

## Supplementary Information

### **Stereocontrolled synthesis and conformational analysis of a series of disaccharides $\alpha,\beta$ -D-GlcA-(1 $\rightarrow$ 3)- $\alpha$ -L-Fuc**

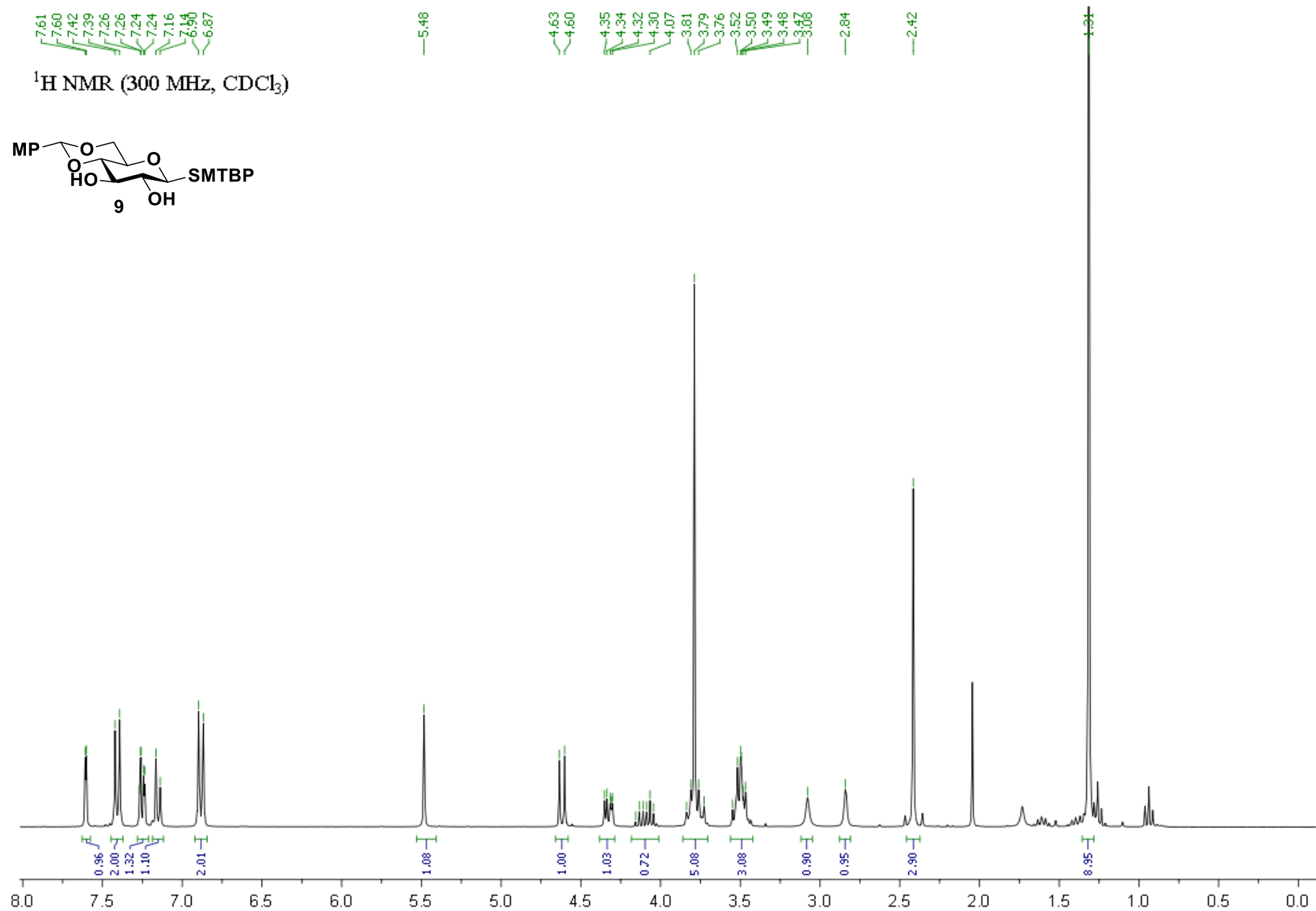
*Alexey G. Gerbst, Dmitry Z. Vinnitsky, Alexandra I. Tokatly, Andrey S. Dmitrenok,  
Vadim B. Krylov, Nadezhda E. Ustuzhanina, Nikolay E. Nifantiev*

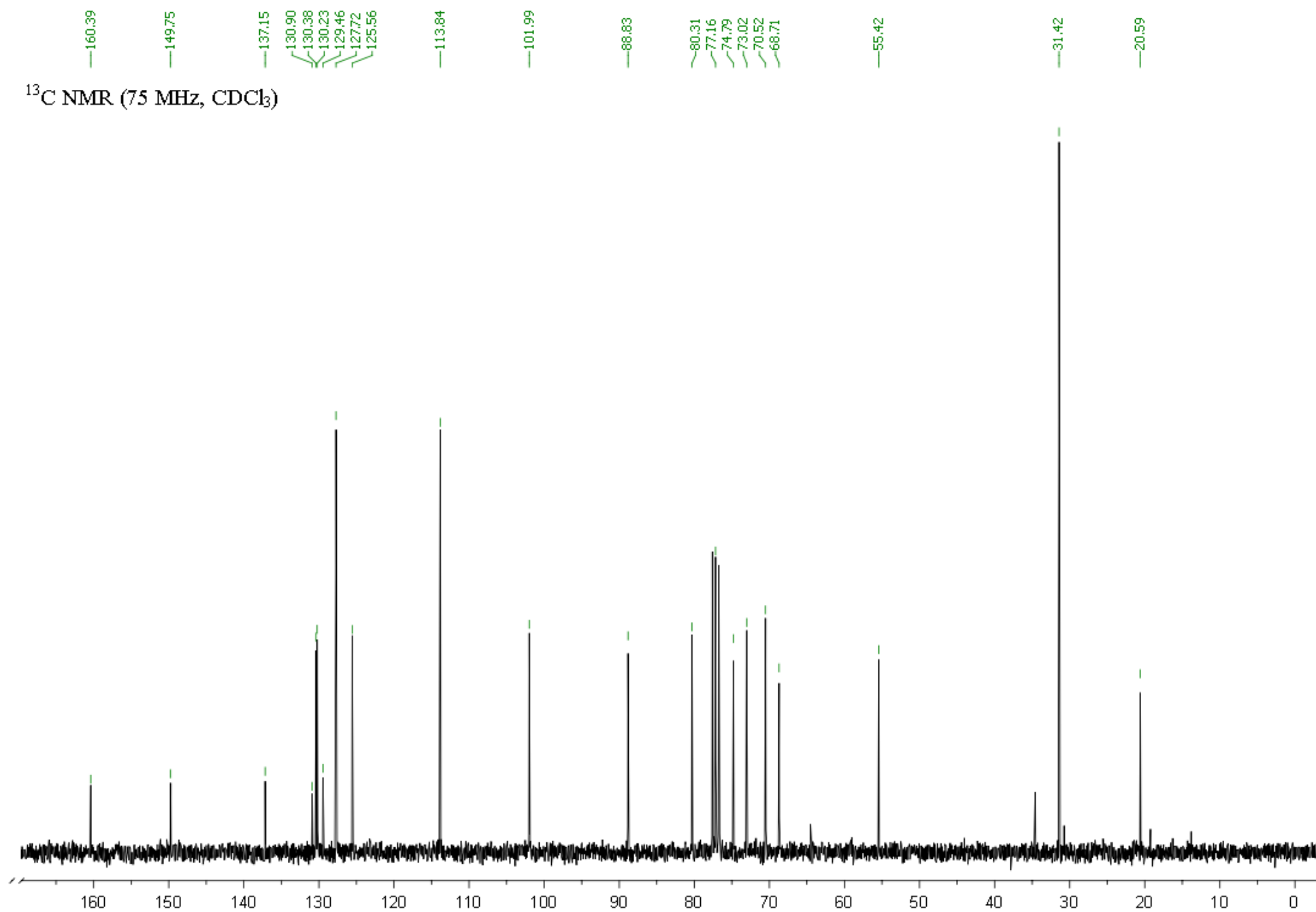
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# **Spectral data**

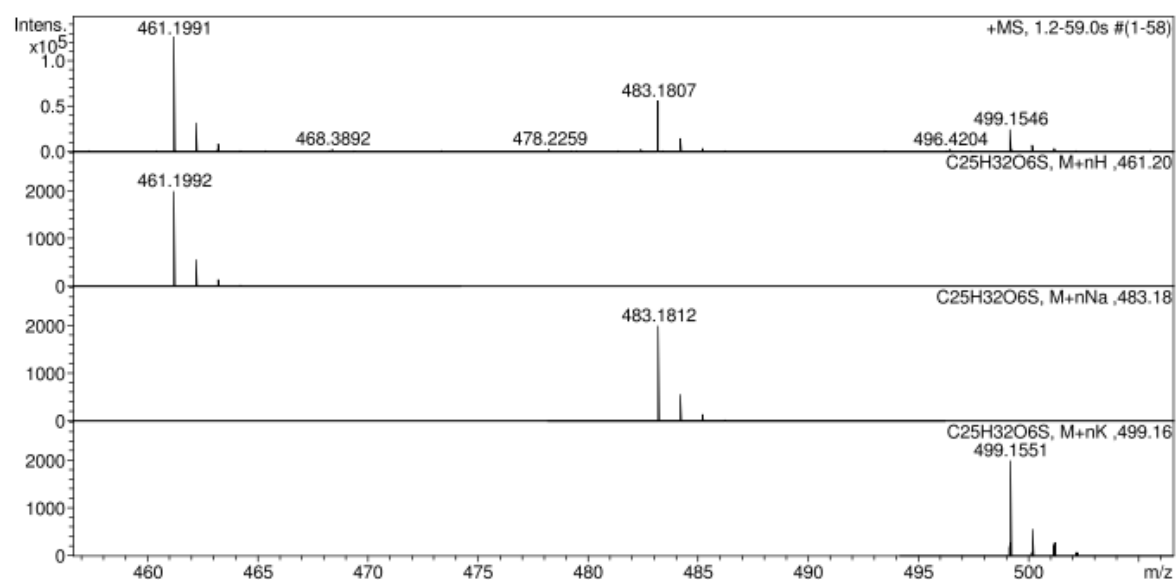
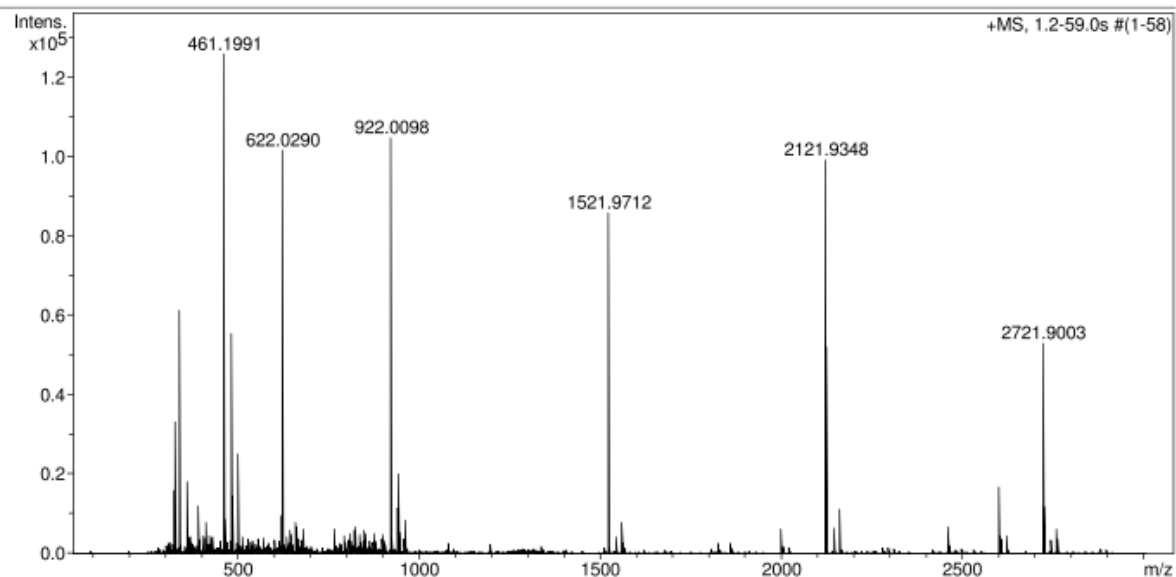
(2-methyl-5-tert-butylphenyl) 4,6-O-(4-methoxybenzylidene)-1-thio- $\beta$ -D-glucopyranoside (9).



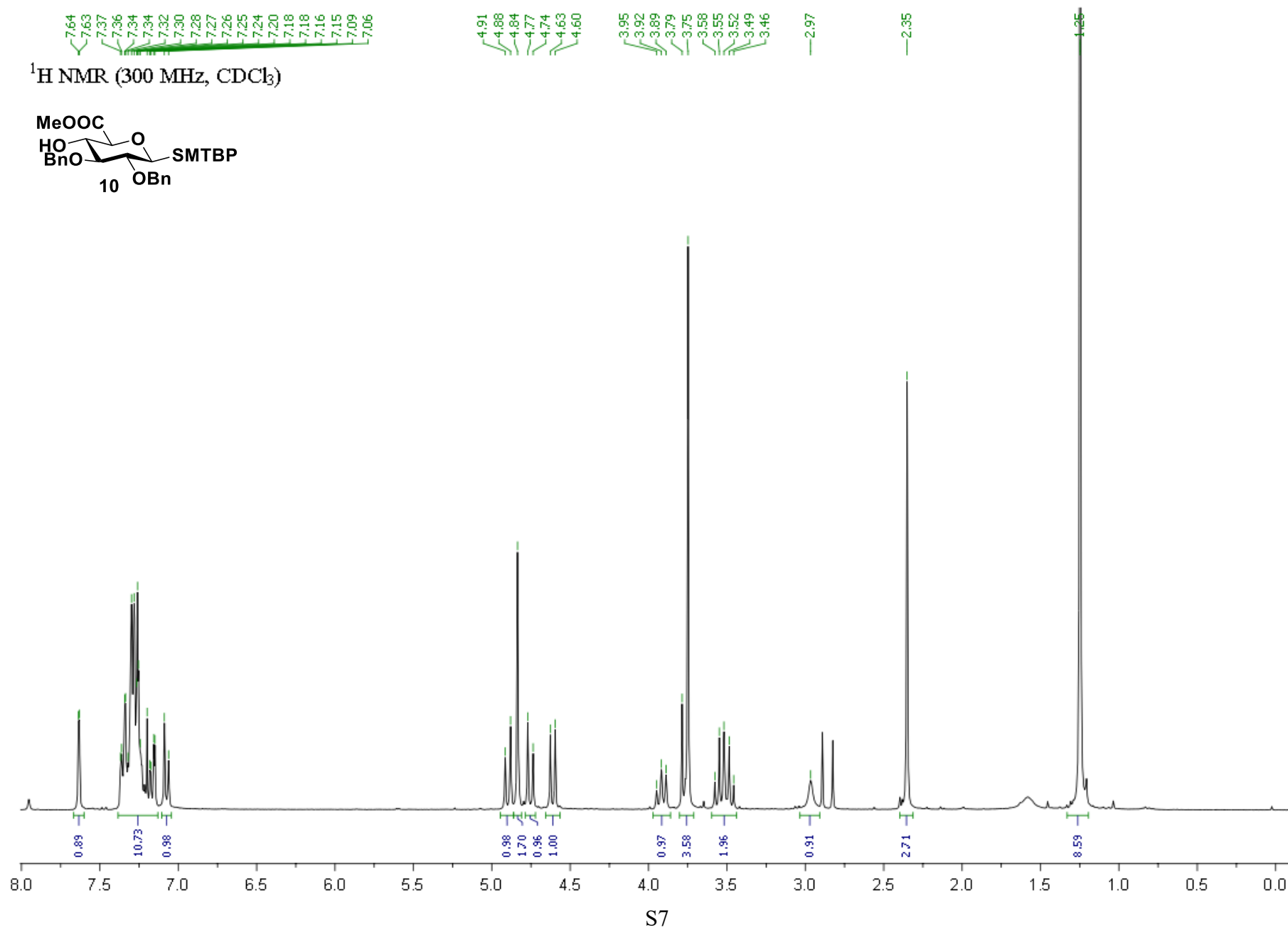


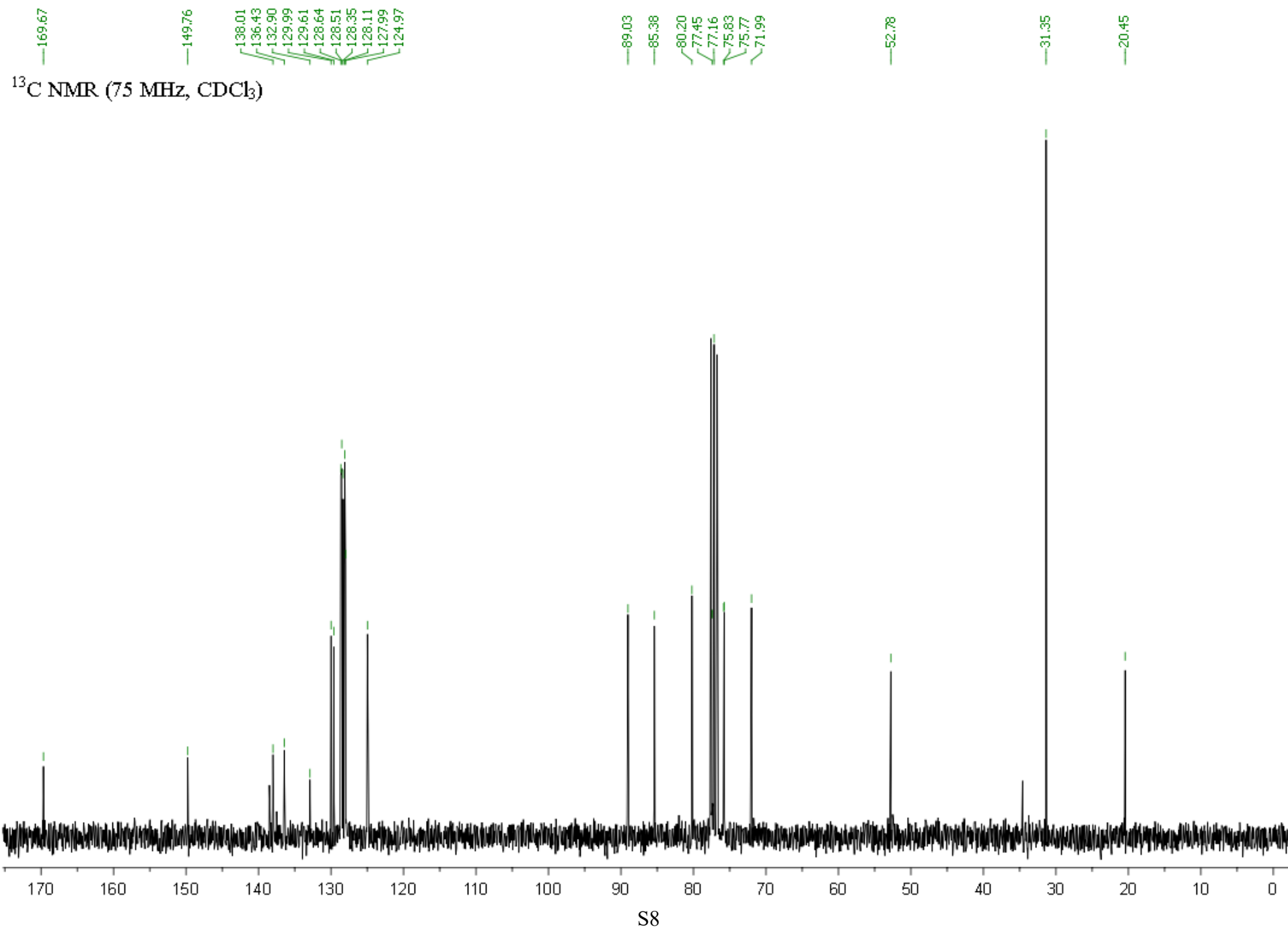
**Acquisition Parameter**

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| Focus       | Active   |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z   | Set Capillary        | 4500 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |



Methyl [(2-methyl-5-tert-butylphenyl) 2,3-di-O-benzyl-1-thio- $\beta$ -D-glucopyranosyl] uronate (10).

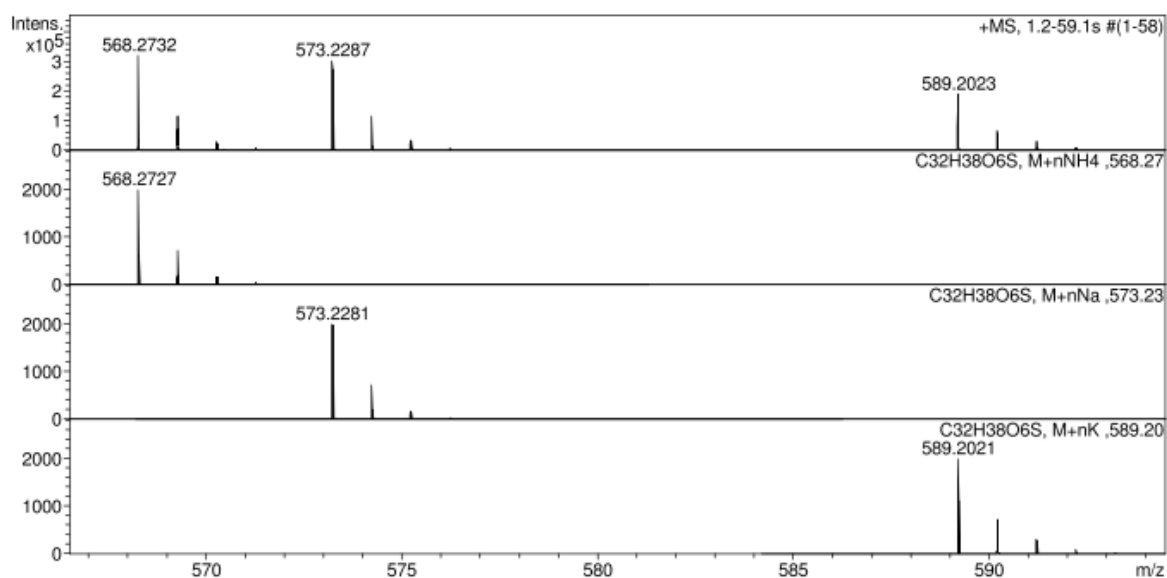
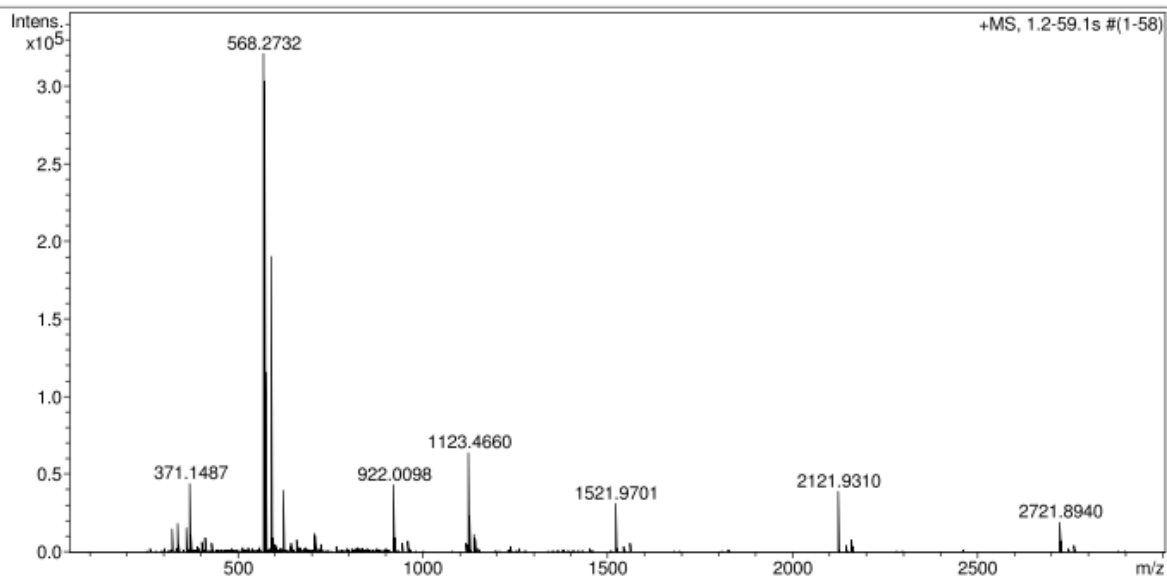




