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

Synthesis of oligosaccharides related to galactomannan from *Aspergillus fumigatus* and their NMR spectra

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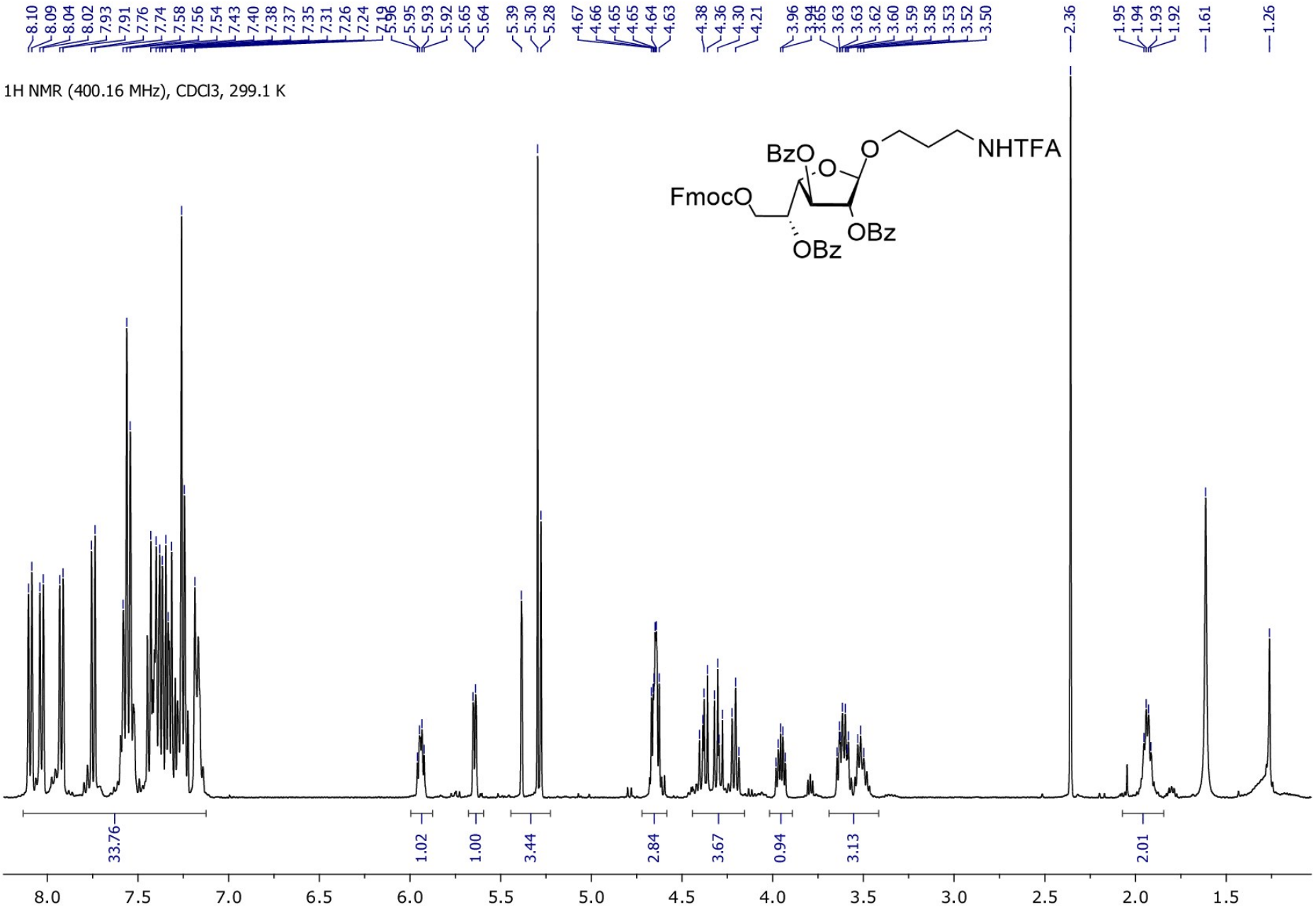
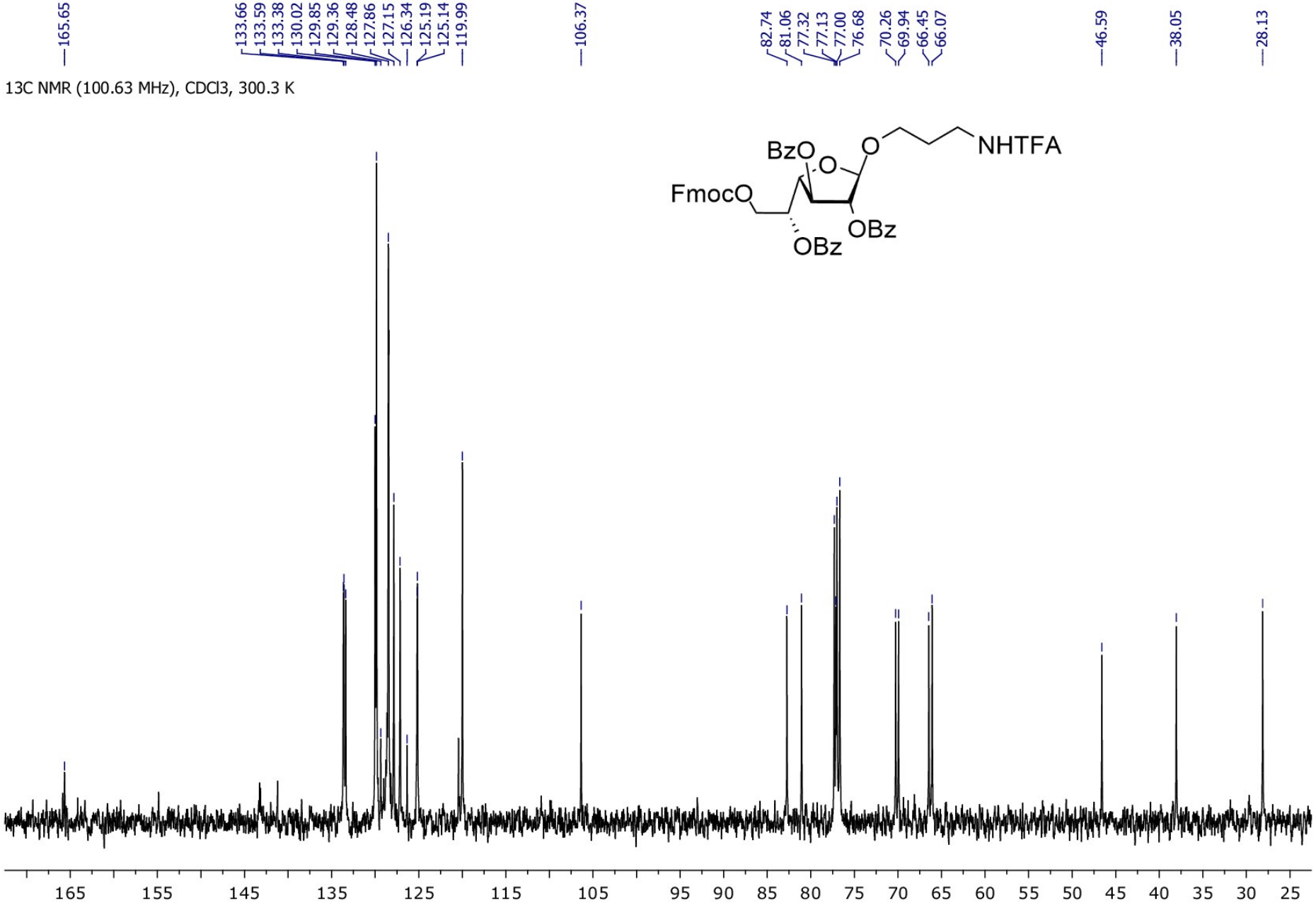
Table S1. ^{1}H NMR chemical shifts (δ, ppm; D_2O) of oligosaccharides **1-13**.[a]

#	Unit	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(6')
1	β-D-Gal*f*-(1→	5.03	4.11	4.07	3.99	3.83	3.71	3.65
	→6)-β-D-Gal*f*-O$(CH_2)_3NH_2$	5.01	4.07	4.07	3.99	3.96	3.87	3.61
2	β-D-Gal*f*-(1→	5.04	4.12	4.07	4.00	3.83	3.71	3.65
	→6)-β-D-Gal*f*-(1→	5.22	4.14	4.07	4.07	3.97	3.88	3.63
	→5)-β-D-Gal*f*-O$(CH_2)_3NH_2$	4.99	4.07	4.12	4.08	3.95	3.79	3.79
3	β-D-Gal*f*-(1→	5.24	4.16	4.09	4.09	3.86	3.73	3.68
	→5)-β-D-Gal*f*-O$(CH_2)_3NH_2$	5.00	4.08	4.15	4.09	3.97	3.80	3.80
4	β-D-Gal*f*-(1→	5.21	4.14	4.07	4.07	3.84	3.72	3.66
	→5)-β-D-Gal*f*-(1→	5.19	4.14	4.11	4.16	3.96	3.79	3.79
	→5)-β-D-Gal*f*-O$(CH_2)_3NH_2$	4.99	4.07	4.13	4.08	3.93	3.79	3.79
5	β-D-Gal*f*-(1→	5.13	4.15	4.07	4.05	3.83	3.68	3.64
	→3)-α-D-Man*p*-O$(CH_2)_3NH_2$	4.89	4.14	3.87	3.71	3.63	3.88	3.75
6	β-D-Gal*f*-(1→	5.20	4.13	4.06	4.05	3.82	3.70	3.66
	→5)-β-D-Gal*f*-(1→	5.10	4.12	4.12	4.14	3.95	3.77	3.77
	→3)-α-D-Man*p*-O$(CH_2)_3NH_2$	4.89	4.13	3.85	3.71	3.63	3.88	3.75
7	β-D-Gal*f*-(1→	5.20	4.13	4.06	4.05	3.82	3.70	3.66
	→5)-β-D-Gal*f*-(1→ [b]	5.18	4.13	4.10	4.14	3.93	3.78	3.78
	→5)-β-D-Gal*f*-(1→	5.10	4.13	4.10	4.14	3.93	3.78	3.78
	→3)-α-D-Man*p*-O$(CH_2)_3NH_2$	4.88	4.12	3.84	3.70	3.63	3.90	3.74
8	β-D-Gal*f*-(1→	5.04	4.10	4.06	3.98	3.81	3.70	3.64
	→6)-α-D-Man*p*-O$(CH_2)_3NH_2$	4.84	3.95	3.79	3.68	3.71	4.00	3.72
9	β-D-Gal*f*-(1→	5.21	4.14	4.07	4.07	3.84	3.72	3.67
	→5)-β-D-Gal*f*-(1→	5.03	4.10	4.11	4.09	3.95	3.79	3.79
	→6)-α-D-Man*p*-O$(CH_2)_3NH_2$	4.85	3.95	3.79	3.70	3.71	4.01	3.72
10	β-D-Gal*f*-(1→	5.21	4.14	4.06	4.06	3.83	3.71	3.66
	→5)-β-D-Gal*f*-(1→ [b]	5.18	4.14	4.10	4.15	3.95	3.79	3.79
	→5)-β-D-Gal*f*-(1→	5.02	4.10	4.10	4.08	3.95	3.79	3.79
	→6)-α-D-Man*p*-O$(CH_2)_3NH_2$	4.84	3.95	3.78	3.69	3.70	4.00	3.71
11	β-D-Gal*f*-(1→	5.21	4.14	4.06	4.06	3.84	3.71	3.67
	→5)-β-D-Gal*f*-(1→ [c]	5.18	4.14	4.10	4.15	3.94	3.80	3.80
	→5)-β-D-Gal*f*-(1→	5.03	4.06	4.10	4.08	3.94	3.80	3.80
	→6)-α-D-Man*p*-O$(CH_2)_3NH_2$	4.84	3.95	3.78	3.69	3.71	4.00	3.72
12	β-D-Gal*f*-(1→	5.21	4.14	4.06	4.06	3.83	3.70	3.67
	→5)-β-D-Gal*f*-(1→	5.01	4.10	4.11	4.09	3.94	3.79	3.79
	→6)-β-D-Gal*f*-(1→	5.22	4.14	4.11	4.07	3.97	3.87	3.63
	→5)-β-D-Gal*f*-(1→	5.03	4.11	4.11	4.09	3.96	3.79	3.79
	→6)-α-D-Man*p*-O$(CH_2)_3NH_2$	4.84	3.95	3.78	3.69	3.71	4.01	3.72
13	β-D-Gal*f*-(1→	5.11	4.13	4.08	4.08	3.82	3.69	3.65
	→2)-α-D-Man*p*-(1→	5.16	4.16	3.90	3.61	3.78	3.89	3.74
	→2)-α-D-Man*p*-O$(CH_2)_3NH_2$	5.10	3.99	3.88	3.68	3.59	3.89	3.74

[a] aglycon signals δ (ppm): Man*p*-OC$\underline{H_2}$-CH_2-CH_2-NH_2 – 3.85, 3.61, Man*p*-OCH_2-C$\underline{H_2}$-CH_2-NH_2 – 1.98, Man*p*-OCH_2-CH_2-C$\underline{H_2}$-NH_2 – 3.13; Gal*f*-OC$\underline{H_2}$-CH_2-CH_2-NH_2 – 3.86, 3.66, Gal*f*-OCH_2-C$\underline{H_2}$-CH_2-NH_2 – 1.98, Gal*f*-OCH_2-CH_2-C$\underline{H_2}$-NH_2 – 3.13, (internal standard C$\underline{H_3}$CN – 2.06). [b] two internal residues. [c] four internal residues

3-Trifluoroacetamidopropyl 2,3,5-tri-*O*-benzoyl-6-*O*-(9-fluorenylmethoxycarbonyl)-β-D-galactofuranoside 17

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127.15
126.34
125.19
125.14
119.99
106.37
82.74
81.06
77.32
77.13
77.00
76.68
70.26
69.94
66.45
66.07
46.59
38.05
28.13
13C NMR (100.63 MHz), CDCl3, 300.3 K
BzO
O
O
NHTFA
FmocO
OBz
OBz
165
155
145
135
125
115
105
95
90
85
80
75
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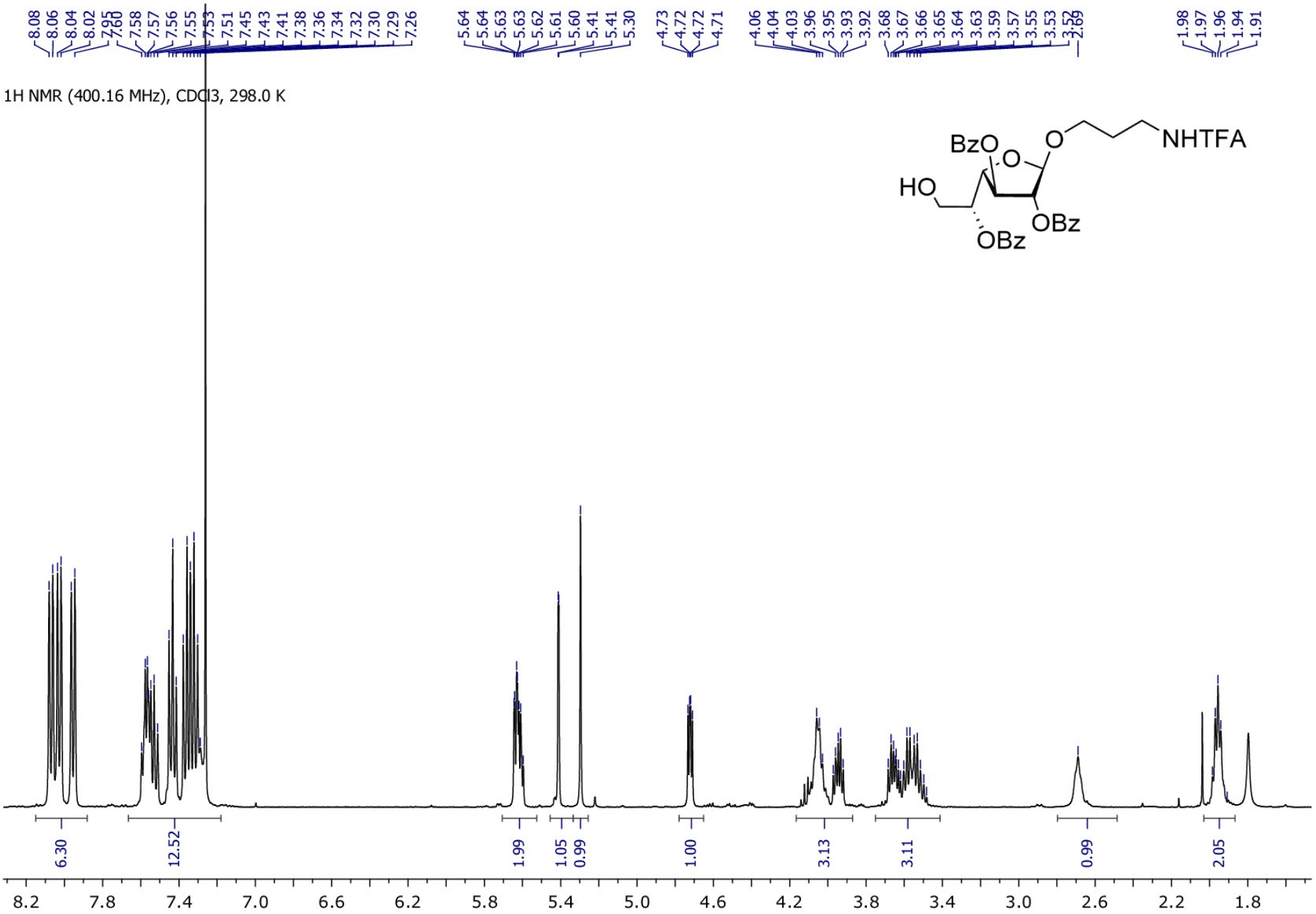
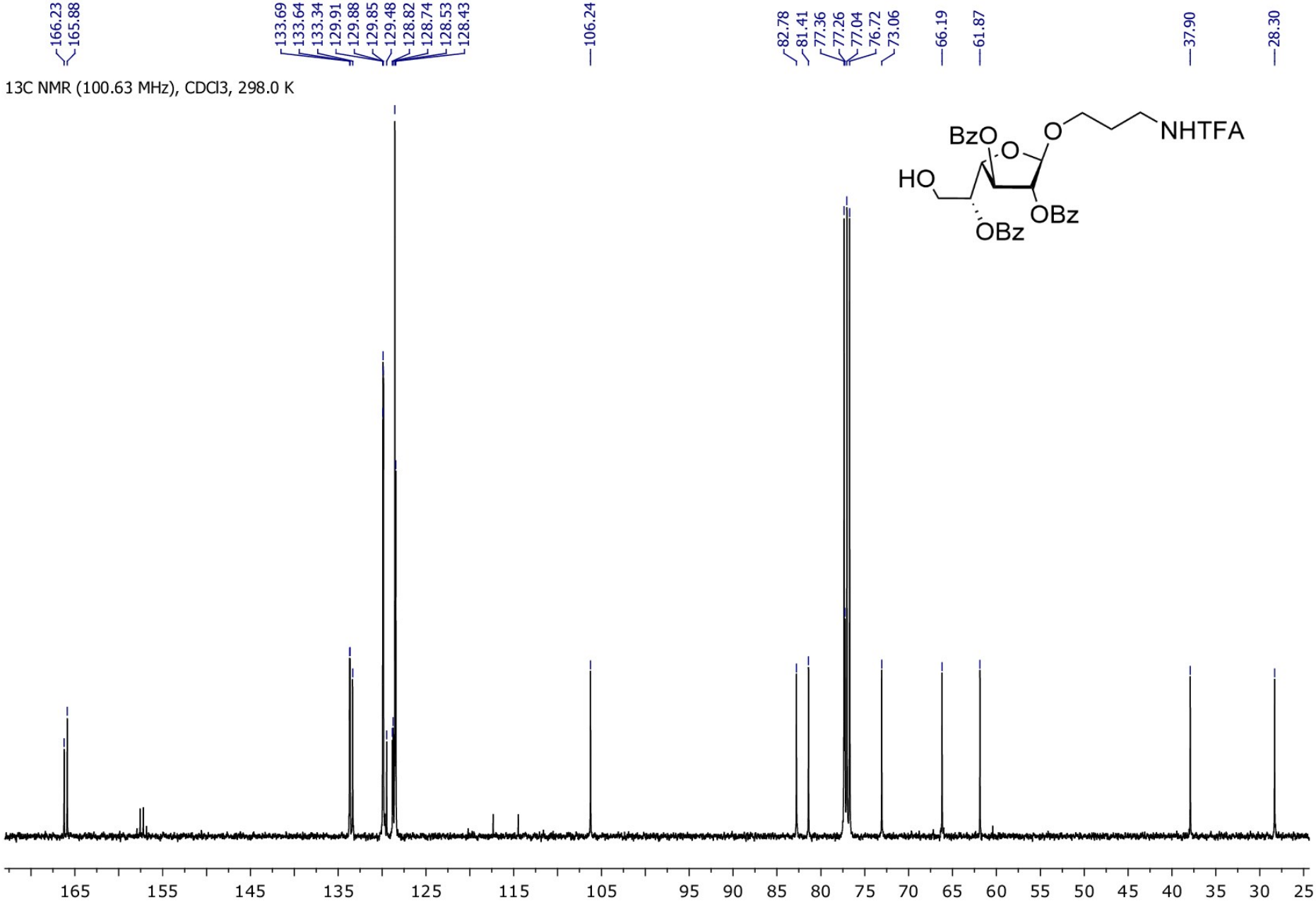
3-Trifluoroacetamidopropyl 2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside 18

