

# Development of an Orthogonal Protection Strategy for the Synthesis of Mycobacterial Arabinomannan Fragments

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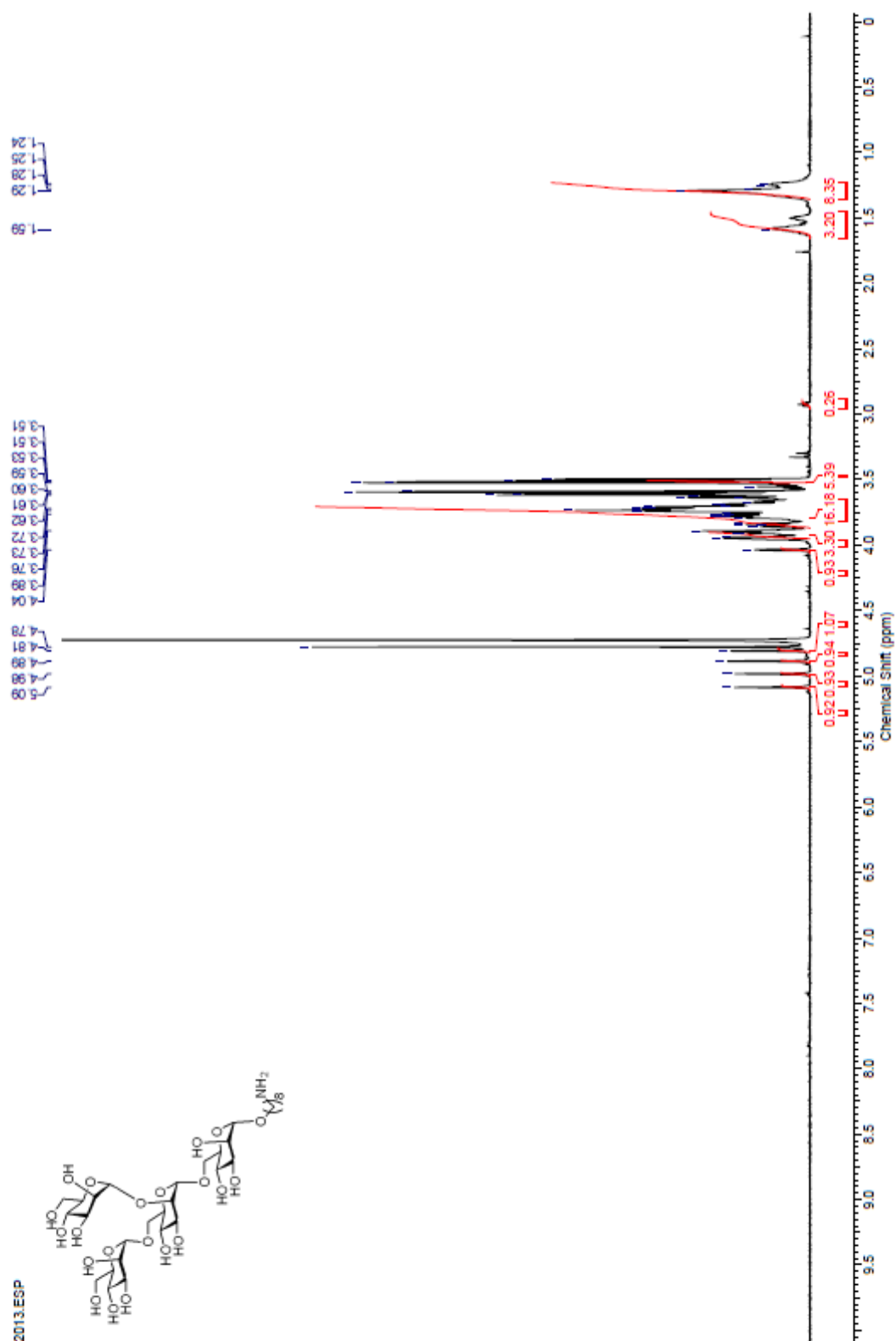
## Supporting Information

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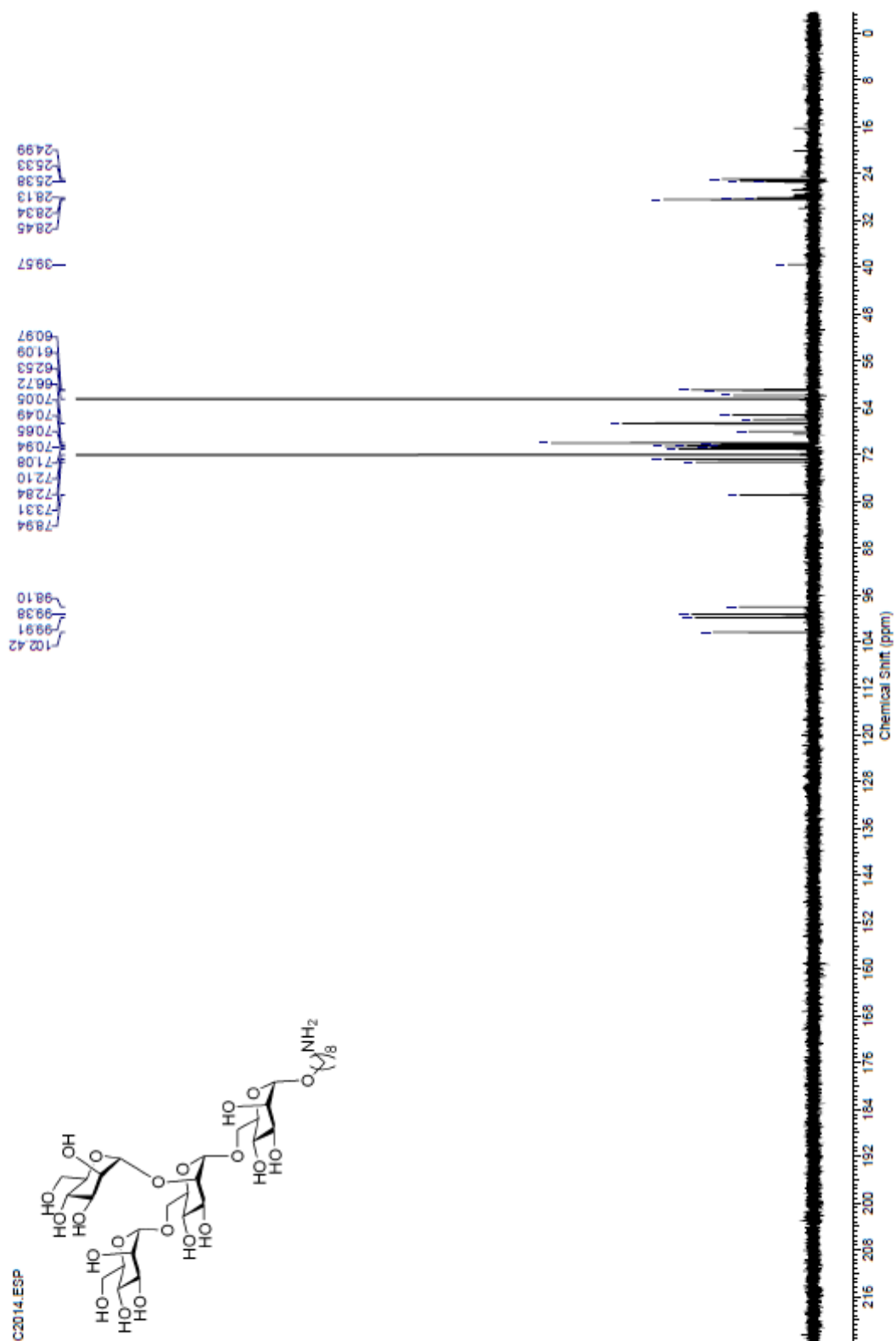
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| Summary of chemical shifts (ppm) of the anomeric carbon and hydrogen resonances |                |

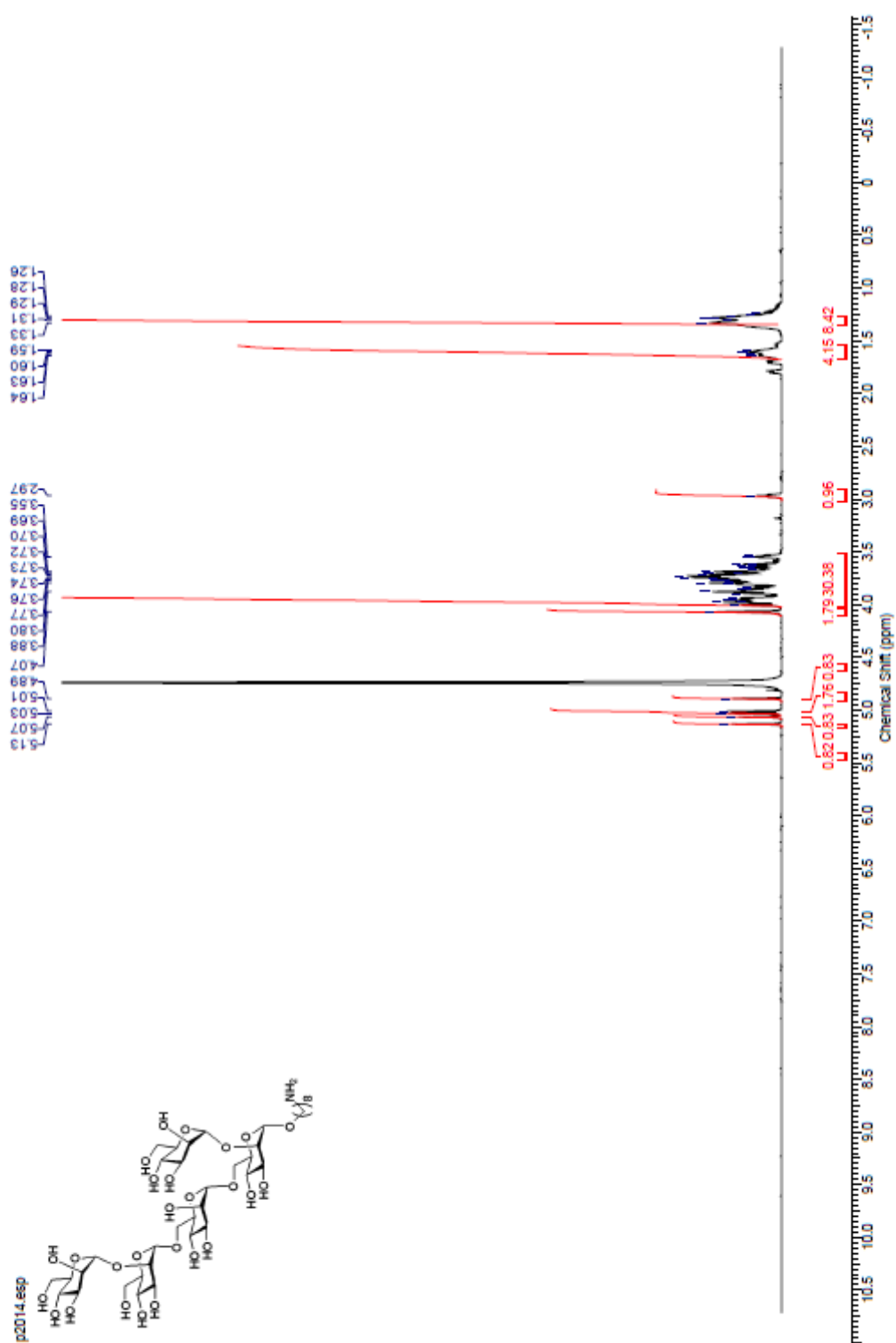
$^1\text{H}$  NMR for compound **1** (600 MHz,  $\text{D}_2\text{O}$ )

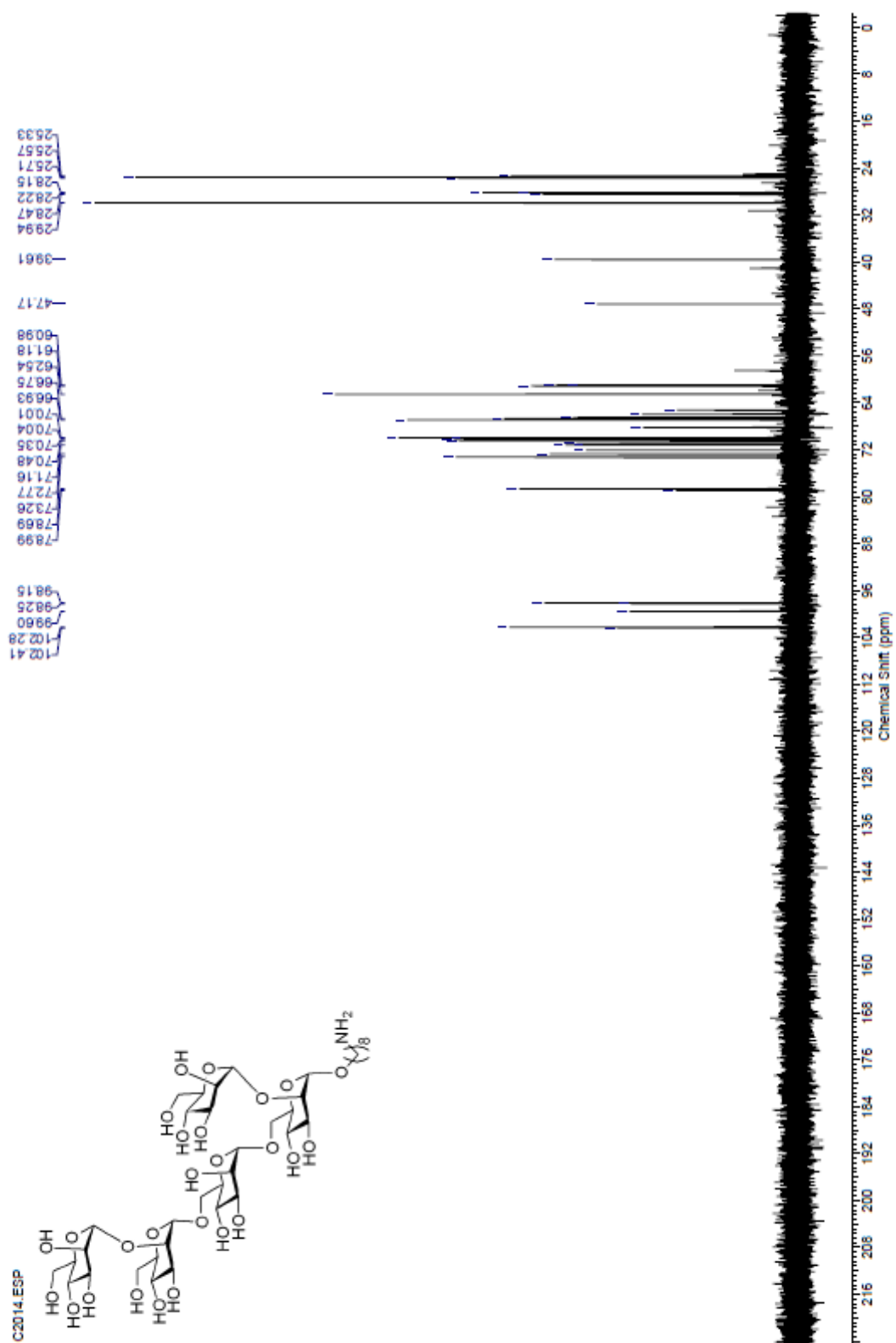


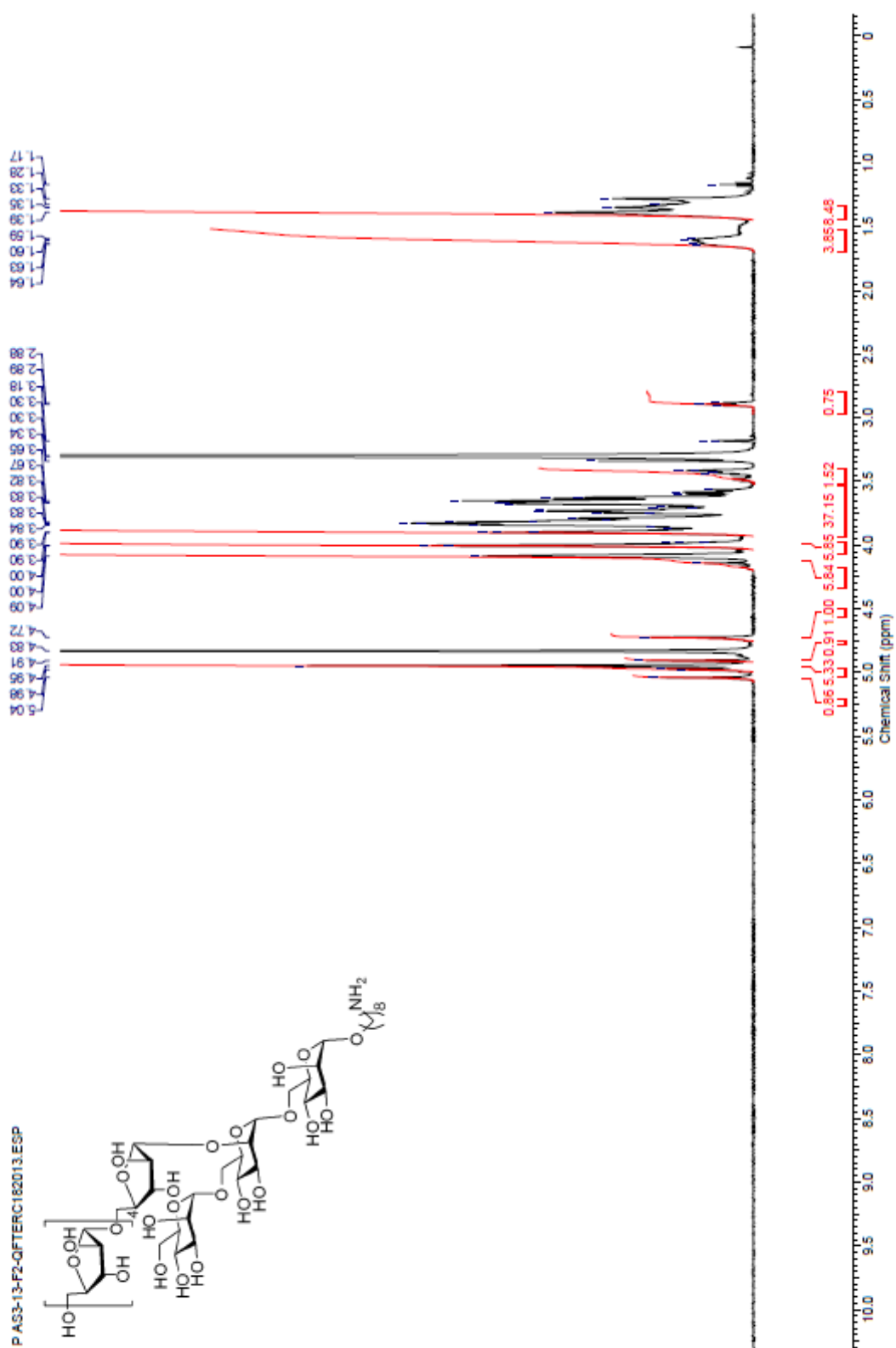
$^{13}\text{C}$  NMR for compound **1** (126 MHz,  $\text{D}_2\text{O}$ )



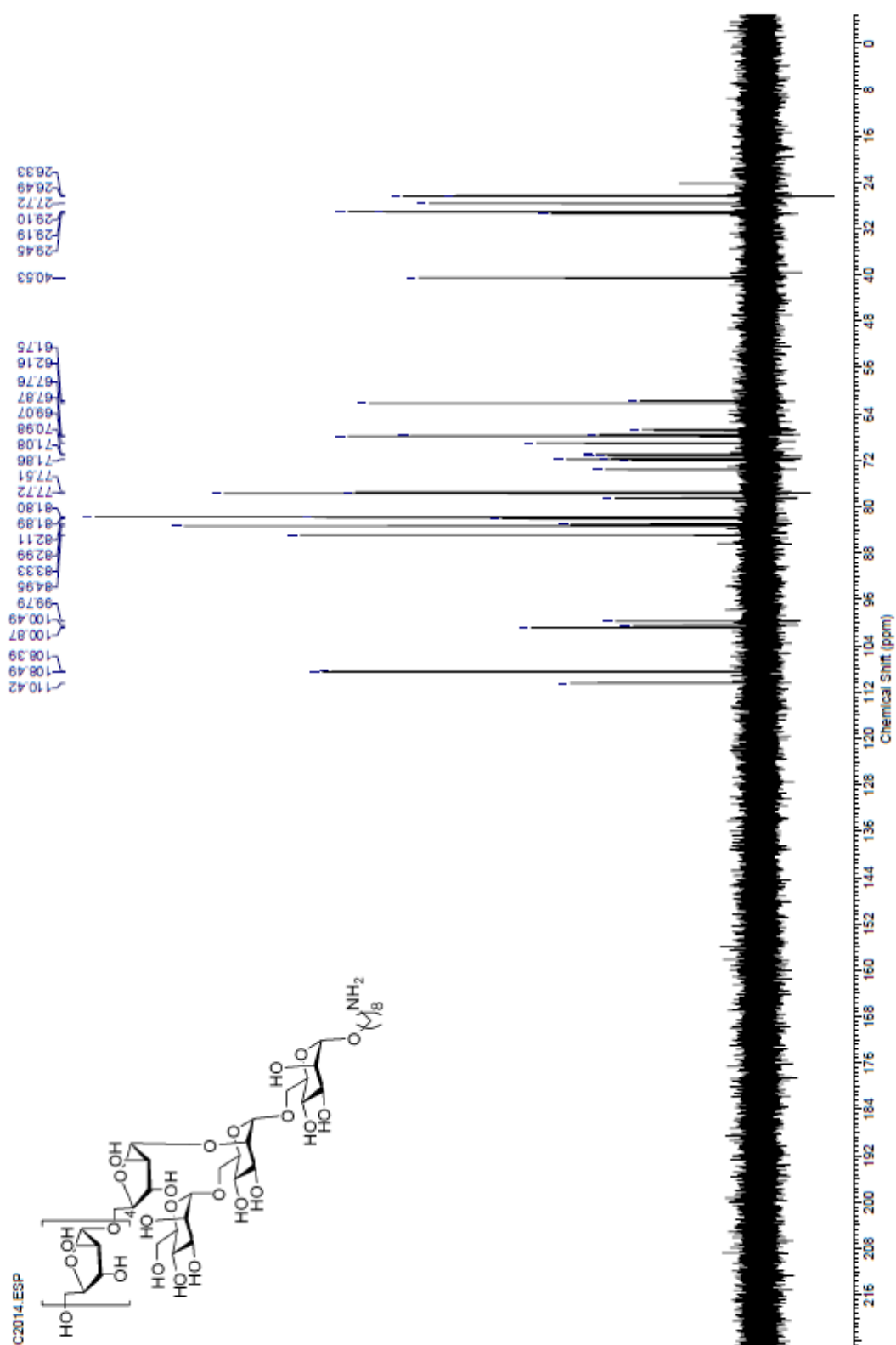
$^1\text{H}$  NMR for compound **2** (700 MHz,  $\text{D}_2\text{O}$ )



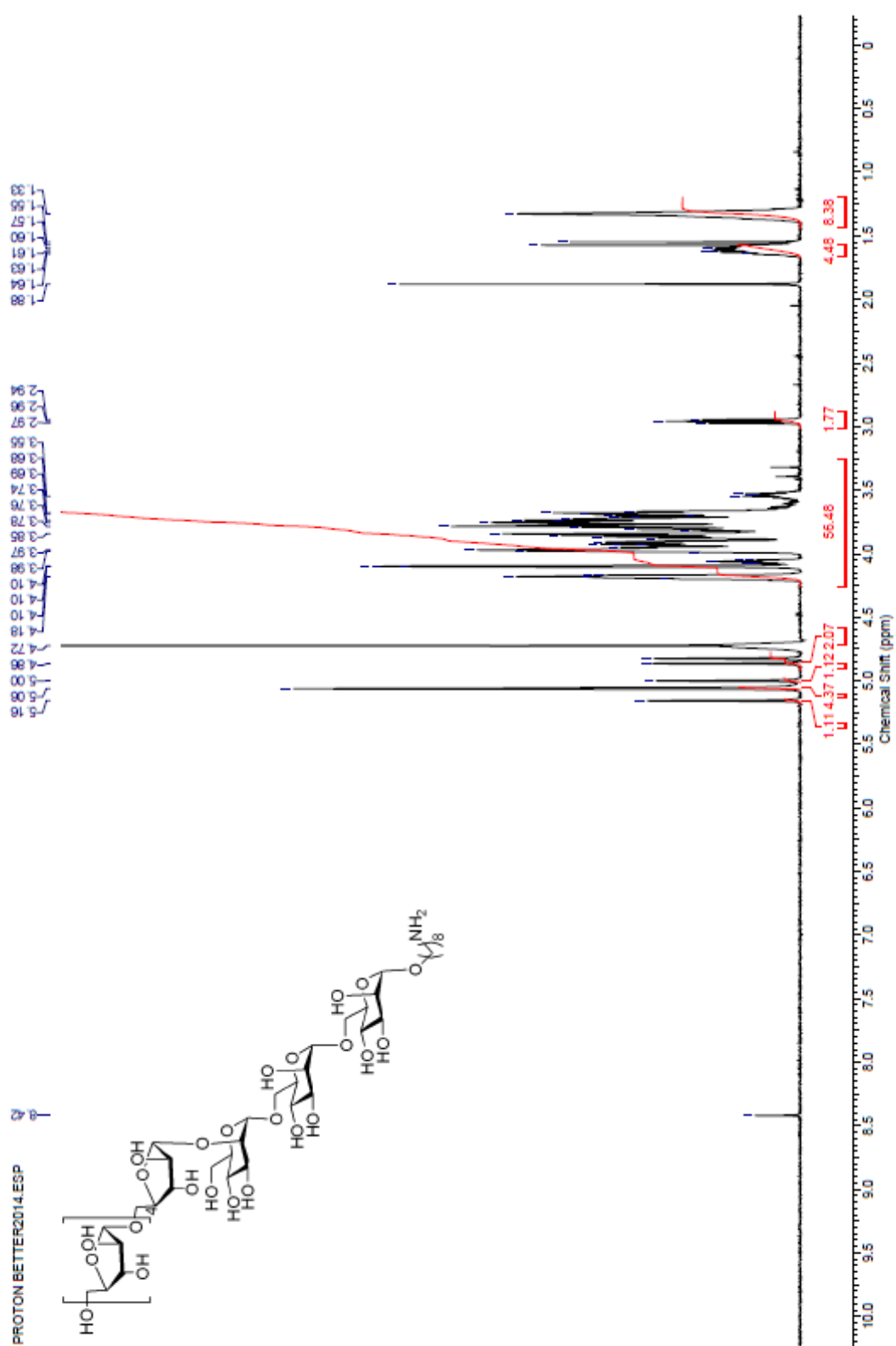
$^{13}\text{C}$  NMR for compound **2** (151 MHz,  $\text{D}_2\text{O}$ )

<sup>1</sup>H NMR for compound **3** (600 MHz, CD<sub>3</sub>OD)

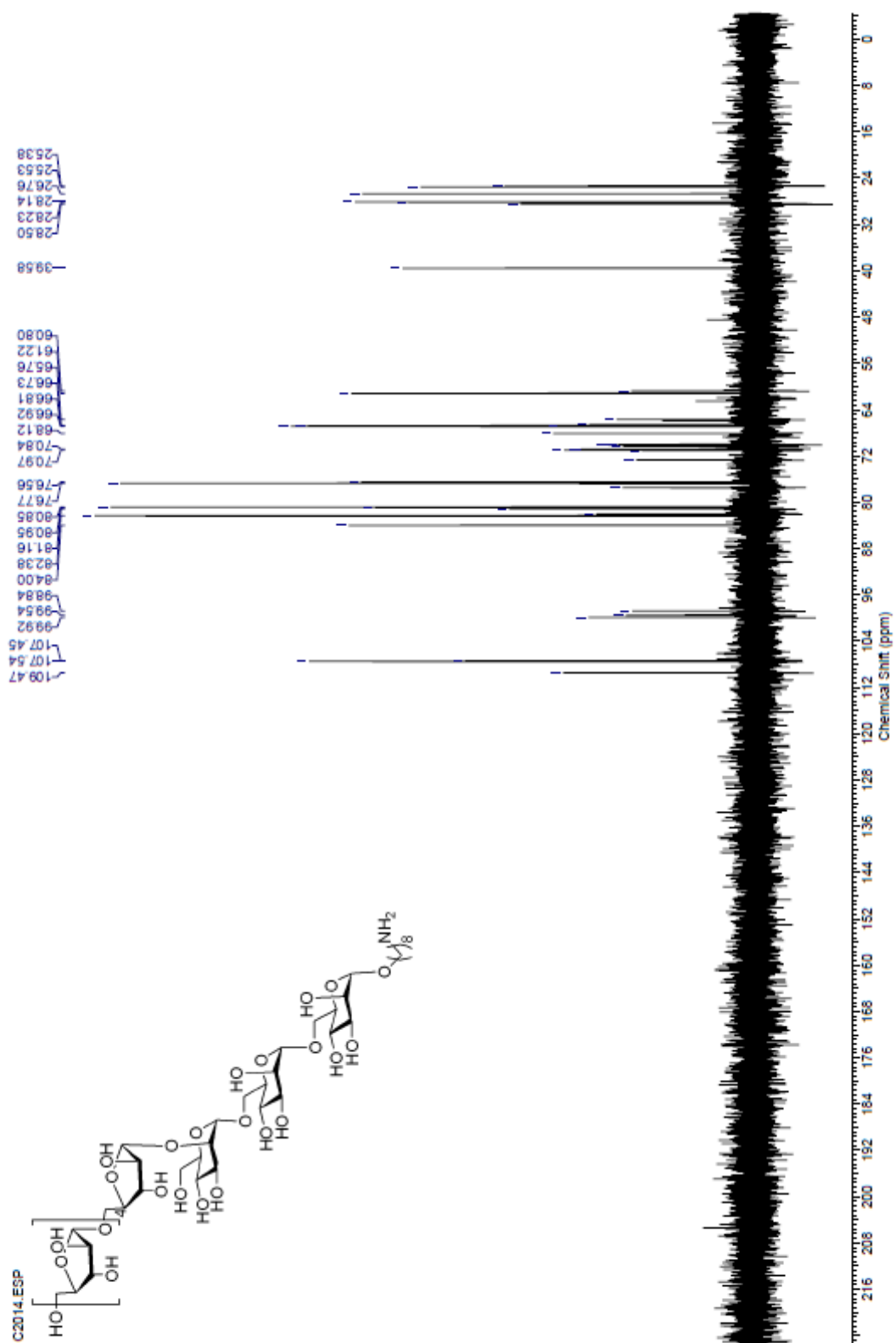
$^{13}\text{C}$  NMR for compound **3** (126 MHz,  $\text{D}_2\text{O}$ )



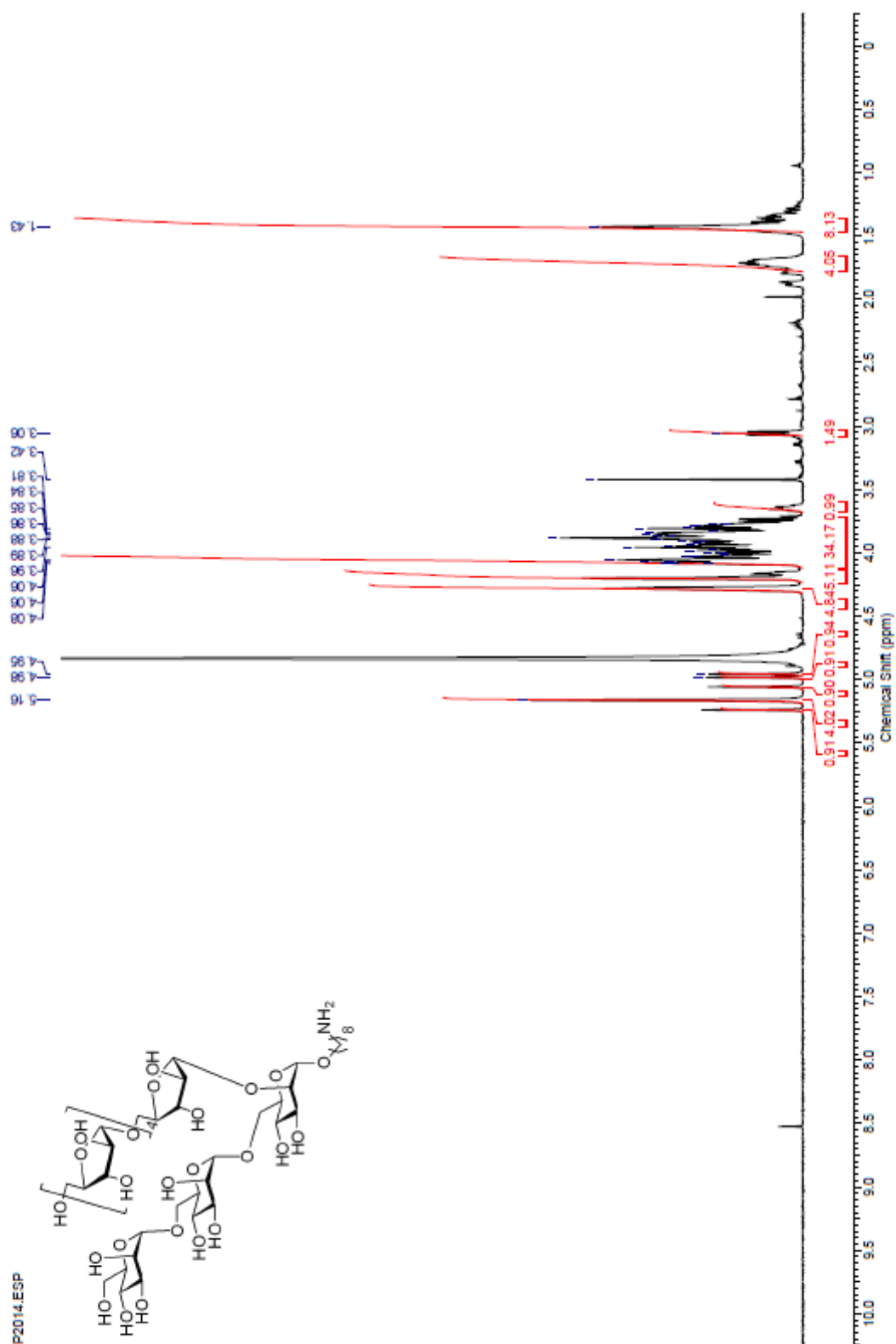
$^1\text{H}$  NMR for compound **4** (500 MHz,  $\text{D}_2\text{O}$ )



