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

Supplementary Information

for

D-Allose, a rare sugar. Synthesis of D-allopyranosyl acceptors from glucose, and their regioselectivity in glycosidation reactions

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Computational methods

Molecular mechanics calculations were carried out using the program MM3(92) (QCPE, Indiana, USA)[1,2] Quantum mechanical calculations were carried out using Gaussian 09W (rev. C.01),[3] with standard termination options.

From a given rotamer, an automated routine was used to generate the starting conformations produced by rotation of ± 120° for each of the exocyclic dihedrals. Those conformers within the first 10 kcal/mol were submitted to DFT optimizations at the B3LYP/6-311+G** level and then to single point calculations with M06-2X at the same level. Charges were then obtained with M06-2X at the same level of theory, for both the ground molecule and the radical cation, using the Mulliken,[4] CHelp,[5] CHelpG,[6] Merz-Singh-Kollman (MK)[7,8] and NPA[9,10] charge distribution schemes. Condensed-to-atom Fukui functions and charges were then obtained as Boltzmann average ratios

Stationary points were characterized by frequency calculations in order to verify that the minima had no imaginary frequencies. Population analysis was carried out using the Boltzmann equation, with a temperature of 298 K and using electronic energies for DFT.

Table S.1. Relative energies and geometries of the conformers found by B3LYP/6-311+G** on analogues of compounds **1-3**

Conformer	ΔE	χ_1[a]	χ_2[a]	χ_3[a]	χ_4[a]	ω[a]	χ_5[a]
1'							
1	0.00	-49	55	-151	-156	75	-178
2	0.33	-45	56	-151	-156	-68	-180
3	0.93	-51	-51	-147	-156	74	-179
4	1.08	-47	56	-151	-156	71	-92
5	1.20	-45	56	-151	-155	-66	94
6	1.37	-48	-47	-147	-156	-68	-179
7	1.47	-52	-58	-89	-160	75	-178
8	1.56	-47	55	-150	-155	74	85
9	1.89	-49	-57	-87	-159	-67	-179
10	2.11	-50	-49	-147	-156	71	-93
11	2.37	-48	-47	-147	-156	-66	94
12	2.47	-49	-50	-146	-156	74	86

13	2.68	-50	-57	-88	-160	71	-94
14	2.73	-51	168	-157	-156	74	-178
15	2.88	-49	-56	-87	-159	-65	94
16	2.93	-50	-57	-88	-159	75	85
17	3.44	-44	59	-151	81	179	-179
18	4.66	-49	-56	-86	86	179	-179
2'							
1	0.00	-48	35	-153	-154	73	-173
2	0.08	-49	-37	-151	-156	73	-173
3	0.19	-46	34	-152	-155	-67	175
4	0.23	-47	-37	-151	-156	-67	173
5	0.88	-47	34	-153	-159	64	85
6	0.91	-47	-38	-151	-161	65	85
7	2.03	-48	35	-155	-151	-172	-75
8	2.10	-49	-38	-153	-153	-171	-74
9	2.26	-47	-38	-151	-157	171	103
10	2.30	-46	35	-153	-155	170	105
11	2.67	-47	-38	-150	-162	150	165
12	2.69	-47	35	-152	-160	150	167
13	2.72	-47	-39	-150	42	-62	-96
14	2.74	-44	-39	68	46	-63	-95
15	2.81	-46	33	-153	41	-63	-96
16	2.83	-43	33	68	45	-64	-95
17	4.63	-50	160	-78	-159	73	-173
3'							
1	0.00	51	-30	-70	-159	75	-178
2	0.46	52	-29	-68	-158	-67	-179
3	1.11	50	-29	-68	-158	-66	91
4	1.20	49	-29	-69	-159	73	-92
5	1.42	52	-31	-69	-157	73	84
6	1.61	48	-28	71	79	-178	180
7	2.15	45	51	73	80	-178	-180
8	2.45	49	-29	-67	82	-179	-180

[a]Dihedral angle χ_n, defined by the atoms H-n-C-n-O-n-H(O)-n, with n = 1 to 4. Angle χ_6 defined by the atoms C-5-C-6-O-6-H(O)-and ω by the atoms O-5-C-5-C-6-O-6.

Table S.2 Relative energies and hydrogen bonding interactions for some conformers of analogues of compounds **1-3**

		Hydrogen bonding					
Confórmero	ΔE (kcal/mol)		d(O···H) (Å)	Θ (°)[a]		d(O···H) (Å)	Θ (°)[a]
1'							
1	0.00	OH-3···O-1	1.99	140	OH-4···O-3	2.17	116
2	0.33	OH-3···O-1	1.98	140	OH-4···O-3	2.16	116
3	0.93	OH-3···O-1	2.02	140	OH-4···O-3	2.16	116
4	1.08	OH-3···O-1	1.99	140	OH-4···O-3	2.17	116
...							
18	4.66	OH-3···O-2	2.23	113	OH-4···O-6	1.95	143
2'							
1	0.00	OH-3···O-1	1.99	140	OH-4···O-3	2.17	116
2	0.08	OH-3···O-1	1.99	140	OH-4···O-3	2.17	116
3	0.19	OH-3···O-1	1.98	140	OH-4···O-3	2.18	116
4	0.23	OH-3···O-1	1.98	141	OH-4···O-3	2.17	116
...							
16	2.83	OH-3···O-4	2.24	109	OH-4···O=C	1.95	152
17	4.63	OH-3···O=C	1.74	154	OH-4···O-3	2.10	114
3'							
1	0.00	OH-3···O-2	2.20	109	OH-4···O-3	2.15	113
2	0.46	OH-3···O-2	2.22	108	OH-4···O-3	2.15	114
3	1.11	OH-3···O-2	2.23	108	OH-4···O-3	2.15	114
4	1.20	OH-3···O-2	2.22	108	OH-4···O-3	2.16	113
...							
6	1.61	OH-3···O-4	2.20	111	OH-4···O-6	1.96	140

[a]Angle Θ defined by the atoms O-H···O.

Table S.3 Differences in Fukui indices on O-3 and O-4 calculated by B3LYP and M06-2X.

	Mulliken	Chelp	ChelpG	MK	NPA	MC
B3LYP						
1'	–0.035	–0.038	–0.045	–0.052	–0.047	–0.062
2'	–0.065	–0.050	–0.079	–0.088	–0.075	–0.211
3'	–0.018	–0.034	–0.052	–0.058	–0.021	–0.033
M06-2x						
1'	–0.067	–0.070	–0.089	–0.098	–0.078	–0.094
2'	–0.128	–0.117	–0.158	–0.168	–0.150	–0.164
3'	–0.039	–0.057	–0.080	–0.085	–0.046	–0.037

Table S.4. Coordinates of minimal energy conformers

1'		**Conformer 1**			**Conformer 2**		
atom	x	Y	z	atom	X	y	z
C	–0.711286	1.160779	–0.559816	C	–0.881415	1.086809	–0.620280
C	–1.712945	0.011177	–0.730474	C	–1.421189	–0.337923	–0.797524
C	–1.308871	–1.189419	0.140590	C	–0.901870	–1.254871	0.320066
C	0.164106	–1.570380	–0.123311	C	0.634212	–1.165916	0.396771
C	1.082160	–0.339265	–0.022439	C	1.116876	0.295638	0.452107
C	2.503549	–0.641096	–0.448804	C	2.623655	0.423958	0.329373
O	0.590408	0.716622	–0.872686	O	0.526741	1.083147	–0.602179
H	–0.923822	1.963447	–1.273744	H	–1.160416	1.708135	–1.477172
O	–0.812397	1.646519	0.760369	O	–1.432452	1.625522	0.565547
O	–3.003904	0.519652	–0.470501	O	–2.828260	–0.251920	–0.889210
H	–1.638795	–0.306294	–1.782352	H	–1.003378	–0.708497	–1.746172
H	–1.921573	–2.060566	–0.108839	H	–1.159439	–2.295891	0.105507
O	–1.509516	–0.961646	1.534097	O	–1.478545	–0.969903	1.594955
H	0.247581	–1.995357	–1.129570	H	1.072327	–1.639774	–0.483990
O	0.563859	–2.584557	0.784820	O	1.099822	–1.881637	1.531899
H	1.101210	0.006810	1.016750	H	0.828221	0.720425	1.422194
H	2.546291	–0.720251	–1.545565	H	3.082513	–0.035109	1.215744
H	2.805301	–1.603398	–0.014709	H	2.890971	1.490666	0.307931
O	3.355309	0.396804	0.006020	O	3.073388	–0.219852	–0.847972
C	4.700291	0.214623	–0.389625	C	4.474548	–0.142436	–1.014741
C	–4.070055	–0.361896	–0.787293	C	–3.479735	–1.457961	–1.256660
C	–0.101906	2.864516	0.994584	C	–1.286895	3.038187	0.697593
H	–1.400266	–0.012811	1.701699	H	–1.694673	–0.025281	1.622079
H	0.148012	–2.366921	1.632035	H	0.445341	–1.732574	2.230024
H	4.800284	0.212825	–1.484188	H	5.005829	–0.617034	–0.177740
H	5.111728	–0.726661	0.001889	H	4.811535	0.900459	–1.099784
H	5.272416	1.048824	0.017394	H	4.719619	–0.670250	–1.936778
H	–4.108164	–1.218708	–0.105657	H	–3.427780	–2.209028	–0.460858
H	–3.993316	–0.724805	–1.821768	H	–3.053837	–1.877132	–2.178879
H	–4.989746	0.213015	–0.680276	H	–4.525140	–1.204313	–1.431989
H	–0.478089	3.655098	0.335169	H	–1.785528	3.552260	–0.132093
H	0.971323	2.733804	0.833131	H	–0.232750	3.329572	0.723318
H	–0.290700	3.140559	2.031181	H	–1.768072	3.317606	1.634109
2'		**Conformer 1**				**Conformer 2**	
atom	x	Y	z	atom	X	y	z

C	0.710588	–1.090277	–1.490414	C	0.890779	–0.848738	–0.115061
C	1.753936	0.029583	0.374541	C	1.791332	0.349581	–0.454353
C	1.404757	1.136305	1.874058	C	1.265978	1.636369	0.176564
C	–0.034748	1.629549	–0.700401	C	–0.207647	1.849065	–0.229066
C	–1.020942	0.446770	1.260610	C	–1.038268	0.583181	0.060502
C	–2.391226	0.892121	1.176870	C	–2.436649	0.693723	–0.503323
O	–0.559149	–0.549241	–1.347200	O	–0.425739	–0.575415	–0.540159
H	0.902235	–1.818517	0.266585	H	1.192668	–1.736915	–0.676271
O	0.755617	–1.724201	0.007740	O	0.979968	–1.089461	1.274020
O	3.042614	–0.551410	–0.460994	O	3.148216	0.157548	–0.019801
H	1.753467	0.461199	–0.753127	H	1.776527	0.448507	–1.542040
H	2.085796	1.978519	0.873522	H	1.852778	2.484071	–0.186991
O	1.541549	0.736971	1.939579	O	1.375029	1.667523	1.598326
H	–0.058011	2.172155	2.084077	H	–0.258603	2.074486	–1.299523
O	–0.419756	2.544957	–1.082830	O	–0.737727	2.969323	0.455966
H	–1.106898	–0.001914	–0.101940	H	–1.101496	0.442944	1.145428
H	–2.394555	1.103525	–0.347737	H	–2.427569	0.582791	–1.589322
H	–2.689811	1.790093	–1.438771	H	–2.866411	1.662964	–0.246479
O	–3.324075	–0.173699	0.139788	O	–3.236756	–0.357299	0.080992
C	–4.582636	–0.011204	0.701004	C	–4.488210	–0.502552	–0.411892
C	4.124456	0.085041	1.877438	C	3.954124	–0.600208	–0.806912
C	–0.001536	–2.934654	0.981268	C	0.362769	–2.307425	1.701289
H	1.320861	–0.204575	–0.546461	H	1.295678	0.760556	1.930403
H	–0.021392	2.226386	–0.468027	H	–0.356254	2.949461	1.346126
O	–4.939425	0.958644	–0.896121	O	–4.944098	0.197262	–1.282022
C	–5.448110	–1.192225	–0.534432	C	–5.205634	–1.642862	0.264536
C	5.397184	–0.607662	0.725271	C	5.345955	–0.663492	–0.237873
O	4.044314	1.073008	–1.490414	O	3.579009	–1.133457	–1.821730
H	0.366121	–3.660843	0.374541	H	0.820490	–3.163735	1.193580
H	–1.064480	–2.747555	1.874058	H	–0.711354	–2.296595	1.499974
H	0.147518	–3.329488	–0.700401	H	0.538542	–2.385947	2.773239
H	–5.461594	–1.331984	1.260610	H	–5.191154	–1.509925	1.348271
H	–5.037830	–2.101995	1.176870	H	–4.695393	–2.582919	0.040527
H	–6.458820	–1.025047	–1.347200	H	–6.231841	–1.688229	–0.093818
H	6.233757	–0.179846	0.266585	H	5.313686	–1.036892	0.787768
H	5.325865	–1.680547	0.007740	H	5.777055	0.339883	–0.205937
H	5.553915	–0.469874	–0.460994	H	5.962271	–1.312552	–0.856143

3'		**Conformer 1**				**Conformer 2**	
atom	x	Y	z	atom	x	Y	z
C	–0.863481	0.860678	0.168220	C	1.056156	0.778811	–0.350355

C	–1.695514	–0.290400	–0.408104	C	1.476159	–0.406939	0.525629
C	–0.991950	–1.633787	–0.170280	C	0.607562	–1.632253	0.218242
C	0.496828	–1.611246	–0.539036	C	–0.889025	–1.310159	0.196079
C	1.179762	–0.363910	0.056844	C	–1.162398	–0.050583	–0.648594
C	2.613213	–0.216896	–0.409967	C	–2.610731	0.399059	–0.585733
O	0.452574	0.793330	–0.367230	O	–0.335524	1.021363	–0.185328
H	–0.812762	0.784591	1.266695	H	1.263882	0.559265	–1.411267
O	–1.437040	2.067172	–0.213593	O	1.754758	1.908259	0.059914
O	–2.971865	–0.407980	0.210935	O	2.820221	–0.809069	0.282353
H	–1.800419	–0.117147	–1.486819	H	1.338840	–0.113294	1.573889
H	–1.497779	–2.405866	–0.763234	H	0.800650	–2.401294	0.976239
O	–1.051663	–1.988911	1.214453	O	0.927690	–2.156262	–1.076254
H	0.587944	–1.564605	–1.628845	H	–1.232110	–1.111393	1.212727
O	1.125281	–2.816828	–0.130067	O	–1.629900	–2.425685	–0.279898
H	1.170858	–0.430965	1.152746	H	–0.926847	–0.269215	–1.700955
H	2.619493	0.111287	–1.460461	H	–3.231876	–0.363076	–1.076398
H	3.109492	–1.194277	–0.345431	H	–2.714679	1.344644	–1.137832
O	3.274178	0.731668	0.409523	O	–3.010457	0.566633	0.760936
C	4.610024	0.963961	0.010483	C	–4.362051	0.957836	0.888080
C	–4.029677	0.334123	–0.393186	C	3.812973	–0.195305	1.101792
C	–0.843783	3.214528	0.396854	C	1.574041	3.048428	–0.778172
H	–1.971464	–1.897822	1.493107	H	1.885514	–2.271164	–1.109326
H	0.767915	–3.039525	0.740094	H	–1.117315	–2.816577	–0.999974
O	4.659828	1.370641	–1.009530	H	–5.039687	0.209639	0.452959
C	5.209156	0.042954	0.050228	H	–4.547679	1.926090	0.401605
C	5.031863	1.692150	0.703888	H	–4.572103	1.051111	1.953897
O	–4.173547	0.025330	–1.436231	H	3.626777	–0.407212	2.162177
H	–3.832625	1.407548	–0.357543	H	3.842449	0.885525	0.948355
H	–4.931136	0.102337	0.174467	H	4.766814	–0.637375	0.812811
H	0.200749	3.322010	0.096778	H	0.538547	3.395534	–0.751535
H	–0.904345	3.145420	1.490151	H	1.856845	2.818040	–1.813294
H	–1.417479	4.076014	0.056804	H	2.231552	3.825467	–0.389657

Experimental methods

The solvents used were distilled, dried and stored according to standard procedures. Analytical thin layer chromatography (TLC) was performed on Silica Gel 60 F254 (Merck) aluminum supported plates (layer thickness 0.2 mm). Visualization of the spots was effected by exposure to UV light and charring with a solution of 5% (v/v) sulfuric acid in EtOH, containing 0.5% *p*-anisaldehyde. Column chromatography was carried out with Silica Gel 60 (230–400 mesh, Merck). Optical rotations were measured at 25 °C with a Perkin-Elmer 343 digital polarimeter. Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AMX 500 instrument. Chemical shifts (δ) are reported in ppm, with TMS (δ 0.00 for ^{1}H) and residual chloroform (δ 77.16 for ^{13}C) as internal references. Assignments of ^{1}H and ^{13}C NMR spectra were assisted by 2D ^{1}H COSY and HSQC experiments. High resolution mass spectra (HRMS) were recorded on a BRUKER micrOTOF-Q II electrospray ionization mass spectrometer.

Glycosyl acceptors

Methyl 2-*O*-benzyl-4.6-*O*-benzylidene-α-D-glucopyranoside (8)

A suspension of **7**[11] (1.0 g, 3.54 mmol) and Bu_2SnO (0.9 g, 3.60 mmol) in anhydrous toluene (60.0 mL) was refluxed for 2 h, using a Dean-Stark trap to remove the water released. After evaporation of the solvent till 2 mL remained, BnBr (0.42 mL, 3.60 mmol) and TBAB (0.15 g, 0.46 mmol) were added and the mixture was allowed to react at 100 °C for 12 h. The TLC analysis (hexane/EtOAc 7:3) showed the formation of a faster moving product *Rf* 0.54, that was obtained as a crystalline solid (1.12 g, 85%) after purification by silica gel column chromatography (hexane/EtOAc 8:2). $[\alpha]_D$ +34 (*c* 1 in $CHCl_3$), mp 130-131 °C, lit.: $[\alpha]_D^{25}$ +35 (*c* 1 in $CHCl_3$), mp 131-132 °C.[12]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52-7.49 (m, 2H, aromatic), 7.42-7.30 (m, 8H, aromatic), 5.52 (s, 1H, C*H*Ph), 4.79, 4.71 (2d, 2H, J_{gem} = 12.2 Hz, CH_2Ph), 4.61 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.26 (dd, 1H, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.1 Hz, H-6a), 4.16 (t, 1H, $J_{2,3}$ = 9.3 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 3.81 (td, 1H, $J_{5,6a}$ = 4.8 Hz, $J_{4,5}$ = 9.5 Hz, $J_{5,6b}$ = 10.2 Hz, H-5), 3.70 (t, 1H, J_{gem} = 10.1 Hz, $J_{5,6b}$ = 10.2 Hz, H-6b), 3.50 (t,

1H, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.47 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.3 Hz, H-2), 3.38 (s, 3H, CH_3O) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 137.8, 137.0, 129.1, 128.5, 128.2, 128.1, 128.0, 126.3 (aromatic), 101.9 (*C*HPh), 98.6 (C-1), 81.2 (C-4), 79.5 (C-2), 73.3 (*C*H_2Ph), 70.2 (C-3), 69.0 (C-6), 62.0 (C-5), 55.4 (*C*H_3O) ppm.

