

Efficient assembly of oligomannosides using the hydrophobically assisted switching phase method

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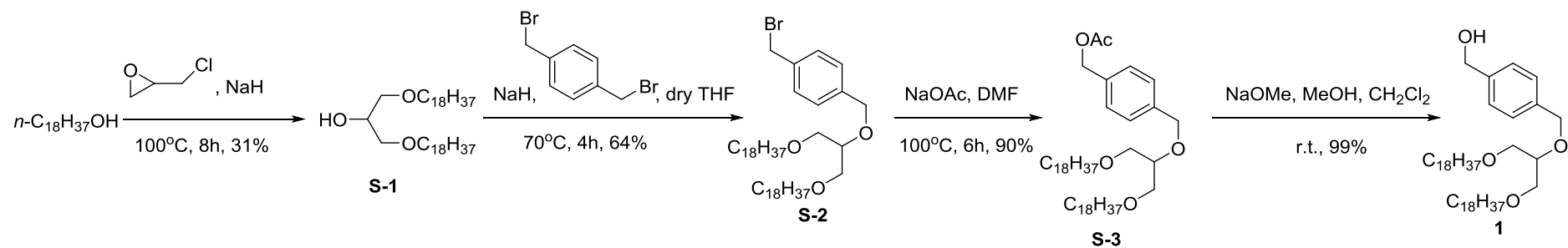
The State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, Beijing 100191, P R China

E-mail: zjli@bjmu.edu.cn

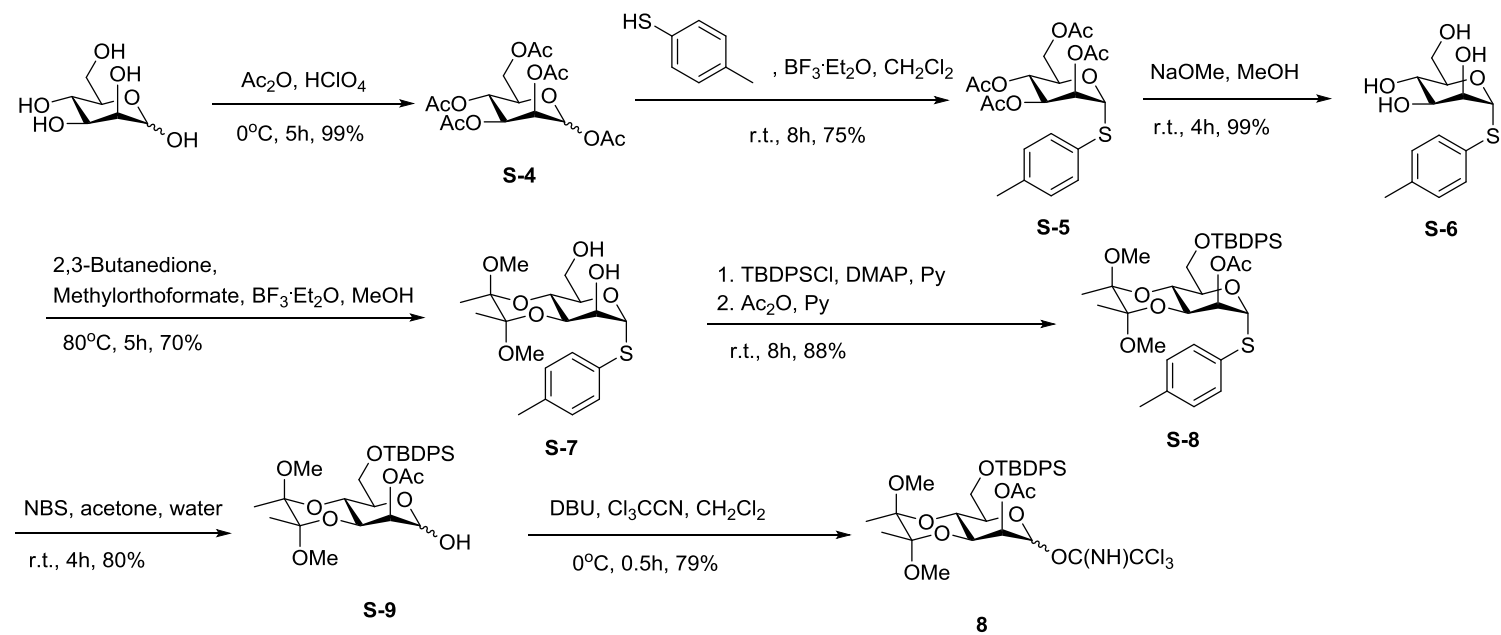
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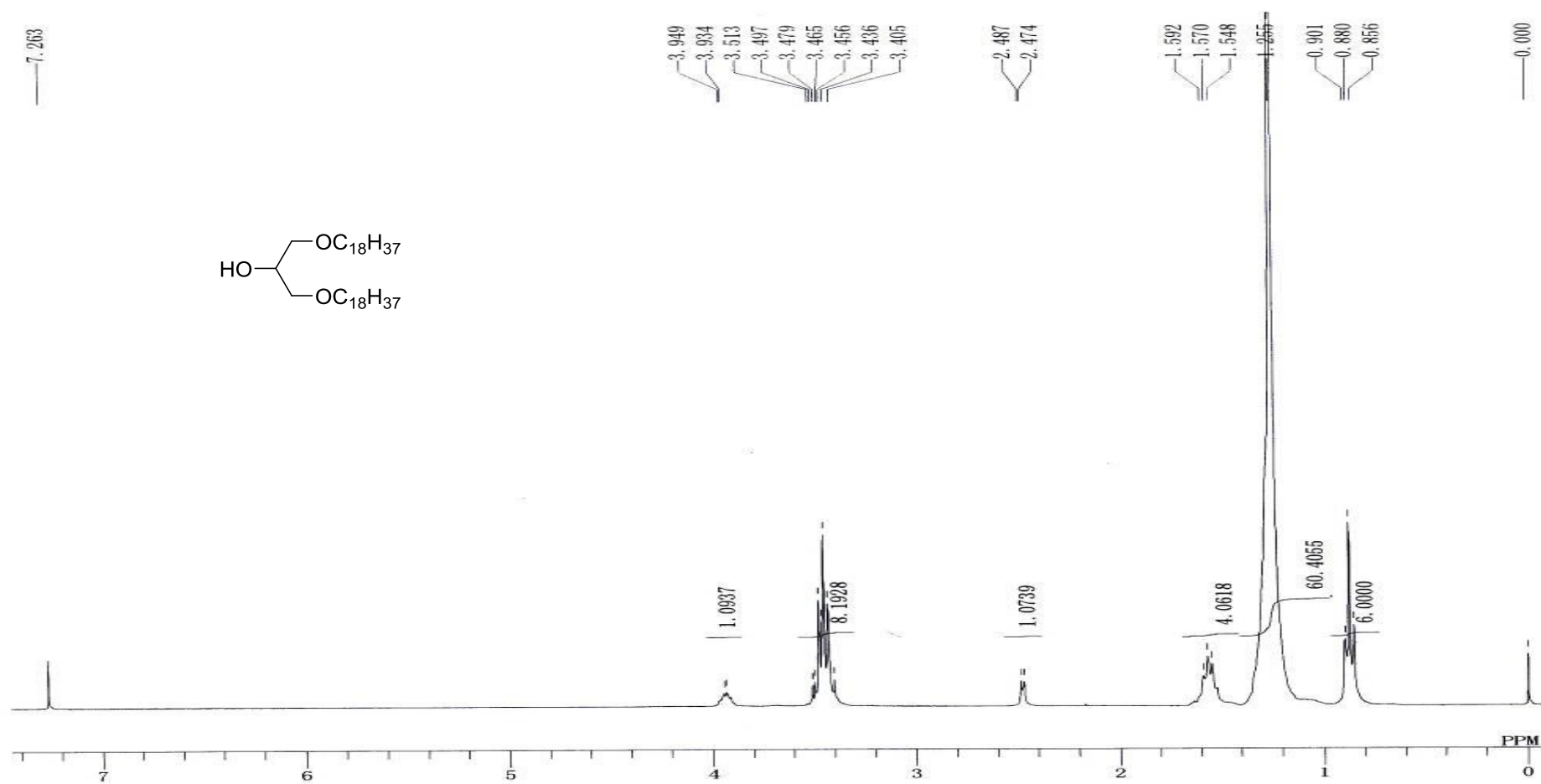
Synthesis of Compound 1:



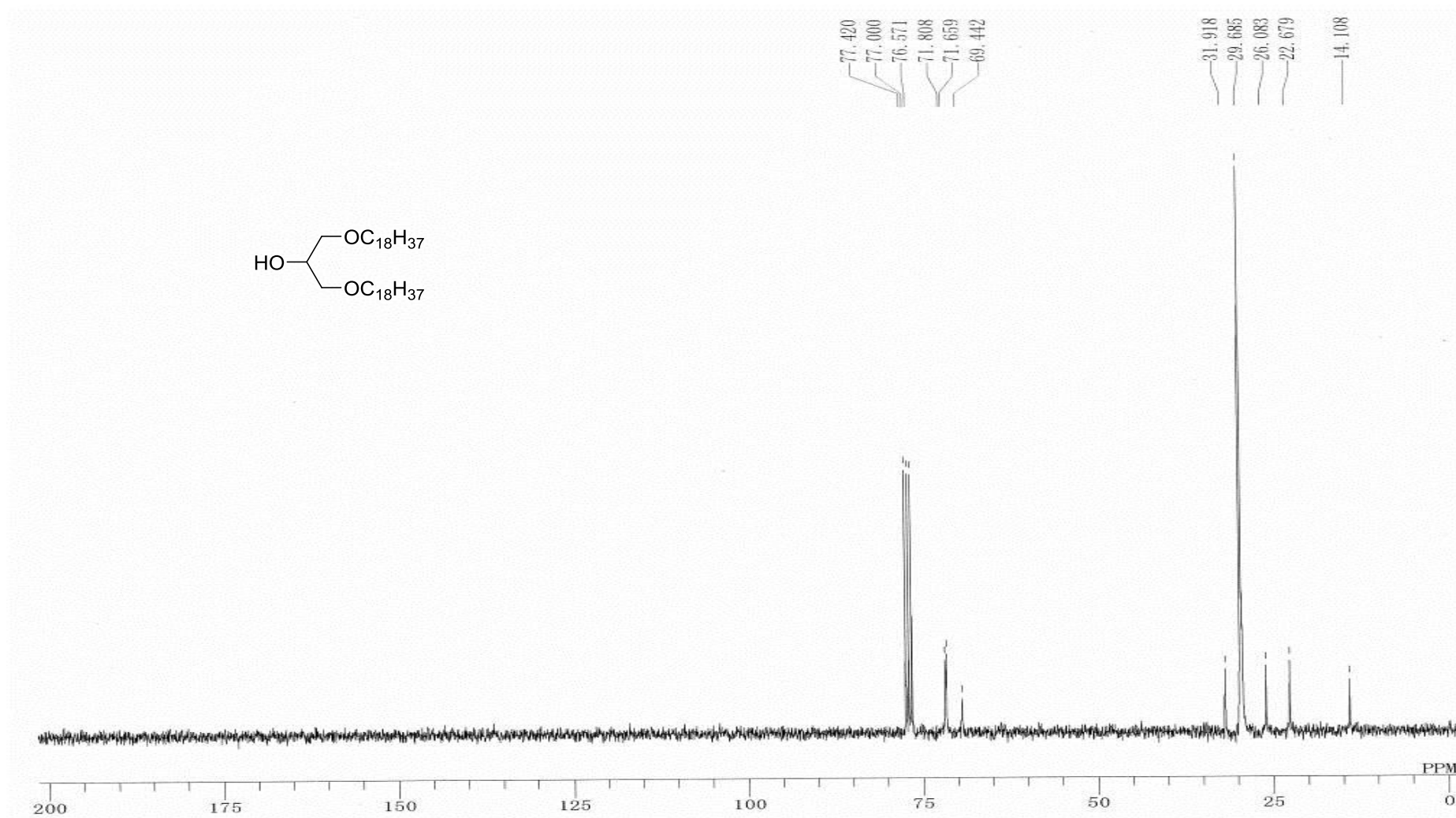
Synthesis of Compound 8:



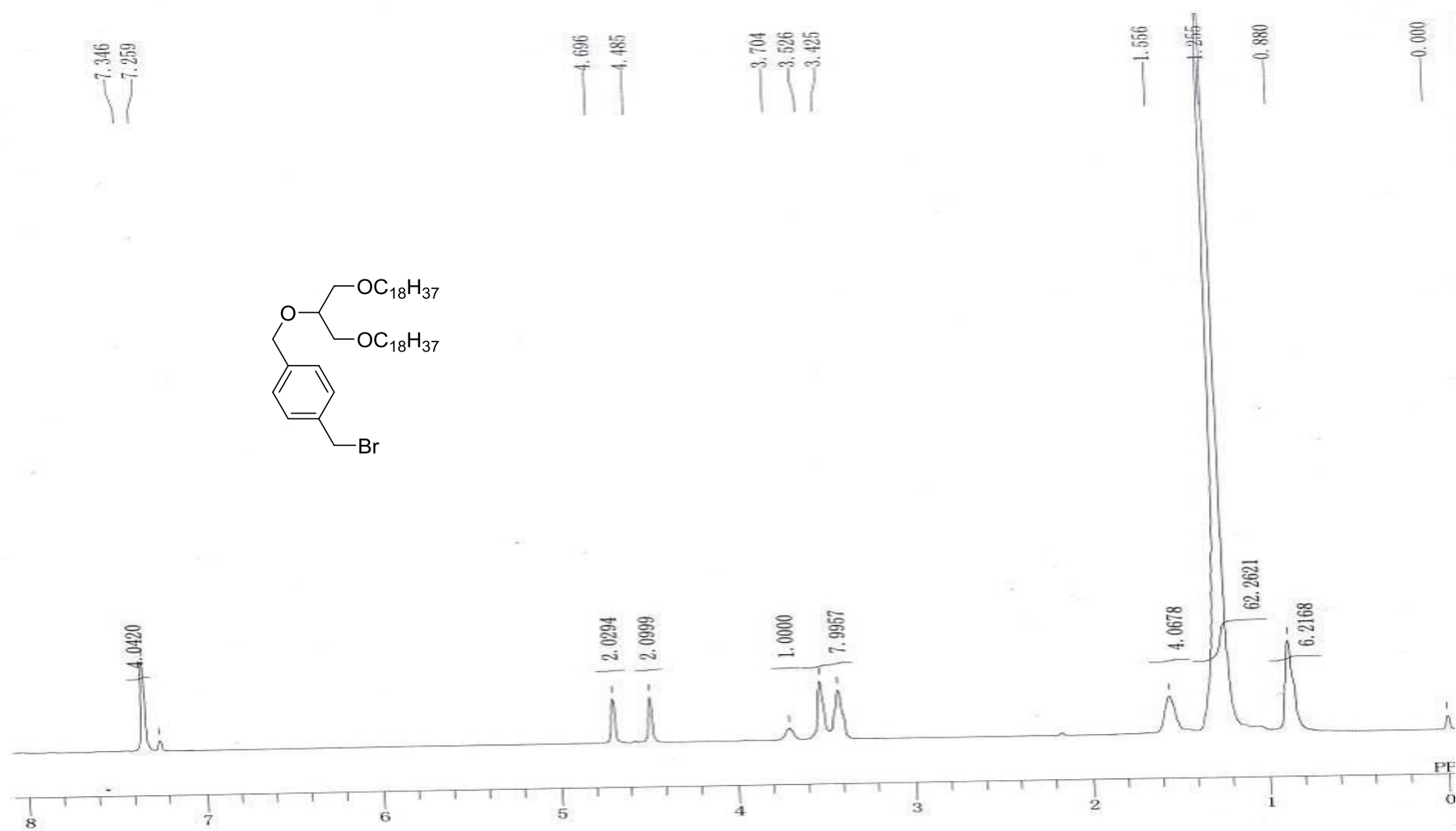
¹H NMR of Compound **S-1** (CDCl₃, 300MHz)



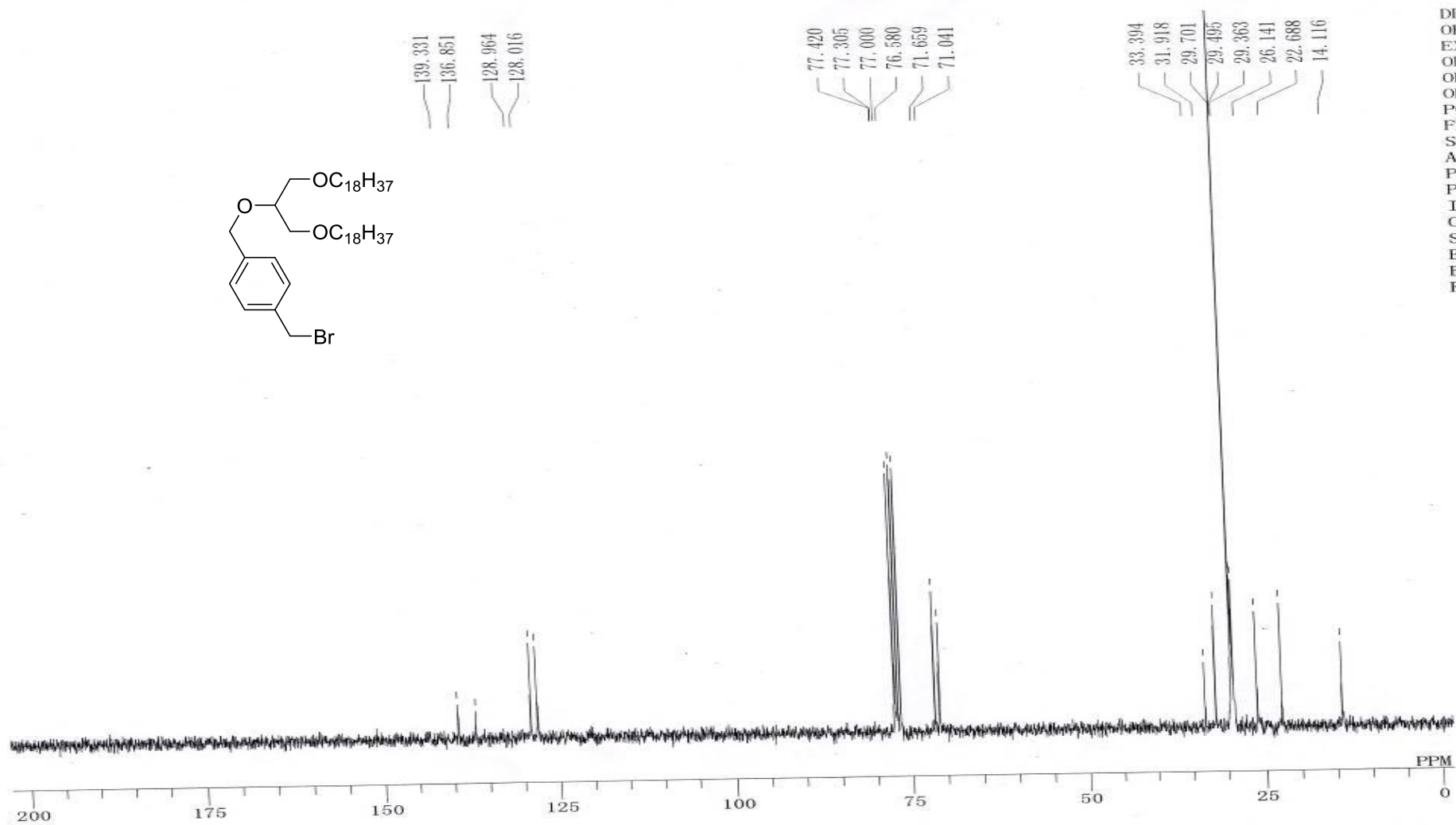
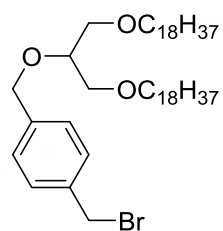
¹³C NMR of Compound **S-1** (CDCl₃, 75MHz)



^1H NMR of Compound S-2 (CDCl_3 , 300MHz)

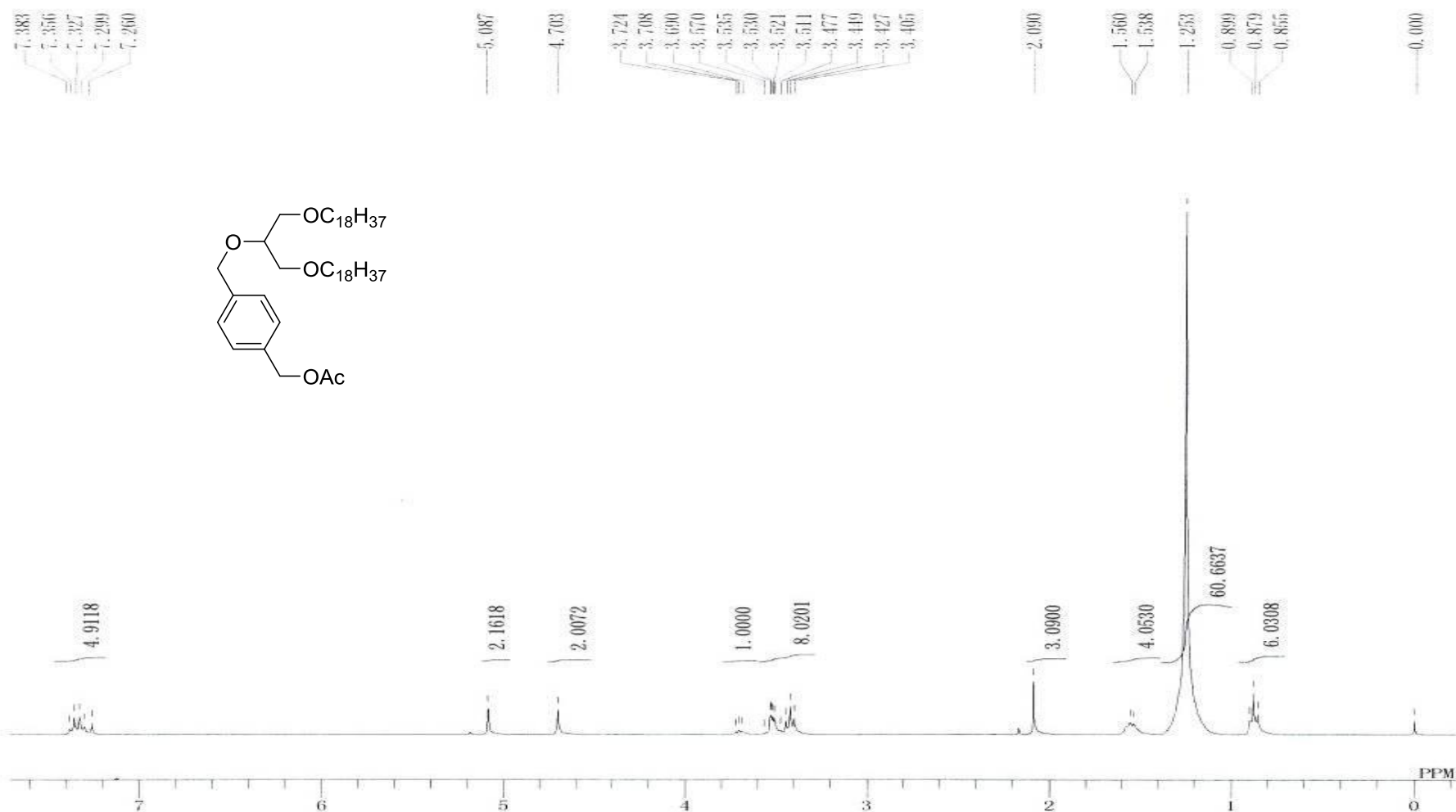


¹³C NMR of Compound **S-2** (CDCl₃, 75MHz)

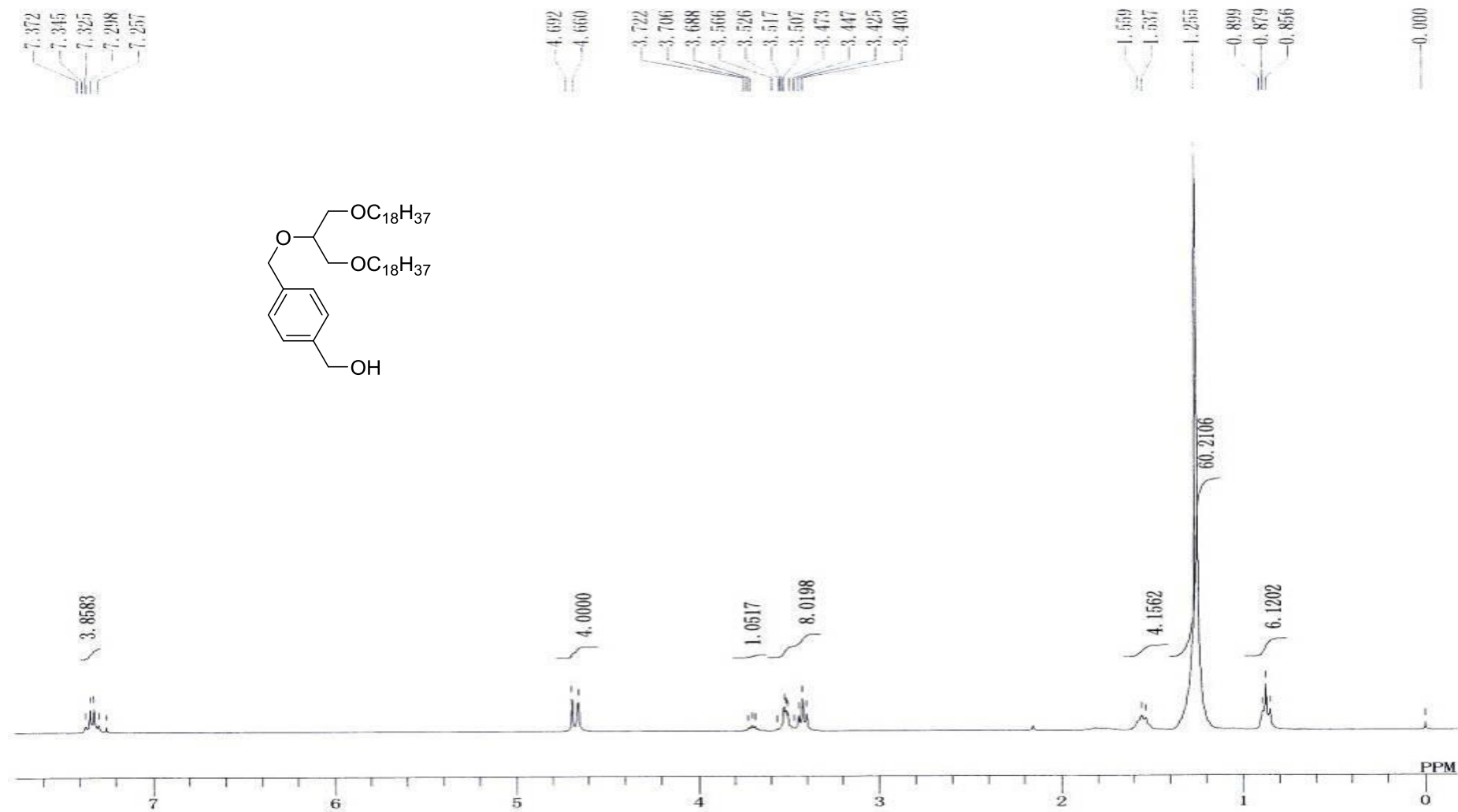


DF
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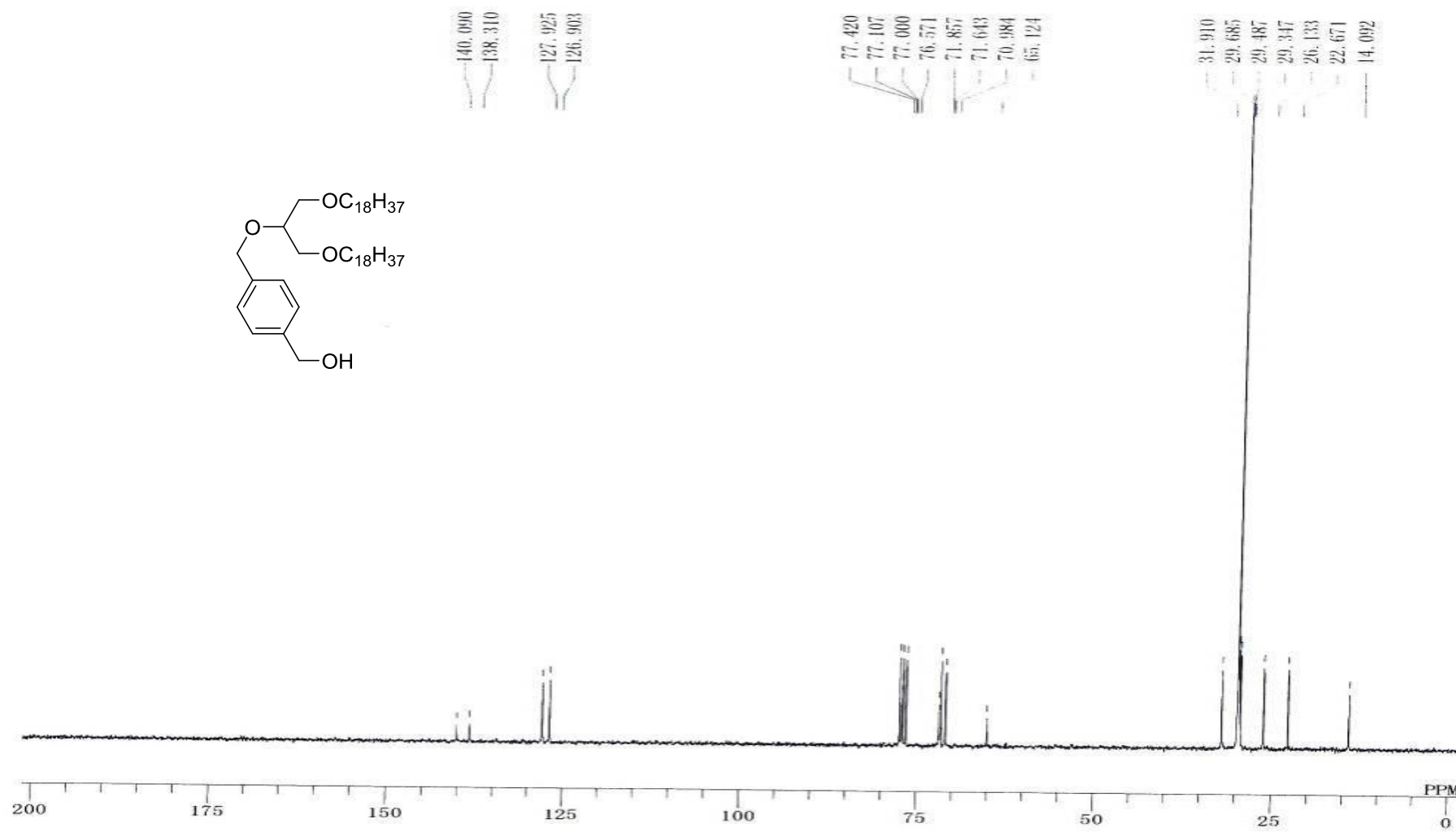
¹H NMR of Compound S-3 (CDCl₃, 300MHz)



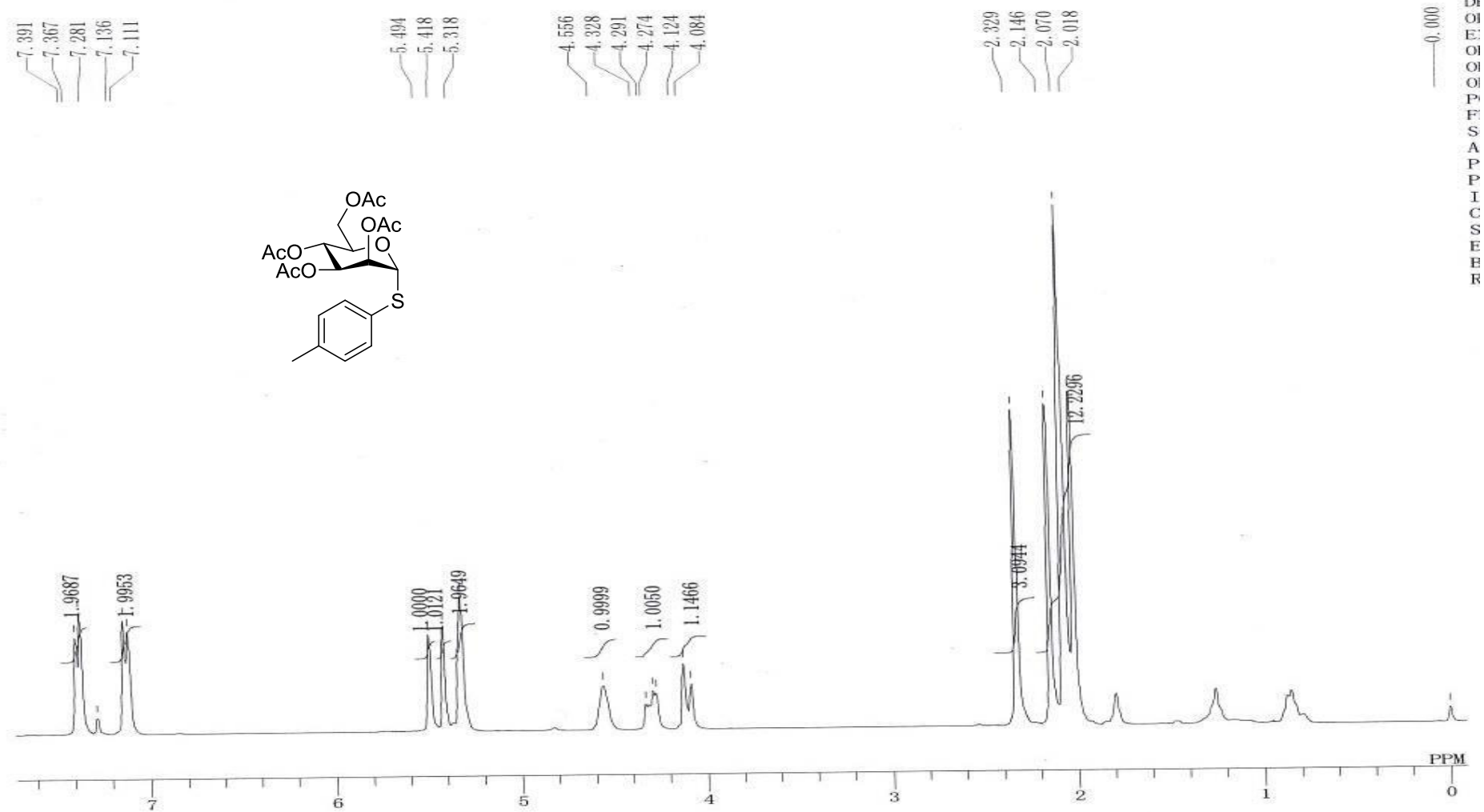
¹H NMR of Compound 1 (CDCl₃, 300MHz)



¹³C NMR of Compound **1** (CDCl₃, 75MHz)



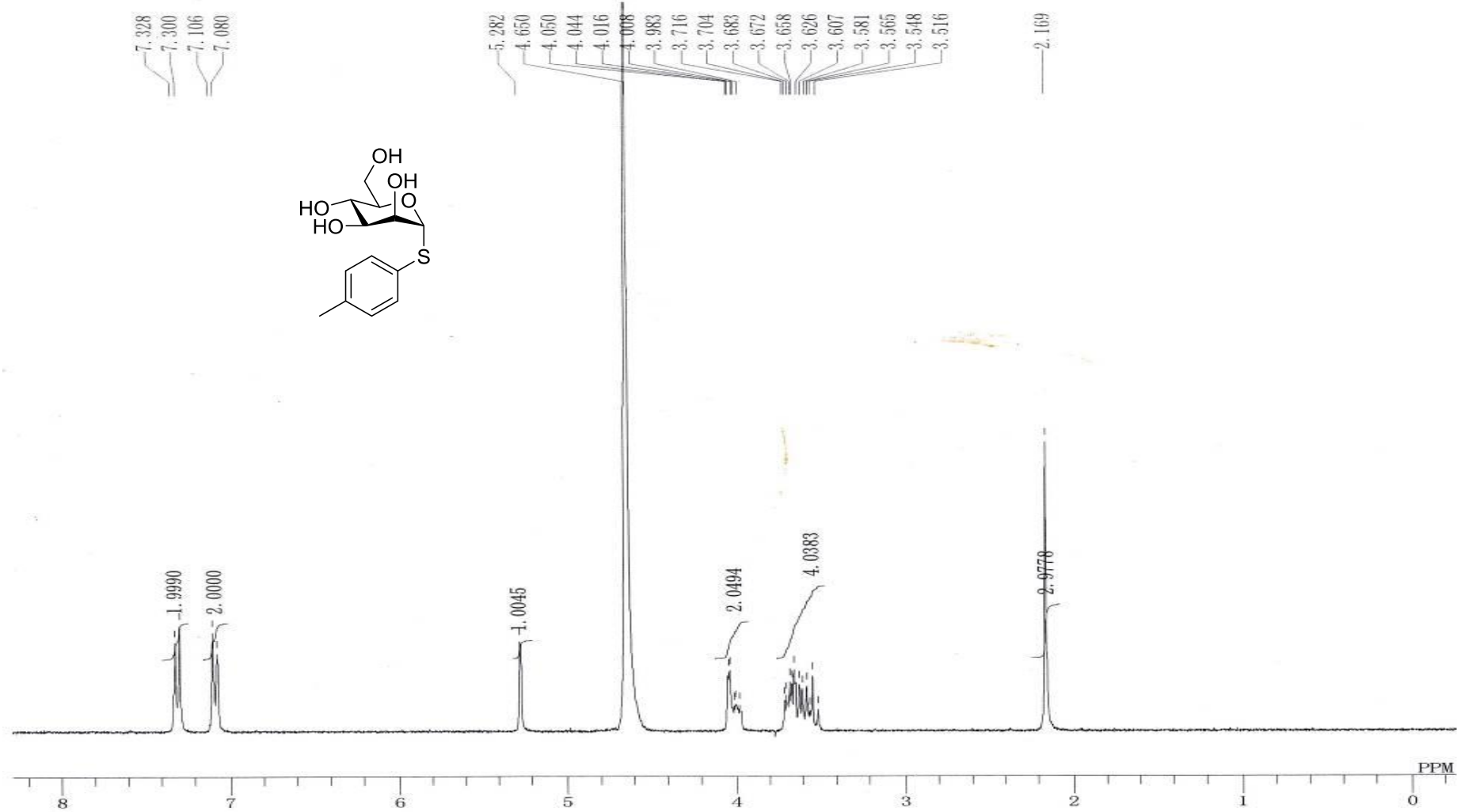
¹H NMR of Compound S-5 (CDCl₃, 300MHz)



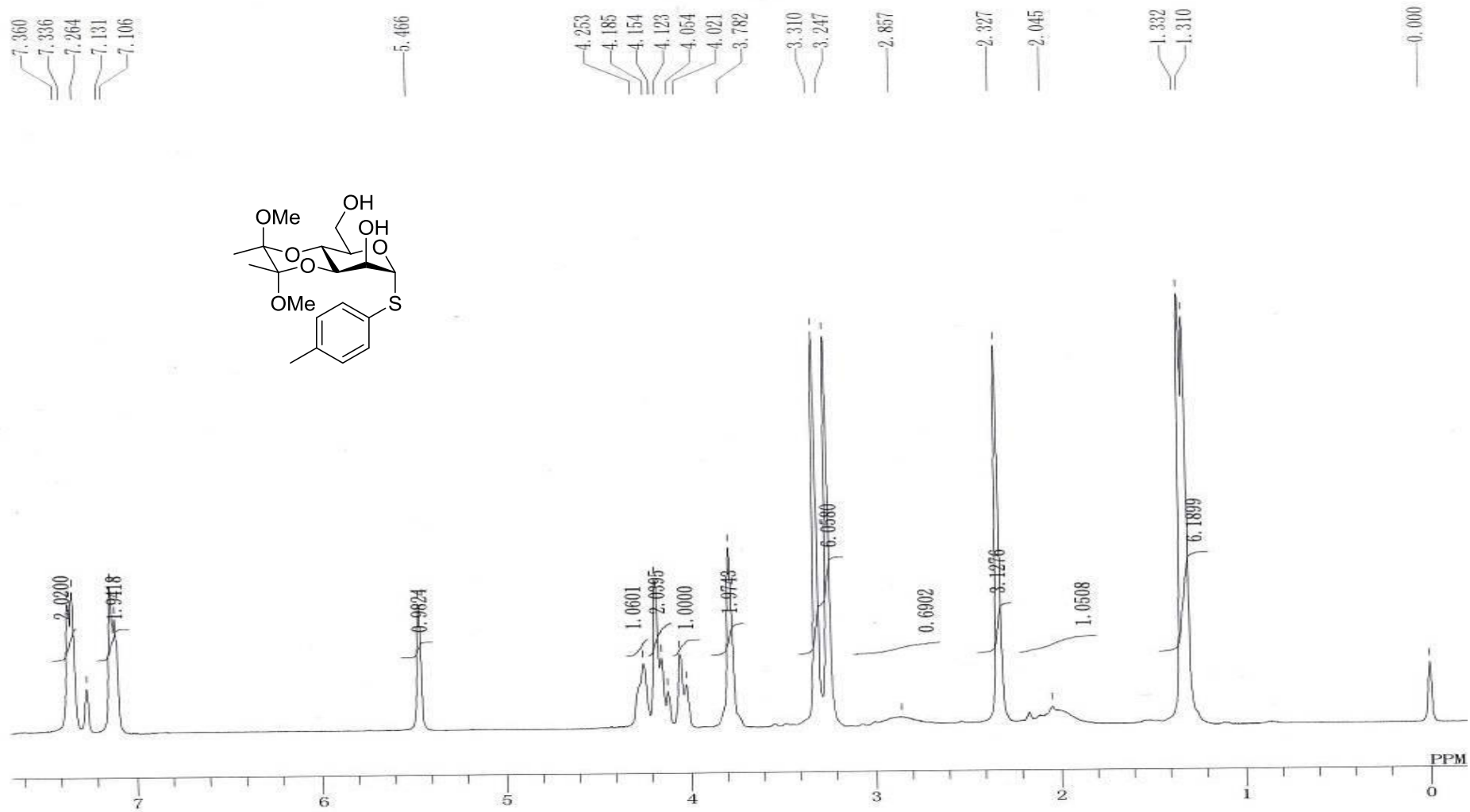
¹³C NMR of Compound **S-5** (CDCl₃, 75MHz)



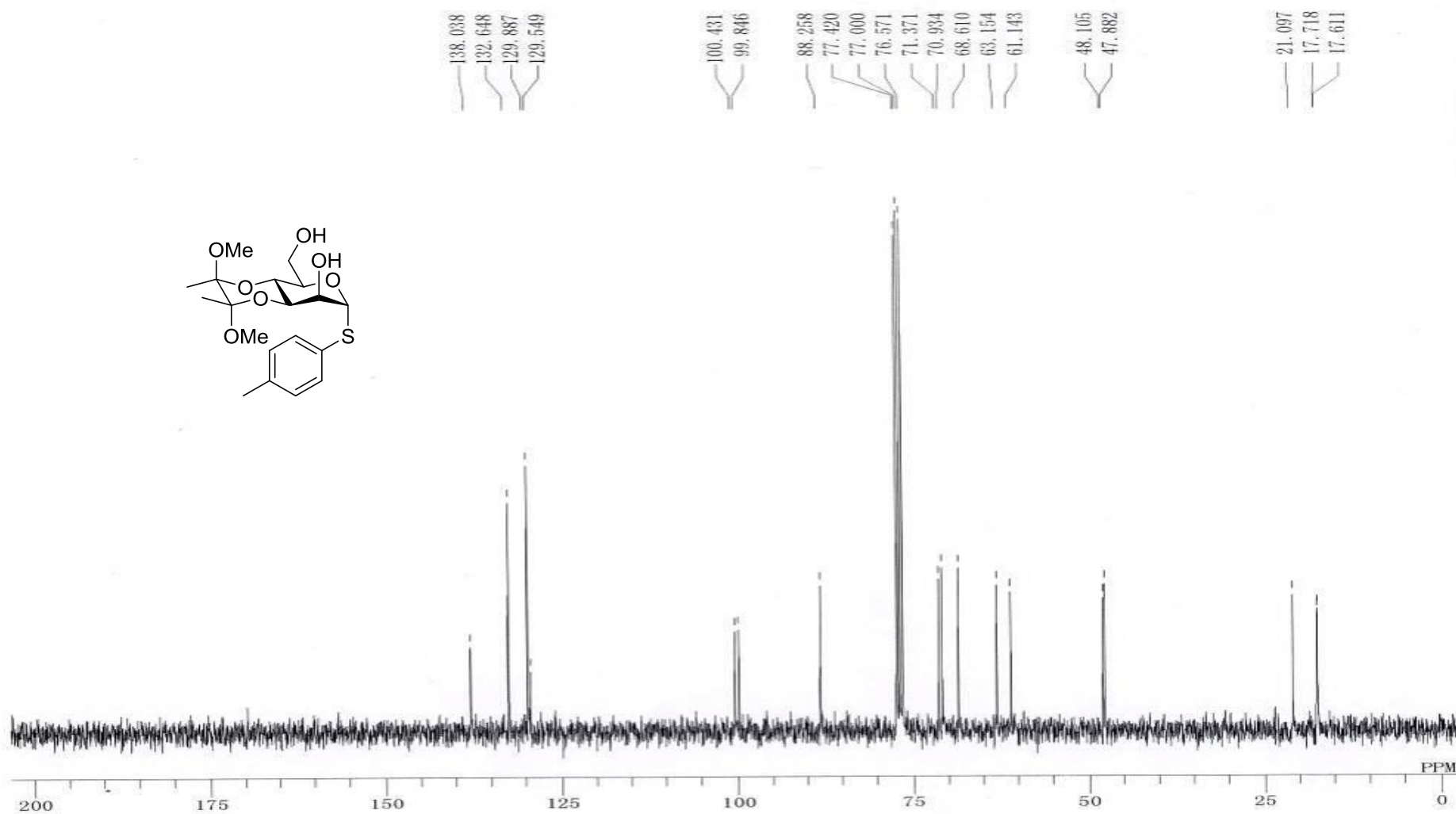
¹H NMR of Compound **S-6** (D₂O, 300MHz)



¹H NMR of Compound S-7 (CDCl₃, 300MHz)



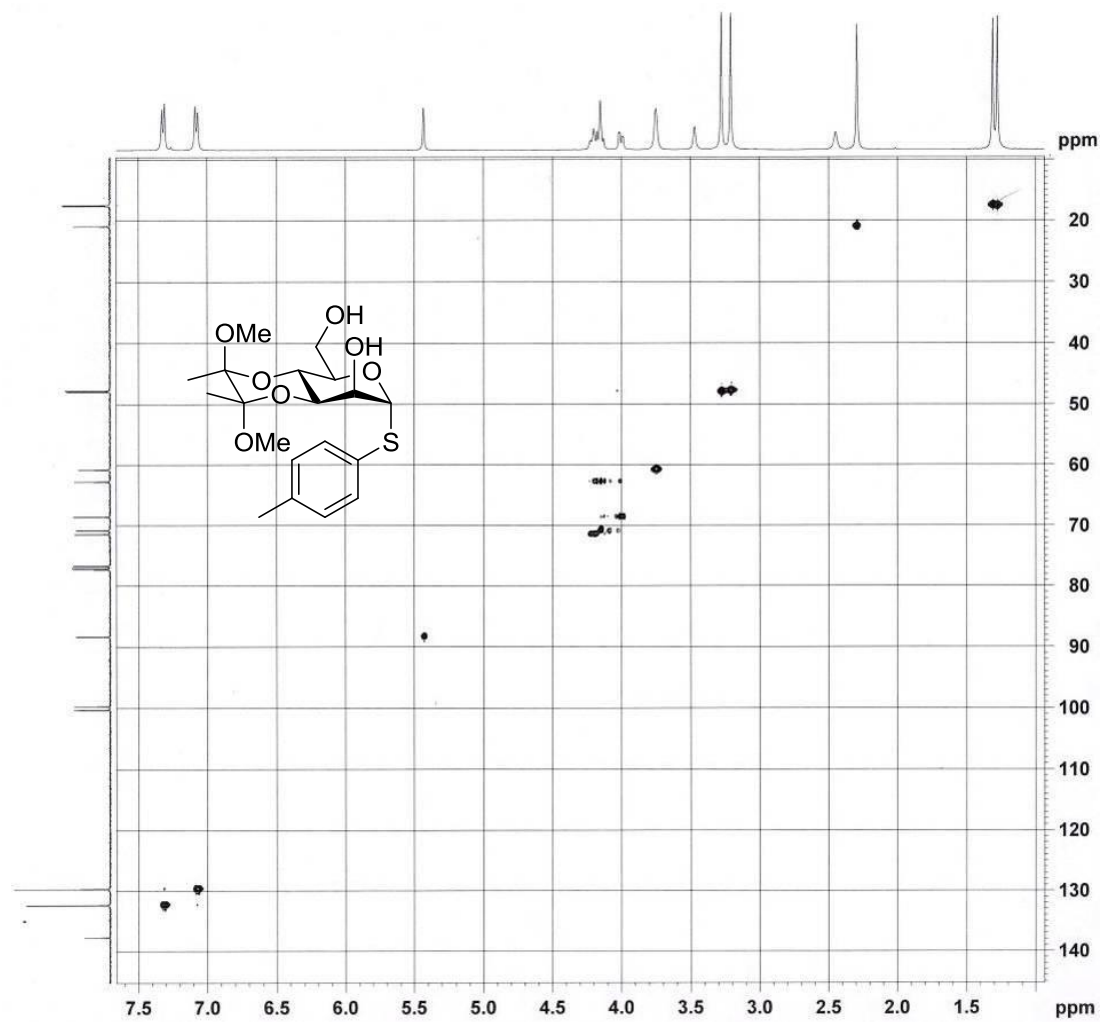
¹³C NMR of Compound **S-7** (CDCl₃, 75MHz)



