SUPPORTING INFORMATION

for

C7 Epimerization of Benzylidene-Protected *β*-D-Idopyranosides Brings Structural Insights into Idose Conformational Flexibility

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1. X-ray Diffraction.

The data for **20a**, crystallised from $CHCl_3$/hexanes, were collected from a shock-cooled single crystal at 150 K on a Bruker Venture Metaljet k-geometry diffractometer with a Metal Jet using Helios MX Mirror Optics as monochromator and a Bruker CMOS Photon III detector. The diffractometer was equipped with an Oxford Cryostream 700 low temperature device and used Ga K_α radiation (λ = 1.34139 Å). All data were integrated with *SAINT* (2020) and a multi-scan absorption correction using *SADABS* 2016/2 was applied.[1] The structure was solved by dual methods with *XT* and refined by full-matrix least-squares methods against F^2 using *XL*.[2-3] Structure solution and refinement cycles were performed within the graphical user interface of *OLEX2*.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and oxygen atoms, and 1.2 times for all other carbon atoms. This report and the CIF file were generated using FinalCif.

Table S1. Crystal Data and Structure Refinement for Compound 20a.

Parameter	Data	Parameter	Data
Empirical formula	$C_{23}H_{30}O_6$	Crystal size [mm^3]	0.03×0.04×0.19
Formula weight	402.47	Crystal colour	clear light colourless
Temperature [K]	150	Crystal shape	needle
Crystal system	orthorhombic	Radiation	Ga K_α (λ=1.34139 Å)
Space group (number)	$P2_12_12_1$ (19)	2Θ range [°]	8.20 to 121.22 (0.77 Å)
a [Å]	10.6168(4)	Index ranges	$-13 \le h \le 11$ $-14 \le k \le 14$ $-21 \le l \le 20$
b [Å]	11.4428(4)	Reflections collected	41569
c [Å]	16.4108(6)	Independent reflections	4567 R_{int} = 0.0696 R_{sigma} = 0.0447
α [°]	90	Completeness to θ = 53.594°	100.0 %
β [°]	90	Data / Restraints / Parameters	4567 / 0 / 266
γ [°]	90	Goodness-of-fit on F^2	1.053
Volume [$Å^3$]	1993.68(13)	Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0440 wR_2 = 0.0705
Z	4	Final *R* indexes [all data]	R_1 = 0.0658 wR_2 = 0.0752
ρ_{calc} [gcm^{-3}]	1.341	Largest peak/hole [$eÅ^{-3}$]	0.20/−0.21
μ [mm^{-1}]	0.500	Extinction coefficient	0.00127(19)
F(000)	864	Flack X parameter	0.0(3)

Table S2. Atomic Coordinates and Ueq [Å^2] for Compound 20a.

Atom	*x*	*y*	*z*	U_{eq}
O1	0.67251(13)	0.30565(13)	0.57814(9)	0.0230(3)
O2	0.59438(14)	0.08841(14)	0.50669(10)	0.0301(4)
H2	0.595538	0.143107	0.472561	0.045
O3	0.92042(15)	0.10810(18)	0.56885(10)	0.0426(5)
H3	0.988920	0.098564	0.544113	0.064
O4	0.58084(14)	0.18093(13)	0.66940(9)	0.0241(4)
O5	0.68079(15)	0.44042(14)	0.42991(9)	0.0293(4)
O6	0.73368(13)	0.24487(15)	0.40923(9)	0.0270(4)
C1	0.6865(2)	0.19653(19)	0.62063(13)	0.0232(5)
H1	0.763418	0.199646	0.655709	0.028
C2	0.6999(2)	0.0984(2)	0.55923(14)	0.0257(5)
H2A	0.709424	0.023283	0.589705	0.031
C3	0.8213(2)	0.1206(2)	0.51135(14)	0.0284(5)
H3A	0.830482	0.061215	0.467037	0.034
C4	0.8237(2)	0.2431(2)	0.47543(13)	0.0261(5)
H4	0.909741	0.260036	0.453675	0.031
C5	0.7876(2)	0.3364(2)	0.53800(14)	0.0246(5)
H5	0.856366	0.343999	0.579305	0.030
C6	0.7674(2)	0.4523(2)	0.49688(15)	0.0292(5)
H6A	0.733533	0.509098	0.536748	0.035
H6B	0.848939	0.482492	0.476575	0.035
C7	0.7285(2)	0.3575(2)	0.37359(14)	0.0292(6)
H7	0.815588	0.381264	0.357414	0.035
C8	0.6467(2)	0.3548(2)	0.29850(15)	0.0326(6)
C9	0.5984(2)	0.4584(3)	0.26765(16)	0.0409(7)
H9	0.610721	0.529478	0.296418	0.049
C10	0.5318(3)	0.4582(3)	0.19460(17)	0.0520(8)
H10	0.498342	0.529232	0.173816	0.062
C11	0.5142(3)	0.3558(4)	0.15242(17)	0.0542(9)
H11	0.469298	0.356258	0.102342	0.065
C12	0.5614(3)	0.2525(3)	0.18257(16)	0.0500(8)
H12	0.548844	0.181714	0.153431	0.060
C13	0.6280(2)	0.2517(3)	0.25621(15)	0.0401(7)
H13	0.660374	0.180362	0.277121	0.048
C14	0.5823(2)	0.2522(2)	0.74250(13)	0.0257(5)
H14	0.599318	0.335337	0.727242	0.031
C15	0.6810(2)	0.2118(2)	0.80391(14)	0.0308(6)
H15	0.766583	0.216578	0.778697	0.037
C16	0.6547(2)	0.0862(2)	0.83017(15)	0.0305(6)
H16A	0.719745	0.060429	0.869482	0.037
H16B	0.658185	0.033957	0.782155	0.037
C17	0.5239(2)	0.0788(2)	0.86986(14)	0.0257(5)
H17	0.506658	−0.003413	0.887162	0.031
C18	0.5184(2)	0.1598(2)	0.94396(14)	0.0340(6)

H18A	0.582439	0.135674	0.984427	0.041
H18B	0.434384	0.154354	0.969900	0.041
C19	0.5432(3)	0.2863(2)	0.91695(16)	0.0409(7)
H19	0.539215	0.339176	0.965369	0.049
C20	0.4449(3)	0.3238(2)	0.85461(16)	0.0390(7)
H20A	0.460595	0.405568	0.837800	0.047
H20B	0.359838	0.319588	0.879171	0.047
C21	0.4516(2)	0.2432(2)	0.78004(14)	0.0281(5)
H21	0.386937	0.267780	0.739143	0.034
C22	0.4257(2)	0.11731(19)	0.80705(14)	0.0251(5)
H22A	0.340383	0.112120	0.831186	0.030
H22B	0.428808	0.064706	0.759204	0.030
C24	0.6747(3)	0.2938(2)	0.87821(16)	0.0432(7)
H24A	0.739363	0.270802	0.918595	0.052
H24B	0.691861	0.375122	0.860970	0.052

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S3. Bond Lengths and Angles for Compound 20a.

Atom–Atom	Length [Å]	Atom–Atom–Atom	Angle [°]	Atom–Atom–Atom	Angle [°]
O1–C1	1.438(3)	C5–O1–C1	110.42(16)	C9–C10–H10	119.9
O1–C5	1.432(3)	C2–O2–H2	109.5	C11–C10–C9	120.3(3)
O2–H2	0.8400	C3–O3–H3	109.5	C11–C10–H10	119.9
O2–C2	1.419(3)	C1–O4–C14	113.29(16)	C10–C11–H11	119.9
O3–H3	0.8400	C7–O5–C6	109.43(17)	C10–C11–C12	120.1(3)
O3–C3	1.420(3)	C7–O6–C4	110.42(17)	C12–C11–H11	119.9
O4–C1	1.389(3)	O1–C1–H1	109.4	C11–C12–H12	120.0
O4–C14	1.451(3)	O1–C1–C2	109.30(17)	C11–C12–C13	120.0(3)
O5–C6	1.439(3)	O4–C1–O1	107.92(17)	C13–C12–H12	120.0
O5–C7	1.418(3)	O4–C1–H1	109.4	C8–C13–C12	120.0(3)
O6–C4	1.447(3)	O4–C1–C2	111.35(18)	C8–C13–H13	120.0
O6–C7	1.416(3)	C2–C1–H1	109.4	C12–C13–H13	120.0
C1–H1	1.0000	O2–C2–C1	112.95(18)	O4–C14–H14	109.3
C1–C2	1.515(3)	O2–C2–H2A	108.3	O4–C14–C15	112.56(18)
C2–H2A	1.0000	O2–C2–C3	111.50(18)	O4–C14–C21	106.66(18)
C2–C3	1.531(3)	C1–C2–H2A	108.3	C15–C14–H14	109.3
C3–H3A	1.0000	C1–C2–C3	107.34(18)	C21–C14–H14	109.3
C3–C4	1.520(3)	C3–C2–H2A	108.3	C21–C14–C15	109.78(18)
C4–H4	1.0000	O3–C3–C2	105.43(18)	C14–C15–H15	109.5
C4–C5	1.531(3)	O3–C3–H3A	110.0	C14–C15–C16	110.27(19)
C5–H5	1.0000	O3–C3–C4	109.76(19)	C14–C15–C24	108.0(2)
C5–C6	1.503(3)	C2–C3–H3A	110.0	C16–C15–H15	109.5
C6–H6A	0.9900	C4–C3–C2	111.44(18)	C16–C15–C24	110.0(2)
C6–H6B	0.9900	C4–C3–H3A	110.0	C24–C15–H15	109.5
C7–H7	1.0000	O6–C4–C3	107.06(17)	C15–C16–H16A	109.7
C7–C8	1.508(3)	O6–C4–H4	109.4	C15–C16–H16B	109.7
C8–C9	1.387(4)	O6–C4–C5	109.17(17)	C15–C16–C17	109.7(2)
C8–C13	1.383(4)	C3–C4–H4	109.4	H16A–C16–H16B	108.2
C9–H9	0.9500	C3–C4–C5	112.29(18)	C17–C16–H16A	109.7
C9–C10	1.392(4)	C5–C4–H4	109.4	C17–C16–H16B	109.7
C10–H10	0.9500	O1–C5–C4	110.51(17)	C16–C17–H17	109.7
C10–C11	1.374(5)	O1–C5–H5	109.4	C18–C17–C16	109.76(19)
C11–H11	0.9500	O1–C5–C6	107.57(18)	C18–C17–H17	109.7
C11–C12	1.376(4)	C4–C5–H5	109.4	C18–C17–C22	109.58(19)
C12–H12	0.9500	C6–C5–C4	110.51(18)	C22–C17–C16	108.33(18)
C12–C13	1.400(4)	C6–C5–H5	109.4	C22–C17–H17	109.7
C13–H13	0.9500	O5–C6–C5	110.54(18)	C17–C18–H18A	109.8
C14–H14	1.0000	O5–C6–H6A	109.5	C17–C18–H18B	109.8
C14–C15	1.525(3)	O5–C6–H6B	109.5	C17–C18–C19	109.54(19)
C14–C21	1.522(3)	C5–C6–H6A	109.5	H18A–C18–H18B	108.2
C15–H15	1.0000	C5–C6–H6B	109.5	C19–C18–H18A	109.8
C15–C16	1.526(3)	H6A–C6–H6B	108.1	C19–C18–H18B	109.8
C15–C24	1.540(3)	O5–C7–H7	108.7	C18–C19–H19	109.5
C16–H16A	0.9900	O5–C7–C8	109.92(19)	C20–C19–C18	110.0(2)
C16–H16B	0.9900	O6–C7–O5	110.71(18)	C20–C19–H19	109.5

C16–C17	1.537(3)	C3–C4–H4	109.4	C20–C19–C24	109.2(2)
C17–H17	1.0000	C3–C4–C5	112.29(18)	C24–C19–C18	109.2(2)
C17–C18	1.530(3)	C5–C4–H4	109.4	C24–C19–H19	109.5
C17–C22	1.531(3)	O1–C5–C4	110.51(17)	C19–C20–H20A	109.8
C18–H18A	0.9900	O1–C5–H5	109.4	C19–C20–H20B	109.8
C18–H18B	0.9900	O1–C5–C6	107.57(18)	C19–C20–C21	109.6(2)
C18–C19	1.536(4)	C4–C5–H5	109.4	H20A–C20–H20B	108.2
C19–H19	1.0000	C6–C5–C4	110.51(18)	C21–C20–H20A	109.8
C19–C20	1.523(4)	C6–C5–H5	109.4	C21–C20–H20B	109.8
C19–C24	1.536(4)	O5–C6–C5	110.54(18)	C14–C21–C20	108.9(2)
C20–H20A	0.9900	O5–C6–H6A	109.5	C14–C21–H21	109.6
C20–H20B	0.9900	O5–C6–H6B	109.5	C14–C21–C22	110.13(19)
C20–C21	1.533(3)	C5–C6–H6A	109.5	C20–C21–H21	109.6
C21–H21	1.0000	C5–C6–H6B	109.5	C22–C21–C20	109.02(19)
C21–C22	1.532(3)	H6A–C6–H6B	108.1	C22–C21–H21	109.6
C22–H22A	0.9900	O5–C7–H7	108.7	C17–C22–C21	110.06(19)
C22–H22B	0.9900	O5–C7–C8	109.92(19)	C17–C22–H22A	109.6
C24–H24A	0.9900	O6–C7–O5	110.71(18)	C17–C22–H22B	109.6
C24–H24B	0.9900	O6–C7–H7	108.7	C21–C22–H22A	109.6
		O6–C7–C8	110.0(2)	C21–C22–H22B	109.6
		C8–C7–H7	108.7	H22A–C22–H22B	108.2
		C9–C8–C7	119.6(2)	C15–C24–H24A	109.8
		C13–C8–C7	120.7(2)	C15–C24–H24B	109.8
		C13–C8–C9	119.5(2)	C19–C24–C15	109.5(2)
		C8–C9–H9	120.0	C19–C24–H24A	109.8
		C8–C9–C10	120.1(3)	C19–C24–H24B	109.8
		C10–C9–H9	120.0	H24A–C24–H24B	108.2

Table S4. Torsion Angles for Compound 20a.

Atom–Atom–Atom–Atom	Torsion Angle [°]	Atom–Atom–Atom–Atom	Torsion Angle [°]
O1–C1–C2–O2	−60.0(2)	C7–O6–C4–C3	178.75(17)
O1–C1–C2–C3	63.3(2)	C7–O6–C4–C5	57.0(2)
O1–C5–C6–O5	−68.8(2)	C7–C8–C9–C10	174.5(2)
O2–C2–C3–O3	−169.98(18)	C7–C8–C13–C12	−174.2(2)
O2–C2–C3–C4	71.0(2)	C8–C9–C10–C11	−0.4(4)
O3–C3–C4–O6	171.63(16)	C9–C8–C13–C12	0.4(4)
O3–C3–C4–C5	−68.6(2)	C9–C10–C11–C12	0.6(4)
O4–C1–C2–O2	59.2(2)	C10–C11–C12–C13	−0.3(4)
O4–C1–C2–C3	−177.53(17)	C11–C12–C13–C8	−0.2(4)
O4–C14–C15–C16	−60.2(2)	C13–C8–C9–C10	−0.1(4)
O4–C14–C15–C24	179.62(18)	C14–O4–C1–O1	−76.2(2)
O4–C14–C21–C20	−176.19(18)	C14–O4–C1–C2	163.80(17)
O4–C14–C21–C22	64.3(2)	C14–C15–C16–C17	−60.1(2)
O5–C7–C8–C9	39.1(3)	C14–C15–C24–C19	60.9(3)
O5–C7–C8–C13	−146.3(2)	C14–C21–C22–C17	59.5(2)
O6–C4–C5–O1	68.1(2)	C15–C14–C21–C20	61.6(2)
O6–C4–C5–C6	−50.8(2)	C15–C14–C21–C22	−57.9(2)
O6–C7–C8–C9	161.3(2)	C15–C16–C17–C18	−59.3(2)
O6–C7–C8–C13	−24.2(3)	C15–C16–C17–C22	60.3(2)
C1–O1–C5–C4	60.7(2)	C16–C15–C24–C19	−59.5(3)
C1–O1–C5–C6	−178.54(17)	C16–C17–C18–C19	60.1(3)
C1–O4–C14–C15	−70.3(2)	C16–C17–C22–C21	−60.1(2)
C1–O4–C14–C21	169.28(17)	C17–C18–C19–C20	59.4(3)
C1–C2–C3–O3	65.8(2)	C17–C18–C19–C24	−60.4(3)
C1–C2–C3–C4	−53.2(2)	C18–C17–C22–C21	59.6(2)
C2–C3–C4–O6	−72.0(2)	C18–C19–C20–C21	−60.1(3)
C2–C3–C4–C5	47.8(2)	C18–C19–C24–C15	59.9(3)
C3–C4–C5–O1	−50.4(2)	C19–C20–C21–C14	−60.2(2)
C3–C4–C5–C6	−169.38(18)	C19–C20–C21–C22	60.0(3)
C4–O6–C7–O5	−65.2(2)	C20–C19–C24–C15	−60.4(3)
C4–O6–C7–C8	173.11(17)	C20–C21–C22–C17	−59.9(2)
C4–C5–C6–O5	51.9(2)	C21–C14–C15–C16	58.5(2)
C5–O1–C1–O4	169.92(16)	C21–C14–C15–C24	−61.7(2)
C5–O1–C1–C2	−68.8(2)	C22–C17–C18–C19	−58.8(3)
C6–O5–C7–O6	65.0(2)	C24–C15–C16–C17	58.9(3)
C6–O5–C7–C8	−173.27(18)	C24–C19–C20–C21	59.7(3)
C7–O5–C6–C5	−58.2(2)		

Table S5. Hydrogen Bonds for Compound 20a.

D–H···A [Å]	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
O2–H2···O6	0.84	2.14	2.820(2)	137.6
O3–H3···O5$^{\#1}$	0.84	2.13	2.820(2)	139.4

Symmetry transformations used to generate equivalent atoms:
#1: 0.5+X, 0.5-Y, 1-Z.

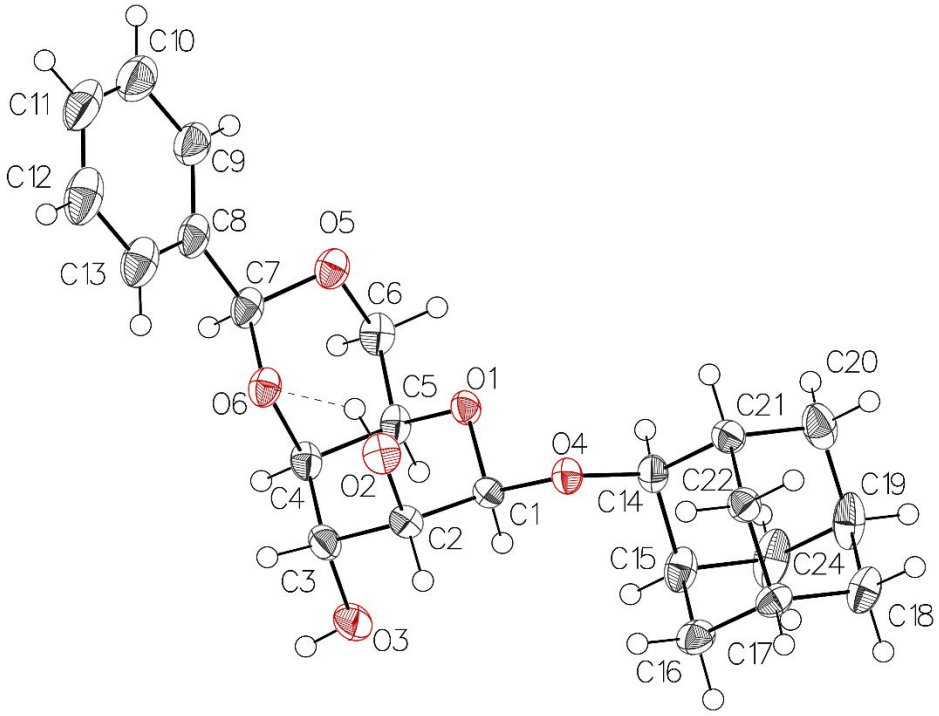
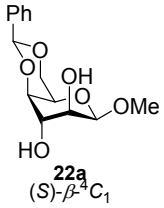


Figure S1. Thermal atomic displacement ellipsoid plot for compound 20a with the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level and hydrogen atoms are shown as sphere of arbitrary size.

2. Molecular Modeling.



22a
(*S*)-β-$^4C_1$

Table S6. 3D Coordinates of B3LYP/6-31+G(d,p) Optimized Geometries of 22aA-22aD.

		22aA *coordinates*			22aB *coordinates*			22aC *coordinates*		
ID	**atom**	**X**	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**
1	C	1.3784	-0.8246	-1.2160	-1.3058	-0.8651	1.1874	-1.3085	-0.8651	1.1862
2	C	2.8360	0.4922	0.1446	-2.9193	0.4065	-0.0010	-2.9193	0.4087	-0.0055
3	C	1.6705	-1.4358	1.2474	-1.6471	-1.3638	-1.2984	-1.6543	-1.3632	-1.3015
4	C	2.2167	-0.0038	1.4590	-2.4257	-0.0354	-1.3856	-2.4265	-0.0366	-1.3895
5	C	0.7548	-1.4999	0.0171	-0.6946	-1.4510	-0.0964	-0.6962	-1.4506	-0.0974
6	O	1.8483	0.4891	-0.8946	-1.8580	0.4336	0.9504	-1.8592	0.4337	0.9479
7	O	1.1957	0.8593	1.9455	-1.5873	0.9469	-1.9808	-1.5829	0.9428	-1.9829
8	O	2.7248	-2.3679	1.0010	-2.5601	-2.4544	-1.1333	-2.6553	-2.3810	-1.1925
9	O	-0.4687	-0.8260	0.3695	0.5213	-0.7730	-0.4359	0.5210	-0.7746	-0.4358
10	C	0.3275	-0.6933	-2.3117	-0.2345	-0.7429	2.2645	-0.2379	-0.7431	2.2639
11	O	-0.8780	-0.0959	-1.8140	0.9520	-0.1152	1.7629	0.9493	-0.1158	1.7632
12	C	-1.4071	-0.8060	-0.7143	1.4638	-0.7989	0.6288	1.4630	-0.7990	0.6301
13	H	2.2096	-1.4426	-1.5857	-2.0952	-1.5423	1.5475	-2.0987	-1.5418	1.5452
14	H	1.0888	-1.7246	2.1312	-1.0567	-1.4809	-2.2153	-1.0699	-1.4826	-2.2219
15	H	2.9991	-0.0225	2.2250	-3.3134	-0.2012	-2.0146	-3.3096	-0.2116	-2.0191
16	H	0.5420	-2.5533	-0.2115	-0.4787	-2.5161	0.0745	-0.4720	-2.5145	0.0824
17	H	0.4050	0.7193	1.3964	-2.0057	1.8088	-1.8310	-1.9999	1.8053	-1.8332
18	H	3.2369	-2.4864	1.8130	-3.1105	-2.5285	-1.9254	-2.2402	-3.2481	-1.3000
19	H	0.6853	-0.0449	-3.1132	-0.5899	-0.1247	3.0909	-0.5935	-0.1244	3.0899
20	H	0.1074	-1.6874	-2.7262	0.0084	-1.7448	2.6472	0.0044	-1.7449	2.6472
21	H	-1.5976	-1.8506	-1.0101	1.6546	-1.8501	0.9051	1.6547	-1.8501	0.9063
22	C	-2.6719	-0.1380	-0.2404	2.7339	-0.1250	0.1771	2.7327	-0.1238	0.1793
23	C	-5.0209	1.0832	0.6812	5.1051	1.1207	-0.6528	5.1030	1.1237	-0.6500
24	C	-2.7000	1.2428	0.0022	3.9414	-0.8316	0.1824	3.9393	-0.8320	0.1771
25	C	-3.8240	-0.9012	-0.0209	2.7174	1.2118	-0.2463	2.7166	1.2154	-0.2365
26	C	-4.9967	-0.2931	0.4392	3.8983	1.8313	-0.6596	3.8971	1.8358	-0.6494
27	C	-3.8706	1.8502	0.4609	5.1255	-0.2114	-0.2312	5.1230	-0.2108	-0.2362
28	H	-1.8105	1.8388	-0.1751	3.9588	-1.8679	0.5096	3.9564	-1.8701	0.4986
29	H	-3.8073	-1.9712	-0.2105	1.7818	1.7618	-0.2524	1.7816	1.7665	-0.2367
30	H	-5.8867	-0.8927	0.6054	3.8790	2.8667	-0.9871	3.8782	2.8731	-0.9708
31	H	-3.8866	2.9203	0.6457	6.0580	-0.7680	-0.2238	6.0549	-0.7685	-0.2346
32	H	-5.9308	1.5574	1.0373	6.0228	1.6042	-0.9748	6.0205	1.6080	-0.9717
33	H	3.6549	-0.1862	-0.1499	-3.6994	-0.2878	0.3559	-3.7026	-0.2820	0.3513
34	O	3.3086	1.7886	0.3041	-3.4277	1.6971	-0.1358	-3.4228	1.7010	-0.1421
35	C	4.1481	2.2469	-0.7635	-4.1469	2.1900	1.0035	-4.1435	2.1965	0.9950
36	H	5.0024	1.5716	-0.9009	-4.9744	1.5151	1.2544	-4.9744	1.5247	1.2432
37	H	4.5089	3.2337	-0.4701	-4.5445	3.1644	0.7172	-4.5365	3.1725	0.7079
38	H	3.5888	2.3248	-1.7008	-3.4856	2.3001	1.8675	-3.4845	2.3039	1.8611

Table S7. 3D Coordinates of B3LYP/6-31+G(d,p) Optimized Geometries of 22aA-22aD (continued).

ID	atom	22aD *coordinates* X	Y	Z
1	C	-1.3784	-0.8246	1.2160
2	C	-2.8360	0.4922	-0.1446
3	C	-1.6705	-1.4358	-1.2474
4	C	-2.2167	-0.0038	-1.4590
5	C	-0.7548	-1.4999	-0.0171
6	O	-1.8484	0.4891	0.8946
7	O	-1.1957	0.8593	-1.9455
8	O	-2.7248	-2.3679	-1.0010
9	O	0.4687	-0.8260	-0.3695
10	C	-0.3275	-0.6933	2.3117
11	O	0.8780	-0.0959	1.8140
12	C	1.4071	-0.8060	0.7143
13	H	-2.2096	-1.4426	1.5857
14	H	-1.0888	-1.7247	-2.1312
15	H	-2.9991	-0.0226	-2.2250
16	H	-0.5420	-2.5533	0.2115
17	H	-0.4050	0.7193	-1.3964
18	H	-3.2369	-2.4864	-1.8130
19	H	-0.6853	-0.0448	3.1132
20	H	-0.1074	-1.6874	2.7262
21	H	1.5976	-1.8506	1.0102
22	C	2.6719	-0.1380	0.2404
23	C	5.0209	1.0832	-0.6812
24	C	2.7000	1.2428	-0.0022
25	C	3.8240	-0.9012	0.0209
26	C	4.9967	-0.2931	-0.4392
27	C	3.8706	1.8502	-0.4609
28	H	1.8105	1.8388	0.1751
29	H	3.8073	-1.9712	0.2105
30	H	5.8867	-0.8927	-0.6054
31	H	3.8866	2.9203	-0.6457
32	H	5.9308	1.5574	-1.0373
33	H	-3.6549	-0.1862	0.1498
34	O	-3.3086	1.7886	-0.3041
35	C	-4.1481	2.2469	0.7635
36	H	-5.0024	1.5716	0.9009
37	H	-4.5090	3.2337	0.4700
38	H	-3.5888	2.3248	1.7008

Table S8. Energy and Abundance of Conformers 22aA-22aD.

conformer	B3LYP/6-31+G(d,p)				B3LYP/6-311++G(2d,2p)			
	ΔE (Ha)	ΔG (Ha)	abundance (%)	imaginary frequencies	ΔE (Ha)	ΔG (Ha)	abundance (%)	imaginary frequencies
22aA	−995.70163	−995.43434	45.0	0	−995.95748	−995.68914	44.4	0
22aB	−995.69900	−995.43242	5.91	0	−995.95503	−995.68731	6.40	0
22aC	−995.69876	−995.43211	4.25	0	−995.95480	−995.68705	4.85	0
22aD	−995.70163	−995.43434	44.9	0	−995.95748	−995.68914	44.3	0

Table S9. Comparison Between Experimental (20a) and Calculated (22aA-22aD) NMR ^{3}J Coupling Constants.

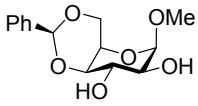
protons	experimental ^{3}J (Hz)	B3LYP/6-31+G(d,p)		B3LYP/6-311++G(2d,2p)	
		calculated ^{3}J (Hz)	Δ	calculated ^{3}J (Hz)	Δ
1-2	N/A	1.05	N/A	1.05	N/A
2-3	2.50	2.84	+0.34	2.83	+0.23
3-4	2.50	2.59	+0.09	2.58	−0.02
4-5	N/A	1.27	N/A	1.27	N/A
5-6a	1.10	1.55	+0.45	1.55	+0.45
5-6b	1.90	1.87	−0.03	1.87	−0.03
6a-6b	12.45	11.82	−0.63	11.82	−0.63
		Rmsd : 0.32		*Rmsd : 0.32*	

Table S10. Comparison Between Experimental (20a) and Calculated (22aA-22aD) NMR ^{1}H and ^{13}C Chemical Shifts.

atom	experimental δ (ppm)	B3LYP/6-31+G(d,p)		B3LYP/6-311++G(2d,2p)	
		calculated δ (ppm)	Δ	calculated δ (ppm)	Δ
H-1	4.94	4.84	−0.10	4.84	−0.10
H-2	3.62	3.48	−0.14	3.48	−0.14
H-3	4.21	4.18	−0.03	4.18	−0.03
H-4	3.93	4.09	+0.16	4.09	+0.16
H-5	3.75	3.78	+0.03	3.78	+0.03
H-6a	4.37	4.35	−0.02	4.35	−0.02
H-6b	4.06	4.16	+0.10	4.16	+0.10
		Rmsd : 0.10		*Rmsd : 0.10*	
C-1	95.9	97.3	+1.4	97.3	+1.4
C-2	70.4	70.7	+0.3	70.7	+0.3
C-3	70.4	71.2	+0.8	71.2	+0.8
C-4	75.6	74.7	-0.9	74.7	-0.9
C-5	66.6	67.1	+0.5	67.1	+0.5
C-6	70.0	69.1	−0.9	69.1	−0.9
C-7	101.5	100.4	−1.1	100.4	−1.1
		Rmsd : 0.93		*Rmsd : 0.93*	

Table S11. Comparison Between Experimental (20a) and Calculated (22aA-22aD) H-H Distances by Quantitative NOESY NMR.

protons	experimental distance (Å)	B3LYP/6-31+G(d,p)		B3LYP/6-311++G(2d,2p)	
		calculated distance (Å)	Δ	calculated distance (Å)	Δ
6ax-7''	2.337	2.422	+0.085	2.422	+0.085
5-1	2.253	2.390	+0.137	2.390	+0.137
4-7''	2.254	2.388	+0.134	2.388	+0.134
2-1	2.430	2.462	+0.032	2.461	+0.031
2-3	2.431	2.563	+0.132	2.563	+0.132
4-3	2.547	2.569	+0.022	2.569	+0.022
5-6eq	2.691	2.572	−0.119	2.572	−0.119
5-6ax	2.453	2.402	−0.051	2.412	−0.041
		Rmsd : 0.30		*Rmsd : 0.30*	



(*S*)-22b
(*S*)-β-$^1C_4$

Table S12. 3D Coordinates of B3LYP/6-31+G(d,p) Optimized Geometries of (*S*)-22bA-(*S*)-22bF.

		(*S*)-22bA *coordinates*			(*S*)-22bB *coordinates*			(*S*)-22bC *coordinates*		
ID	**atom**	**X**	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**
1	C	-1.3796	-1.3512	-0.9595	-1.4400	-1.2841	-1.0029	-1.4400	1.2841	1.0029
2	C	-2.7831	0.1122	0.4285	-2.7768	0.2460	0.3839	-2.7769	-0.2460	-0.3839
3	C	-0.7837	1.1195	-0.7605	-0.6777	1.1250	-0.7001	-0.6777	-1.1250	0.7001
4	C	-2.2297	1.3443	-0.2953	-2.1227	1.4449	-0.3119	-2.1226	-1.4448	0.3120
5	C	-0.7323	-0.1297	-1.6434	-0.6921	-0.0948	-1.6326	-0.6921	0.0949	1.6326
6	O	-2.6565	-1.0540	-0.3700	-2.7160	-0.9027	-0.4617	-2.7160	0.9027	0.4617
7	O	-2.3231	2.5114	0.5182	-2.2047	2.5839	0.5329	-2.2047	-2.5839	-0.5328
8	O	-0.3419	2.2346	-1.5327	-0.1720	2.2900	-1.3580	-0.1719	-2.2900	1.3581
9	O	0.5843	-0.4721	-2.1189	0.6087	-0.5119	-2.0905	0.6087	0.5120	2.0905
10	C	-0.4001	-2.0016	0.0219	-0.5377	-2.0001	0.0079	-0.5377	2.0001	-0.0079
11	O	0.7804	-2.3582	-0.7145	0.6667	-2.3993	-0.6705	0.6667	2.3993	0.6704
12	C	1.4441	-1.2446	-1.2819	1.4037	-1.3319	-1.2297	1.4037	1.3319	1.2297
13	H	-1.6058	-2.0889	-1.7339	-1.6827	-1.9952	-1.7972	-1.6827	1.9953	1.7972
14	H	-0.1405	1.0005	0.1196	-0.0978	0.9339	0.2080	-0.0978	-0.9339	-0.2080
15	H	-2.8554	1.5362	-1.1726	-2.6948	1.6245	-1.2341	-2.6947	-1.6245	1.2342
16	H	-1.2854	0.1028	-2.5593	-1.2037	0.2094	-2.5512	-1.2037	-0.2093	2.5512
17	H	-2.0062	2.2684	1.4037	-1.6856	3.2834	0.1071	-1.6856	-3.2834	-0.1070
18	H	-0.5064	3.0293	-1.0025	0.7948	2.2587	-1.3452	0.7948	-2.2587	1.3452
19	H	-0.1558	-1.3404	0.8589	-0.3125	-1.3673	0.8701	-0.3125	1.3673	-0.8702
20	H	-0.8114	-2.9333	0.4153	-1.0056	-2.9216	0.3595	-1.0056	2.9216	-0.3596
21	H	2.1592	-1.6813	-1.9861	2.1082	-1.8131	-1.9148	2.1082	1.8132	1.9147
22	C	2.2210	-0.4194	-0.2515	2.2005	-0.5199	-0.2050	2.2005	0.5199	0.2050
23	C	3.8475	1.0196	1.5361	3.8151	0.9385	1.5790	3.8151	-0.9386	-1.5790
24	C	2.6723	-1.0136	0.9355	2.4219	-0.9876	1.0960	2.4219	0.9876	-1.0961
25	C	2.6076	0.8957	-0.5442	2.8264	0.6678	-0.6156	2.8264	-0.6678	0.6156
26	C	3.4131	1.6119	0.3457	3.6241	1.3958	0.2705	3.6241	-1.3958	-0.2705
27	C	3.4748	-0.2960	1.8279	3.2173	-0.2572	1.9858	3.2173	0.2571	-1.9859
28	H	2.3941	-2.0381	1.1608	1.9767	-1.9243	1.4143	1.9767	1.9242	-1.4144
29	H	2.2613	1.3623	-1.4596	2.7056	1.0104	-1.6400	2.7056	-1.0103	1.6400
30	H	3.7000	2.6326	0.1089	4.0998	2.3138	-0.0621	4.0998	-2.3138	0.0622
31	H	3.8095	-0.7665	2.7480	3.3708	-0.6269	2.9955	3.3708	0.6268	-2.9956
32	H	4.4728	1.5769	2.2277	4.4328	1.5040	2.2704	4.4328	-1.5041	-2.2703
33	H	-3.8627	0.2100	0.5934	-3.8518	0.4209	0.5138	-3.8518	-0.4210	-0.5137
34	O	-2.1139	0.0292	1.6662	-2.1653	0.0457	1.6288	-2.1653	-0.0458	-1.6288
35	C	-2.7531	-0.8070	2.6402	-2.9033	-0.7982	2.5204	-2.9033	0.7981	-2.5205
36	H	-3.7768	-0.4616	2.8295	-3.9062	-0.3889	2.6957	-3.9062	0.3887	-2.6958
37	H	-2.1648	-0.7249	3.5548	-2.3496	-0.8169	3.4601	-2.3496	0.8168	-3.4601
38	H	-2.7734	-1.8503	2.3098	-2.9895	-1.8164	2.1268	-2.9897	1.8163	-2.1269

Table S13. 3D Coordinates of B3LYP/6-31+G(d,p) Optimized Geometries of (*S*)-22bA-(*S*)-22bF (continued).

		(*S*)-22bD *coordinates*			(*S*)-22bE *coordinates*			(*S*)-22bF *coordinates*		
ID	**atom**	**X**	**Y**	**X**	**X**	**X**	**Z**	**X**	**Y**	**Z**
1	C	-1.4118	-1.1721	-1.2117	-1.4225	-1.4094	-0.8480	1.3795	1.2336	-1.0933
2	C	-3.1857	-0.0163	0.0510	-2.7973	0.2723	0.2904	2.7486	-0.0077	0.5262
3	C	-1.0068	1.2021	-0.3618	-0.6832	1.0419	-0.8650	0.8281	-1.2119	-0.5963
4	C	-2.5291	1.3372	-0.2418	-2.1239	1.4121	-0.4945	2.2677	-1.3302	-0.0900
5	C	-0.6793	0.1703	-1.4455	-0.6925	-0.2990	-1.6177	0.7641	-0.0781	-1.6240
6	O	-2.8092	-0.9930	-0.9078	-2.7078	-0.9771	-0.3754	2.6453	1.0357	-0.4427
7	O	-2.8783	2.3080	0.7428	-2.2104	2.6265	0.2393	2.3007	-2.4202	0.8293
8	O	-0.4312	2.4528	-0.7441	-0.1675	2.0790	-1.6976	0.4340	-2.4214	-1.2420
9	O	0.7268	-0.0444	-1.6202	0.6240	-0.7416	-2.0090	-0.5519	0.1681	-2.1569
10	C	-0.6533	-2.0329	-0.1706	-0.5211	-1.9753	0.2522	0.3668	1.9949	-0.2320
11	O	0.5070	-1.3459	0.3238	0.6870	-2.4471	-0.3704	-0.7998	2.2290	-1.0371
12	C	1.3655	-0.9769	-0.7345	1.4210	-1.4527	-1.0532	-1.4374	1.0358	-1.4511
13	H	-1.4342	-1.7066	-2.1639	-1.6473	-2.2210	-1.5453	1.6143	1.8649	-1.9547
14	H	-0.5929	0.8816	0.6009	-0.0858	0.9715	0.0517	0.1674	-1.0131	0.2552
15	H	-2.9259	1.7129	-1.1902	-2.6897	1.5733	-1.4177	2.9210	-1.5426	-0.9458
16	H	-1.0080	0.5903	-2.4014	-1.2024	-0.1270	-2.5712	1.3357	-0.4119	-2.4962
17	H	-2.7776	1.8821	1.6101	-1.9473	2.4257	1.1520	3.1934	-2.7900	0.8594
18	H	-0.7770	3.1209	-0.1325	0.7481	1.8544	-1.9172	0.6455	-3.1442	-0.6312
19	H	-1.2789	-2.2340	0.6964	-0.3042	-1.2319	1.0239	0.1090	1.4486	0.6798
20	H	-0.3405	-2.9858	-0.6178	-0.9803	-2.8476	0.7213	0.7559	2.9779	0.0406
21	H	1.6034	-1.8758	-1.3262	2.1262	-2.0102	-1.6770	-2.1471	1.3563	-2.2204
22	C	2.6332	-0.3852	-0.1586	2.2167	-0.5260	-0.1299	-2.2189	0.3507	-0.3257
23	C	4.9784	0.6372	0.9903	3.8309	1.1261	1.4771	-3.8530	-0.8493	1.6240
24	C	3.7234	-1.2280	0.0925	2.4224	-0.8318	1.2212	-2.7211	1.1052	0.7440
25	C	2.7243	0.9760	0.1599	2.8593	0.5954	-0.6769	-2.5577	-1.0060	-0.4202
26	C	3.8938	1.4832	0.7337	3.6560	1.4201	0.1205	-3.3671	-1.6031	0.5506
27	C	4.8922	-0.7209	0.6674	3.2174	-0.0049	2.0223	-3.5275	0.5073	1.7173
28	H	3.6594	-2.2827	-0.1636	1.9659	-1.7183	1.6482	-2.4786	2.1606	0.8150
29	H	1.8882	1.6337	-0.0556	2.7530	0.8120	-1.7365	-2.1711	-1.5965	-1.2436
30	H	3.9601	2.5399	0.9766	4.1433	2.2859	-0.3181	-3.6162	-2.6573	0.4686
31	H	5.7331	-1.3818	0.8566	3.3587	-0.2492	3.0711	-3.9019	1.1024	2.5454
32	H	5.8871	1.0351	1.4327	4.4484	1.7669	2.0996	-4.4809	-1.3140	2.3786
33	H	-4.2755	0.0521	-0.0492	-3.8748	0.4563	0.3741	3.8228	-0.0523	0.7479
34	O	-2.8480	-0.3566	1.3776	-2.2111	0.2652	1.5734	2.0235	0.2482	1.6975
35	C	-3.6997	-1.3392	1.9807	-2.9645	-0.4315	2.5748	2.5970	1.2550	2.5396
36	H	-4.7428	-1.0007	1.9727	-3.9707	-0.0043	2.6641	3.6226	0.9833	2.8202
37	H	-3.3609	-1.4551	3.0109	-2.4275	-0.3011	3.5150	1.9759	1.3025	3.4351
38	H	-3.6244	-2.3000	1.4604	-3.0387	-1.4981	2.3400	2.6021	2.2326	2.0464

Table S14. Energy and Abundance of Conformers (*S*)-22bA-(*S*)-22bF.

conformer	B3LYP/6-31+G(d,p)				B3LYP/6-311++G(2d,2p)			
	ΔE (Ha)	ΔG (Ha)	abundance (%)	imaginary frequencies	ΔE (Ha)	ΔG (Ha)	abundance (%)	imaginary frequencies
(*S*)-22bA	−995.69310	−995.42434	32.9	0	−995.94854	−995.67915	45.7	0
(*S*)-22bB	−995.69053	−995.42188	2.43	0	−995.94598	−995.67689	4.14	0
(*S*)-22bC	−995.69053	−995.42188	2.43	0	−995.94598	−995.67689	4.16	0
(*S*)-22bD	−995.69161	−995.42486	57.0	0	−995.94724	−995.67896	37.2	0
(*S*)-22bE	−995.69105	−995.42248	4.60	0	−995.94661	−995.67750	7.90	0
(*S*)-22bF	−995.68894	−995.42052	0.58	0	−995.94462	−995.67552	0.98	0

Table S15. Comparison Between Experimental (20b) and Calculated [(*S*)-22bA-(*S*)-22bF] NMR ^{3}J Coupling Constants.

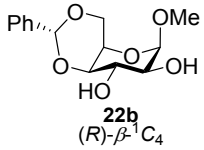
protons	experimental ^{3}J (Hz)	B3LYP/6-31+G(d,p)		B3LYP/6-311++G(2d,2p)	
		calculated ^{3}J (Hz)	Δ	calculated ^{3}J (Hz)	Δ
1-2	4.30	3.97	−0.33	3.94	−0.36
2-3	8.60	9.44	+0.84	9.42	+0.82
3-4	8.70	9.86	+1.16	9.92	+1.22
4-5	5.20	7.11	+1.91	6.89	+1.69
5-6a	9.90	7.33	−2.57	8.82	−1.08
5-6b	5.20	6.98	+1.78	6.33	+1.13
6a-6b	11.10	11.14	+0.05	10.88	-0.22
		Rmsd : 1.49		*Rmsd : 1.04*	

Table S16. Comparison Between Experimental (20b) and Calculated [(*S*)-22bA-(*S*)-22bF] NMR ^{1}H and ^{13}C Chemical Shifts.

atom	experimental δ (ppm)	B3LYP/6-31+G(d,p)		B3LYP/6-311++G(2d,2p)	
		calculated δ (ppm)	Δ	calculated δ (ppm)	Δ
H-1	4.96	4.78	−0.18	4.73	−0.23
H-2	3.57	3.53	−0.04	3.63	+0.06
H-3	4.55	4.22	−0.33	4.09	−0.46
H-4	4.06	4.20	+0.14	4.25	+0.19
H-5	4.20	4.48	+0.28	4.48	+0.28
H-6a	4.30	4.36	+0.06	4.40	+0.10
H-6b	4.06	4.12	+0.06	4.12	+0.06
		Rmsd : 0.19		*Rmsd : 0.24*	
C-1	96.1	96.7	+0.6	96.9	+0.8
C-2	72.4	71.8	−0.6	72.2	−0.2
C-3	65.7	69.2	+3.5	69.1	+3.4
C-4	74.4	72.1	−2.3	73.2	−1.2
C-5	66.9	68.4	+1.5	68.8	+1.9
C-6	67.2	65.1	−2.1	63.9	−3.3
C-7	95.6	95.0	−0.6	94.3	−1.3
		Rmsd : 1.91		*Rmsd : 2.06*	

Table S17. Comparison between Experimental (20b) and Calculated [(*S*)-22bA-(*S*)-22bF] H-H Distances by Quantitative NOESY NMR.

protons	experimental distance (Å)	B3LYP/6-31+G(d,p)		B3LYP/6-311++G(2d,2p)	
		calculated distance (Å)	Δ	calculated distance (Å)	Δ
3-7''	2.244	4.056	+1.812	4.075	+1.831
6a-7''	2.362	3.599	+1.237	3.630	+1.268
6a-3	2.656	2.706	+0.050	2.591	−0.065
5-7''	3.552	3.339	−0.213	3.456	−0.096
5-1	2.807	3.963	+1.156	3.968	+1.161
4-7''	3.516	3.817	+0.310	3.852	+0.336
2-1	2.319	2.425	+0.106	2.425	+0.106
2-4	2.392	2.528	+0.136	2.528	+0.136
2-3	2.894	3.055	+0.161	3.054	+0.160
		Rmsd : 0.76		*Rmsd : 0.76*	



22b
(*R*)-β-$^1C_4$

Table S18. 3D Coordinates of B3LYP/6-31+G(d,p) Optimized Geometries of (*R*)-22bA-(*R*)-22bE.

		(*R*)-22bA *coordinates*			(*R*)-22bB *coordinates*			(*R*)-22bC *coordinates*		
ID	**atom**	**X**	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**
1	C	-1.4356	1.3552	-0.0109	1.3991	1.3464	-0.1394	-1.4104	1.3691	-0.0528
2	C	-3.3299	-0.2812	-0.2561	3.3321	-0.2299	0.3216	-3.3254	-0.2537	-0.3159
3	C	-1.1226	-0.9222	-1.1369	1.1221	-0.7752	1.2480	-1.1107	-0.9514	-1.1117
4	O	-2.5555	-1.0277	-1.1955	2.5547	-0.8822	1.3126	-2.5419	-1.0494	-1.1911
5	C	-0.6534	0.5447	-1.0498	0.6392	0.6717	1.0048	-0.6435	0.5134	-1.0707
6	C	-2.9276	1.1981	-0.2953	2.9050	1.2318	0.1378	-2.9113	1.2301	-0.3222
7	H	-0.8064	1.0277	-2.0199	0.8116	1.2666	1.9071	-0.7961	0.9663	-2.0557
8	H	-4.3609	-0.4022	-0.6104	4.3586	-0.2882	0.7029	-4.3474	-0.3607	-0.6982
9	H	-0.7816	-1.3271	-2.0936	0.7830	-1.0741	2.2433	-0.7556	-1.3936	-2.0464
10	O	-3.2097	-0.7551	1.0569	3.2589	-0.8373	-0.9495	-3.2691	-0.6810	1.0279
11	C	-3.8916	-1.9897	1.3034	3.9749	-2.0739	-1.0655	-3.9990	-1.8827	1.3064
12	H	-3.7705	-2.2049	2.3659	3.8878	-2.3876	-2.1064	-3.9149	-2.0564	2.3799
13	H	-3.4641	-2.8074	0.7134	3.5438	-2.8405	-0.4138	-3.5775	-2.7344	0.7630
14	H	-4.9596	-1.8922	1.0705	5.0324	-1.9300	-0.8124	-5.0551	-1.7617	1.0358
15	O	0.7693	0.6170	-0.8373	-0.7887	0.6780	0.8435	0.7807	0.5870	-0.8608
16	C	-0.4908	-1.7733	-0.0259	0.4965	-1.7469	0.2350	-0.5000	-1.7599	0.0413
17	H	-0.8721	-1.5019	0.9648	0.8753	-1.5776	-0.7798	-0.8906	-1.4453	1.0159
18	H	-0.6786	-2.8346	-0.2002	0.7019	-2.7803	0.5213	-0.6926	-2.8265	-0.0901
19	O	0.9328	-1.5884	-0.0733	-0.9277	-1.5823	0.2649	0.9252	-1.5856	0.0000
20	C	1.2782	-0.2395	0.1870	-1.2889	-0.2635	-0.0961	1.2816	-0.2294	0.2014
21	H	0.8475	0.0521	1.1574	-0.8536	-0.0486	-1.0869	0.8526	0.1087	1.1572
22	C	2.7795	-0.1032	0.2153	-2.7971	-0.1378	-0.1518	2.7838	-0.1039	0.2251
23	C	5.5716	0.1368	0.2868	-5.5860	0.1245	-0.3539	5.5771	0.1215	0.2878
24	C	3.5417	-0.3995	-0.9236	-3.5989	-1.2650	-0.3732	3.5451	-0.4646	-0.8956
25	C	3.4219	0.3124	1.3863	-3.3995	1.1230	-0.0391	3.4275	0.3689	1.3734
26	C	4.8153	0.4328	1.4236	-4.7874	1.2522	-0.1382	4.8216	0.4820	1.4063
27	C	4.9319	-0.2799	-0.8871	-4.9876	-1.1334	-0.4710	4.9360	-0.3525	-0.8634
28	H	3.0448	-0.7211	-1.8332	-3.1366	-2.2417	-0.4613	3.0474	-0.8303	-1.7880
29	H	2.8350	0.5420	2.2719	-2.7824	1.9981	0.1336	2.8412	0.6492	2.2447
30	H	5.3053	0.7565	2.3370	-5.2436	2.2336	-0.0449	5.3128	0.8506	2.3019
31	H	5.5171	-0.5109	-1.7724	-5.6001	-2.0149	-0.6371	5.5206	-0.6335	-1.7346
32	H	6.6534	0.2297	0.3131	-6.6648	0.2255	-0.4298	6.6595	0.2087	0.3106
33	H	-1.2303	1.0107	1.0098	1.1828	0.8588	-1.0994	-1.2058	1.0360	0.9736
34	H	-3.1197	1.5509	-1.3190	3.1324	1.7753	1.0603	-3.1262	1.6432	-1.3128
35	O	-3.7314	1.9245	0.6235	3.6594	1.8679	-0.8903	-3.7119	1.9641	0.5934
36	H	-3.4184	2.8413	0.6144	3.6990	1.2501	-1.6388	-3.7239	1.4640	1.4252
37	O	-1.1402	2.7503	-0.1148	1.0077	2.7151	-0.2011	-1.0459	2.7408	-0.1910
38	H	-0.1954	2.8774	0.0536	1.6161	3.1568	-0.8133	-0.0784	2.7884	-0.1651

Table S19. 3D Coordinates of B3LYP/6-31+G(d,p) Optimized Geometries of (*R*)-22bA-(*R*)-22bE.

ID	atom	(*R*)-22bD *coordinates* X	Y	Z	(*R*)-22bE *coordinates* X	Y	Z
1	C	-1.2323	1.7858	-0.2841	-1.4275	1.3720	-0.0025
2	C	-2.9992	0.0033	-0.2802	-3.3219	-0.2676	-0.2584
3	C	-0.7920	-0.6506	-0.9068	-1.1260	-0.9208	-1.1372
4	O	-1.9793	-0.9996	-0.1886	-2.5576	-1.0159	-1.2039
5	C	-0.1919	0.6603	-0.3749	-0.6605	0.5430	-1.0438
6	C	-2.5285	1.2951	0.4041	-2.9212	1.2241	-0.2736
7	H	0.6200	0.9834	-1.0382	-0.8151	1.0274	-2.0133
8	H	-3.1919	0.2073	-1.3480	-4.3548	-0.3825	-0.6129
9	H	-1.0197	-0.5336	-1.9767	-0.7810	-1.3227	-2.0939
10	O	-4.1468	-0.4691	0.3419	-3.2040	-0.7555	1.0499
11	C	-4.8155	-1.5160	-0.3709	-3.8840	-1.9933	1.2829
12	H	-5.7289	-1.7327	0.1849	-3.7651	-2.2189	2.3436
13	H	-4.1960	-2.4164	-0.4241	-3.4544	-2.8049	0.6860
14	H	-5.0752	-1.1887	-1.3864	-4.9518	-1.8958	1.0484
15	O	0.3067	0.4572	0.9617	0.7631	0.6178	-0.8334
16	C	0.2198	-1.7748	-0.7322	-0.4969	-1.7756	-0.0274
17	H	-0.2456	-2.7441	-0.9196	-0.8778	-1.5060	0.9638
18	H	1.0443	-1.6309	-1.4425	-0.6837	-2.8366	-0.2043
19	O	0.7147	-1.8307	0.6133	0.9270	-1.5896	-0.0751
20	C	1.2480	-0.6097	1.0841	1.2730	-0.2418	0.1893
21	H	1.3579	-0.7487	2.1633	0.8425	0.0482	1.1600
22	C	2.6055	-0.2624	0.4696	2.7742	-0.1054	0.2165
23	C	5.1752	0.3525	-0.4910	5.5663	0.1348	0.2866
24	C	3.4622	-1.2810	0.0303	3.5353	-0.3955	-0.9247
25	C	3.0528	1.0657	0.4371	3.4176	0.3043	1.3891
26	C	4.3291	1.3720	-0.0437	4.8110	0.4247	1.4256
27	C	4.7386	-0.9751	-0.4508	4.9255	-0.2759	-0.8889
28	H	3.1282	-2.3131	0.0667	3.0376	-0.7123	-1.8356
29	H	2.4012	1.8593	0.7888	2.8314	0.5296	2.2763
30	H	4.6614	2.4058	-0.0672	5.3018	0.7439	2.3402
31	H	5.3906	-1.7741	-0.7918	5.5099	-0.5019	-1.7761
32	H	6.1671	0.5903	-0.8642	6.6481	0.2279	0.3123
33	H	-0.8096	2.6057	0.3095	-1.2214	1.0245	1.0179
34	H	-3.3103	2.0531	0.2861	-3.1256	1.6039	-1.2833
35	O	-2.3299	1.1364	1.8022	-3.6484	1.9746	0.6899
36	H	-1.5147	0.6210	1.9267	-4.5210	2.1873	0.3331
37	O	-1.4776	2.2006	-1.6297	-1.0686	2.7476	-0.1228
38	H	-2.0119	3.0068	-1.6181	-0.1009	2.7955	-0.1012

Table S20. Energy and Abundance of Conformers (*R*)-22bA-(*R*)-22bE.

conformer	B3LYP/6-31+G(d,p)				B3LYP/6-311++G(2d,2p)			
	ΔE (Ha)	ΔG (Ha)	abundance (%)	imaginary frequencies	ΔE (Ha)	ΔG (Ha)	abundance (%)	imaginary frequencies
(*R*)-22bA	−995.70054	−995.43419	27.0	0	−995.95595	−995.68804	19.6	0
(*R*)-22bB	−995.70163	−995.43448	36.5	0	−995.95715	−995.68853	33.0	0
(*R*)-22bC	−995.70175	−995.43433	31.1	0	−995.95721	−995.68870	39.4	0
(*R*)-22bD	−995.70023	−995.43230	3.62	0	−995.95575	−995.68701	6.57	0
(*R*)-22bE	−995.69773	−995.43160	1.73	0	−995.95344	−995.68551	1.35	0

Table S21. Comparison Between Experimental (20b) and Calculated [(*R*)-22bA-(*R*)-22bE] NMR ^{3}J Coupling Constants.

