Convergent synthesis of isomeric heterosaccharides related to the fragments of galactomannan from *Aspergillus fumigatus*

D.A. Argunov, V.B. Krylov, N.E. Nifantiev*

Supporting information

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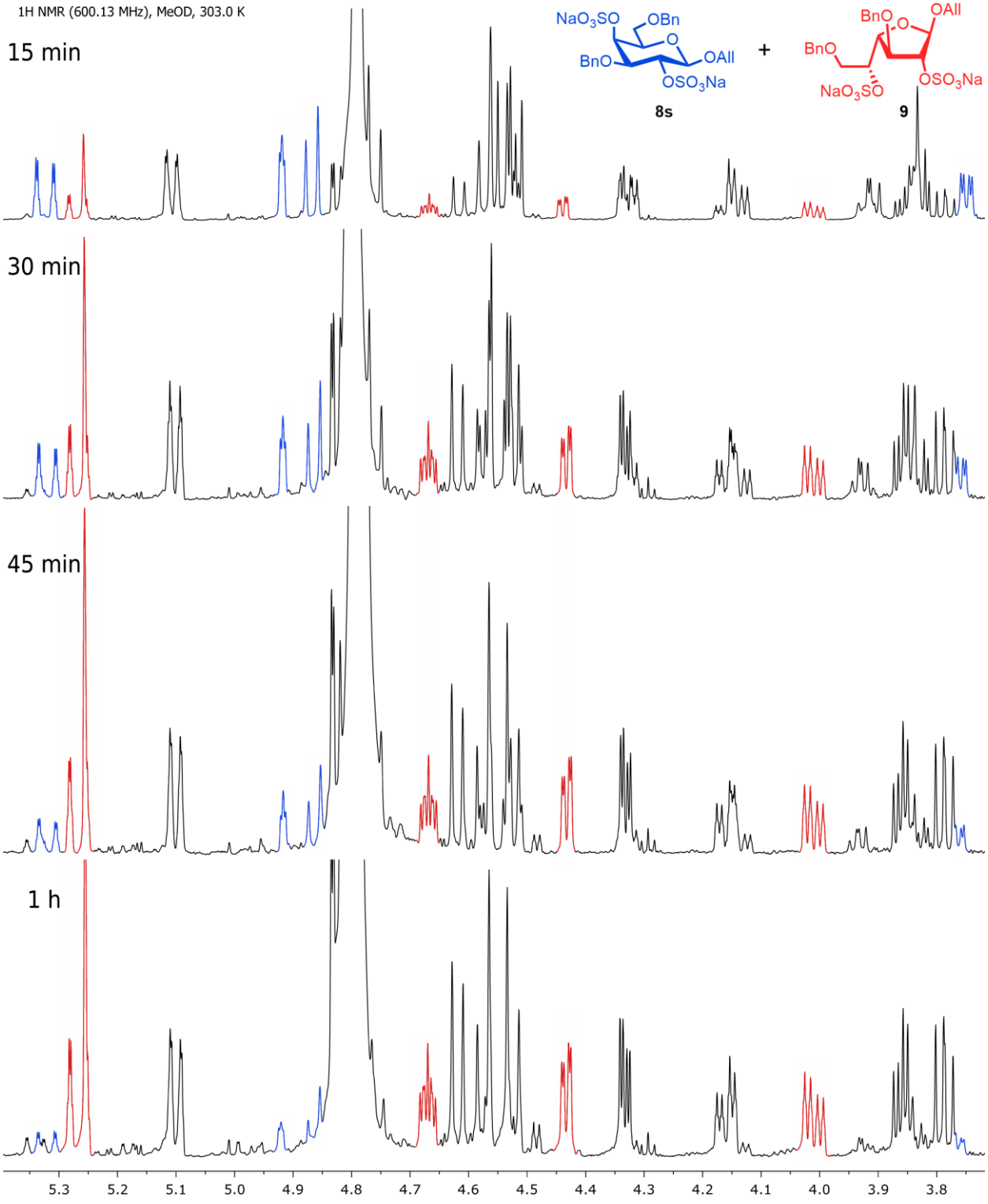
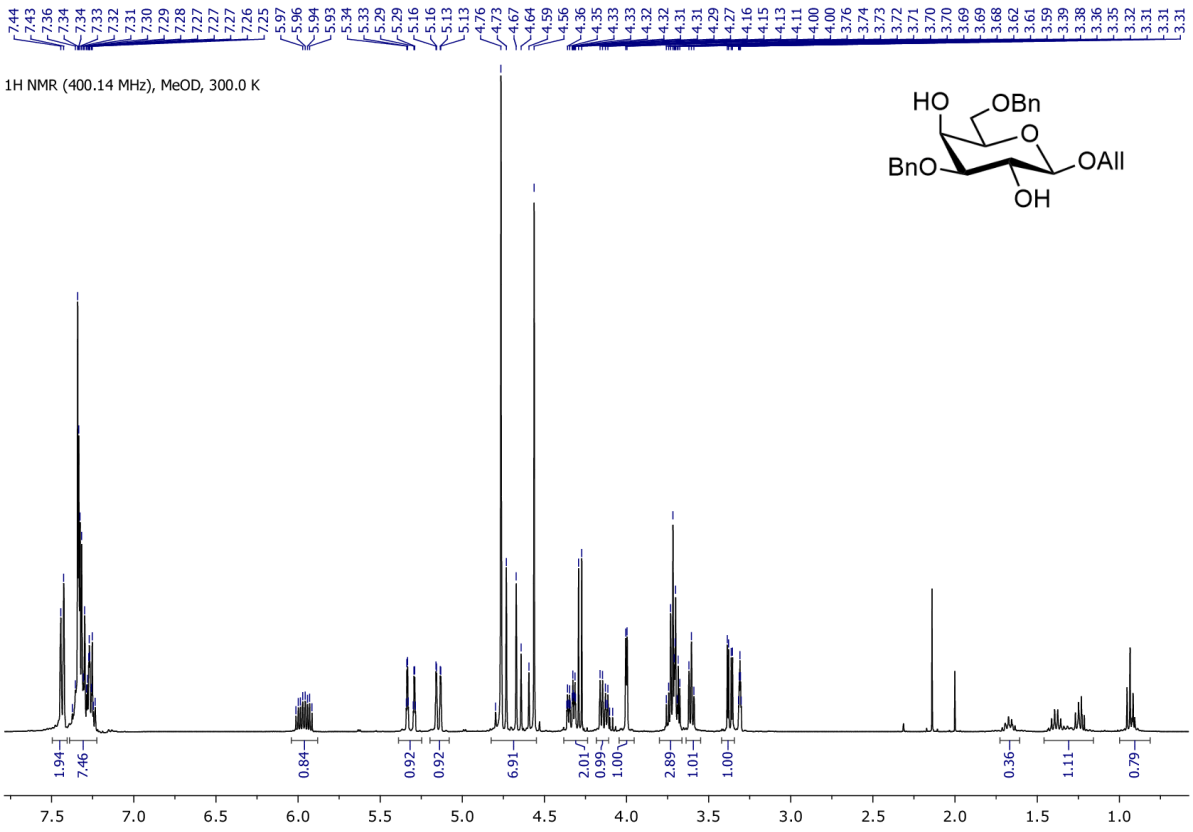
NMR-monitoring of rearrangement of pyranoside 8*

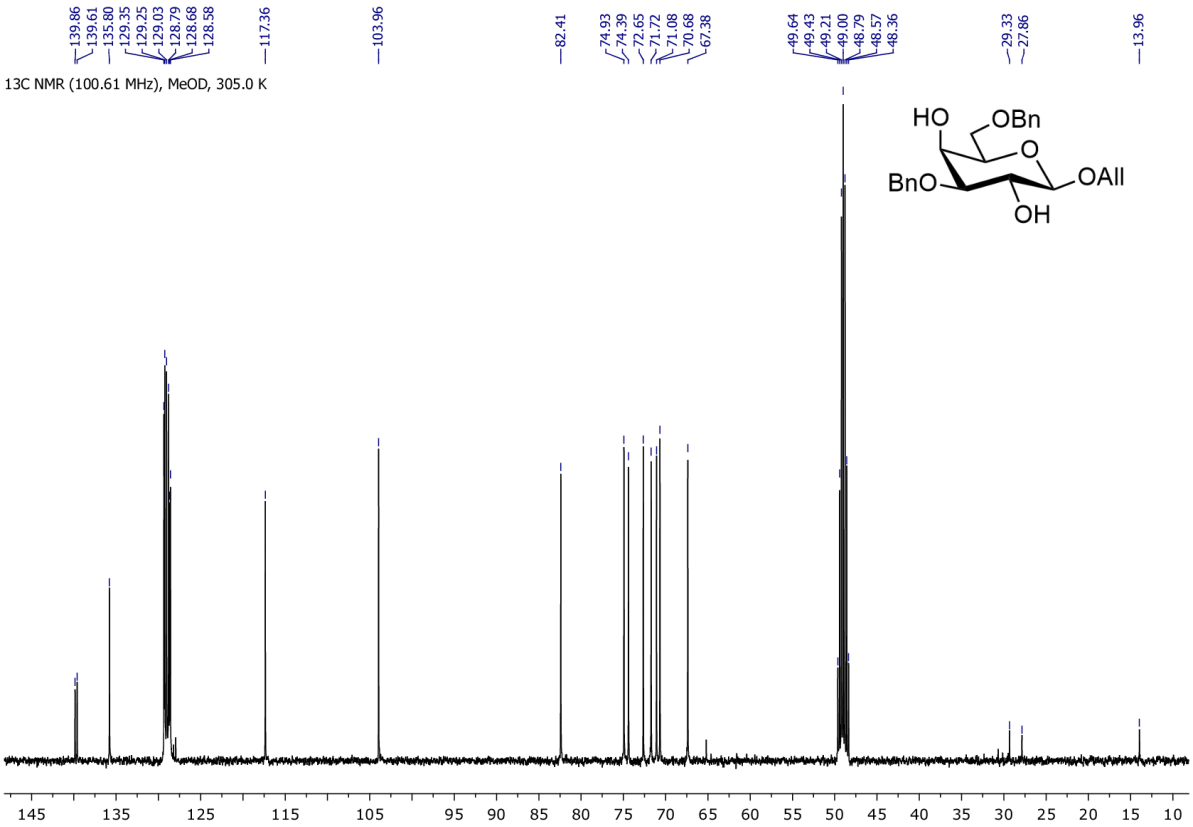


* Conditions: **8** (1 eq.), Py·SO_3 (8 eq.), HSO_3Cl (3.2 eq.), DMF (0.8 mL/1 mmol Py·SO_3), 40 °C. Probes were treated by excess of aq. $NaHCO_3$, concentrated *in vacuo* and extracted from solid by MeOH.

NMR and ESI-mass spectra of compounds

Allyl 3,6-di-O-benzyl-β-D-galactopyranoside (8)





Acquisition Parameter

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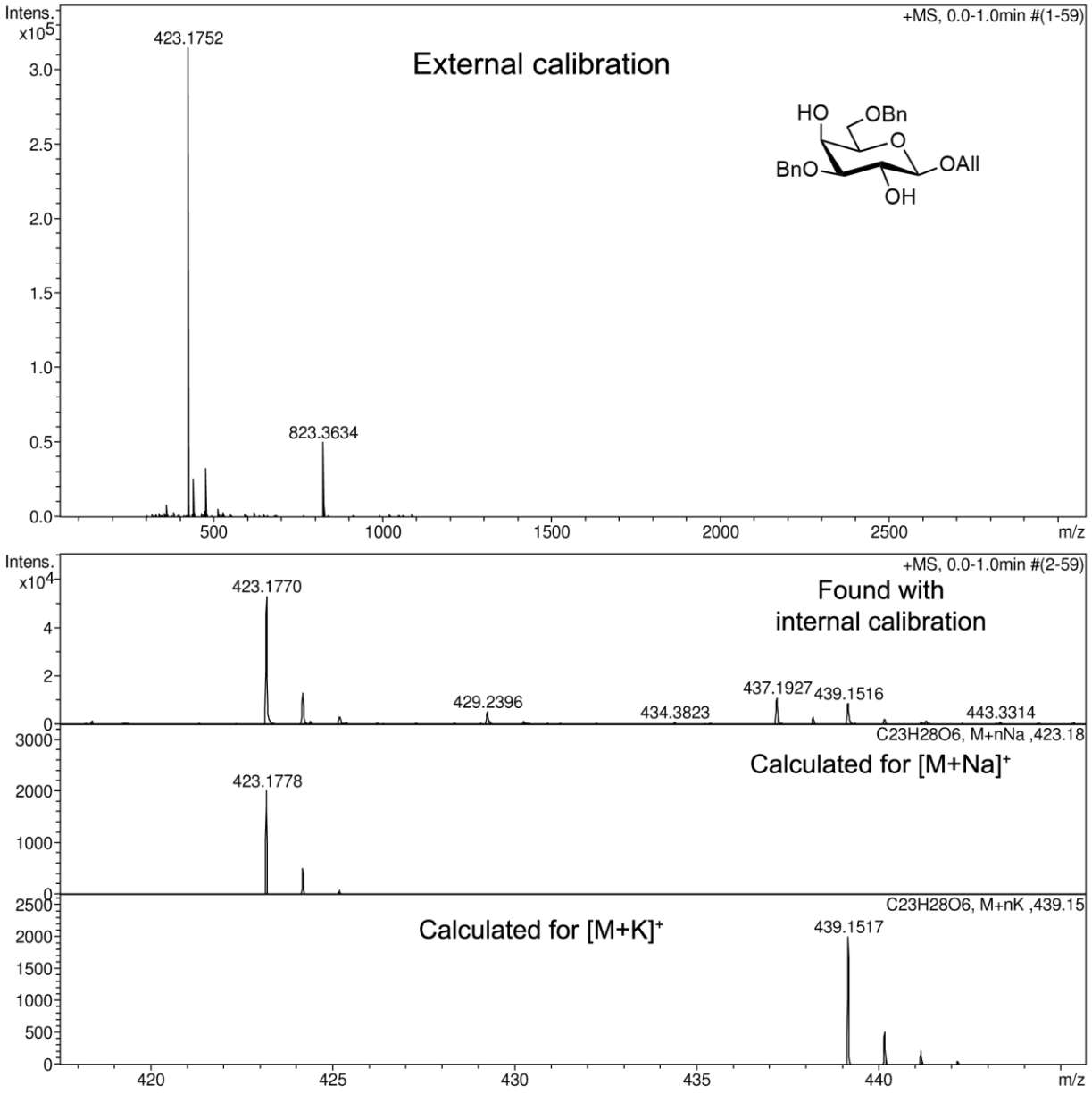
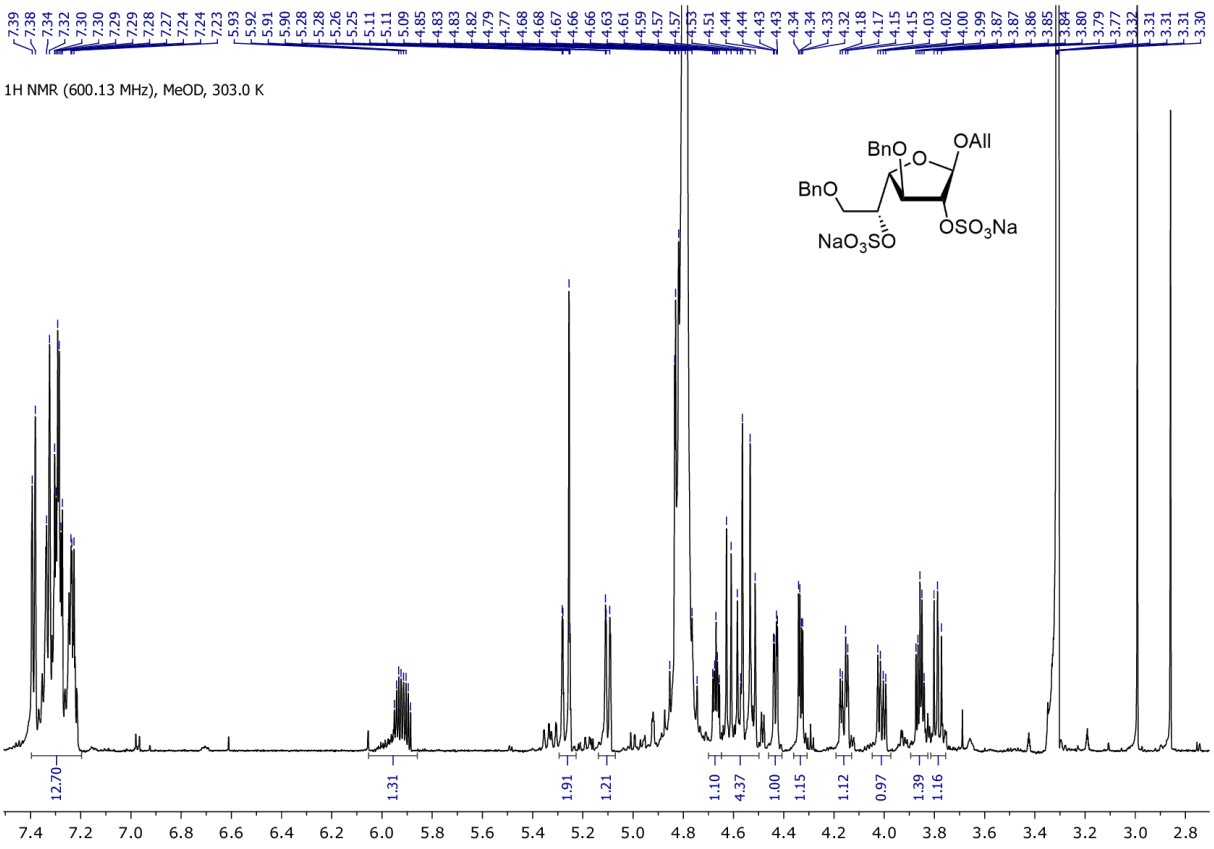
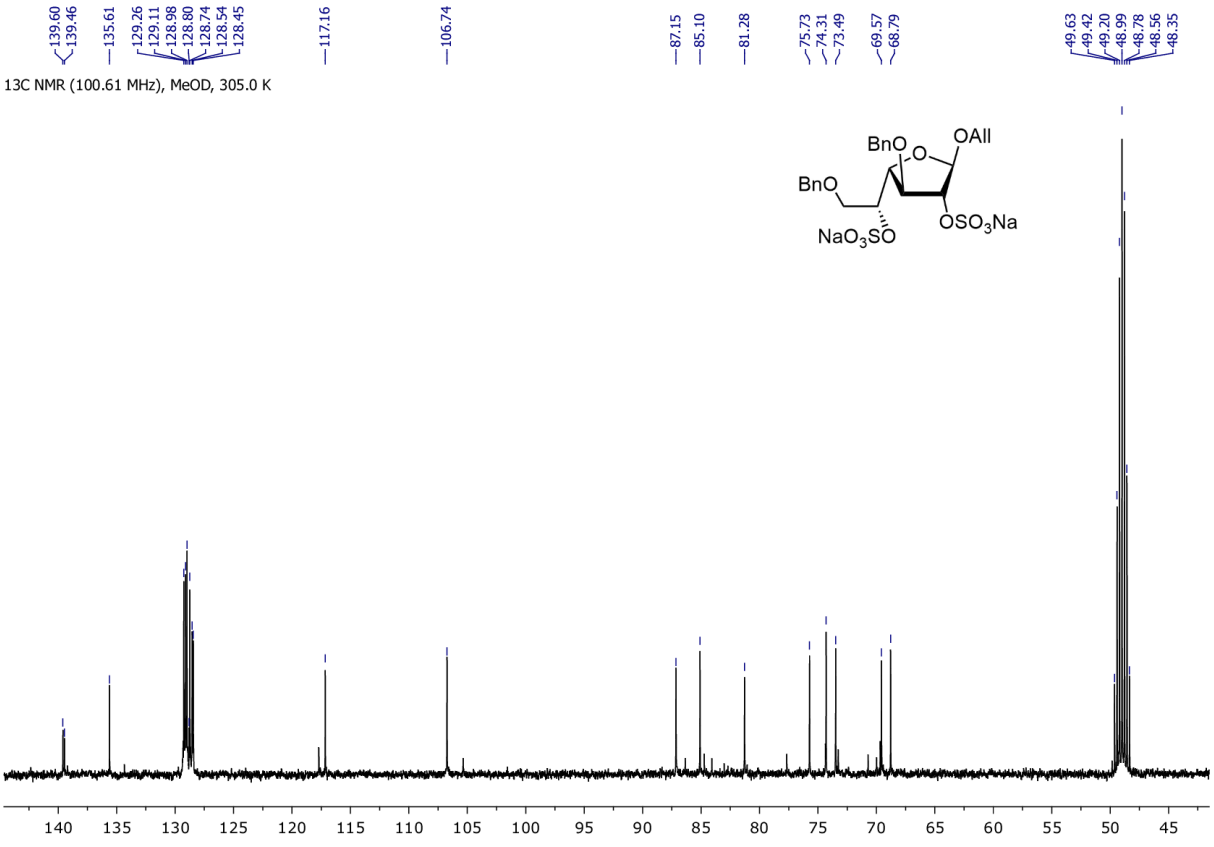


Disodium salt of allyl 3,6-di-O-benzyl-2,5-di-O-sulfo-β-D-galactofuranoside (9)





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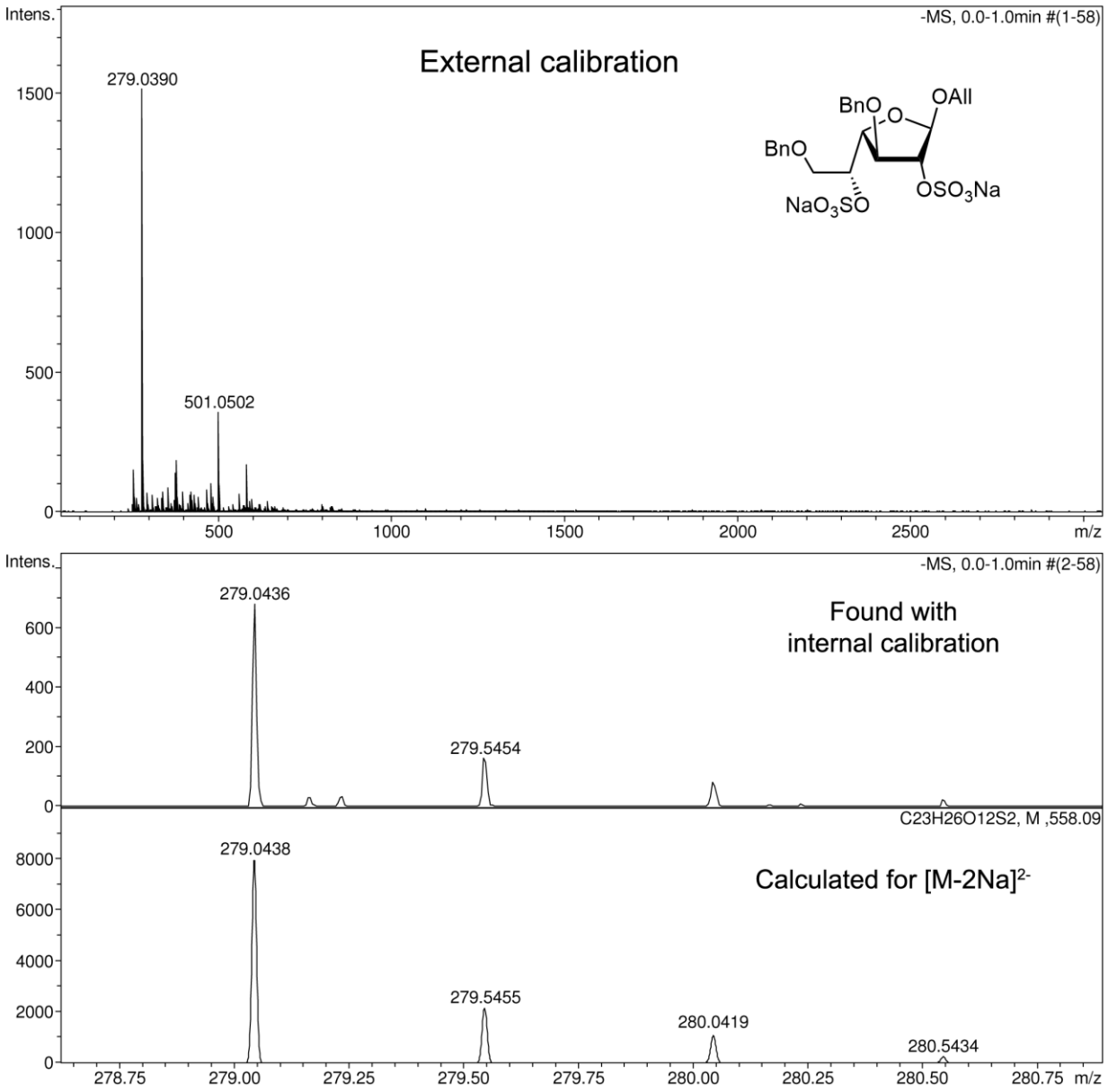
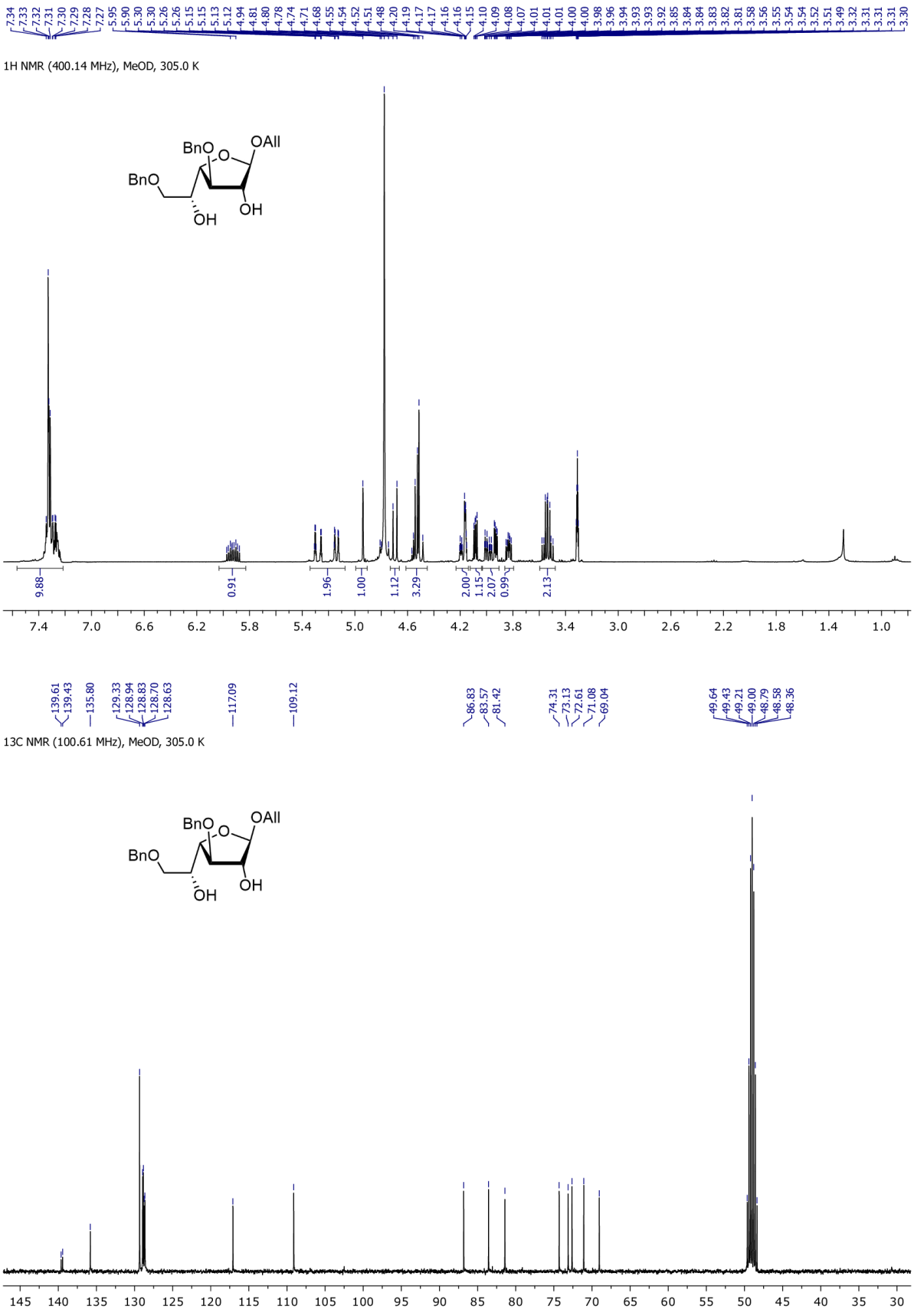


Allyl 3,6-di-O-benzyl-β-D-galactofuranoside (10)



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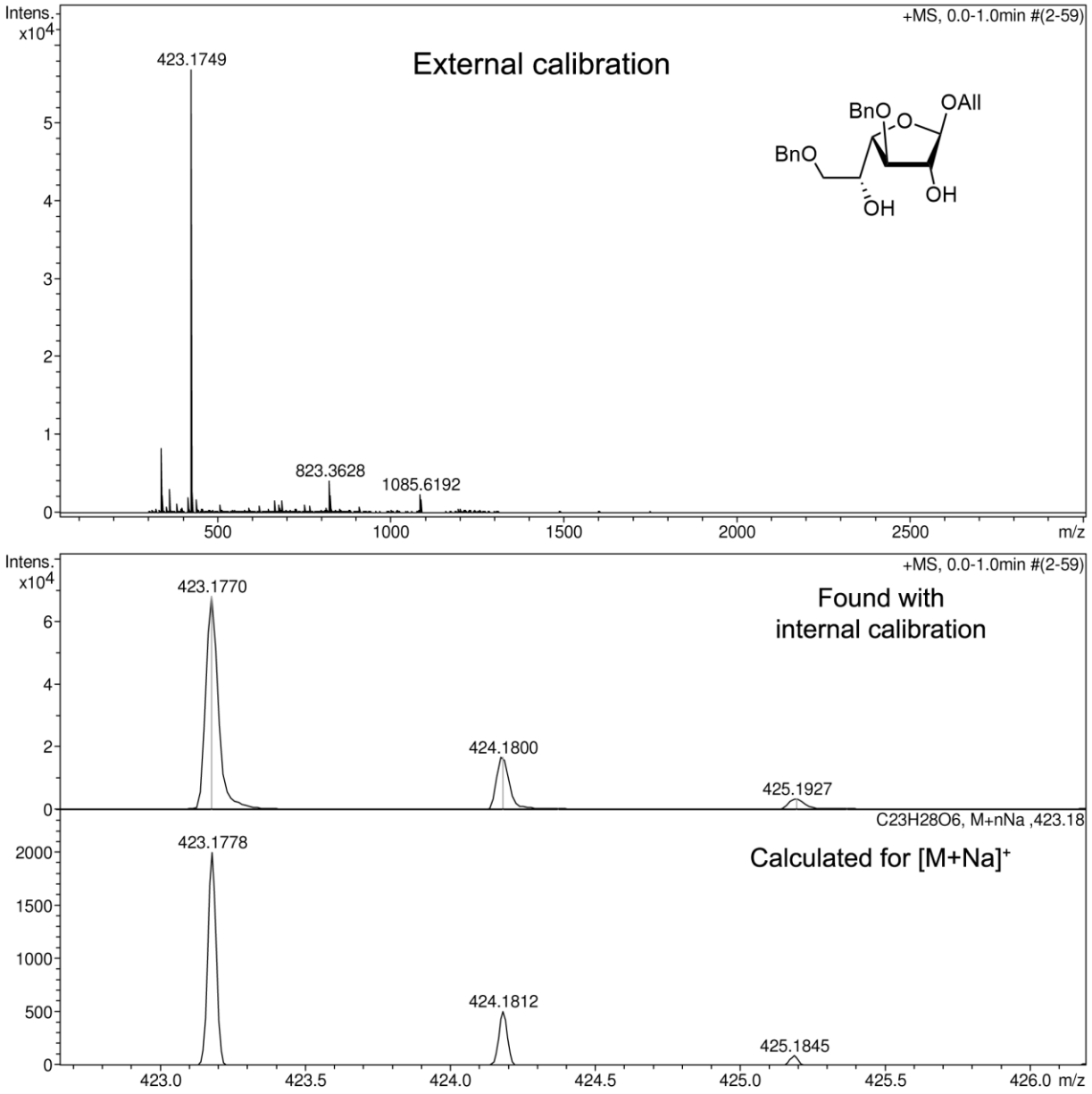

