ELECTRONIC SUPPLEMENTARY INFORMATION

The Stereoselectivities of Tributyltin Hydride-Mediated Reductions of 5-Bromo-D-Glucuronides to L-Iduronides are Dependent on the Anomeric Substituent: Syntheses and DFT Calculations

Shifaza Mohamed,[a] Elizabeth H. Krenske*[a] and Vito Ferro*[a]

[a] *The University of Queensland*

School of Chemistry and Molecular Biosciences

Brisbane, QLD 4072, Australia

E-mail: v.ferro@uq.edu.au, e.krenske@uq.edu.au

Contents

Computational details S3-S5

Computational data S6-S38

Copies of ^{1}H and ^{13}C NMR spectra for compounds **1**-**12**, **14**-**15** S39-S66

Computational details

Entropy calculations. The correct prediction of the major stereoisomer of product in the reduction of bromide **10** was found to depend on the method used for computing vibrational entropy. When all vibrational modes were treated as harmonic, the predicted L-ido:D-gluco selectivity was almost zero (48:52). The use of Truhlar's quasiharmonic approximation for correcting the entropy associated with low-frequency vibrational modes (i.e. where all harmonic frequencies below 100 cm^{-1} were raised to exactly 100 cm^{-1} before evaluation of the vibrational component of the thermal contribution to entropy) led to a correct prediction that the major stereoisomer of product is the L-ido isomer, albeit underestimating the degree of selectivity relative to experiment (calcd 77:23, c.f. expt 100:0). We explored a second approach to reducing the errors associated with low-frequency vibrations, namely, the rigid rotor harmonic oscillator / free rotor approximation as implemented in Paton's *GoodVibes* software program.[1] In this method, frequencies higher than a specified cutoff are treated as rigid rotors / harmonic oscillators (as in Truhlar's approximation) while frequencies below the cutoff are treated as free rotors, and a damping function is employed to give a smooth transition from one regime to the other. When the energies of **TS1'**–**TS6'** were computed with this approach, employing a cutoff of 100 cm^{-1}, the energy of the lowest-energy D-gluco transition state (**TS4'**) was 0.4 kcal mol^{-1} higher than that of the lowest-energy L-ido transition state (**TS3'**). The predicted L-ido:D-gluco selectivity was 62:38. The results of calculations employing different treatments of vibrational entropy are summarized in Table S1. In the data set recorded in the following section, the Gibbs free energies listed as "G" refer to values corrected with Truhlar's quasiharmonic approximation. Uncorrected values are listed as "G_{raw}" and values corrected using Paton's approximation are listed as "G_{RRHO}" (all at a standard state of 298.15 K and 1 mol L^{-1}).

Comparison with other density functional methods. For certain structures, single-point energies were also computed with two other functionals: M06-2X/TZP[2] and B97-D3/TZP.[3,4] In each case the calculation was performed in implicit (SMD) benzene. The predicted L-ido:D-gluco selectivities obtained with these two functionals were similar to those obtained with B3LYP-D3: i.e., 75:25 with M06-2X and 70:30 with B97-D3, as compared to 77:23 with B3LYP-D3 (Table S1). In the accompanying data set, the M06-2X total potential energy plus solvation energy (0 K) is listed as E_{M06-2X}, while the B97-D3 total potential energy plus solvation energy (0 K) is listed as E_{B97-D3}.

[1] R. S. Paton, *GoodVibes*, https://github.com/bobbypaton/compchem (accessed 11 January 2016).
[2] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.
[3] S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787–1799.
[4] S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.

Table S1. Comparison between Experimental and Theoretical L-Ido:D-Gluco Selectivities for the Reduction of Bromide **10** by Bu_3SnH.[a]

Method	Calcd stereoselectivity L-ido:D-gluco
Experiment	100:0
B3LYP-D3//B3LYP with no entropy correction	48:52
B3LYP-D3//B3LYP with Truhlar's entropy correction	77:23
B3LYP-D3//B3LYP with Paton's entropy correction	62:38
M06-2X//B3LYP	75:25
B97X-D3//B3LYP	70:30

[a] In the theoretical calculations, Bu_3SnH was modelled as Me_3SnH.

Computations on other C1-substituted bromides (1, 4, and 7). The transition states for reductions of bromides **1**, **4**, and **7** were computed at the B3LYP-D3(BJ)/Def2-TZVPP–SMD//B3LYP/6-31G(d)–LANL2DZ–SMD level of theory. Table S2 shows the relative activation barriers ($\Delta G^{\ddagger}_{rel}$) and the corresponding L-ido:D-gluco selectivities. The conformations of the transition states for **1**, **4**, and **7** were generally similar to those of **10**. In Table S2, the transition states are each labelled **TS1'**–**TS6'**, by analogy with the structures shown in Figure 1 of the paper. In the accompanying list of coordinates (below), the labelling system for the transition states for **1**, **4**, and **7** also includes the C1-substituent (β-OAc, α-OAc, or β-OMe).

The agreement between the L-ido:D-gluco selectivities predicted by the computations, and those measured experimentally, is variable. For bromide **7**, bearing a β-OMe substituent at C1, the calculations correctly predict that the D-gluco isomer is favoured, but overestimate the degree of selectivity (L-ido:D-gluco ratio 27:73, compared with 1:1.1). For the C1-acetates **1** and **4**, the calculations do not correctly predict the major stereoisomer. One possible reason for the discrepancy between theory and experiment is the use of Me_3SnH as a model for Bu_3SnH, which neglects the role of non-bonded interactions involving the longer butyl chains. However, because the experimental selectivities are based on measurements of isolated yields, rather than spectroscopic measurements of the crude reaction mixtures, it is not certain that there should be an exact correspondence between the theoretical and experimental selectivities. Decomposition or incomplete isolation of one or other isomer may cause the measured selectivity to differ from that predicted on the basis of transition-state calculations.

Table S2. Experimental and Theoretical Activation Barriers and L-Ido:D-Gluco Selectivities for the Reduction of Bromides **1**, **4**, **7**, and **10** by Bu_3SnH.[a]

C-1 substituent	$\Delta G^{\ddagger}_{rel}$ (kcal mol^{-1})						Calcd (exptal) stereoselectivity L-ido:D-gluco
	L-ido			D-gluco			
	TS1'	TS2'	TS3'	TS4'	TS5'	TS6'	
1 (β-OAc)	3.2	–	0	2.9	2.4	1.7	88:12 (1:1.8)
4 (α-OAc)	2.8	1.1	0.7	0	4.8	5.9	37:63 (5:1)
7 (β-OMe)	3.8	–	0.7	0	3.9	2.8	27:73 (1:1.1)
10 (β-F)	4.1	–	0	1.0	3.7	2.4	77:23 (1:0)

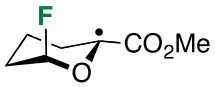
[a] In the theoretical calculations, Bu_3SnH was modelled as Me_3SnH.

Computational data

In this section are listed the Cartesian coordinates of optimized structures considered in the paper. The structures were optimized in implicit benzene at the B3LYP/6-31G(d)–LANL2DZ–SMD level of theory. All radicals had total spin $\langle S^2 \rangle = 0.7500$ after annihilation of the first spin contaminant. Underneath each set of coordinates are listed the following energies (in Hartree):

- B3LYP/6-31G(d)–LANL2DZ–SMD total potential energy plus solvation energy in benzene at 0 K (E)
- B3LYP/6-31G(d)–LANL2DZ–SMD Gibbs free energy in benzene at 298.15 K and 1 mol L^{-1} (after application of Truhlar's quasiharmonic approximation) (G)
- B3LYP-D3(BJ)/Def2-TZVPP–SMD single-point total potential energy plus solvation energy in benzene at 0 K (E_{D3})

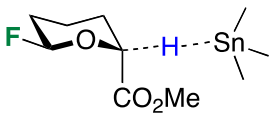
Pyranosyl radical A



O	0.392654	-0.828370	-0.558863
C	-0.125667	0.361461	-0.144642
C	0.723024	1.591548	-0.072176
C	2.174358	1.271951	0.316510
C	2.672928	0.087602	-0.516961
C	1.758191	-1.104480	-0.315608
C	-1.561254	0.425002	0.024969
O	-2.183473	-0.765388	-0.158985
C	-3.607069	-0.735692	0.005664
H	0.257013	2.299750	0.617880
H	2.808804	2.149423	0.157927
H	3.689143	-0.210718	-0.238504
H	1.992381	-1.954589	-0.959769
O	-2.152648	1.463675	0.312108
H	2.229949	1.014093	1.379996
H	2.681883	0.339206	-1.585158
F	1.873143	-1.536428	1.001962
H	0.718130	2.082529	-1.061249
H	-3.946525	-1.752272	-0.200592
H	-3.879120	-0.449254	1.026443
H	-4.069275	-0.034000	-0.695253

0 imaginary frequencies
E = -598.252456
G = -598.117073
E_{D3} = -598.539944

TS1

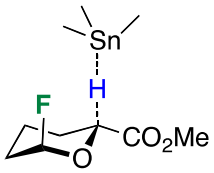


C	-1.623991	-0.676166	1.703738
C	-1.310341	0.089681	0.443312
O	-1.662352	-0.540761	-0.741565
C	-3.019859	-0.955983	-0.814066
C	-3.406312	-1.841421	0.356145
C	-3.097414	-1.134247	1.683555
C	-1.388557	1.564399	0.477179

O	-1.208255	2.227629	1.489394
O	-1.597127	2.106442	-0.744969
C	-1.599115	3.541890	-0.784510
Sn	2.102165	-0.264398	-0.035146
C	2.373960	-1.775823	-1.543713
C	3.145575	-0.819442	1.766930
C	2.831096	1.633014	-0.744933
H	-3.663669	-0.069427	-0.903335
F	-3.118002	-1.659691	-1.991161
H	-2.826352	-2.769010	0.271077
H	-4.468145	-2.099605	0.273095
H	-3.755086	-0.263057	1.804808
H	-3.298658	-1.804279	2.526956
H	-1.413567	-0.045887	2.570900
H	-0.974889	-1.560419	1.759943
H	-1.801495	3.805256	-1.823962
H	-0.628518	3.940759	-0.475247
H	-2.376287	3.951366	-0.132518
H	0.285199	-0.057720	0.318418
H	4.226249	-0.849344	1.583957
H	2.956156	-0.097830	2.568610
H	2.832075	-1.808955	2.116364
H	3.436125	-1.872801	-1.797715
H	1.824950	-1.517198	-2.454984
H	2.016060	-2.750323	-1.194892
H	2.285611	1.951783	-1.639635
H	3.895135	1.565259	-1.000422
H	2.714472	2.406659	0.021643

1 imaginary frequency
E = -721.942190
G = -721.704239
E_{D3} = -933.311471

TS2



O	2.027650	0.521766	-0.936646
C	1.704476	-0.019203	0.303622
C	2.009236	0.811941	1.529083
C	1.647350	2.287210	1.316657
C	2.240417	2.776617	-0.008367
C	1.789801	1.882224	-1.149161
C	1.965620	-1.466307	0.395413
O	2.020162	-2.077113	-0.808652
C	2.206437	-3.500050	-0.763656
H	1.480395	0.382638	2.384818
H	2.021963	2.891343	2.149480
H	1.942097	3.805556	-0.235092
H	2.273896	2.113692	-2.100664
O	2.037863	-2.060379	1.462180
C	-2.627042	1.690684	0.823867
Sn	-1.751322	-0.125667	0.056498
C	-2.142758	-0.285187	-2.055527
C	-2.630429	-1.804843	1.087517
H	0.122801	-0.090932	0.309786
H	0.558357	2.407727	1.293885
H	3.337136	2.749466	0.027113

F	0.411747	2.083805	-1.344886
H	3.084342	0.727179	1.754254
H	2.219132	-3.825613	-1.805087
H	1.387587	-3.986388	-0.225328
H	3.152972	-3.754719	-0.277562
H	-3.216888	-0.209205	-2.261831
H	-1.786231	-1.243012	-2.449360
H	-1.627364	0.517771	-2.591719
H	-3.716203	-1.815453	0.933023
H	-2.439803	-1.749585	2.164786
H	-2.225032	-2.753367	0.719435
H	-3.716823	1.664924	0.703252
H	-2.246885	2.564491	0.284559
H	-2.409118	1.819916	1.889563

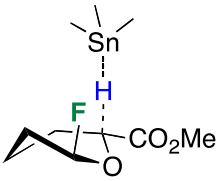
1 imaginary frequency

E = -721.950084

G = -721.711306

E_{D3} = -933.319368

TS3

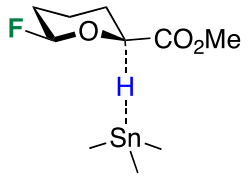


C	-1.659999	-1.906847	-1.120004
O	-2.030701	-0.576612	-0.897383
C	-1.710209	0.007663	0.321720
C	-2.076226	-0.777613	1.573913
C	-2.527093	-2.198601	1.206649
C	-1.580993	-2.760631	0.141706
C	-1.934320	1.464285	0.353541
O	-2.007960	2.097887	1.397037
H	-2.854963	-0.239341	2.125585
H	-2.528203	-2.837271	2.095471
H	-1.811464	-3.799420	-0.115637
F	-0.415986	-1.930654	-1.766720
O	-1.950701	2.030248	-0.872071
C	-2.097845	3.458267	-0.884350
Sn	1.742587	0.102094	0.111985
C	2.629210	1.329716	1.648147
C	2.577948	-1.883348	0.226807
C	2.159884	0.944261	-1.825415
H	-3.555134	-2.183929	0.822586
H	-0.549642	-2.738434	0.512490
H	-2.384276	-2.283233	-1.846951
H	-1.205394	-0.826304	2.241999
H	-2.094827	3.743100	-1.937725
H	-3.039893	3.758003	-0.415718
H	-1.269172	3.942792	-0.359442
H	-0.144549	0.044878	0.325414
H	3.238797	0.951560	-2.020744
H	1.670722	0.354595	-2.607406
H	1.792145	1.973477	-1.893822
H	3.715448	1.384305	1.506969

H	2.229400	2.348835	1.619553
H	2.435911	0.915821	2.643589
H	3.659662	-1.847179	0.050191
H	2.412952	-2.335256	1.211104
H	2.129771	-2.530893	-0.533233

1 imaginary frequency
E = -721.944547
G = -721.705343
E_{D3} = -933.314531

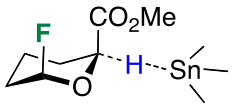
TS4



O	2.176388	0.002301	-0.677367
C	1.523526	0.415223	0.469132
C	1.950571	-0.228609	1.771367
C	2.121997	-1.745688	1.617172
C	2.955291	-2.058343	0.367290
C	2.322368	-1.397563	-0.840247
C	1.228687	1.860588	0.496969
O	1.244148	2.429416	-0.727068
C	0.897165	3.822306	-0.759575
H	1.219238	0.018500	2.545643
H	2.599952	-2.165766	2.508241
H	3.026495	-3.136316	0.185467
F	3.128832	-1.542608	-1.943724
O	0.913412	2.453664	1.519261
C	-2.896968	-0.972179	1.718341
Sn	-1.814233	-0.375561	-0.050215
C	-2.063423	-1.877339	-1.581418
C	-2.556323	1.521031	-0.756480
H	0.044618	-0.093588	0.302611
H	1.136889	-2.223950	1.531219
H	3.974155	-1.664193	0.468383
H	1.342761	-1.832246	-1.085016
H	2.906121	0.219427	2.086345
H	0.922992	4.105105	-1.813124
H	-0.101644	3.988990	-0.347092
H	1.620974	4.416506	-0.193450
H	-3.125142	-1.992039	-1.830340
H	-1.529783	-1.598035	-2.496247
H	-1.688975	-2.851822	-1.249060
H	-3.606452	1.440087	-1.061549
H	-2.490673	2.277622	0.032732
H	-1.977969	1.869046	-1.618791
H	-2.747654	-0.253029	2.530640
H	-3.971069	-1.025068	1.504014
H	-2.571615	-1.957301	2.069747

1 imaginary frequency
E = -721.944617
G = -721.705785
E_{D3} = -933.316256

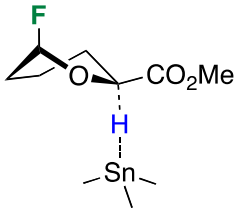
TS5



O	-1.576831	0.555708	-0.969335
C	-2.861203	1.086431	-1.172249
F	-3.798571	0.054886	-1.062115
H	-2.874081	1.427016	-2.210727
C	-3.229586	2.172922	-0.174828
H	-2.584568	3.039427	-0.369419
H	-4.263884	2.482233	-0.360642
C	-3.035667	1.671759	1.261540
H	-3.766698	0.884248	1.477776
H	-3.208362	2.483415	1.977181
C	-1.606188	1.114408	1.424254
H	-1.475554	0.624951	2.392141
H	-0.891332	1.947129	1.365951
C	-1.300529	0.126572	0.328639
C	-1.467260	-1.315070	0.601802
O	-1.471221	-1.789539	1.729844
O	-1.509240	-2.061837	-0.522404
C	-1.610580	-3.477458	-0.310832
H	-1.635188	-3.921042	-1.307487
H	-0.748945	-3.852711	0.249234
H	-2.526222	-3.726835	0.233548
H	0.302423	0.163128	0.242961
Sn	2.143162	0.207951	-0.058846
C	2.527877	1.069899	-1.994613
C	3.116583	1.374307	1.470805
C	2.873705	-1.816530	0.006782
H	3.954658	-1.837578	-0.174874
H	2.387654	-2.433173	-0.756688
H	2.683889	-2.270378	0.985373
H	4.200075	1.386614	1.302727
H	2.760713	2.410152	1.467753
H	2.931305	0.950819	2.463645
H	2.170778	2.104038	-2.042230
H	3.603734	1.070183	-2.206172
H	2.024043	0.498736	-2.781380

1 imaginary frequency
E = -721.945797
G = -721.707003
E_{D3} = -933.314089

TS6



O	-2.001072	-0.381523	1.099922
C	-1.557061	0.344772	0.003271
C	-2.063976	-0.095439	-1.348566
C	-1.855457	-1.611227	-1.575055
C	-1.893129	-2.405995	-0.248884
C	-2.592002	-1.623143	0.845411
C	-1.419969	1.775976	0.345940
O	-1.219326	2.524236	-0.770905
C	-0.979619	3.920398	-0.536817

H	-1.567818	0.490470	-2.124780
H	-2.629662	-1.975128	-2.256816
H	-0.878941	-2.619952	0.107529
F	-3.926498	-1.423378	0.466093
O	-1.389615	2.230212	1.475186
Sn	1.853001	-0.291387	0.043491
C	2.337311	-1.211604	1.933157
C	2.492402	-1.585668	-1.564766
C	2.885106	1.593812	-0.135809
H	-0.893332	-1.784154	-2.068398
H	-2.400110	-3.368499	-0.368581
H	-2.612671	-2.140941	1.807050
H	-3.135972	0.138991	-1.403626
H	-0.842285	4.363805	-1.524608
H	-1.832412	4.383088	-0.031569
H	-0.082036	4.065790	0.071132
H	-0.028619	0.020870	-0.069573
H	3.970455	1.437420	-0.130030
H	2.619435	2.098935	-1.070804
H	2.632292	2.259518	0.696368
H	3.416411	-1.392872	2.004698
H	2.042330	-0.565837	2.766895
H	1.823383	-2.172034	2.047898
H	3.583699	-1.693554	-1.550462
H	2.055550	-2.586086	-1.473372
H	2.207232	-1.174748	-2.539280

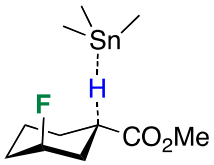
1 imaginary frequency

E = -721.941579

G = -721.702779

E_{D3} = -933.313097

Transition state analogous to TS2, with pyranosyl oxygen replaced by CH_2 (fully optimized)

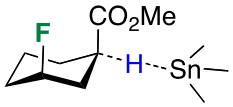


C	2.023810	0.639800	-1.100718
C	1.775007	-0.018929	0.241867
C	2.083111	0.802131	1.475266
C	1.595441	2.254217	1.365199
C	2.059615	2.910432	0.058113
C	1.610499	2.109997	-1.157758
C	2.005010	-1.464595	0.373963
O	1.961787	-2.113312	-0.823303
C	2.130810	-3.536218	-0.758574
H	1.663497	0.310989	2.358993
H	1.959574	2.831628	2.222838
H	1.676244	3.934077	-0.025568
H	1.979671	2.561385	-2.085641
O	2.166606	-2.053896	1.433815
C	-2.586947	1.634957	0.873507
Sn	-1.712048	-0.162920	0.073797
C	-2.123698	-0.306683	-2.035059
C	-2.526599	-1.879206	1.093401
H	0.141775	-0.105131	0.276711
H	0.500332	2.280265	1.409251
H	3.156681	2.974502	0.035678
F	0.195469	2.186956	-1.231522

H	3.176788	0.802091	1.627216
H	2.066886	-3.887654	-1.790028
H	1.344828	-3.997584	-0.153423
H	3.104478	-3.795836	-0.332187
H	-3.202198	-0.271428	-2.229096
H	-1.734538	-1.242775	-2.450238
H	-1.649427	0.527437	-2.561684
H	-3.613316	-1.921972	0.952106
H	-2.324172	-1.832100	2.168869
H	-2.096285	-2.809630	0.707585
H	-3.673519	1.629311	0.726115
H	-2.176335	2.511879	0.363078
H	-2.391592	1.732862	1.946643
H	3.102792	0.601367	-1.325629
H	1.527501	0.091957	-1.907063

1 imaginary frequency
E = -686.049519
G = -685.786642
E_{D3} = -897.406386

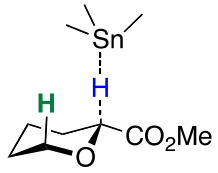
Transition state analogous to TS5, with pyranosyl oxygen replaced by CH_2
(fully optimized)



C	1.738468	0.605495	1.203378
C	3.212939	1.033021	1.165791
F	3.987314	-0.112272	0.881129
H	3.532211	1.389122	2.153011
C	3.493496	2.072433	0.085079
H	2.979671	3.002866	0.364781
H	4.567882	2.291772	0.069547
C	3.016005	1.595196	-1.294569
H	3.623141	0.738748	-1.609214
H	3.163674	2.386642	-2.039567
C	1.528556	1.175180	-1.263957
H	1.230644	0.765838	-2.232717
H	0.911899	2.065204	-1.070626
C	1.290166	0.158571	-0.171014
C	1.434574	-1.255457	-0.555418
O	1.512083	-1.662029	-1.707193
O	1.389920	-2.096722	0.511413
C	1.501630	-3.491401	0.198965
H	1.433335	-4.013872	1.155104
H	0.692750	-3.811600	-0.464404
H	2.461666	-3.708215	-0.279097
H	-0.339488	0.188018	-0.024056
Sn	-2.199182	0.220246	0.065906
C	-2.825961	1.048966	1.955511
C	-2.957459	1.432037	-1.546314
C	-2.915168	-1.801601	-0.121670
H	-4.010808	-1.825979	-0.094764
H	-2.539193	-2.425388	0.696209
H	-2.586880	-2.244834	-1.067852
H	-4.053723	1.446171	-1.532301
H	-2.602779	2.465017	-1.463785
H	-2.634605	1.037299	-2.515508
H	-2.466103	2.076702	2.074189
H	-3.920380	1.062714	2.020226
H	-2.443863	0.454609	2.792338

H 1.149723 1.475504 1.527157
H 1.605030 -0.182836 1.947391
1 imaginary frequency
E = -686.047331
G = -685.784283
E_{D3} = -897.403329

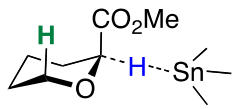
Transition state analogous to TS2, with F replaced by H
(single-point calculation, C–H bond length 1.09 Å)