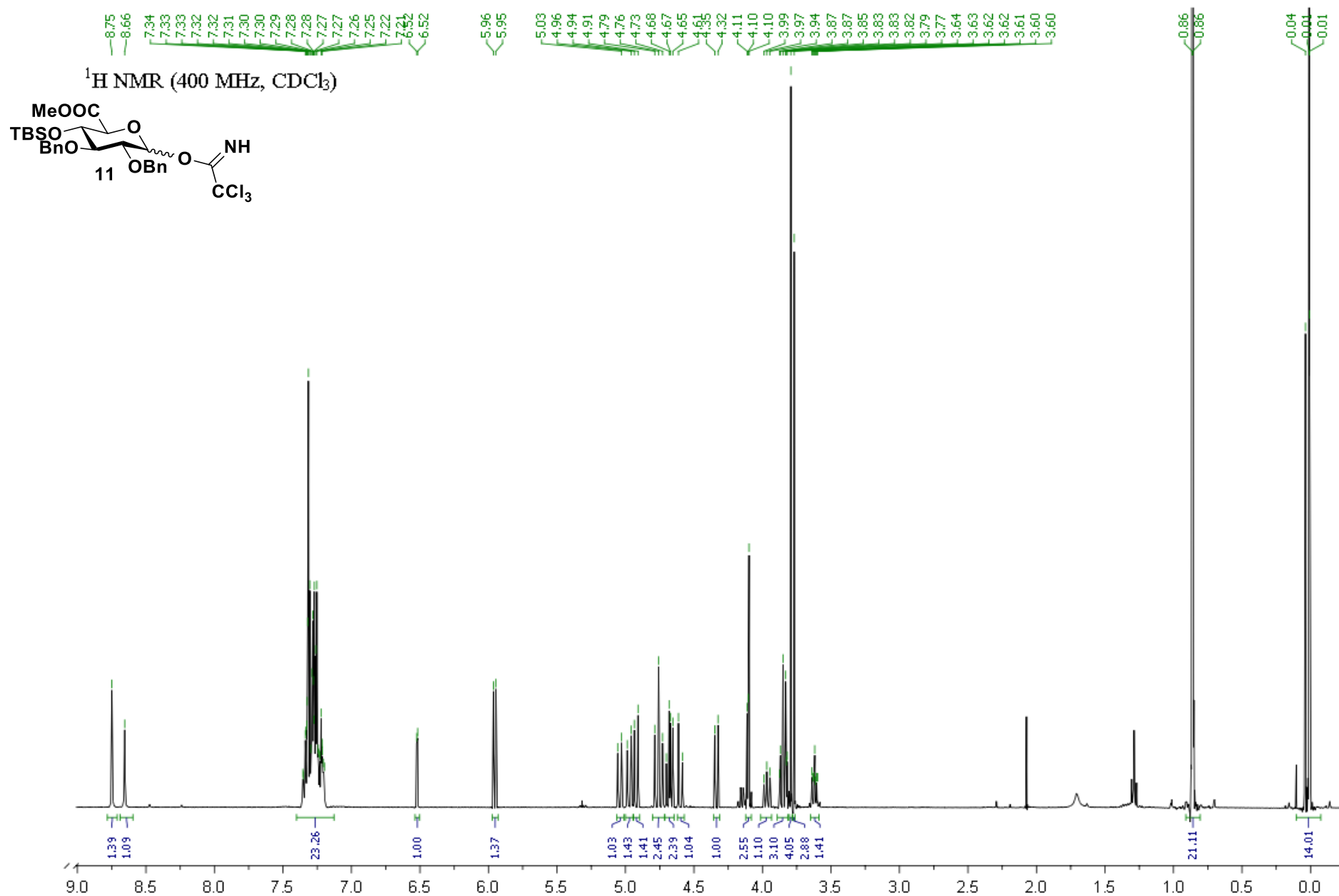


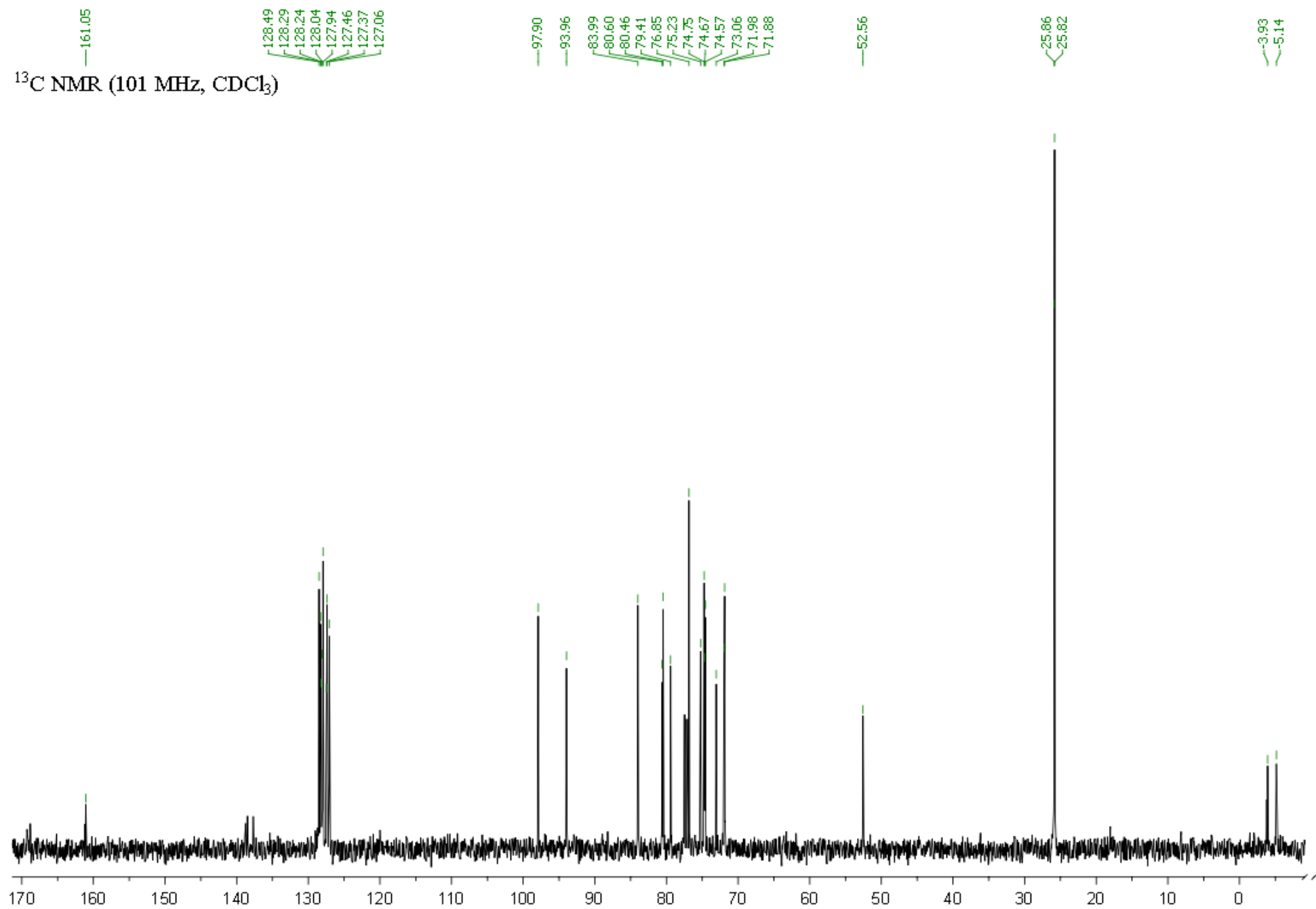
**Acquisition Parameter**

|             |          |                      |          |                  |           |
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| Source Type | ESI      | Ion Polarity         | Positive | Set Nebulizer    | 0.5 Bar   |
| Focus       | Active   |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z   | Set Capillary        | 4500 V   | Set Dry Gas      | 4.0 l/min |
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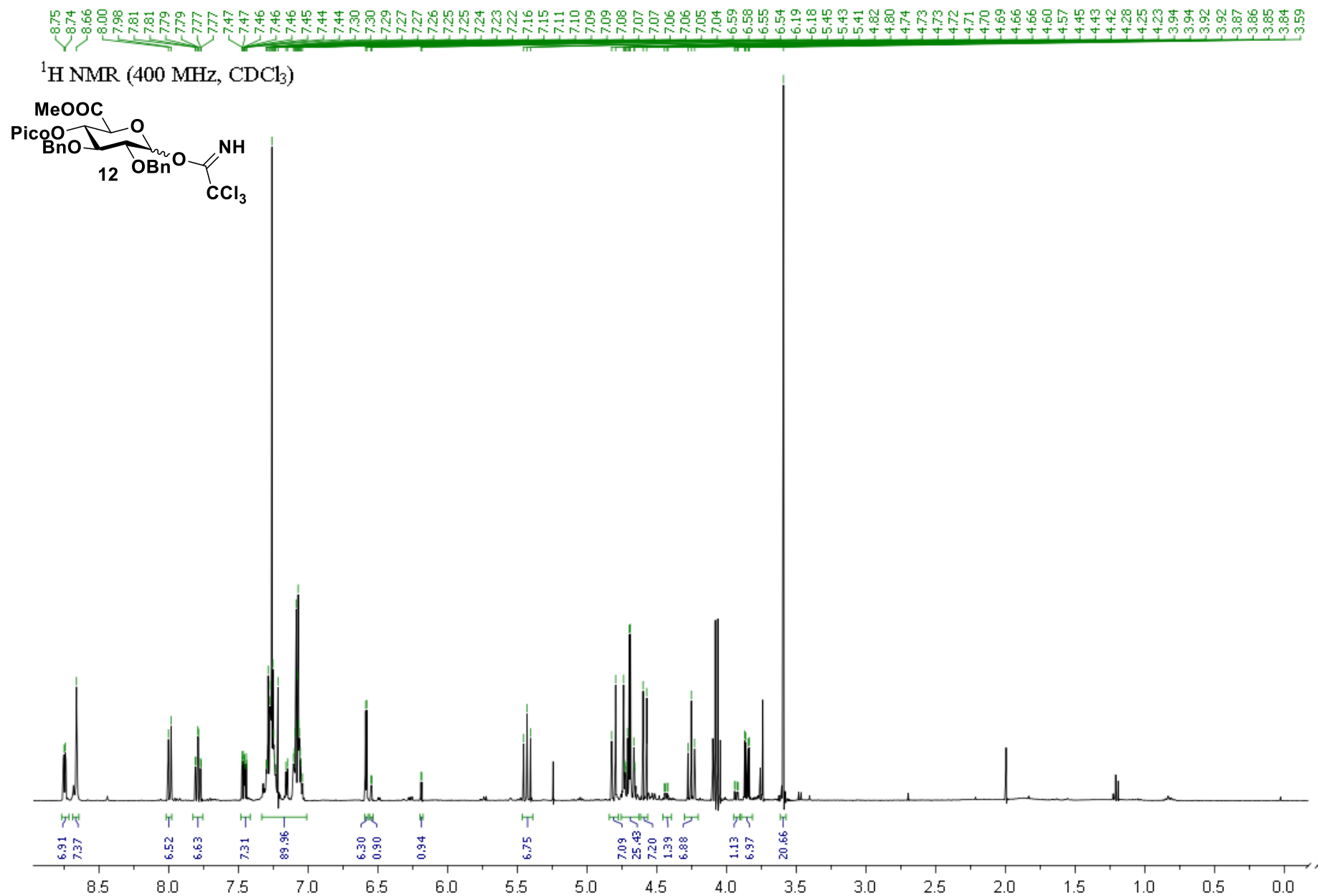


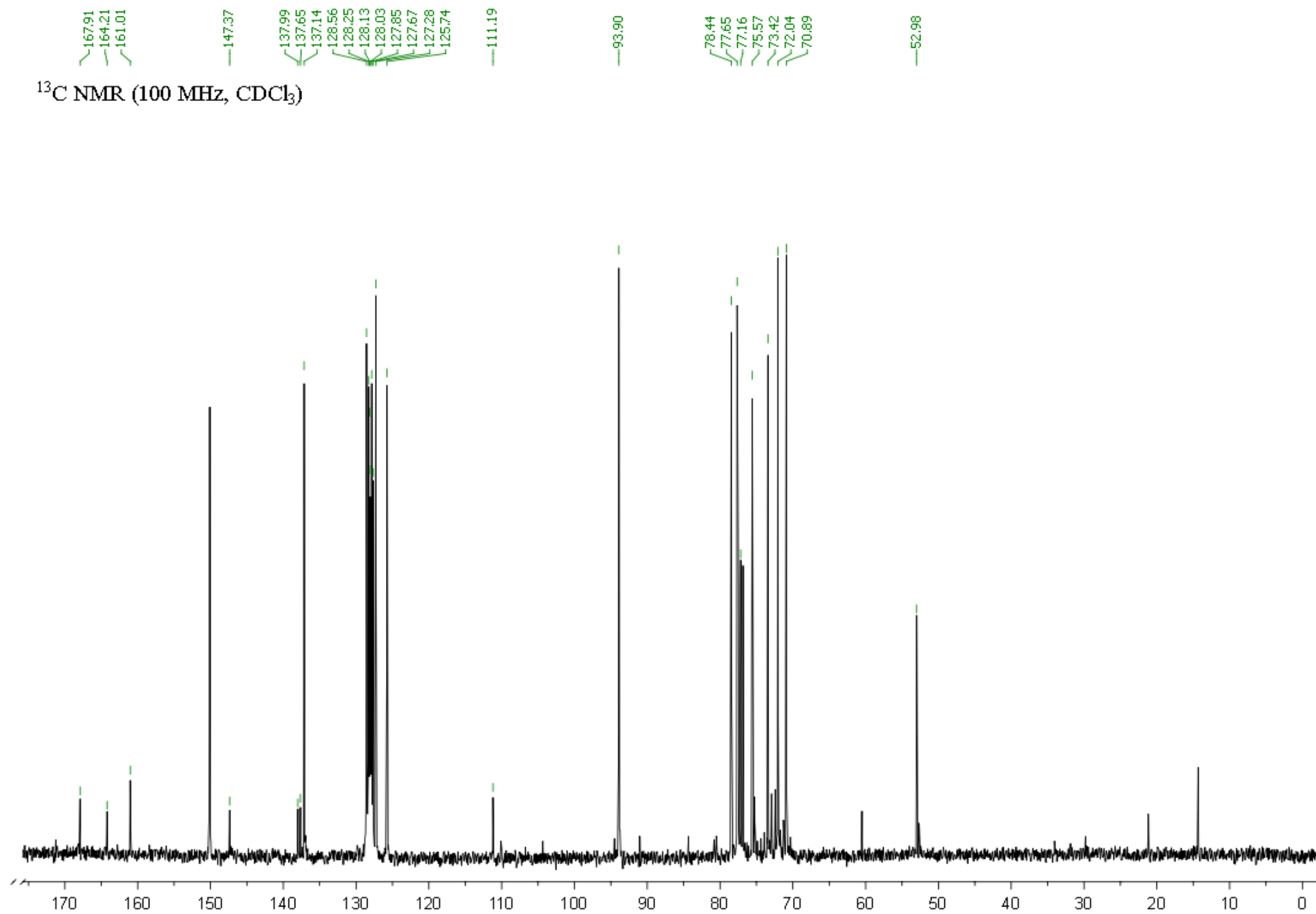
**Methyl (2,3-di-O-benzyl-4-O-tert-butyldimethylsilyl- $\alpha,\beta$ -D-glucopyranosyl) uronate trichloroacetimidate (11).**





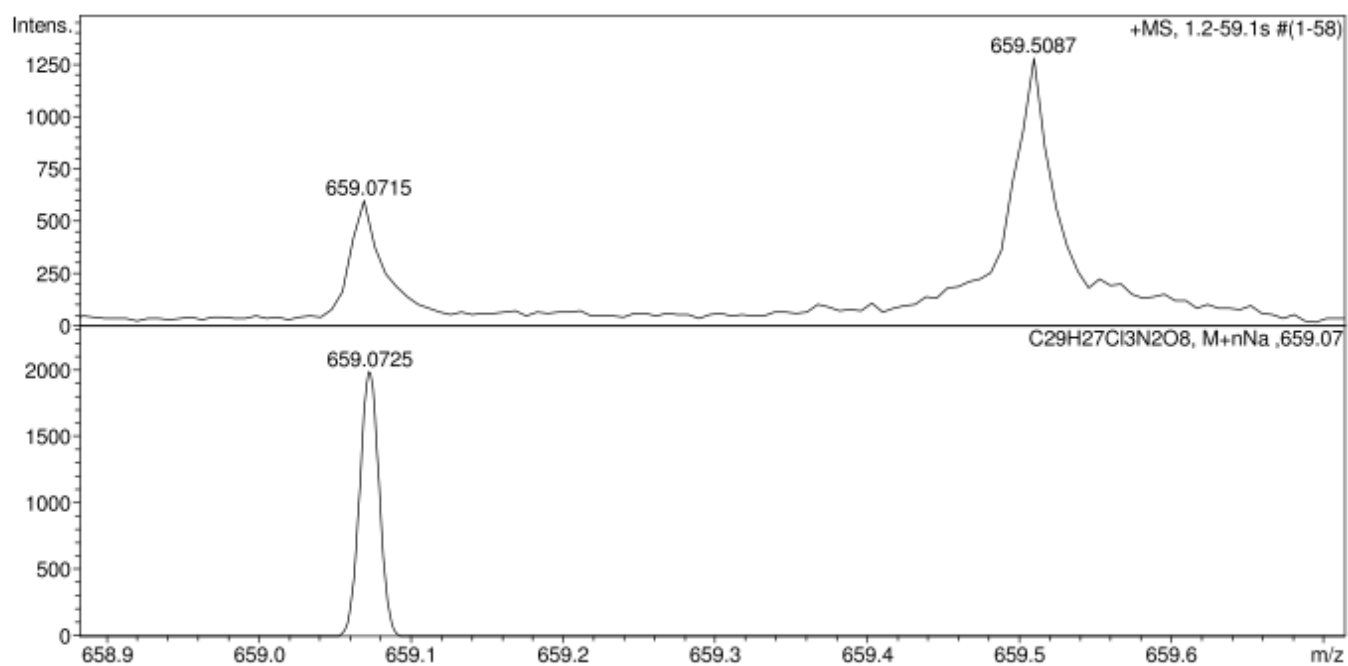
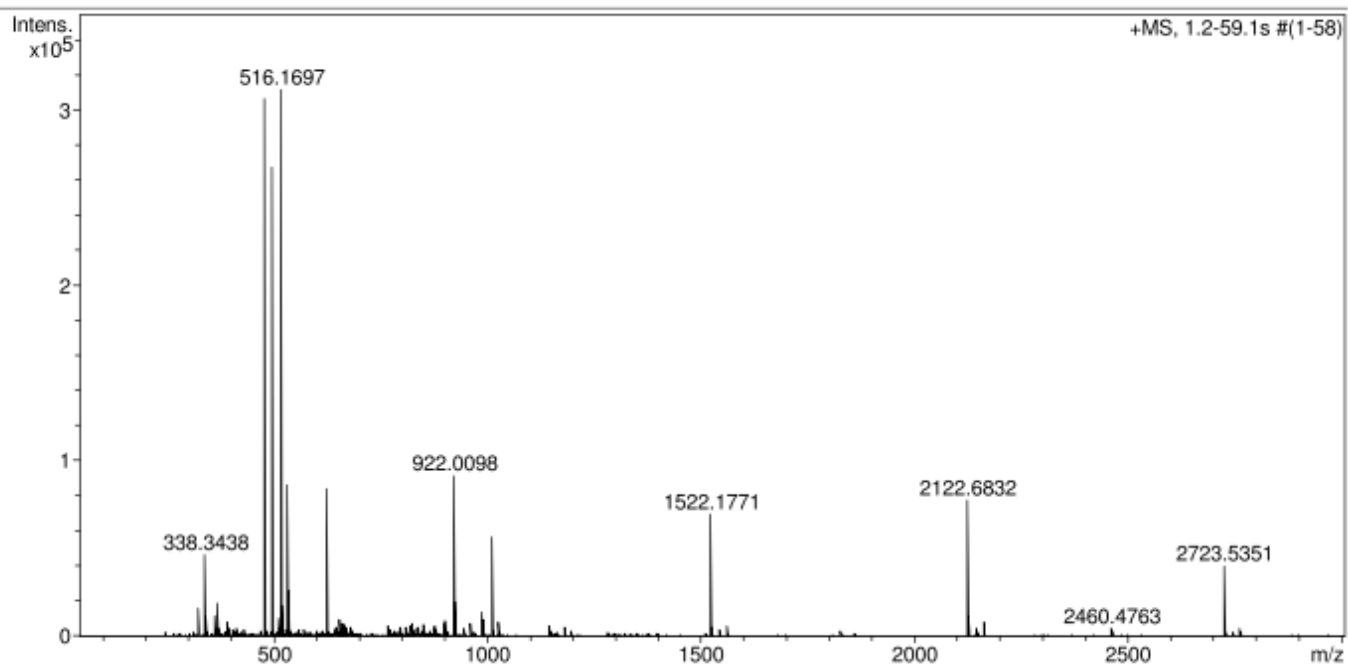
**Methyl (2,3-di-O-benzyl-4-O-picoloyl- $\alpha,\beta$ -D-glucopyranosyl) uronate trichloroacetimidate (12).**



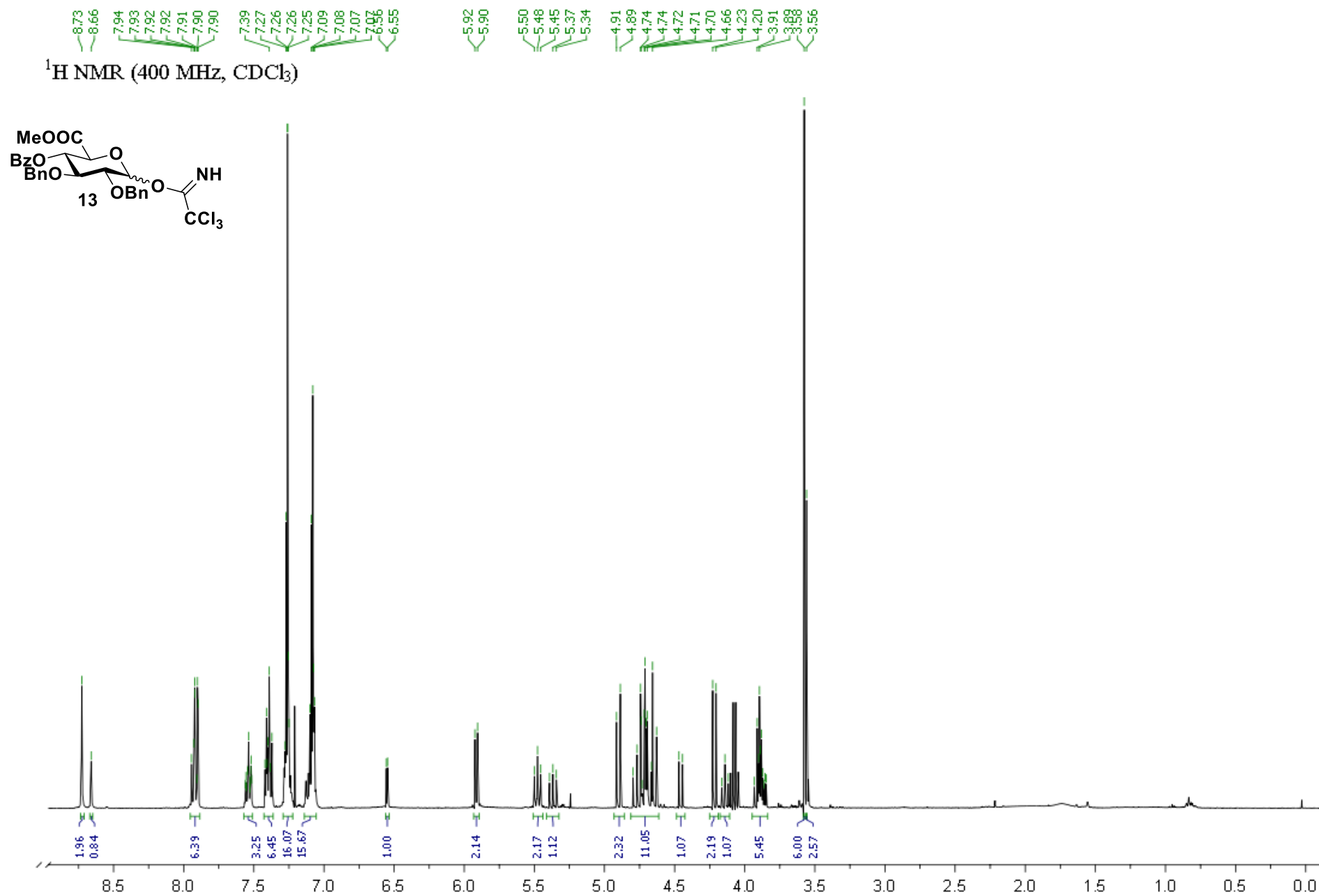


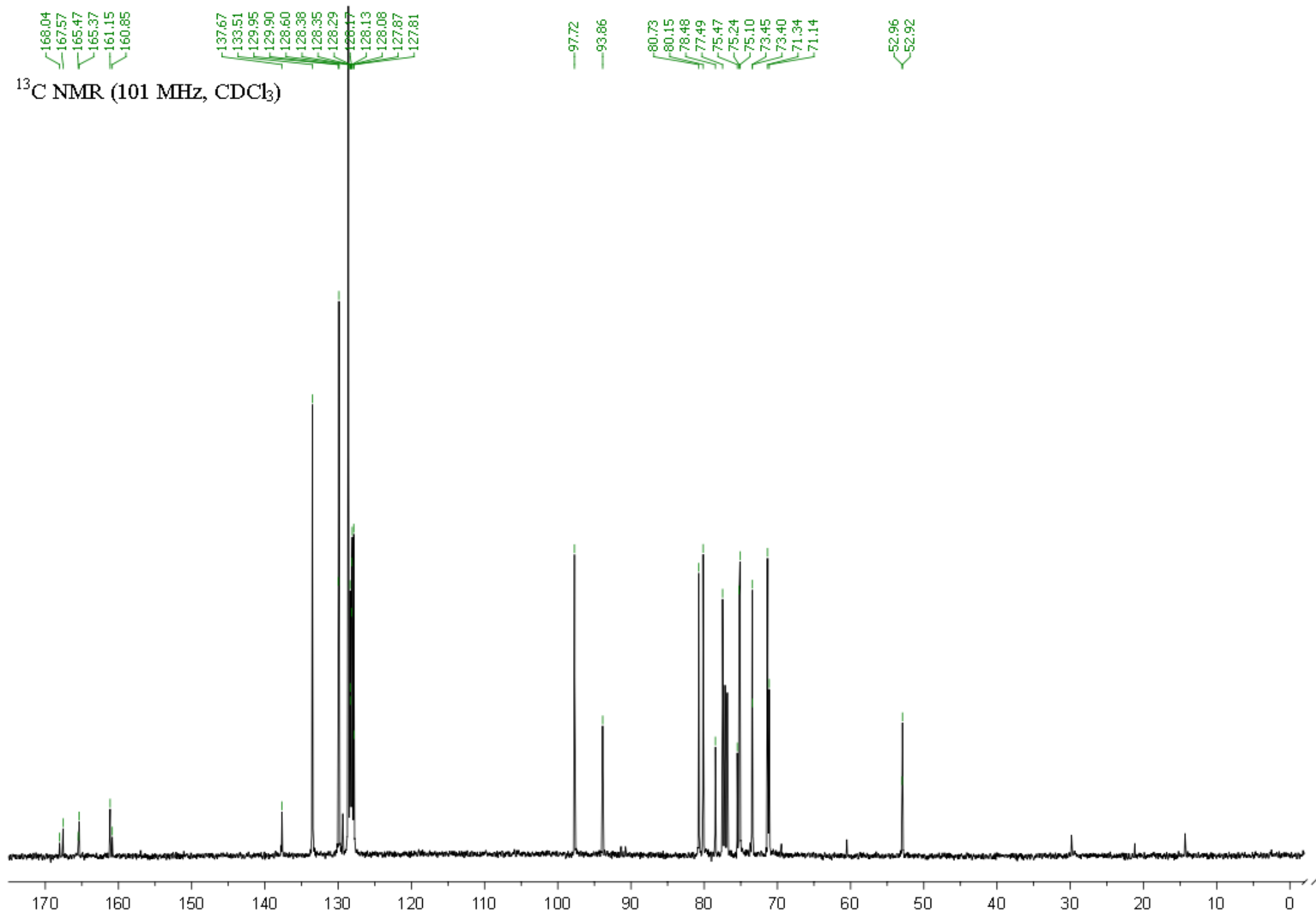
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| Scan Begin  | 50 m/z   | Set Capillary        | 4500 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |



Methyl (2,3-di-O-benzyl-4-O-benzoyl- $\alpha,\beta$ -D-glucopyranosyl) uronate trichloroacetimidate (13).

