

Regioselective galactofuranosylation for the synthesis of disaccharide patterns found in pathogenic microorganisms

Laurent Legentil,*^a Yari Cabezas,^a Olivier Tasseau,^a Charles Tellier,^b Franck Daligault^b and Vincent Ferrières*^a

(a) Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France

(b) Université de Nantes, UMR CNRS 6286, 2 Rue de la Houssinière, 44322 Nantes Cedex 3, France

laurent.legentil@ensc-rennes.fr or vincent.ferrieres@ensc-rennes.fr

Table of content

Details of computational calculation by DFT	p S2
Cartesian coordinates of borinate adducts	p S4
NMR spectrum of acceptors 2b, 2c, 4a, 4b, 12	p S17
NMR spectrum of isolated disaccharides and their corresponding orthoester 5b/6b, 5c, 8a/9a, 8b, 17, 18/18', 19/19'	p S27
NMR spectrum of isolated disaccharides from the glycosylation of <i>p</i> NP-Galf in presence of Ag ₂ O or AgOTf	p S49

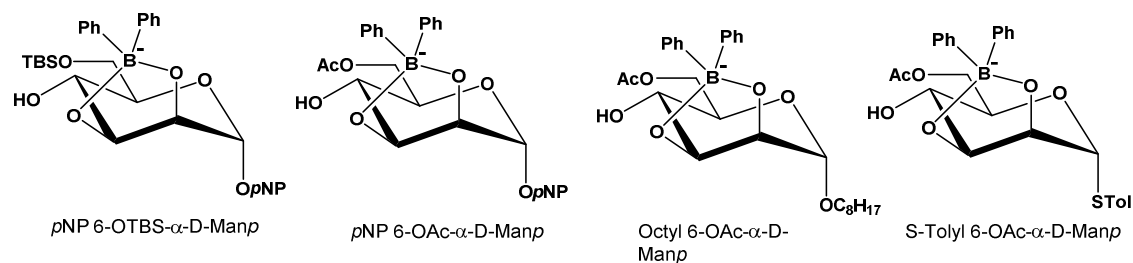
Details of computational calculations by DFT

Calculations were performed with the Gaussian '09 software package¹ on a Mac OS workstation with an Intel Core i5 processor. Geometrical models of Manp, Rhap, Galp, GalpNAc and Galf derivatives were built using Glycam-web. Preliminary Restricted Hartree-Fock / AM1 geometry optimization^{2, 3}, parametrization and viewing of the diphenyl borinate esters of α -D-mannopyranoside derivatives were carried out using Yasara⁴ and Gaussview⁵, energy minimizations were performed using the density functional theory (B3LYP functional), with the 6-31+G* basis set⁶.

Considering glycosylation reaction, computational models were built as tetracoordinate borinate complexes of diols (O-2, O-3 or O-3, O4) as proposed by Taylor & al⁷.

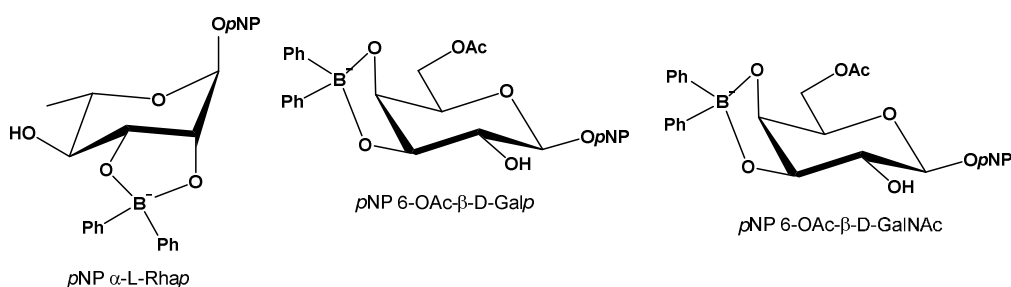
For each borinate complexes, calculations have included DFT condensed reactivity indicator or condensed Fukui function in order to rationalize the observed experimental selectivity.

To predict where are located the most electrophilic and nucleophilic sites, condensed Fukui functions (f_k , defining measure of relative nucleophilic reactivity) were calculated according to the method of Yang and Mortier⁸: a single-point energy calculation of the one-electron-oxidized form was performed and the difference in Mulliken charges between the diphenylborinate adduct and its oxidized form for each oxygen atom was calculated.



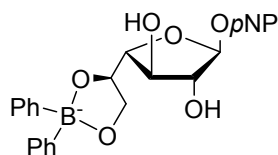
Diphenylborinate ester derivatives	Mulliken charge O-3	Fukui function f_k at O-3
p NP 6-OTBS- α -D-Manp	- 0.35	0.180
p NP 6-OAc- α -D-Manp	- 0.31	0.115
Octyl 6-OAc- α -D-Manp	- 0.32	0.134
S-Tolyl 6-OAc- α -D-Manp	- 0.33	0.115

Table S1: Mulliken charges, condensed Fukui functions for diphenylborinate esters of α -D-mannopyranoside derivatives (B3LYP/6-31G* basis set).



Diphenylborinate ester derivatives	Mulliken charge O-3	Fukui function f_k at O-3
p NP α -L-Rhap	- 0,29	0,134
p NP 6-OAc- β -D-Galp	- 0,31	0,121
p NP 6-OAc- β -D-GalNAc	- 0,25	0, 101

Table S2: Mulliken charges, condensed Fukui functions for diphenylborinate esters of Rhap, Galp and GalNAc derivatives (B3LYP/6-31G* basis set).



Diphenylborinate ester derivatives	Mulliken charge O-6	Fukui function f_k at O-6
β -D-Galf-OpNP	- 0.31	0.157

Table S3: Mulliken charges, condensed Fukui functions for diphenylborinate esters of p NP β -D-Galf (B3LYP/6-31G* basis set)

- (1) Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
- (2) Cramer, C. J. in *Essentials of Computational Chemistry*; John Wiley & Sons, Ltd.: Chichester, **2002**, p 153–189.
- (3) Dewar, M.J.S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.
- (4) Krieger, E; Vriend, G. *Bioinformatics* **2014**, *30*, 2981-2982.
- (5) GaussView version 5_ Dennington, R.; Keith, T.; Millam, J. *Semichem Inc.* **2009**, Shawnee Mission, KS.
- (6) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652 ; (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789 ; (c) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200–1211.
- (7) Chan, L.; Taylor, M.S. *Org Lett.* **2011**, *12*, 3090-3093.
- (8) Yang W.; Mortier, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 5708-5711.

Cartesian Coordinates of borinate adducts

*p*NP 6-OTBS- α -D-Man ρ 2,3-diphenylborinate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.214899	-0.707716	1.446212
2	6	0	5.088489	-1.795077	1.618987
3	6	0	3.805560	-0.039299	2.610662
4	6	0	5.521628	-2.203528	2.880141
5	1	0	5.436168	-2.335902	0.742851
6	6	0	4.238663	-0.431399	3.879904
7	1	0	3.126506	0.801892	2.512834
8	6	0	5.098901	-1.519421	4.021719
9	1	0	6.192243	-3.053330	2.975705
10	1	0	3.902828	0.111232	4.759729
11	1	0	5.436681	-1.830181	5.005868
12	6	0	4.920374	0.351817	-0.941039
13	6	0	5.456745	1.622548	-0.669036
14	6	0	5.485095	-0.350128	-2.017371
15	6	0	6.495311	2.165136	-1.424900
16	1	0	5.043136	2.201241	0.152363
17	6	0	6.530386	0.177851	-2.780035
18	1	0	5.082492	-1.328158	-2.262901
19	6	0	7.041908	1.441242	-2.486924
20	1	0	6.881771	3.152955	-1.188120
21	1	0	6.943285	-0.394812	-3.606563
22	1	0	7.852689	1.858126	-3.077009
23	6	0	-1.130364	2.797796	-0.437982
24	6	0	-2.198090	2.228649	0.275346
25	1	0	-2.251954	1.160278	0.426935
26	6	0	-3.224713	3.042556	0.733225
27	1	0	-4.056991	2.622274	1.280912
28	6	0	-3.197210	4.411391	0.471728
29	7	0	-4.286009	5.257925	0.950462
30	8	0	-4.244464	6.460285	0.688730
31	8	0	-5.194512	4.731549	1.591954
32	6	0	-2.148470	4.985768	-0.251888
33	1	0	-2.150894	6.050089	-0.441759
34	6	0	-1.120925	4.179374	-0.701563
35	1	0	-0.285590	4.590961	-1.253910
36	8	0	-0.074325	2.112010	-0.924956
37	6	0	0.214210	0.797962	-0.461895
38	1	0	0.152955	0.792773	0.634286
39	6	0	1.634508	0.431589	-0.907075
40	1	0	1.844401	0.971915	-1.843096
41	6	0	1.758327	-1.095450	-1.136424

42	1	0	1.568424	-1.368028	-2.184648
43	6	0	0.756030	-1.834323	-0.249233
44	1	0	0.972847	-1.552224	0.791359
45	6	0	-0.680313	-1.440588	-0.610266
46	1	0	-0.983511	-2.022822	-1.483507
47	6	0	-1.628737	-1.719445	0.555916
48	1	0	-1.530035	-2.778673	0.819620
49	1	0	-1.311961	-1.138232	1.428158
50	8	0	-2.981984	-1.366073	0.307522
51	14	0	-4.209901	-2.052378	-0.598664
52	6	0	-3.774552	-2.120378	-2.433782
53	1	0	-2.963394	-2.819654	-2.651600
54	1	0	-3.460542	-1.131061	-2.778829
55	1	0	-4.642443	-2.423045	-3.029309
56	6	0	-5.644435	-0.861976	-0.344390
57	1	0	-5.955115	-0.819849	0.703159
58	1	0	-6.515278	-1.138459	-0.946072
59	1	0	-5.341449	0.146637	-0.639337
60	6	0	-4.655265	-3.810997	0.052336
61	6	0	-3.589285	-4.850442	-0.356824
62	1	0	-3.859816	-5.840739	0.033501
63	1	0	-2.595828	-4.611474	0.031903
64	1	0	-3.504371	-4.941914	-1.443450
65	6	0	-6.012916	-4.246800	-0.542090
66	1	0	-6.268068	-5.257861	-0.197960
67	1	0	-5.993460	-4.273607	-1.636646
68	1	0	-6.826791	-3.582518	-0.237205
69	6	0	-4.769628	-3.784482	1.590891
70	1	0	-5.051548	-4.776322	1.968720
71	1	0	-5.530483	-3.075812	1.932839
72	1	0	-3.824810	-3.506223	2.064961
73	8	0	-0.756406	-0.064596	-1.038091
74	8	0	0.889737	-3.248356	-0.381151
75	1	0	1.844362	-3.405525	-0.336416
76	8	0	3.063348	-1.437874	-0.766060
77	8	0	2.565369	0.719373	0.092766
78	5	0	3.702664	-0.262011	-0.034223

*p*NP 6-OAc- α -D-Manp 2,3-diphenylborinate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.551520	0.599239	1.041126
2	6	0	-4.515563	1.565432	0.775373
3	6	0	-3.034704	0.488935	2.328606
4	6	0	-4.946399	2.422052	1.778677
5	1	0	-4.936267	1.649679	-0.224484

6	6	0	-3.469497	1.342077	3.333570
7	1	0	-2.292311	-0.272892	2.555712
8	6	0	-4.421320	2.312663	3.057825
9	1	0	-5.694750	3.179944	1.562010
10	1	0	-3.064124	1.250034	4.337982
11	1	0	-4.756618	2.985136	3.843206
12	6	0	-4.082101	-1.649641	-0.348526
13	6	0	-4.838167	-2.108410	0.725056
14	6	0	-4.214807	-2.267619	-1.587859
15	6	0	-5.723950	-3.164177	0.558870
16	1	0	-4.738822	-1.639660	1.701207
17	6	0	-5.096444	-3.326973	-1.752864
18	1	0	-3.633365	-1.914611	-2.436420
19	6	0	-5.851602	-3.775907	-0.679370
20	1	0	-6.318647	-3.512039	1.399536
21	1	0	-5.202124	-3.799661	-2.725906
22	1	0	-6.548633	-4.599608	-0.810568
23	6	0	2.717903	-1.636147	-0.277465
24	6	0	3.363364	-0.582683	0.363586
25	1	0	2.865335	0.367350	0.524855
26	6	0	4.672457	-0.729956	0.798866
27	1	0	5.178963	0.098594	1.291728
28	6	0	5.339087	-1.929485	0.596049
29	7	0	6.732854	-2.079635	1.048899
30	8	0	7.276618	-3.148155	0.827636
31	8	0	7.242070	-1.121110	1.604210
32	6	0	4.701000	-2.983094	-0.042178
33	1	0	5.230160	-3.920449	-0.208438
34	6	0	3.391936	-2.832739	-0.477385
35	1	0	2.892739	-3.656678	-0.979261
36	8	0	1.413486	-1.546043	-0.719490
37	6	0	0.625724	-0.356127	-0.516922
38	1	0	0.633329	-0.118202	0.557733
39	6	0	-0.818764	-0.633981	-1.002794
40	1	0	-0.849763	-1.495247	-1.675381
41	6	0	-1.485020	0.573025	-1.679726
42	1	0	-1.308565	0.571394	-2.758763
43	6	0	-1.034770	1.917279	-1.066005
44	1	0	-1.394263	1.972741	-0.034398
45	6	0	0.510726	2.068247	-1.084230
46	1	0	0.781182	2.693629	-1.939661
47	6	0	0.991826	2.762513	0.212707
48	1	0	0.581913	3.775015	0.266164
49	1	0	0.653760	2.195751	1.084196
50	8	0	2.438649	2.841092	0.249874
51	6	0	3.052844	3.605308	-0.674814

52	6	0	4.555001	3.527051	-0.580667
53	1	0	4.885715	3.851944	0.407659
54	1	0	5.013882	4.166111	-1.337791
55	1	0	4.885575	2.498060	-0.735903
56	8	0	2.464778	4.290579	-1.485934
57	8	0	1.179922	0.773685	-1.247927
58	8	0	-1.638192	2.957528	-1.832494
59	1	0	-2.570673	2.693343	-1.942008
60	8	0	-2.878250	0.391406	-1.412646
61	8	0	-1.650367	-0.906363	0.127626
62	5	0	-3.047350	-0.392894	-0.149834

Octyl 6-OAc- α -D-Manp 2,3-diphenylborinate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.210920	-0.826260	-0.951250
2	1	0	1.520927	-1.602192	-0.607278
3	1	0	2.694532	-0.354327	-0.091722
4	6	0	3.260538	-1.430476	-1.902626
5	1	0	2.754905	-2.091207	-2.610182
6	1	0	3.735792	-0.635341	-2.481631
7	6	0	4.346765	-2.227648	-1.153915
8	1	0	3.884371	-2.939720	-0.465843
9	1	0	4.921863	-2.802975	-1.883339
10	6	0	5.306647	-1.293321	-0.390238
11	1	0	5.710835	-0.548954	-1.080633
12	1	0	4.767103	-0.760432	0.395711
13	6	0	6.469204	-2.086237	0.232723
14	1	0	6.080513	-2.798532	0.964337
15	1	0	6.982244	-2.654042	-0.547134
16	6	0	7.469772	-1.134612	0.912833
17	1	0	7.837599	-0.410021	0.182281
18	1	0	6.966519	-0.579812	1.708167
19	6	0	8.658498	-1.915647	1.500261
20	1	0	8.299765	-2.629868	2.244955
21	1	0	9.155745	-2.480346	0.708228
22	6	0	9.668310	-0.958136	2.153257
23	1	0	10.508748	-1.519901	2.566180
24	1	0	9.195629	-0.397168	2.962531
25	1	0	10.054169	-0.249795	1.416735
26	6	0	-3.517011	-0.477962	1.288041
27	6	0	-4.876330	-0.185992	1.262231
28	6	0	-2.812599	-0.333736	2.479317
29	6	0	-5.522052	0.258288	2.407667
30	1	0	-5.437841	-0.307035	0.338074
31	6	0	-3.457914	0.111130	3.625071

32	1	0	-1.752549	-0.573300	2.519993
33	6	0	-4.812307	0.408779	3.589777
34	1	0	-6.583030	0.493380	2.377210
35	1	0	-2.902168	0.225044	4.552418
36	1	0	-5.317396	0.754713	4.488111
37	6	0	-3.053026	-2.572801	-0.347647
38	6	0	-3.145541	-3.449948	0.727609
39	6	0	-3.197049	-3.064816	-1.641499
40	6	0	-3.389506	-4.799689	0.514238
41	1	0	-3.028635	-3.078494	1.742988
42	6	0	-3.440198	-4.414856	-1.855042
43	1	0	-3.130364	-2.390834	-2.492441
44	6	0	-3.540441	-5.282615	-0.777317
45	1	0	-3.468922	-5.478236	1.359869
46	1	0	-3.560654	-4.791306	-2.867744
47	1	0	-3.738183	-6.338415	-0.944424
48	8	0	1.488634	0.187879	-1.680444
49	6	0	0.366835	0.782291	-0.994340
50	1	0	0.607150	0.856048	0.077651
51	6	0	-0.893008	-0.088629	-1.233043
52	1	0	-0.699531	-0.853532	-1.989878
53	6	0	-2.140034	0.711626	-1.630658
54	1	0	-2.174883	0.880891	-2.710312
55	6	0	-2.271469	2.054239	-0.871600
56	1	0	-2.554513	1.848738	0.164762
57	6	0	-0.956399	2.880899	-0.888564
58	1	0	-1.124972	3.775301	-1.495207
59	6	0	-0.584230	3.316722	0.550903
60	1	0	-1.327951	4.023313	0.929885
61	1	0	-0.558556	2.443813	1.208410
62	8	0	0.719595	3.947836	0.579750
63	6	0	0.864442	5.120022	-0.068590
64	6	0	2.282450	5.629025	-0.031375
65	1	0	2.598938	5.778643	1.002776
66	1	0	2.356361	6.577259	-0.567419
67	1	0	2.952173	4.903421	-0.497398
68	8	0	-0.046735	5.710782	-0.610814
69	8	0	0.142079	2.126699	-1.496872
70	8	0	-3.317677	2.792020	-1.501233
71	1	0	-4.070734	2.171789	-1.580668
72	8	0	-3.214252	-0.145826	-1.233045
73	8	0	-1.280674	-0.731241	-0.011937
74	5	0	-2.770870	-0.989923	-0.079720

Thiotolyl 6-OAc- α -D-Manp 2,3-diphenylborinate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.238292	0.881359	1.019928
2	6	0	-4.187168	1.853979	0.726071
3	6	0	-2.682549	0.834762	2.295065
4	6	0	-4.567389	2.778143	1.689158
5	1	0	-4.633966	1.890728	-0.265398
6	6	0	-3.064053	1.757800	3.258990
7	1	0	-1.947727	0.072482	2.543980
8	6	0	-4.002176	2.733390	2.955000
9	1	0	-5.303525	3.541307	1.449578
10	1	0	-2.625677	1.718247	4.253000
11	1	0	-4.295388	3.460424	3.708085
12	6	0	-3.913383	-1.376213	-0.290441
13	6	0	-4.544985	-1.885220	0.839066
14	6	0	-4.235116	-1.894570	-1.541511
15	6	0	-5.495951	-2.889400	0.720146
16	1	0	-4.294093	-1.495095	1.822710
17	6	0	-5.184094	-2.900854	-1.660529
18	1	0	-3.750158	-1.507224	-2.434496
19	6	0	-5.818312	-3.395713	-0.530374
20	1	0	-5.992240	-3.275932	1.606683
21	1	0	-5.436986	-3.295473	-2.641312
22	1	0	-6.566878	-4.178338	-0.624482
23	6	0	3.248409	-2.148286	-0.099181
24	6	0	3.763811	-0.974354	0.437593
25	1	0	3.249178	-0.030689	0.306531
26	6	0	4.959036	-0.993057	1.142503
27	1	0	5.354449	-0.069248	1.558202
28	6	0	5.649687	-2.183795	1.317389
29	6	0	6.953951	-2.199739	2.087049
30	1	0	7.214853	-3.218511	2.380666
31	1	0	6.871837	-1.592478	2.990792
32	1	0	7.762857	-1.799339	1.472229
33	6	0	5.143289	-3.355481	0.772720
34	1	0	5.682972	-4.291422	0.897254
35	6	0	3.947921	-3.335994	0.067554
36	1	0	3.557810	-4.257466	-0.357218
37	16	0	1.721812	-2.188695	-1.012337
38	6	0	0.866258	-0.626460	-0.609596
39	1	0	0.964832	-0.443157	0.470976
40	6	0	-0.631882	-0.698285	-1.002014
41	1	0	-0.829715	-1.574325	-1.625076
42	6	0	-1.159413	0.558250	-1.706337
43	1	0	-0.992365	0.512729	-2.785871

44	6	0	-0.558637	1.853781	-1.118429
45	1	0	-0.921716	1.978678	-0.094172
46	6	0	0.992580	1.825028	-1.113874
47	1	0	1.341535	2.445356	-1.943925
48	6	0	1.528303	2.419808	0.211142
49	1	0	1.170956	3.446928	0.326954
50	1	0	1.173241	1.823496	1.055552
51	8	0	2.977376	2.429576	0.231546
52	6	0	3.618680	3.214413	-0.656066
53	6	0	5.116602	3.070109	-0.574147
54	1	0	5.463457	3.333426	0.427059
55	1	0	5.598697	3.725498	-1.302257
56	1	0	5.403666	2.036892	-0.779894
57	8	0	3.057510	3.965533	-1.426918
58	8	0	1.512110	0.469684	-1.323203
59	8	0	-1.026880	2.937971	-1.918153
60	1	0	-1.990256	2.788111	-2.020063
61	8	0	-2.566285	0.542661	-1.424621
62	8	0	-1.432490	-0.762148	0.189668
63	5	0	-2.796022	-0.186618	-0.129300

