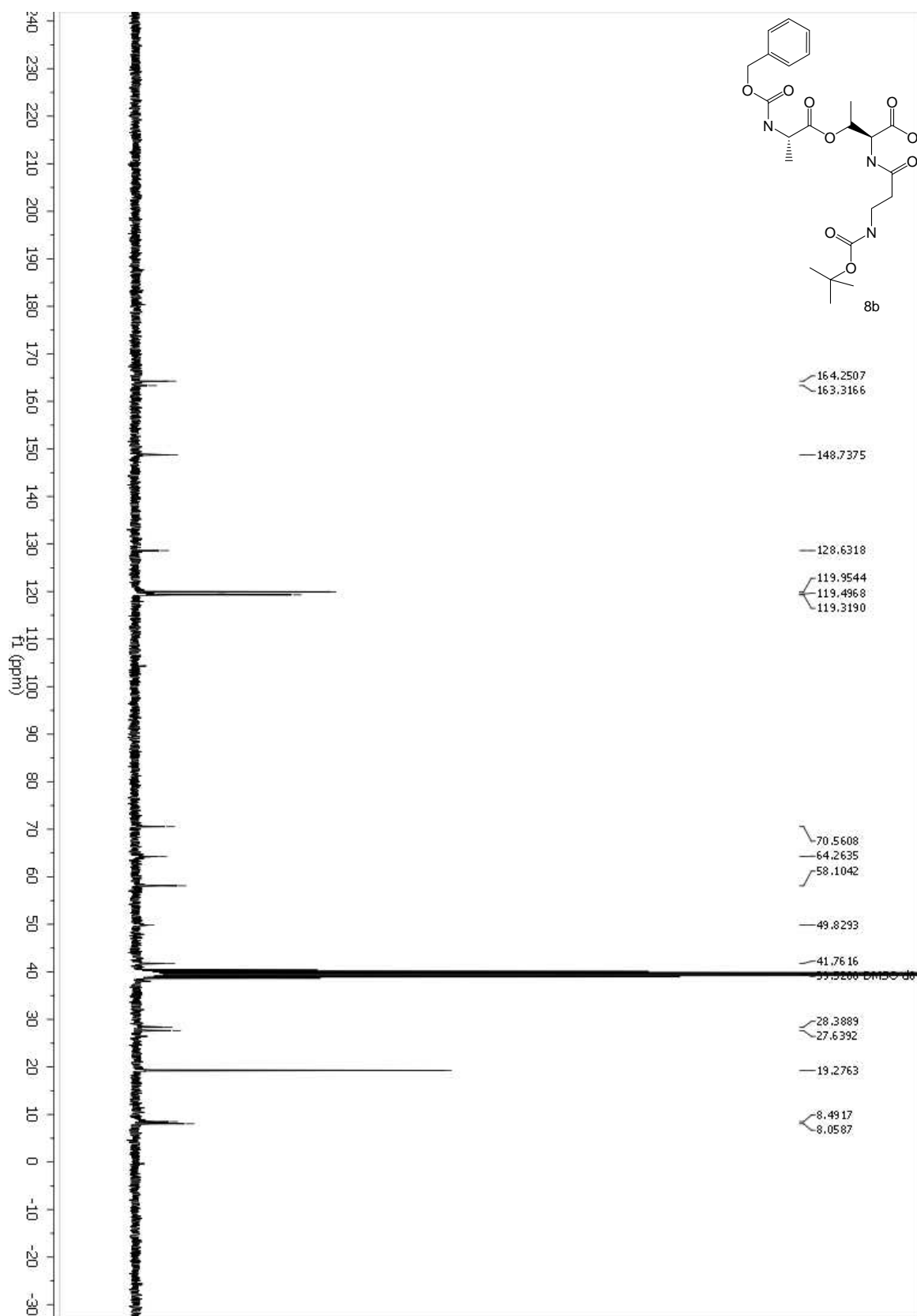


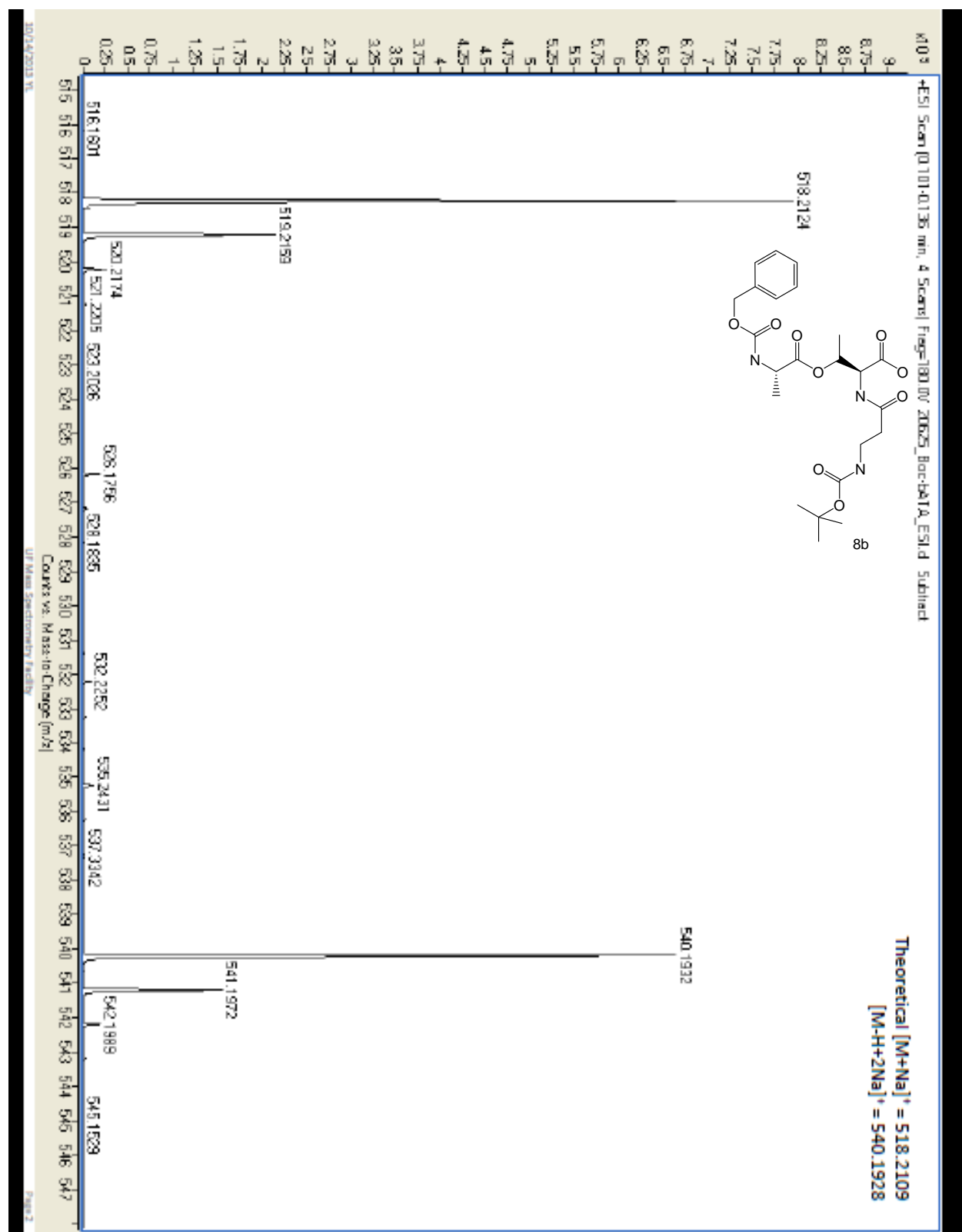


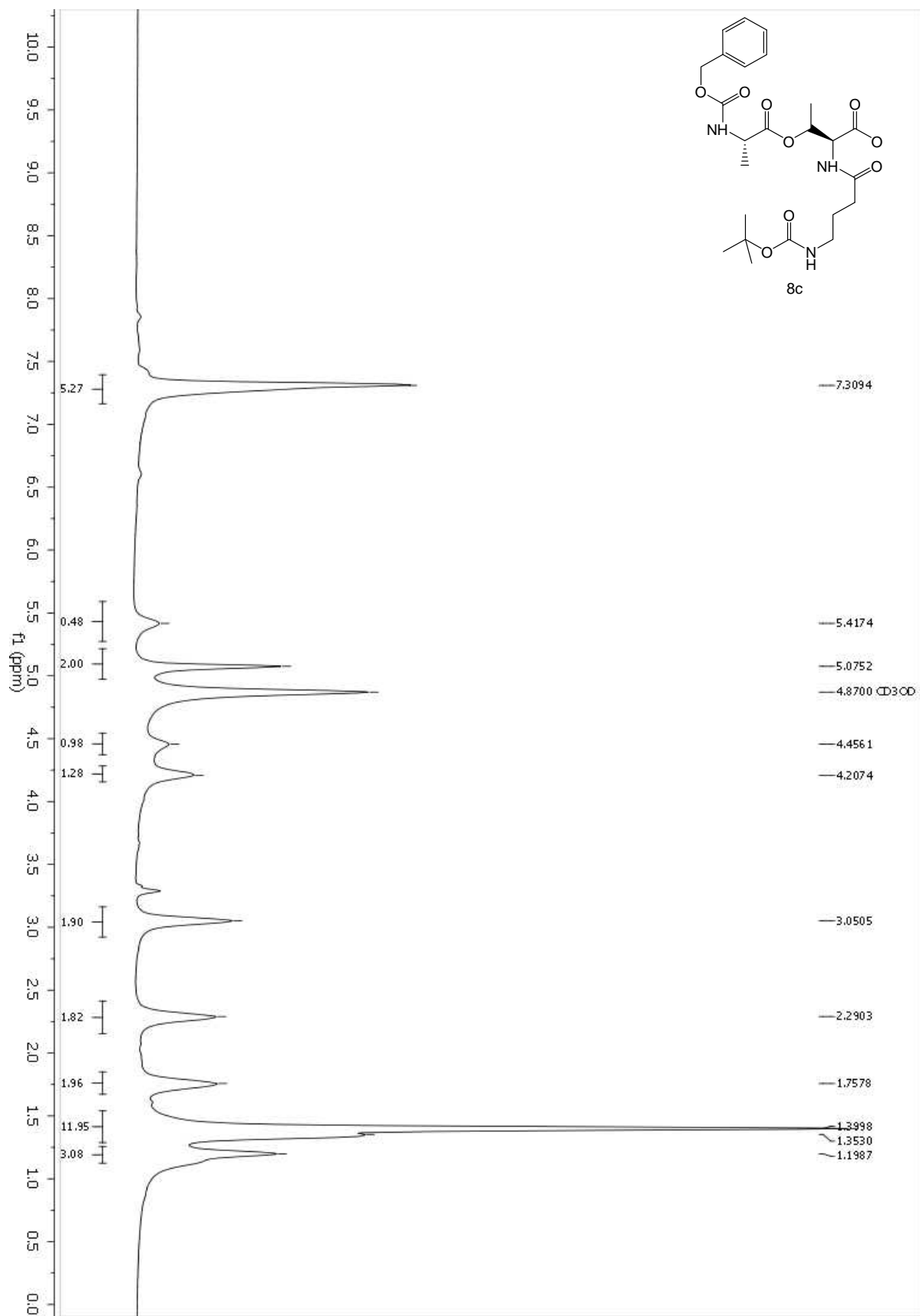


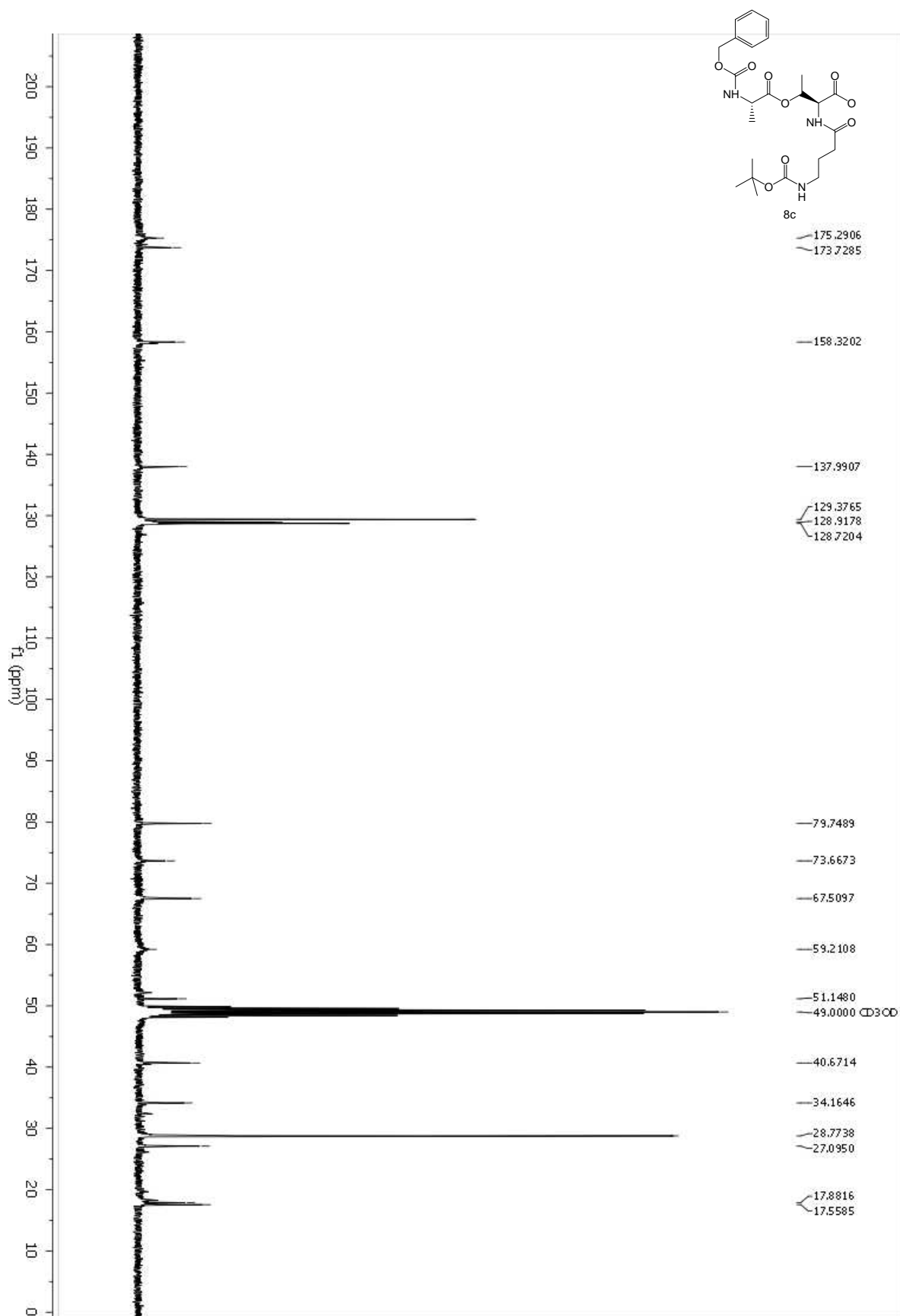


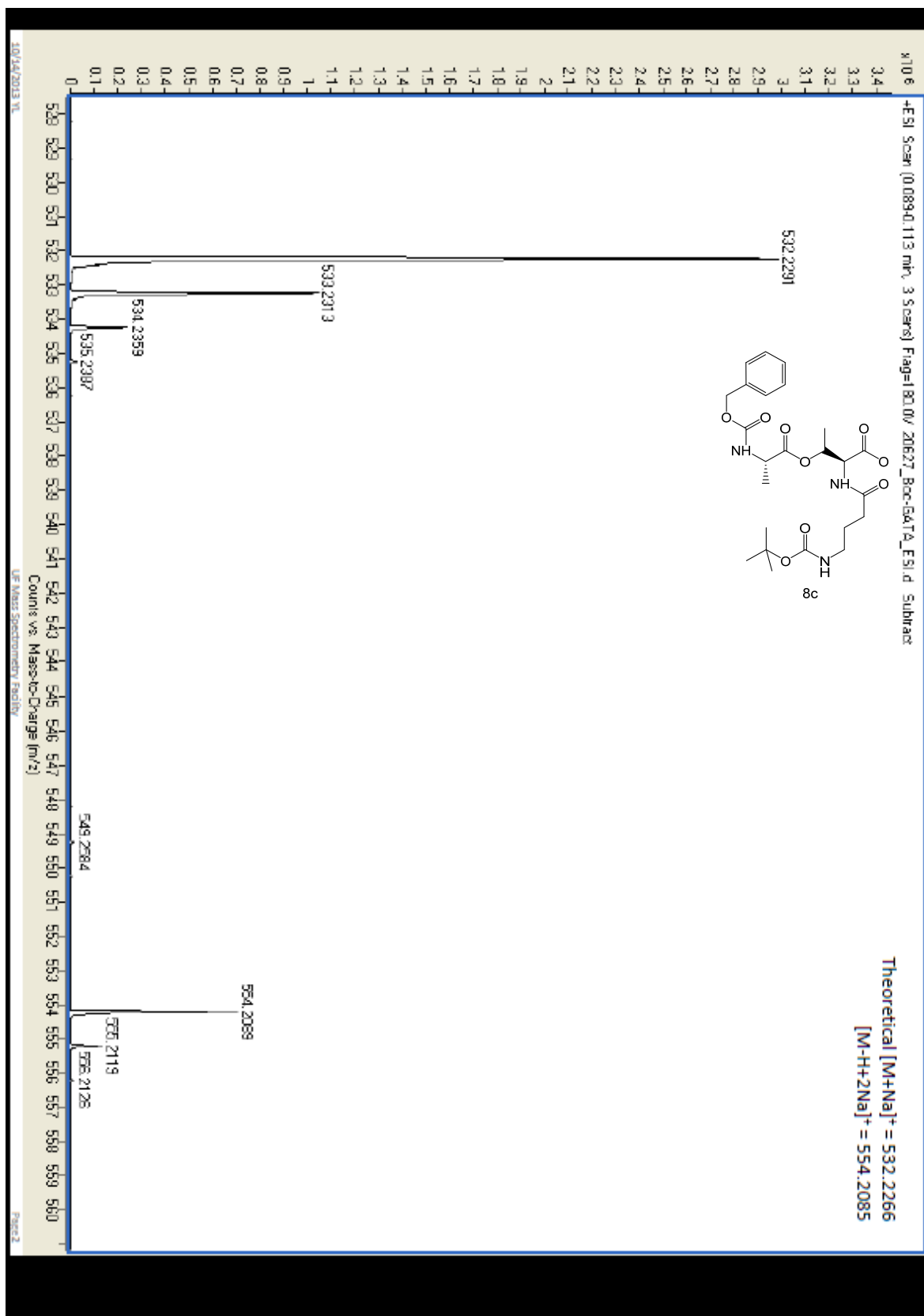