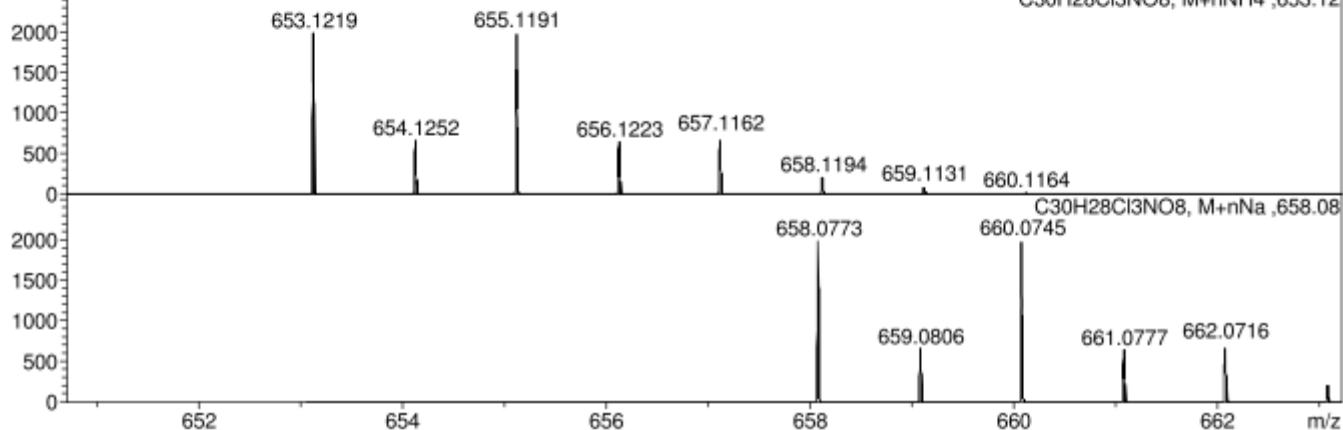
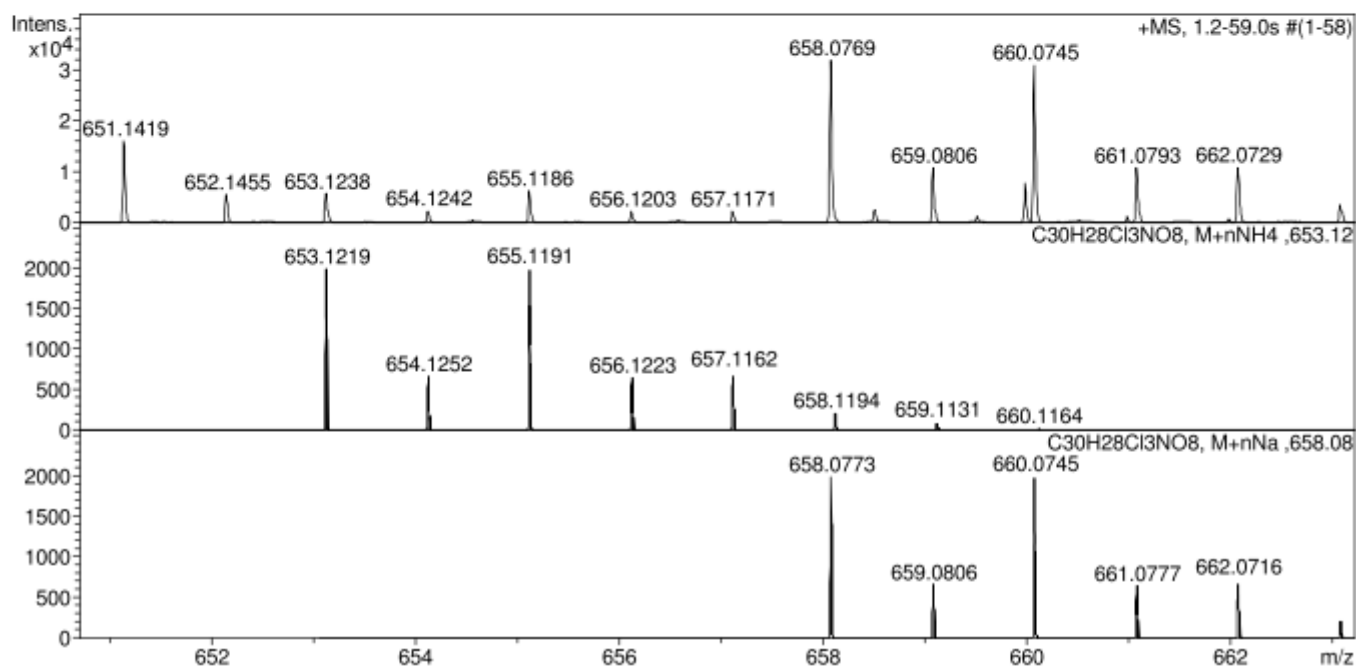
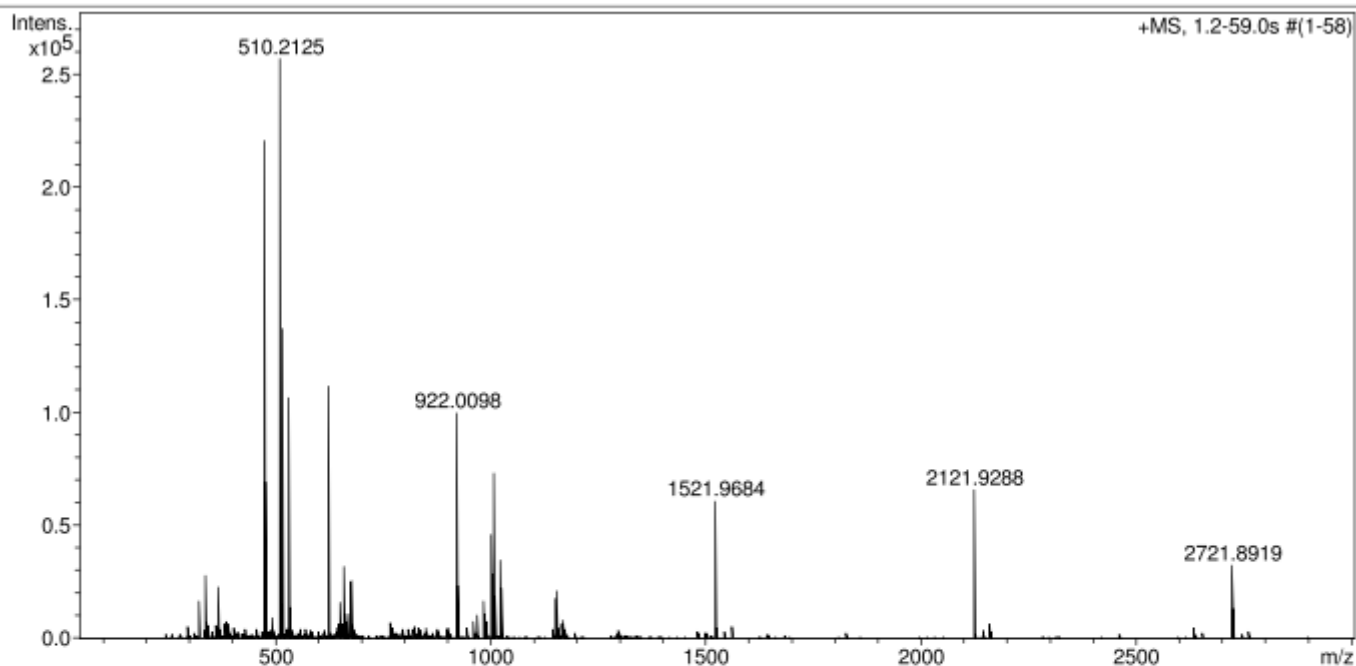




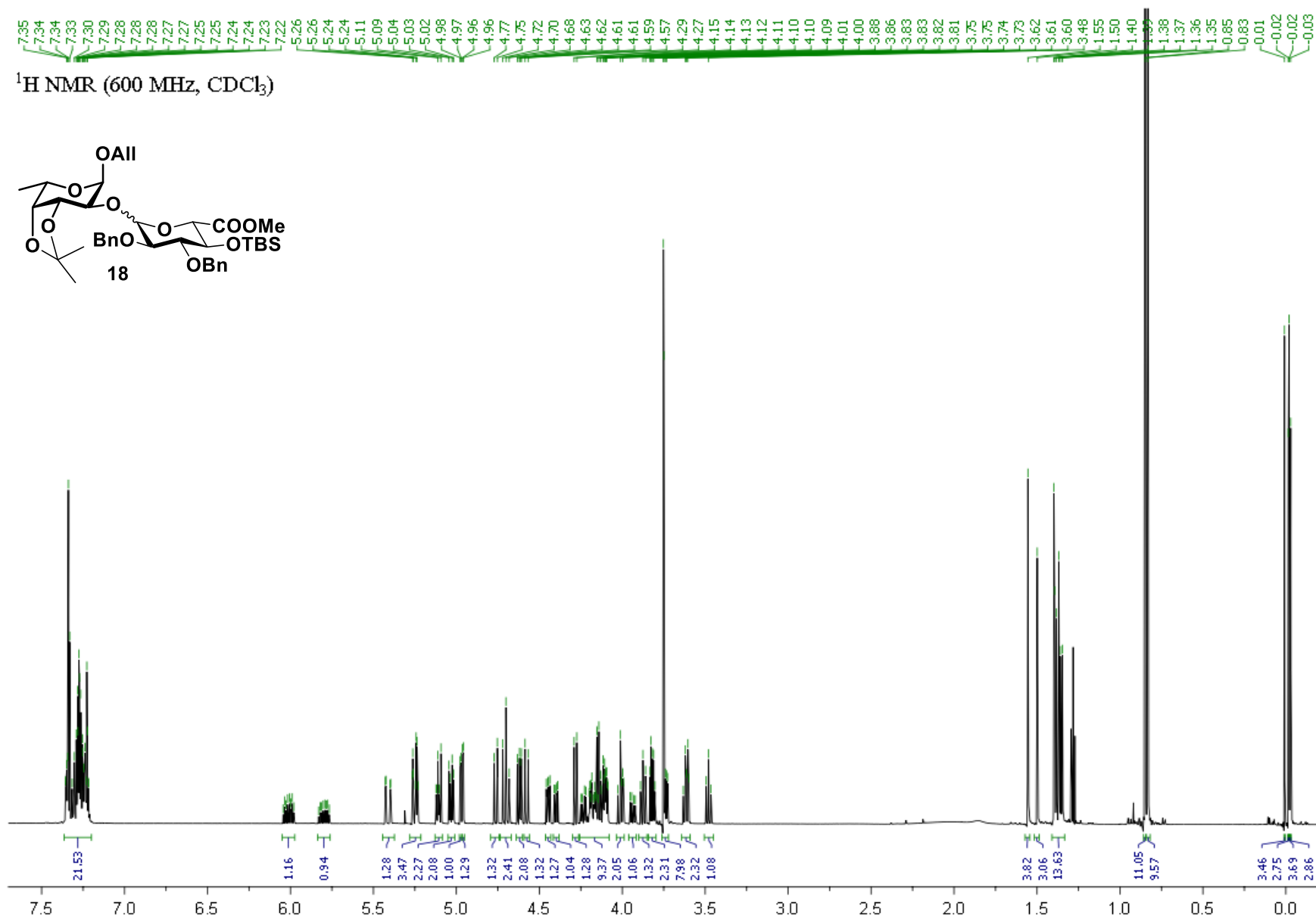


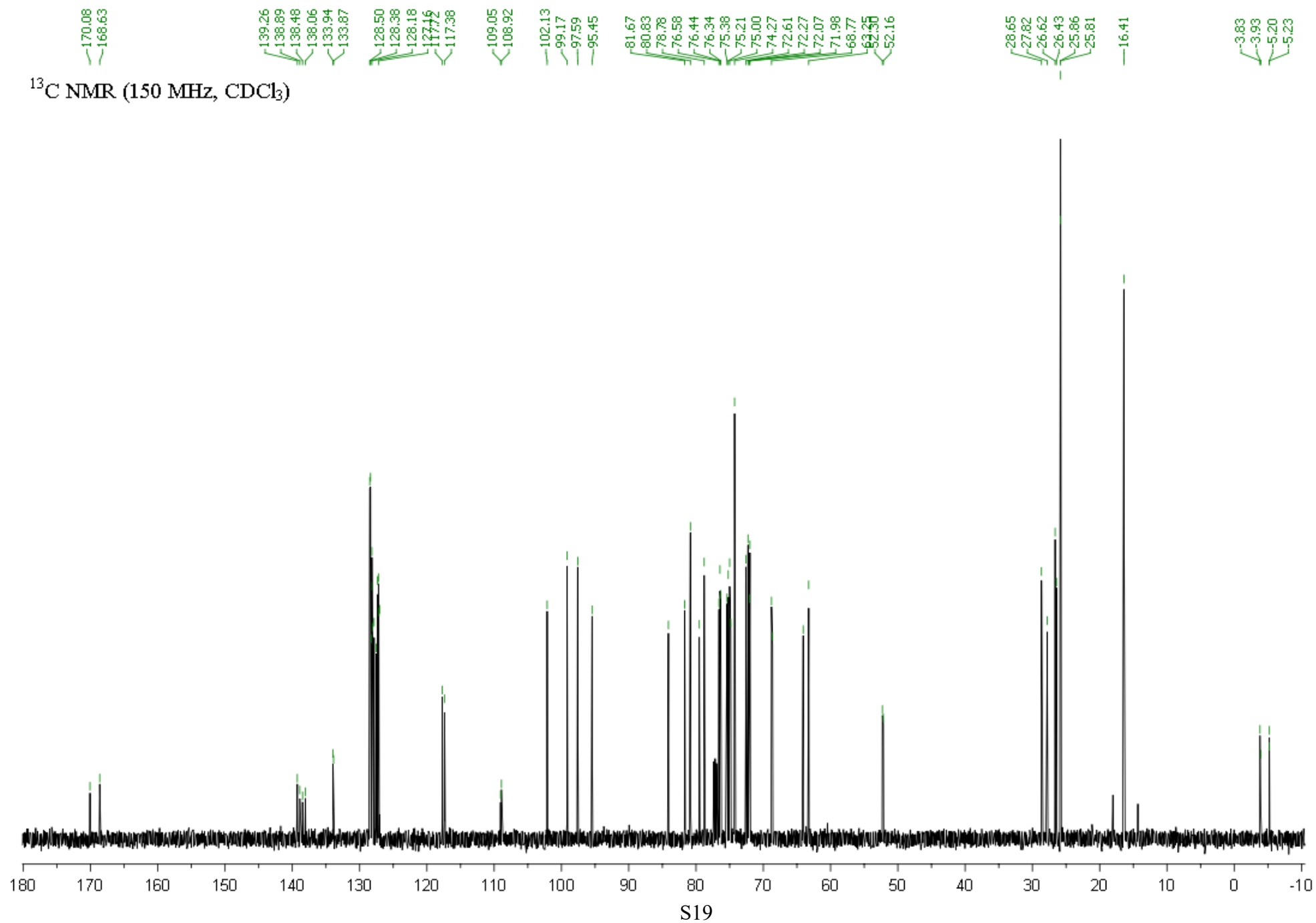
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| Scan Begin  | 50 m/z   | Set Capillary        | 4500 V   | Set Dry Gas      | 4.0 l/min |
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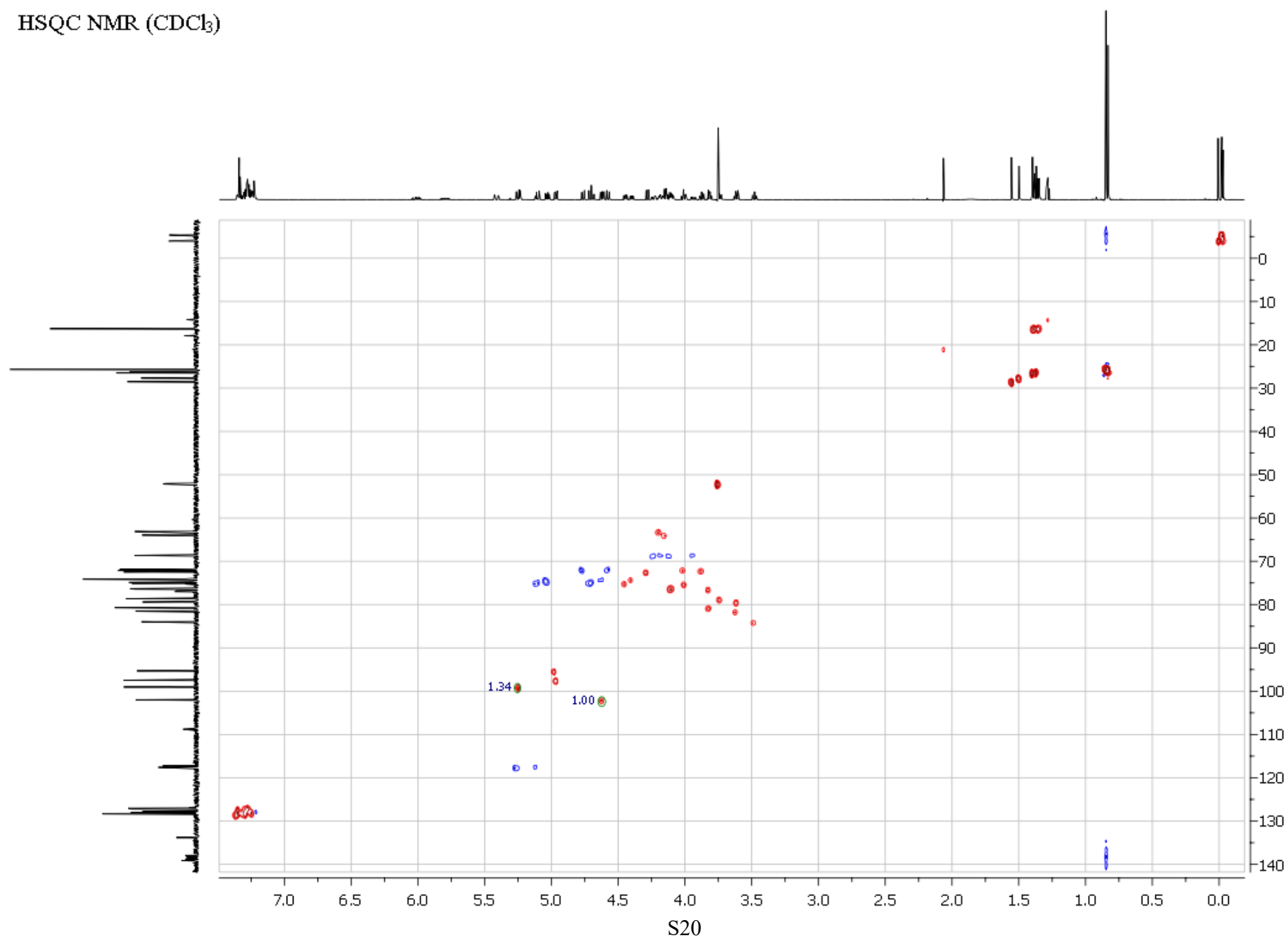


Allyl 3,4-O-isopropylidene-2-O-(methyl 2,3-di-O-benzyl-4-O-tert-butyldimethylsilyl- $\alpha,\beta$ -D-glucopyranosyluronate)- $\alpha$ -L-fucopyranoside (18).



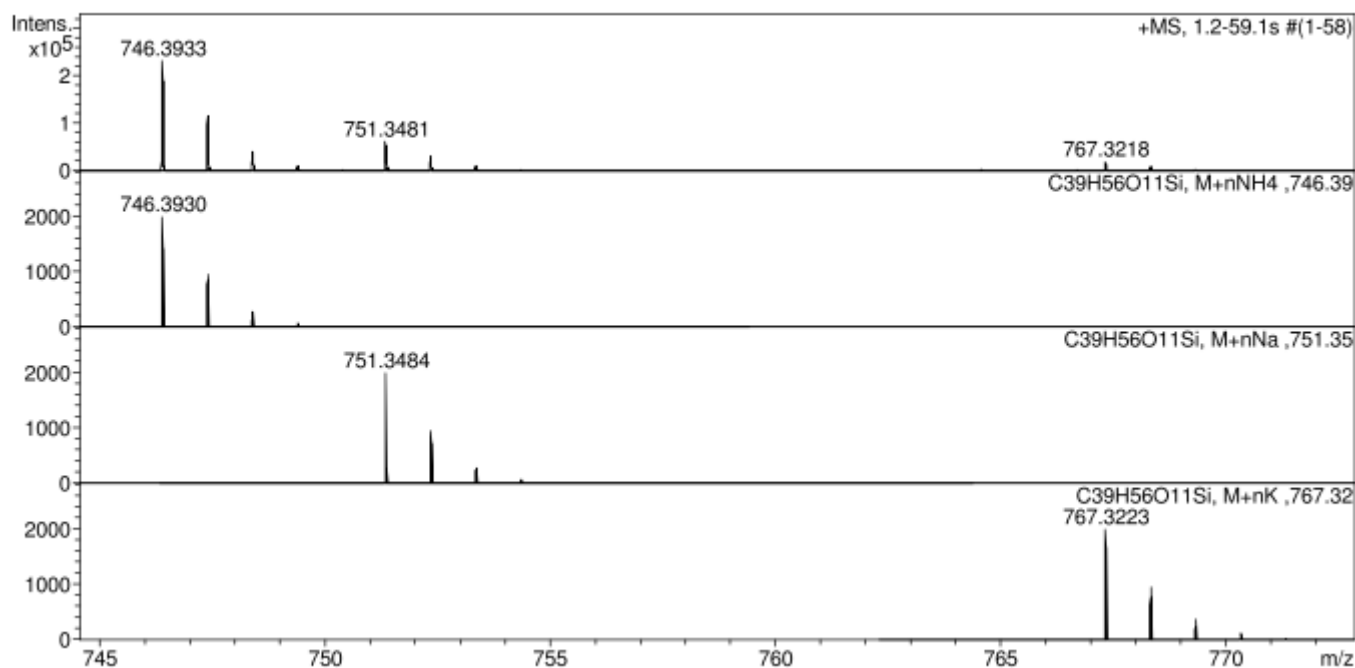
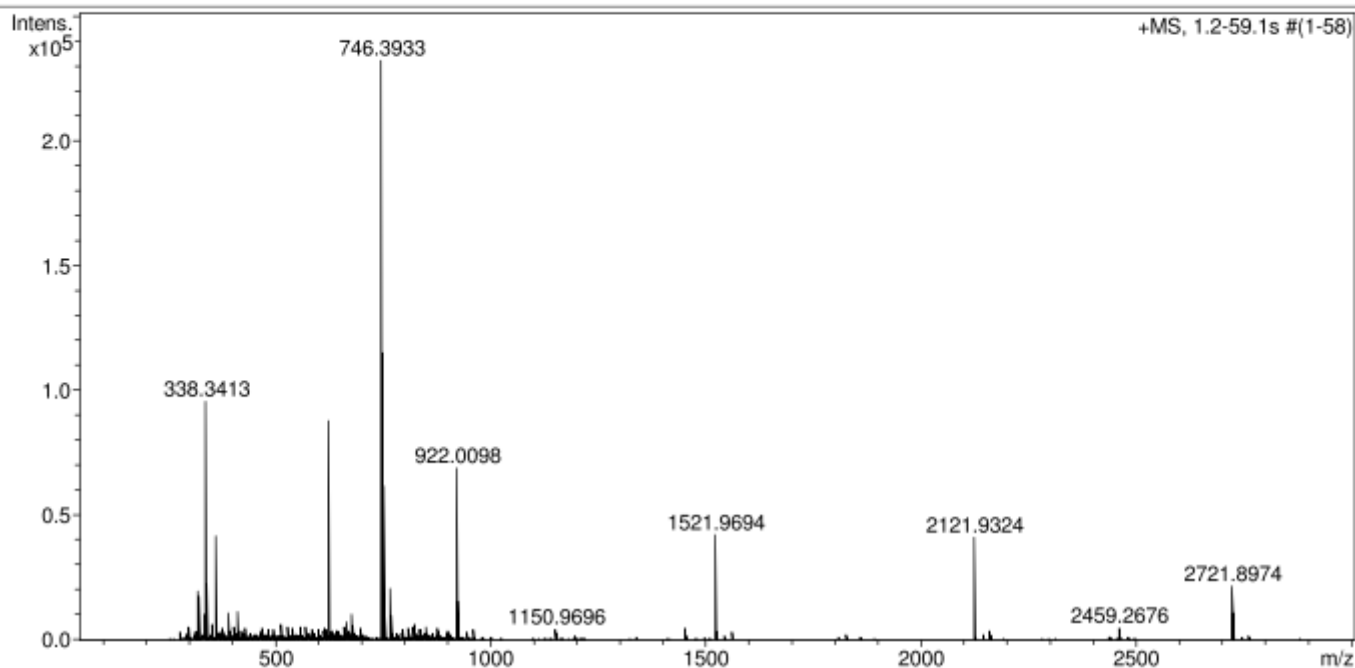


HSQC NMR (CDCl<sub>3</sub>)

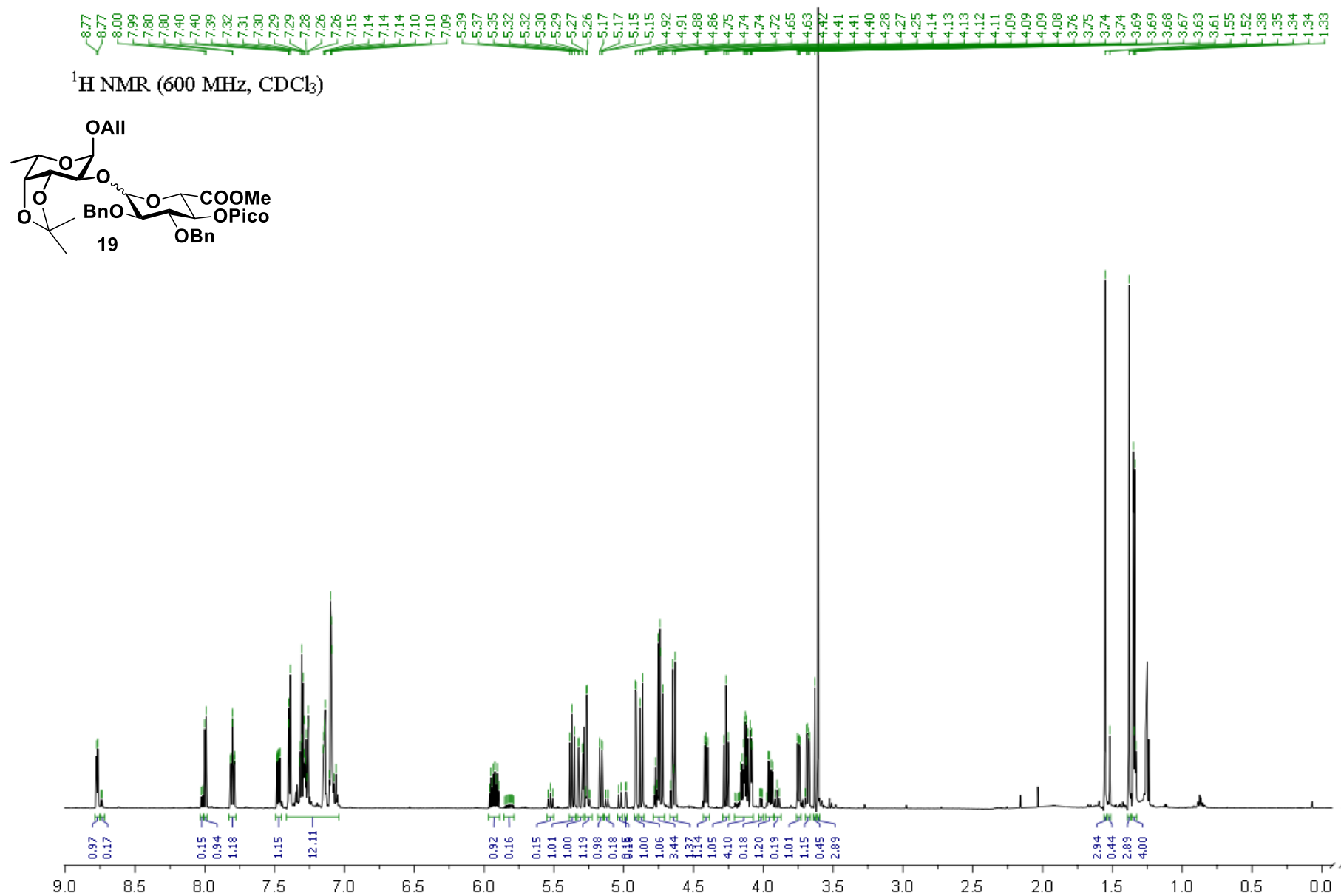


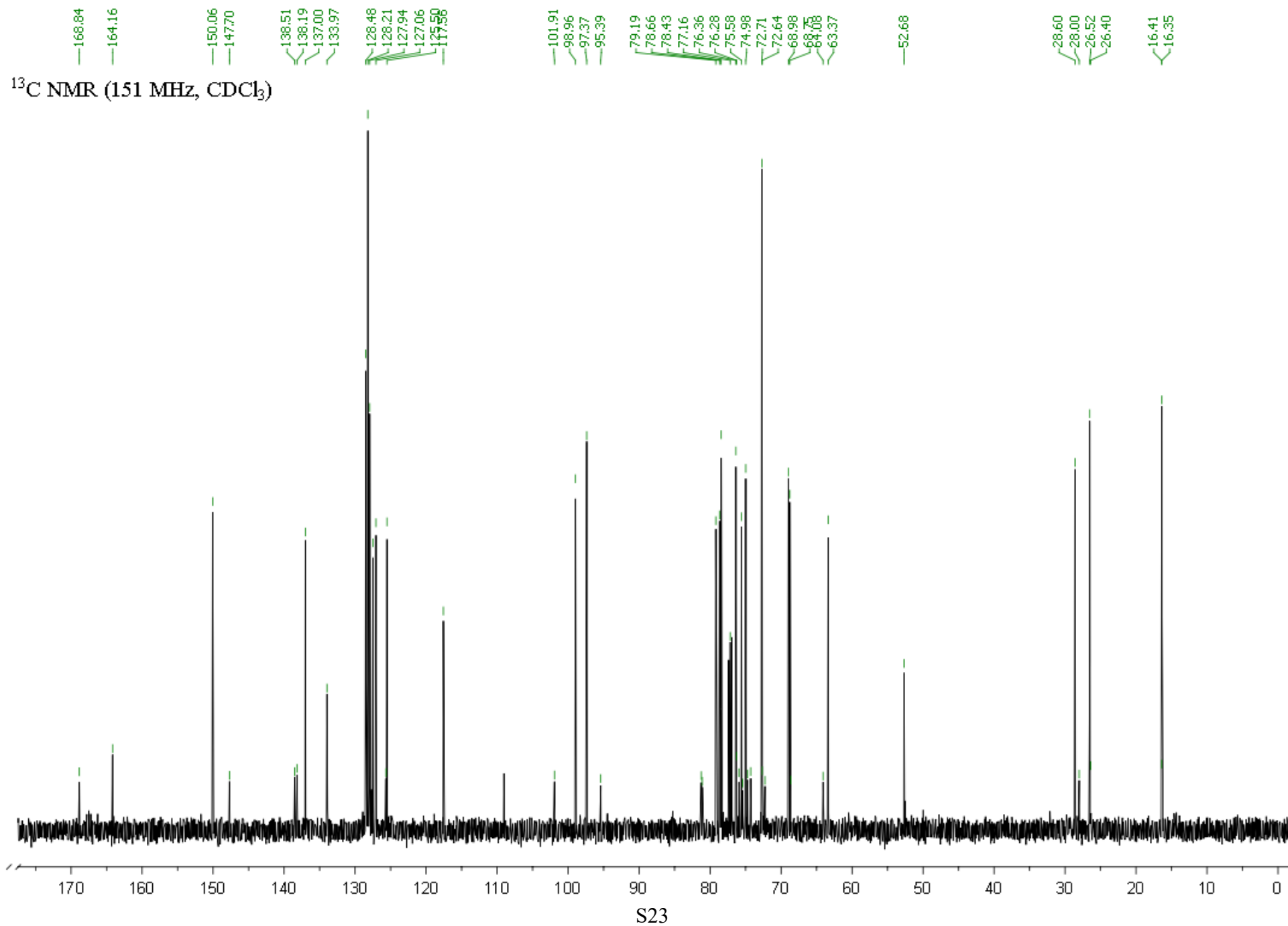
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| Focus       | Active   |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z   | Set Capillary        | 4500 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |