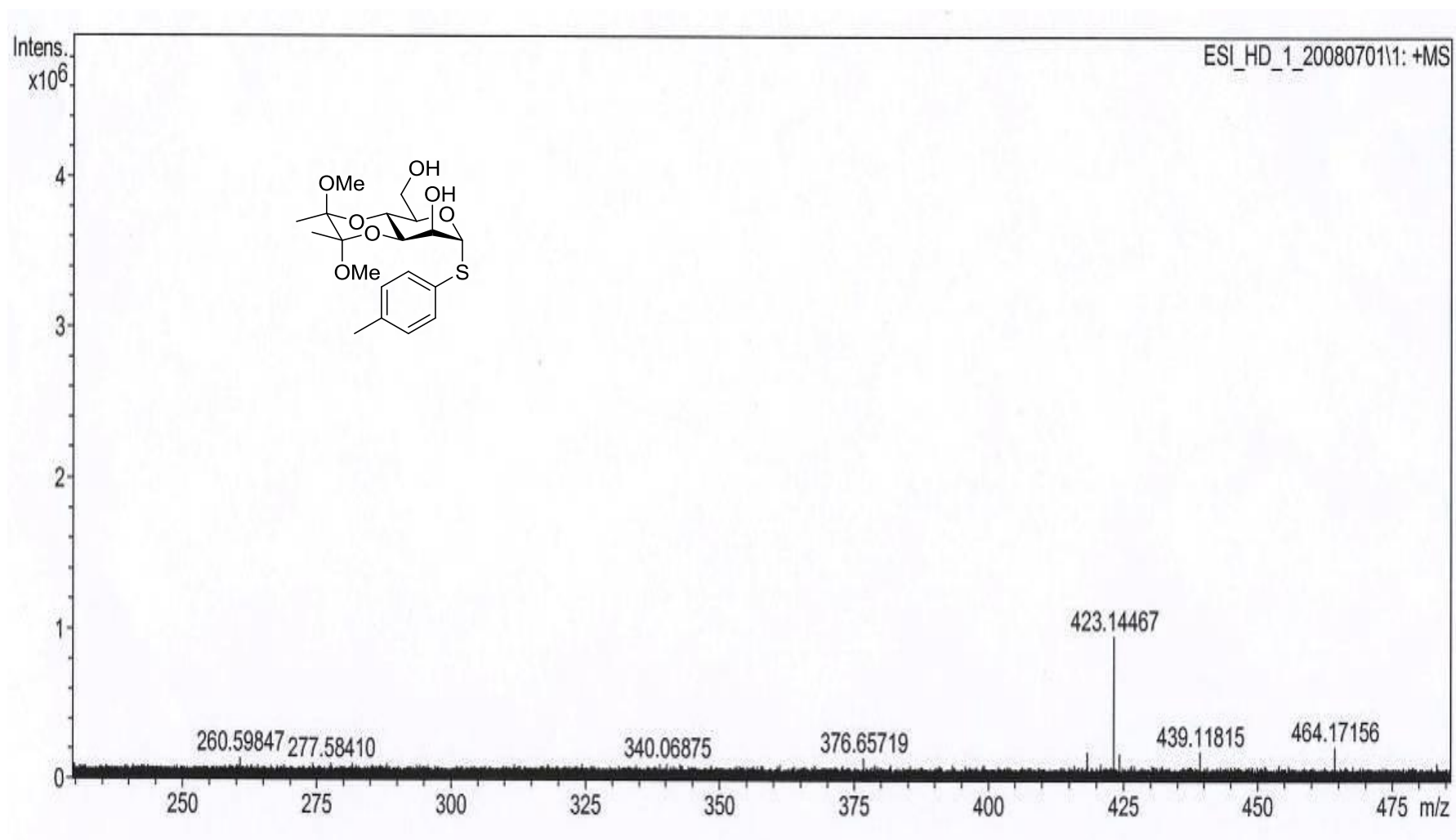
HHCOSY of Compound S-7 (CDCl₃, 300 MHz)



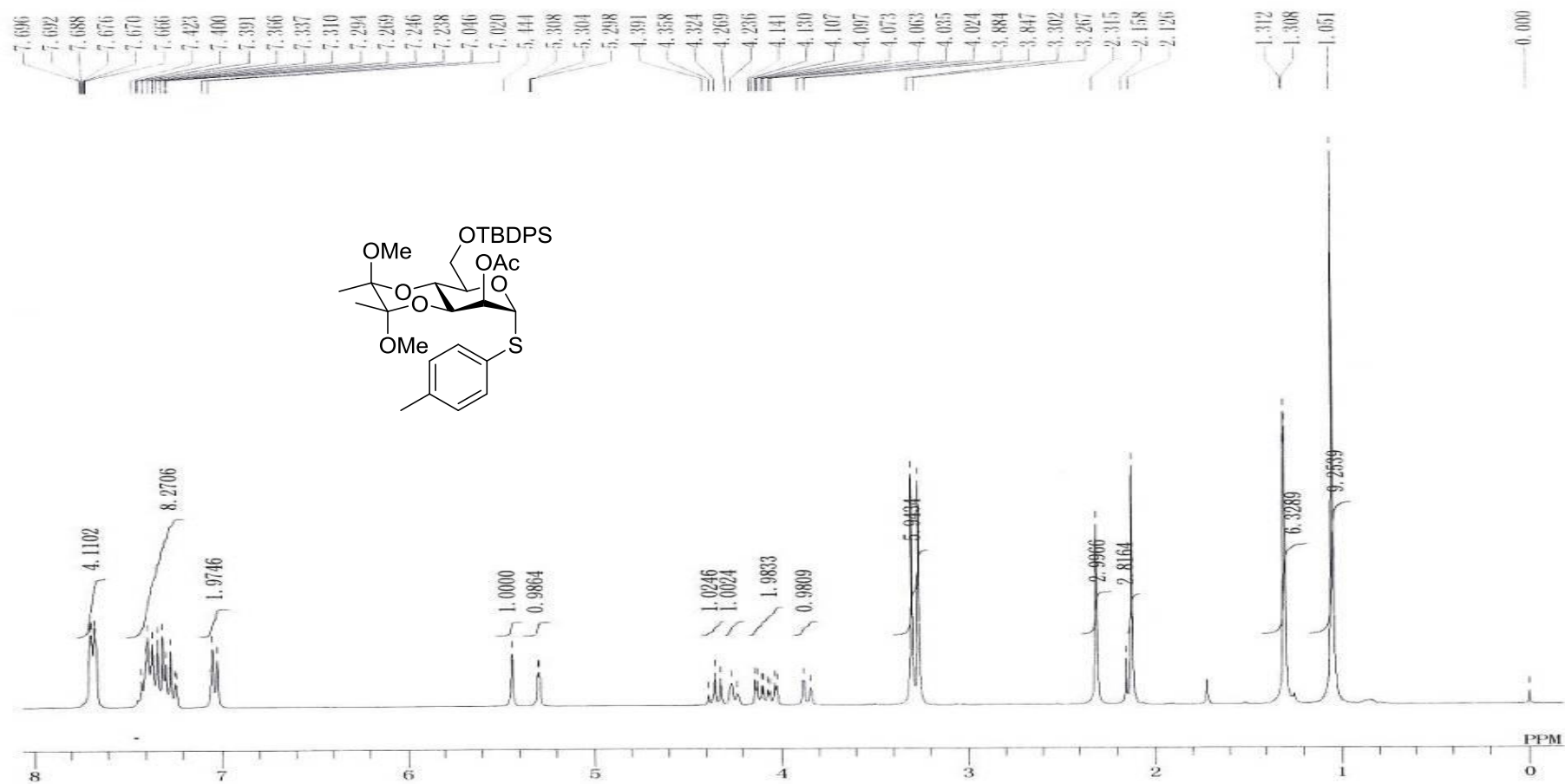
HSQC of Compound S-7 (CDCl₃, 300 MHz)



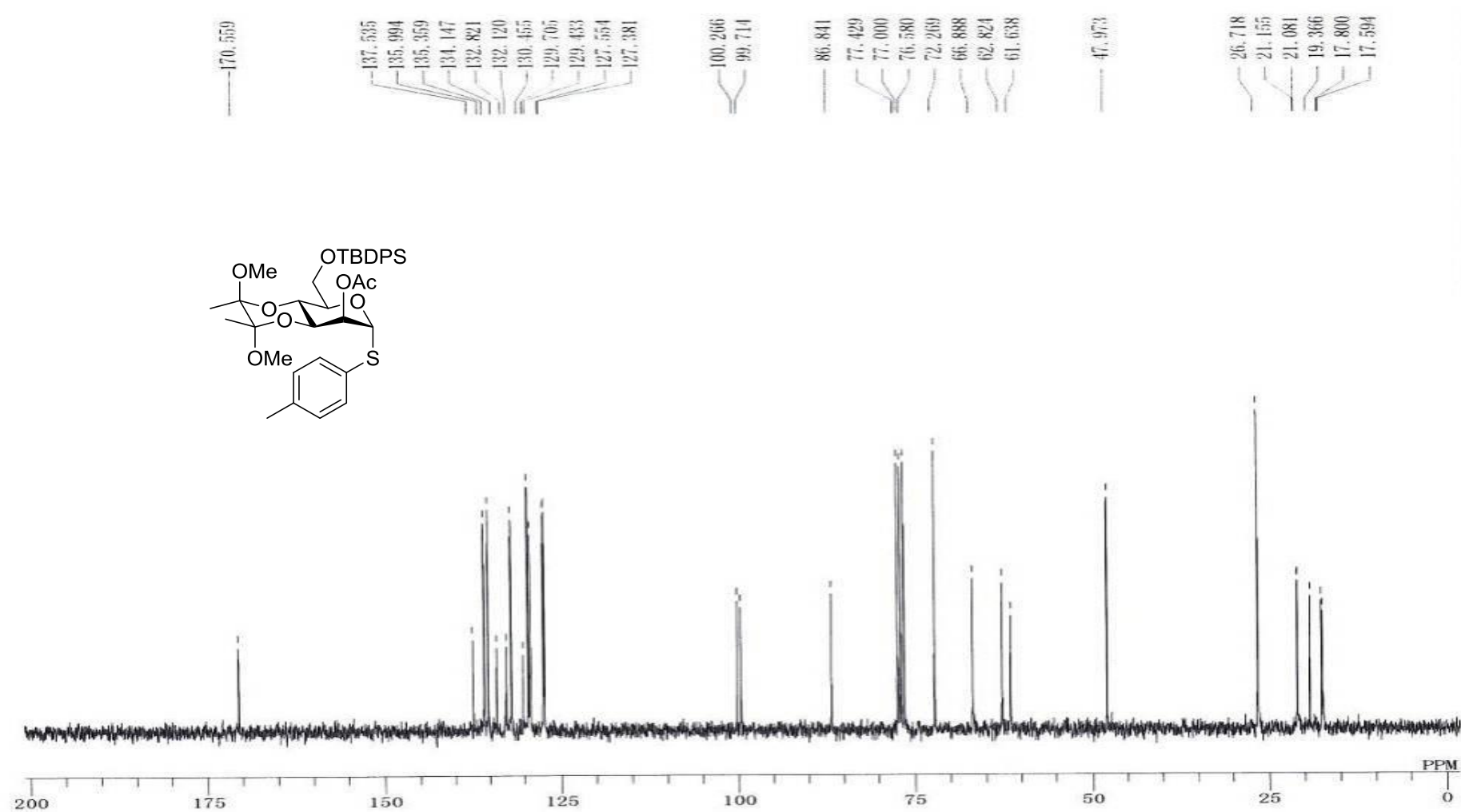
HRMS (ESI) of Compound S-7



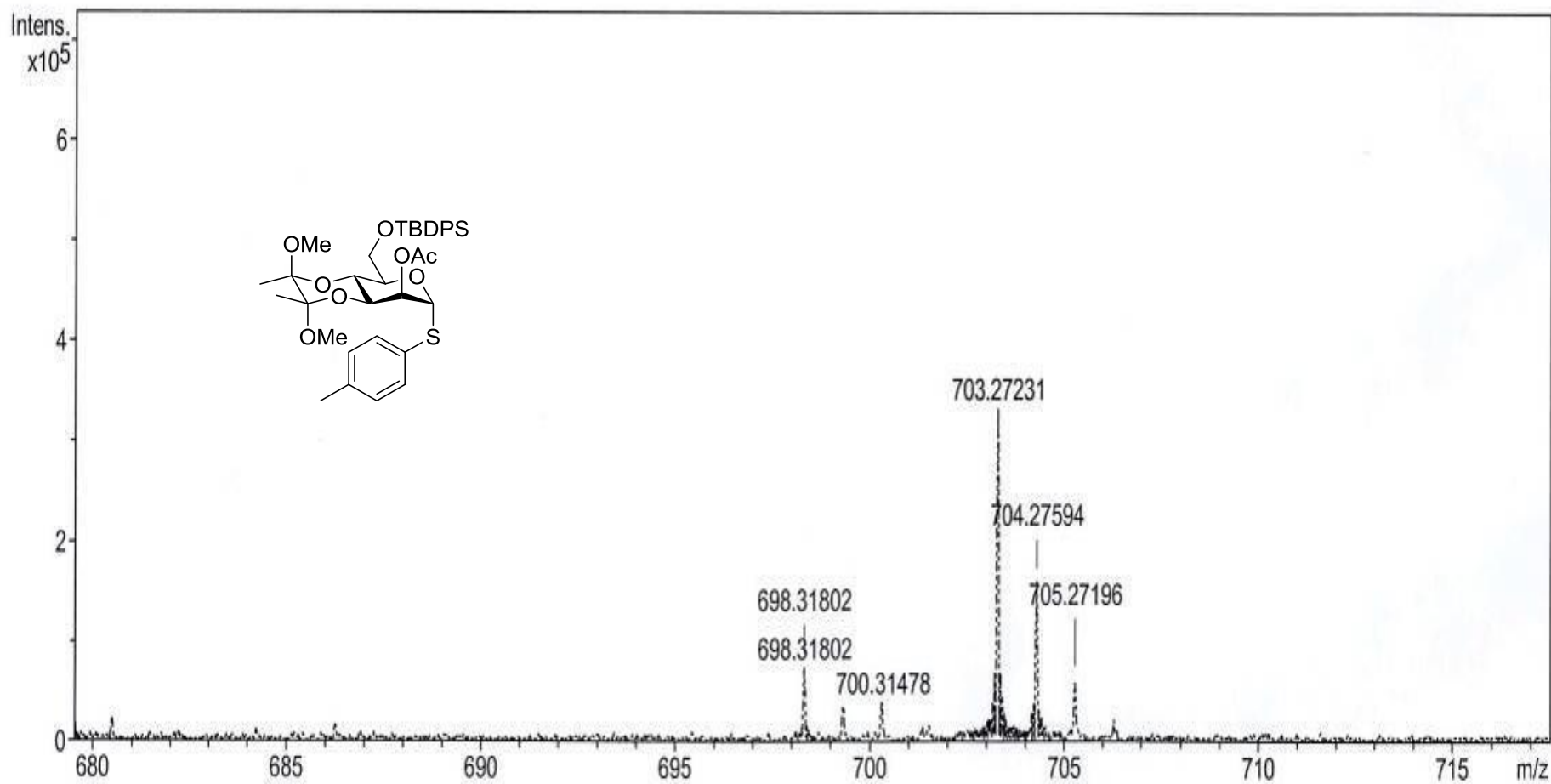
^1H NMR of Compound **S-8** (CDCl_3 , 300MHz)



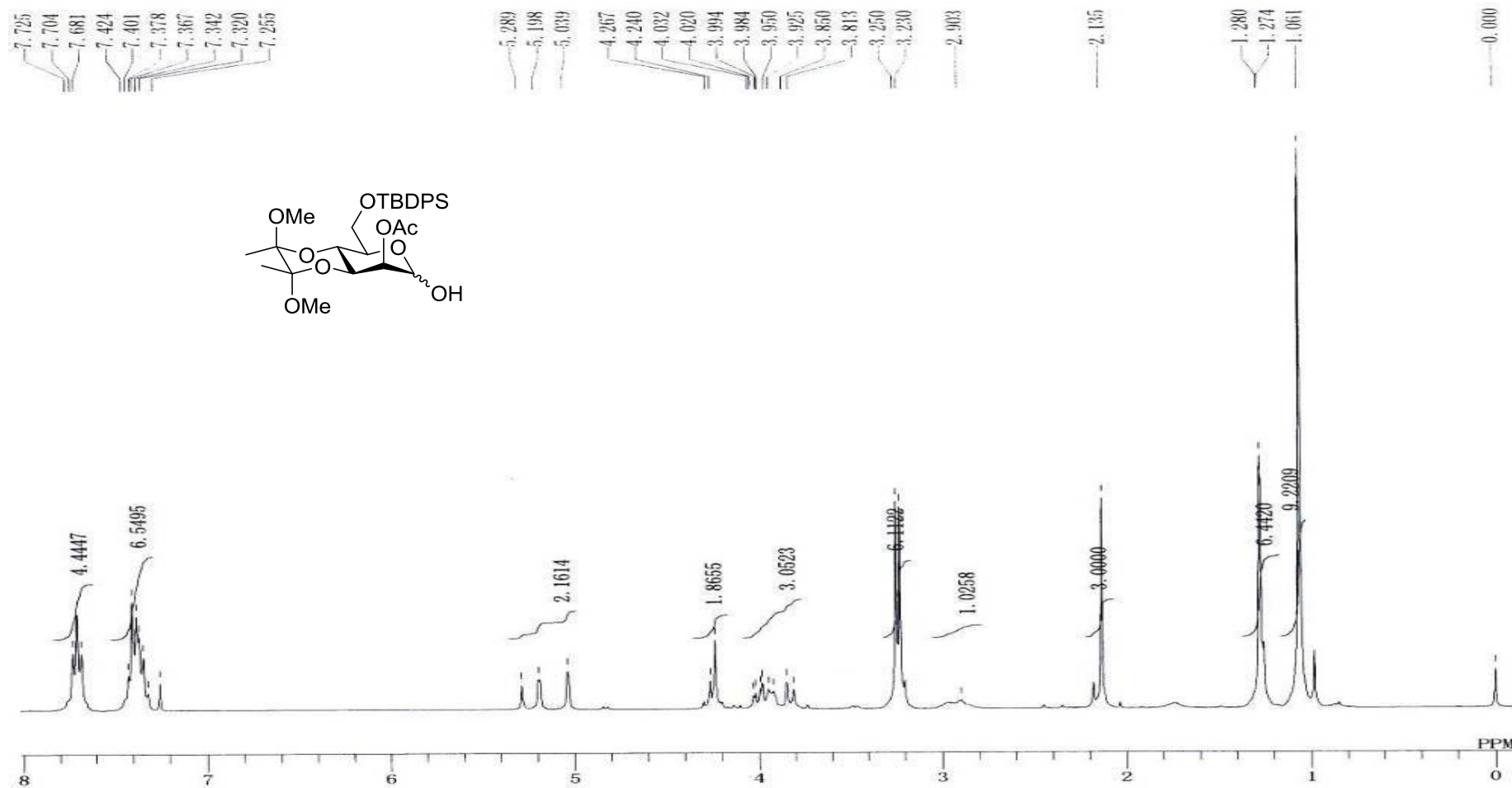
¹³C NMR of Compound **S-8** (CDCl₃, 75MHz)



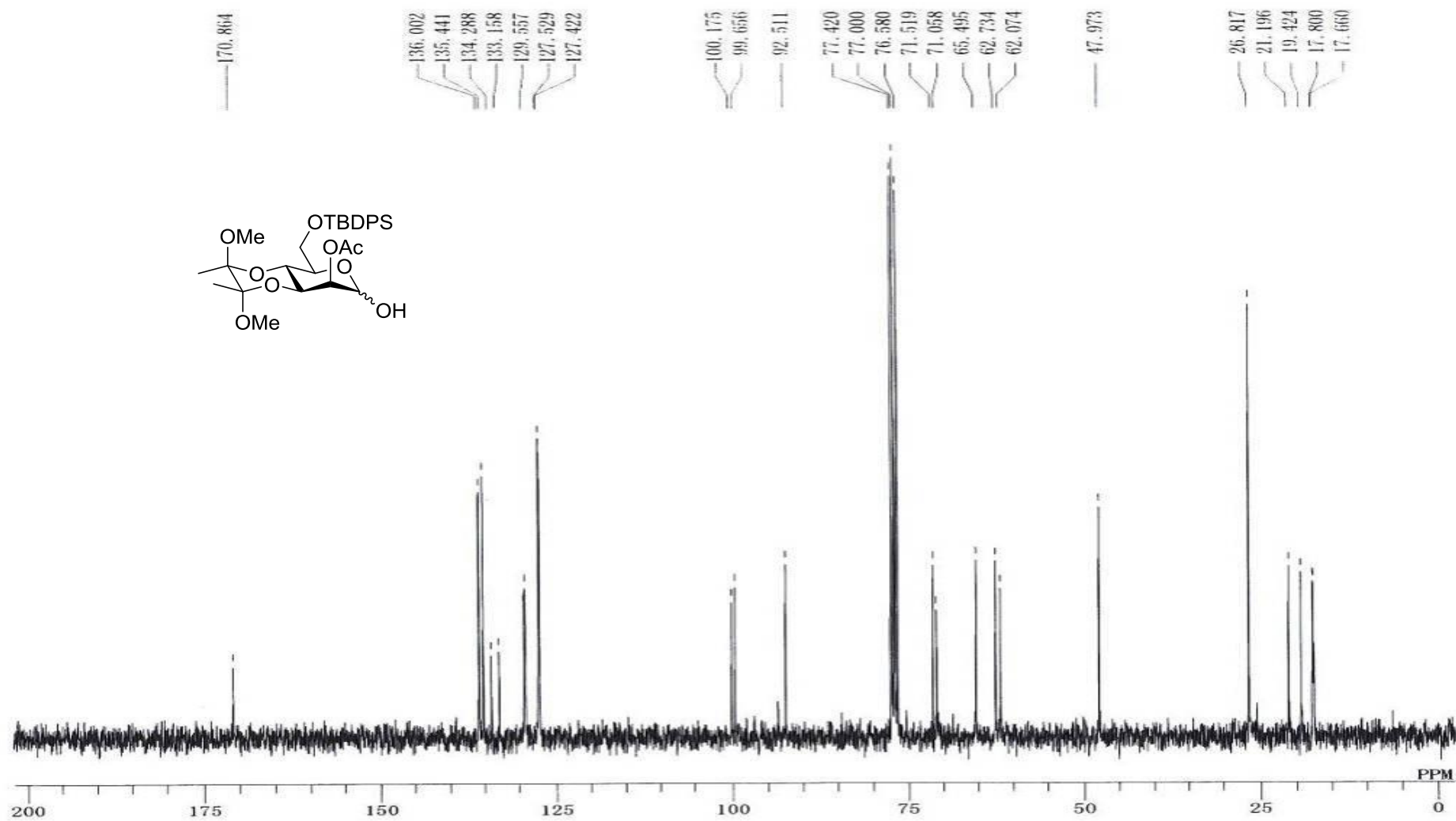
HRMS (ESI) of Compound S-8

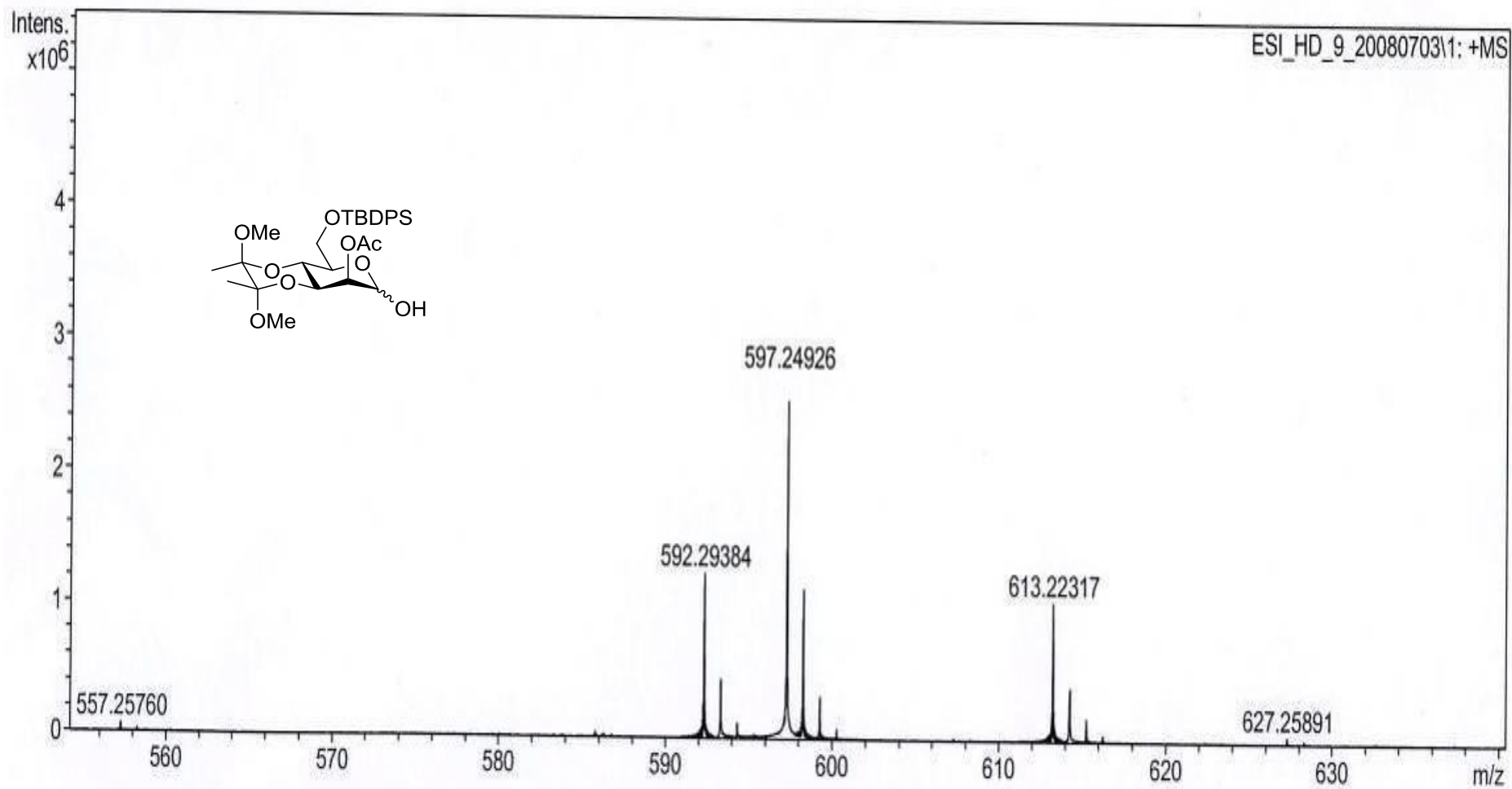


^1H NMR of Compound **S-9** (CDCl_3 , 300MHz)

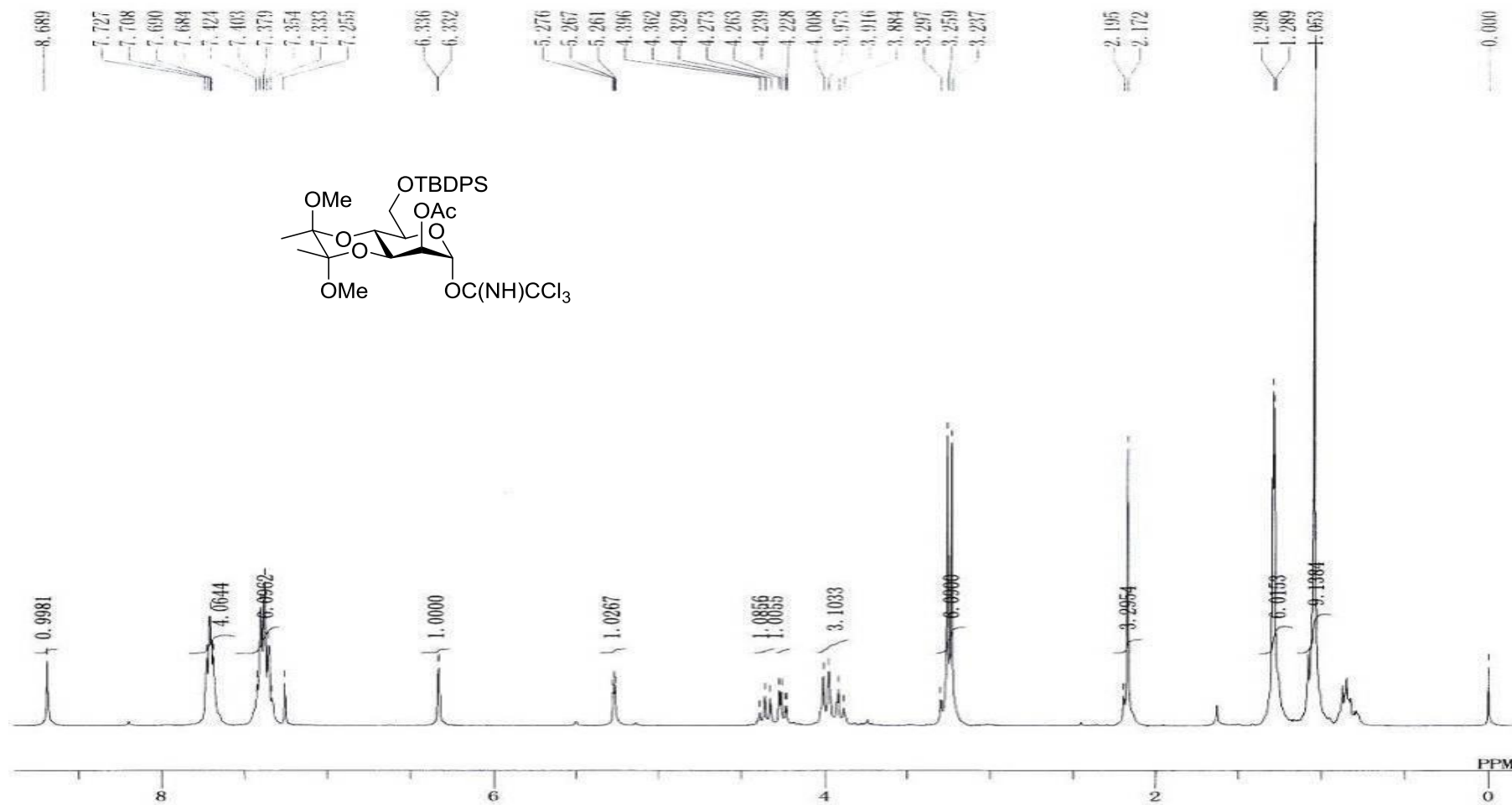


^{13}C NMR of Compound **S-9** (CDCl_3 , 75MHz)

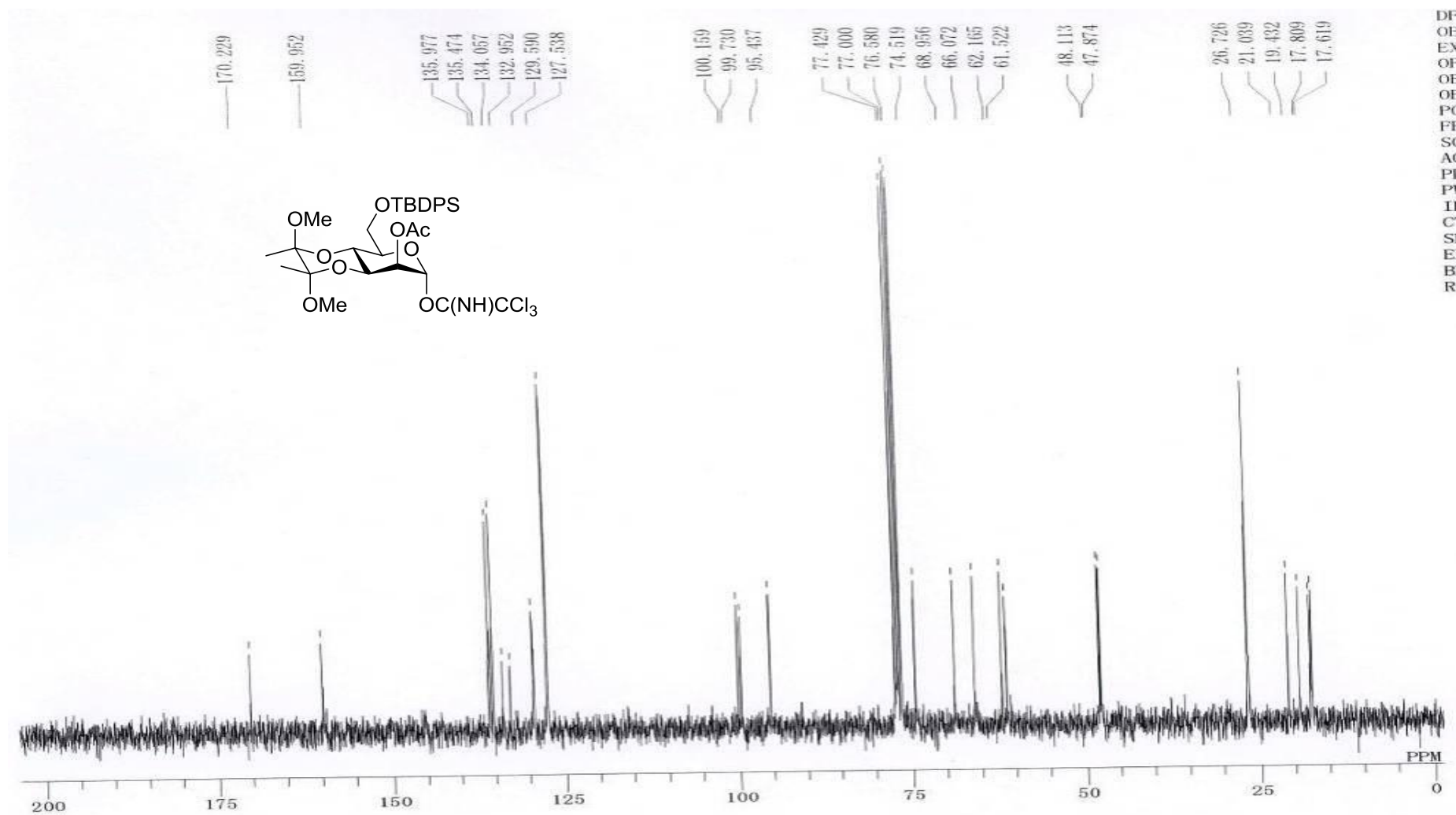


HRMS (ESI) of Compound **S-9**

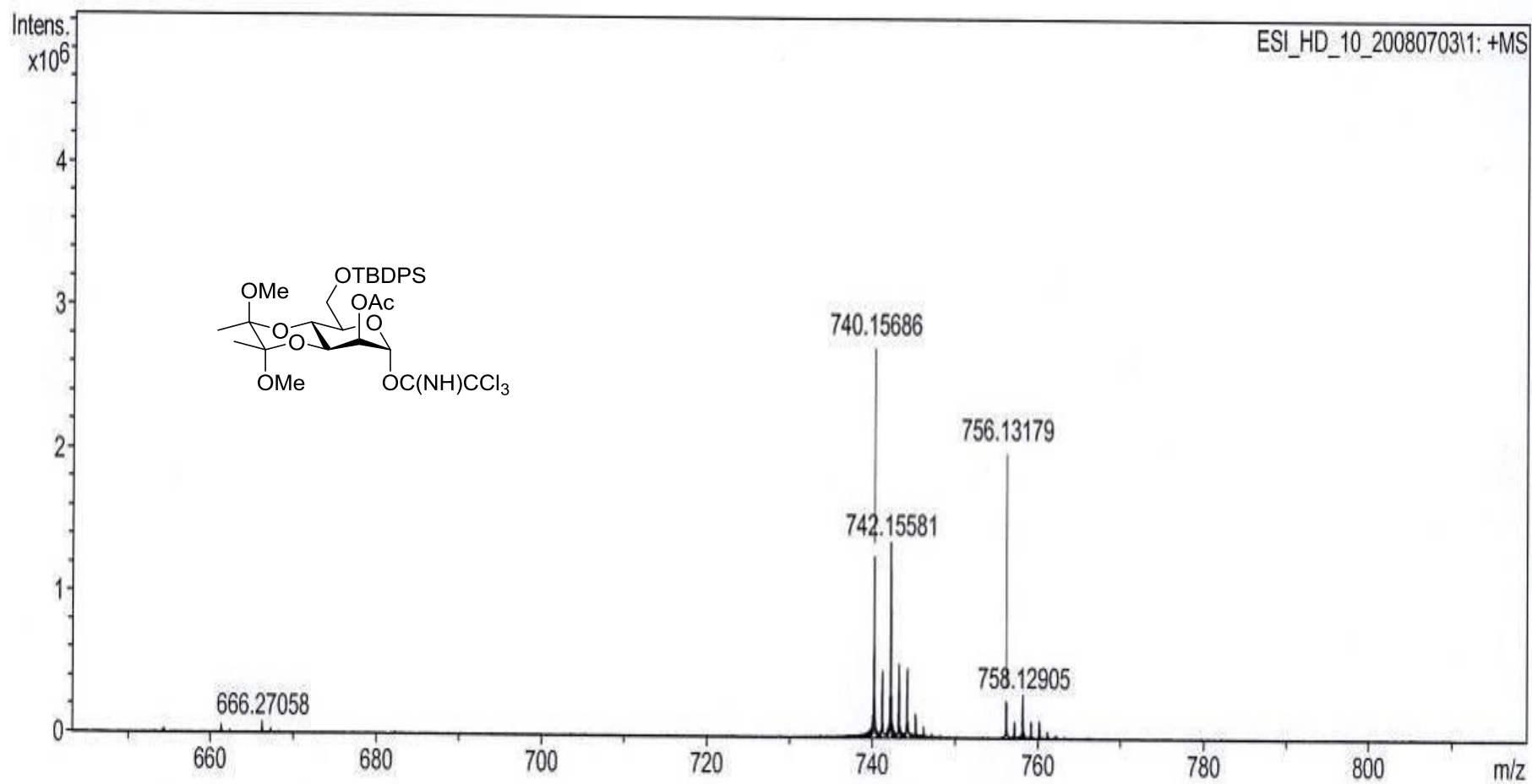
¹H NMR of Compound **8** (CDCl₃, 300MHz)



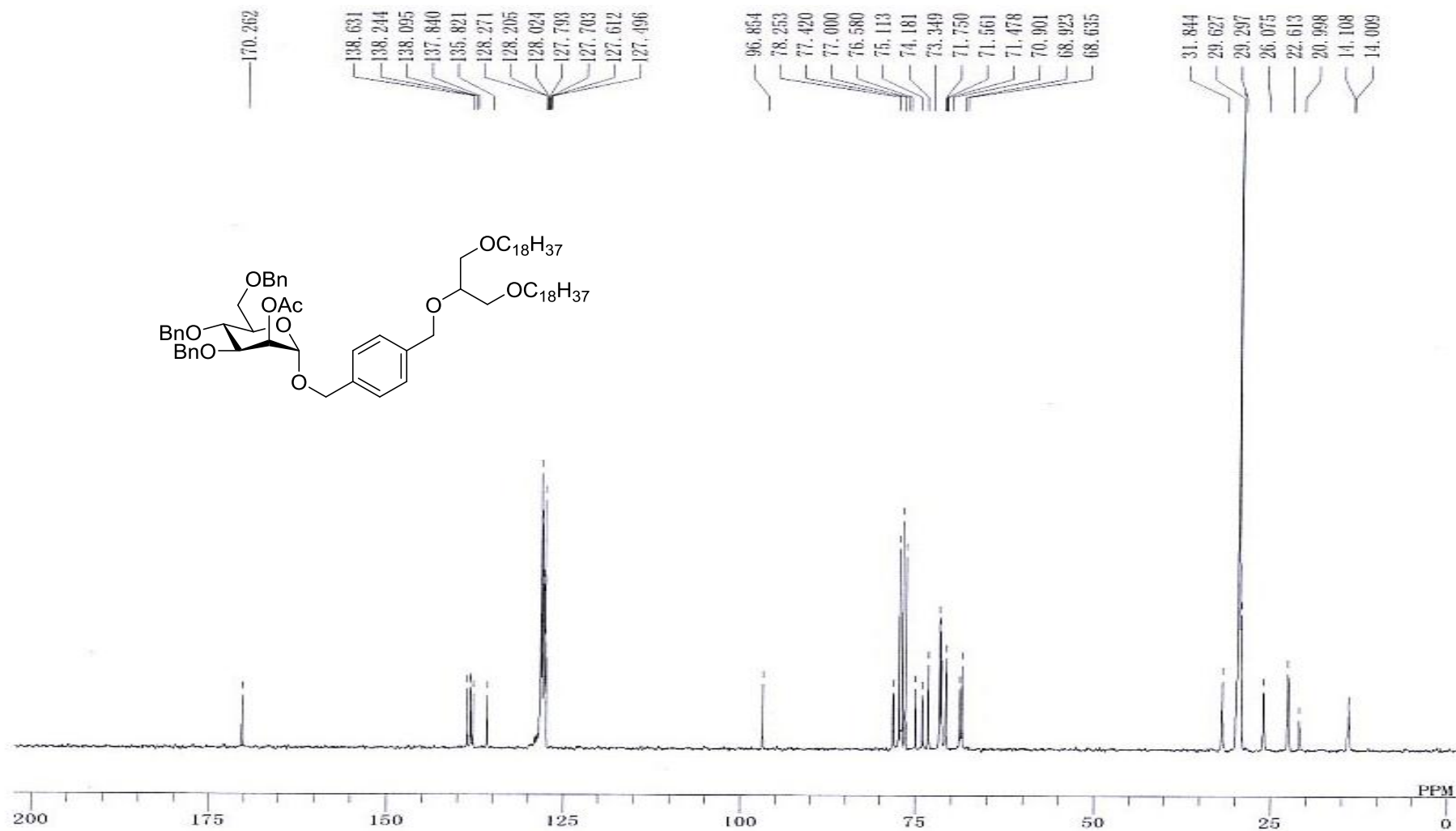
^{13}C NMR of Compound **8** (CDCl_3 , 75MHz)



HRMS (ESI) of Compound 8

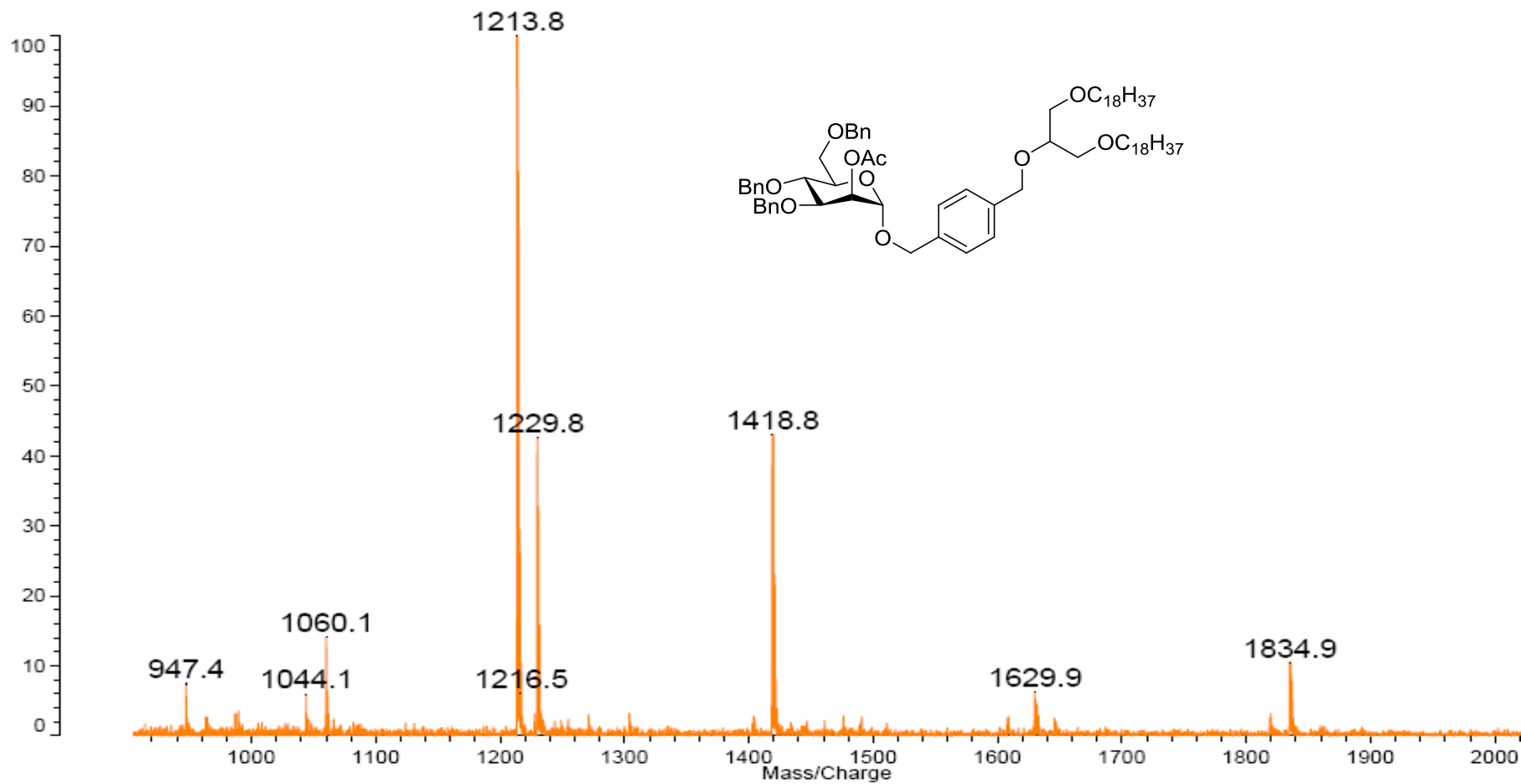


^{13}C NMR of Compound **3-1a** (CDCl_3 , 75MHz)