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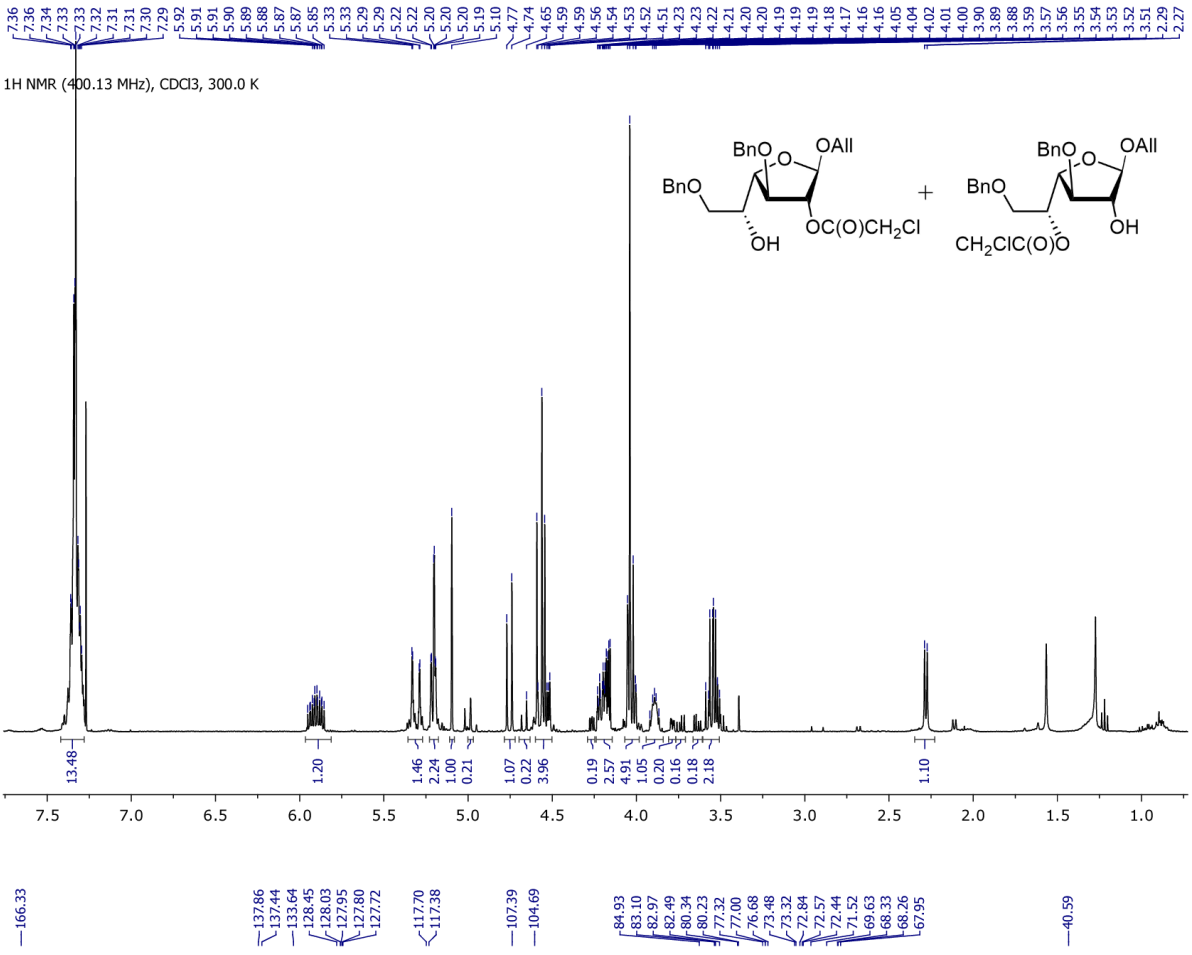

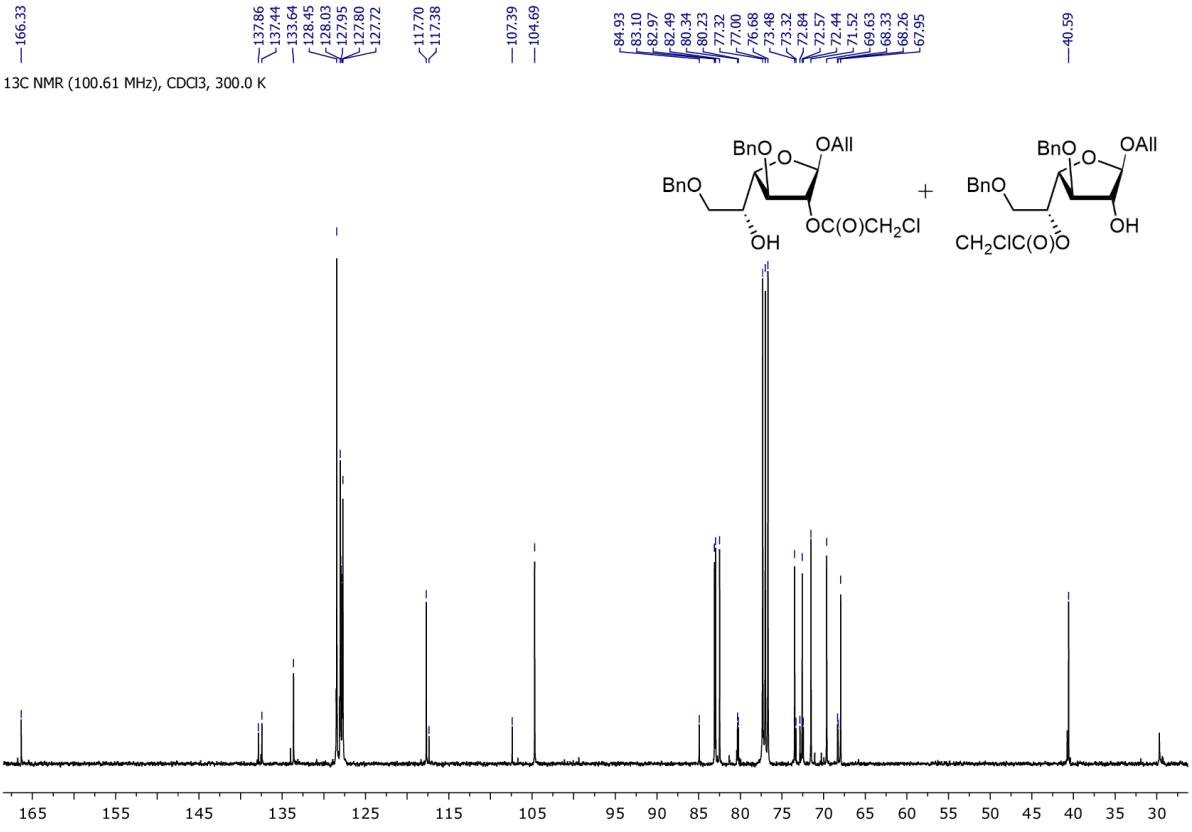

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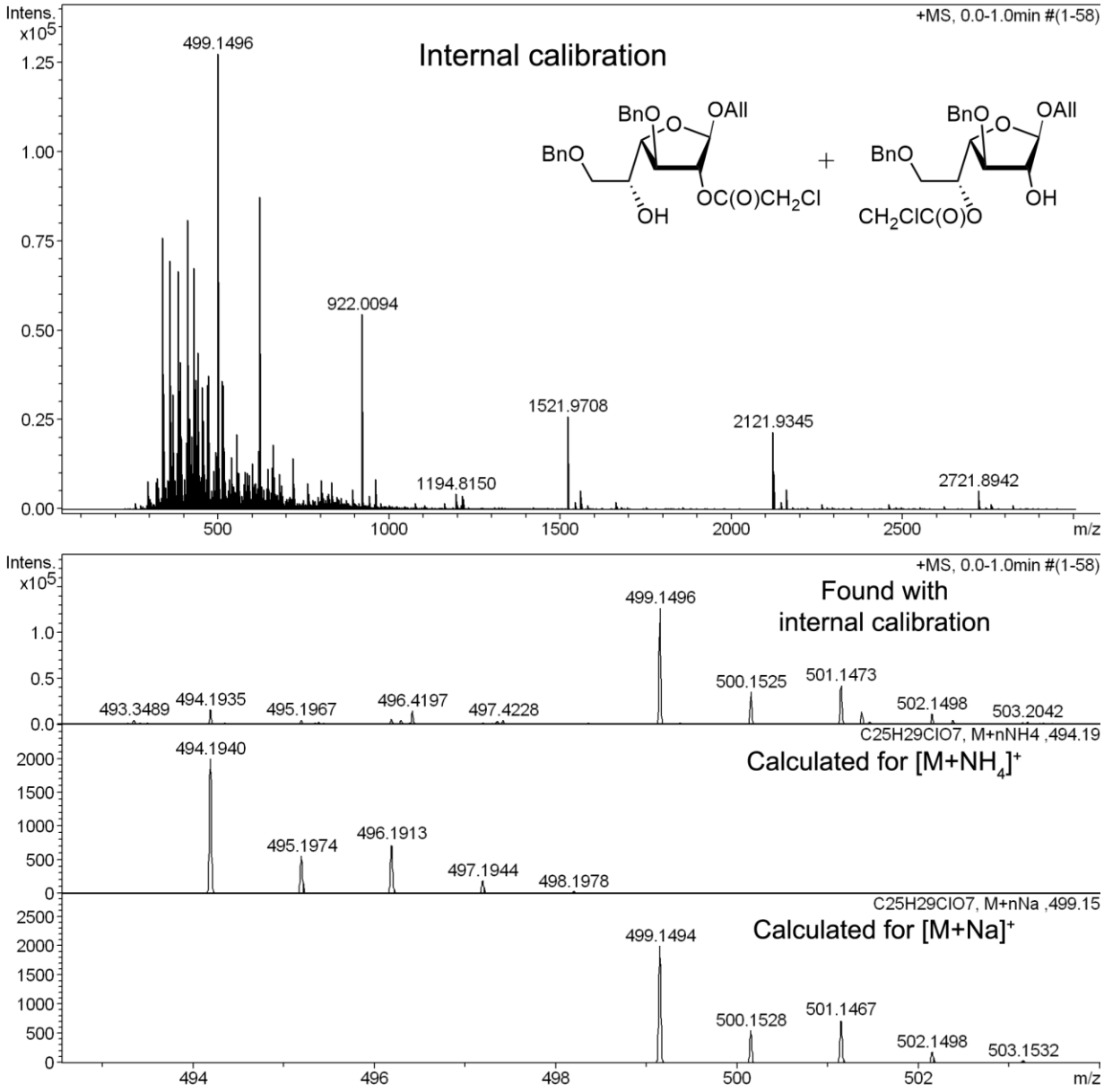
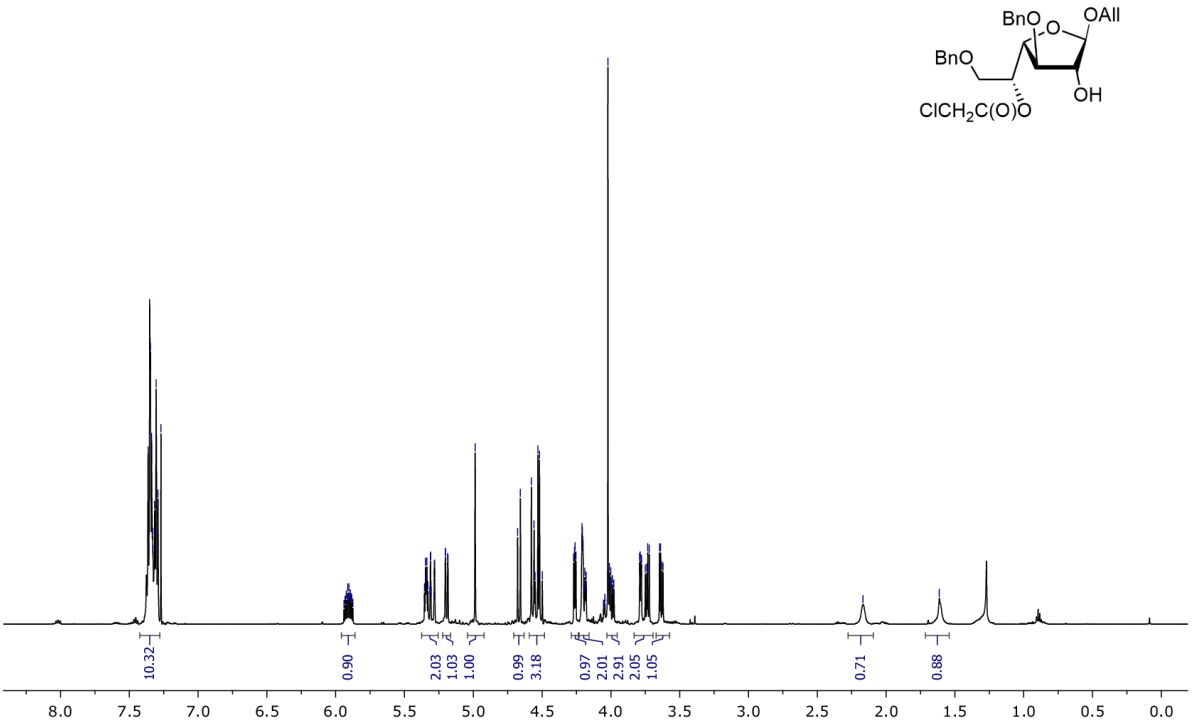
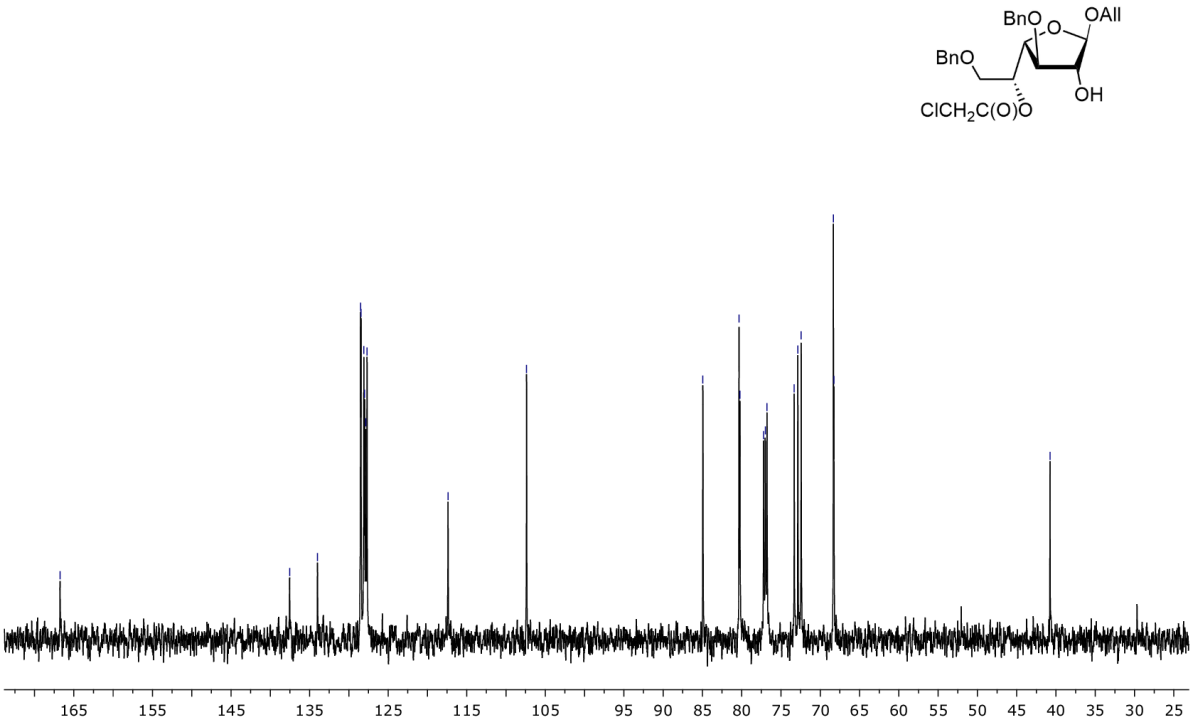


Allyl 3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranoside (12)

1H NMR (600.13 MHz), CDCl3, 300.3 K



13C NMR (150.92 MHz), CDCl3, 300.6 K



Acquisition Parameter

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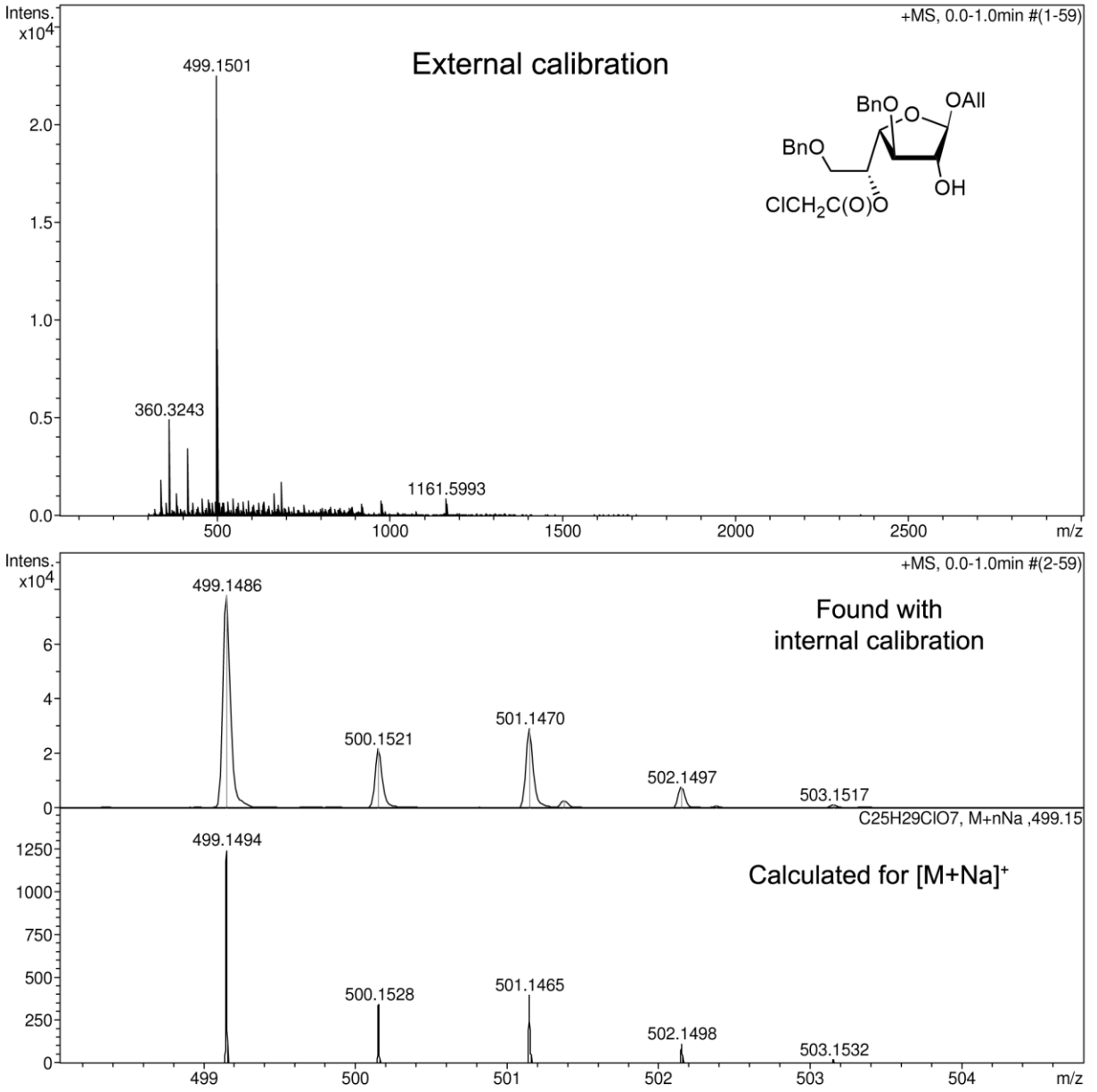
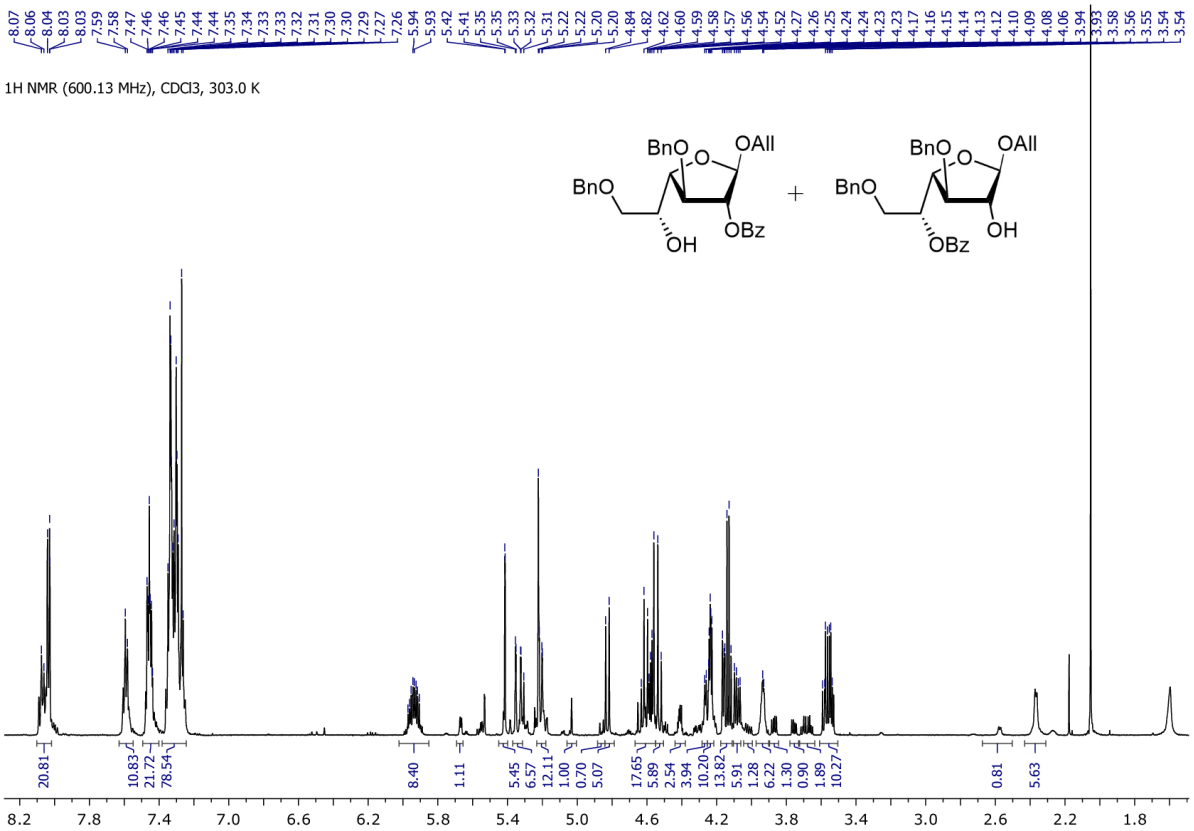
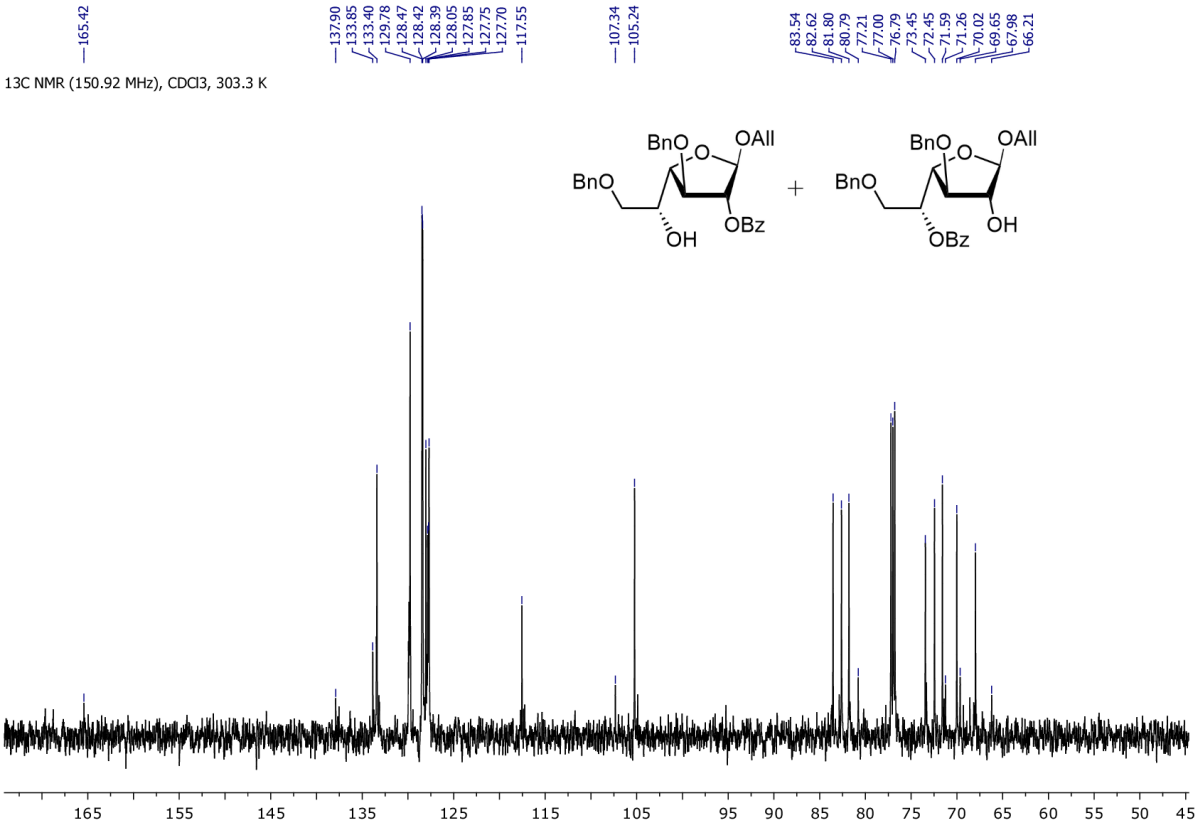


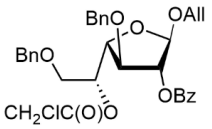
Allyl 2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside (13) from diol 10

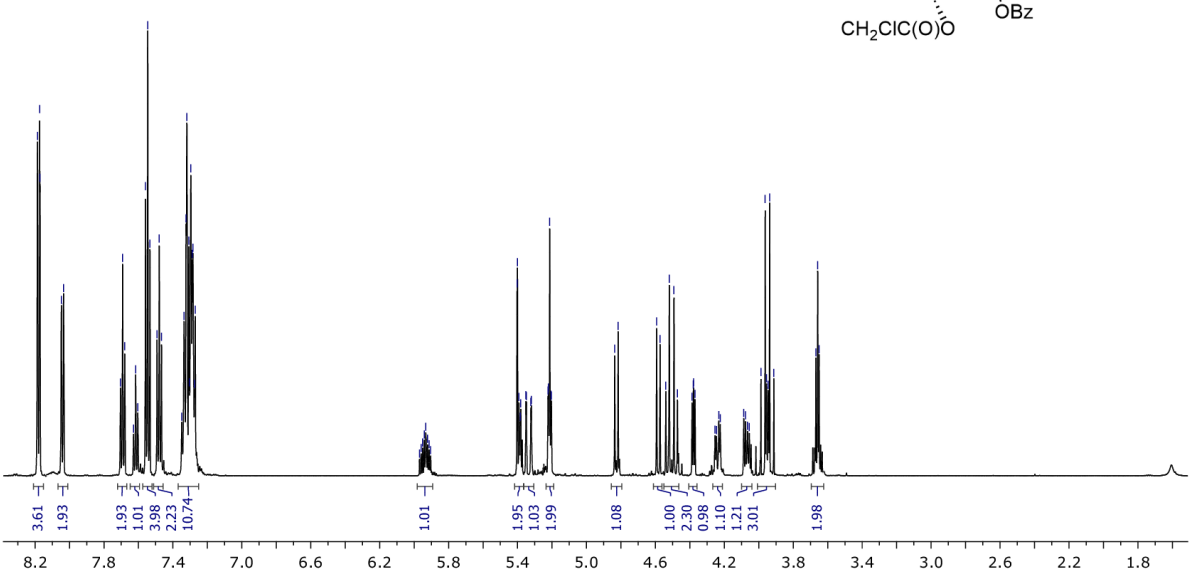




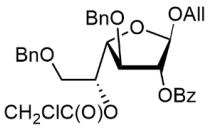
Allyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranoside (15)