Methyl 2-*O*-benzyl-4.6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-uloside (9)

Method A: A solution of oxalyl chloride (0.17 mL, 1.88 mmol) in anh. CH_2Cl_2 (10 mL) was cooled to –70 °C and DMSO (0.16 mL, 2.15 mmol) was added dropwise. After 15 min, a solution of **8** (0.5 g, 1.34 mmol) in anh. CH_2Cl_2 (3.5 mL) was slowly added. After another 2 h of stirring, EtN(*i*Pr)$_2$ (0.7 mL, 4.02 mmol) was added, and the mixture was allowed to warm to room temperature slowly. TLC analysis of the mixture showed total conversion of the starting material (*Rf* 0.54, hexane/EtOAc 7:3) into a lower moving compound (*Rf* 0.40), that was obtained as an amorphous solid (**9**, 0.46 g, 93%) after purification by silica gel column chromatography (hexane/EtOAc 85:15).

Method B: To a solution of **8** (0.5 g, 1.34 mmol) in anh. Acetonitrile (15 mL), IBX (0.75 g, 2.68 mmol) was added and the suspension was refluxed for 4 h. As in the previous treatment, TLC analysis showed total conversion of the starting material into a lower moving compound (*Rf* 0.40). Purification of the crude mixture by column chromatography gave **9** (0.45 g, 91%) as an amorphous solid, $[\alpha]_D$ –18 (*c* 1 in $CHCl_3$), lit.: $[\alpha]_D^{20}$ –17.4 (*c* 1.07 in $CHCl_3$).[13]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54-7.46 (m, 2H, aromatic), 7.41-7.29 (m, 8H, aromatic), 5.53 (s, 1H, C*H*Ph), 5.06 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.96, 4.59 (2d, 2H, J_{gem} = 12.5 Hz, CH_2Ph), 4.38 (dd, 1H, $J_{5,6a}$ = 4.7 Hz, J_{gem} = 10.3 Hz, H-6a), 4.19 (dd, 1H, $^4J_{2,4}$ = 1.4 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 4.13 (dd, 1H, $^4J_{2,4}$ = 1.4 Hz, $J_{1,2}$ = 4.2 Hz, H-2), 4.08 (td, 1H, $J_{5,6a}$ = 4.7 Hz, $J_{4,5}$ = 9.8 Hz, $J_{5,6b}$ = 10.3 Hz, H-5), 3.87 (t, 1H, $J_{5,6b}$ = 10.2 Hz, J_{gem} = 10.3 Hz, H-6b), 3.44 (s, 3H, CH_3O) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 196.2 (*C*O), 136.8, 136.3, 129.3, 128.6, 128.29, 128.23, 126.3 (aromatic), 102.5 (C-1), 101.9 (*C*HPh), 82.1 (C-4), 79.5 (C-2), 72.6 (*C*H_2Ph), 69.4 (C-6), 65.4 (C-5), 55.6 (*C*H_3O) ppm.

Methyl 2-*O*-benzyl-4.6-*O*-benzylidene-α-D-allopyranoside (10)

A suspension of uloside **9** (0.8 g, 2.16 mmol) in MeOH (30 mL) was cooled to 0 °C and $NaBH_4$ (102.0 mg, 2.7 mmol) was added in small portions. After 5 h, TLC analysis showed total conversion of the starting material (*Rf* 0.40, hexane/EtOAc 7:3) into a faster moving compound (*Rf* 0.50). A few drops of AcOH were added and the solvent was evaporated. The residue was redisolved in CH_2Cl_2 and the organic phase was washed (H_2O), dried and concentrated under reduced pressure. Purification of the mixture by short column chromatography (hexane/EtOAc 8:2) gave **10** (0.77 g, 96%) as a crystalline solid, mp 75-76 °C, $[\alpha]_D$ +5 (*c* 1 in $CHCl_3$), lit.: mp 75-77 °C, $[\alpha]_D$ +4.7 (c 1 in $CHCl_3$).[14]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H, aromatic), 7.41-7.30 (m, 8H, aromatic), 5.53 (s, 1H, C*H*Ph), 4.79 (d, 1H, J_{gem} = 12.4 Hz, C*H*$_2$Ph), 4.76 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.61 (d, 1H, J_{gem} = 12.4 Hz, C*H*$_2$Ph), 4.43 (ddd, 1H, $J_{3,4}$ = 2.6 Hz, $J_{2,3}$ = 3.2 Hz, $J_{3,OH}$ = 6.3 Hz, H-3), 4.34 (dd, 1H, $J_{5,6a}$ = 5.2 Hz, J_{gem} = 10.3 Hz, H-6a), 4.16 (ddd, 1H, $J_{5,6a}$ = 5.2 Hz, $J_{4,5}$ = 9.7 Hz, $J_{5,6b}$ = 10.3 Hz, H-5), 3.71 (t, 1H, $J_{5,6b}$ = 10.3 Hz, J_{gem} = 10.3 Hz, H-6b), 3.51 (t, 1H, $J_{2,3}$ = 3.2 Hz, $J_{1,2}$ = 3.6 Hz, H-2), 3.45 (s, 3H, C*H*$_3$O), 3.42 (dd, 1H, $J_{3,4}$ = 2.6 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 3.21 (d, 1H, $J_{3,OH}$ = 6.3 Hz, OH-3) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$) δ 137.3, 137.2, 129.2, 128.7, 128.3, 128.2, 128.1, 126.4 (aromatic), 102.1 (*C*HPh), 99.7 (C-1), 78.9 (C-4), 73.9 (*C*H_2Ph), 70.5 (C-2), 69.2 (C-6), 67.0 (C-3), 57.9 (C-5), 56.0 (*C*H_3O) ppm.

Methyl 2,6-di-*O*-benzyl-α-D-allopyranoside (1)

A solution of alloside **10** (0.5 g, 1.34 mmol) and trimethylamine borane (182.0 mg, 2.50 mmol) in acetonitrile (12.0 mL), was cooled to 0 °C and boron trifluoride diethyl etherate (333 µL, 2.70 mmol) was added dropwise. After 1 h of stirring at 0 °C and 1 h at room temperature, TLC analysis of the mixture (hexane/EtOAc 7:3) showed total conversion of the starting material (*Rf* 0.50) into a more polar compound (*Rf* 0.28). Et_3N and MeOH were added, and the solvent was evaporated under reduced pressure. The residue was redisolved in CH_2Cl_2 and the organic phase was washed (H_2O), dried and concentrated under reduced pressure. Purification of the mixture

by column chromatography (hexane/EtOAc 8:2) gave **1** (0.44 g, 87%) as an amorphous solid, $[\alpha]_D$ +45 (*c* 1 in $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40-7.27 (m, 10H, aromatic), 4.79 (dd, 1H, $^4J_{1,3}$ = 0.9 Hz, $J_{1,2}$ = 3.5 Hz, H-1), 4.76 (d, 1H, J_{gem} = 12.3 Hz, C*H*$_2$Ph), 4.62-4.58 (m, 3H, C*H*$_2$Ph), 4.23 (ddt, 1H, $^4J_{1,3}$ = 0.9 Hz, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ = 3.3 Hz, $J_{4,OH}$ = 8.5 Hz, H-3), 3.82-3.77 (m, 1H, H-6a), 3.76-3.69 (m, 2H, H-5 and H-6b), 3.51 (td, 1H, $J_{3,4}$ = 3.3 Hz, $J_{4,5}$ = 10.0 Hz, $J_{4,OH}$ = 10.5 Hz, H-4), 3.48 (t, 1H, $J_{2,3}$ = 3.2 Hz, $J_{1,2}$ = 3.5 Hz, H-2), 3.43 (s, 3H, C*H*$_3$O), 3.41 (d, 1H, $J_{3,OH}$ = 8.5 Hz, OH-3), 2.67 (d, 1H, $J_{4,OH}$ = 10.5 Hz, OH-4) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 138.0, 137.2, 128.5, 128.3, 128.1, 127.9, 127.58, 127.57 (aromatic), 98.9 (C-1), 73.56 (*C*H$_2$Ph), 73.51 (C-2), 70.6 (*C*H$_2$Ph), 69.2 (C-6), 69.0 (C-3), 67.5 (C-5), 66.8 (C-4), 55.7 (*C*H$_3$O) ppm.

HRMS-ESI: calculated *m*/*z* for $C_{21}H_{26}NaO_6$ $[M+Na]^+$ 397.1622. Found: 397.1620.

Methyl 2-*O*-benzoyl-4.6-*O*-benzylidene-α-D-glucopyranoside (11)

A solution of **91** (1.0 g, 3.54 mmol) in anh. acetonitrile (35.0 mL) and Et_3N (5.0 mL, 35.6 mmol) was cooled to –25 °C and then, a 0.2 M solution of benzoyl cyanide in acetonitrile (19.5 mL, 3.90 mmol) was slowly added over 2 h. After 1 h of stirring TLC analysis of the mixture (hexane/EtOAc 7:3) showed total conversion of the starting material (*Rf* 0.20) into a less polar compound (*Rf* 0.45), so the mixture was allowed to warm to room temperature slowly and a few drops of MeOH were added. The solvent was evaporated under reduced pressure, the residue was redisolved in CH_2Cl_2 and the organic phase was washed (H_2O), dried and concentrated under reduced pressure again. Purification of the mixture by column chromatography (hexane/EtOAc 85:15) gave **11** (1.16 g, 85%) as a crystalline solid, mp 168-169 °C, $[\alpha]_D$ +114 (*c* 1 in $CHCl_3$), lit.: mp 169-170, $[\alpha]_D^{25}$ +111.2 (*c* 1.64 in $CHCl_3$).[15]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12-8.07 (m, 2H, aromatic), 7.61-7.34 (m, 8H, aromatic), 5.57 (s, 1H, C*H*Ph), 5.07 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 5.04 (dd, 1H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 4.35 (t, 1H, $J_{3,4}$ = 9.5 Hz, $J_{2,3}$ = 9.6 Hz, H-3), 4.32 (dd, 1H, $J_{5,6a}$ = 4.8 Hz, J_{gem} = 10.3 Hz, H-6a), 3.91 (td, 1H,

$J_{5,6a}$ = 4.8 Hz, $J_{4,5}$ = 9.5 Hz, $J_{5,6b}$ = 10.3 Hz, H-5), 3.79 (t, 1H, J_{gem} = 10.3 Hz, $J_{5,6b}$ = 10.3 Hz, H-6b), 3.63 (t, 1H, $J_{3,4}$ = 9.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.39 (s, 3H, C*H*$_3$O), 2.55 (bs, 1H, OH-3) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 166.2 (*C*OPh), 136.9, 133.3, 129.9, 129.4, 129.2, 128.4, 128.3, 126.3 (aromatic), 102.0 (*C*HPh), 97.7 (C-1), 81.4 (C-4), 74.0 (C-2), 68.9 (C-6), 68.8 (C-3), 62.0 (C-5), 55.5 (*C*H$_3$O) ppm.

Methyl 2-*O*-benzoyl-4.6-*O*-benzylidene-α-D-*ribo*-hexopyranosid-3-uloside (12)

Method B used for the synthesis of uloside **9** was applied to glucoside **11** (1.0 g, 2.59 mmol). Purification of the mixture by short column chromatography (hexane/EtOAc 85:15) gave **12** (0.91 g, 91%) as a crystalline solid, mp 209-211, $[\alpha]_D$ +92 (*c* 1 in $CHCl_3$), lit.: mp 211-213,[16] $[\alpha]_D^{32}$ +96 (*c* 0.64 in $CHCl_3$).[17]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19-7.35 (m, 10H, aromatic), 5.63 (dd, 1H, $^4J_{2,4}$ = 1.3 Hz, $J_{1,2}$ = 4.3 Hz, H-2), 5.60 (s, 1H, C*H*Ph), 5.35 (d, 1H, $J_{1,2}$ = 4.3 Hz, H-1), 4.45 (dd, 1H, $J_{5,6a}$ = 4.7 Hz, J_{gem} = 10.3 Hz, H-6a), 4.43 (dd, 1H, $^4J_{2,4}$ = 1.3 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 4.19 (td, 1H, $J_{5,6a}$ = 4.7 Hz, $J_{4,5}$ = 9.8 Hz, $J_{5,6b}$ = 10.3 Hz, H-5), 3.99 (t, 1H, $J_{5,6b}$ = 10.3 Hz, J_{gem} = 10.3 Hz, H-6b), 3.50 (s, 3H, C*H*$_3$O) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 191.8 (*C*O), 165.2 (*C*OPh), 136.2, 133.6, 130.1, 129.3, 128.7, 128.4, 128.3, 126.3 (aromatic), 102.1 (*C*HPh), 101.4 (C-1), 82.1 (C-4), 74.8 (C-2), 69.3 (C-6), 65.4 (C-5), 55.7 (*C*H$_3$O) ppm.

Methyl 2-*O*-benzoyl-4.6-*O*-benzylidene-α-D-allopyranoside (13)

Uloside **12** (0.90 g, 2.34 mmol) was treated with $NaBH_4$, following the same procedure employed for the synthesis of **10**. The reaction temperature was lowered to –18 °C to improve diastereoselectivity. After 5 h TLC analysis of the mixture (hexane/EtOAc 7:3) showed total conversion of the starting material (*Rf* 0.35) into a faster moving compound (*Rf* 0.40) that was characterized as **13** (0.87 g, 97%), after purification by short column chromatography (hexane/EtOAc 85:15), mp 115-117, $[\alpha]_D$ +75 (*c* 1 in $CHCl_3$), lit.: mp 114-116 °C, $[\alpha]_D^{23}$ +71 (*c* 1 in $CHCl_3$).[18]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15-8.11 (m, 2H, aromatic), 7.62-7.33 (m, 8H, aromatic), 5.62 (s, 1H, C*H*Ph), 5.09 (t, 1H, $J_{2,3}$ = 3.2 Hz, $J_{1,2}$ = 3.7 Hz, H-2), 5.04 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.50 (ddd, 1H, $J_{3,4}$ = 2.6 Hz, $J_{2,3}$ = 3.2 Hz, $J_{3,OH}$ = 7.3 Hz, H-3), 4.42 (dd, 1H, $J_{5,6a}$ = 5.1 Hz, J_{gem} = 10.3 Hz, H-6a), 4.25 (td, 1H, $J_{5,6a}$ = 4.8 Hz, $J_{4,5}$ = 9.5 Hz, $J_{5,6b}$ = 10.3 Hz, H-5), 3.83 (t, 1H, J_{gem} = 10.3 Hz, $J_{5,6b}$ = 10.3 Hz, H-6b), 3.67 (dd, 1H, $J_{3,4}$ = 2.6 Hz, $J_{4,5}$ = 9.7 Hz, H-4), 3.48 (s, 3H, CH_3O), 3.23 (d, 1H, $J_{3,OH}$ = 7.3 Hz, OH-3) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 165.6 (*C*OPh), 137.0, 133.5, 130.0, 129.2, 129.1, 128.4, 128.2, 126.2 (aromatic), 101.9 (*C*HPh), 98.7 (C-1), 78.6 (C-4), 69.7 (C-2), 69.0 (C-6), 68.2 (C-3), 57.9 (C-5), 56.1 (CH_3O) ppm.

Methyl 2-*O*-benzoyl-α-D-allopyranoside (14)

A solution of **13** (0.85 g, 2.20 mmol) in CH_2Cl_2 (15 mL) was treated with TFA-H_2O (9:1 v/v, 2 mL). After 10 mim, TLC analysis of the mixture showed total consumption of the starting material (*Rf* 0.40, hexane/EtOAc 85:15) and the presence of lower moving compound (*Rf* 0.50, EtOAc/MeOH 4:1). The mixture was diluted with CH_2Cl_2, and the organic phase was washed (H_2O), dried and concentrated under reduced pressure. **14** was obtained as an amorphous solid (0.62 g, 95%) and was used without further purification.

Methyl 2,6-di-*O*-benzoyl-α-D-allopyranoside (2)

The same methodology employed for the synthesis of **11** was applied to alloside **14** (0.5 g, 1.68 mmol). The temperature was lowered to –40 °C to improve regioselectivity. Purification of the reaction mixture by column chromatography (hexane/EtOAc 2:1) gave **2** (0.53 g, 85%) as an amorphous solid, $[\alpha]_D$ +10 (*c* 1 in $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15-7.40 (m, 30H, aromatic), 5.08-5.04 (m, 2H, H-1 and H-2), 4.78 (dd, 1H, $J_{5,6a}$ = 2.1 Hz, J_{gem} = 12.0 Hz, H-6a), 4.63 (dd, 1H, $J_{5,6b}$ = 5.7 Hz, J_{gem} = 12.0 Hz, H-6b), 4.37-4.32 (m, 1H, H-3), 4.03 (ddd, 1H, $J_{5,6a}$ = 2.1 Hz, $J_{5,6b}$ = 5.7 Hz, $J_{4,5}$ = 10.2 Hz, H-5), 3.71 (td, 1H, $J_{3,4}$ = 3.2 Hz, $J_{4,5}$ = 10.2 Hz, $J_{4,OH}$ = 10.4 Hz, H-4), 3.59 (d, 1H, $J_{3,OH}$ = 9.2 Hz, OH-3), 3.48 (s, 3H, CH_3O), 2.93 (d, 1H, $J_{4,OH}$ = 10.4 Hz, OH-4) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 166.5, 165.5 (*C*OPh), 133.5, 133.1, 129.9, 129.8, 129.7, 129.6, 129.2, 128.47, 128.41 (aromatic), 98.1 (C-1), 69.9 (C-3), 69.3 (C-2), 67.0 (C-4), 66.7 (C-5), 63.9 (C-6), 56.0 (*C*H_3O) ppm.

HRMS-ESI: calculated *m*/*z* for $C_{21}H_{22}NaO_8$ $[M+Na]^+$ 425.1207. Found: 425.1202.

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-β-D-allopyranoside (25)

Obtained from **28**[12] (0.15 g, 0,78 mmol) with the same procedures described for **9** and **10.** TLC analysis of the mixture (hexane/EtOAc 7:3) showed total conversion of the starting material (*Rf* 0.50) into a lower moving compound (*Rf* 0.47). Purification by column chromatography (hexane/EtOAc 8:2) gave **29** (0.13 g, 88%) as an amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.30 (m, 10H, aromatic), 5.51 (s, 1H, C*H*Ph), 4.86 (d, 1H, J_{gem} = 12.1 Hz, CH_2Ph), 4.77 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.71 (d, 1H, J_{gem} = 12.1 Hz, CH_2Ph), 4.40 (dd, 1H, $J_{5,6a}$ = 5.2 Hz, J_{gem} = 10.4 Hz, H-6a), 4.33-4.29 (m, 1H, H-3), 4.04 (ddd, 1H, $J_{5,6a}$ = 5.2 Hz, $J_{4,5}$ = 9.5 Hz, $J_{5,6b}$ = 10.4 Hz, H-5), 3.72 (t, 1H, $J_{5,6b}$ = 10.4 Hz, J_{gem} = 10.4 Hz, H-6b), 3.59 (s, 3H, CH_3O), 3.50 (dd, 1H, $J_{3,4}$ = 2.4 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.31 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{1,2}$ = 7.8 Hz, H-2), 3.21 (bs, 1H, OH-3) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$) δ 137.8, 137.0, 129.1, 128.4, 128.2, 128.0, 127.9, 126.2 (aromatic), 102.3 (C-1), 101.9 (*C*HPh), 78.6 (C-4), 77.2 (C-2), 72.8 (*C*H_2Ph), 69.1 (C-6), 68.3 (C-3), 62.6 (C-5), 57.4 (*C*H_3O) ppm.