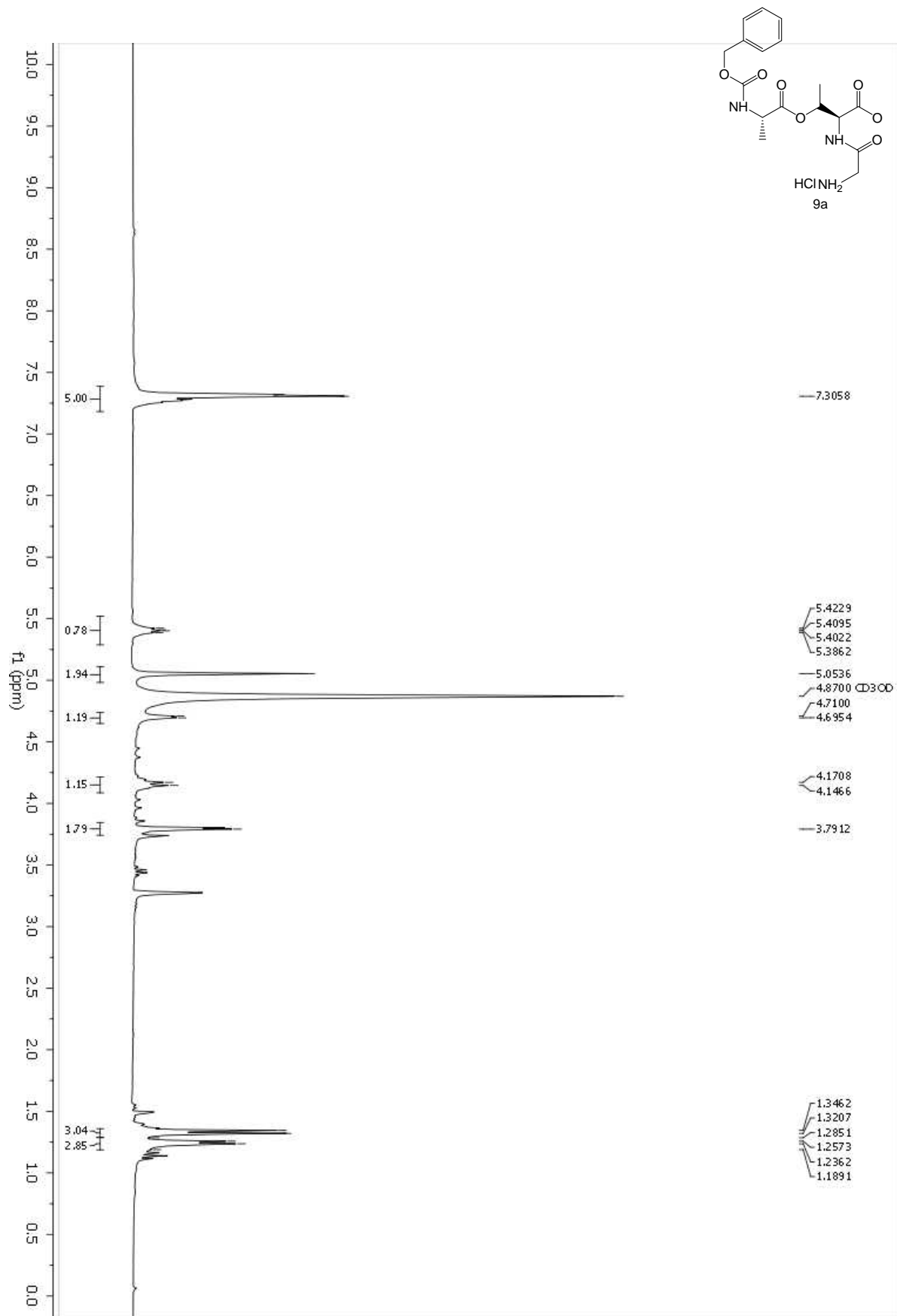




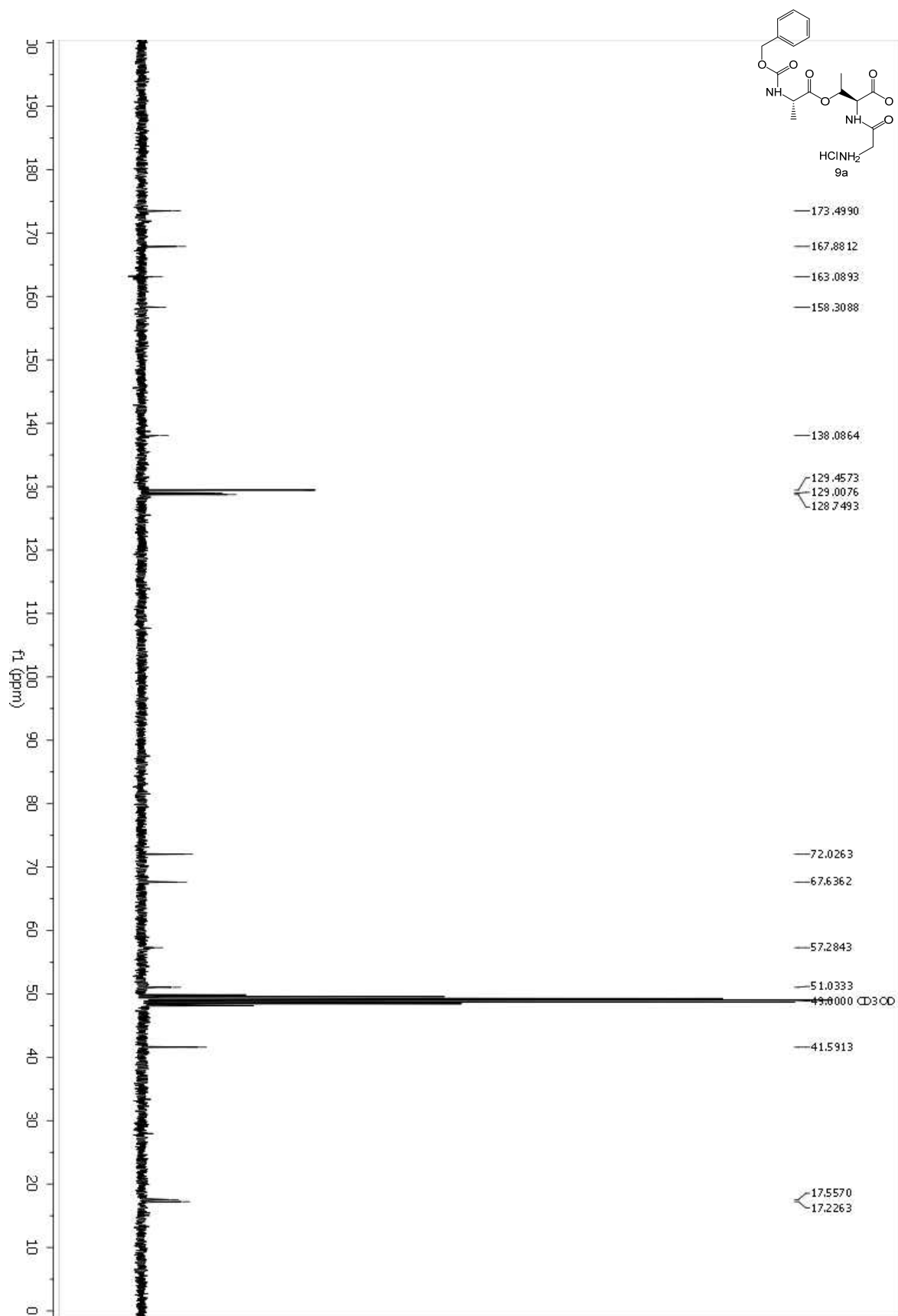


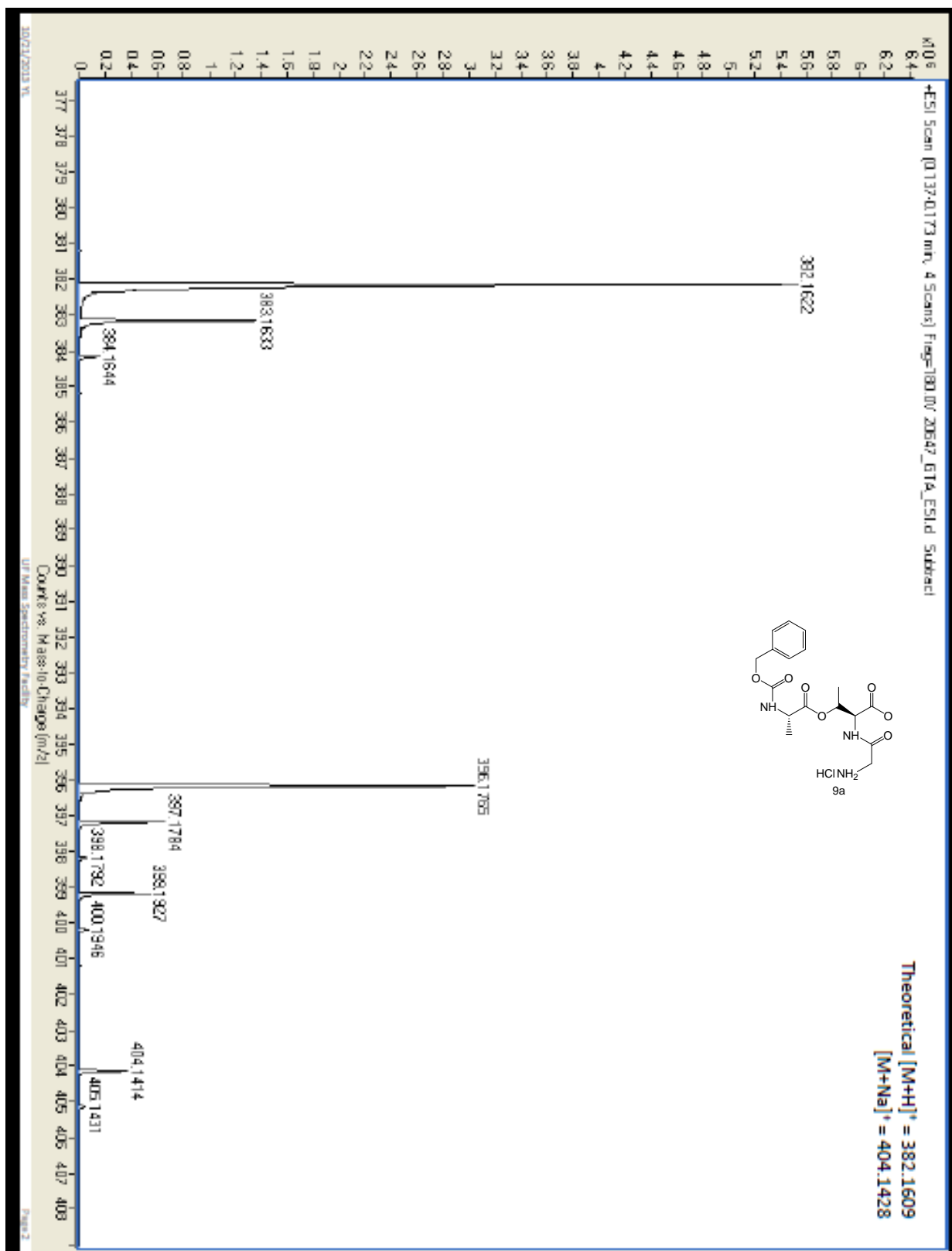


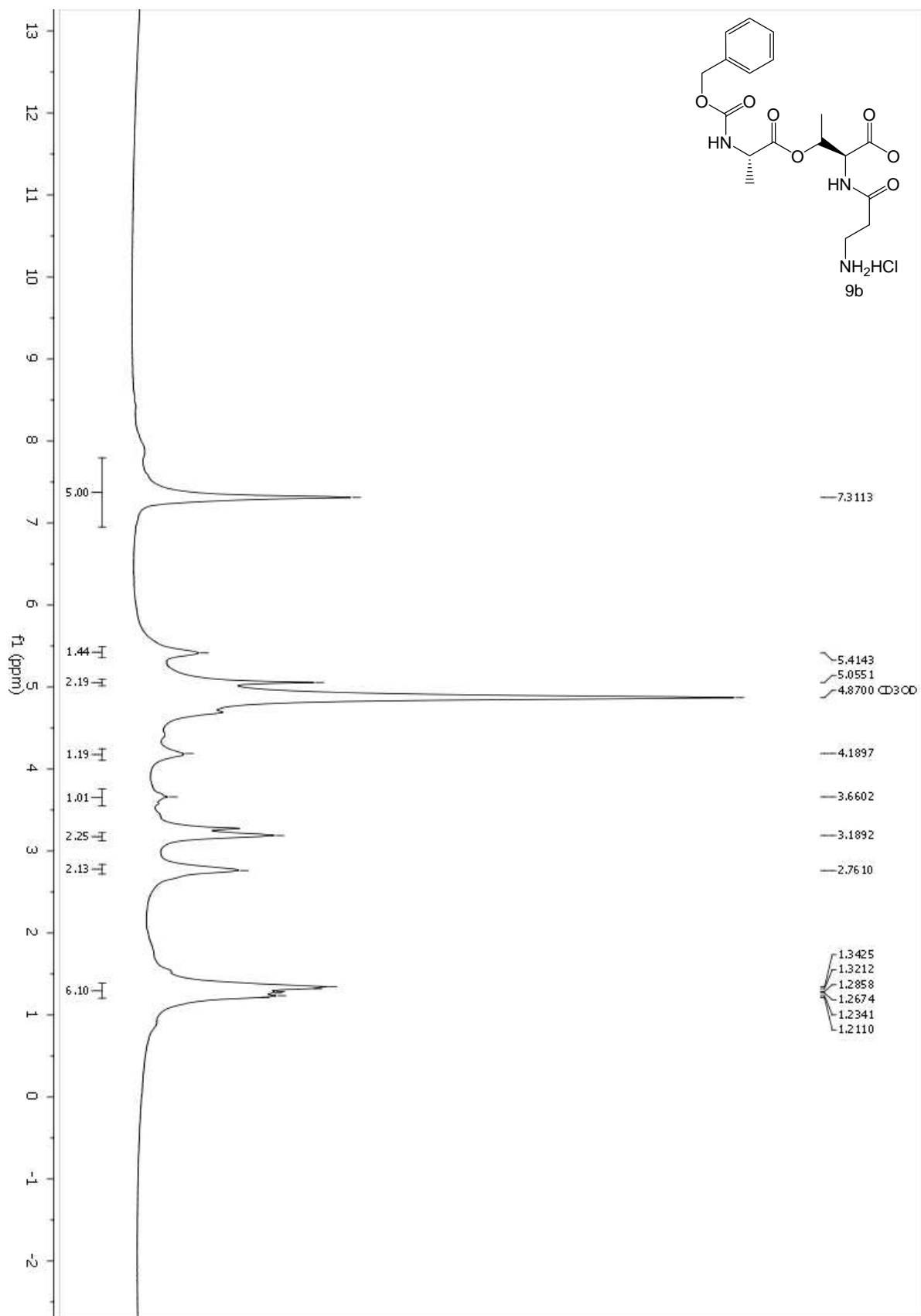


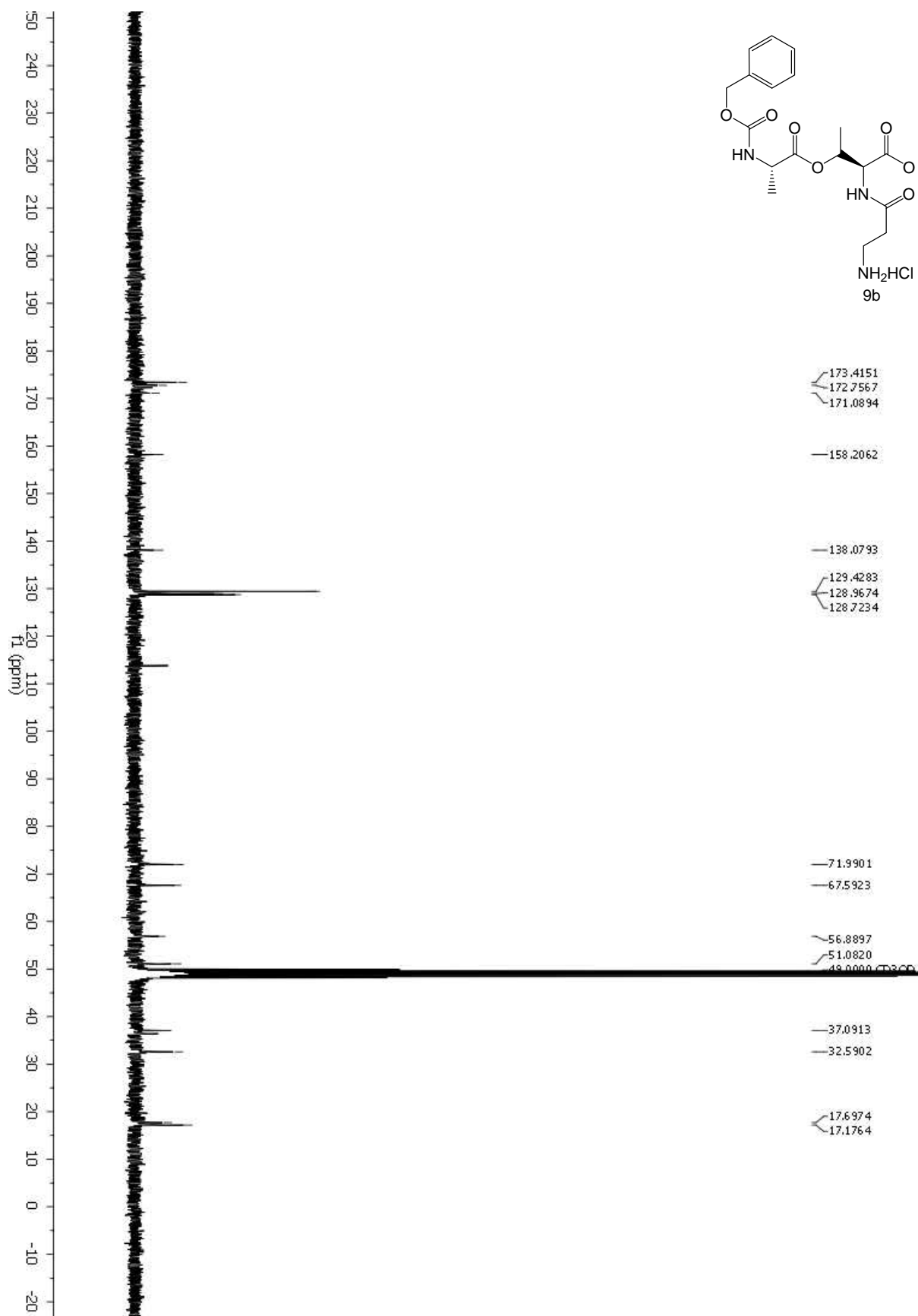


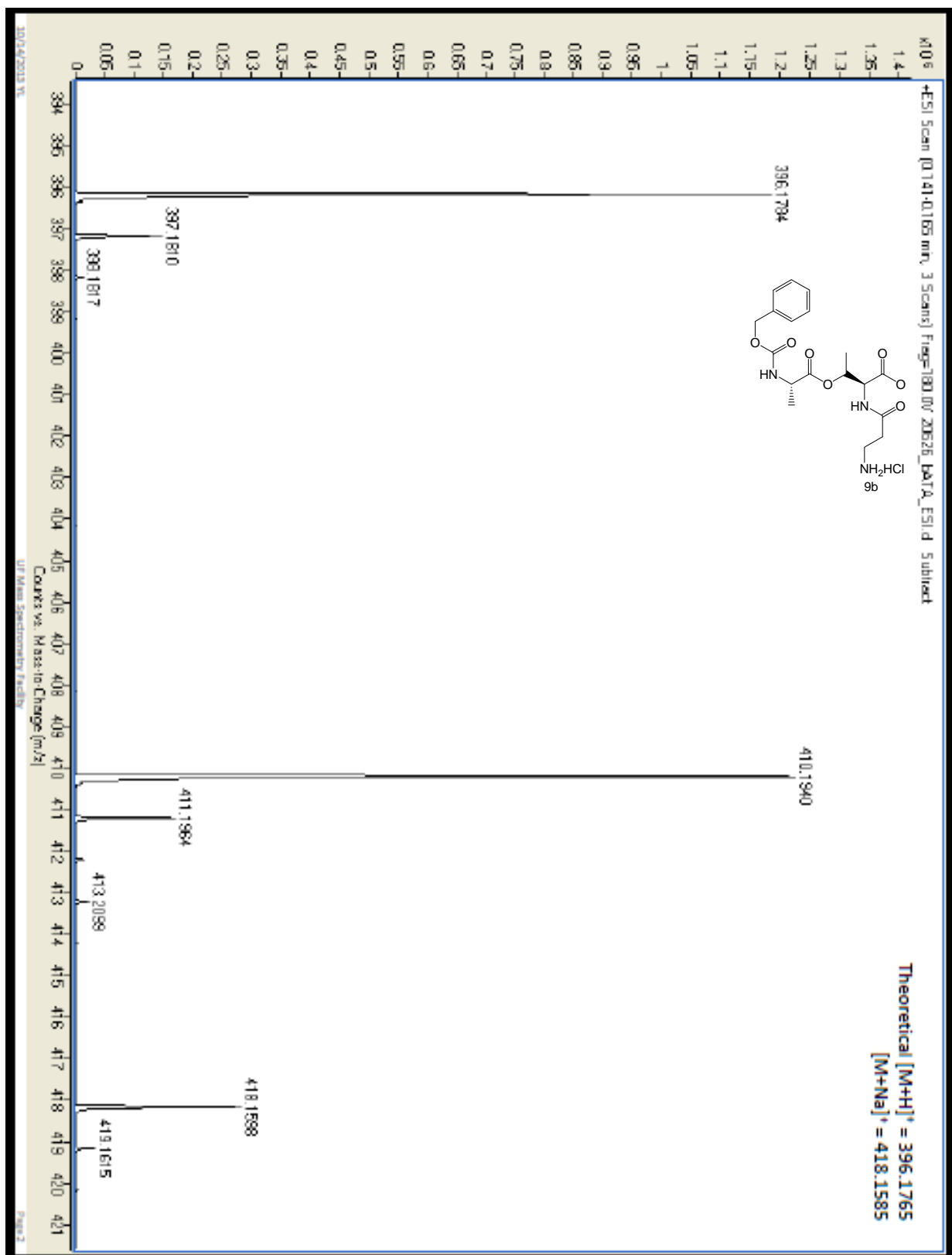