*p*NP 6-OAc- β -D-Galp 3,4-diphenylborinate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.192867	-1.522597	0.889400
2	6	0	-2.658019	-1.335101	2.160702
3	1	0	-2.175206	-0.394722	2.418543
4	6	0	-2.736378	-2.345308	3.109440
5	1	0	-2.320900	-2.191471	4.102229
6	6	0	-3.354299	-3.547009	2.796472
7	1	0	-3.421144	-4.335367	3.541966
8	6	0	-3.894312	-3.737822	1.533419
9	1	0	-4.386427	-4.676025	1.289593
10	6	0	-3.816160	-2.727773	0.584798
11	1	0	-4.245596	-2.880622	-0.402934
12	6	0	3.267518	-1.482915	-0.316652
13	6	0	4.054571	-1.191487	-1.424004
14	1	0	3.628188	-1.204956	-2.422958
15	6	0	5.401075	-0.897526	-1.258187
16	1	0	6.022971	-0.672321	-2.123301
17	6	0	5.956843	-0.898336	0.014114
18	7	0	7.385562	-0.581858	0.189432
19	8	0	7.819301	-0.579257	1.329048
20	8	0	8.026526	-0.337730	-0.818603
21	6	0	5.173152	-1.198039	1.120419
22	1	0	5.610949	-1.192296	2.117365

23	6	0	3.827968	-1.493968	0.951649
24	1	0	3.209698	-1.723134	1.815053
25	8	0	1.932587	-1.778801	-0.462546
26	6	0	1.084967	-0.825340	-1.130155
27	1	0	1.524702	-0.573782	-2.105915
28	8	0	0.979390	0.376175	-0.322915
29	6	0	0.137070	1.439481	-0.850020
30	1	0	0.569974	1.792942	-1.789977
31	6	0	0.110583	2.610311	0.151675
32	1	0	-0.686715	3.311712	-0.109409
33	1	0	-0.050362	2.236841	1.166830
34	8	0	1.373555	3.306756	0.087715
35	6	0	1.528893	4.332295	0.944084
36	6	0	2.886421	4.975567	0.833566
37	1	0	3.019047	5.403553	-0.161910
38	1	0	3.666537	4.229903	0.996759
39	1	0	2.989774	5.767568	1.579751
40	8	0	0.667423	4.705638	1.714024
41	6	0	-1.292054	0.907639	-1.127660
42	1	0	-1.864568	1.646354	-1.696216
43	8	0	-2.002989	0.625595	0.101310
44	5	0	-3.097923	-0.345756	-0.248857
45	6	0	-1.328016	-0.437510	-1.858459
46	1	0	-1.198722	-0.316075	-2.937110
47	8	0	-2.646600	-0.913448	-1.577853
48	6	0	-0.314280	-1.459361	-1.292495
49	1	0	-0.658707	-1.796283	-0.309711
50	8	0	-0.257682	-2.565063	-2.206379
51	1	0	-1.184549	-2.863554	-2.331185
52	6	0	-4.510083	0.456897	-0.384698
53	6	0	-4.813945	1.480443	0.506594
54	1	0	-4.107355	1.745390	1.290422
55	6	0	-6.009333	2.176673	0.395036
56	1	0	-6.238285	2.978542	1.092500
57	6	0	-6.912109	1.850126	-0.606086
58	1	0	-7.847040	2.397481	-0.695680
59	6	0	-6.619224	0.824518	-1.493084
60	1	0	-7.328212	0.564628	-2.275019
61	6	0	-5.422955	0.129097	-1.382413
62	1	0	-5.199627	-0.669175	-2.086548

*p*NP 6-OAc- β -D-GalpNAc 3,4-diphenylborinate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.506222	0.852723	-0.209257
2	6	0	-4.839955	1.909838	0.629302
3	1	0	-4.122322	2.267745	1.364539
4	6	0	-6.086116	2.513381	0.534245
5	1	0	-6.343449	3.336301	1.196411
6	6	0	-7.003731	2.067006	-0.405371
7	1	0	-7.980226	2.539128	-0.480335
8	6	0	-6.677738	1.009053	-1.241435
9	1	0	-7.399734	0.652511	-1.971954
10	6	0	-5.435003	0.399000	-1.140714
11	1	0	-5.195875	-0.436820	-1.794913
12	6	0	3.286225	-1.235861	-0.083230
13	6	0	3.876243	-0.168356	-0.752587
14	1	0	3.292558	0.481123	-1.394562
15	6	0	5.230485	0.088598	-0.593264
16	1	0	5.686106	0.929731	-1.110711
17	6	0	5.998713	-0.719132	0.233632
18	7	0	7.434105	-0.436511	0.411181
19	8	0	8.053046	-1.160291	1.172485
20	8	0	7.895171	0.506676	-0.208987
21	6	0	5.411843	-1.785182	0.901627
22	1	0	6.008374	-2.417736	1.555194
23	6	0	4.058426	-2.042600	0.737349
24	1	0	3.595703	-2.874375	1.259673
25	8	0	1.946179	-1.538792	-0.213688
26	6	0	1.057864	-0.693954	-0.968598
27	1	0	1.468556	-0.584929	-1.983917
28	8	0	0.979782	0.608208	-0.349514
29	6	0	0.230991	1.601442	-1.088506
30	1	0	0.697047	1.731290	-2.069082
31	6	0	0.296512	2.937365	-0.323409
32	1	0	-0.431270	3.644561	-0.730459
33	1	0	0.089889	2.771030	0.737792
34	8	0	1.620940	3.494656	-0.474825
35	6	0	1.880145	4.618788	0.215956
36	6	0	3.298501	5.092096	0.038107
37	1	0	3.496073	5.292964	-1.016423
38	1	0	3.992789	4.322149	0.380867
39	1	0	3.465313	6.004428	0.613643
40	8	0	1.057536	5.195384	0.897962
41	6	0	-1.226287	1.116515	-1.278667
42	1	0	-1.731511	1.740105	-2.021415
43	8	0	-1.961400	1.215095	-0.051734

44	5	0	-3.033034	0.145760	-0.069548
45	6	0	-1.353504	-0.360293	-1.694160
46	1	0	-1.278481	-0.466341	-2.779123
47	8	0	-2.687802	-0.663347	-1.279519
48	6	0	-0.354338	-1.329814	-0.995290
49	1	0	-0.672836	-1.460517	0.043966
50	7	0	-0.334442	-2.658971	-1.646307
51	1	0	0.371254	-2.843887	-2.339000
52	6	0	-1.177839	-3.651482	-1.333683
53	8	0	-2.035418	-3.523722	-0.494021
54	6	0	-0.966526	-4.926311	-2.092013
55	1	0	0.042508	-5.299634	-1.913120
56	1	0	-1.690056	-5.671034	-1.757813
57	1	0	-1.098380	-4.749126	-3.159548
58	6	0	-2.943122	-0.760160	1.282533
59	6	0	-3.518842	-2.024678	1.304761
60	1	0	-4.006943	-2.416958	0.415043
61	6	0	-3.452438	-2.806697	2.449125
62	1	0	-3.895991	-3.798963	2.453282
63	6	0	-2.809204	-2.328741	3.580867
64	1	0	-2.749749	-2.945017	4.474479
65	6	0	-2.232335	-1.067566	3.565713
66	1	0	-1.719787	-0.694981	4.448946
67	6	0	-2.298280	-0.285287	2.421071
68	1	0	-1.833123	0.697742	2.422257

*p*NP β-L-Rhap 2,3-diphenylborinate

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.005535	-0.793814	-0.510175
2	6	0	-4.254525	-1.235691	-1.806043
3	1	0	-3.532261	-1.043033	-2.596308
4	6	0	-5.423831	-1.924004	-2.099089
5	1	0	-5.608393	-2.274140	-3.111589
6	6	0	-6.354436	-2.169758	-1.100391
7	1	0	-7.269860	-2.713497	-1.329769
8	6	0	-6.115198	-1.726456	0.191929
9	1	0	-6.841556	-1.921455	0.976871
10	6	0	-4.946031	-1.038339	0.484494
11	1	0	-4.763492	-0.687679	1.498143
12	6	0	-2.910218	1.639217	-0.114775
13	6	0	-3.972979	2.184508	-0.827069
14	1	0	-4.626924	1.539466	-1.409277
15	6	0	-4.206144	3.552573	-0.801271
16	1	0	-5.043975	3.970899	-1.352775
17	6	0	-3.376537	4.385421	-0.064868

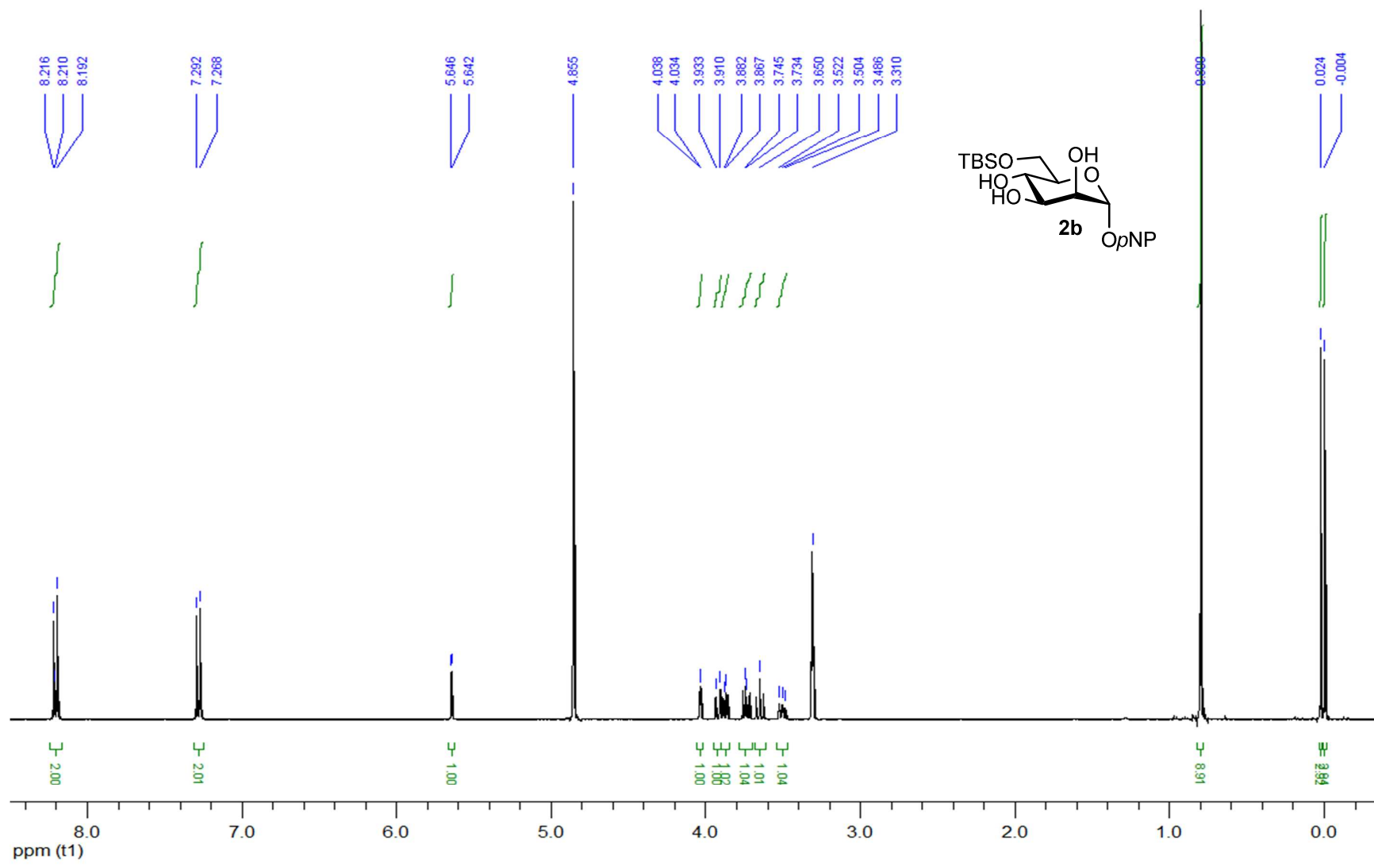
18	1	0	-3.563731	5.455791	-0.038830
19	6	0	-2.308581	3.848988	0.639035
20	1	0	-1.656646	4.499088	1.216586
21	6	0	-2.076877	2.480922	0.613600
22	1	0	-1.242053	2.066467	1.167707
23	8	0	1.890200	-1.156175	-0.535936
24	6	0	0.770852	-0.258464	-0.372700
25	1	0	0.815677	0.488921	-1.178418
26	8	0	0.812539	0.431337	0.908696
27	6	0	0.834901	-0.395806	2.106214
28	1	0	1.857379	-0.751026	2.263745
29	6	0	0.427960	0.502880	3.284605
30	1	0	-0.602071	0.844400	3.163290
31	1	0	1.081540	1.375828	3.337265
32	1	0	0.504101	-0.045684	4.225651
33	6	0	-0.098771	-1.635753	1.986711
34	1	0	-0.612879	-1.801575	2.937536
35	8	0	0.711900	-2.782222	1.696775
36	1	0	0.173154	-3.581097	1.858666
37	6	0	-1.143331	-1.501141	0.852681
38	1	0	-1.694021	-2.437834	0.733165
39	8	0	-2.083277	-0.463491	1.148717
40	6	0	-0.532166	-1.091870	-0.497849
41	1	0	-0.346110	-1.976030	-1.112682
42	8	0	-1.545487	-0.308176	-1.143914
43	5	0	-2.635650	0.032900	-0.150230
44	6	0	3.190916	-0.696575	-0.549898
45	6	0	4.207215	-1.629591	-0.695528
46	1	0	3.961880	-2.684535	-0.776705
47	6	0	5.533248	-1.223703	-0.728577
48	1	0	6.328478	-1.959460	-0.839609
49	6	0	5.843398	0.123959	-0.619375
50	7	0	7.249827	0.559468	-0.666182
51	8	0	7.464330	1.755783	-0.570531
52	8	0	8.095320	-0.308574	-0.800731
53	6	0	4.832681	1.062482	-0.465834
54	1	0	5.079704	2.119011	-0.371264
55	6	0	3.506604	0.654219	-0.433704
56	1	0	2.731629	1.403323	-0.304327

*p*NP β-D-Galf 5,6-diphenylborinate

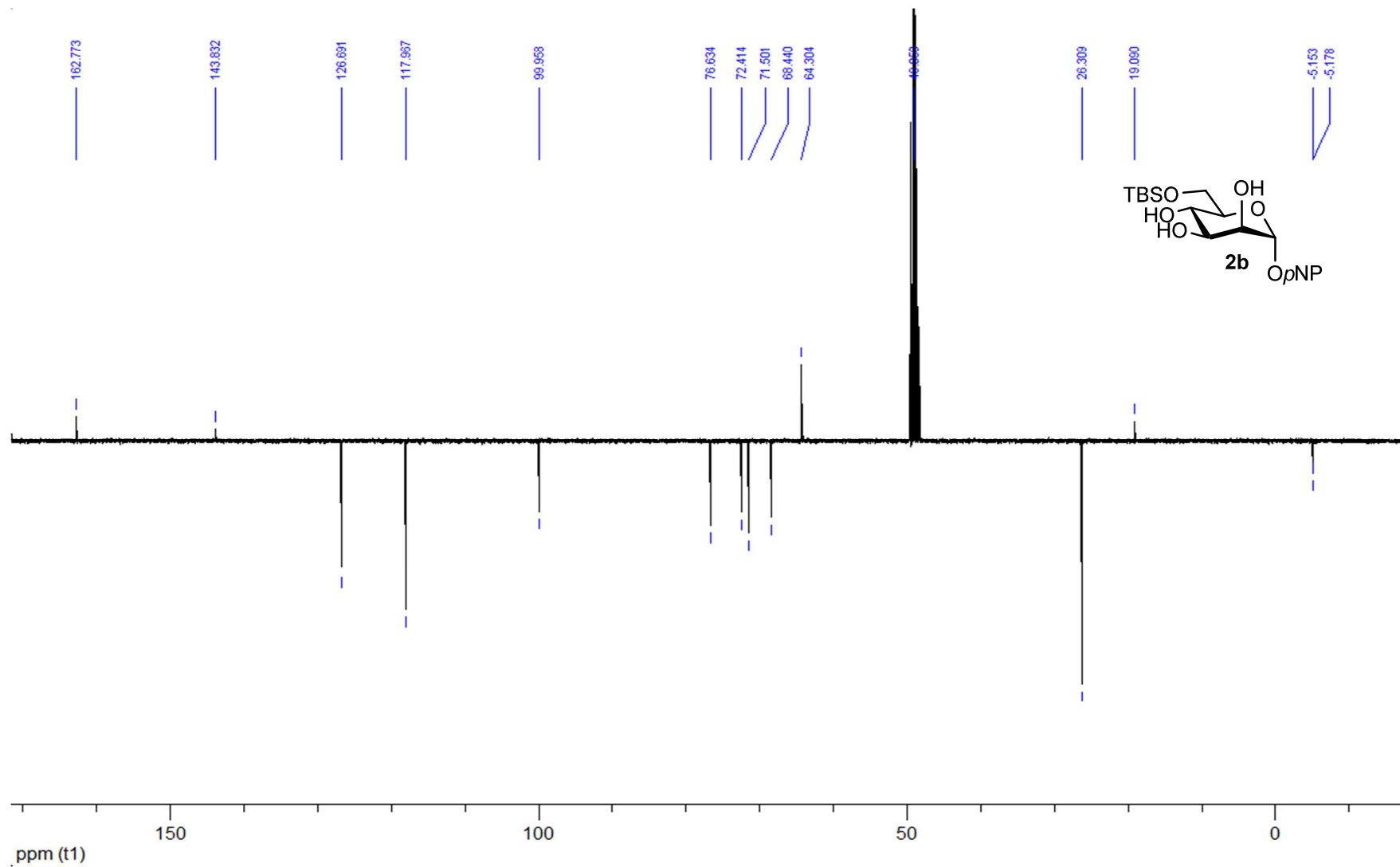
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.079223	3.279185	-0.305838
2	1	0	-1.809242	2.894414	0.411031
3	8	0	-1.452736	4.587247	-0.755446

4	1	0	-1.426645	5.161053	0.035758
5	6	0	-0.878872	2.302610	-1.482009
6	1	0	-0.607974	2.879967	-2.370308
7	6	0	-2.131908	1.447816	-1.811352
8	1	0	-2.845994	2.060306	-2.367938
9	8	0	-2.768961	0.987021	-0.626764
10	5	0	-2.404755	-0.459443	-0.367359
11	6	0	-1.802512	0.167771	-2.585335
12	1	0	-2.655996	-0.125385	-3.202451
13	1	0	-0.901644	0.263406	-3.197573
14	8	0	-1.603859	-0.831898	-1.575531
15	8	0	0.279766	1.493487	-1.148390
16	6	0	0.867303	1.923314	0.102775
17	1	0	0.572731	1.222010	0.897982
18	6	0	0.301930	3.331636	0.352332
19	1	0	0.929652	4.065772	-0.161547
20	8	0	0.196511	3.648964	1.752850
21	1	0	1.099873	3.624245	2.134722
22	8	0	2.306461	2.006873	0.030030
23	6	0	3.133008	0.907650	-0.105976
24	6	0	4.501635	1.114140	0.026391
25	1	0	4.874754	2.114989	0.219005
26	6	0	5.392432	0.049182	-0.086856
27	1	0	6.458361	0.235095	0.025815
28	6	0	4.918648	-1.242527	-0.339684
29	7	0	5.867667	-2.381327	-0.471230
30	8	0	5.416444	-3.513345	-0.529413
31	8	0	7.063183	-2.142948	-0.524632
32	6	0	3.541344	-1.445963	-0.479342
33	1	0	3.147630	-2.438220	-0.688434
34	6	0	2.654856	-0.377249	-0.365683
35	1	0	1.596468	-0.558282	-0.494876
36	6	0	-3.728441	-1.406453	-0.278318
37	6	0	-4.944727	-0.900140	0.197678
38	6	0	-3.659958	-2.756056	-0.645624
39	6	0	-6.070054	-1.717812	0.283367
40	1	0	-5.021666	0.139508	0.509331
41	6	0	-4.784747	-3.574772	-0.558628
42	1	0	-2.721364	-3.177948	-0.998239
43	6	0	-5.991632	-3.054766	-0.098227
44	1	0	-7.009988	-1.311991	0.649804
45	1	0	-4.719909	-4.620482	-0.848621
46	1	0	-6.870675	-3.691308	-0.035643
47	6	0	-1.499263	-0.580557	0.994631
48	6	0	-1.734103	0.269067	2.082795
49	6	0	-0.487643	-1.542090	1.098017