HRMS-ESI: calculated *m*/*z* for $C_{21}H_{24}NaO_6$ $[M+Na]^+$ 395.1465. Found: 395.1460.

Methyl 2,6-di-*O*-benzyl-β-D-allopyranoside (3)

Obtained from **29** (0.7 g, 1.88 mmol) with the same procedure described for **1**. TLC analysis of the mixture (hexane/EtOAc 7:3) showed total conversion of the starting material (*Rf* 0.47) into a lower moving compound (*Rf* 0.25). Purification by short column chromatography (hexane/EtOAc 7:3) gave **3** (1.14 g, 95%) as an amorphous solid, $[\alpha]_D$ –24 (*c* 1 in $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37-7.26 (m, 10H, aromatic), 4.85. 4.76 (2d, 2H, J_{gem} = 11.9 Hz, CH_2Ph), 4.65 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.59 (s, 2H, CH_2Ph), 4.16-4.11 (m, 1H, H-3), 3.84 (ddd,

1H, $J_{5,6a}$ = 4.1 Hz, $J_{5,6b}$ = 5.4 Hz, $J_{4,5}$ = 9.5 Hz, H-5), 3.77 (dd, 1H, $J_{5,6a}$ = 4.1 Hz, J_{gem} = 10.3 Hz, H-6a), 3.70 (dd, 1H, $J_{5,6b}$ = 5.4 Hz, J_{gem} = 10.3 Hz, H-6b), 3.58-3.52 (m, 1H, H-4), 3.55 (s, 3H, CH_3O), 3.28 (dd, 1H, $J_{2,3}$ = 3.1 Hz, $J_{1,2}$ = 7.7 Hz, H-2), 2.84 (d, 1H, $J_{4,OH}$ = 8.0 Hz, OH-4), 2.73 (bs, 1H, OH-3) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 137.97, 137.94, 128.4, 128.3, 127.9, 127.8, 127.69. 127.66 (aromatic), 101.4 (C-1), 77.2 (C-2), 73.5 (*C*H_2Ph), 72.9 (*C*H_2Ph), 72.3 (C-5), 70.5 (C-6), 69.8 (C-3), 69.0 (C-4), 56.9 (*C*H_3O) ppm.

HRMS-ESI: calculated *m*/*z* for $C_{21}H_{26}NaO_6$ $[M+Na]^+$ 397.1622. Found: 397.1621.

General procedure for glycosidations using trichloroacetimidates 4 or 5 as glycosyl donors

A suspension of trichloroacetimidate **4**[19] or **5**[20] (74 mg, 0.10 mmol), glycosyl acceptor **1**, **2** or **3** (0.14 mmol, 1.4 equiv) and 4 Å powdered molecular sieves (0.1 g) in anh. CH_2Cl_2 (10 mL) was stirred for 30 min under Ar. Then, the mixture was cooled to −30 °C and TMSOTf (8 μL, 0.04 mmol) was added. When TLC analysis showed optimal conversion (normally 2 h of stirring at −30 °C) the reaction mixture was quenched with triethylamine, filtered, diluted with CH_2Cl_2 (20 mL) and successively washed with $NaHCO_3$ (ss) and water (30 mL). After drying with anh. Na_2SO_4, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography, as indicated in each case.

Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2,6-di-*O*-benzyl-α-D-allopyranoside (15) and methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,6-di-*O*-benzyl-α-D-allopyranoside (16)

Obtained according to the general procedure by condensation of **4** with **1.** TLC analysis of the mixture showed, among the excess of **1** (*Rf* 0.05, 85:15 toluene-EtOAc), the presence of a major product of *Rf* 0.20 and a minor product of *Rf* 0.13. According to the integration of the ^{1}H NMR signals corresponding to H-1' of both disaccharides (5.25 and 4.92 ppm) they were in a 2.4:1 ratio.

After purification by column chromatography (9:1 toluene-EtOAc) fractions of *Rf* 0.20 afforded syrupy compound **15** (0.05 g, 56%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20-7.10 (m, 30H, aromatic), 6.00 (d, 1H, $J_{3',4'}$ = 3.7 Hz, H-4'), 5.98 (dd, 1H, $J_{1',2'}$ = 8.2 Hz, $J_{2',3'}$ = 10.5 Hz, H-2'), 5.62 (dd, 1H, $J_{3',4'}$ = 3.7 Hz, $J_{2',3'}$ = 10.5 Hz, H-3'), 5.25 (d, 1H, $J_{1',2'}$ = 8.2 Hz, H-1'), 4.79 (d, 1H, J_{gem} = 12.6 Hz, CH_2Ph), 4.69 (dd, 1H, $J_{5',6'a}$ = 6.8 Hz, J_{gem} = 11.4 Hz, H-6'a), 4.62 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 4.55 (d, 1H, J_{gem} = 12.6 Hz, CH_2Ph), 4.49-4.42 (m, 2H, H-3 and H-6'b), 4.40 (d, 1H, J_{gem} = 12.3 Hz, CH_2Ph), 4.35 (ddd, 1H, $J_{4',5'}$ = 1.1 Hz, $J_{5',6'a}$ = 6.8 Hz, $J_{5',6'b}$ = 6.8 Hz, H-5'), 4.25 (d, 1H, J_{gem} = 12.3 Hz, CH_2Ph), 3.63 (ddd, 1H, $J_{3,4}$ = 2.8 Hz, $J_{4,OH}$ = 8.2 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.59-3.53 (m, 1H, H-5), 3.43 (t, 1H, $J_{1,2}$ = 3.8 Hz, $J_{2,3}$ = 3.8 Hz, H-2), 3.32 (s, 3H, CH_3O), 3.20 (dd, 1H, $J_{5,6a}$ = 3.3 Hz, J_{gem} = 10.5 Hz, H-6a), 3.07 (dd, 1H, $J_{5,6b}$ = 3.9 Hz, J_{gem} = 10.5 Hz, H-6b), 2.55 (d, 1H, $J_{4,OH}$ = 8.2 Hz, OH-4) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 166.0, 165.8, 165.5, 164.7 (*C*OPh), 137.7, 137.4, 133.5, 133.24, 133.21, 133.1, 130.3, 129.77, 129.74, 129.6, 129.39, 129.34, 129.0, 128.8, 128.7, 128.5, 128.45, 128.40, 128.3, 128.24, 128.21, 127.9, 127.8, 127.7, 127.5 (aromatic), 102.1 (C-1'), 98.0 (C-1), 75.0 (C-3), 73.29 (*C*H_2Ph), 73.25 (C-2), 71.77 (C-5'), 71.75 (C-3'), 70.3 (*C*H_2Ph), 70.1 (C-2'), 68.75 (C-6), 68.74 (C-4), 68.3 (C-4'), 66.4 (C-5), 62.4 (C-6'), 55.3 (*C*H_3O) ppm.

HRMS-ESI: calculated *m/z* for $C_{55}H_{52}NaO_{15}$ $[M+Na]^+$ 975.3198. Found: 975.3185.

Fractions of *Rf* 0.19 afforded syrupy compound **16** (0.02 g, 23%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18-7.20 (m, 30H, aromatic), 5.96 (dd, 1H, $J_{4',5'}$ = 0.8 Hz, $J_{3',4'}$ = 3.5 Hz, H-4'), 5.83 (dd, 1H, $J_{1',2'}$ = 8.0 Hz, $J_{2',3'}$ = 10.4 Hz, H-2'), 5.50 (dd, 1H, $J_{3',4'}$ = 3.5 Hz, $J_{2',3'}$ = 10.4 Hz, H-3'), 4.92 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.72 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 4.70 (d, 1H, J_{gem} = 12.3 Hz, CH_2Ph), 4.66 (dd, 1H, $J_{5',6'a}$ = 6.5 Hz, J_{gem} = 11.3 Hz, H-6'a), 4.51-4.50 (m, 1H, H-3), 4.46 (d, 1H, J_{gem} = 12.3 Hz, CH_2Ph), 4.42 (d, 1H, J_{gem} = 12.1 Hz, CH_2Ph), 4.39 (dd, 1H, $J_{5',6'b}$ = 6.6 Hz, J_{gem} = 11.3 Hz, H-6'b), 4.25 (d, 1H, J_{gem} = 12.1 Hz, CH_2Ph), 4.19 (td, 1H, $J_{4',5'}$ = 0.8 Hz, $J_{5',6'a}$ = 6.5 Hz, $J_{5',6'b}$ = 6.6 Hz, H-5'), 4.00-3.94 (m, 1H, H-5), 3.78 (dd, 1H, $J_{3,4}$ = 2.7 Hz, $J_{4,5}$ = 10.2 Hz, H-4), 3.57 (dd, 1H, $J_{5,6a}$ = 3.2 Hz, J_{gem} = 10.8 Hz, H-6a), 3.50 (dd, 1H, $J_{5,6b}$ = 1.3 Hz, J_{gem} = 10.8 Hz, H-6b), 3.43 (t, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 3.6 Hz, H-2), 3.35 (s, 3H, CH_3O), 3.29 (d, 1H, $J_{3,OH}$ = 6.5 Hz, OH-3) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 166.0, 165.6, 165.5, 164.7 (*C*OPh), 138.0, 137.4, 133.6, 133.3, 133.2, 130.1, 129.76, 129.73, 129.3, 129.2, 128.9, 128.67, 128.64, 128.53, 128.51, 128.4, 128.2, 128.0, 127.9, 127.7 (aromatic), 102.1 (C-1'), 99.0 (C-1), 75.7 (C-4), 73.8 (C-2), 73.3 (*C*H_2Ph), 71.6

(C-3'), 71.3 (C-5'), 70.5 (*C*H_2Ph), 69.6 (C-2'), 69.1 (C-3), 68.2 (C-6), 67.9 (C-4'), 64.9 (C-5), 62.0 (C-6'), 55.7 (*C*H_3O) ppm.

HRMS-ESI: calculated *m*/*z* for $C_{55}H_{52}NaO_{15}$ $[M+Na]^+$ 975.3198. Found: 975.3168.

Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2,6-di-*O*-benzoyl-α-D-allopyranoside (17) and methyl 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl-(1→3)-2,6-di-*O*-benzoyl-α-D-allopyranoside (19)

Obtained according to the general procedure by condensation of **4** with **2.** After 2 h, TLC analysis of the mixture showed total consumption of **4** (*Rf* 0.65, 85:15 toluene-EtOAc) and the presence of two products of *Rf* 0.28 and 0.43. Analysis of the ^{1}H NMR spectrum indicated the presence of two isomers, both with 1→3 glycosidic linkage and in an α/β ratio of 1.0:1.3.

After purification by column chromatography (92:8 toluene-EtOAc) fractions of *Rf* 0.43 afforded **19** (0.04 g, 42%) as an amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14-7.20 (m, 30H, aromatic), 6.12-6.05 (m, 2H, H-3' and H-4'), 5.96 (d, 1H, $J_{1',2'}$ = 3.6 Hz, H-1'), 5.83-5.77 (m, 1H, H-2'), 5.26 (t, 1H, $J_{5',6'b}$ = 6.1 Hz, $J_{5',6'a}$ = 6.7 Hz, H-5'), 5.06 (dd, 1H, $J_{2,3}$ = 3.1 Hz, $J_{1,2}$ = 4.1 Hz, H-2), 4.91 (dd, 1H, $J_{5,6a}$ = 3.6 Hz, J_{gem} = 12.3 Hz, H-6a), 4.86 (d, 1H, $J_{1,2}$ = 4.1 Hz, H-1), 4.61 (t, 1H, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 3.1 Hz, H-3), 4.53 (dd, 1H, $J_{5',6'a}$ = 6.7 Hz, J_{gem} = 11.4 Hz, H-6'a), 4.50 (dd, 1H, $J_{5,6b}$ = 2.1 Hz, J_{gem} = 12.3 Hz, H-6b), 4.39 (dd, 1H, $J_{5',6'b}$ = 6.1 Hz, J_{gem} = 11.4 Hz, H-6'b), 4.34 (ddd, 1H, $J_{5,6b}$ = 2.1 Hz, $J_{5,6a}$ = 3.6 Hz, $J_{4,5}$ = 10.0 Hz, H-5), 3.70 (ddd, 1H, $J_{3,4}$ = 3.1 Hz, $J_{4,OH}$ = 6.6 Hz, $J_{4,5}$ = 10.0 Hz, H-4), 3.58 (d, 1H, $J_{4,OH}$ = 6.6 Hz, OH-4), 2.99 (s, 3H, C*H*$_3$O), ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 167.6, 166.1, 166.0, 165.8, 165.7, 165.6 (*C*OPh), 133.44, 133.40, 133.1, 133.0, 130.0, 129.94, 129.90, 129.73, 129.70, 129.6, 129.5, 129.4, 129.27, 129.20, 129.0, 128.5, 128.46, 128.40, 128.3, 128.2, 128.1 (aromatic), 97.3 (C-1), 96.0 (C-1'), 72.9 (C-3), 70.8 (C-2), 69.4 (C-4'), 69.0 (C-2'), 68.5 (C-3'), 66.9 (C-5'), 66.8 (C-4), 66.5 (C-5), 63.9 (C-6), 62.6 (C-6'), 55.6 (*C*H_3O) ppm.

HRMS-ESI: calculated *m*/*z* for $C_{55}H_{48}NaO_{17}$ $[M+Na]^+$ 1003.2784. Found: 1003.2762.

Further elution gave **17** (0.05 g, 53%) as an amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23-7.23 (m, 30H, aromatic), 5.95 (dd, 1H, $J_{1',2'}$ = 8.0 Hz, $J_{2',3'}$ = 10.5 Hz, H-2'), 5.90 (dd, 1H, $J_{4',5'}$ = 0.8 Hz, $J_{3',4'}$ = 3.6 Hz, H-4'), 5.60 (dd, 1H, $J_{3',4'}$ = 3.6 Hz, $J_{2',3'}$ = 10.5 Hz, H-3'), 5.09 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.97 (dd, 1H, $J_{2,3}$ = 3.7 Hz, $J_{1,2}$ = 4.2 Hz, H-2), 4.93 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.60 (t, 1H, $J_{3,4}$ = 2.9 Hz, $J_{2,3}$ = 3.6 Hz, H-3), 4.20-4.13 (m, 2H, H-5' and H-6a), 4.04 (dd, 1H, $J_{5',6'a}$ = 6.4 Hz, J_{gem} = 11.4 Hz, H-6'a), 4.01-3.95 (m, 2H, H-6b and H-6'b), 3.77 (ddd, 1H, $J_{5,6b}$ = 2.0 Hz, $J_{5,6a}$ = 3.8 Hz, $J_{4,5}$ = 10.0 Hz, H-5), 3.62 (ddd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{4,OH}$ = 8.1 Hz, $J_{4,5}$ = 10.0 Hz, H-4), 3.44 (s, 3H, CH_3O), 3.01 (d, 1H, $J_{4,OH}$ = 8.1 Hz, OH-4) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 167.3, 165.8, 165.7, 165.5, 165.4, 165.0 (*C*OPh), 133.5, 133.49, 133.41, 133.28, 133.24, 133.17, 130.1, 129.8, 129.78, 129.75, 129.4, 129.3, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1 (aromatic), 102.3 (C-1'), 97.0 (C-1), 75.7 (C-3), 71.4 (C-3' and C-5'), 70.5 (C-2'), 68.9 (C-2), 68.1 (C-4'), 67.1 (C-4), 65.9 (C-5), 63.2 (C-6), 61.6 (C-6'), 55.4 (*C*H_3O) ppm.

HRMS-ESI: calculated *m/z* for $C_{55}H_{48}NaO_{17}$ $[M+Na]^+$ 1003.2784. Found: 1003.2791.

Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2,6-di-*O*-benzyl-α-D-allopyranoside (20) and methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-2,6-di-*O*-benzyl-α-D-allopyranoside (21)

Obtained according to the general procedure by condensation of **5** with **1.** After 2 h, TLC analysis of the mixture showed total consumption of **5** (*Rf* 0.65, 85:15 toluene-EtOAc) and the presence of two products of *Rf* 0.25 and 0.30. According to the integration of the ^{1}H NMR signals corresponding to H-4' of both disaccharides (4.96 and 4.94 ppm) they were in a 1.0:1.3 ratio.

After purification by column chromatography (8:2 toluene-EtOAc) fractions of *Rf* 0.30 afforded **20** (0.04 g, 42%) as an amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20-7.16 (m, 30H, aromatic), 5.96 (dt, 1H, $J_{5',6'b}$ = 3.1 Hz, $J_{4',5'}$ = 3.3 Hz, $J_{5',6'a}$ = 8.1 Hz, H-5'), 5.67 (dd, 1H, $J_{2',3'}$ = 1.6 Hz, $J_{3',4'}$ = 6.0 Hz, H-3'), 5.51 (s, 1H, H-1'), 5.43 (d, 1H, $J_{2',3'}$ = 1.6 Hz, H-2'), 4.96 (dd, 1H, $J_{4',5'}$ = 3.3 Hz, $J_{3',4'}$ = 6.0 Hz, H-4'), 4.75 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 4.72 (d, 1H, J_{gem} = 12.4 Hz, CH_2Ph), 4.68-4.60 (m, 3H, H-6'a and CH_2Ph), 4.58 (d, 1H, J_{gem} = 12.3 Hz, CH_2Ph), 4.47 (dd, 1H, $J_{5',6'b}$ = 3.1 Hz, J_{gem} = 12.1 Hz, H-6'b), 4.37 (t, 1H, $J_{3,4}$ = 3.2 Hz, $J_{2,3}$ =

3.3 Hz, H-3), 4.02 (ddd, 1H, $J_{5,6a}$ = 3.0 Hz, $J_{5,6b}$ = 4.4 Hz, $J_{4,5}$ = 9.9 Hz, H-5), 3.79 (dd, 1H, $J_{5,6a}$ = 3.0 Hz, J_{gem} = 10.6 Hz, H-6a), 3.76 (dd, 1H, $J_{5,6b}$ = 4.4 Hz, J_{gem} = 10.6 Hz, H-6b), 3.70 (td, 1H, $J_{3,4}$ = 3.2 Hz, $J_{4,5}$ = 9.9 Hz, $J_{4,OH}$ = 10.7 Hz, H-4), 3.50 (t, 1H, $J_{2,3}$ = 3.3 Hz, $J_{1,2}$ = 3.9 Hz, H-2), 3.38 (s, 3H, CH_3O), 2.93 (d, 1H, $J_{4,OH}$ = 10.7 Hz, OH-4) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 166.6, 166.1, 165.72, 165.70 (*C*OPh), 137.54, 133.5, 133.4, 133.1, 132.9, 130.0, 129.9, 129.7, 129.6, 129.5, 129.2, 129.0, 128.7, 128.4, 128.39, 128.36, 128.35, 128.2, 128.0, 127.9, 127.6, 127.5 (aromatic), 107.0 (C-1'), 98.0 (C-1), 83.7 (C-2'), 80.6 (C-4'), 76.9 (C-3'), 74.9 (C-3), 73.6 (*C*H_2Ph), 73.5 (C-2), 70.7 (*C*H_2Ph), 70.2 (C-5'), 69.5 (C-6), 67.9 (C-4), 67.2 (C-5), 64.2 (C-6'), 55.7 (*C*H_3O) ppm.