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128.82
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128.53
128.43
106.24
82.78
81.41
77.36
77.26
77.04
76.72
73.06
66.19
61.87
37.90
28.30
13C NMR (100.63 MHz), CDCl3, 298.0 K
BzO
O
O
NHTFA
HO
OBz
OBz
165
155
145
135
125
115
105
95
90
85
80
75
70
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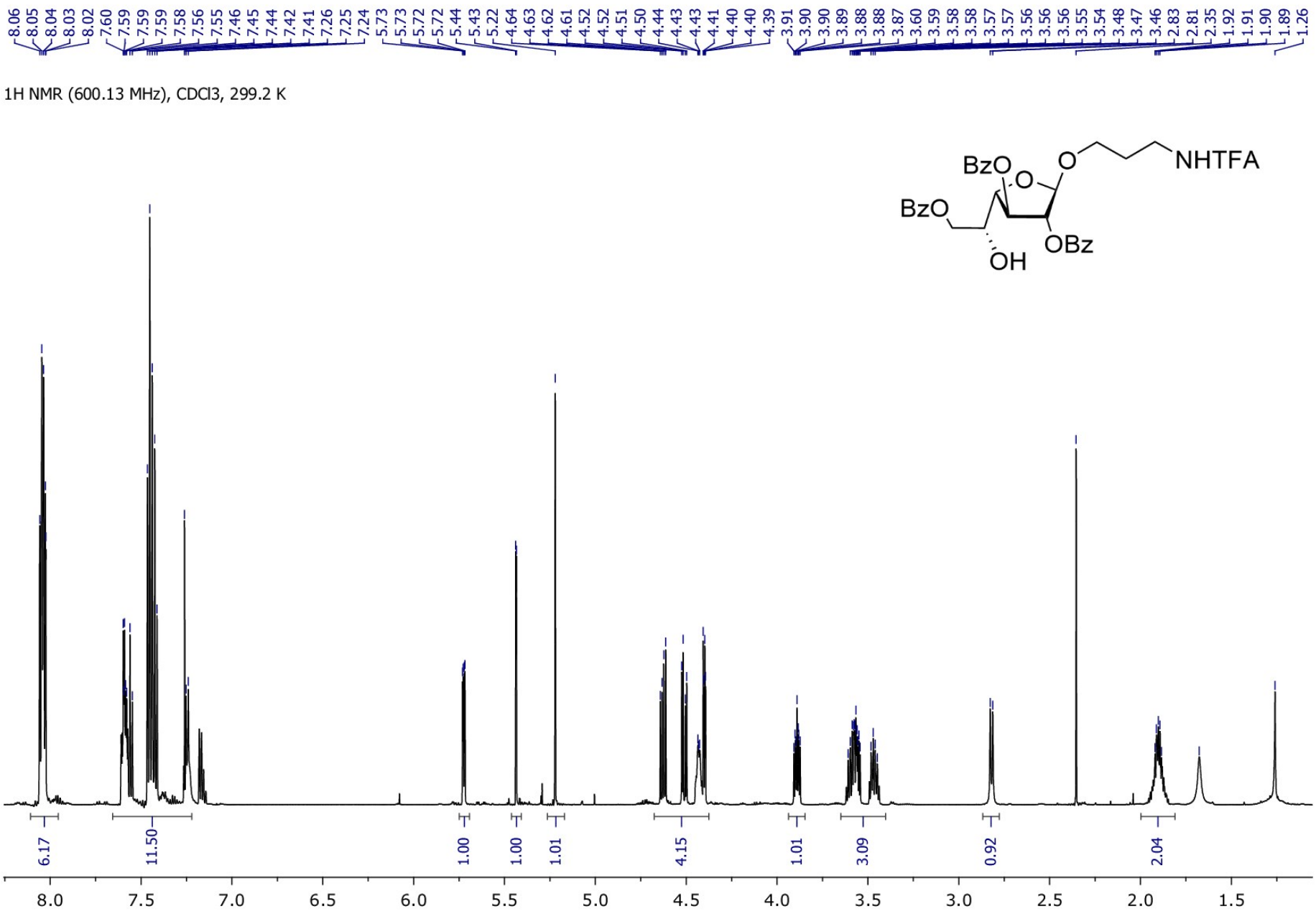
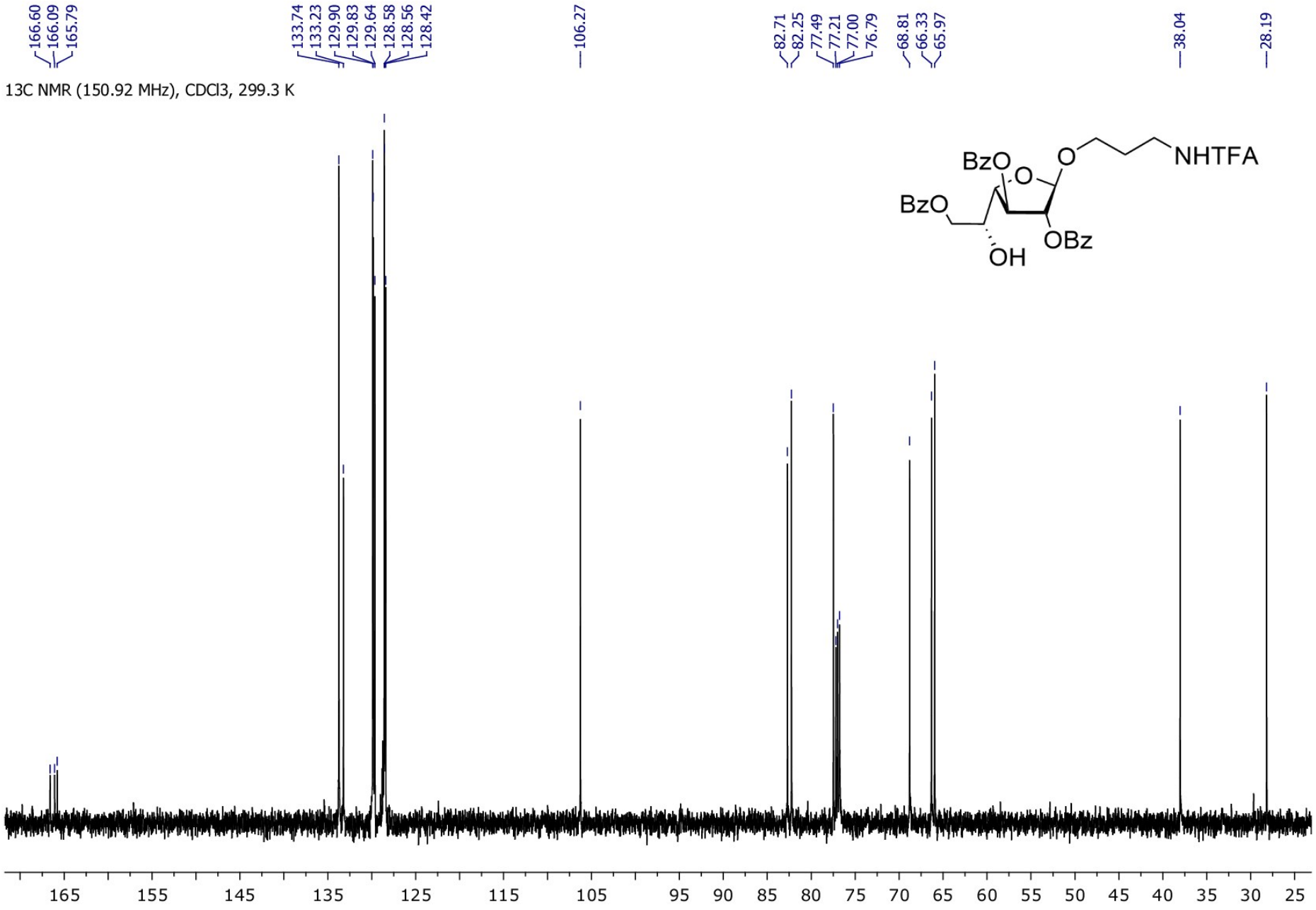
3-trifluoroacetamidopropyl 2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside 19

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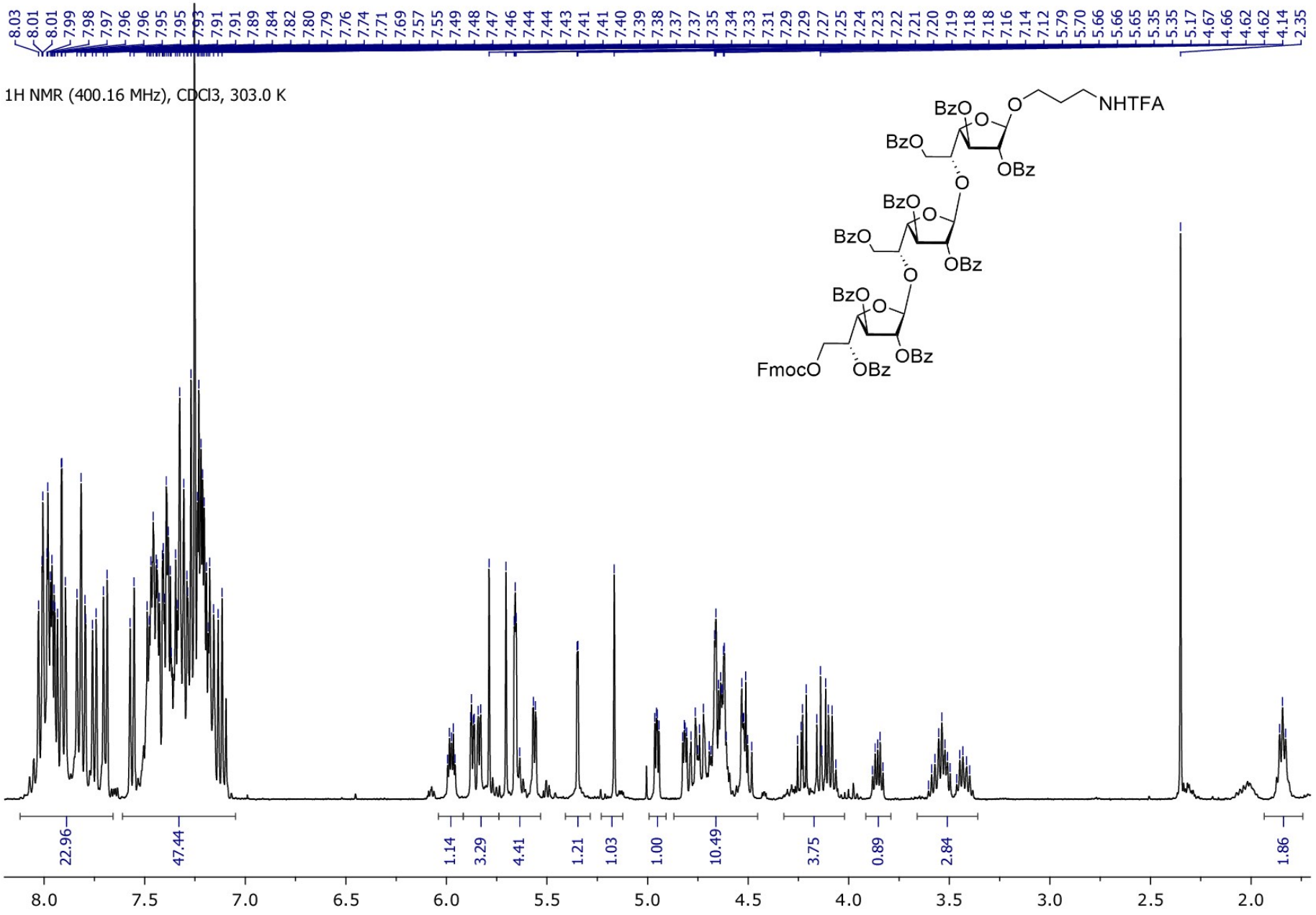
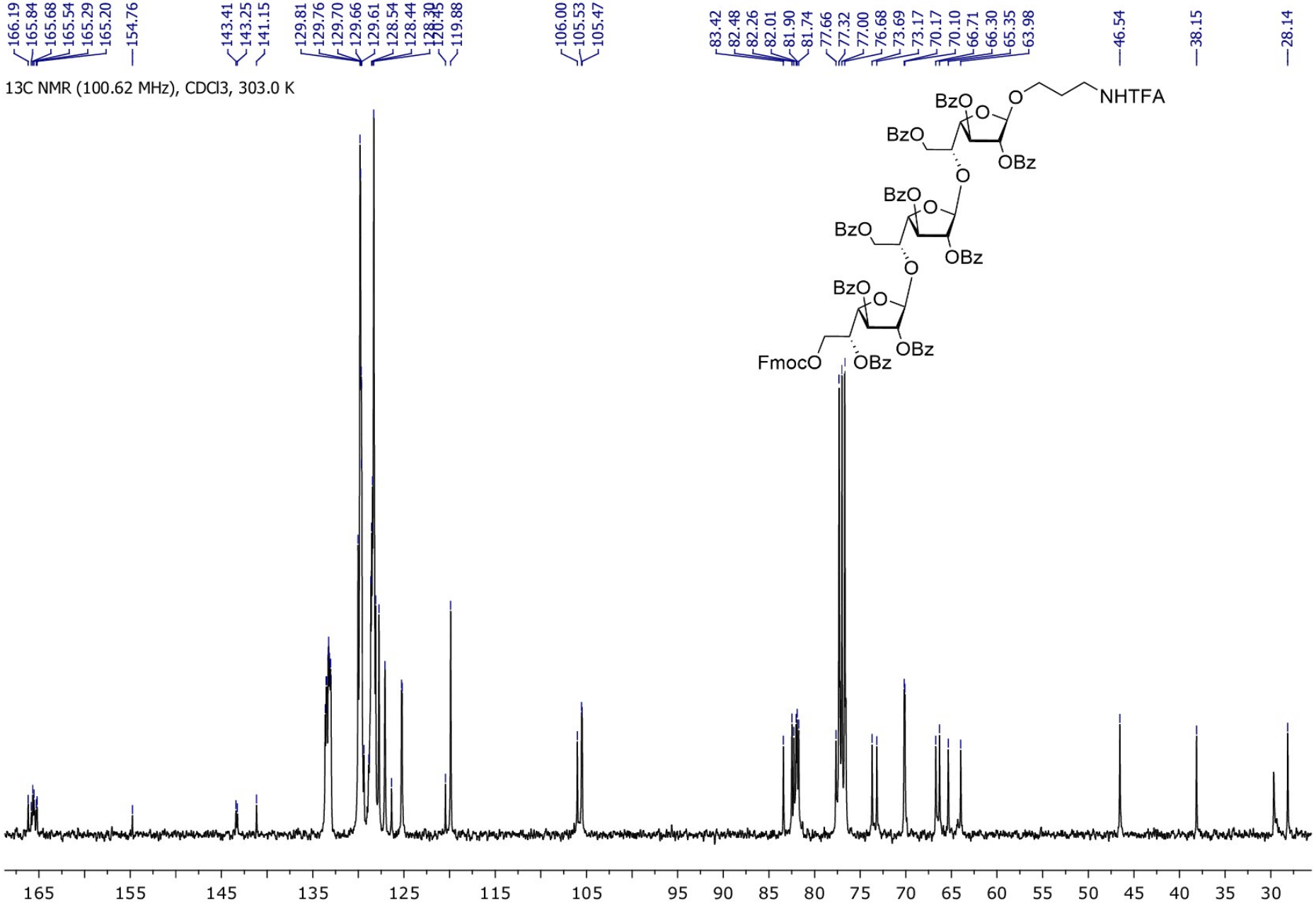
82.71
82.25
77.49
77.21
77.00
76.79
68.81
66.33
65.97
38.04
28.19
13C NMR (150.92 MHz), CDCl3, 299.3 K
BzO
O
O
NHTFA
BzO
OBz
OH
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25

3-Trifluoroacetamidopropyl 2,3,5-tri-*O*-benzoyl-6-*O*-(9-fluorenylmethoxycarbonyl)-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside 21

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82.01
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81.74
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77.32
77.00
76.68
73.69
73.17
70.17
70.10
66.71
66.30
65.35
63.98
46.54
38.15
28.14
13C NMR (100.62 MHz), CDCl3, 303.0 K
BzO
O
NHTFA
OBz
FmocO
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
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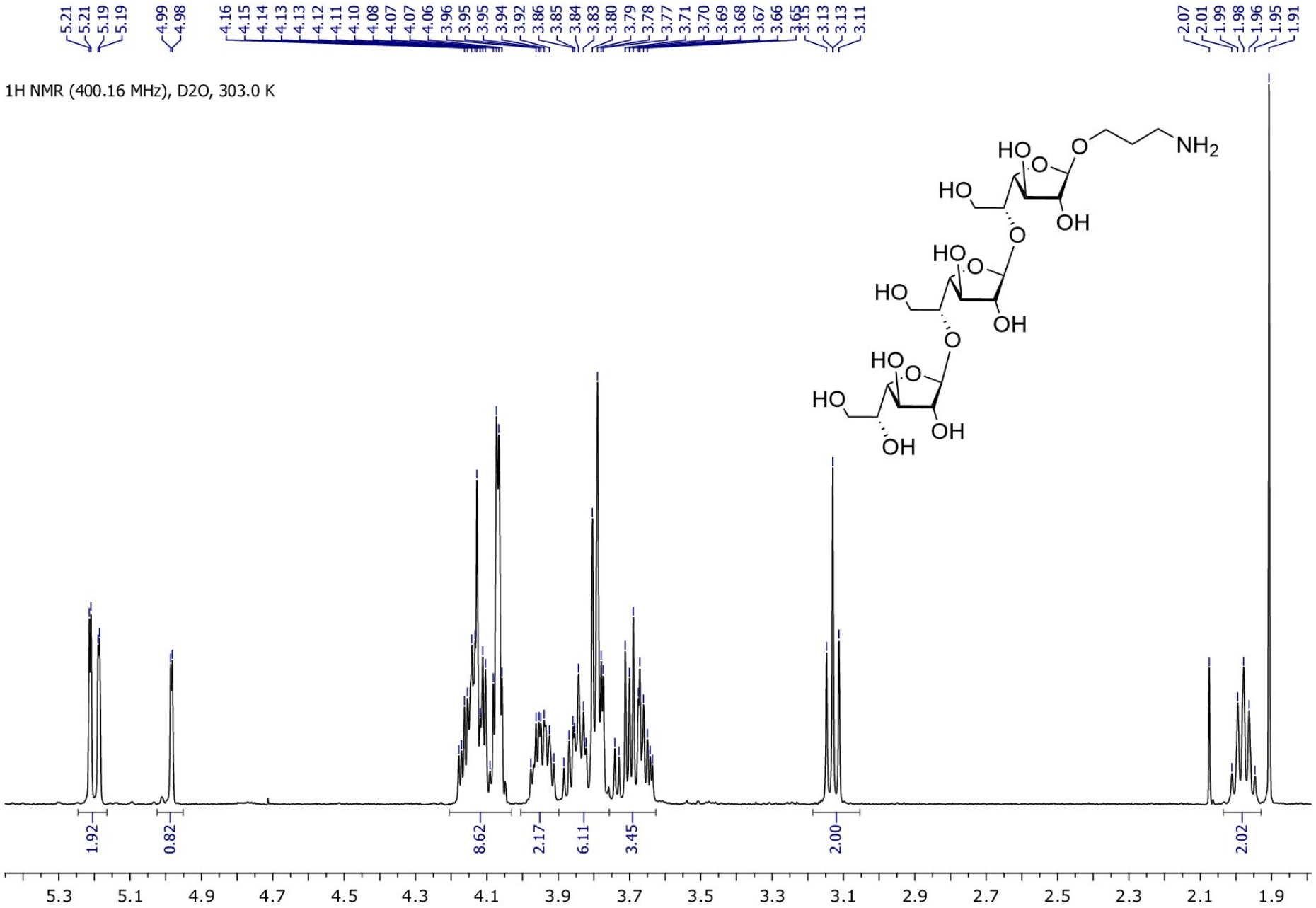
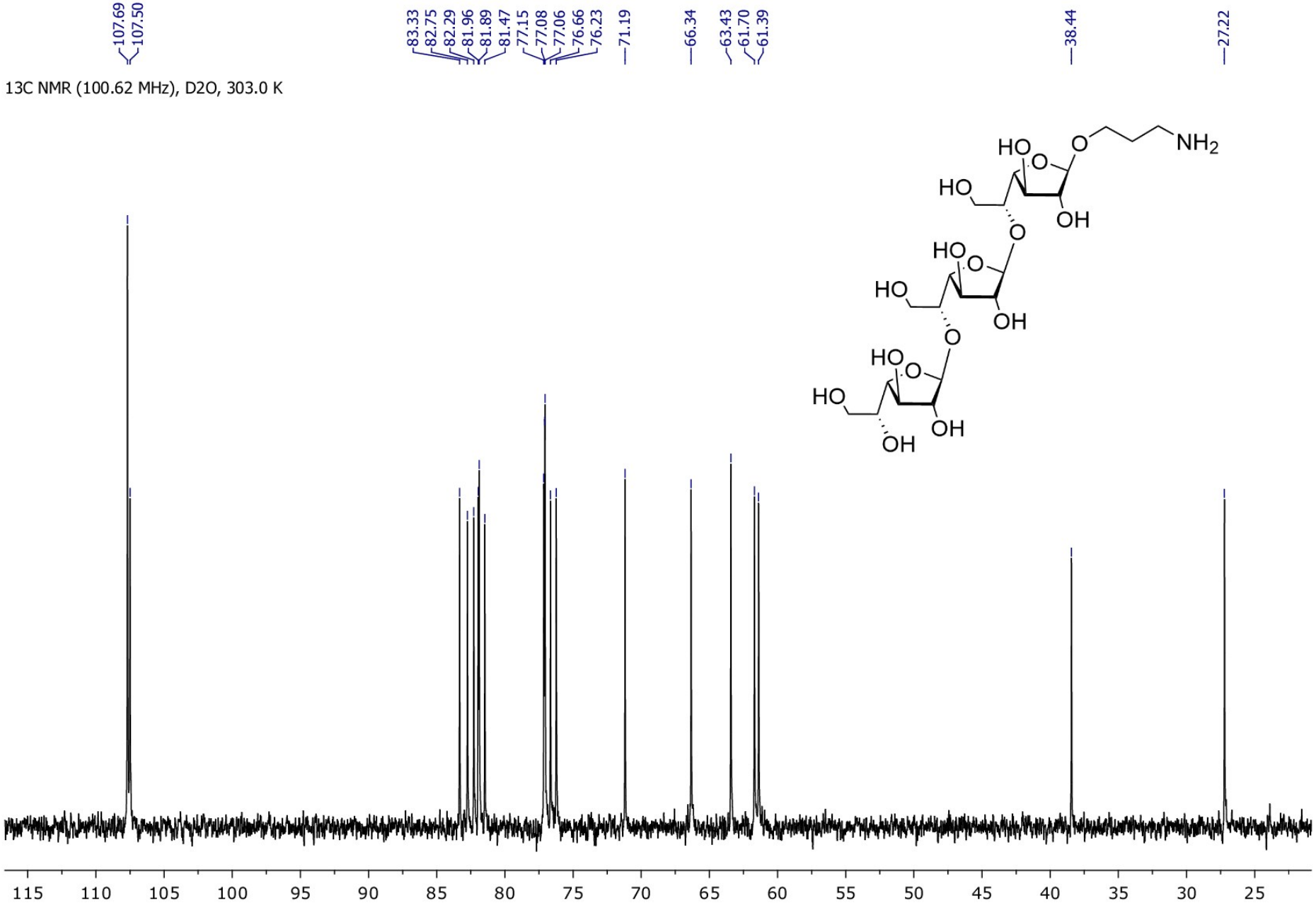
35
30