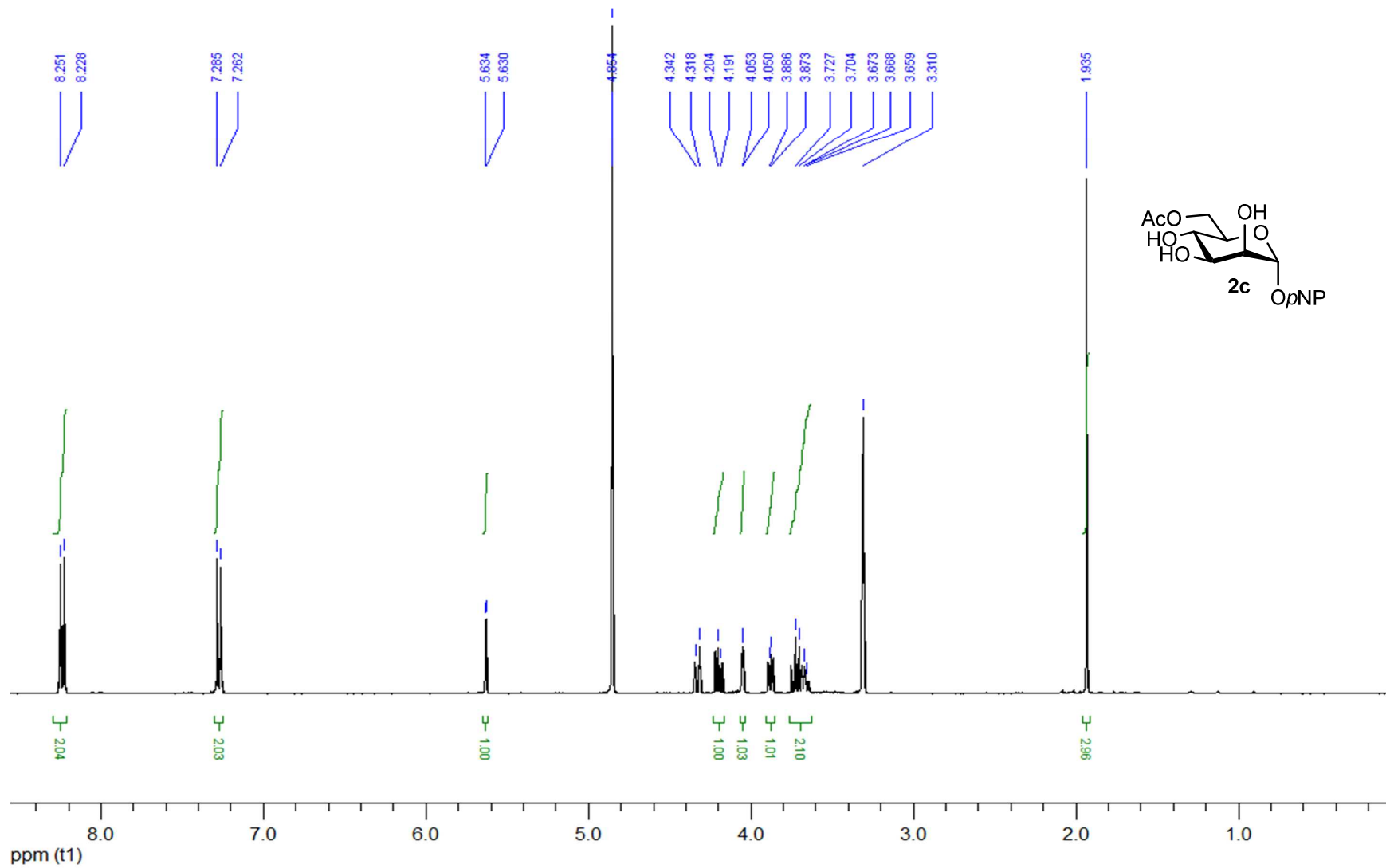
50	6	0	-0.952092	0.182648	3.232740
51	1	0	-2.529616	1.009346	2.037460
52	6	0	0.294179	-1.629547	2.248182
53	1	0	-0.296587	-2.225895	0.272985
54	6	0	0.066815	-0.762794	3.313844
55	1	0	-1.136217	0.855706	4.066391
56	1	0	1.085374	-2.372809	2.312236
57	1	0	0.682445	-0.825968	4.207585



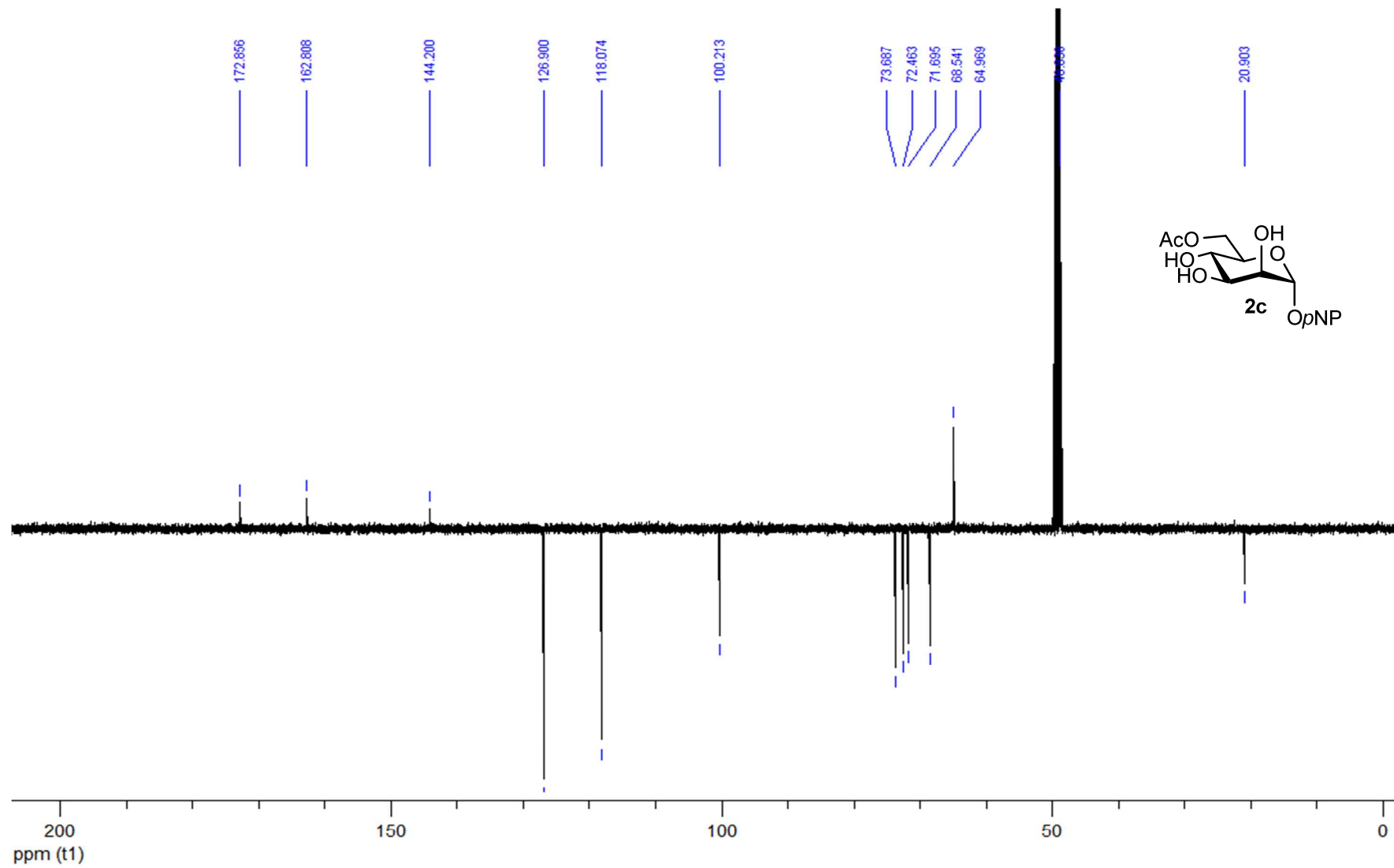
¹H NMR Spectrum of **2b** (400 MHz, CD₃OD)

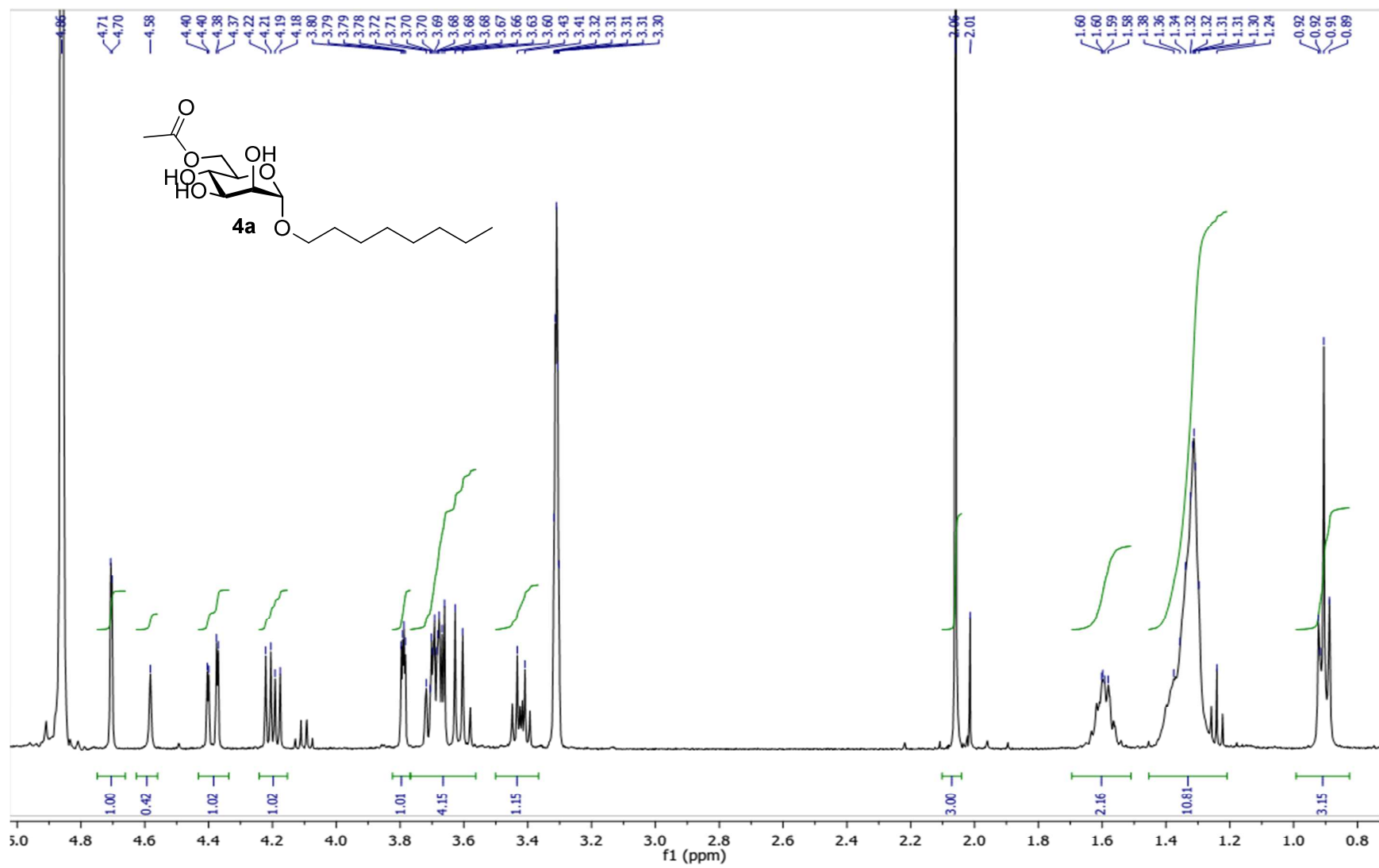


^{13}C NMR Spectrum of **2b** (100 MHz, CD_3OD)

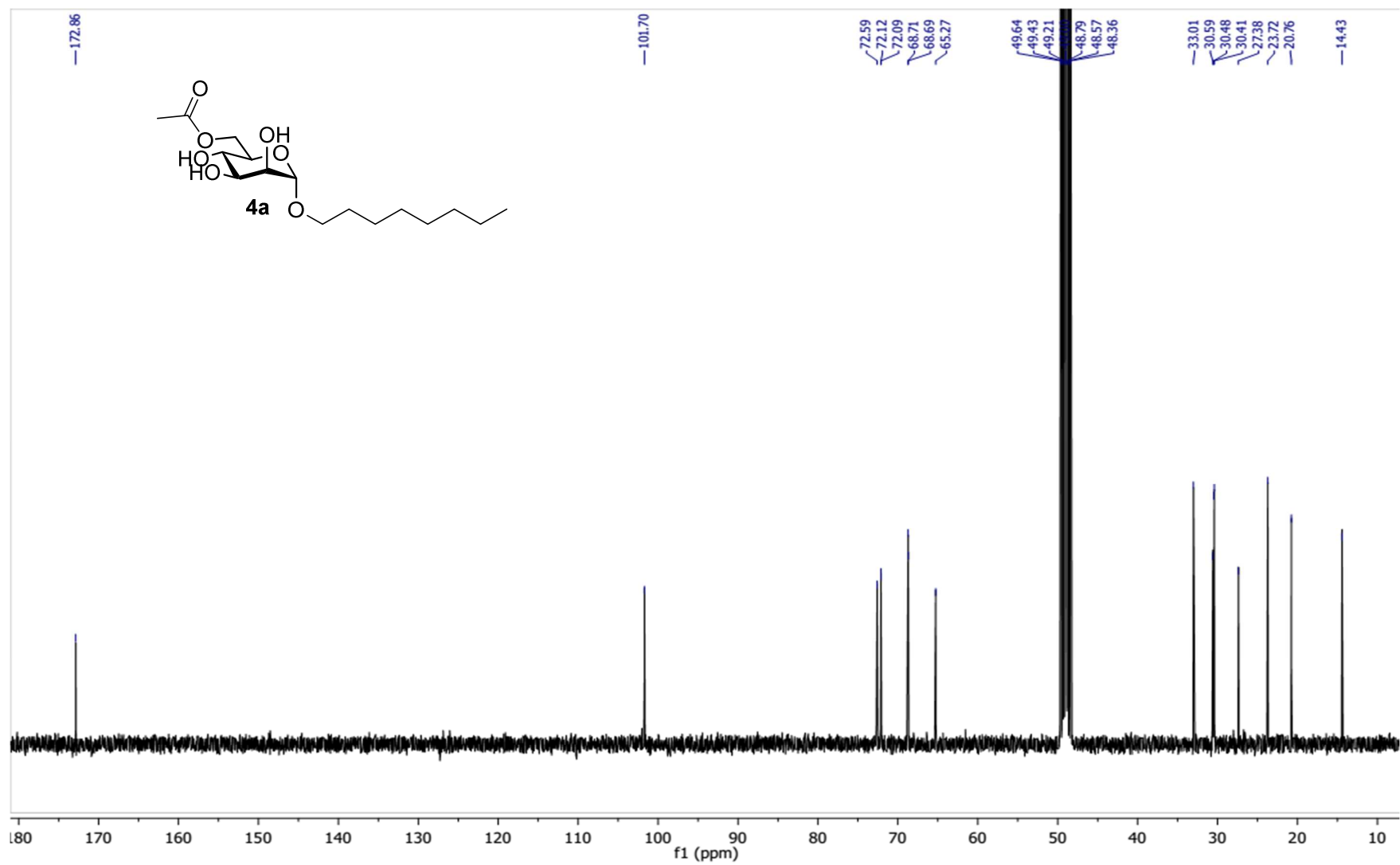


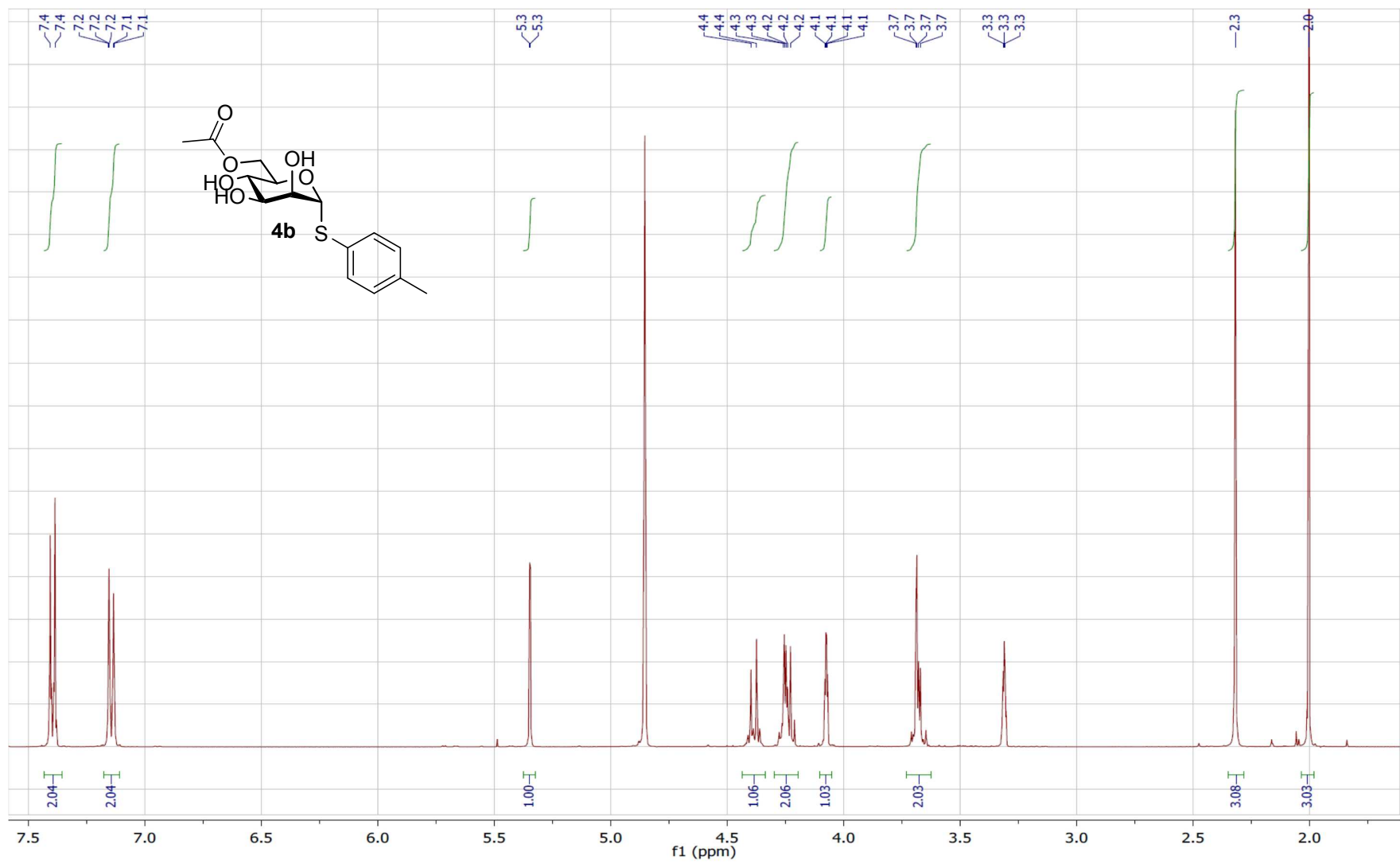
^1H NMR Spectrum of **2c** (400 MHz, CD_3OD)



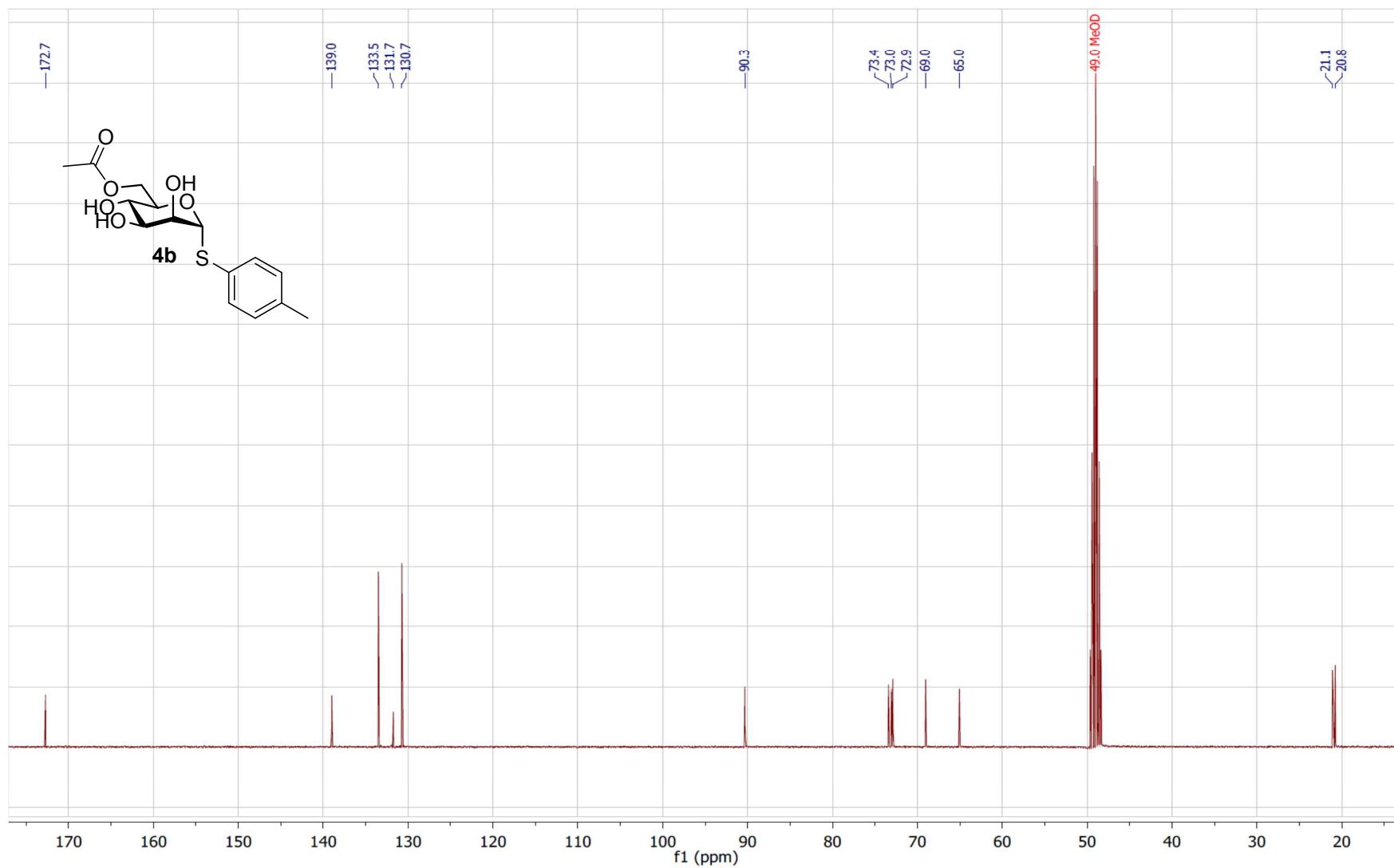


¹H NMR Spectrum of **4a** (400 MHz, CD₃OD)

