Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

The synthesis of heterosaccharides related to the fucoidan from *Chordaria flagelliformis* bearing L-fucofuranosyl unit

Dmitry Z. Vinnitskiy, Vadim B. Krylov, Nadezhda E. Ustyuzhanina, Andrey S. Dmitrenok, Nikolay E. Nifantiev

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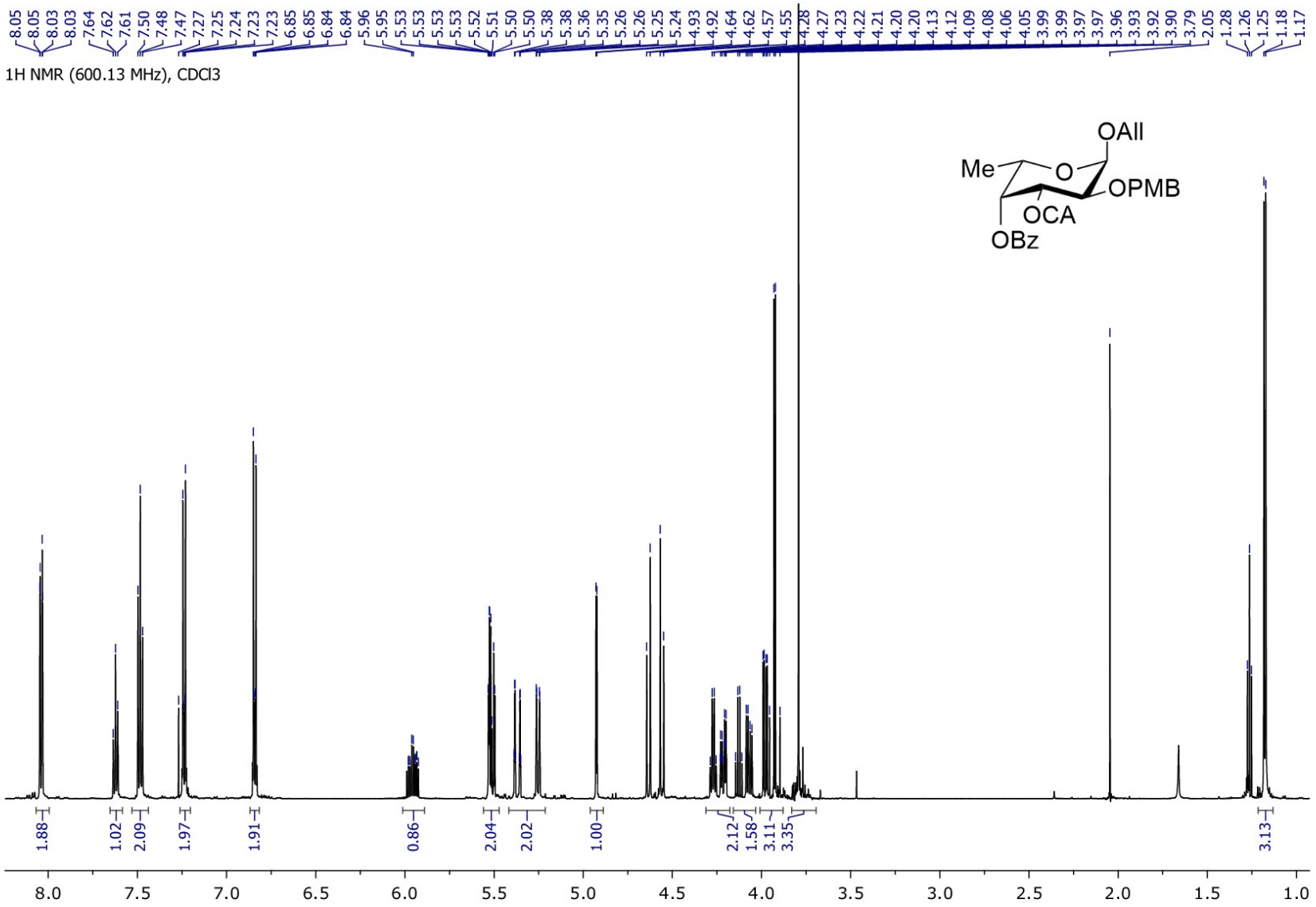
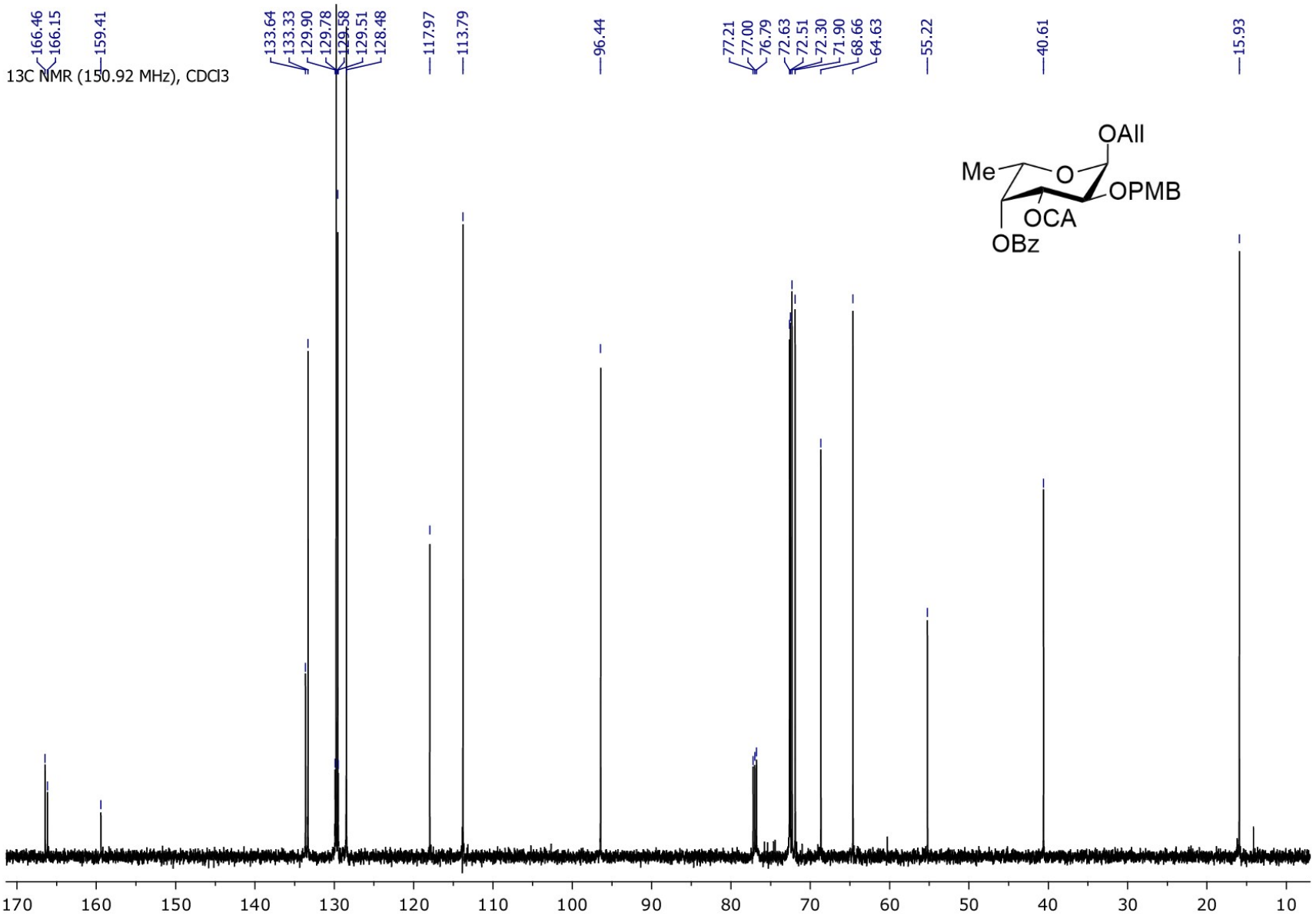
Allyl 2-*O*-*p*-methoxybenzyl-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranoside (12)




13C NMR (150.92 MHz), CDCl3
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166.15
159.41
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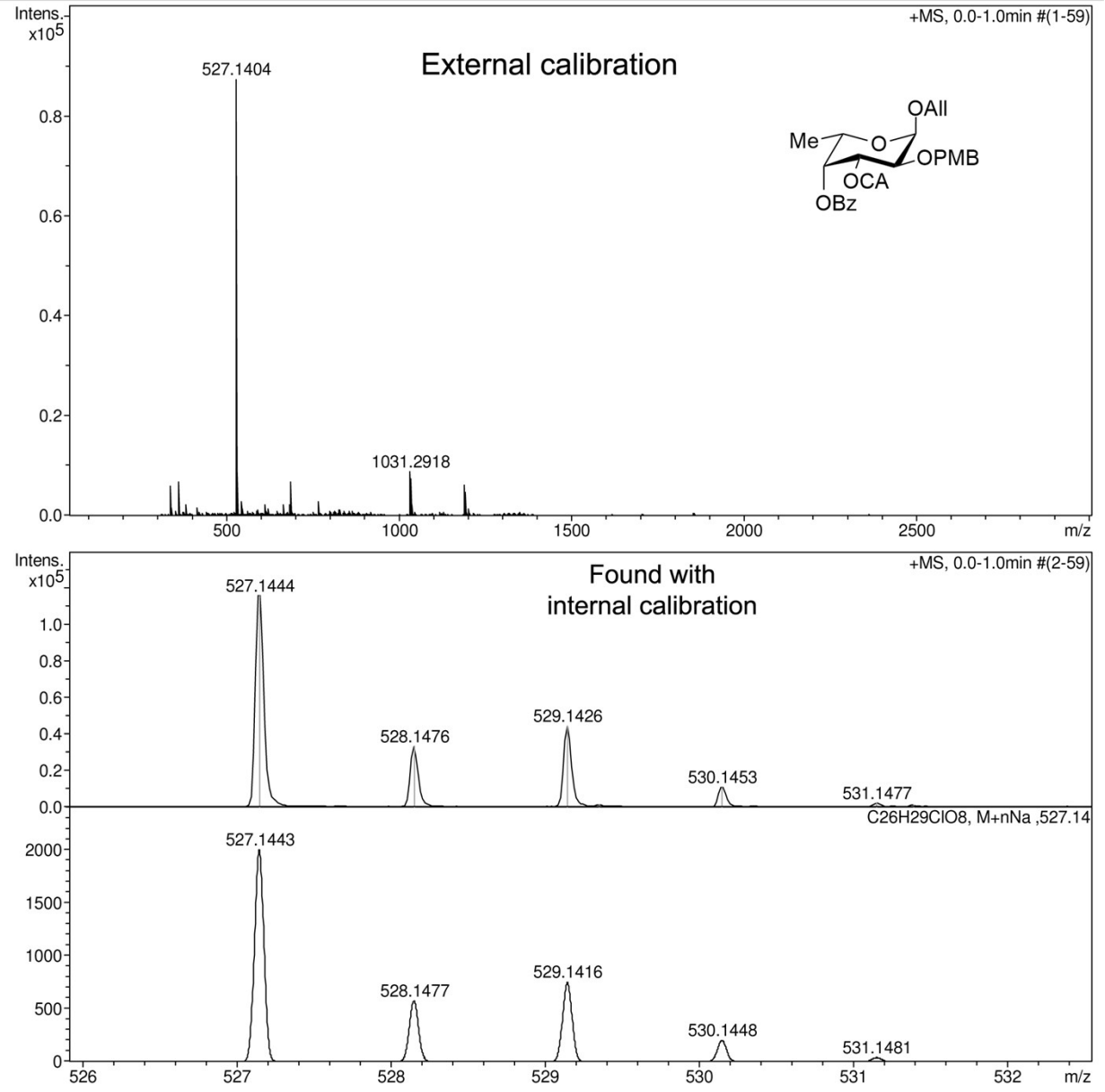
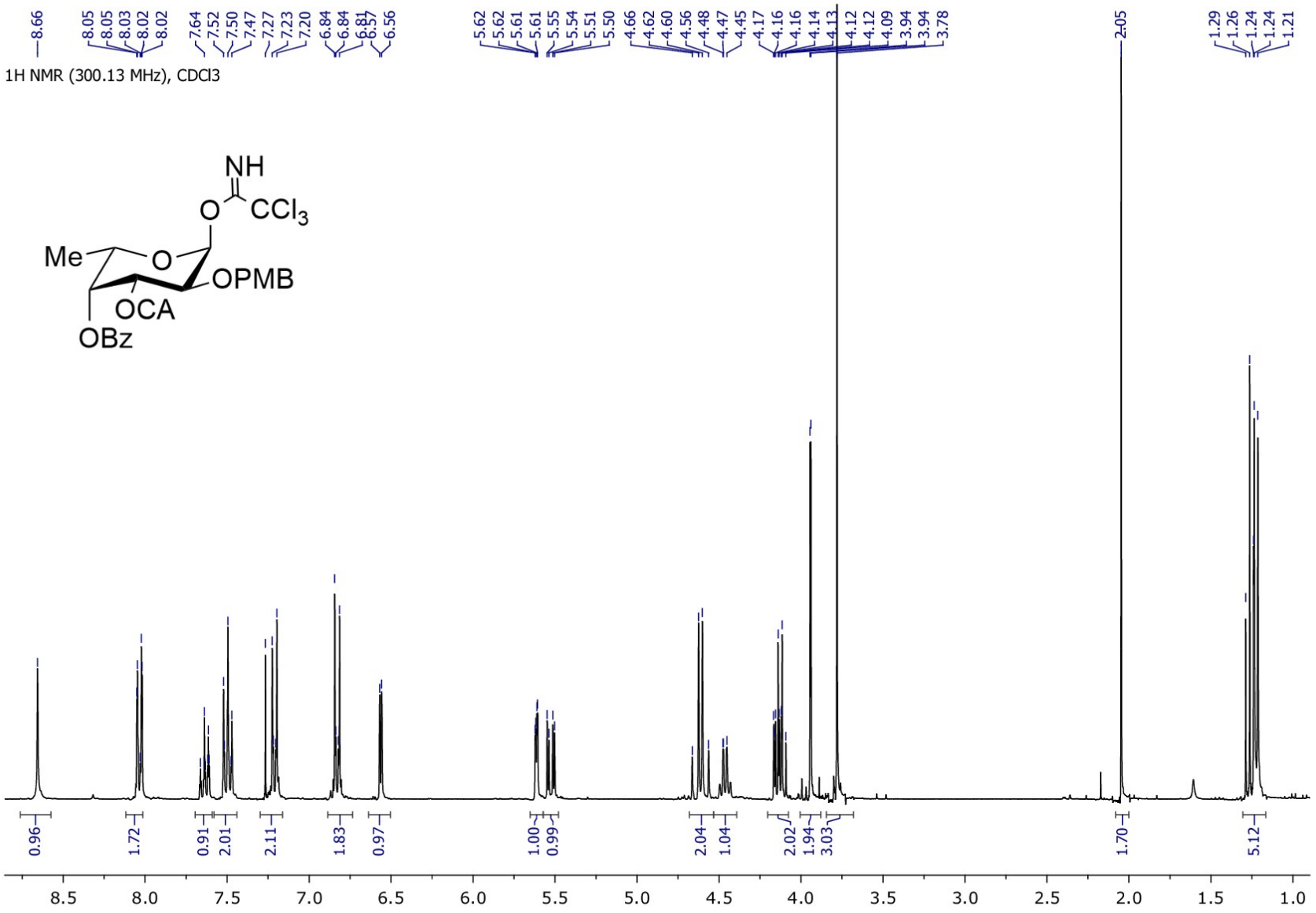
129.78
129.58
129.51
128.48
117.97
113.79
96.44
77.21
77.00
76.79
72.63
72.51
72.30
71.90
68.66
64.63
55.22
40.61
15.93
OAll
Me
O
OPMB
OCA
OBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

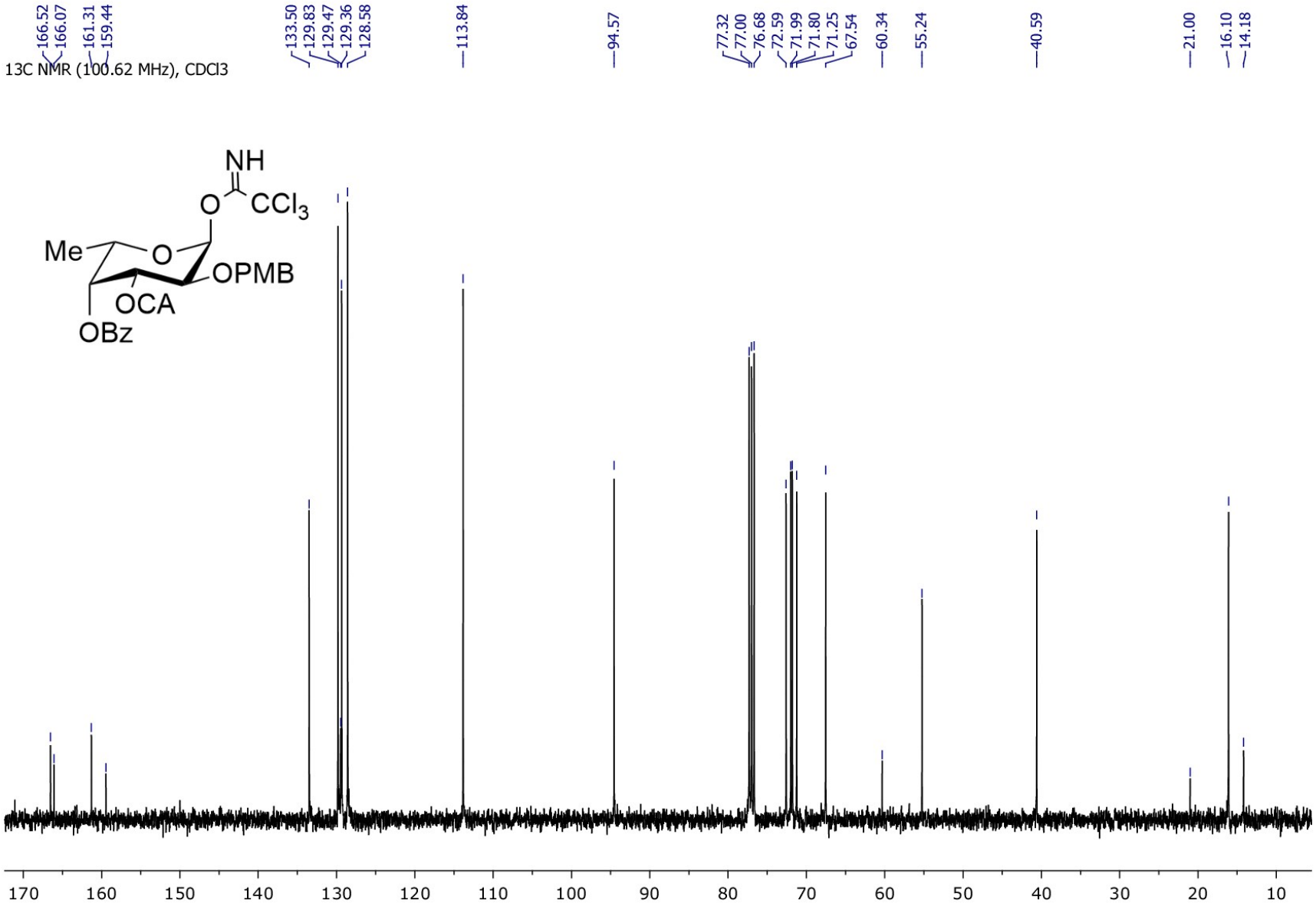
Acquisition Parameter

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



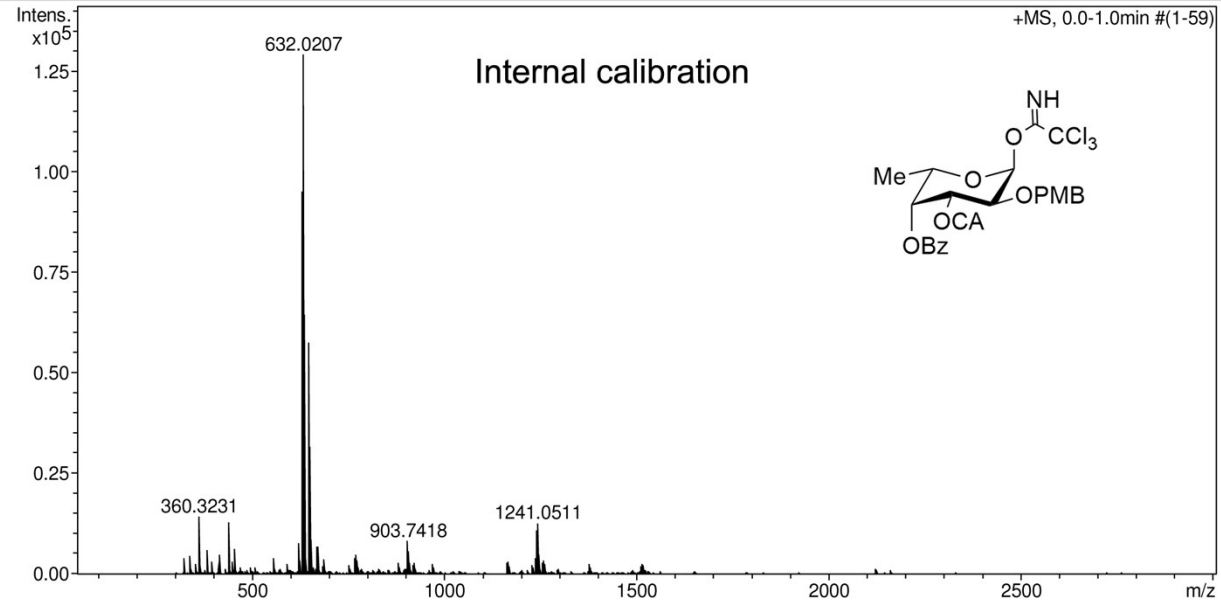
2-*O*-*p*-methoxybenzyl-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranoside trichloroacetimidates (13α)

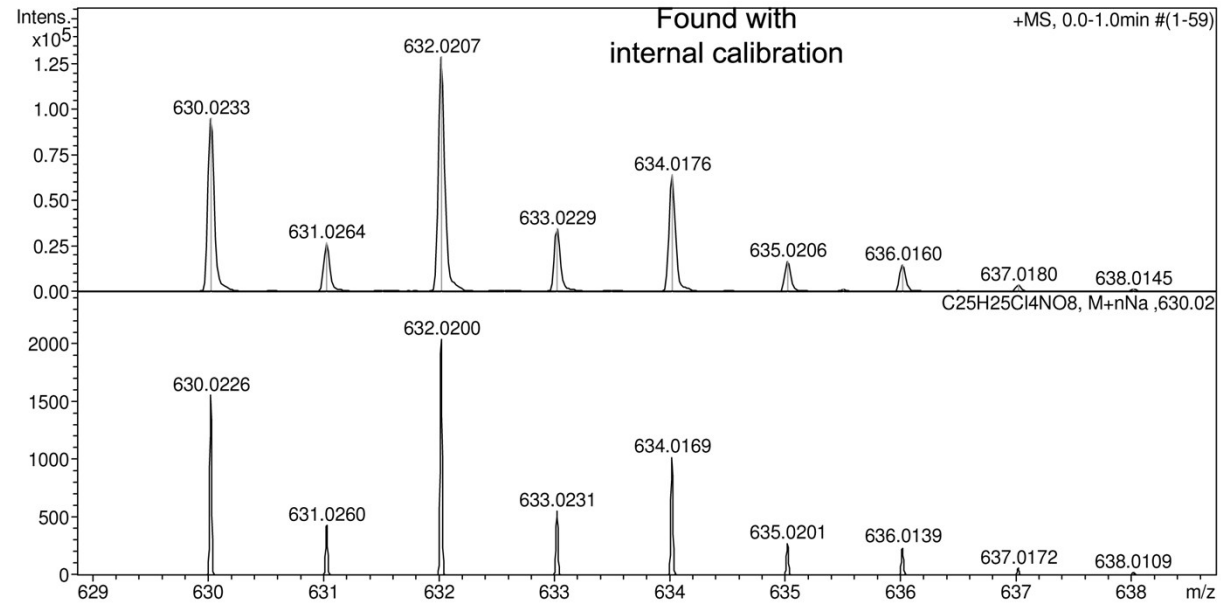



166.52
166.07
161.31
159.44
133.50
129.83
129.47
129.36
128.58
113.84
94.57
77.32
77.00
76.68
72.59
71.99
71.80
71.25
67.54
60.34
55.24
40.59
21.00
16.10
14.18
13C NMR (100.62 MHz), CDCl3
NH
O
CCl3
Me
O
OPMB
OCA
OBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

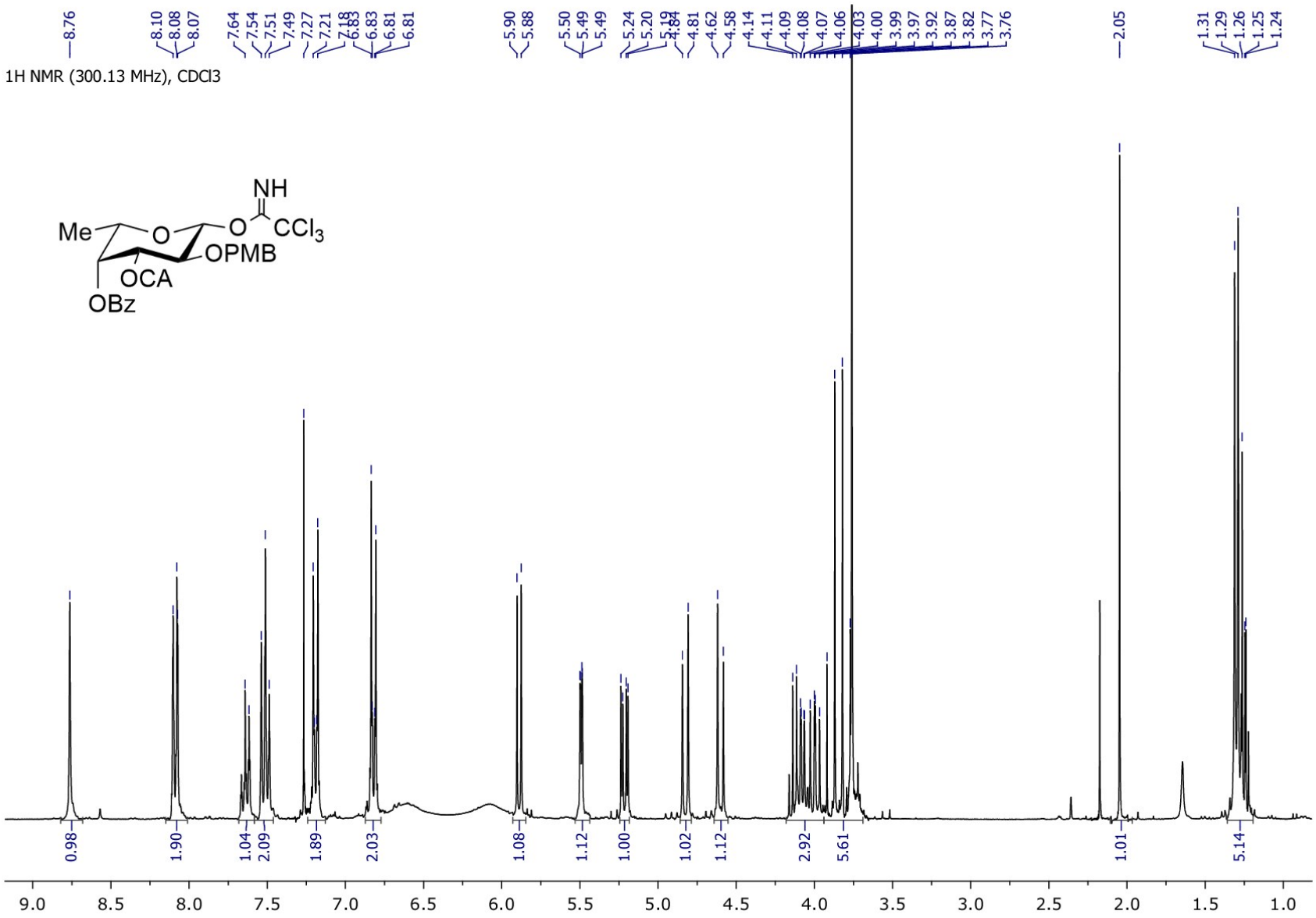
Acquisition Parameter

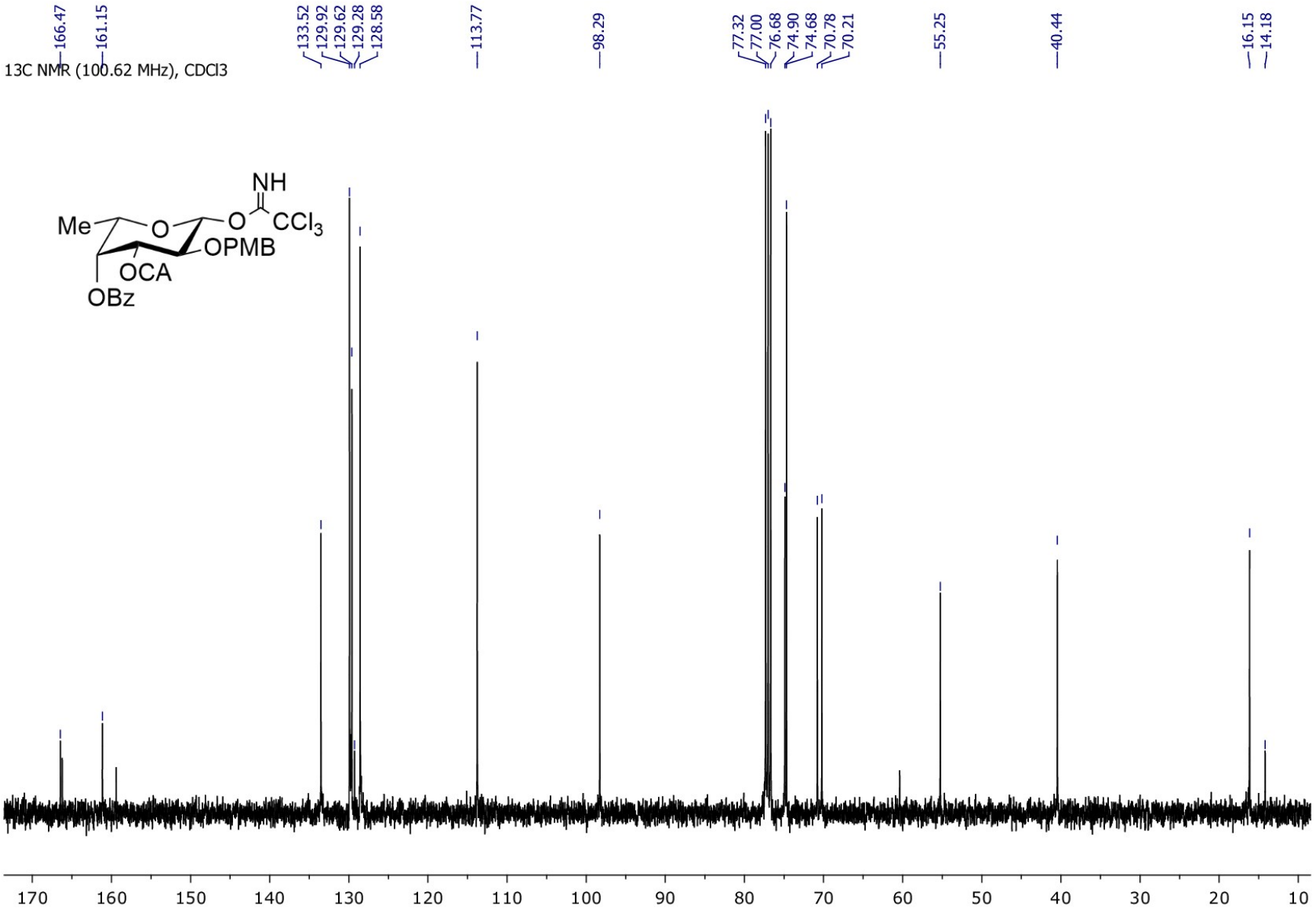
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





2-*O*-*p*-methoxybenzyl-3-*O*-chloroacetyl-4-*O*-benzoyl-β-L-fucopyranoside trichloroacetimidates (13β)

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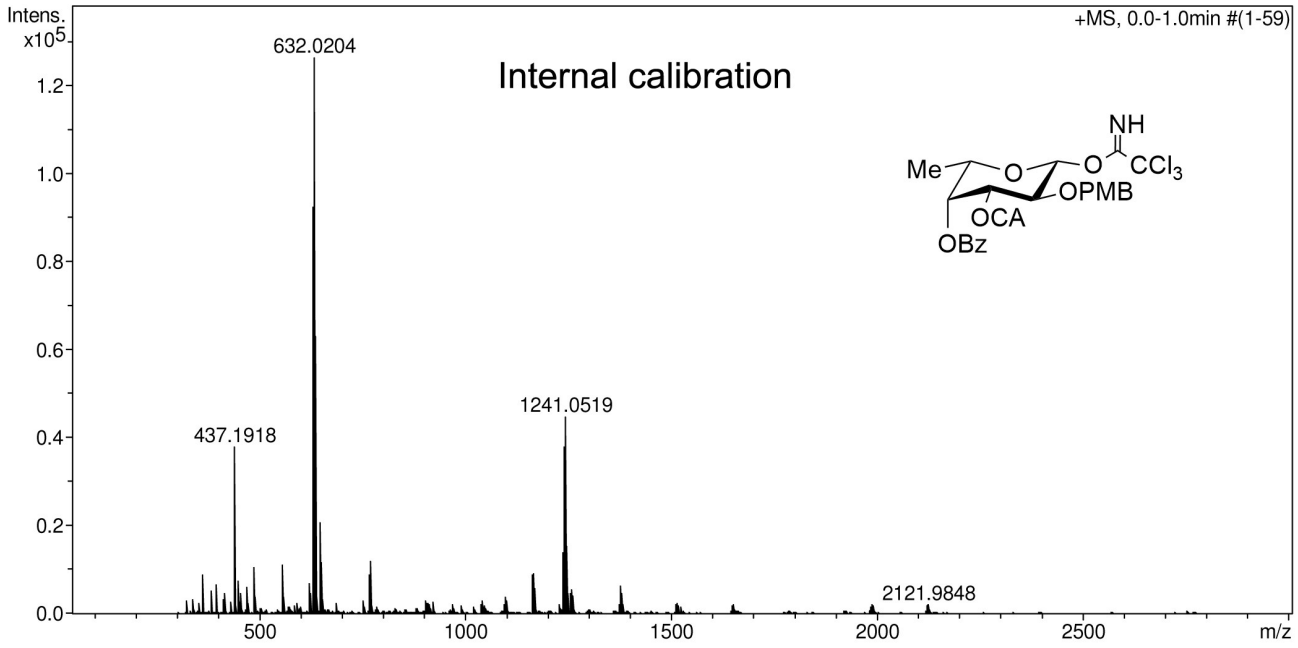
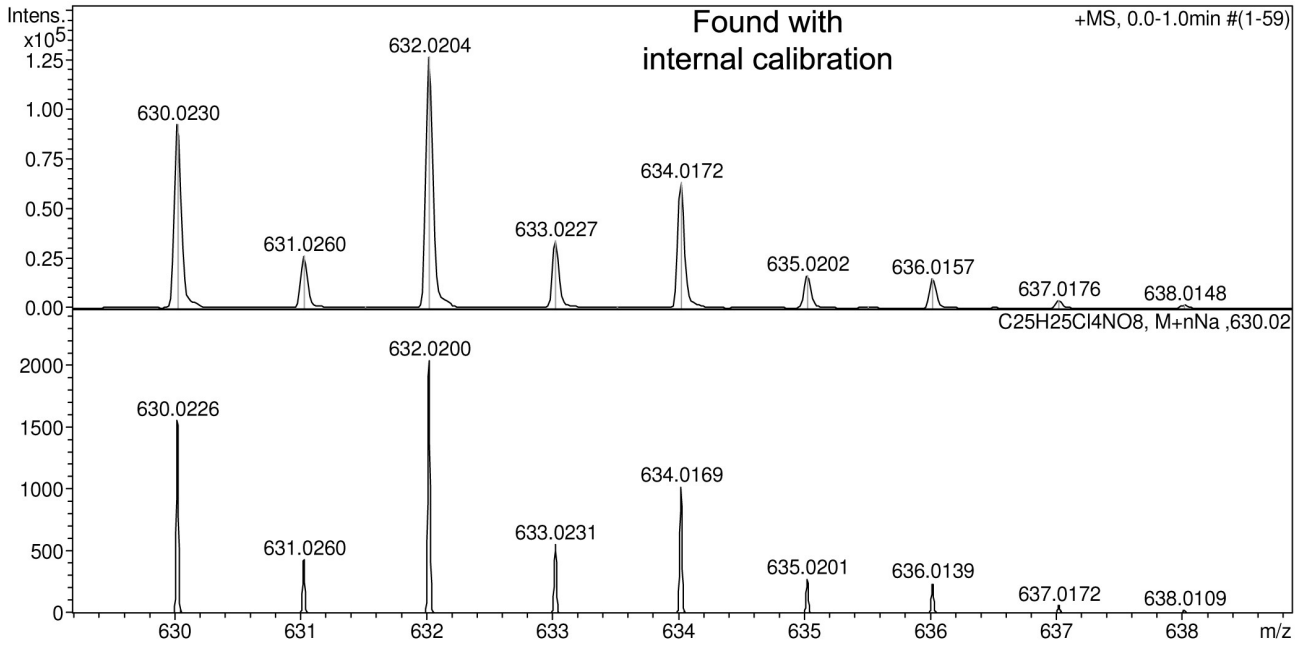
128.58
113.77
98.29
77.32
77.00
76.68
74.90
74.68
70.78
70.21
55.25
40.44
16.15
14.18
13C NMR (100.62 MHz), CDCl3
NH
Me
O
O
CCl3
OPMB
OCA
OBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

