Electronic Supplementary Material (ESI) for RSC Advances.

Oligosaccharide Synthesis on Soluble High-Molecular Weight Polymer pHEMA Using a Photo-Cleavable Linker

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Supplementary Information

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Percentage loading calculations:

Polymer bound monosaccharide **7** (20 mg) was dissolved in 0.8 mL of $CDCl_3$ containing 1% TMS V/V. The TMS peak was integrated as 1 proton at chemical shift value 0.0 and remaining saccharide peaks were integrated accordingly.

The ratio between analyte and internal standard:

$r_{A/IS}$ = (0.007/1) / (1/12) = 0.084

The sample contains 5.2 mg of TMS:

n_{IS} = 5.2 / 88 = 0.059 mmol.

$n_A = n_{IS} * r_{A/IS}$ = 0.005 mmol / 20 mg of polymer = 0.25 mmol/g of polymer.

Figure S1. ^{1}H NMR of pHEMA bound monosaccharide

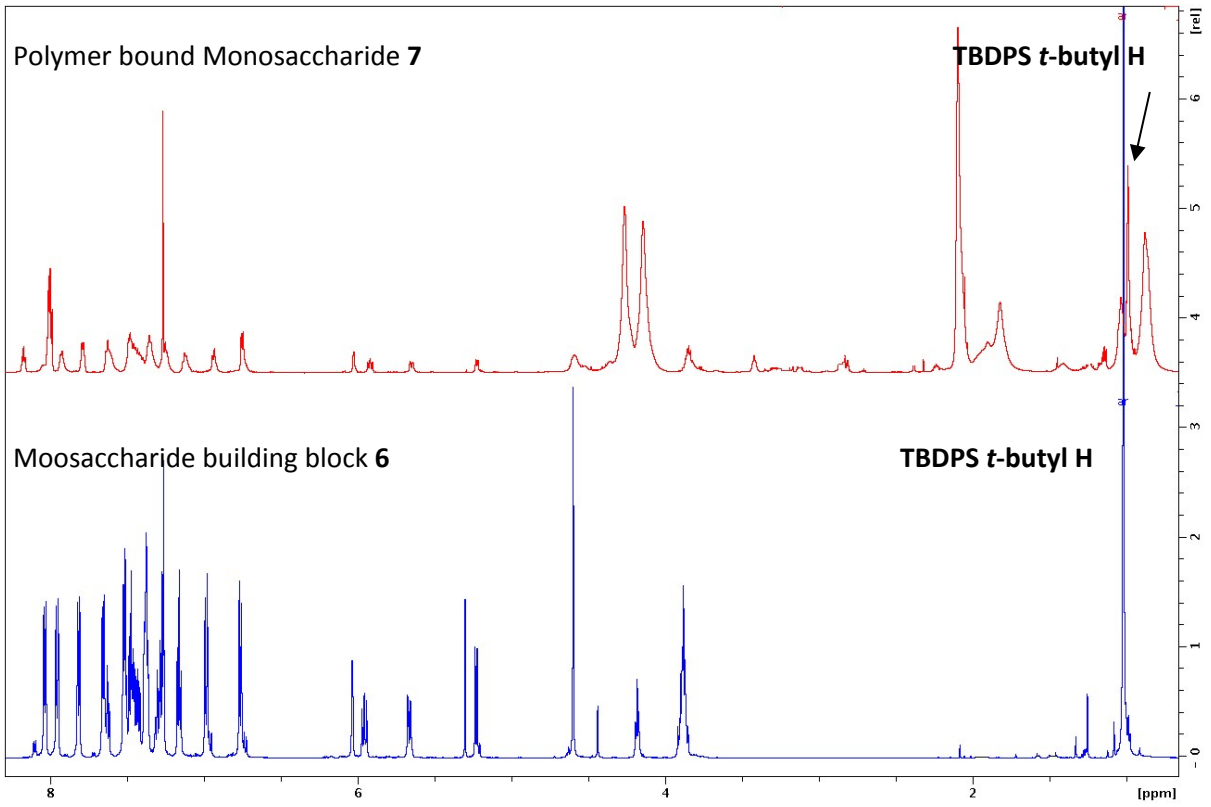
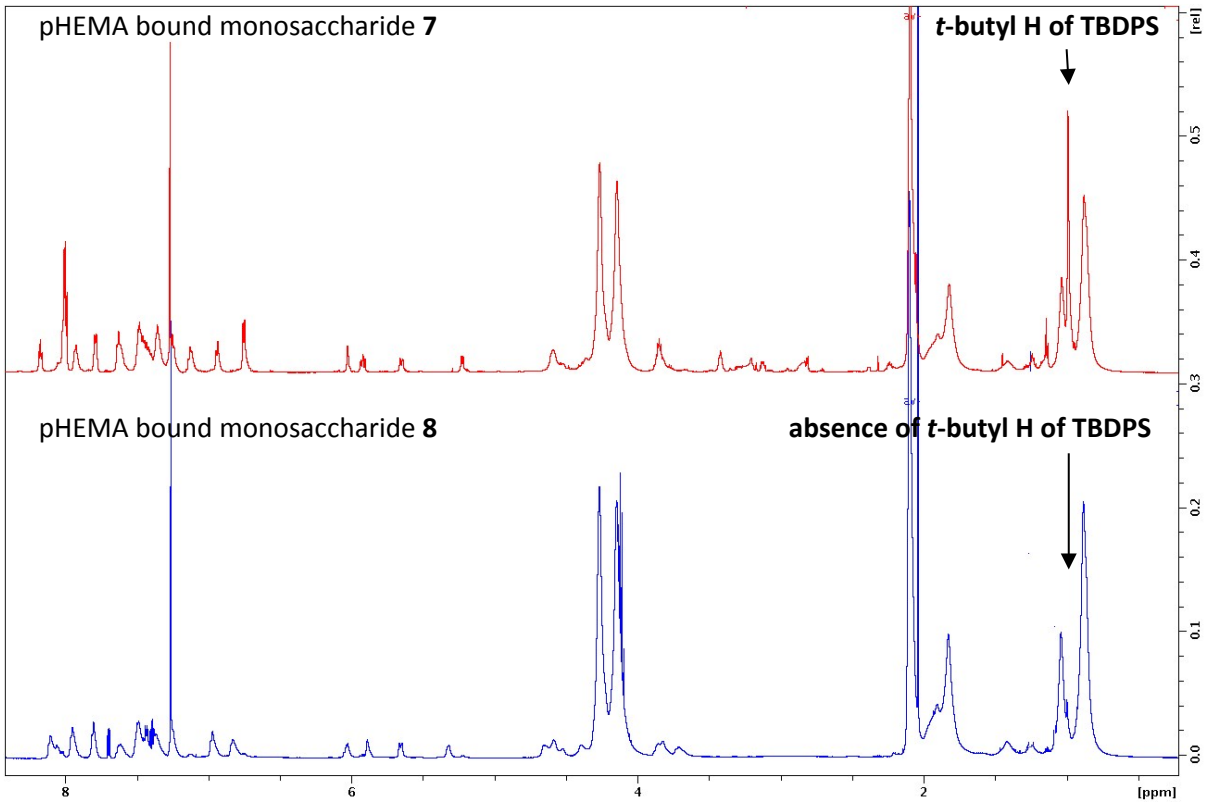


Figure S2. ^{1}H NMR of pHEMA bound oligosaccharide **7** and **8** (TBDPS de-protection)



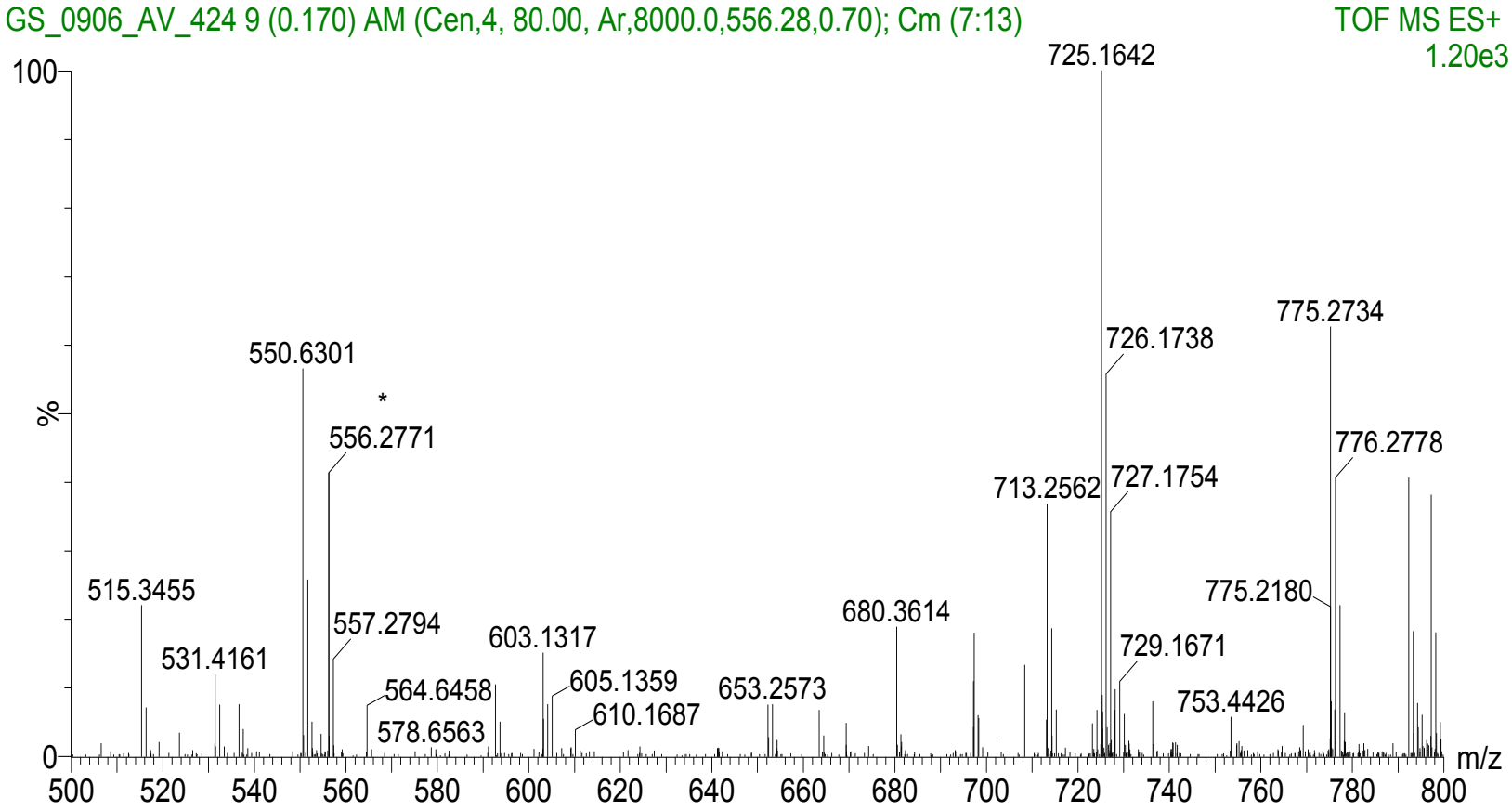
Polymer percentage recovery comparison between pHEMA and Boltron H40

To compare pHEMA recovery with other polymer support, we decided to use hyper branched Boltron H40 polymer for model tri-galactoside synthesis. Both polymers were recovered using precipitation method. The average recovery of pHEMA over 2 cycles of de-protections and glycosylations was 91% compared to 64% of Boltron H40.

Polymer bound product	pHEMA Recovery (%)	Boltron H40 Recovery (%)
Loading and Capping **7**	80	58
1st De-protection **8**	94	71
Glycosylation **9**	90	55
2nd De-protection **10**	92	64
Glycosylation **11**	89	65

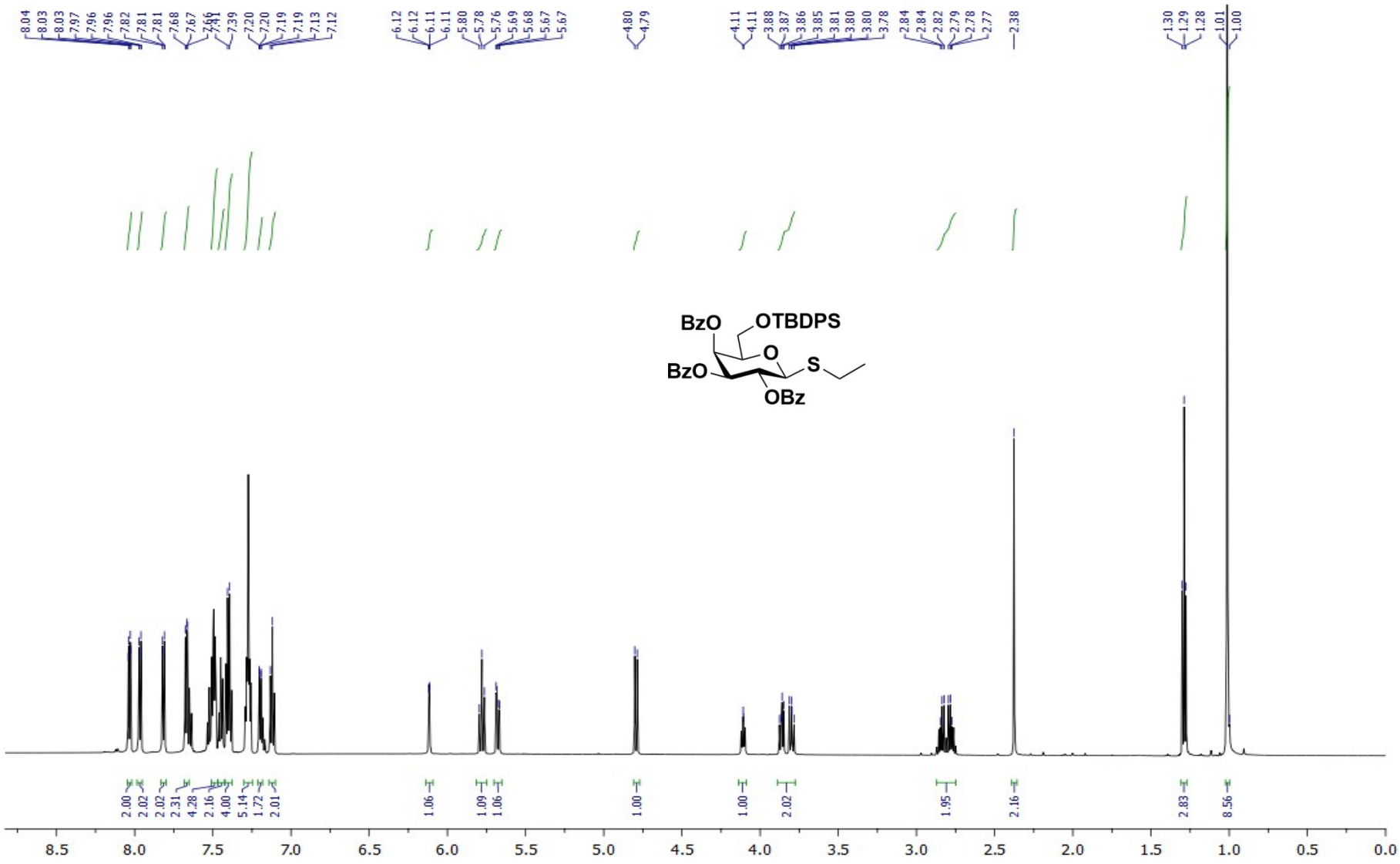
Table S1. Percentage recovery comparison between pHEMA and Boltron H40 using Precipitation method.

HRMS data of ethyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl 1-thio-*β*-D-galactopyranoside (A)

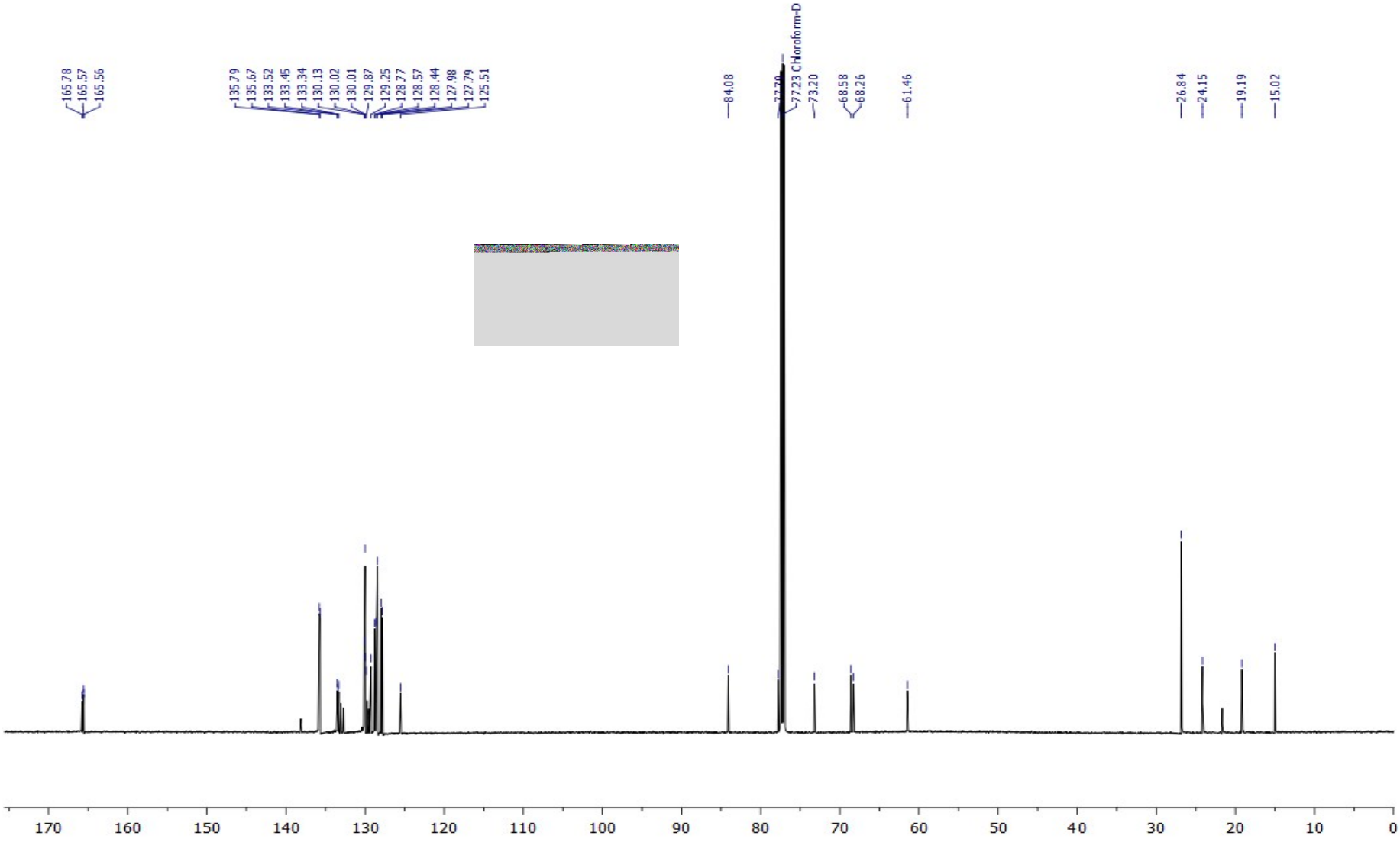


Mass accuracy = ((775.2761-775.2734)/ 775.2761)* 106 = 3.5 ppm

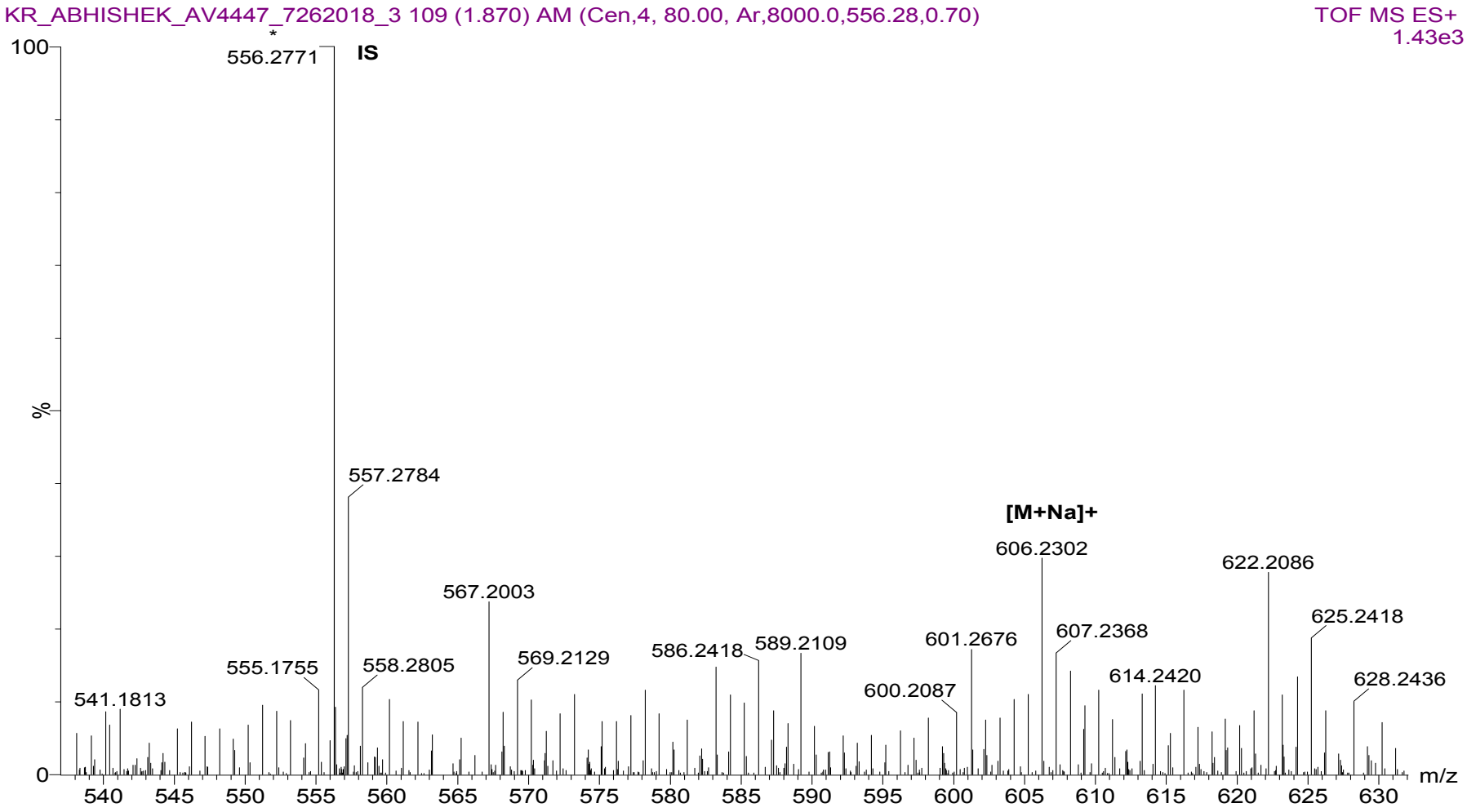
^{1}H NMR of ethyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl 1-thio-*β*-D-galactopyranoside (A)