HRMS-ESI: calculated *m/z* for $C_{55}H_{52}NaO_{15}$ $[M+Na]^+$ 975.3198. Found: 975.3199.

Fractions of *Rf* 0.25 afforded **21** (0.03 g, 32%) as an amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15-7.12 (m, 30H, aromatic), 6.00 (dt, 1H, $J_{4',5'}$ = 3.9 Hz, $J_{5',6'a}$ = 5.5 Hz, $J_{5',6'b}$ = 5.5 Hz, H-5'), 5.66 (dd, 1H, $J_{2',3'}$ = 1.7 Hz, $J_{3',4'}$ = 6.0 Hz, H-3'), 5.47 (d, 1H, $J_{2',3'}$ = 1.7 Hz, H-2'), 5.42 (s, 1H, H-1'), 4.94 (dd, 1H, $J_{4',5'}$ = 3.9 Hz, $J_{3',4'}$ = 6.0 Hz, H-4'), 4.77-4.73 (m, 3H, H-1, H-6'a and H-6'b), 4.68 (d, 1H, J_{gem} = 12.4 Hz, CH_2Ph), 4.54 (s, 2H, CH_2Ph), 4.51-4.34 (m, 2H, H-3 and CH_2Ph), 4.09-4.04 (m, 1H, H-5), 3.90 (dd, 1H, $J_{5,6a}$ = 3.1 Hz, J_{gem} = 10.8 Hz, H-6a), 3.83 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{4,5}$ = 10.2 Hz, H-4), 3.76 (dd, 1H, $J_{5,6b}$ = 1.5 Hz, J_{gem} = 10.8 Hz, H-6b), 3.48 (t, 1H, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 3.4 Hz, H-2), 3.41 (s, 3H, CH_3O), 3.24 (d, 1H, $J_{3,OH}$ = 7.1 Hz, OH-3) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 166.1, 165.7, 165.6, 165.5 (*C*OPh), 137.9, 137.4, 133.46, 133.41, 133.2, 133.1, 130.0, 129.9, 129.8, 129.7, 129.5, 128.94, 128.91, 128.5, 128.4, 128.3, 128.2, 127.98, 127.95, 127.7, 127.4 (aromatic), 107.0 (C-1'), 99.2 (C-1), 82.5 (C-2'), 80.7 (C-4'), 77.2 (C-3'), 73.9 (C-4), 73.5 (C-2), 73.4 (*C*H_2Ph), 70.4 (*C*H_2Ph), 70.2 (C-5'), 69.2 (C-3), 68.3 (C-6), 65.2 (C-5), 63.4 (C-6'), 55.7 (*C*H_3O) ppm.

HRMS-ESI: calculated *m/z* for $C_{55}H_{52}NaO_{15}$ $[M+Na]^+$ 975.3198. Found: 975.3171.

Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2,6-di-*O*-benzoyl-α-D-allopyranoside (22) and methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-2,6-di-*O*-benzoyl-α-D-allopyranoside (23)

Obtained according to the general procedure by condensation of **5** with **2.** TLC analysis of the mixture showed, among the excess of **2** (*Rf* 0.05, 85:15 toluene-EtOAc), the presence of two products of *Rf* 0.32 and 0.48. According to the integration of the ^{1}H NMR signals corresponding to H-2 of **22** and H-4 of **23** they were in a 1.2:1.0 ratio.

After purification by column chromatography (92:8 toluene-EtOAc) fractions of *Rf* 0.48 (85:15 toluene-EtOAc) afforded **23** (0.05 g, 45%) as an amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12-7.12 (m, 30H, aromatic), 5.97 (dt, 1H, $J_{4',5'}$ = 3.9 Hz, $J_{5',6'a}$ = 4.5 Hz, $J_{5',6'b}$ = 6.5 Hz, H-5'), 5.66 (dd, 1H, $J_{2',3'}$ = 1.8 Hz, $J_{3',4'}$ = 5.9 Hz, H-3'), 5.51 (d, 1H, $J_{2',3'}$ = 1.8 Hz, H-2'), 5.49 (s, 1H, H-1'), 4.06 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 5.03 (t, 1H, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 3.4 Hz, H-2), 4.93 (dd, 1H, $J_{4',5'}$ = 3.9 Hz, $J_{3',4'}$ = 5.9 Hz, H-4'), 4.84 (dd, 1H, $J_{5,6a}$ = 1.9 Hz, J_{gem} = 12.1 Hz, H-6a), 4.75 (dd, 1H, $J_{5',6'a}$ = 4.5 Hz, J_{gem} = 12.0 Hz, H-6'a), 4.73-4.67 (m, 2H, H-6b and H-6'b), 4.64-4.59 (m, 1H, H-3), 4.39 (ddd, 1H, $J_{5,6a}$ = 1.9 Hz, $J_{5,6b}$ = 4.4 Hz, $J_{4,5}$ = 10.2 Hz, H-5), 3.97 (dd, 1H, $J_{3,4}$ = 2.9 Hz, $J_{4,5}$ = 10.2 Hz, H-4), 3.48 (s, 3H, CH_3O), 3.45 (d, 1H, $J_{3,OH}$ = 7.9 Hz, OH-3) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 166.1, 166.0, 165.7, 165.6, 165.5 (*C*OPh), 133.49, 133.44, 133.3, 133.2, 132.9, 130.07, 130.03, 129.96, 129.90, 129.8, 129.7, 129.6, 128.43, 128.40, 128.37, 128.32, 128.28, 128.21 (aromatic), 107.4 (C-1'), 98.1 (C-1), 82.8 (C-2'), 81.2 (C-4'), 77.1 (C-3'), 75.2 (C-4), 70.2 (C-5'), 69.9 (C-3), 69.3 (C-2), 64.2 (C-5), 63.3 (C-6), 63.2 (C-6'), 56.0 (*C*H_3O) ppm.

HRMS-ESI: calculated *m/z* for $C_{55}H_{48}NaO_{17}$ $[M+Na]^+$ 1003.2784. Found: 1003.2752.

Fractions of *Rf* 0.38 afforded **22** (0.05 g, 52%) as an amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20-7.13 (m, 30H, aromatic), 5.77 (dd, 1H, $J_{2',3'}$ = 1.2 Hz, $J_{3',4'}$ = 4.7 Hz, H-3'), 5.63-5.58 (m, 1H, H-5'), 5.56 (s, 1H, H-1'), 5.48 (d, 1H, $J_{2',3'}$ = 1.2 Hz, H-2'), 5.11 (t, 1H, $J_{2,3}$ = 3.5 Hz, $J_{1,2}$ = 4.2 Hz, H-2), 4.96 (d, 1H, $J_{1,2}$ = 4.2 Hz, H-1), 4.76 (dd, 1H, $J_{5,6a}$ = 4.9 Hz, J_{gem} = 12.1 Hz, H-6a), 4.71 (dd, 1H, $J_{5,6b}$ = 2.3 Hz, J_{gem} = 12.1 Hz, H-6b), 4.64 (t, 1H, $J_{3,4}$ = 3.1 Hz, $J_{2,3}$ = 3.5 Hz, H-3), 4.59 (dd, 1H, $J_{4',5'}$ = 4.1 Hz, $J_{3',4'}$ = 4.7 Hz, H-4'), 4.37 (ddd, 1H, $J_{5,6b}$ = 2.3 Hz, $J_{5,6a}$ = 4.9 Hz, $J_{4,5}$ = 10.1 Hz, H-5), 4.32 (dd, 1H, $J_{5',6'a}$ = 7.8 Hz, J_{gem} = 12.1 Hz, H-6'a), 4.05 (dd, 1H, $J_{5',6'b}$ = 3.0 Hz, J_{gem} = 12.1 Hz, H-6'b), 3.86 (ddd, 1H, $J_{3,4}$ = 3.1 Hz, $J_{4,5}$ =10.1 Hz, $J_{4,OH}$ = 10.2 Hz, H-4), 3.49 (s, 3H, CH_3O), 3.42 (d, 1H, $J_{4,OH}$ = 10.2 Hz, OH-4) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$): δ 166.9, 166.6, 165.8, 165.6, 165.53, 165.52 (*C*OPh), 133.53, 133.51, 133.16, 133.10, 132.9, 129.97, 129.91, 129.8, 129.7, 129.6, 129.5, 128.5, 128.43, 128.41, 128.36, 128.30, 128.26 (aromatic), 108.0 (C-1'), 97.4 (C-1), 83.6 (C-2'), 81.2 (C-4'), 77.2 (C-3'), 75.2 (C-3), 70.1 (C-5'), 69.3 (C-2), 67.7 (C-4), 66.5 (C-5), 64.1 (C-6), 63.3 (C-6'), 55.8 (*C*H_3O) ppm.

HRMS-ESI: calculated *m/z* for $C_{55}H_{48}NaO_{17}$ $[M+Na]^+$ 1003.2784. Found: 1003.2790.

Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2,6-di-*O*-benzyl-β-D-allopyranoside (24) and methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,6-di-*O*-benzyl-β-D-allopyranoside (25)

Obtained according to the general glycosidation procedure by condensation of **4** with **3**. TLC analysis of the mixture showed, among the excess of **3** (*Rf* 0.05, 85:15 toluene-EtOAc), the presence of one product of *Rf* 0.37. Analysis of the reaction mixture by ^{1}H NMR showed that two regioisomers (**24** and **25**) were formed in a 1.0:5.8 ratio.

After purification by column chromatography (90:10 toluene-EtOAc) fractions of *Rf* 0.37 (85:15 toluene-EtOAc) afforded an inseparable mixture of **24** and **25** (0.09 g, 82%) as an amorphous solid.

From the mixture, signals for **25**:

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95 (dd, 1H, $J_{4',5'}$ = 0.8 Hz, $J_{3',4'}$ = 3.5 Hz, H-4'), 5.78 (dd, 1H, $J_{1',2'}$ = 8.0 Hz, $J_{2',3'}$ = 10.4 Hz, H-2'), 5.52 (dd, 1H, $J_{3',4'}$ = 3.5 Hz, $J_{2',3'}$ = 10.4 Hz, H-3'), 4.89 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.75 (d, 1H, J_{gem} = 12.0 Hz, CH_2Ph), 4.69 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 4.61 (dd, 1H, $J_{5',6'a}$ = 6.8 Hz, J_{gem} = 11.4 Hz, H-6'a), 4.60 (d, 1H, J_{gem} = 12.0 Hz, CH_2Ph), 4.45-4.41 (m, 1H, H-3), 4.40 (dd, 1H, $J_{5',6'b}$ = 6.2 Hz, J_{gem} = 11.4 Hz, H-6'b), 4.32 (d, 1H, J_{gem} = 12.2 Hz, CH_2Ph), 4.22 (td, 1H, $J_{4',5'}$ = 0.8 Hz, $J_{5',6'b}$ = 6.2 Hz, $J_{5',6'a}$ = 6.8 Hz, H-5'), 4.18 (d, 1H, J_{gem} = 12.2 Hz, CH_2Ph), 3.87 (ddd, 1H, $J_{5,6a}$ = 1.7 Hz, $J_{5,6b}$ = 3.8 Hz, $J_{4,5}$ = 9.8 Hz, H-5), 3.80 (dd, 1H, $J_{3,4}$ = 2.6 Hz, $J_{4,5}$ = 8.8 Hz, H-4), 3.51 (s, 3H, CH_3O), 3.49 (dd, 1H, $J_{5,6a}$ = 1.7 Hz, J_{gem} = 11.0 Hz, H-6a), 3.42 (dd, 1H, $J_{5,6b}$ = 3.8 Hz, J_{gem} = 11.0 Hz, H-6b), 3.22 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{1,2}$ = 7.9 Hz, H-2), 2.66 (bs, 1H, OH-3) ppm.

^{13}C NMR (125.8 MHz, $CDCl_3$) δ 102.00 (C-1'), 101.36 (C-1), 77.03 (C-2), 76.63 (C-4), 73.10 (*C*H_2Ph), 72.55 (*C*H_2Ph), 71.54 (C-5'), 71.43 (C-3'), 71.03 (C-5), 69.85 (C-3), 69.59 (C-2'), 68.46 (C-6), 67.99 (C-4'), 62.04 (C-6'), 56.92 (*C*H_3O) ppm.

Signals for **24**:

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.97 (dd, 1H, $J_{4',5'}$ = 0.9 Hz, $J_{3',4'}$ = 3.6 Hz, H-4'), 5.86 (dd, 1H, $J_{1',2'}$ = 8.1 Hz, $J_{2',3'}$ = 10.4 Hz, H-2'), 5.63 (dd, 1H, $J_{3',4'}$ = 3.6 Hz, $J_{2',3'}$ = 10.4 Hz, H-3'), 5.25 (d, 1H, $J_{1',2'}$ = 8.1 Hz, H-1'), 4.73 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.73 (s, 2H, C*H*$_2$Ph), 4.56 (dd, 1H, $J_{5',6'a}$ = 6.7 Hz, J_{gem} = 11.4 Hz, H-6'a), 4.44-4.38 (m, 2H, H-3 and H-6'b), 4.37, 4.31 (2d, 2H, J_{gem} = 12.1 Hz, C*H*$_2$Ph), 4.35 (ddd, 1H, $J_{4',5'}$ = 0.9 Hz, $J_{5',6'a}$ = 6.6 Hz, $J_{5',6'b}$ = 6.6 Hz, H-5'), 3.66-3.60 (m, 1H, H-5), 3.59 (ddd, 1H, $J_{3,4}$ = 2.5 Hz, $J_{4,5}$ = 8.8 Hz, $J_{4,OH}$ = 6.3 Hz, H-4), 3.50 (s, 3H, C*H*$_3$O), 3.42 (dd, 1H, $J_{5,6a}$ = 4.7 Hz, J_{gem} = 10.1 Hz, H-6a), 3.31 (dd, 1H, $J_{5,6b}$ = 4.6 Hz, J_{gem} = 10.1 Hz, H-6b), 3.27 (dd, 1H, $J_{2,3}$ = 2.8 Hz, $J_{1,2}$ = 7.8 Hz, H-2), 2.86 (d, 1H, $J_{4,OH}$ = 6.3 Hz, OH-4) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 102.05 (C-1'), 101.13 (C-1), 77.11 (C-3), 77.03 (C-2), 73.41 (*C*H_2Ph), 72.07 (*C*H_2Ph), 71.74 (C-5), 71.64 (C-3'), 71.47 (C-5'), 70.48 (C-2' and C-4), 70.23 (C-6), 68.18 (C-4'), 62.11(C-6'), 56.87(*C*H_3O) ppm.

Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→3)-2,6-di-*O*-benzyl-β-D-allopyranoside (26) and methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-2,6-di-*O*-benzyl-β-D-allopyranoside (27)

Obtained according to the general glycosidation procedure by condensation of **5** with **3**. TLC analysis of the mixture showed, among the excess of **3** (*Rf* 0.05, 85:15 toluene-EtOAc), the presence of two products of *Rf* 0.28 and *Rf* 0.30. According to the integration of the ^{1}H NMR signals corresponding to H-4' of **26** and H-5' of **27** they were in a 1.0:2.3 ratio.

After purification by column chromatography (88:12 toluene-EtOAc) fractions of *Rf* 0.28 (85:15 toluene-EtOAc) afforded an inseparable mixture of **26** and **27** (0.09 g, 82%) as an amorphous solid.

The first fractions of *Rf* 0.30 afforded **26** (0.05 g, 49%) unpurified with **27**. Selected signals for **26**:

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.93 (dt, 1H, $J_{5',6'b}$ = 3.0 Hz, $J_{4',5'}$ = 3.4 Hz, $J_{5',6'a}$ = 8.2 Hz, H-5'), 5.66 (s, 1H, H-1'), 5.61 (da, 1H, $J_{3',4'}$ = 5.2 Hz, H-3'), 5.44 (d, 1H, $J_{2',3'}$ = 1.2 Hz, H-2'), 4.88 (dd, 1H, $J_{4',5'}$ = 3.4 Hz, $J_{3',4'}$ = 5.2 Hz, H-4'), 4.84 (d, 1H, J_{gem} = 12.1 Hz, CH_2Ph), 4.73 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 4.69 (d, 1H, J_{gem} = 12.1 Hz, CH_2Ph), 4.62 (dd, 1H, $J_{5',6'a}$ = 8.2 Hz, J_{gem} = 12.1 Hz, H-6'a), 4.61, 4.58 (2d, 2H, J_{gem} = 12.2 Hz, CH_2Ph), 4.38 (t, 1H, $J_{3,4}$ = 2.5 Hz, $J_{2,3}$ = 2.9 Hz, H-3), 4.33 (dd, 1H, $J_{5',6'b}$ = 3.0 Hz, J_{gem} = 12.1 Hz, H-6'b), 3.96 (dt, 1H, $J_{5,6a}$ = 4.5 Hz, $J_{5,6b}$ = 5.3 Hz, $J_{4,5}$ = 9.5 Hz, H-5), 3.79 (dd, 1H, $J_{5,6a}$ = 4.5 Hz, J_{gem} = 10.4 Hz, H-6a), 3.74 (dd, 1H, $J_{5,6b}$ = 5.3 Hz, J_{gem} = 10.4 Hz, H-6b), 3.68-3.62 (m, 1H, H-4), 3.52 (s, 3H, CH_3O), 3.28 (dd, 1H, $J_{2,3}$ = 2.9 Hz, $J_{1,2}$ = 7.9 Hz, H-2), 3.02 (d, 1H, $J_{4,OH}$ = 7.0 Hz, OH-4) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 106.26 (C-1'), 101.94 (C-1), 82.66 (C-2'), 81.36 (C-4'), 77.32 (C-3'), 76.32 (C-2), 75.34 (C-3), 73.70 (*C*H_2Ph), 72.68 (*C*H_2Ph), 72.42 (C-5), 70.74 (C-6), 70.68 (C-4), 70.32 (C-5'), 64.17 (C-6'), 56.88 (*C*H_3O) ppm.