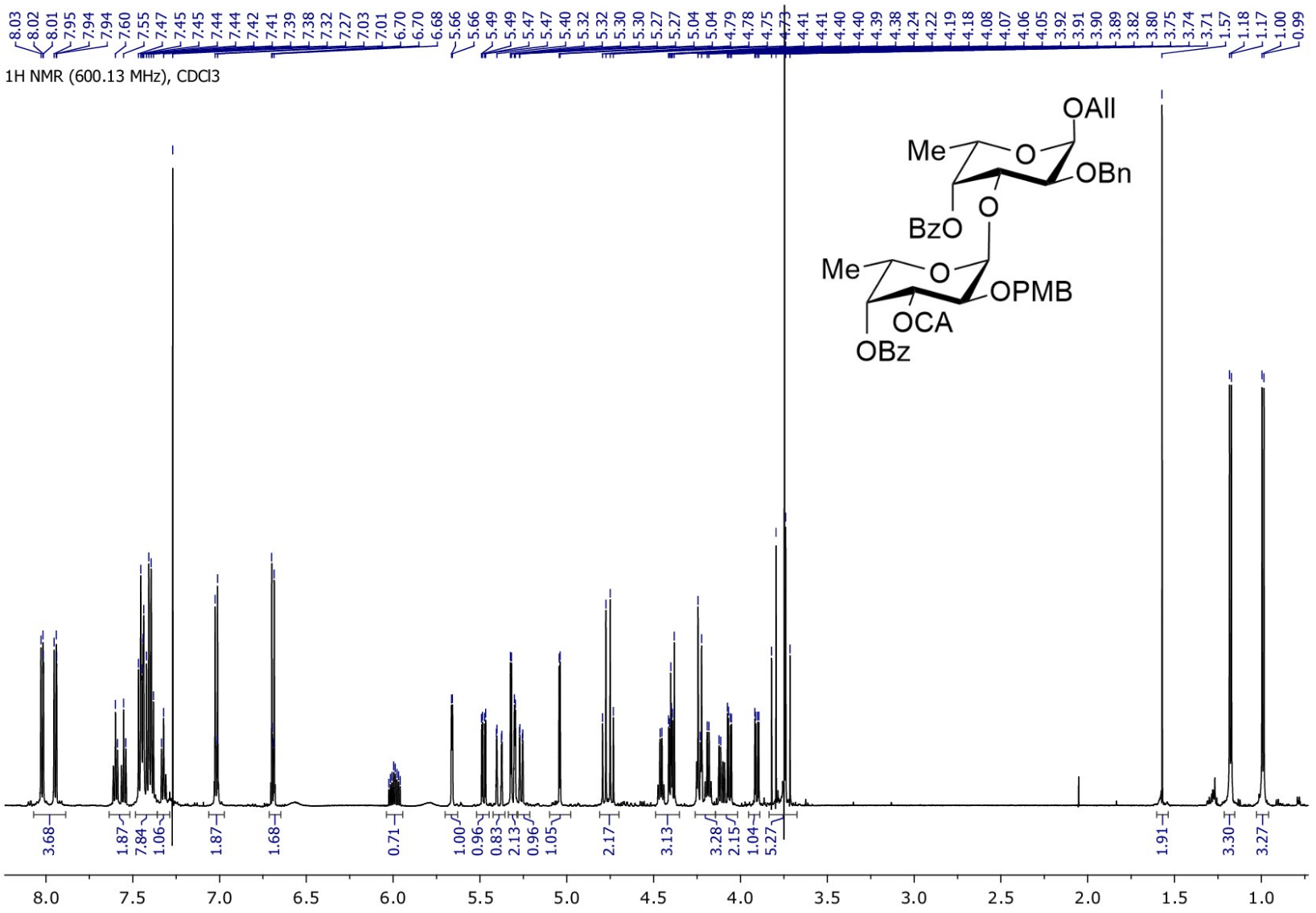
Acquisition Parameter

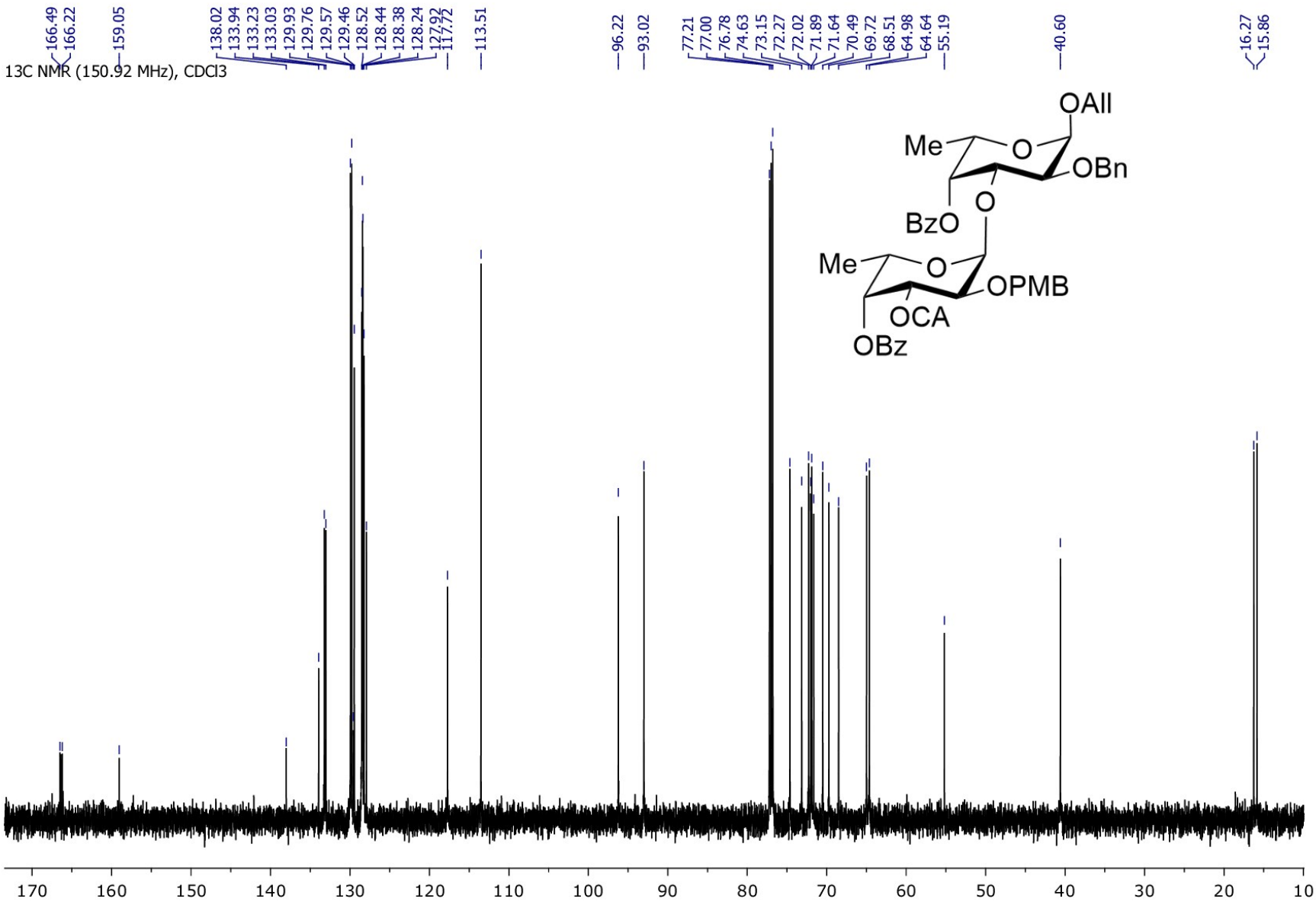
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





Allyl 2-*O*-*p*-methoxybenzyl-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (5)

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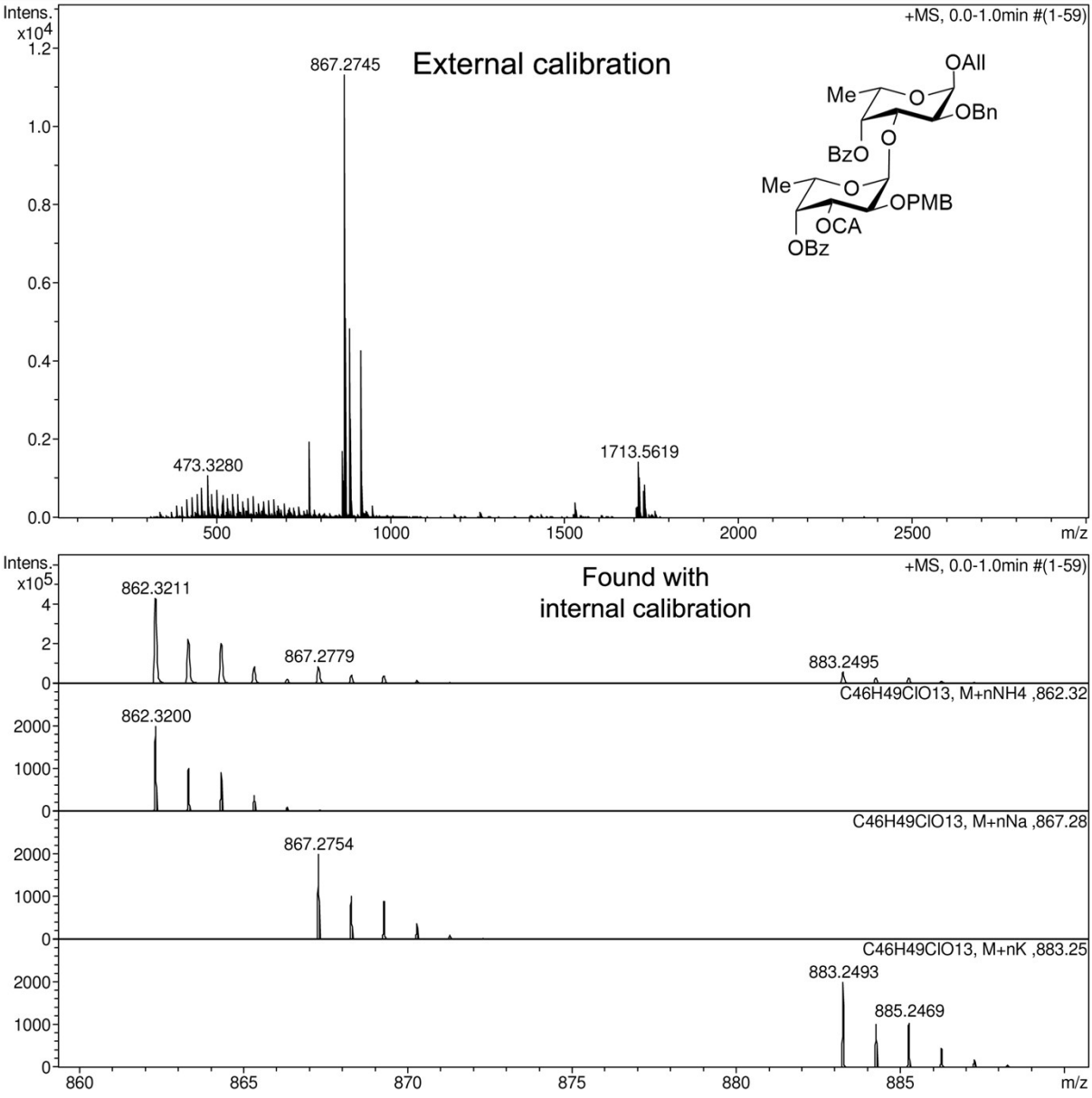
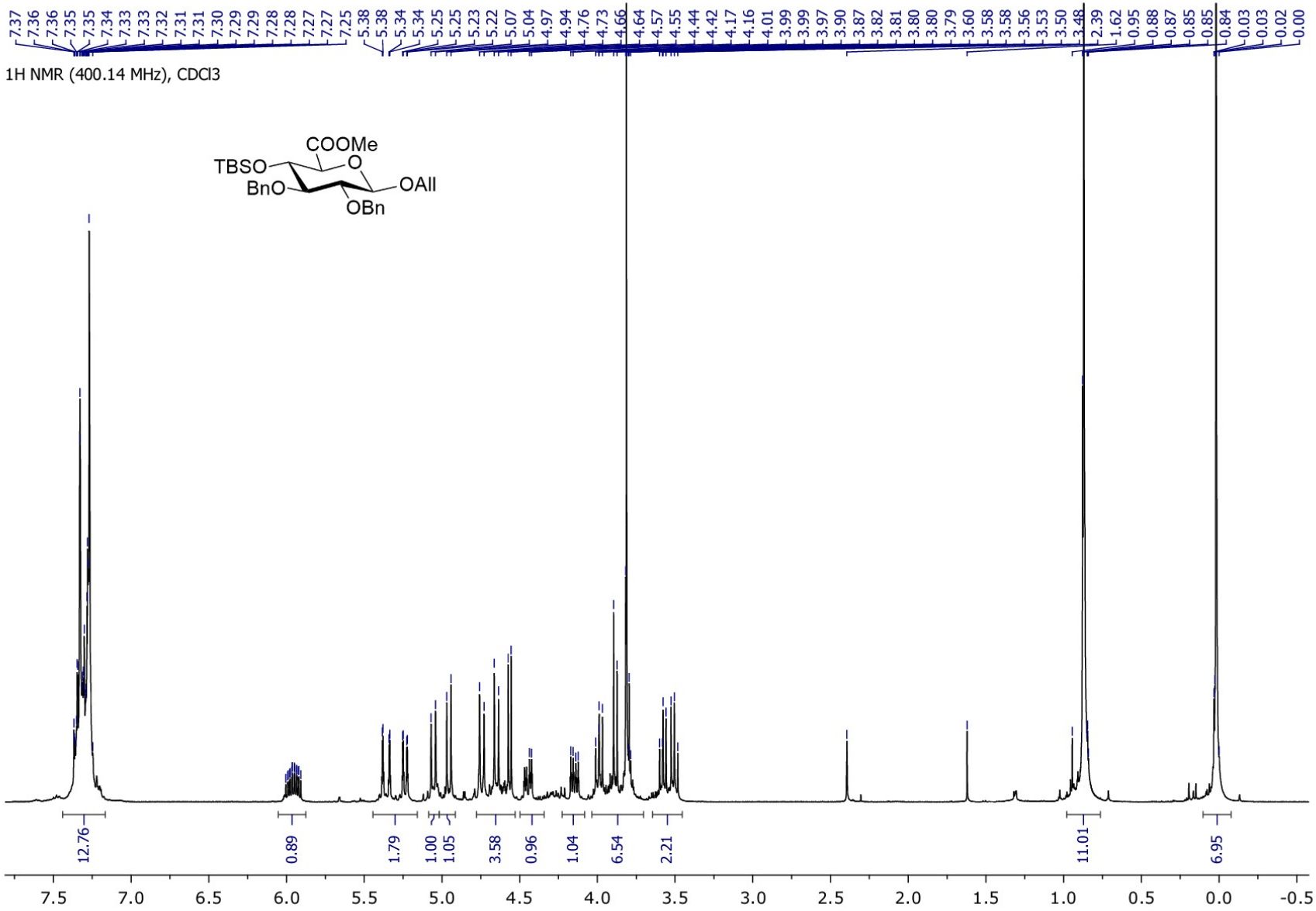
159.05
138.02
133.94
133.23
133.03
129.93
129.76
129.57
129.46
128.52
128.44
128.38
128.24
127.92
117.72
113.51
96.22
93.02
77.21
77.00
76.78
74.63
73.15
72.27
72.02
71.89
71.64
70.49
69.72
68.51
64.98
64.64
55.19
40.60
16.27
15.86
13C NMR (150.92 MHz), CDCl3
OAll
Me
O
OBn
O
BzO
Me
O
OPMB
OCA
OBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

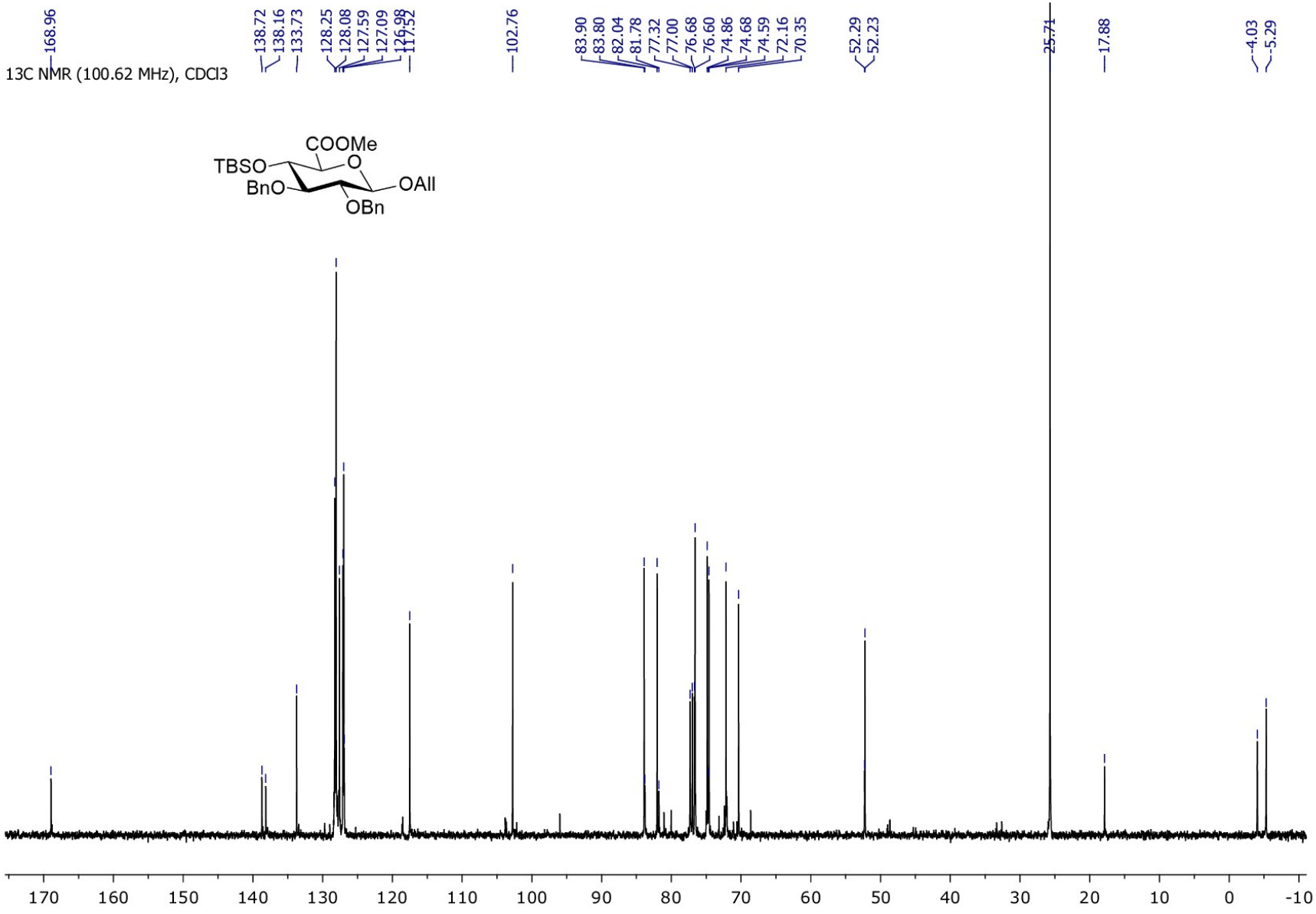
Acquisition Parameter

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



Methyl (allyl 2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl β-D-glucopyranosyl)uronate (15)




13C NMR (100.62 MHz), CDCl3
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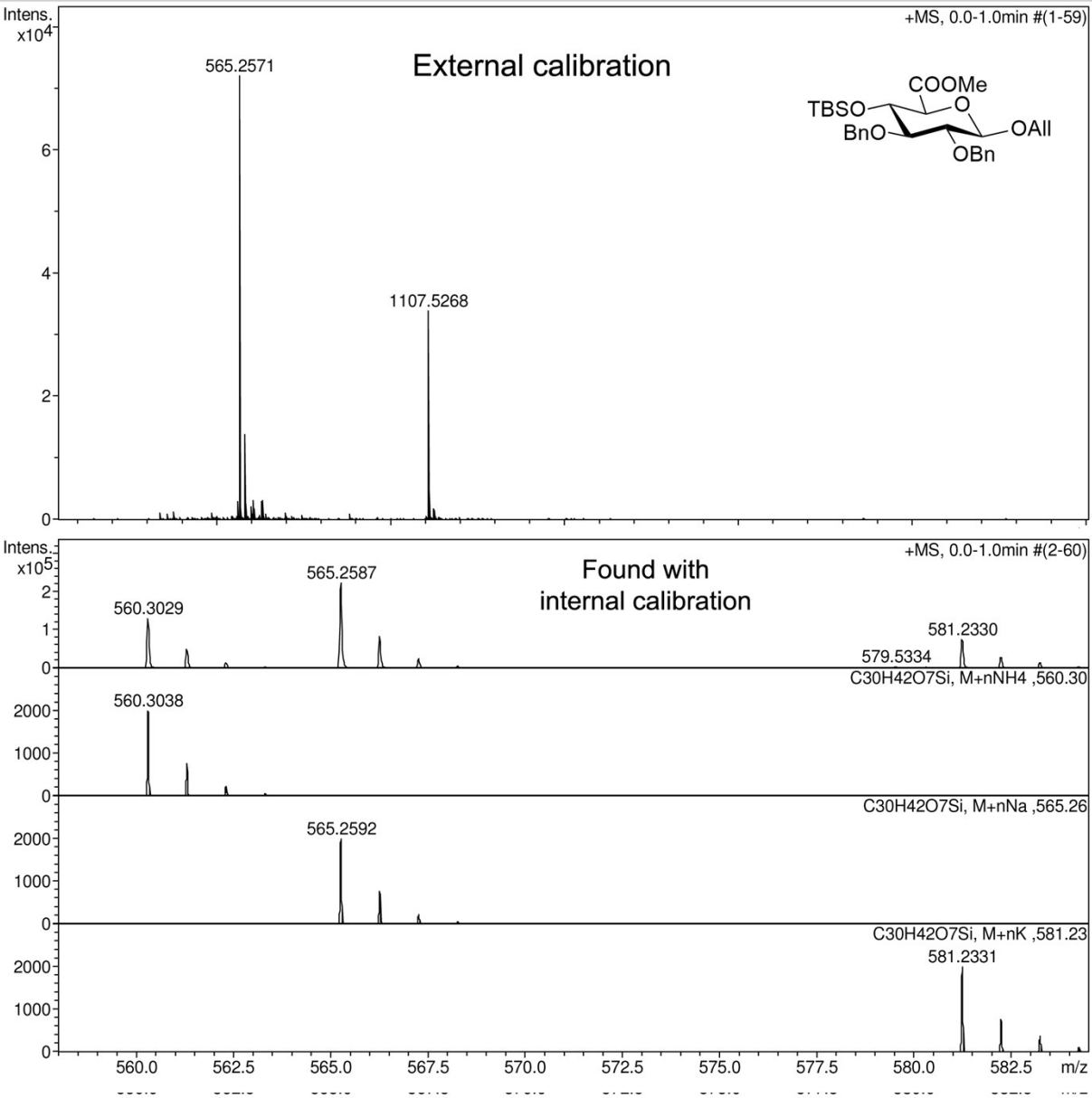
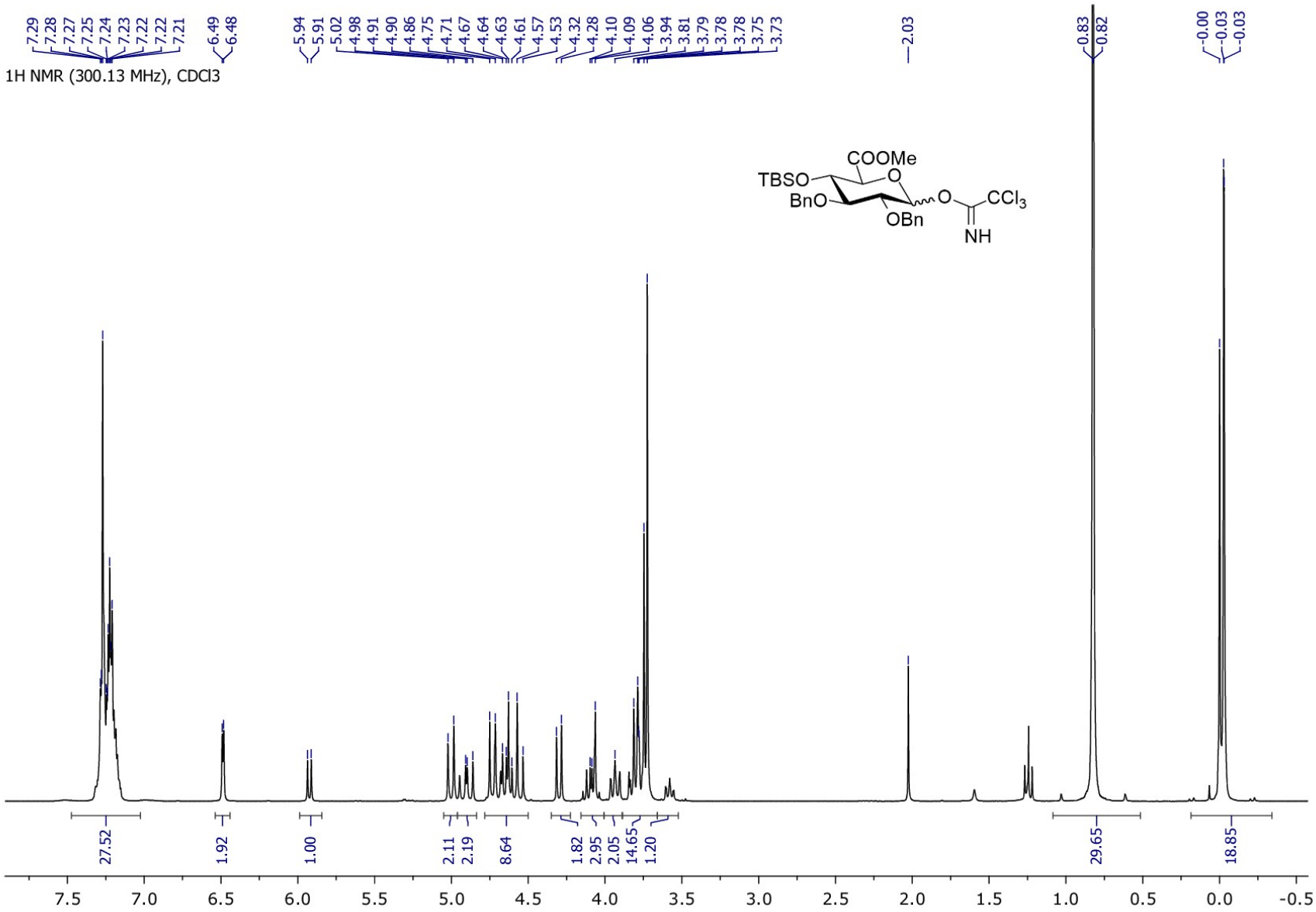
138.72
138.16
133.73
128.25
128.08
127.59
127.09
126.98
117.52
102.76
83.90
83.80
82.04
81.78
77.32
77.00
76.68
76.60
74.86
74.68
74.59
72.16
70.35
52.29
52.23
25.71
17.88
-4.03
-5.29
COOMe
TBSO
O
BnO
OAll
OBn
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

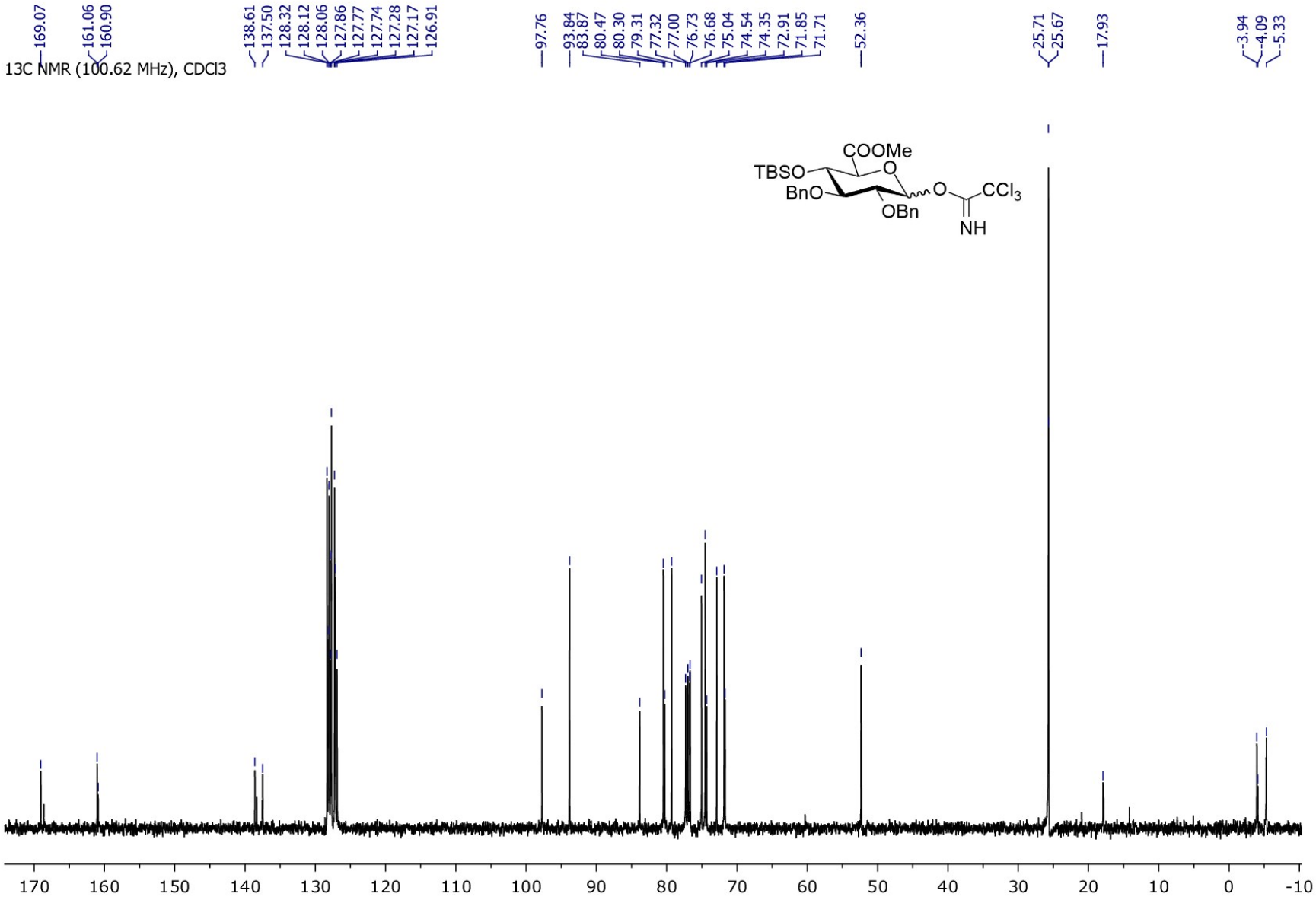
Acquisition Parameter

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



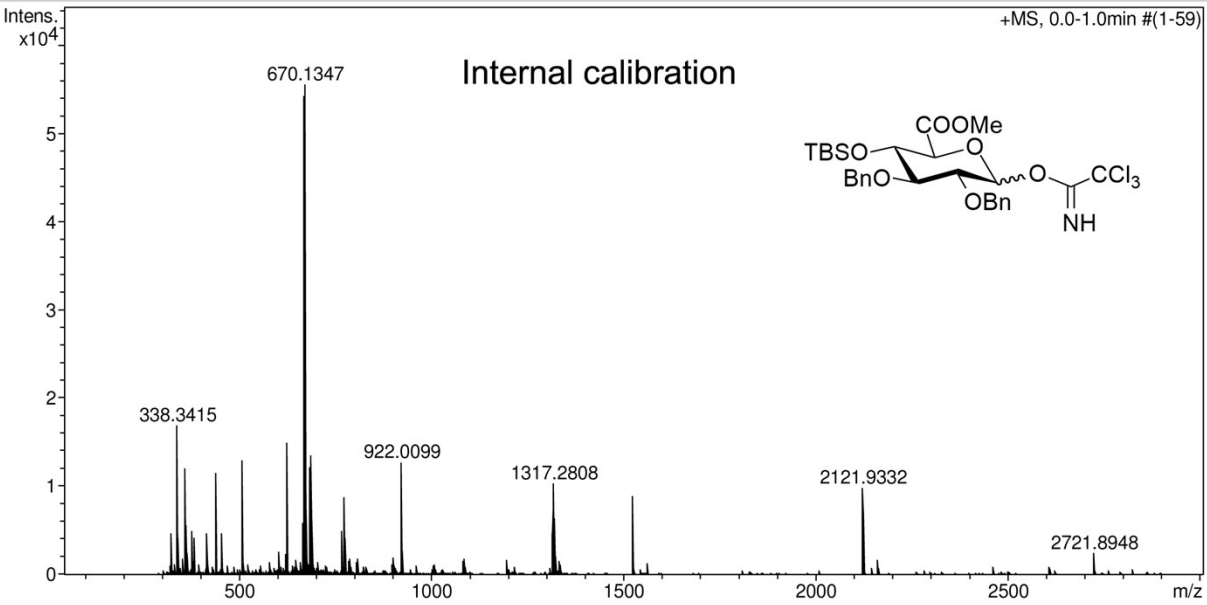
Methyl (2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl α,β-D-glucopyranosyl)uronate trichloroacetimidates (8)

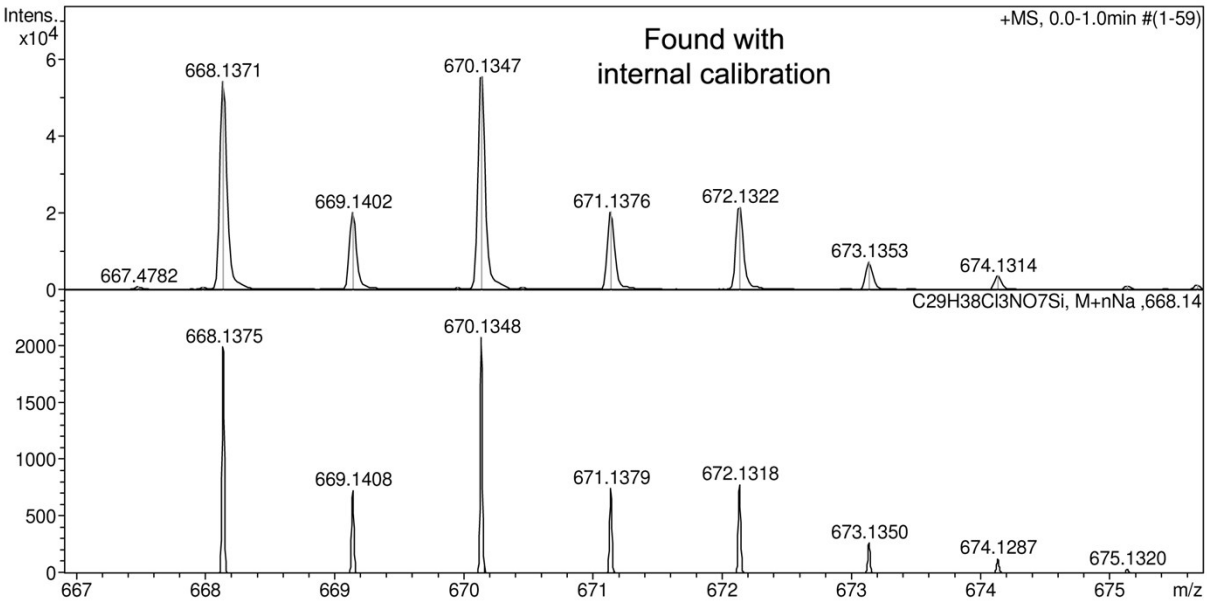



13C NMR (100.62 MHz), CDCl3
169.07
161.06
160.90
138.61
137.50
128.32
128.12
128.06
127.86
127.77
127.74
127.28
127.17
126.91
97.76
93.84
83.87
80.47
80.30
79.31
77.32
77.00
76.73
76.68
75.04
74.54
74.35
72.91
71.85
71.71
52.36
25.71
25.67
17.93
-3.94
-4.09
-5.33
COOMe
TBSO
BnO
OBn
O
O
CCl3
NH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