^{13}C NMR of Ethyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl 1-thio-*β*-D-galactopyranoside (A)

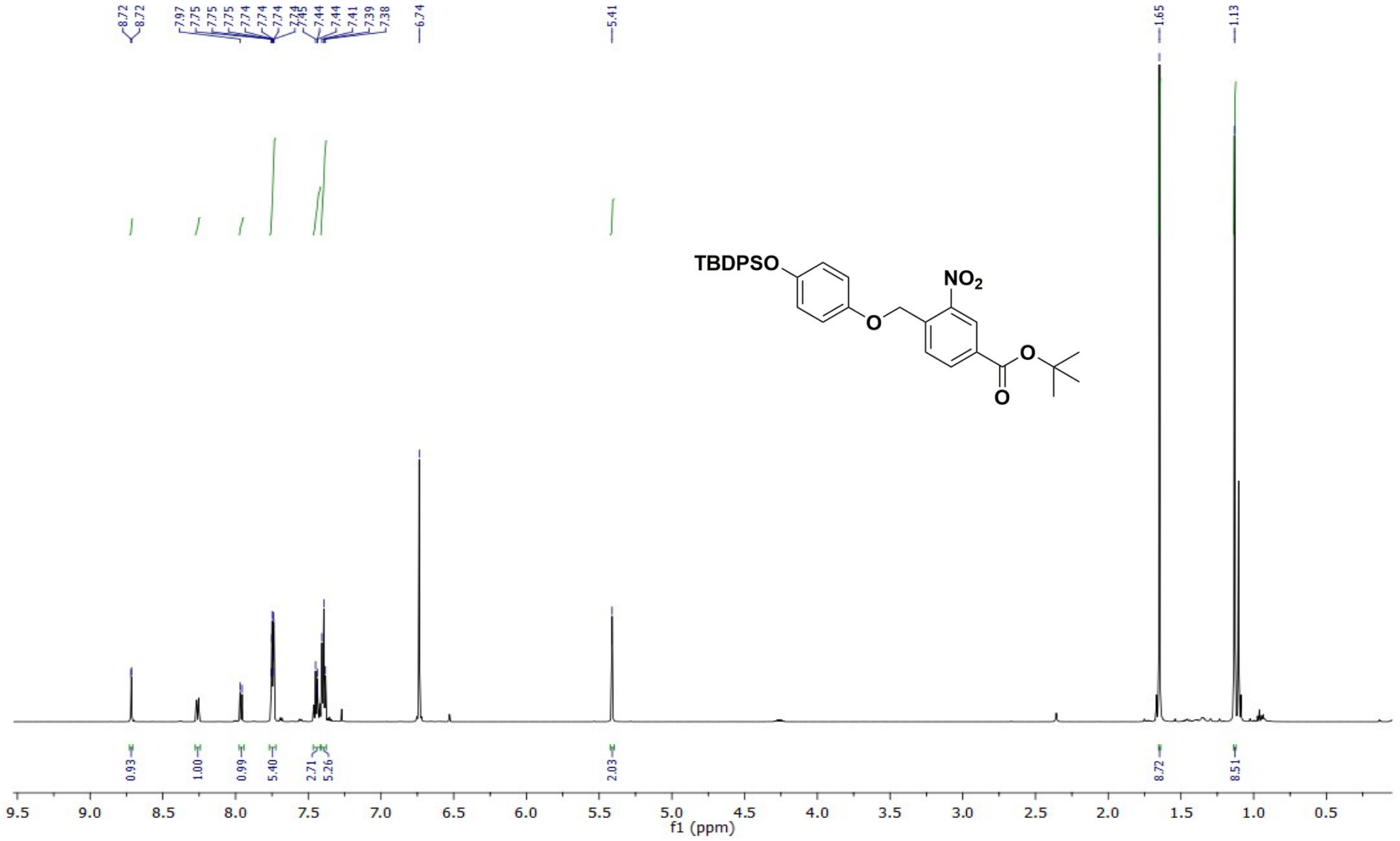


HRMS data of *t*-butyl 4-((4-((*t*-butyldiphenylsilyl)oxy)phenoxy)methyl)-3-nitrobenzoate (3)

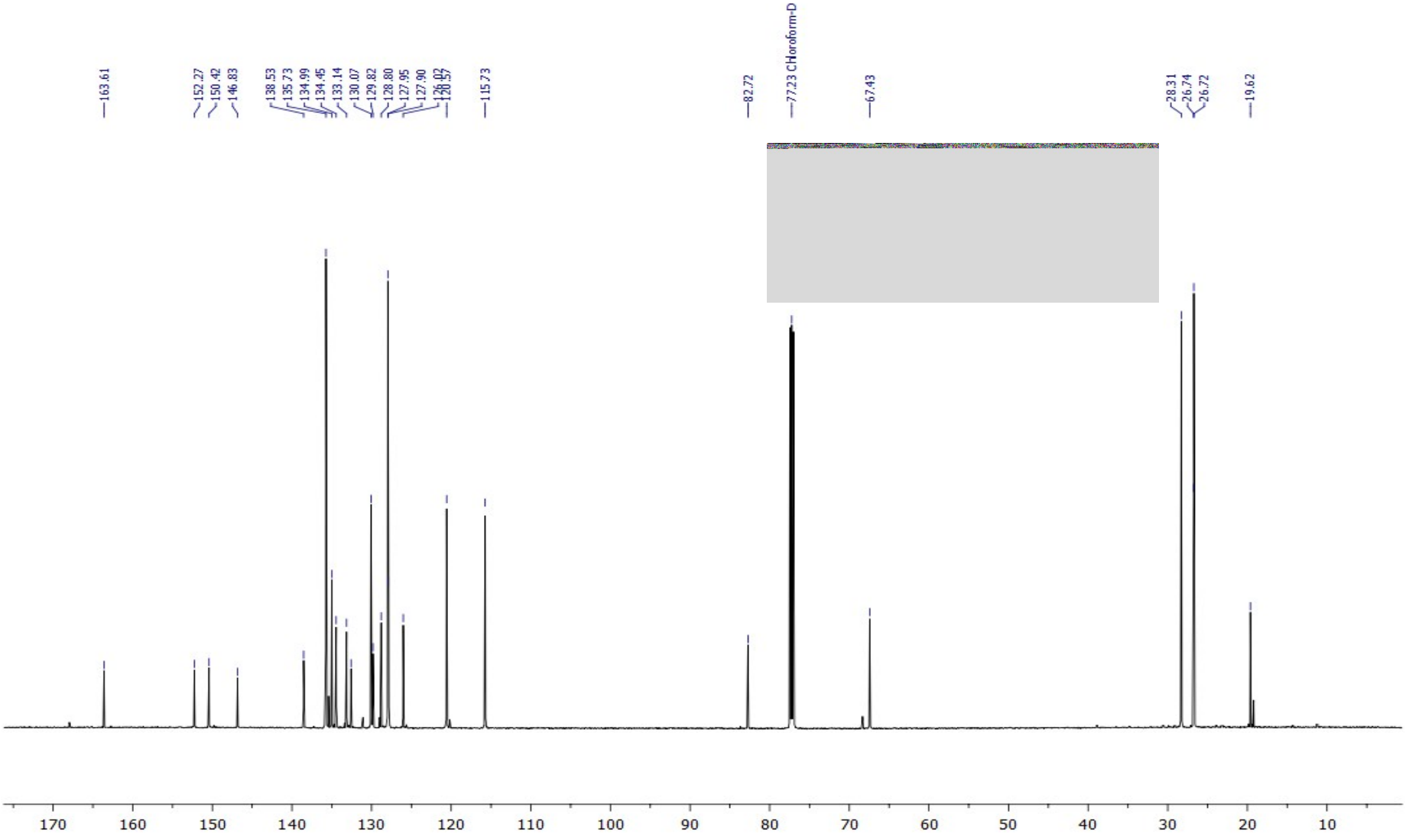


Mass accuracy = ((606.2288-606.2302)/606.2288)* 106 = 2.3 ppm

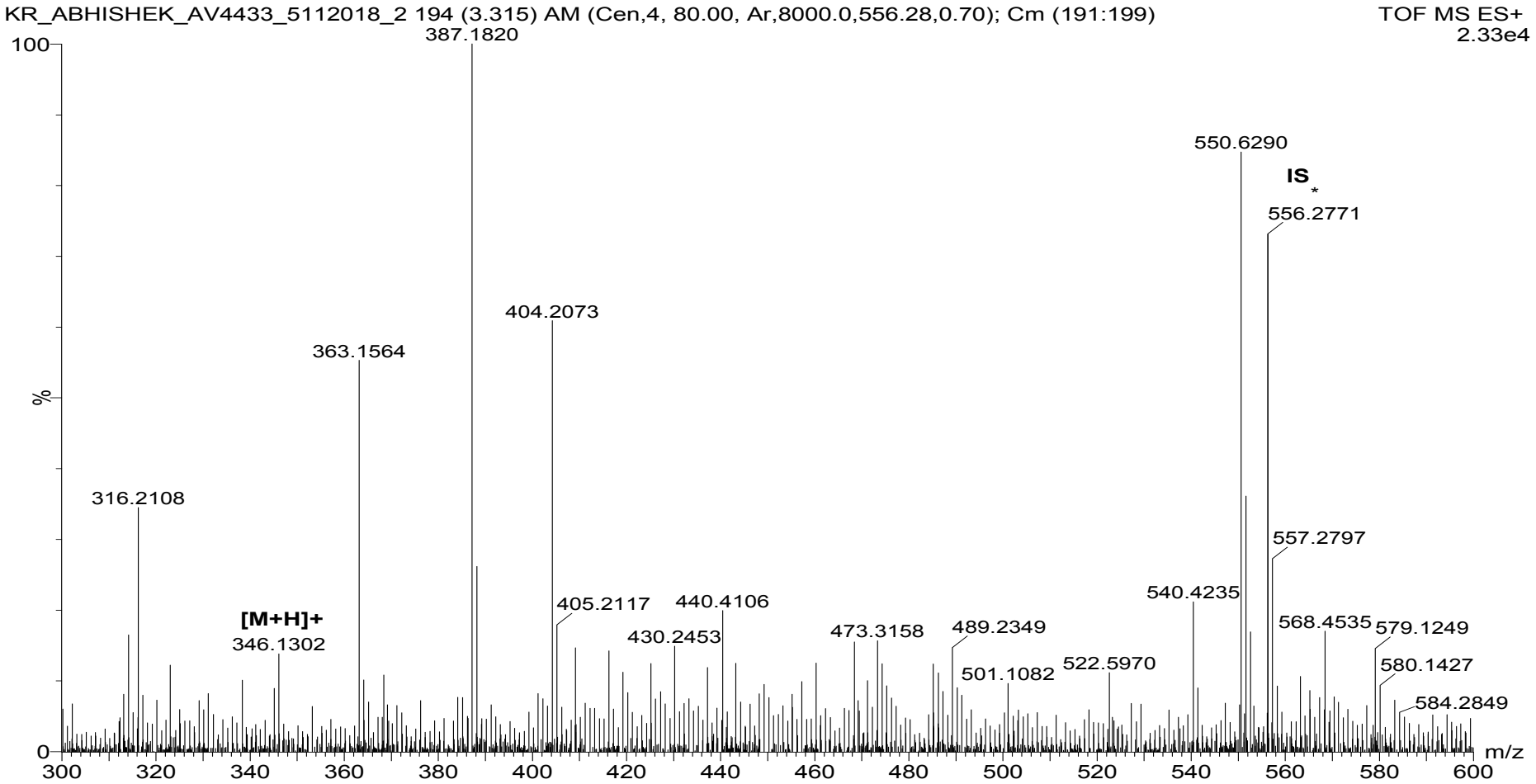
^{1}H NMR of *t*-butyl 4-((4-((*t*-butyldiphenylsilyl)oxy)phenoxy)methyl)-3-nitrobenzoate (3)



^{13}C NMR of *t*-butyl 4-((4-((*t*-butyldiphenylsilyl)oxy)phenoxy)methyl)-3-nitrobenzoate (3)



HRMS data of *t*-butyl 4-((4-hydroxyphenoxy)methyl)-3-nitrobenzoate (4)



Mass accuracy = ((346.1291-346.1302)/346.1291)* 106 = 3.2 ppm

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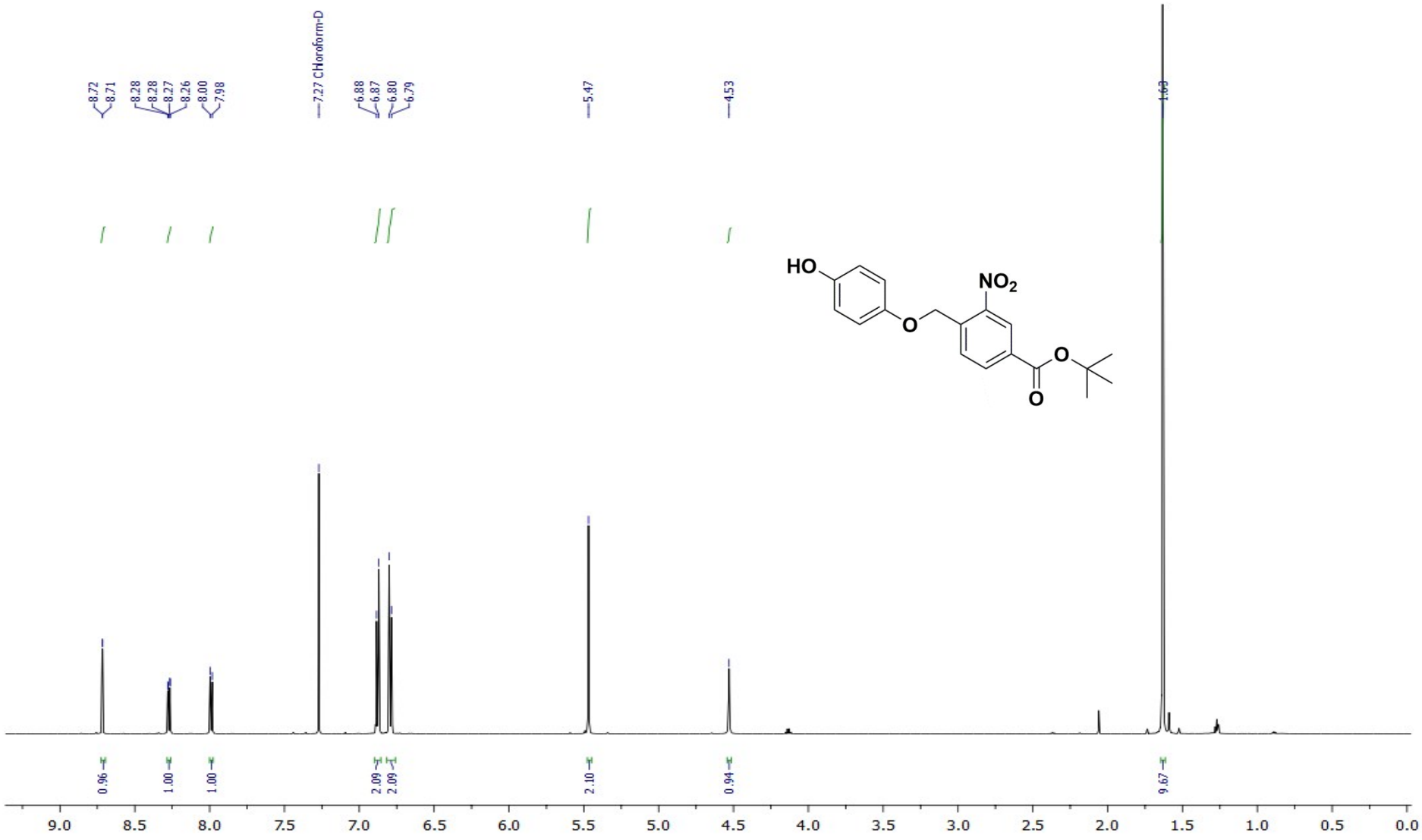
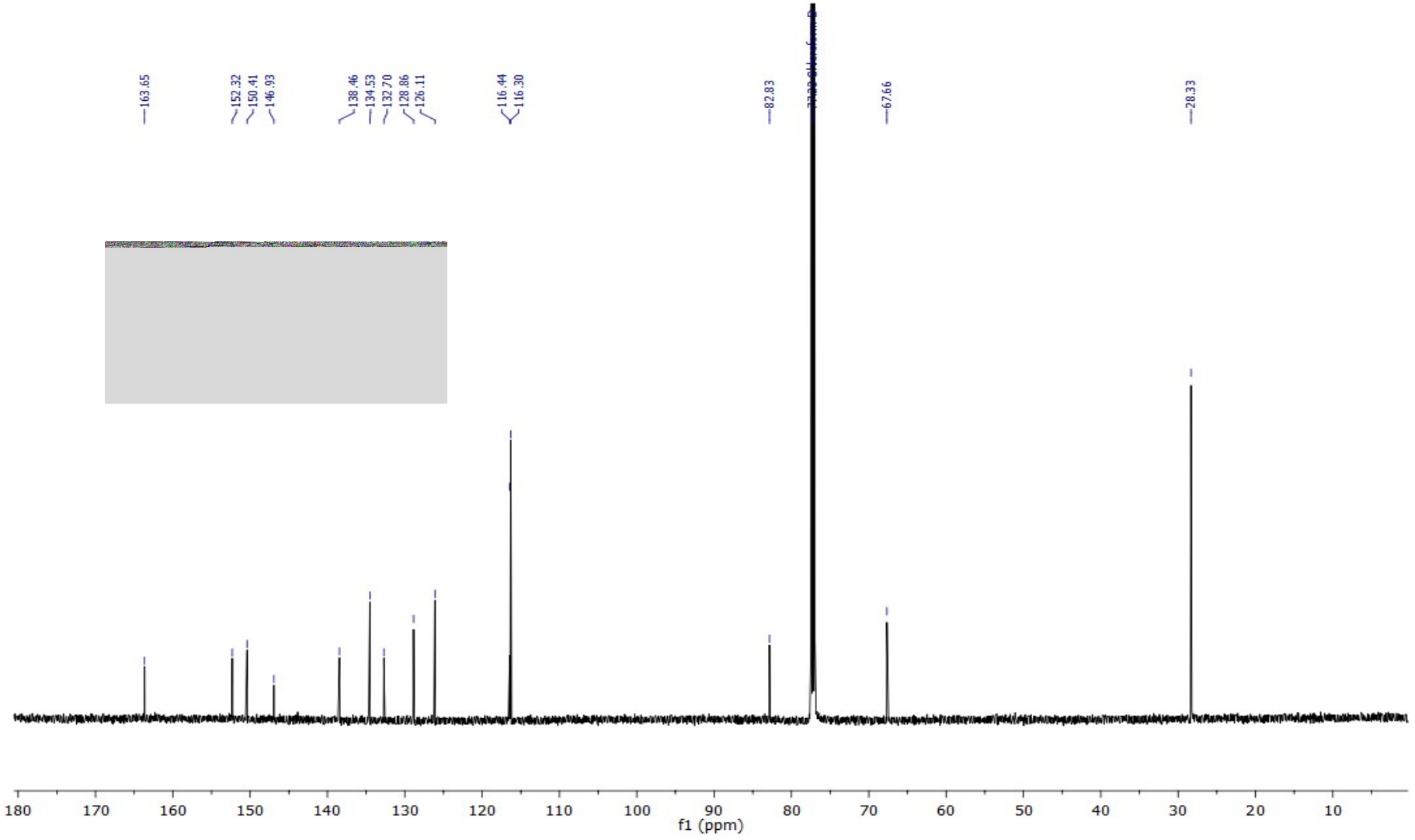
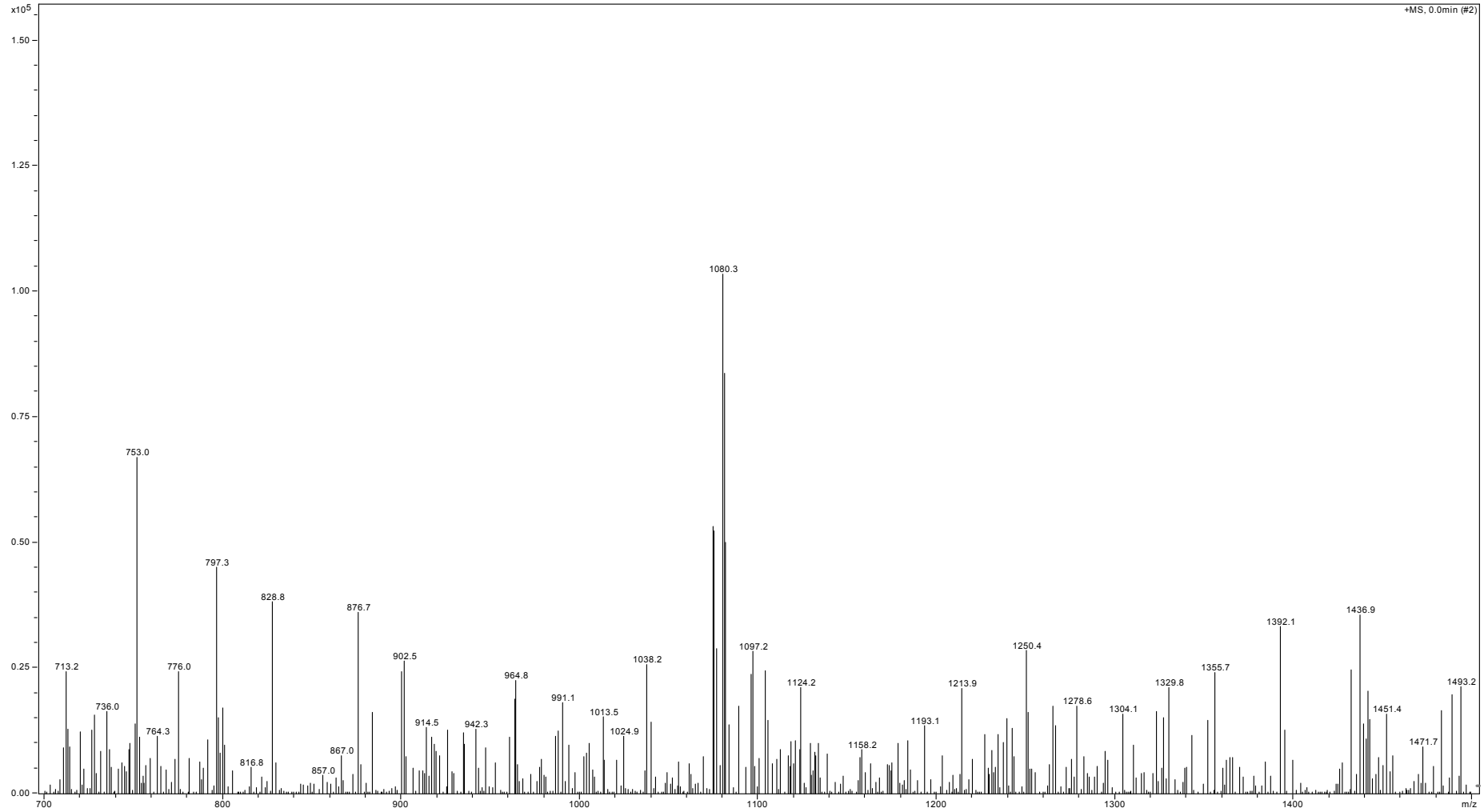


