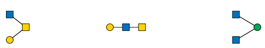
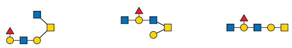
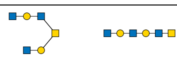
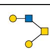
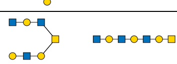
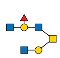
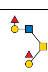
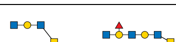
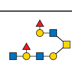
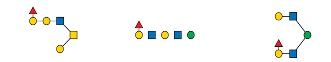
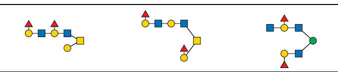
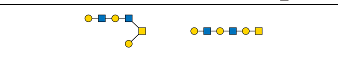
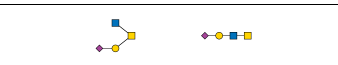
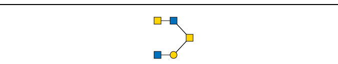
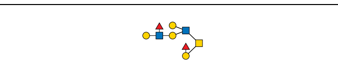
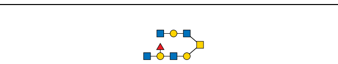
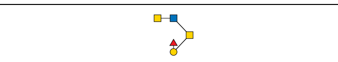
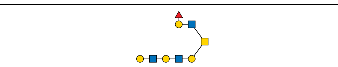
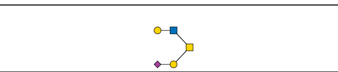
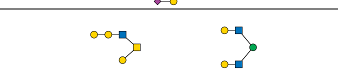
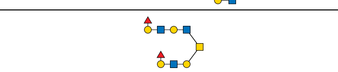
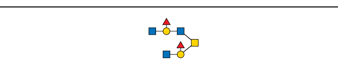
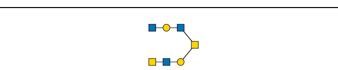
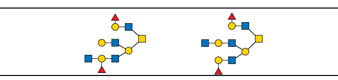
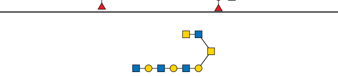
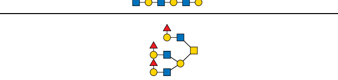
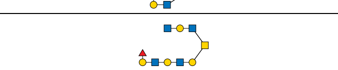
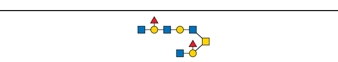
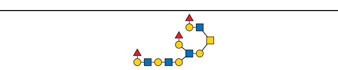
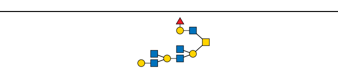
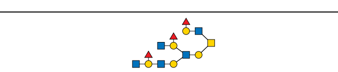
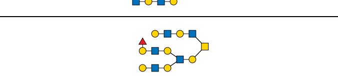
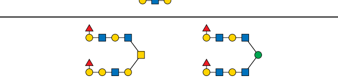
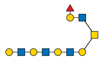
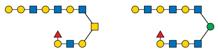
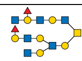
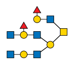
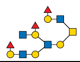
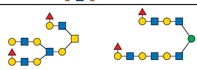
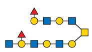
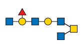
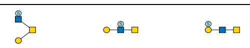
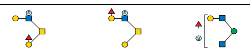
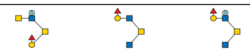
Supplementary Table 1: Glycan profiles for MUC5AC preparations.
Glycans released from each mucin were permethylated and analyzed by NSI-MS. Table 1 presents details (glycan reference number, structural representation, composition, GlyTouCan accession, theoretical m/z, detected m/z, amount, and relative abundance) for the glycans released from MUC5AC only.

					MUC5AC			
Glycan #	Representative Structure	Composition	GlyTouCan Accession(s)	Theoretical m/z (M+Na)[1+]	Detected m/z (M+Na)[1+]	pmol/mg of total released glycan	% Total Profile	% Total Profile w/o Peeling
1		(Hex)1 (HexNAc)1	G76355TG, G85856KC	518.257	518.26	91.72	16.83	17.91
2		(Hex)1 (HexNAc)1 (Deoxyhexose)1	G94435QH	692.346	692.35	73.00	13.40	14.26
3		(Hex)2 (HexNAc)1 (Deoxyhexose)1	G73318SN, G33986KK	896.446	896.45	10.38	1.91	2.03
4		(Hex)1 (HexNAc)1 (NeuAc)1	G65562ZE	879.431	879.44	5.99	1.10	1.17
5		(HexNAc)1	G57321FI	314.157	314.16	2.50	0.46	0.49
6		(Hex)1 (HexNAc)1 (Deoxyhexose)1 (NeuAc)1	G47180UC	1053.520	1053.53	1.37	0.25	0.27
7		(Hex)2 (HexNAc)1 (Deoxyhexose)2	G68200GL	1070.535	1070.54	0.88	0.16	0.17
8		(Hex)1 (HexNAc)2	G00033MO, G61730RY, G56868BH	763.384	763.39	87.06	15.98	17.00
9		(Hex)2 (HexNAc)3 (Deoxyhexose)1	G91459EI, G26724PP, G52132CU	1386.699	1386.71	24.48	4.49	4.78
10		(Hex)2 (HexNAc)4	G34764BK, G12074QJ	1457.736	1457.74	23.39	4.29	4.57
11		(Hex)2 (HexNAc)2 (Deoxyhexose)1	G94514IB, G61216ZY	1141.573	1141.58	20.85	3.83	4.07
12		(Hex)2 (HexNAc)3	G96915PP, G13483MW	1212.610	1212.62	17.89	3.28	3.49
13		(Hex)2 (HexNAc)2	G64973KT	967.483	967.49	17.03	3.13	3.33
14		(Hex)3 (HexNAc)2 (Deoxyhexose)2	G20310DM, G78177LC	1519.762	1519.77	12.29	2.26	2.40
15		(Hex)3 (HexNAc)3 (Deoxyhexose)1	G66741QE, G16458JH	1590.799	1590.81	12.21	2.24	2.38
16		(Hex)3 (HexNAc)4	G94517VF, G57672ST	1661.836	1661.84	11.04	2.03	2.15
17		(Hex)2 (HexNAc)4 (Deoxyhexose)1	G23700TV	1631.825	1631.83	10.85	1.99	2.12
18		(Hex)1 (HexNAc)2 (Deoxyhexose)1	G32426JY, G74353FF	937.473	937.48	10.15	1.86	1.98
19		(Hex)2 (HexNAc)2 (Deoxyhexose)2	G23119MJ	1315.662	1315.67	7.98	1.46	1.56
20		(Hex)1 (HexNAc)3	G68893BQ, G23438NR	1008.510	1008.51	7.48	1.37	1.46
21		(Hex)3 (HexNAc)4 (Deoxyhexose)1	G02990AF, G29956GF	1835.925	1835.93	7.29	1.34	1.42
22		(Hex)3 (HexNAc)4 (Deoxyhexose)2	G93333OF	1016.502	1016.51	5.07	0.93	0.99

23		(Hex)3 (HexNAc)2 (Deoxyhexose)1	G15849KC, G81911LP, G41486OC	1345.672	1345.68	4.93	0.90	0.96
24		(Hex)3 (HexNAc)3 (Deoxyhexose)2	G35949CT, G71094KR, G08426KY	1764.888	1764.90	4.80	0.88	0.94
25		(Hex)3 (HexNAc)3	G86537AD, G89585FG	1416.709	1416.72	3.25	0.60	0.64
26		(Hex)1 (HexNAc)2 (NeuAc)1	G85608AG, G64844ET	1124.557	1124.56	2.52	0.46	0.49
27		(Hex)1 (HexNAc)4	G59229NY	1253.636	1253.64	2.25	0.41	0.44
28		(Hex)4 (HexNAc)3 (Deoxyhexose)2	G68308CM	1968.988	1968.99	2.02	0.37	0.39
29		(Hex)3 (HexNAc)5 (Deoxyhexose)1	G05252QE	1052.020	1052.03	2.00	0.37	0.39
30		(Hex)1 (HexNAc)3 (Deoxyhexose)1	G28878FC	1182.599	1182.61	1.86	0.34	0.36
31		(Hex)4 (HexNAc)4 (Deoxyhexose)1	G94768NG	1031.507	1031.51	1.75	0.32	0.34
32		(Hex)2 (HexNAc)2 (NeuAc)1	G46748BU	1328.657	1328.66	1.72	0.31	0.34
33		(Hex)3 (HexNAc)2	G16404NW, G25323VU	1171.583	1171.59	1.60	0.29	0.31
34		(Hex)2 (HexNAc)3 (Deoxyhexose)2	G68384KC, G39326PP	1560.788	1560.79	1.51	0.28	0.29
35		(Hex)4 (HexNAc)4 (Deoxyhexose)2	G98518WL	1118.552	1118.56	1.35	0.25	0.26
36		(Hex)2 (HexNAc)4 (Deoxyhexose)2	G90965BZ	1805.914	1805.92	1.21	0.22	0.24
37		(Hex)2 (HexNAc)5	G23048PE	1702.862	1702.87	0.98	0.18	0.19
38		(Hex)4 (HexNAc)5 (Deoxyhexose)2	G82251ZP, G18603ZQ	1241.115	1241.12	0.93	0.17	0.18
39		(Hex)3 (HexNAc)6	G62609ZF	1087.539	1087.54	0.91	0.17	0.18
40		(Hex)4 (HexNAc)4 (Deoxyhexose)3	G66166BF	1205.596	1205.60	0.84	0.15	0.16
41		(Hex)4 (HexNAc)5 (Deoxyhexose)1	G92547QZ	1154.070	1154.08	0.82	0.15	0.16
42		(Hex)3 (HexNAc)5 (Deoxyhexose)2	G28921PH	1139.065	1139.07	0.64	0.12	0.13
43		(Hex)6 (HexNAc)5 (Deoxyhexose)3	G18501TC	1532.259	1532.27	0.56	0.10	0.11
44		(Hex)4 (HexNAc)6 (Deoxyhexose)1	G32752FJ	1276.633	1276.64	0.51	0.09	0.10
45		(Hex)5 (HexNAc)6 (Deoxyhexose)3	G65612SS	1552.772	1552.78	0.39	0.07	0.08
46		(Hex)7 (HexNAc)6 (Deoxyhexose)1	G61898SS	1582.783	1582.80	0.39	0.07	0.08
47		(Hex)5 (HexNAc)4 (Deoxyhexose)2	G21630AC	1220.601	1220.61	0.31	0.06	0.06

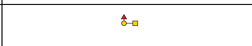
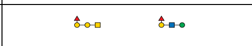
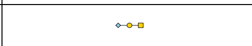
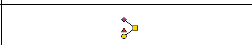
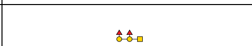
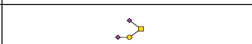
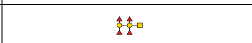
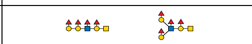
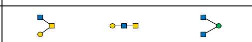
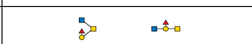
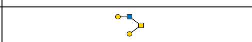
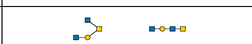
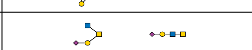
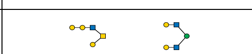
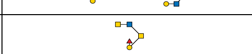
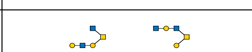
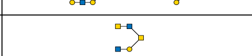
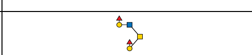
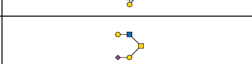
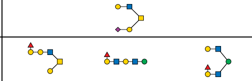
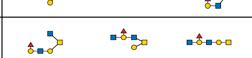
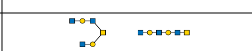
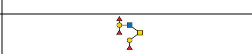
48		(Hex)5 (HexNAc)5 (Deoxyhexose)1	G25957KN	1256.120	1256.13	0.29	0.05	0.06
49		(Hex)6 (HexNAc)5 (Deoxyhexose)1	G37901JE, G84713IO	1358.170	1358.18	0.25	0.05	0.05
50		(Hex)6 (HexNAc)7 (Deoxyhexose)2	G29852ZH	1690.341	1690.36	0.25	0.05	0.05
51		(Hex)4 (HexNAc)6 (Deoxyhexose)2	G99804SJ	1363.678	1363.69	0.21	0.04	0.04
52		(Hex)5 (HexNAc)5 (Deoxyhexose)3	G90829NZ	1430.209	1430.22	0.14	0.03	0.03
53		(Hex)6 (HexNAc)5 (Deoxyhexose)2	G70999YJ, G02681FY	1445.215	1445.22	0.13	0.02	0.03
54		(Hex)5 (HexNAc)6 (Deoxyhexose)2	G44467ZE	1465.728	1465.73	0.11	0.02	0.02
55		(Hex)3 (HexNAc)5	G00505CR	1906.962	1906.97	2.51	0.46	0.49
56		(Hex)2 (HexNAc)5 (Deoxyhexose)1	G09396HG	949.970	949.98	0.62	0.11	0.12
57		(Hex)2 (HexNAc)1	G28052FT	722.357	722.36	4.80	0.88	0.94
58		$(Hex)_2$ $(HexNAc)_1$ $(NeuAc)_1$	G59126YU	1083.531	1083.54	1.84	0.34	0.36
59		(Hex)1 (Deoxyhexose)1	G00068MO	447.220	447.22	32.79	6.02	na
					Total w/ Peel:	544.90	100.00	100.00
Note 1:	Glycan 59 is the expected product of peeling reactions				**Total w/o Peel:**	512.11		

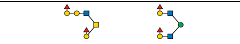
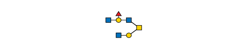
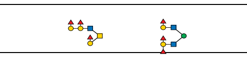
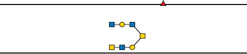
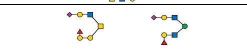
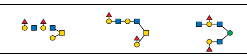
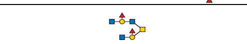
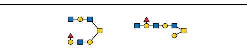
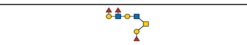
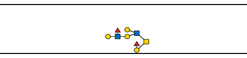
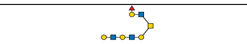
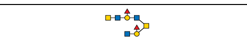
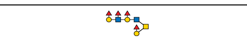
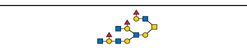
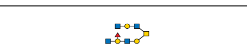
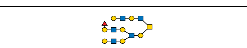
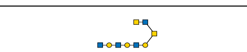
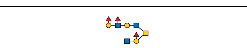
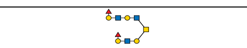
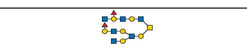
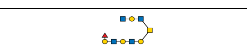
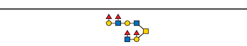
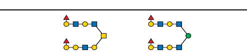
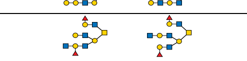
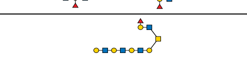
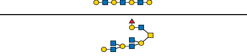
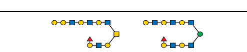
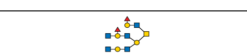
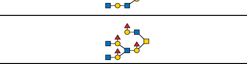
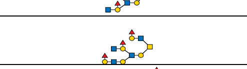
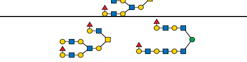
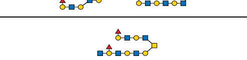
Supplementary Table 2: Sulfated glycan profiles for MUC2, MUC5B, and MUC5AC preparations.
Glycans released from each mucin were permethylated and analyzed by NSI-MS. Table 2 presents details (glycan reference number, structural representation, composition, GlyTouCan accession, theoretical m/z, detected m/z, amount, and relative abundance) for the top 5 sulfated glycans detected from each mucin preparation by negative mode NSI-MS.

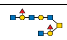
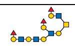
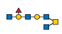
					MUC2				MUC5B				MUC5AC			
Glycan #	Representative Structure	Composition	GlyTouCan Accession(s)	Theoretical m/z $(M-H)^{1-}$	Detected m/z $(M-H)^{1-}$	Signal Intensity	% of Total sulfated glycans	% of Top 5 sulfated glycans	Detected m/z $(M-H)^{1-}$	Signal Intensity	% of Total sulfated glycans	% of Top 5 sulfated glycans	Detected m/z $(M-H)^{1-}$	Signal Intensity	% of Total sulfated glycans	% of Top 5 sulfated glycans
S1		S1 (Hex)1 (HexNAc)1	G10634LC	560.202					560.201	887059	8.36	21.96				
S2		S1 (Hex)1 (HexNAc)1 (Deoxyhexose)1	G08671QK	734.291					734.290	1025409	9.67	25.39				
S3		S1 (Hex)1 (HexNAc)2	G32406CO	805.328	805.33	4010391	19.68	34.30					805.33	360757	6.34	9.97
S4		S1 (Hex)2 (HexNAc)1 (Deoxyhexose)1	G24803MV	938.391					938.389	1172196	11.05	29.02	938.39	543225	9.55	15.01
S5		S1 (Hex)1 (HexNAc)2 (Deoxyhexose)1	G10520JC	979.417	979.41	2695001	13.22	23.05					979.42	1275559	22.43	35.25
S6		S1 (Hex)1 (HexNAc)2 (NeuAc)1	G96888OD	1166.502	1166.50	1909453	9.37	16.33								
S7		S1 (Hex)2 (HexNAc)2 (Deoxyhexose)1	G24803MV	1183.517					1183.515	478521	4.51	11.85	1183.52	972794	17.11	26.88
S8		S1 (Hex)1 (HexNAc)2 (NeuGc)1	not currently supported by repository	1196.512	1196.51	1486979	7.30	12.72								
S9		S1 (Hex)1 (HexNAc)3 (Deoxyhexose)1	G72091WB, G60644GY	1224.544	1224.540	1588826	7.80	13.59								
S10		S1 (Hex)2 (HexNAc)3 (Deoxyhexose)1	G35891PL	1428.644					1428.641	476006	4.49	11.78	1428.64	466419	8.20	12.89
					Total subset:	11690650		100.00	**Total subset:**	4039191		100.00	**Total subset:**	3618754		100.00
Note 1:	GlyTouCan Accessions are for the indicated compositions				**Total sulfated:**	20381869	57.36		**Total sulfated:**	10606784	38.08		**Total sulfated:**	5686243	63.64	

Supplementary Table 3: Glycan profiles for MUC2, MUC5B, and MUC5AC preparations

Glycans released from each mucin were permethylated and analyzed by NSI-MS. Table 3 presents details (glycan reference number, structural representation, composition, GlyTouCan accession, theoretical m/z, detected m/z, amount, and relative abundance) for the glycans released from all three mucins for cross-comparison.

					MUC2				MUC5B				MUC5AC			
Glycan #	Representative Structure	Composition	GlyTouCan Accession(s)	Theoretical m/z $(M+Na)^{1+}$	Detected m/z $(M+Na)^{1+}$	pmol/mg of total released glycan	% Total Profile	% Total Profile w/o Peeling	Detected m/z $(M+Na)^{1+}$	pmol/mg of total released glycan	% Total Profile	% Total Profile w/o Peeling	Detected m/z $(M+Na)^{1+}$	pmol/mg of total released glycan	% Total Profile	% Total Profile w/o Peeling
1		(HexNAc)1	G57321FI	314.157	314.16	6.23	1.68	2.42	314.158	0.73	0.40	0.44	314.159	2.50	0.46	0.49
2		(Hex)1 (HexNAc)1	G76355TG, G85856KC	518.257	518.26	37.53	10.10	14.57	518.258	14.30	7.90	8.66	518.26	91.72	16.83	17.91
3		(Hex)1 (HexNAc)1 (Deoxyhexose)1	G94435QH	692.346	692.35	89.58	24.11	34.77	692.349	38.27	21.15	23.16	692.35	73.00	13.40	14.26
4		(Hex)1 (HexNAc)1 (NeuAc)1	G65562ZE	879.431	879.43	17.29	4.65	6.71	879.434	4.38	2.42	2.65	879.44	5.99	1.10	1.17
5		(Hex)2 (HexNAc)1 (Deoxyhexose)1	G73318SN, G33986KK	896.446					896.449	3.64	2.01	2.21	896.45	10.38	1.91	2.03
6		(Hex)1 (HexNAc)1 (NeuGc)1	G64527IJ	909.441	909.444	11.40	3.07	4.42								
7		(Hex)1 (HexNAc)1 (Deoxyhexose)1 (NeuAc)1	G47180UC	1053.520	1053.523	1.25	0.34	0.49	1053.522	1.15	0.63	0.69	1053.53	1.37	0.25	0.27
8		(Hex)2 (HexNAc)1 (Deoxyhexose)2	G68200GL	1070.535	1070.540	0.20	0.05	0.08	1070.539	2.73	1.51	1.65	1070.54	0.88	0.16	0.17
9		(Hex)1 (HexNAc)1 (NeuAc)2	G01614ZM	1240.605	1240.608	1.86	0.50	0.72								
10		(Hex)2 (HexNAc)1 (Deoxyhexose)3	G82961CS	1244.625					1244.628	0.60	0.33	0.36				
11		(Hex)2 (HexNAc)1 (Deoxyhexose)1 (NeuAc)1	G49549VN, G95742RK	1257.620					1257.625	0.87	0.48	0.53				
12		(Hex)1 (HexNAc)1 (NeuAc)1 (NeuGc)1	G49527BY	1270.615	1270.616	0.41	0.11	0.16								
13		(Hex)1 (HexNAc)2 (Deoxyhexose)1 (NeuAc)1	G75749JP, G40270LS	1298.646	1298.649	1.21	0.32	0.47	1298.650	1.33	0.73	0.80				
14		(Hex)3 (HexNAc)2 (Deoxyhexose)4	G93469SN, G15747RC	1867.940					1867.946	1.30	0.72	0.79				
15		(Hex)1 (HexNAc)2	G00033MO, G61730RY, G56868BH	763.384	763.386	9.26	2.49	3.59	763.388	4.25	2.35	2.57	763.39	87.06	15.98	17.00
16		(Hex)1 (HexNAc)2 (Deoxyhexose)1	G32426JY, G74353FF	937.473	937.475	22.56	6.07	8.76	937.476	11.24	6.21	6.80	937.48	10.15	1.86	1.98
17		(Hex)2 (HexNAc)2	G64973KT	967.483	967.486	4.19	1.13	1.63	967.486	1.89	1.05	1.15	967.49	17.03	3.13	3.33
18		(Hex)1 (HexNAc)3	G68893BQ, G23438NR	1008.510	1008.514	2.78	0.75	1.08	1008.514	0.72	0.40	0.44	1008.51	7.48	1.37	1.46
19		(Hex)1 (HexNAc)2 (Deoxyhexose)2	G89748NG, G09520ZQ	1111.562					1111.565	4.05	2.24	2.45				
20		(Hex)1 (HexNAc)2 (NeuAc)1	G85608AG, G64844ET	1124.557	1124.559	2.50	0.67	0.97	1124.562	1.22	0.67	0.74	1124.56	2.52	0.46	0.49
21		(Hex)2 (HexNAc)2 (Deoxyhexose)1	G94514IB, G61216ZY	1141.573	1141.576	3.00	0.81	1.16	1141.575	3.99	2.20	2.41	1141.58	20.85	3.83	4.07
22		(Hex)1 (HexNAc)2 (NeuGc)1	G60426XC	1154.568	1154.573	1.56	0.42	0.61								
23		(Hex)3 (HexNAc)2	G16404NW, G25323VU	1171.583	1171.586	0.14	0.04	0.05	1171.586	1.65	0.91	1.00	1171.59	1.60	0.29	0.31
24		(Hex)1 (HexNAc)3 (Deoxyhexose)1	G28878FC	1182.599	1182.602	4.86	1.31	1.89	1182.602	2.98	1.65	1.81	1182.61	1.86	0.34	0.36
25		(Hex)2 (HexNAc)3	G96915PP, G13483MW	1212.610	1212.612	1.94	0.52	0.75	1212.612	1.87	1.03	1.13	1212.62	17.89	3.28	3.49
26		(Hex)1 (HexNAc)4	G59229NY	1253.636									1253.64	2.25	0.41	0.44
27		(Hex)2 (HexNAc)2 (Deoxyhexose)2	G23119MJ	1315.662	1315.666	2.54	0.68	0.99	1315.666	4.94	2.73	2.99	1315.67	7.98	1.46	1.56
28		(Hex)2 (HexNAc)2 (NeuAc)1	G46748BU	1328.657	1328.659	4.55	1.23	1.77	1328.659	2.42	1.34	1.46	1328.66	1.72	0.31	0.34
29		(Hex)3 (HexNAc)2 (Deoxyhexose)1	G15849KC, G81911LP, G41486OC	1345.672	1345.676	0.25	0.07	0.10	1345.676	3.30	1.82	2.00	1345.68	4.93	0.90	0.96
30		(Hex)2 (HexNAc)3 (Deoxyhexose)1	G91459EI, G26724PP, G52132CU	1386.699	1386.703	0.41	0.11	0.16	1386.702	3.40	1.88	2.06	1386.71	24.48	4.49	4.78
31		(Hex)3 (HexNAc)3	G86537AD, G89585FG	1416.709	1416.713	0.10	0.03	0.04	1416.714	0.17	0.09	0.10	1416.72	3.25	0.60	0.64
32		(Hex)2 (HexNAc)4	G34764BK, G12074QJ	1457.736	1457.729	0.32	0.09	0.12	1457.734	0.27	0.15	0.17	1457.74	23.39	4.29	4.57
33		(Hex)2 (HexNAc)2 (Deoxyhexose)3	G01532FF	1489.751					1489.755	1.78	0.98	1.07				

34		(Hex)2 (HexNAc)2 (Deoxyhexose)1 (NeuAc)1	G77740PR, G59155GF	1502.750					1502.751	0.22	0.12	0.13				
35		(Hex)3 (HexNAc)2 (Deoxyhexose)2	G20310DM, G78177LC	1519.762					1519.766	4.35	2.40	2.63	1519.77	12.29	2.26	2.40
36		(Hex)2 (HexNAc)3 (Deoxyhexose)2	G68384KC, G39326PP	1560.788	1560.792	2.48	0.67	0.96	1560.792	3.40	1.88	2.06	1560.79	1.51	0.28	0.29
37		(Hex)3 (HexNAc)3 (Deoxyhexose)1	G66741QE, G16458JH	1590.799	1590.806	0.32	0.09	0.12	1590.803	2.15	1.19	1.30	1590.81	12.21	2.24	2.38
38		(Hex)3 (HexNAc)4 (Deoxyhexose)1	G23700TV	1631.825	1631.822	0.40	0.11	0.15	1631.830	1.05	0.58	0.64	1631.83	10.85	1.99	2.12
39		(Hex)3 (HexNAc)4	G94517VF, G57672ST	1661.836	1661.831	0.49	0.13	0.19	1661.837	0.05	0.03	0.03	1661.84	11.04	2.03	2.15
40		(Hex)3 (HexNAc)2 (Deoxyhexose)3	G70416EY, G13012GZ	1693.851					1693.856	2.22	1.23	1.34				
41		(Hex)2 (HexNAc)5	G23048PE	1702.862									1702.87	0.98	0.18	0.19
42		(Hex)3 (HexNAc)2 (Deoxyhexose)1 (NeuAc)1	G74607VK, G81461IK	1706.846					1706.851	0.91	0.50	0.55				
43		(Hex)3 (HexNAc)3 (Deoxyhexose)2	G35949CT, G71094KR, G08426KY	1764.888					1764.897	5.23	2.89	3.17	1764.90	4.80	0.88	0.94
44		(Hex)2 (HexNAc)4 (Deoxyhexose)2	G90965BZ	1805.914	1805.921	0.95	0.26	0.37	1805.919	2.17	1.20	1.31	1805.92	1.21	0.22	0.24
45		(Hex)3 (HexNAc)4 (Deoxyhexose)1	G02990AF, G29956GF	1835.925	1835.927	1.03	0.28	0.40	1835.927	1.45	0.80	0.88	1835.93	7.29	1.34	1.42
46		(Hex)3 (HexNAc)3 (Deoxyhexose)3	G23021IW	1938.977					1938.979	2.11	1.17	1.28				
47		(Hex)4 (HexNAc)3 (Deoxyhexose)2	G68308CM	1968.988					1968.990	1.14	0.63	0.69	1968.99	2.02	0.37	0.39
48		(Hex)3 (HexNAc)4 (Deoxyhexose)2	G93333OF	1016.502					1016.504	1.34	0.74	0.81	1016.51	5.07	0.93	0.99
49		(Hex)4 (HexNAc)4 (Deoxyhexose)1	G94768NG	1031.507	1031.509	0.47	0.13	0.18	1031.510	0.57	0.32	0.35	1031.51	1.75	0.32	0.34
50		(Hex)2 (HexNAc)5 (Deoxyhexose)2	G25612EW	1037.015					1037.018	0.58	0.32	0.35				
51		(Hex)3 (HexNAc)3 (Deoxyhexose)4	G84853WN	1068.028					1068.031	0.84	0.47	0.51				
52		(Hex)5 (HexNAc)6 (Deoxyhexose)3	G65612SS	1552.772					1552.776	0.19	0.10	0.11	1552.78	0.39	0.07	0.08
53		(Hex)3 (HexNAc)5 (Deoxyhexose)1	G05252QE	1052.020	1052.023	0.94	0.25	0.36	1052.023	0.13	0.07	0.08	1052.03	2.00	0.37	0.39
54		(Hex)7 (HexNAc)6 (Deoxyhexose)1	G61898SS	1582.783					1582.796	0.05	0.03	0.03	1582.80	0.39	0.07	0.08
55		(Hex)3 (HexNAc)6	G62609ZF	1087.539									1087.54	0.91	0.17	0.18
56		(Hex)3 (HexNAc)4 (Deoxyhexose)3	G59787TQ	1103.546					1103.549	2.94	1.62	1.78				
57		(Hex)4 (HexNAc)4 (Deoxyhexose)2	G98518WL	1118.552					1118.555	1.13	0.62	0.68	1118.56	1.35	0.25	0.26
58		(Hex)6 (HexNAc)7 (Deoxyhexose)2	G29852ZH	1690.341									1690.36	0.25	0.05	0.05
59		(Hex)4 (HexNAc)5 (Deoxyhexose)1	G92547QZ	1154.070	1154.073	1.18	0.32	0.46	1154.073	0.25	0.14	0.15	1154.08	0.82	0.15	0.16
60		(Hex)3 (HexNAc)4 (Deoxyhexose)4	G89469SP	1190.591					1190.594	1.72	0.95	1.04				
61		(Hex)5 (HexNAc)4 (Deoxyhexose)2	G21630AC	1220.601					1220.604	0.84	0.46	0.51	1220.61	0.31	0.06	0.06
62		(Hex)4 (HexNAc)5 (Deoxyhexose)2	G82251ZP, G18603ZQ	1241.115	1241.118	0.35	0.09	0.13	1241.118	0.49	0.27	0.30	1241.12	0.93	0.17	0.18
63		(Hex)5 (HexNAc)5 (Deoxyhexose)1	G25957KN	1256.120	1256.123	0.32	0.09	0.13	1256.123	0.46	0.25	0.28	1256.13	0.29	0.05	0.06
64		(Hex)4 (HexNAc)6 (Deoxyhexose)1	G32752FJ	1276.633	1276.637	0.30	0.08	0.12					1276.64	0.51	0.09	0.10
65		(Hex)6 (HexNAc)5 (Deoxyhexose)1	G37901JE, G84713IO	1358.170									1358.18	0.25	0.05	0.05
66		(Hex)4 (HexNAc)6 (Deoxyhexose)2	G99804SJ	1363.678	1363.682	0.17	0.05	0.07					1363.69	0.21	0.04	0.04
67		(Hex)4 (HexNAc)5 (Deoxyhexose)4	G11381FO	1415.204					1415.208	0.51	0.28	0.31				
68		(Hex)5 (HexNAc)5 (Deoxyhexose)3	G90829NZ	1430.209					1430.213	0.08	0.04	0.05	1430.22	0.14	0.03	0.03
69		(Hex)6 (HexNAc)5 (Deoxyhexose)2	G70999YJ, G02681FY	1445.215					1445.215	0.22	0.12	0.14	1445.22	0.13	0.02	0.03
70		(Hex)5 (HexNAc)6 (Deoxyhexose)2	G44467ZE	1465.728	1465.730	0.11	0.03	0.04	1465.729	0.22	0.12	0.14	1465.73	0.11	0.02	0.02

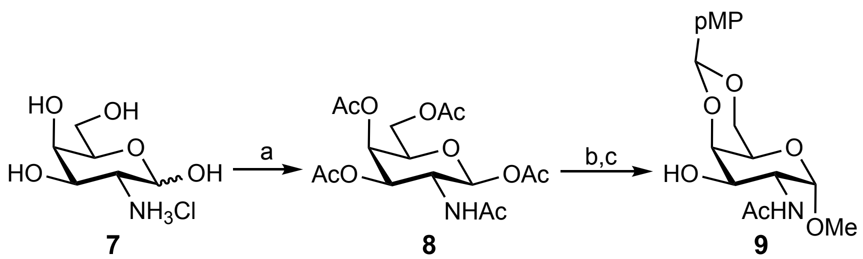
71		(Hex)3 (HexNAc)5 (Deoxyhexose)2	G28921PH	1139.065									1139.07	0.64	0.12	0.13
72		(Hex)6 (HexNAc)5 (Deoxyhexose)3	G18501TC	1532.259									1532.27	0.56	0.10	0.11
73		(Hex)4 (HexNAc)4 (Deoxyhexose)3	G66166BF	1205.596					1205.599	1.07	0.59	0.65	1205.60	0.84	0.15	0.16
74		(HexNAc(2)	G00041MO, G00057MO	559.284	559.285	8.86	2.38	3.44	559.285	1.11	0.62	0.67				
75		(HexNAc)2 (NeuAc)1	G63334FZ	920.457	920.460	3.84	1.03	1.49	920.460	1.37	0.76	0.83				
76		(HexNAc)2 (NeuGc)1	G09441IP	950.468	950.471	2.76	0.74	1.07								
77		(Hex)3 (HexNAc)5	G00505CR	1906.962	1906.970	0.38	0.10	0.15					1906.97	2.51	0.46	0.49
78		(Hex)2 (HexNAc)5 (Deoxyhexose)1	G09396HG	949.970									949.98	0.62	0.11	0.12
79		(Hex)2 (HexNAc)1	G28052FT	722.357	722.359	3.79	1.02	1.47	722.359	3.13	1.73	1.89	722.36	4.80	0.88	0.94
80		(Hex)2 (HexNAc)1 (NeuAc)1	G59126YU	1083.531	1083.530	0.59	0.16	0.23	1083.530	0.07	0.04	0.04	1083.54	1.84	0.34	0.36
81		(Hex)1 (Deoxyhexose)1	G00068MO	447.220	447.221	38.66	10.40	na	447.221	7.66	4.23	na	447.22	32.79	6.02	na
82		(Hex)1 (NeuAc)1	G30207PZ, G63069TR	634.305	634.306	43.37	11.67	na	634.307	7.83	4.33	na				
83		(Hex)1 (NeuGc)1	G38557KR, G59867EM	664.315	664.317	31.92	8.59	na	664.317	0.24	0.13	na				
					Total w/ Peel:	371.58	100.00	100.00	**Total w/ Peel:**	180.95	100.00	100.00	**Total w/ Peel:**	544.90	100.00	100.00
Note 1:	Glycans 81, 82, 83 are the expected products of peeling reactions				**Total w/o Peel:**	257.62			**Total w/o Peel:**	165.23			**Total w/o Peel:**	512.11		

Supplementary Table 4: Primer sequences

ECE1_F	TGCCATTTGTTGTCAGAGCTG
ECE1_R	TAGCTTGTTGAACAGTTTCCAGG
HWP1_F	GCTGGTTCAGAATCATCCATGC
HWP1_R	AAGGTTCAGTGGCAGGAGCTG
HGC1_F	GTCAGCTTCCTGCACCTCATC
HGC1_R	AAACAGCACGAGAACCAGCG
NRG1_F	GGTTGCACGTTGTCGAAACC
NRG1_R	TGTTGCTGCTGCTGCTTGG
ACT1_F	CCCAGGTATTGCTGAACGTA
ACT1_R	GAACCACCAATCCAGACAGA
YWP1_F	TGCTAGTACTGCTAACAAAGTCAC
YWP1_R	CACCATTAACACCACCAGCA
UME6_F	TCATTCAATCCTACTCGTCCACC
UME6_R	CCAGATCCAGTAGCAGTGCTG
RIP1_F	TGCTGACAGAGTCAAGAAACC
RIP1_R	GAACCAACCACCGAAATCAC
EFG1_F	CATCACAACCAGGTTCTACAACCAAT
EFG1_R	CTACTATTAGCAGCACCACCC
18S_F	GGATTTACTGAAGACTAACTACTG
18S_R	GAACAACAACCGATCCCTAGT
ALS3_F	ACTTCCACAGCTGCTTCCACTTCT
ALS3_R	TCCACGGAACCGGTTGTTGCT
HYR1_F	CGGTTCTGGAAGTGGTCATAA
HYR1_R	AGAGTGTGAACCTGCGTTAG
EED1_F	TGCTCTACCACCACAACAAG
EED1_R	TTGCGGTGCTTGCTCATA

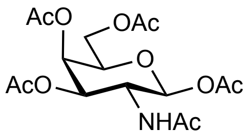
Supplementary Note: Glycan synthesis protocols with NMR spectra and HPLC traces of synthesized glycans

General methods. All commercial reagents were used as supplied unless otherwise stated, and solvents were dried and distilled using standard techniques. Thin layer chromatography was performed on silica-coated glass plates (TLC Silica Gel 60 F_{254}, Merck) with detection by fluorescence, charring with 5% $H_2SO_{4(aq)}$, or staining with a ceric ammonium molybdate solution. Organic solutions were concentrated and/or evaporated to dry under vacuum in a water bath (<50 °C). Molecular sieves were dried at 400 °C under vacuum for 20-30 minutes prior to use. Amberlite IR-120H resin was washed extensively with MeOH and dried under vacuum prior to use. Medium-pressure liquid chromatography (MPLC) was performed using a CombiFlash Companion equipped with RediSep normal-phase flash columns, and solvent gradients refer to sloped gradients with concentrations reported as % *v*/*v*. NMR spectra were recorded on a Bruker Avance DMX-500 (500 MHz) spectrometer, and assignments achieved with the assistance of 2D gCOSY, 2D gTOCSY, 2D gHSQC, and 2D gHMBC; chemical shifts are expressed in ppm and referenced to either $Si(CH_3)_4$ (for $CDCl_3$), residual CHD_2OD (for CD_3OD), or a MeOH internal standard (for D_2O). Low resolution electron-spray ionization mass spectrometry (ESI-MS) was performed using a Waters micromass ZQ. High resolution mass spectrometry was performed using an Agilent 1100 LC equipped with a photodiode array detector, and a Micromass QTOF I equipped with a 4 GHz digital-time converter. Optical rotation was determined in a 10 cm cell at 20 °C using a Perkin-Elmer Model 341 polarimeter. HPLC analysis was performed using an Agilent 1100 LC equipped with an Atlantis T3 (3 µm, 2.1x100 mm) C18 column and ELSD detection.



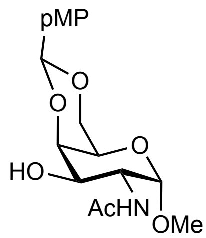
(a) Ac_2O, Pyr, 0 ˚C → rt, 97%; (b) HCl, MeOH, 60 ˚C; (c) *p*MPCH$(OMe)_2$, DMF, 69% (2 steps).

Acetyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-galactopyranoside (8)



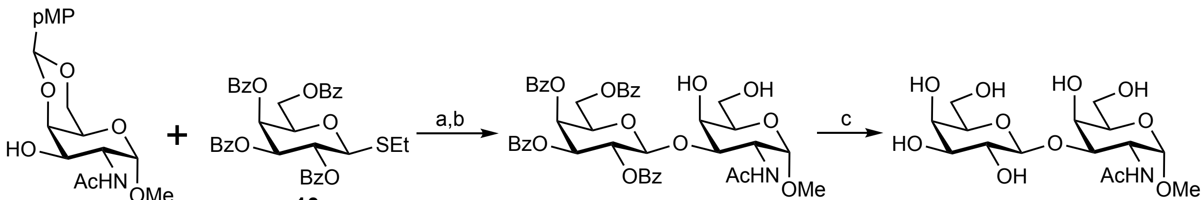
D-Galactosamine hydrochloride (**7**; 12.35 g, 57.27 mmol) in anhydrous pyridine (80 mL) was cooled to 0 °C, and then Ac_2O (40 mL) added dropwise over 15 min and the flask slowly warmed to rt. After 16 hours, the reaction mixture was concentrated to a syrup via co-evaporation with toluene (2 x 50 mL), and then the crude material was purified via MPLC on silica gel using 0→60% acetone – CH_2Cl_2 to afford the pure product as a white solid (21.63 g, 55.55 mmol, 97% yield). R_f = 0.11 (3:7 acetone : CH_2Cl_2). $[\alpha]_D^{20}$: +9.8° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δH 5.70 (d, 1H, *J* = 8.8 Hz, H-1), 5.43 (d, 1H, *J* = 9.5 Hz, NH), 5.38 (dd, 1H, *J* = 3.3, <1 Hz, H-4), 5.09 (dd, 1H, *J* = 11.3, 3.3 Hz, H-3), 4.45 (ddd, 1H, *J* = 11.2, 9.2, 9.2 Hz, H-2), 4.17 (dd, 1H, *J* = 11.3, 6.6 Hz, H-6^a), 4.12 (dd, 1H, *J* = 11.3, 6.5 Hz, H-6^b), 4.02 (ddd, 1H, *J* = 6.5, 6.5, 1.0 Hz, H-5), 2.17 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.94 (s, 3H, NHAc). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 170.97 (C=O), 170.62 (C=O), 170.47 (C=O), 170.39 (C=O), 169.79 (C=O), 93.28 (C-1), 72.11 (C-5), 70.55 (C-3), 66.56 (C-4), 61.52 (C-6), 50.06 (C-2), 23.54 (NHAc), 21.11 (OAc), 20.89 (2x OAc), 20.86 (OAc). LRMS *m*/*z* calc'd for $C_{16}H_{23}NNaO_{10}$ $(M+Na)^+$: 412.12; found: 412.10.

Methyl 2-acetamido-2-deoxy-4,6-*O*-(*p*-methoxybenzylidene)-α-D-galactopyranoside (9)



The starting material (**8**; 5.953 g, 15.29 mmol) was dissolved into 2% *v*/*v* conc. HCl in MeOH and left heating at 60 °C. After 3 days, the mixture was evaporated to dry to afford the desired methyl α-glycoside crude product: R_f = 0.29 (1:4 CH_3OH : CH_2Cl_2); LRMS *m*/*z* calc'd for $C_9H_{17}NNaO_6$ $(M+Na)^+$: 258.10; found: 258.06. The crude material and *p*-methoxybenzylidene dimethyl acetal (3.2 mL, 19 mmol) were added to anhydrous DMF (35 mL) under Ar (acidity maintained from previous step). After 18 hours of mixing at ambient temperature, the reaction mixture was neutralized with Et_3N (to pH 8), concentrated to a syrup, and then purified via MPLC on silica gel using 0→60% acetone (w/ 0.1% NH_4OH) – CH_2Cl_2 to afford the desired product as a white solid (3.722 g, 10.53 mmol, 69% yield over 2 steps). R_f = 0.57

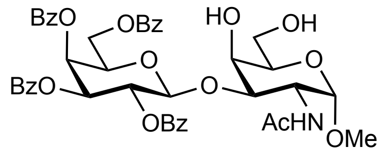
(0.01:10:29.99:60 NH_4OH : MeOH : acetone : CH_2Cl_2). $[\alpha]_D^{20}$: +135° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δH 7.46 – 7.43 (m, 2H, Ar), 6.90 – 6.87 (m, 2H, Ar), 5.91 (d, 1H, *J* = 8.9 Hz, NH), 5.50 (s, 1H, PhC*H*), 4.83 (d, 1H, *J* = 3.5 Hz, H-1), 4.44 (ddd, 1H, *J* = 10.9, 9.0, 3.5 Hz, H-2), 4.24 (dd, 1H, *J* = 12.5, 1.4 Hz, H-6[a]), 4.15 (dd, 1H, *J* = 3.4, <1 Hz, H-4), 4.03 (dd, 1H, *J* = 12.5, 1.6 Hz, H-6[b]), 3.82 – 3.79 (m, 4H, H-3 and $ArOCH_3$), 3.60 – 3.59 (m, 1H, H-5), 3.38 (s, 3H, OCH_3), 2.94 (d, 1H, *J* = <1 Hz, 3-OH), 2.02 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 171.39 (C=O), 160.30 (Ar), 130.30 (Ar), 127.85 (Ar), 113.70 (Ar), 101.30 (Ph*C*H), 99.49 (C-1), 75.59 (C-4), 69.40 (C-6), 68.97 (C-3), 62.86 (C-5), 55.56 (OCH_3), 55.43 (ArO*C*H_3), 50.54 (C-2), 23.51 (Ac). LRMS *m/z* calc'd for $C_{17}H_{23}NNaO_7$ $(M+Na)^+$: 376.14; found: 376.08.



9 **10** **11** **1**

(a) NIS, TfOH, CH_2Cl_2/CH_3CN, 0 ˚C; (b) AcOH/H_2O, 73% (2 steps); (c) NaOMe, MeOH, 50 ˚C, 89%.

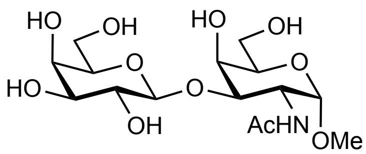
Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (11)



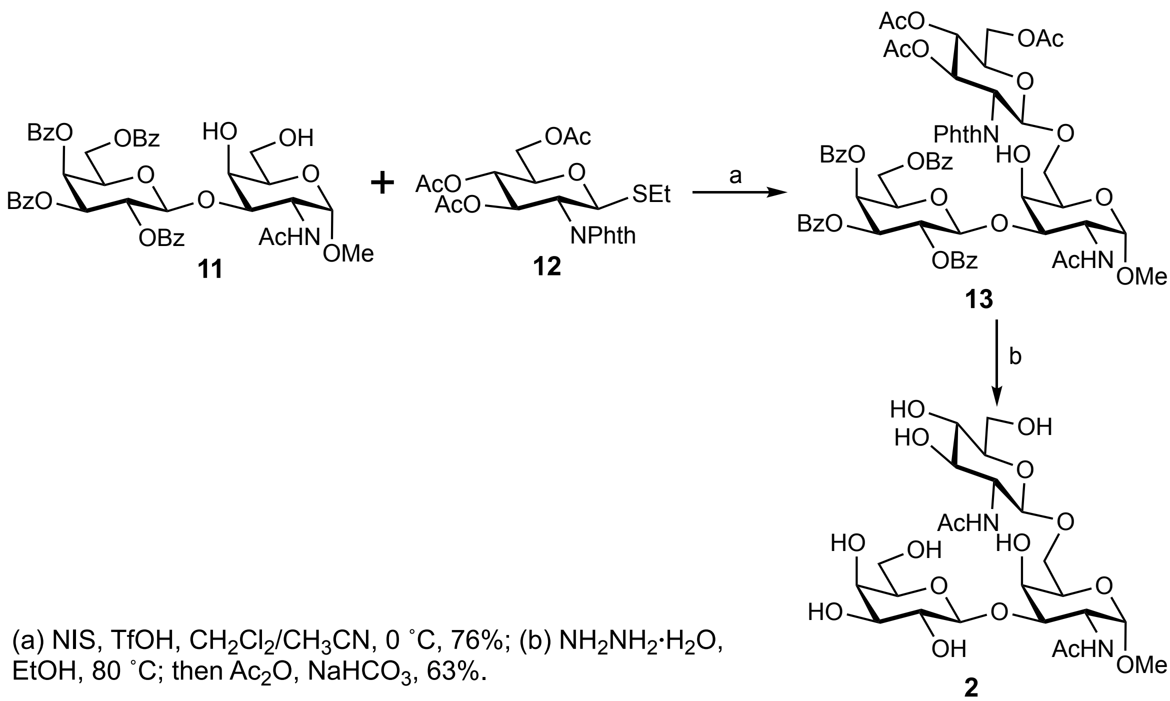
The glycosyl acceptor (**9**; 602 mg, 1.70 mmol), glycosyl donor [ref 1] (**10**; 2.726 g, 4.255 mmol), and crushed molecular sieves (3 Å, 1.905 mg) in anhydrous CH_2Cl_2 (10 mL) and anhydrous acetonitrile (20 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to 0 °C, and then *N*-iodosuccinimide (NIS) was added (777 mg, 3.45 mmol) followed by the drop-wise addition of triflic acid (TfOH) (23 µL, 0.26 mmol). After 5 hours, the mixture was neutralized with Et_3N (to pH 8), warmed to ambient temperature, filtered over Celite, and diluted with CH_2Cl_2 (100 mL). The organic phase was washed with sat'd $Na_2S_2O_{3(aq)}$ solution (100 mL), sat'd $NaCl_{(aq)}$ solution (100 mL), dried with Na_2SO_4, filtered, and evaporated to dry to afford the crude product: LRMS *m/z* calc'd for $C_{51}H_{49}NNaO_{16}$

$(M+Na)^+$: 954.30; found: 954.29. The crude mixture was then dissolved into AcOH (16 mL) and H_2O (4 mL). After 3 hours at ambient temperature, the mixture was neutralized with excess sat'd $NaHCO_{3(aq)}$ solution and the product extracted with CH_2Cl_2 (2 x 100 mL). The combined organic phases were washed with sat'd $NaHCO_{3(aq)}$ (3 x 100 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→10% MeOH – CH_2Cl_2 to afford the pure product as a white solid (1.007 g, 1.237 mmol, 73% yield over 2 steps). R_f = 0.38 (1:19 MeOH : CH_2Cl_2). $[\alpha]_D^{20}$: +170° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δH 8.07 – 8.05 (m, 2H, Ar), 8.04 – 8.02 (m, 2H, Ar), 7.99 – 7.97 (m, 2H, Ar), 7.74 – 7.71 (m, 2H, Ar), 7.61 – 7.55 (m, 2H, Ar), 7.53 – 7.50 (m, 1H, Ar), 7.48 – 7.44 (m, 2H, Ar), 7.44 – 7.38 (m, 5H, Ar), 7.22 – 7.18 (m, 2H, Ar), 5.95 (dd, 1H, *J* = 3.5, <1 Hz, Gal_H4), 5.84 (dd, 1H, *J* = 10.4, 8.0 Hz, Gal_H2), 5.64 (dd, 1H, *J* = 10.4, 3.5 Hz, Gal_H3), 5.45 (d, 1H, *J* = 8.9 Hz, NH), 5.04 (d, 1H, *J* = 8.0 Hz, Gal_H1), 4.73 (d, 1H, *J* = 3.6 Hz, GalN_H1), 4.62 – 4.54 (m, 3H, Gal_H6^a, Gal_H6^b, and GalN_H2), 4.44 – 4.41 (m, 1H, Gal_H5), 4.21 – 4.19 (m, 1H, GalN_H4), 3.84 (dd, 1H, *J* = 10.8, 3.0 Hz, GalN_H3), 3.77 (ddd, 1H, *J* = 11.2, 6.2, 2.7 Hz, GalN_H6^a), 3.71 – 3.69 (m, 1H, GalN_H5), 3.54 (ddd, 1H, *J* = 11.3, 8.9, 4.3 Hz, GalN_H6^b), 3.27 (s, 3H, OCH_3), 3.10 (d, 1H, *J* = <1 Hz, 4-OH), 2.44 (dd, 1H, *J* = 8.8, 3.0 Hz, 6-OH), 1.34 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 170.10 (Ac), 166.27 (C=O), 165.81 (C=O), 165.70 (C=O), 164.94 (C=O), 133.91 (Ar), 133.77 (Ar), 133.71 (Ar), 133.53 (Ar), 130.18 (Ar), 130.00 (Ar), 129.91 (Ar), 129.90 (Ar), 129.44 (Ar), 129.26 (Ar), 128.85 (Ar), 128.81 (Ar), 128.79 (Ar), 128.71 (Ar), 128.47 (Ar), 102.07 (Gal_C1), 98.82 (GalN_C1), 79.86 (GalN_C3), 72.24 (Gal_C5), 71.62 (Gal_C3), 69.90 (Gal_C2), 69.44 (GalN_C5), 68.87 (GalN_C4), 68.36 (Gal_C4), 62.85 (GalN_C6), 62.83 (Gal_C6), 55.30 (OCH_3), 48.05 (GalN_C2), 22.56 (Ac). LRMS *m/z* calc'd for $C_{43}H_{43}NNaO_{15}$ $(M+Na)^+$: 836.25; found: 836.23.

Methyl β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (1)

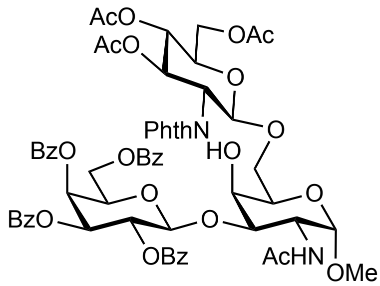


The starting material (**11**; 83 mg, 0.10 mmol) was dissolved into anhydrous MeOH (1.5 mL), and then NaOMe solution was added drop-wise (1.5 M NaOMe in MeOH; to pH 10) and the mixture heated at 50 °C. After 14 hours, the reaction mixture was cooled to rt, neutralized with acidic resin (Amberlite IR-120H; to pH 6), filtered, and then evaporated to dry. The crude material was purified via RPLC on C-18 silica gel using 0→40% acetonitrile – H_2O to afford the pure product as a white solid (36 mg, 0.091 mmol, 89% yield); data characterization is in agreement with that previously published [ref 2]. $[\alpha]_D^{20}$: +95° (*c* 1.0, H_2O). ^{1}H NMR (D_2O, 500 MHz): δH 4.77 – 4.76 (m, 1H, GalN_H1), 4.45 (d, 1H, *J* = 7.8 Hz, Gal_H1), 4.32 (dd, 1H, *J* = 11.1, 3.7 Hz, GalN_H2), 4.22 (dd, 1H, *J* = 2.9, <1 Hz, GalN_H4), 3.99 (dd, 1H, *J* = 11.1, 3.1 Hz, GalN_H3), 3.95 (ddd, 1H, *J* = 7.4, 4.9, <1 Hz, GalN_H5), 3.90 (dd, 1H, *J* = 3.4, <1 Hz, Gal_H4), 3.77 (dd, 1H, *J* = 11.7, 7.4 Hz, Gal_H6^a), 3.78 – 3.72 (m, 2H, Gal_H6^a and GalN_H6^b), 3.72 (dd, 1H, *J* = 11.7, 4.5 Hz, Gal_H6^b), 3.64 (ddd, 1H, *J* = 7.7, 4.5, <1 Hz, Gal_H5), 3.60 (dd, 1H, *J* = 9.9, 3.4 Hz, Gal_H3), 3.50 (dd, 1H, *J* = 9.9, 7.8 Hz, Gal_H2), 3.38 (s, 3H, OCH_3), 2.01 (s, 3H, Ac). ^{13}C NMR (D_2O, 125 MHz): δC 175.23 (C=O), 105.34 (Gal_C1), 98.95 (GalN_C1), 77.92 (GalN_C3), 75.59 (Gal_C5), 73.17 (Gal_C3), 71.24 (Gal_C2), 71.07 (GalN_C5), 69.38 (GalN_C4), 69.21 (Gal_C4), 61.86 (GalN_C6), 61.59 (Gal_C6), 55.72 (OCH_3), 49.22 (GalN_C2), 22.64 (Ac). ESI-HRMS *m*/*z* calc'd for $C_{15}H_{27}NNaO_{11}$ $(M+Na)^+$: 420.1482; found: 420.1482. HPLC purity analysis: 99.1%, R_t 4.54 minutes, Atlantis T3 C18 column.



(a) NIS, TfOH, CH_2Cl_2/CH_3CN, 0 °C, 76%; (b) $NH_2NH_2{\cdot}H_2O$, EtOH, 80 °C; then Ac_2O, $NaHCO_3$, 63%.

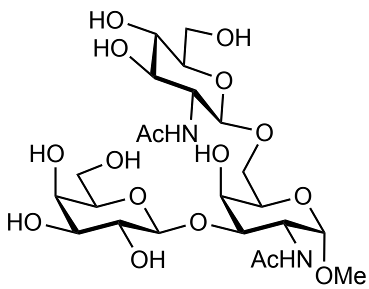
Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-D-galactopyranoside (13)



The glycosyl acceptor (**11**; 135 mg, 0.166 mmol), glycosyl donor [ref 6] (**12**; 87 mg, 0.18 mmol), and crushed molecular sieves (3 Å, 190 mg) in anhydrous CH_2Cl_2 (1.0 mL) and anhydrous acetonitrile (1.0 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to 0 °C, and then NIS was added (67 mg, 0.30 mmol) followed by the drop-wise addition of TfOH solution (15% *v*/*v* in CH_2Cl_2; 10 μL, 0.017 mmol). After 3 hours, the mixture was neutralized with Et_3N (to pH 8), warmed to ambient temperature, and diluted with CH_2Cl_2 (60 mL). The organic phase was washed with saturated $Na_2S_2O_{3(aq)}$ solution (60 mL), saturated $NaCl_{(aq)}$ solution (60 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→20% acetone (containing 0.05% *v*/*v* $NH_4OH_{(aq)}$) – CH_2Cl_2 to afford the pure product as a white solid (156 mg, 0.127 mmol, 76% yield). R_f = 0.58 (0.01:19.99:80 NH_4OH : acetone : CH_2Cl_2). $[\alpha]_D^{20}$: +123° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δH 8.09 – 8.06 (m, 2H, Ar), 8.02 – 7.99 (m, 2H, Ar), 7.93 – 7.90 (m, 2H, Ar), 7.87 – 7.71 (m, 6H, Ar), 7.65 – 7.59 (m, 2H, Ar), 7.52 – 7.46 (m, 5H, Ar), 7.43 – 7.40 (m, 1H, Ar), 7.39 – 7.35 (m, 2H, Ar), 7.24 – 7.20 (m, 2H, Ar), 5.93 (dd, 1H, *J* = 3.2, <1 Hz, Gal_H4), 5.82 (dd, 1H, *J* = 10.7, 9.1 Hz, GlcN_H3), 5.76 (dd, 1H, *J* = 10.4, 8.0 Hz, Gal_H2), 5.56 (dd, 1H, *J* = 10.4, 3.4 Hz, Gal_H3), 5.33 (d, 1H, *J* = 8.4 Hz, GlcN_H1), 5.18 (dd, 1H, *J* = 9.6, 9.6 Hz, GlcN_H4), 5.06 (d, 1H, *J* = 8.9 Hz, NH), 4.85 (d, 1H, *J* = 8.0 Hz, Gal_H1), 4.53 – 4.50 (m, 2H, Gal_H6^a and Gal_H6^b), 4.35 (dd, 1H, *J* = 12.2, 4.2 Hz, GlcN_H6^a), 4.35 – 4.29 (m, 2H, GalN_H2 and Gal_H5), 4.29 (dd, 1H, *J* = 10.8, 8.5 Hz, GlcN_H2), 4.22 (d, 1H, *J* = 3.5 Hz, GalN_H1), 4.19 (dd, 1H, *J* = 12.2, 2.0 Hz, GlcN_H6^b), 3.96 – 3.95 (m, 1H, GalN_H4), 3.87 (ddd, 1H, *J* = 10.1, 4.3, 2.3 Hz, GlcN_H5), 3.76 (dd, 1H, *J* = 10.6, 2.4 Hz, GalN_H6^a), 3.69 (dd, 1H, *J* = 10.7, 8.5 Hz, GalN_H6^b), 3.65 – 3.61 (m, 2H, GalN_H3 and GalN_H5), 2.81 (s, 3H, OCH_3), 2.76 (d, 1H, *J* = <1 Hz, GalN_4-OH), 2.10 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.86 (s, 3H, OAc), 1.28 (s, 3H, NHAc). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 170.91 (C=O), 170.28 (C=O), 169.87 (C=O), 169.77 (C=O), 167.71

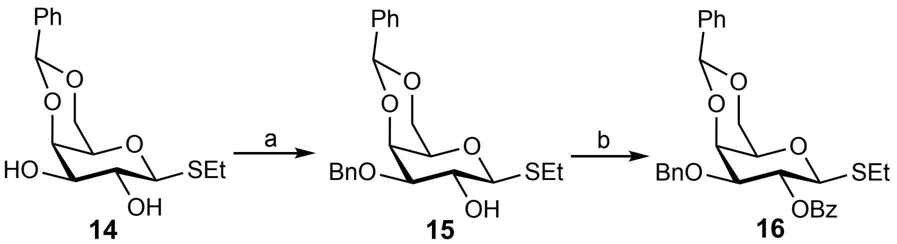
(C=O), 166.18 (C=O), 165.79 (C=O), 165.72 (C=O), 164.84 (C=O), 134.52 (Ar), 134.01 (Ar), 133.74 (Ar), 133.71 (Ar), 133.60 (Ar), 131.68 (Ar), 130.27 (Ar), 129.96 (Ar), 129.38 (Ar), 129.26 (Ar), 128.94 (Ar), 128.86 (Ar), 128.76 (Ar), 128.72 (Ar), 128.53 (Ar), 102.02 (Gal_C1), 99.13 (GlcN_C1), 98.23 (Fuc_C1), 79.92 (GalN_C3), 72.19 (Gal_C5), 72.05 (GlcN_C5), 71.61 (Gal_C3), 71.09 (GalN_C6), 70.83 (GalN_C3), 69.82 (Gal_C2), 69.19 (GlcN_C4), 68.54 (GalN_C5), 68.25 (GalN_C4), 68.16 (Gal_C4), 62.57 (Gal_C6), 62.24 (GlcN_C6), 54.89 (GlcN_C2), 54.50 (OCH_3), 47.88 (GalN_C2), 22.62 (NHAc), 20.99 (OAc), 20.86 (OAc), 20.67 (OAc). LRMS *m/z* calc'd for $C_{63}H_{62}N_2NaO_{24}$ $(M+Na)^+$: 1253.36; found: 1253.32.

Methyl β-D-galactopyranosyl-(1→3)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-D-galactopyranoside (2)



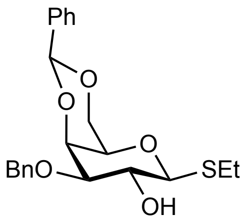
The protected trisaccharide (**13**; 146 mg, 0.119 mmol) and $NH_2NH_2 \cdot H_2O$ (47 μL, 0.98 mmol) were added to EtOH (3.0 mL) and left mixing at 80 °C. After 16 hours, the mixture was cooled to ambient temperature and then $NaHCO_3$ (406 mg, 4.83 mmol) and Ac_2O added (0.23 mL, 2.4 mmol). After another 4 hours, the solution was evaporated to dry and the crude mixture purified via RPLC on C-18 silica gel using 0→30% acetonitrile – H_2O to afford the pure product as a white solid (45 mg, 0.075 mmol, 63% yield over 2 steps). $[\alpha]_D^{20}$: +54° (*c* 0.3, H_2O). ^1H NMR (D_2O, 500 MHz): δH 4.75 (d, 1H, *J* = 3.8 Hz, GalN_H1), 4.52 (d, 1H, *J* = 8.5 Hz, GlcN_H1), 4.44 (d, 1H, *J* = 7.8 Hz, Gal_H1), 4.31 (dd, 1H, *J* = 11.1, 3.7 Hz, GalN_H2), 4.20 (dd, 1H, *J* = 3.0, <1 Hz, GalN_H4), 4.06 (dd, 1H, *J* = 10.6, 3.0 Hz, GalN_H6^a), 4.03 (ddd, 1H, *J* = 11.0, 2.6, <1 Hz, GalN_H5), 3.99 (dd, 1H, *J* = 11.1, 3.1 Hz, GalN_H3), 3.93 (dd, 1H, *J* = 12.3, 1.8 Hz, GlcN_H6^a), 3.90 (dd, 1H, *J* = 3.3, <1 Hz, Gal_H4), 3.77 – 3.70 (m, 4H, Gal_H6^a, GlcN_H6^b, Gal_H6^b, and GalN_H6^b), 3.71 (dd, 1H, *J* = 10.4, 8.5 Hz, GlcN_H2), 3.63 (ddd, 1H, *J* = 7.6, 4.7, <1 Hz, Gal_H5), 3.60 (dd, 1H, *J* = 9.9, 3.4 Hz, Gal_H3), 3.53 (dd, 1H, *J* = 10.3, 8.3 Hz, GlcN_H3), 3.50 (dd, 1H, *J* = 10.0, 7.9 Hz, Gal_H2), 3.46 – 3.41 (m, 2H, GlcN_H5 and GlcN_H4), 3.35 (s, 3H, OCH_3), 2.00 (s, 6H, 2x Ac). ^{13}C NMR (D_2O, 125 MHz): δC 175.25 (C=O), 175.09 (C=O), 105.34 (Gal_C1), 102.27 (GlcN_C1), 98.82 (GalN_C1), 77.73

(GalN_C3), 76.49 (GlcN_C5), 75.61 (Gal_C5), 74.43 (GlcN_C3), 73.17 (Gal_C3), 71.25 (Gal_C2), 70.67 (GalN_C6), 70.59 (GlcN_C4), 69.93 (GalN_C5), 69.62 (GalN_C4), 69.22 (Gal_C4), 61.60 (Gal_C6), 61.36 (GlcN_C6), 56.15 (GlcN_C2), 55.51 (OCH_3), 49.17 (GalN_C2), 22.81 (Ac), 22.65 (Ac). ESI-HRMS *m*/*z* calc'd for $C_{23}H_{40}N_2NaO_{16}$ $(M+Na)^+$: 623.2276; found: 623.2276. HPLC purity analysis: >99.5%, R_t 5.39 minutes, Atlantis T3 C18 column.



(a) NaH, DMF/THF; then $NiCl_2$; then BnBr, 57%; (b) BzCl, Py, CH_2Cl_2, 86%.

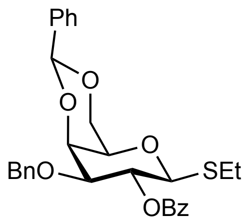
Ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (15)



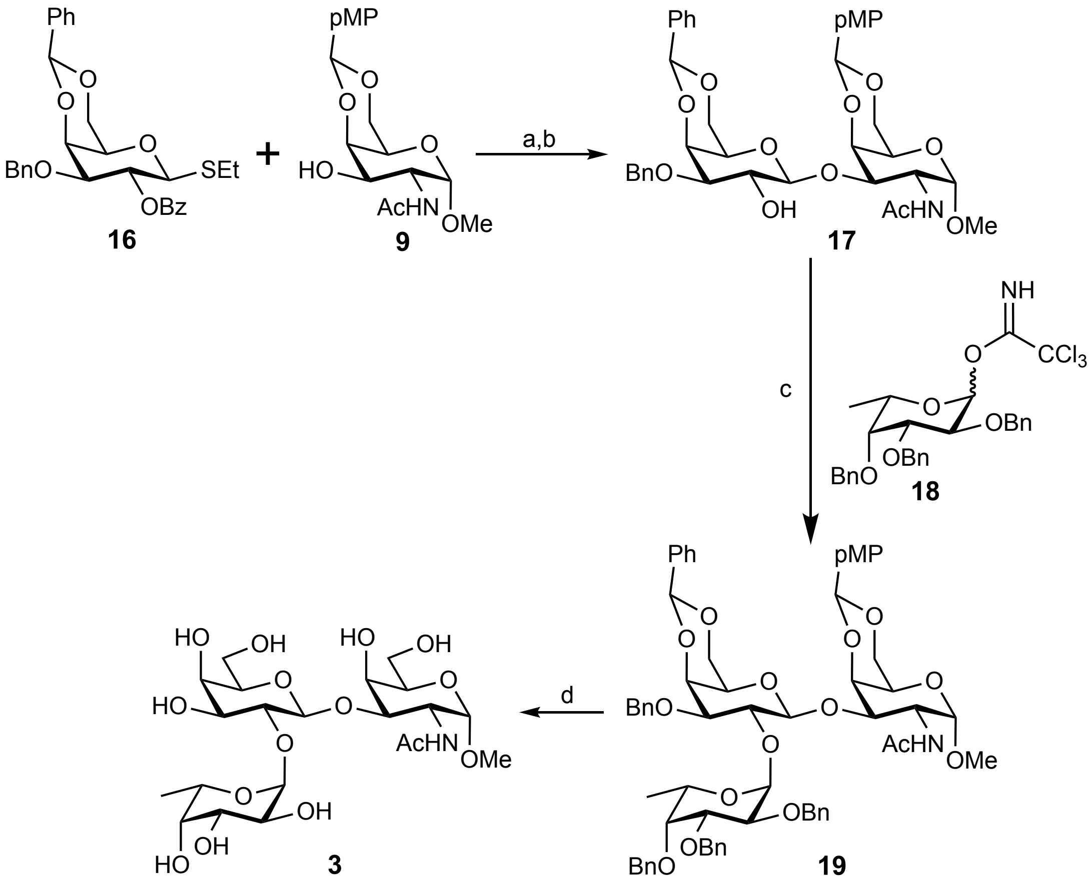
The starting material [ref 3] (**14**; 506 mg, 1.62 mmol) and NaH (60% oil dispersion; 138 mg, 3.45 mmol) were added to anhydrous THF (20 mL) and anhydrous DMF (2 mL) and left mixing at ambient temperature for 1 hour. Anhydrous $NiCl_2$ was added [ref 4] (209 mg, 1.6 mmol), and after another hour benzyl bromide was added drop-wise over 5 min (212 µL, 1.78 mmol). After 20 hours the reaction was quenched via the slow addition of MeOH (2 mL), 3 drops of AcOH were added, and then the mixture evaporated to dry. The crude material was redissolved into CH_2Cl_2 (120 mL) and then washed with sat'd $NaCl_{(aq)}$ solution (2 x 120 mL), dried with Na_2SO_4, filtered, and then evaporated to dry. The crude material was purified via MPLC using 0→30% EtOAc – toluene to afford the pure product as a white solid (374 mg, 0.929 mmol, 57% yield). R_f = 0.53 (1:4 acetone : toluene). $[\alpha]_D^{20}$: +6.7° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δH 7.52 – 7.48 (m, 2H, Ar), 7.41 – 7.27 (m, 8H, Ar), 5.44 (s, 1H, PhC*H*), 4.79 (d, 1H, *J* = 12.3 Hz, PhCH^aH^b), 4.76 (d, 1H, *J* = 12.3 Hz, PhCH^aH^b), 4.35 (d, 1H, *J* = 9.6 Hz, H-

1), 4.31 (dd, 1H, J = 12.4, 1.5 Hz, H-6[a]), 4.18 (dd, 1H, J = 3.4, <1 Hz, H-4), 4.06 (ddd, 1H, J = 9.4, 9.4, 1.6 Hz, H-2), 3.97 (dd, 1H, J = 12.4, 1.8 Hz, H-6[b]), 3.50 (dd, 1H, J = 9.2, 3.4 Hz, H-3), 3.41 – 3.40 (m, 1H, H-5), 2.83 (dq, 1H, J = 12.6, 7.5 Hz, $SCH^aH^bCH_3$), 2.75 (dq, 1H, J = 12.6, 7.5 Hz, $SCH^aH^bCH_3$), 2.55 (d, 1H, J = 1.6 Hz, 2-OH), 1.33 (dd, 3H, J = 7.5, 7.5 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 138.29 (Ar), 138.05 (Ar), 129.21 (Ar), 128.68 (Ar), 128.38 (Ar), 128.08 (Ar), 126.60 (Ar), 101.48 (Ph*C*H), 85.52 (C-1), 80.54 (C-3), 73.75 (C-4), 71.76 (Ph*C*H_2), 70.36 (C-5), 69.65 (C-6), 68.24 (C-2), 23.15 (S*C*H_2CH_3), 15.50 (SCH_2*C*H_3). LRMS *m/z* calc'd for $C_{22}H_{26}NaO_5S$ $(M+Na)^+$: 425.14; found: 425.22.

Ethyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (16)

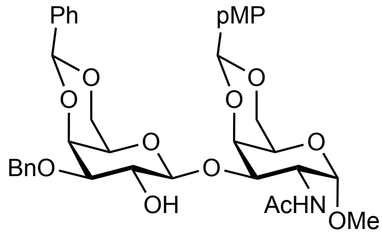


The starting material (**15**; 1.112 g, 2.763 mmol) and benzoyl chloride (0.42 mL, 3.6 mmol) were added to anhydrous pyridine (2.0 mL) and anhydrous CH_2Cl_2 (8.0 mL). After 3 hours, the mixture was quenched via the dropwise addition of MeOH (1 mL), evaporated to dry, and then purified via MPLC using 0→10% EtOAc – toluene to afford the pure product as a white solid (1.207 g, 2.382 mmol, 86% yield). R_f = 0.47 (1:9 acetone : toluene). $[\alpha]_D^{20}$: +25° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δH 8.05 – 8.02 (m, 2H, Ar), 7.60 – 7.53 (m, 3H, Ar), 7.47 – 7.44 (m, 2H, Ar), 7.40 – 7.34 (m, 3H, Ar), 7.24 – 7.16 (m, 5H, Ar), 5.73 (dd, 1H, J = 9.7, 9.7 Hz, H-2), 5.51 (s, 1H, PhC*H*), 4.68 (d, 1H, J = 12.8 Hz, $PhCH^aH^b$), 4.61 (d, 1H, J = 12.8 Hz, $PhCH^aH^b$), 4.53 (d, 1H, J = 9.8 Hz, H-1), 4.35 (dd, 1H, J = 12.3, 1.5 Hz, H-6[a]), 4.27 (dd, 1H, J = 3.4, <1 Hz, H-4), 4.01 (dd, 1H, J = 12.3, 1.7 Hz, H-6[b]), 3.74 (dd, 1H, J = 9.6, 3.4 Hz, H-3), 3.46 – 3.45 (m, 1H, H-5), 2.91 (dq, 1H, J = 12.3, 7.5 Hz, $SCH^aH^bCH_3$), 2.76 (dq, 1H, J = 12.3, 7.5 Hz, $SCH^aH^bCH_3$), 1.27 (dd, 3H, J = 7.5, 7.5 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 165.46 (C=O), 138.01 (Ar), 137.94 (Ar), 133.21 (Ar), 130.33 (Ar), 130.07 (Ar), 129.25 (Ar), 128.53 (Ar), 128.51 (Ar), 128.41 (Ar), 127.92 (Ar), 127.88 (Ar), 126.68 (Ar), 101.56 (Ph*C*H), 83.09 (C-1), 78.32 (C-3), 73.63 (C-4), 71.20 (Ph*C*H_2), 70.34 (C-5), 69.58 (C-6), 68.95 (C-2), 22.92 (S*C*H_2CH_3), 15.05 (SCH_2*C*H_3). LRMS *m/z* calc'd for $C_{29}H_{30}NaO_6S$ $(M+Na)^+$: 529.17; found: 529.22.



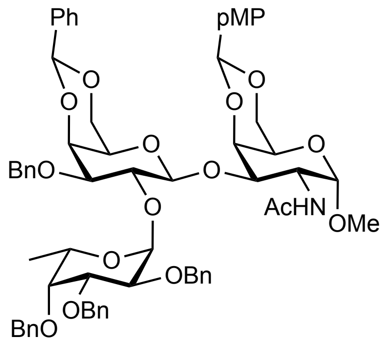
(a) NIS, TfOH, CH_2Cl_2/ACN; (b) NaOMe, MeOH, 50 ˚C, 56% (2 steps);
(c) TMSOTf, CH_2Cl_2, -78 ˚C, 72%; (d) H_2, $Pd(OH)_2$, H_2O/MeOH, 78%.

Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-*O*-(*p*-methoxybenzylidene)-α-D-galactopyranoside (17)



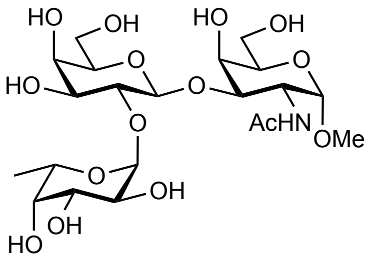
The glycosyl acceptor (**9**; 209 mg, 0.591 mmol), glycosyl donor (**16**; 359 mg, 0.709 mmol), and molecular sieves (3 Å; 343 mg) in anhydrous CH_2Cl_2 (4.0 mL) and anhydrous acetonitrile (2.0 mL) were left mixing at rt under Ar. After 1 hour, the mixture was cooled to -40 °C and then *N*-iodosuccinimide (239 mg, 1.06 mmol) and dropwise triflic acid (7 µL, 0.08 mmol) were added. Three equivalent batches were prepared in parallel (2.527 mmol glycosyl donor combined), and after 4 hours, the mixture was neutralized with Et_3N, warmed to ambient temperature, filtered over Celite, combined and diluted with CH_2Cl_2 (250 mL). The organic phase was washed with sat'd $Na_2S_2O_{3(aq)}$ solution (250 mL), sat'd $NaCl_{(aq)}$ solution (250 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→30% acetone (w/ 0.1% NH_4OH) – CH_2Cl_2 to afford the semi-pure product: R_f = 0.28 (1:4 acetone w/ 0.1% NH_4OH : CH_2Cl_2). LRMS *m*/*z* calc'd for $C_{44}H_{47}NNaO_{13}$ $(M+Na)^+$: 820.29; found: 820.15. The mixture was then added to anhydrous MeOH (5.0 mL), and NaOMe solution added (1.5 M NaOMe in MeOH; to pH 10). After 14 hours at 50 °C, the mixture was neutralized with acidic resin (Amberlite IR-120H; to pH 6), filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→30% acetone (w/ 0.1% NH_4OH) – CH_2Cl_2 to afford the pure product as a white solid (989 mg, 1.43 mmol, 56% yield over 2 steps). R_f = 0.13 (1:4 acetone w/ 0.1% $NH_4OH_{(aq)}$: CH_2Cl_2). $[\alpha]_D^{20}$: +127° (*c* 0.67, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δH 7.52 – 7.46 (m, 4H, Ar), 7.39 – 7.37 (m, 2H, Ar), 7.35 – 7.26 (m, 6H, Ar), 6.88 – 6.85 (m, 2H, Ar), 5.87 (d, 1H, *J* = 8.4 Hz, NH), 5.56 (s, 1H, pMPC*H*), 5.45 (s, 1H, PhC*H*), 4.95 (d, 1H, *J* = 3.6 Hz, GalNAc_H1), 4.81 (d, 1H, *J* = 12.4 Hz, $PhCH^aH^b$), 4.77 (d, 1H, *J* = 12.4 Hz, $PhCH^aH^b$), 4.67 (ddd, 1H, *J* = 11.0, 8.5, 3.6 Hz, GalNAc_H2), 4.39 (d, 1H, *J* = 7.7 Hz, Gal_H1), 4.38 – 4.37 (m, 1H, GalNAc_H4), 4.25 (dd, 1H, *J* = 12.3, 1.5 Hz, Gal_H6[a]), 4.23 (dd, 1H, *J* = 12.4, 1.5 Hz, GalNAc_H6[a]), 4.09 – 4.08 (m, 1H, Gal_H4), 4.06 (ddd, 1H, *J* = 9.7, 7.8, 1.6 Hz, Gal_H2), 4.02 (dd, 1H, *J* = 12.3, 1.7 Hz, Gal_H6[b]), 4.02 (dd, 1H, *J* = 12.4, 1.5 Hz, GalNAc_H6[b]), 3.94 (dd, 1H, *J* = 11.0, 3.2 Hz, GalNAc_H3), 3.80 (s, 3H, OCH_3), 3.62 – 3.61 (m, 1H, GalNAc_H5), 3.43 (dd, 1H, *J* = 9.8, 3.5 Hz, Gal_H3), 3.41 (s, 3H, OCH_3), 3.34 – 3.33 (m, 1H, Gal_H5), 2.85 (d, 1H, *J* = 1.7 Hz, 2-OH), 2.00 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 171.13 (C=O), 160.23 (Ar), 138.61 (Ar), 137.99 (Ar), 130.64 (Ar), 129.27 (Ar), 128.56 (Ar), 128.45 (Ar), 128.11 (Ar), 128.07 (Ar), 127.90 (Ar), 126.63 (Ar), 113.73 (Ar), 105.05 (Gal_C1), 101.47 (Ph*C*H), 101.20 (pMP*C*H), 99.65 (GalNAc_C1), 78.68 (Gal_C3), 76.13 (GalNAc_C4), 75.67 (GalNAc_C3), 73.96 (Gal_C4), 71.88 (PhCH_2), 69.63 (Gal_C2), 69.50, 69.38 (Gal_C6 and GalNAc_C6), 67.03 (Gal_C5), 63.31 (GalNAc_C5), 55.64 (OCH_3), 55.53 (OCH_3), 48.73 (GalNAc_C2), 23.87 (Ac). LRMS *m*/*z* calc'd for $C_{37}H_{43}NNaO_{12}$ $(M+Na)^+$: 716.27; found: 716.26.

Methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-*O*-(*p*-methoxybenzylidene)-α-D-galactopyranoside (19)

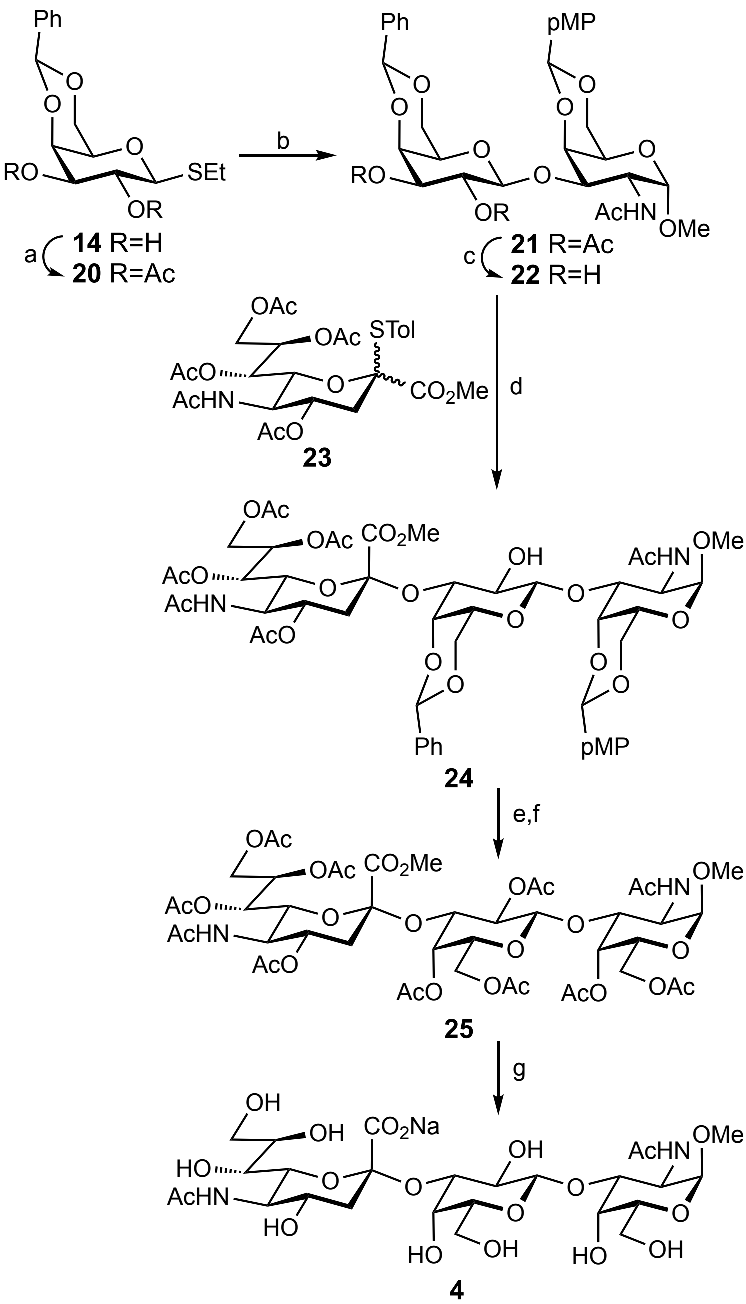


The glycosyl acceptor (**17**; 198 mg, 0.285 mmol), glycosyl donor [ref 5] (**18**; 212 mg, 0.366 mmol), and molecular sieves (3 Å; 246 mg) in anhydrous CH_2Cl_2 (5.0 mL) were left mixing at rt under Ar. After 1 hour, the mixture was cooled to -78 °C and then trimethylsilyl triflate was added dropwise (7.5 μL, 0.041 mmol). Three equivalent batches were prepared in parallel (0.836 mmol glycosyl donor combined), and after 3 hours the mixtures were neutralized with Et_3N, filtered over Celite, combined and then diluted with CH_2Cl_2 (500 mL). The organic phase was washed with sat'd $NaHCO_{3(aq)}$ solution (500 mL), sat'd $NaCl_{(aq)}$ solution (500 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→30% acetone (w/ 0.1% NH_4OH) – CH_2Cl_2 to afford the pure product as a white solid (670 mg, 0.603 mmol, 72% yield). R_f = 0.45 (1:4 acetone w/ 0.1% NH_4OH : CH_2Cl_2). $[\alpha]_D^{20}$: +34° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δH 7.54 – 7.50 (m, 2H, Ar), 7.48 – 7.45 (m, 2H, Ar), 7.35 – 7.32 (m, 5H, Ar), 7.29 – 7.20 (m, 13H, Ar), 7.19 – 7.12 (m, 5H, Ar), 6.78 – 6.75 (m, 2H, Ar), 6.11 (d, 1H, *J* = 8.3 Hz, NH), 5.50 (s, 1H, *p*MPC*H*), 5.48 (d, 1H, *J* = 3.8 Hz, Fuc_H1), 5.43 (s, 1H, PhC*H*), 4.89 (d, 1H, *J* = 11.4 Hz, PhC$H^a$$H^b$), 4.89 (d, 1H, *J* = 3.5 Hz, GalNAc_H1), 4.81 (d, 1H, *J* = 11.9 Hz, PhC$H^a$$H^b$), 4.76 (d, 1H, *J* = 11.9 Hz, PhC$H^a$$H^b$), 4.70 (d, 1H, *J* = 12.0 Hz, PhC$H^a$$H^b$), 4.64 – 4.59 (m, 4H, PhC$H^a$$H^b$, GalNAc_H2, PhC$H^a$$H^b$, and Gal_H1), 4.54 (d, 1H, *J* = 11.4 Hz, PhC$H^a$$H^b$), 4.53 (d, 1H, *J* = 12.1 Hz, PhC$H^a$$H^b$), 4.39 (dd, 1H, *J* = 3.0, <1 Hz, GalNAc_H4), 4.25 – 4.18 (m, 4H, Gal_H6^a, GalNAc_H6^a, Gal_H2, and Fuc_H5), 4.12 (dd, 1H, *J* = 3.6, <1 Hz, Gal_H4), 4.04 – 3.96 (m, 3H, Gal_H6^b, GalNAc_H6^b, and GalNAc_H3), 3.94 (dd, 1H, *J* = 10.1, 3.8 Hz, Fuc_H2), 3.89 (dd, 1H, *J* = 10.2, 2.6 Hz, Fuc_H3), 3.74 (s, 3H, OCH_3), 3.73 – 3.72 (m, 1H, Fuc_H4), 3.66 (dd, 1H, *J* = 9.5, 3.7 Hz, Gal_H3), 3.58 – 3.57 (m, 1H, GalNAc_H5), 3.37 (s, 3H, OCH_3), 3.34 – 3.32 (m, 1H, Gal_H5), 1.87 (s, 3H, Ac), 0.92 (d, 3H, *J* = 6.4 Hz, Fuc_H6). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 170.03 (C=O), 160.09 (Ar), 139.51 (Ar), 139.41 (Ar), 138.86 (Ar), 138.73 (Ar), 138.05 (Ar), 130.71 (Ar), 129.15 (Ar), 128.41 (Ar), 128.39 (Ar), 128.24 (Ar), 128.21 (Ar), 128.11 (Ar), 128.02 (Ar), 127.96 (Ar), 127.60 (Ar), 127.41 (Ar), 127.38 (Ar), 127.35 (Ar), 126.54 (Ar), 113.54 (Ar), 103.35 (Gal_C1), 101.34 (*p*MP*C*H), 101.09 (Ph*C*H), 99.60 (GalNAc_C1), 97.66 (Fuc_C1), 80.51 (Gal_C3), 79.28 (Fuc_C3), 78.53 (Fuc_C4), 76.43 (GalNAc_C4), 76.10 (Fuc_C2), 75.12 (Ph*C*H_2), 74.54 (Gal_C2), 73.73 (GalNAc_C3), 73.26 (Gal_C4), 72.70 (Ph*C*H_2), 72.47 (Ph*C*H_2), 71.31 (Ph*C*H_2), 69.41 (Gal_C6 and GalNAc_C6), 67.17 (Fuc_C5), 66.54 (Gal_C5), 63.32 (GalNAc_C5), 55.65 (OCH_3), 55.47 (OCH_3), 48.85 (GalNAc_C2), 23.65 (Ac), 16.41 (Fuc_C6). LRMS *m/z* calc'd for $C_{64}H_{71}NNaO_{16}$ $(M+Na)^+$: 1132.46; found: 1132.38.

Methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (3)

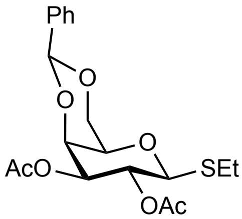


The starting material (**19**; 37 mg, 0.033 mmol) and $Pd(OH)_2$ (20% *w/w* on carbon, 13 mg) in MeOH (0.8 mL) and H_2O (0.8 mL) were left mixing under H_2 at atmospheric pressure. After 48 hours, the solid catalyst was removed via filtration and the solution evaporated to dry. The crude material was purified via RPLC on C-18 silica gel using 0→60% acetonitrile – H_2O to afford the pure product as a white solid (14 mg, 0.026 mmol, 78% yield); data characterization is in agreement with that previously published [ref 2]. $[\alpha]_D^{20}$: +42° (*c* 0.5, H_2O). ^1H NMR (D_2O, 500 MHz): δH 5.22 (d, 1H, *J* = 4.1 Hz, Fuc_H1), 4.75 (m, 1H, GalN_H1), 4.62 (d, 1H, *J* = 7.7 Hz, Gal_H1), 4.21 (dq, 1H, *J* = 6.6, <1 Hz, Fuc_H5), 4.13 – 4.09 (m, 2H, GalN_H2 and GalN_H4), 4.11 (dd, 1H, *J* = 11.2, 2.9 Hz, GalN_H3), 3.96 (ddd, 1H, *J* = 6.2, 6.2, <1 Hz, GalN_H5), 3.89 (dd, 1H, *J* = 3.4, <1 Hz, Gal_H4), 3.82 (dd, 1H, *J* = 9.7, 3.4 Hz, Gal_H3), 3.79 – 3.71 (m, 5H, GalN_H6^a, Fuc_H2, GalN_H6^b, Gal_H6^a, and Gal_H6^b), 3.67 – 3.60 (m, 4H, Fuc_H4, Fuc_H3, Gal_H5, and Gal_H2), 3.35 (s, 3H, OCH_3), 2.03 (s, 3H, Ac), 1.18 (d, 3H, *J* = 6.6 Hz, Fuc_H6). ^{13}C NMR (D_2O, 125 MHz): δC 174.31 (C=O), 102.63 (Gal_C1), 99.94 (Fuc_C1), 98.53 (GalN_C1), 76.93 (Gal_C2), 75.66 (Gal_C5), 74.41 (GalN_C3), 74.21 (Gal_C3), 72.51 (Fuc_C4), 71.06 (GalN_C5), 70.21 (Fuc_C3), 69.71 (Gal_C4 and GalN_C4), 68.72 (Fuc_C2), 67.44 (Fuc_C5), 61.88 (GalN_C6), 61.56 (Gal_C6), 55.74 (OCH_3), 50.06 (GalN_C2), 22.59 (Ac), 16.00 (Fuc_C6). ESI-HRMS *m/z* calc'd for $C_{21}H_{37}NNaO_{15}$ $(M+Na)^+$: 566.2061; found: 566.2061. HPLC purity analysis: >99.5%, R_t 5.55 minutes, Atlantis T3 C18 column.



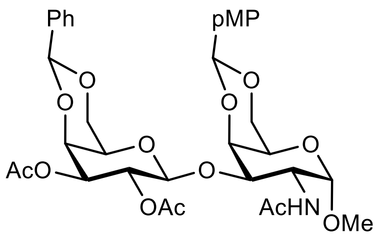
(a) Ac_2O, Py, 96%; (b) **9**, NIS, TfOH, CH_2Cl_2/ACN, 0 °C, 73%; (c) NaOMe, MeOH, 98%; (d) NIS, TfOH, -40 °C, 47%; (e) AcOH, H_2O, 70 °C; (f) Ac_2O, Py, 71% (2 steps); (g) NaOMe, MeOH/H_2O, 66%.

Ethyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (20)



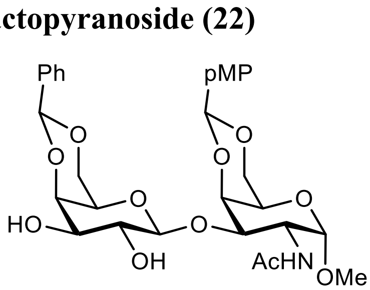
The starting material (**14**; 1.071 g, 3.429 mmol) was dissolved into anhydrous pyridine (6.0 mL) and Ac_2O (6.0 mL), and left mixing at rt. After 3 hours, the reaction mixture was evaporated to dry via co-evaporation with toluene (3 x 10 mL), and then the crude material was purified via MPLC on silica gel using 0→40% acetone – toluene to afford the pure product as a white solid (1.306 g, 3.294 mmol, 96% yield). R_f = 0.64 (1:4 acetone : toluene). $[\alpha]_D^{20}$: +28° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δH 7.51 – 7.46 (m, 2H, Ar), 7.40 – 7.34 (m, 3H, Ar), 5.48 (s, 1H, PhC*H*), 5.46 (dd, 1H, *J* = 9.9, 9.9 Hz, H-2), 4.98 (dd, 1H, *J* = 10.0, 3.5 Hz, H-3), 4.45 (d, 1H, *J* = 9.8 Hz, H-1), 4.39 (dd, 1H, *J* = 3.5, <1 Hz, H-4), 4.31 (dd, 1H, *J* = 12.5, 1.5 Hz, H-6^a), 3.99 (dd, 1H, *J* = 12.5, 1.6 Hz, H-6^b), 3.53 – 3.52 (m, 1H, H-5), 2.87 (dq, 1H, *J* = 12.3, 7.5 Hz, $SCH^aH^bCH_3$), 2.72 (dq, 1H, *J* = 12.3, 7.5 Hz, $SCH^aH^bCH_3$), 2.06 (s, 3H, Ac), 2.05 (s, 3H, Ac), 1.28 (dd, 3H, *J* = 7.5, 7.5 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 170.69 (C=O), 169.53 (C=O), 137.72 (Ar), 129.21 (Ar), 128.30 (Ar), 126.46 (Ar), 101.20 (Ph*C*H), 82.86 (C-1), 73.71 (C-4), 73.10 (C-3), 69.80 (C-5), 69.18 (C-6), 66.70 (C-2), 22.90 (SCH_2CH_3), 20.96 (Ac), 20.95 (Ac), 14.88 (SCH_2CH_3). LRMS *m/z* calc'd for $C_{19}H_{24}NaO_7S$ $(M+Na)^+$: 419.11; found: 419.11.

Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-*O*-(*p*-methoxybenzylidene)-α-D-galactopyranoside (21)



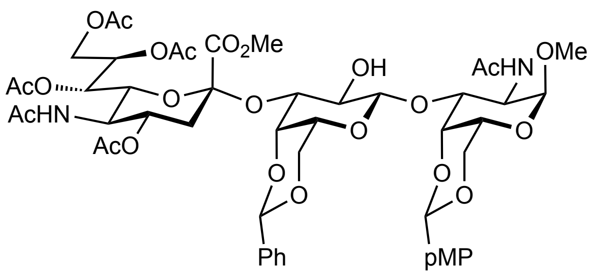
The glycosyl acceptor (**9**; 504 mg, 1.43 mmol), glycosyl donor (**20**; 1.119 g, 2.823 mmol), and crushed molecular sieves (3 Å, 1.476 g) in anhydrous CH_2Cl_2 (10 mL) and anhydrous acetonitrile (5 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to 0 °C, and then NIS added (641 mg, 2.85 mmol) followed by the drop-wise addition of TfOH (12 μL, 0.14 mmol). After 5 hours, the mixture was neutralized with Et_3N (to pH 8), warmed to ambient temperature, diluted with CH_2Cl_2 (100 mL), and filtered over Celite. The organic phase was washed with saturated $Na_2S_2O_{3(aq)}$ solution (100 mL), saturated $NaCl_{(aq)}$ solution (100 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→40% acetone (containing 0.05% *v*/*v* conc'd $NH_4OH_{(aq)}$) – CH_2Cl_2 to afford the mostly pure intermediate as a white solid (722 mg, 1.05 mmol, 73% yield). R_f = 0.39 (3:7 acetone w/ 0.1% NH_4OH : CH_2Cl_2). $[\alpha]_D^{20}$: +122° (*c* 1.0, CH_3OH). ^1H NMR (CD_3OD, 500 MHz): δH 7.53 – 7.49 (m, 2H, Ar), 7.46 – 7.43 (m, 2H, Ar), 7.36 – 7.33 (m, 3H, Ar), 6.85 – 6.82 (m, 2H, Ar), 5.59 (s, 1H, PhC*H*), 5.57 (s, 1H, *p*MPC*H*), 5.27 (dd, 1H, *J* = 10.4, 8.0 Hz, Gal_H2), 5.05 (dd, 1H, *J* = 10.4, 3.7 Hz, Gal_H3), 4.88 (d, 1H, *J* = 8.0 Hz, Gal_H1), 4.72 (d, 1H, *J* = 3.5 Hz, GalNAc_H1), 4.56 (dd, 1H, *J* = 11.2, 3.5 Hz, GalNAc_H2), 4.49 (dd, 1H, *J* = 3.3, <1 Hz, GalNAc_H4), 4.42 (dd, 1H, *J* = 3.7, 0.7 Hz, Gal_H4), 4.25 (dd, 1H, *J* = 12.4, 1.5 Hz, Gal_H6[a]), 4.17 (dd, 1H, *J* = 12.5, 1.6 Hz, Gal_H6[b]), 4.16 – 4.13 (m, 1H, GalNAc_H6[a]), 4.12 – 4.09 (m, 2H, GalNAc_H6[b] and GalNAc_H3), 3.77 (s, 3H, ArOC*H*3), 3.71 – 3.70 (m, 1H, GalNAc_H5), 3.67 – 3.66 (m, 1H, Gal_H5), 3.42 (s, 3H, OCH_3), 2.03 (s, 3H, NHAc), 2.01 (s, 3H, OAc), 2.00 (s, 3H, OAc). ^{13}C NMR (CD_3OD, 125 MHz): δC 173.24 (C=O), 172.03 (C=O), 171.69 (C=O), 161.52 (Ar), 139.58 (Ar), 132.31 (Ar), 130.16 (Ar), 129.25 (Ar), 128.96 (Ar), 127.71 (Ar), 114.40 (Ar), 102.94 (Gal_C1), 102.32 (Ar*C*H), 102.05 (Ar*C*H), 101.12 (GalNAc_C1), 77.34 (GalNAc_C4), 75.49 (GalNAc_C3), 75.09 (Gal_C4), 73.39 (Gal_C3), 70.51 (Gal_C2), 70.38 (GalNAc_C6), 70.12 (Gal_C6), 67.95 (Gal_C5), 64.62 (GalNAc_C5), 55.98 (OCH_3), 55.83 (ArO*C*H3), 50.05 (GalNAc_C2), 23.09 (NHAc), 21.08 (OAc), 20.73 (OAc). LRMS *m*/*z* calc'd for $C_{34}H_{41}NNaO_{14}$ $(M+Na)^+$: 710.24; found: 710.21.

Methyl 4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-*O*-(*p*-methoxybenzylidene)-α-D-galactopyranoside (22)



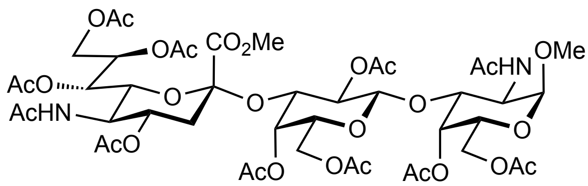
The starting material (**21**; 548 mg, 0.797 mmol) was dissolved into anhydrous MeOH (6.0 mL), and then NaOMe solution was added drop-wise (1.5 M NaOMe in MeOH; to pH 10). After 2 hours at ambient temperature, the reaction mixture was neutralized with acidic resin (Amberlite IR-120H; to pH 6), filtered, and then evaporated to dry. The crude material was purified via MPLC on silica gel using 0→100% acetone (w/ 0.1% NH_4OH) – CH_2Cl_2 to afford the pure product as a white solid (470 mg, 0.779 mmol, 98% yield). R_f = 0.07 (1:1 acetone w/ 0.1% NH_4OH : CH_2Cl_2). $[\alpha]_D^{20}$: +104° (*c* 1.0, CH_3OH). ^1H NMR (CD_3OD, 500 MHz): δH 7.59 – 7.55 (m, 2H, Ar), 7.49 – 7.46 (m, 2H, Ar), 7.39 – 7.33 (m, 3H, Ar), 6.90 – 6.86 (m, 2H, Ar), 5.65 (s, 1H, PhC*H*), 5.61 (s, 1H, *p*MPC*H*), 4.82 (d, 1H, *J* = 3.4 Hz, GalNAc_H1), 4.62 (dd, 1H, *J* = 11.2, 3.4 Hz, GalNAc_H2), 4.55 (dd, 1H, *J* = 3.2, <1 Hz, GalNAc_H4), 4.52 (d, 1H, *J* = 7.4 Hz, Gal_H1), 4.26 (dd, 1H, *J* = 12.4, 1.4 Hz, Gal_H6^a), 4.22 (dd, 1H, *J* = 3.5, 0.8 Hz, Gal_H4), 4.19 (dd, 1H, *J* = 12.4, 1.7 Hz, Gal_H6^b), 4.17 (dd, 1H, *J* = 12.5, 1.4, GalNAc_H6^a), 4.15 – 4.11 (m, 2H, GalNAc_H6^b and GalNAc_H3), 3.81 (s, 3H, ArOCH_3), 3.75 – 3.74 (m, 1H, GalNAc_H5), 3.67 (dd, 1H, *J* = 9.9, 7.4 Hz, Gal_H2), 3.61 (dd, 1H, *J* = 9.9, 3.5 Hz, Gal_H3), 3.58 – 3.57 (m, 1H, Gal_H5), 3.46 (s, 3H, OCH_3), 2.00 (s, 3H, NHAc). ^{13}C NMR (CD_3OD, 125 MHz): δC 174.61 (C=O), 162.06 (Ar), 140.19 (Ar), 132.69 (Ar), 130.34 (Ar), 129.50 (Ar), 129.49 (Ar), 128.10 (Ar), 114.78 (Ar), 106.75 (Gal_C1), 102.83, 102.76 (Ph*C*H and *p*MP*C*H), 101.50 (GalNAc_C1), 78.01 (GalNAc_C4), 77.92 (Gal_C4), 76.14 (GalNAc_C3), 74.01 (Gal_C3), 72.23 (Gal_C2), 70.83 (Gal_C6), 70.80 (GalNAc_C6), 68.64 (Gal_C5), 64.99 (GalNAc_C5), 56.35 (OCH_3), 56.20 (ArO*C*H_3), 50.74 (GalNAc_C2), 23.33 (NHAc). LRMS *m/z* calc'd for $C_{30}H_{37}NNaO_{12}$ $(M+Na)^+$: 626.22; found: 626.18.

Methyl 4,6-*O*-benzylidene-3-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-4,6-*O*-(*p*-methoxybenzylidene)-α-D-galactopyranoside (24)



The glycosyl acceptor (**22**; 399 mg, 0.661 mmol), glycosyl donor (**23**; 601 mg, 1.01 mmol), and crushed molecular sieves (3 Å, 866 mg) in anhydrous CH_2Cl_2 (5.0 mL) and anhydrous acetonitrile (5.0 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to -40 °C, and then NIS (298 mg, 1.32 mmol) and TfOH (9 μL, 0.10 mmol) were added. After 24 hours, the mixture was neutralized with Et_3N (to pH 8), warmed to ambient temperature, filtered over Celite, and evaporated to dry. The crude material was redissolved into CH_2Cl_2 (30 mL), washed with saturated $NaHCO_{3(aq)}$ solution (2x 30 mL), saturated $NaCl_{(aq)}$ solution (30 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→30% acetone (w/ 0.1% NH_4OH) – CH_2Cl_2 to afford the pure product as a white solid (333 mg, 0.309 mmol, 47% yield). ^1H NMR ($CDCl_3$, 500 MHz) δ 7.49 – 7.46 (m, 4H, Ar), 7.34 – 7.31 (m, 3H, Ar), 6.85 – 6.82 (m, 2H, Ar), 6.50 (d, 1H, J = 7.8 Hz, GalNAc_NH), 5.55 (s, 1H, ArC*H*), 5.51 (ddd, 1H, J = 9.7, 7.1, 2.5 Hz, Neu5Ac_H8), 5.40 – 5.37 (m, 2H, Neu5Ac_NH and ArC*H*), 5.24 (dd, 1H, J = 9.4, 1.3 Hz, Neu5Ac_H7), 5.04 (d, 1H, J = 3.3 Hz, GalNAc_H1), 4.87 (ddd, 1H, J = 12.2, 9.8, 4.5 Hz, Neu5Ac_H4), 4.64 (ddd, 1H, J = 11.1, 7.8, 3.3 Hz, GalNAc_H2), 4.55 (d, 1H, J = 7.7 Hz, Gal_H1), 4.41 (dd, 1H, J = 2.8, <1 Hz, GalNAc_H4), 4.38 (dd, 1H, J = 12.2, 2.4 Hz, Neu5Ac_H9^a), 4.25 – 4.20 (m, 3H, GalNAc_H6^a, Gal_H6^a, and Gal_H3), 4.11 (dd, 1H, J = 12.4, <2 Hz, Gal_H6^b), 4.07 – 4.01 (m, 4H, Neu5Ac_H5, GalNAc_H3, GalNAc_H6^b, and Neu5Ac_H6), 3.95 – 3.89 (m, 3H, Neu5Ac_H9^b, Gal_H4, and Gal_H2), 3.78 (s, 3H, OCH_3), 3.64 – 3.62 (s, 4H, GalNAc_H5 and OCH_3), 3.50 – 3.49 (m, 1H, Gal_H5), 3.40 (s, 3H, OCH_3), 2.91 – 2.89 (broad s, 1H, Gal_2-OH), 2.71 (dd, 1H, J = 12.9, 4.5 Hz, Neu5Ac_H3$_{eq}$), 2.19 (s, 3H, OAc), 2.15 (s, 3H, OAc), 2.05 – 2.00 (m, 10H, OAc, NHAc, Neu5Ac_H3$_{ax}$, and OAc), 1.88 (s, 3H, NHAc). LRMS m/z calc'd for $C_{50}H_{64}N_2NaO_{24}$ $(M+Na)^+$: 1099.37; found: 1099.27.

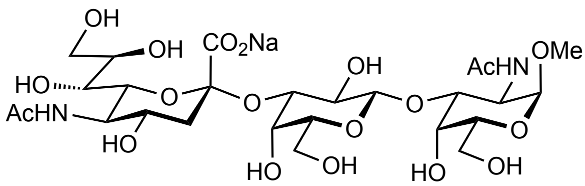
Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-β-D-galactopyranosyl-(1→3)-2-acetamido-4,6-di-*O*-acetyl-2-deoxy-α-D-galactopyranoside (25)



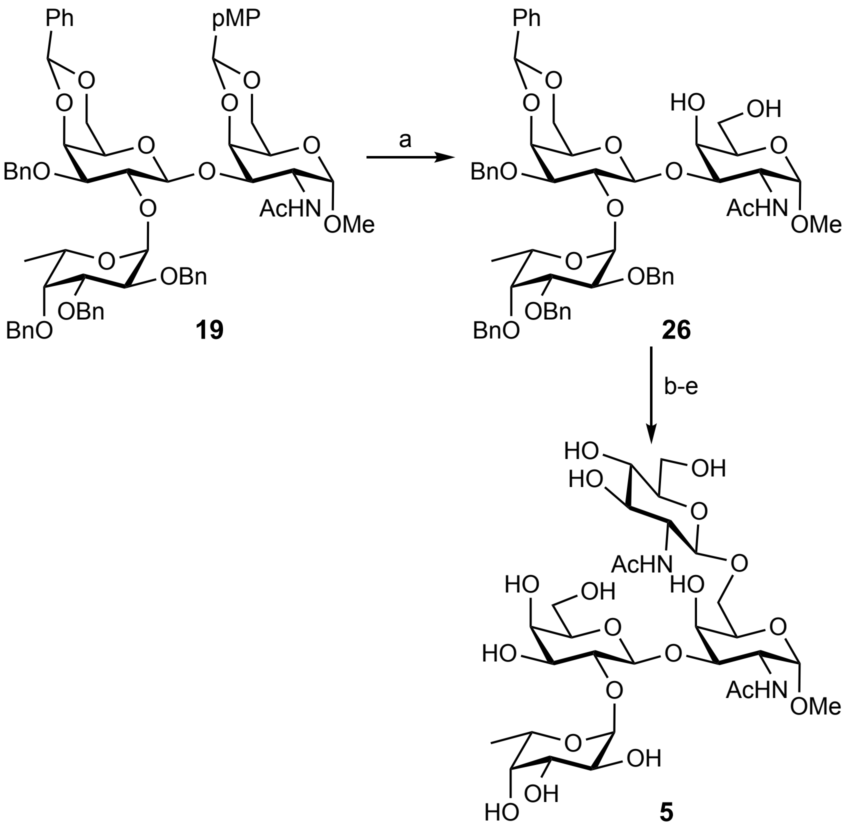
The starting material (**24**; 96 mg, 0.089 mmol) was dissolved into AcOH (1.2 mL) and H_2O (0.3 mL) and left mixing at 70 °C. After 7 hours, the mixture was evaporated to dry via co-evaporation with toluene (3 x 2 mL), and then redissolved into pyridine (1.0 mL) and Ac_2O (1.0 mL). After 18 hours, the reaction mixture was concentrated to a syrup via co-evaporation with toluene (3 x 2 mL), and then the crude material was purified via MPLC on silica gel using 0→15% MeOH – CH_2Cl_2 to afford the pure product as a white solid (68 mg, 0.063 mmol, 71%

yield over 2 steps). ^{1}H NMR (CDCl$_3$, 500 MHz): δH 6.40 (d, 1H, J = 8.1 Hz, GalNAc_NH), 5.70 (ddd, 1H, J = 9.3, 7.7, 2.6 Hz, Neu5Ac_H8), 5.42 (dd, 1H, J = 2.8, <1 Hz, GalNAc_H4), 5.31 (dd, 1H, J = 9.4, 2.7 Hz, Neu5Ac_H7), 5.23 (d, 1H, J = 10.2 Hz, Neu5Ac_NH), 5.00 (dd, 1H, J = 10.1, 8.1 Hz, Gal_H2), 4.91 (d, 1H, J = 3.5 Hz, GalNAc_H1), 4.89 – 4.83 (m, 2H, Gal_H4 and Neu5Ac_H4), 4.68 (d, 1H, J = 8.0 Hz, Gal_H1), 4.50 – 4.45 (m, 2H, Gal_H3 and GalNAc_H2), 4.39 (dd, 1H, J = 12.1, 2.6 Hz, Neu5Ac_H9^a), 4.21 (dd, 1H, J = 11.4, 4.6 Hz, GalNAc_H6^a), 4.11 – 4.04 (m, 3H, Neu5Ac_H5, GalNAc_H5, and Gal_H6^a), 4.01 (dd, 1H, J = 11.4, 6.5 Hz, Gal_H6^b), 3.95 (dd, 1H, J = 11.4, 7.6 Hz, GalNAc_H6^b), 3.93 – 3.84 (m, 6H, GalNAc_H3, Neu5Ac_H9^b, Gal_H5, and OCH$_3$), 3.67 (dd, 1H, J = 10.7, 2.7 Hz, Neu5Ac_H6), 3.35 (s, 3H, OCH$_3$), 2.59 (dd, 1H, J = 12.6, 4.5 Hz, Neu5Ac_H3$_{eq}$), 2.27 (s, 3H, OAc), 2.20 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.01 (s, 6H, OAc and NHAc), 1.86 (s, 3H, NHAc), 1.69 (dd, 1H, J = 12.4, 12.4 Hz, Neu5Ac_H3$_{ax}$). ^{13}C NMR (CDCl$_3$, 125 MHz): δC 171.50 (Ac), 171.11 (Ac), 171.03 (Ac), 170.81 (Ac), 170.55 (Ac), 170.51 (Ac), 170.49 (Ac), 170.26 (Ac), 170.24 (Ac), 170.07 (Ac), 170.06 (Ac), 168.12 (Neu5Ac_C1), 101.63 (Gal_C1), 98.66 (GalNAc_C1), 96.93 (Neu5Ac_C2), 74.42 (GalNAc_C3), 72.07 (Neu5Ac_C6), 71.51 (Gal_C3), 70.95 (Gal_C5), 69.58 (GalNAc_C4), 69.41 (Neu5Ac_C4), 69.02 (Gal_C2), 67.75 (Gal_C4), 67.61 (Neu5Ac_C7), 67.49 (GalNAc_C5), 67.40 (Neu5Ac_C8), 63.47 (Neu5Ac_C9), 63.24 (GalNAc_C6), 62.03 (Gal_C6), 55.38 (OCH$_3$), 53.35 (OCH$_3$), 49.35 (GalNAc_C2), 49.15 (Neu5Ac_C5), 37.59 (Neu5Ac_C3), 23.30 (NHAc), 23.28 (NHAc), 21.62 (OAc), 21.25 (OAc), 21.02 (2x OAc), 20.93 (4x OAc), 20.85 (OAc). LRMS m/z calc'd for $C_{45}H_{64}N_2NaO_{28}$ (M+Na)$^+$: 1103.35; found: 1103.29.

Methyl 3-*O*-(sodium 5-acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (4)

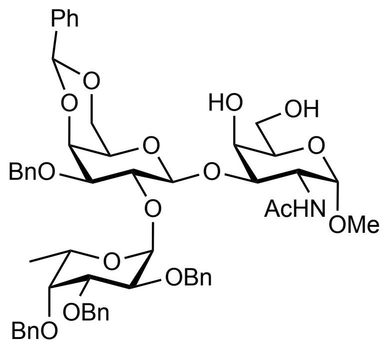


The starting material (**25**; 55 mg, 0.051 mmol) was dissolved into 50% aqueous MeOH (1.0 mL), and then NaOMe solution was added drop-wise (1.5 M NaOMe in MeOH; to pH 10). After 14 hours, the reaction mixture was neutralized with acidic resin (Amberlite IR-120H; to pH 8), filtered, and evaporated to dry. The crude material was purified via RPLC on C-18 silica gel using 0→20% acetonitrile – H_2O to afford the pure product as a white solid (24 mg, 0.034 mmol, 66% yield). $[\alpha]_D^{20}$: +32° (*c* 1.0, H_2O). ^{1}H NMR (D_2O, 500 MHz): δH 4.79 (d, 1H, *J* = 3.7 Hz, GalNAc_H1), 4.52 (d, 1H, *J* = 7.9 Hz, Gal_H1), 4.31 (dd, 1H, *J* = 11.1, 3.7 Hz, GalNAc_H2), 4.22 (dd, 1H, *J* = 2.7, <1 Hz, GalNAc_H4), 4.06 (dd, 1H, *J* = 9.8, 3.2 Hz, Gal_H3), 4.00 (dd, 1H, *J* = 11.1, 3.0 Hz, GalNAc_H3), 3.96 – 3.92 (m, 2H, GalNAc_H5 and Gal_H4), 3.87 (ddd, 1H, *J* = 8.9, 6.3, 2.5 Hz, NeuNAc_H8), 3.86 – 3.81 (m, 2H, NeuNAc_H9^a and NeuNAc_H5), 3.79 – 3.60 (m, 8H, GalNAc_H6^a, GalNAc_H6^b, Gal_H6^a, Gal_H6^b, NeuNAc_H4, NeuNAc_H9^b, Gal_H5, and NeuNAc_H6), 3.58 (dd, 1H, *J* = 8.9, 1.7 Hz, NeuNAc_H7), 3.53 (dd, 1H, *J* = 9.8, 7.9 Hz, Gal_H2), 3.38 (s, 3H, OCH_3), 2.75 (dd, 1H, *J* = 12.4, 4.6 Hz, NeuNAc_H3$_{eq}$), 2.02 (s, 3H, Ac), 2.01 (s, 3H, Ac), 1.77 (dd, 1H, *J* = 12.2, 12.2 Hz, NeuNAc_H3$_{ax}$). ^{13}C NMR (D_2O, 125 MHz): δC 175.64 (C=O), 175.26 (C=O), 174.55 (NeuNAc_C1), 105.12 (Gal_C1), 100.33 (NeuNAc_C2), 98.93 (GalNAc_C1), 78.07 (GalNAc_C3), 76.30 (Gal_C3), 75.41 (Gal_C5), 73.44 (NeuNAc_C6), 72.48 (NeuNAc_C8), 71.09 (GalNAc_C5), 69.68 (Gal_C2), 69.23 (GalNAc_C4), 69.02 (NeuNAc_C4), 68.72 (NeuNAc_C7), 68.00 (Gal_C4), 63.16 (NeuNAc_C9), 61.90 (GalNAc_C6), 61.60 (Gal_C6), 55.73 (OCH_3), 52.30 (NeuNAc_C5), 49.22 (GalNAc_C2), 40.39 (NeuNAc_C3), 22.71 (Ac), 22.68 (Ac). ESI-HRMS *m/z* calc'd for $C_{26}H_{43}N_2NaO_{19}$ $(M+Na)^+$: 733.2255; found: 733.2250. HPLC purity analysis: 98.2%, R_t 5.40 minutes, Atlantis T3 C18 column.



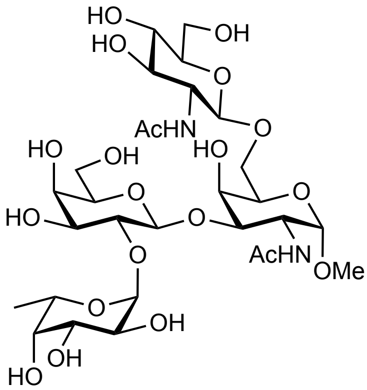
(a) AcOH, H_2O, 71%; (b) **12**, NIS, TfOH, CH_2Cl_2/ACN, 0 ˚C; (c) $NH_2NH_2{\cdot}H_2O$, EtOH, 80 ˚C; (d) Ac_2O, $NaHCO_3$, MeOH; (e) H_2, $Pd(OH)_2$, H_2O/MeOH, 63% (4 steps).

Methyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→2)-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-galactopyranosyl-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (26)

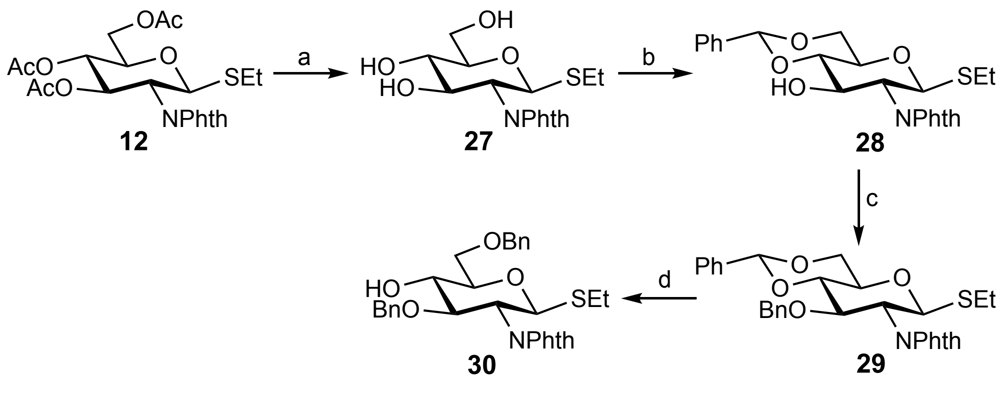


The starting material (**19**; 440 mg, 0.396 mmol) was dissolved into AcOH (3.2 mL) and H_2O (0.8 mL) and left mixing at ambient temperature. After 3 hours, the mixture was diluted with CH_2Cl_2 (50 mL) and sat'd $NaHCO_{3(aq)}$ solution (50 mL), and then solid $NaHCO_3$ added until gas evolution subsided. The aqueous layer was removed and re-extracted with CH_2Cl_2 (2 x 20 mL), and then the combined organic layers washed with sat'd $NaHCO_{3(aq)}$ solution (50 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→100% acetone – CH_2Cl_2 to afford the pure product as a white solid (280 mg, 0.282 mmol, 71% yield). R_f = 0.49 (1:1 acetone : CH_2Cl_2). $[\alpha]_D^{20}$: +20° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δH 7.53 – 7.50 (m, 2H, Ar), 7.38 – 7.20 (m, 20H, Ar), 7.19 – 7.14 (m, 3H, Ar), 6.95 (d, 1H, *J* = 7.6 Hz, NH), 5.45 (s, 1H, PhC*H*), 5.29 (d, 1H, *J* = 3.8 Hz, Fuc_H1), 5.00 (d, 1H, *J* = 11.3 Hz, PhC$H^a$$H^b$), 4.85 (d, 1H, *J* = 3.4 Hz, GalNAc_H1), 4.82 (d, 1H, *J* = 12.0 Hz, PhC$H^a$$H^b$), 4.78 (d, 1H, *J* = 12.2 Hz, PhC$H^a$$H^b$), 4.73 (d, 1H, *J* = 12.1 Hz, PhC$H^a$$H^b$), 4.72 – 4.67 (m, 2H, PhC$H^a$$H^b$ and PhC$H^a$$H^b$), 4.64 (d, 1H, *J* = 11.9 Hz, PhC$H^a$$H^b$), 4.60 (d, 1H, *J* = 11.4 Hz, PhC$H^a$$H^b$), 4.54 (d, 1H, *J* = 7.3 Hz, Gal_H1), 4.40 (ddd, 1H, *J* = 11.1, 7.7, 3.4 Hz, GalNAc_H2), 4.19 – 4.15 (m, 2H, Gal_H6^a and Fuc_H5), 4.13 – 4.10 (m, 3H, Gal_H2, Gal_H4, and GalNAc_H4), 4.00 (dd, 1H, *J* = 10.2, 3.8 Hz, Fuc_H2), 3.99 (dd, 1H, *J* = 12.4, 1.4 Hz, Gal_H6^b), 3.92 – 3.86 (m, 3H, Fuc_H3, GalNAc_H6^a, and GalNAc_H3), 3.79 – 3.73 (m, 3H, Fuc_H4, GalNAc_H5, and GalNAc_H6^b), 3.60 (dd, 1H, *J* = 9.5, 3.4 Hz, Gal_H3), 3.38 – 3.37 (m, 1H, Gal_H5), 3.28 (s, 3H, OCH_3), 3.26 – 3.25 (m, 1H, 4-OH), 2.87 – 2.84 (m, 1H, 6-OH), 1.80 (s, 3H, Ac), 1.24 (d, 3H, *J* = 6.5 Hz, Fuc_H6). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 170.45 (C=O), 139.10 (Ar), 139.05 (Ar), 138.75 (Ar), 138.48 (Ar), 137.77 (Ar), 129.18 (Ar), 128.44 (Ar), 128.36 (Ar), 128.26 (Ar), 128.12 (Ar), 127.93 (Ar), 127.63 (Ar), 127.60 (Ar), 127.58 (Ar), 127.54 (Ar), 127.50 (Ar), 127.35 (Ar), 126.47 (Ar), 103.24 (Gal_C1), 101.08 (Ph*C*H), 98.61, 98.53 (GalNAc_C1 and Fuc_C1), 78.89 (Fuc_C3), 78.51 (Gal_C3), 78.22 (Fuc_C4), 78.16 (Gal_C2), 77.07 (GalNAc_C3), 76.32 (Fuc_C2), 75.05 (Ph*C*H_2), 73.89 (Gal_C4), 73.15 (Ph*C*H_2), 72.94 (Ph*C*H_2), 72.25 (Ph*C*H_2), 69.34 (GalNAc_C5), 69.30 (Gal_C6), 69.20 (GalNAc_C4), 67.92 (Fuc_C5), 66.74 (Gal_C5), 63.03 (GalNAc_C6), 55.42 (OCH_3), 48.99 (GalNAc_C2), 23.06 (Ac), 16.78 (Fuc_C6). LRMS *m*/*z* calc'd for $C_{56}H_{65}NNaO_{15}$ $(M+Na)^+$: 1014.43; found: 1014.54.

Methyl α-L-fucopyranosyl-(1→2)-β-D-galactopyranosyl-(1→3)-[2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)]-2-acetamido-2-deoxy-α-D-galactopyranoside (5)

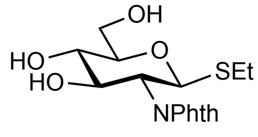


The glycosyl acceptor (**26**; 188 mg, 0.189 mmol), glycosyl donor [ref 6] (**12**; 118 mg, 0.246 mmol), and crushed molecular sieves (3 Å, 171 mg) in anhydrous CH_2Cl_2 (1.5 mL) and anhydrous acetonitrile (1.5 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to 0 °C, and then NIS was added (78 mg, 0.35 mmol) followed by the drop-wise addition of TfOH (10 µL, 0.02 mmol). After 2 hours, the mixture was neutralized with Et_3N (to pH 8), warmed to ambient temperature, and diluted with CH_2Cl_2 (60 mL). The organic phase was washed with saturated $Na_2S_2O_{3(aq)}$ solution (60 mL), saturated $NaCl_{(aq)}$ solution (60 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→40% acetone (containing 0.1% *v*/*v* $NH_4OH_{(aq)}$) – CH_2Cl_2 to afford a mostly pure product (containing a small amount of a lower R_f by-product): R_f = 0.75 (0.01:19.99:80 NH_4OH : acetone : CH_2Cl_2). LRMS *m*/*z* calc'd for $C_{76}H_{84}N_2NaO_{24}$ $(M+Na)^+$: 1431.53; found: 1431.54. The product and $NH_2NH_2{\cdot}H_2O$ (112 µL, 2.34 mmol) were then added to EtOH (4.0 mL) and left mixing at 80 °C. After 20 hours, the mixture was evaporated to dry, redissolved into MeOH (4.0 mL), and then $NaHCO_3$ (788 mg, 9.38 mmol) and Ac_2O added (0.44 mL, 4.7 mmol). After another 4 hours, the solution was evaporated to dry and the crude mixture purified via MPLC on silica gel using 0→30% MeOH – CH_2Cl_2 to afford the partially deprotected product: R_f = 0.07 (3:7 acetone : CH_2Cl_2). LRMS *m*/*z* calc'd for $C_{57}H_{72}N_2NaO_{20}$ $(M+Na)^+$: 1127.46; found: 1127.28. The starting material and $Pd(OH)_2$ (20% *w*/*w* on carbon; 40 mg) were added to 50% aqueous MeOH (2.0 mL), the atmosphere evacuated, and the flask flushed with $H_{2(g)}$ (via balloon). After 24 hours, the catalyst was removed via filtration, the mixture evaporated to dry, and the crude material purified via RPLC on C-18 silica gel using 0→60% acetonitrile – H_2O to afford the pure product as a white solid (92 mg, 0.12 mmol, 63% yield over 4 steps). $[\alpha]_D^{20}$: +5.4° (*c* 0.5, H_2O). ^1H NMR (D_2O, 500 MHz): δH 5.21 (d, 1H, *J* = 4.0 Hz, Fuc_H1), 4.73 (d, 1H, *J* = 3.4 Hz, GalN_H1), 4.61 (d, 1H, J = 7.7 Hz, Gal_H1), 4.53 (d, 1H, J = 8.5 Hz, GlcN_H1), 4.20 (dq, 1H, J = 6.6, <1 Hz, Fuc_H5), 4.16 (dd, 1H, J = 11.0, 3.4 Hz, GalN_H2), 4.14 (dd, 1H, J = 2.8, <1 Hz, GalN_H4), 4.11 (dd, 1H, J = 11.1, 2.9 Hz, GalN_H3), 4.08 – 4.03 (m, 2H, GalN_H6[a] and GalN_H5), 3.93 (dd, 1H, J = 12.5, 1.6 Hz, GlcN_H6[a]), 3.88 (dd, 1H, J = 3.4, <1 Hz, Gal_H4), 3.82 (dd, 1H, J = 9.7, 3.4 Hz, Gal_H3), 3.78 – 3.71 (m, 5H, Fuc_H2, Gal_H6[a], GlcN_H6[b], Gal_H6[b], and GalN_H6[b]), 3.71 (dd, 1H, J = 10.2, 8.5 Hz, GlcN_H2), 3.67 – 3.61 (m, 3H, Fuc_H4, Fuc_H3, and Gal_H5), 3.61 (dd, 1H, J = 9.6, 7.8 Hz, Gal_H2), 3.53 (dd, 1H, J = 10.3, 8.2 Hz, GlcN_H3), 3.48 – 3.41 (m, 2H, GlcN_H5 and GlcN_H4), 3.32 (s, 3H, OCH_3), 2.03 (s, 3H, Ac), 2.00 (s, 3H, Ac), 1.18 (d, 3H, J = 6.6 Hz, Fuc_H6). ^{13}C NMR (D_2O, 125 MHz): δC 175.11 (C=O), 174.31 (C=O), 102.60 (Gal_C1), 102.29 (GlcN_C1), 99.93 (Fuc_C1), 98.37 (GalN_C1), 76.94 (Gal_C2), 76.49 (GlcN_C5), 75.67 (Gal_C5), 74.45 (GlcN_C3), 74.21 (GalN_C3 and Gal_C3), 72.50 (Fuc_C4), 70.82 (GalN_C6), 70.58 (GlcN_C4), 70.20 (Fuc_C3), 69.98, 69.93 (GalN_C4 and GalN_C5), 69.72 (Gal_C4), 68.72 (Fuc_C2), 67.43 (Fuc_C5), 61.57 (Gal_C6), 61.35 (GlcN_C6), 56.15 (GlcN_C2), 55.48 (OCH_3), 49.97 (GalN_C2), 22.81 (Ac), 22.58 (Ac), 15.99 (Fuc_C6). ESI-HRMS *m*/*z* calc'd for $C_{29}H_{50}N_2NaO_{20}$ $(M+Na)^+$: 769.2855; found: 769.2853. HPLC purity analysis: >99.5%, R_t 5.49 minutes, Atlantis T3 C18 column.



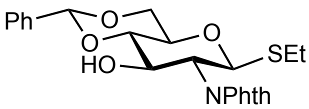
(a) NaOMe, MeOH, 97%; (b) $PhCH(OMe)_2$, camphorsulfonic acid, DMF, 80%; (c) NaH, BnBr, DMF, 72%; (g) Et_3SiH, $BF_3{\cdot}Et_2O$, CH_2Cl_2, 89%.

Ethyl 2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (27)



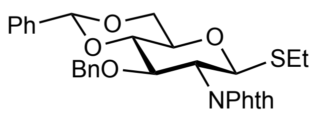
The starting material (**12**; 6.98 g, 14.6 mmol) was dissolved into anhydrous MeOH (50 mL) and anhydrous CH_2Cl_2 (20 mL), and then NaOMe solution was added drop-wise (1.5 M NaOMe in MeOH; to pH 10). After 4 hours at ambient temperature, the reaction mixture was neutralized with acidic resin (Amberlite IR-120H; to pH 6), filtered, and then evaporated to dry to afford the pure product as a white solid (4.97 g, 14.1 mmol, 97% yield). R_f = 0.21 (2:3 acetone : toluene). $[\alpha]_D^{20}$: +8.8° (*c* 1.0, CH_3OH). ^{1}H NMR (CD_3OD, 500 MHz): δH 7.90 – 7.81 (m, 4H, Ar), 5.32 (d, 1H, *J* = 10.5 Hz, H-1), 4.27 (dd, 1H, *J* = 10.2, 8.4 Hz, H-3), 4.05 (dd, 1H, *J* = 10.3, 10.3 Hz, H-2), 3.92 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6^a), 3.73 (dd, 1H, *J* = 12.0, 5.6 Hz, H-6^b), 3.45 (ddd, 1H, *J* = 9.8, 5.5, 2.0 Hz, H-5), 3.40 (dd, 1H, *J* = 9.8, 8.4 Hz, H-4), 2.73 (dq, 1H, *J* = 12.7, 7.4 Hz, $SCH^aH^bCH_3$), 2.63 (dq, 1H, *J* = 12.7, 7.5 Hz, $CH^aH^bCH_3$), 1.17 (dd, 3H, *J* = 7.4, 7.4 Hz, SCH_2CH_3). ^{13}C NMR (CD_3OD, 125 MHz): δC 169.86 (C=O), 169.58 (C=O), 135.77 (Ar), 135.69 (Ar), 133.36 (Ar), 133.09 (Ar), 124.57 (Ar), 124.24 (Ar), 82.73 (C-5), 82.62 (C-1), 73.87 (C-3), 72.61 (C-4), 63.09 (C-6), 57.88 (C-2), 25.00 (SCH_2CH_3), 15.44 (SCH_2CH_3). LRMS *m*/*z* calc'd for $C_{16}H_{19}NNaO_6S$ $(M+Na)^+$: 376.08; found: 376.01.

Ethyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (28)



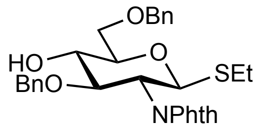
The starting material (**27**; 4.974 g, 14.08 mmol), benzylidene dimethyl acetal (2.6 mL, 17 mmol), and camphorsulfonic acid (to pH 3) were added to anhydrous DMF (40 mL) under Ar. After 16 hours of mixing at ambient temperature, the reaction mixture was neutralized with Et_3N (to pH 8), evaporated to dry, and then purified via MPLC on silica gel using 0→70% acetone – toluene to afford the desired product as a white solid (4.977 g, 11.27 mmol, 80% yield). R_f = 0.56 (1:4 acetone : toluene). $[\alpha]_D^{20}$: –4.2° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δH 7.83 – 7.79 (m, 2H, Ar), 7.69 – 7.64 (m, 2H, Ar), 7.50 – 7.46 (m, 2H, Ar), 7.36 – 7.32 (m, 3H, Ar), 5.54 (s, 1H, PhC*H*), 5.36 (d, 1H, *J* = 10.6 Hz, H-1), 4.60 (ddd, 1H, *J* = 9.6, 9.6, 3.8 Hz, H-3), 4.35 (dd, 1H, *J* = 10.4, 4.9 Hz, H-6^a), 4.27 (dd, 1H, *J* = 10.3, 10.3 Hz, H-2), 3.76 (dd, 1H, *J* = 10.2, 10.2 Hz, H-6^b), 3.62 (ddd, 1H, *J* = 9.6, 9.6, 4.9 Hz, H-5), 3.54 (dd, 1H, *J* = 9.2, 9.2 Hz, H-4), 3.05 (d, 1H, *J* = 3.8 Hz, 3-OH), 2.68 (dq, 1H, *J* = 12.5, 7.4 Hz, $SCH^aH^bCH_3$), 2.63 (dq, 1H, *J* = 12.5, 7.4 Hz, $SCH^aH^bCH_3$), 1.17 (dd, 3H, *J* = 7.4, 7.4 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 168.35 (C=O), 167.82 (C=O), 137.10 (Ar), 134.29 (Ar), 131.74 (Ar), 131.60 (Ar), 129.41 (Ar), 128.43 (Ar), 126.44 (Ar), 123.93 (Ar), 123.41 (Ar), 101.93 (Ph*C*H), 82.14 (C-4), 81.94 (C-1), 70.46 (C-5), 69.53 (C-3), 68.67 (C-6), 55.69 (C-2), 24.27 (S*C*H_2CH_3), 14.98 (SCH_2*C*H_3). LRMS *m/z* calc'd for $C_{23}H_{23}NNaO_6S$ $(M+Na)^+$: 464.11; found: 464.11.

Ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (29)

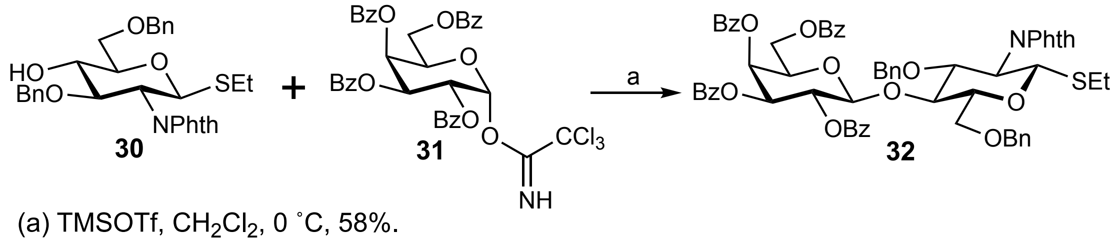


The starting material (**28**; 3.001 g, 6.797 mmol) and benzyl bromide (1.1 mL, 9.3 mmol) were added to anhydrous DMF (30 mL), and then NaH added portion-wise (60% oil dispersion; 385 mg, 9.62 mmol). After 1 hour, the reaction was quenched via the drop-wise addition of H_2O and the mixture diluted with EtOAc (200 mL) and saturated $NaCl_{(aq)}$ solution (500 mL). The aqueous layer was removed and then re-extracted with EtOAc (200 mL). The combined organic phases were washed with sat'd $NaCl_{(aq)}$ solution (2 x 500 mL), dried with Na_2SO_4, filtered, and then evaporated to dry. The crude material was purified via MPLC using 0→10% EtOAc – toluene to afford the pure product as a white solid (2.604 g, 4.899 mmol, 72% yield). R_f = 0.71 (1:4 EtOAc : toluene). $[\alpha]_D^{20}$: +54° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δH 7.85 – 7.82 (m, 1H, Ar), 7.73 – 7.63 (m, 3H, Ar), 7.54 – 7.51 (m, 2H, Ar), 7.42 – 7.35 (m, 3H, Ar), 7.01 – 6.98 (m, 2H, Ar), 6.94 – 6.86 (m, 3H, Ar), 5.63 (s, 1H, PhC*H*), 5.35 (d, 1H, *J* = 10.6 Hz, H-1), 4.80 (d, 1H, *J* = 12.3 Hz, $PhCH^aH^b$), 4.51 (d, 1H, *J* = 12.3 Hz, $PhCH^aH^b$), 4.46 (dd, 1H, *J* = 9.9, 9.0 Hz, H-3), 4.41 (dd, 1H, *J* = 10.4, 4.9 Hz, $H\text{-}6^a$), 4.30 (dd, 1H, *J* = 10.5, 10.0 Hz, H-2), 3.83 (dd, 1H, *J* = 10.2, 10.2 Hz, $H\text{-}6^b$), 3.82 (dd, 1H, *J* = 9.2, 9.2 Hz, H-4), 3.70 (ddd, 1H, *J* = 9.6, 9.6, 4.9 Hz, H-5), 2.68 (dq, 1H, *J* = 12.5, 7.4 Hz, $SCH^aH^bCH_3$), 2.62 (dq, 1H, *J* = 12.5, 7.4 Hz, $SCH^aH^bCH_3$), 1.16 (dd, 3H, *J* = 7.4, 7.4 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 167.90 (C=O), 167.58 (C=O), 137.99 (Ar), 137.49 (Ar), 134.13 (Ar), 134.01 (Ar), 131.80 (Ar), 131.74 (Ar), 129.20 (Ar), 128.46 (Ar), 128.27 (Ar), 128.21 (Ar), 127.59 (Ar), 126.23 (Ar), 123.72 (Ar), 123.49 (Ar), 101.48 (Ph*C*H), 83.22 (C-4), 81.96 (C-1), 75.60 (C-3), 74.37 (Ph*C*H_2), 70.63 (C-5), 68.90 (C-6), 54.85 (C-2), 24.24 (S*C*H_2CH_3), 15.03 (SCH_2*C*H_3). LRMS *m/z* calc'd for $C_{30}H_{29}NNaO_6S$ $(M+Na)^+$: 554.16; found: 554.09.

Ethyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (30)

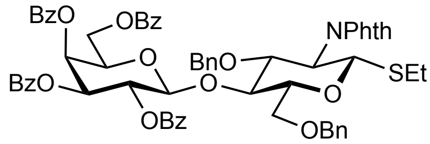


A solution of the starting material (**29**; 2.726 g, 5.128 mmol) in anhydrous CH_2Cl_2 (25 mL) was cooled to 0 °C under Ar, and then Et_3SiH (4.1 mL, 26 mmol) and $BF_3{\cdot}Et_2O$ (1.3 mL, 10 mmol) were slowly added. After 5 hours, the reaction mixture was neutralized with Et_3N (to pH 8), warmed back to ambient temperature, and then quenched via the slow addition of MeOH (10 mL). The crude mixture was evaporated to dry, and then purified via MPLC on silica gel using 0→30% EtOAc – toluene to afford the pure product as a white solid (2.430 g, 4.554 mmol, 89% yield). R_f = 0.43 (1:4 EtOAc : toluene). $[\alpha]_D^{20}$: +38° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δH 7.82 – 7.80 (m, 1H, Ar), 7.72 – 7.66 (m, 3H, Ar), 7.38 – 7.29 (m, 5H, Ar), 7.06 – 7.02 (m, 2H, Ar), 6.98 – 6.92 (m, 3H, Ar), 5.27 (d, 1H, *J* = 10.0 Hz, H-1), 4.75 (d, 1H, *J* = 12.2 Hz, PhCH^aH^b), 4.63 (d, 1H, *J* = 11.9 Hz, PhCH^aH^b), 4.58 (d, 1H, *J* = 11.9 Hz, PhCH^aH^b), 4.54 (d, 1H, *J* = 12.2 Hz, PhCH^aH^b), 4.28 (dd, 1H, *J* = 10.2, 7.9 Hz, H-3), 4.23 (dd, 1H, *J* = 10.1, 10.1 Hz, H-2), 3.85 (dd, 1H, *J* = 10.1, 4.8 Hz, H-6^a), 3.85 – 3.81 (m, 1H, H-4), 3.77 (dd, 1H, *J* = 10.1, 5.2 Hz, H-6^b), 3.68 (ddd, 1H, *J* = 9.6, 5.0, 5.0 Hz, H-5), 2.97 (d, 1H, *J* = 2.5 Hz, 4-OH), 2.66 (dq, 1H, *J* = 12.5, 7.4 Hz, SCH^aH^{b}CH$_3$), 2.59 (dq, 1H, *J* = 12.5, 7.4 Hz, SCH^aH^bCH$_3$), 1.16 (dd, 3H, *J* = 7.4, 7.4 Hz, SCH$_2$CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 168.28 (C=O), 167.72 (C=O), 138.33 (Ar), 137.79 (Ar), 134.12 (Ar), 134.02 (Ar), 131.86 (Ar), 128.72 (Ar), 128.36 (Ar), 128.12 (Ar), 128.10 (Ar), 128.02 (Ar), 127.65 (Ar), 123.74 (Ar), 123.48 (Ar), 81.38 (C-1), 79.78 (C-3), 77.77 (C-5), 74.77 (C-4), 74.67 (Ph*C*H$_2$), 74.00 (Ph*C*H$_2$), 71.13 (C-6), 54.60 (C-2), 24.17 (S*C*H$_2$CH$_3$), 15.11 (SCH$_2$*C*H$_3$). LRMS *m*/*z* calc'd for $C_{30}H_{31}NNaO_6S$ $(M+Na)^+$: 556.18; found: 556.11.