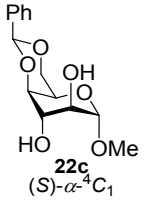
protons	experimental ^{3}J (Hz)	B3LYP/6-31+G(d,p)		B3LYP/6-311++G(2d,2p)	
		calculated ^{3}J (Hz)	Δ	calculated ^{3}J (Hz)	Δ
1-2	4.30	3.76	−0.54	3.70	−0.60
2-3	8.60	9.04	+0.44	8.85	+0.25
3-4	8.70	9.71	+1.01	9.49	+0.79
4-5	5.20	6.35	+1.15	6.18	+0.98
5-6a	9.90	11.15	+1.25	10.85	+0.95
5-6b	5.20	5.41	+0.21	5.30	+0.10
6a-6b	11.10	10.44	+0.66	10.48	+0.62
		Rmsd : 0.83		*Rmsd : 0.69*	

Table S22. Comparison Between Experimental (20b) and Calculated [(*R*)-22bA-(*R*)-22bE] NMR ^{1}H and ^{13}C Chemical Shifts.

atom	experimental δ (ppm)	B3LYP/6-31+G(d,p)		B3LYP/6-311++G(2d,2p)	
		calculated δ (ppm)	Δ	calculated δ (ppm)	Δ
H-1	4.96	4.79	−0.17	4.80	−0.16
H-2	3.57	3.49	-0.08	3.47	-0.10
H-3	4.55	4.61	+0.06	4.59	+0.04
H-4	4.06	4.10	+0.04	4.08	+0.02
H-5	4.20	4.31	+0.11	4.28	+0.08
H-6a	4.30	4.35	+0.05	4.33	+0.03
H-6b	4.06	4.04	−0.02	4.04	−0.02
		Rmsd : 0.09		*Rmsd : 0.08*	
C-1	96.1	97.6	+1.5	97.6	+1.5
C-2	72.4	72.2	+0.2	72.1	−0.3
C-3	65.7	65.2	−0.5	65.5	−0.2
C-4	74.4	75.5	+1.1	75.3	+0.9
C-5	66.9	67.6	+0.7	67.6	+0.7
C-6	67.2	66.7	−0.5	66.6	−0.6
C-7	95.6	93.7	−2.1	93.5	−2.1
		Rmsd : 1.15		*Rmsd : 1.10*	

Table S23. Comparison Between Experimental (20b) and Calculated [(*R*)-22bA-(*R*)-22bE] H-H Distances by Quantitative NOESY NMR.

protons	experimental distance (Å)	B3LYP/6-31+G(d,p)		B3LYP/6-311++G(2d,2p)	
		calculated distance (Å)	Δ	calculated distance (Å)	Δ
3-7’’	2.244	2.272	+0.028	2.282	+0.038
6a-7’’	2.362	2.345	−0.017	2.358	−0.004
6a-3	2.656	2.518	−0.138	2.529	−0.127
5-7’’	3.552	3.890	+0.338	3.905	+0.353
5-1	2.807	3.621	+0.814	3.445	+0.638
4-7’’	3.516	3.696	+0.180	3.698	+0.182
2-1	2.319	2.426	+0.107	2.428	+0.109
2-4	2.392	2.527	+0.135	2.545	+0.153
2-3	2.894	3.015	+0.121	2.991	+0.097
		Rmsd : 0.46		*Rmsd : 0.43*	



22c
(*S*)-α-$^4C_1$

Table S24. 3D Coordinates of B3LYP/6-31+G(d,p) Optimized Geometries of 22cA-22cC.

		22cA *coordinates*			**22cB** *coordinates*			**22cC** *coordinates*		
ID	**atom**	**X**	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**
1	C	-1.4076	1.1978	0.2835	-1.1849	0.6928	0.9913	1.1957	-0.7806	0.9004
2	C	-2.6235	-0.4714	-0.9691	-2.9108	0.3705	-0.6337	2.9285	-0.3379	-0.6881
3	C	-1.6863	-1.1399	1.2836	-1.4829	-1.6152	-0.0074	1.4982	1.5962	0.0792
4	C	-2.0373	-1.6276	-0.1372	-2.9079	-1.0654	-0.0793	2.9234	1.0527	-0.0282
5	C	-0.8178	0.1305	1.2165	-0.5915	-0.7232	0.8653	0.6035	0.6423	0.8800
6	O	-1.7532	0.6471	-1.0016	-1.7399	1.0948	-0.2707	1.7548	-1.0855	-0.3867
7	O	-3.8836	-0.1564	-0.4046	-4.0853	0.9839	-0.1588	4.0995	-0.9863	-0.2529
8	O	-0.9042	-2.1817	-0.7971	-3.6496	-1.9458	-0.9234	3.6683	1.9939	-0.8006
9	O	-2.8542	-0.9006	2.0663	-1.4724	-2.9396	0.5208	1.4863	2.8774	0.7052
10	O	0.4826	-0.2712	0.7367	0.7054	-0.6990	0.2440	-0.6909	0.6645	0.2545
11	C	-0.3822	2.2992	0.0446	-0.1286	1.7003	1.4289	0.1377	-1.8195	1.2558
12	O	0.8896	1.7610	-0.3421	1.1051	1.5428	0.7200	-1.0937	-1.6043	0.5594
13	C	1.3820	0.8382	0.6056	1.6033	0.2204	0.8507	-1.5811	-0.2988	0.7937
14	C	-4.6701	0.7744	-1.1634	-4.4134	2.2169	-0.8107	4.4278	-2.1711	-0.9886
15	H	-2.2969	1.6393	0.7510	-1.9739	0.6888	1.7551	1.9822	-0.8355	1.6648
16	H	-2.7339	-0.7674	-2.0185	-2.9110	0.3529	-1.7312	2.9351	-0.2390	-1.7812
17	H	-1.1149	-1.9206	1.7944	-1.0628	-1.6153	-1.0226	1.0817	1.6724	-0.9346
18	H	-2.7860	-2.4217	-0.0711	-3.3488	-1.0598	0.9257	3.3600	0.9714	0.9755
19	H	-0.7213	0.5487	2.2279	-0.5066	-1.1680	1.8673	0.5156	1.0111	1.9122
20	H	-0.1460	-1.5948	-0.6274	-4.5943	-1.8175	-0.7614	4.6124	1.8552	-0.6435
21	H	-3.5249	-0.4924	1.4898	-2.1003	-3.4601	-0.0034	2.1188	3.4341	0.2254
22	H	-0.7017	2.9527	-0.7690	-0.4745	2.7181	1.2394	0.4832	-2.8186	0.9849
23	H	-0.2717	2.8961	0.9611	0.0502	1.5813	2.5074	-0.0430	-1.7874	2.3400
24	H	-4.8285	0.3942	-2.1794	-4.5273	2.0643	-1.8915	4.5452	-1.9433	-2.0558
25	H	-5.6283	0.8600	-0.6501	-5.3630	2.5489	-0.3886	5.3757	-2.5333	-0.5882
26	H	-4.1860	1.7545	-1.2100	-3.6464	2.9762	-0.6278	3.6590	-2.9399	-0.8616
27	H	1.4531	1.3268	1.5907	1.6962	-0.0212	1.9228	-1.6448	-0.1417	1.8863
28	C	2.7250	0.3189	0.1623	2.9408	0.1222	0.1632	-2.9424	-0.1292	0.1534
29	C	5.2199	-0.6842	-0.6296	5.4353	-0.0595	-1.1045	-5.5082	0.2164	-0.9361
30	C	2.9148	-0.1439	-1.1476	3.0573	0.3973	-1.2070	-3.7454	-1.2412	-0.1304
31	C	3.7890	0.2778	1.0703	4.0777	-0.2433	0.8921	-3.4344	1.1578	-0.1061
32	C	5.0343	-0.2229	0.6766	5.3231	-0.3345	0.2610	-4.7103	1.3291	-0.6495
33	C	4.1582	-0.6428	-1.5412	4.2996	0.3068	-1.8375	-5.0221	-1.0679	-0.6748
34	H	2.0940	-0.1050	-1.8567	2.1769	0.6811	-1.7748	-3.3701	-2.2382	0.0710
35	H	3.6466	0.6384	2.0857	3.9921	-0.4572	1.9543	-2.8166	2.0224	0.1124
36	H	5.8550	-0.2495	1.3872	6.2000	-0.6190	0.8350	-5.0797	2.3308	-0.8492
37	H	4.2998	-0.9981	-2.5576	4.3835	0.5213	-2.8989	-5.6345	-1.9376	-0.8948
38	H	6.1865	-1.0719	-0.9378	6.4010	-0.1295	-1.5965	-6.4999	0.3498	-1.3586

Table S25. Energy and Abundance of Conformers 22cA-22cC.

conformer	B3LYP/6-31+G(d,p)				B3LYP/6-311++G(2d,2p)			
	ΔE (Ha)	ΔG (Ha)	abundance (%)	imaginary frequencies	ΔE (Ha)	ΔG (Ha)	abundance (%)	imaginary frequencies
22cA	−995.70793	−995.43926	97.1	0	−995.96321	−995.69375	97.5	0
22cB	−995.70123	−995.43569	2.22	0	−995.95704	−995.68997	1.77	0
22cC	−995.70046	−995.43456	0.67	0	−995.95639	−995.68908	0.69	0

Table S26. Comparison between experimental (20c) and calculated (22cA-22cC) NMR ^3J coupling constants

protons	experimental ^3J (Hz)	B3LYP/6-31+G(d,p)		B3LYP/6-311++G(2d,2p)	
		calculated ^3J (Hz)	Δ	calculated ^3J (Hz)	Δ
1-2	N/A	1.70	N/A	1.68	N/A
2-3	1.20	2.98	−1.78	2.95	−1.75
3-4	2.70	3.12	−0.42	3.11	−0.41
4-5	N/A	1.38	N/A	1.38	N/A
5-6a	1.30	1.56	−0.26	1.56	+0.26
5-6b	1.70	1.90	+0.20	1.90	+0.20
6a-6b	12.60	11.92	−0.68	11.92	−0.68
		Rmsd : 0.75		*Rmsd : 0.74*	

Table S27. Comparison Between Experimental (20c) and Calculated (22cA-22cC) NMR ^{1}H and ^{13}C Chemical Shifts.

atom	experimental δ (ppm)	B3LYP/6-31+G(d,p)		B3LYP/6-311++G(2d,2p)	
		calculated δ (ppm)	Δ	calculated δ (ppm)	Δ
H-1	5.20	5.12	−0.08	5.12	−0.08
H-2	3.71	3.66	−0.05	3.66	−0.05
H-3	4.00	3.91	−0.09	3.91	−0.09
H-4	4.14	4.24	+0.10	4.24	+0.10
H-5	4.00	3.97	−0.03	3.97	−0.03
H-6a	4.36	4.42	+0.06	4.42	+0.06
H-6b	4.13	4.22	+0.09	4.22	+0.09
		Rmsd : 0.08		*Rmsd : 0.08*	
C-1	99.2	100.6	+1.4	100.6	+1.4
C-2	67.2	67.3	+0.1	67.2	+0.0
C-3	68.0	68.4	+0.4	68.4	+0.4
C-4	76.0	75.7	−0.3	75.7	−0.3
C-5	59.5	60.4	+0.9	60.4	+0.9
C-6	70.2	68.9	−1.3	68.9	−1.3
C-7	101.6	100.5	−1.1	100.5	−1.1
		Rmsd : 0.93		*Rmsd : 0.93*	

3. NMR Spectra of New Compounds.

Figure S2. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **1,2,3,4,6-penta-*O*-acetyl *α*-D-idopyranose (2)**

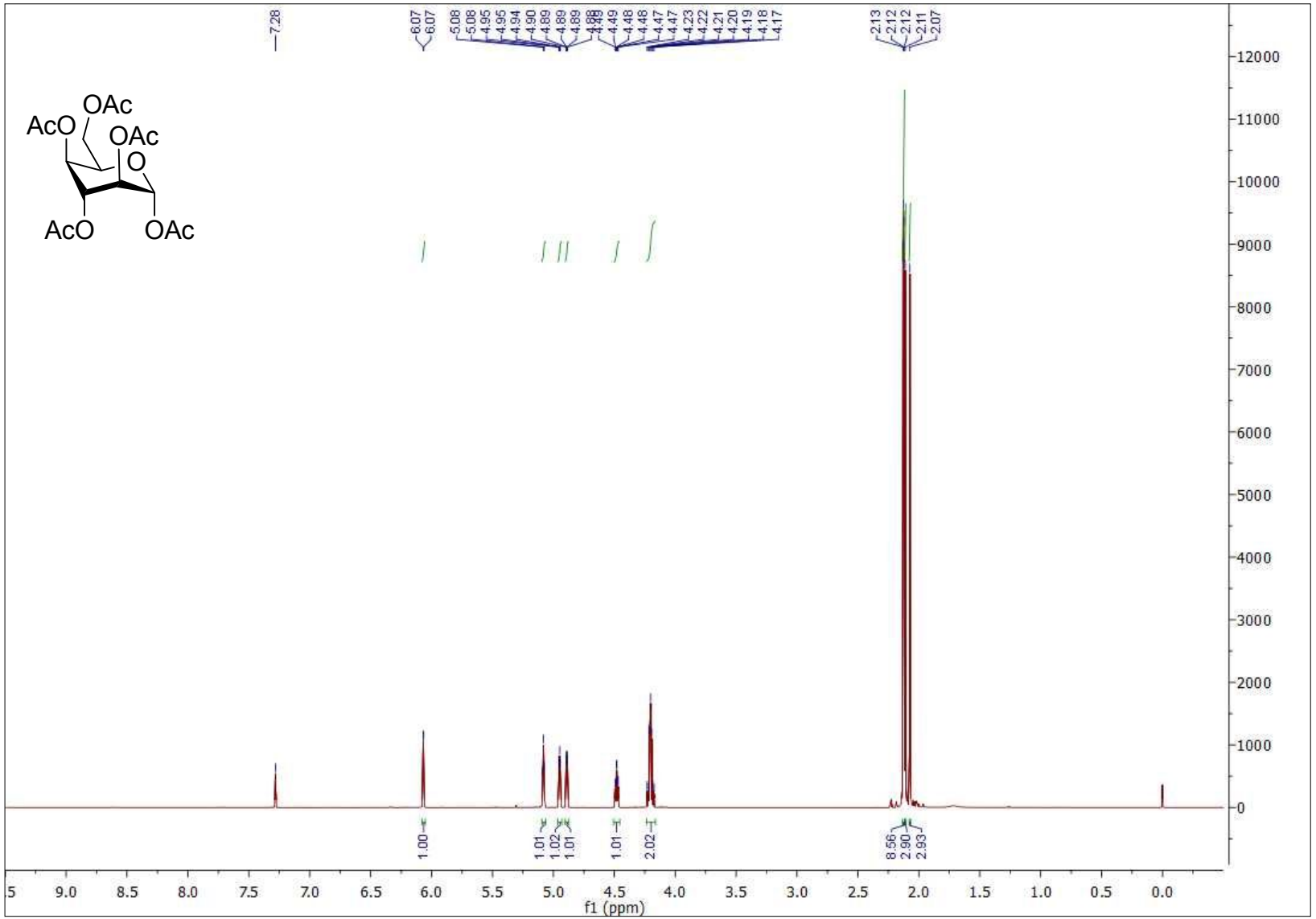


Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-idopyranoside (3a)**

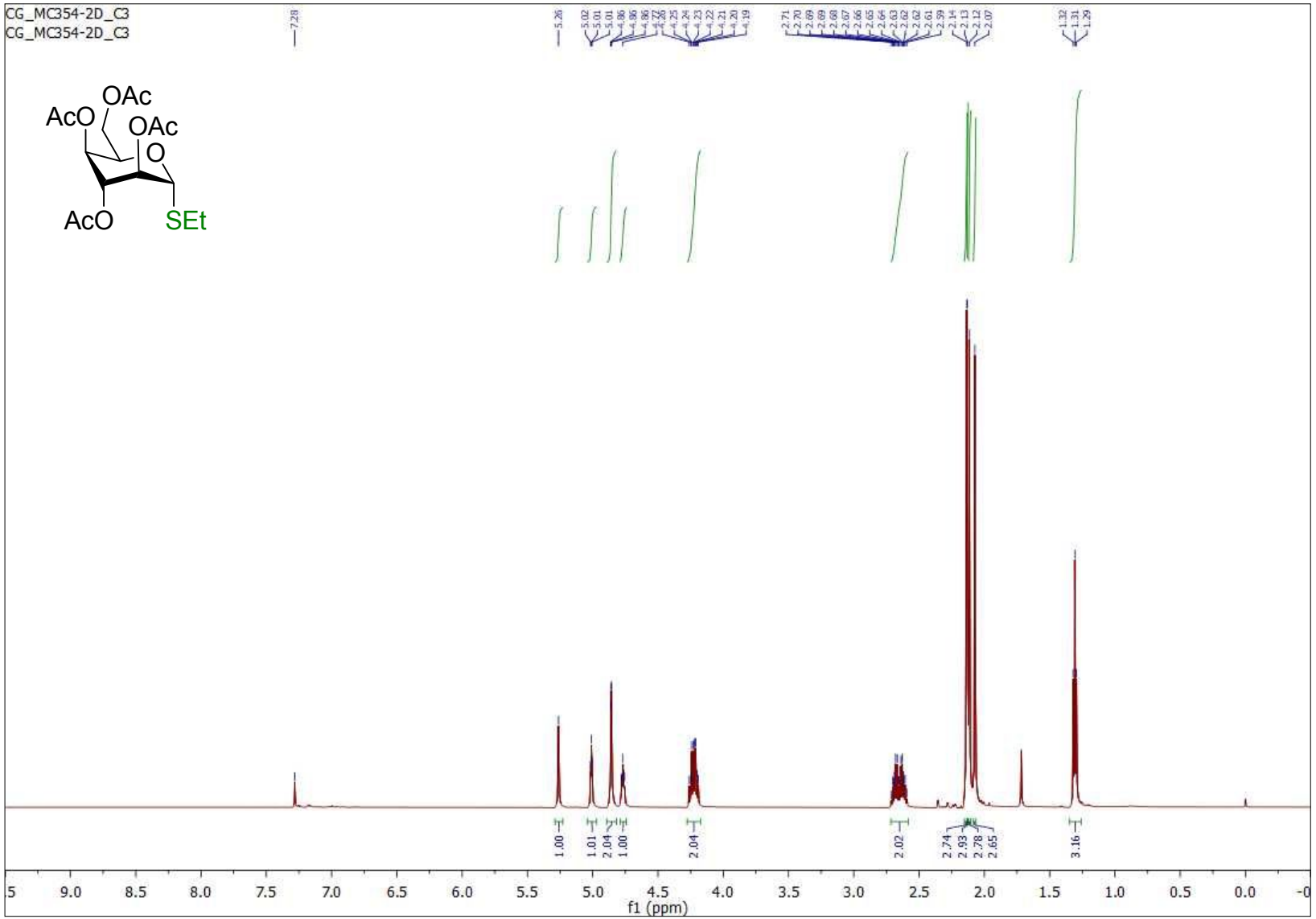


Figure S4. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-idopyranoside (3a)**

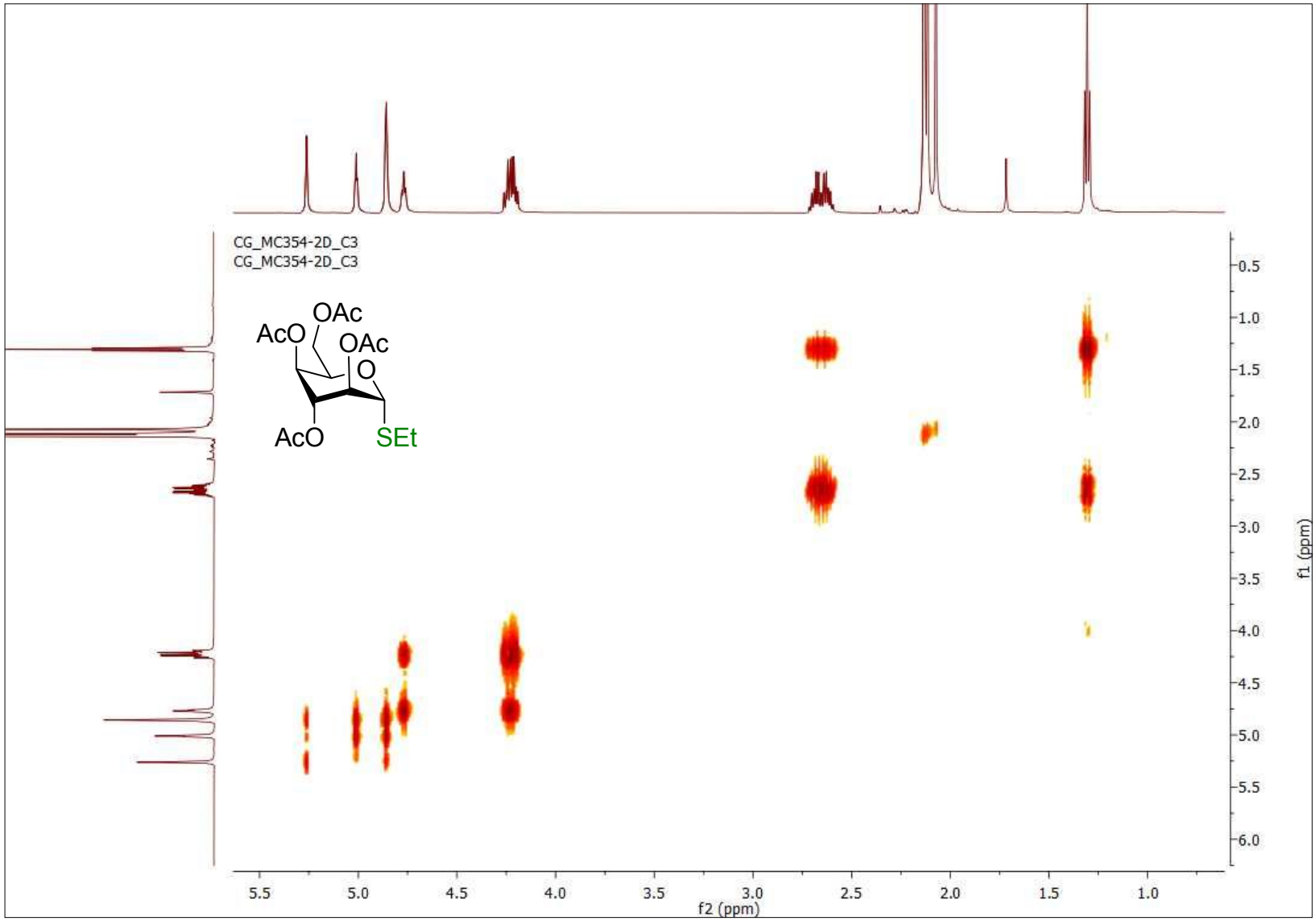


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-idopyranoside (3a)**

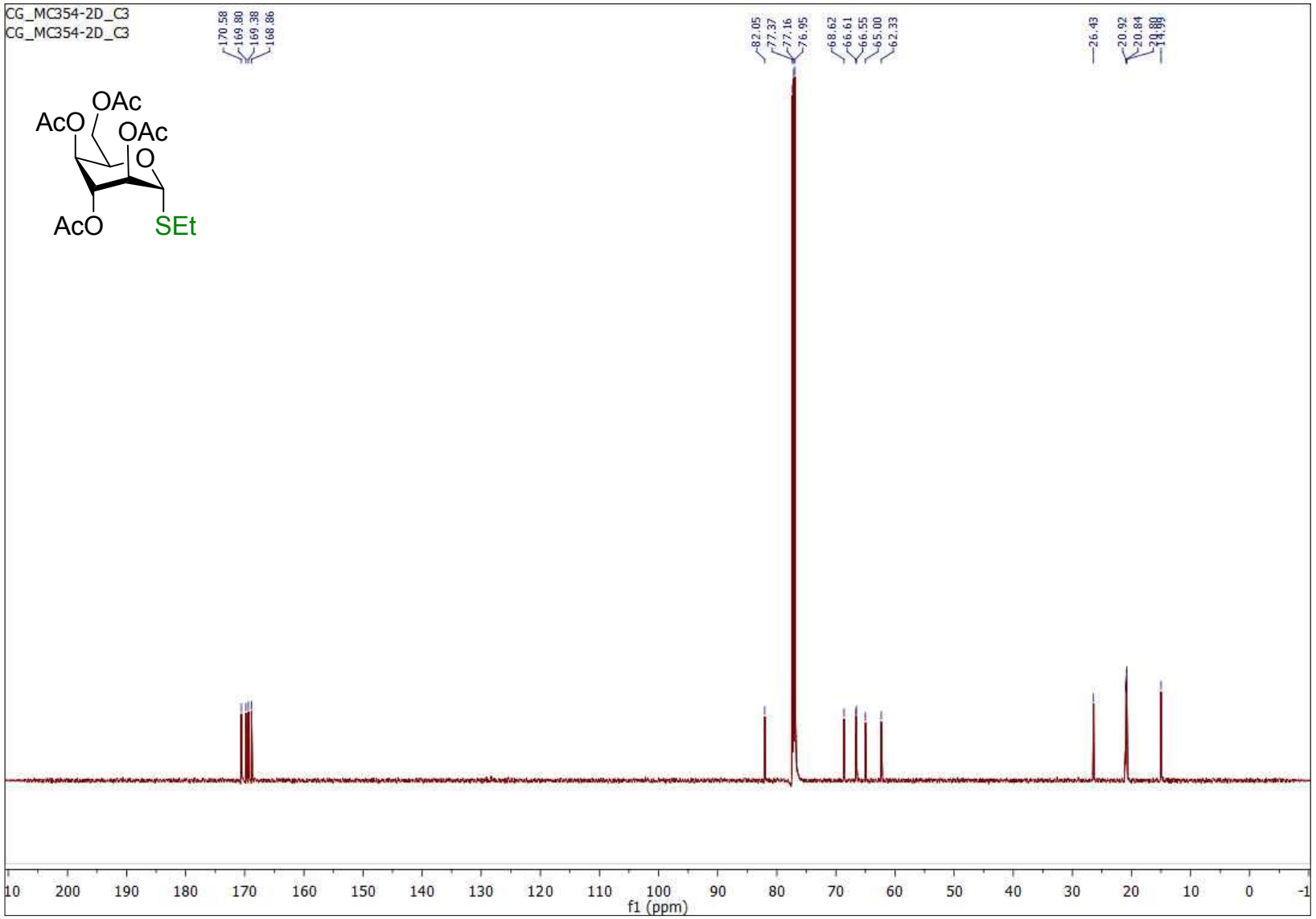


Figure S6. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-idopyranoside (3a)**

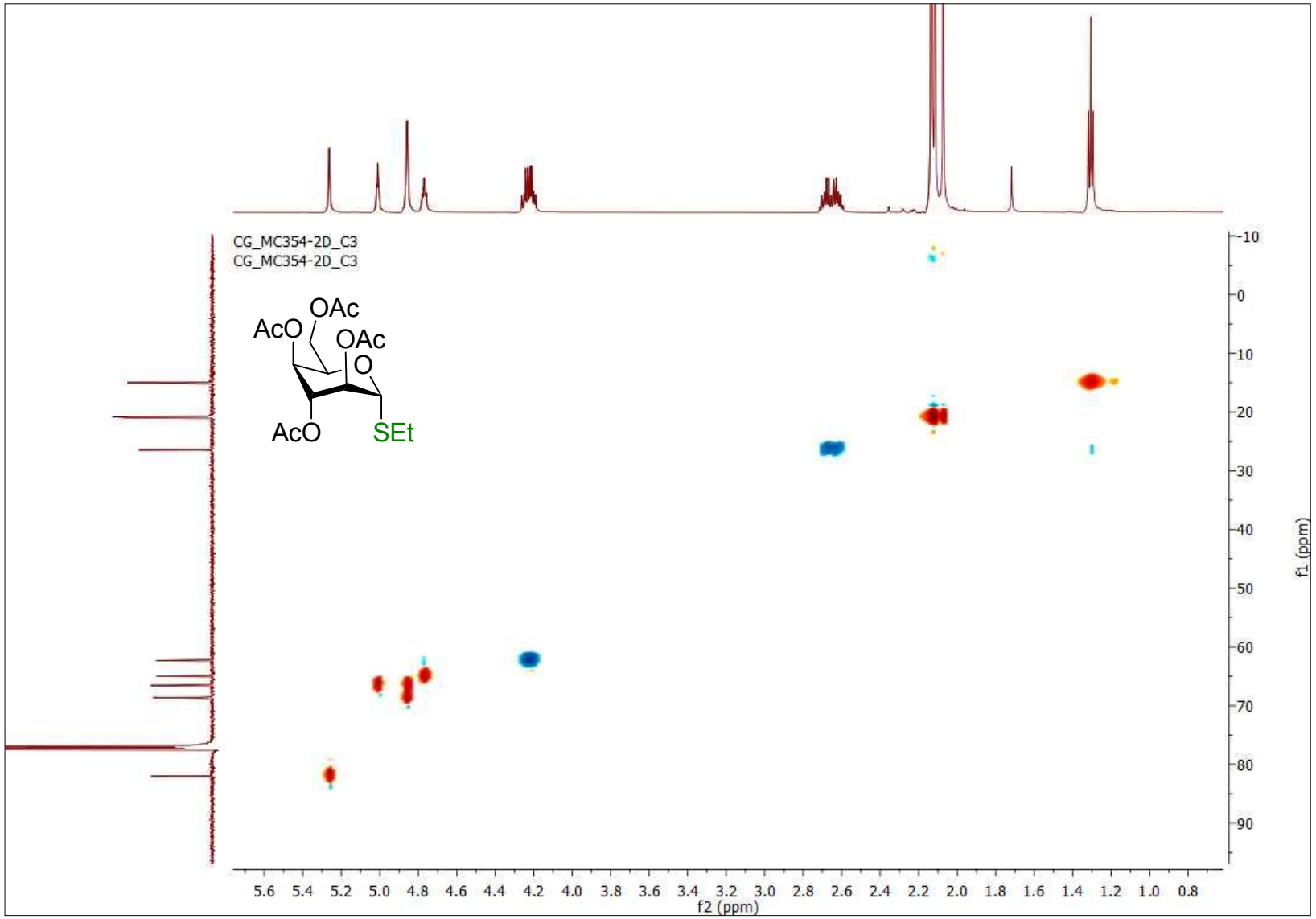


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-idopyranoside (3b)**

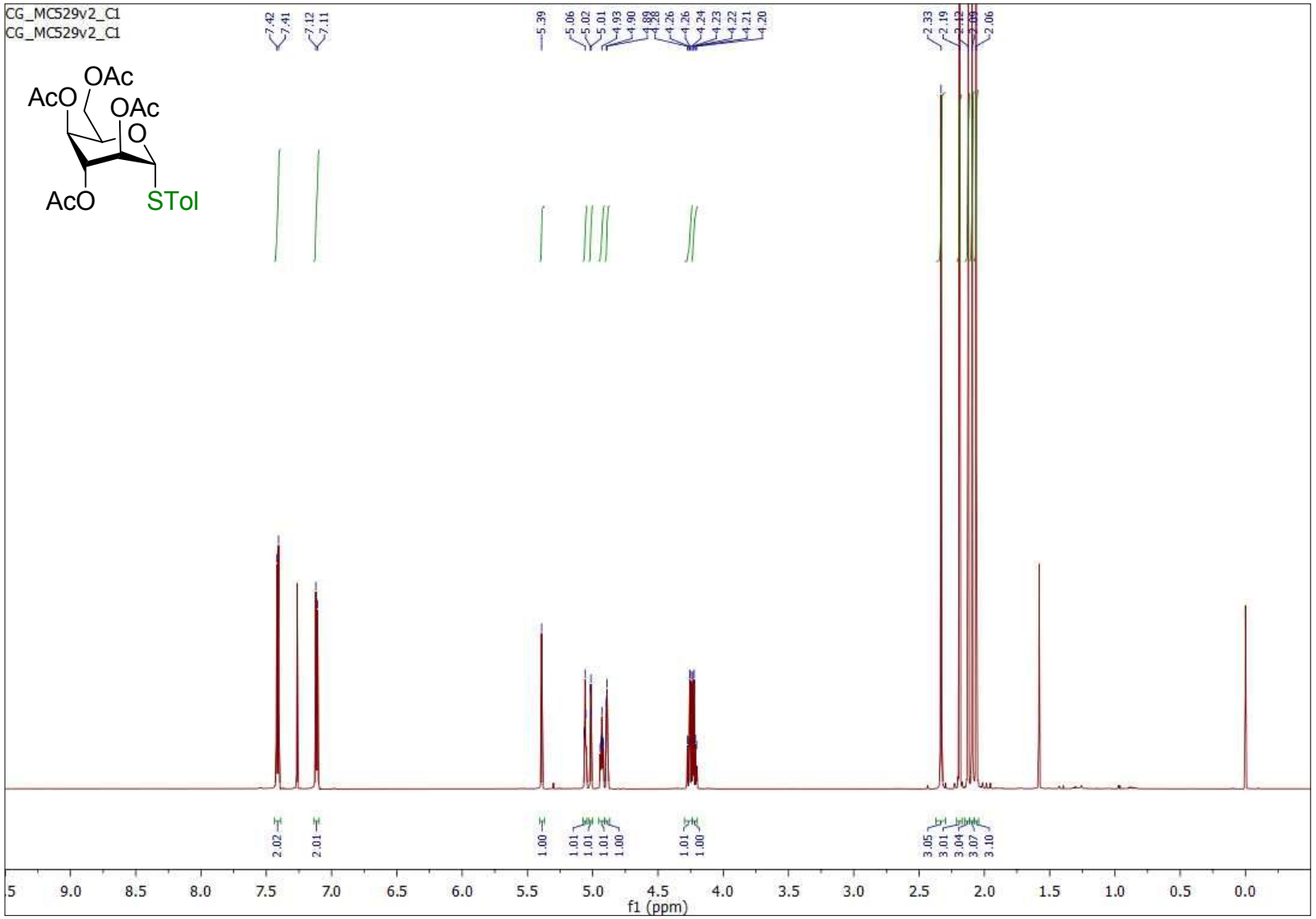


Figure S8. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-idopyranoside (3b)**

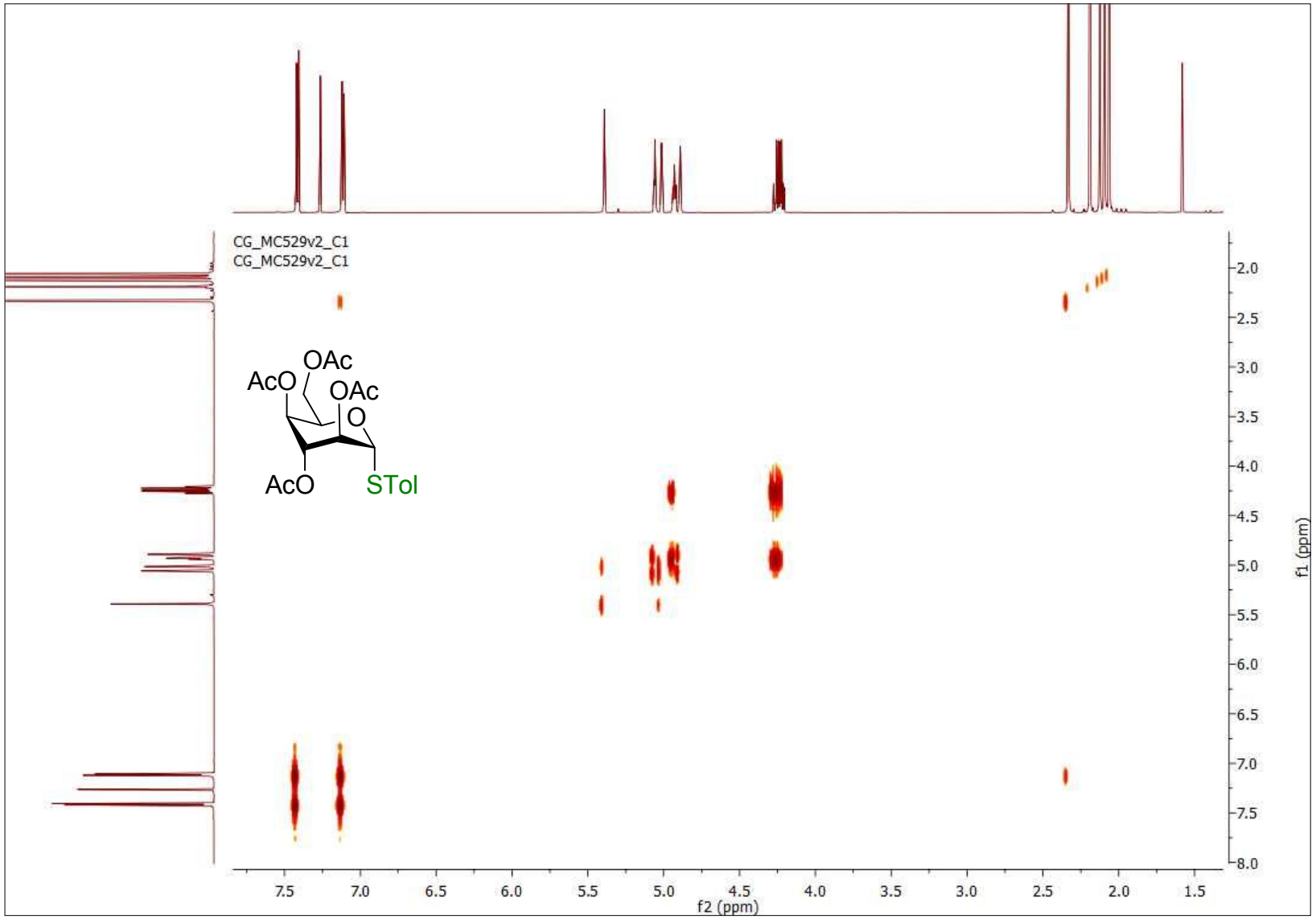


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***para*-methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-idopyranoside (3b)**

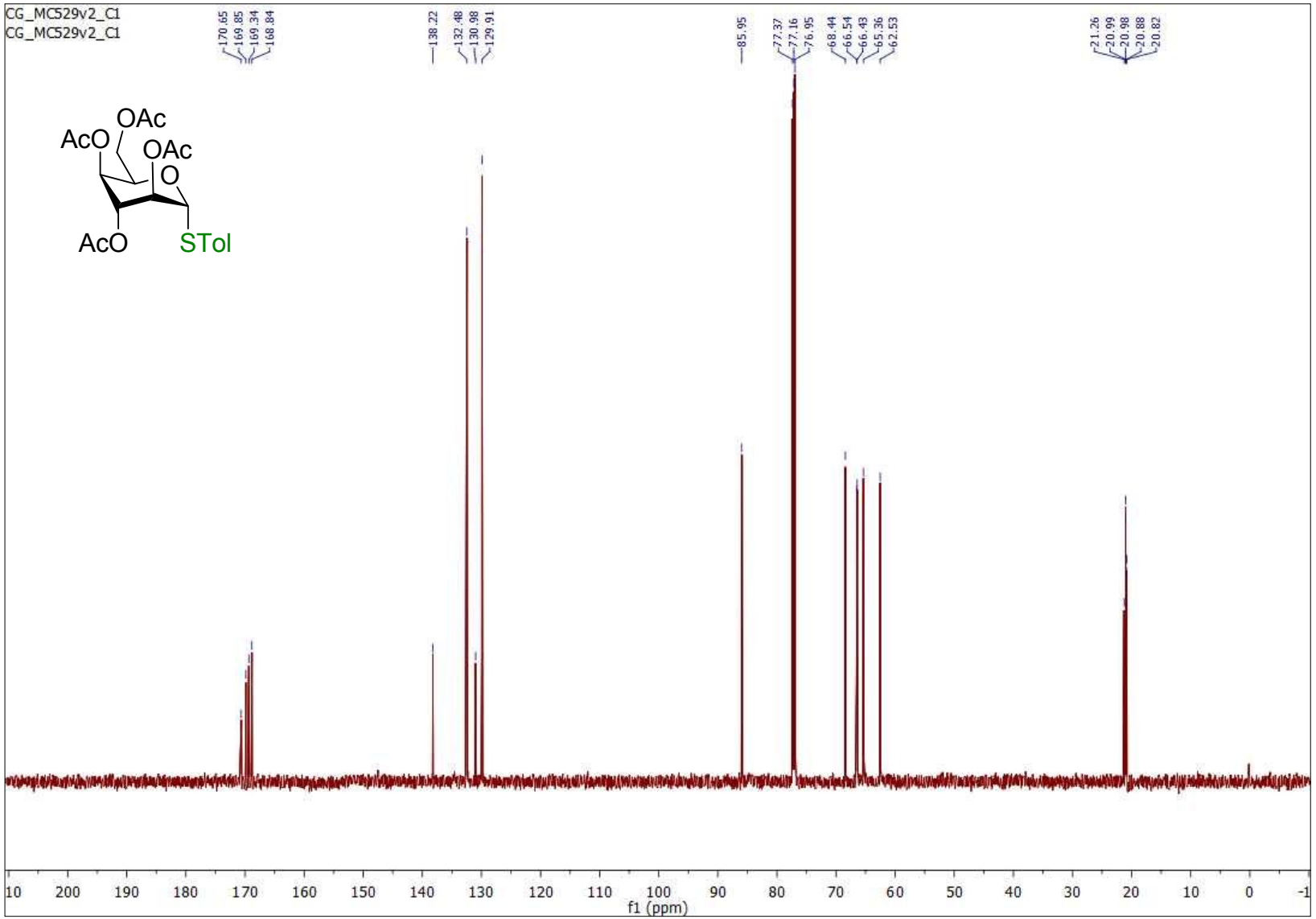


Figure S10. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-idopyranoside (3b)**

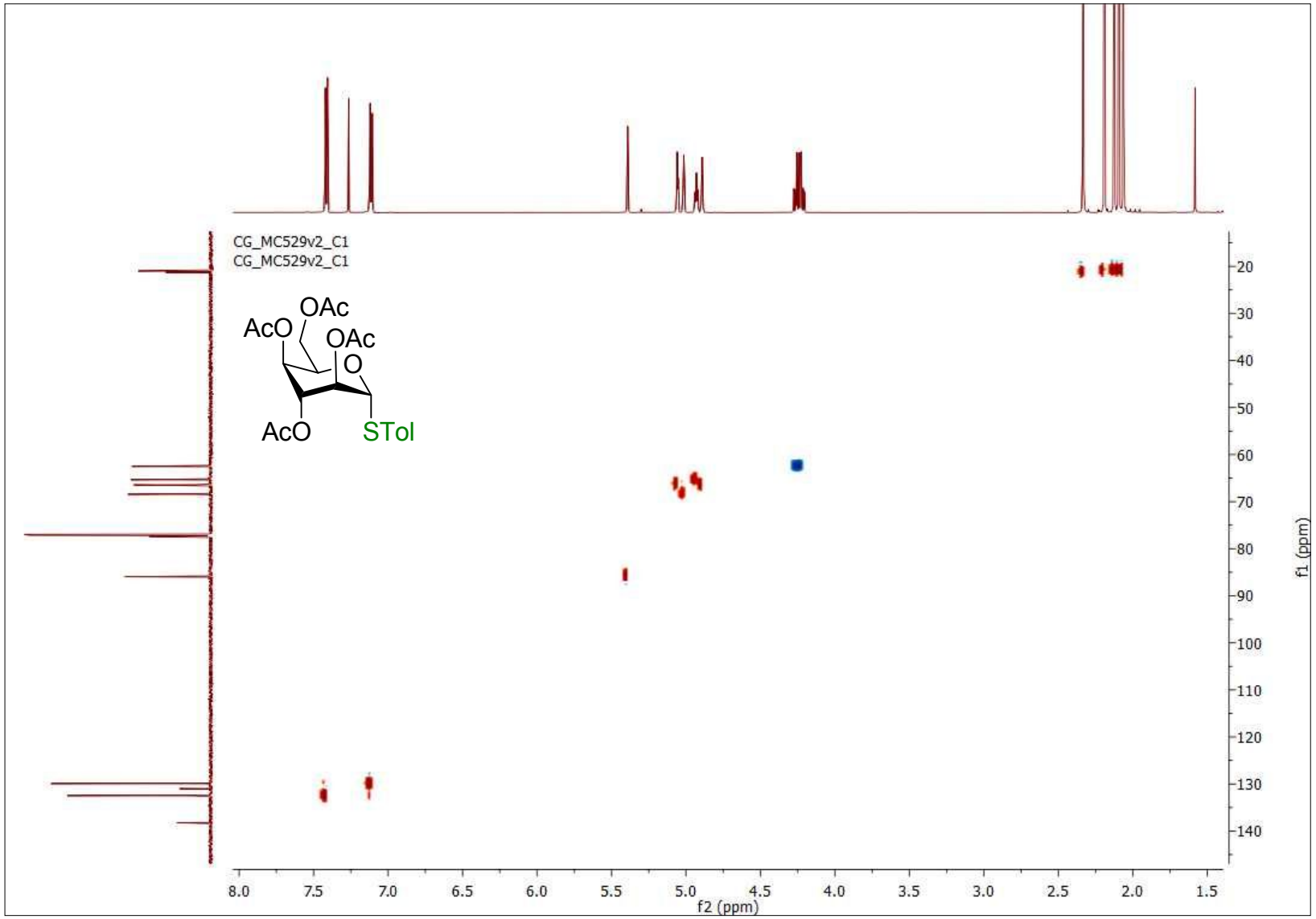


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (4a)**

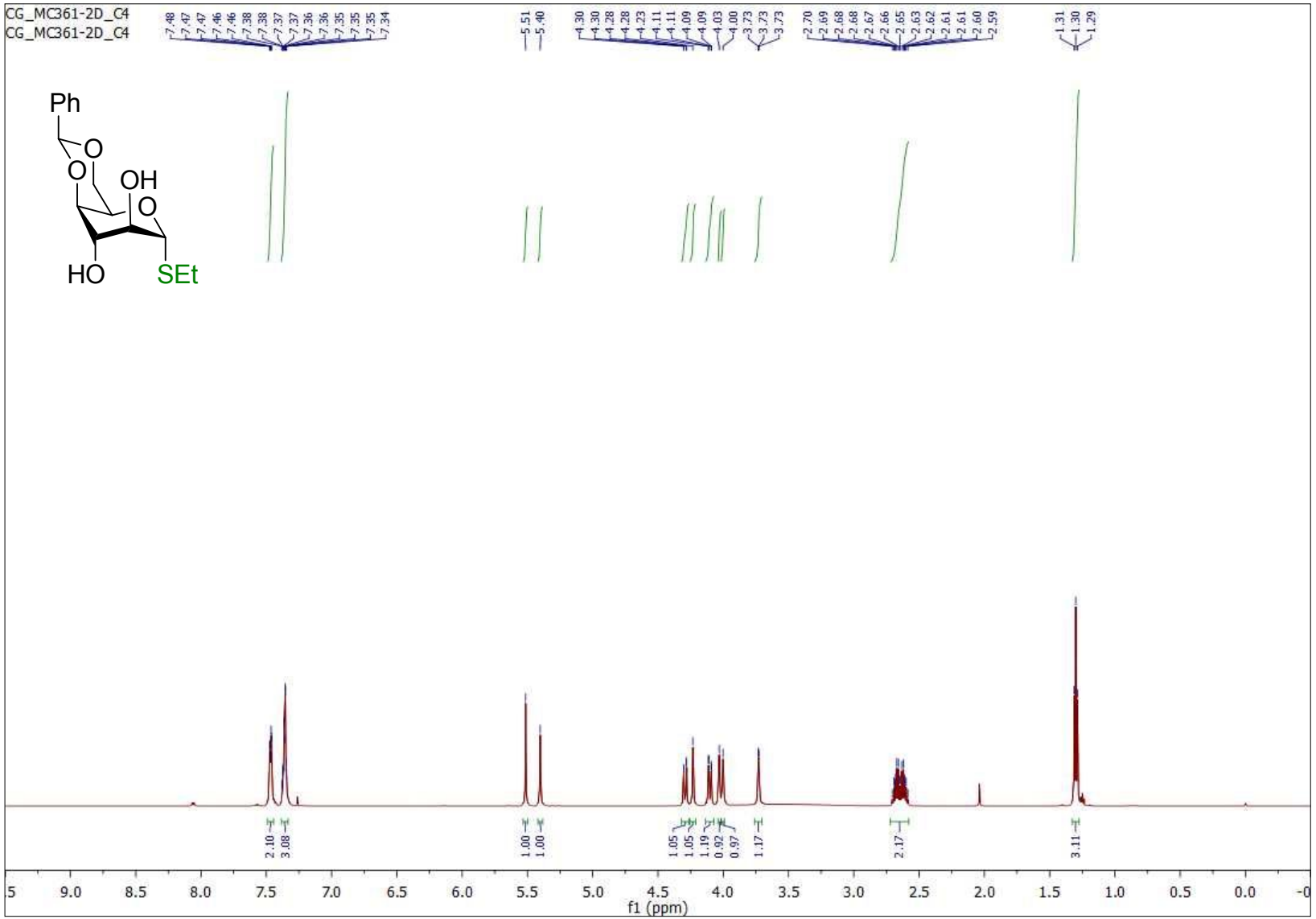


Figure S12. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (4a)**

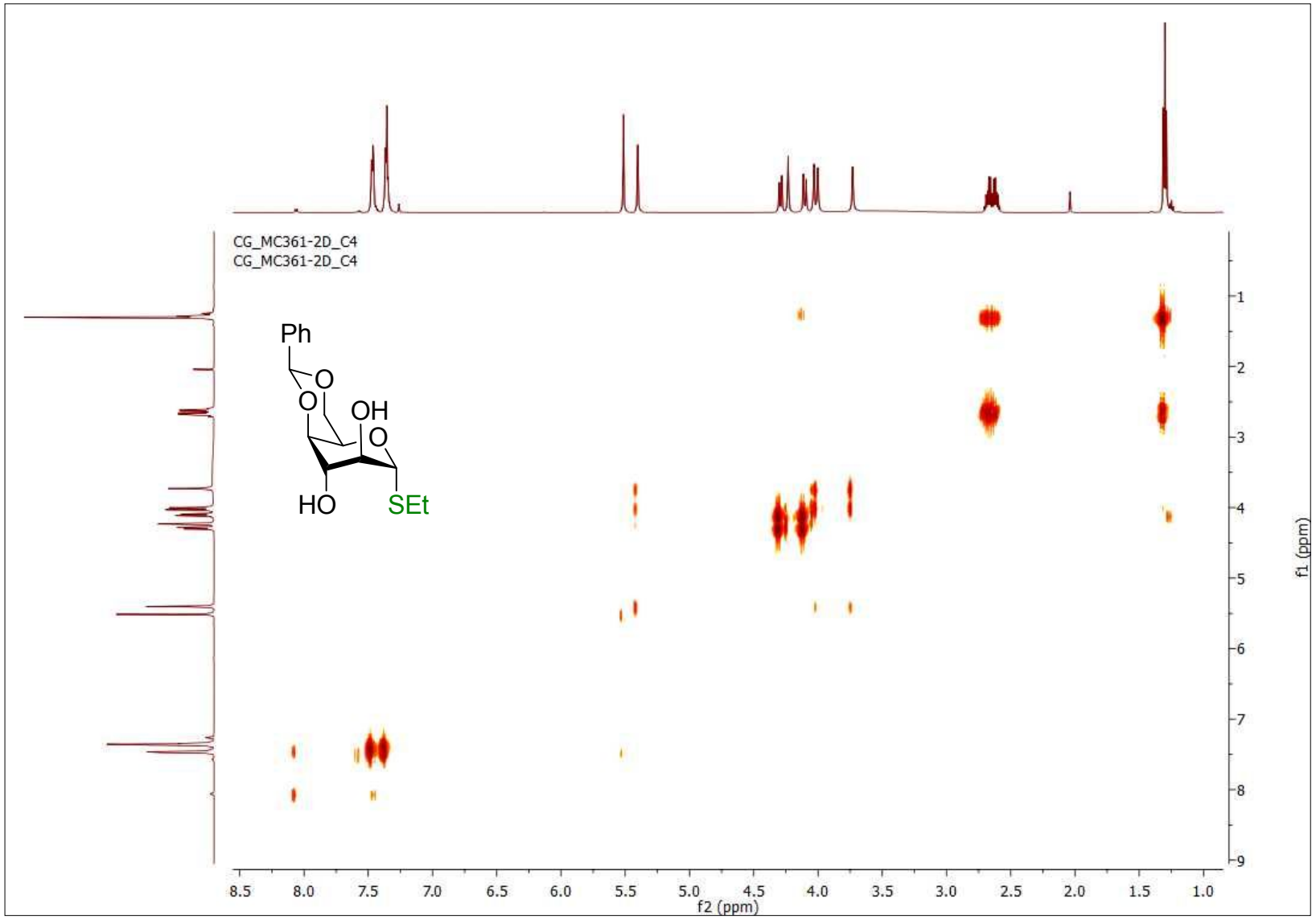


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **ethyl 4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (4a)**