Further elution gave **27** (0.04 g, 34%) unpurified with **26**. Selected signals for **27**:

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10-7.10 (m, 30H, aromatic), 6.00 (dt, 1H, $J_{4',5'}$ = 3.8 Hz, $J_{5',6'b}$ = 4.4 Hz, $J_{5',6'a}$ = 6.9 Hz, H-5'), 5.65 (dd, 1H, $J_{2',3'}$ = 1.5 Hz, $J_{3',4'}$ = 5.5 Hz, H-3'), 5.47 (d, 1H, $J_{2',3'}$ = 1.5 Hz, H-2'), 5.43 (s, 1H, H-1'), 4.80 (dd, 1H, $J_{4',5'}$ = 3.8 Hz, $J_{3',4'}$ = 5.5 Hz, H-4'), 4.79 (d, 1H, J_{gem} = 12.0 Hz, CH_2Ph), 4.76 (dd, 1H, $J_{5',6'a}$ = 4.4 Hz, J_{gem} = 11.9 Hz, H-6'a), 4.70 (dd, 1H, $J_{5',6'b}$ = 6.9 Hz, J_{gem} = 11.9 Hz, H-6'b), 4.68 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 4.65 (d, 1H, J_{gem} = 12.0 Hz, CH_2Ph), 4.59, 4.54 (2d, 2H, J_{gem} = 12.1 Hz, CH_2Ph), 4.37 (t, 1H, $J_{3,4}$ = 2.8 Hz, $J_{2,3}$ = 3.2 Hz, H-3), 3.99 (dt, 1H, $J_{5,6a}$ = 2.7 Hz, $J_{5,6b}$ = 2.7 Hz, $J_{4,5}$ = 9.8 Hz, H-5), 3.87 (dd, 1H, $J_{3,4}$ = 2.8 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 3.81 (d, 2H, $J_{5,6}$ = 2.7 Hz, H-6a and H-6b), 3.55 (s, 3H, CH_3O), 3.30 (dd, 1H, $J_{2,3}$ = 3.0 Hz, $J_{1,2}$ = 7.9 Hz, H-2), 2.52 (bs, 1H, OH-3) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ 166.08, 165.66, 165.63, 165.41 (*C*OPh), 138.24, 138.04, 133.54, 133.41, 133.29, 133.16, 129.94, 129.91, 129.88, 129.82, 129.71, 129.69, 129.46, 129.42, 129.02, 128.86, 128.78, 128.48, 128.43, 128.41, 128.40, 128.37, 128.35, 128.20, 128.16, 127.94, 127.78, 127.74, 127.58, 127.36 (aromatic), 106.96 (C-1'), 101.57 (C-1), 82.13 (C-2'), 81.45 (C-4'), 77.25 (C-3'), 77.08 (C-2), 74.29 (C-4), 73.29 (*C*H_2Ph), 72.70 (*C*H_2Ph), 71.45 (C-5), 70.20 (C-5'), 70.11 (C-3), 68.72 (C-6), 63.35 (C-6'), 56.94 (*C*H_3O) ppm.