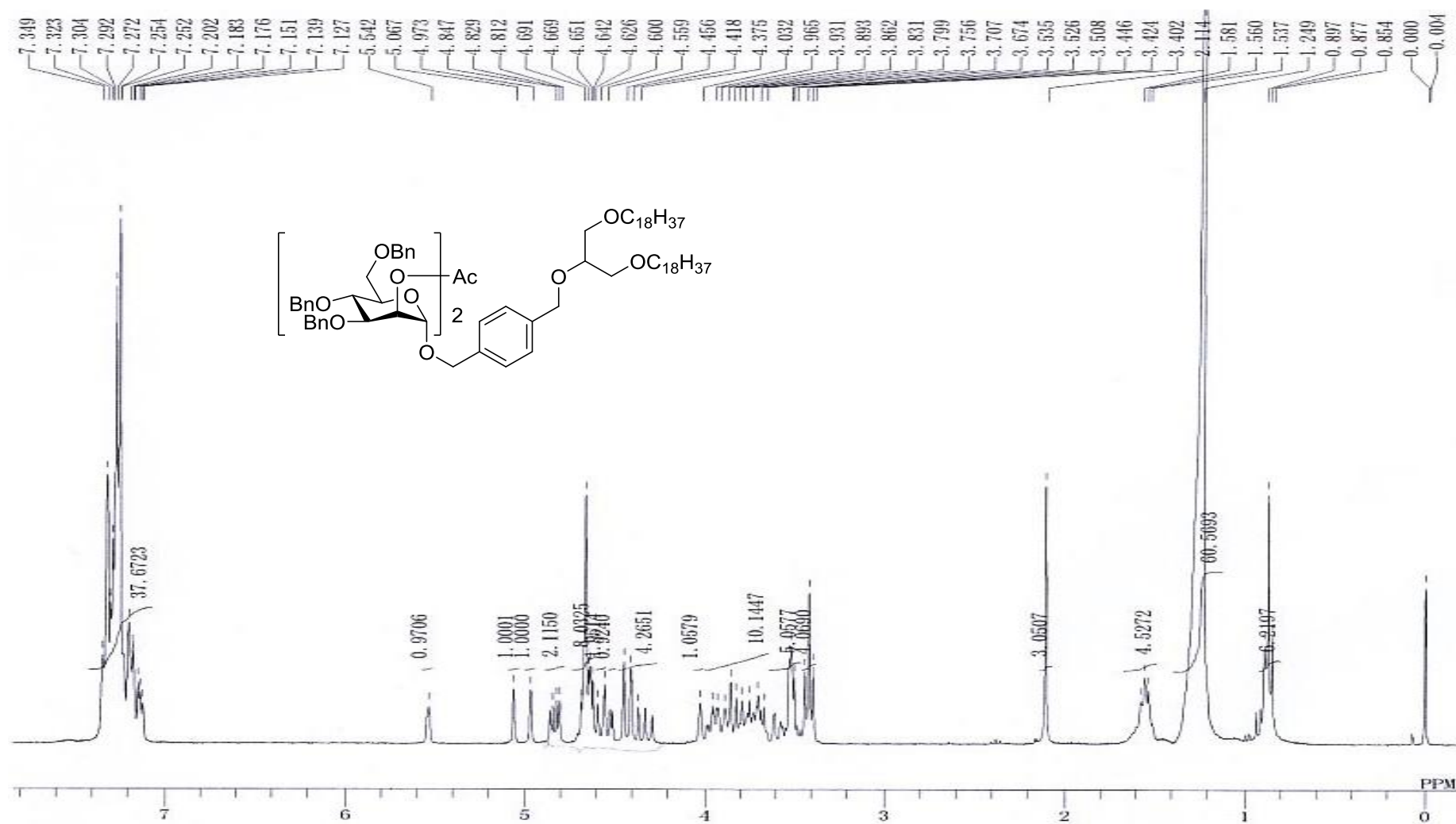


MALDI-TOF-MS of Compound 3-1a

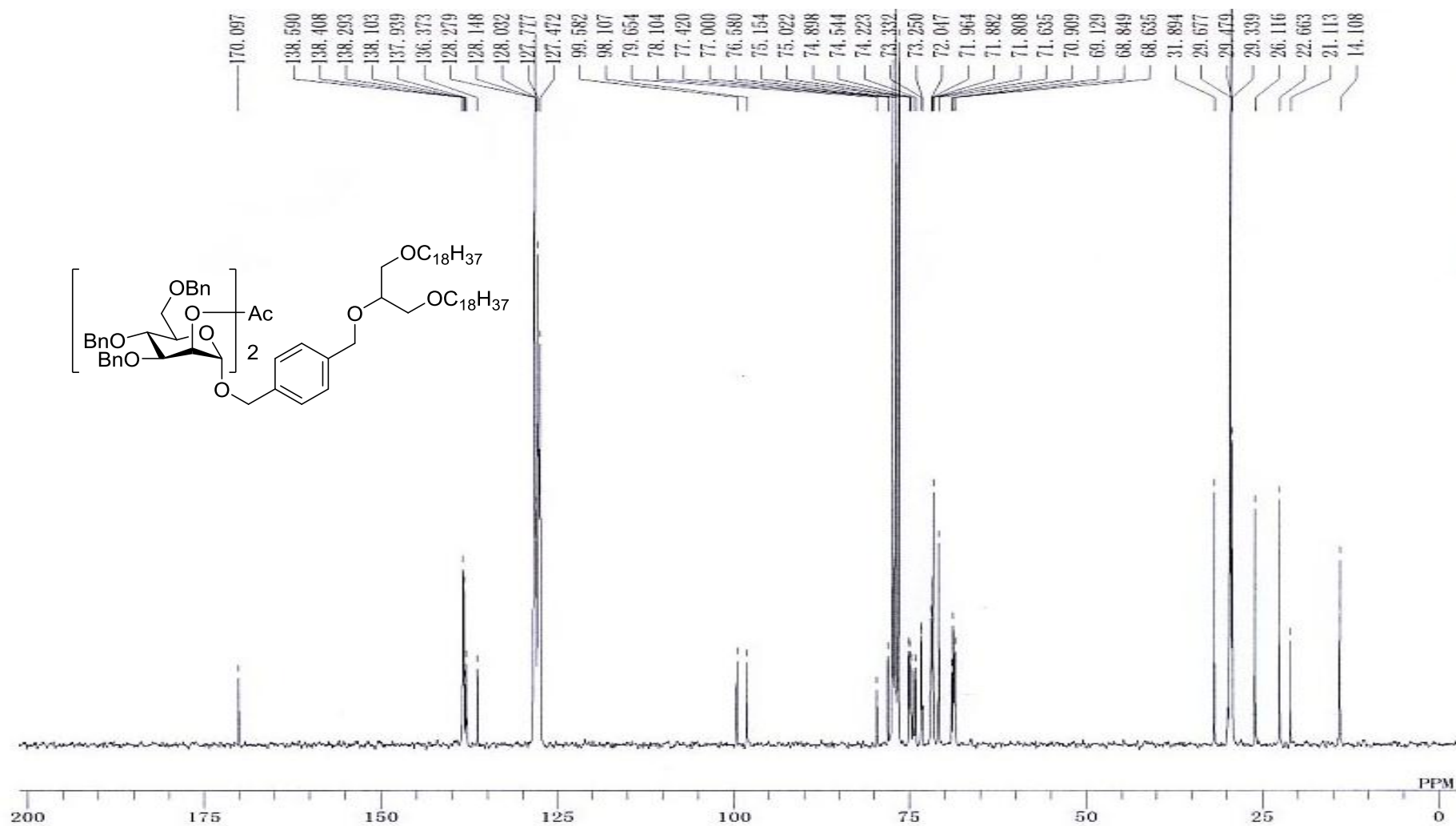
Data: 12-10003.A5 9 Apr 2007 11:31 Cal: tof 9 Apr 2007 11:27
Kratos PC Axima CFRplus V2.4.0: Mode Linear, Power: 53, Blanked, P.Ext. @ 1000 (bin 52)
%Int. 283 mV[sum= 16142 mV] Profiles 1-57 Smooth Av 2 -Baseline 20



¹H NMR of Compound 3-2a (CDCl₃, 300MHz)



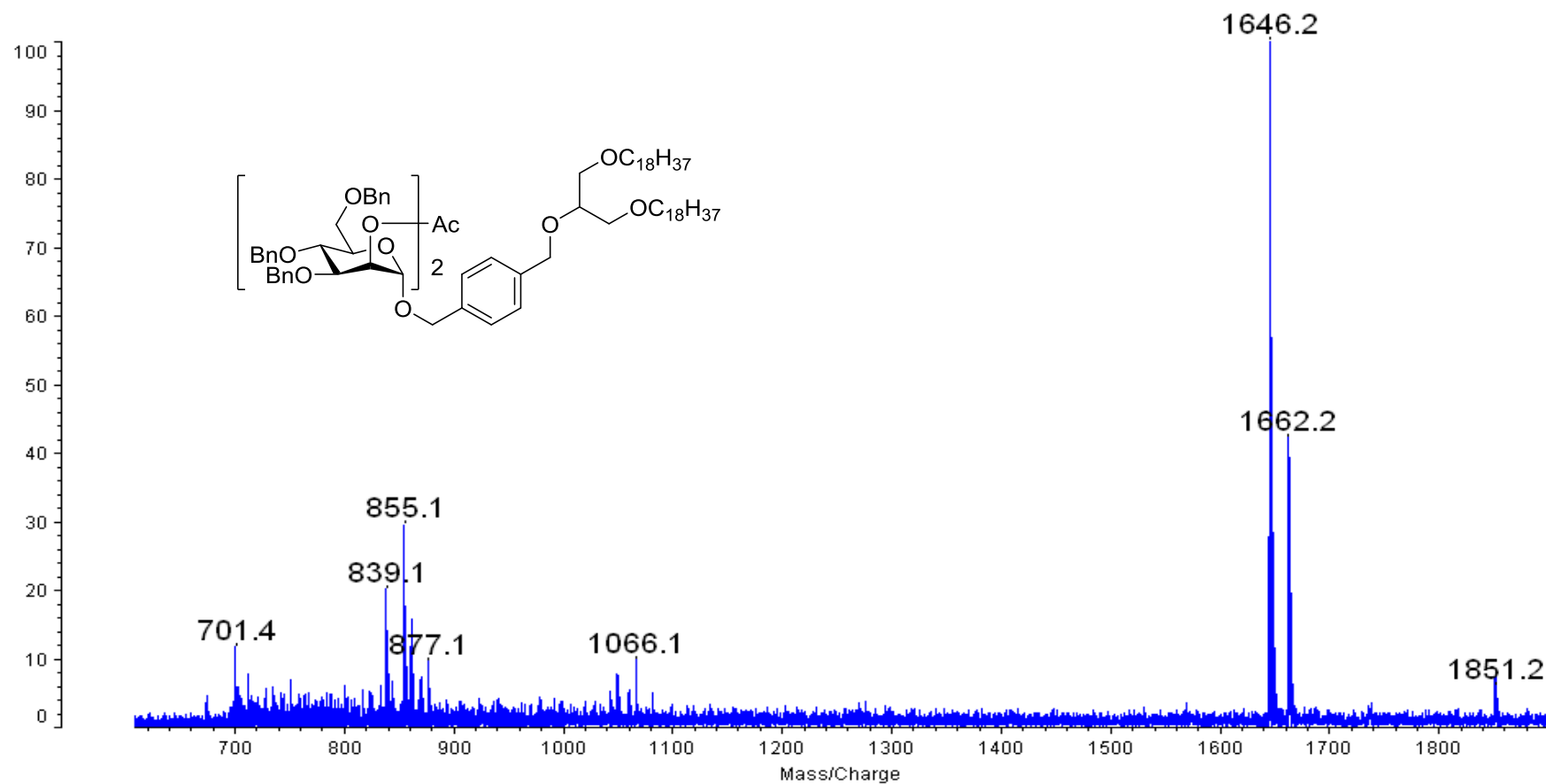
¹³C NMR of Compound **3-2a** (CDCl₃, 75MHz)



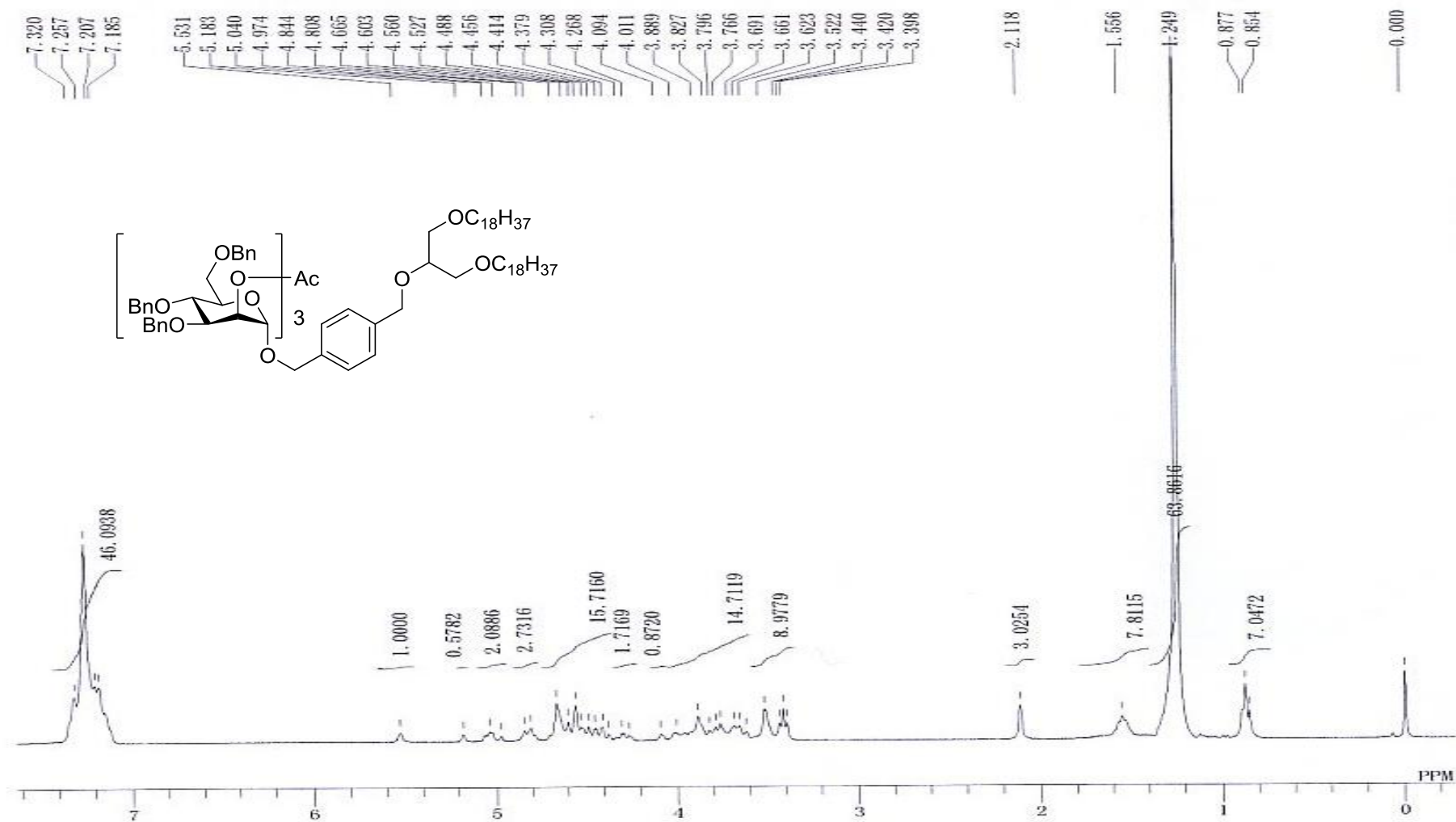
MALDI-TOF-MS of Compound 3-2a

12-2

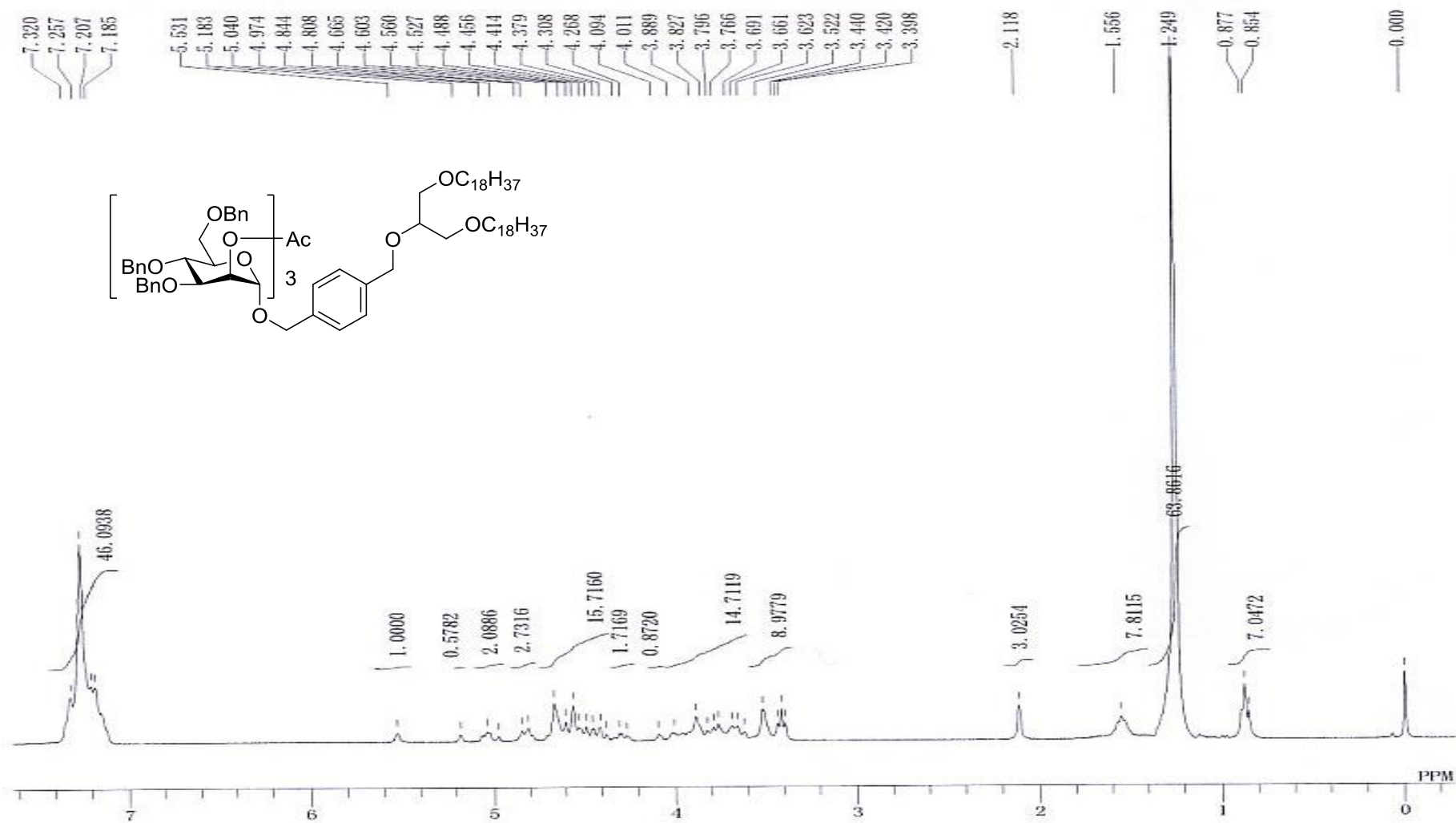
Data: 12-20002.D1 23 Apr 2007 9:28 Cal: LIUDAN 23 Apr 2007 9:27
 Kratos PC Axima CFRplus V2.4.0: Mode Reflectron, Power: 62, Blanked, P.Ext. @ 2300 (bin 114)
 %Int. 93 mV[sum= 7010 mV] Profiles 1-75 Smooth Av 2 -Baseline 20



¹H NMR of Compound 3-3a (CDCl₃, 300MHz)



¹³C NMR of Compound **3-2a** (CDCl₃, 75MHz)

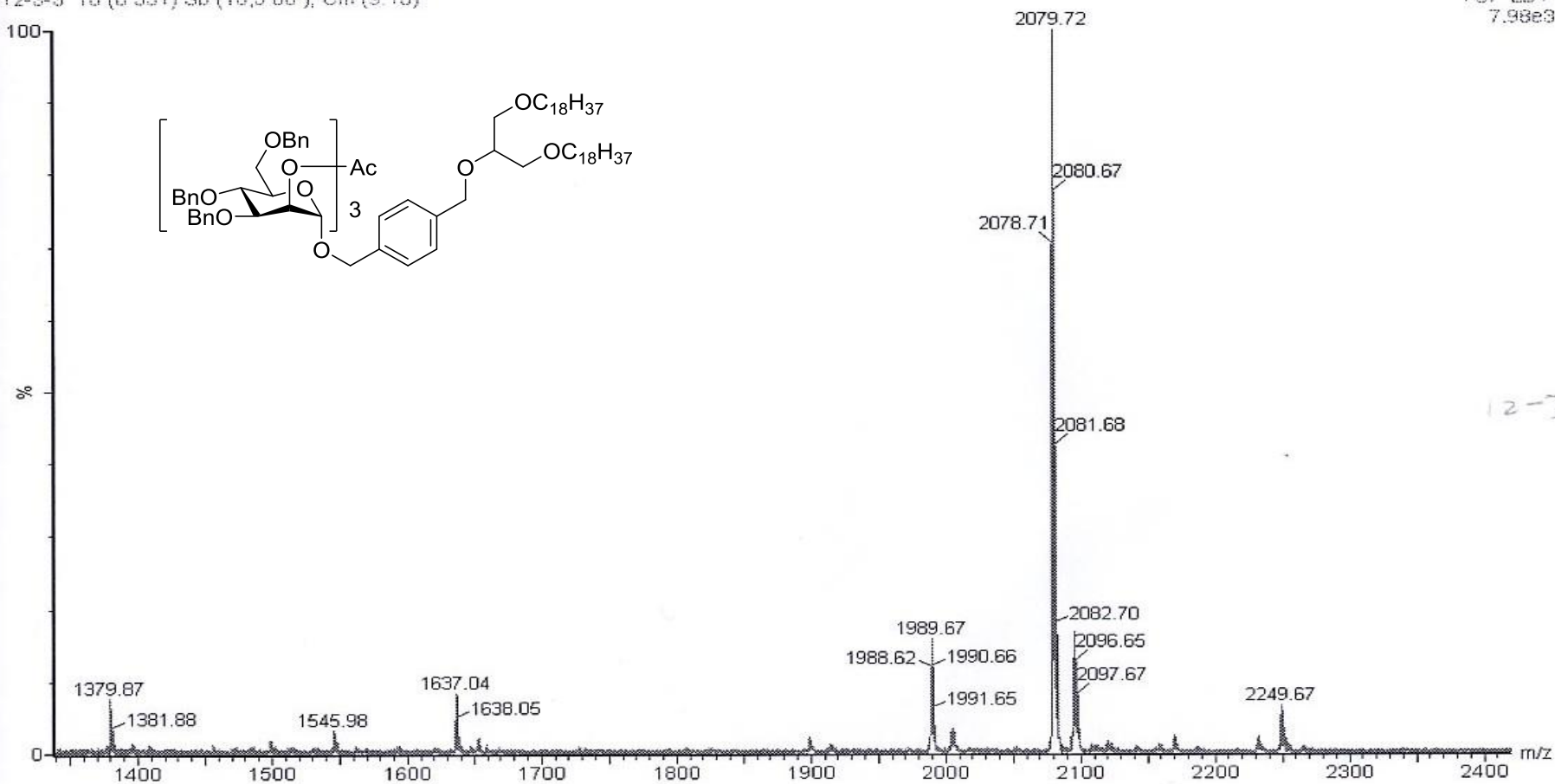


MALDI-TOF-MS of Compound **3-3a**

12-3-3

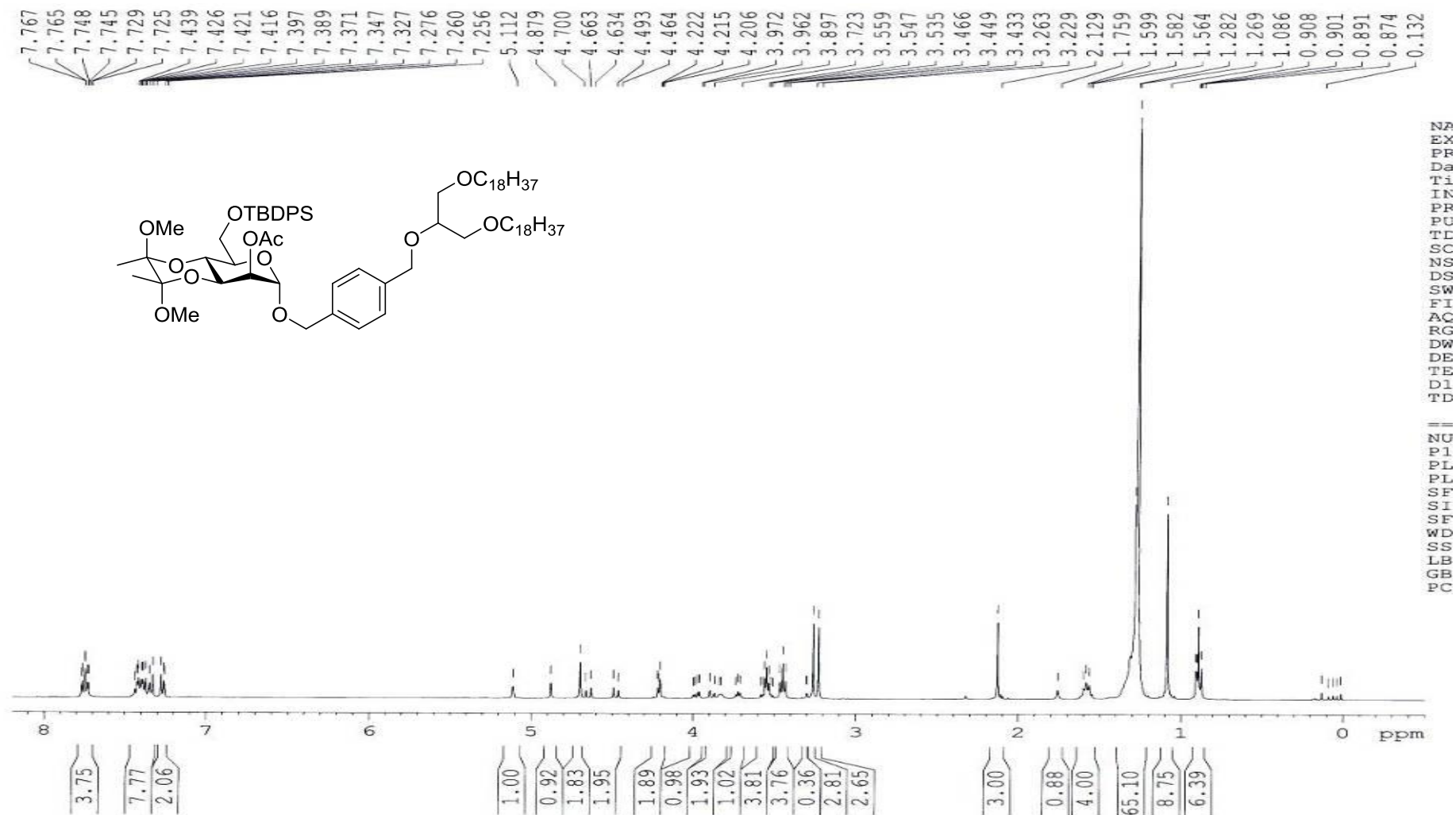
12-3-3 10 (0.331) Sb (10,5 00); Cm (9:18)

TOF LD+
7.98e9

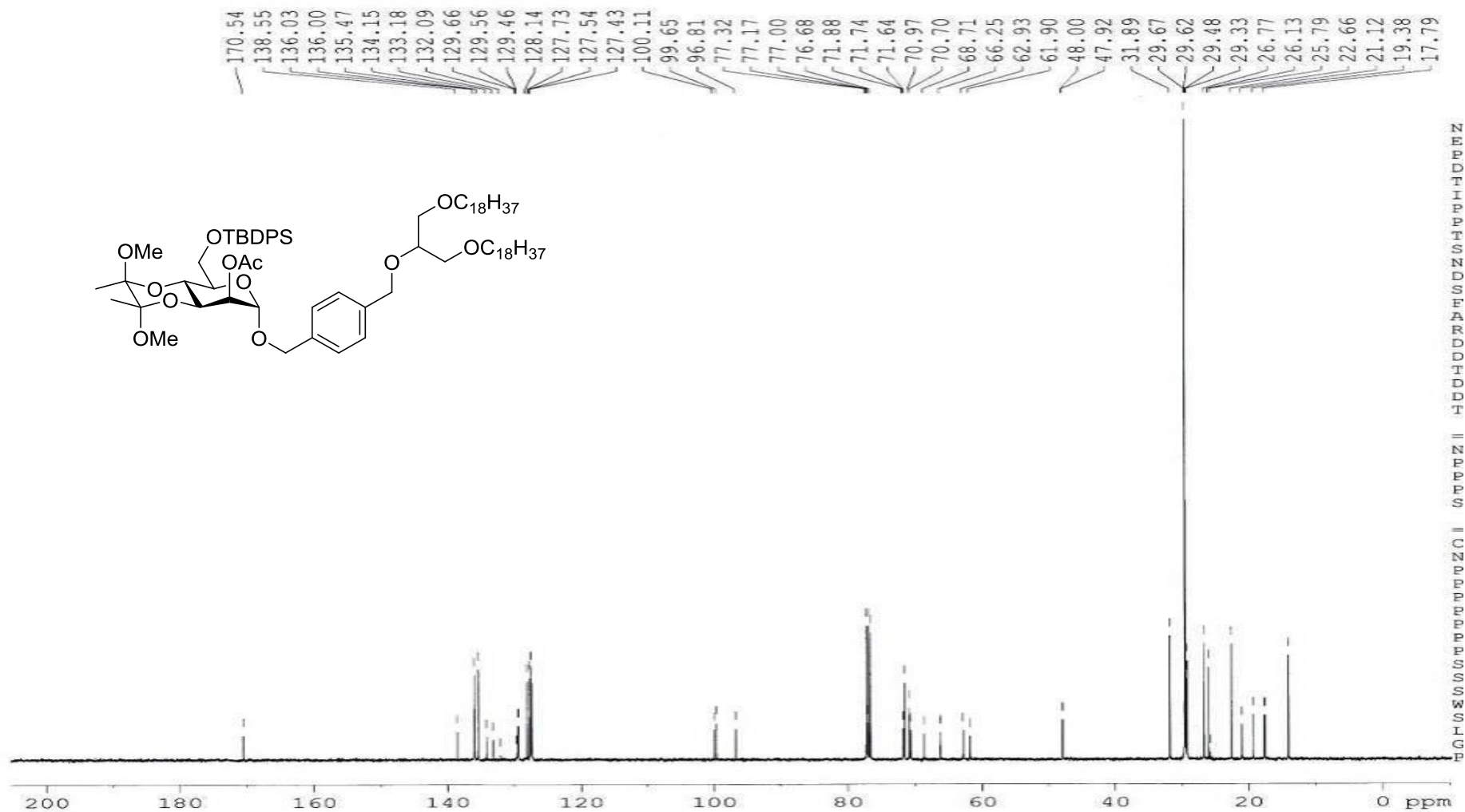


12-3

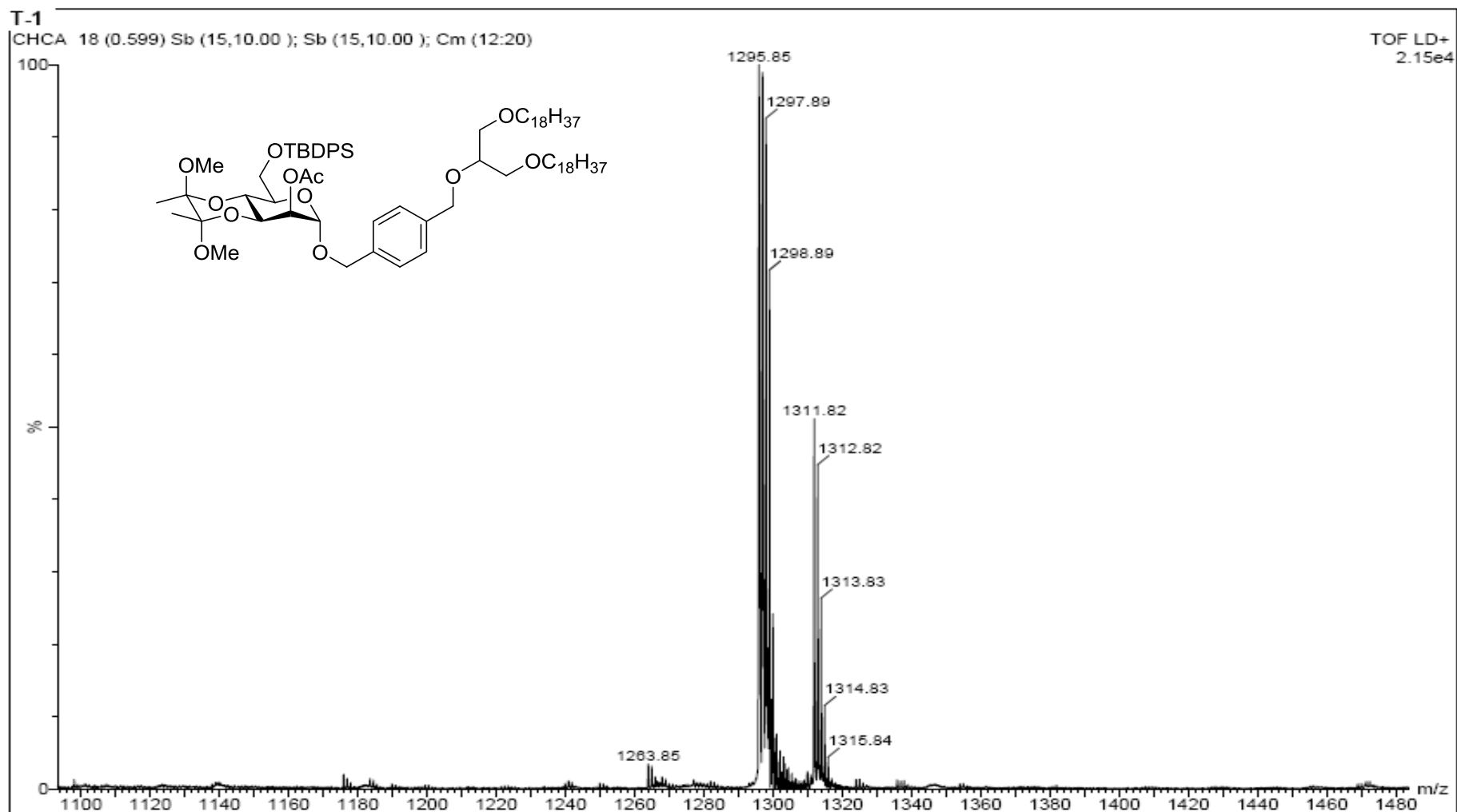
¹H NMR of Compound 9 (CDCl₃, 400MHz)



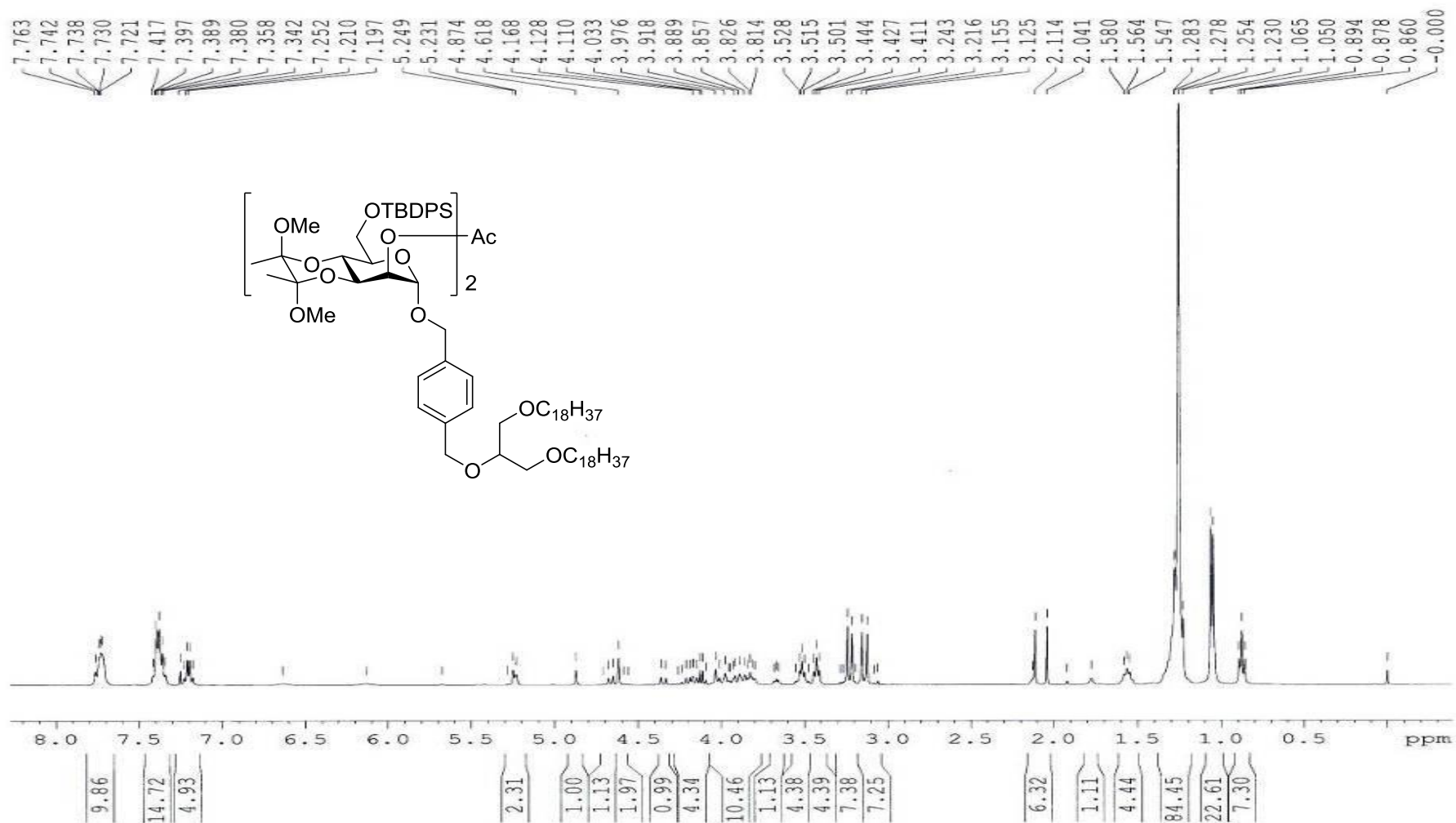
^{13}C NMR of Compound **9** (CDCl_3 , 100MHz)



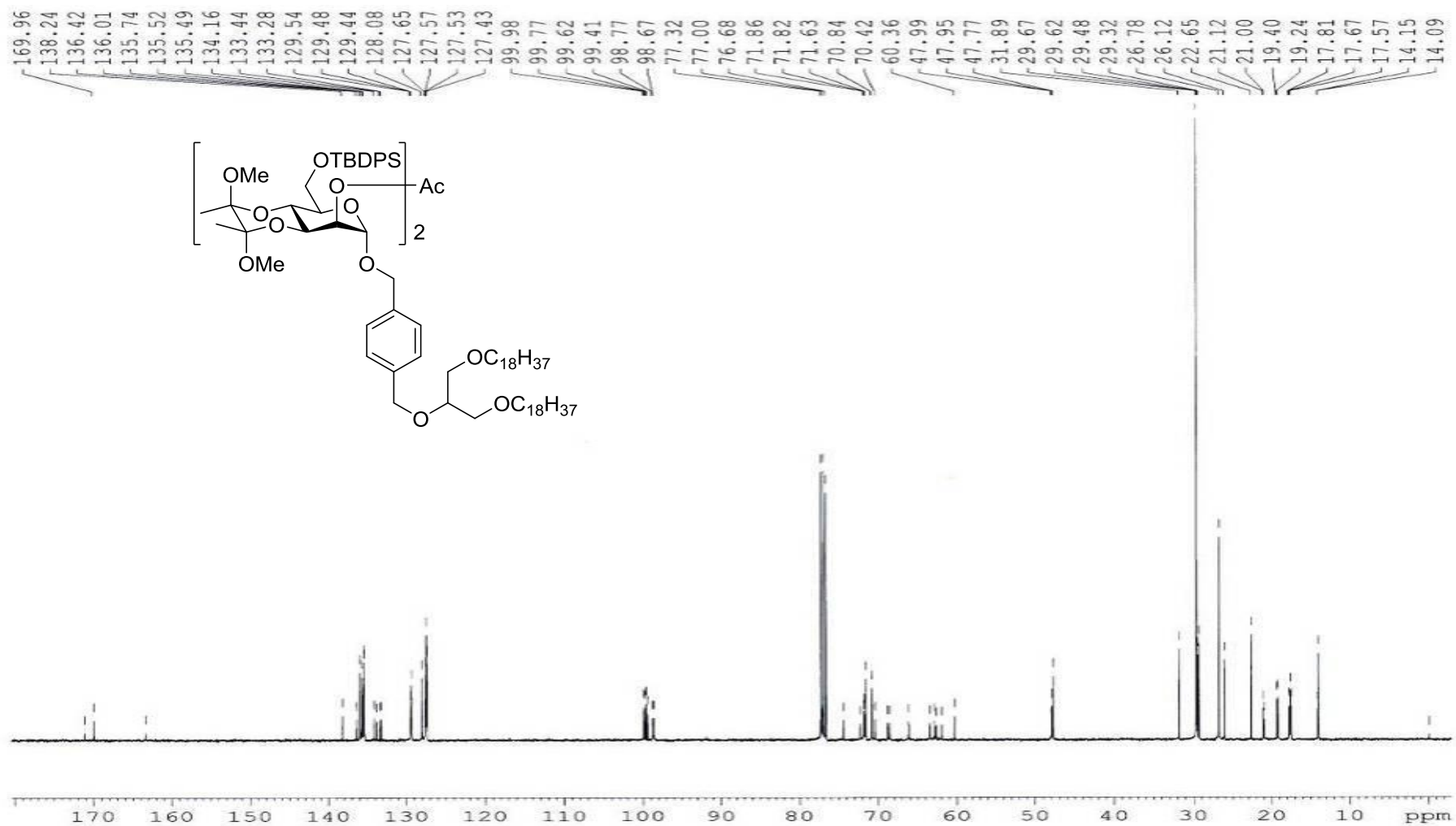
MALDI-TOF-MS of Compound 9



¹H NMR of Compound 10-2a (CDCl₃, 400MHz)



^{13}C NMR of Compound **10-2a** (CDCl_3 , 100MHz)



MALDI-TOF-MS of Compound **10-2a**

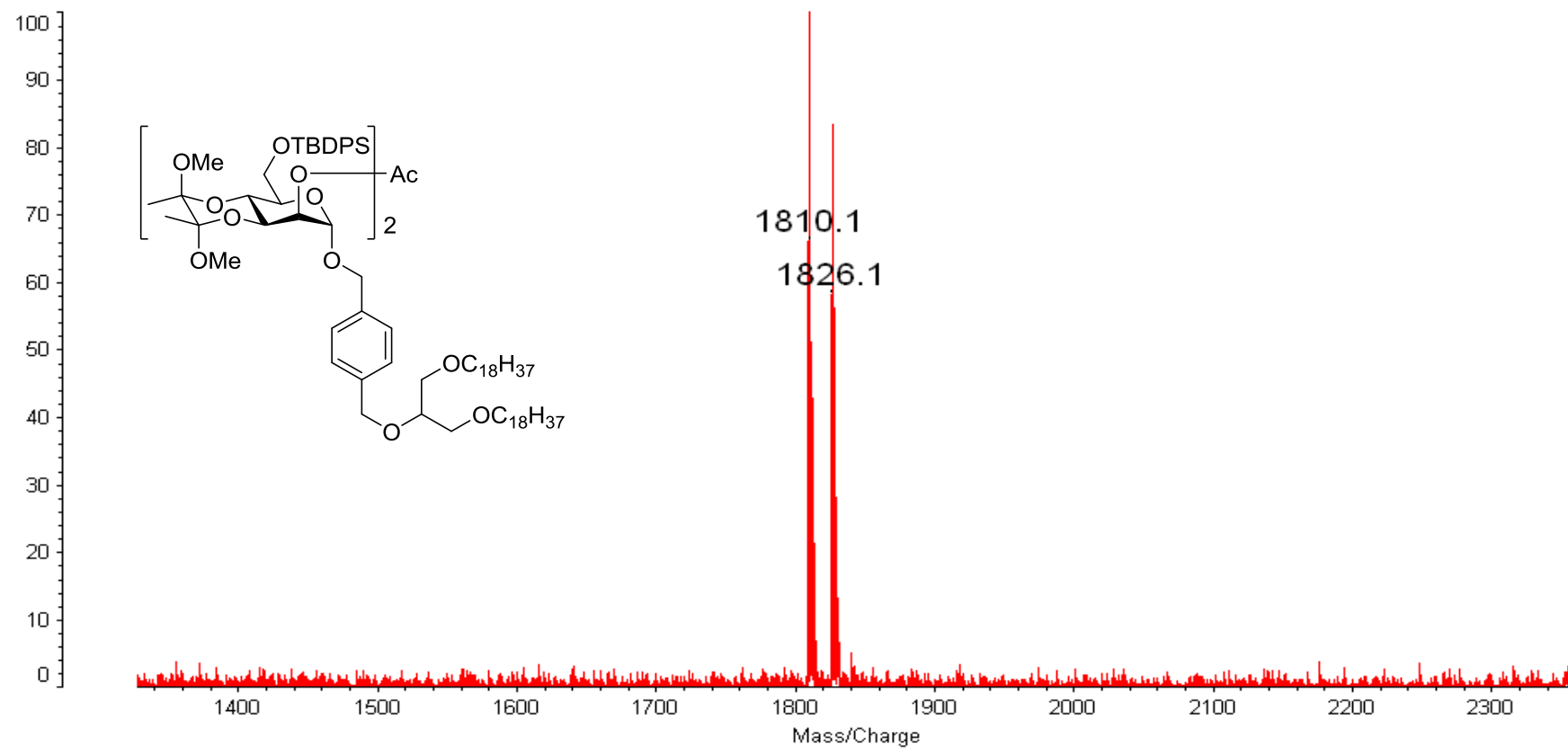
42D-2

CHCA

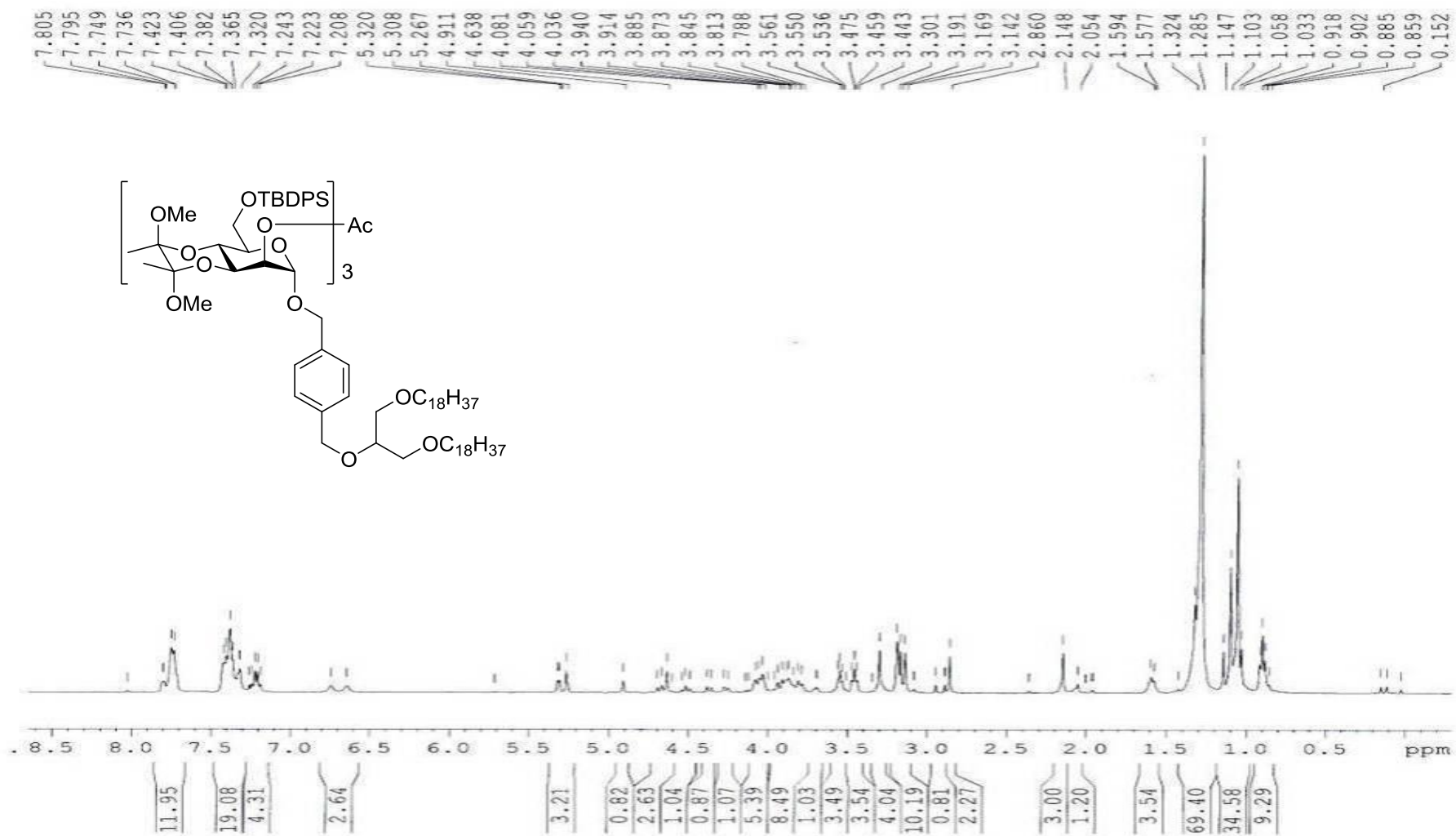
Data: 42D-20002.M21 1 Sep 2008 16:34 Cal: 080111 1 Sep 2008 16:21