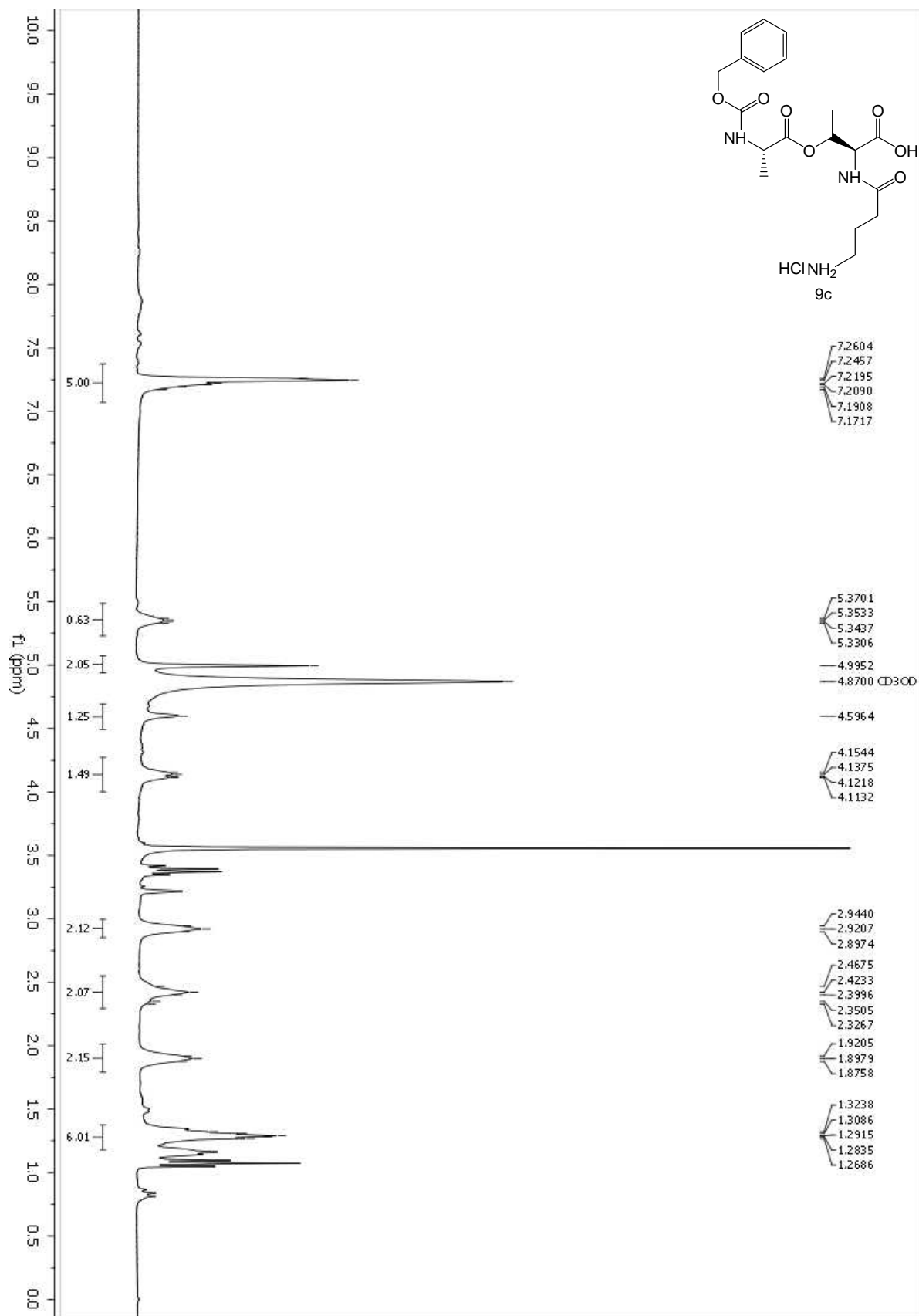


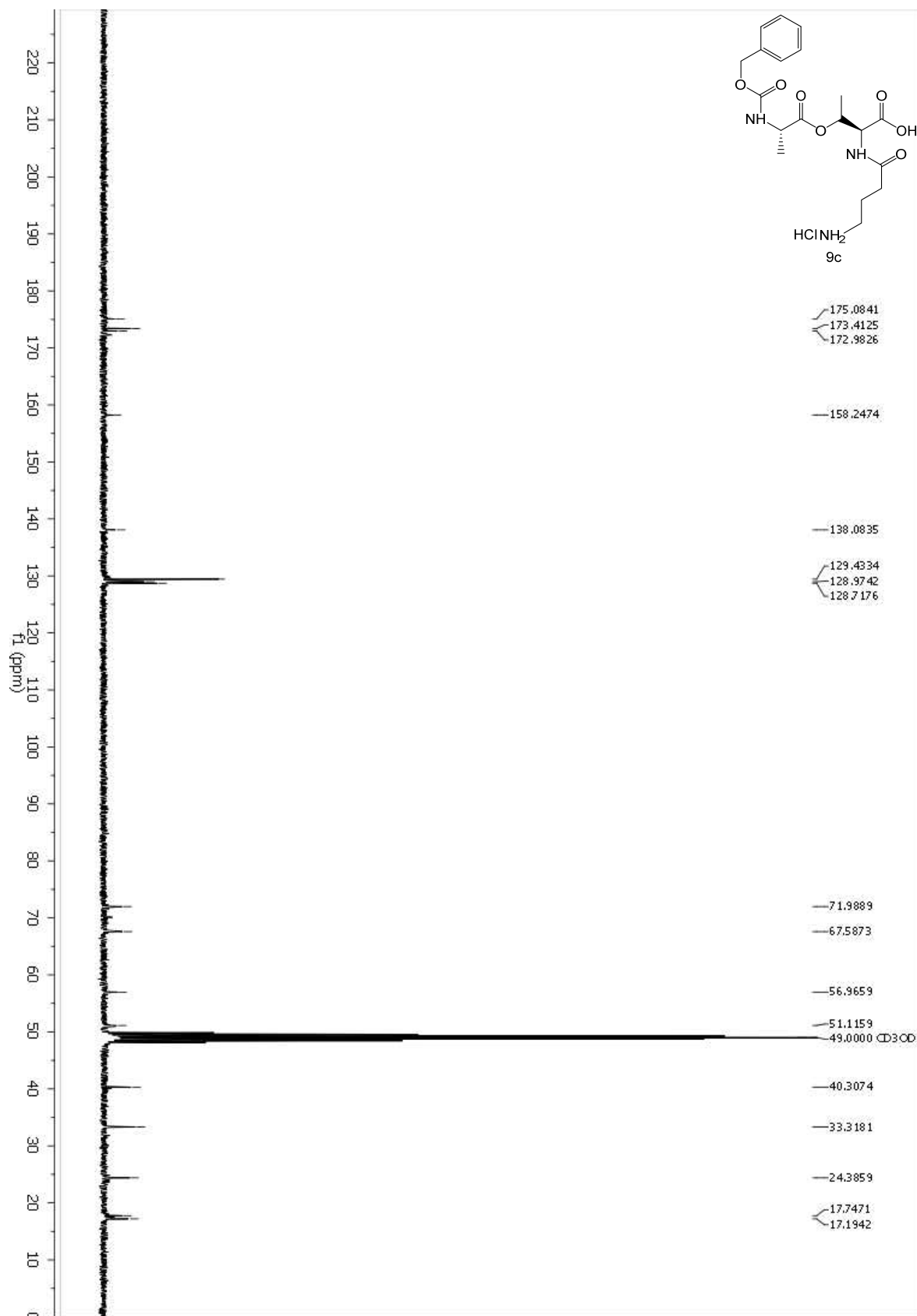


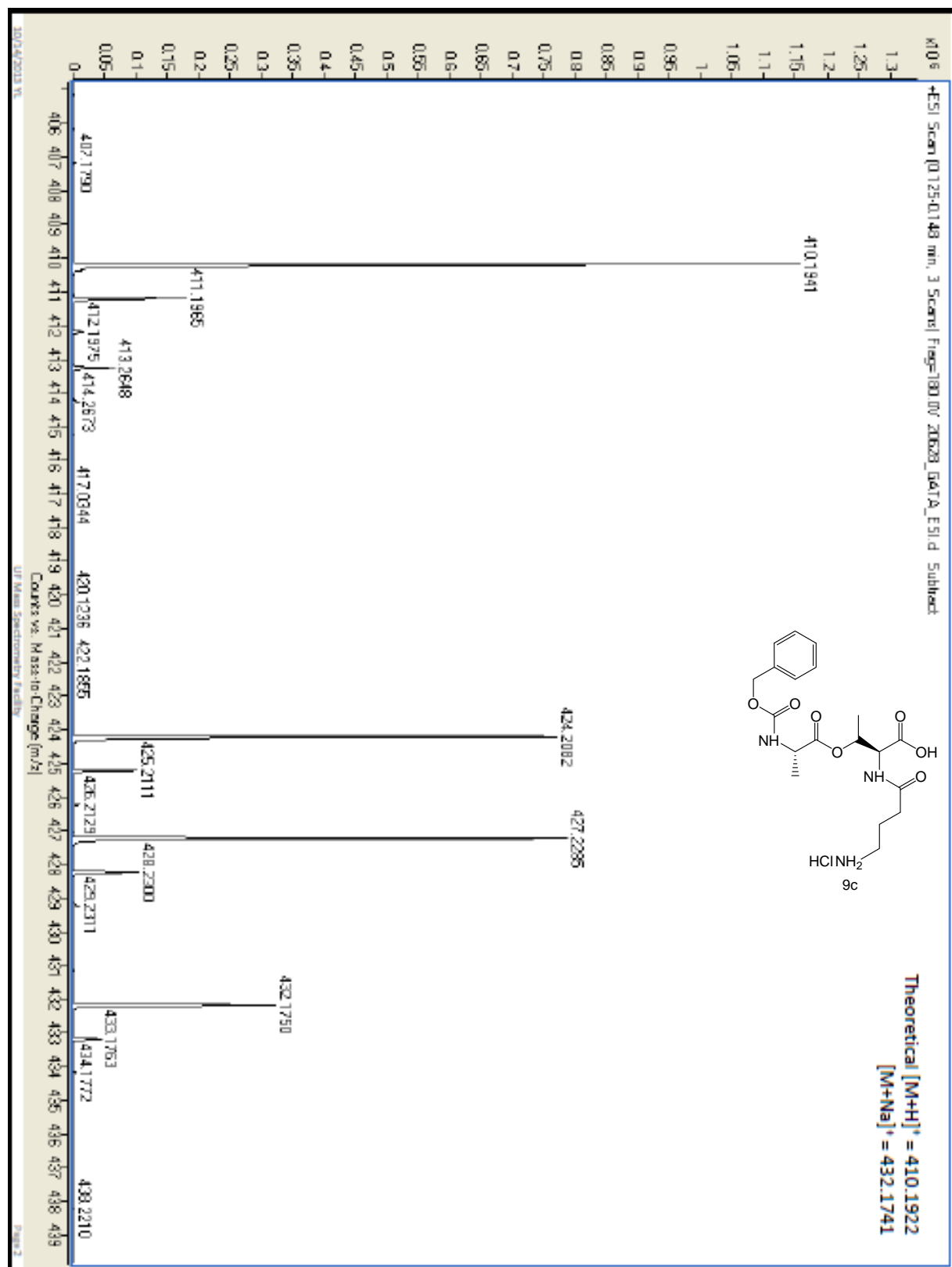








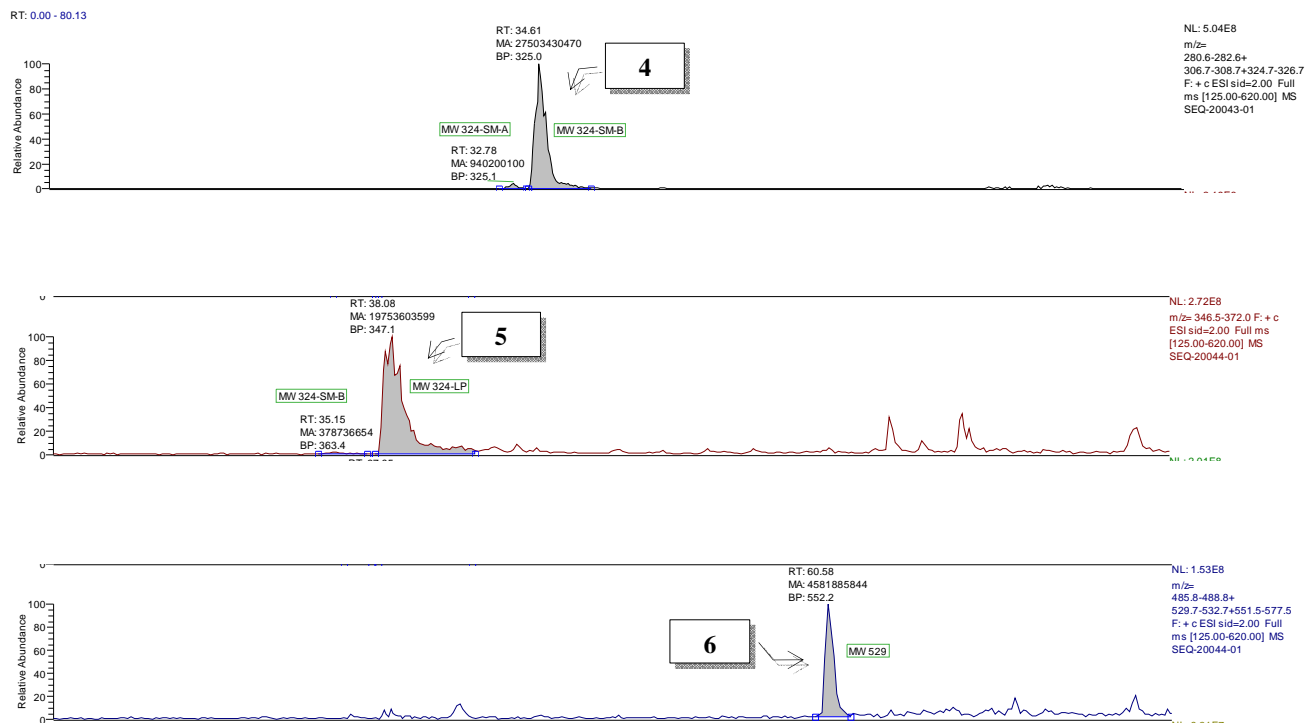