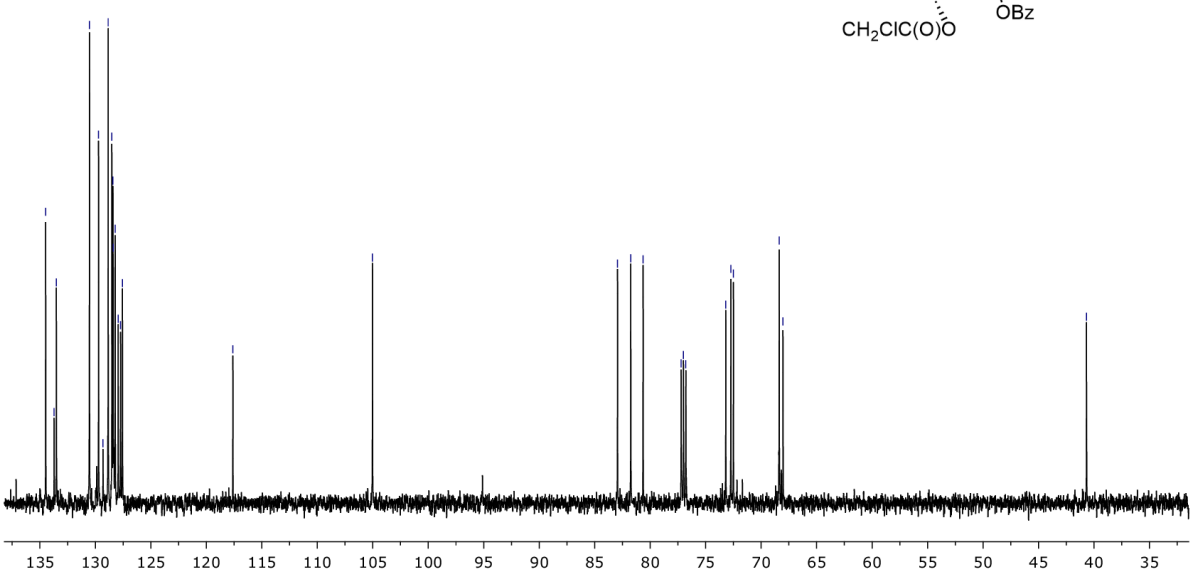
1H NMR (600.13 MHz), CDCl3, 303.0 K





13C NMR (150.91 MHz), CDCl3, 303.1 K





Acquisition Parameter

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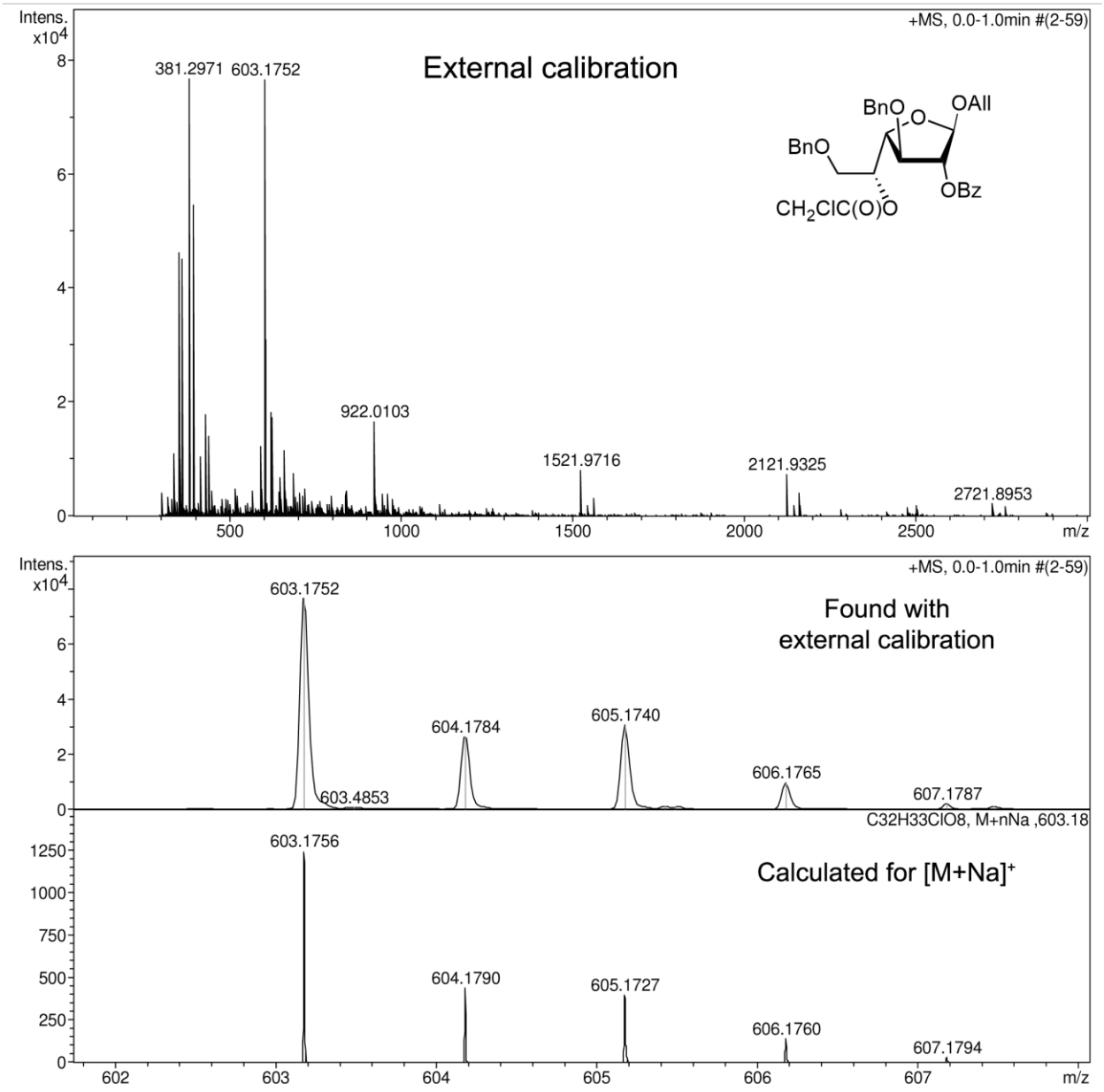
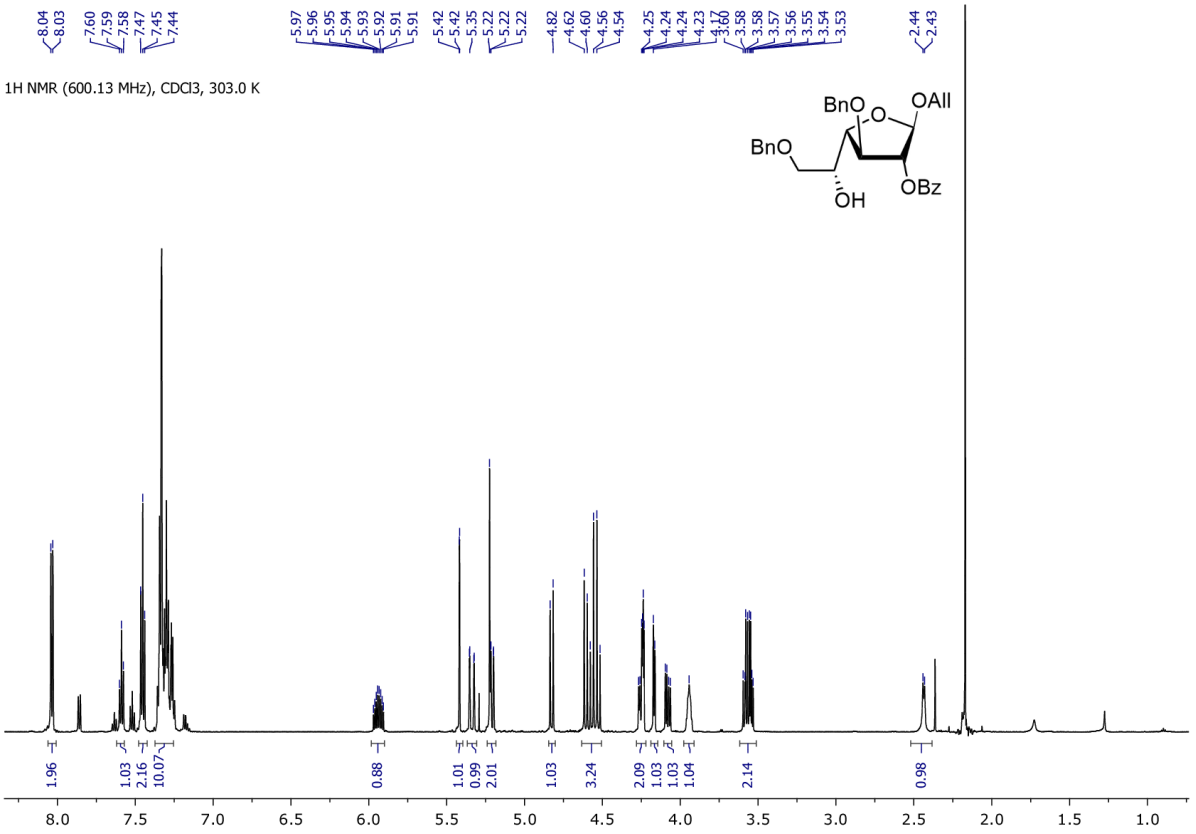
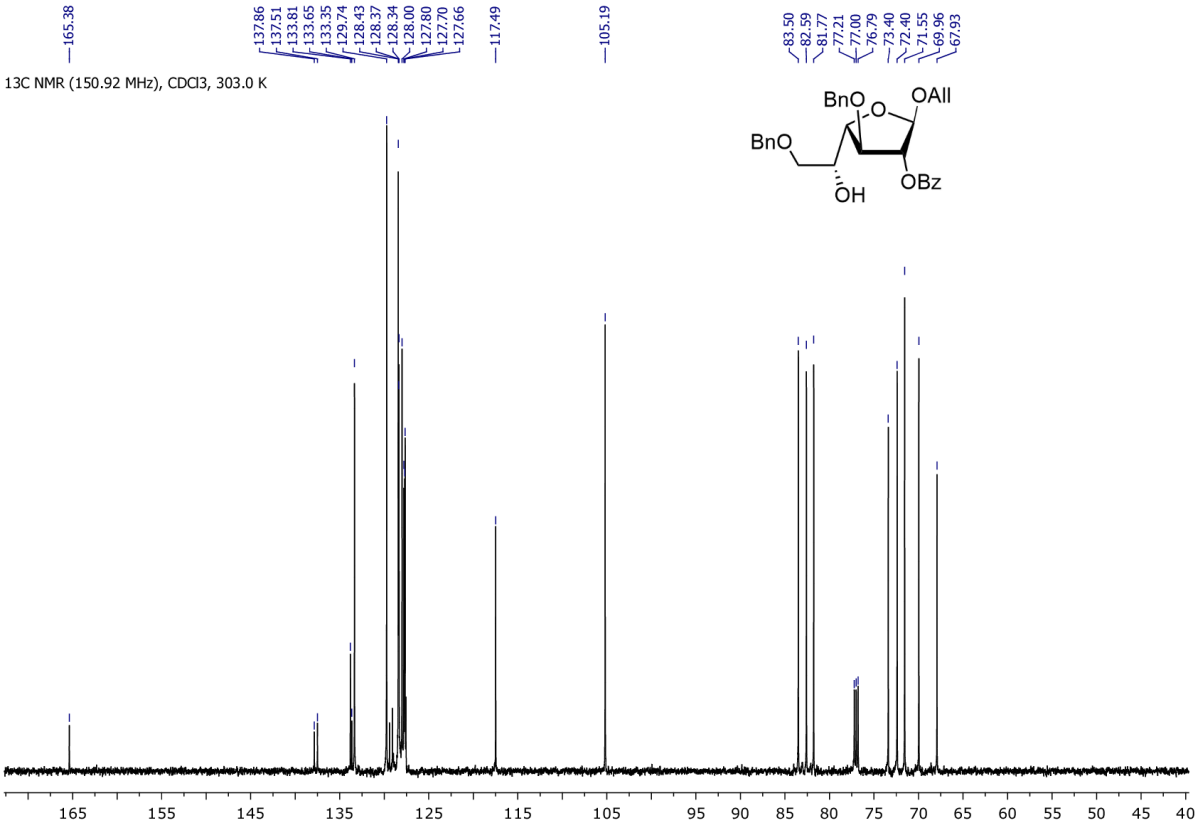


Allyl 2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside (13) (pure, from 15)





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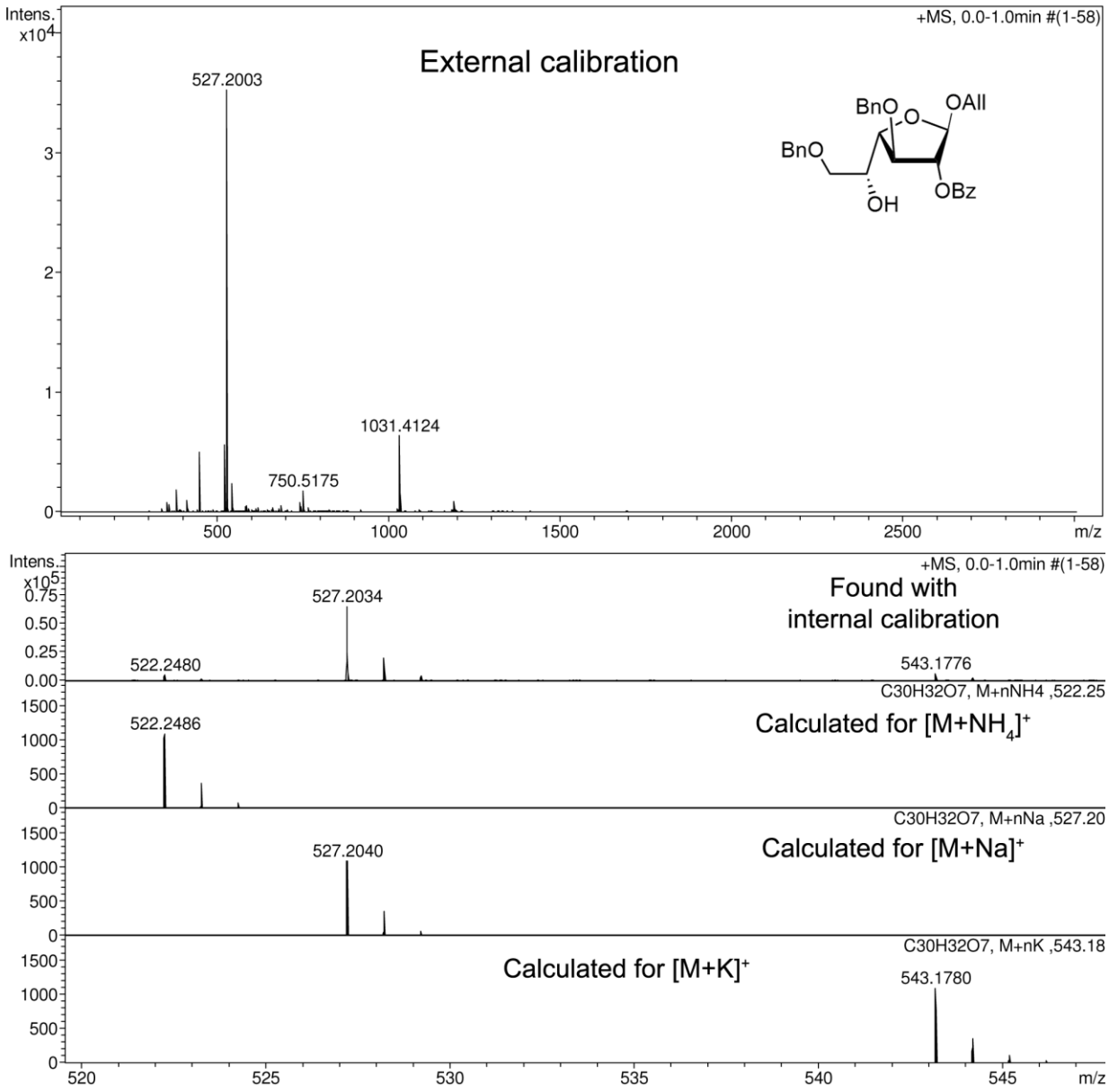
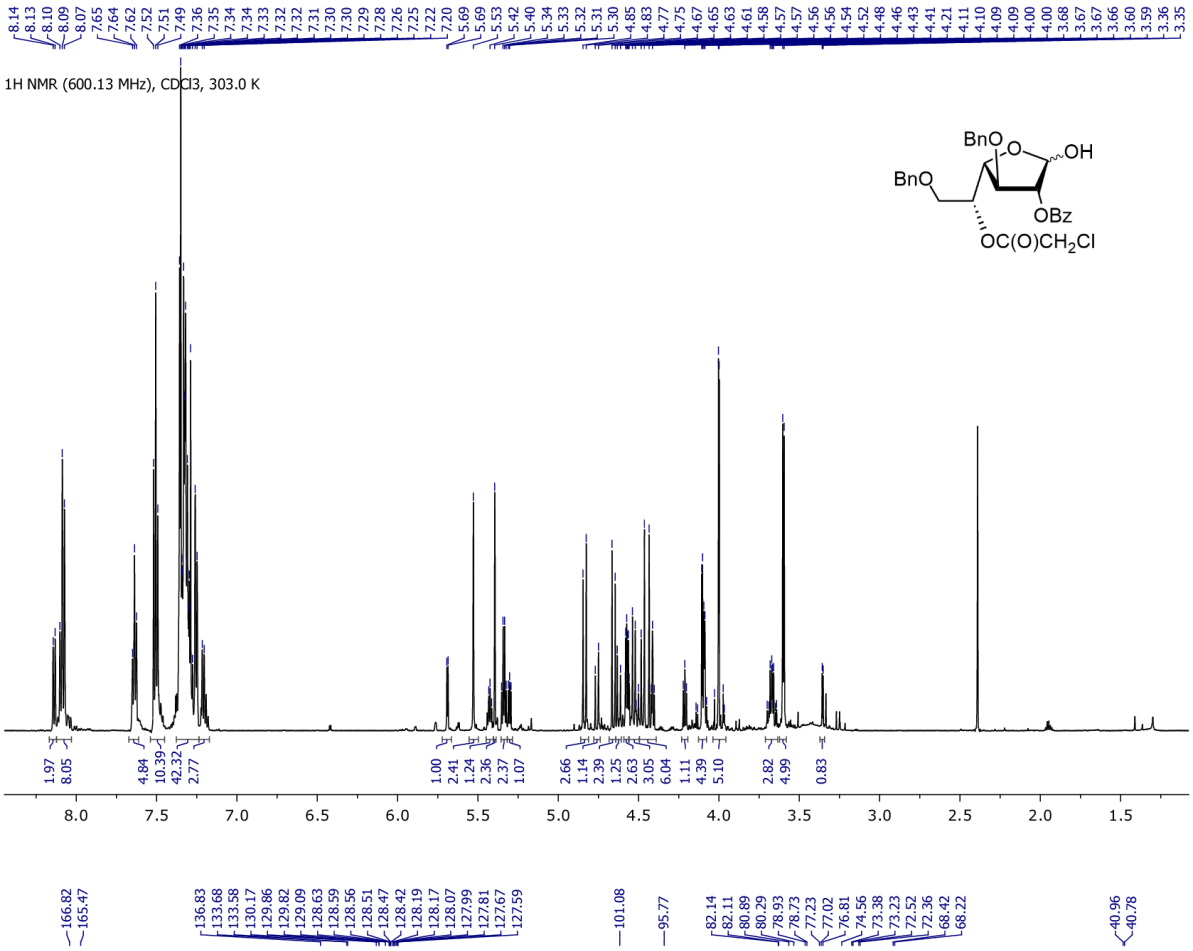
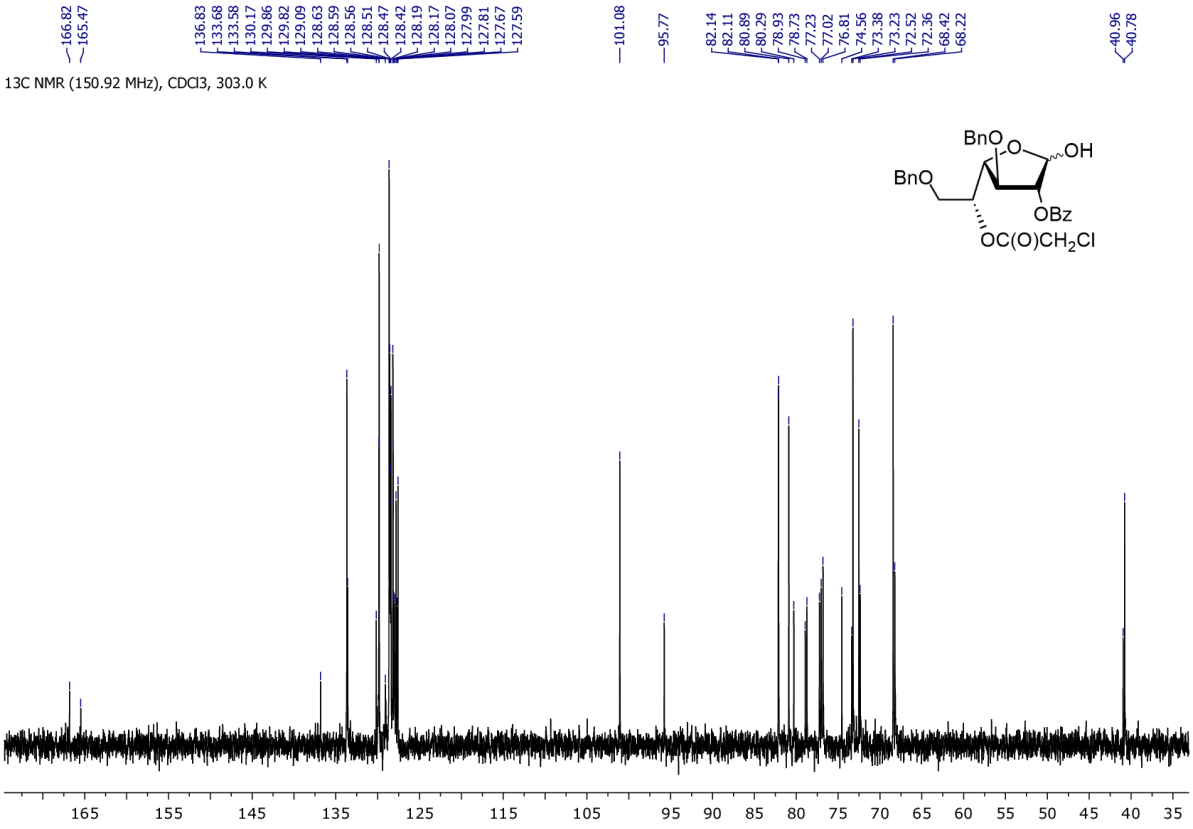
Scan End	3000 m/z	Set Collision Cell RF	1200.0 Vpp	Set Divert Valve	Waste



2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-D-galactofuranose (16)





Acquisition Parameter

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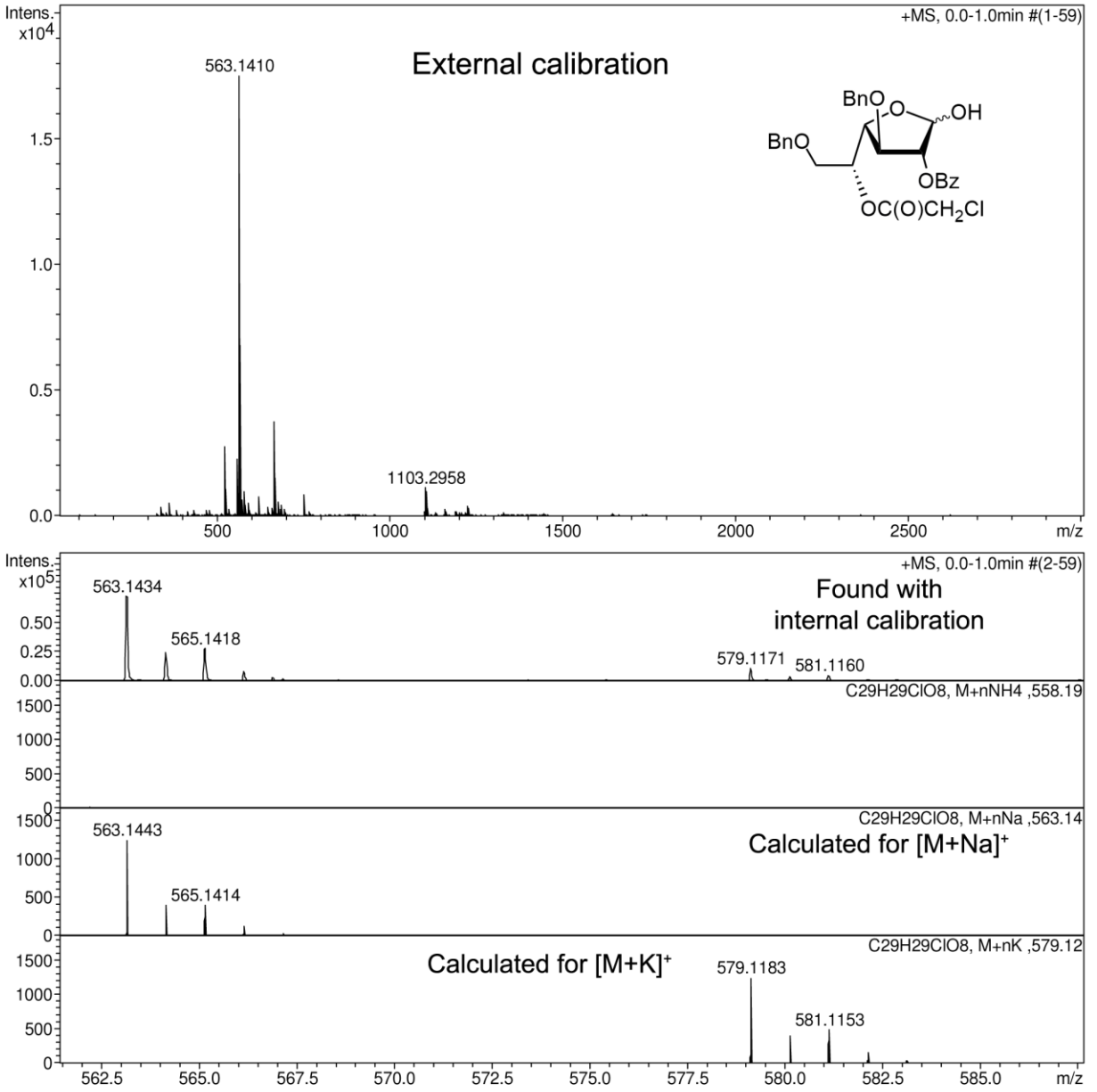
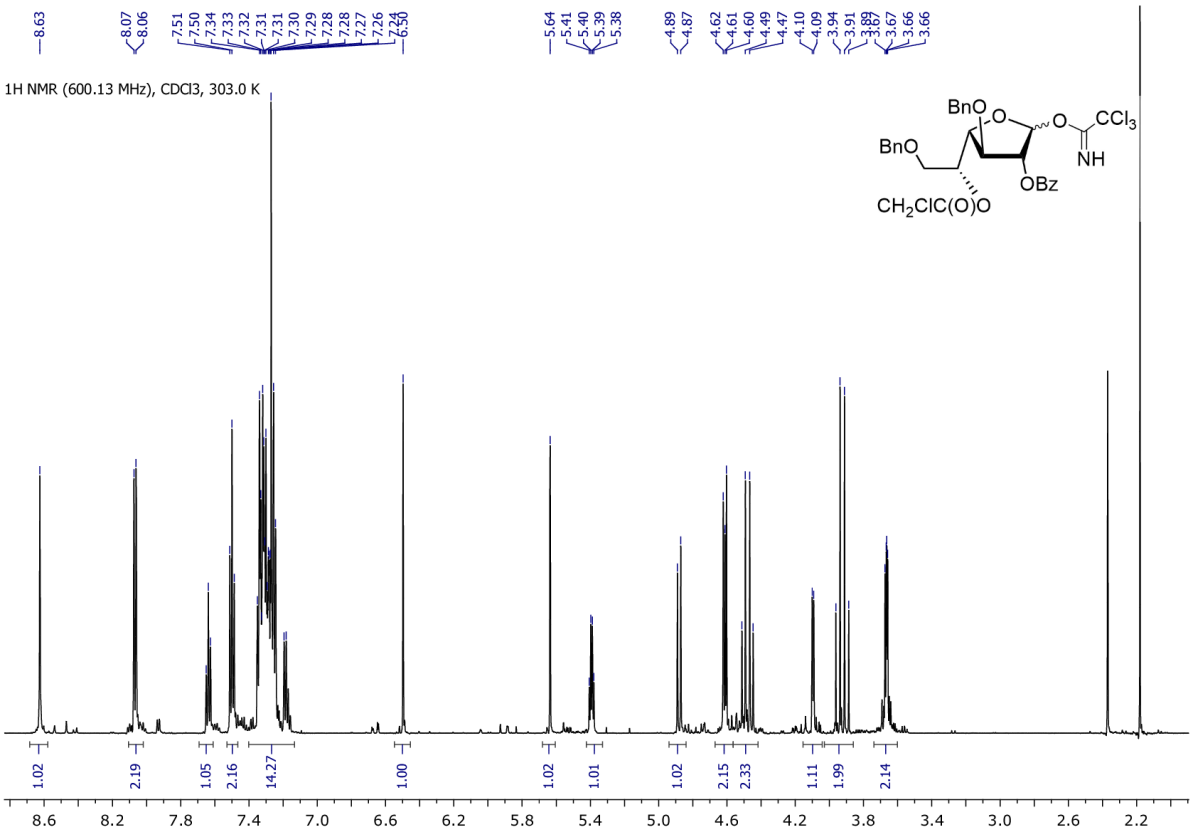
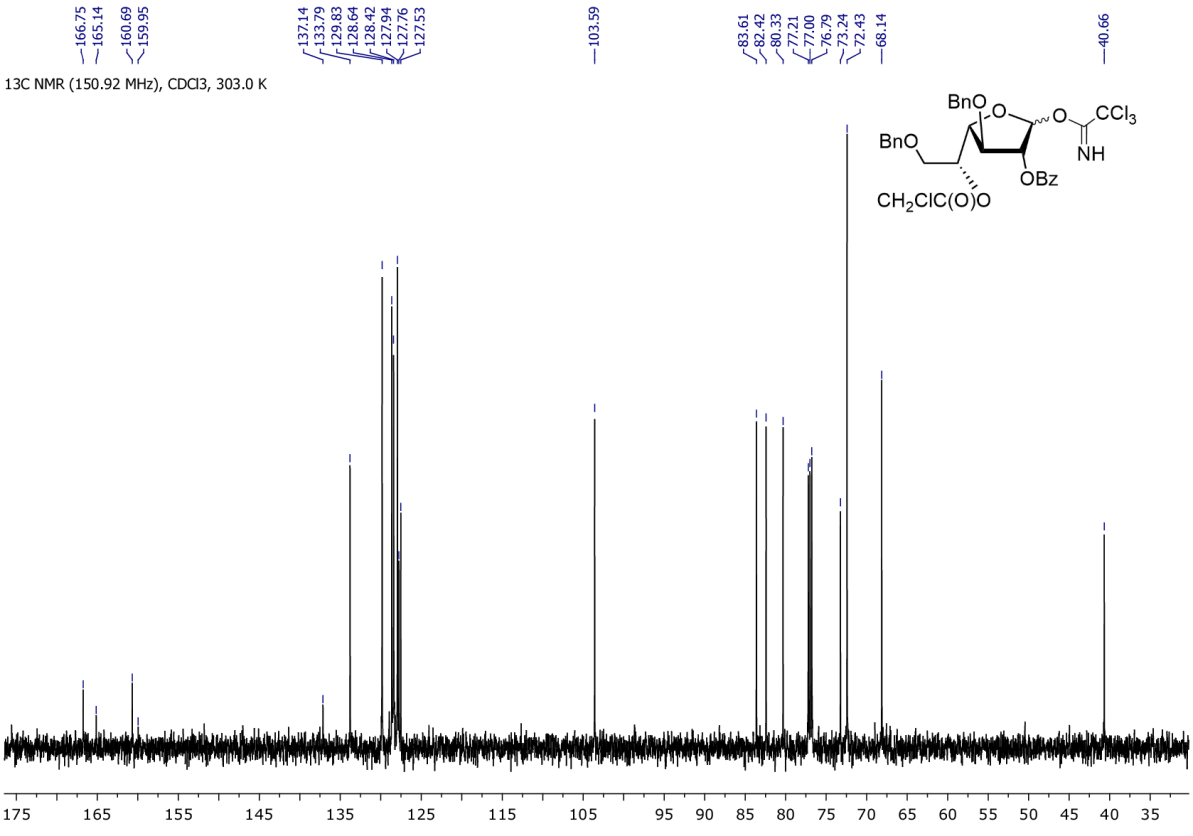
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranoside trichloroacetimidate (17)