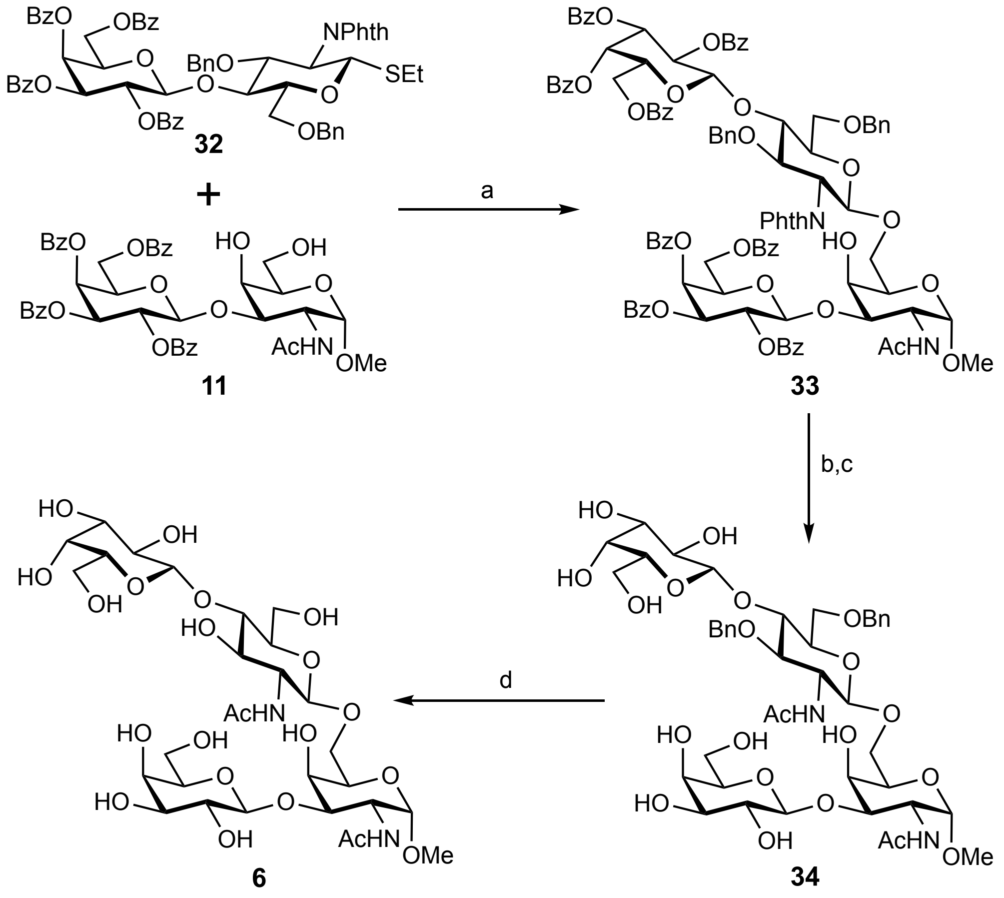
(a) TMSOTf, CH_2Cl_2, 0 ˚C, 58%.

Ethyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (32)



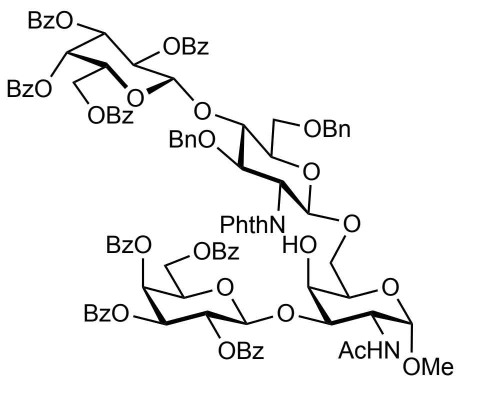
The glycosyl acceptor (**30**; 621 mg, 1.16 mmol), glycosyl donor [ref 7] (**31**; 1.715 g, 2.315 mmol), and crushed molecular sieves (3 Å, 1.006 mg) in anhydrous CH_2Cl_2 (25 mL) were left mixing at ambient temperature under Ar. After 1 hour, the reaction flask was cooled to 0 °C, and then trimethylsilyl triflate (32 μL, 0.18 mmol) was added dropwise. The flask was slowly warmed to rt, and after 6 hours was neutralized with Et_3N (to pH 8), filtered over Celite, and diluted with CH_2Cl_2 (250 mL). The organic phase was washed with saturated $NaHCO_{3(aq)}$ solution (250 mL), saturated $NaCl_{(aq)}$ solution (250 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→10% EtOAc – toluene to afford the pure product as a white solid (747 mg, 0.672 mmol, 58% yield). R_f = 0.58 (1:4 EtOAc : toluene). $[\alpha]_D^{20}$: +51° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δH 8.06 – 8.03 (m, 2H, Ar), 7.95 – 7.91 (m, 4H, Ar), 7.81 – 7.76 (m, 4H, Ar), 7.70 – 7.34 (m, 15H, Ar), 7.32 – 7.28 (m, 2H, Ar), 7.25 – 7.21 (m, 2H, Ar), 7.10 – 7.06 (m, 2H, Ar), 6.85 – 6.82 (m, 3H, Ar), 5.88 (dd, 1H, *J* = 3.4, <1 Hz, Gal_H4), 5.79 (dd, 1H, *J* = 10.4, 8.0 Hz, Gal_H2), 5.43 (dd, 1H, *J* = 10.4, 3.5 Hz, Gal_H3), 5.16 (d, 1H, *J* = 10.5 Hz, GlcN_H1), 5.02 (d, 1H, *J* = 12.2 Hz, $PhCH^aH^b$), 4.97 (d, 1H, *J* = 8.0 Hz, Gal_H1), 4.76 (d, 1H, *J* = 12.1 Hz, $PhCH^aH^b$), 4.69 (d, 1H, *J* = 12.3 Hz, $PhCH^aH^b$), 4.41 (d, 1H, *J* = 12.2 Hz, $PhCH^aH^b$), 4.40 (dd, 1H, *J* = 11.3, 6.7 Hz, Gal_H6^a), 4.37 (dd, 1H, *J* = 10.2, 8.6 Hz, GlcN_H3), 4.30 (dd, 1H, *J* = 11.3, 6.9 Hz, Gal_H6^b), 4.26 (dd, 1H, *J* = 10.4, 10.4 Hz, GlcN_H2), 4.24 (dd, 1H, *J* = 9.8, 8.7 Hz, GlcN_H4), 4.03 (ddd, 1H, *J* = 6.8, 6.8, <1 Hz, Gal_H5), 3.73 (dd, 1H, *J* = 11.2, 3.1 Hz, GlcN_H6^a), 3.60 (dd, 1H, *J* = 11.2, 1.4 Hz, GlcN_H6^b), 3.43 (ddd, 1H, *J* = 9.9, 2.8, 1.4 Hz, GlcN_H5), 2.63 (dq, 1H, *J* = 12.5, 7.4 Hz, $SCH^aH^bCH_3$), 2.55 (dq, 1H, *J* = 12.5, 7.5 Hz, $SCH^aH^bCH_3$), 1.14 (dd, 3H, *J* = 7.4, 7.4 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 168.12 (C=O), 167.65 (C=O), 166.20 (C=O), 165.67 (C=O), 165.53 (C=O), 165.23 (C=O), 138.74 (Ar), 138.27 (Ar), 134.02 (Ar), 133.88 (Ar), 133.64 (Ar), 133.45 (Ar), 131.87 (Ar), 129.71 (Ar), 129.28 (Ar), 129.27 (Ar), 129.01 (Ar), 128.89 (Ar), 128.76 (Ar), 128.74 (Ar), 128.48 (Ar), 128.38 (Ar), 128.30 (Ar), 128.11 (Ar), 128.01 (Ar), 127.28 (Ar), 123.67 (Ar), 123.44 (Ar), 100.64 (Gal_C1), 81.28 (GlcN_C1), 79.02 (GlcN_C5), 77.96 (GlcN_C4), 77.72 (GlcN_C3), 74.76 ($PhCH_2$), 73.74 ($PhCH_2$), 71.96 (Gal_C3), 71.27 (Gal_C5), 70.55 (Gal_C2), 68.24 (Gal_C4), 67.91

(GlcN_C6), 61.78 (Gal_C6), 54.95 (GlcN_C2), 24.09 (S*C*$H_2$$CH_3$), 15.09 ($SCH_2$*C*$H_3$). LRMS *m*/*z* calc'd for $C_{64}H_{57}NNaO_{15}S$ $(M+Na)^+$: 1134.33; found: 1134.27.



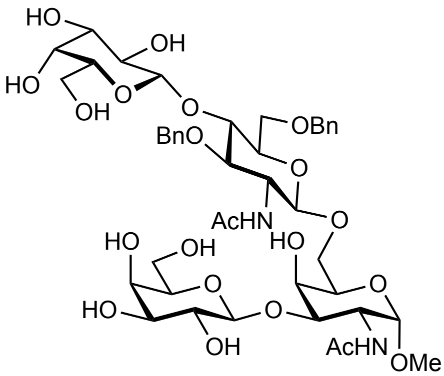
(a) NIS, TfOH, CH_2Cl_2/CH_3CN, 0 ˚C, 74%; (b) $NH_2NH_2{\cdot}H_2O$, EtOH; (c) Ac_2O, MeOH, 72% (2 steps); (d) H_2, $Pd(OH)_2$, H_2O, 93%.

Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-[2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl-(1→3)]-2-acetamido-2-deoxy-α-D-galactopyranoside (33)



The glycosyl acceptor (**11**; 132 mg, 0.162 mmol), glycosyl donor (**32**; 203 mg, 0.183 mmol), and crushed molecular sieves (3 Å, 273 mg) in anhydrous CH_2Cl_2 (2.0 mL) and anhydrous acetonitrile (2.0 mL) were left mixing for 1 hour at ambient temperature under Ar. The reaction flask was cooled to 0 °C, and then *N*-iodosuccinimide was added (67 mg, 0.30 mmol) followed by the drop-wise addition of triflic acid (3 µL, 0.017 mmol; in 20 µL CH_2Cl_2). After 6 hours, the mixture was neutralized with Et_3N (to pH 8), warmed to ambient temperature, filtered over Celite, and diluted further with CH_2Cl_2 (60 mL). The organic phase was washed with sat'd $Na_2S_2O_{3(aq)}$ solution (60 mL), sat'd $NaCl_{(aq)}$ solution (2 x 60 mL), dried with Na_2SO_4, filtered, and evaporated to dry. The crude material was purified via MPLC on silica gel using 0→30% acetone (w/ 0.1% NH_4OH) – CH_2Cl_2 to afford the pure product as a white solid (224 mg, 0.120 mmol, 74% yield). R_f = 0.21 (1:9 acetone w/ 0.1% NH_4OH : CH_2Cl_2). $[\alpha]_D^{20}$: +110° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δH 8.08 – 8.03 (m, 4H, Ar), 7.96 – 7.89 (m, 8H, Ar), 7.79 – 7.76 (m, 2H, Ar), 7.74 – 7.72 (m, 2H, Ar), 7.68 – 7.64 (m, 2H, Ar), 7.64 – 7.60 (m, 1H, Ar), 7.58 – 7.54 (m, 2H, Ar), 7.53 – 7.30 (m, 24H, Ar), 7.26 – 7.20 (m, 4H, Ar), 7.10 – 7.06 (m, 2H, Ar), 6.84 – 6.81 (m, 3H, Ar), 5.92 (dd, 1H, *J* = 3.5, <1 Hz, Gal_H4'), 5.87 (dd, 1H, *J* = 3.5, <1 Hz, Gal_H4), 5.78 (dd, 1H, *J* = 10.4, 8.0 Hz, Gal_H2), 5.75 (dd, 1H, *J* = 10.4, 8.0 Hz, Gal_H2'), 5.53 (dd, 1H, *J* = 10.4, 3.5 Hz, Gal_H3'), 5.41 (dd, 1H, *J* = 10.4, 3.5 Hz, Gal_H3), 5.04 – 5.00 (m, 2H, NH and PhCH^aH^b), 4.99 (d, 1H, *J* = 8.5 Hz, GlcN_H1), 4.90 (d, 1H, *J* = 8.0 Hz, Gal_H1), 4.79 – 4.76 (m, 2H, Gal_H1' and PhCH^aH^b), 4.68 (d, 1H, *J* = 12.3 Hz, PhCH^aH^b), 4.51 (dd, 1H, *J* = 11.7, 5.0 Hz, Gal_H6^{a}'), 4.45 (dd, 1H, *J* = 11.7, 7.7 Hz, Gal_H6^{b}'), 4.39 (dd, 1H, *J* = 11.2, 6.7 Hz, Gal_H6^a), 4.38 (d, 1H, *J* = 12.2 Hz, PhCH^aH^b), 4.37 (dd, 1H, *J* = 10.7, 8.9 Hz, GlcN_H3), 4.34 – 4.28 (m, 2H, GalNAc_H2 and Gal_H6^b), 4.26 – 4.22 (m, 2H, Gal_H5' and GlcN_H4), 4.21 (d, 1H, *J* = 3.6 Hz, GalNAc_H1), 4.15 (dd, 1H, *J* = 10.8, 8.5 Hz, GlcN_H2), 4.02 (ddd, 1H, *J* = 6.8, 6.8, <1 Hz, Gal_H5), 3.91 – 3.89 (m, 1H, GalNAc_H4), 3.75 (dd, 1H, *J* = 10.8, 2.8 Hz, GlcN_H6^a), 3.71 – 3.69 (m, 1H, GalNAc_H6^a), 3.59 – 3.49 (m, 4H, GalNAc_H3, GalNAc_H5, GalNAc_H6^b, and GlcN_H6^b), 3.38 – 3.35 (m, 1H, GlcN_H5), 2.77 – 2.74 (m, 4H, OCH_3 and GalNAc_4-OH), 1.28 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 125 MHz): δC 169.85 (C=O, Ac), 167.98 (C=O, Phth), 167.75 (C=O, Phth), 166.22 (C=O, Bz), 166.20 (C=O, Bz), 165.78 (C=O, Bz), 165.73 (C=O, Bz), 165.67 (C=O, Bz), 165.52 (C=O, Bz), 165.18 (C=O, Bz), 164.82 (C=O, Bz), 138.84 (Ar), 138.11 (Ar), 133.98 (Ar), 133.88 (Ar), 133.70 (Ar), 133.66 (Ar), 133.59 (Ar), 133.45 (Ar), 131.95 (Ar), 130.27 (Ar), 130.05 (Ar), 129.95 (Ar), 129.90 (Ar), 129.71 (Ar), 129.28 (Ar), 129.26 (Ar), 129.01 (Ar), 128.97 (Ar), 128.92 (Ar), 128.87 (Ar), 128.85 (Ar), 128.78 (Ar), 128.76 (Ar), 128.73 (Ar), 128.71 (Ar), 128.58 (Ar), 128.52 (Ar), 128.49 (Ar), 128.43 (Ar), 127.25 (Ar), 123.50 (Ar), 123.21 (Ar), 101.92 (Gal_C1'), 100.68 (Gal_C1), 99.16 (GlcN_C1), 98.13 (GalNAc_C1), 80.07 (GalNAc_C3), 78.06 (GlcN_C4), 76.67 (GlcN_C3), 74.64 (Ph*C*H_2), 74.56 (GlcN_C5), 73.85 (Ph*C*H_2), 72.14 (Gal_C5'), 71.88 (Gal_C3), 71.60 (Gal_C3'), 71.23 (Gal_C5), 70.50 (Gal_C2), 70.29 (GalNAc_C6), 69.77 (Gal_C2'), 68.44 (GalNAc_C5), 68.21 (Gal_C4), 68.14 (Gal_C4' and GalNAc_C4), 67.73 (GlcN_C6), 62.52 (Gal_C6'), 61.78 (Gal_C6), 55.96 (GlcN_C2), 54.45 (OCH_3), 47.86 (GalNAc_C2), 22.62 (Ac). LRMS *m*/*z* calc'd for $C_{105}H_{94}N_2NaO_{30}$ $(M+Na)^+$: 1886.58; found: 1886.29.

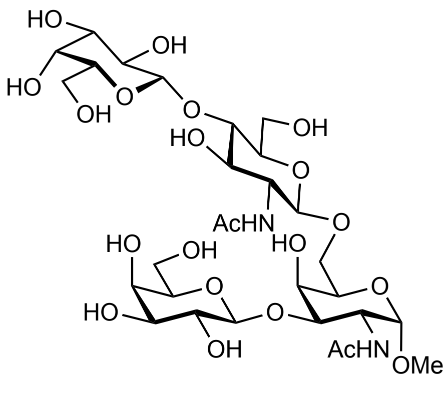
Methyl β-D-galactopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl-(1→6)-[β-D-galactopyranosyl-(1→3)]-2-acetamido-2-deoxy-α-D-galactopyranoside (34)



The starting material (**33**; 124 mg, 0.0665 mmol) and $NH_2NH_2 \cdot H_2O$ (48 μL, 1.0 mmol) in EtOH (1.5 mL) were left heating at 80 ºC. After 24 hours, additional $NH_2NH_2 \cdot H_2O$ was added (16 μL, 0.33 mmol), and after another 24 hours the mixture was evaporated to dry to afford the crude product: LRMS *m*/*z* calc'd for $C_{41}H_{61}N_2O_{20}$ $(M+H)^+$: 901.38; found: 901.44. The mixture was redissolved into MeOH (2.0 mL) and Ac_2O added (157 μL, 1.66 mmol), and after 4 hours the mixture was evaporated to dry and purified via RPLC on C-18 silica gel using 0→100% acetonitrile – H_2O to afford the pure product as a white solid (45 mg, 0.048 mmol, 72% yield over 2 steps) $[\alpha]_D^{20}$: +35° (*c* 1.0, H_2O). ^1H NMR (D_2O, 500 MHz): δH 7.49 – 7.35 (m, 10H, Ar), 4.91 (d, 1H, *J* = 11.4 Hz, PhCH^aH^b), 4.73 (d, 1H, *J* = 4.0 Hz, GalNAc_H1), 4.72 (d, 1H, *J* = 11.8 Hz, PhCH^aH^b), 4.64 (d, 1H, *J* = 11.4 Hz, PhCH^aH^b), 4.55 (d, 1H, *J* = 11.9 Hz, PhCH^aH^b), 4.50 (d, 1H, *J* = 8.4 Hz, GlcNAc_H1), 4.42 (d, 1H, *J* = 7.8 Hz, Gal_H1'), 4.30 (dd, 1H, *J* = 11.0, 3.7 Hz, GalNAc_H2), 4.20 – 4.17 (m, 2H, Gal_H1 and GalNAc_H4), 4.03 – 4.00

(m, 2H, GalNAc_H5 and GalNAc_H6[a]), 3.97 – 3.91 (m, 4H, GalNAc_H3, GlcNAc_H6[a], GlcNAc_H6[b], and GlcNAc_H4), 3.89 (dd, 1H, J = 3.4, <1 Hz, Gal_H4'), 3.84 (dd, 1H, J = 3.5, <1 Hz, Gal_H4), 3.77 (dd, 1H, J = 10.5, 8.5 Hz, GlcNAc_H2), 3.76 – 3.58 (m, 9H, Gal_H6[a]', Gal_H6[b]', GalNAc_H6[b], Gal_H6[a], GlcNAc_H3, GlcNAc_H5, Gal_H6[b], Gal_H5', and Gal_H3'), 3.51 (dd, 1H, J = 7.8, 7.8 Hz, Gal_H2), 3.50 (dd, 1H, J = 7.8, 7.8 Hz, Gal_H2'), 3.39 – 3.35 (m, 2H, Gal_H3 and Gal_H5), 3.31 (s, 3H, OCH_3), 2.00 (s, 3H, Ac), 1.83 (s, 3H, Ac). ^{13}C NMR (D_2O, 125 MHz): δC 175.23 (C=O), 174.53 (C=O), 138.23 (Ar), 137.92 (Ar), 129.50 (Ar), 129.39 (Ar), 129.29 (Ar), 129.23 (Ar), 129.03 (Ar), 128.89 (Ar), 105.33 (Gal_C1'), 103.17 (Gal_C1), 102.25 (GlcNAc_C1), 98.77 (GalNAc_C1), 80.56 (GlcNAc_C3), 77.79 (GalNAc_C3), 76.57 (GlcNAc_C4), 75.96 (Gal_C5), 75.58 (Gal_C5'), 75.14 (Ph*C*H_2), 74.58 (GlcNAc_C5), 73.62 (Ph*C*H_2), 73.16 (Gal_C3'), 73.08 (Gal_C3), 71.71 (Gal_C2), 71.24 (Gal_C2'), 70.92 (GalNAc_C6), 69.92 (GalNAc_C5), 69.61 (GalNAc_C4), 69.31 (Gal_C4), 69.18 (Gal_C4'), 68.23 (GlcNAc_C6), 61.84 (Gal_C6), 61.55 (Gal_C6'), 55.45 (OCH_3), 54.98 (GlcNAc_C2), 49.14 (GalNAc_C2), 22.78 (Ac), 22.64 (Ac). LRMS *m*/*z* calc'd for $C_{43}H_{62}N_2NaO_{21}$ $(M+Na)^+$: 965.37; found: 965.40.

Methyl β-D-galactopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→6)-[β-D-galactopyranosyl-(1→3)]-2-acetamido-2-deoxy-α-D-galactopyranoside (6)



The starting material (**34**; 36 mg, 0.038 mmol) and $Pd(OH)_2$ (20% *w*/*w* on carbon, 9 mg) in H_2O (1.5 mL) were left mixing under H_2 at atmospheric pressure. After 24 hours, the solid catalyst was removed via filtration and the solution evaporated to dry. The crude material was purified via RPLC on C-18 silica gel using 0→60% acetonitrile – H_2O to afford the pure product as a white solid (27 mg, 0.035 mmol, 93% yield). $[\alpha]_D^{20}$: +29° (*c* 0.7, H_2O). ^{1}H NMR (D_2O, 500 MHz): δH 4.74 (d, 1H, J = 3.8 Hz, GalNAc_H1), 4.54 (d, 1H, J = 8.2 Hz, GlcNAc_H1), 4.46 (d, 1H, J = 7.8 Hz, Gal_H1), 4.43 (d, 1H, J = 7.8 Hz, Gal_H1'), 4.31 (dd, 1H, J = 11.0, 3.7 Hz, GalNAc_H2), 4.19 (dd, 1H, J = 3.2, <1 Hz, GalNAc_H4), 4.07 – 3.97 (m, 4H, GalNAc_H6^a, GalNAc_H5, GalNAc_H3, and GlcNAc_H6^a), 3.91 (dd, 1H, J = 3.4, <1 Hz, Gal_H4), 3.89 (dd, 1H, J = 3.4, <1 Hz, Gal_H4'), 3.83 (dd, 1H, J = 12.3, 5.1 Hz, GlcNAc_H6^b), 3.79 – 3.69 (m, 9H, GlcNAc_H2, Gal_H6^a, Gal_H6^{a}', Gal_H6^b, Gal_H6^{b}', GalNAc_H6^b, Gal_H5, GlcNAc_H4, and GlcNAc_H3), 3.65 (dd, 1H, J = 10.0, 3.4 Hz, Gal_H3), 3.65 – 3.58 (m, 3H, Gal_H5', Gal_H3', and GlcNAc_H5), 3.53 (dd, 1H, J = 9.9, 7.8 Hz, Gal_H2), 3.49 (dd, 1H, J = 9.9, 7.8 Hz, Gal_H2'), 3.34 (s, 3H, OCH_3), 2.00 (s, 3H, Ac), 2.00 (s, 3H, Ac). ^{13}C NMR (D_2O, 125 MHz): δC 175.25 (C=O), 175.05 (C=O), 105.35 (Gal_C1'), 103.55 (Gal_C1), 102.17 (GlcNAc_C1), 98.83 (GalNAc_C1), 79.15 (GlcNAc_C4), 77.72 (GalNAc_C3), 76.01 (Gal_C5), 75.62 (Gal_C5'), 75.38 (GlcNAc_C5), 73.17, 73.16 (Gal_C3 and Gal_C3'), 73.04 (GlcNAc_C3), 71.61 (Gal_C2), 71.26 (Gal_C2'), 70.68 (GalNAc_C6), 69.93 (GalNAc_C5), 69.63 (GalNAc_C4), 69.23, 69.20 (Gal_C4 and Gal_C4'), 61.67, 61.61 (Gal_C6 and Gal_C6'), 60.69 (GlcNAc_C6), 55.67 (GlcNAc_C2), 55.53 (OCH_3), 49.17 (GalNAc_C2), 22.83 (Ac), 22.66 (Ac). ESI-HRMS *m/z* calc'd for $C_{29}H_{50}N_2NaO_{21}$ $(M+Na)^+$: 785.2804; found: 785.2806. HPLC purity analysis: >99.5%, R_t 5.34 minutes, Atlantis T3 C18 column.

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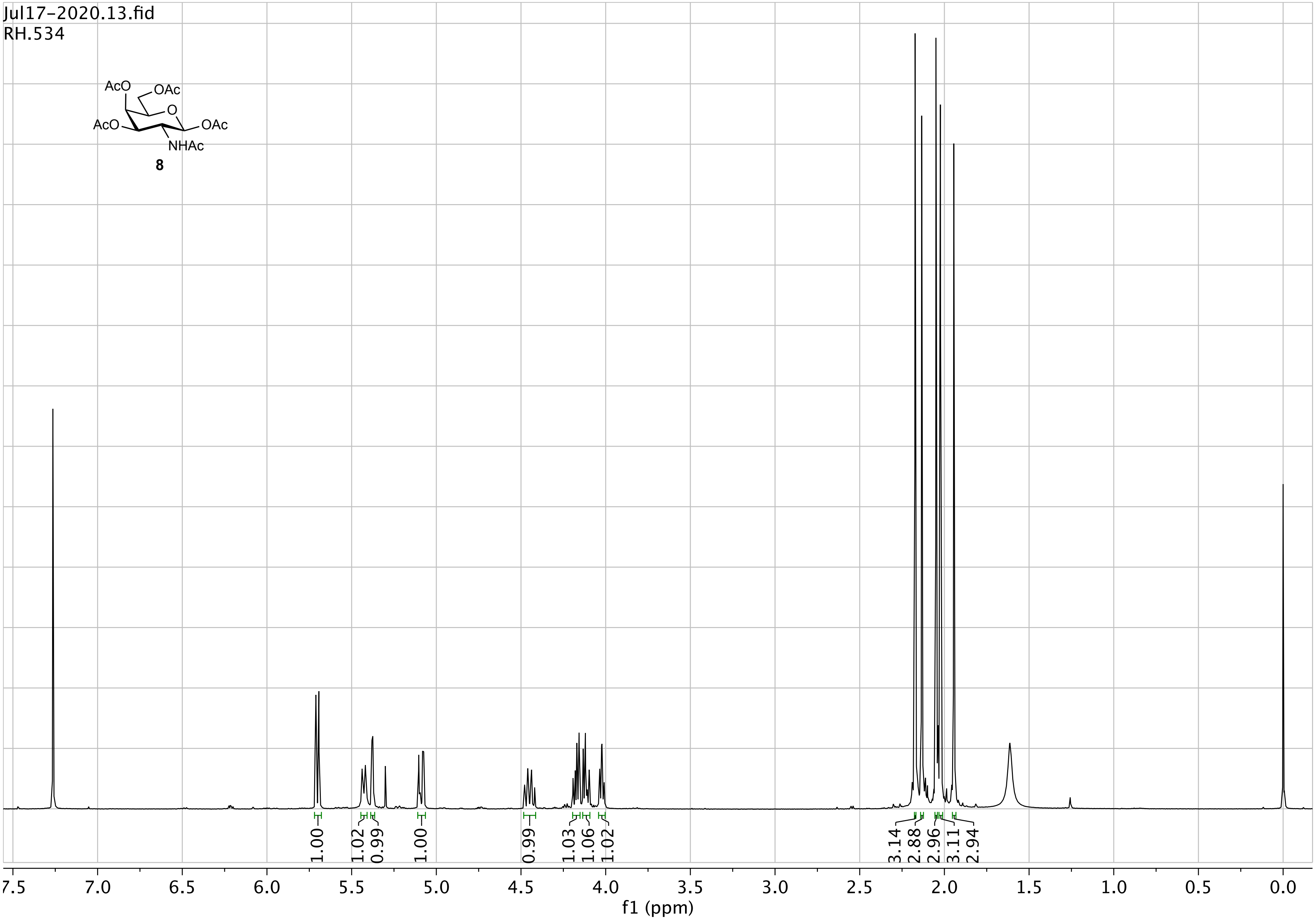
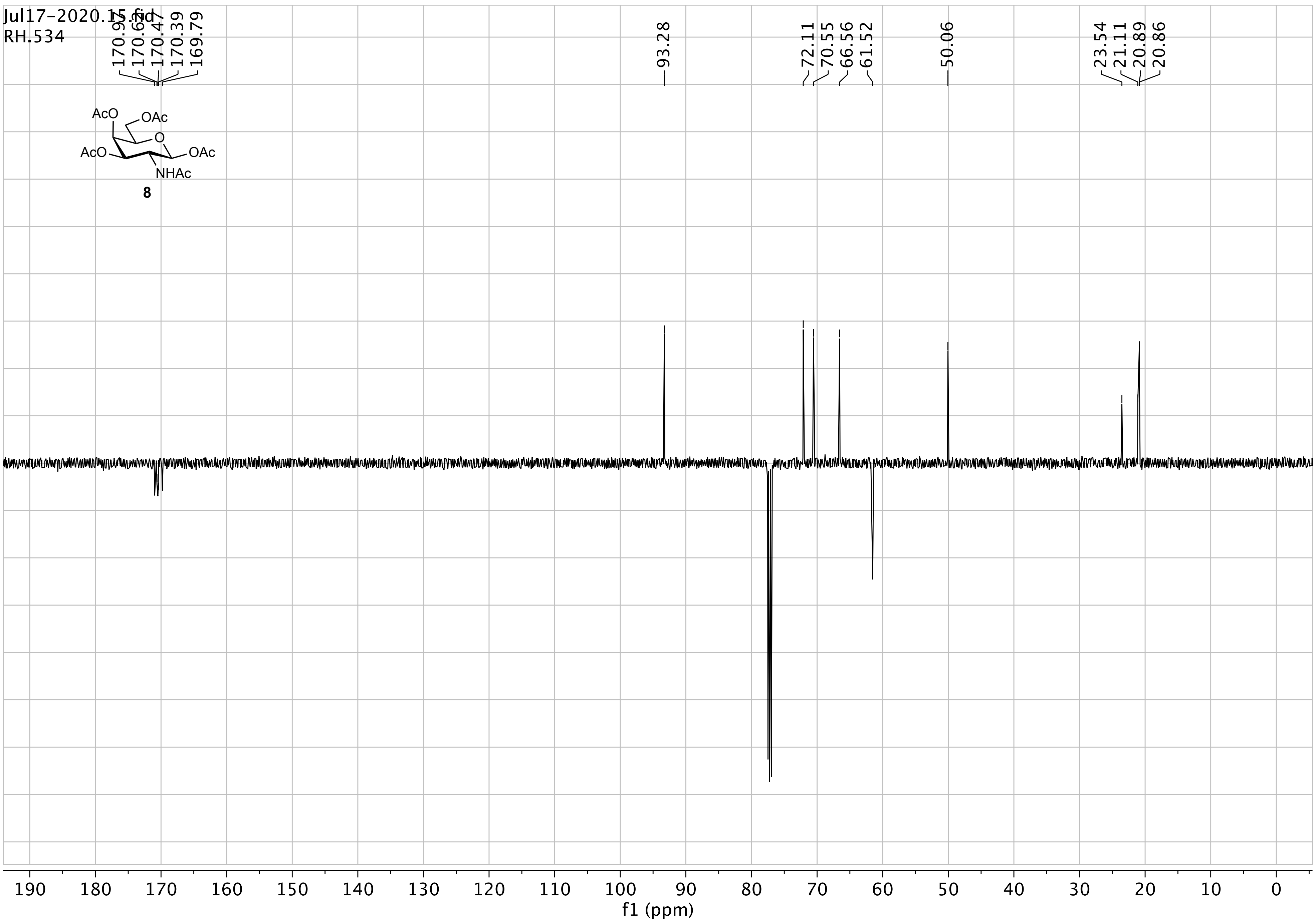
^{1}H NMR in $CDCl_3$ (500 MHz)



^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



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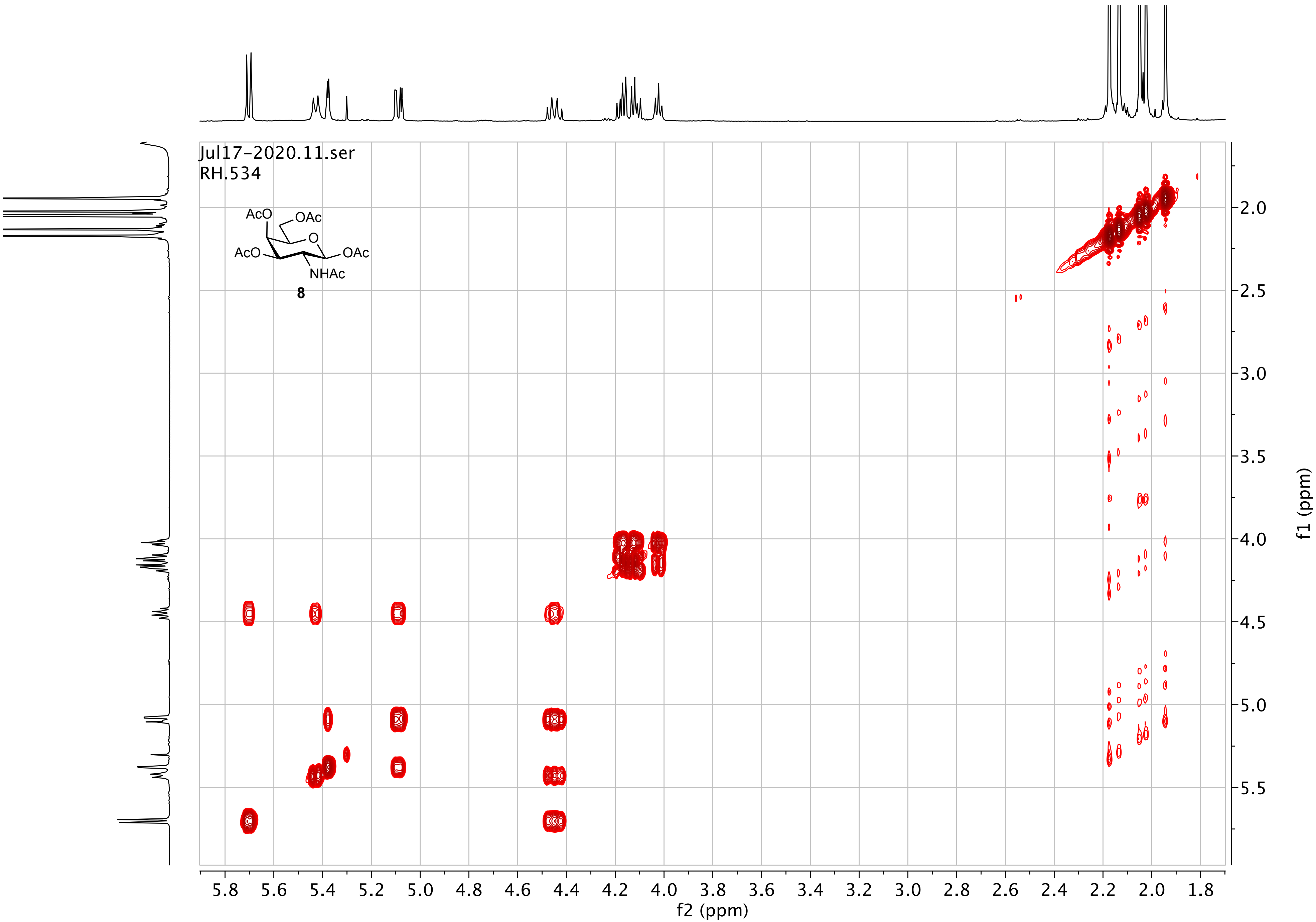

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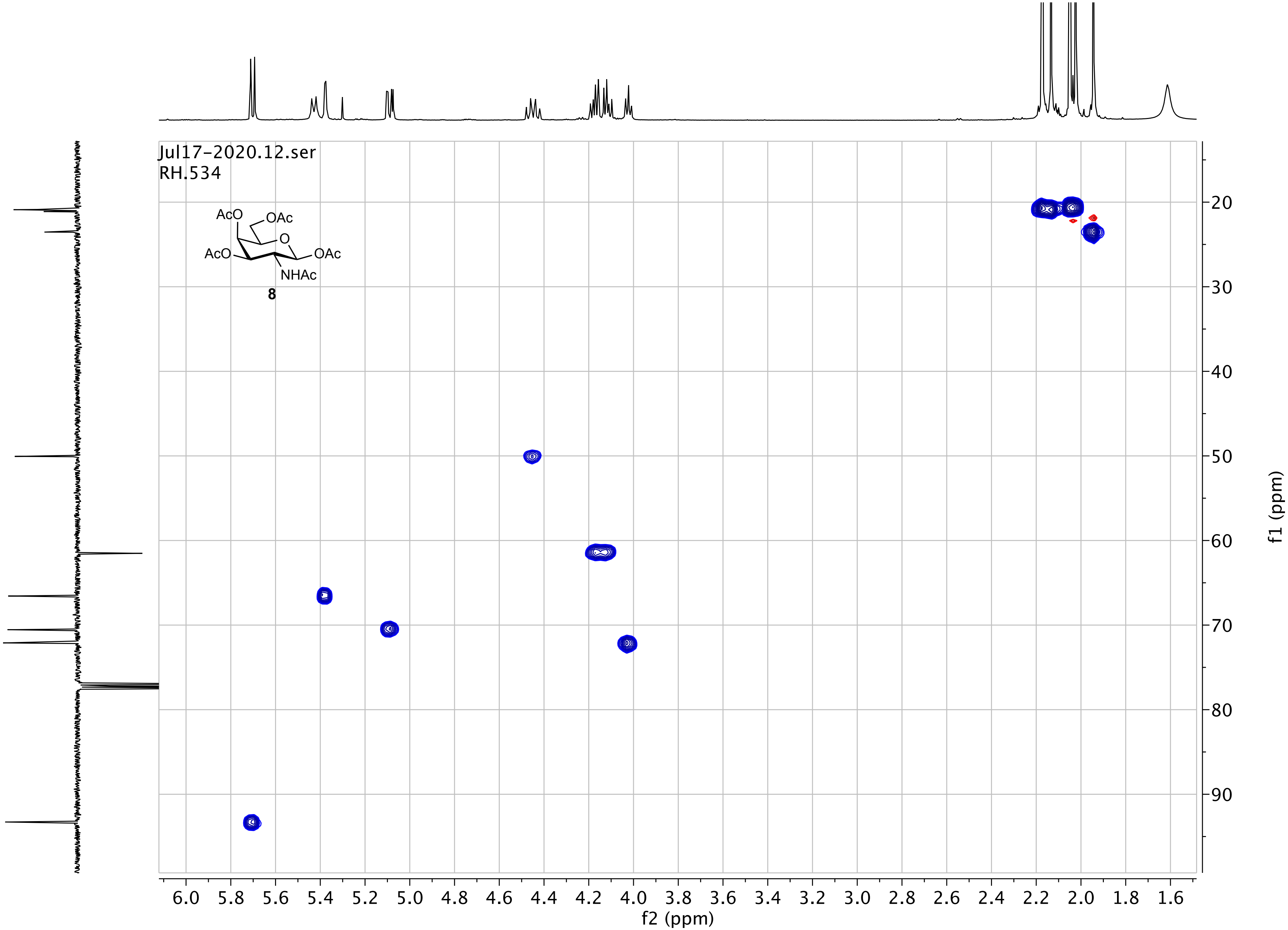
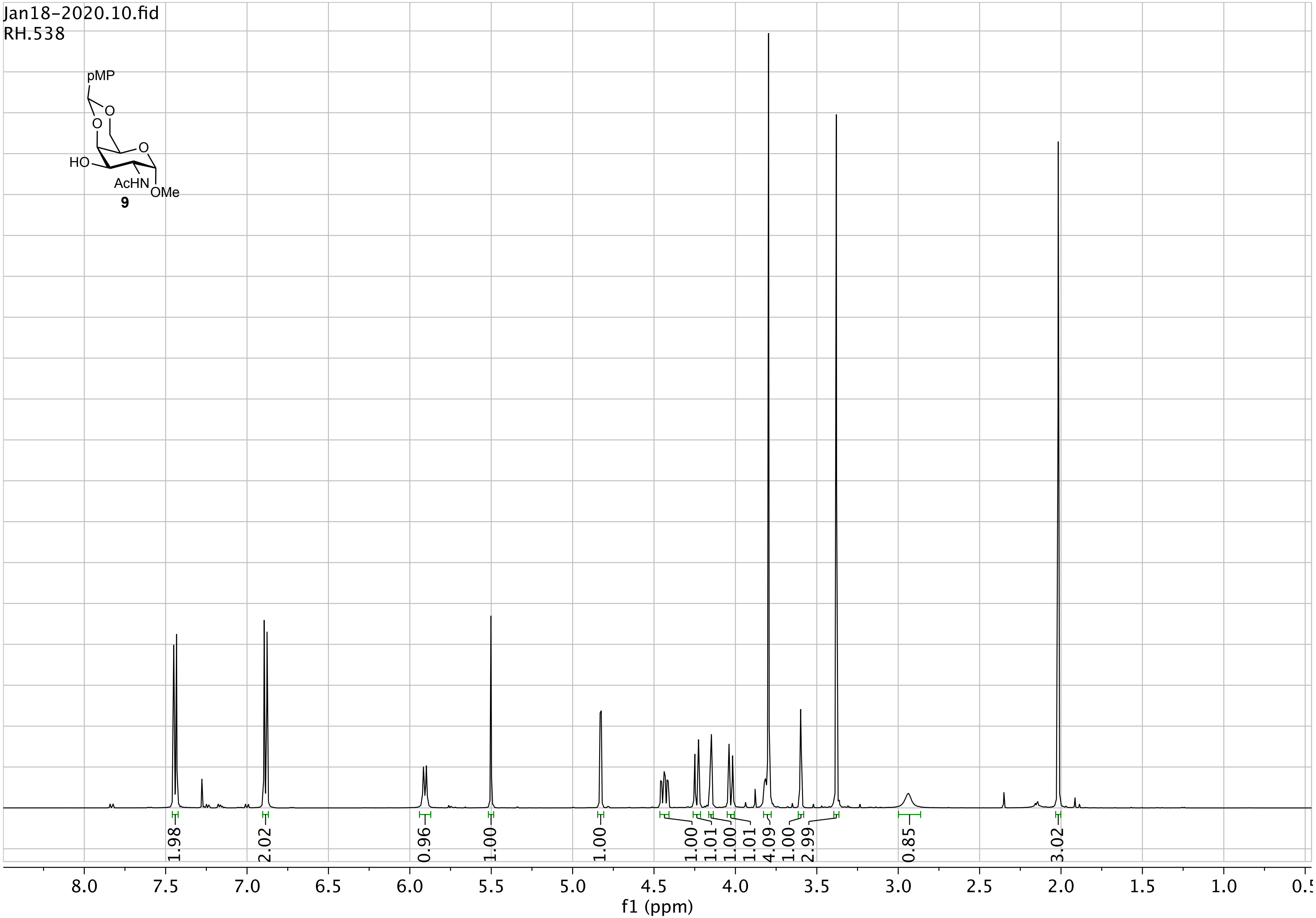
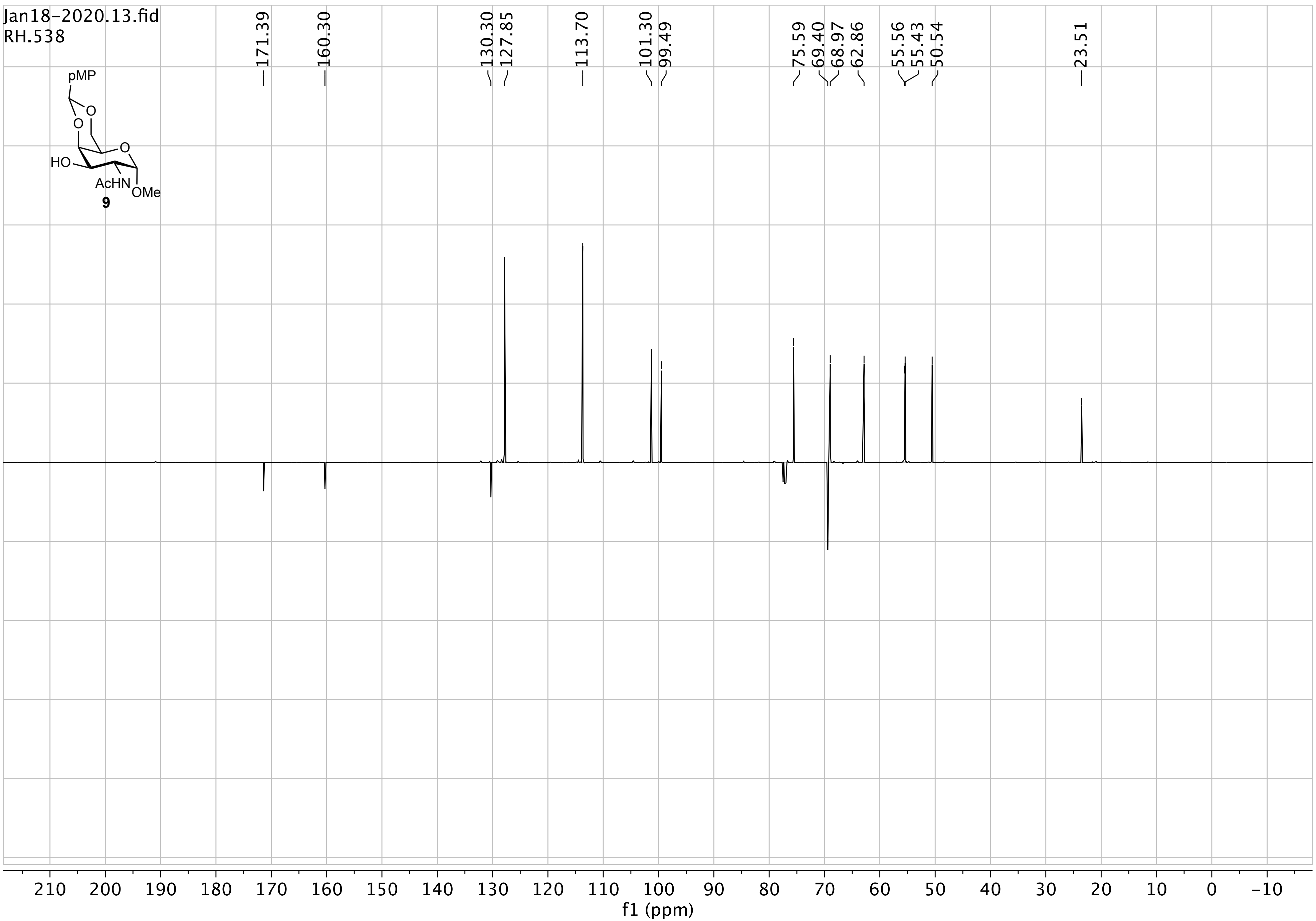


^1H NMR in $CDCl_3$ (500 MHz)



^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



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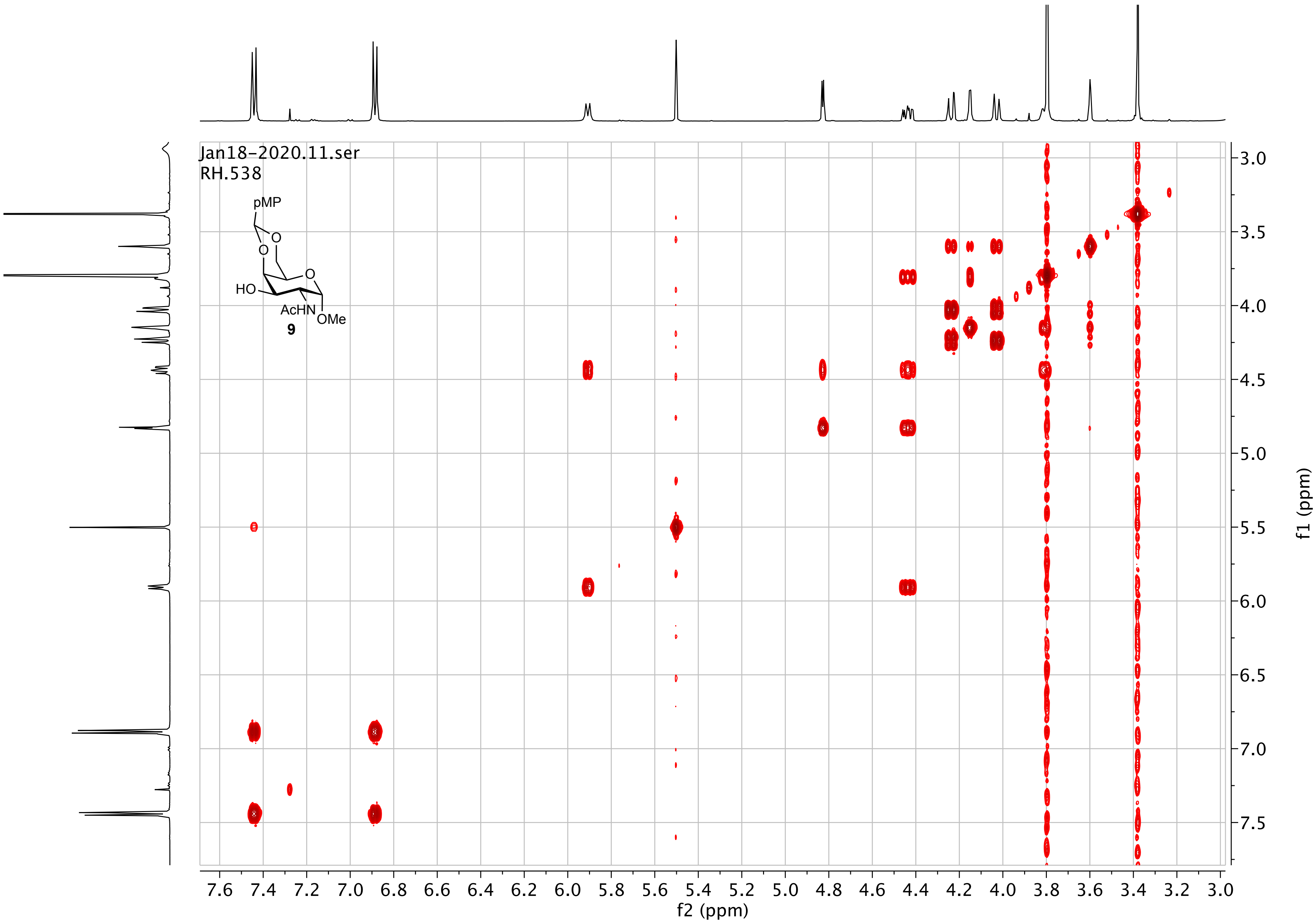

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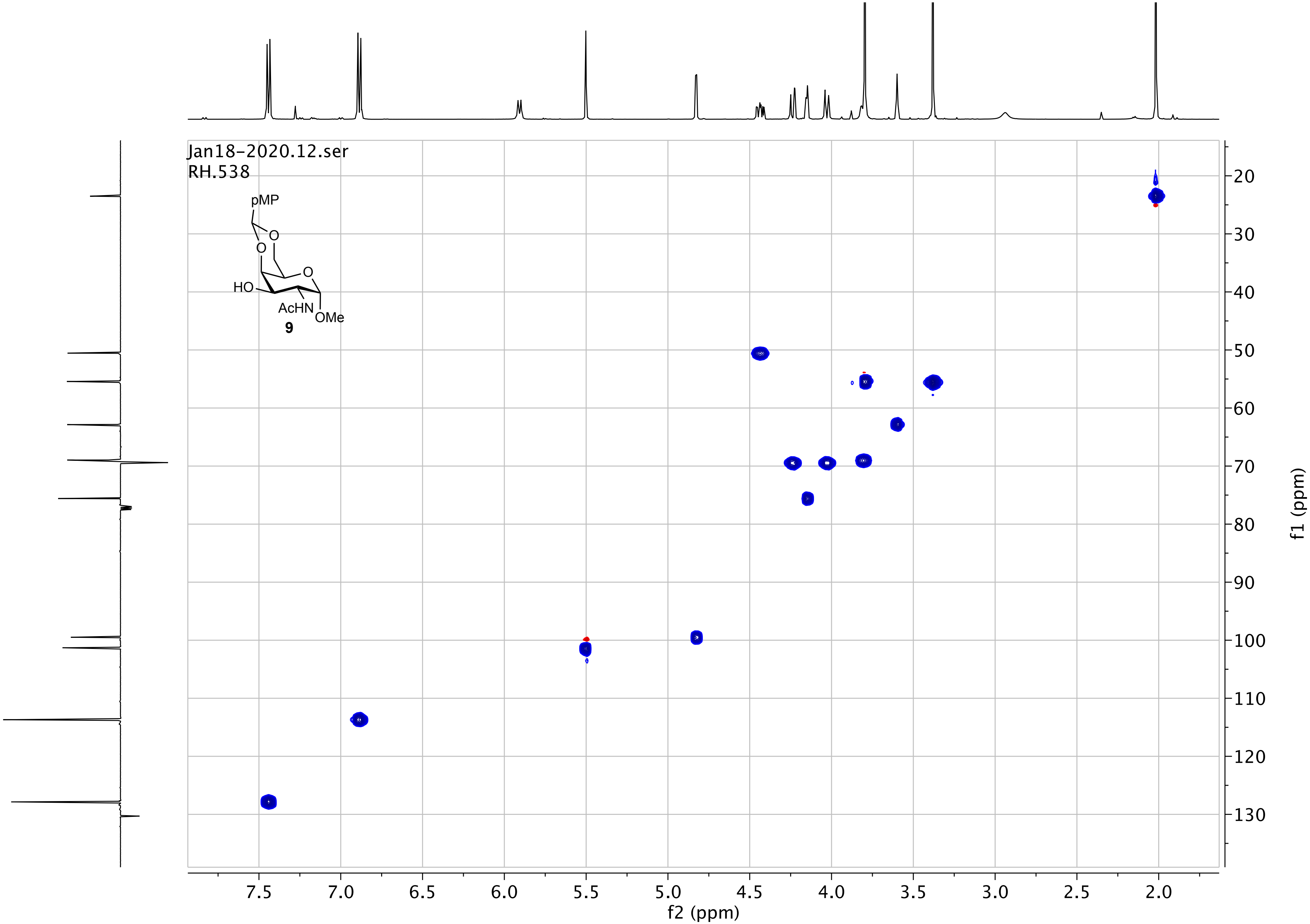

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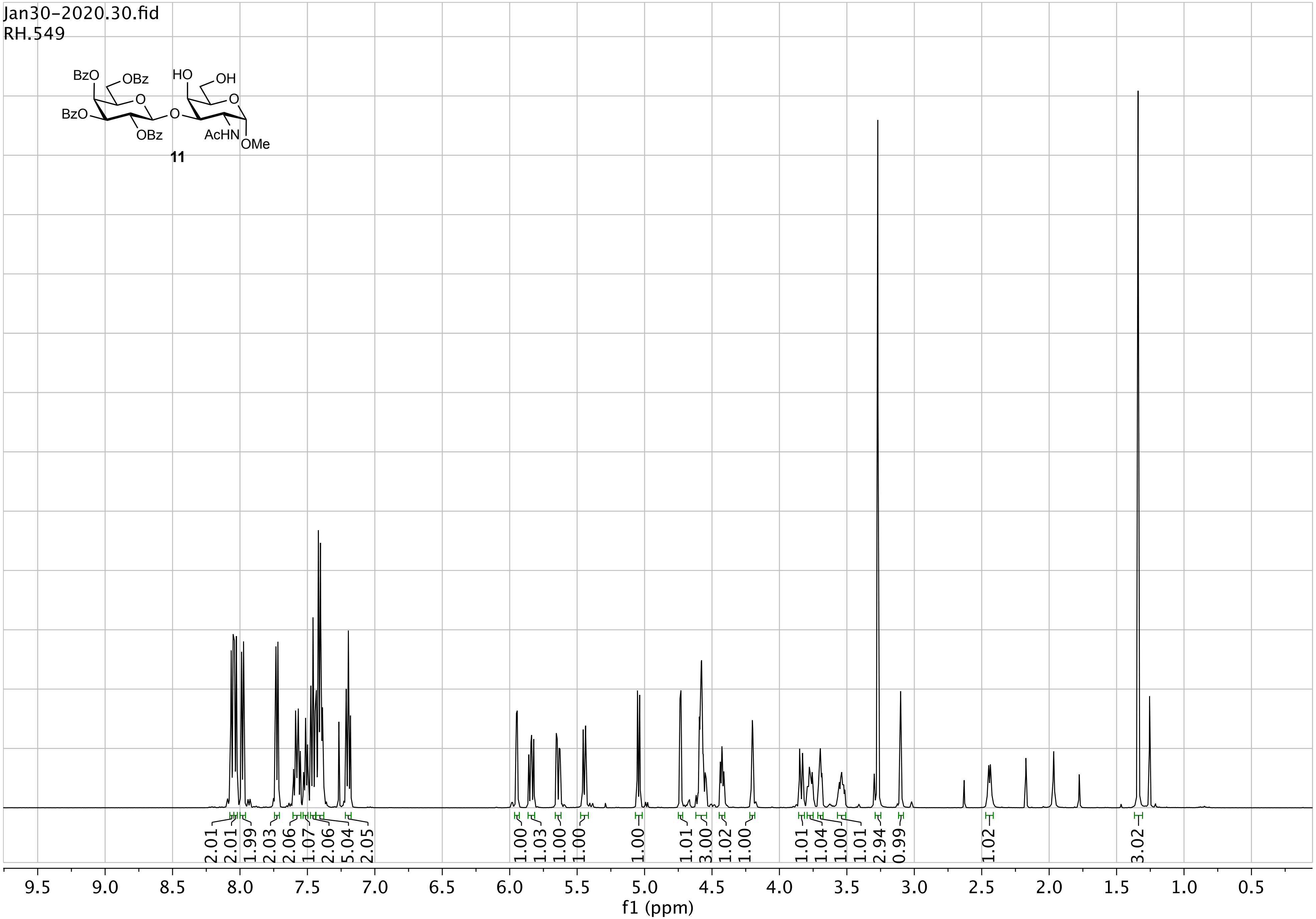
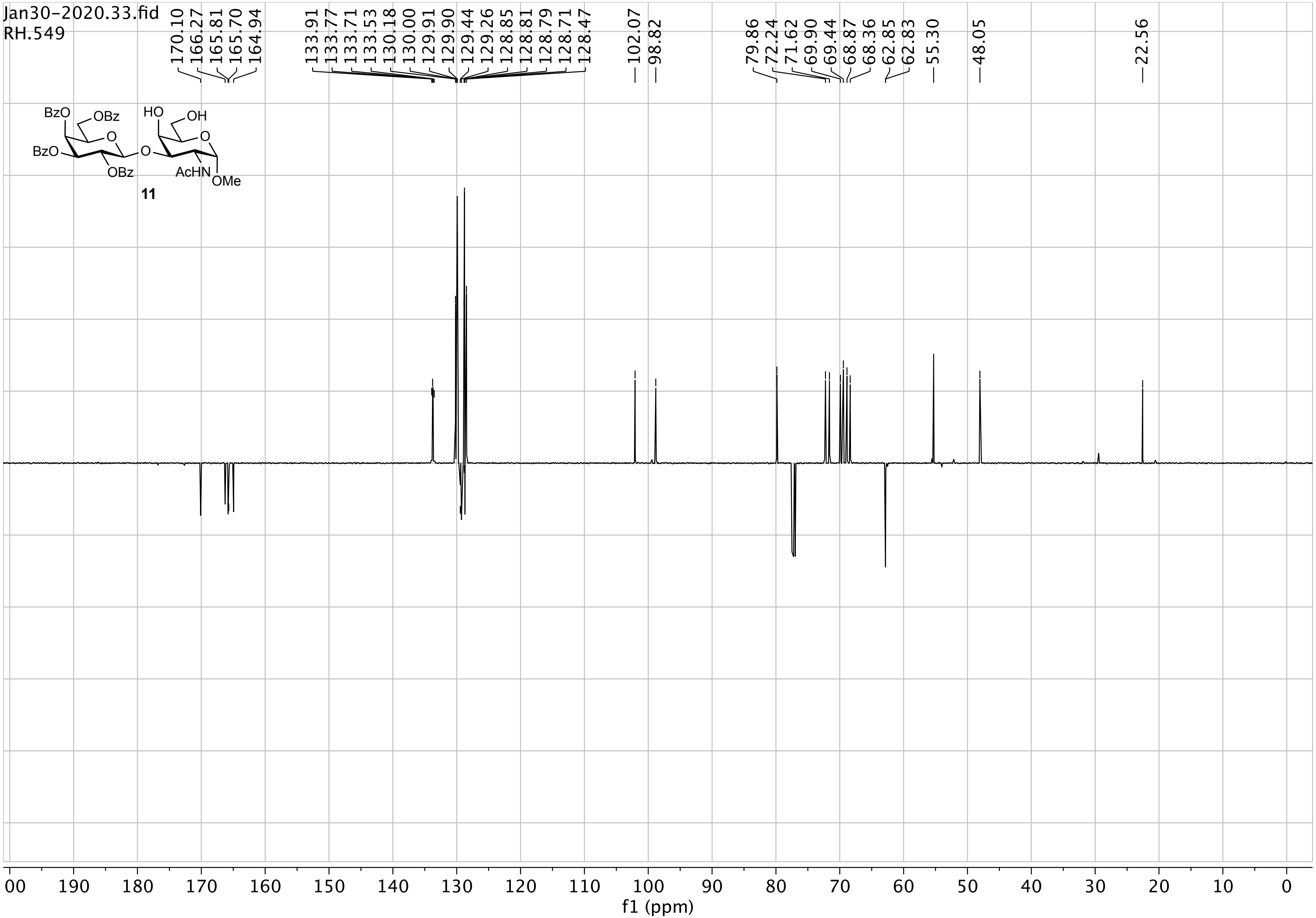


^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



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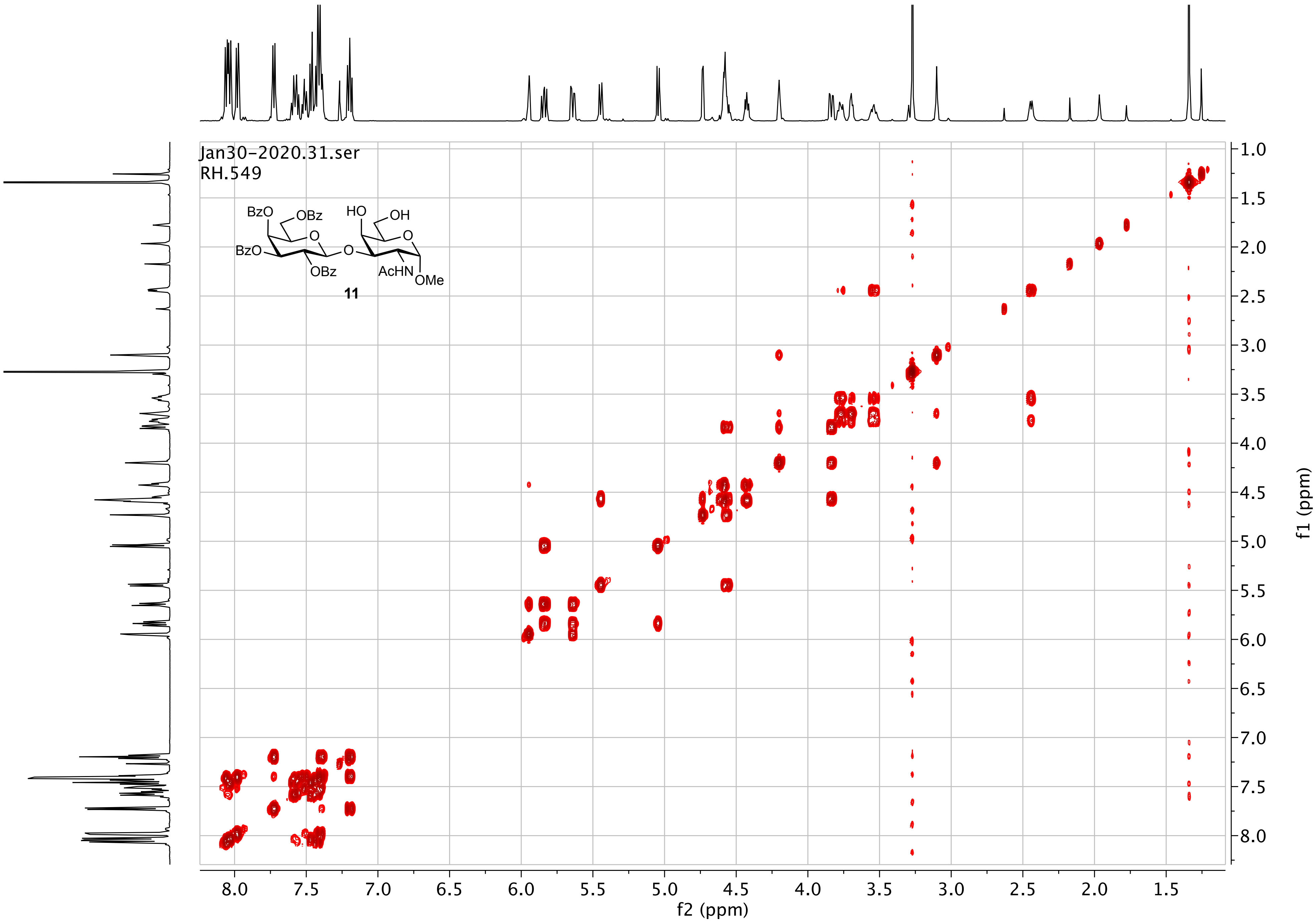

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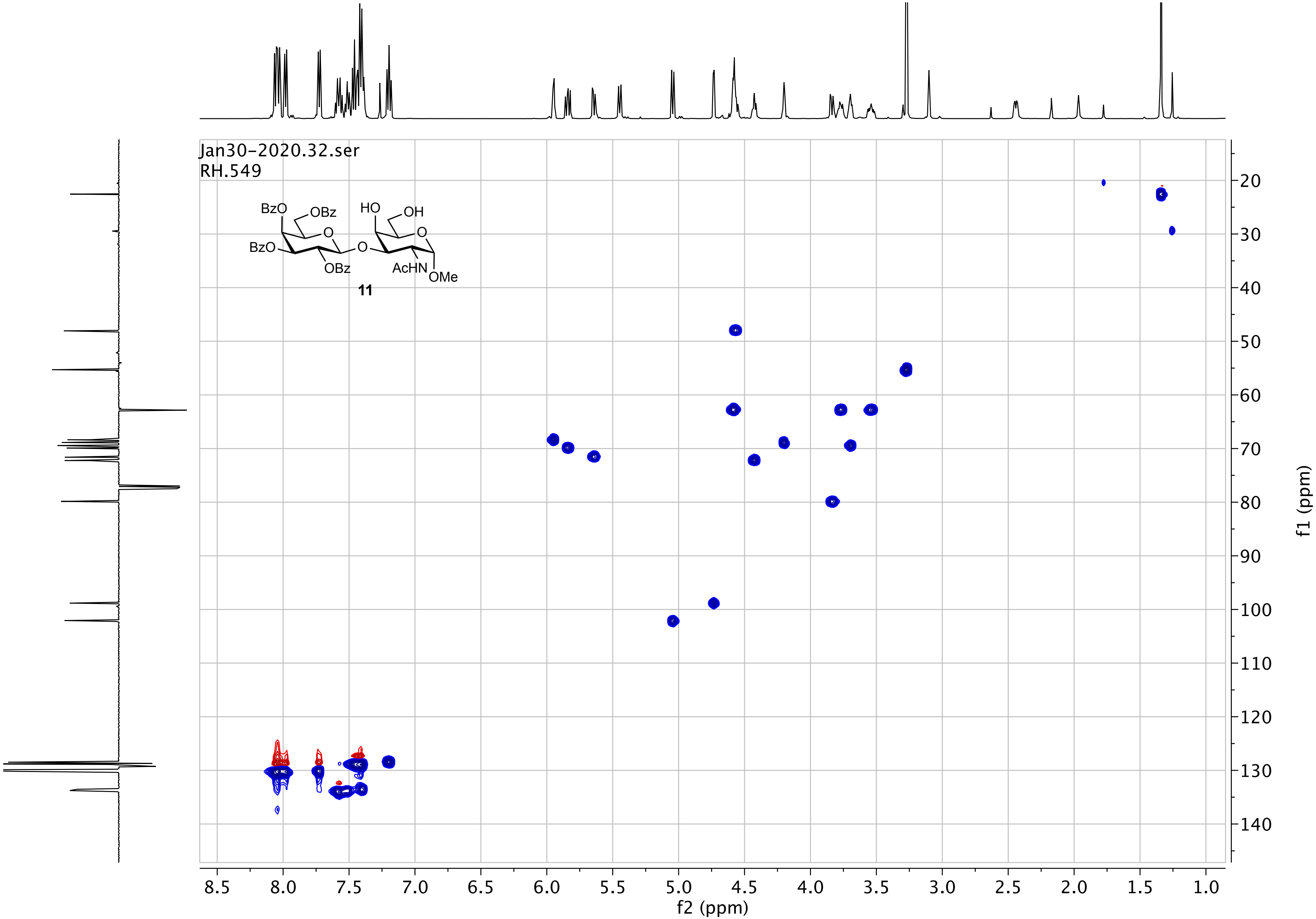

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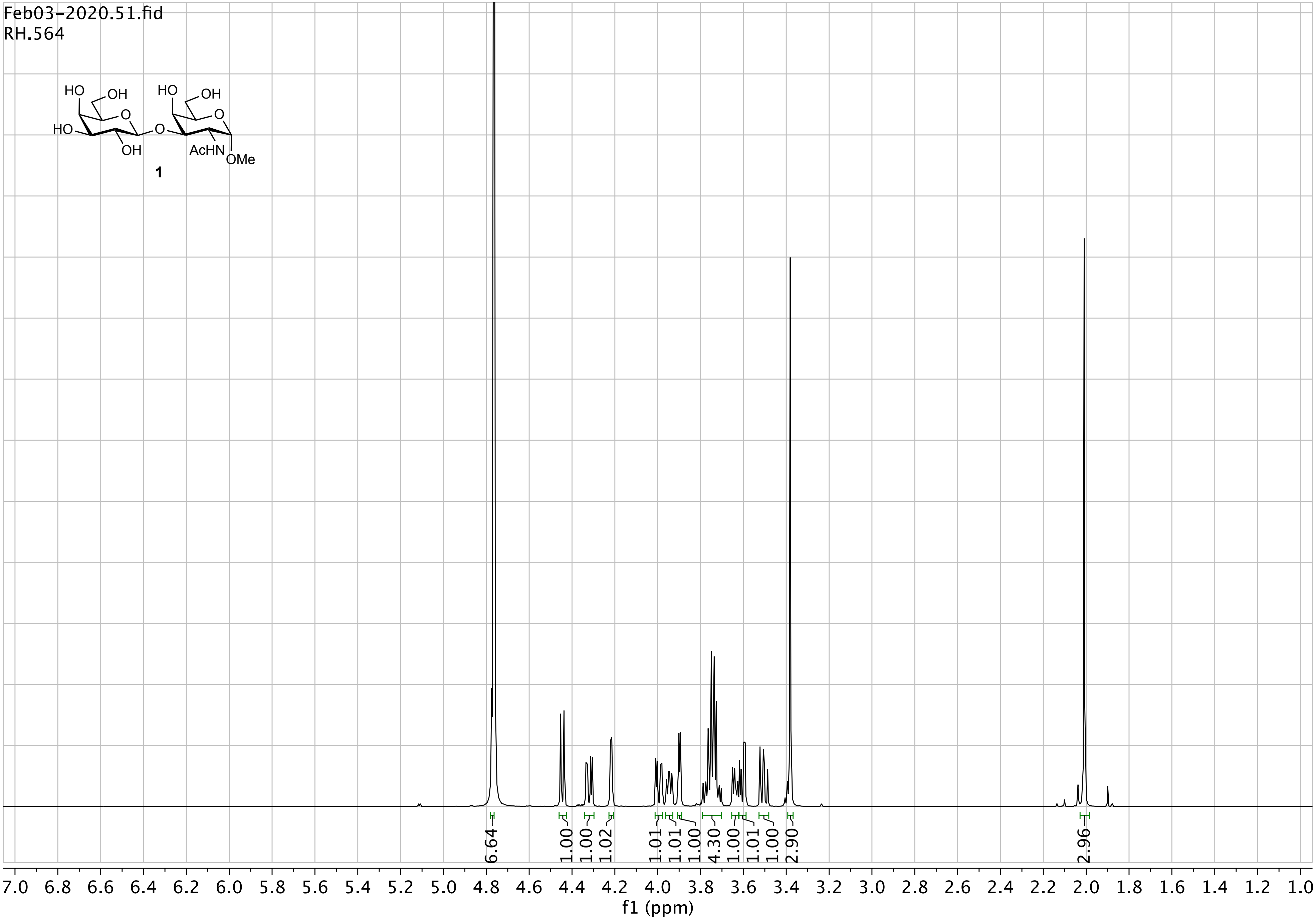