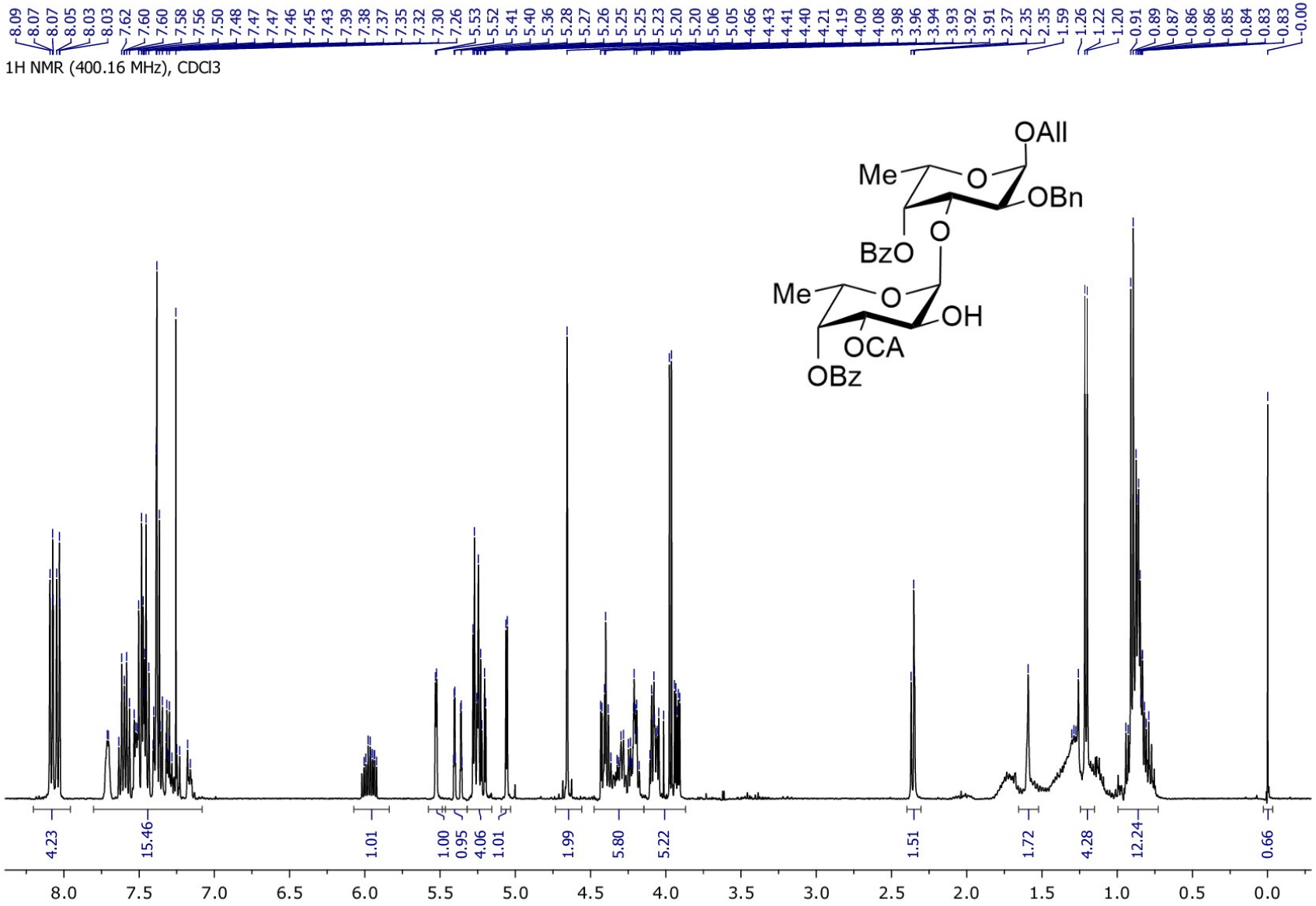
Acquisition Parameter

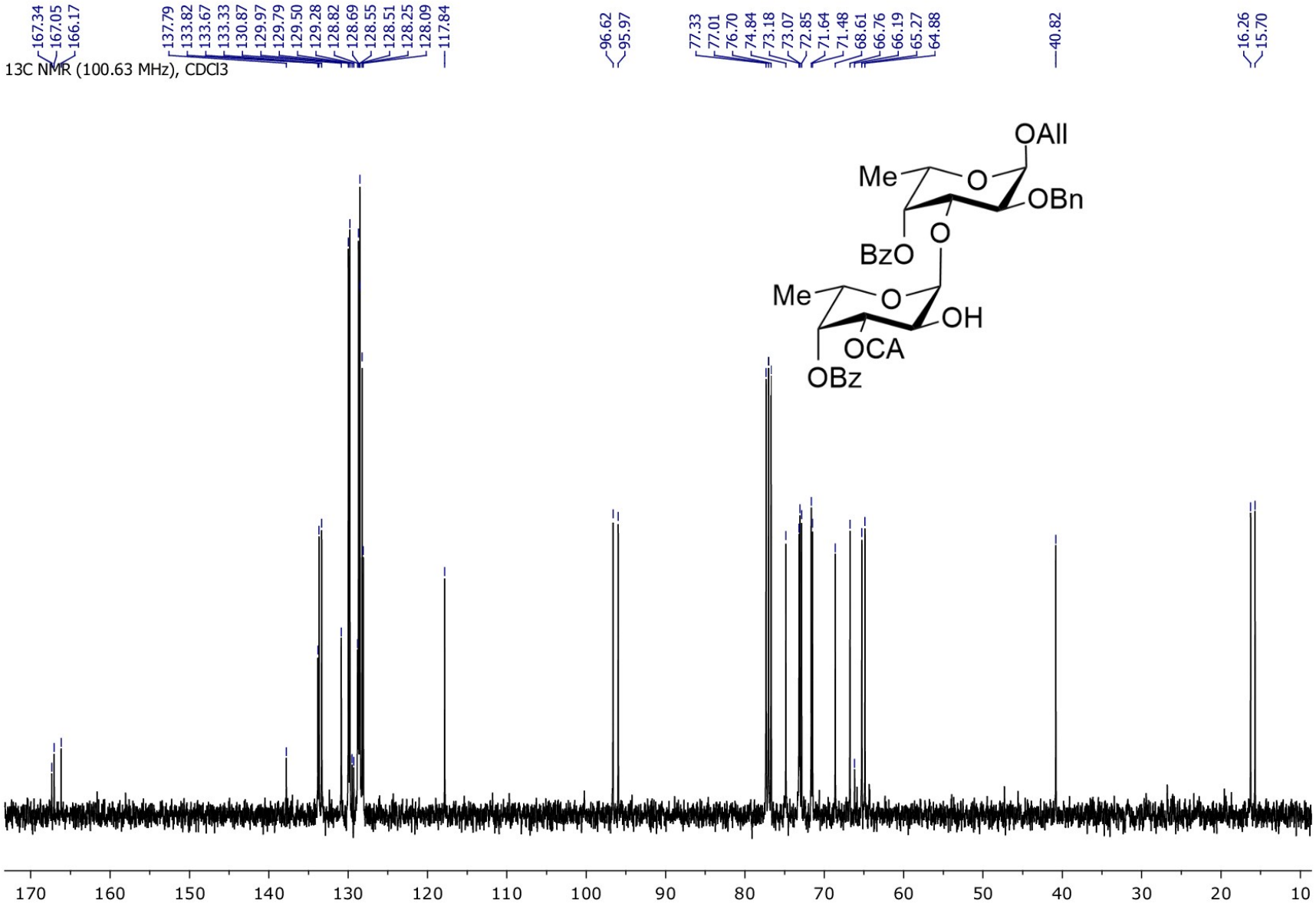
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





Allyl 3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (16)




13C NMR (100.63 MHz), CDCl3
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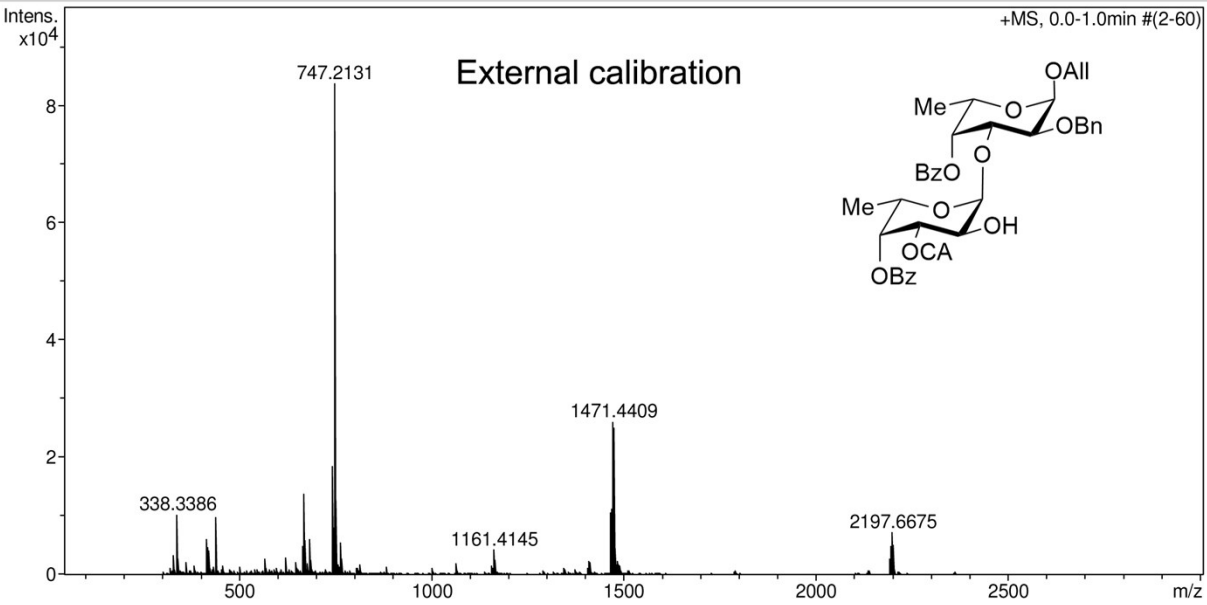
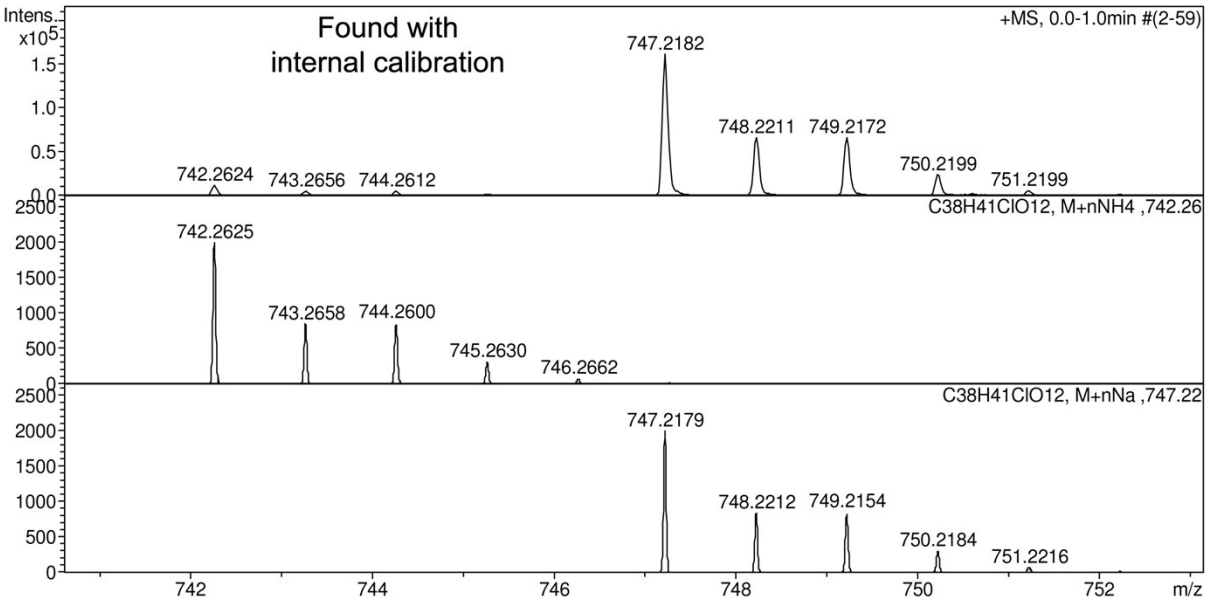
167.05
166.17
137.79
133.82
133.67
133.33
130.87
129.97
129.79
129.50
129.28
128.82
128.69
128.55
128.51
128.25
128.09
117.84
96.62
95.97
77.33
77.01
76.70
74.84
73.18
73.07
72.85
71.64
71.48
68.61
66.76
66.19
65.27
64.88
40.82
16.26
15.70
OAll
Me
O
OBn
O
BzO
Me
O
OH
OCA
OBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

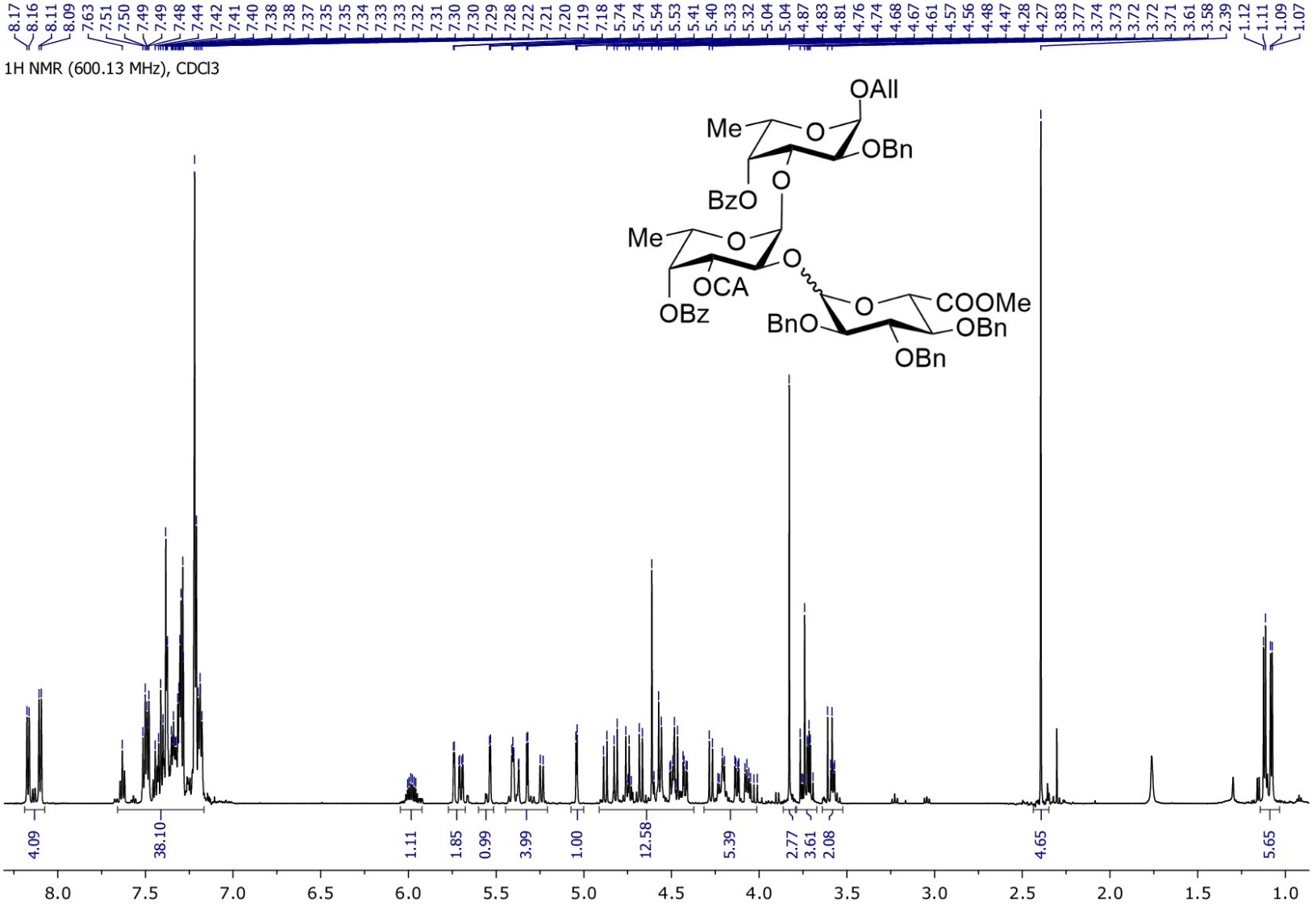
Acquisition Parameter

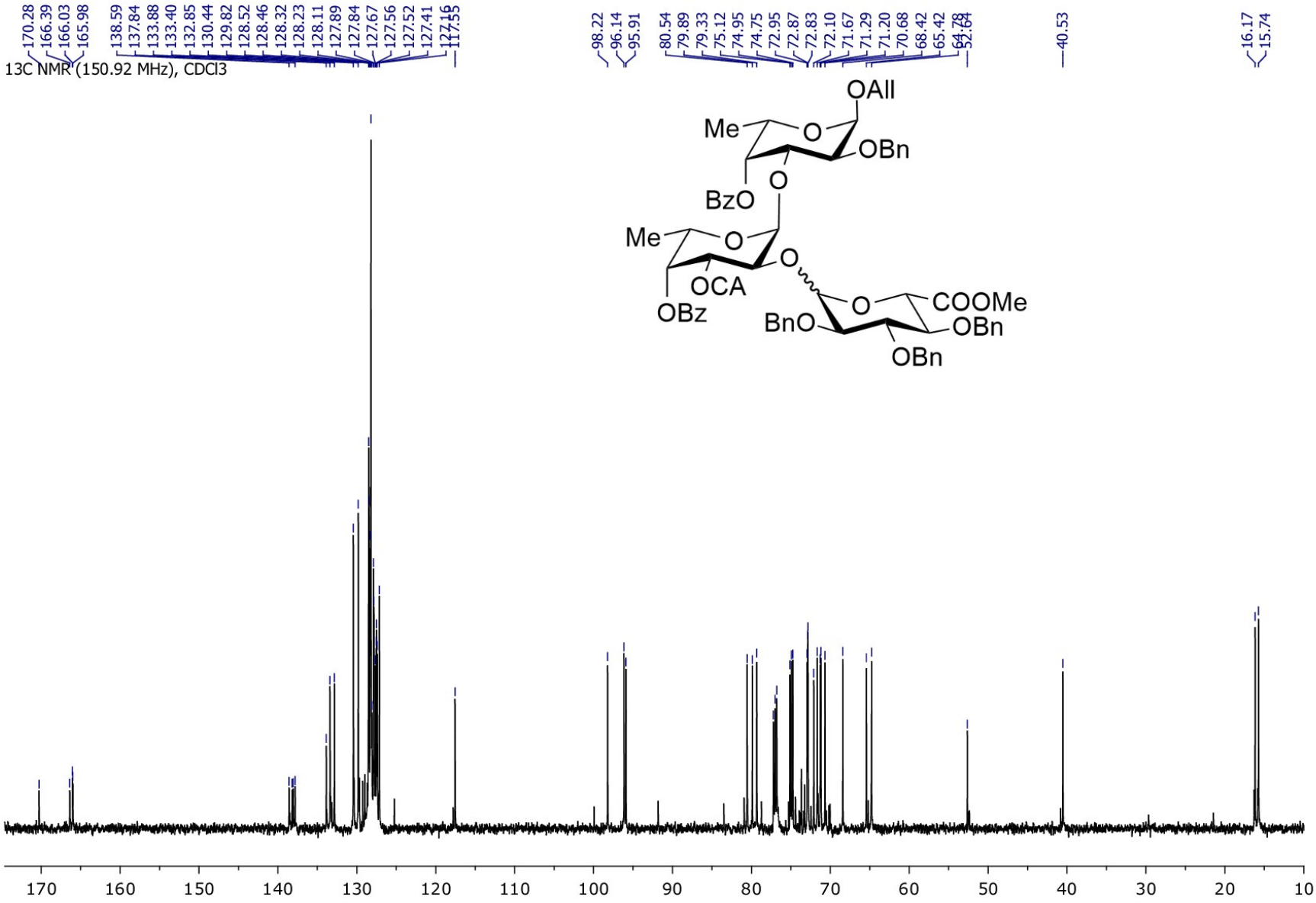
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





Allyl methyl 2,3,4-tri-*O*-benzyl-α,β-D-glucopyranosyluronate-(1→2)-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranosides (17)




13C NMR (150.92 MHz), CDCl3
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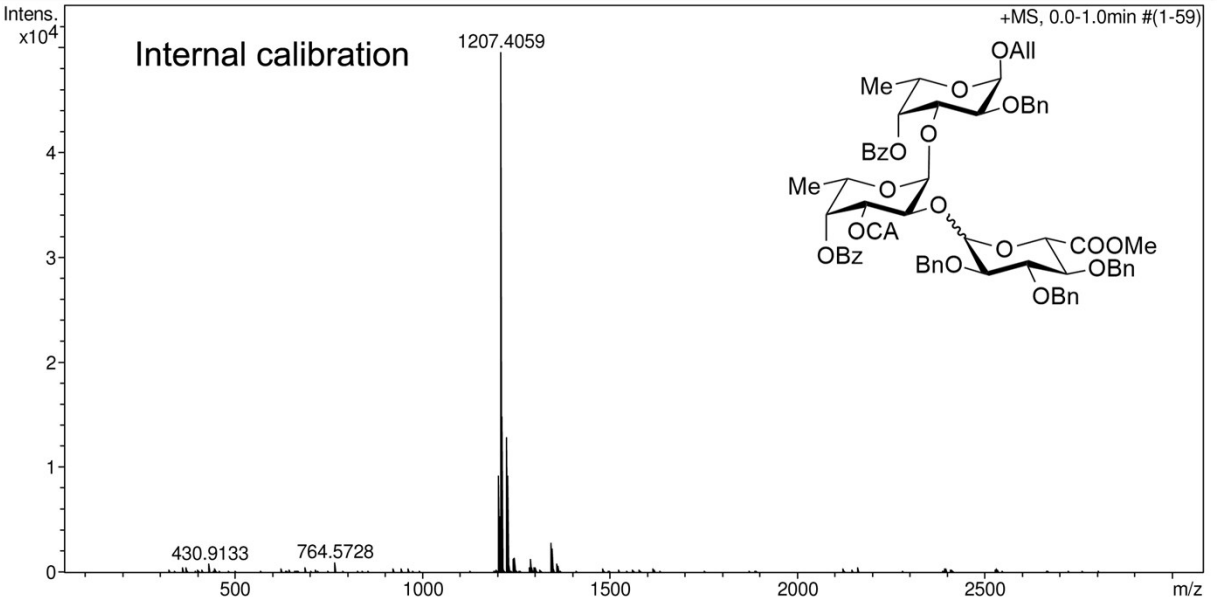
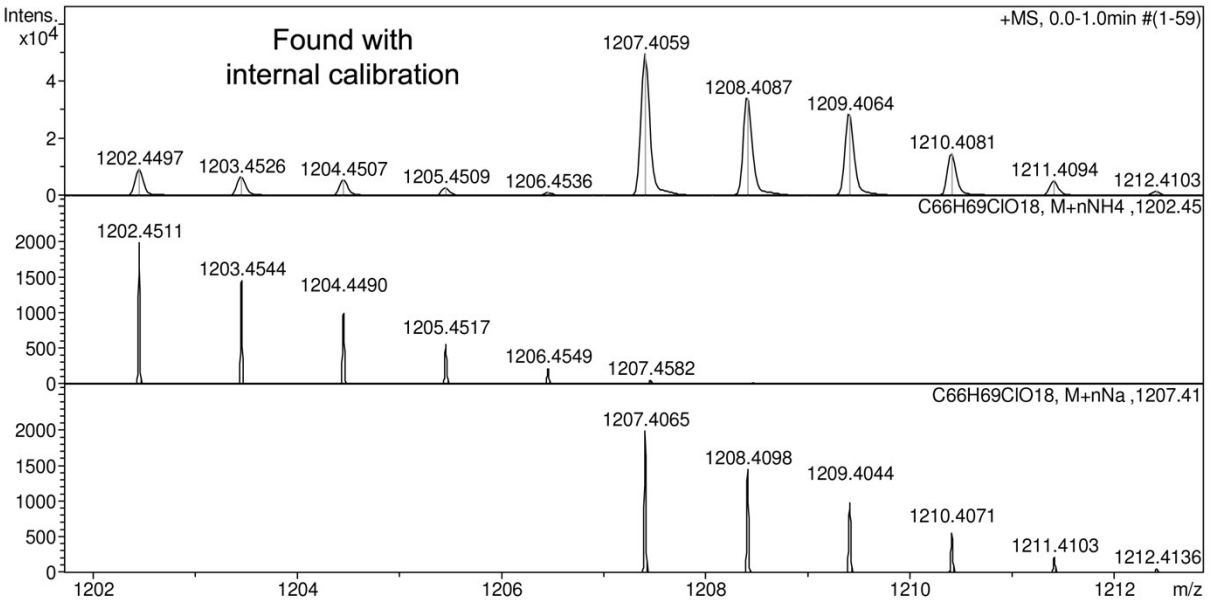
166.39
166.03
165.98
138.59
137.84
133.88
133.40
132.85
130.44
129.82
128.52
128.46
128.32
128.23
128.11
127.89
127.84
127.67
127.56
127.52
127.41
98.22
96.14
95.91
80.54
79.89
79.33
75.12
74.95
74.75
72.95
72.87
72.83
72.10
71.67
71.29
71.20
70.68
68.42
65.42
40.53
16.17
15.74
OAll
Me
O
OBn
BzO
O
Me
O
O
OCA
OBz
O
COOMe
BnO
OBn
OBn
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

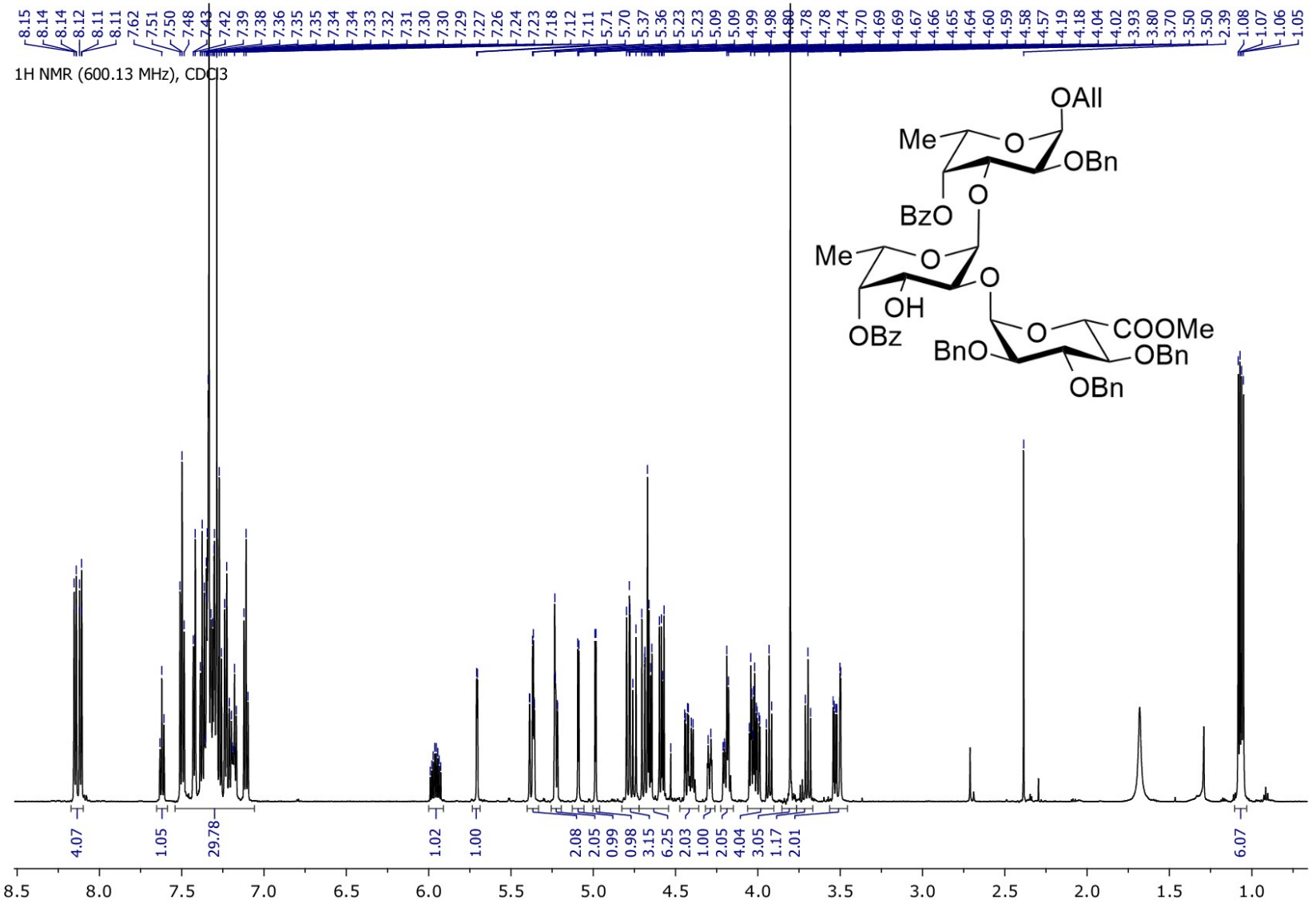
Acquisition Parameter

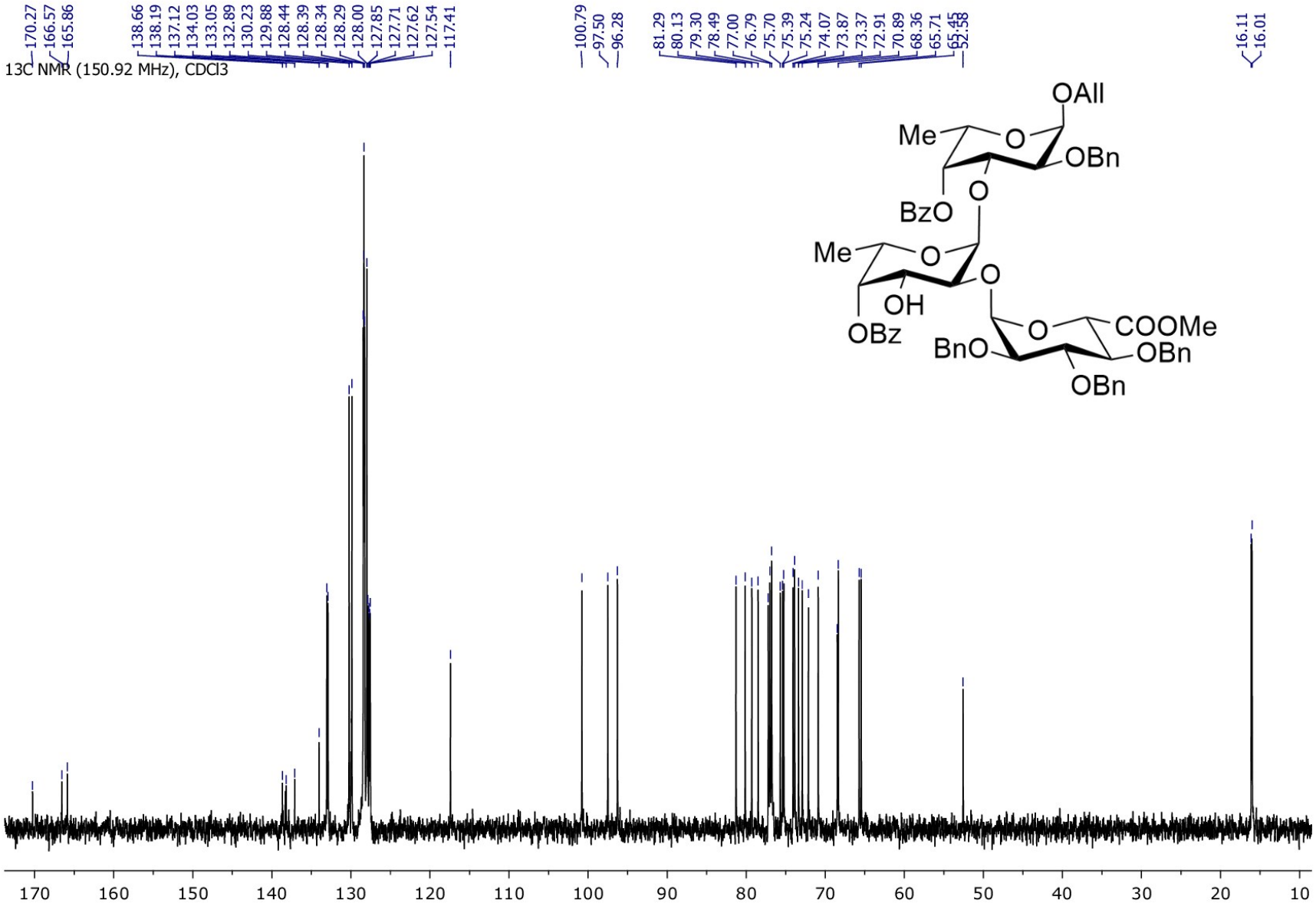
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





Allyl methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyluronate-(1→2)-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (18)




13C NMR (150.92 MHz), CDCl3
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165.86
138.66
138.19
137.12
134.03
133.05
132.89
130.23
129.88
128.44
128.39
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128.29
128.00
127.85
127.71
127.62
127.54
117.41
100.79
97.50
96.28
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80.13
79.30
78.49
77.00
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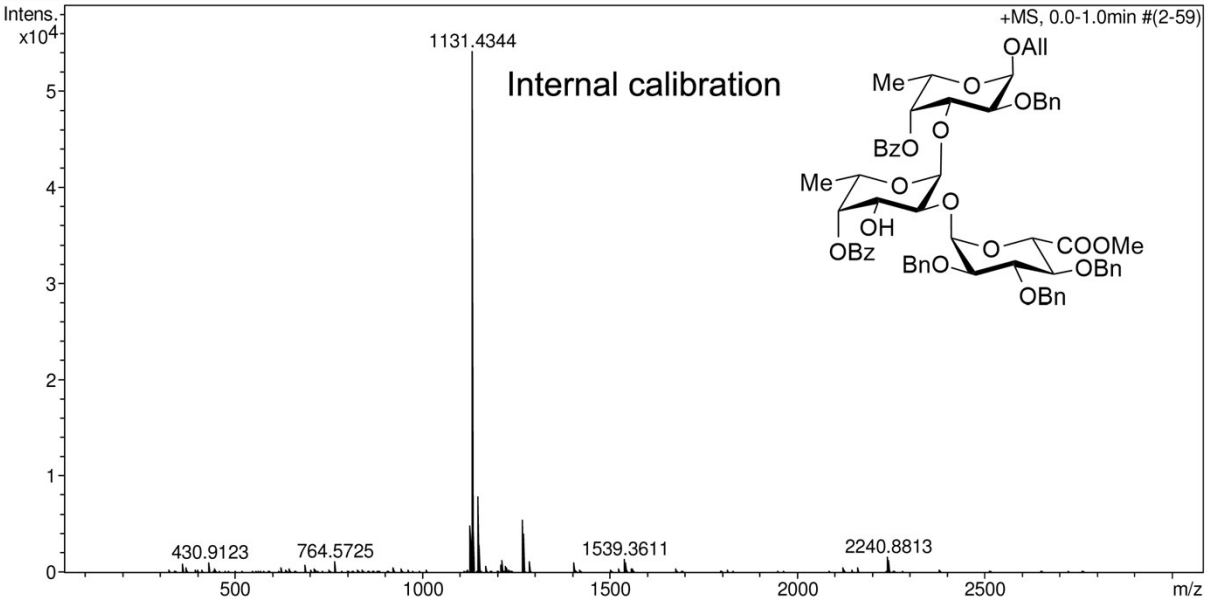
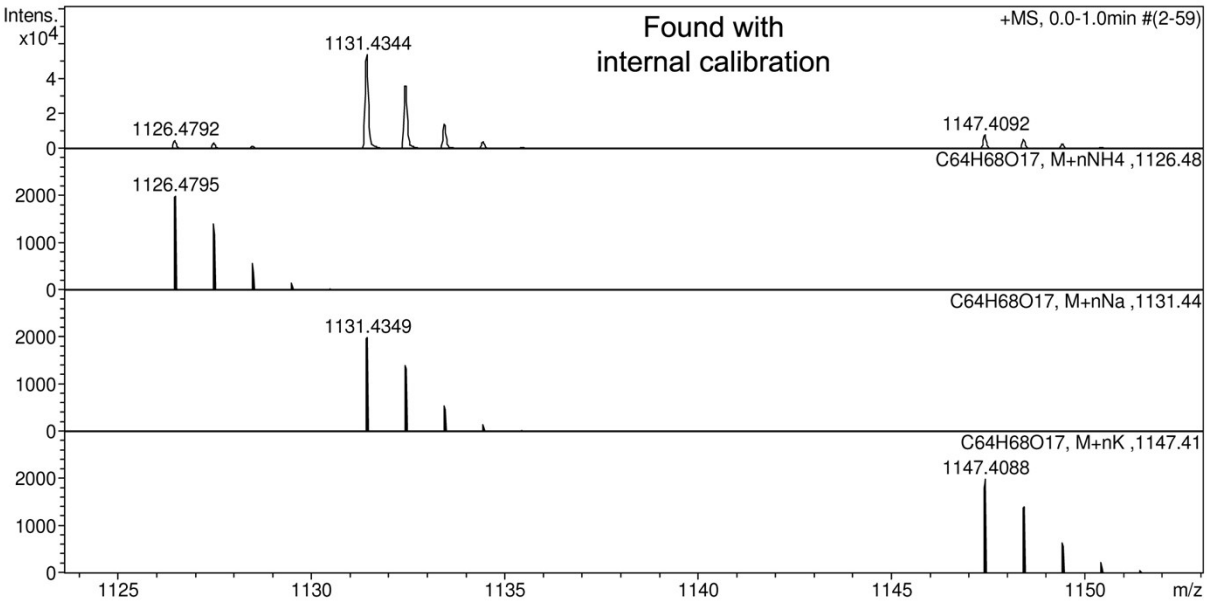
75.70
75.39
75.24
74.07
73.87
73.37
72.91
70.89
68.36
65.71
65.45
52.58
16.11
16.01
OAll
Me
O
OBn
BzO
O
Me
O
O
OH
OBz
O
COOMe
BnO
OBn
OBn
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