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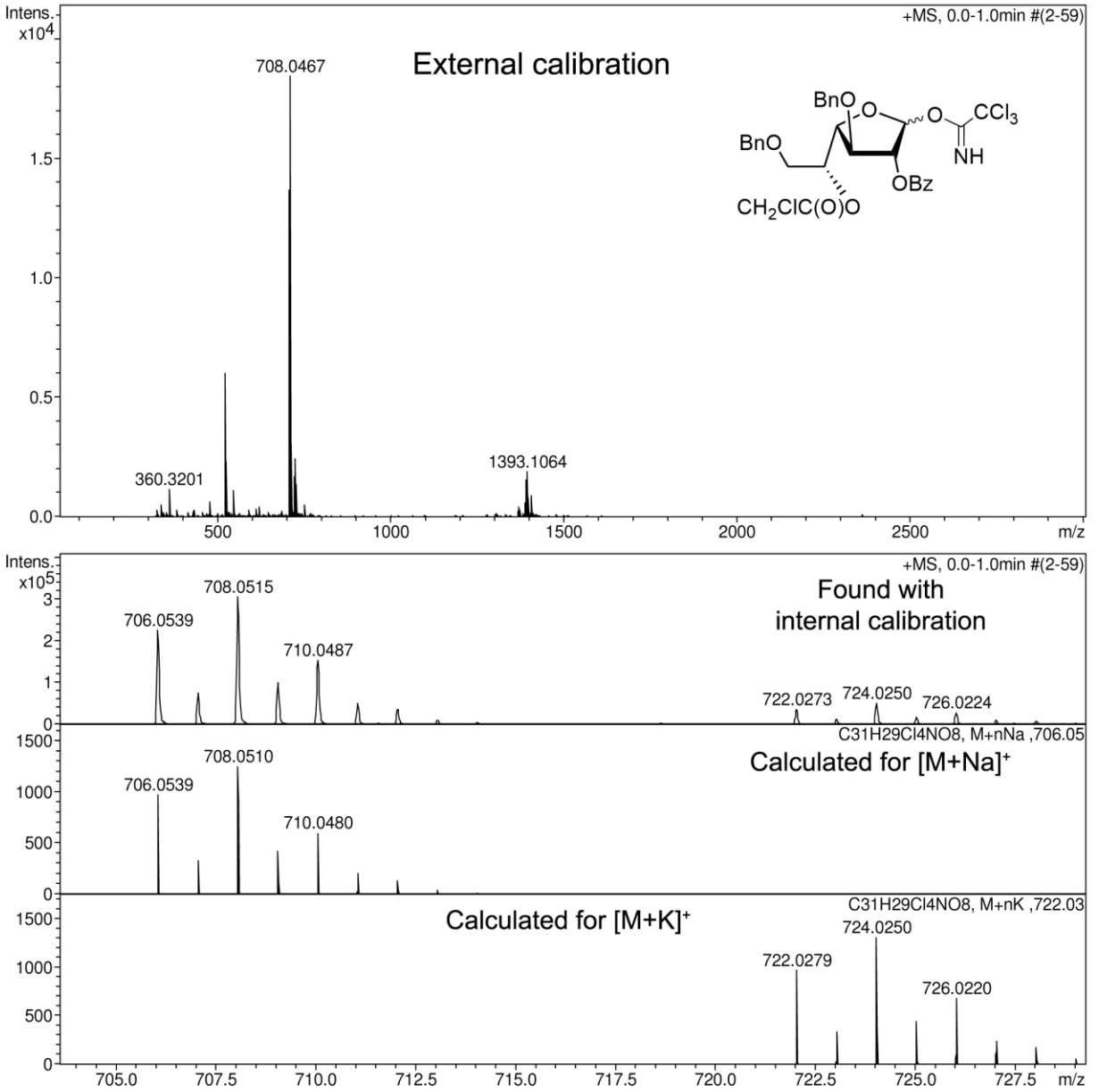
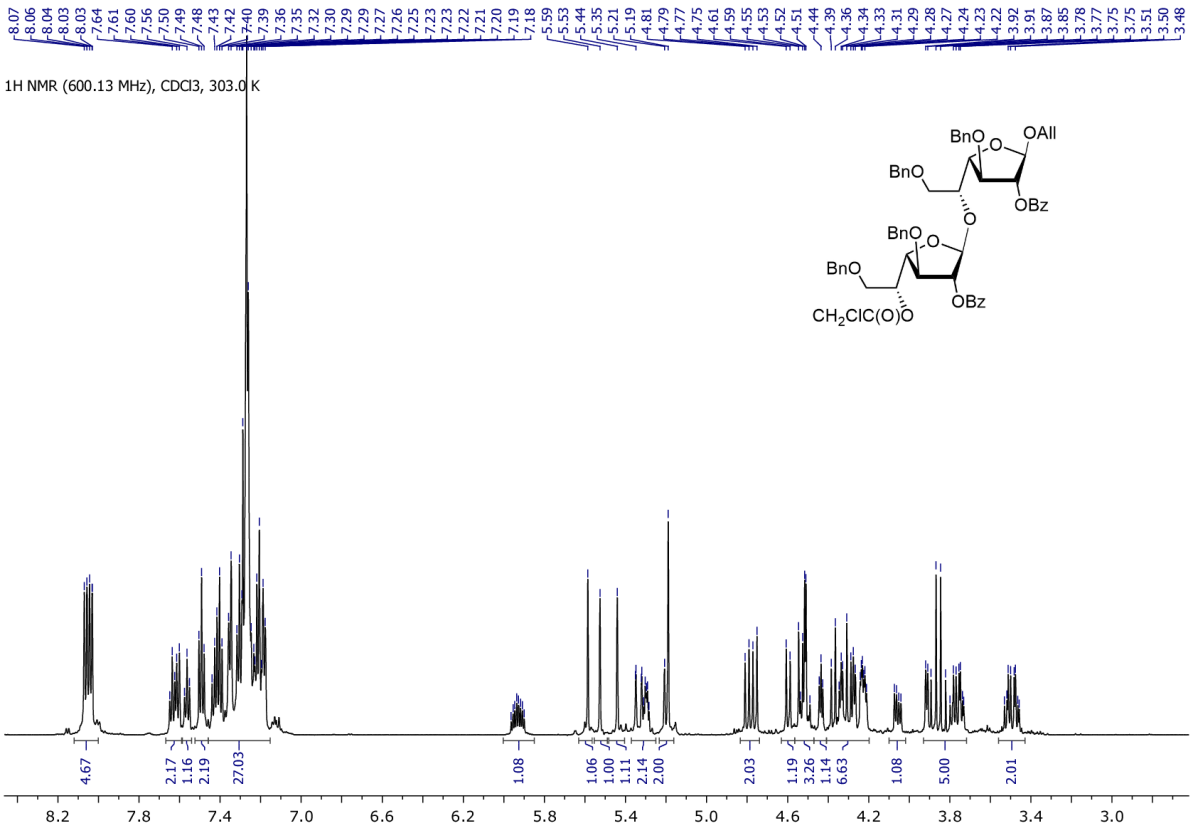
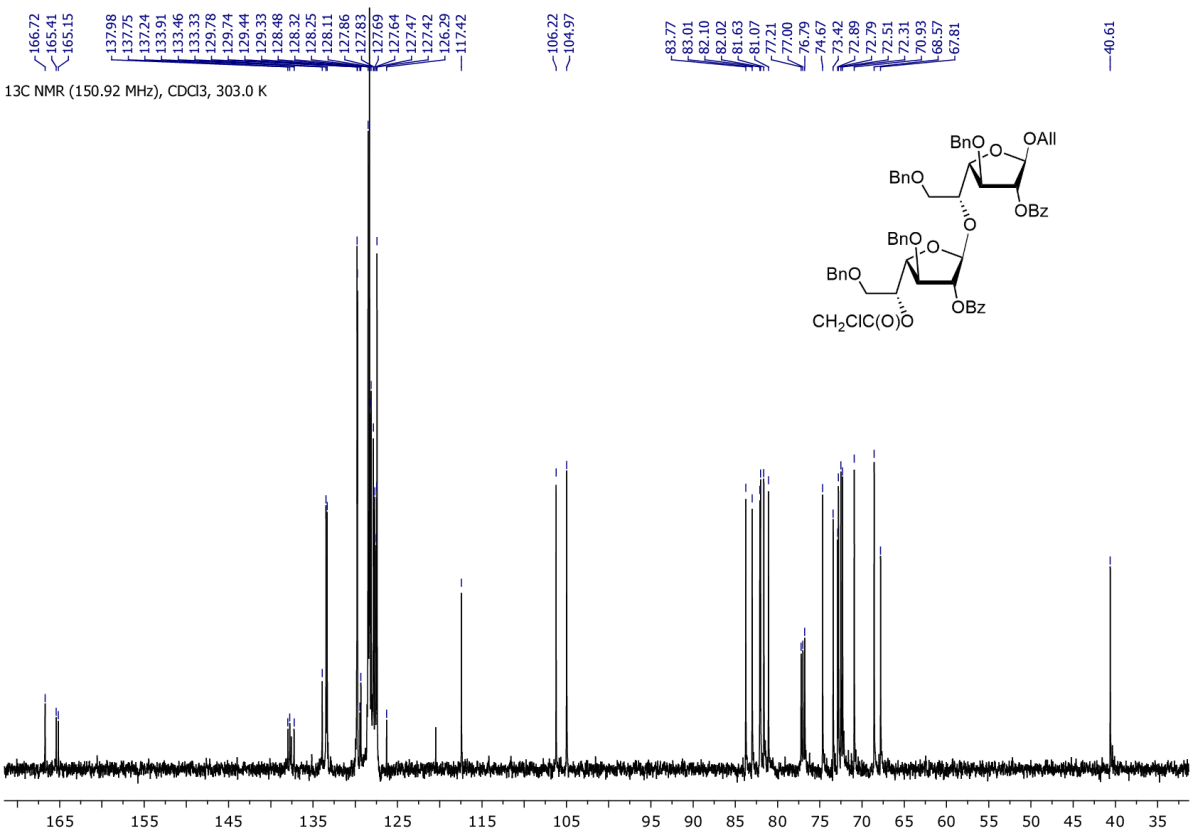


Allyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside (18)





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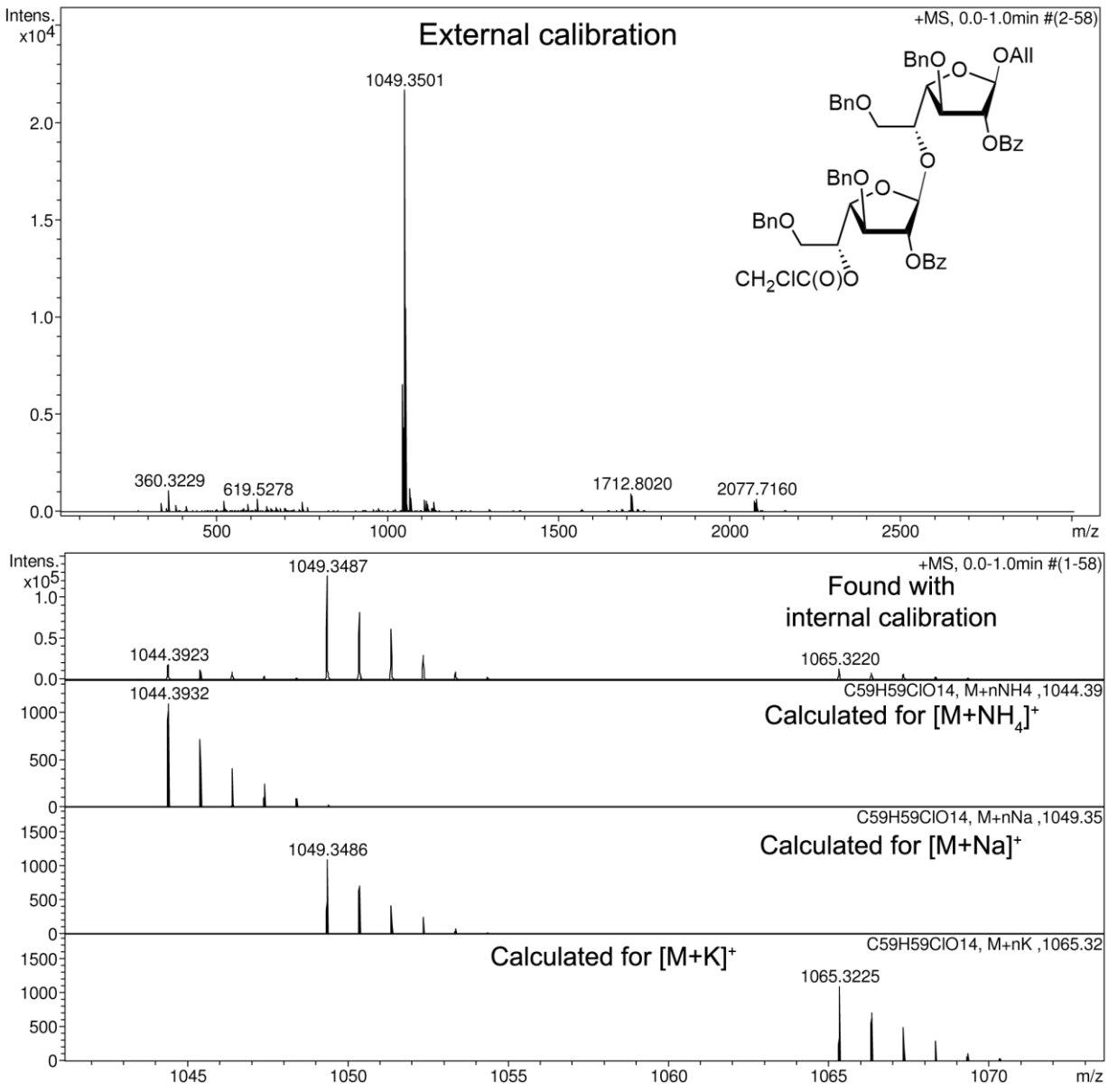
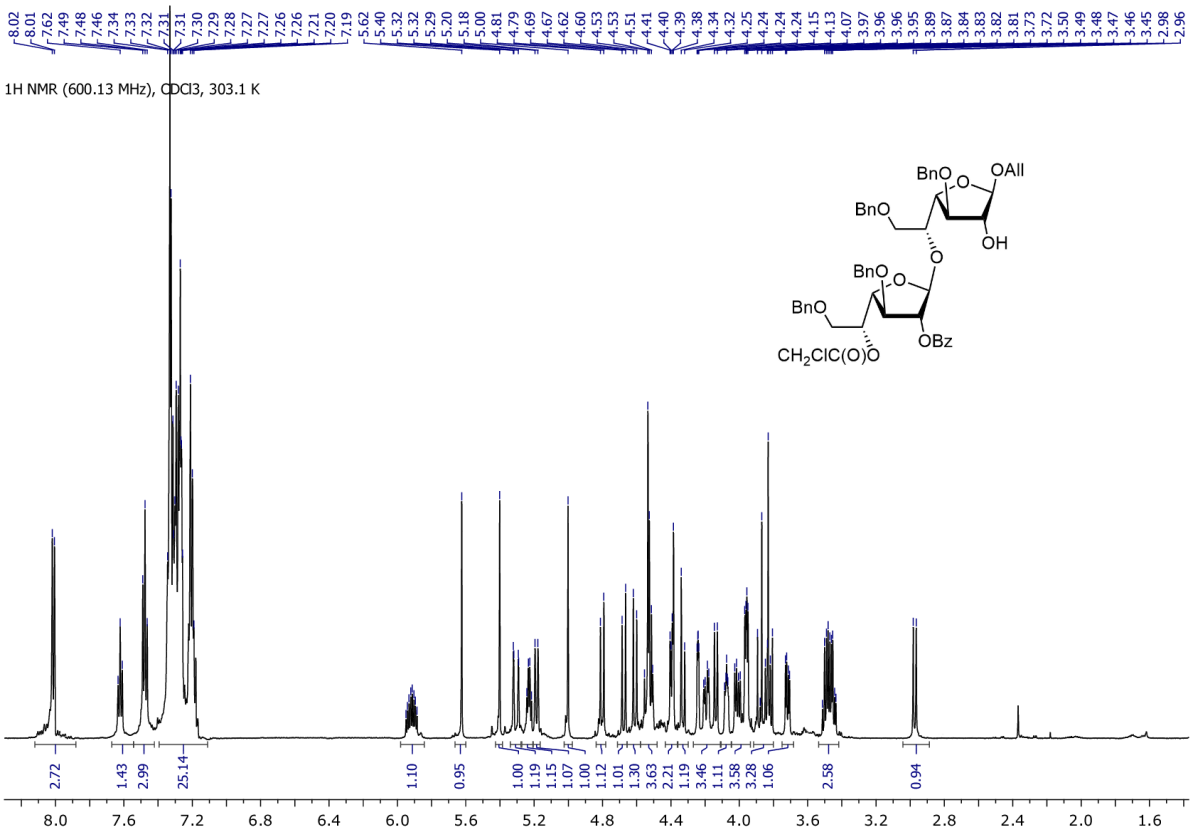
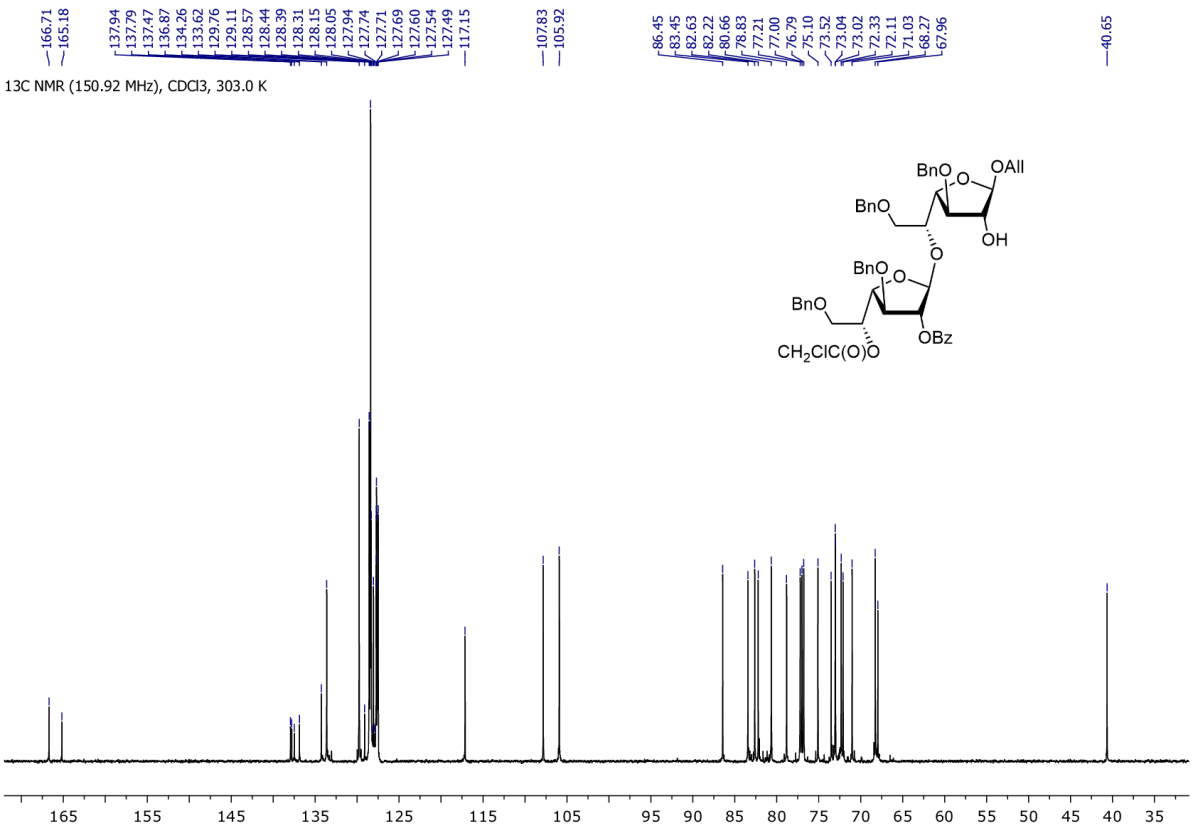


Allyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-3,6-di-O-benzyl-β-D-galactofuranoside (19)





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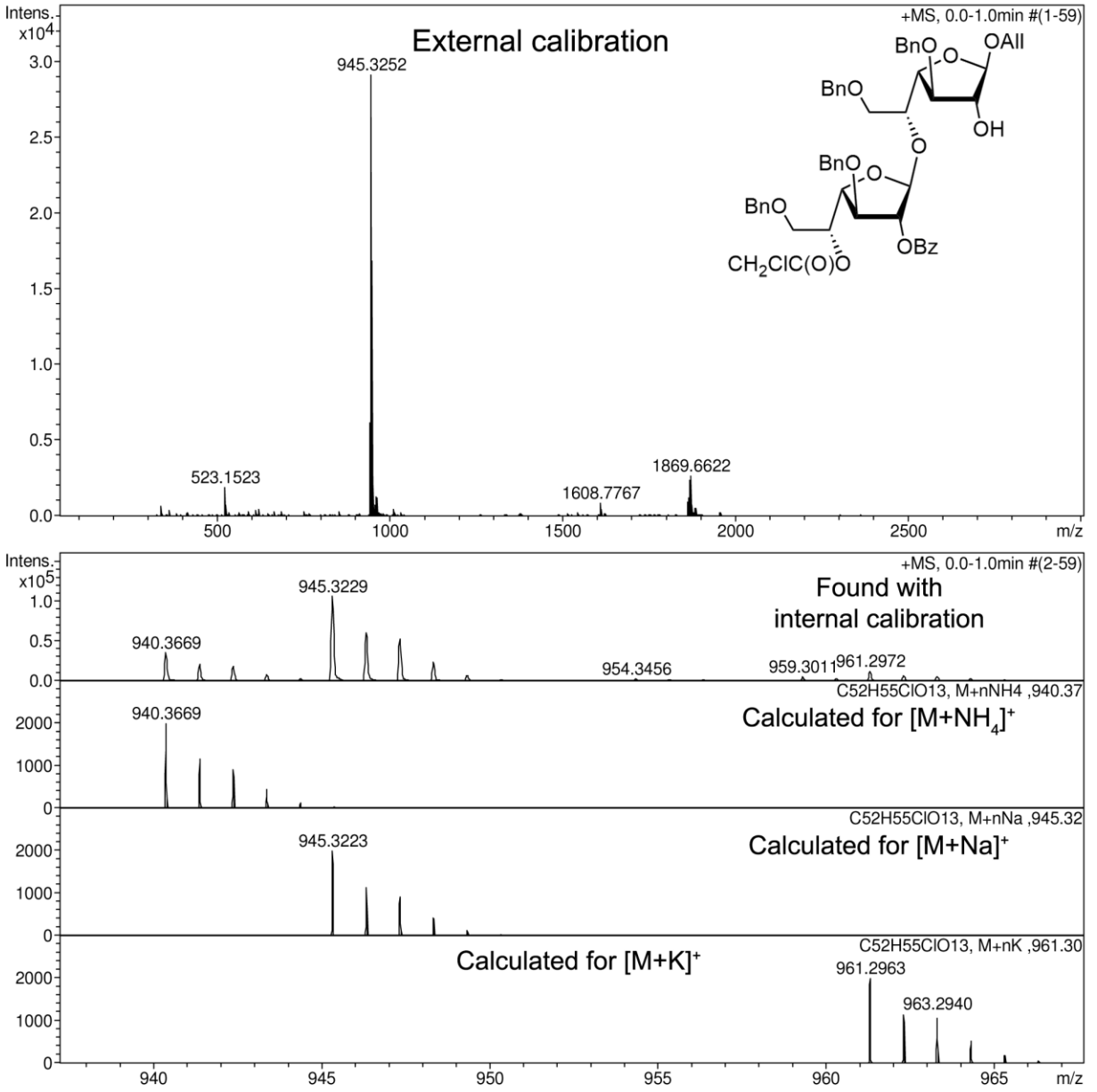
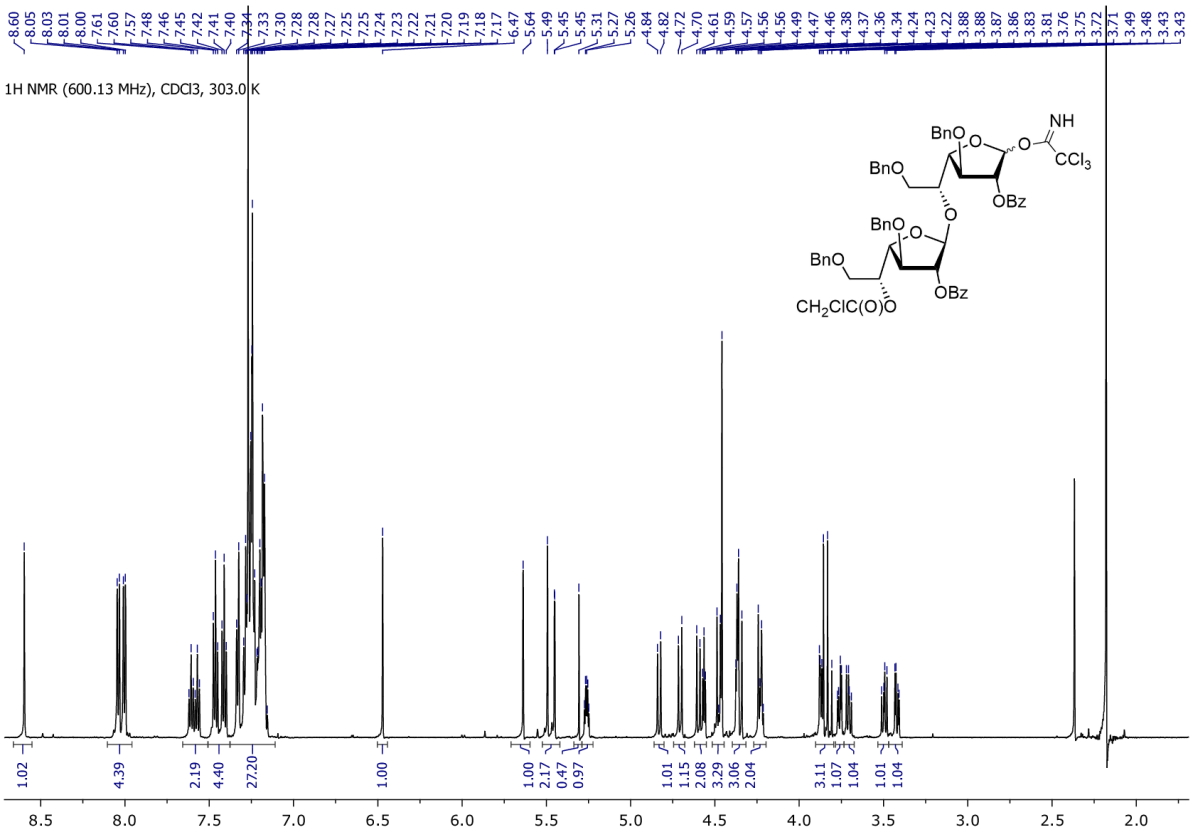
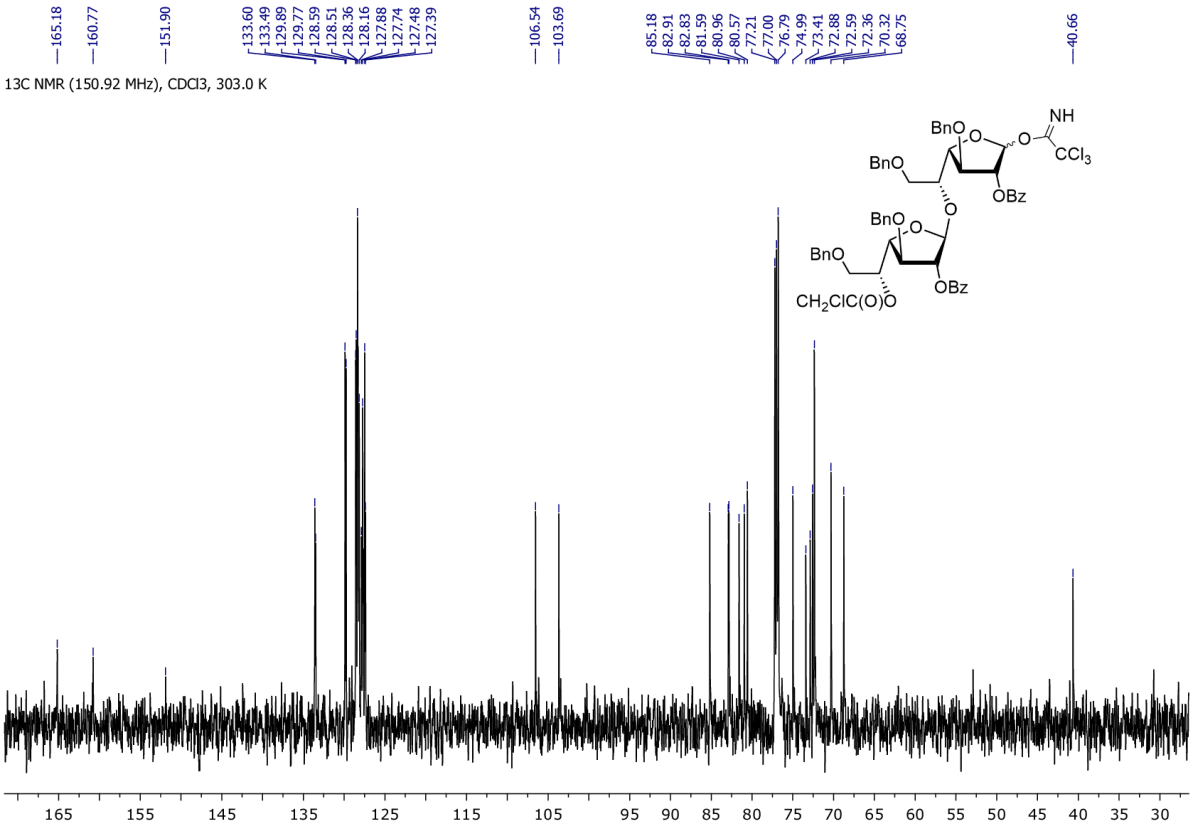
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside trichloroacetimidate (5)