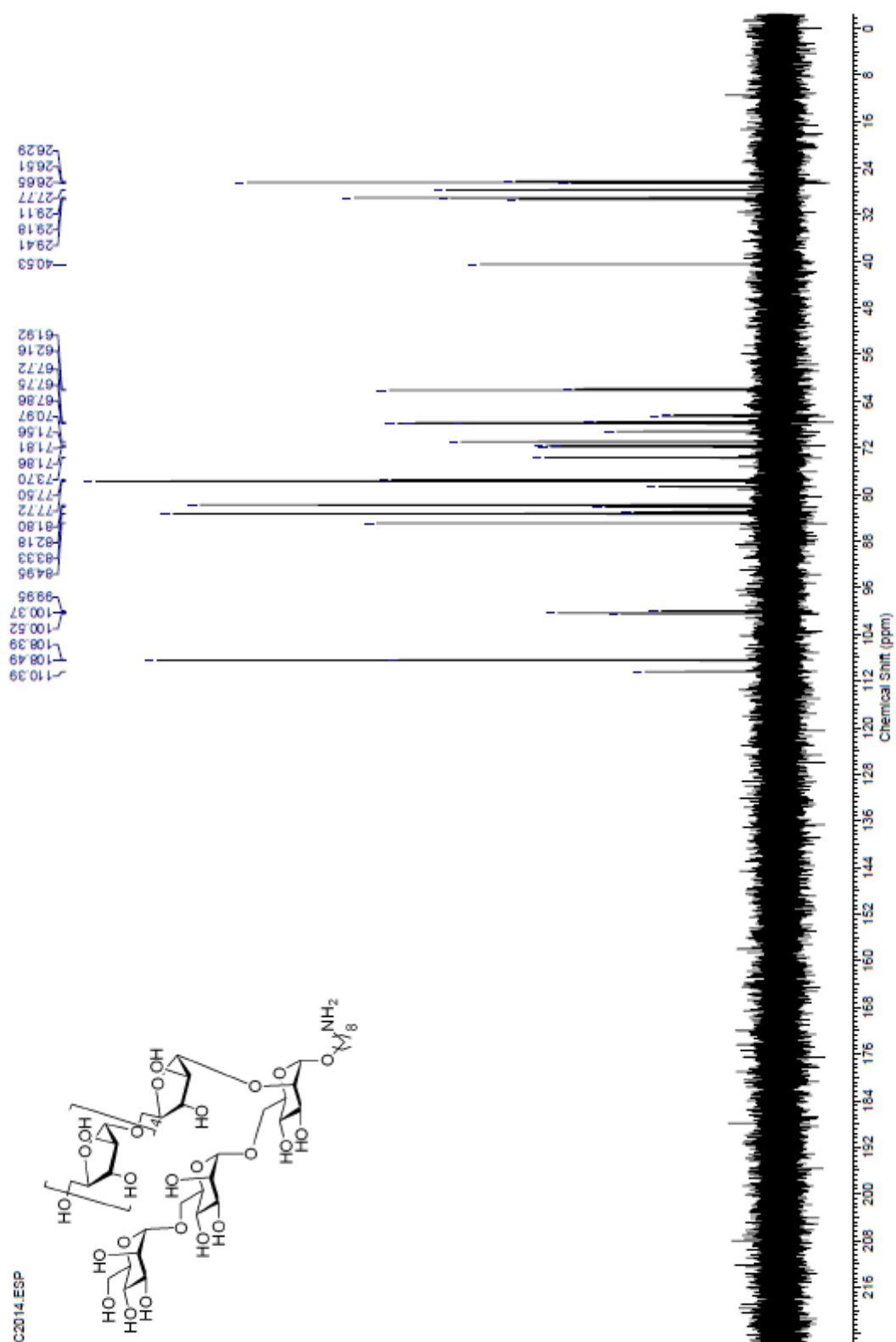
$^{13}\text{C}$  NMR for compound **4** (126 MHz,  $\text{D}_2\text{O}$ )



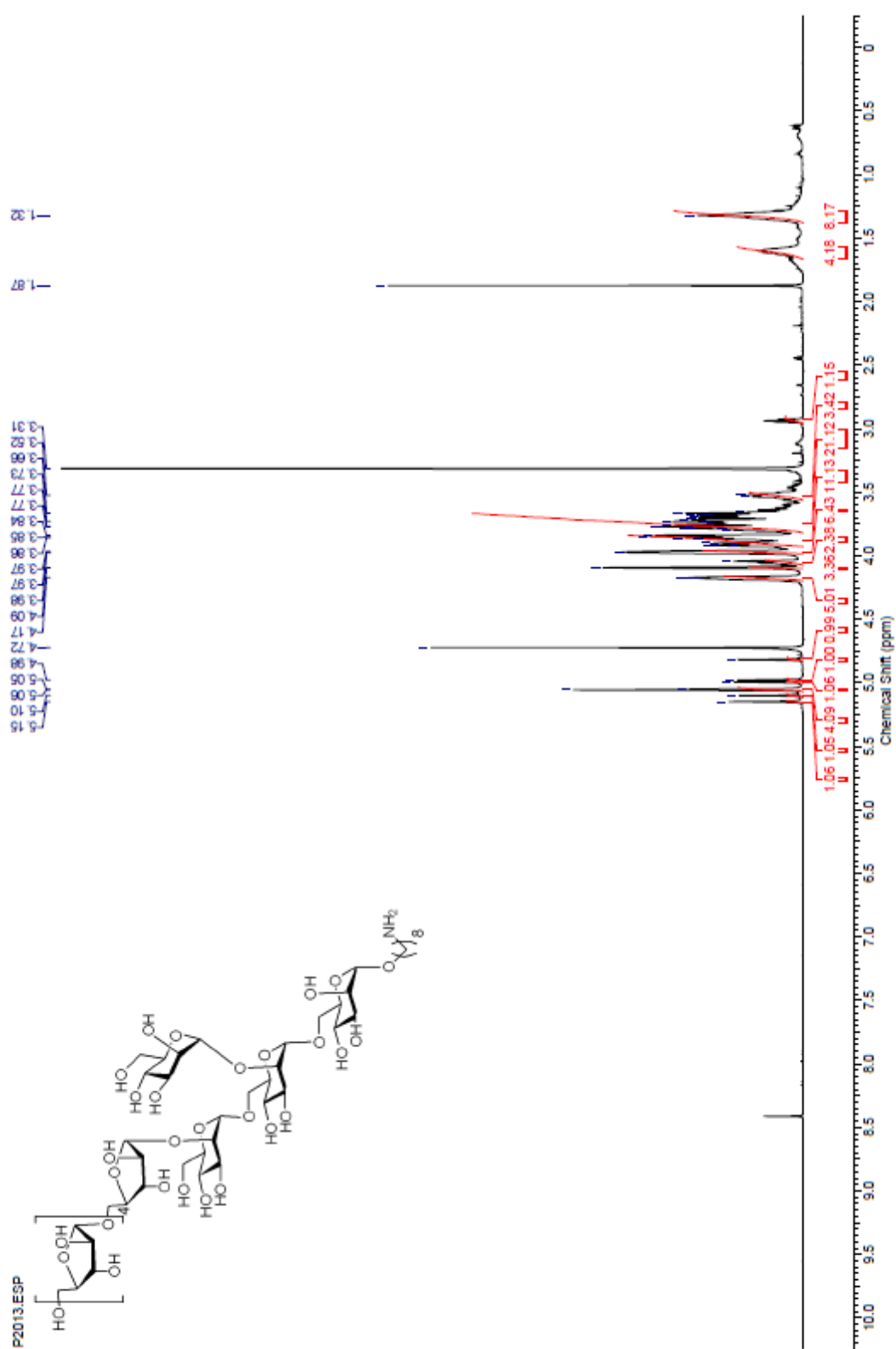
$^1\text{H}$  NMR for compound **5** (700 MHz,  $\text{D}_2\text{O}$ )



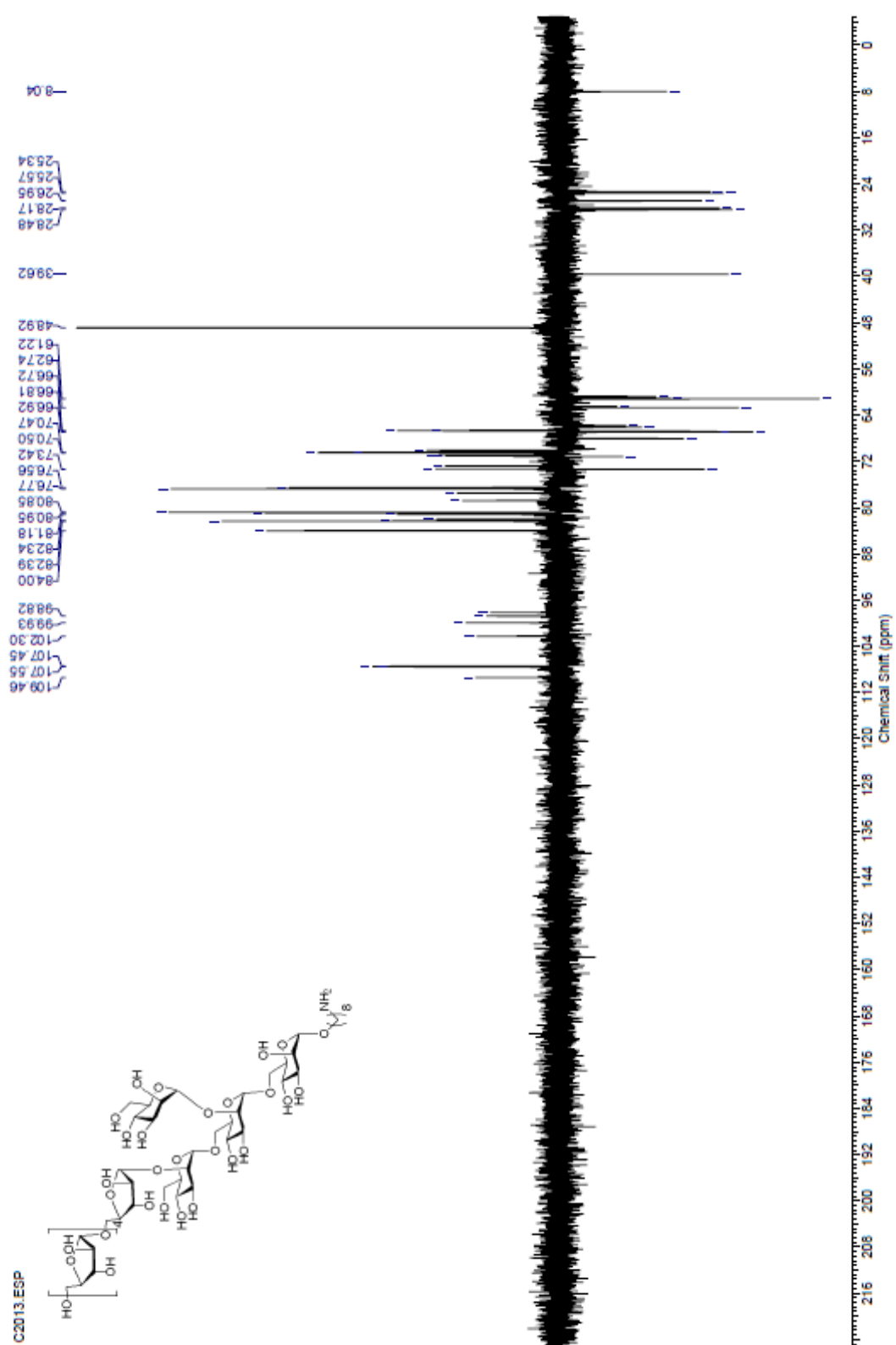
$^{13}\text{C}$  NMR for compound **5** (126 MHz,  $\text{D}_2\text{O}$ )



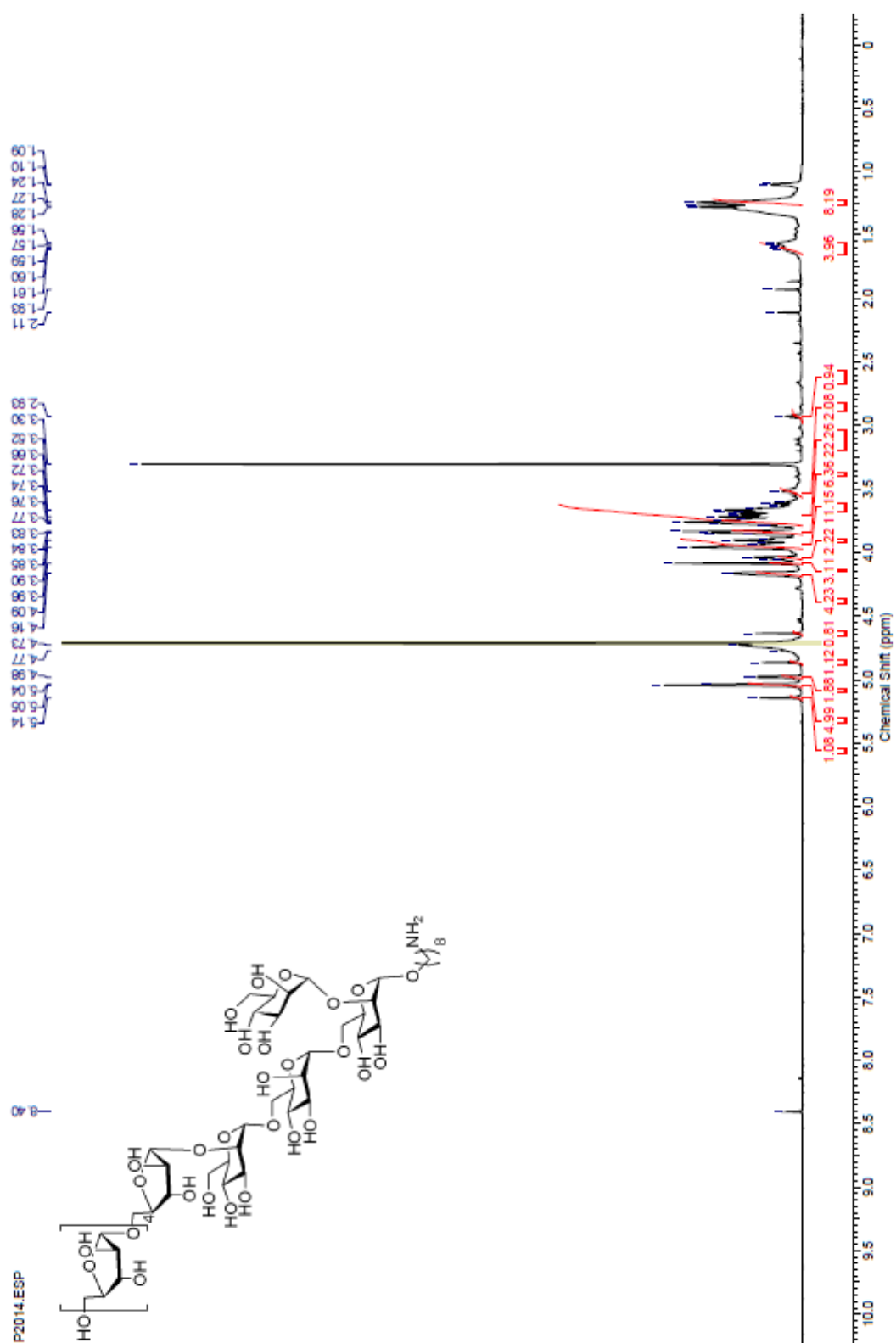
$^1\text{H}$  NMR for compound **6** (600 MHz,  $\text{D}_2\text{O}$ )



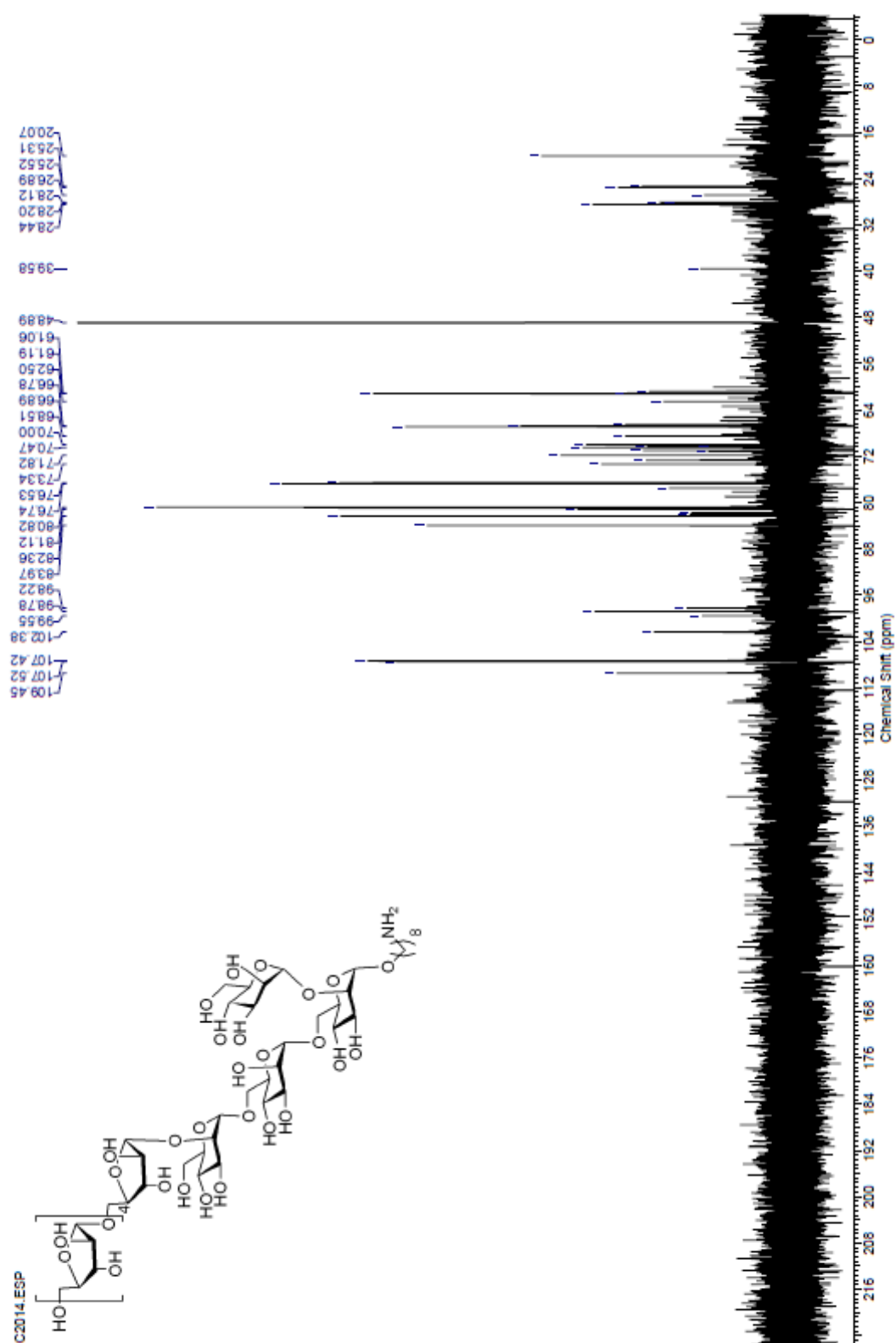
$^{13}\text{C}$  NMR for compound **6** (126 MHz,  $\text{D}_2\text{O}$ )

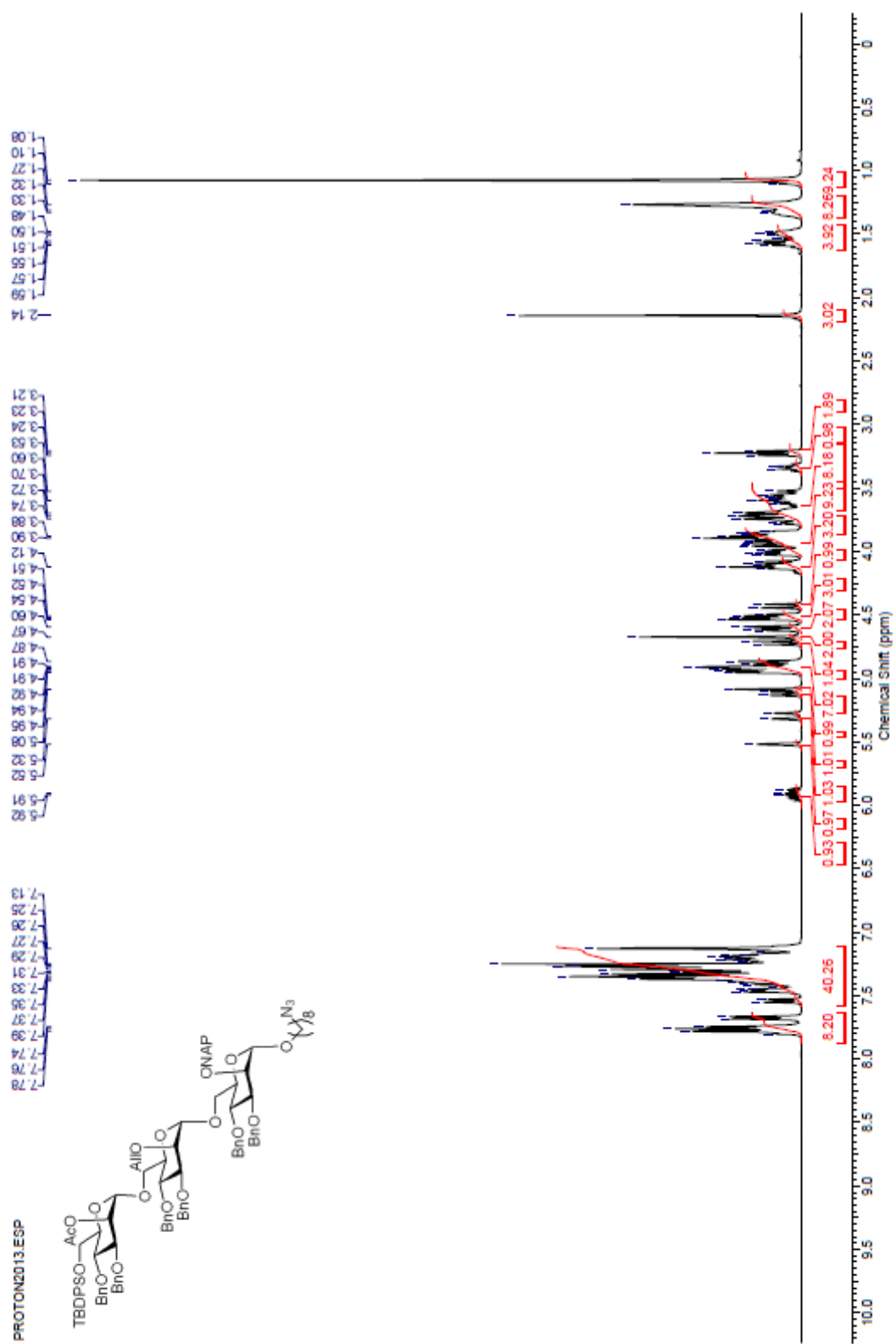


$^1\text{H}$  NMR for compound **7** (700 MHz,  $\text{D}_2\text{O}$ )

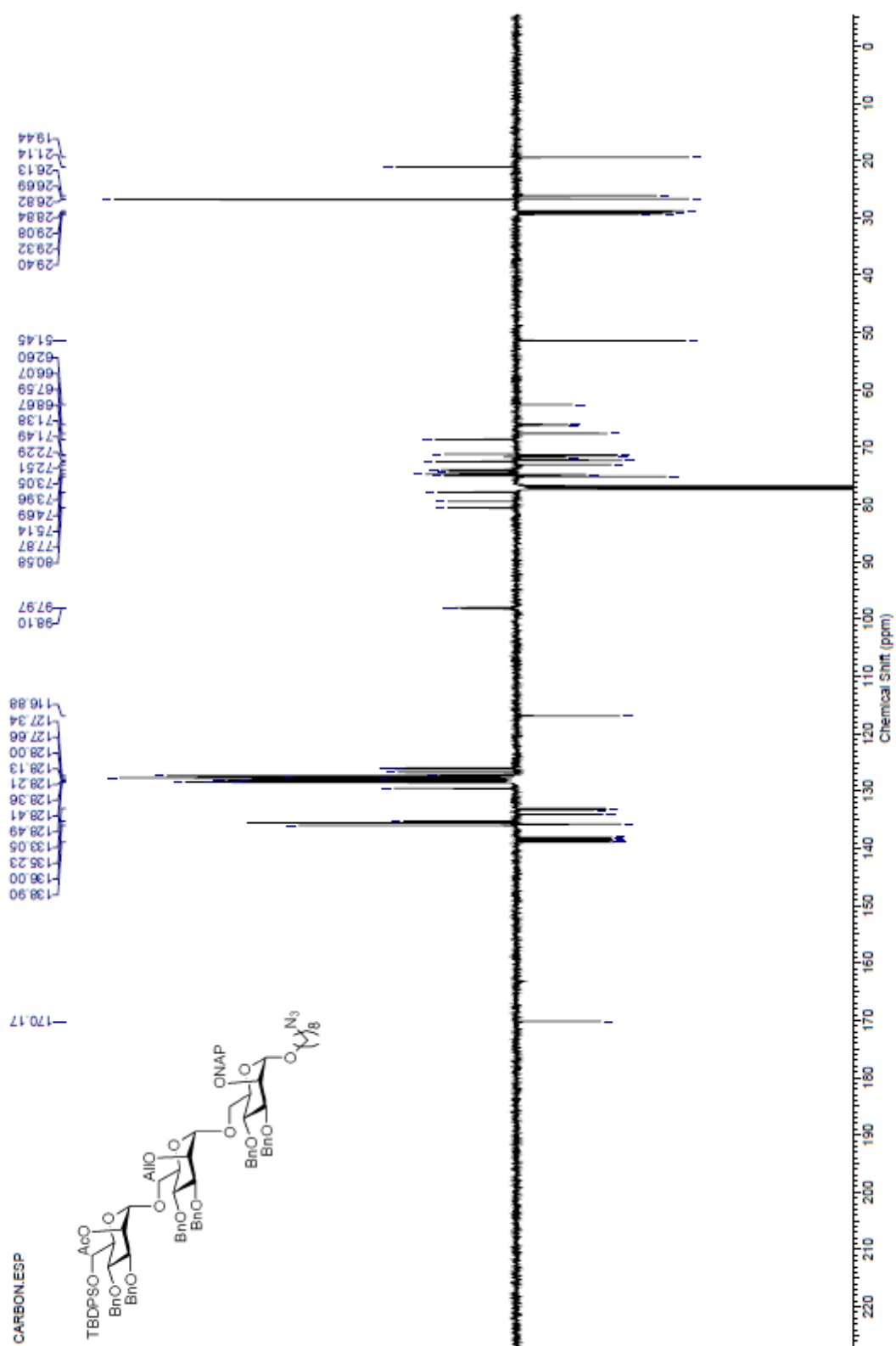


$^{13}\text{C}$  NMR for compound **7** (176 MHz,  $\text{D}_2\text{O}$ )

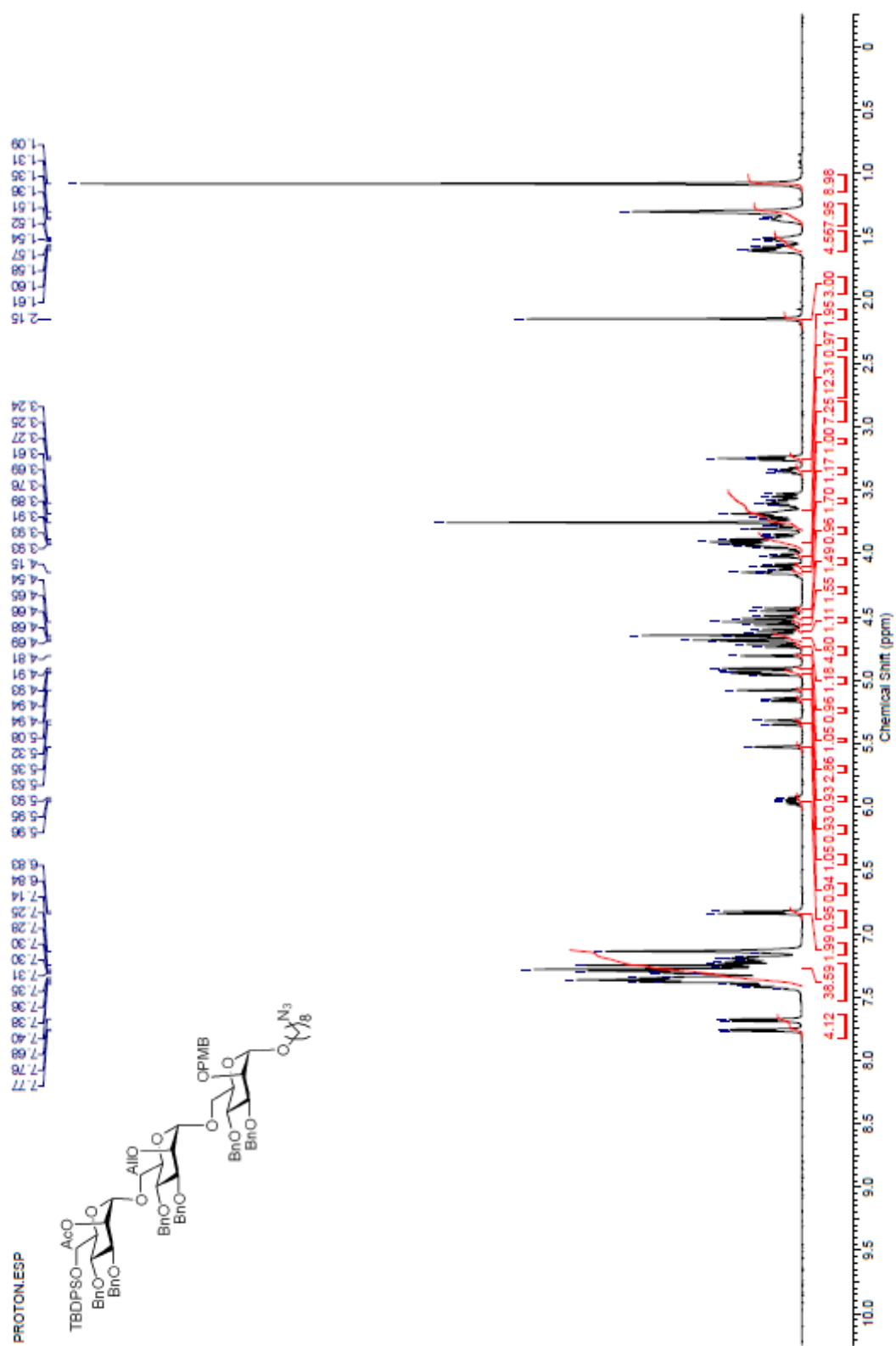


<sup>1</sup>H NMR for compound **8** (400 MHz, CDCl<sub>3</sub>)