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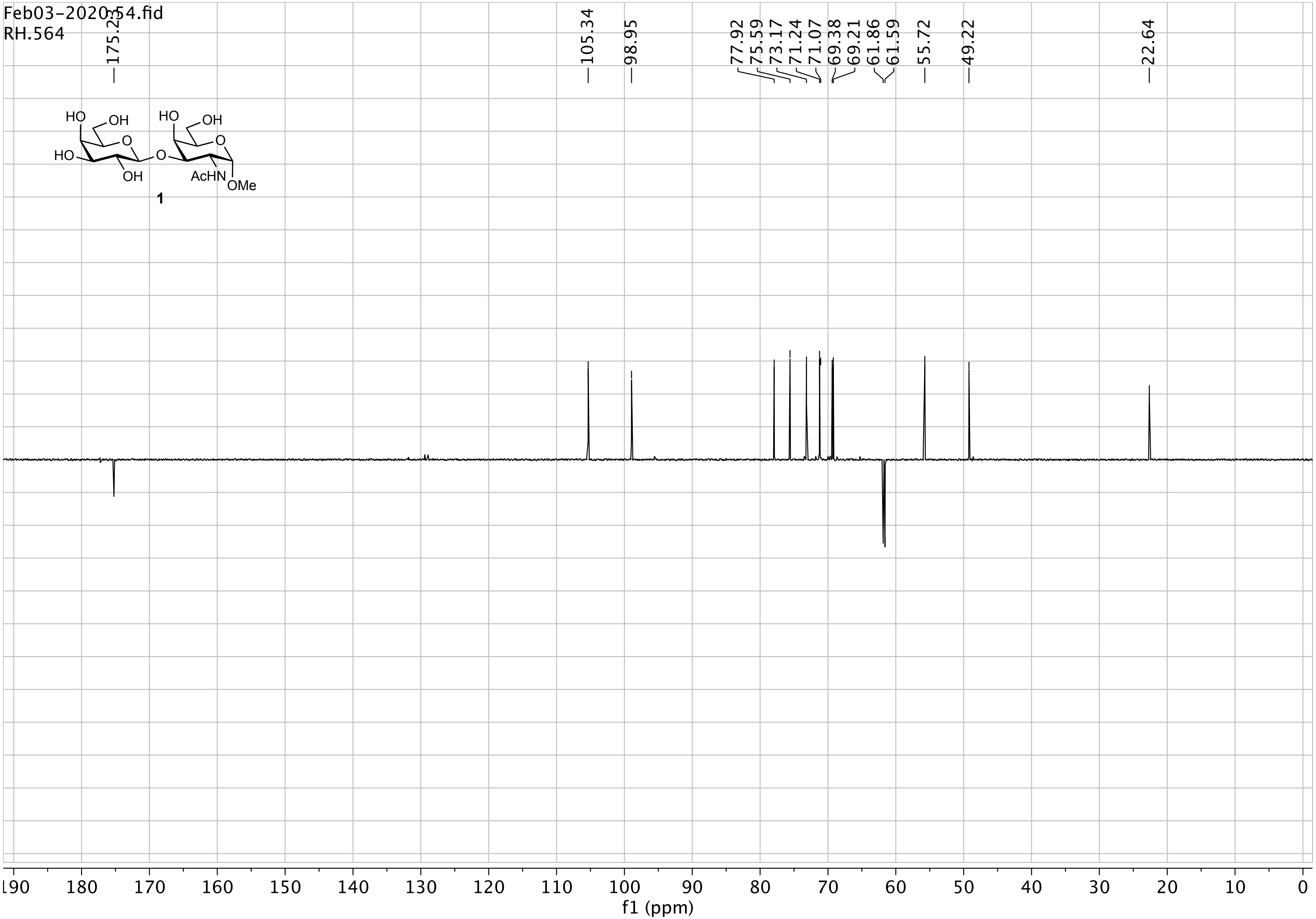

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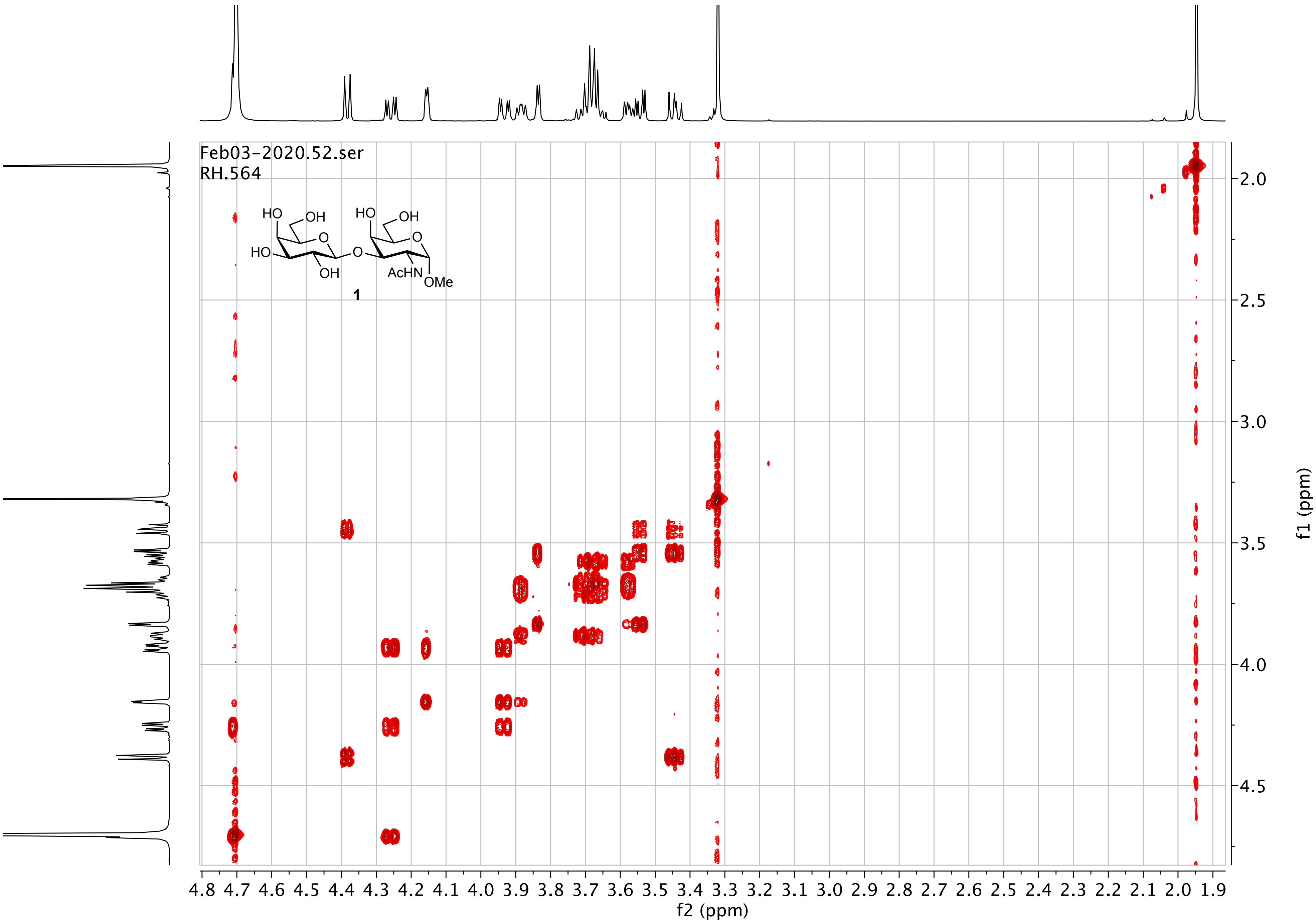

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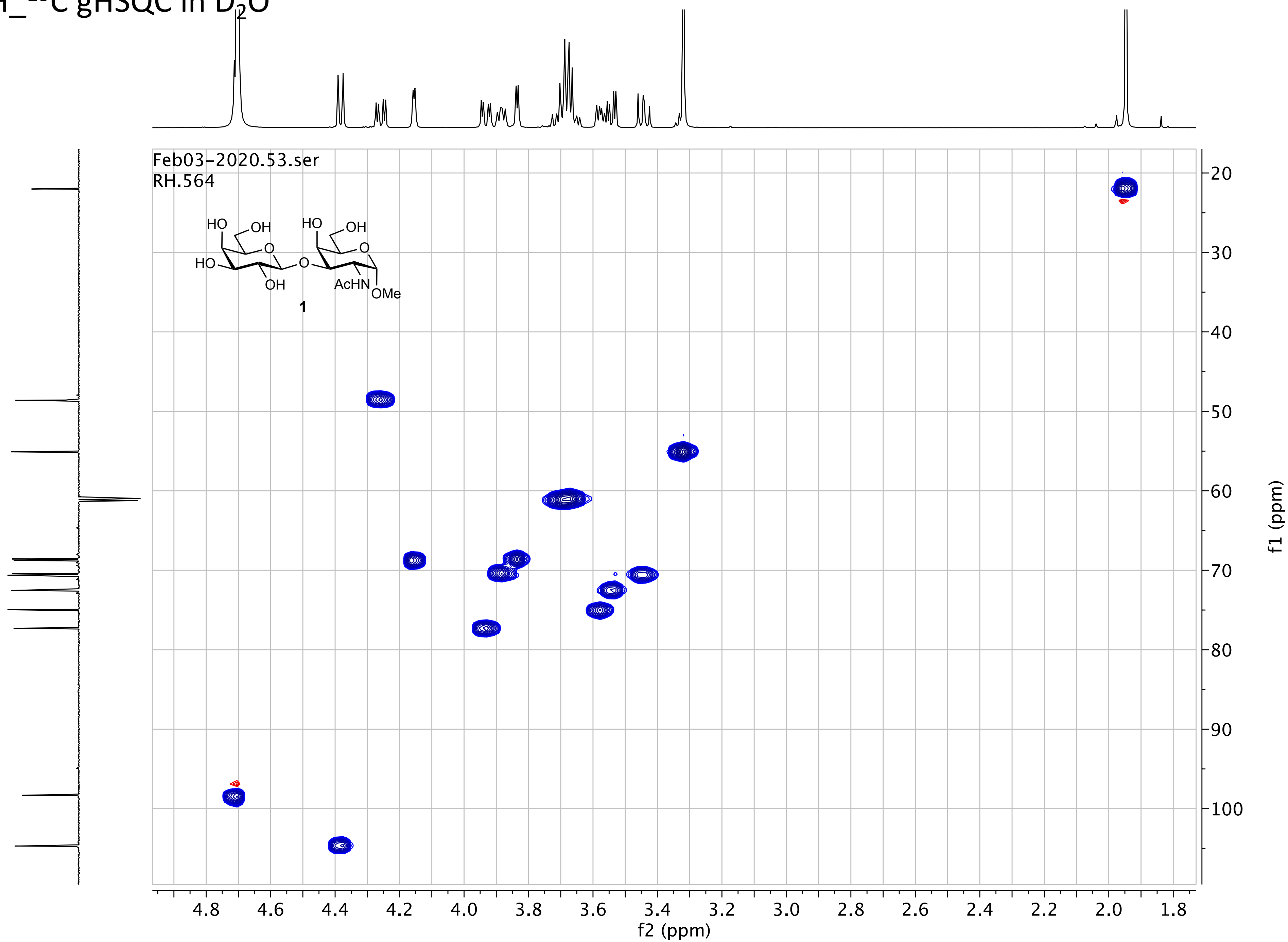

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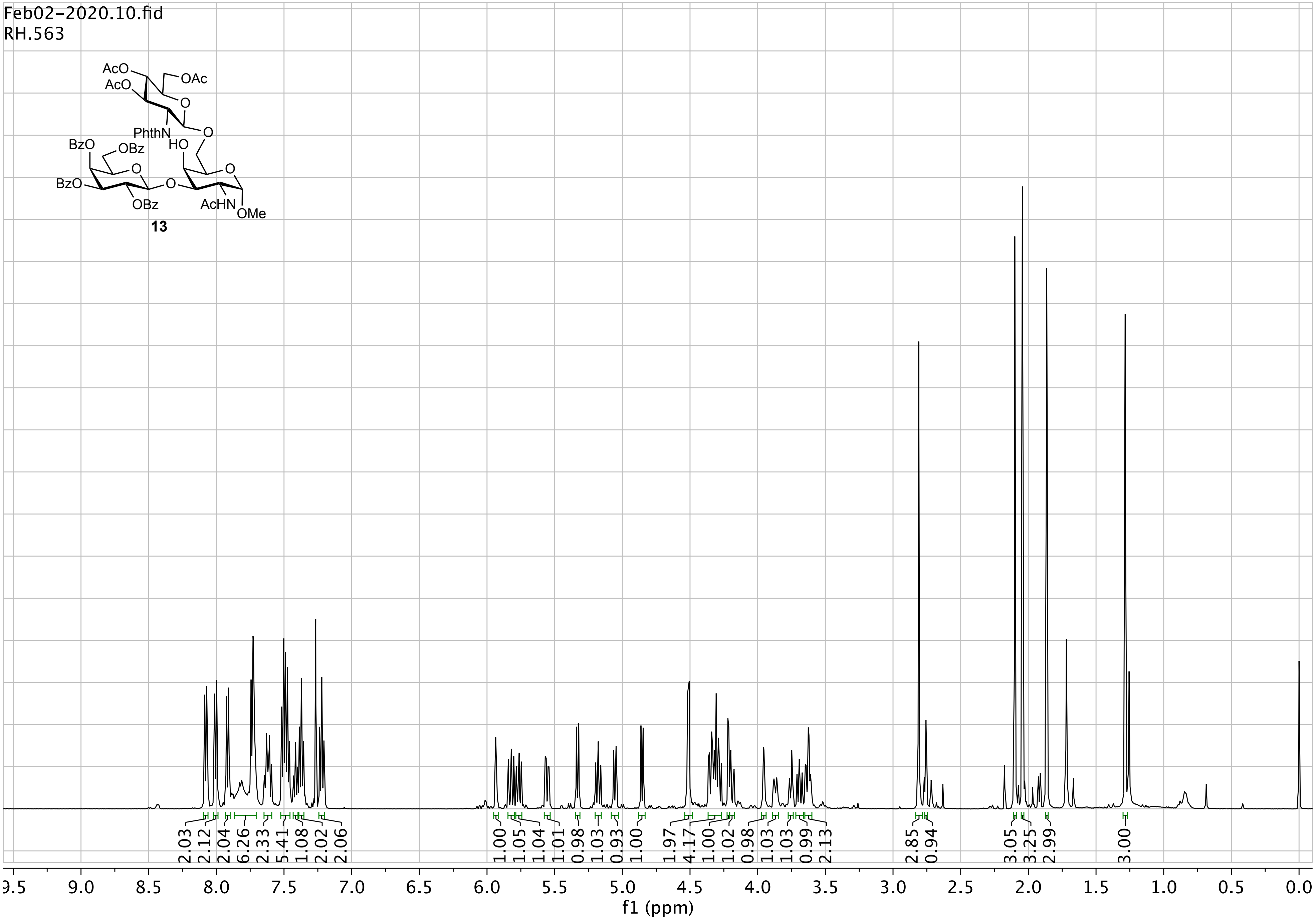

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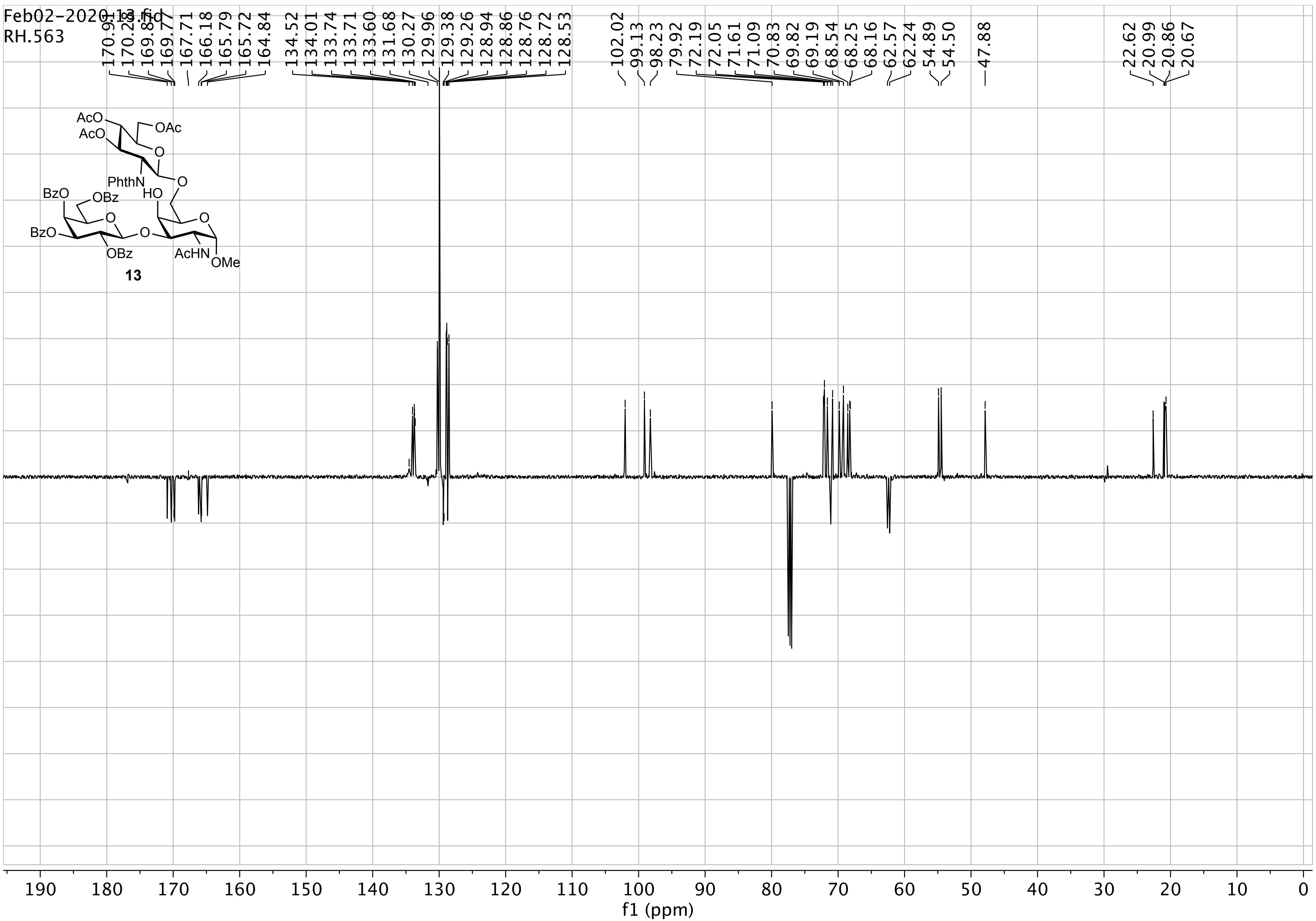

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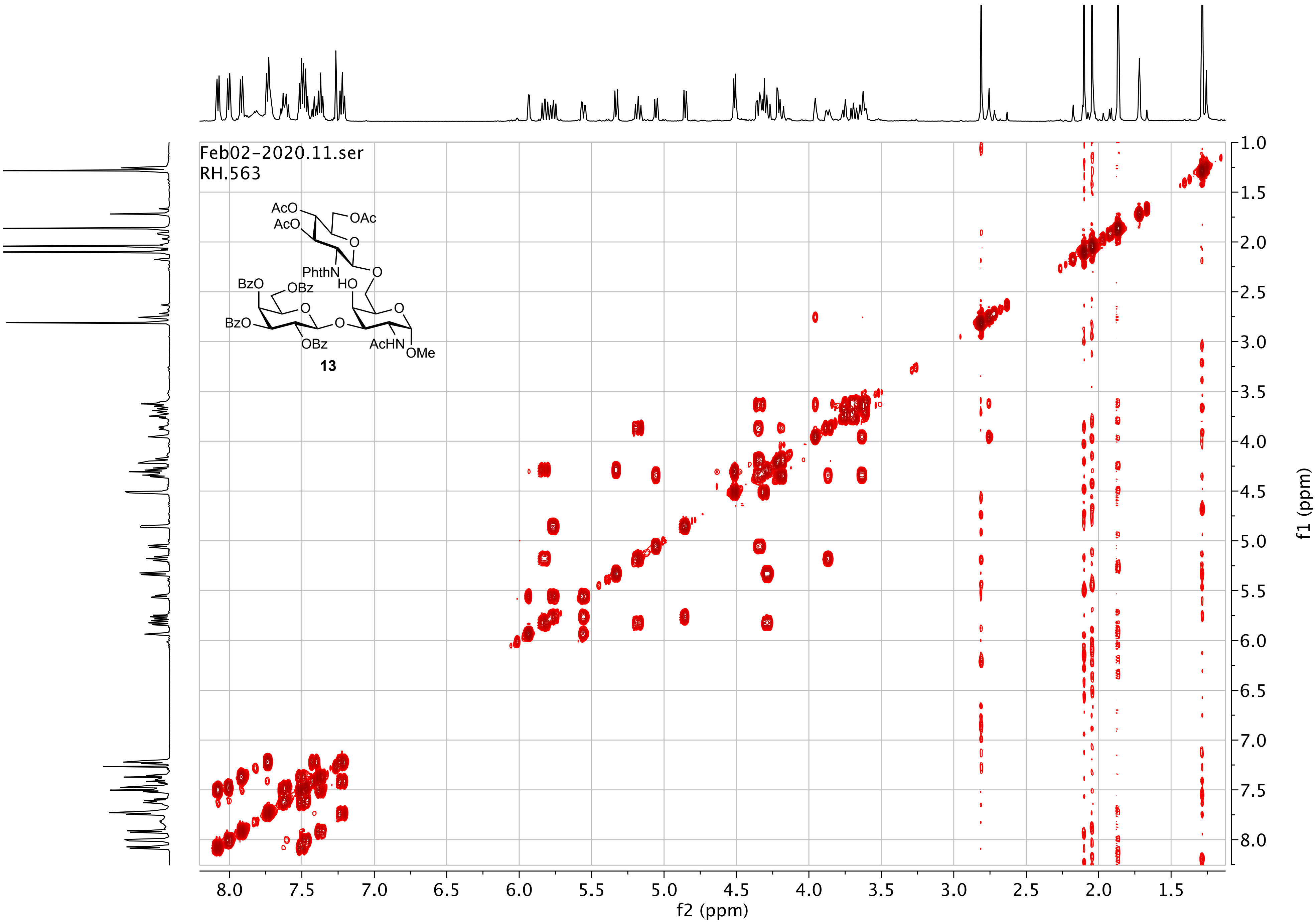

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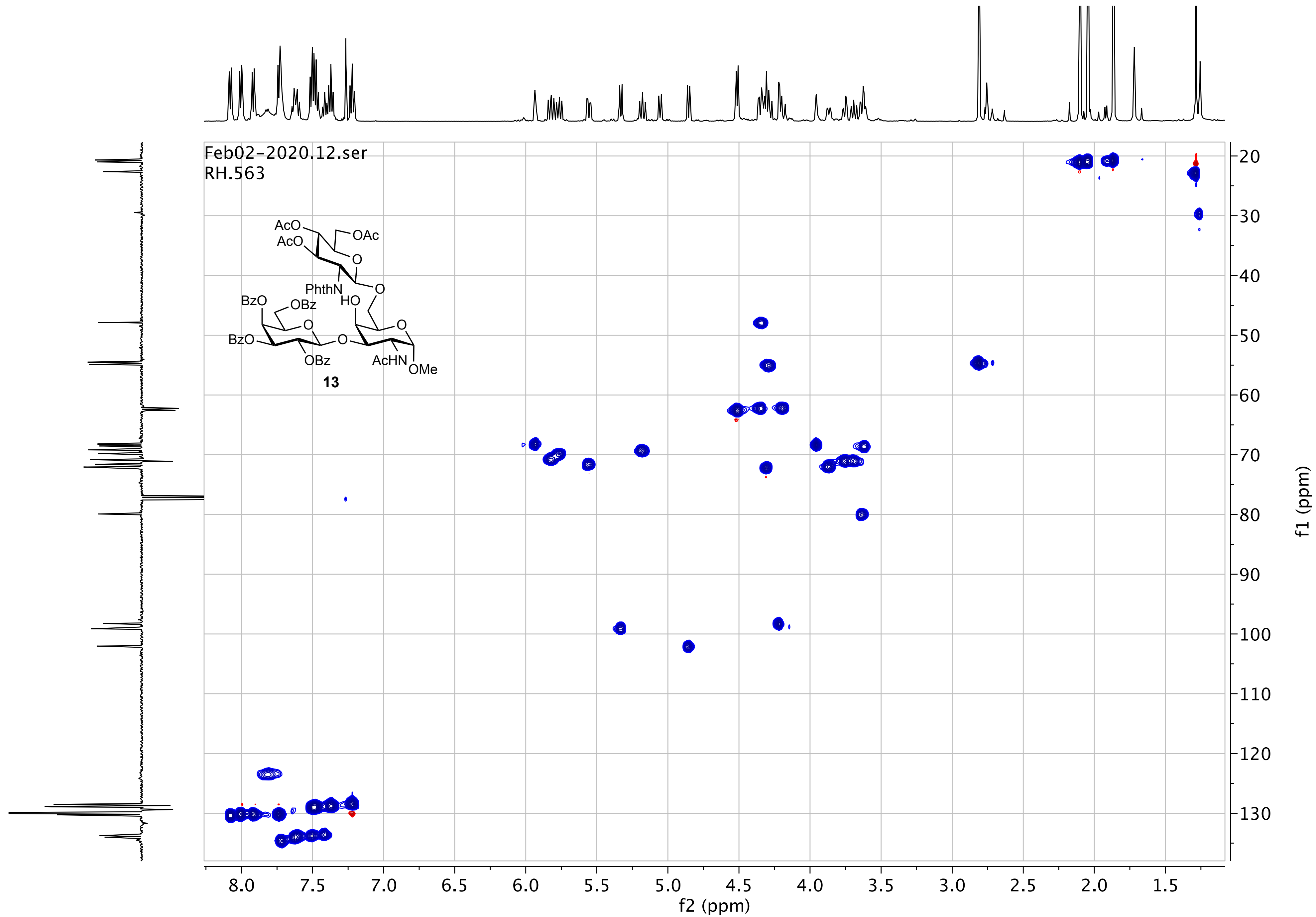

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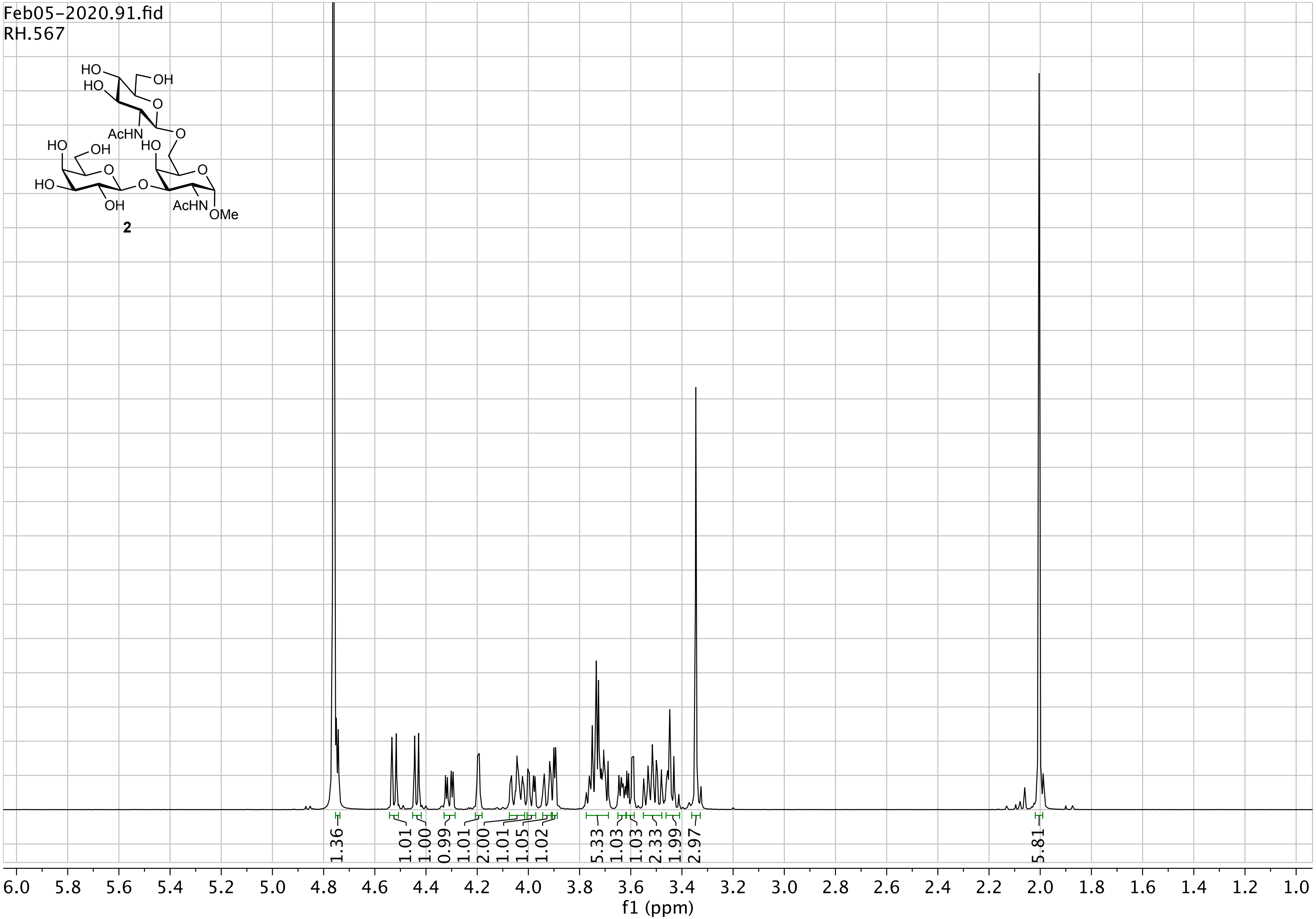
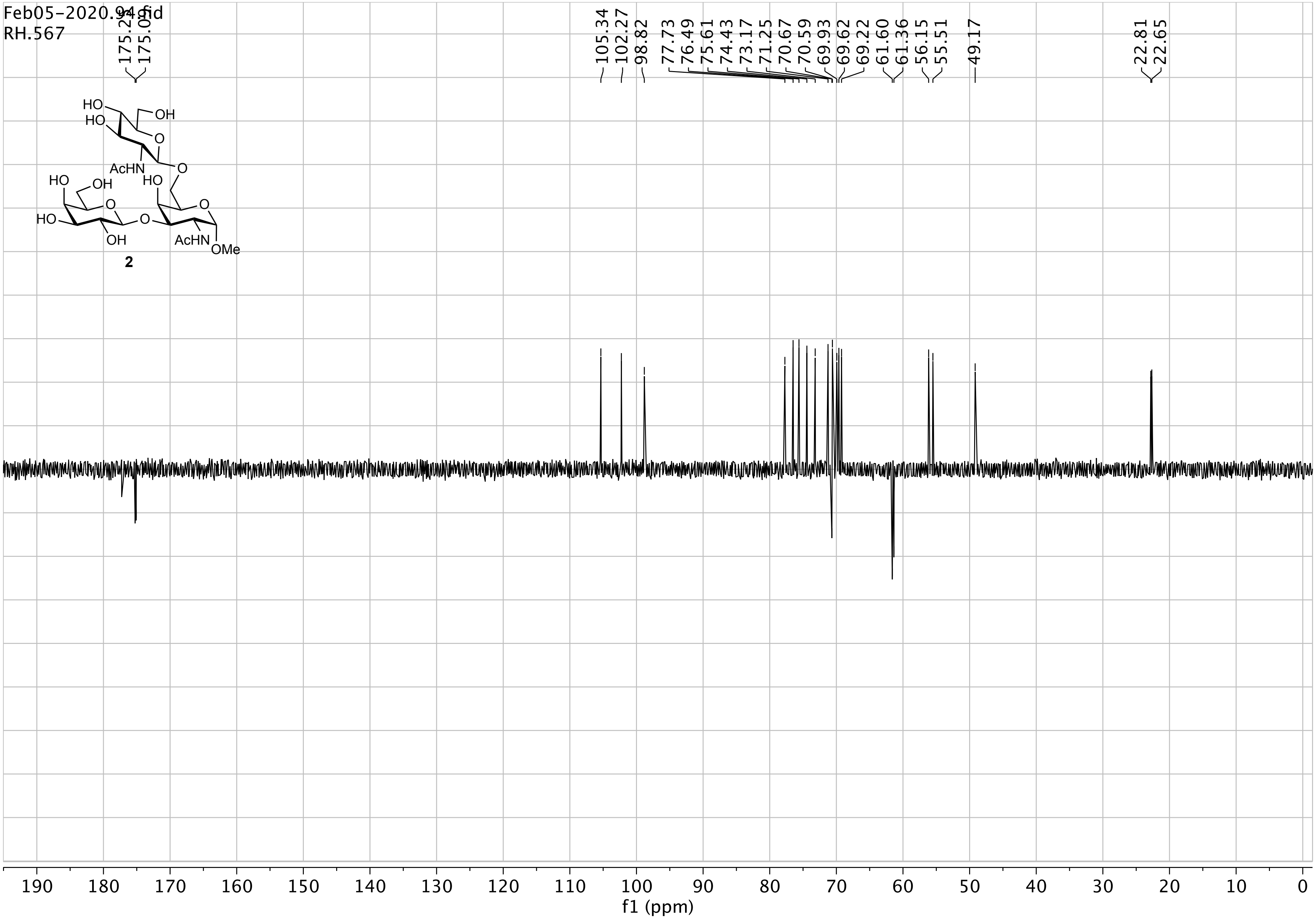


^{13}C NMR (APT) in D_2O (125 MHz)



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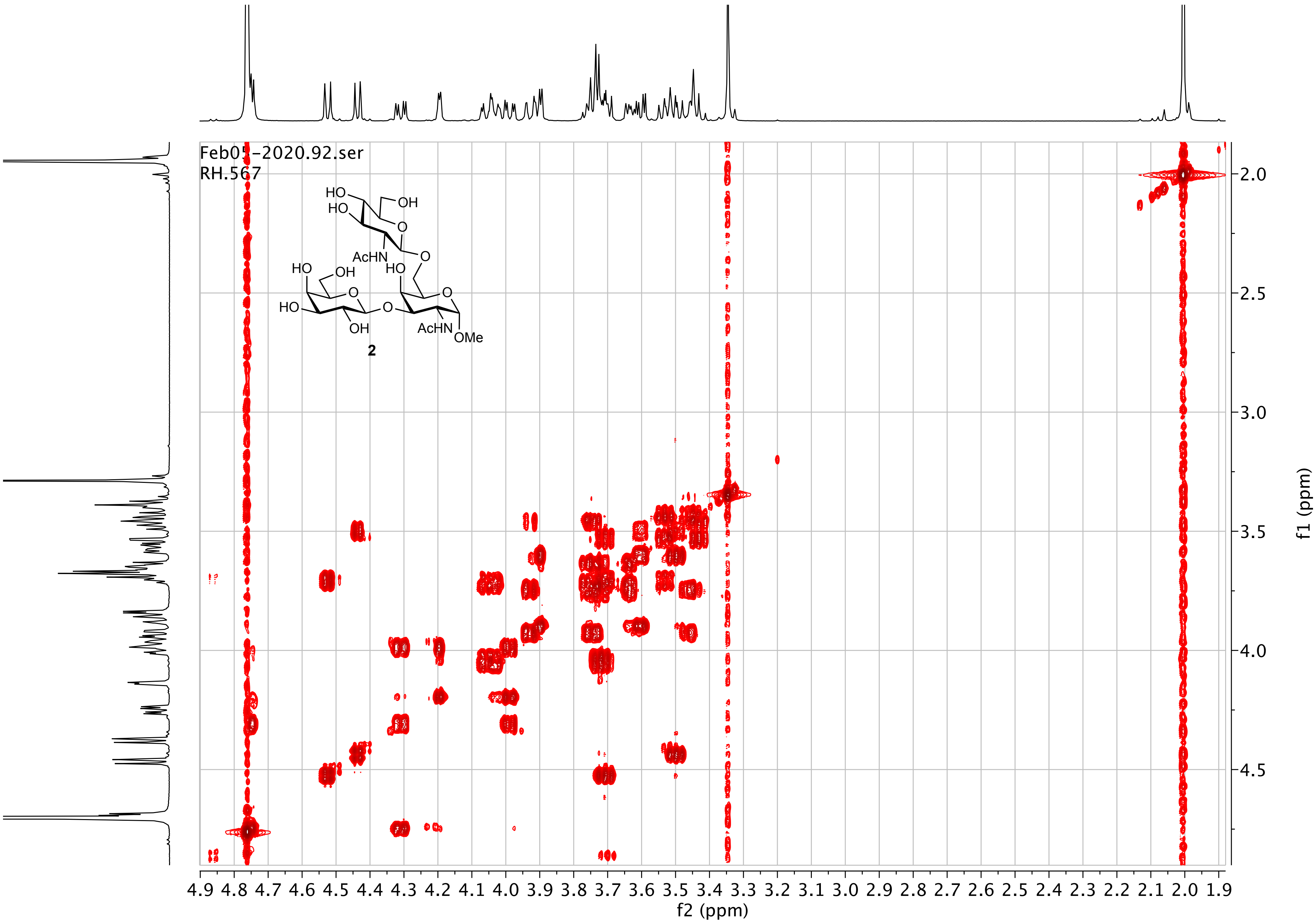

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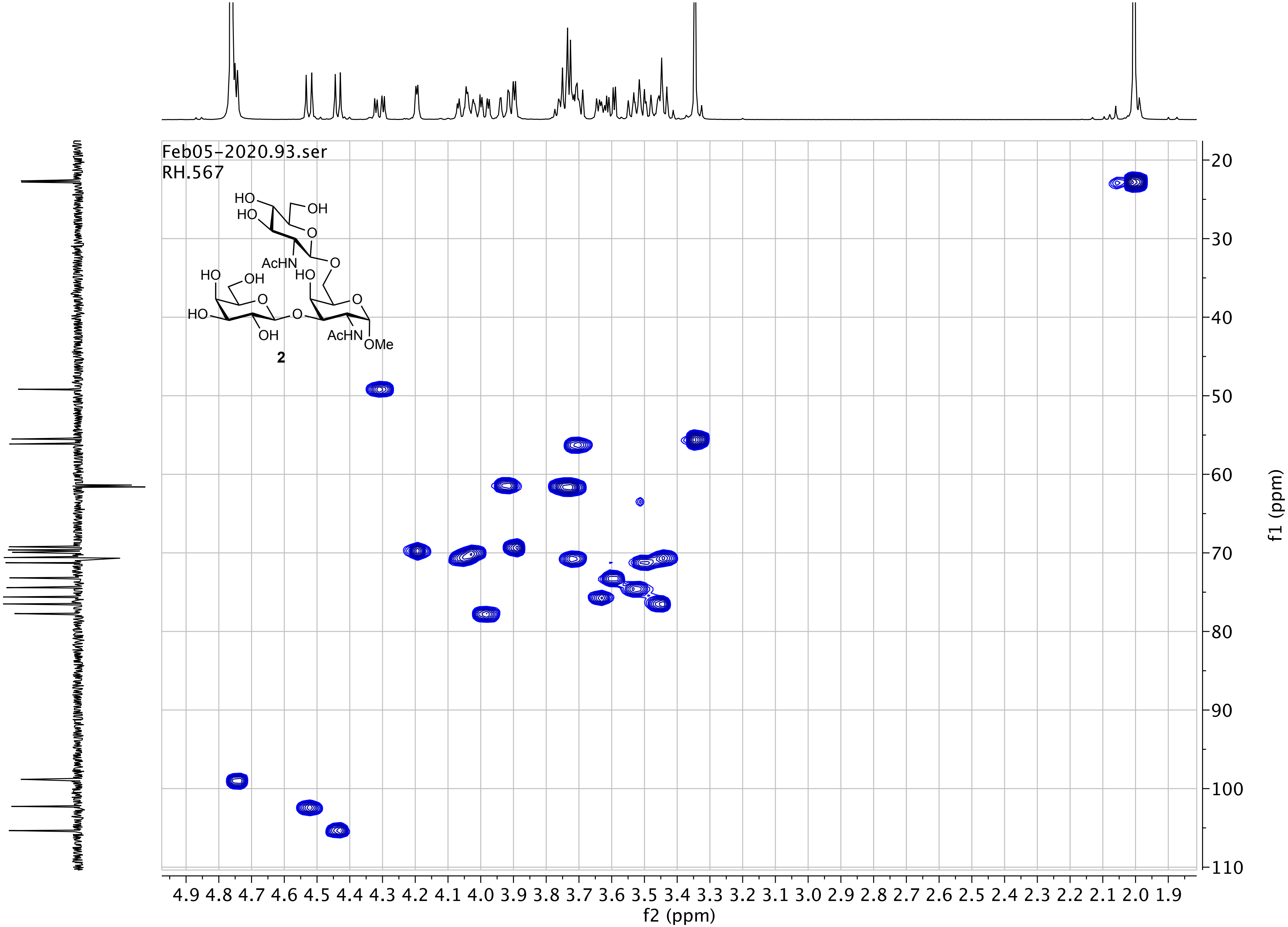
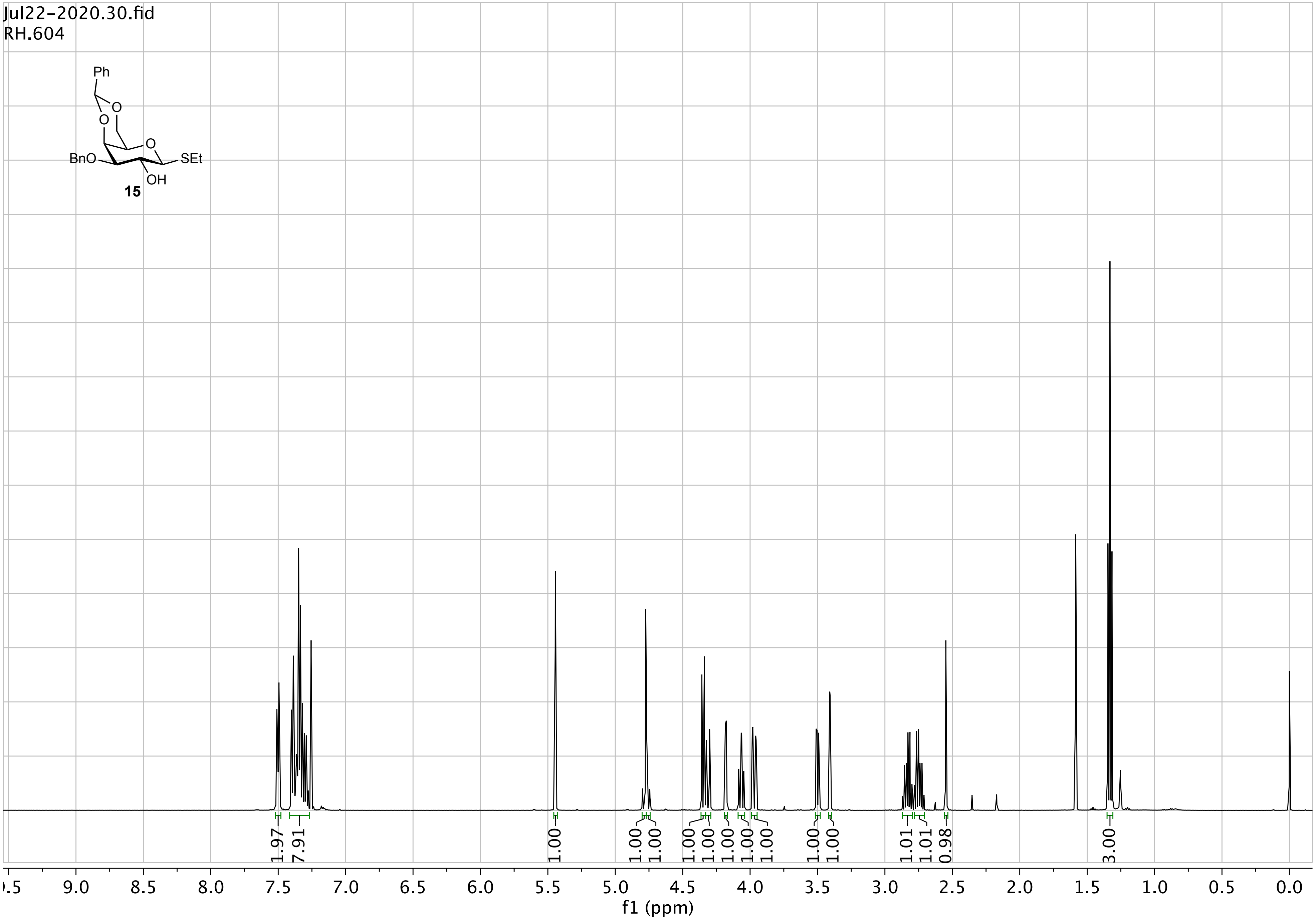
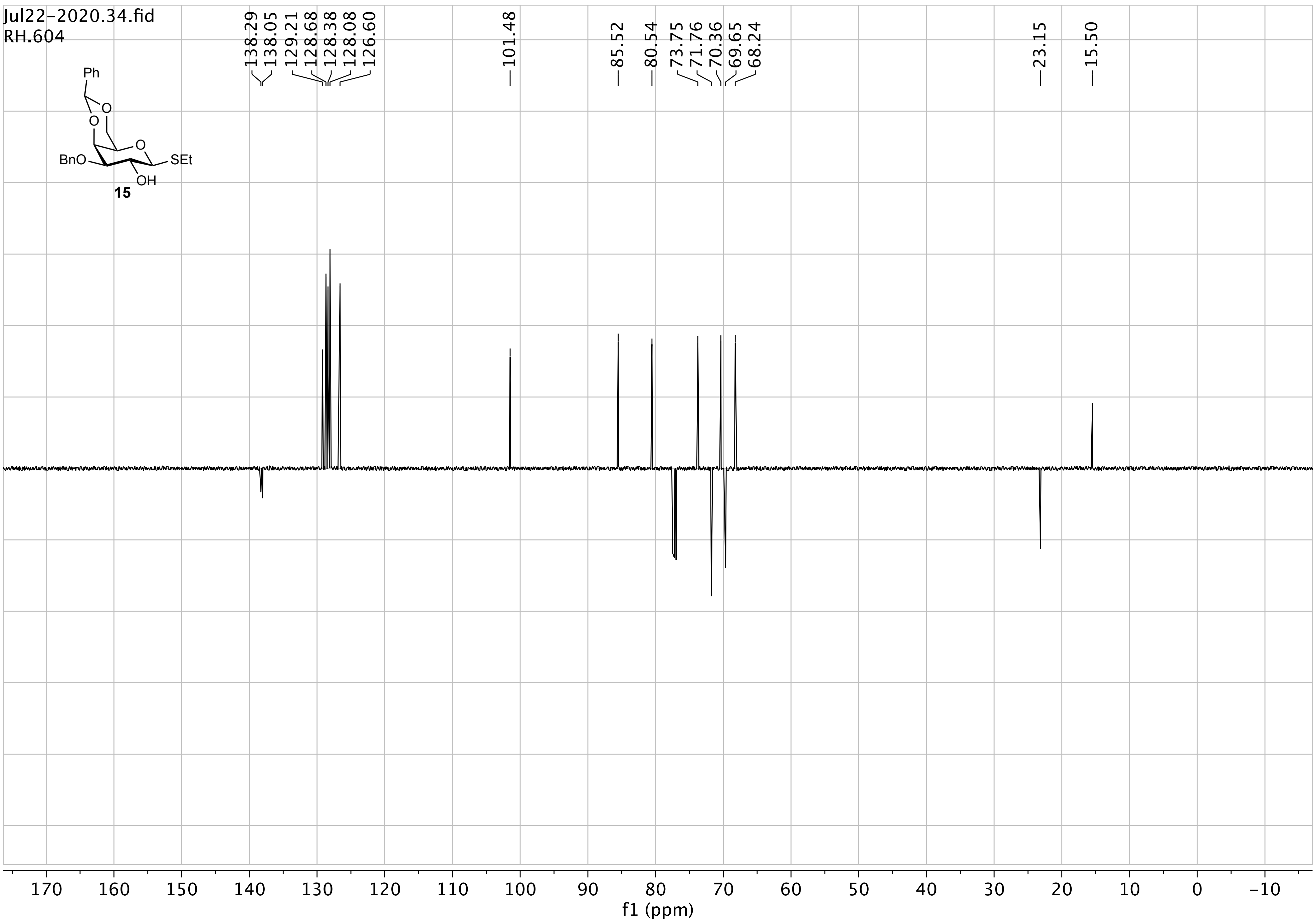


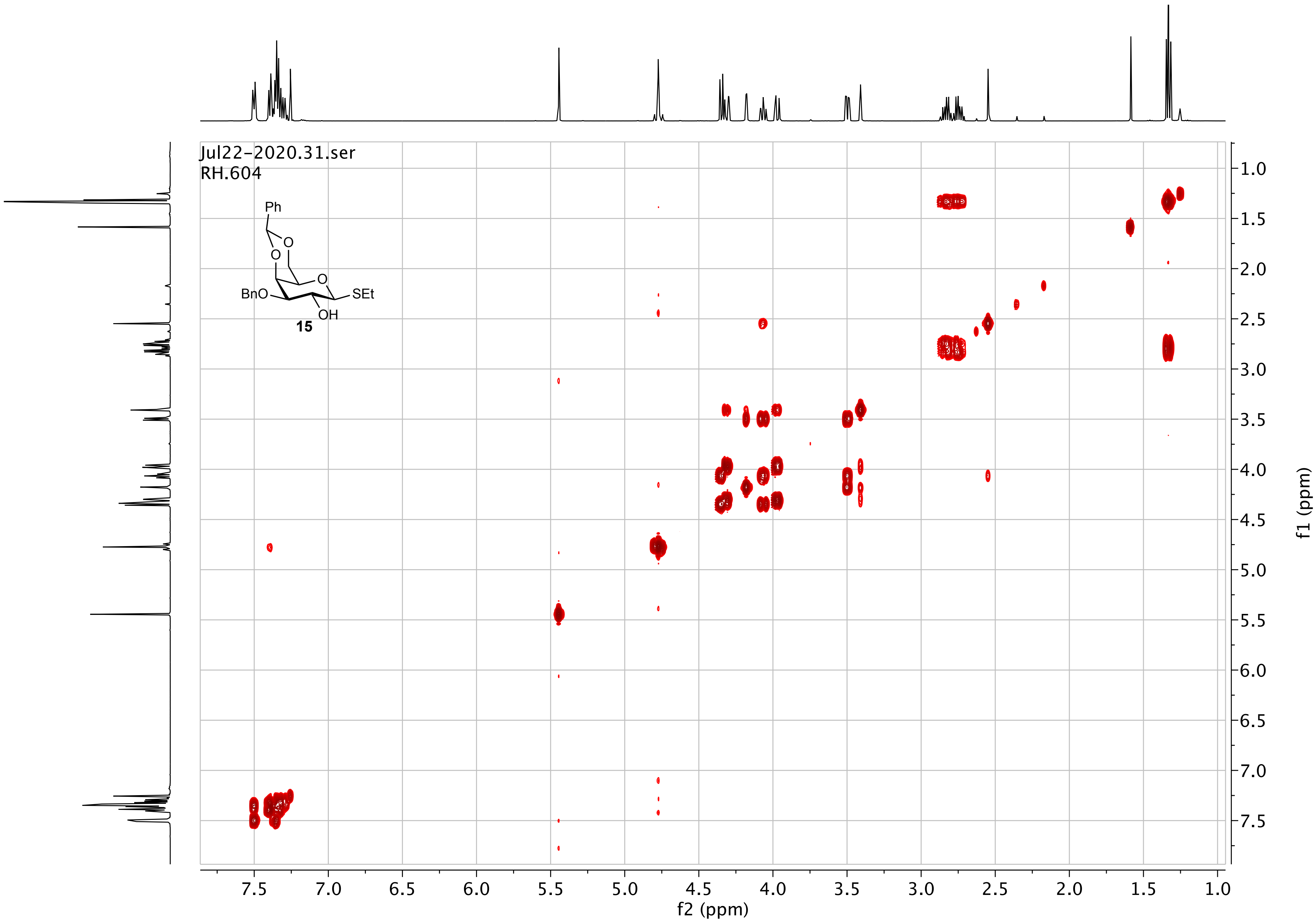
^{1}H NMR in $CDCl_3$ (500 MHz)



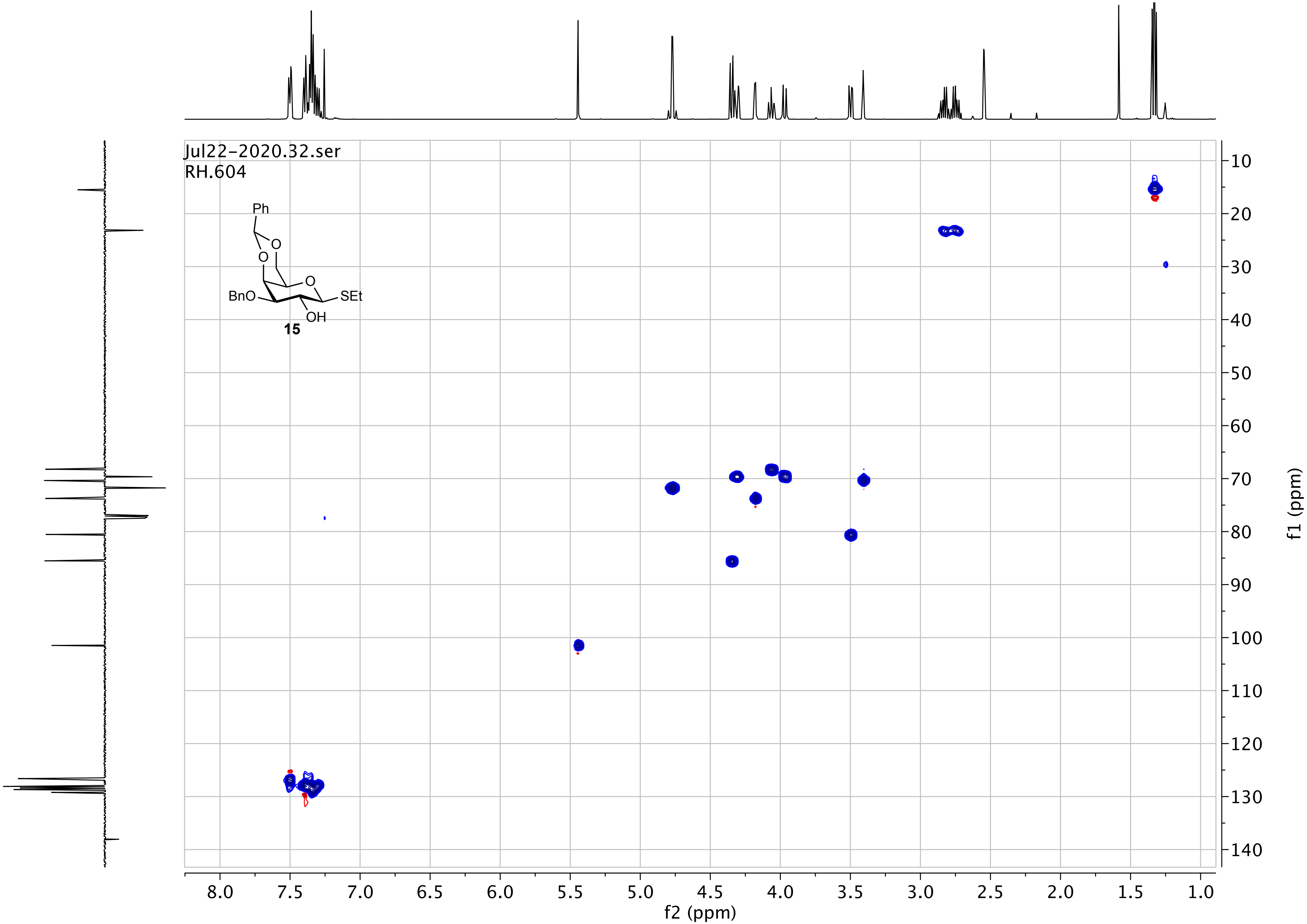
^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



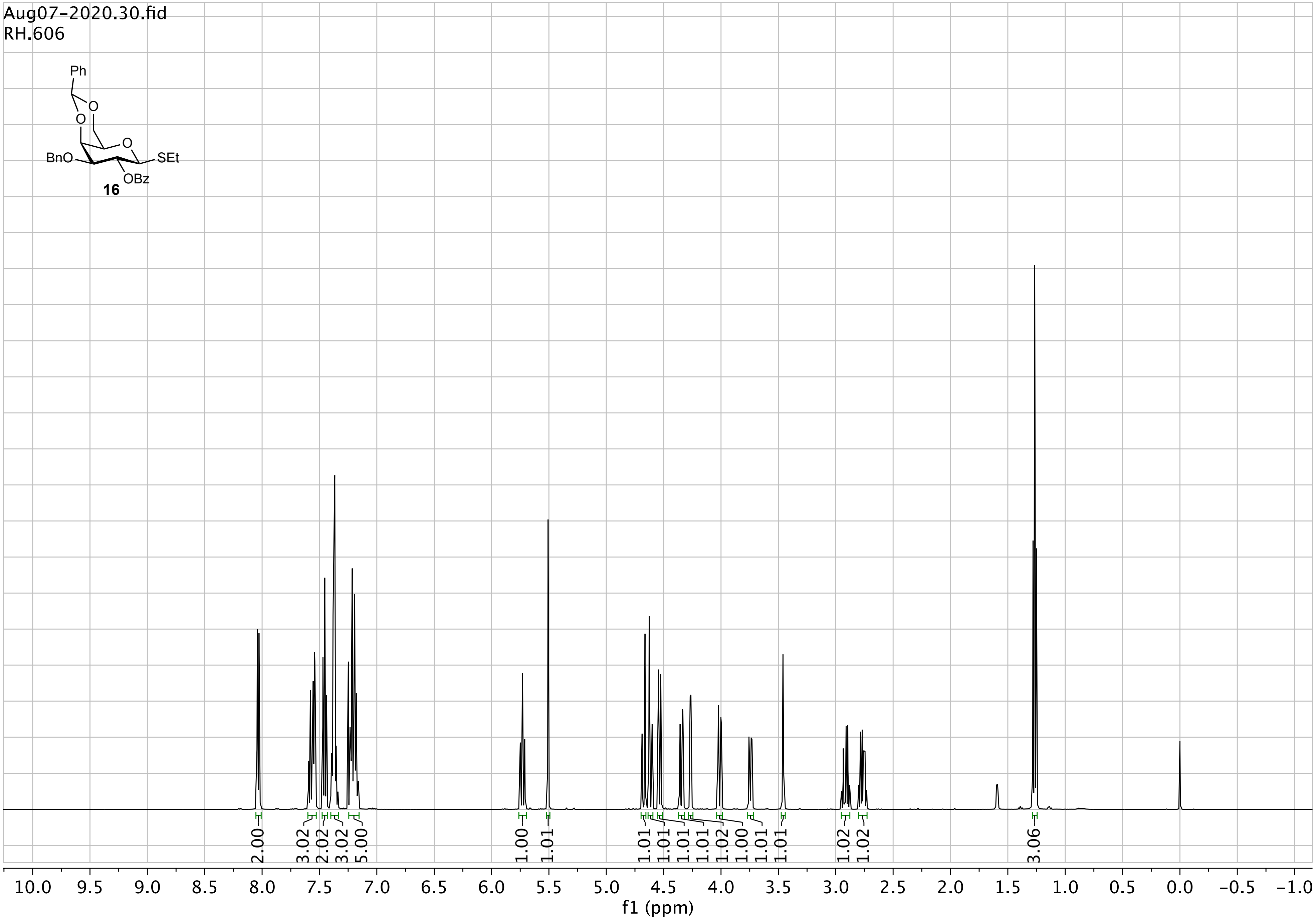
$^1H\_^1H$ gCOSY in $CDCl_3$



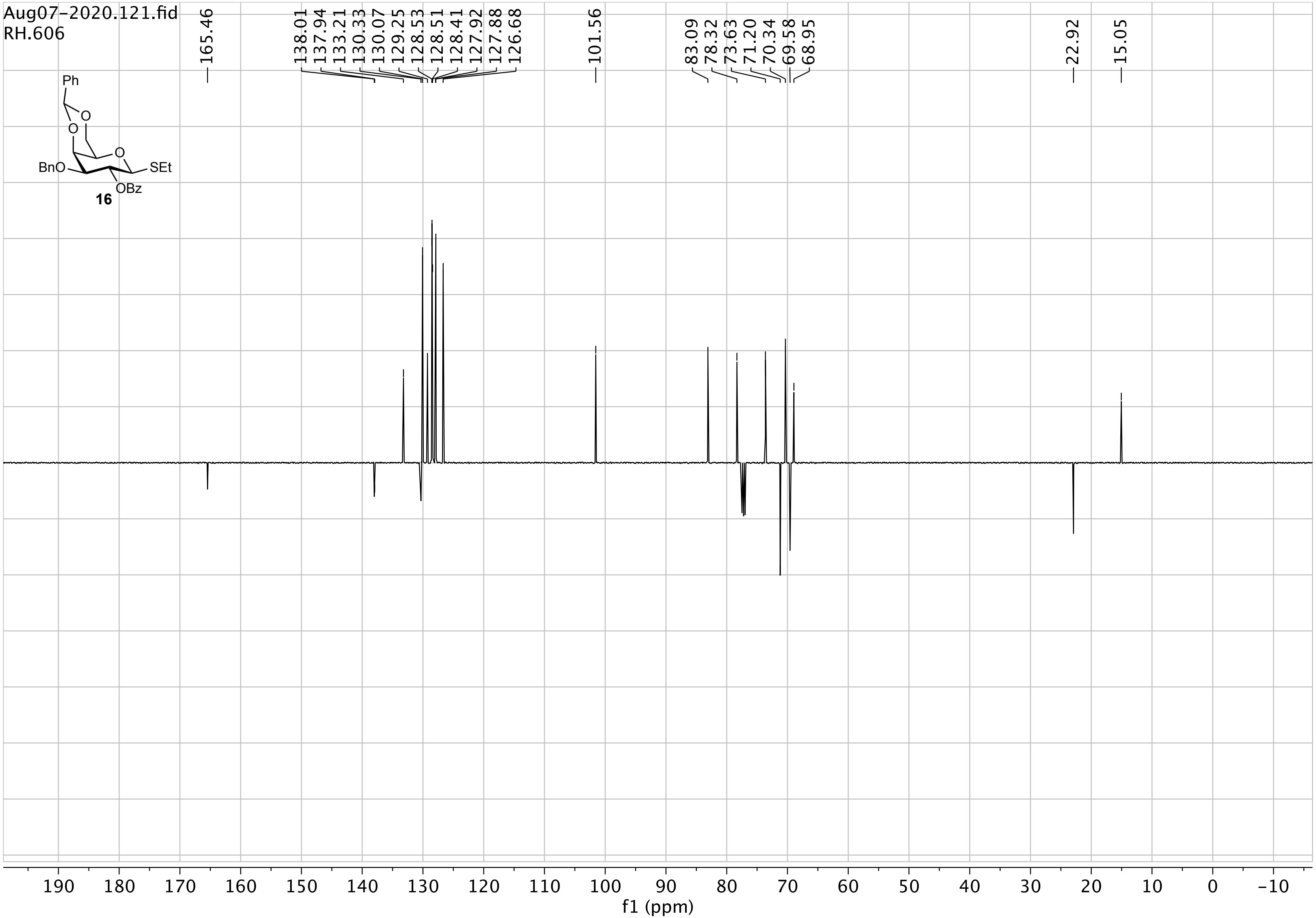
$^1H\_^{13}C$ gHSQC in $CDCl_3$



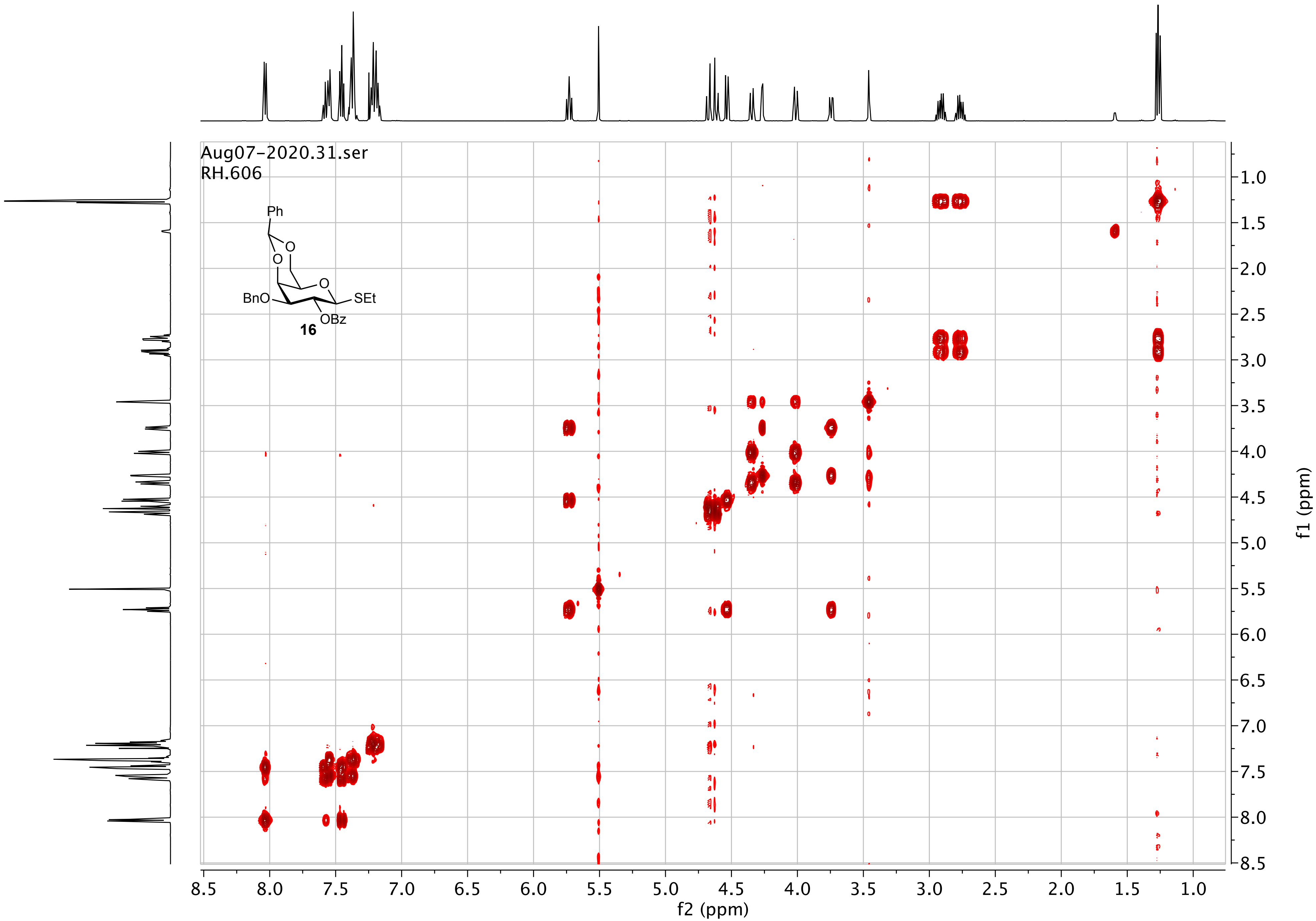
^{1}H NMR in $CDCl_3$ (500 MHz)



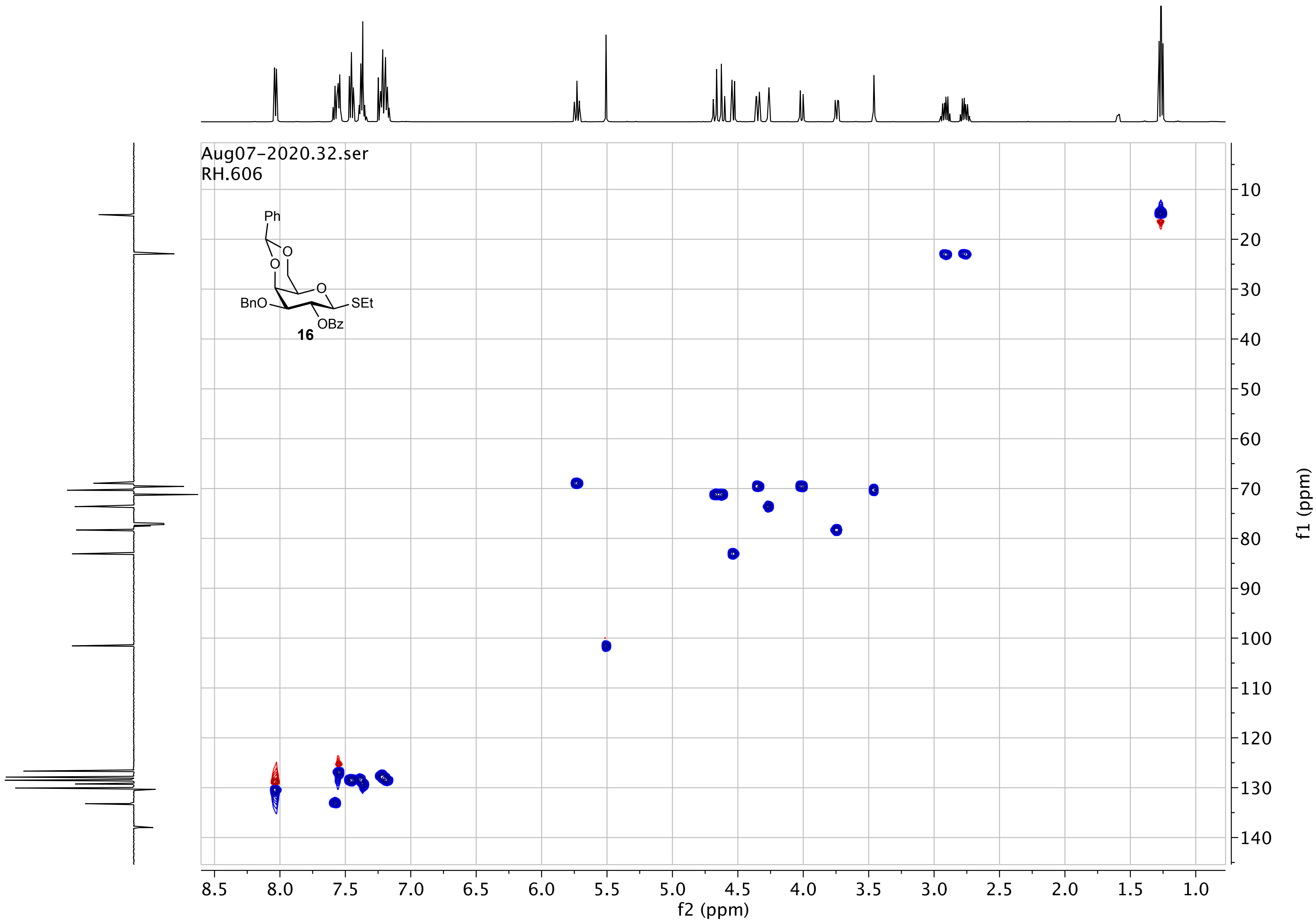
^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