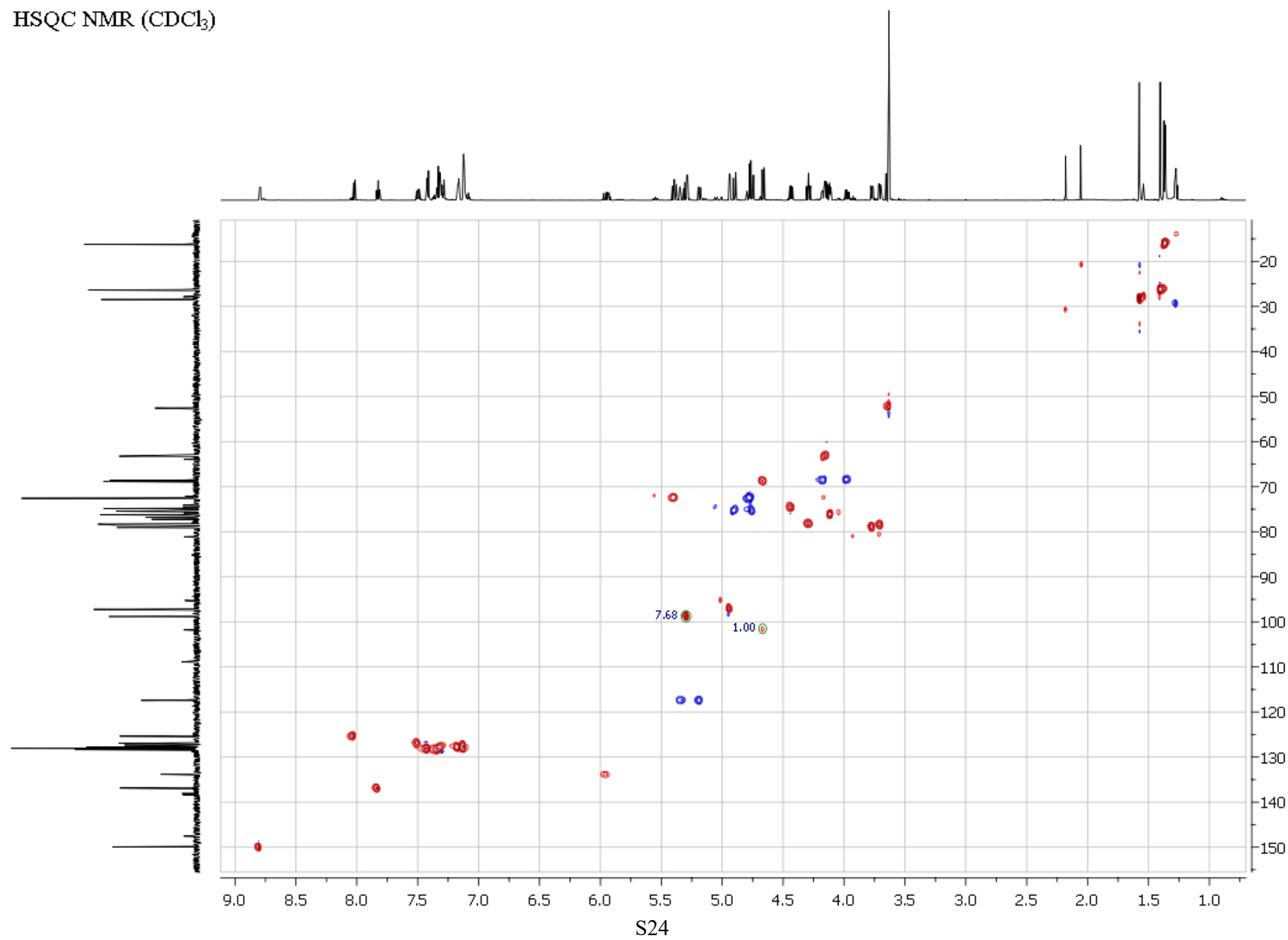


Allyl 3,4-O-isopropylidene-2-O-(methyl 2,3-di-O-benzyl-4-O-picoloyl- $\alpha,\beta$ -D-glucopyranosyluronate)- $\alpha$ -L-fucopyranoside (19).





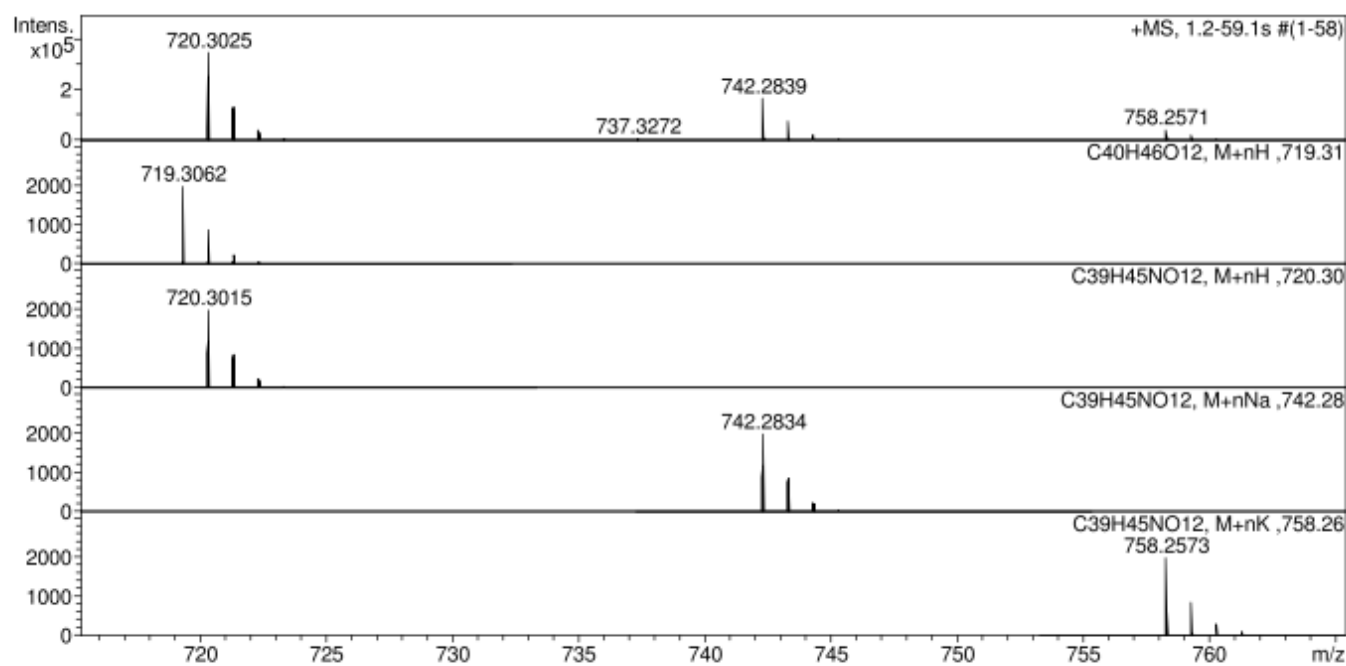
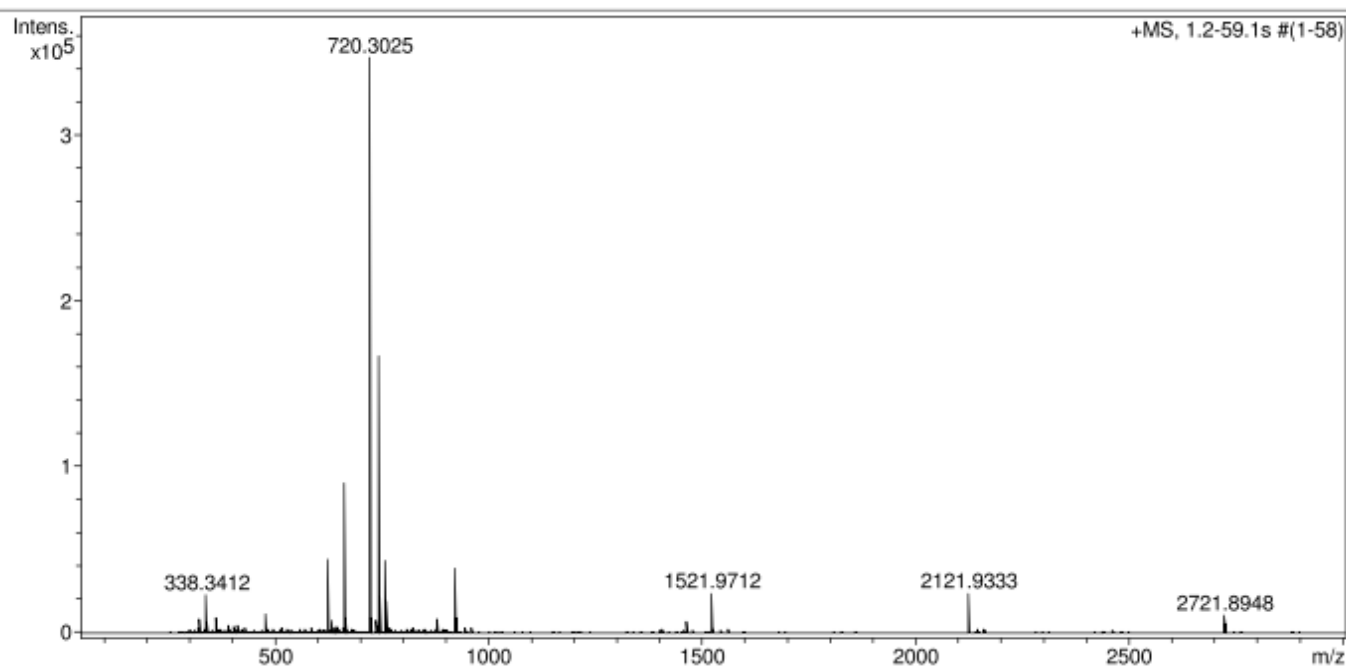
HSQC NMR (CDCl<sub>3</sub>)



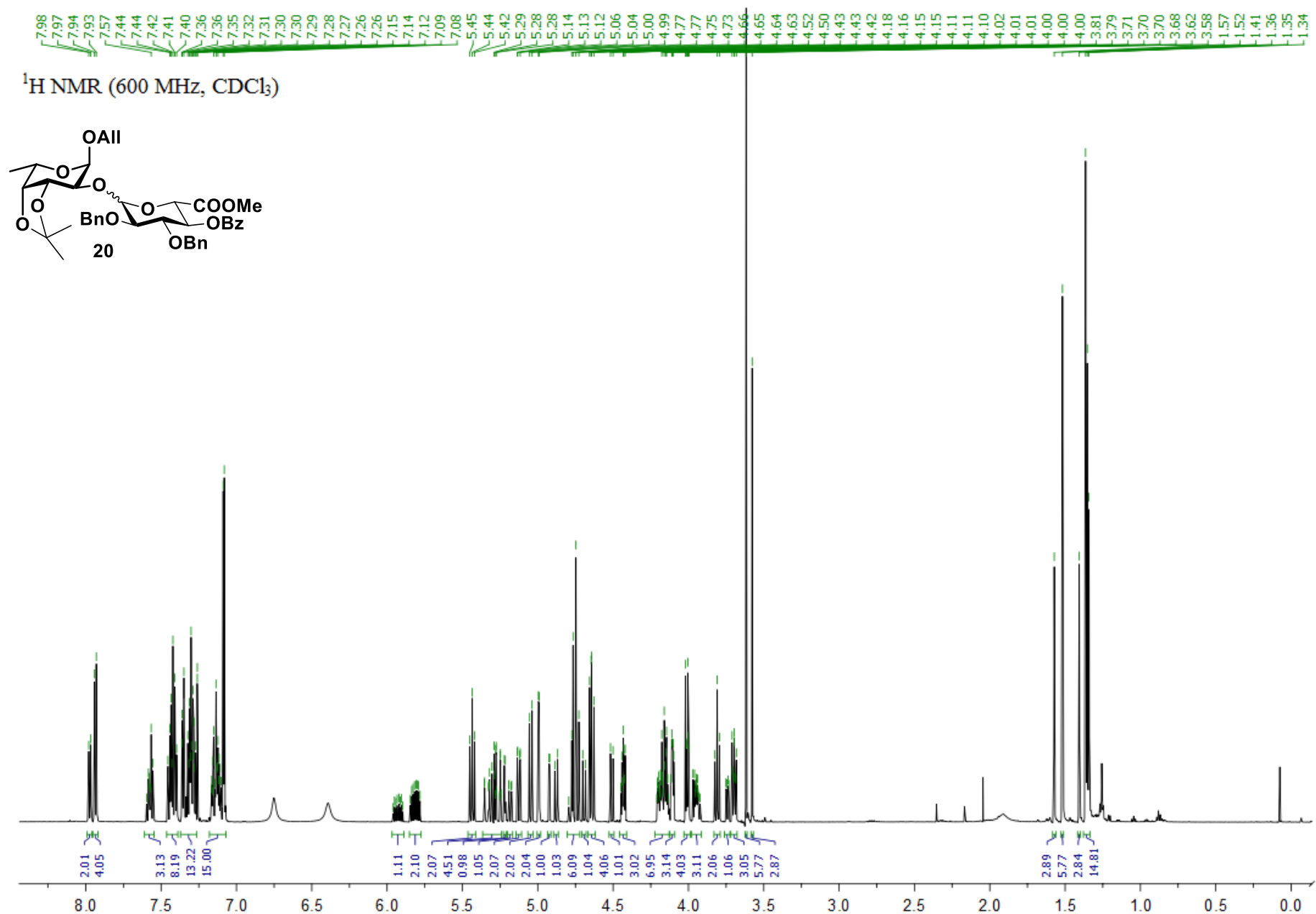


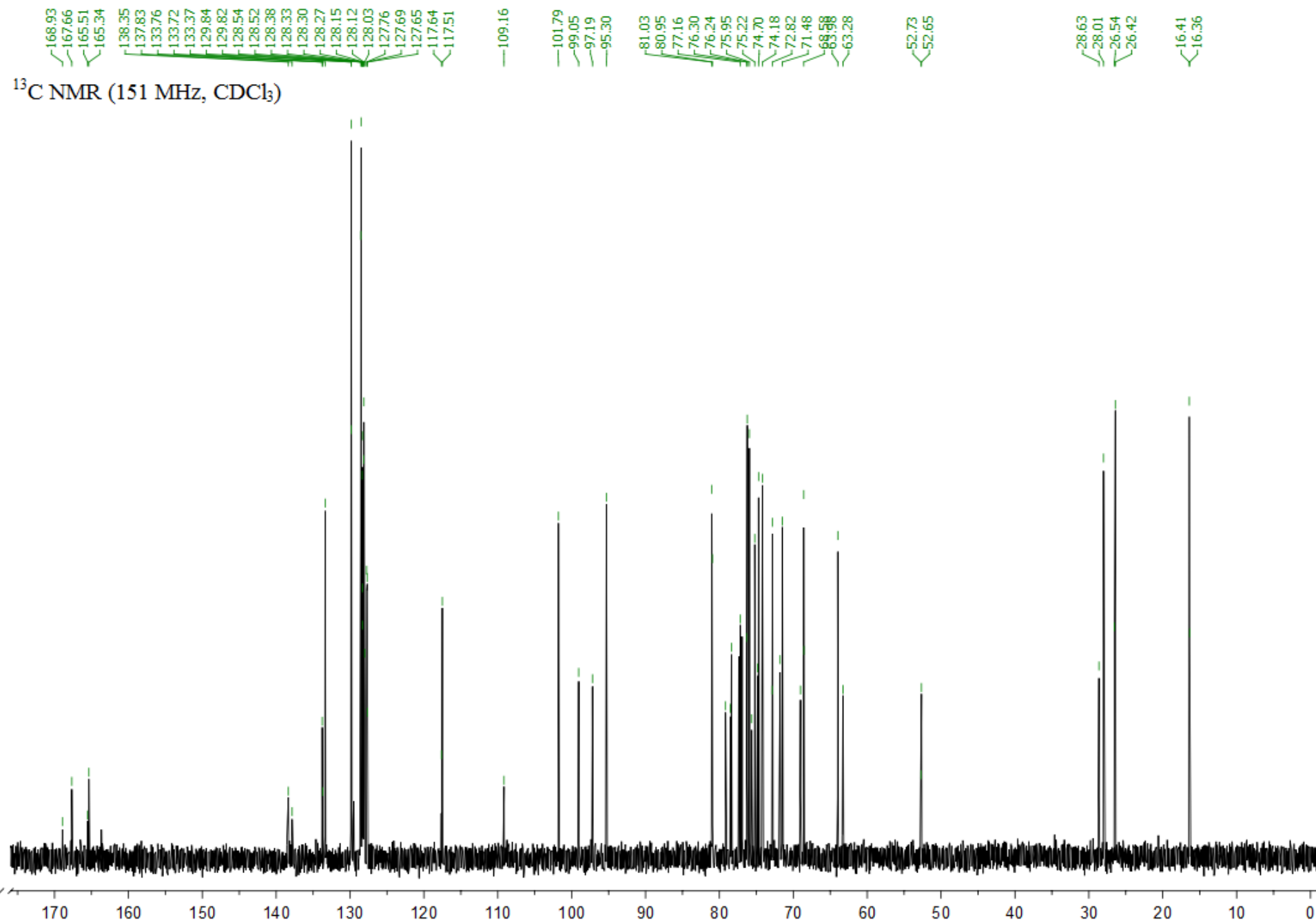
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| Focus       | Active   |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z   | Set Capillary        | 4500 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |

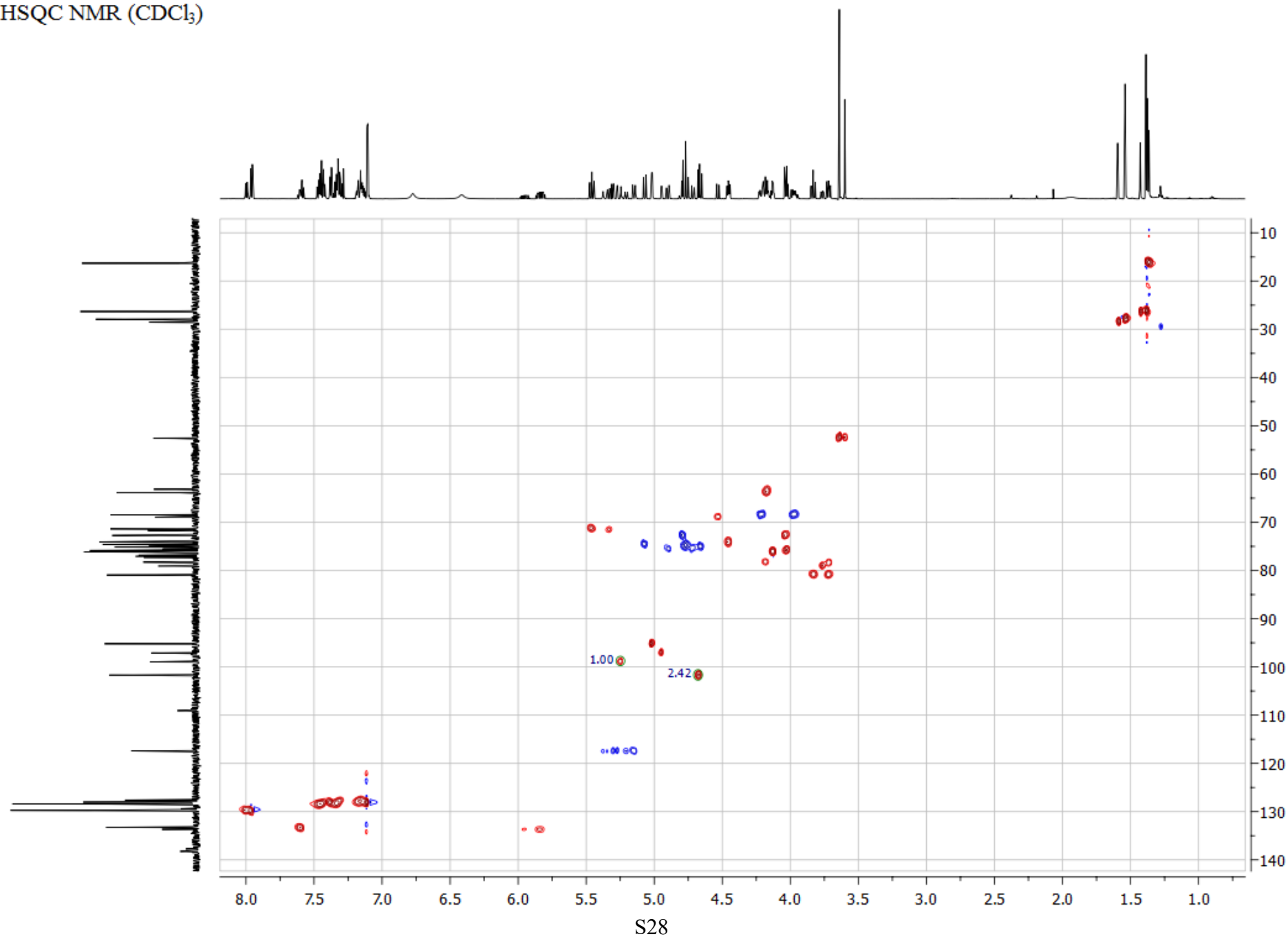


Allyl 3,4-O-isopropylidene-2-O-(methyl 2,3-di-O-benzyl-4-O-benzoyl- $\alpha,\beta$ -D-glucopyranosyluronate)- $\alpha$ -L-fucopyranoside (20).



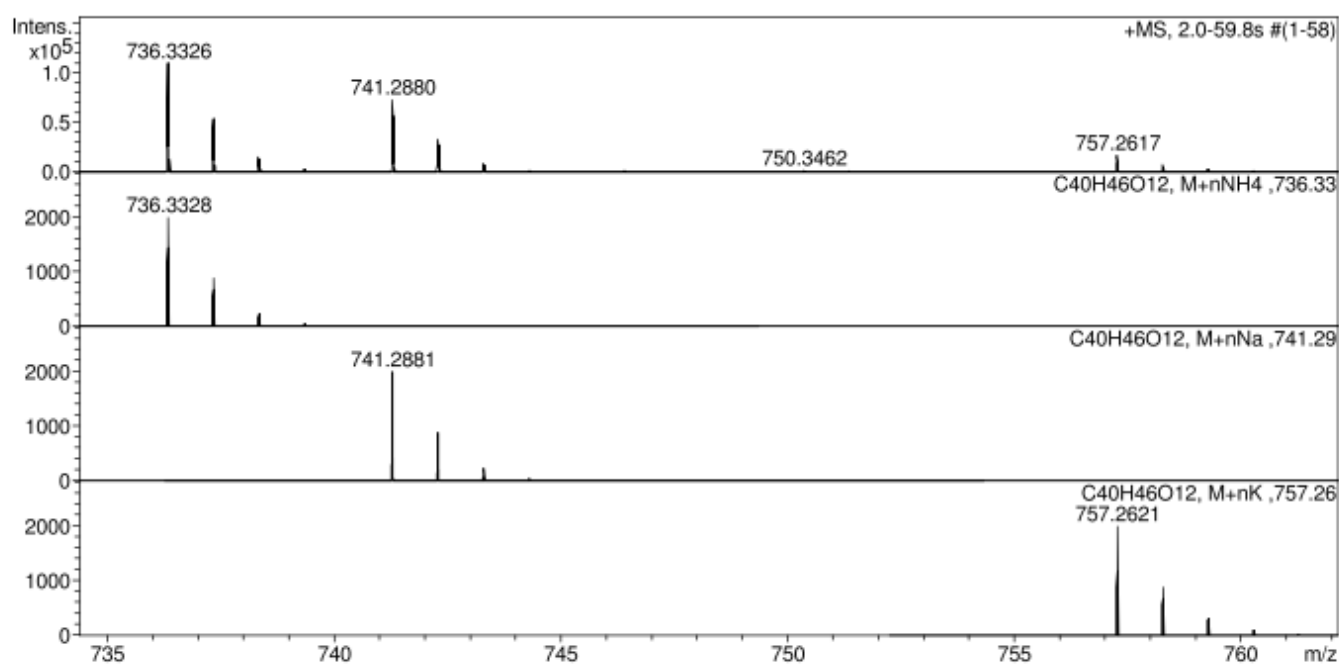
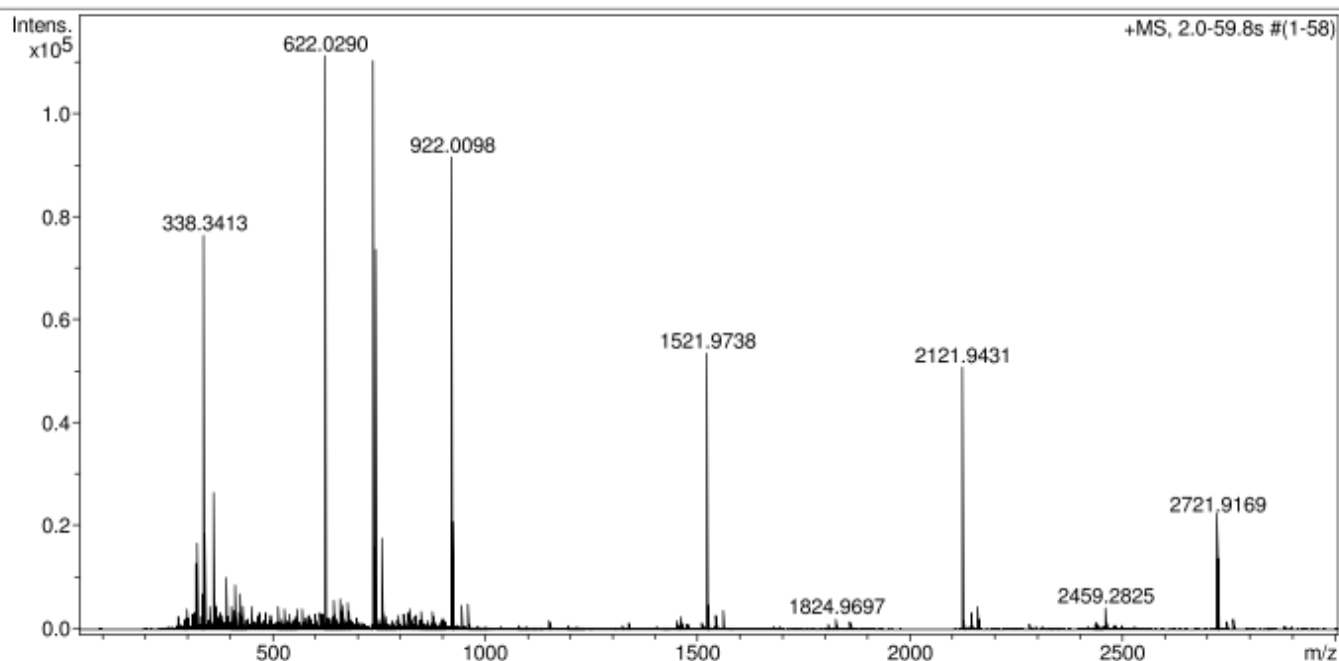