Sn	-1.730930	-0.066415	0.005614
H	0.143285	0.042548	0.236149
C	-2.133264	-0.427884	-2.079281
H	-1.752787	-1.407404	-2.388185
H	-3.210600	-0.400434	-2.280982
H	-1.644678	0.336846	-2.691120
C	-2.554726	-1.668405	1.193239
H	-2.357800	-1.510269	2.259125
H	-3.640877	-1.722765	1.051095
H	-2.125470	-2.634985	0.908650
C	-2.651832	1.787472	0.613821
H	-2.429792	2.018944	1.661207
H	-3.741313	1.720997	0.506829
H	-2.300446	2.618740	-0.006204
C	1.722220	0.156743	0.207856
C	2.024728	-1.268326	0.427844
O	2.121549	-1.760789	1.543299
O	2.087595	-1.984305	-0.716382
C	2.314240	-3.391623	-0.544443
H	3.271135	-3.575024	-0.046660
H	2.328434	-3.810013	-1.552153
H	1.513416	-3.849285	0.043828
C	2.012448	1.103857	1.349861
H	1.502240	0.739766	2.246178
H	3.091146	1.069408	1.571137
O	2.020866	0.591412	-1.079478
C	1.743196	1.919894	-1.412065
H	2.213549	2.077112	-2.385376
C	2.176812	2.926274	-0.361550
H	3.274091	2.932529	-0.334611
H	1.847939	3.921786	-0.677640
C	1.607557	2.543240	1.008184
H	1.971116	3.230601	1.779072
H	0.515461	2.631297	0.985362
H	0.670100	2.032361	-1.566715

E_{D3} = -834.024675

Transition state analogous to TS5, with F replaced by H
(single-point calculation, C–H bond length 1.09 Å)

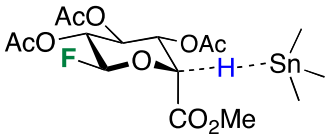


C	-2.989343	1.091519	-1.384198
H	-2.948128	1.430555	-2.422445
C	-3.406488	2.180190	-0.408593
H	-4.429267	2.491108	-0.647817
H	-2.750666	3.045220	-0.570969
C	-3.287679	1.680850	1.036559
H	-3.495422	2.493903	1.741214
H	-4.030363	0.895003	1.216012
C	-1.869527	1.121137	1.273397

H	-1.151037	1.952463	1.250771
H	-1.789794	0.632908	2.247417
C	-1.509783	0.131088	0.196362
O	-1.718123	0.558760	-1.114716
C	-1.693088	-1.309832	0.462629
O	-1.755982	-1.782585	1.589645
O	-1.678592	-2.058223	-0.661187
C	-1.793374	-3.473336	-0.453102
H	-1.767517	-3.918382	-1.449073
H	-0.962411	-3.849312	0.151086
H	-2.736284	-3.720216	0.043799
H	0.095520	0.164587	0.193221
Sn	1.949431	0.205592	-0.013541
C	2.671781	-1.820116	0.092459
H	2.431007	-2.272135	1.060630
H	3.760606	-1.843413	-0.033311
H	2.224482	-2.437026	-0.694133
C	2.434867	1.063905	-1.928171
H	2.082659	2.098619	-1.995564
H	1.971094	0.492472	-2.739008
H	3.520184	1.061905	-2.084095
C	2.845079	1.372484	1.562512
H	2.608162	0.950840	2.545104
H	3.935805	1.382560	1.450387
H	2.491808	2.408973	1.539686
H	-3.725084	0.288802	-1.334910

E_{D3} = -834.020223

TS1'



C	-0.229201	-0.316965	0.808397
O	0.119569	-1.597076	0.400653
C	1.479985	-1.934211	0.591256
C	2.361288	-0.989472	-0.219171
C	2.064844	0.463945	0.145842
C	0.555202	0.758943	0.064386
F	1.626218	-3.207360	0.114909
C	-0.682605	-0.138546	2.203710
O	-0.650468	-1.303163	2.893276
C	-1.176733	-1.239165	4.230129
O	-1.114825	0.906295	2.664211
Sn	-3.278251	-0.420922	-0.898240
C	-2.777895	-0.346423	-2.987338
C	-4.600098	1.178576	-0.345479
C	-4.162447	-2.323909	-0.418075
H	1.733800	-1.936726	1.658159
H	2.178543	-1.168379	-1.281425
O	3.732263	-1.272133	0.087203
H	2.432856	0.690072	1.149804
O	2.739648	1.308720	-0.798107
O	0.390442	2.067796	0.612159
H	0.245926	0.758403	-0.986483
H	-1.118737	-2.258614	4.614029
H	-2.214175	-0.893741	4.222052
H	-0.578521	-0.566334	4.851567
H	-1.716060	-0.293251	0.068135
H	-3.679899	-0.470691	-3.597878

H	-2.320401	0.614717	-3.241228
H	-2.077207	-1.146155	-3.249787
H	-5.101826	-2.455667	-0.968136
H	-4.382681	-2.396290	0.652441
H	-3.490888	-3.146815	-0.684525
H	-4.821866	1.153621	0.726686
H	-5.546455	1.099714	-0.893359
H	-4.135540	2.140072	-0.581047
C	4.523601	-1.758939	-0.915572
O	4.143938	-1.930596	-2.049916
C	5.907493	-2.036206	-0.392698
H	6.328124	-1.134607	0.064887
H	5.864623	-2.807673	0.384110
H	6.546668	-2.373679	-1.209520
C	3.677602	2.182828	-0.330061
O	3.991461	2.281709	0.833338
C	4.249068	2.981366	-1.471994
H	4.705471	2.310890	-2.208156
H	3.451184	3.530479	-1.983327
H	4.996042	3.680809	-1.094311
C	-0.655833	2.814419	0.174745
O	-1.399829	2.469121	-0.718085
C	-0.752093	4.093916	0.957321
H	0.227110	4.573522	1.046591
H	-1.463703	4.768128	0.478605
H	-1.096448	3.854201	1.969679

1 imaginary frequency

E = -1405.575879

G = -1405.225290

G_{raw} = -1405.235847

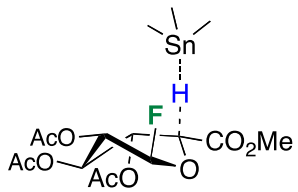
G_{RRHO} = -1405.225868

E_{D3} = -1617.270282

$E_{M06\text{-}2X}$ = -7422.885363

$E_{B97\text{-}D3}$ = -7425.635276

TS3'



O	0.179980	0.465368	-2.097387
C	0.304248	1.086371	-0.859374
C	-0.960266	1.137122	-0.024942
C	-1.920969	0.004541	-0.425717
C	-1.138962	-1.218269	-0.898185
C	-0.270574	-0.852741	-2.106843
C	1.149630	2.297121	-0.856340
O	1.875034	2.437645	-1.980734
C	2.740630	3.585426	-2.010429
O	-1.622873	2.403288	-0.261489
C	-2.114005	3.065712	0.820488
C	-2.689411	4.392720	0.403345
O	-2.711581	-0.395988	0.702882
C	-3.984299	0.084946	0.793578
O	-4.497441	0.792527	-0.043853
O	-2.053071	-2.236362	-1.323554
C	-2.085558	-3.404386	-0.614086
C	-3.114463	-4.333901	-1.199517

F	0.820662	-1.717307	-2.143498
O	-2.090377	2.625753	1.948899
C	-4.625677	-0.374501	2.074639
O	-1.376744	-3.635985	0.336923
O	1.222061	3.042637	0.107758
C	2.300778	-2.920468	0.780701
Sn	2.673864	-0.804249	0.869958
C	4.449327	-0.308798	-0.239305
C	2.840103	-0.130527	2.907015
H	-2.584904	0.361339	-1.217235
H	-0.516095	-1.612644	-0.093574
H	-0.815050	-0.991458	-3.043739
H	-0.726921	1.067506	1.039305
H	-4.098955	-3.854341	-1.202269
H	-2.861207	-4.565573	-2.239894
H	-3.151346	-5.254810	-0.616295
H	-4.177867	0.173018	2.912048
H	-5.696807	-0.169089	2.043691
H	-4.445369	-1.440197	2.243171
H	-1.919655	4.995182	-0.090133
H	-3.501572	4.236270	-0.314878
H	-3.068993	4.919579	1.279834
H	3.236898	3.549478	-2.981050
H	2.162427	4.508530	-1.912820
H	3.479892	3.538792	-1.205775
H	1.271964	0.150808	0.014187
H	5.308939	-0.871351	0.143506
H	4.325339	-0.552393	-1.299504
H	4.678357	0.759037	-0.157565
H	3.743479	-0.544215	3.370821
H	2.899490	0.961754	2.951030
H	1.975031	-0.450128	3.497386
H	3.185671	-3.467969	1.126523
H	1.451530	-3.207189	1.408091
H	2.083446	-3.225017	-0.247023

1 imaginary frequency

E = -1405.580833

G = -1405.229919

G_{raw} = -1405.239468

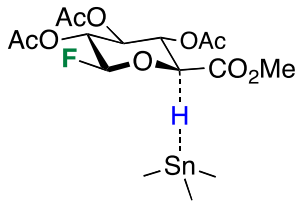
G_{RRHO} = -1405.229904

E_{D3} = -1617.277132

$E_{M06\text{-}2X}$ = -7422.891149

$E_{B97\text{-}D3}$ = -7425.643597

TS4'



C	-1.033121	-1.722518	1.208103
O	-0.085980	-1.042388	1.997946
C	0.490153	0.085447	1.439217
C	-0.492533	1.097919	0.859997
C	-1.585103	0.402849	0.036710
C	-2.165020	-0.787076	0.794115
C	1.629370	0.601489	2.226980
O	2.052033	1.744688	2.143888
F	-1.531475	-2.719576	1.998456

O	2.201690	-0.357184	2.981850
C	3.348447	0.063028	3.740979
Sn	2.351433	-0.947933	-1.335900
C	4.389240	-0.993115	-0.645505
C	2.113361	0.505490	-2.903867
C	1.753432	-2.902265	-2.023350
O	0.201652	2.000442	-0.009021
O	-2.633249	1.347601	-0.213833
O	-3.043554	-1.508524	-0.076589
H	1.266236	-0.435166	0.136096
H	-1.174685	0.073924	-0.920958
H	-2.709219	-0.467364	1.686277
H	-0.546455	-2.185495	0.339568
H	-0.958919	1.678311	1.664137
H	3.670094	-0.820763	4.293570
H	4.148036	0.408465	3.079477
H	3.082017	0.866893	4.432745
H	2.422331	-3.240827	-2.823467
H	1.796660	-3.637952	-1.213025
H	0.733363	-2.887879	-2.422267
H	5.065158	-1.268981	-1.463475
H	4.694777	-0.011130	-0.268600
H	4.512716	-1.723465	0.161108
H	2.541957	1.466166	-2.600643
H	2.623863	0.174295	-3.815696
H	1.056003	0.662210	-3.139424
C	-4.314200	-1.760215	0.364119
O	-4.747567	-1.371715	1.422689
C	-5.062274	-2.574740	-0.656690
H	-5.050973	-2.070435	-1.628550
H	-4.574283	-3.547022	-0.786487
H	-6.090714	-2.722618	-0.324848
C	-2.905648	1.683339	-1.508010
O	-2.340728	1.205622	-2.465455
C	-3.994947	2.721679	-1.550812
H	-4.890997	2.351881	-1.041331
H	-3.669113	3.623479	-1.021021
H	-4.230602	2.965798	-2.587534
C	0.144164	3.333995	0.283551
O	-0.543731	3.805265	1.158510
C	1.046840	4.105422	-0.640746
H	0.859692	3.830540	-1.683484
H	0.887464	5.175488	-0.500420
H	2.089738	3.859684	-0.411497

1 imaginary frequency

E = -1405.579216

G = -1405.227929

G_{raw} = -1405.239027

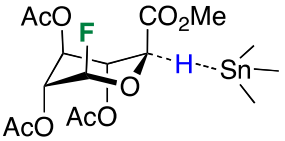
G_{RRHO} = -1405.228790

E_{D3} = -1617.275984

$E_{M06\text{-}2X}$ = -7422.890124

$E_{B97\text{-}D3}$ = -7425.642927

TS5'



C	-0.004202	0.822350	-0.037251
O	0.203720	0.362698	-1.334345

C	1.529908	0.285851	-1.768235
C	2.453583	-0.460903	-0.798534
C	2.258254	-0.007144	0.655866
C	0.767681	0.119499	1.046113
F	2.050710	1.563821	-1.926833
C	-0.288823	2.260158	0.152328
O	-0.572438	2.888840	-1.004426
C	-0.927671	4.275654	-0.876351
O	-0.351397	2.788775	1.252148
Sn	-3.307308	-0.245251	-0.116792
C	-4.499754	1.544653	-0.163953
C	-3.431863	-1.293771	-1.990461
C	-3.952653	-1.507819	1.503063
H	1.498169	-0.191741	-2.748647
O	2.159002	-1.868819	-0.837501
H	3.486049	-0.298007	-1.110636
O	2.799053	1.316095	0.816480
H	2.773871	-0.697296	1.324916
H	0.692308	0.679759	1.977349
O	0.212464	-1.206017	1.227874
H	-1.088404	4.630566	-1.895369
H	-1.841760	4.390225	-0.286455
H	-0.120820	4.840851	-0.402041
H	-1.548096	0.280461	0.123490
H	-5.552796	1.298560	-0.343781
H	-4.165606	2.216376	-0.961536
H	-4.431309	2.081068	0.788360
H	-5.046836	-1.578872	1.503568
H	-3.549420	-2.520702	1.400986
H	-3.640404	-1.101761	2.470731
H	-2.854391	-2.223659	-1.958403
H	-4.474023	-1.545012	-2.220157
H	-3.040236	-0.675784	-2.804939
C	2.763196	-2.591101	-1.822770
O	3.476003	-2.096758	-2.667467
C	2.416558	-4.050593	-1.698334
H	1.330980	-4.186289	-1.751619
H	2.898447	-4.611087	-2.500298
H	2.749381	-4.433972	-0.727664
C	4.141504	1.412111	1.026300
O	4.873525	0.449074	1.083404
C	4.552025	2.853404	1.158562
H	4.333712	3.385344	0.225615
H	3.980003	3.340402	1.955005
H	5.619502	2.912983	1.374798
C	0.473923	-1.812362	2.415216
O	1.128309	-1.302260	3.298612
C	-0.170088	-3.173248	2.470198
H	0.084397	-3.752490	1.577141
H	0.161358	-3.699248	3.366663
H	-1.260440	-3.065955	2.495249

1 imaginary frequency

E = -1405.577469

G = -1405.225913

G_{raw} = -1405.236222

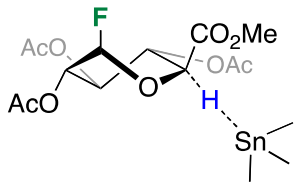
G_{RRHO} = -1405.226355

E_{D3} = -1617.271908

E_{M06-2X} = -7422.887094

E_{B97-D3} = -7425.637463

TS6'



C	0.667944	-0.821610	-1.205138
C	-0.302277	-1.449867	-0.218077
C	-1.513006	-0.528111	-0.028970
C	-2.194273	-0.179471	-1.361508
C	-1.213933	-0.309453	-2.531965
O	0.100927	-0.007531	-2.184058
O	0.332859	-1.588177	1.063684
C	0.372527	-2.830122	1.625132
O	-0.128139	-3.815703	1.135865
O	-2.439176	-1.195178	0.840892
C	-2.971510	-0.482974	1.872136
C	-3.957314	-1.326121	2.634368
O	-2.626837	1.194054	-1.340199
C	-3.920193	1.439749	-0.980876
O	-4.723721	0.567753	-0.738721
F	-1.277455	-1.625393	-2.979926
C	1.860492	-1.543444	-1.698070
O	2.449614	-1.275801	-2.728208
O	-2.688056	0.669976	2.114183
C	-4.174357	2.921112	-0.920233
O	2.267227	-2.491160	-0.818543
C	3.441452	-3.224235	-1.206287
C	1.134052	-2.782368	2.924225
Sn	2.029699	1.870656	0.514380
C	0.338559	3.054095	1.126227
C	3.203137	1.300407	2.226006
C	3.235024	2.961115	-0.894286
H	-1.184168	0.398853	0.445059
H	-3.053545	-0.829980	-1.533476
H	-1.477437	0.354438	-3.356954
H	-0.622832	-2.443019	-0.548087
H	-3.638854	3.339569	-0.060073
H	-3.798154	3.418596	-1.819221
H	-5.243121	3.106138	-0.804378
H	-3.532879	-2.307898	2.864957
H	-4.248721	-0.812705	3.551704
H	-4.845082	-1.488101	2.012275
H	2.187602	-2.559436	2.721071
H	0.747981	-1.986759	3.569369
H	1.056408	-3.745419	3.430823
H	3.626458	-3.930107	-0.395473
H	3.271559	-3.762467	-2.143058
H	4.295821	-2.552651	-1.328608
H	1.371234	0.335362	-0.312833
H	3.545698	2.191351	2.765044
H	2.612237	0.689786	2.916748
H	4.084990	0.724308	1.925932
H	3.610366	3.884854	-0.438124
H	4.094115	2.365952	-1.220755
H	2.650320	3.229702	-1.780135
H	0.676945	3.971105	1.623112
H	-0.265351	3.340711	0.258567
H	-0.304996	2.505478	1.821564

1 imaginary frequency
E = -1405.577395
G = -1405.226371
G_{raw} = -1405.236336
G_{RRHO} = -1405.226646
E_{D3} = -1617.273416
E_{M06-2X} = -7422.887446
E_{B97-D3} = -7425.639581

TS1'-βOAc

C	-0.212264	-1.189729	0.128944
C	0.380559	0.058862	0.772576
O	-0.119250	1.223310	0.210279
C	-1.535402	1.388515	0.312240
C	-2.235212	0.234326	-0.403730
C	-1.749265	-1.106120	0.147007
C	0.785445	0.092148	2.194249
O	1.313438	-0.835373	2.787957
O	-1.834941	2.580524	-0.375084
O	-3.643897	0.346829	-0.157147
C	-4.477424	0.484170	-1.229870
C	-5.903419	0.606012	-0.761908
O	-2.264291	-2.150987	-0.692750
C	-3.112211	-3.066243	-0.140894
C	-3.512359	-4.085452	-1.175577
O	0.112637	-2.401379	0.812322
C	1.266779	-3.033592	0.481624
C	1.497770	-4.208798	1.390103
O	0.581425	1.311953	2.740433
C	1.008894	1.457011	4.104664
O	-4.102660	0.506324	-2.379053
O	-3.477814	-3.044723	1.011521
O	1.995708	-2.676391	-0.419197
Sn	3.371238	0.458145	-0.951324
C	3.881513	2.543043	-0.768943
C	2.839769	0.011700	-2.986395
C	5.002884	-0.769928	-0.287526
H	-1.833250	1.472414	1.360404
H	-2.045550	0.302762	-1.477241
H	-2.116572	-1.256216	1.165217
H	0.134033	-1.249584	-0.908717
H	0.790046	2.492715	4.367976
H	2.079779	1.256815	4.200833
H	0.456527	0.776399	4.758956
H	1.880109	0.166483	0.086594
H	3.672820	0.247823	-3.659100
H	2.601733	-1.050980	-3.094379
H	1.970109	0.596674	-3.304330
H	4.725419	2.787648	-1.425093
H	4.166282	2.790337	0.259397
H	3.034648	3.178337	-1.049552
H	5.277978	-0.536617	0.746466
H	5.882942	-0.609167	-0.921065
H	4.718759	-1.824716	-0.341248
H	-6.167763	-0.242764	-0.122732
H	-6.021345	1.514919	-0.161293
H	-6.570448	0.647416	-1.624075
H	-3.977447	-3.590095	-2.034588
H	-2.625928	-4.612627	-1.544660
H	-4.209678	-4.800299	-0.736568

H	0.588768	-4.809503	1.490256
H	2.316720	-4.818918	1.006302
H	1.755640	-3.831153	2.386038
C	-2.117498	3.702853	0.366421
O	-2.208661	3.705582	1.569459
C	-2.290562	4.887465	-0.543198
H	-2.990557	4.653916	-1.351519
H	-2.648675	5.742448	0.031668
H	-1.328519	5.135493	-1.006404

1 imaginary frequency
E = -1534.224960
G = -1533.828076
E_{D3} = -1745.978666

TS3'-βOAc

C	-0.000917	1.332458	1.672190
O	0.255419	-0.007975	2.041322
C	0.104553	-0.982412	1.072856
C	-1.239145	-1.030459	0.375198
C	-1.906303	0.356204	0.368745
C	-0.854098	1.461376	0.407345
C	0.726934	-2.281854	1.394669
O	0.536990	-3.283225	0.720918
O	-2.095571	-1.958625	1.086458
C	-2.850954	-2.808810	0.340490
O	-2.909722	-2.775847	-0.869240
O	-2.667440	0.531439	-0.836238
C	-4.018927	0.365695	-0.765916
C	-4.634254	0.491279	-2.133278
O	-1.511862	2.734343	0.462494
C	-1.300028	3.611184	-0.561786
O	-0.560003	3.398077	-1.494684
O	1.232813	2.004457	1.420450
O	1.577568	-2.217148	2.434999
C	2.261276	-3.443050	2.746105
C	-3.590940	-3.769206	1.233009
O	-4.615875	0.130567	0.260383
C	-2.119345	4.856792	-0.354122
Sn	2.192509	-0.522451	-1.687274
C	1.100359	-1.344124	-3.350982
C	2.750711	1.520875	-2.071929
C	3.937424	-1.708737	-1.261827
H	-2.576499	0.437763	1.228048
H	-0.223858	1.427891	-0.482112
H	-0.489932	1.795833	2.528813
H	-1.127592	-1.387580	-0.650115
H	-3.185840	4.606181	-0.357366
H	-1.892493	5.303367	0.619582
H	-1.907049	5.571523	-1.150176
H	-4.461863	-0.442447	-2.681835
H	-5.709273	0.653208	-2.038666
H	-4.173091	1.302502	-2.703249
H	-2.877252	-4.358554	1.818495
H	-4.221184	-3.215460	1.936966
H	-4.208760	-4.432763	0.626432
H	2.888669	-3.214976	3.608933
H	1.547508	-4.233348	2.994909
H	2.878957	-3.768771	1.904356
H	1.065818	-0.623262	-0.160773
H	4.628666	-1.694823	-2.112914

H	4.469784	-1.323526	-0.385416
H	3.659439	-2.749454	-1.064839
H	1.742258	-1.407191	-4.237724
H	0.738636	-2.350653	-3.116945
H	0.237210	-0.717666	-3.599524
H	3.239821	1.598333	-3.050327
H	1.875100	2.177543	-2.072231
H	3.451626	1.881086	-1.311566
C	1.824392	2.645184	2.480914
O	1.329033	2.711487	3.580390
C	3.144668	3.233967	2.065487
H	3.028172	3.836081	1.158995
H	3.543526	3.845776	2.875751
H	3.850804	2.427342	1.837172