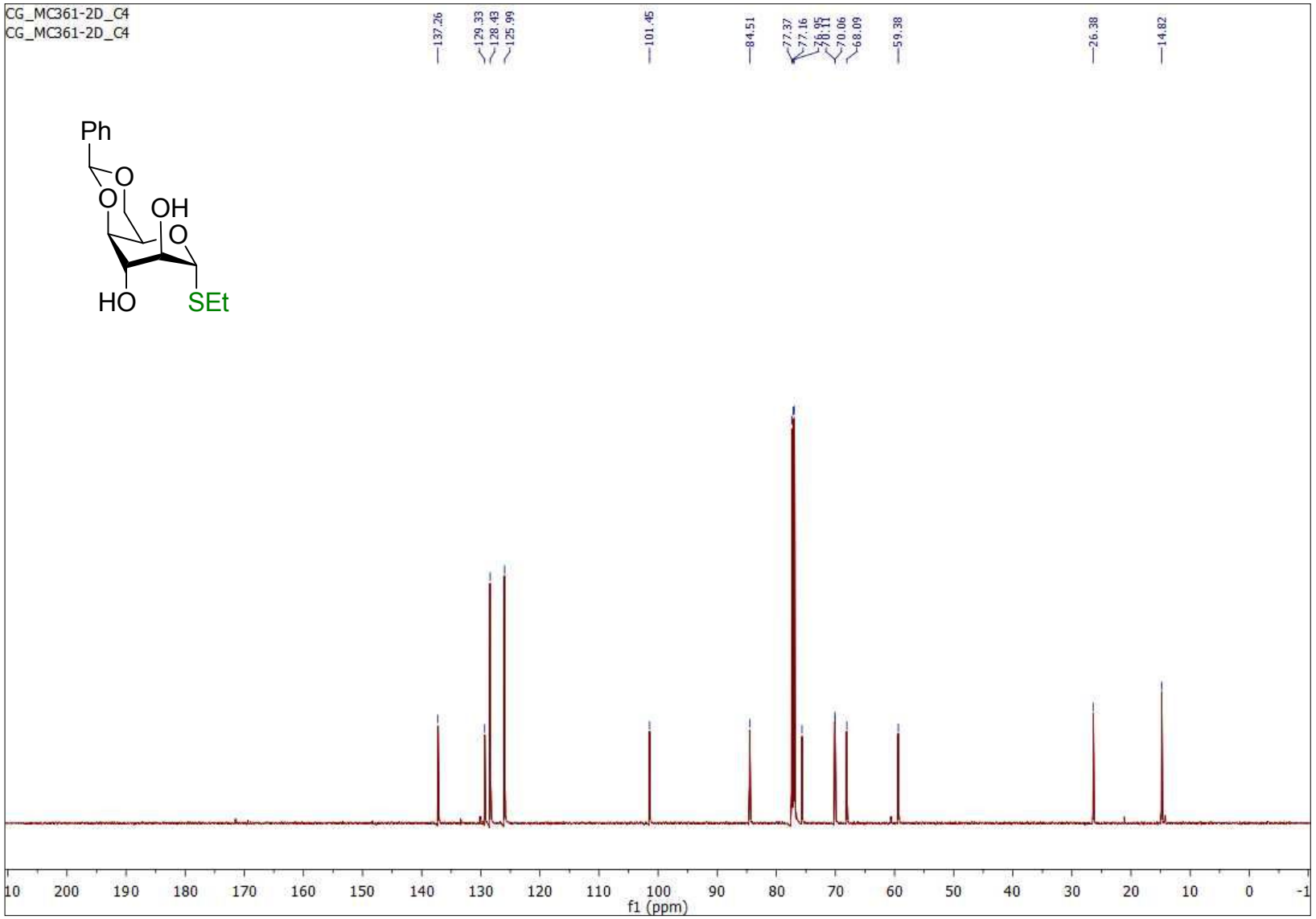


Figure S14. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (4a)**

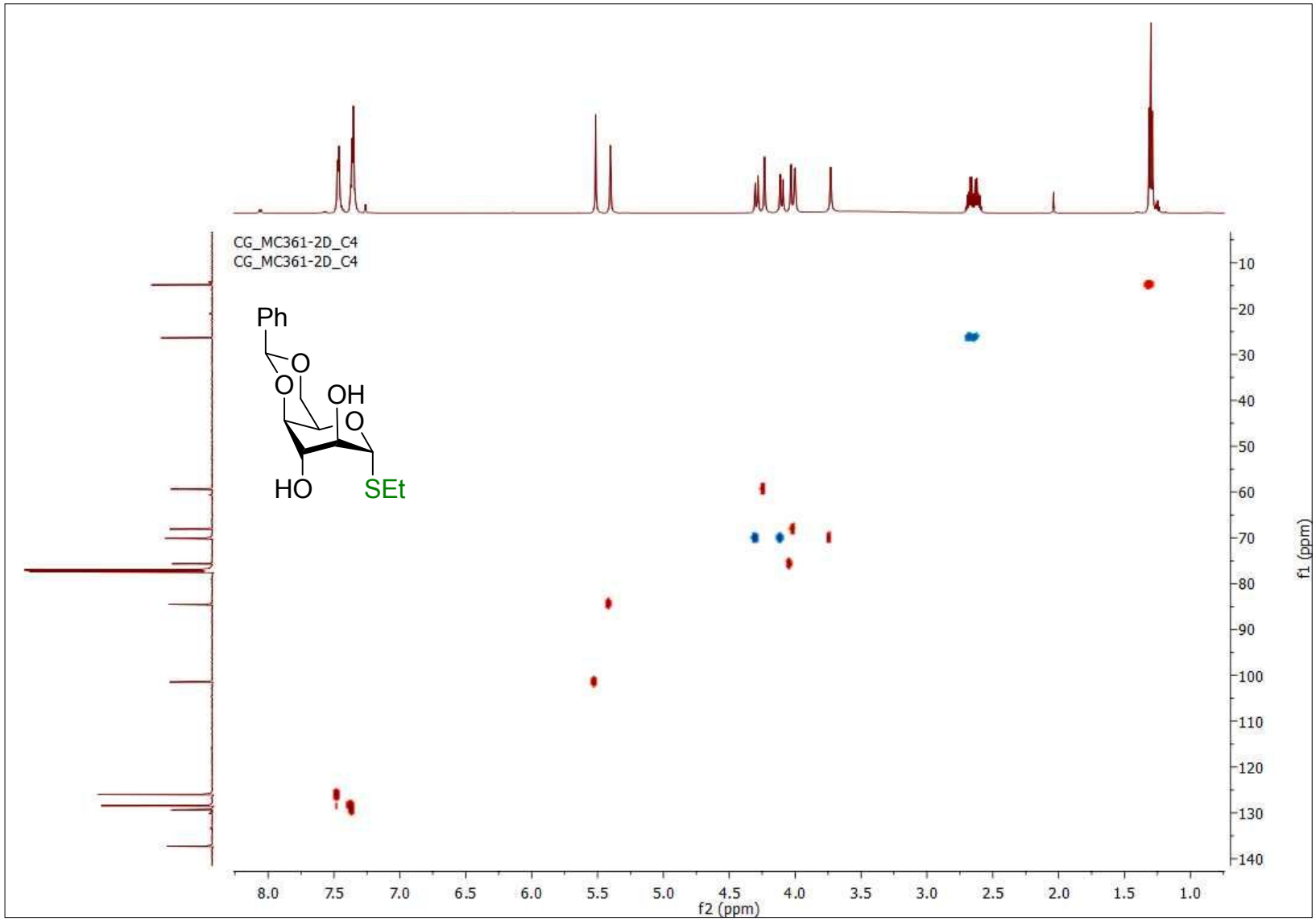


Figure S15. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (4b)**

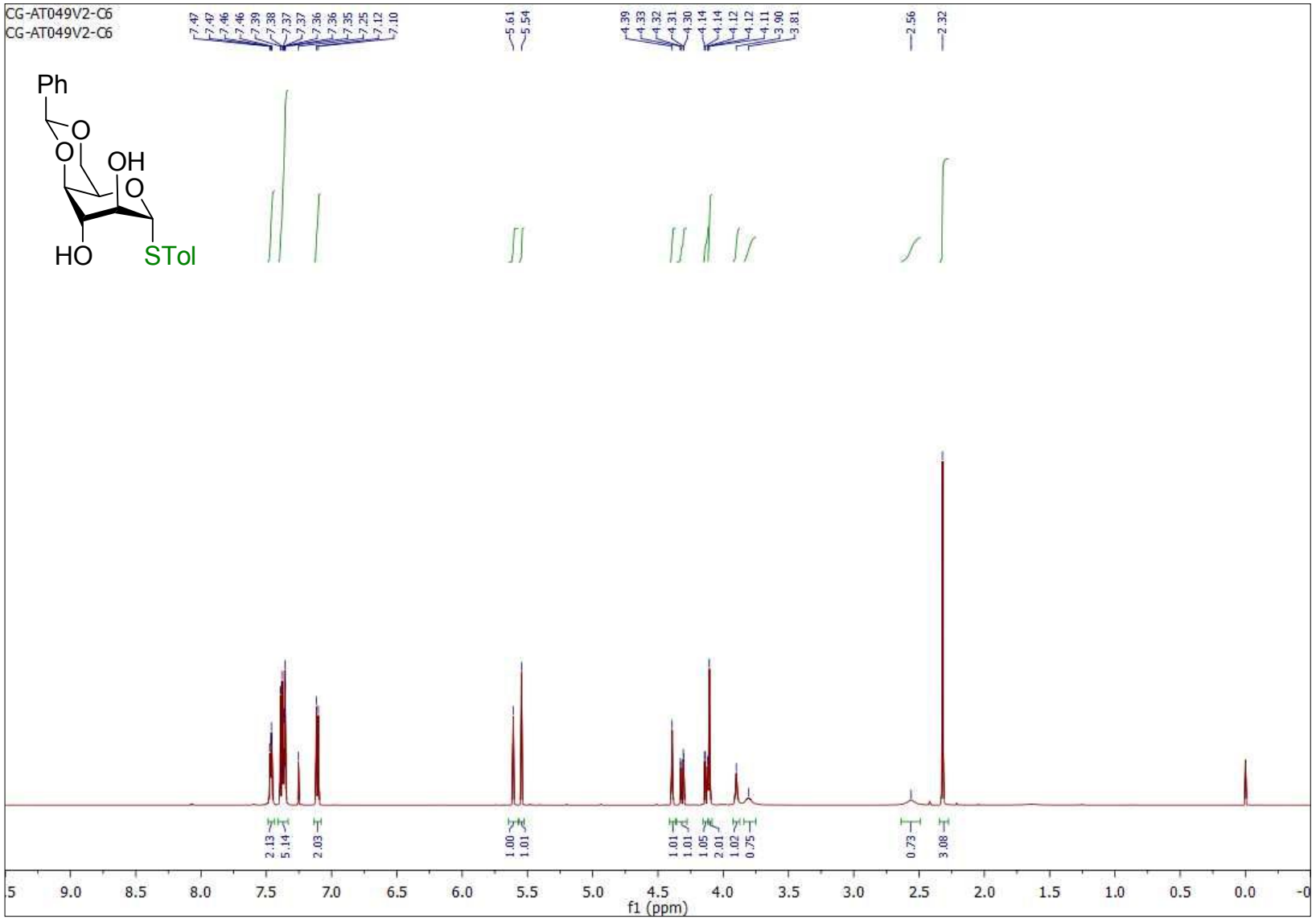


Figure S16. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (4b)**

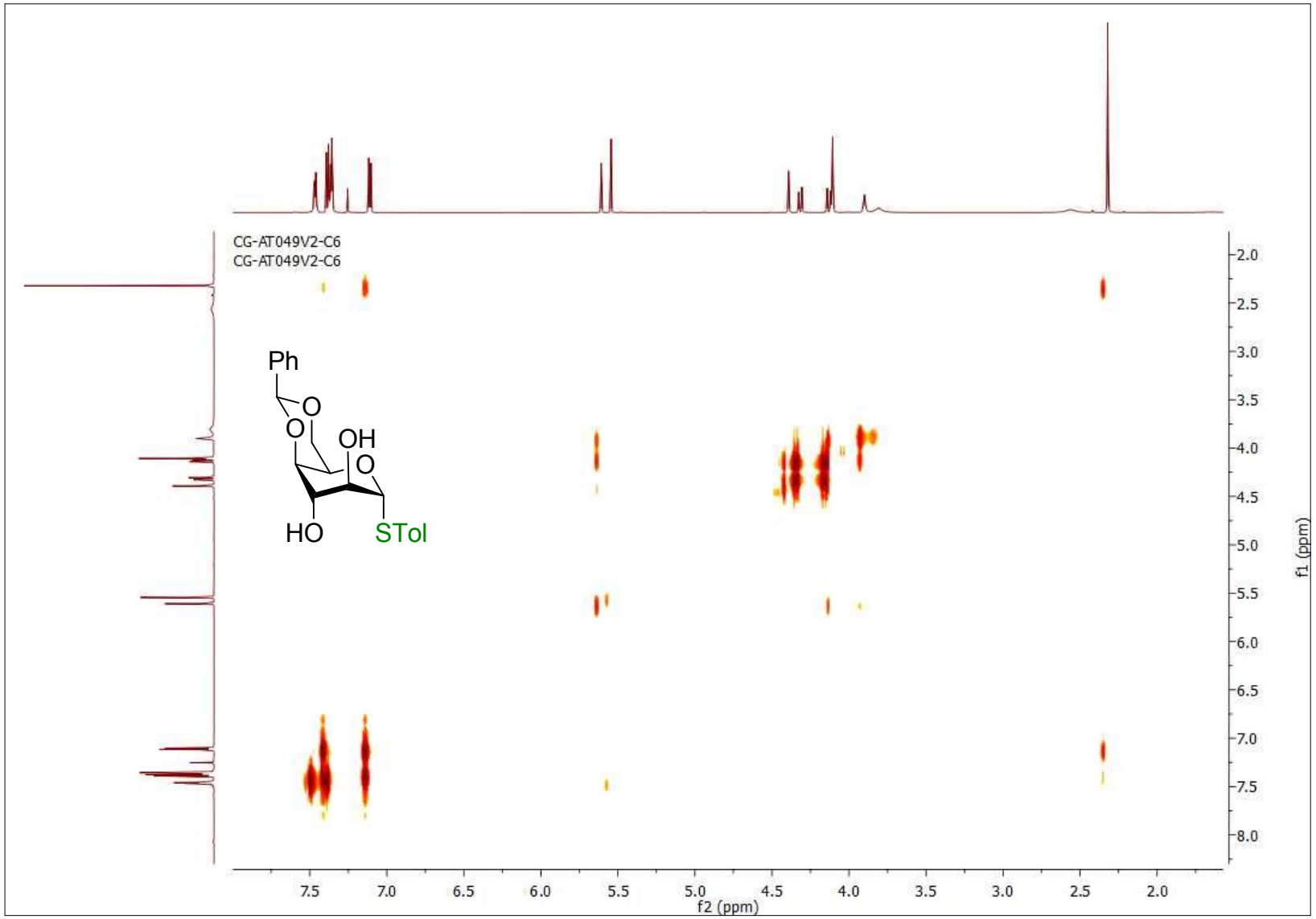


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (4b)**

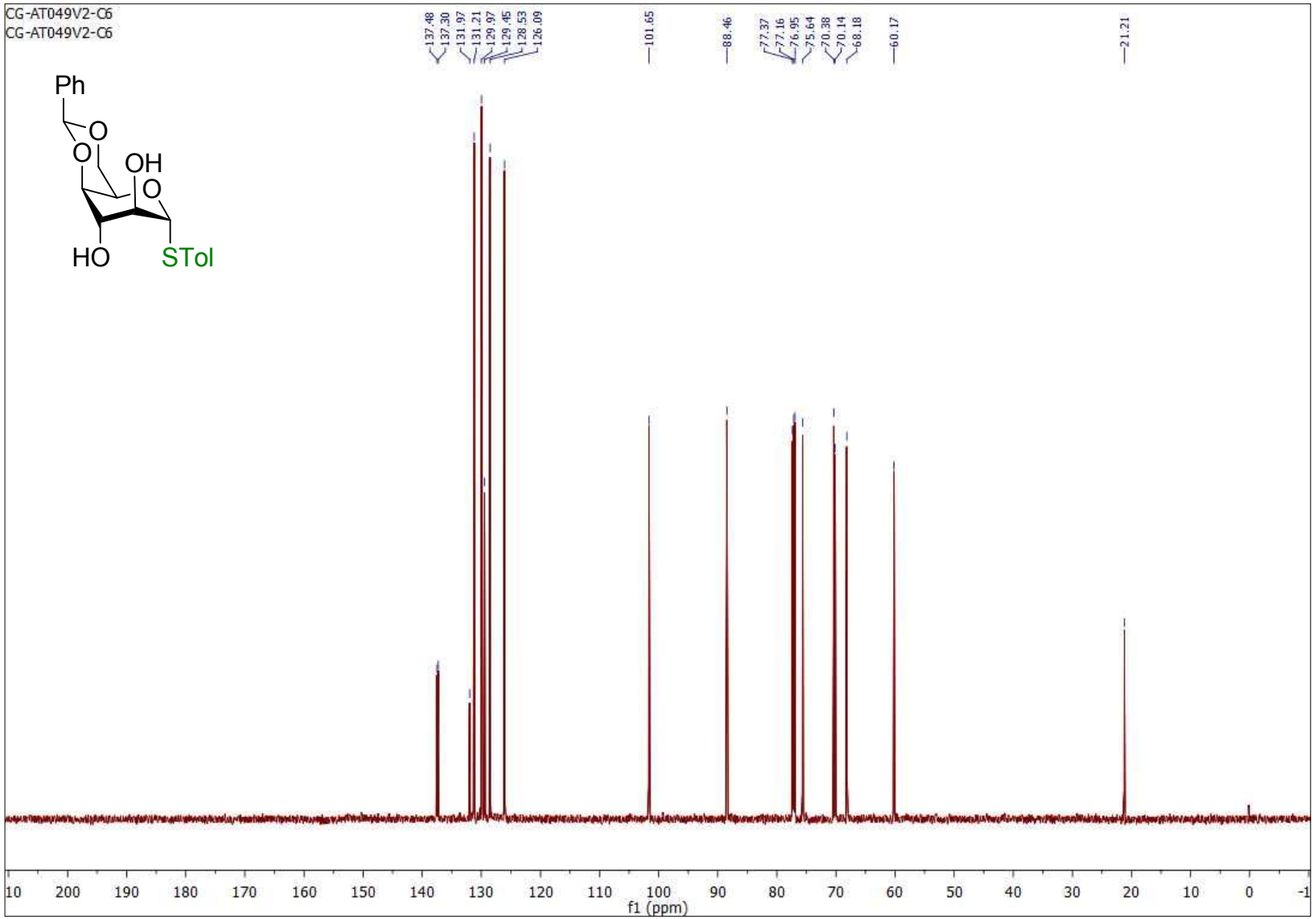


Figure S18. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (4b)**

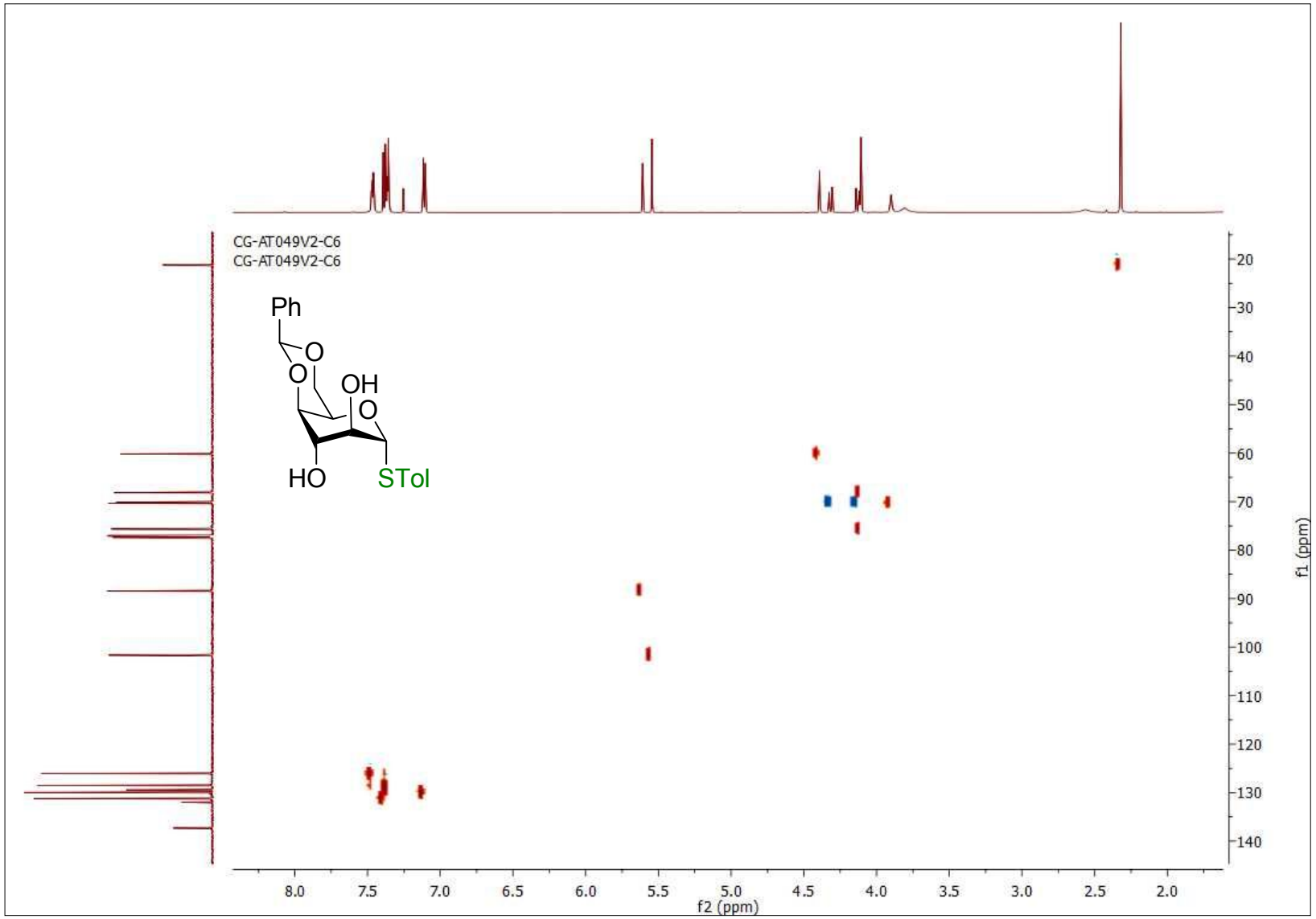


Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (5a)**

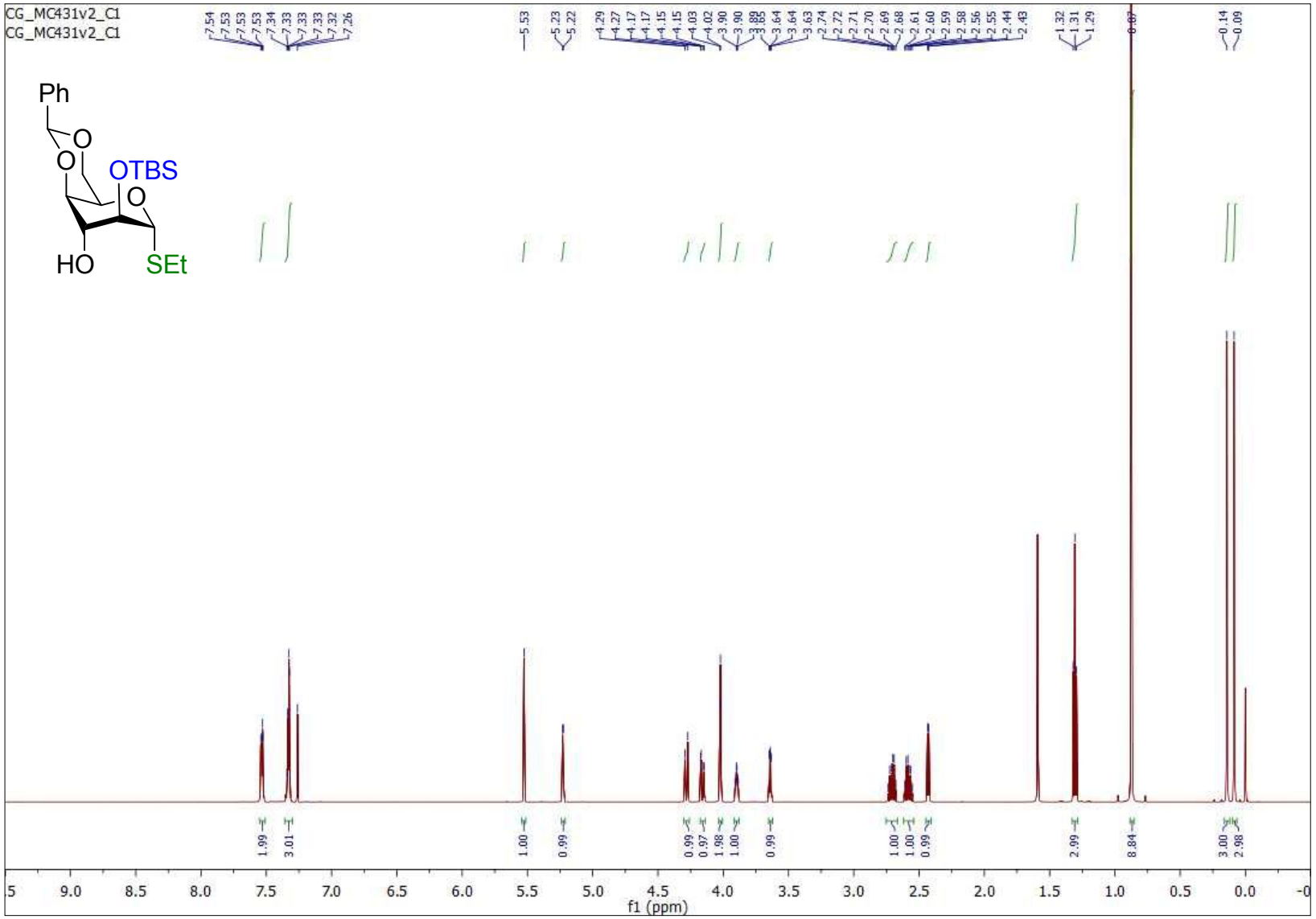


Figure S20. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (5a)**

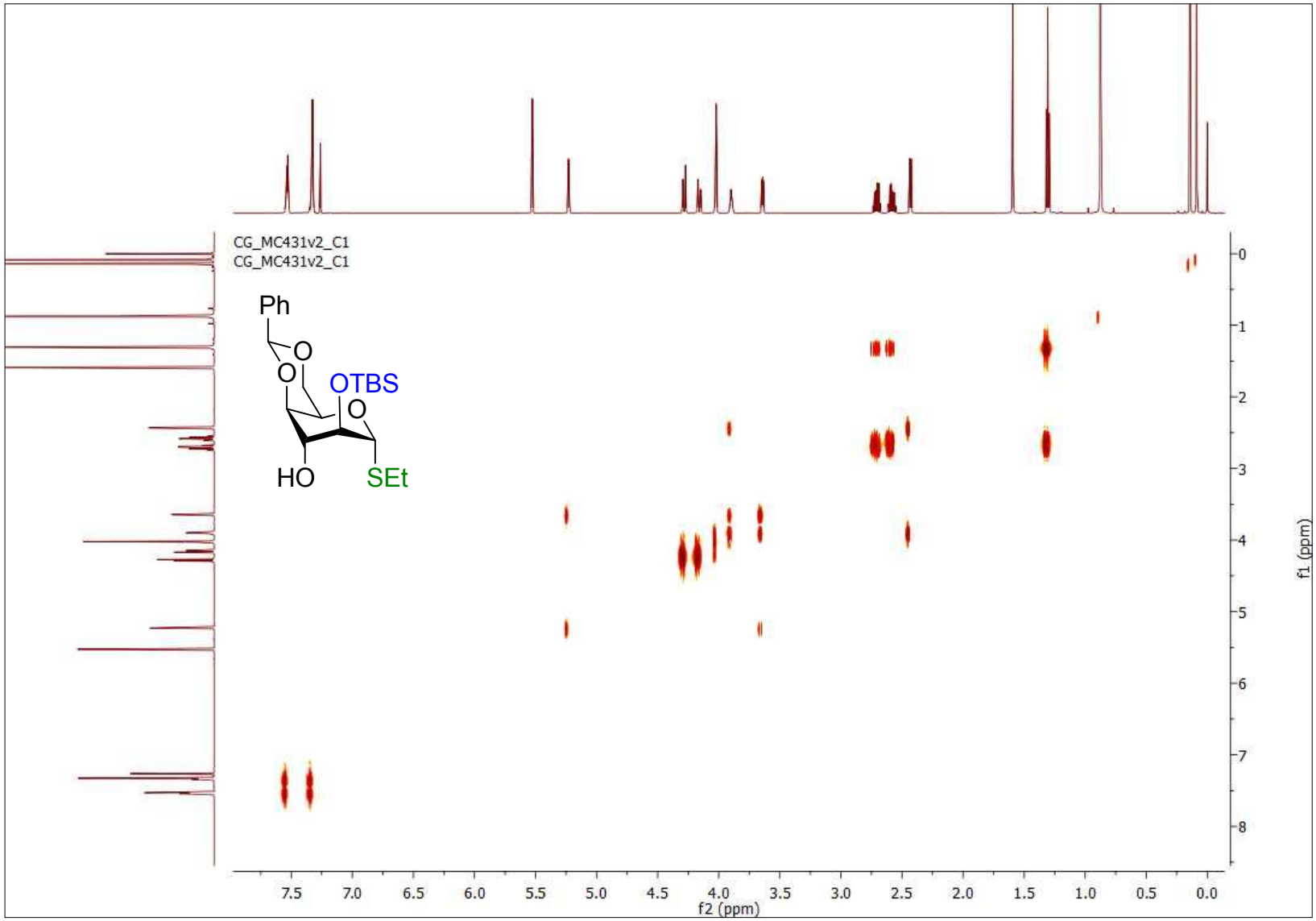


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **ethyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (5a)**

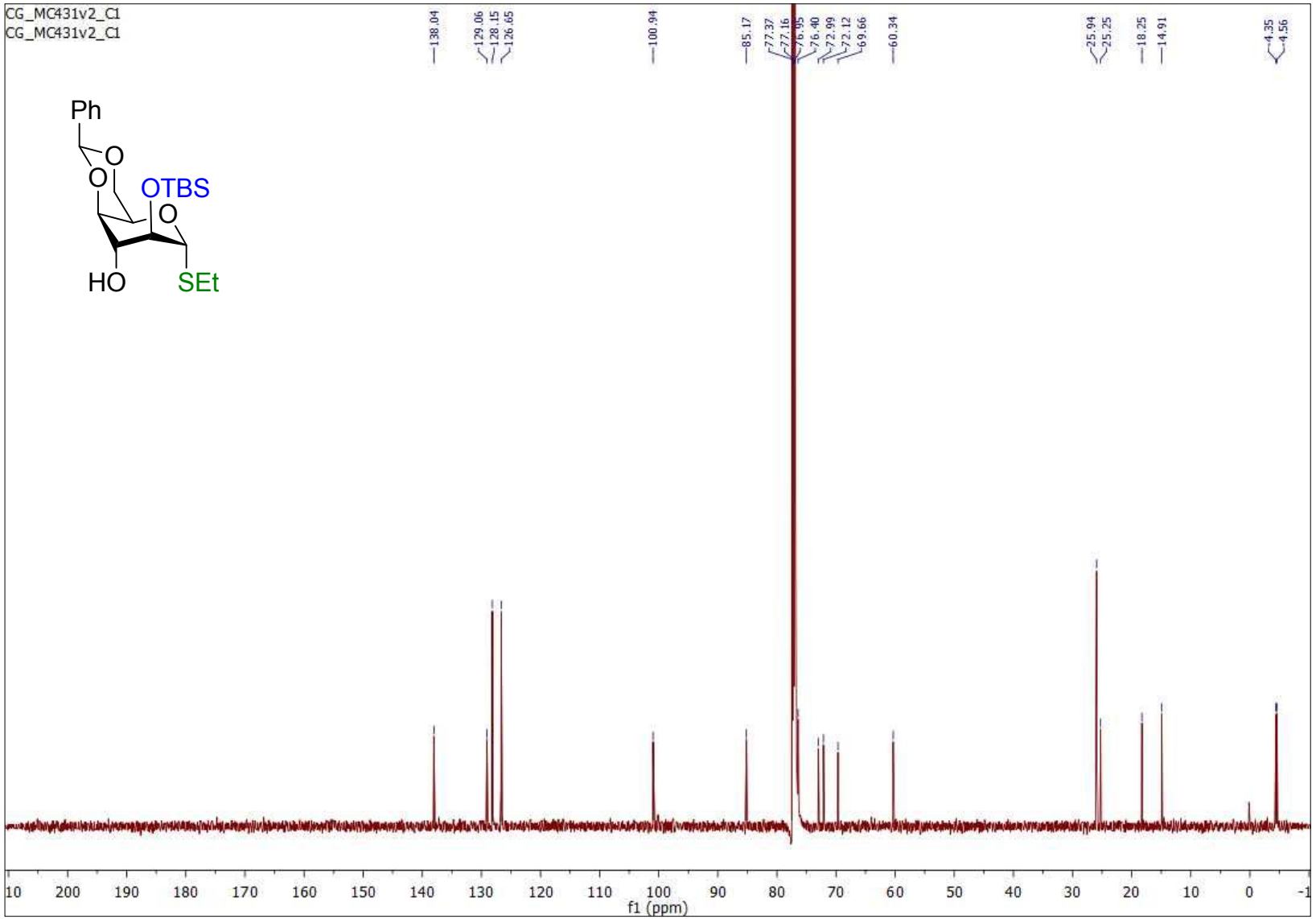


Figure S22. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (5a)**

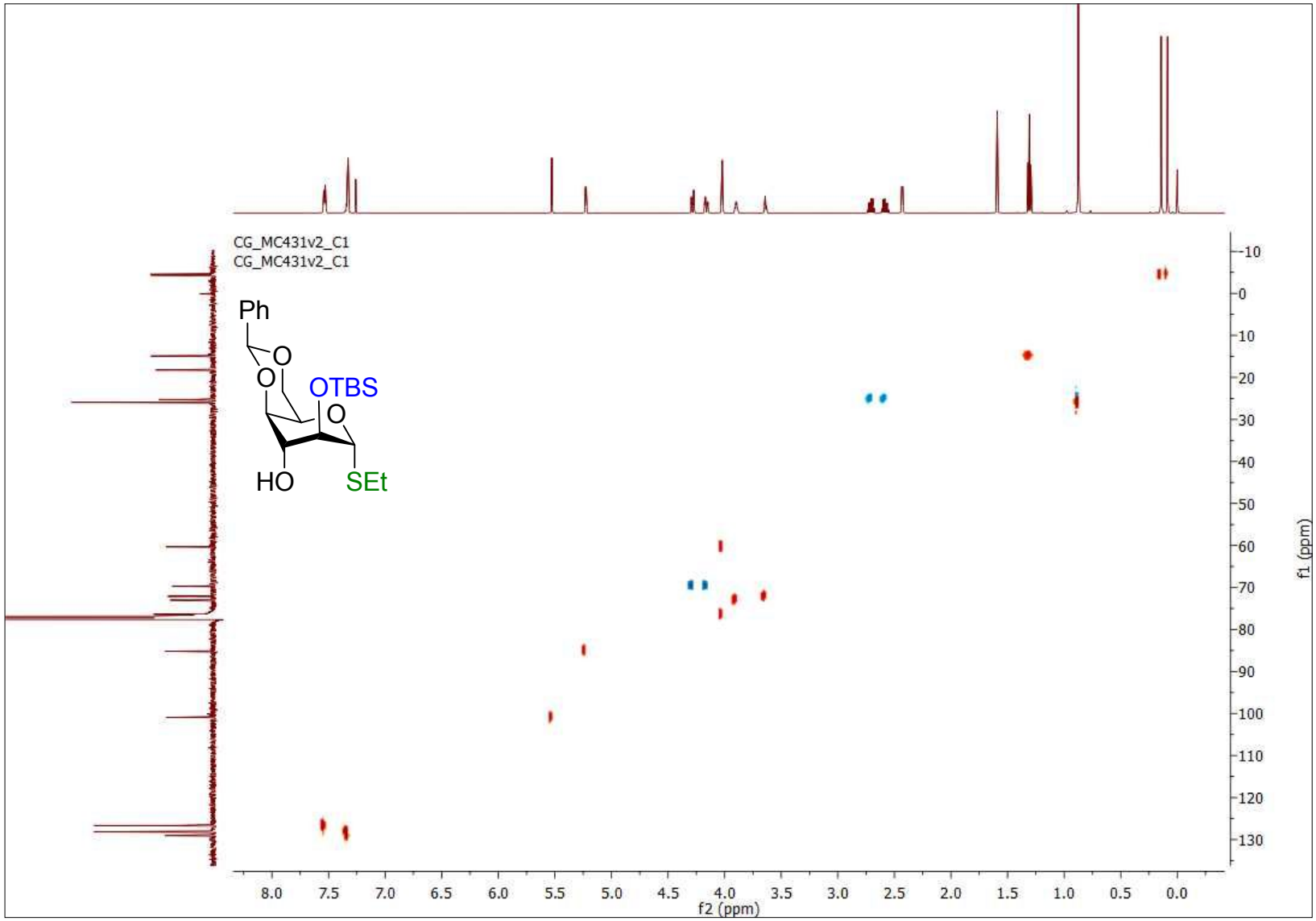


Figure S23. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (10)**

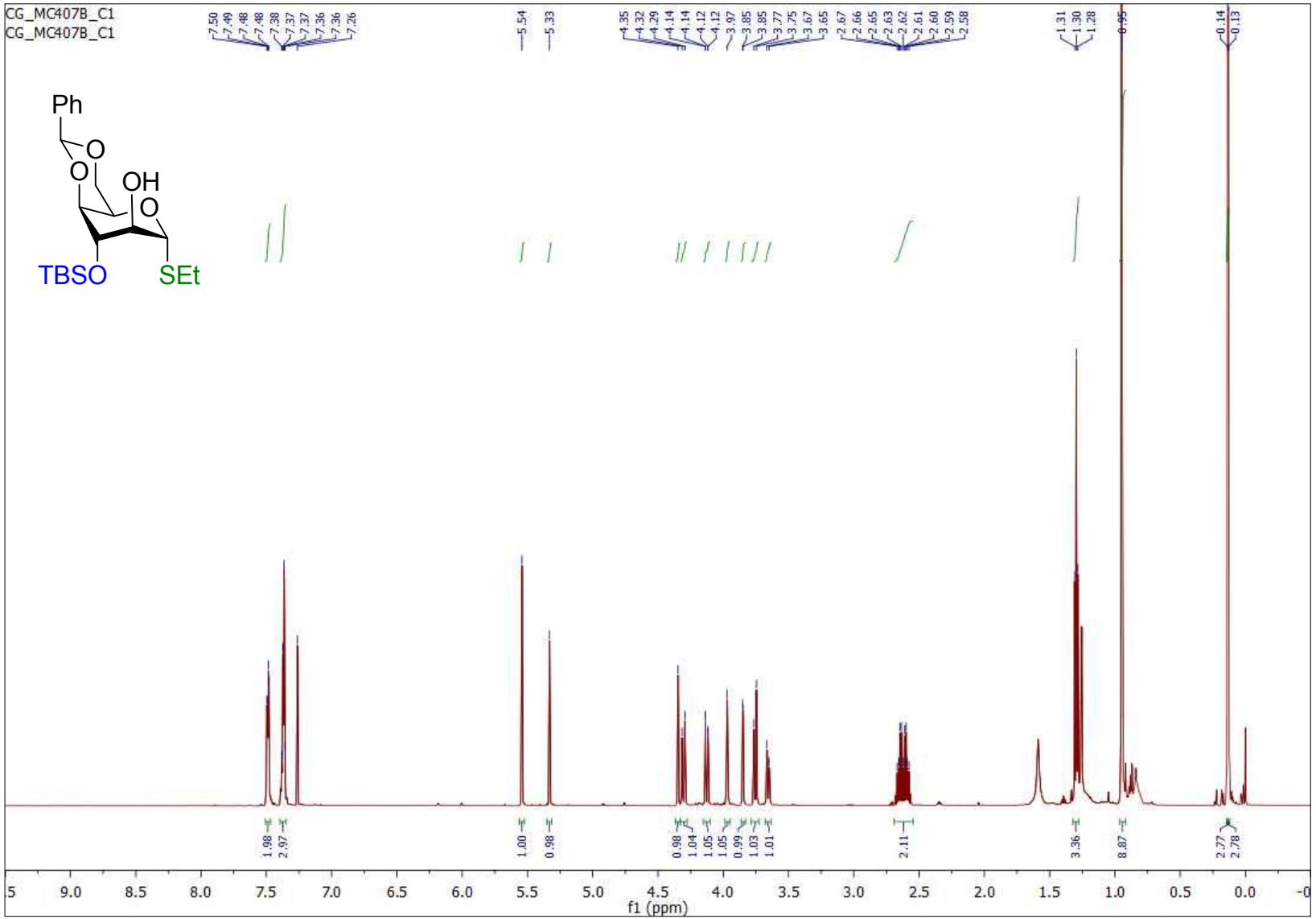


Figure S24. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (10)**

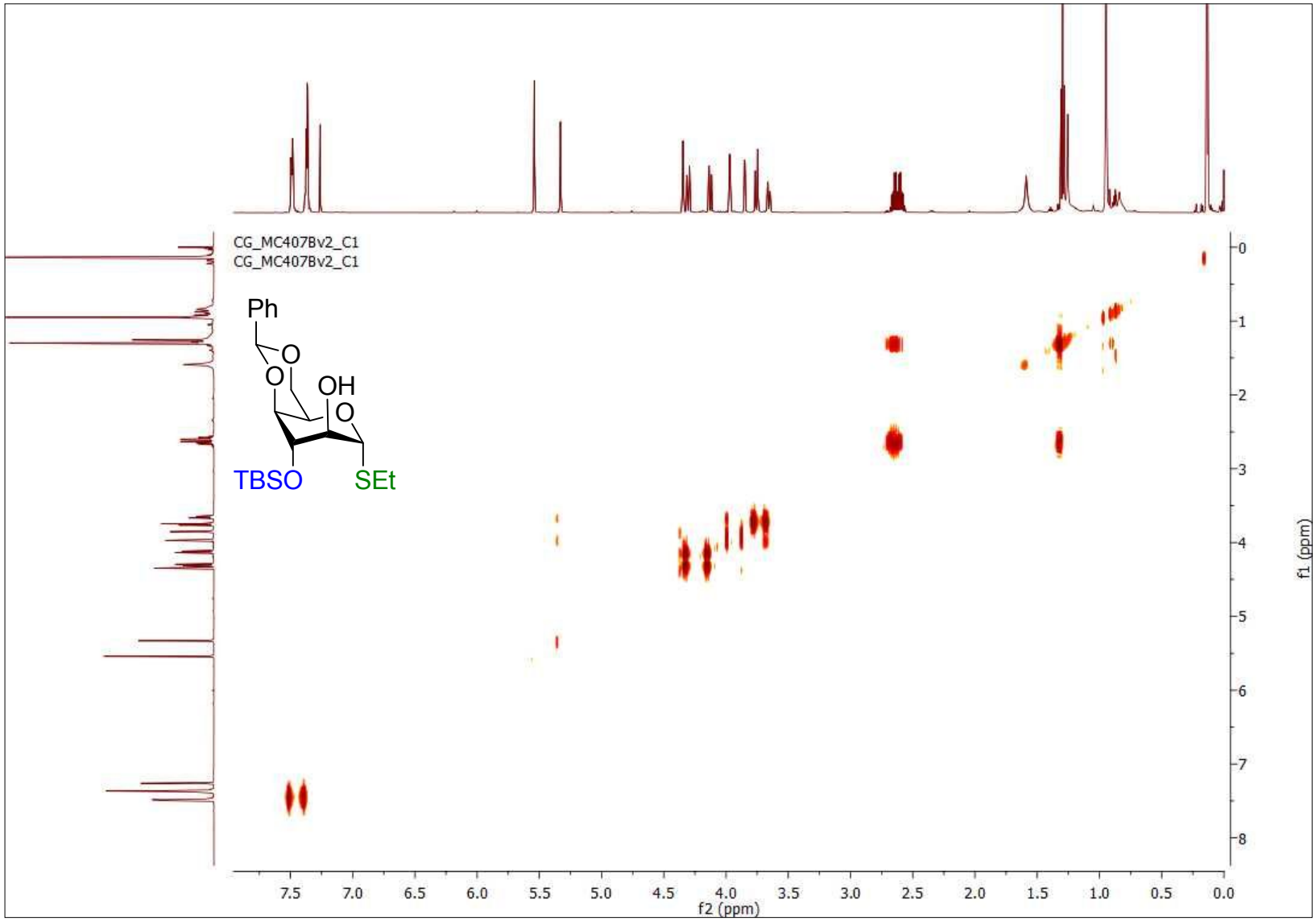


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **ethyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (10)**