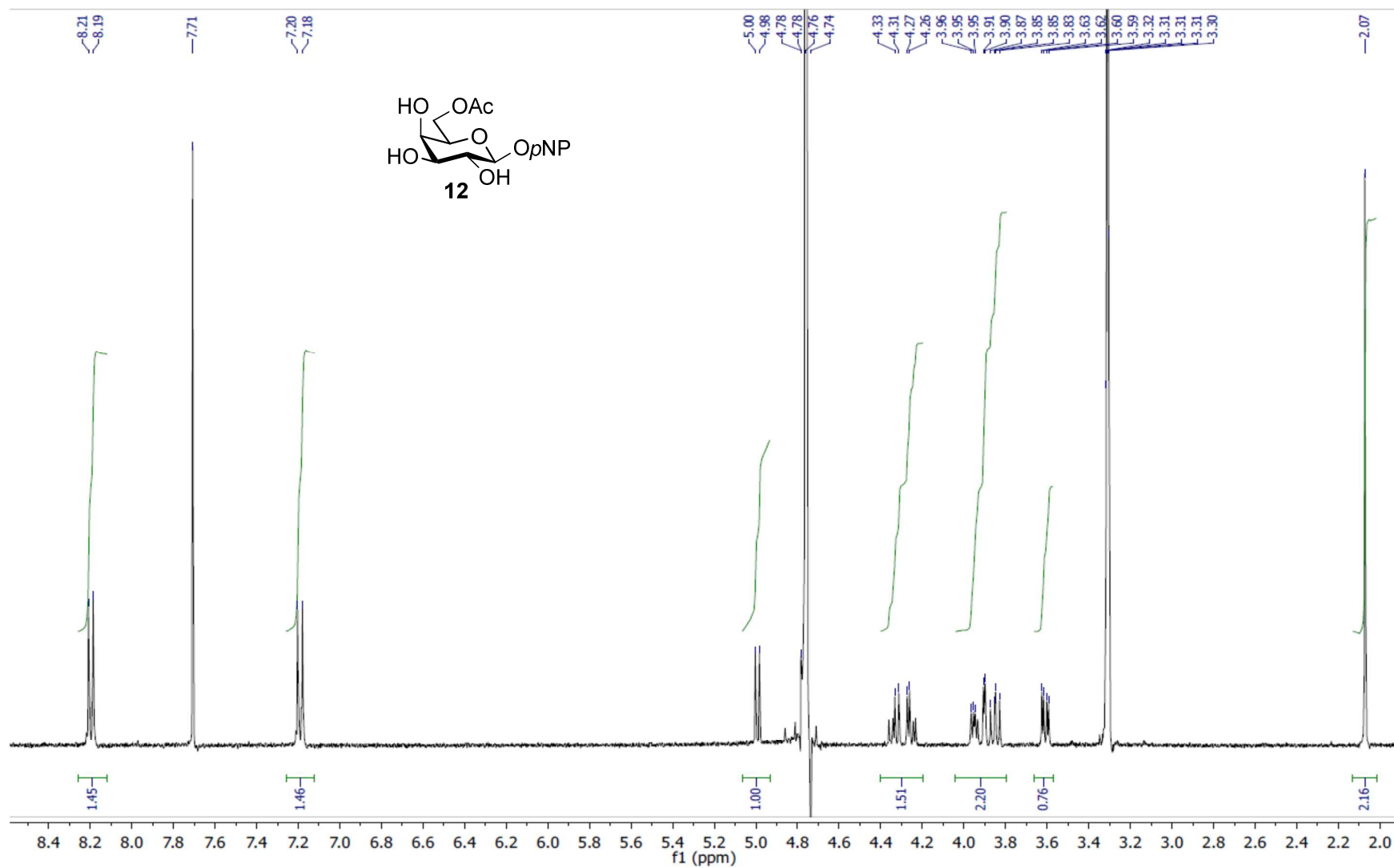




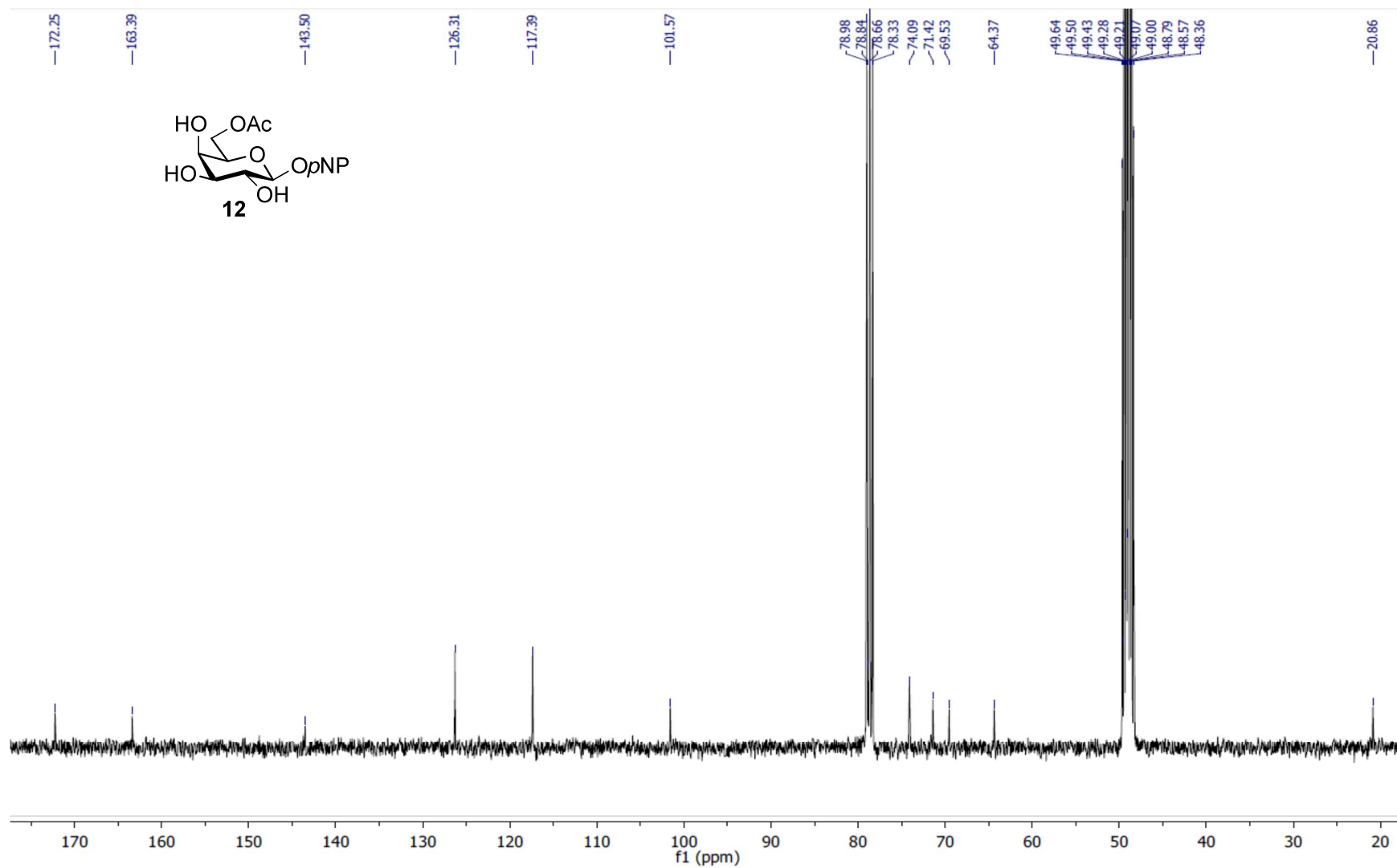
¹H NMR Spectrum of **4b** (400 MHz, CD₃OD)



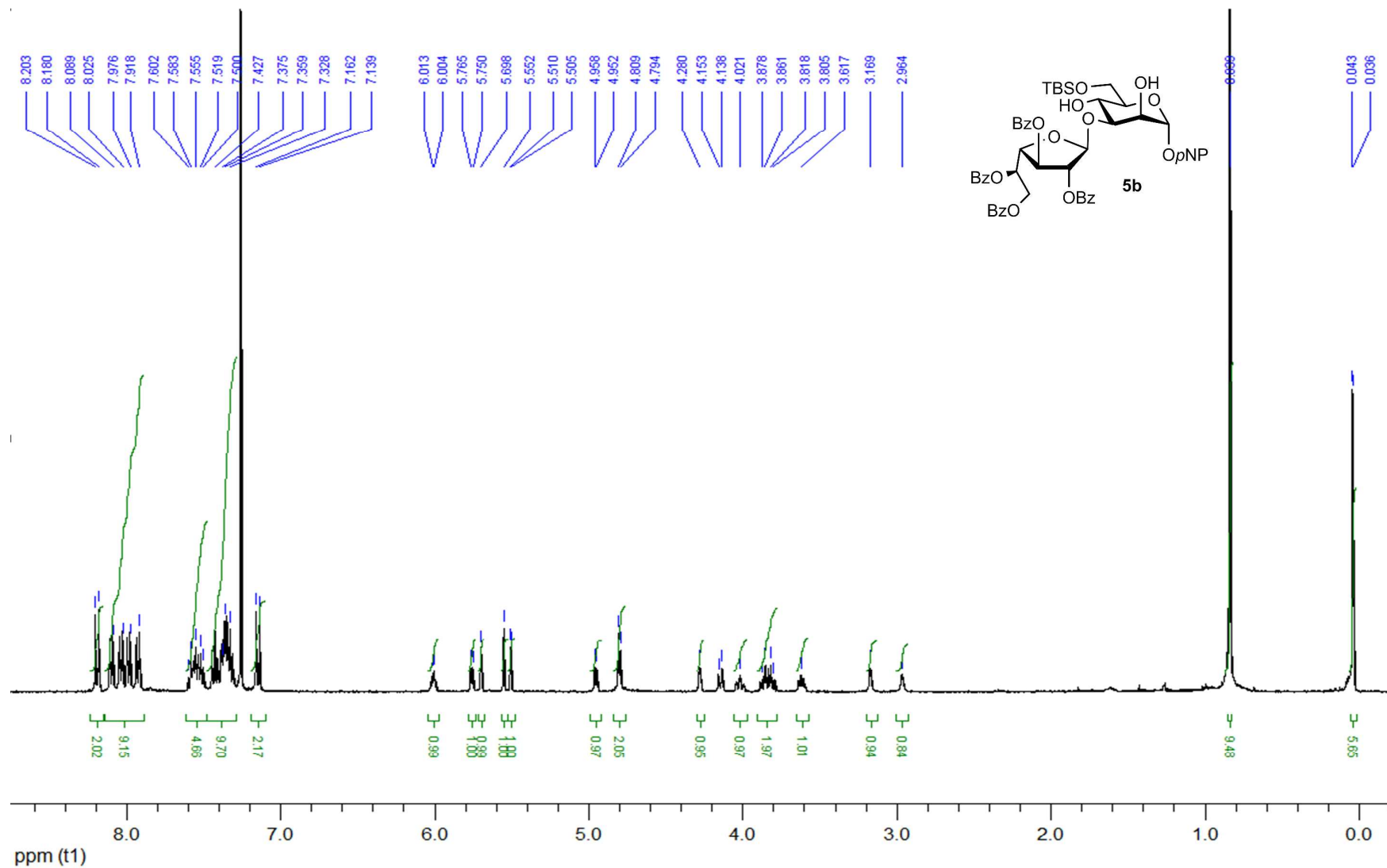
^{13}C NMR Spectrum of **4b** (100 MHz, CD_3OD)



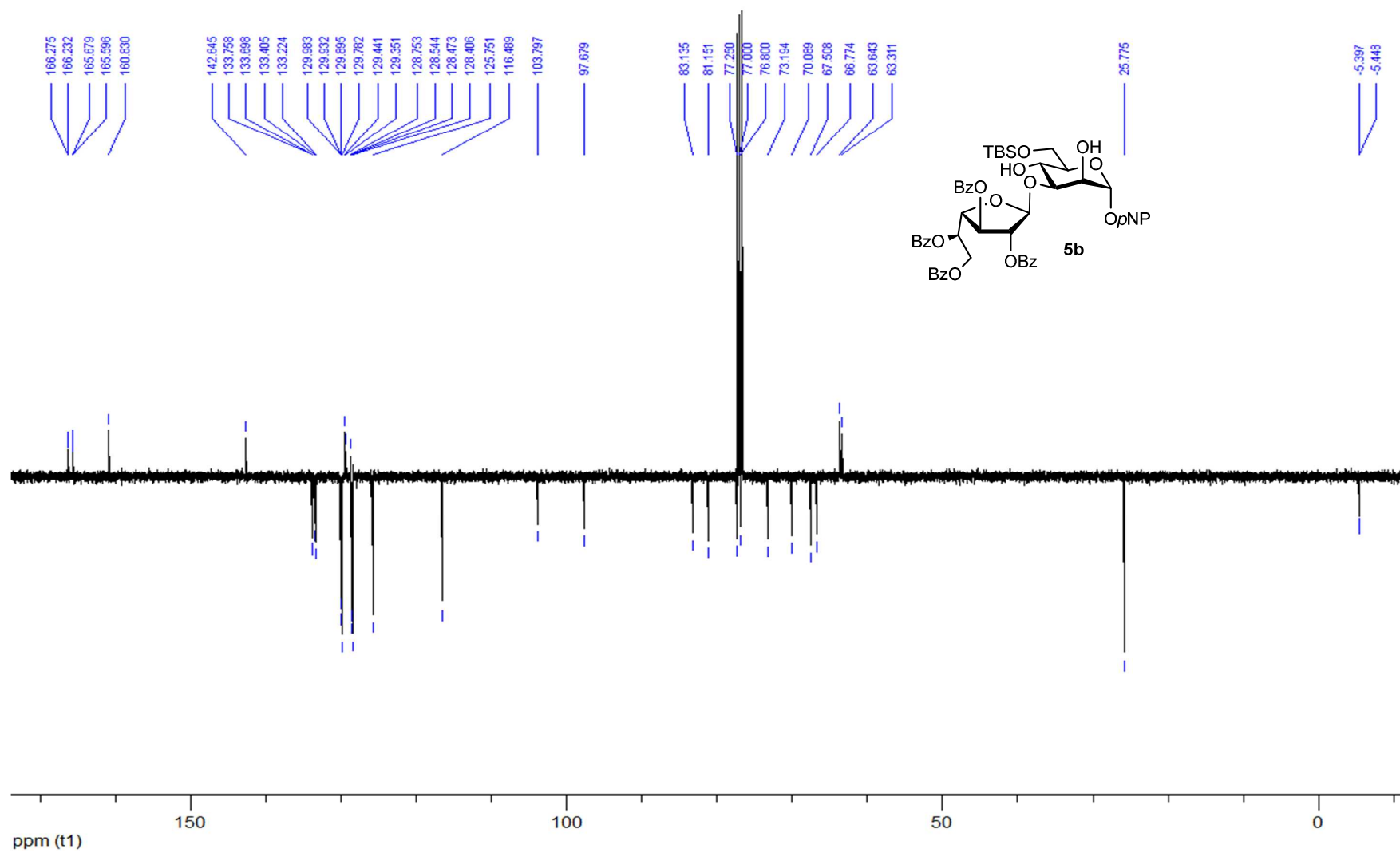
¹H NMR Spectrum of **12** (400 MHz, CD₃OD)



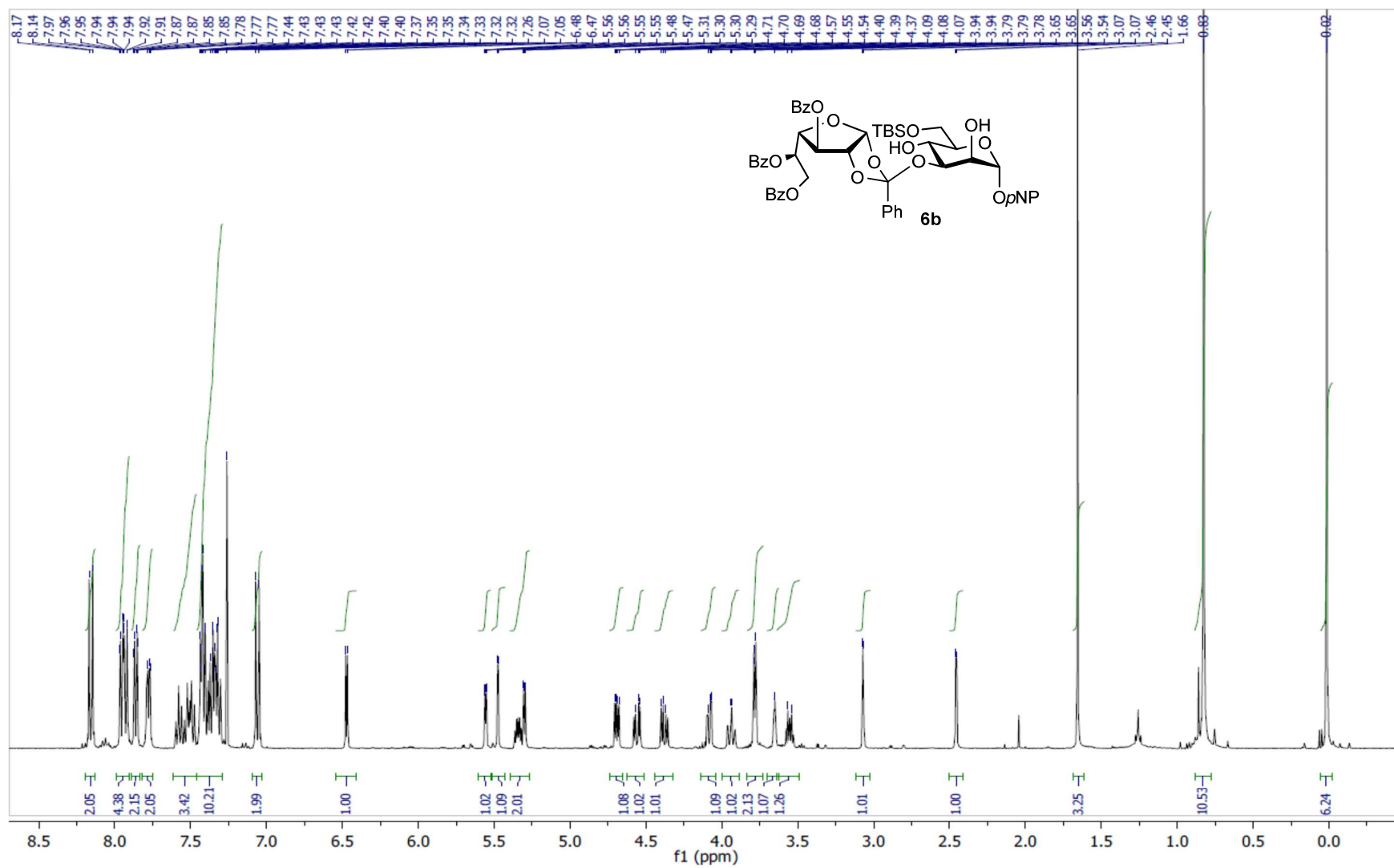
^{13}C NMR Spectrum of **12** (100 MHz, CD_3OD)



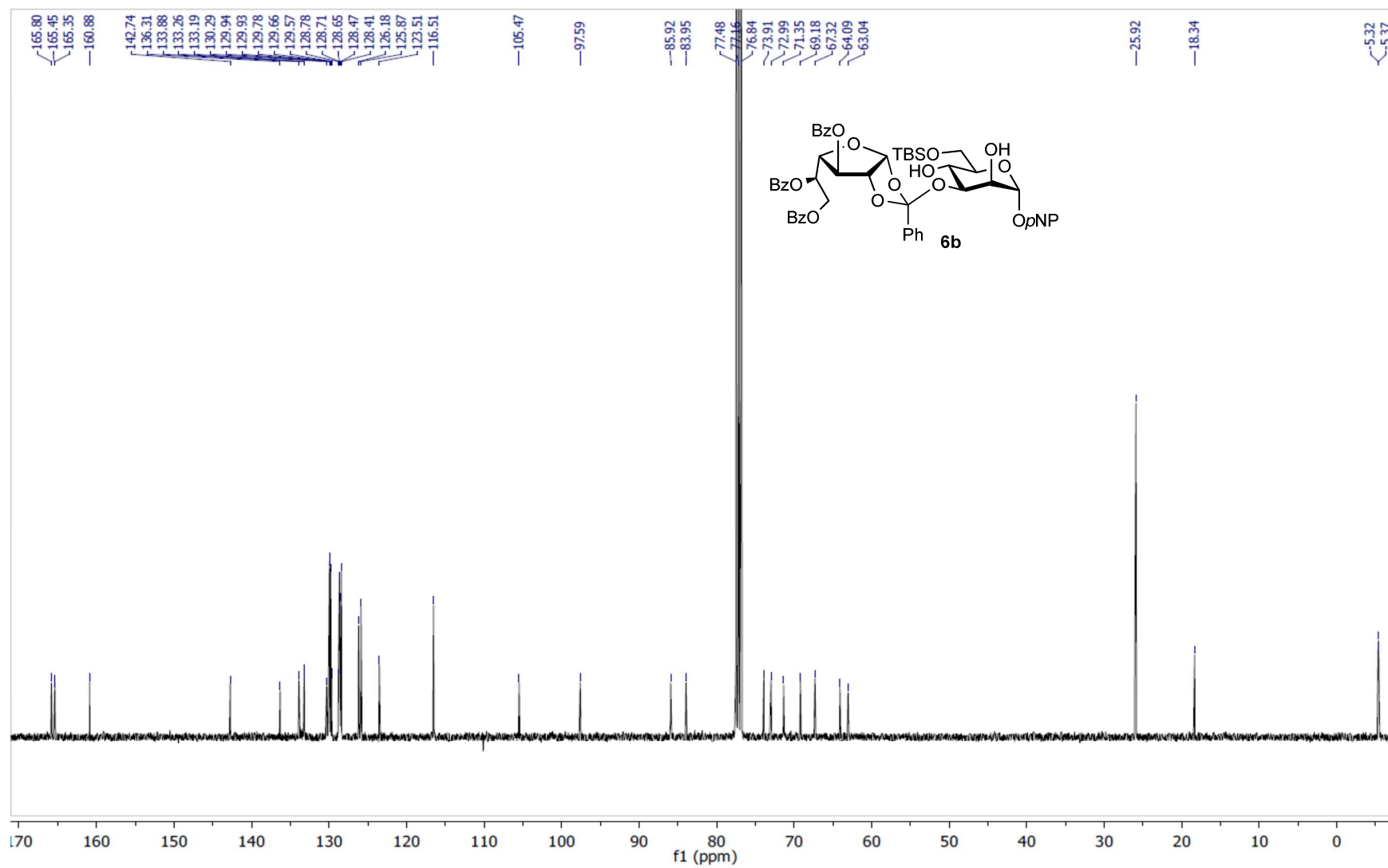
¹H NMR Spectrum of **5b** (400 MHz, CDCl₃)