Kratos PC Axima CFRplus V2.4.0: Mode Reflectron, Power: 64, Blanked, P.Ext. @ 1000 (bin 75)

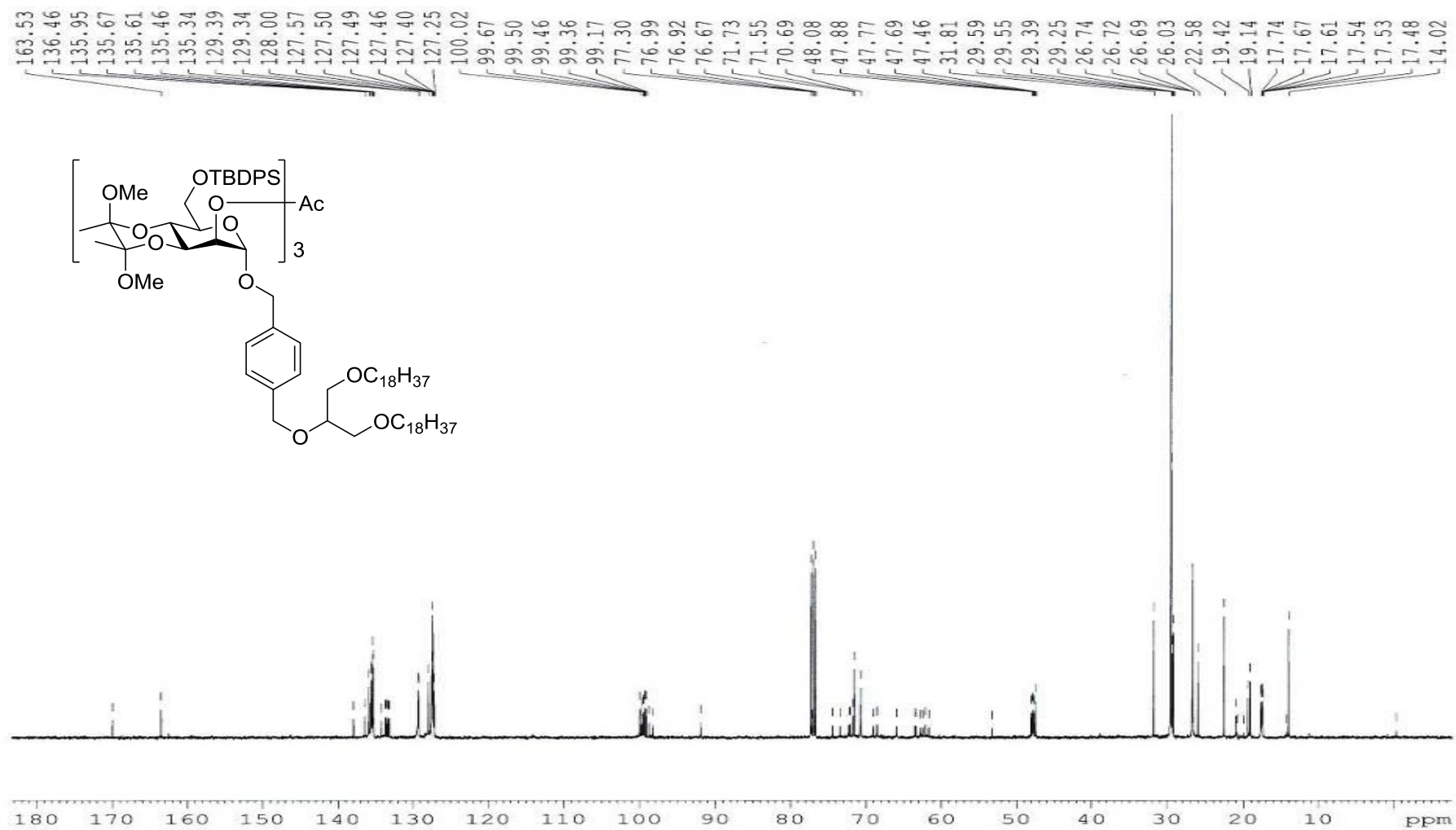
%Int. 4.0 mV[sum= 377 mV] Profiles 1-94 Smooth Av 2



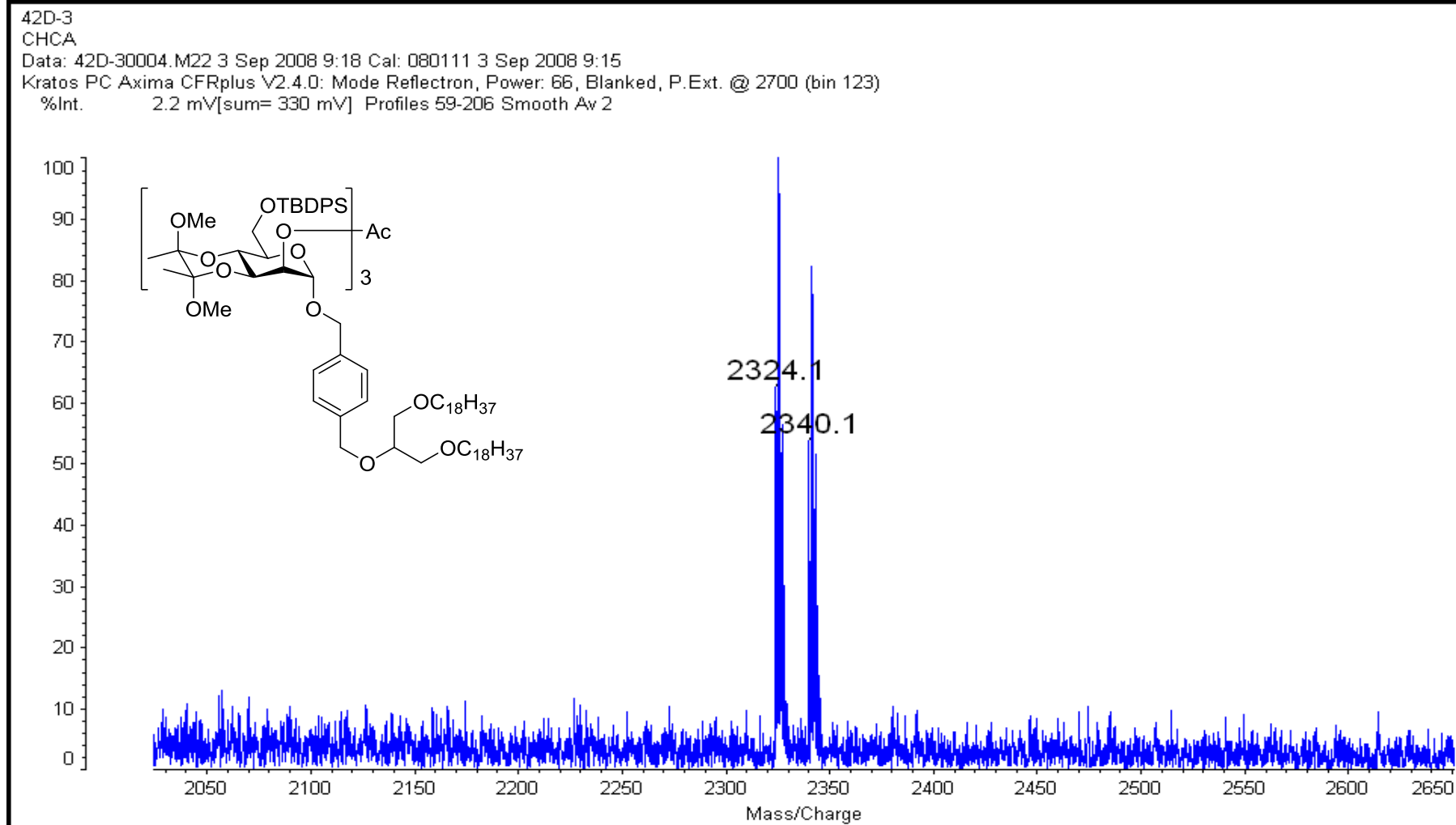
^1H NMR of Compound **10-3a** (CDCl_3 , 400MHz)



^{13}C NMR of Compound **10-3a** (CDCl_3 , 100MHz)



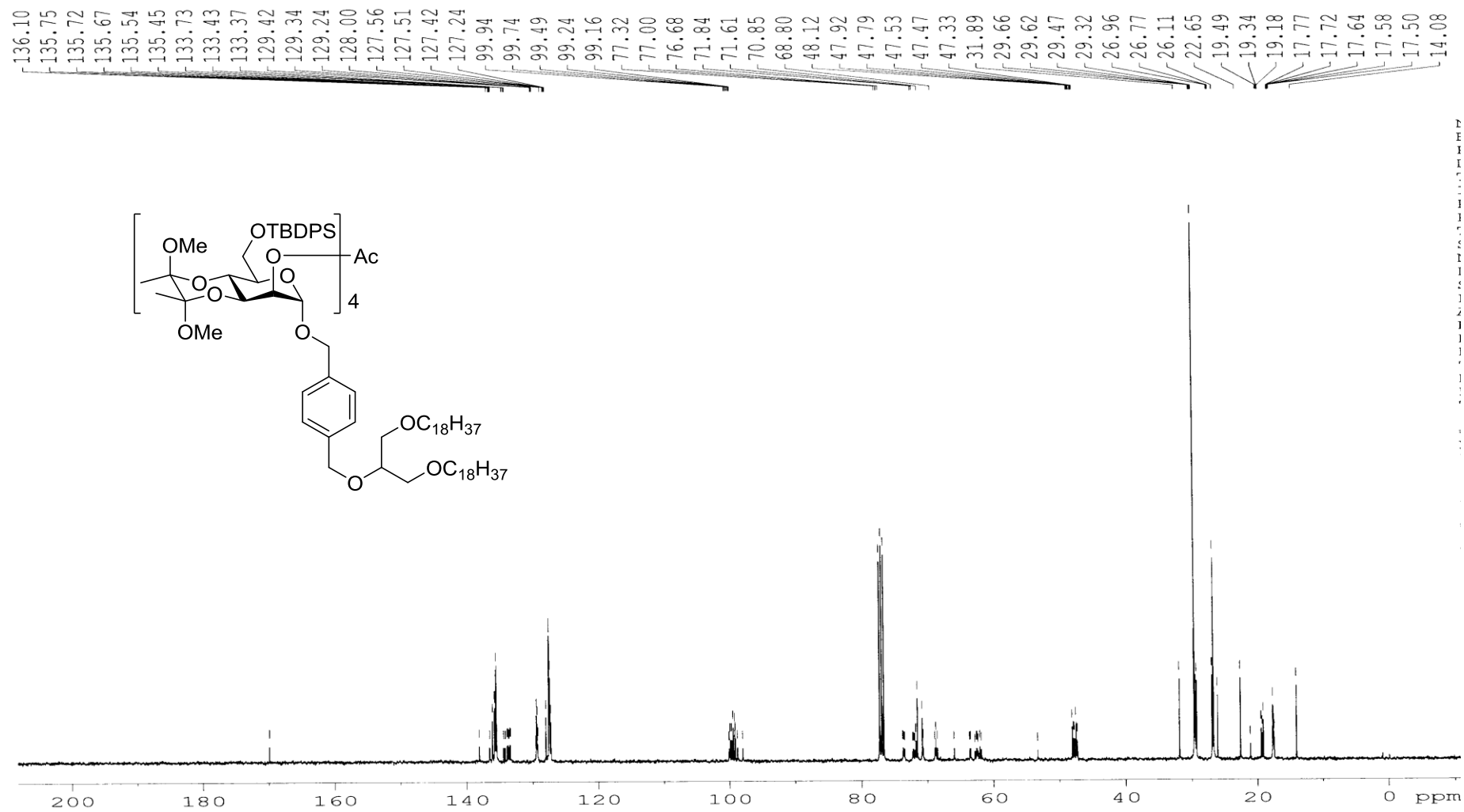
MALDI-TOF-MS of Compound **10-3a**



THE
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S
J
2
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H
C
I
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=
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S
C



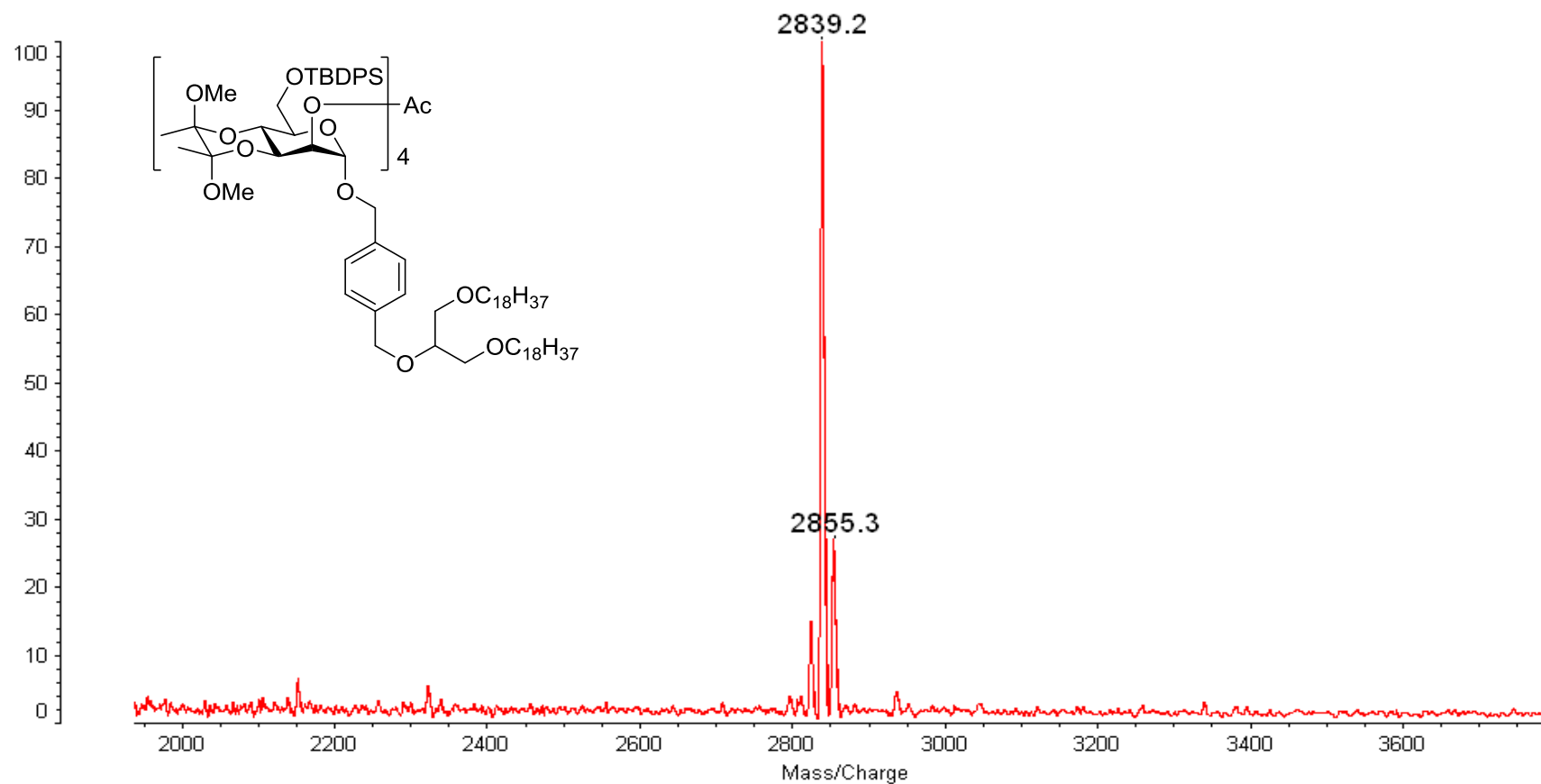
¹³C NMR of Compound **10-4a** (CDCl₃, 100MHz)



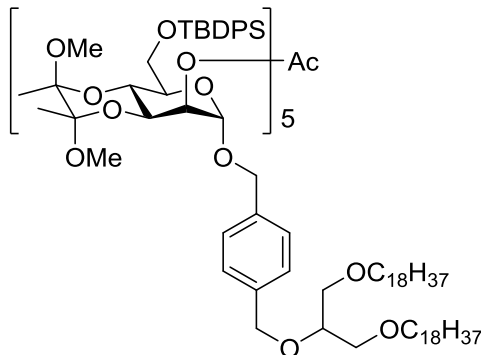
MALDI-TOF-MS of Compound **10-4a**

HD42-4

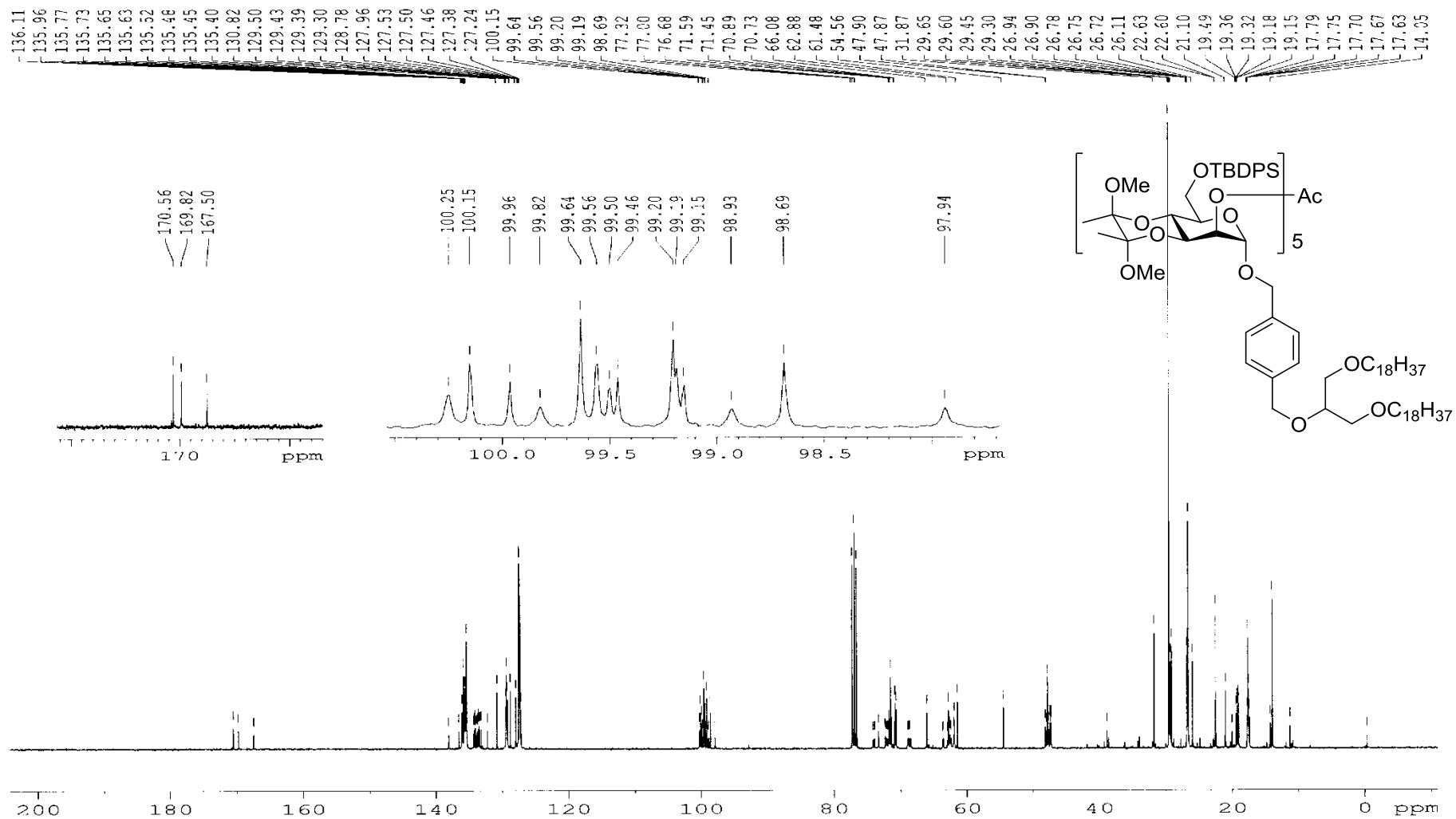
Data: HD42-40001.A14 24 Feb 2009 17:24 Cal: ZHONG 24 Feb 2009 17:23
 Kratos PC Axima CFRplus V2.4.0: Mode Linear, Power: 37, Blanked, P.Ext. @ 2300 (bin 65)
 %Int. 25 mV[sum= 2400 mV] Profiles 1-95 Smooth Av 50 -Baseline 80



7.733
7.731
7.726
7.715
7.712
7.704
7.696
7.691
7.687
7.391
7.386
7.381
7.373
7.368
7.362
7.357
7.355
7.344
7.326
7.315
7.310
7.298
7.280
7.263
4.355
3.323
3.266
3.257
3.245
3.214
3.102
3.057
2.935
2.899
2.888
2.707
2.690
2.128
2.123
1.377
1.359
1.341
1.307
1.300
1.282
1.260
1.238
1.228
1.152
1.114
1.098
1.081
1.073
1.054
1.030
1.015
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0.893
0.877
0.873
0.859
0.857
0.848
0.835
0.832



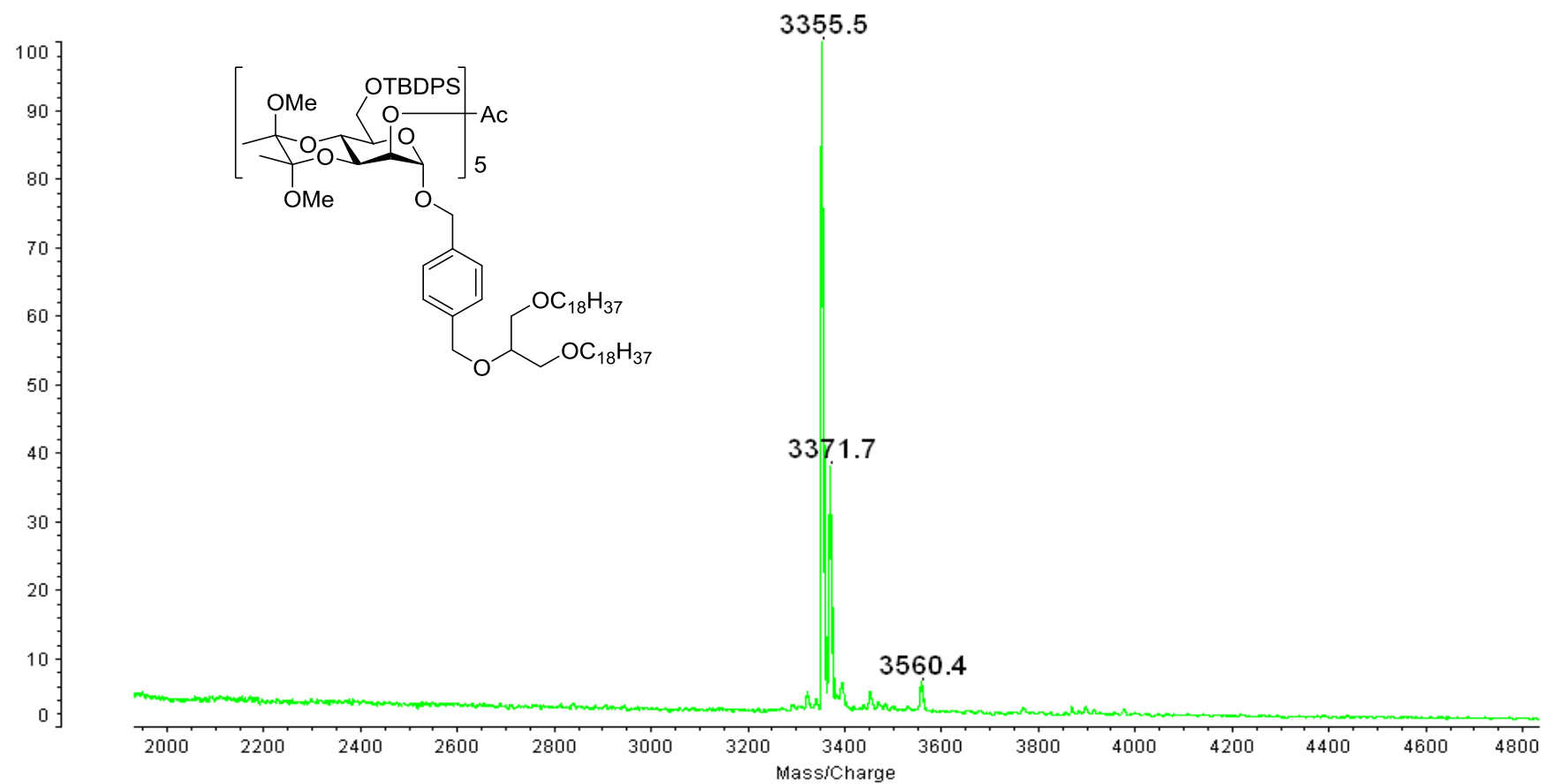
¹³C NMR of Compound **10-5a** (CDCl₃, 100MHz)



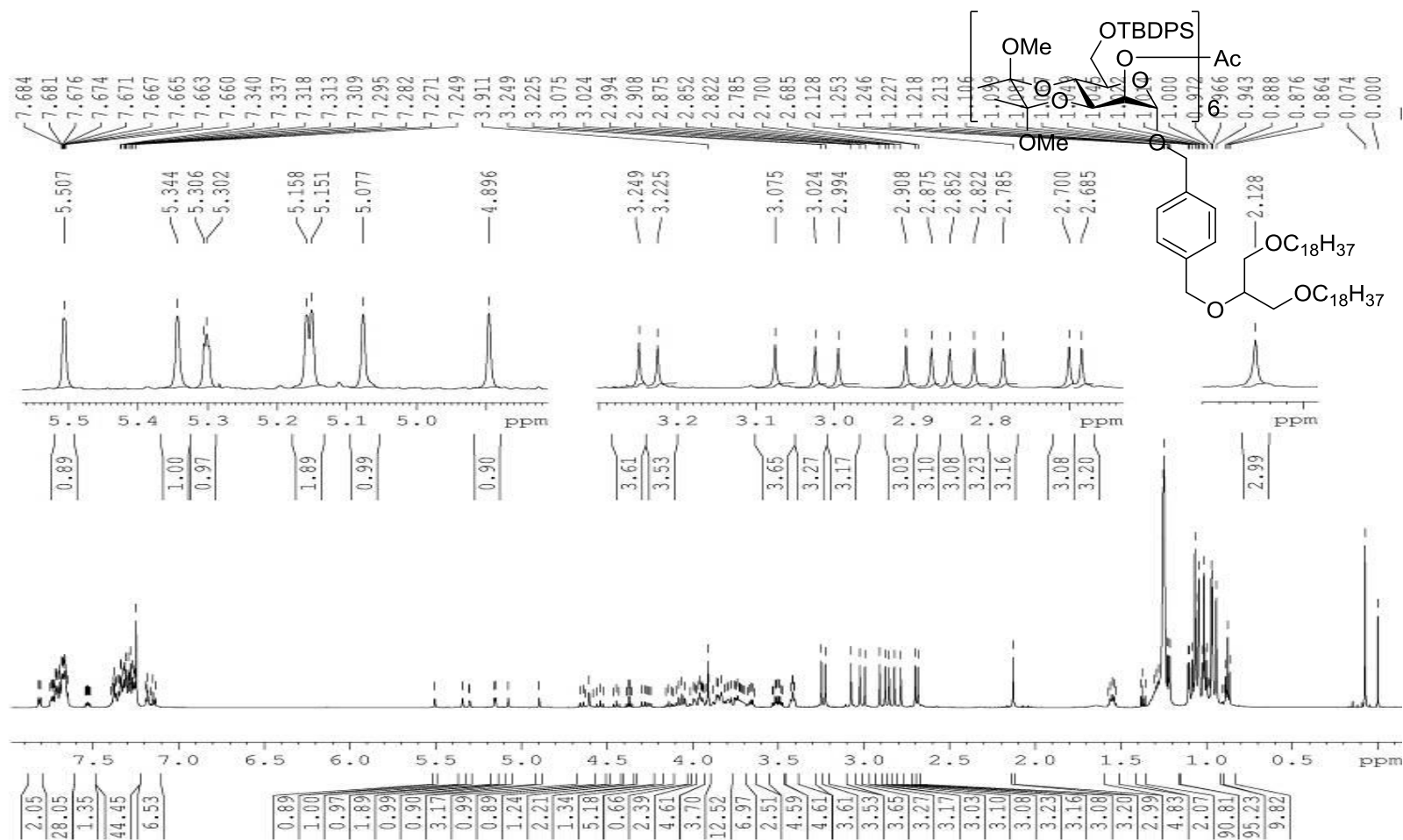
MALDI-TOF-MS of Compound **10-5a**

HD42-5

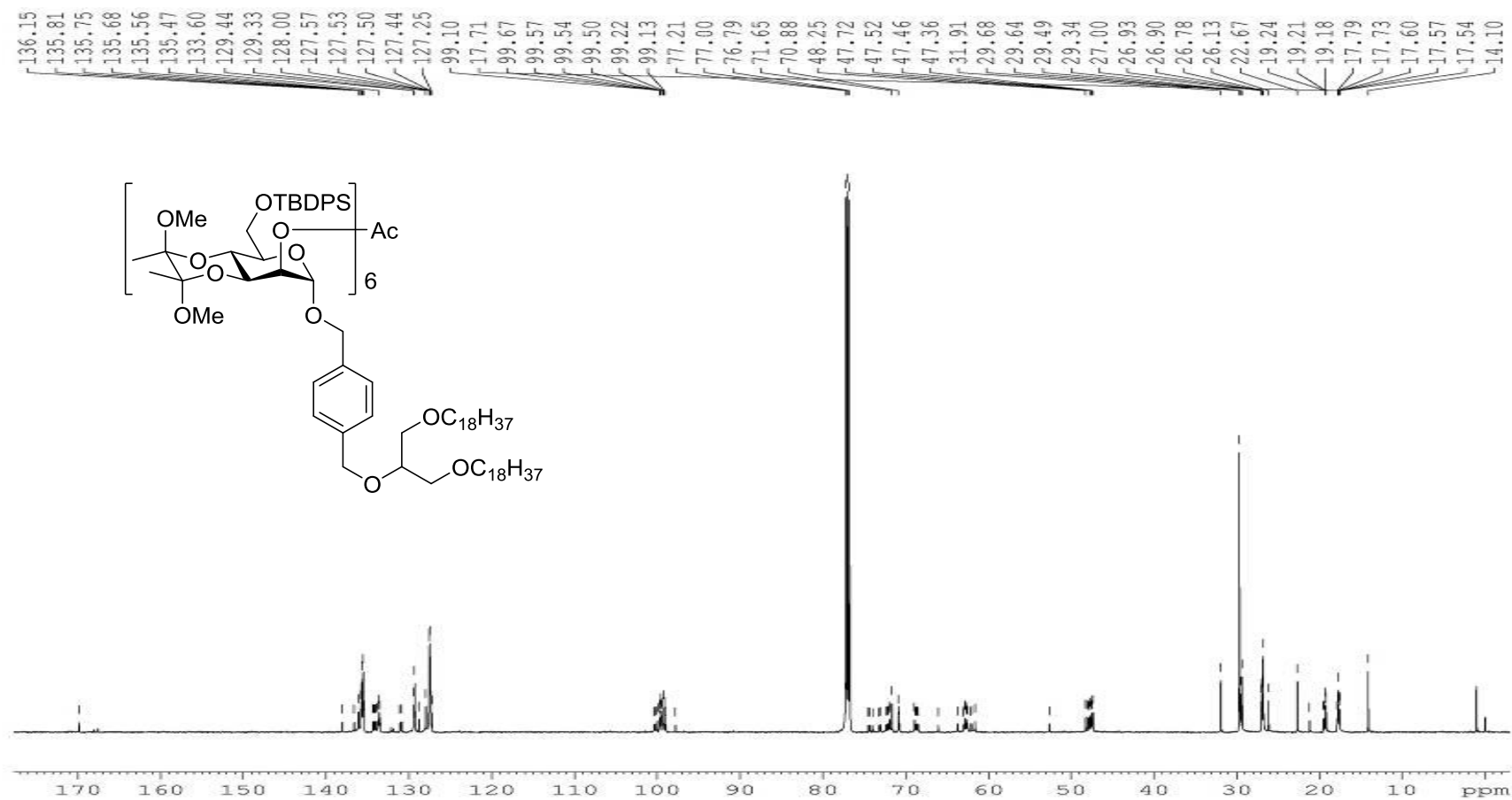
Data: HD42-50001.J4 6 Mar 2009 16:26 Cal: zhong 6 Mar 2009 16:25
 Kratos PC Axima CFRplus V2.4.0: Mode Linear, Power: 40, Blanked, P.Ext. @ 2300 (bin 65)
 %Int. 169 mV[sum= 12368 mV] Profiles 1-73 Smooth Av 50



¹H NMR of Compound 10-6a (CDCl₃, 600MHz)



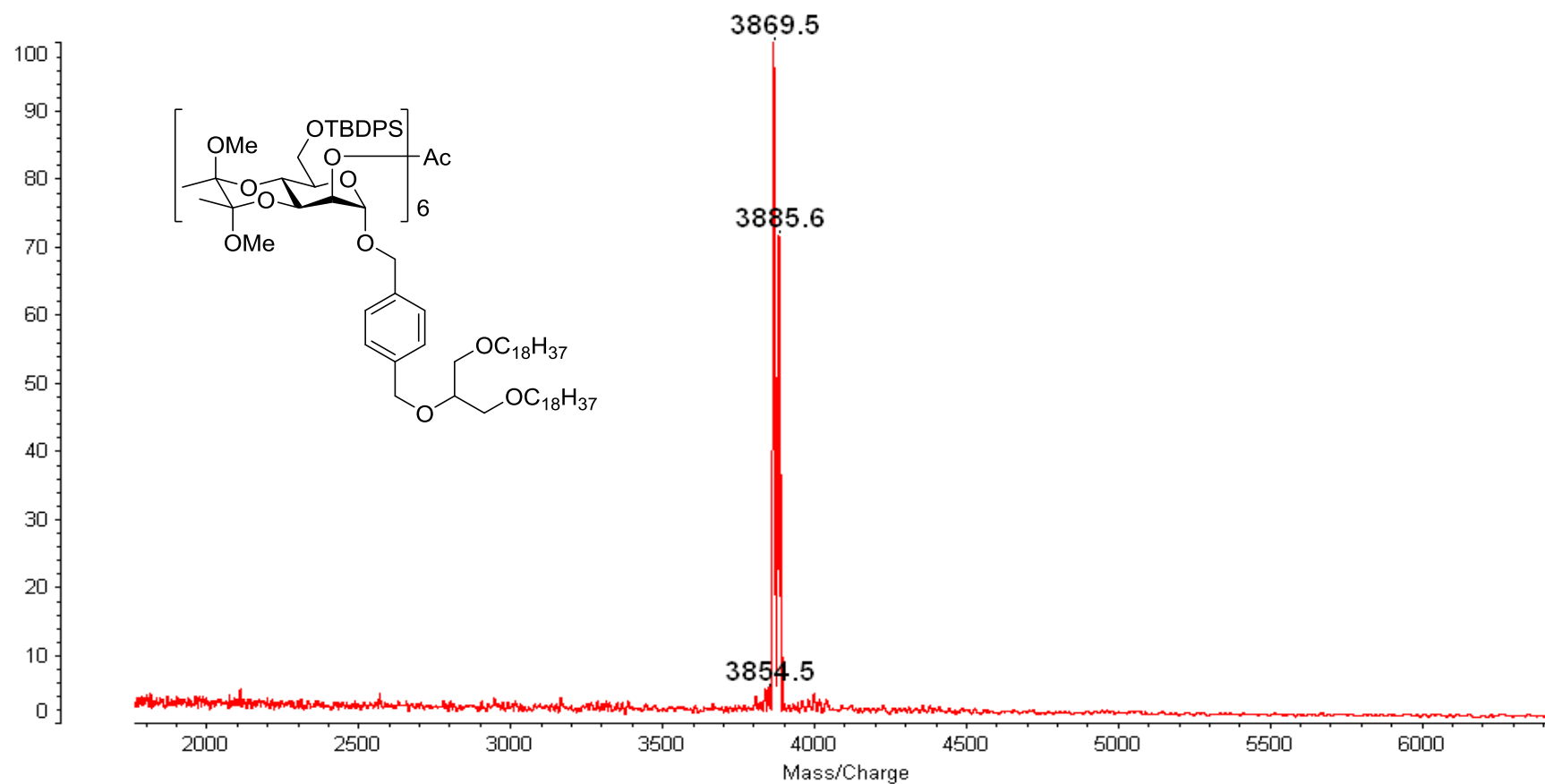
^{13}C NMR of Compound **10-6a** (CDCl_3 , 150MHz)



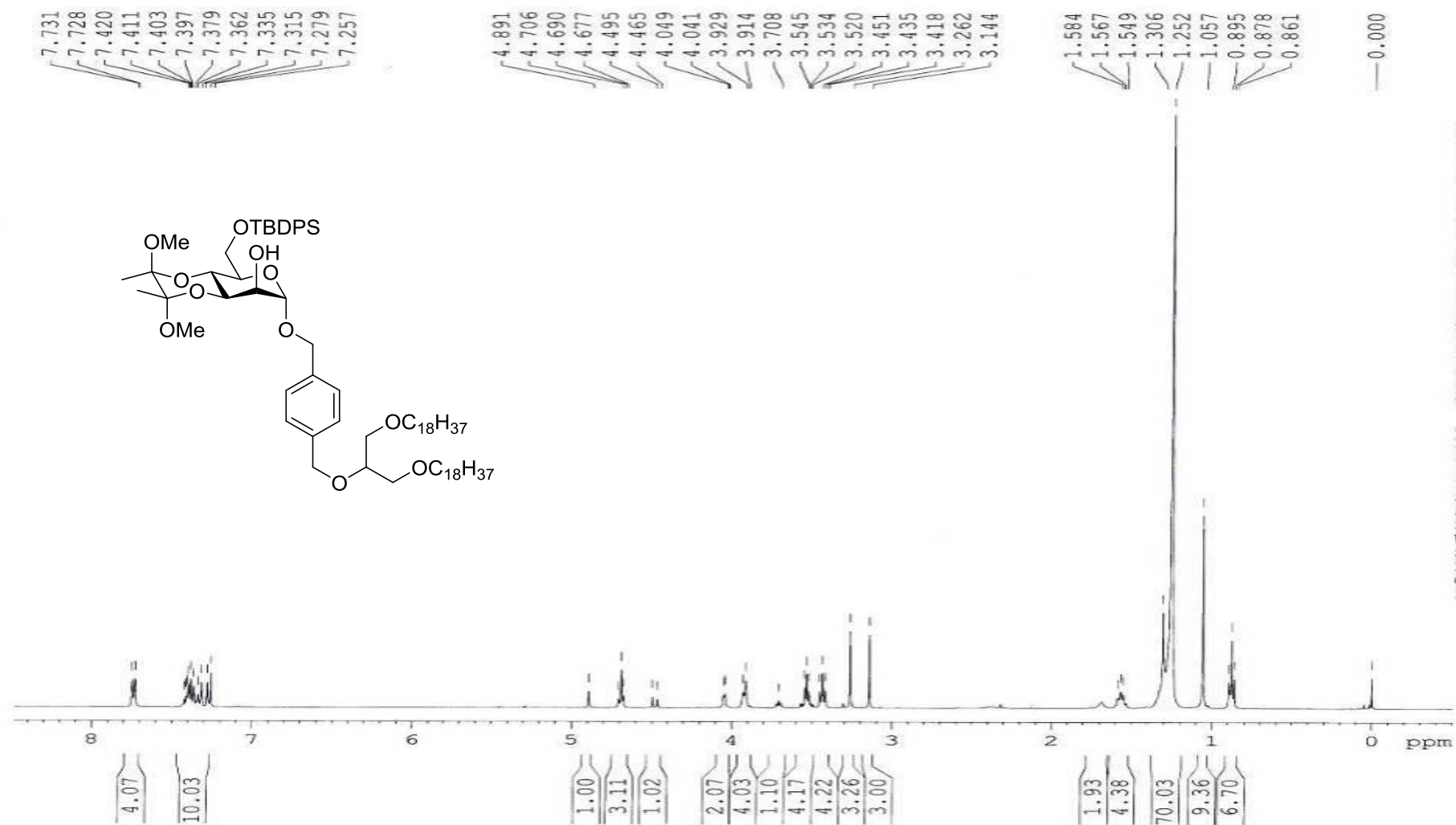
MALDI-TOF-MS of Compound **10-6a**

HD42-6

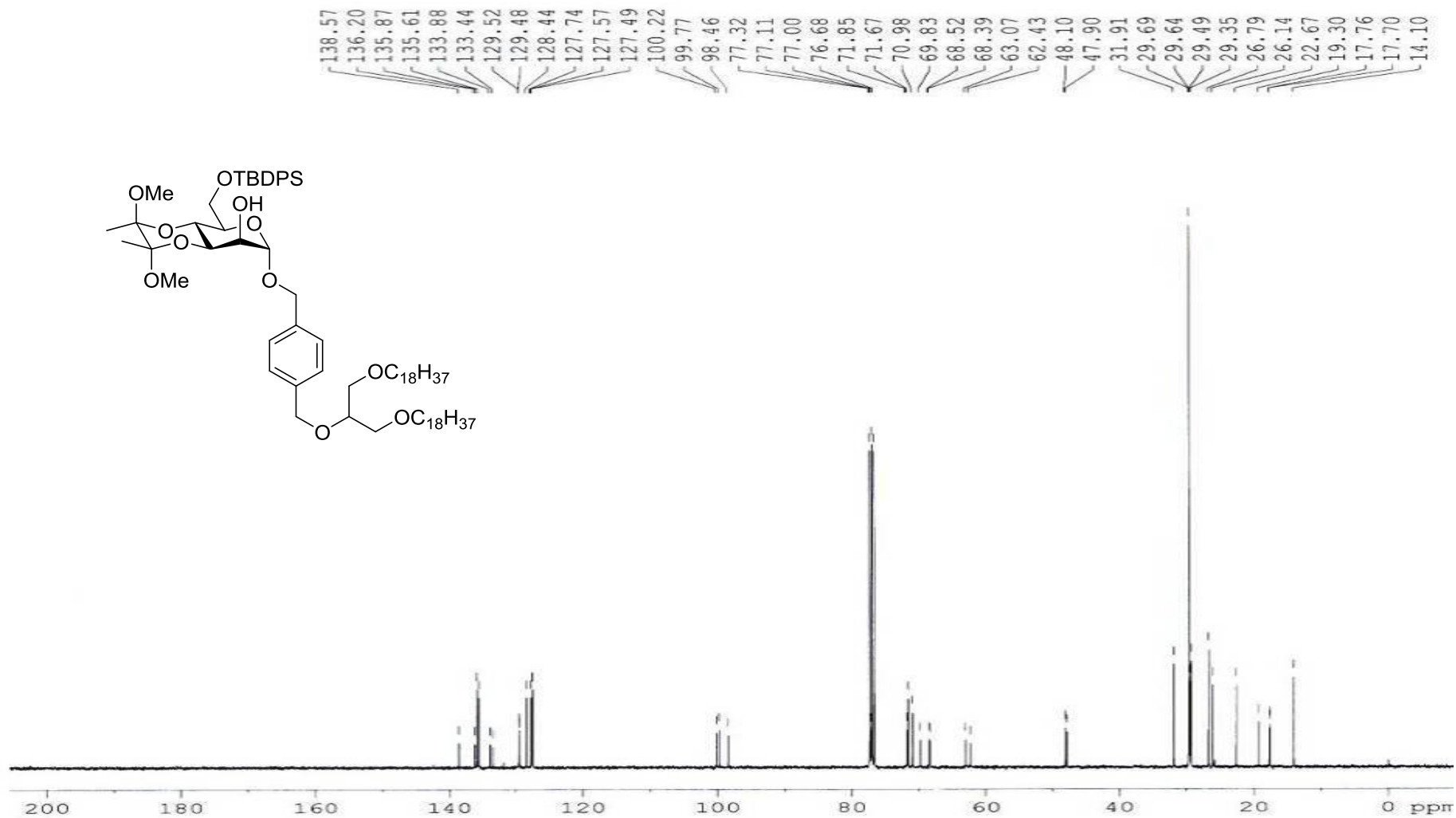
Data: HD42-60001.11 30 Mar 2009 17:22 Cal: zhong 30 Mar 2009 17:22
 Kratos PC Axima CFRplus V2.4.0: Mode Linear, Power: 58, Blanked, P.Ext. @ 4000 (bin 86)
 %Int. 34 mV[sum= 2439 mV] Profiles 16-86 Smooth Av 80 -Baseline 80



^1H NMR of Compound **10-1b** (CDCl_3 , 400MHz)



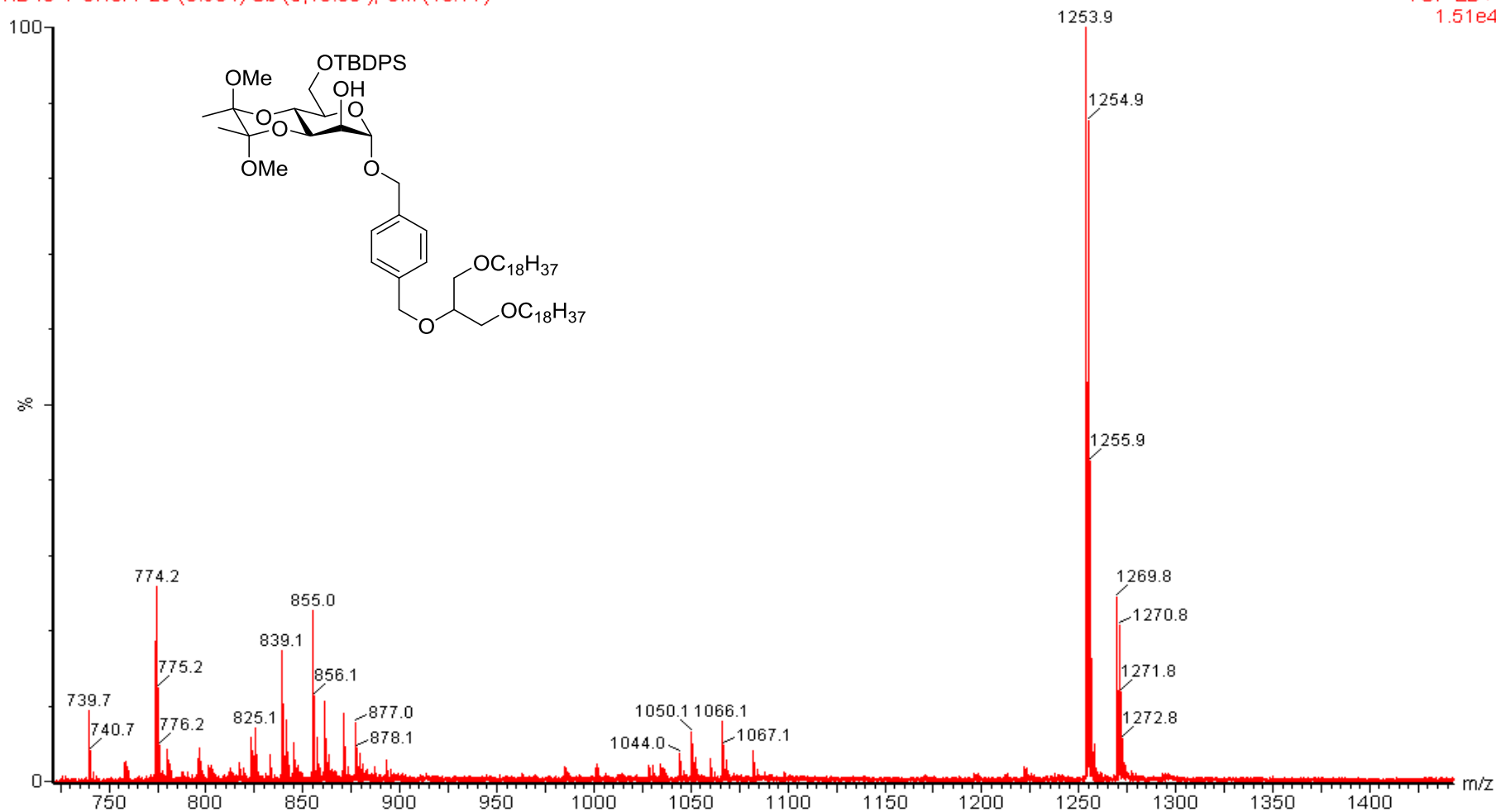
^{13}C NMR of Compound **10-1b** (CDCl_3 , 100MHz)