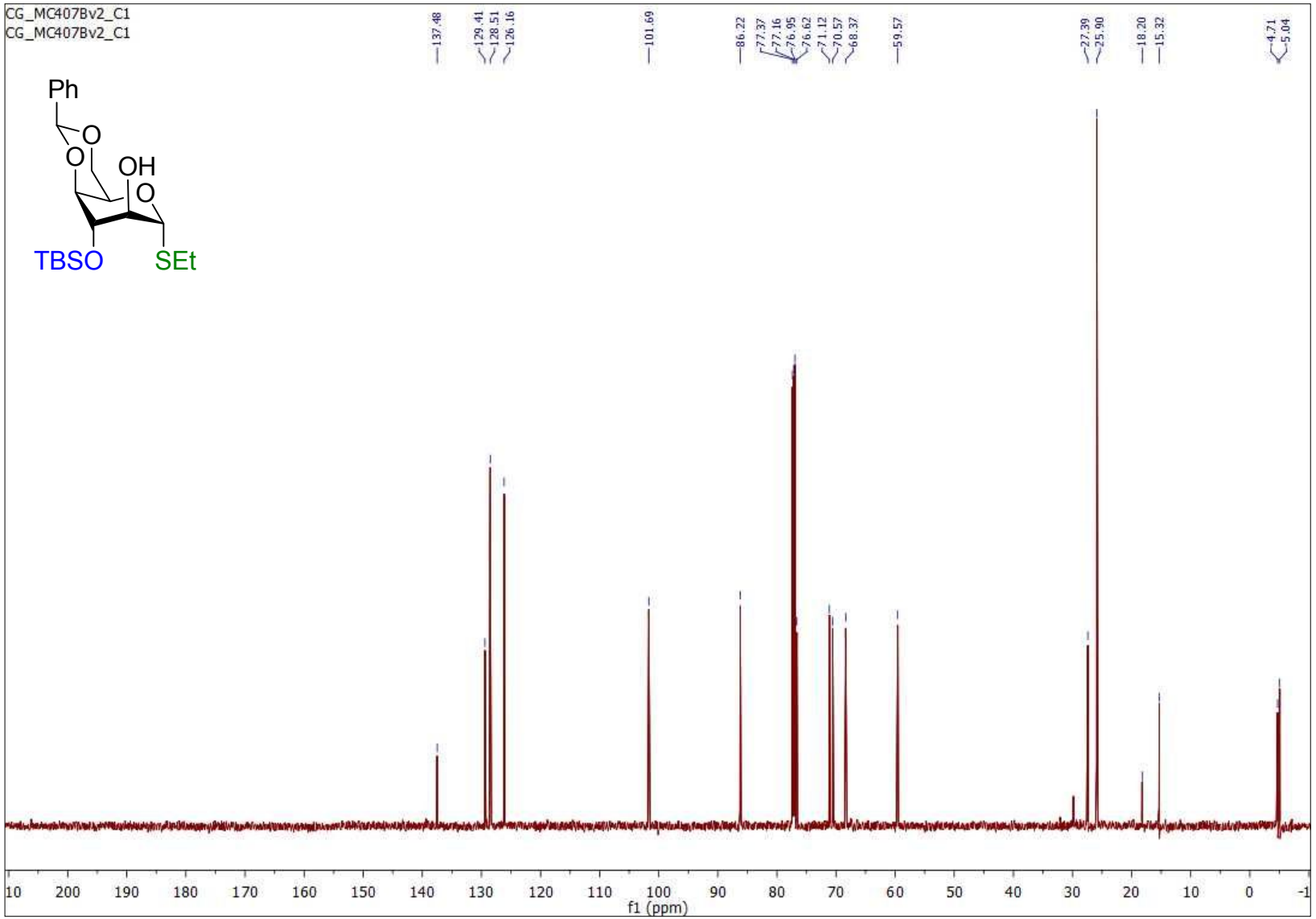


Figure S26. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (10)**

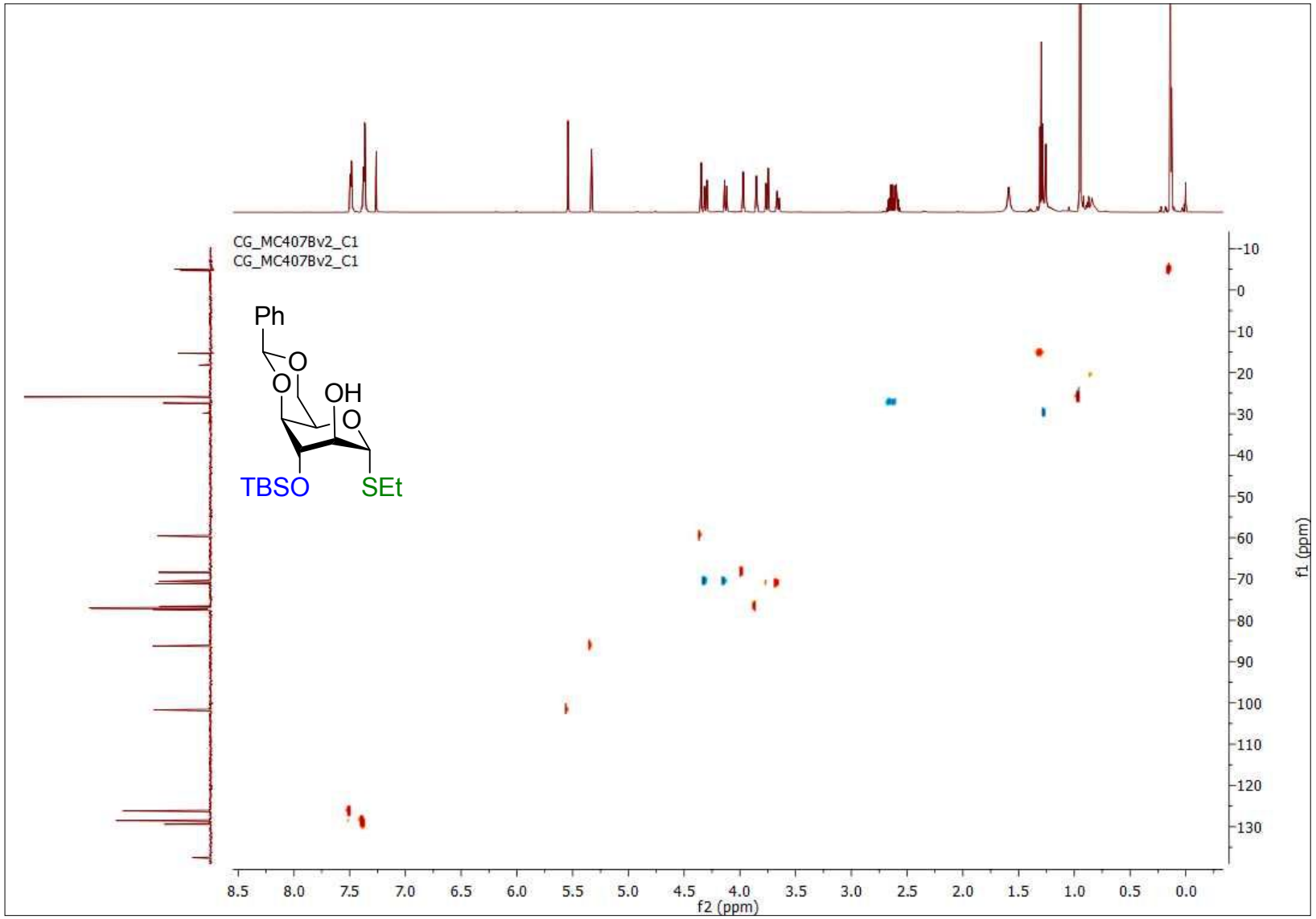


Figure S27. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (5b)**

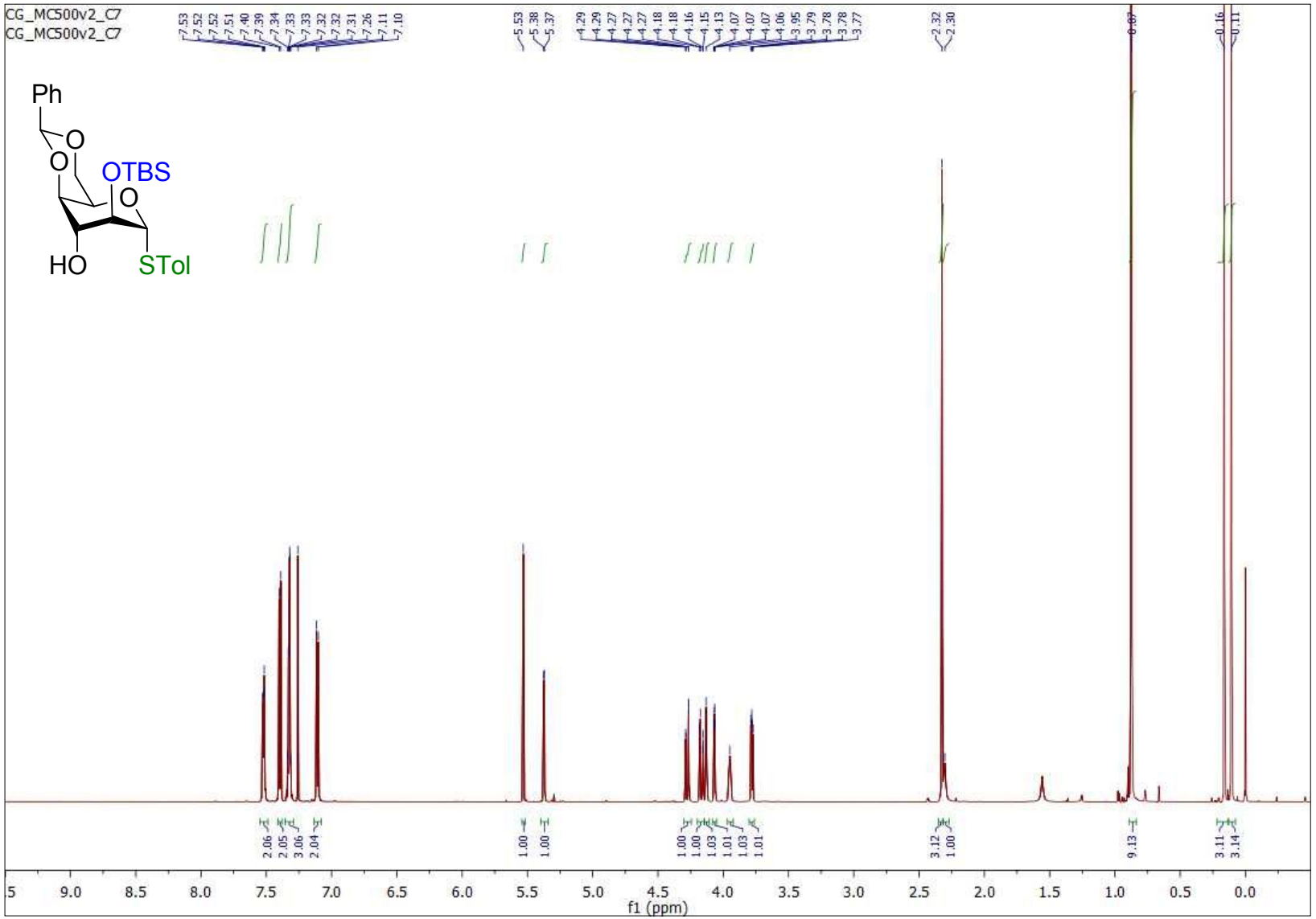


Figure S28. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (5b)**

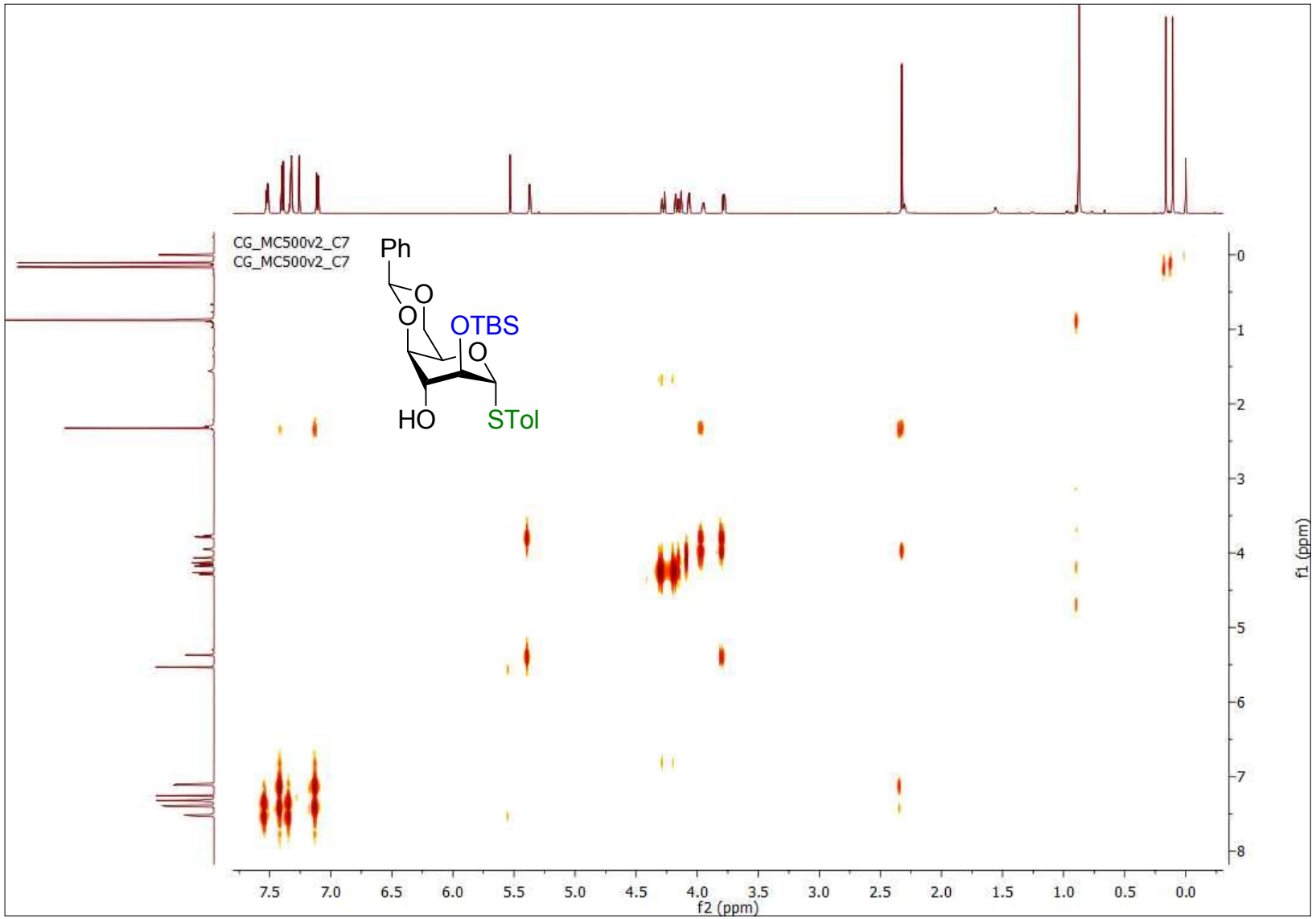


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (5b)**

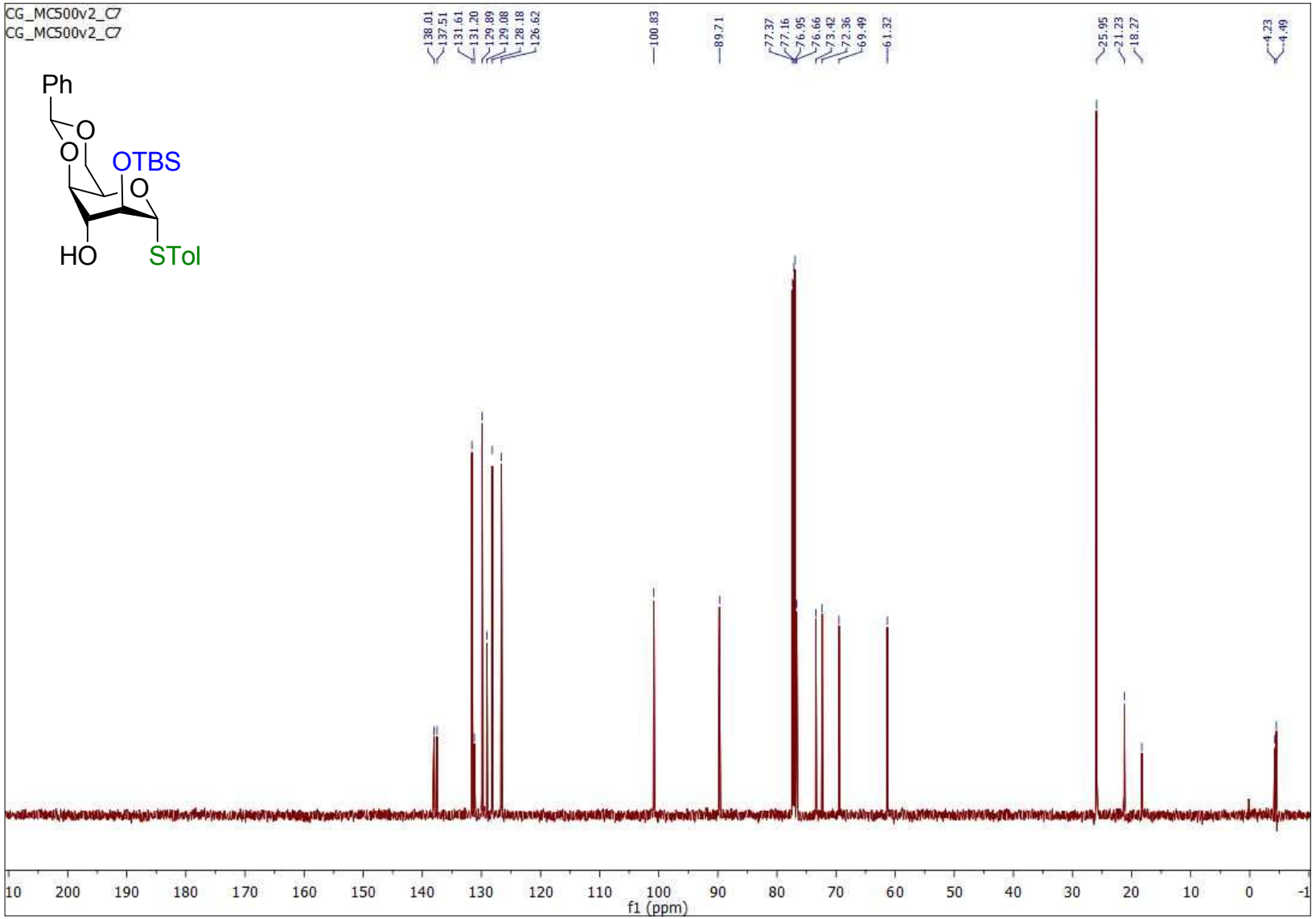


Figure S30. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (5b)**

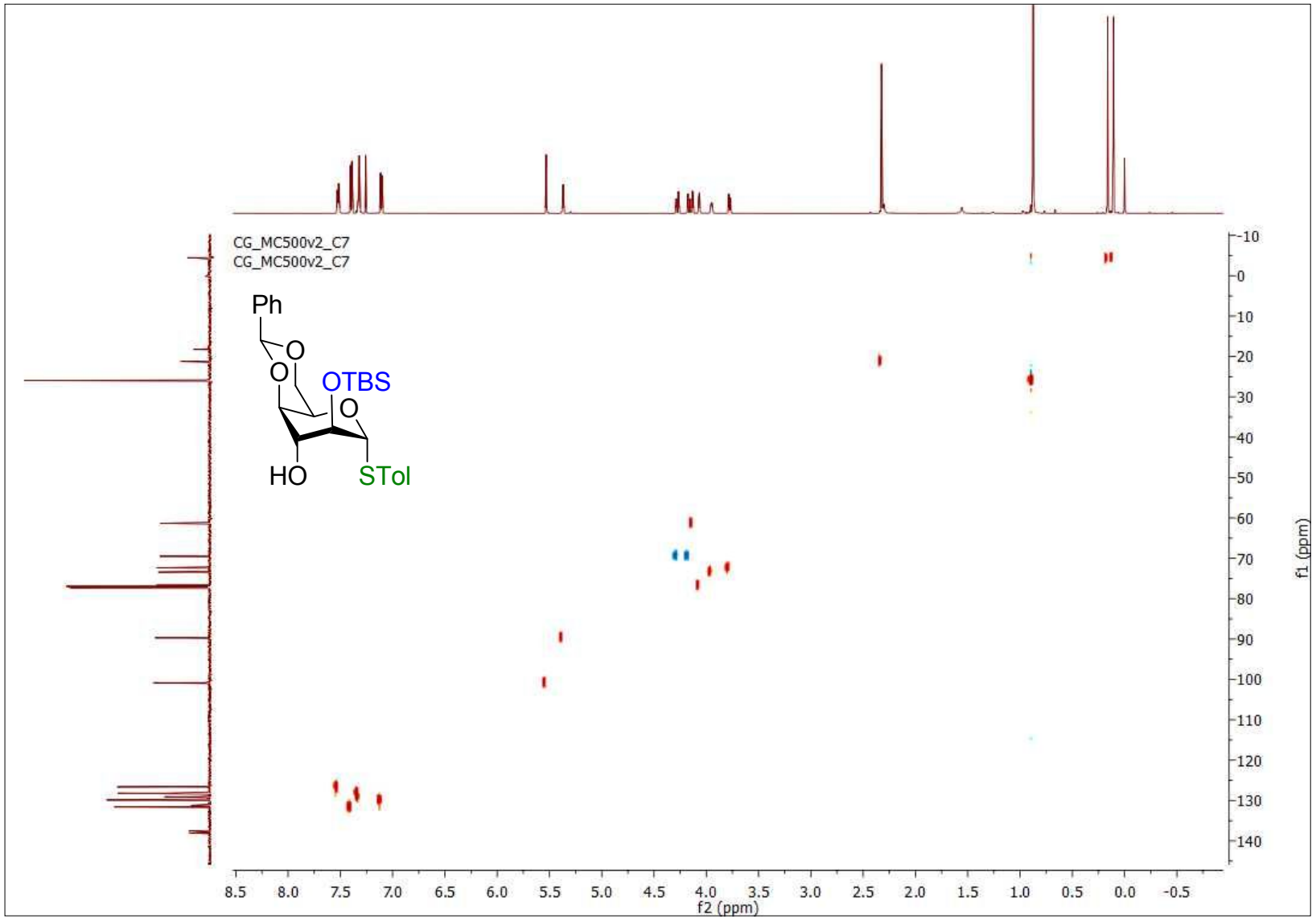


Figure S31. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (6a)**

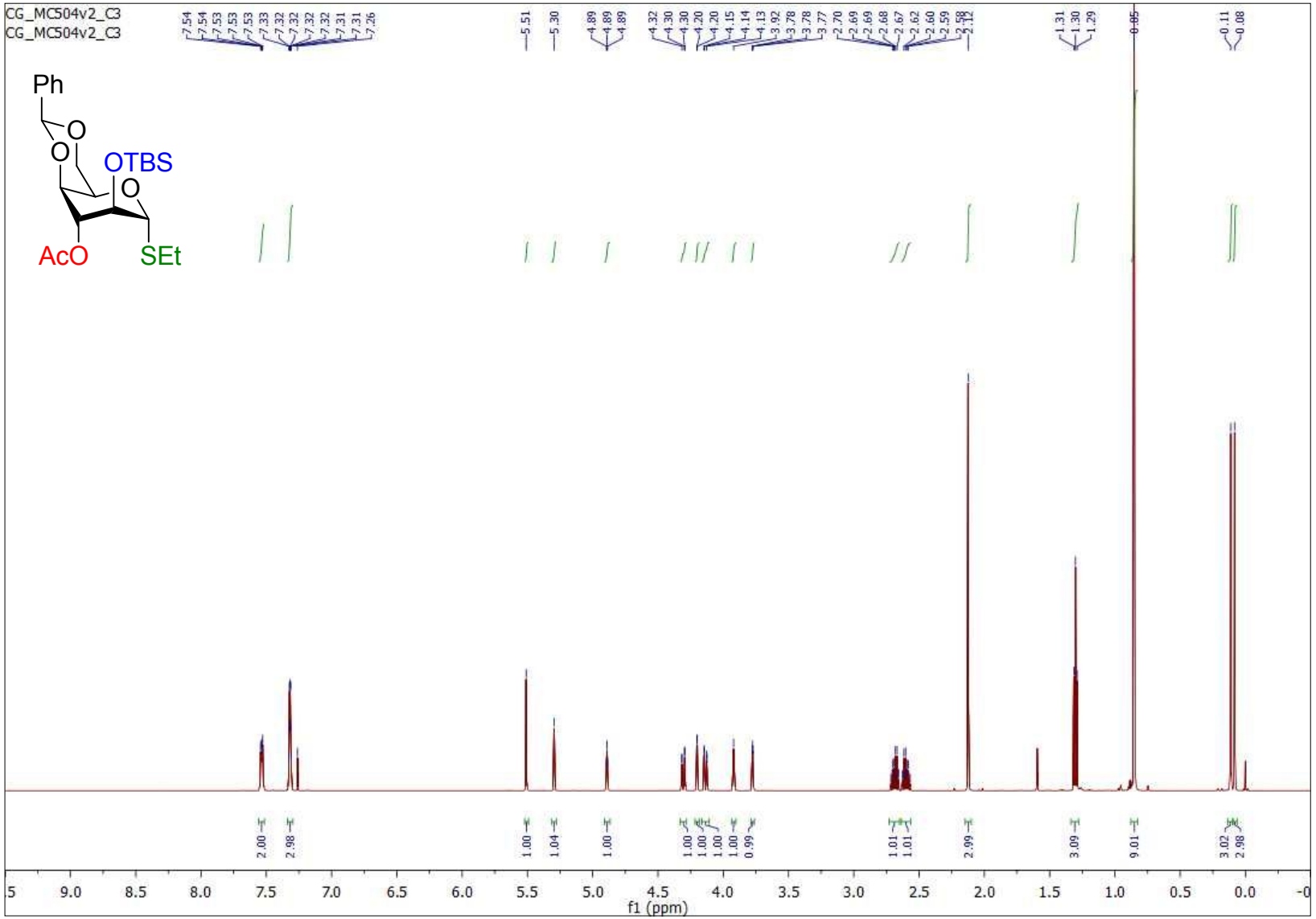


Figure S32. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (6a)**

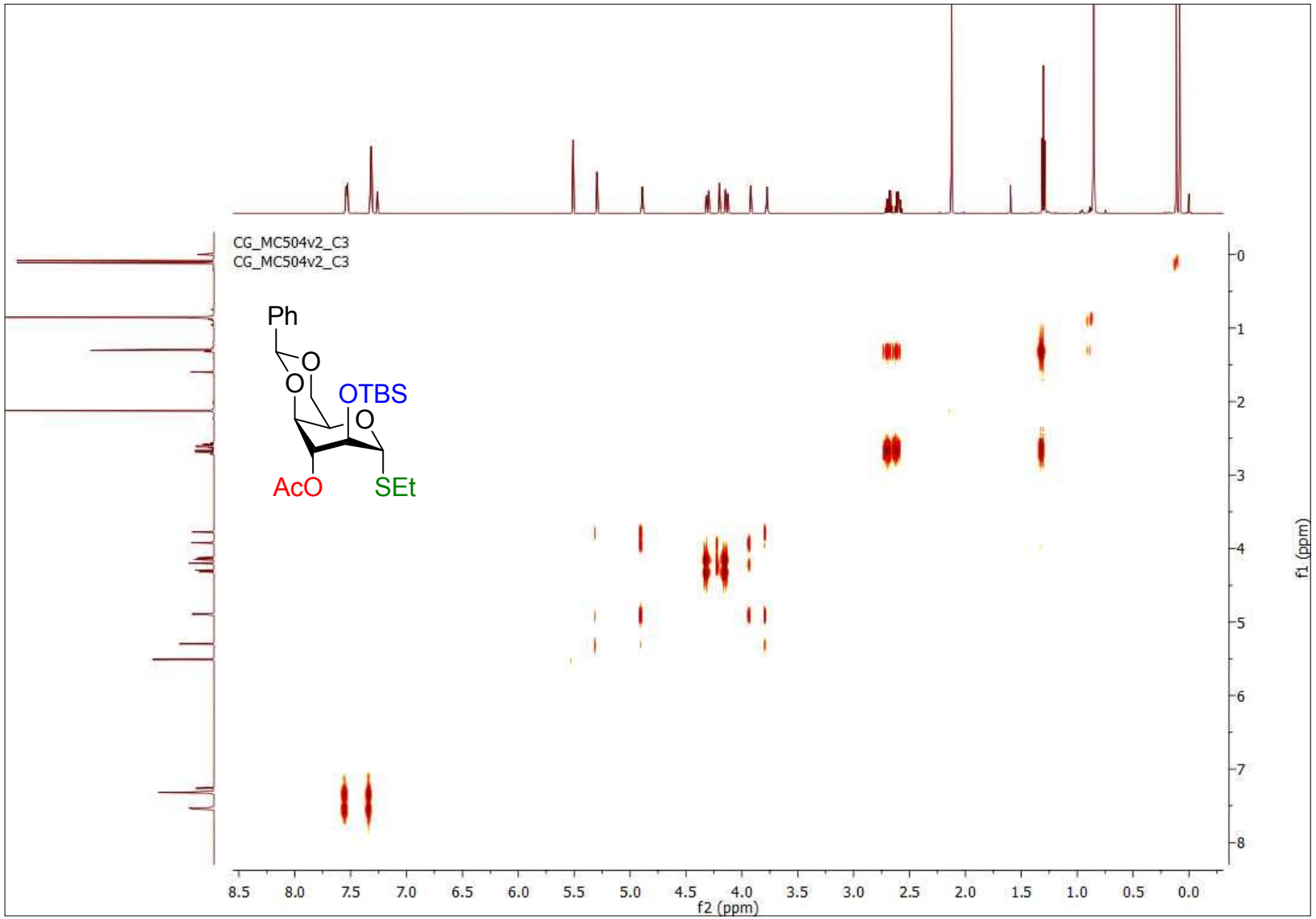


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (6a)**

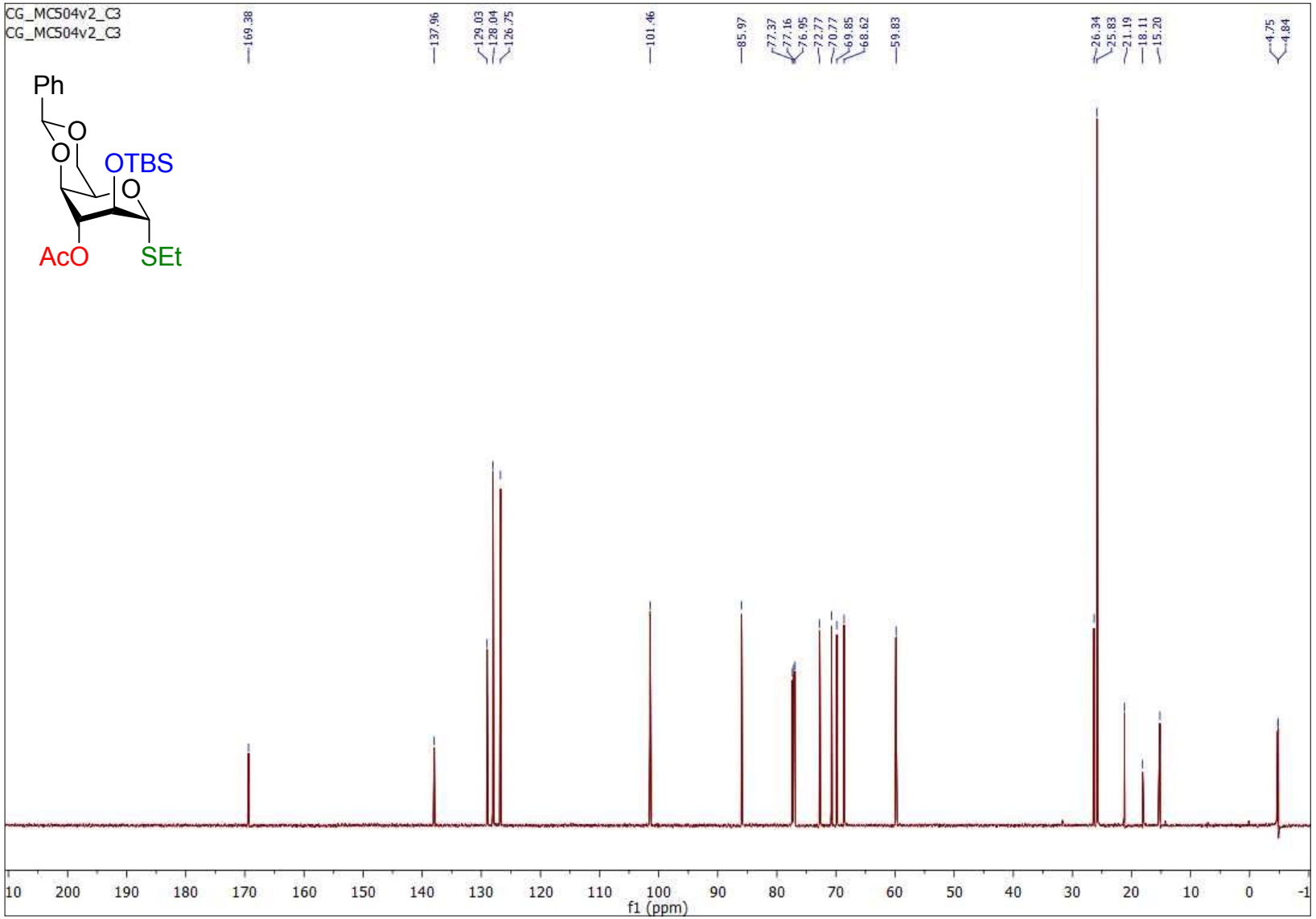


Figure S34. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (6a)**

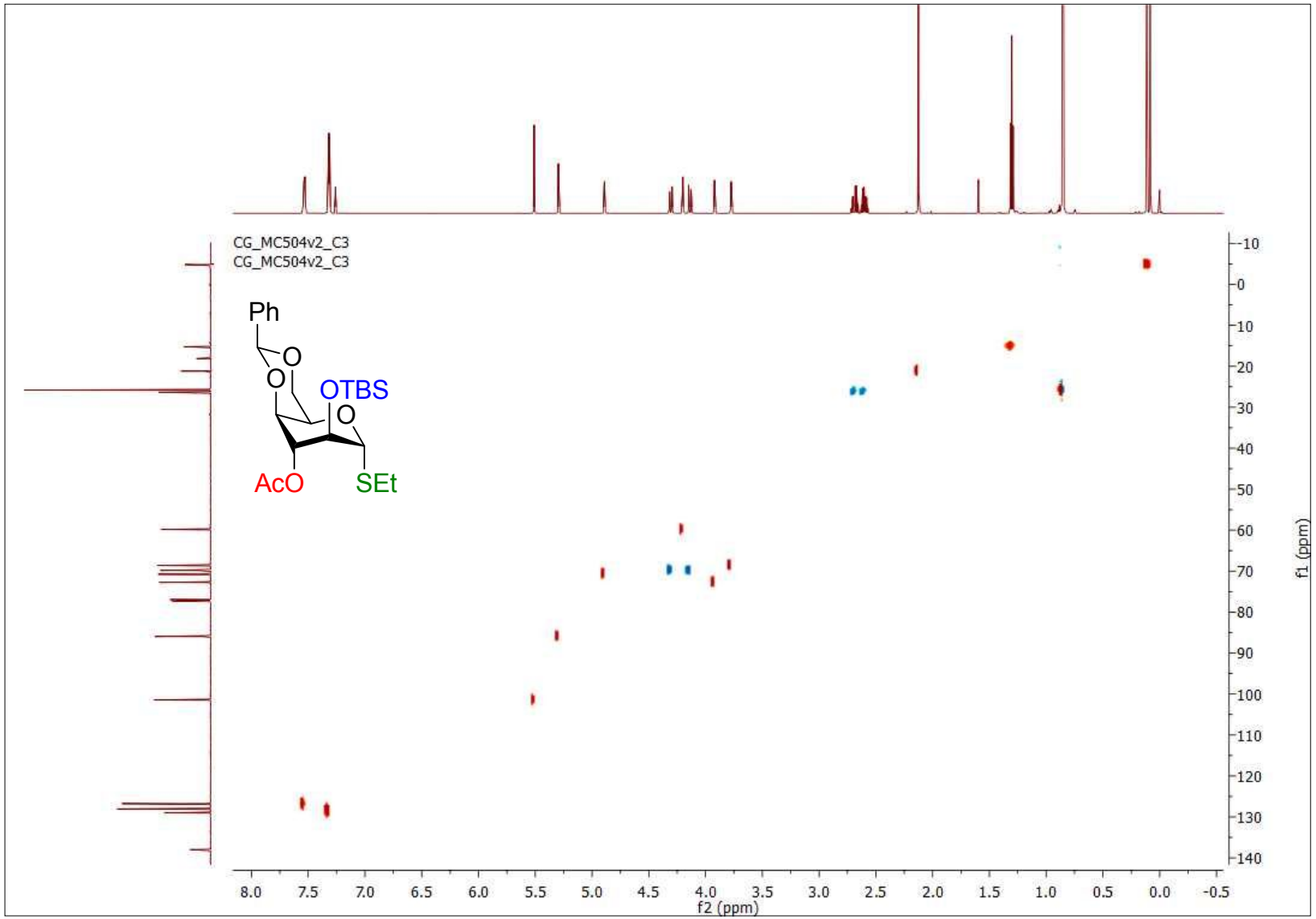


Figure S35. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (6b)**

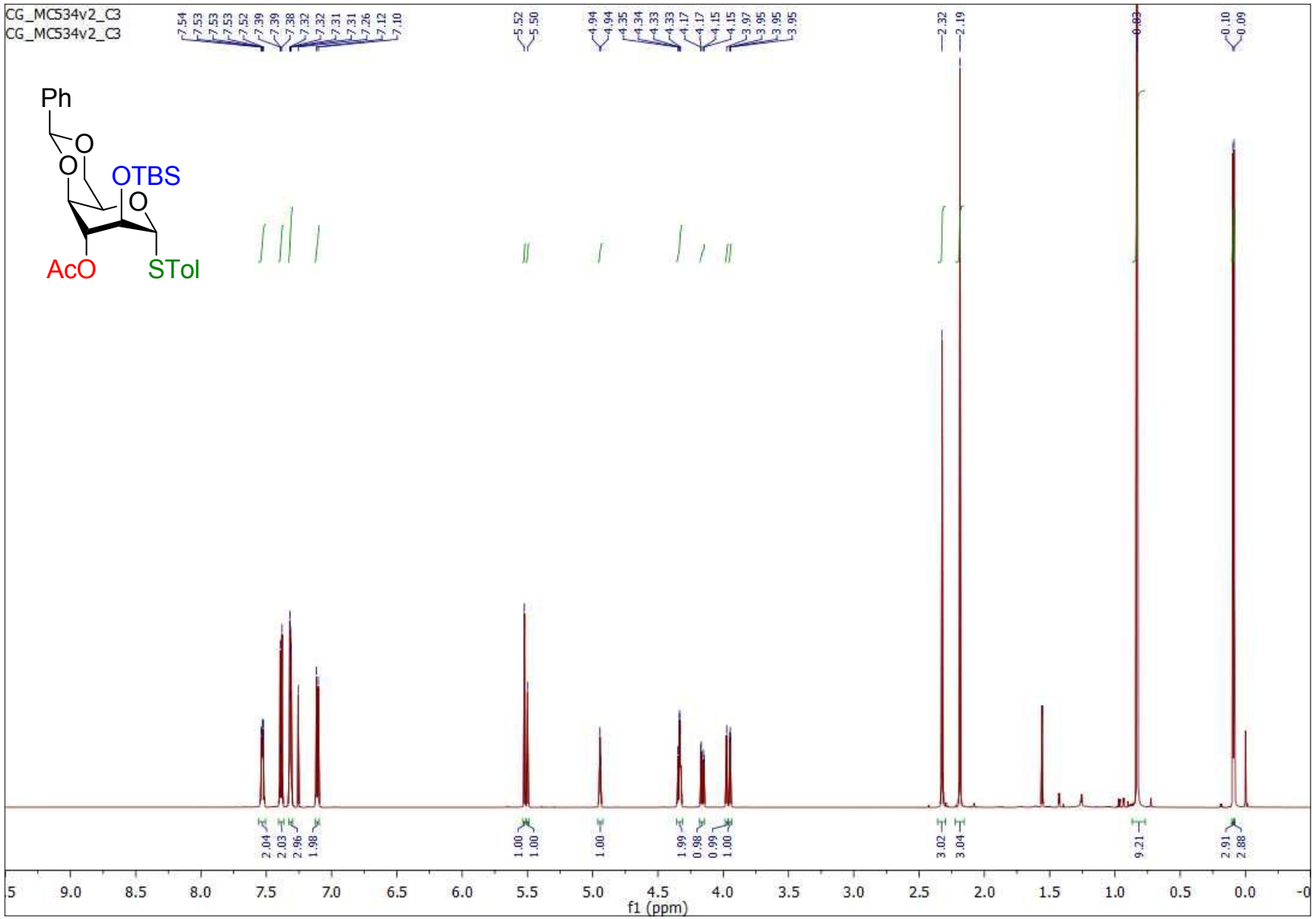


Figure S36. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (6b)**

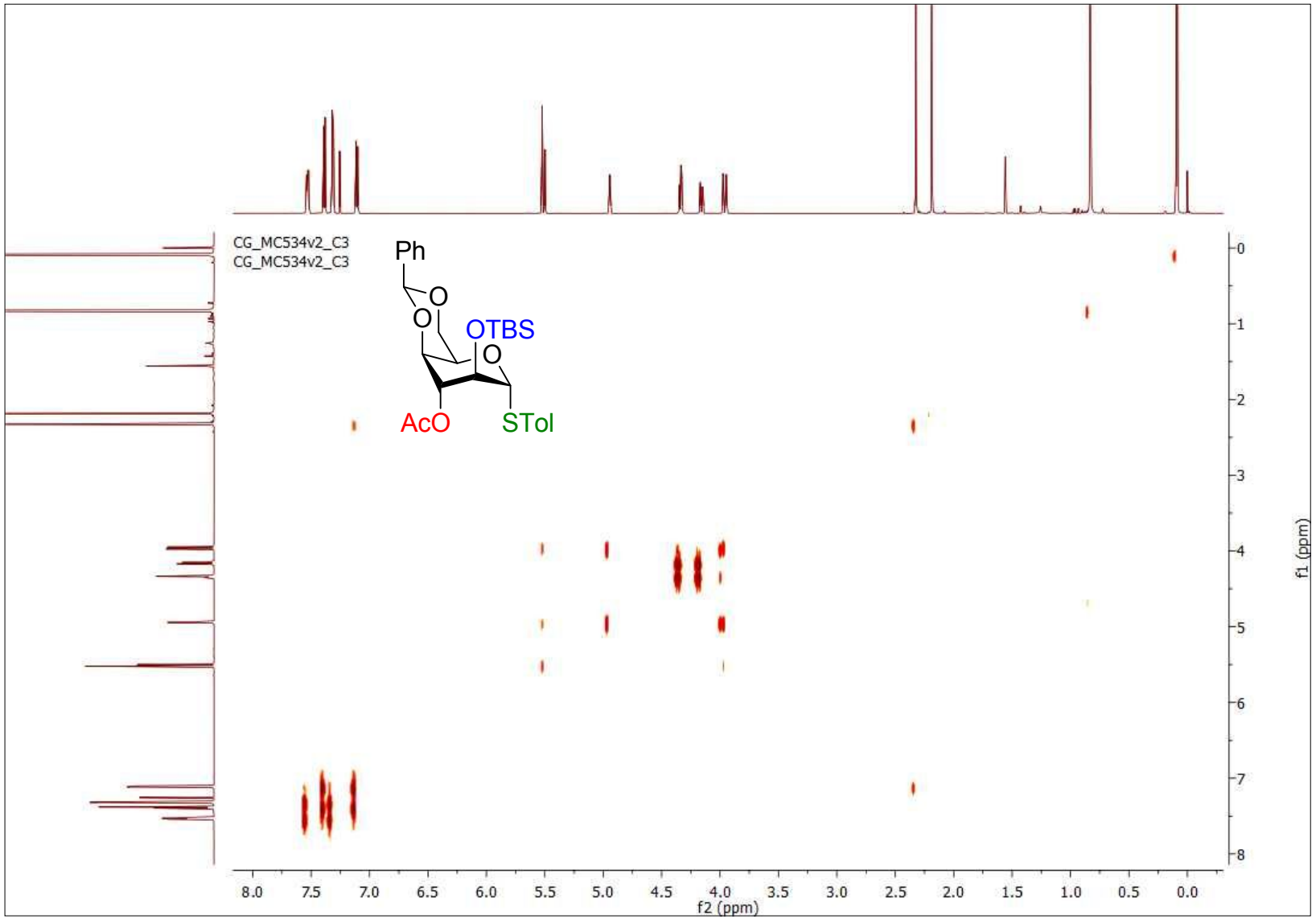


Figure S37. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***para*-methylphenyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (6b)**

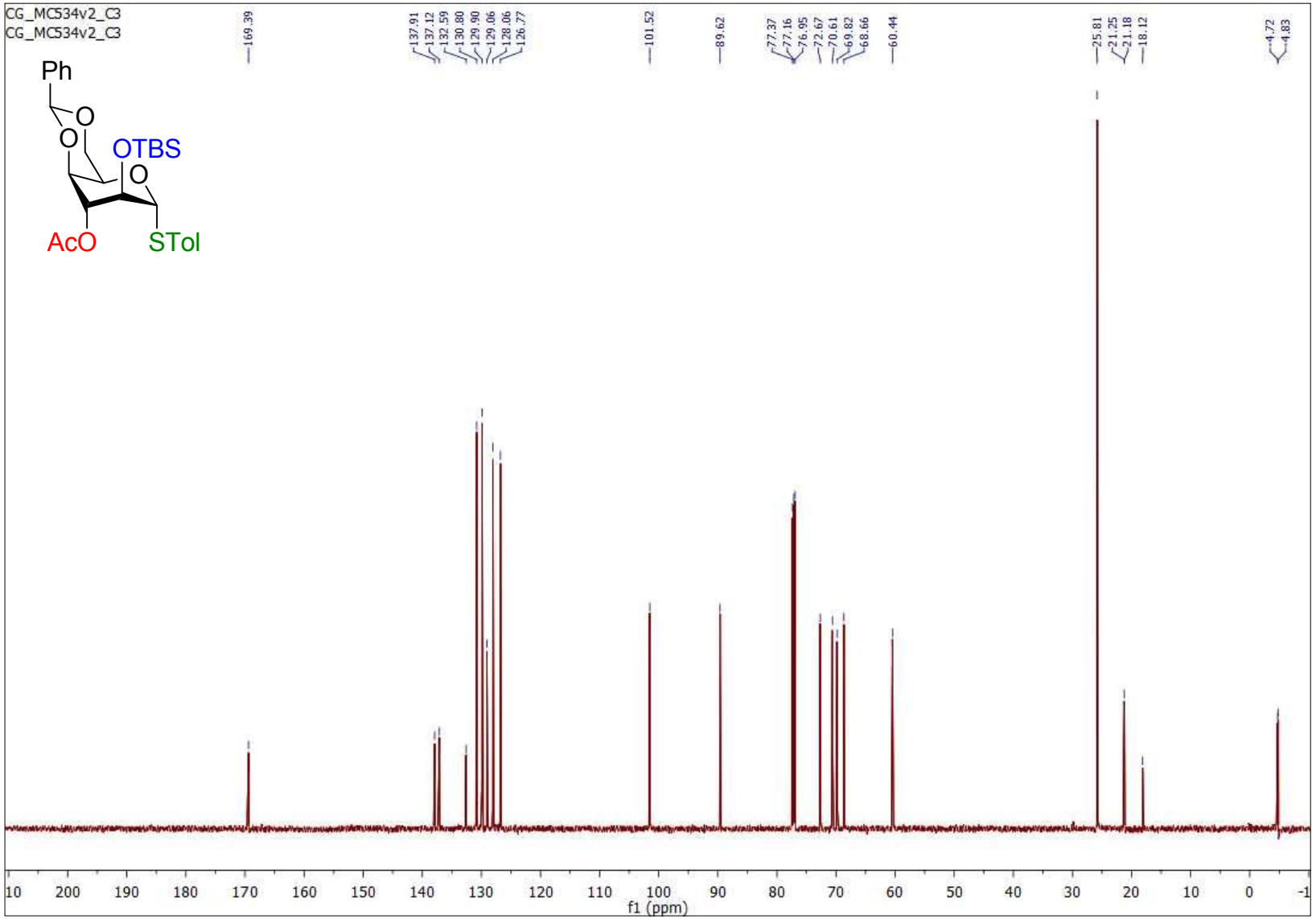


Figure S38. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (6b)**

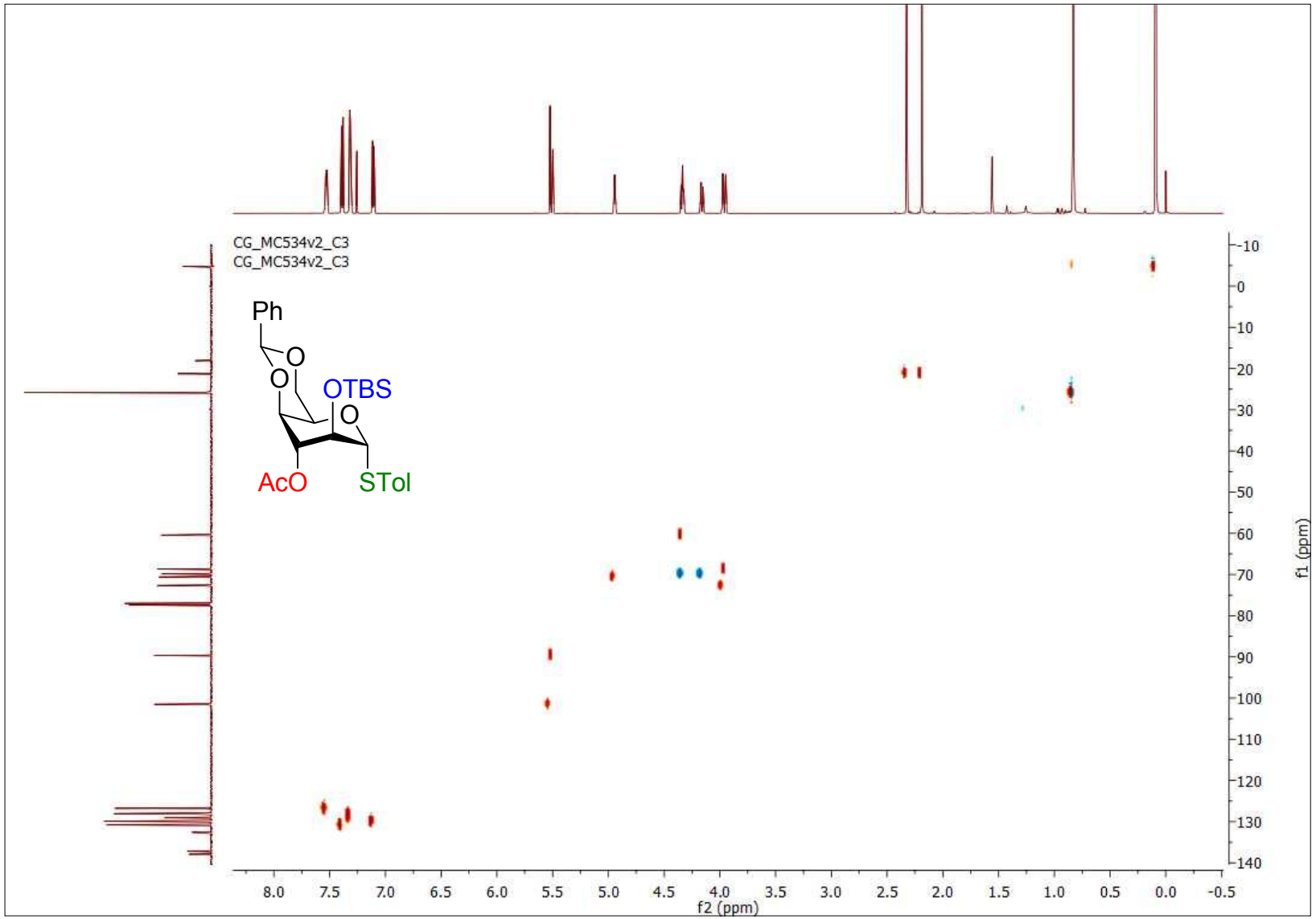


Figure S39. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-1-thio-*α*-D-idopyranoside (7)**

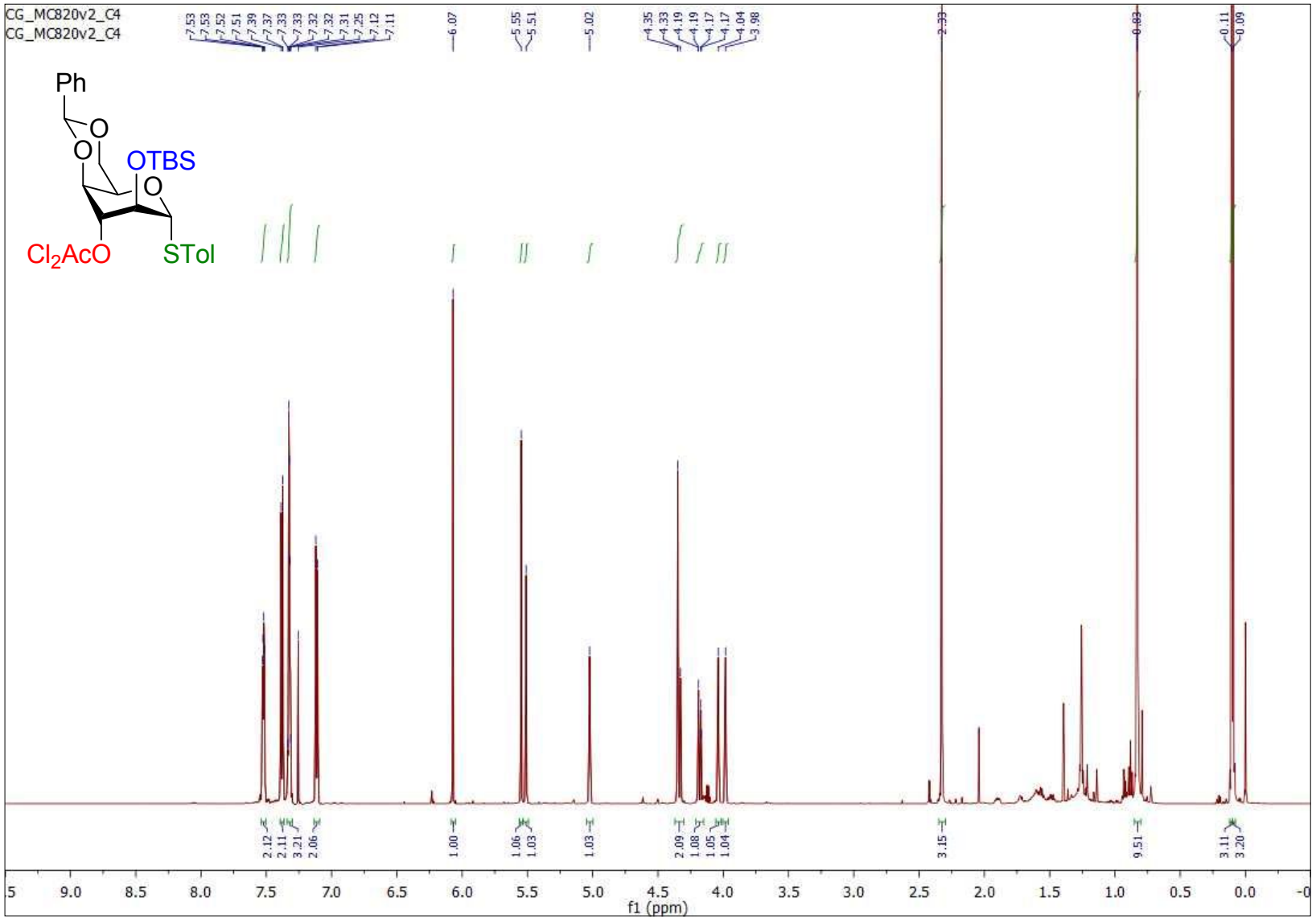


Figure S40. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-1-thio-*α*-D-idopyranoside (7)**

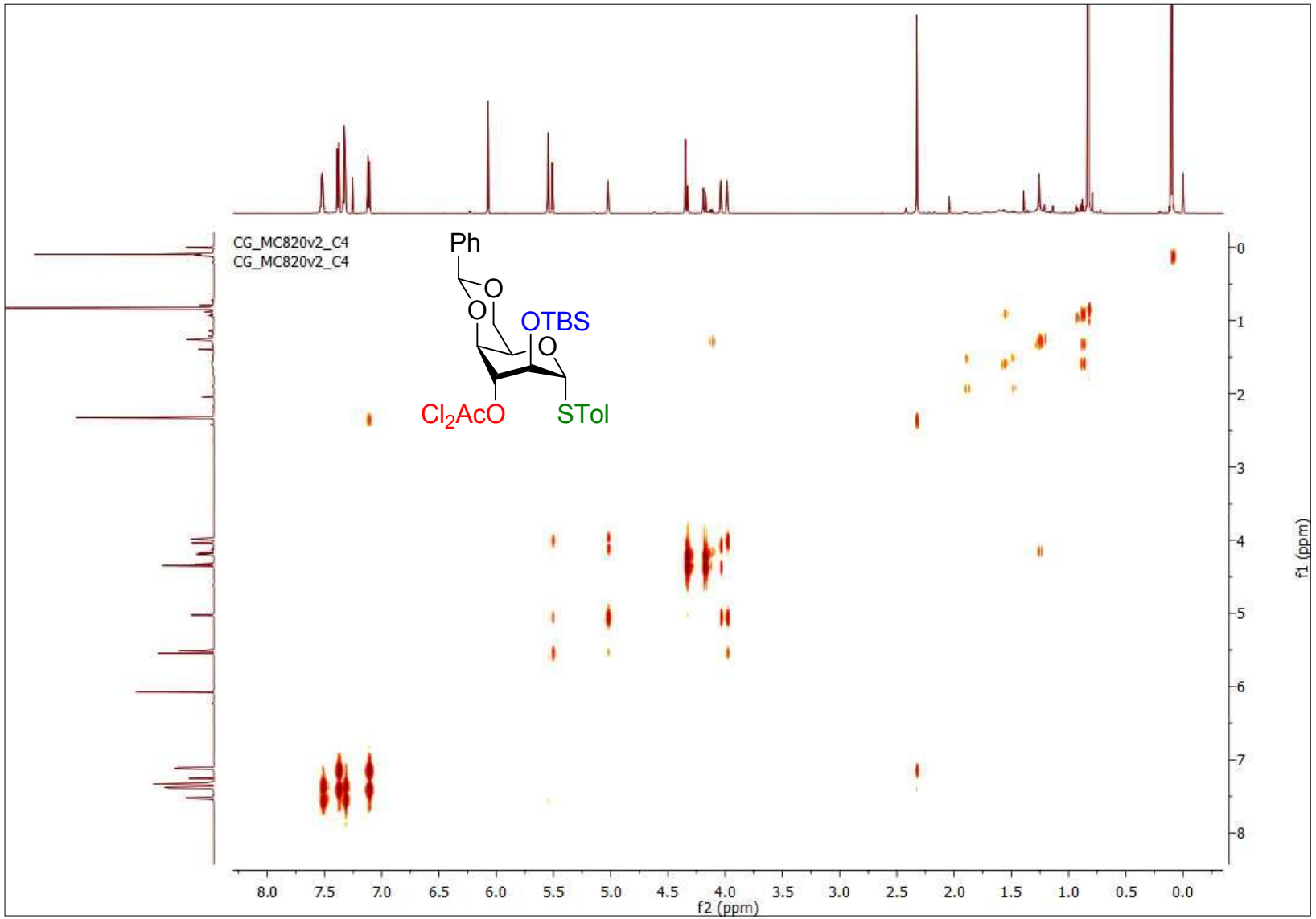


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-1-thio-*α*-D-idopyranoside (7)**

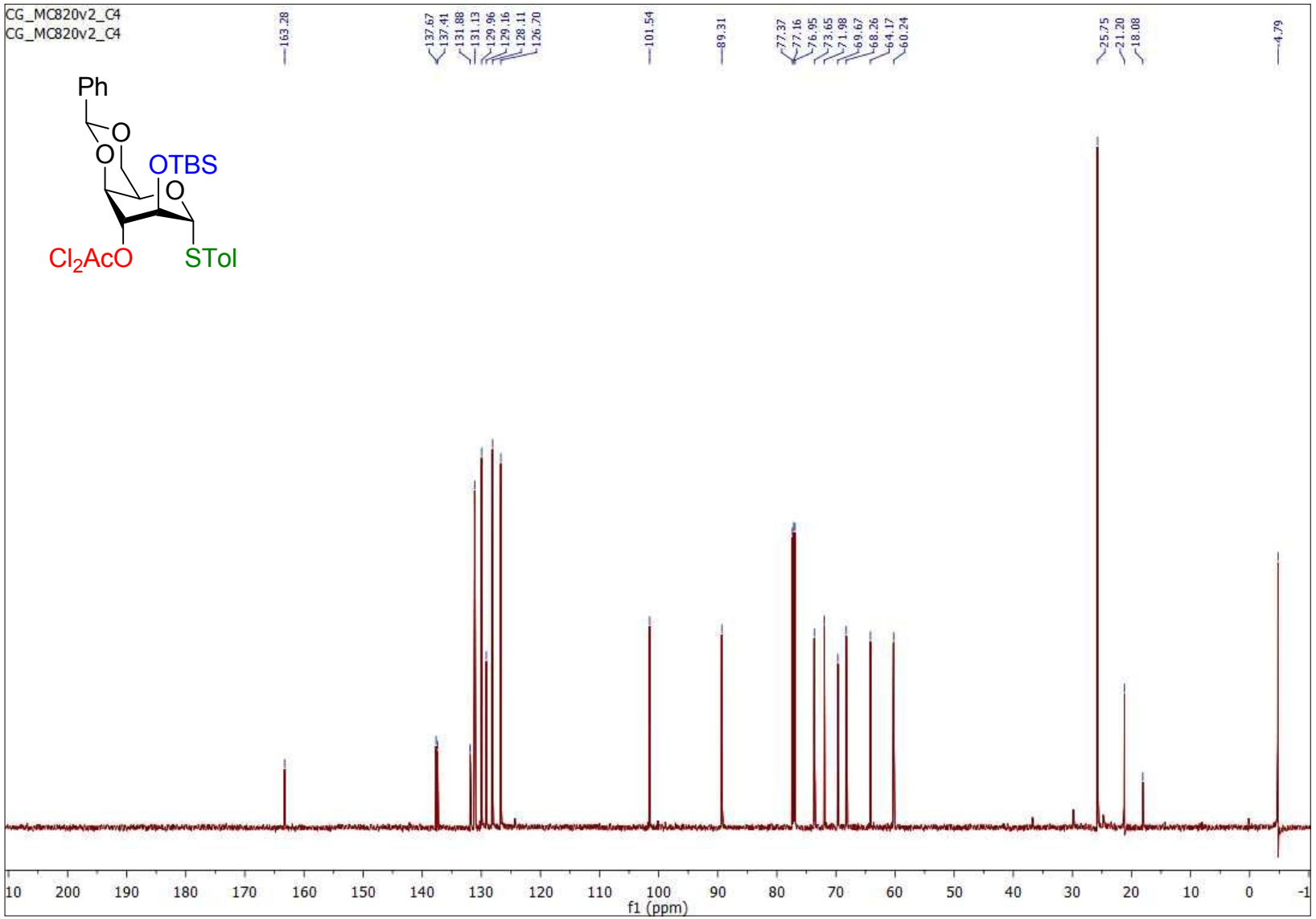


Figure S42. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-1-thio-*α*-D-idopyranoside (7)**

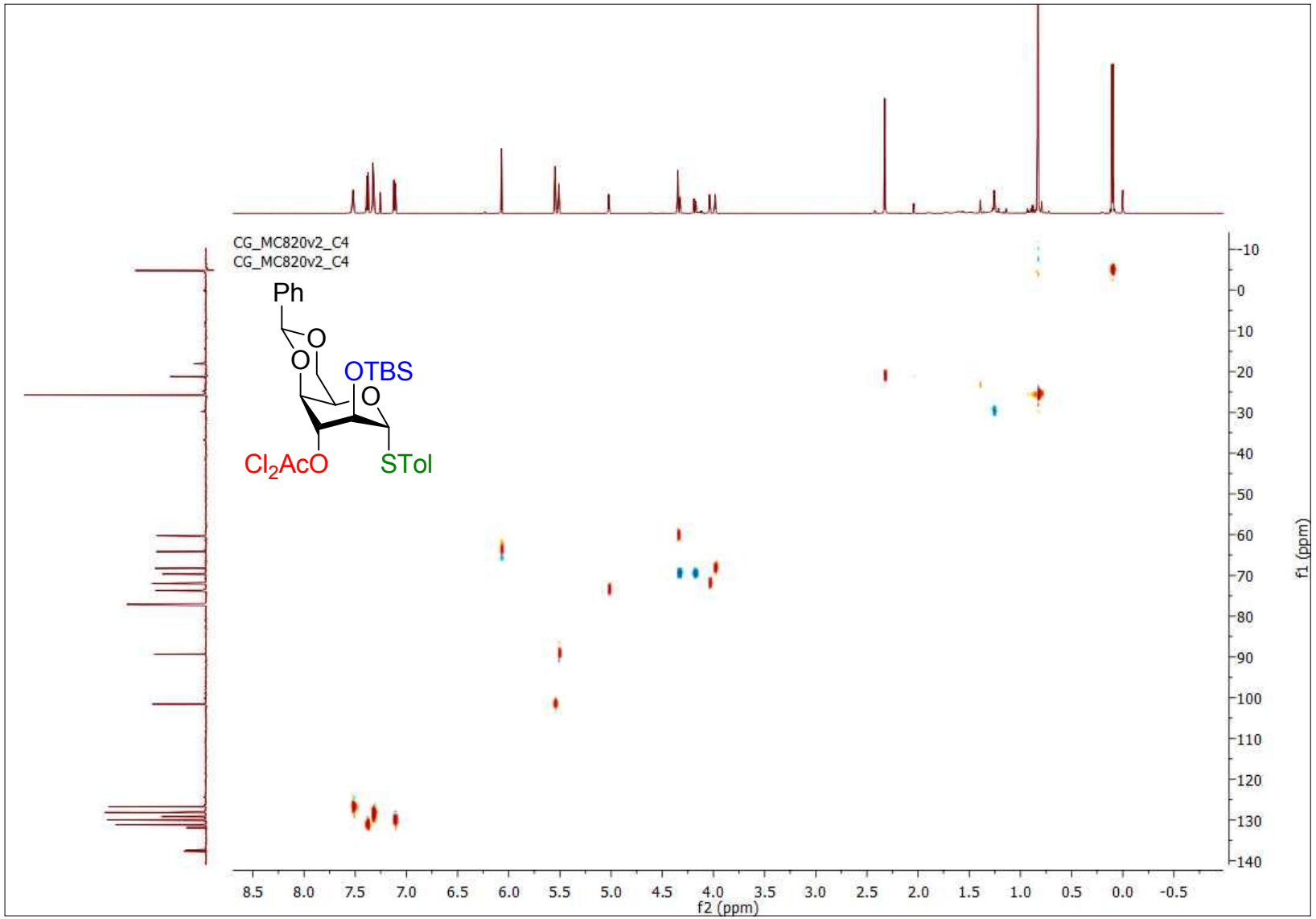


Figure S43. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-(2-azidomethyl)benzoyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (8)**