1 imaginary frequency

E = -1534.227911

G = -1533.829893

E_{D3} = -1745.984872

TS4'-βOAc

C	-2.128852	0.012532	-0.004697
C	-1.429373	-1.351029	-0.137751
O	-0.494810	-1.590299	0.899800
C	0.445554	-0.613458	1.154614
C	-0.102720	0.801981	1.283892
C	-1.082740	1.110356	0.146221
O	-2.326613	-2.440615	-0.171150
C	1.474597	-1.050793	2.123025
O	1.627827	-2.390747	2.127814
C	2.647597	-2.887614	3.010692
O	0.973929	1.743065	1.194743
C	1.167941	2.586443	2.250947
C	2.433533	3.376811	2.056082
O	-1.758009	2.340677	0.443714
C	-1.538711	3.411386	-0.371397
C	-2.294814	4.609817	0.138431
O	-2.828229	0.270422	-1.236619
C	-4.173670	0.056097	-1.274375
C	-4.716035	0.399124	-2.636671
O	2.164108	-0.287302	2.781607
O	-4.819580	-0.350768	-0.335727
O	-0.834854	3.383874	-1.355577
O	0.419416	2.670846	3.196261
Sn	2.523395	-0.497790	-1.648403
C	1.588539	-1.442821	-3.347751
C	4.282748	-1.604680	-1.081918
C	3.030219	1.541485	-2.116822
H	1.331742	-0.525613	-0.165667
H	-0.531853	1.232737	-0.789188
H	-2.827874	0.009732	0.830711
H	-0.917536	-1.394546	-1.106678
H	-0.604018	0.932238	2.249506
H	2.639034	-3.971045	2.882667
H	3.627161	-2.481871	2.742460
H	2.422308	-2.628450	4.049027
H	2.297951	-1.498874	-4.181971
H	1.272644	-2.463273	-3.105366
H	0.712530	-0.880720	-3.689062
H	5.022702	-1.591599	-1.890917
H	4.746814	-1.170128	-0.190014

H	4.033511	-2.648549	-0.863418
H	3.626769	1.983384	-1.312095
H	3.614388	1.588825	-3.043357
H	2.129197	2.149250	-2.247064
H	-4.476368	1.437277	-2.889678
H	-4.249786	-0.237779	-3.396411
H	-5.796907	0.253017	-2.647708
H	-3.367722	4.392443	0.174255
H	-1.977037	4.845602	1.159901
H	-2.112148	5.464408	-0.514328
H	2.488305	3.783077	1.041735
H	2.480360	4.183211	2.789590
H	3.291519	2.709588	2.196878
C	-3.104887	-2.719772	0.932053
O	-3.063097	-2.097965	1.963527
C	-3.985300	-3.904145	0.640285
H	-3.378929	-4.765924	0.341987
H	-4.569810	-4.148972	1.528077
H	-4.659168	-3.667783	-0.190048

1 imaginary frequency

E = -1534.224117

G = -1533.826224

E_{D3} = -1745.980158

TS5'-βOAc

C	-0.401082	-0.667538	-1.208363
C	0.096338	0.534730	-0.451935
O	-0.202052	0.570117	0.900759
C	-1.555707	0.395887	1.274813
C	-2.230767	-0.800758	0.589869
C	-1.896305	-0.913319	-0.905695
C	0.188830	1.809627	-1.192002
O	0.350170	1.872312	-2.401440
O	-2.325998	1.549621	0.934897
O	-1.770433	-2.021305	1.200928
C	-2.420475	-2.415089	2.332502
C	-1.875667	-3.727925	2.828449
O	-2.596052	0.110660	-1.635414
C	-3.885363	-0.151987	-1.985586
C	-4.461986	0.995291	-2.770724
O	0.360388	-1.827196	-0.789802
C	0.346634	-2.894491	-1.629841
C	1.168866	-4.026719	-1.069751
O	0.187023	2.888731	-0.379405
C	0.393266	4.149193	-1.038570
O	-3.312615	-1.775172	2.842947
O	-4.458305	-1.177462	-1.691580
O	-0.244612	-2.907787	-2.687739
Sn	3.469342	0.117626	0.227191
C	4.652020	-0.515253	-1.457022
C	4.137848	2.046675	0.904334
C	3.593247	-1.322522	1.820004
H	-1.537730	0.276109	2.356655
H	-3.309401	-0.717187	0.727122
H	-2.205207	-1.894320	-1.268562
H	-0.276869	-0.514024	-2.279774
H	0.390260	4.897727	-0.244788
H	1.351852	4.161228	-1.565110
H	-0.407392	4.351667	-1.756056
H	1.700471	0.283792	-0.296765

H	5.159958	1.979933	1.295327
H	3.490062	2.426618	1.701026
H	4.134079	2.772629	0.084200
H	5.707166	-0.590129	-1.168716
H	4.330595	-1.493015	-1.830835
H	4.573049	0.205557	-2.277624
H	3.139900	-2.274270	1.525036
H	4.640781	-1.508517	2.084385
H	3.072953	-0.958013	2.711734
H	-0.798838	-3.645998	3.010635
H	-2.386028	-4.011101	3.749897
H	-2.024263	-4.505631	2.071233
H	-4.405410	1.917910	-2.183385
H	-3.880352	1.153415	-3.685312
H	-5.500488	0.780015	-3.025388
H	0.913470	-4.204852	-0.020765
H	0.996060	-4.928960	-1.658395
H	2.233888	-3.770816	-1.113512
C	-2.285760	2.595019	1.821070
O	-1.710019	2.549438	2.881104
C	-3.066286	3.763681	1.283705
H	-2.605666	4.119091	0.355736
H	-4.091588	3.459870	1.047670
H	-3.078301	4.567322	2.021188

1 imaginary frequency

E = -1534.225432

G = -1533.827941

E_{D3} = -1745.980520

TS6'-βOAc

C	-2.092003	-1.718157	-2.523553
Sn	-2.815079	0.033123	-1.505178
C	-3.182264	1.624452	-2.904477
C	-4.607801	-0.419674	-0.404056
C	-0.094426	1.010784	0.412158
C	-0.519444	2.250640	1.093071
O	-0.383032	3.377830	0.651331
C	0.280753	-0.221807	1.217269
O	-0.904852	-0.909122	1.661269
C	-1.006036	-1.209543	2.986760
O	-0.142438	-0.986549	3.804333
C	1.095964	-1.167929	0.329223
O	1.511366	-2.305126	1.099120
C	0.945049	-3.513778	0.825748
C	1.526247	-4.570898	1.727738
C	2.350113	-0.464988	-0.185700
O	2.811039	-1.242793	-1.306404
C	4.132224	-1.134892	-1.621981
O	4.895531	-0.402485	-1.032967
C	2.035883	0.983999	-0.622171
O	2.576047	1.861155	0.359390
C	2.981418	3.101742	-0.080458
C	3.313455	3.988878	1.085151
O	-1.144652	1.967571	2.262119
C	-1.612612	3.104293	3.006316
C	-2.343590	-1.841217	3.272869
O	0.106030	-3.695857	-0.027196
C	4.477186	-2.036078	-2.777459
O	3.042993	3.399583	-1.247509
H	0.486506	-1.508372	-0.510284

H	3.126069	-0.445549	0.581800
H	2.453480	1.211264	-1.601181
H	0.858119	0.041856	2.109445
H	4.237656	-3.076059	-2.531192
H	3.882716	-1.764038	-3.656396
H	5.539219	-1.945022	-3.008779
H	1.447142	-4.262342	2.775029
H	1.001886	-5.514931	1.573095
H	2.591280	-4.703428	1.506389
H	-3.132552	-1.088535	3.161117
H	-2.551284	-2.646366	2.561359
H	-2.356435	-2.227517	4.293144
H	-2.045247	2.696996	3.921260
H	-0.786576	3.778868	3.248246
H	-2.370926	3.652722	2.440010
H	-1.487832	0.570572	-0.328904
H	-3.934592	1.316465	-3.640109
H	-3.548058	2.521564	-2.394270
H	-2.264896	1.888355	-3.440665
H	-2.882442	-2.145692	-3.151856
H	-1.244575	-1.466655	-3.170545
H	-1.765017	-2.484077	-1.813241
H	-5.420469	-0.674412	-1.094585
H	-4.449212	-1.271535	0.265296
H	-4.929600	0.437062	0.197447
H	3.870965	4.859392	0.736396
H	2.376489	4.323312	1.545745
H	3.886339	3.446493	1.842706
O	0.642608	1.214358	-0.745517

1 imaginary frequency

E = -1534.225653

G = -1533.829083

E_{D3} = -1745.980648

TS1'-αOAc

C	-1.844124	-0.807301	0.101364
C	-0.313755	-0.922568	0.232504
C	0.318136	0.442422	0.493031
O	-0.111965	1.401962	-0.415478
C	-1.513814	1.605135	-0.509814
C	-2.201283	0.294152	-0.893021
O	-0.078994	-1.884698	1.264343
C	0.991977	-2.709030	1.137357
O	1.755991	-2.684869	0.196663
C	0.692004	0.991802	1.817252
O	1.227109	0.058403	2.638177
C	1.679396	0.553098	3.910126
O	-2.045667	2.036198	0.732238
C	-2.071082	3.390572	0.967898
C	-2.460648	3.663632	2.392133
O	-3.622550	0.480587	-0.892593
C	-4.280804	0.361694	-2.082762
O	-3.734622	0.123314	-3.135509
O	-2.335207	-2.054733	-0.416655
C	-3.210341	-2.771124	0.345241
O	-3.625017	-2.412606	1.423240
O	0.631009	2.175854	2.105078
C	-5.756672	0.581202	-1.883338
C	-3.573423	-4.054354	-0.356077
C	1.077233	-3.642032	2.315150

O	-1.818597	4.213102	0.121519
Sn	3.385307	0.201613	-1.104202
C	4.891213	-0.861154	0.002068
C	3.998908	2.235114	-1.449975
C	2.985513	-0.779529	-2.976304
H	-1.646527	2.377754	-1.266359
H	-1.877152	0.015175	-1.898394
H	-2.301710	-0.617962	1.073312
H	0.086679	-1.309007	-0.711071
H	2.061689	-0.318383	4.443578
H	0.854423	1.004972	4.467881
H	2.473176	1.294222	3.780250
H	1.813501	0.260501	-0.123006
H	3.895409	-0.813336	-3.587342
H	2.647082	-1.806831	-2.808841
H	2.214432	-0.248380	-3.544449
H	4.928960	2.263089	-2.030249
H	4.170069	2.760798	-0.504593
H	3.230221	2.781421	-2.006528
H	5.116375	-0.360296	0.949647
H	5.818207	-0.921080	-0.580433
H	4.549405	-1.877712	0.217968
H	-6.150334	-0.126316	-1.146049
H	-5.933870	1.589822	-1.494372
H	-6.277063	0.457234	-2.833873
H	-4.016559	-3.839103	-1.334330
H	-2.673498	-4.653645	-0.531840
H	-4.279759	-4.618626	0.254244
H	0.131310	-4.177027	2.448306
H	1.891265	-4.352261	2.164613
H	1.255911	-3.063631	3.227812
H	-3.336516	3.072214	2.676533
H	-1.629340	3.367473	3.041301
H	-2.663639	4.727780	2.521182

1 imaginary frequency

E = -1534.226587

G = -1533.829509

E_{D3} = -1745.980384

TS2'-αOAc

C	-1.317308	0.441442	1.298549
C	-2.000774	-0.595947	0.392629
C	-1.029299	-1.060635	-0.694539
O	-0.521459	0.023109	-1.453111
C	0.141163	0.984319	-0.719808
C	-0.549358	1.518481	0.513920
O	-3.142734	0.036726	-0.202873
C	-4.254364	-0.727492	-0.391783
O	-4.333377	-1.894293	-0.077609
O	-1.690483	-1.863795	-1.652982
C	-1.614216	-3.219787	-1.494399
C	-2.435000	-3.913517	-2.544773
C	0.855364	1.991130	-1.533791
O	1.295100	3.027920	-1.061380
O	-1.498605	2.523967	0.066372
C	-1.674815	3.597334	0.882426
O	-1.167200	3.697569	1.977905
O	-0.353195	-0.240203	2.128517
C	-0.818308	-0.726325	3.320105
O	-1.974738	-0.637280	3.662715

O	1.046872	1.597460	-2.806731
C	1.796611	2.511411	-3.625468
C	-2.567629	4.617796	0.226102
C	0.294696	-1.355528	4.112858
C	-5.346805	0.090022	-1.027914
O	-0.982150	-3.751869	-0.610795
Sn	3.116034	-0.567878	0.166668
C	3.940237	-0.037222	2.084599
C	2.921077	-2.708737	0.009584
C	4.393068	0.169148	-1.404679
H	-0.206871	-1.619344	-0.236615
H	0.172748	1.997222	1.175459
H	-2.066084	0.913604	1.935205
H	-2.325321	-1.455849	0.982001
H	1.420111	0.246616	-0.137057
H	2.785545	2.697760	-3.198642
H	1.264995	3.461703	-3.729513
H	1.888278	2.023468	-4.596887
H	5.369983	-0.327341	-1.366927
H	4.555289	1.246931	-1.298609
H	3.952250	-0.021940	-2.388431
H	3.946195	1.048687	2.224152
H	4.973273	-0.397362	2.158009
H	3.364918	-0.486253	2.900639
H	3.905174	-3.182969	0.106474
H	2.500796	-2.995500	-0.959989
H	2.271200	-3.114272	0.792030
H	-5.583321	0.957006	-0.402005
H	-5.012010	0.468178	-1.999874
H	-6.237551	-0.526096	-1.157442
H	0.770289	-2.154344	3.534148
H	1.060507	-0.606037	4.340364
H	-0.106455	-1.763026	5.041680
H	-3.487597	4.147322	-0.134859
H	-2.804815	5.410318	0.937241
H	-2.054365	5.047323	-0.641864
H	-3.496405	-3.734970	-2.337891
H	-2.216472	-3.511012	-3.538498
H	-2.236256	-4.985784	-2.517650

1 imaginary frequency

E = -1534.226406

G = -1533.828975

E_{D3} = -1745.983404

TS3'-αOAc

C	1.379622	-0.413349	-1.603483
O	0.374428	-1.363661	-1.329190
C	-0.166519	-1.390645	-0.053933
C	0.575798	-0.721772	1.074581
C	1.194952	0.639789	0.681189
C	1.144151	0.881889	-0.832836
C	-0.857827	-2.651481	0.294496
O	-1.274516	-2.880722	1.419715
O	1.613357	-1.638726	1.521433
C	1.971371	-1.538277	2.828957
O	1.544286	-0.683796	3.574585
O	0.448316	1.669066	1.358229
C	1.147133	2.693522	1.921054
C	0.215621	3.639084	2.629983
O	2.165404	1.804963	-1.236958

C	1.817767	3.113073	-1.393476
O	0.686674	3.529072	-1.270529
H	1.362557	-0.256094	-2.680743
O	-1.051346	-3.458380	-0.764234
C	-1.774328	-4.670430	-0.488096
C	2.940243	-2.629781	3.202179
O	2.350228	2.808671	1.841385
C	3.031825	3.943372	-1.708009
Sn	-3.085544	0.471111	-0.325792
C	-3.740428	1.245265	1.573870
C	-2.852278	2.057089	-1.766634
C	-4.508620	-0.974965	-1.052324
H	2.232165	0.679125	1.012936
H	0.164979	1.277709	-1.111629
O	2.657016	-0.926219	-1.221436
H	-0.111661	-0.563123	1.905002
H	3.654353	3.456798	-2.464326
H	2.722866	4.932679	-2.048697
H	3.632438	4.046024	-0.796706
H	-0.355875	3.103413	3.395208
H	0.792045	4.441425	3.092372
H	-0.498011	4.062525	1.915037
H	2.421890	-3.595535	3.192373
H	3.757970	-2.686646	2.477120
H	3.336717	-2.442165	4.201094
H	-1.803401	-5.212894	-1.433987
H	-1.261687	-5.262989	0.274643
H	-2.789851	-4.447894	-0.148327
H	-1.426273	-0.466636	-0.133765
H	-5.483496	-0.502449	-1.221630
H	-4.172286	-1.412729	-1.998218
H	-4.644737	-1.785366	-0.328009
H	-4.693184	1.775137	1.456305
H	-3.886088	0.432535	2.293019
H	-3.008277	1.944766	1.989527
H	-3.768745	2.657734	-1.813045
H	-2.020231	2.720423	-1.509909
H	-2.668364	1.644786	-2.764870
C	3.389173	-1.579061	-2.177783
O	3.032829	-1.699647	-3.325857
C	4.670525	-2.096005	-1.583325
H	5.238465	-1.272183	-1.138156
H	4.444840	-2.808651	-0.782477
H	5.265573	-2.584169	-2.356156

1 imaginary frequency
E = -1534.227192
G = -1533.830023
E_{D3} = -1745.983817

TS4'-αOAc

C	-2.281126	0.027582	0.814173
C	-1.450359	-1.168711	1.296638
O	-0.302237	-0.764033	1.989906
C	0.495802	0.250298	1.478462
C	-0.218138	1.425168	0.822450
C	-1.418915	0.969436	-0.013624
H	-2.020371	-1.787503	1.987825
C	1.626591	0.579755	2.373419
O	2.008772	-0.471226	3.126024
C	3.123110	-0.225171	4.001345

O	0.703969	2.111830	-0.036072
C	0.853936	3.457749	0.141219
C	1.965182	3.975261	-0.732319
O	-2.198166	2.128060	-0.343662
C	-2.340582	2.458763	-1.658091
C	-3.154950	3.718830	-1.785815
O	-3.360945	-0.434756	-0.004041
C	-4.544336	-0.703476	0.626736
C	-5.552758	-1.238878	-0.351959
O	2.195500	1.660520	2.374867
O	-4.717971	-0.538428	1.812119
O	-1.866420	1.824423	-2.572904
O	0.182867	4.120277	0.897478
Sn	2.463572	-0.979833	-1.123892
C	2.819039	-3.106358	-0.996769
C	4.341905	0.049297	-0.894588
C	1.592298	-0.488905	-3.031393
H	1.332628	-0.383170	0.253083
H	-1.088032	0.486888	-0.935172
H	-2.683552	0.543007	1.690170
O	-1.060558	-1.970111	0.168630
H	-0.564124	2.133653	1.583847
H	3.271475	-1.155885	4.550753
H	4.020819	0.024651	3.428326
H	2.899382	0.591732	4.692904
H	3.868432	-3.322327	-1.229279
H	2.609838	-3.489406	0.007174
H	2.196085	-3.651409	-1.713838
H	5.012492	-0.196765	-1.726636
H	4.197967	1.134446	-0.880528
H	4.837247	-0.240261	0.038530
H	1.356864	0.578323	-3.090392
H	2.288413	-0.732627	-3.842790
H	0.665067	-1.046124	-3.200288
H	-5.532873	-0.672738	-1.287466
H	-5.300989	-2.280162	-0.584832
H	-6.548469	-1.205432	0.092745
H	-4.125591	3.595818	-1.293957
H	-2.638237	4.544067	-1.283596
H	-3.299181	3.958367	-2.840180
H	1.880642	3.580325	-1.749151
H	1.943067	5.066050	-0.747901
H	2.925019	3.641598	-0.321688
C	-1.757230	-3.126681	-0.048718
O	-2.686866	-3.486371	0.637756
C	-1.208901	-3.862409	-1.240045
H	-0.144531	-4.074699	-1.096260
H	-1.758271	-4.795147	-1.374985
H	-1.306763	-3.244428	-2.139359

1 imaginary frequency
E = -1534.228789
G = -1533.830523
E_{D3} = -1745.986030

TS5'-αOAc

C	0.385346	-1.197255	0.893985
C	-0.193416	0.192613	0.859399
O	0.205821	0.985111	-0.199907
C	1.621743	1.155576	-0.313045
C	2.346897	-0.187207	-0.436360

C	1.918989	-1.135642	0.696104
C	-0.463938	0.840668	2.160625
O	-0.767344	0.225260	3.171413
H	1.992916	1.713183	0.550949
O	2.025631	-0.817087	-1.684931
C	2.937553	-0.704124	-2.692837
C	2.420696	-1.375112	-3.938130
O	2.436813	-0.609244	1.935539
C	3.653046	-1.073838	2.351955
C	4.015330	-0.472426	3.682538
O	-0.202504	-1.980483	-0.172505
C	-0.135770	-3.330340	-0.037369
C	-0.794282	-4.016844	-1.206231
O	-0.414590	2.186059	2.080723
C	-0.735195	2.886565	3.294094
O	4.005793	-0.147889	-2.580369
O	4.315463	-1.860238	1.715558
O	0.376959	-3.885466	0.910193
Sn	-3.454513	0.093831	-0.335674
C	-4.637219	-1.586606	0.302458
C	-4.343171	1.922298	0.368165
C	-3.266559	0.118410	-2.477670
O	1.821693	1.897976	-1.491751
H	3.424976	-0.017316	-0.389989
H	2.329352	-2.130664	0.522555
H	0.172025	-1.668626	1.853021
H	-0.661471	3.946476	3.047105
H	-1.748284	2.642694	3.626202
H	-0.027371	2.632910	4.088372
H	-1.767110	-0.014051	0.392508
H	-5.317870	2.080011	-0.108212
H	-3.705778	2.782067	0.137127
H	-4.495952	1.889156	1.452236
H	-5.659034	-1.498411	-0.085032
H	-4.218240	-2.532120	-0.057892
H	-4.689316	-1.631759	1.395308
H	-2.771799	-0.790130	-2.836289
H	-4.254077	0.182735	-2.949306
H	-2.674139	0.980099	-2.802093
H	1.501452	-0.881653	-4.272142
H	3.175322	-1.320767	-4.723942
H	2.176151	-2.422190	-3.731121
H	4.015097	0.620810	3.616769
H	3.270349	-0.755545	4.433987
H	5.001107	-0.825270	3.988139
H	-0.439801	-3.592214	-2.150300
H	-0.580866	-5.086242	-1.169842
H	-1.879161	-3.865356	-1.162901
C	2.139026	3.228731	-1.371968
O	2.296315	3.787753	-0.313795
C	2.272222	3.844224	-2.736889
H	1.328537	3.747623	-3.284618
H	2.539704	4.897293	-2.641902
H	3.040760	3.313559	-3.309287

1 imaginary frequency

E = -1534.223306

G = -1533.826286

E_{D3} = -1745.977194

TS6'-αOAc

```
O   -0.818440   -1.259298    0.526988
C    0.258901   -0.618682    1.115078
C    0.137851    0.895350    1.213580
C   -0.807813    1.397904    0.112135
C   -2.192002    0.743073    0.195739
C   -2.076712   -0.654652    0.834608
C    0.923695   -1.412735    2.171787
O    1.794805   -0.655568    2.884986
C    2.518901   -1.355178    3.910923
O    1.425813    1.501612    1.008115
C    1.870648    2.390117    1.940780
C    3.258657    2.856208    1.586233
O   -0.973032    2.817941    0.243083
C   -0.413252    3.628076   -0.699512
O    0.207010    3.229056   -1.658968
O   -2.694041    0.671365   -1.147245
C   -4.035617    0.828070   -1.322866
C   -4.392883    0.662245   -2.776187
H   -2.183932   -0.582456    1.921022
O    1.231902    2.741060    2.906384
C   -0.689273    5.070863   -0.366201
O   -4.809254    1.068017   -0.423446
O    0.768138   -2.607873    2.338546
Sn   2.249852   -1.198682   -1.651666
C    2.220613   -3.330595   -1.938094
C    1.266610   -0.203893   -3.287360
C    4.275440   -0.495464   -1.455968
H   -0.366535    1.179672   -0.862195
H   -2.872164    1.349556    0.797598
O   -3.064430   -1.500835    0.312778
H   -0.221735    1.214557    2.198149
H   -3.782877    1.324472   -3.398952
H   -4.183188   -0.366411   -3.090258
H   -5.451591    0.881212   -2.922056
H   -0.300881    5.306385    0.630354
H   -0.222099    5.716732   -1.110863
H   -1.769616    5.251728   -0.345397
H    3.954659    2.011527    1.639253
H    3.283310    3.237173    0.560123
H    3.574427    3.634809    2.282217
H    3.157675   -0.605985    4.380896
H    1.832782   -1.781685    4.648007
H    3.125812   -2.156130    3.479238
H    1.310060   -0.804930   -0.086610
H    4.845645   -0.718717   -2.365366
H    4.297034    0.587905   -1.297881
H    4.780705   -0.976524   -0.611587
H    2.748510   -3.601615   -2.860154
H    2.704515   -3.845788   -1.101812
H    1.191095   -3.696045   -2.011993
H    1.816153   -0.374633   -4.220805
H    0.247646   -0.584017   -3.417067
H    1.210548    0.875549   -3.114621
C   -3.685999   -2.365972    1.188045
O   -3.467167   -2.383318    2.373440
C   -4.659786   -3.233582    0.442969
H   -5.419504   -2.608887   -0.039465
H   -4.140382   -3.790395   -0.344109
H   -5.136971   -3.927152    1.136204
1 imaginary frequency
E = -1534.220063
```