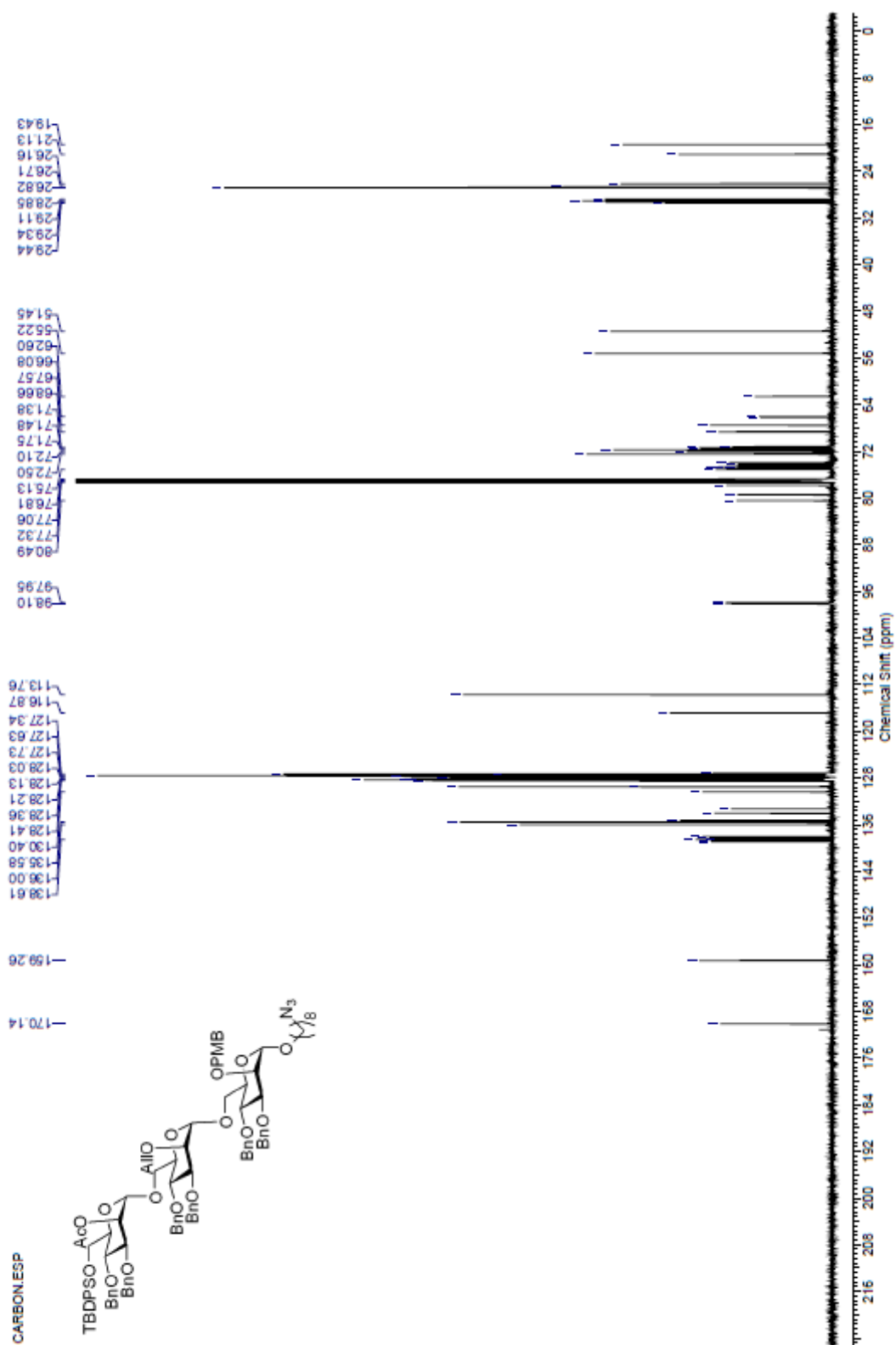
$^{13}\text{C}$  NMR for compound **8** (126 MHz,  $\text{CDCl}_3$ )



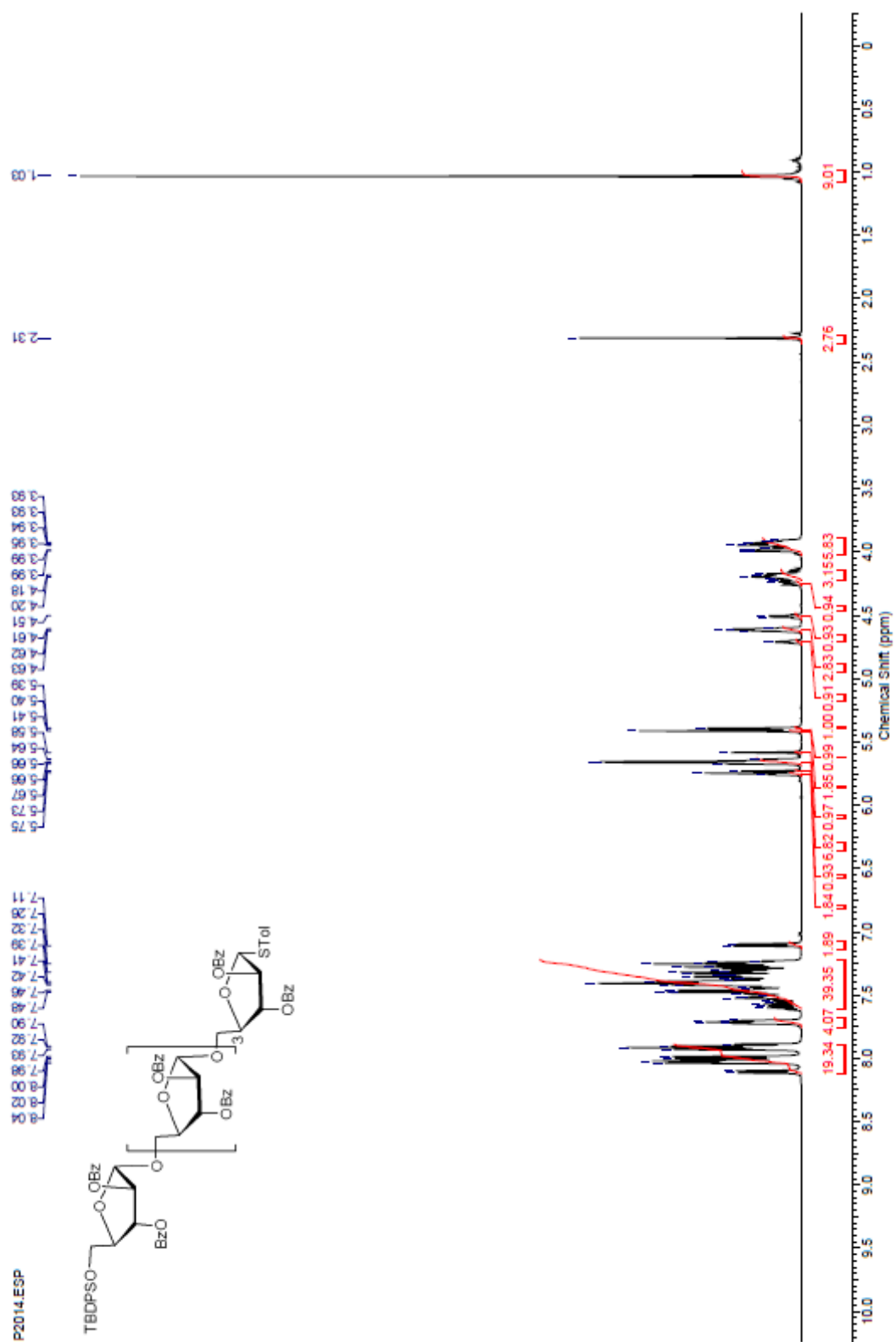
$^1\text{H}$  NMR for compound **9** (500 MHz,  $\text{CDCl}_3$ )



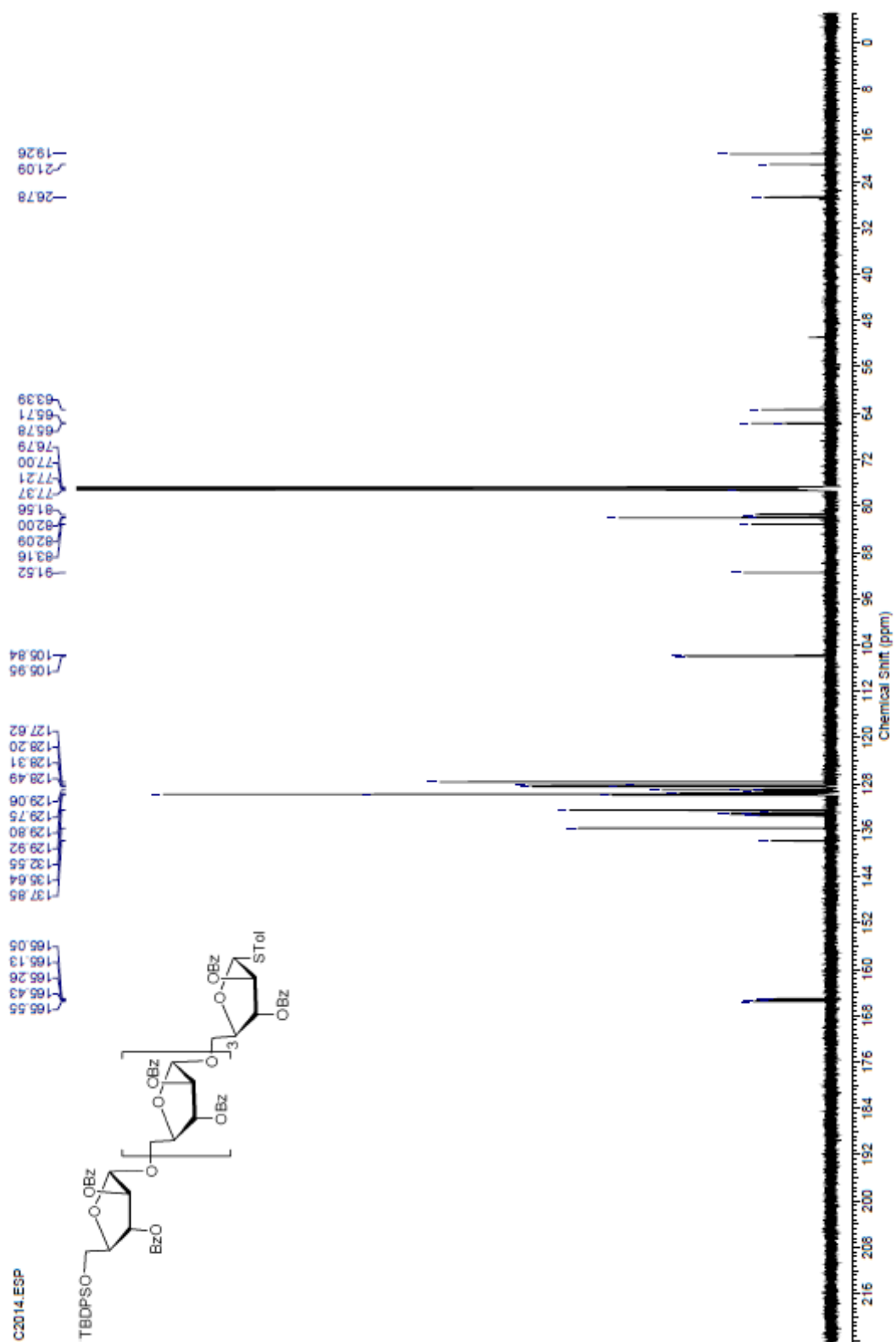
$^{13}\text{C}$  NMR for compound **9** (126 MHz,  $\text{CDCl}_3$ )



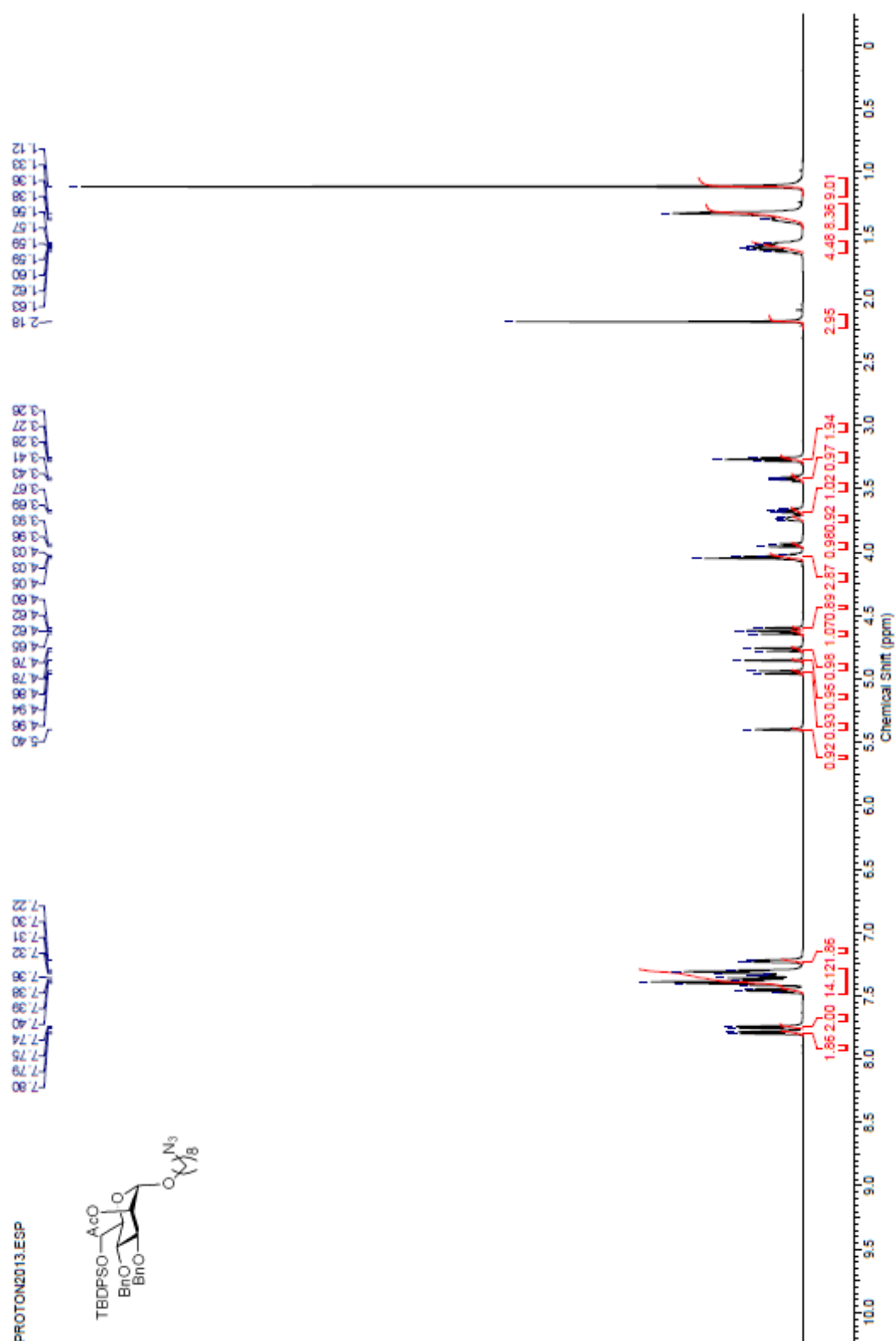
$^1\text{H}$  NMR for compound **12** (600 MHz,  $\text{CDCl}_3$ )



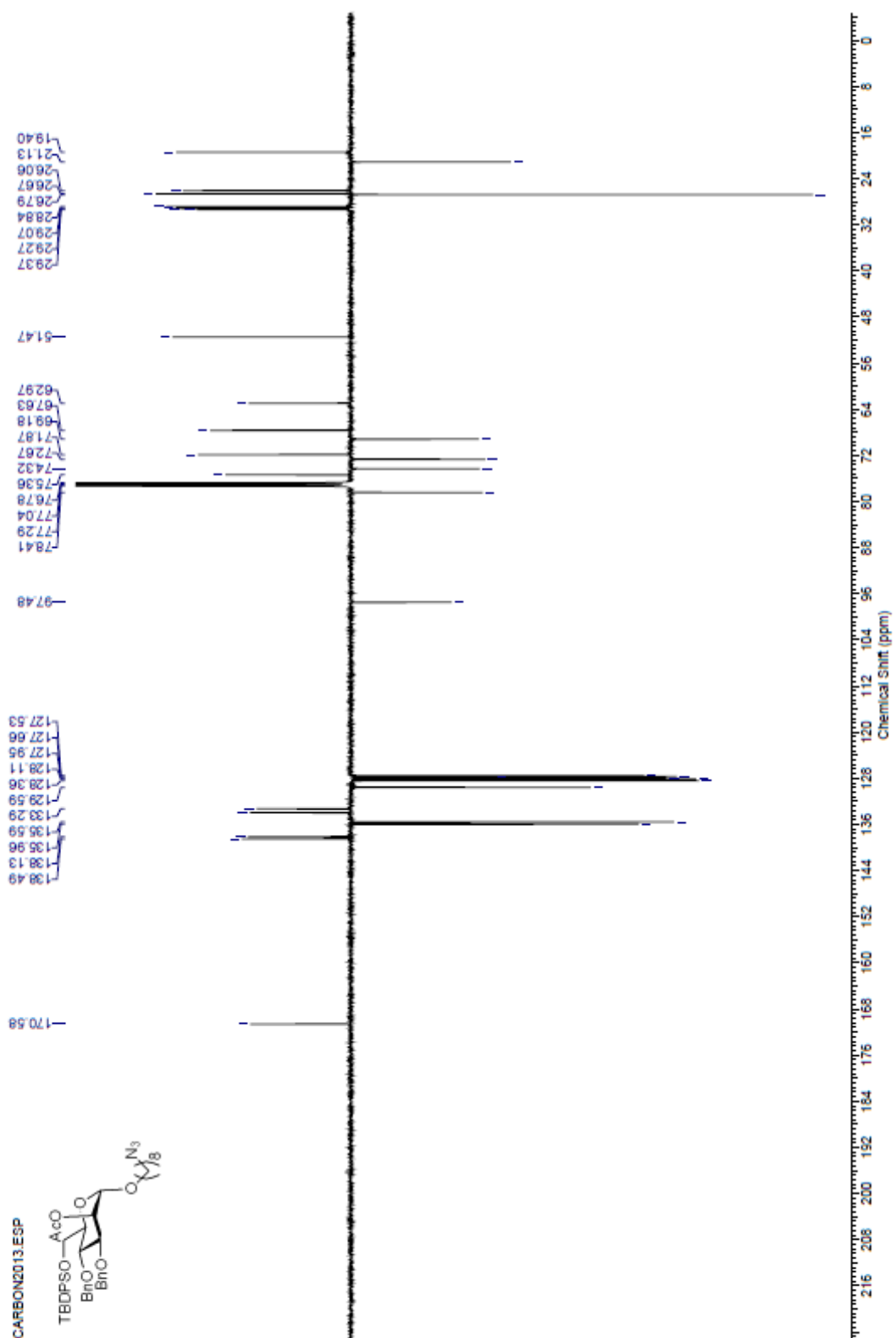
$^{13}\text{C}$  NMR for compound **12** (151 MHz,  $\text{CDCl}_3$ )

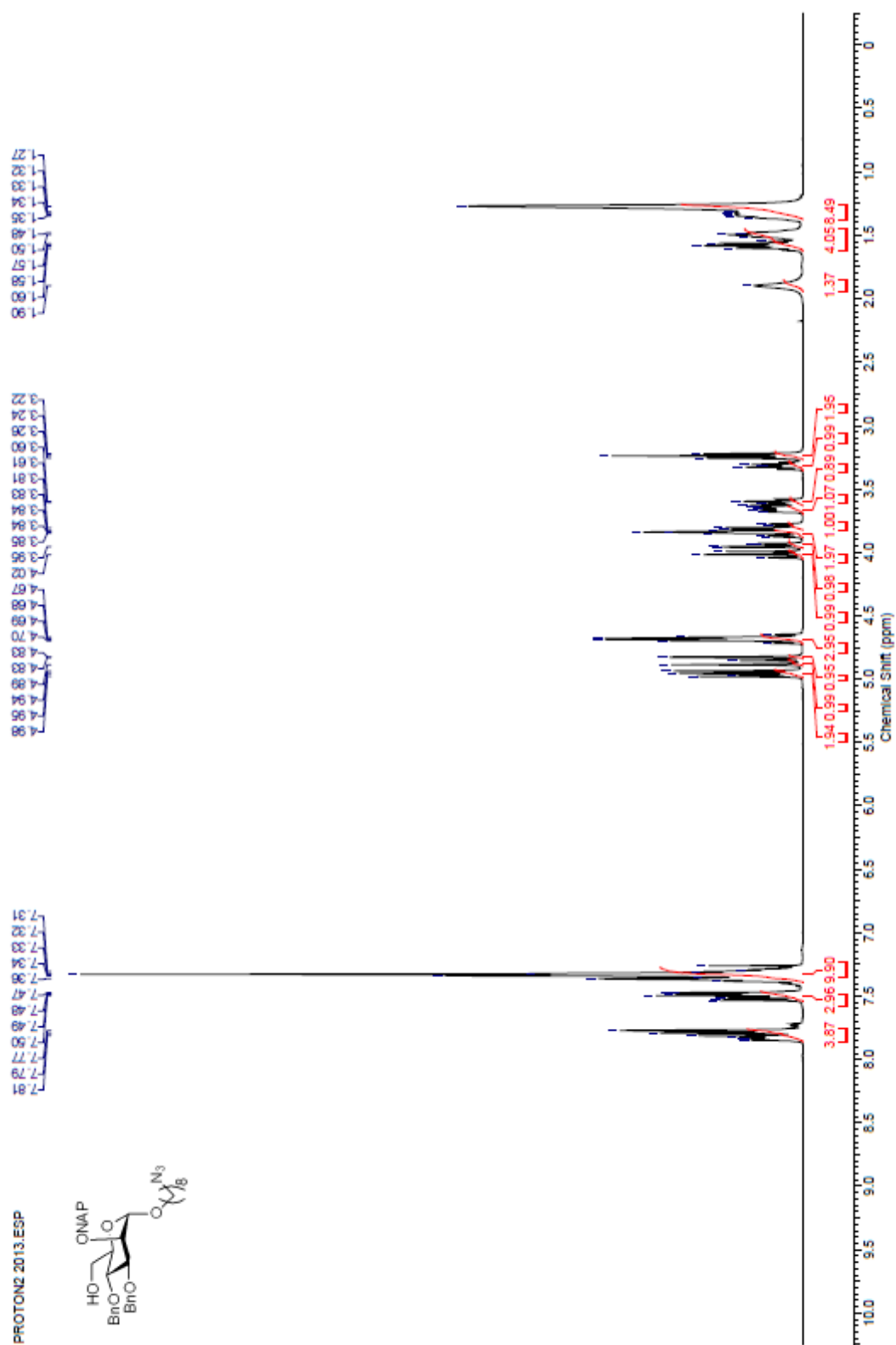


$^1\text{H}$  NMR for compound **13** (500 MHz,  $\text{CDCl}_3$ )

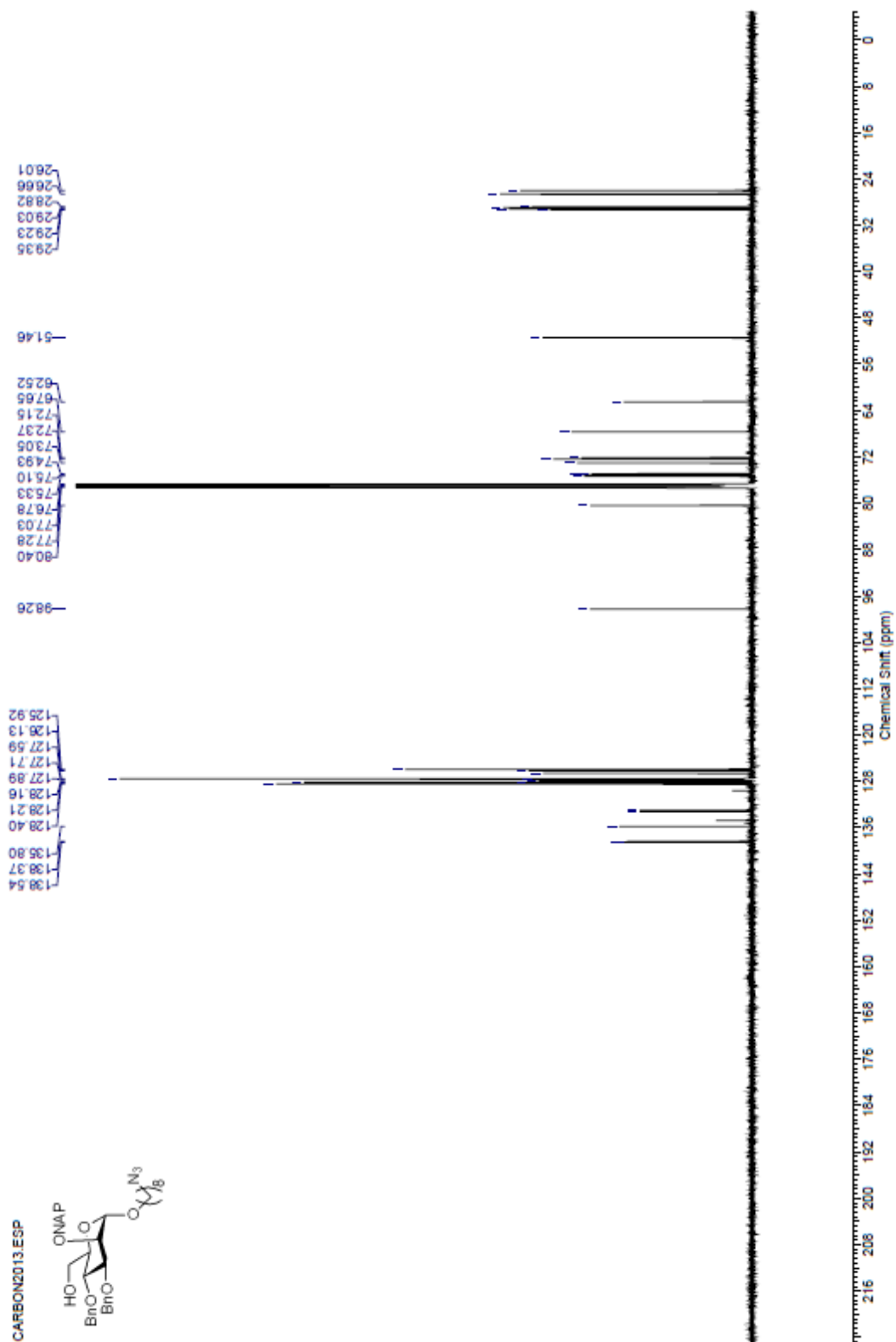


$^{13}\text{C}$  NMR for compound **13** (126 MHz,  $\text{CDCl}_3$ )

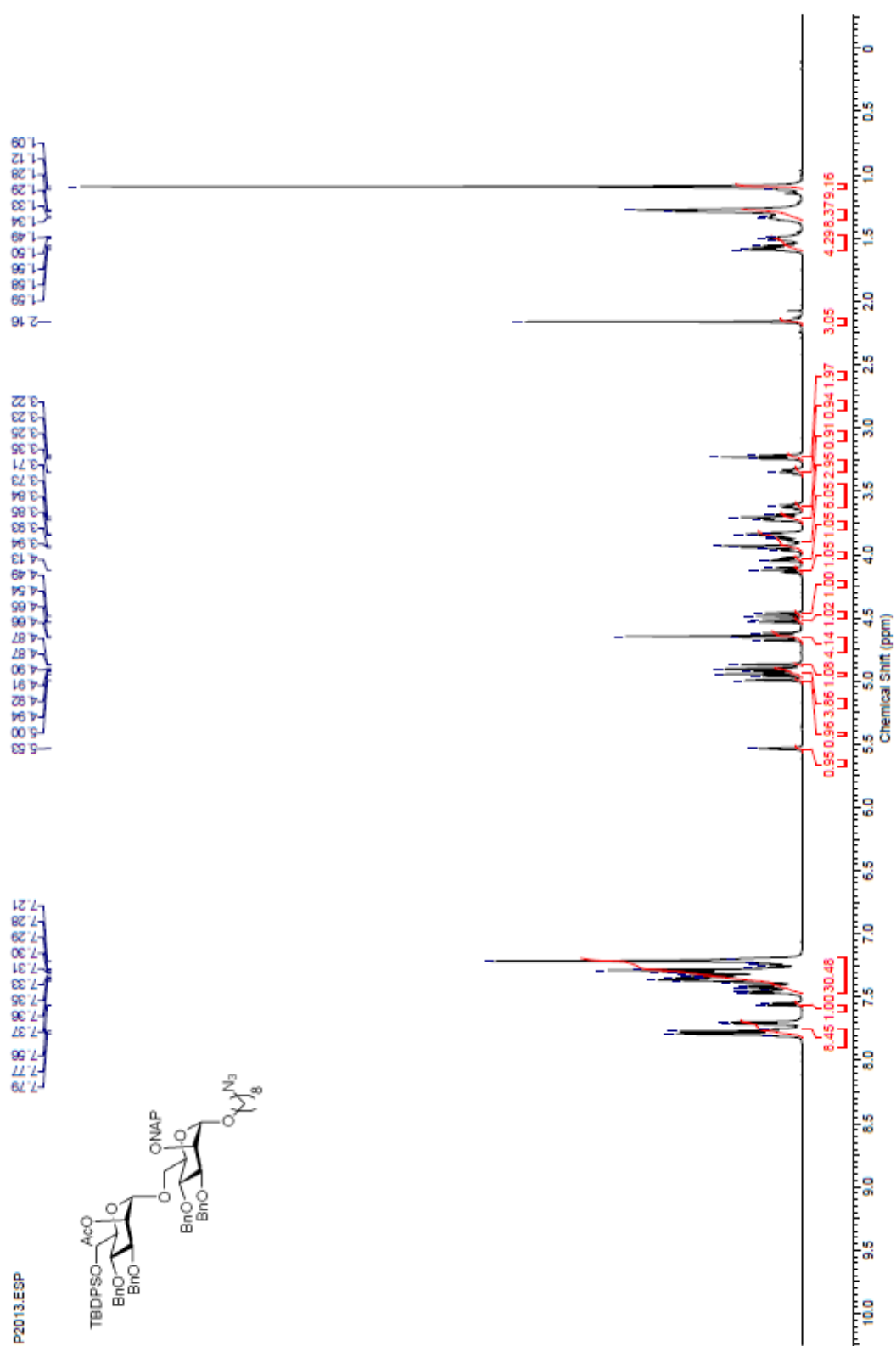


<sup>1</sup>H NMR for compound **14** (500 MHz, CDCl<sub>3</sub>)

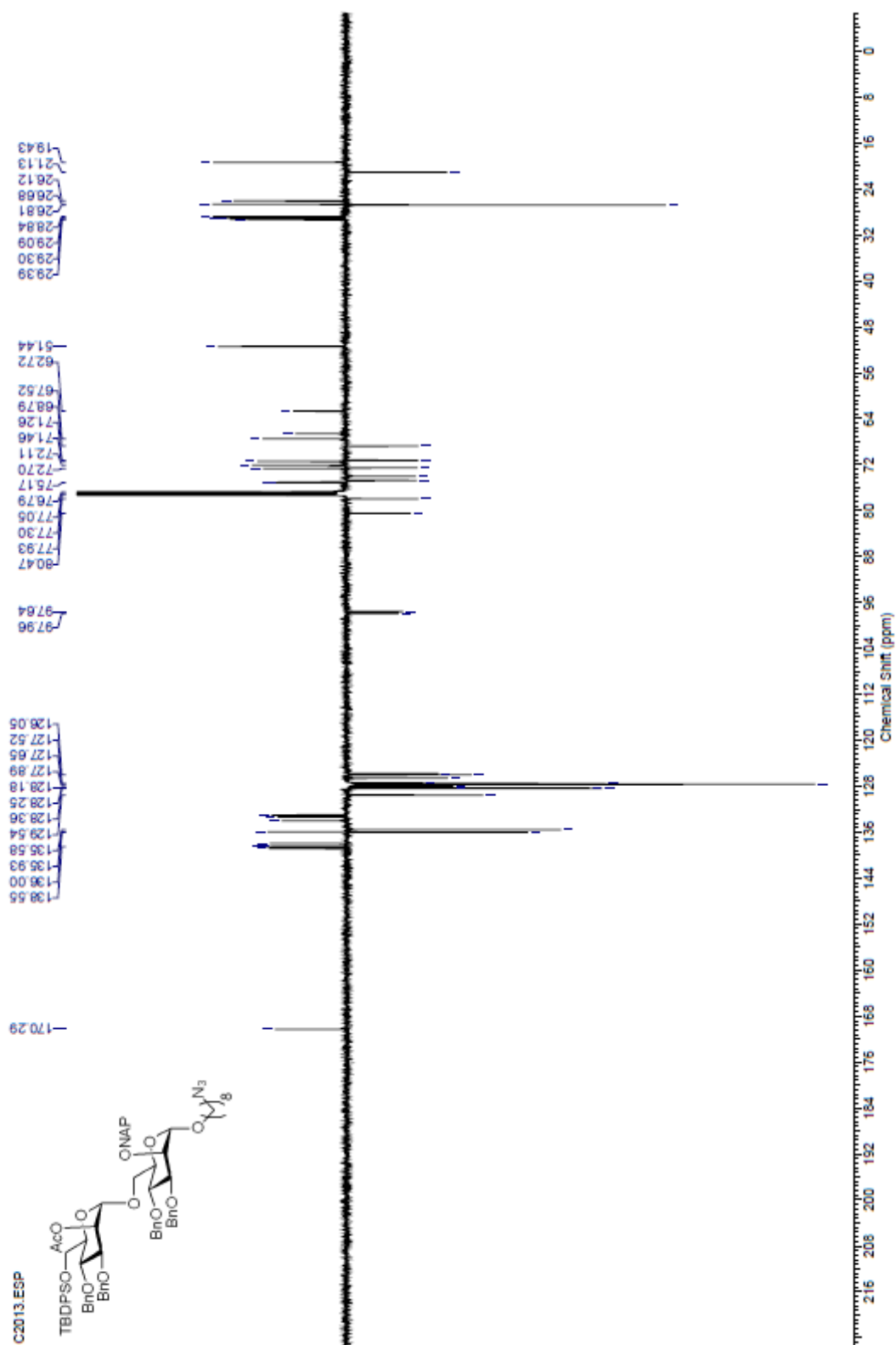
$^{13}\text{C}$  NMR for compound **14** (126 MHz,  $\text{CDCl}_3$ )