**HPLC chromatograms and ESI-MS for chemical ligation of 4 in buffer**

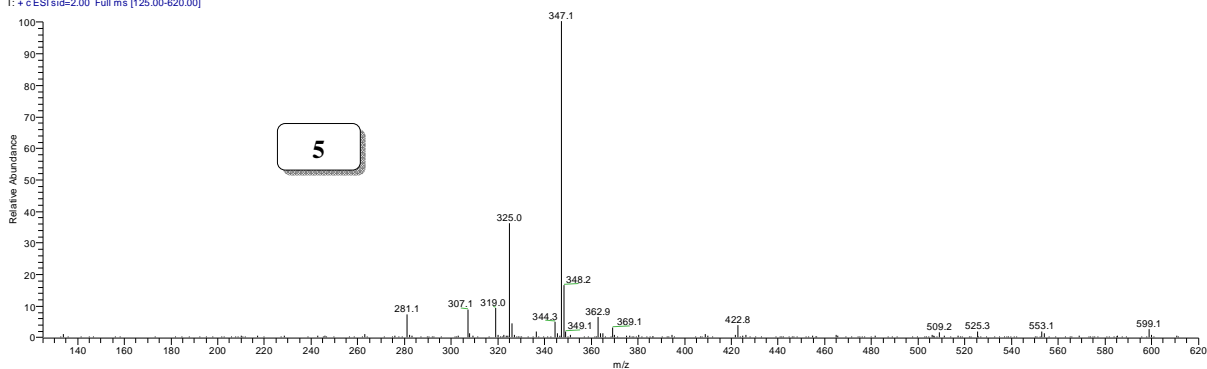
Summary Chromatogram: HPLC/(+)ESI-MS integrated ion-peaks for the **4** (top, rt 34.61), **5** (middle, rt 38.08), and **6** (bottom, rt 60.58).