Acquisition Parameter

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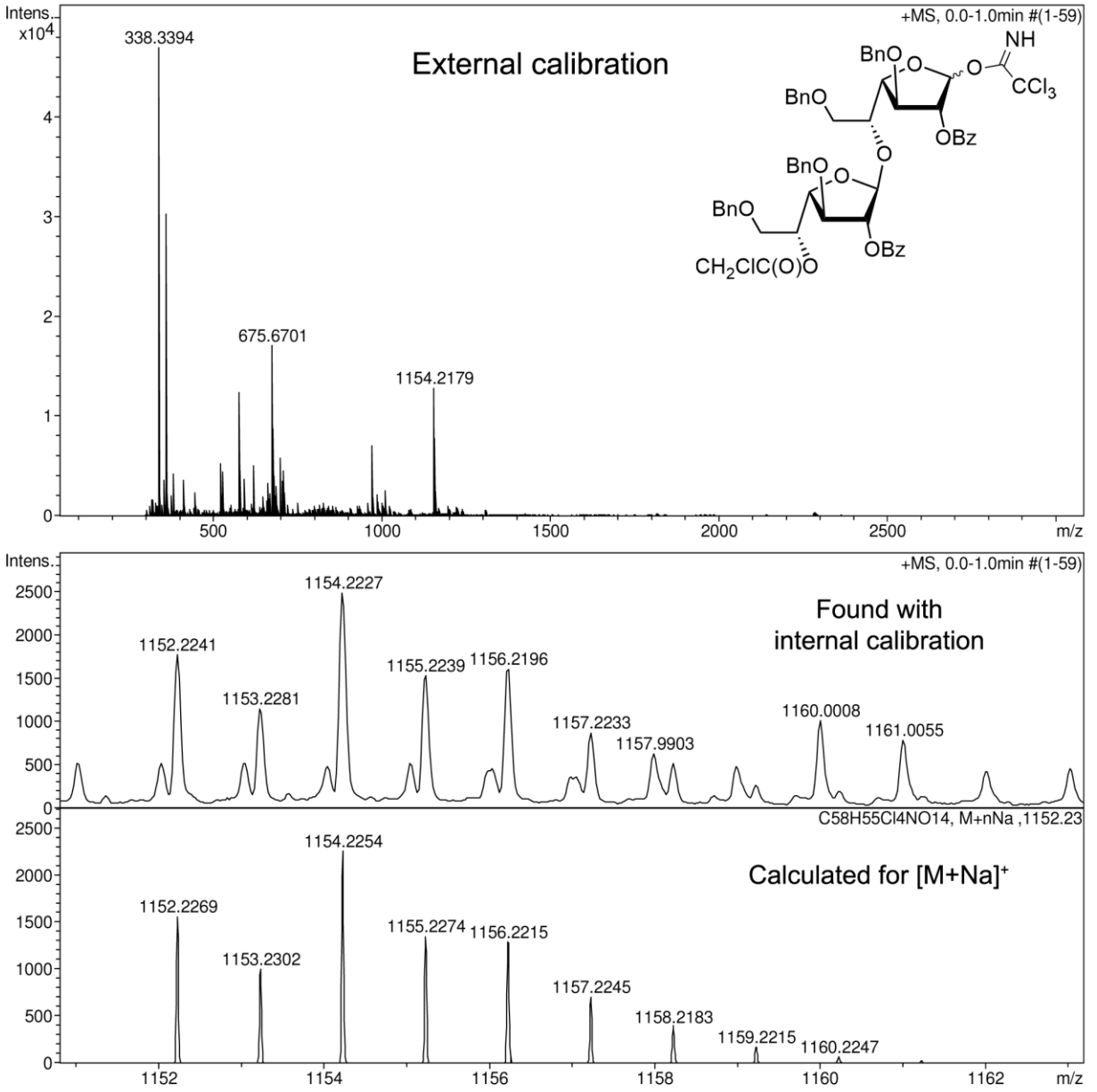
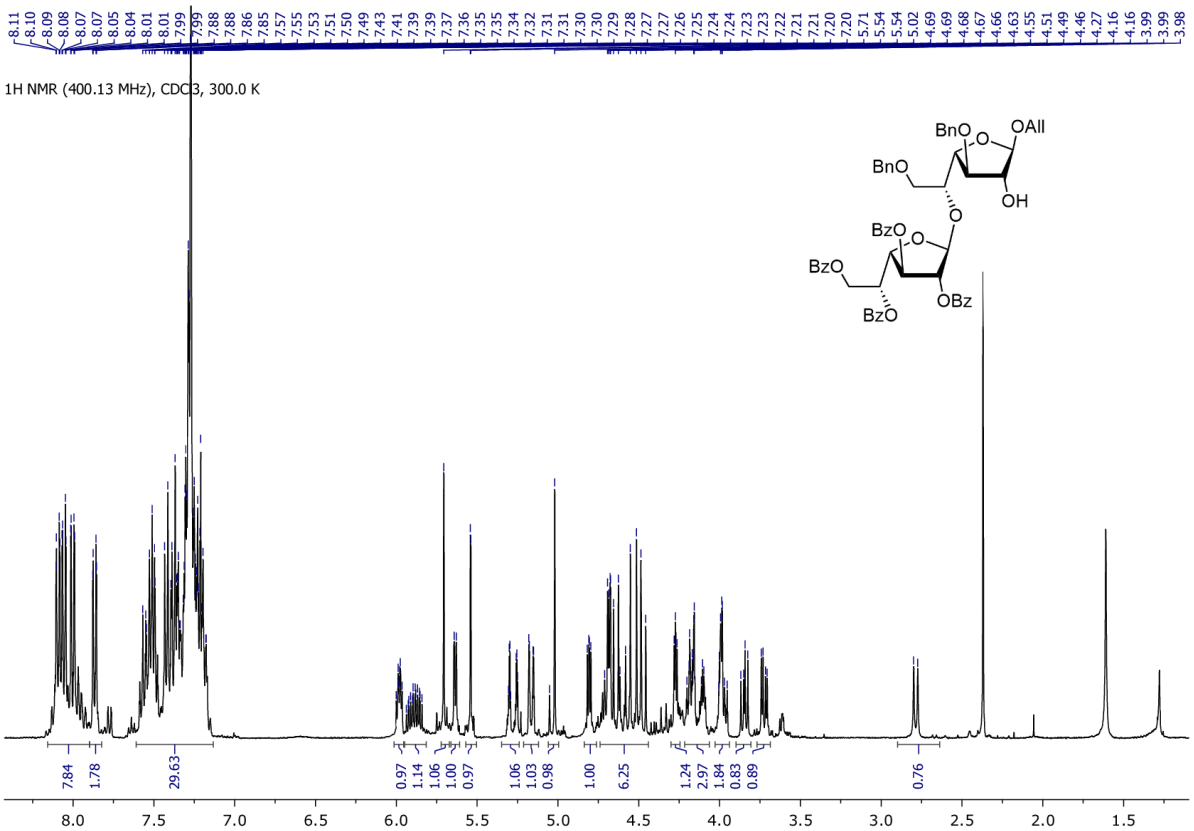
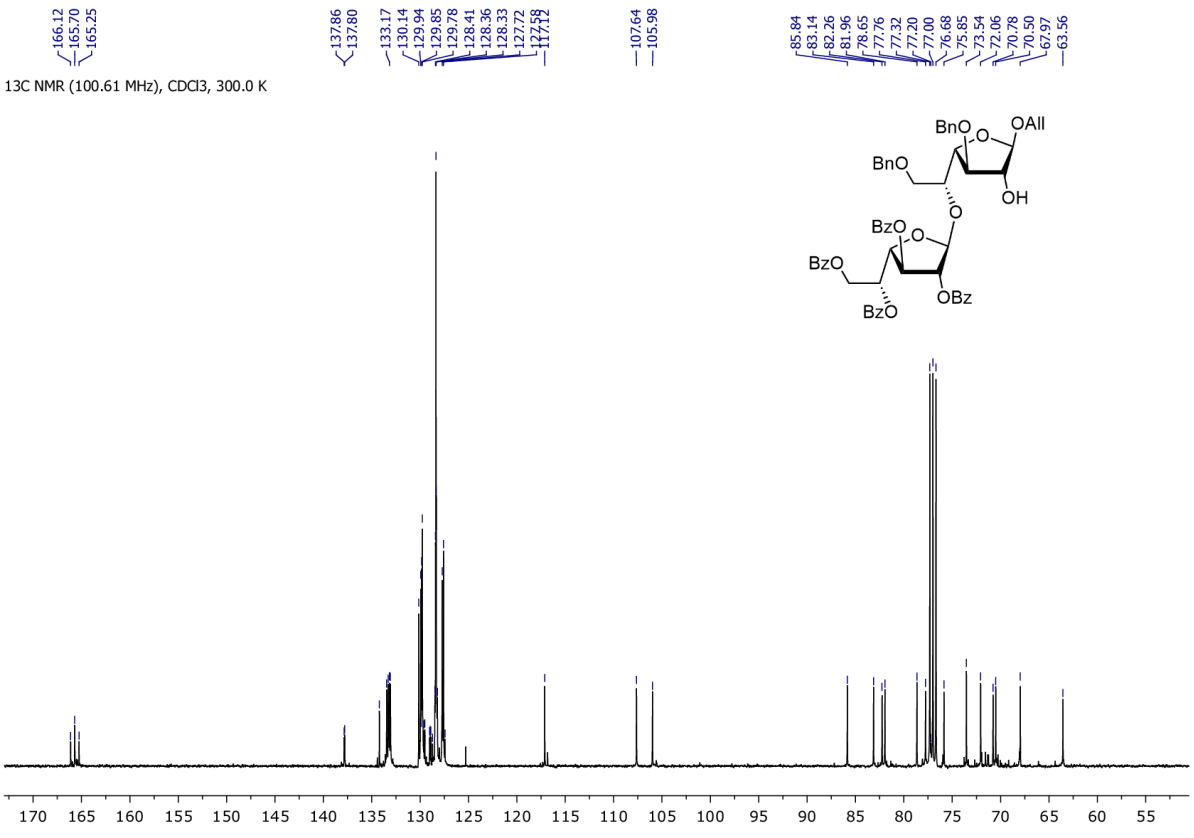
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Allyl 2,3,5,6-tetra-O-benzoyl-β-D-galactofuranosyl-(1→5)-3,6-di-O-benzyl-β-D-galactofuranoside (21)





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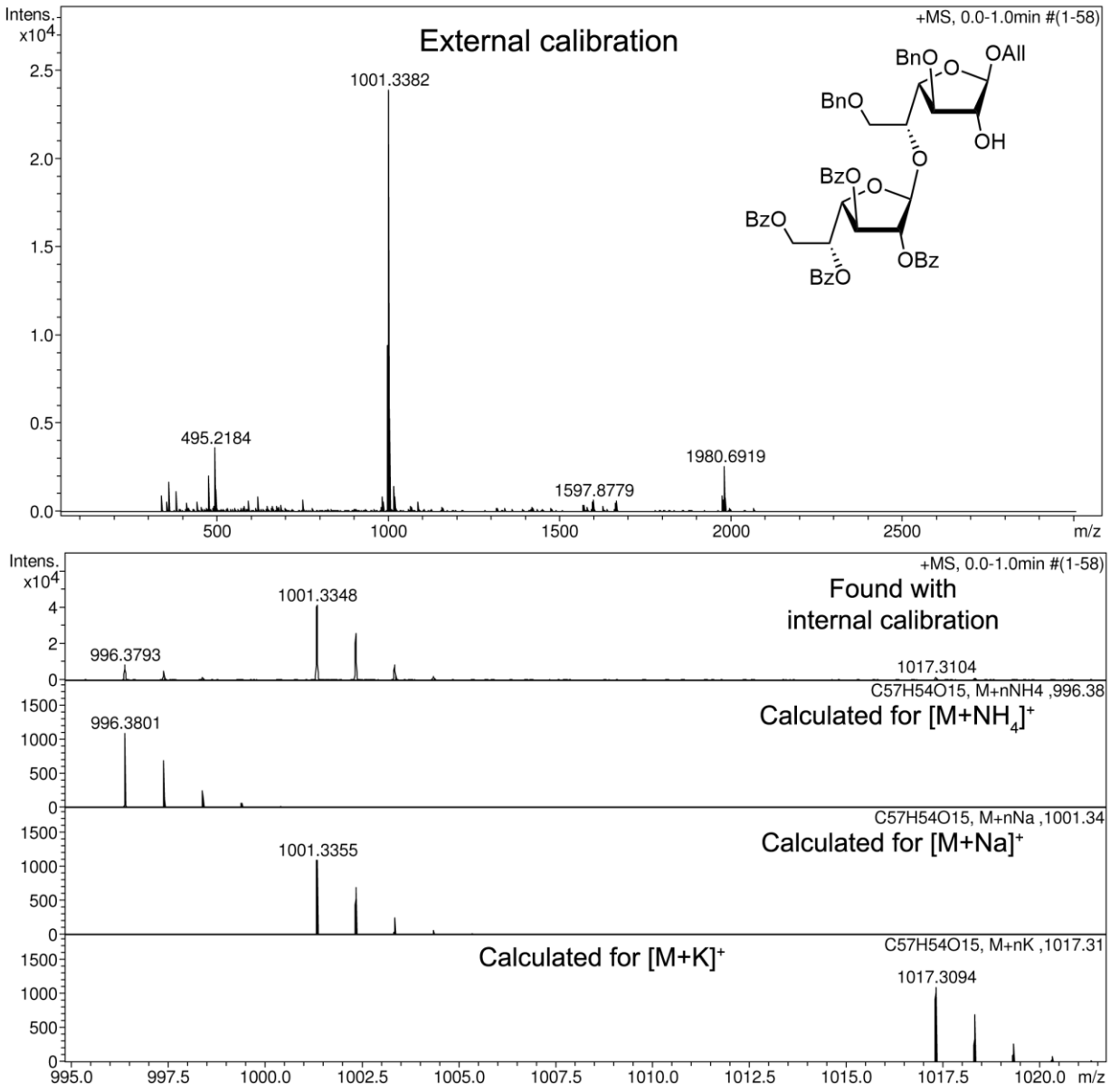
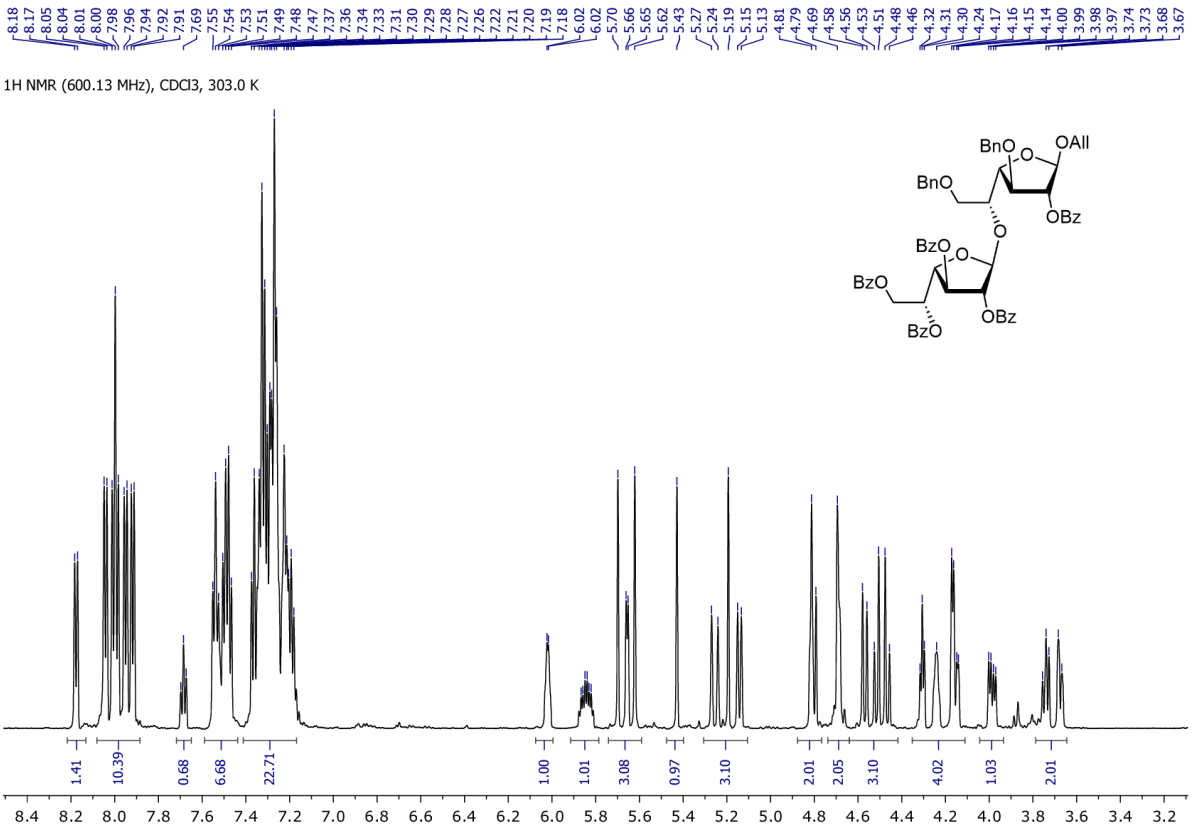
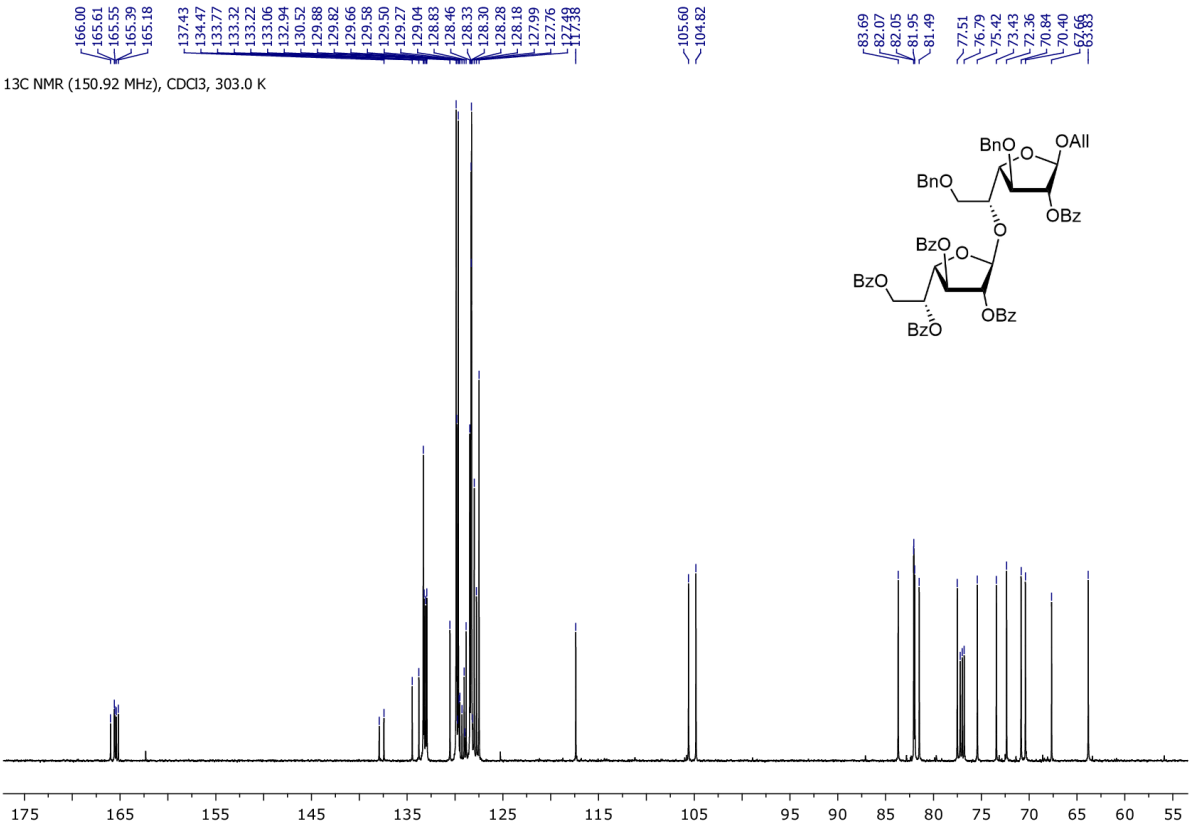


Allyl 2,3,5,6-tetra-O-benzoyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside (22)





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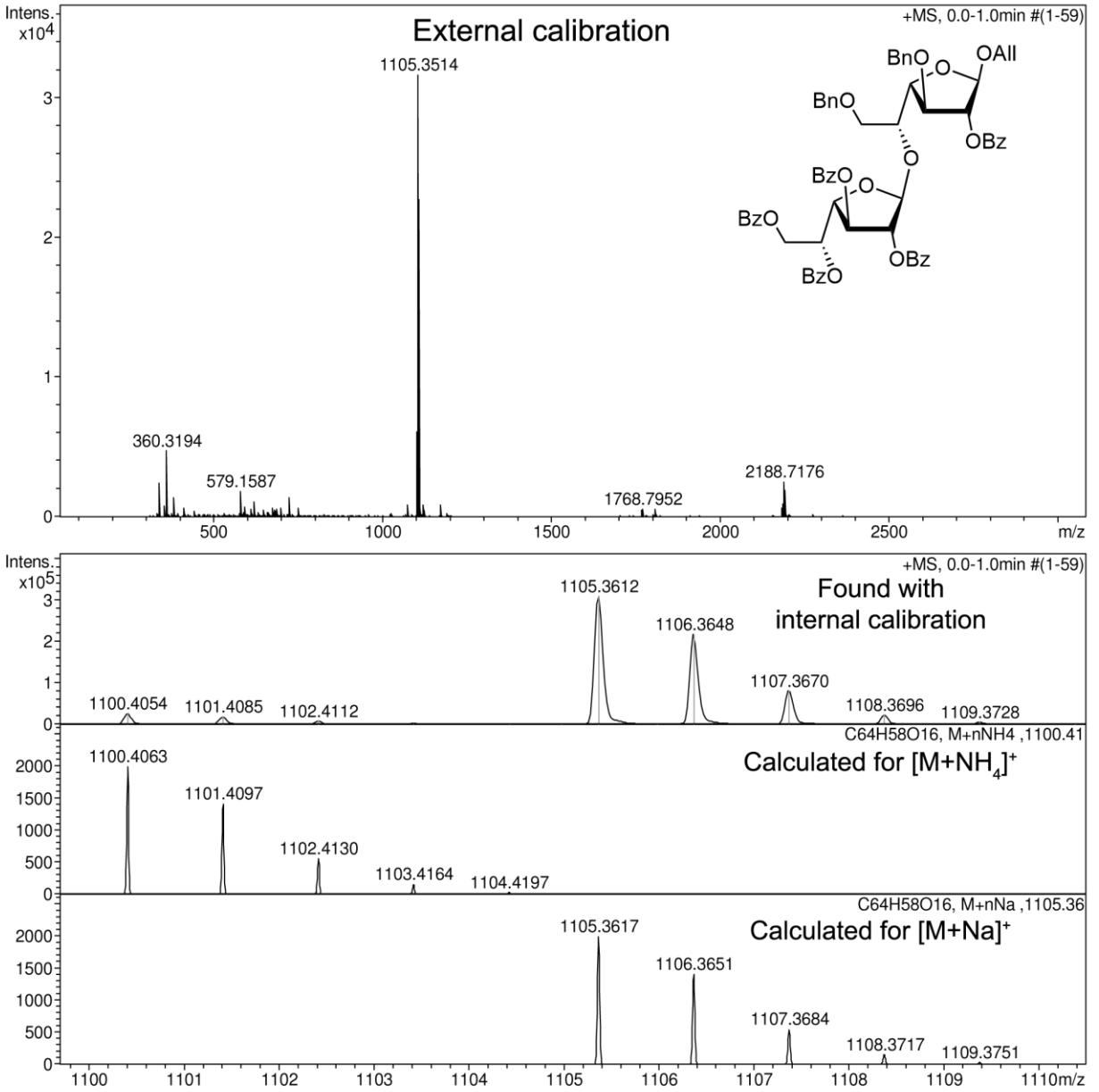
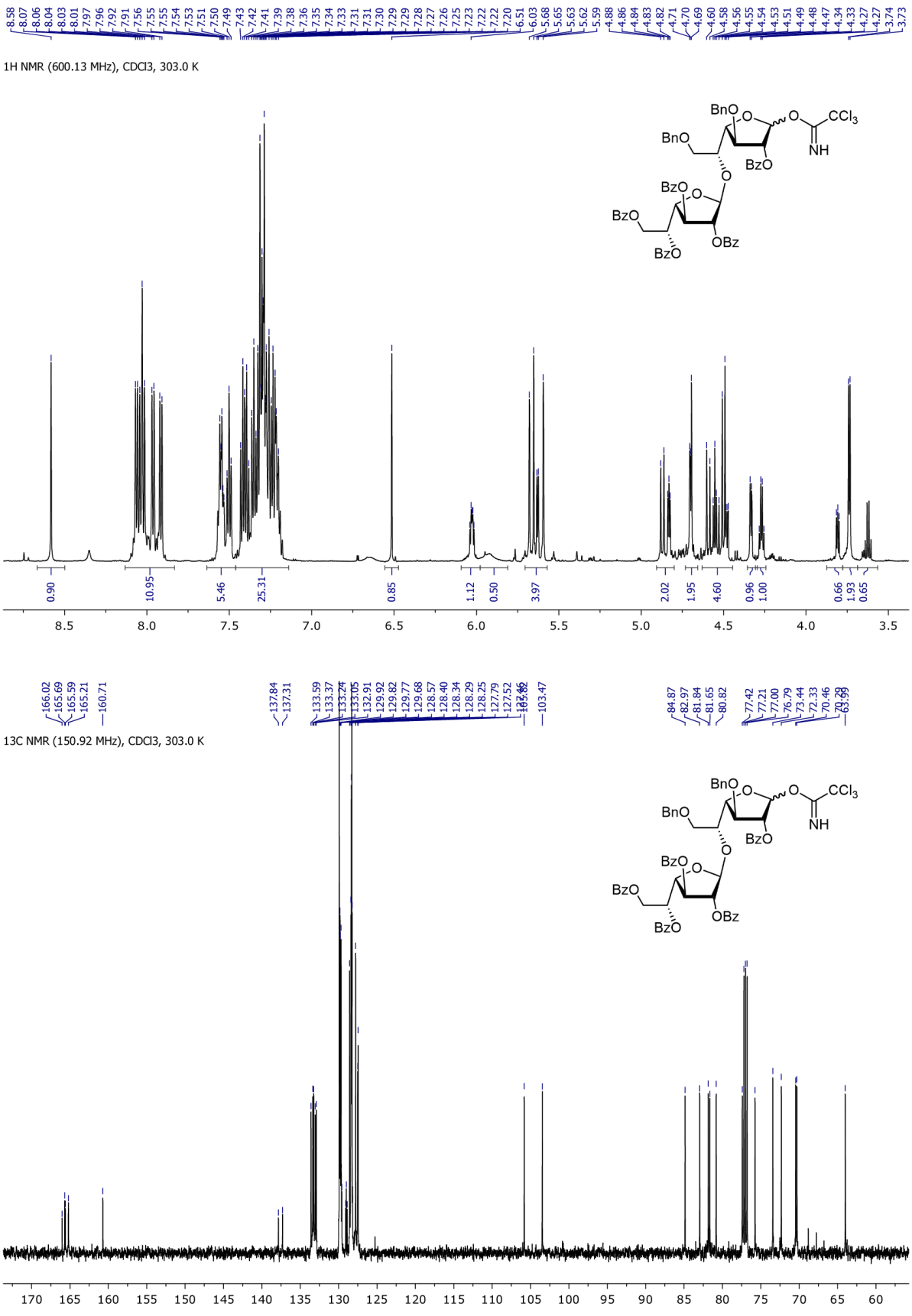
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

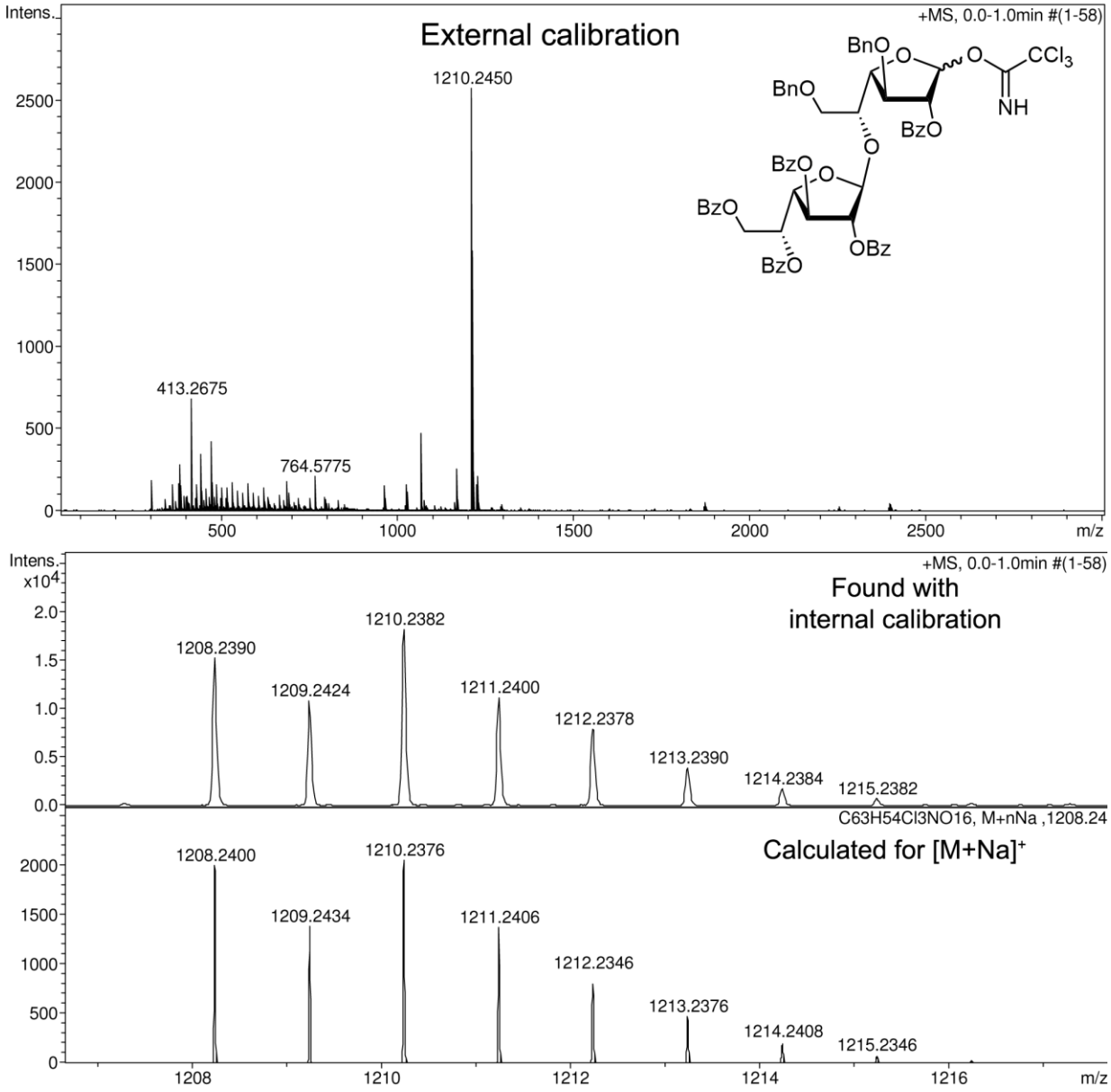


2,3,5,6-tetra-O-benzoyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranoside trichloroacetimidate (6)