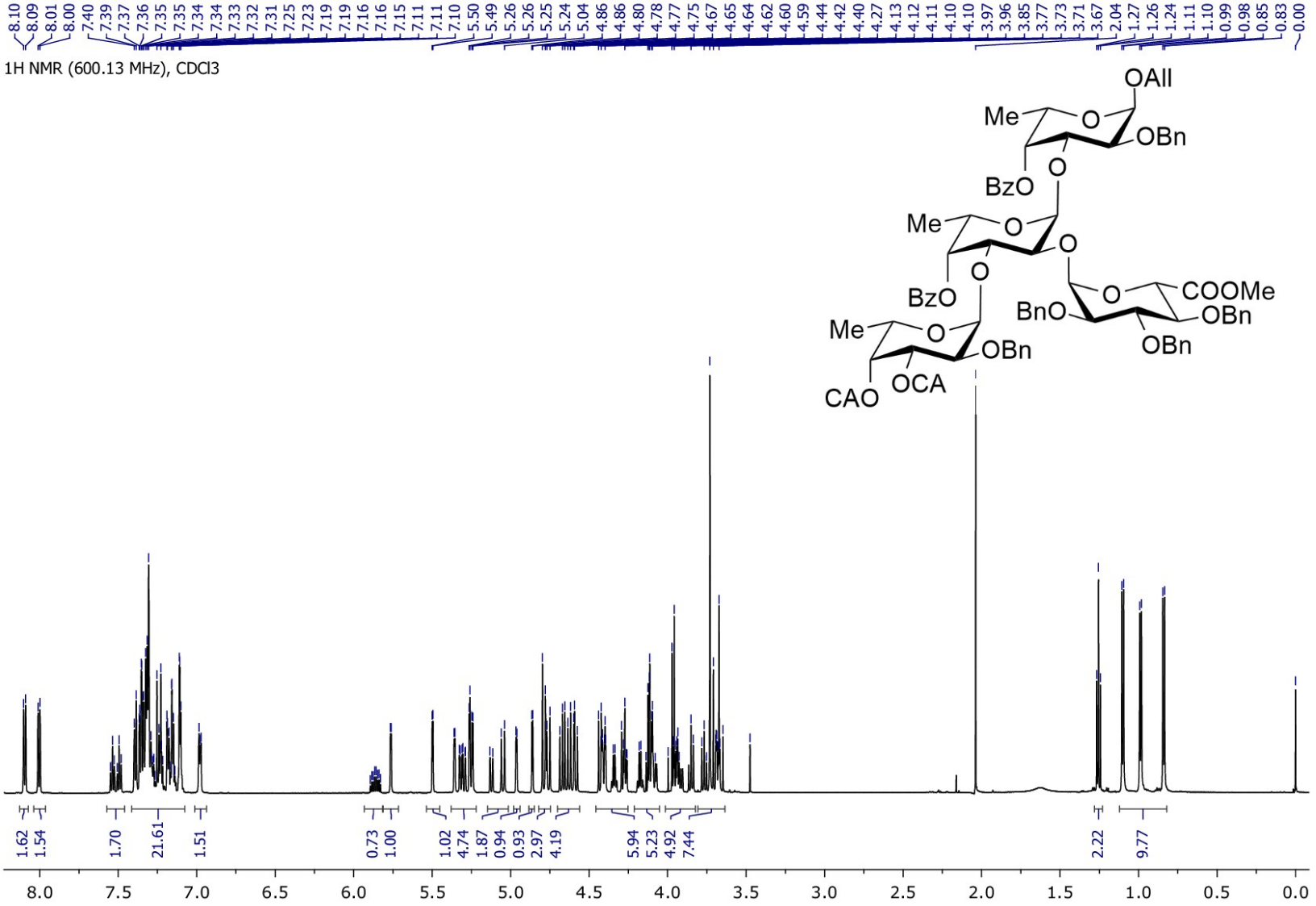
Acquisition Parameter

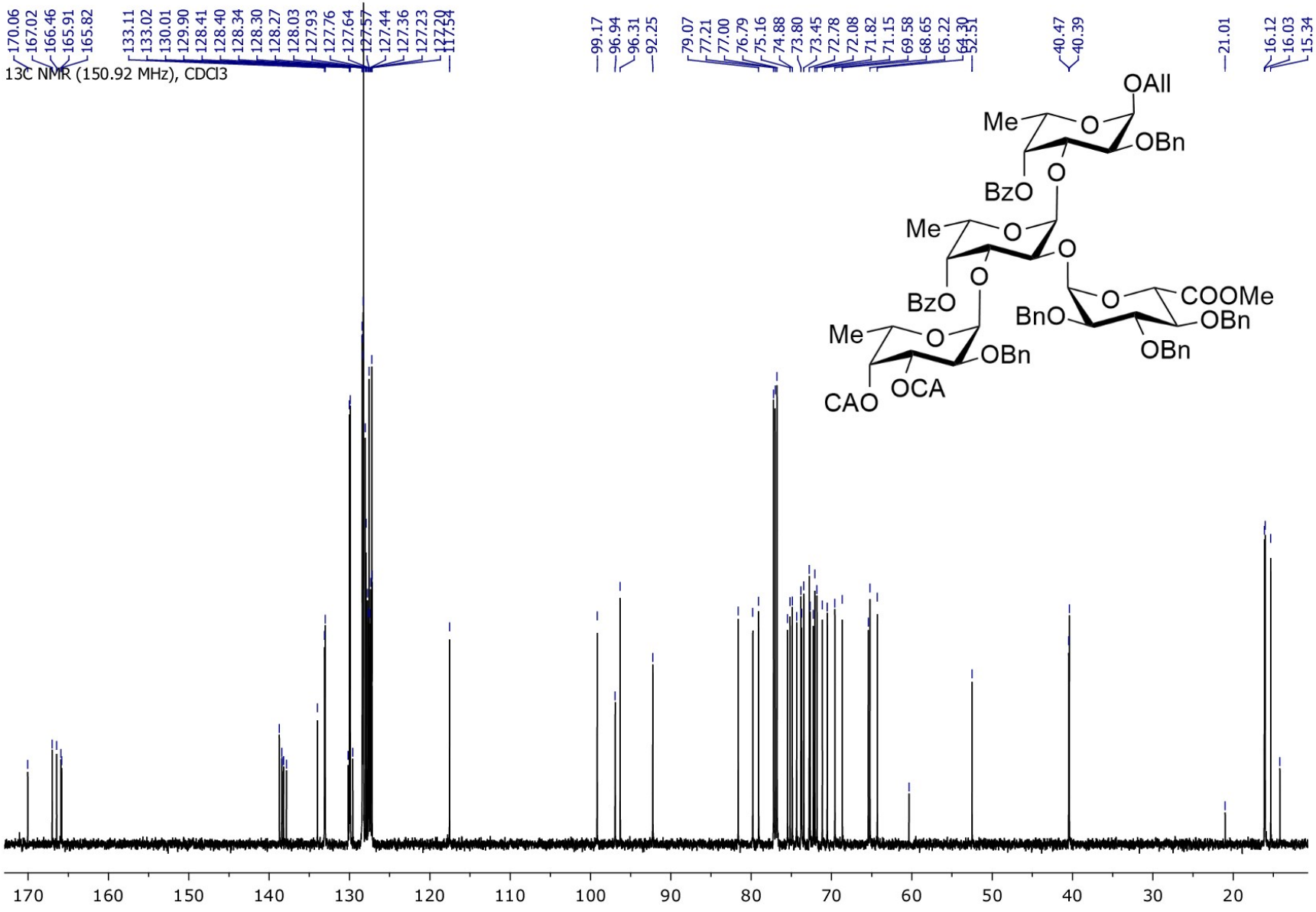
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





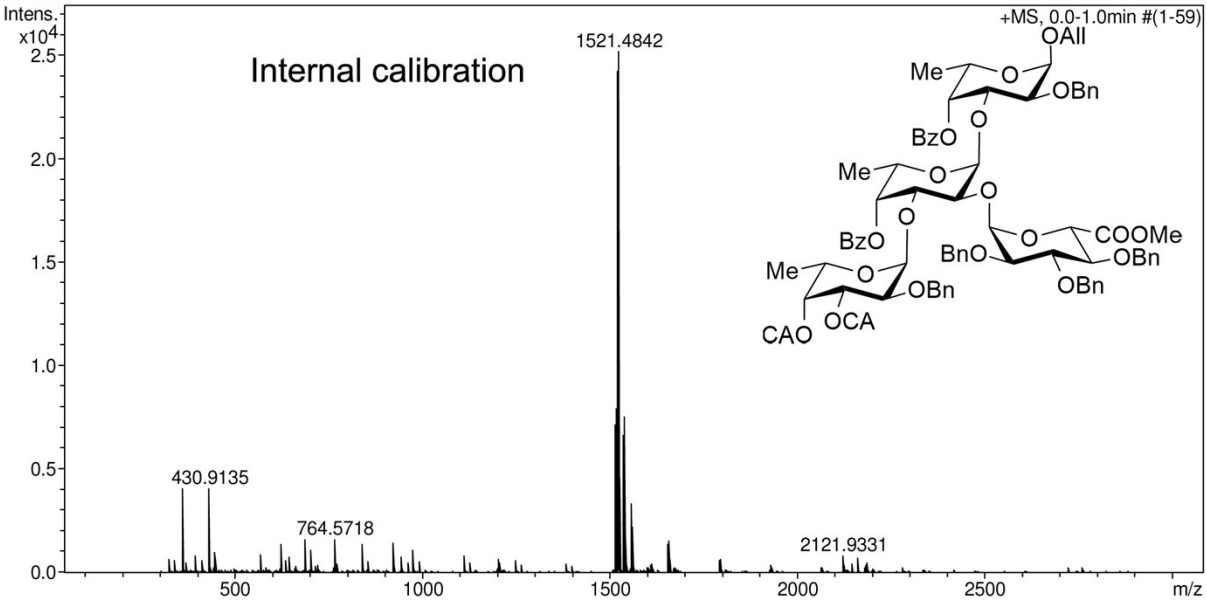
Allyl 2-*O*-benzyl-3,4-di-*O*-chloroacetyl-α-L-fucopyranosyl-(1→3)-{methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosyluronate-(1→2)}-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (19)

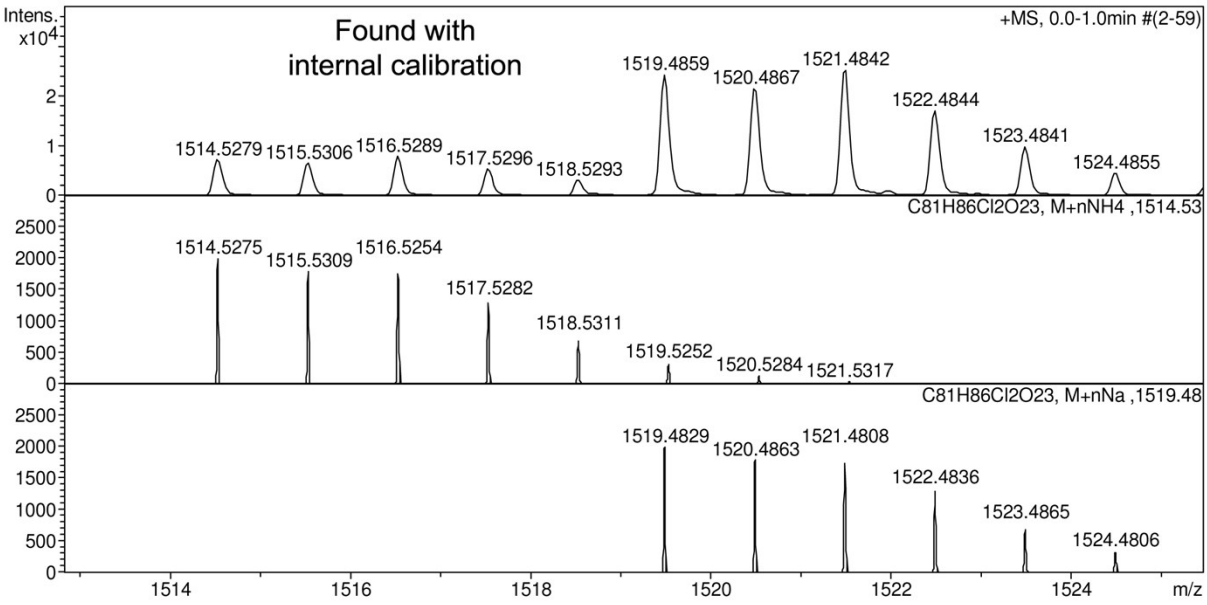



13C NMR (150.92 MHz), CDCl3
170.06
167.02
166.46
165.91
165.82
133.11
133.02
130.01
129.90
128.41
128.40
128.34
128.30
128.27
128.03
127.93
127.76
127.64
127.57
127.44
127.36
127.23
127.20
117.54
99.17
96.94
96.31
92.25
79.07
77.21
77.00
76.79
75.16
74.88
73.80
73.45
72.78
72.08
71.82
71.15
69.58
68.65
65.22
64.30
32.51
40.47
40.39
21.01
16.12
16.03
15.34
OAll
Me
O
OBn
BzO
O
Me
O
O
O
BzO
O
COOMe
BnO
OBn
Me
O
OBn
OBn
CAO
OCA
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

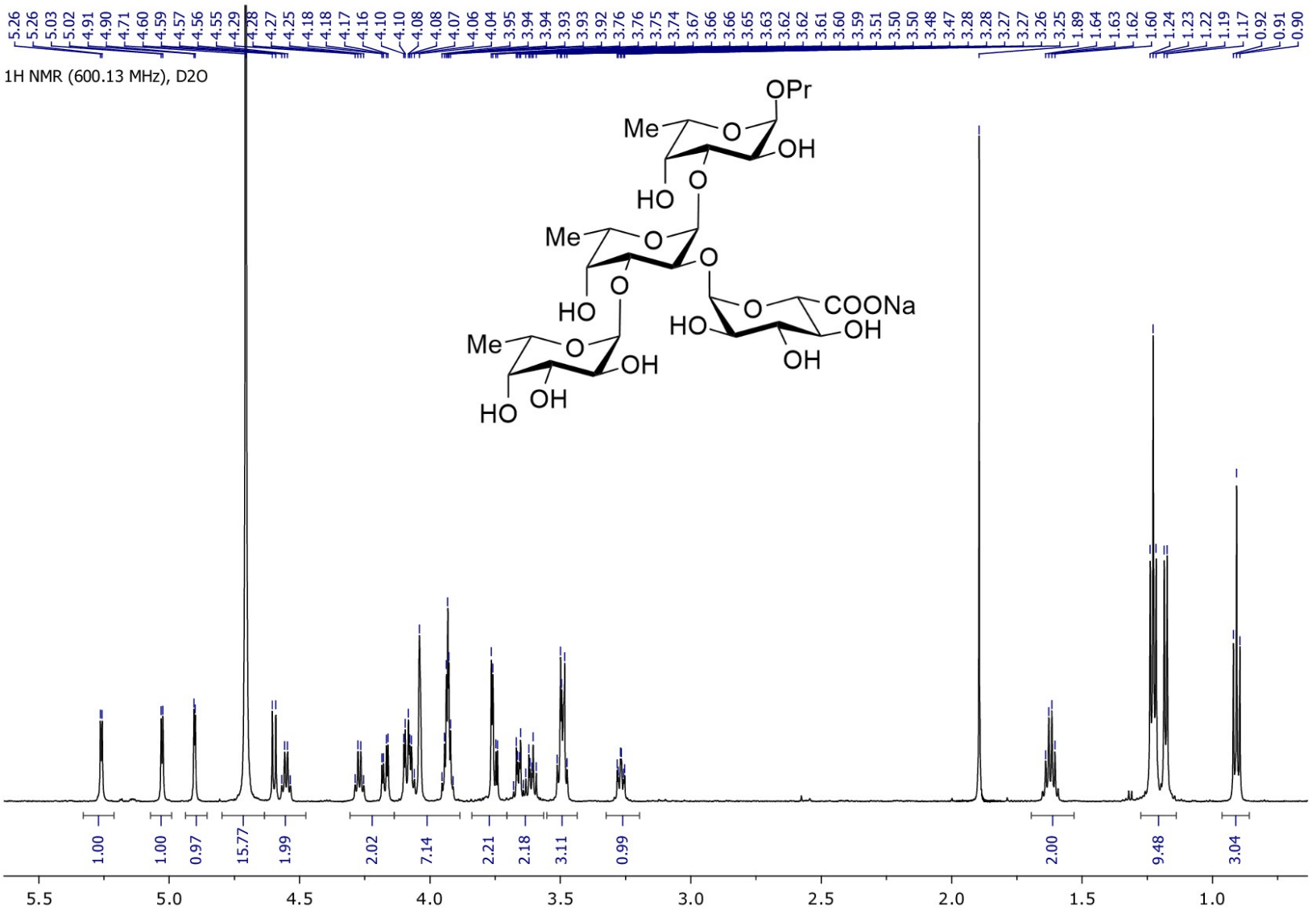
Acquisition Parameter

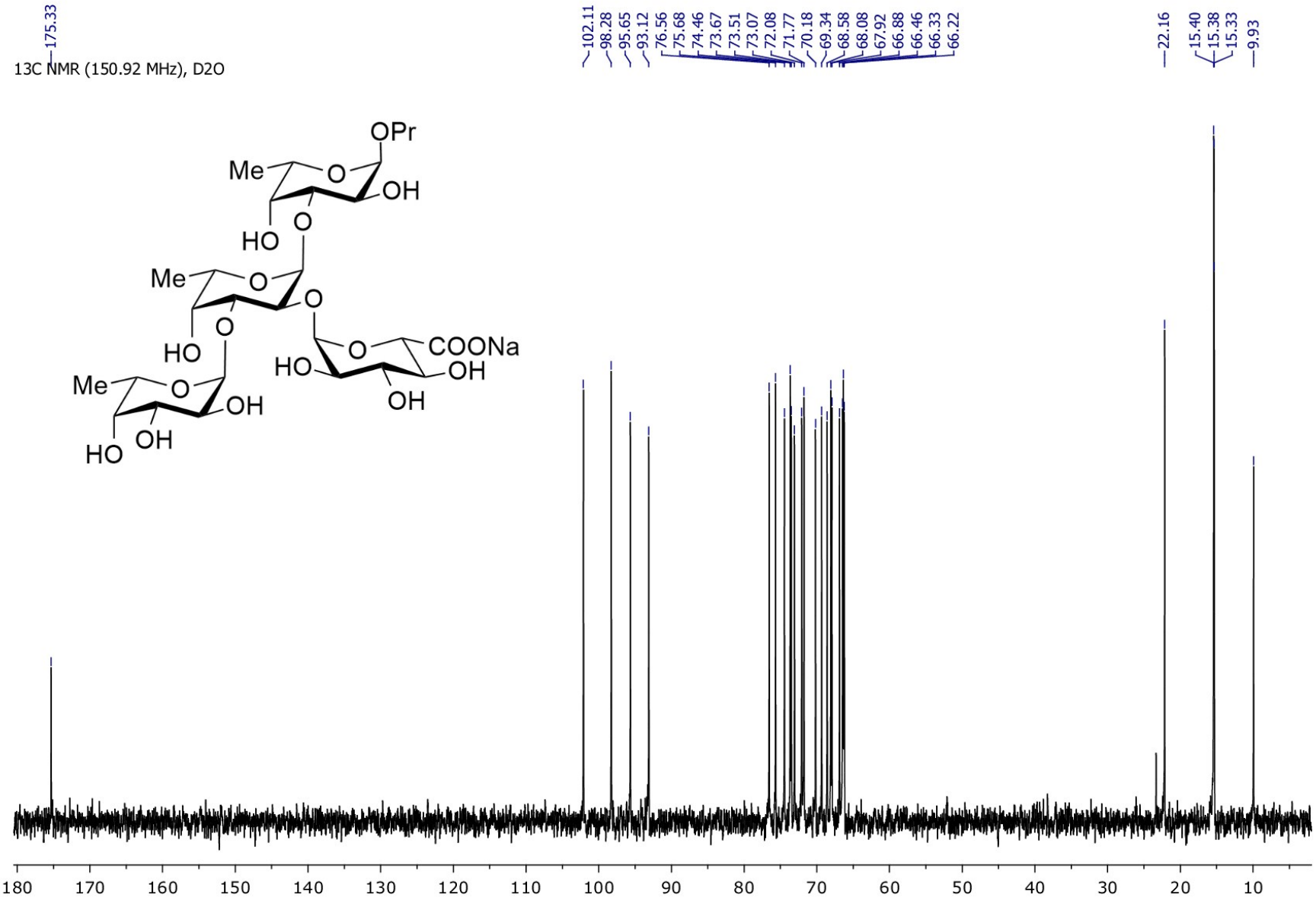
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





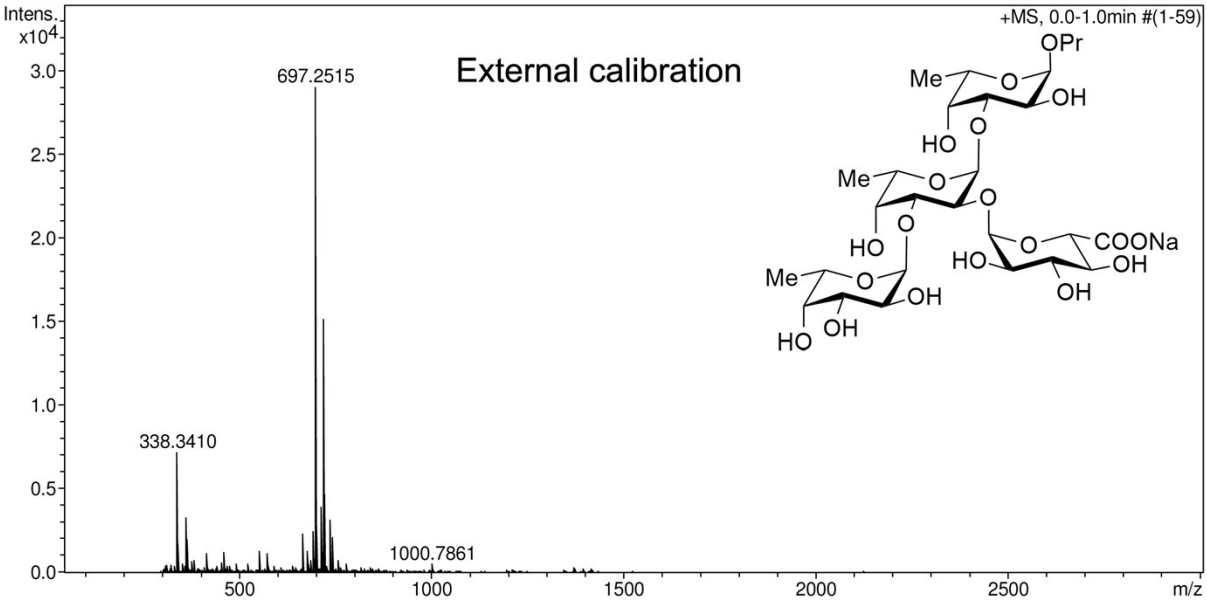
Sodium salt propyl α-L-fucopyranosyl-(1→3)-{ α-D-glucopyranosyluronate-(1→2)}-α-L-fucopyranosyl-(1→3)-α-L-fucopyranoside (1)

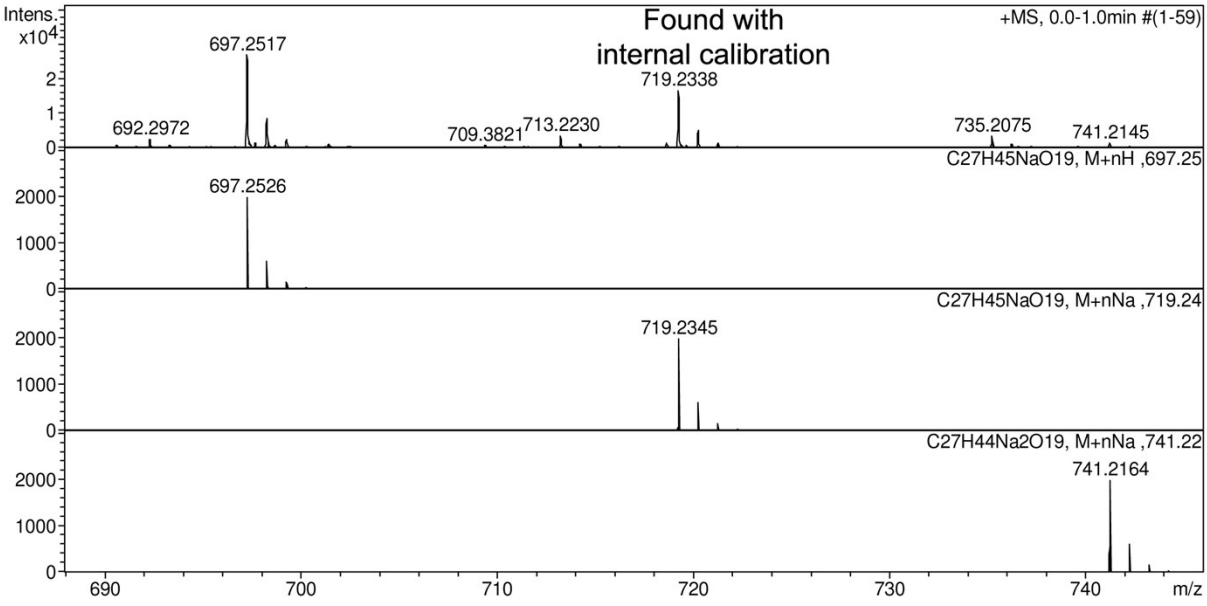



13C NMR (150.92 MHz), D2O
175.33
102.11
98.28
95.65
93.12
76.56
75.68
74.46
73.67
73.51
73.07
72.08
71.77
70.18
69.34
68.58
68.08
67.92
66.88
66.46
66.33
66.22
22.16
15.40
15.38
15.33
9.93
OPr
Me
O
OH
HO
O
Me
O
O
HO
O
COONa
HO
OH
OH
Me
O
OH
HO
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

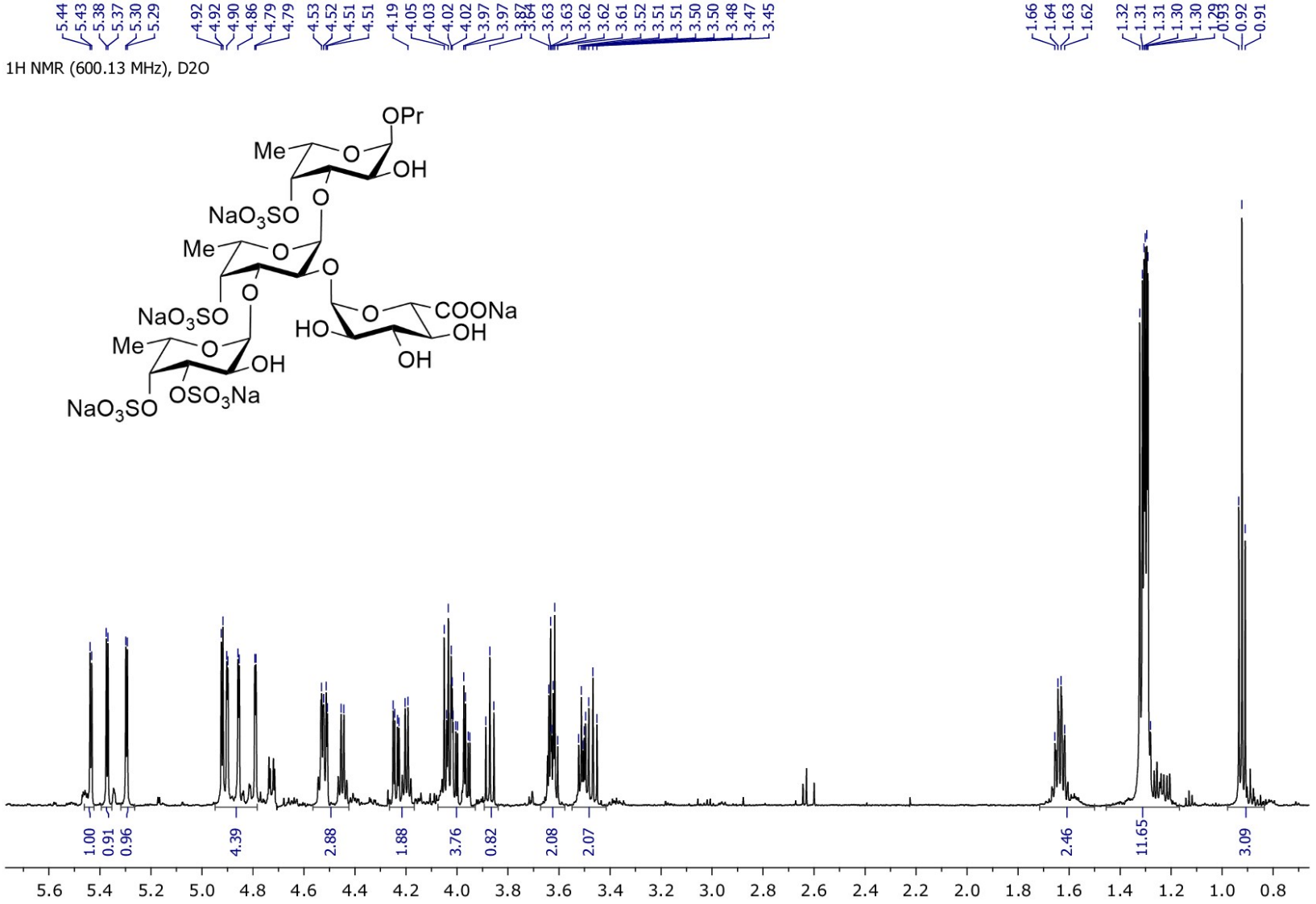
Acquisition Parameter

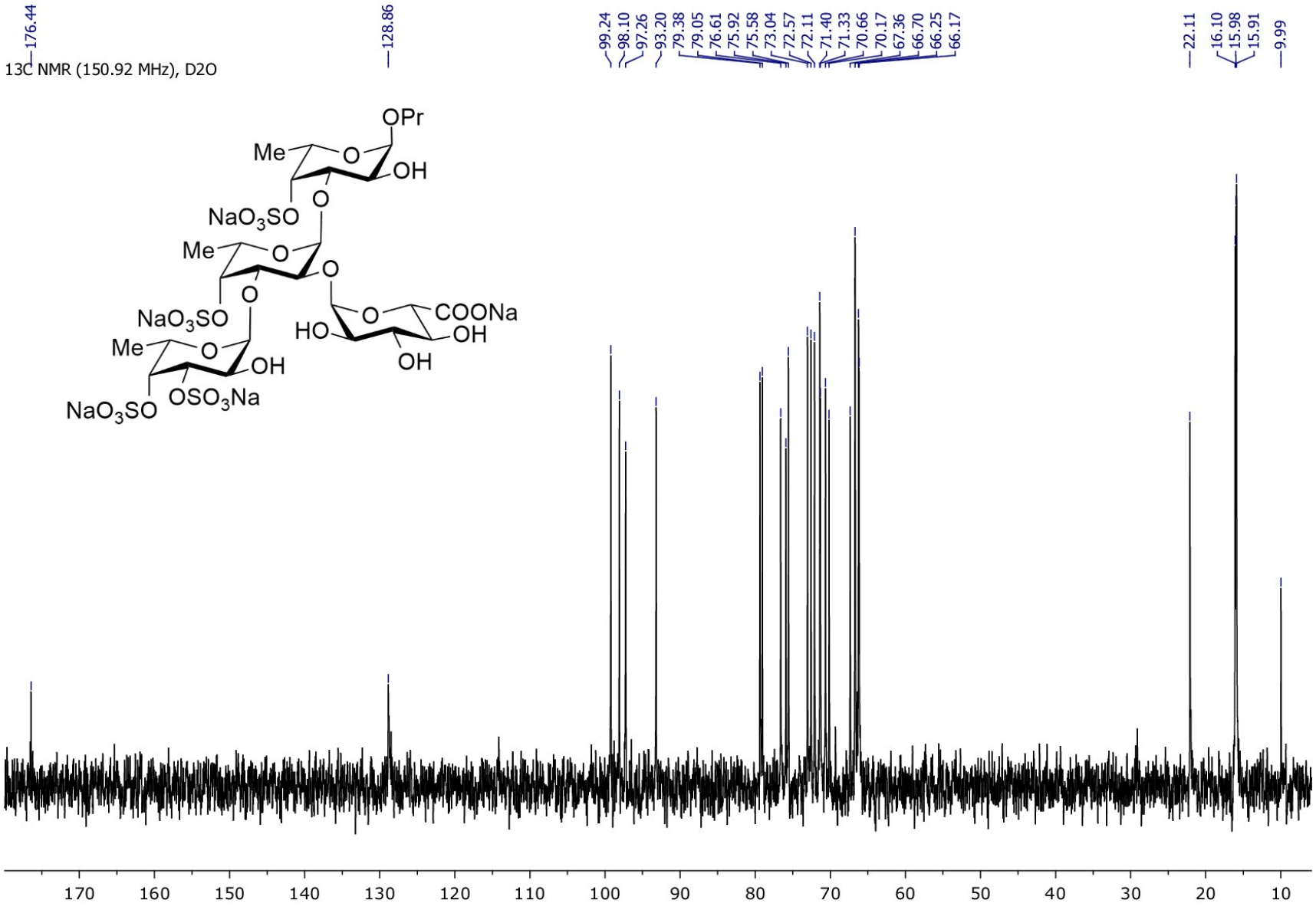
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