G = -1533.822764
E_{D3} = -1745.975692

TS1'-βOMe

C	0.467036	0.860051	0.173672
C	-0.277332	-0.330938	0.769158
O	0.115096	-1.522910	0.193672
C	1.515118	-1.856051	0.352199
C	2.338142	-0.779215	-0.354261
C	1.985028	0.605536	0.189378
C	-0.731548	-0.350565	2.175330
O	-1.188785	0.609996	2.775167
O	1.749598	-3.065665	-0.256743
O	3.728272	-1.020922	-0.094505
C	4.553694	-1.238036	-1.157861
C	5.952508	-1.519522	-0.674803
O	2.601949	1.594135	-0.652079
C	3.550450	2.408509	-0.109507
C	4.032566	3.394715	-1.141748
O	0.277964	2.079458	0.897228
C	-0.782672	2.857884	0.569689
C	-0.893181	4.021888	1.514752
O	-0.677197	-1.599250	2.702111
C	-1.210513	-1.722372	4.030799
O	4.196964	-1.205872	-2.312838
O	3.933295	2.337419	1.035807
O	-1.531072	2.622371	-0.355525
Sn	-3.273699	-0.230360	-0.981578
C	-4.058432	-2.237783	-0.966954
C	-2.725060	0.327242	-2.984277
C	-4.726725	1.127375	-0.167133
H	1.740739	-1.892443	1.429989
H	2.151125	-0.837116	-1.428540
H	2.369183	0.720200	1.205914
H	0.138688	0.995914	-0.862329
H	-1.102143	-2.775991	4.292909
H	-2.265252	-1.433721	4.053484
H	-0.652910	-1.098115	4.734818
H	-1.743403	-0.235210	0.056249
H	-3.601988	0.306570	-3.642199
H	-2.311657	1.340260	-2.991568
H	-1.976450	-0.358915	-3.394503
H	-4.970462	-2.294948	-1.573423
H	-4.307979	-2.557016	0.050759
H	-3.330233	-2.945094	-1.378100
H	-4.949154	0.889189	0.878383
H	-5.661513	1.071723	-0.737431
H	-4.347042	2.151923	-0.215394
H	6.288230	-0.728727	0.003797
H	5.968404	-2.460988	-0.114248
H	6.627732	-1.593122	-1.528431
H	4.386825	2.868290	-2.034133
H	3.204742	4.041999	-1.452103
H	4.835639	4.002446	-0.722658
H	0.078997	4.502440	1.659414
H	-1.619326	4.741255	1.133510
H	-1.225256	3.646893	2.489474
C	1.196554	-4.188134	0.432922
H	1.535716	-5.076353	-0.104772
H	1.559219	-4.230663	1.469503

```
H    0.102012   -4.156285    0.434055
```
1 imaginary frequency
E = -1420.866411
G = -1420.476357
E_{D3} = -1632.568099

TS3'-βOMe

```
C    0.276836   -0.975125    2.038279
O   -0.185614    0.380497    2.118341
C   -0.316090    1.069081    0.928985
C    0.949637    1.193632    0.103064
C    1.917378    0.041341    0.421503
C    1.149562   -1.222477    0.800106
C   -1.194450    2.254326    0.979023
O   -1.245165    3.079512    0.080431
O    1.602509    2.444886    0.432143
C    2.073781    3.197929   -0.596516
O    2.059701    2.846245   -1.755921
O    2.708880   -0.267178   -0.737305
C    3.986885    0.200275   -0.785549
C    4.629034   -0.173987   -2.094646
O    2.086978   -2.257954    1.130878
C    2.067677   -3.400834    0.387008
O    1.303885   -3.604819   -0.528331
O   -0.776054   -1.882881    1.999020
O   -1.994995    2.268902    2.064545
C   -2.911628    3.373856    2.132626
C    2.612186    4.505961   -0.080356
O    4.508650    0.834393    0.104199
C    3.128785   -4.352082    0.874353
Sn  -2.467850   -0.646979   -1.203321
C   -1.379552   -1.796324   -2.662921
C   -3.804209   -1.911022   -0.082394
C   -3.561598    0.940331   -2.163780
H    2.580457    0.344257    1.235487
H    0.530410   -1.561326   -0.031395
H    0.871674   -1.106374    2.951905
H    0.721702    1.201062   -0.964529
H    4.118904   -3.895133    0.769587
H    2.981150   -4.571267    1.937150
H    3.086664   -5.276071    0.296288
H    4.165752    0.406599   -2.900509
H    5.696391    0.048725   -2.057090
H    4.469171   -1.233140   -2.318044
H    1.817778    5.056591    0.434542
H    3.413193    4.321394    0.643418
H    2.995796    5.099133   -0.911623
H   -3.465043    3.236603    3.062884
H   -2.372101    4.325021    2.151700
H   -3.597267    3.367743    1.280268
H   -1.239236    0.203213   -0.020040
H   -4.286468    0.534762   -2.879982
H   -4.107093    1.543273   -1.430245
H   -2.878162    1.602836   -2.704358
H   -2.077992   -2.326869   -3.321108
H   -0.757427   -1.143309   -3.284584
H   -0.730163   -2.536031   -2.183730
H   -4.666781   -2.193414   -0.697599
H   -3.291086   -2.825423    0.230689
H   -4.175460   -1.397861    0.810956
```

C	-1.564606	-1.911952	3.189324
H	-2.277166	-2.730716	3.070650
H	-0.936725	-2.104875	4.071285
H	-2.106345	-0.970836	3.331420

1 imaginary frequency
E = -1420.868996
G = -1420.477976
E_{D3} = -1632.573950

TS4'-βOMe

C	-2.137296	-0.818661	0.586904
C	-1.007727	-1.829811	0.786377
O	-0.048966	-1.293738	1.717721
C	0.527910	-0.085679	1.396326
C	-0.460744	1.023961	1.054073
C	-1.559056	0.512389	0.113778
O	-1.533195	-2.982326	1.320841
C	1.683369	0.258068	2.251389
O	2.261946	-0.837083	2.789046
C	3.421210	-0.579030	3.598249
O	0.217057	2.095306	0.385448
C	0.177582	3.332524	0.960456
C	1.052994	4.285954	0.192230
O	-2.616335	1.482458	0.082764
C	-2.899056	2.095068	-1.101013
C	-4.023573	3.079333	-0.913876
O	-3.010506	-1.317569	-0.435143
C	-4.317069	-1.539354	-0.111017
C	-5.052609	-2.110641	-1.294983
O	2.117884	1.391008	2.394347
O	-4.795166	-1.307325	0.974581
O	-2.318608	1.869741	-2.139077
O	-0.475416	3.604776	1.940787
Sn	2.341523	-0.533871	-1.556130
C	1.693580	-2.297242	-2.617926
C	4.395126	-0.779297	-0.950807
C	2.132053	1.210816	-2.798255
H	1.287922	-0.314183	0.011948
H	-1.157216	0.404608	-0.896599
H	-2.691941	-0.704775	1.520929
H	-0.483815	-2.023881	-0.164732
H	-0.918137	1.419207	1.968246
H	3.750170	-1.556325	3.954947
H	4.211780	-0.105442	3.009182
H	3.169667	0.066701	4.444385
H	2.322480	-2.454418	-3.502341
H	1.774281	-3.188763	-1.986347
H	0.655962	-2.205957	-2.956576
H	5.038768	-0.911254	-1.828597
H	4.747361	0.098831	-0.399159
H	4.511987	-1.658030	-0.307620
H	2.567772	2.084638	-2.302862
H	2.646734	1.066765	-3.755436
H	1.078042	1.424309	-3.003026
H	-4.895228	-1.488192	-2.181458
H	-4.664382	-3.109881	-1.522839
H	-6.117329	-2.177776	-1.067347
H	-4.902408	2.575380	-0.498195
H	-3.724060	3.852671	-0.198095
H	-4.274359	3.538800	-1.870878

```
H    0.825043    4.243839   -0.877441
H    0.909474    5.300421    0.567161
H    2.101415    3.995026    0.322233
C   -0.627455   -4.087200    1.348194
H   -1.194600   -4.939946    1.727526
H   -0.259110   -4.318339    0.338466
H    0.222594   -3.889664    2.009938
1 imaginary frequency
E = -1420.869575
G = -1420.479964
E_D3 = -1632.573646
```

TS5'-βOMe

```
C   -0.606155   -0.121156   -1.099122
C    0.030637    0.779931   -0.071534
O   -0.278166    0.516628    1.248415
C   -1.673800    0.417681    1.595906
C   -2.450138   -0.505621    0.643441
C   -2.121259   -0.259626   -0.836459
C    0.295953    2.175184   -0.484033
O    0.452659    2.514171   -1.647568
O   -2.311175    1.652477    1.588384
O   -2.114003   -1.883126    0.906055
C   -2.781261   -2.490997    1.923325
C   -2.390728   -3.942381    2.021094
O   -2.688459    0.994480   -1.253716
C   -4.003728    0.992937   -1.599841
C   -4.443064    2.375072   -2.001098
O    0.008910   -1.431460   -1.007033
C   -0.144215   -2.251587   -2.077611
C    0.503827   -3.588619   -1.822482
O    0.468745    3.008948    0.564733
C    0.822753    4.358423    0.220673
O   -3.582589   -1.921850    2.631466
O   -4.698377    0.000790   -1.572831
O   -0.729167   -1.933288   -3.090441
Sn   3.350766   -0.189647    0.159861
C    4.133437   -0.894316   -1.717693
C    4.468818    1.537844    0.796189
C    3.477878   -1.739300    1.649554
H   -1.649578   -0.013134    2.602683
H   -3.515884   -0.358751    0.820133
H   -2.541899   -1.066341   -1.437983
H   -0.453817    0.284013   -2.098955
H    0.930630    4.883187    1.171236
H    1.764434    4.385774   -0.334969
H    0.038113    4.825111   -0.381660
H    1.570375    0.310319   -0.058939
H    5.514678    1.266974    0.983132
H    4.054564    1.956003    1.719507
H    4.451030    2.317931    0.027584
H    5.187138   -1.176039   -1.605528
H    3.584832   -1.769786   -2.080885
H    4.070386   -0.112680   -2.482108
H    2.846244   -2.593431    1.383673
H    4.511215   -2.093165    1.744468
H    3.152174   -1.366022    2.626161
H   -1.301542   -4.044343    2.058703
H   -2.838653   -4.384381    2.912160
H   -2.743018   -4.479310    1.132823
```

```
H   -4.333729    3.056516   -1.150326
H   -3.809222    2.755099   -2.808907
H   -5.484947    2.351292   -2.323158
H    0.104541   -4.029266   -0.903089
H    0.314306   -4.253056   -2.666733
H    1.584473   -3.470059   -1.686971
C   -1.966645    2.490545    2.692278
H   -2.525122    3.420472    2.560494
H   -2.265851    2.024284    3.641885
H   -0.895042    2.708923    2.707269
1 imaginary frequency
E = -1420.864933
G = -1420.475086
E_D3 = -1632.567635
```

TS6'-βOMe

```
O   -0.076734    0.527773   -1.957443
C   -0.646312    1.053410   -0.810317
C    0.314072    1.347844    0.332528
C    1.491557    0.370229    0.267796
C    2.219015    0.419874   -1.084280
C    1.287494    0.894503   -2.210640
C   -1.807805    1.927938   -1.083283
O   -2.276008    2.509823    0.047161
C   -3.418174    3.364547   -0.127257
O   -0.340339    1.140144    1.596467
C   -0.365084    2.177371    2.478612
C   -1.116531    1.776830    3.721840
O    2.398362    0.710368    1.328881
C    2.859913   -0.293328    2.121991
O    2.536996   -1.455417    2.001586
O    2.661249   -0.907253   -1.438962
C    3.934448   -1.258980   -1.108772
C    4.192023   -2.698259   -1.465650
O    1.448907    2.271134   -2.324505
O    0.144940    3.255925    2.280014
C    3.828225    0.247909    3.139010
O    4.726543   -0.507038   -0.585458
O   -2.335019    2.059999   -2.175273
Sn  -2.107895   -1.965582    0.010888
C   -3.402264   -2.454618   -1.639846
C   -0.468744   -3.358856    0.106682
C   -3.219840   -1.987171    1.855464
H    1.122505   -0.644454    0.429663
H    3.081618    1.084801   -1.024149
H    1.524363    0.372455   -3.145180
H    0.669882    2.381924    0.299235
H    3.684809   -3.339982   -0.735392
H    3.790557   -2.937393   -2.454493
H    5.264092   -2.898116   -1.432494
H    3.429282    1.148162    3.615842
H    4.041940   -0.516527    3.887580
H    4.758848    0.527616    2.631894
H   -2.158656    1.553406    3.468417
H   -0.683340    0.869093    4.154772
H   -1.081750    2.588174    4.450346
H   -3.645807    3.753588    0.866155
H   -3.187740    4.187602   -0.809608
H   -4.269573    2.800815   -0.519009
H   -1.394721   -0.256558   -0.288928
```

H	-3.676271	-2.971639	2.012430
H	-2.565674	-1.773665	2.707381
H	-4.019328	-1.238783	1.840400
H	-3.844519	-3.448275	-1.500264
H	-4.215934	-1.727324	-1.730547
H	-2.842197	-2.457061	-2.580724
H	-0.846110	-4.382068	0.220985
H	0.126003	-3.315012	-0.811977
H	0.192578	-3.140219	0.951379
C	0.819751	2.839915	-3.479645
H	1.040840	3.909178	-3.451800
H	1.240197	2.407694	-4.398636
H	-0.262780	2.683067	-3.462828

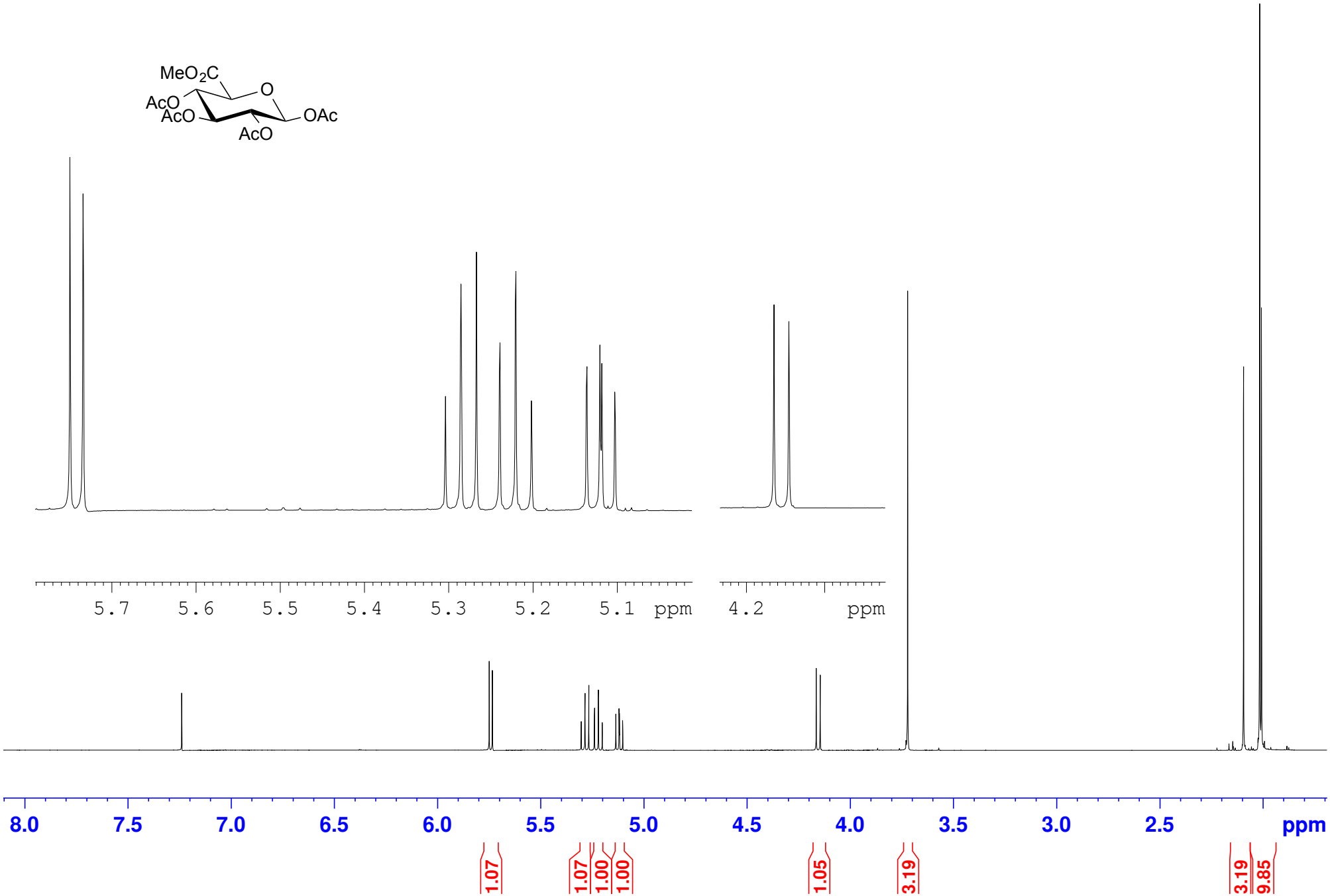
1 imaginary frequency

E = -1420.867362

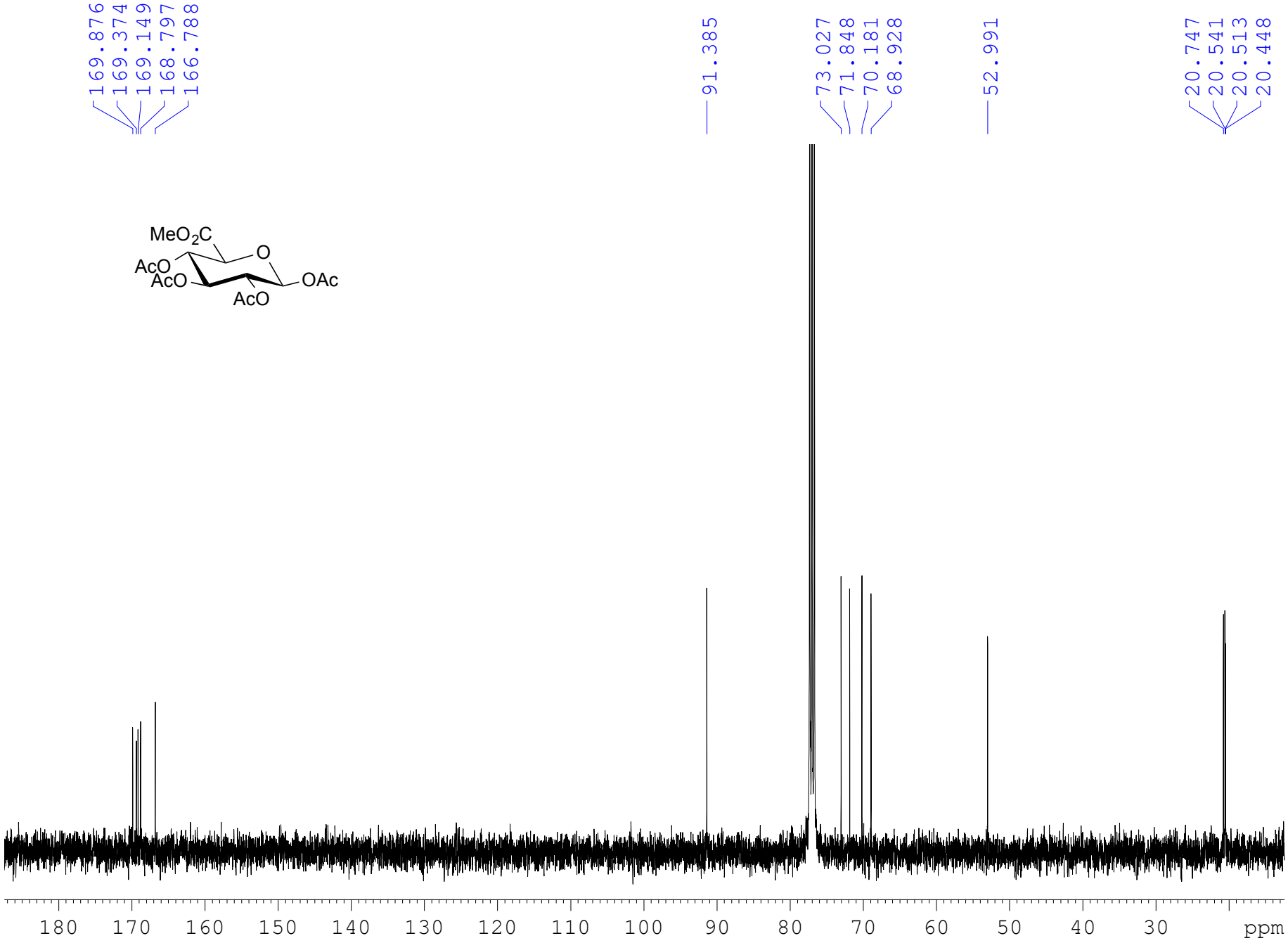
G = -1420.476481

E_{D3} = -1632.570469

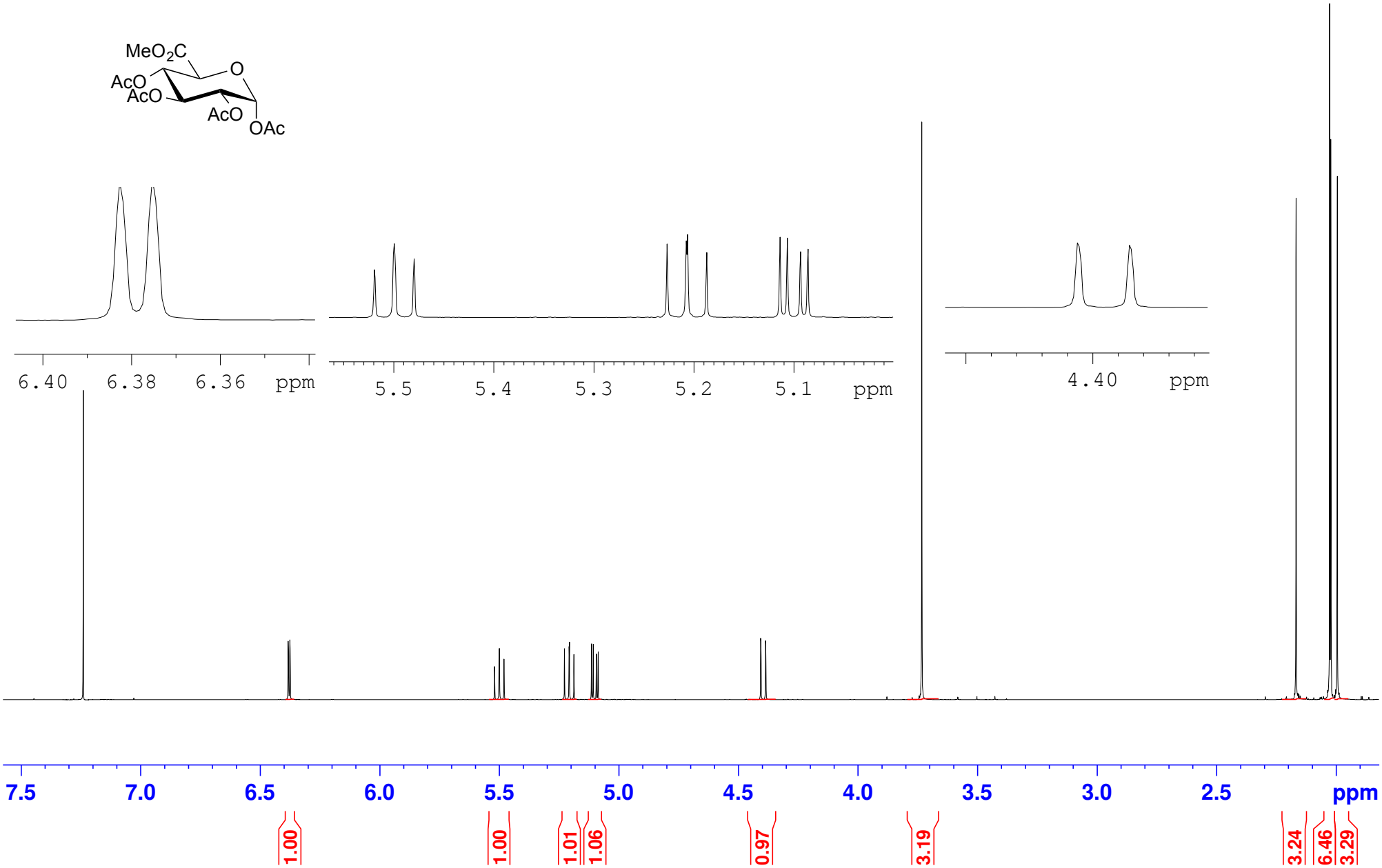
[1]H NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranuronate **(3)**