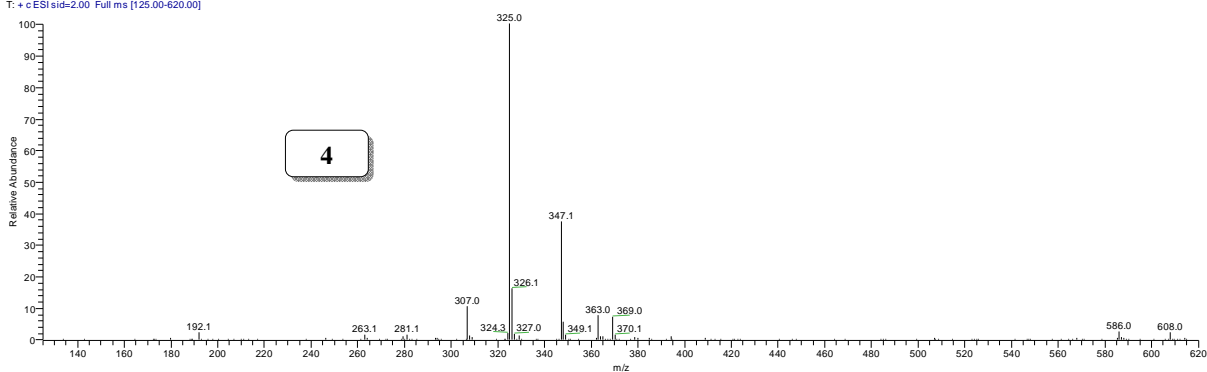
MW 324-LP **5** (top) and MW 324-SM **4** (bottom): (+)ESI-MS.

SEQ-20044-01 7/18/2013 6:47:02 PM 2181-5RS-LP; 5 uL  
Xerra MS C18:0.15:95:5(0)>65:35(10)>25:75(50)>5:95(60-75)