3-Aminopropyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranoside 4

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82.29
81.96
81.89
81.47
77.15
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77.06
76.66
76.23
71.19
66.34
63.43
61.70
61.39
38.44
27.22
13C NMR (100.62 MHz), D2O, 303.0 K
HO
O
O
NH2
HO
OH
HO
O
HO
OH
O
HO
O
HO
OH
OH
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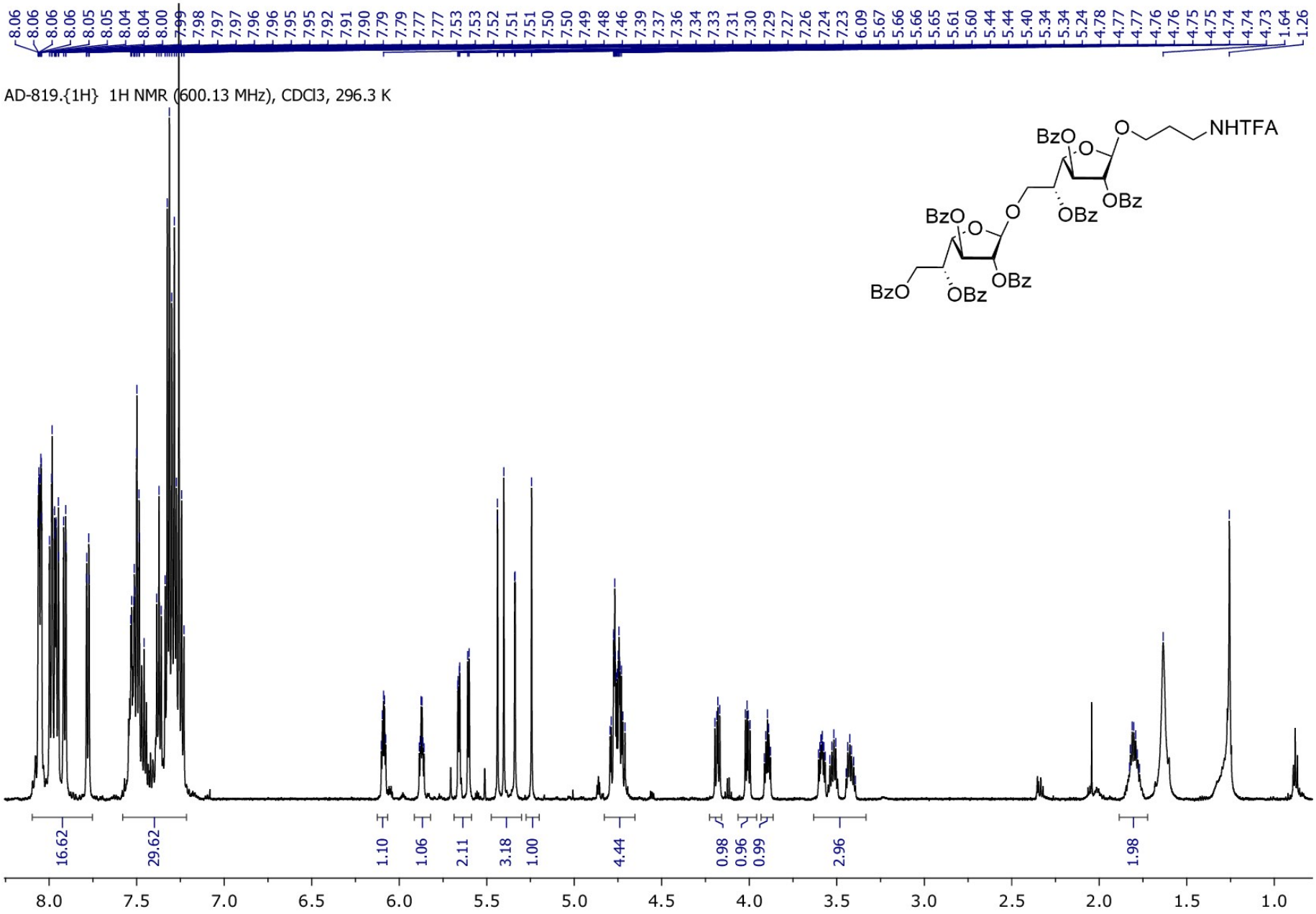
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2.11
3.18
1.00
4.44
0.98
0.96
0.99
2.96
1.98
8.0
7.5
7.0
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3.0
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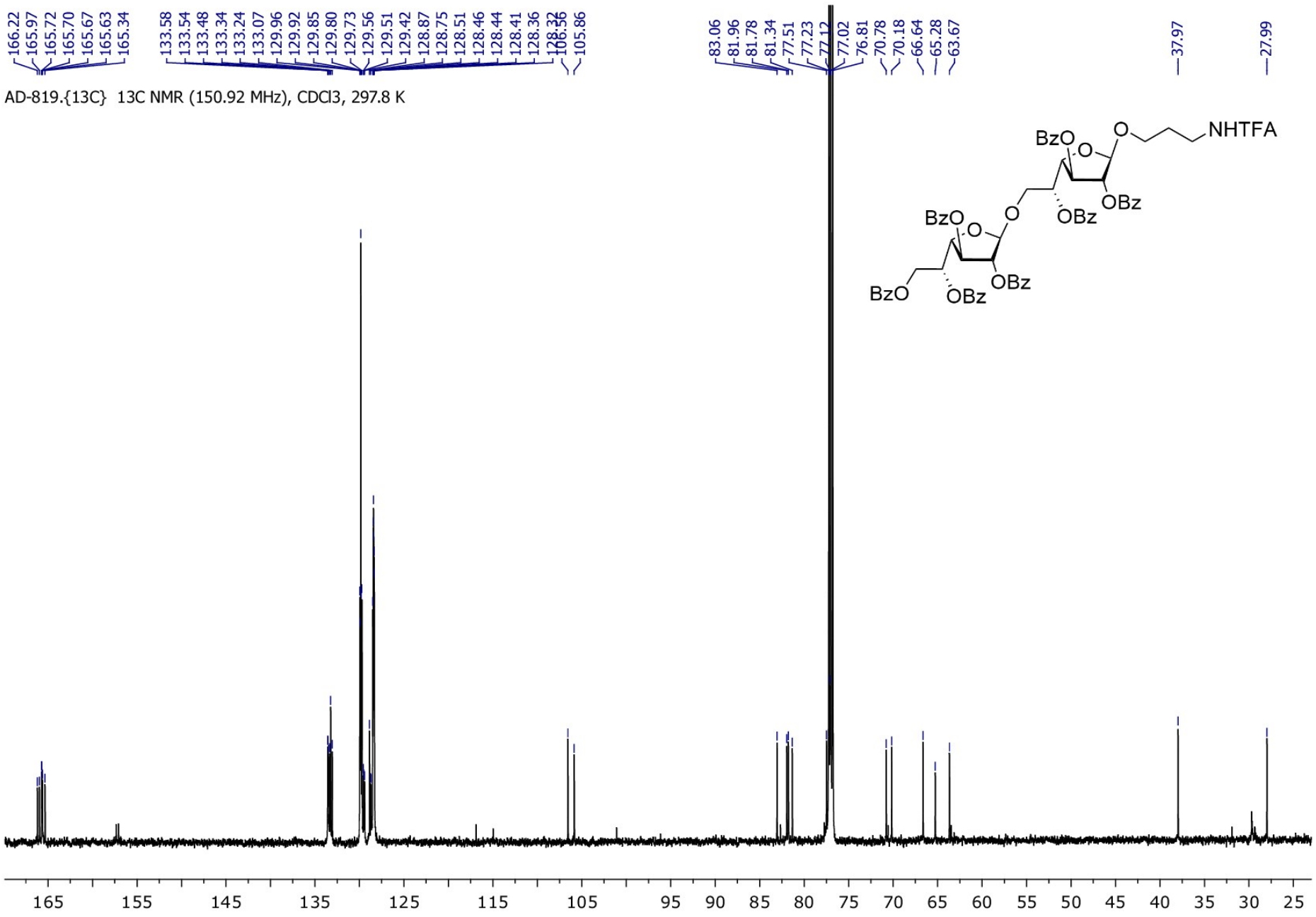
2.0
1.5
1.0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129.85
129.80
129.73
129.56
129.51
129.42
128.87
128.75
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128.46
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128.41
128.36
105.86
83.06
81.96
81.78
81.34
77.51
77.23
77.12
77.02
76.81
70.78
70.18
66.64
65.28
63.67
37.97
27.99
AD-819.{13C} 13C NMR (150.92 MHz), CDCl3, 297.8 K
BzO
O
O
NHTFA
OBz
OBz
BzO
O
O
OBz
OBz
BzO
OBz
165
155
145
135
125
115
105
95
90
85
80
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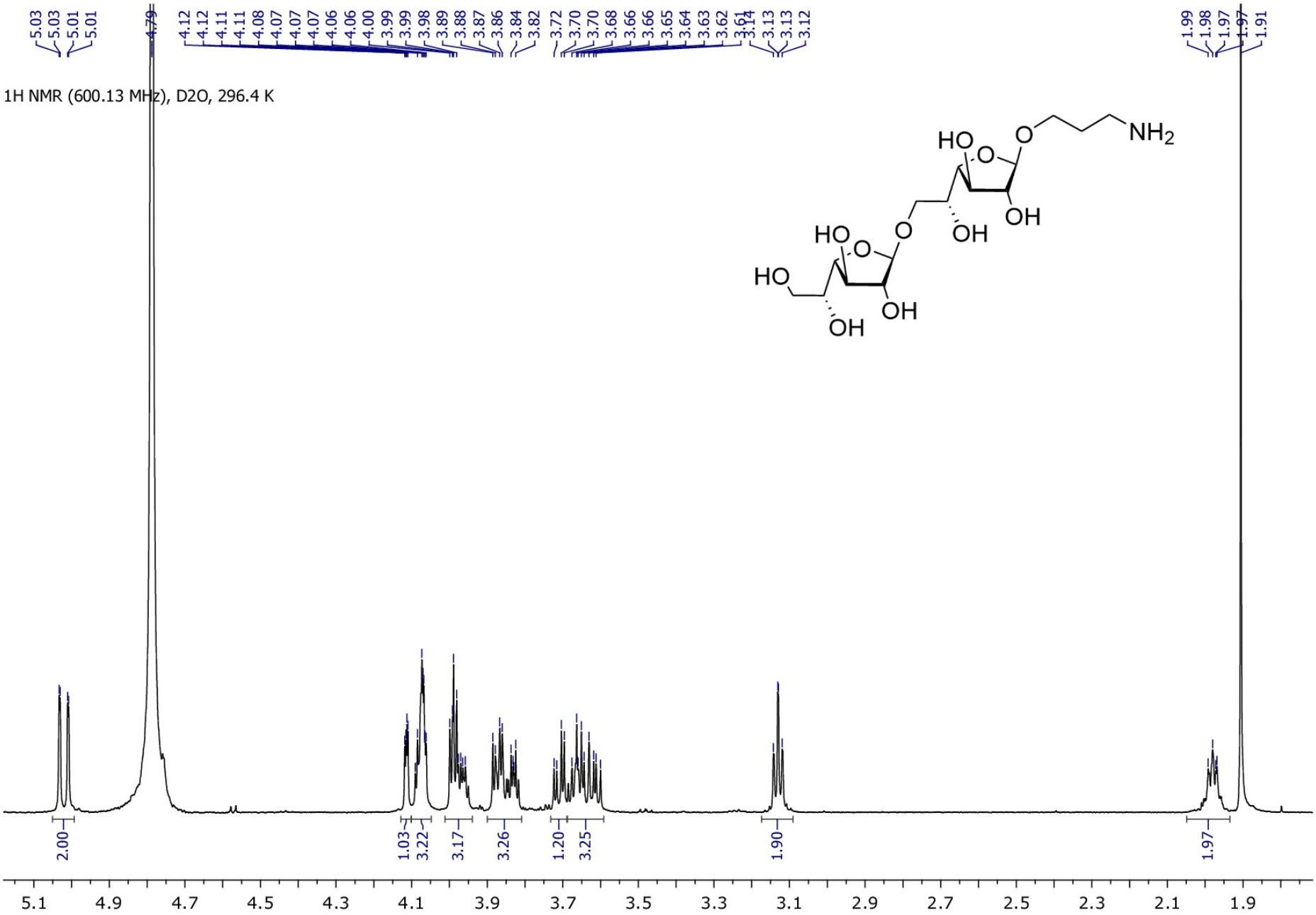
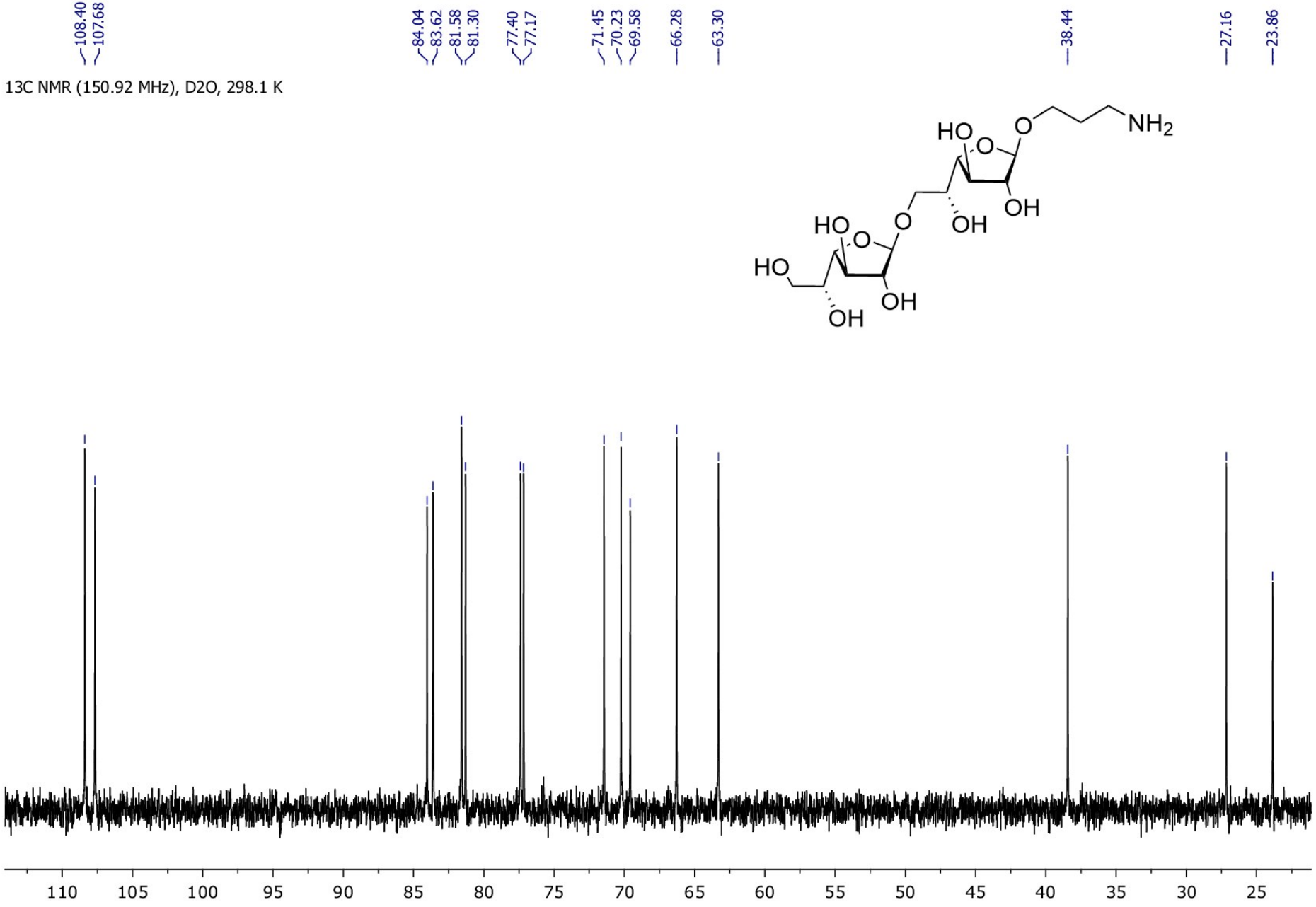
25