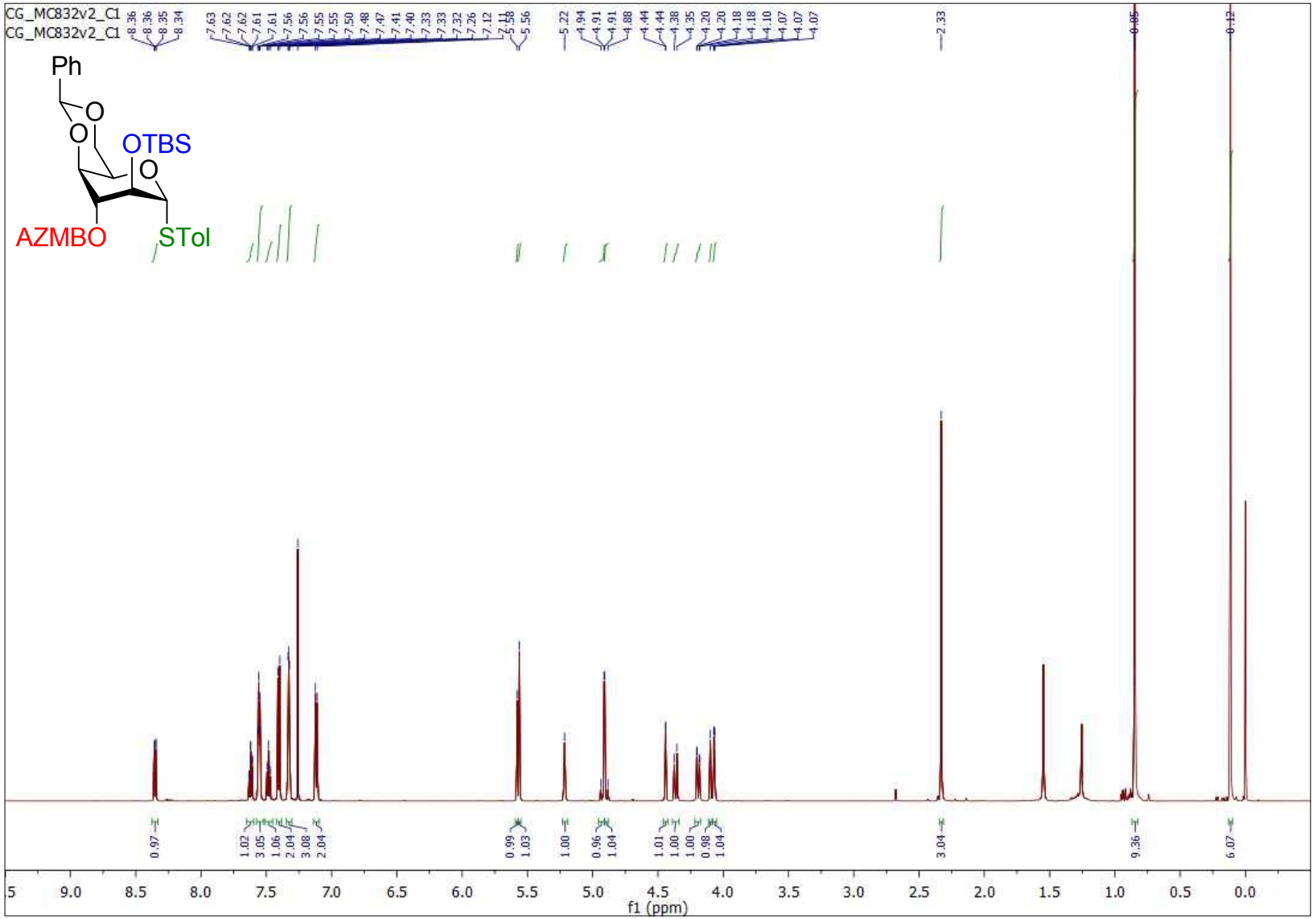


Figure S44. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-(2-azidomethyl)benzoyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (8)**

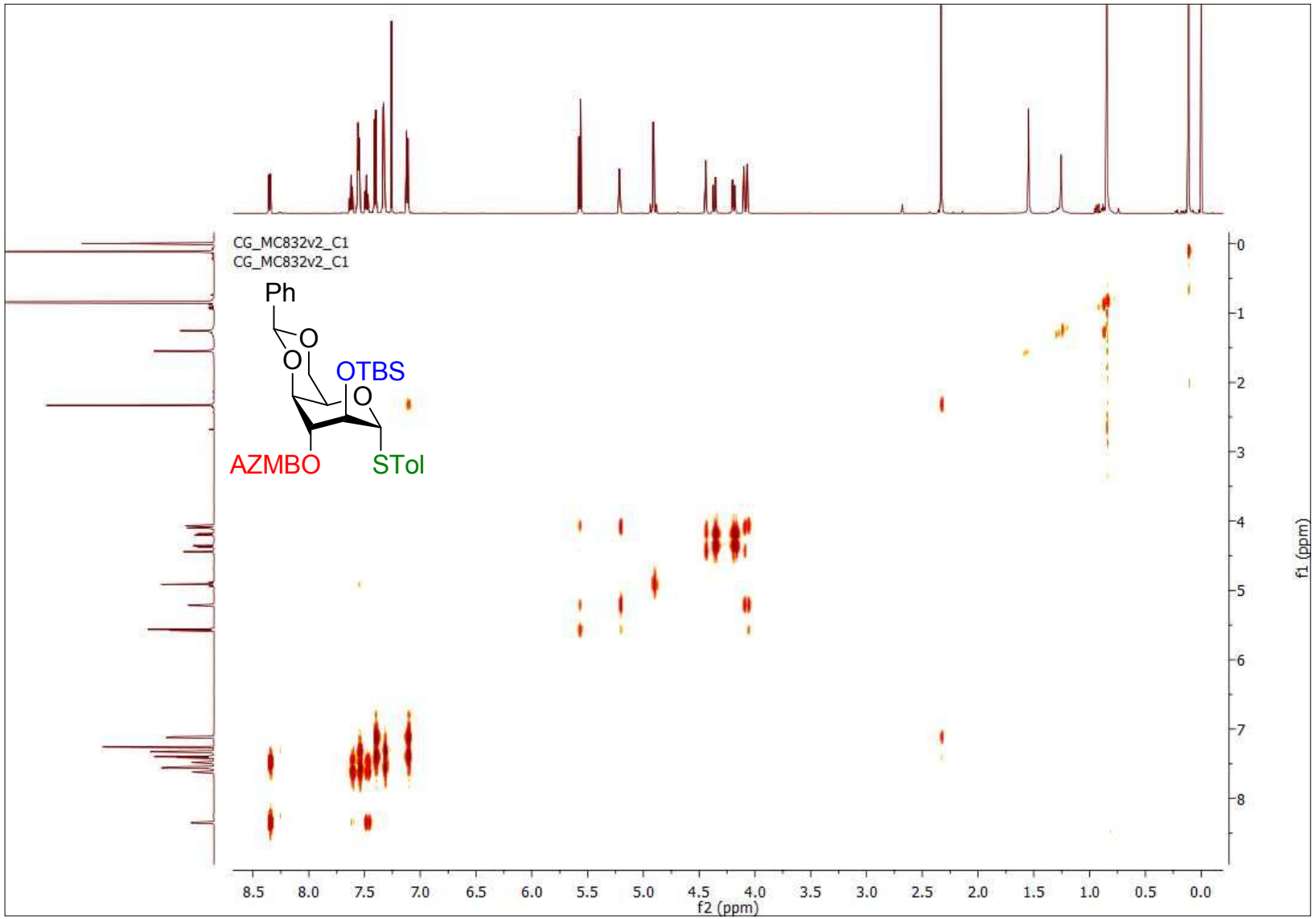


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***para*-methylphenyl 3-*O*-(2-azidomethyl)benzoyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (8)**

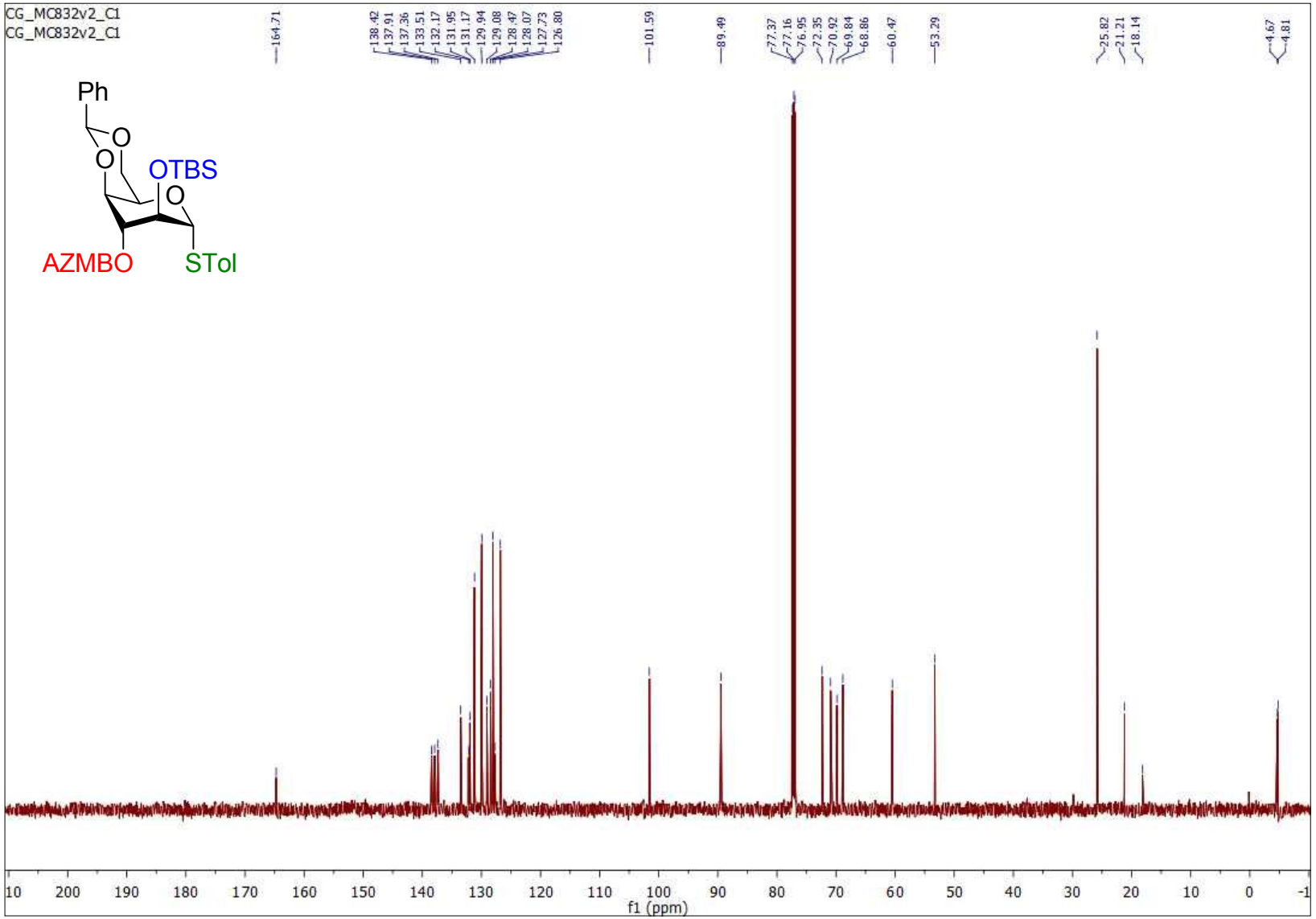


Figure S46. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-(2-azidomethyl)benzoyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (8)**

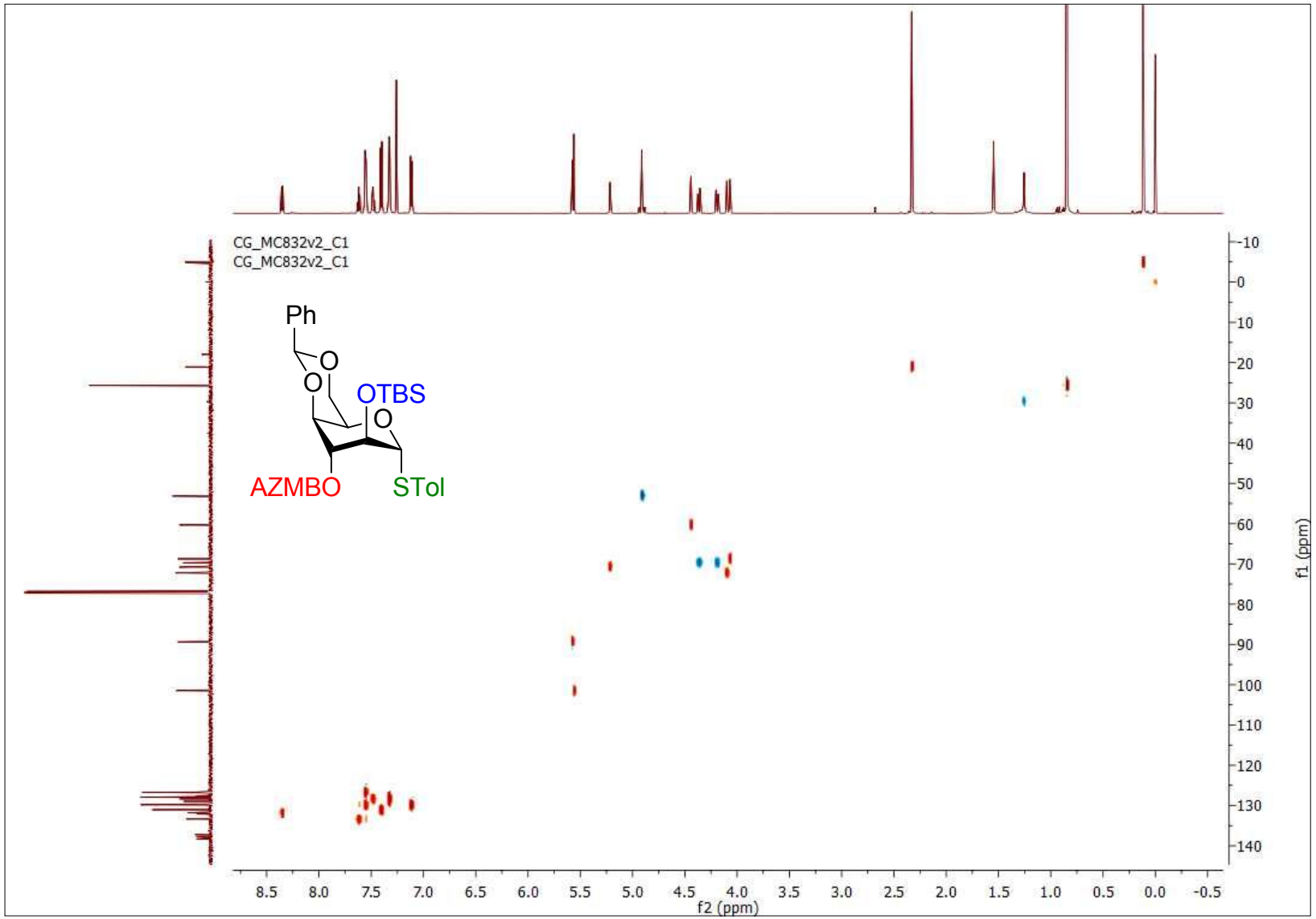


Figure S47. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-1-thio-*α*-D-idopyranoside (9)**

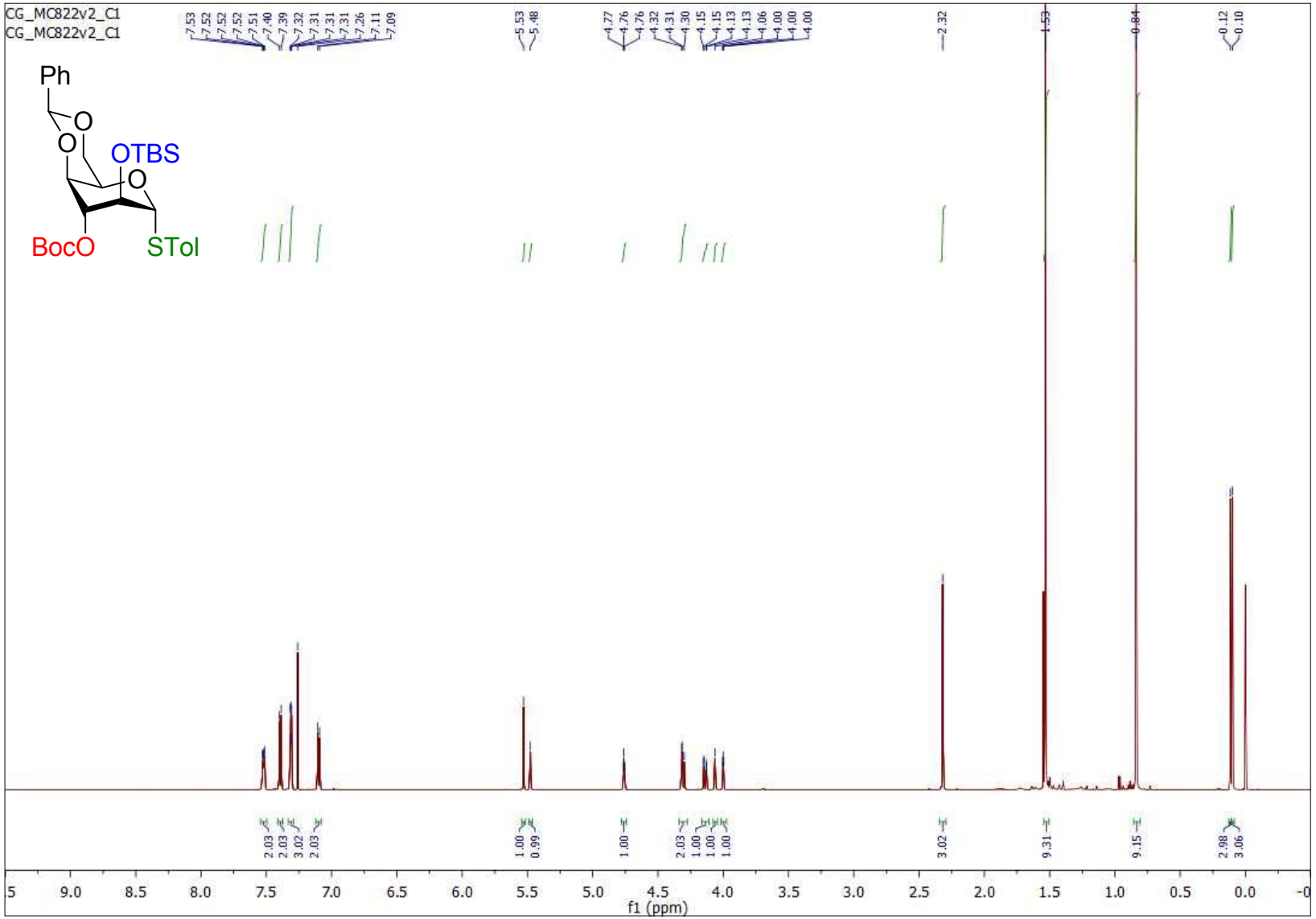


Figure S48. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-1-thio-*α*-D-idopyranoside (9)**

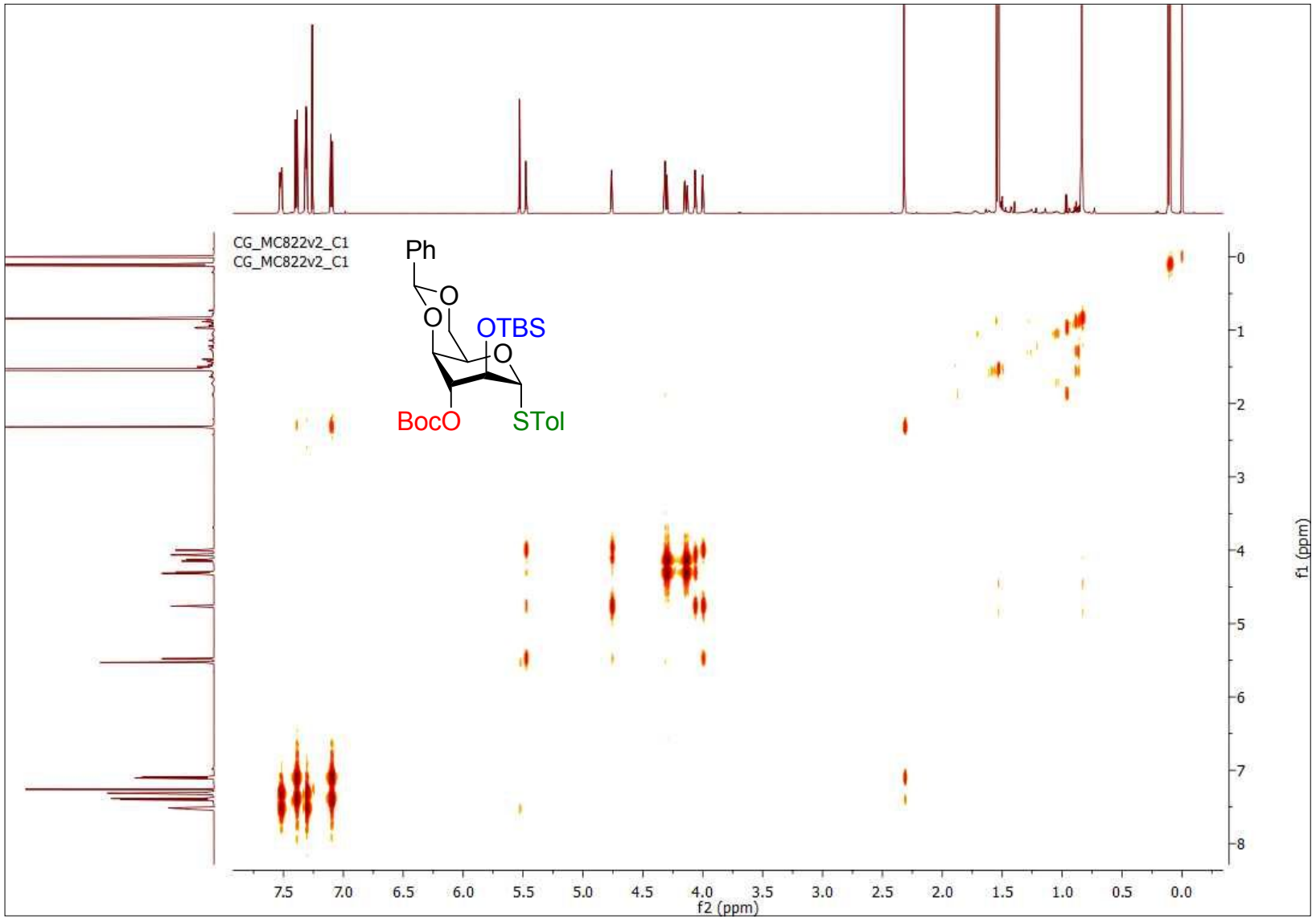


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-1-thio-*α*-D-idopyranoside (9)**

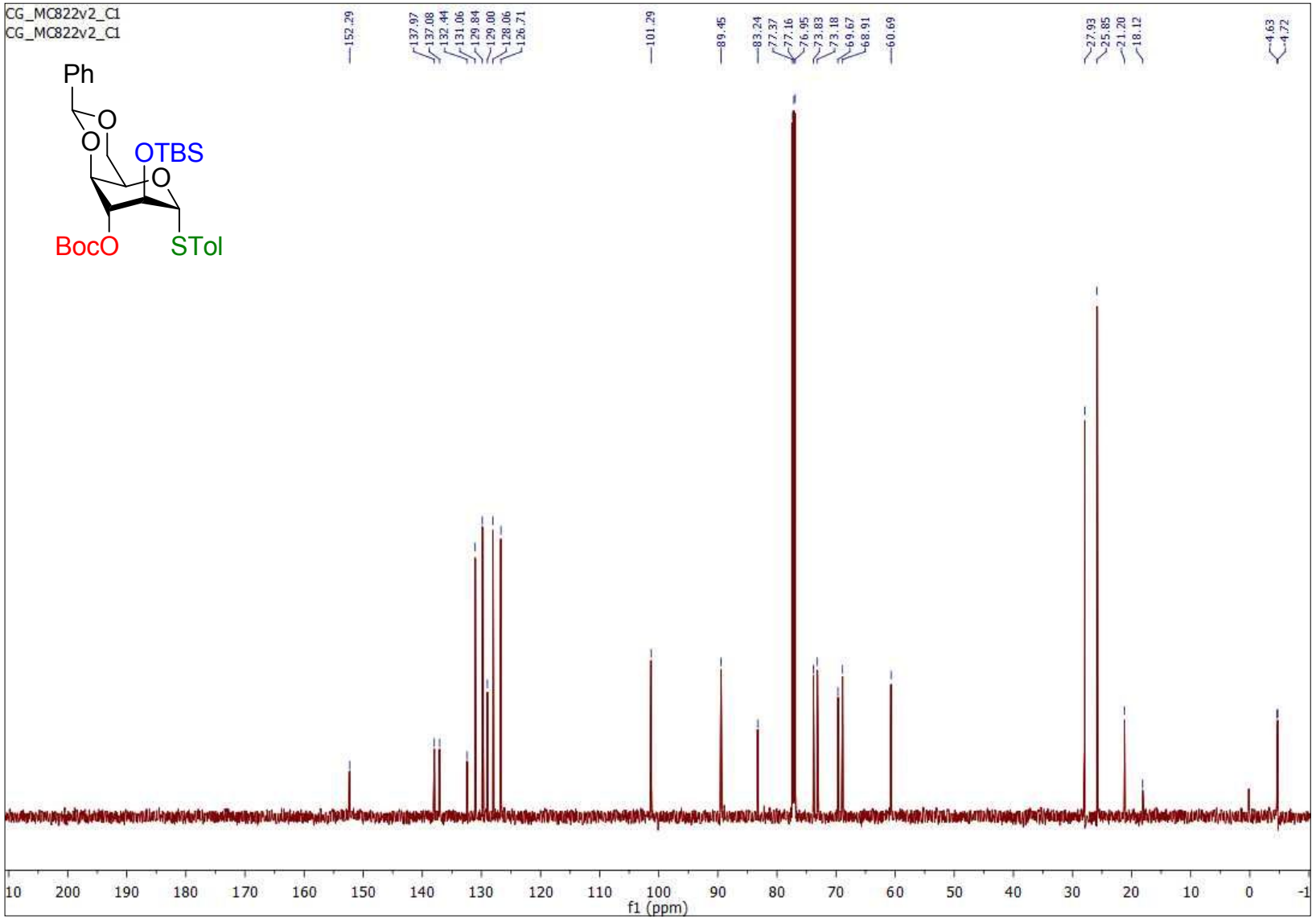


Figure S50. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-1-thio-*α*-D-idopyranoside (9)**