HSQC NMR (CDCl<sub>3</sub>)

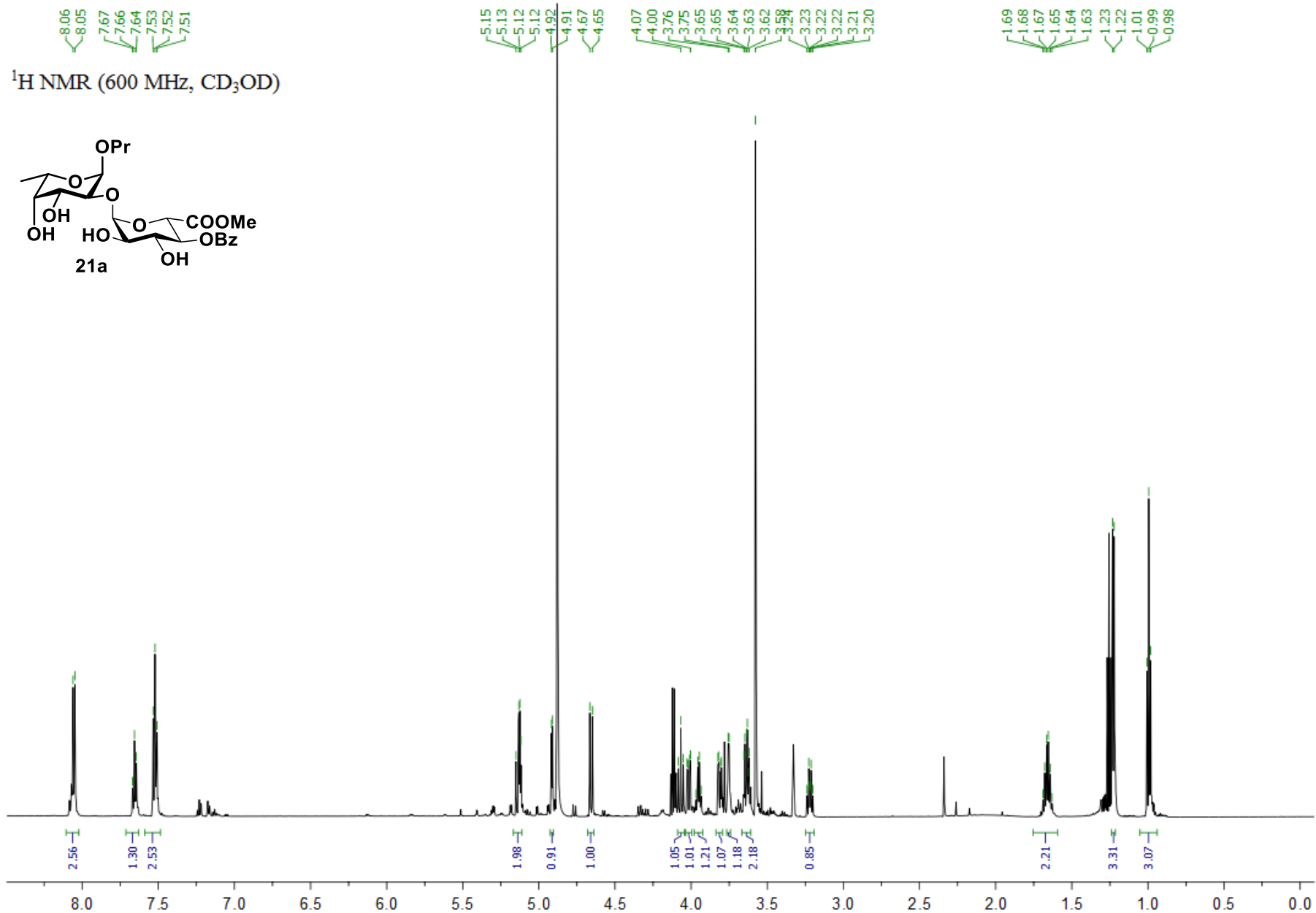


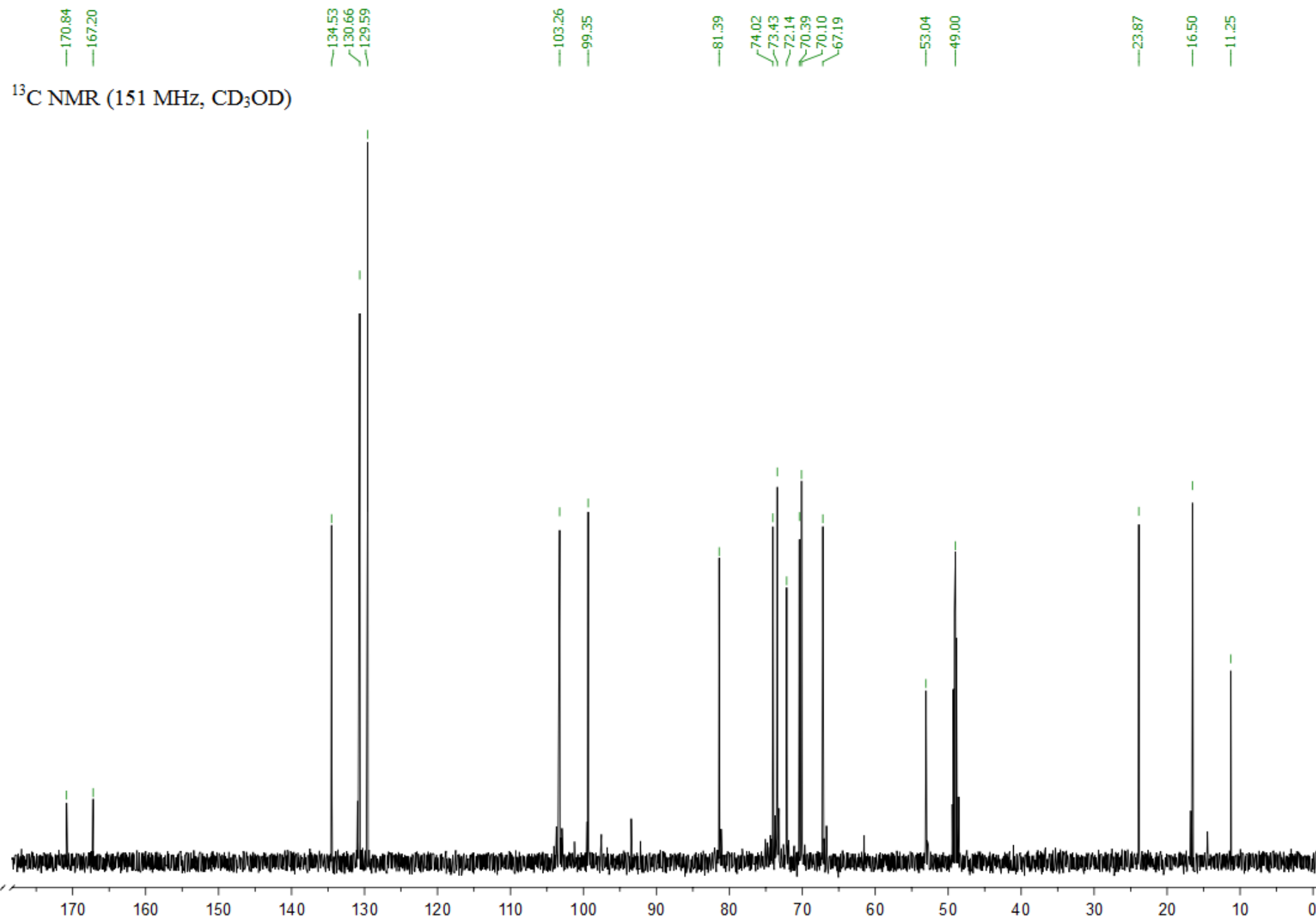
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|             |          |                      |          |                  |           |
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| Focus       | Active   |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z   | Set Capillary        | 4500 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |



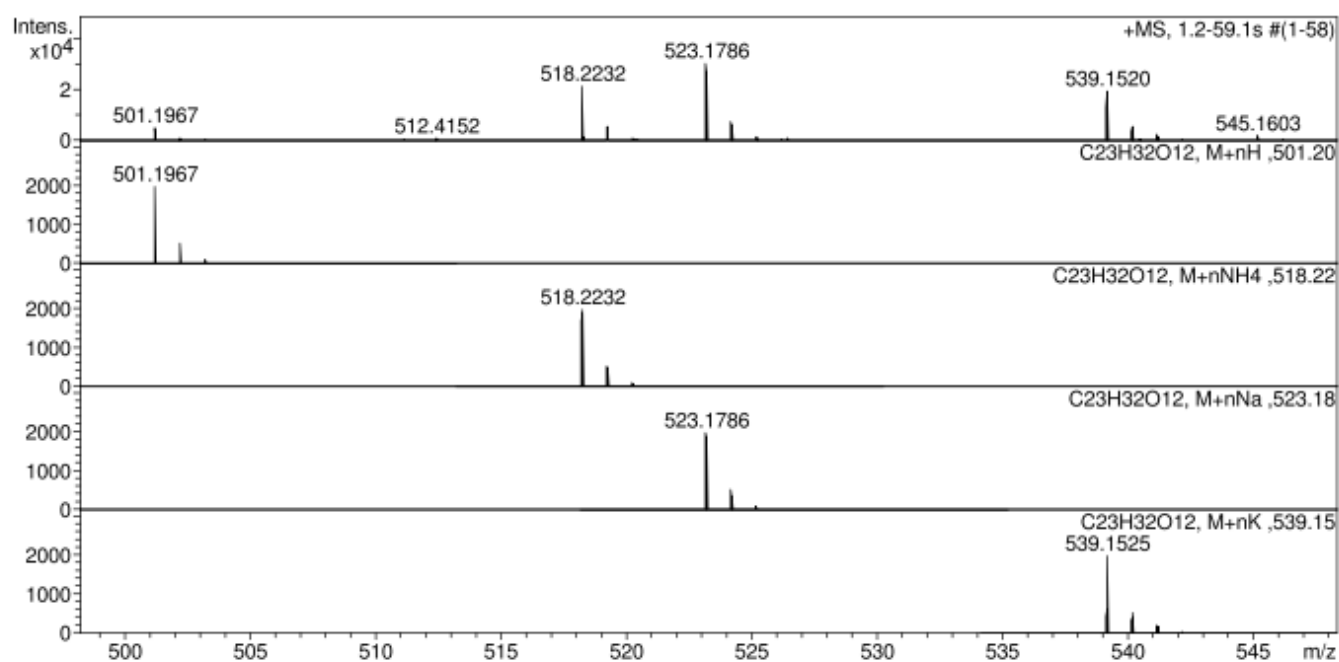
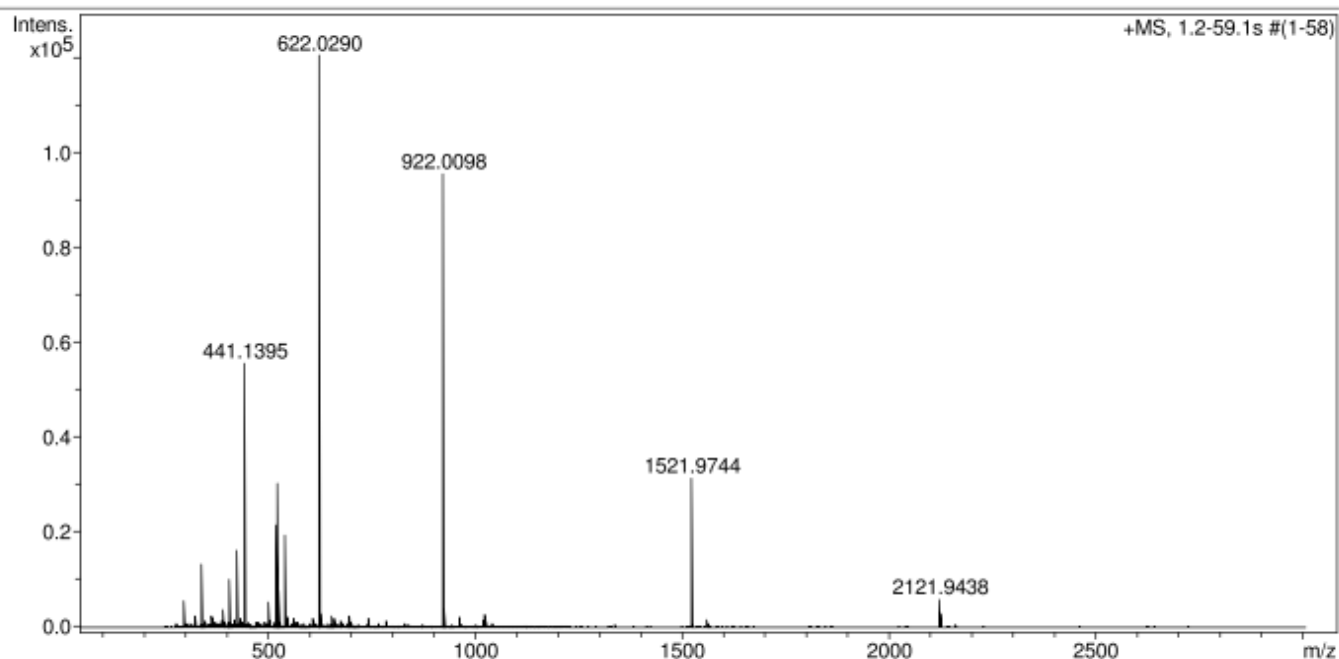
Propyl 2-O-(methyl 4-O-benzoyl- $\alpha$ -D-glucopyranosyluronate)- $\alpha$ -L-fucopyranoside (21a).





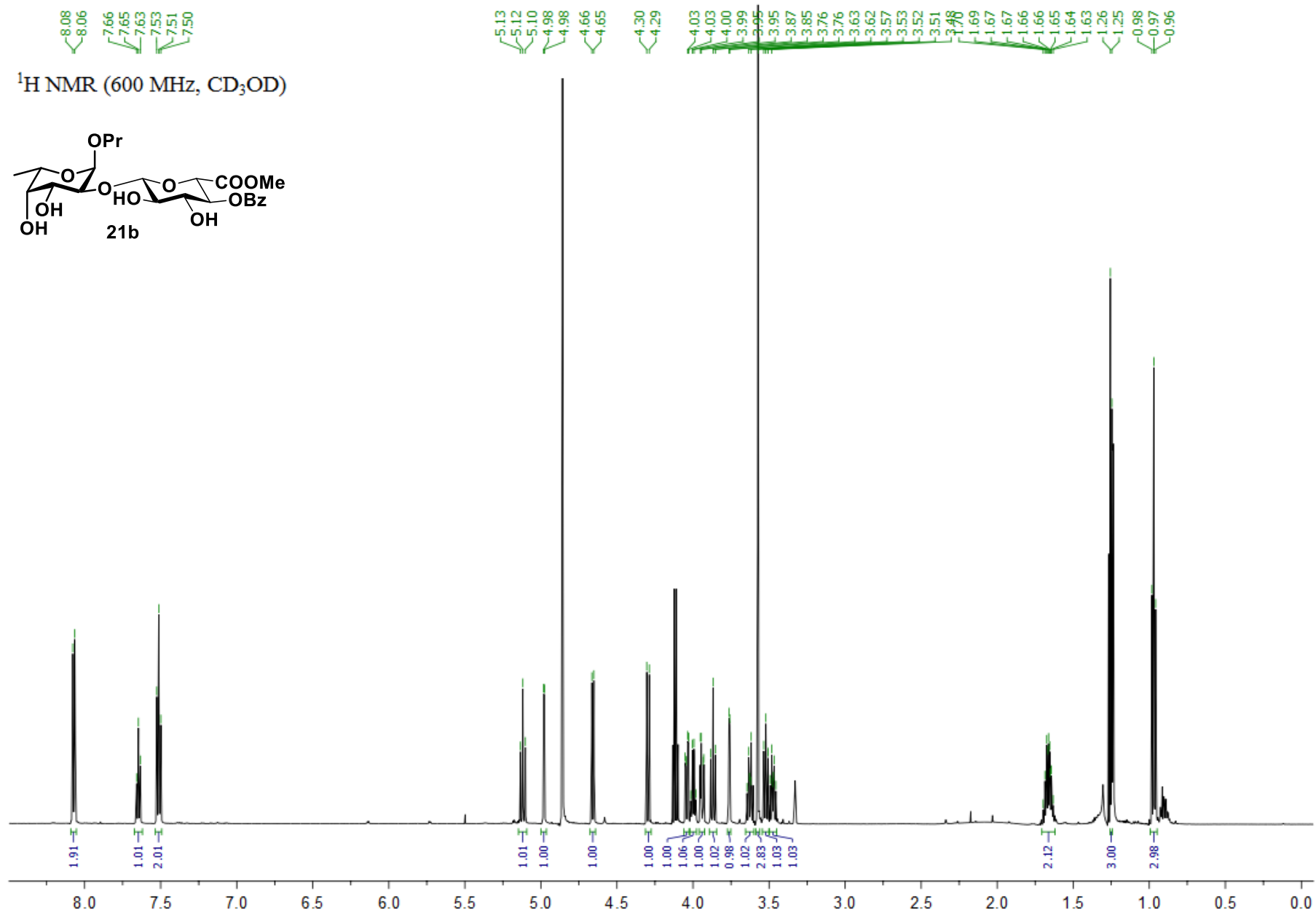
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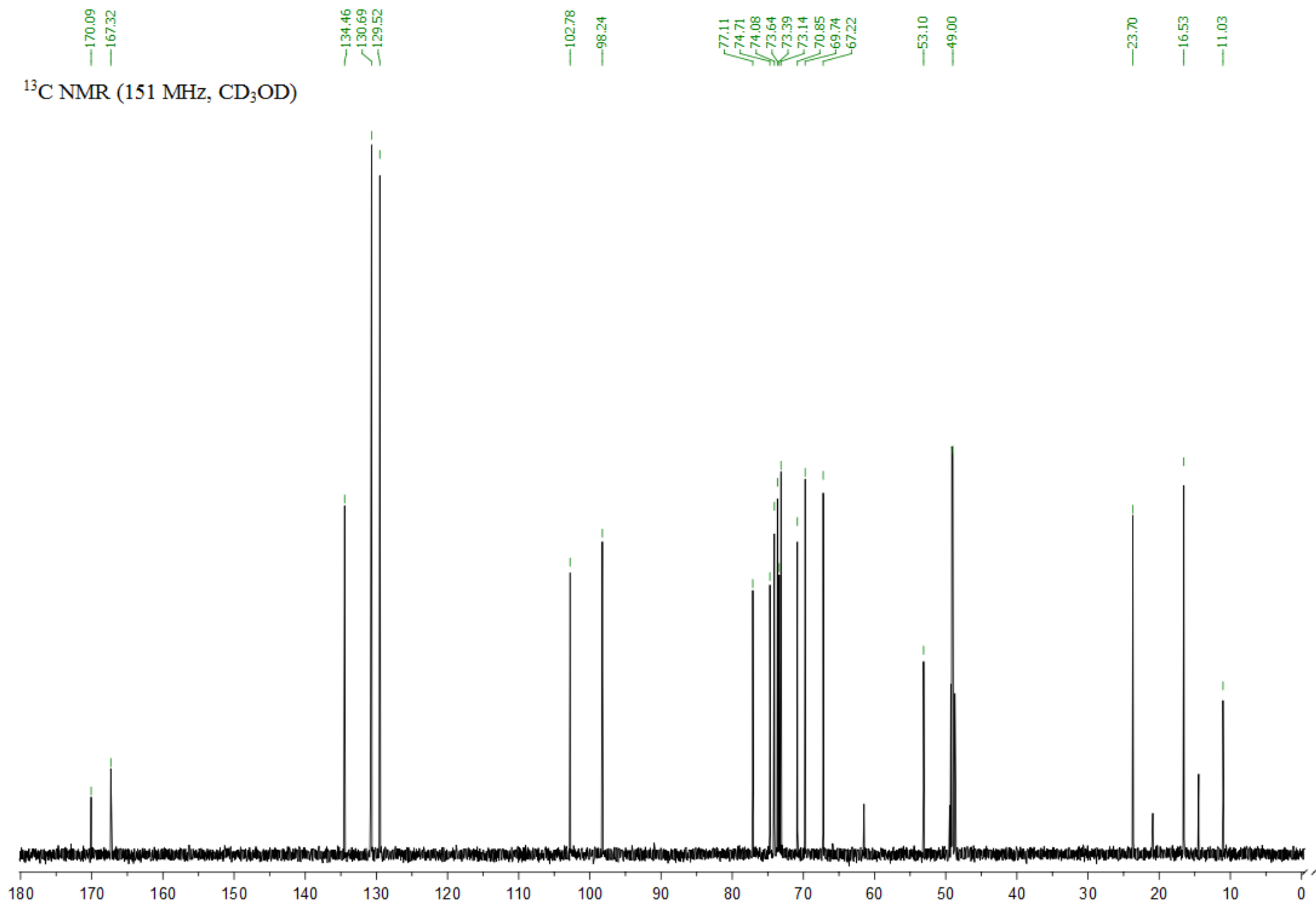
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| Focus       | Active   |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z   | Set Capillary        | 4500 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |





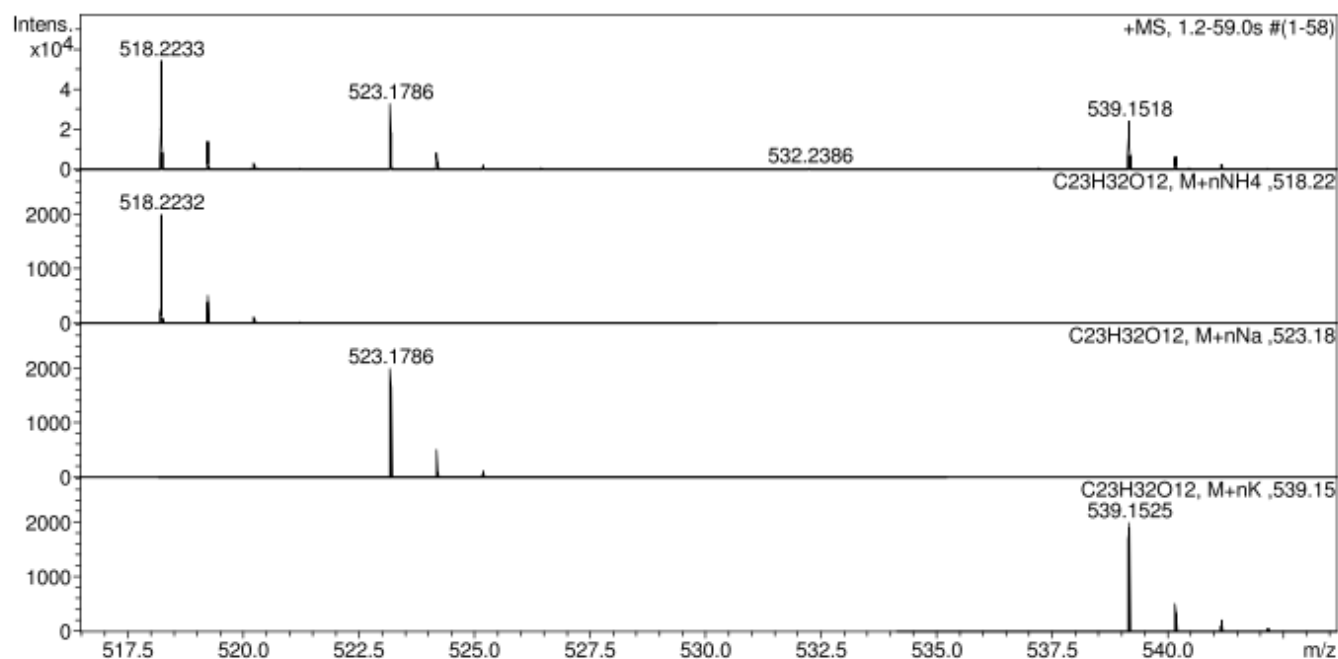
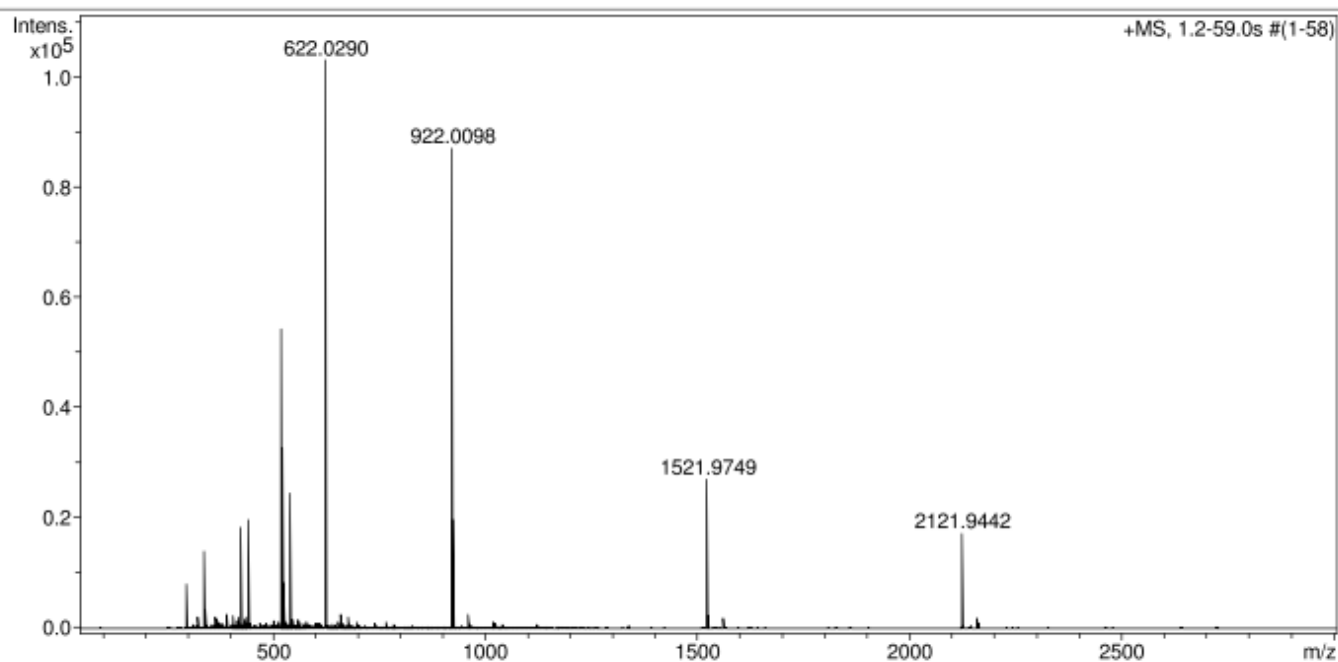
Propyl 2-O-(methyl 4-O-benzoyl- $\beta$ -D-glucopyranosyluronate)- $\alpha$ -L-fucopyranoside (21b).