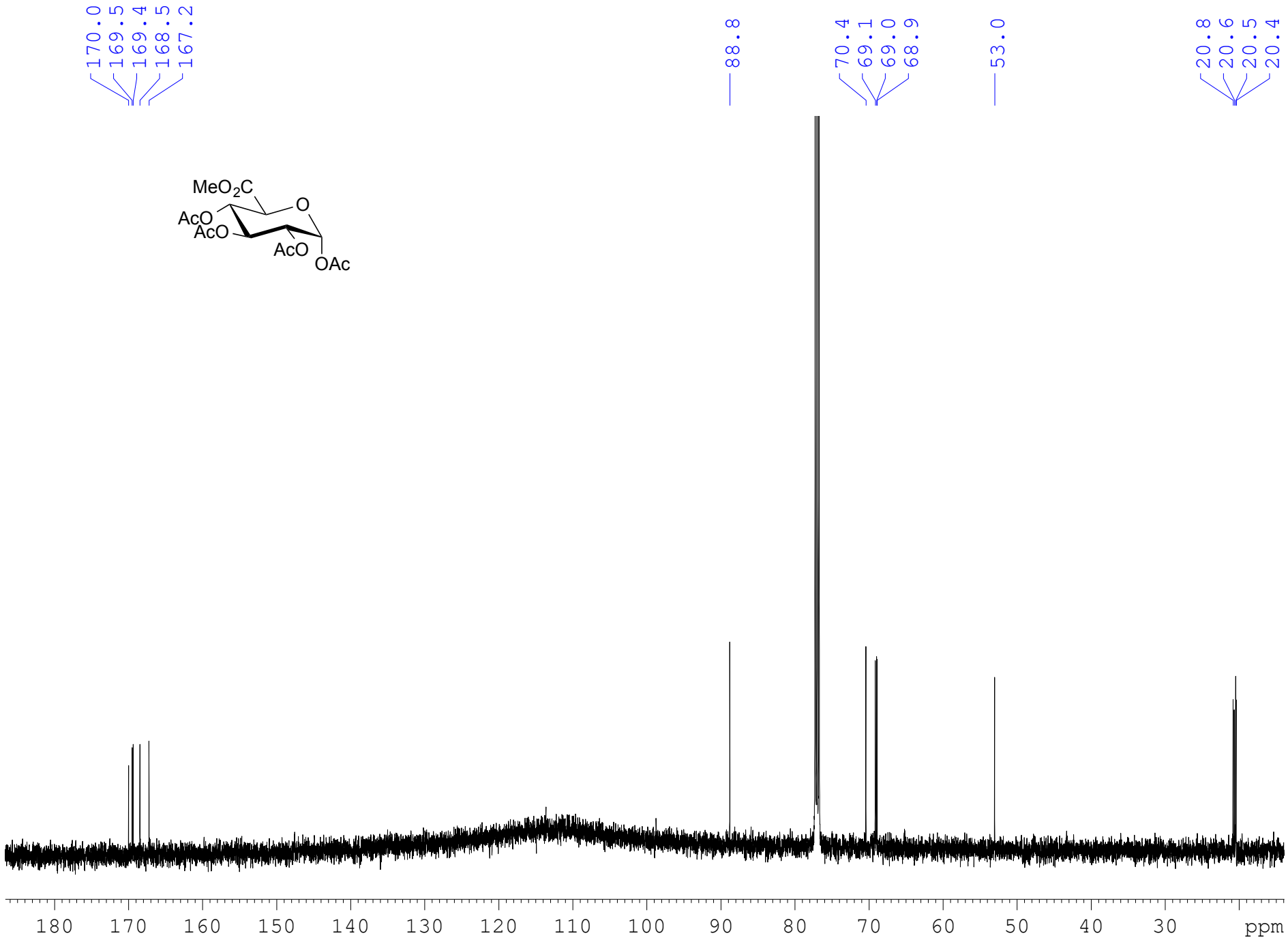
^{13}C NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranuronate **(3)**



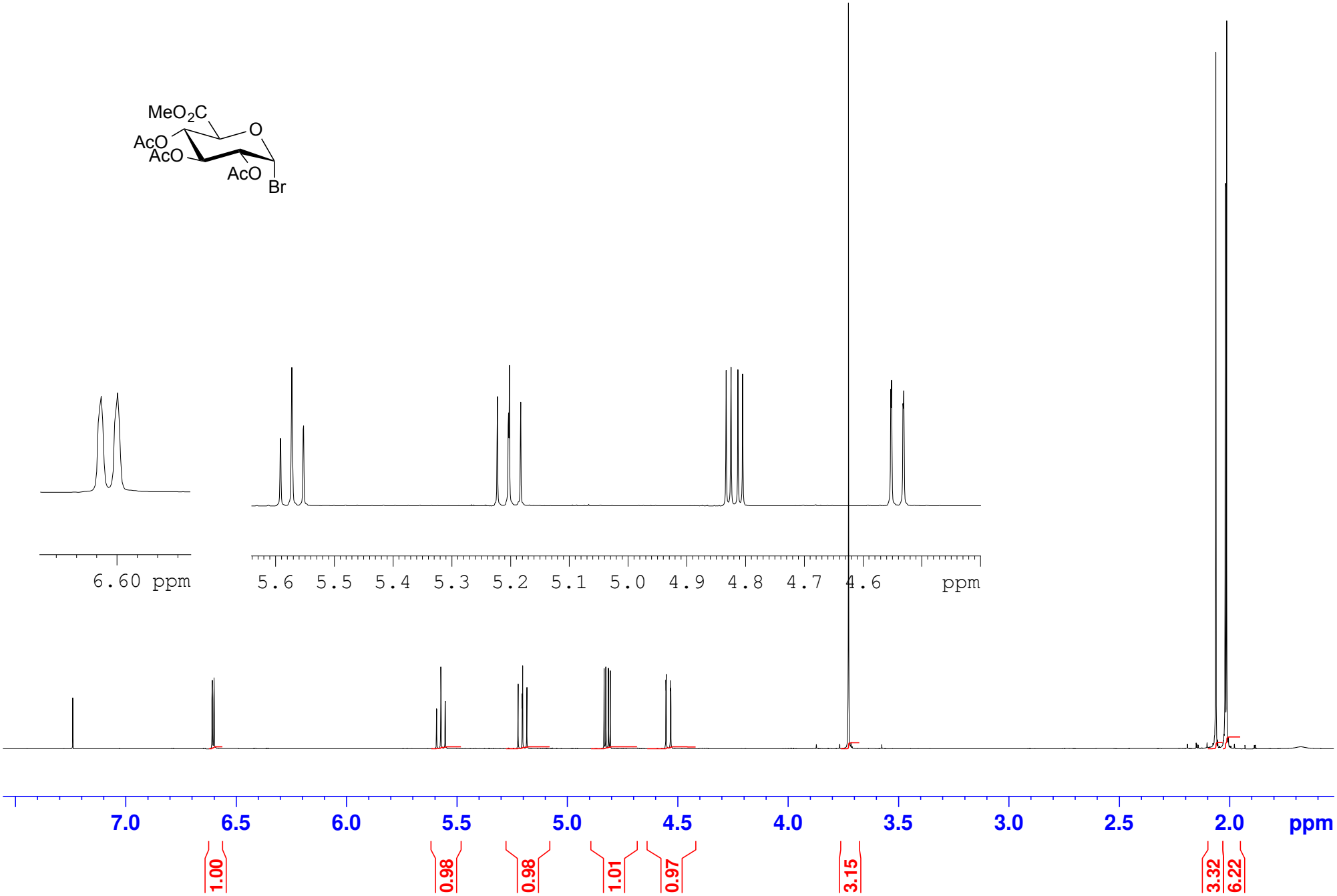
^{1}H NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-α-D-glucopyranuronate **(6)**



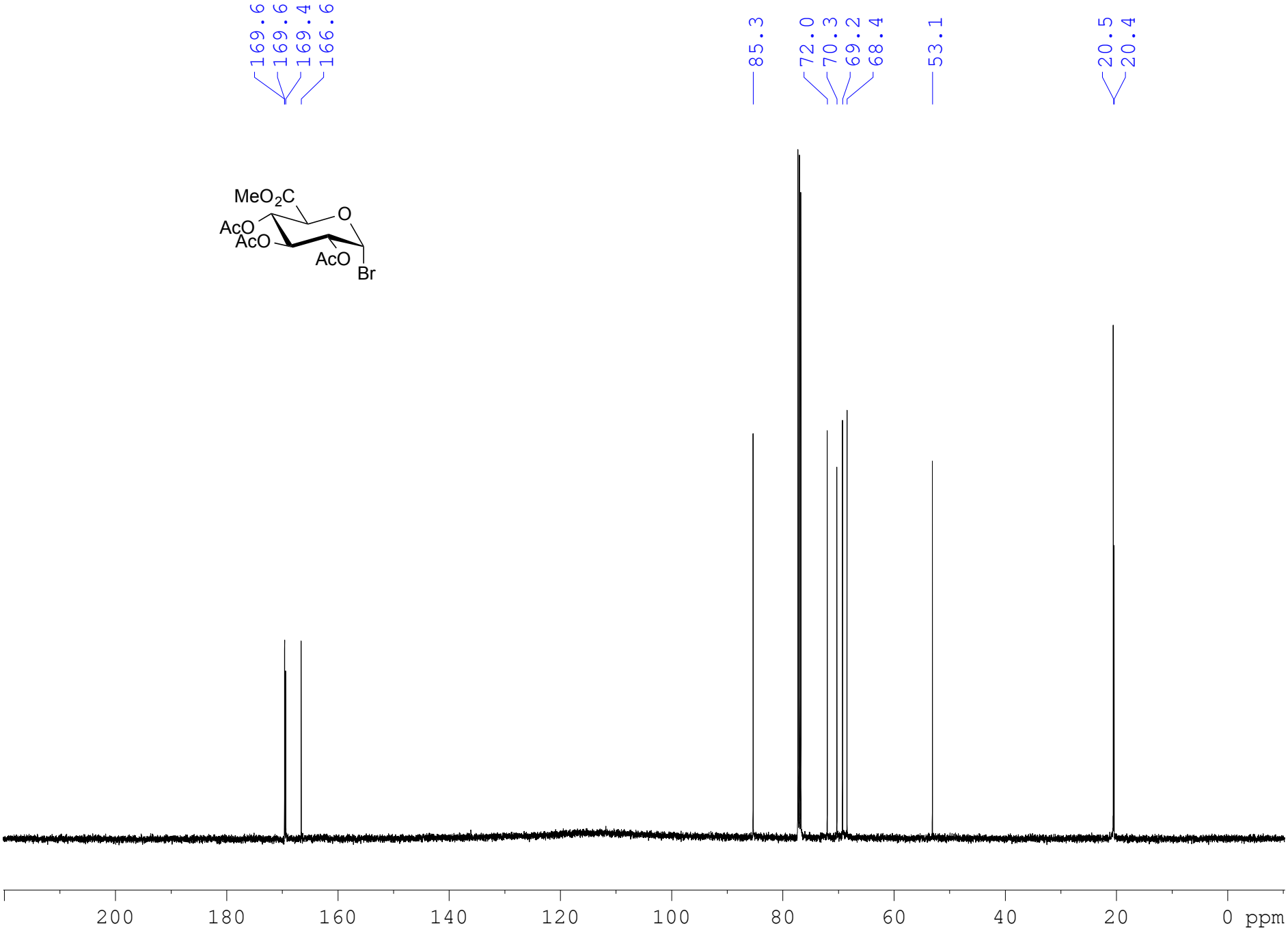
^{13}C NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-α-D-glucopyranuronate **(6)**



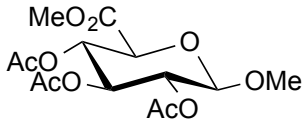
[1]H NMR Spectrum of Methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl bromide) uronate **(14)**

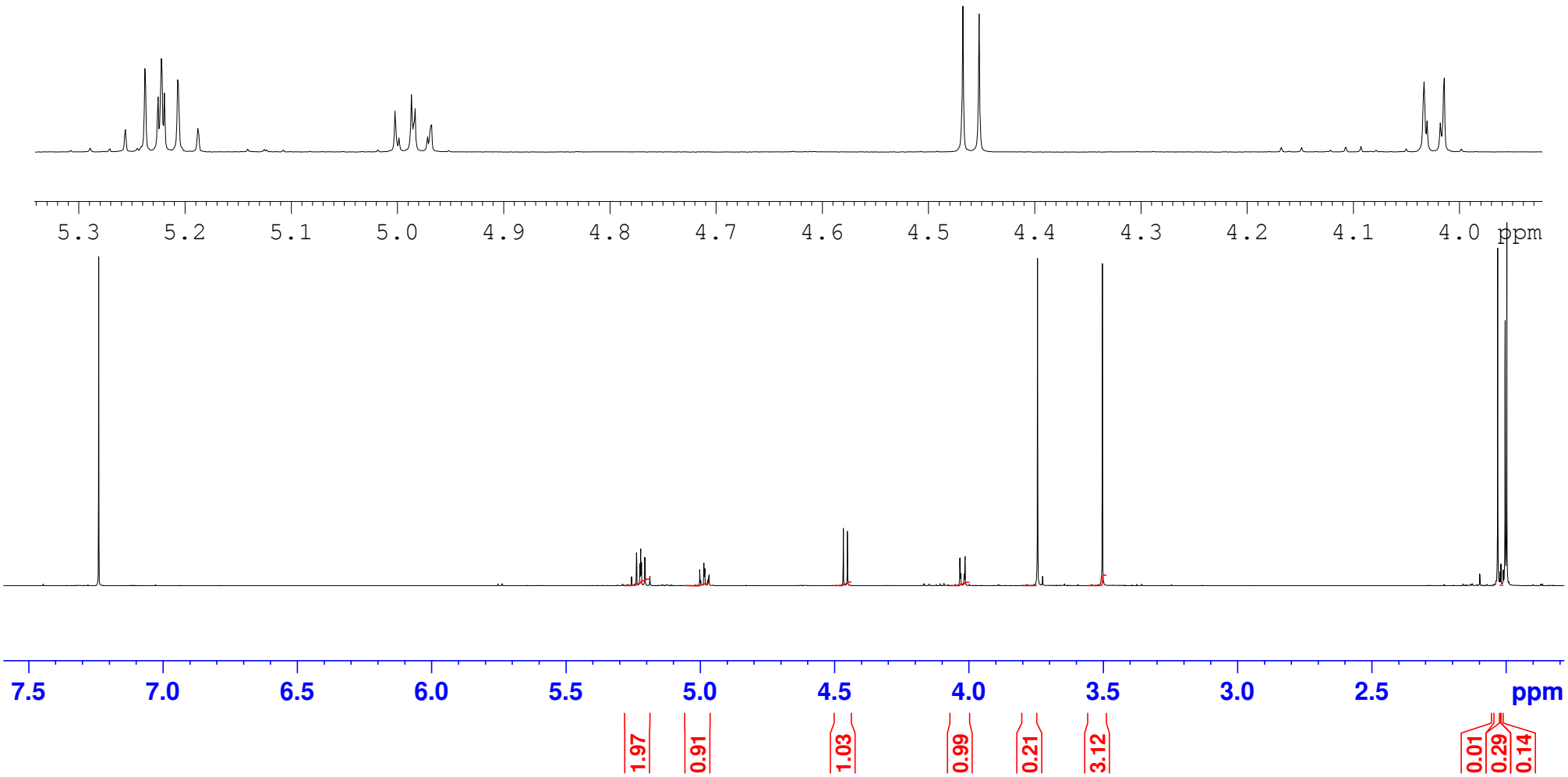


^{13}C NMR Spectrum of Methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl bromide) uronate **(14)**

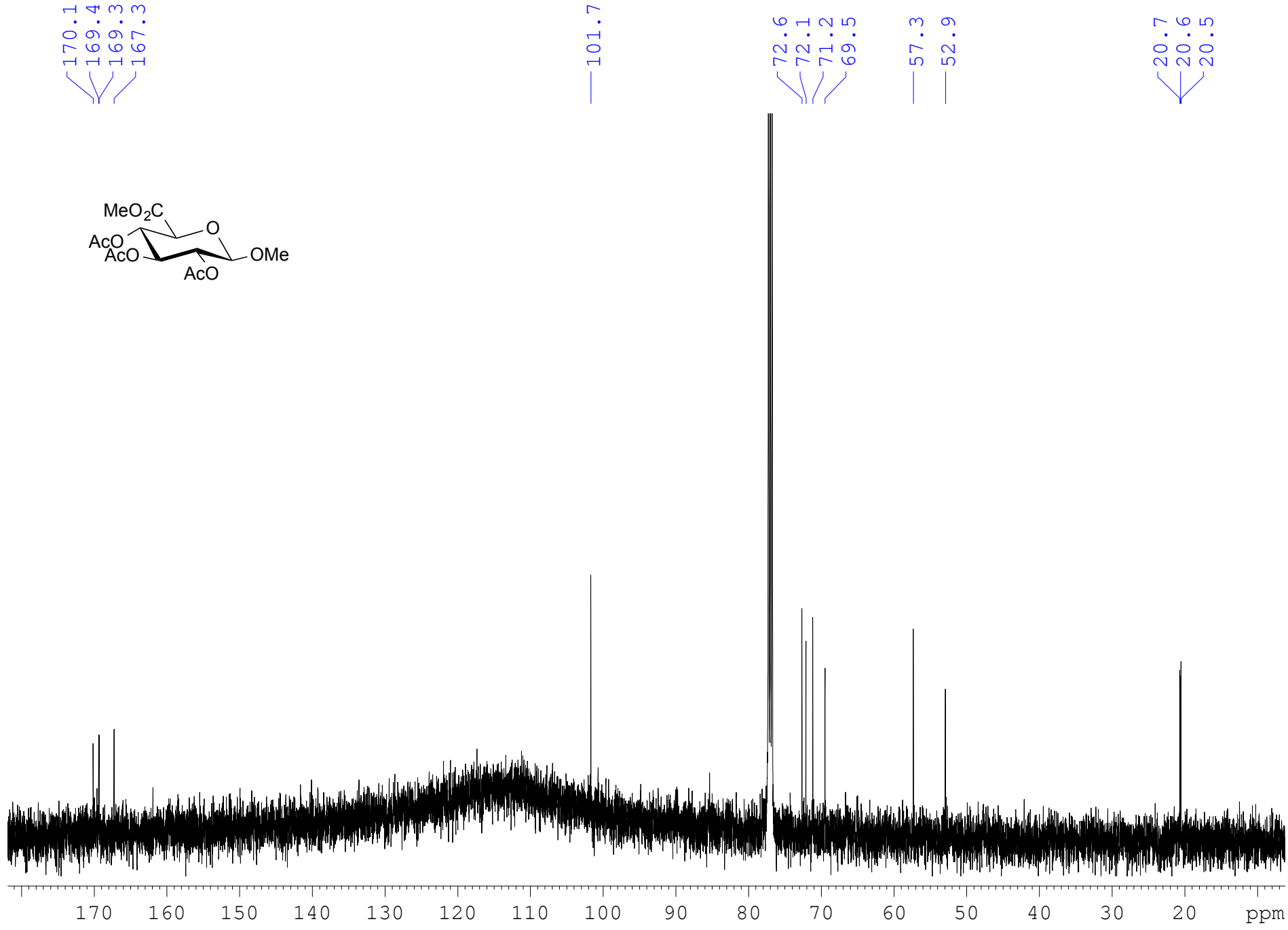


[1]H NMR Spectrum of Methyl (methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosid) uronate **(9)**