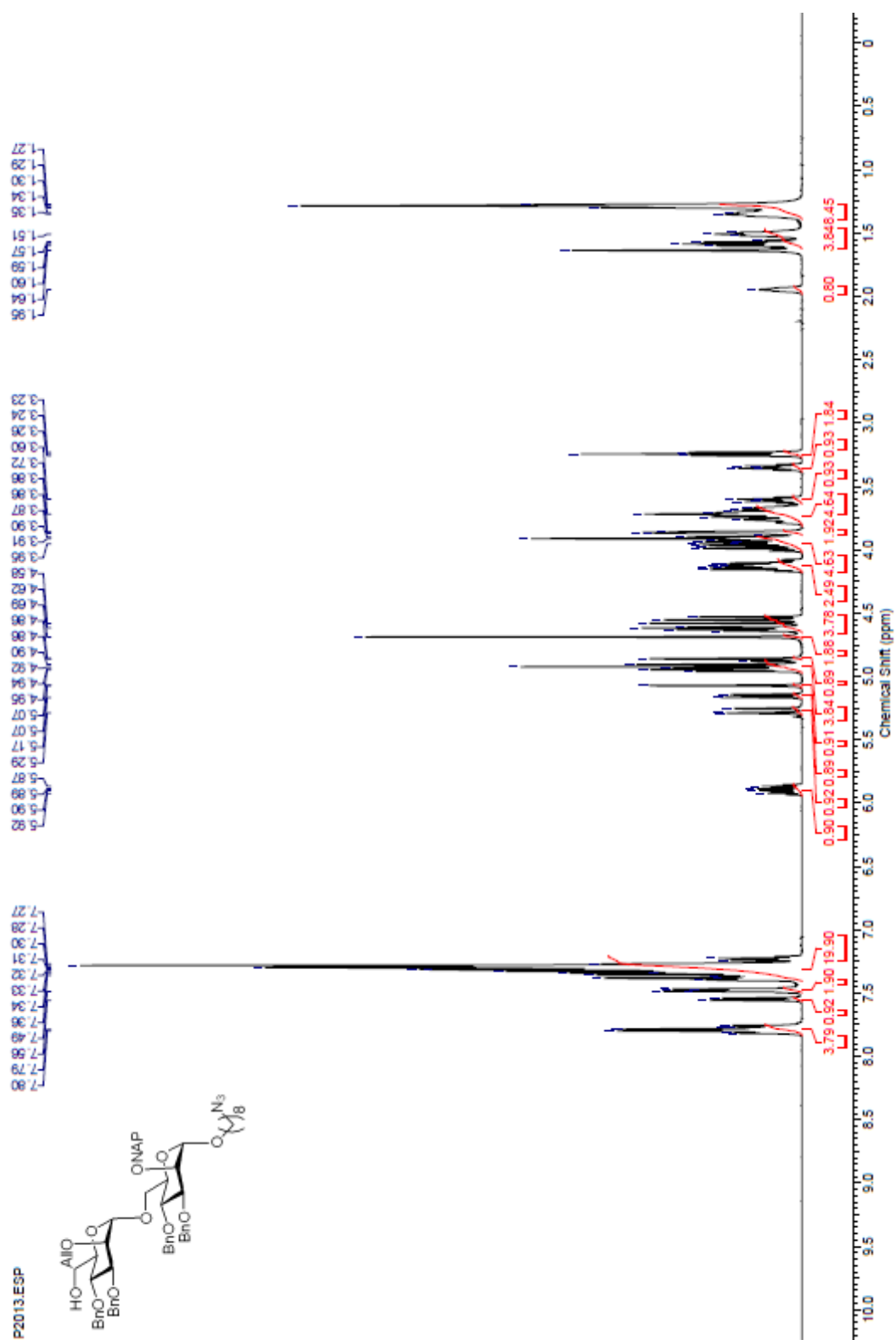
$^1\text{H}$  NMR for compound **15** (500 MHz,  $\text{CDCl}_3$ )



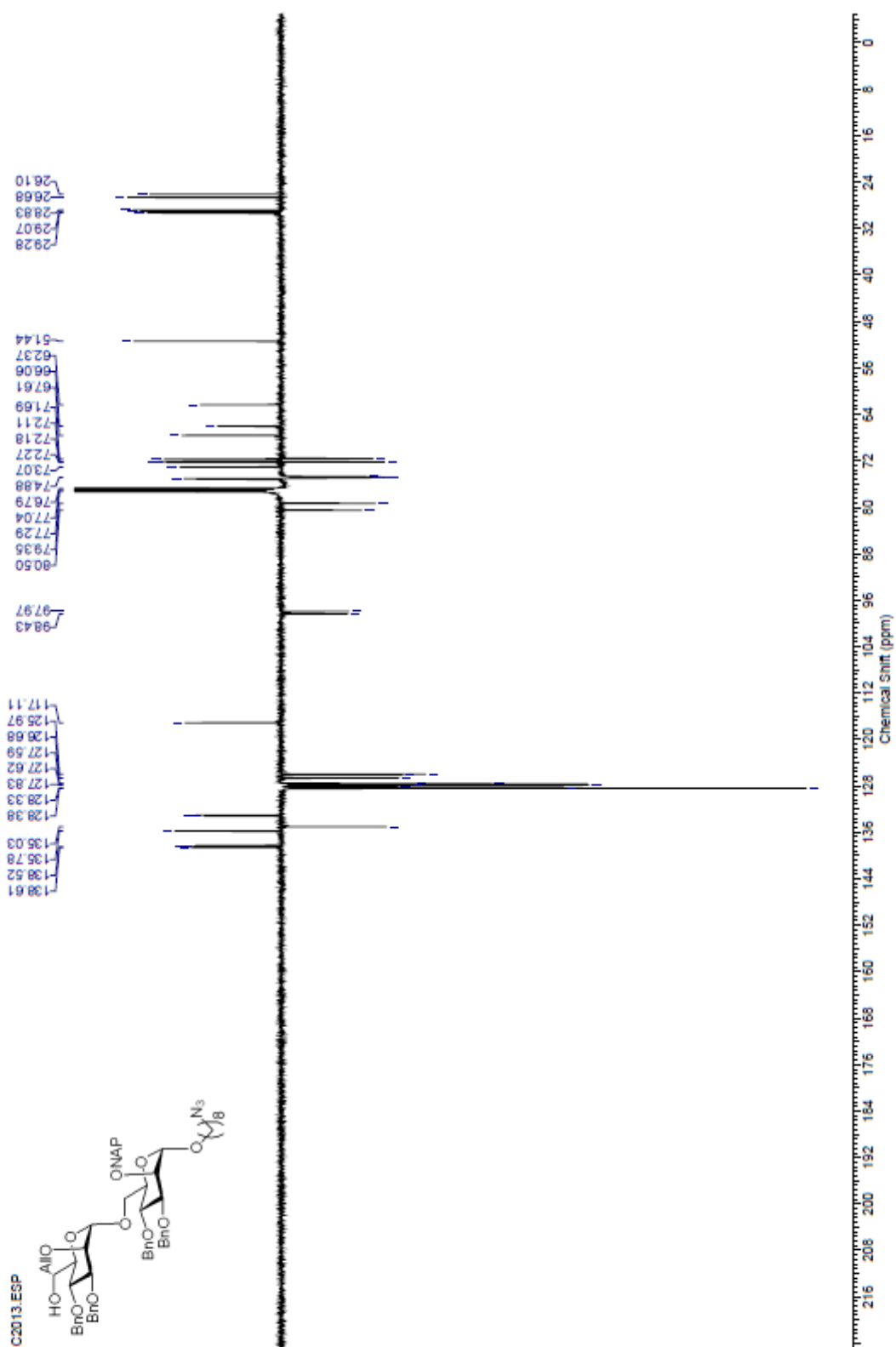
$^{13}\text{C}$  NMR for compound **15** (126 MHz,  $\text{CDCl}_3$ )

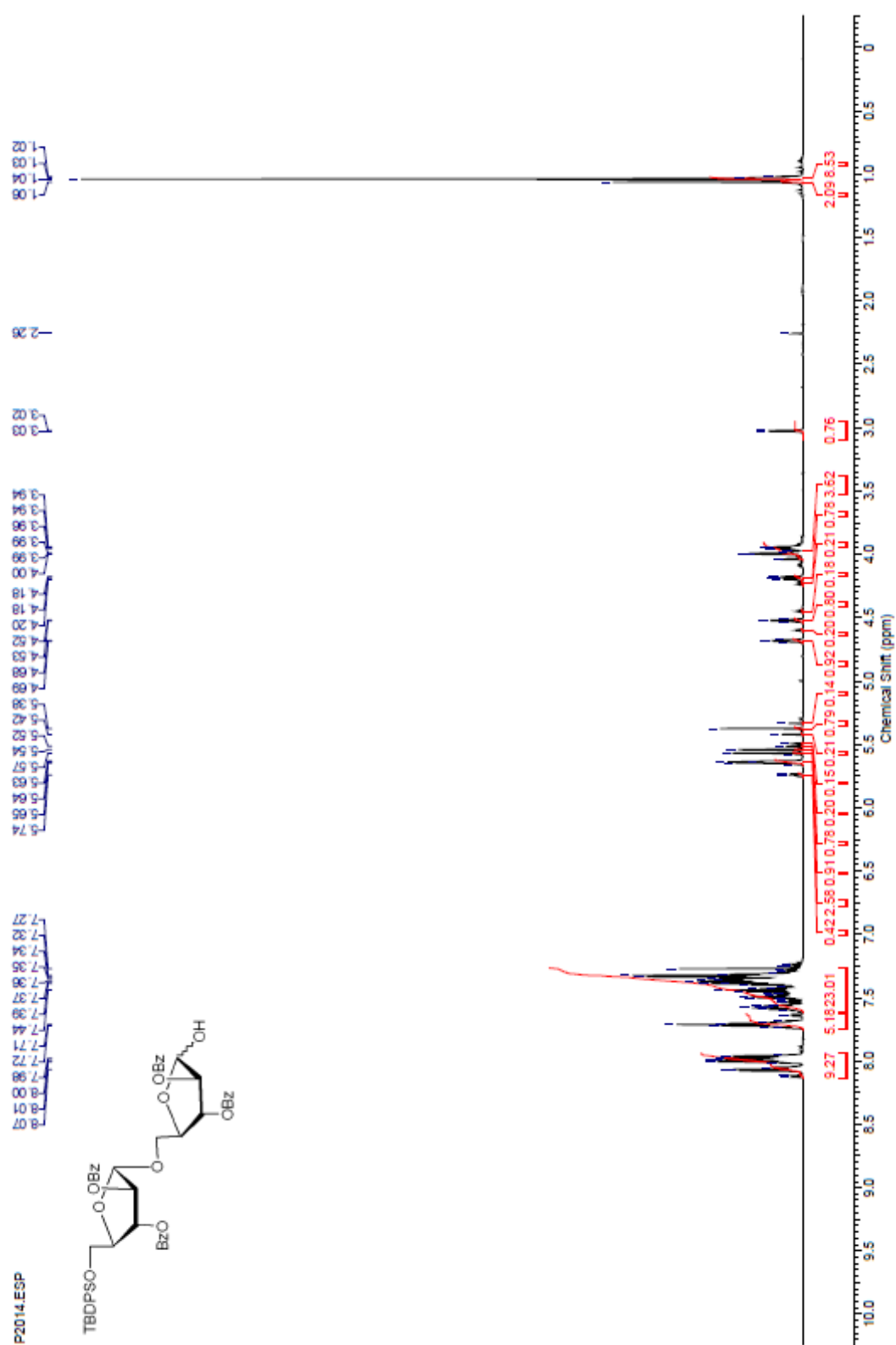


$^1\text{H}$  NMR for compound **16** (400 MHz,  $\text{CDCl}_3$ )

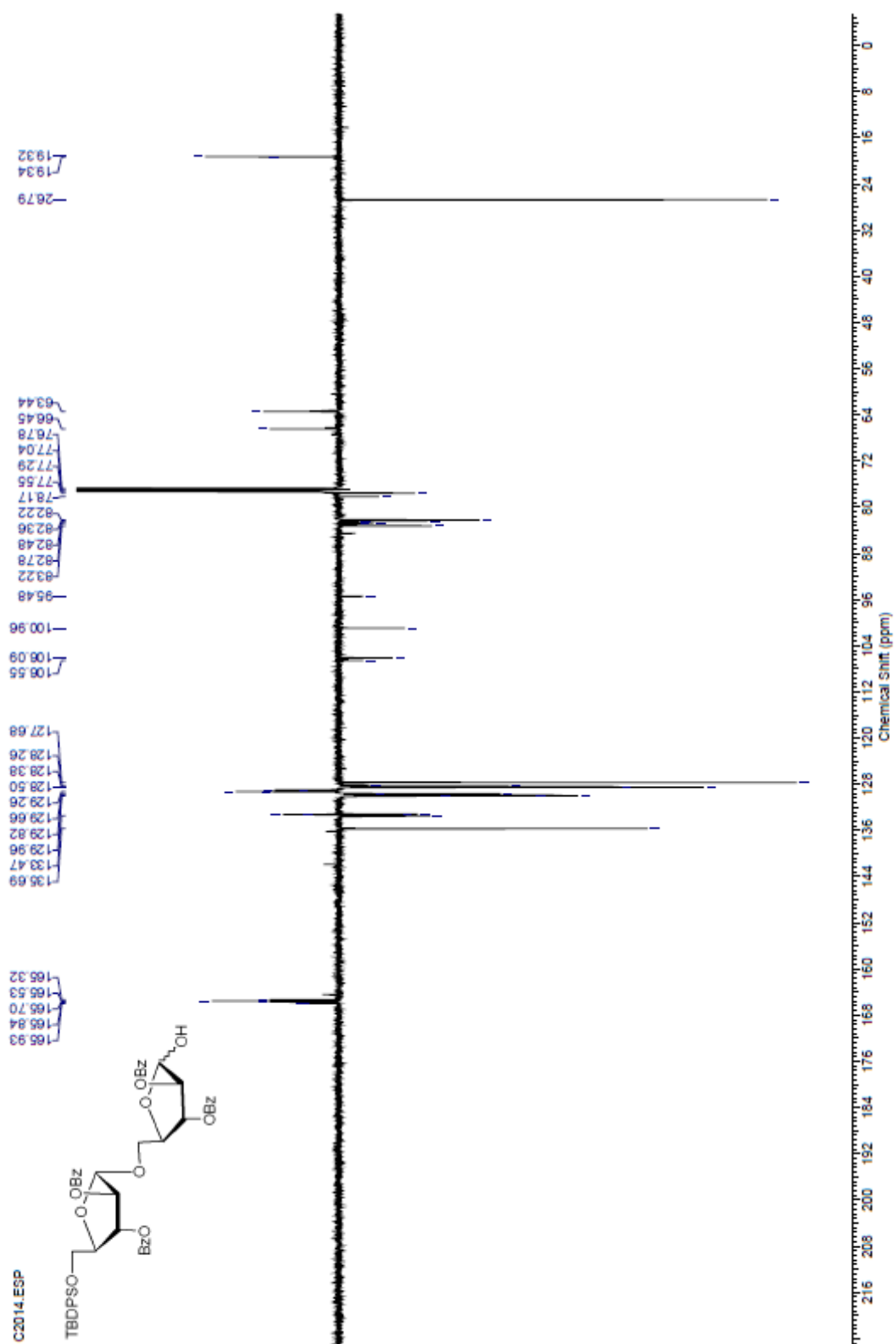


$^{13}\text{C}$  NMR for compound **16** (126 MHz,  $\text{CDCl}_3$ )

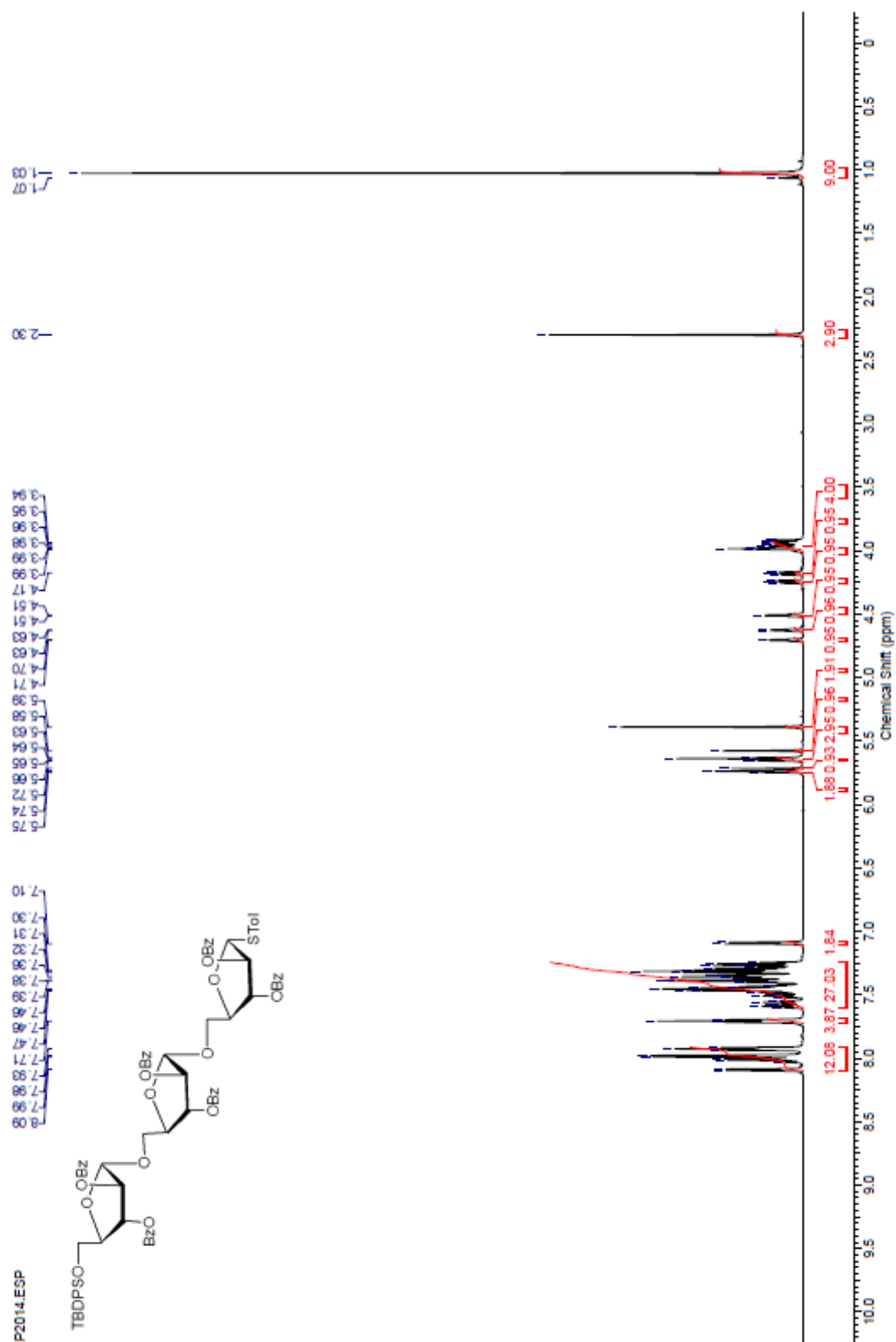


<sup>1</sup>H NMR for compound **18** (700 MHz, CDCl<sub>3</sub>)

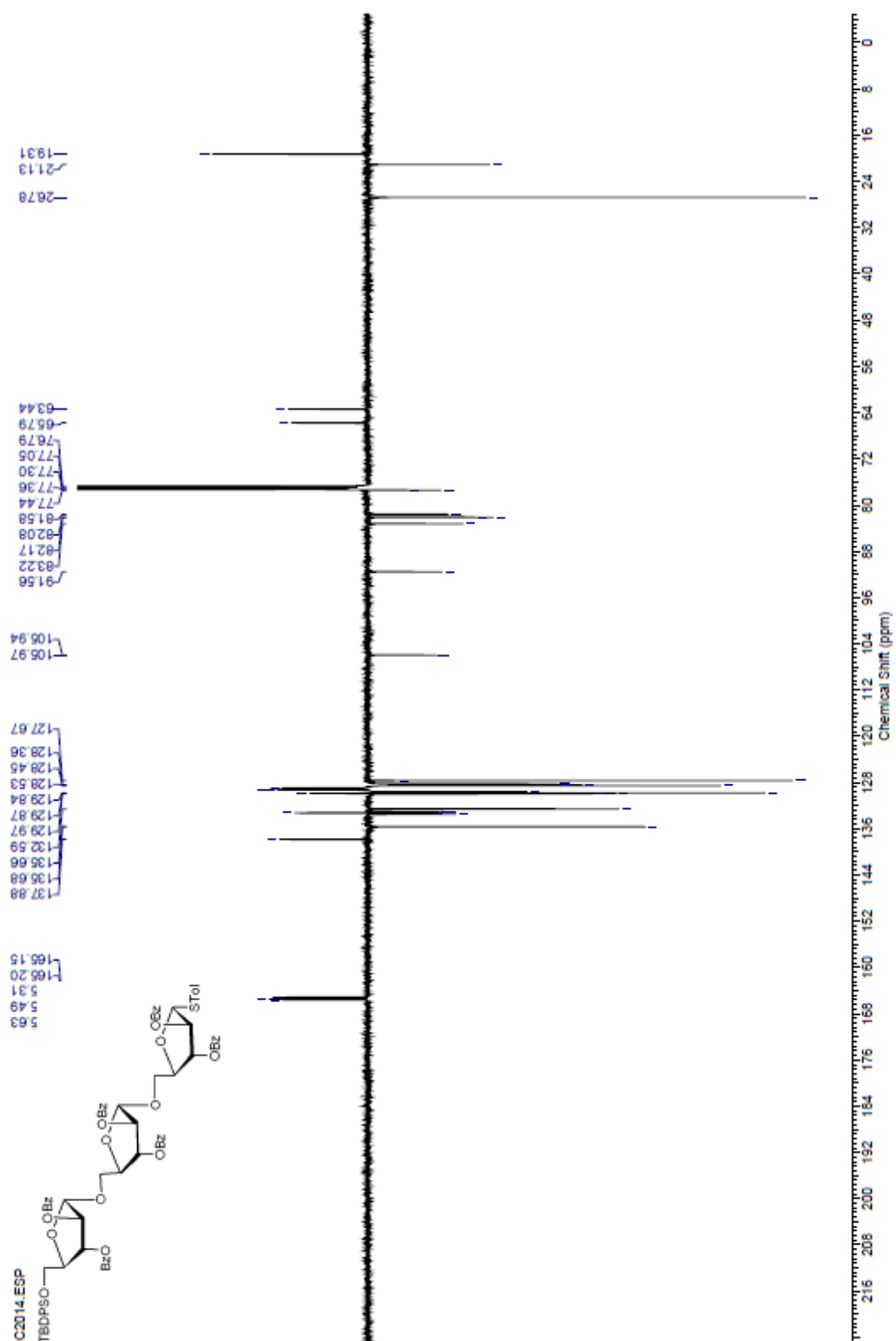
$^{13}\text{C}$  NMR for compound **18** (126 MHz,  $\text{CDCl}_3$ )

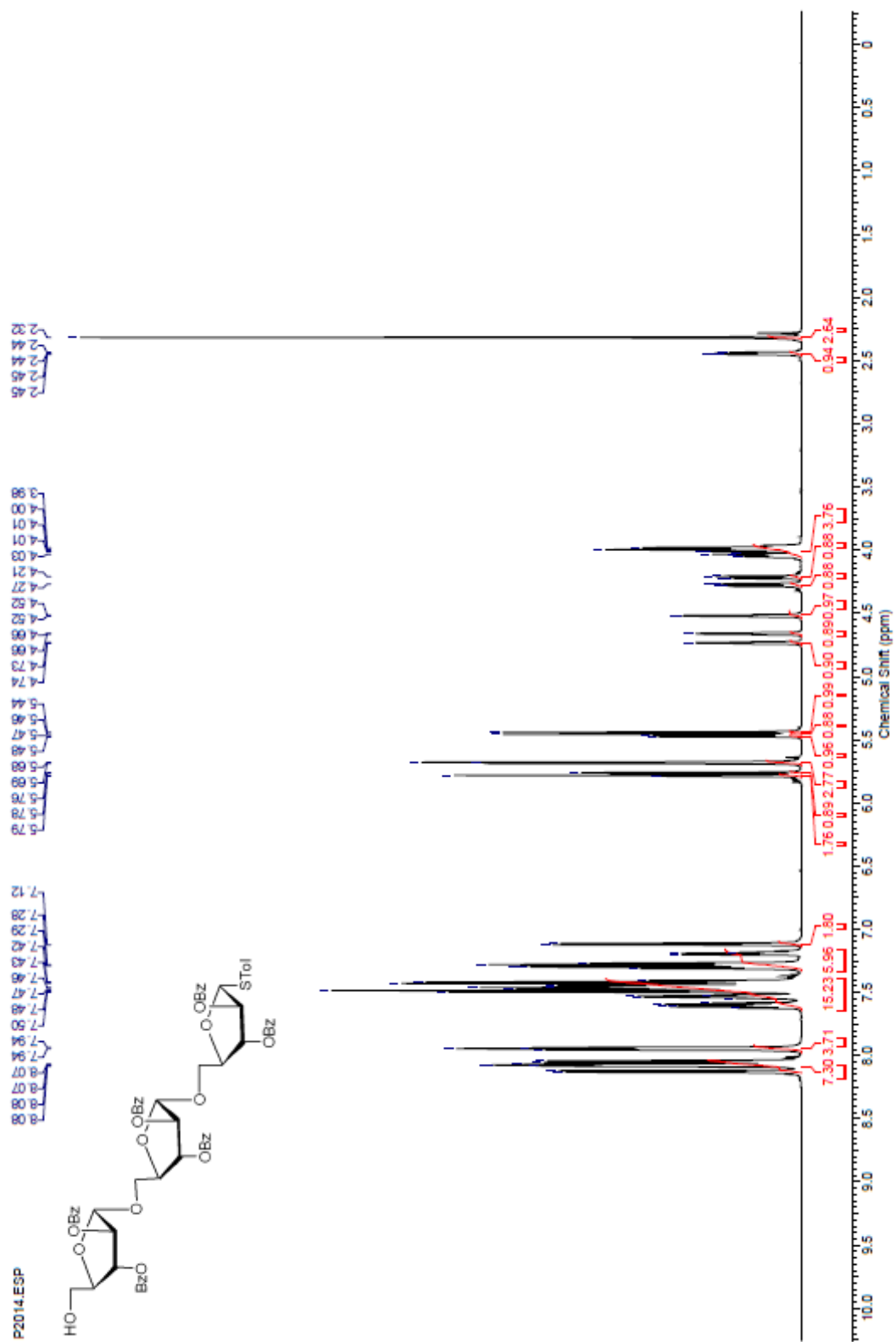


$^1\text{H}$  NMR for compound **22** (700 MHz,  $\text{CDCl}_3$ )

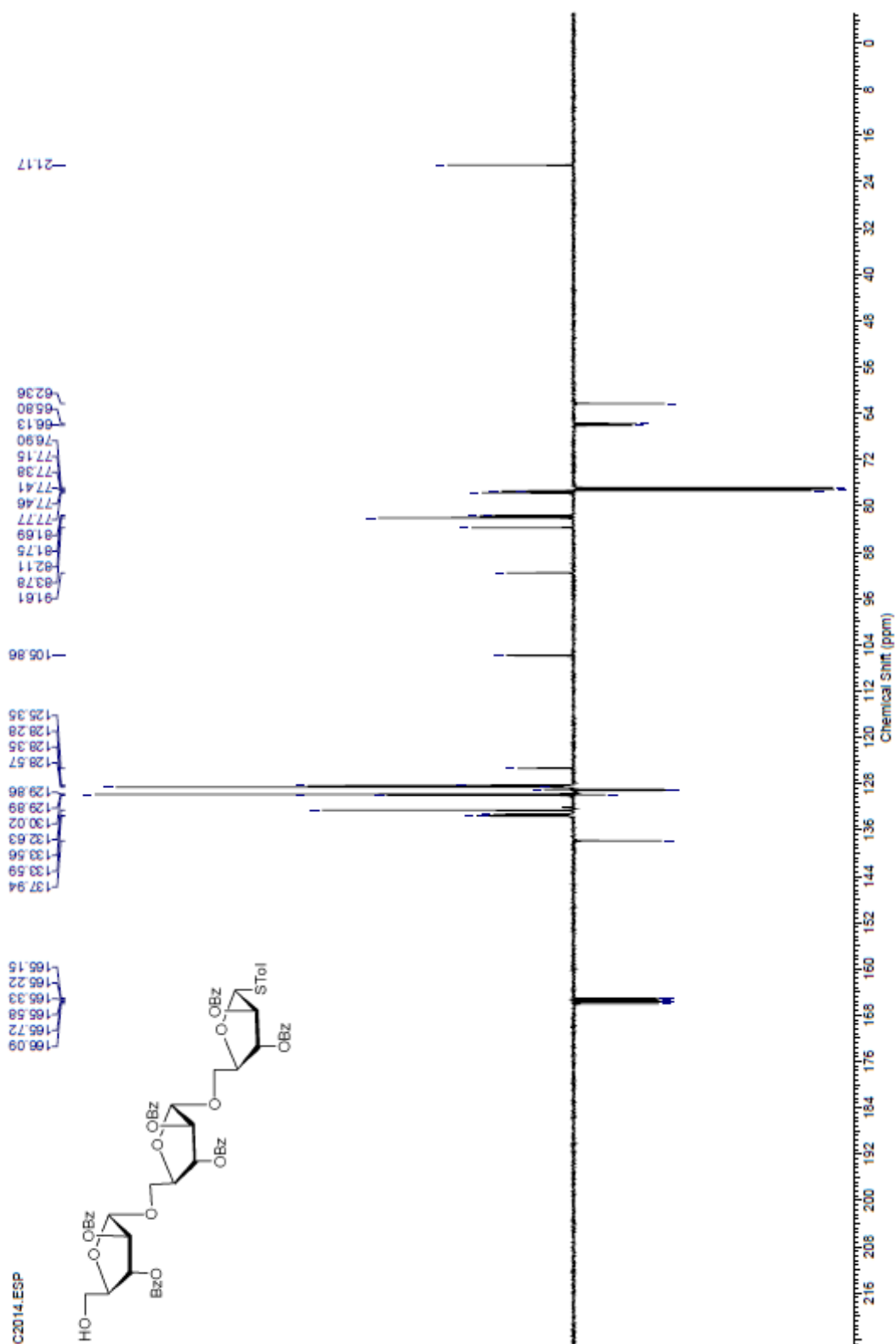


$^{13}\text{C}$  NMR for compound **22** (126 MHz,  $\text{CDCl}_3$ )