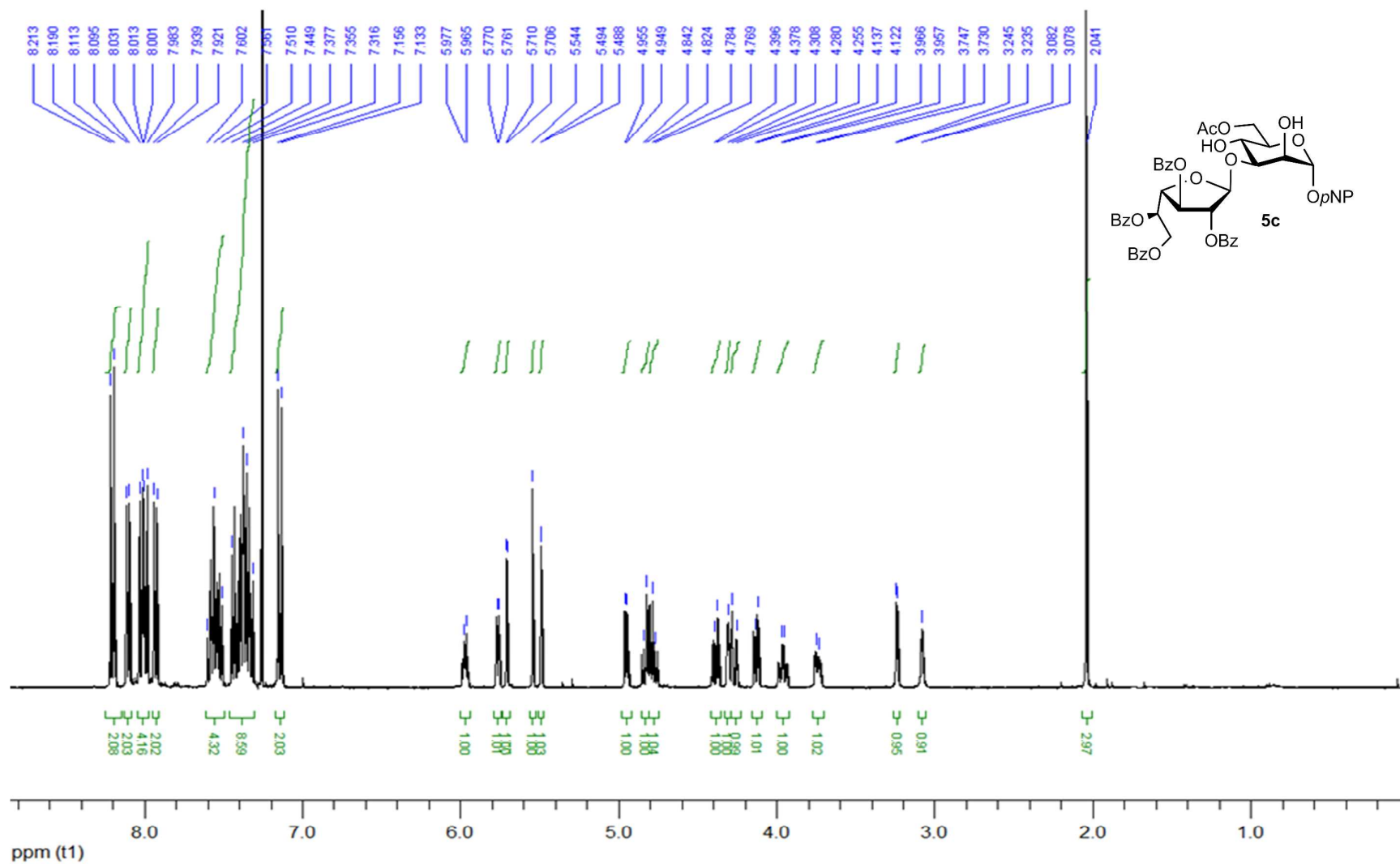
^{13}C NMR Spectrum of **5b** (100 MHz, CDCl_3)



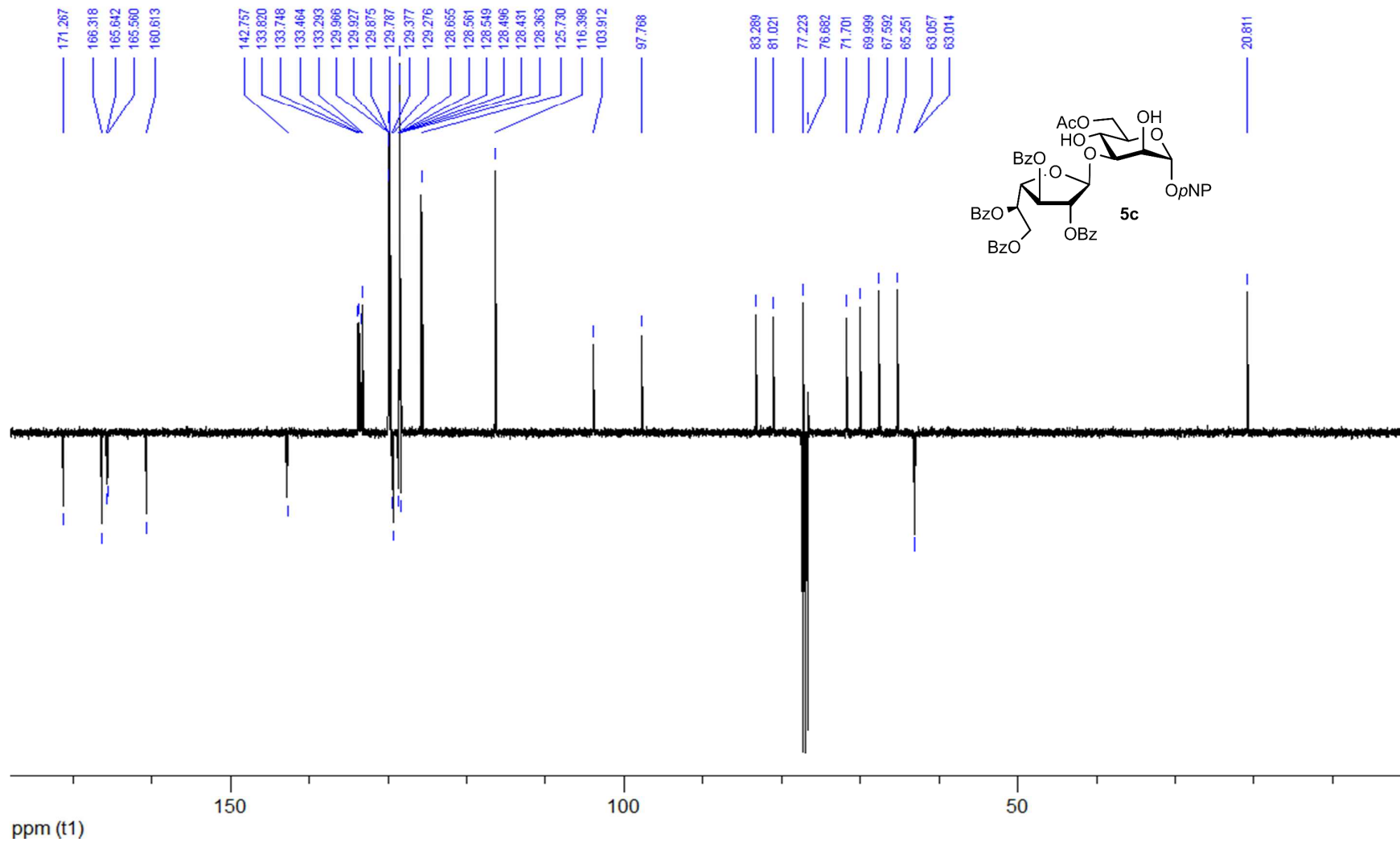
¹H NMR Spectrum of **6b** (400 MHz, CDCl₃)



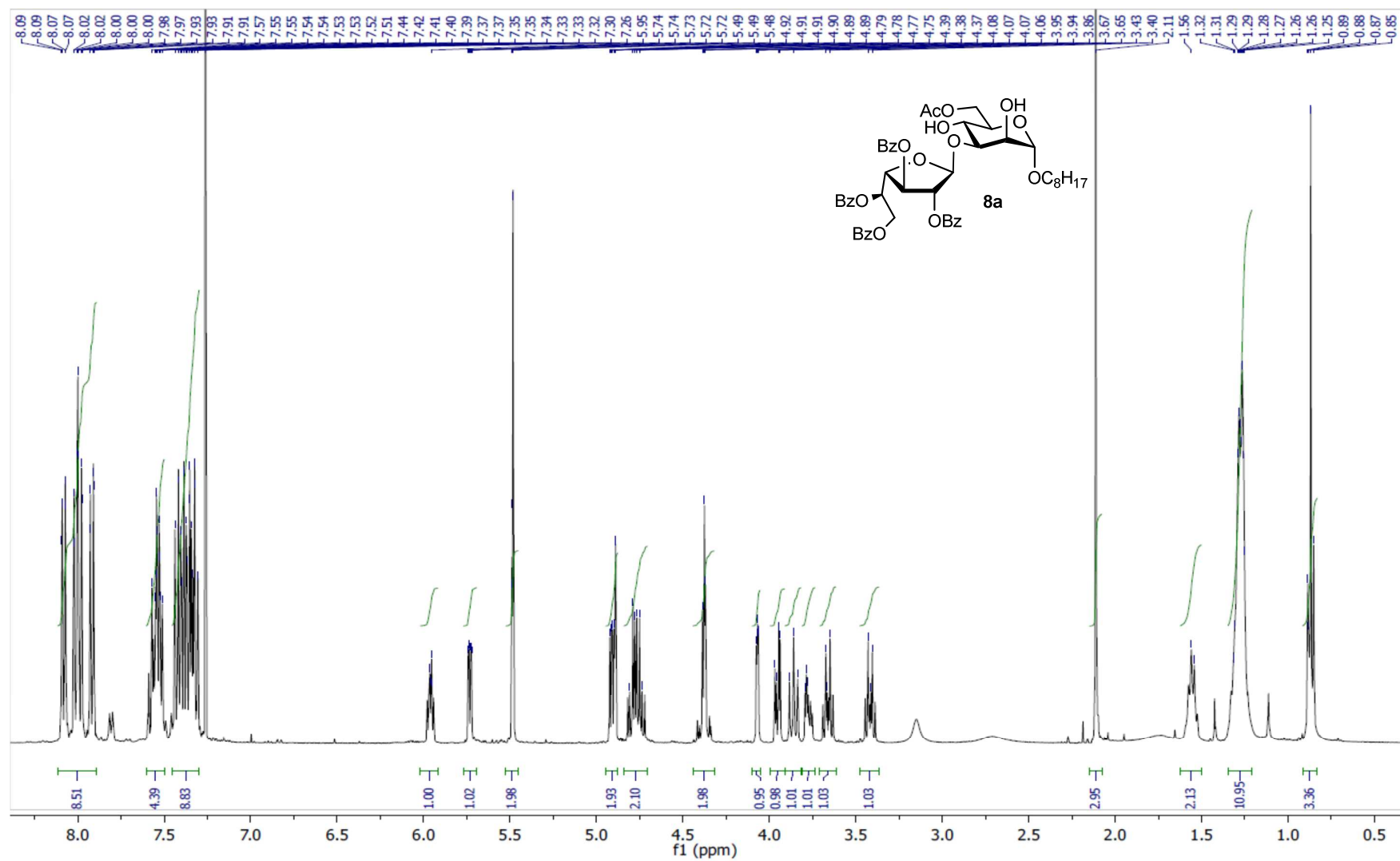
^{13}C NMR Spectrum of **6b** (100 MHz, CDCl_3)



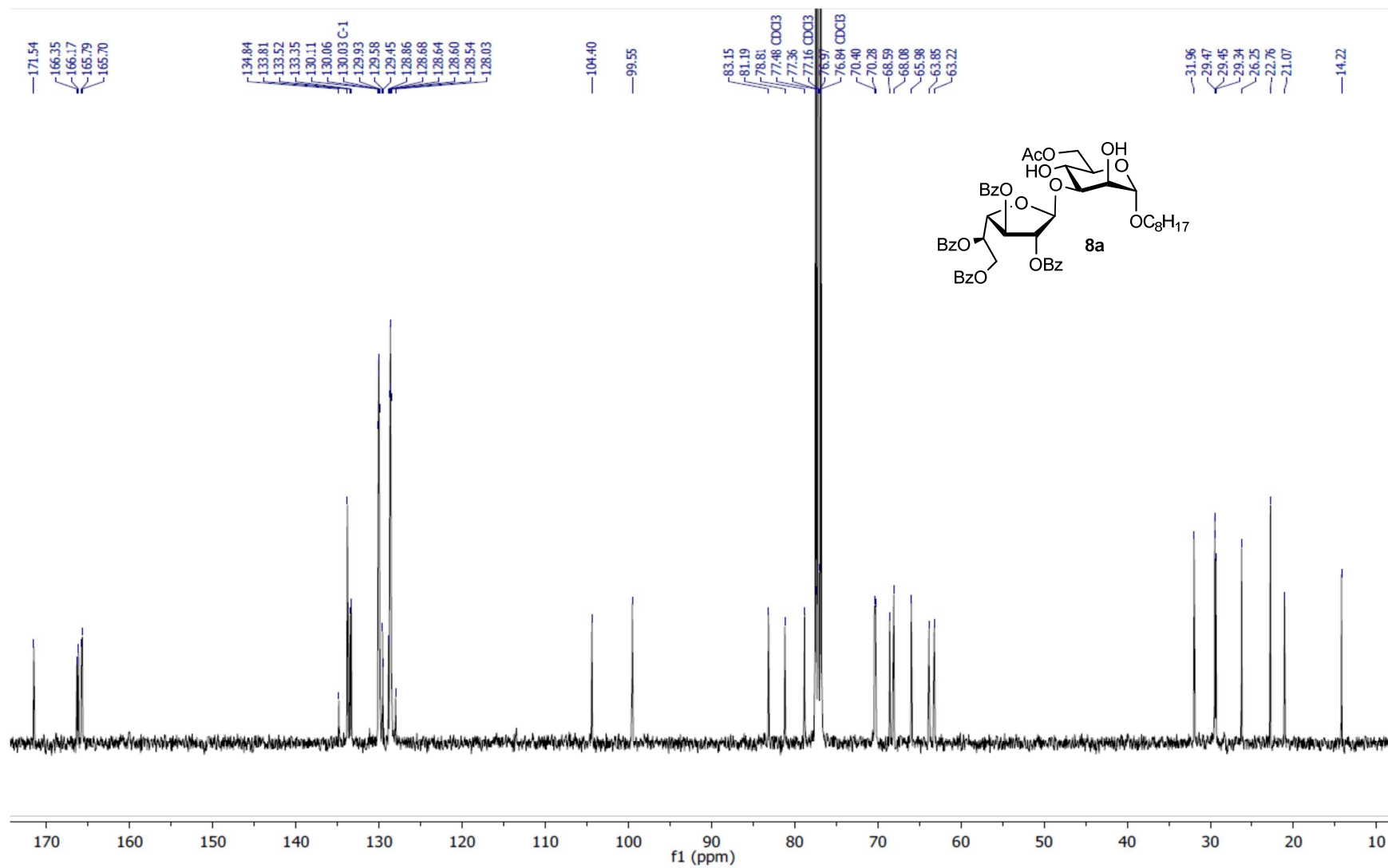
¹H NMR Spectrum of **5c** (400 MHz, CDCl₃)



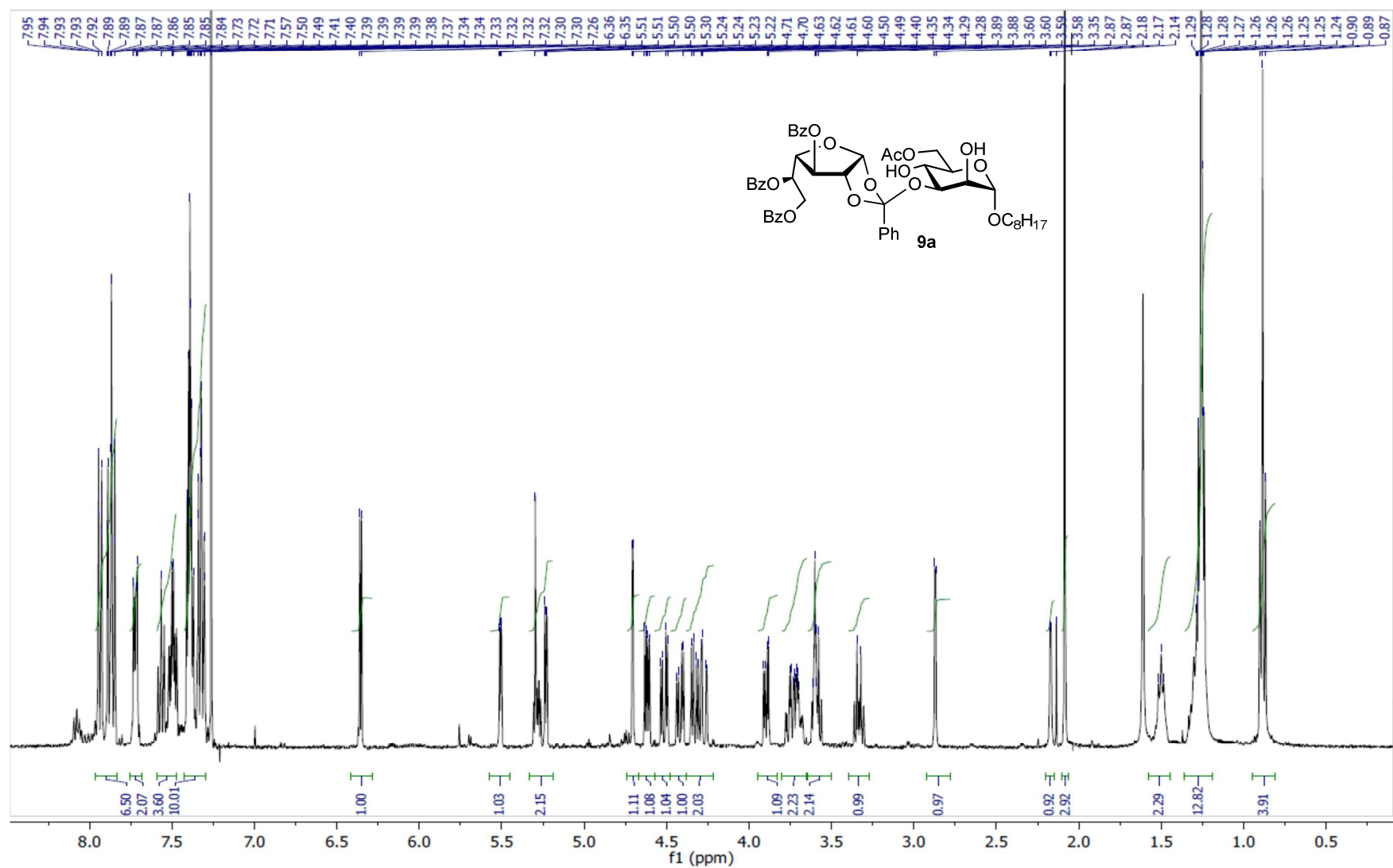
¹³C NMR Spectrum of **5c** (100 MHz, CDCl₃)