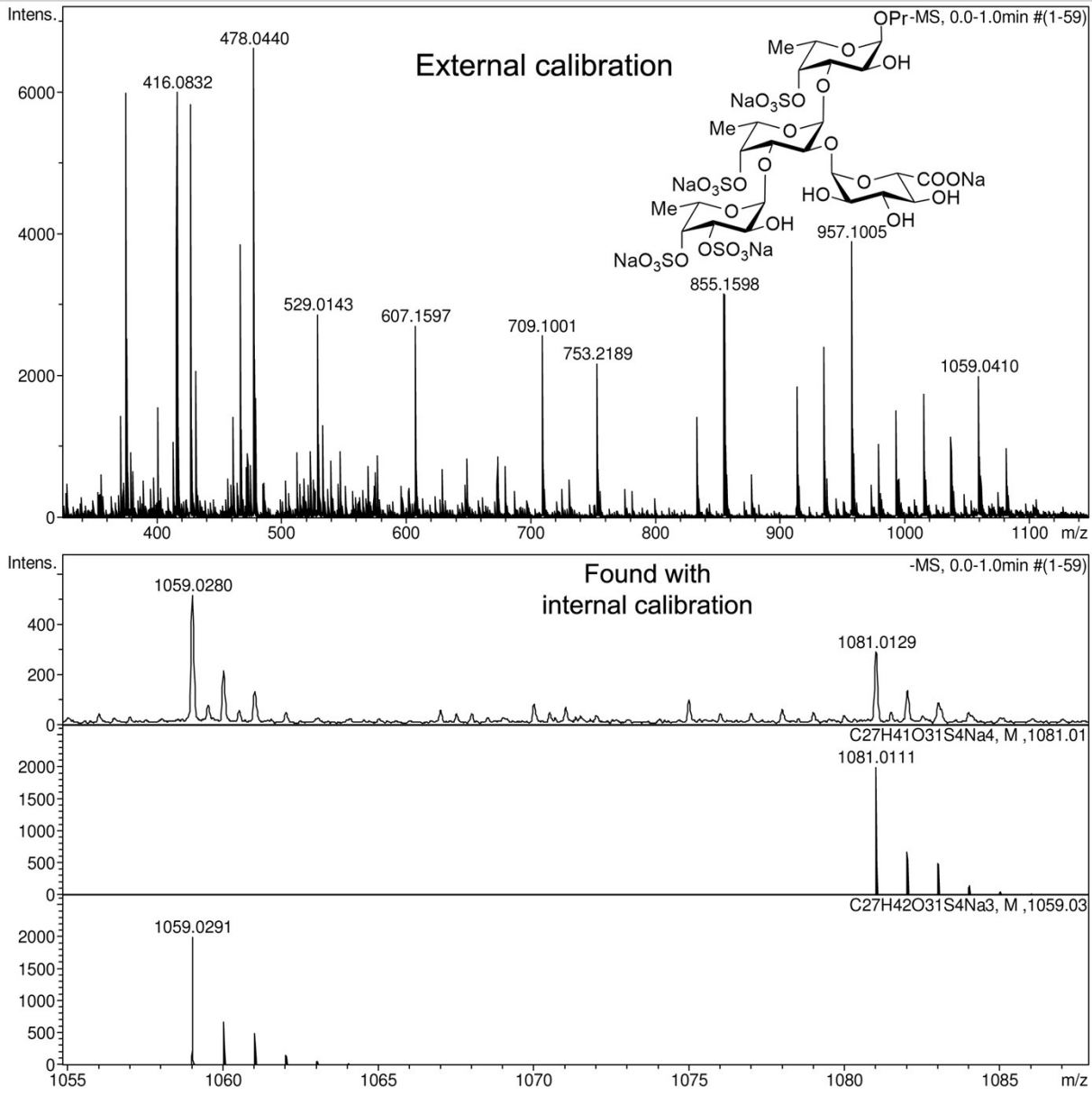
Sodium salt propyl 3,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-{ α-D-glucopyranosyluronate-(1→2)}-4-*O*-sulfonato-α-L-fucopyranosyl-(1→3)- 4-*O*-sulfonato-α-L-fucopyranoside (2)



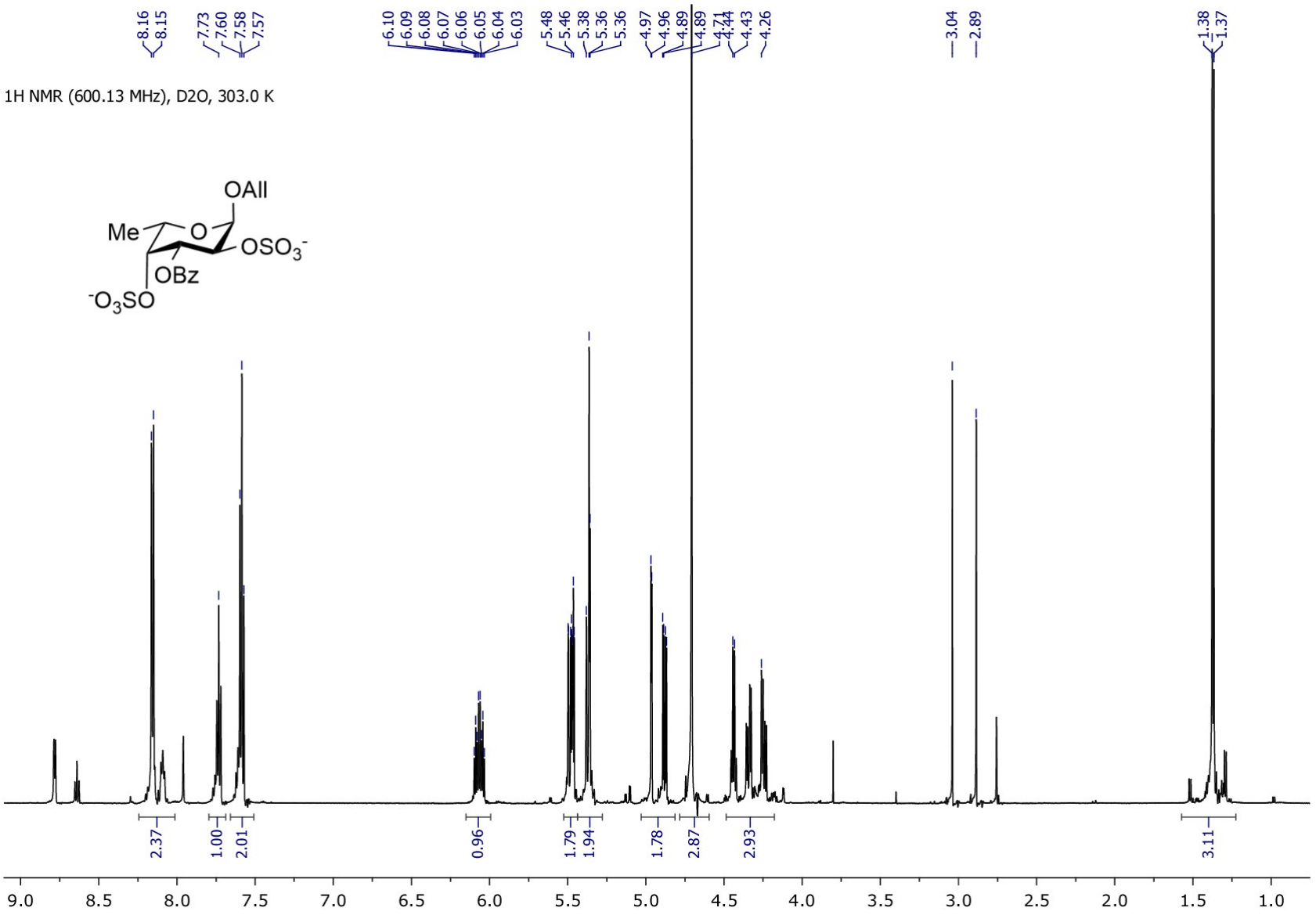

176.44
128.86
99.24
98.10
97.26
93.20
79.38
79.05
76.61
75.92
75.58
73.04
72.57
72.11
71.40
71.33
70.66
70.17
67.36
66.70
66.25
66.17
22.11
16.10
15.98
15.91
9.99
13C NMR (150.92 MHz), D2O
OPr
Me
O
OH
O
NaO3SO
Me
O
O
O
NaO3SO
HO
O
COONa
OH
OH
Me
O
OH
NaO3SO
OSO3Na
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

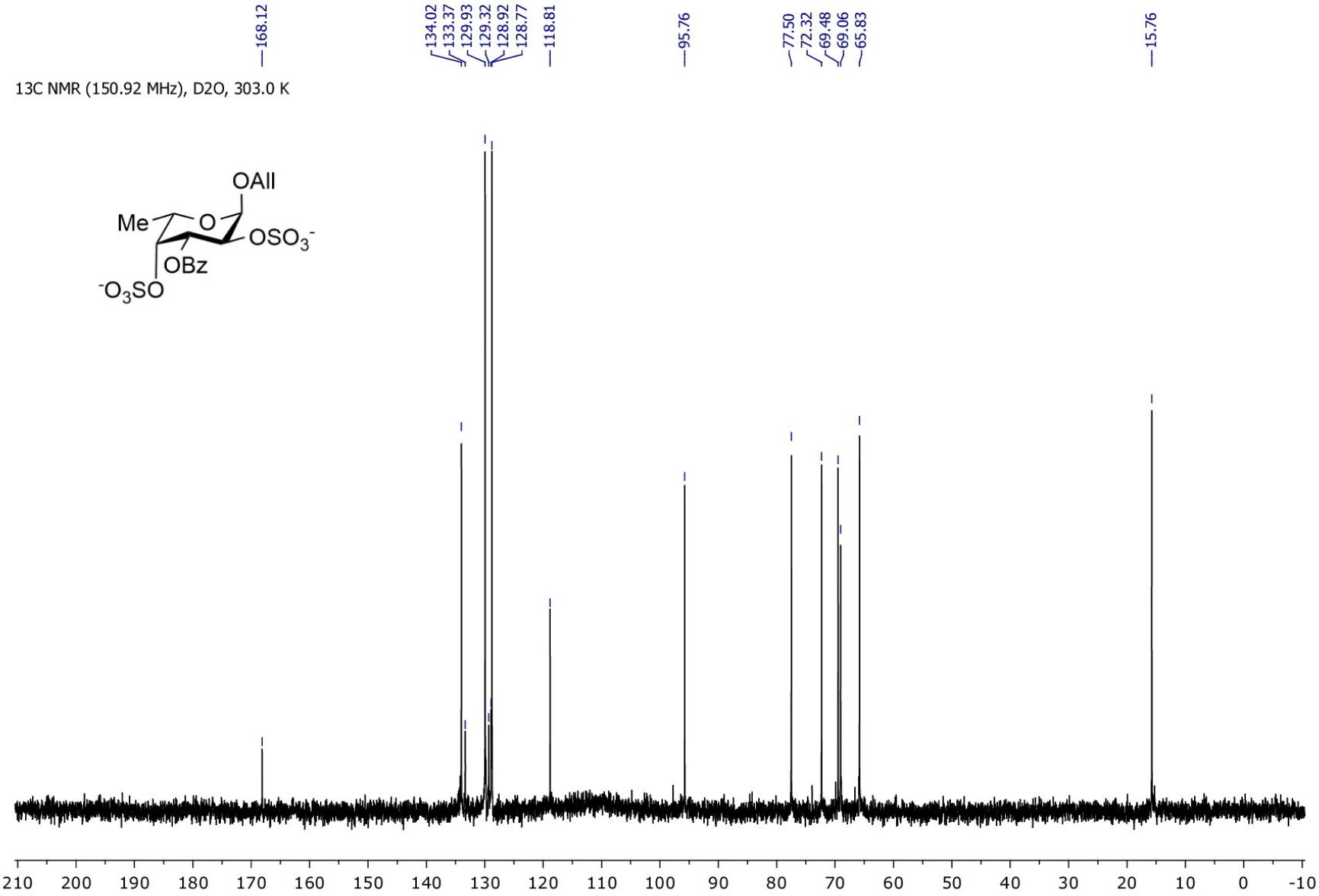
Acquisition Parameter

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

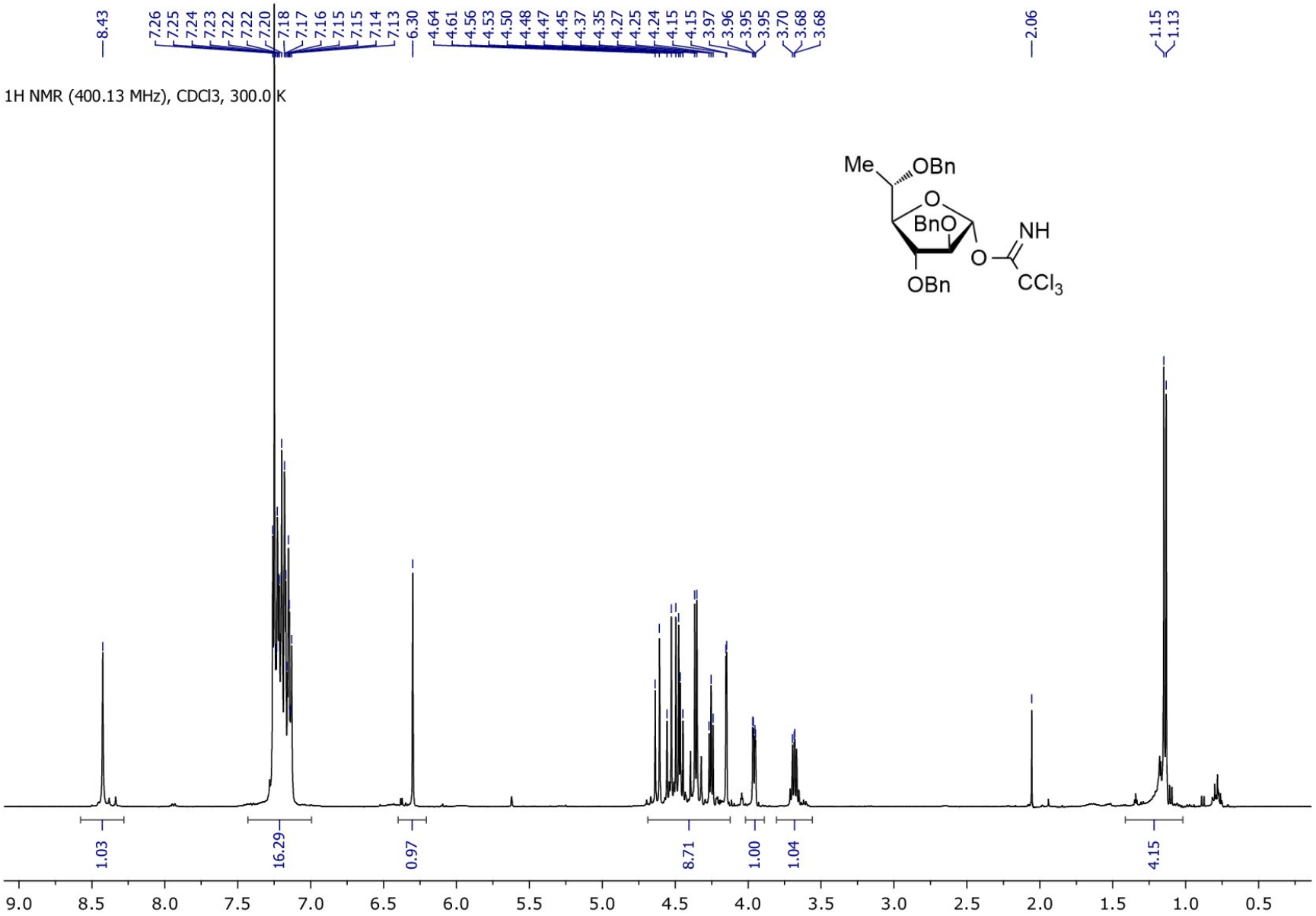


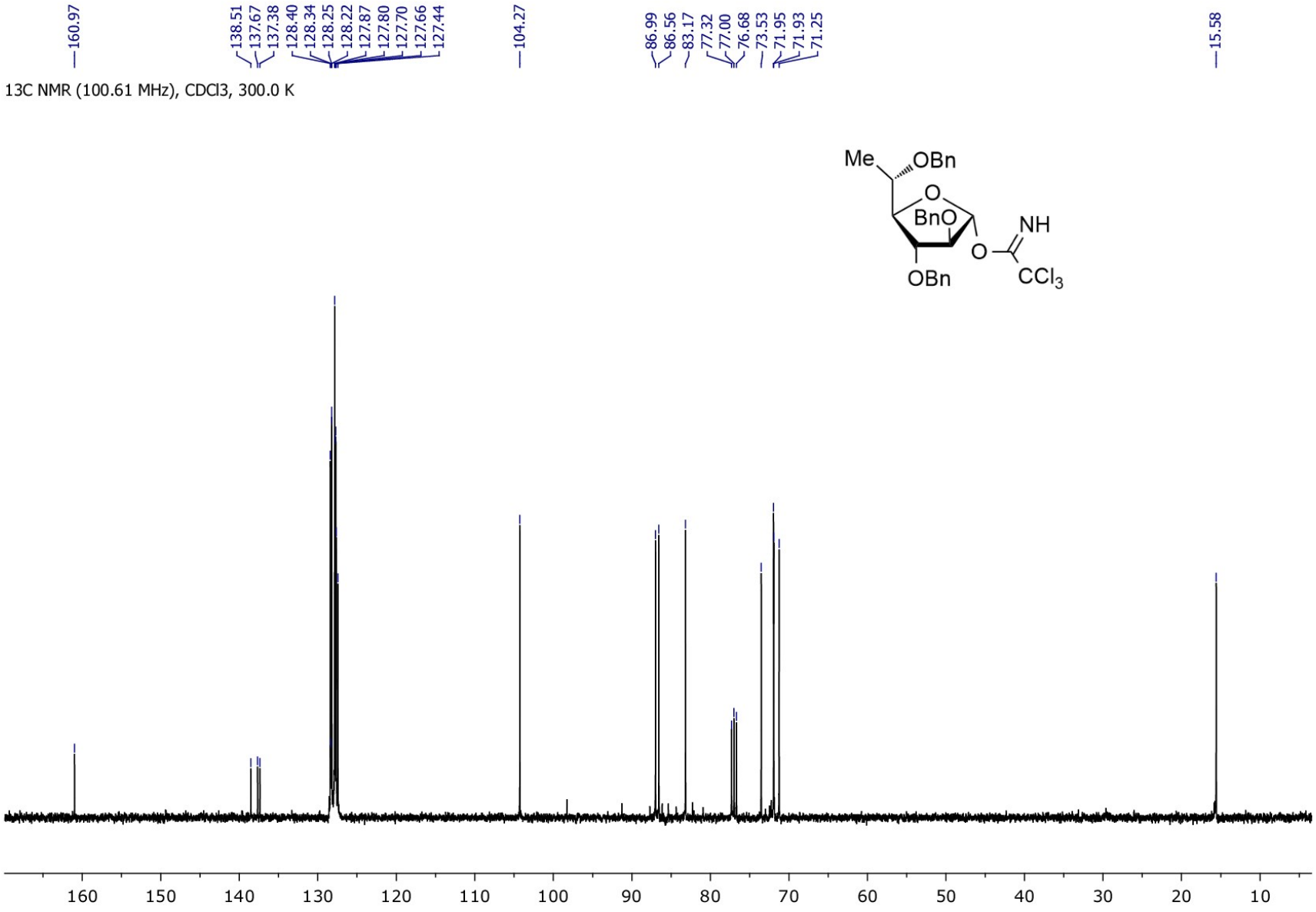
Sodium salt allyl 2,4-di-O-sulfonato-3-O-benzyl-α-L-fucopyranoside (21)




168.12
134.02
133.37
129.93
129.32
128.92
128.77
118.81
95.76
77.50
72.32
69.48
69.06
65.83
15.76
13C NMR (150.92 MHz), D2O, 303.0 K
OAll
Me
O
OSO3-
OBz
-O3SO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

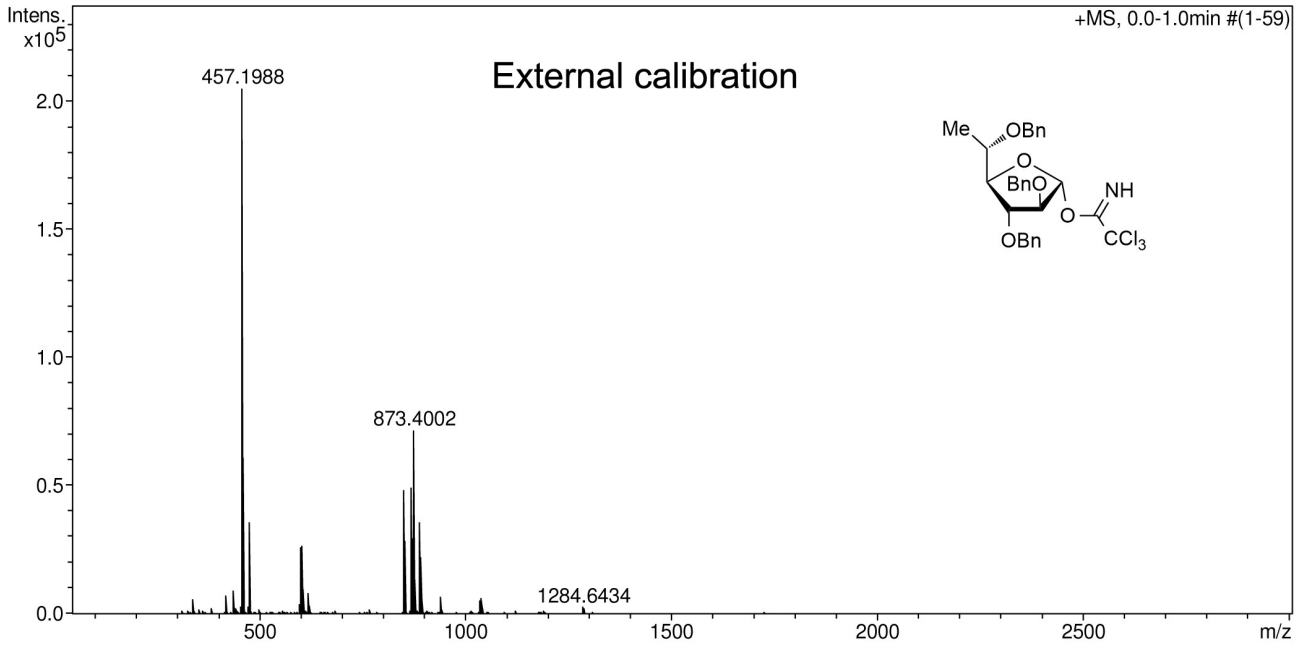
2,3,5-tri-O-benzyl-β-L-fucofuranoside trichloroacetoimidates (24)

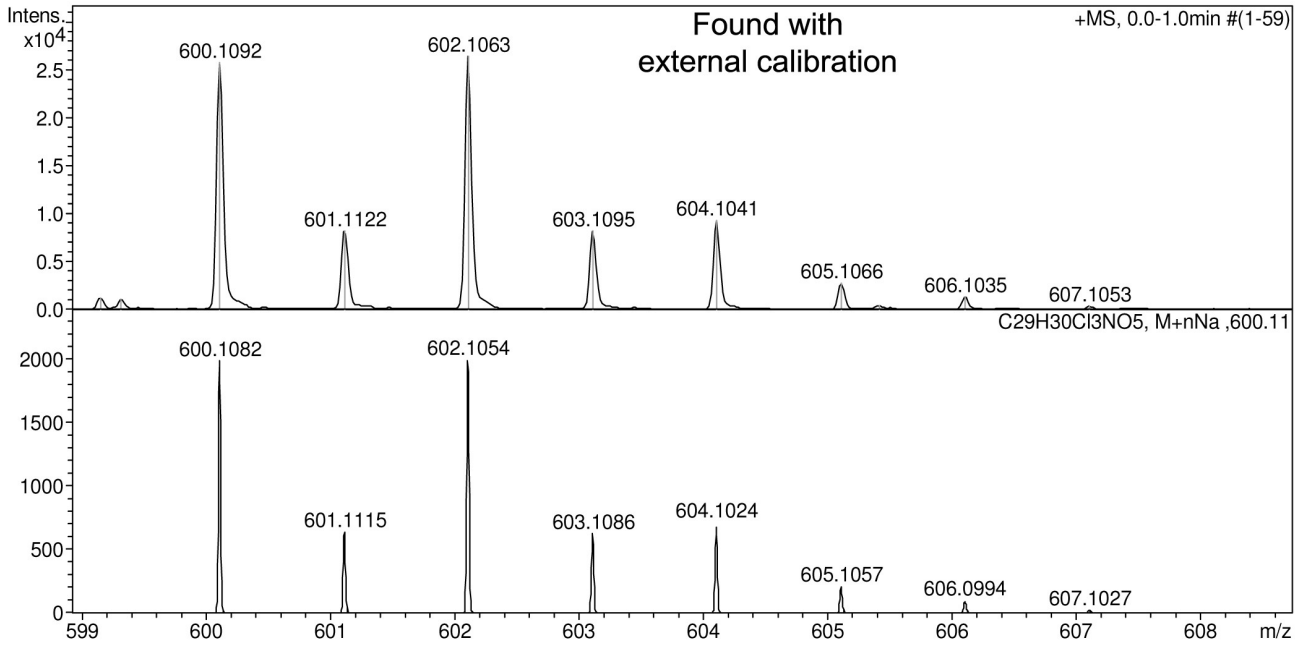



160.97
138.51
137.67
137.38
128.40
128.34
128.25
128.22
127.87
127.80
127.70
127.66
127.44
104.27
86.99
86.56
83.17
77.32
77.00
76.68
73.53
71.95
71.93
71.25
15.58
13C NMR (100.61 MHz), CDCl3, 300.0 K
Me
OBn
O
BnO
NH
O
CCl3
OBn
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

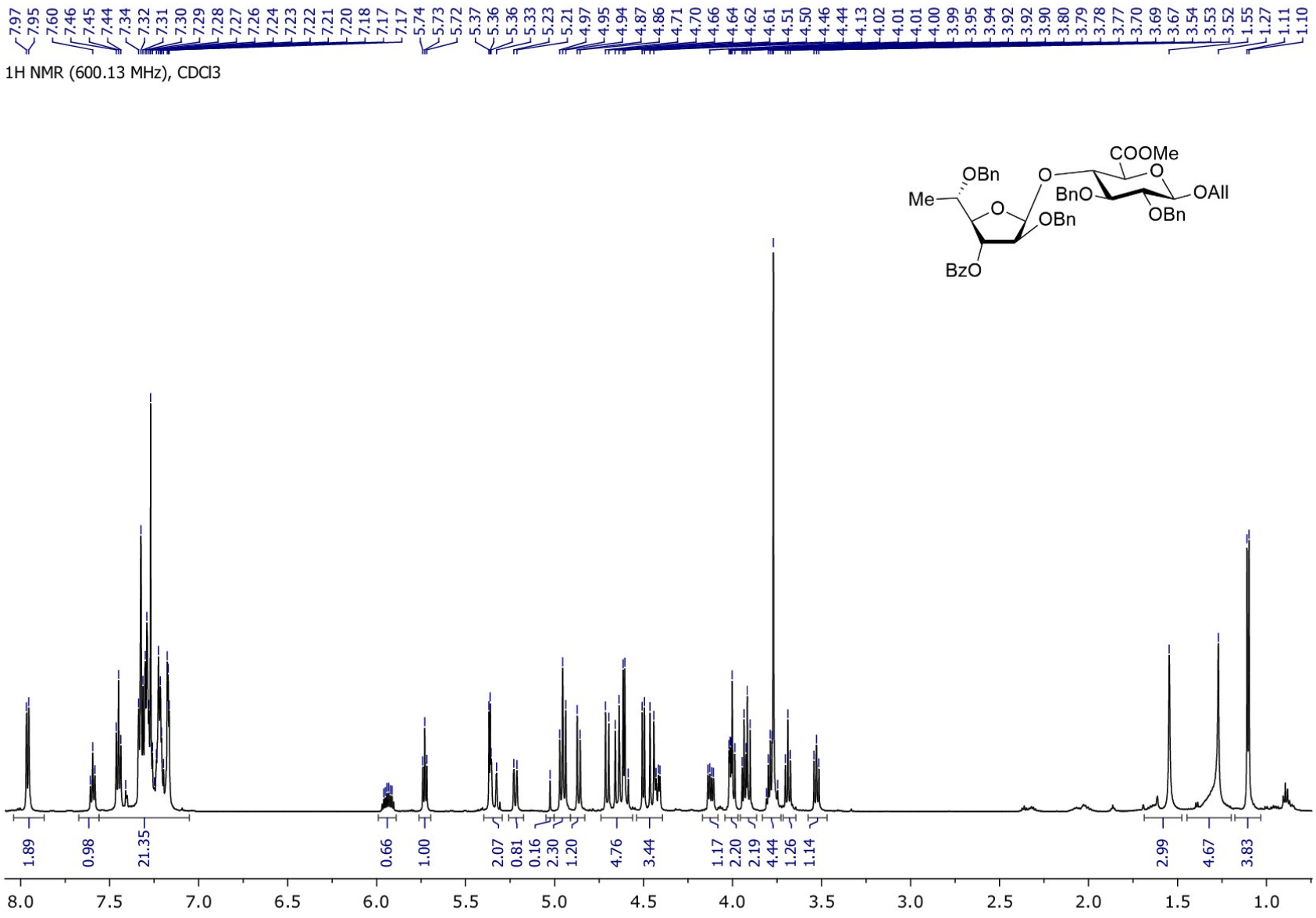
Acquisition Parameter

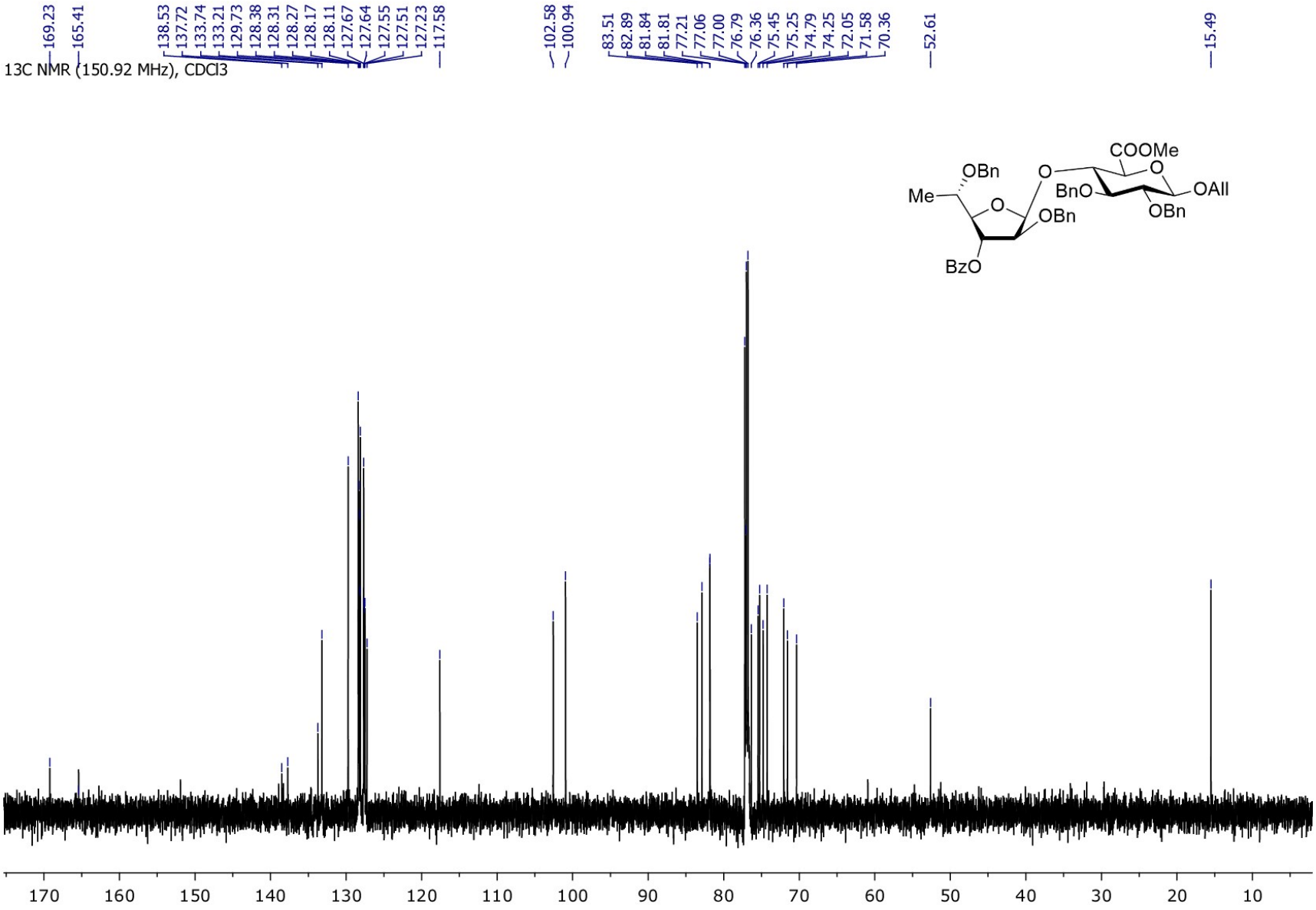
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





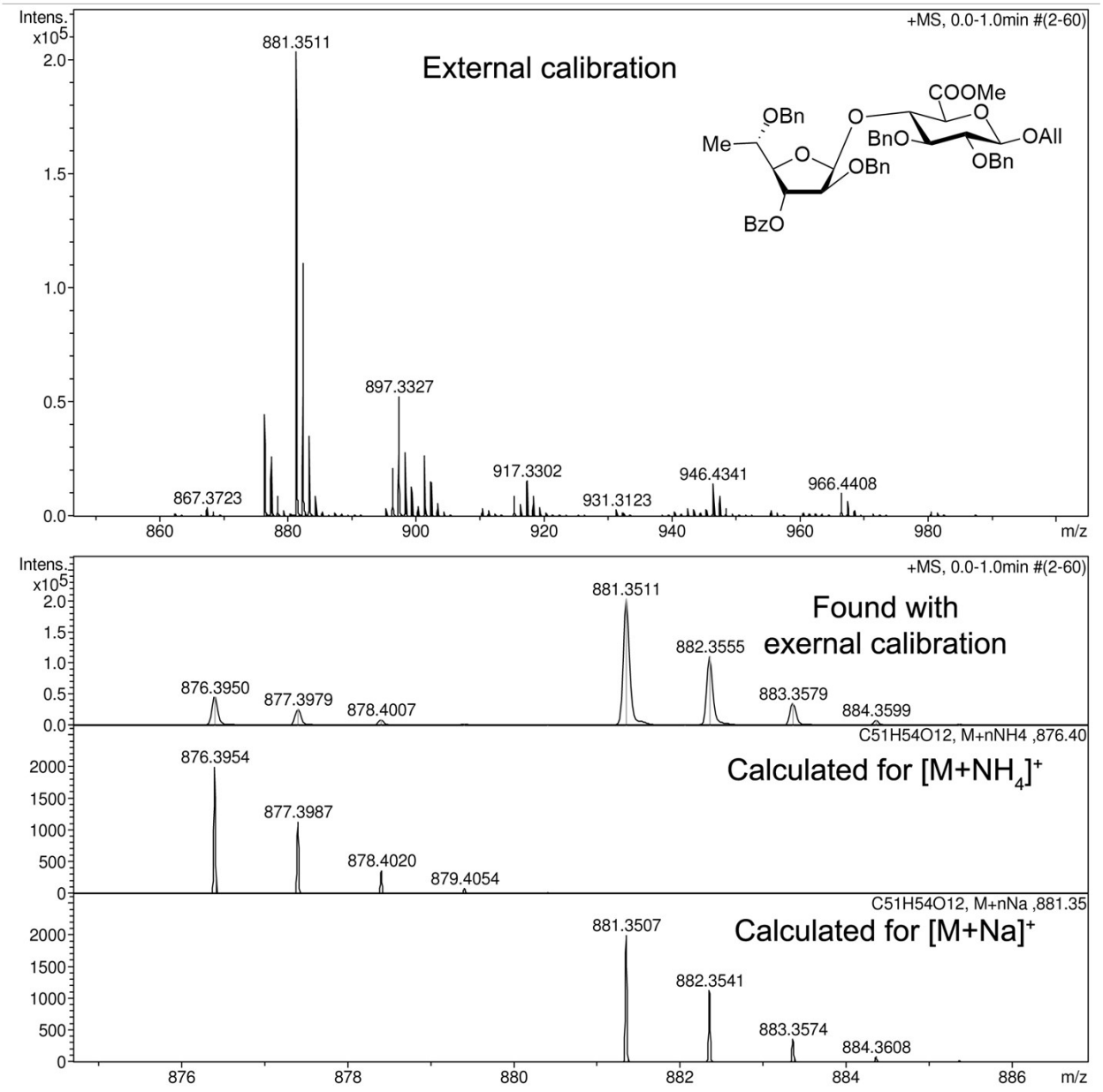
Allyl 2,5-di-*O*-benzyl-3-*O*-benzoyl-α-L-fucofuranosyl-(1→4)-methyl-2,3-di-*O*-benzyl-β-D-glucopyranozyl uronate (25α)