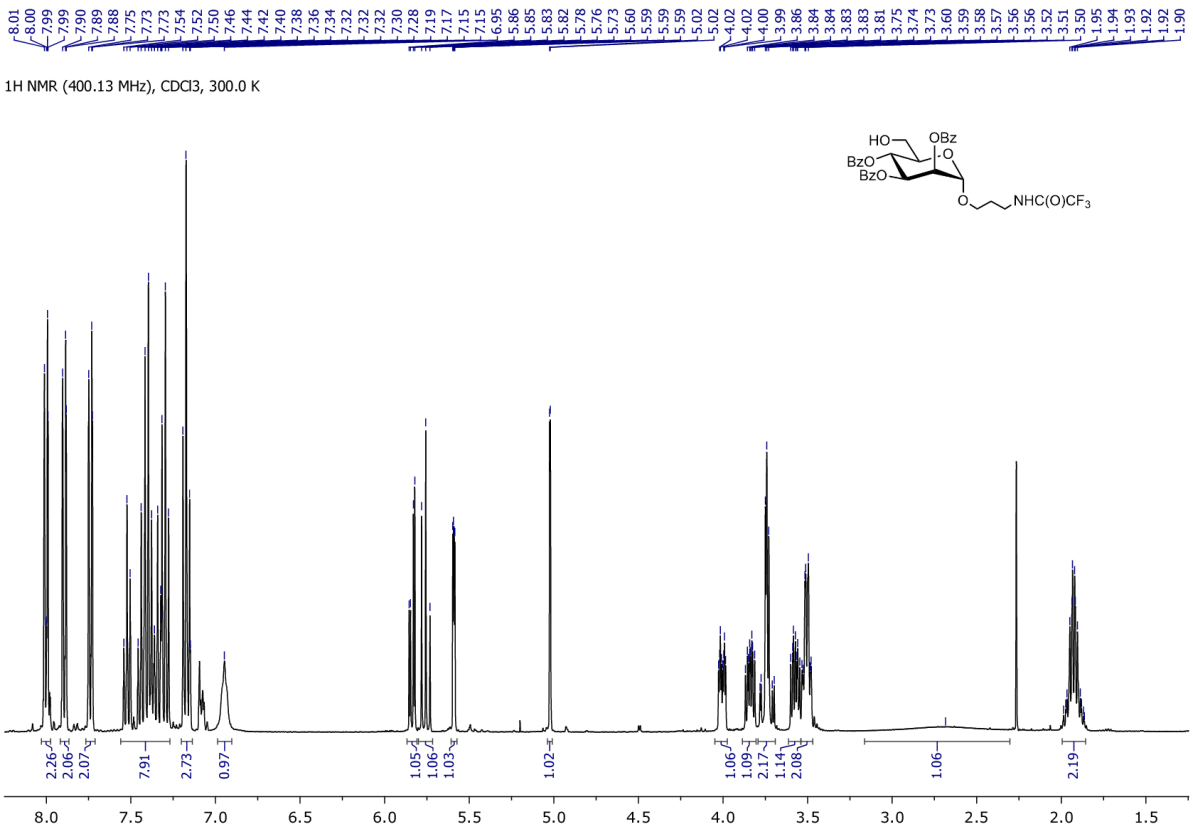


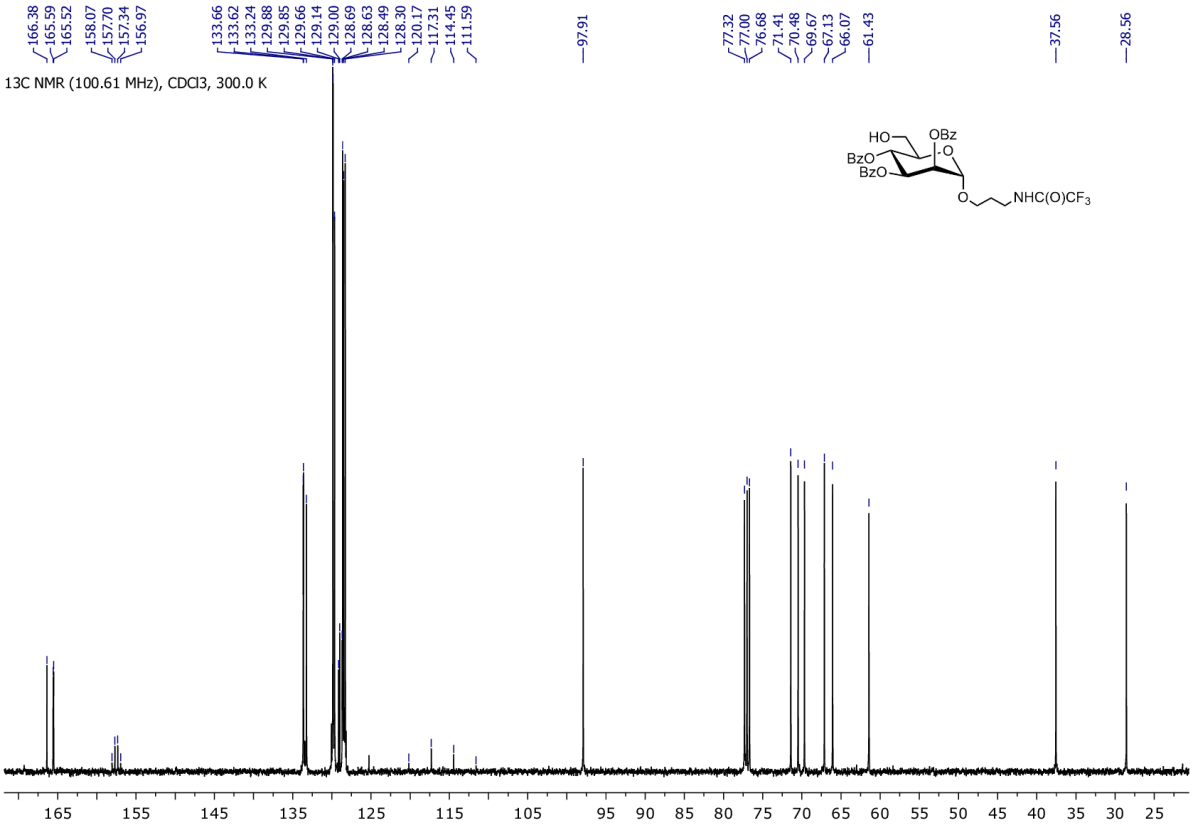
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	1200.0 Vpp	Set Divert Valve	Waste



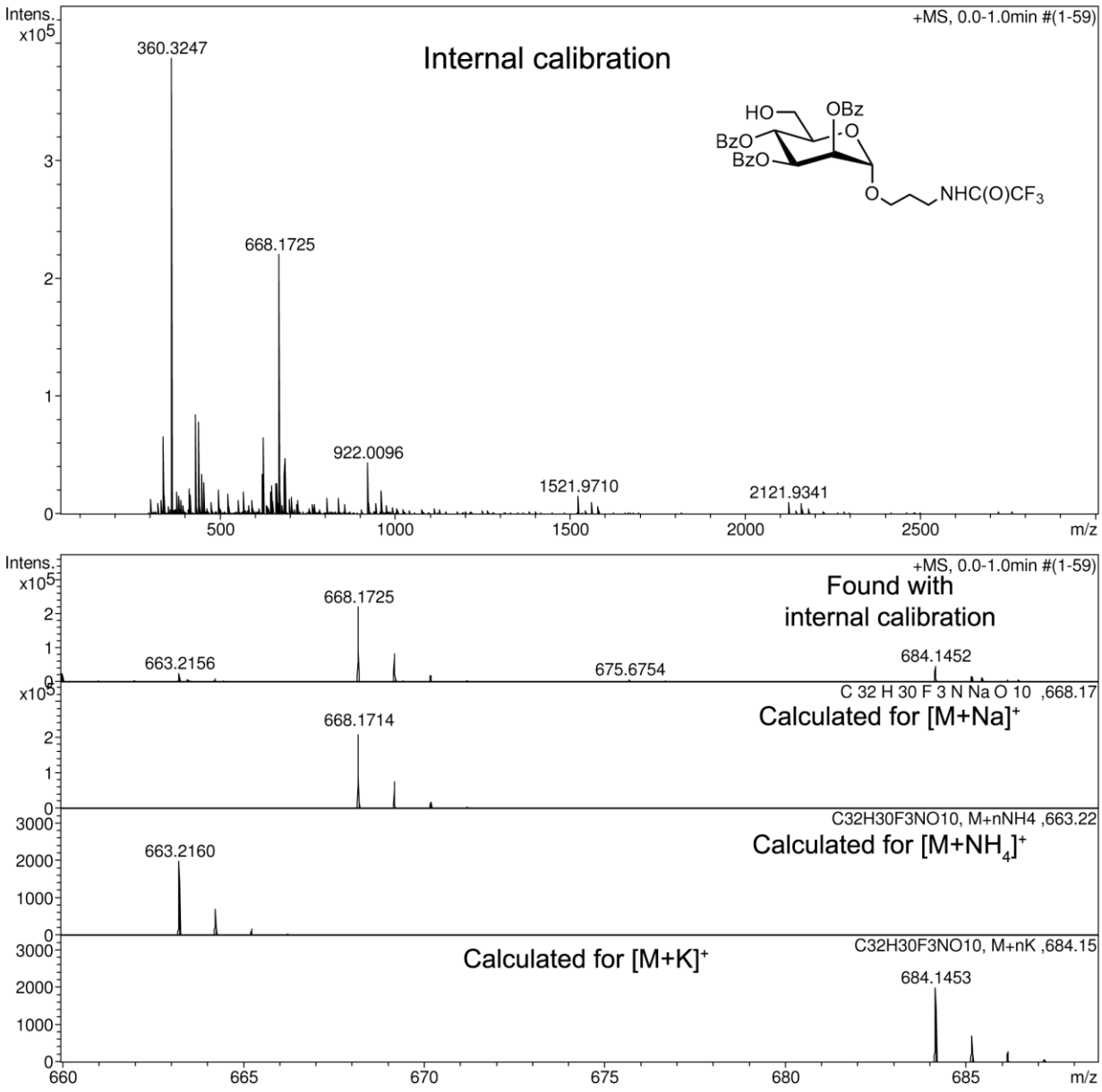
3-trifluoroacetamidopropyl 2,3,4-tri-O-benzoyl-α-D-mannopyranoside (3)





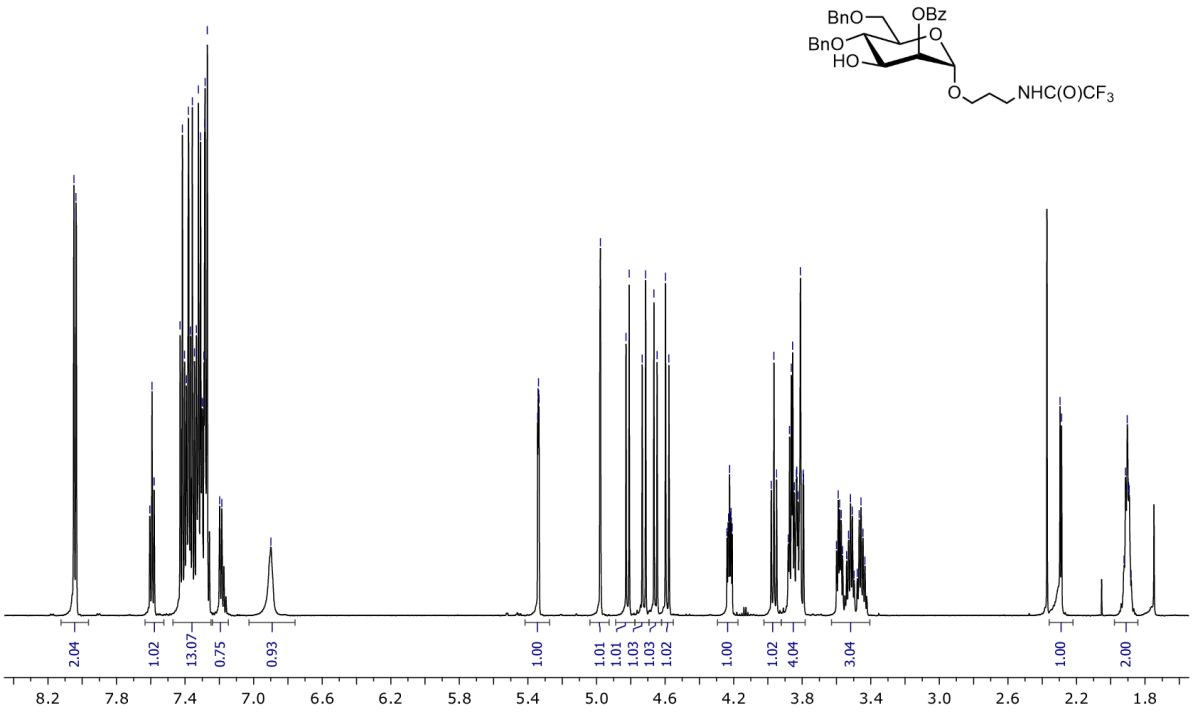
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	1200.0 Vpp	Set Divert Valve	Waste

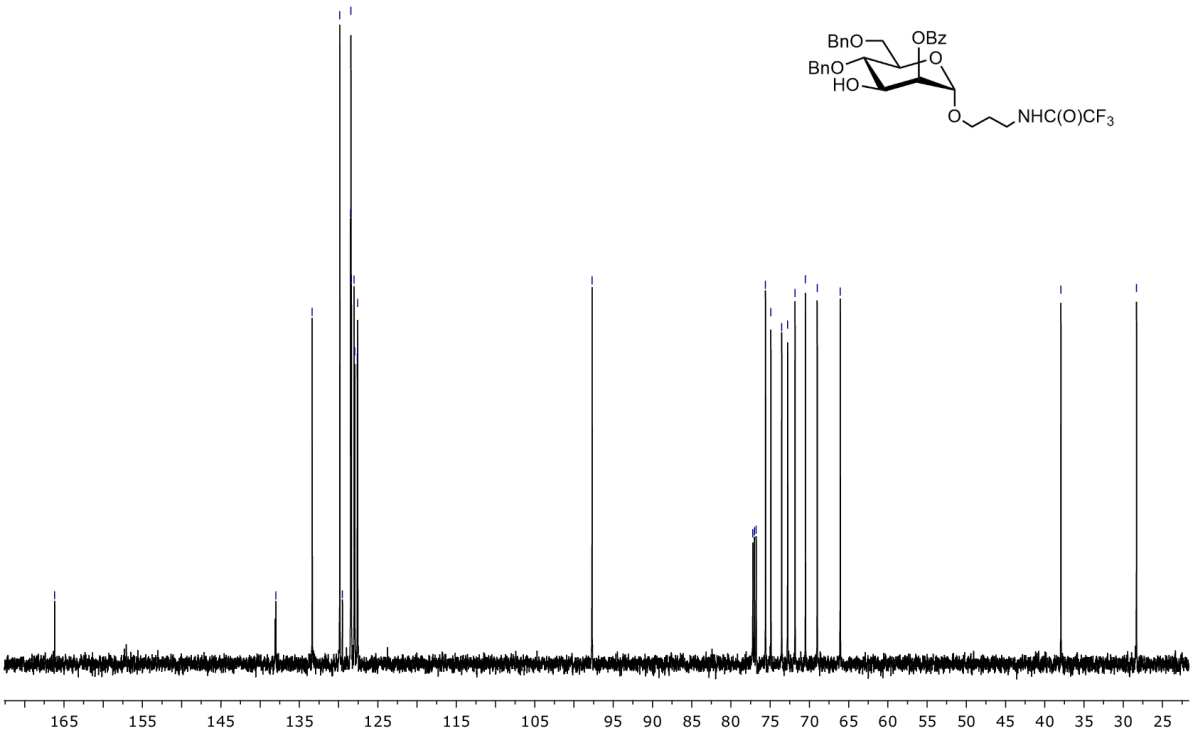


3-trifluoroacetamidopropyl 2-O-benzoyl-4,5-di-O-benzyl-α-D-mannopyranoside (4)

1H NMR (600.13 MHz), CDCl3, 303.0 K

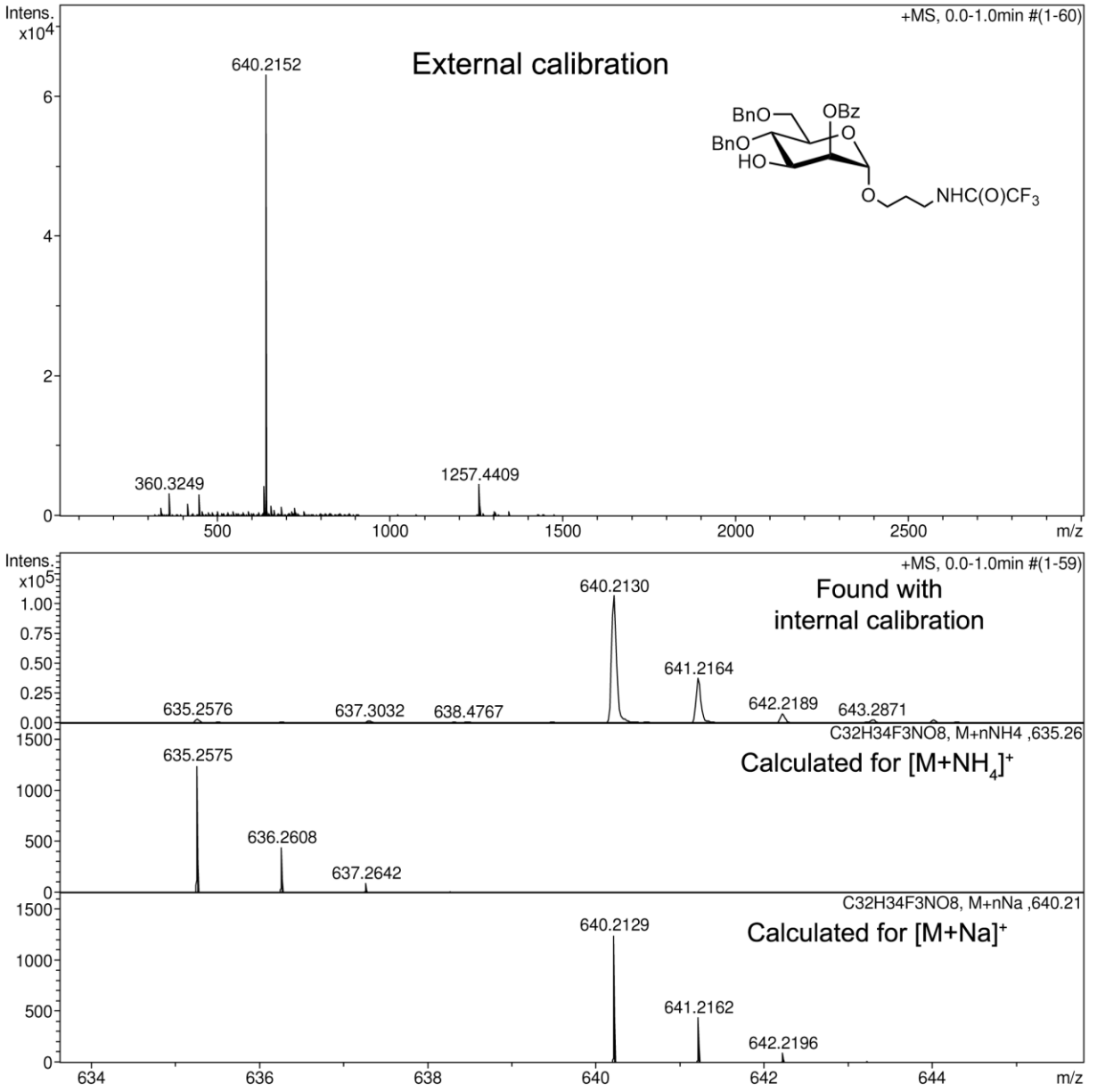


13C NMR (150.92 MHz), CDCl3, 303.2 K

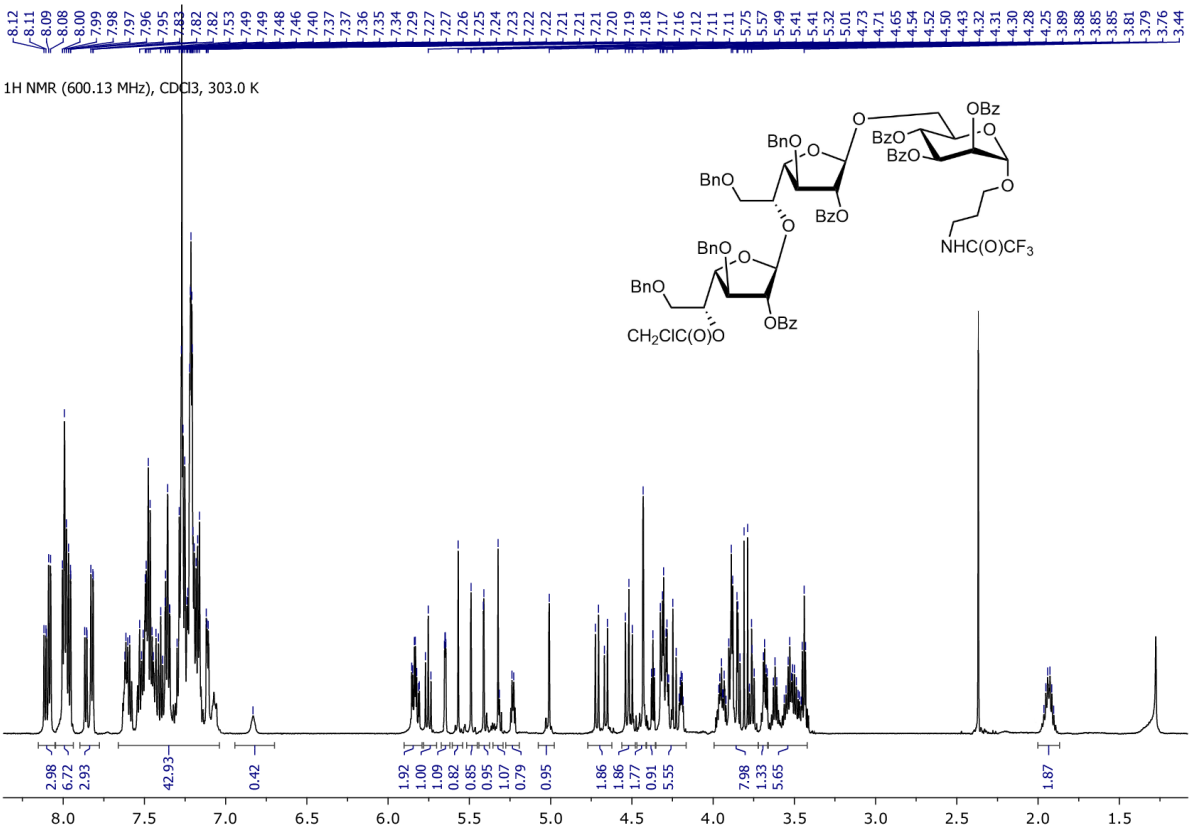


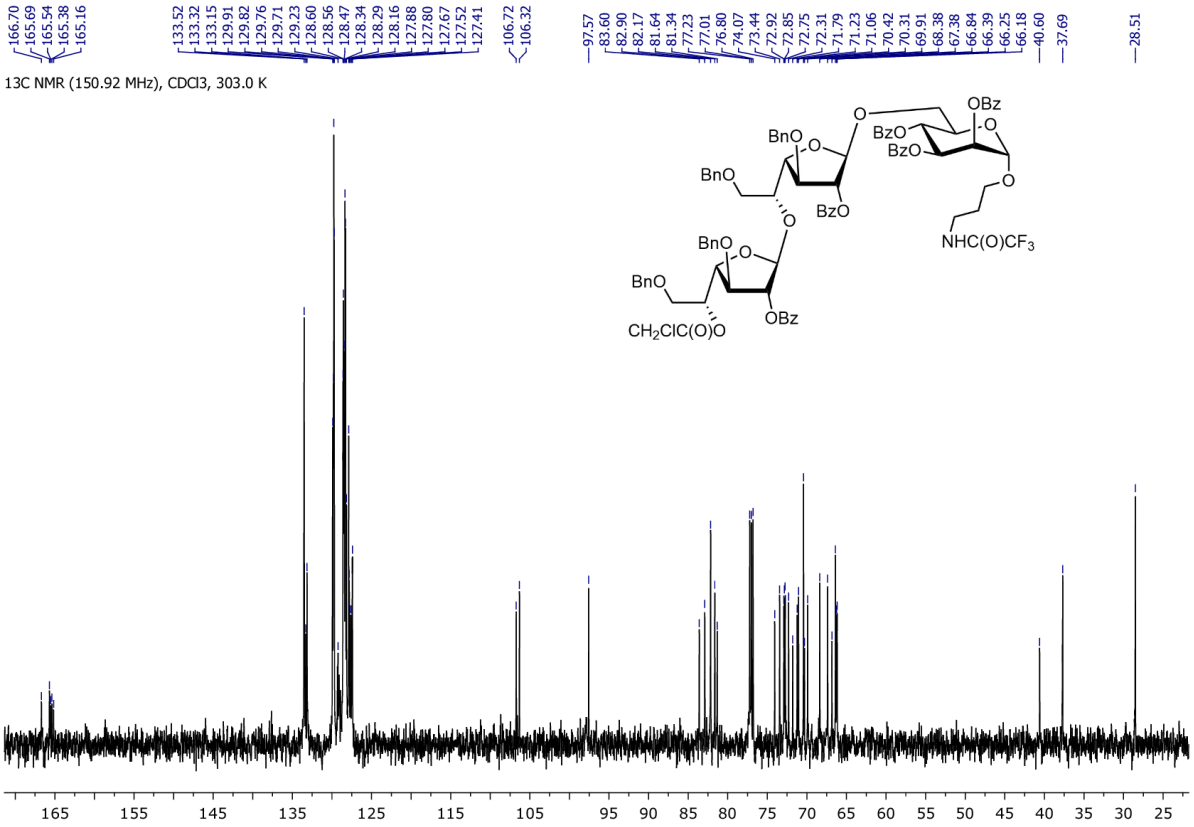
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not 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



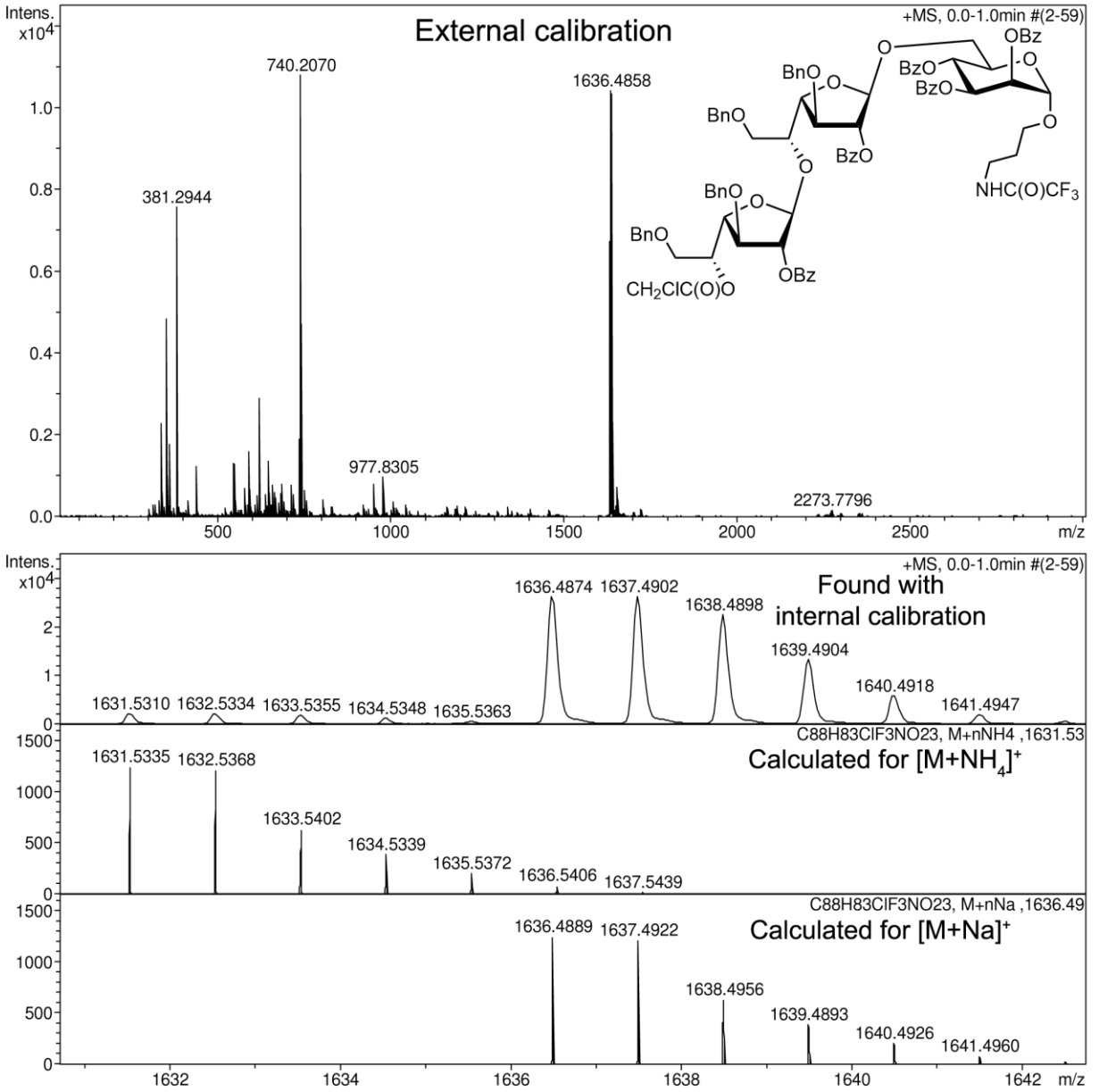
3-trifluoroacetamidopropyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (25)



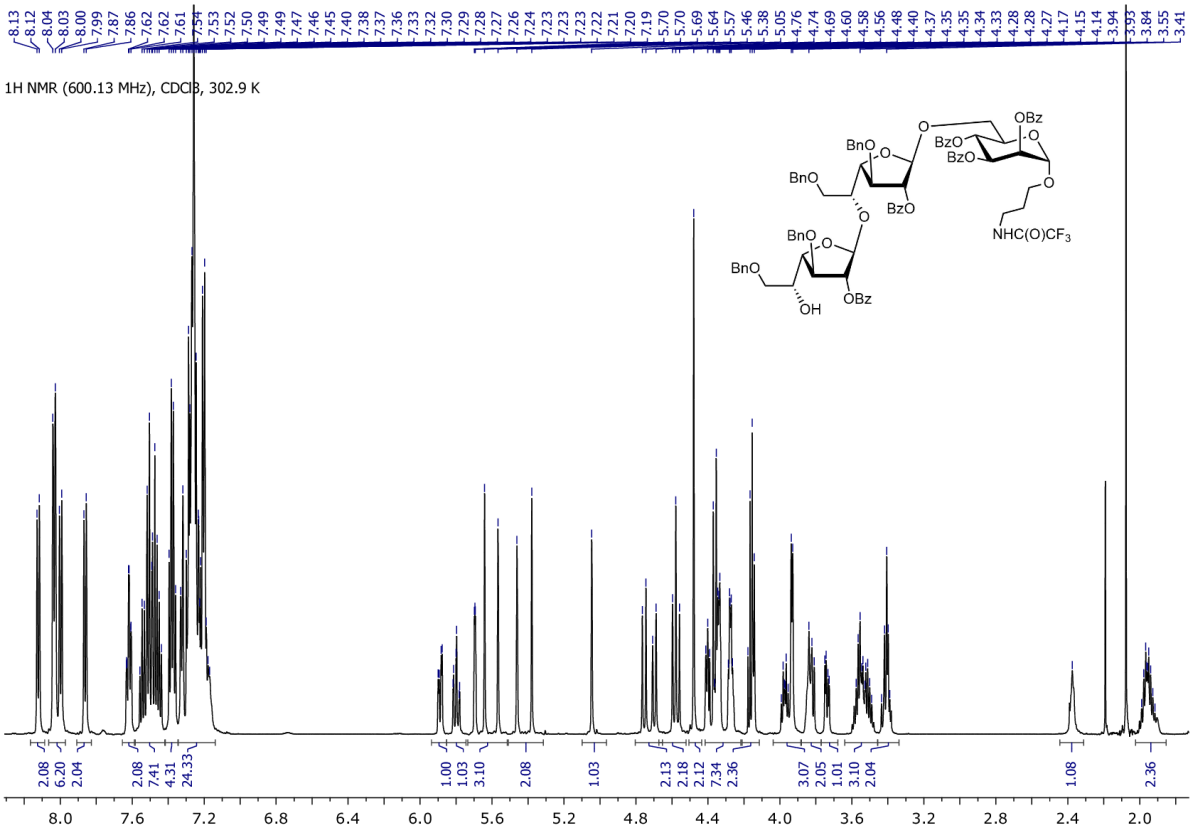


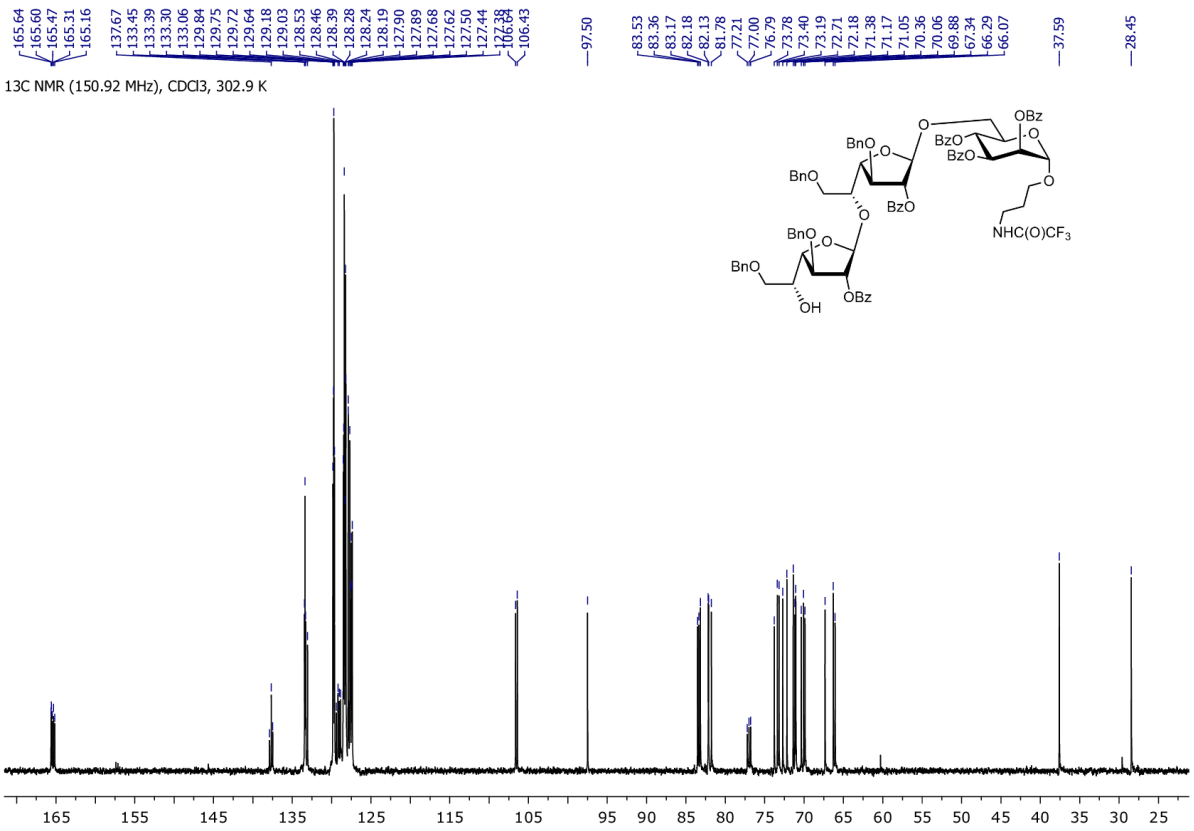
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not 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