3-Aminopropyl β-D-galactofuranosyl-(1→6)-β-D-galactofuranoside 1

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63.30
38.44
27.16
23.86
13C NMR (150.92 MHz), D2O, 298.1 K
HO
O
O
NH2
OH
HO
O
O
OH
HO
OH
OH
110
105
100
95
90
85
80
75
70
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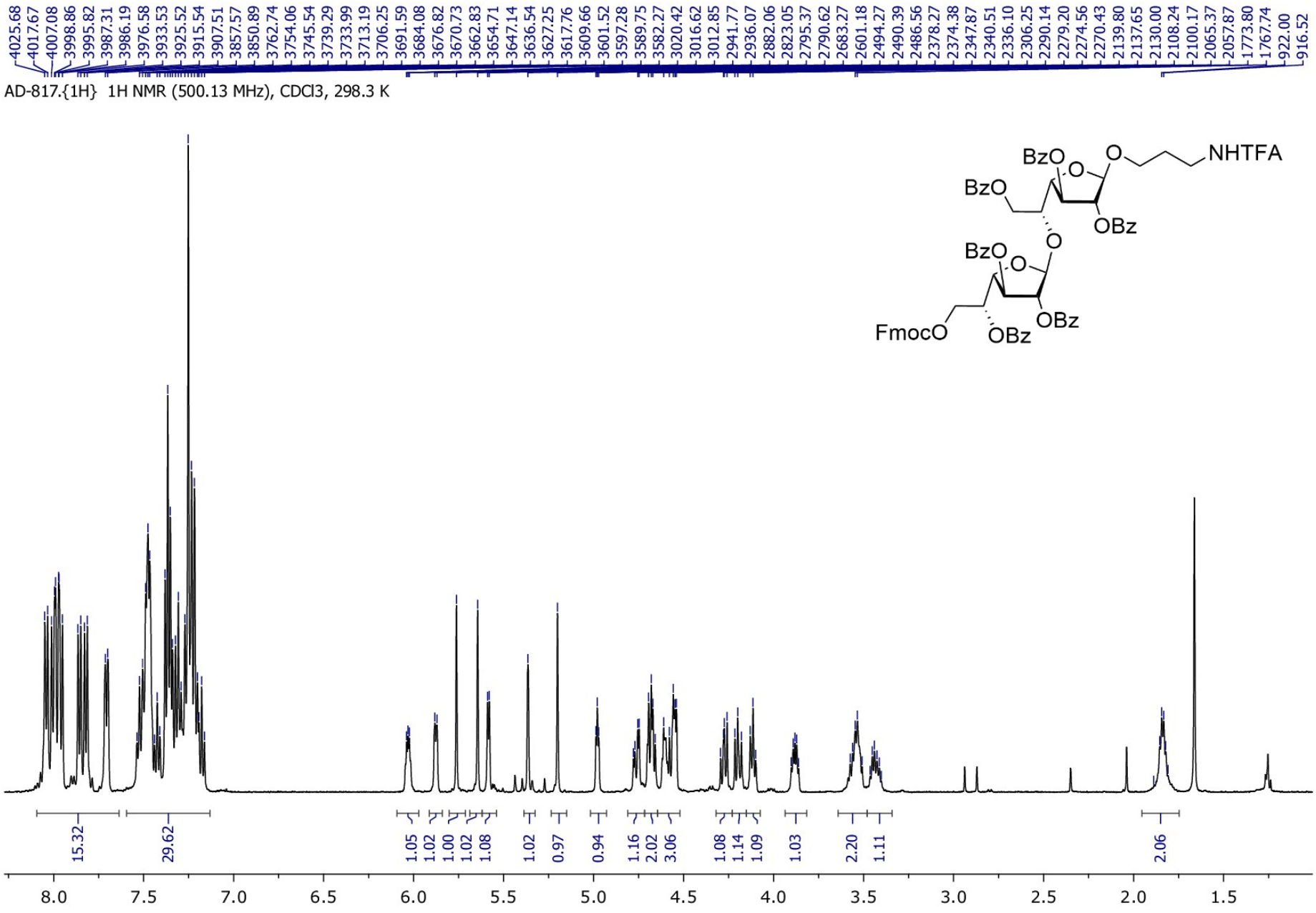
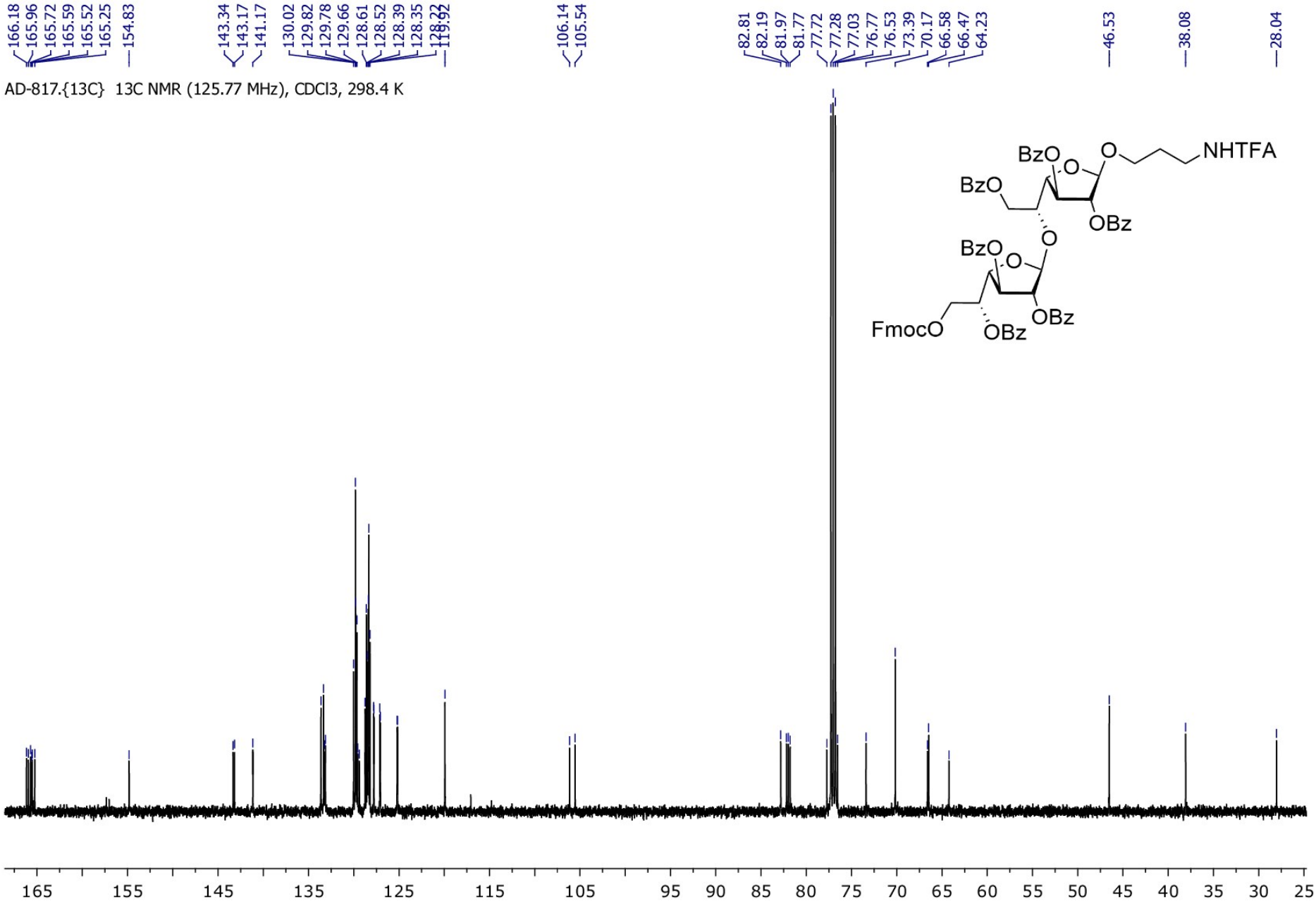
60
55
50
45
40
35
30
25

3-Trifluoroacetamidopropyl 2,3,5-tri-*O*-benzoyl-6-*O*-(9-fluorenylmethoxycarbonyl)-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside 24

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129.66
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128.52
128.39
128.35
106.14
105.54
82.81
82.19
81.97
81.77
77.72
77.28
77.03
76.77
76.53
73.39
70.17
66.58
66.47
64.23
46.53
38.08
28.04
AD-817.{13C} 13C NMR (125.77 MHz), CDCl3, 298.4 K
BzO
O
O
NHTFA
BzO
OBz
BzO
O
O
OBz
FmocO
OBz
165
155
145
135
125
115
105
95
90
85
80
75
70
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50
45
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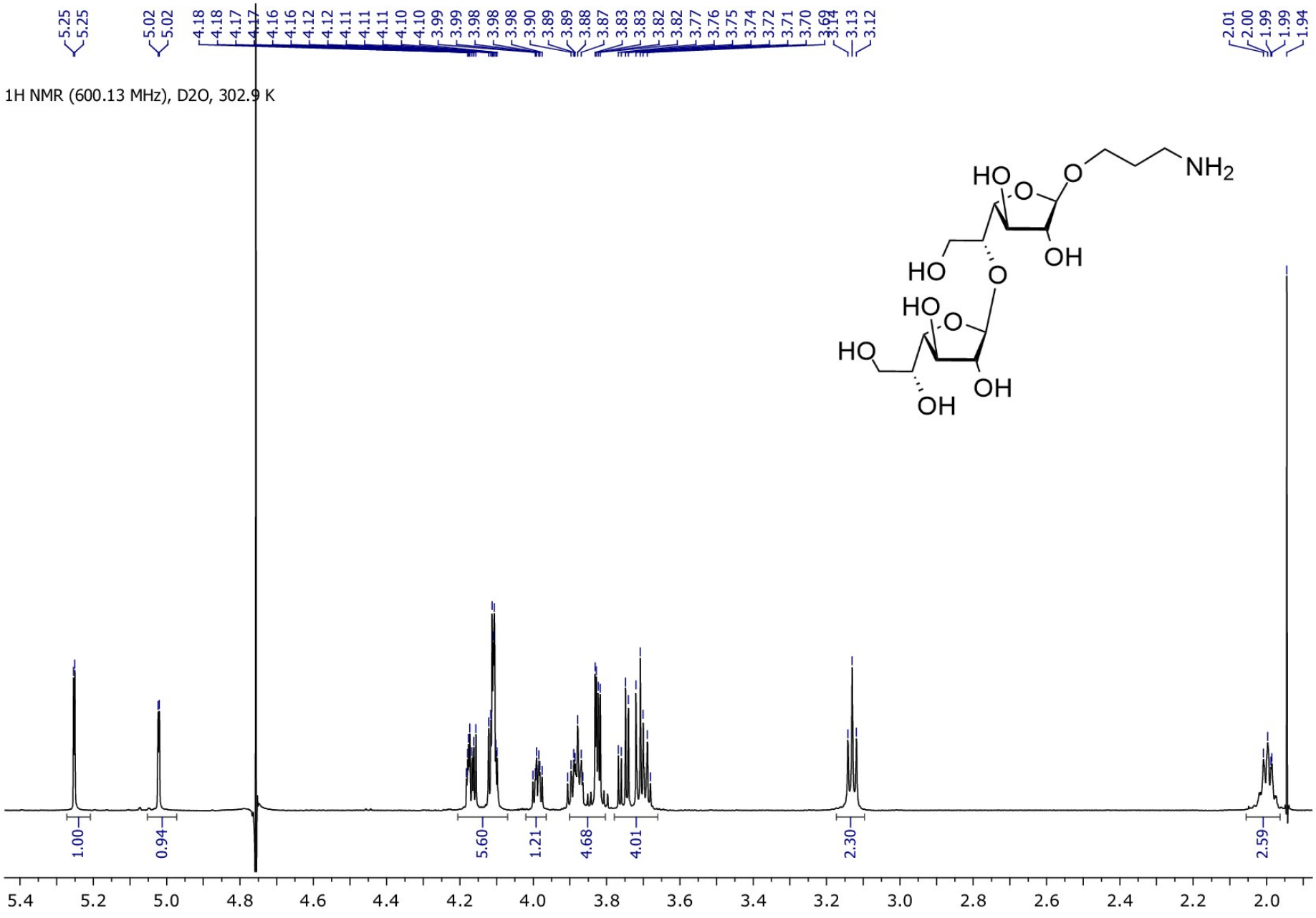
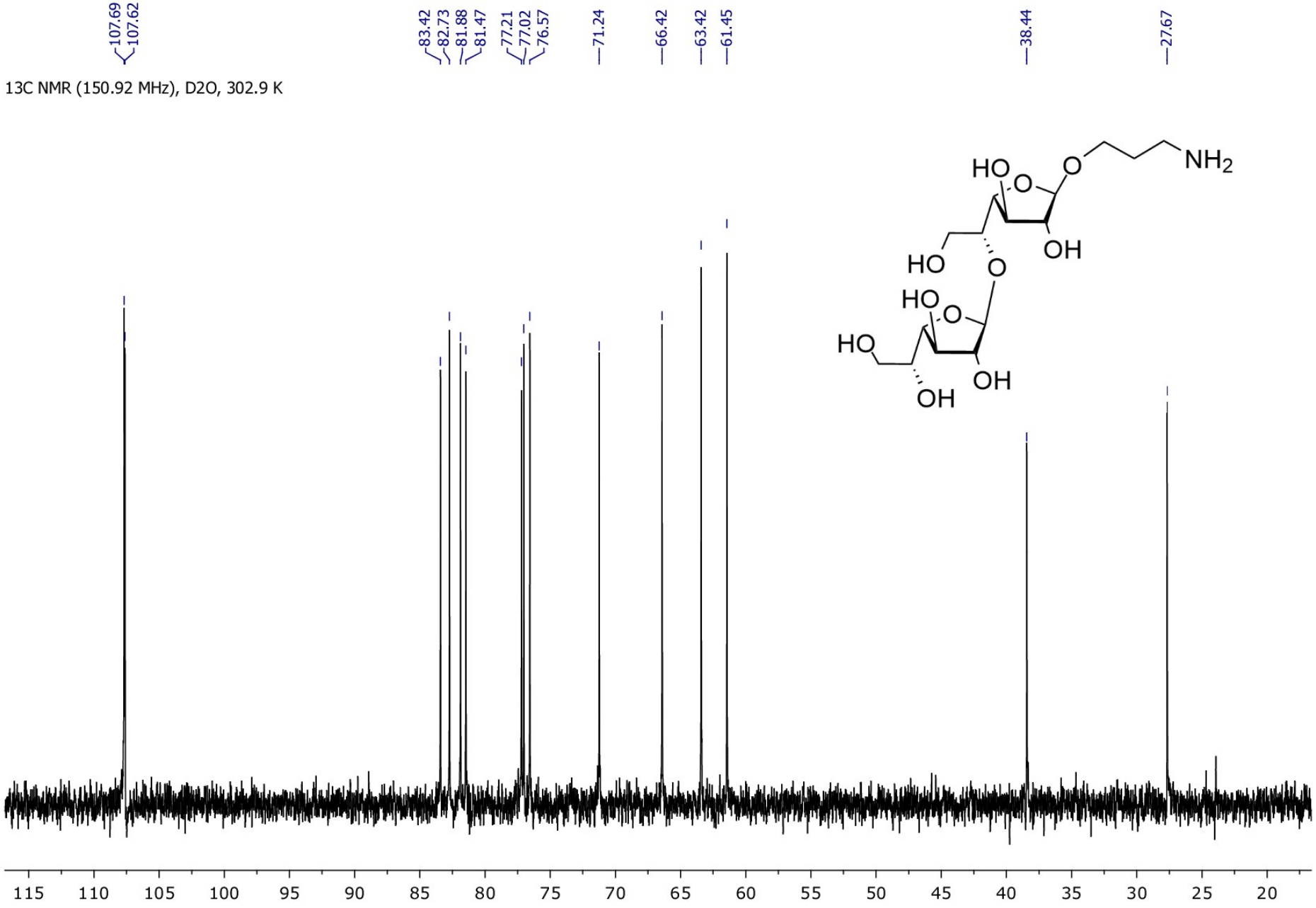
25

3-Aminopropyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranoside 3

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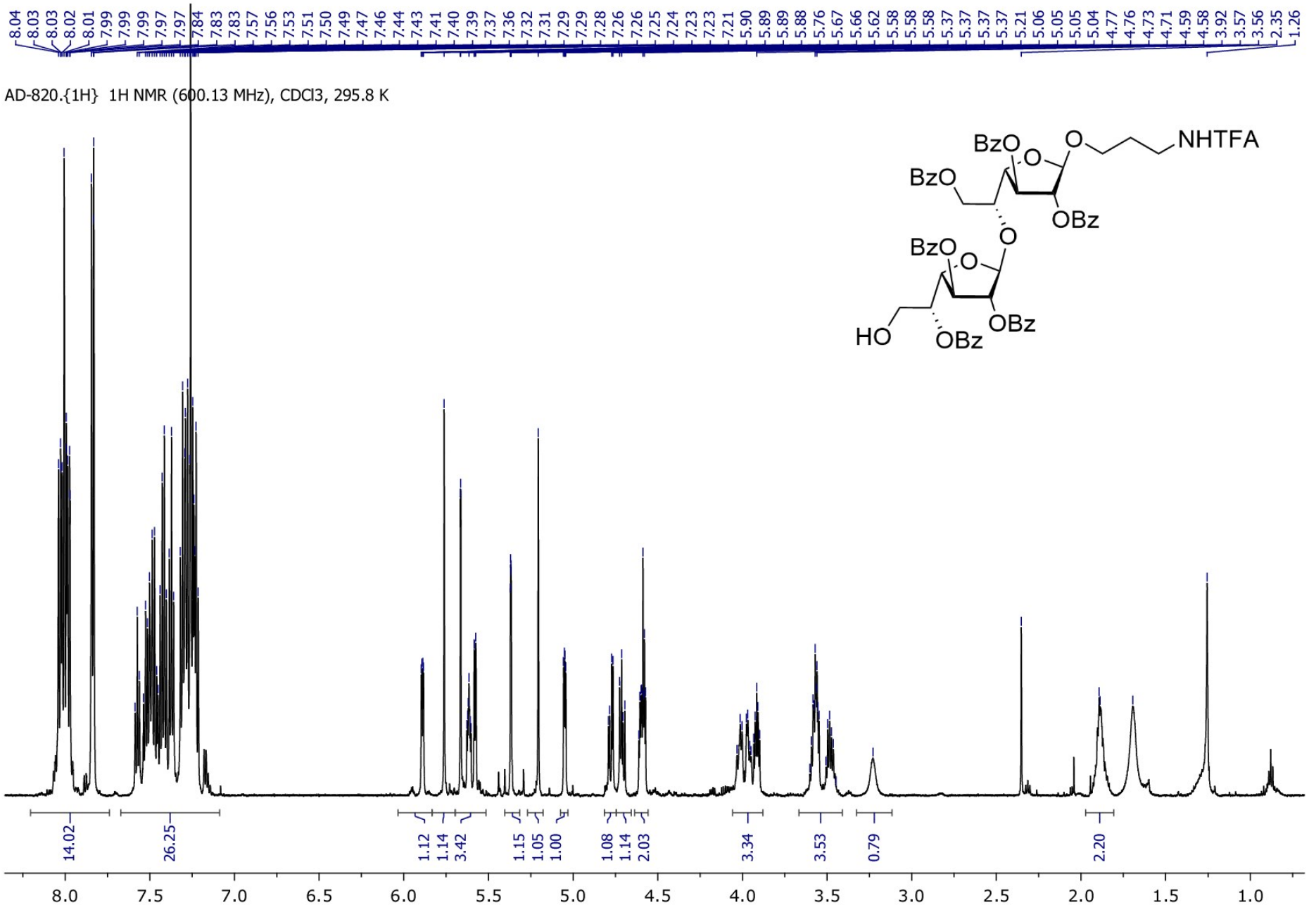
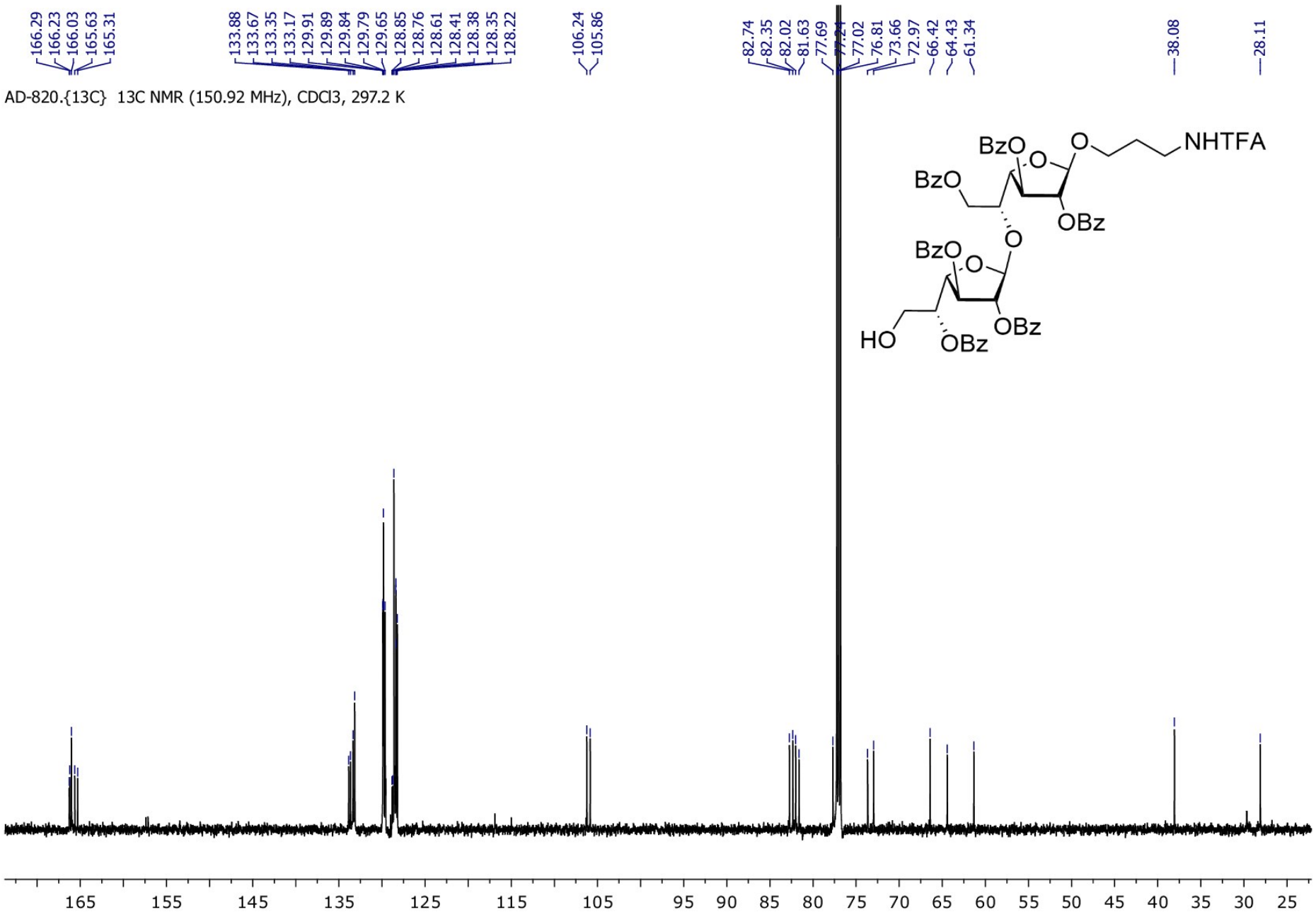
107.62
83.42
82.73
81.88
81.47
77.21
77.02
76.57
71.24
66.42
63.42
61.45
38.44
27.67
13C NMR (150.92 MHz), D2O, 302.9 K
HO
O
O
NH2
OH
HO
O
HO
O
HO
OH
OH
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20