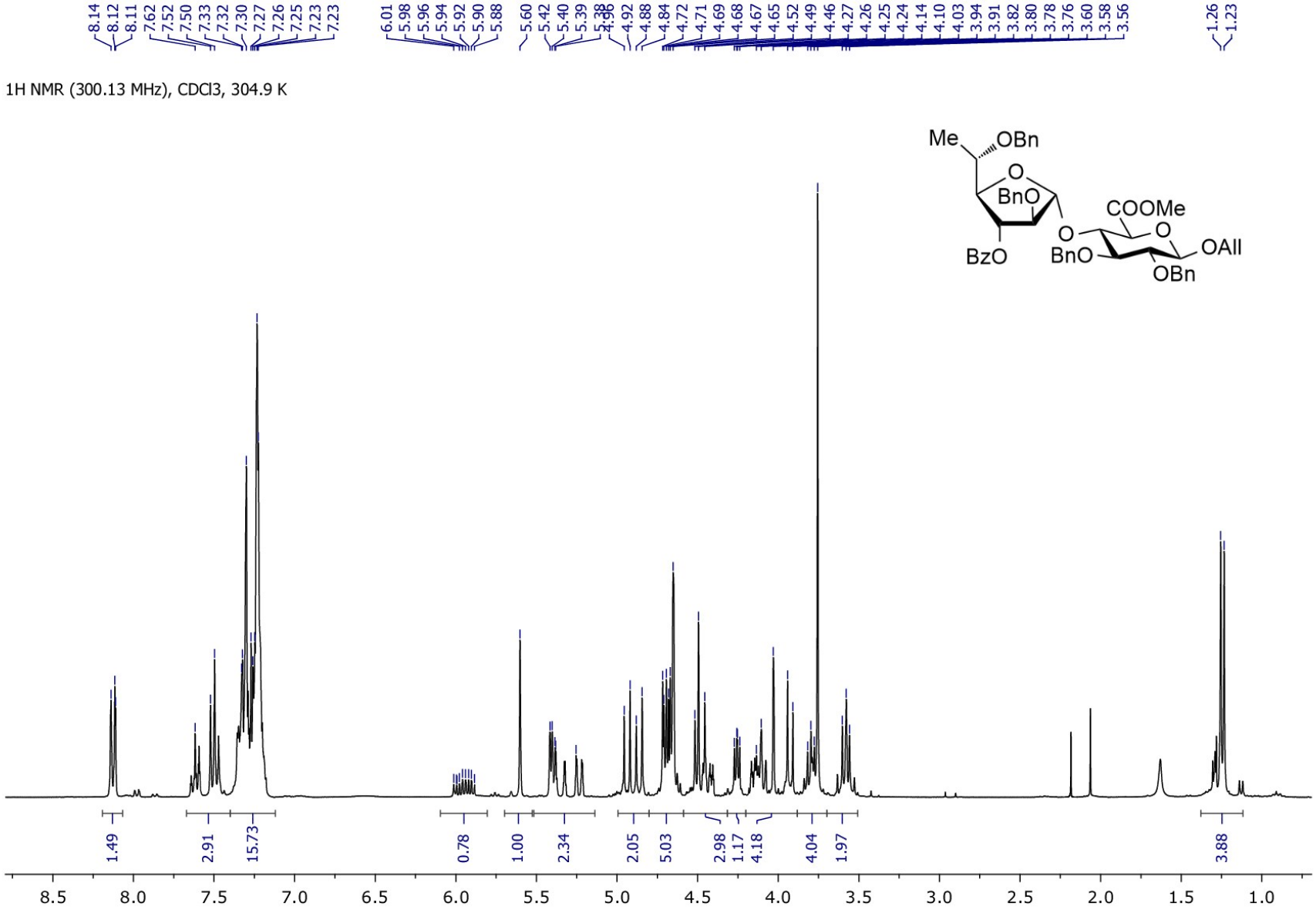

169.23
165.41
138.53
137.72
133.74
133.21
129.73
128.38
128.31
128.27
128.17
128.11
127.67
127.64
127.55
127.51
127.23
117.58
102.58
100.94
83.51
82.89
81.84
81.81
77.21
77.06
77.00
76.79
76.36
75.45
75.25
74.79
74.25
72.05
71.58
70.36
52.61
15.49
13C NMR (150.92 MHz), CDCl3
COOMe
OBn
O
O
Me
BnO
OAll
O
OBn
OBn
BzO
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

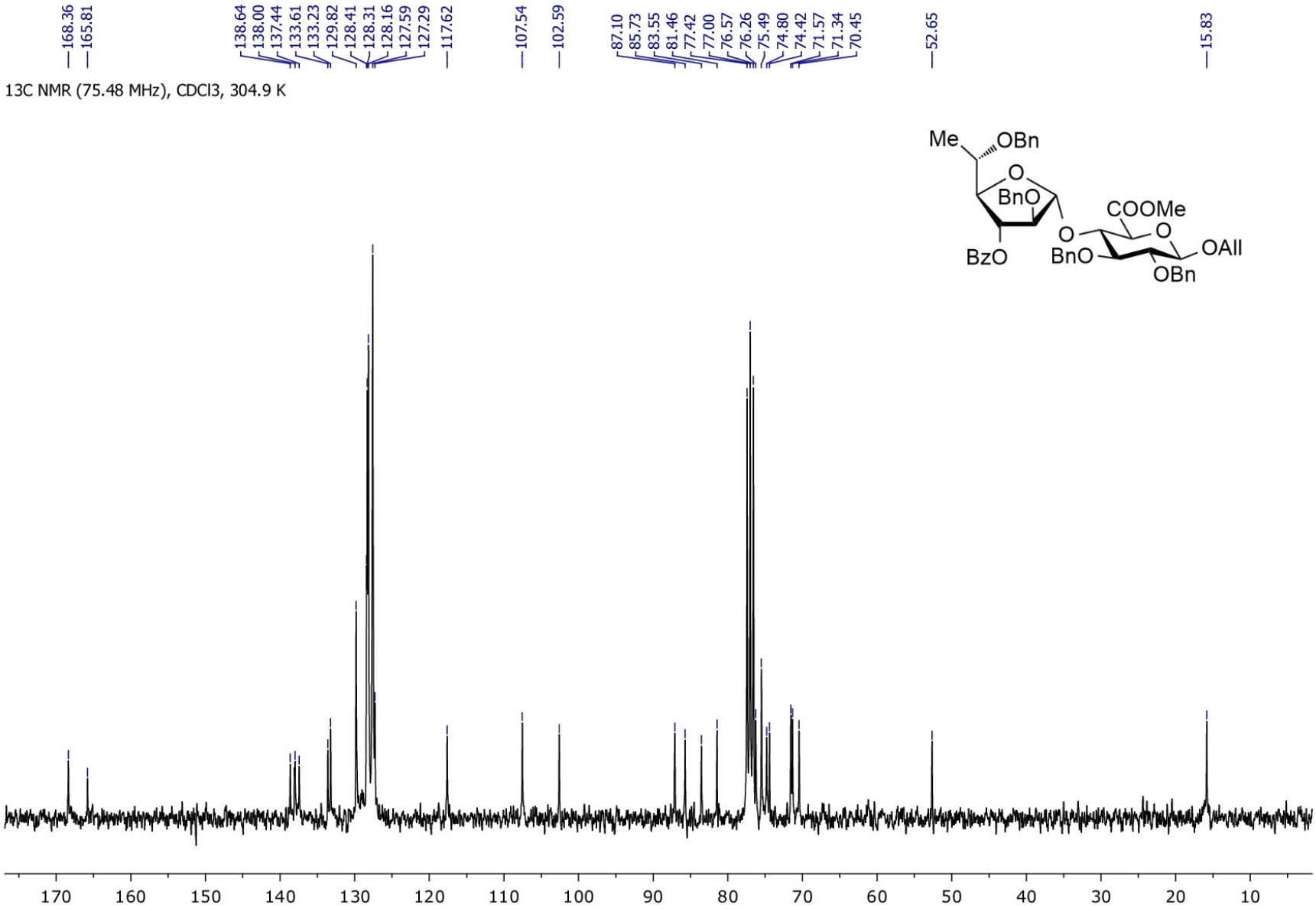
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
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



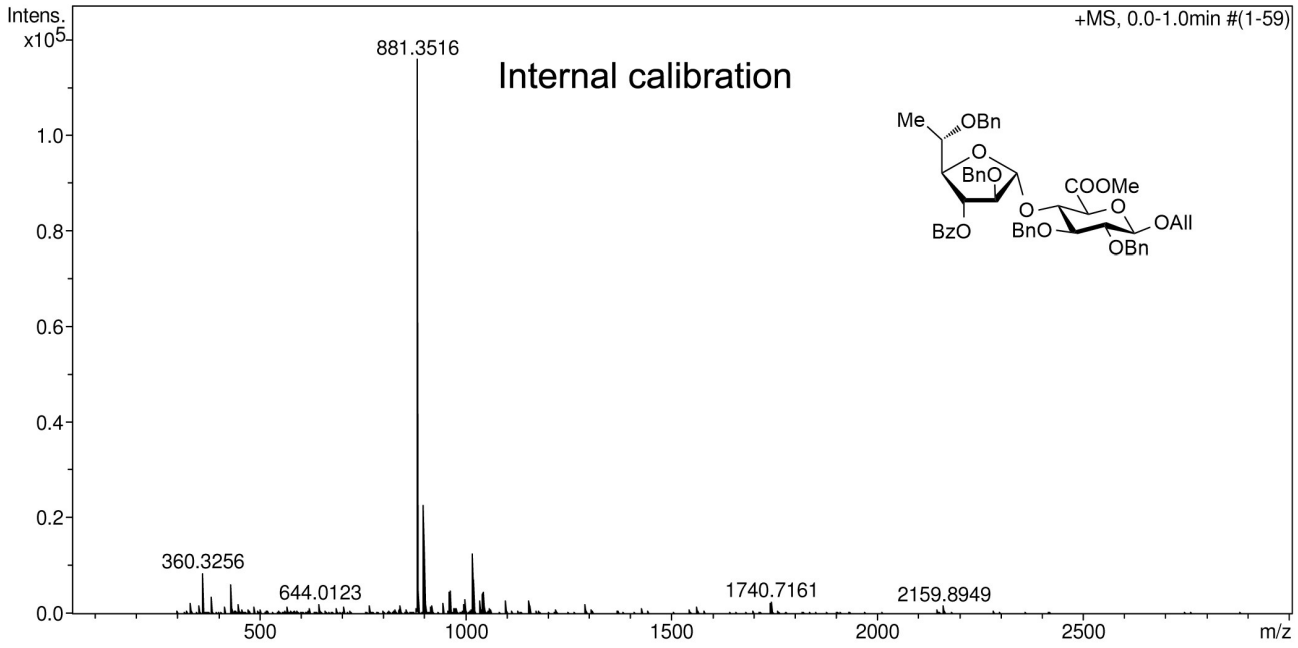
Allyl 2,5-di-*O*-benzyl-3-*O*-benzoyl-β-L-fucofuranosyl-(1→4)-methyl-2,3-di-*O*-benzyl-β-D-glucopyranozyl uronate (25β)

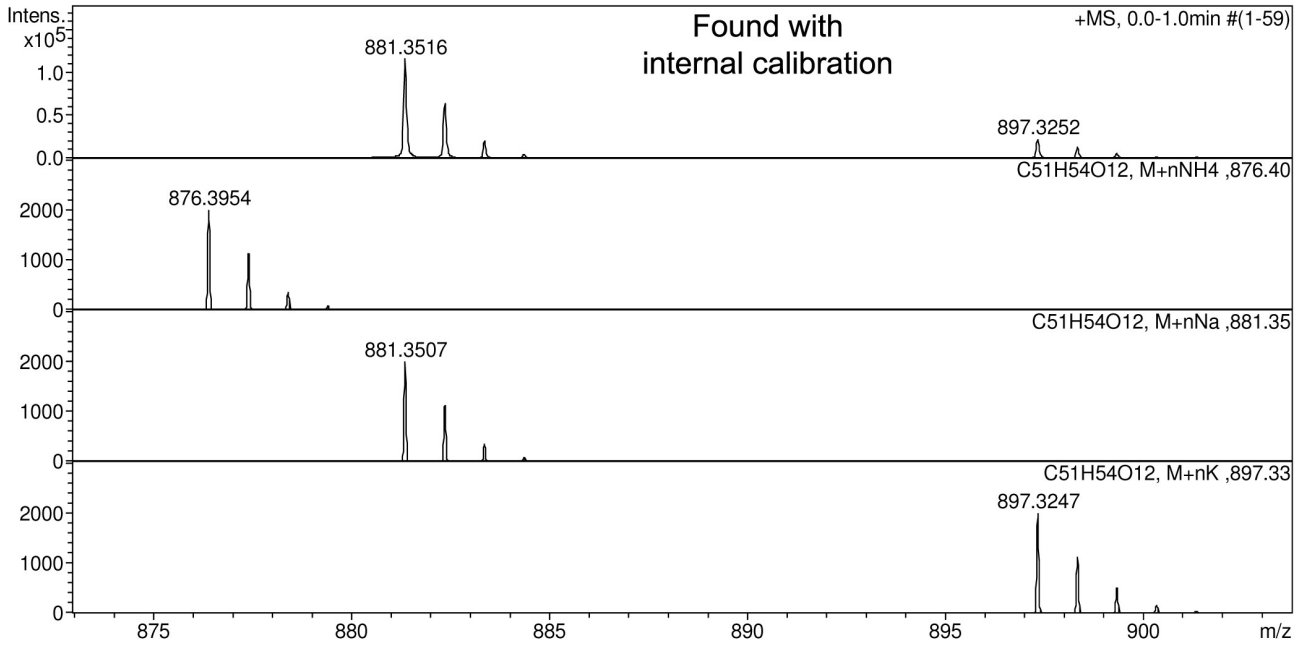



168.36
165.81
138.64
138.00
137.44
133.61
133.23
129.82
128.41
128.31
128.16
127.59
127.29
117.62
107.54
102.59
87.10
85.73
83.55
81.46
77.42
77.00
76.57
76.26
75.49
74.80
74.42
71.57
71.34
70.45
52.65
15.83
13C NMR (75.48 MHz), CDCl3, 304.9 K
Me
OBn
O
BnO
BzO
COOMe
O
O
BnO
OAll
OBn
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

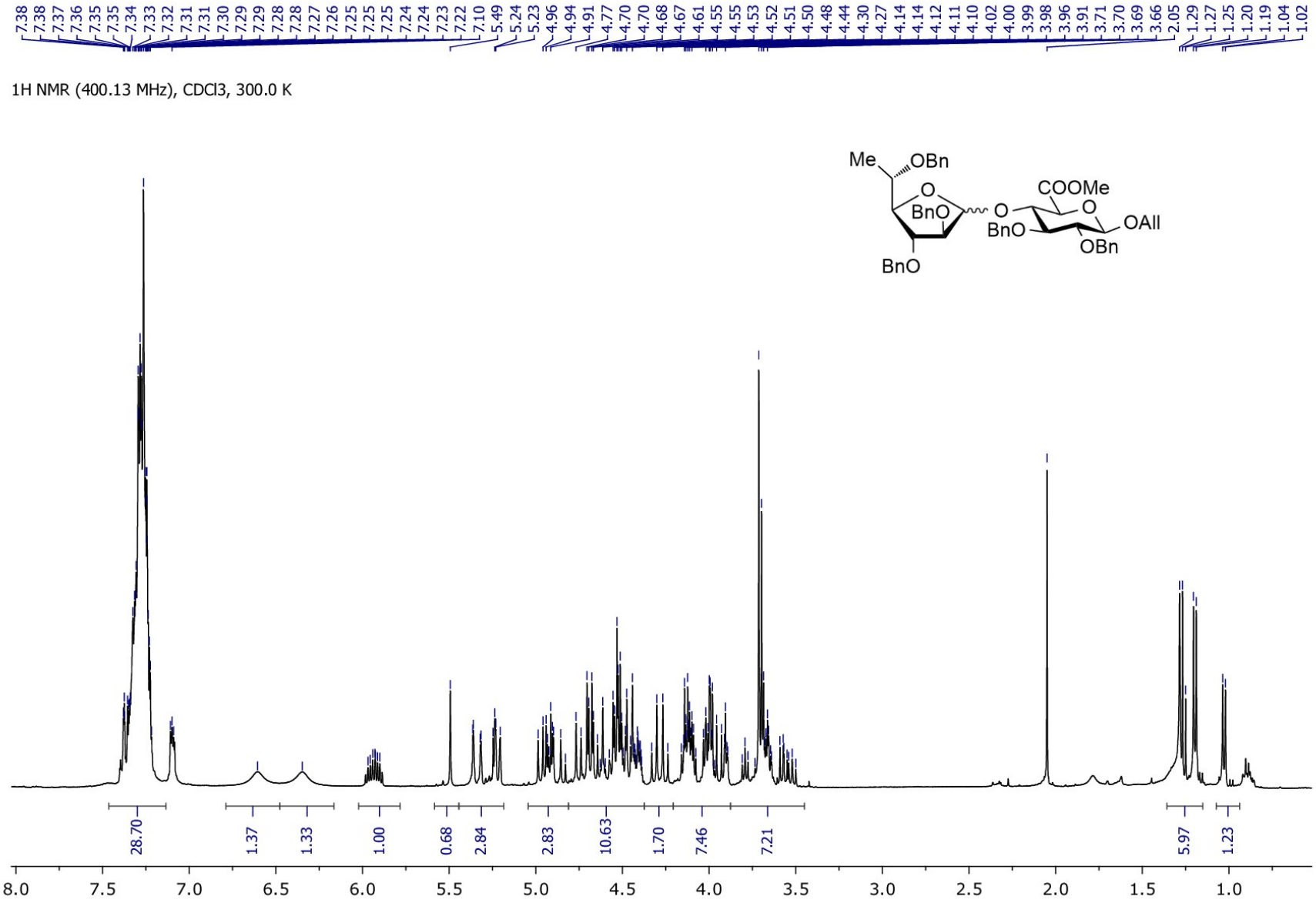
Acquisition Parameter

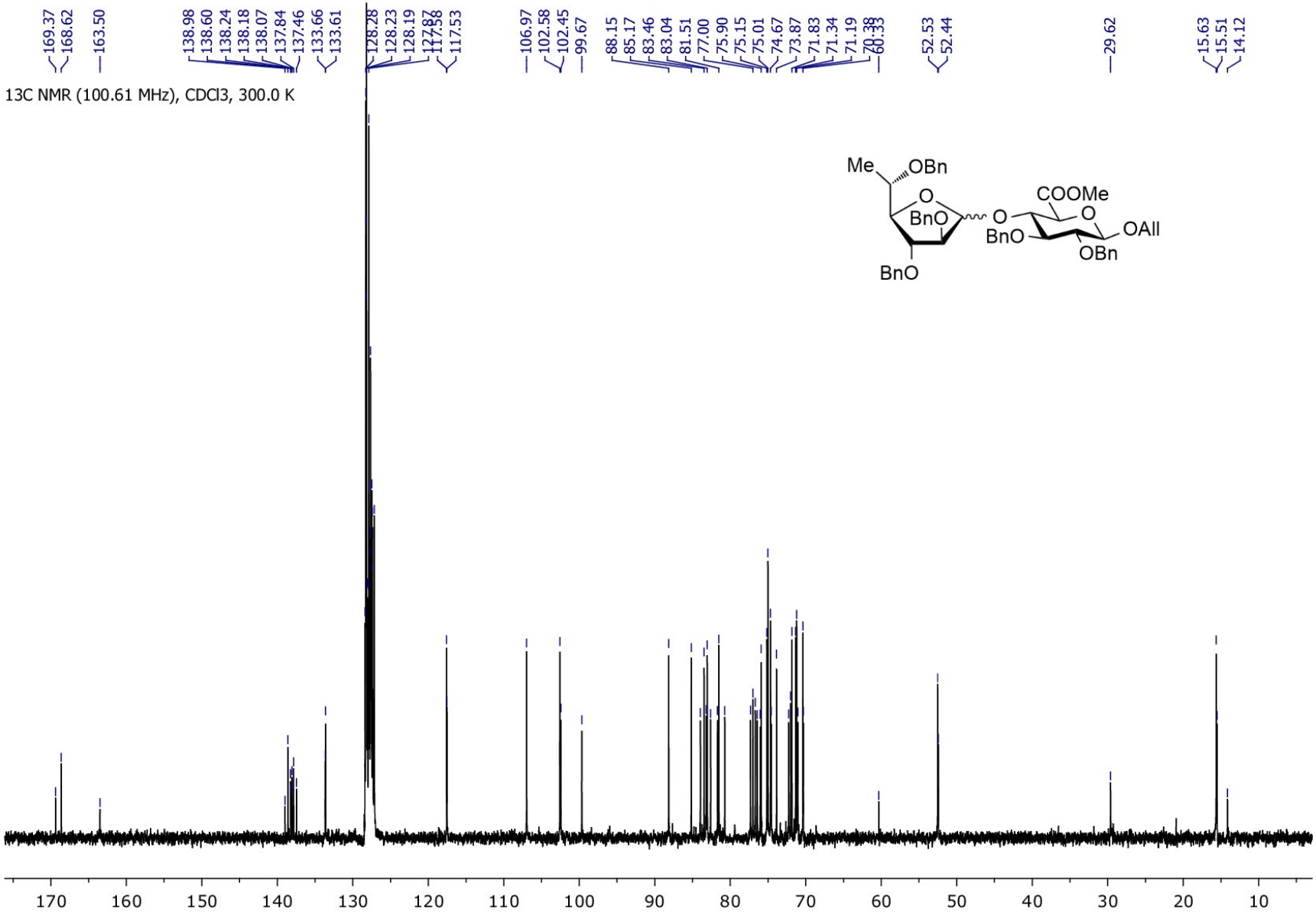
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





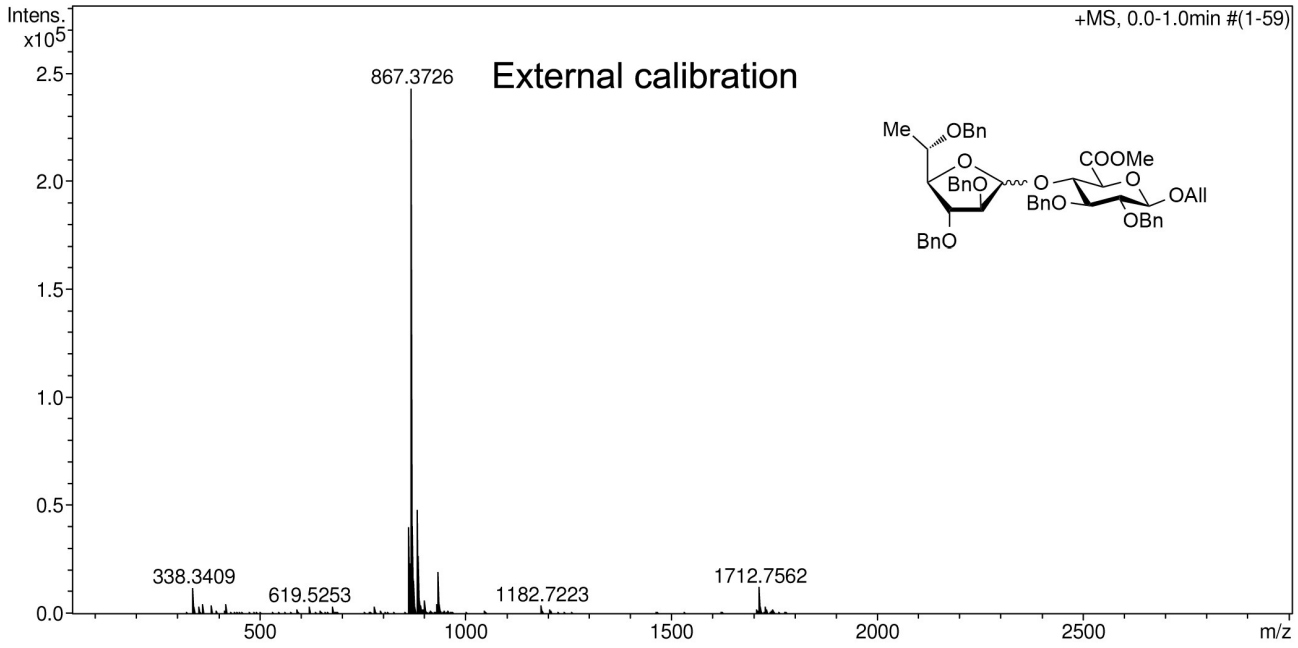
Allyl 2,3,5-tri-*O*-benzyl-α,β-L-fucofuranosyl-(1→4)-methyl-2,3-di-*O*-benzyl-β-D-glucopyranozyl uronate (26)

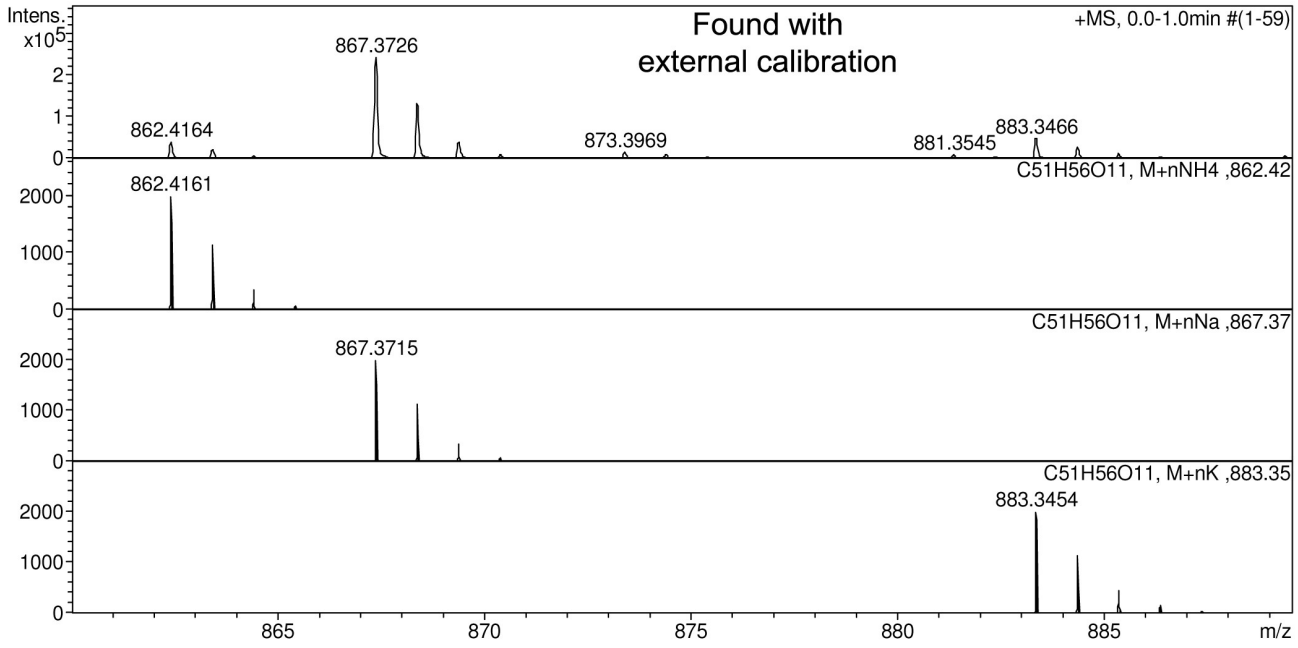



169.37
168.62
163.50
138.98
138.60
138.24
138.18
138.07
137.84
137.46
133.66
133.61
128.28
128.23
128.19
117.53
106.97
102.58
102.45
99.67
88.15
85.17
83.46
83.04
81.51
77.00
75.90
75.15
75.01
74.67
73.87
71.83
71.34
71.19
52.53
52.44
29.62
15.63
15.51
14.12
13C NMR (100.61 MHz), CDCl3, 300.0 K
Me
OBn
O
BnO
BnO
O
COOMe
O
BnO
OAll
OBn
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

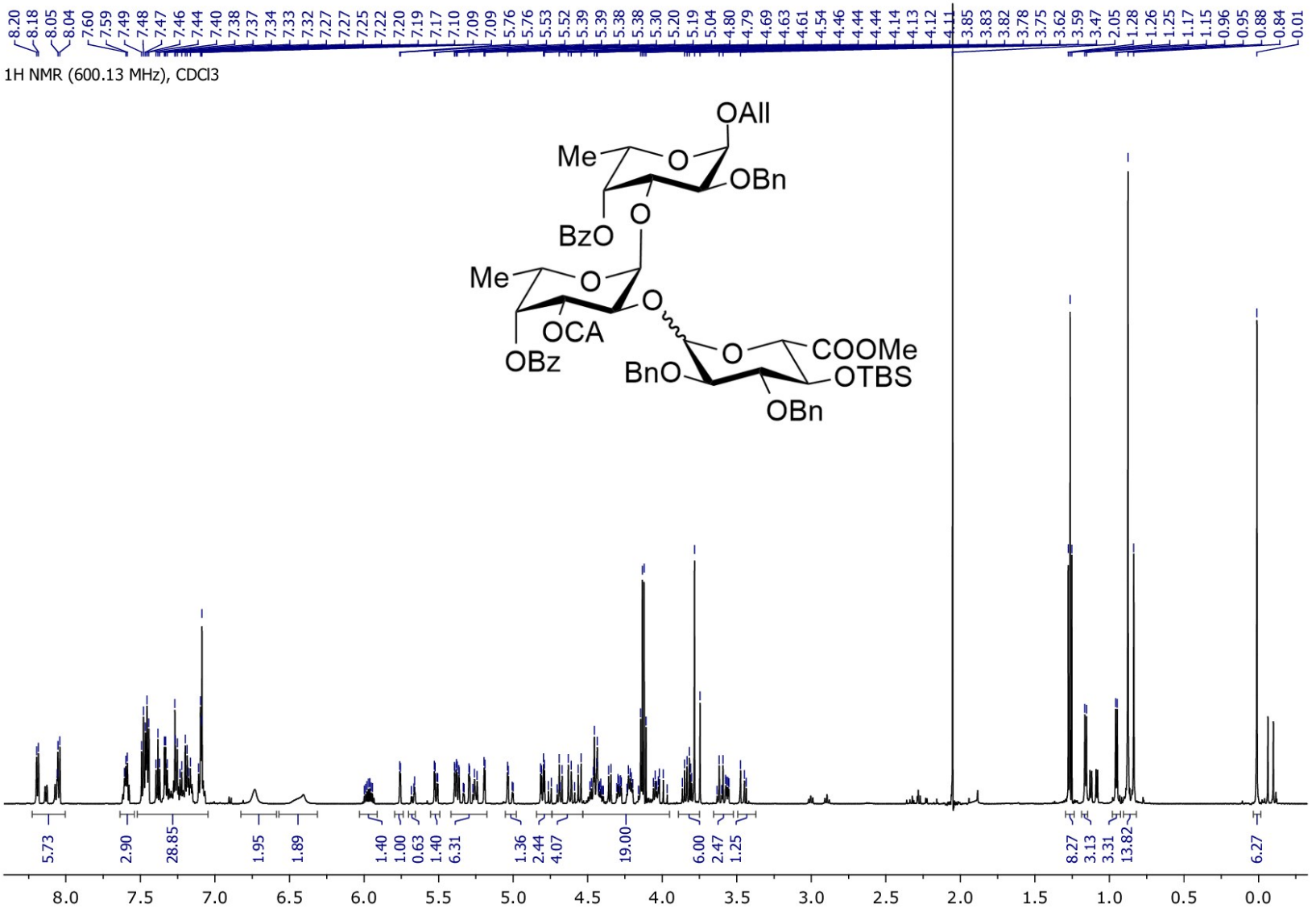
Acquisition Parameter

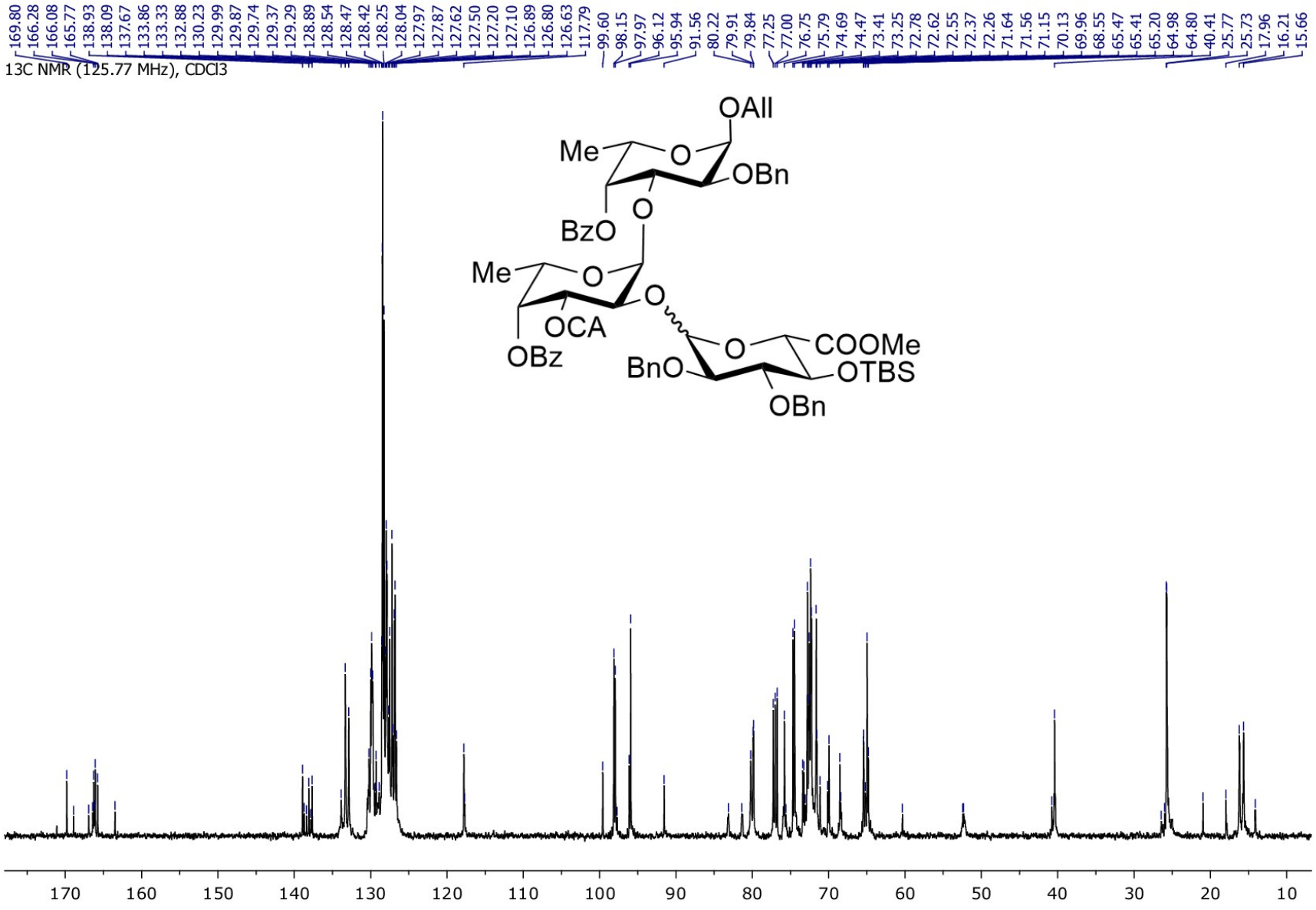
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