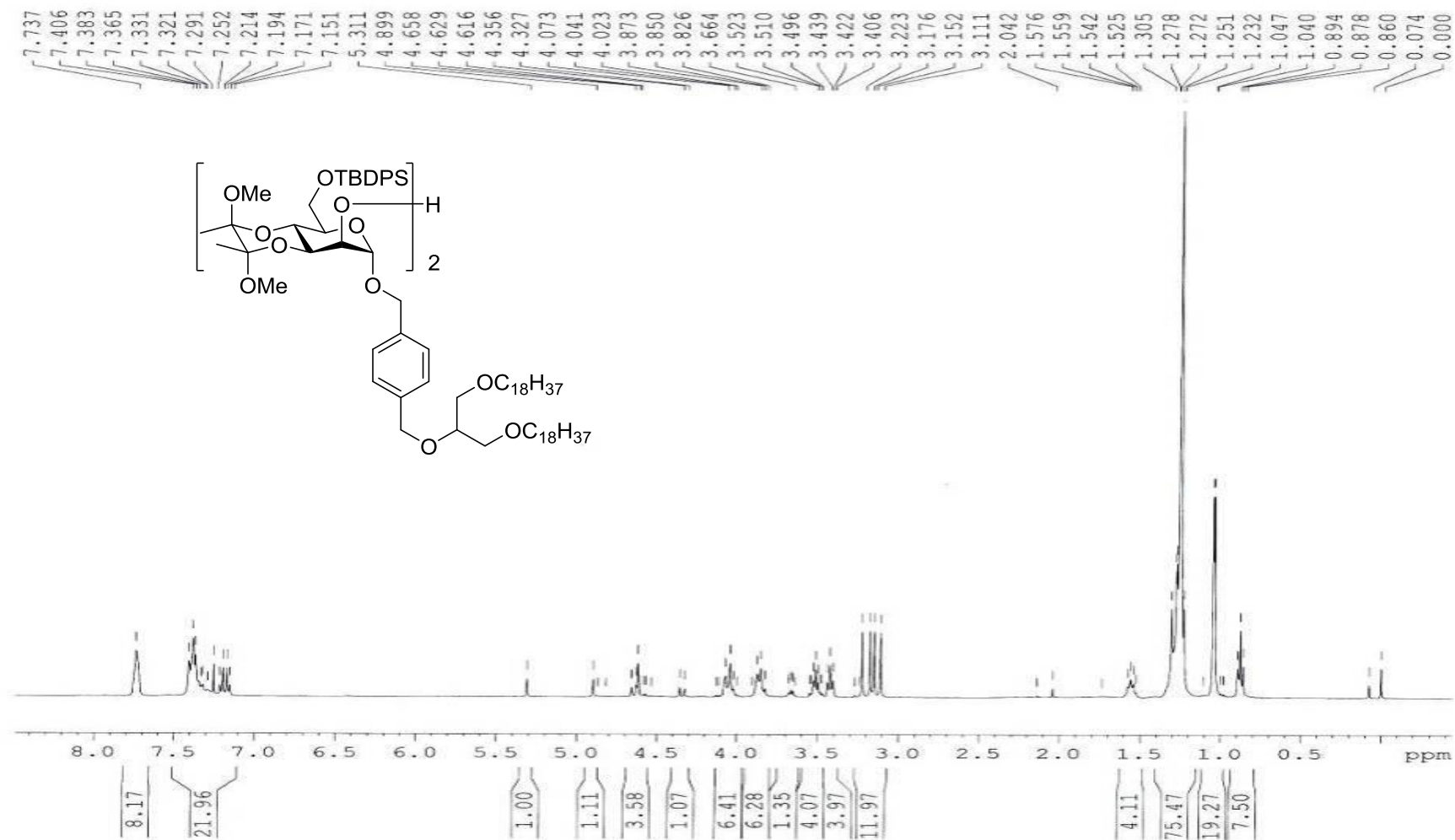
MALDI-TOF-MS of Compound **10-1b**

HD43-1-CHCA 29 (0.964) Sb (5,10.00); Cm (16:77)

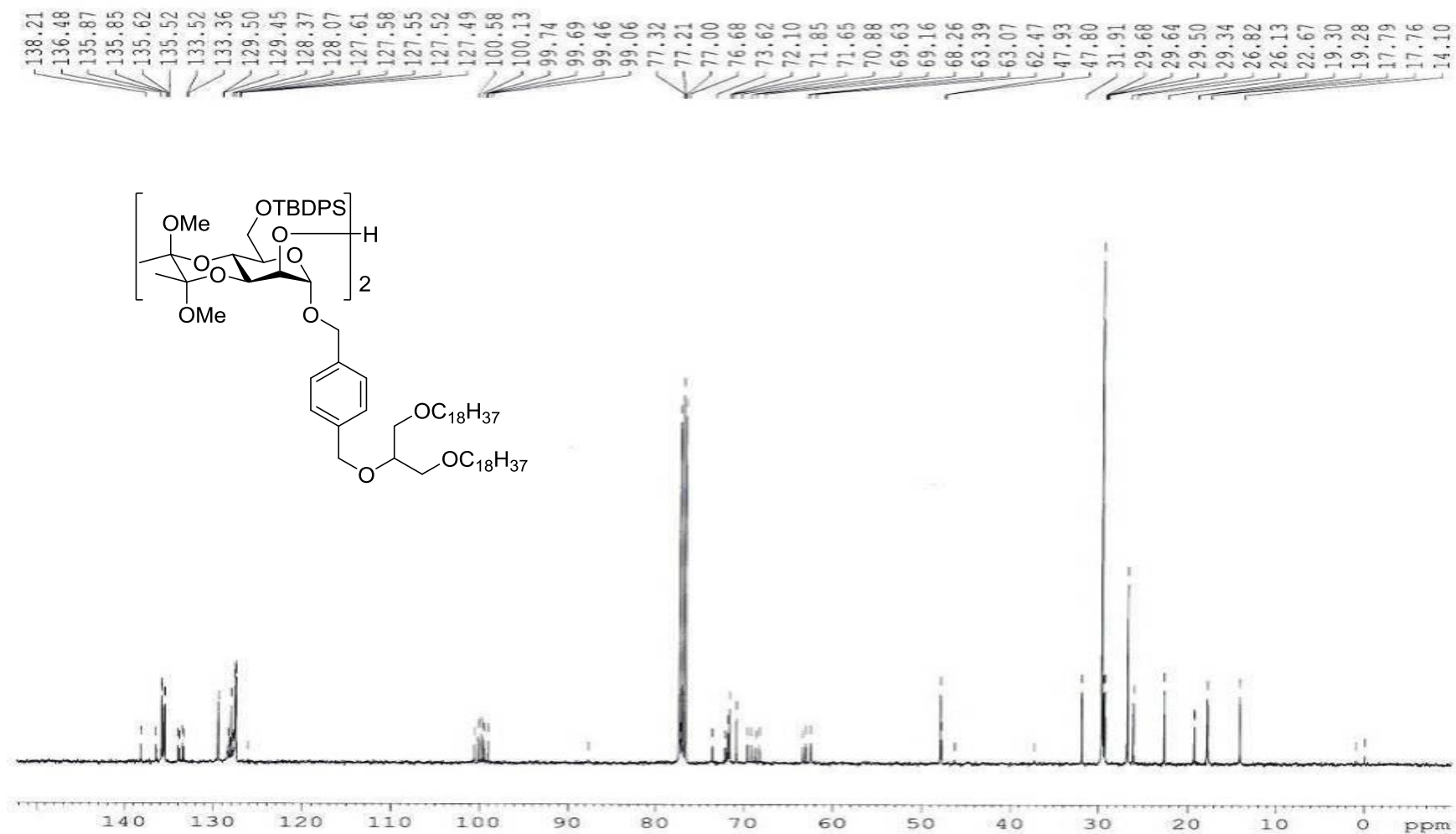
TOF LD+
1.51e4



¹H NMR of Compound **10-2b** (CDCl₃, 400MHz)



^{13}C NMR of Compound **10-2b** (CDCl_3 , 100MHz)



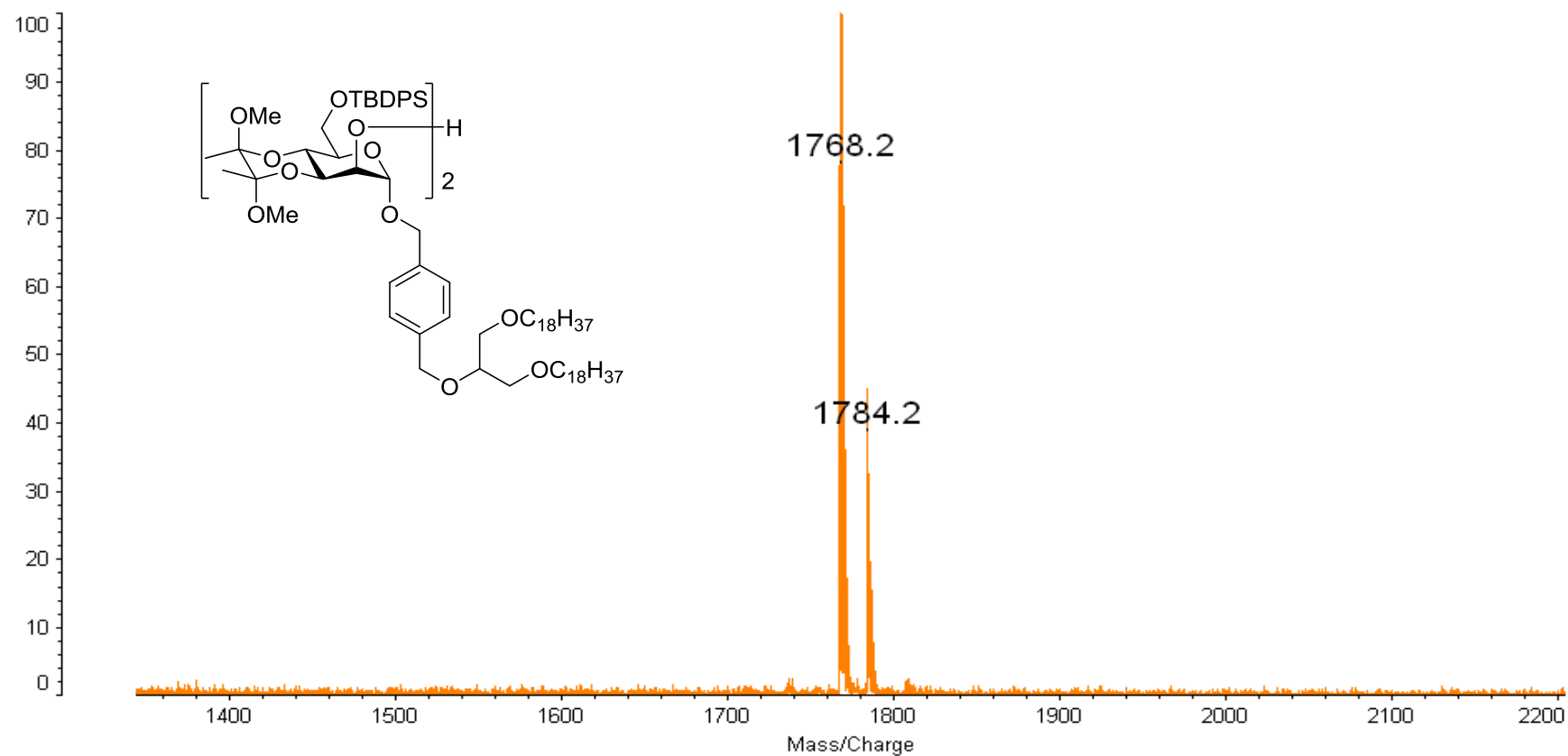
MALDI-TOF-MS of Compound **10-2b**

43D-2
CHCA

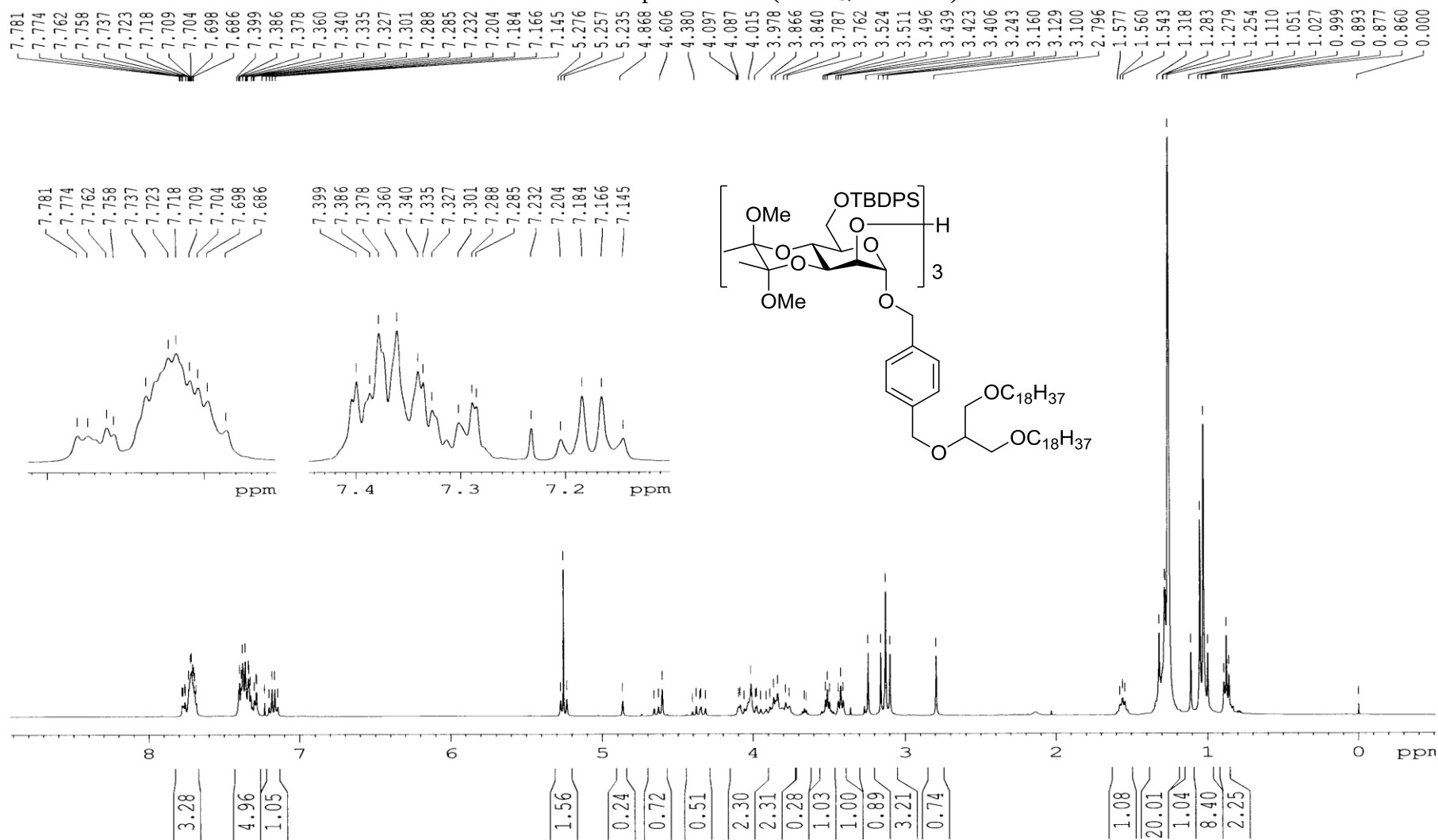
Data: 43D-20002.H19 2 Sep 2008 14:57 Cal: 080111 2 Sep 2008 14:53

Kratos PC Axima CFRplus V2.4.0: Mode Reflectron, Power: 68, Blanked, P.Ext. @ 1000 (bin 75)

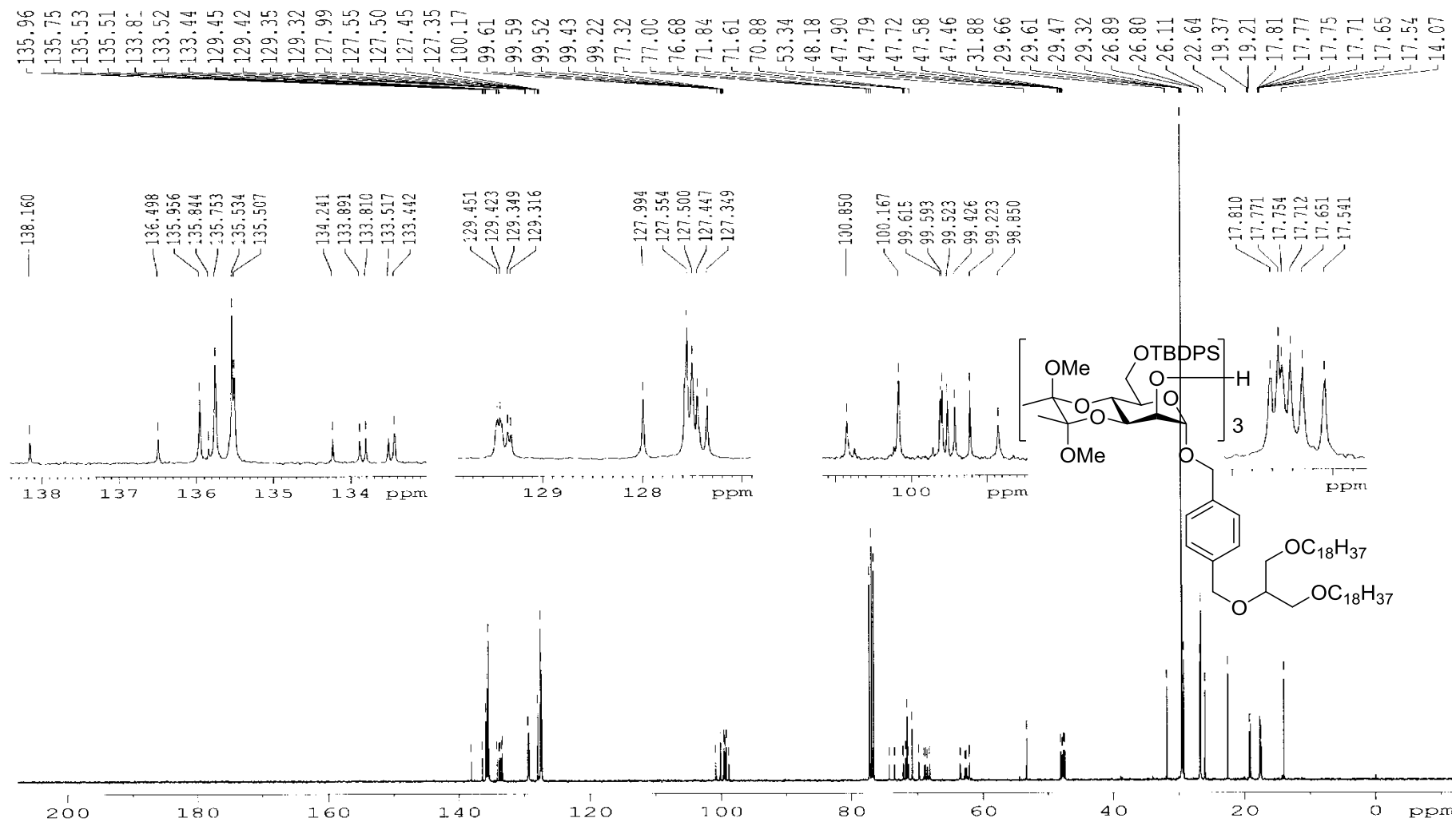
%Int. 33 mV[sum= 1238 mV] Profiles 1-37 Smooth Av 2



¹H NMR of Compound 10-3b (CDCl₃, 400MHz)



¹³C NMR of Compound **10-3b** (CDCl₃, 100MHz)



MALDI-TOF-MS of Compound **10-3b**

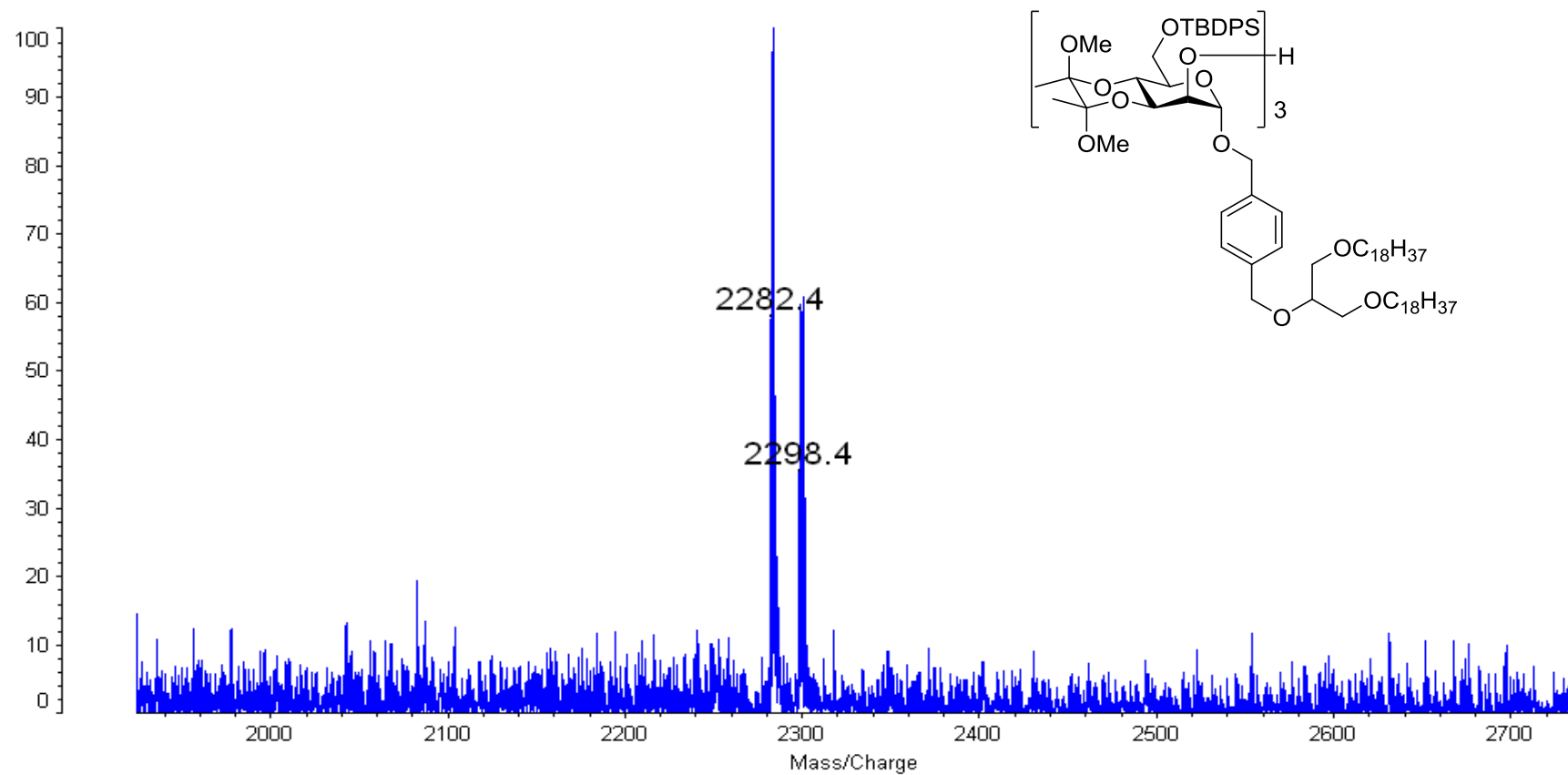
42D-4

CHCA

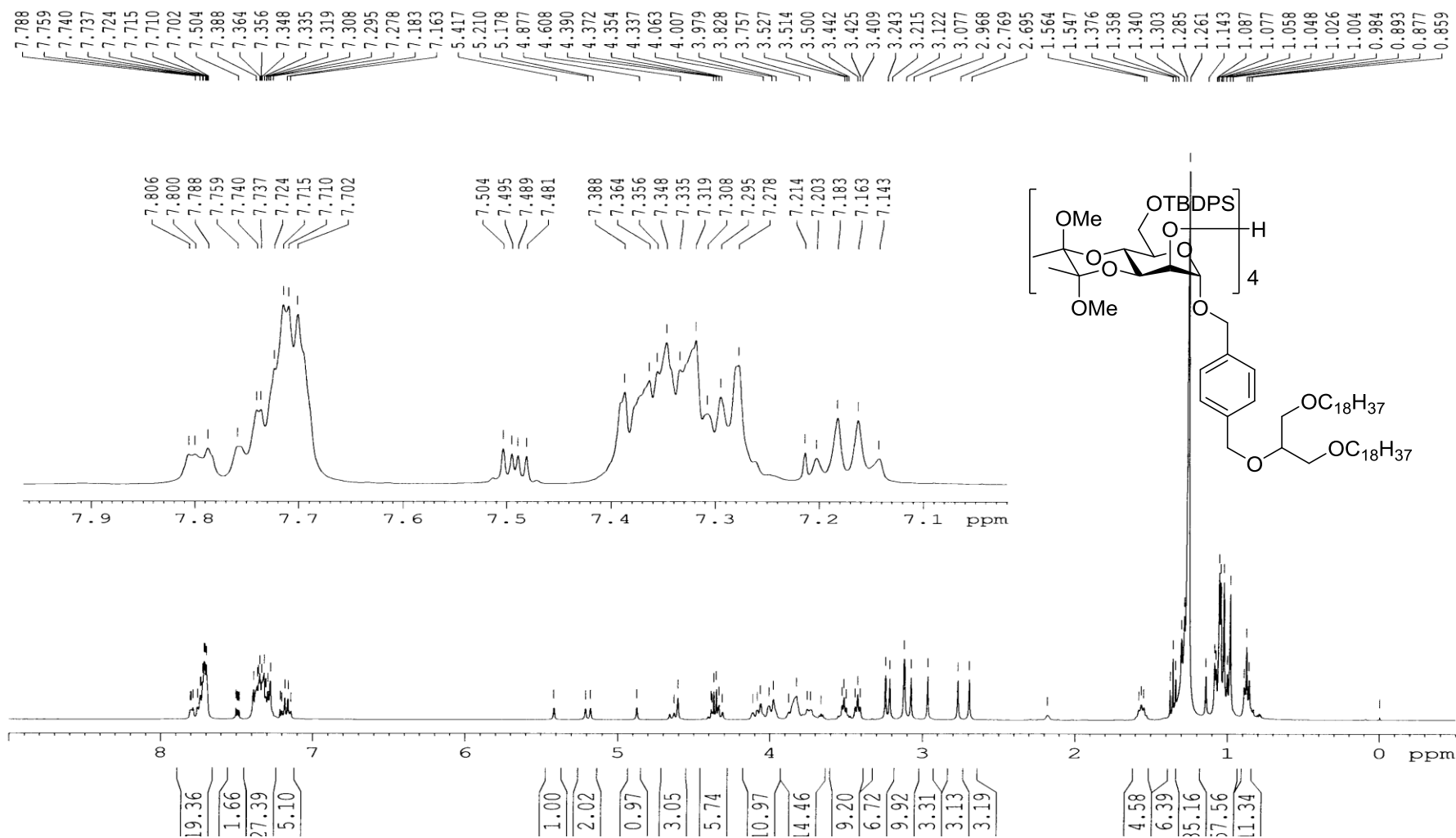
Data: 42D-40002.117 2 Sep 2008 14:58 Cal: 080111 2 Sep 2008 14:53

Kratos PC Axima CFRplus V2.4.0: Mode Reflectron, Power: 68, Blanked, P.Ext. @ 1000 (bin 75)

%Int. 2.5 mV[sum= 132 mV] Profiles 1-53 Smooth Av 2



¹H NMR of Compound **10-4b** (CDCl₃, 400MHz)



135.996
135.779
135.705
135.671
135.496
135.436
133.511
133.424
130.793
129.411
129.369
129.306
128.748
127.943
127.515
127.468
127.438
127.396
127.346
127.276
127.276
100.188
100.055
99.644
99.552
99.479
99.279
99.218
99.156
98.814
77.318
77.000
76.682
71.560
70.862
61.462
48.008
48.026
47.853
47.683
47.558
47.479
47.403
47.283
31.845
29.622
29.577
29.567
29.424
29.280
26.916
26.839
26.738
26.084
22.603
19.333
19.285
19.148
19.119
17.840
17.783
17.710
17.647
17.562
17.485
14.034
14.014

167.471

170 ppm

100 ppm

48 ppm

200 180 160 140 120 100 80 60 40 20 0 ppm

Chemical structure of the repeating unit:

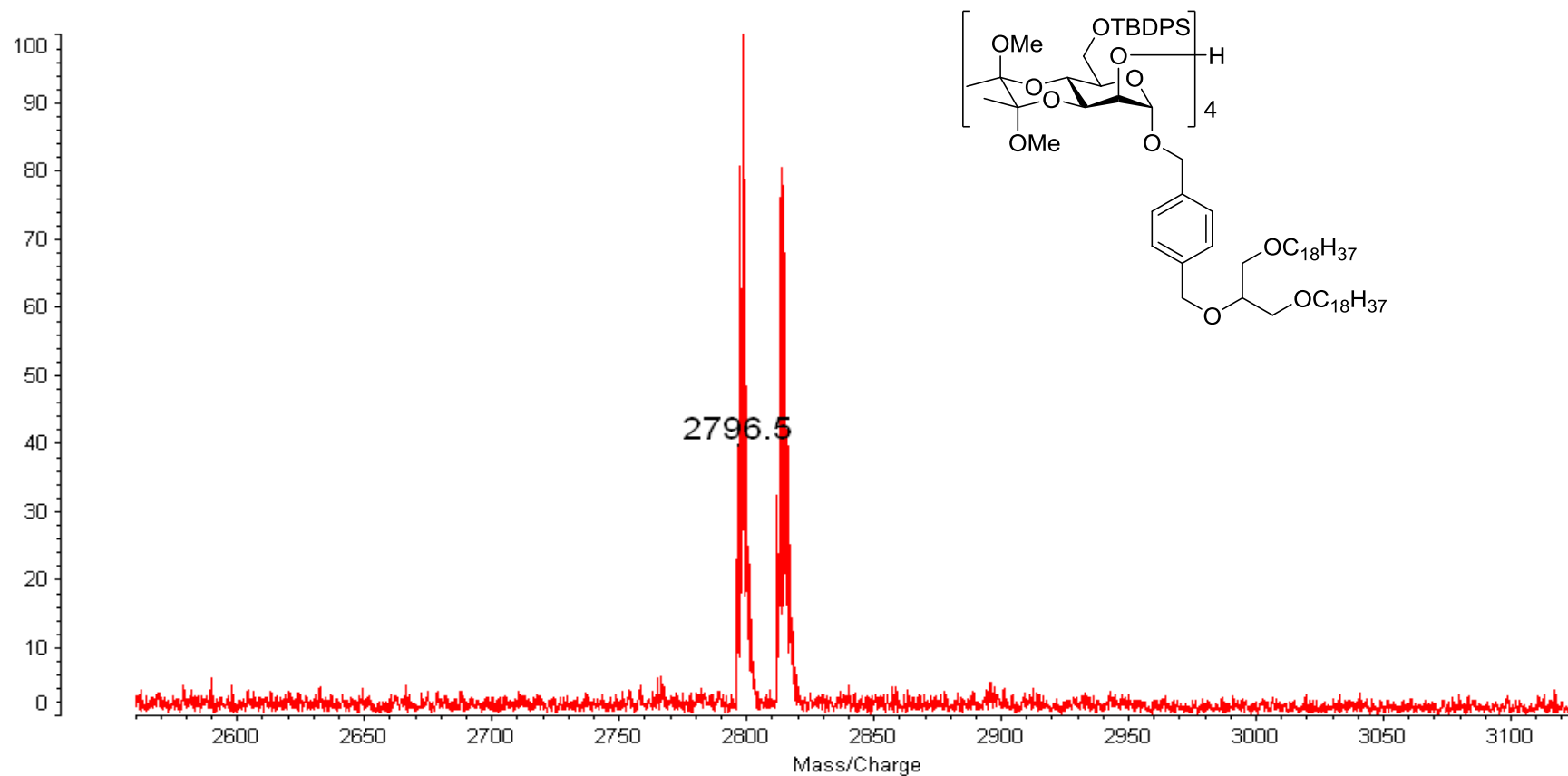
*C1(C(C(C1OC(C2=CC=CC=C2COCC(C)CC(C)OC)OC3=CC=CC=C3OC4C(C(C(C4)OC)OC)OC)OC)OC)OC

Labels in the structure: OMe, OTBDPS, H, OC₁₈H₃₇.

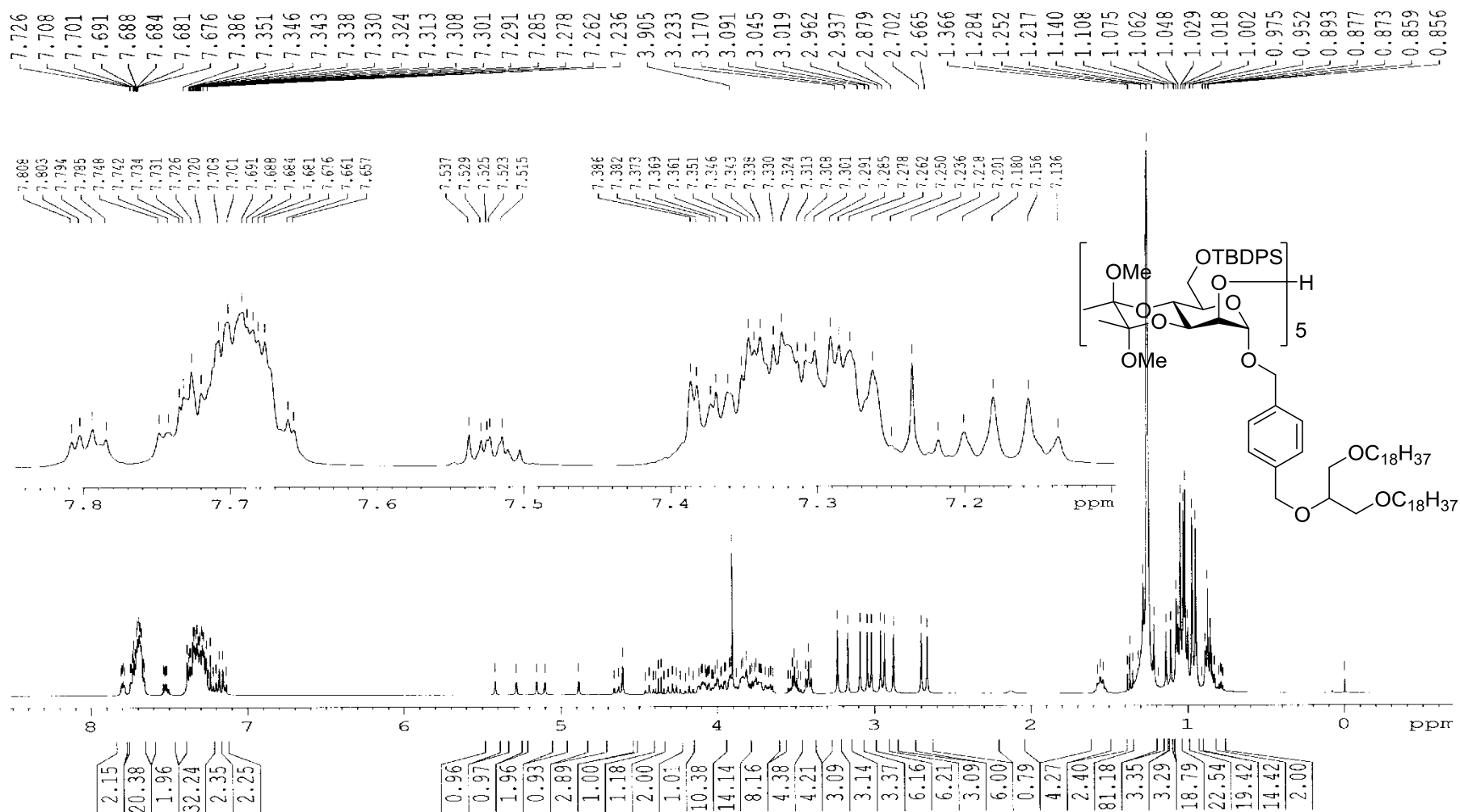
MALDI-TOF-MS of Compound **10-4b**

43D-4

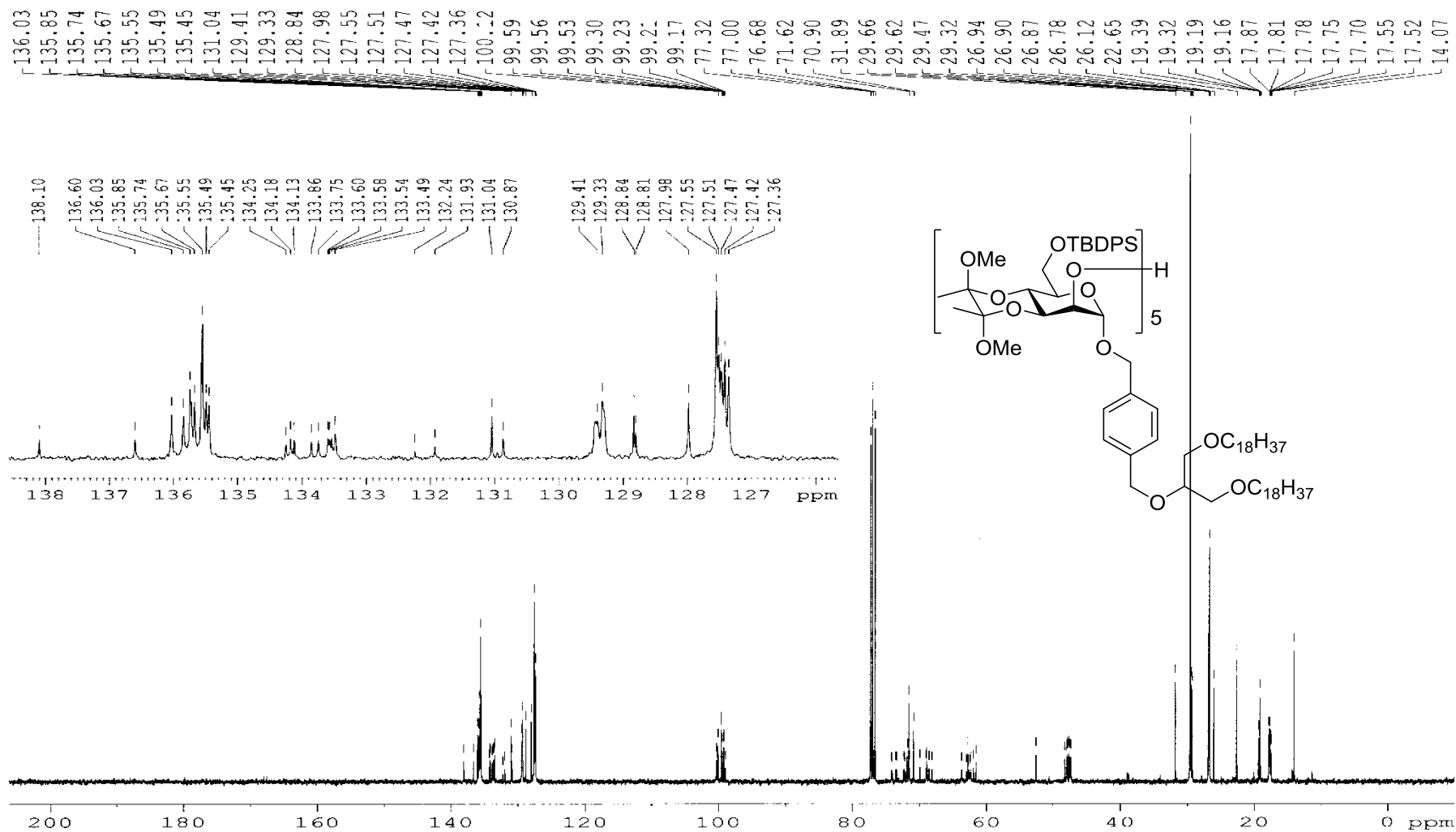
Data: 43D-40001.I11 18 Sep 2008 17:41 Cal: zouxj 18 Sep 2008 17:37
 Kratos PC Axima CFRplus V2.4.0: Mode Reflectron, Power: 74, Blanked, P.Ext. @ 2300 (bin 114)
 %Int. 16 mV[sum= 1334 mV] Profiles 1-81 Smooth Av 2



¹H NMR of Compound 10-5b (CDCl₃, 400MHz)



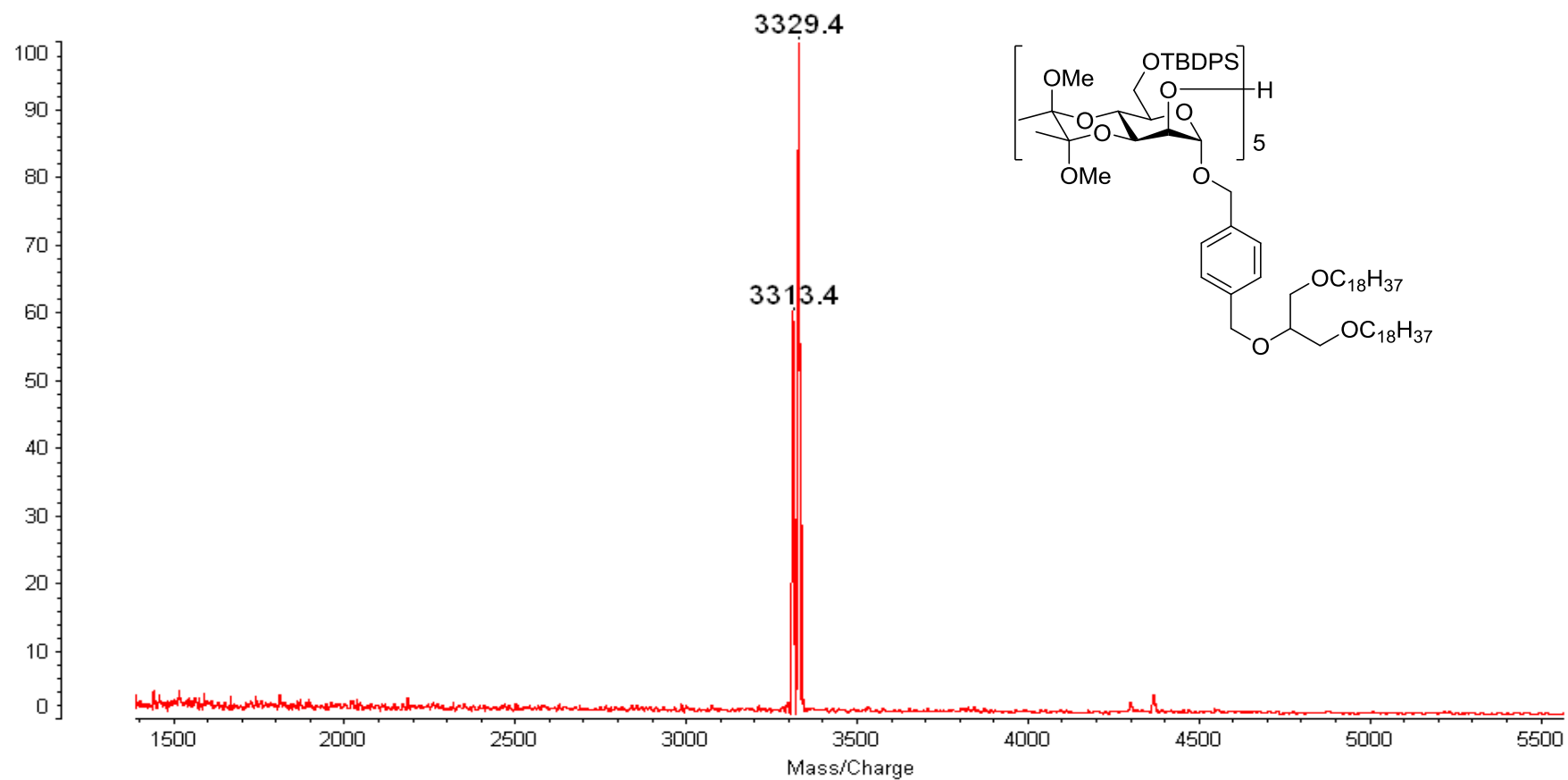
¹³C NMR of Compound **10-5b** (CDCl₃, 100MHz)