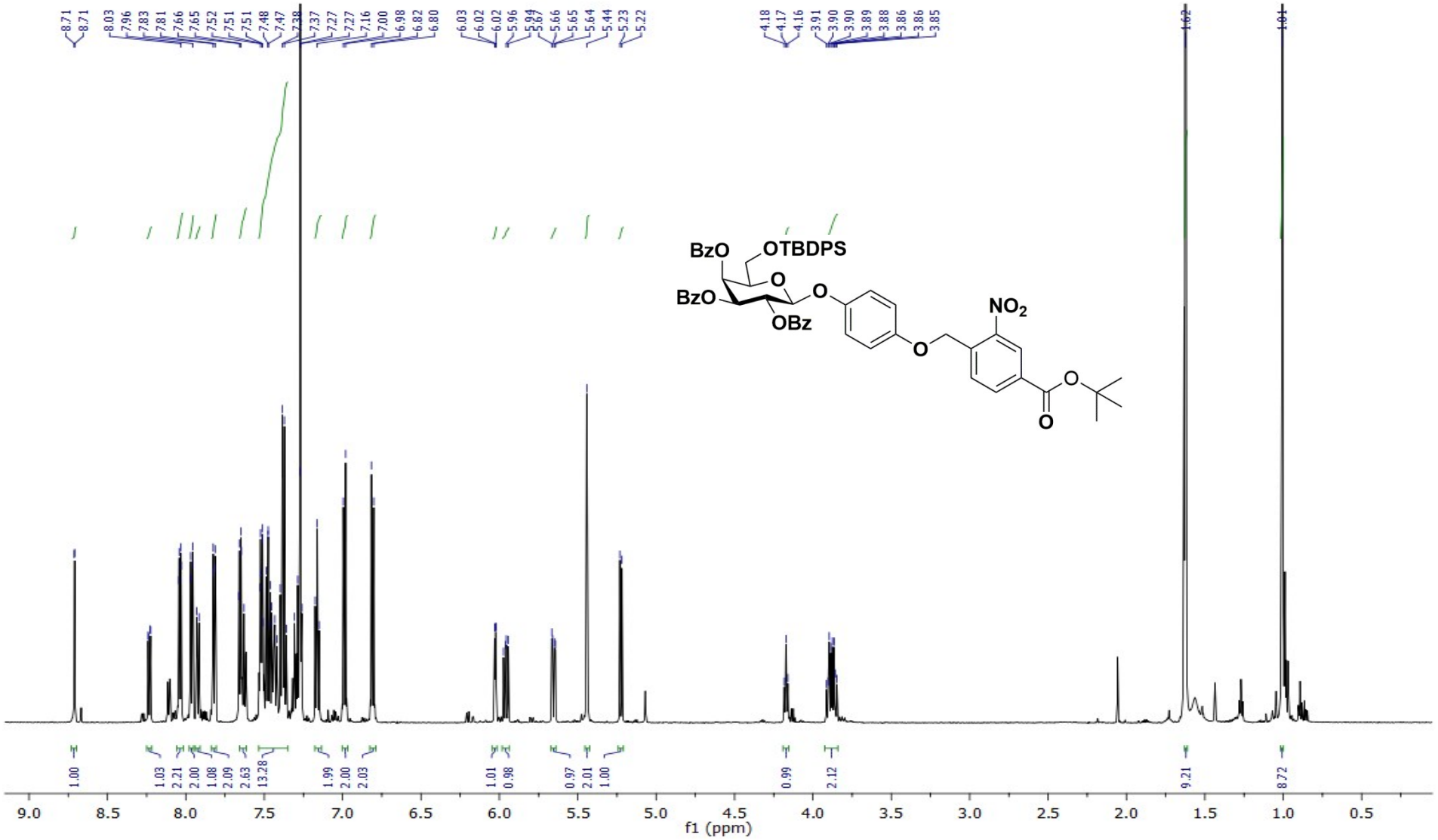
^{13}C NMR of *t*-butyl 4-((4-hydroxyphenoxy)methyl)-3-nitrobenzoate (4)



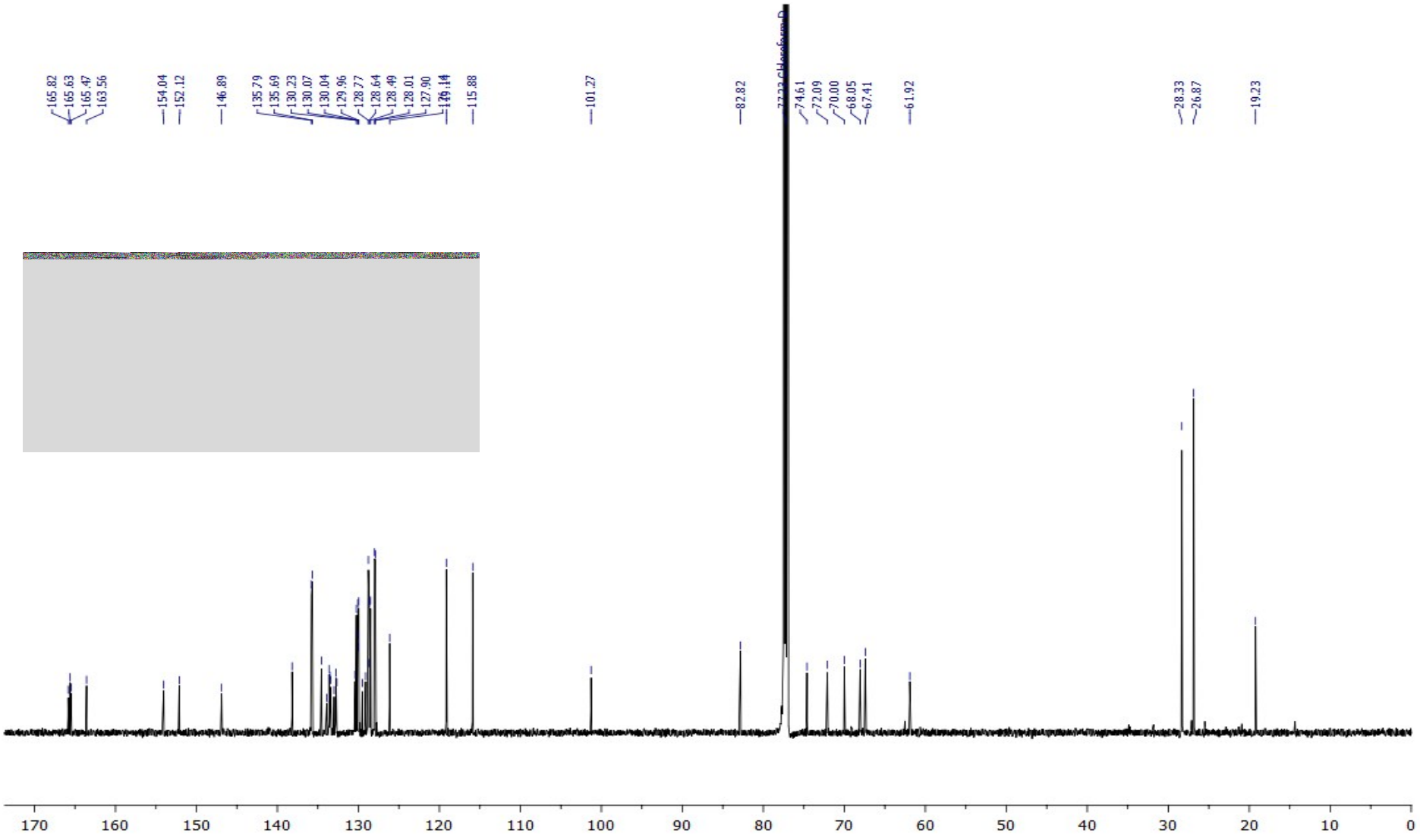
ESI-MS data of **4-((4-(*t*-butoxycarbonyl)-2-nitrobenzyl)oxy)phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl *β*-D-galactopyranoside (5)**



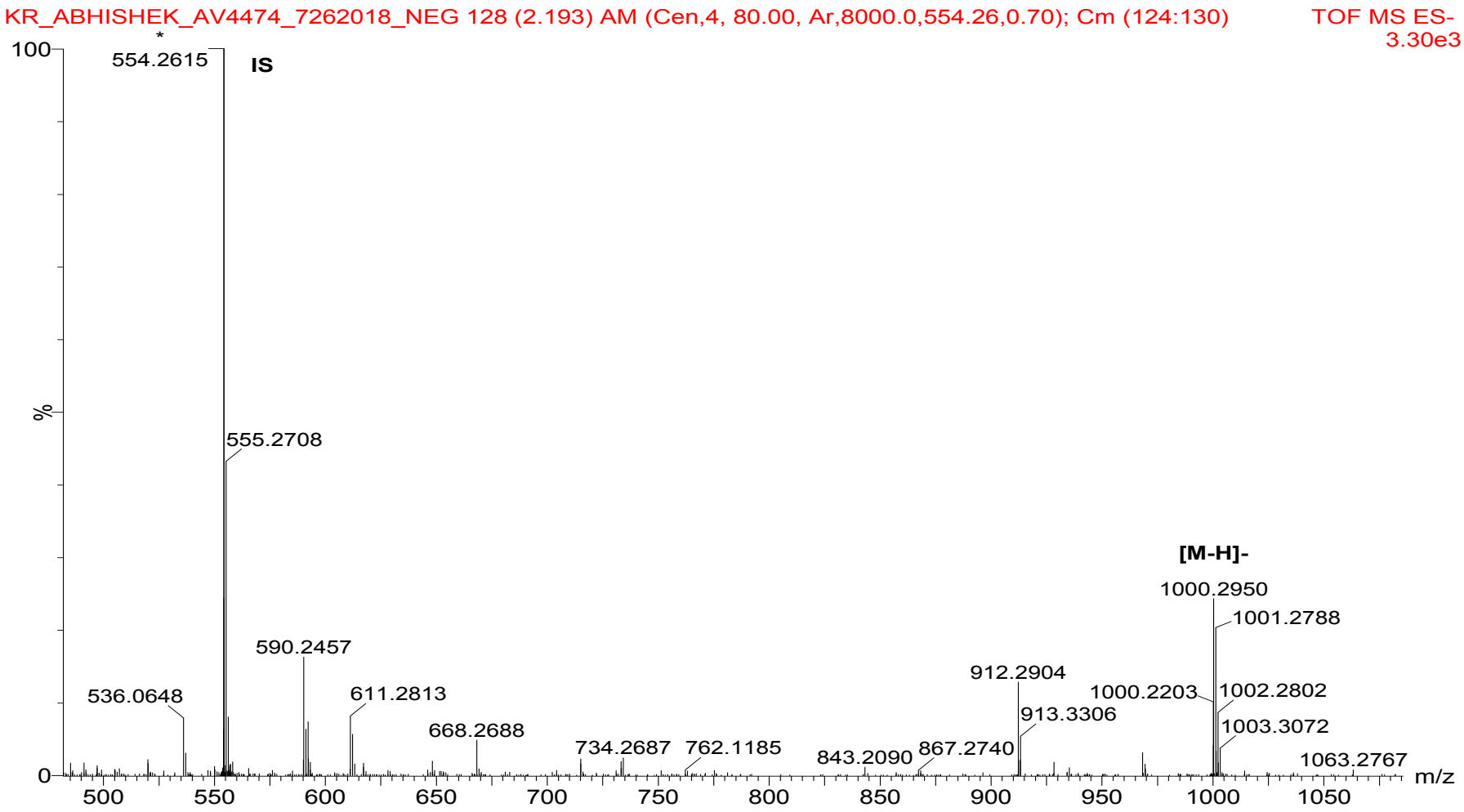
^{1}H NMR of 4-((4-(*t*-butoxycarbonyl)-2-nitrobenzyl)oxy)phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl *β*-D-galactopyranoside (5)



^{13}C NMR of 4-((4-(*t*-butoxycarbonyl)-2-nitrobenzyl)oxy)phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl *β*-D-galactopyranoside (5)

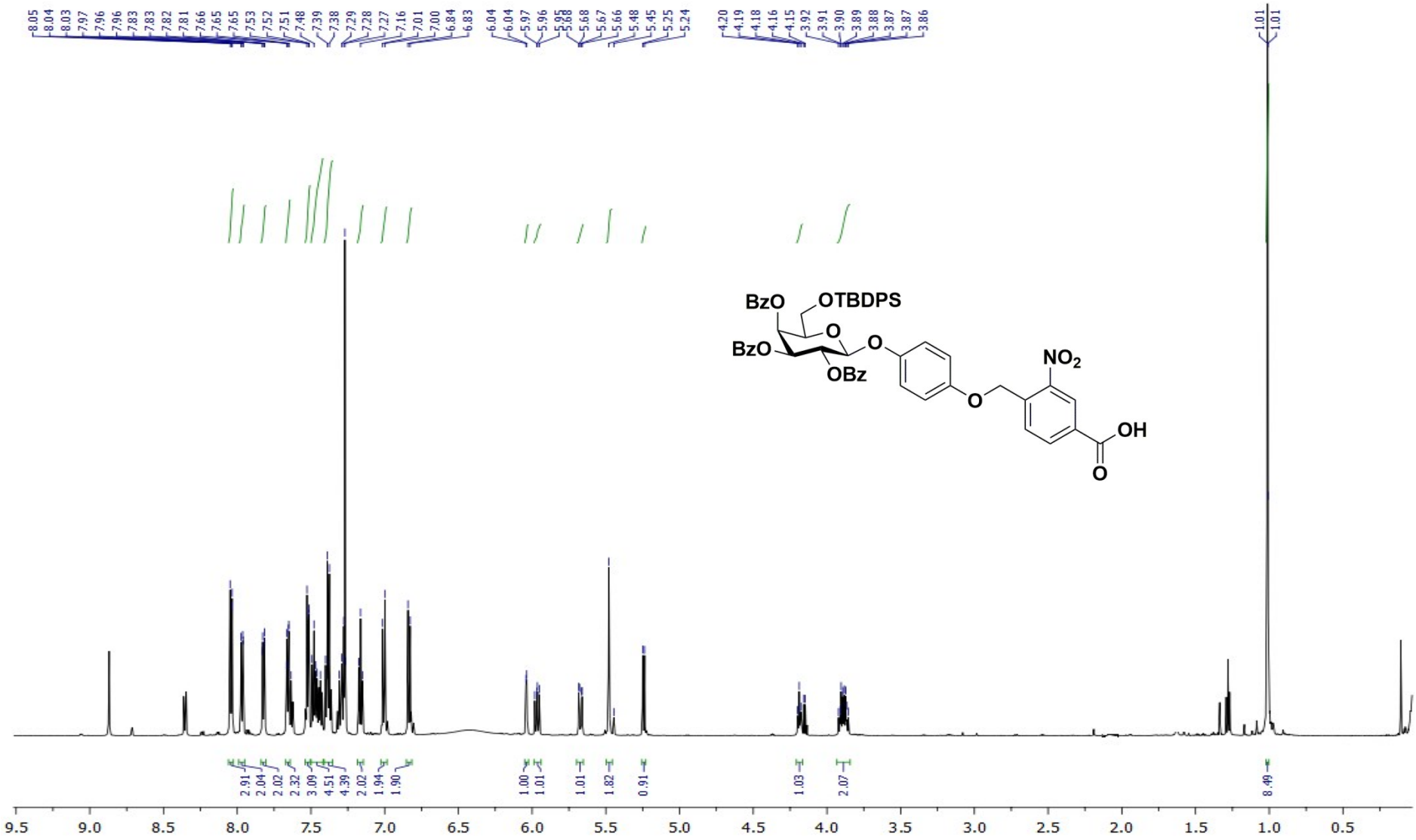


HRMS data of 4-((4-carboxylate-2-nitrobenzyl)oxy)phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl *β*-D-galactopyranoside (6)