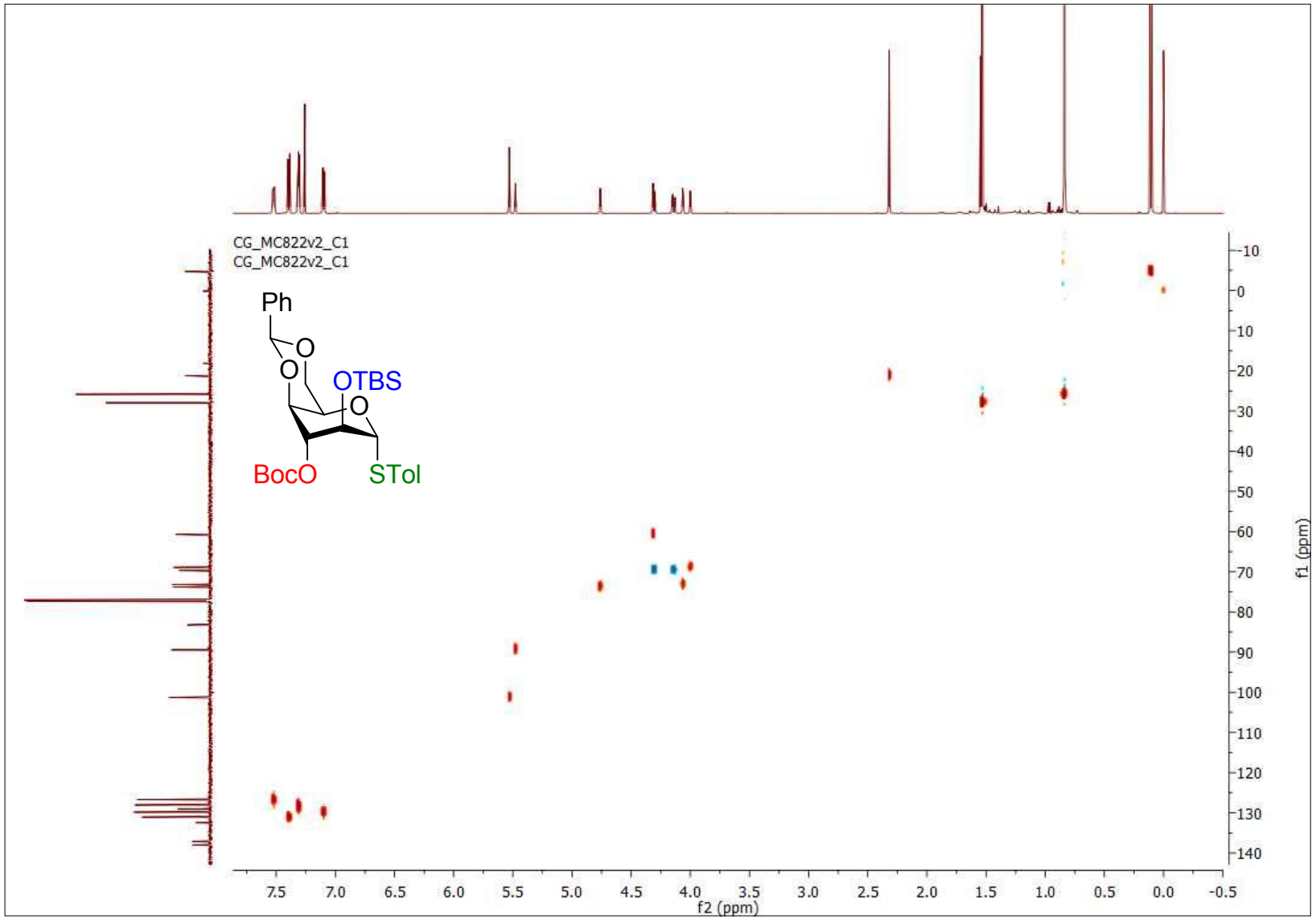


Figure S51. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (14a)**

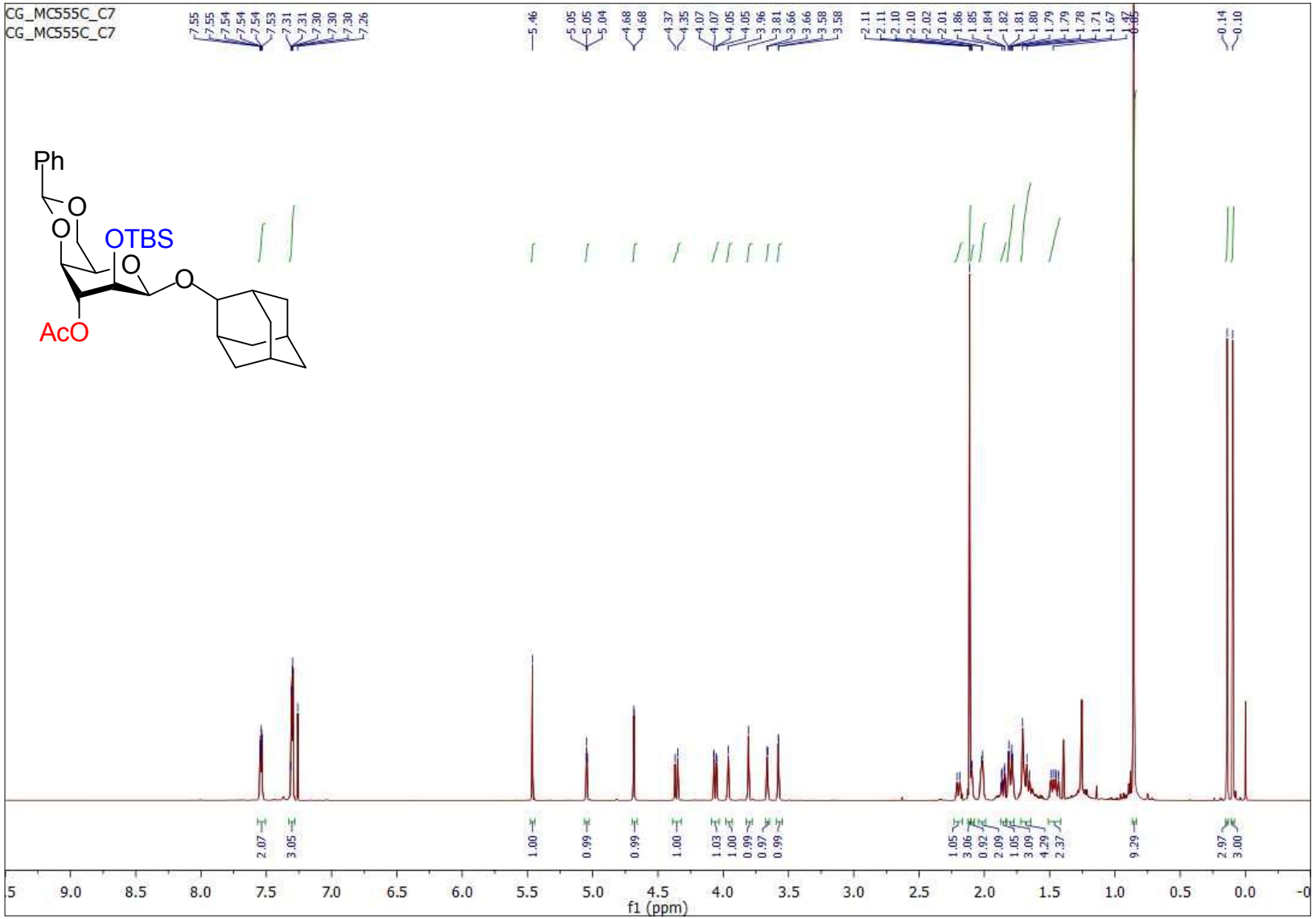


Figure S52. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (14a)**

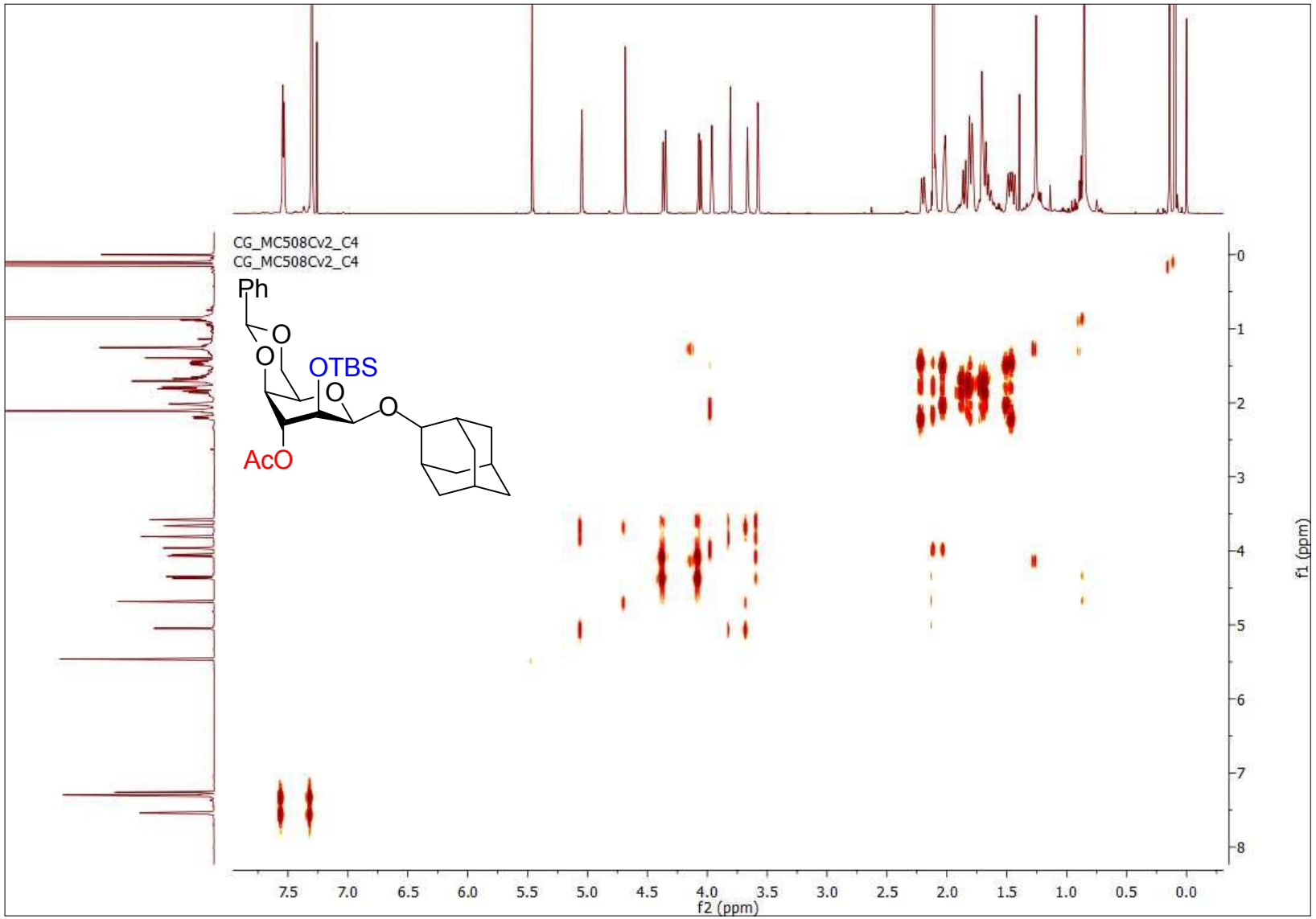


Figure S53. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (14a)**

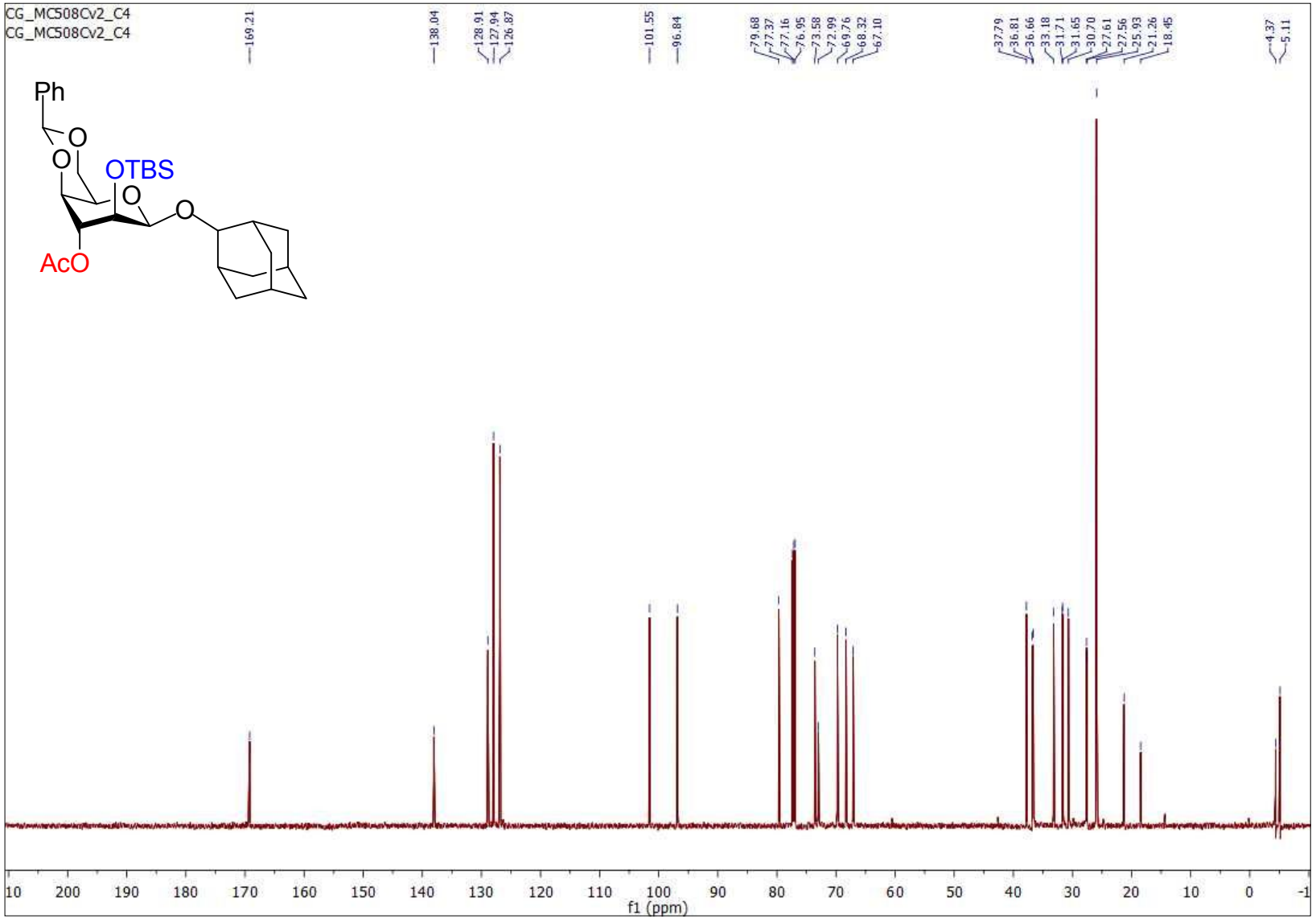


Figure S54. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (14a)**

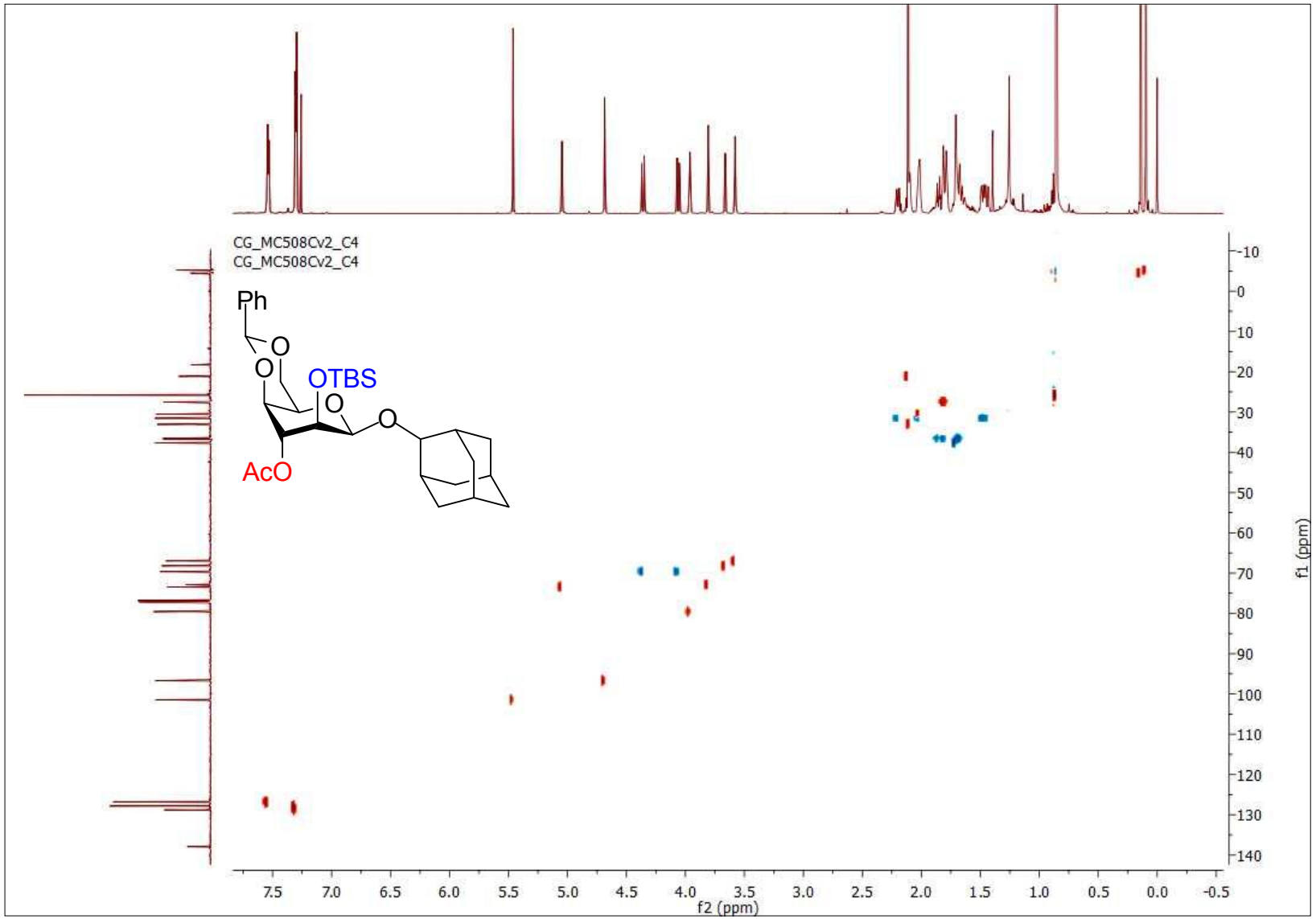


Figure S55. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (14a)**

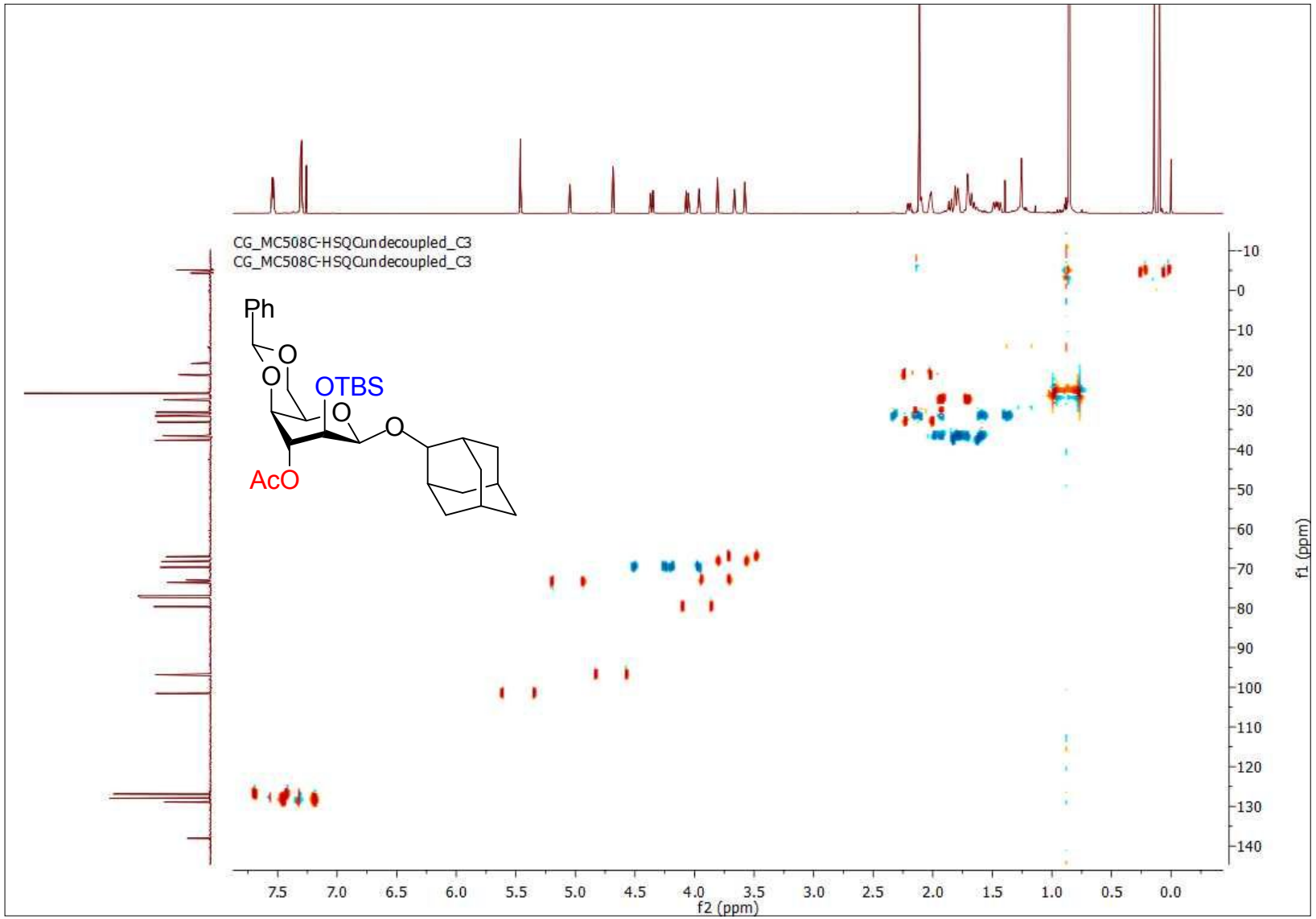


Figure S56. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (14b)**

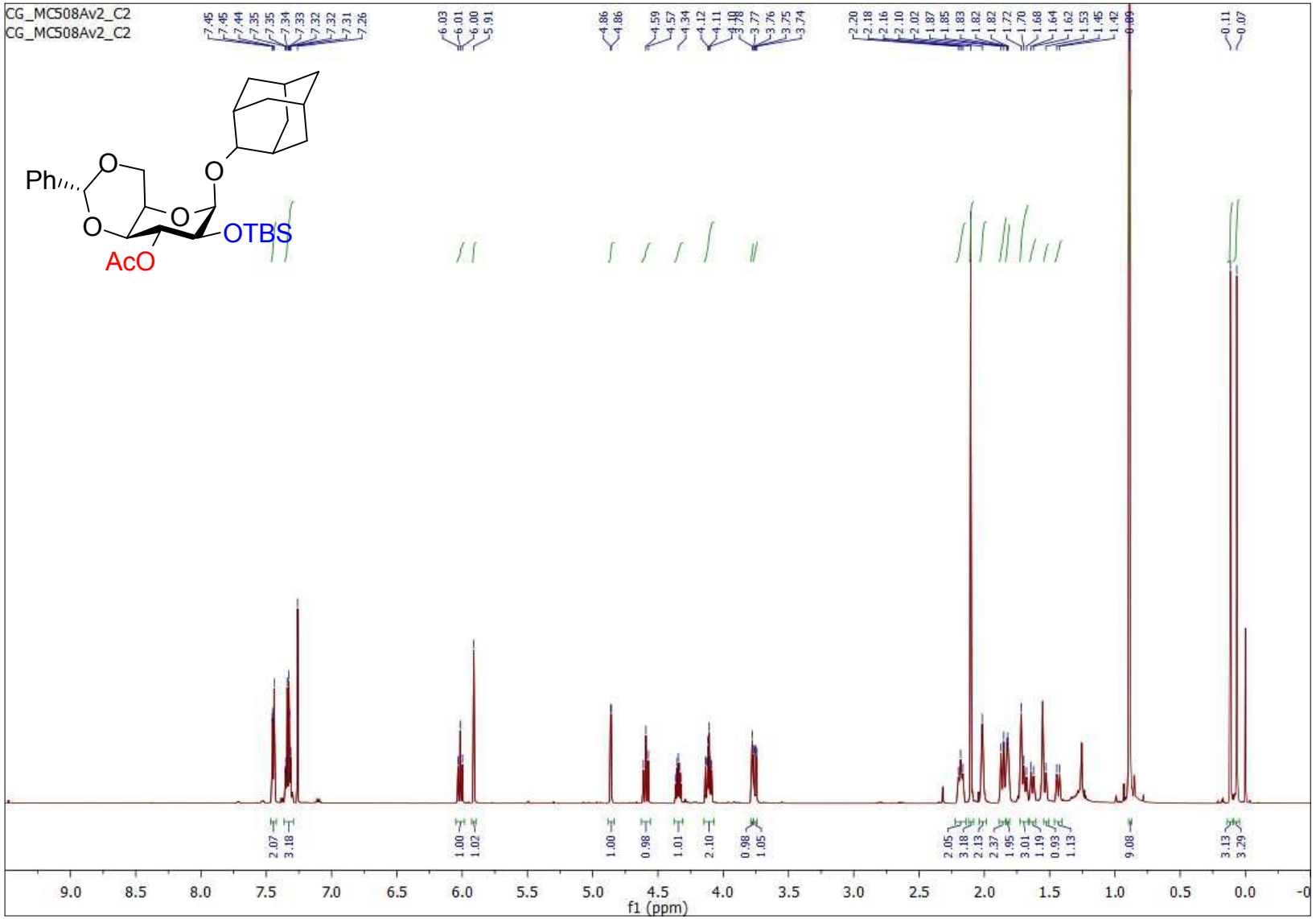


Figure S57. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (14b)**

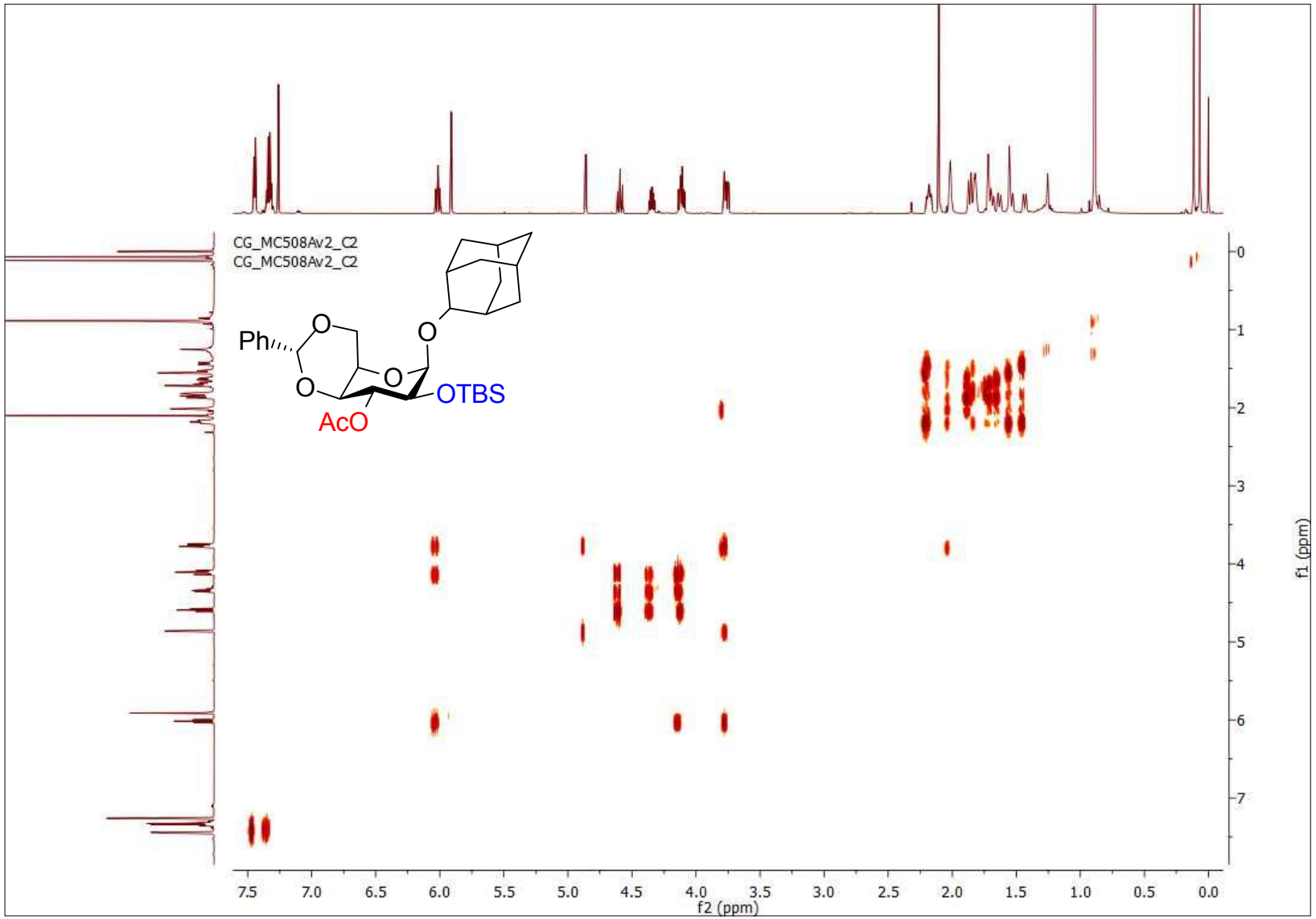


Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (14b)**

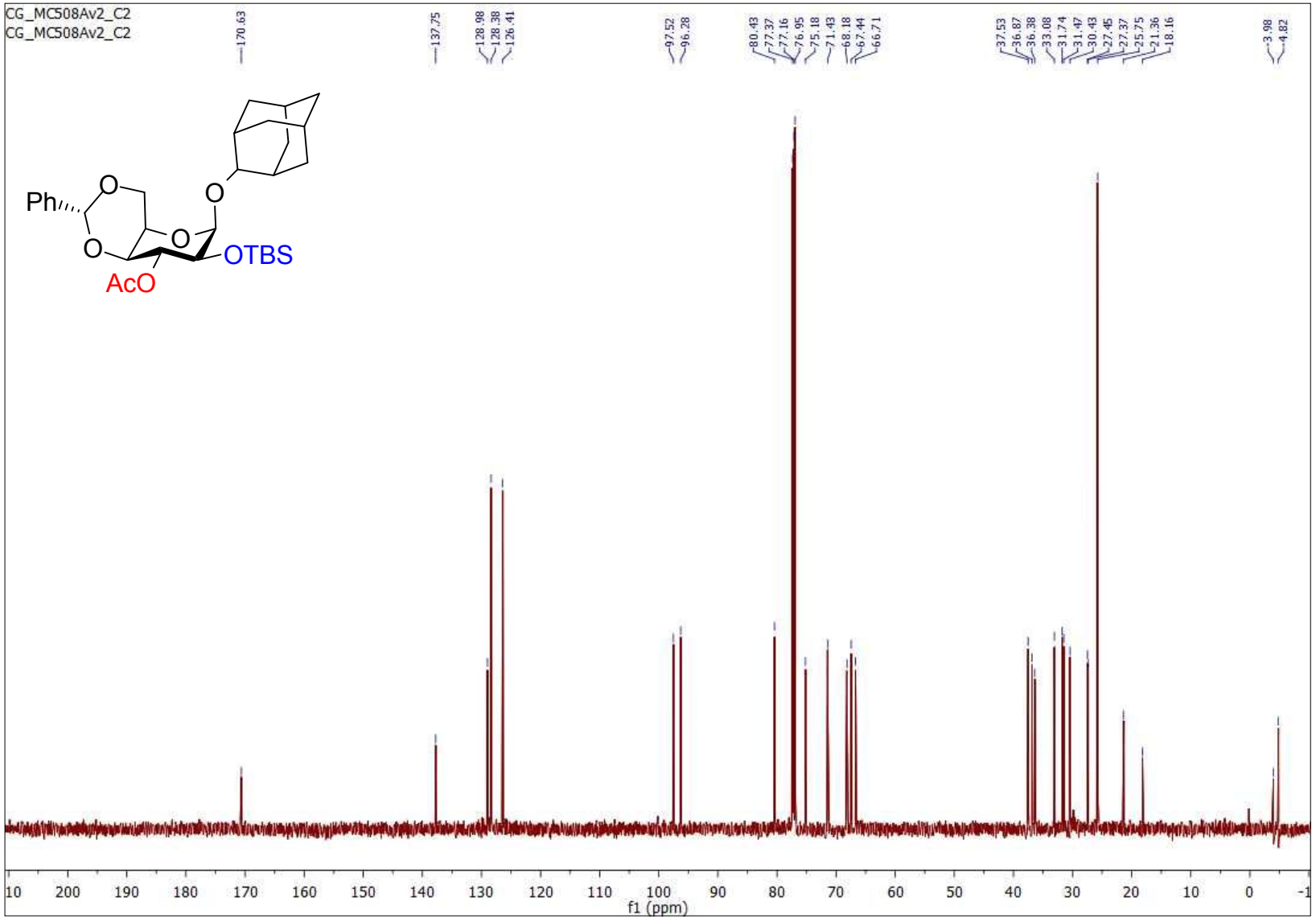


Figure S59. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (14b)**

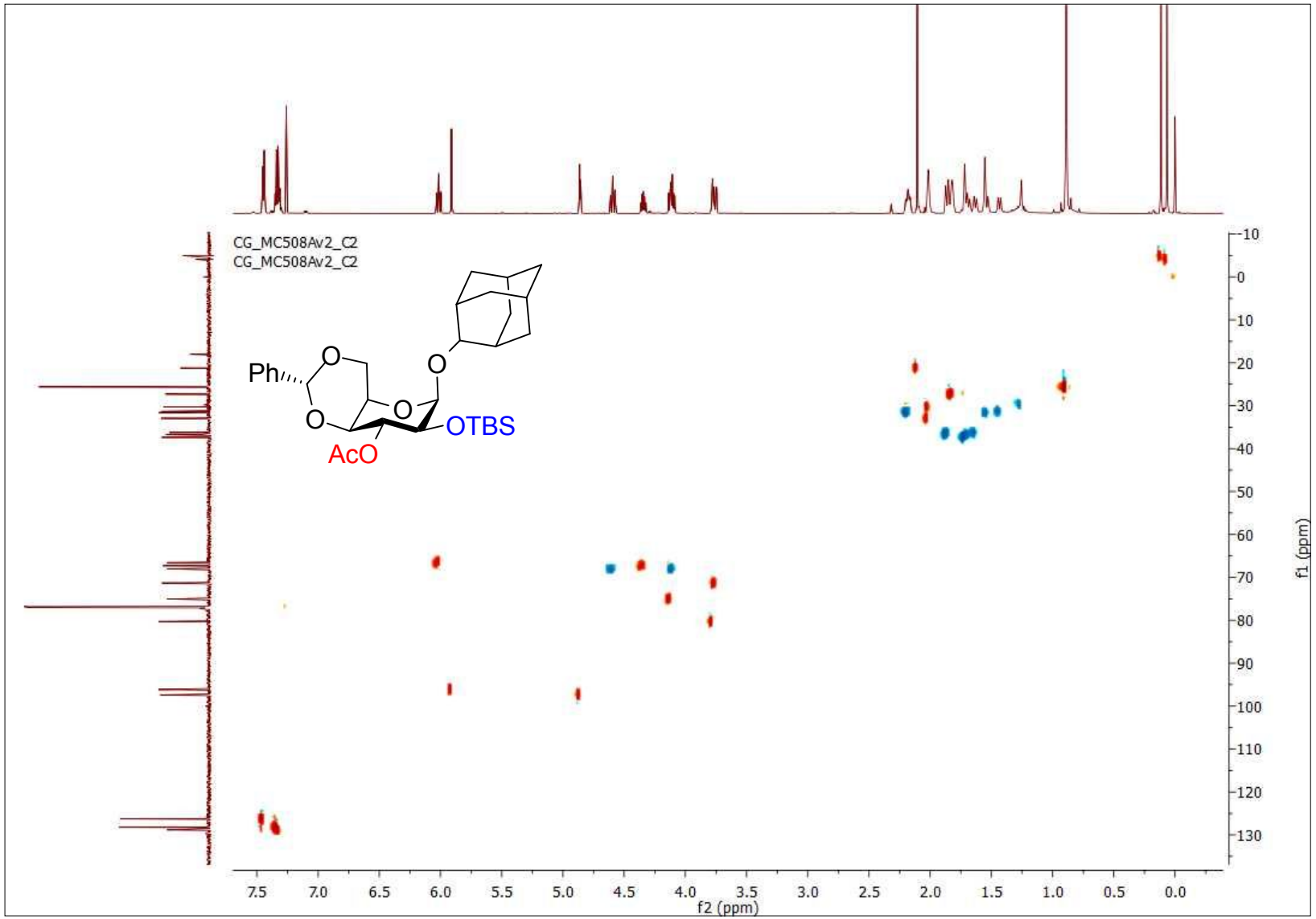


Figure S60. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (14b)**

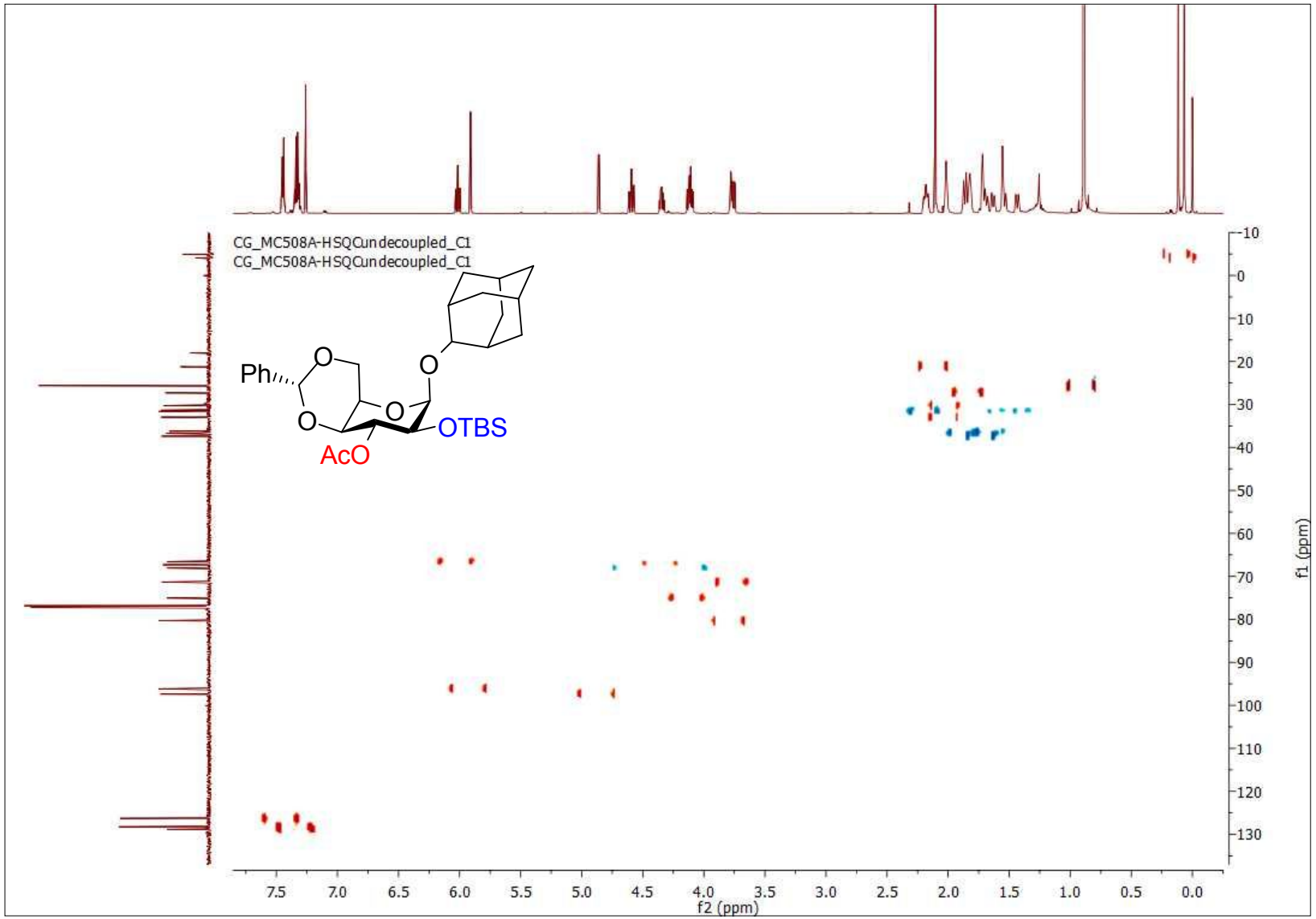


Figure S61. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (14c)**

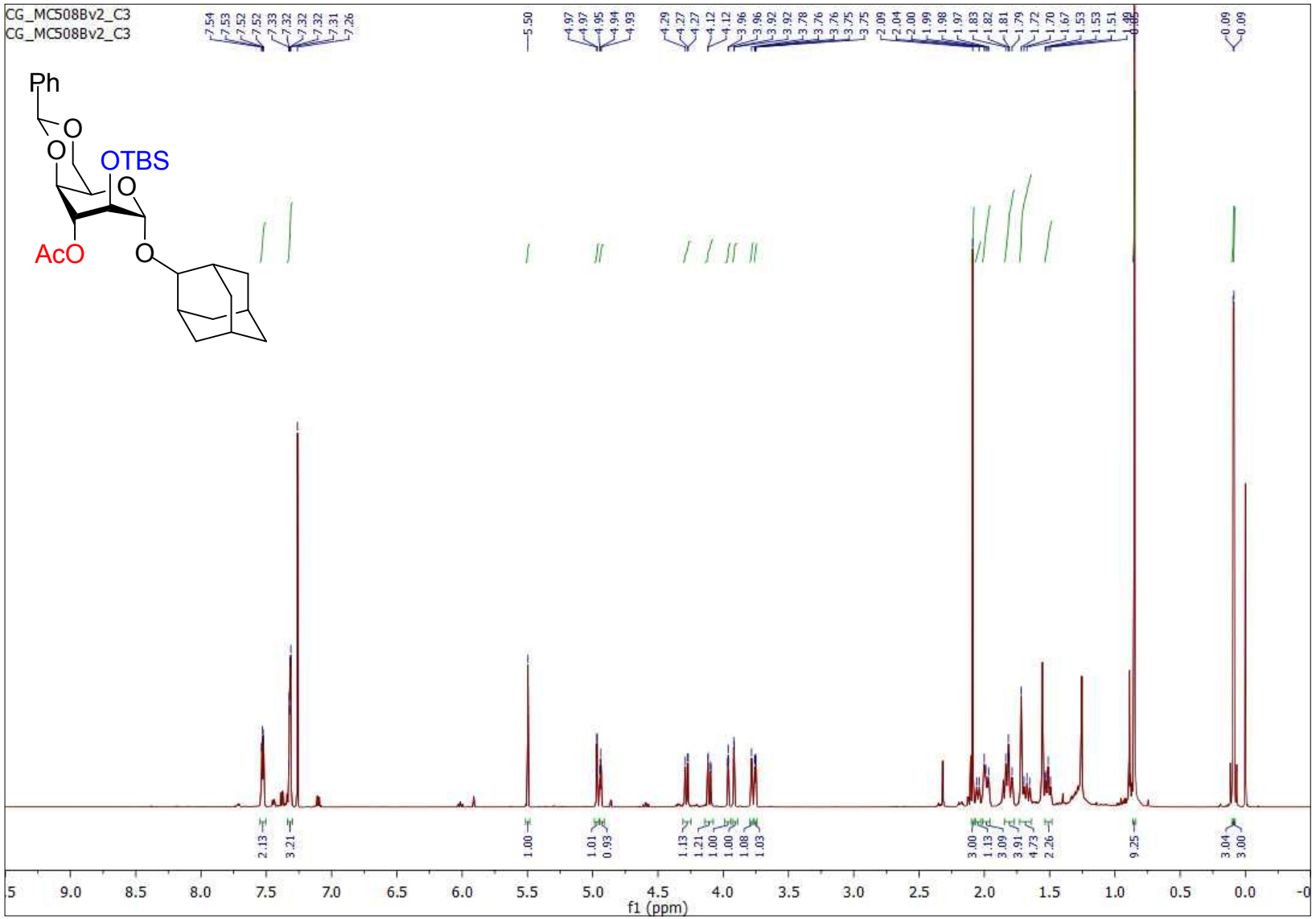


Figure S62. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (14c)**

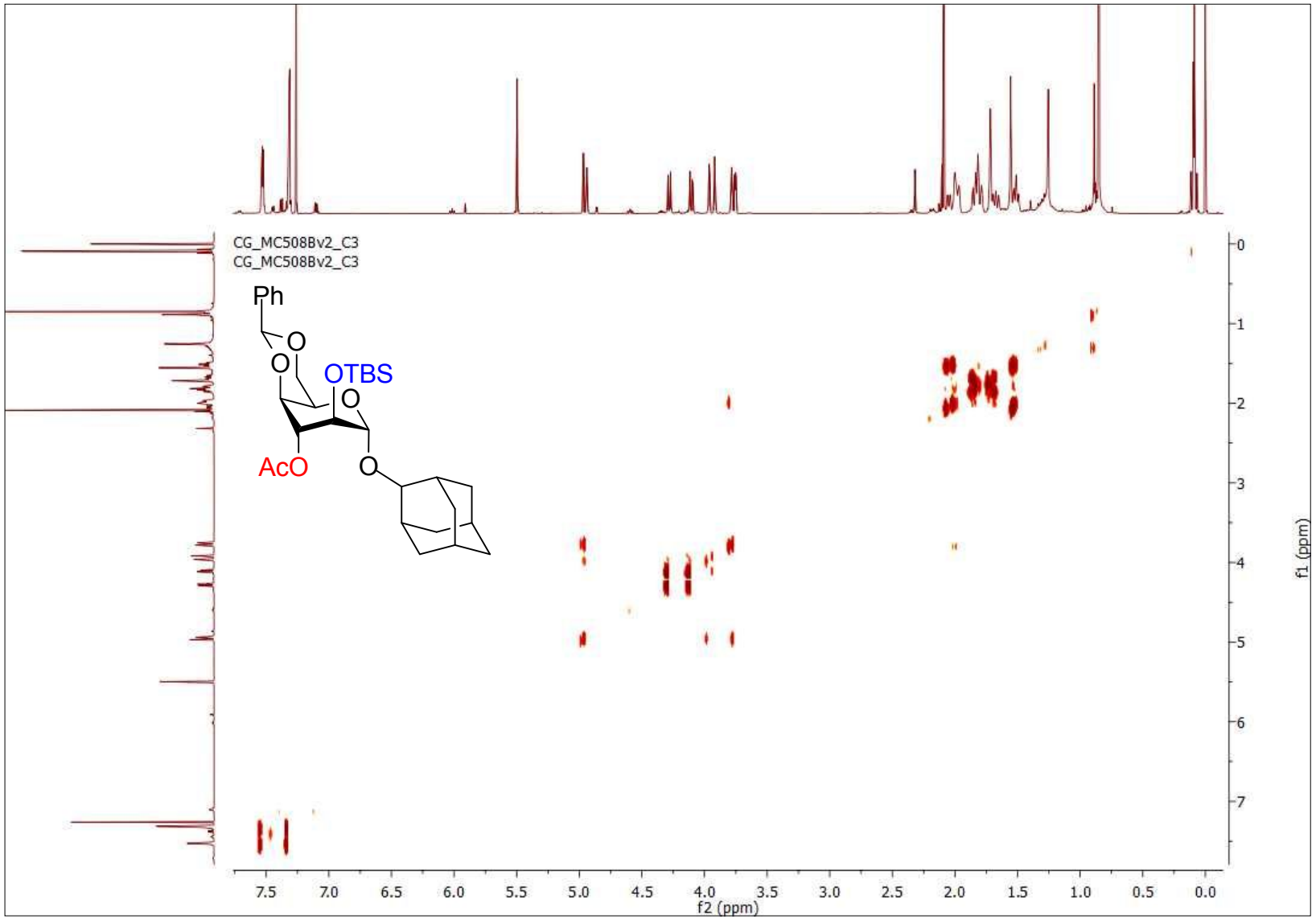


Figure S63. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (14c)**

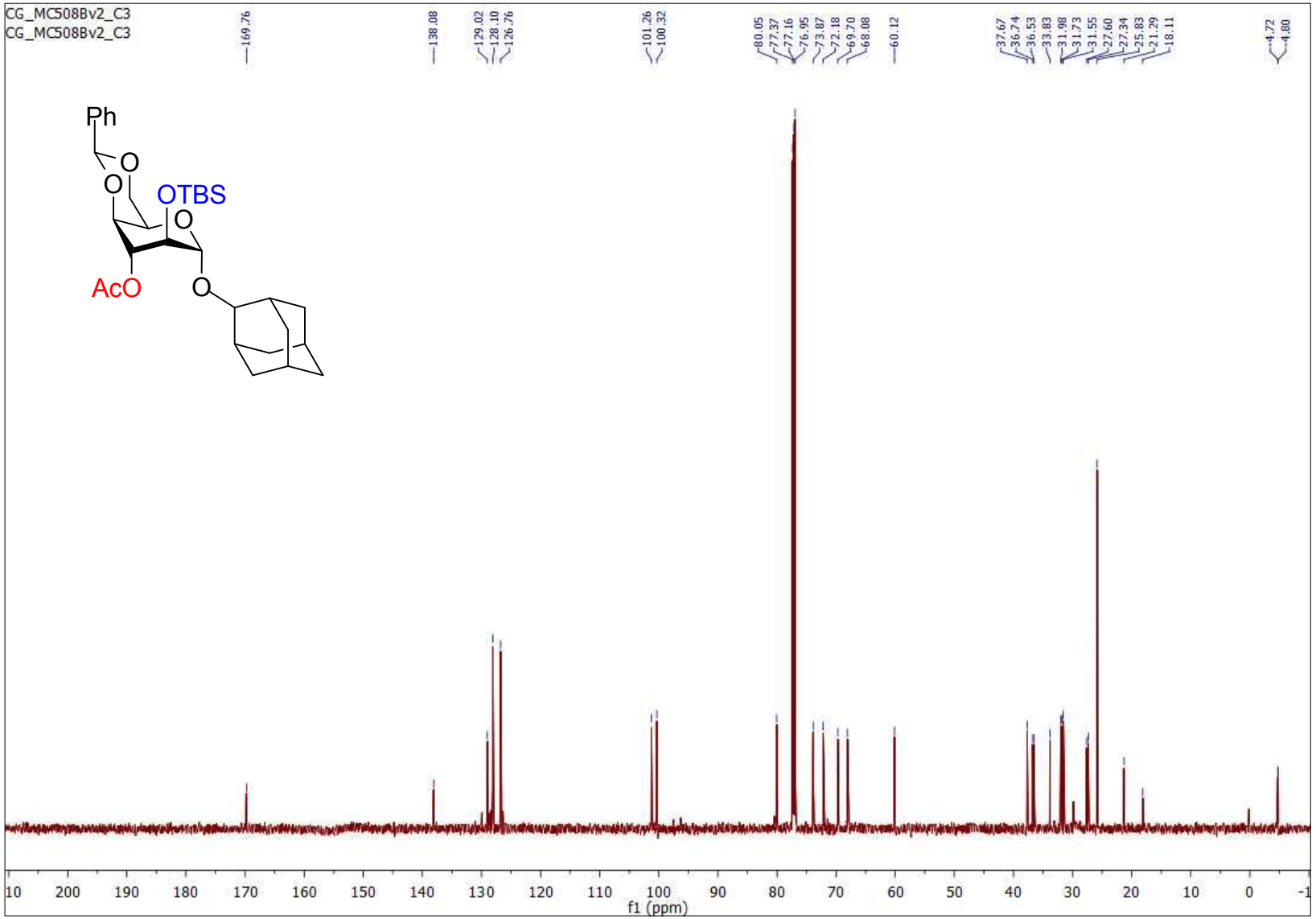


Figure S64. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (14c)**

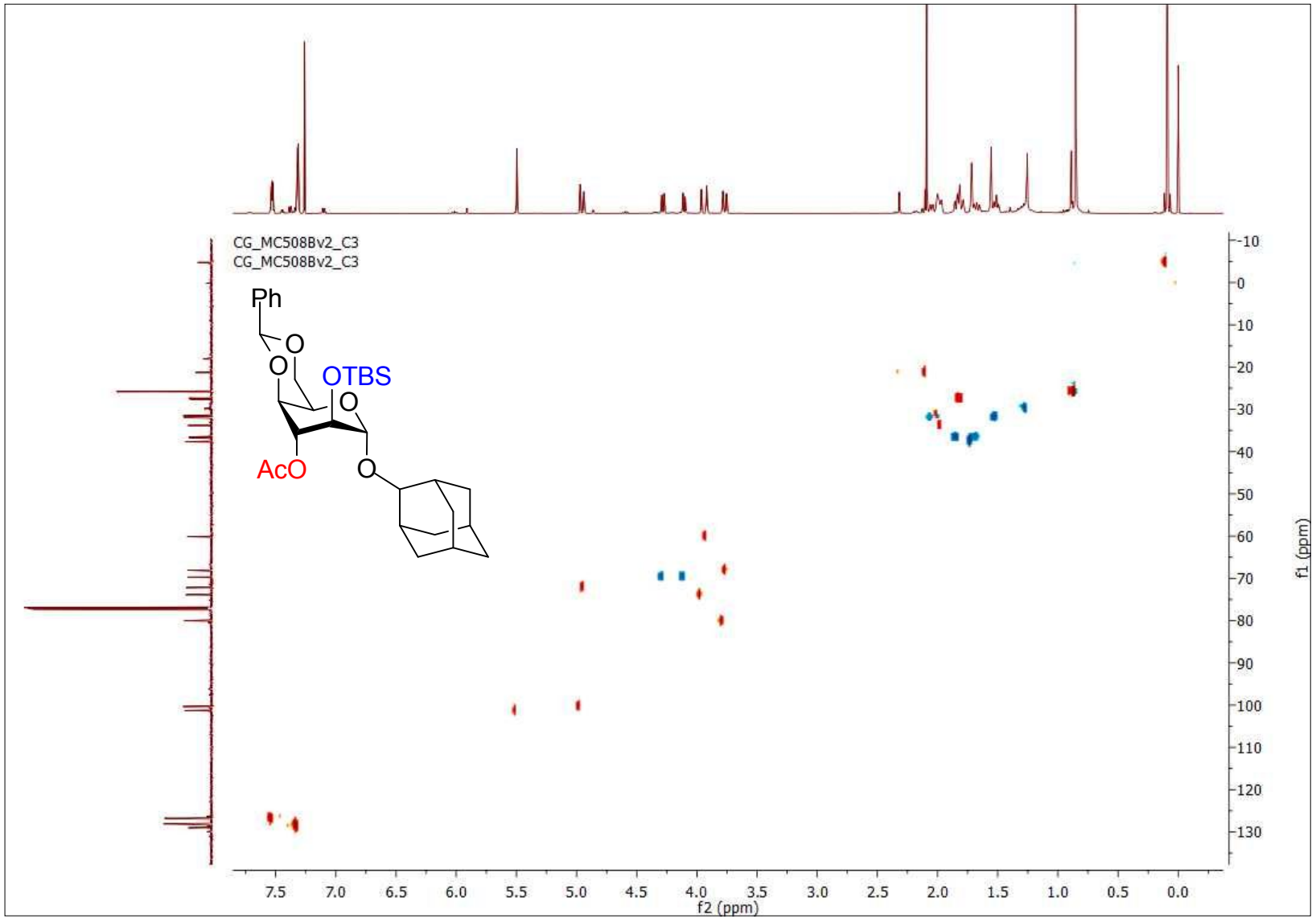


Figure S65. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (14c)**

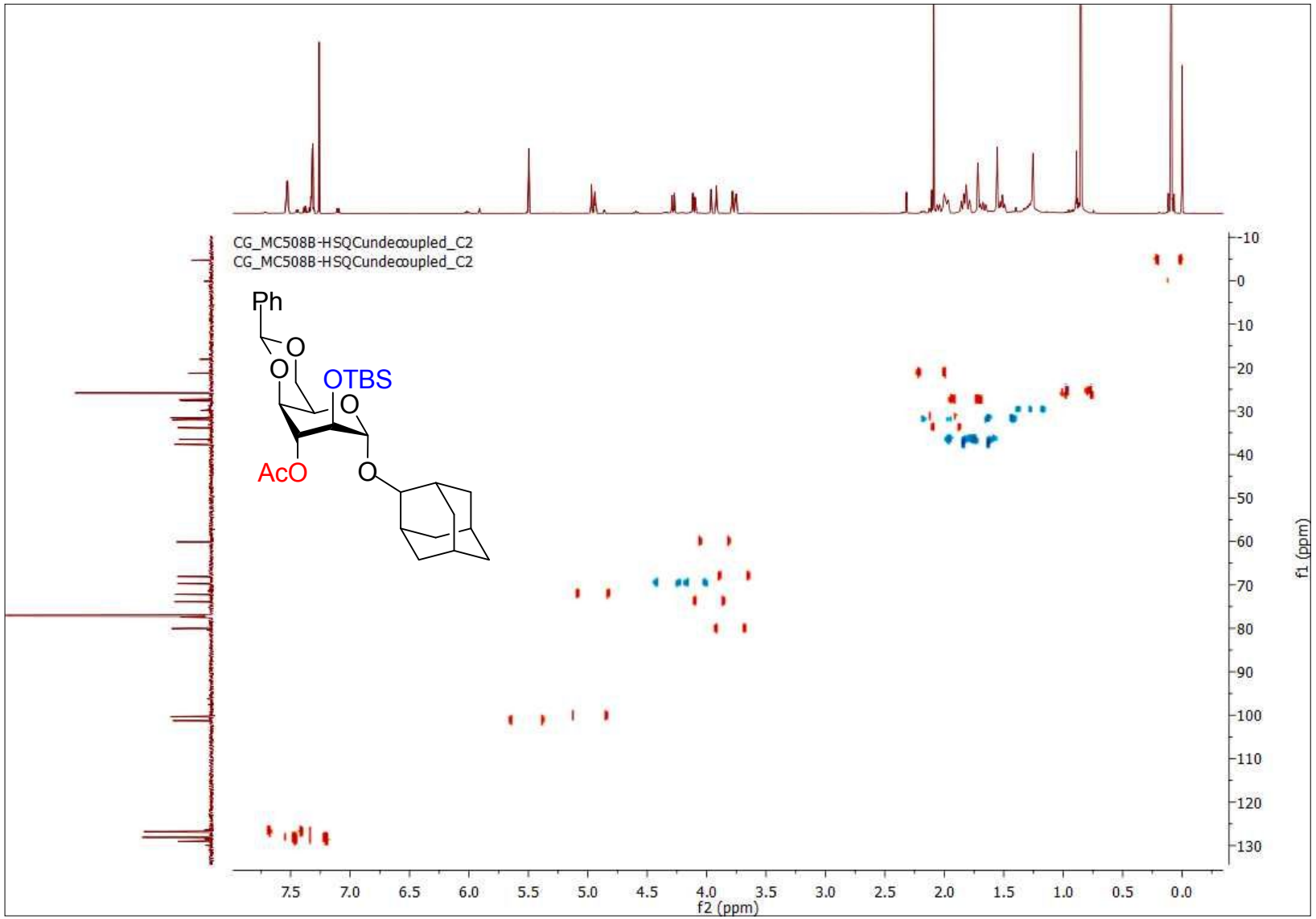