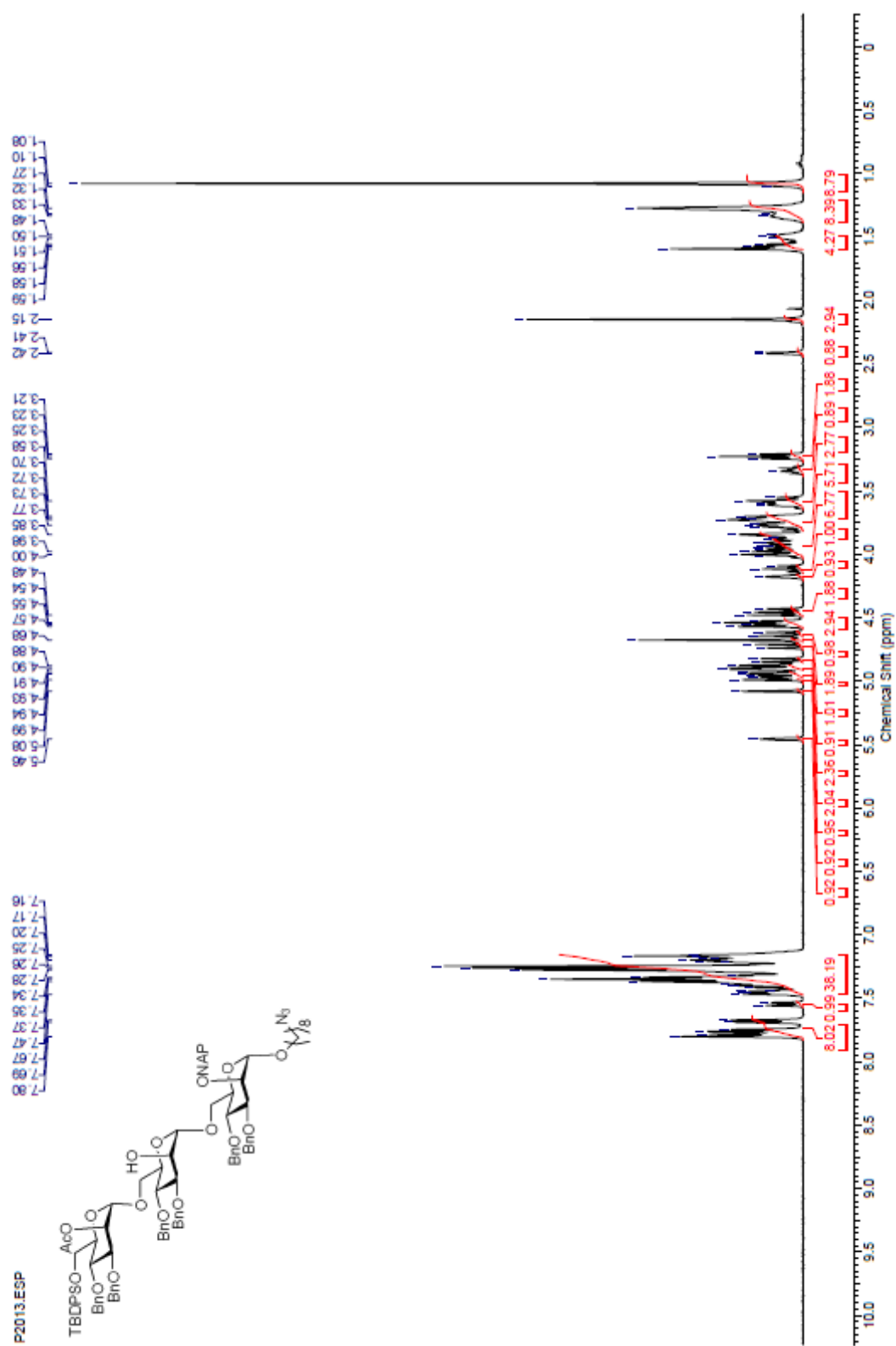


<sup>1</sup>H NMR for compound **23** (700 MHz, CDCl<sub>3</sub>)

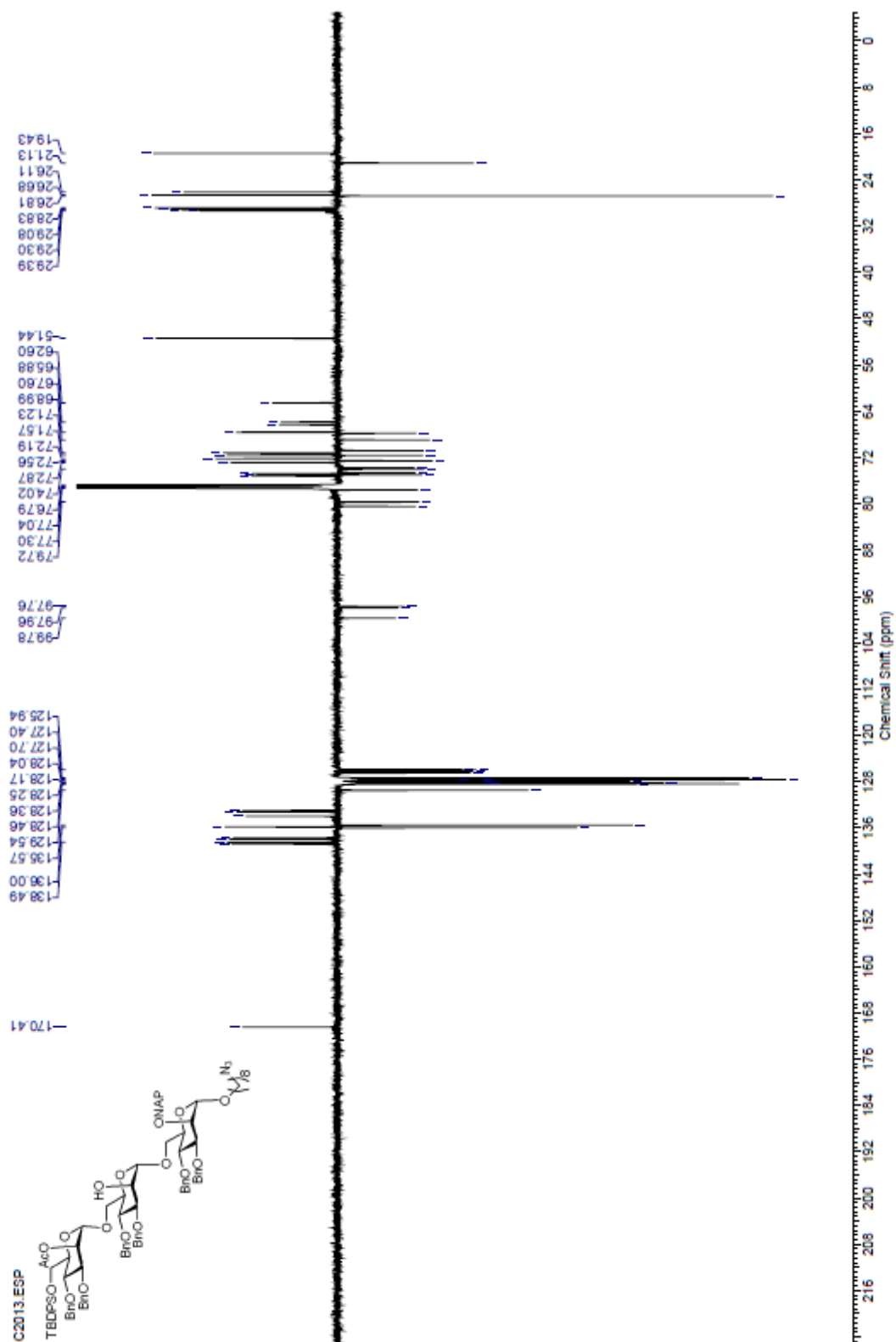
$^{13}\text{C}$  NMR for compound **23** (126 MHz,  $\text{CDCl}_3$ )

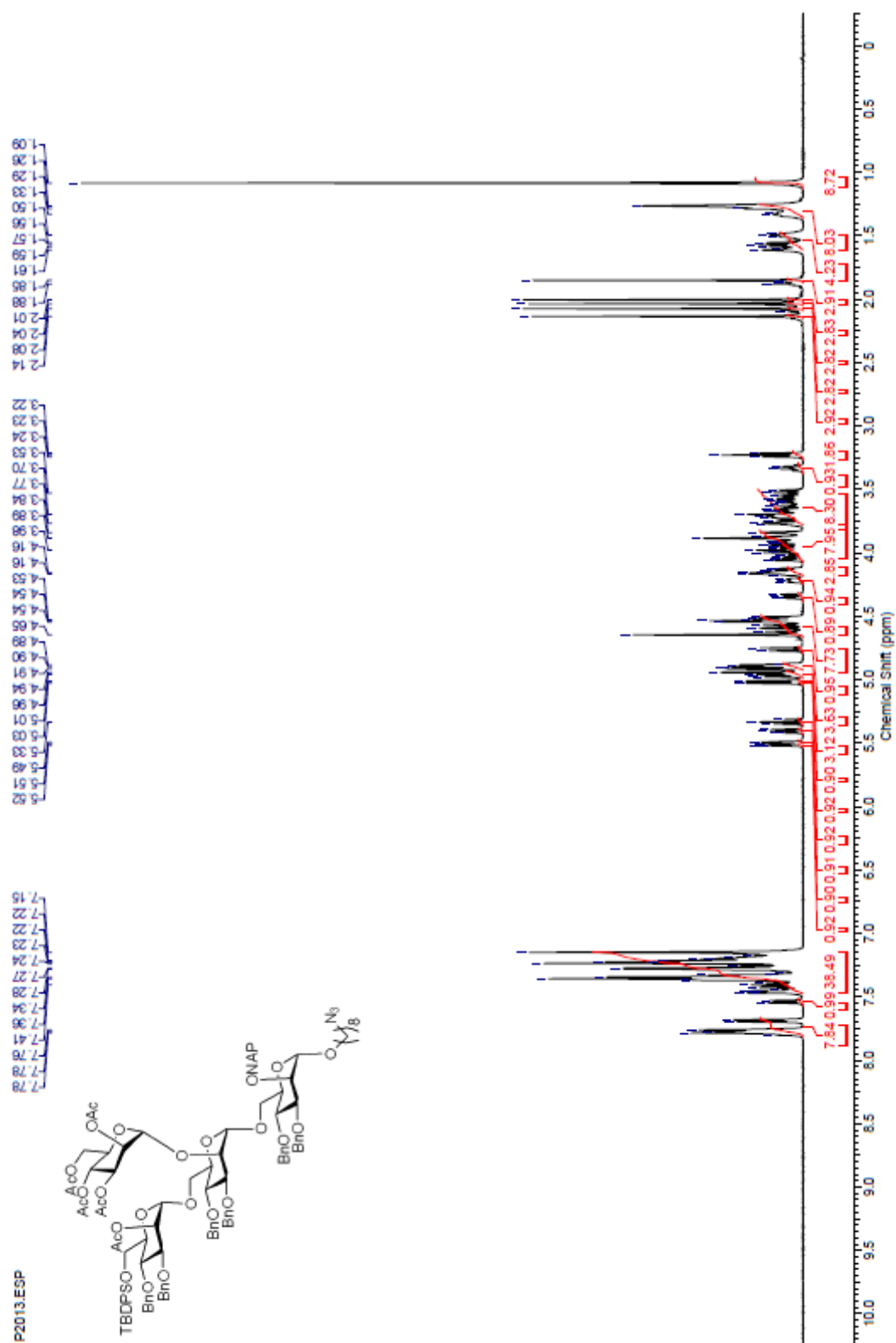


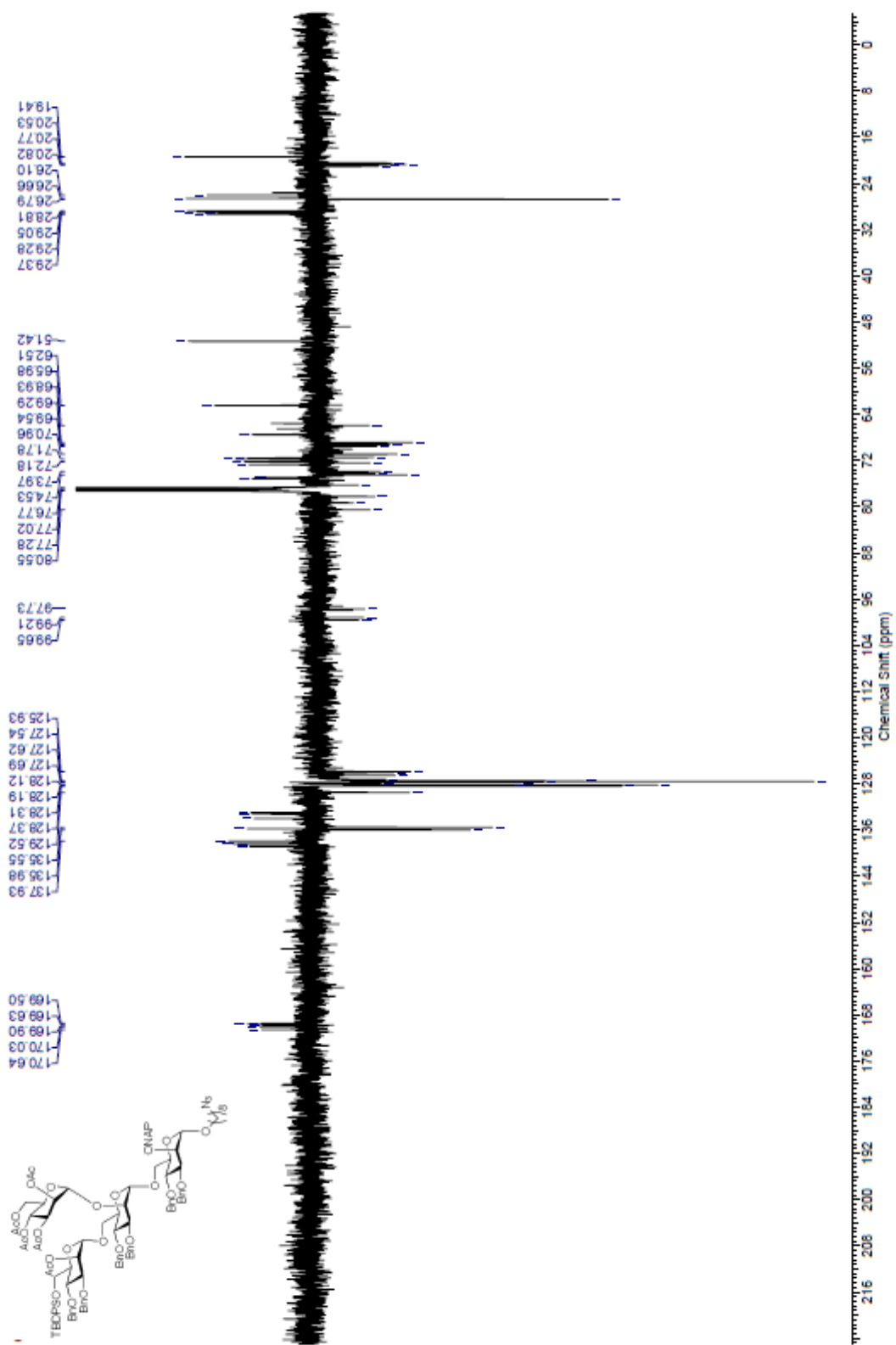
$^1\text{H}$  NMR for compound **24** (400 MHz,  $\text{CDCl}_3$ )



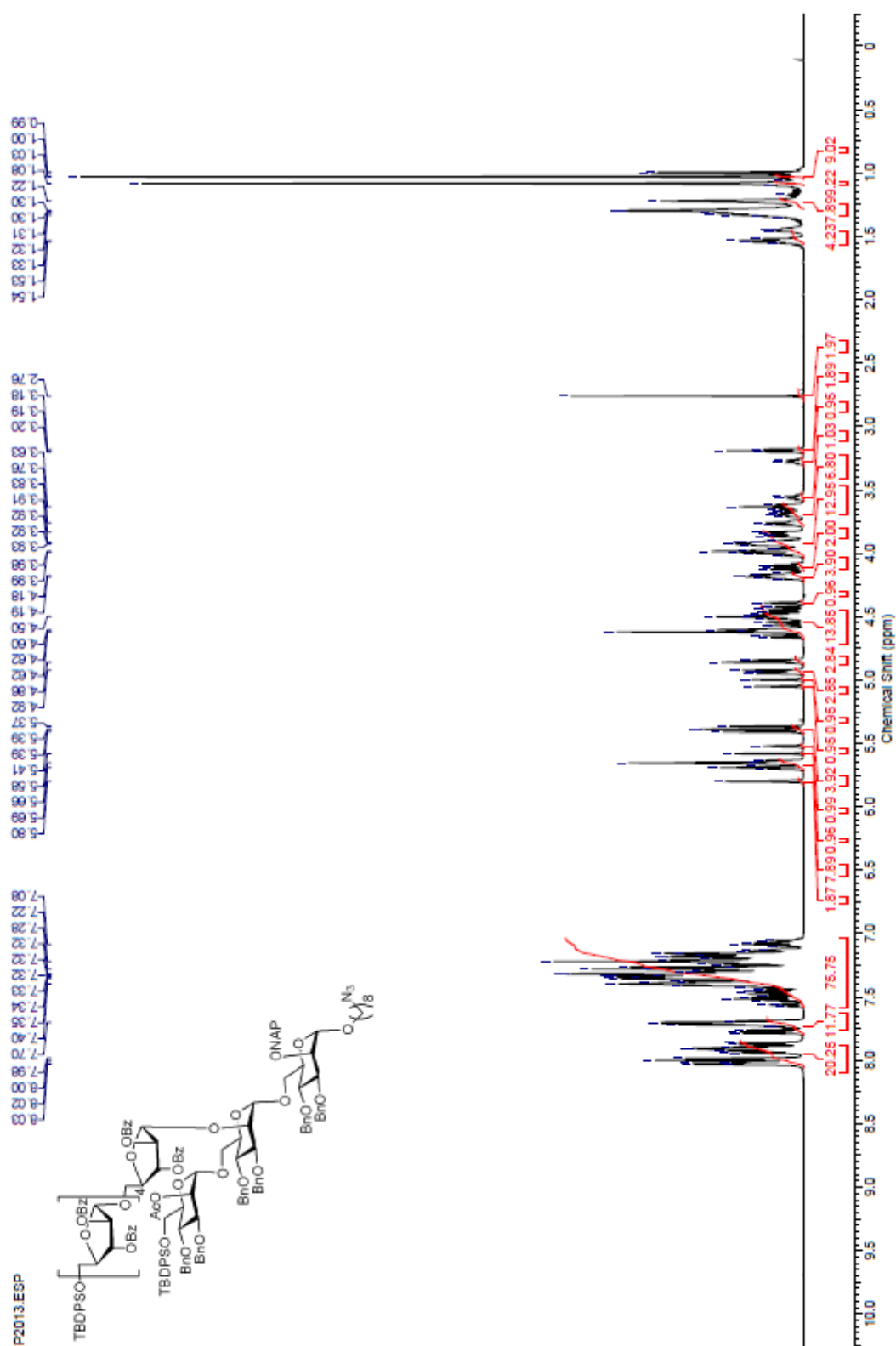
$^{13}\text{C}$  NMR for compound **24** (126 MHz,  $\text{CDCl}_3$ )

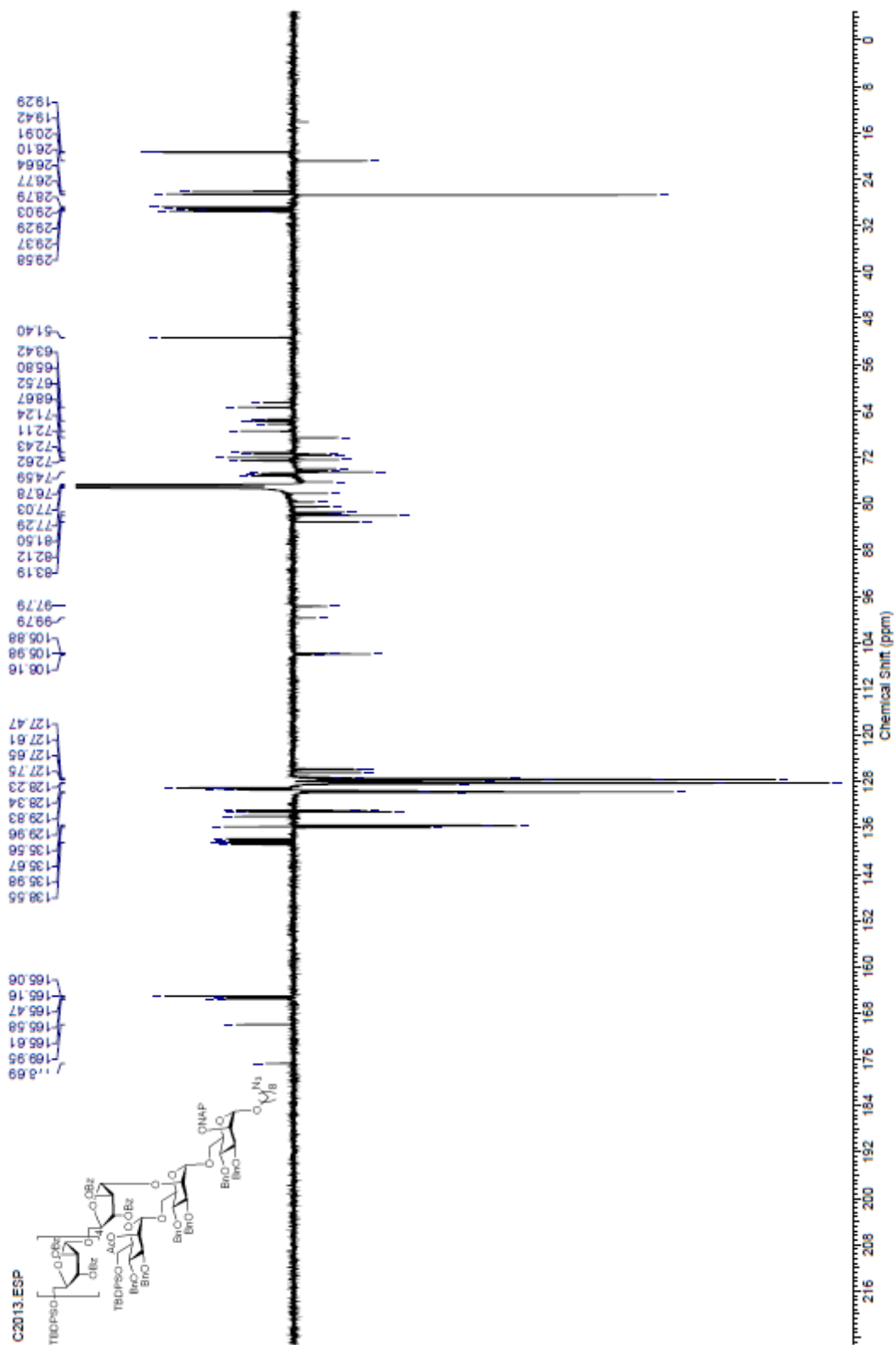


<sup>1</sup>H NMR for compound **25** (500 MHz, CDCl<sub>3</sub>)

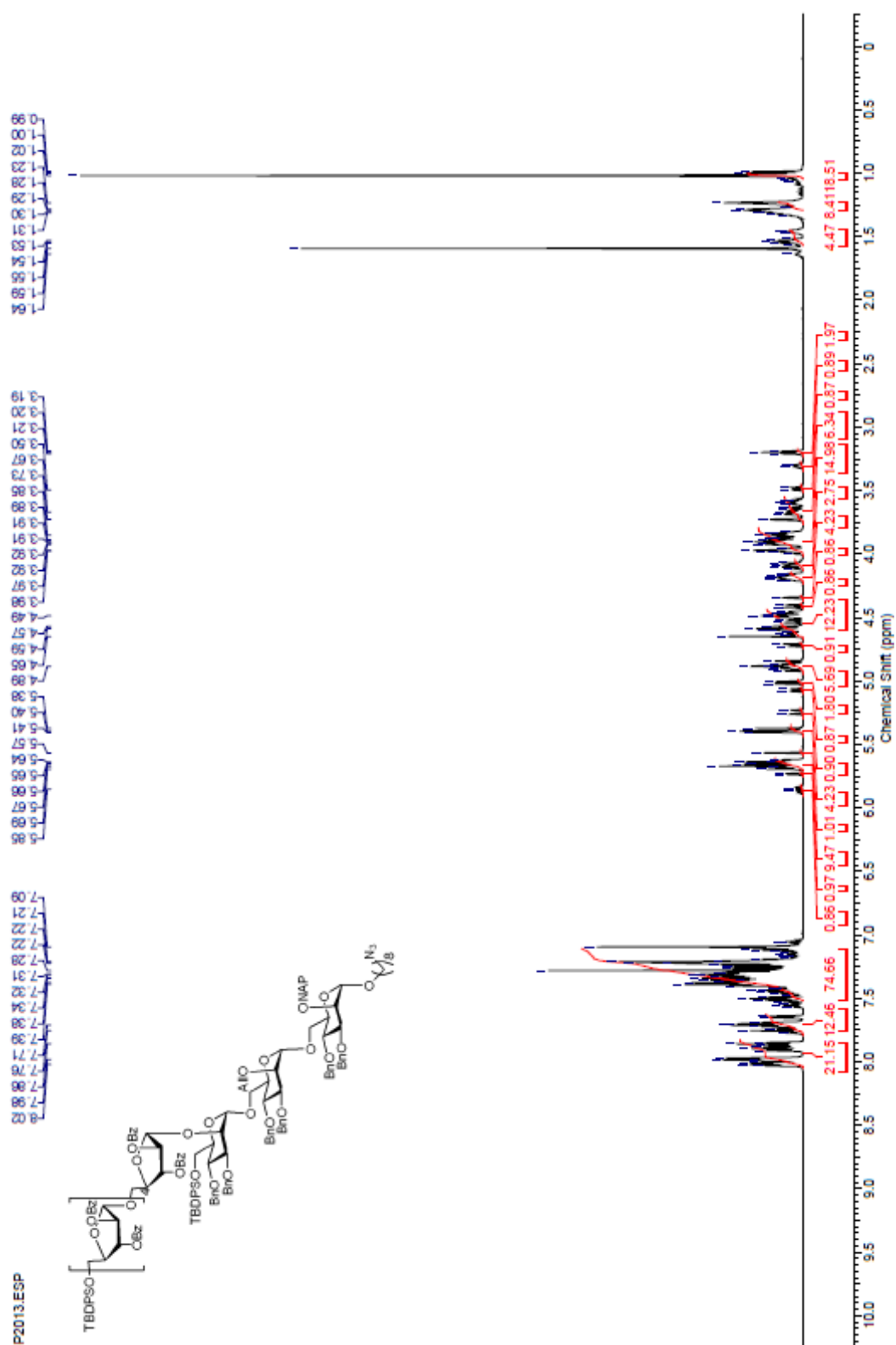
$^{13}\text{C}$  NMR for compound **25** (126 MHz,  $\text{CDCl}_3$ )

$^1\text{H}$  NMR for compound **26** (600 MHz,  $\text{CDCl}_3$ )

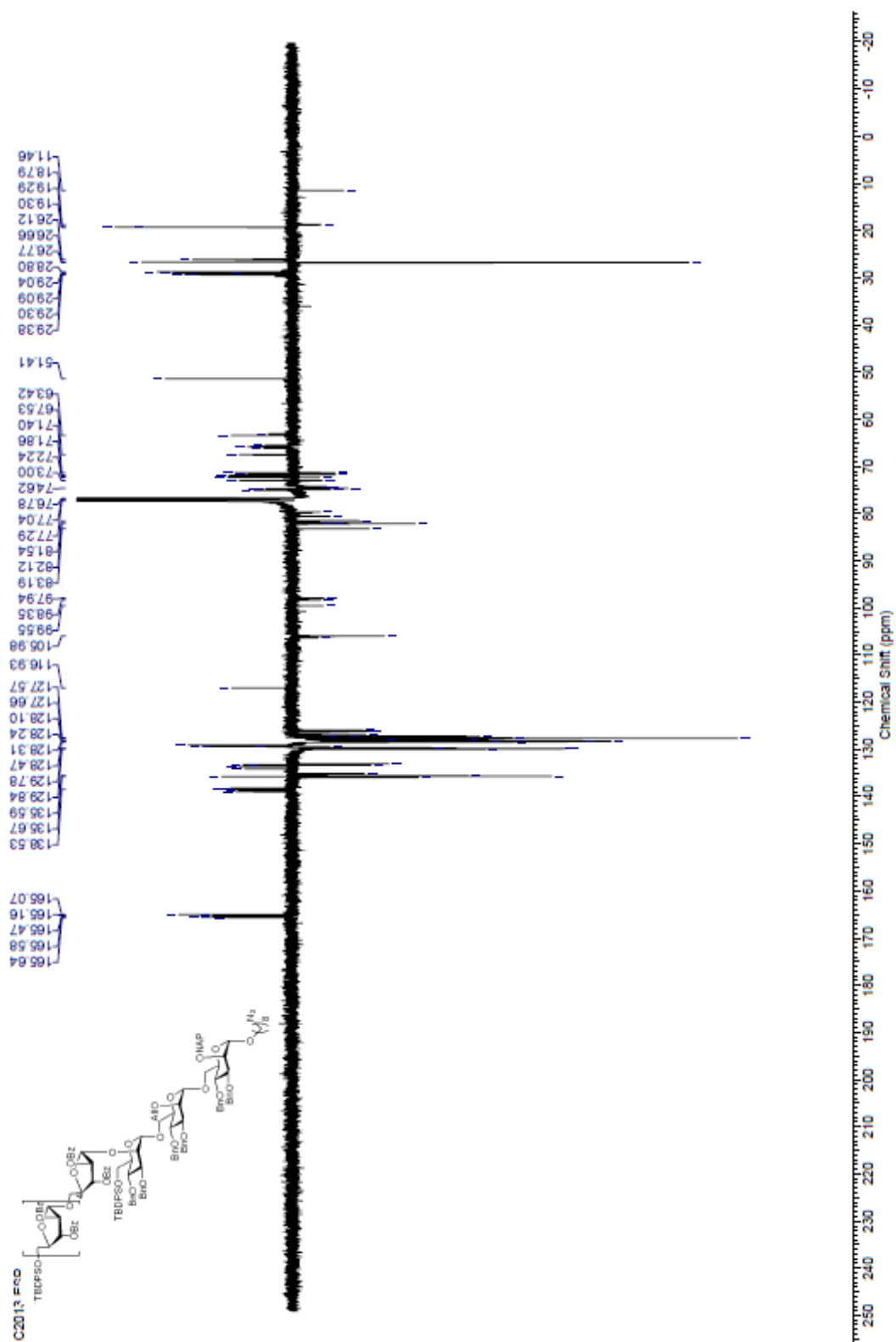


$^{13}\text{C}$  NMR for compound **26** (126 MHz,  $\text{CDCl}_3$ )

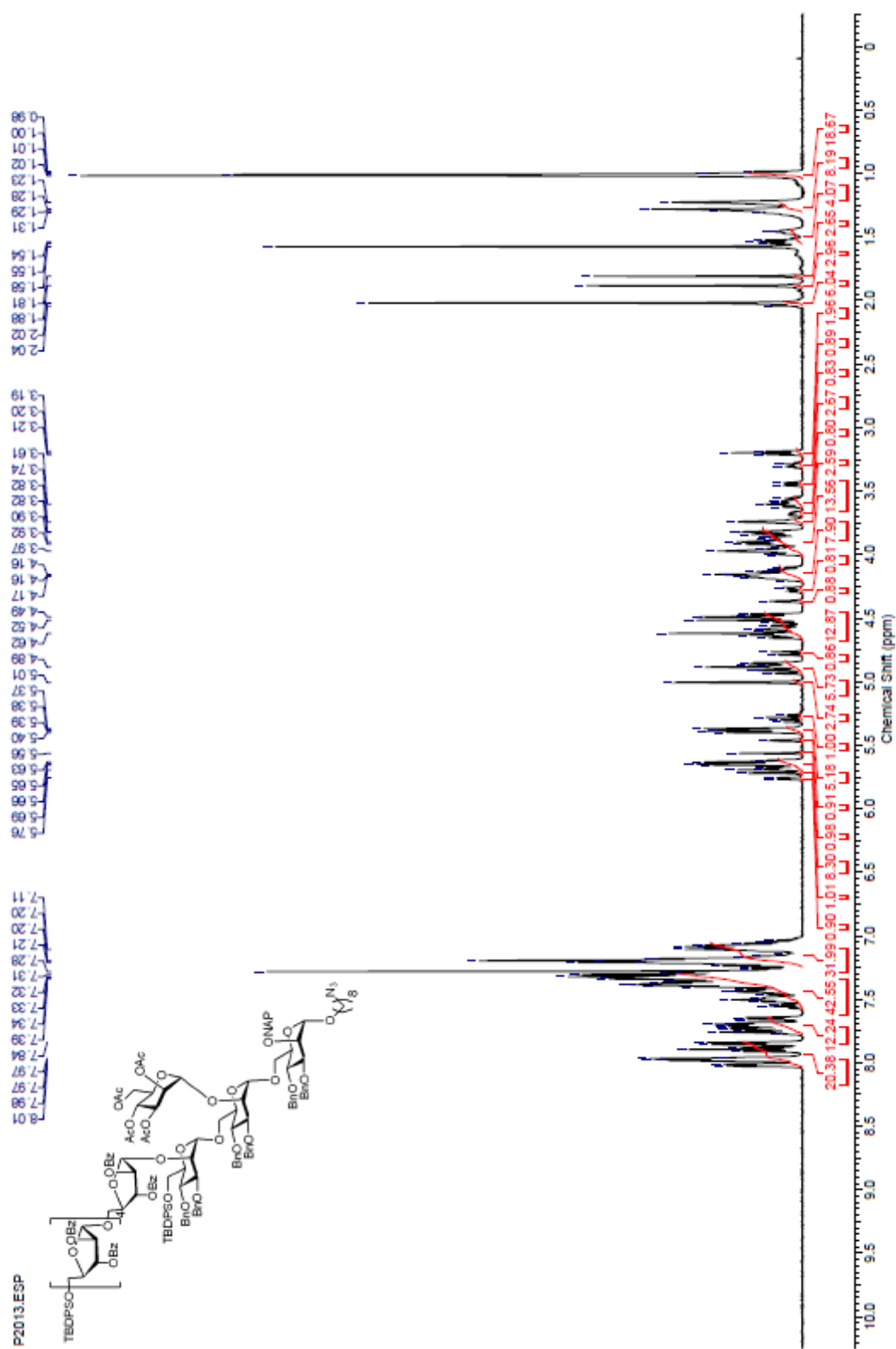
$^1\text{H}$  NMR for compound **28** (600 MHz,  $\text{CDCl}_3$ )