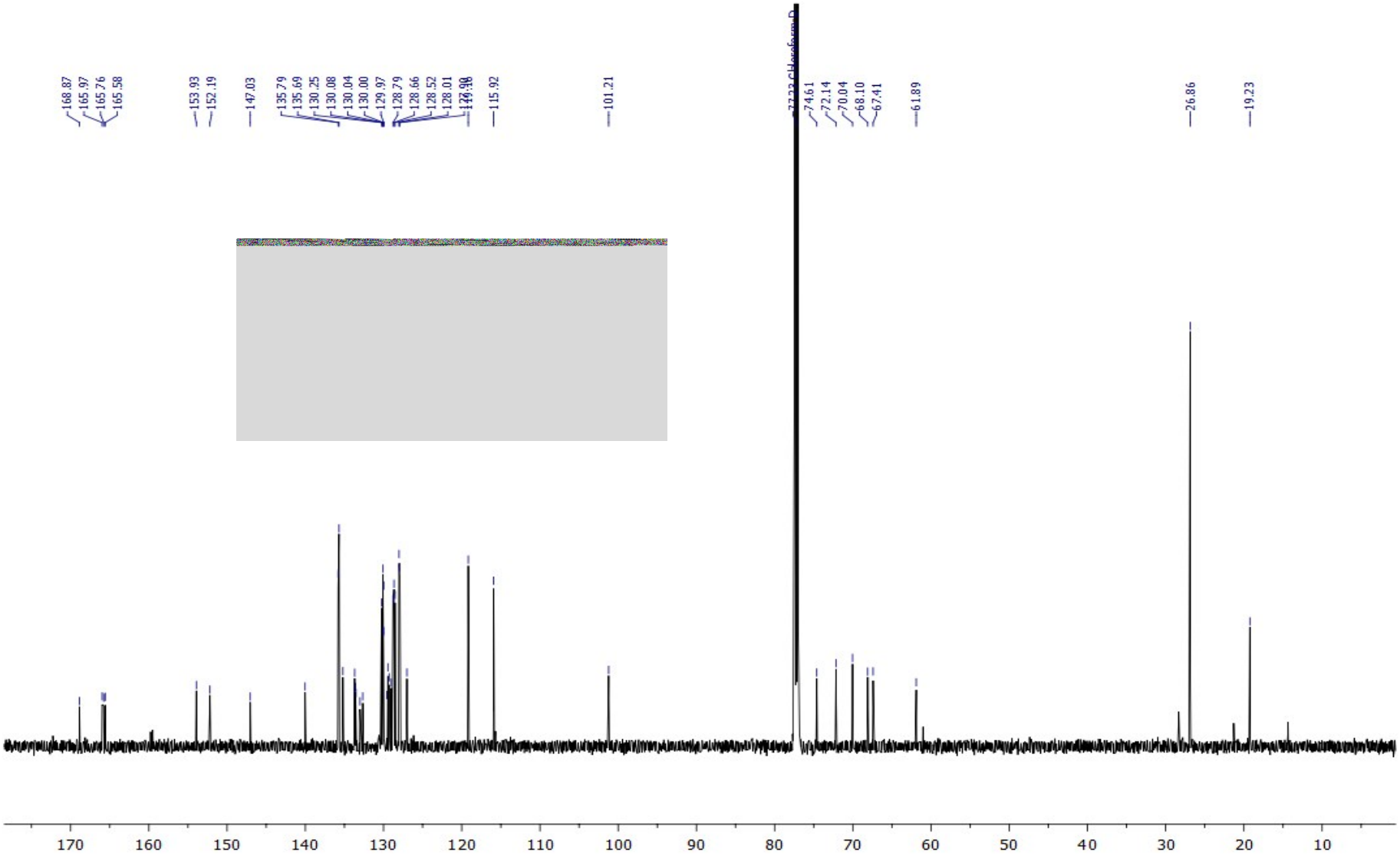


Mass accuracy = ((1000.3000-1000.2950)/1000.3000)* 106 = 5.0 ppm

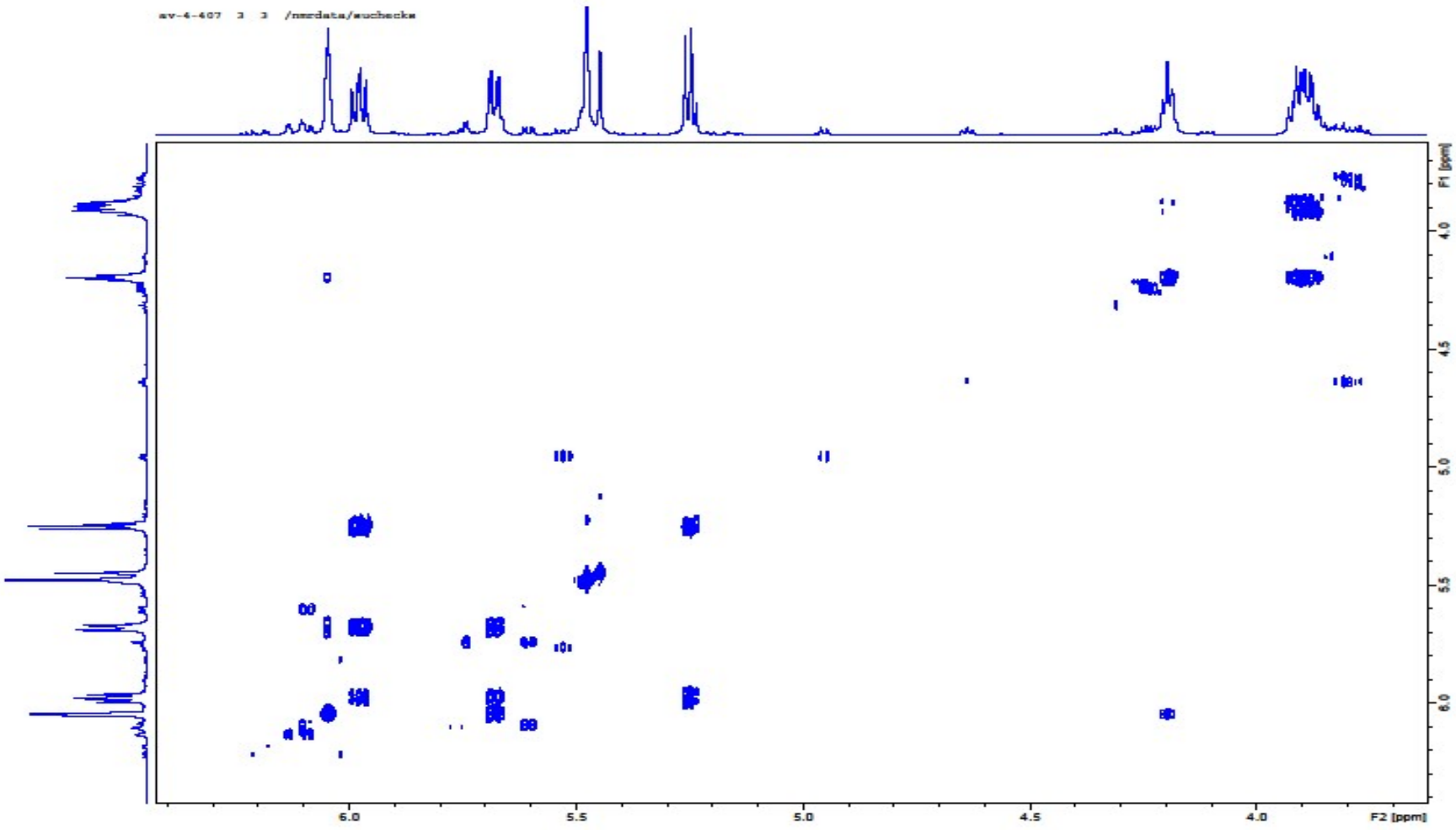
^{1}H NMR of 4-((4-carboxylate-2-nitrobenzyl)oxy)phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl *β*-D-galactopyranoside (6)



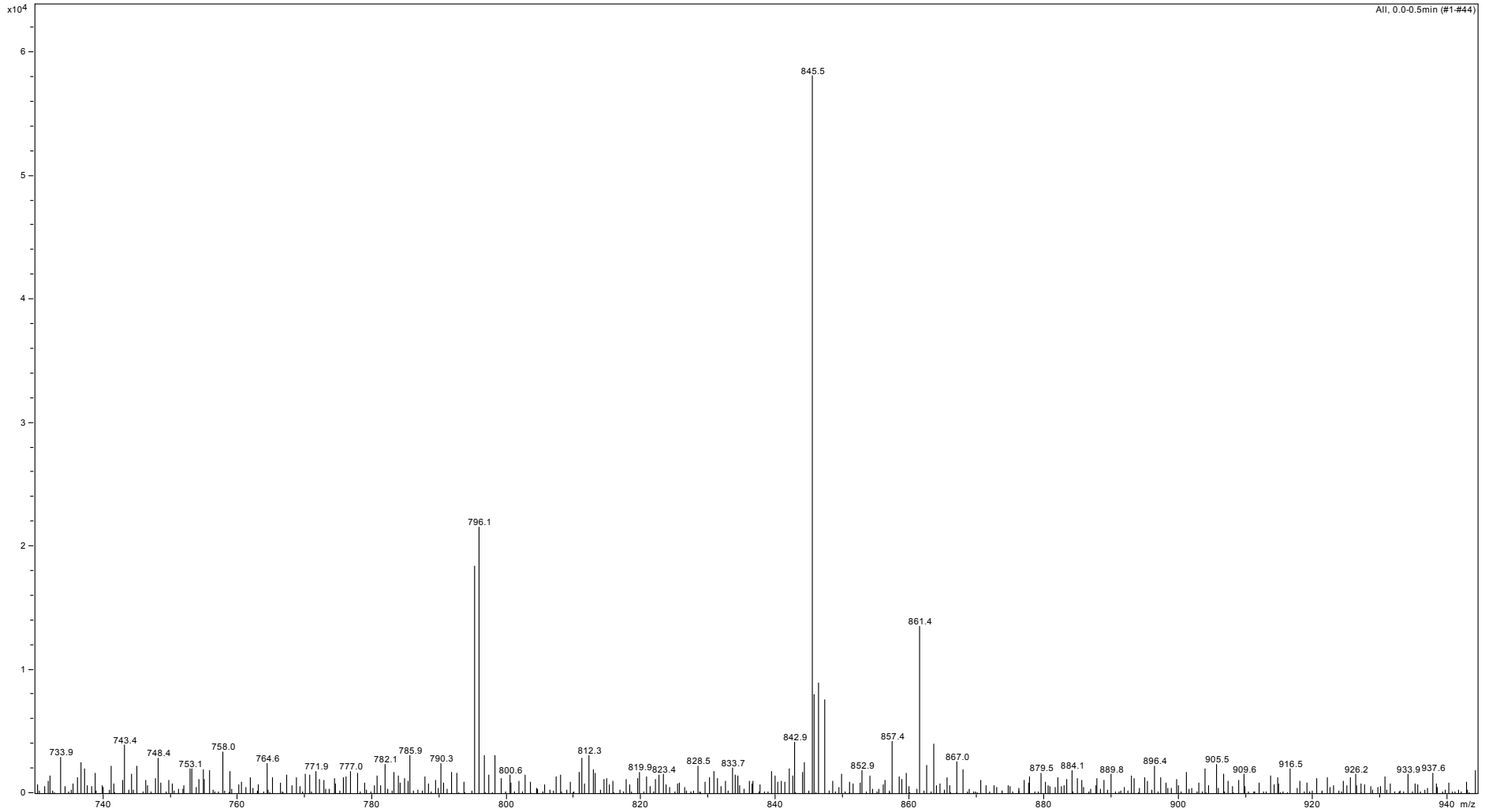
^{13}C NMR of 4-((4-carboxylate-2-nitrobenzyl)oxy)phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl *β*-D-galactopyranoside (6)



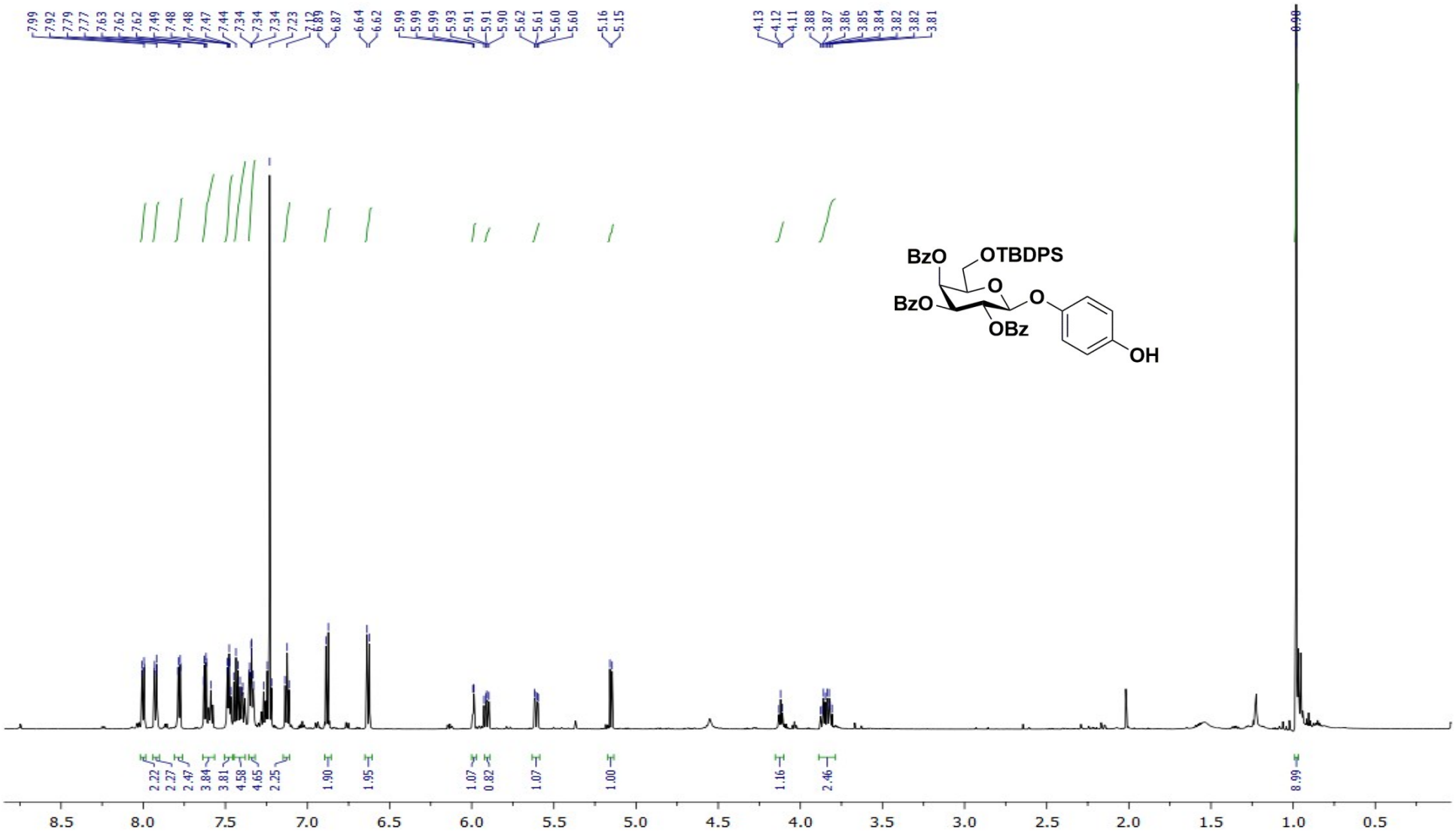
COSY NMR of 4-((4-carboxylate-2-nitrobenzyl)oxy)phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl *β*-D-galactopyranoside (6)



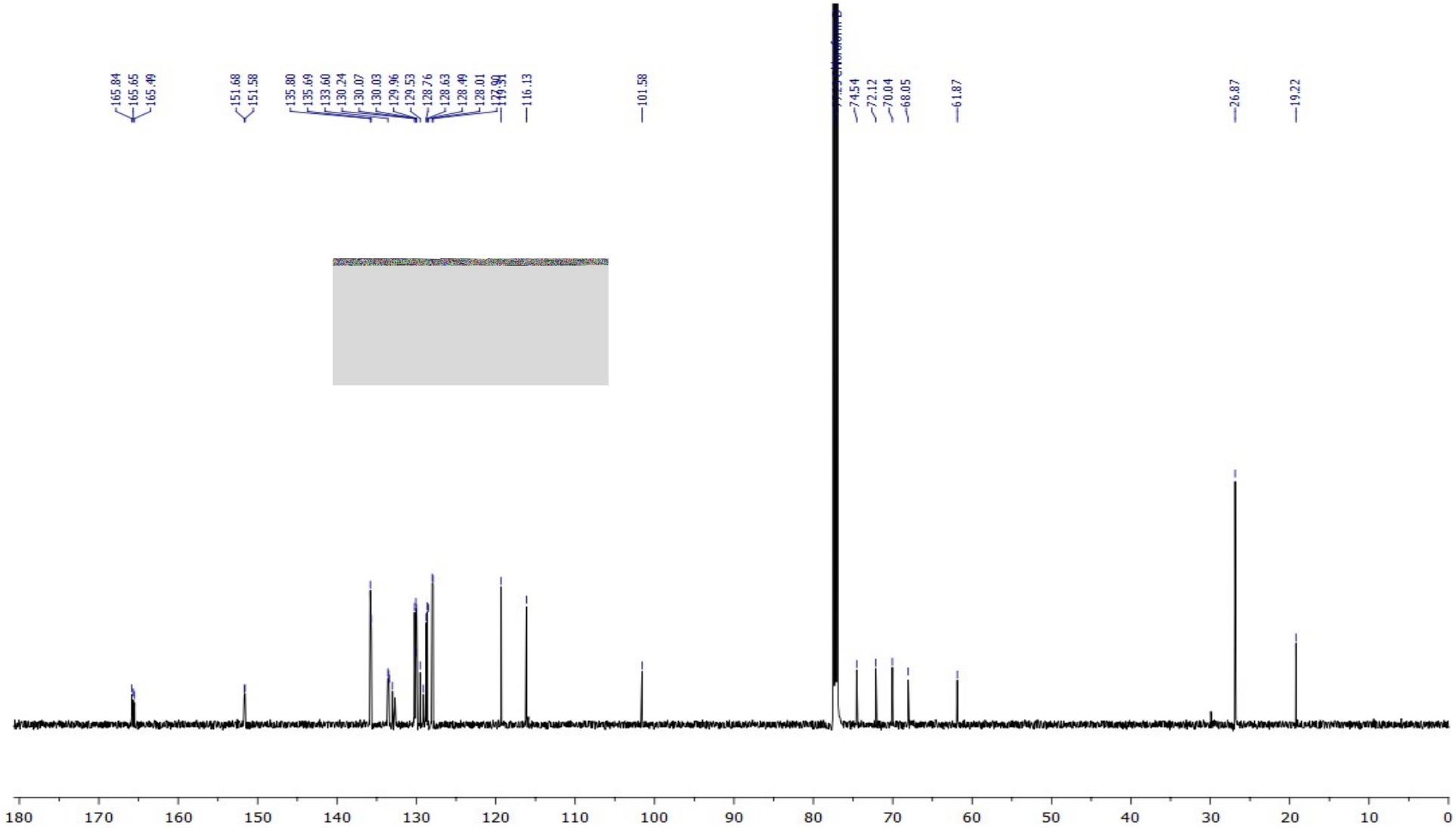
ESI-MS data of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galacopyranoside (7a)



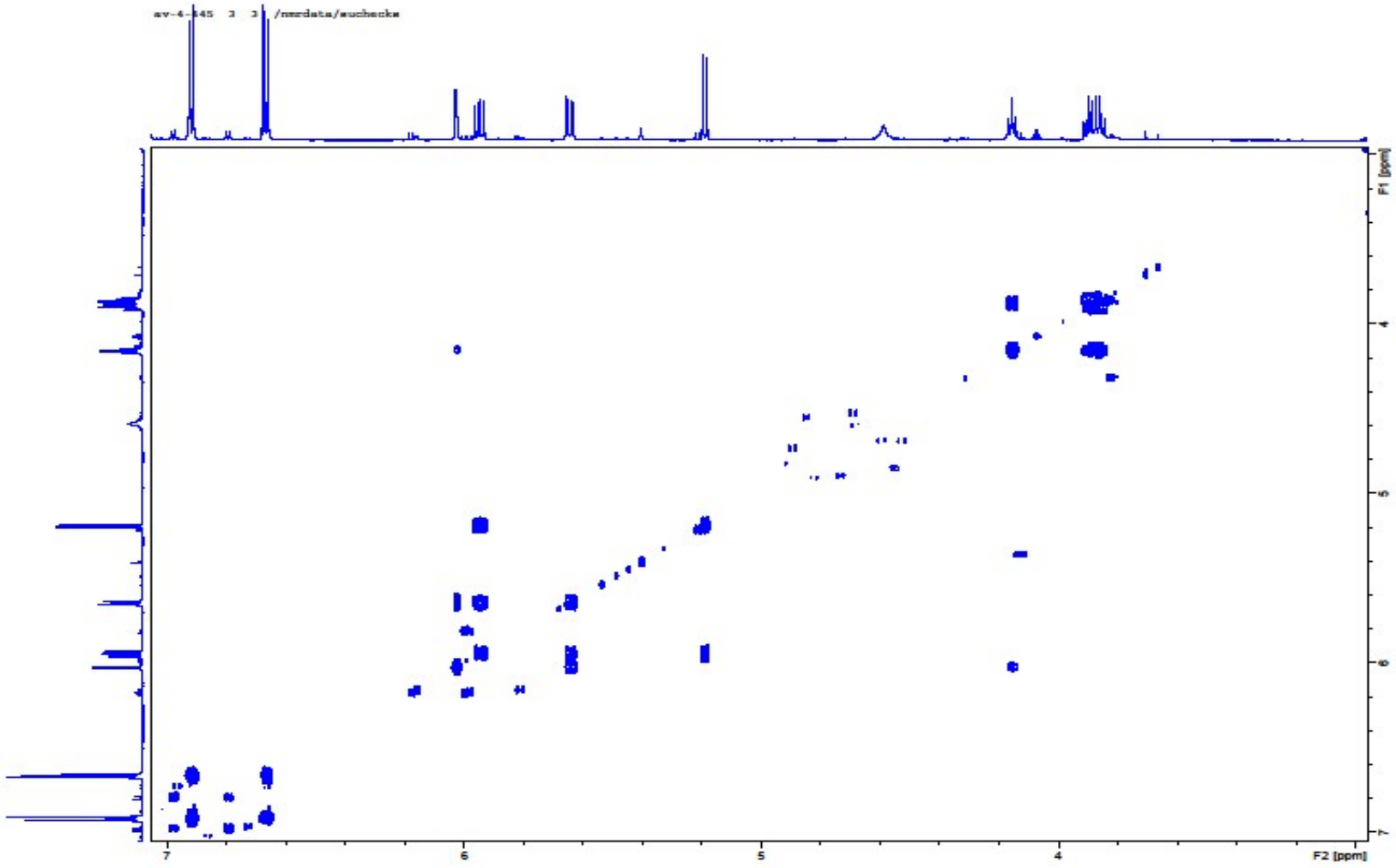
^{1}H NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranoside (7a)