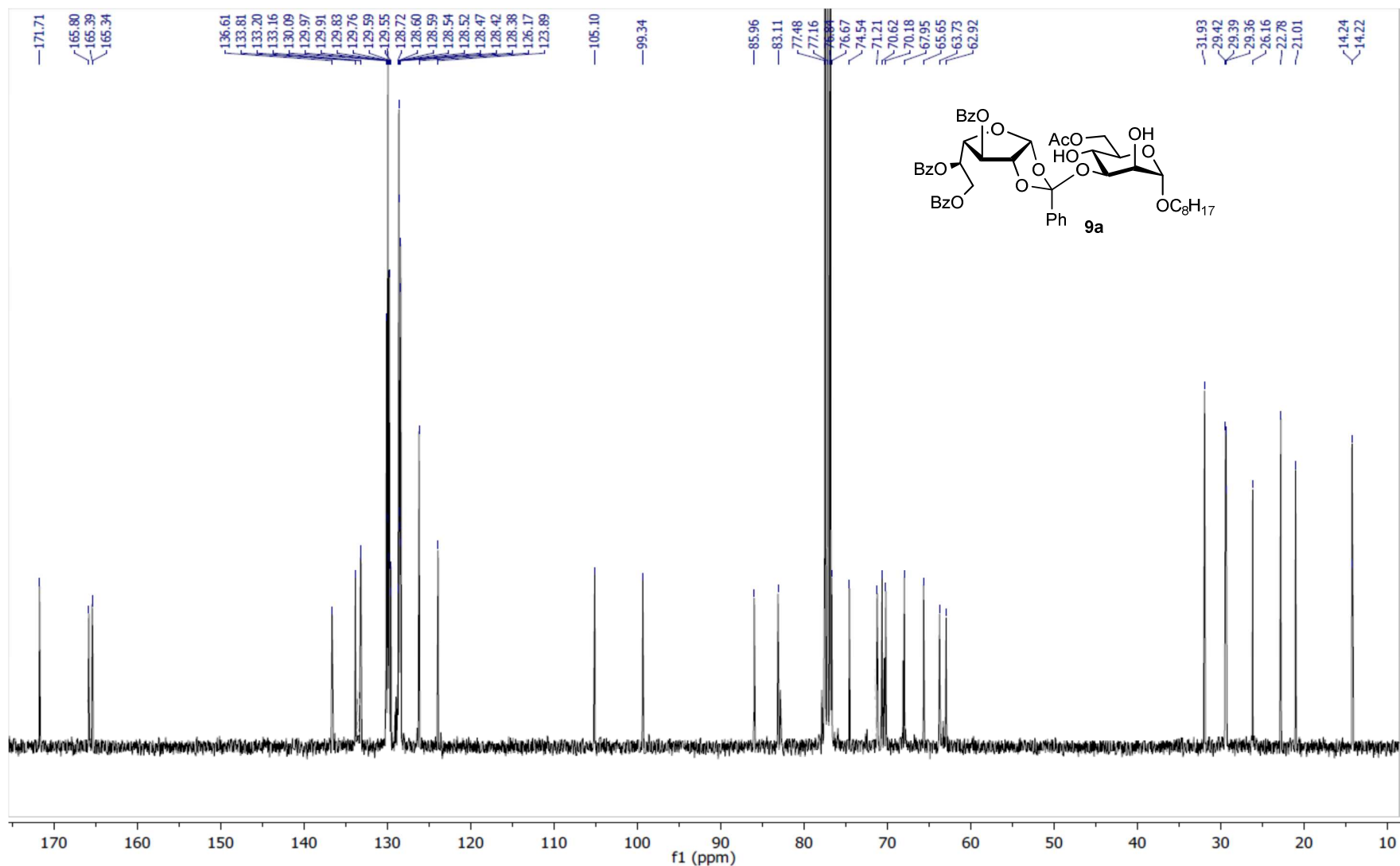
¹H NMR Spectrum of **8a** (400 MHz, CDCl₃)



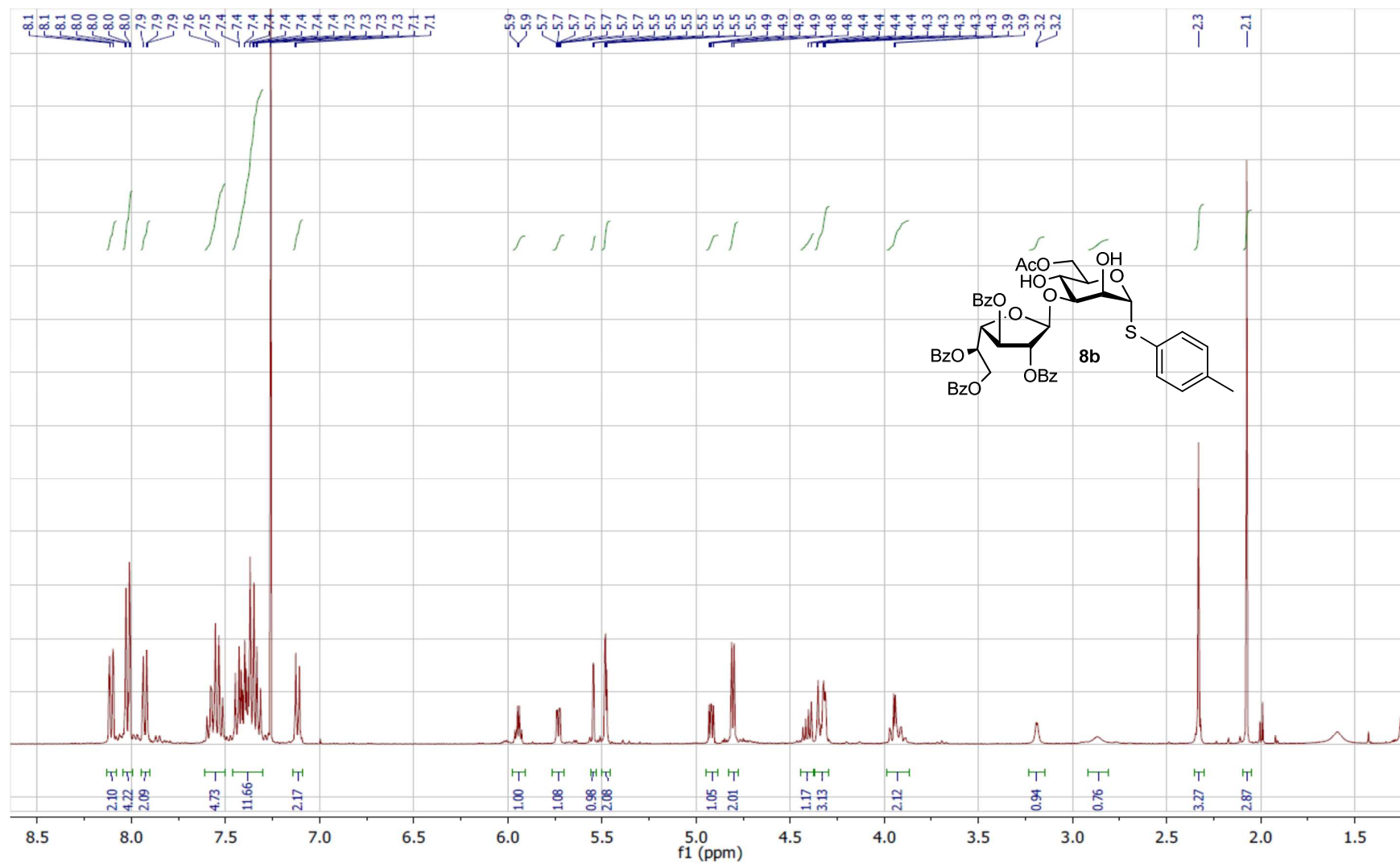
¹³C NMR Spectrum of **8a** (100 MHz, CDCl₃)



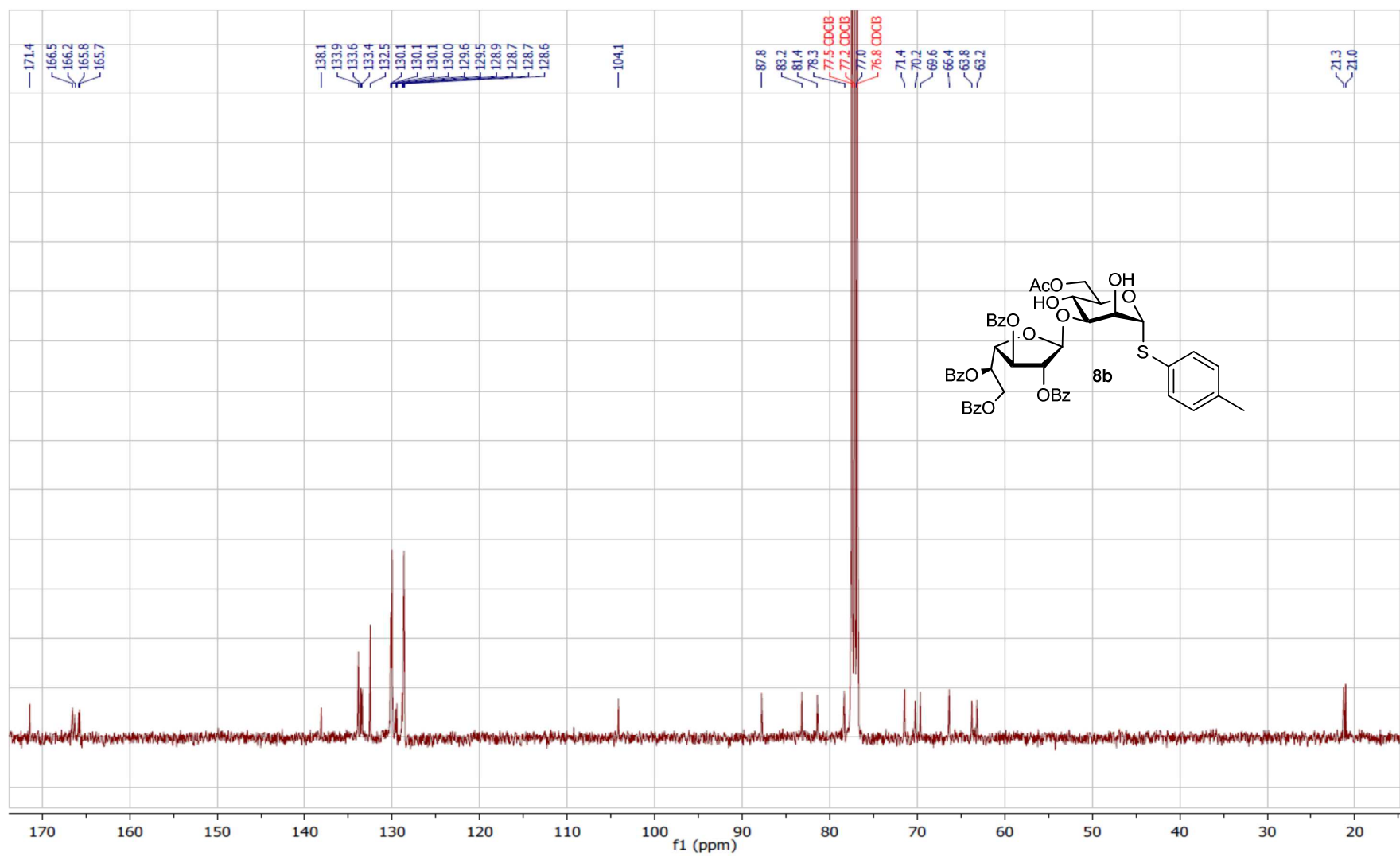
¹H NMR Spectrum of **9a** (400 MHz, CDCl₃)



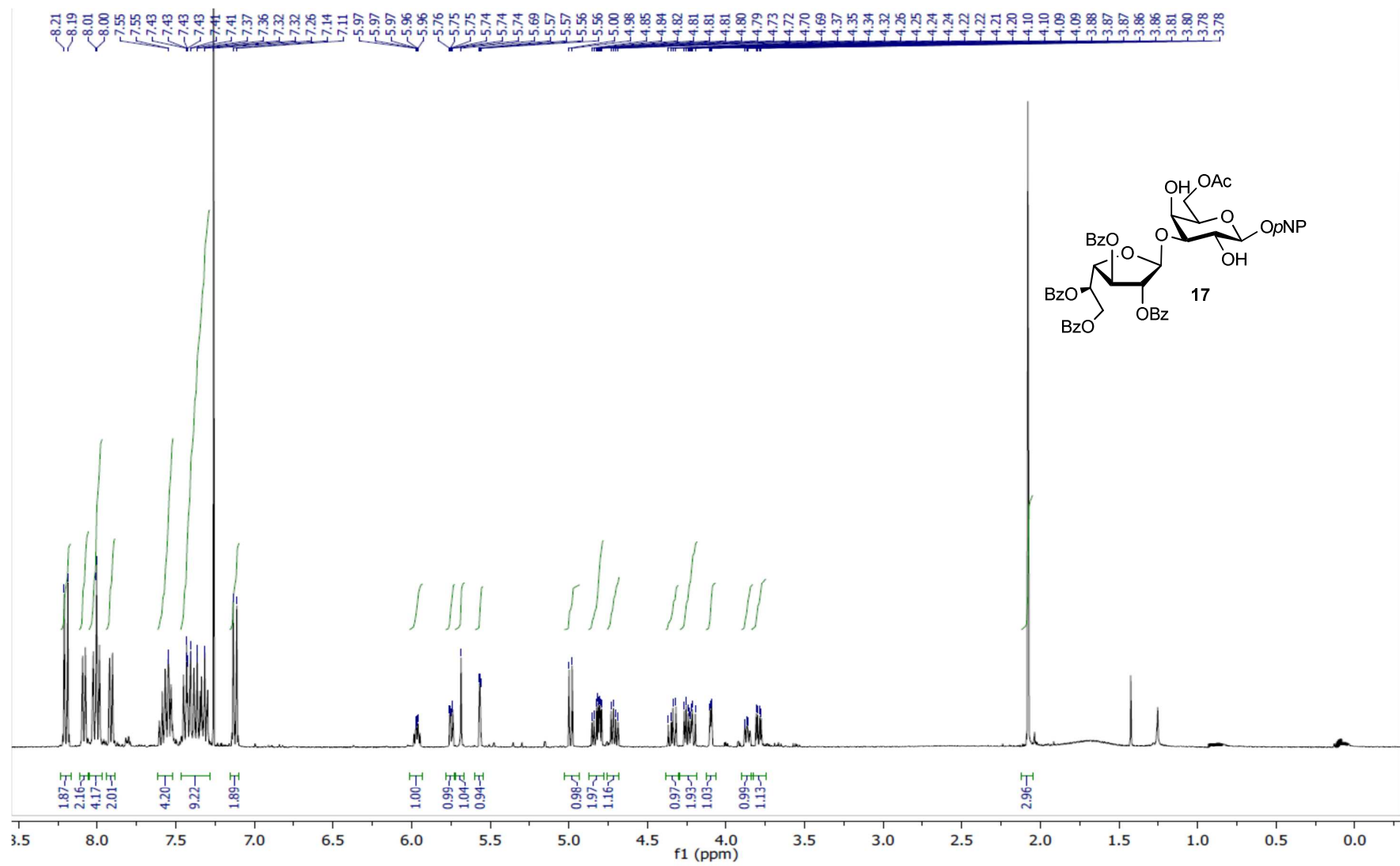
^{13}C NMR Spectrum of **9a** (100 MHz, CDCl_3)



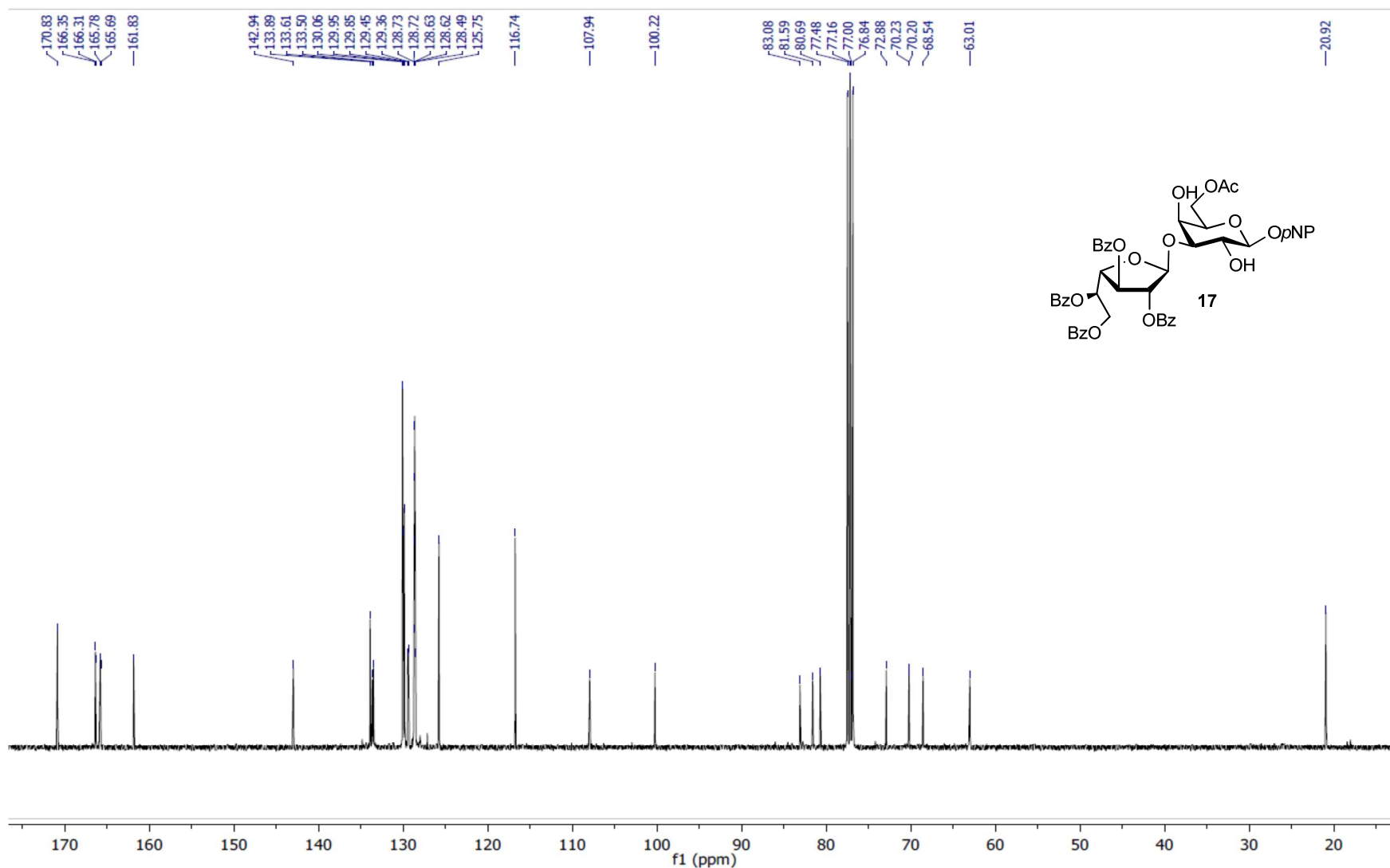
¹H NMR Spectrum of **8b** (400 MHz, CDCl₃)



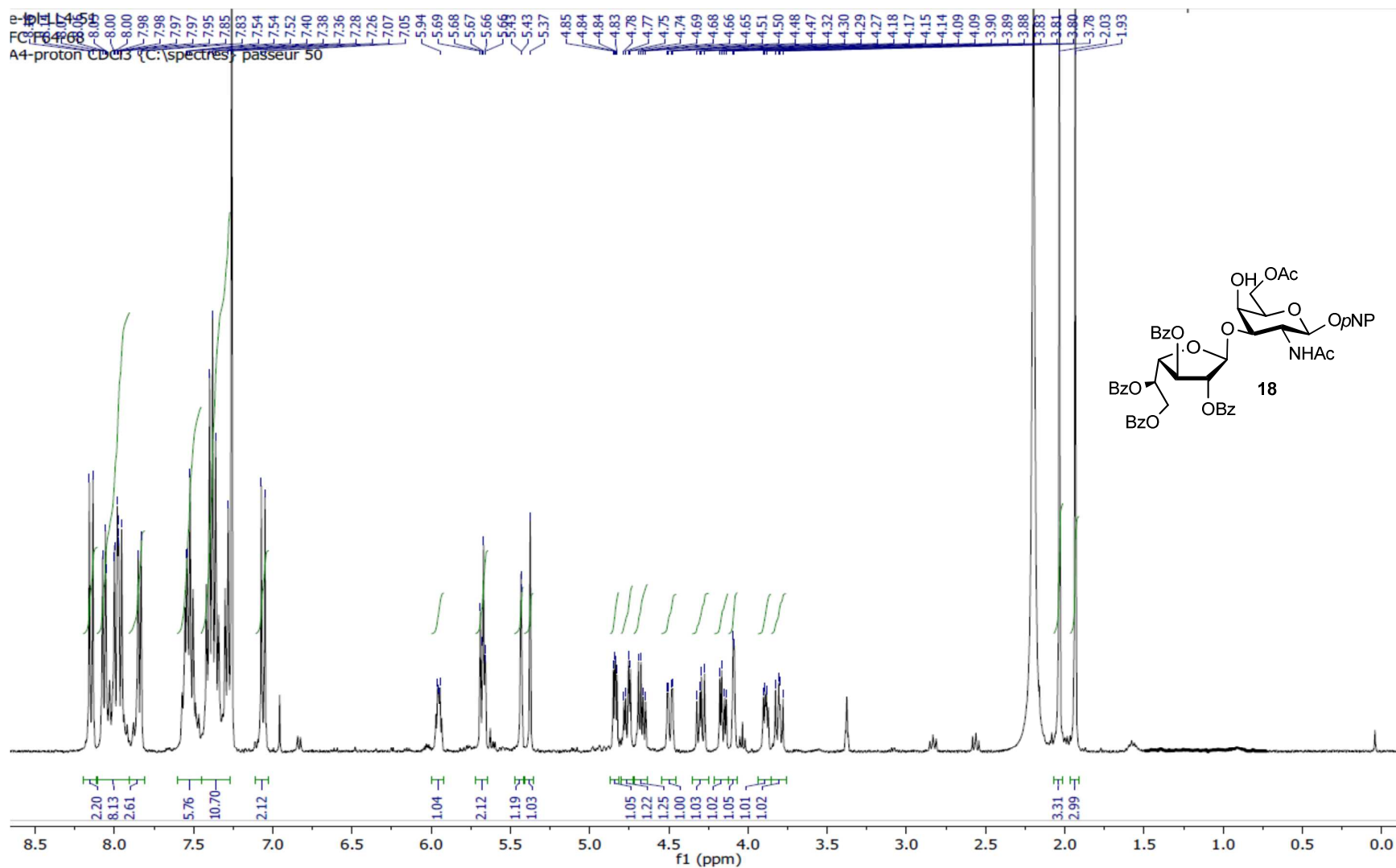
¹³C NMR Spectrum of **8b** (100 MHz, CDCl₃)