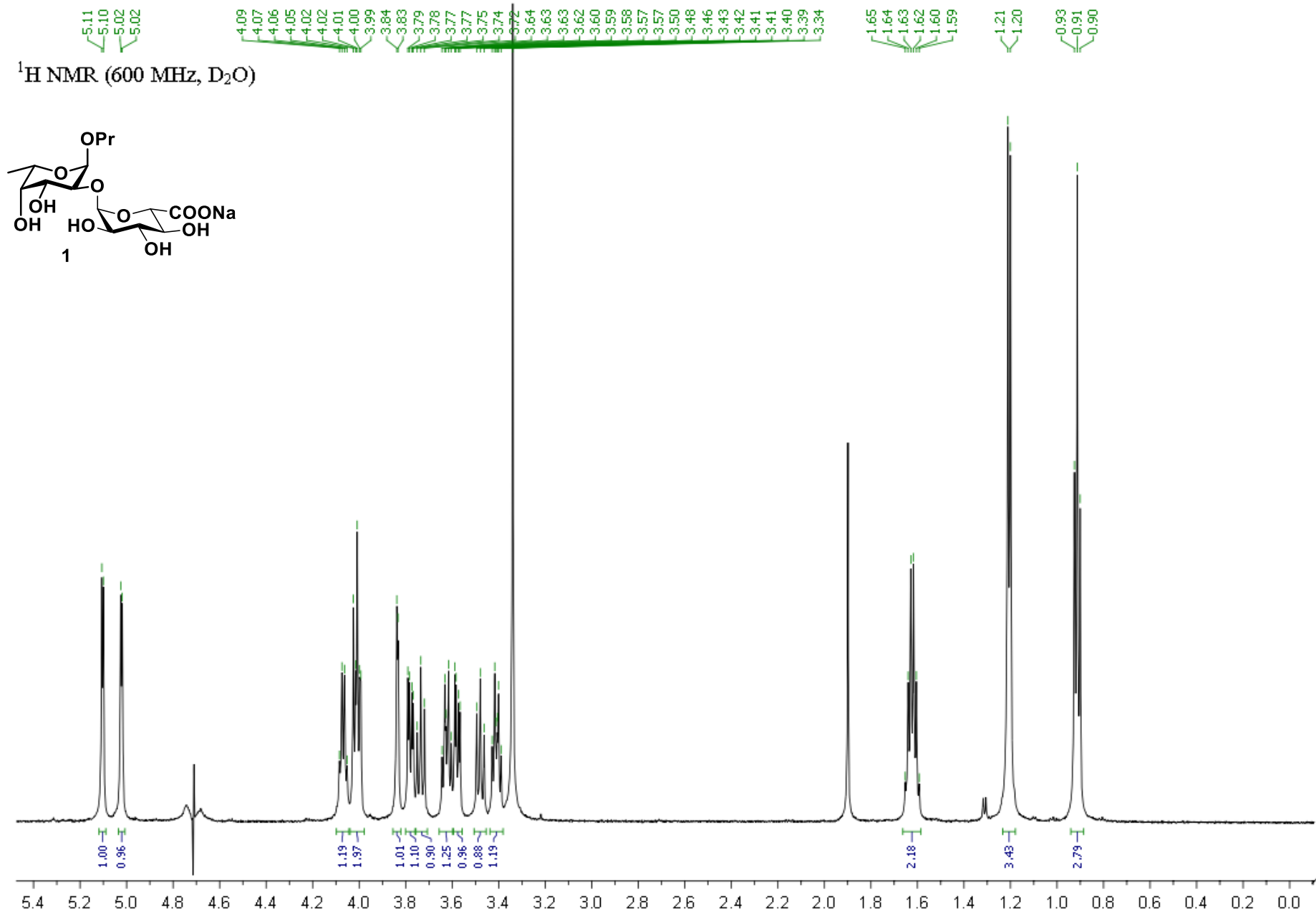


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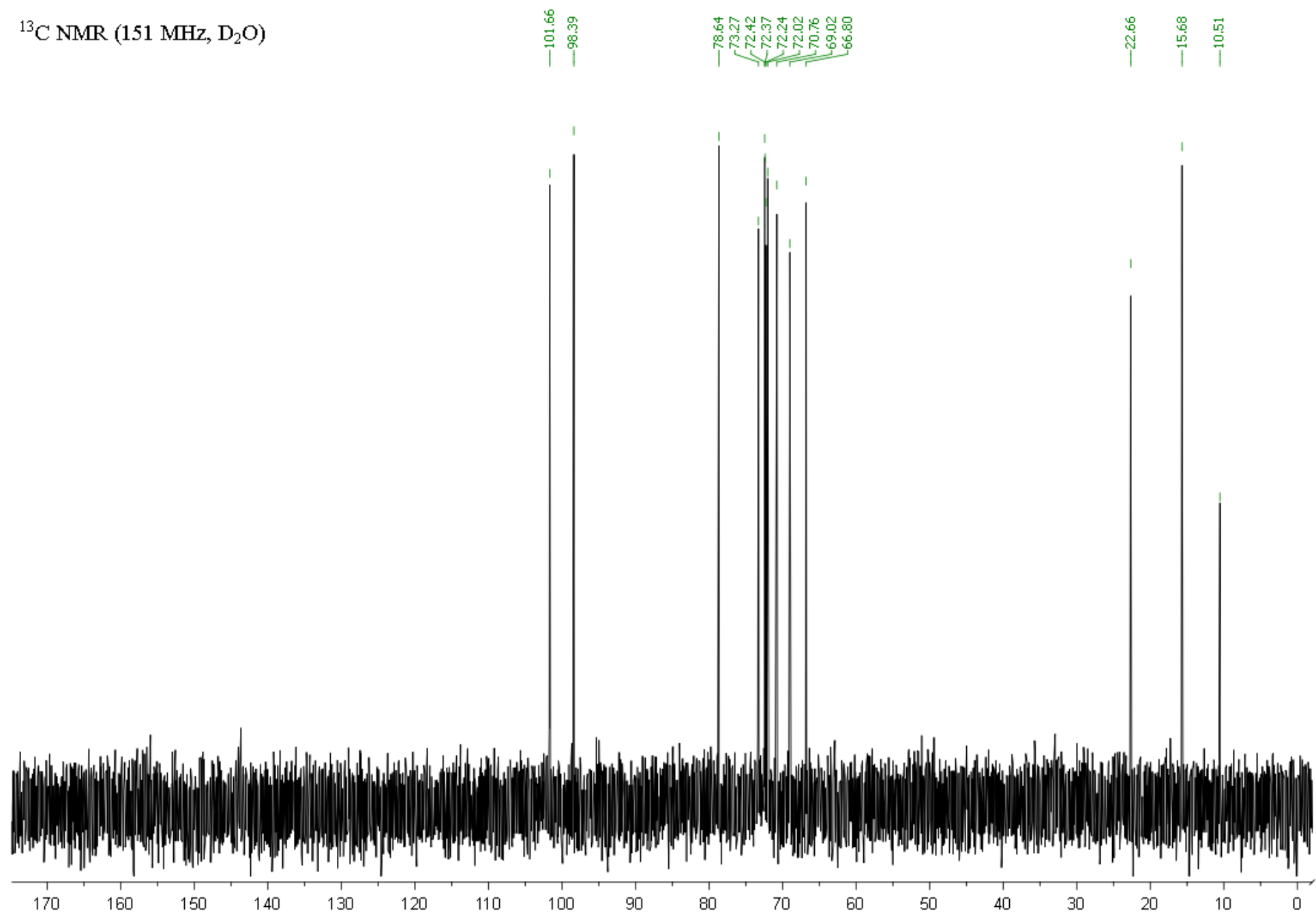
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| Focus       | Active   |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z   | Set Capillary        | 4500 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |



Propyl 2-O-( $\alpha$ -D-glucopyranosyluronic acid)- $\alpha$ -L-fucopyranoside sodium salt (1).



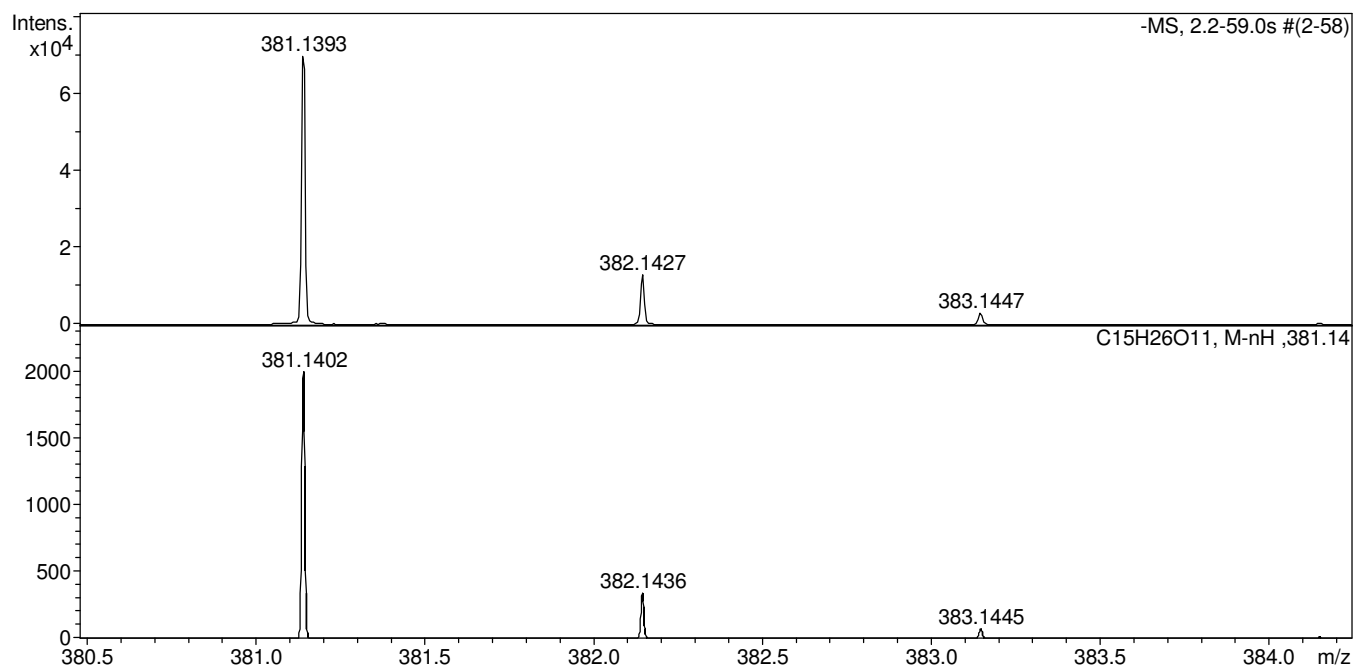
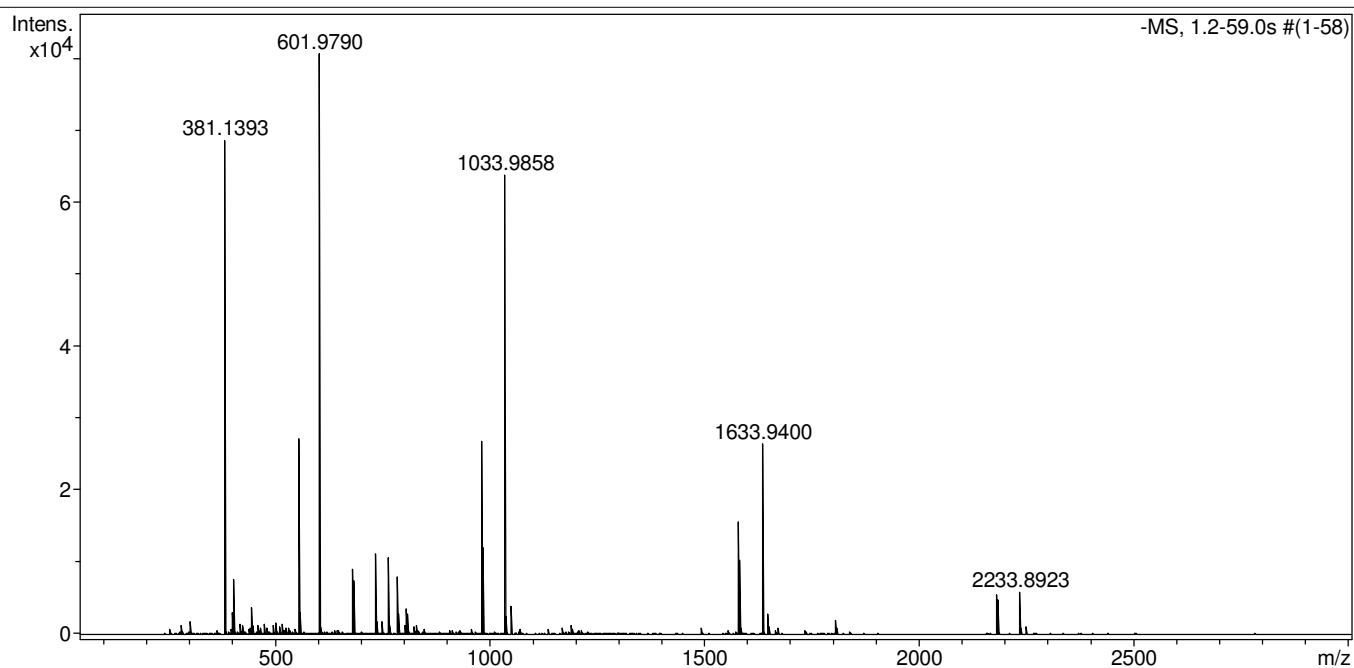
$^{13}\text{C}$  NMR (151 MHz,  $\text{D}_2\text{O}$ )



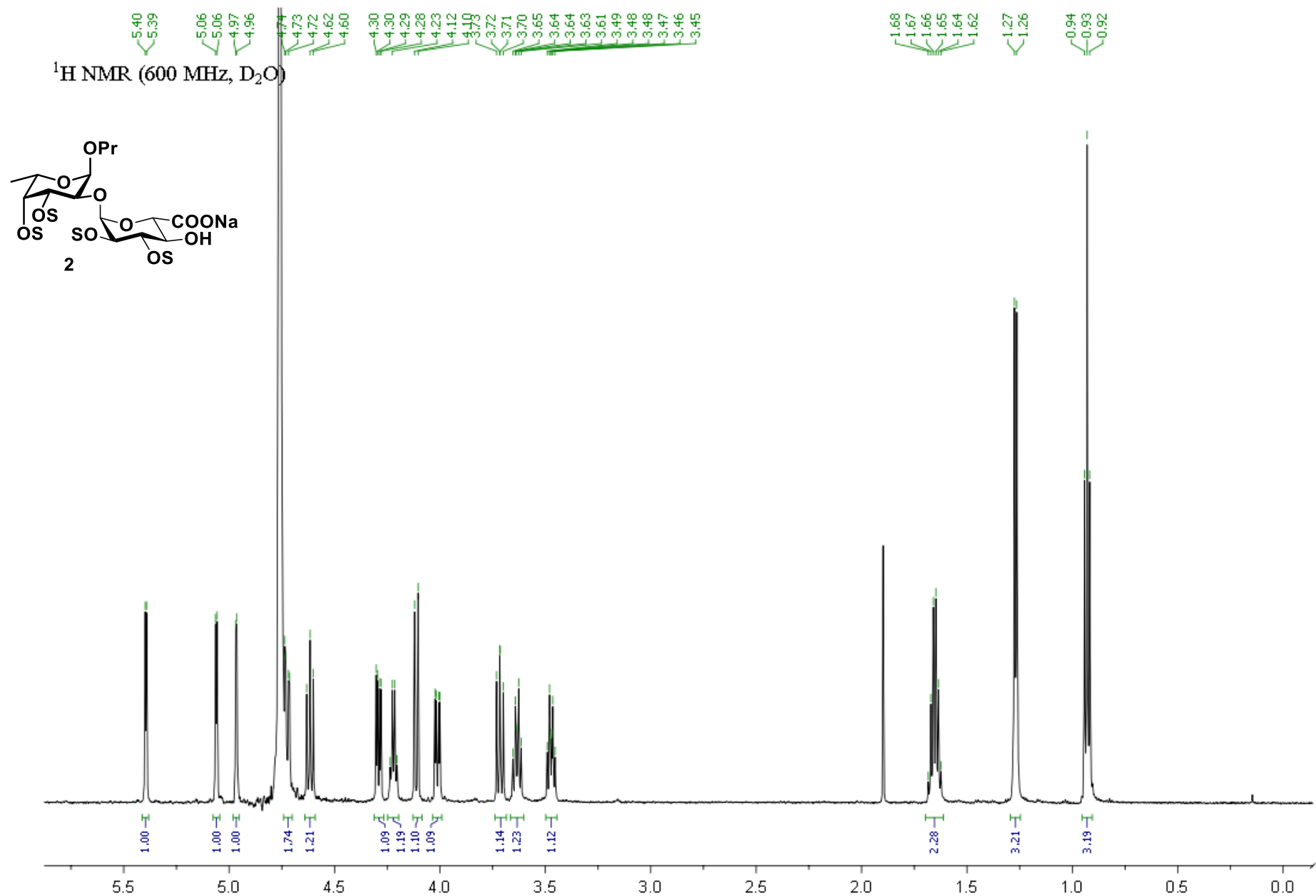
S37

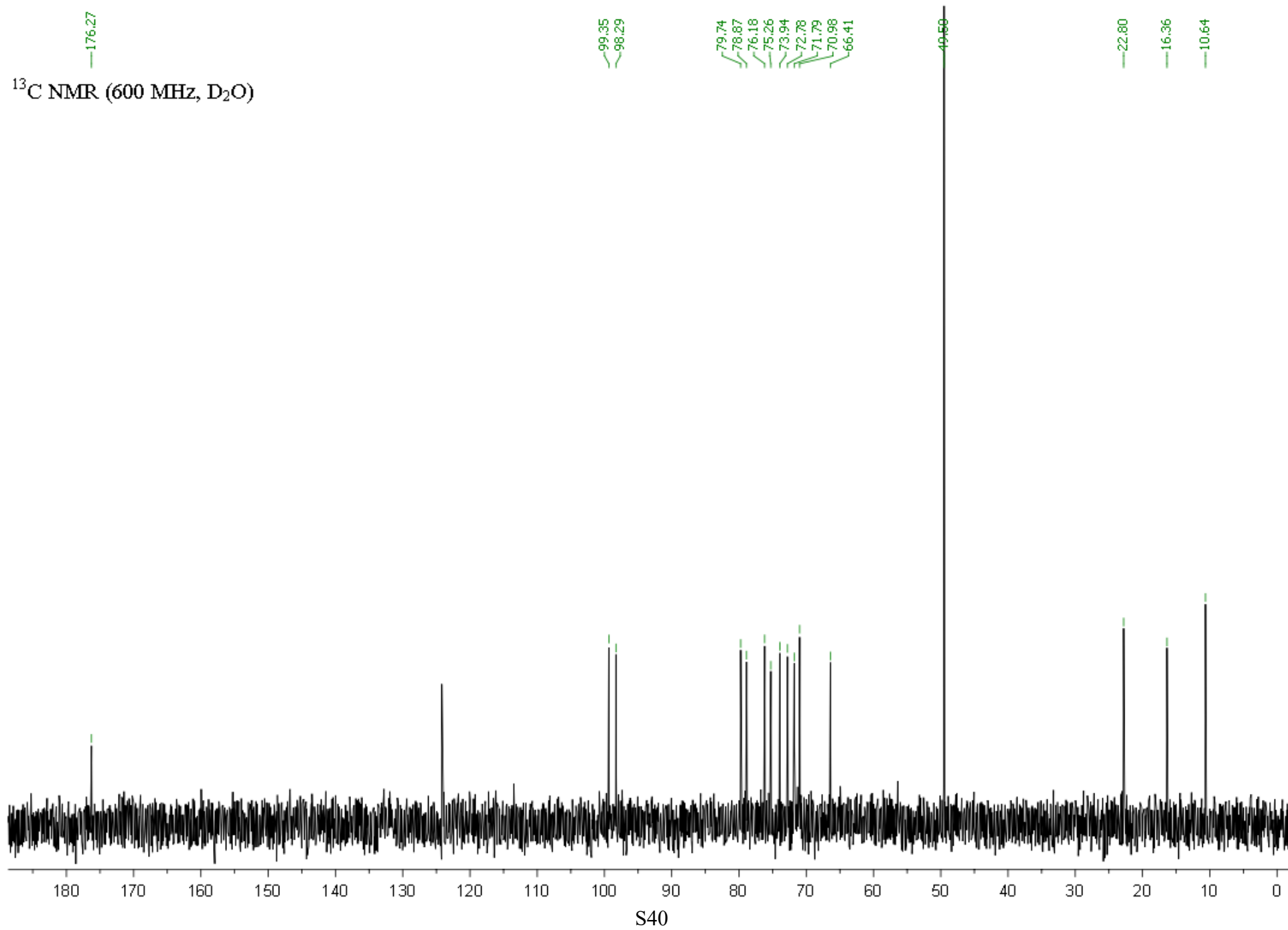
**Acquisition Parameter**

|             |          |                      |          |                  |           |
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| Focus       | Active   |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z   | Set Capillary        | 3000 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |



Propyl 2-O-(2,3-di-O-sulfo- $\alpha$ -D-glucopyranosyluronic acid)-3,4-di-O-sulfo- $\alpha$ -L-fucopyranoside sodium salt (2).

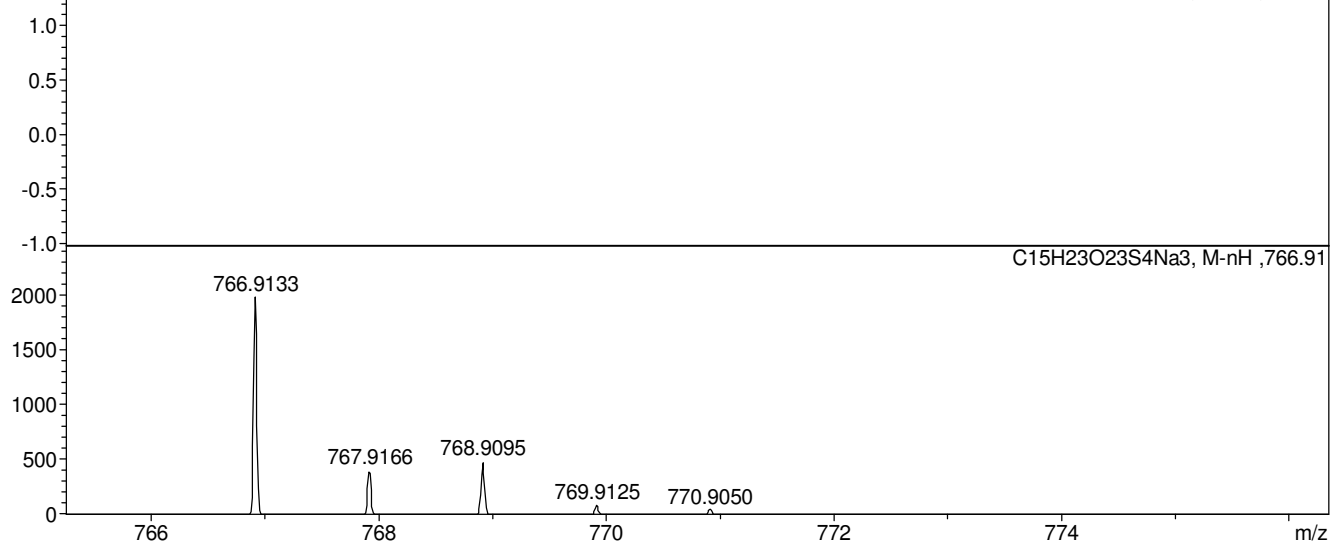
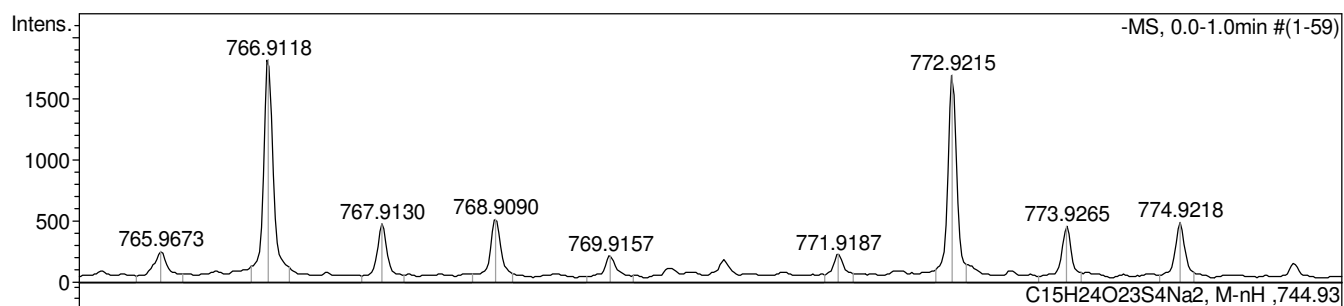
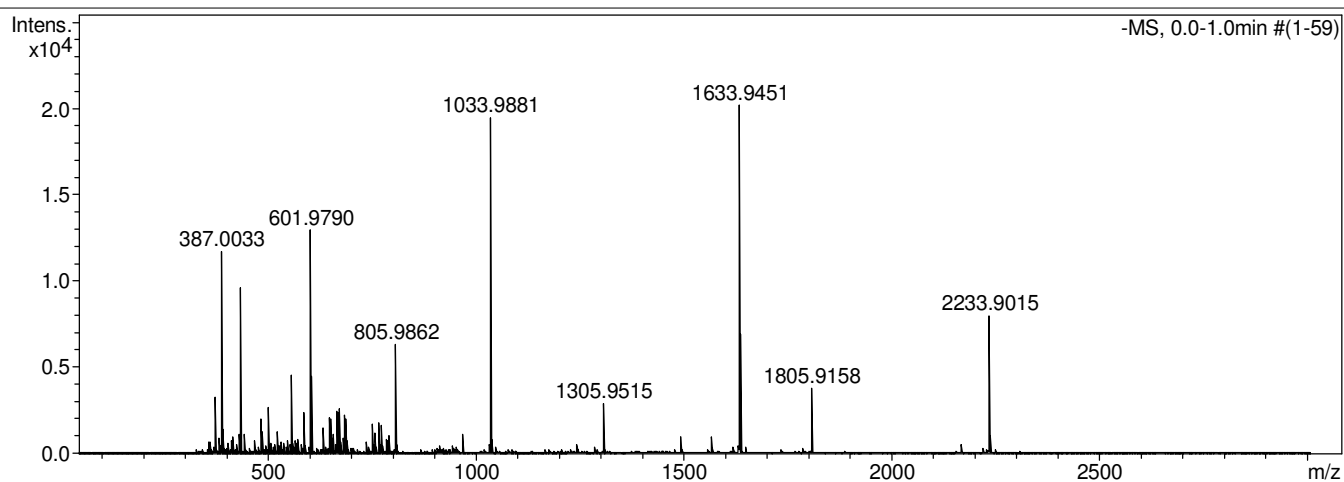