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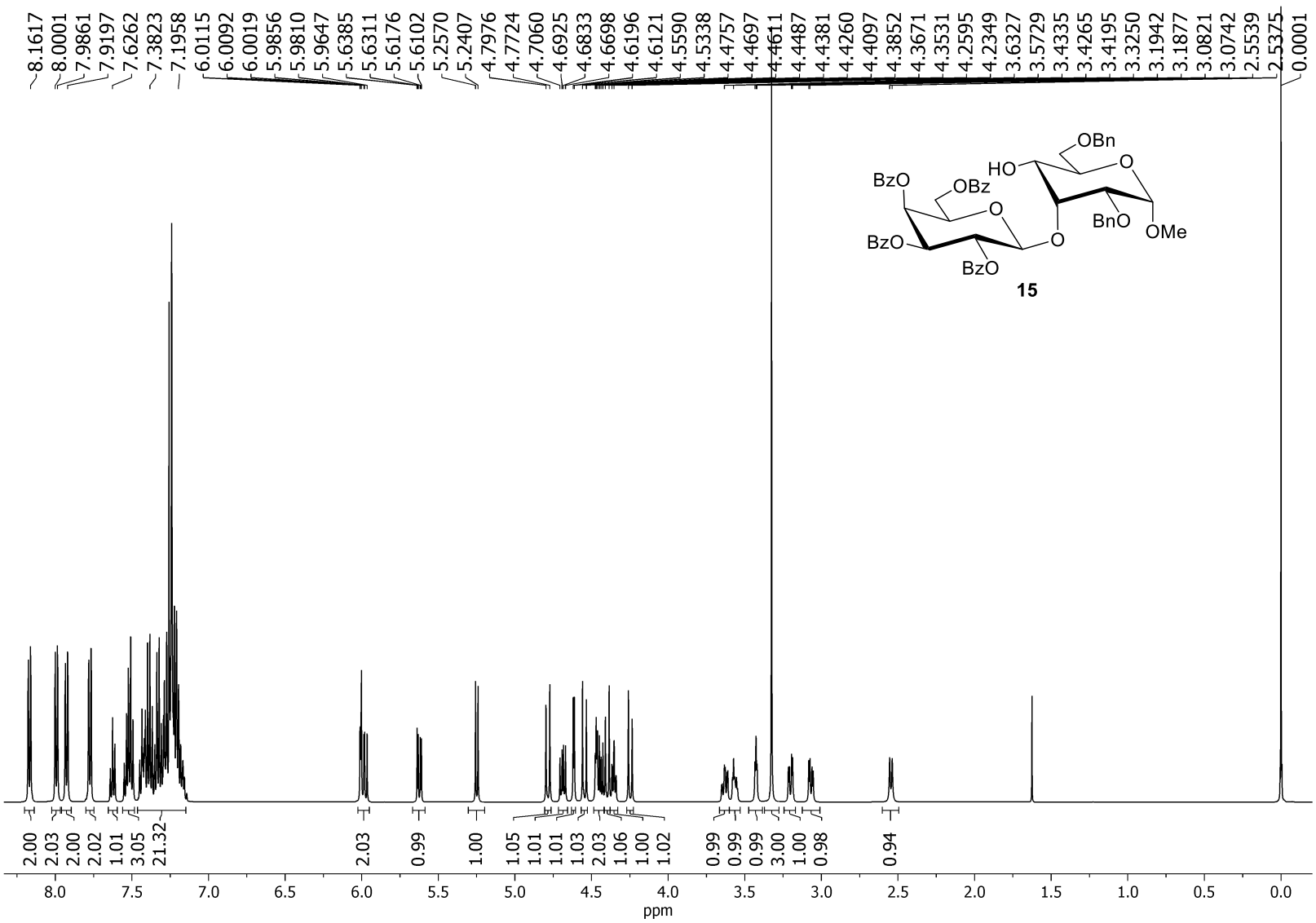
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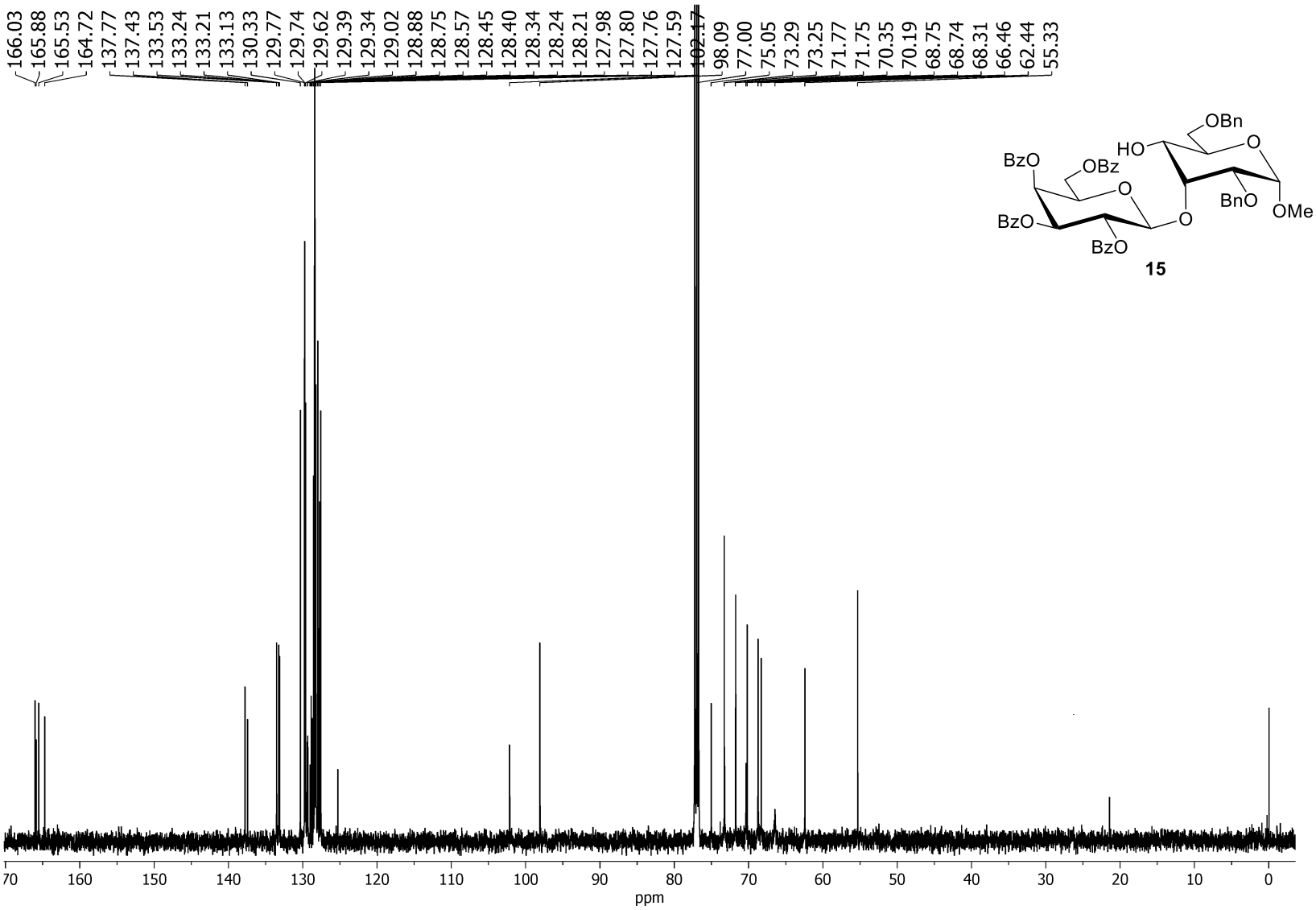
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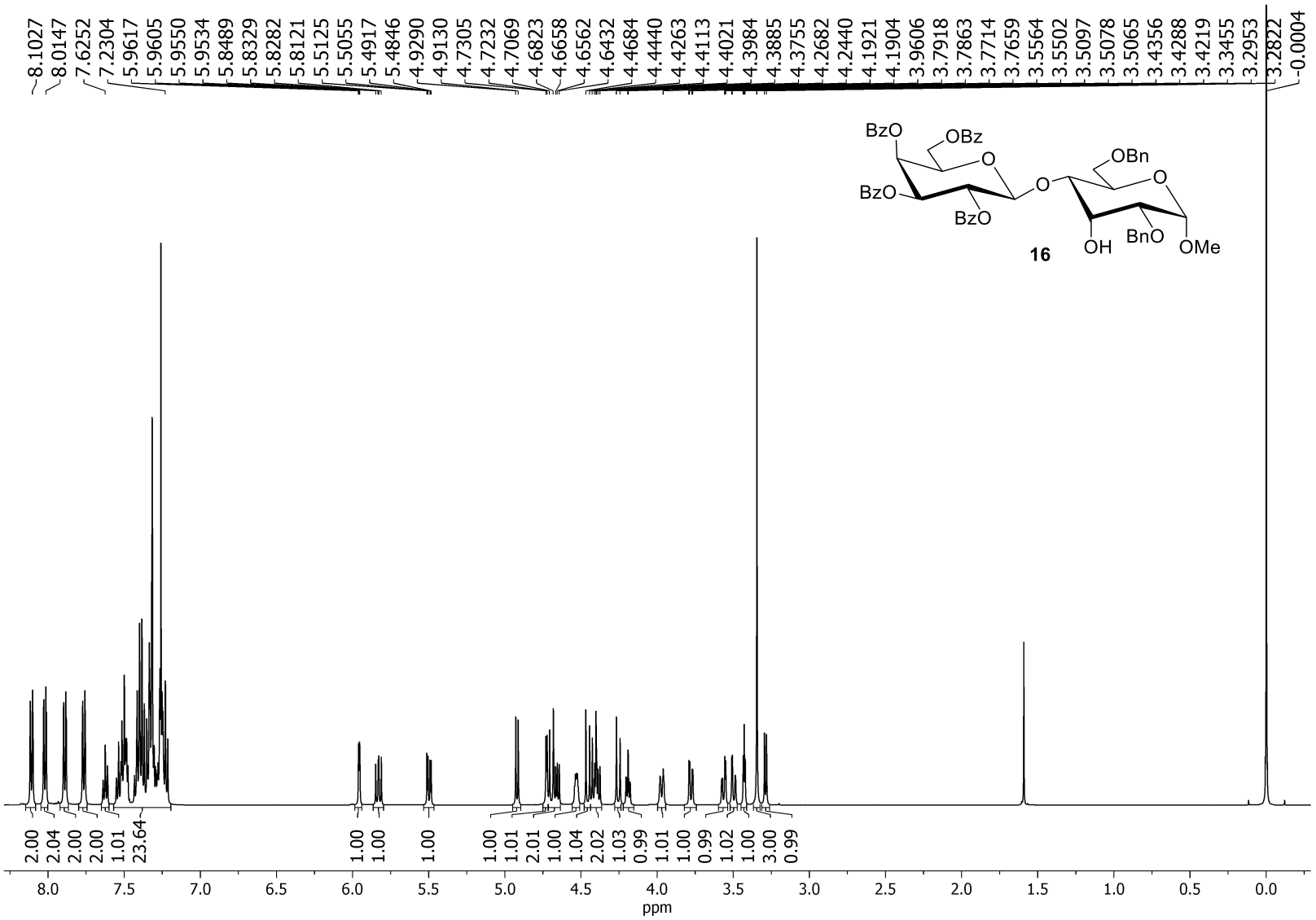
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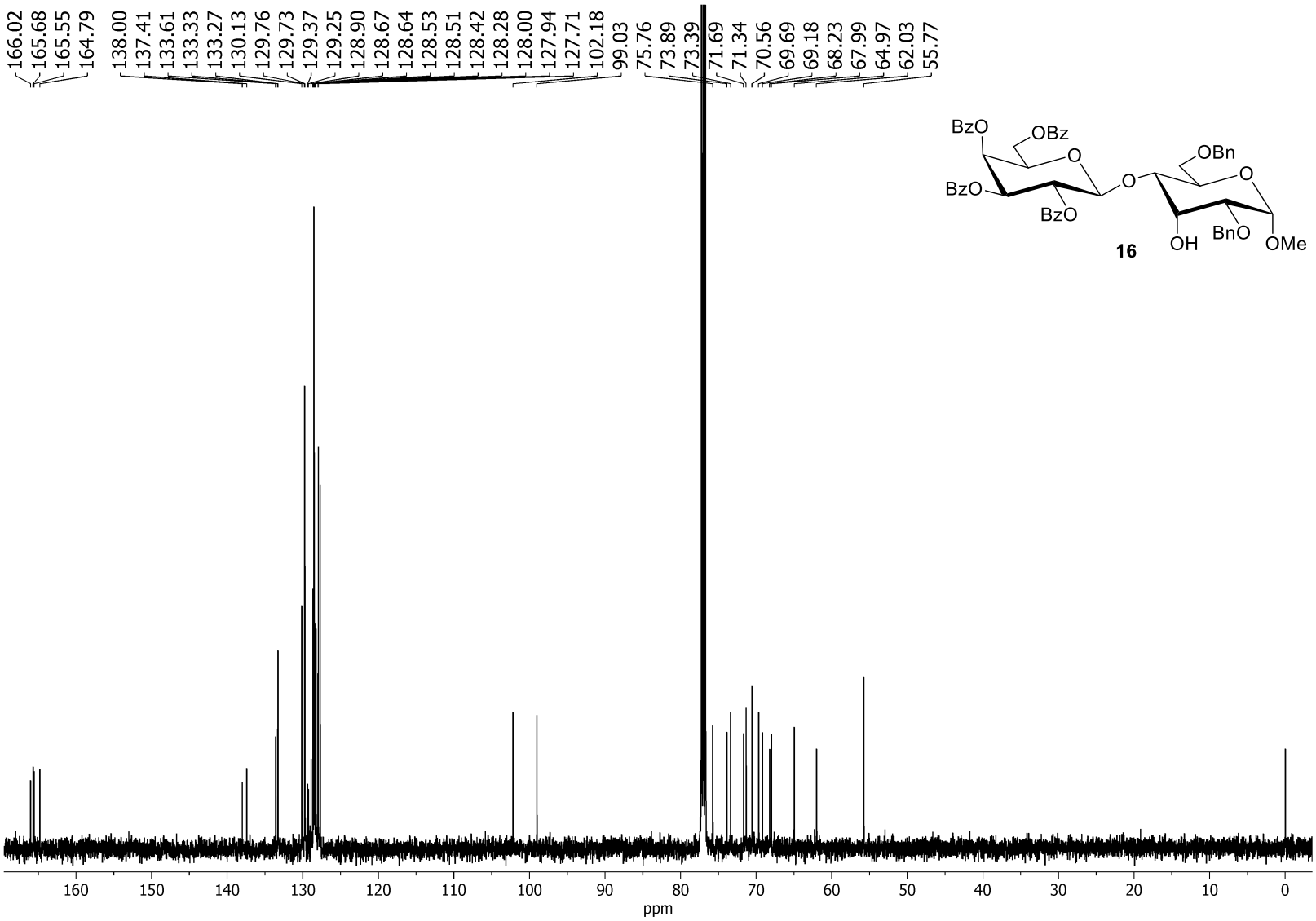
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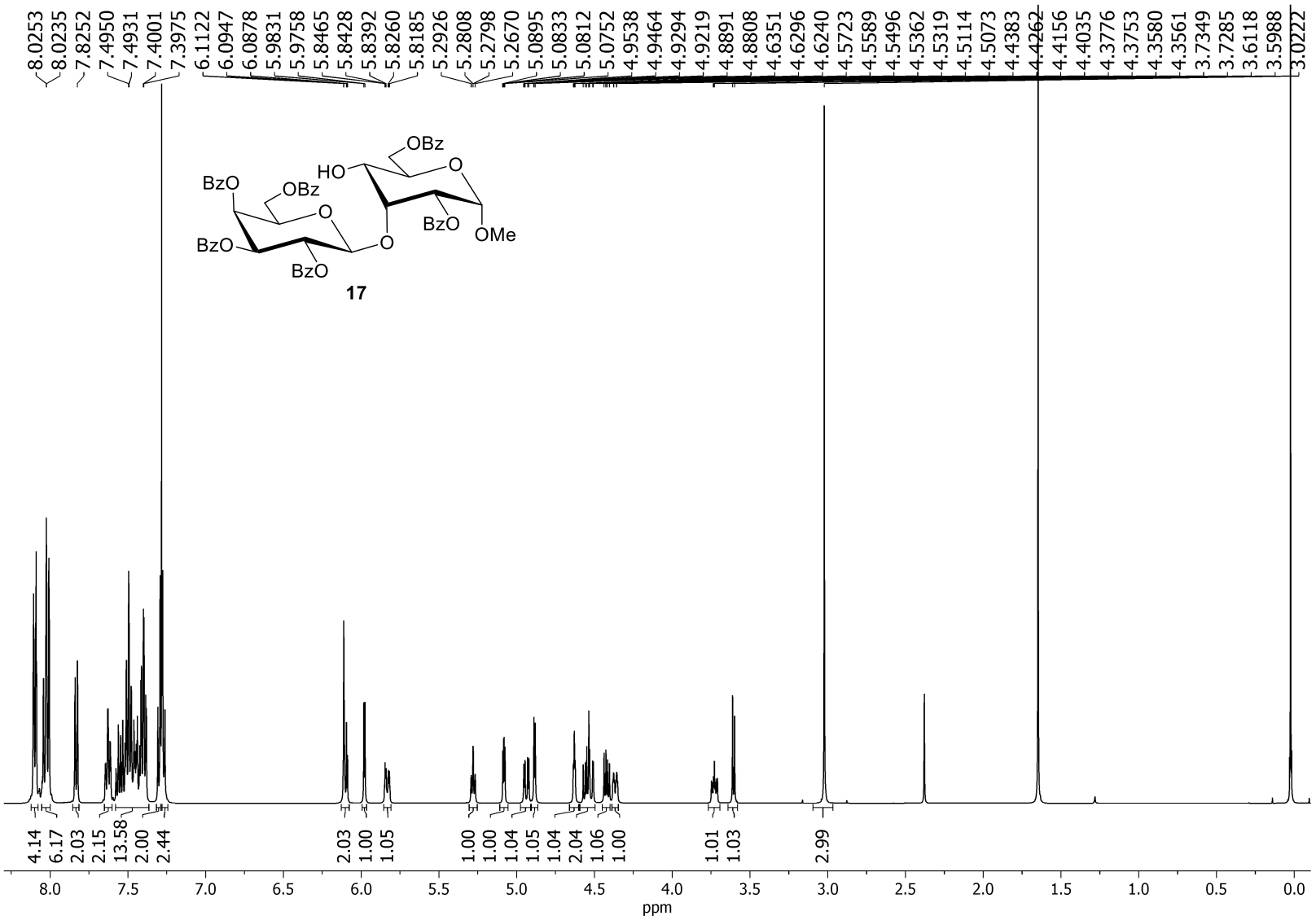
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BzO
OBz
O
BzO
OMe
BzO
O
BzO
17
4.14
6.17
2.03
2.15
13.58
2.00
2.44
2.03
1.00
1.05
1.00
1.00
1.04
1.05
1.04
2.04
1.06
1.00
1.01
1.03
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7.0
6.5
6.0
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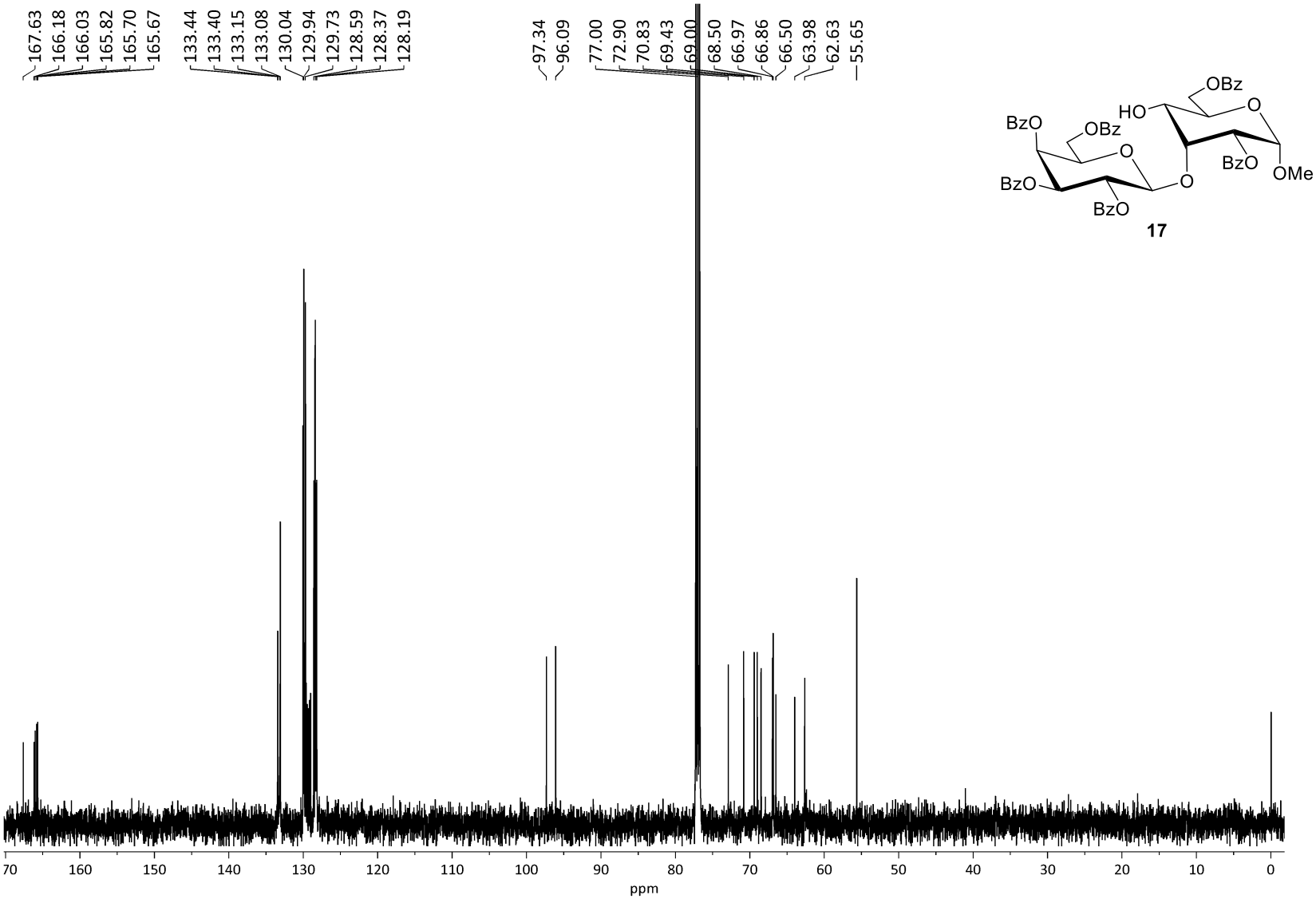
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128.59
128.37
128.19
97.34
96.09
77.00
72.90
70.83
69.43
69.00
68.50
66.97
66.86
66.50
63.98
62.63
55.65
OBz
HO
O
BzO
OBz
O
BzO
OMe
BzO
O
BzO
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100
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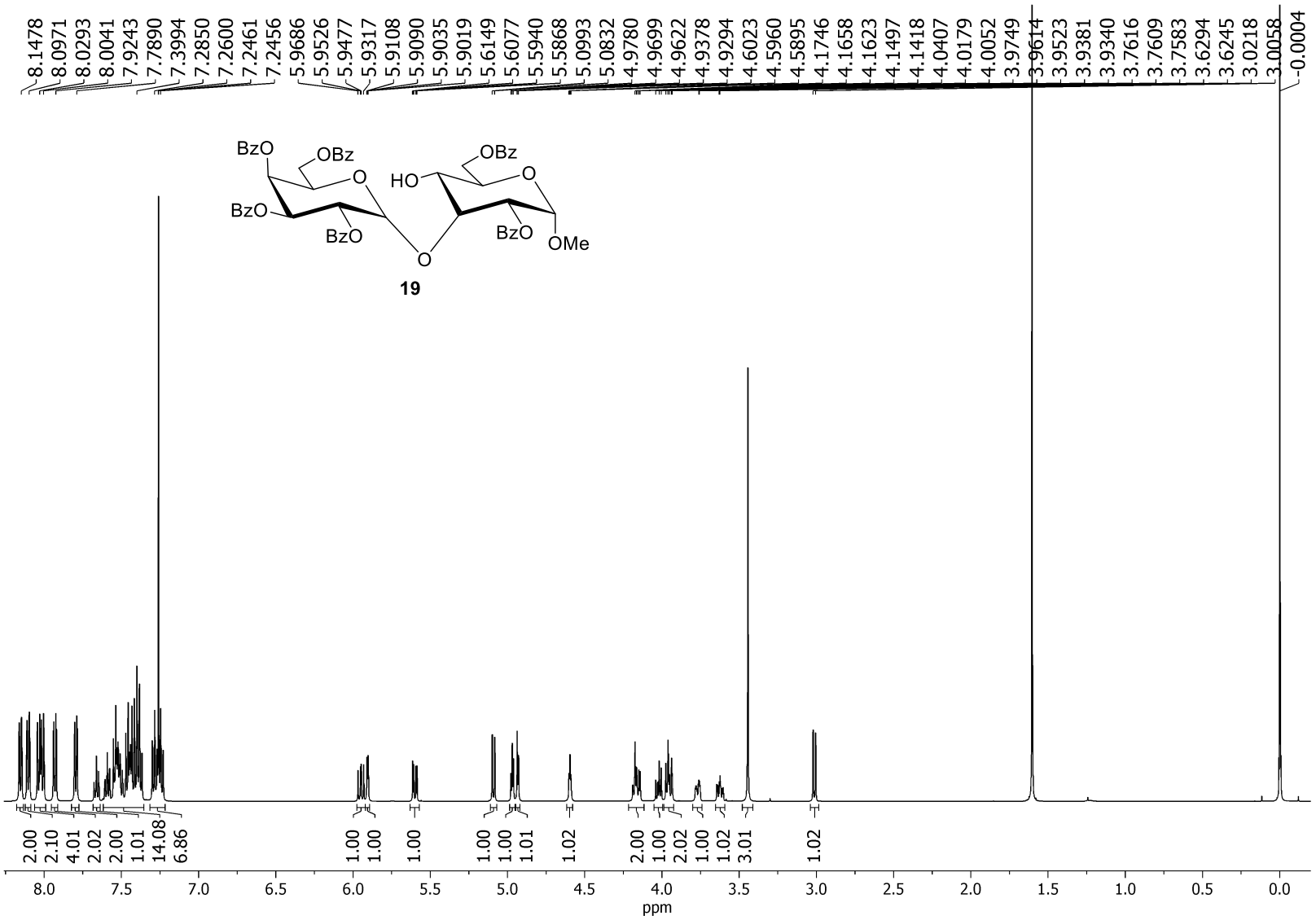
ppm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7.2456
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5.9526
5.9477
5.9317
5.9108
5.9090
5.9035
5.9019
5.6149
5.6077
5.5940
5.5868
5.0993
5.0832
4.9780
4.9699
4.9622
4.9378
4.9294
4.6023
4.5960
4.5895
4.1746
4.1658
4.1623
4.1497
4.1418
4.0407
4.0179
4.0052
3.9749
3.9614
3.9523
3.9381
3.9340
3.7616
3.7609
3.7583
3.6294
3.6245
3.0218
3.0058
-0.0004
BzO
OBz
O
BzO
BzO
O
HO
OBz
O
BzO
OMe
19
2.00
2.10
4.01
2.02
2.00
1.01
14.08
6.86
1.00
1.00
1.00
1.00
1.00
1.01
1.02
2.00
1.00
2.02
1.00
1.02
3.01
1.02
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7.0
6.5
6.0
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4.0
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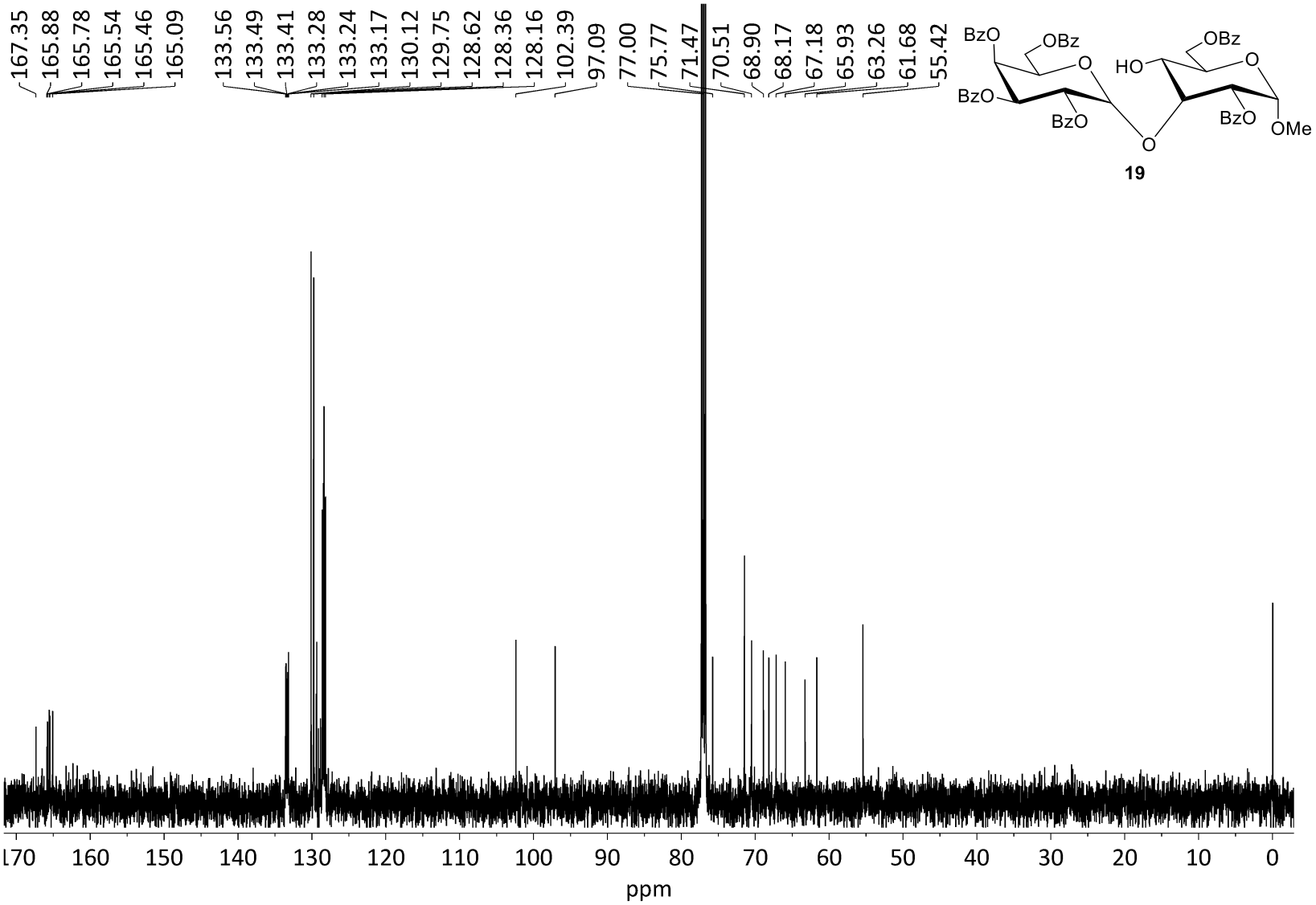
ppm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133.49
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133.28
133.24
133.17
130.12
129.75
128.62
128.36
128.16
102.39
97.09
77.00
75.77
71.47
70.51
68.90
68.17
67.18
65.93
63.26
61.68
55.42
BzO
OBz
O
BzO
BzO
HO
OBz
O
BzO
OMe
O
19
170
160
150
140
130
120
110
100
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30
20
10
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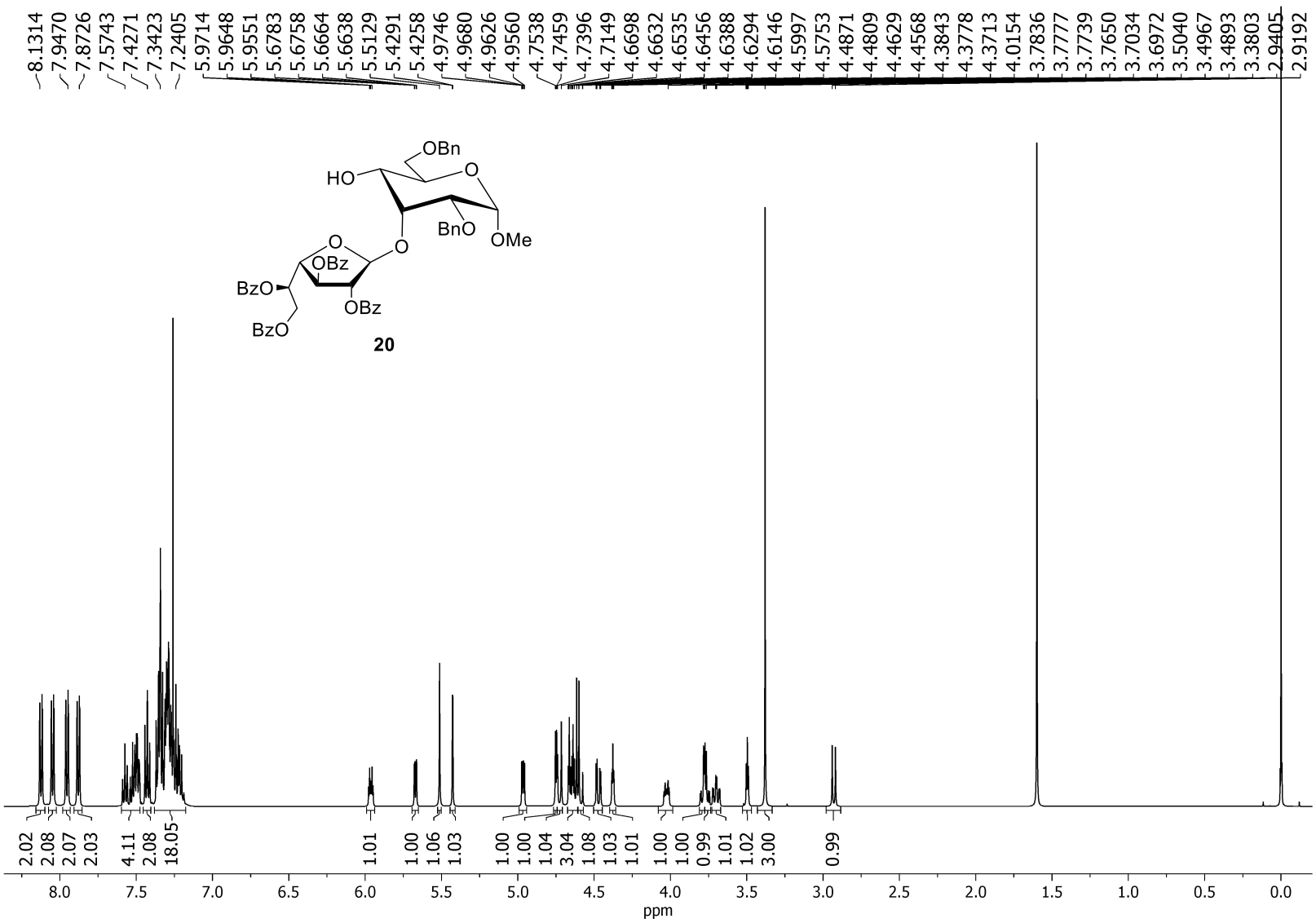
ppm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5.6664
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5.5129
5.4291
5.4258
4.9746
4.9680
4.9626
4.9560
4.7538
4.7459
4.7396
4.7149
4.6698
4.6632
4.6535
4.6456
4.6388
4.6294
4.6146
4.5997
4.5753
4.4871
4.4809
4.4629
4.4568
4.3843
4.3778
4.3713
4.0154
3.7836
3.7777
3.7739
3.7650
3.7034
3.6972
3.5040
3.4967
3.4893
3.3803
2.9405
2.9192
OBn
HO
O
BnO
OMe
O
O
OBz
BzO
OBz
BzO
20
2.02
2.08
2.07
2.03
4.11
2.08
18.05
1.01
1.00
1.06
1.03
1.00
1.00
1.04
3.04
1.08
1.03
1.01
1.00
1.00
0.99
1.01
1.02
3.00
0.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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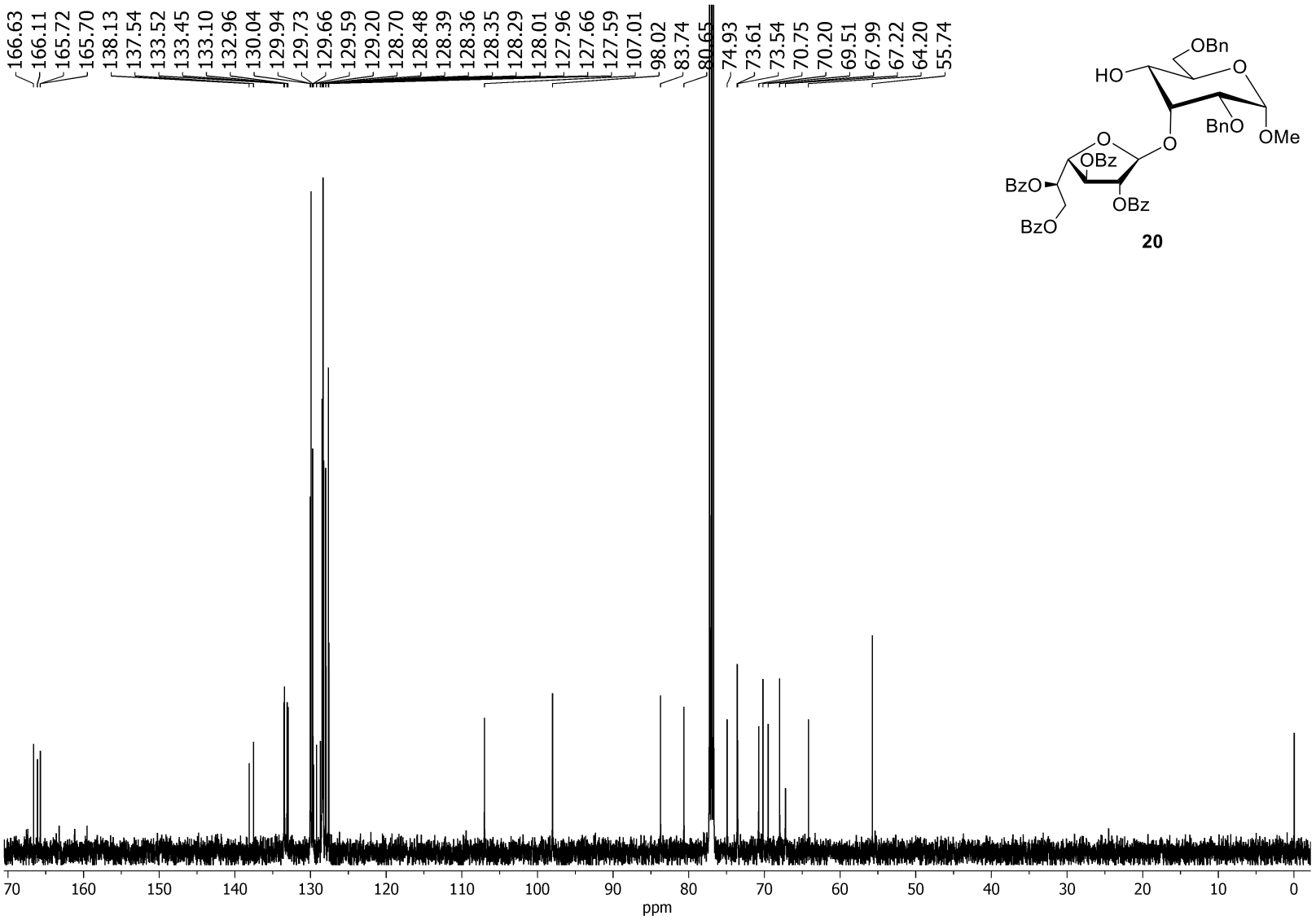
1.0
0.5
0.0
ppm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137.54
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133.45
133.10
132.96
130.04
129.94
129.73
129.66
129.59
129.20
128.70
128.48
128.39
128.36
128.35
128.29
128.01
127.96
127.66