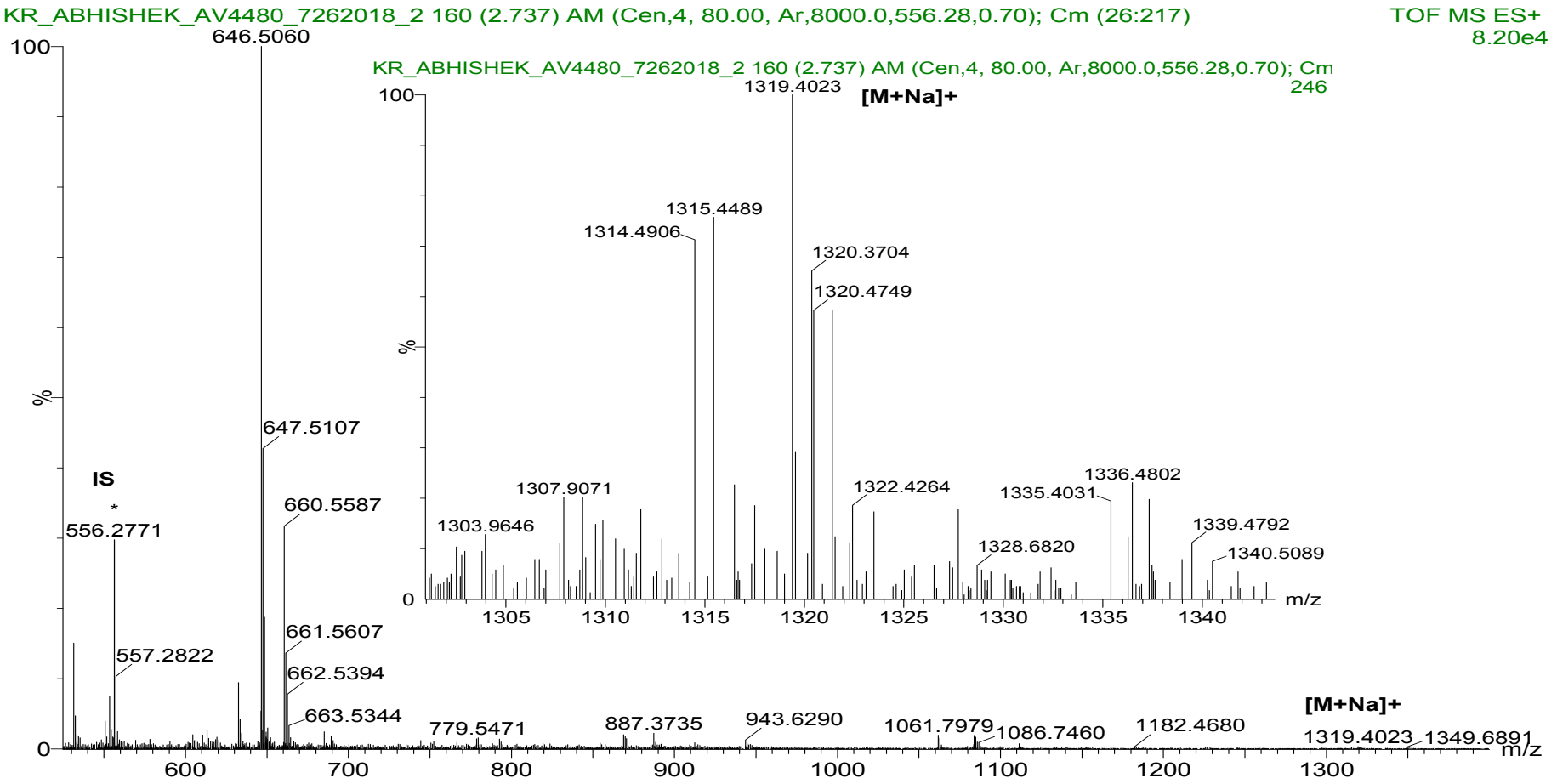
^{13}C NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranoside (7a)



COSY NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranoside (7a)

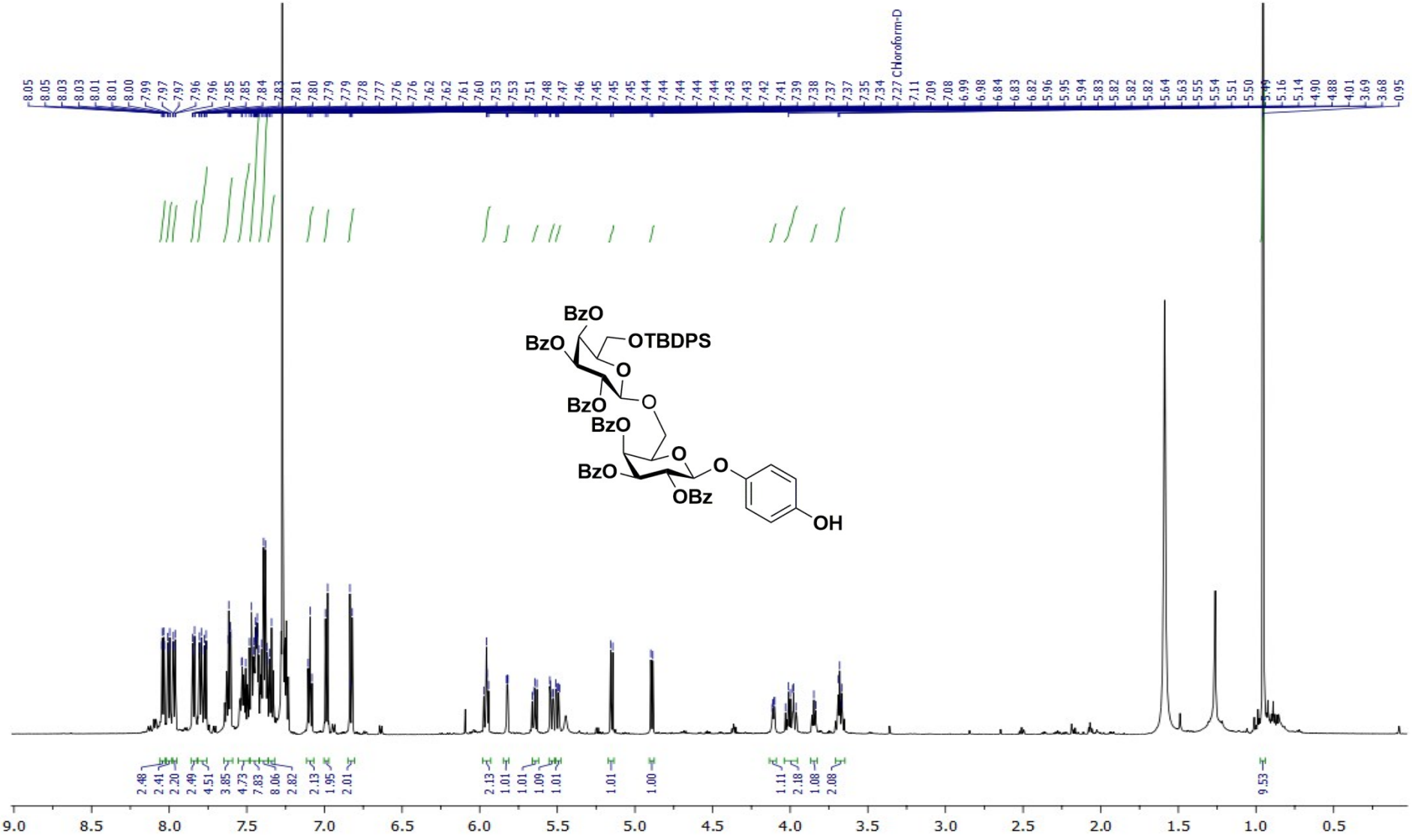


HRMS data of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranoside (9a)

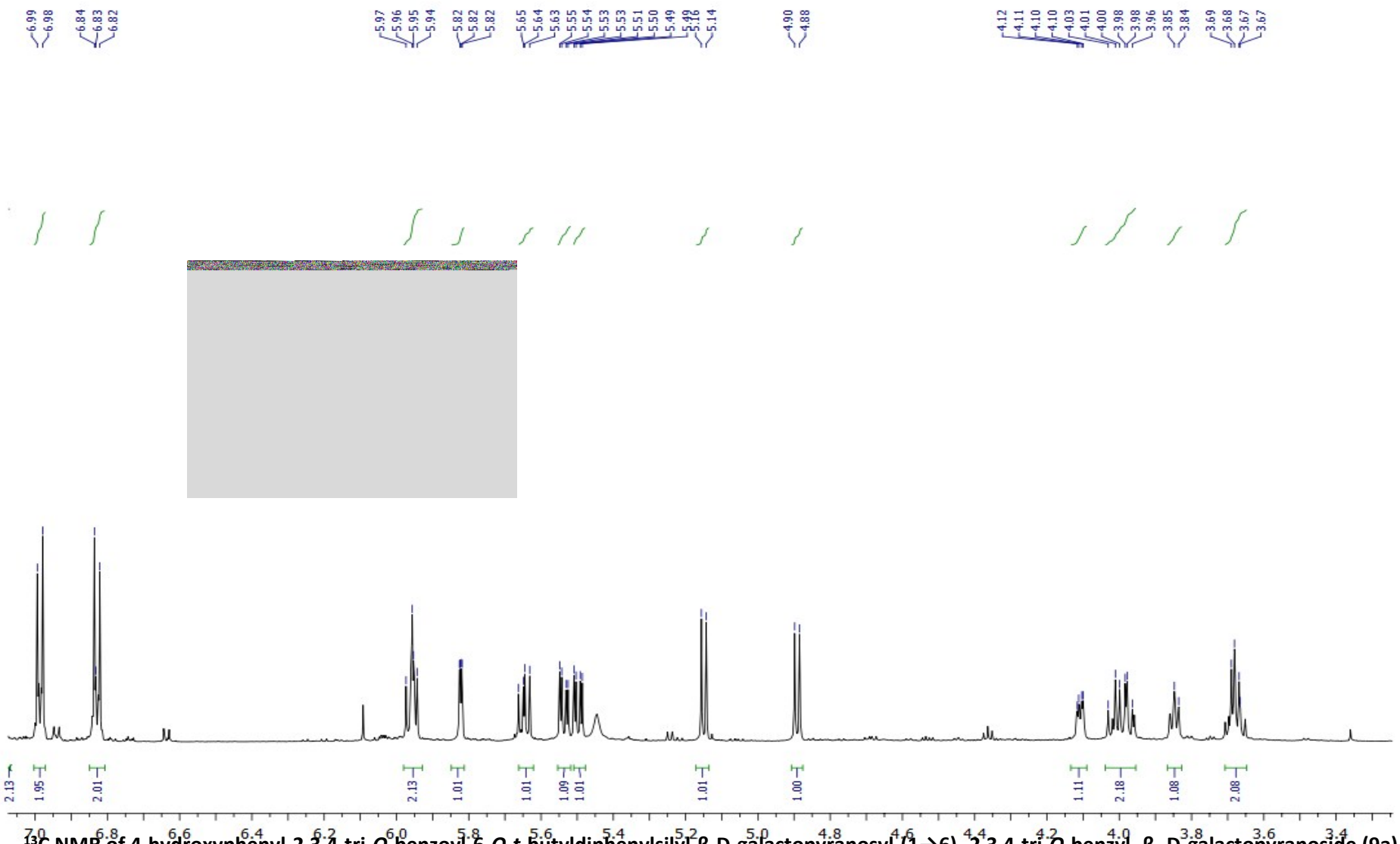


Mass accuracy = ((1319.4072-1319.4023)/1319.4072)* 106 = 3.7 ppm

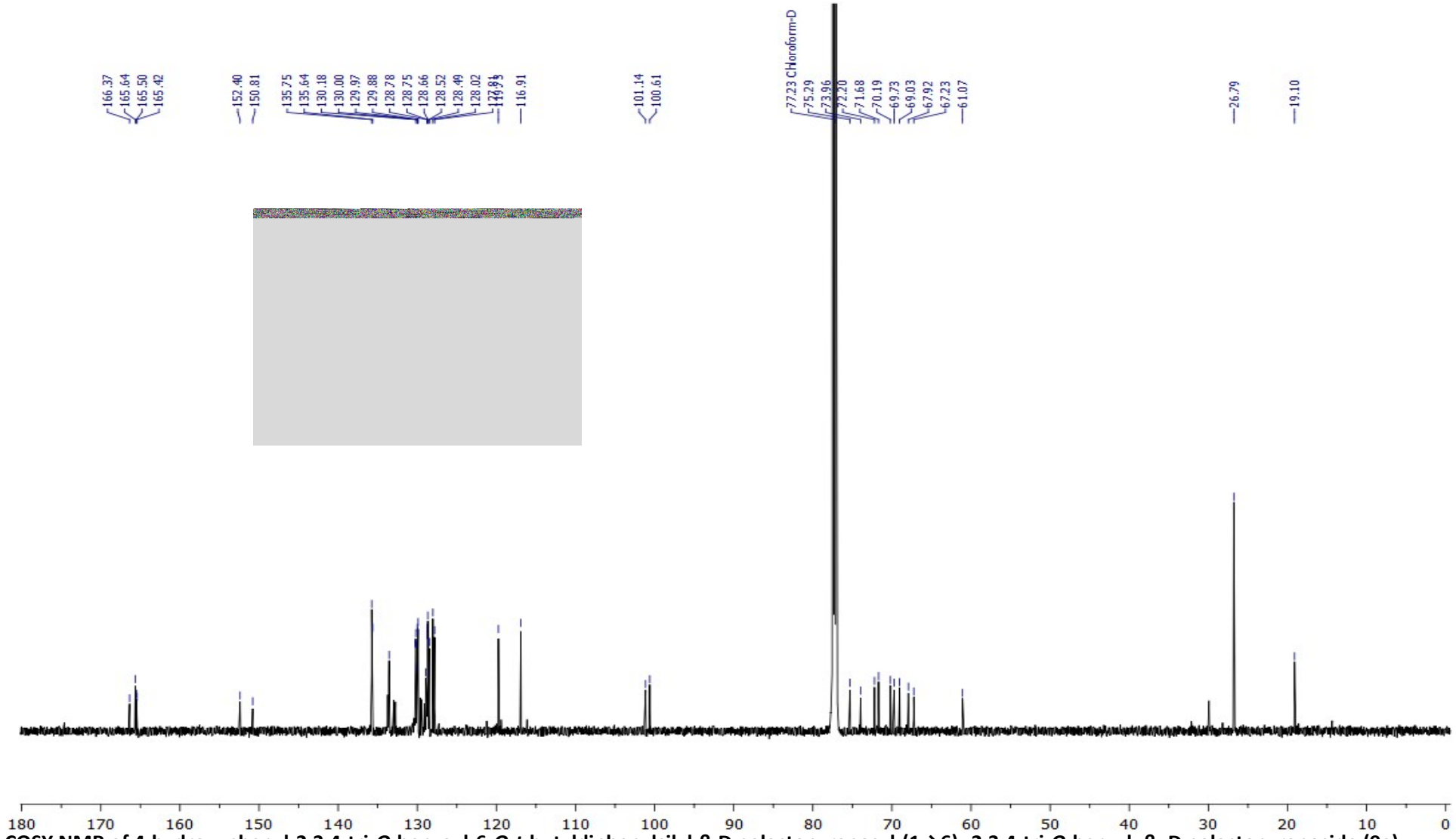
^{1}H NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranoside (9a)



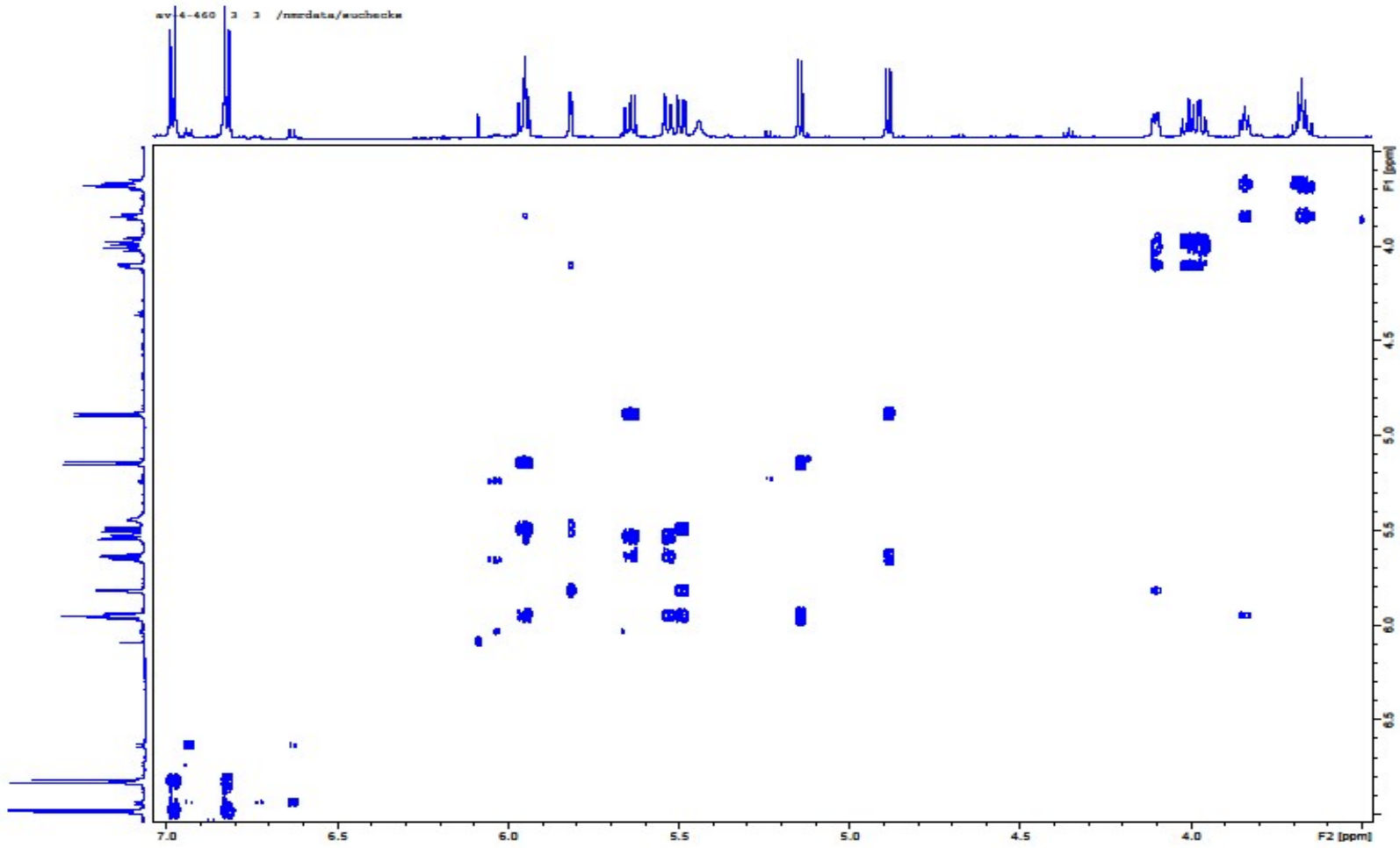
^{1}H NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranoside (9a)