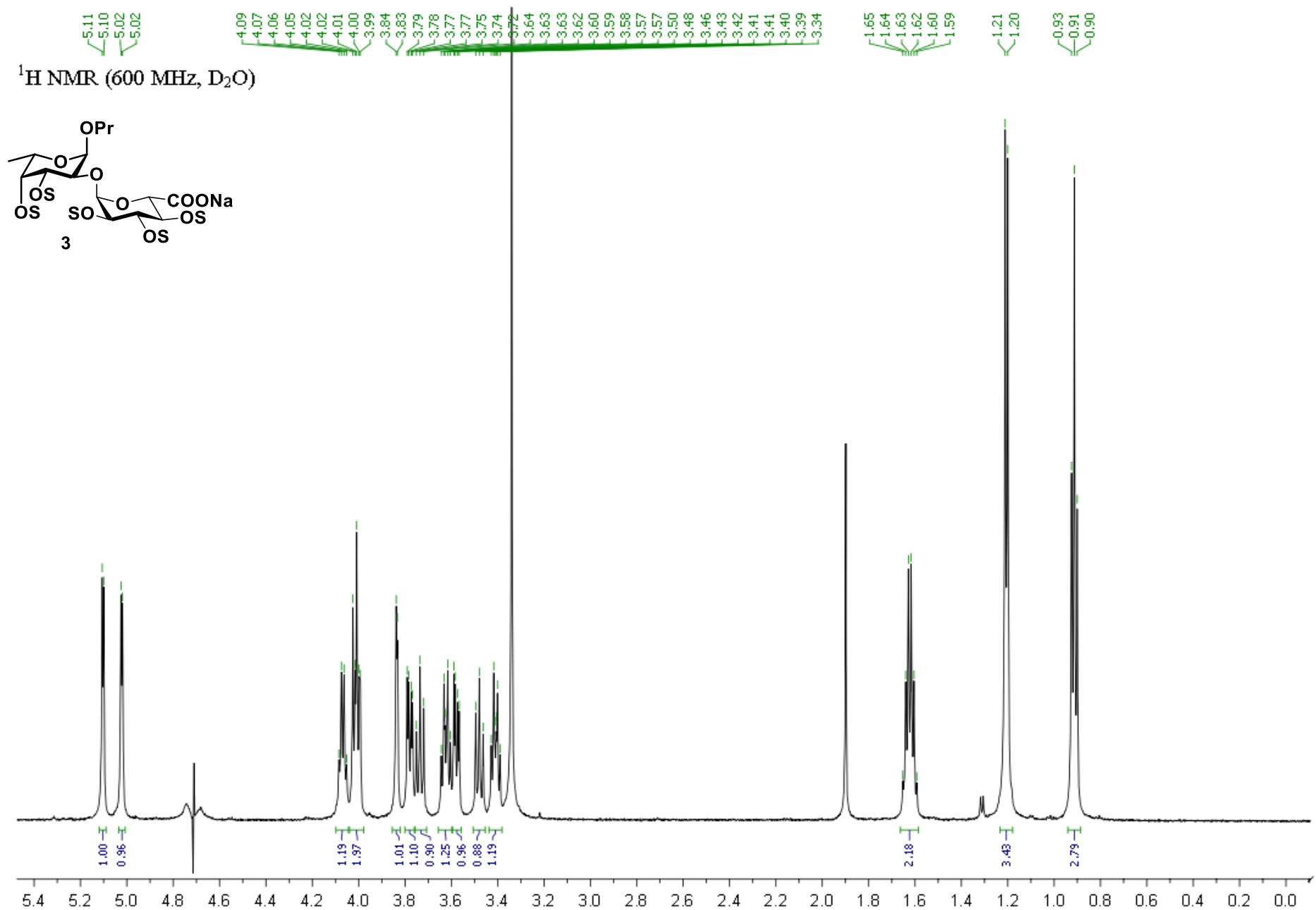


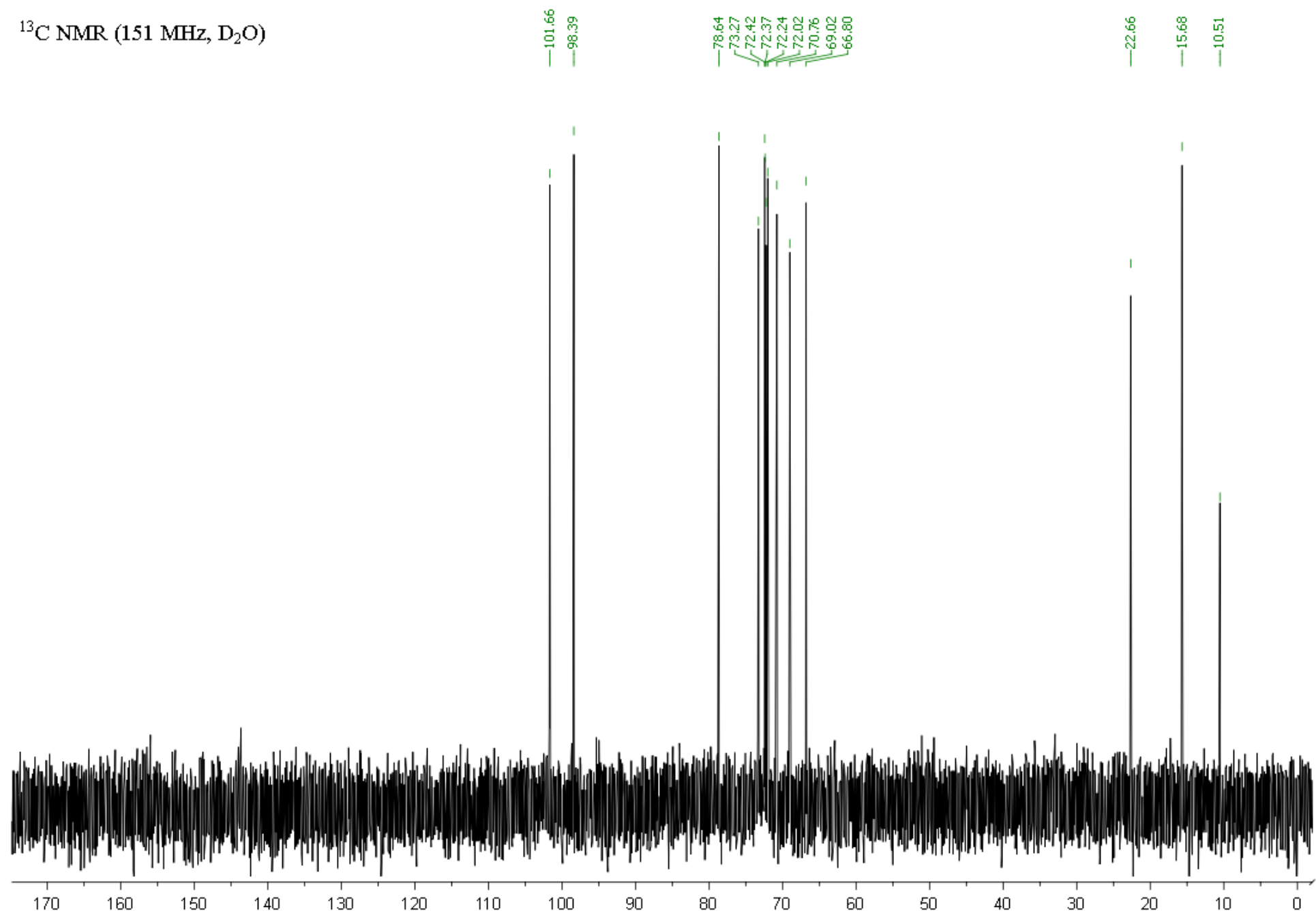
**Acquisition Parameter**

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|-------------|------------|----------------------|----------|------------------|-----------|
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| Focus       | Not active |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z     | Set Capillary        | 3200 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z   | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |



Propyl 2-O-(2,3,4-tri-O-sulfo- $\alpha$ -D-glucopyranosyluronic acid)-3,4-di-O-sulfo- $\alpha$ -L-fucopyranoside sodium salt (3).

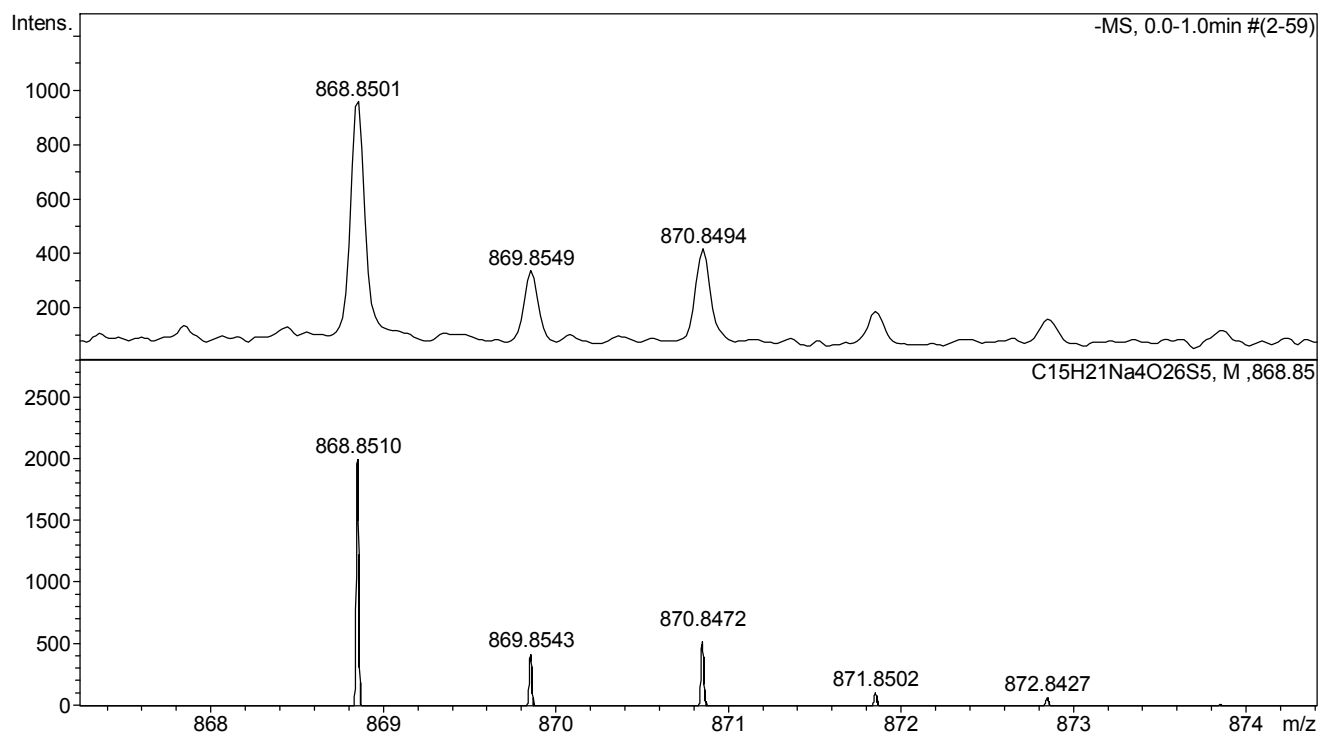
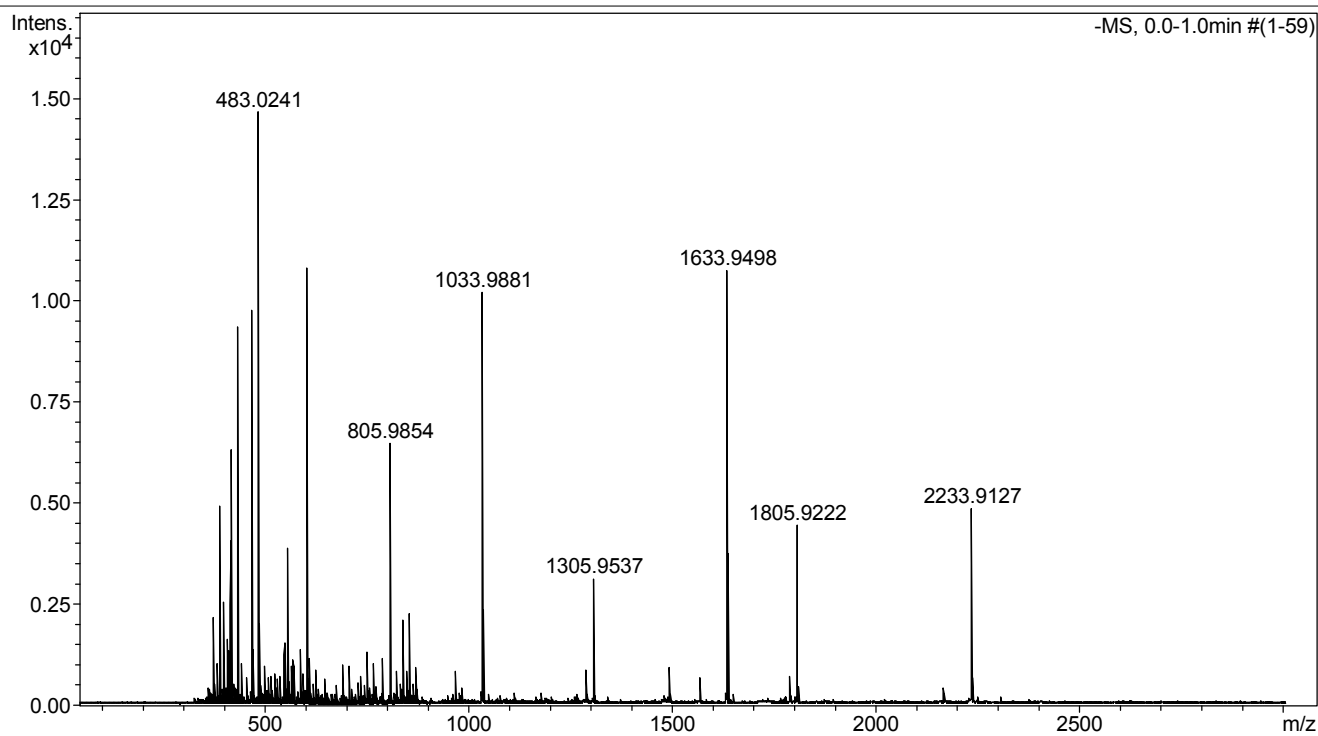


<sup>13</sup>C NMR (151 MHz, D<sub>2</sub>O)

S43

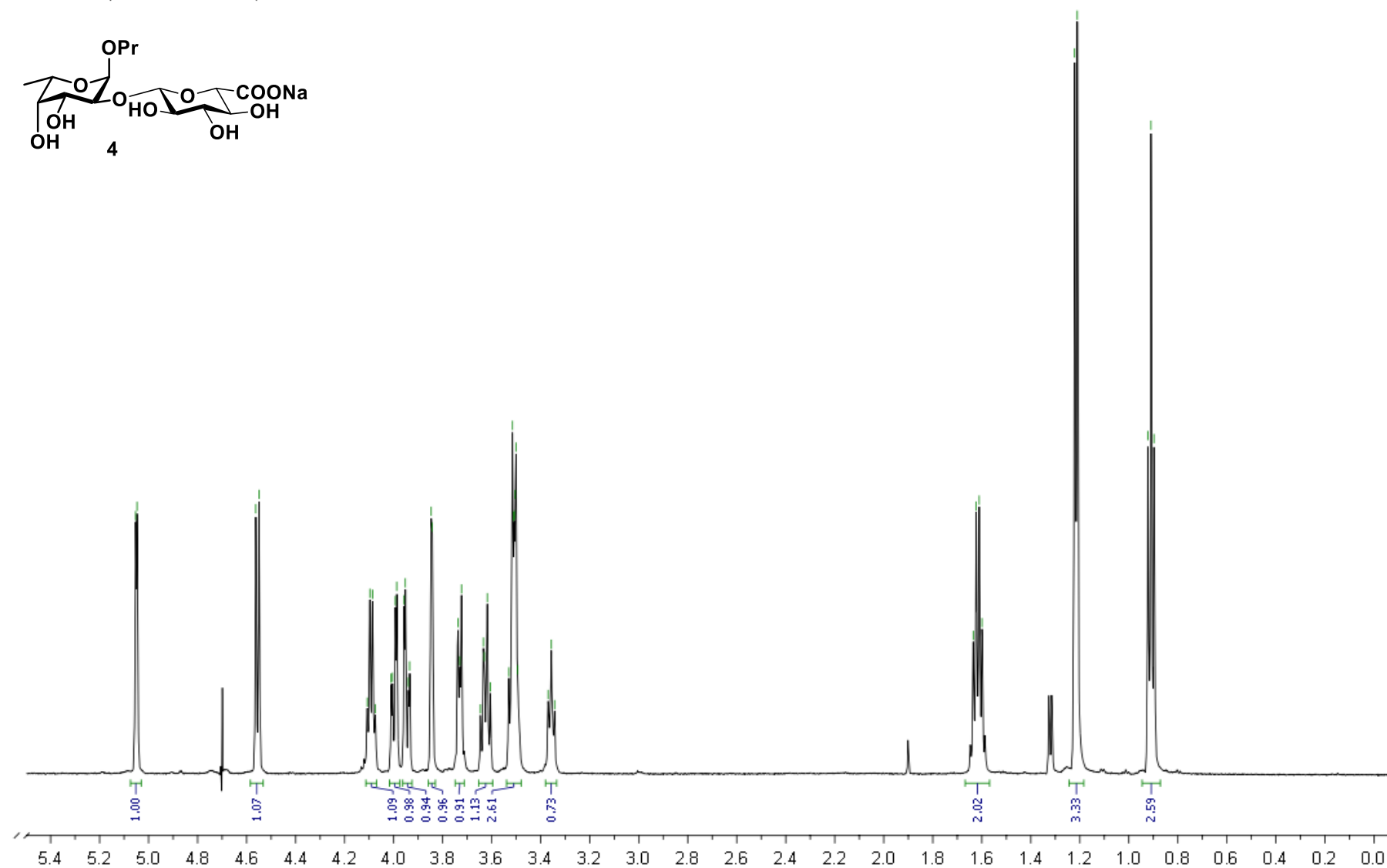
**Acquisition Parameter**

|             |            |                      |          |                  |           |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI        | Ion Polarity         | Negative | Set Nebulizer    | 0.4 Bar   |
| Focus       | Not active |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z     | Set Capillary        | 3200 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z   | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |

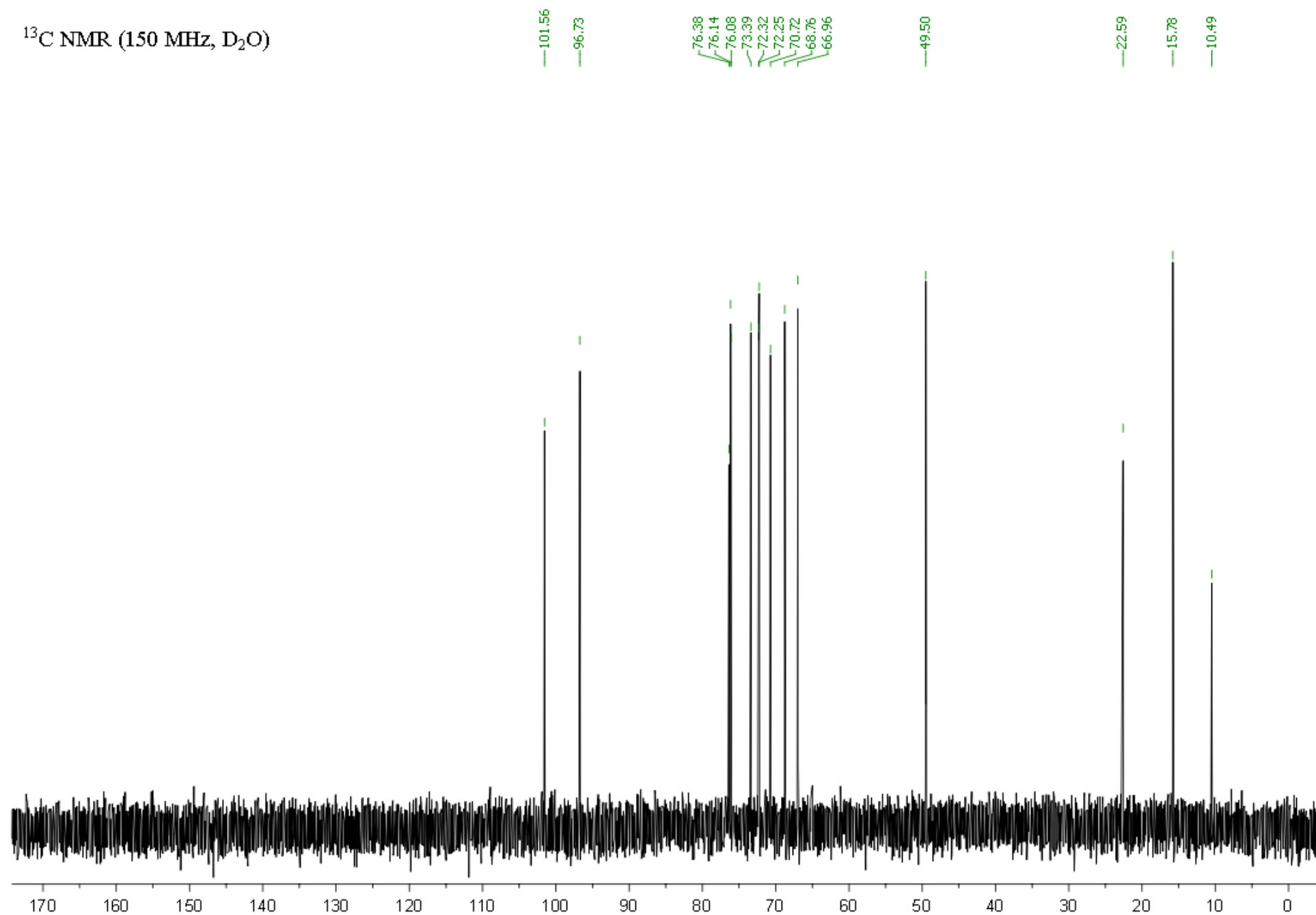


Propyl 2-O-( $\beta$ -D-glucopyranosyluronic acid)- $\alpha$ -L-fucopyranoside sodium salt (4).

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

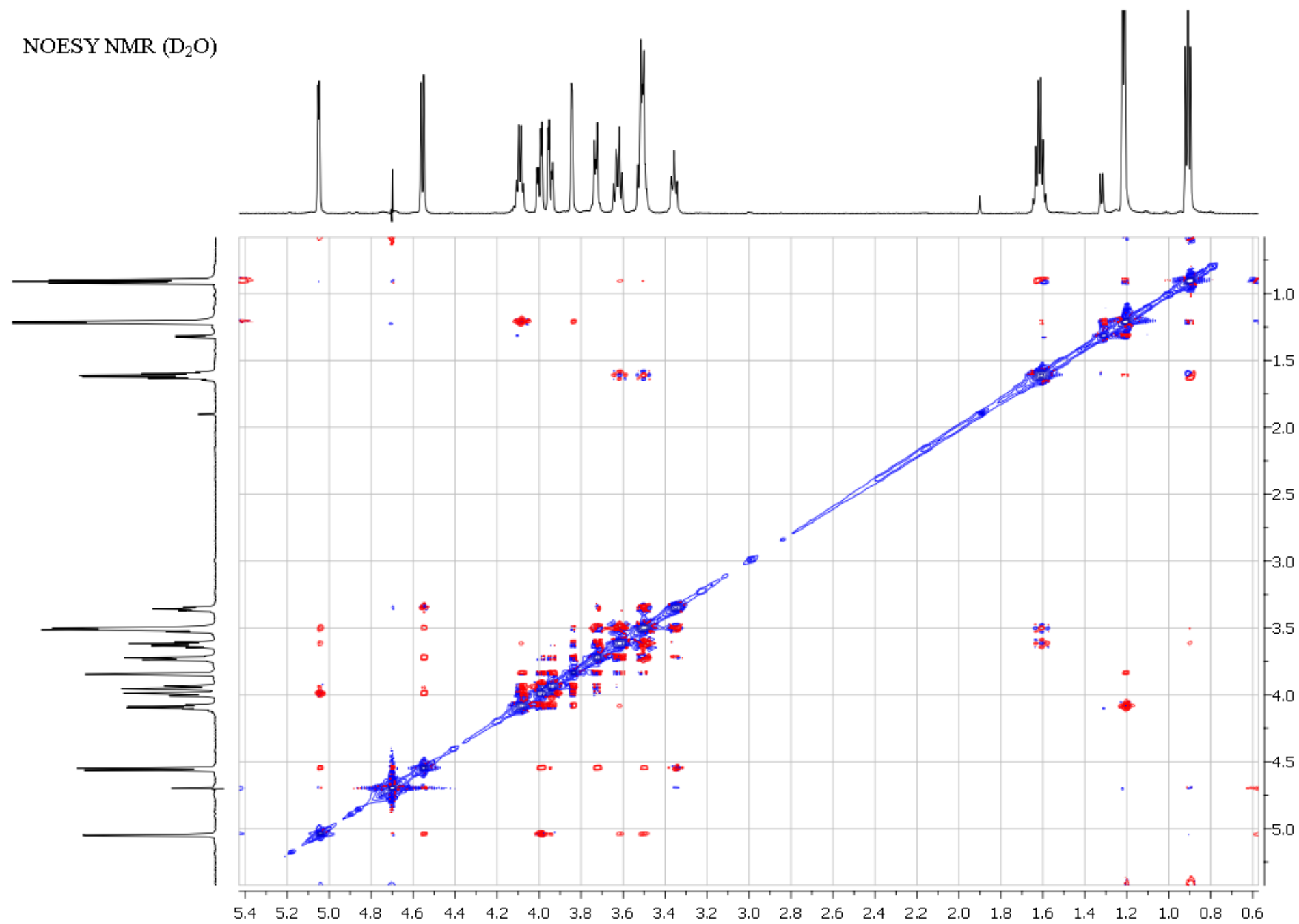


$^{13}\text{C}$  NMR (150 MHz,  $\text{D}_2\text{O}$ )



S46

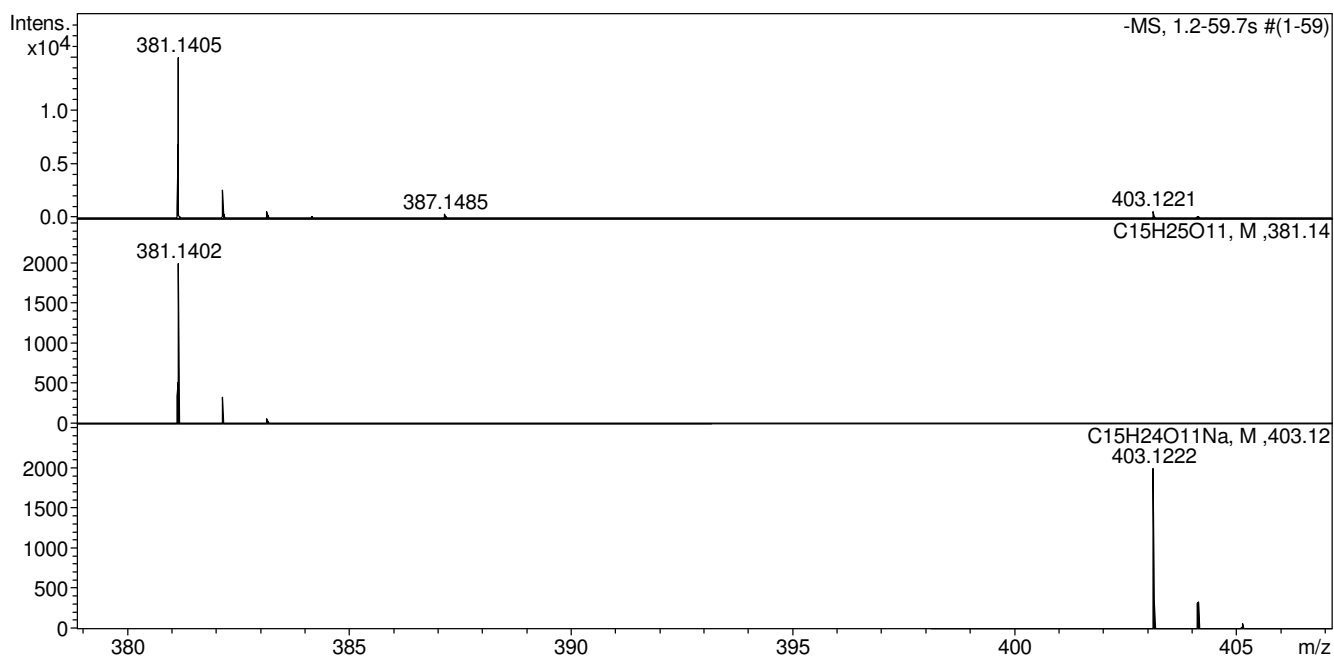
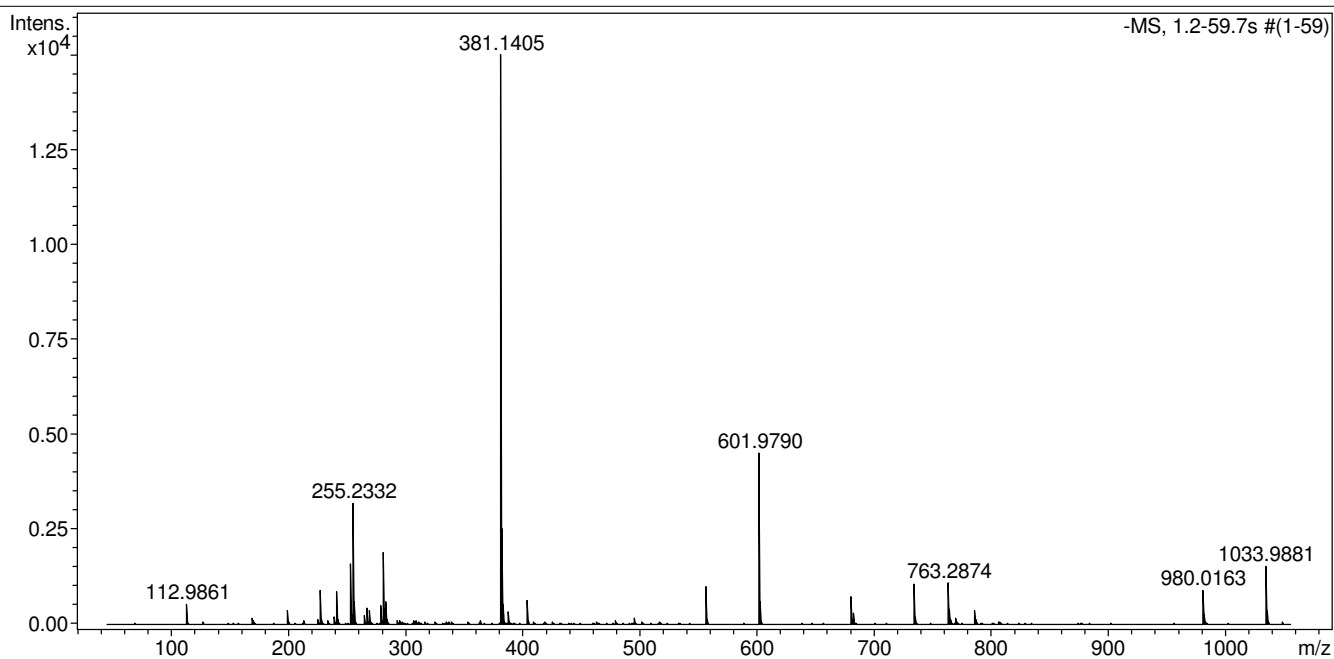
NOESY NMR (D<sub>2</sub>O)