127.59
107.01
98.02
83.74
80.65
74.93
73.61
73.54
70.75
70.20
69.51
67.99
67.22
64.20
55.74
OBn
HO
O
BnO
OMe
O
O
OBz
BzO
OBz
BzO
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140
130
120
110
100
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60
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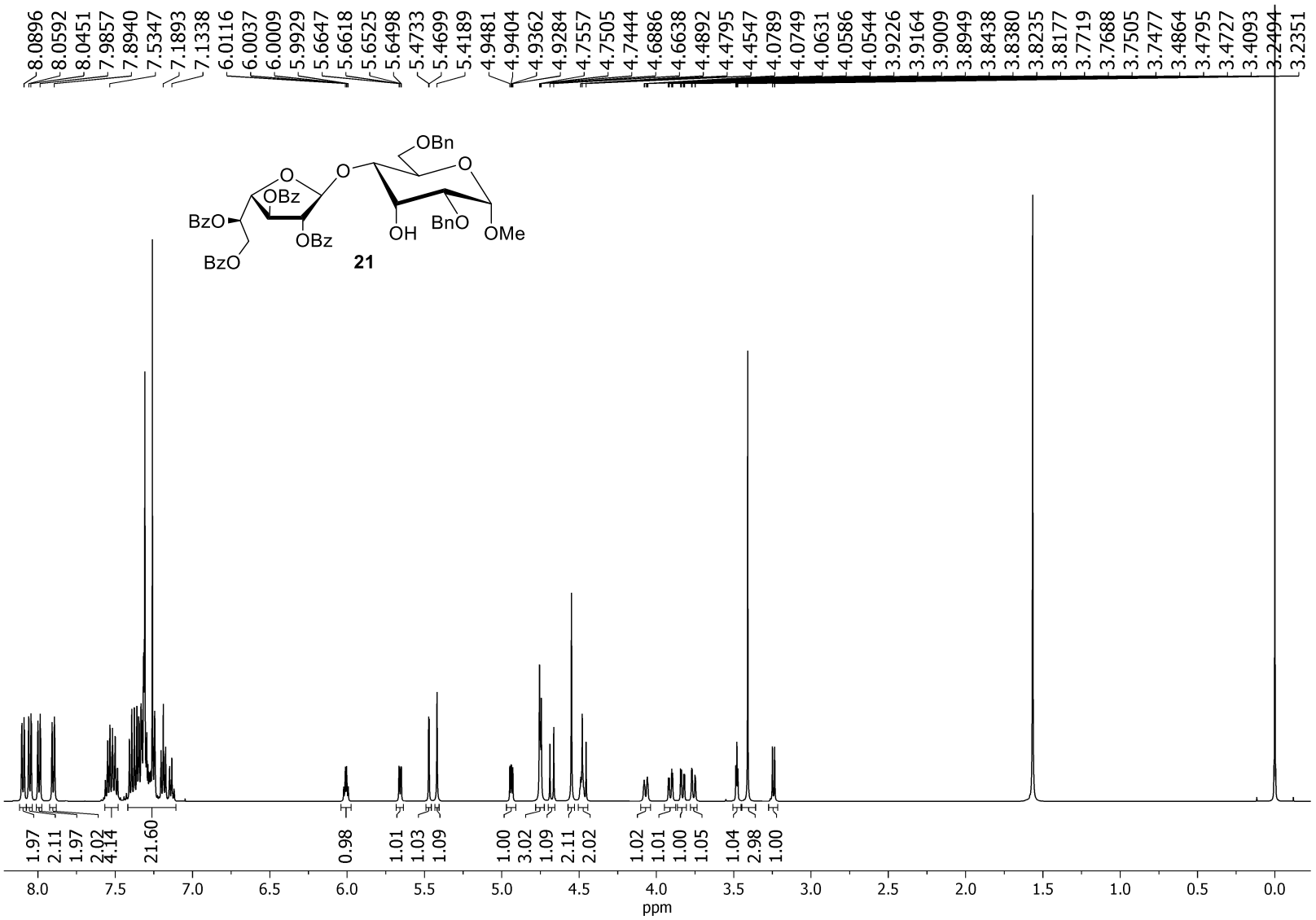
ppm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7.1893
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6.0009
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5.6618
5.6525
5.6498
5.4733
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4.9481
4.9404
4.9362
4.9284
4.7557
4.7505
4.7444
4.6886
4.6638
4.4892
4.4795
4.4547
4.0789
4.0749
4.0631
4.0586
4.0544
3.9226
3.9164
3.9009
3.8949
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3.8380
3.8235
3.8177
3.7719
3.7688
3.7505
3.7477
3.4864
3.4795
3.4727
3.4093
3.2494
3.2351
OBn
O
O
O
OBz
BzO
OBz
OH
BnO
OMe
BzO
21
1.97
2.11
1.97
2.02
4.14
21.60
0.98
1.01
1.03
1.09
1.00
3.02
1.09
2.11
2.02
1.02
1.01
1.00
1.05
1.04
2.98
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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1.5
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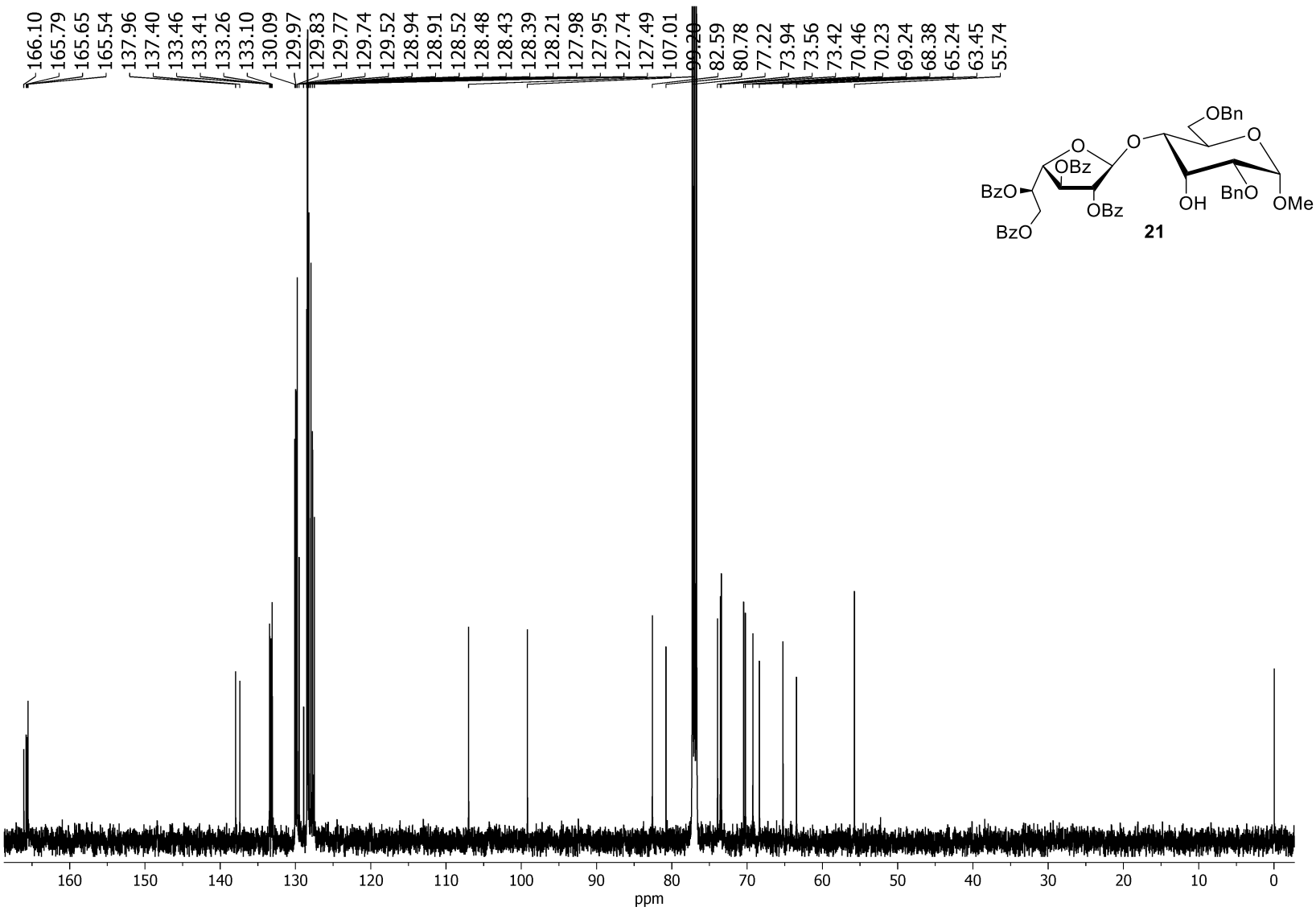
0.0
ppm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129.83
129.77
129.74
129.52
128.94
128.91
128.52
128.48
128.43
128.39
128.21
127.98
127.95
127.74
127.49
107.01
99.20
82.59
80.78
77.22
73.94
73.56
73.42
70.46
70.23
69.24
68.38
65.24
63.45
55.74
OBn
O
O
O
OBz
BzO
OBz
OH
BnO
OMe
BzO
21
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150
140
130
120
110
100
90
80
70
60
50
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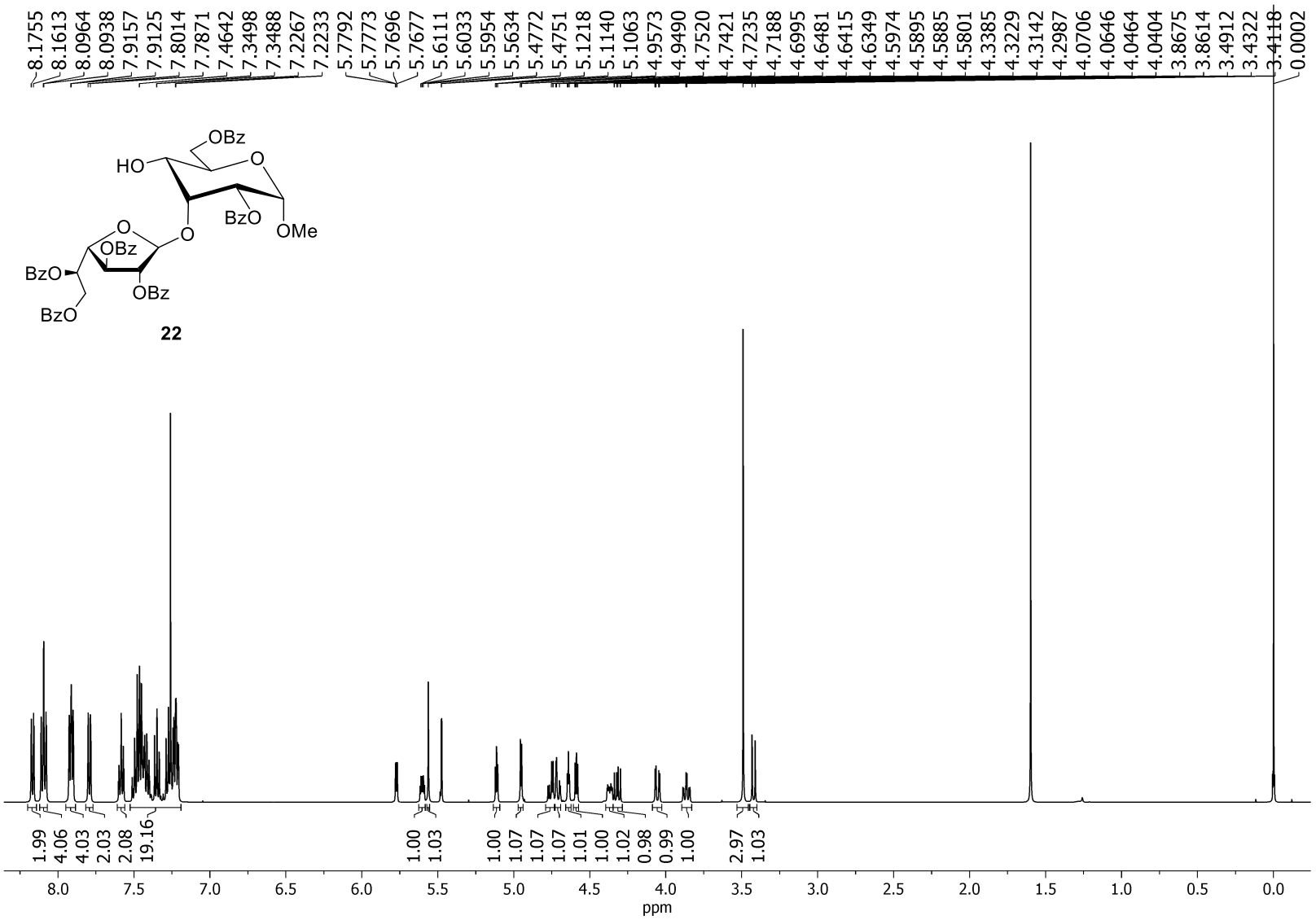
30
20
10
0
ppm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7.2267
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5.7773
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5.7677
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5.5634
5.4772
5.4751
5.1218
5.1140
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4.9490
4.7520
4.7421
4.7235
4.7188
4.6995
4.6481
4.6415
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4.5974
4.5895
4.5885
4.5801
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4.3229
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4.2987
4.0706
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4.0404
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3.8614
3.4912
3.4322
3.4118
0.0002
OBz
HO
O
BzO
OMe
O
O
OBz
BzO
OBz
BzO
22
1.99
4.06
4.03
2.03
2.08
19.16
1.00
1.03
1.00
1.07
1.07
1.07
1.01
1.00
1.02
0.98
0.99
1.00
2.97
1.03
8.0
7.5
7.0
6.5
6.0
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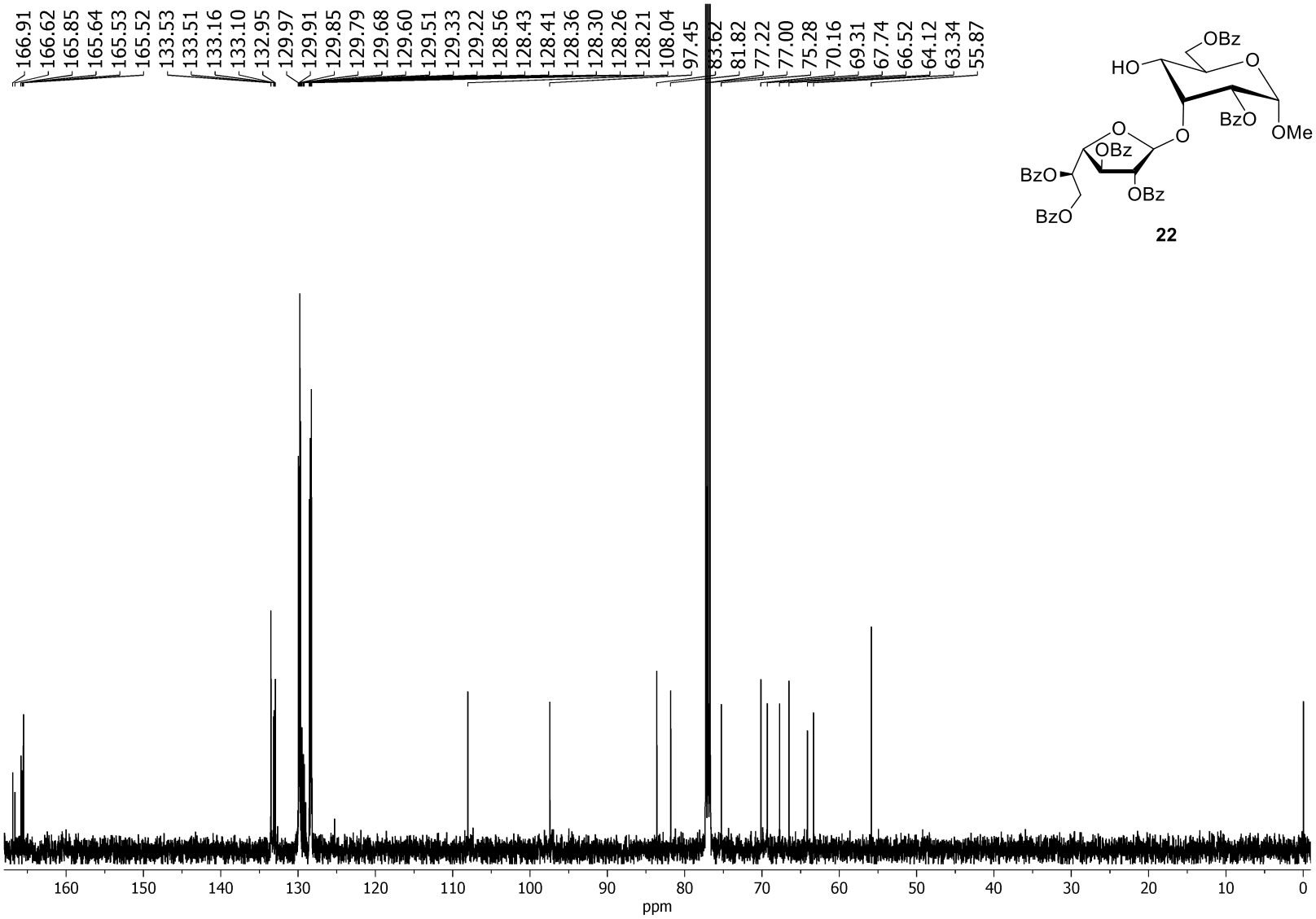
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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133.51
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132.95
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129.51
129.33
129.22
128.56
128.43
128.41
128.36
128.30
128.26
128.21
108.04
97.45
83.62
81.82
77.22
77.00
75.28
70.16
69.31
67.74
66.52
64.12
63.34
55.87
OBz
HO
O
BzO
OMe
O
O
OBz
BzO
OBz
BzO
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130
120
110
100
90
80
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50
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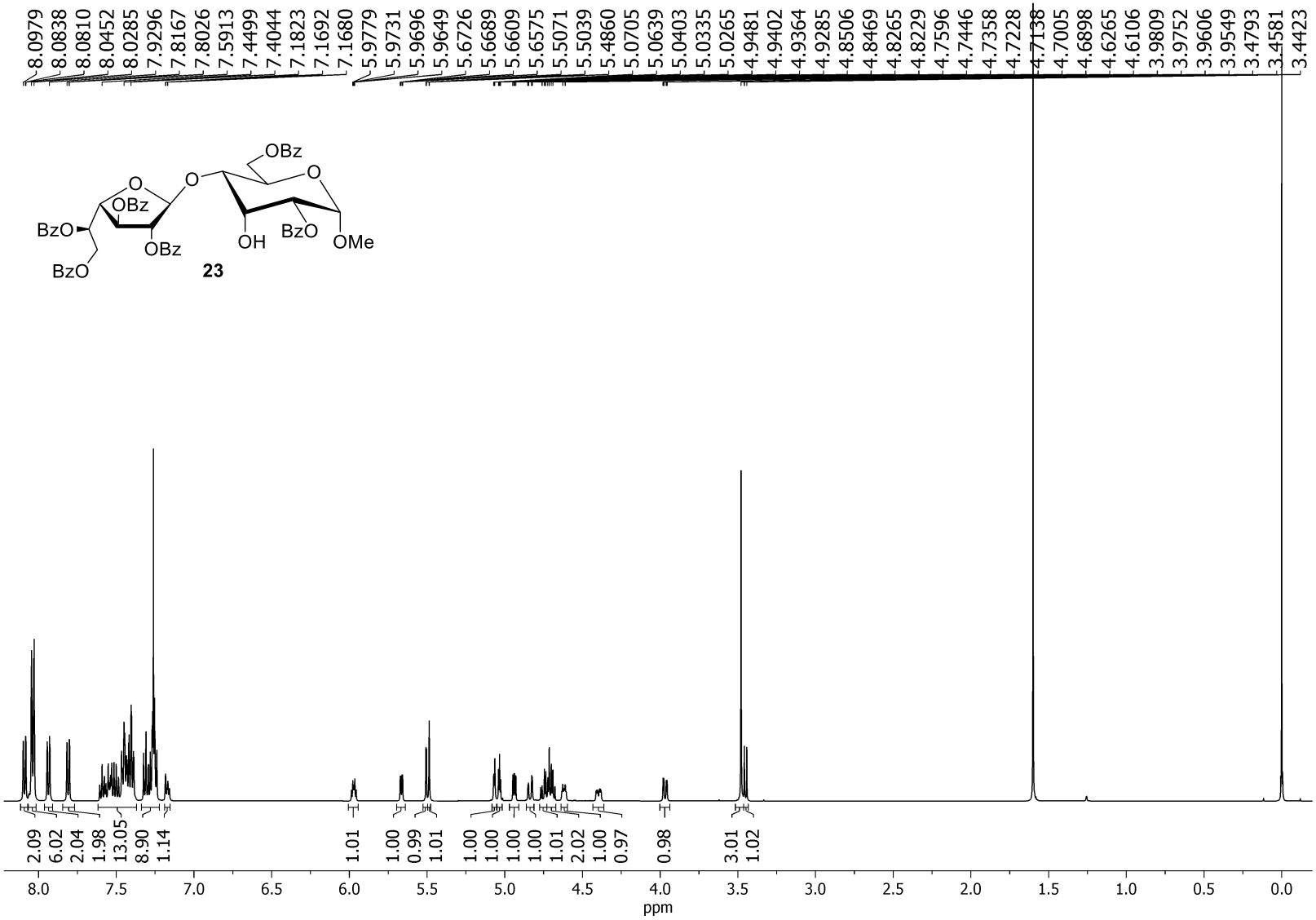
ppm