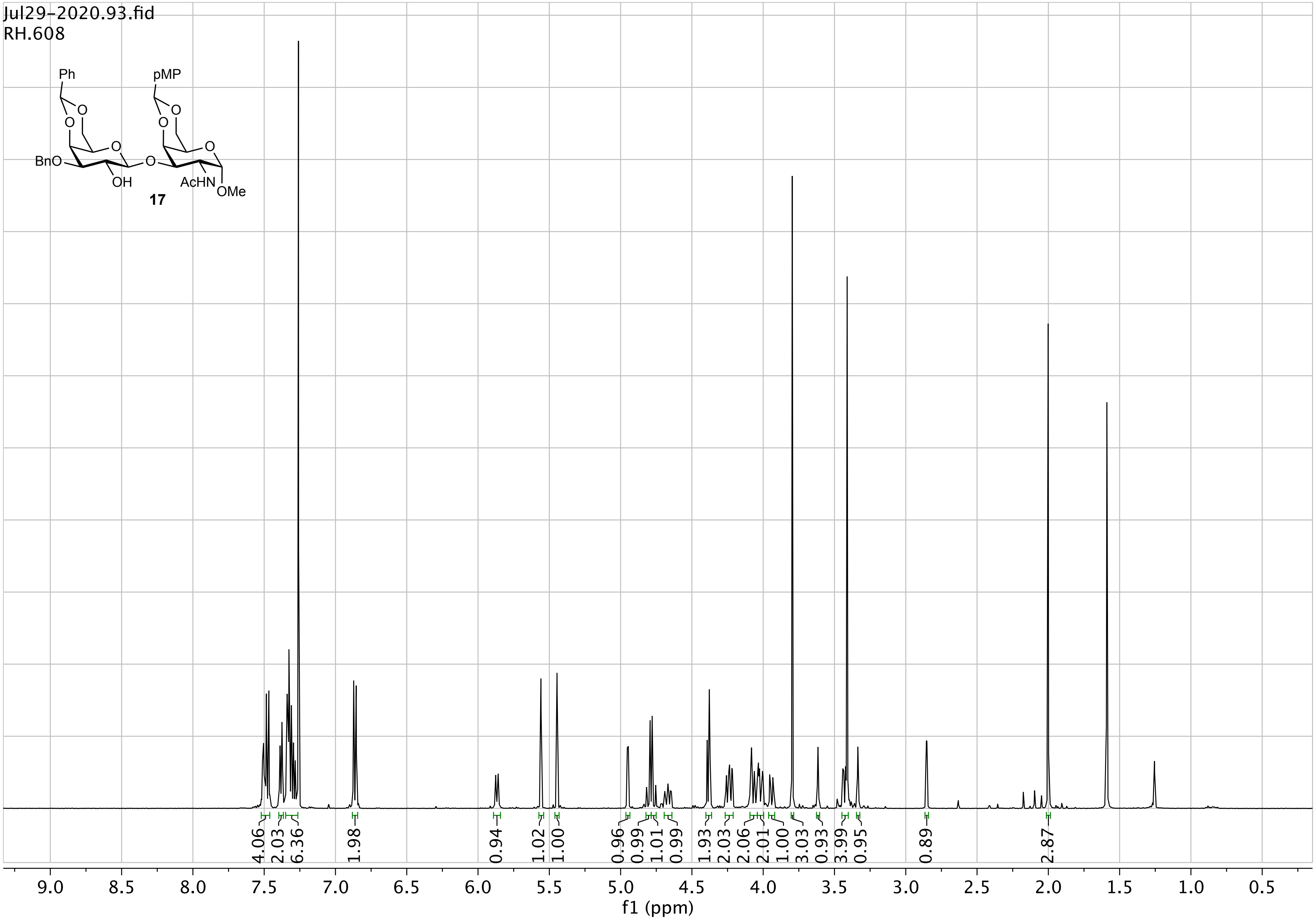
$^{1}H\_^{1}H$ gCOSY in $CDCl_3$



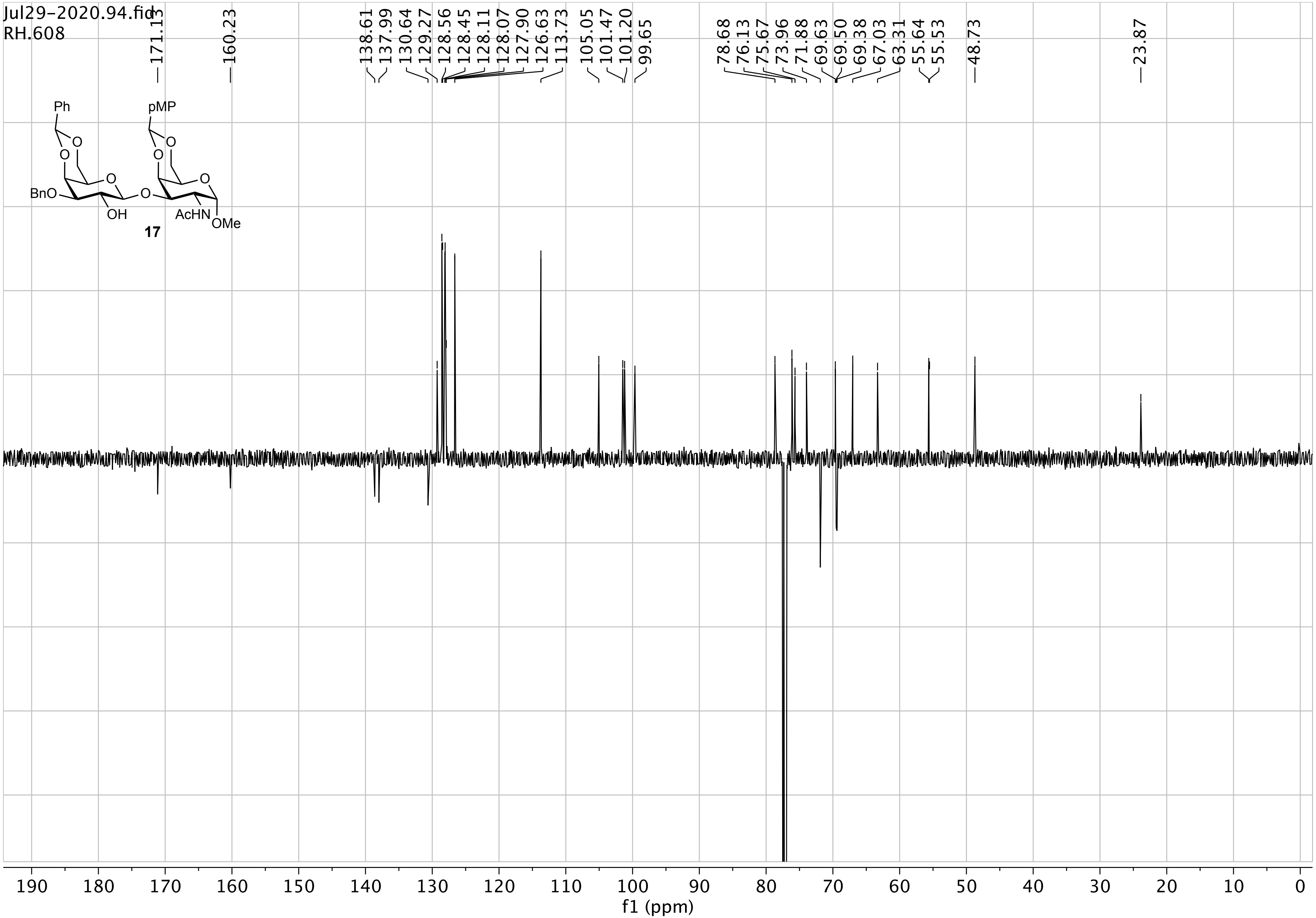
$^{1}H\_^{13}C$ gHSQC in $CDCl_3$



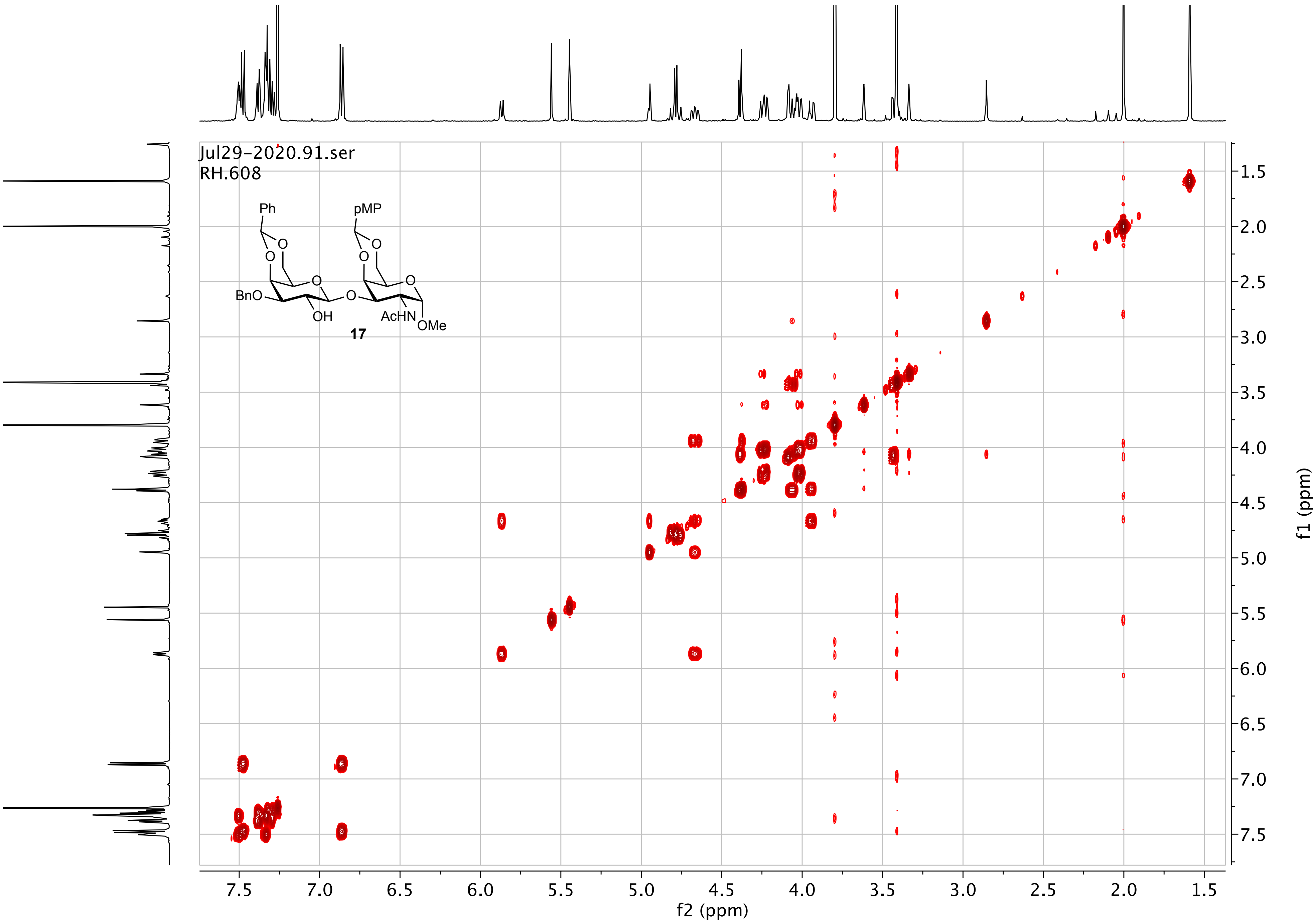
^{1}H NMR in $CDCl_3$ (500 MHz)



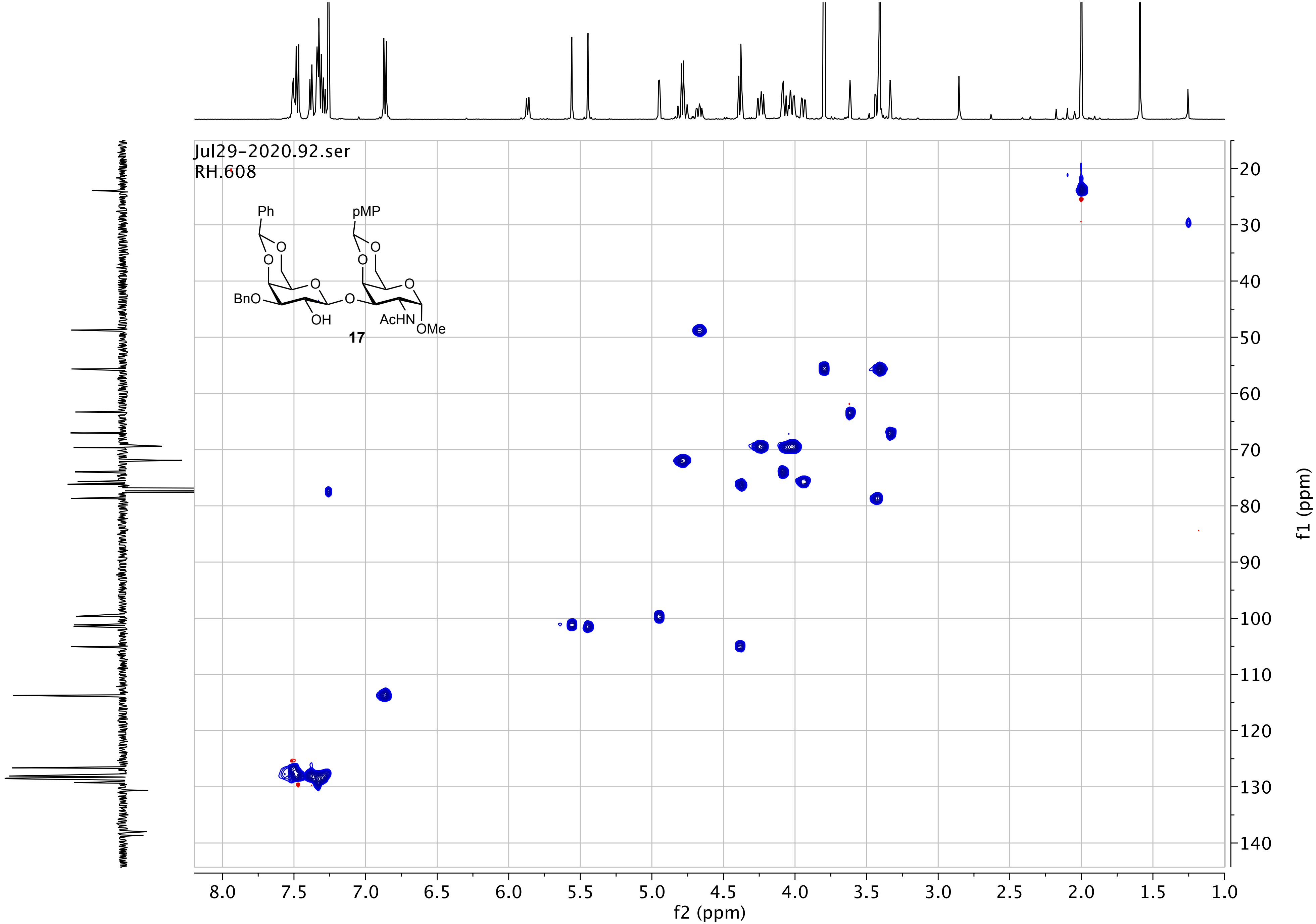
^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



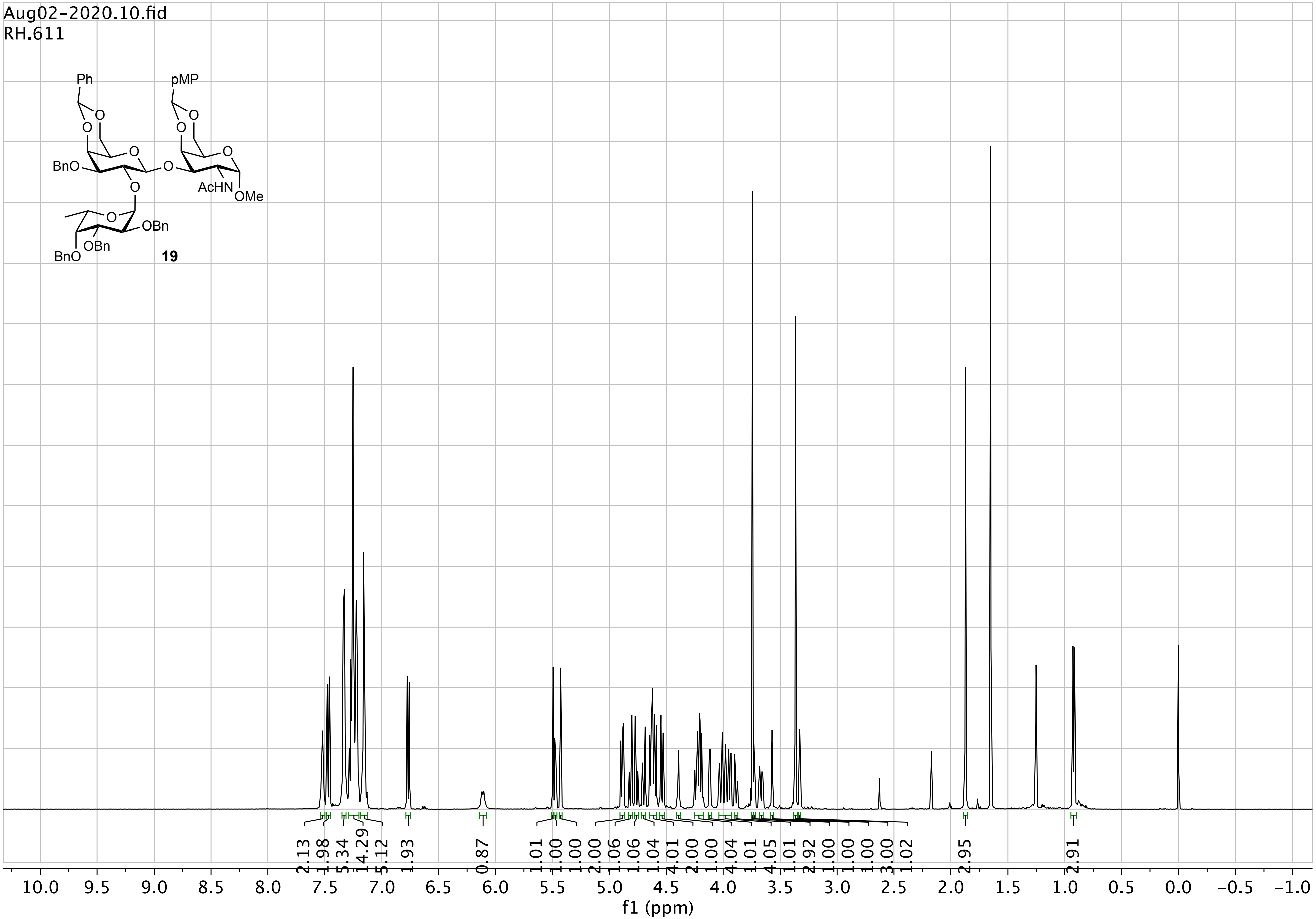
$^1H\_^1H$ gCOSY in $CDCl_3$



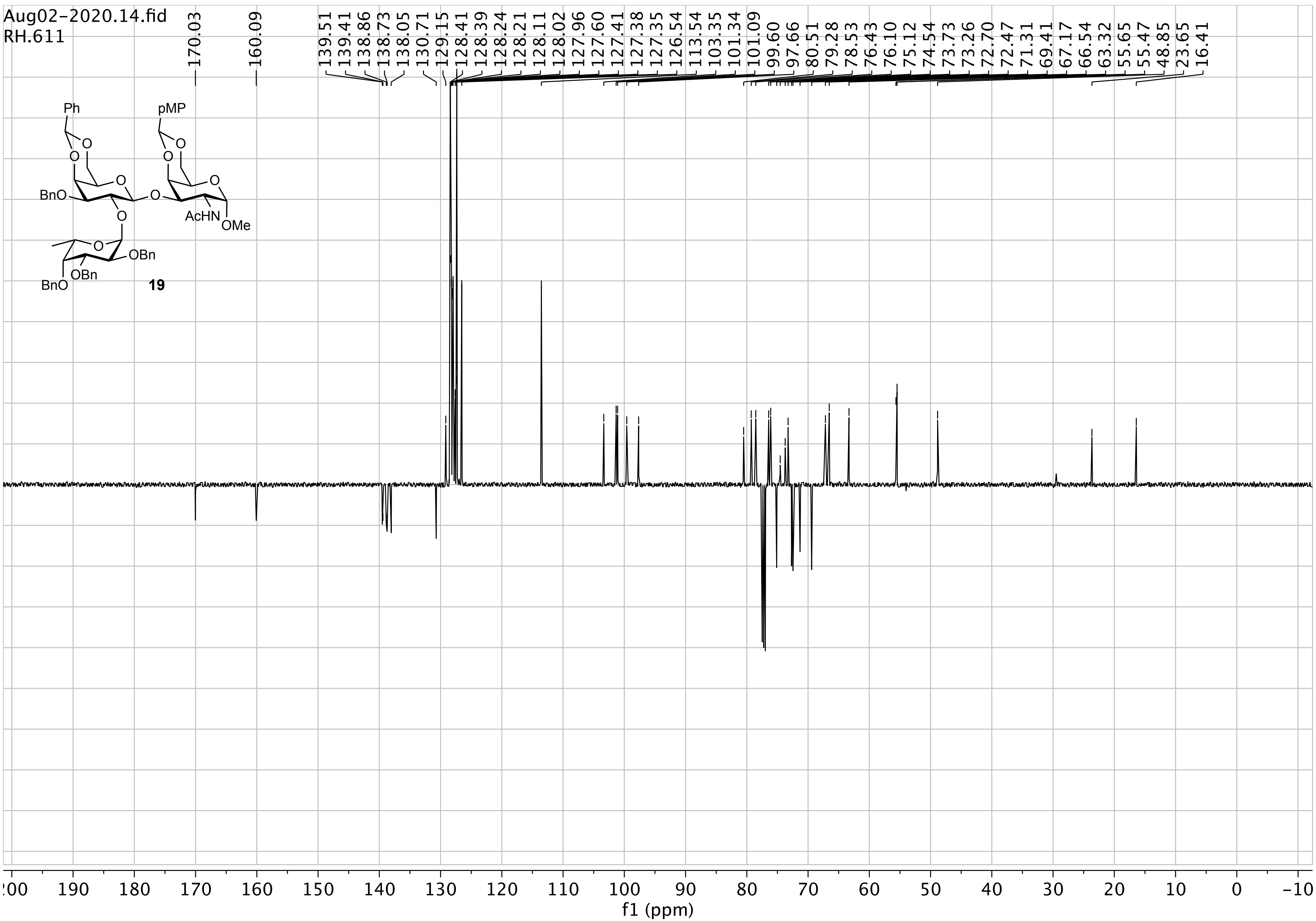
$^1H\_^{13}C$ gHSQC in $CDCl_3$



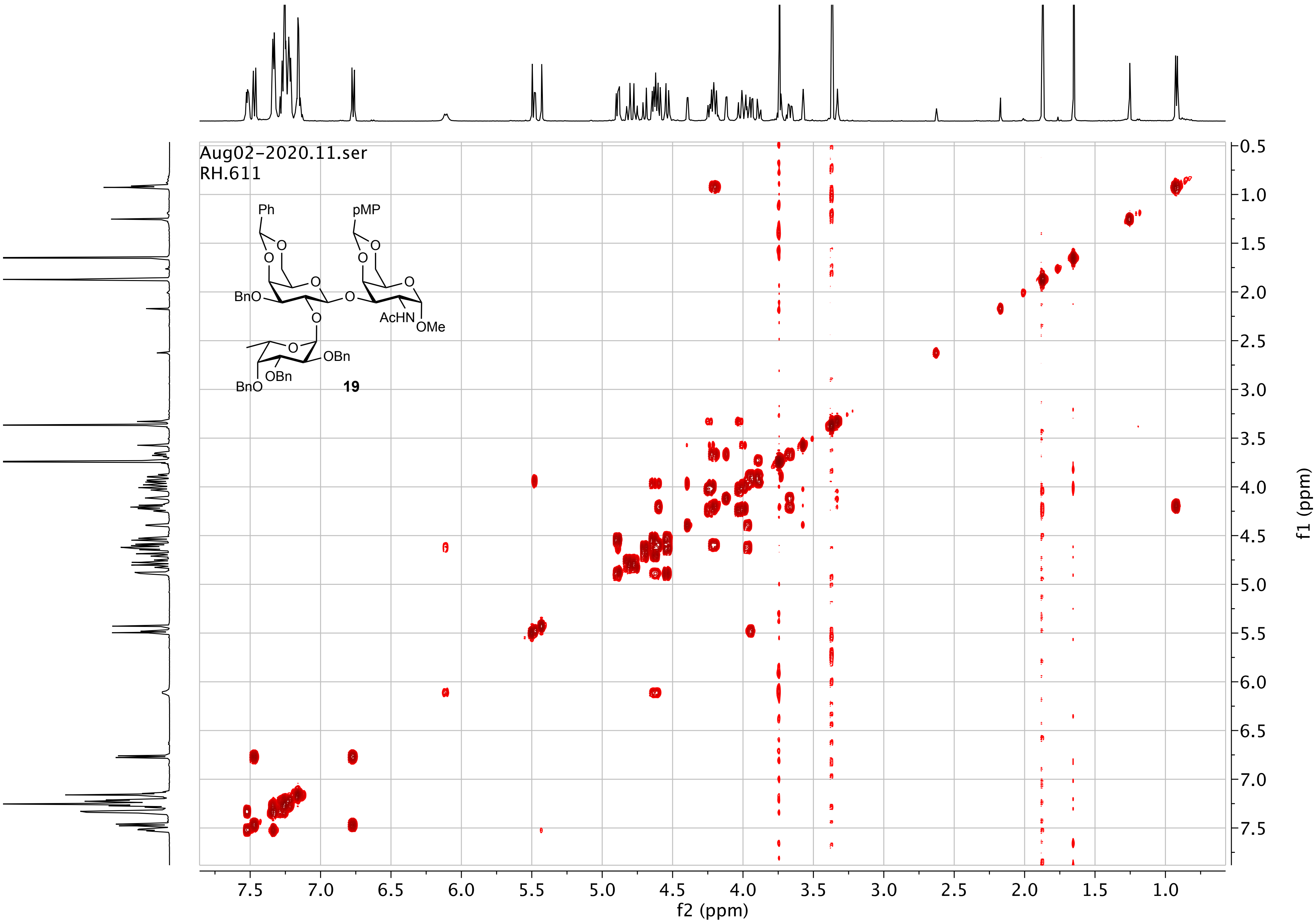
^1H NMR in $CDCl_3$ (500 MHz)



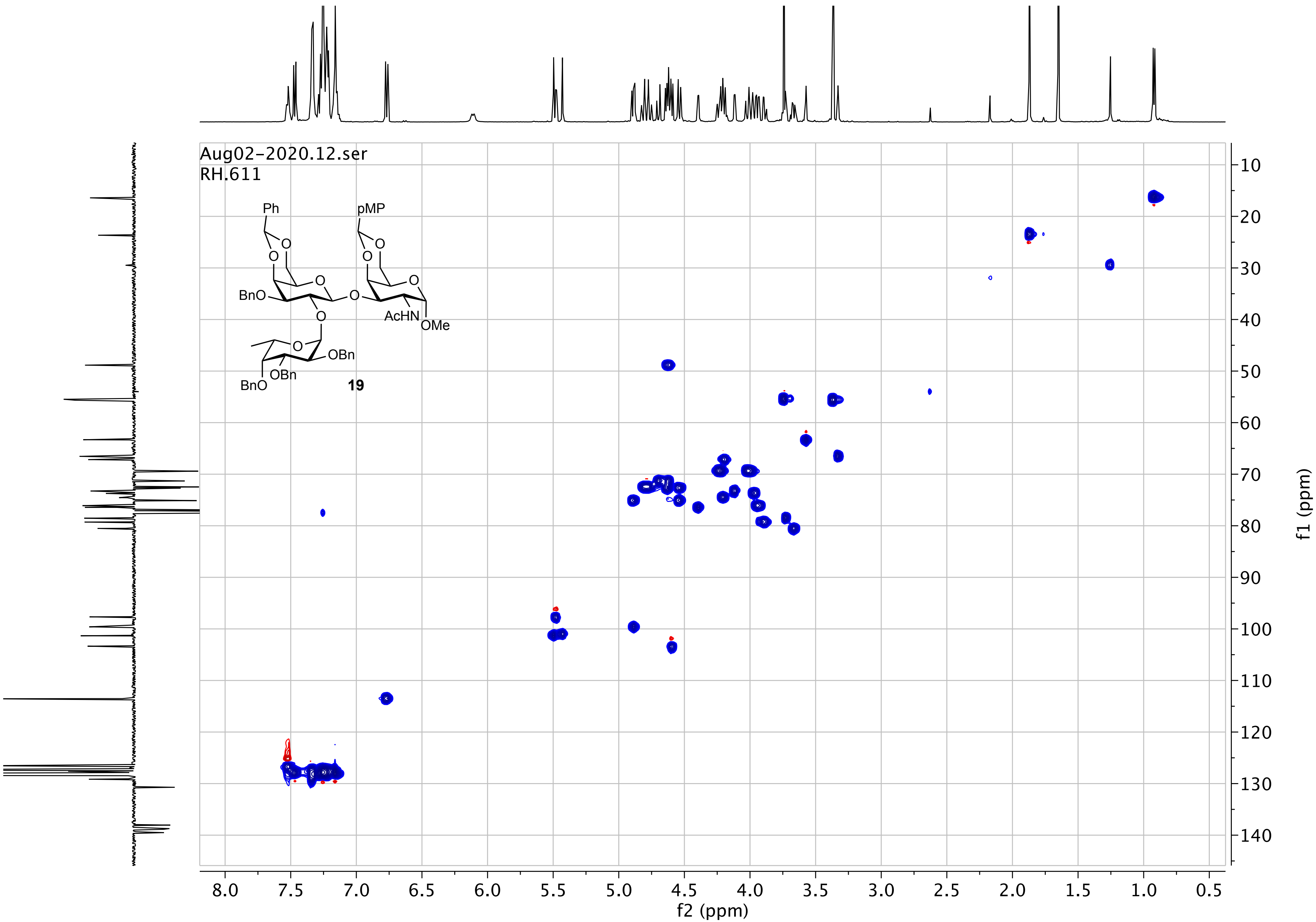
^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



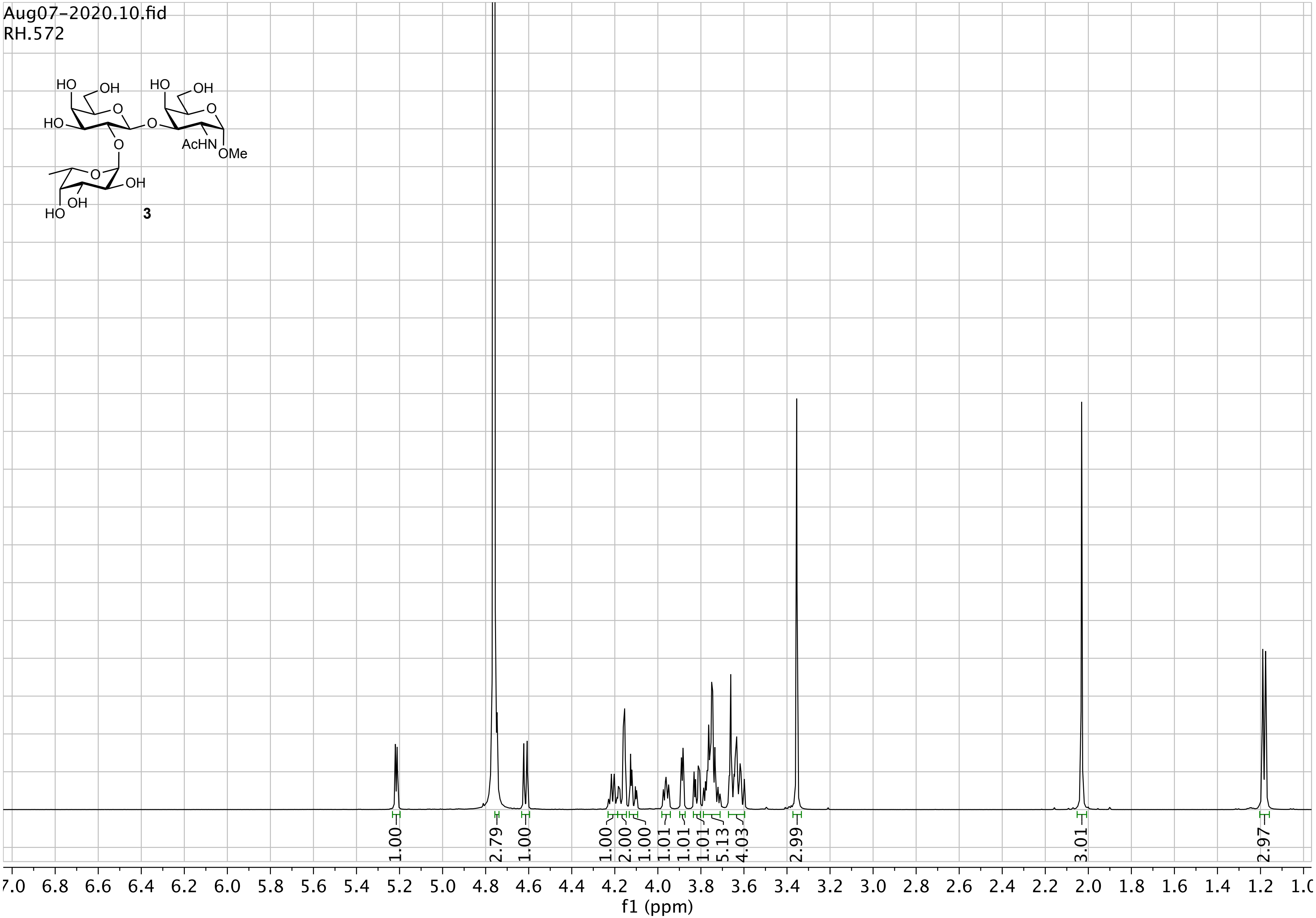
^1H_^1H gCOSY in $CDCl_3$



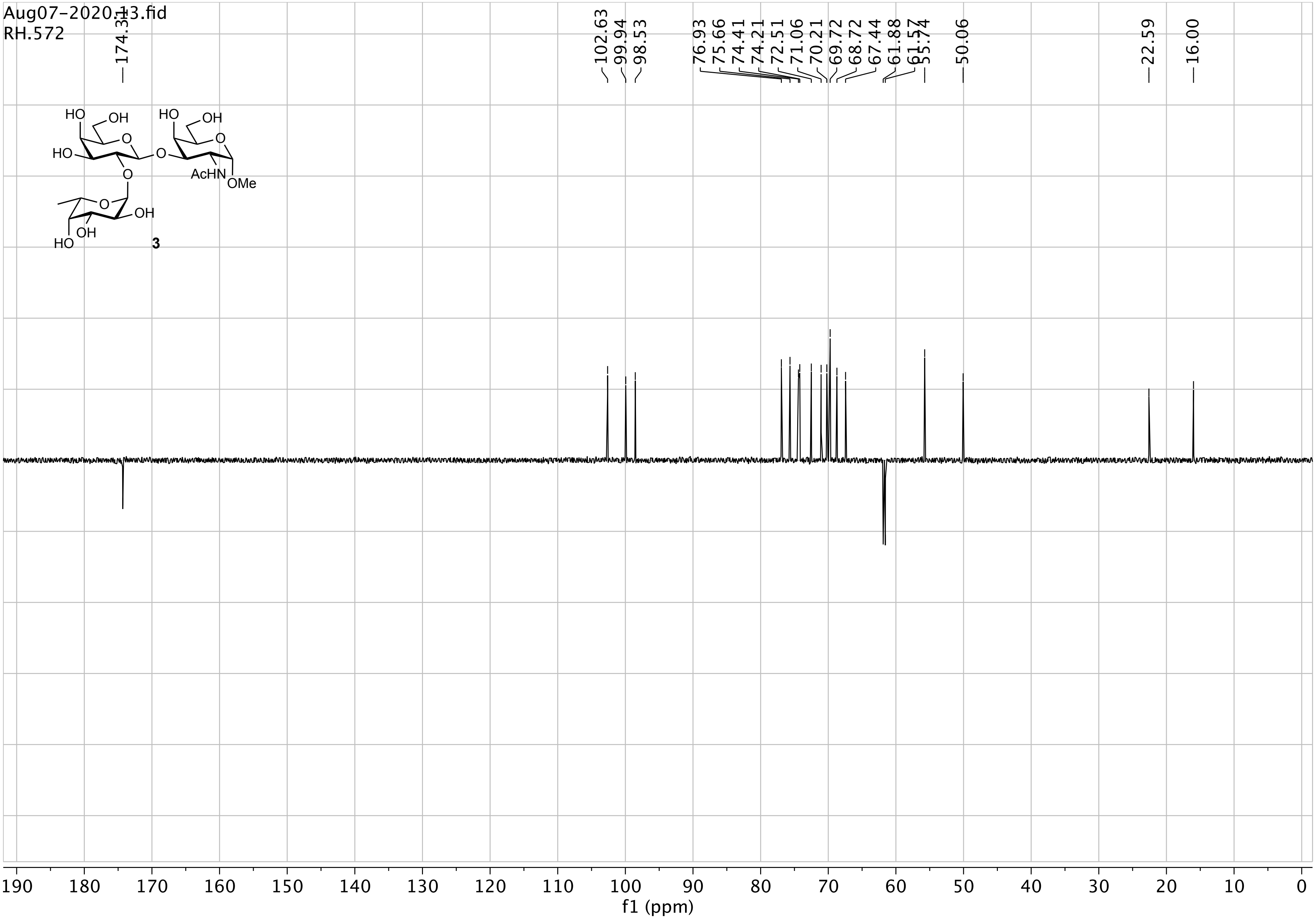
$^{1}H\_^{13}C$ gHSQC in $CDCl_3$



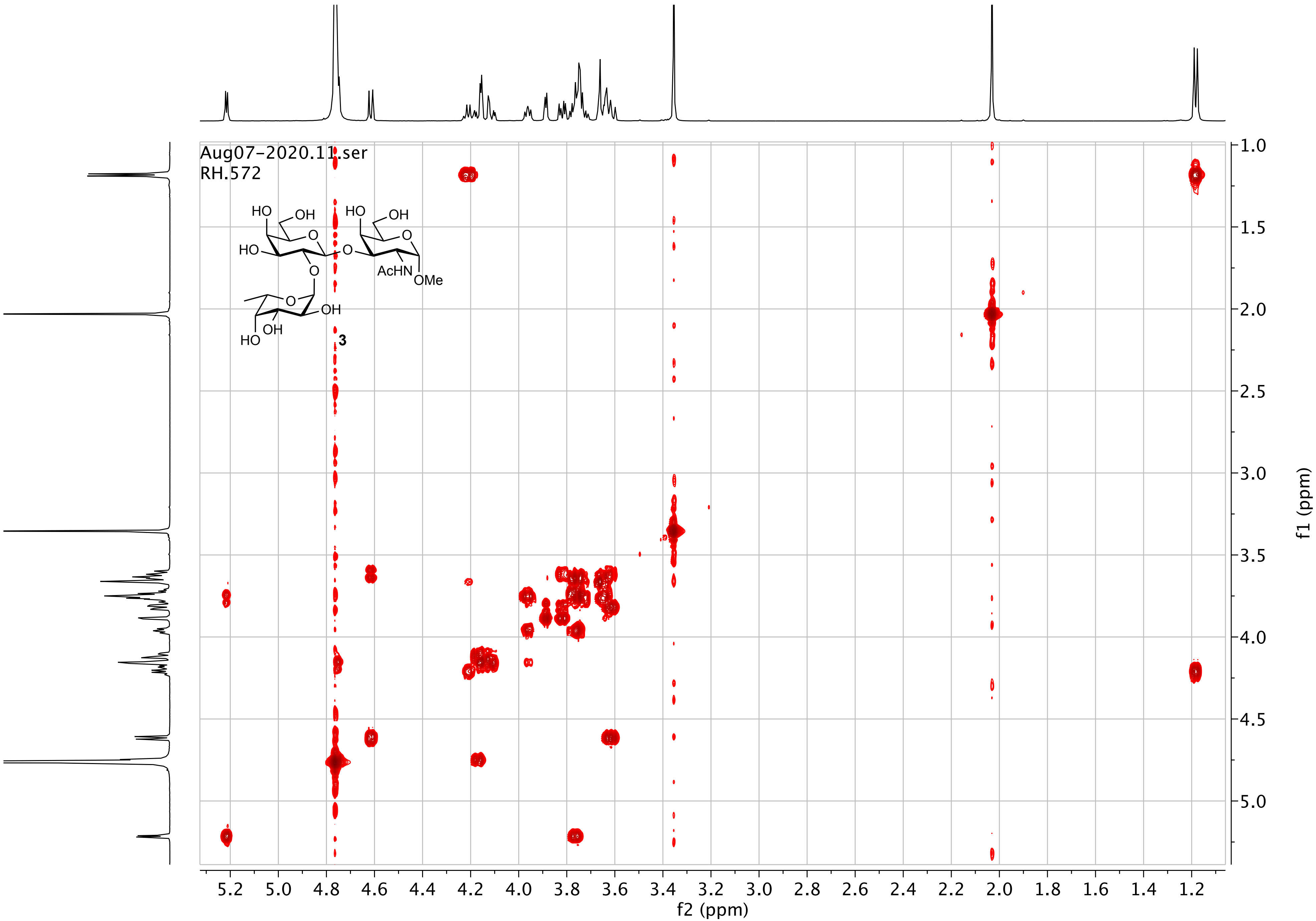
^1H NMR in D_2O (500 MHz)



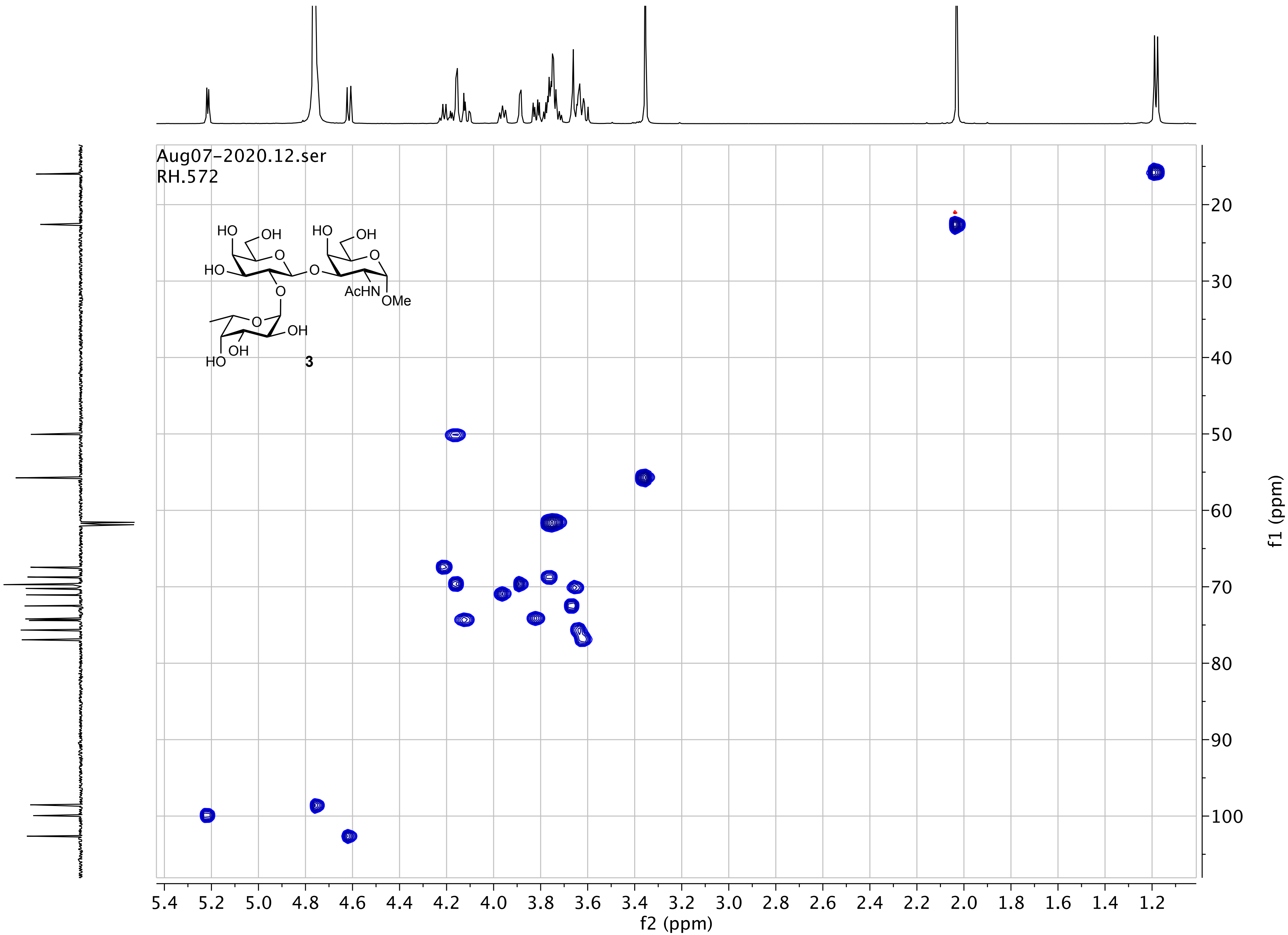
^{13}C NMR (APT) in D_2O (125 MHz)



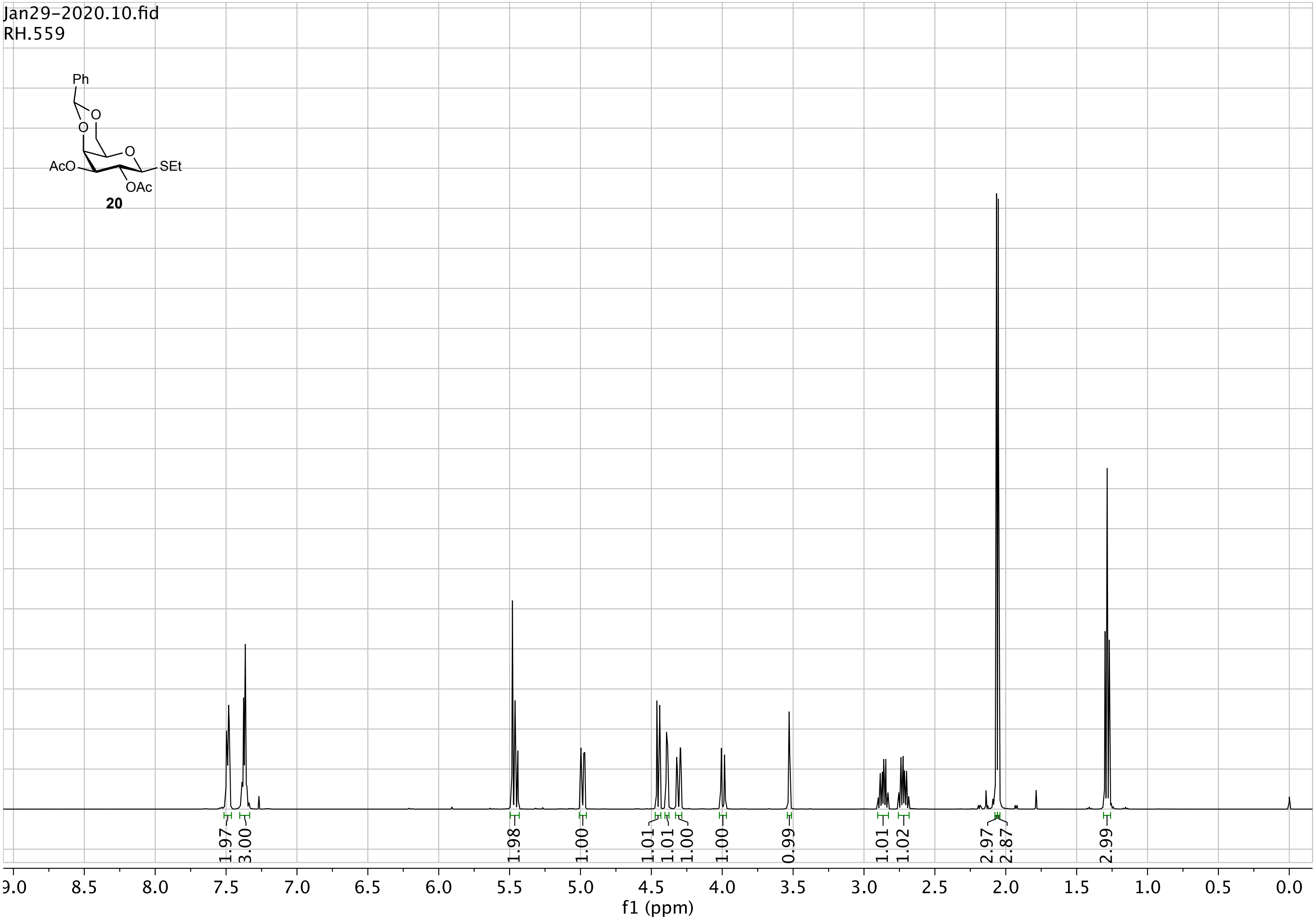
$^{1}H\_^{1}H$ gCOSY in D_2O



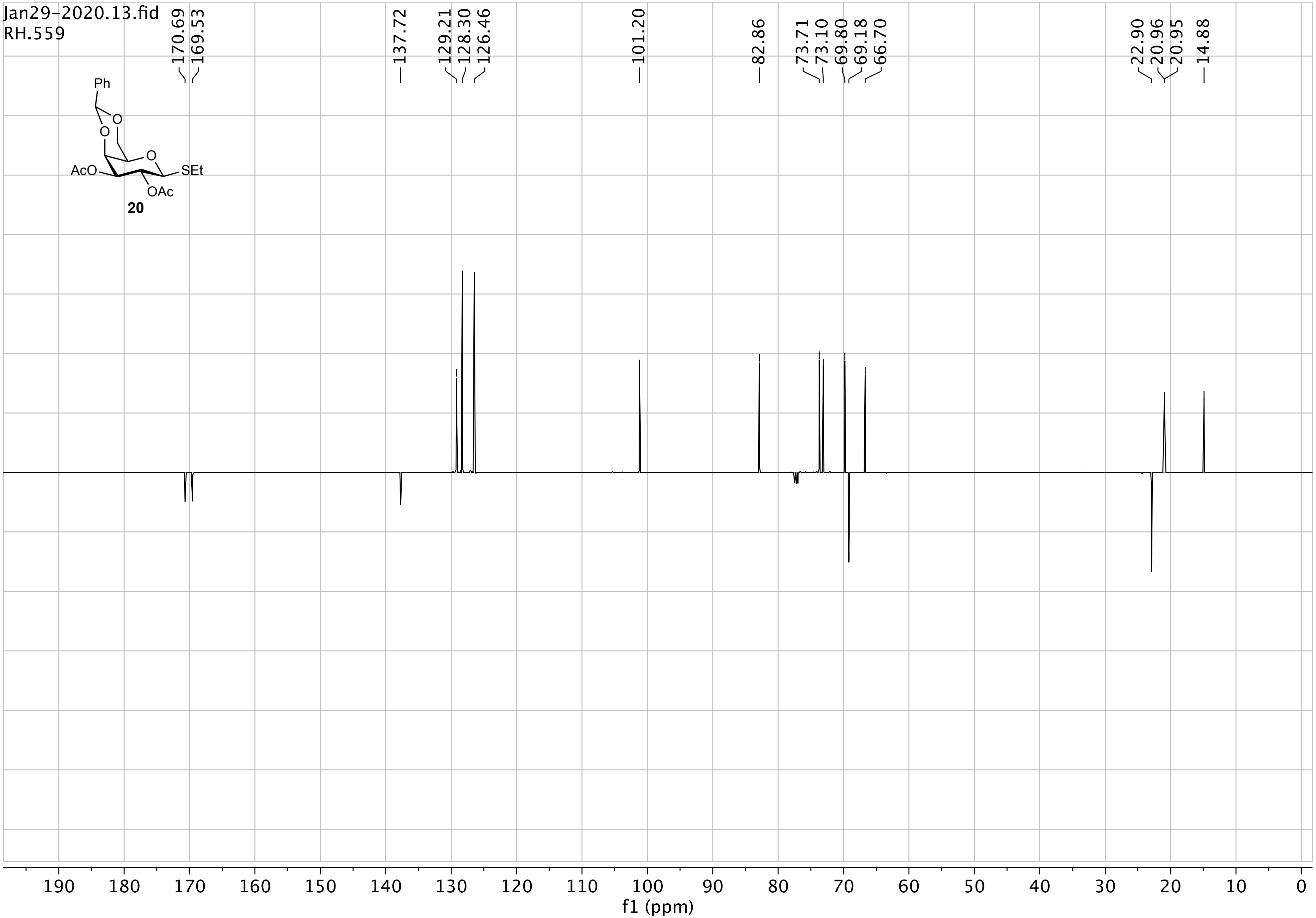
$^{1}H\_^{13}C$ gHSQC in D_2O



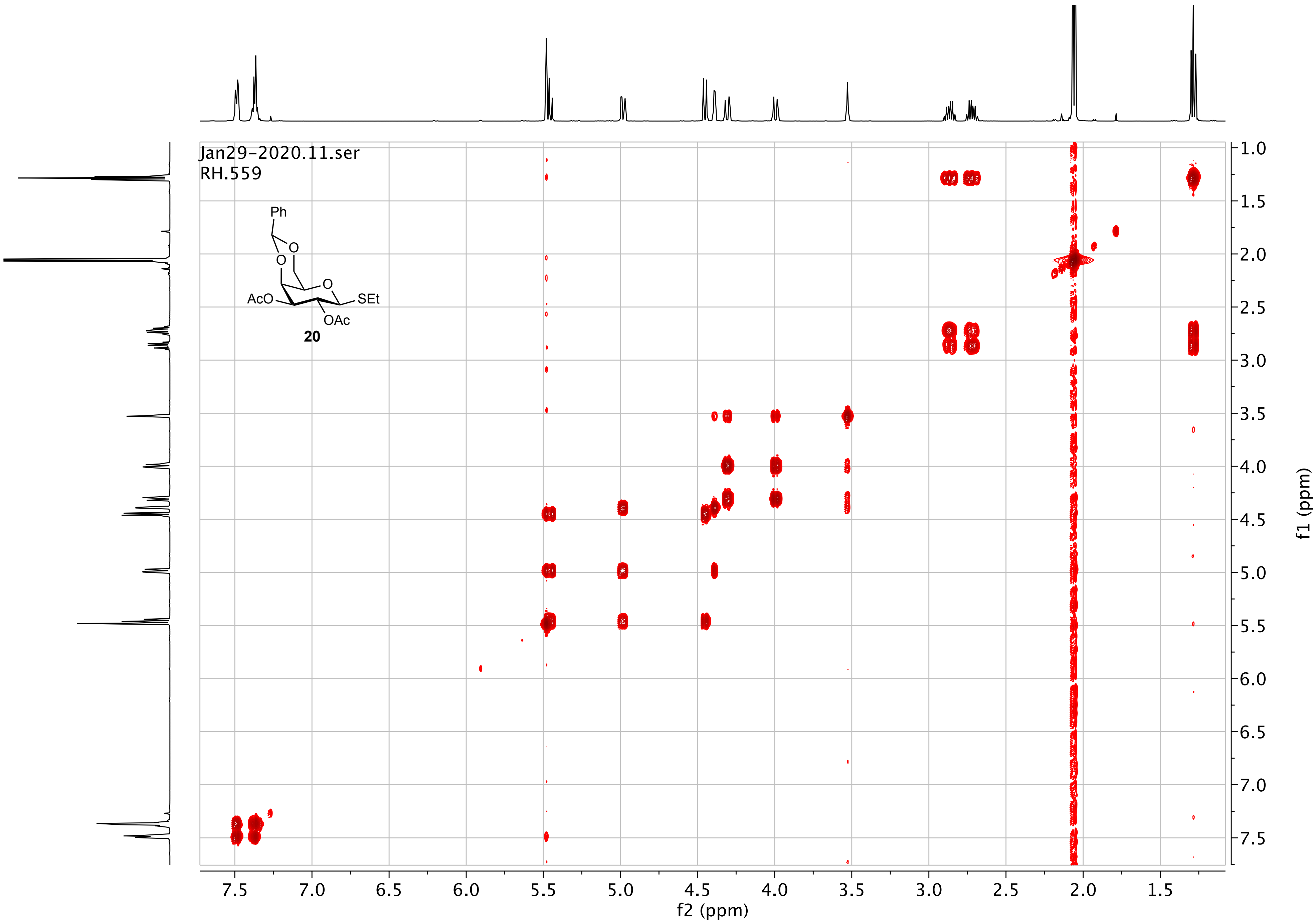
^{1}H NMR in $CDCl_3$ (500 MHz)



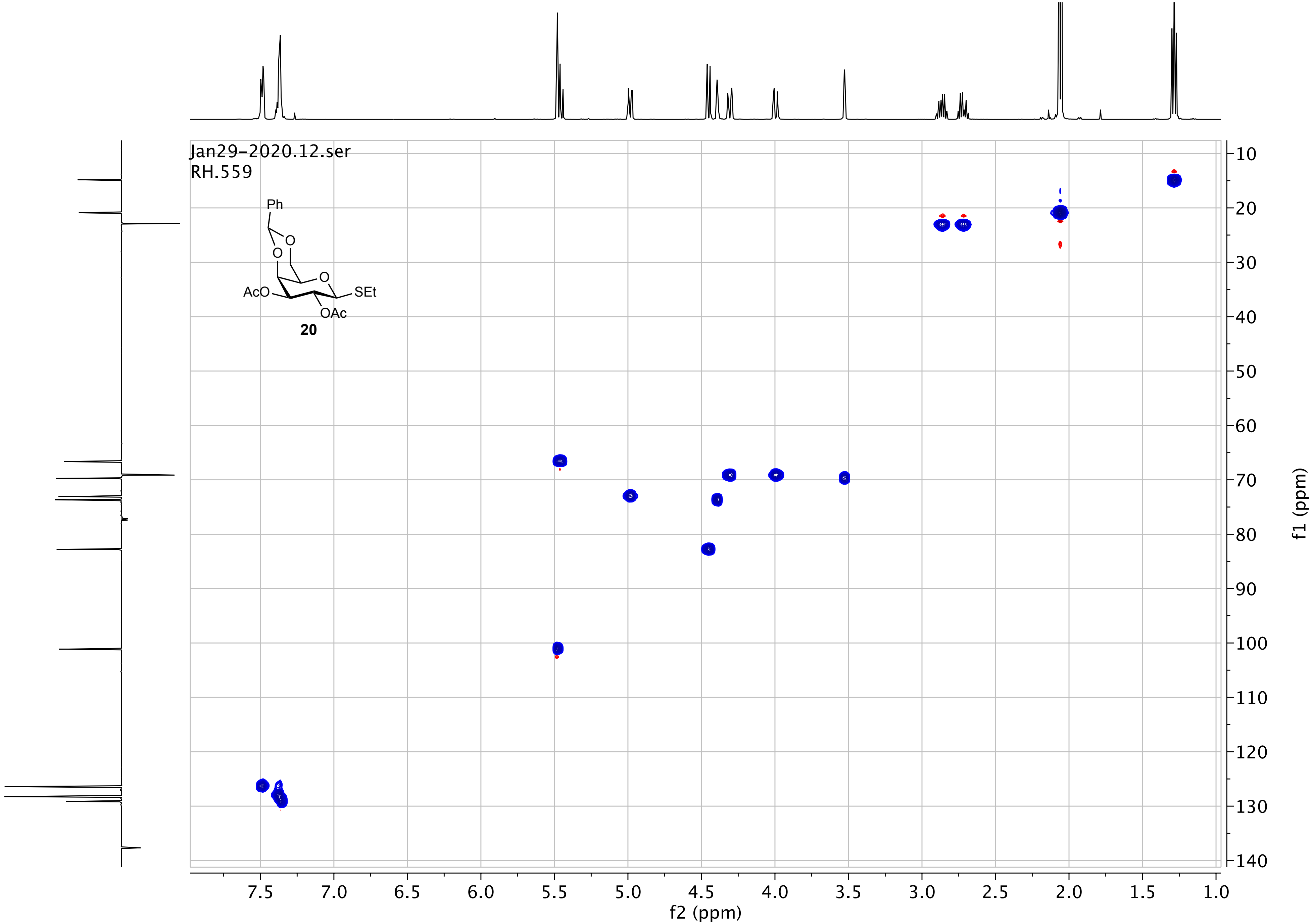
^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



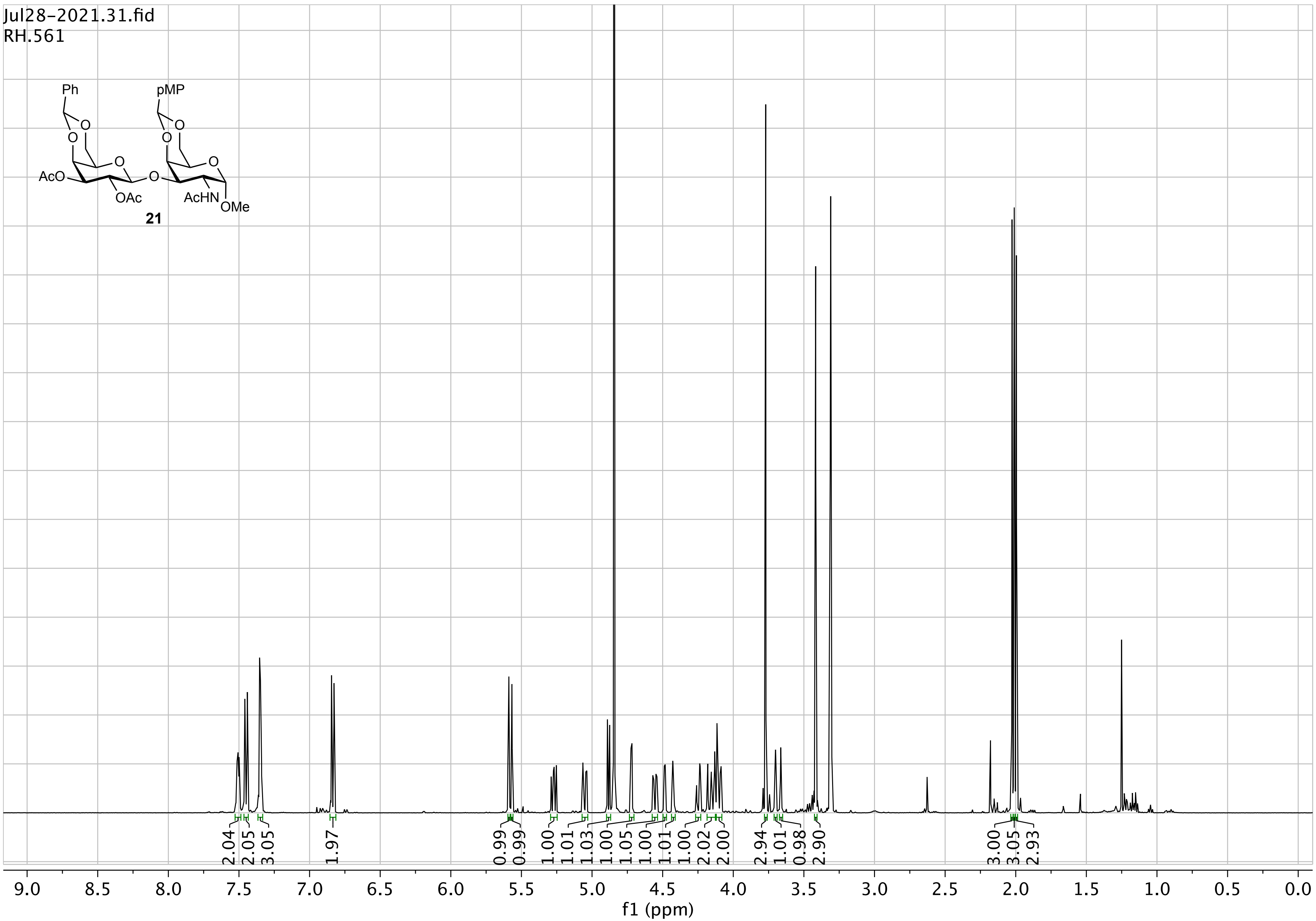
$^1H\_^1H$ gCOSY in $CDCl_3$



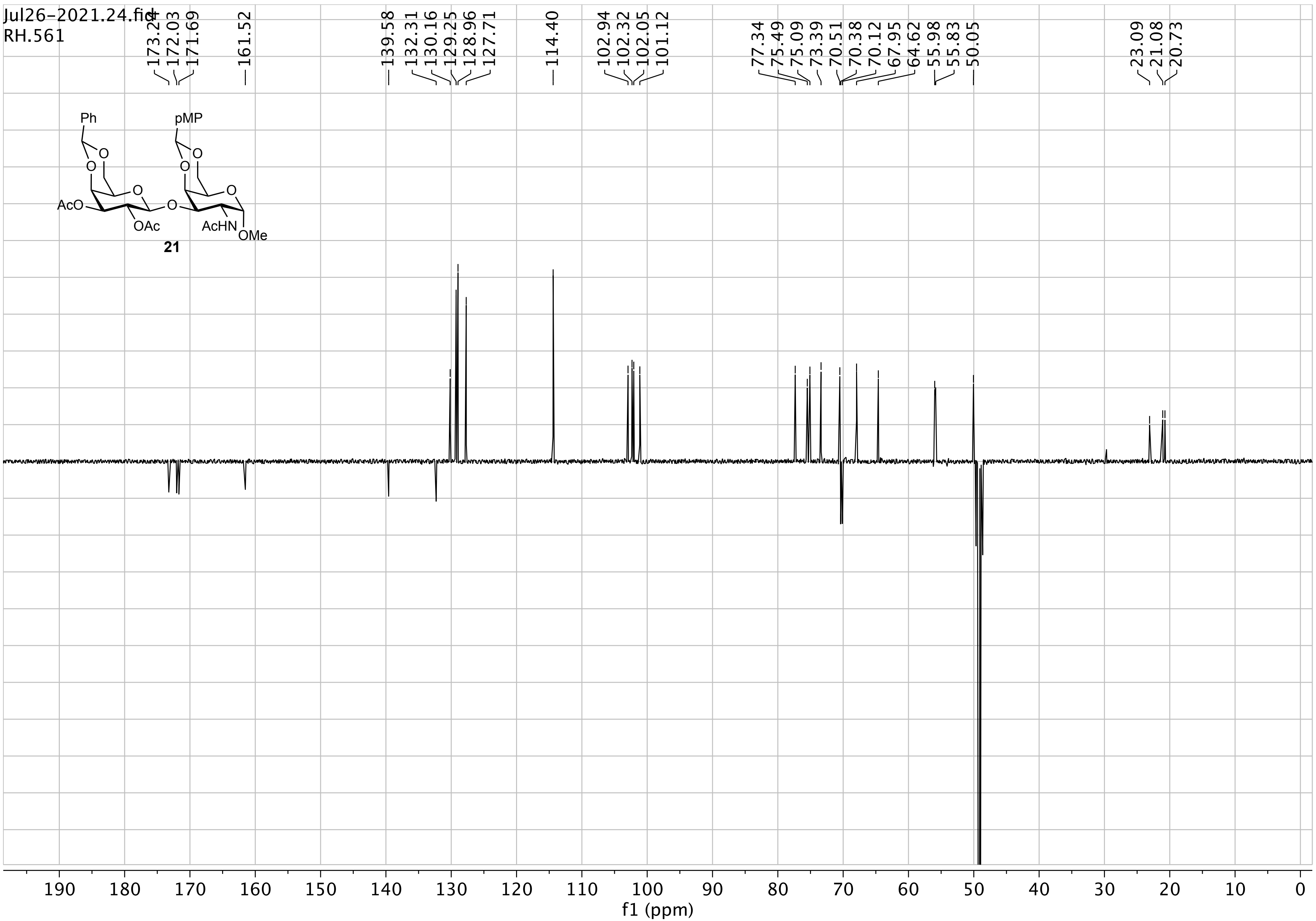
$^{1}H\_^{13}C$ gHSQC in $CDCl_3$



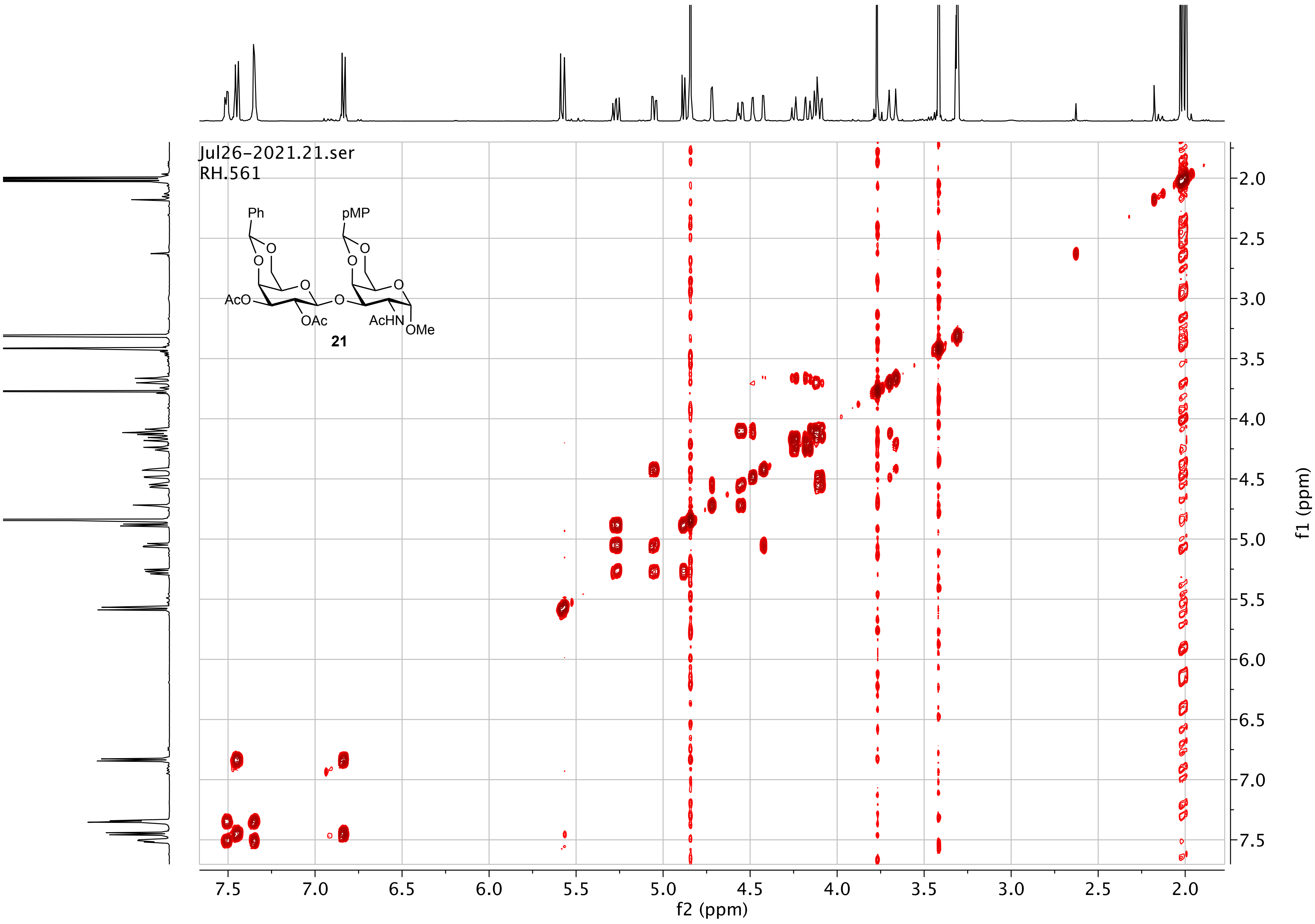
^{1}H NMR in CD_3OD (500 MHz)