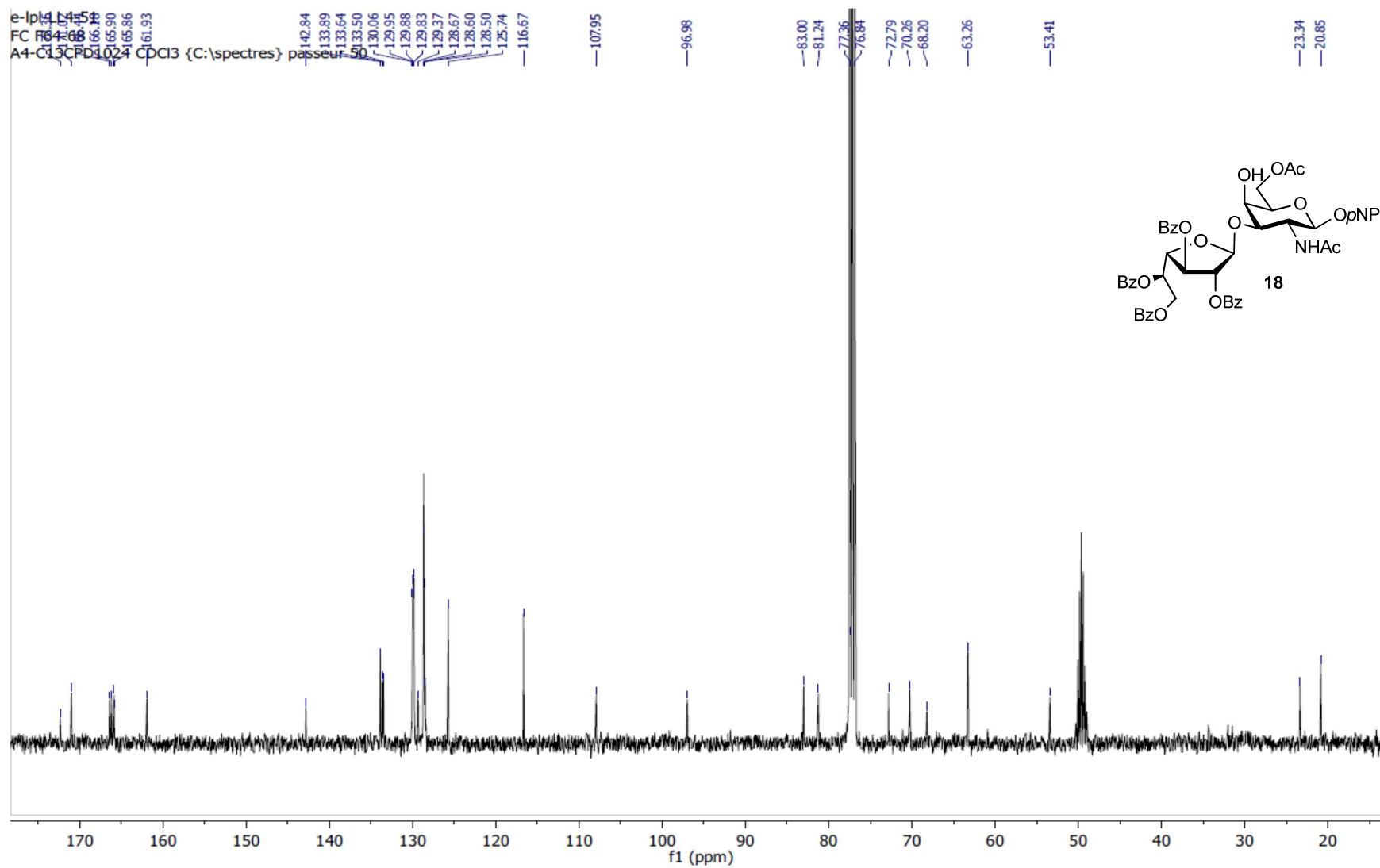
¹H NMR Spectrum of 17 (400 MHz, CDCl₃)



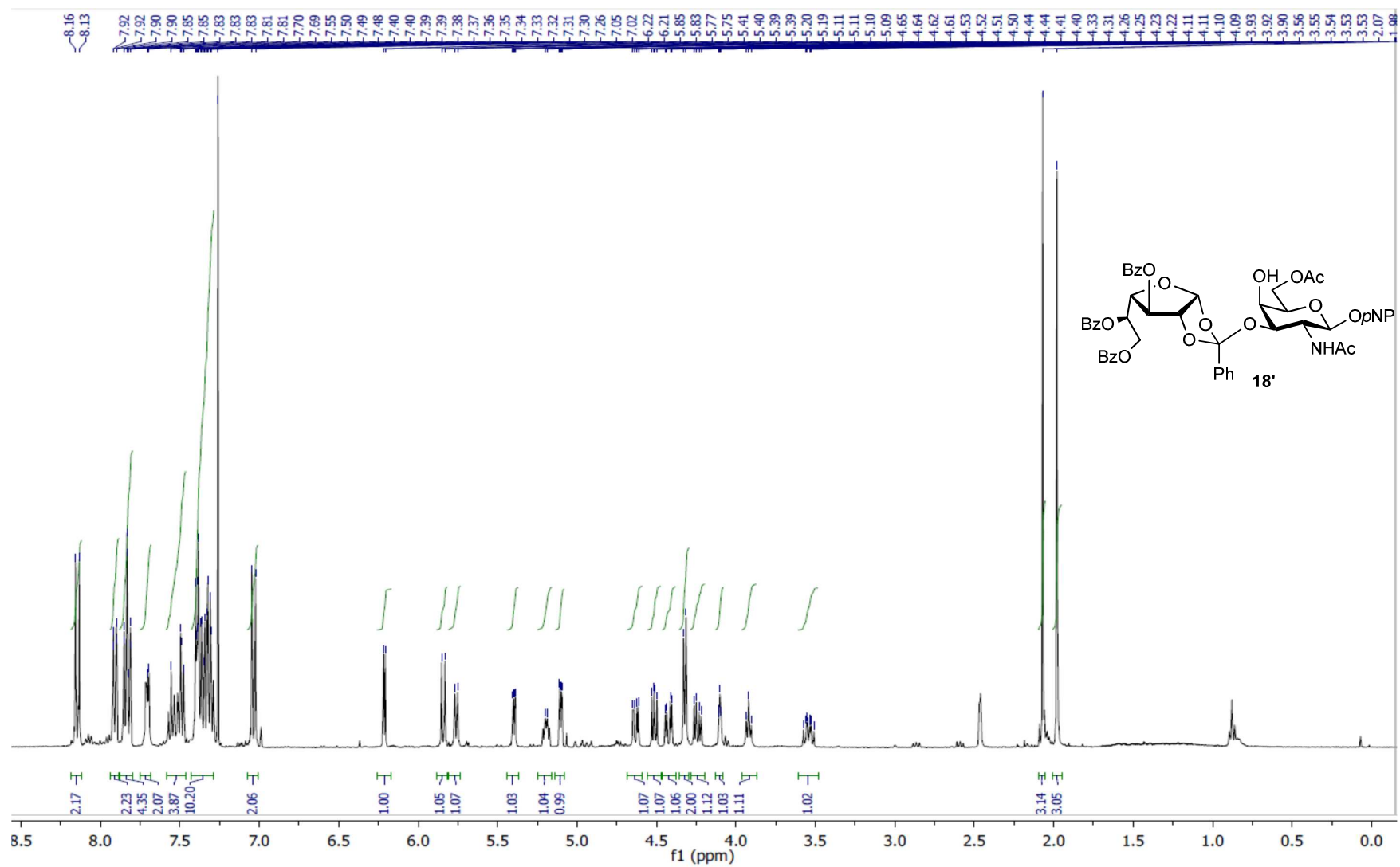
^{13}C NMR Spectrum of **17** (100 MHz, CDCl_3)



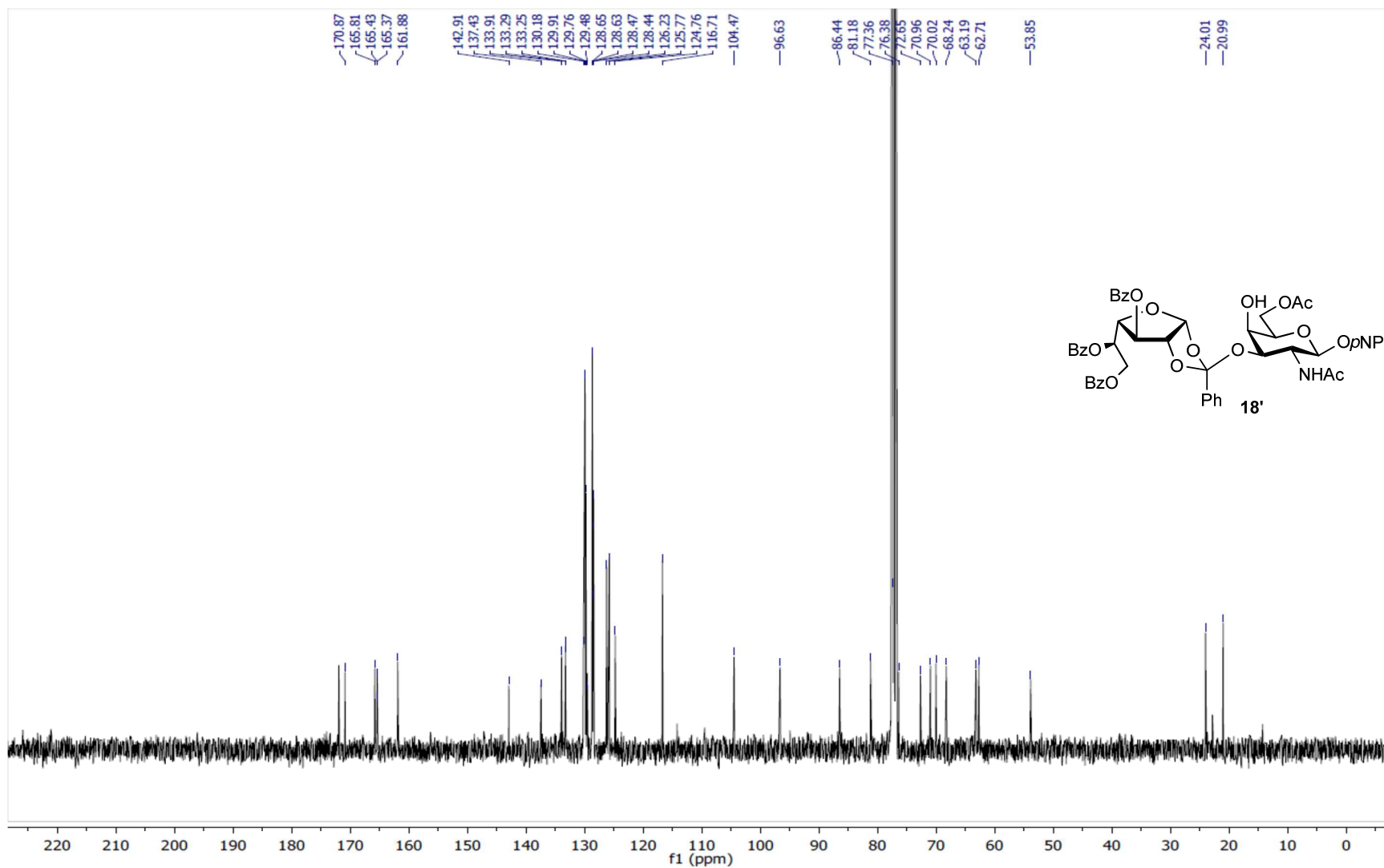
¹H NMR Spectrum of **18** (400 MHz, CDCl₃)



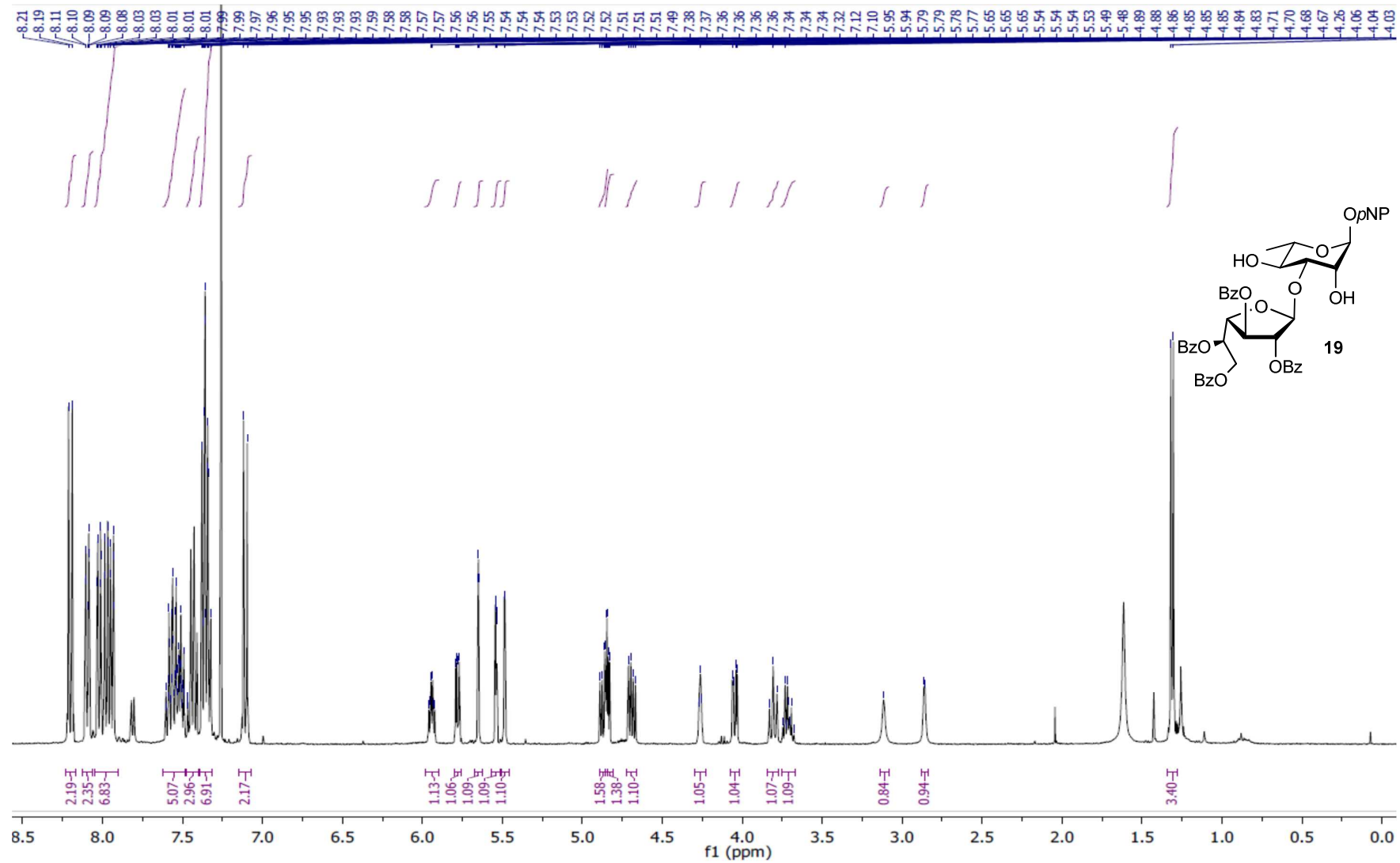
¹³C NMR Spectrum of **18** (100 MHz, CDCl₃)



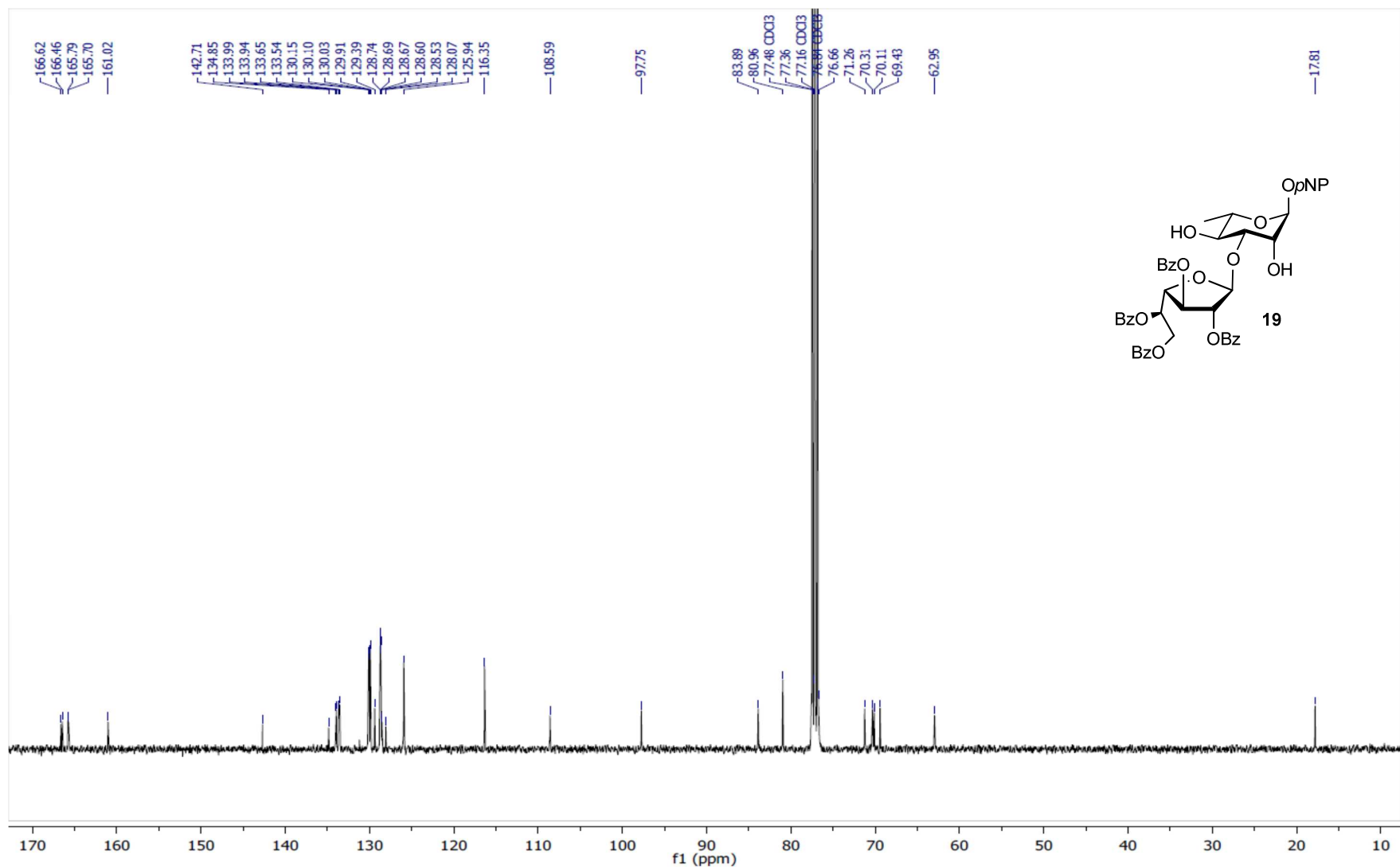
¹H NMR Spectrum of **18'** (400 MHz, CDCl₃)