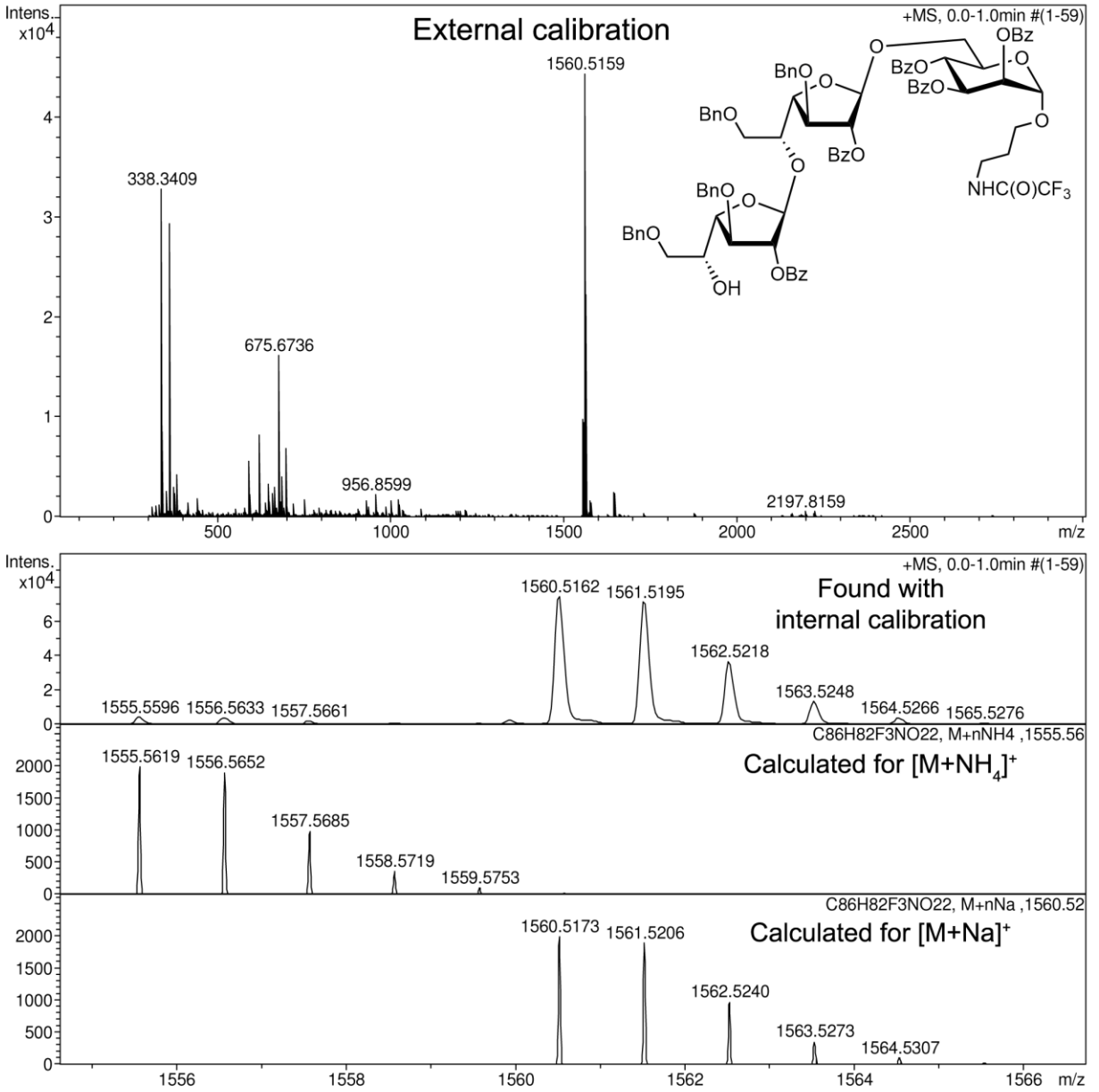
3-trifluoroacetamidopropyl 2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (26)





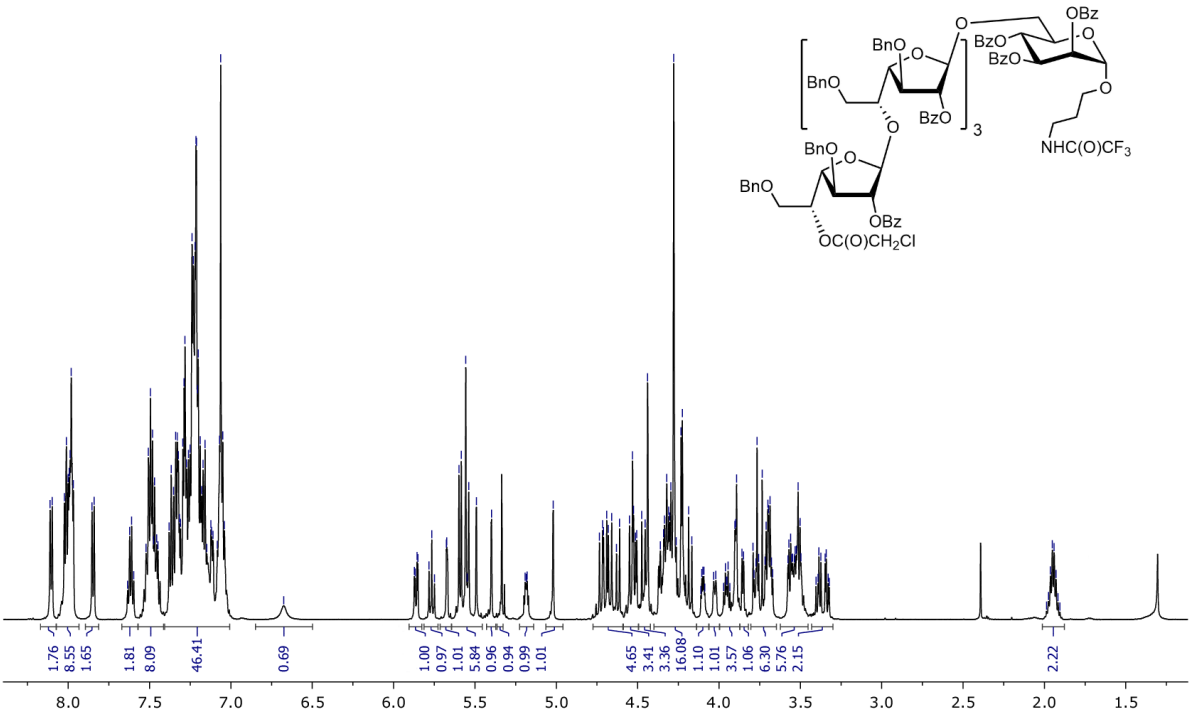
Acquisition Parameter

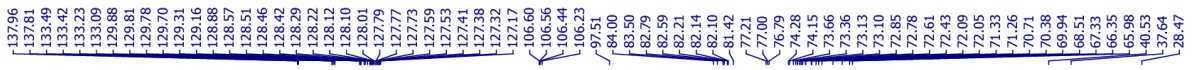
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



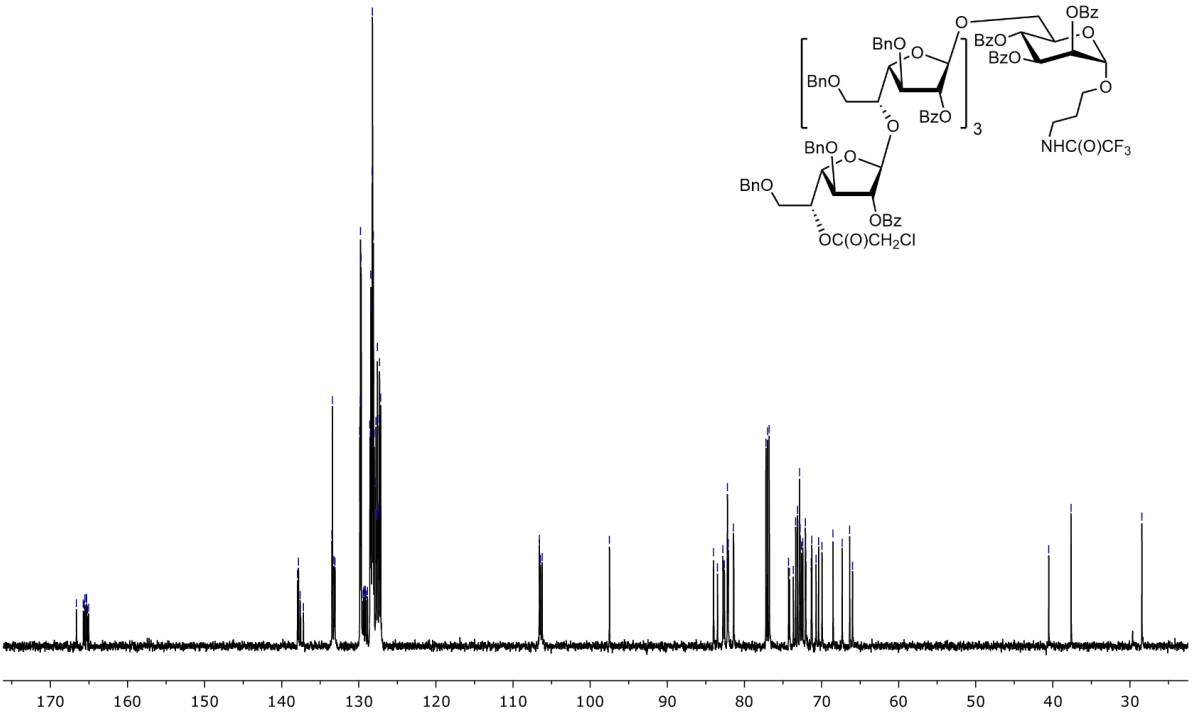
3-trifluoroacetamidopropyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-O-benzoyl-α-D-mannopyranoside (27)

1H NMR (600.13 MHz), CDCl3, 303.0 K



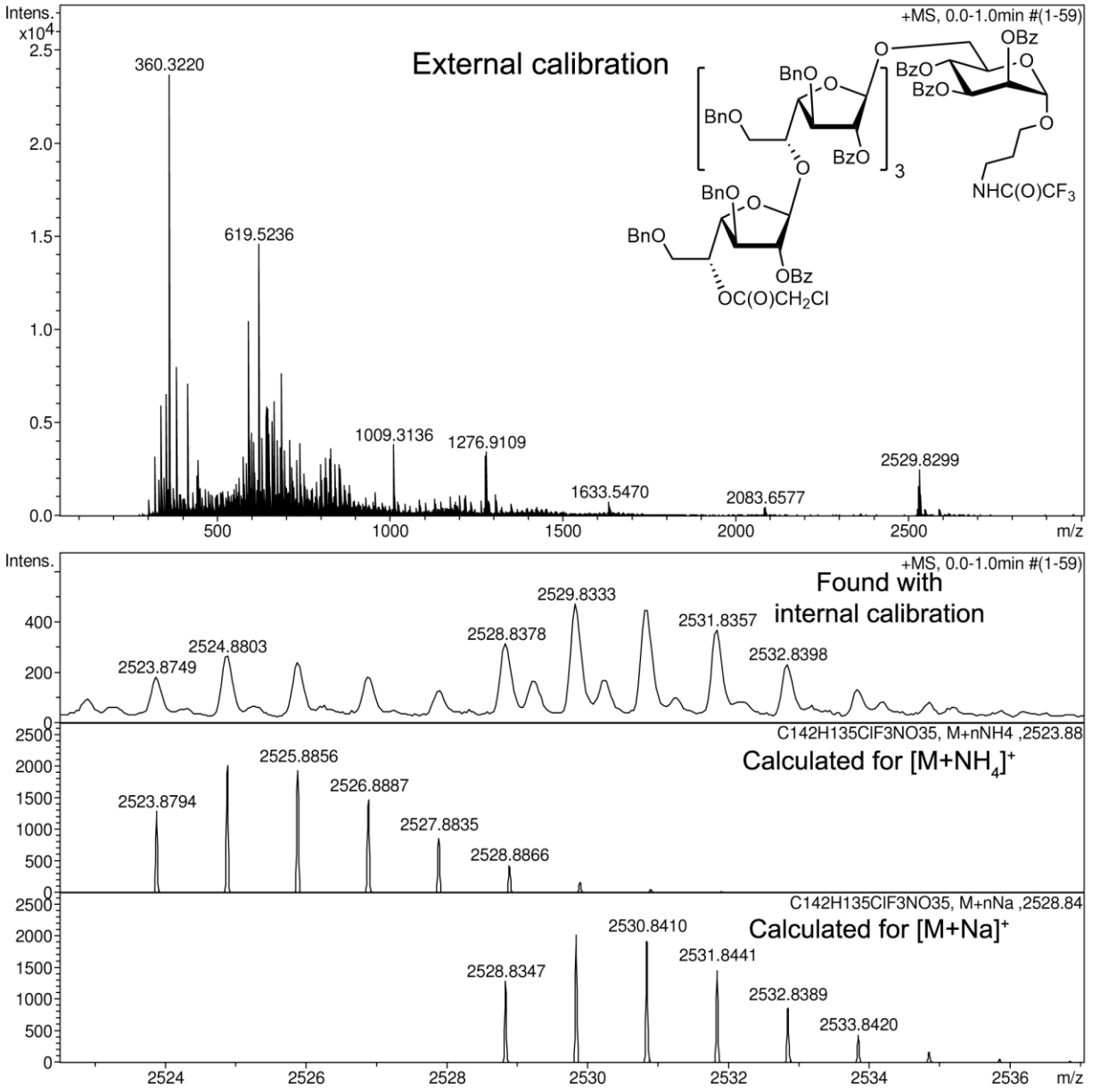


13C NMR (150.92 MHz), CDCl3, 303.1 K

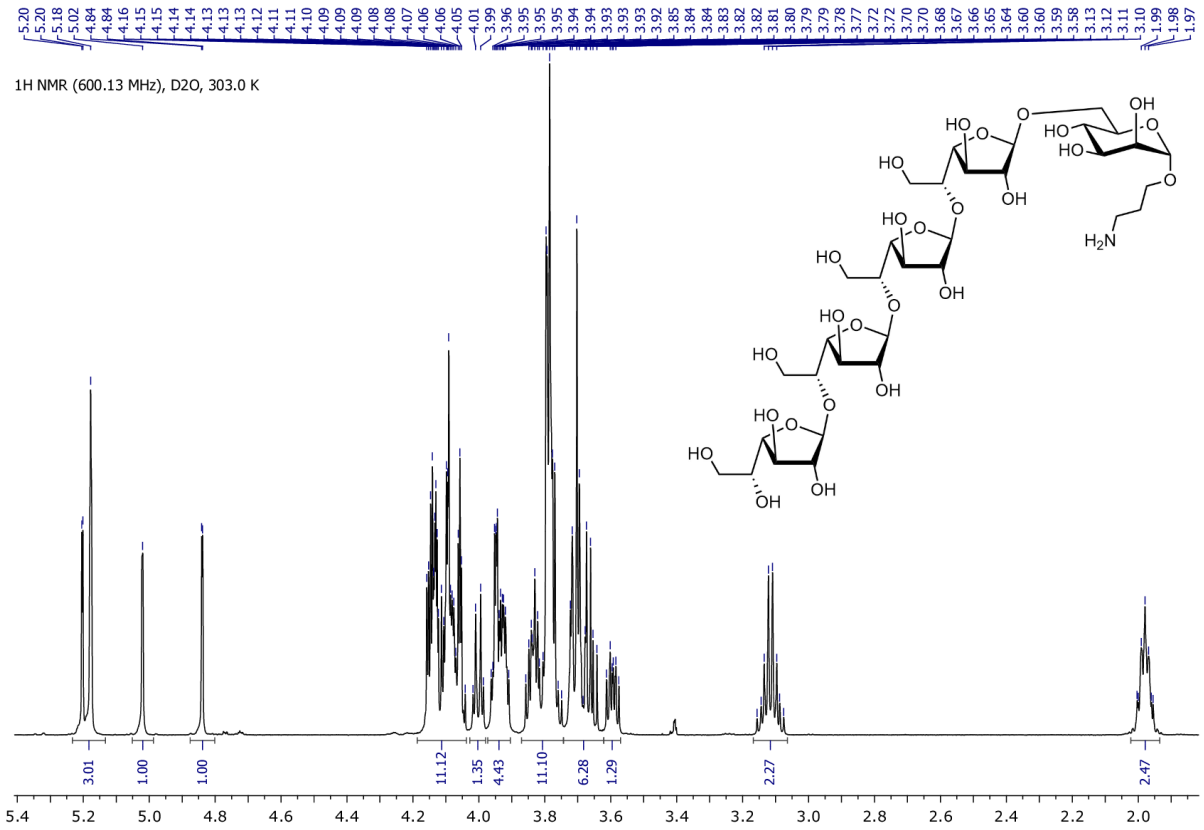


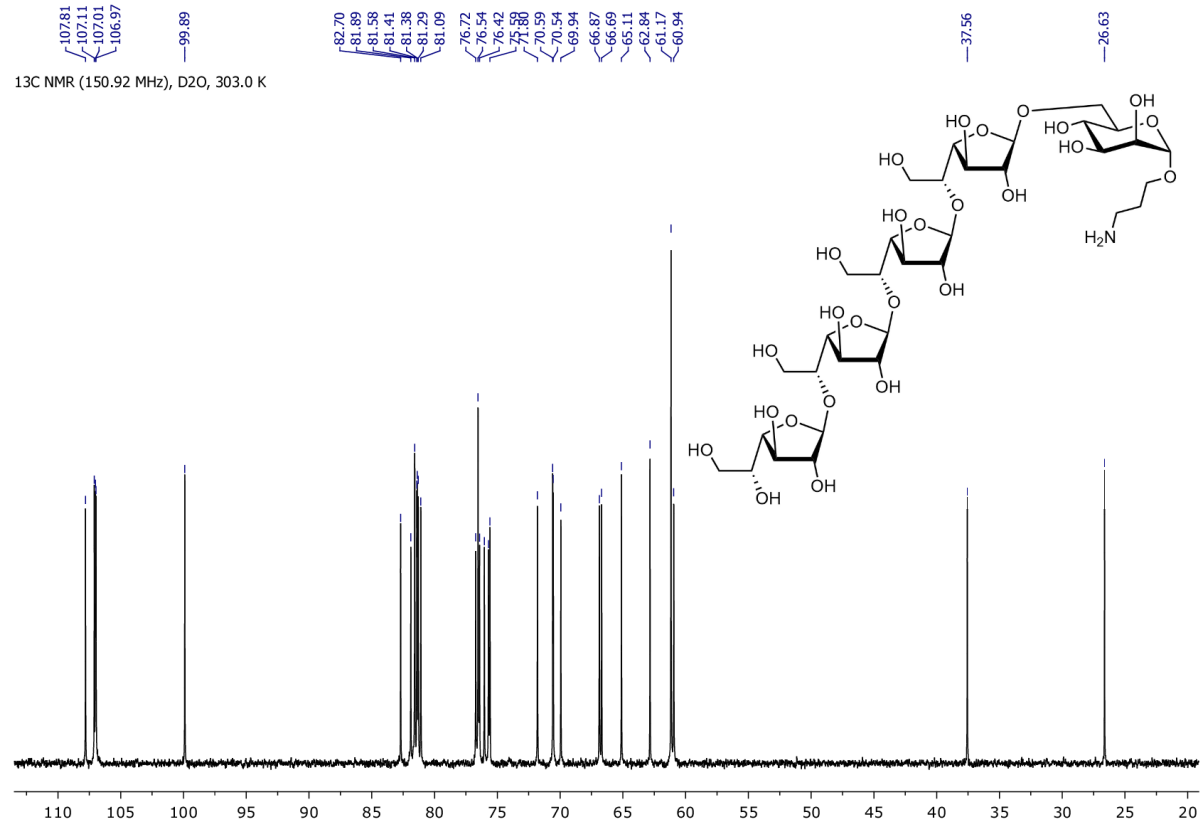
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not 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



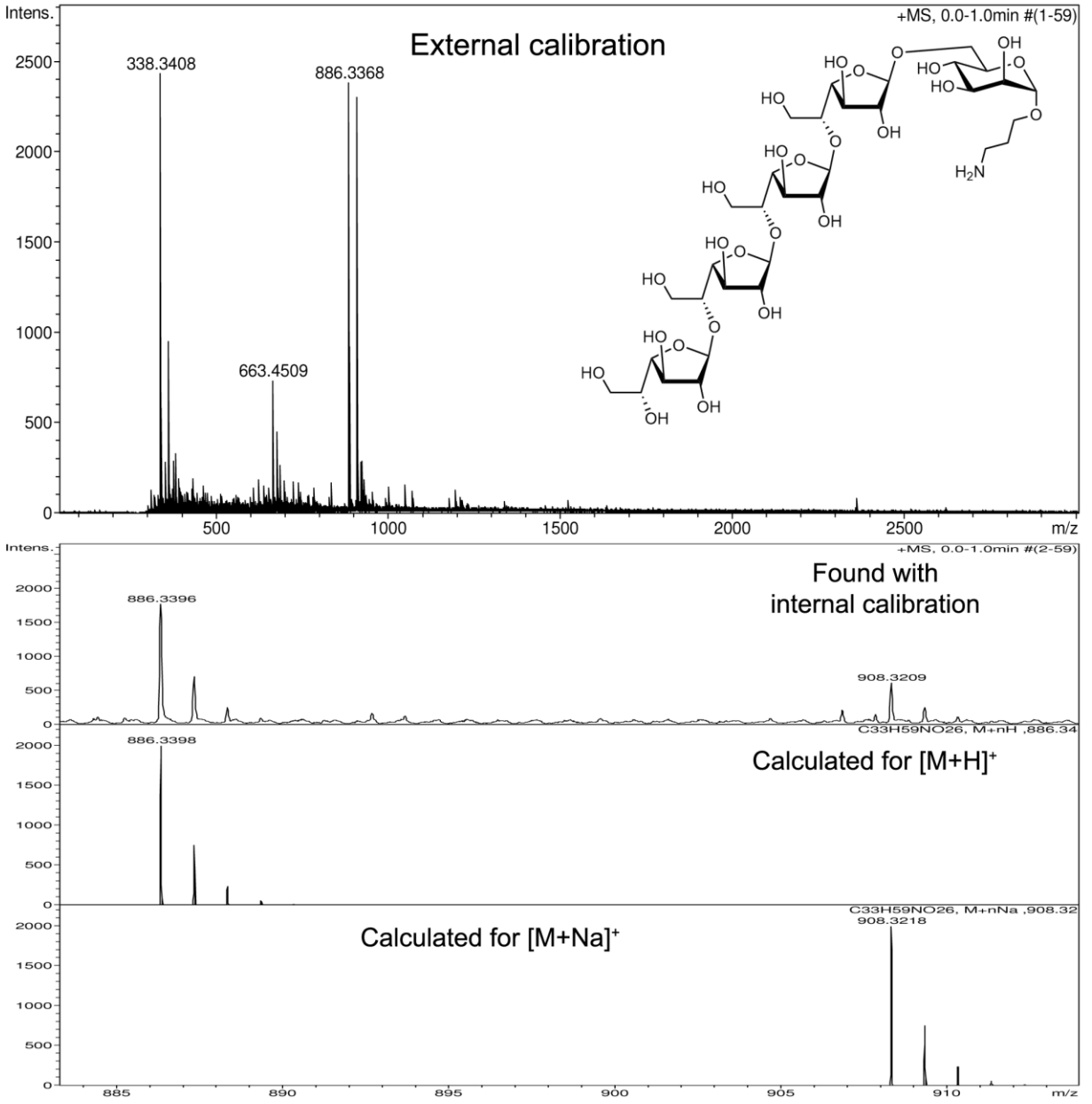
3-aminopropyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→6)-α-D-mannopyranoside (1)



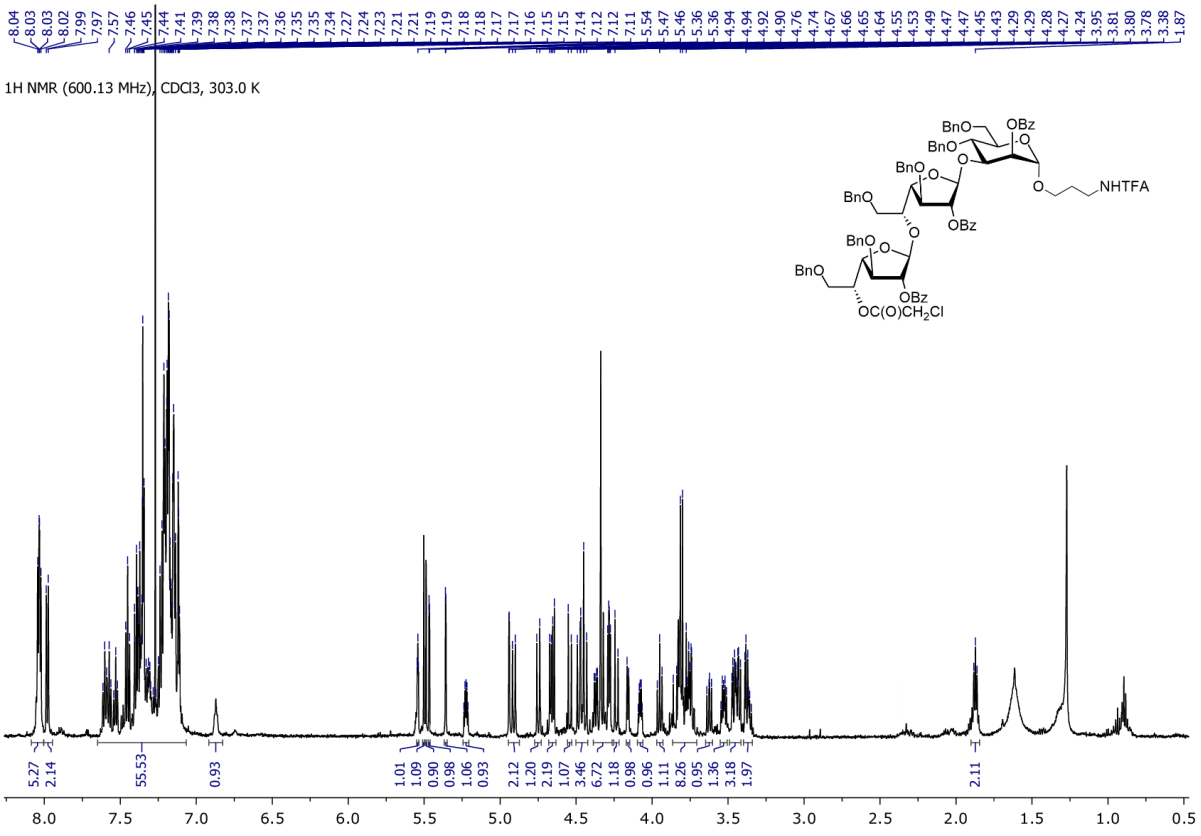


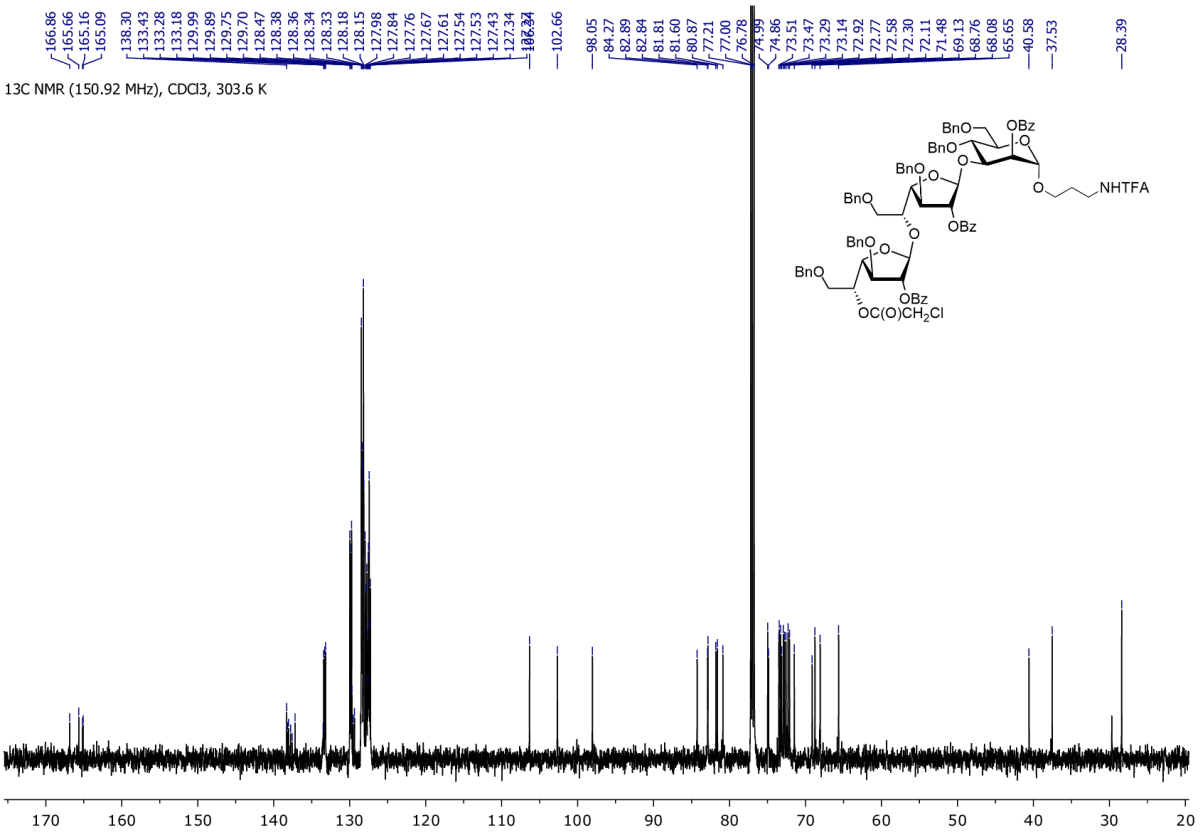
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not 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