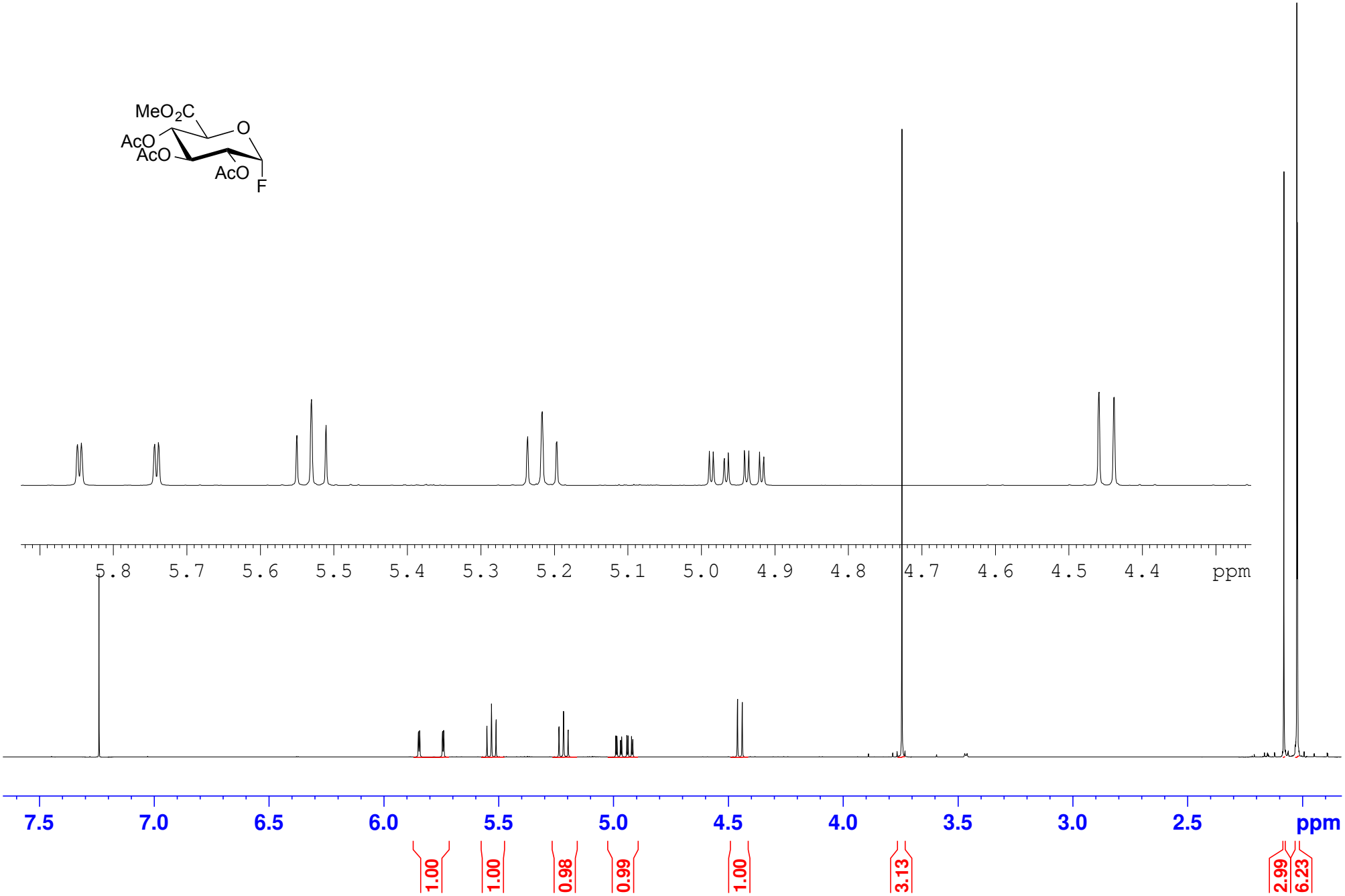




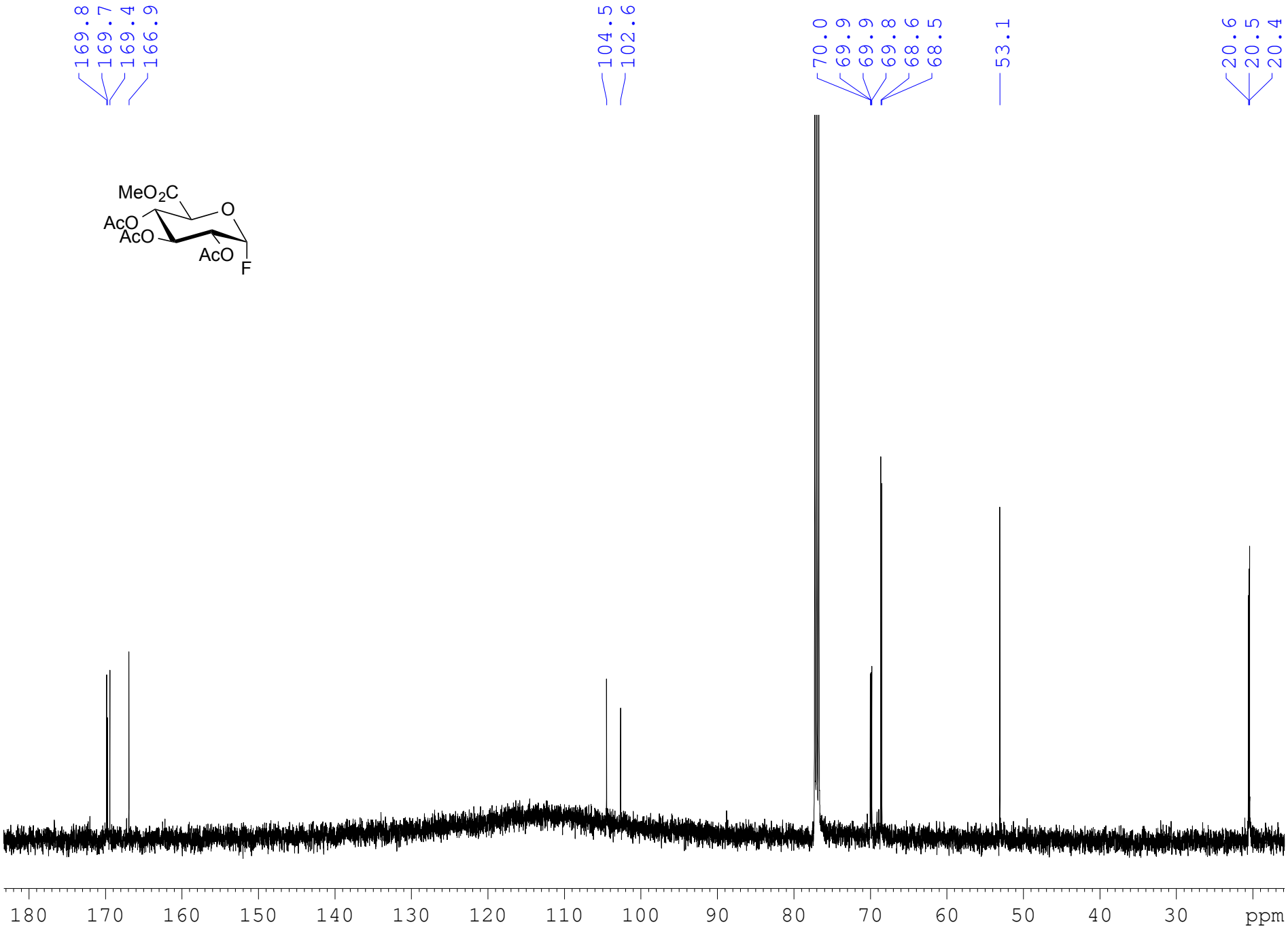
^{13} C NMR Spectrum of Methyl (methyl 2,3,4-tri-*O*-acetyl-β-D-glucopyranosid) uronate **(9)**



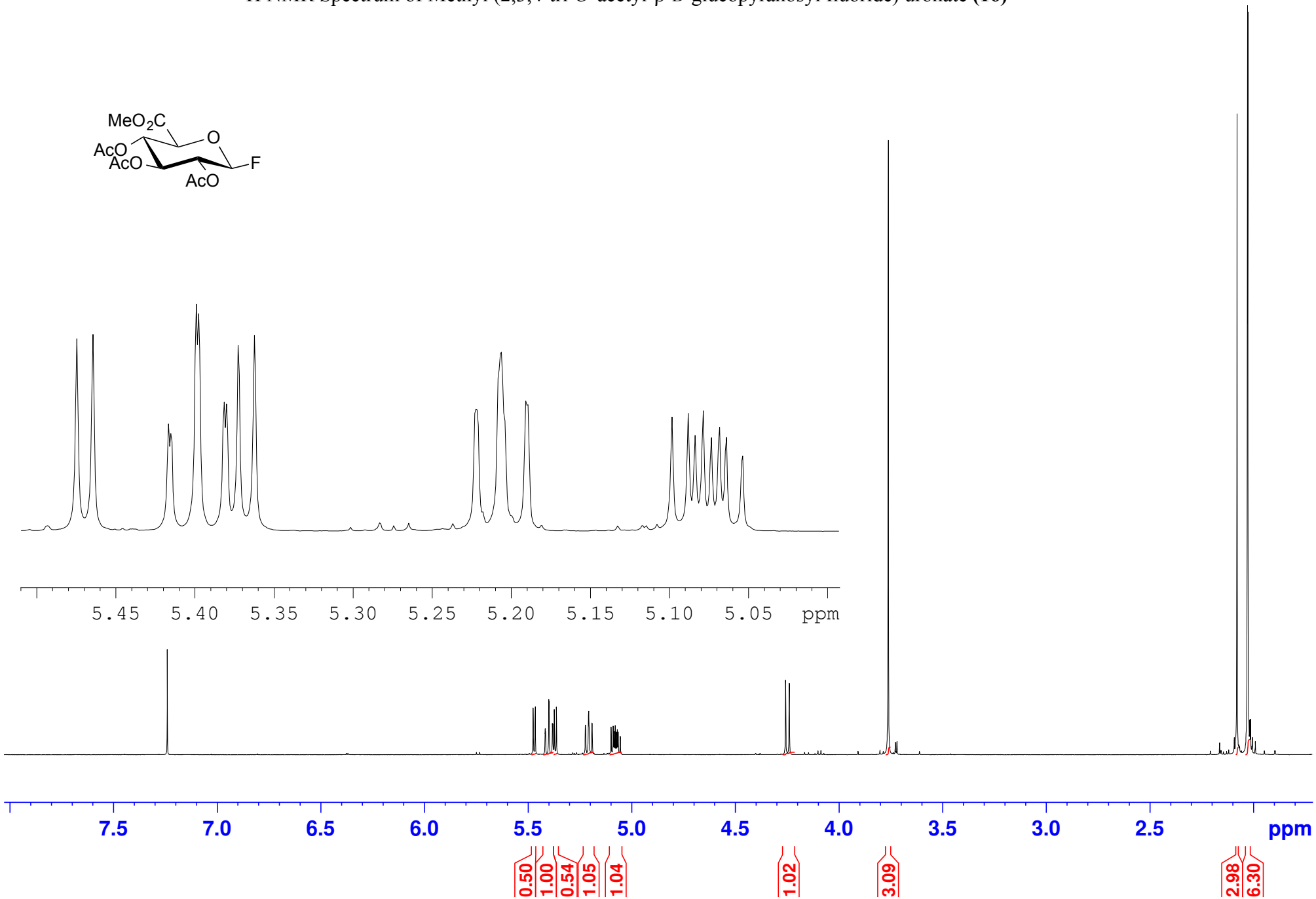
[1]H NMR Spectrum of Methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl fluoride) uronate **(15)**



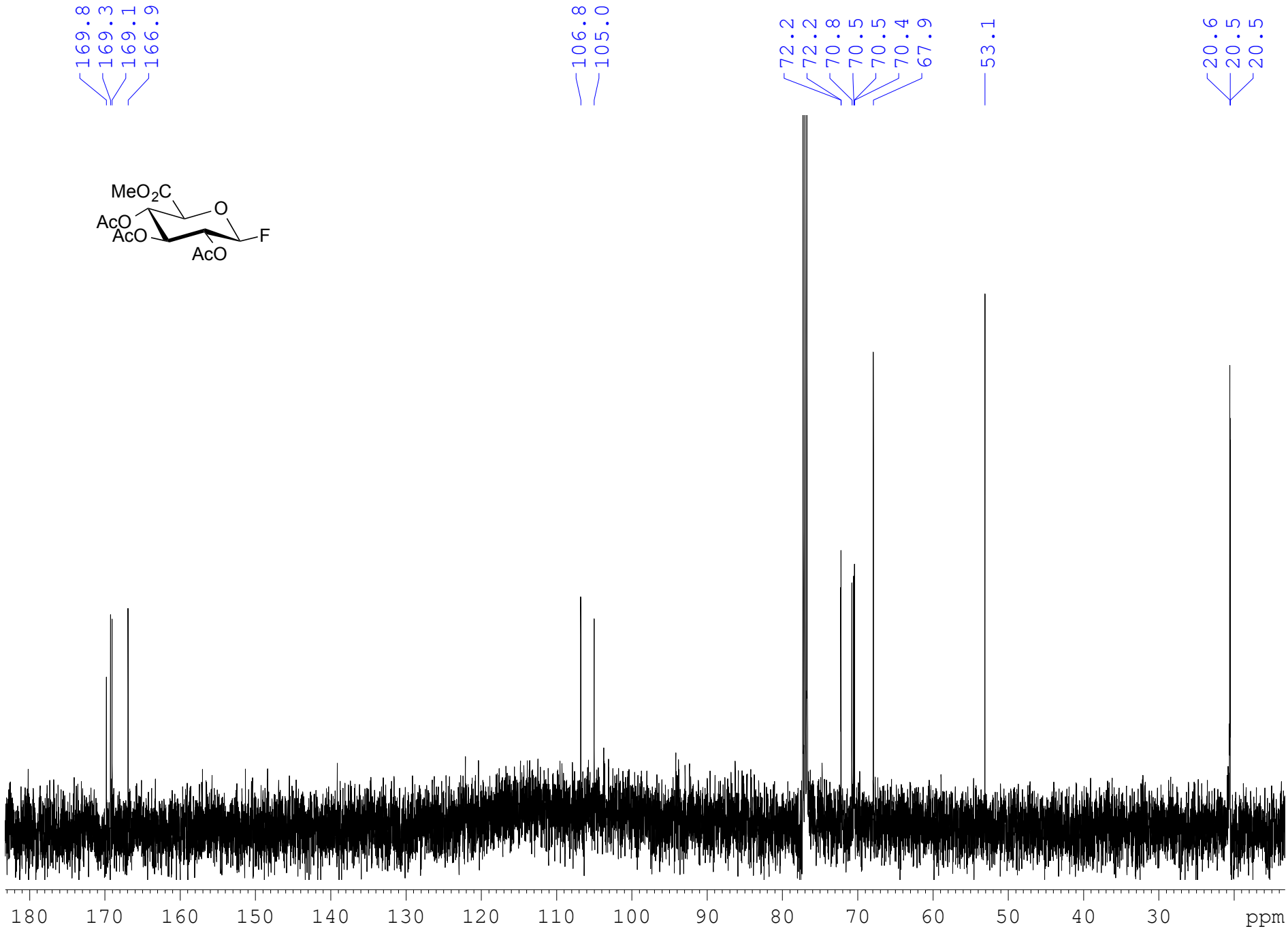
^{13}C NMR Spectrum of Methyl (2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl fluoride) uronate **(15)**



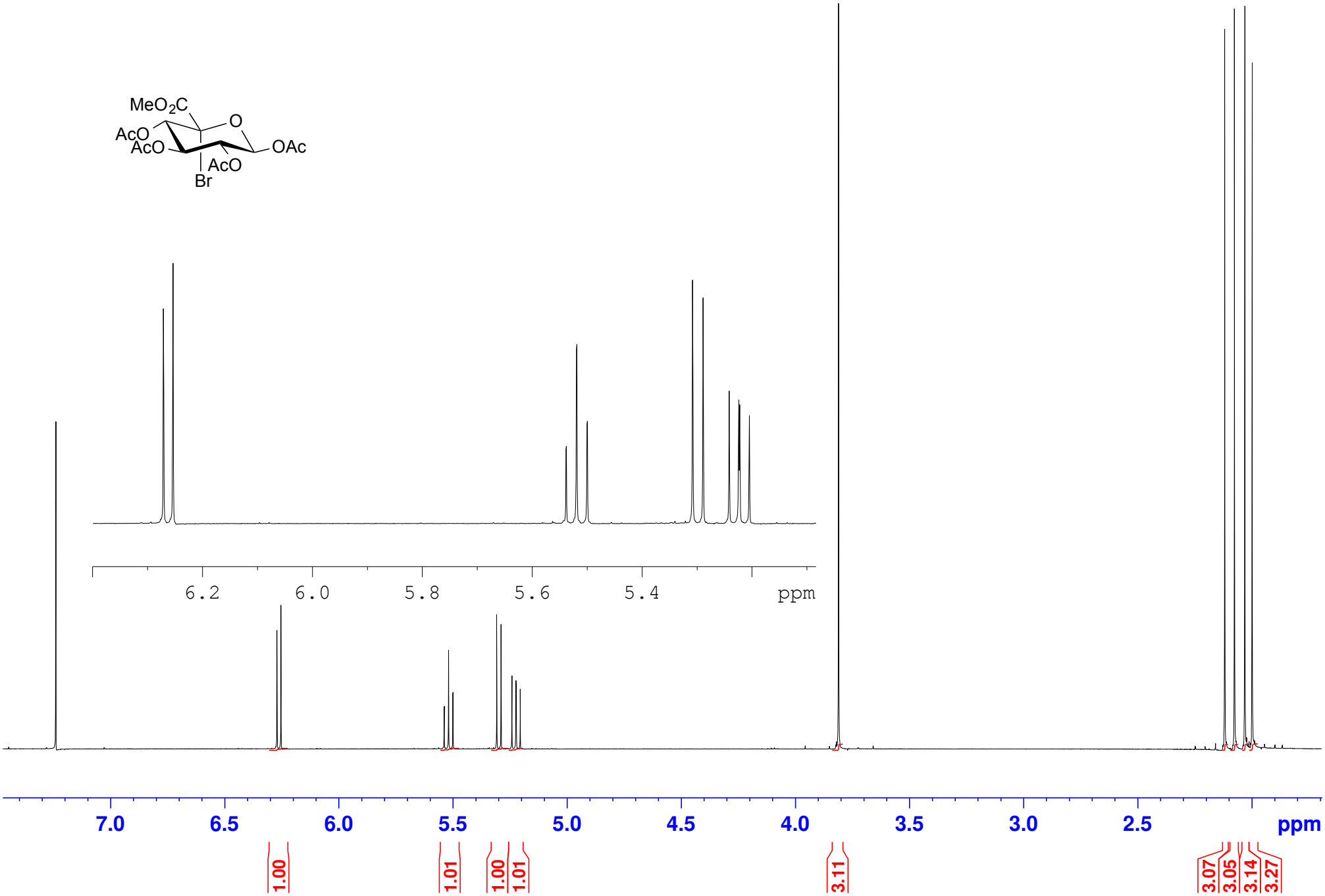
[1]H NMR Spectrum of Methyl (2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl fluoride) uronate **(16)**



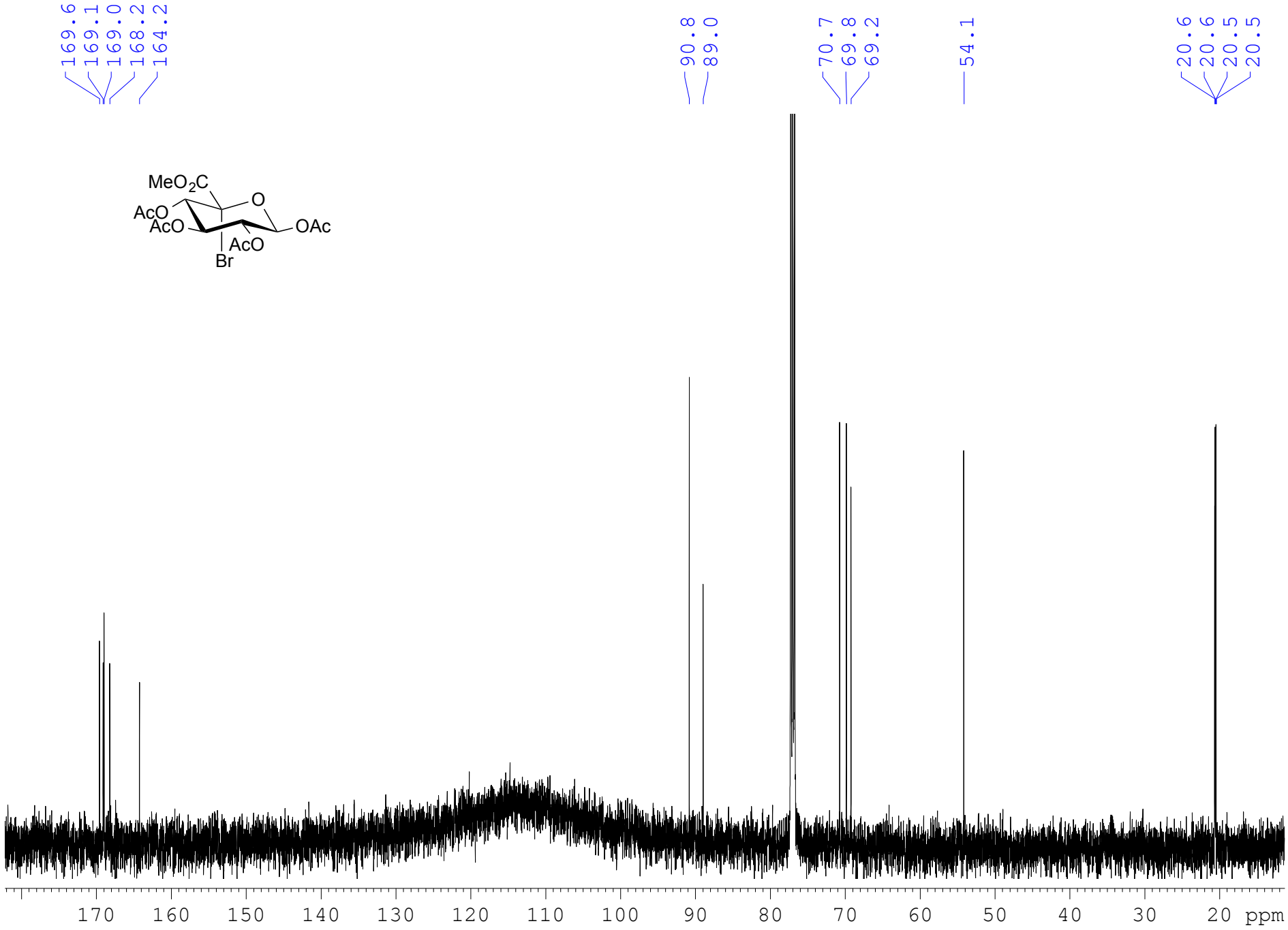
^{13}C NMR Spectrum of Methyl (2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl fluoride) uronate **(16)**



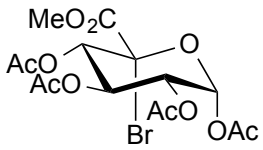
[1]H NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-5-*C*-bromo-β-D-glucopyranosyluronate **(1)**

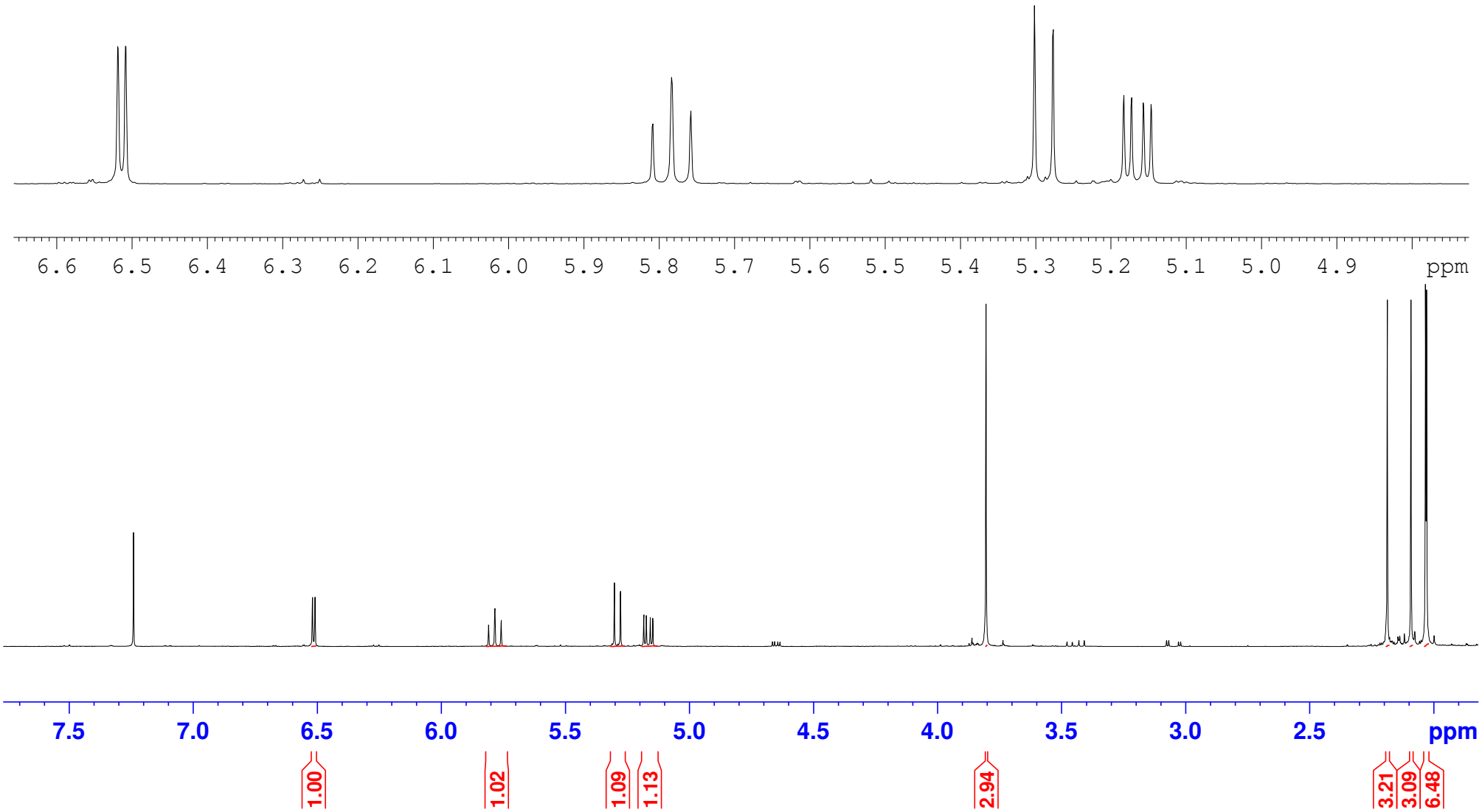


^{13}C NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-5-*C*-bromo-β-D-glucopyranosyluronate **(1)**