3-Trifluoroacetamidopropyl 2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranoside 25

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128.35
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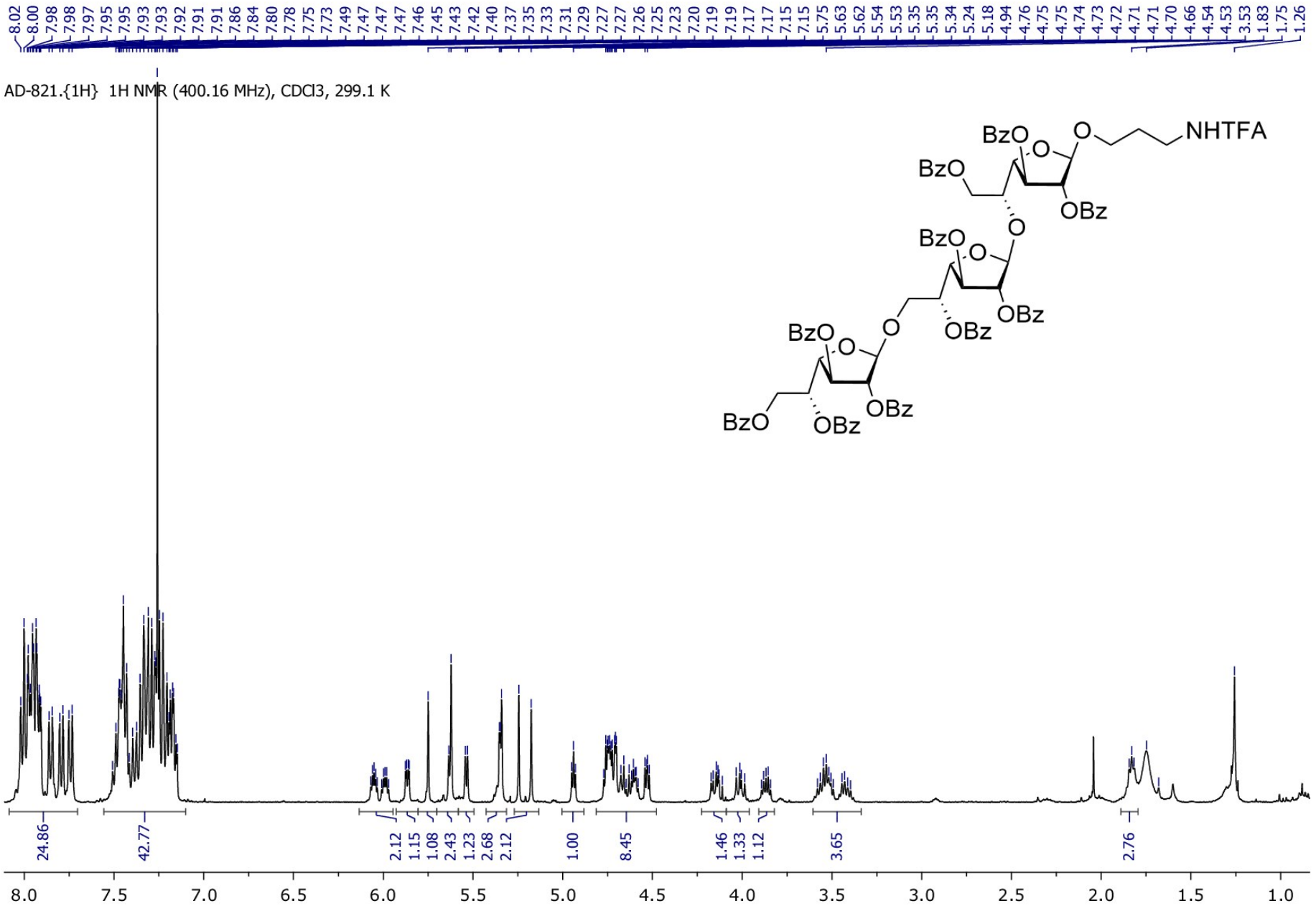
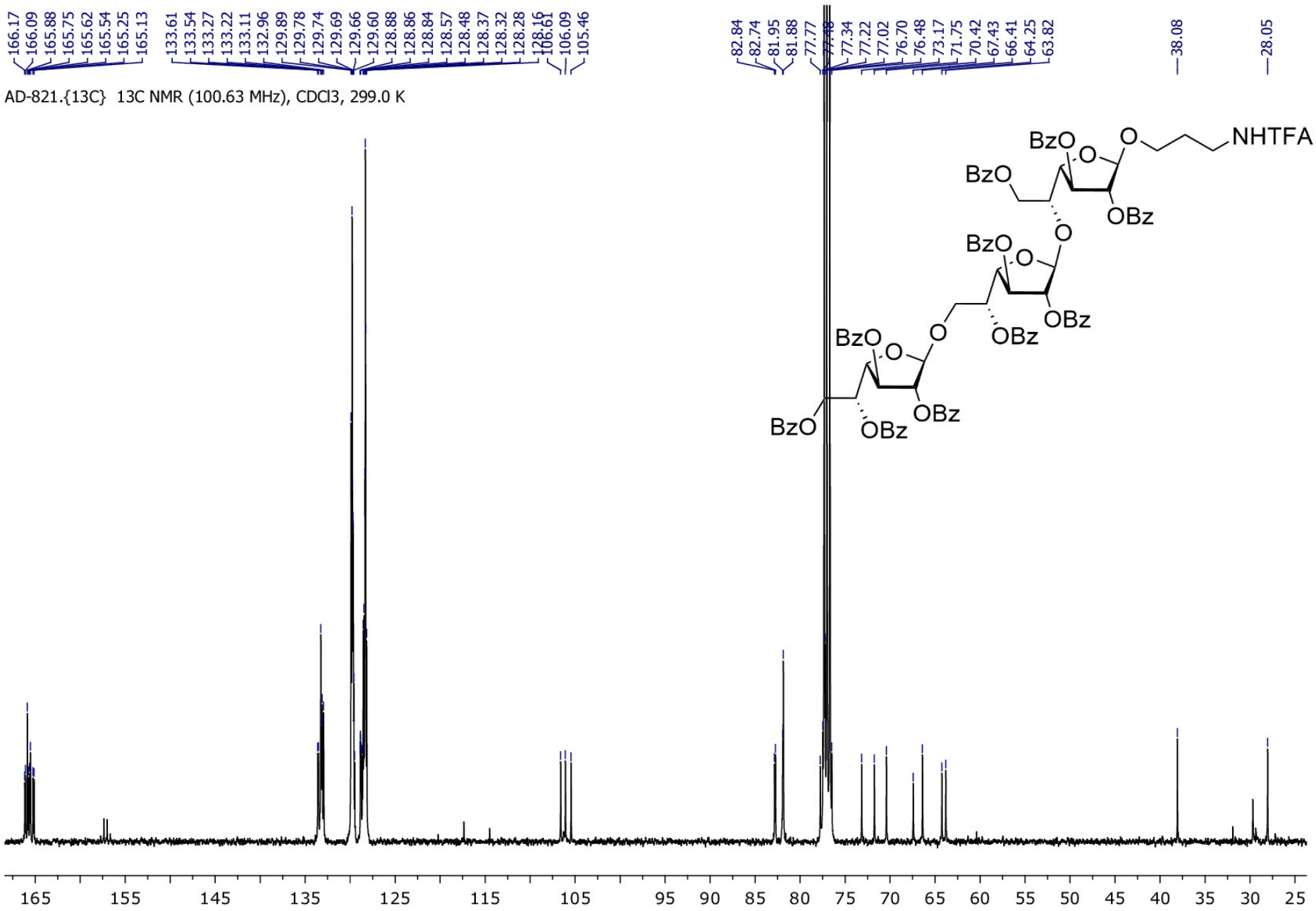
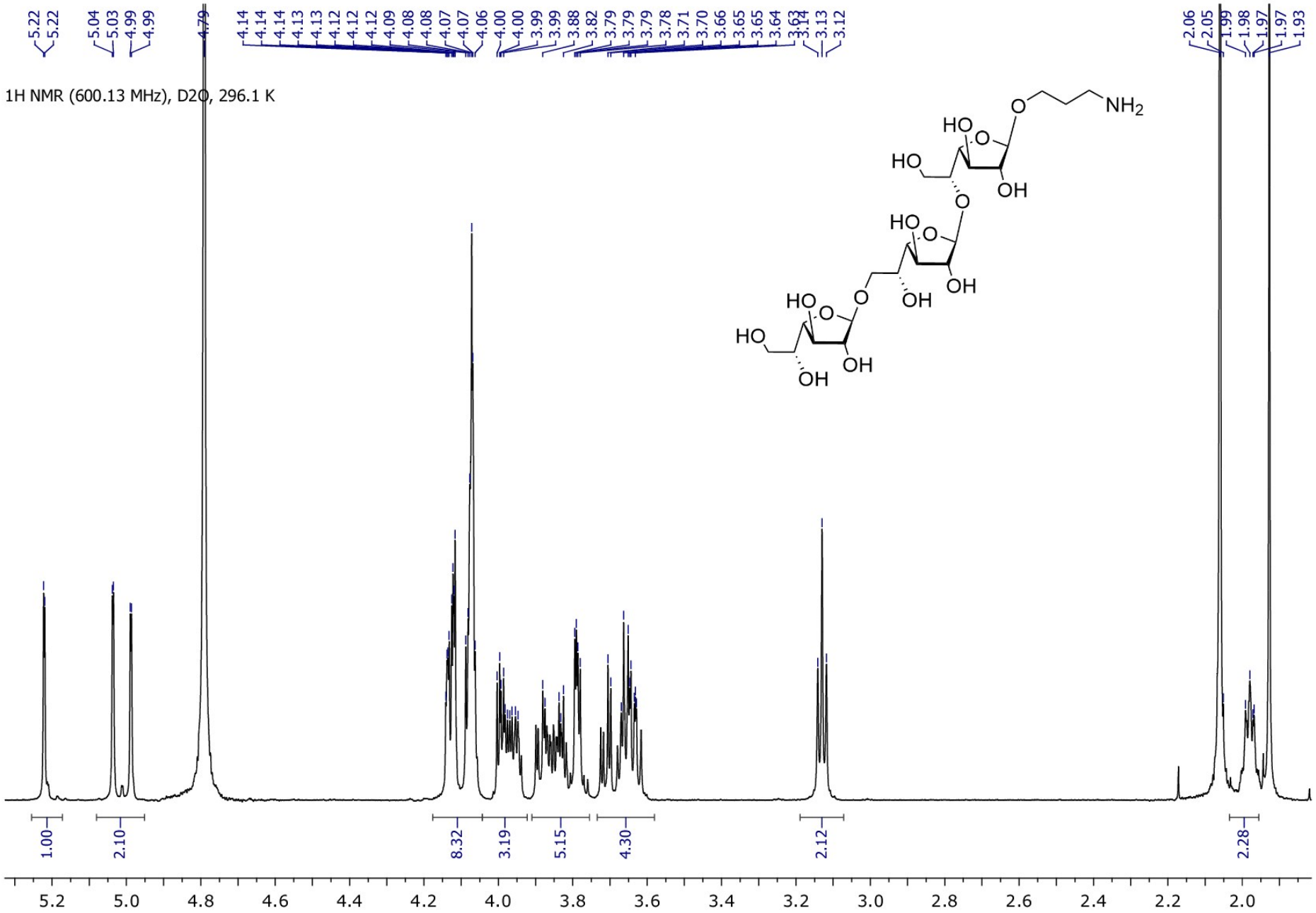
105.86
82.74
82.35
82.02
81.63
77.69
77.24
77.02
76.81
73.66
72.97
66.42
64.43
61.34
38.08
28.11
AD-820.{13C} 13C NMR (150.92 MHz), CDCl3, 297.2 K
BzO
O
O
NHTFA
BzO
OBz
O
BzO
O
HO
OBz
OBz
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25

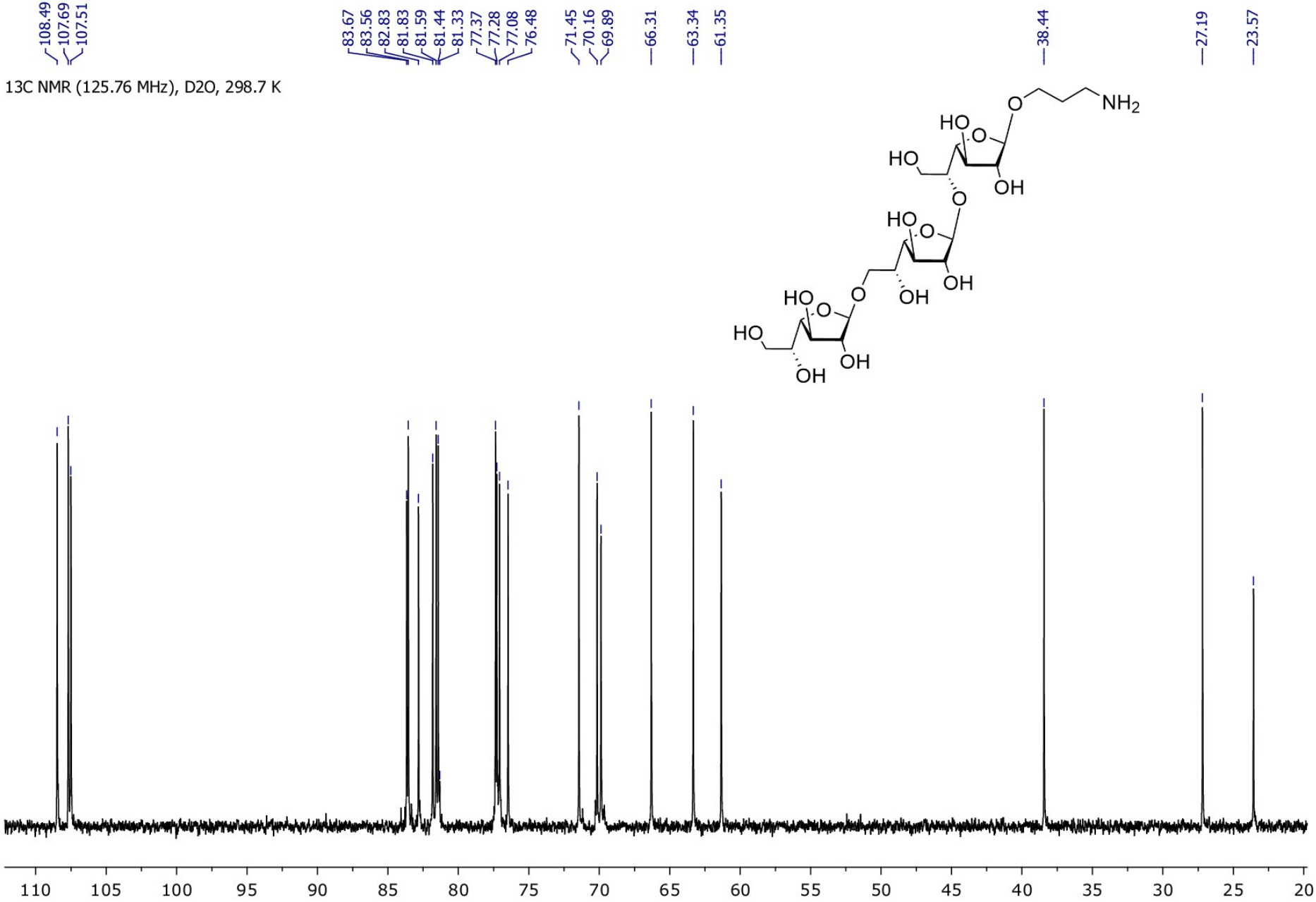
3-Trifluoroacetamidopropyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranoside 26



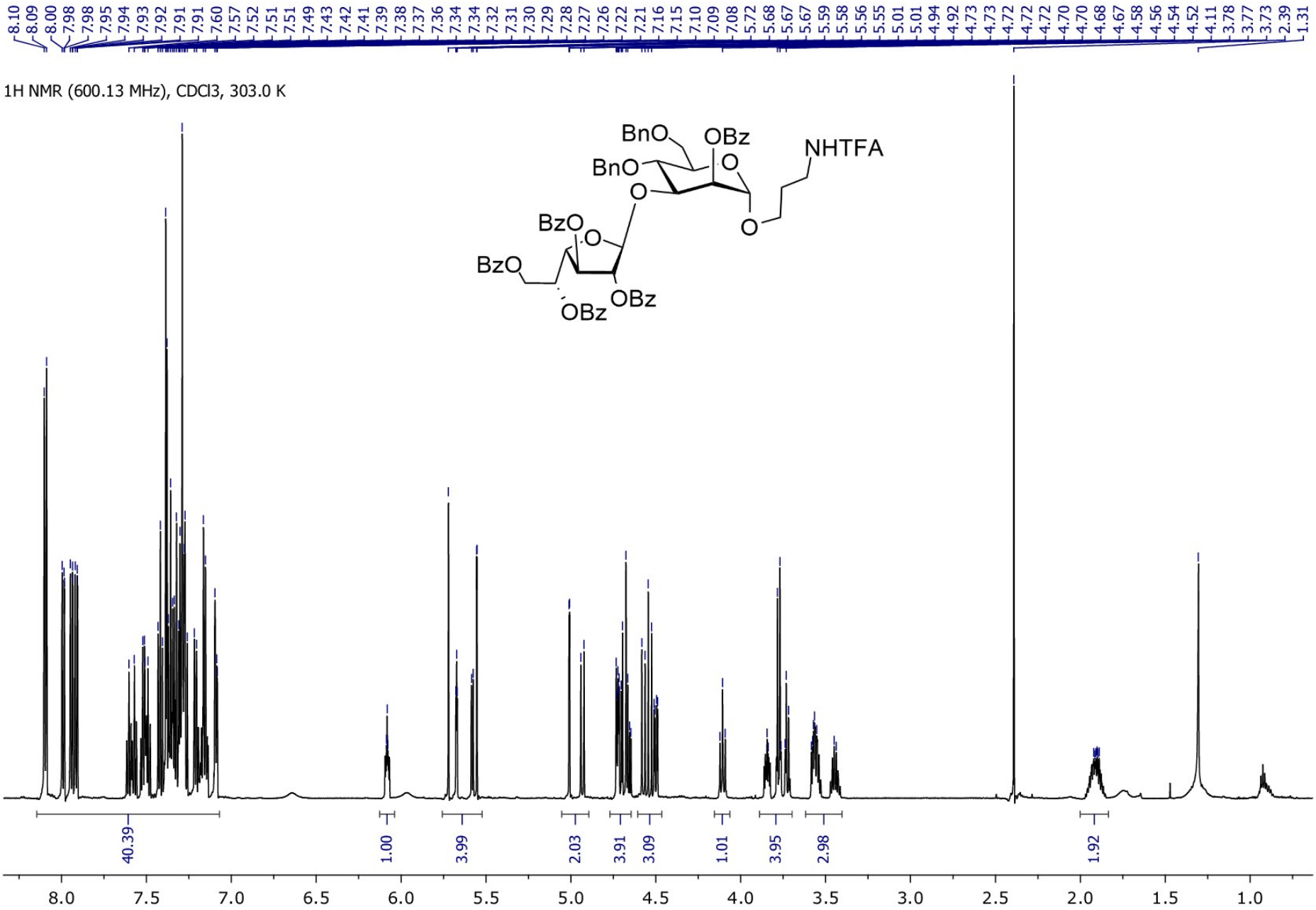

166.17
166.09
165.88
165.75
165.62
165.54
165.25
165.13
133.61
133.54
133.27
133.22
133.11
132.96
129.89
129.78
129.74
129.69
129.66
129.60
128.88
128.86
128.84
128.57
128.48
128.37
128.32
128.28
106.09
105.46
82.84
82.74
81.95
81.88
77.77
77.34
77.22
77.02
76.70
76.48
73.17
71.75
70.42
67.43
66.41
64.25
63.82
38.08
28.05
AD-821.{13C} 13C NMR (100.63 MHz), CDCl3, 299.0 K
BzO
O
NHTFA
OBz
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25