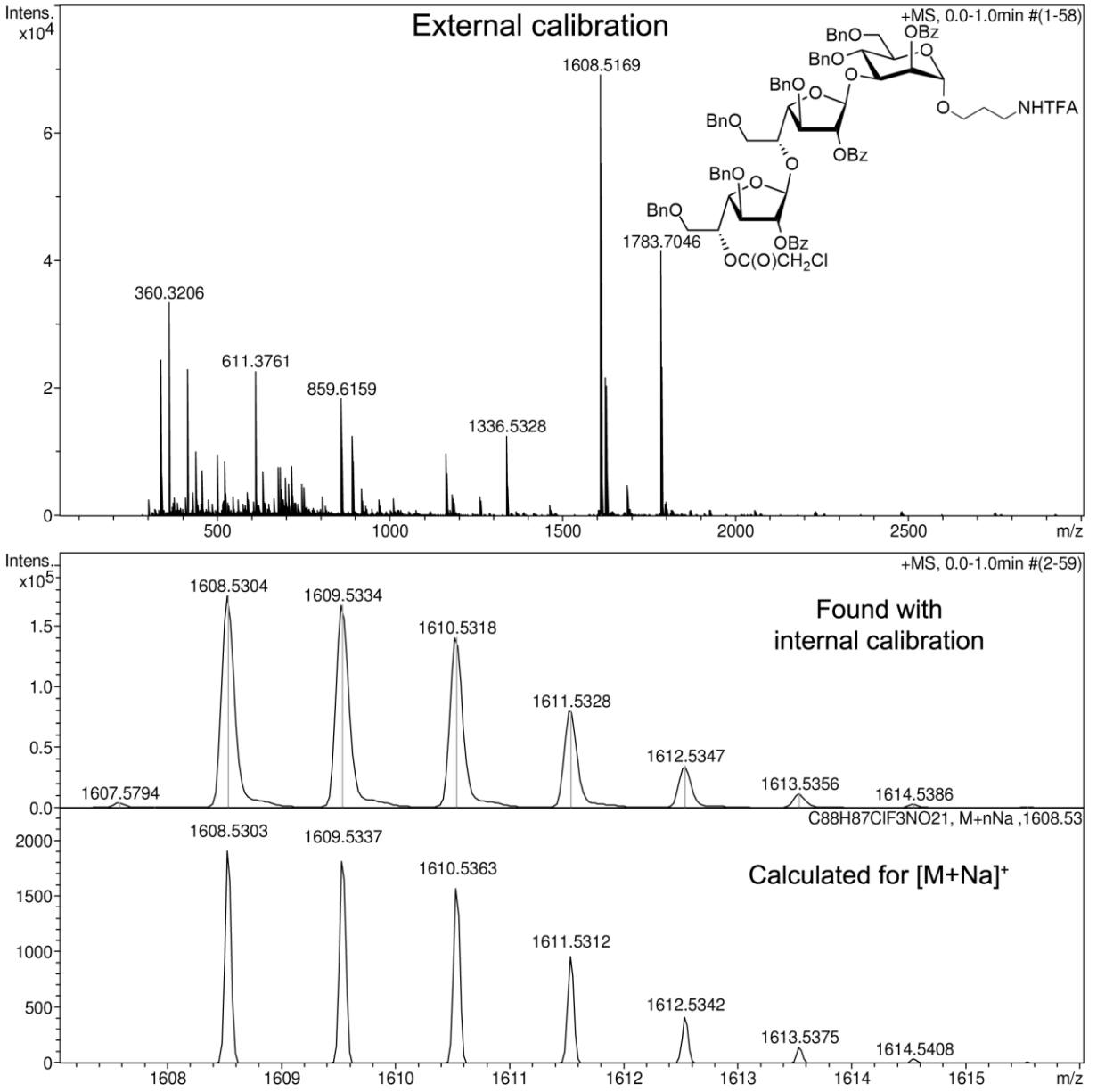
3-trifluoroacetamidopropyl 2-O-benzoyl-3,6-di-O-benzyl-5-O-chloroacetyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-α-D-mannopyranoside (28)



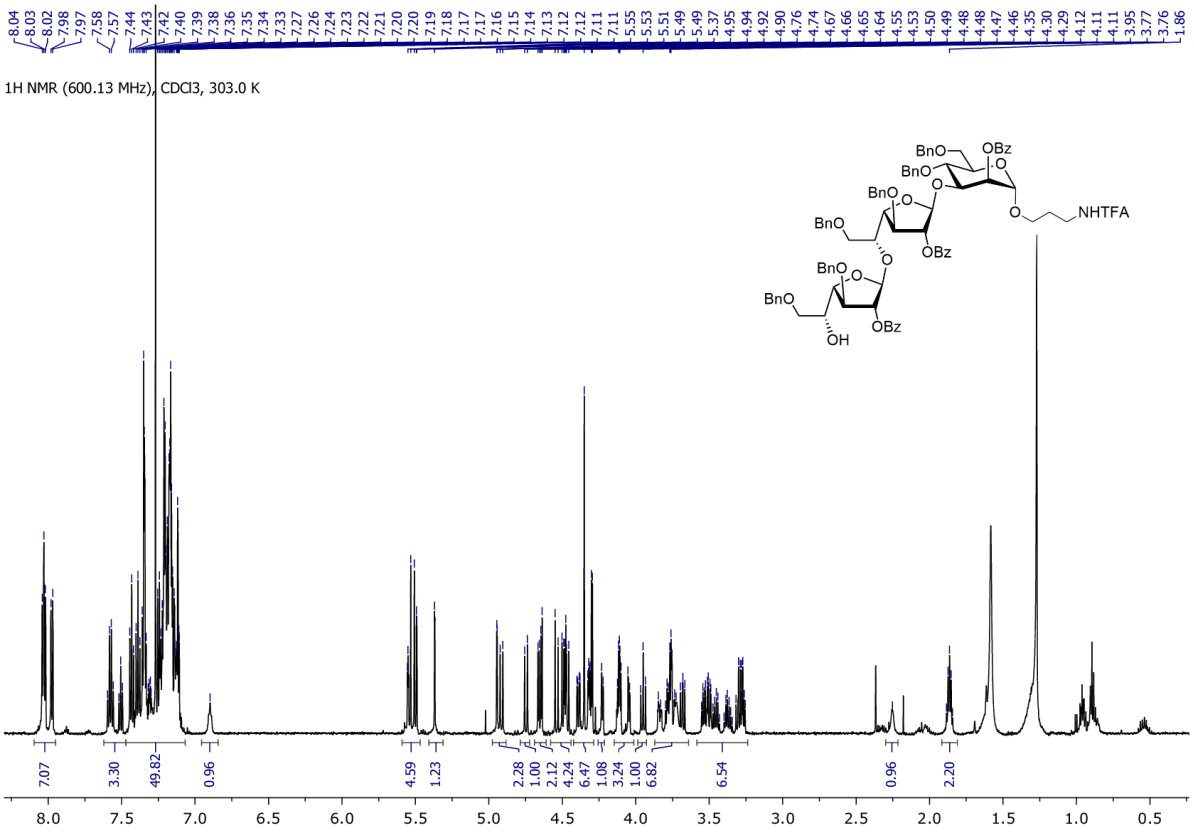


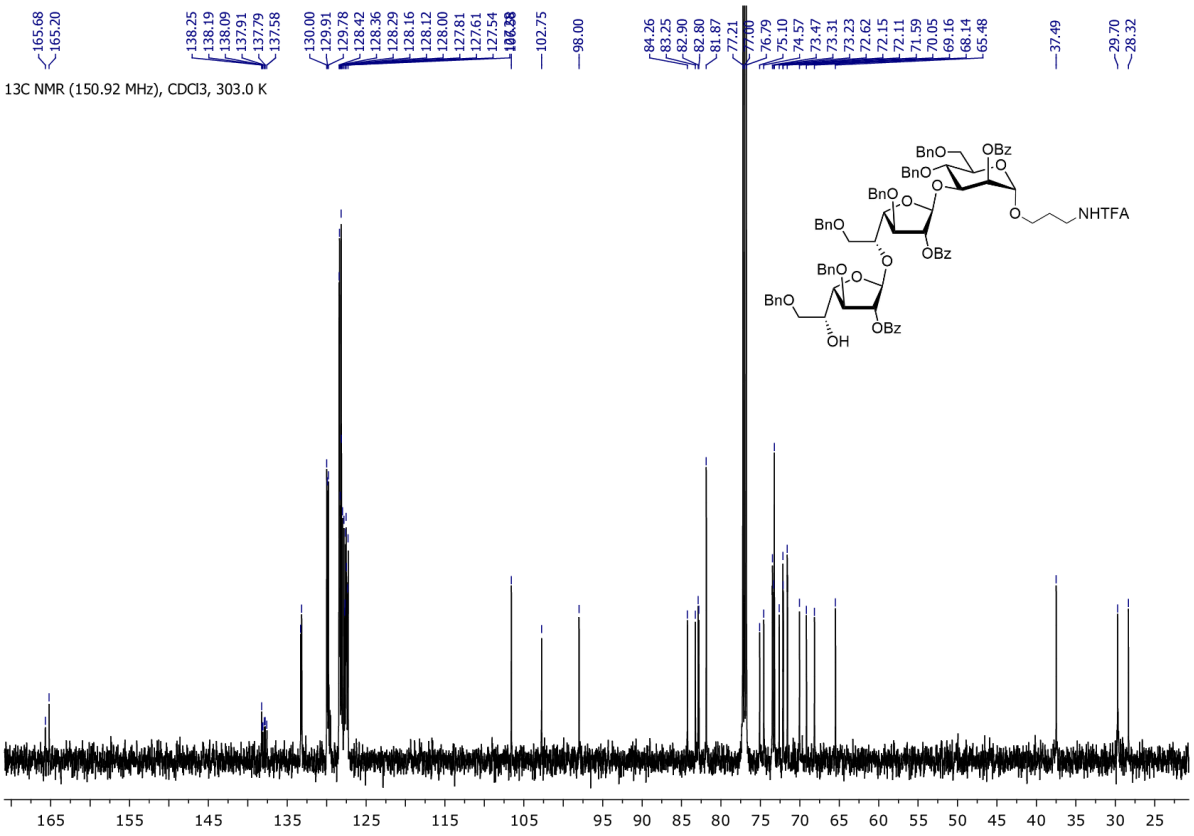
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not 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



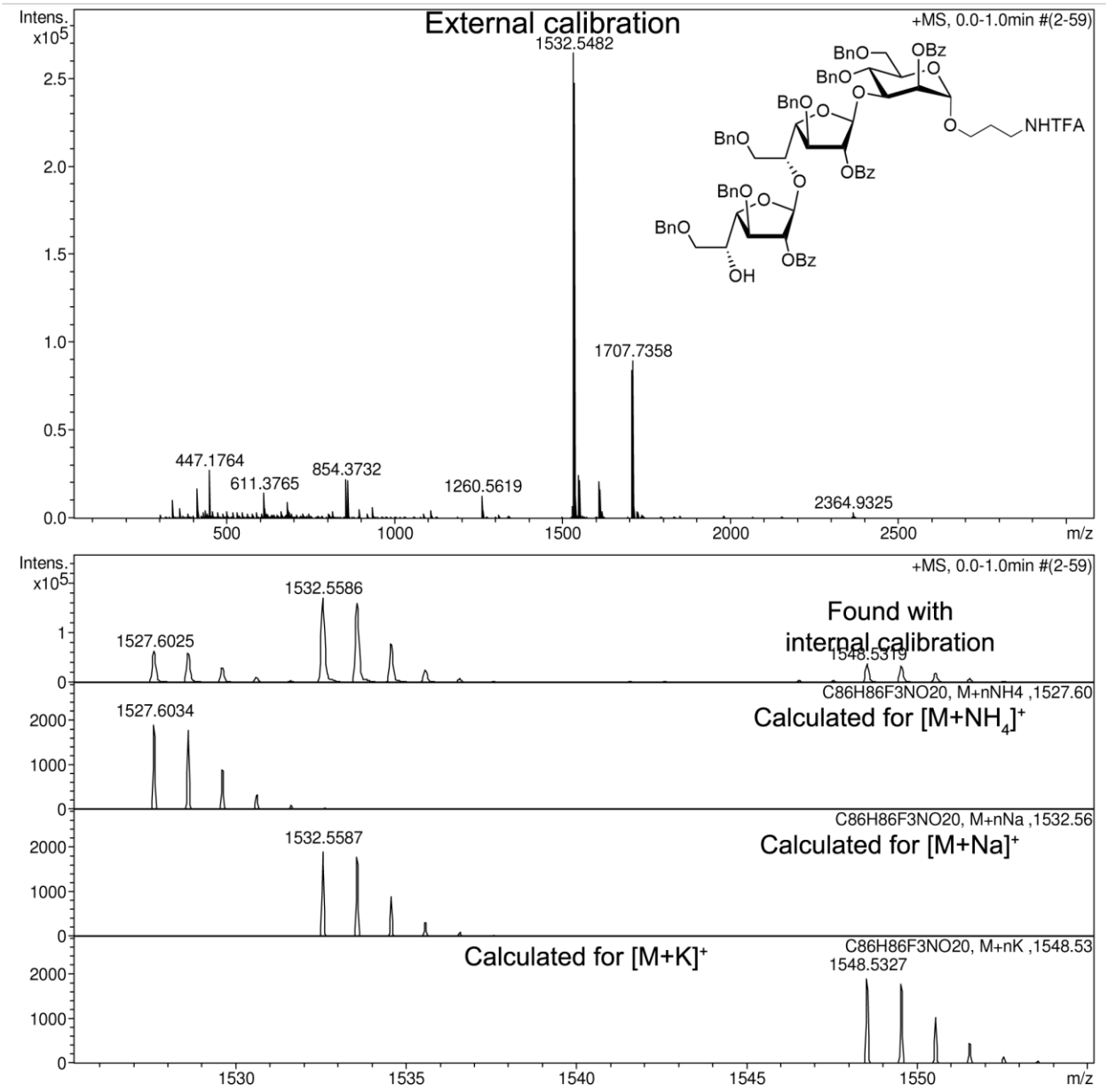
3-trifluoroacetamidopropyl 2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-α-D-mannopyranoside (29)



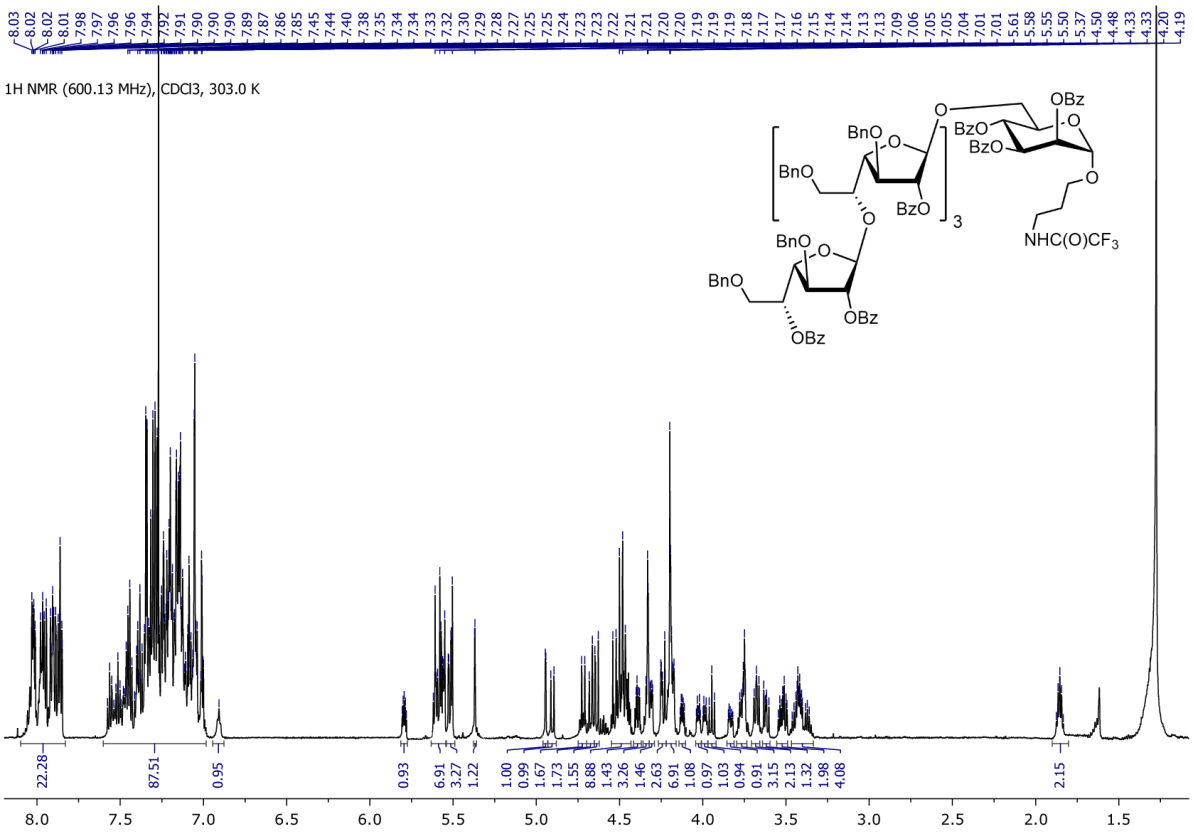


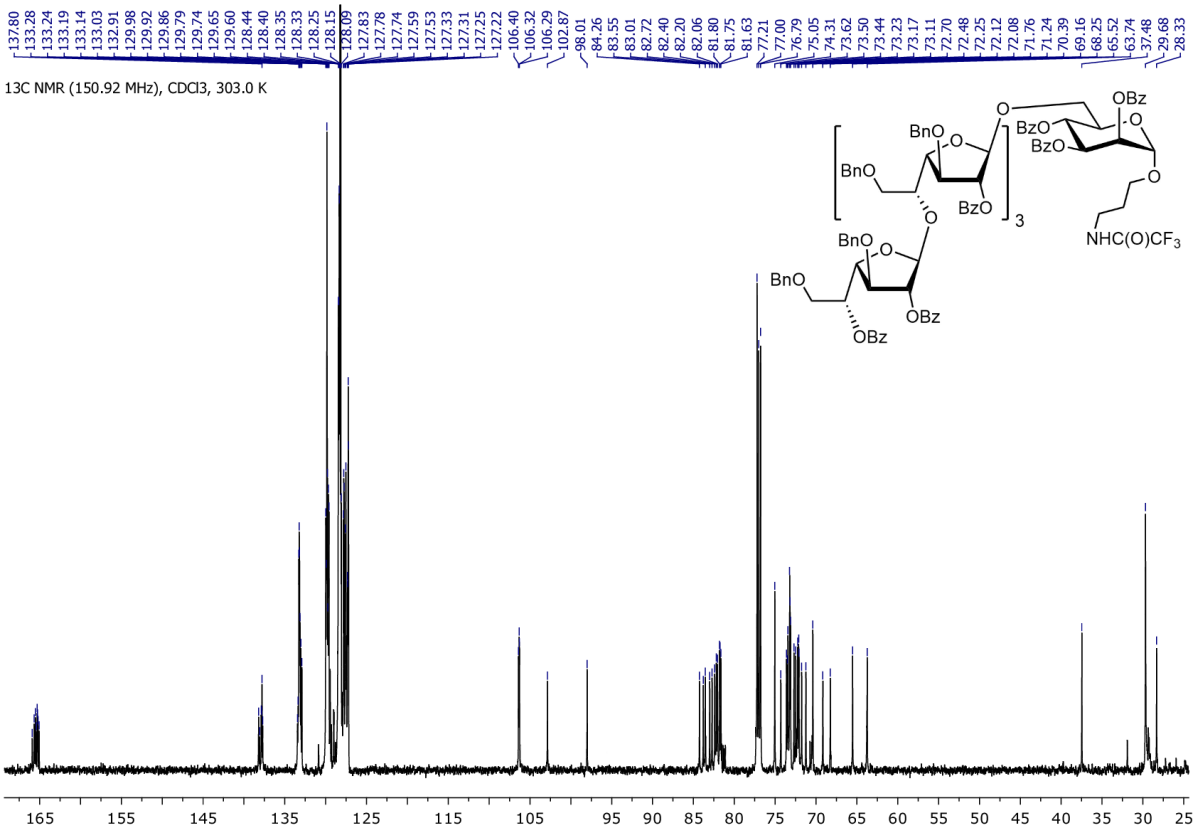
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not 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



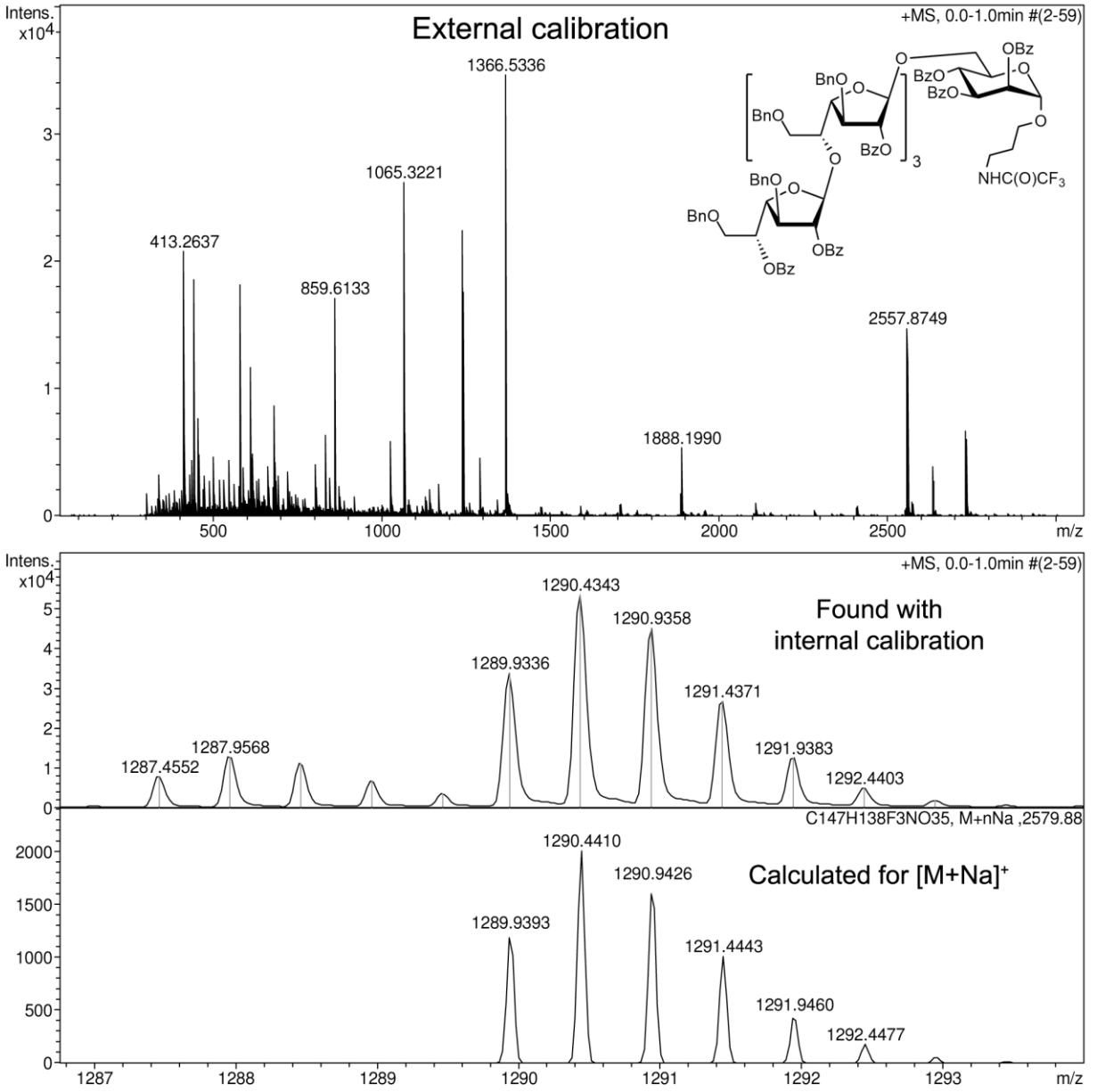
3-trifluoroacetamidopropyl 2,3,5,6-tetra-O-benzoyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→5)-2-O-benzoyl-3,6-di-O-benzyl-β-D-galactofuranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-α-D-mannopyranoside (30)



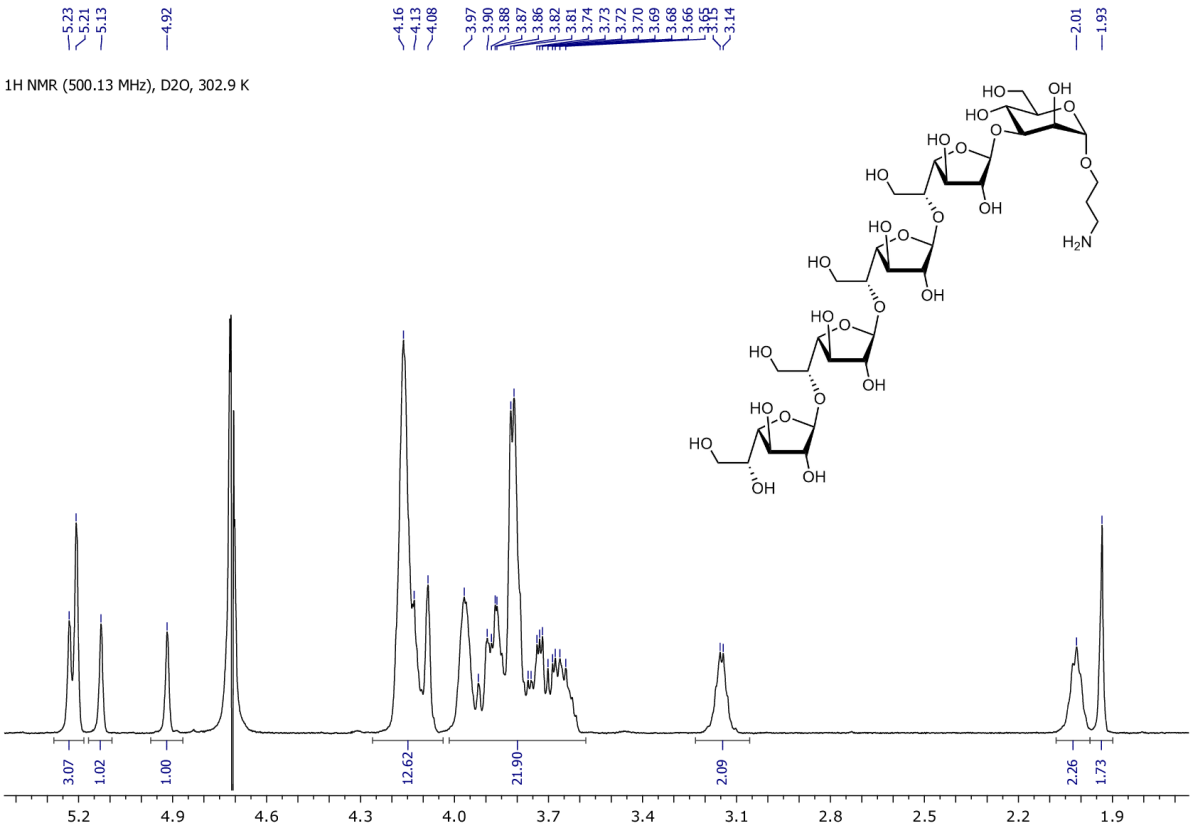


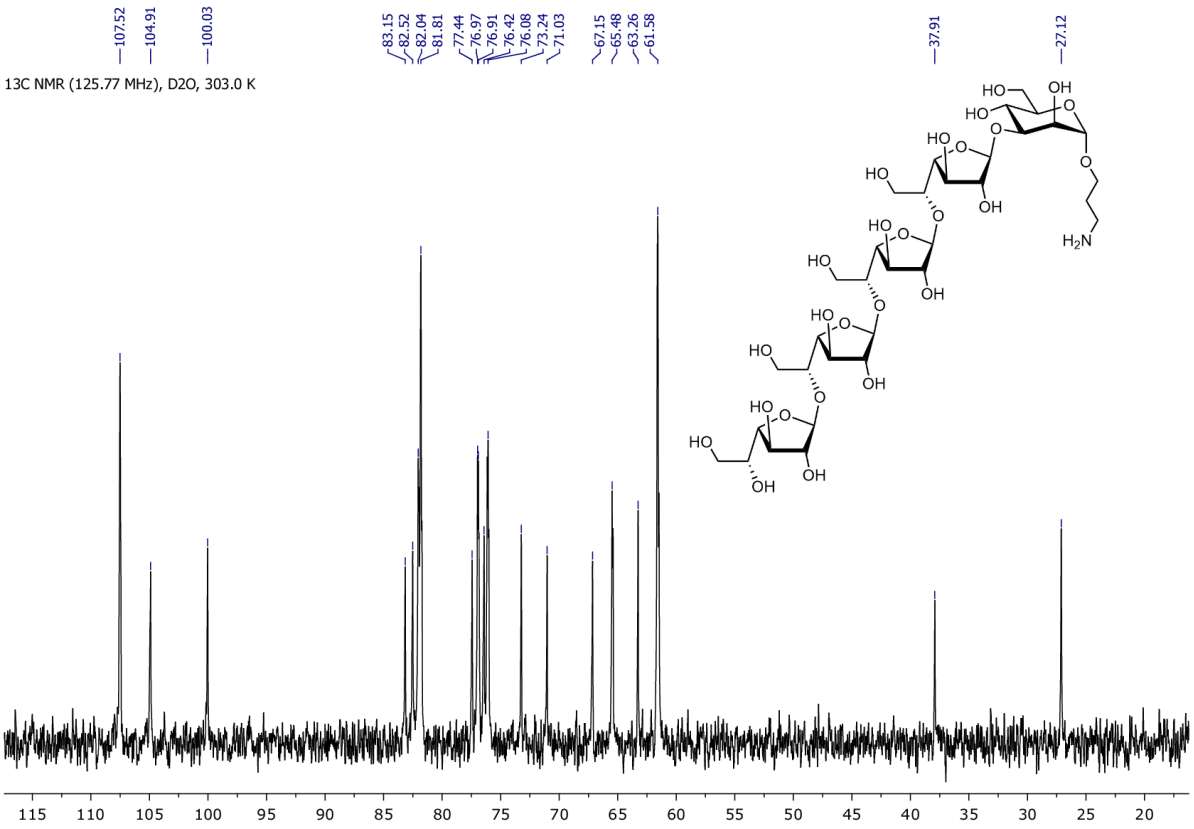
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not 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



3-aminopropyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→3)-α-D-mannopyranoside (2)





Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	1200.0 Vpp	Set Divert Valve	Waste