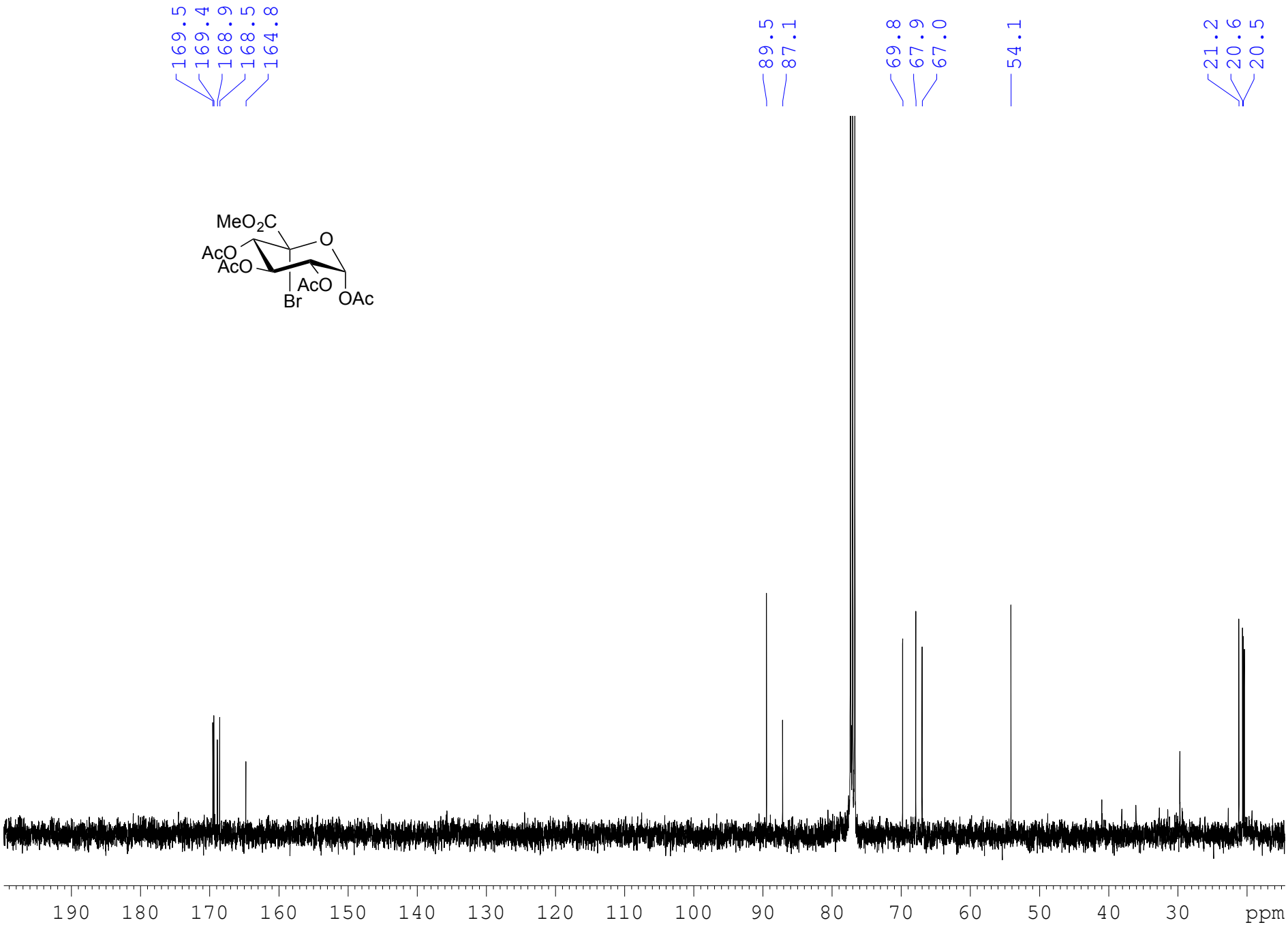


[1] H NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-5-*C*-bromo-α-D-glucopyranosyluronate **(4)**

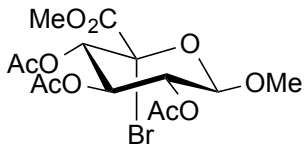


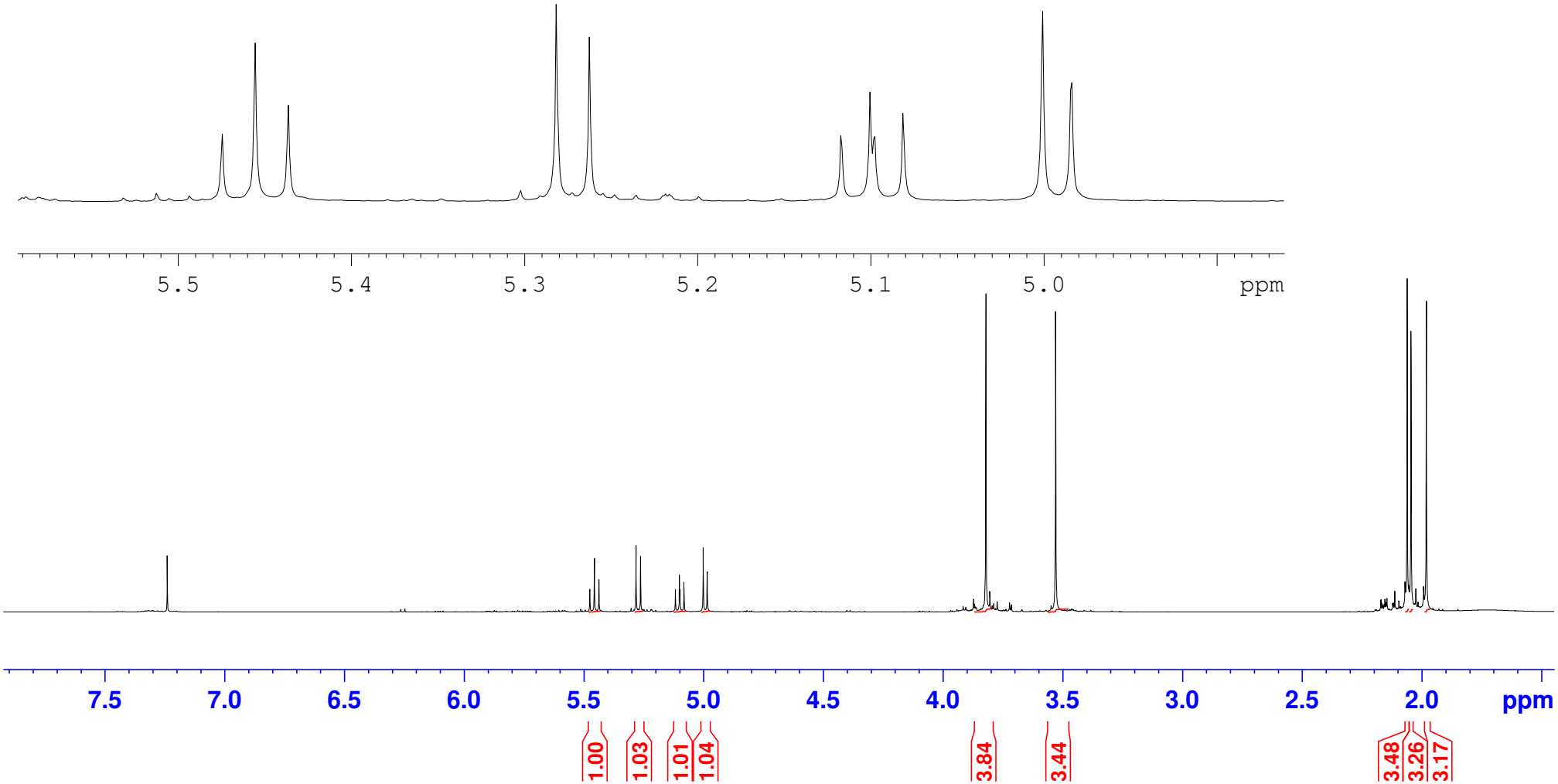


^{13}C NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-5-*C*-bromo-α-D-glucopyranosyluronate **(4)**

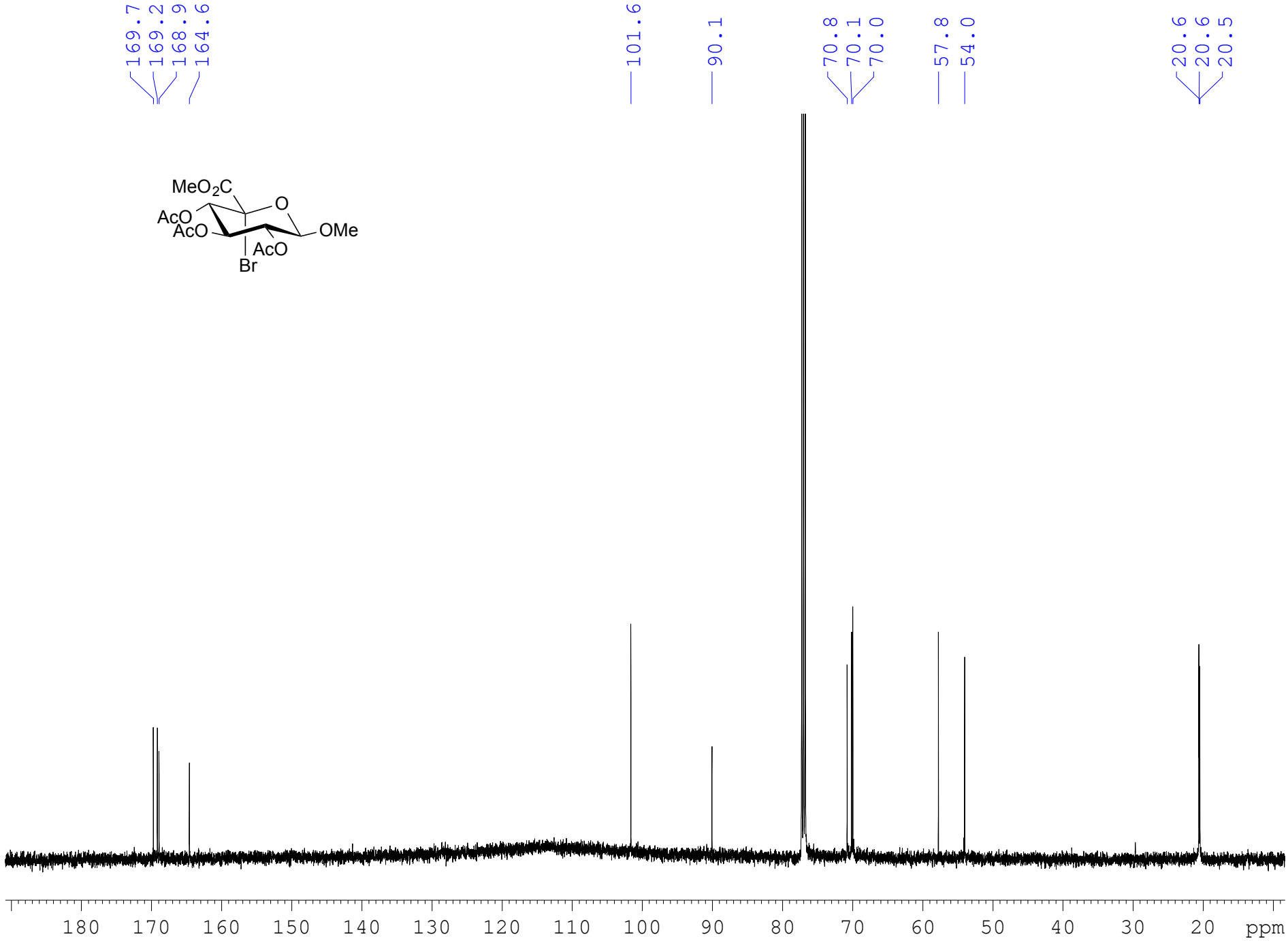


[1]H NMR Spectrum of Methyl (methyl-2,3,4-tri-*O*-acetyl-5-*C*-bromo-β-D-glucopyranosid) uronate **(7)**

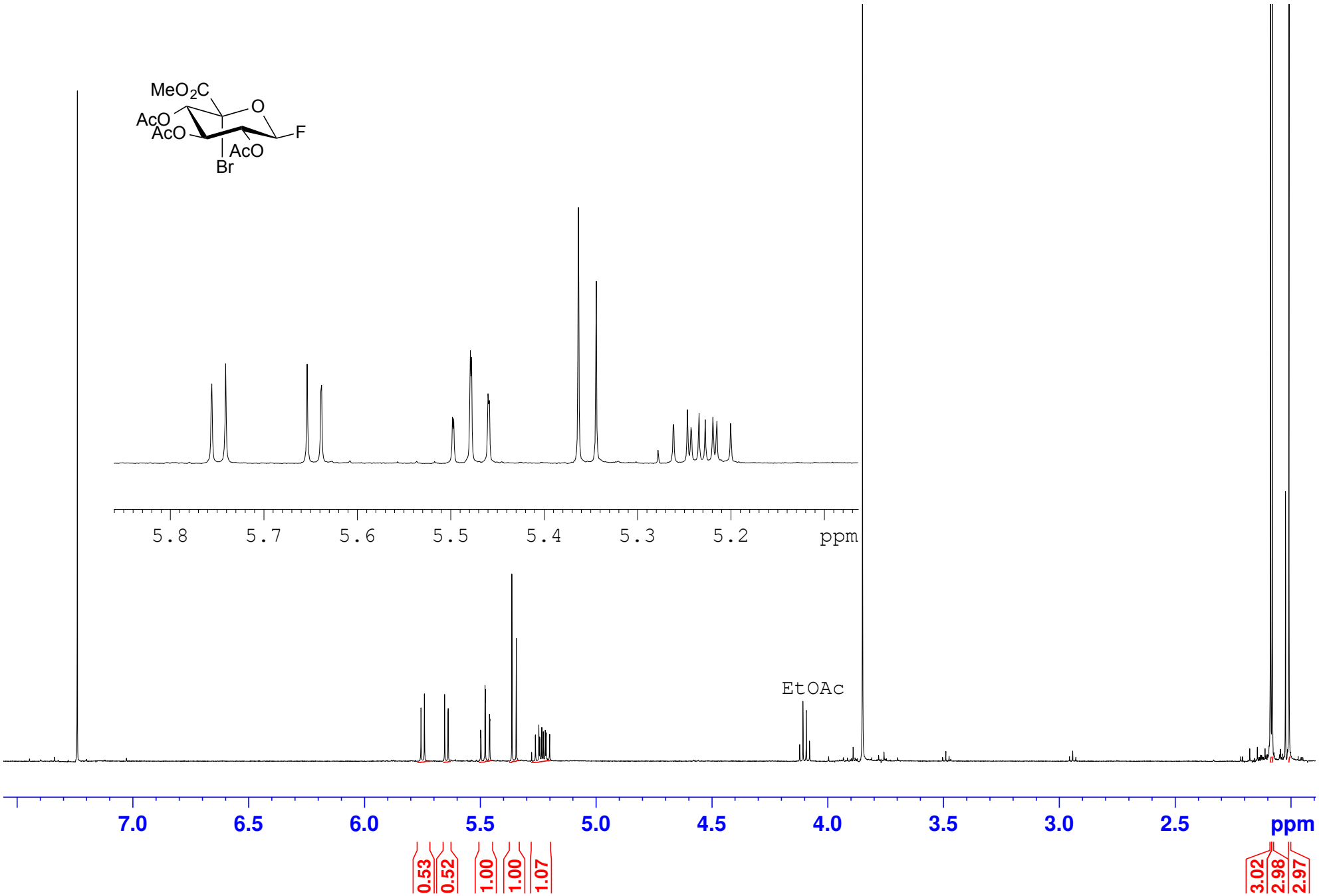




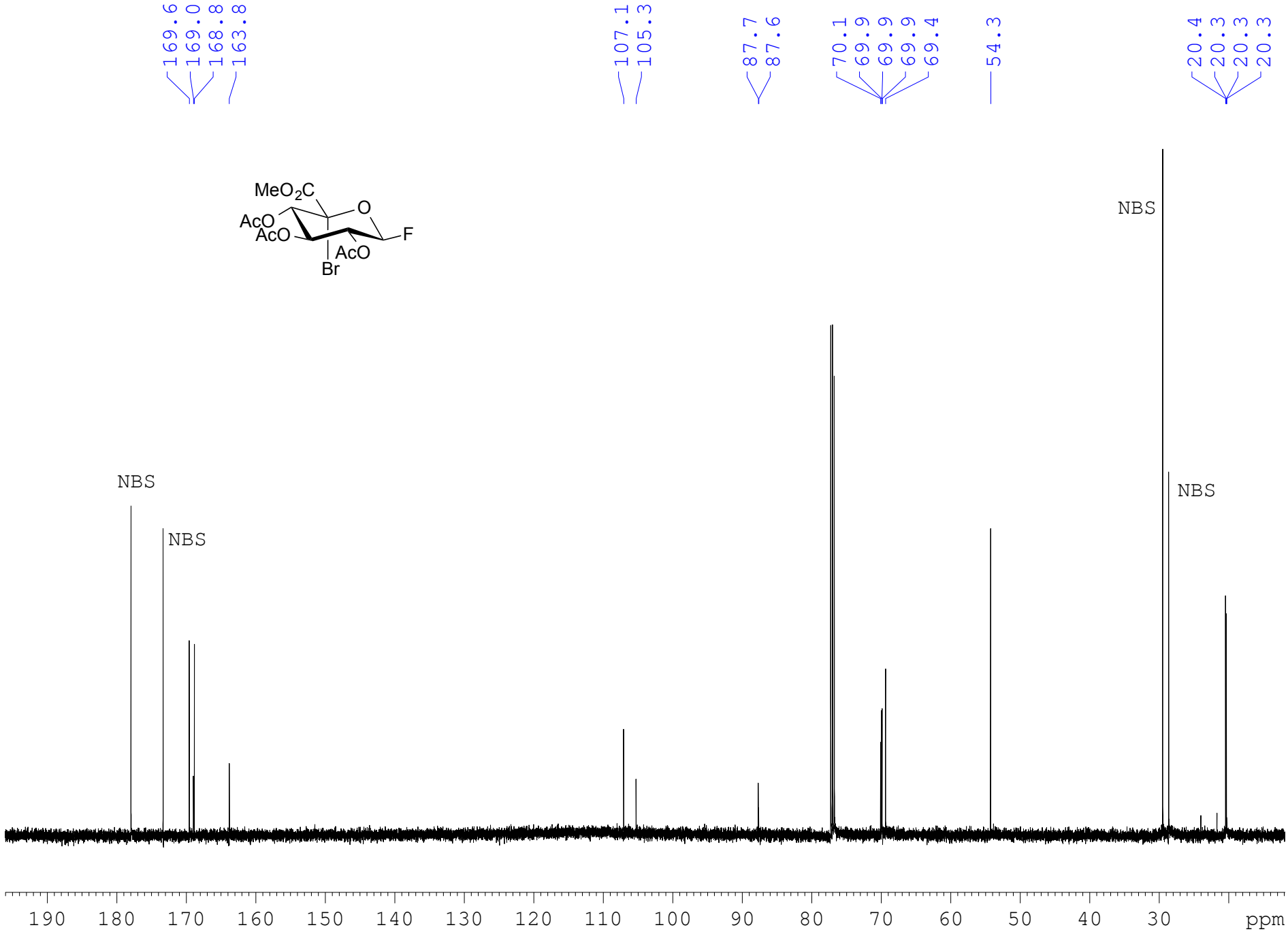
^{13}C NMR Spectrum of Methyl (methyl-2,3,4-tri-*O*-acetyl-5-*C*-bromo-β-D-glucopyranosid) uronate **(7)**



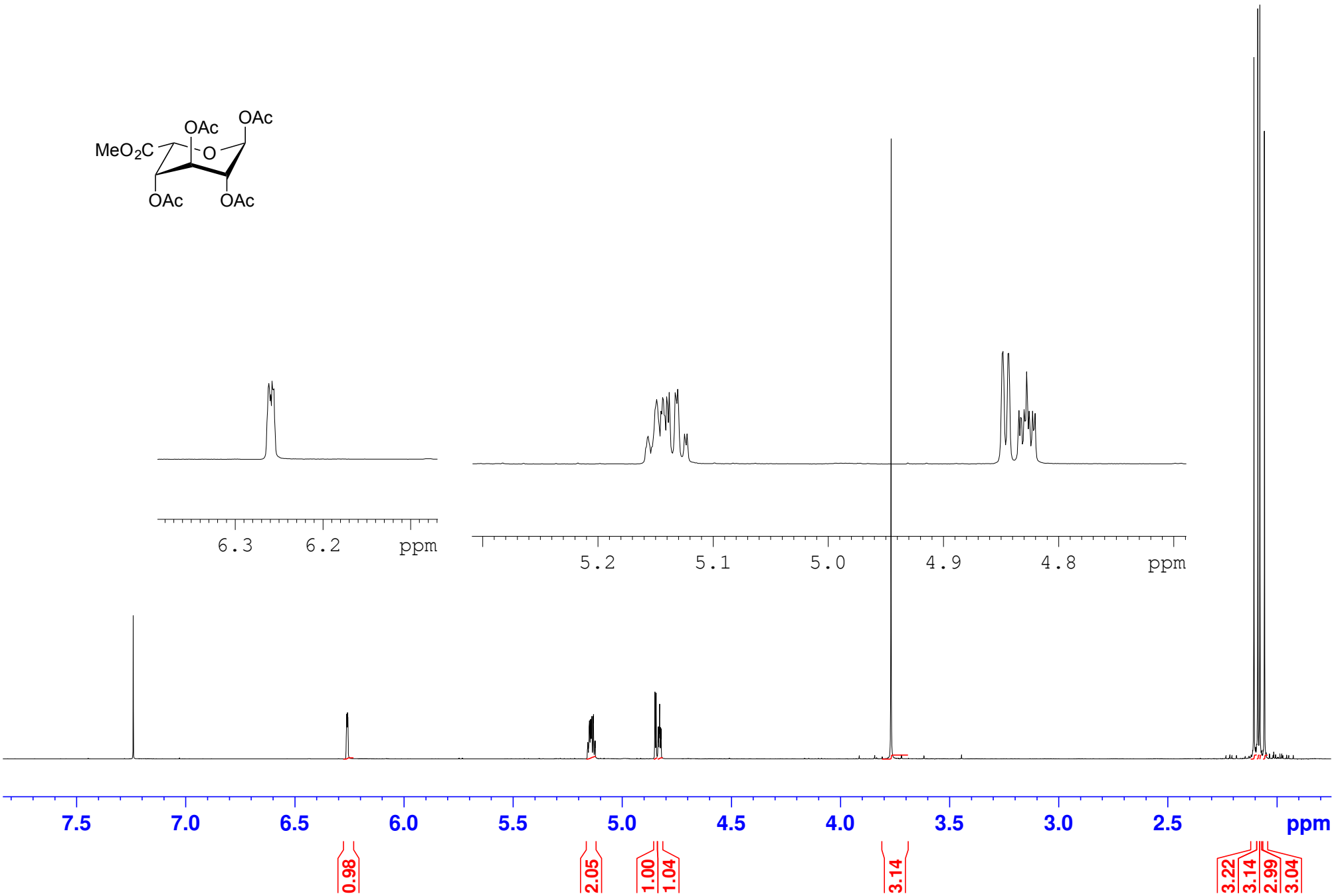
[1] H NMR Spectrum of Methyl (5-bromo-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl fluoride) uronate **(10)**