Figure S66. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (15a)**

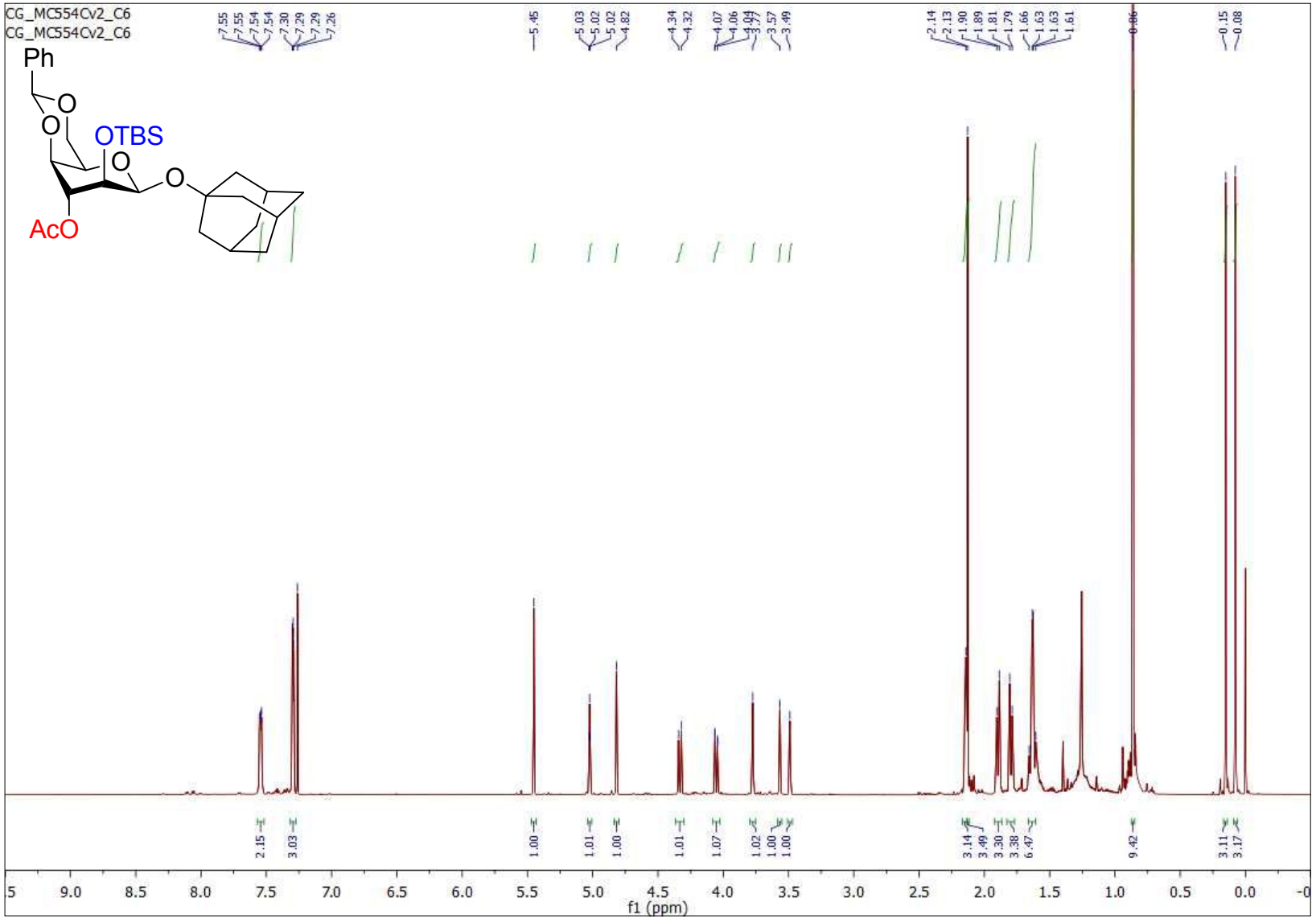


Figure S67. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (15a)**

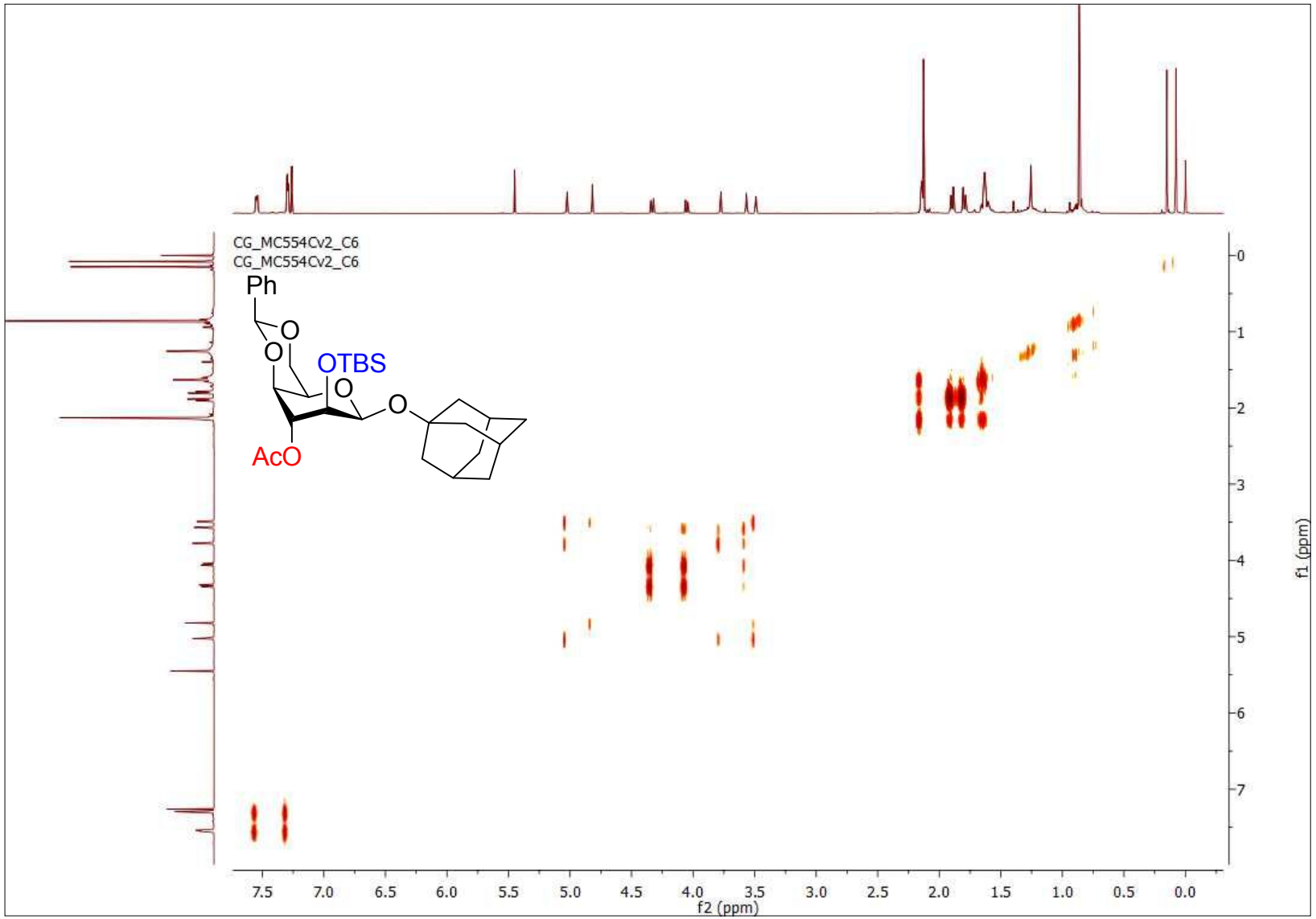


Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (15a)**

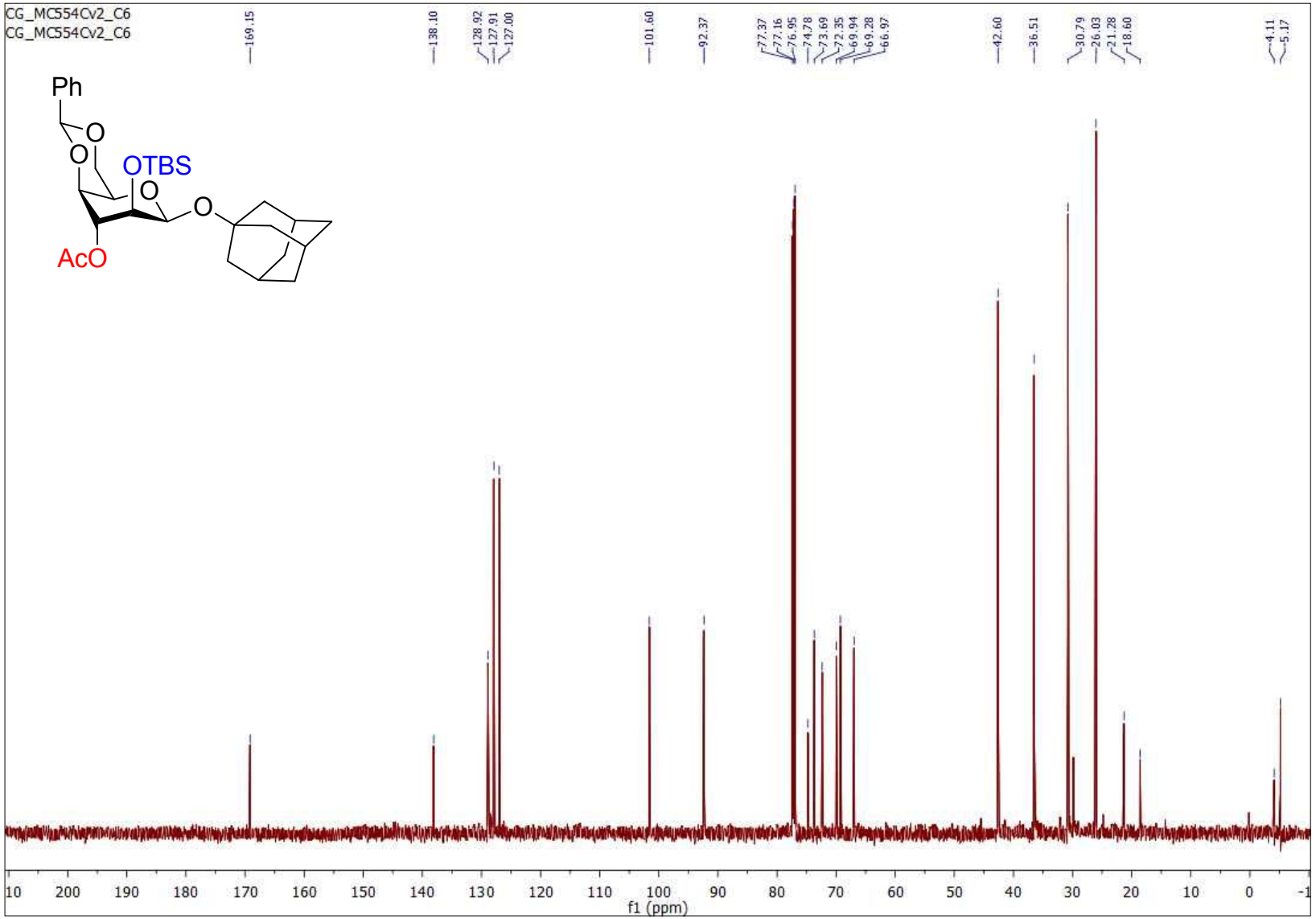


Figure S69. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (15a)**

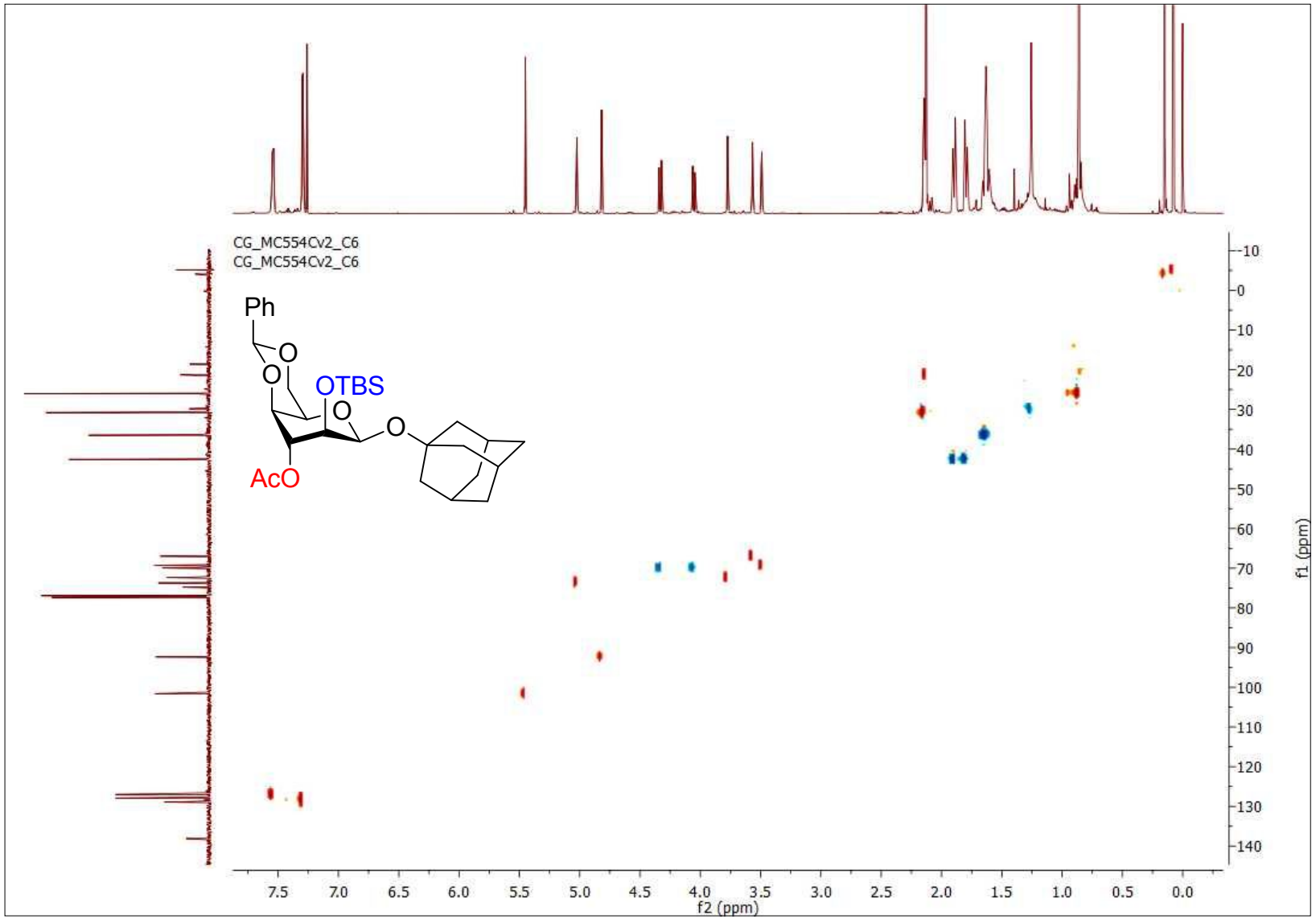


Figure S70. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (15a)**

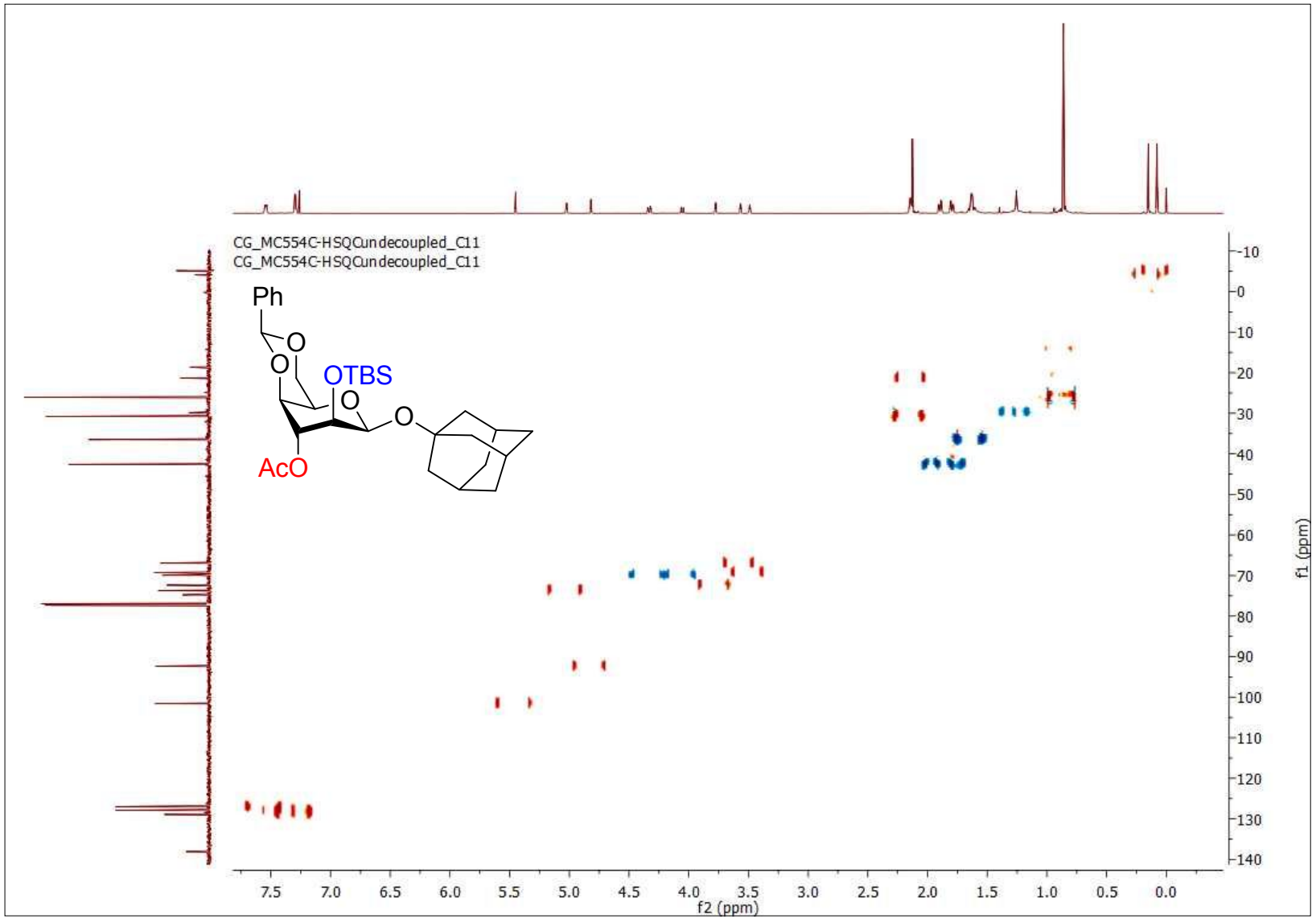


Figure S71. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (15b)**

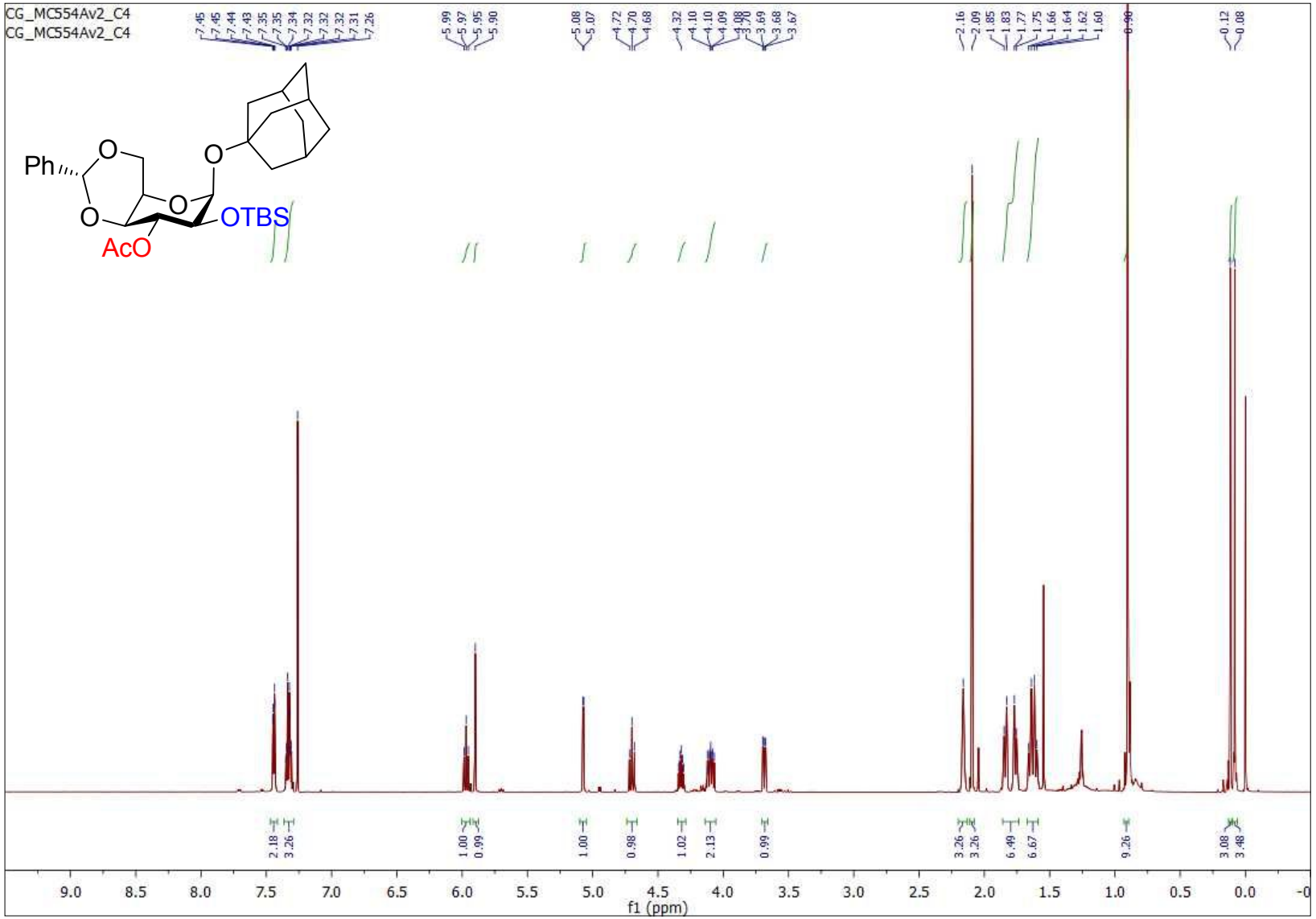


Figure S72. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (15b)**

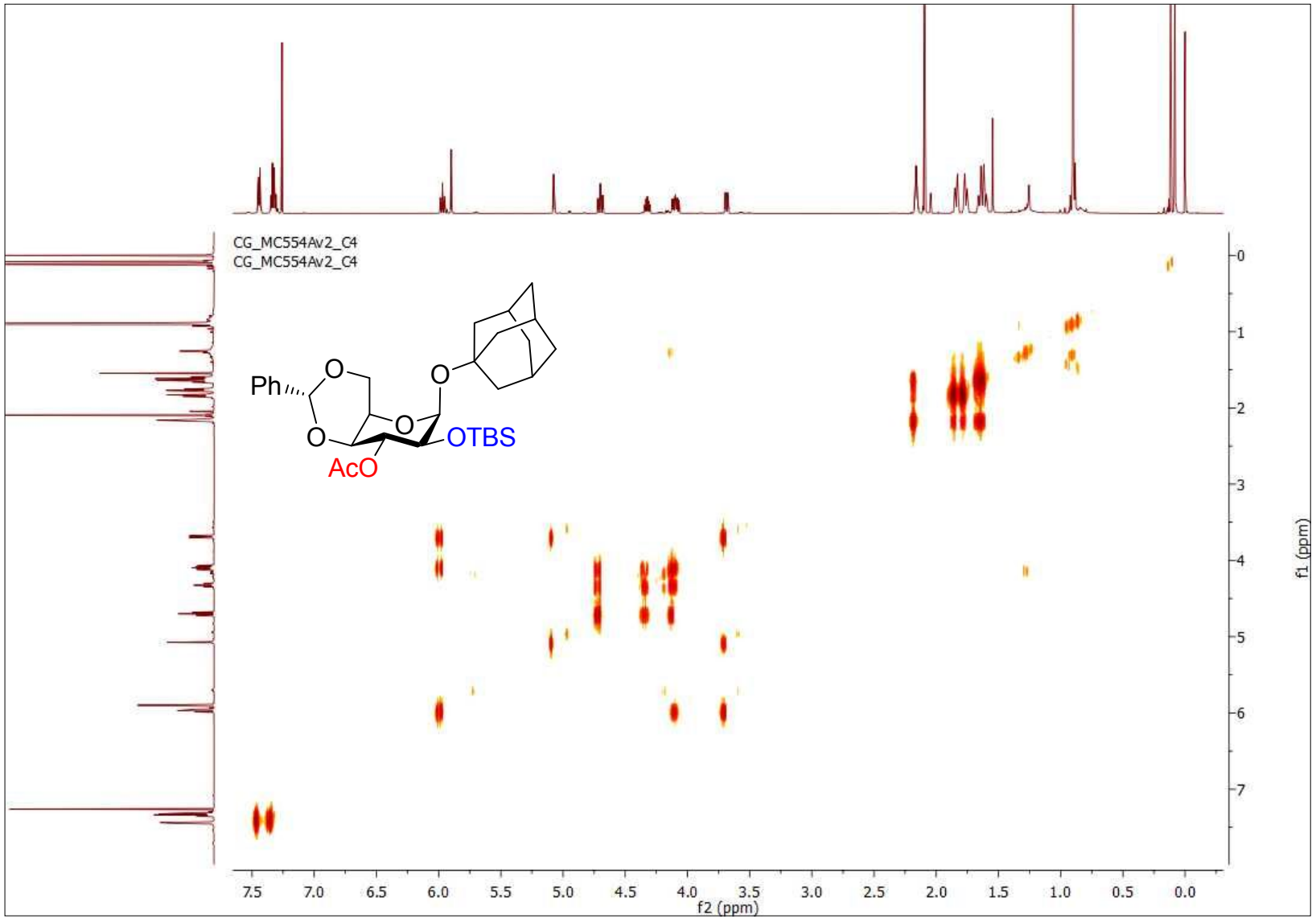


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (15b)**

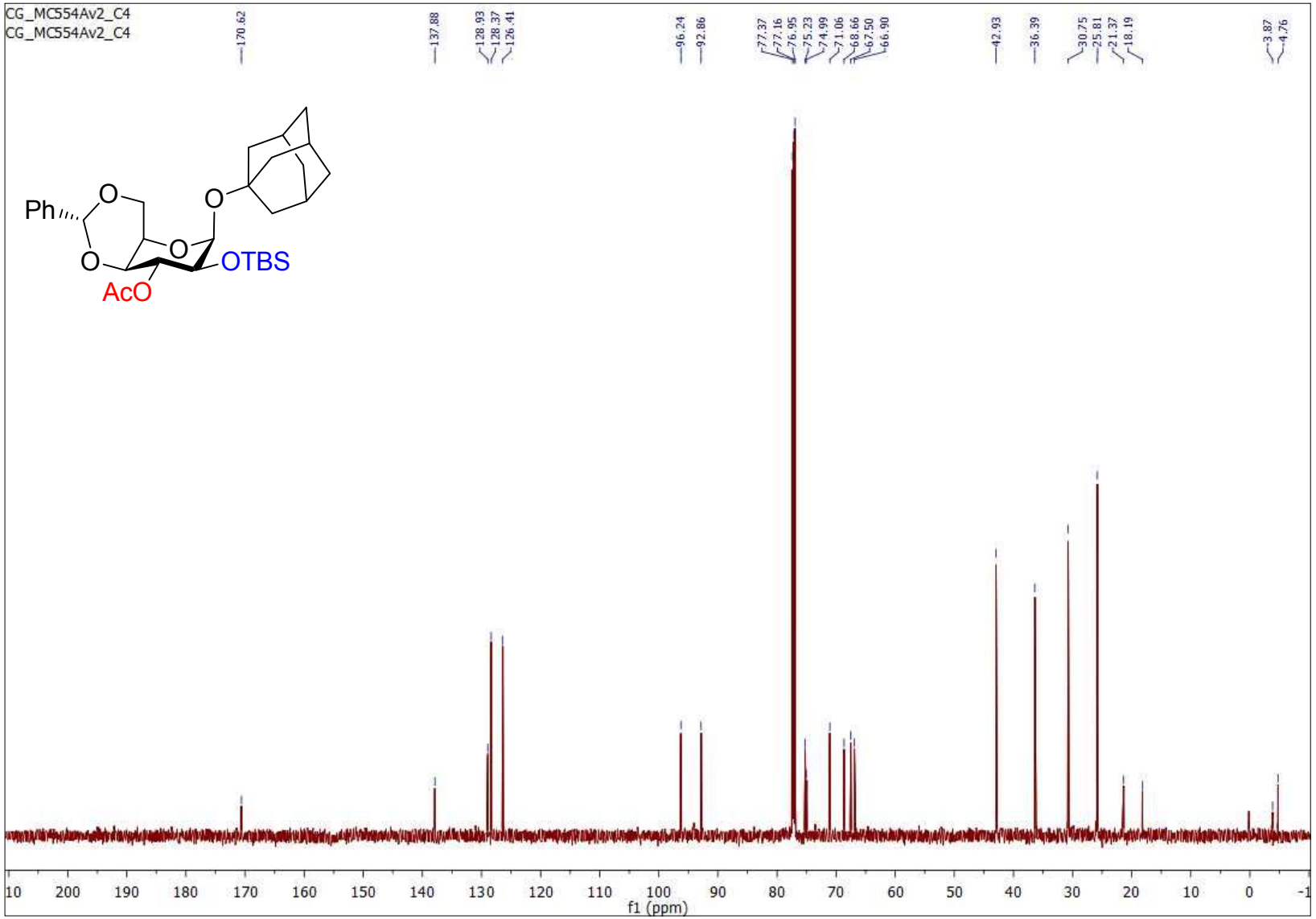


Figure S74. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (15b)**

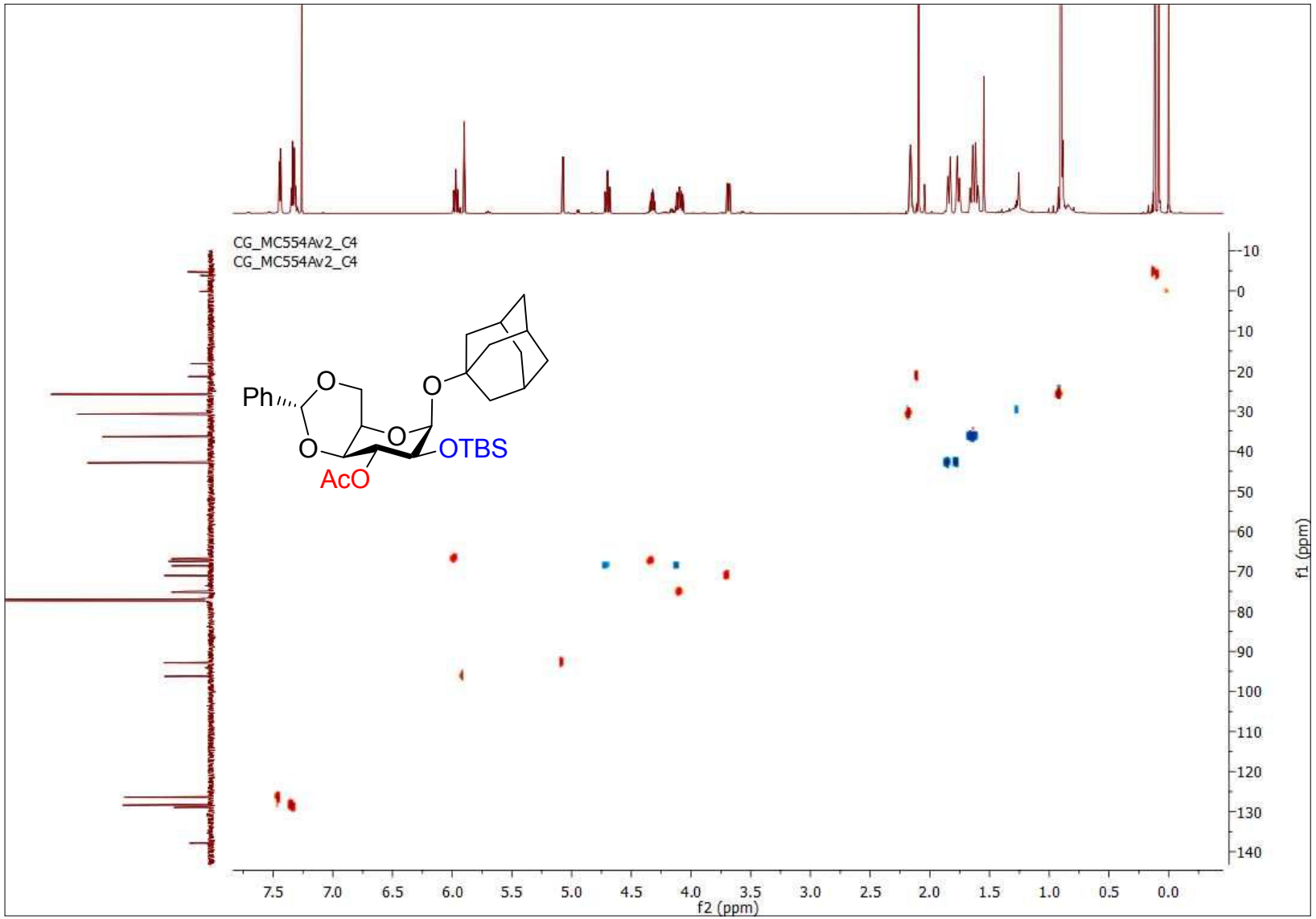


Figure S75. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (15b)**

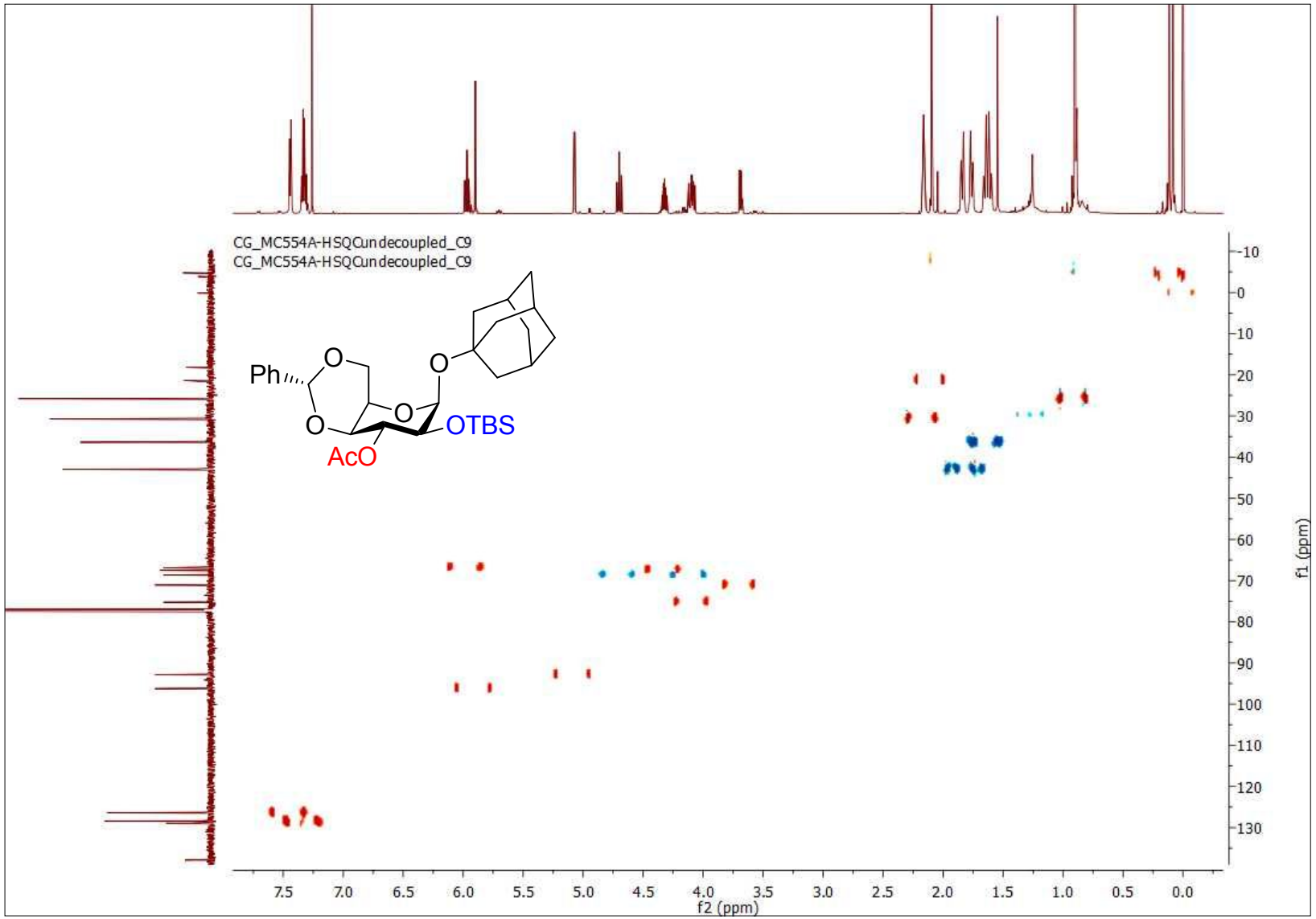


Figure S76. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (15c)**

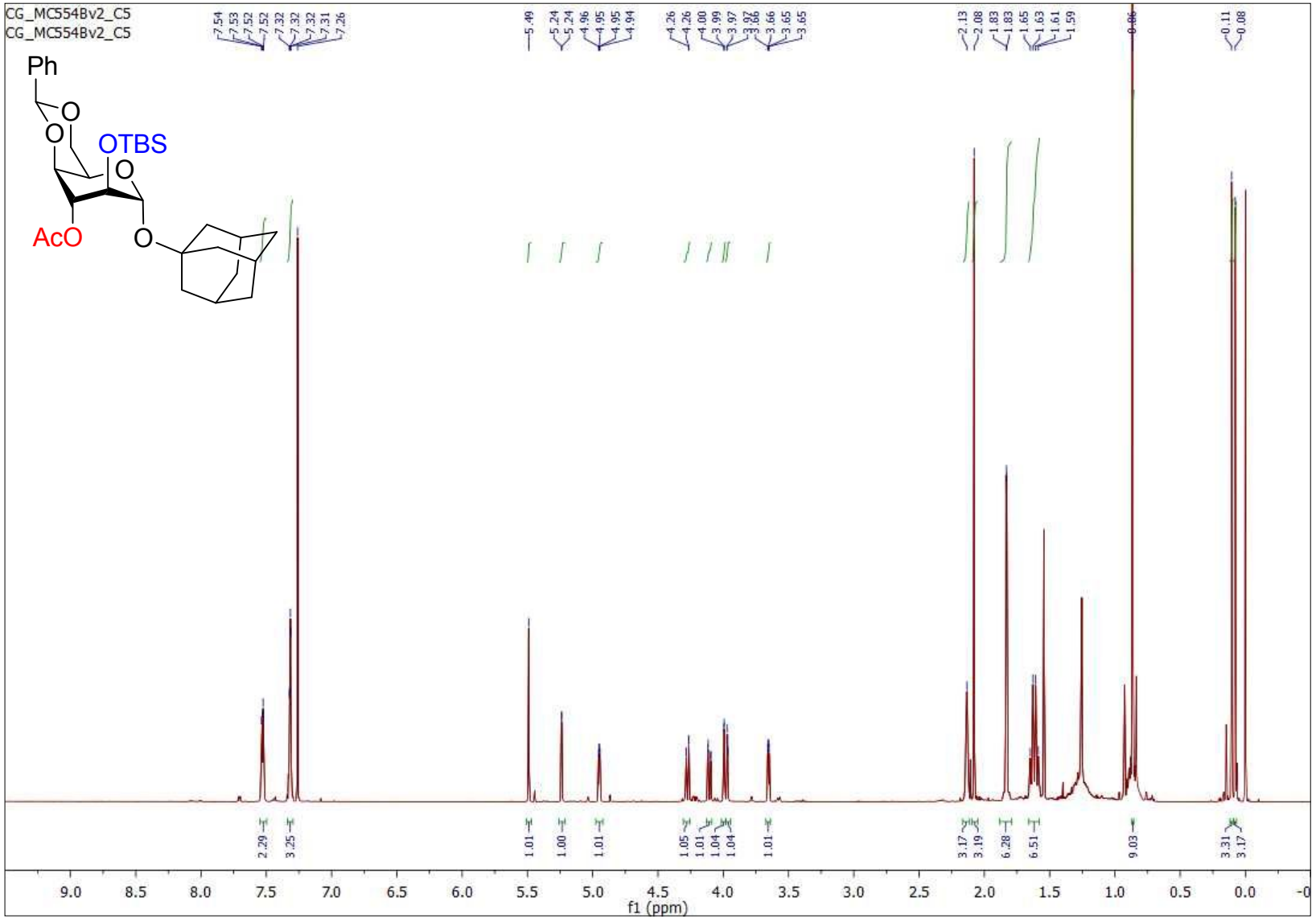


Figure S77. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (15c)**

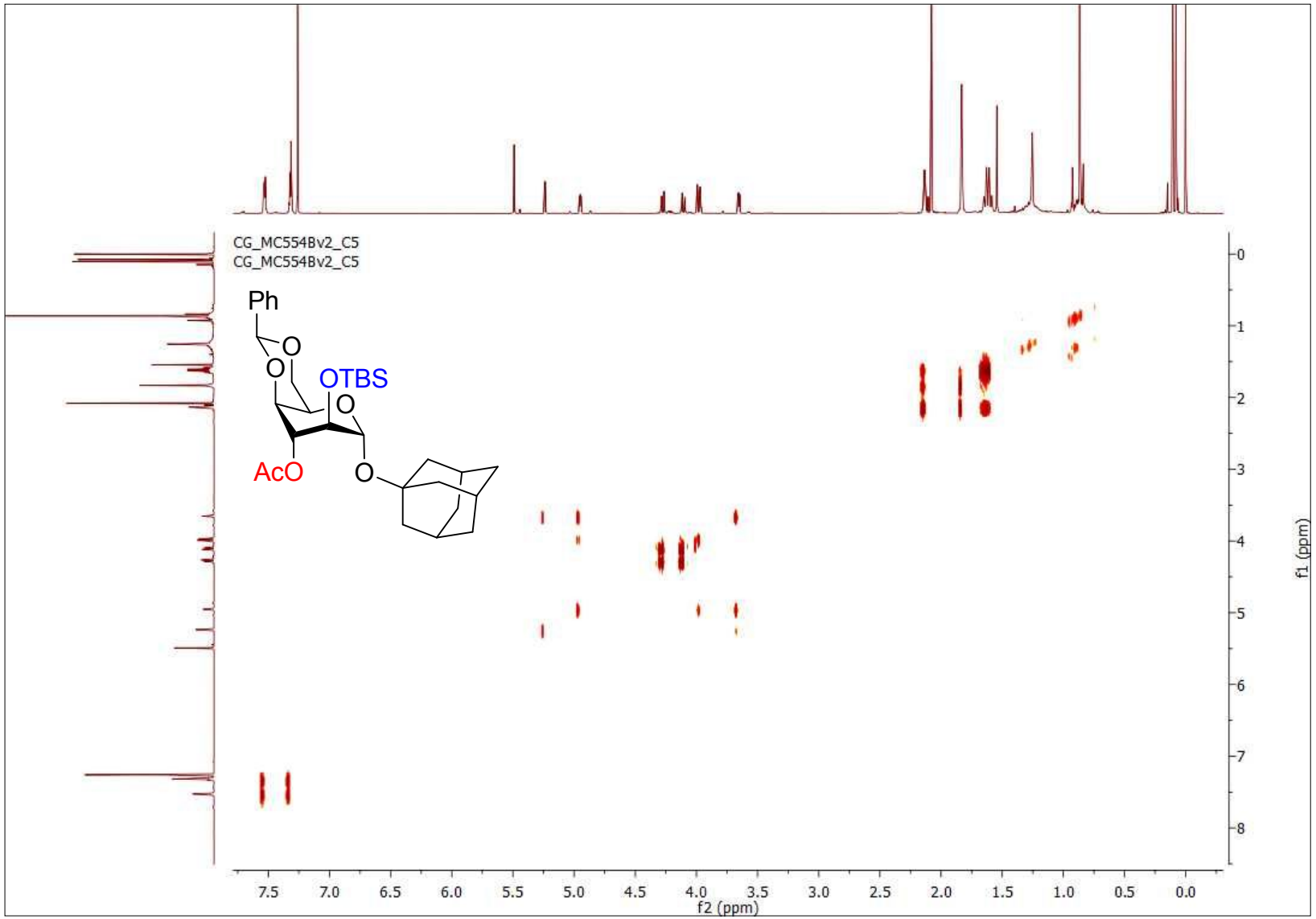


Figure S78. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (15c)**

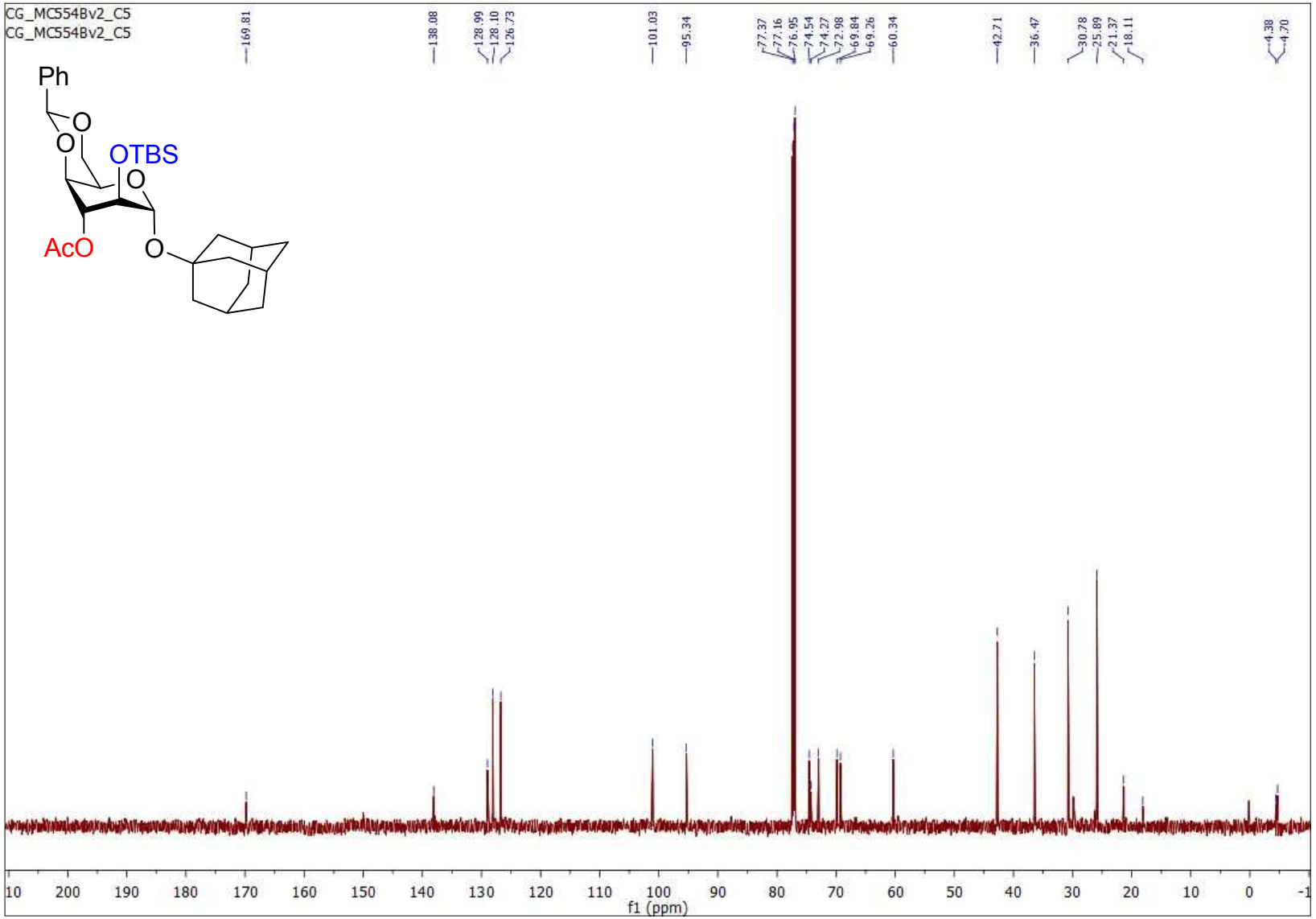


Figure S79. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (15c)**

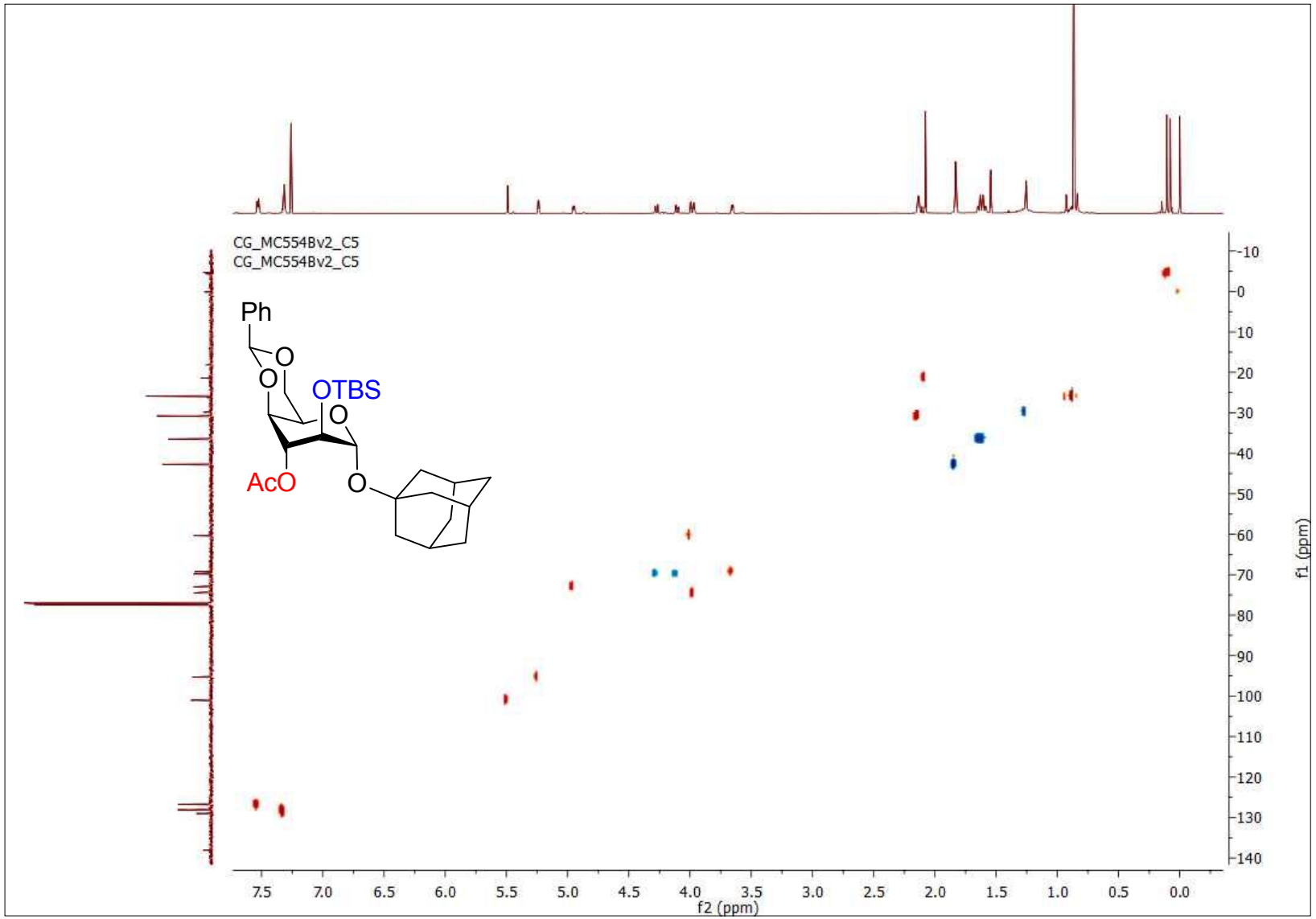


Figure S80. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(1-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (15c)**