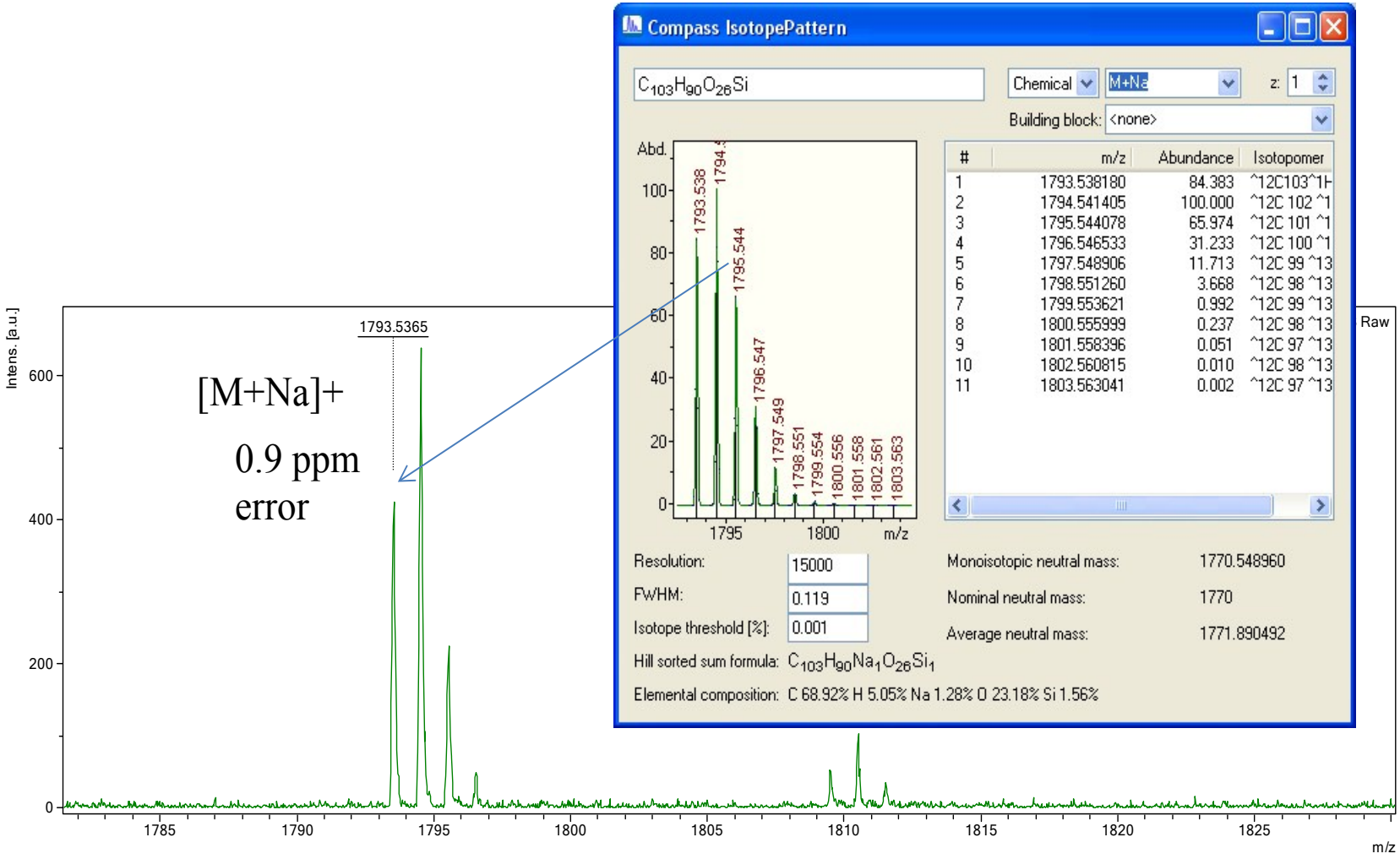
^{13}C NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranoside (9a)



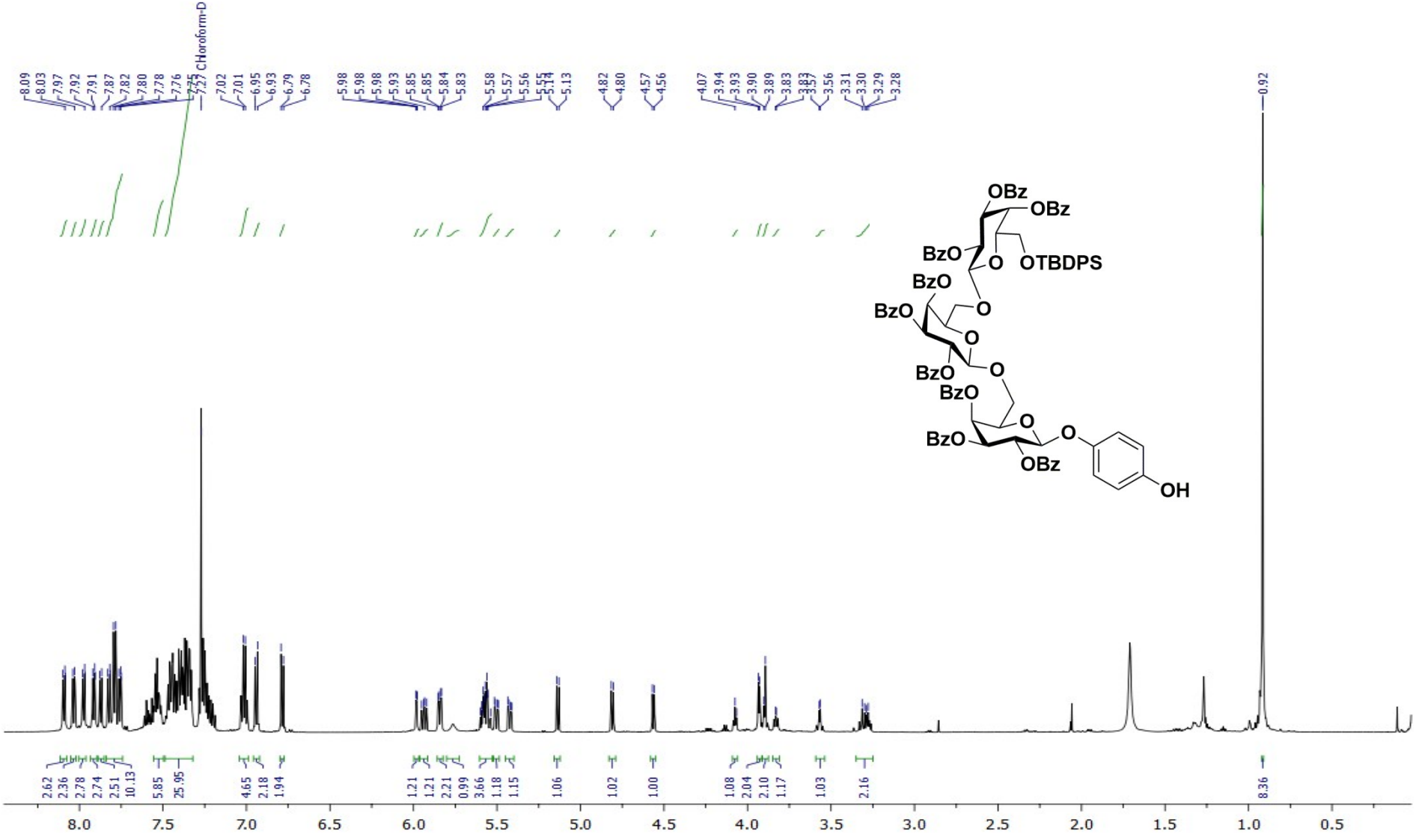
COSY NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranoside (9a)


7.0
6.5
6.0
5.5
5.0
4.5
4.0
F2 [ppm]
F1 [ppm]

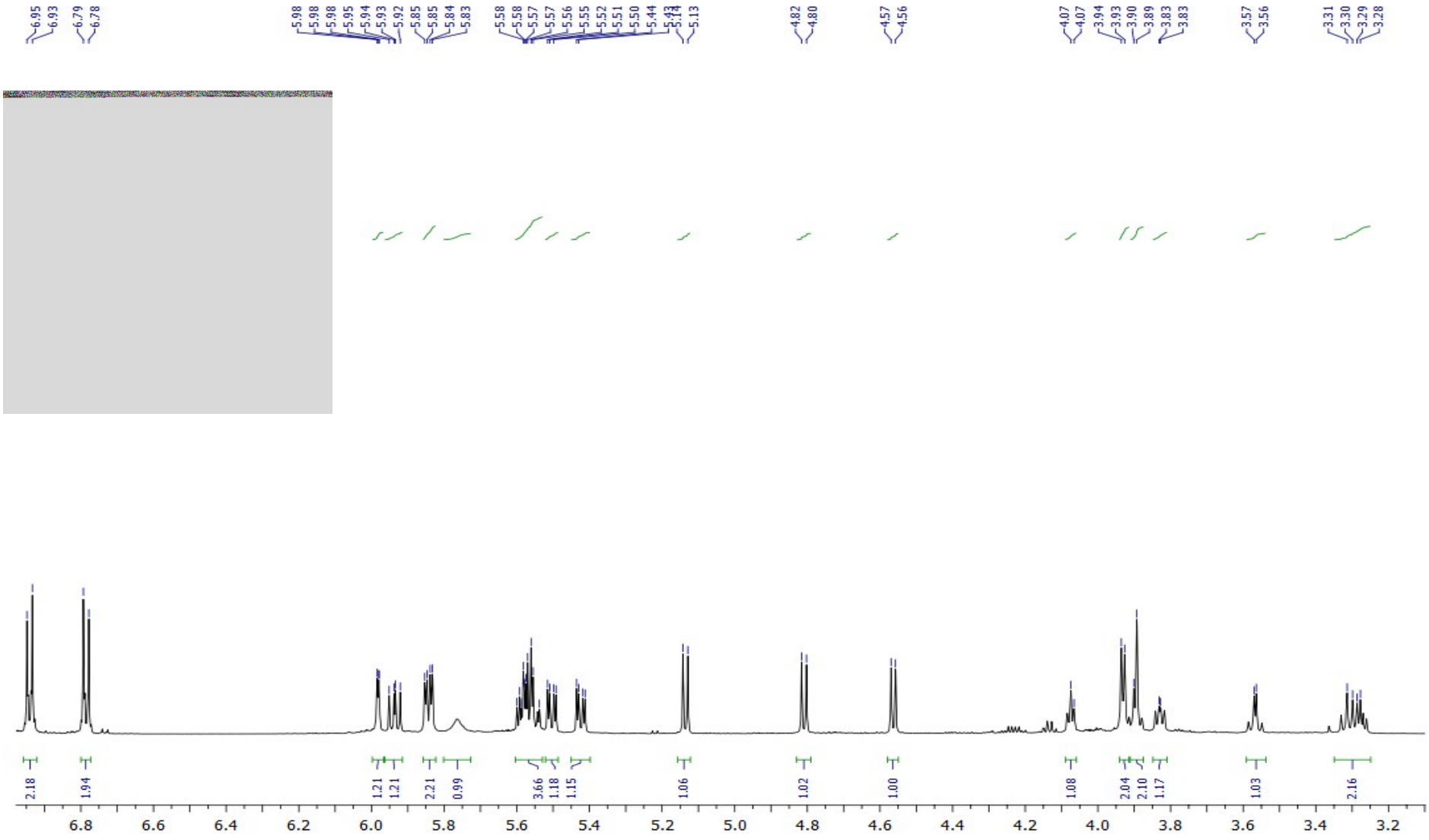
HRMS data of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranoside (11a)



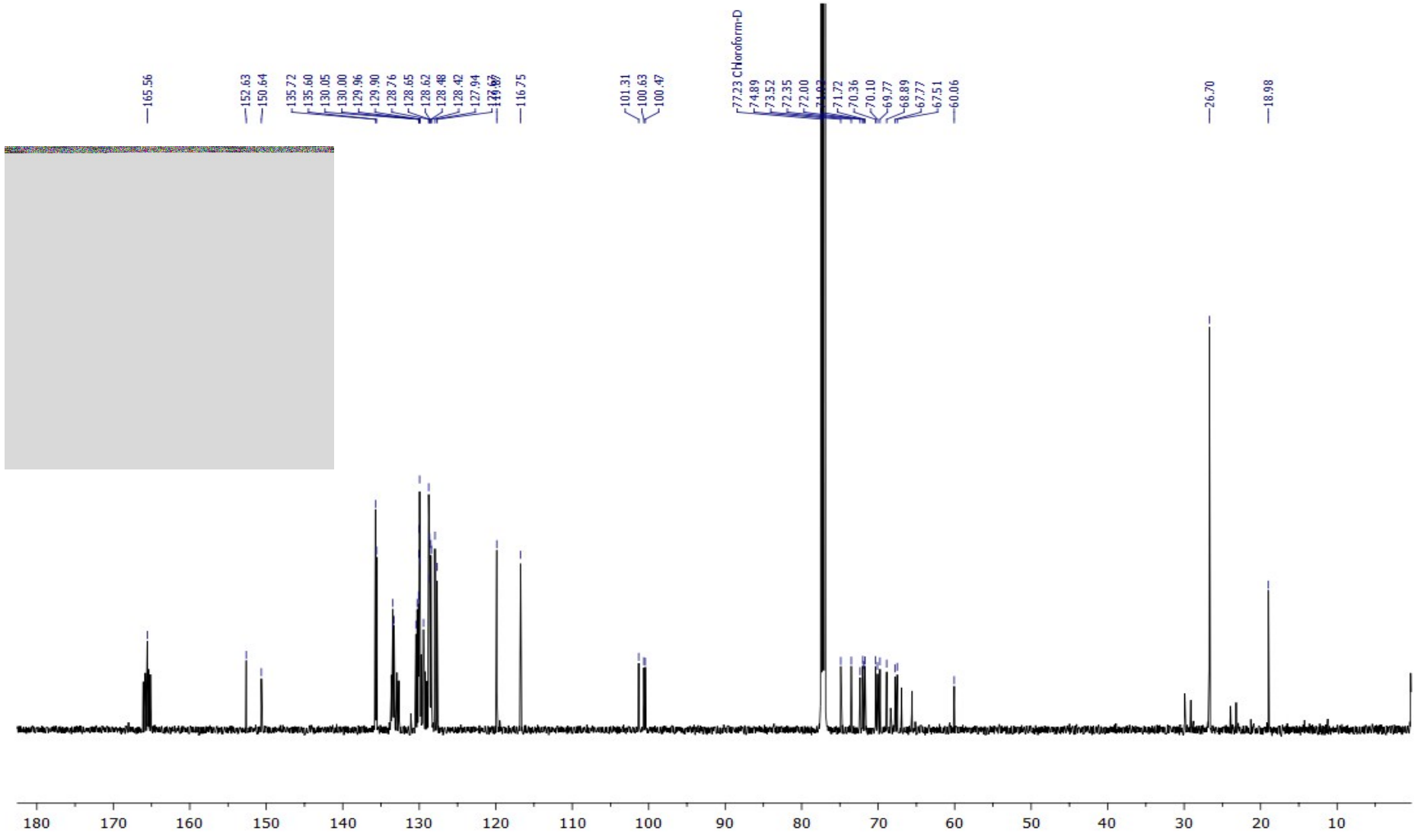
^{1}H NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl- β -D-galactopyranoside (11a)



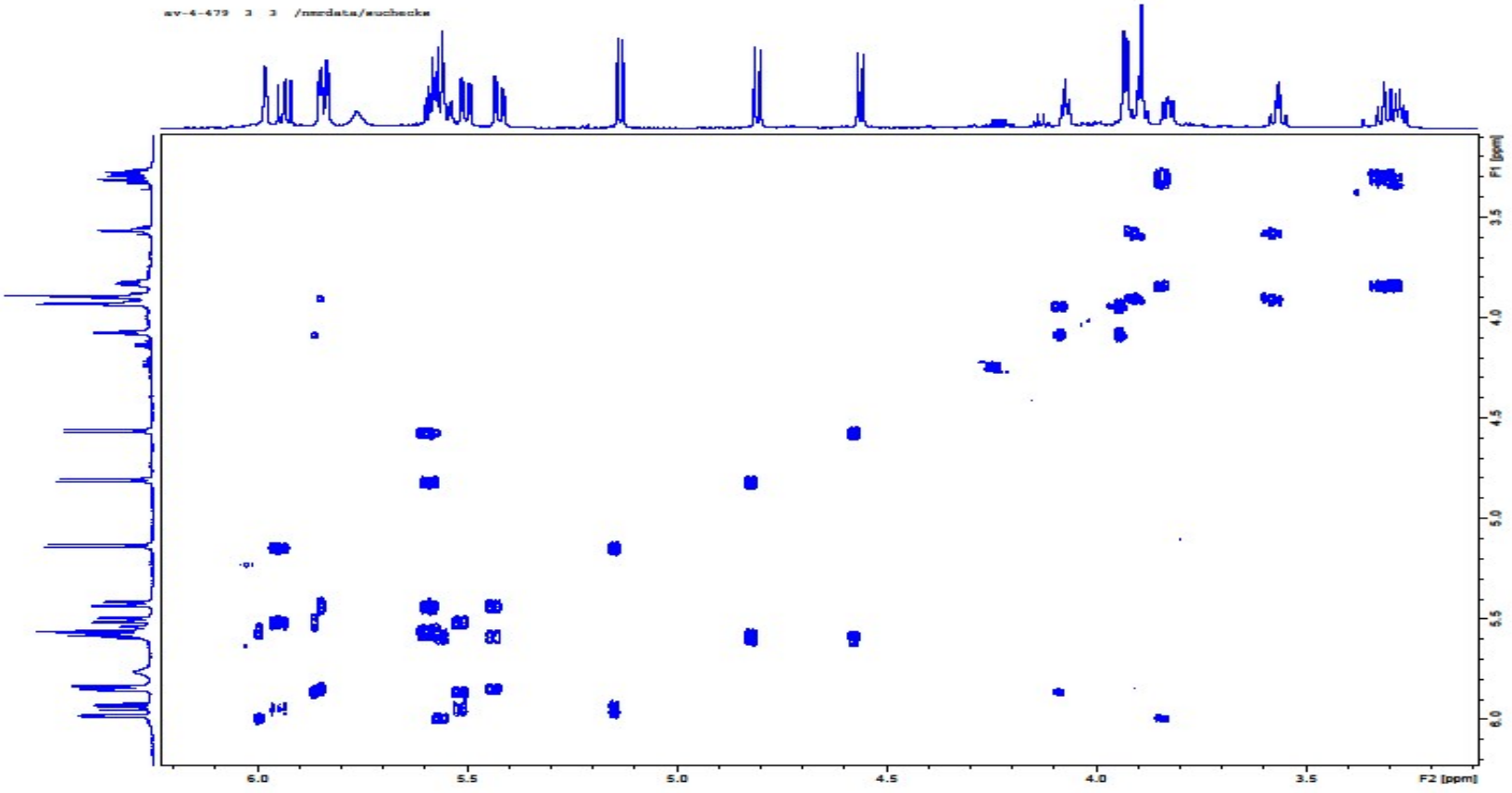
^{1}H NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl- β -D-galactopyranoside (11a)



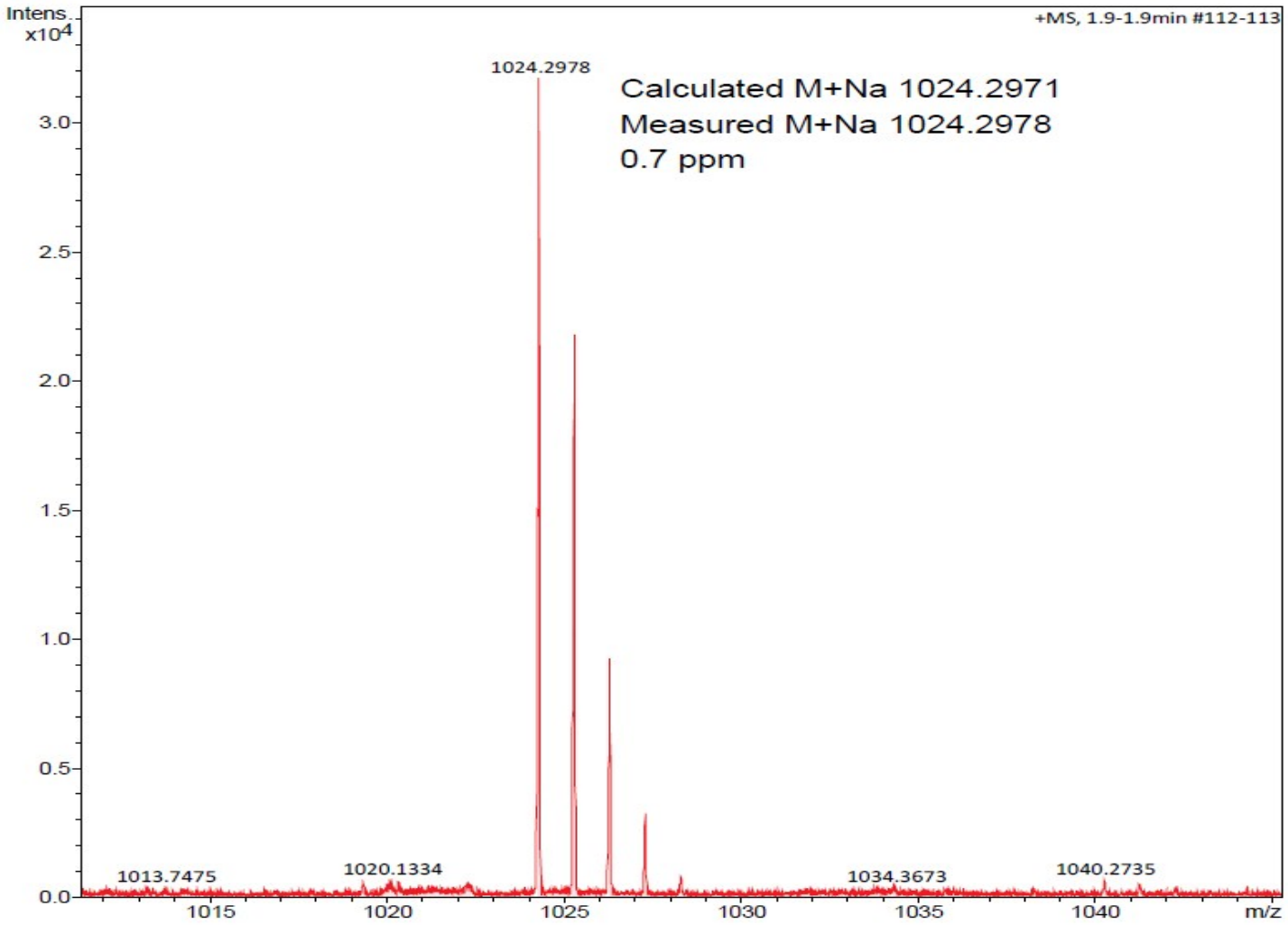
^{13}C NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl- β -D-galactopyranoside (11a)