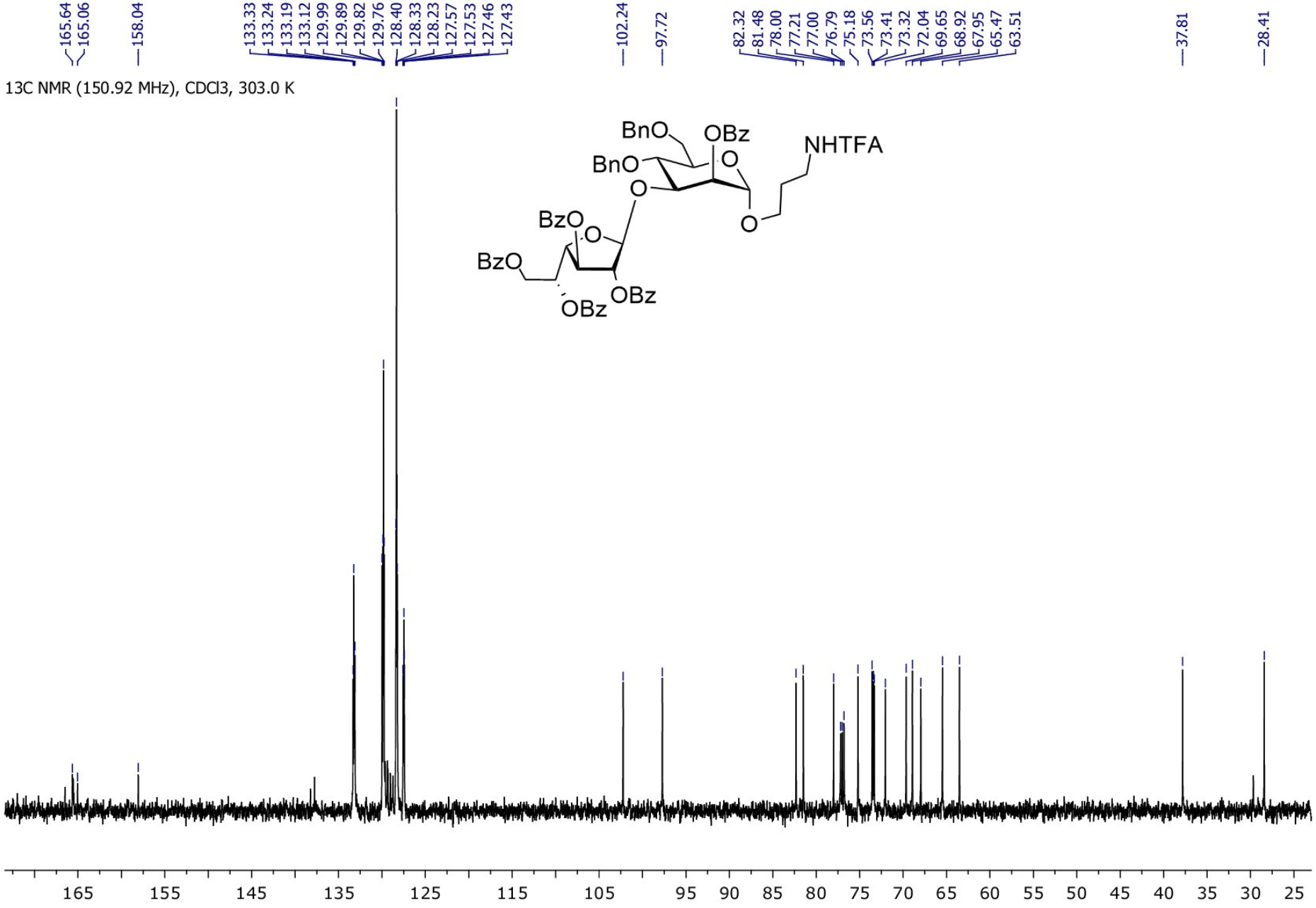
3-Aminopropyl β-D-galactofuranosyl-(1→6)-β-D-galactofuranosyl-(1→5)-β-D-galactofuranoside 2



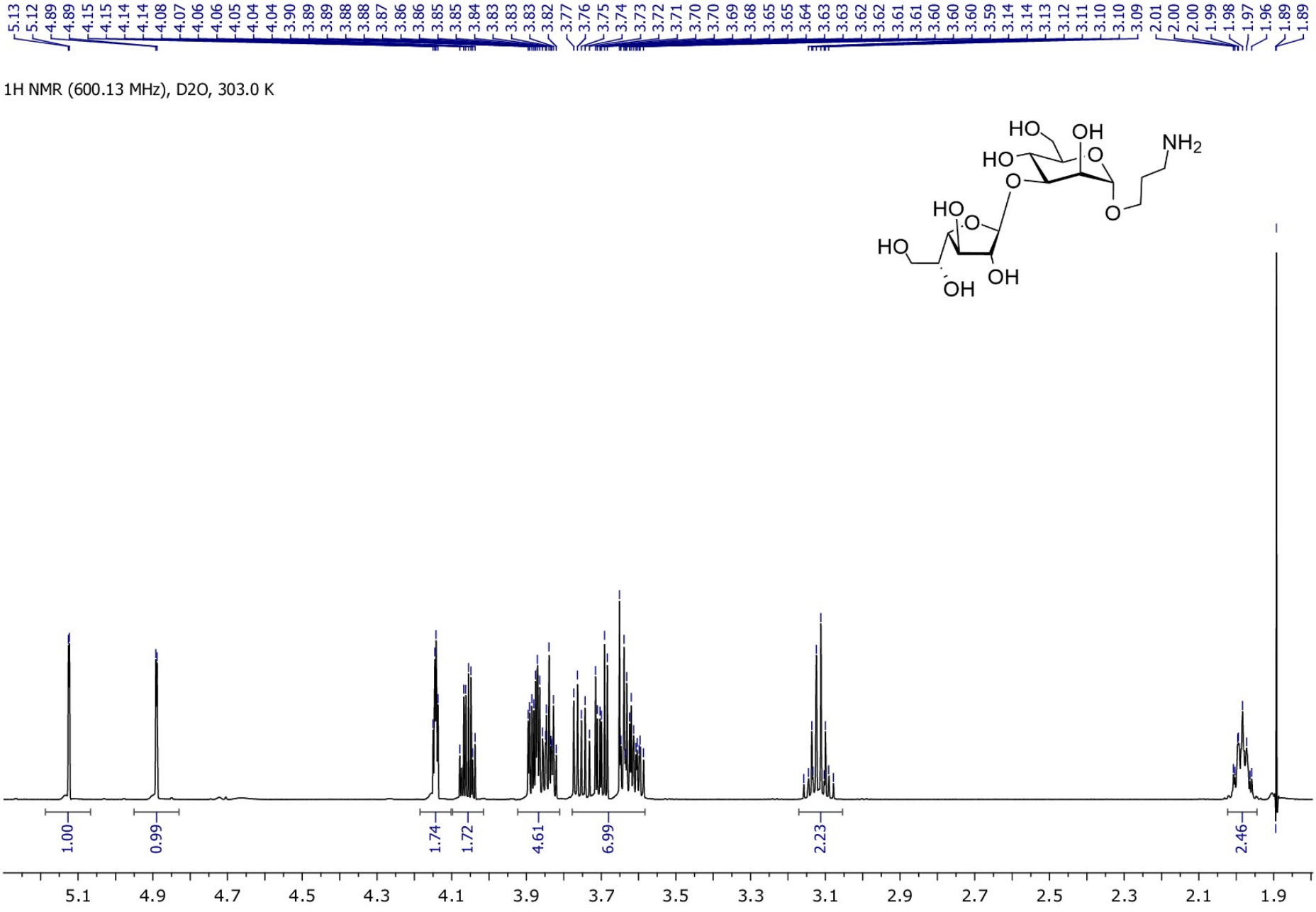

108.49
107.69
107.51
83.67
83.56
82.83
81.83
81.59
81.44
81.33
77.37
77.28
77.08
76.48
71.45
70.16
69.89
66.31
63.34
61.35
38.44
27.19
23.57
13C NMR (125.76 MHz), D2O, 298.7 K
NH2
HO
OH
O
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20

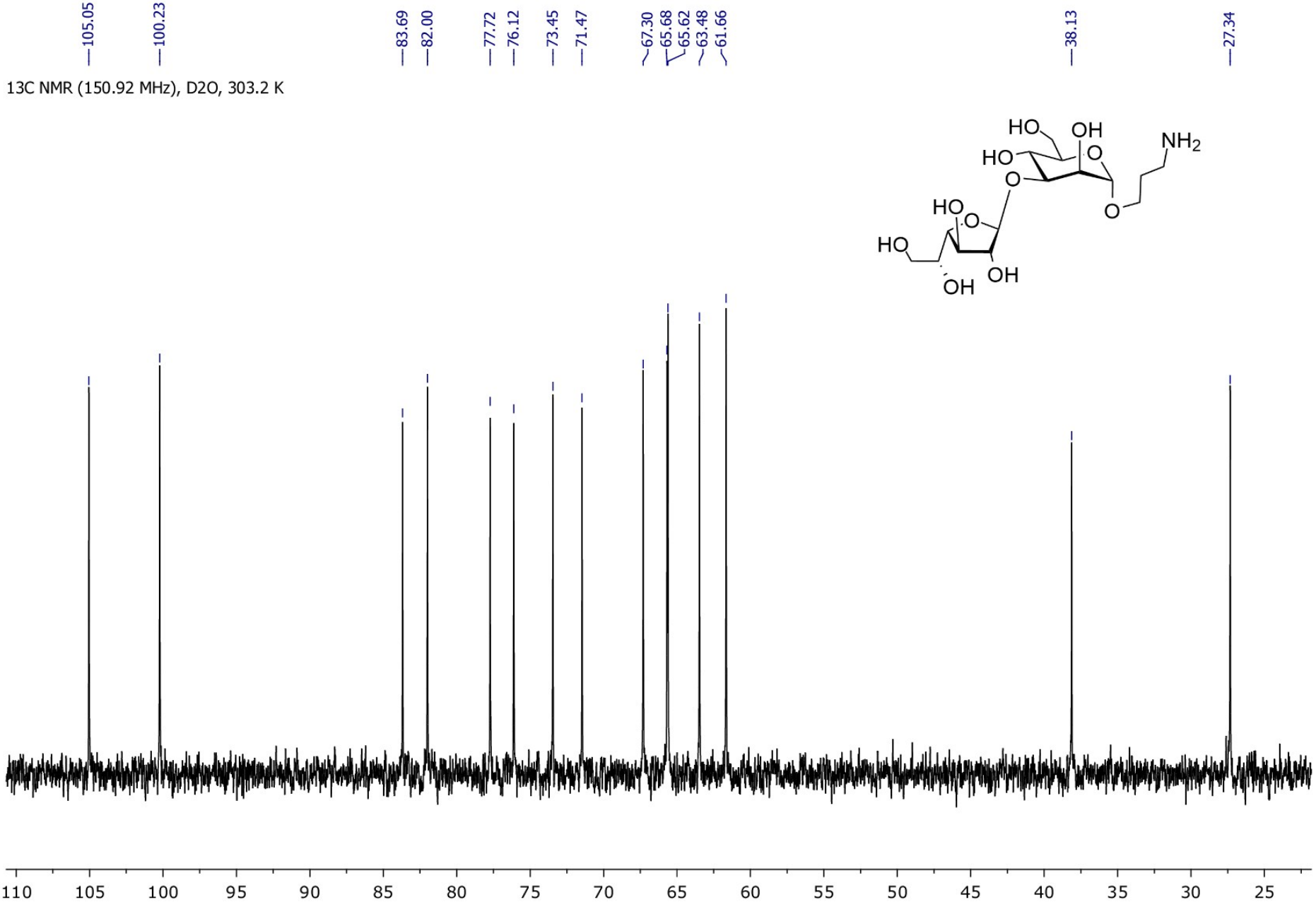
3-Trifluoroacetamidopropyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-α-D-mannopyranoside 28



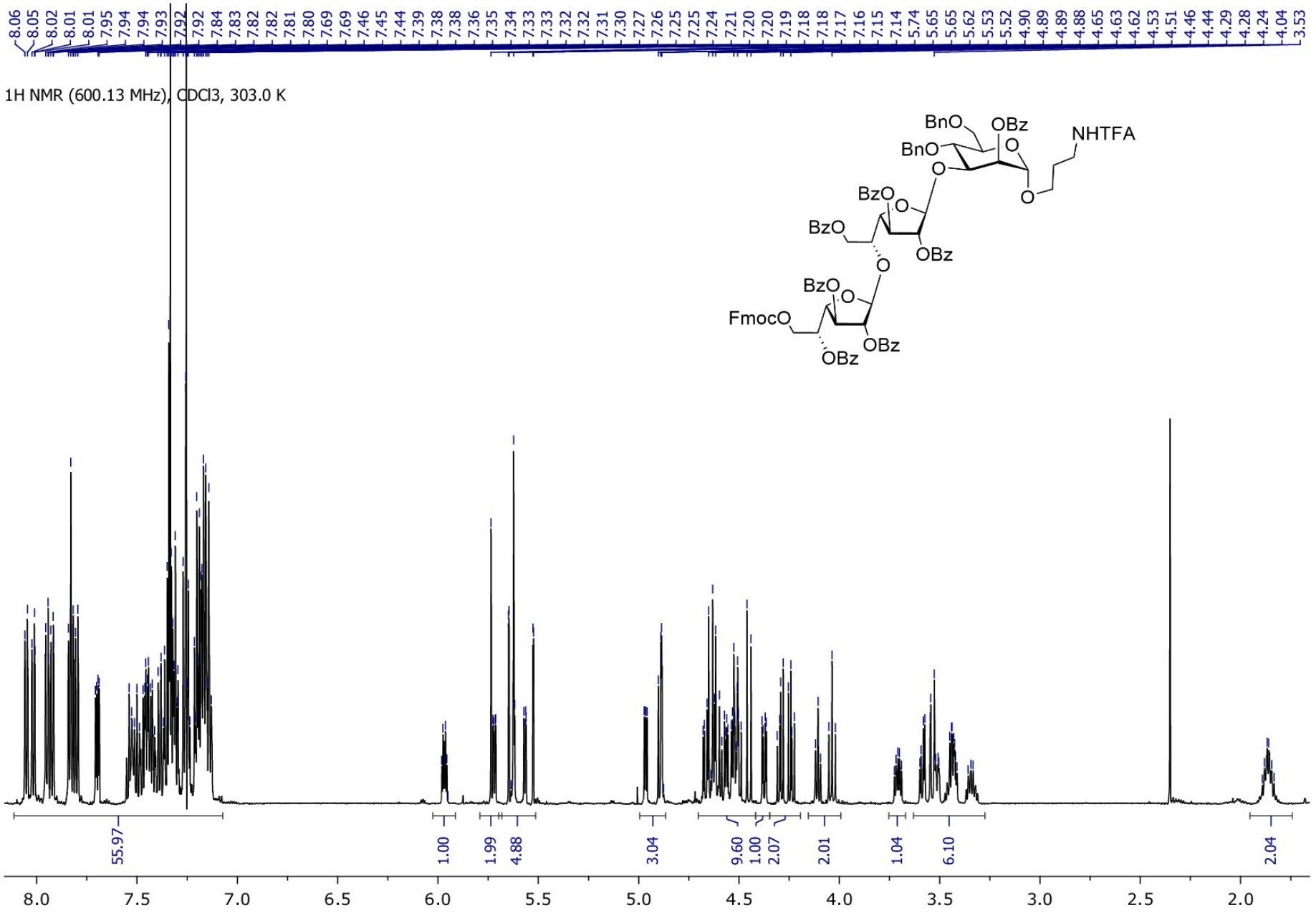

165.64
165.06
158.04
133.33
133.24
133.19
133.12
129.99
129.89
129.82
129.76
128.40
128.33
128.23
127.57
127.53
127.46
127.43
102.24
97.72
82.32
81.48
78.00
77.21
77.00
76.79
75.18
73.56
73.41
73.32
72.04
69.65
68.92
67.95
65.47
63.51
37.81
28.41
13C NMR (150.92 MHz), CDCl3, 303.0 K
BnO
OBz
NHTFA
BnO
O
O
BzO
O
BzO
OBz
OBz
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25

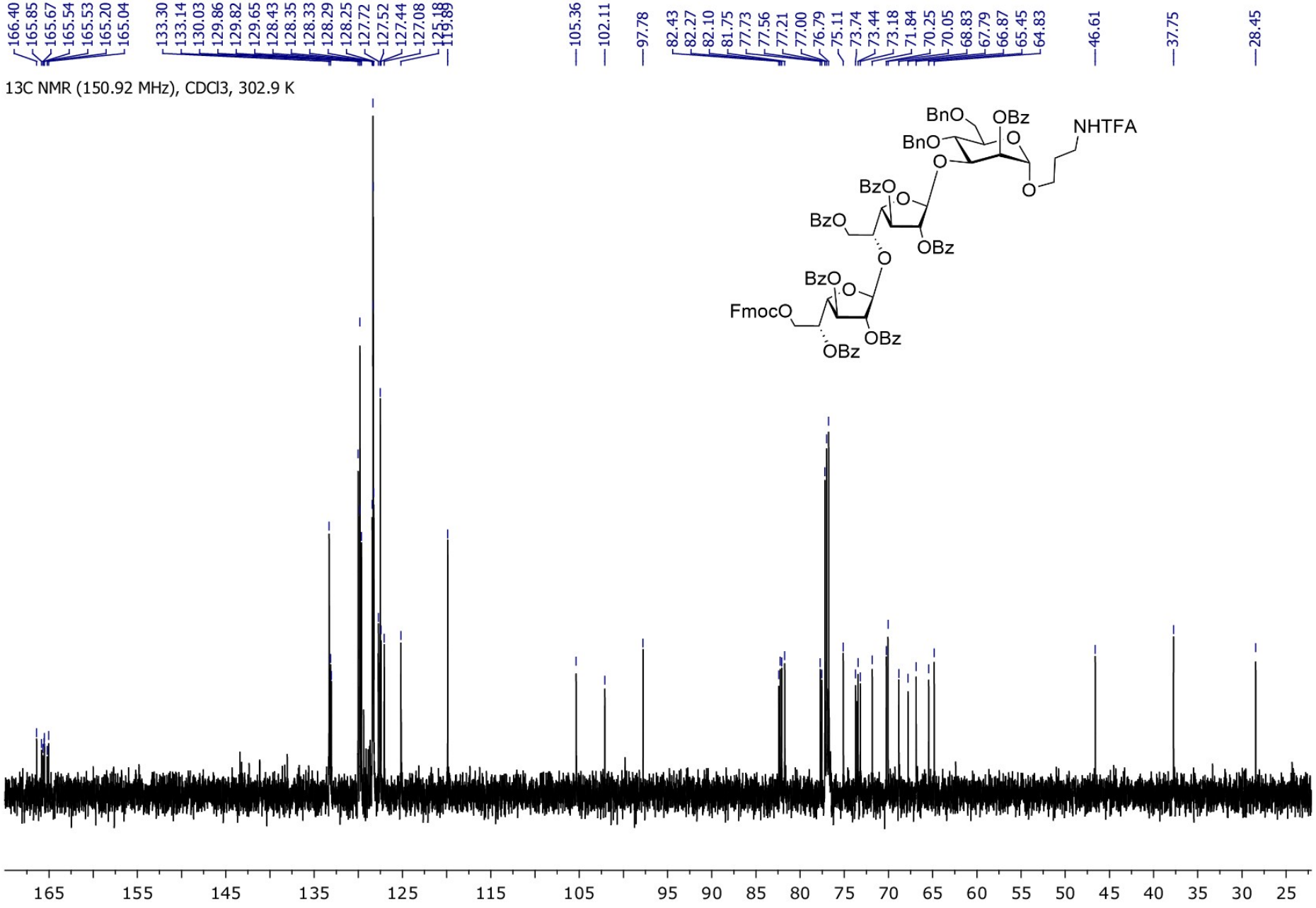
3-Aminopropyl β-D-galactofuranosyl-(1→3)-α-D-mannopyranoside 5