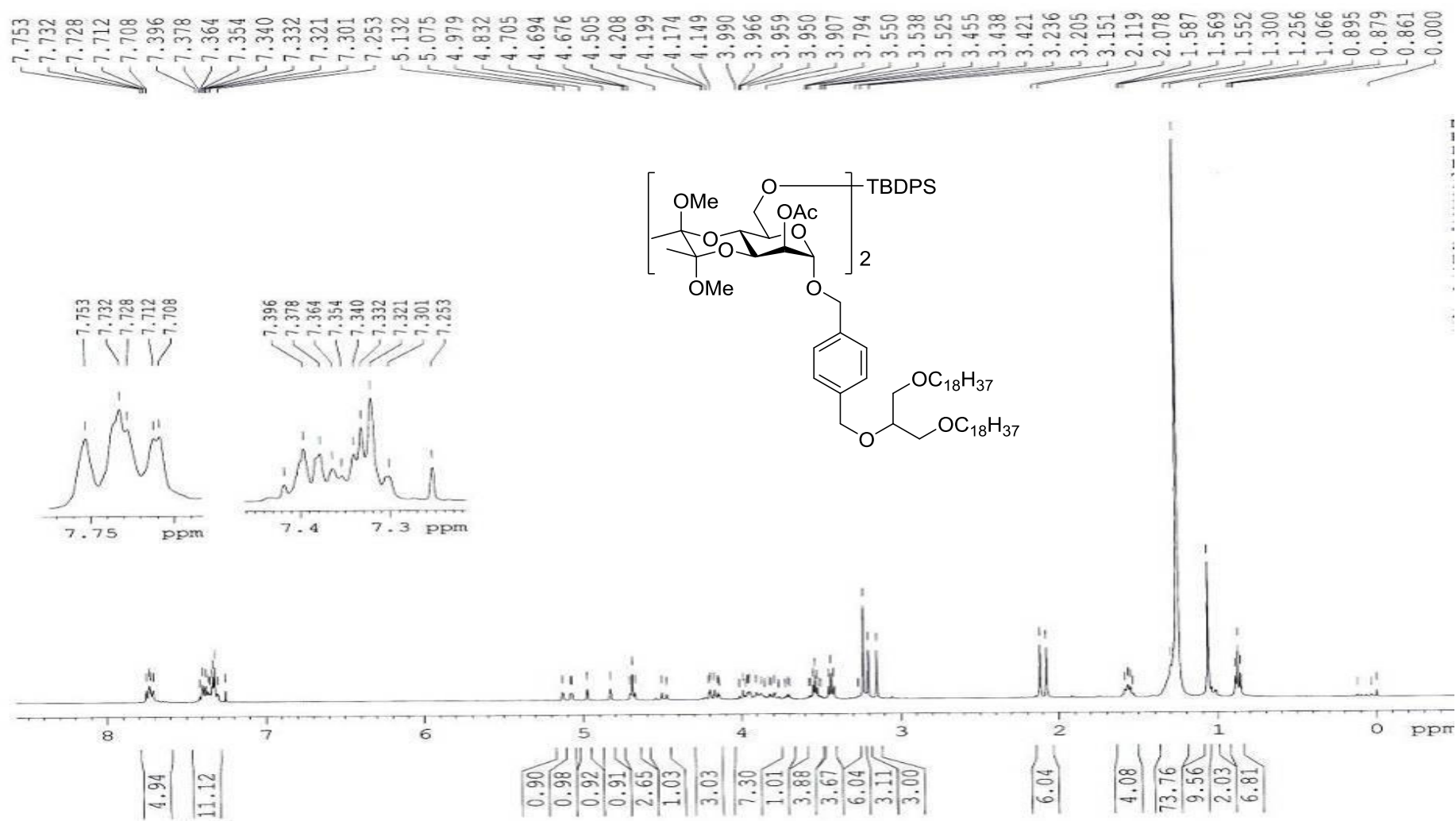
MALDI-TOF-MS of Compound **10-5b**

HD43-5

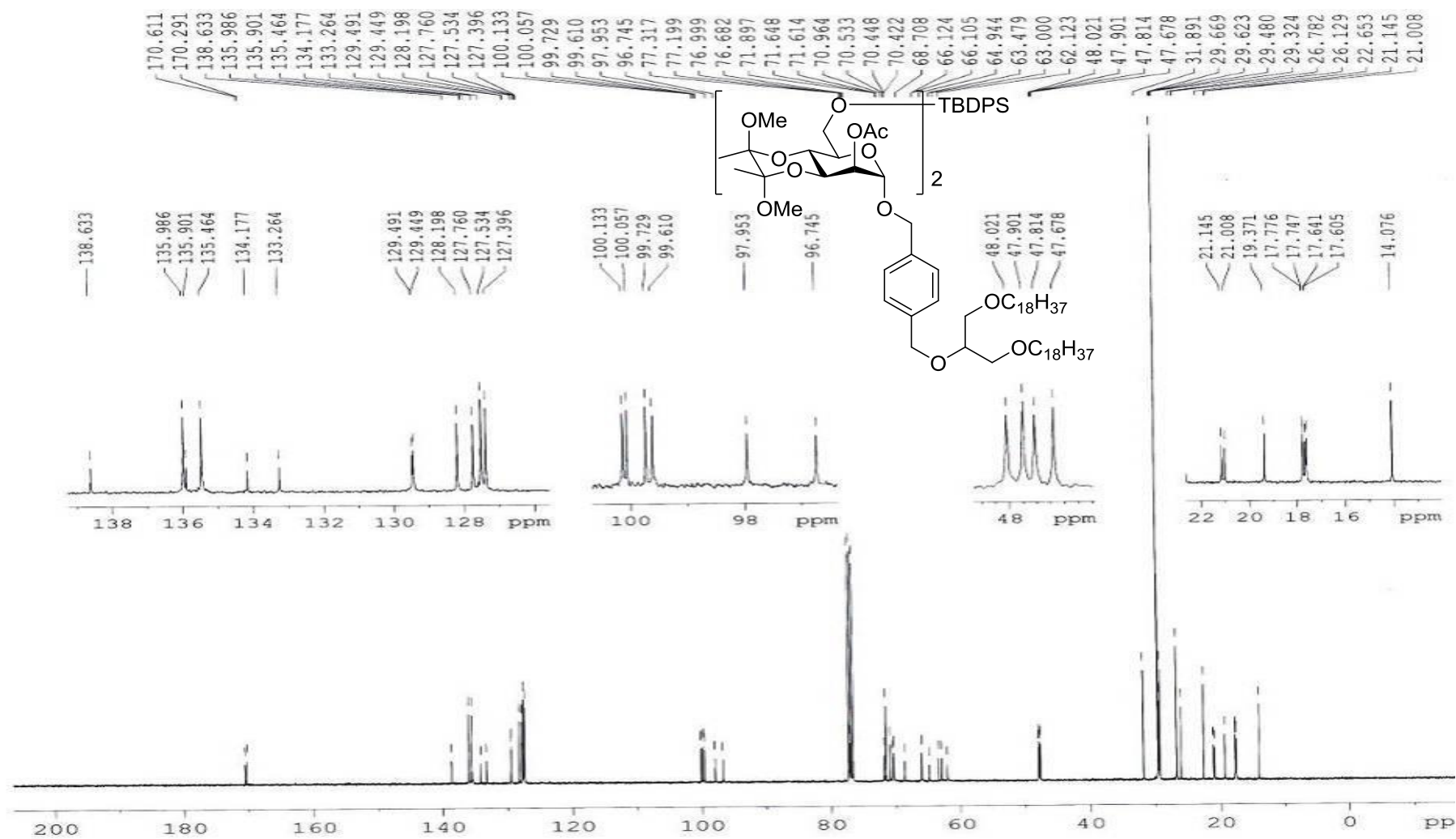
Data: HD43-50001.A24 12 Mar 2009 17:22 Cal: zhong 12 Mar 2009 17:22
 Kratos PC Axima CFRplus V2.4.0: Mode Linear, Power: 40, Blanked, P.Ext. @ 3122 (bin 76)
 %Int. 45 mV[sum= 4860 mV] Profiles 1-108 Smooth Av 80 -Baseline 80



¹H NMR of Compound 11-2a (CDCl₃, 400MHz)



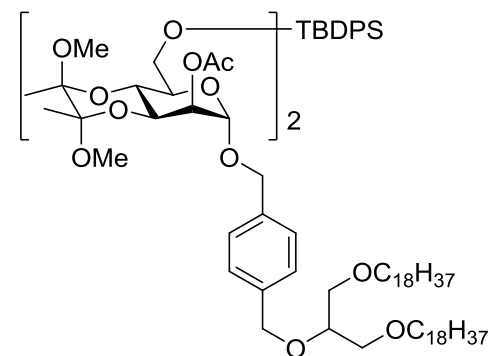
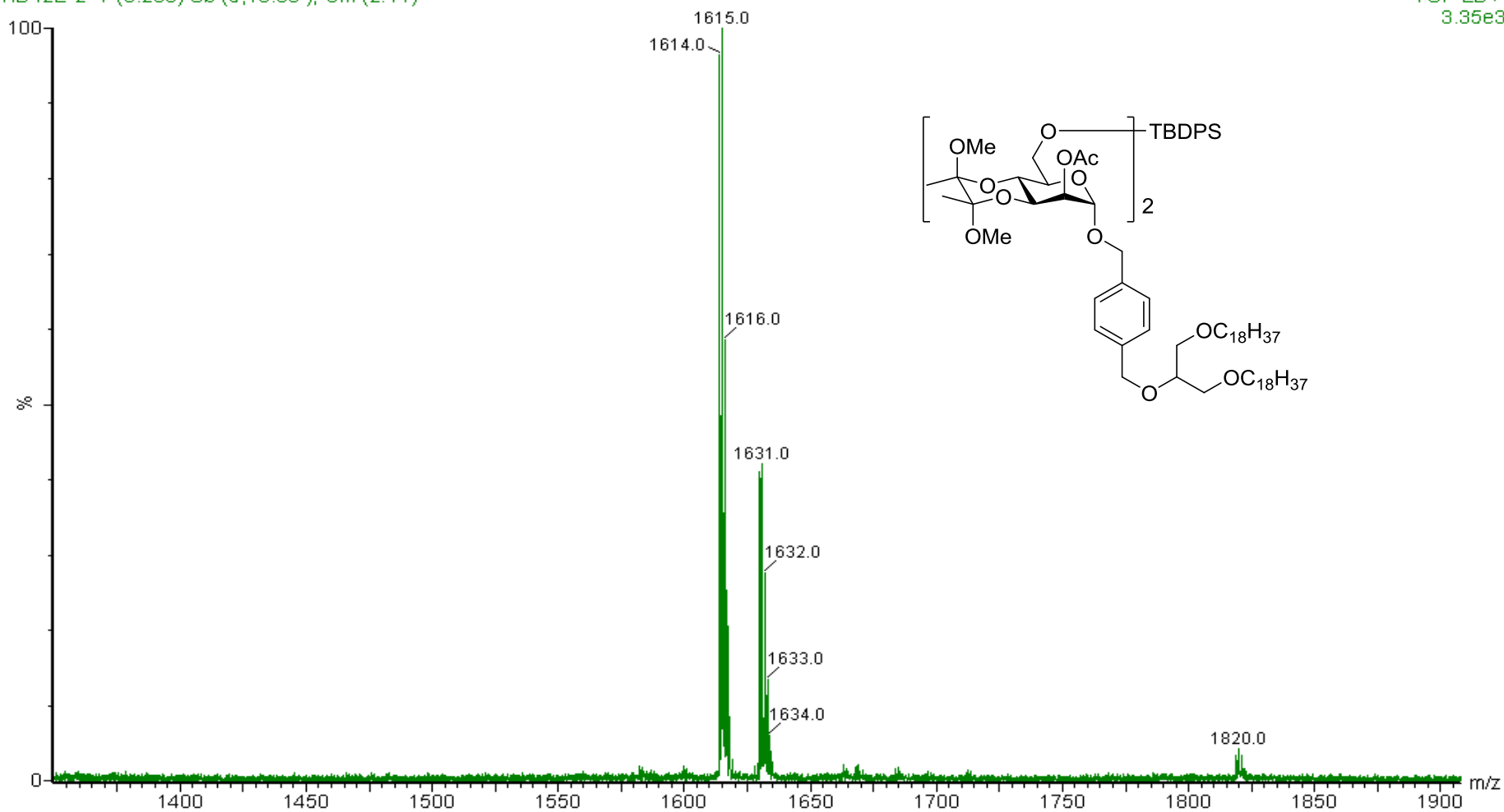
^{13}C NMR of Compound **11-2a** (CDCl_3 , 100MHz)



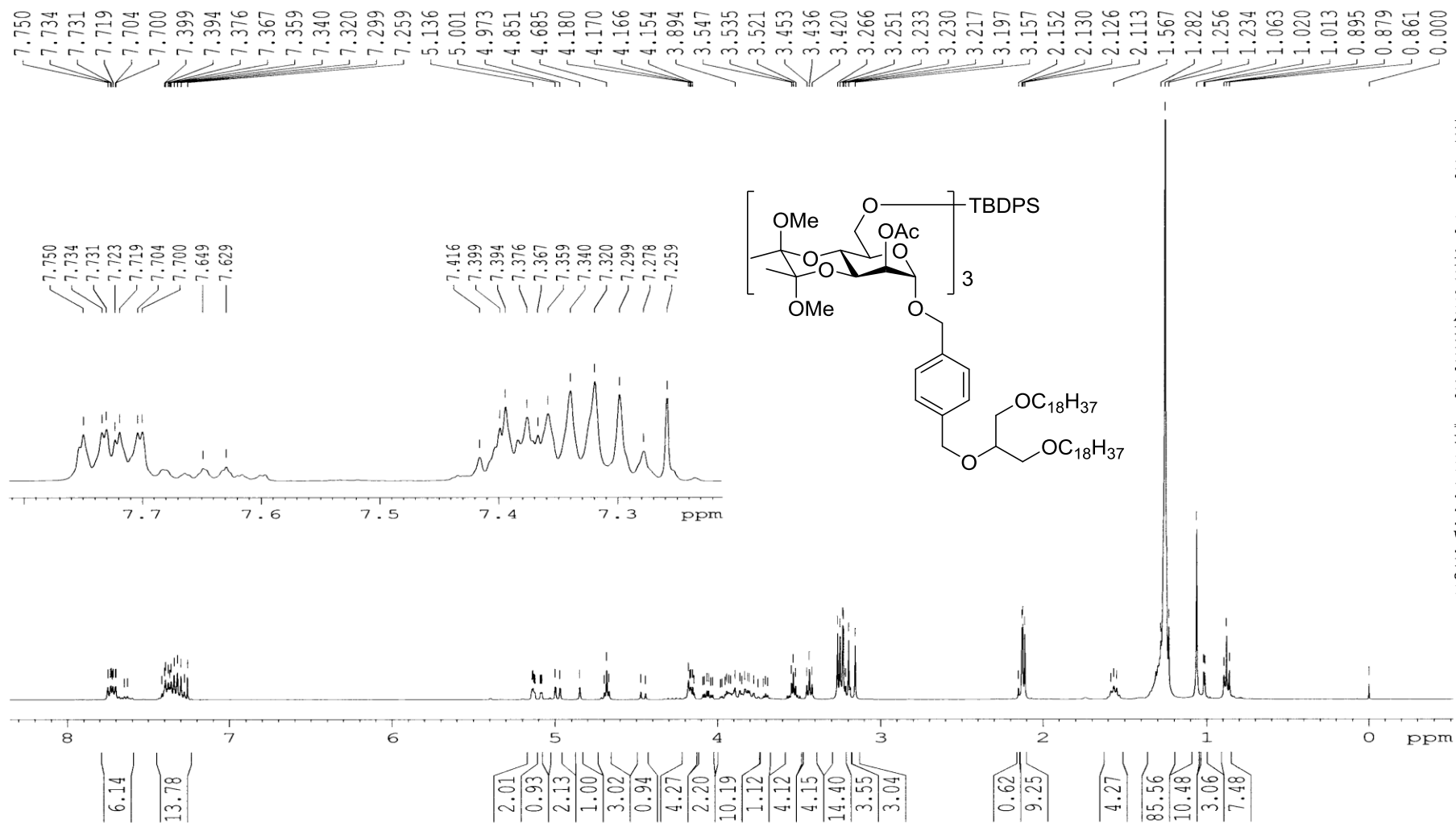
MALDI-TOF-MS of Compound **11-2a**

HD42E-2 7 (0.233) Sb (5,10.00); Cm (2:11)

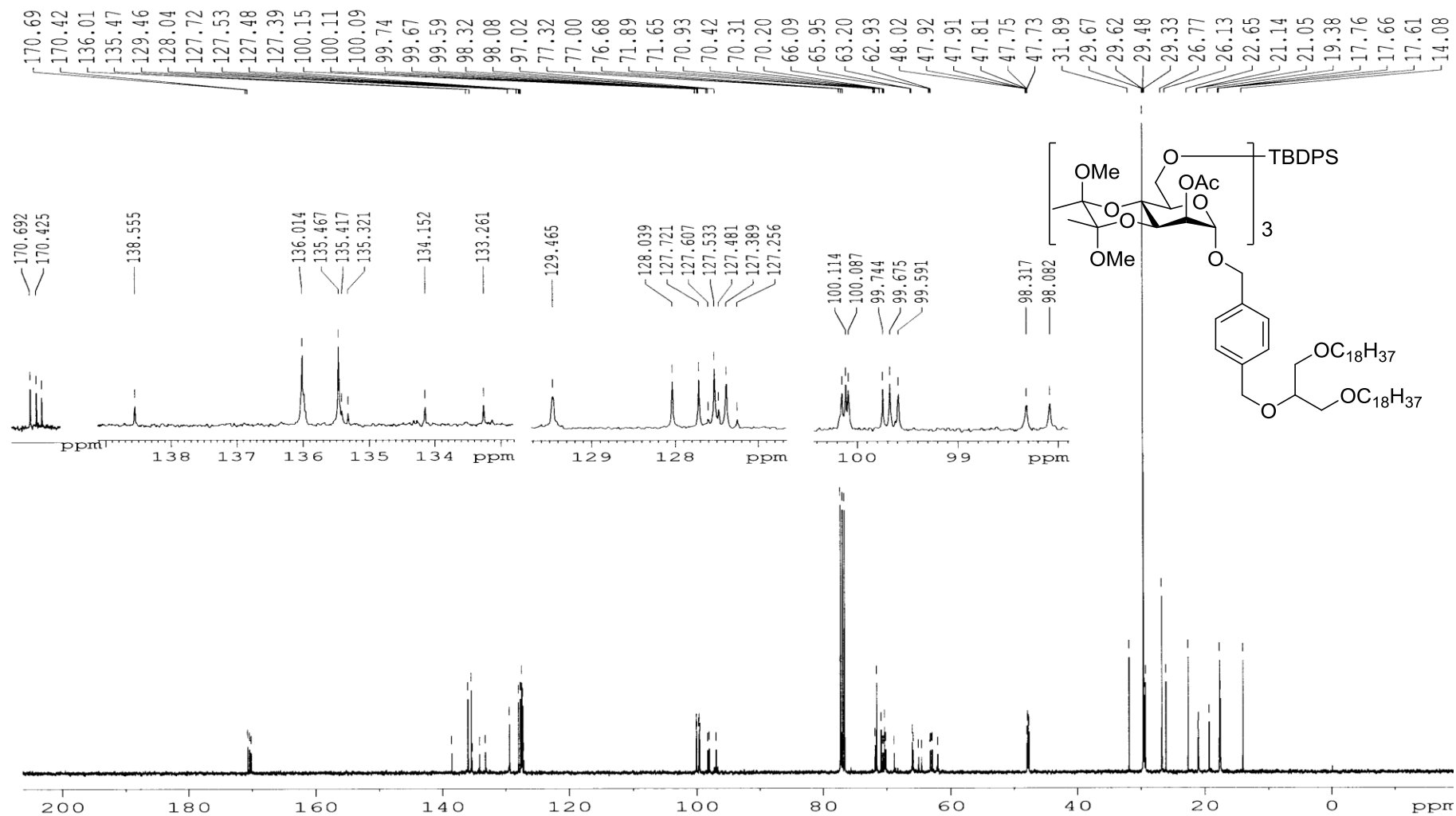
TOF LD+
3.35e3



¹H NMR of Compound 11-3a (CDCl₃, 400MHz)



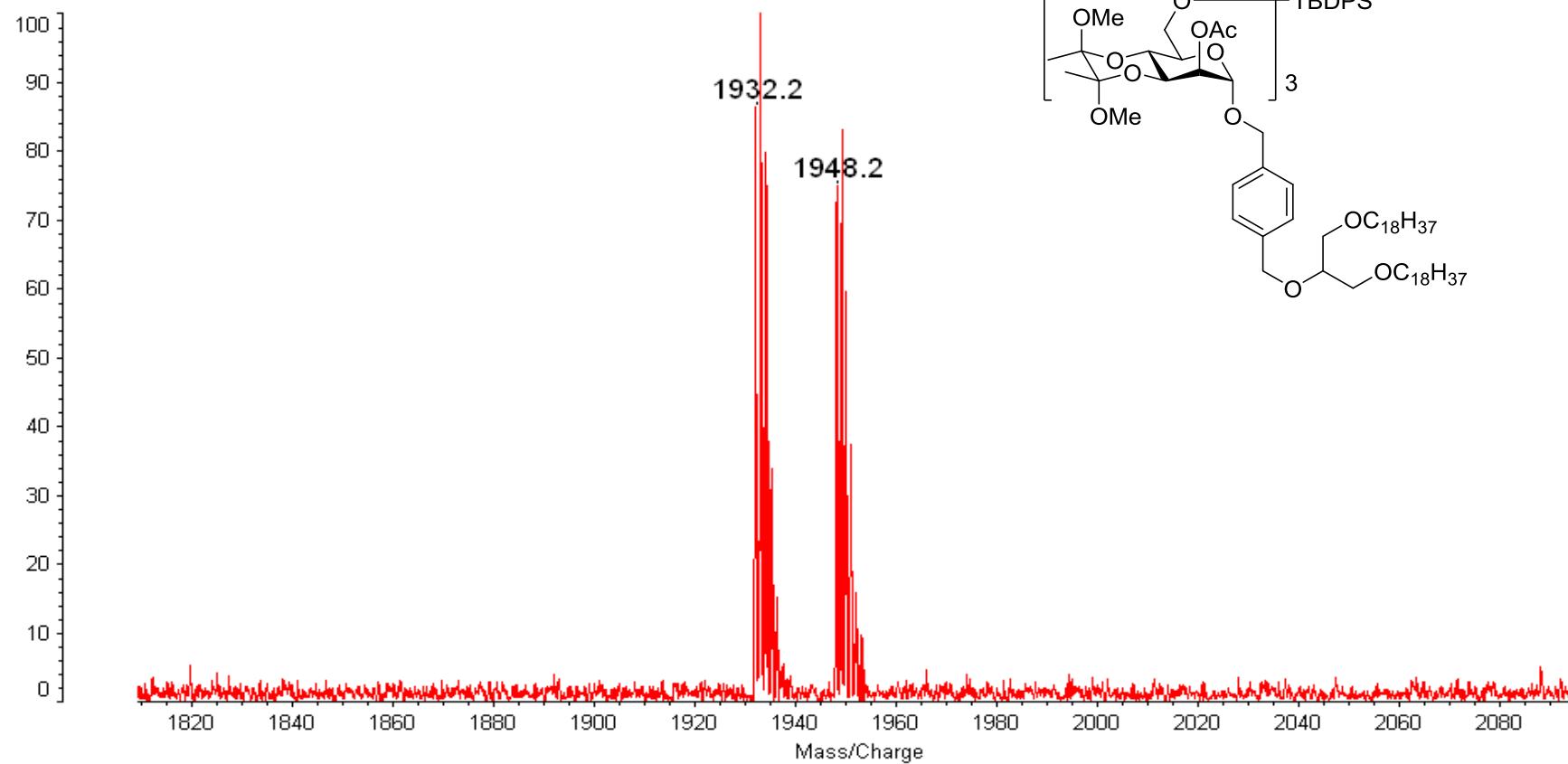
¹³C NMR of Compound **11-3a** (CDCl₃, 100MHz)



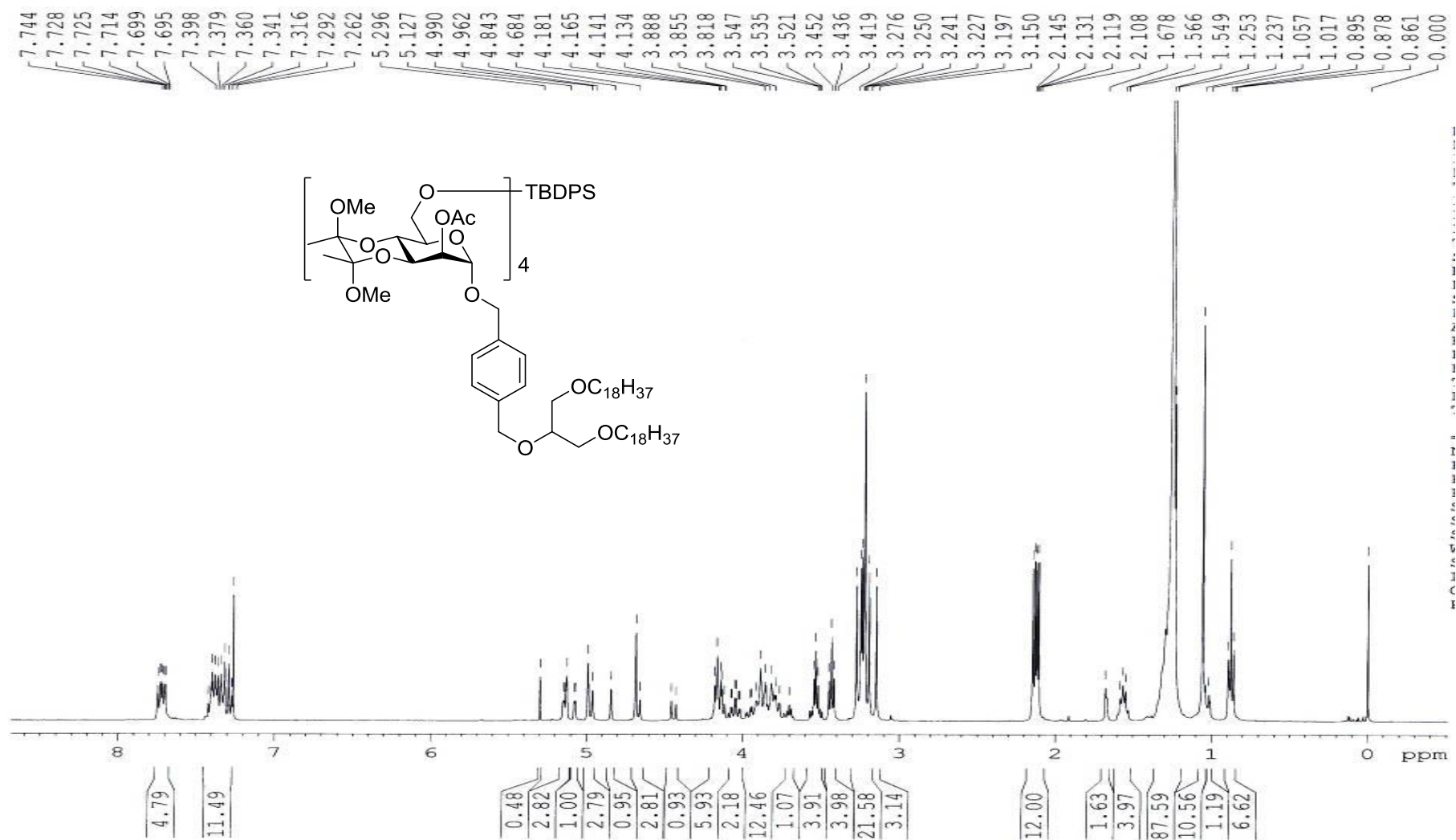
MALDI-TOF-MS of Compound **11-3a**

HD-45-3

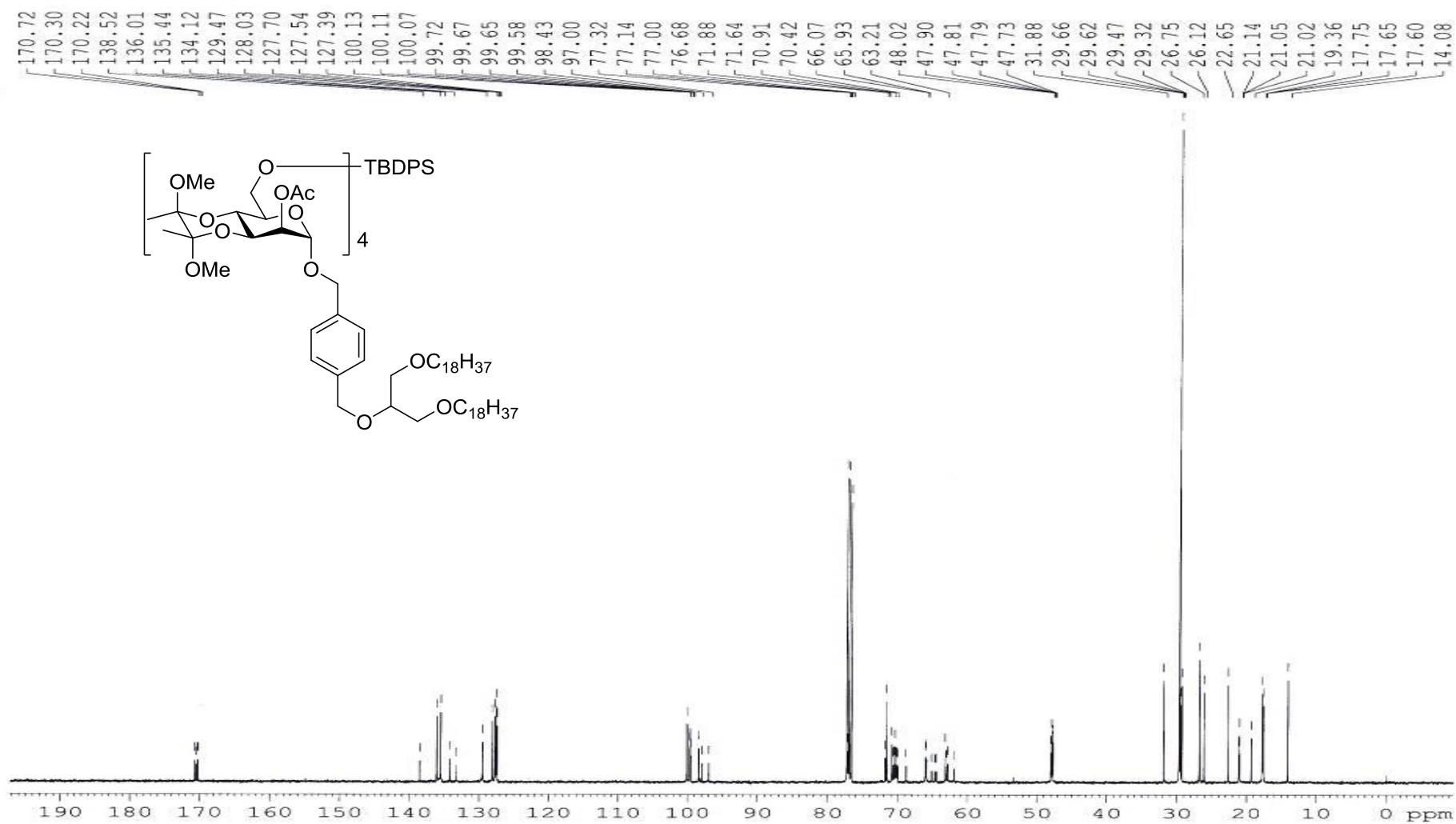
Data: HD45-30001.J15 16 Feb 2009 17:57 Cal: zouxj 16 Feb 2009 17:56
 Kratos PC Axima CFRplus V2.4.0: Mode Reflectron, Power: 35, Blanked, P.Ext. @ 2300 (bin 129)
 %Int. 13 mV[sum= 2054 mV] Profiles 1-158 Smooth Av 2 -Baseline 80



¹H NMR of Compound **11-4a** (CDCl₃, 400MHz)



^{13}C NMR of Compound **11-4a** (CDCl_3 , 100MHz)



MALDI-TOF-MS of Compound **11-4a**

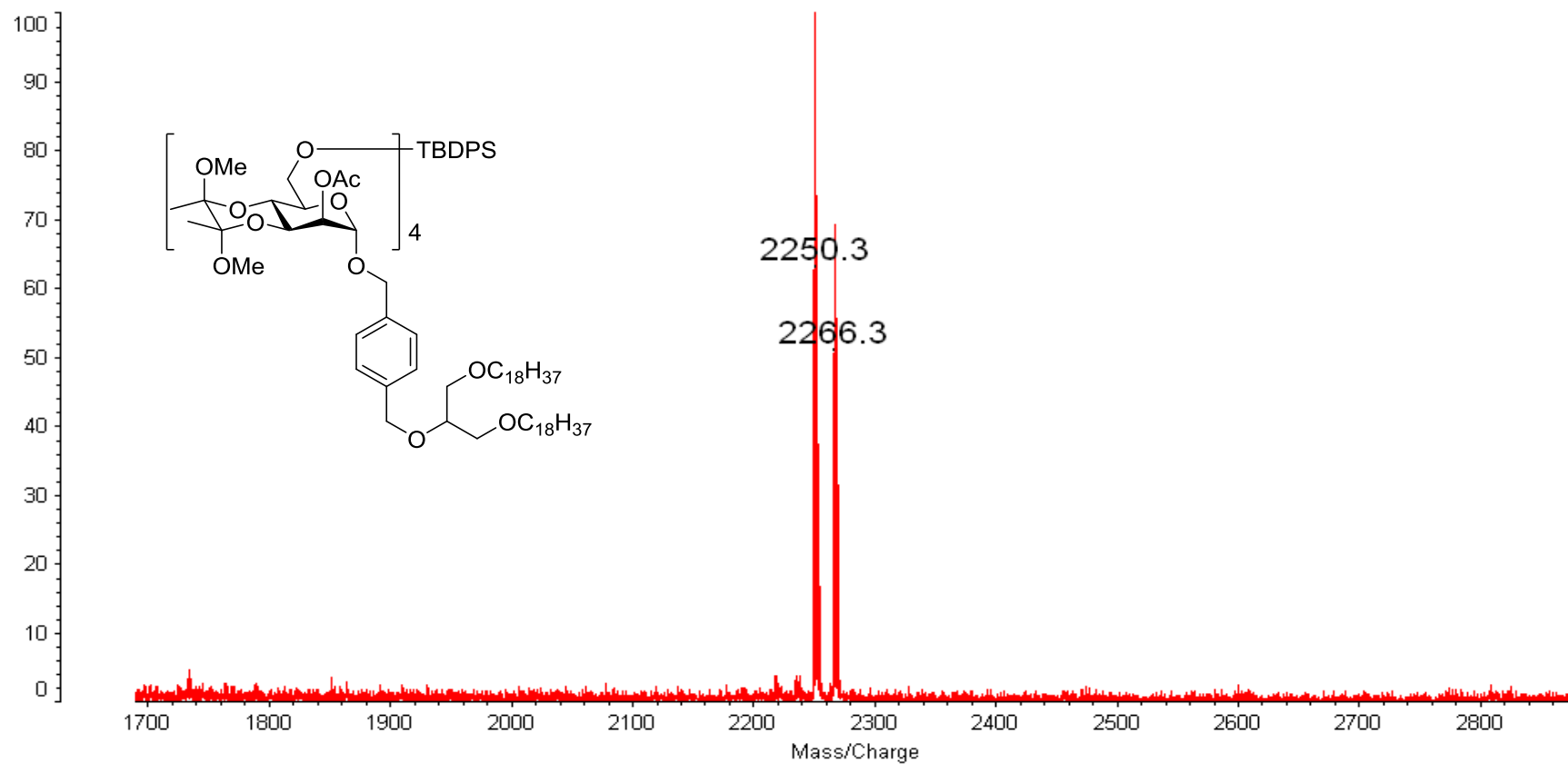
42E-4

CHCA

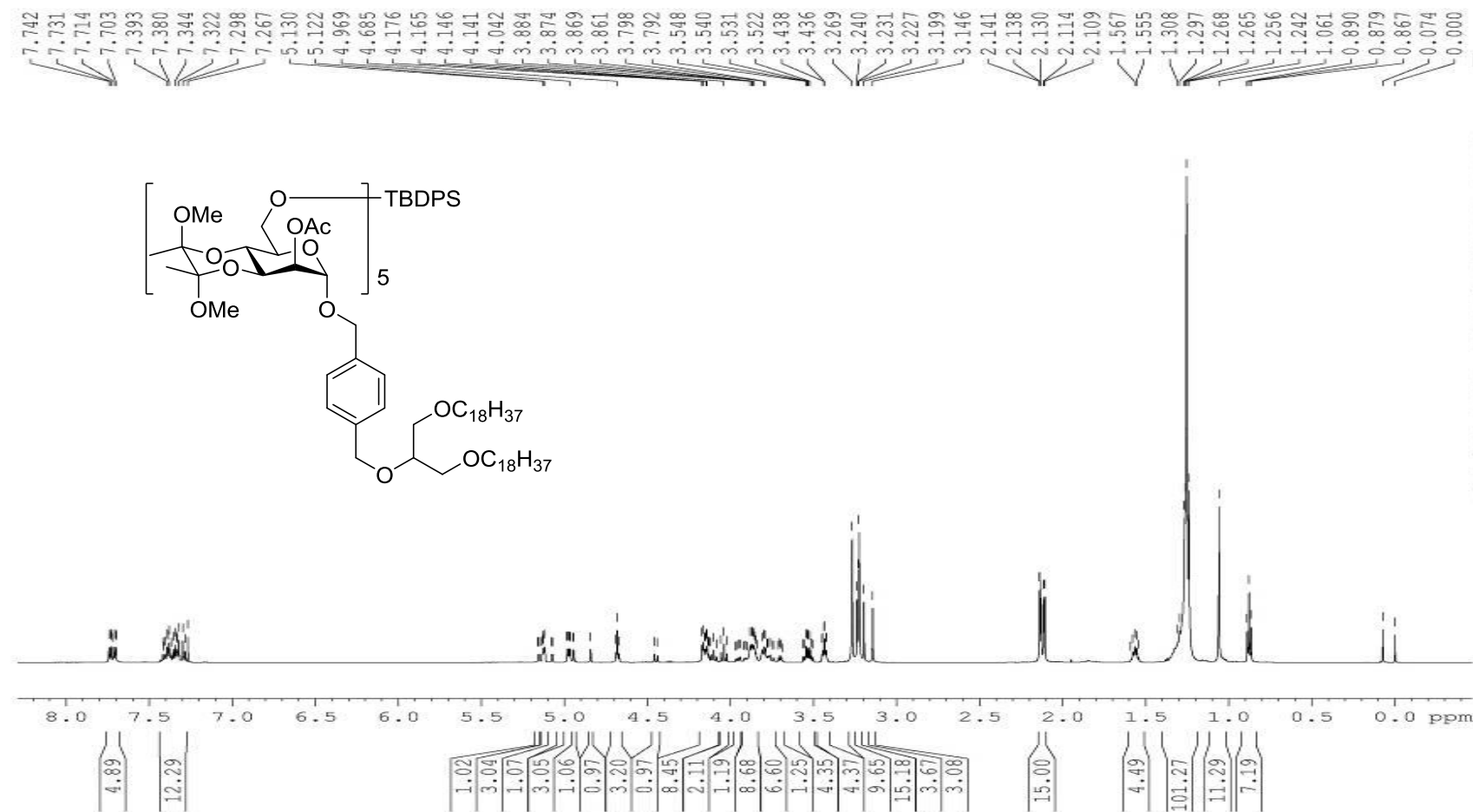
Data: 42E-40001.F21 11 Sep 2008 11:48 Cal: 080111 11 Sep 2008 11:47

Kratos PC Axima CFRplus V2.4.0: Mode Reflectron, Power: 69, Blanked, P.Ext. @ 2300 (bin 114)

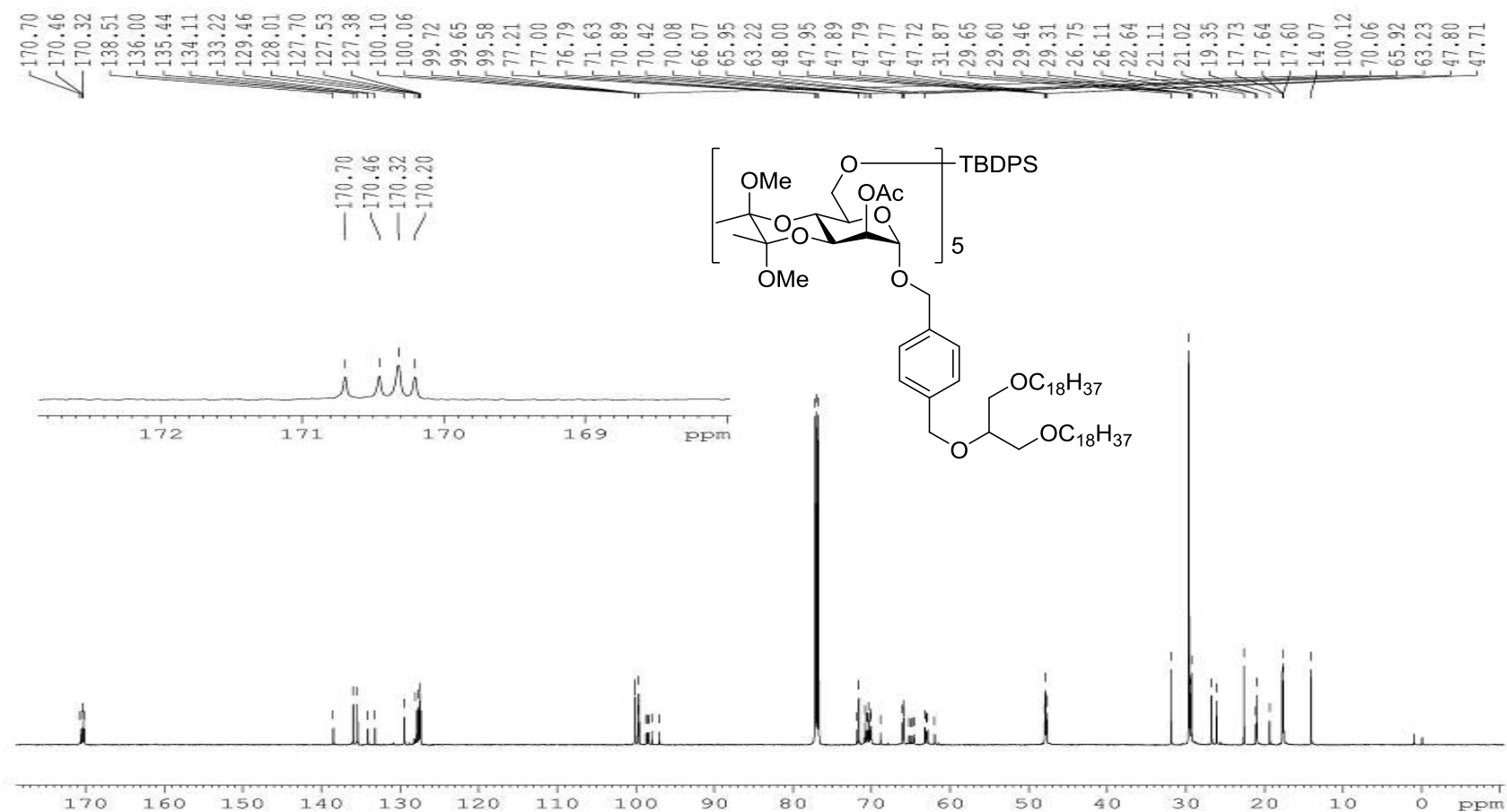
%Int. 11 mV[sum= 1144 mV] Profiles 1-100 Smooth Av 2



¹H NMR of Compound **11-5a** (CDCl₃, 600MHz)



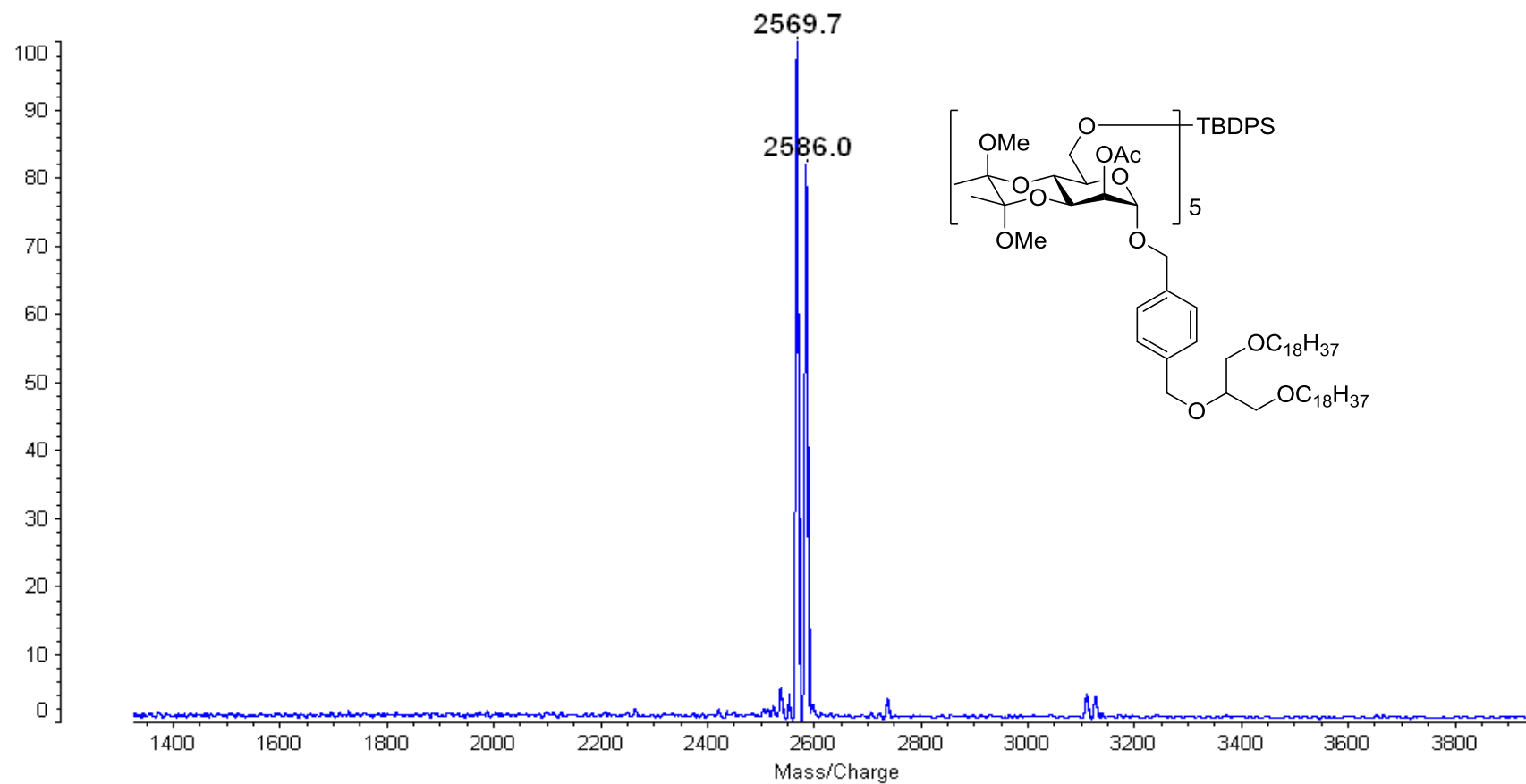
^{13}C NMR of Compound **11-5a** (CDCl_3 , 150MHz)