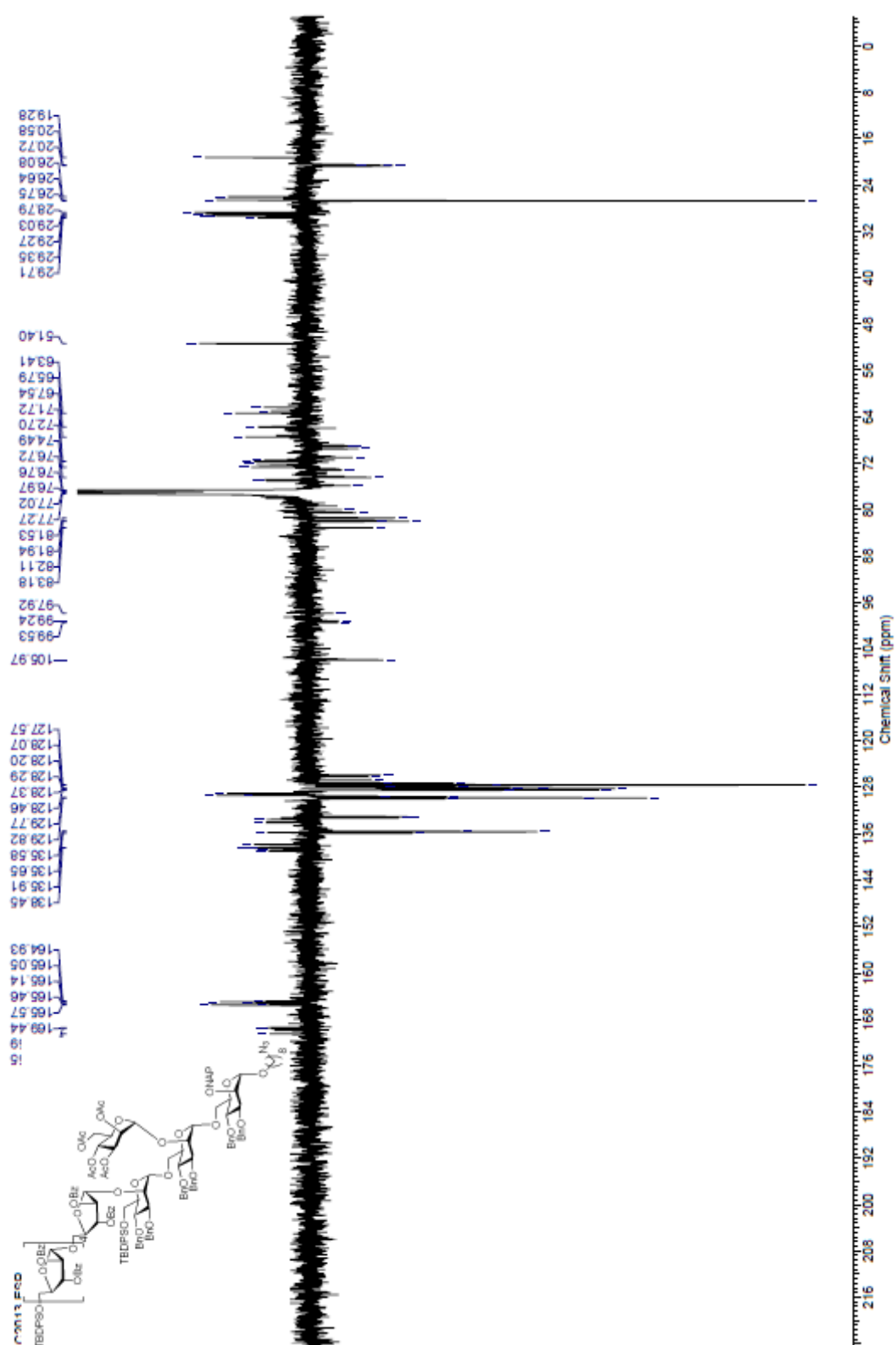
$^{13}\text{C}$  NMR for compound **28** (126 MHz,  $\text{CDCl}_3$ )



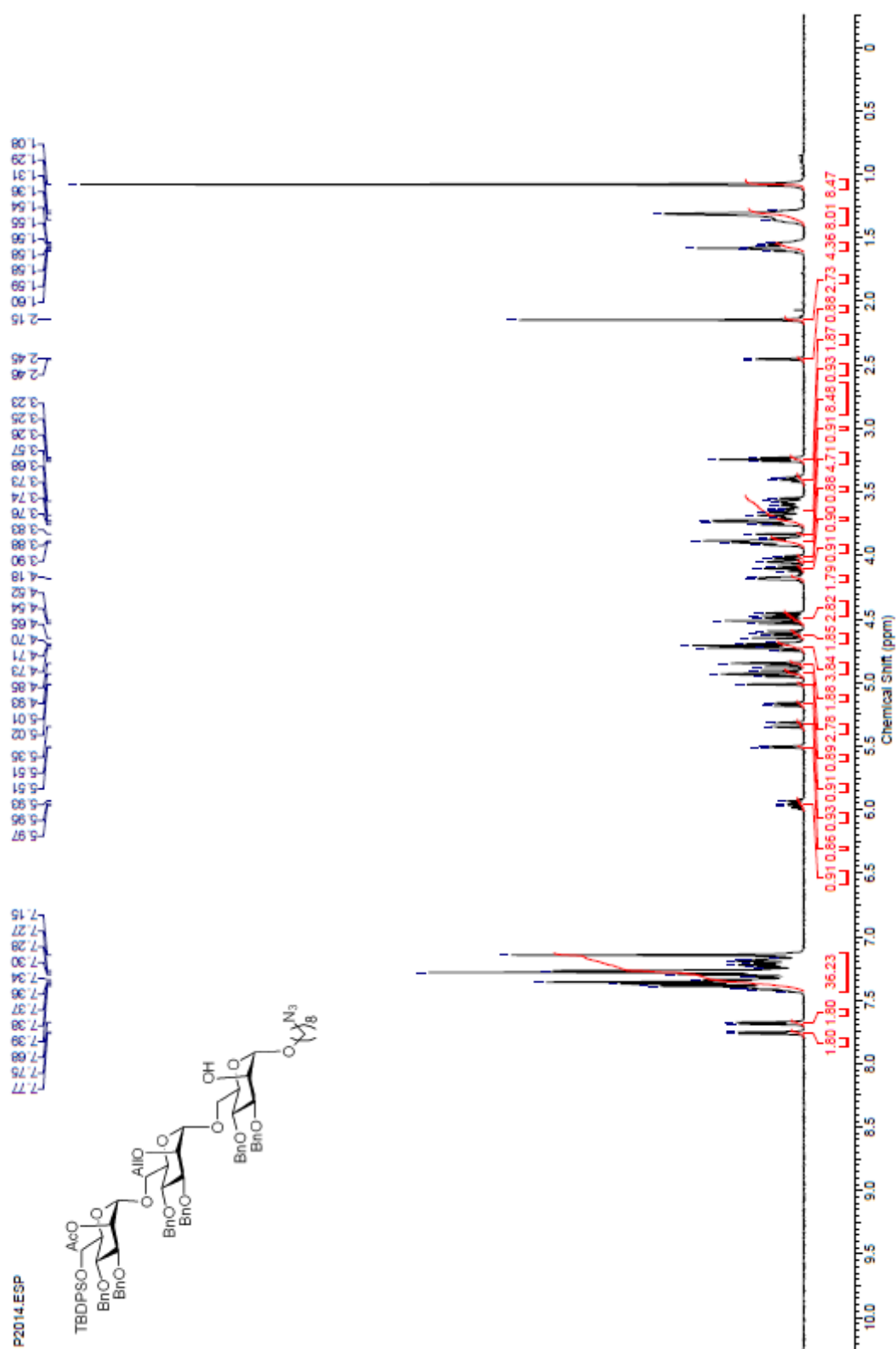
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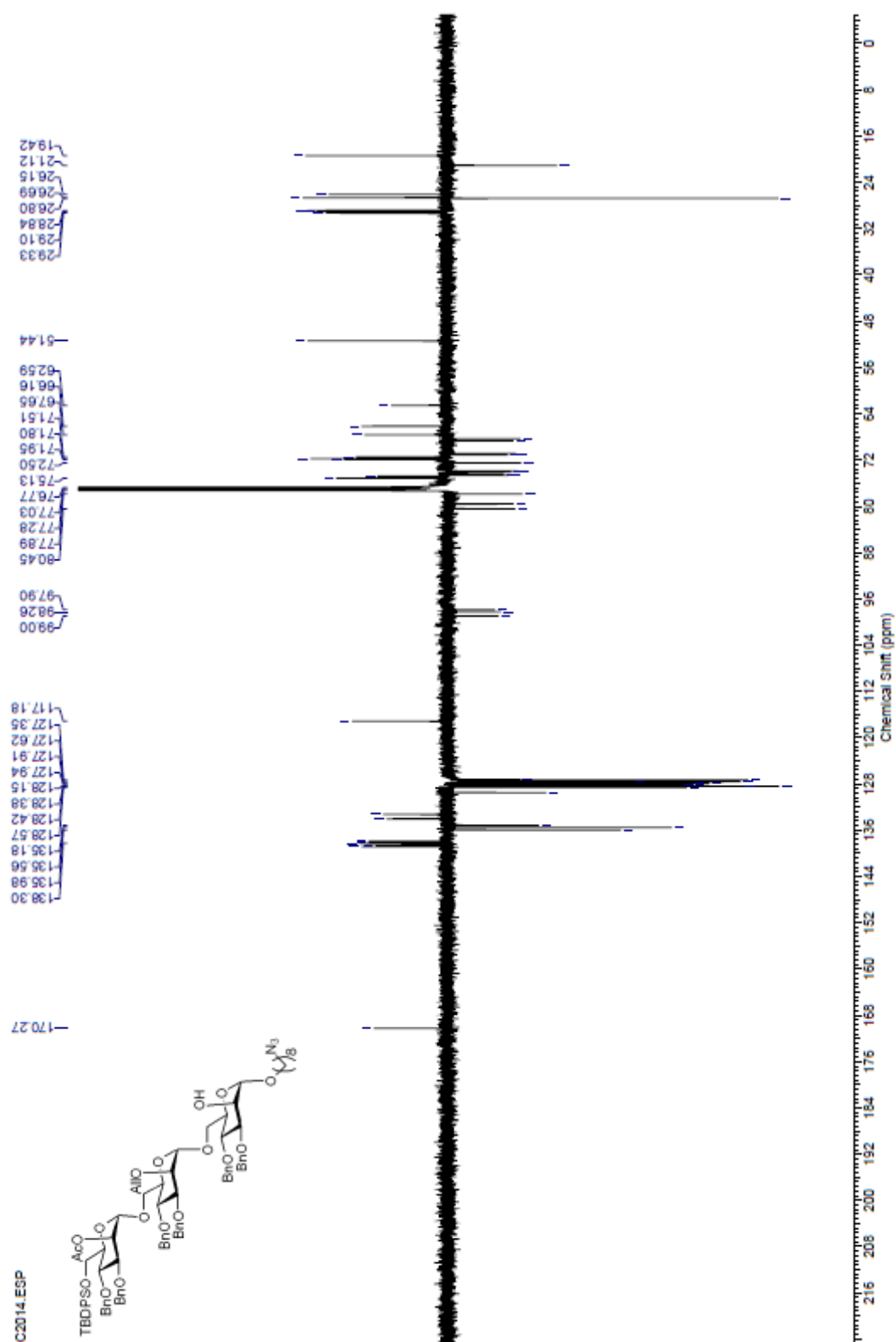
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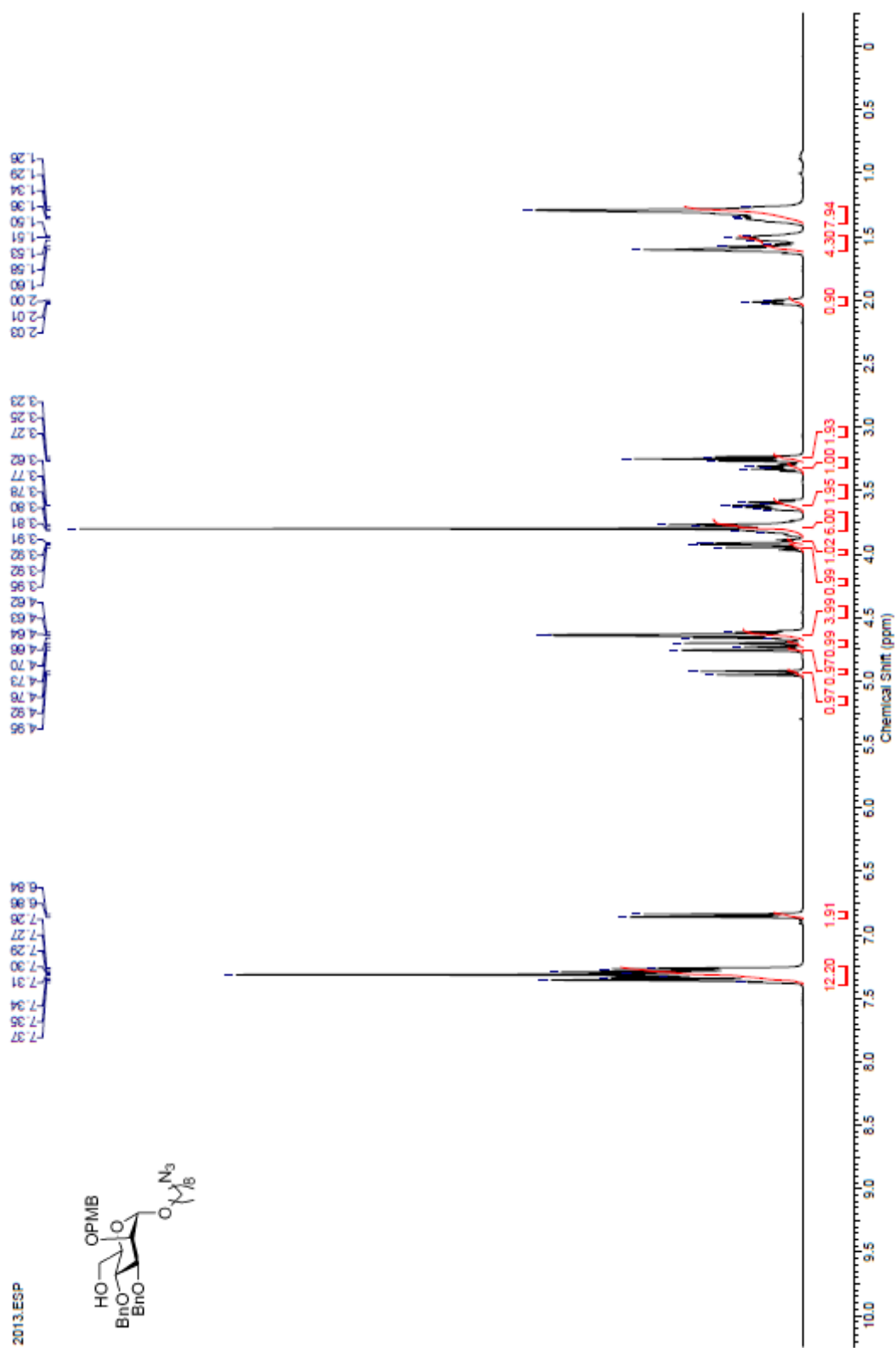


$^1\text{H}$  NMR for compound **30** (500 MHz,  $\text{CDCl}_3$ )

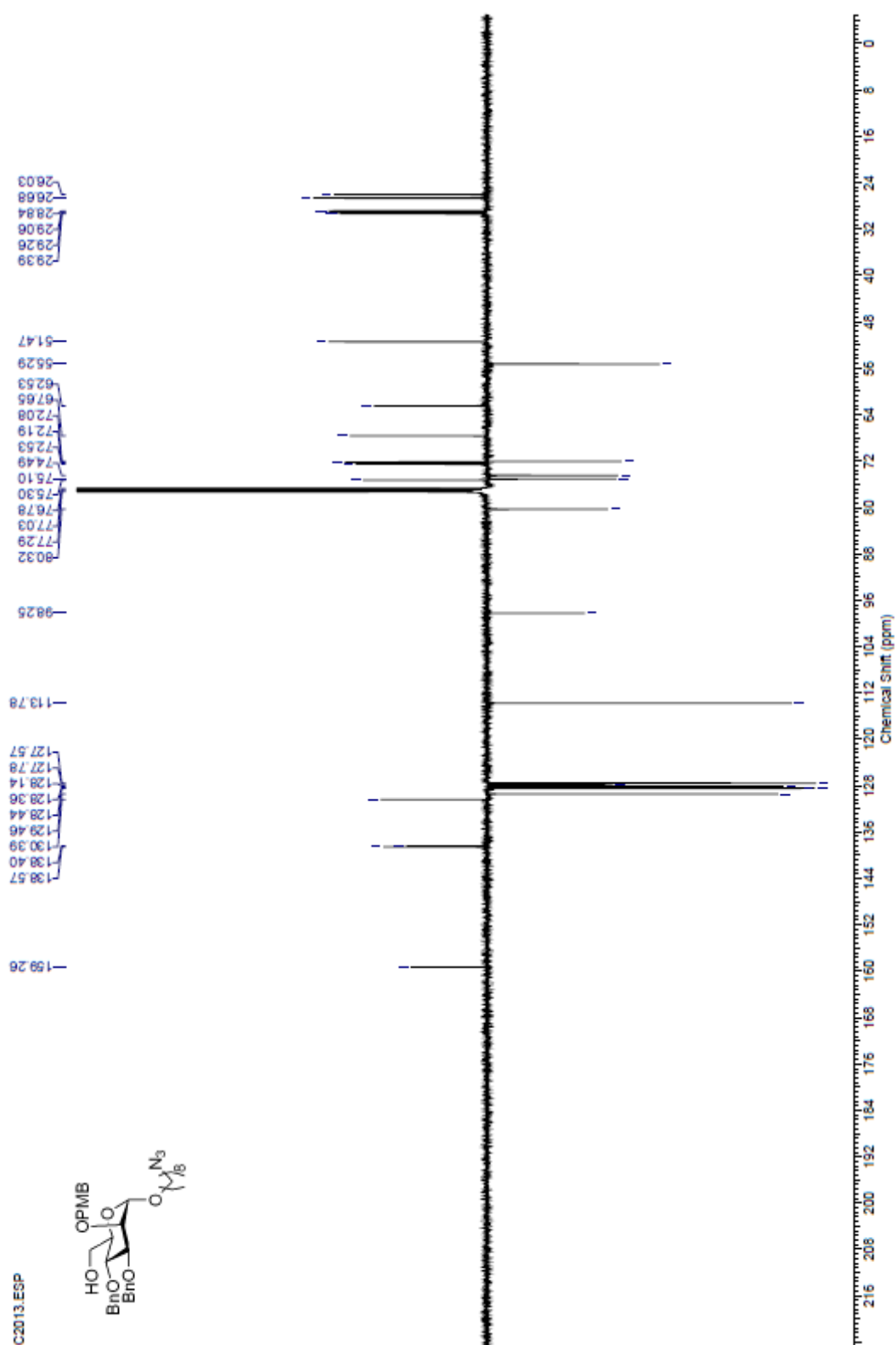


$^{13}\text{C}$  NMR for compound **30** (126 MHz,  $\text{CDCl}_3$ )

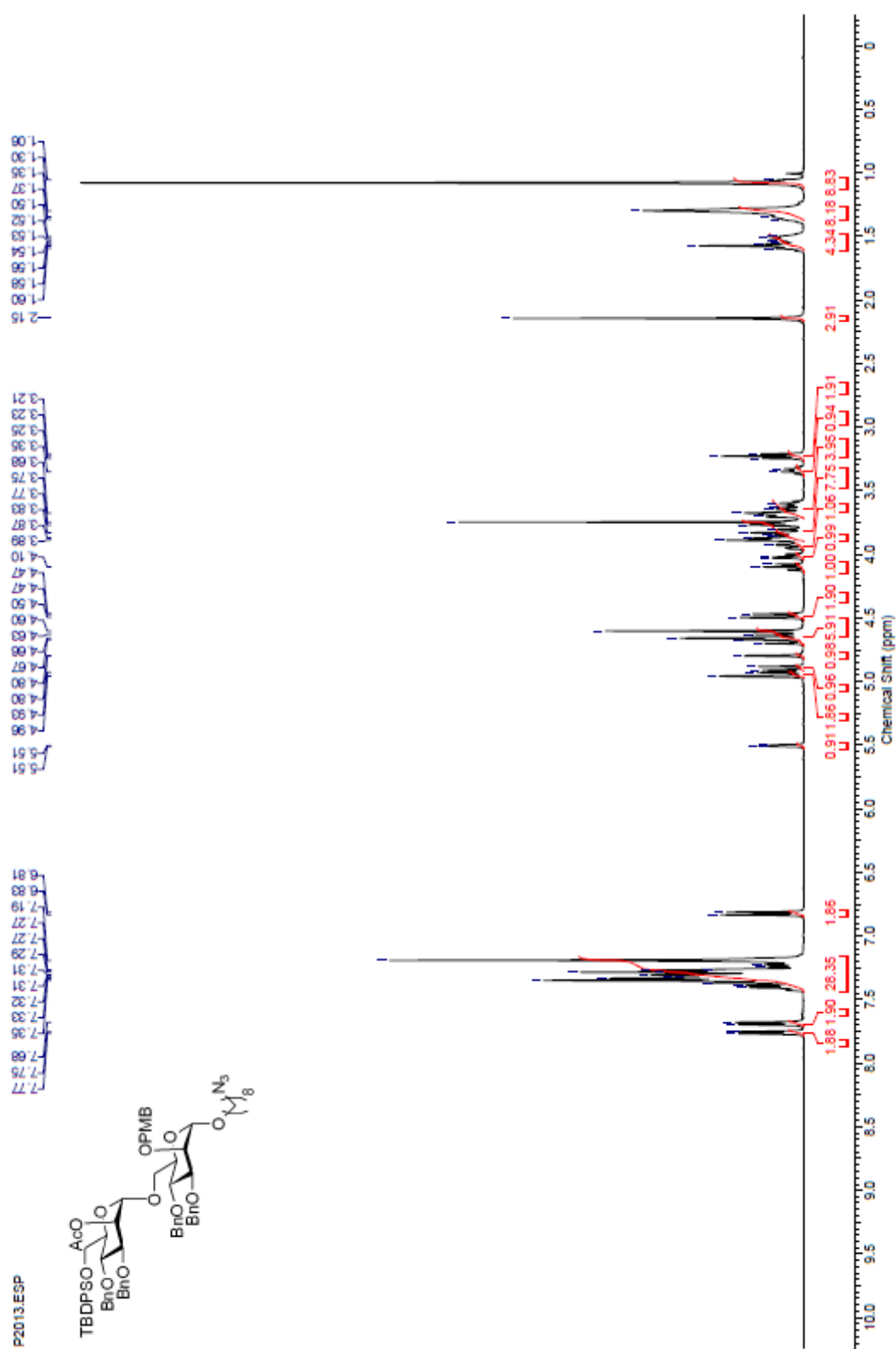


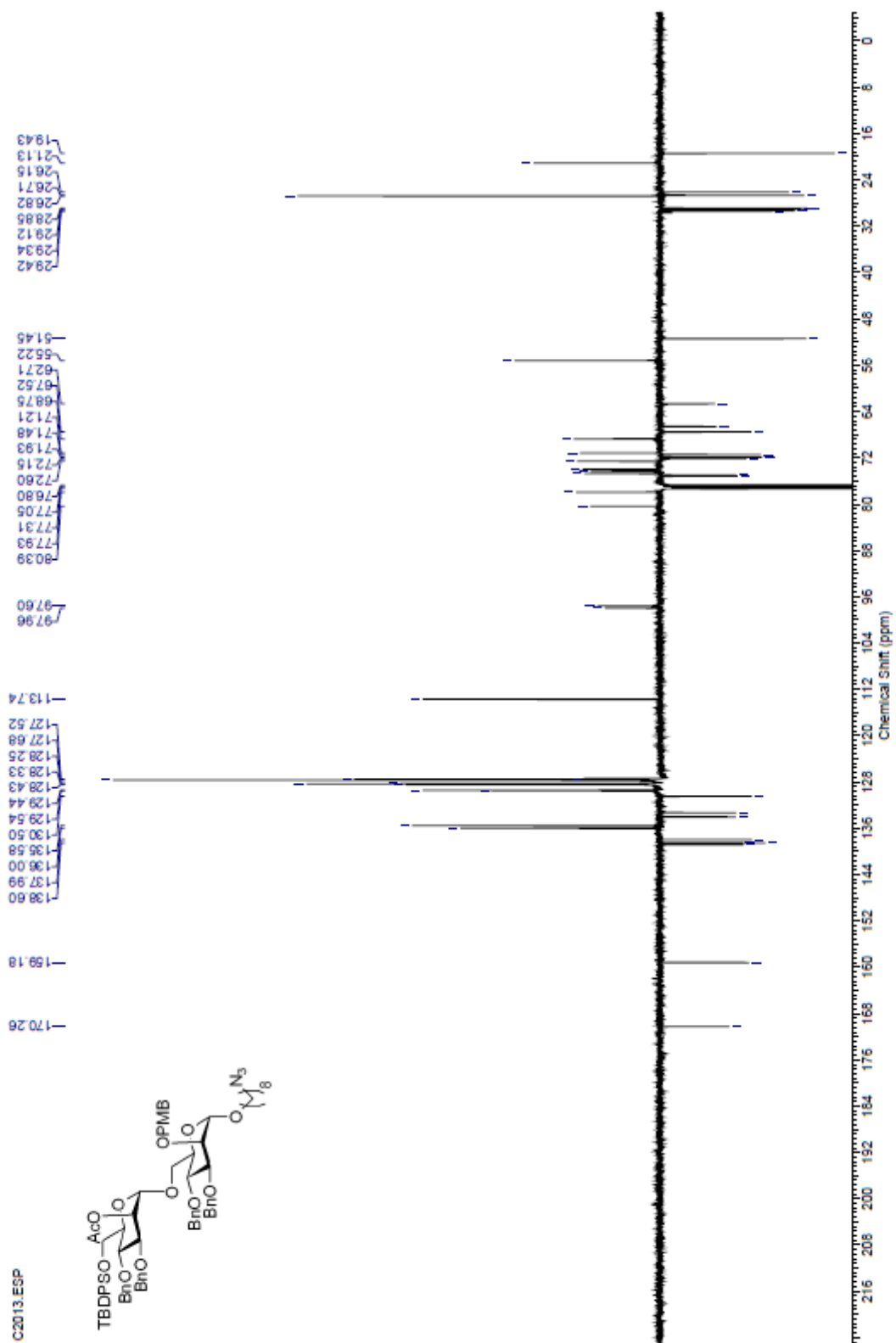
<sup>1</sup>H NMR for compound **31** (400 MHz, CDCl<sub>3</sub>)

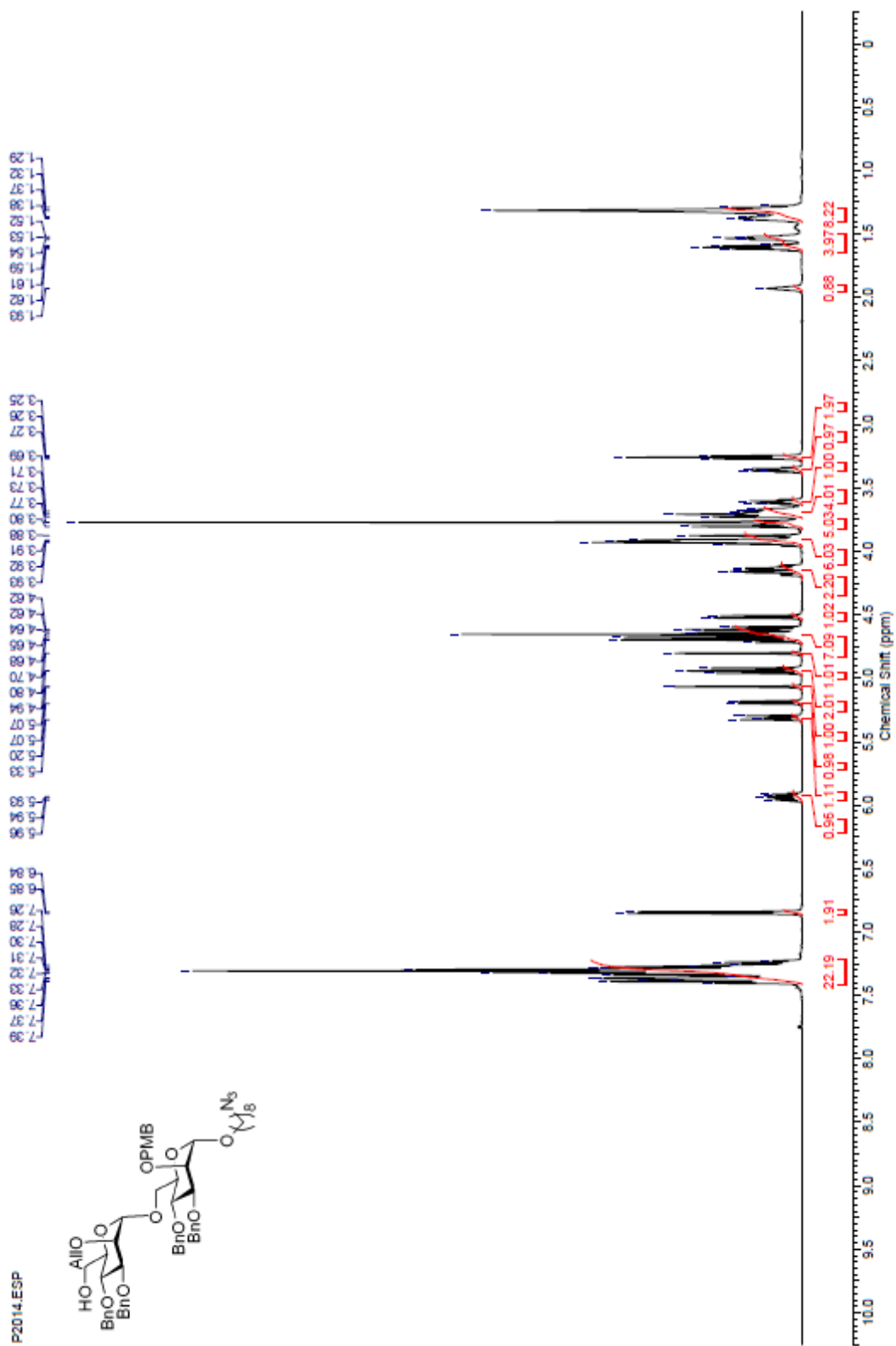
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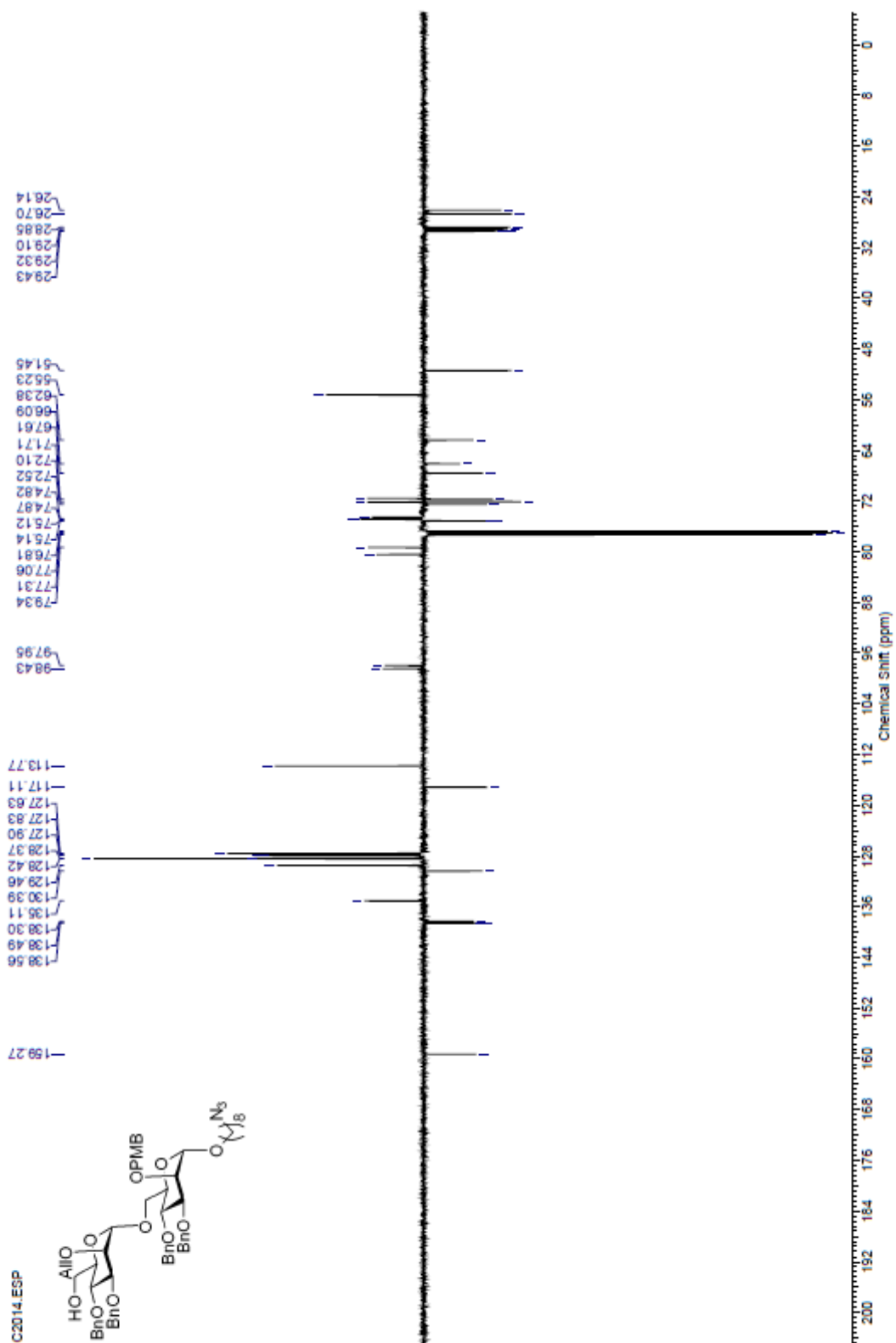
$^1\text{H}$  NMR for compound **32** (400 MHz,  $\text{CDCl}_3$ )