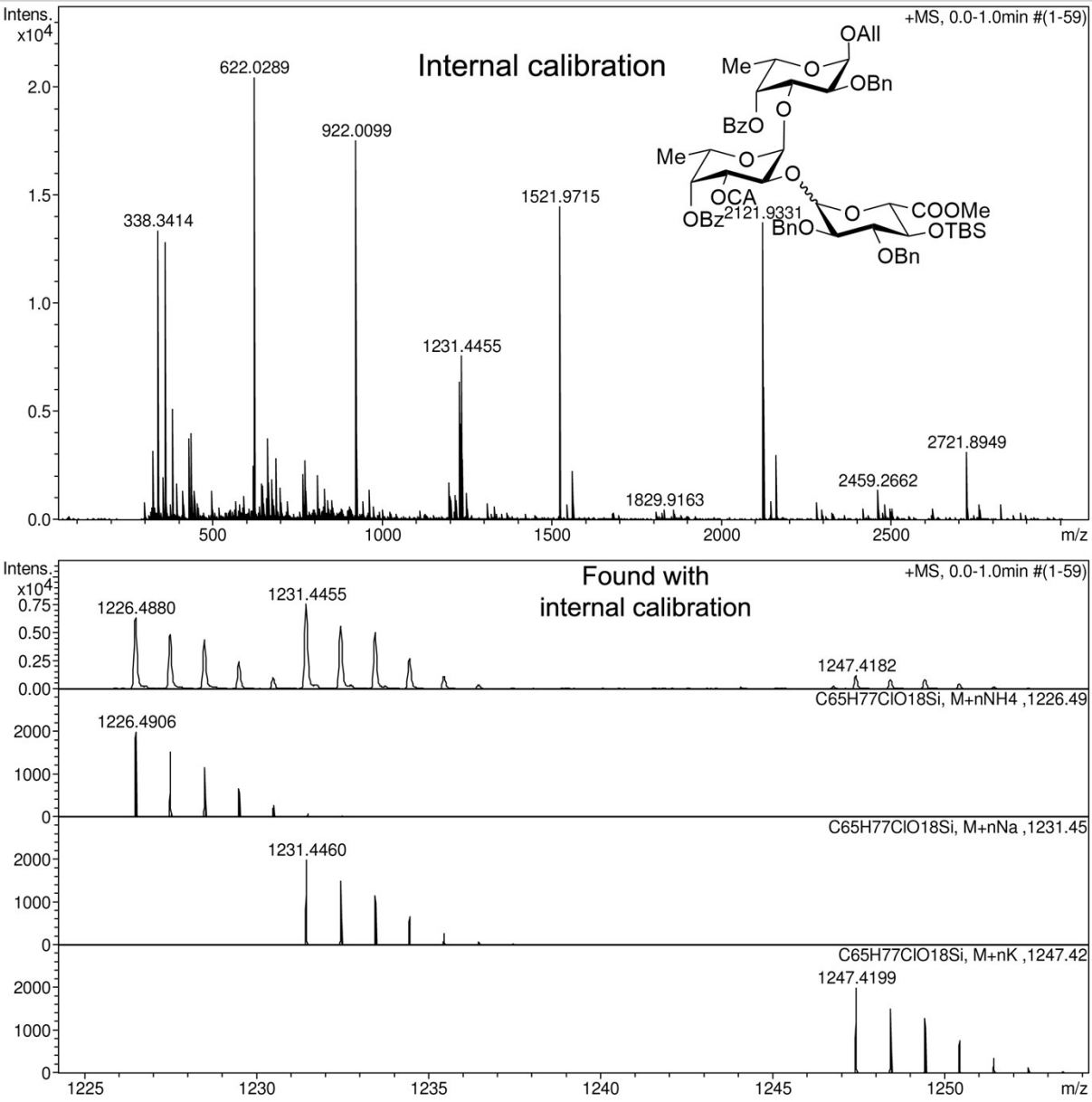
Allyl methyl 2,3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-α,β-D-glucopyranosyluronate-(1→2)-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranosides (27)



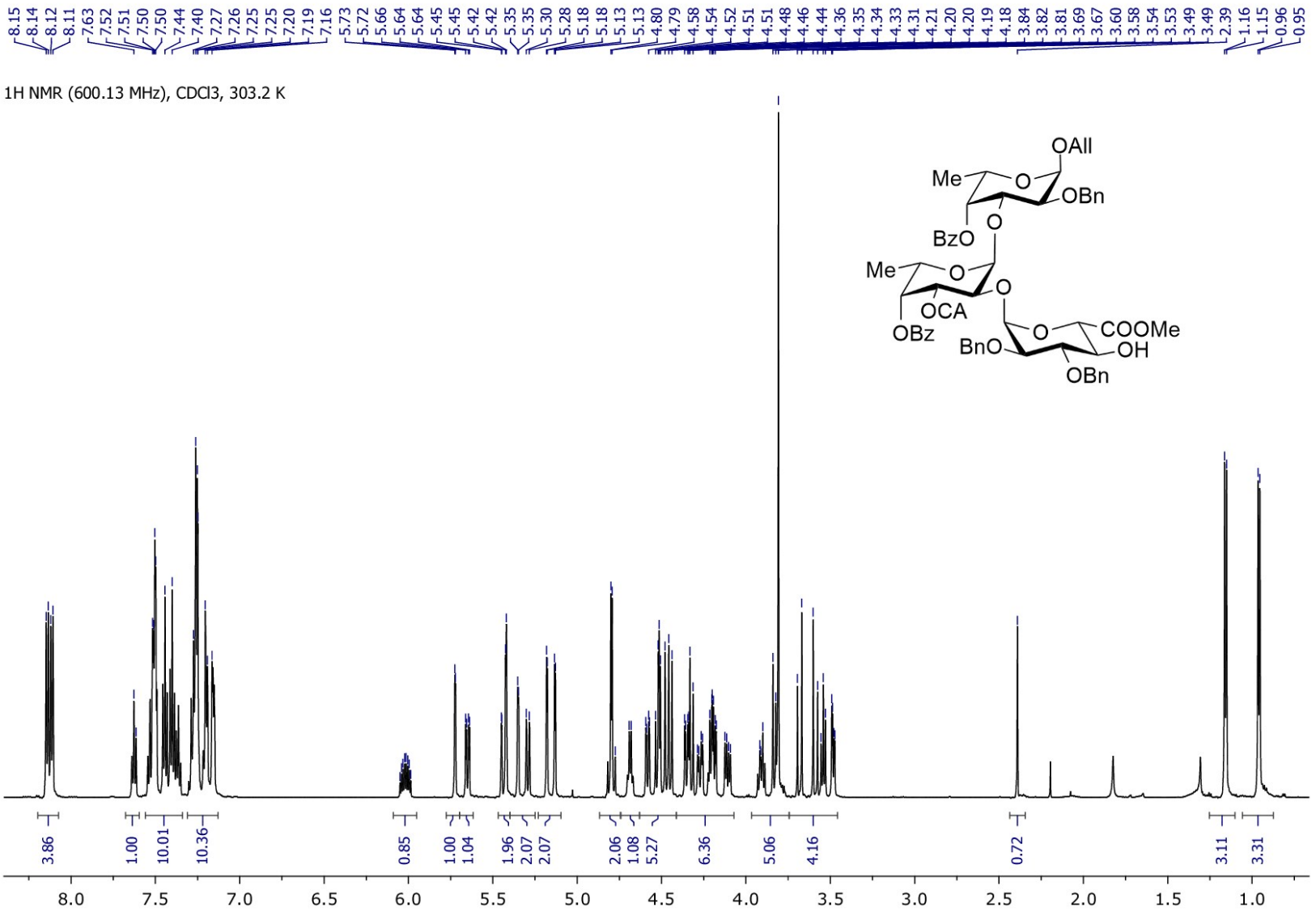

169.80
166.28
166.08
165.77
138.93
138.09
137.67
133.86
133.33
132.88
130.23
129.99
129.87
129.74
129.37
129.29
128.89
128.54
128.47
128.42
128.25
128.04
127.97
127.87
127.62
127.50
127.20
127.10
126.89
126.80
126.63
117.79
99.60
98.15
97.97
96.12
95.94
91.56
80.22
79.91
79.84
77.25
77.00
76.75
75.79
74.69
74.47
73.41
73.25
72.78
72.62
72.55
72.37
72.26
71.64
71.56
71.15
70.13
69.96
68.55
65.47
65.41
65.20
64.98
64.80
40.41
25.77
25.73
17.96
16.21
15.66
13C NMR (125.77 MHz), CDCl3
OAll
Me
O
OBn
O
BzO
Me
O
O
OCA
OBz
O
COOMe
BnO
OTBS
OBn
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

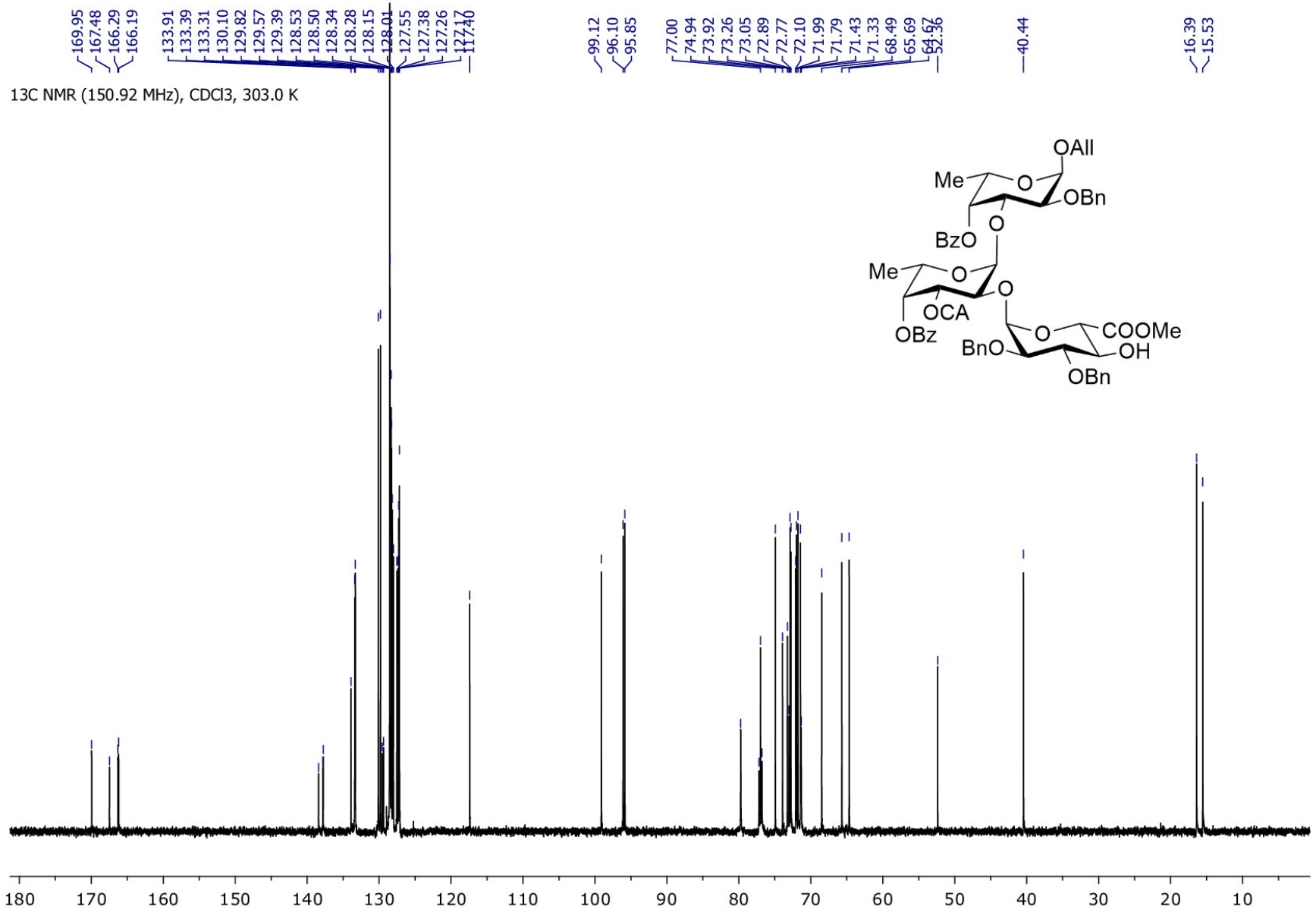
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
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



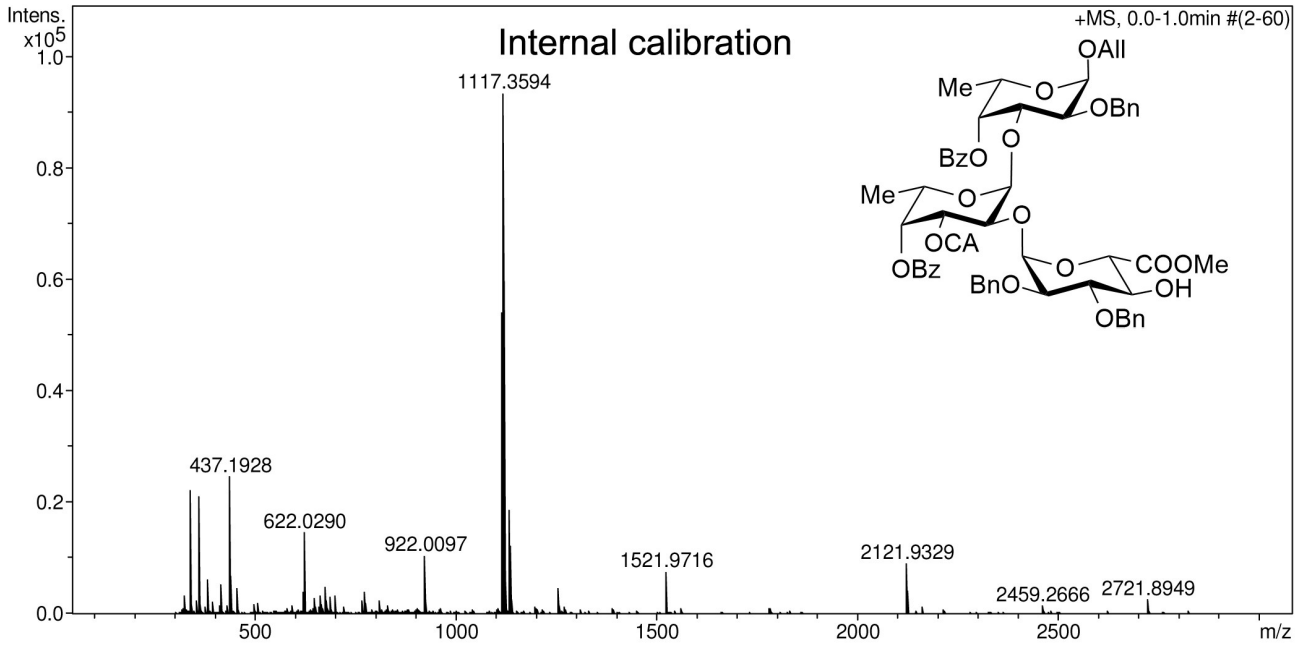
Allyl methyl 2,3-di-*O*-benzyl-α-D-glucopyranosyluronate-(1→2)-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (28)

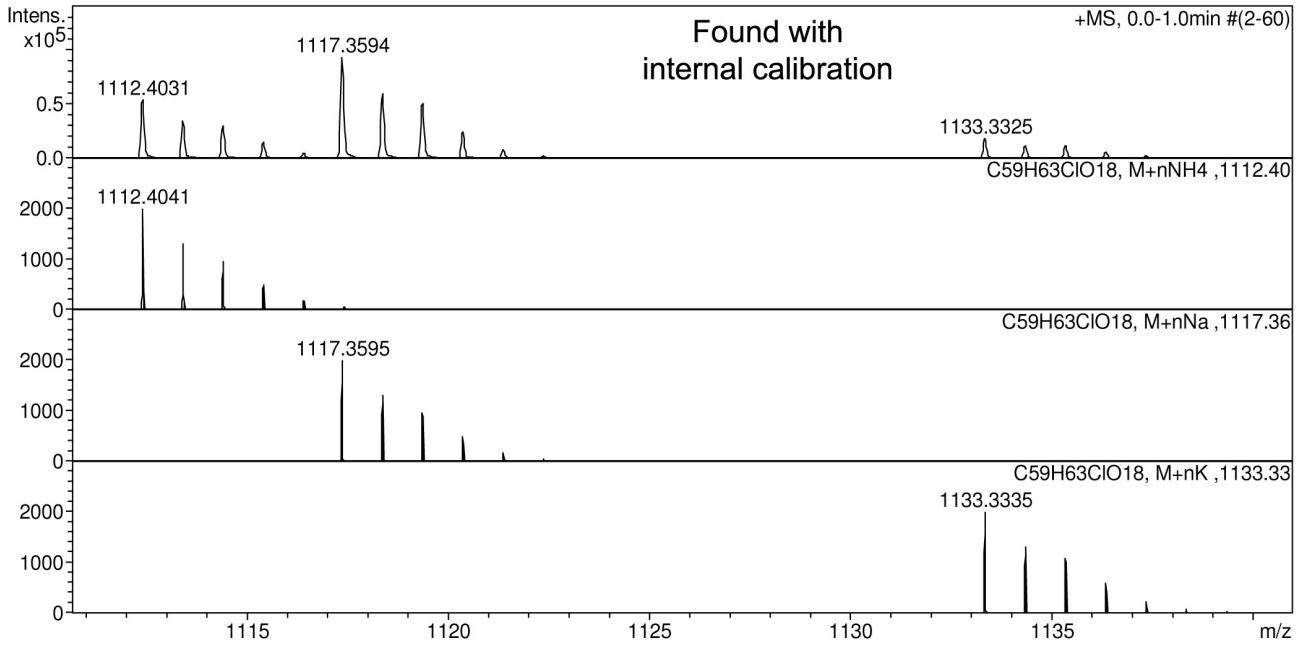



169.95
167.48
166.29
166.19
133.91
133.39
133.31
130.10
129.82
129.57
129.39
128.53
128.50
128.34
128.28
128.15
128.01
127.55
127.38
127.26
99.12
96.10
95.85
77.00
74.94
73.92
73.26
73.05
72.89
72.77
72.10
71.99
71.79
71.43
71.33
68.49
65.69
52.36
40.44
16.39
15.53
13C NMR (150.92 MHz), CDCl3, 303.0 K
OAll
Me
O
OBn
O
BzO
Me
O
O
OCA
OBz
O
COOMe
BnO
OH
OBn
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

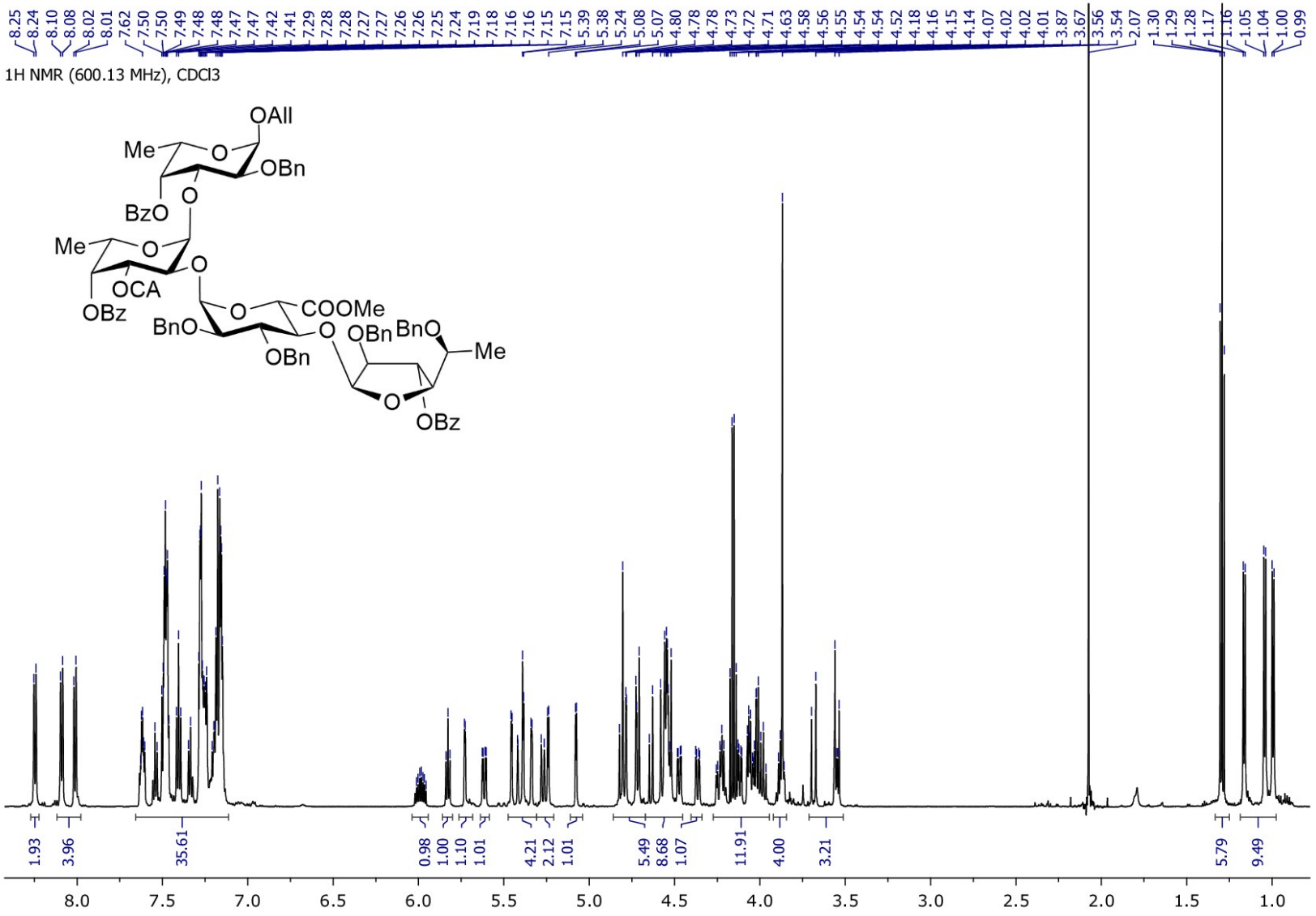
Acquisition Parameter

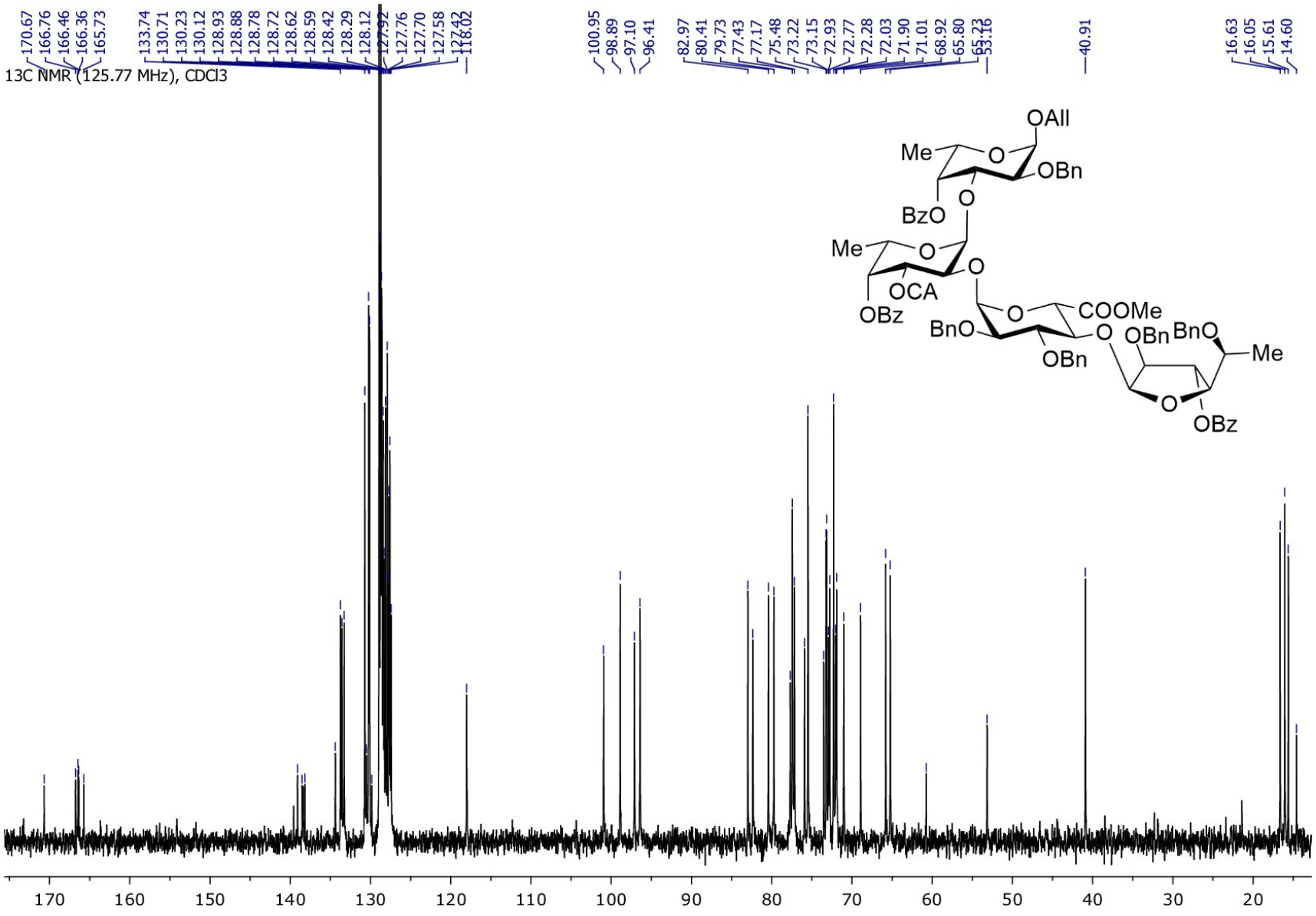
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 ℃
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





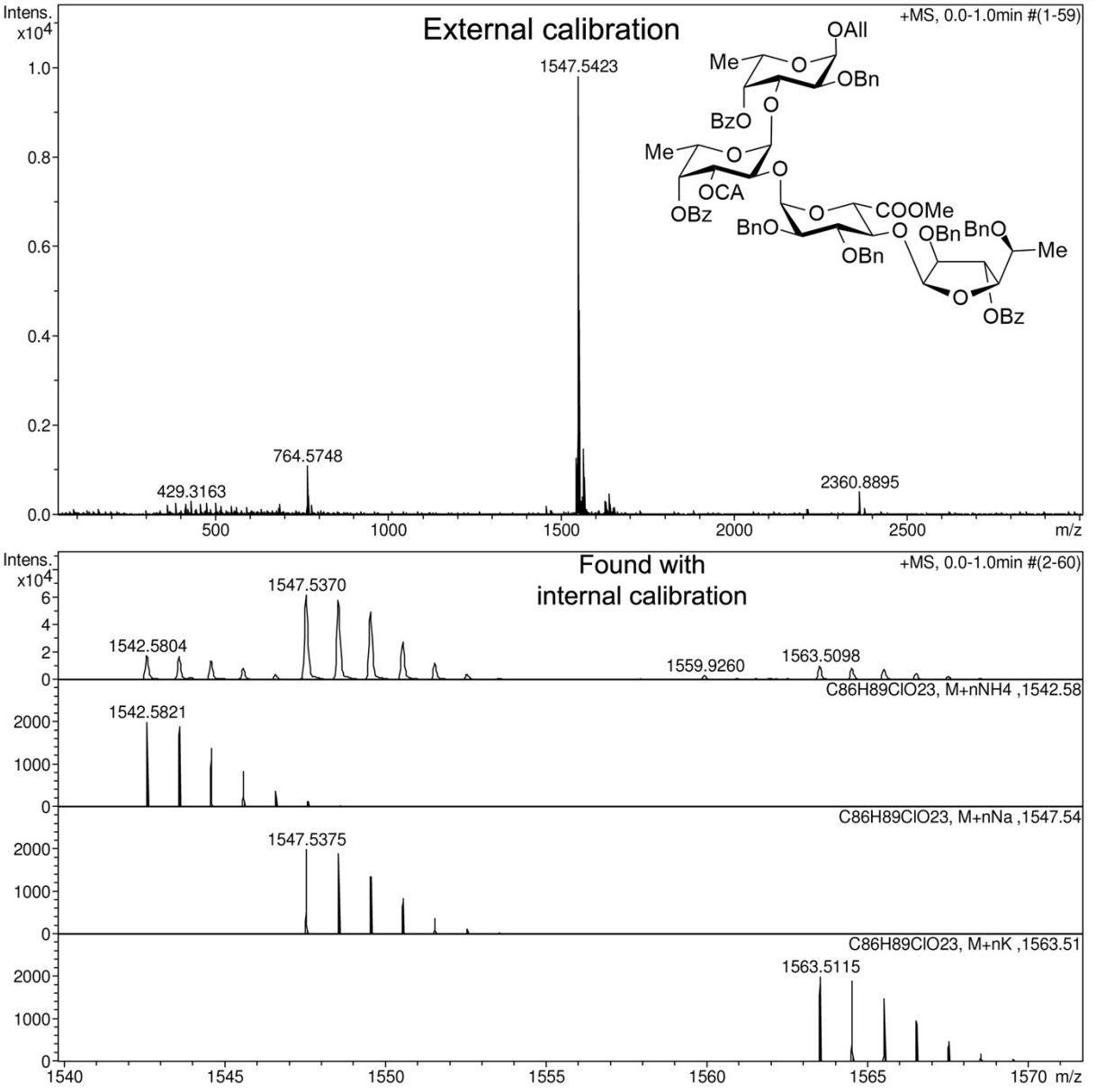
Allyl methyl 2,5-di-*O*-benzyl-3-*O*-benzoyl-α-L-fucofuranosyl-(1→4)-2,3-di-*O*-benzyl-α-D-glucopyranosyluronate-(1→2)-3-*O*-chloroacetyl-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (29)



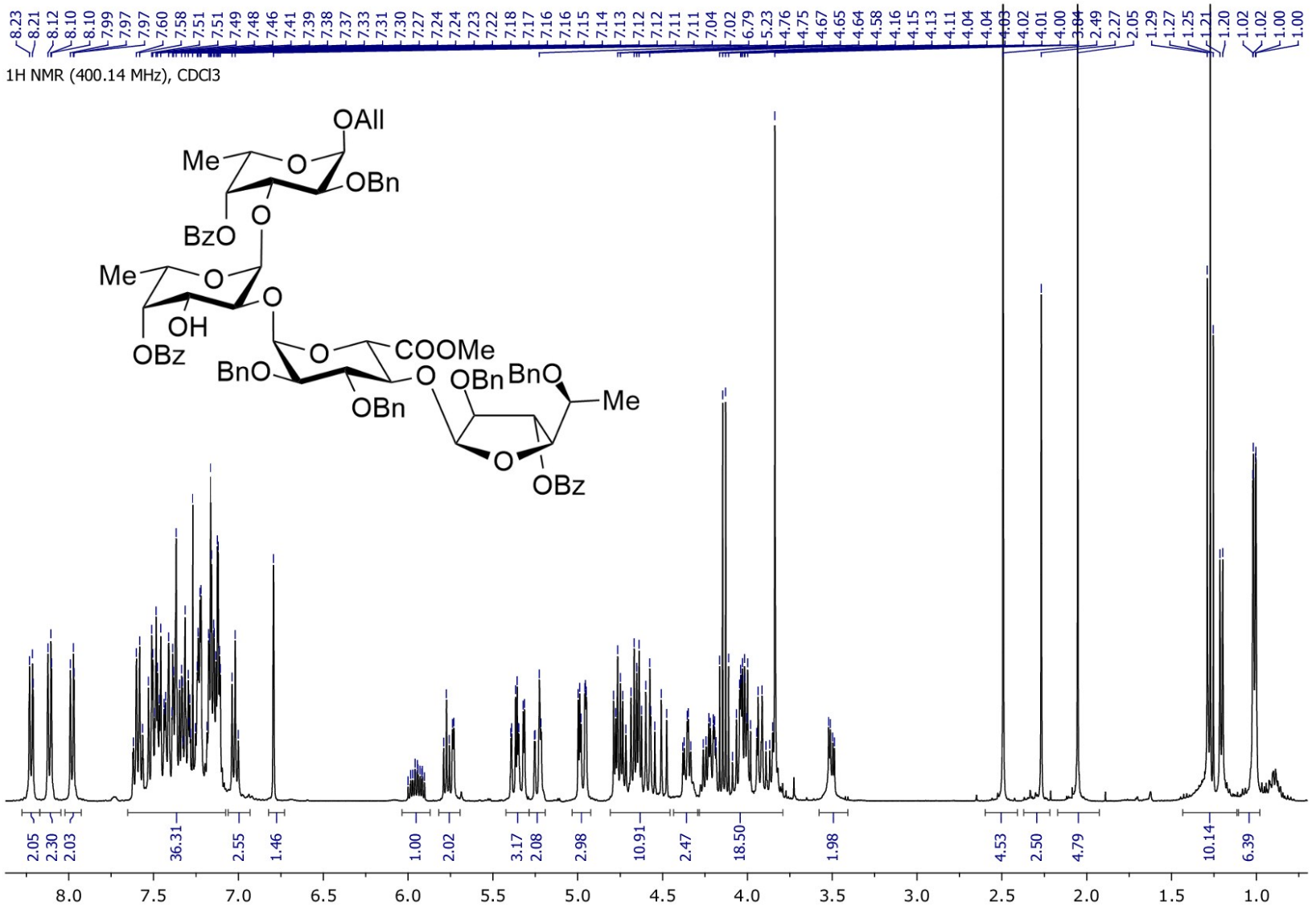

13C NMR (125.77 MHz), CDCl3
170.67
166.76
166.46
166.36
165.73
133.74
130.71
130.23
130.12
128.93
128.88
128.78
128.72
128.62
128.59
128.42
128.29
128.12
127.92
127.76
127.70
127.58
100.95
98.89
97.10
96.41
82.97
80.41
79.73
77.43
77.17
75.48
73.22
73.15
72.93
72.77
72.28
72.03
71.90
71.01
68.92
65.80
40.91
16.63
16.05
15.61
14.60
OAll
Me
O
OBn
BzO
O
Me
O
O
OCA
OBz
O
COOMe
BnO
O
OBn
BnO
OBn
Me
O
OBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

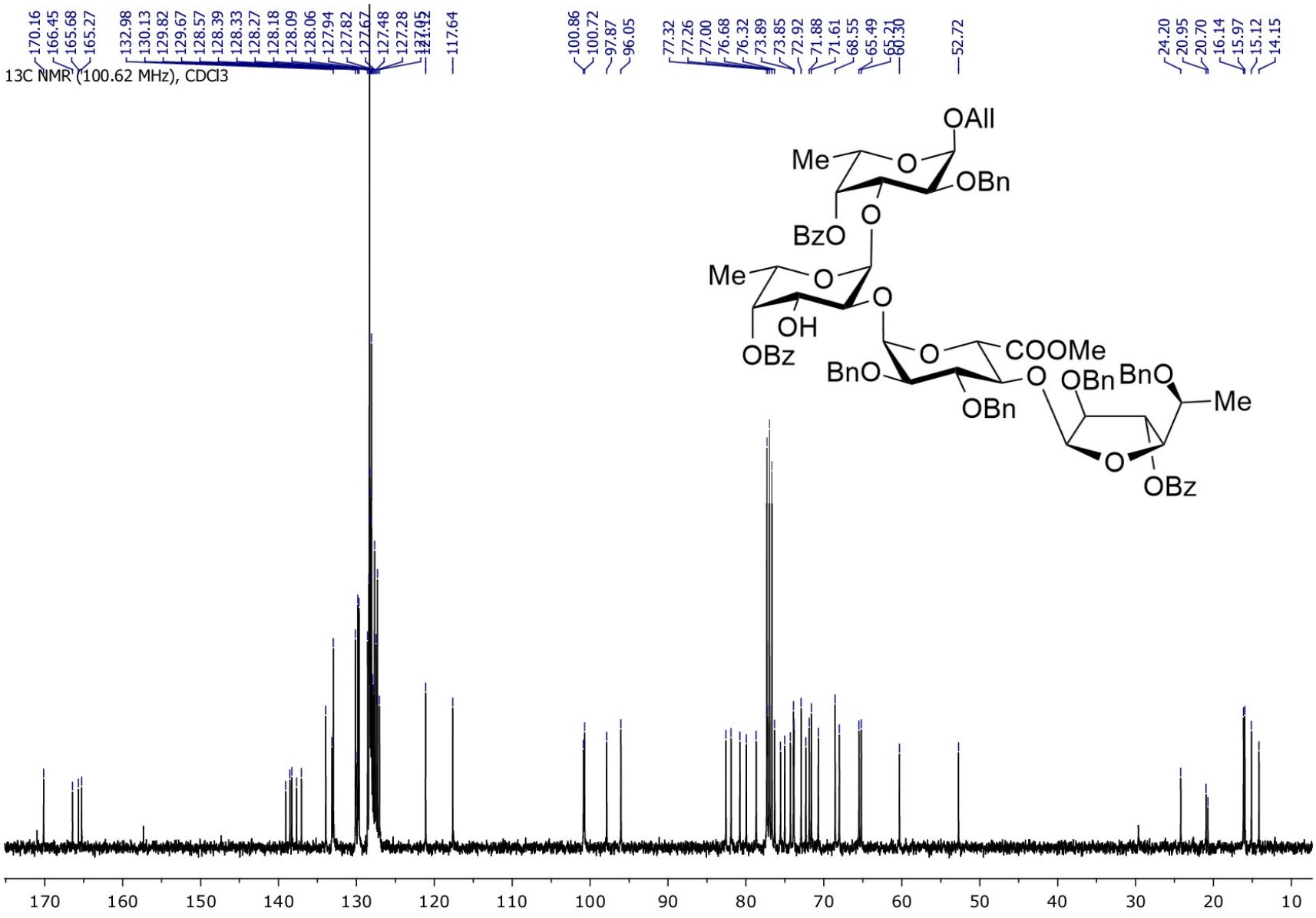
Acquisition Parameter

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



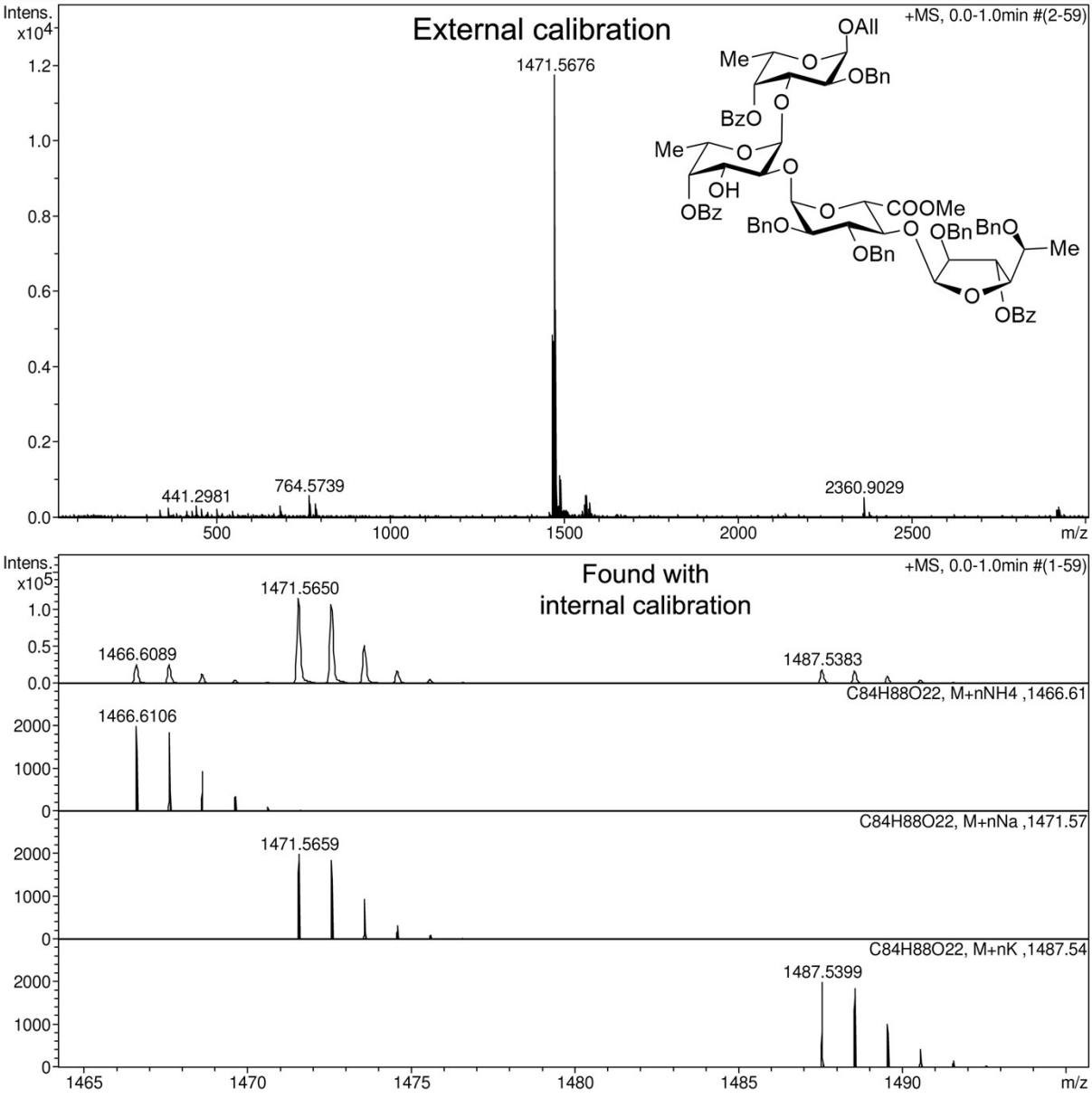
Allyl 2,5-di-*O*-benzyl-3-*O*-benzoyl-α-L-fucofuranosyl-(1→4)-methyl 2,3-di-*O*-benzyl-α-D-glucopyranosyluronate-(1→2)-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (30)