SEQ-20044-01 #1654-1726 RT: 37.60-38.56 AV: 9 SB: 4 36.90-37.18, 40.25-40.69 NL: 1.51E8  
T: + c ESI: sid=2.00 Full ms [125.00-620.00]

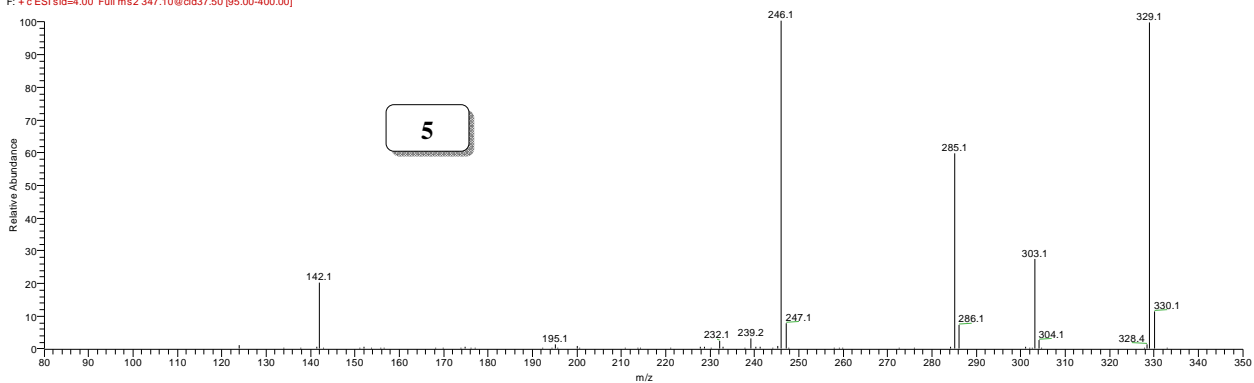


SEQ-20043-01 #1603-1660 RT: 34.40-35.04 AV: 7 SB: 4 