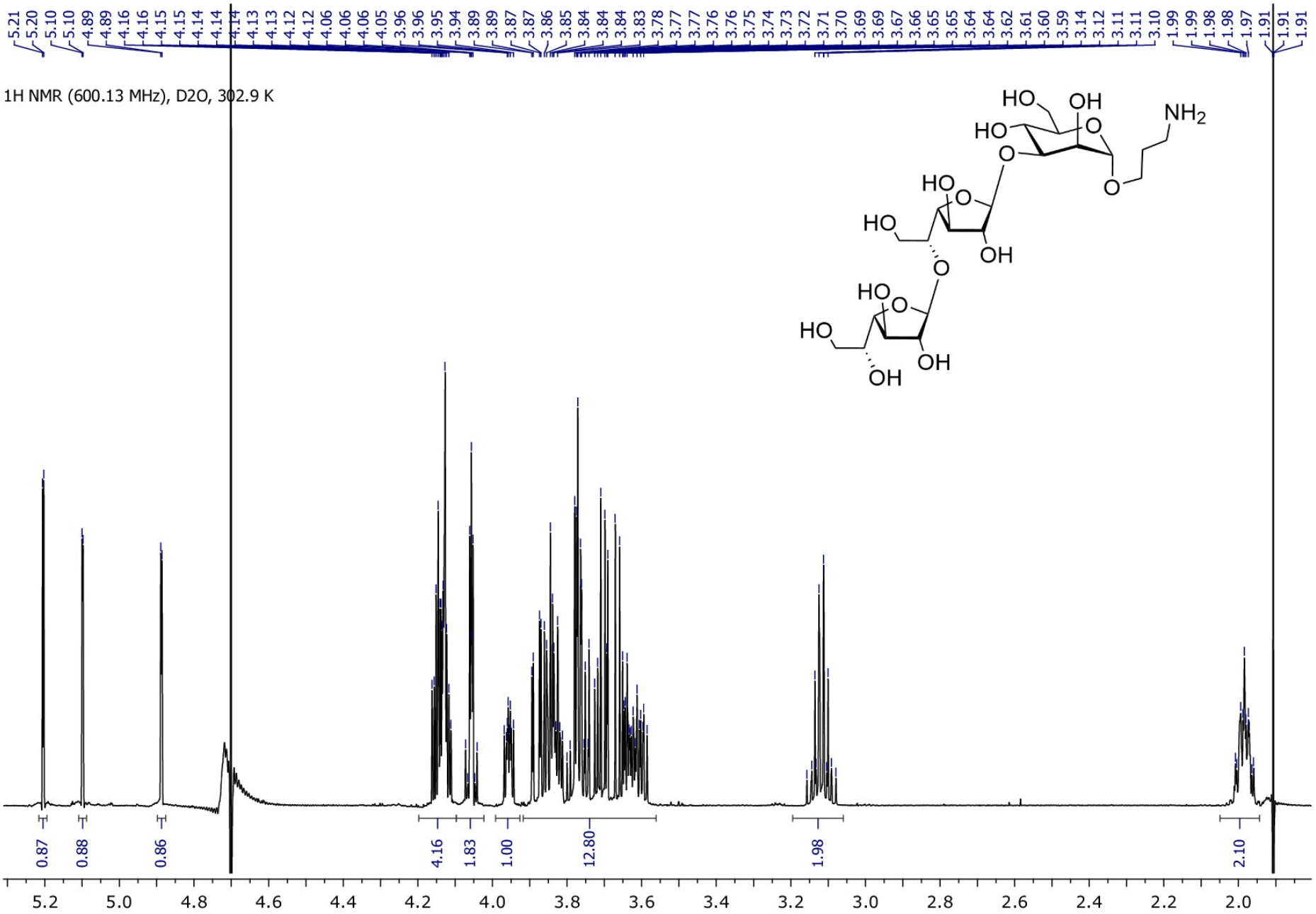

105.05
100.23
83.69
82.00
77.72
76.12
73.45
71.47
67.30
65.68
65.62
63.48
61.66
38.13
27.34
13C NMR (150.92 MHz), D2O, 303.2 K
HO
OH
NH2
HO
O
O
HO
O
HO
OH
OH
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25

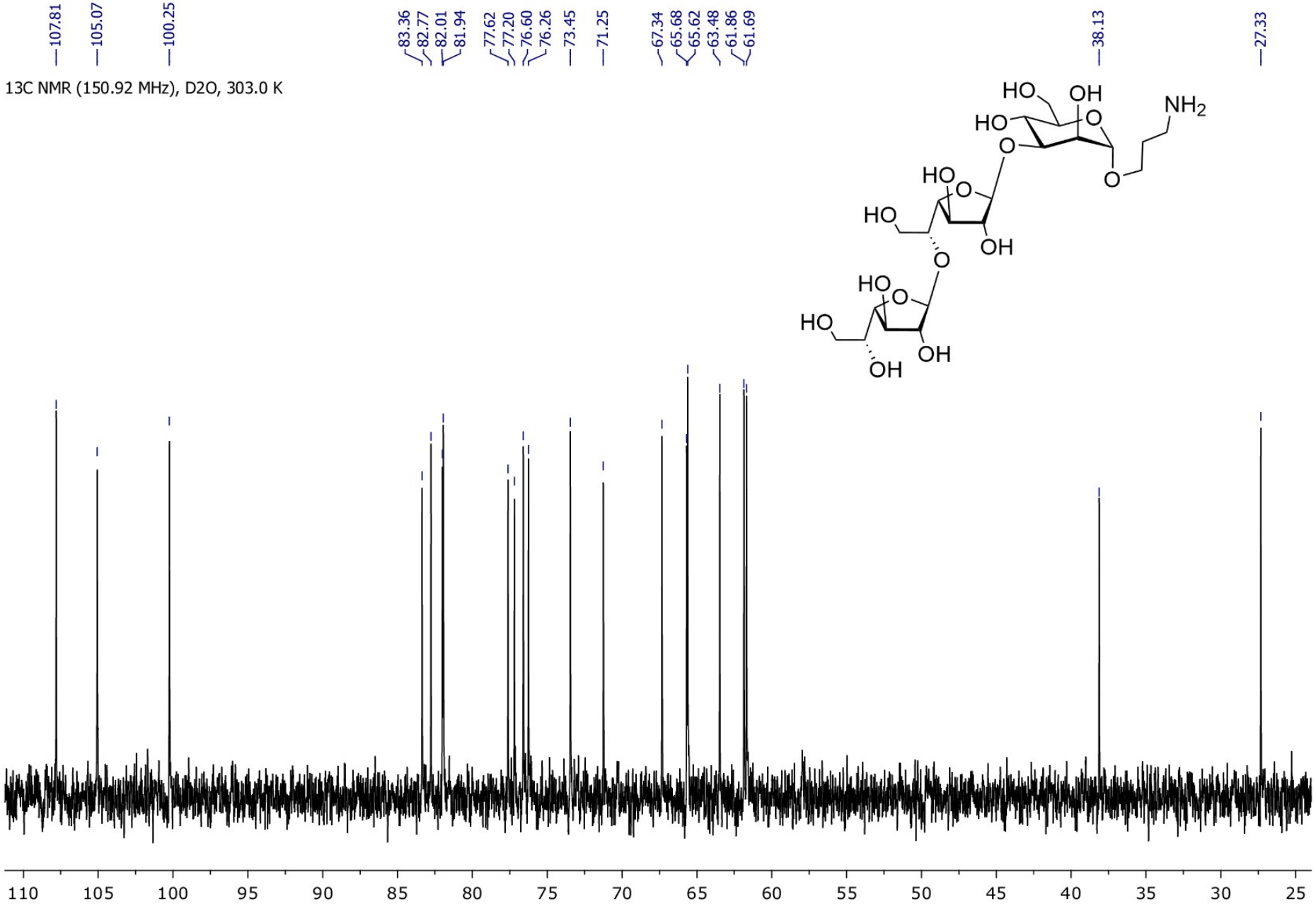
3-Trifluoroacetamidopropyl 2,3,5-tri-*O*-benzoyl-6-*O*-(9-fluorenylmethoxycarbonyl)-β-D-galactofuranosyl-(1→5)-2,3,6-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2-O-benzoyl-4,6-di-O-benzyl-α-D-mannopyranoside 29



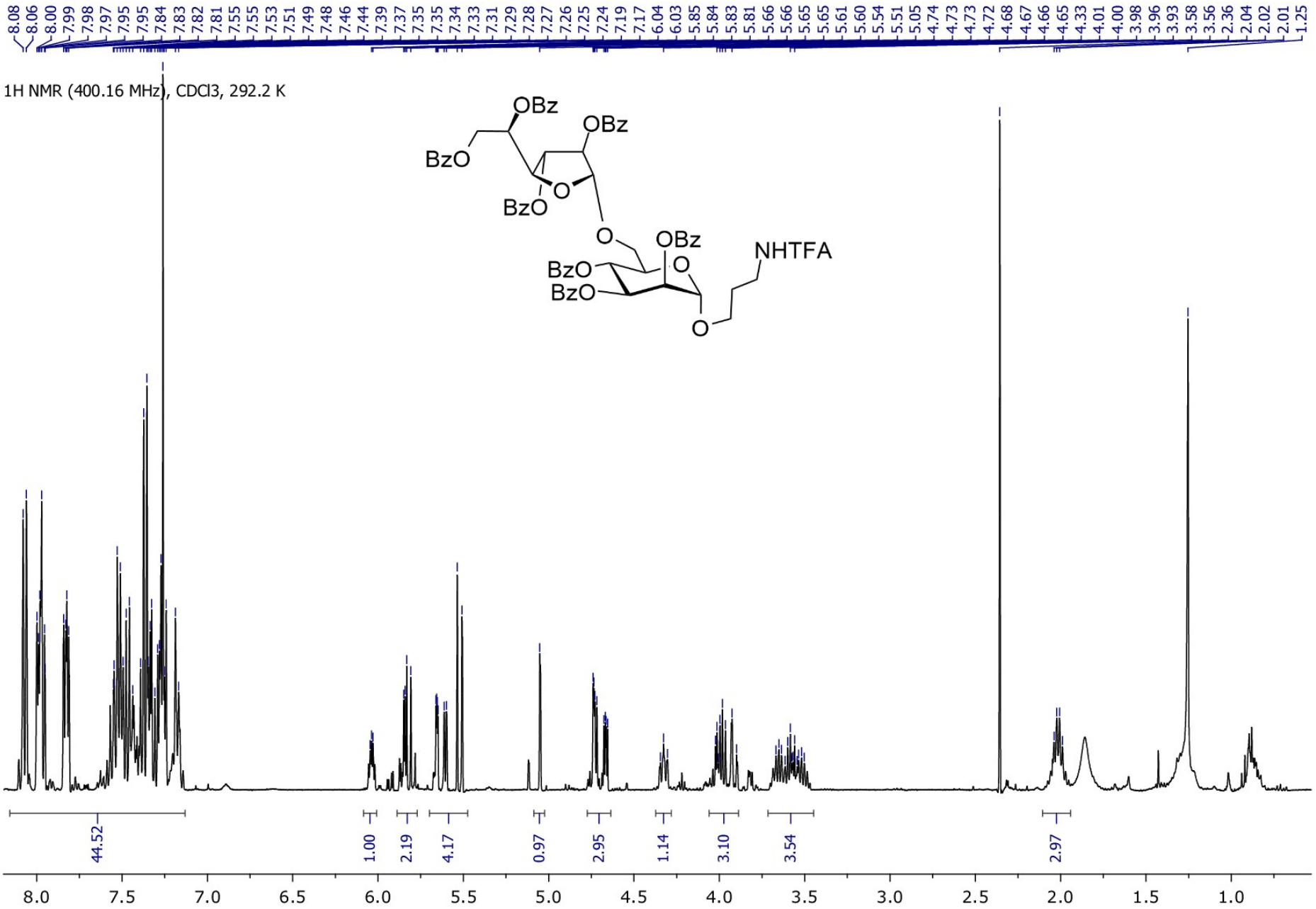

166.40
165.85
165.67
165.54
165.53
165.20
165.04
133.30
133.14
130.03
129.86
129.82
129.65
128.43
128.35
128.33
128.29
128.25
127.72
127.52
127.44
127.08
125.18
119.89
105.36
102.11
97.78
82.43
82.27
82.10
81.75
77.73
77.56
77.21
77.00
76.79
75.11
73.74
73.44
73.18
71.84
70.25
70.05
68.83
67.79
66.87
65.45
64.83
46.61
37.75
28.45
13C NMR (150.92 MHz), CDCl3, 302.9 K
BnO
OBz
NHTFA
BnO
O
O
BzO
O
BzO
OBz
O
BzO
O
FmocO
OBz
OBz
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25

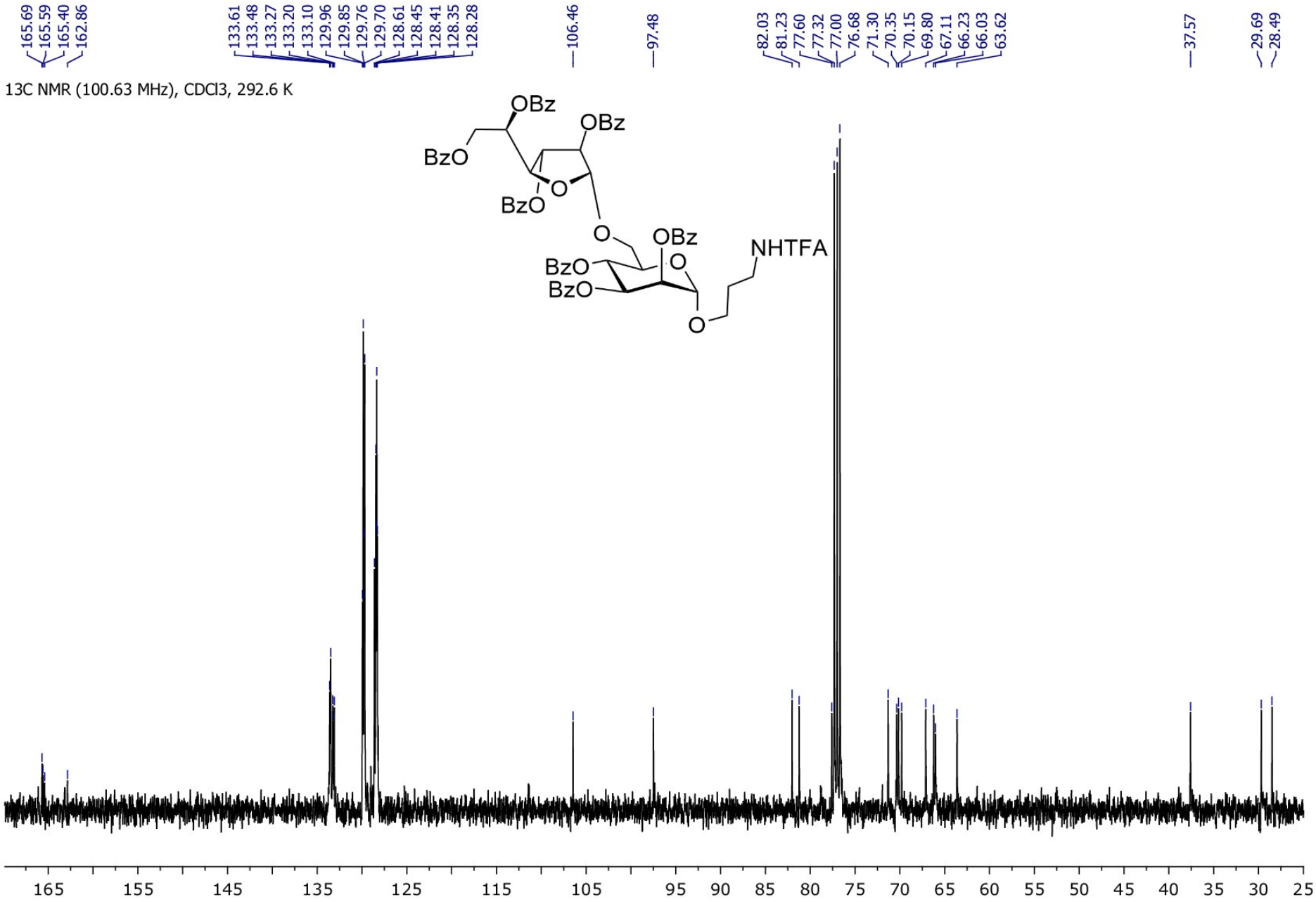
3-Aminopropyl β-D-galactofuranosyl-(1→5)-β-D-galactofuranosyl-(1→3)-α-D-mannopyranoside 6



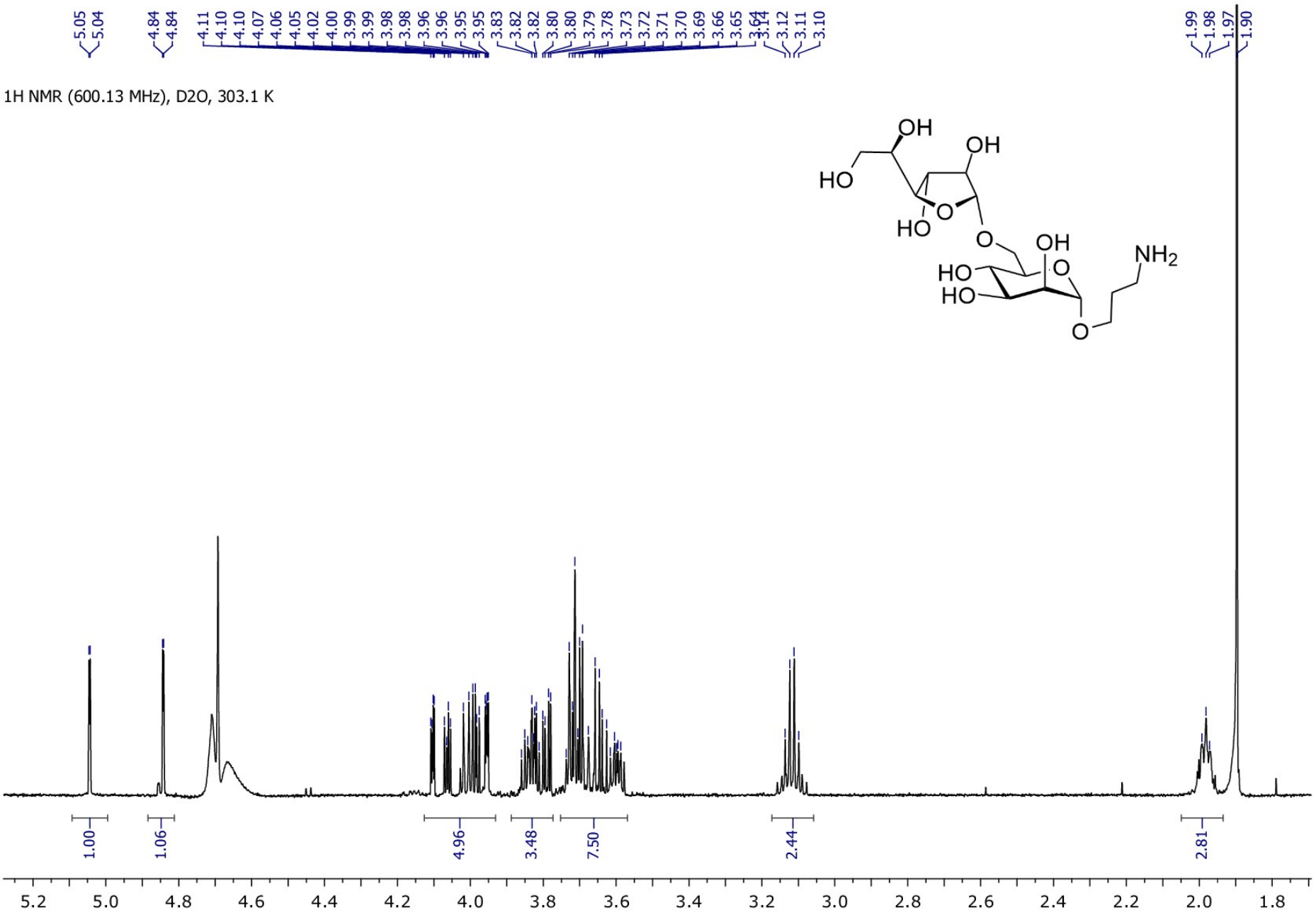

107.81
105.07
100.25
83.36
82.77
82.01
81.94
77.62
77.20
76.60
76.26
73.45
71.25
67.34
65.68
65.62
63.48
61.86
61.69
38.13
27.33
13C NMR (150.92 MHz), D2O, 303.0 K
HO
OH
NH2
O
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25