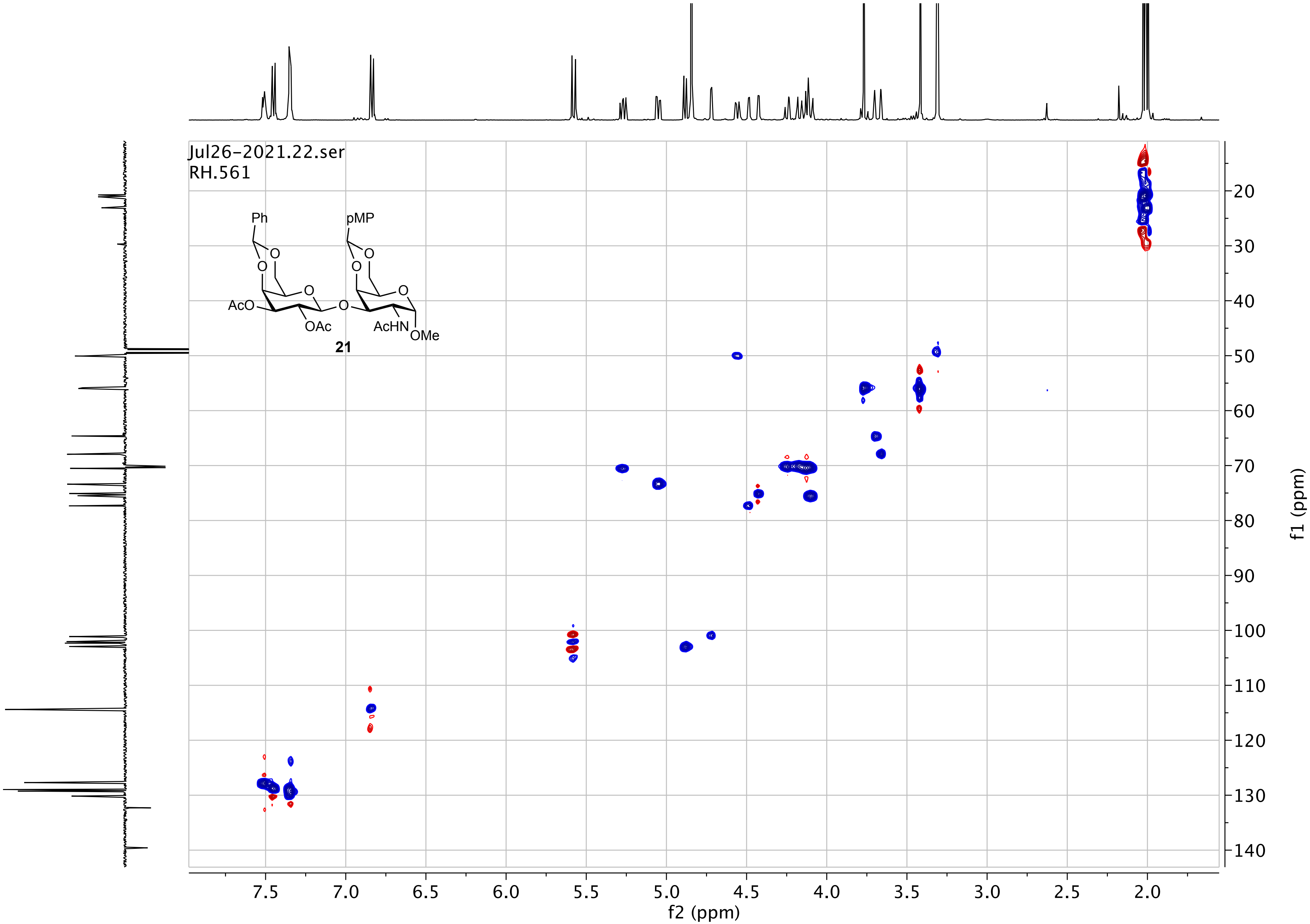
^{13}C NMR (APT) in CD_3OD (125 MHz)



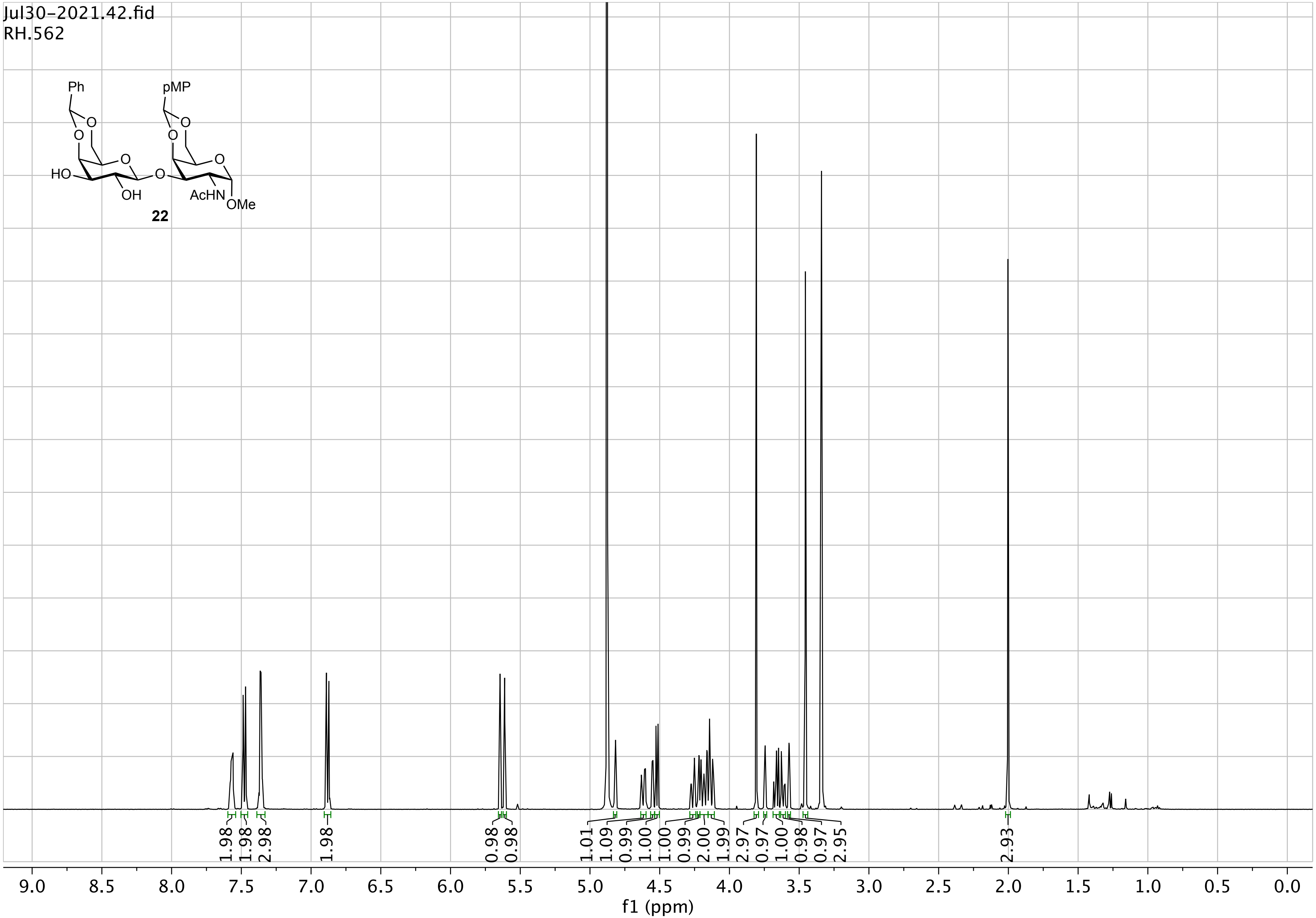
$^{1}H\_^{1}H$ gCOSY in CD_3OD



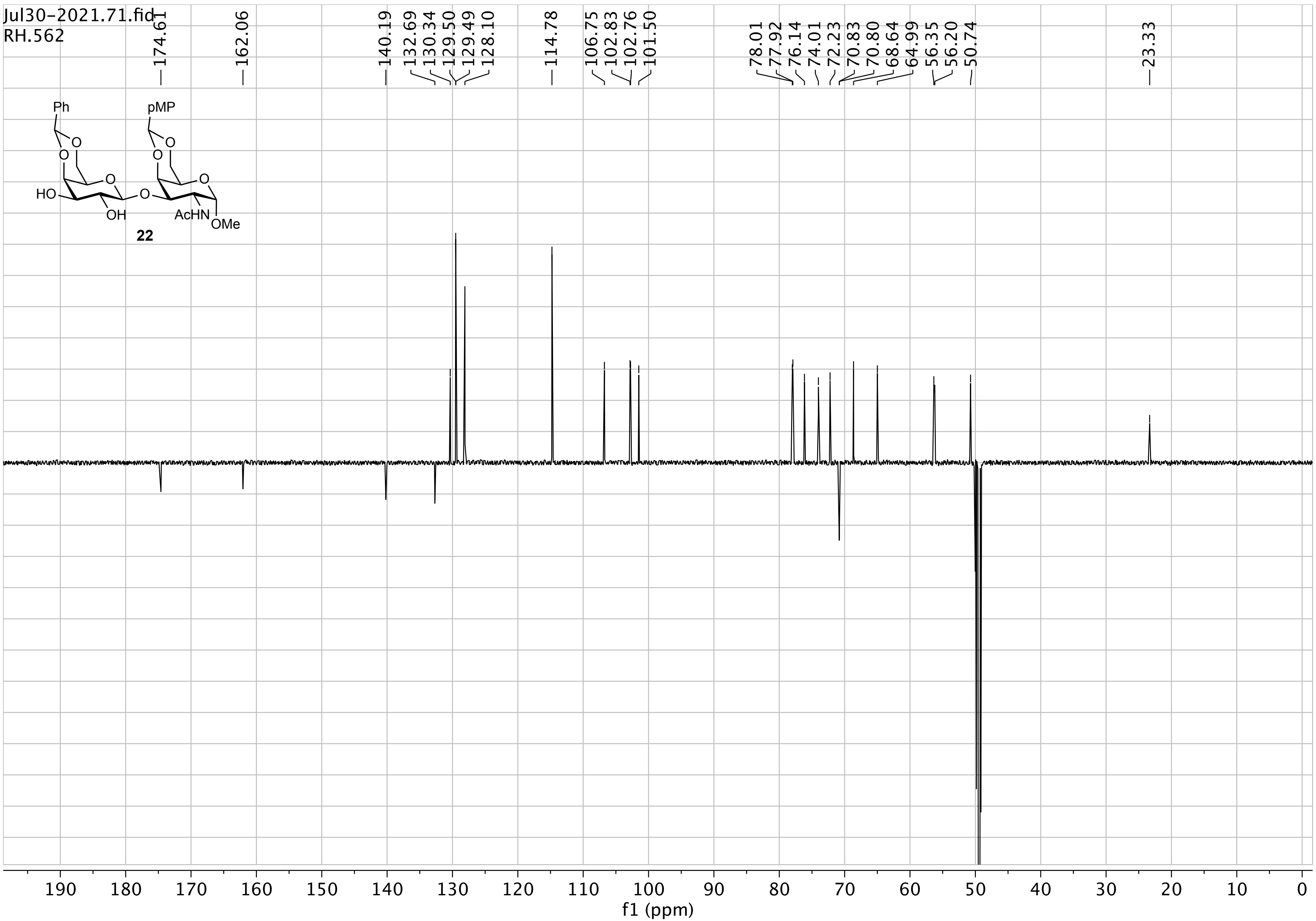
$^1H\_^{13}C$ gHSQC in CD_3OD



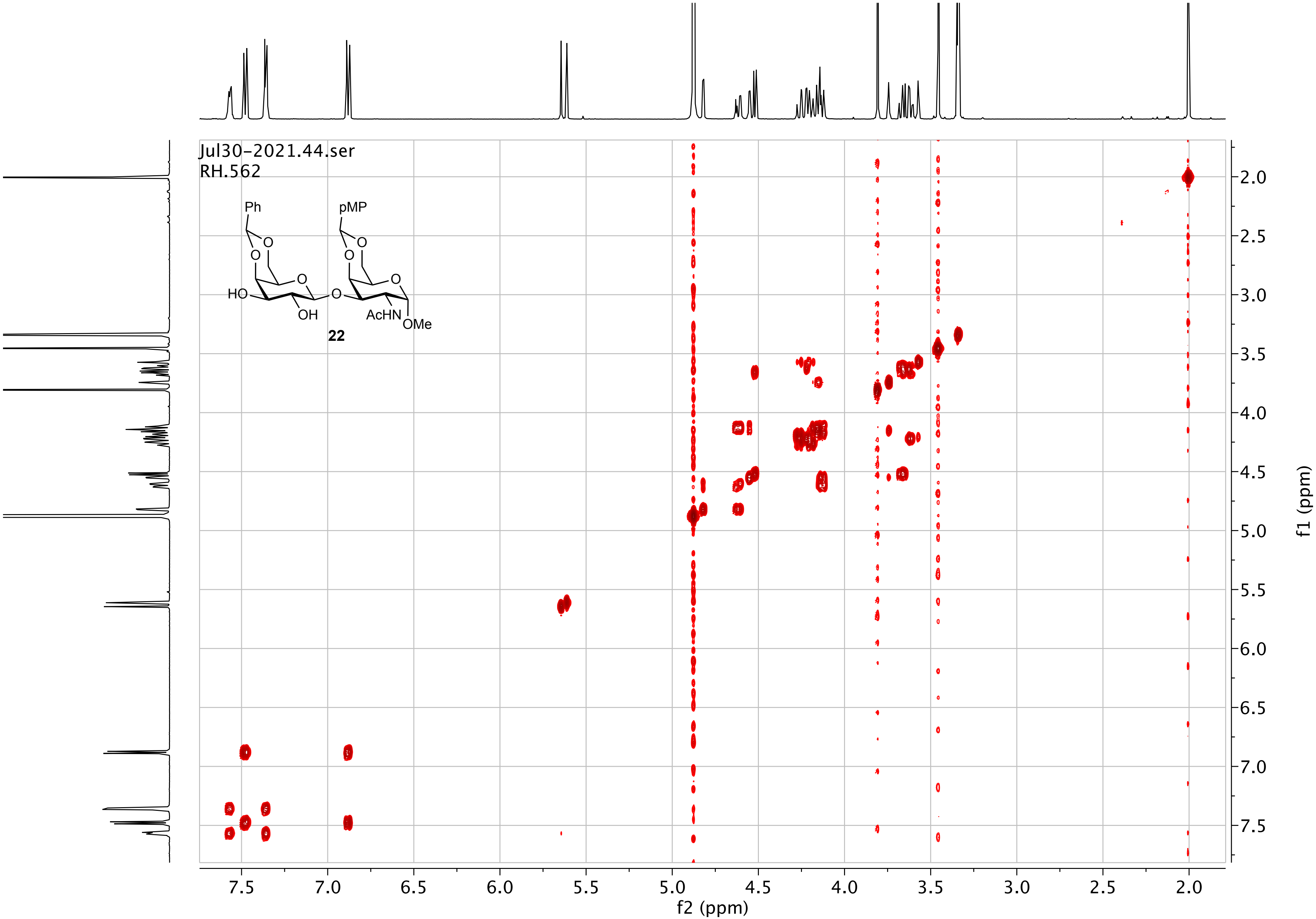
^{1}H NMR in CD_3OD (500 MHz)



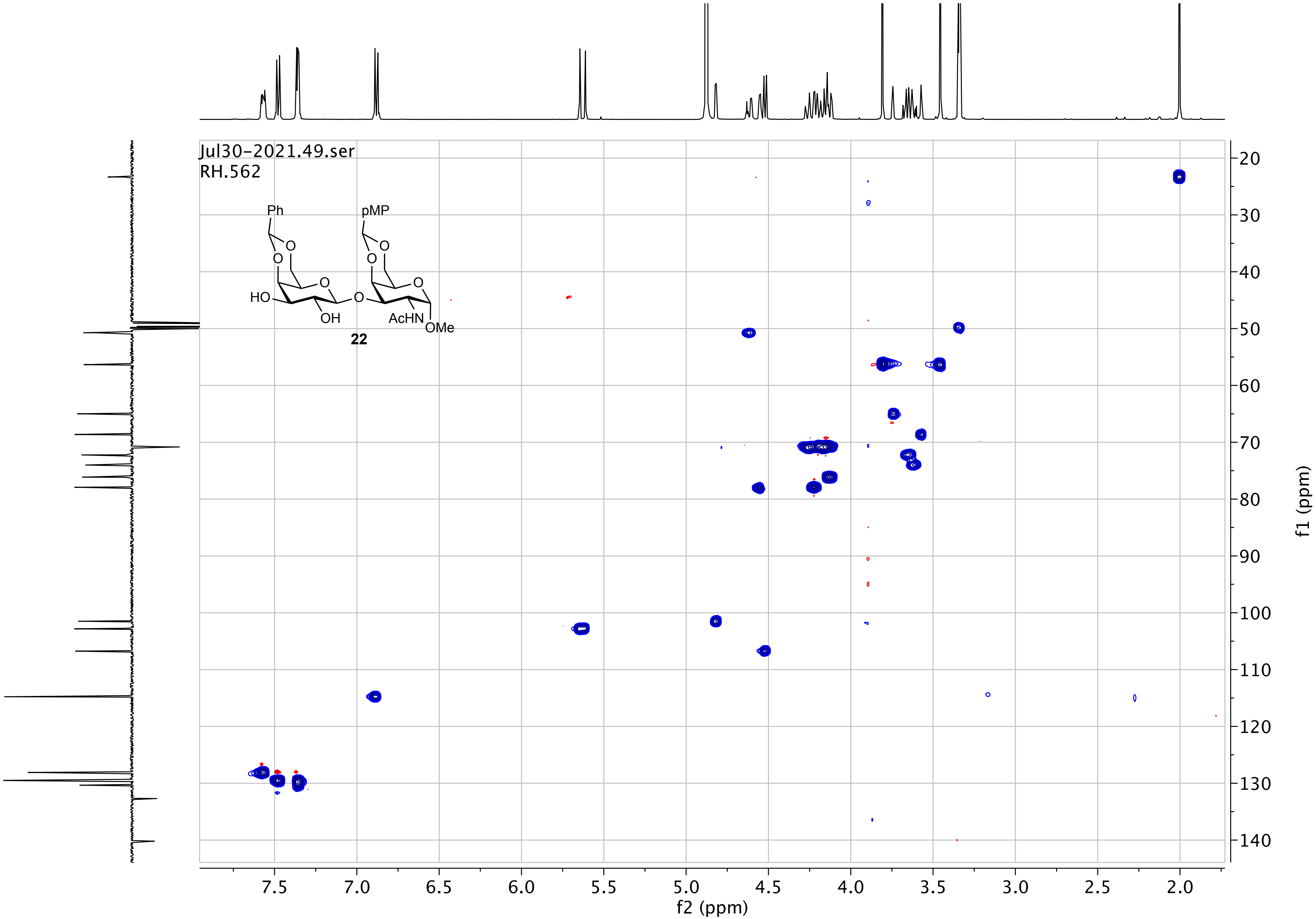
^{13}C NMR (APT) in CD_3OD (125 MHz)



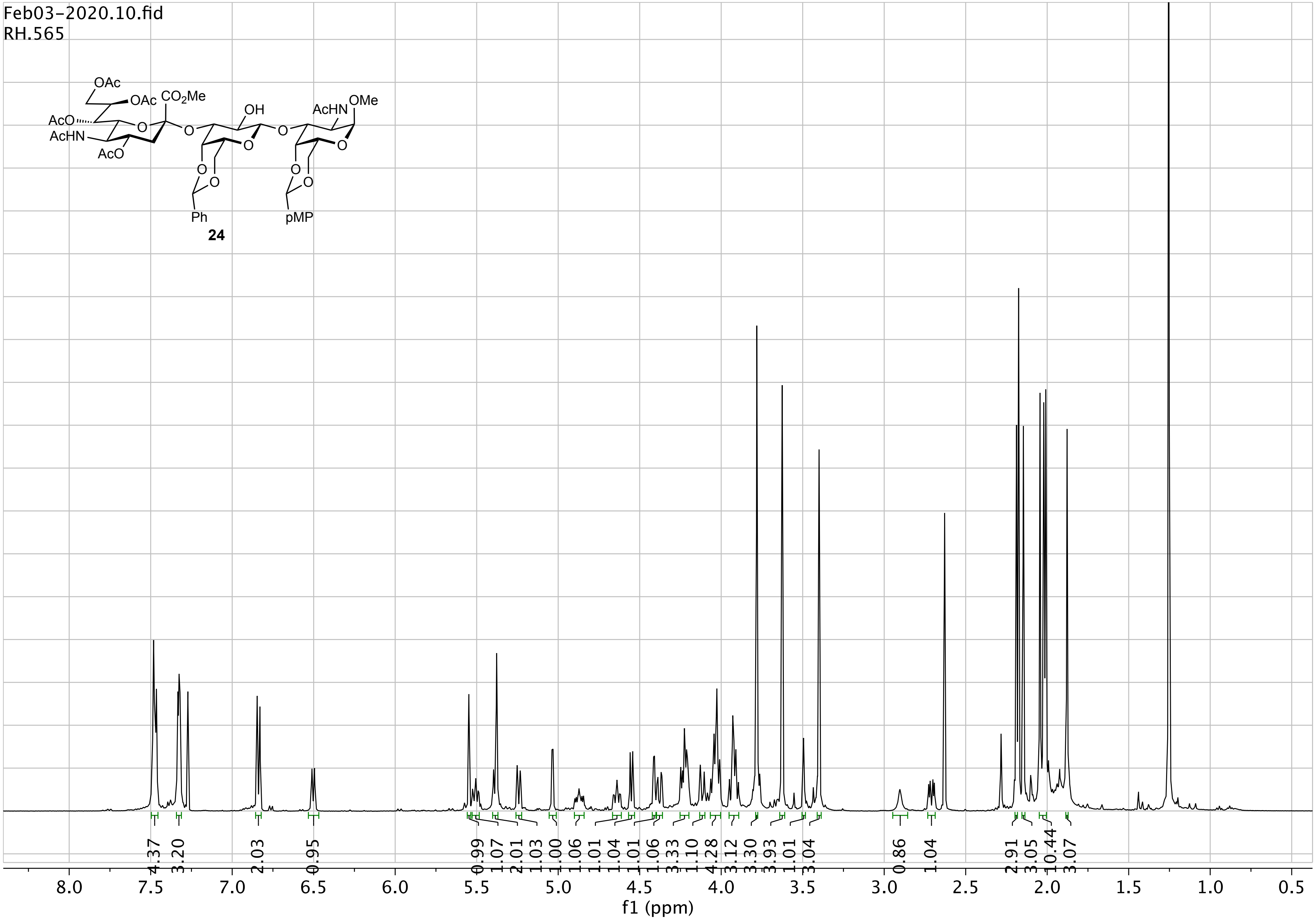
$^1H\_^1H$ gCOSY in CD_3OD



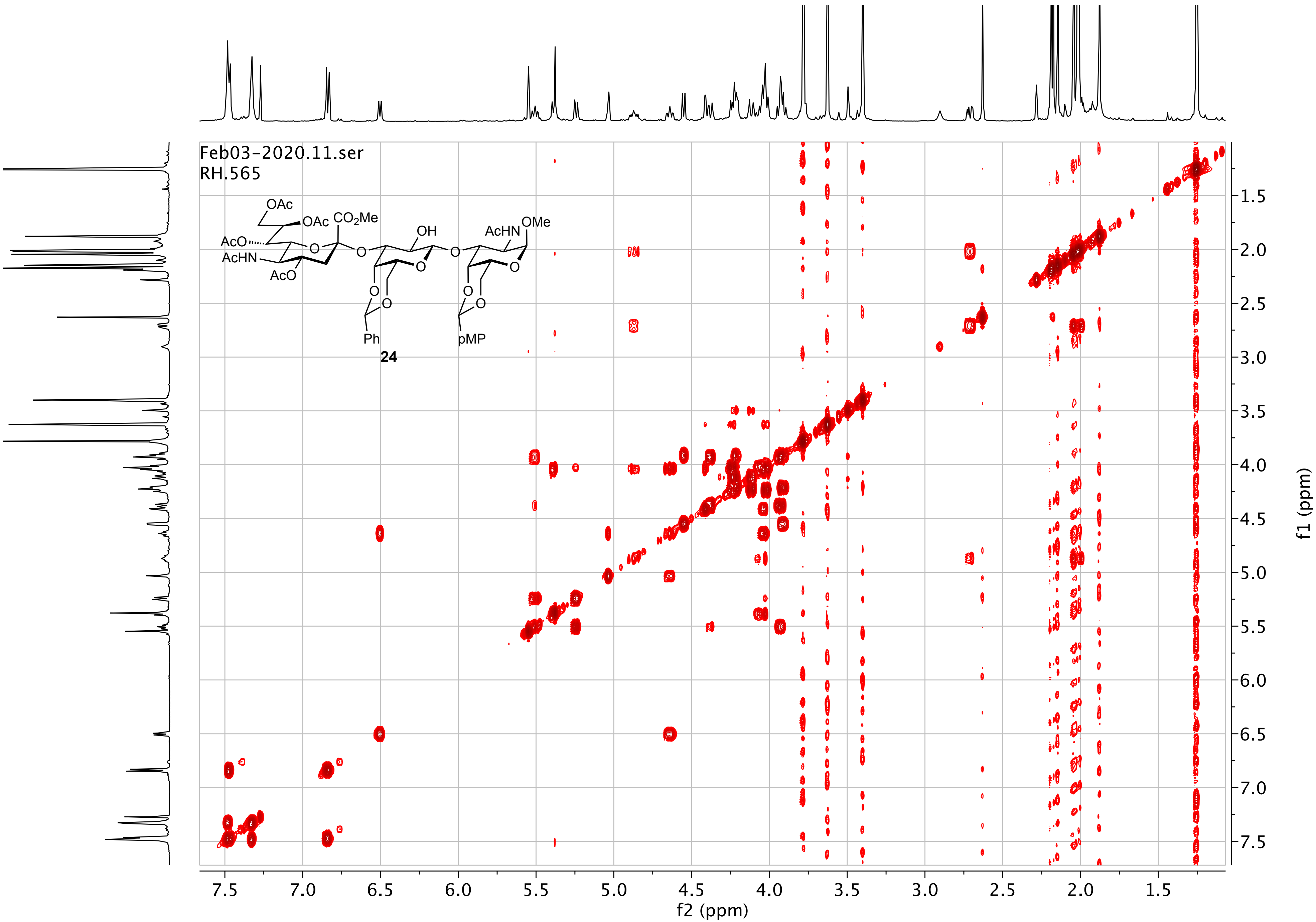
$^{1}H\_^{13}C$ gHSQC in CD_3OD



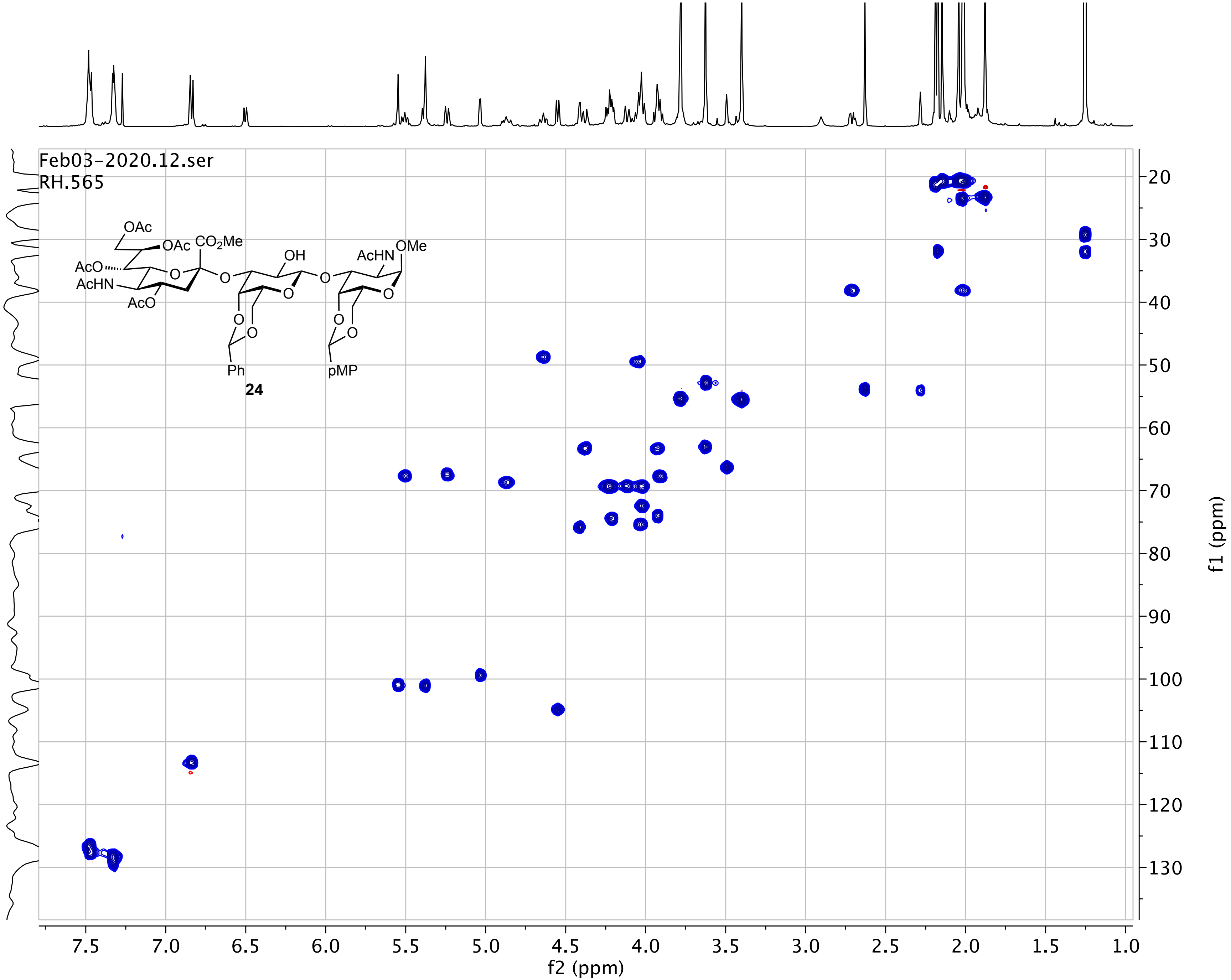
^{1}H NMR in $CDCl_3$ (500 MHz)



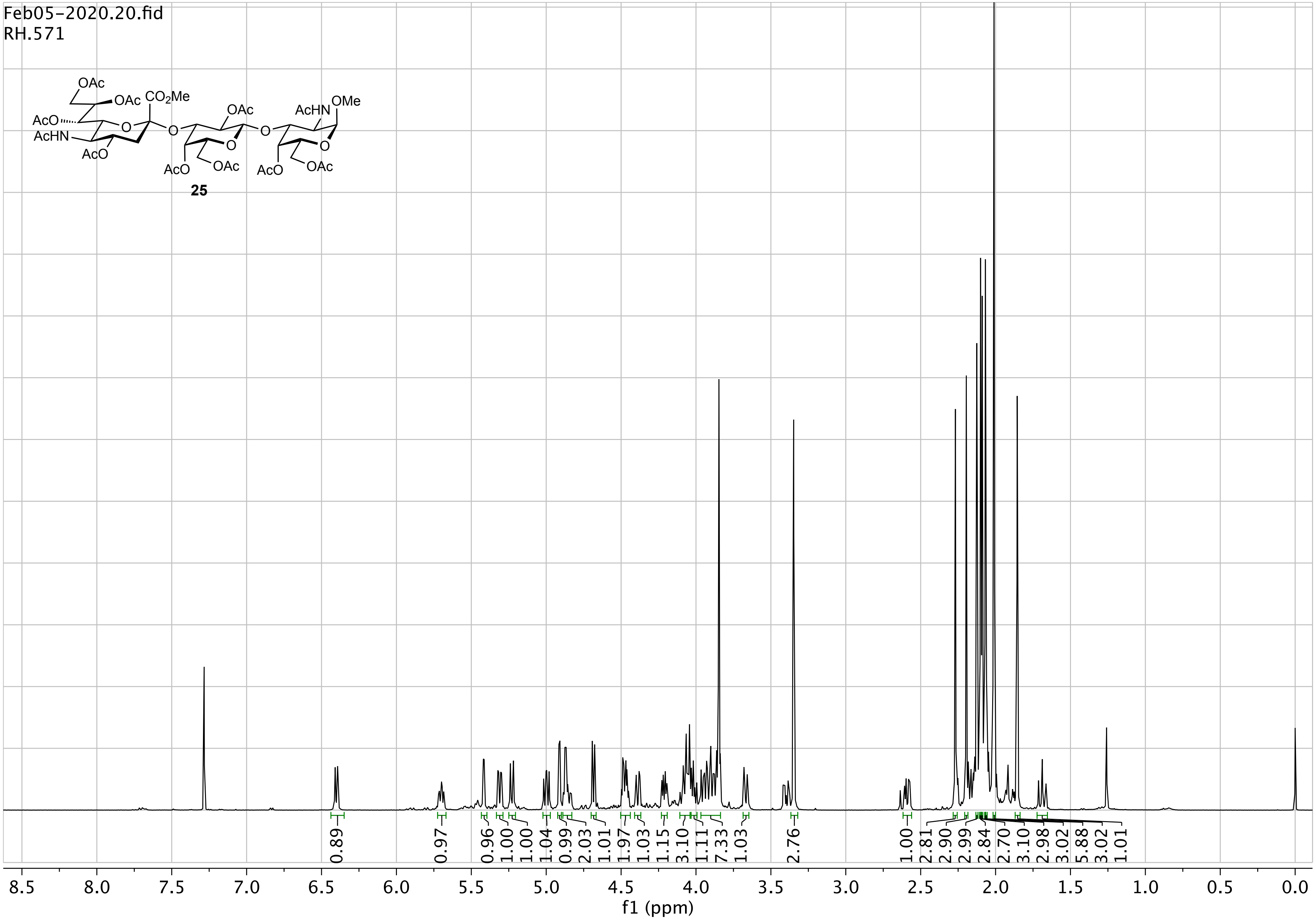
$^{1}H\_^{1}H$ gCOSY in $CDCl_3$



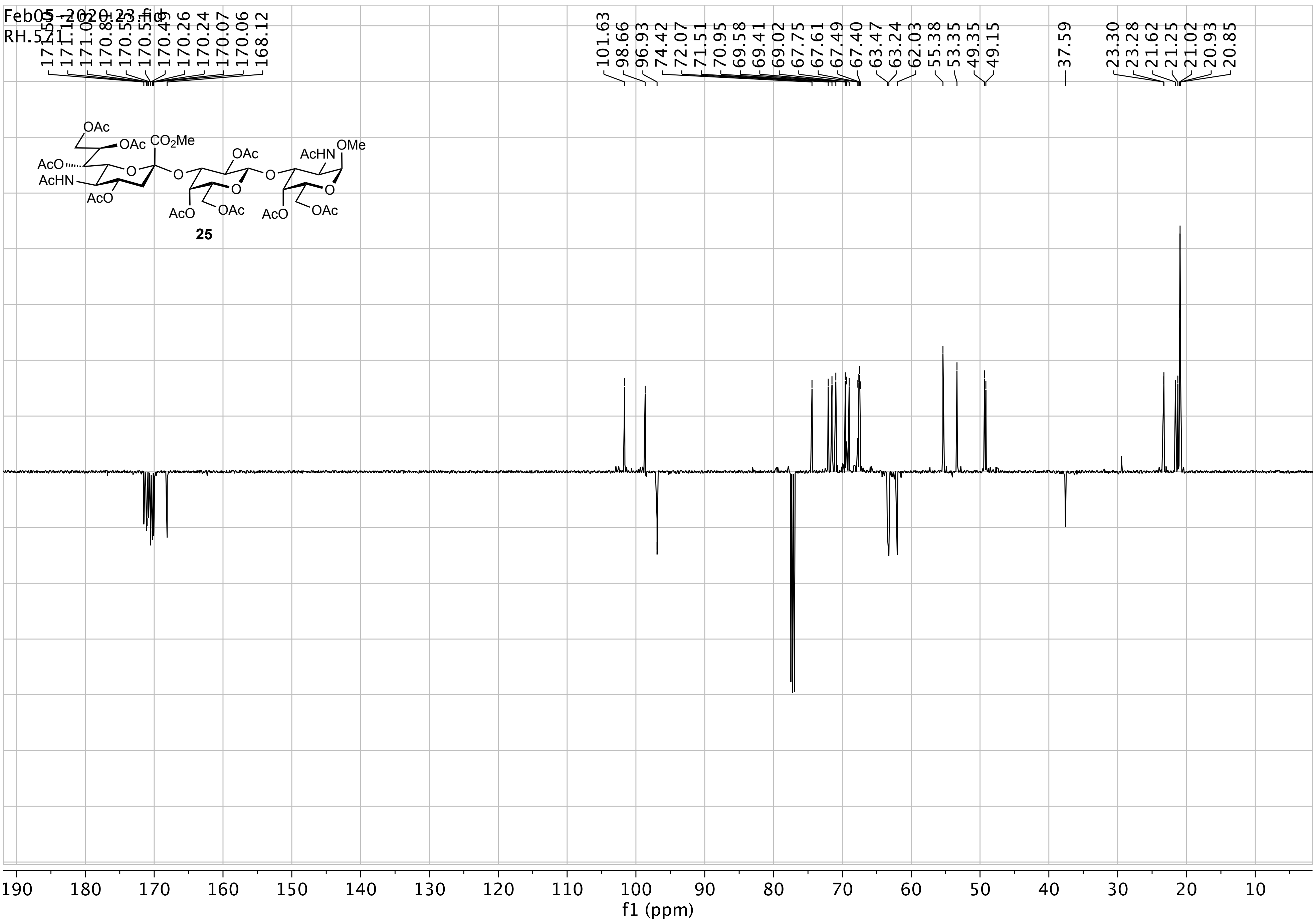
$^1H\_^{13}C$ gHSQC in $CDCl_3$



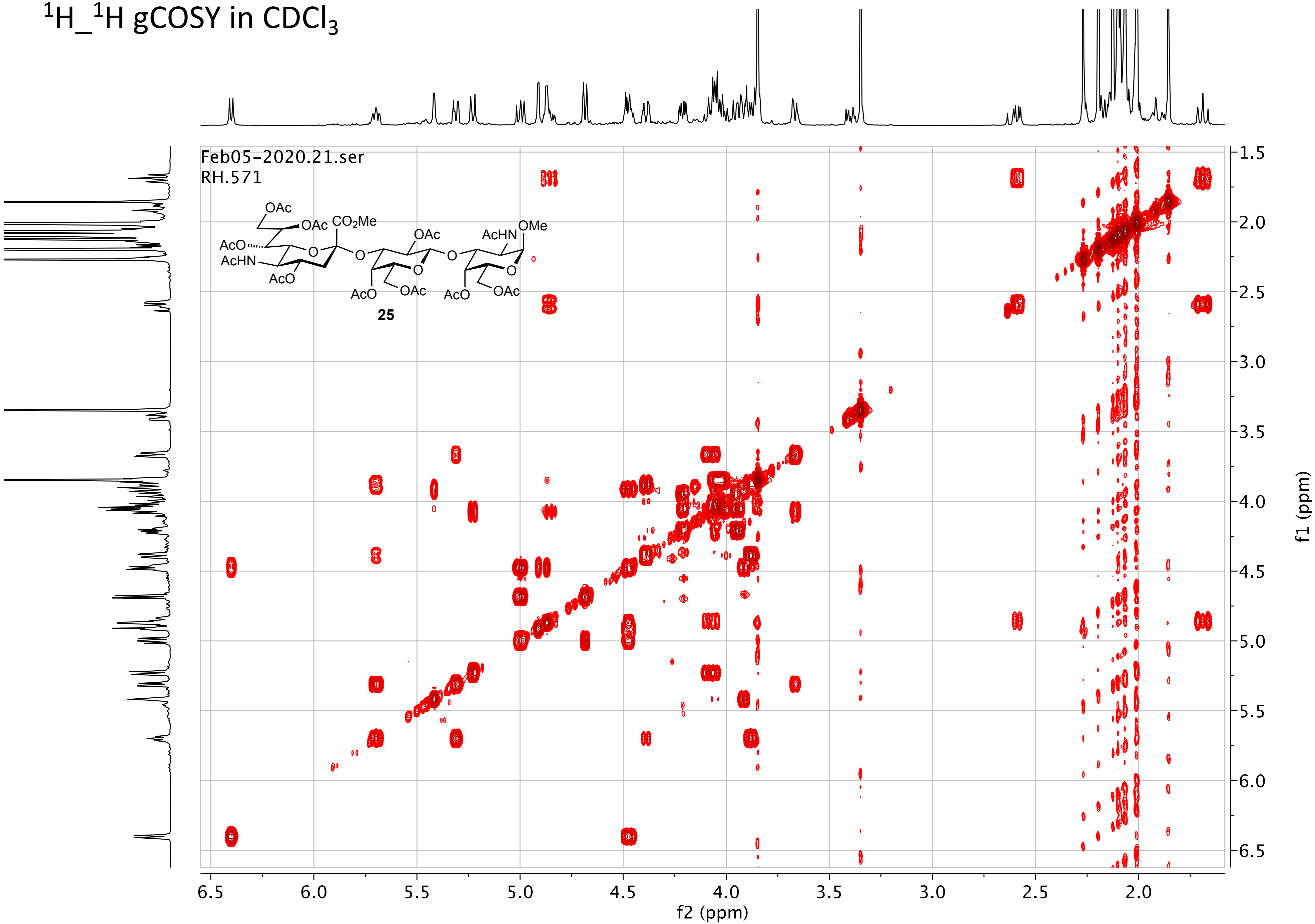
^1H NMR in $CDCl_3$ (500 MHz)

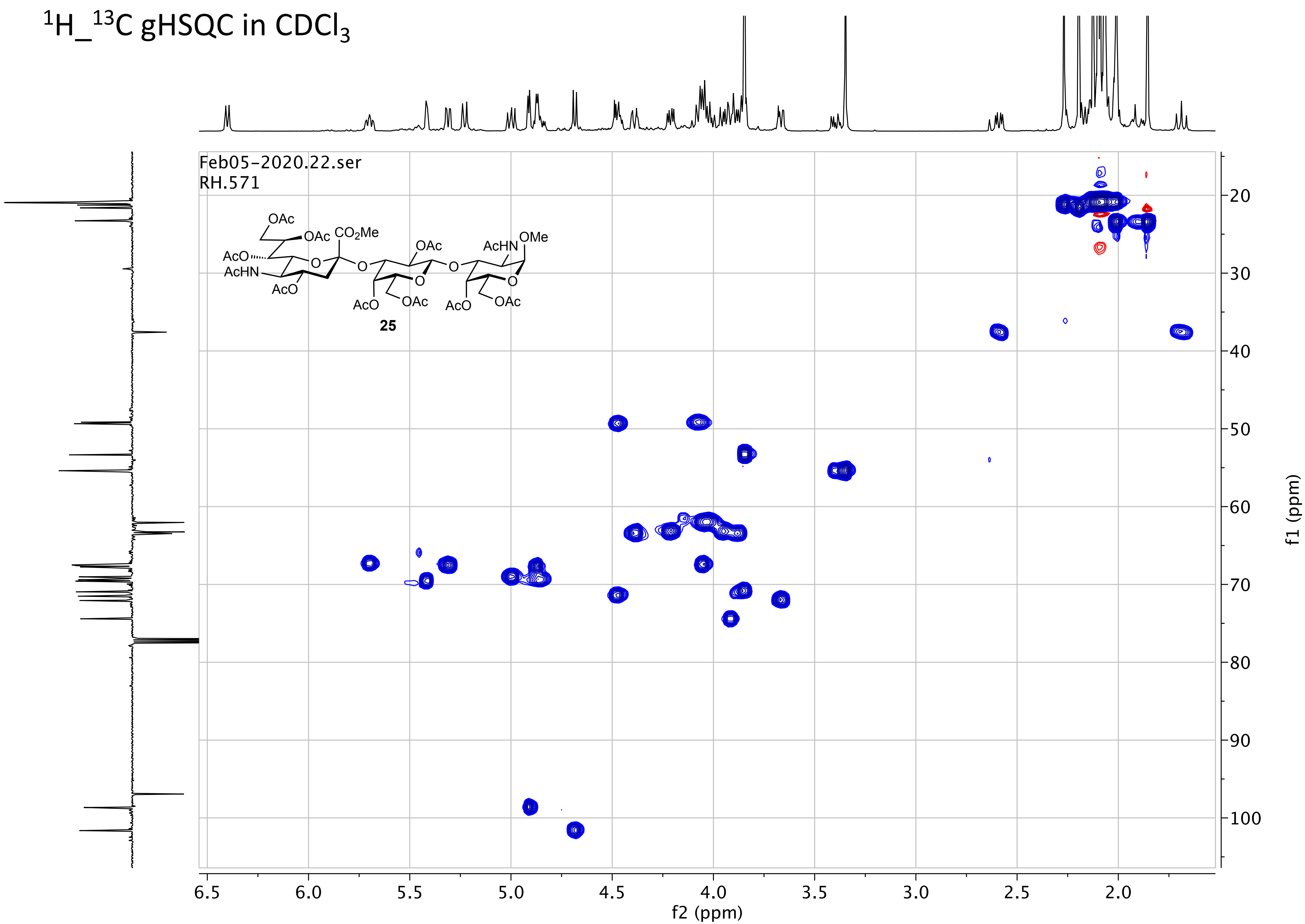


^{13}C NMR (APT) in $CDCl_3$ (125 MHz)

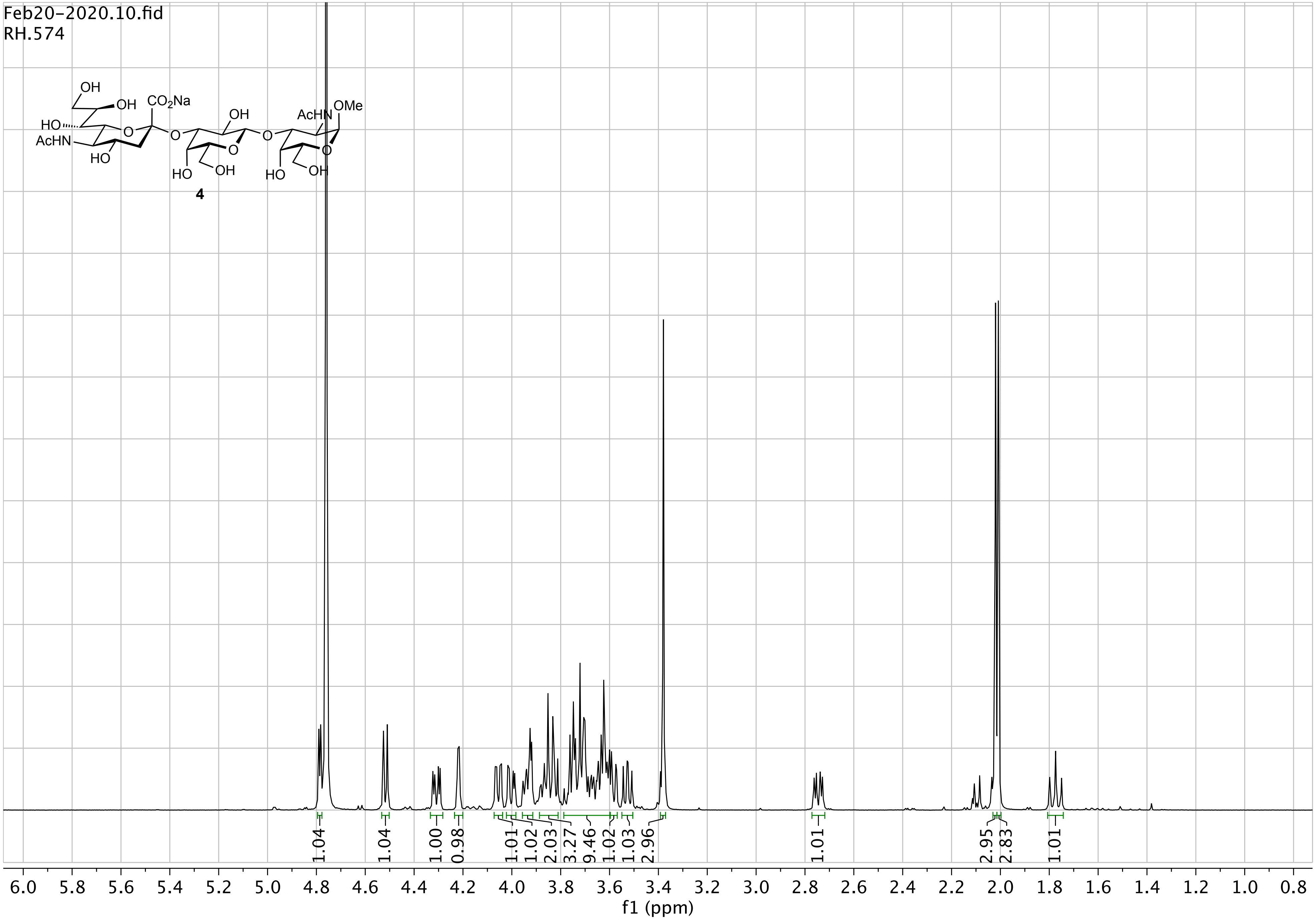


$^1H\_^1H$ gCOSY in $CDCl_3$

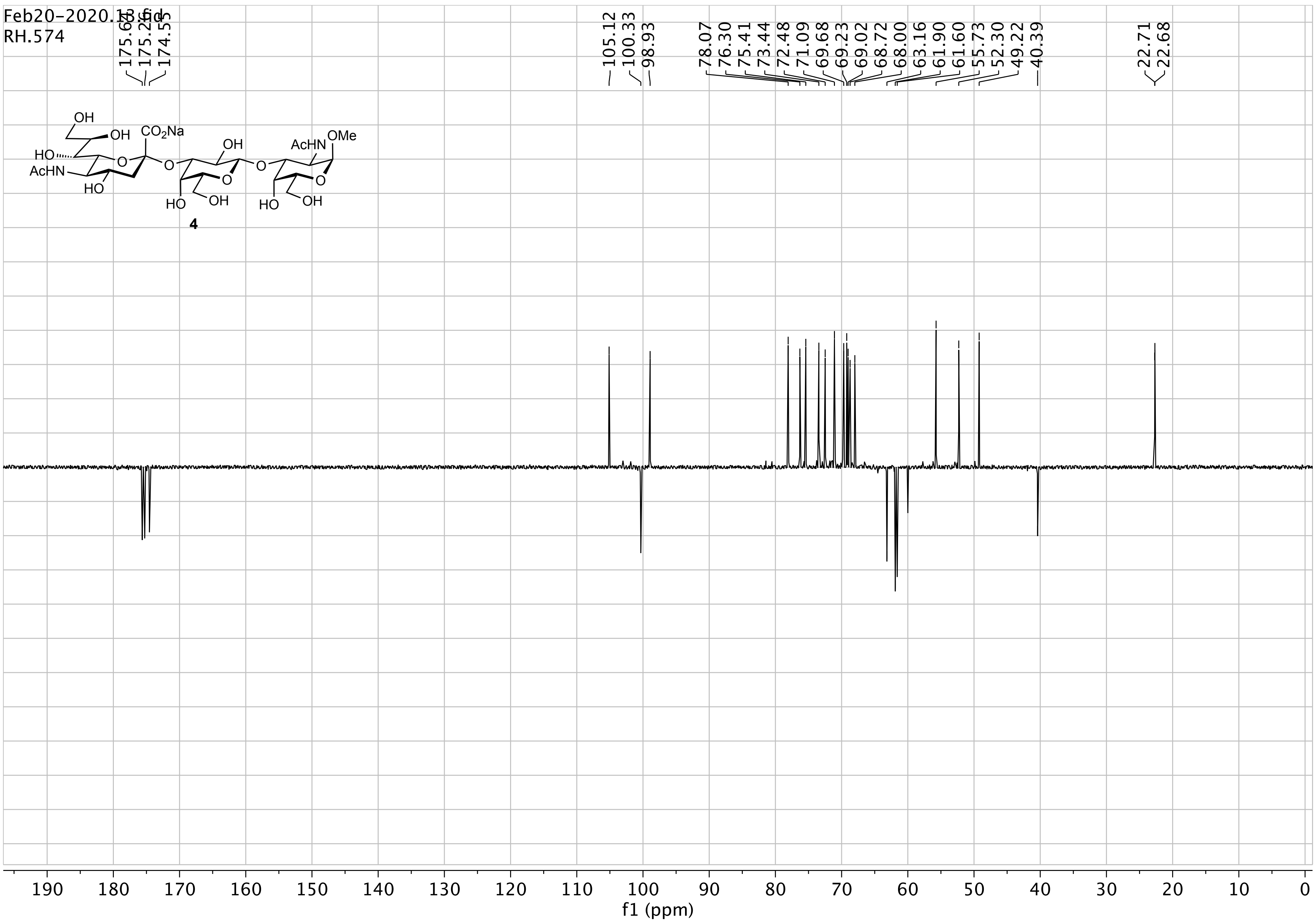



^1H_^{13}C gHSQC in $CDCl_3$
Feb05-2020.22.ser
RH.571
OAc
OAc
CO_2Me
AcO
AcHN
O
O
AcO
OAc
O
AcO
OAc
O
AcHN
OMe
O
AcO
OAc
25
f2 (ppm)
f1 (ppm)

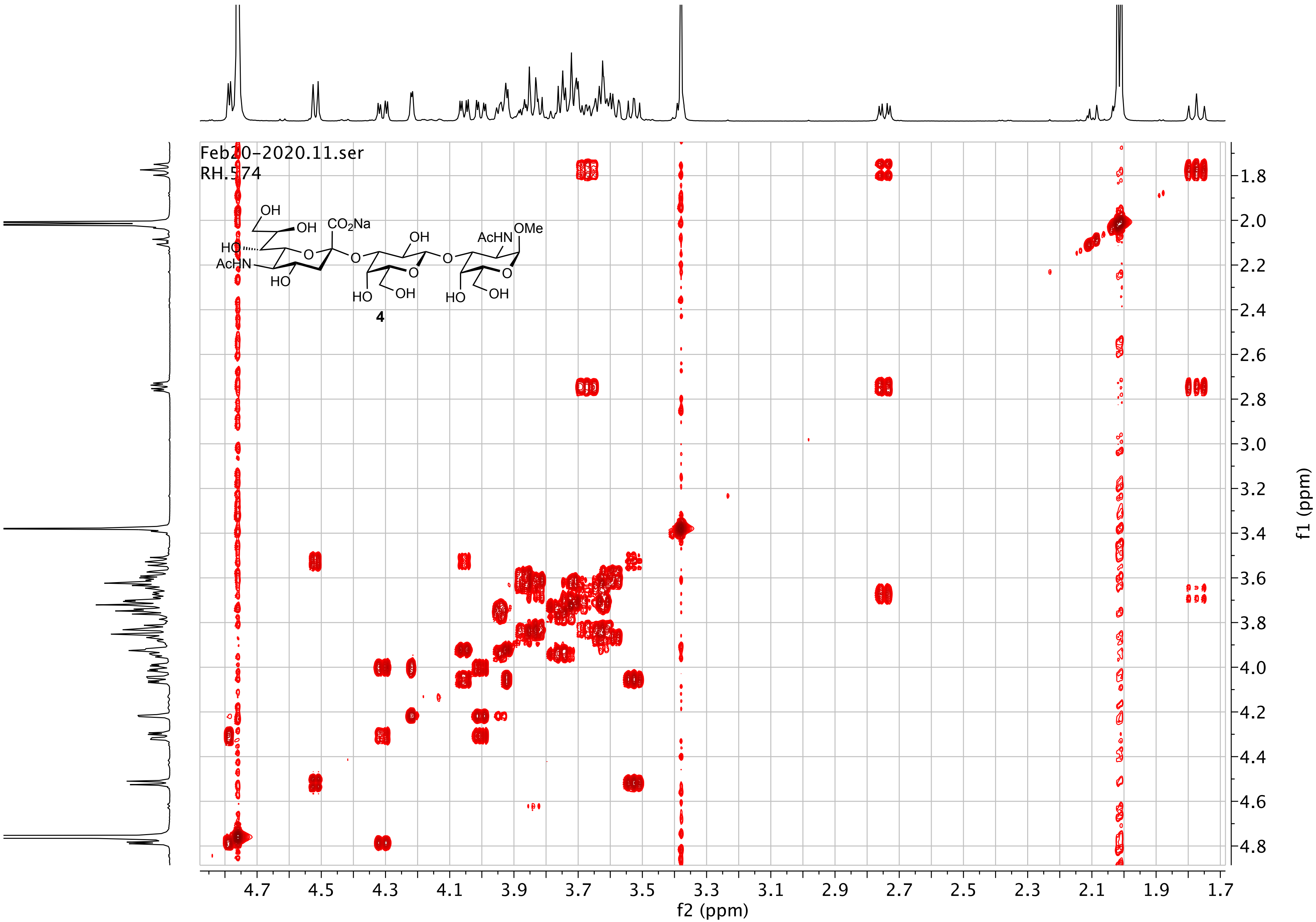
^{1}H NMR in D_2O (500 MHz)



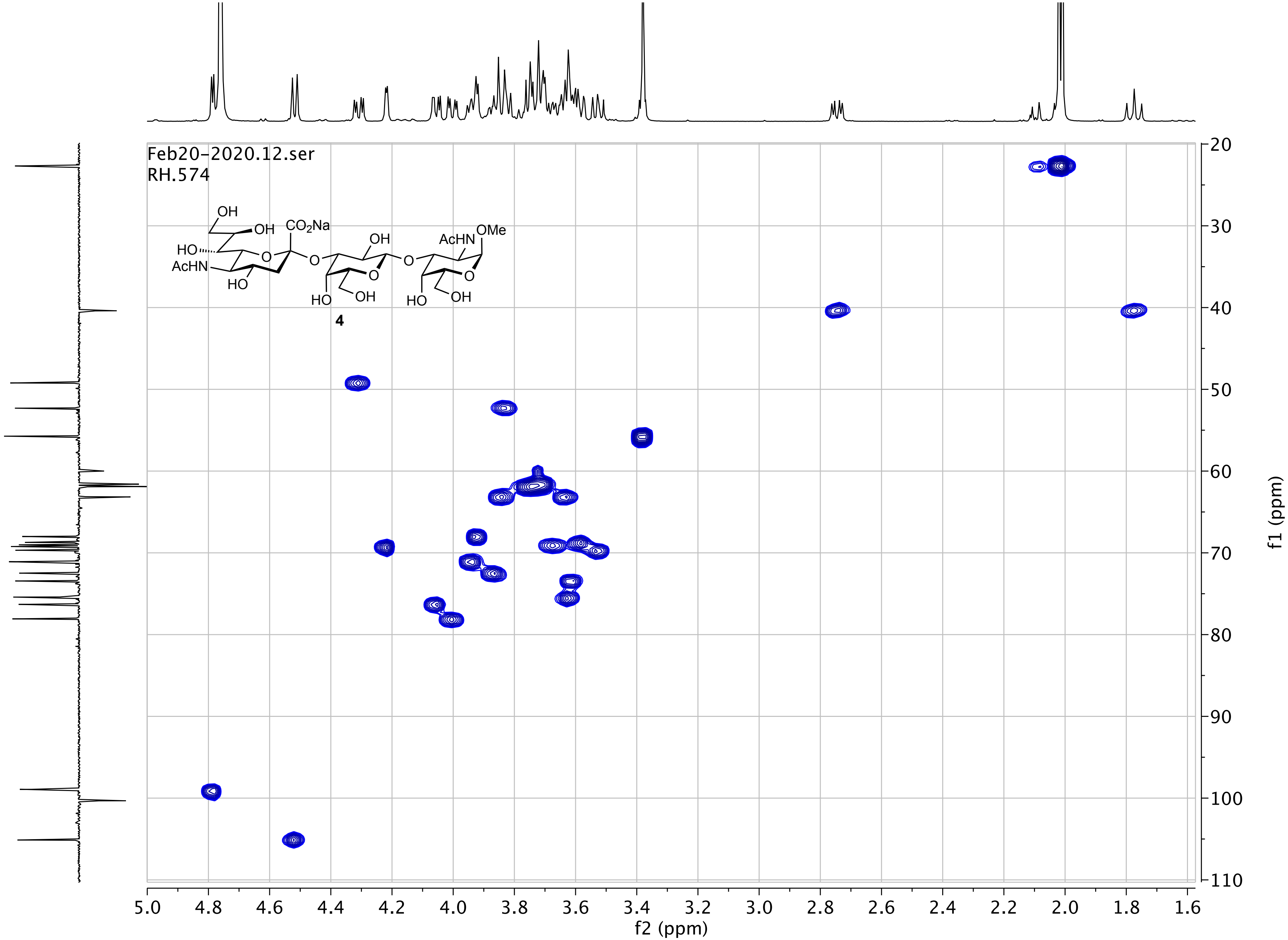
^{13}C NMR (APT) in D_2O (125 MHz)



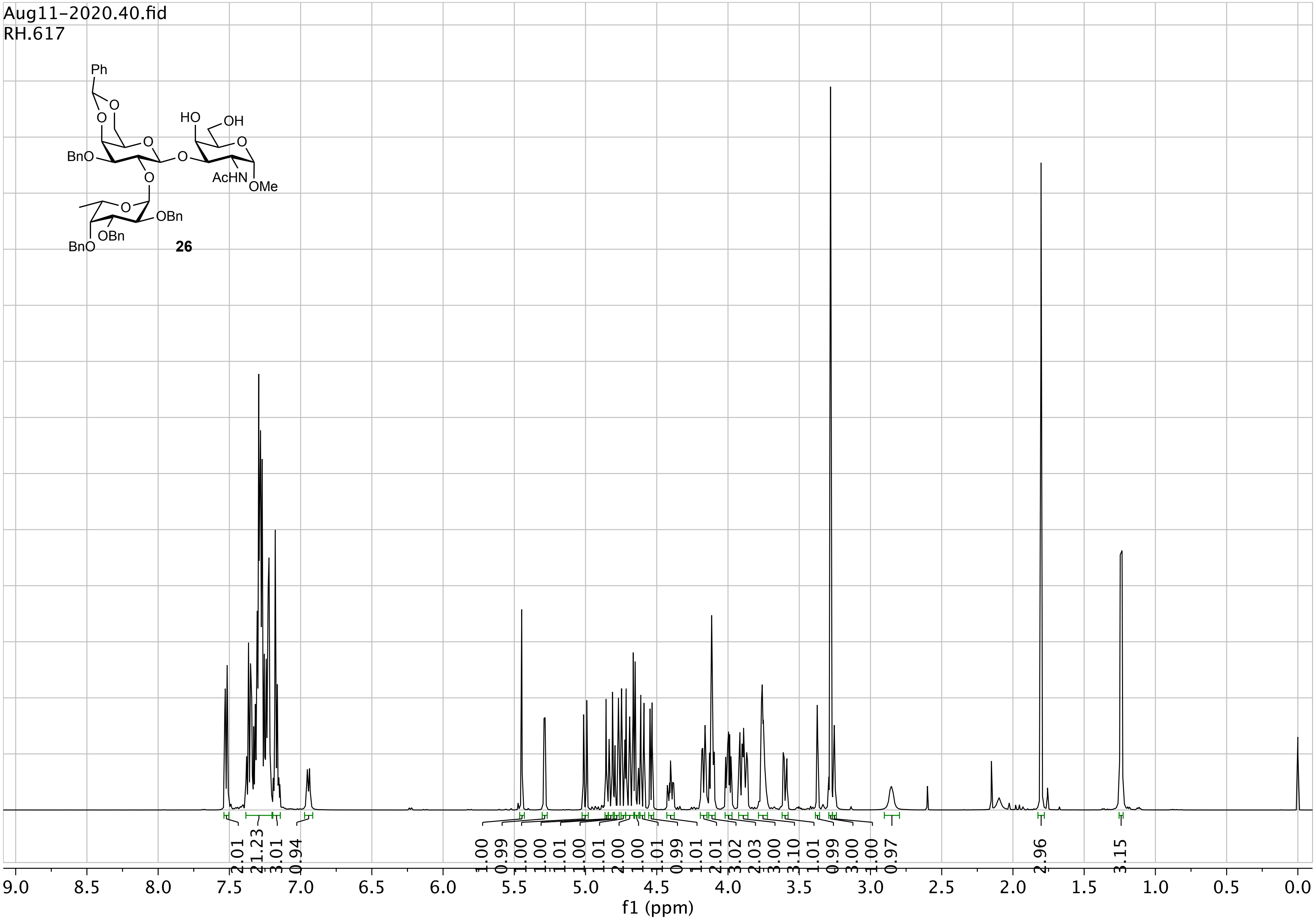
$^{1}H\_^{1}H$ gCOSY in D_2O



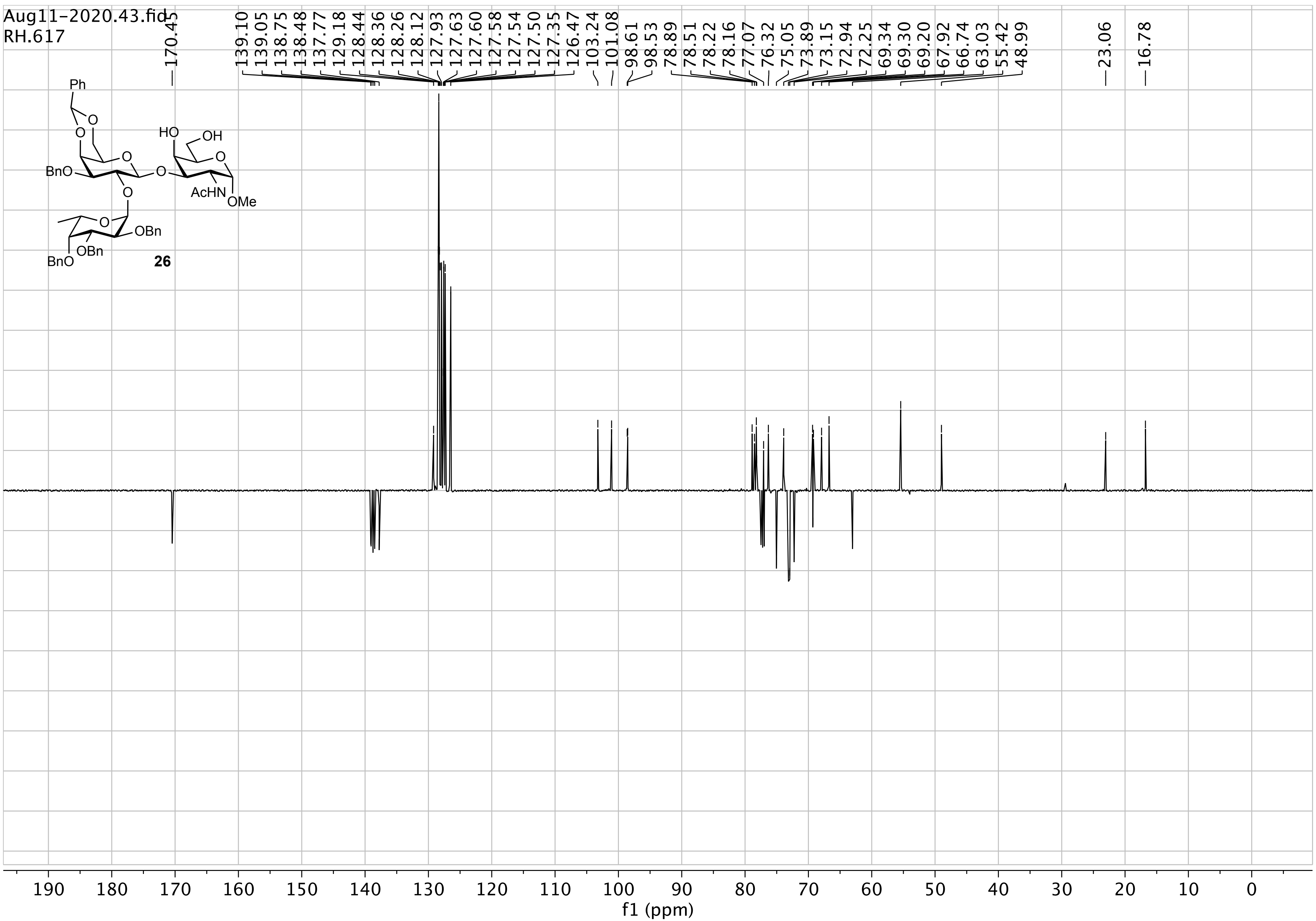
$^{1}H\_^{13}C$ gHSQC in D_2O



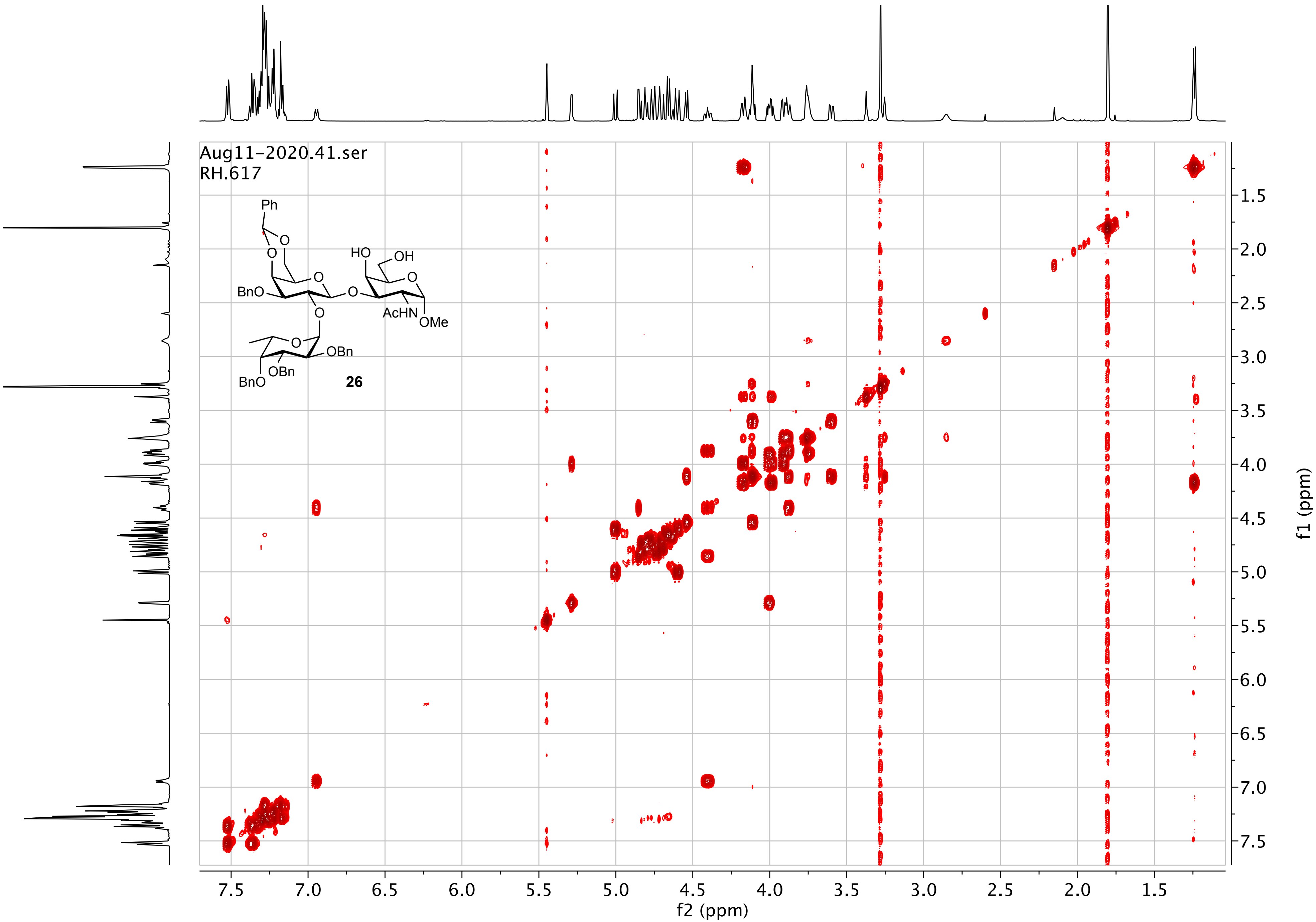
^{1}H NMR in $CDCl_3$ (500 MHz)