S47

# Acquisition Parameter

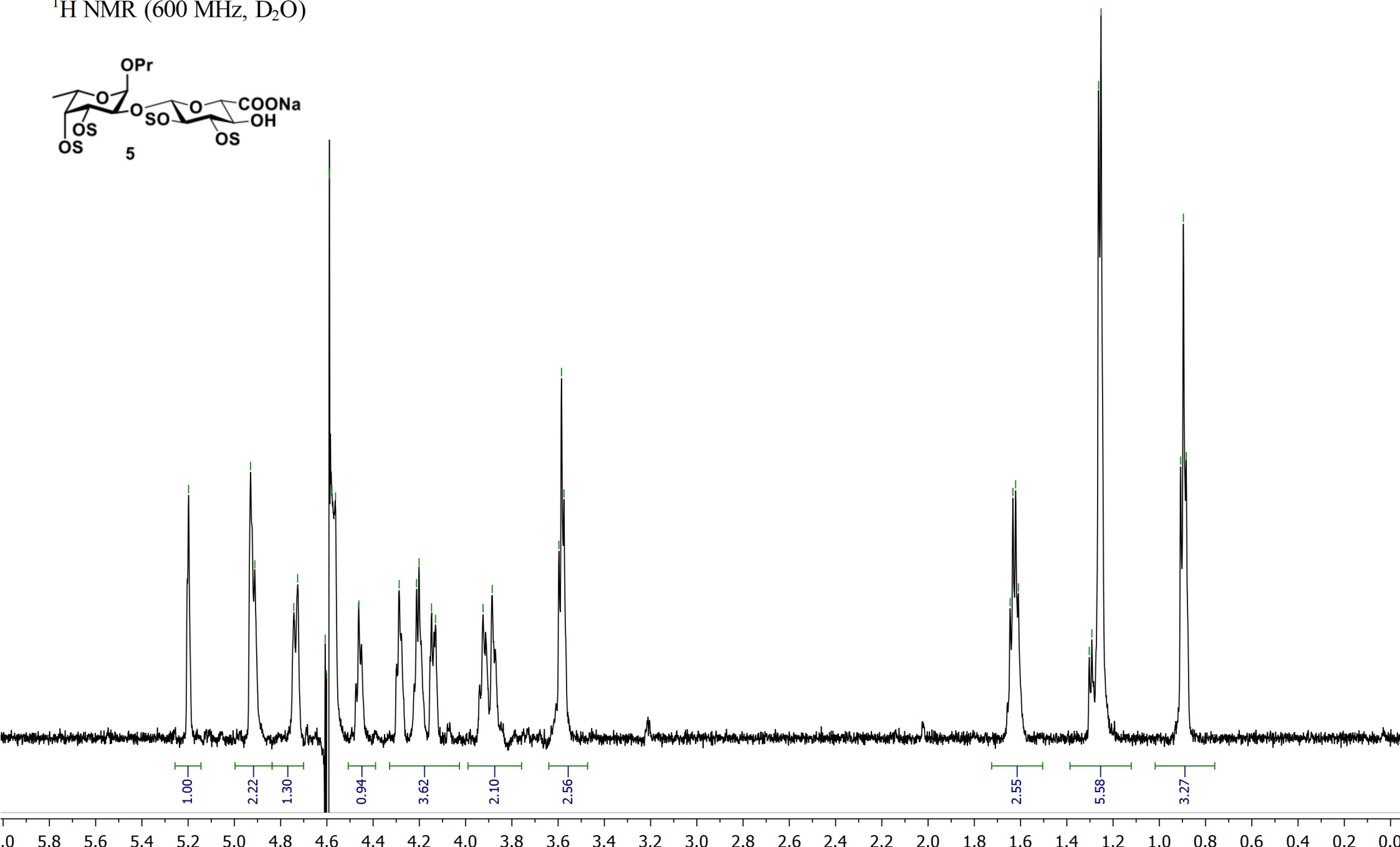
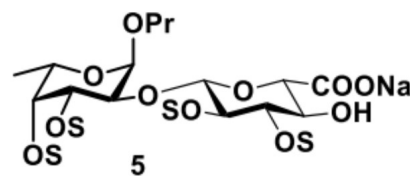
|             |            |                      |          |                  |           |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI        | Ion Polarity         | Negative | Set Nebulizer    | 0.4 Bar   |
| Focus       | Not active |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z     | Set Capillary        | 2000 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 1050 m/z   | Set End Plate Offset | -500 V   | Set Divert Valve | Source    |



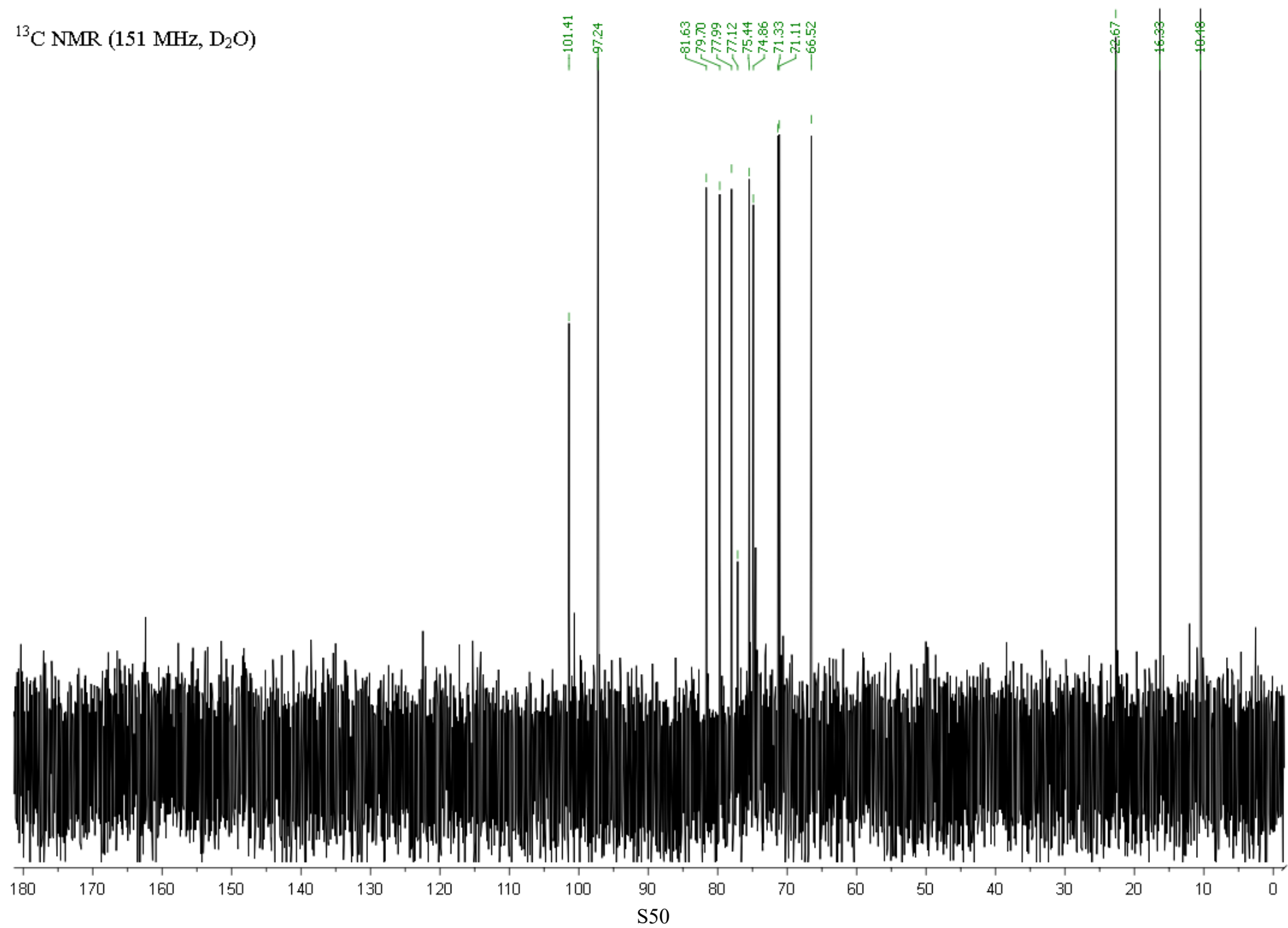


**Propyl 2-O-(2,3-di-O-sulfo- $\beta$ -D-glucopyranosyluronic acid)-3,4-di-O-sulfo- $\alpha$ -L-fucopyranoside sodium salt (5).**

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

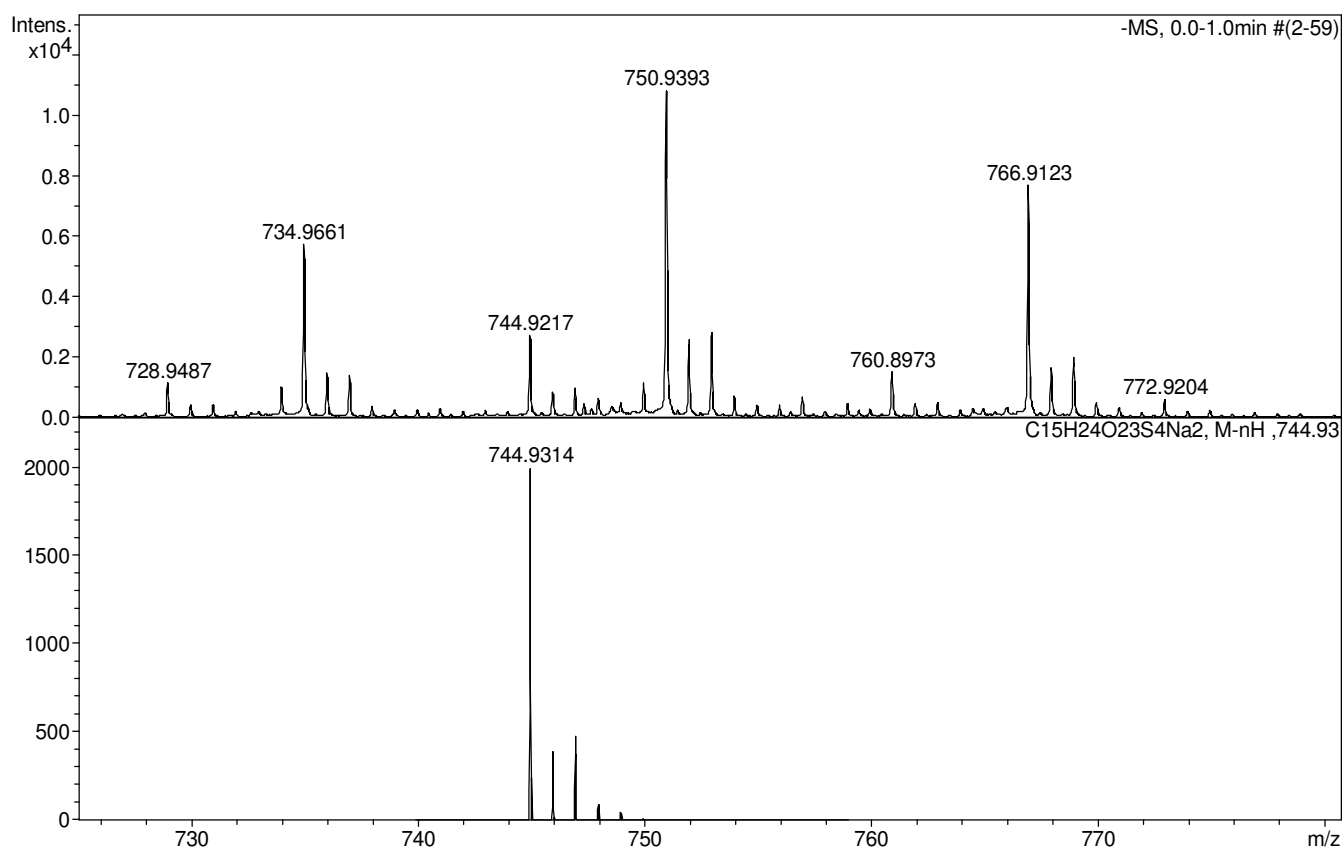
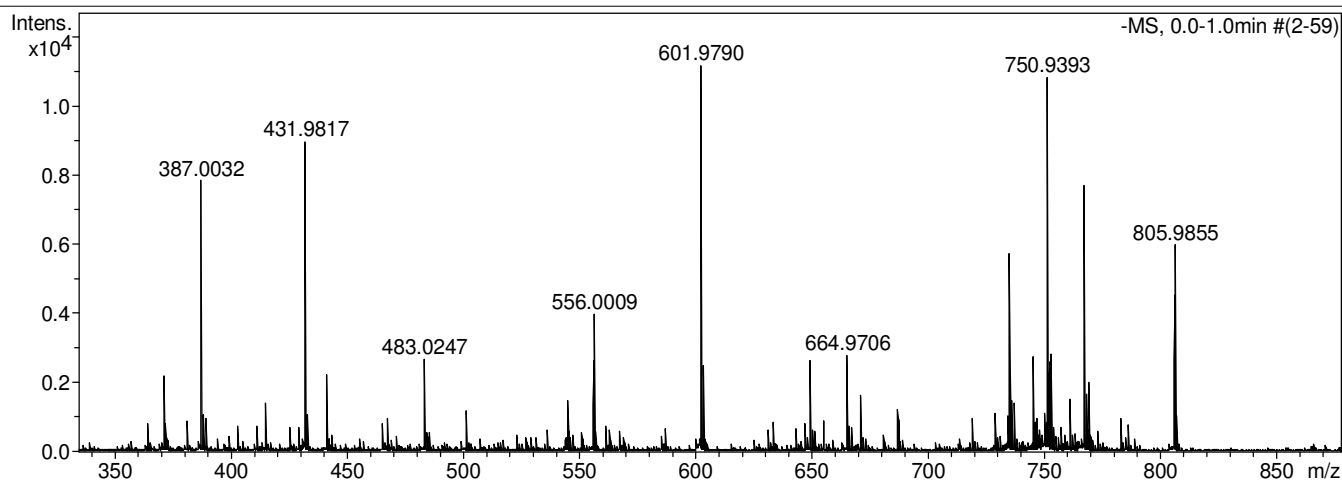


$^{13}\text{C}$  NMR (151 MHz,  $\text{D}_2\text{O}$ )



**Acquisition Parameter**

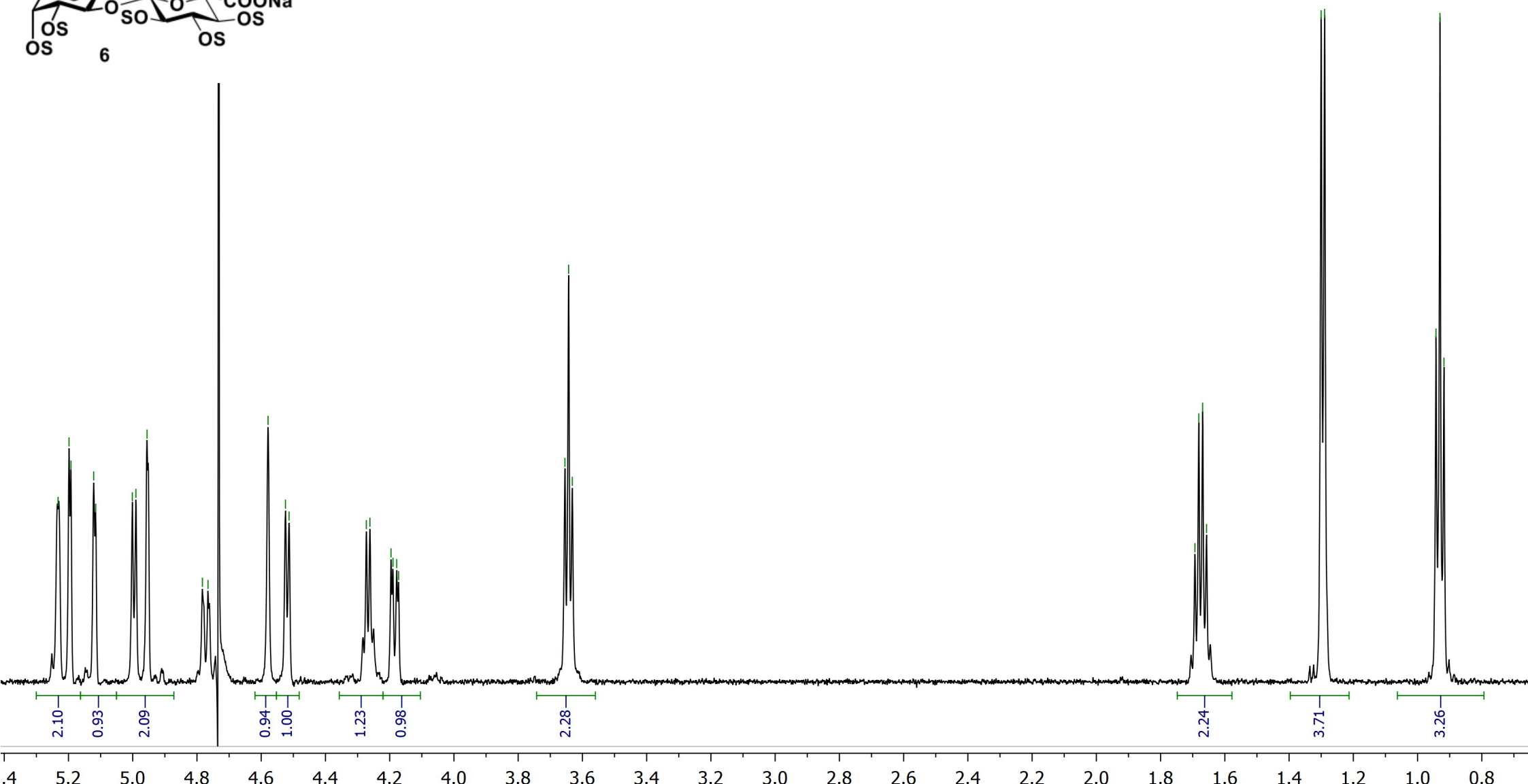
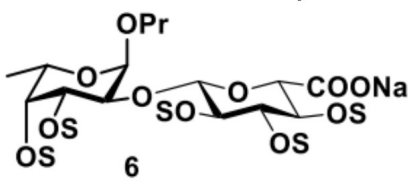
|             |            |                      |          |                  |           |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI        | Ion Polarity         | Negative | Set Nebulizer    | 0.4 Bar   |
| Focus       | Not active |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z     | Set Capillary        | 3200 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z   | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |



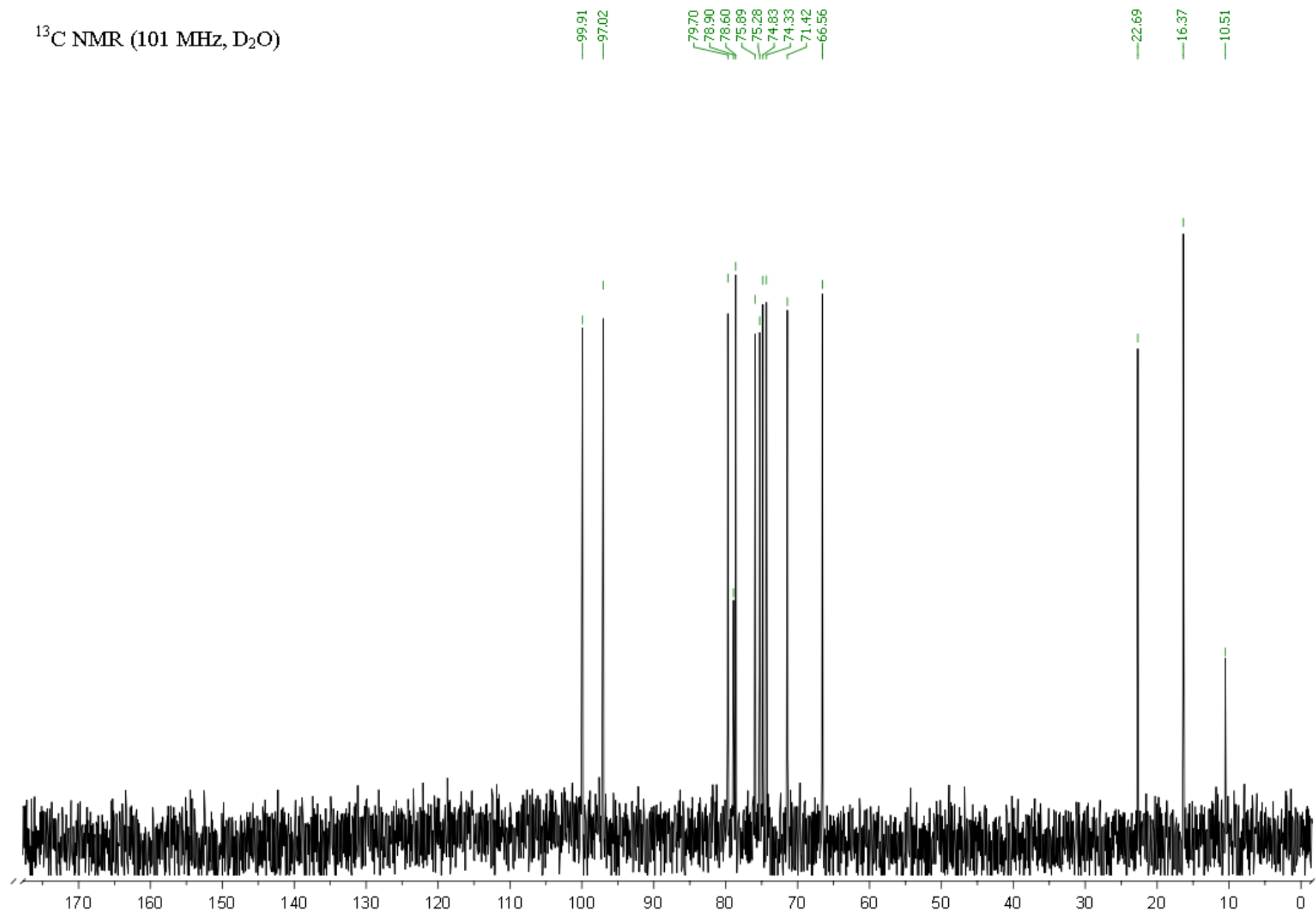
5.23 5.20 5.19 5.12 5.12 5.00 4.99 4.96 4.78 4.77 4.73 4.58 4.52 4.51 4.27 4.26 4.20 4.19 4.18 4.17 3.65 3.64 3.63 1.69 1.68 1.67 1.66 1.30 1.29 0.94 0.93 0.92

**Propyl 2-O-(2,3,4-tri-O-sulfo-β-D-glucopyranosyluronic acid)-3,4-di-O-sulfo-α-L-fucopyranoside sodium salt (6).**

<sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O)

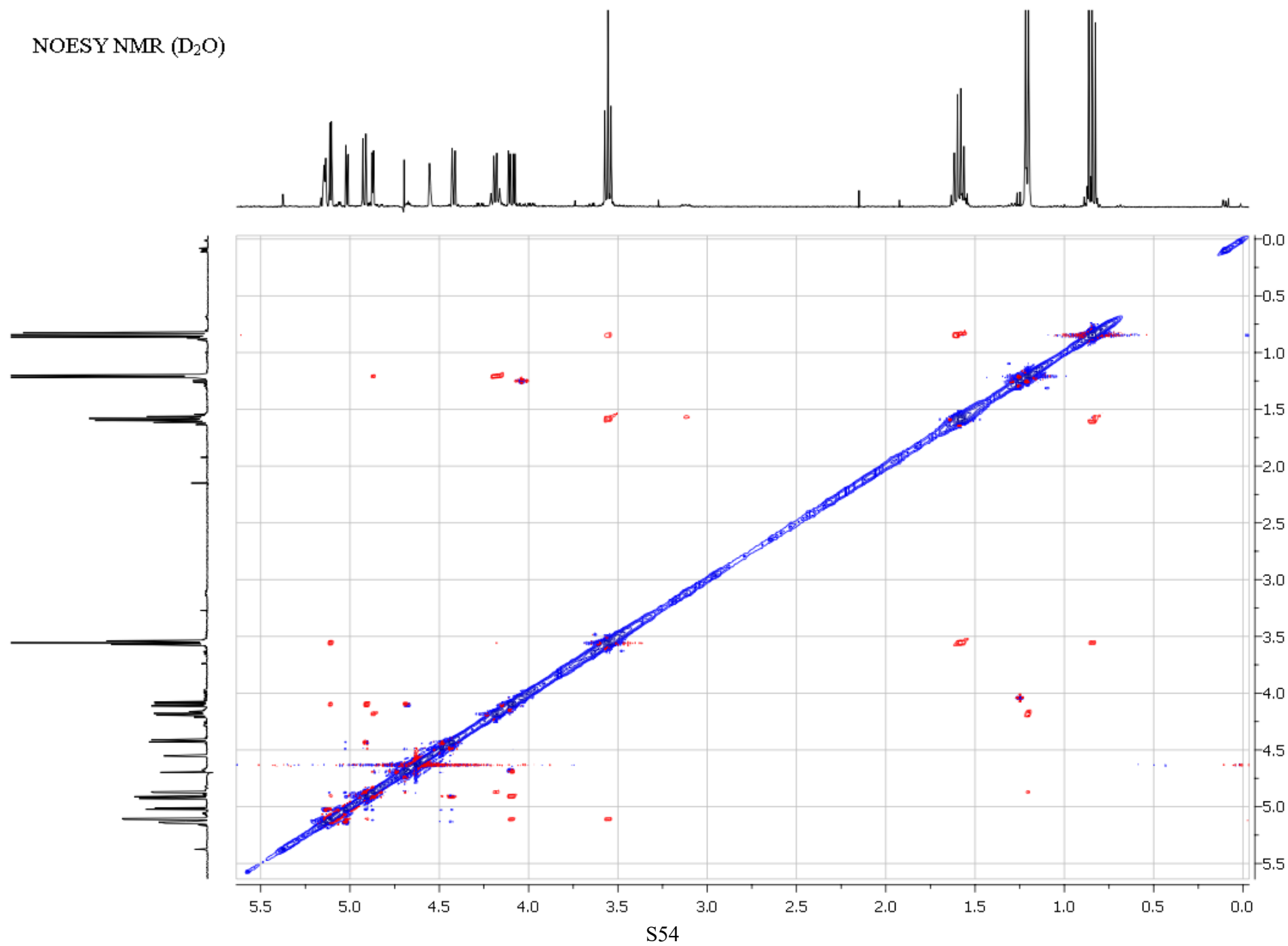


$^{13}\text{C}$  NMR (101 MHz,  $\text{D}_2\text{O}$ )



S53

NOESY NMR (D<sub>2</sub>O)



**Acquisition Parameter**

|             |            |                      |          |                  |           |
|-------------|------------|----------------------|----------|------------------|-----------|
| Source Type | ESI        | Ion Polarity         | Negative | Set Nebulizer    | 0.4 Bar   |
| Focus       | Not active |                      |          | Set Dry Heater   | 180 °C    |
| Scan Begin  | 50 m/z     | Set Capillary        | 3200 V   | Set Dry Gas      | 4.0 l/min |
| Scan End    | 3000 m/z   | Set End Plate Offset | -500 V   | Set Divert Valve | Waste     |