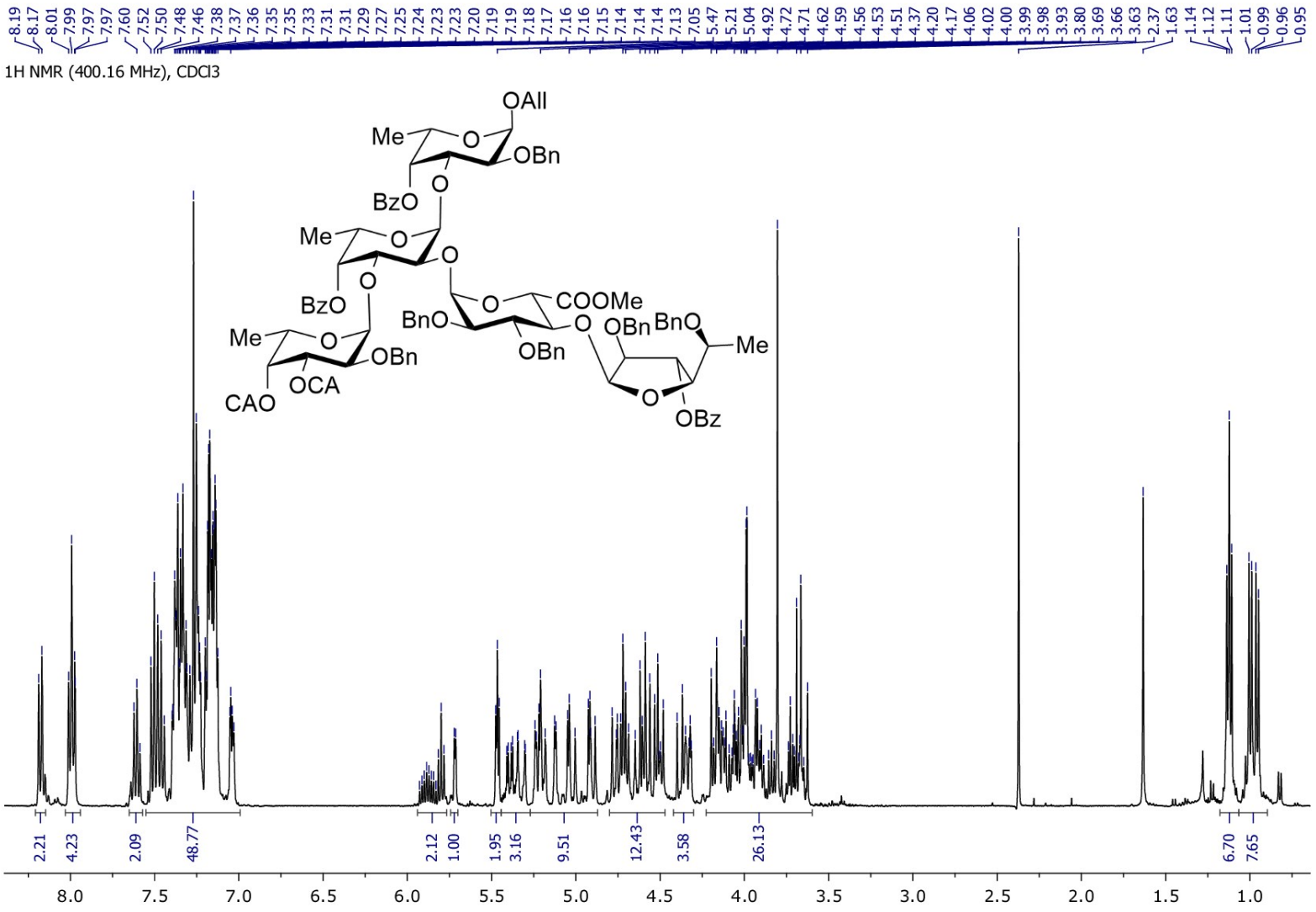

13C NMR (100.62 MHz), CDCl3
170.16
166.45
165.68
165.27
132.98
130.13
129.82
129.67
128.57
128.39
128.33
128.27
128.18
128.09
128.06
127.94
127.82
127.67
127.48
127.28
117.64
100.86
100.72
97.87
96.05
77.32
77.26
77.00
76.68
76.32
73.89
73.85
72.92
71.88
71.61
68.55
65.49
52.72
24.20
20.95
20.70
16.14
15.97
15.12
14.15
OAll
Me
O
OBn
O
BzO
Me
O
O
OH
OBz
O
COOMe
BnO
O
OBn
BnO
OBn
Me
O
OBz
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

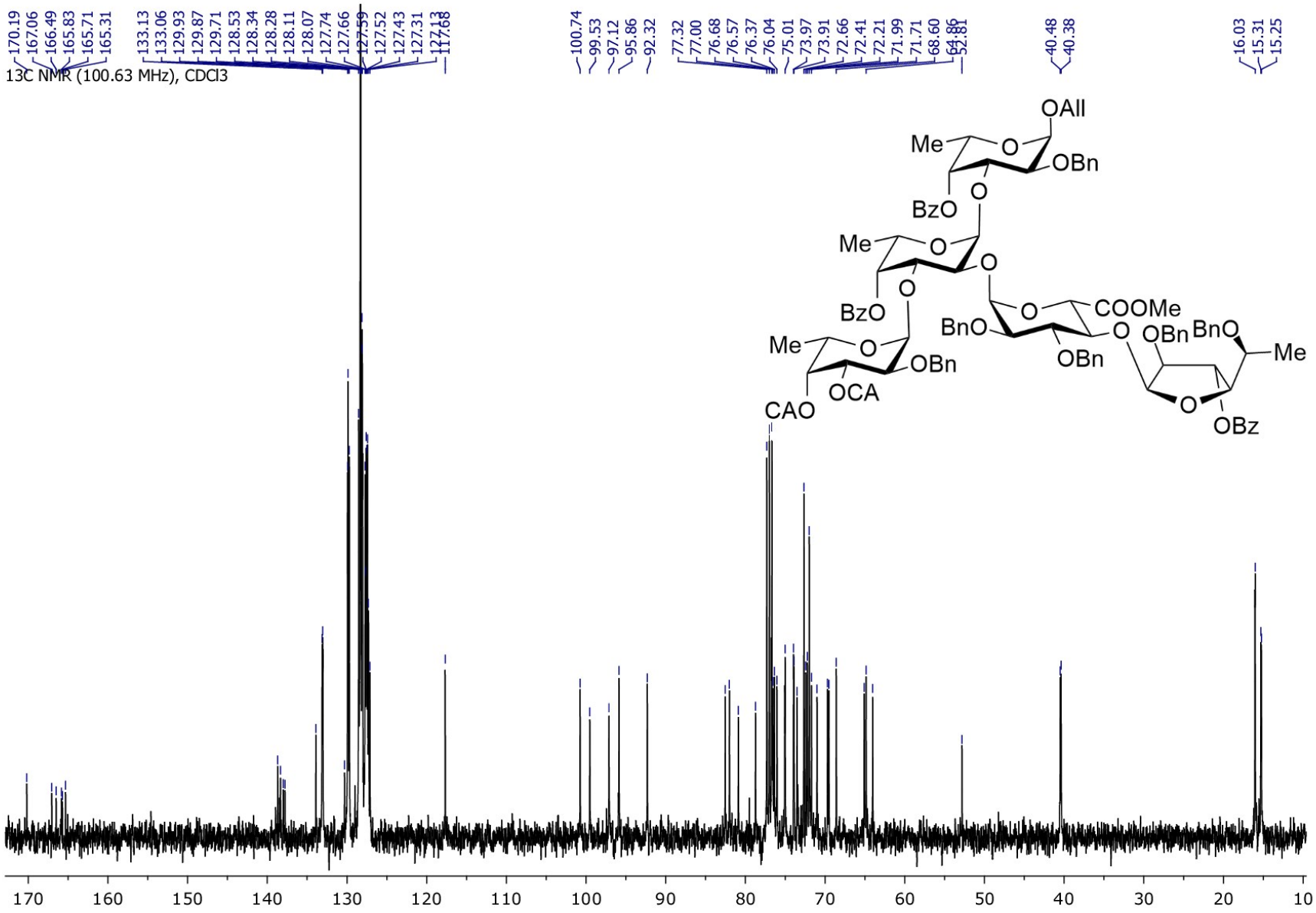
Acquisition Parameter

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



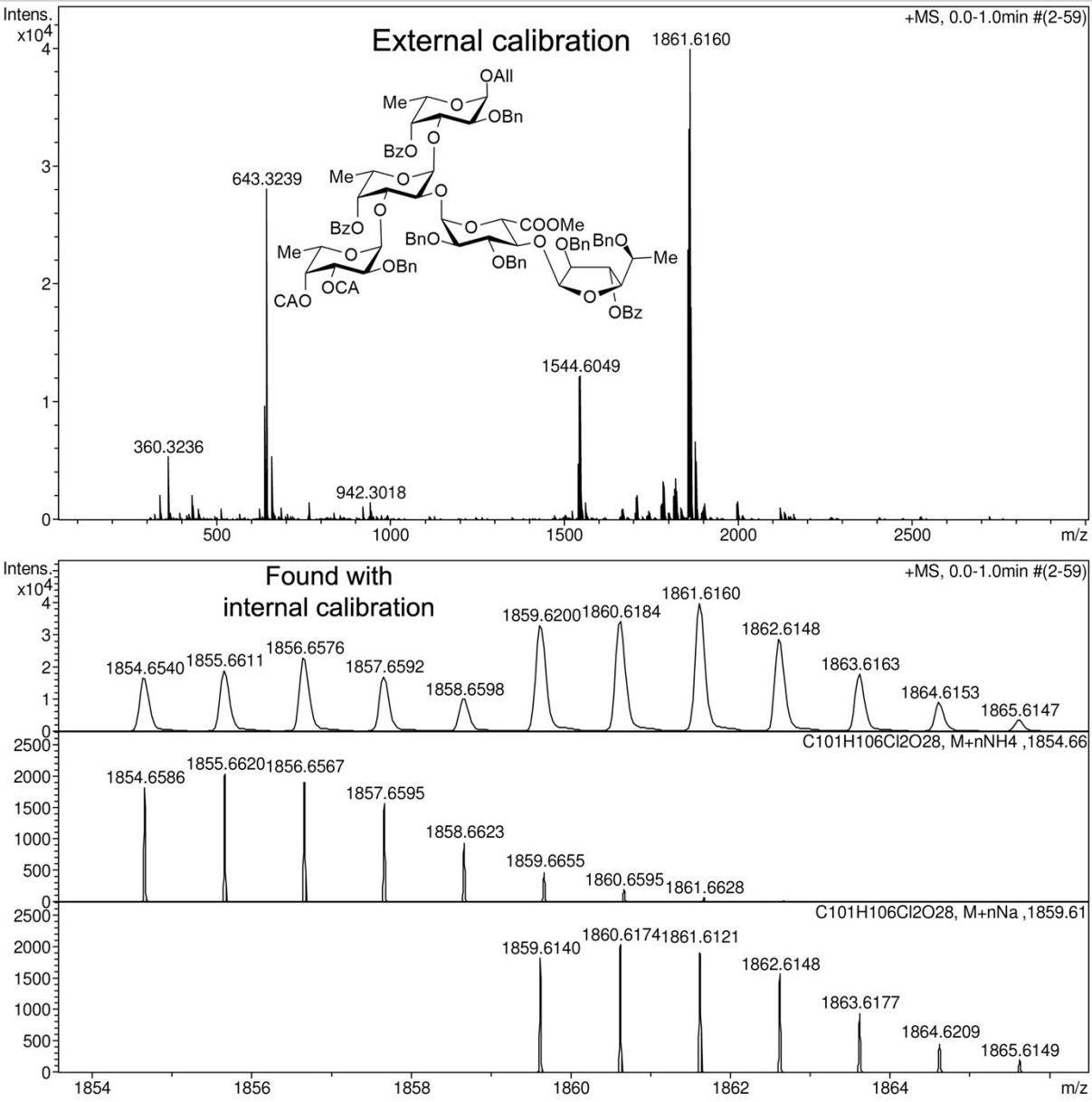
Allyl 2-*O*-benzyl-3,4-di-*O*-chloroacetyl-α-L-fucopyranosyl-(1→3)-{2,5-di-*O*-benzyl-3-*O*-benzoyl-α-L-fucofuranosyl-(1→4)-methyl-2,3-di-*O*-benzyl-α-D-glucopyranosyluronate-(1→2)}-4-*O*-benzoyl-α-L-fucopyranosyl-(1→3)-2-*O*-benzyl-4-*O*-benzoyl-α-L-fucopyranoside (31)



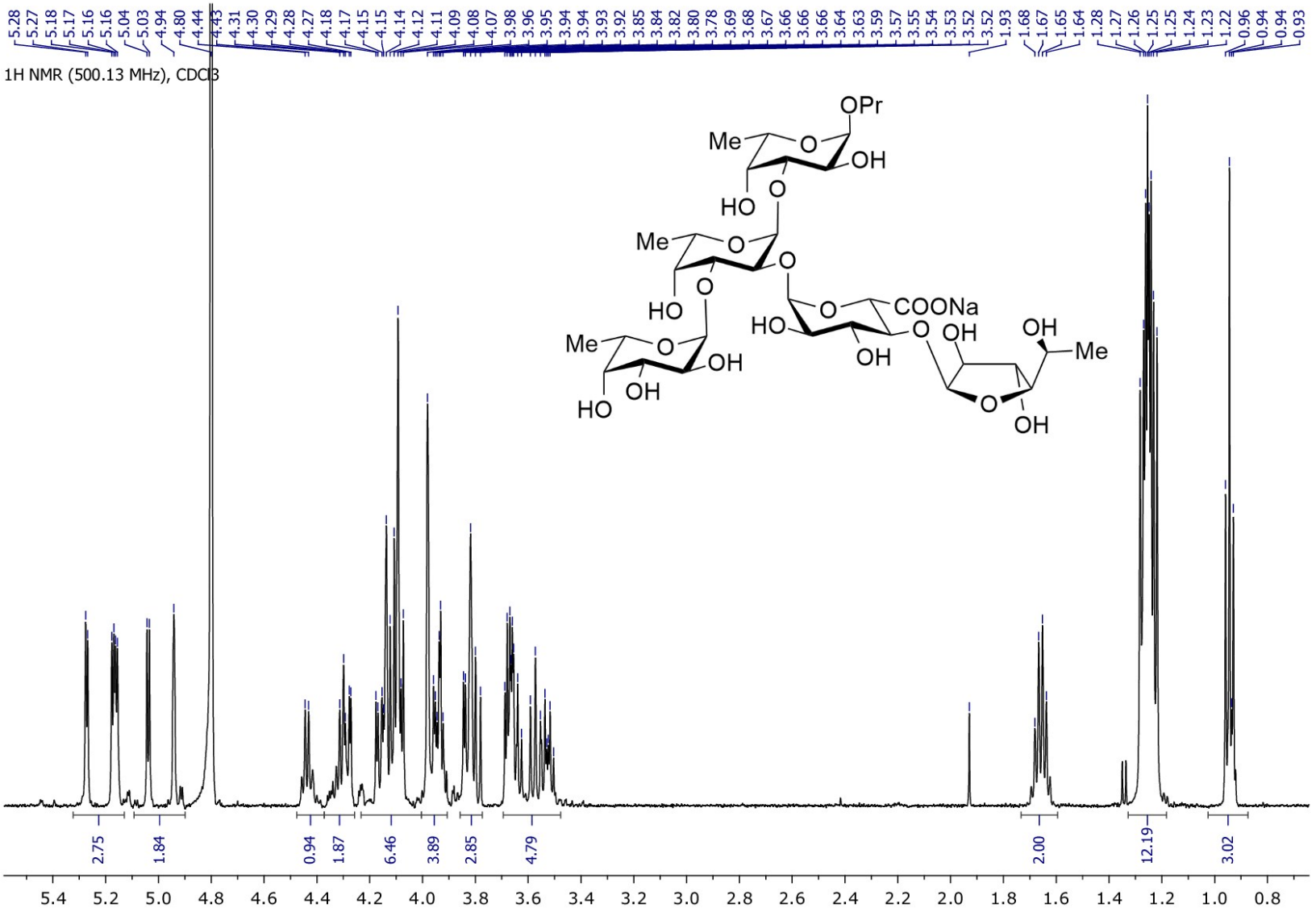

13C NMR (100.63 MHz), CDCl3
170.19
167.06
166.49
165.83
165.71
165.31
133.13
133.06
129.93
129.87
129.71
128.53
128.34
128.28
128.11
128.07
127.74
127.66
127.59
127.52
127.43
127.31
100.74
99.53
97.12
95.86
92.32
77.32
77.00
76.68
76.57
76.37
76.04
75.01
73.97
73.91
72.66
72.41
72.21
71.99
71.71
68.60
40.48
40.38
16.03
15.31
15.25
OAll
Me
O
OBn
BzO
O
Me
O
O
BzO
O
COOMe
BnO
O
OBn BnO
Me
Me
O
OBn
OBn
O
OBz
CAO
OCA
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

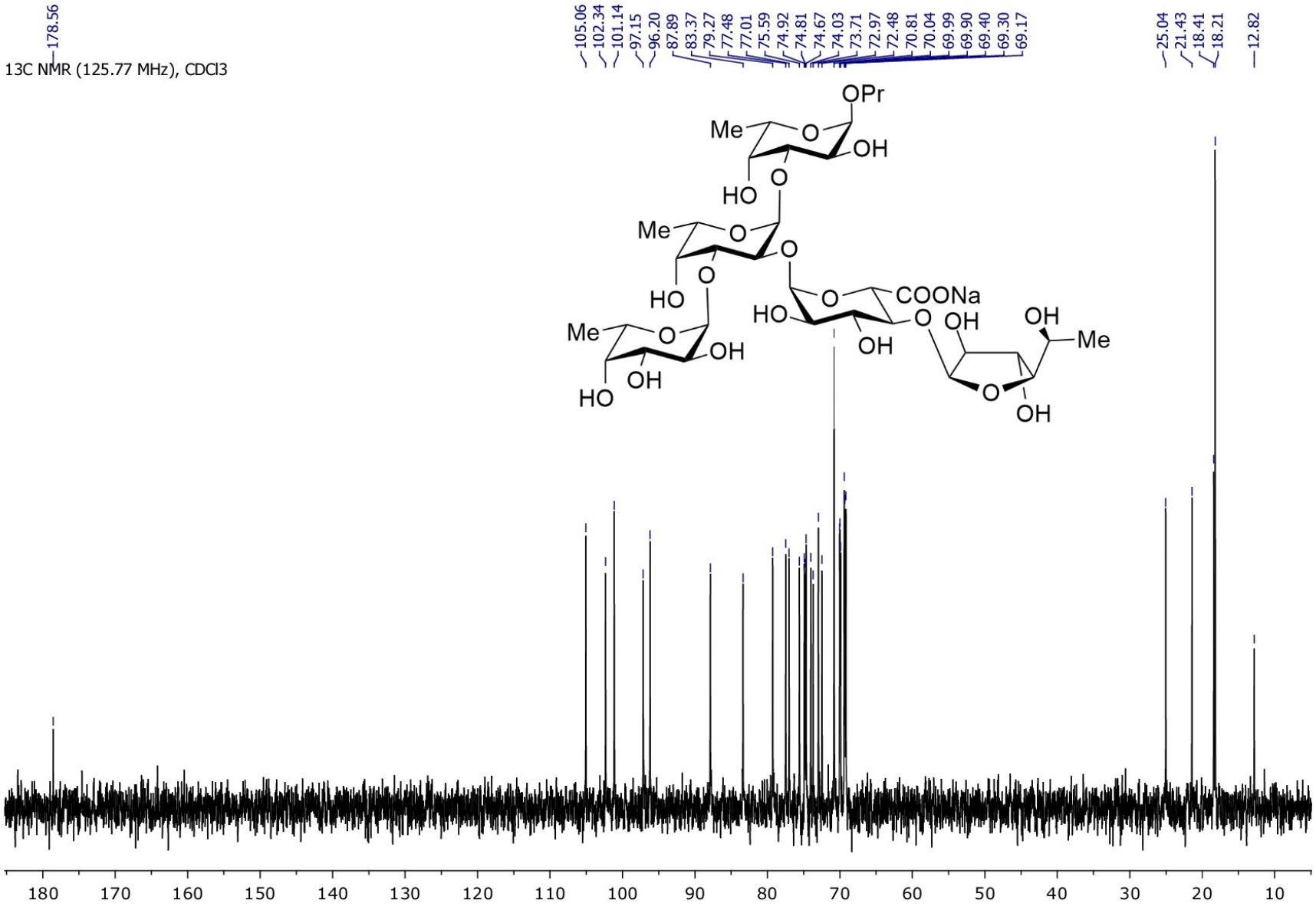
Acquisition Parameter

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



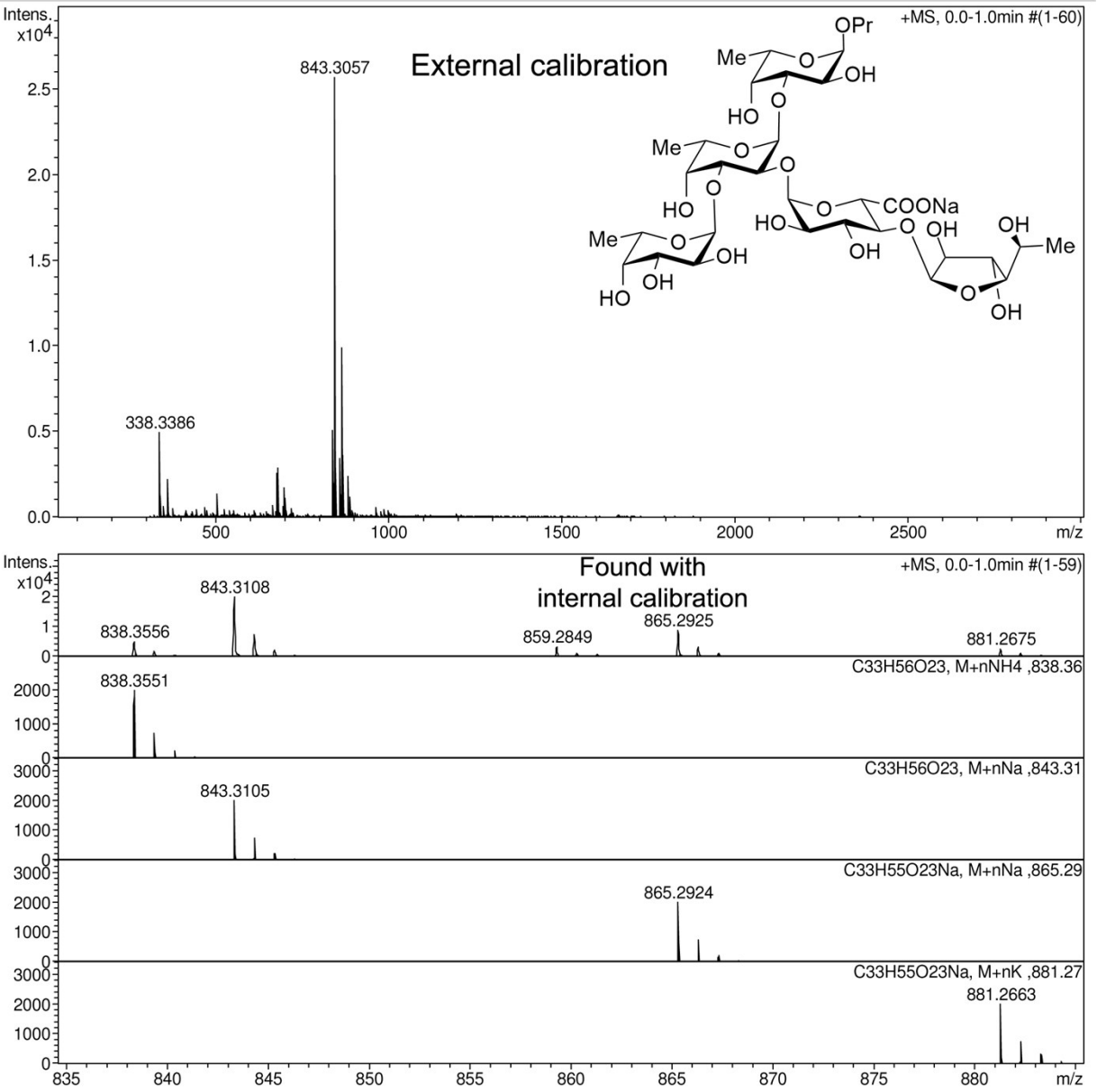
Sodium salt proryl α-L-fucopyranosyl-(1→3)-{α-L-fucofuranosyl-(1→4)-α-D-glucopyranosyluronate-(1→2)}-α-L-fucopyranosyl-(1→3)-α-L-fucopyranoside (3)



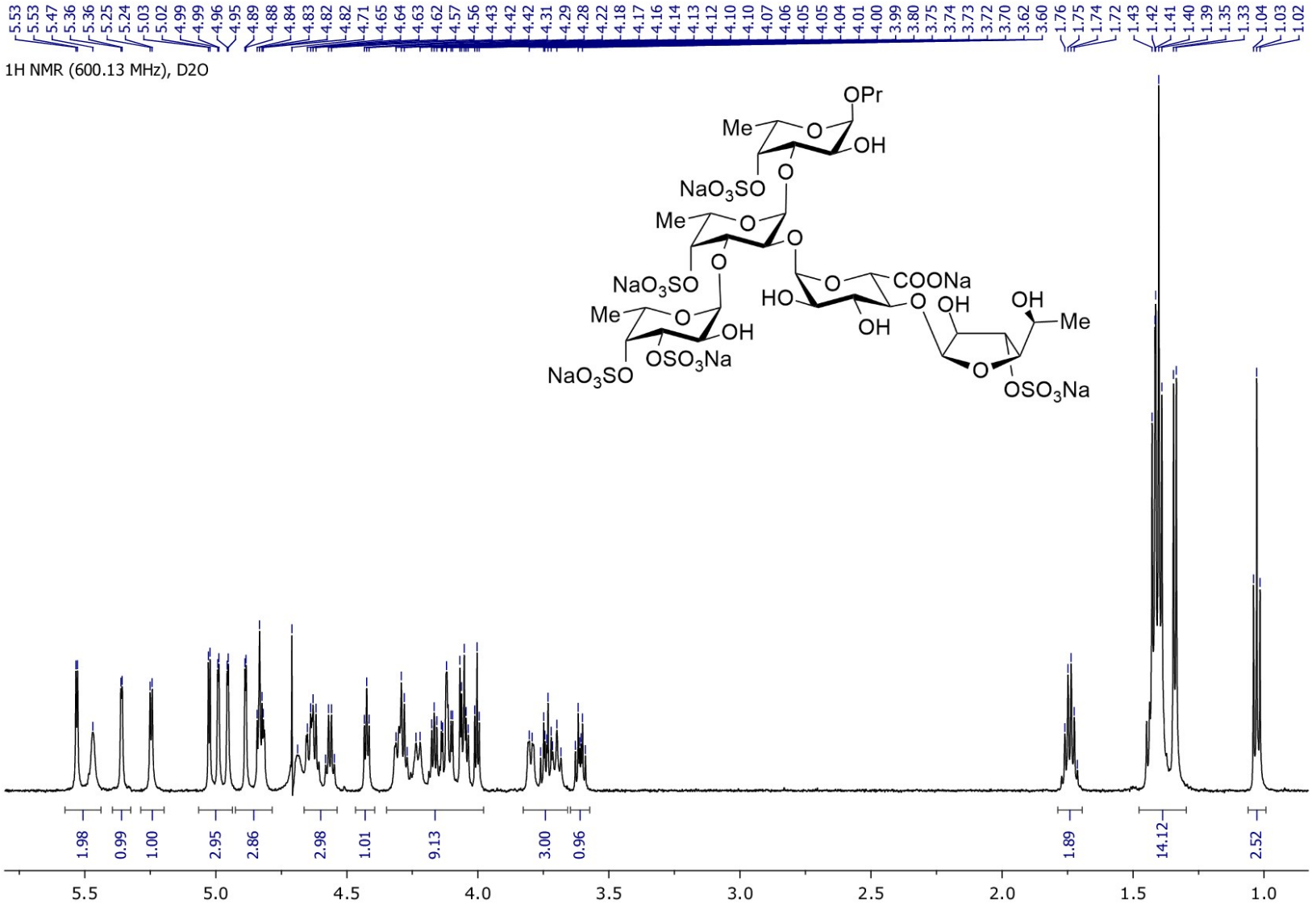

13C NMR (125.77 MHz), CDCl3
178.56
105.06
102.34
101.14
97.15
96.20
87.89
83.37
79.27
77.48
77.01
75.59
74.92
74.81
74.67
74.03
73.71
72.97
72.48
70.81
70.04
69.99
69.90
69.40
69.30
69.17
25.04
21.43
18.41
18.21
12.82
OPr
Me
O
OH
HO
COONa
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

Acquisition Parameter

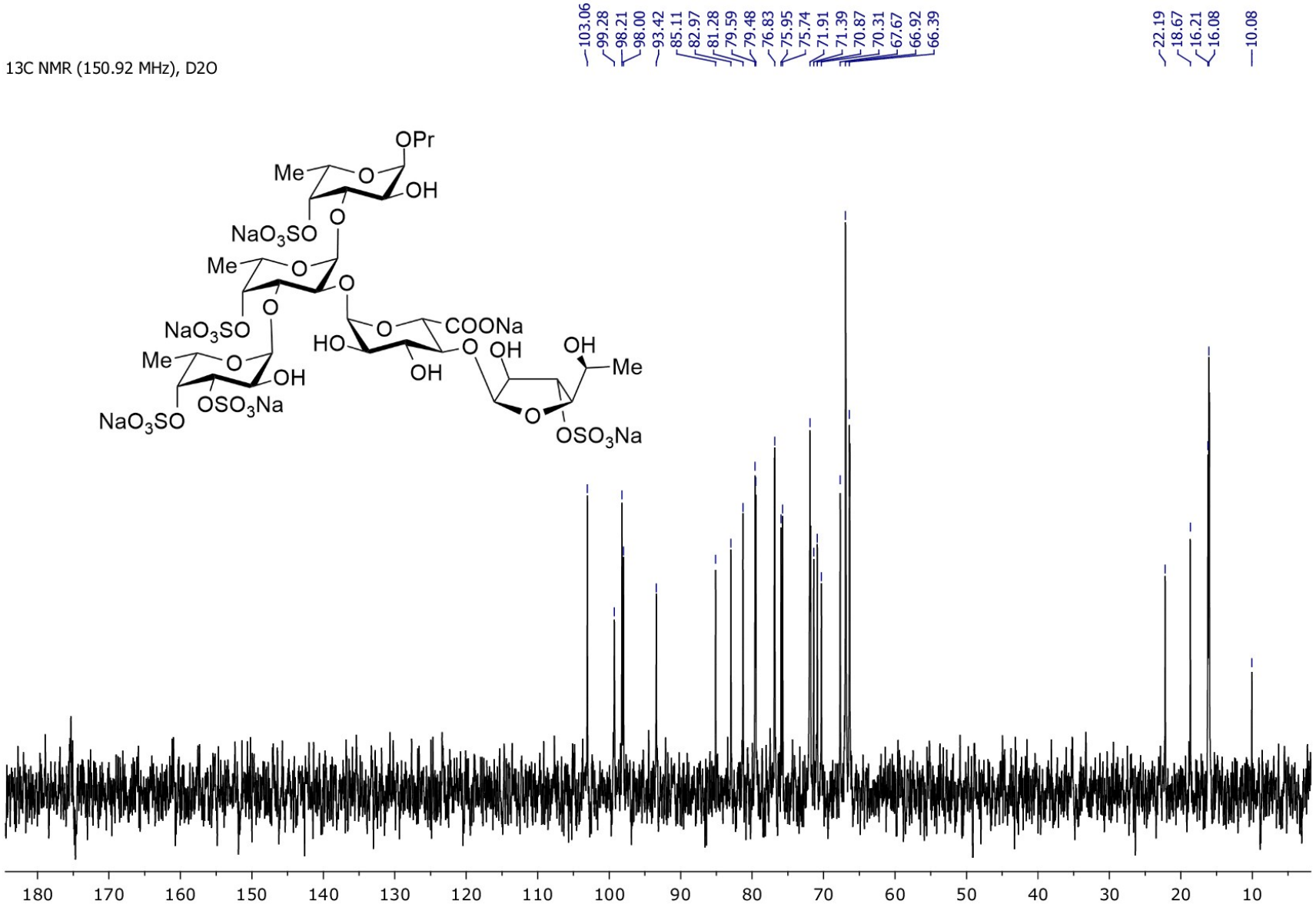
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Sodium salt proryl 3,4-di-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-{3-*O*-sulfonato-α-L-fucofuranosyl-(1→4)-α-D-glucopyranosyluronate-(1→2)}-4-*O*-sulfonato-α-L-fucopyranosyl-(1→3)-4-*O*-sulfonato-α-L-fucopyranoside (4)



13C NMR (150.92 MHz), D2O



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