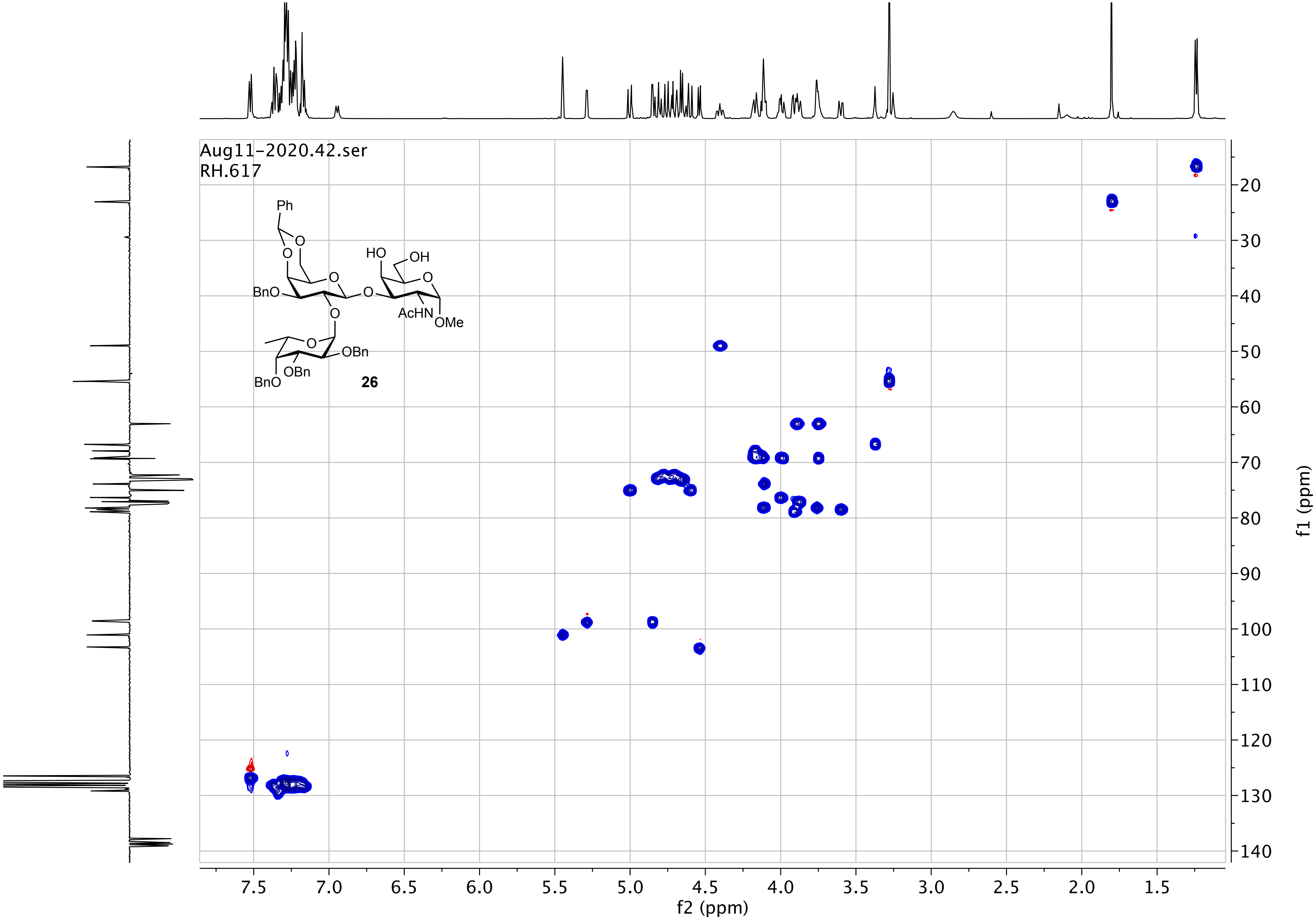
^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



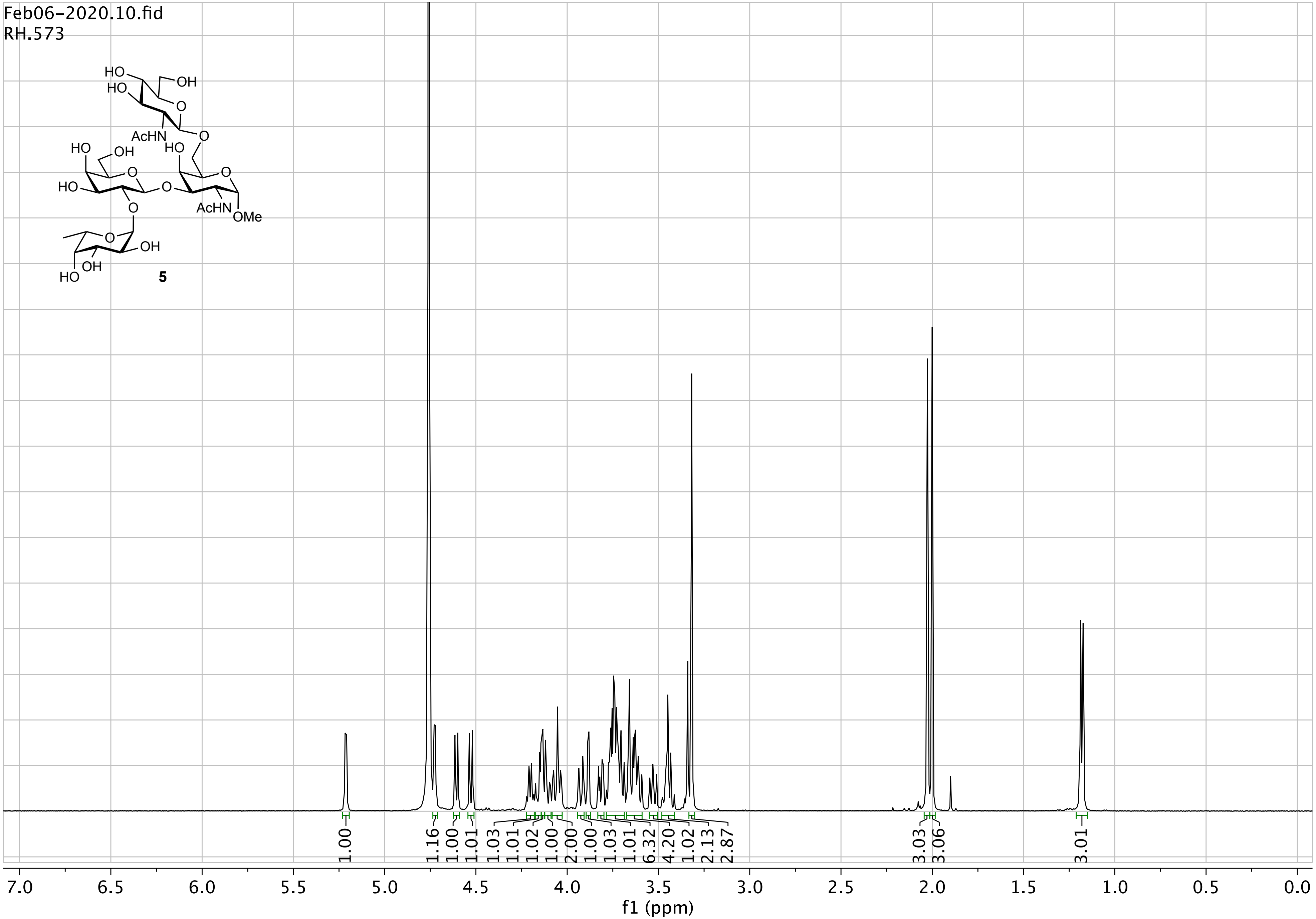
$^1H\_^1H$ gCOSY in $CDCl_3$



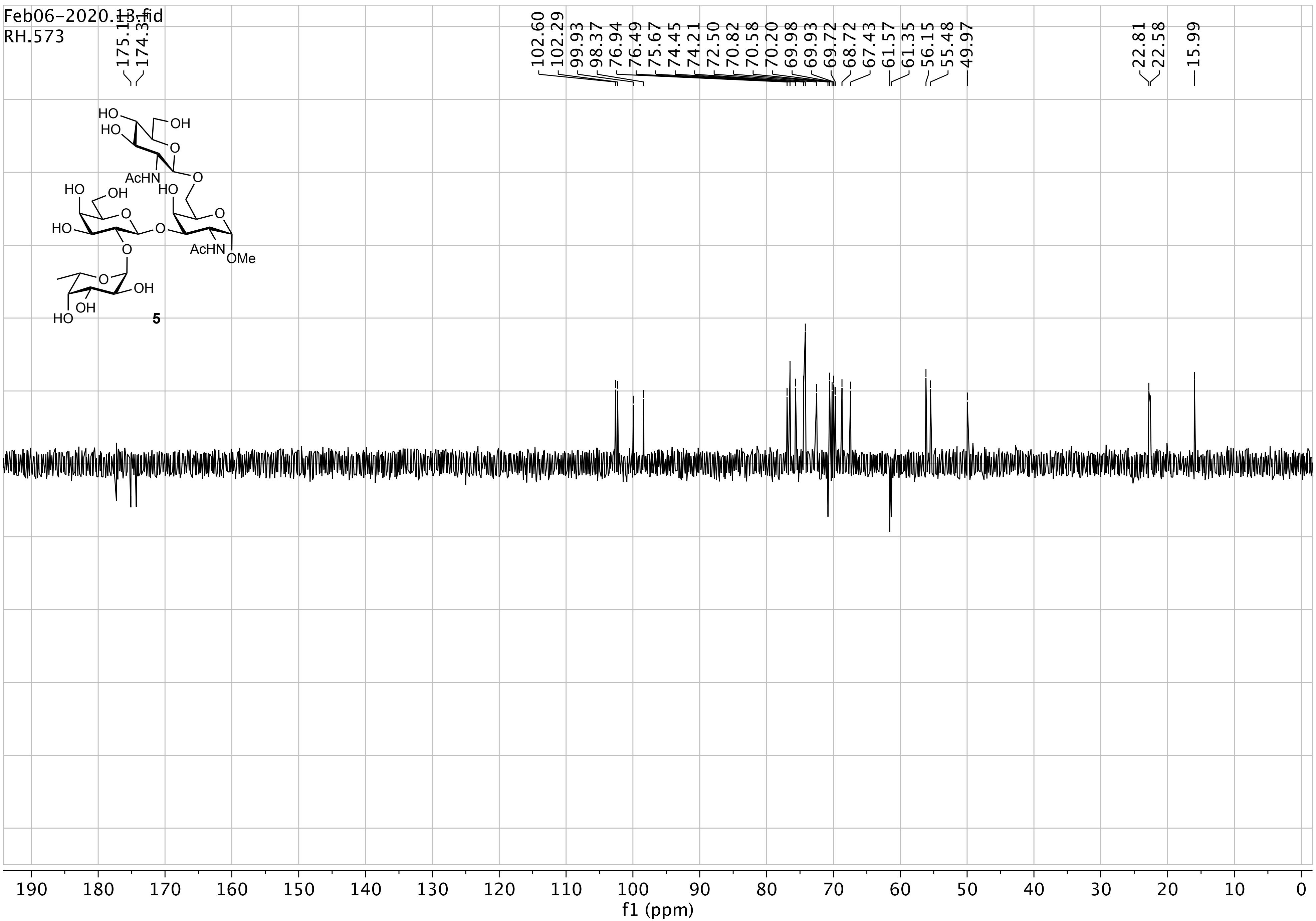
$^{1}H\_^{13}C$ gHSQC in $CDCl_3$



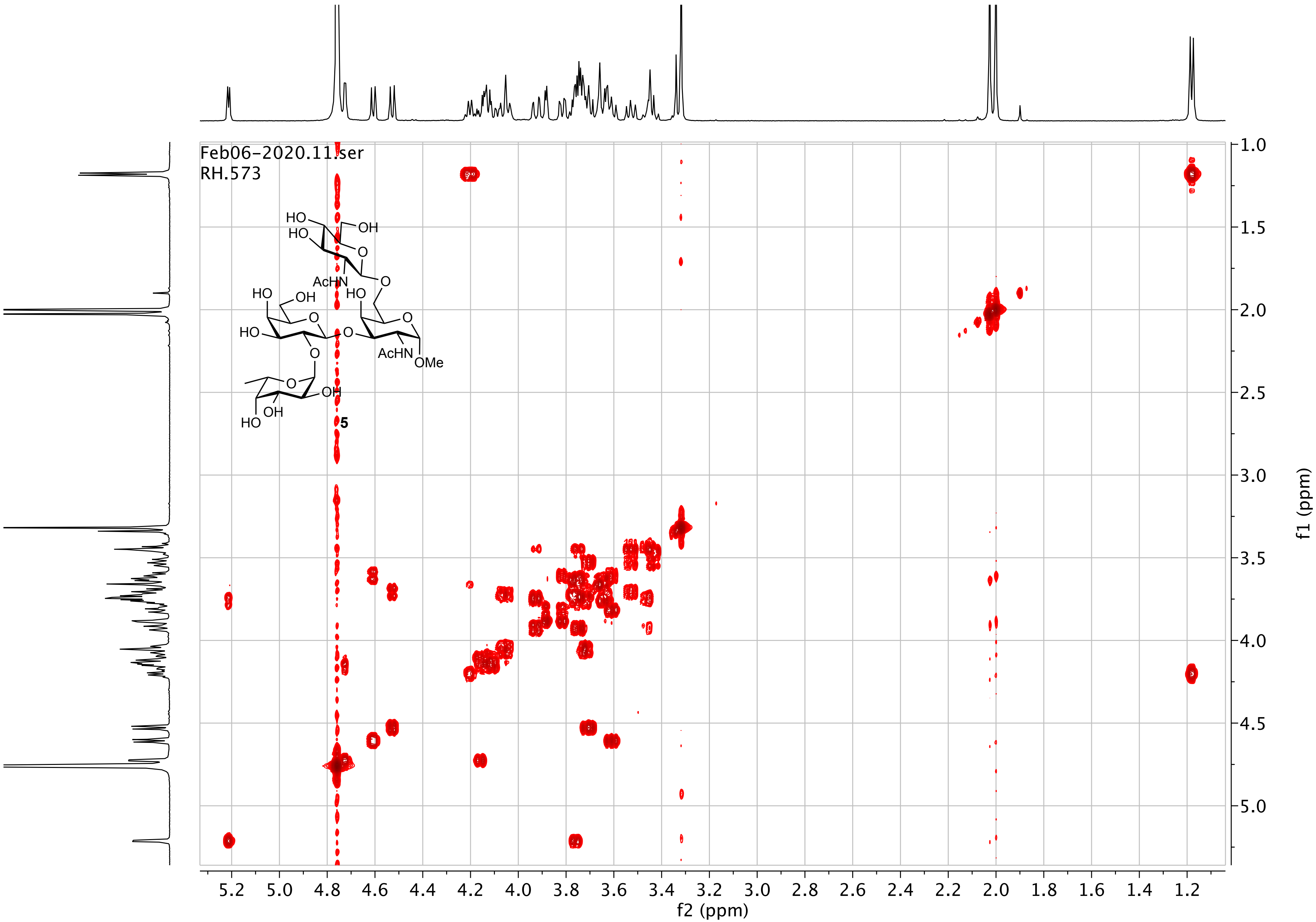
^{1}H NMR in D_2O (500 MHz)



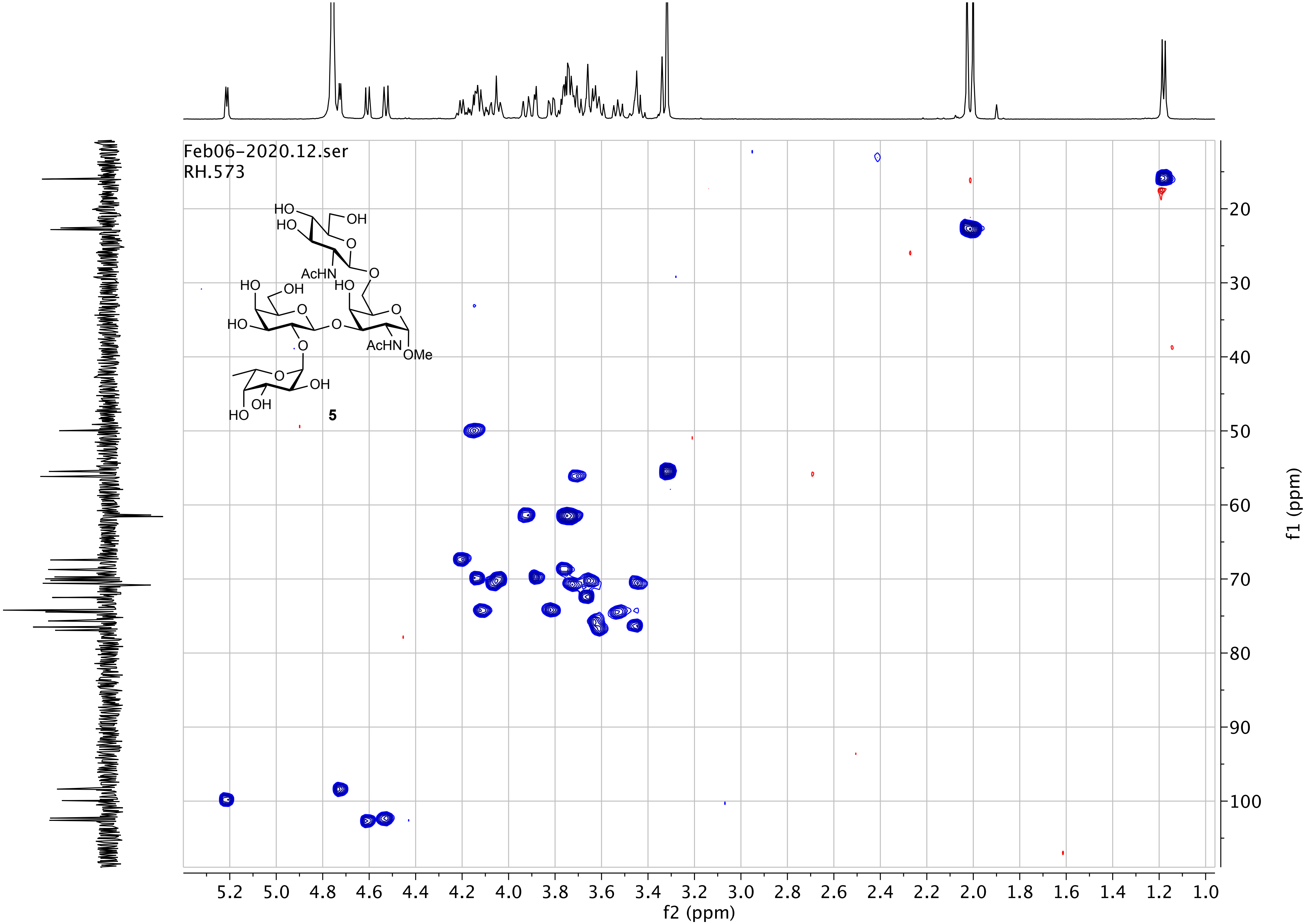
^{13}C NMR (APT) in D_2O (125 MHz)



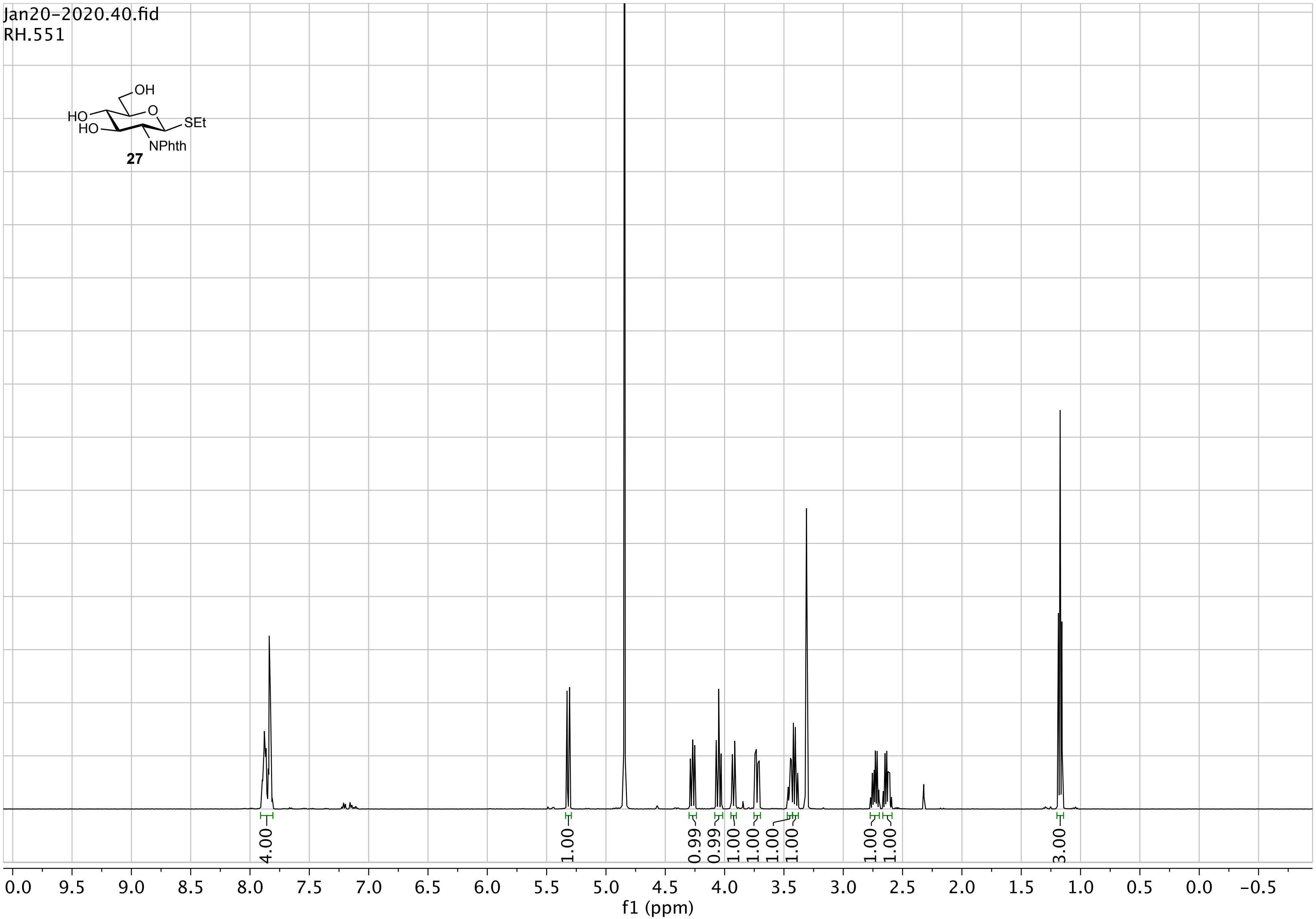
$^1H\_^1H$ gCOSY in D_2O



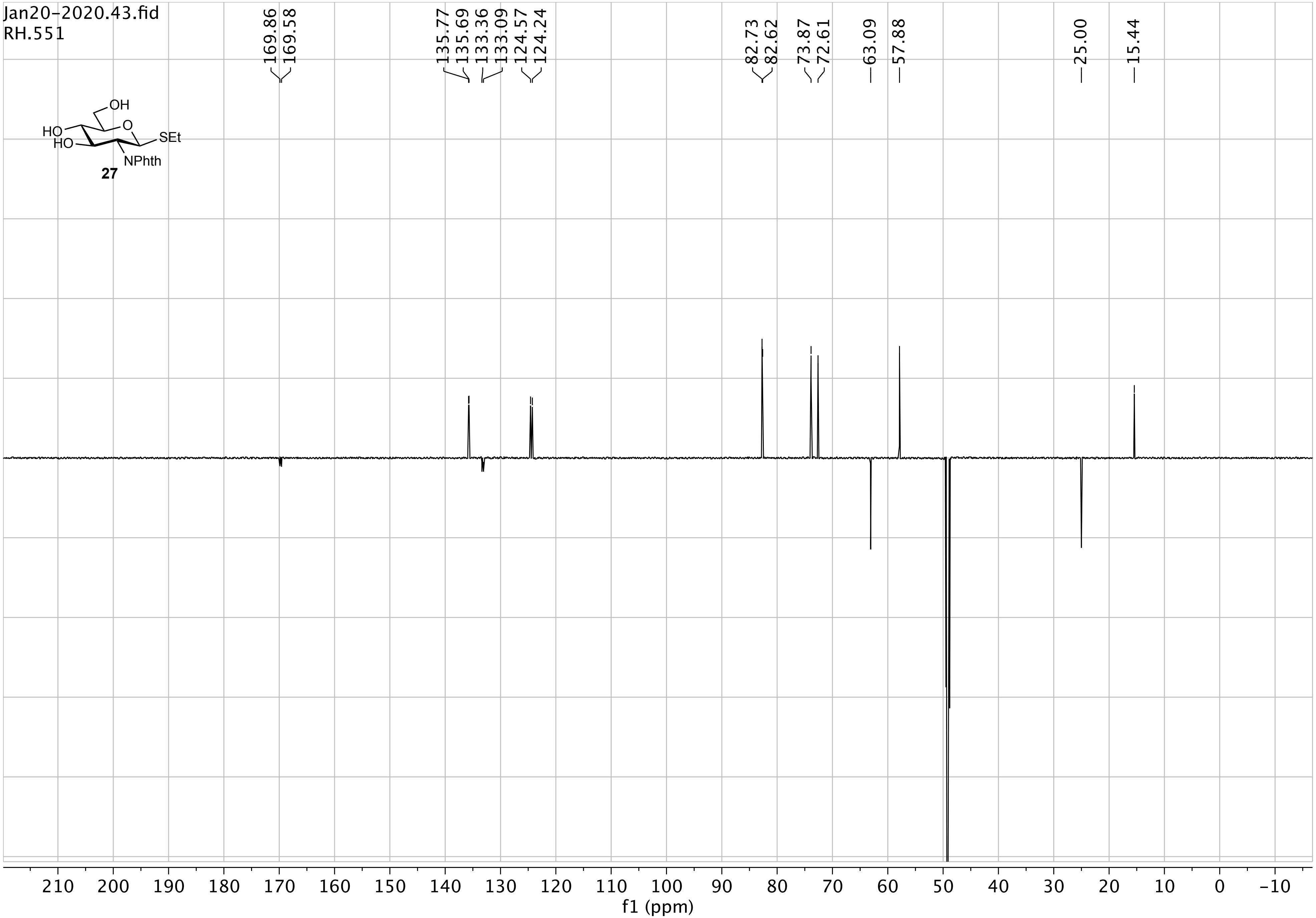
$^{1}H\_^{13}C$ gHSQC in D_2O



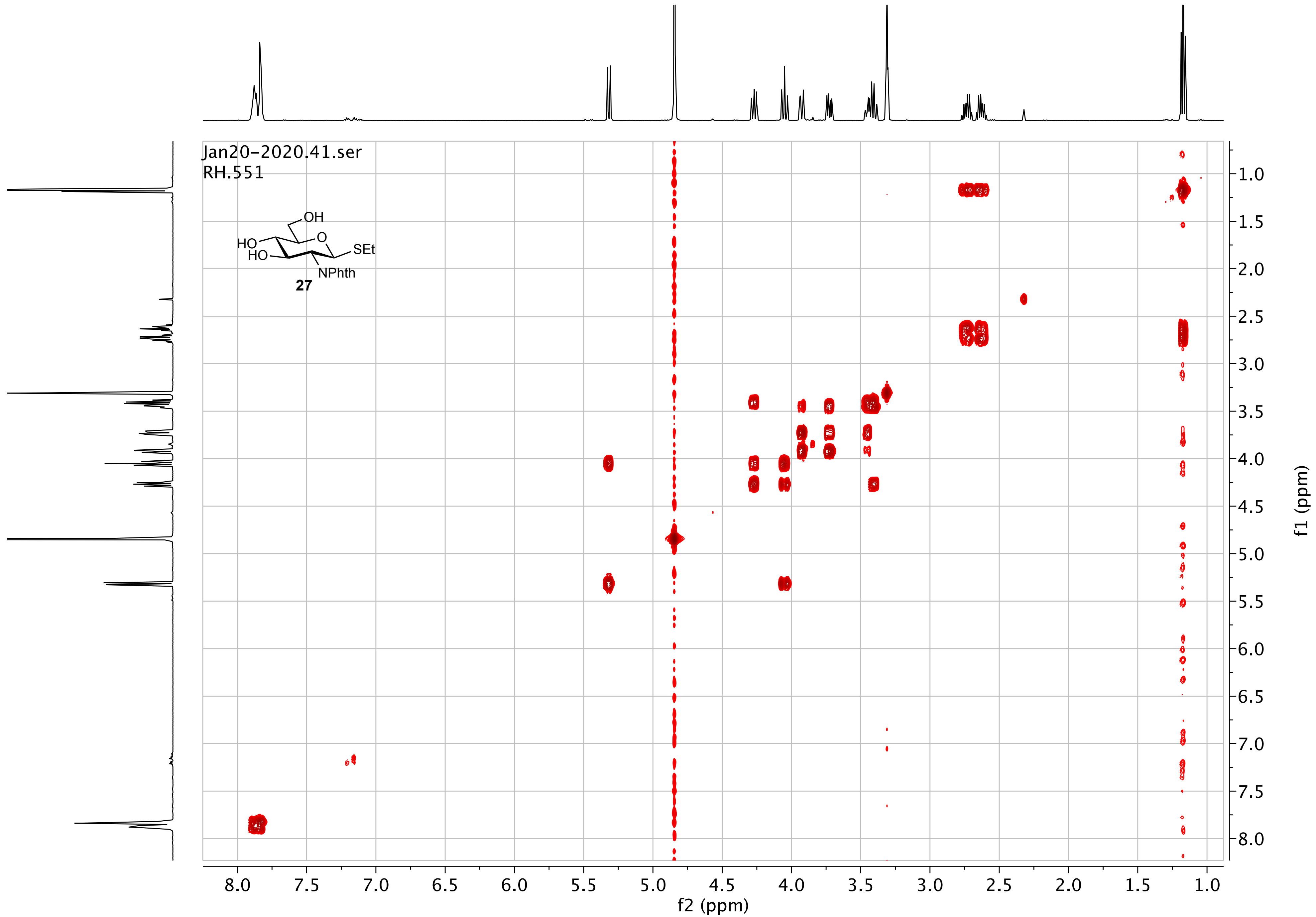
^{1}H NMR in CD_3OD (500 MHz)



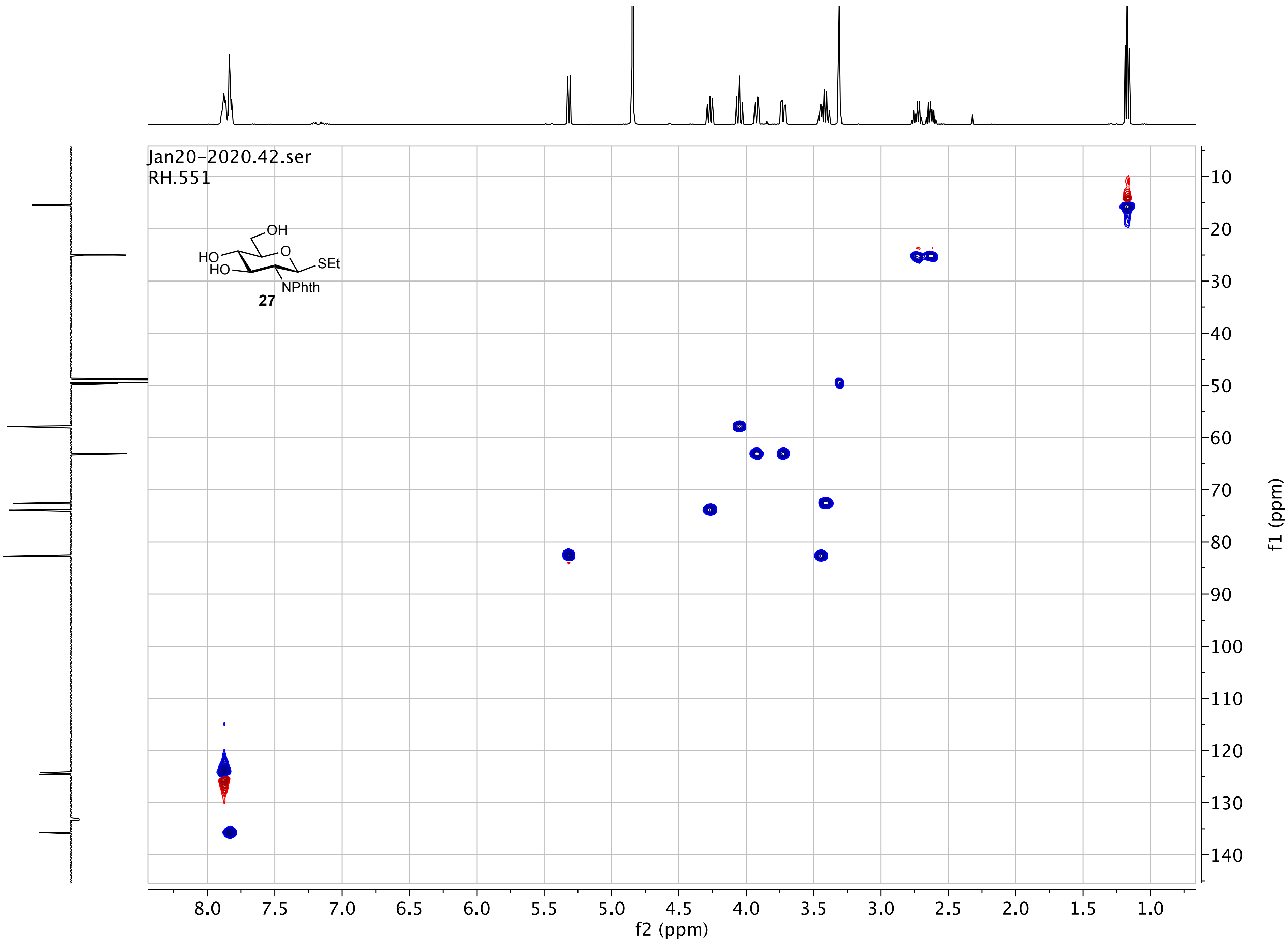
^{13}C NMR (APT) in CD_3OD (125 MHz)



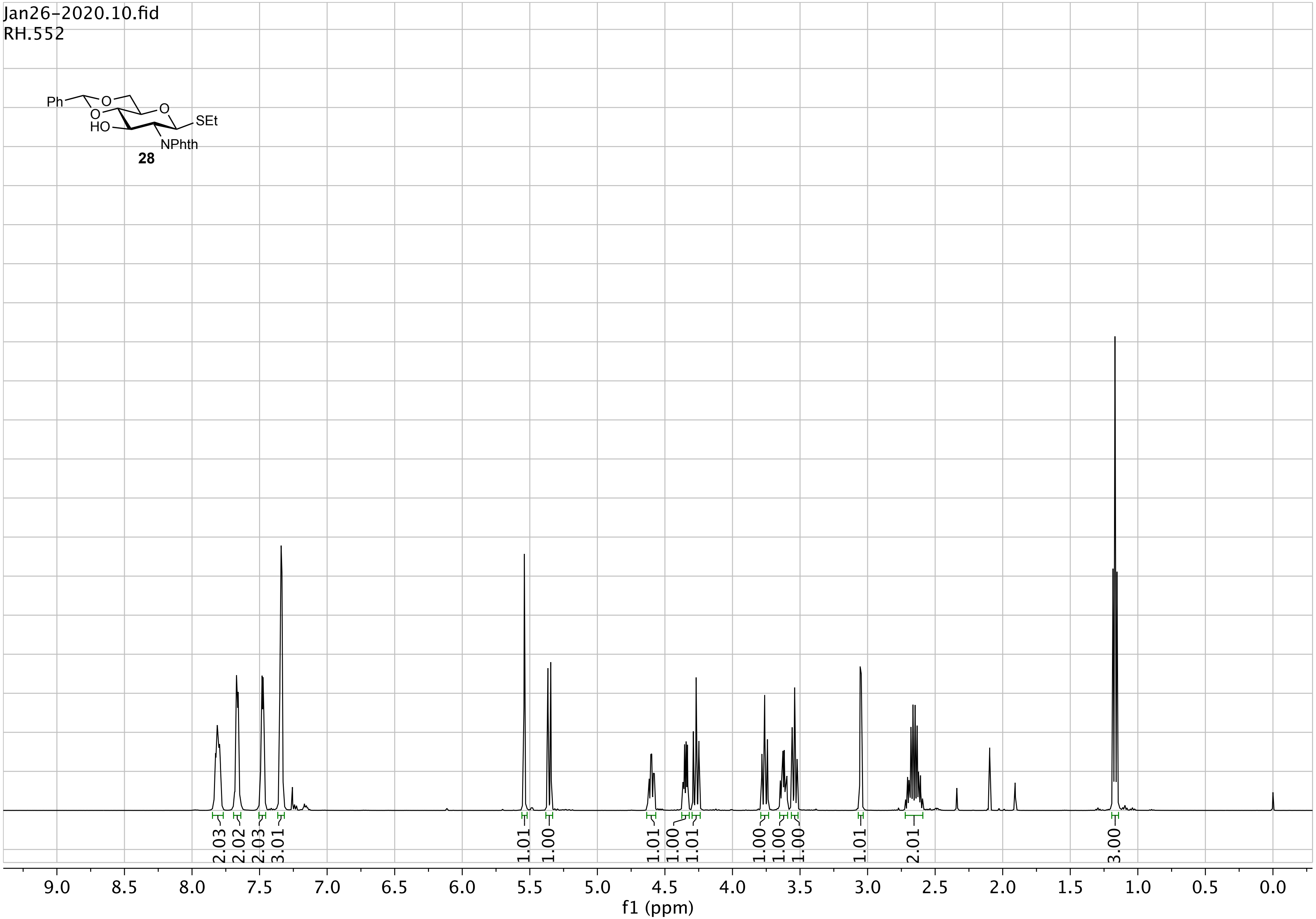
$^1H\_^1H$ gCOSY in CD_3OD



$^{1}H\_^{13}C$ gHSQC in CD_3OD



^1H NMR in $CDCl_3$ (500 MHz)



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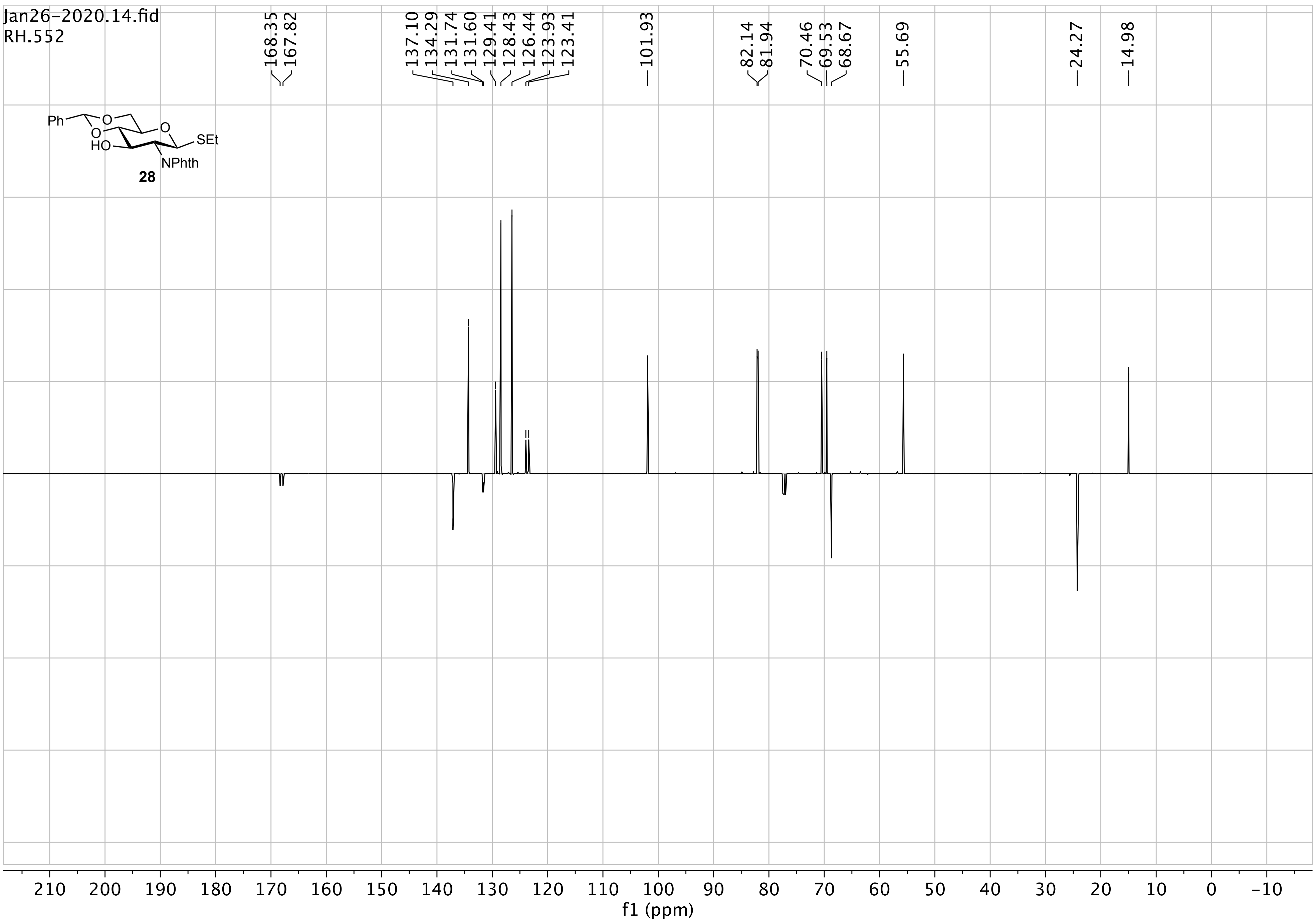
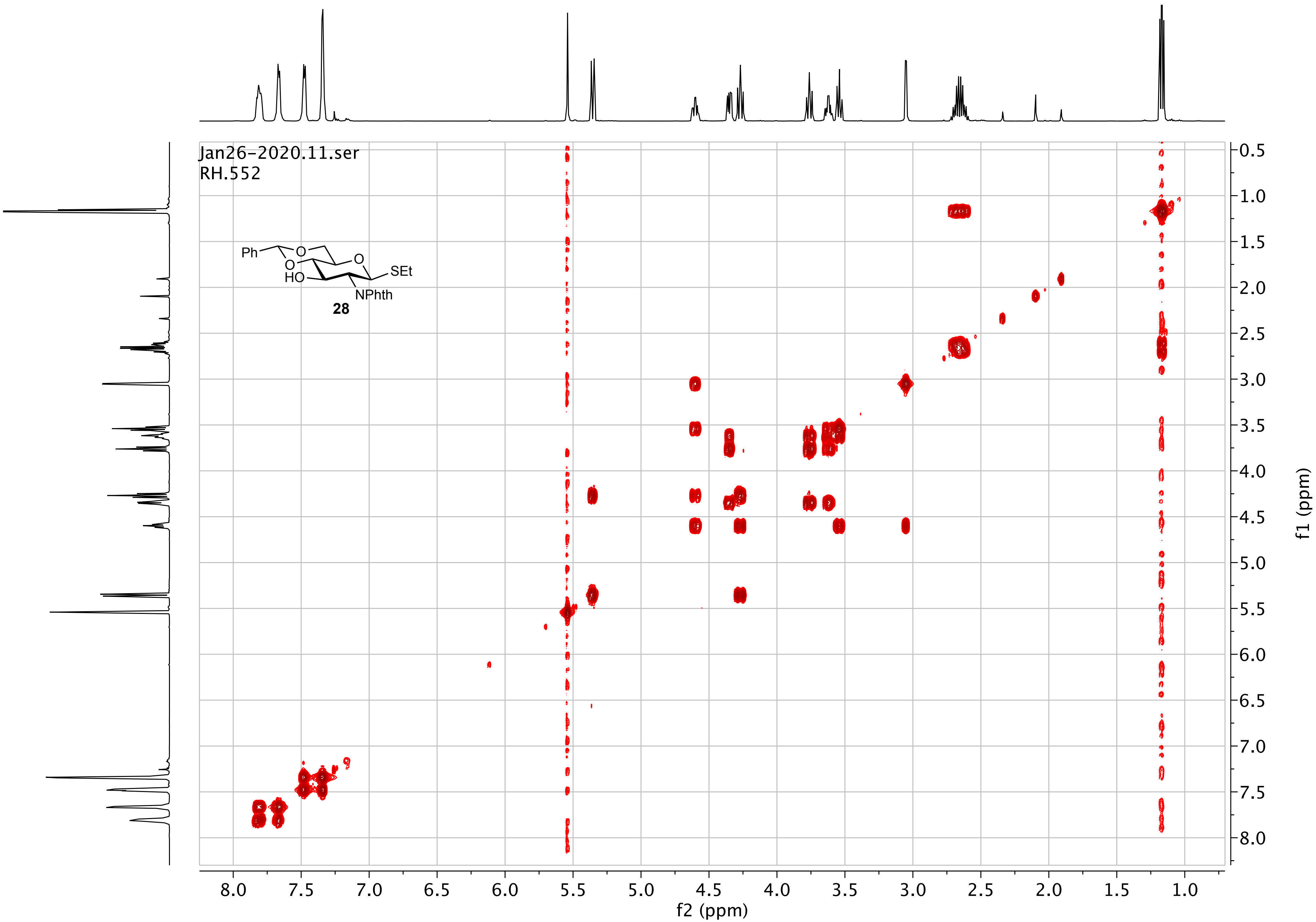
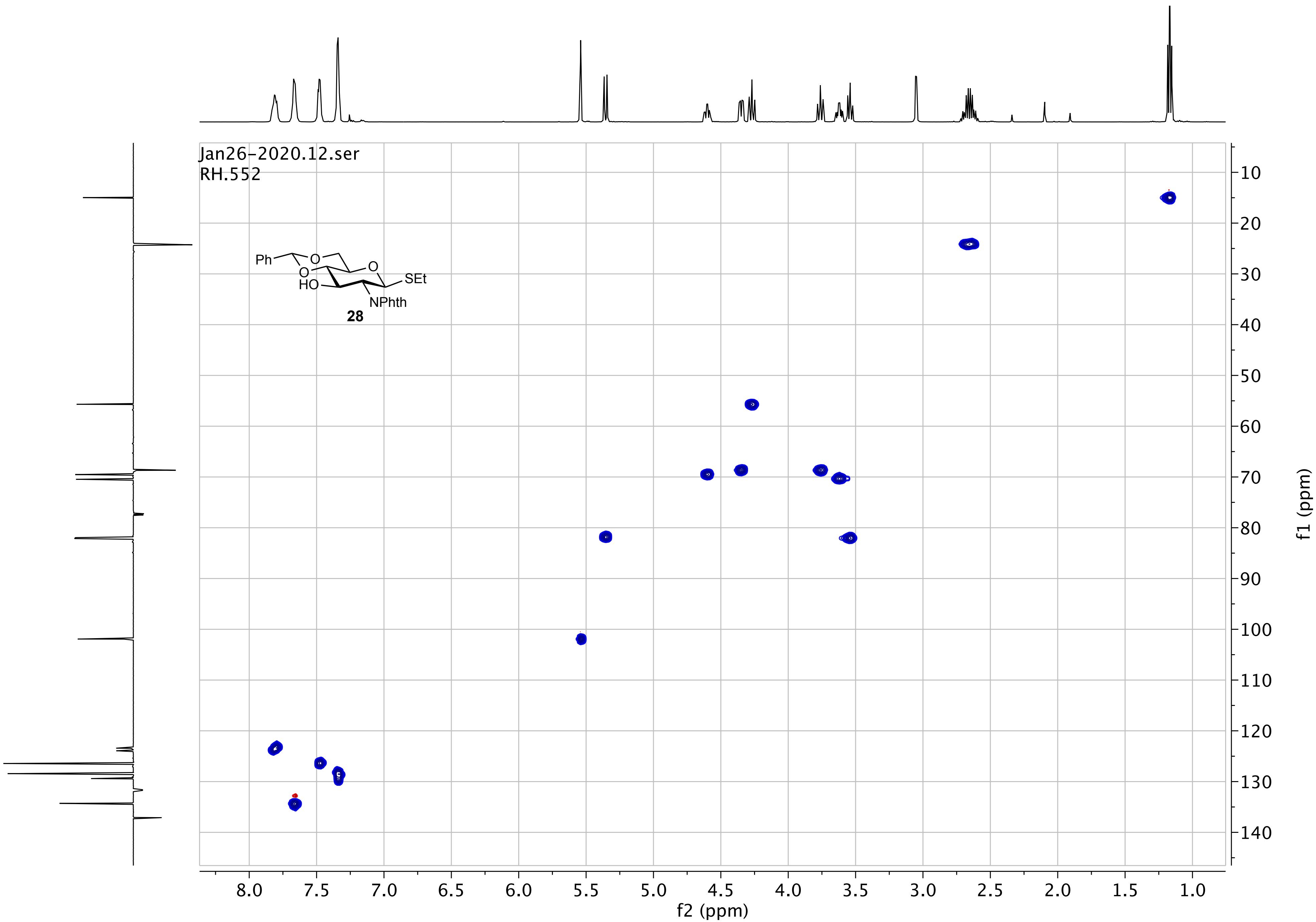
^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



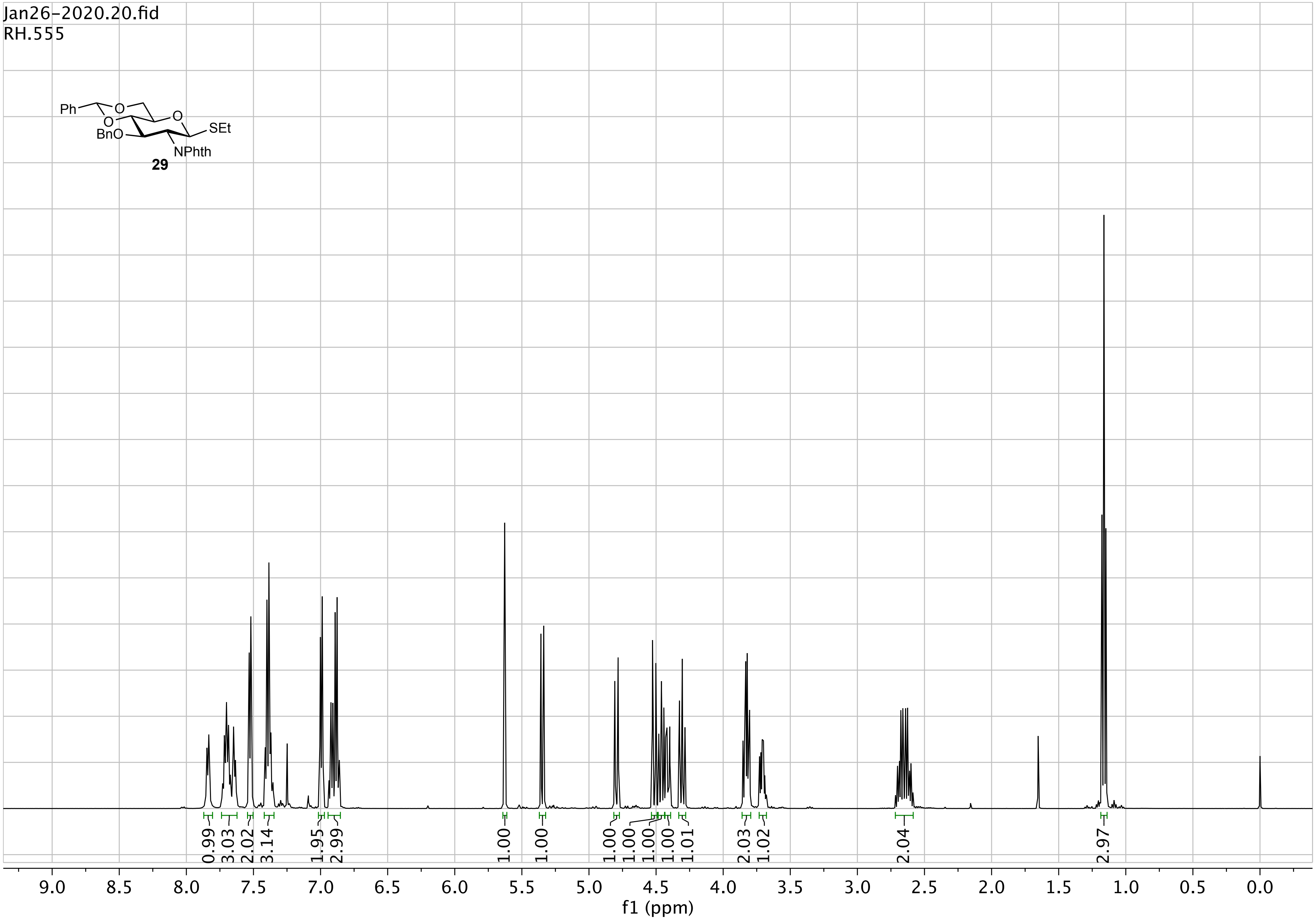
^1H_^1H gCOSY in $CDCl_3$



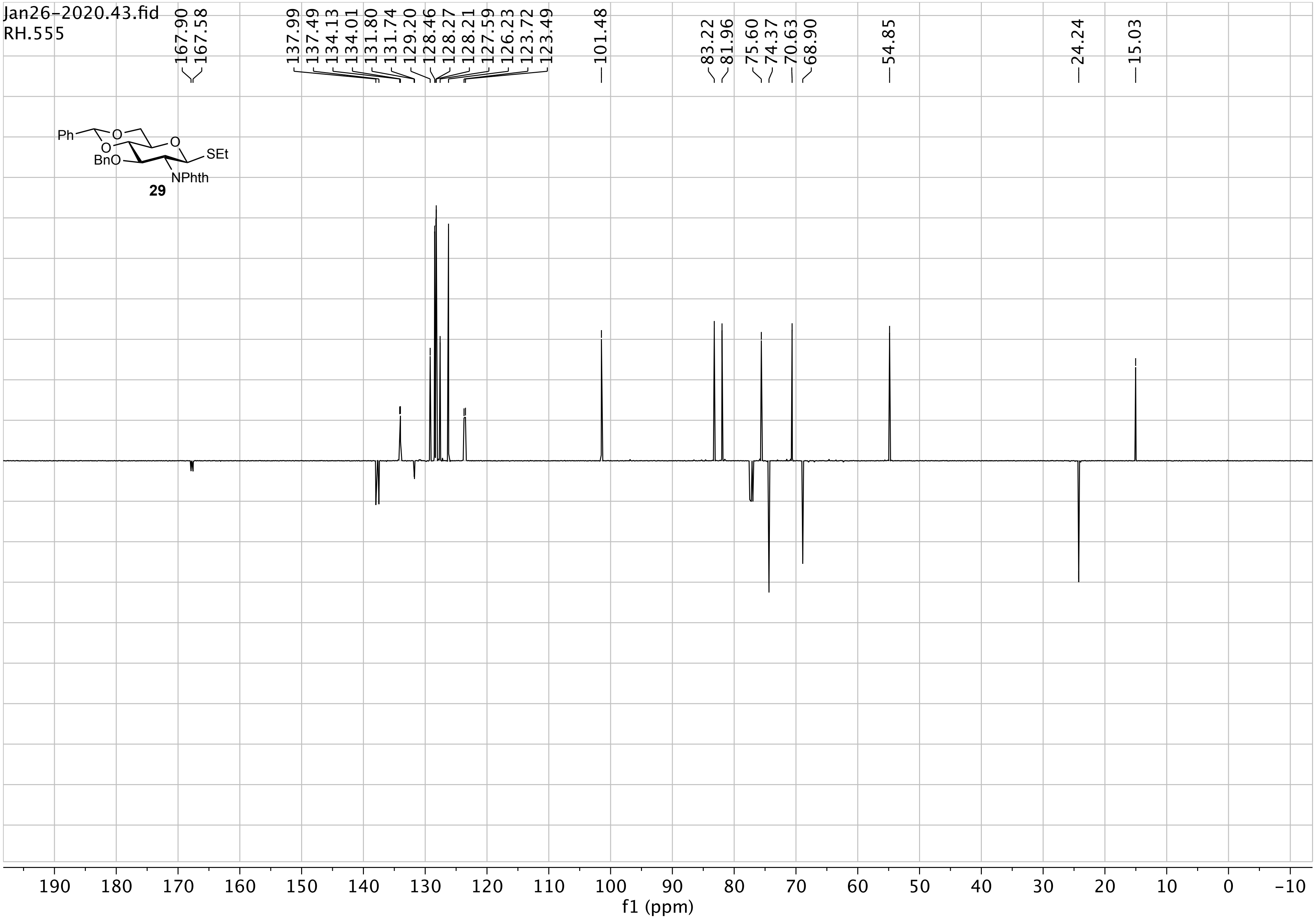
$^1H\_^{13}C$ gHSQC in $CDCl_3$



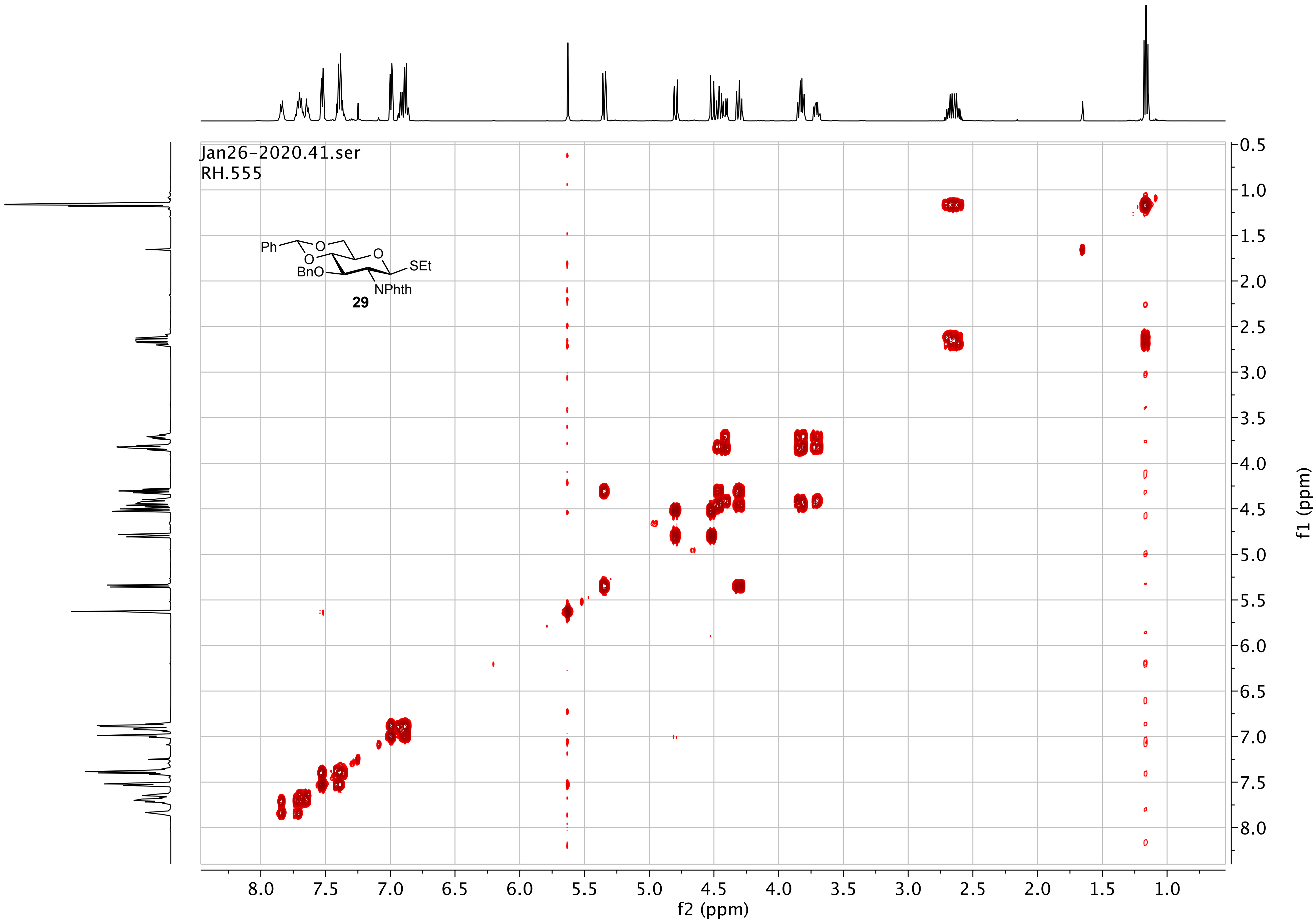
^{1}H NMR in $CDCl_3$ (500 MHz)



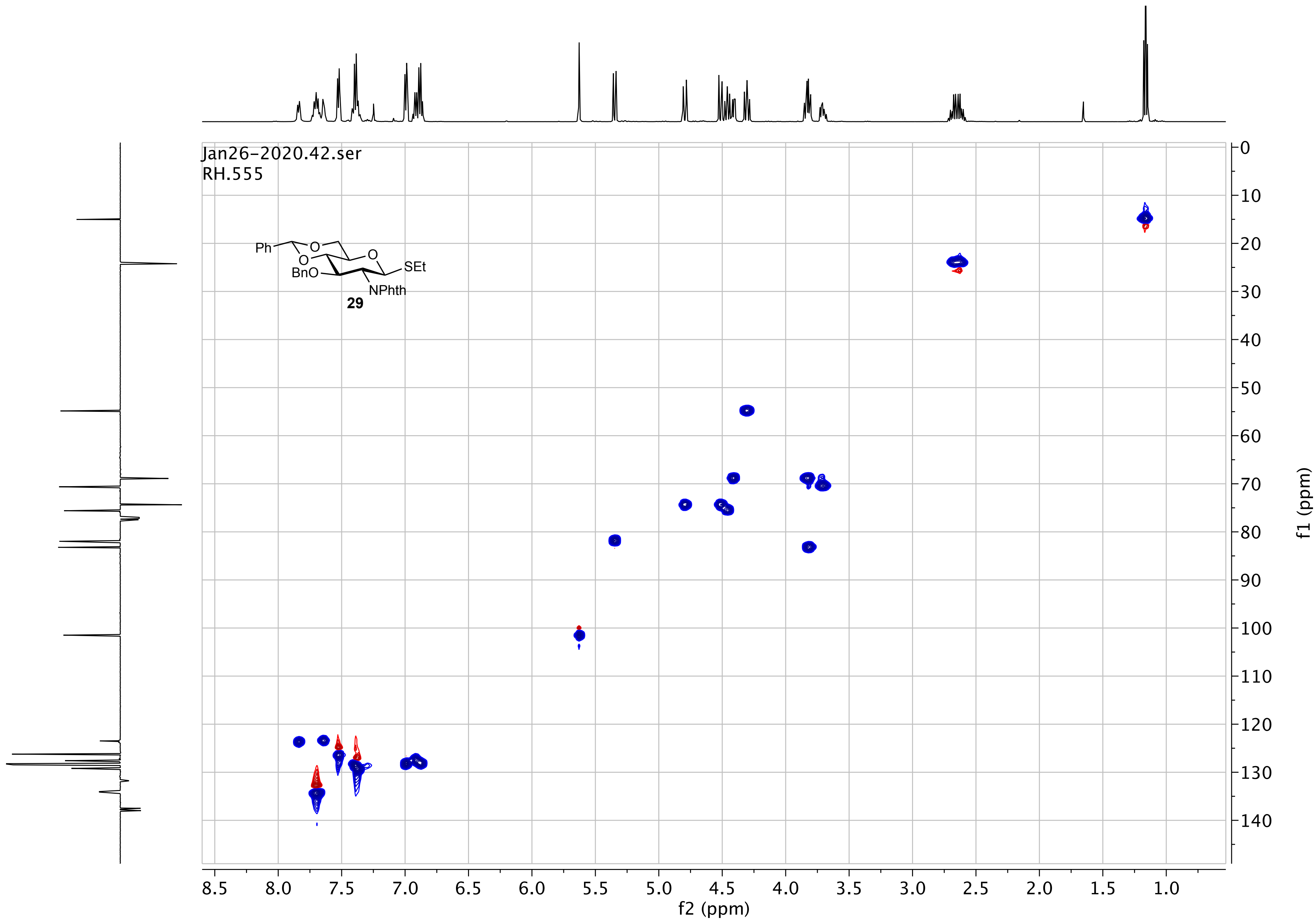
^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



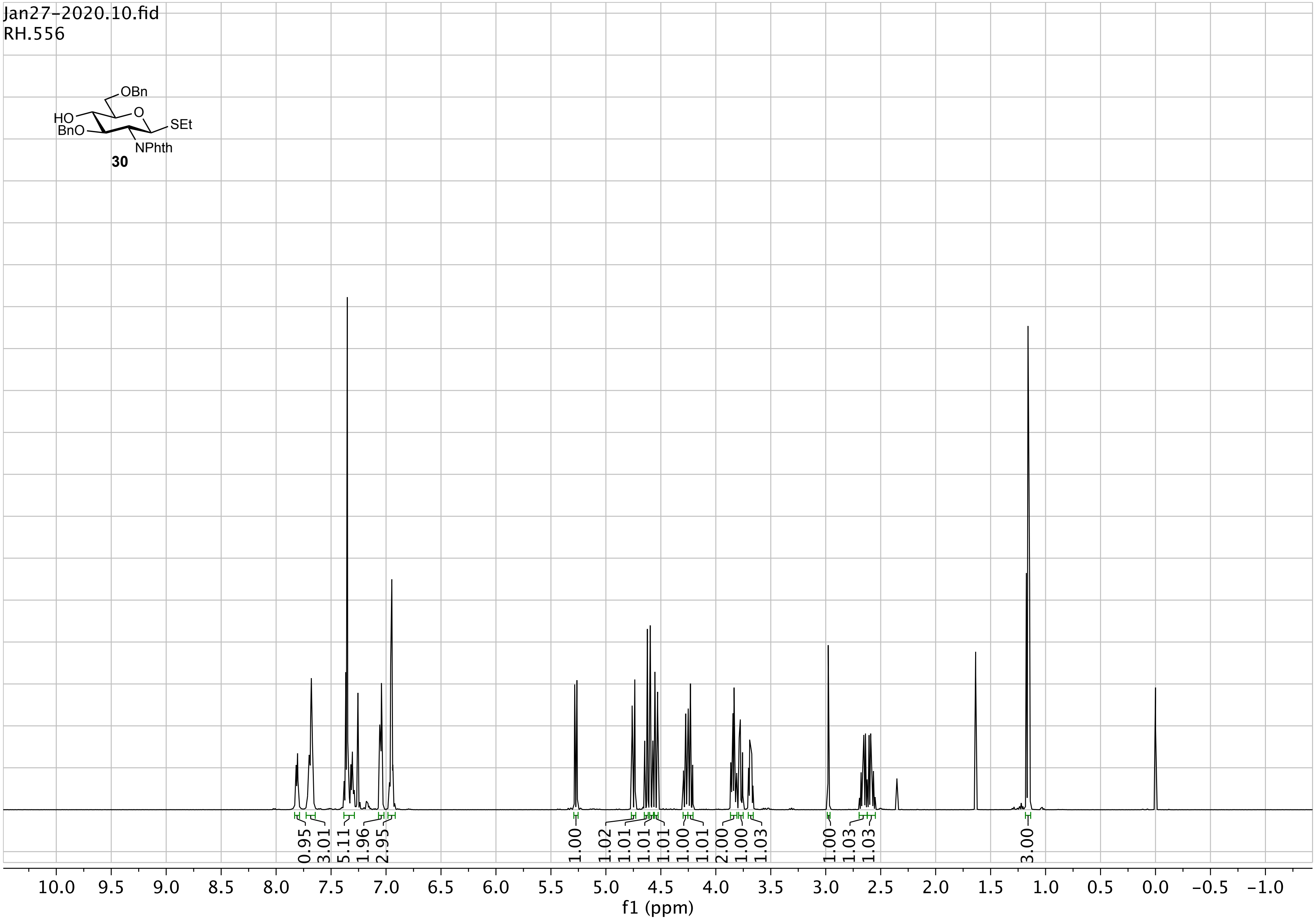
$^{1}H\_^{1}H$ gCOSY in $CDCl_3$



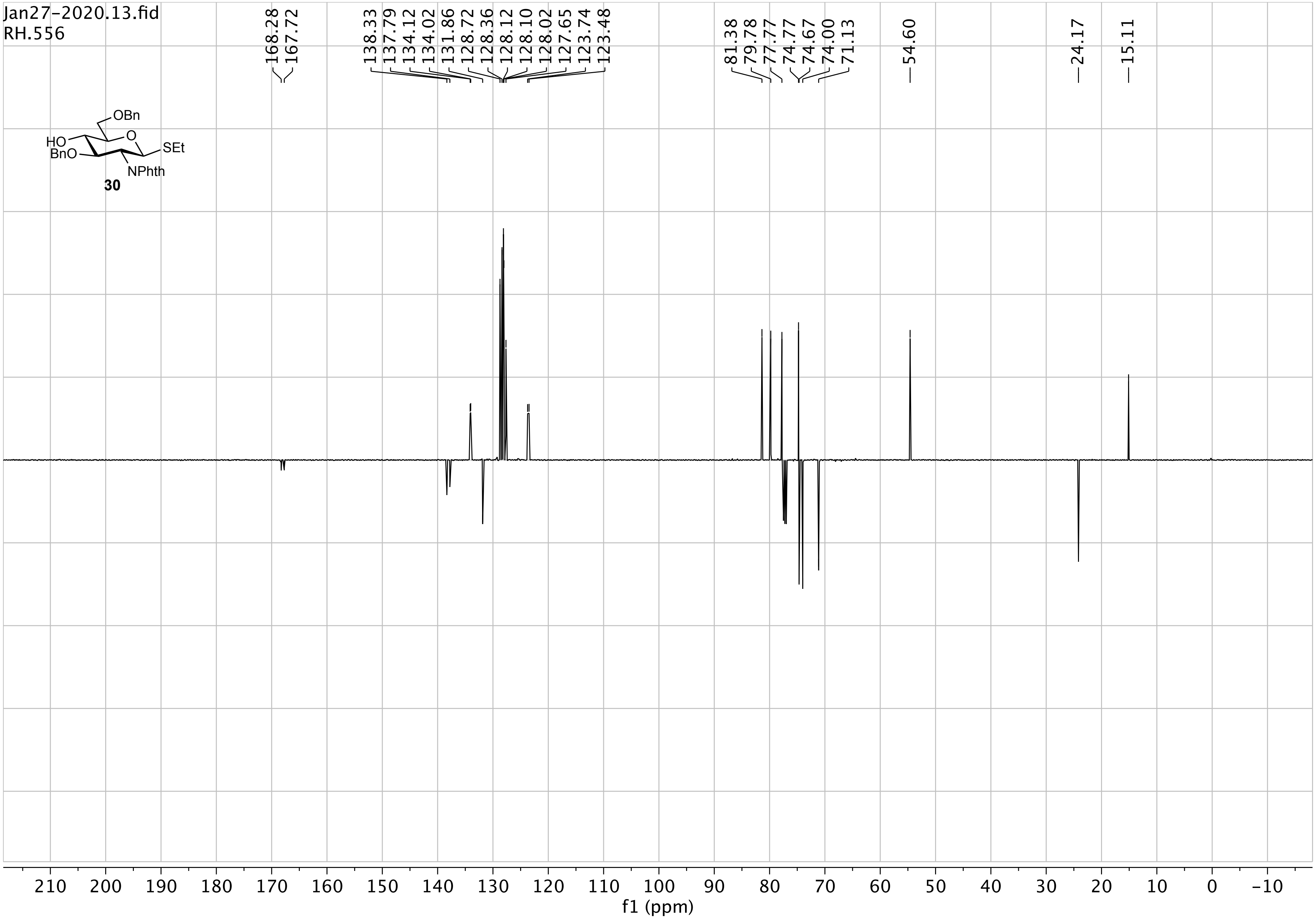
$^{1}H\_^{13}C$ gHSQC in $CDCl_3$



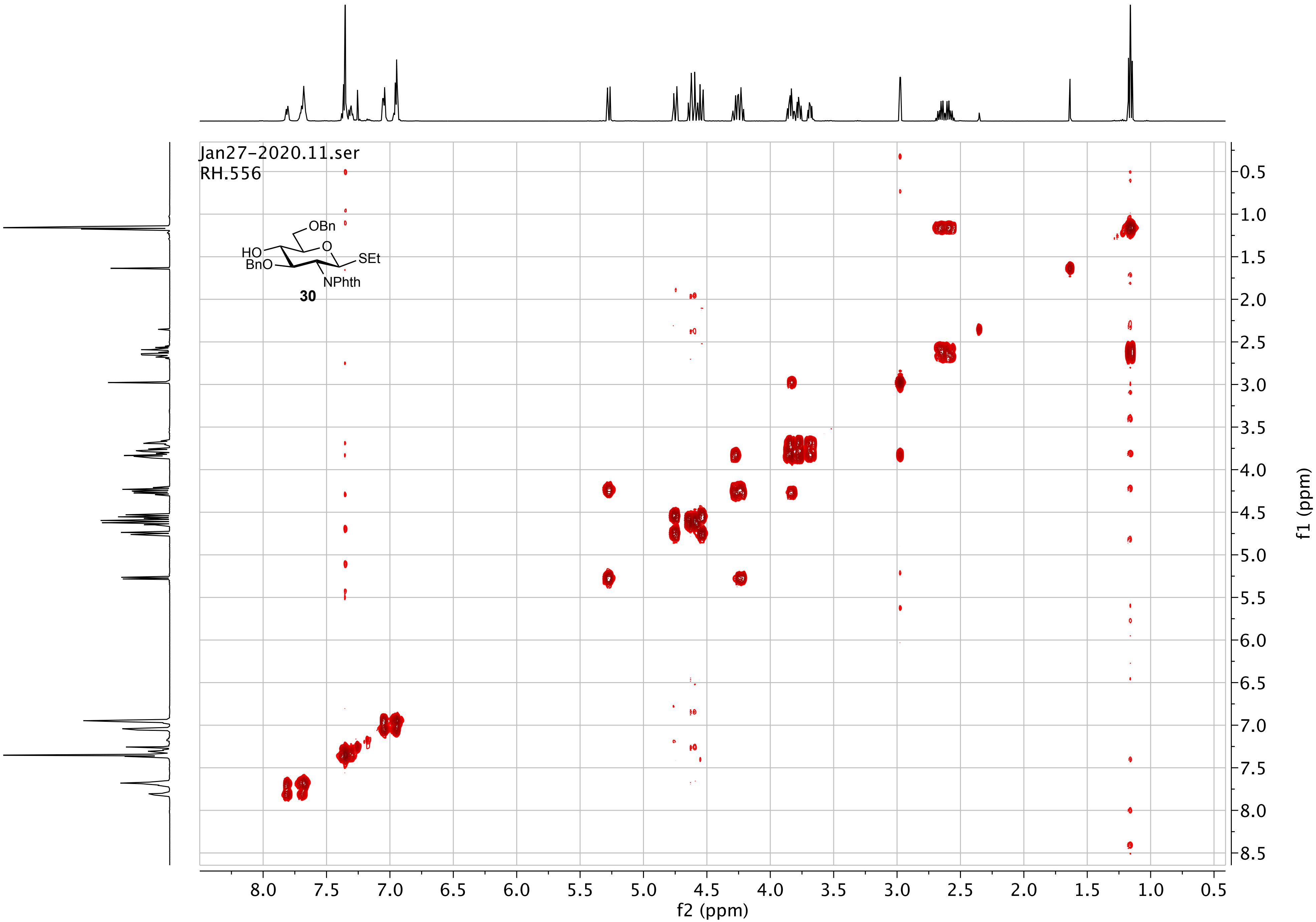
^1H NMR in $CDCl_3$ (500 MHz)