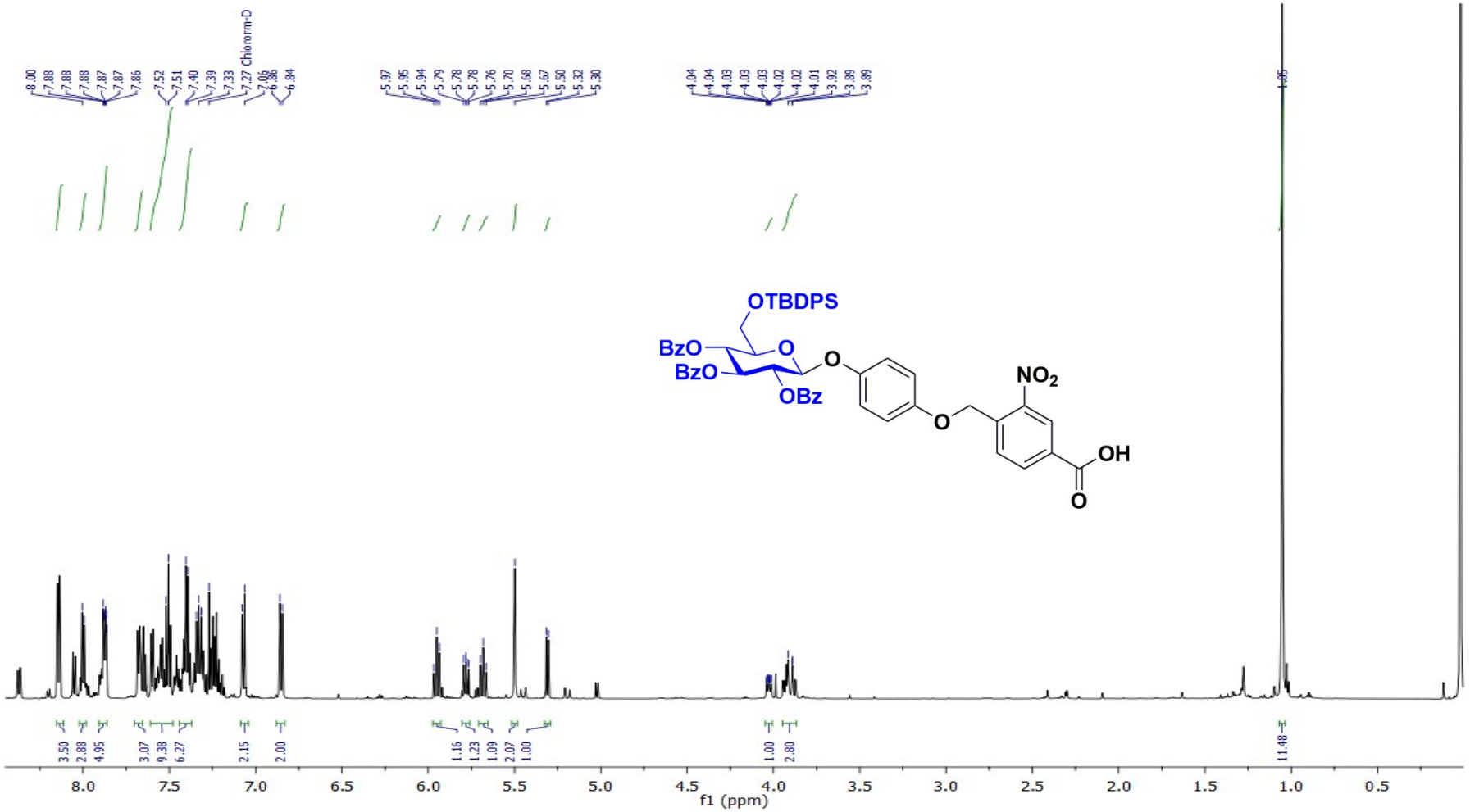
COSY NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl- β -D-galactopyranoside (11a)



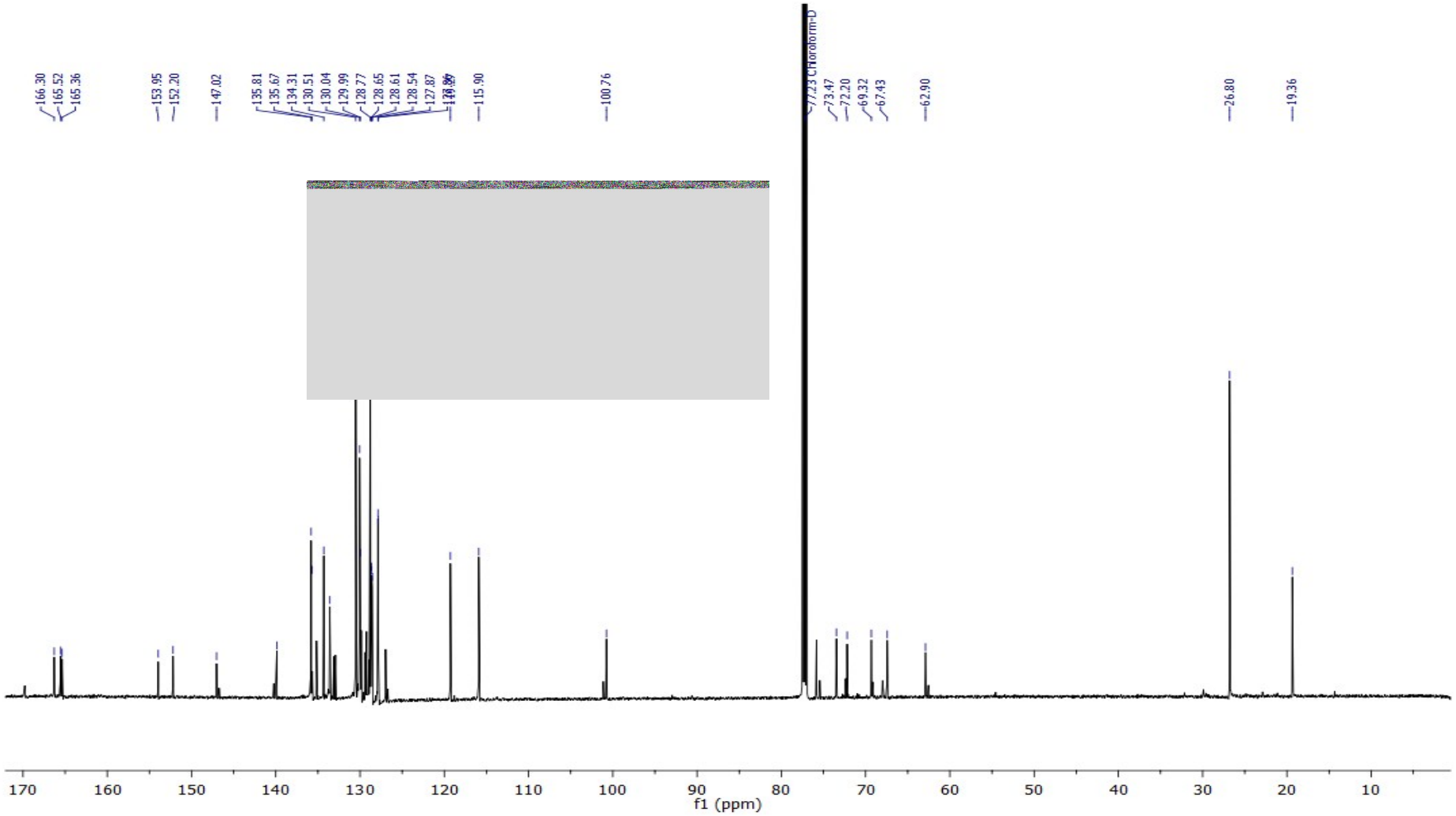
HRMS data of 4-((4-carboxylate-2-nitrobenzyl)oxy)phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl *β*-D-glucopyranoside (12)



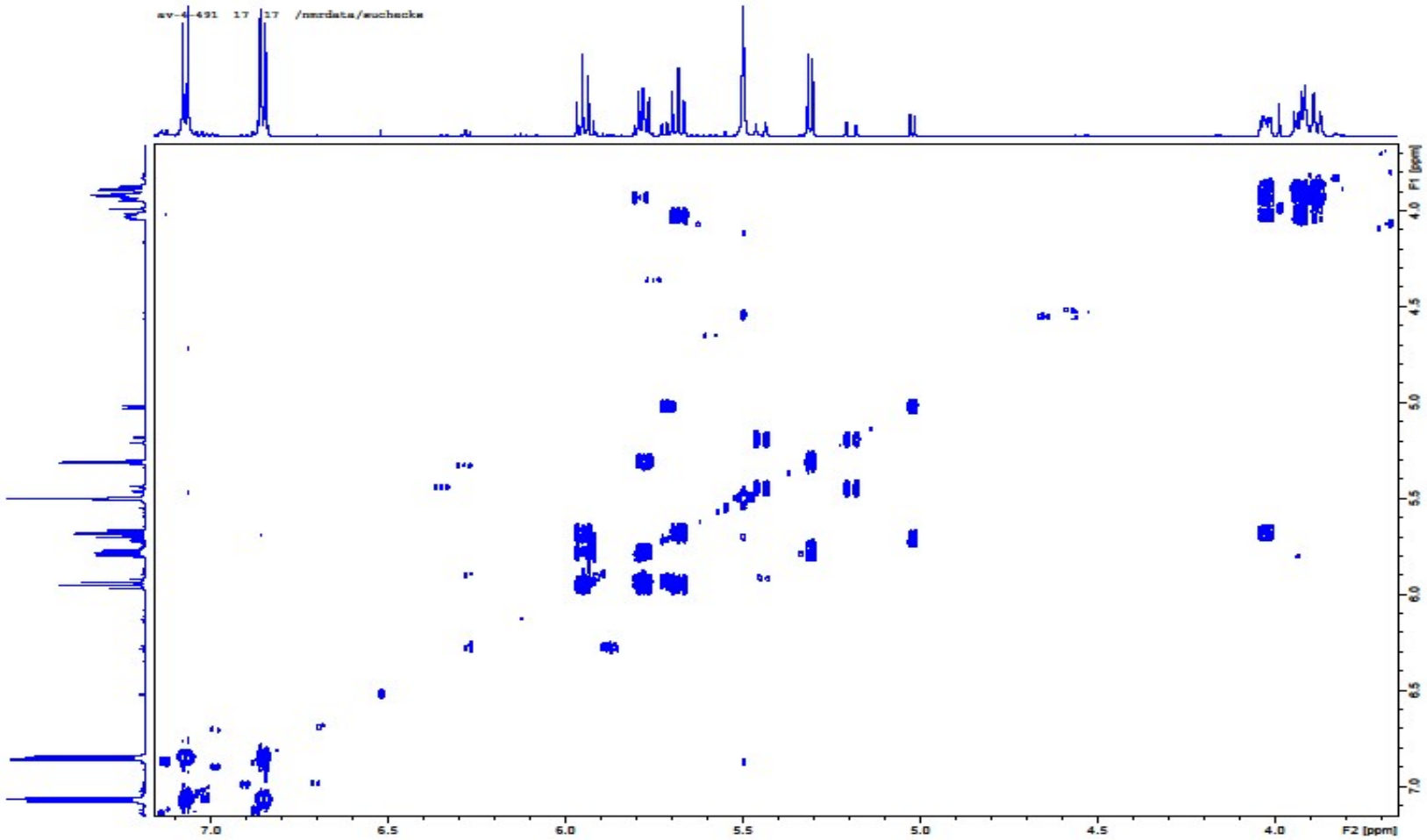
^{1}H NMR of 4-((4-carboxylate-2-nitrobenzyl)oxy)phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl *β*-D-glucopyranoside (12)



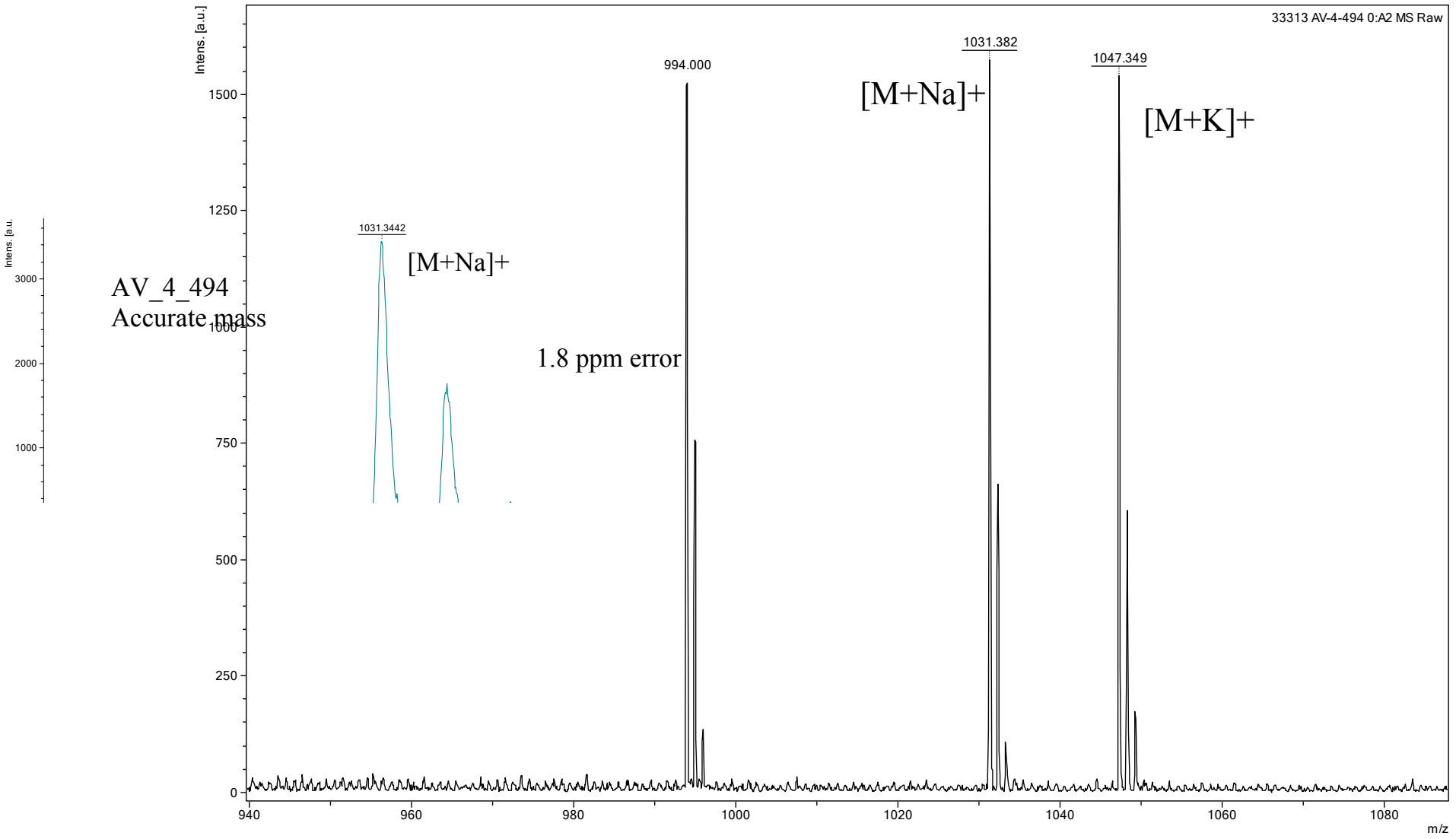
^{13}C NMR of 4-((4-carboxylate-2-nitrobenzyl)oxy)phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl *β*-D-glucopyranoside (12)



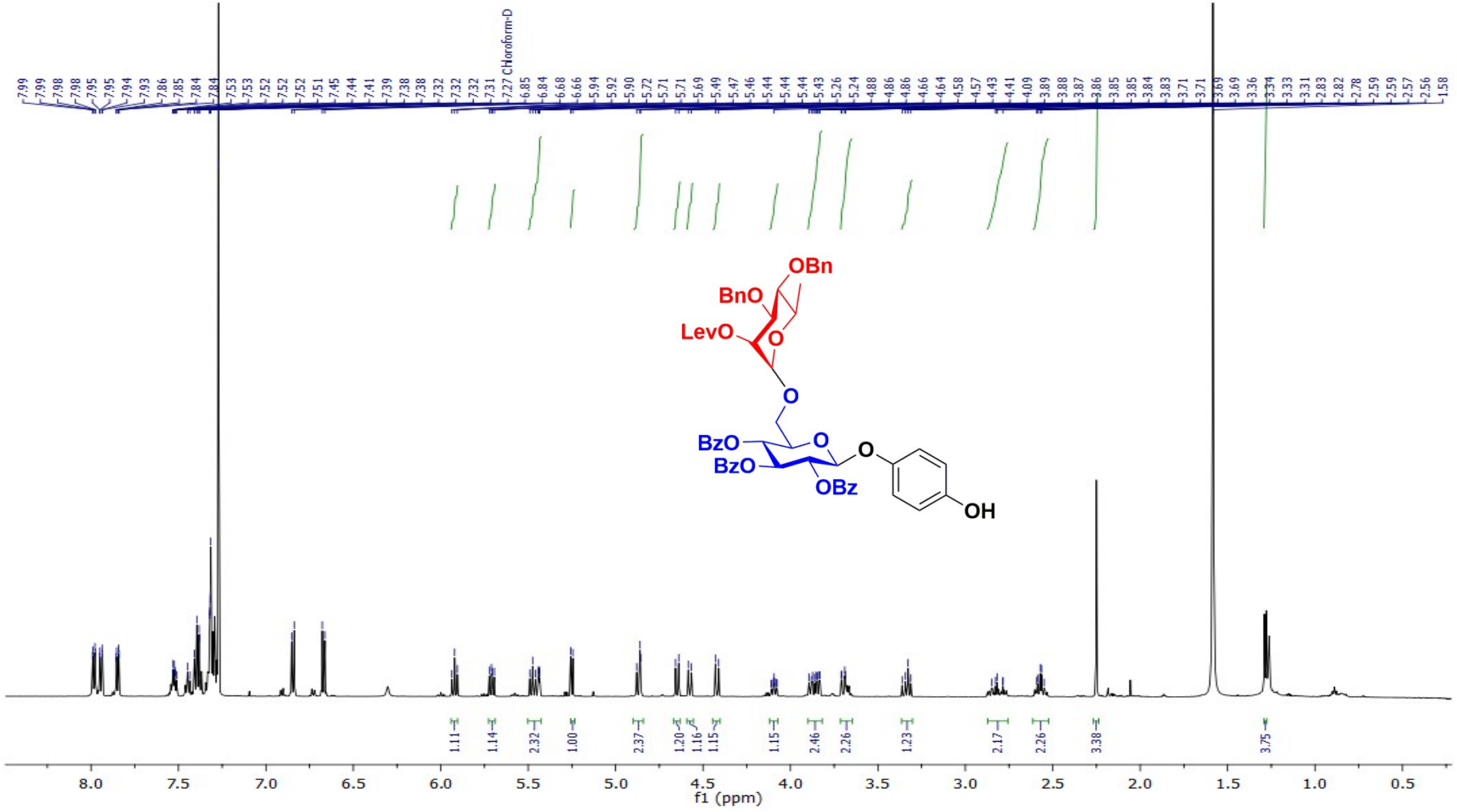
COSY NMR of 4-((4-carboxylate-2-nitrobenzyl)oxy)phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl *β*-D-glucopyranoside (12)