22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5.0639
5.0403
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3.9809
3.9752
3.9606
3.9549
3.4793
3.4581
3.4423
OBz
O
O
O
OBz
BzO
OBz
OH
BzO
OMe
BzO
23
2.09
6.02
2.04
1.98
13.05
8.90
1.14
1.01
1.00
0.99
1.01
1.00
1.00
1.00
1.00
1.01
2.02
1.00
0.97
0.98
3.01
1.02
8.0
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6.5
6.0
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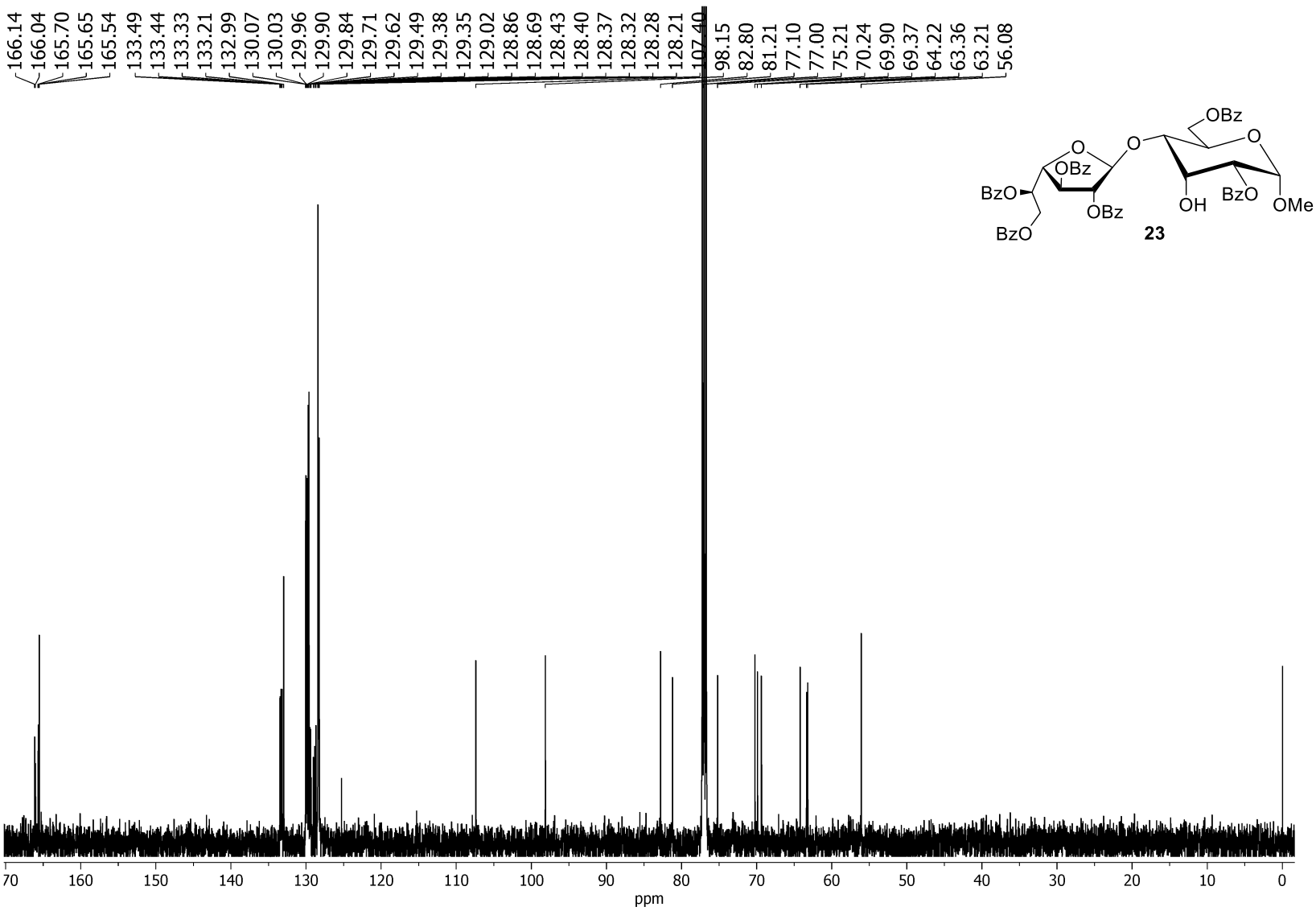
1.5
1.0
0.5
0.0
ppm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133.33
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129.96
129.90
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129.71
129.62
129.49
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129.02
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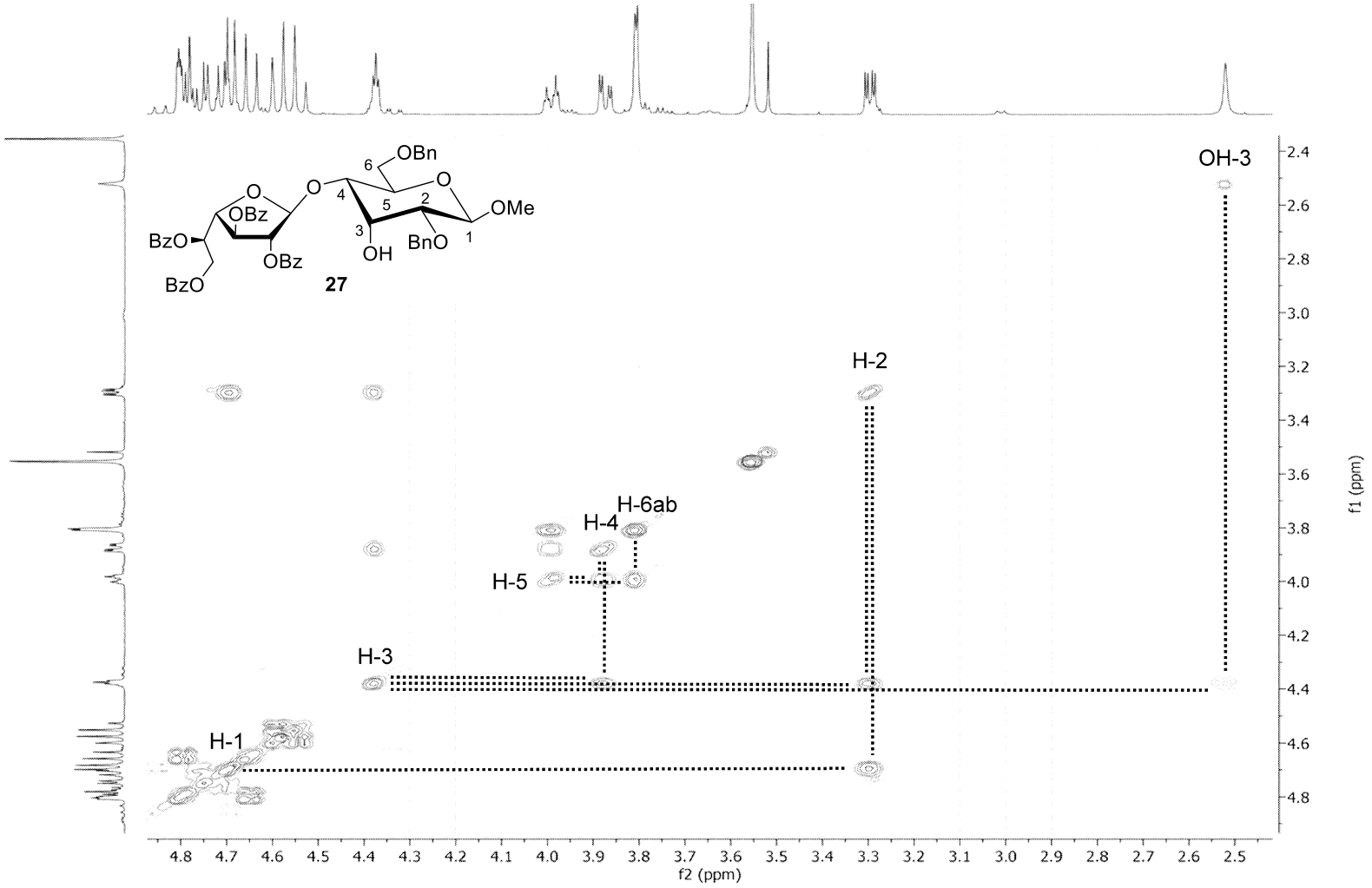
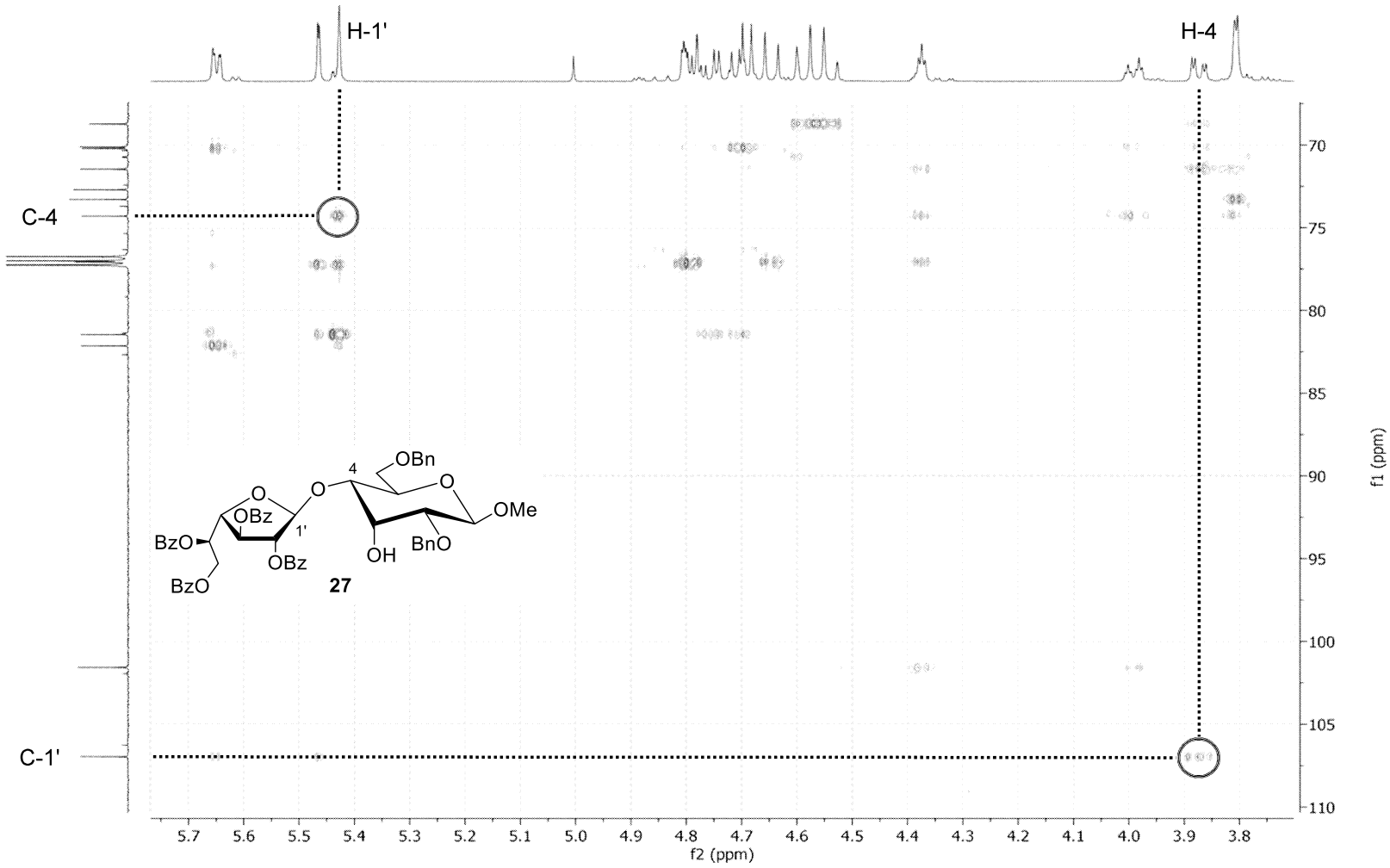
128.69
128.43
128.40
128.37
128.32
128.28
128.21
107.40
98.15
82.80
81.21
77.10
77.00
75.21
70.24
69.90
69.37
64.22
63.36
63.21
56.08
OBz
O
O
O
OBz
BzO
OBz
OH
BzO
OMe
BzO
23
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

2D NMR analysis of disaccharide 27 glycosidic linkage.




H-1'
H-4
C-4
C-1'
f2 (ppm)
f1 (ppm)
OBn
OMe
OBz
BzO
BzO
OBz
OH
BnO
1'
4
27