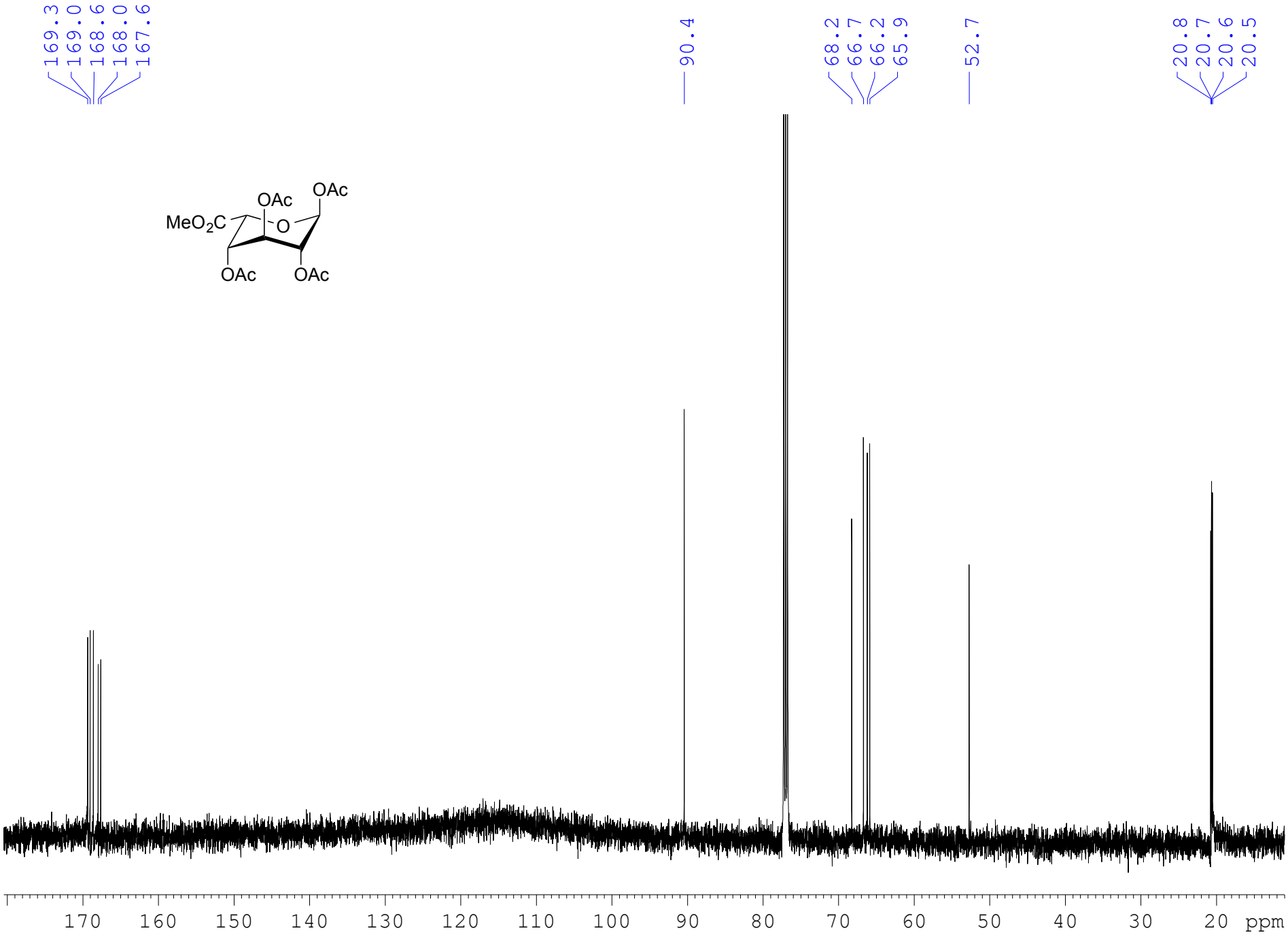
^{13}C NMR Spectrum of Methyl (5-bromo-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl fluoride) uronate **(10)**



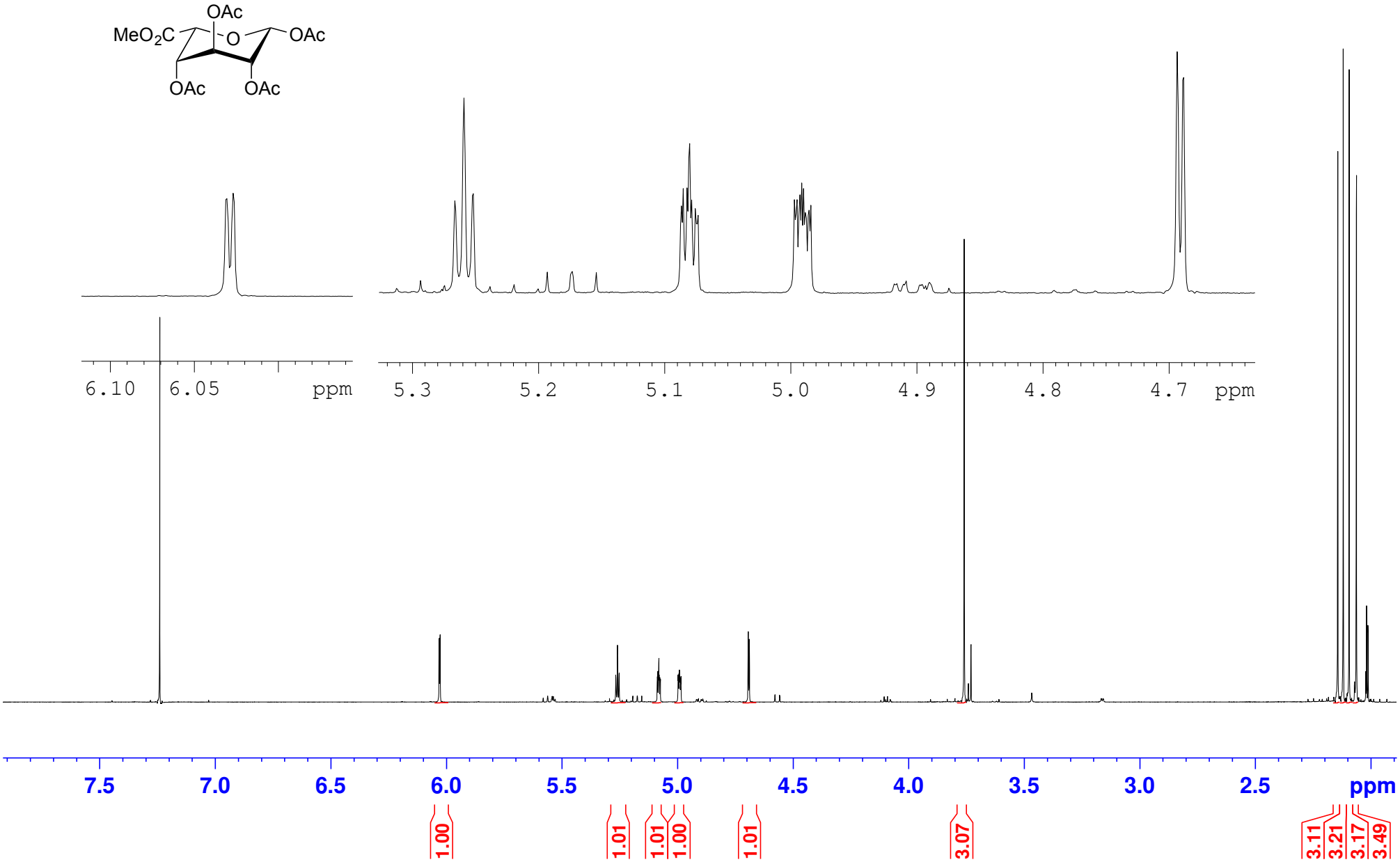
[1]H NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-α-L-idopyranuronate **(2)**



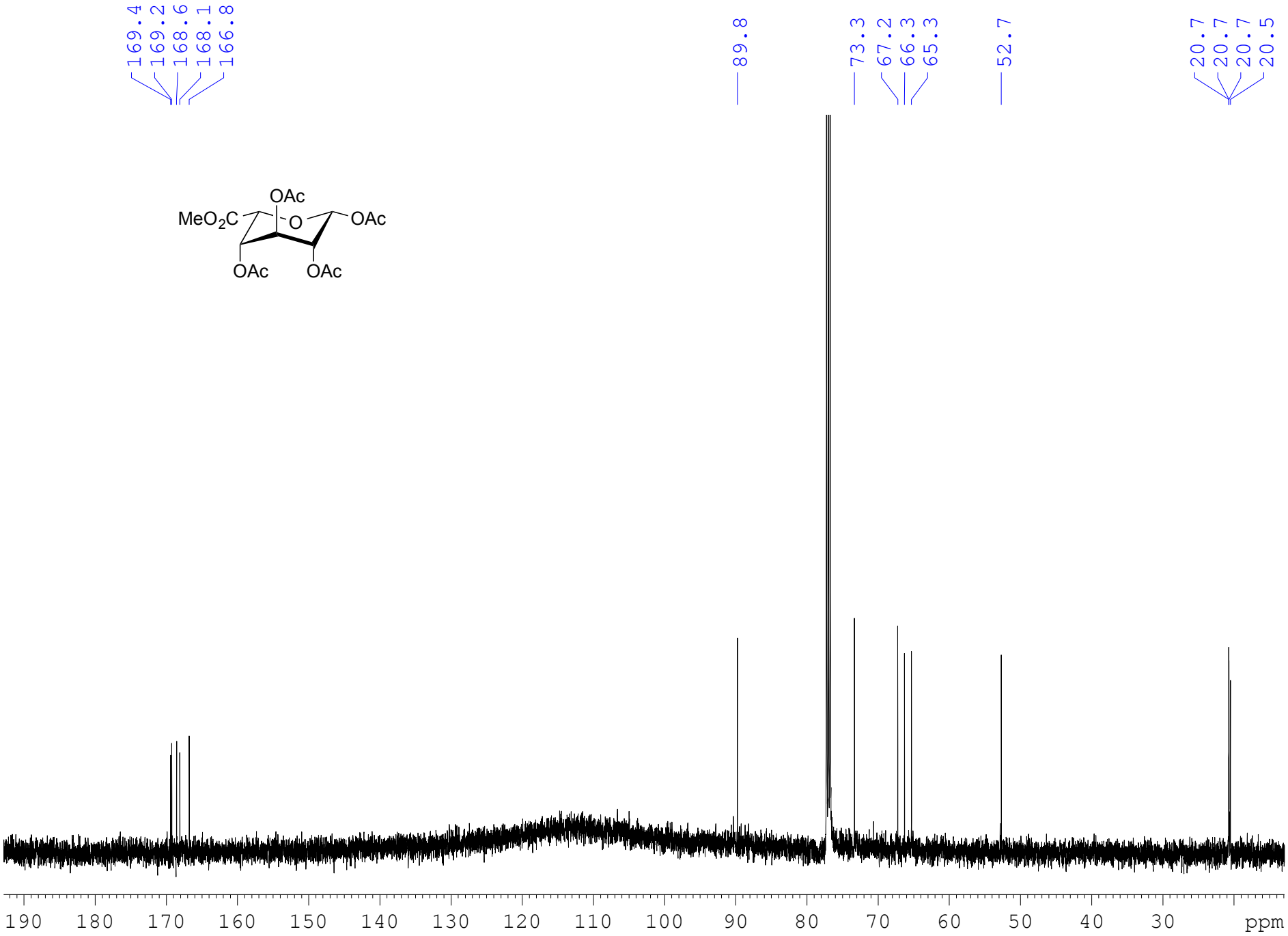
^{13}C NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-α-L-idopyranuronate **(2)**



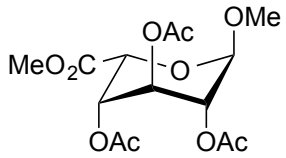
^{1}H NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-β-L-idopyranuronate **(5)**

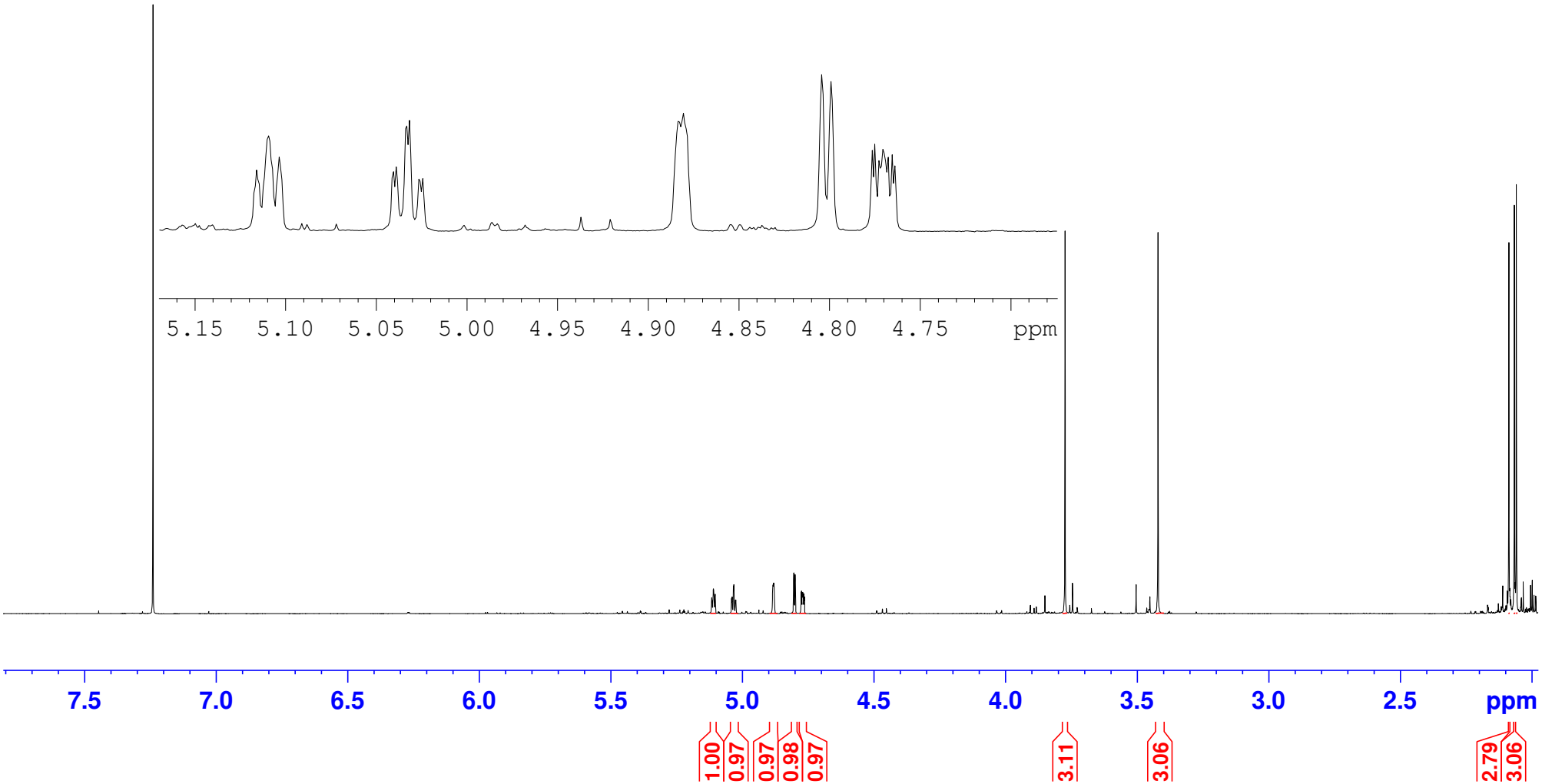


^{13}C NMR Spectrum of Methyl 1,2,3,4-tetra-*O*-acetyl-β-L-idopyranuronate **(5)**

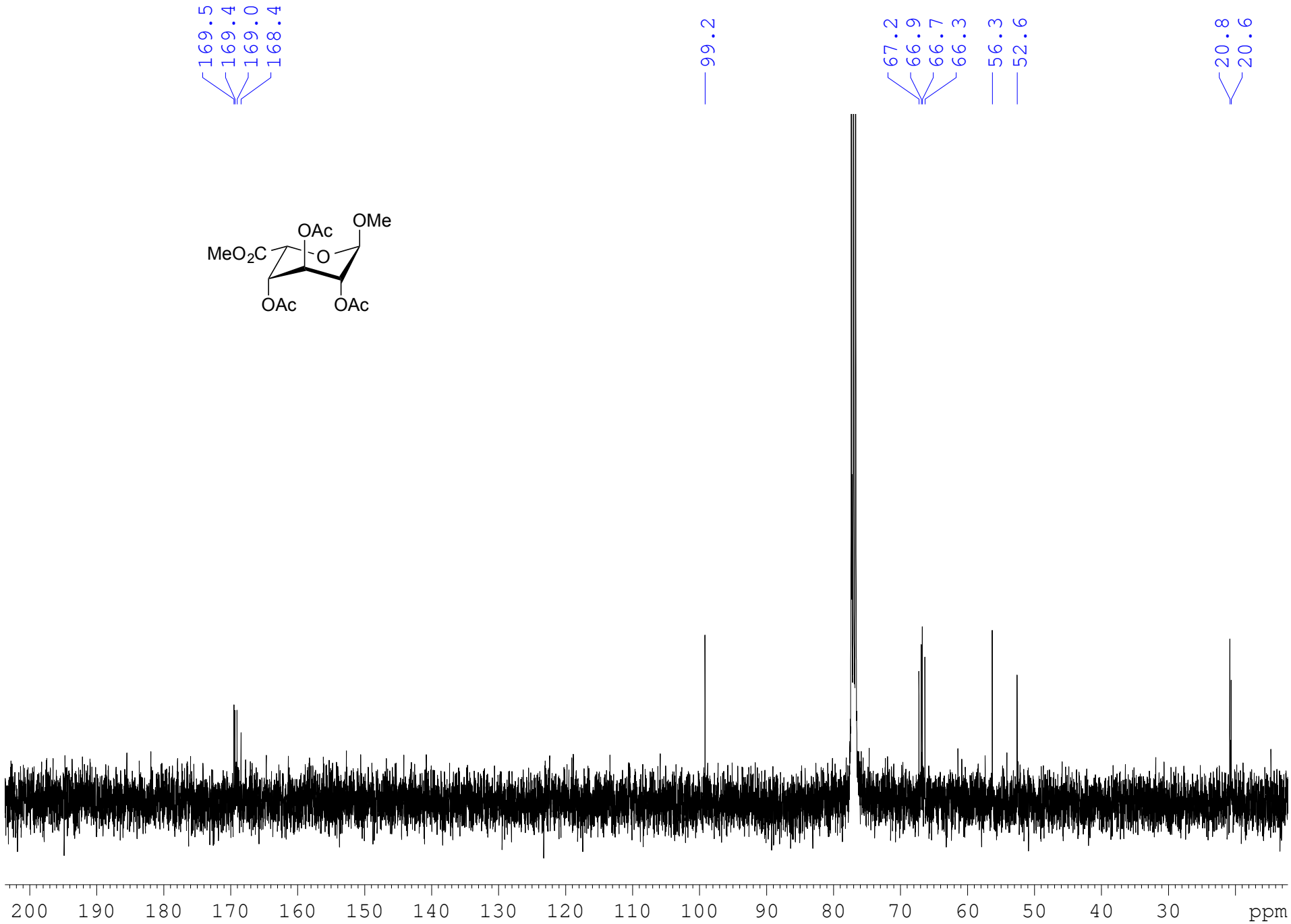


[1]H NMR Spectrum of Methyl (methyl 2,3,4-tri-*O*-acetyl-α-L-idopyranoside) uronate **(8)**

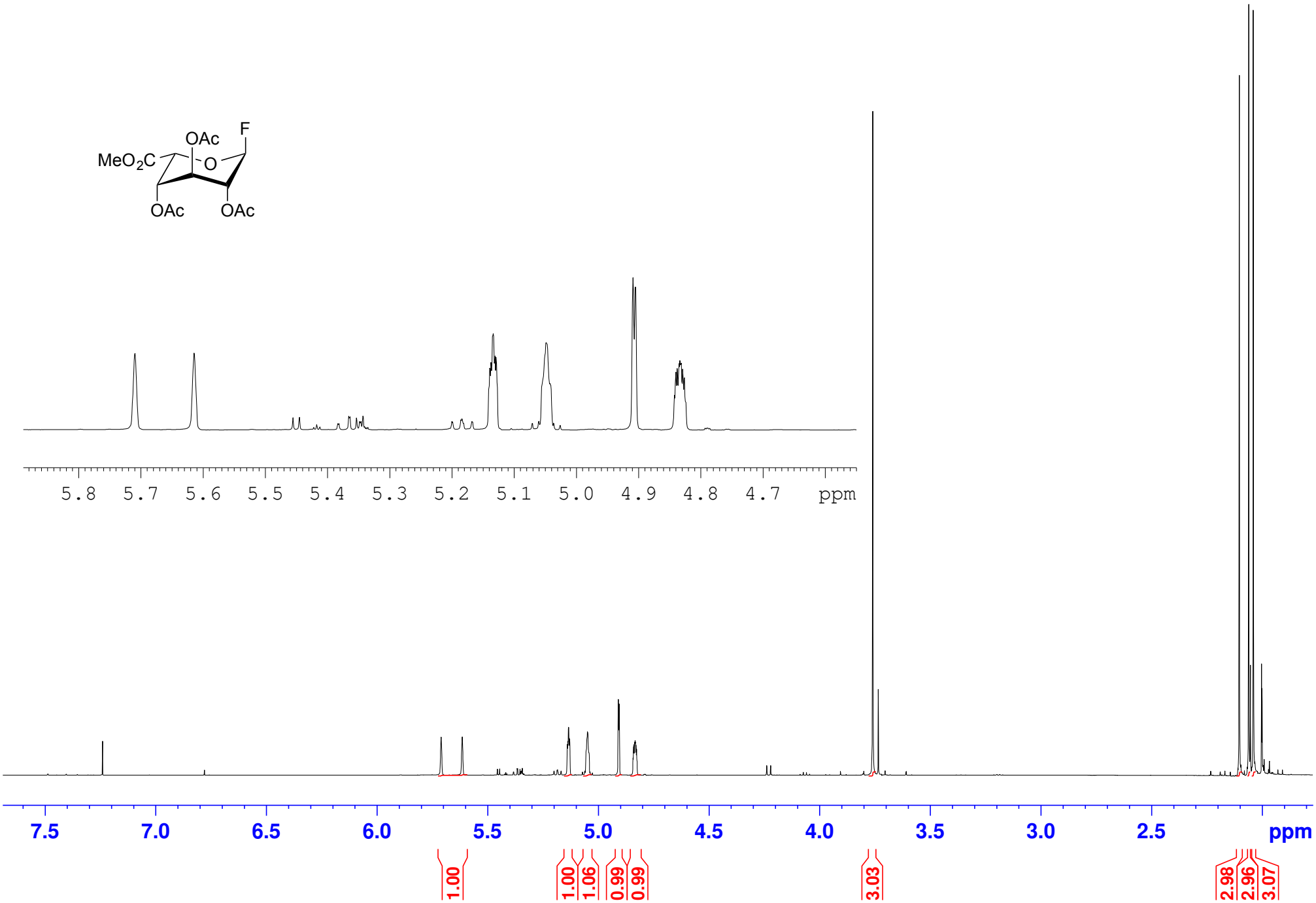




^{13}C NMR Spectrum of Methyl (methyl 2,3,4-tri-*O*-acetyl-α-L-idopyranoside) uronate **(8)**



[1] H NMR Spectrum of Methyl (2,3,4-tri-*O*-acetyl-α-L-idopyranosylfluoride) uronate **(11)**



[13] C NMR Spectrum of Methyl (2,3,4-tri-*O*-acetyl-α-L-idopyranosylfluoride) uronate **(11)**