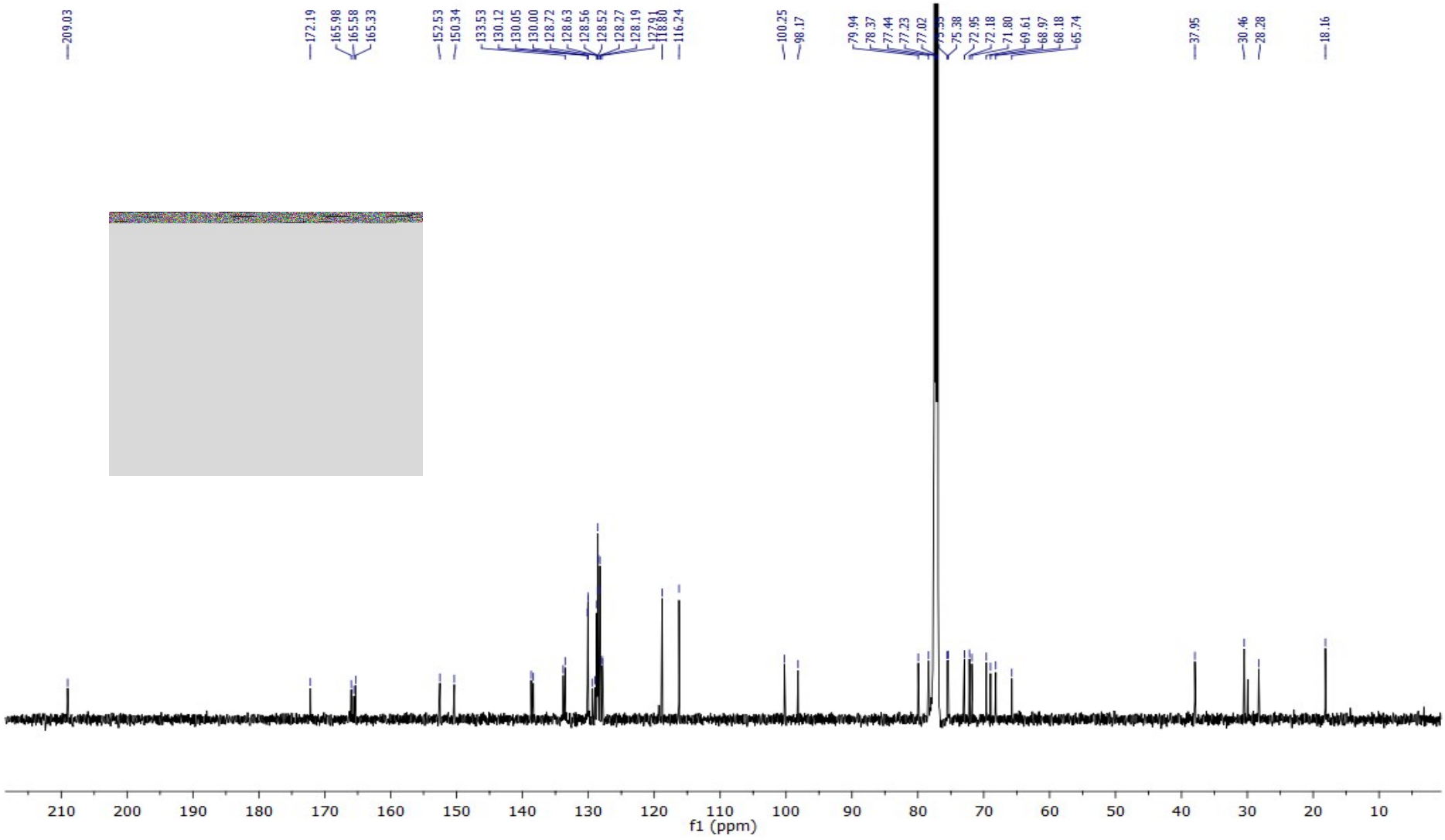
HRMS data of 4-hydroxyphenyl-2-*O*-levulinate-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (15a)



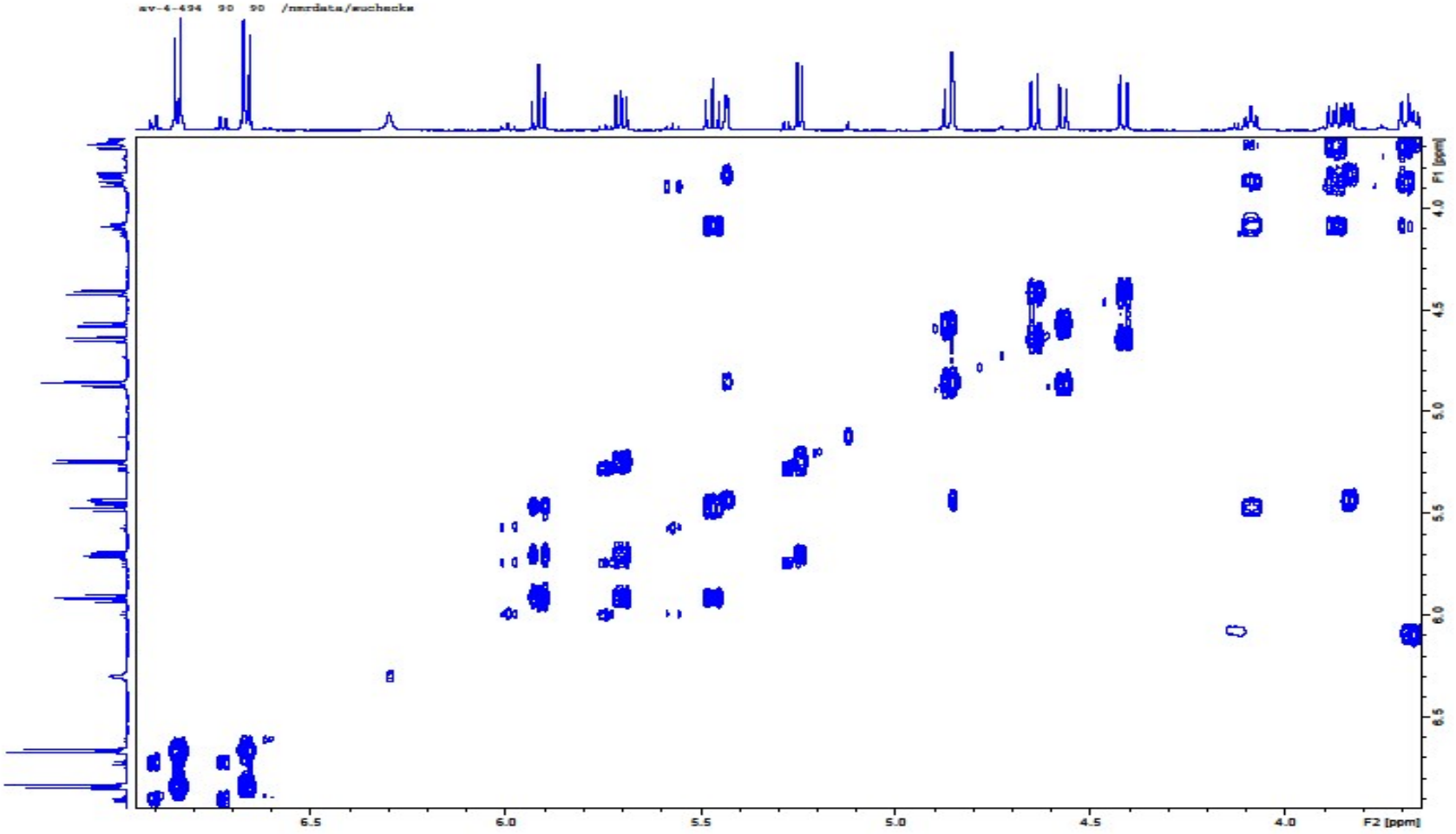
^{1}H NMR of 4-hydroxyphenyl-2-*O*-levulinate-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (15a)



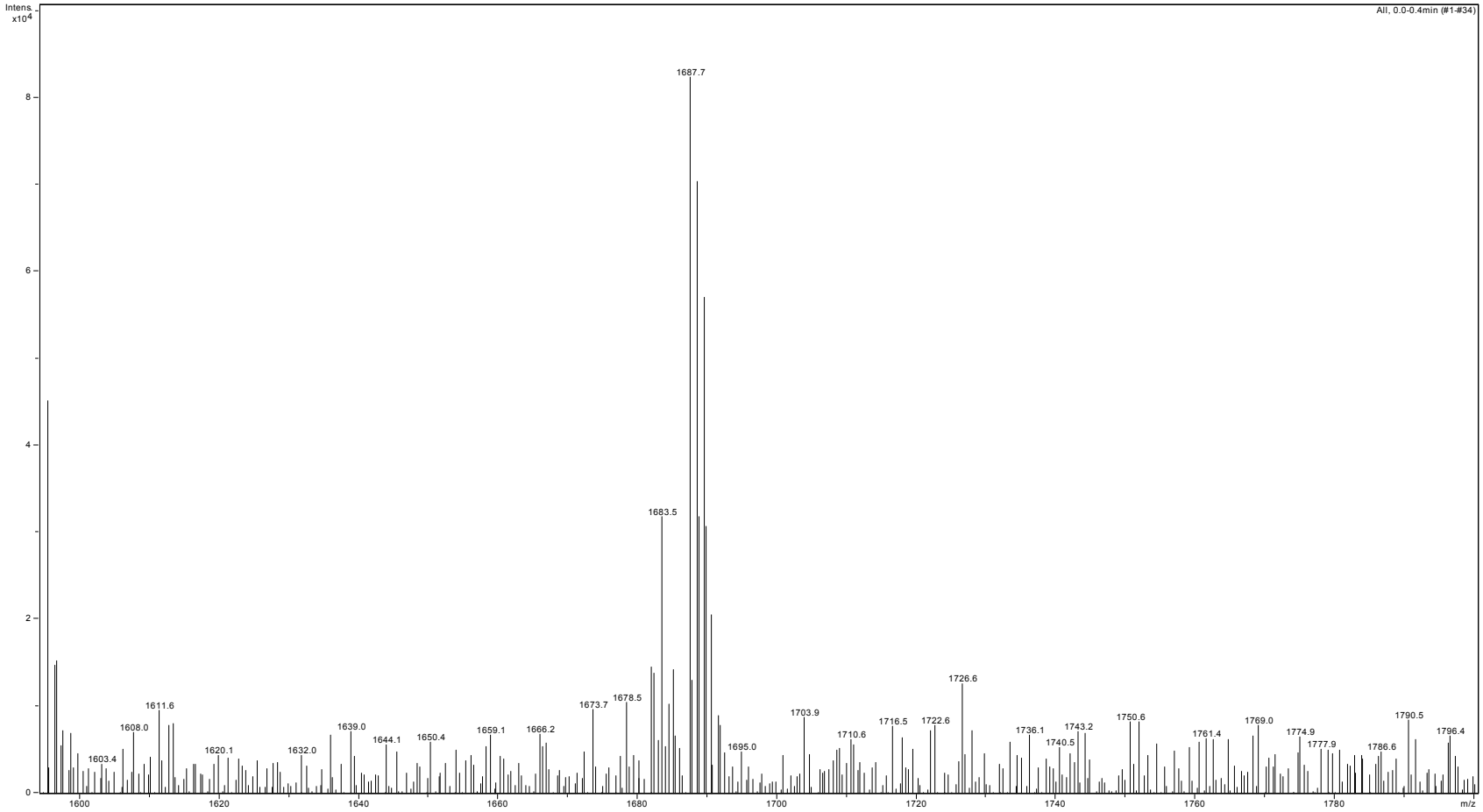
^{13}C NMR of 4-hydroxyphenyl-2-*O*-levulinate-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (15a)



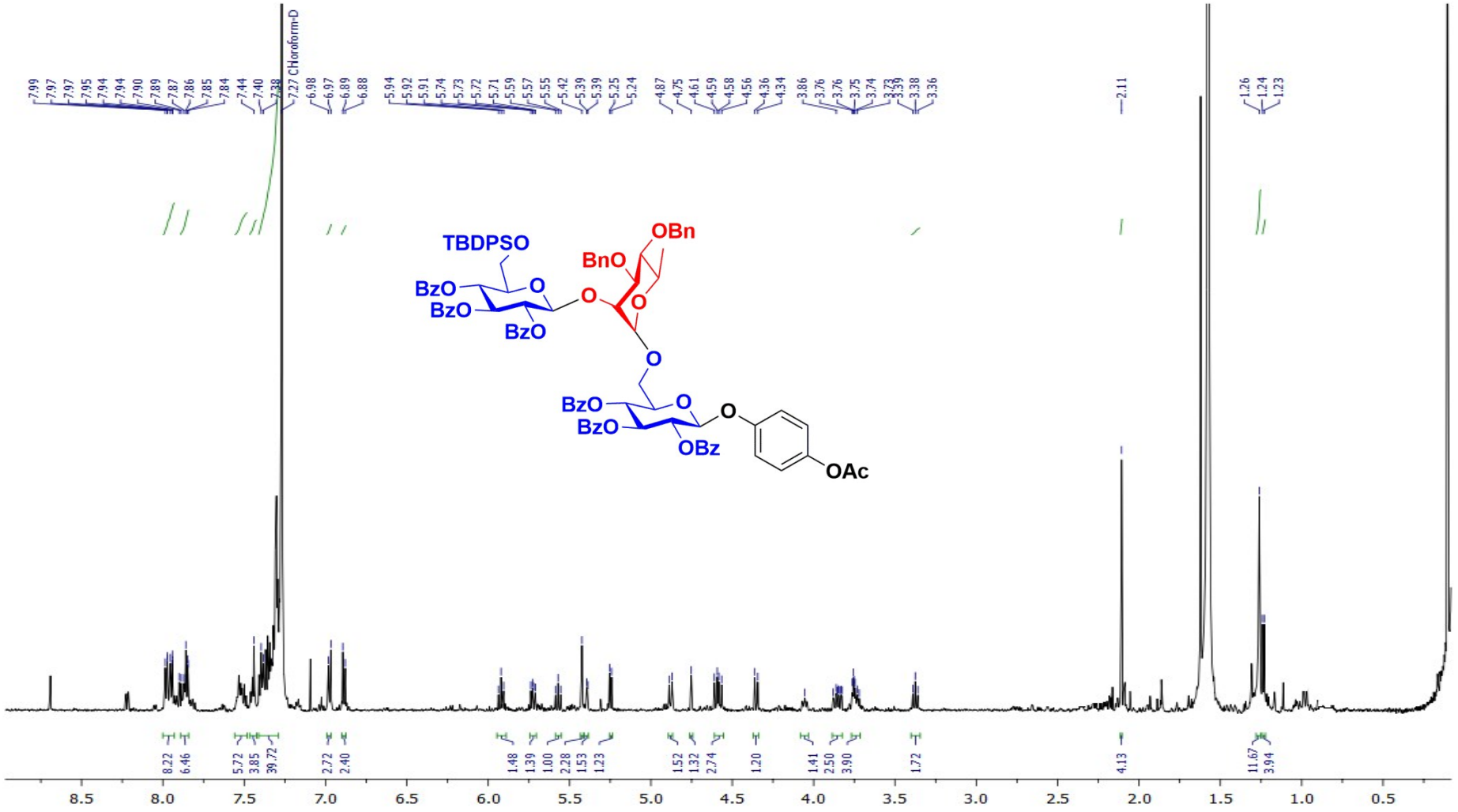
COSY NMR of 4-hydroxyphenyl-2-*O*-levulinate-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (15a)



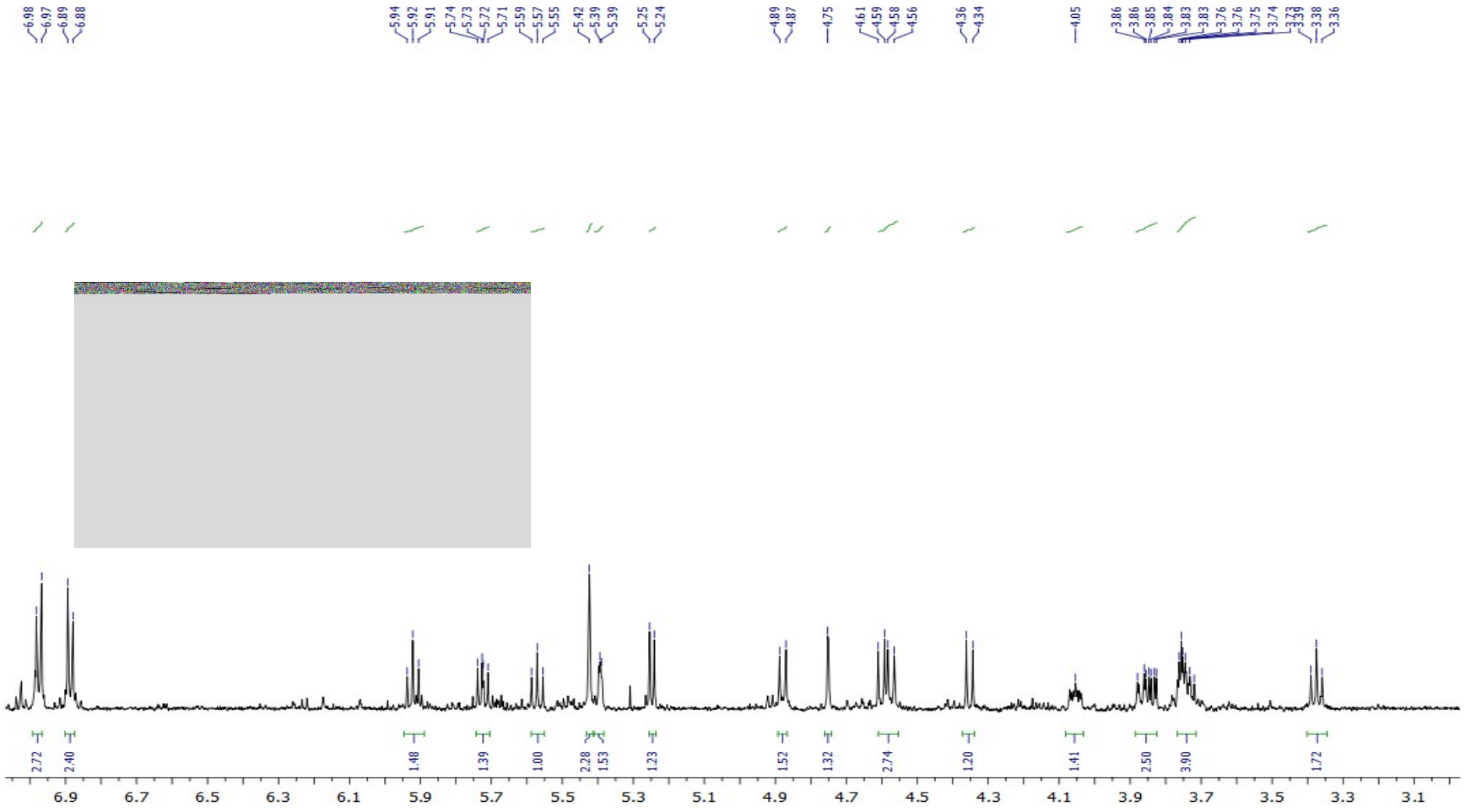
ESI-MS data of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (17a)



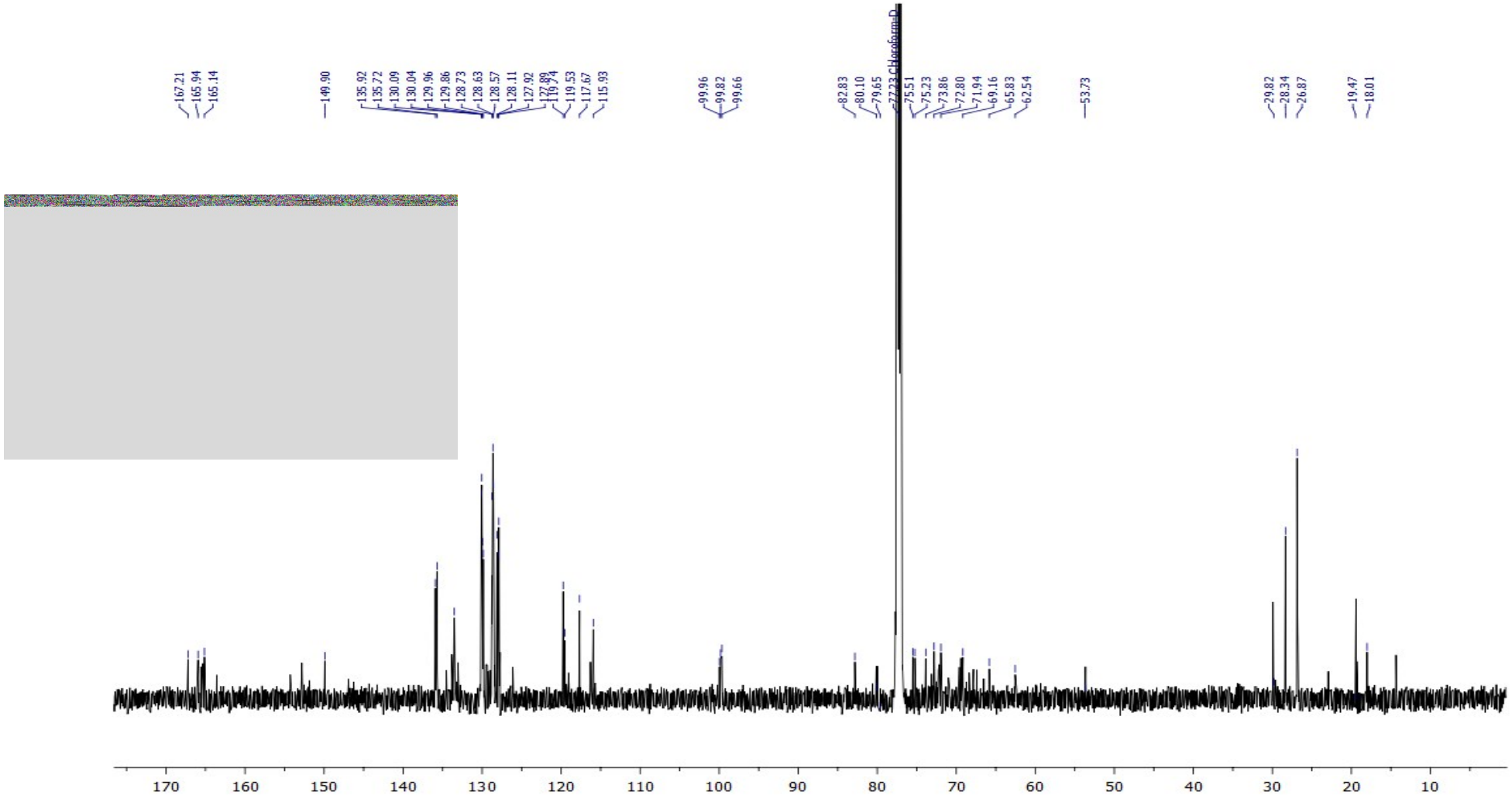
^{1}H NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (17a)



^{1}H NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (17a)



^{13}C NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (17a)



COSY NMR of 4-hydroxyphenyl-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (17a)