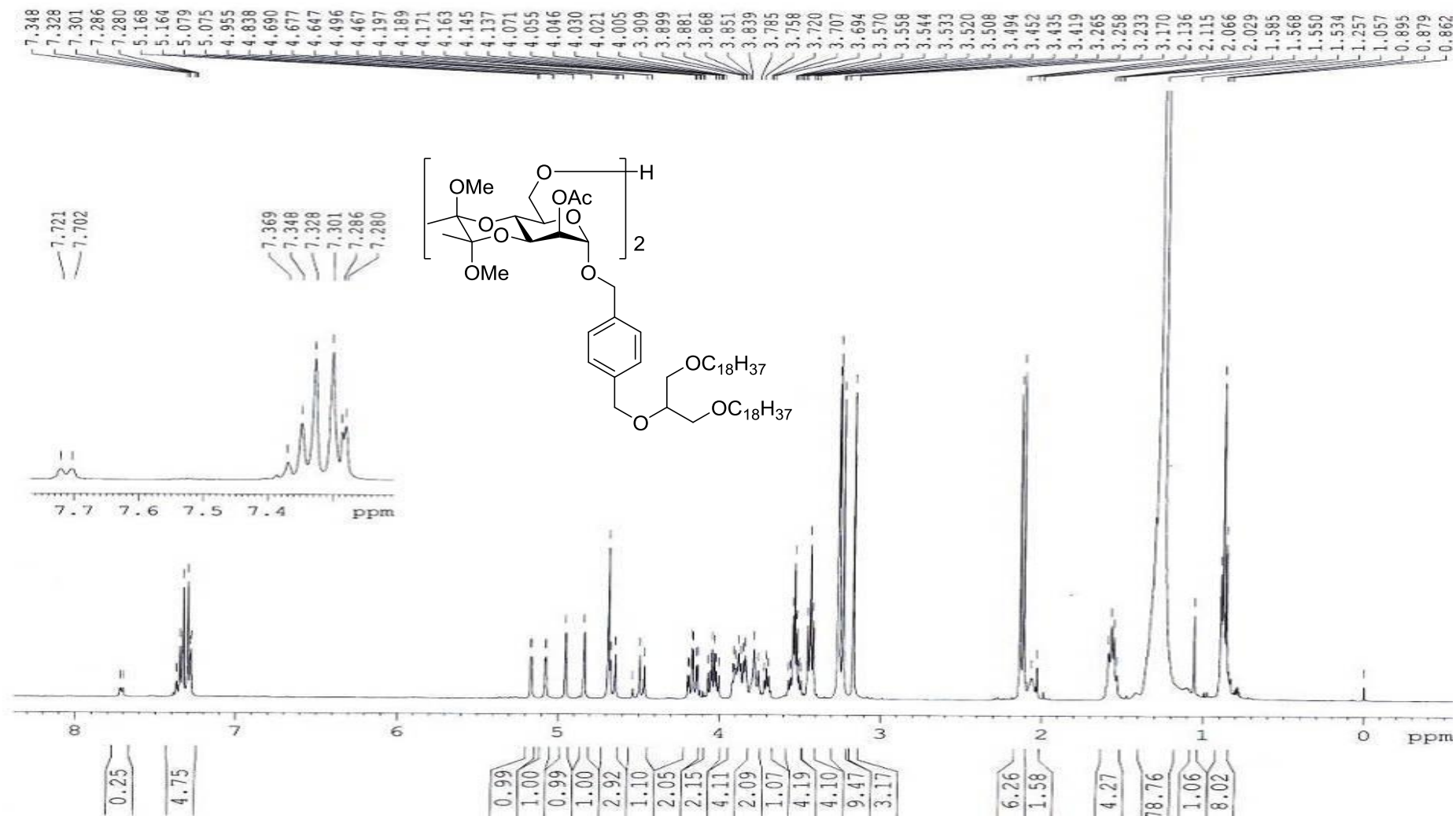
MALDI-TOF-MS of Compound **11-5a**

HD45-5

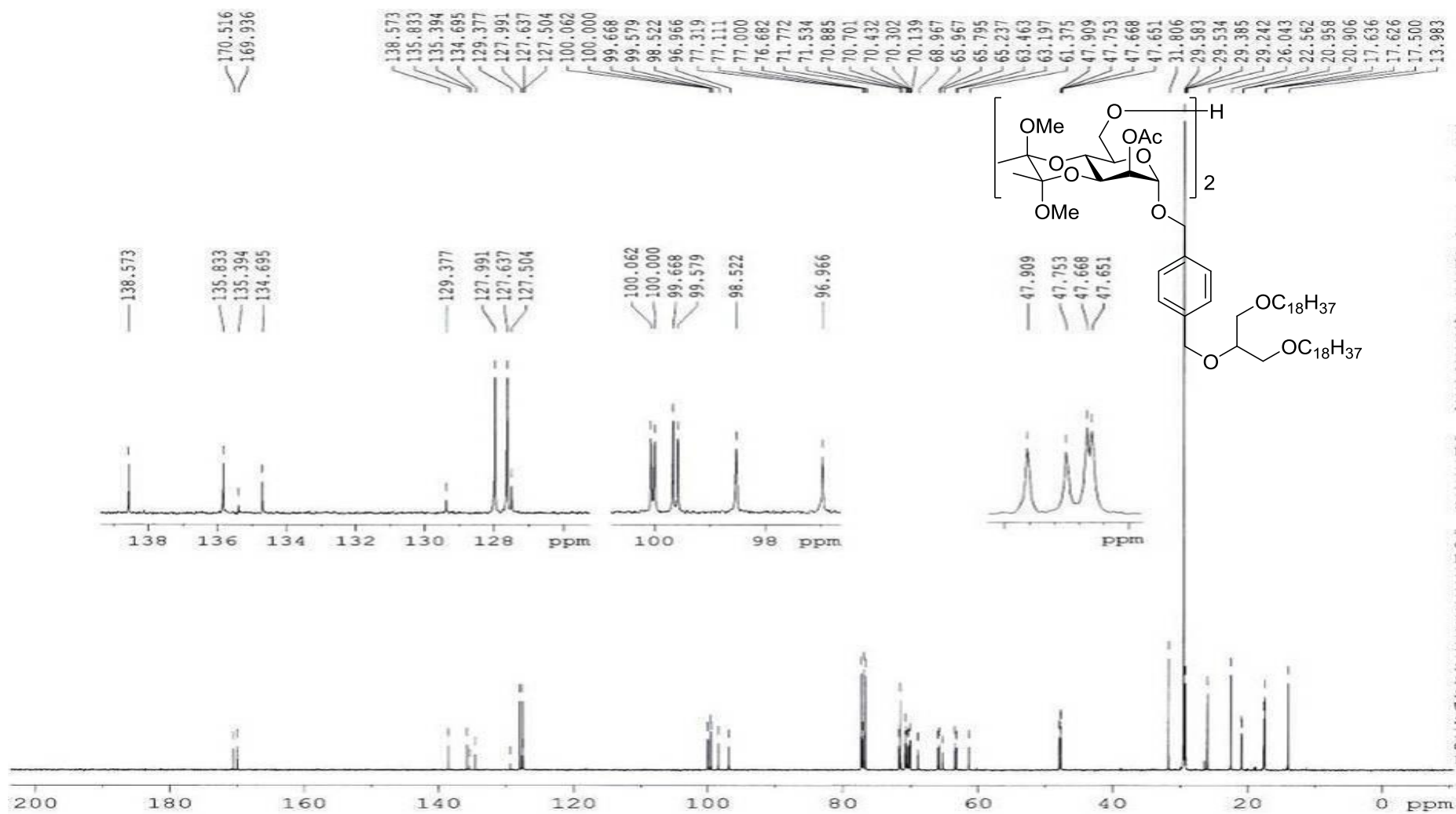
Data: HD45-50002.L1 30 Mar 2009 18:02 Cal: zhong 30 Mar 2009 18:01
 Kratos PC Axima CFRplus V2.4.0: Mode Linear, Power: 58, Blanked, P.Ext. @ 4000 (bin 86)
 %Int. 118 mV[sum= 5094 mV] Profiles 1-43 Smooth Av 80 -Baseline 80



¹H NMR of Compound 11-2b (CDCl₃, 400MHz)



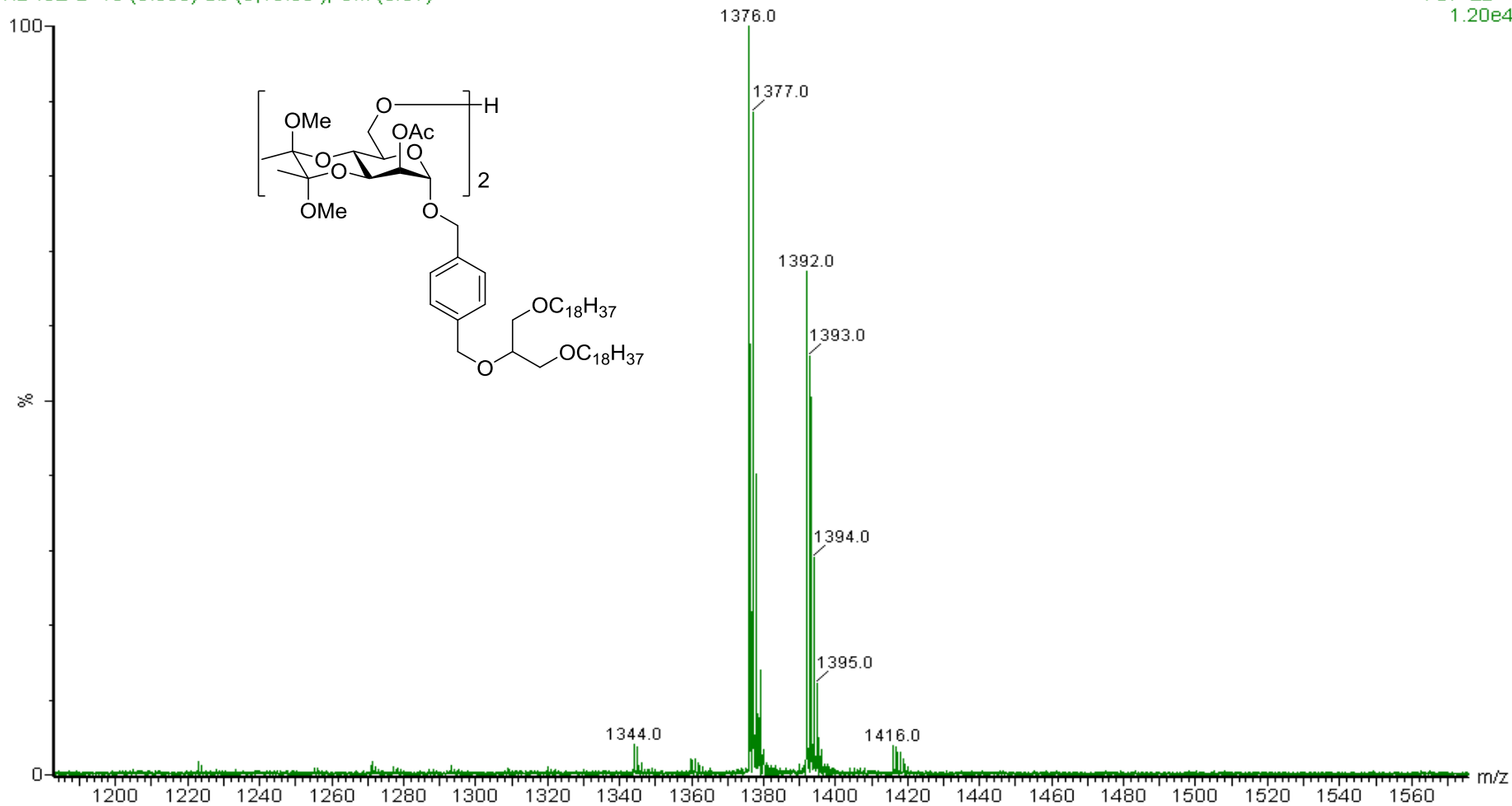
^{13}C NMR of Compound **11-2b** (CDCl_3 , 100MHz)



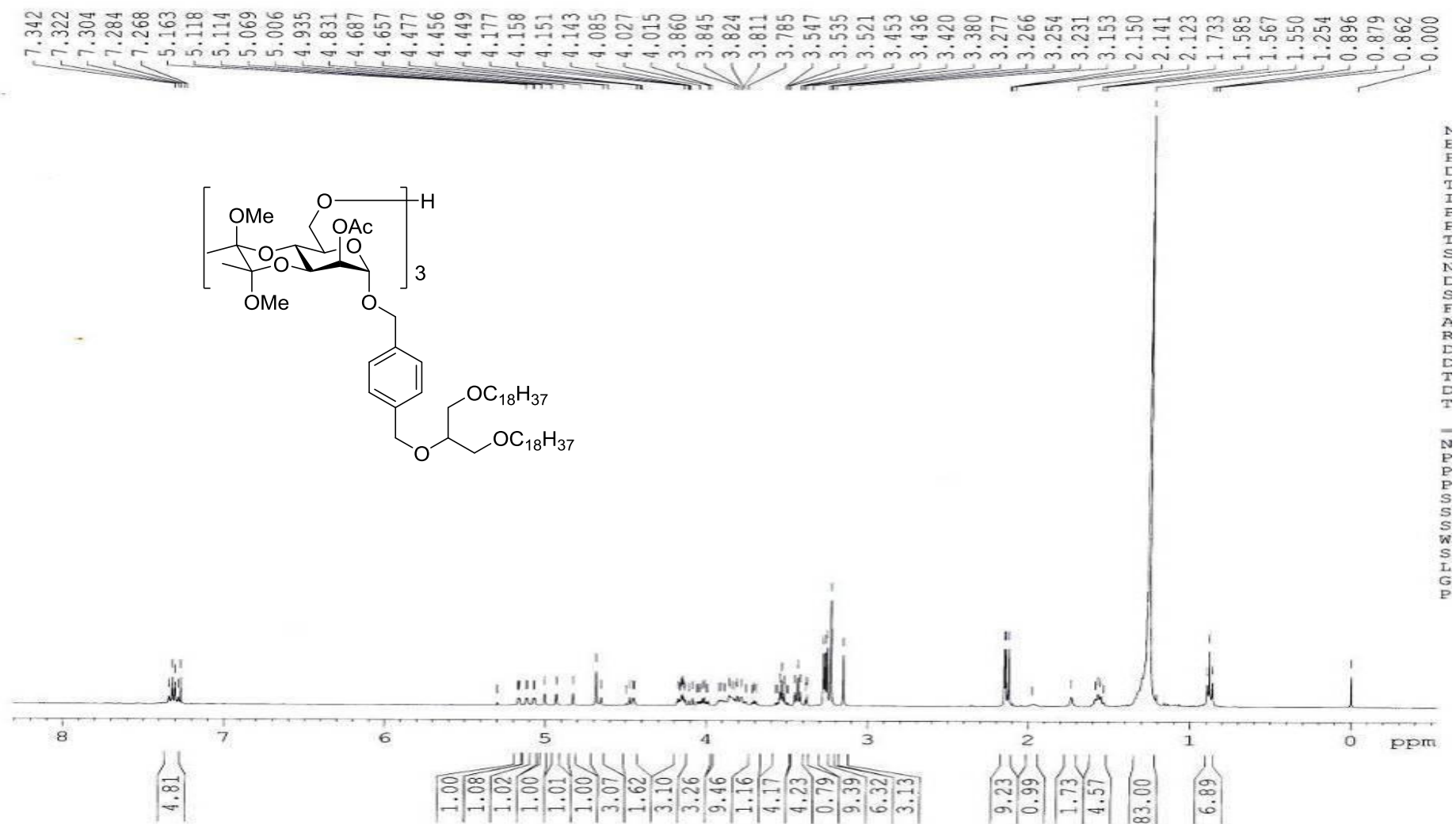
MALDI-TOF-MS of Compound **11-2b**

HD43E-2 15 (0.500) Sb (5,10.00); Cm (6:57)

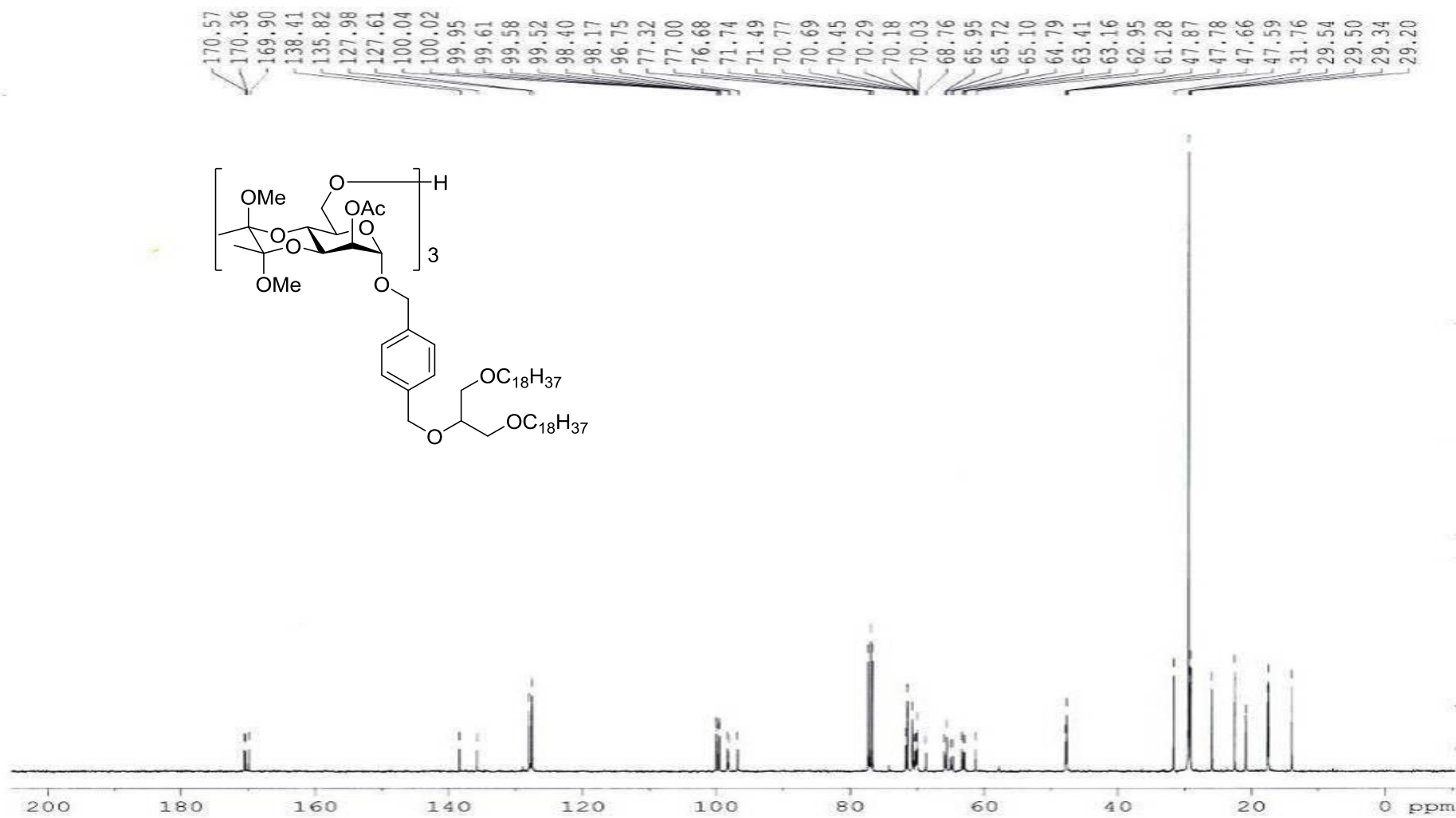
TOF LD+
1.20e4

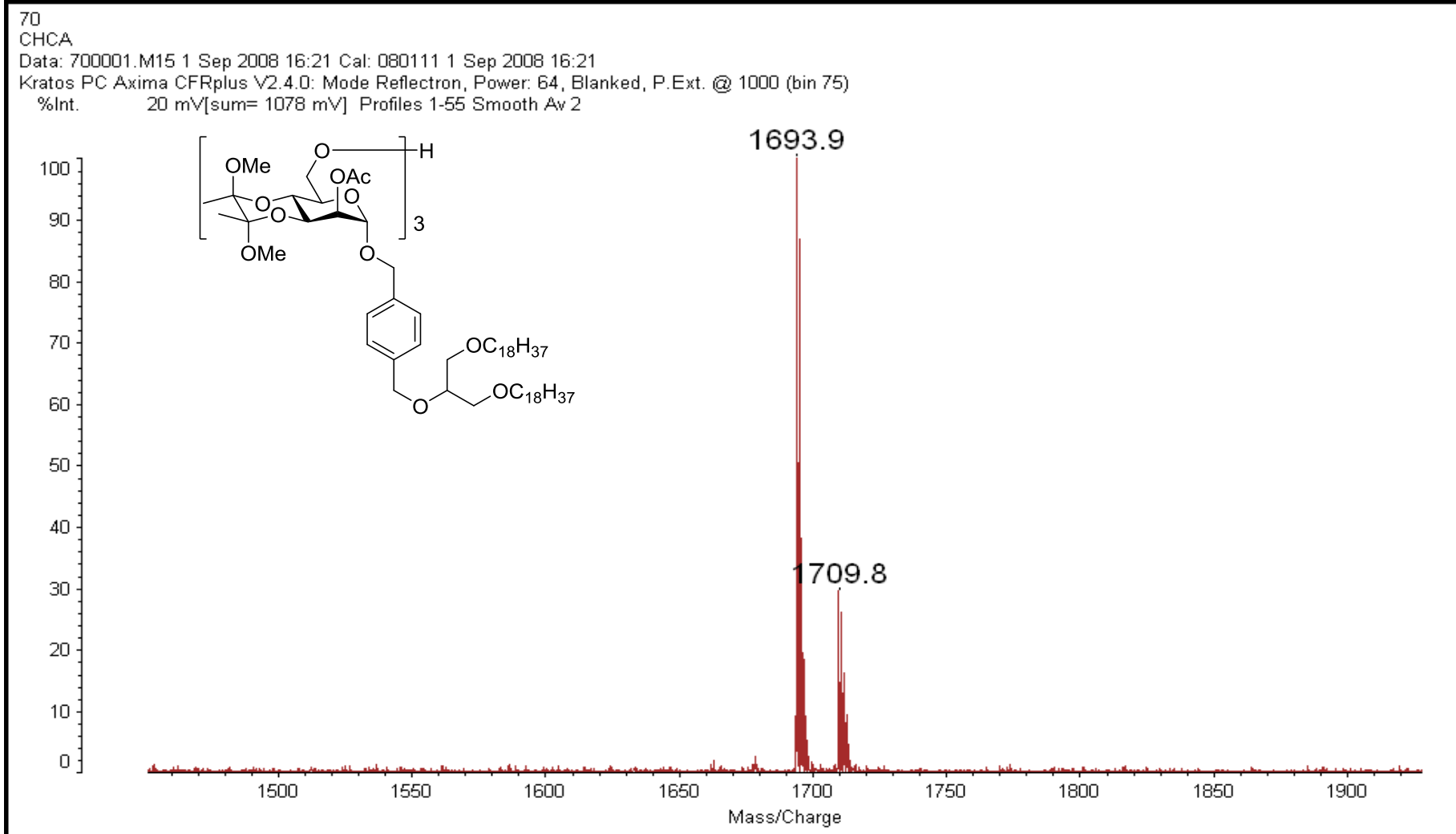


¹H NMR of Compound 11-3b (CDCl₃, 400MHz)

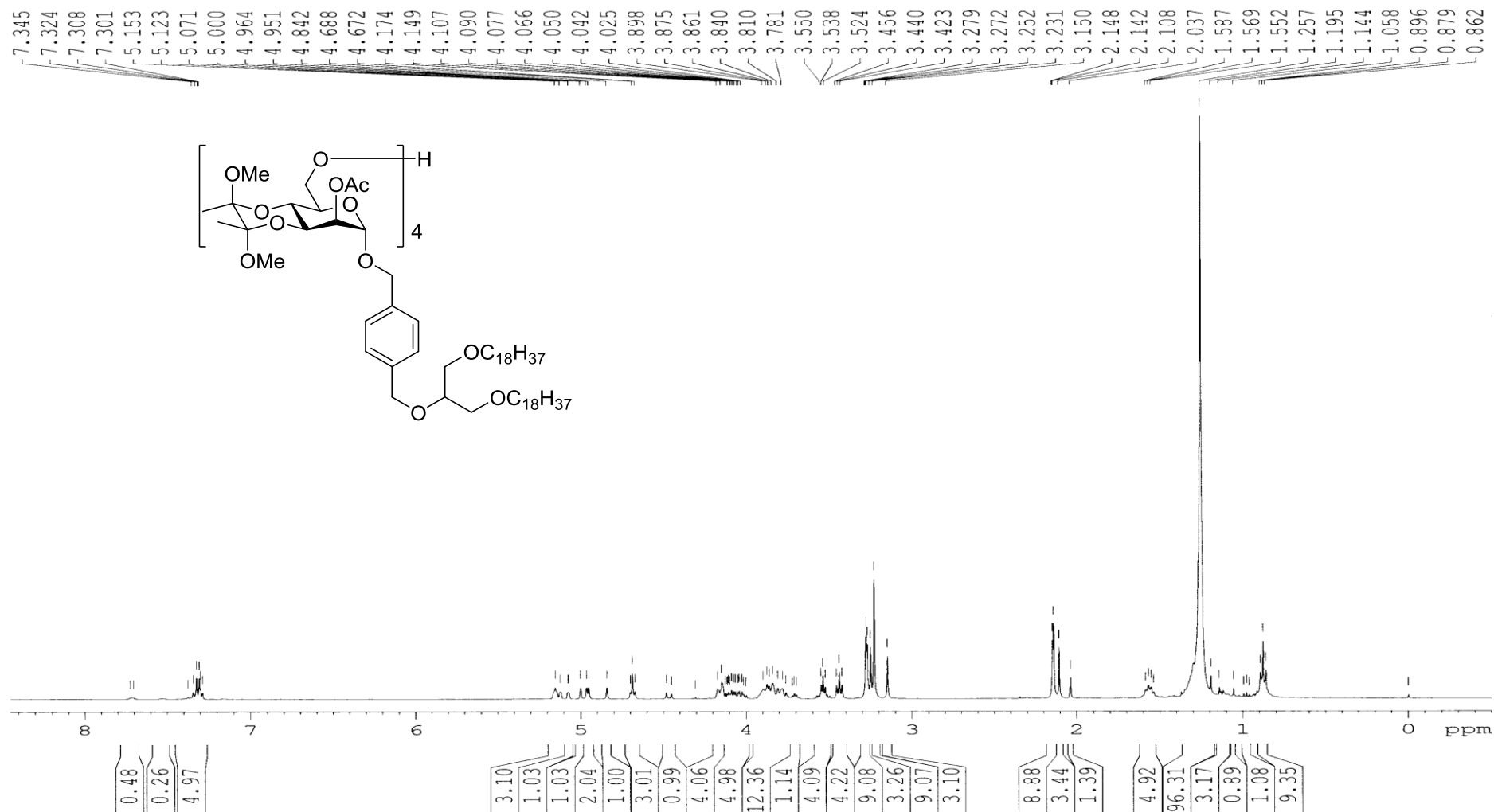


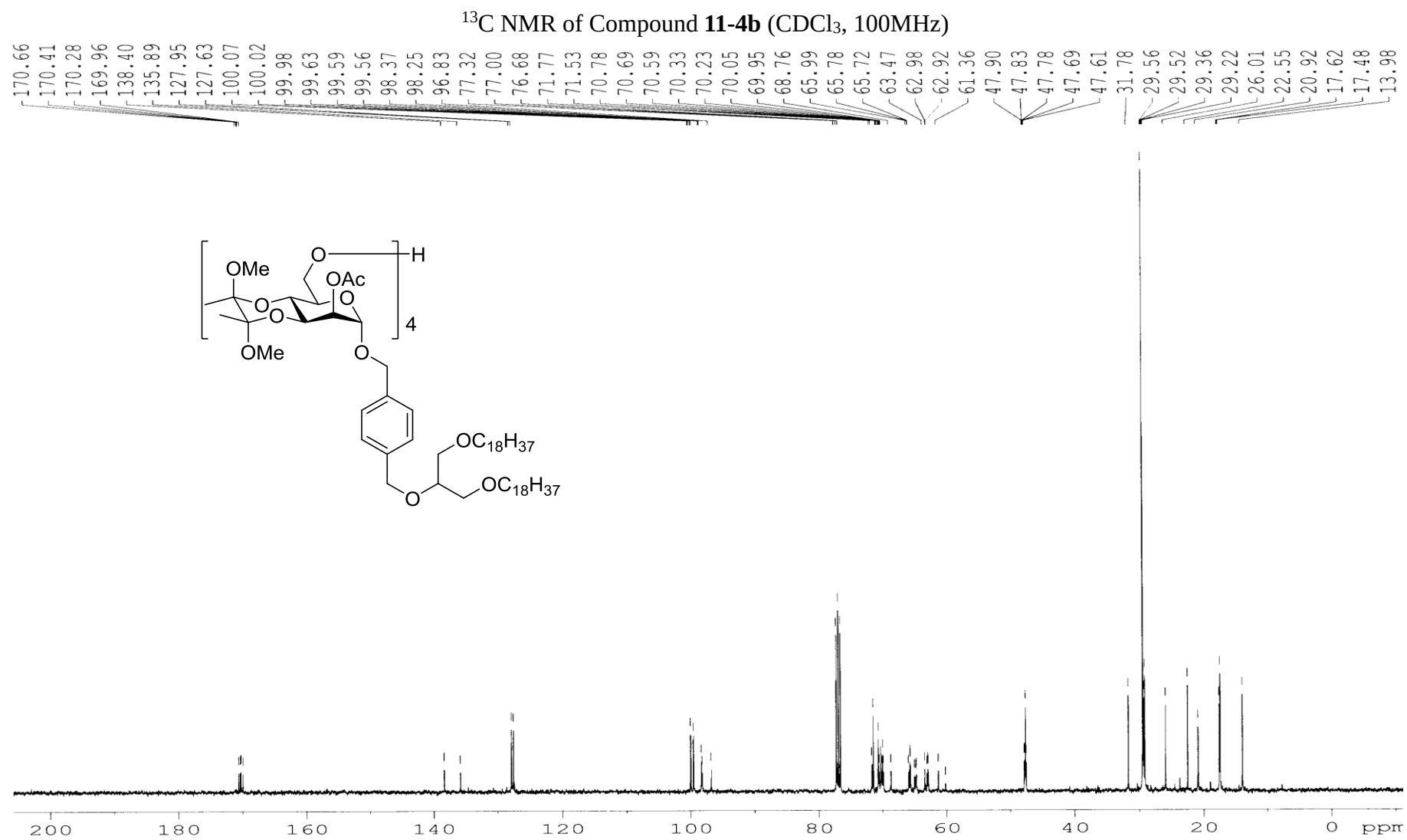
^{13}C NMR of Compound **11-3b** (CDCl_3 , 100MHz)



MALDI-TOF-MS of Compound **11-3b**

¹H NMR of Compound **11-4b** (CDCl₃, 400MHz)

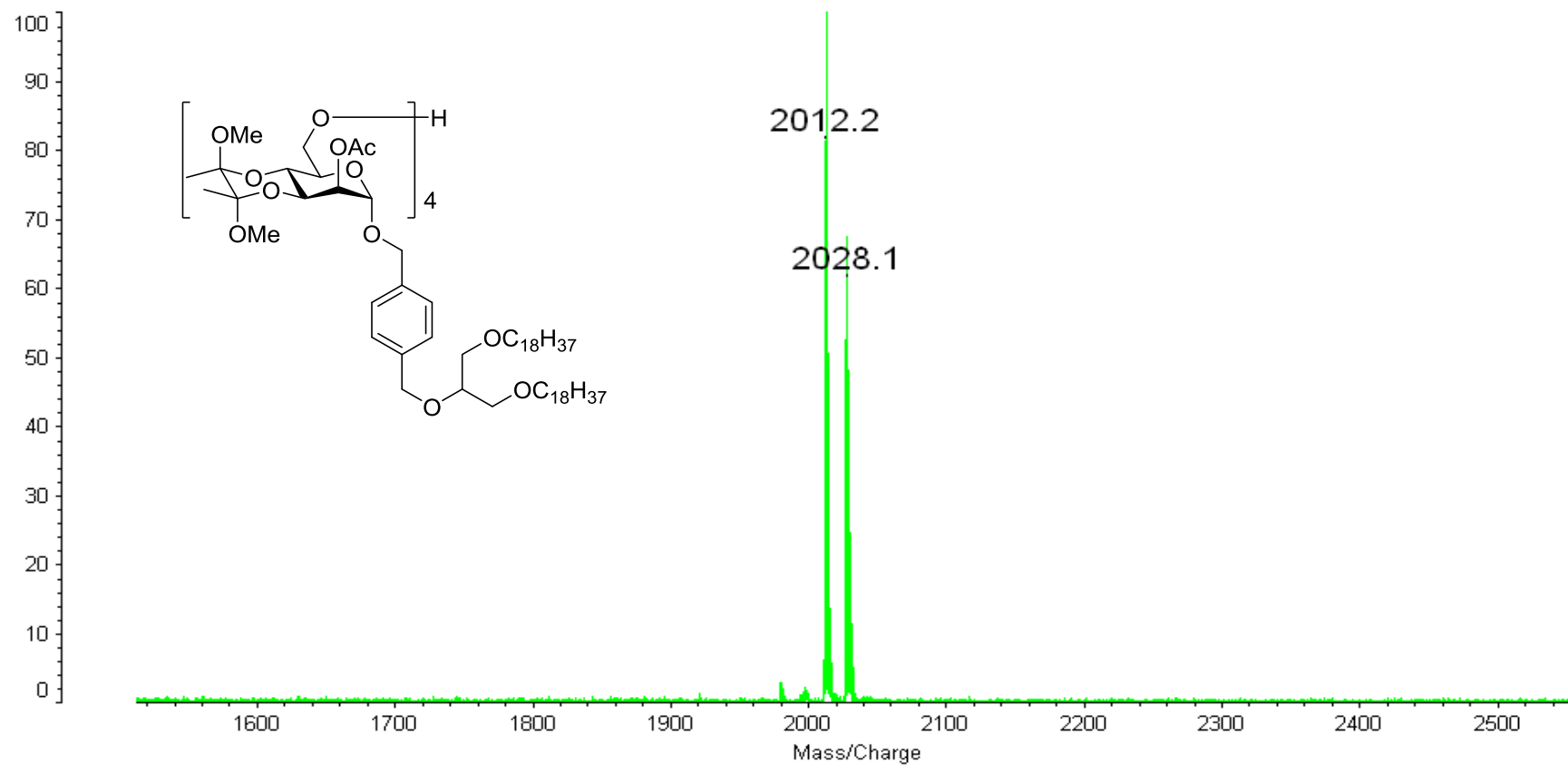




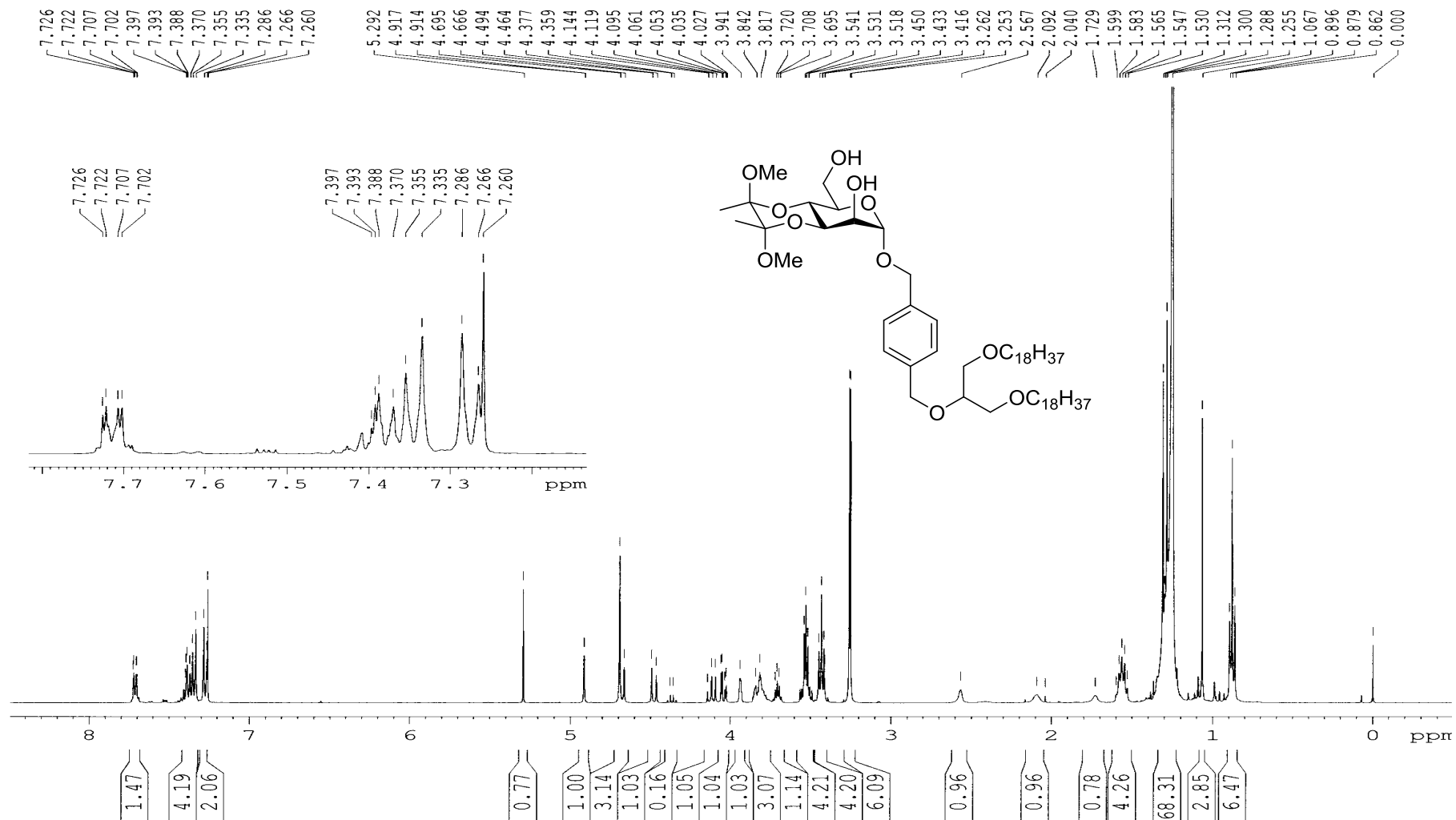
MALDI-TOF-MS of Compound **11-4b**

43E-4

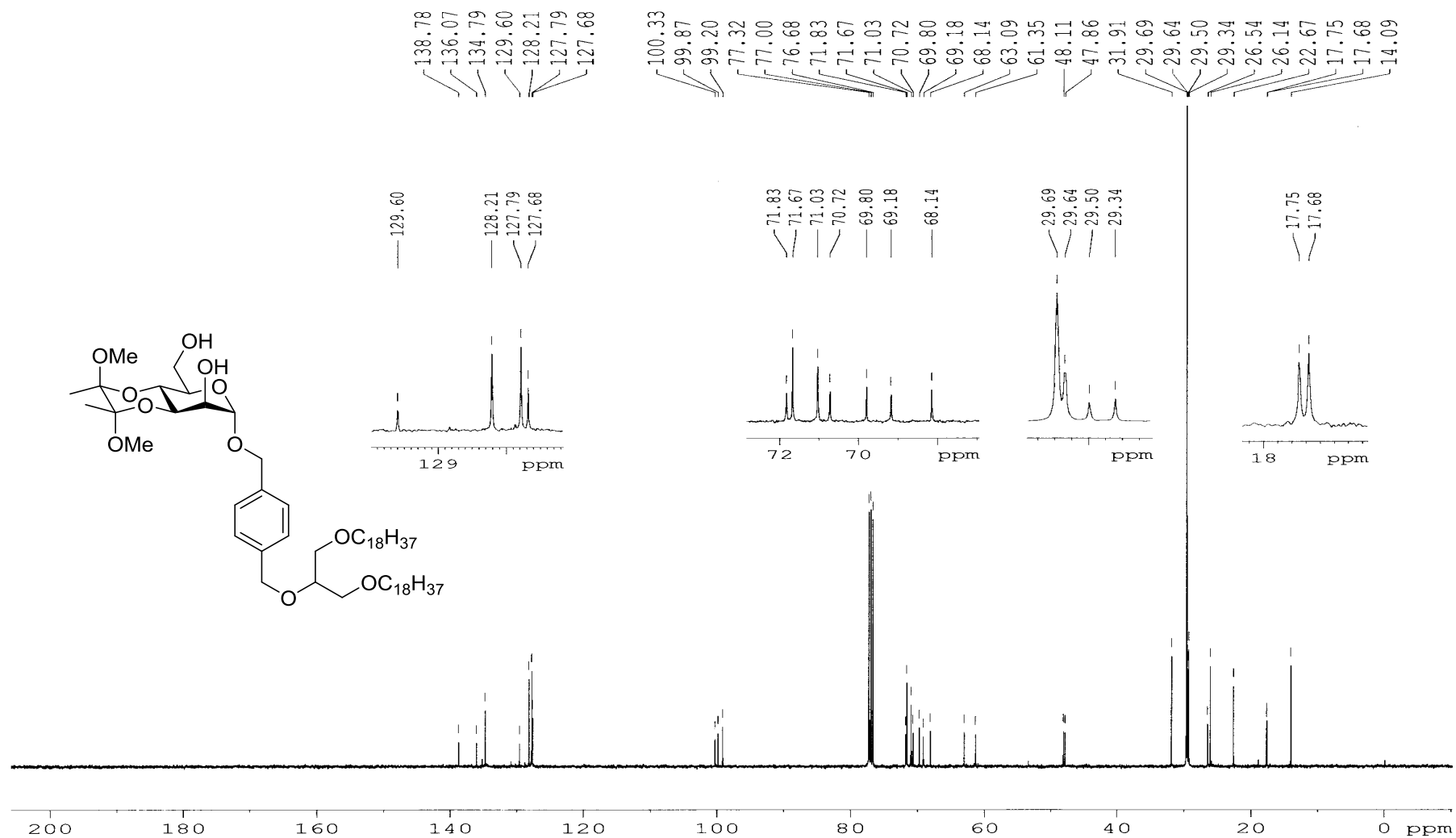
Data: 43E-40001.J12 18 Sep 2008 17:40 Cal: zouxj 18 Sep 2008 17:37
 Kratos PC Axima CFRplus V2.4.0: Mode Reflectron, Power: 69, Blanked, P.Ext. @ 2300 (bin 114)
 %Int. 185 mV[sum= 2406 mV] Profiles 1-13 Smooth Av 2



¹H NMR of Compound 12 (CDCl₃, 400MHz)



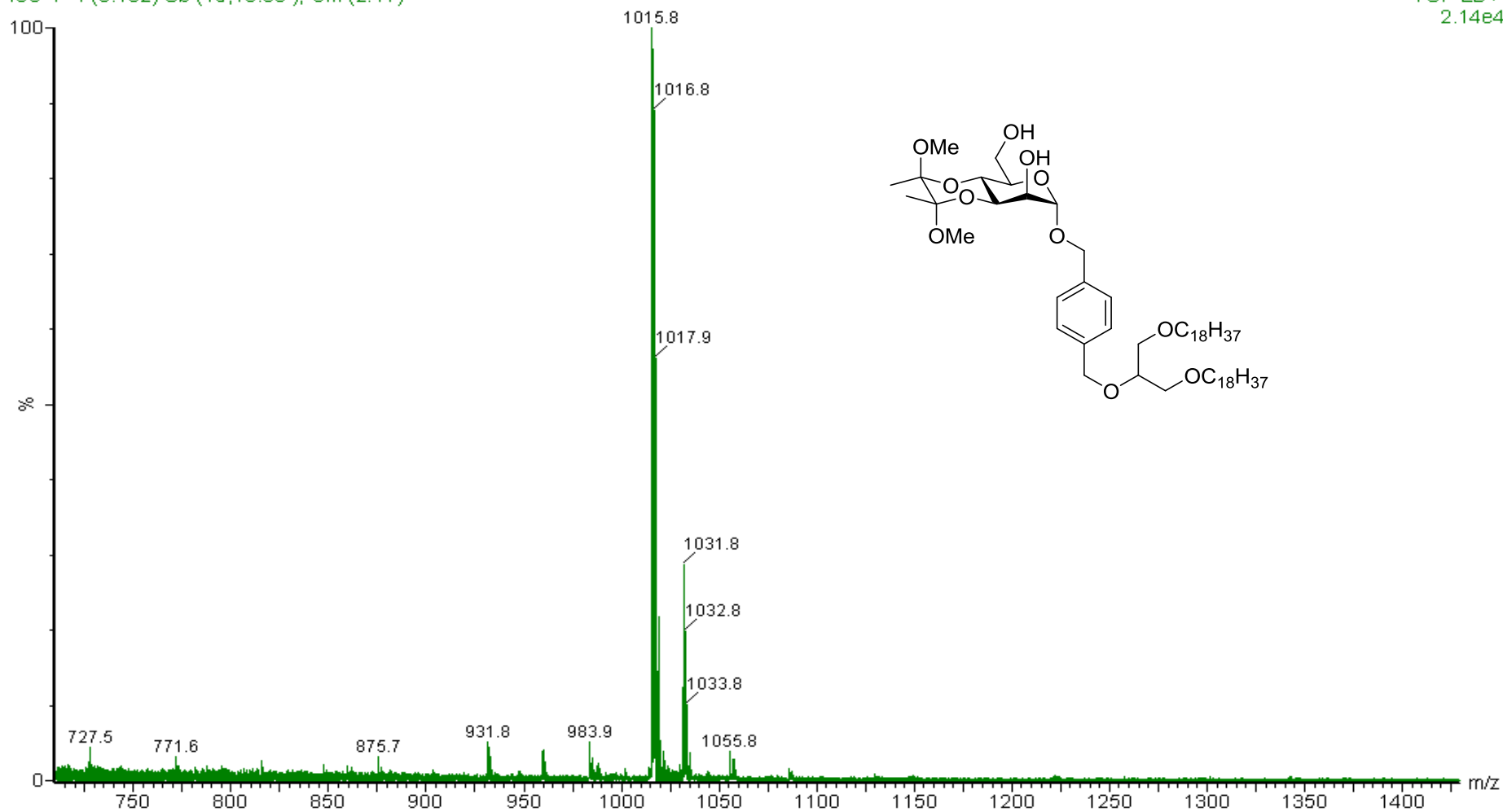
¹³C NMR of Compound **12** (CDCl₃, 100MHz)



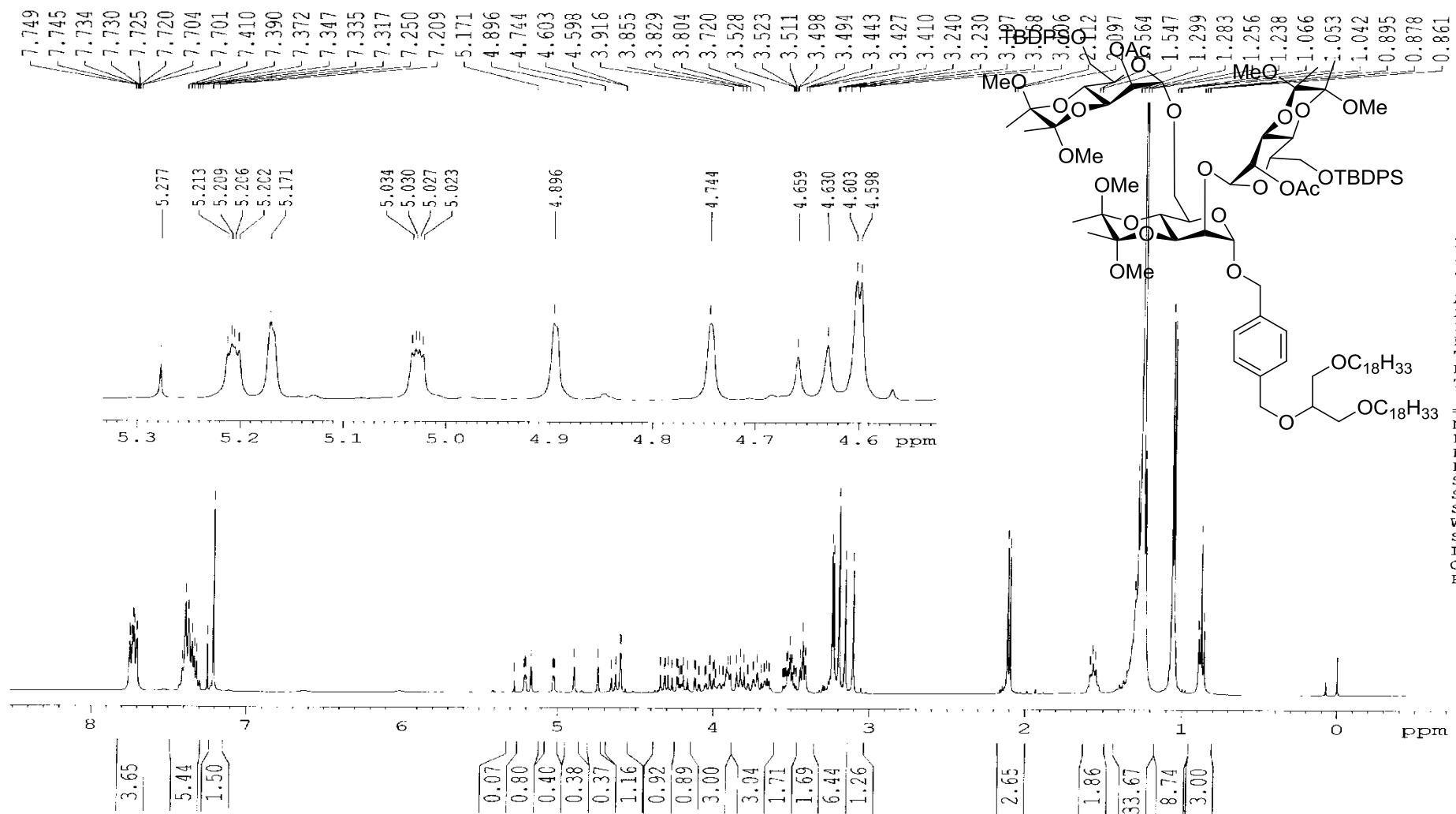
MALDI-TOF-MS of Compound 12

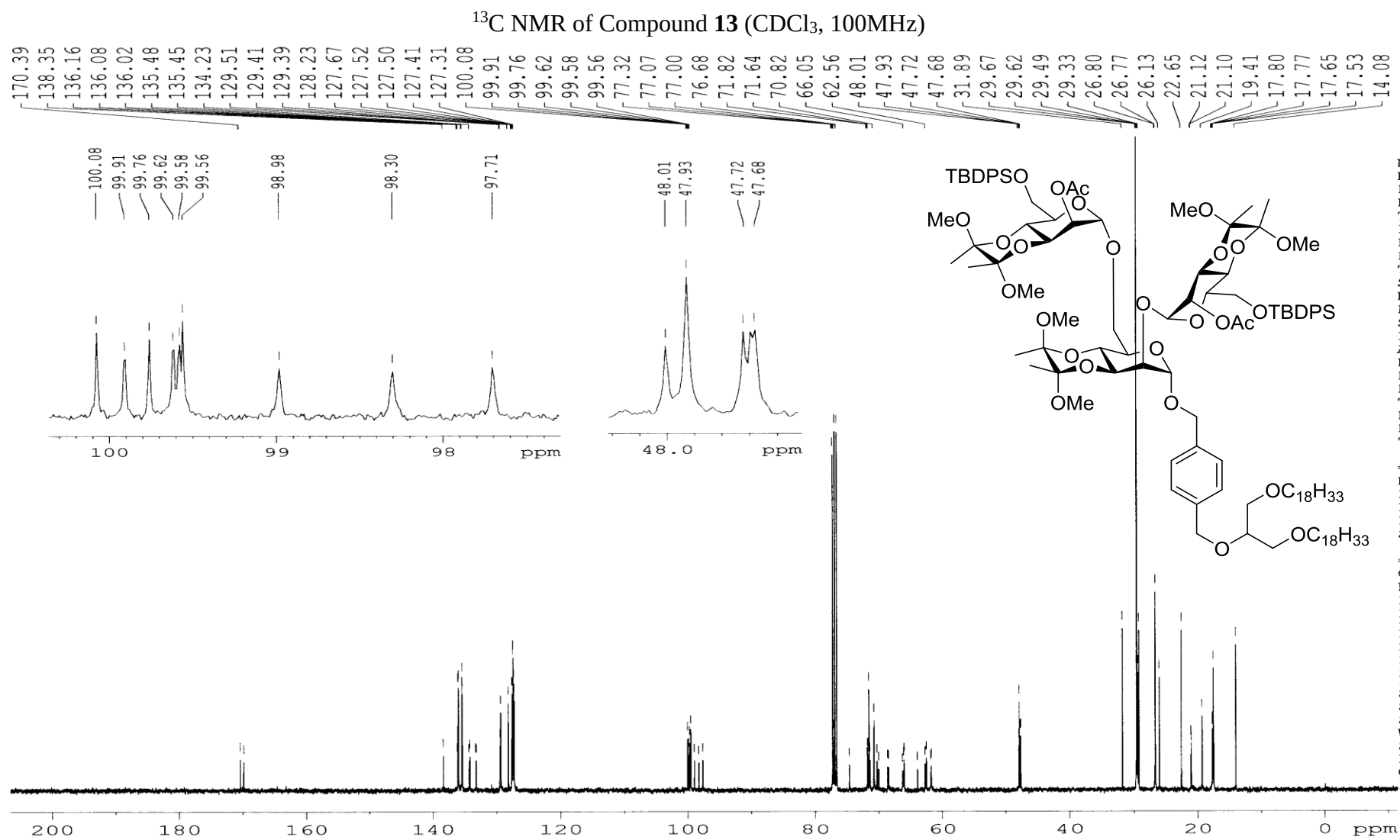
43C-1 4 (0.132) Sb (15,10.00); Cm (2:17)