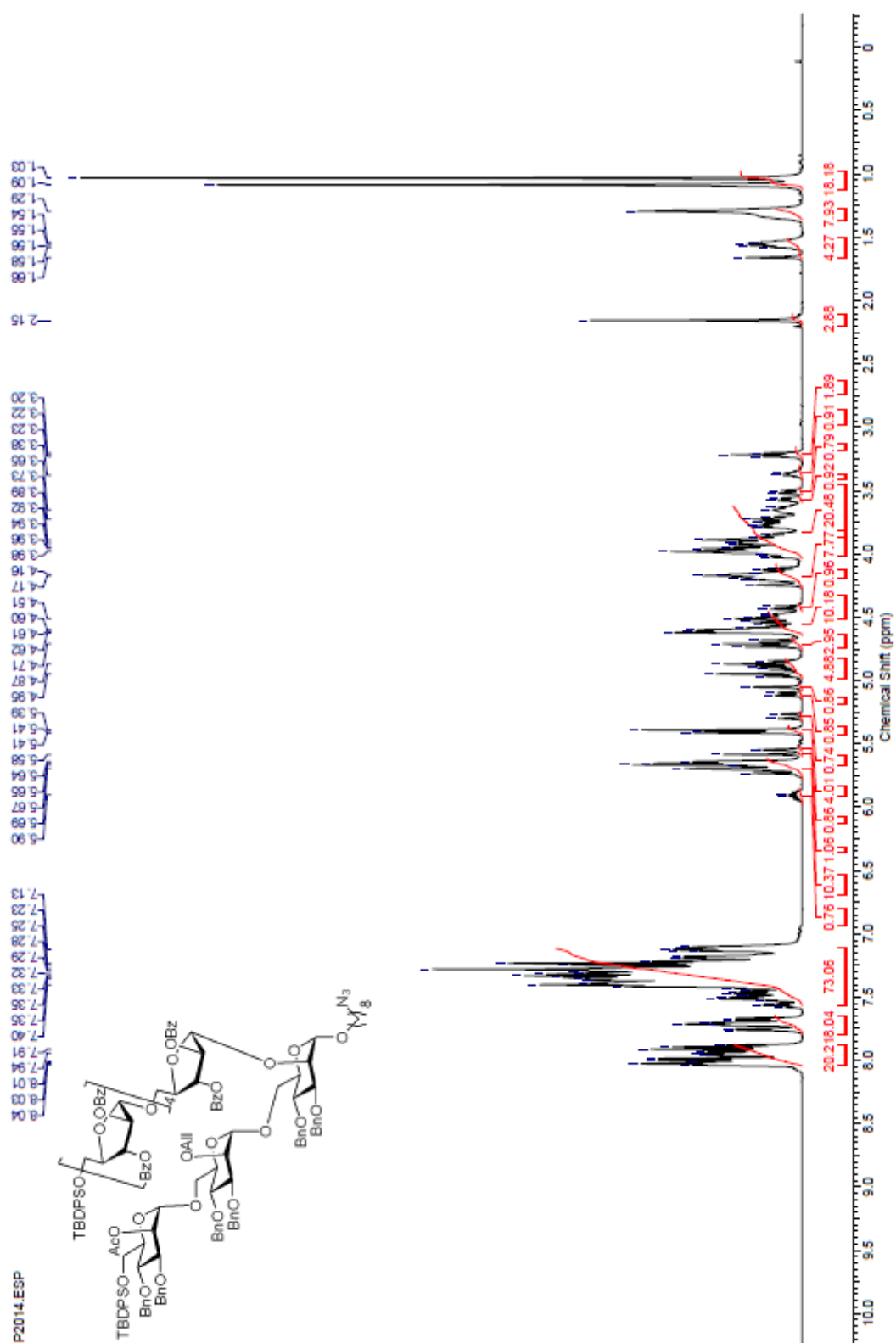
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<sup>1</sup>H NMR for compound **33** (600 MHz, CDCl<sub>3</sub>)

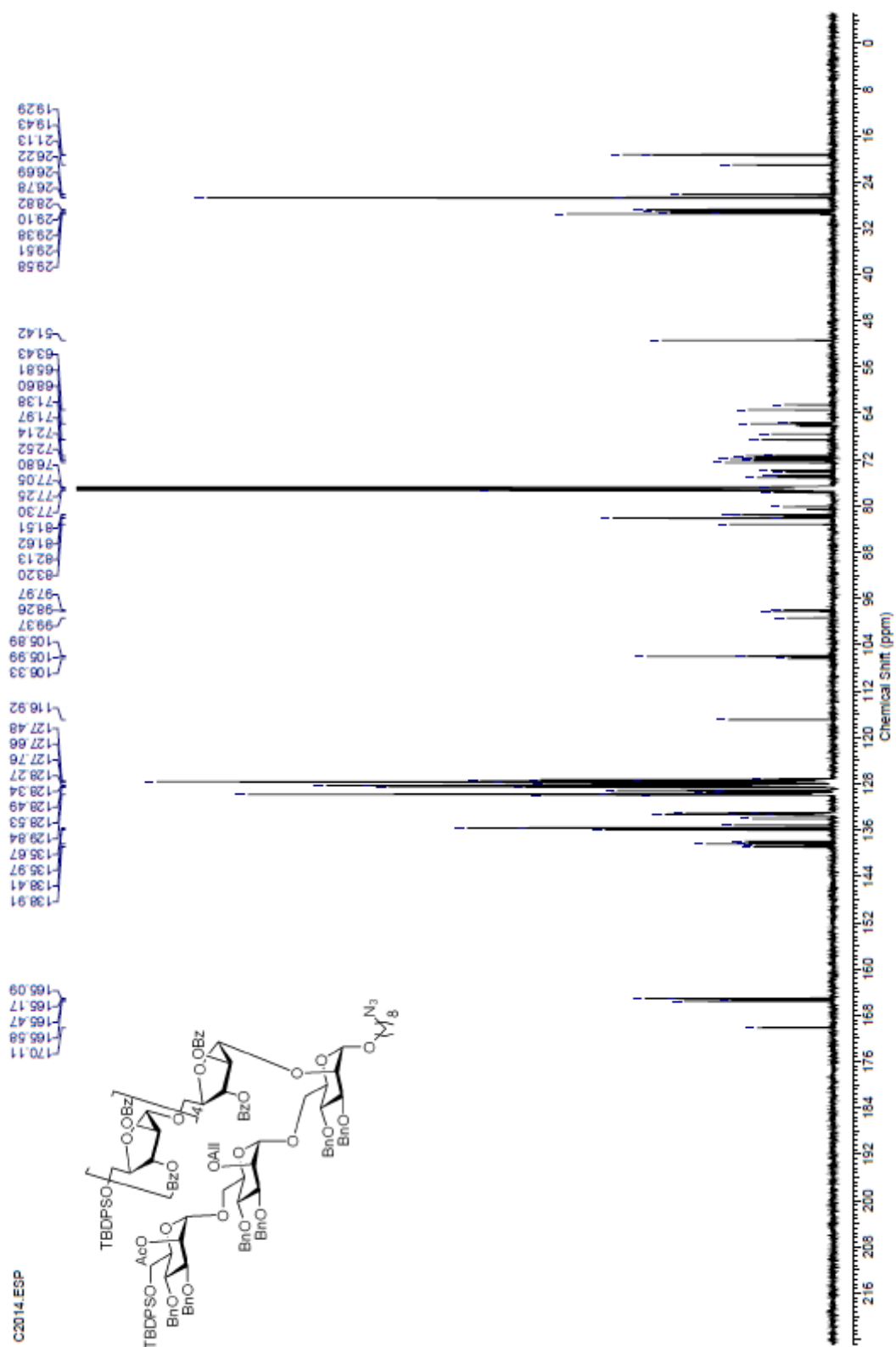
$^{13}\text{C}$  NMR for compound **33** (126 MHz,  $\text{CDCl}_3$ )



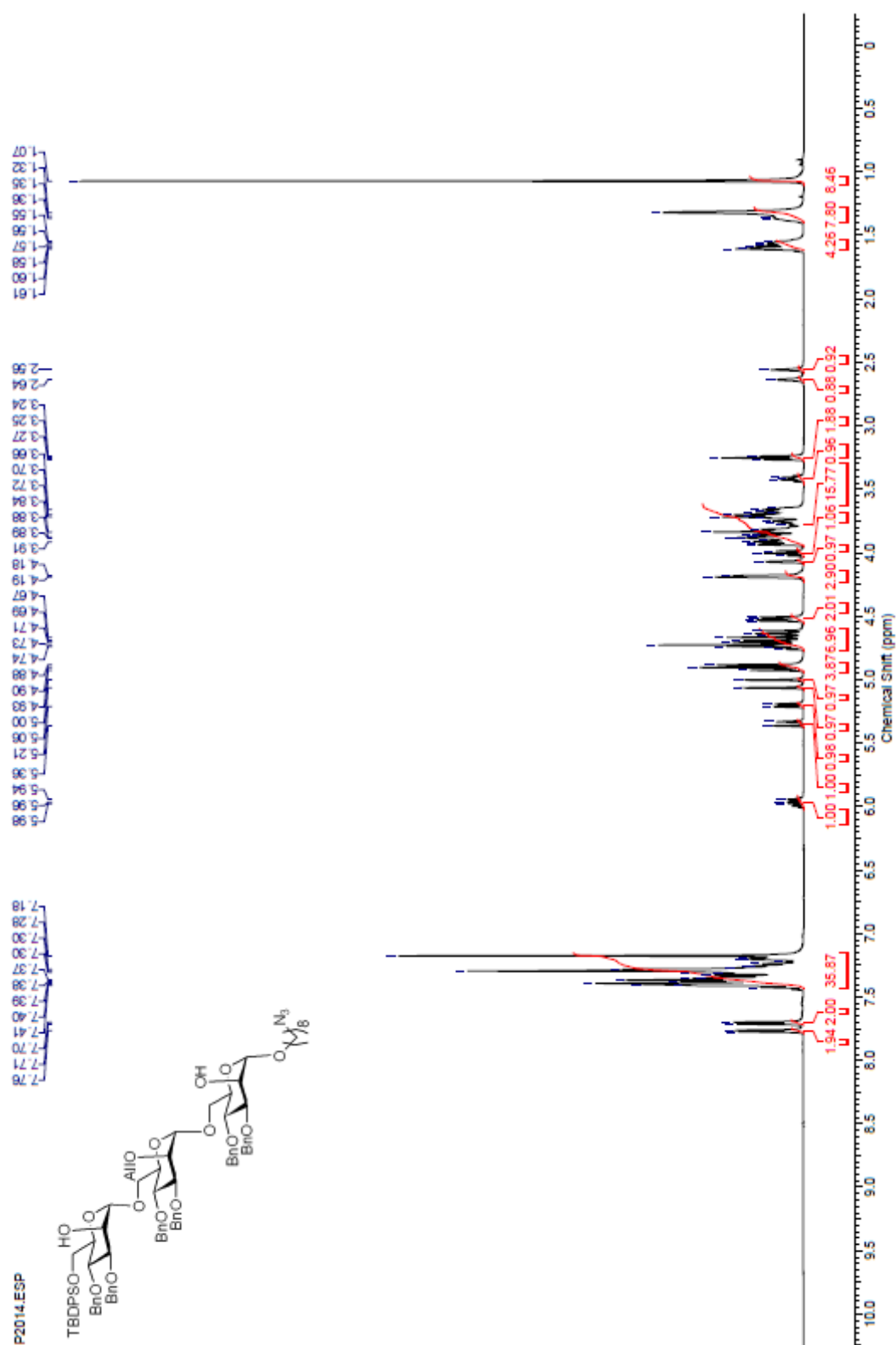
$^1\text{H}$  NMR for compound **34** (600 MHz,  $\text{CDCl}_3$ )



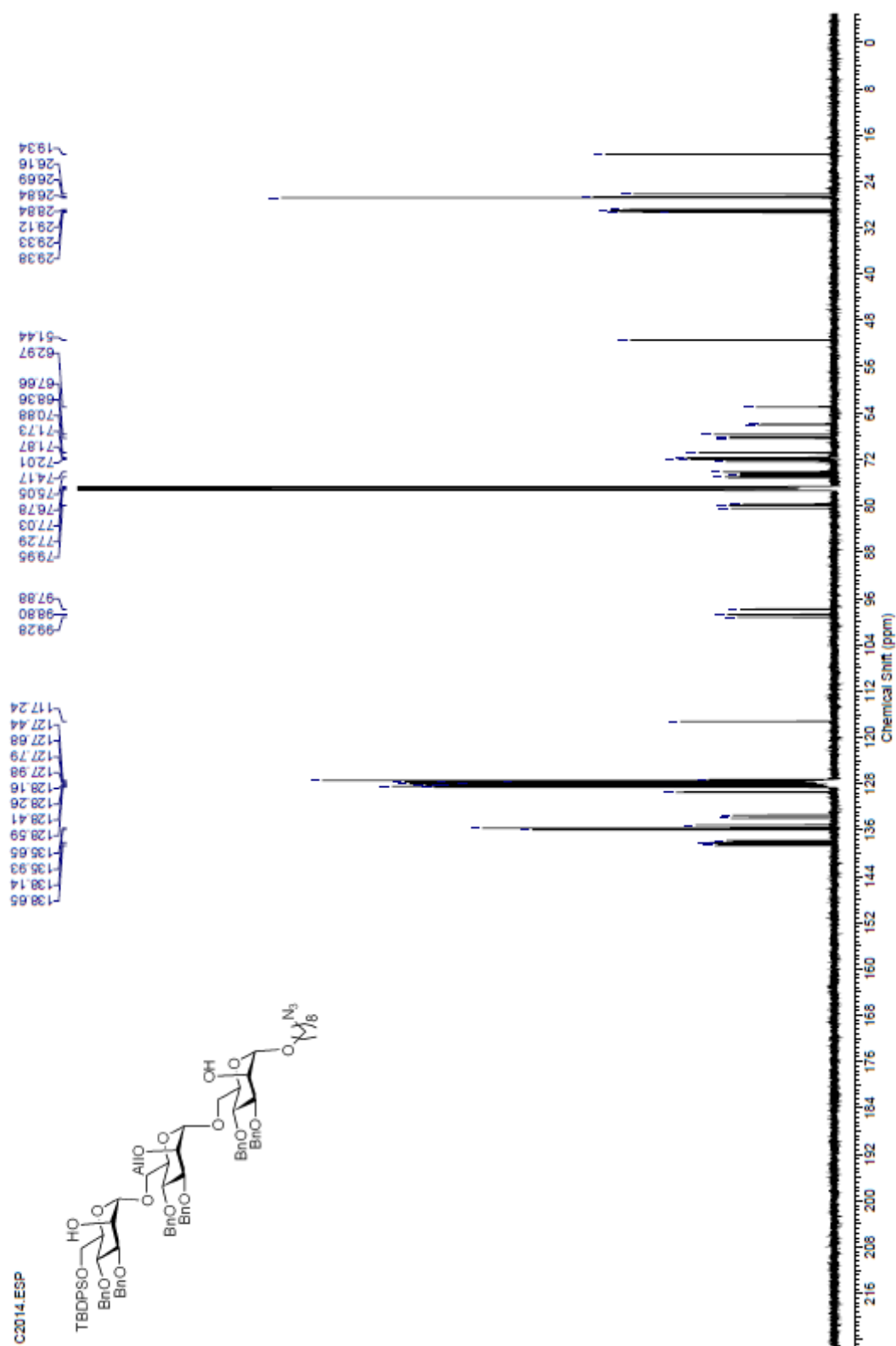
$^{13}\text{C}$  NMR for compound **34** (126 MHz,  $\text{CDCl}_3$ )



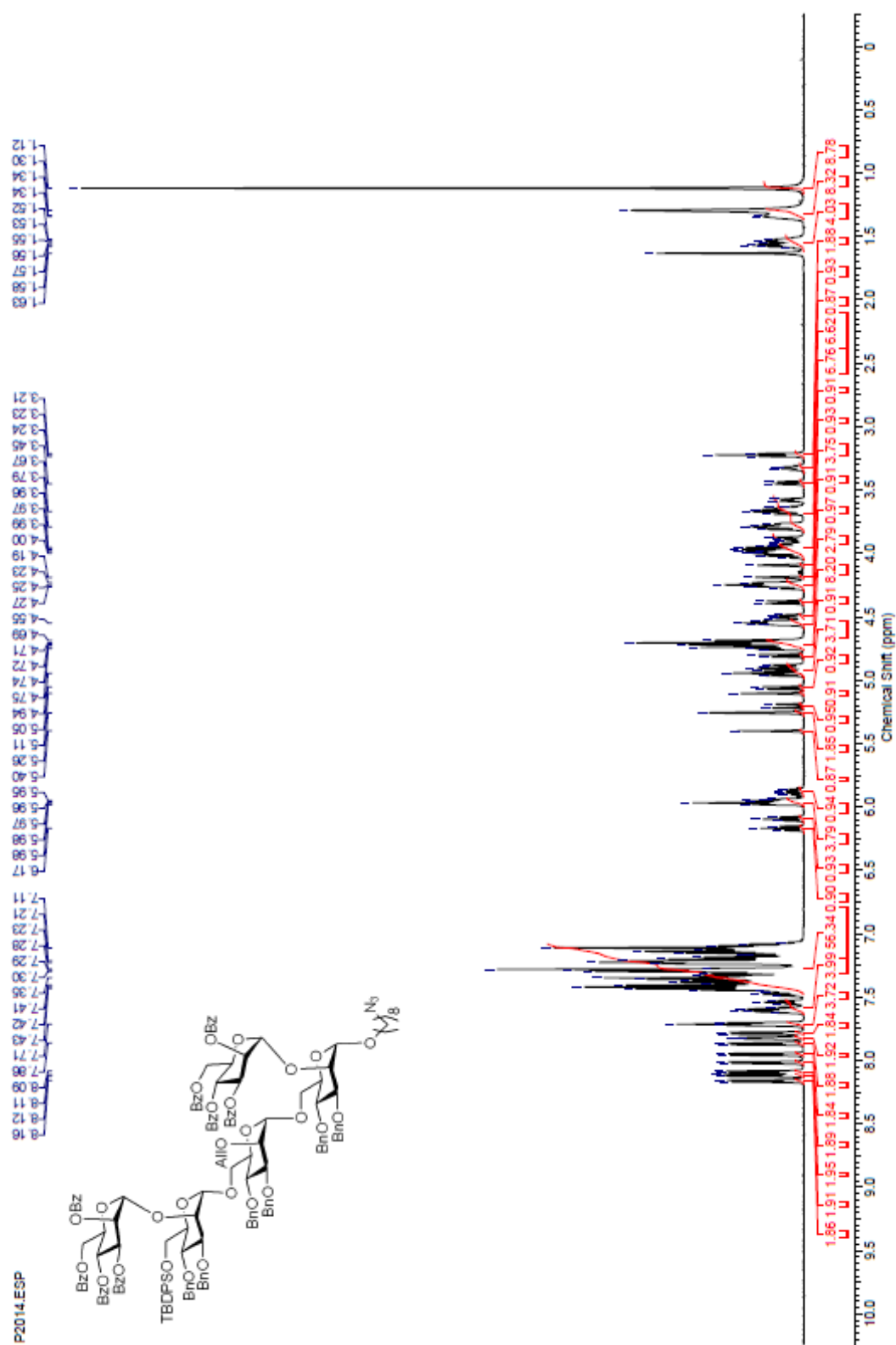
$^1\text{H}$  NMR for compound **35** (500 MHz,  $\text{CDCl}_3$ )



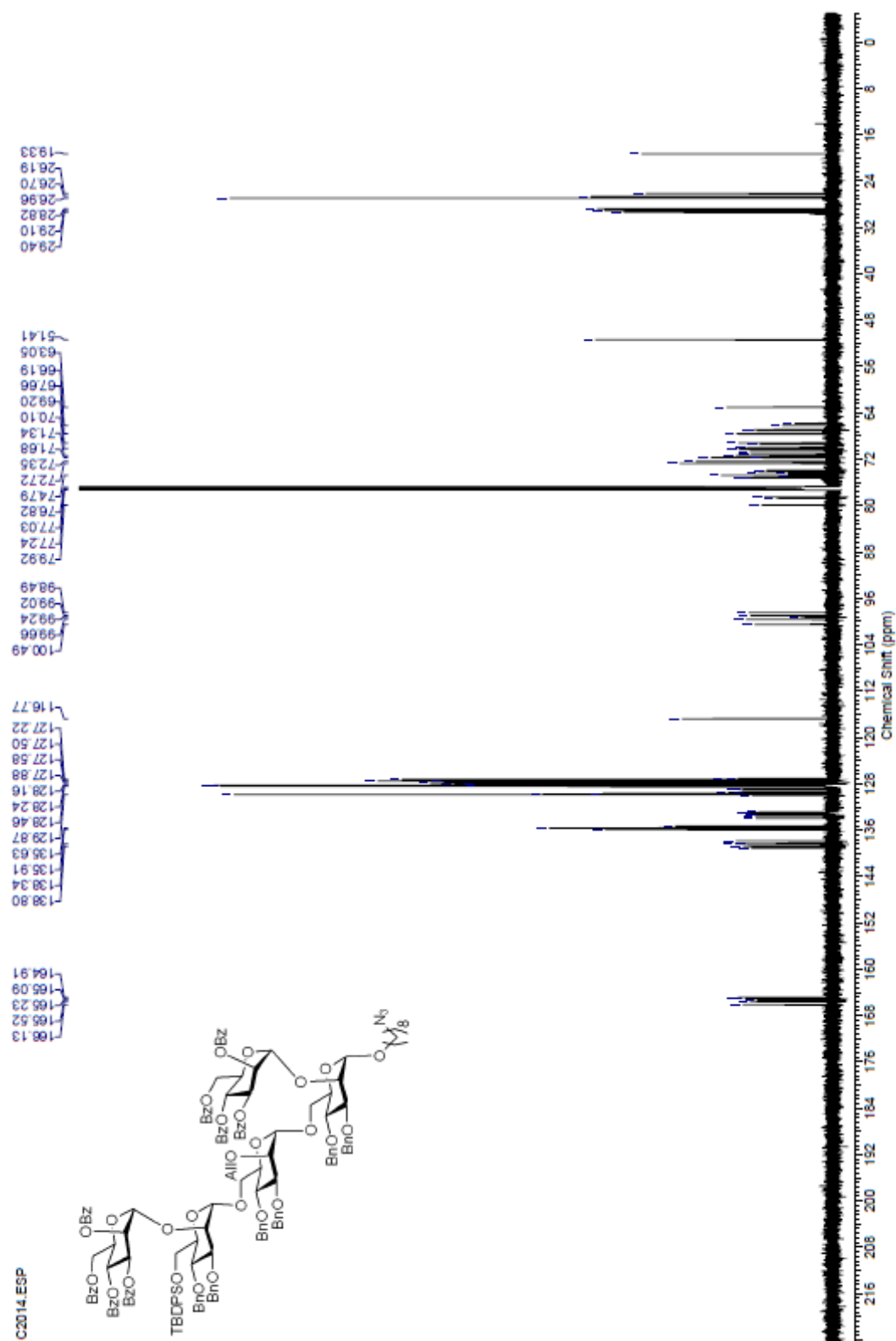
$^{13}\text{C}$  NMR for compound **35** (126 MHz,  $\text{CDCl}_3$ )

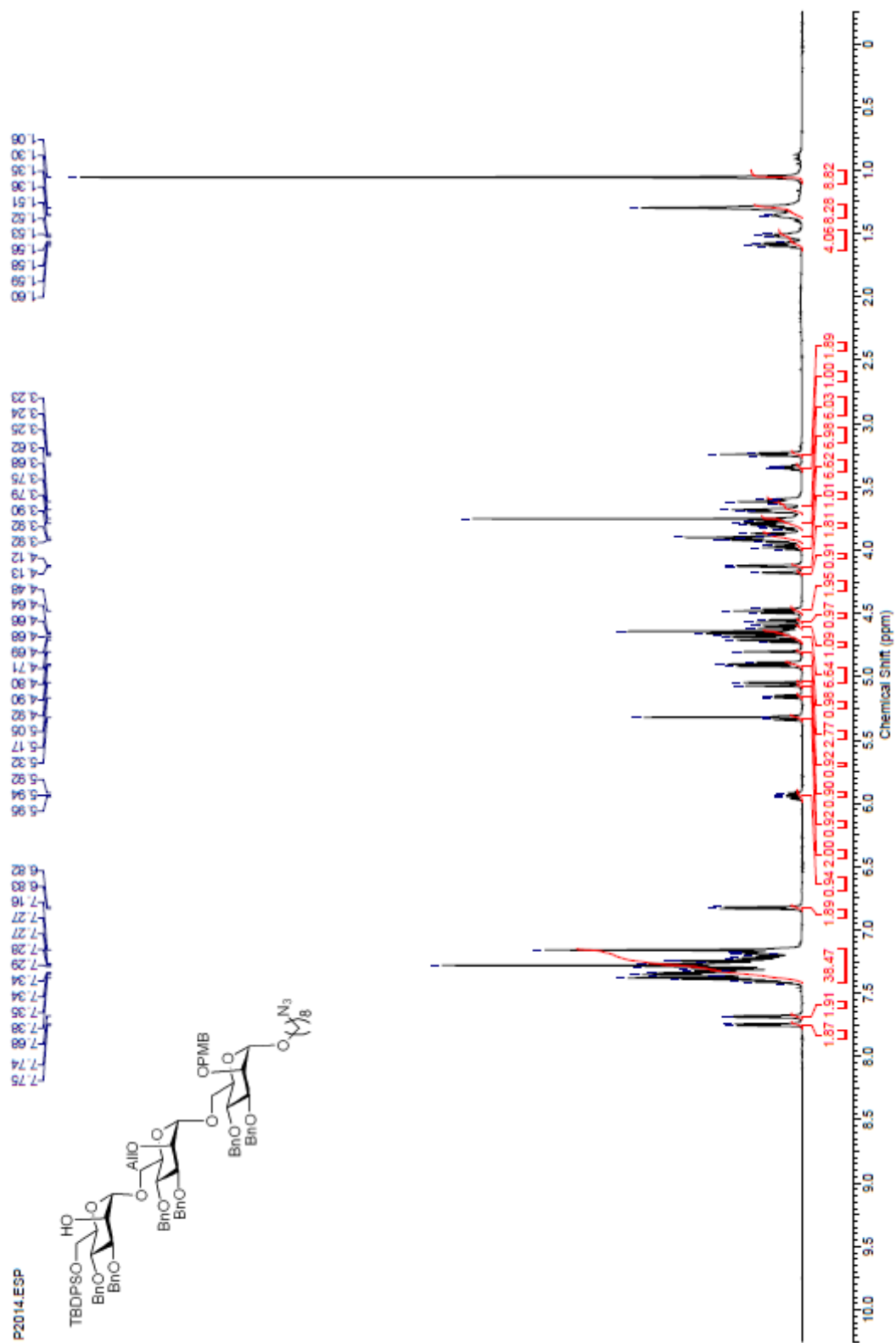


$^1\text{H}$  NMR for compound **36** (600 MHz,  $\text{CDCl}_3$ )

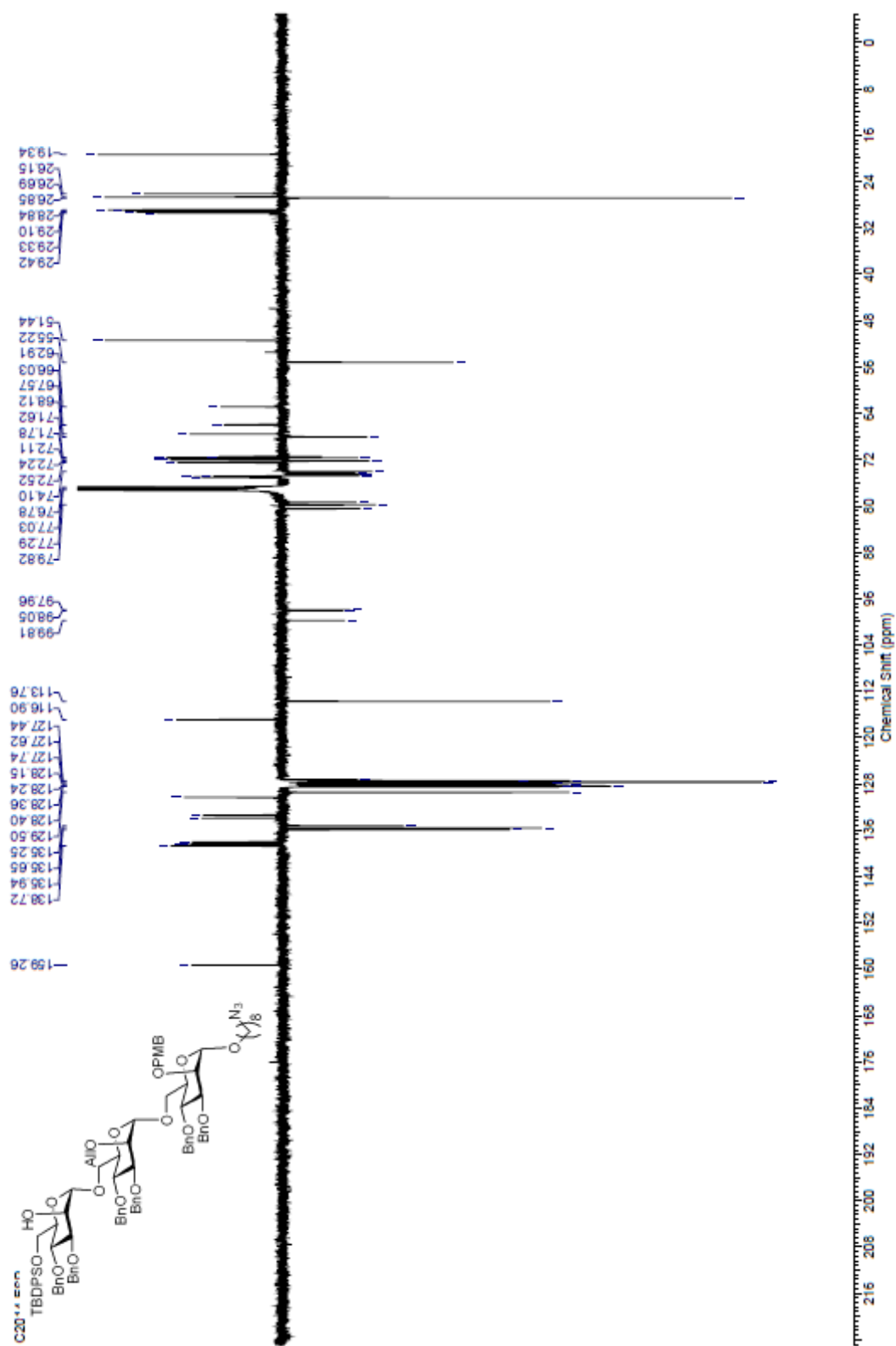


$^{13}\text{C}$  NMR for compound **36** (151 MHz,  $\text{CDCl}_3$ )