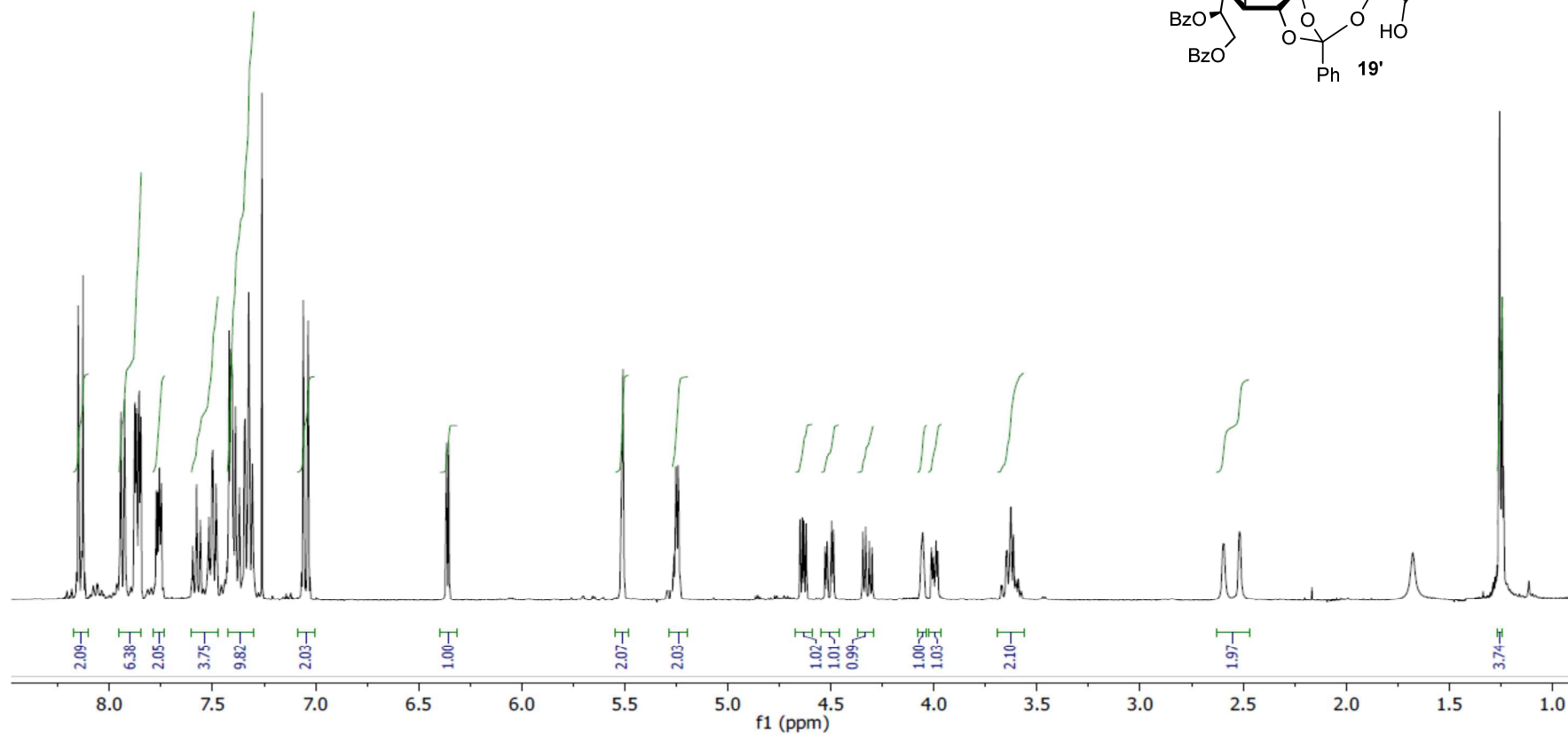
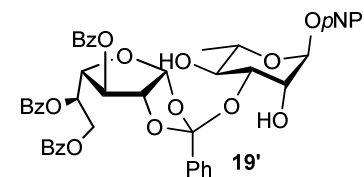
^{13}C NMR Spectrum of **18'** (100 MHz, CDCl_3)



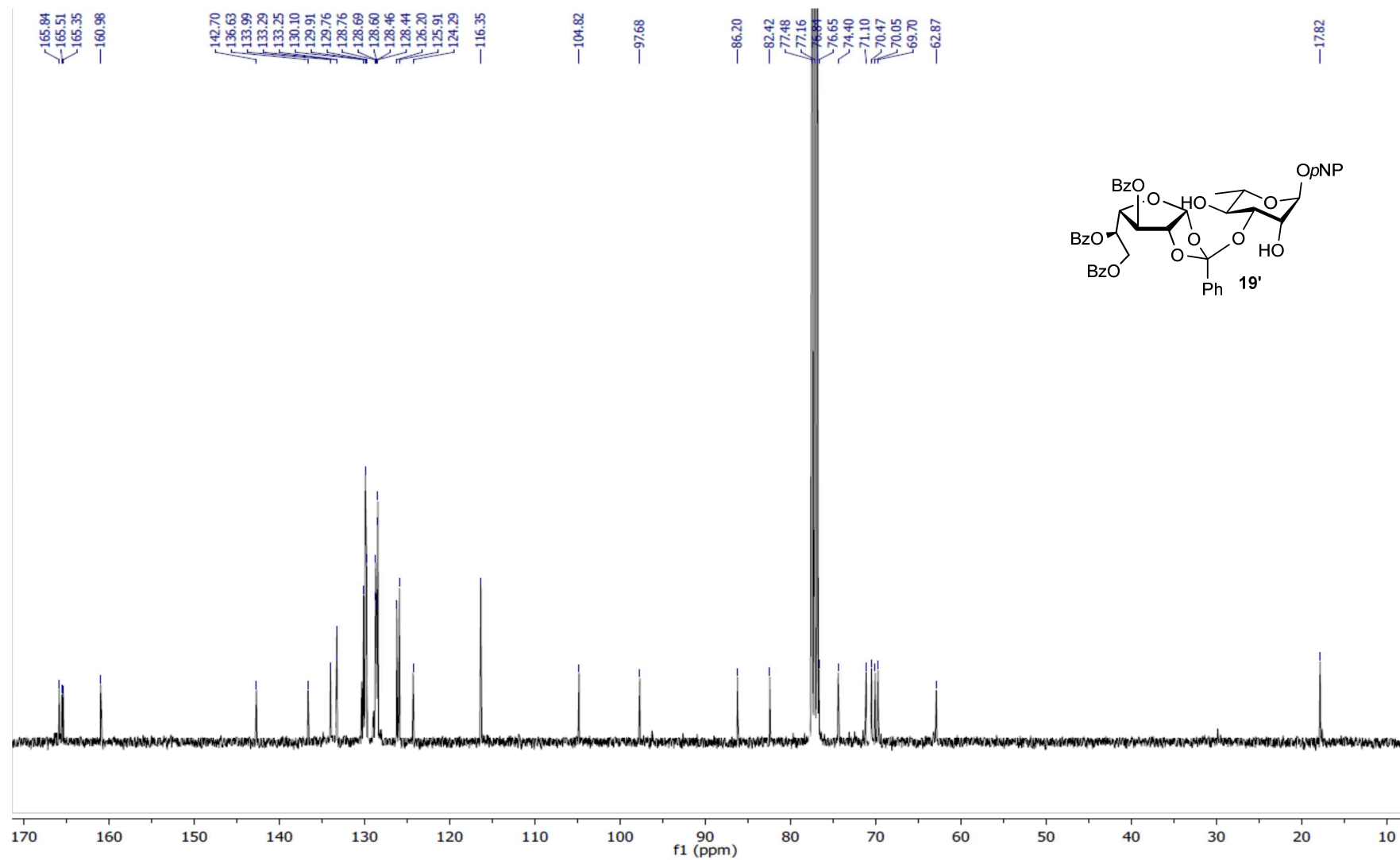
¹H NMR Spectrum of **19** (400 MHz, CDCl₃)



¹³C NMR Spectrum of **19** (100 MHz, CDCl₃)

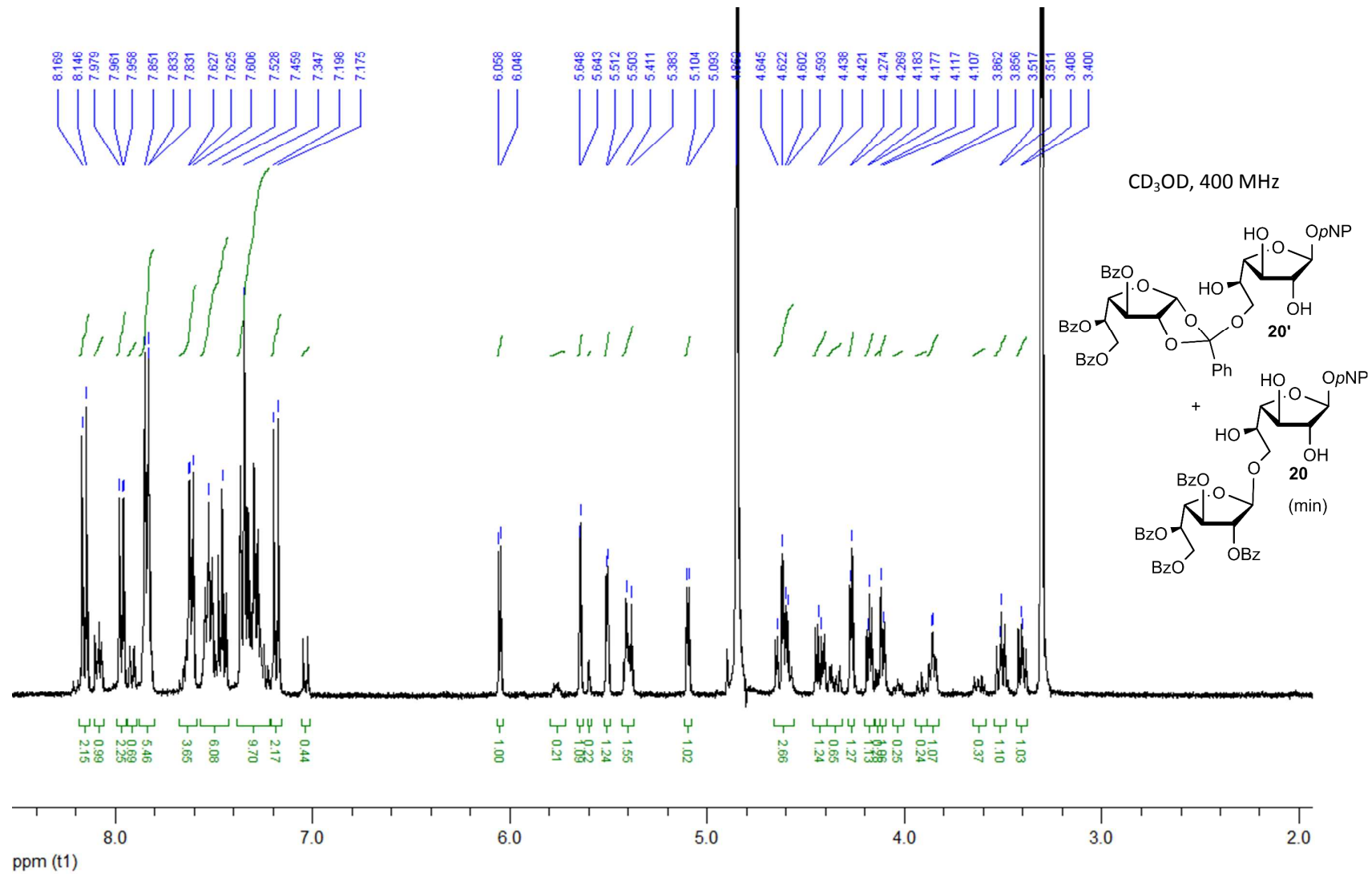


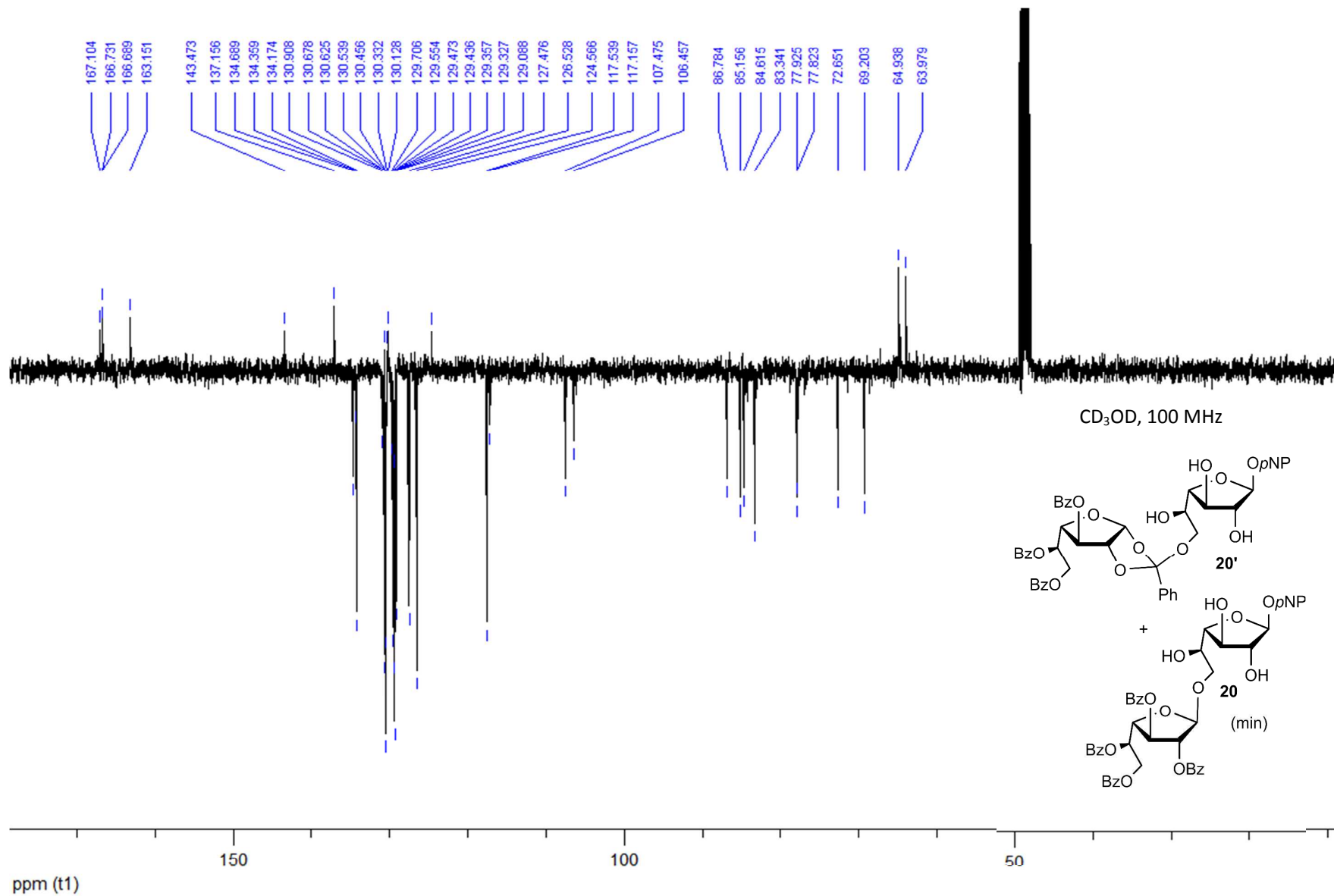
¹H NMR Spectrum of **19'** (400 MHz, CDCl₃)



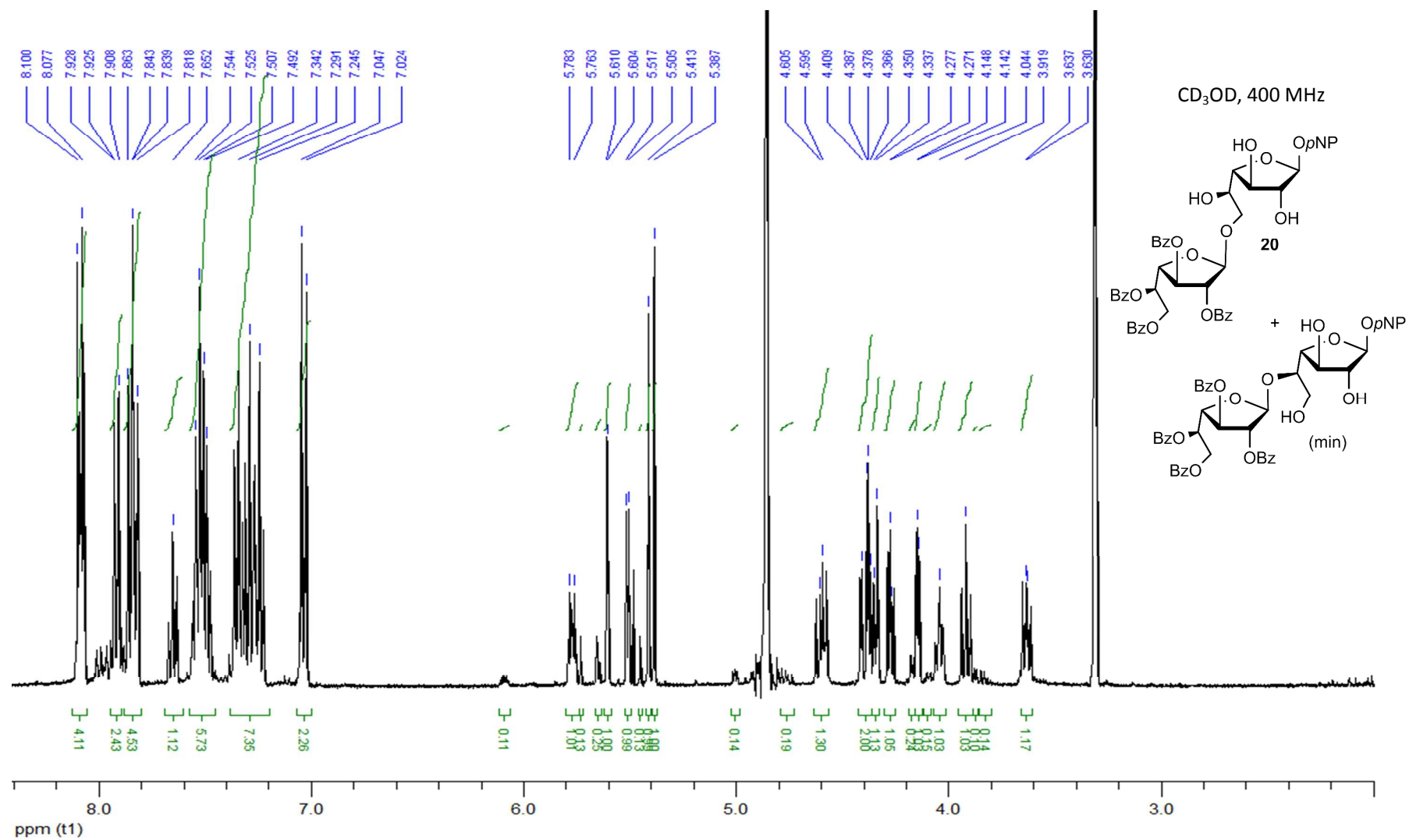
^{13}C NMR Spectrum of **19'** (100 MHz, CDCl_3)

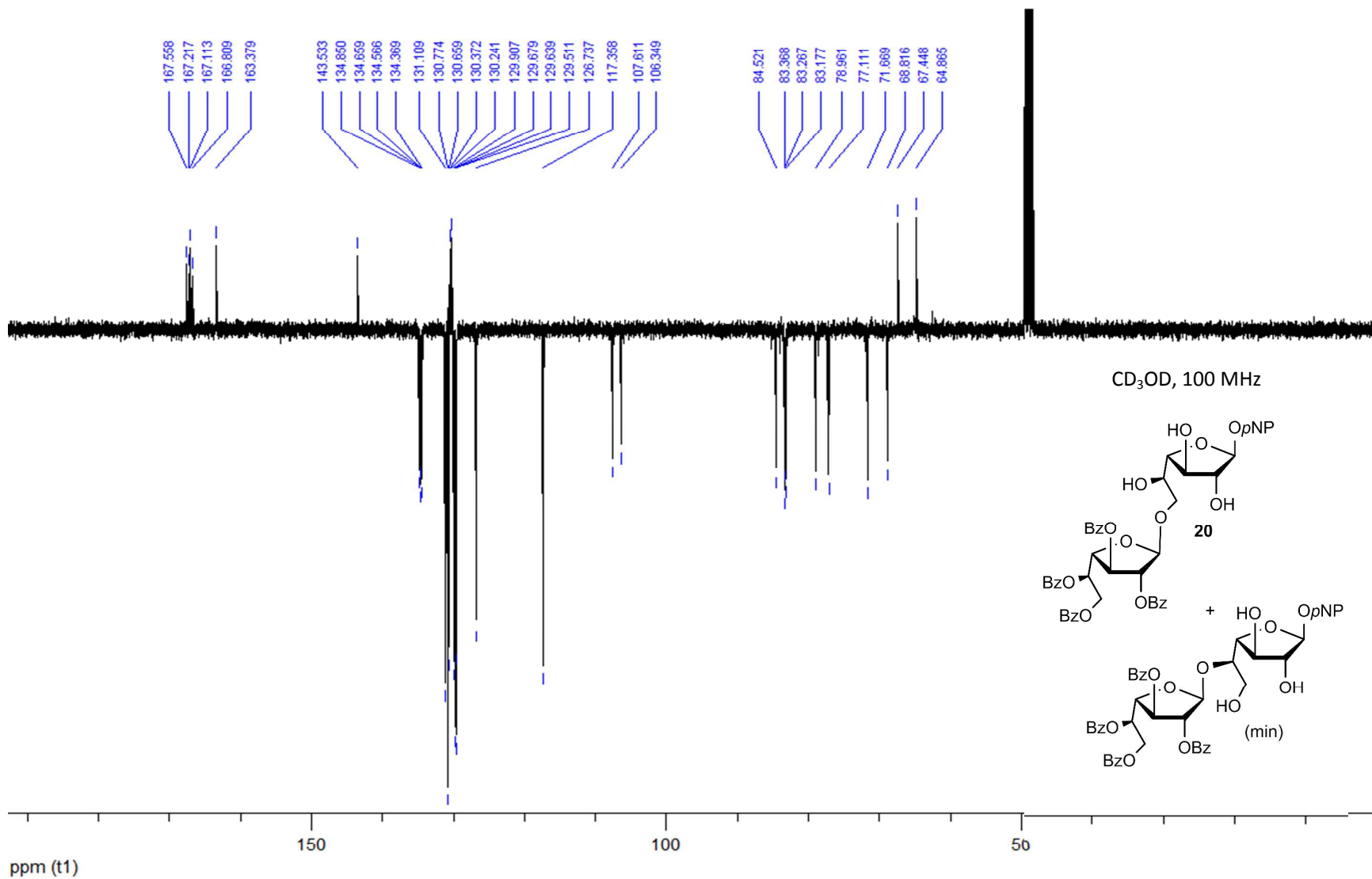
^1H and ^{13}C NMR spectrum of isolated disaccharides from the glycosylation of pNP-Galf in presence of Ag_2O





^1H and ^{13}C NMR spectrum of isolated disaccharides from the glycosylation of pNP-Galf in presence of AgOTf





167.598
167.217
167.113
166.809
163.379

143.533
134.850
134.659
134.586
134.389
131.109
130.774
130.659
130.372
130.241
129.907
129.679
129.639
129.511
126.737
117.358
107.611
106.349

84.521
83.368
83.267
83.177
78.961
77.111
71.669
68.816
67.448
64.865