33.64-33.79, 36.03-36.31 NL: 2.76E8  
T: + c ESI: sid=2.00 Full ms [125.00-620.00]

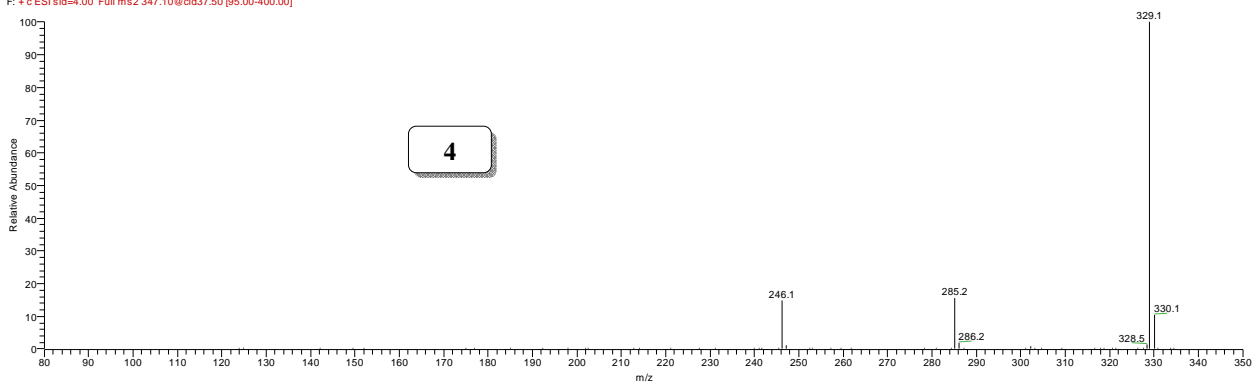


MW 324-LP **5** (top) and MW 324-SM **4** (bottom): (+)ESI-MS/MS of the  $m/z$  347  $[M+Na]^+$  ions.