TOF LD+
2.14e4



¹H NMR of Compound 13 (CDCl₃, 400MHz)

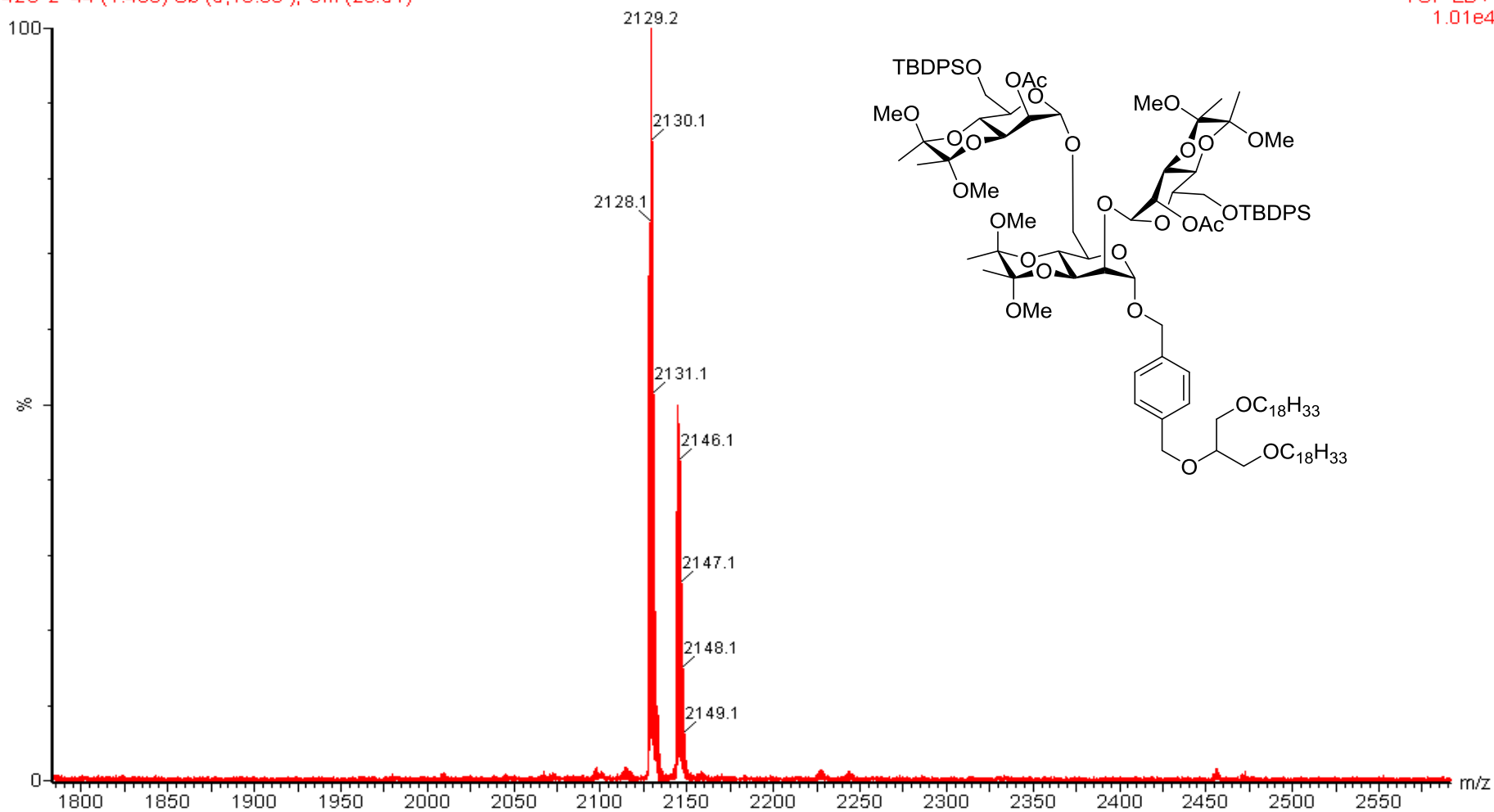




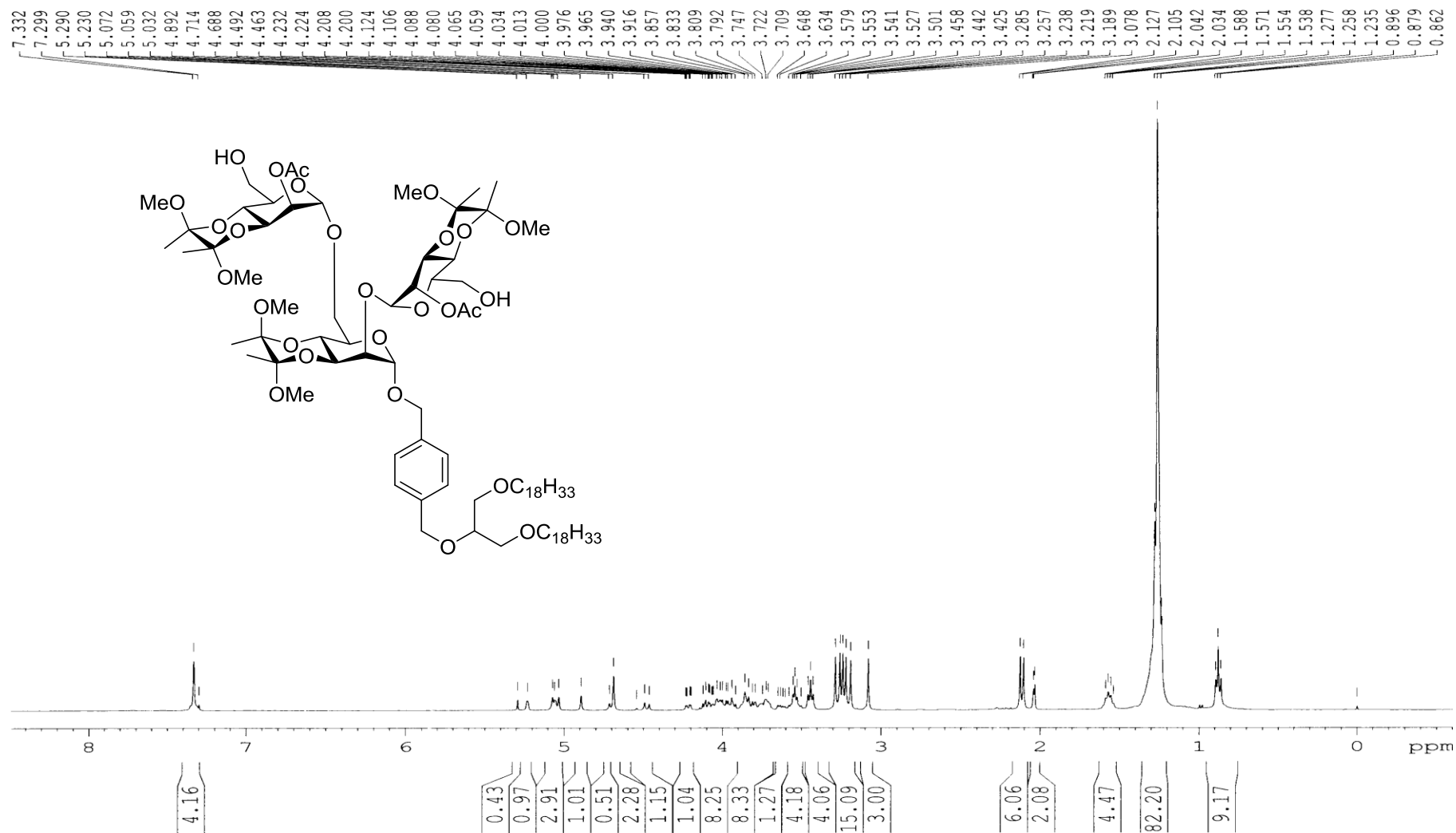
MALDI-TOF-MS of Compound 13

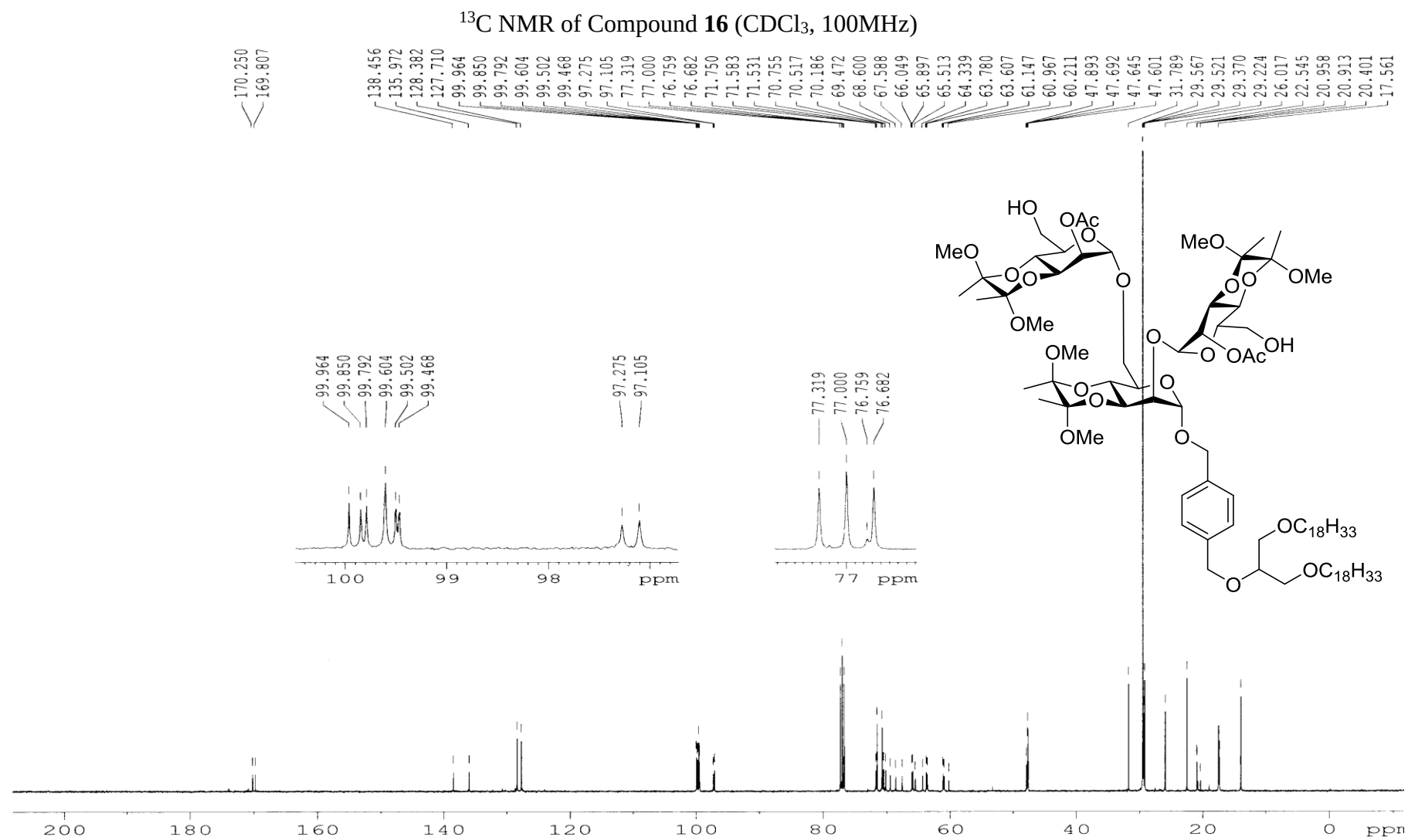
42C-2 44 (1.466) Sb (5,10.00); Cm (20:51)

TOF LD+
1.01e4



¹H NMR of Compound 16 (CDCl₃, 400MHz)

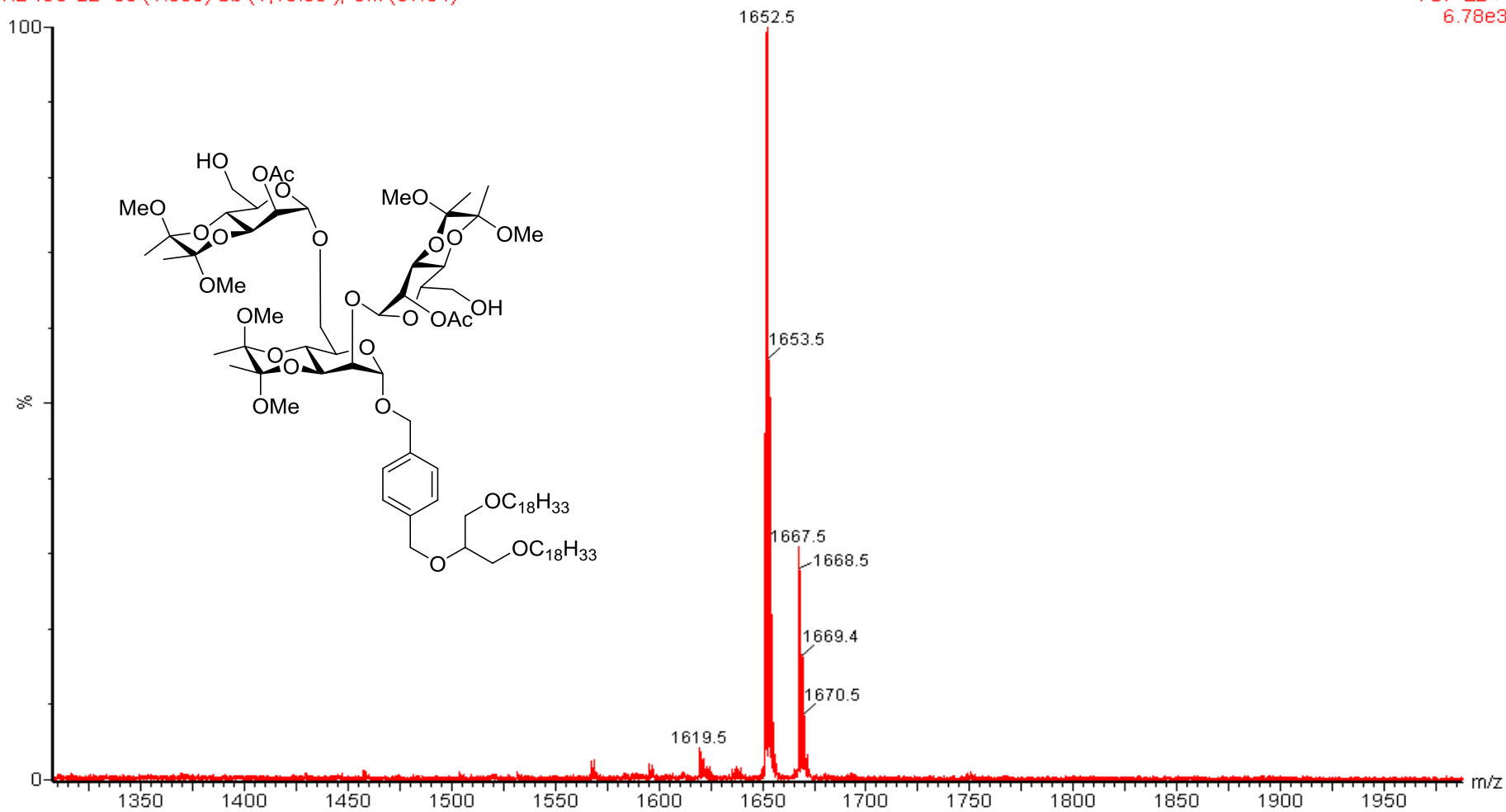




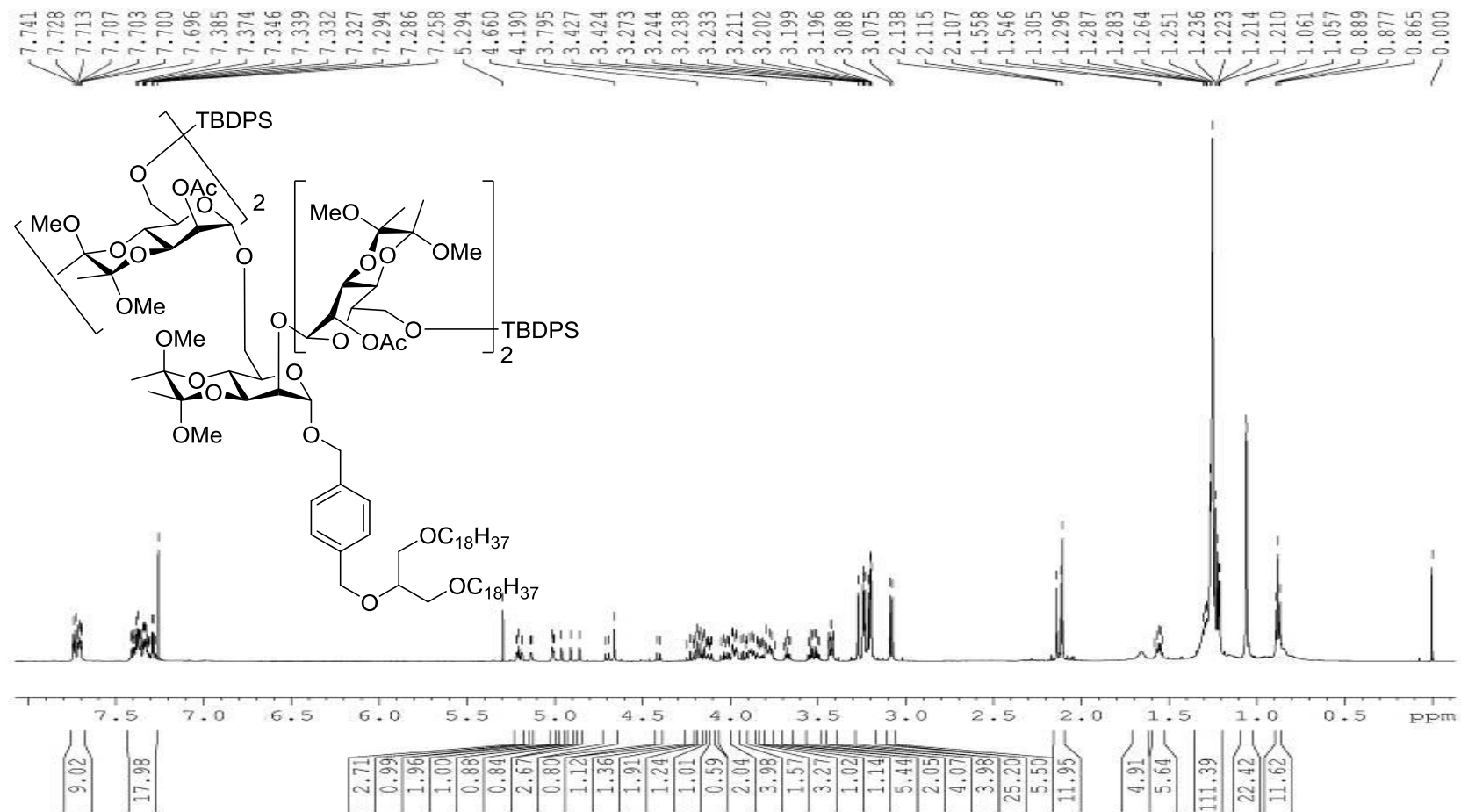
MALDI-TOF-MS of Compound **16**

HD43C-2B 50 (1.665) Sb (1,10.00); Cm (37:54)

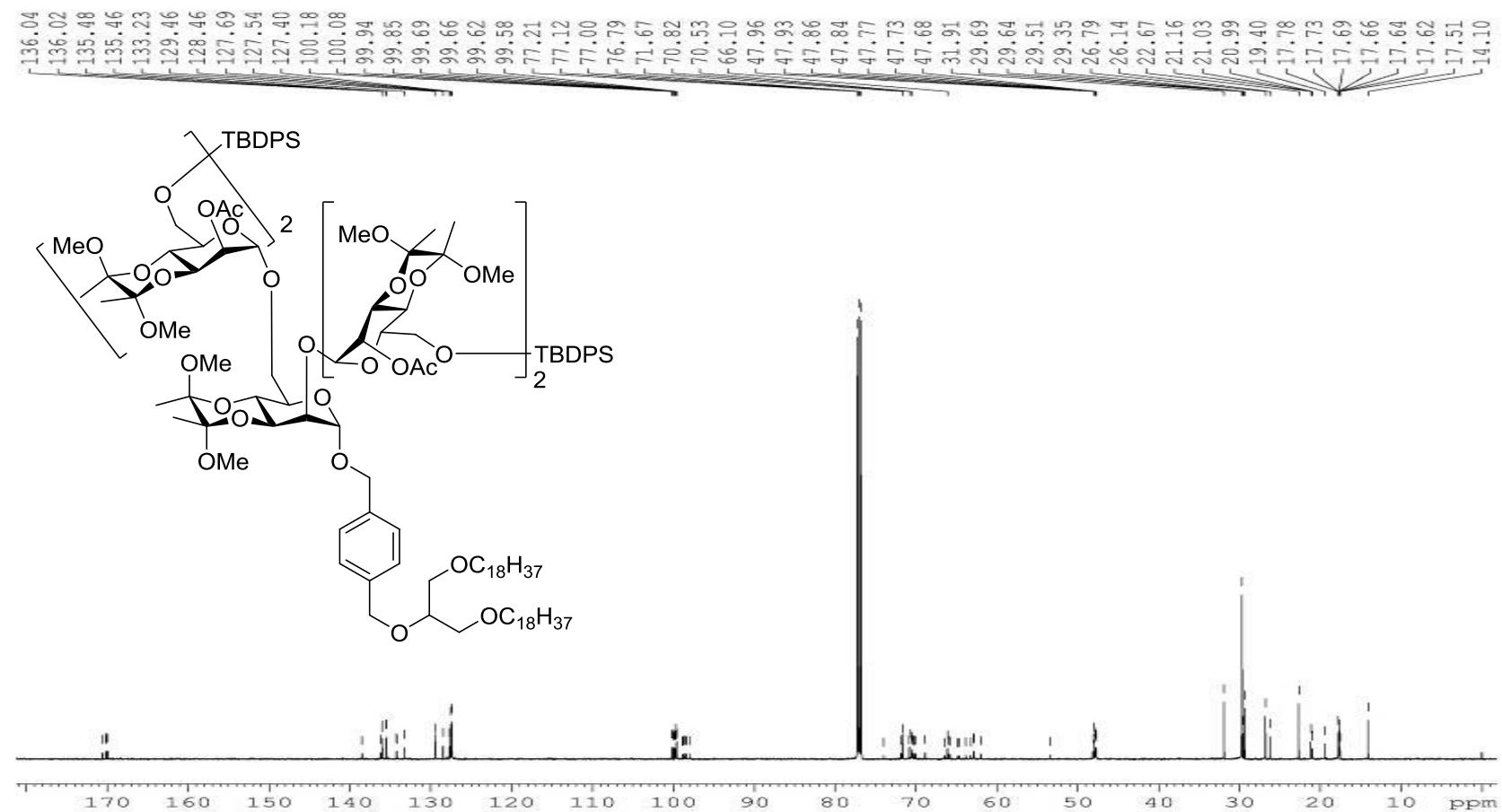
TOF LD+
6.78e3



¹H NMR of Compound 17 (CDCl₃, 600MHz)



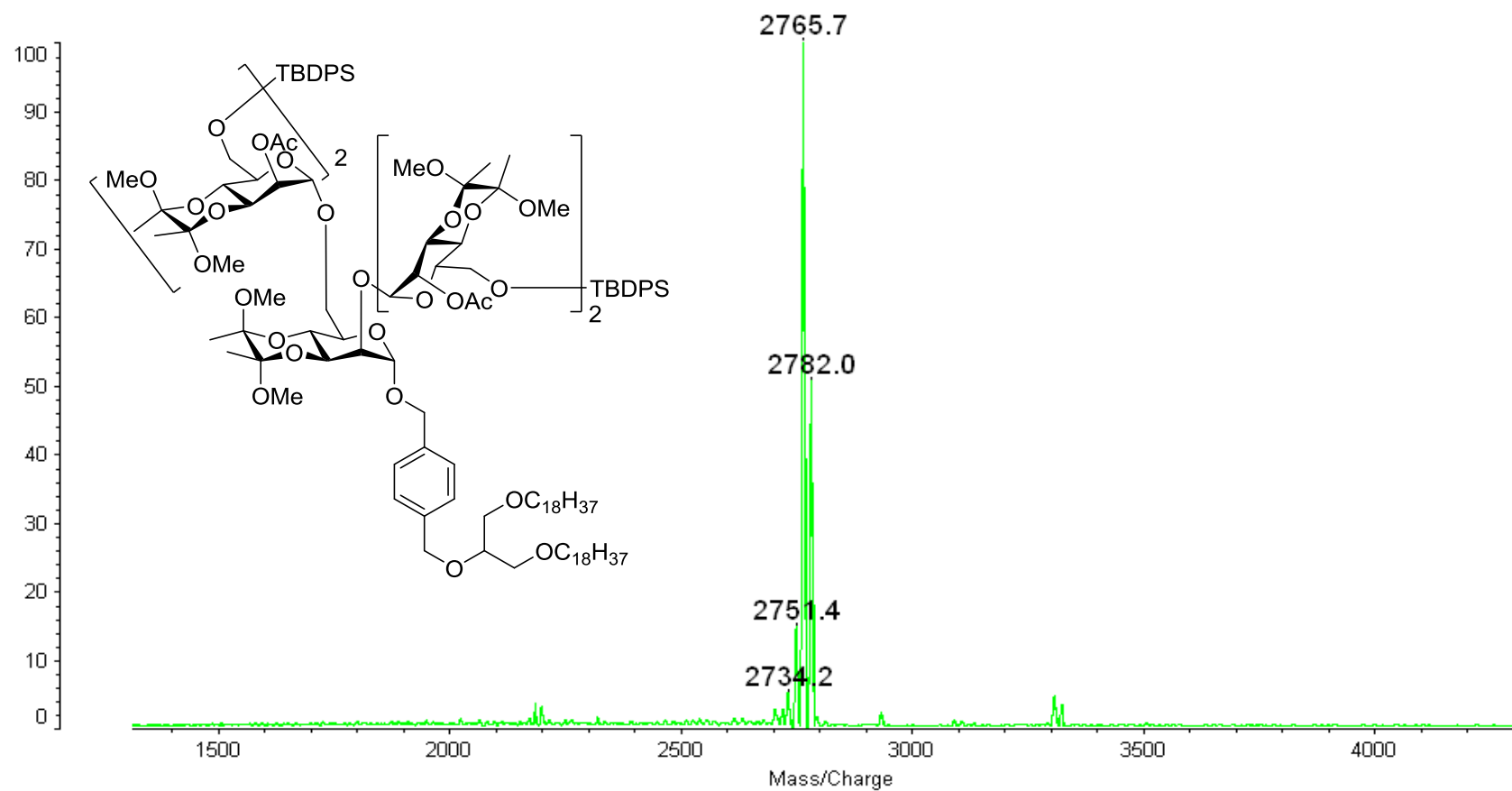
¹³C NMR of Compound **17** (CDCl₃, 150MHz)

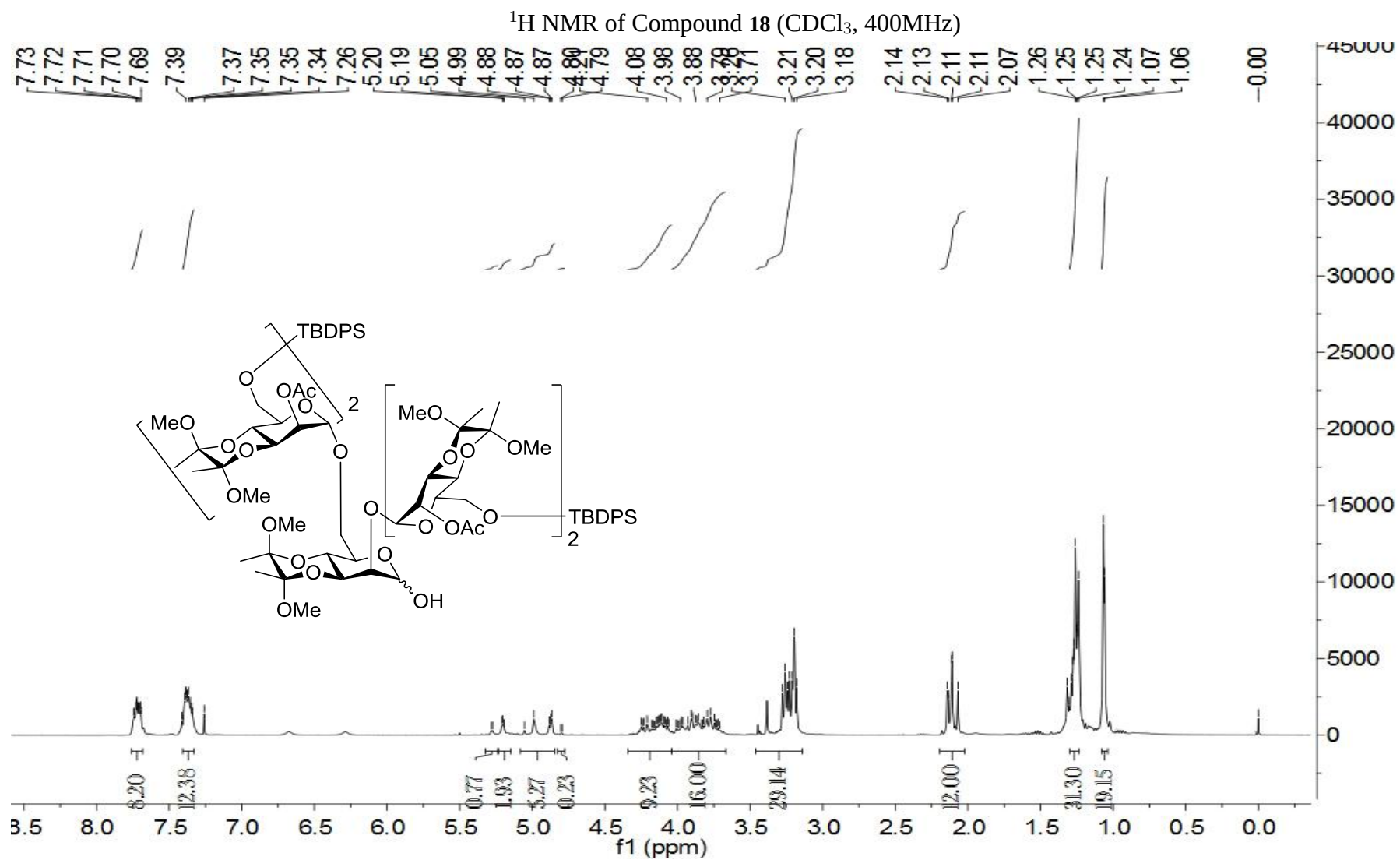


MALDI-TOF-MS of Compound 17

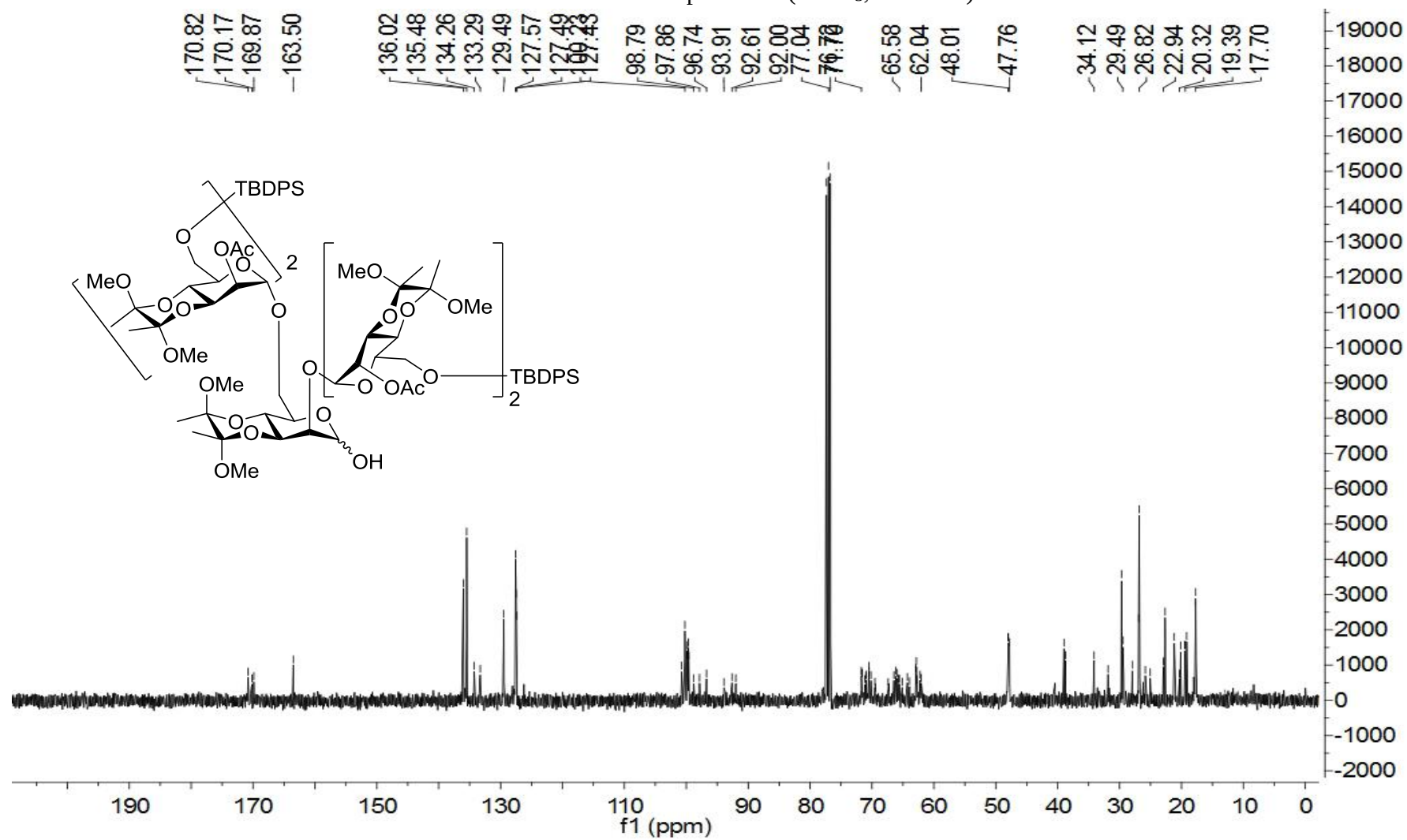
HD56

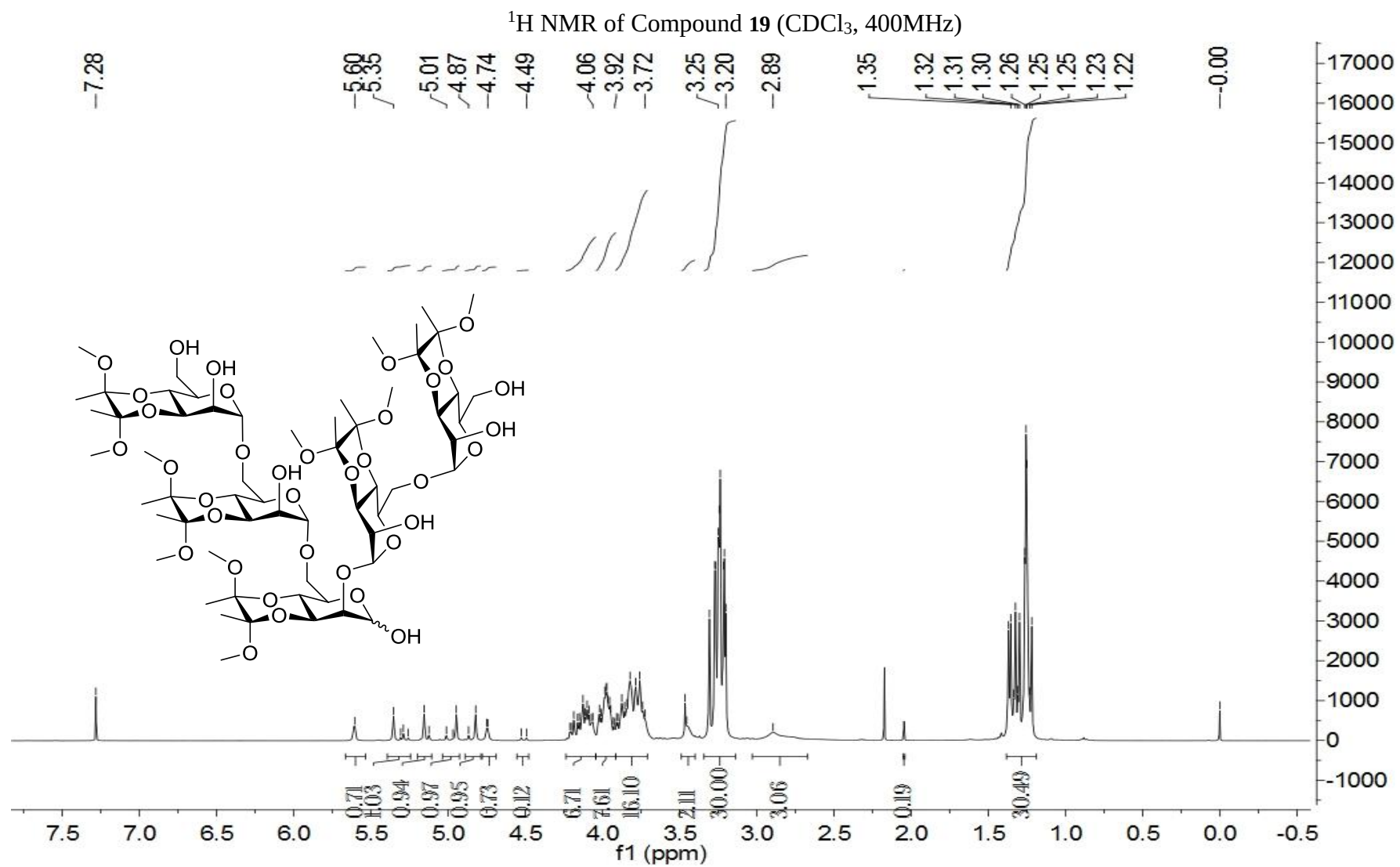
Data: HD560002.M2 30 Mar 2009 18:03 Cal: zhong 30 Mar 2009 18:01
 Kratos PC Axima CFRplus V2.4.0: Mode Linear, Power: 58, Blanked, P.Ext. @ 4000 (bin 86)
 %Int. 450 mV[sum= 8091 mV] Profiles 1-18 Smooth Av 80 -Baseline 80



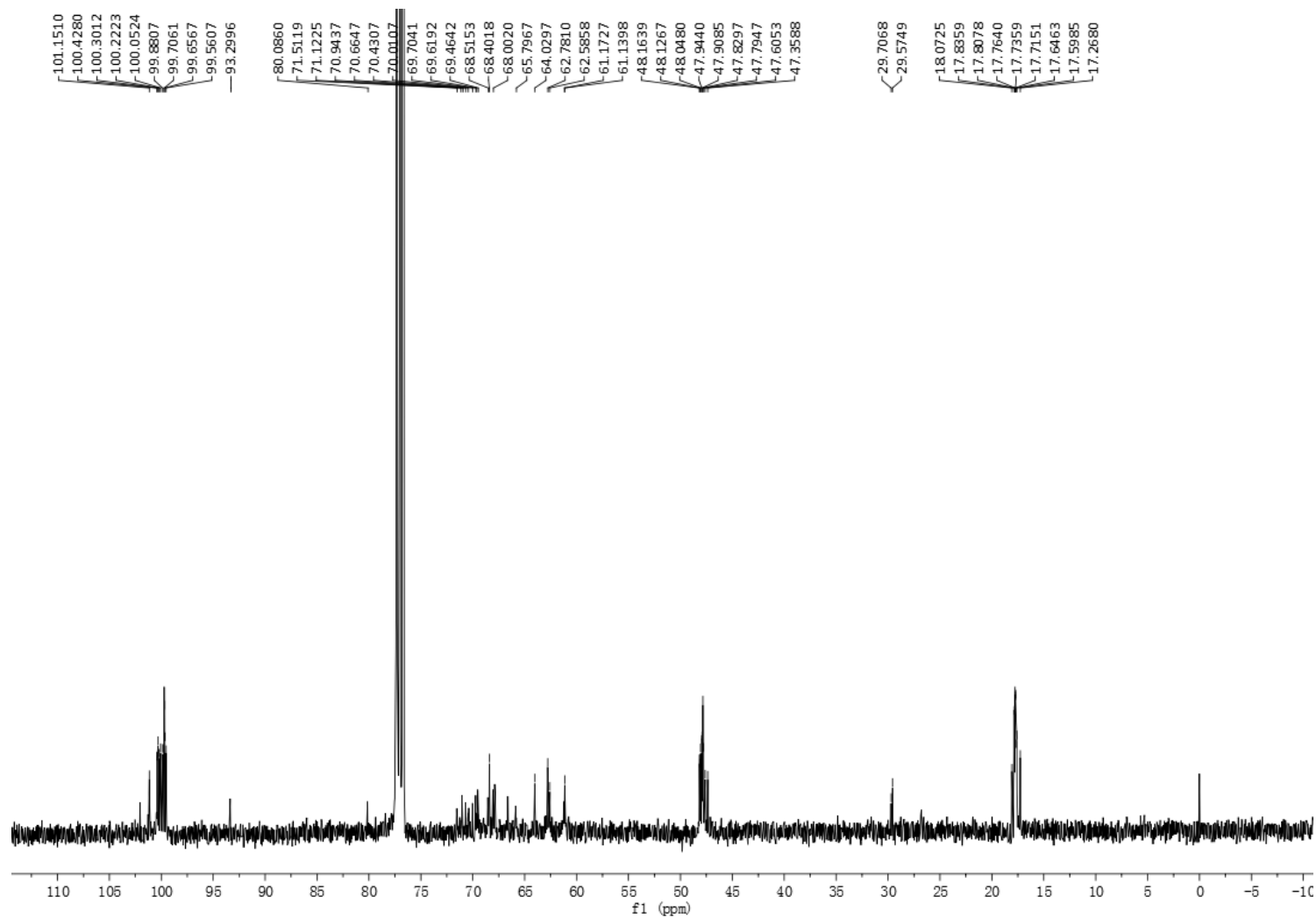


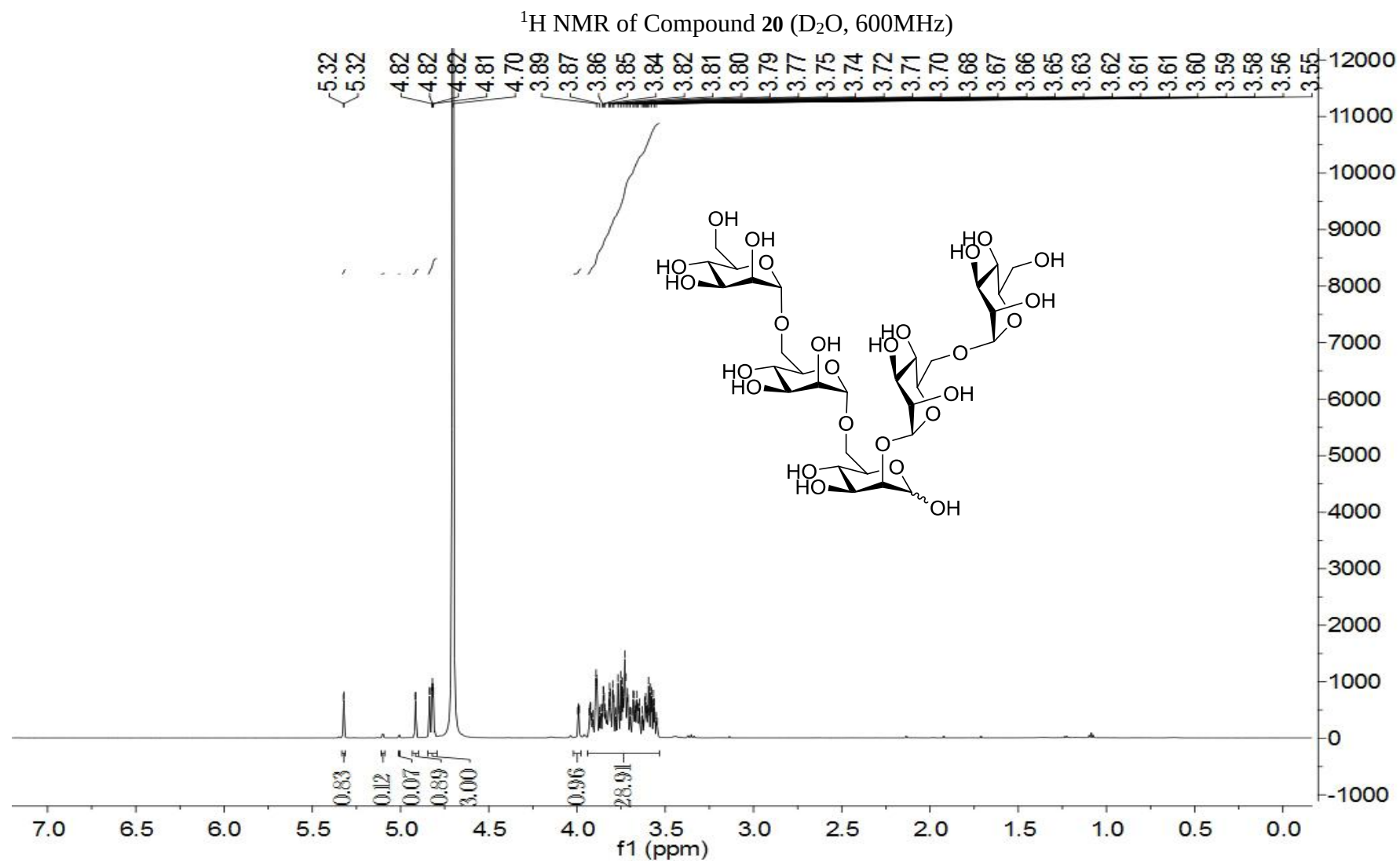
¹³C NMR of Compound **18** (CDCl₃, 100MHz)





^{13}C NMR of Compound **19** (CDCl_3 , 100MHz)





^{13}C NMR of Compound **20** (D_2O , 150MHz)