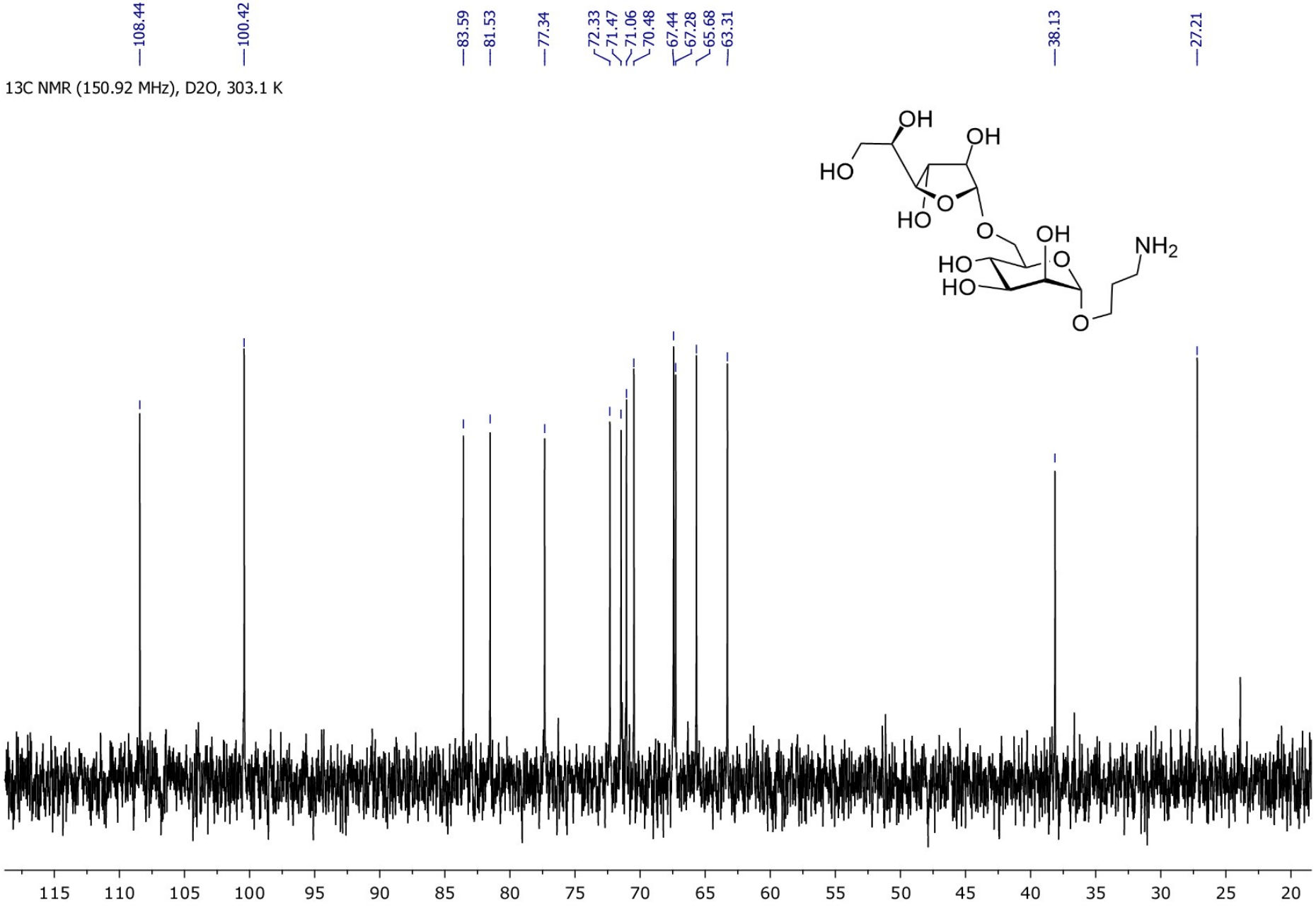
3-Trifluoroacetamidopropyl 2,3,5,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-O-benzoyl-α- d-mannopyranoside 31



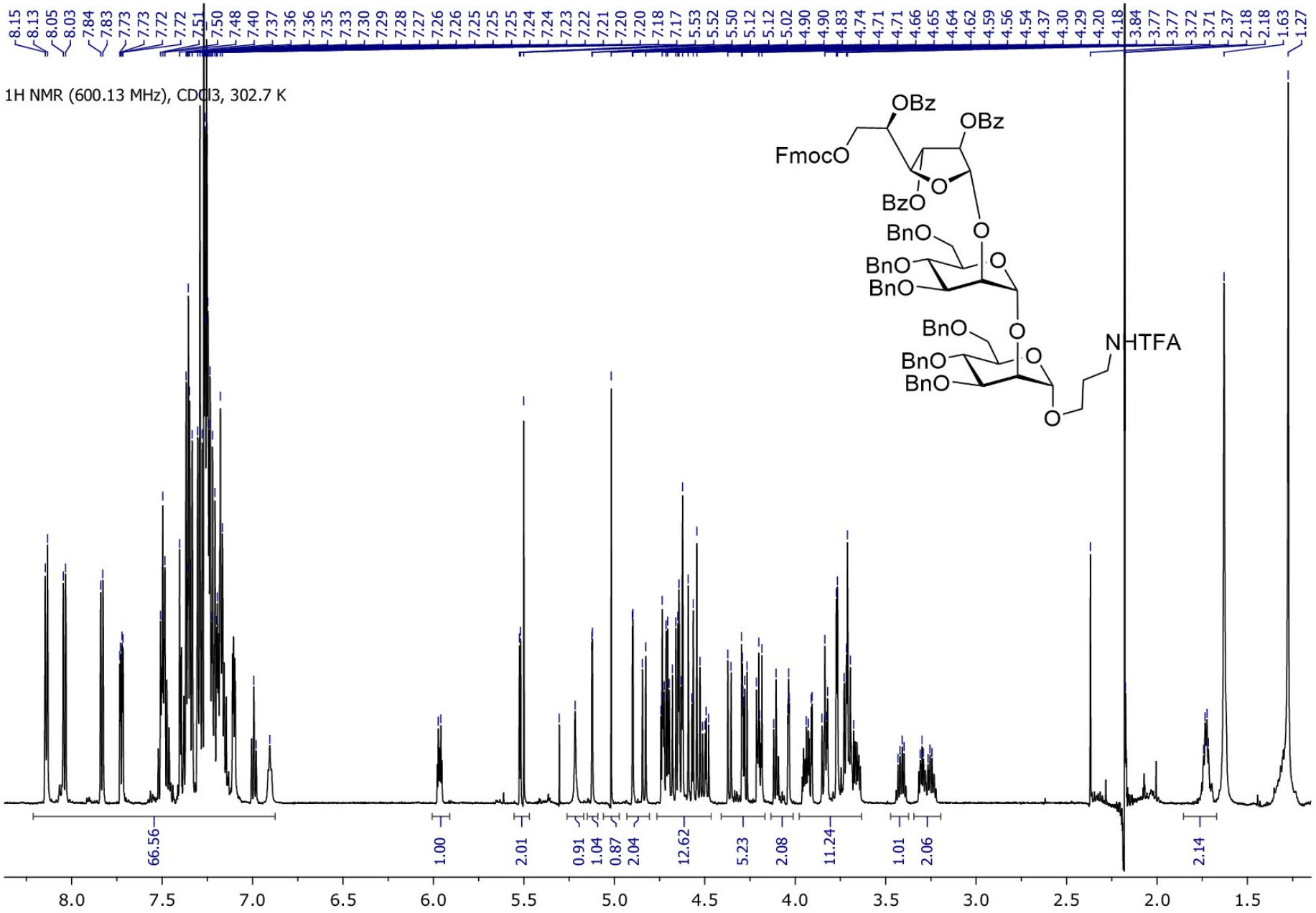

165.69
165.59
165.40
162.86
133.61
133.48
133.27
133.20
133.10
129.96
129.85
129.76
129.70
128.61
128.45
128.41
128.35
128.28
106.46
97.48
82.03
81.23
77.60
77.32
77.00
76.68
71.30
70.35
70.15
69.80
67.11
66.23
66.03
63.62
37.57
29.69
28.49
13C NMR (100.63 MHz), CDCl3, 292.6 K
OBz
OBz
BzO
BzO
O
O
OBz
BzO
BzO
O
NHTFA
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25

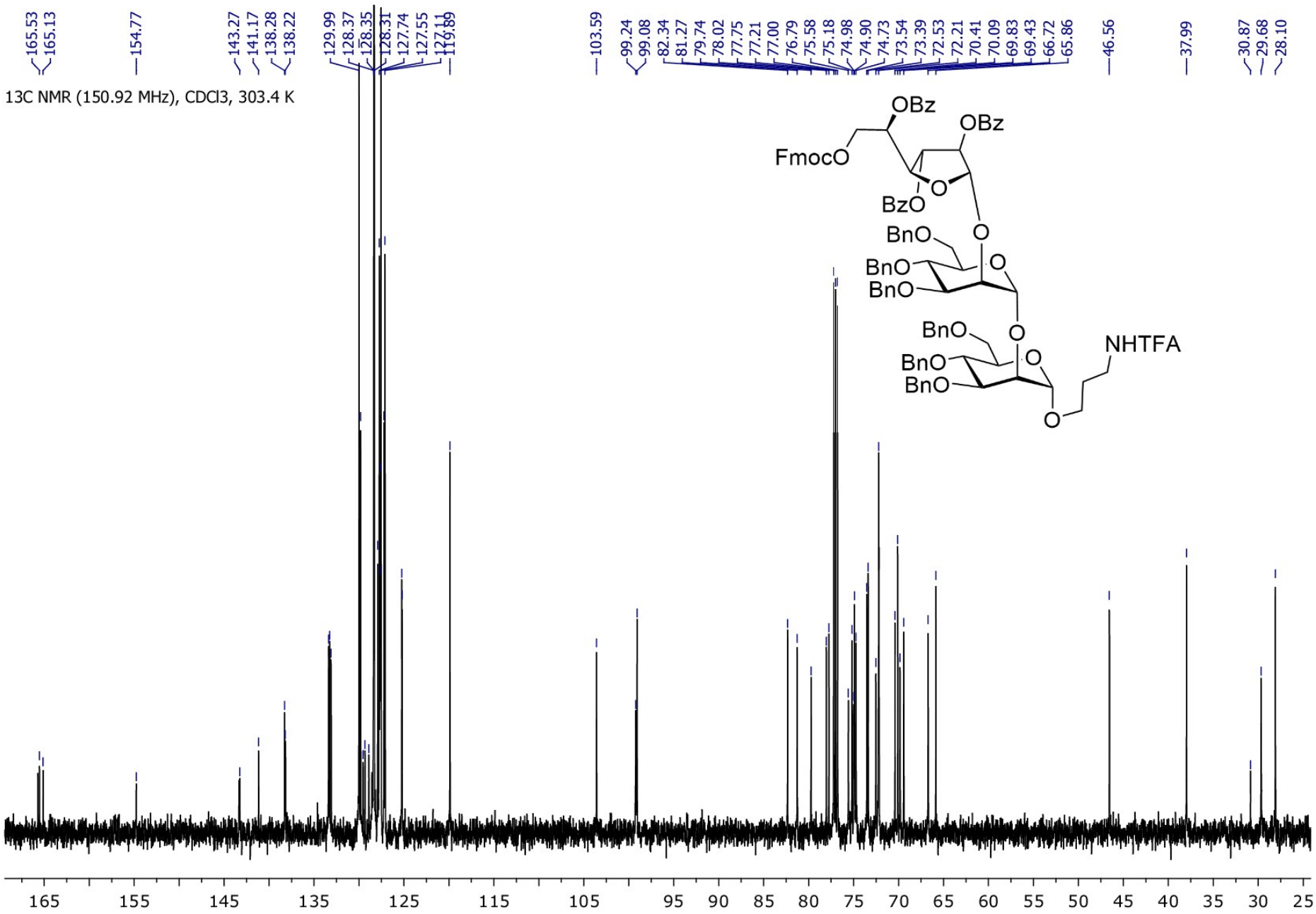
3-Aminopropyl β-D-galactofuranosyl-(1→6)-α-D-mannopyranoside 8



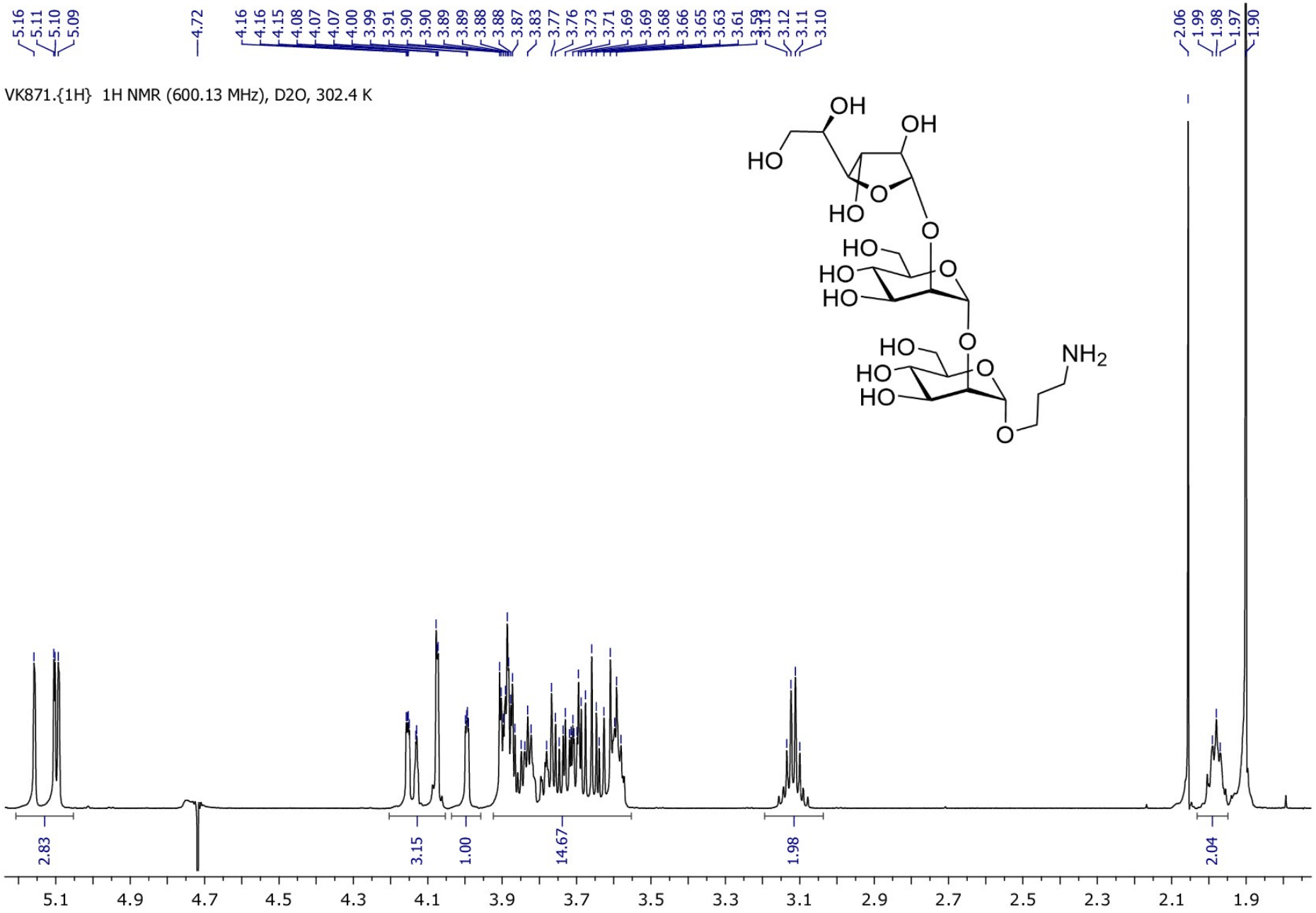

108.44
100.42
83.59
81.53
77.34
72.33
71.47
71.06
70.48
67.44
67.28
65.68
63.31
38.13
27.21
13C NMR (150.92 MHz), D2O, 303.1 K
OH
OH
HO
HO
O
O
OH
HO
HO
O
NH2
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20

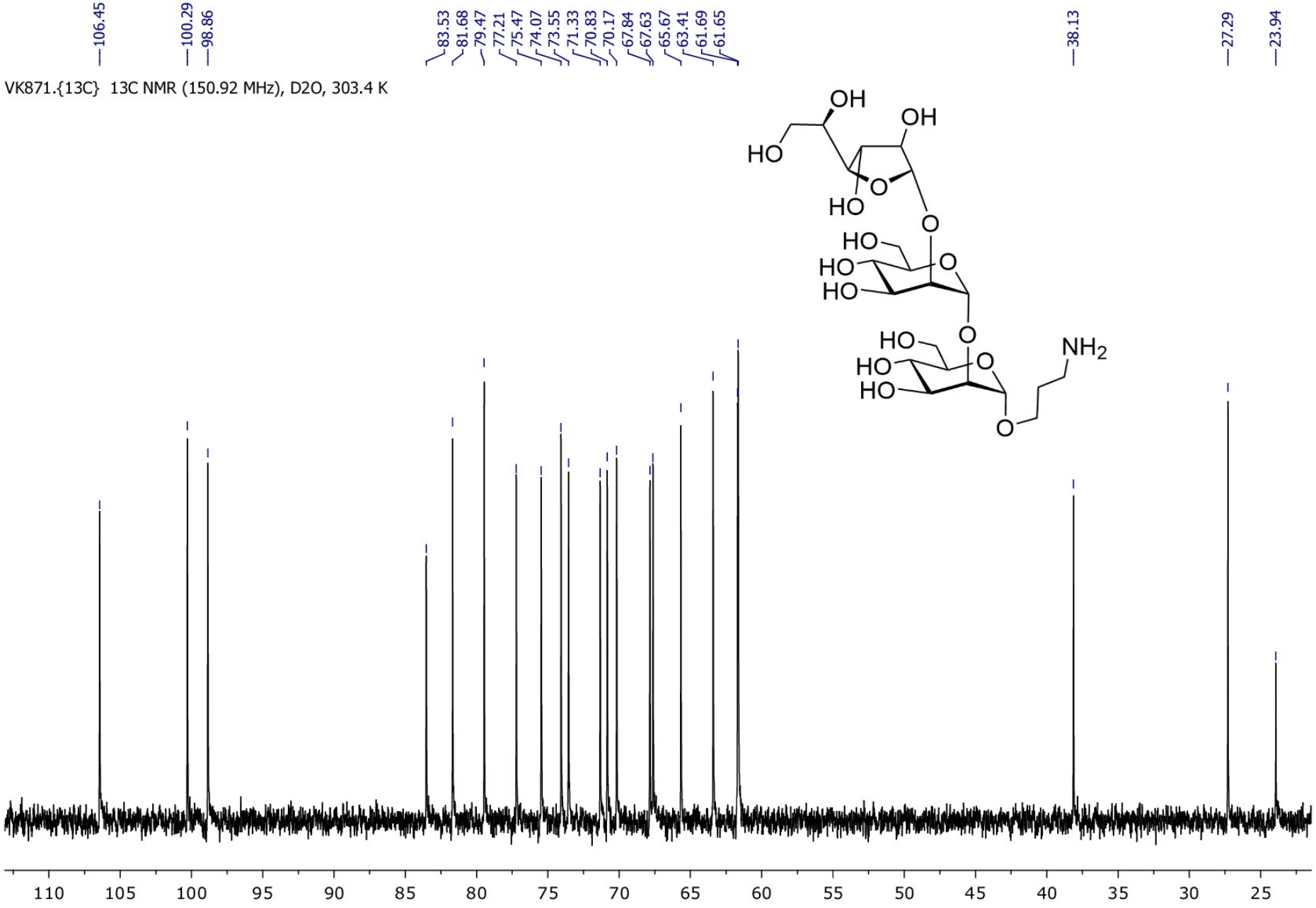
3-Trifluoroacetamidopropyl 2,3,5-tri-*O*-benzoyl-6-*O*-(9-fluorenylmethoxycarbonyl)-β-D-galactofuranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 33




165.53
165.13
154.77
143.27
141.17
138.28
138.22
129.99
128.37
128.35
128.31
127.74
127.55
103.59
99.24
99.08
82.34
81.27
79.74
78.02
77.75
77.21
77.00
76.79
75.58
75.18
74.98
74.90
74.73
73.54
73.39
72.53
72.21
70.41
70.09
69.83
69.43
66.72
65.86
46.56
37.99
30.87
29.68
28.10
13C NMR (150.92 MHz), CDCl3, 303.4 K
OBz
OBz
FmocO
BzO
BnO
BnO
BnO
BnO
BnO
BnO
NHTFA
165
155
145
135
125
115
105
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25

3-Aminopropyl β-D-galactofuranosyl-(1→2)-α-D-mannopyranosyl-(1→2)-α-D-mannopyranoside 13




106.45
100.29
98.86
83.53
81.68
79.47
77.21
75.47
74.07
73.55
71.33
70.83
70.17
67.84
67.63
65.67
63.41
61.69
61.65
38.13
27.29
23.94
VK871.{13C} 13C NMR (150.92 MHz), D2O, 303.4 K
OH
OH
HO
HO
O
HO
HO
HO
O
O
HO
HO
HO
O
NH2
O
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25