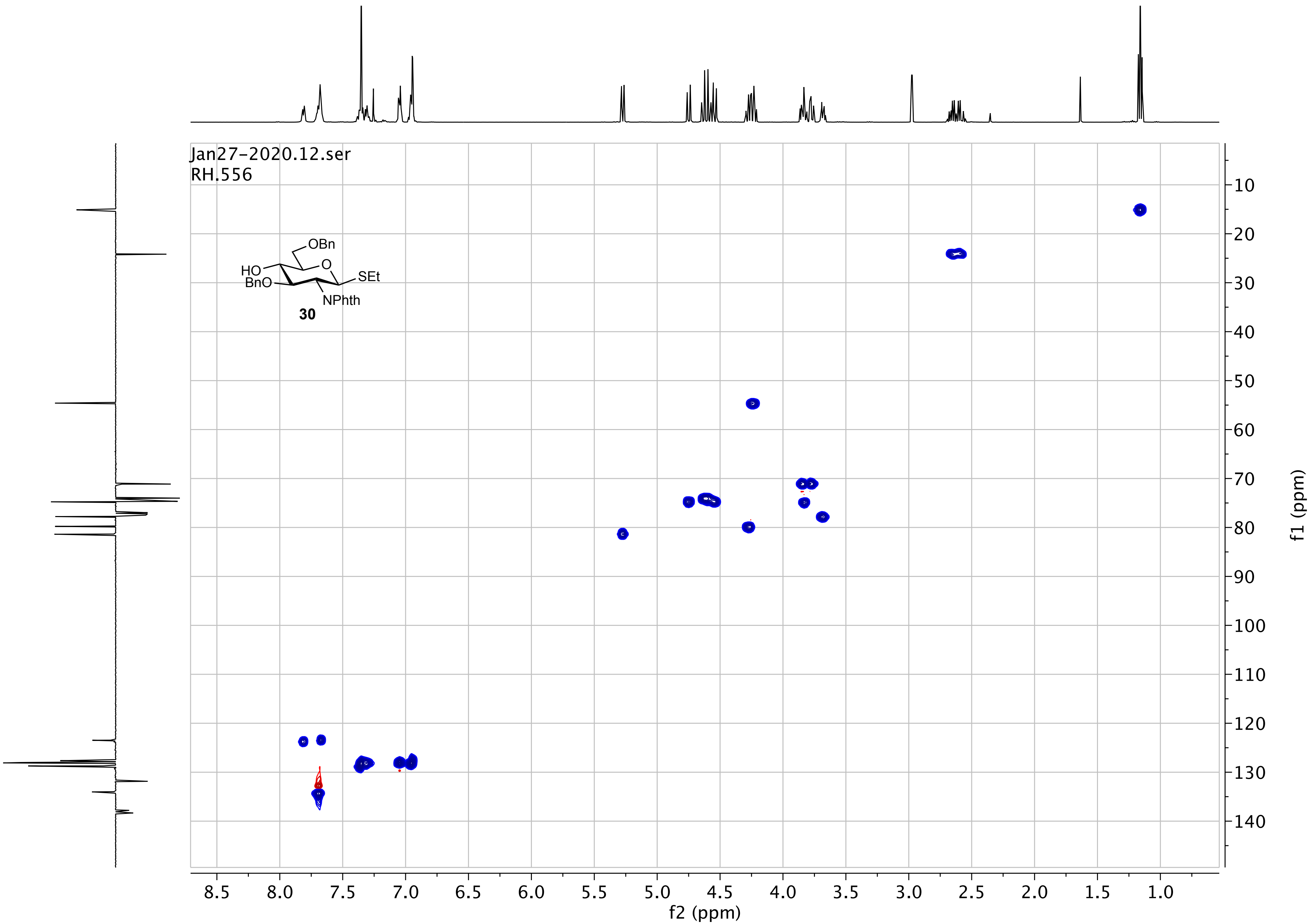
^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



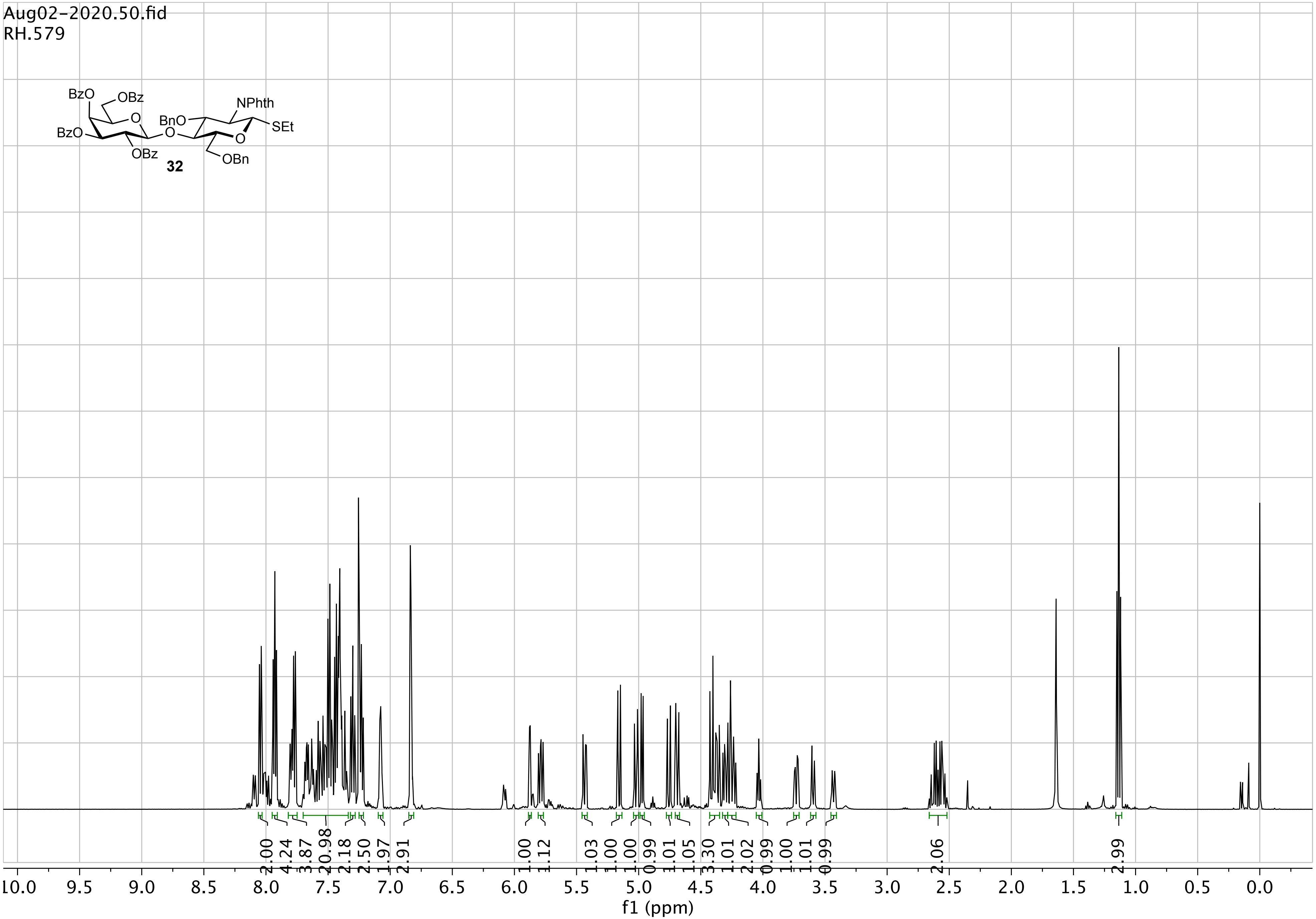
$^1H\_^1H$ gCOSY in $CDCl_3$



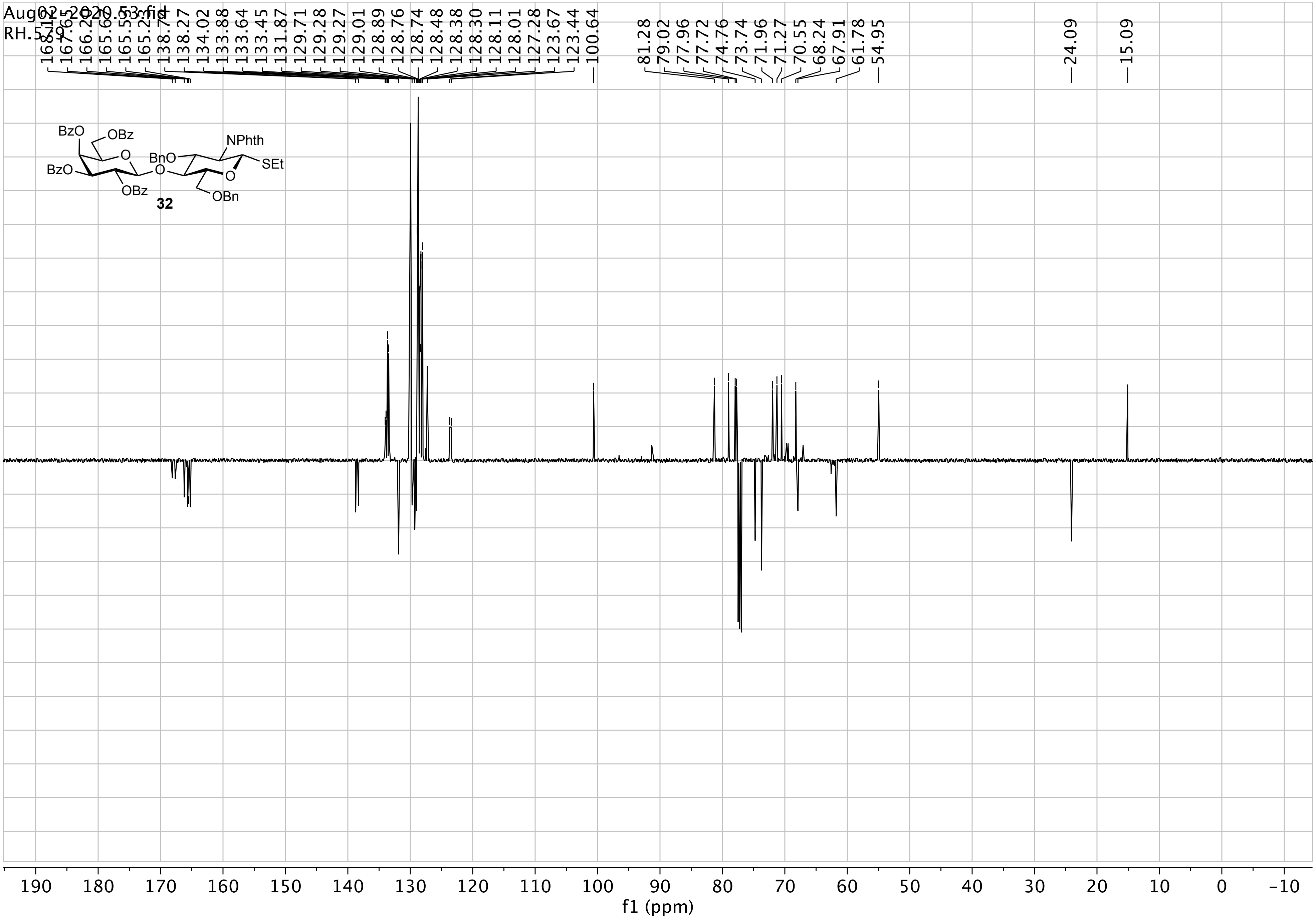
$^{1}H\_^{13}C$ gHSQC in $CDCl_3$



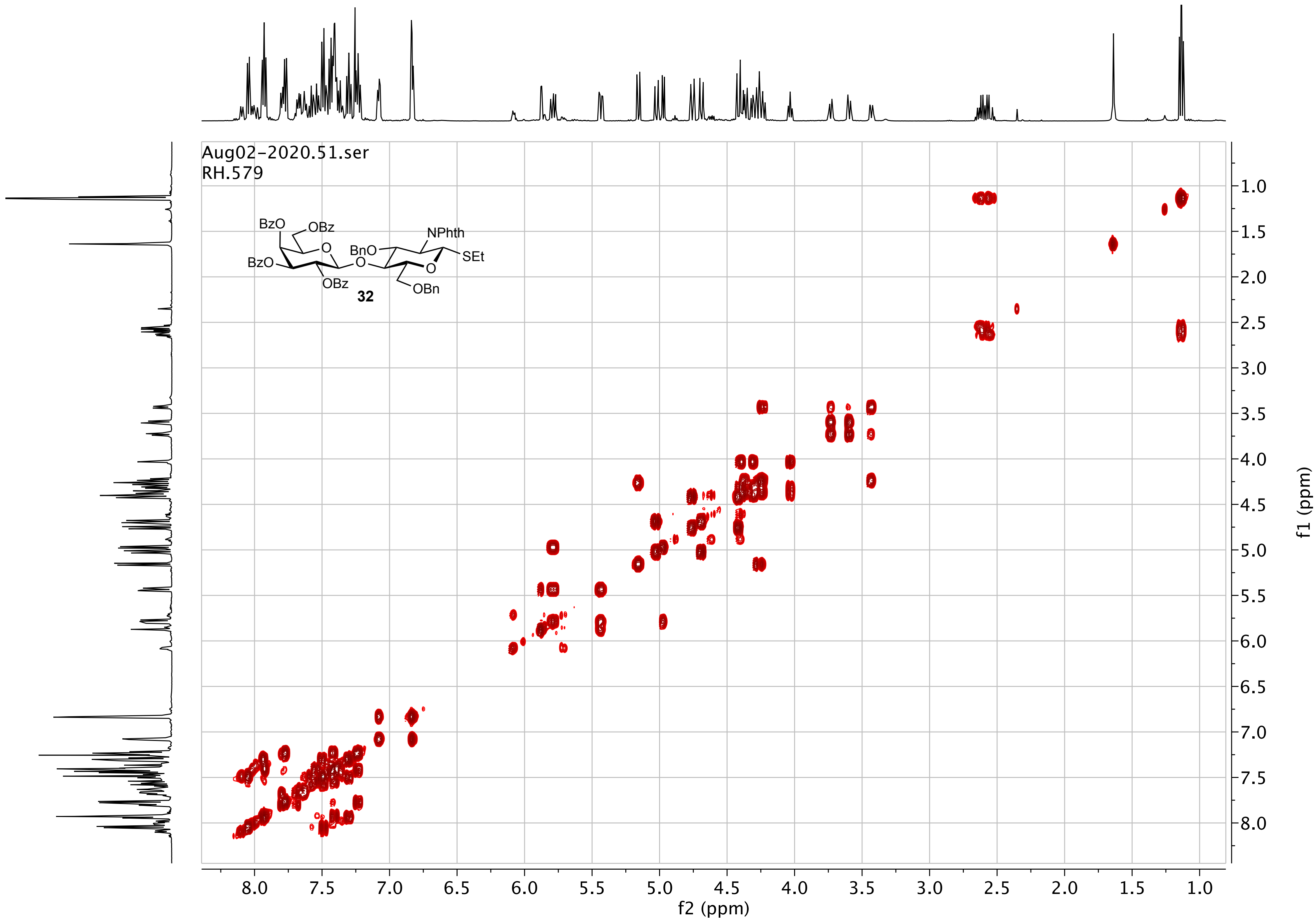
^{1}H NMR in $CDCl_3$ (500 MHz)



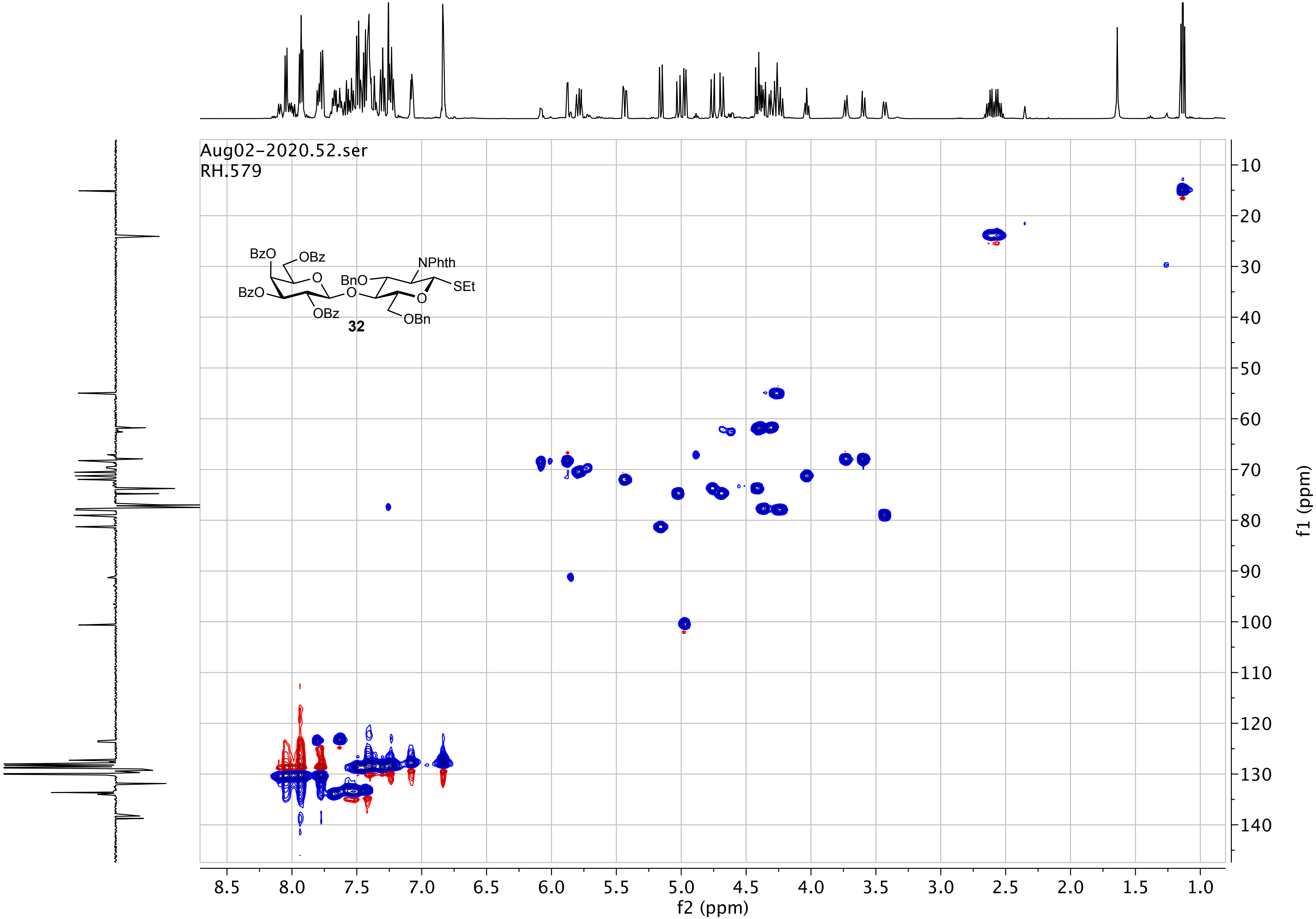
^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



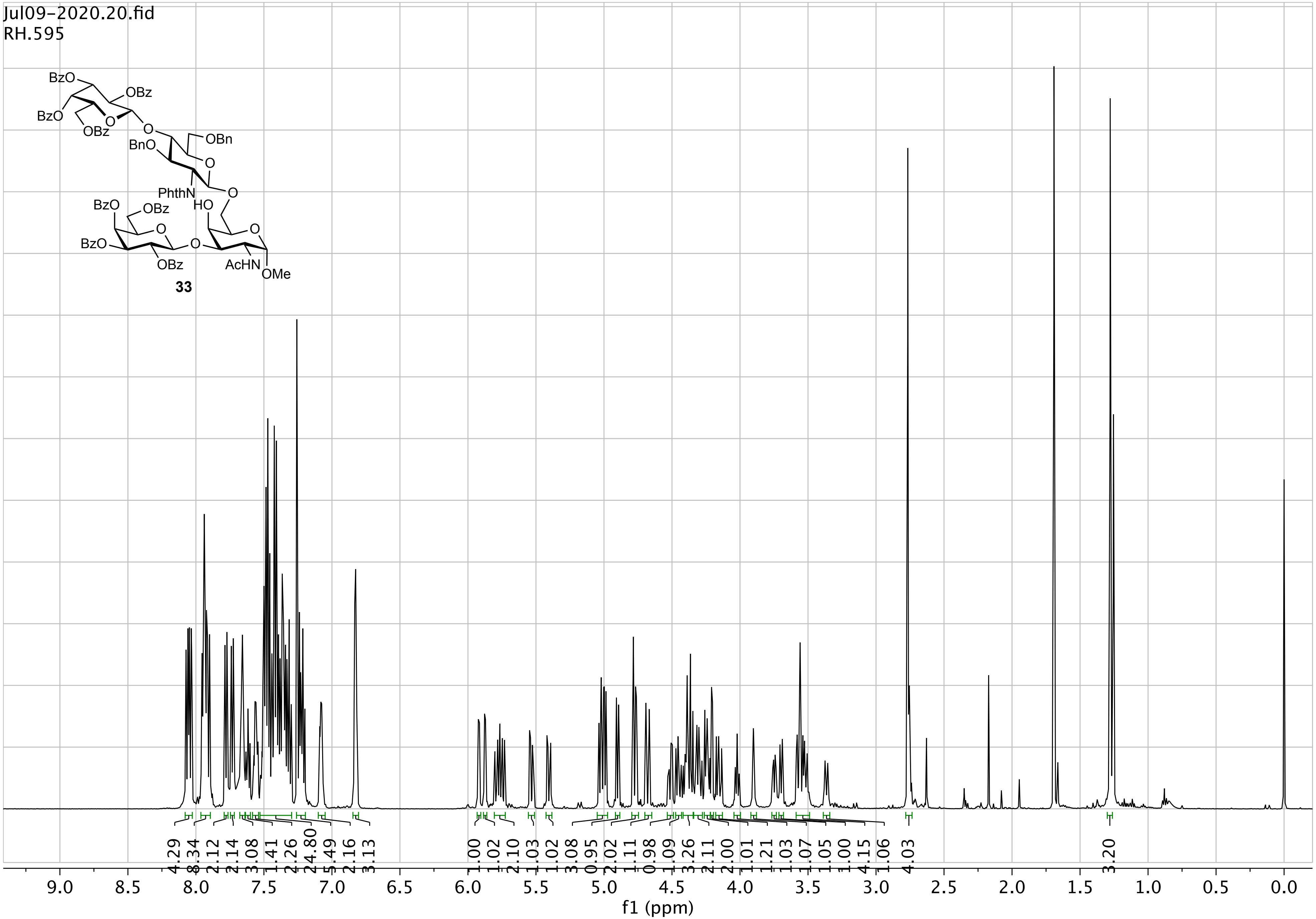
$^{1}H\_^{1}H$ gCOSY in $CDCl_3$



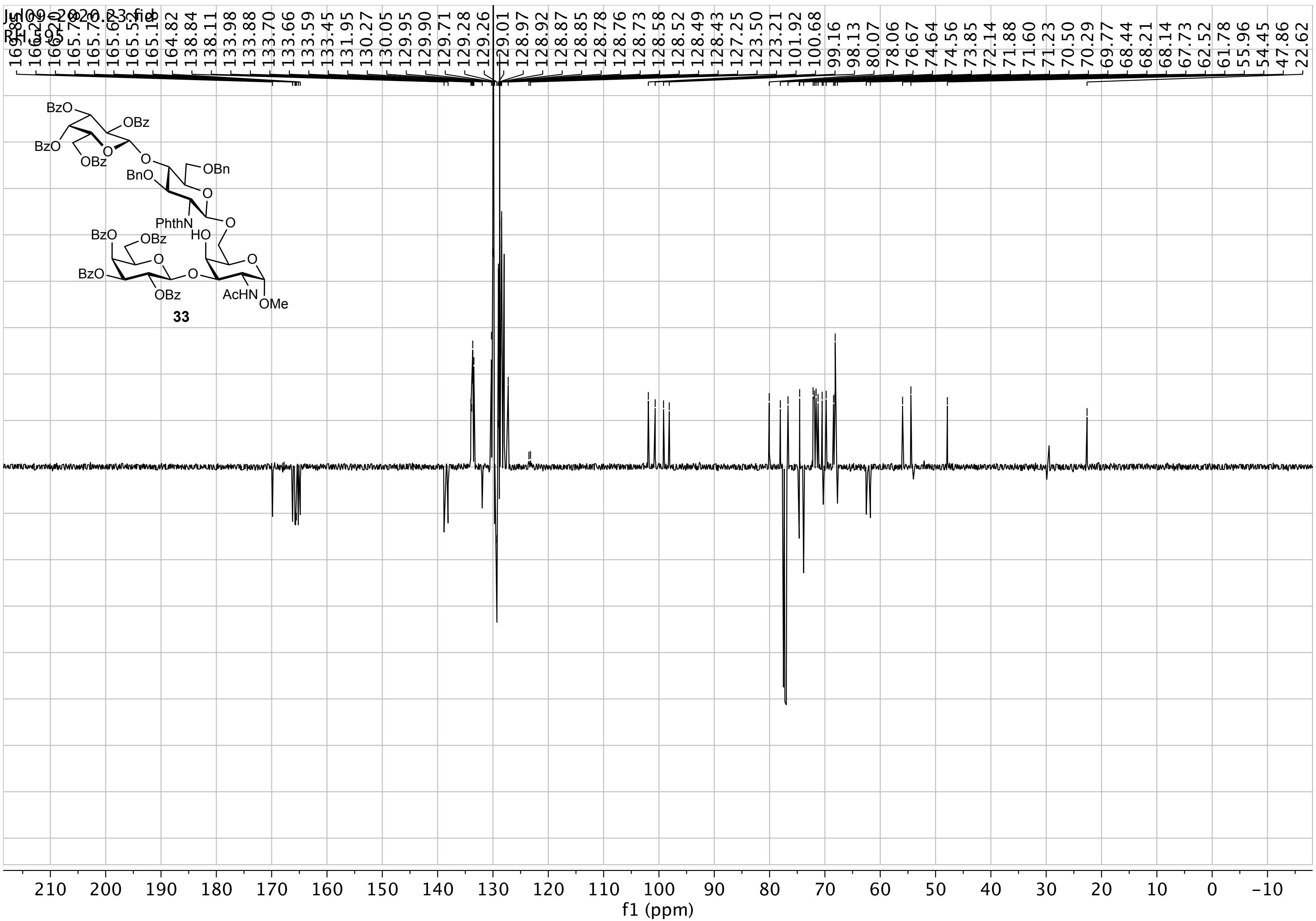
$^{1}H\_^{13}C$ gHSQC in $CDCl_3$



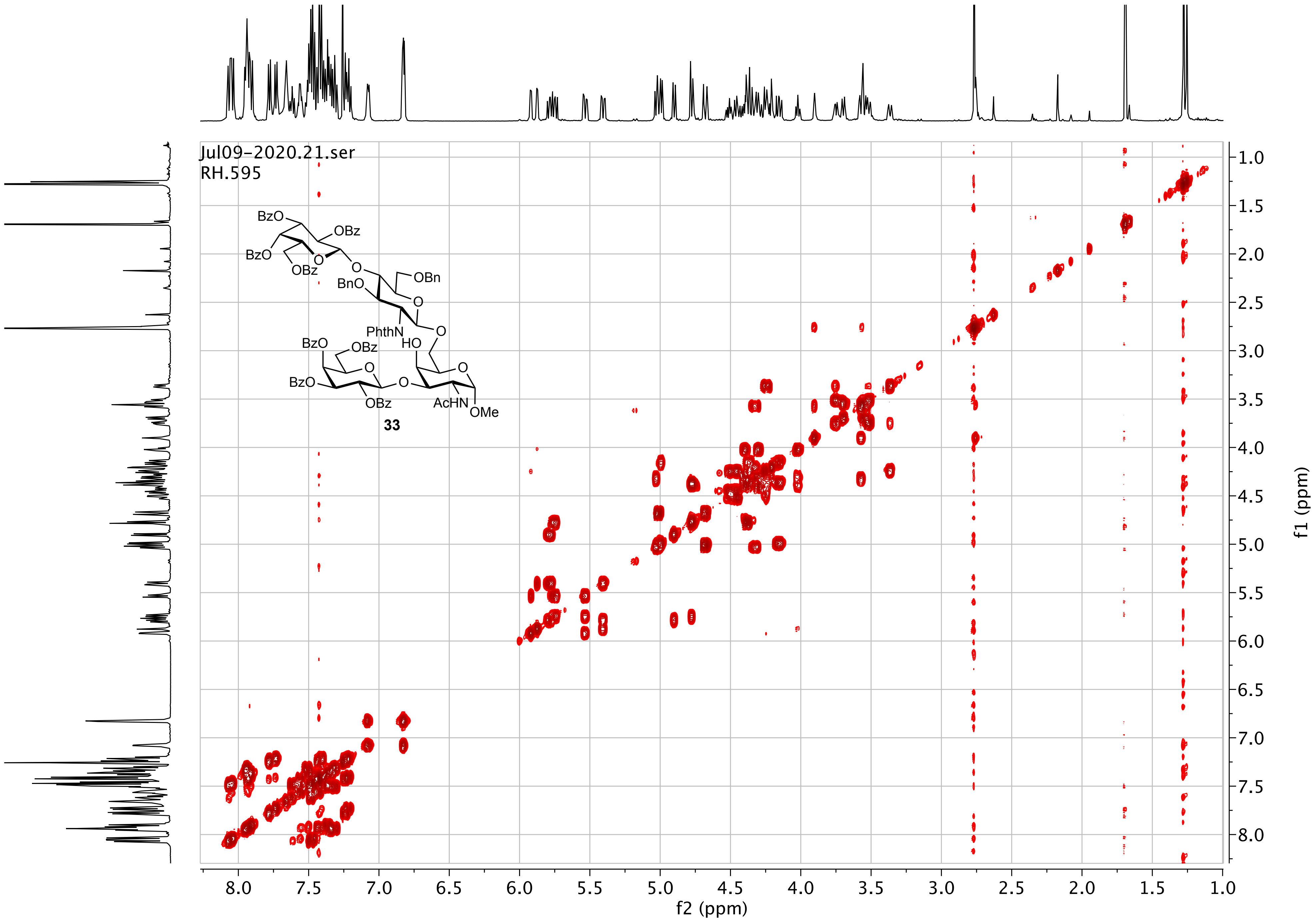
[1]H NMR in $CDCl_3$ (500 MHz)



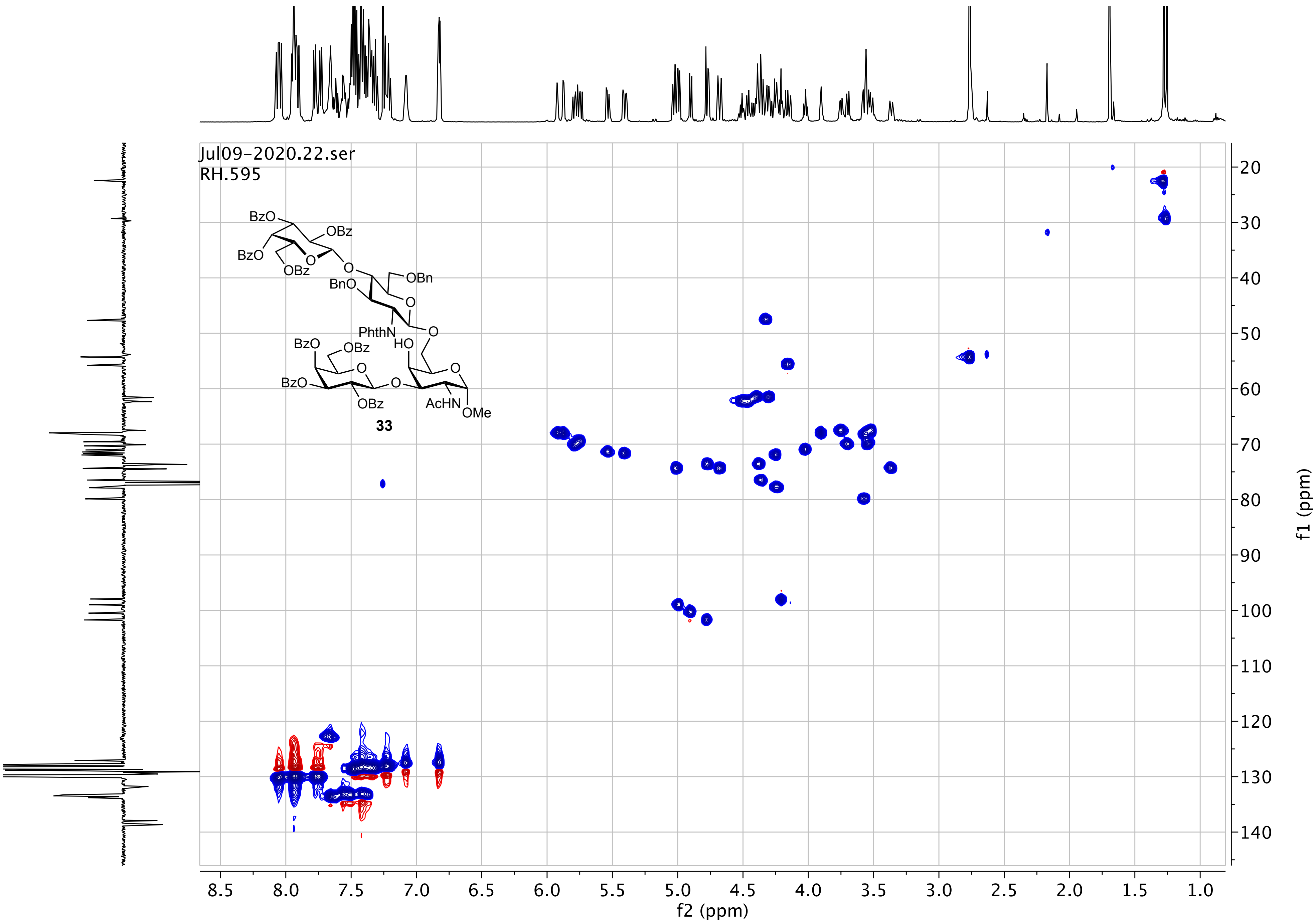
^{13}C NMR (APT) in $CDCl_3$ (125 MHz)



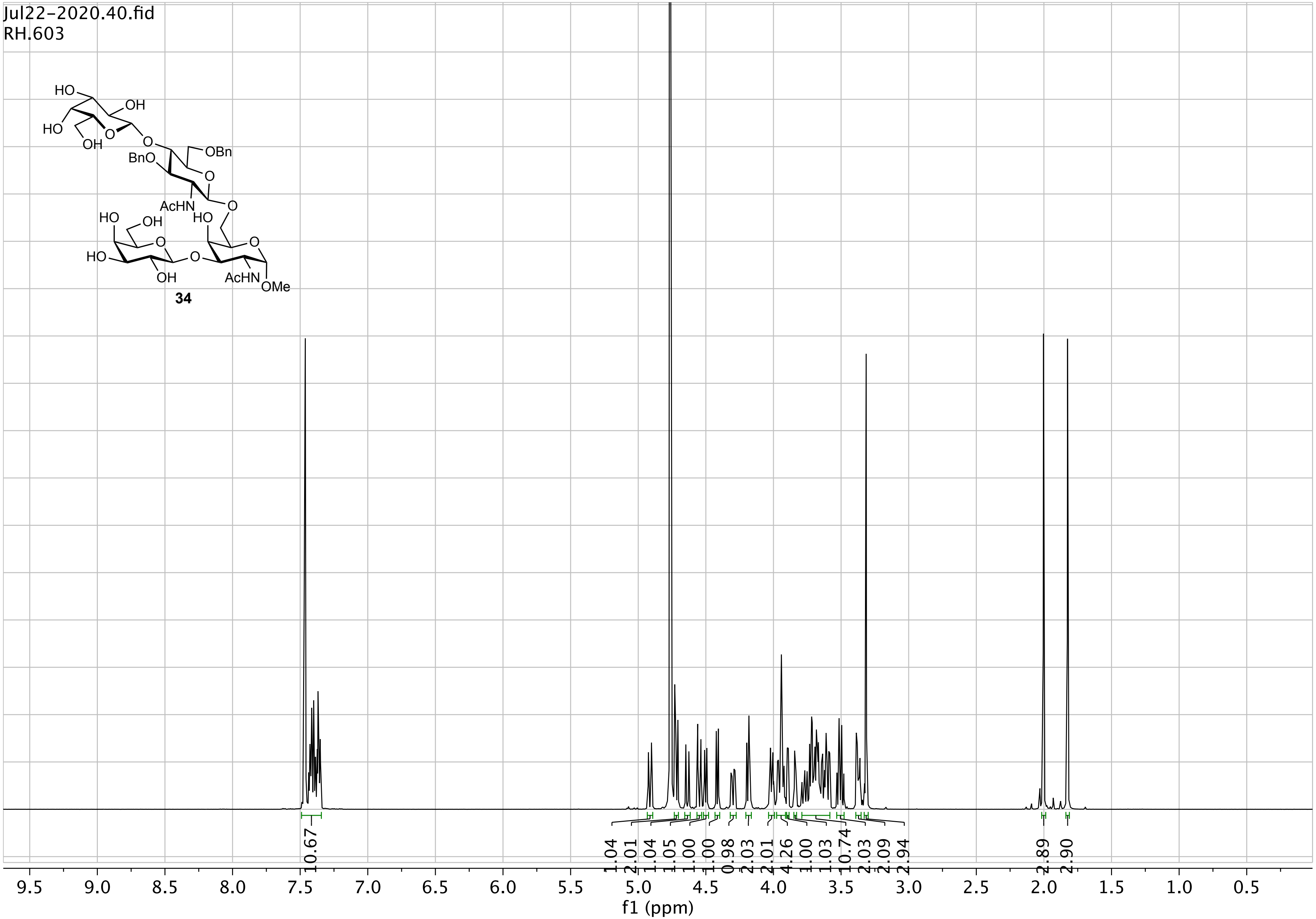
$^1H\_^1H$ gCOSY in $CDCl_3$



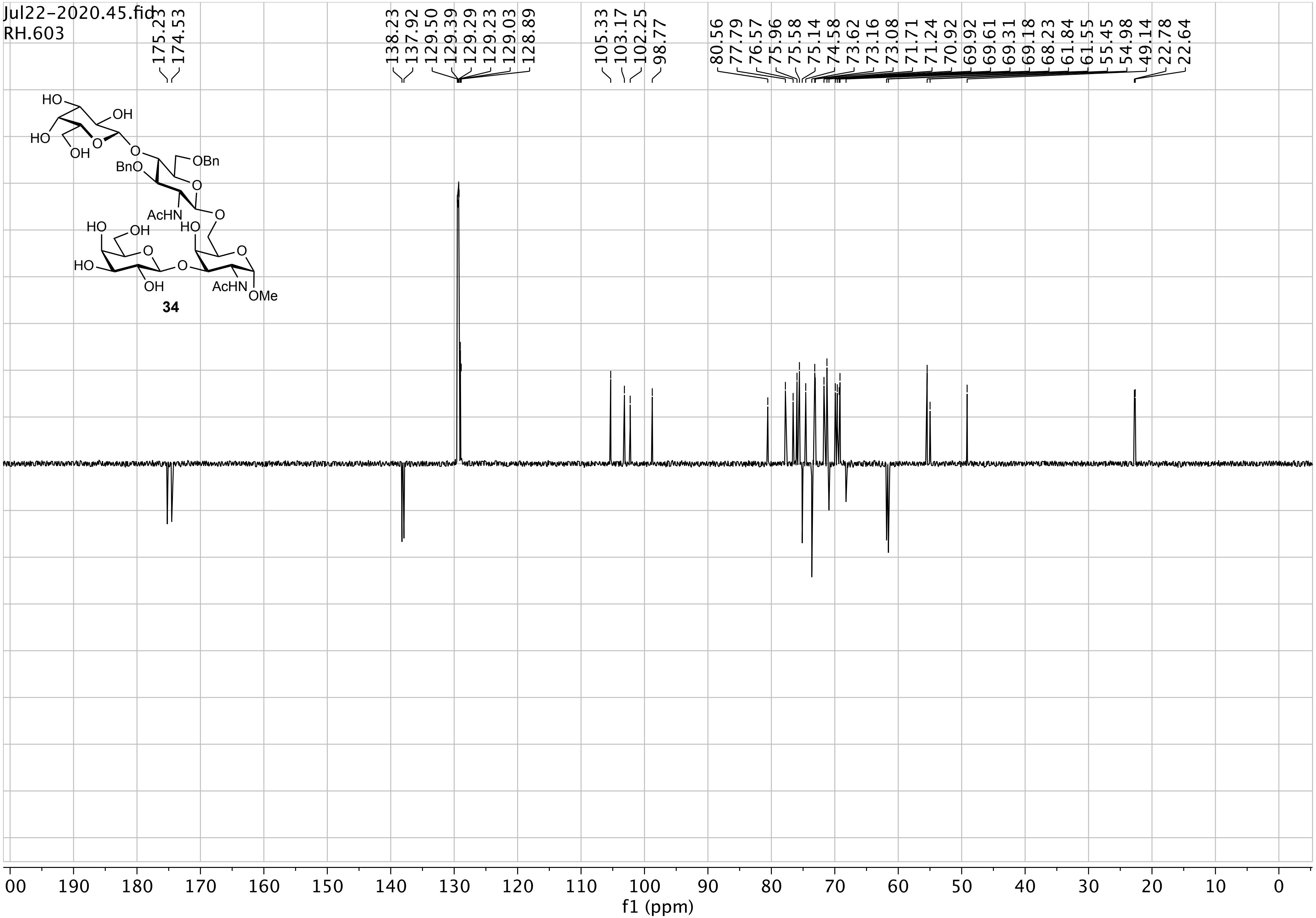
$^{1}H\_^{13}C$ gHSQC in $CDCl_3$



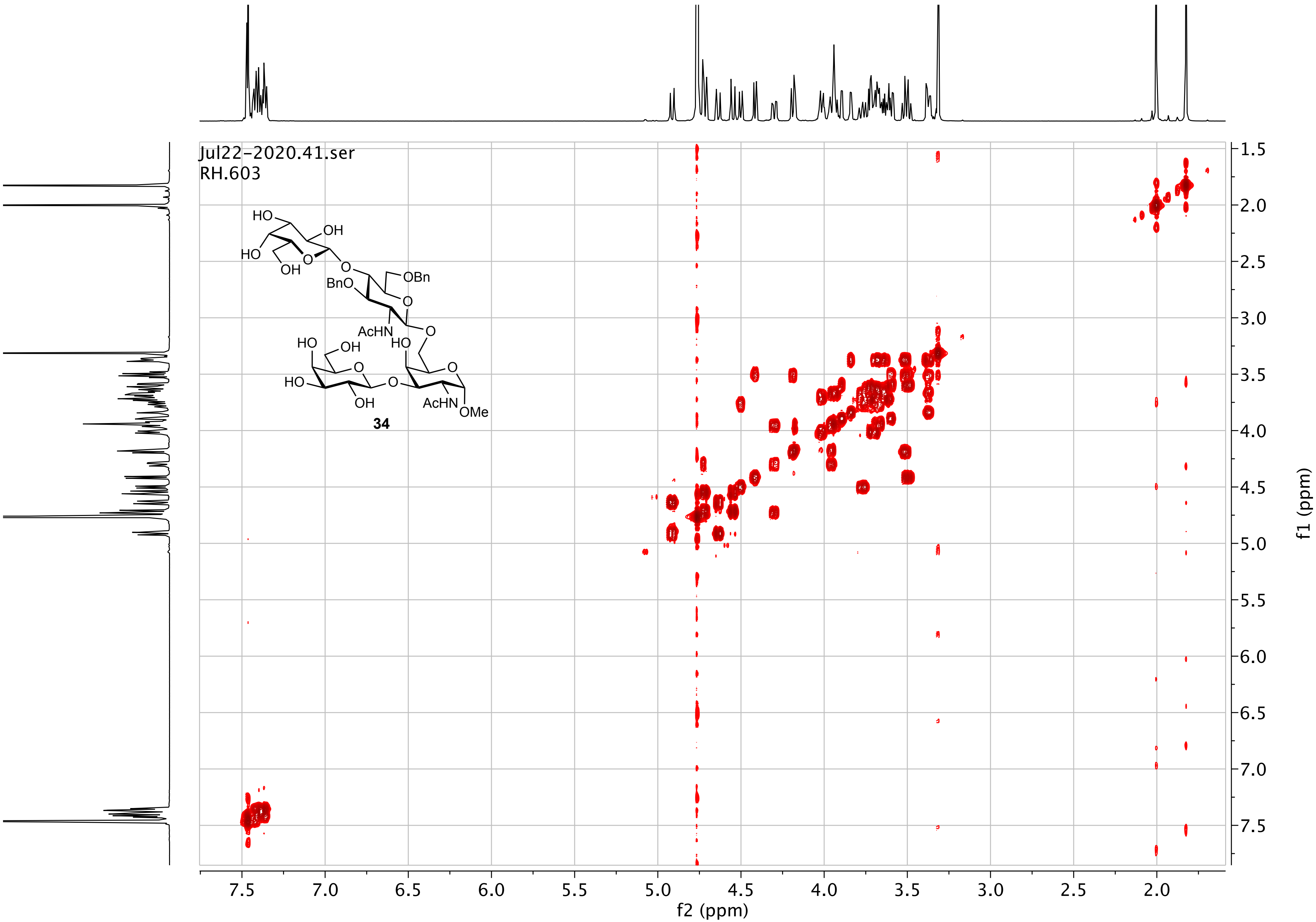
^{1}H NMR in D_2O (500 MHz)



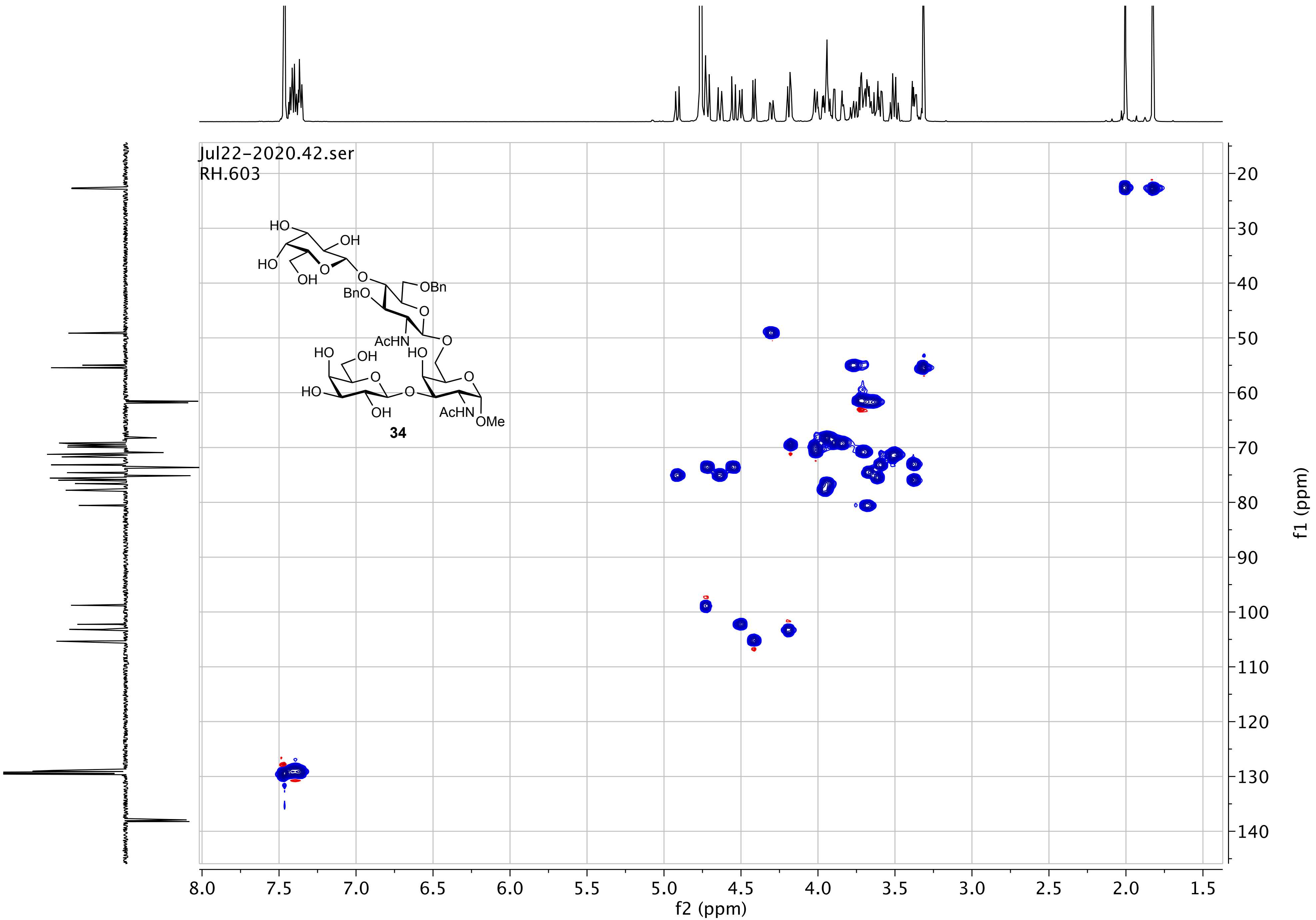
^{13}C NMR (APT) in D_2O (125 MHz)



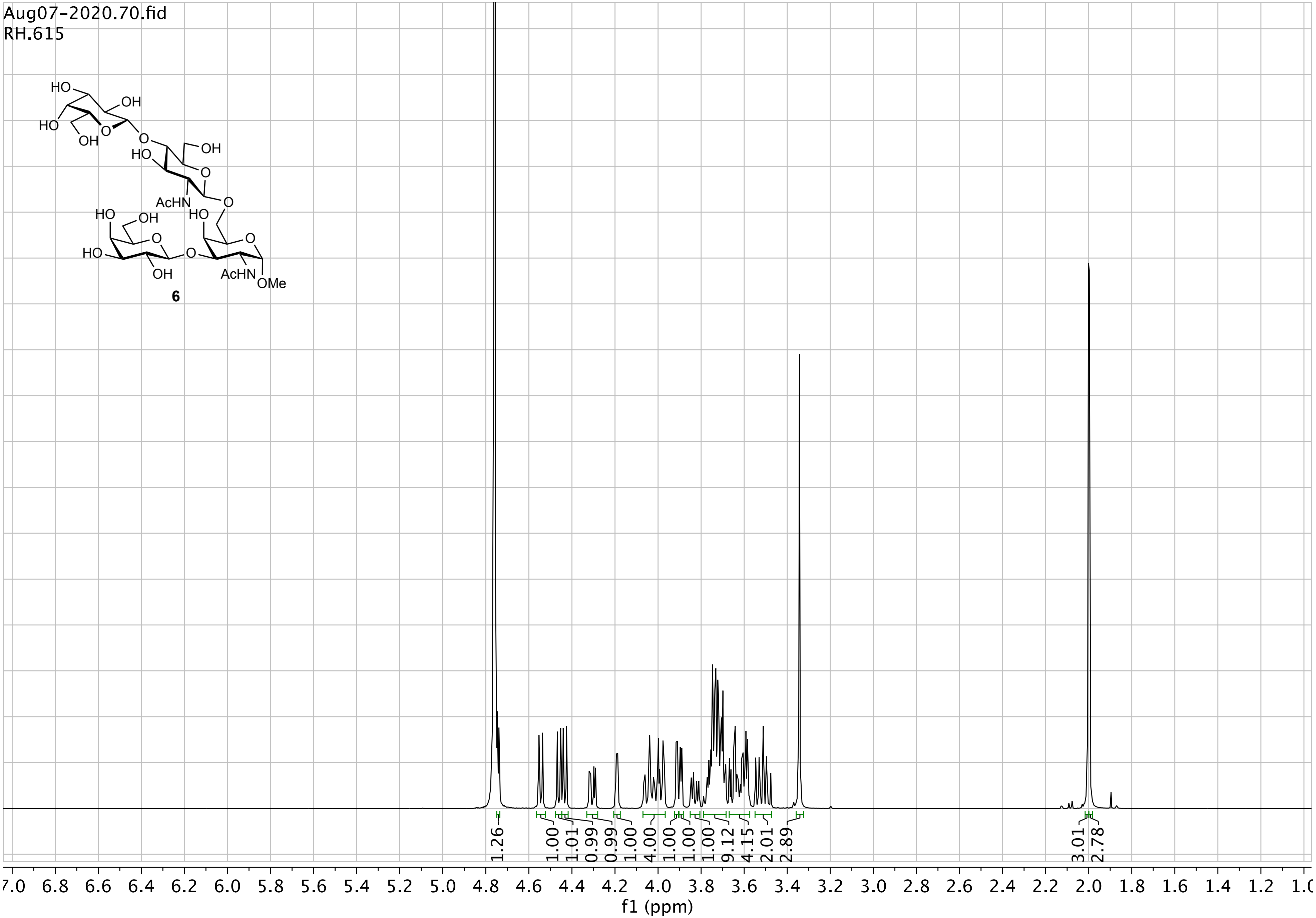
$^1H\_^1H$ gCOSY in D_2O



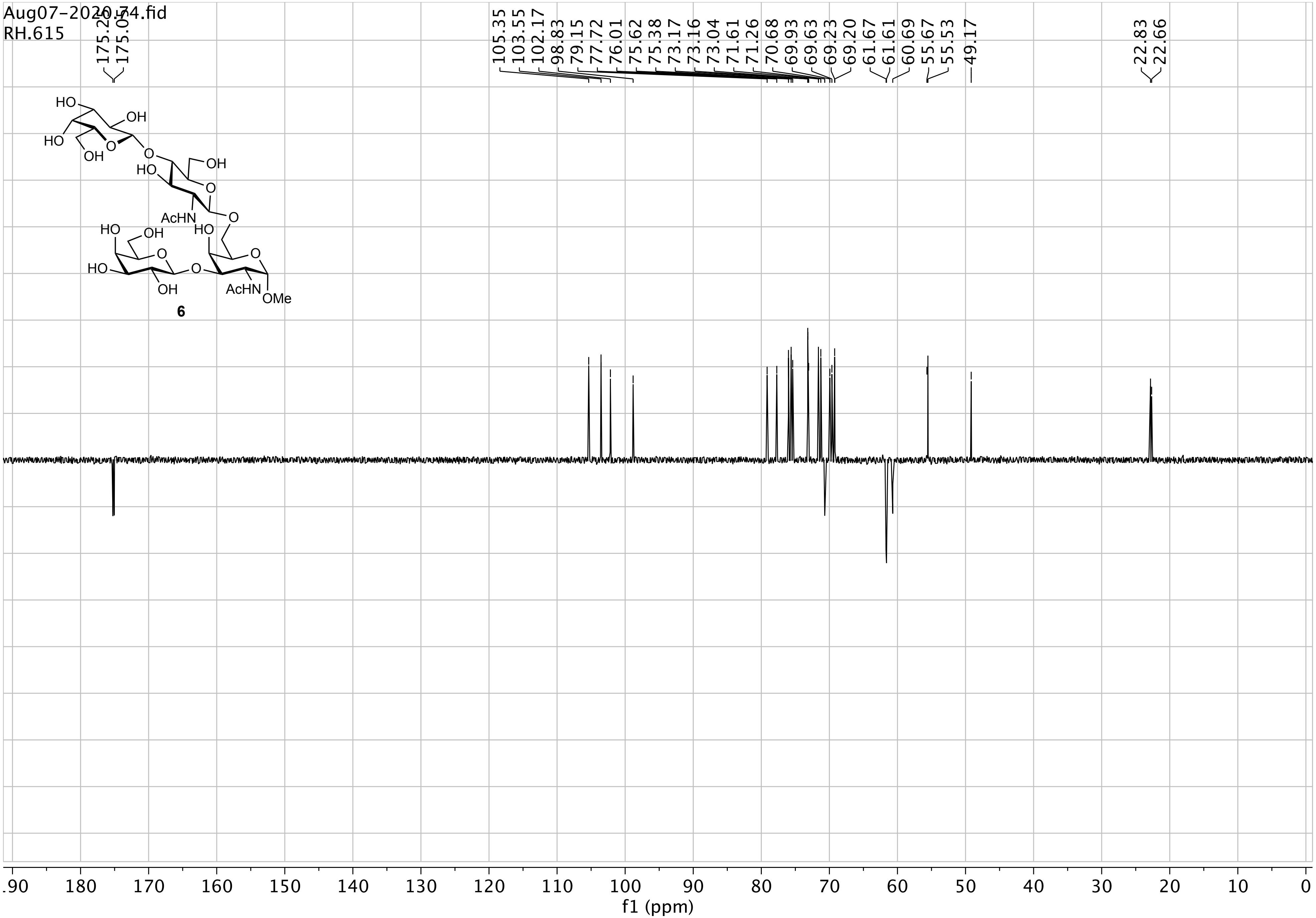
$^{1}H\_^{13}C$ gHSQC in D_2O



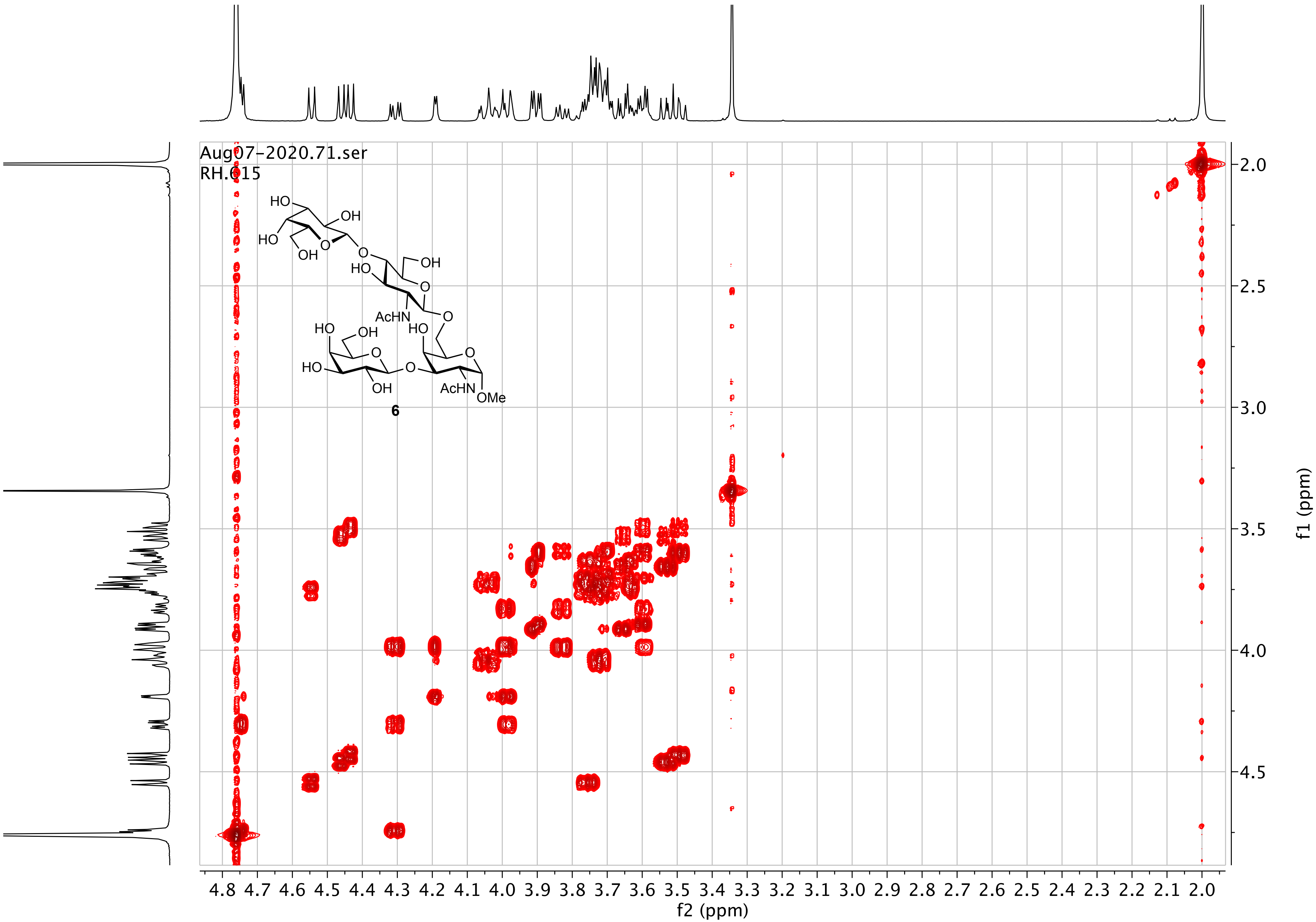
^{1}H NMR in D_2O (500 MHz)



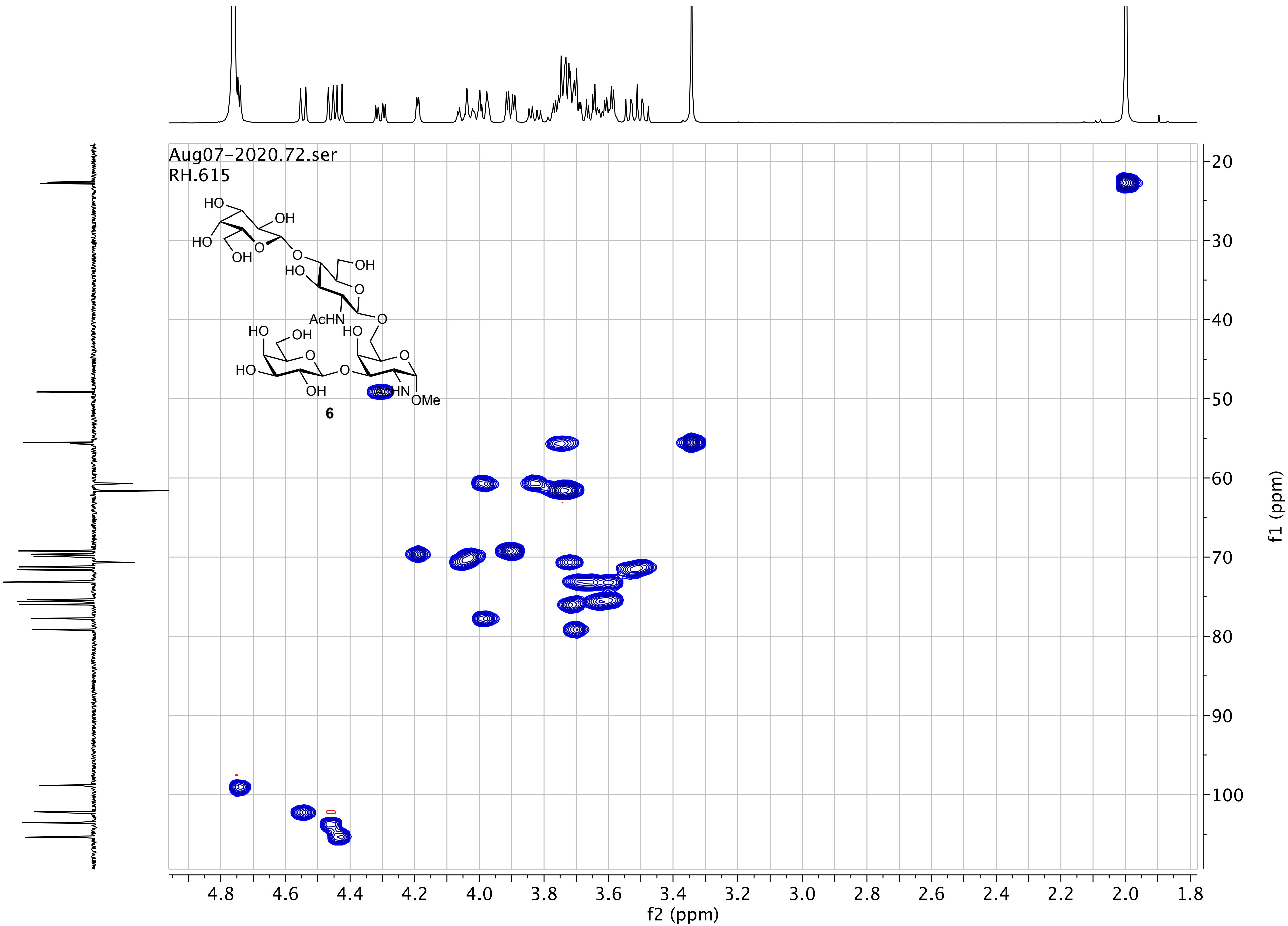
^{13}C NMR (APT) in D_2O (125 MHz)



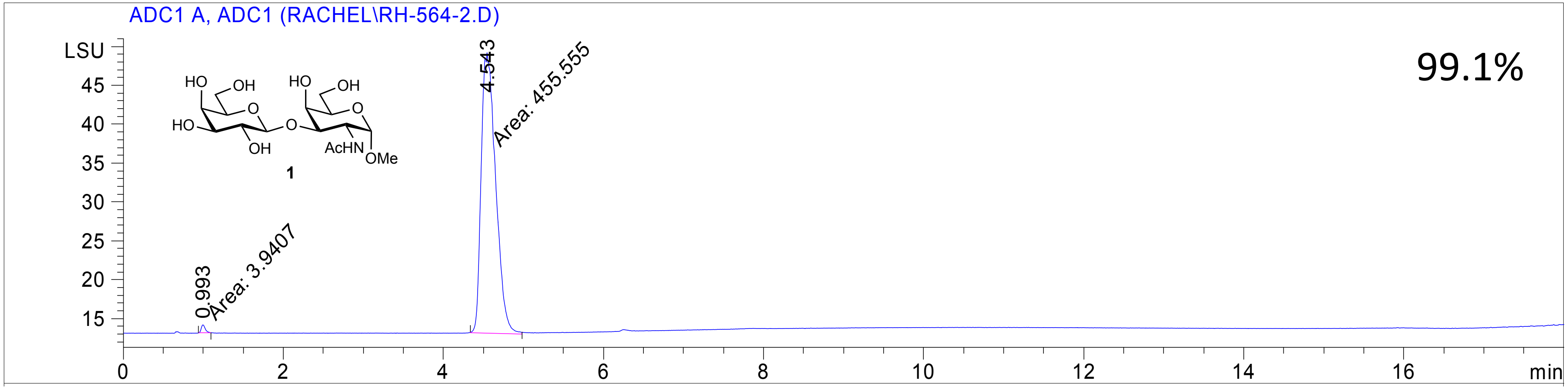
$^1H\_^1H$ gCOSY in D_2O

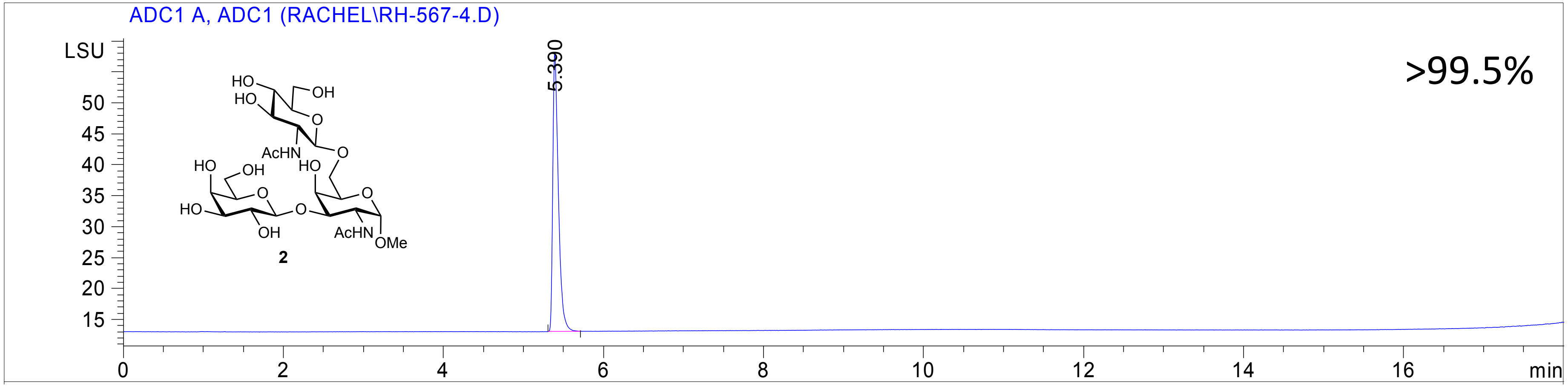


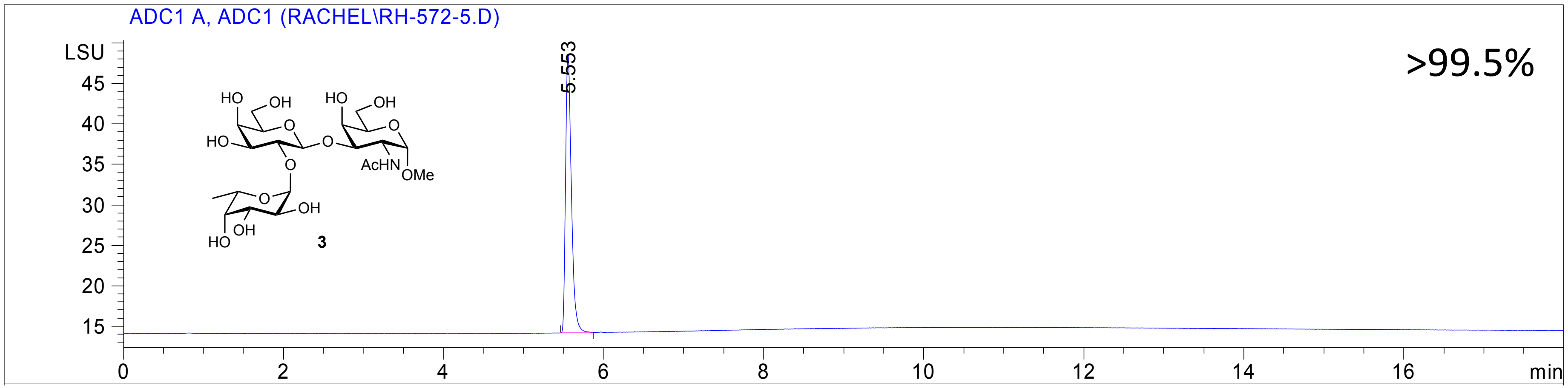
$^1H\_^{13}C$ gHSQC in D_2O



HPLC Purity Analysis







HPLC Purity Analysis