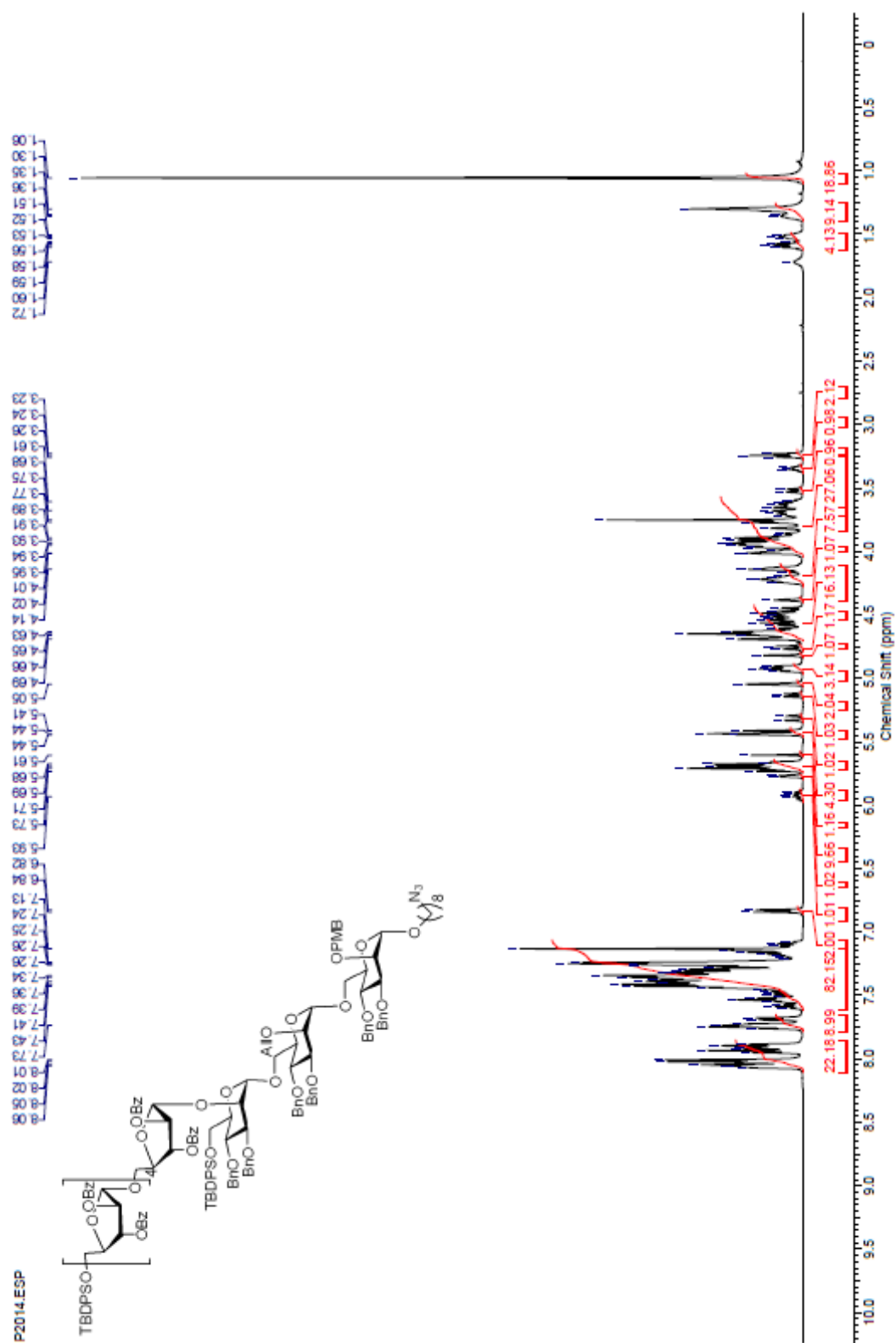


<sup>1</sup>H NMR for compound **37** (500 MHz, CDCl<sub>3</sub>)

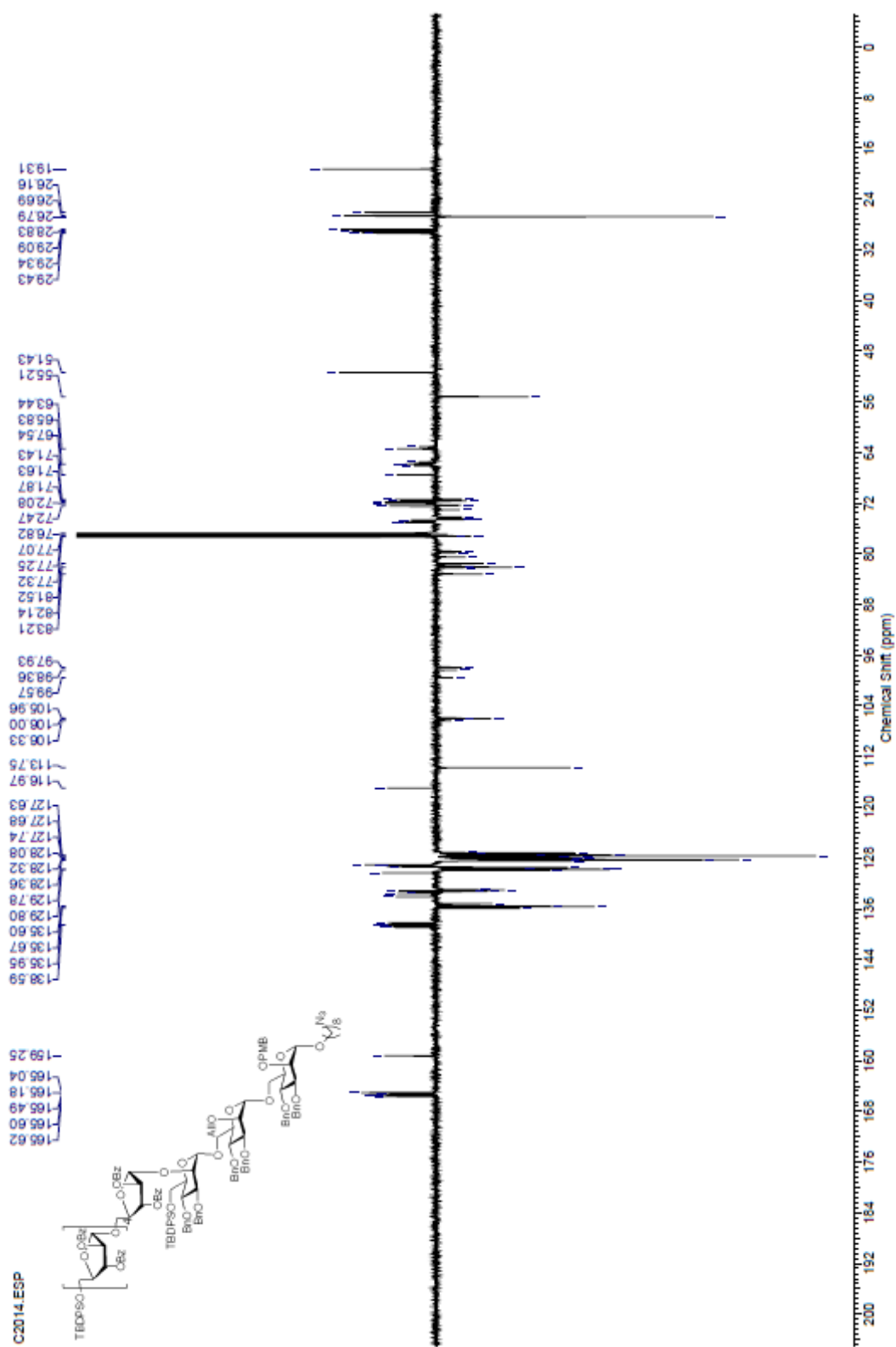
$^{13}\text{C}$  NMR for compound **37** (126 MHz,  $\text{CDCl}_3$ )

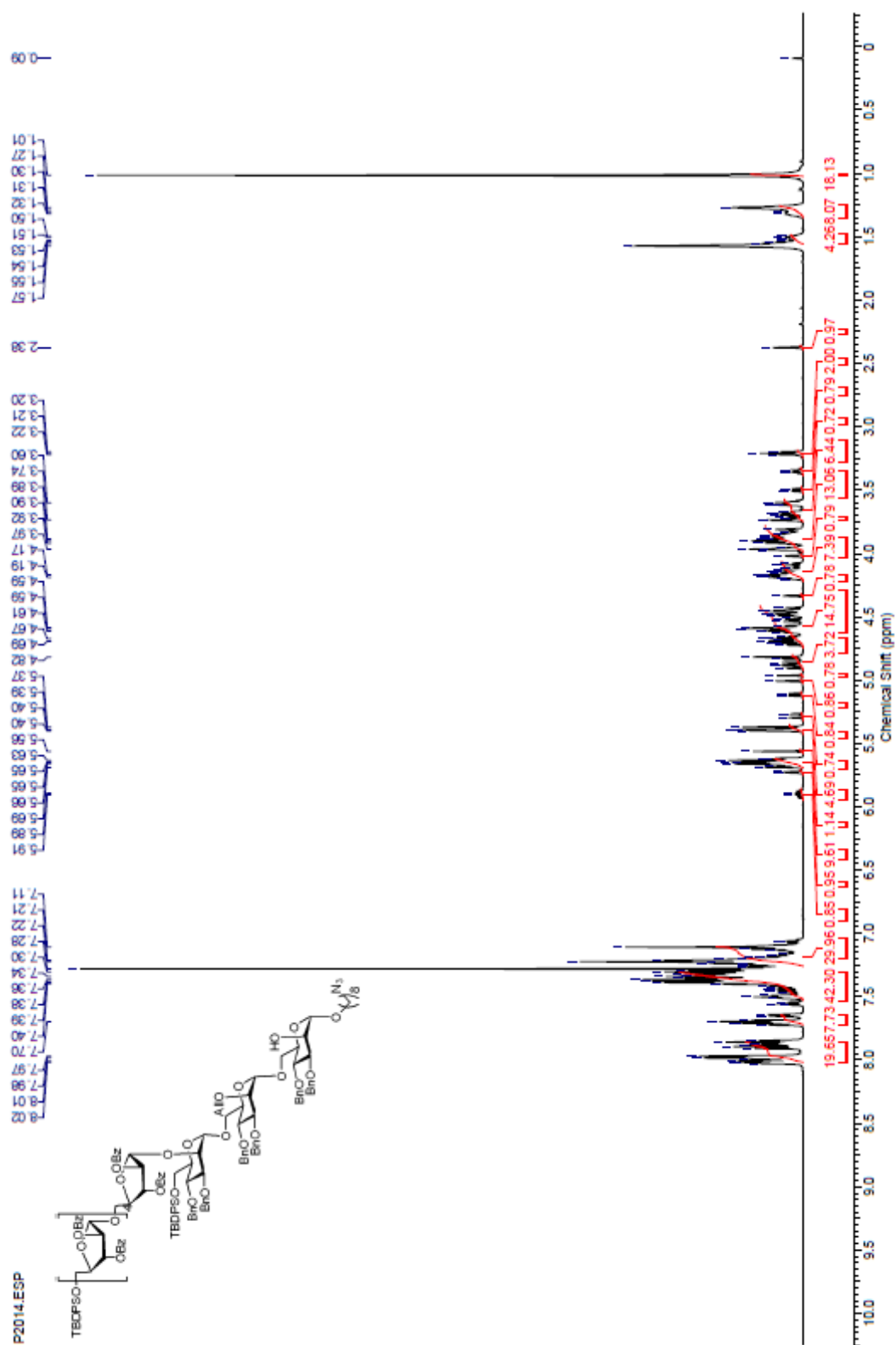


$^1\text{H}$  NMR for compound **38** (600 MHz,  $\text{CDCl}_3$ )

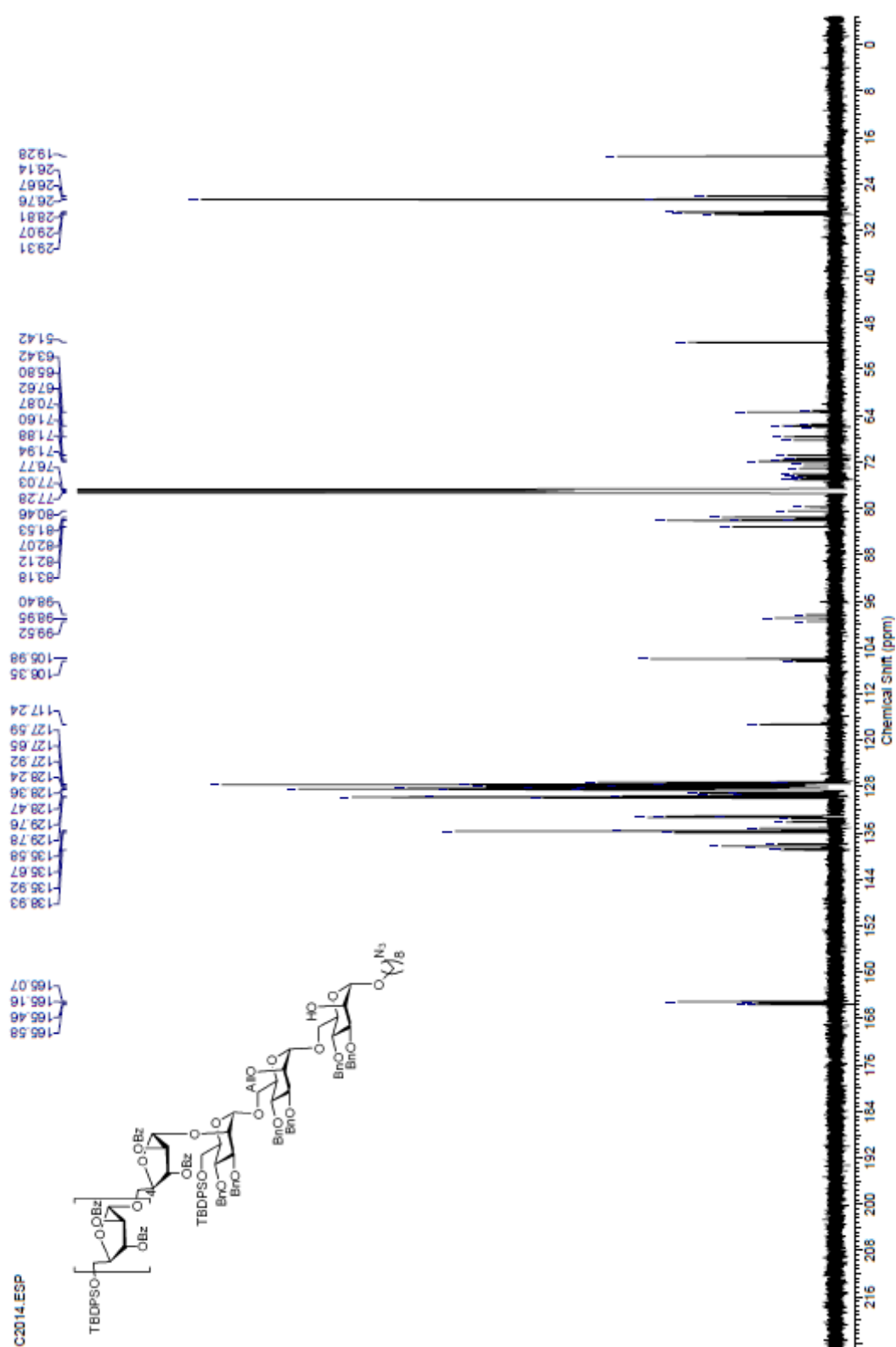


$^{13}\text{C}$  NMR for compound **38** (126 MHz,  $\text{CDCl}_3$ )

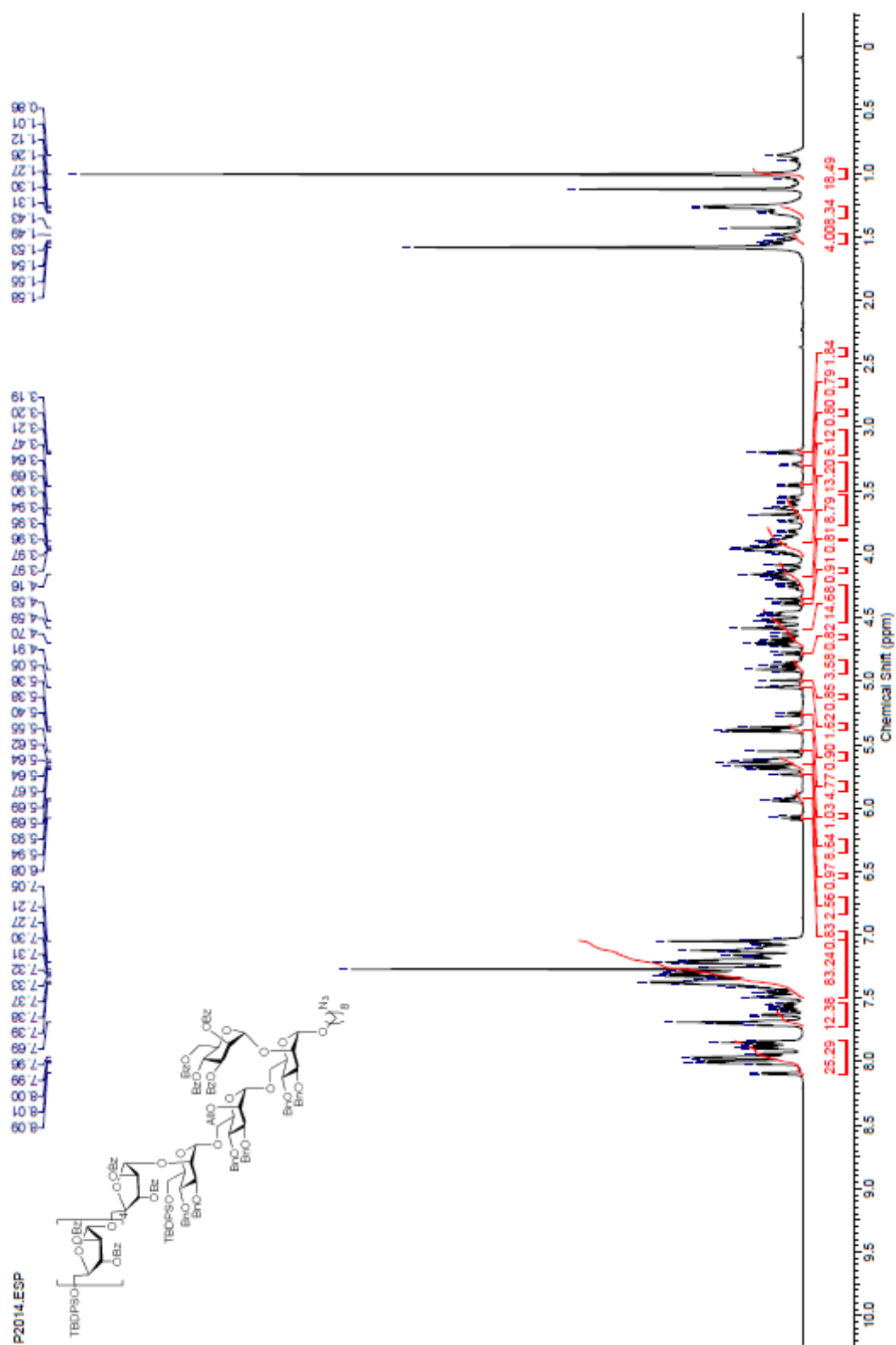


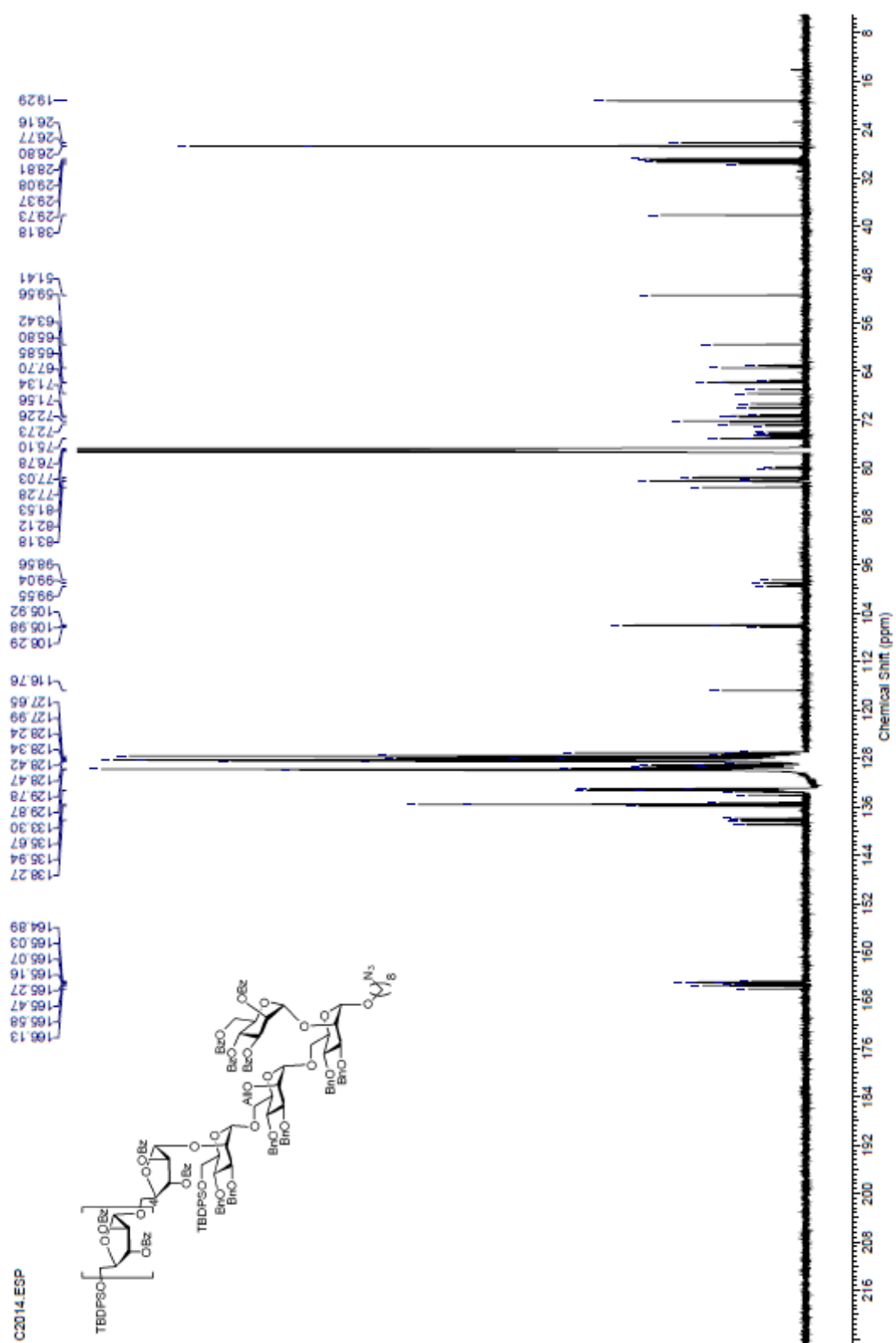
<sup>1</sup>H NMR for compound **39** (600 MHz, CDCl<sub>3</sub>)

$^{13}\text{C}$  NMR for compound **39** (126 MHz,  $\text{CDCl}_3$ )



$^1\text{H}$  NMR for compound **40** (600 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR for compound **40** (126 MHz,  $\text{CDCl}_3$ )

**Table S1.** Summary of chemical shifts (ppm) of the anomeric carbon and hydrogen resonances

| Com-<br>pound |                 |           |           |           |           |       |       |       |           |      |
|---------------|-----------------|-----------|-----------|-----------|-----------|-------|-------|-------|-----------|------|
| <b>1</b>      | <sup>1</sup> H  | 5.09      | 4.98      | 4.89      | 4.81      |       |       |       |           |      |
|               | <sup>13</sup> C | 102.4     | 99.9      | 99.4      | 98.1      |       |       |       |           |      |
| <b>2</b>      | <sup>1</sup> H  | 5.13      | 5.07      | 5.03      | 5.01      | 4.89  |       |       |           |      |
|               | <sup>13</sup> C | 102.4     | 102.3     | 99.6      | 98.3      | 98.1  |       |       |           |      |
| <b>3</b>      | <sup>1</sup> H  | 5.13      | 5.07–5.03 |           |           |       | 4.99  | 4.87  | 4.82      |      |
|               | <sup>13</sup> C | 110.4     | 108.5     | 108.5     | 108.5     | 108.4 | 100.8 | 100.8 | 99.8      |      |
| <b>4</b>      | <sup>1</sup> H  | 5.17      | 5.07      | 5.07      | 5.07      | 5.07  | 5.01  | 4.88  | 4.84      |      |
|               | <sup>13</sup> C | 109.5     | 107.6     | 107.6     | 107.5     | 107.4 | 99.9  | 99.5  | 98.8      |      |
| <b>5</b>      | <sup>1</sup> H  | 5.12      | 5.04      | 5.04      | 5.04      | 5.04  | 4.94  | 4.86  | 4.84      |      |
|               | <sup>13</sup> C | 110.4     | 108.5     | 108.5     | 108.5     | 108.4 | 100.5 | 100.4 | 100.0     |      |
| <b>6</b>      | <sup>1</sup> H  | 5.15      | 5.10      | 5.08–5.04 |           |       |       | 5.00  | 4.98      | 4.82 |
|               | <sup>13</sup> C | 109.5     | 107.5     | 107.5     | 107.4     | 107.4 | 102.3 | 99.9  | 98.8      | 98.2 |
| <b>7</b>      | <sup>1</sup> H  | 5.14      | 5.07–5.02 |           |           |       |       |       | 5.00–4.96 | 4.87 |
|               | <sup>13</sup> C | 109.4     | 107.5     | 107.5     | 107.4     | 107.4 | 102.4 | 99.5  | 98.8      | 98.2 |
| <b>8</b>      | <sup>1</sup> H  | 5.08      | 4.97–4.88 | 4.87      |           |       |       |       |           |      |
|               | <sup>13</sup> C | 98.2      | 98.1      | 98.0      |           |       |       |       |           |      |
| <b>9</b>      | <sup>1</sup> H  | 5.08      | 4.95      | 4.81      |           |       |       |       |           |      |
|               | <sup>13</sup> C | 98.2      | 98.2      | 97.9      |           |       |       |       |           |      |
| <b>12</b>     | <sup>1</sup> H  | 5.76–5.73 | 5.40      | 5.40      | 5.39      | 5.58  |       |       |           |      |
|               | <sup>13</sup> C | 106.0     | 106.0     | 105.9     | 105.9     | 91.6  |       |       |           |      |
| <b>13</b>     | <sup>1</sup> H  | 4.83      |           |           |           |       |       |       |           |      |
|               | <sup>13</sup> C | 97.5      |           |           |           |       |       |       |           |      |
| <b>14</b>     | <sup>1</sup> H  | 4.84      |           |           |           |       |       |       |           |      |
|               | <sup>13</sup> C | 98.3      |           |           |           |       |       |       |           |      |
| <b>15</b>     | <sup>1</sup> H  | 5.00      | 4.88      |           |           |       |       |       |           |      |
|               | <sup>13</sup> C | 98.0      | 97.6      |           |           |       |       |       |           |      |
| <b>16</b>     | <sup>1</sup> H  | 5.07      | 4.86      |           |           |       |       |       |           |      |
|               | <sup>13</sup> C | 98.5      | 97.9      |           |           |       |       |       |           |      |
| <b>18</b>     | <sup>1</sup> H  | 5.67–5.62 | 5.38      |           |           |       |       |       |           |      |
|               | <sup>13</sup> C | 106.1     | 101.0     |           |           |       |       |       |           |      |
| <b>22</b>     | <sup>1</sup> H  | 5.76–5.73 | 5.39      | 5.39      |           |       |       |       |           |      |
|               | <sup>13</sup> C | 106.0     | 106.0     | 91.6      |           |       |       |       |           |      |
| <b>23</b>     | <sup>1</sup> H  | 5.80–5.77 | 5.46      | 5.44      |           |       |       |       |           |      |
|               | <sup>13</sup> C | 105.9     | 105.9     | 91.6      |           |       |       |       |           |      |
| <b>24</b>     | <sup>1</sup> H  | 5.06      | 4.97      | 4.87      |           |       |       |       |           |      |
|               | <sup>13</sup> C | 98.8      | 98.0      | 97.7      |           |       |       |       |           |      |
| <b>25</b>     | <sup>1</sup> H  | 5.03      | 5.01      | 4.99–4.93 | 4.93–4.85 |       |       |       |           |      |
|               | <sup>13</sup> C | 99.7      | 99.2      | 98.0      | 97.8      |       |       |       |           |      |
| <b>26</b>     | <sup>1</sup> H  | 5.72–5.62 | 5.43–5.35 |           |           |       | 5.05  | 5.00  | 4.87–4.82 |      |
|               | <sup>13</sup> C | 106.2     | 106.0     | 106.0     | 105.8     | 105.8 | 99.8  | 97.8  | 97.8      |      |
| <b>28</b>     | <sup>1</sup> H  | 5.71–5.61 | 5.42–5.36 |           |           |       | 5.02  | 5.01  | 4.85      |      |
|               | <sup>13</sup> C | 106.3     | 106.0     | 106.0     | 106.0     | 105.9 | 99.6  | 98.4  | 97.9      |      |
| <b>29</b>     | <sup>1</sup> H  | 5.69      | 5.43–5.35 |           |           |       | 5.01  | 5.01  | 5.01      | 4.86 |
|               | <sup>13</sup> C | 106.5     | 106.0     | 106.0     | 106.0     | 105.9 | 99.6  | 99.6  | 99.2      | 97.9 |
| <b>30</b>     | <sup>1</sup> H  | 5.02      | 4.96–4.89 | 4.88–4.83 |           |       |       |       |           |      |

|           |                 |           |           |           |       |       |      |           |      |      |
|-----------|-----------------|-----------|-----------|-----------|-------|-------|------|-----------|------|------|
|           | <sup>13</sup> C | 99.0      | 98.2      | 97.8      |       |       |      |           |      |      |
| <b>31</b> | <sup>1</sup> H  | 4.76      |           |           |       |       |      |           |      |      |
|           | <sup>13</sup> C | 98.3      |           |           |       |       |      |           |      |      |
| <b>32</b> | <sup>1</sup> H  | 4.96      | 4.80      |           |       |       |      |           |      |      |
|           | <sup>13</sup> C | 98.0      | 97.6      |           |       |       |      |           |      |      |
| <b>33</b> | <sup>1</sup> H  | 5.07      | 4.80      |           |       |       |      |           |      |      |
|           | <sup>13</sup> C | 98.4      | 97.8      |           |       |       |      |           |      |      |
| <b>34</b> | <sup>1</sup> H  | 5.75–5.61 | 5.44–5.36 |           |       |       | 5.05 | 4.97–4.82 |      |      |
|           | <sup>13</sup> C | 106.4     | 106.0     | 106.0     | 105.9 | 105.9 | 99.4 | 98.3      | 97.9 |      |
| <b>35</b> | <sup>1</sup> H  | 5.05      | 4.99      | 4.92–4.84 |       |       |      |           |      |      |
|           | <sup>13</sup> C | 99.3      | 98.8      | 97.9      |       |       |      |           |      |      |
| <b>36</b> | <sup>1</sup> H  | 5.40      | 5.26      | 5.26      | 5.11  | 4.93  |      |           |      |      |
|           | <sup>13</sup> C | 100.5     | 99.7      | 99.3      | 99.0  | 98.5  |      |           |      |      |
| <b>37</b> | <sup>1</sup> H  | 5.07      | 5.05      | 4.81      |       |       |      |           |      |      |
|           | <sup>13</sup> C | 99.8      | 98.1      | 98.0      |       |       |      |           |      |      |
| <b>38</b> | <sup>1</sup> H  | 5.75–5.65 | 5.47–5.39 |           |       |       | 5.05 | 5.05      | 4.82 |      |
|           | <sup>13</sup> C | 106.3     | 106.0     | 106.0     | 106.0 | 105.9 | 99.6 | 98.4      | 97.9 |      |
| <b>39</b> | <sup>1</sup> H  | 5.70–5.60 | 5.43–5.33 |           |       |       | 5.01 | 4.97      | 4.82 |      |
|           | <sup>13</sup> C | 106.4     | 106.0     | 106.0     | 105.9 | 105.9 | 99.5 | 99.0      | 98.4 |      |
| <b>40</b> | <sup>1</sup> H  | 5.71–5.59 | 5.43–5.33 |           |       |       |      | 5.07–5.03 | 5.01 | 4.97 |
|           | <sup>13</sup> C | 106.3     | 106.0     | 106.0     | 105.9 | 105.9 | 99.6 | 99.3      | 99.0 | 98.5 |