SEQ-20044-01 7/18/2013 6:47:02 PM 2181-5RS-LP; 5  $\mu$ L  
Xterra MS C18.0.15.95.5(0)>65.35(10)>25.75(60)>5.95(60-75)  
SEQ-20044-01 #1650-1742 RT: 37.59-38.79 AV: 11 SB: 1 36.96-37.18 NL: 1.62E7  
F: + c ESI sid=4.00 Full ms2 347.10@cid37.50 [95.00-400.00]



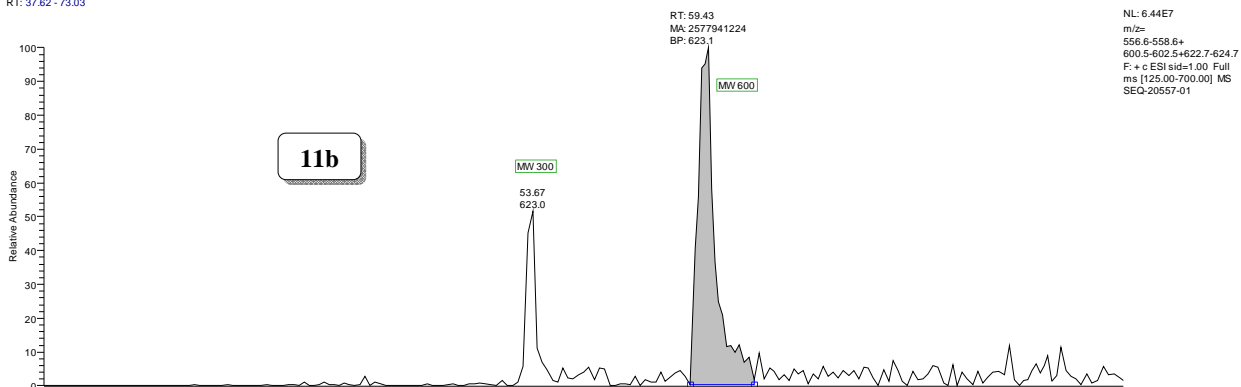
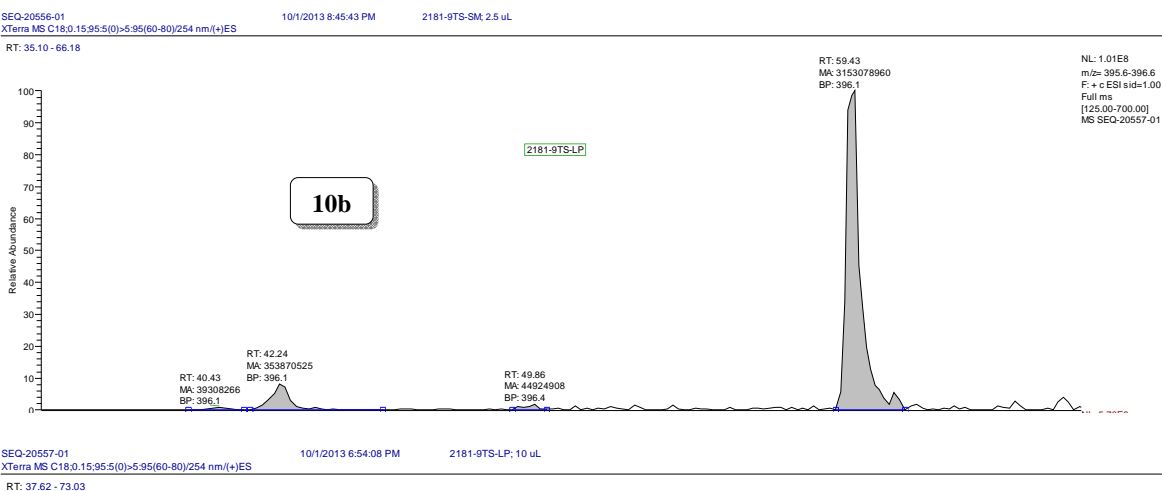
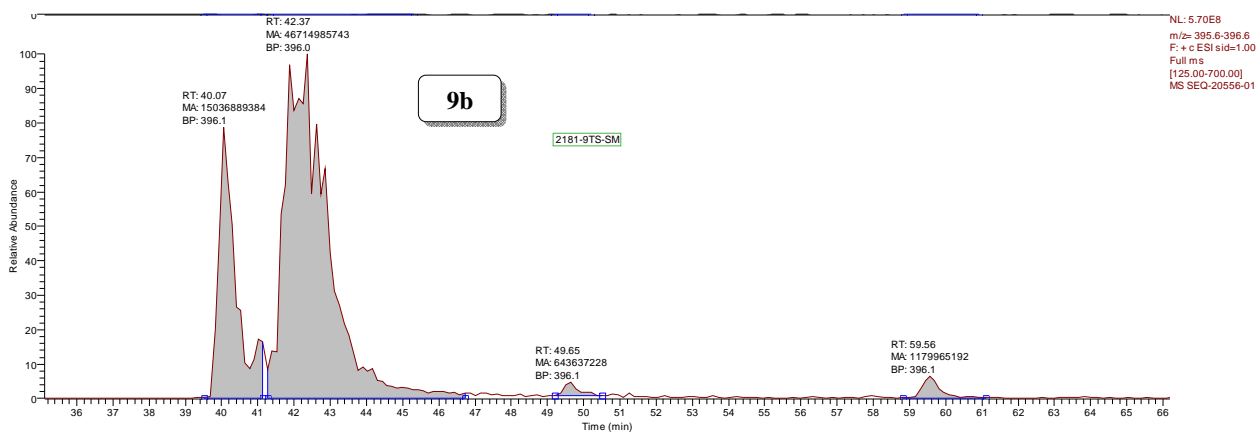
SEQ-20043-01 #1589-1678 RT: 34.17-35.25 AV: 11 SB: 2 33.61-33.88 NL: 5.63E7  
F: + c ESI sid=4.00 Full ms2 347.10@cid37.50 [95.00-400.00]

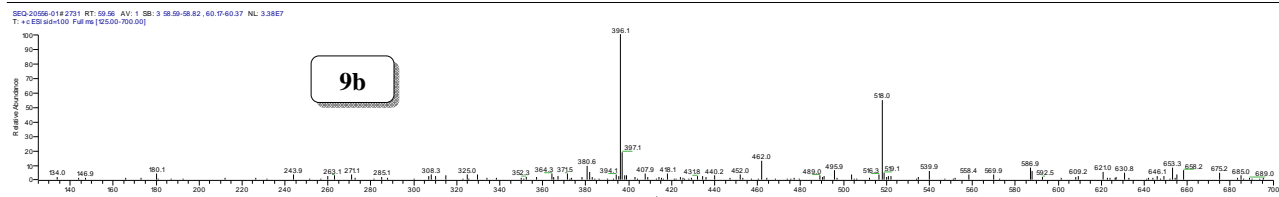
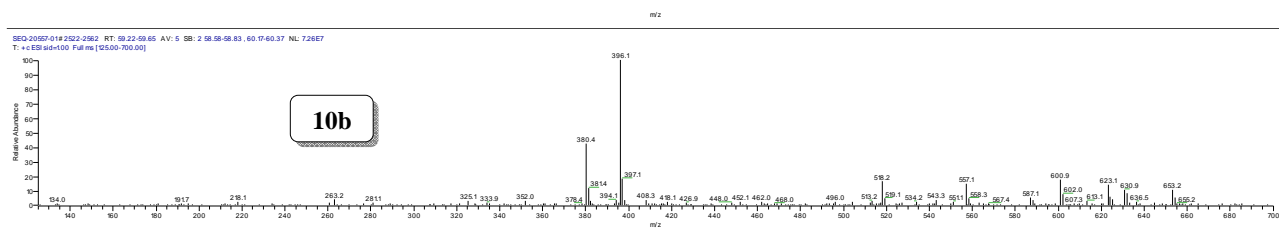


MW 324-LP **5** (top two) and MW 324-SM **4** (bottom two): (+)ESI-MS/MS (top and 3<sup>rd</sup>) and -MS/MS/MS (2<sup>nd</sup> and bottom) of the m/z 325 [M+H]<sup>+</sup> ions.



Summary Chromatogram: HPLC/(+)ESI-MS integrated ion-peaks for the **4** (top, rt 34.61), **5** (middle, rt 38.08), and **6** (bottom, rt 60.58).



MW 395 isomers: (+)ESI-MS for RT 59.5 min LP **10b** (top) and SM **9b** (bottom).MW 395, RT 59.5 min: (+)ESI-MS/MS of m/z 396 [M+H]<sup>+</sup> ions for LP (top) and SM (bottom).