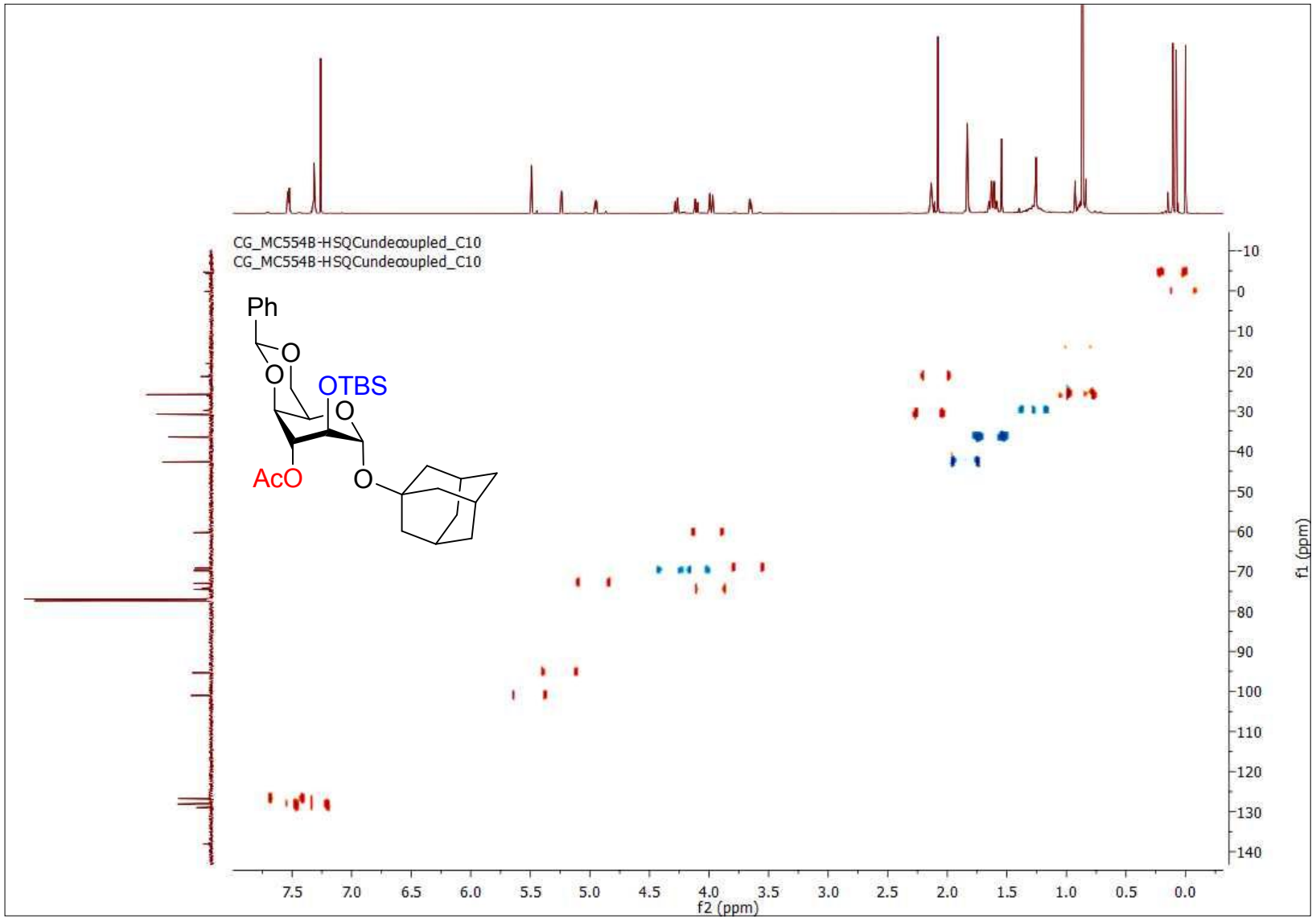


Figure S81. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (16a)**

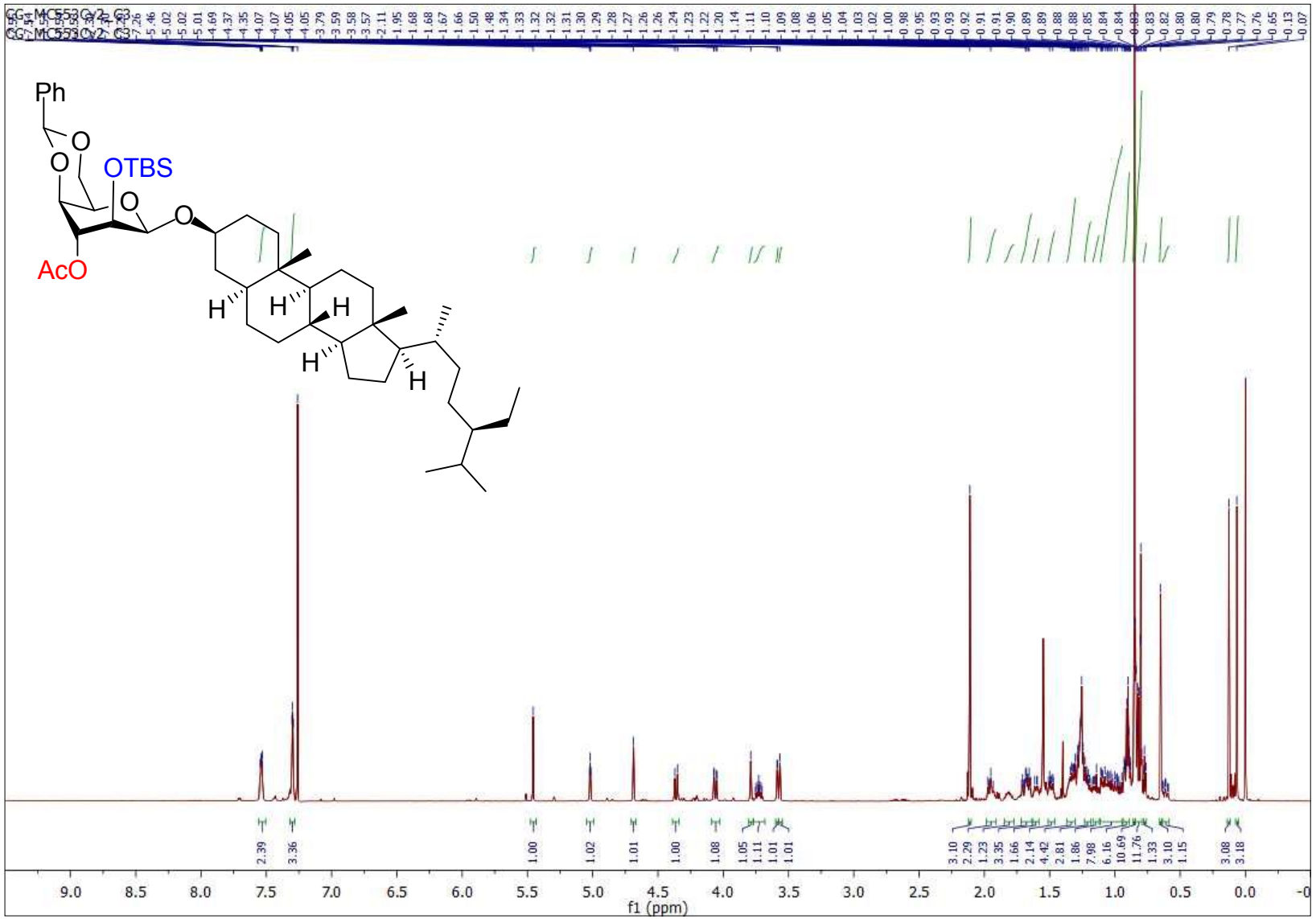


Figure S82. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (16a)**

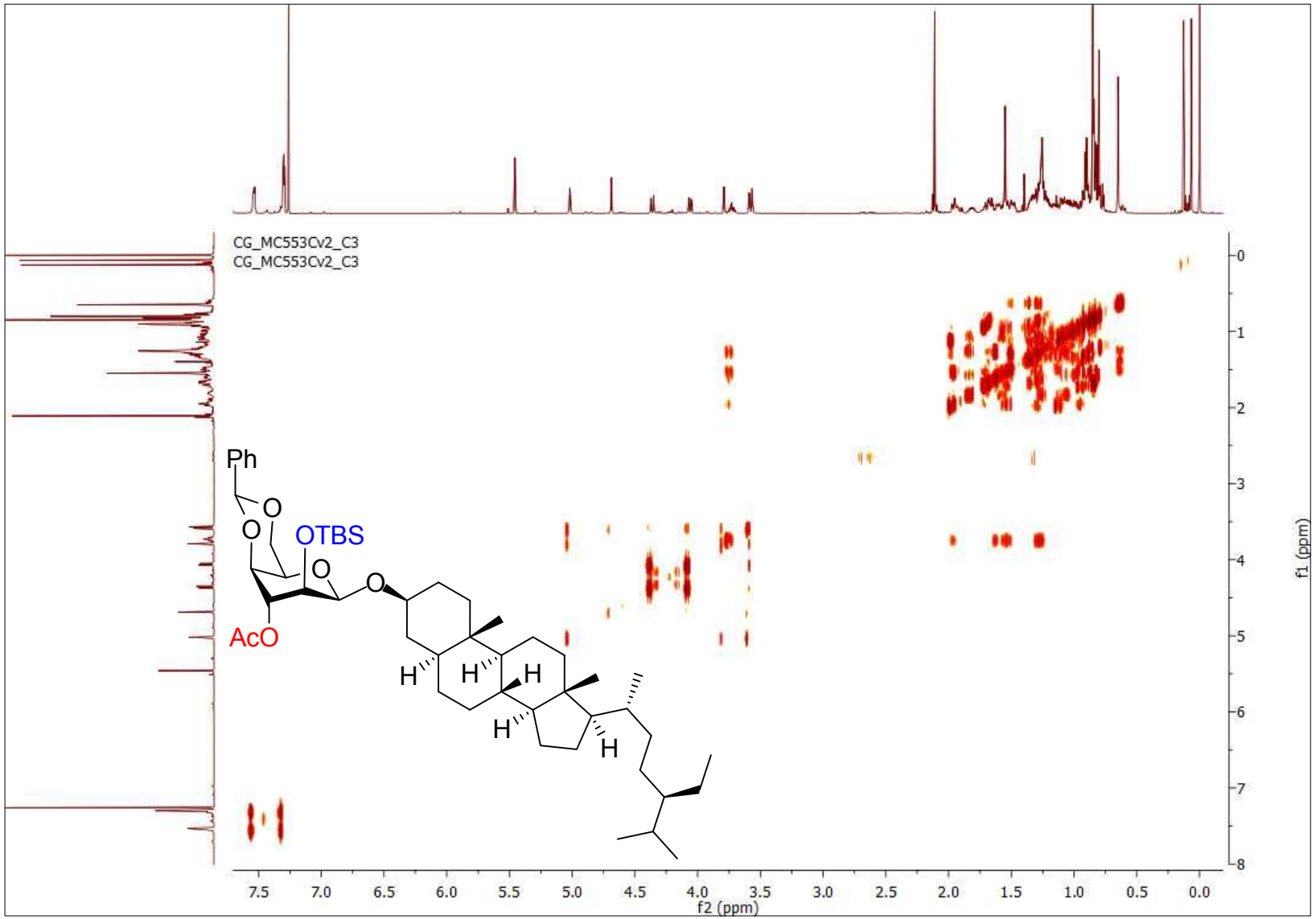


Figure S83. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (16a)**

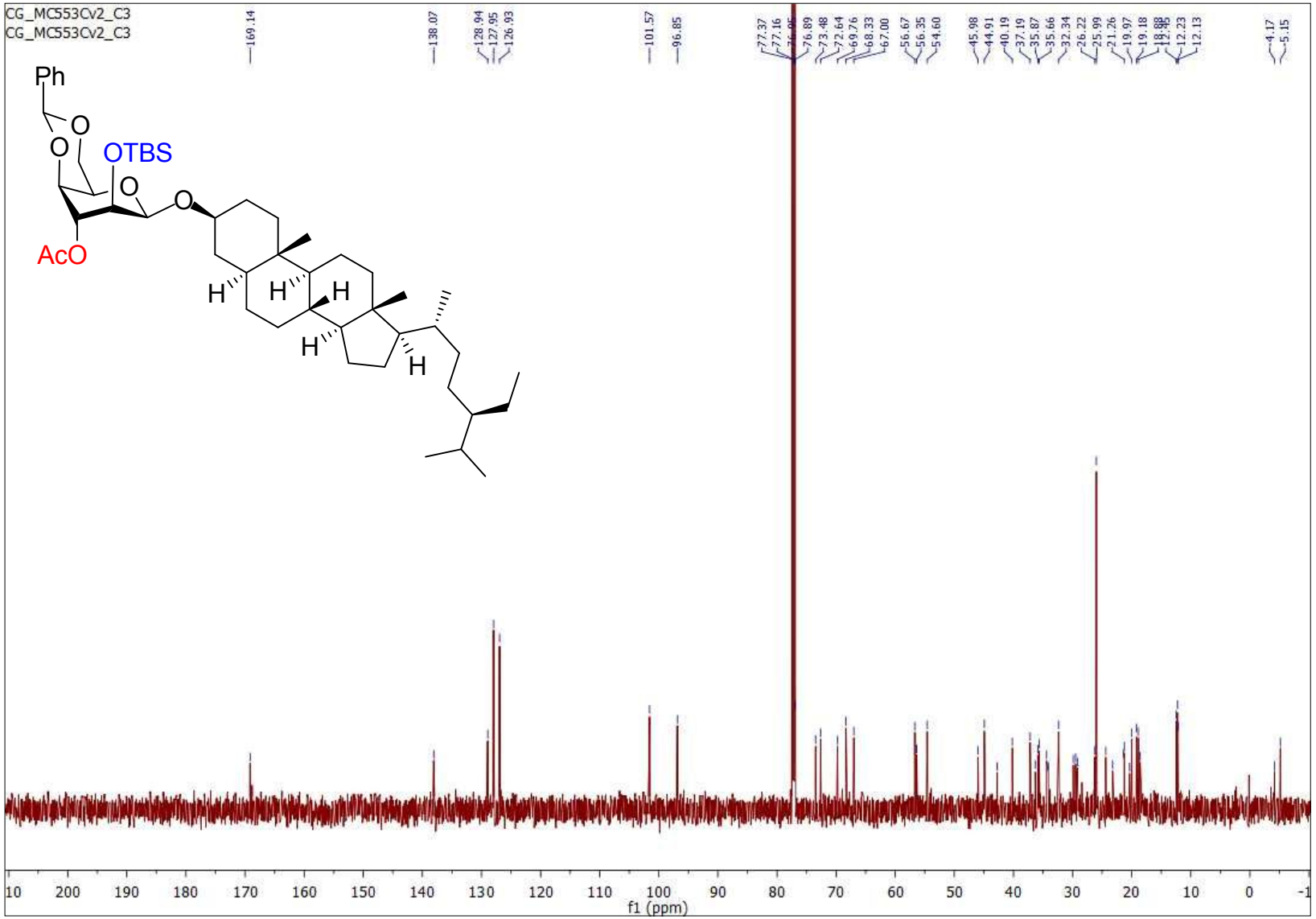


Figure S84. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (16a)**

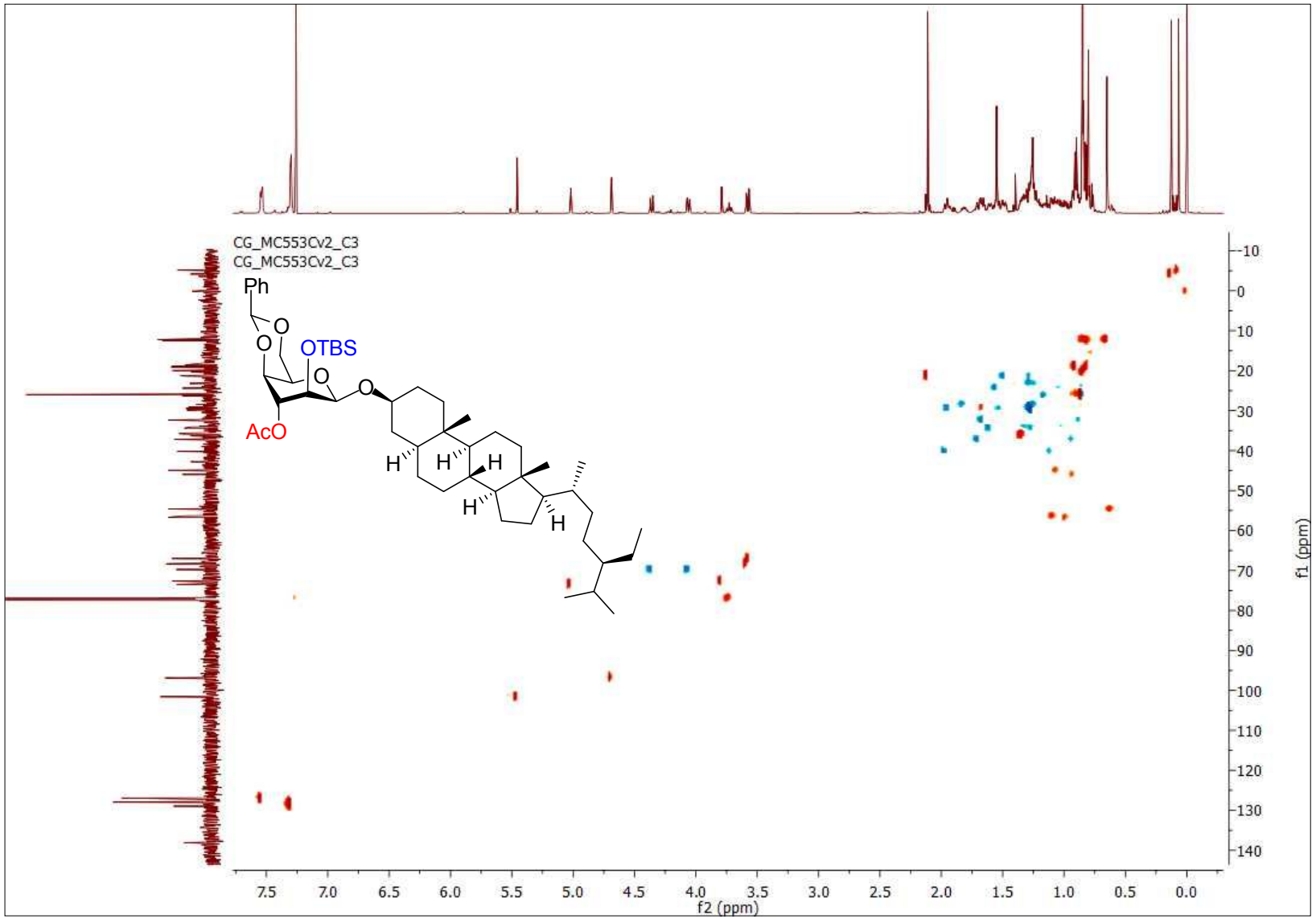


Figure S85. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (16a)**

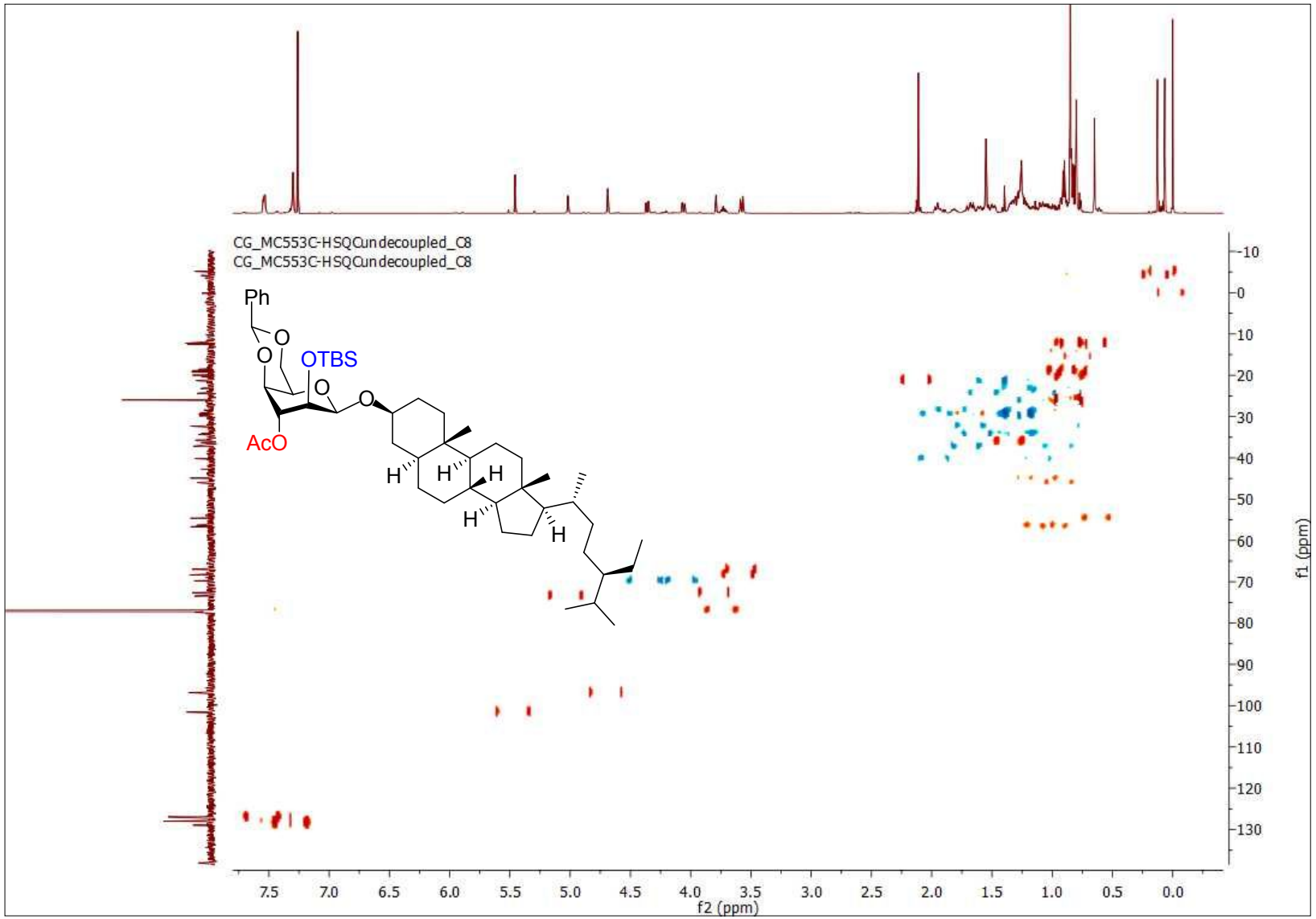


Figure S86. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (16b)**

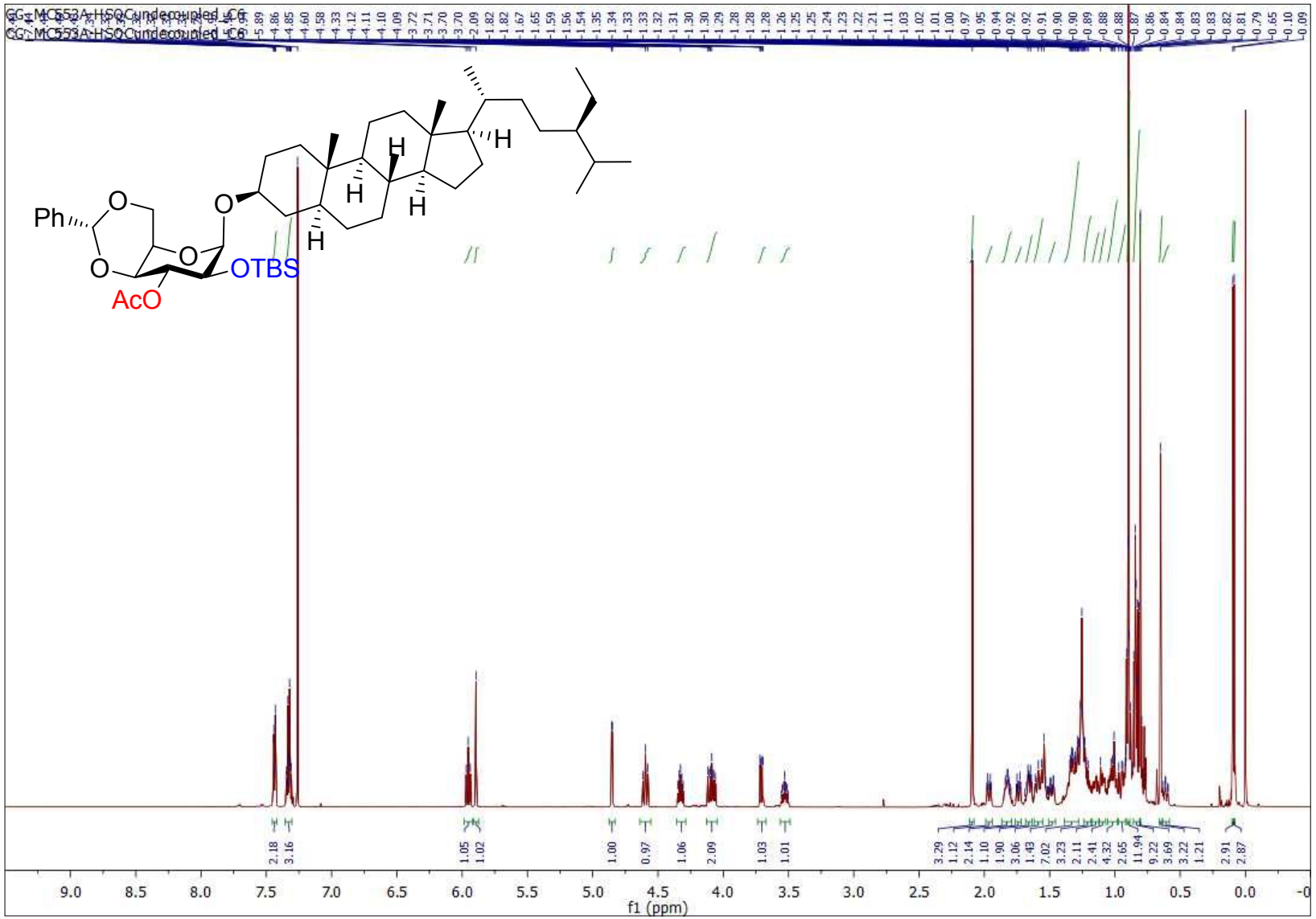


Figure S87. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (16b)**

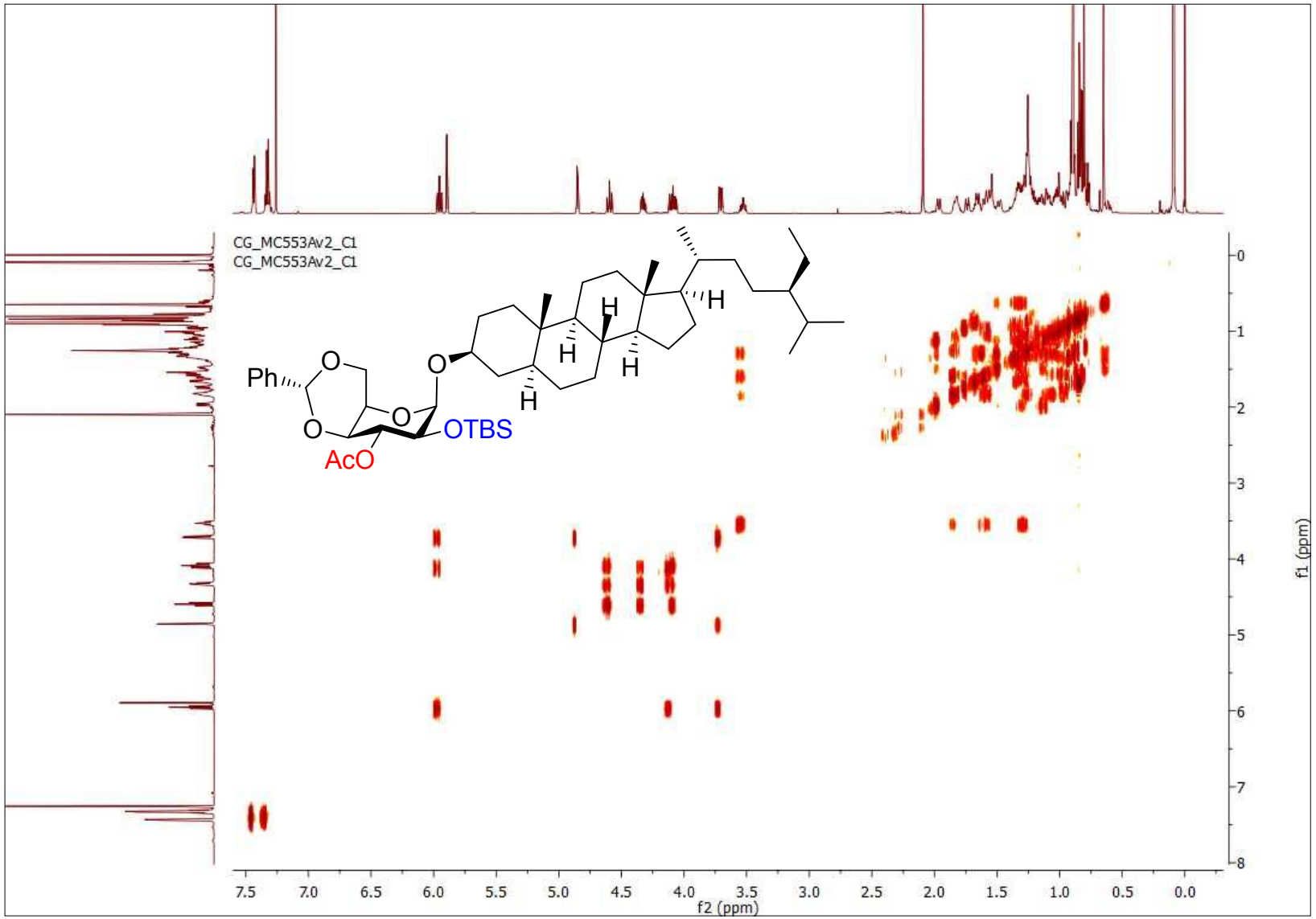


Figure S88. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (16b)**

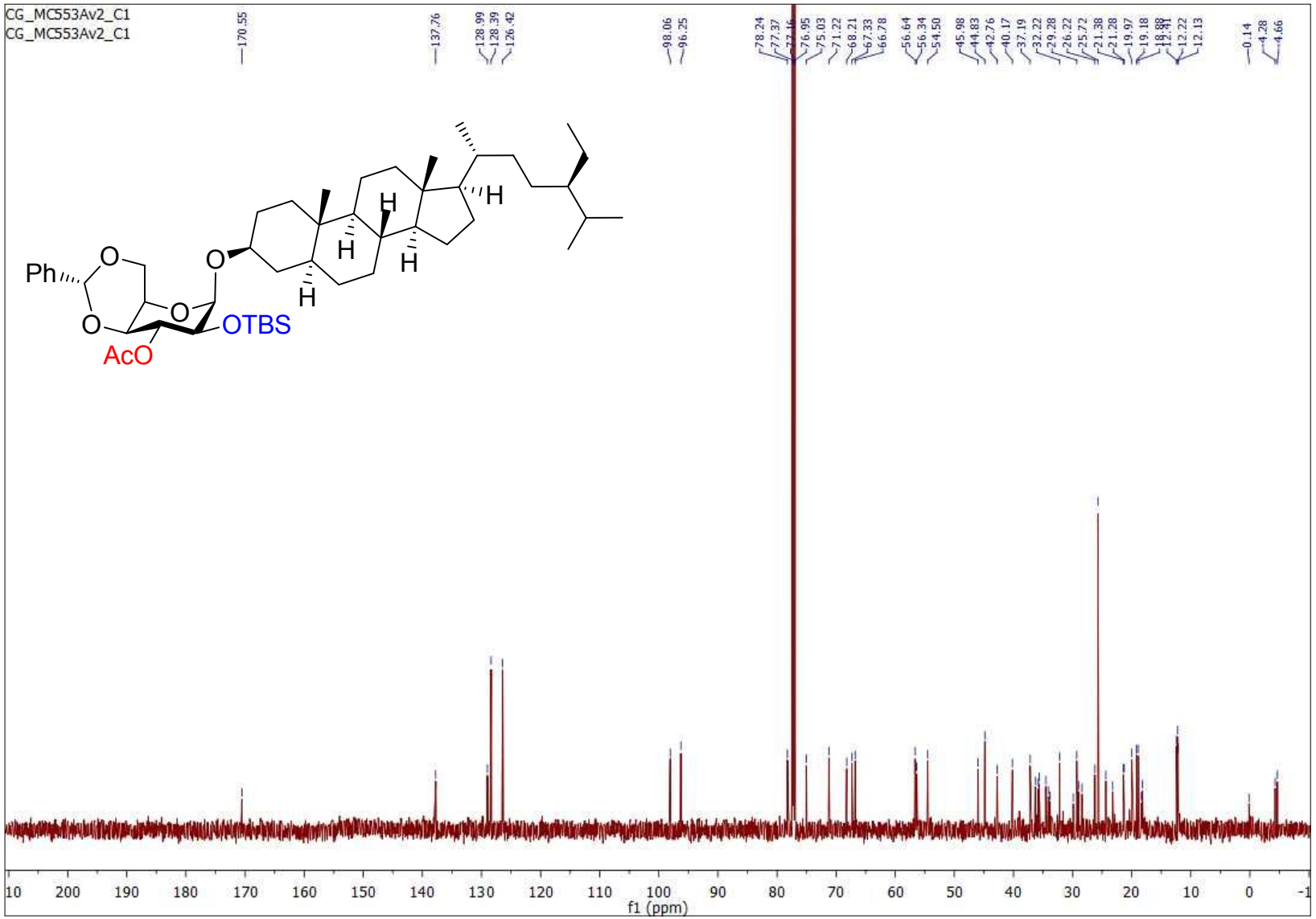


Figure S89. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (16b)**

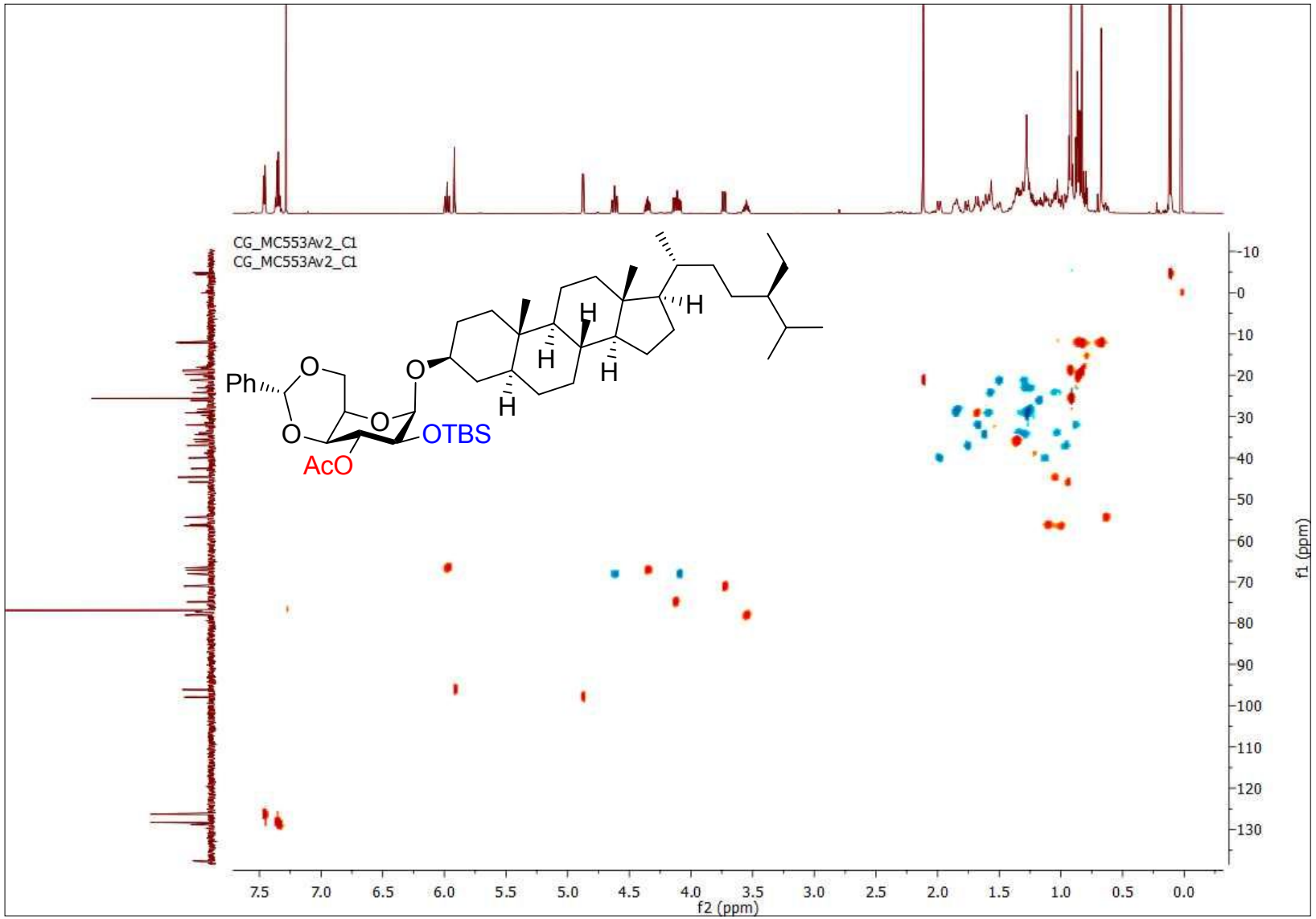


Figure S90. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (16b)**

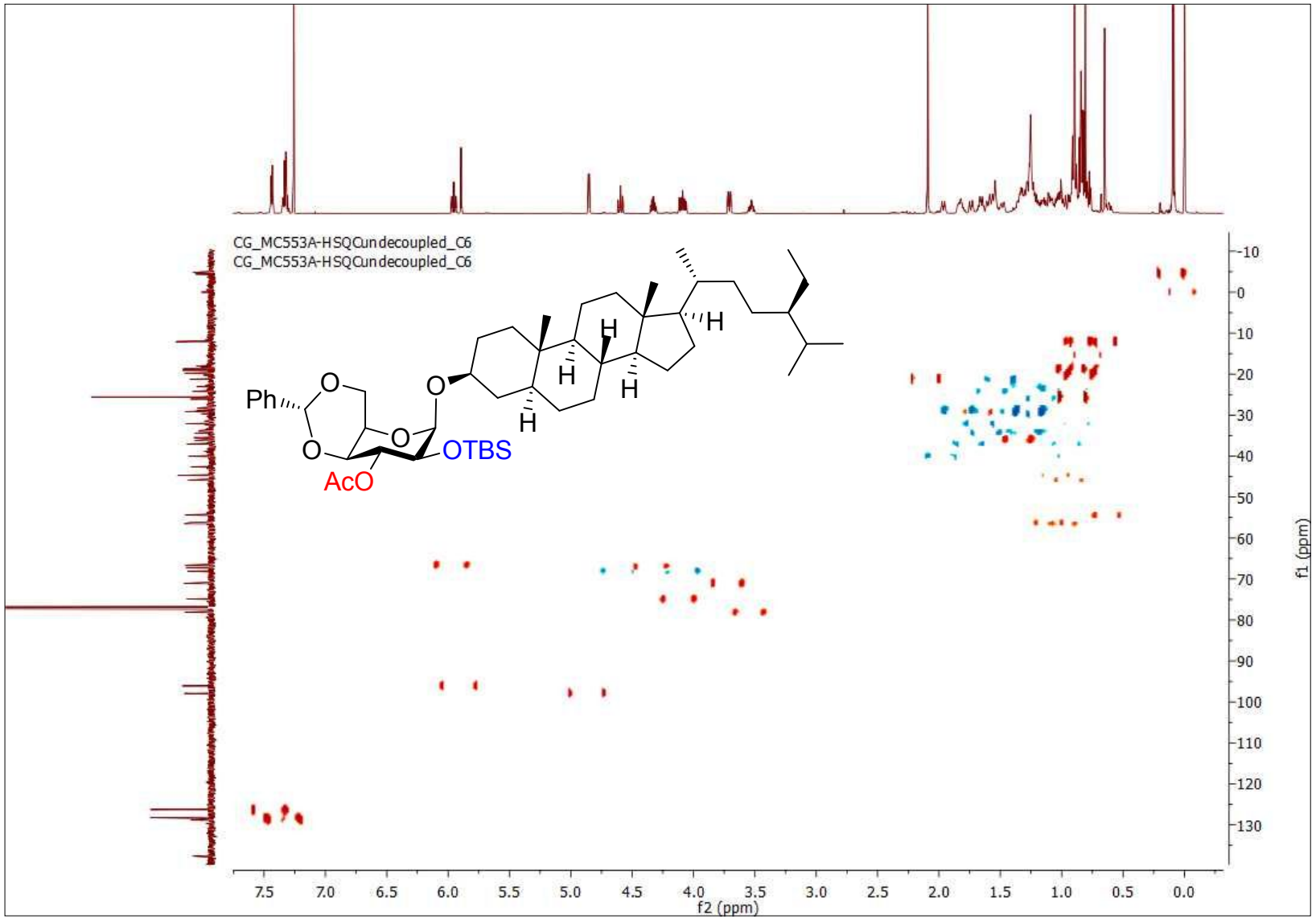


Figure S91. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (16c)**

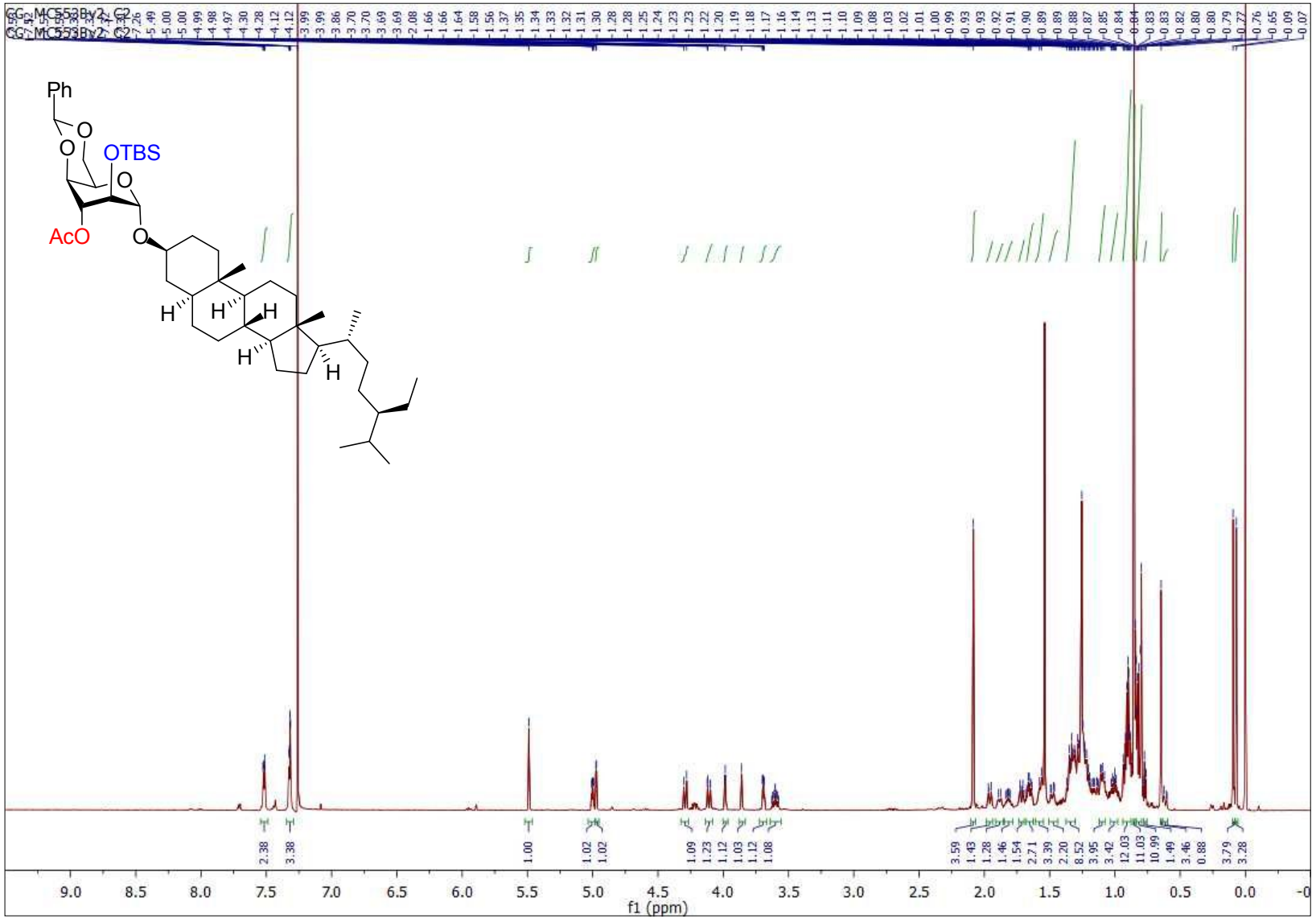


Figure S92. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (16c)**

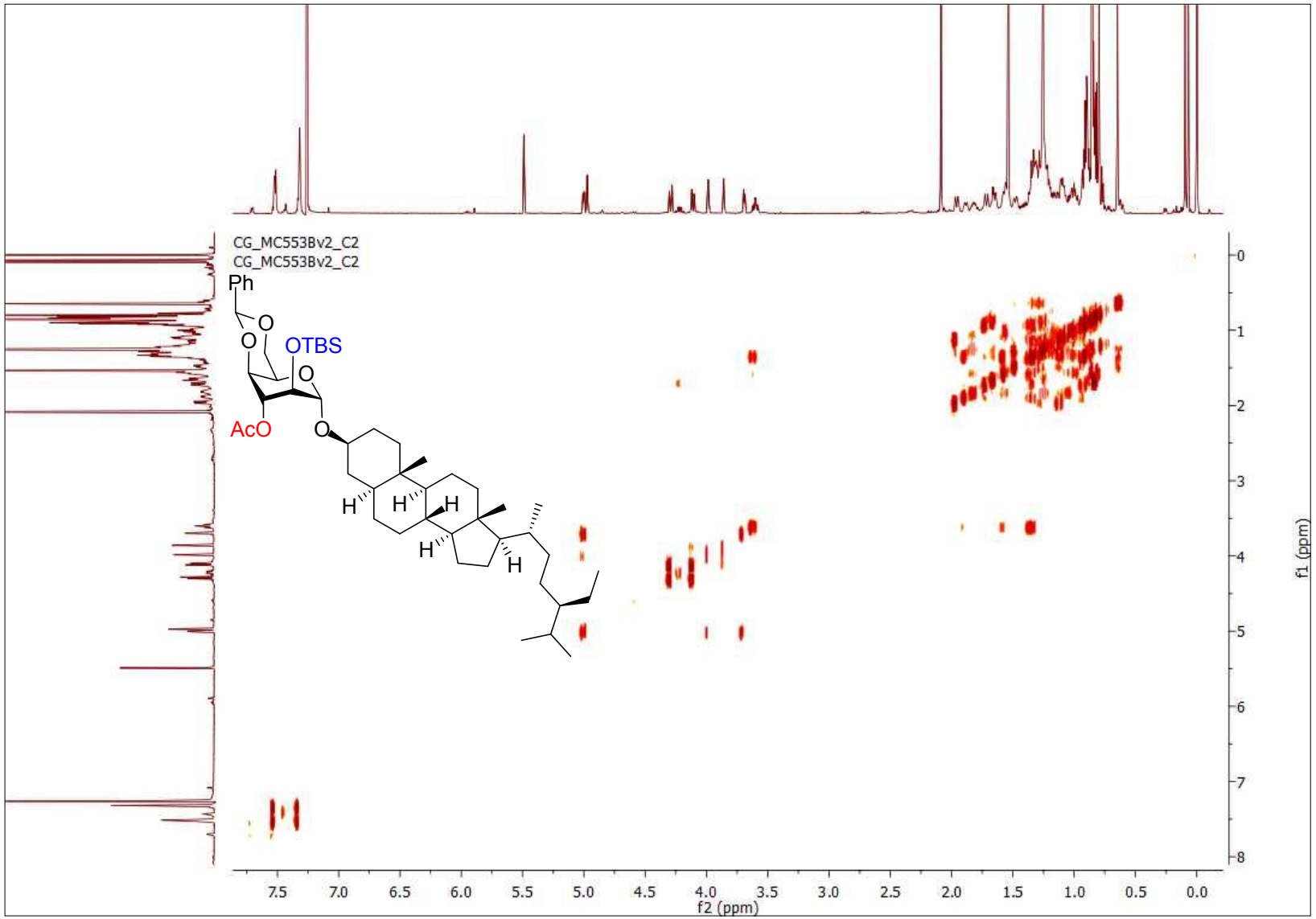


Figure S93. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (16c)**

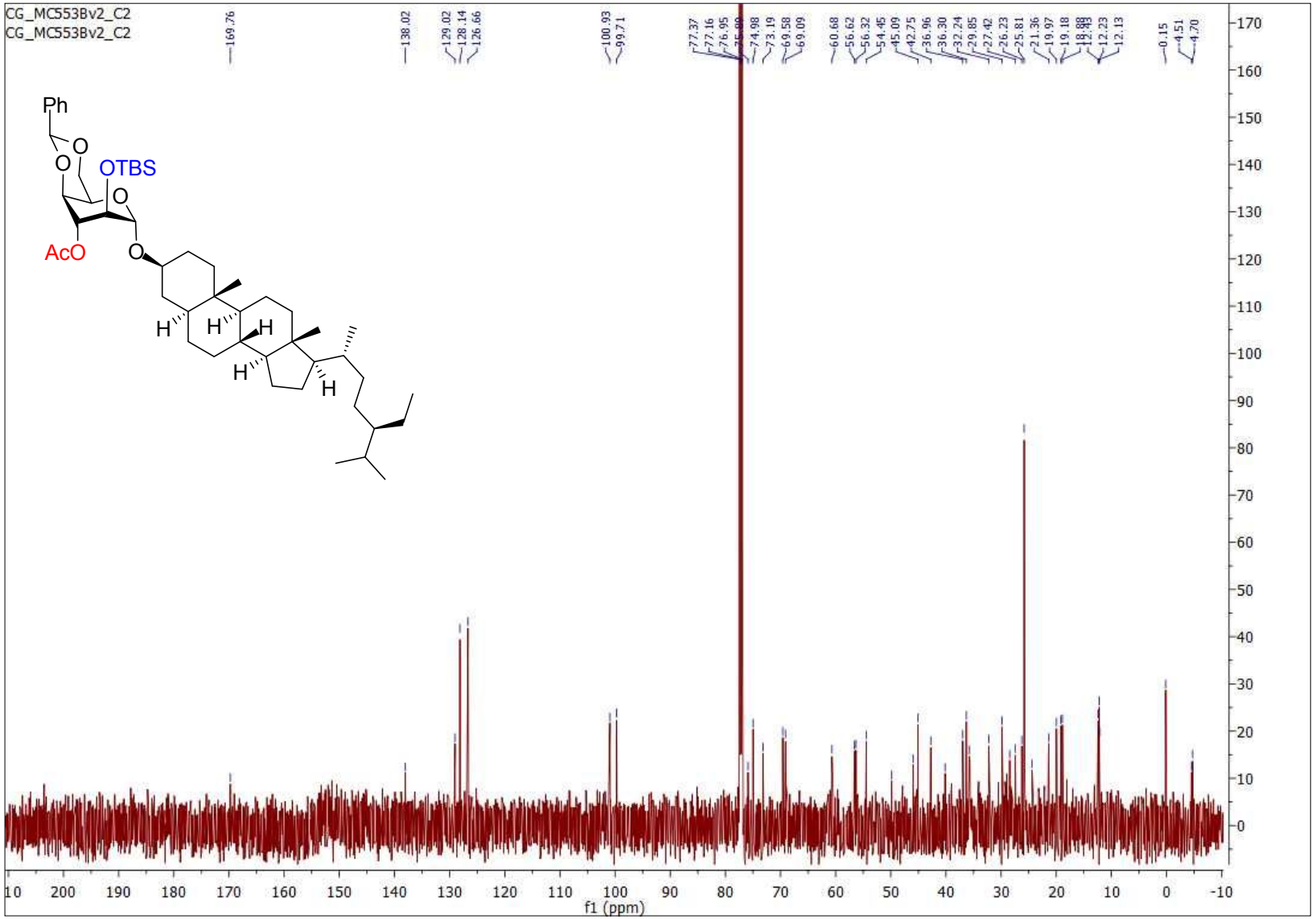


Figure S94. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (16c)**

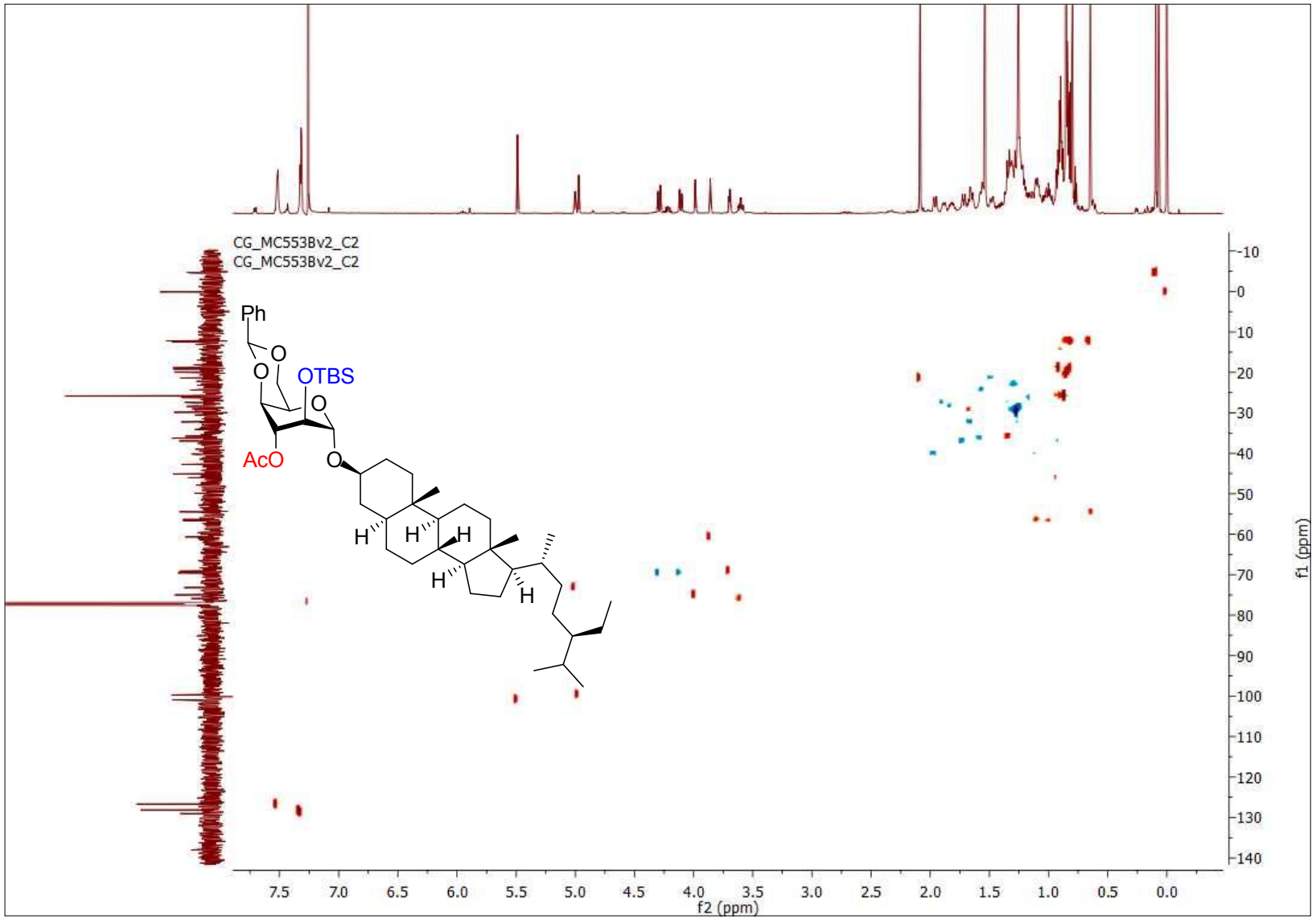


Figure S95. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(3-stigmastanyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (16c)**

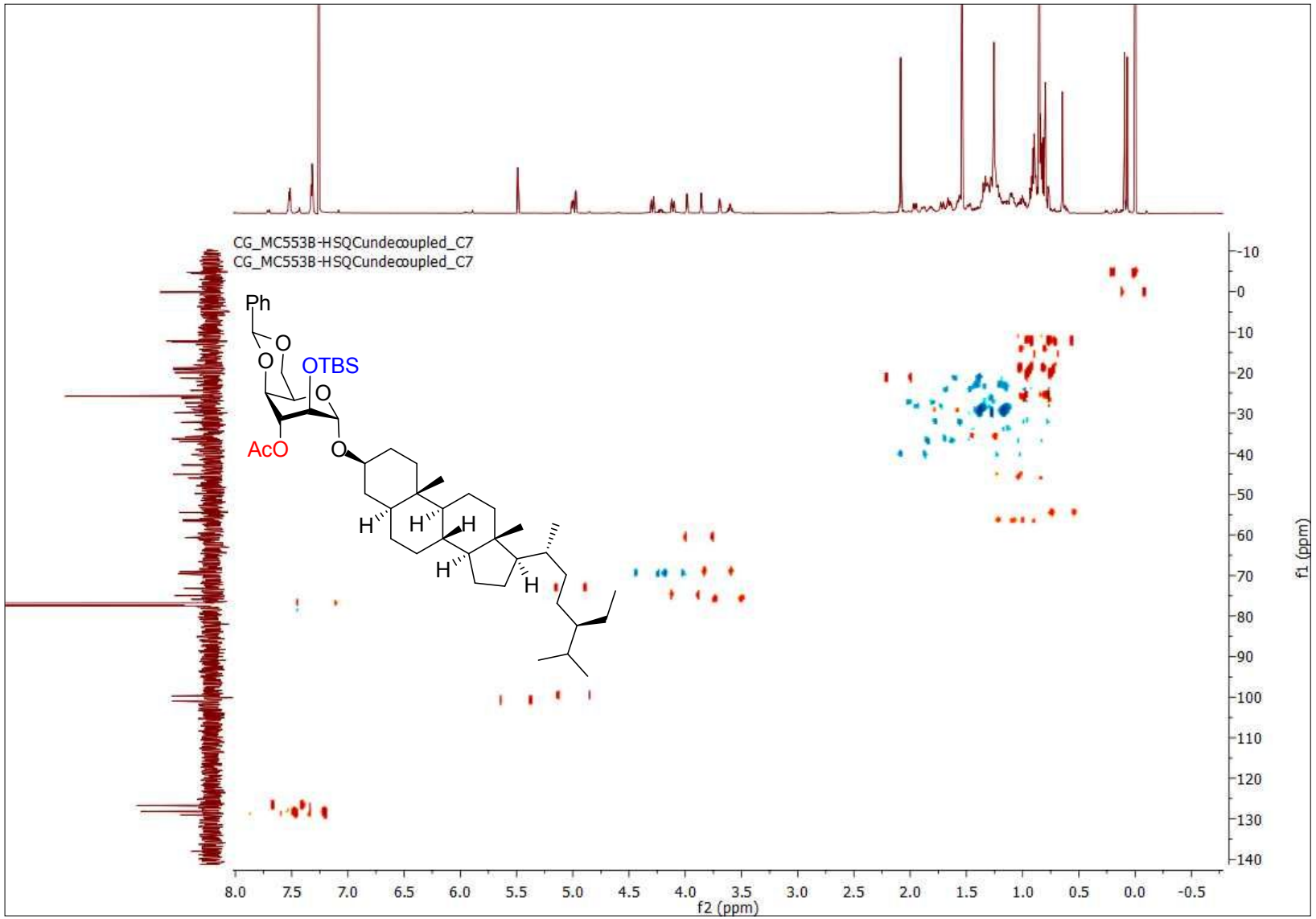


Figure S96. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*β*-D-idopyranoside (17a)**

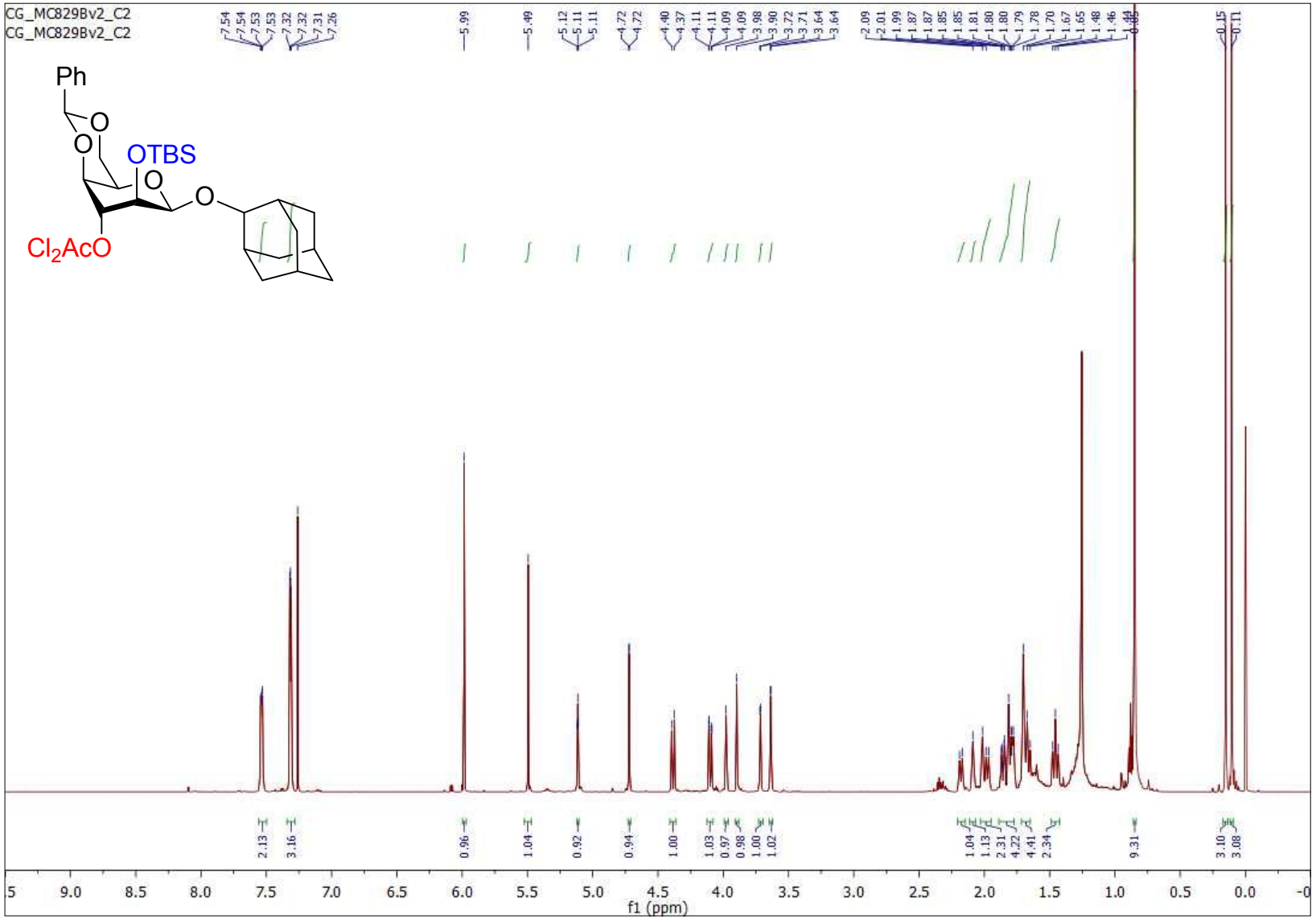


Figure S97. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*β*-D-idopyranoside (17a)**

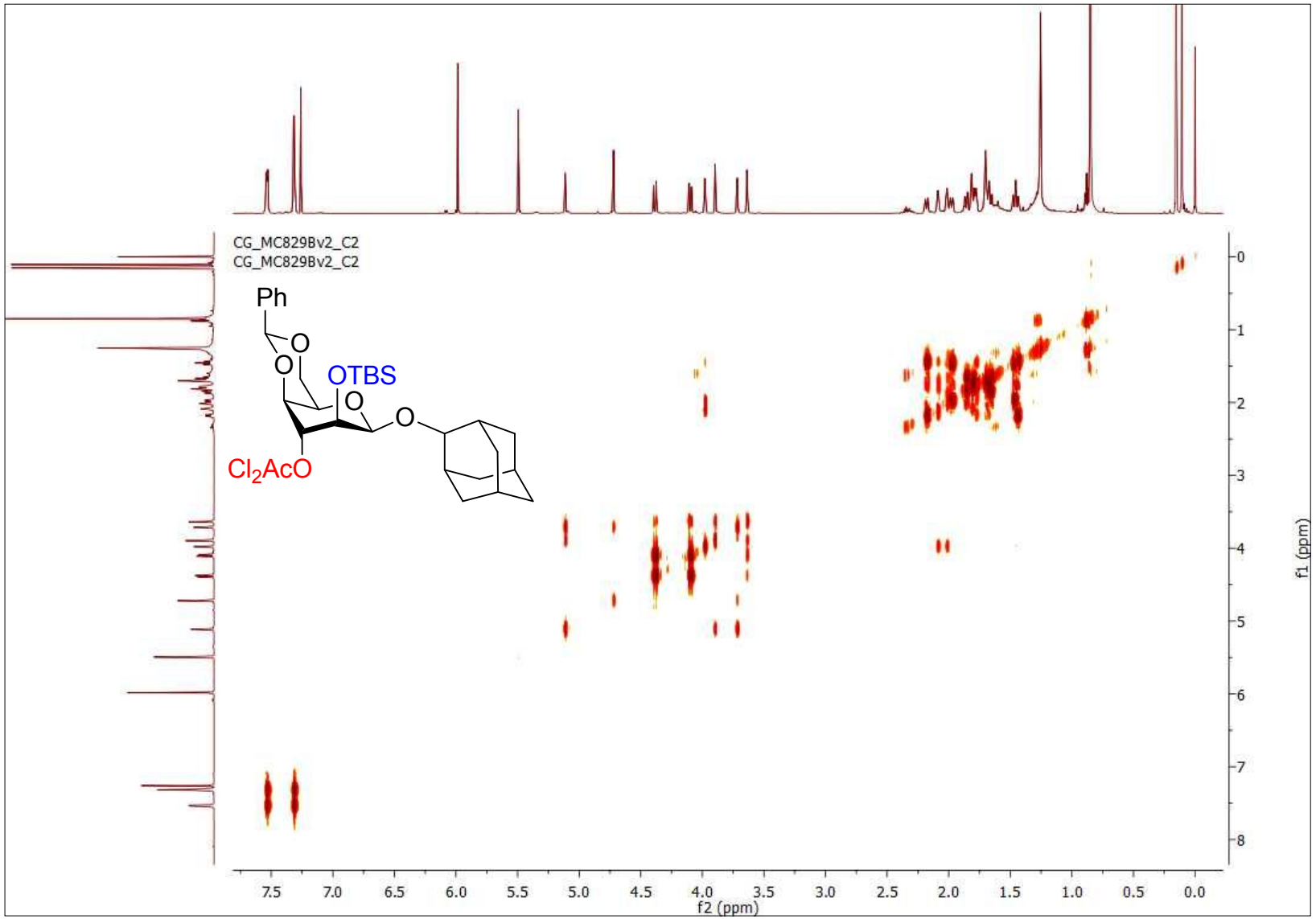


Figure S98. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*β*-D-idopyranoside (17a)**

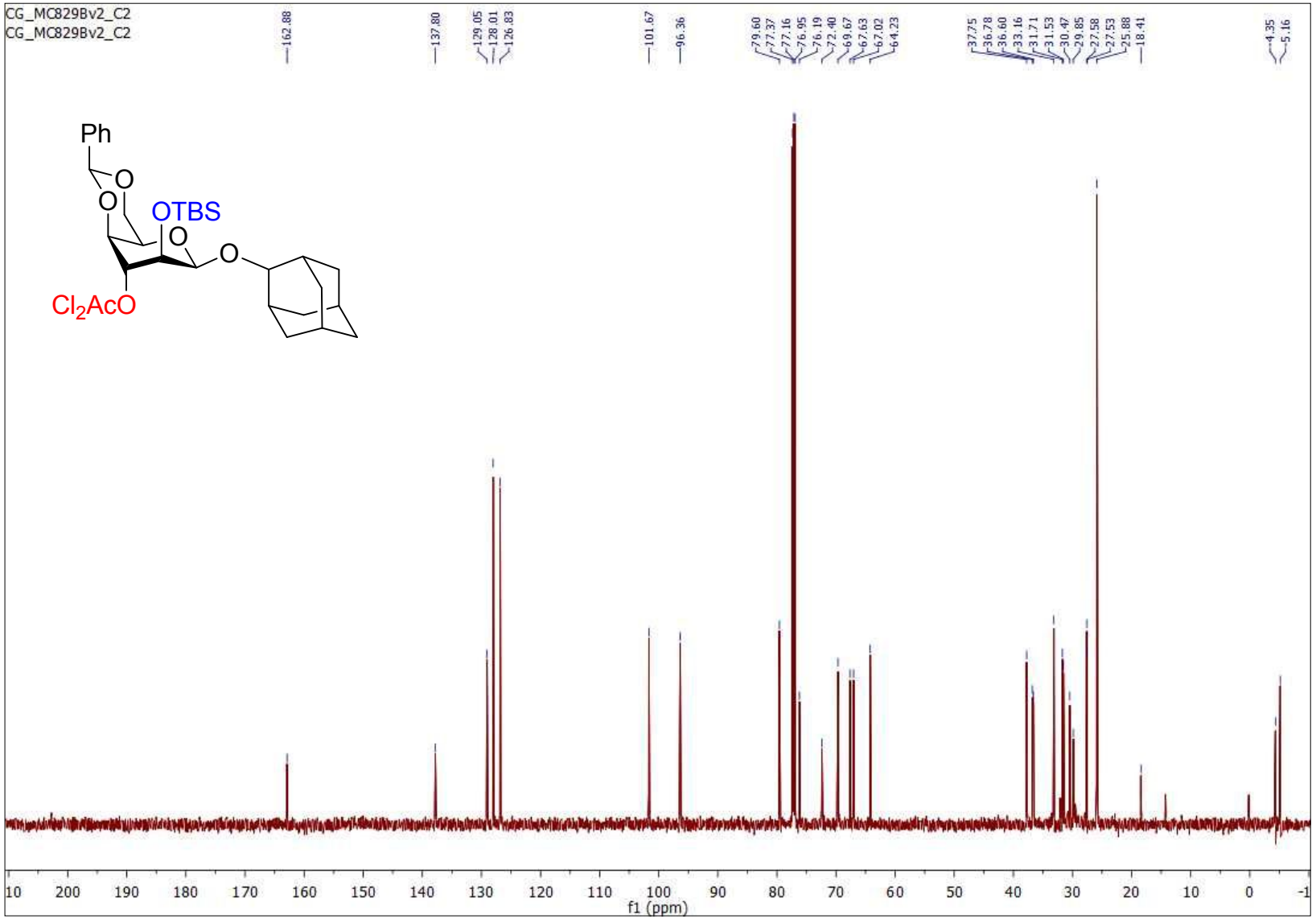


Figure S99. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*β*-D-idopyranoside (17a)**

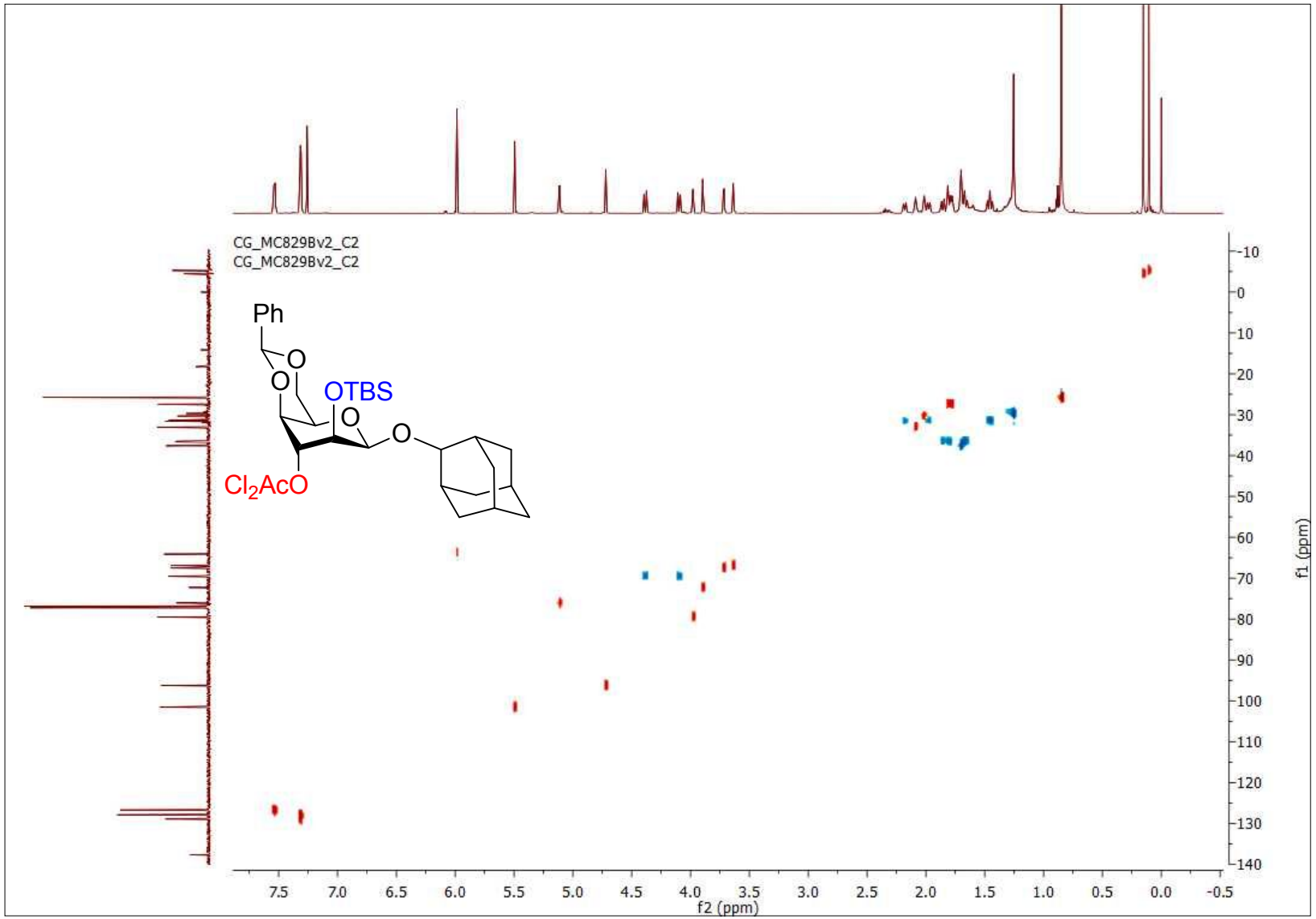


Figure S100. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*β*-D-idopyranoside (17a)**

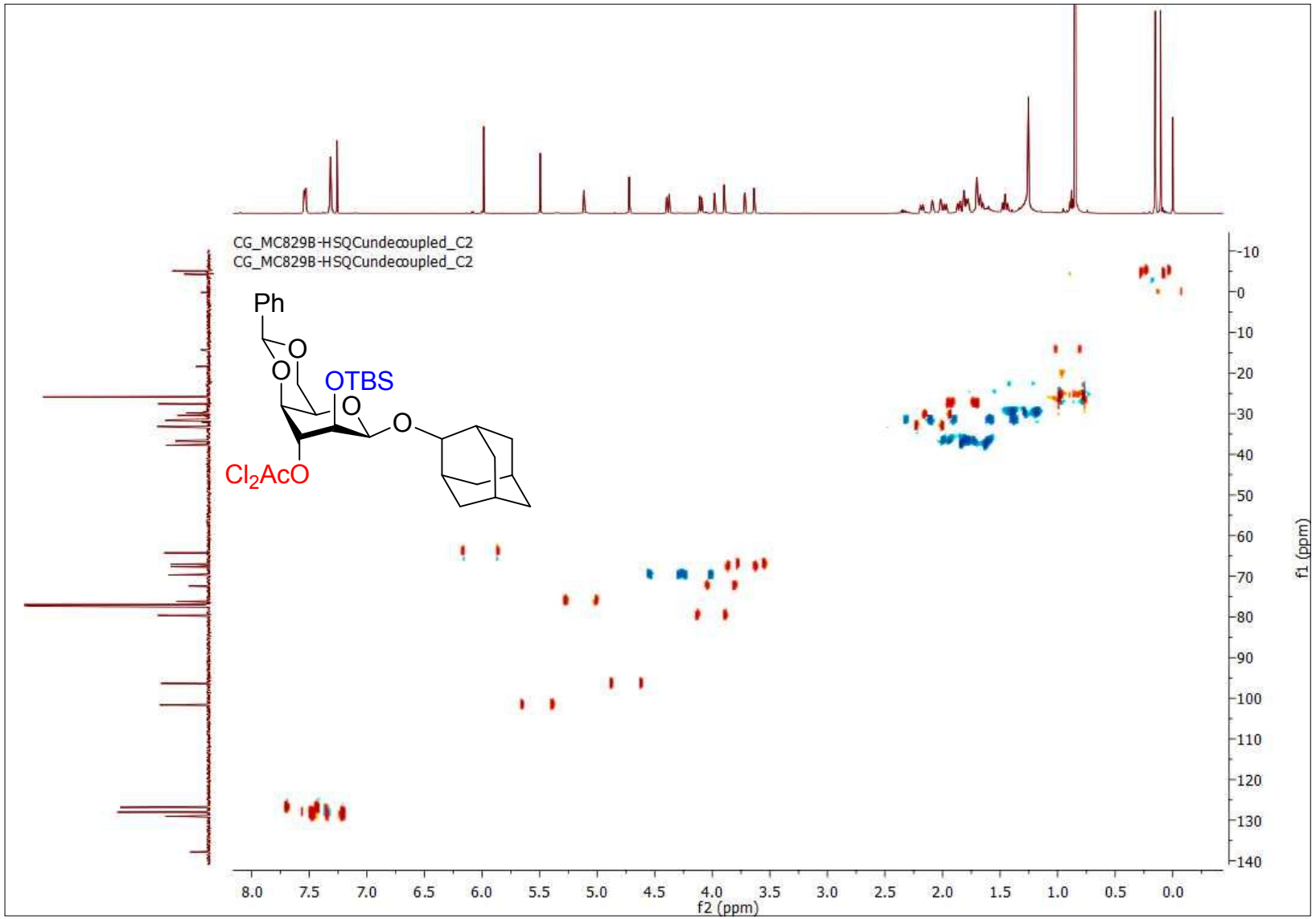


Figure S101. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*β*-D-idopyranoside (17b)** and **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*α*-D-idopyranoside (17c)**

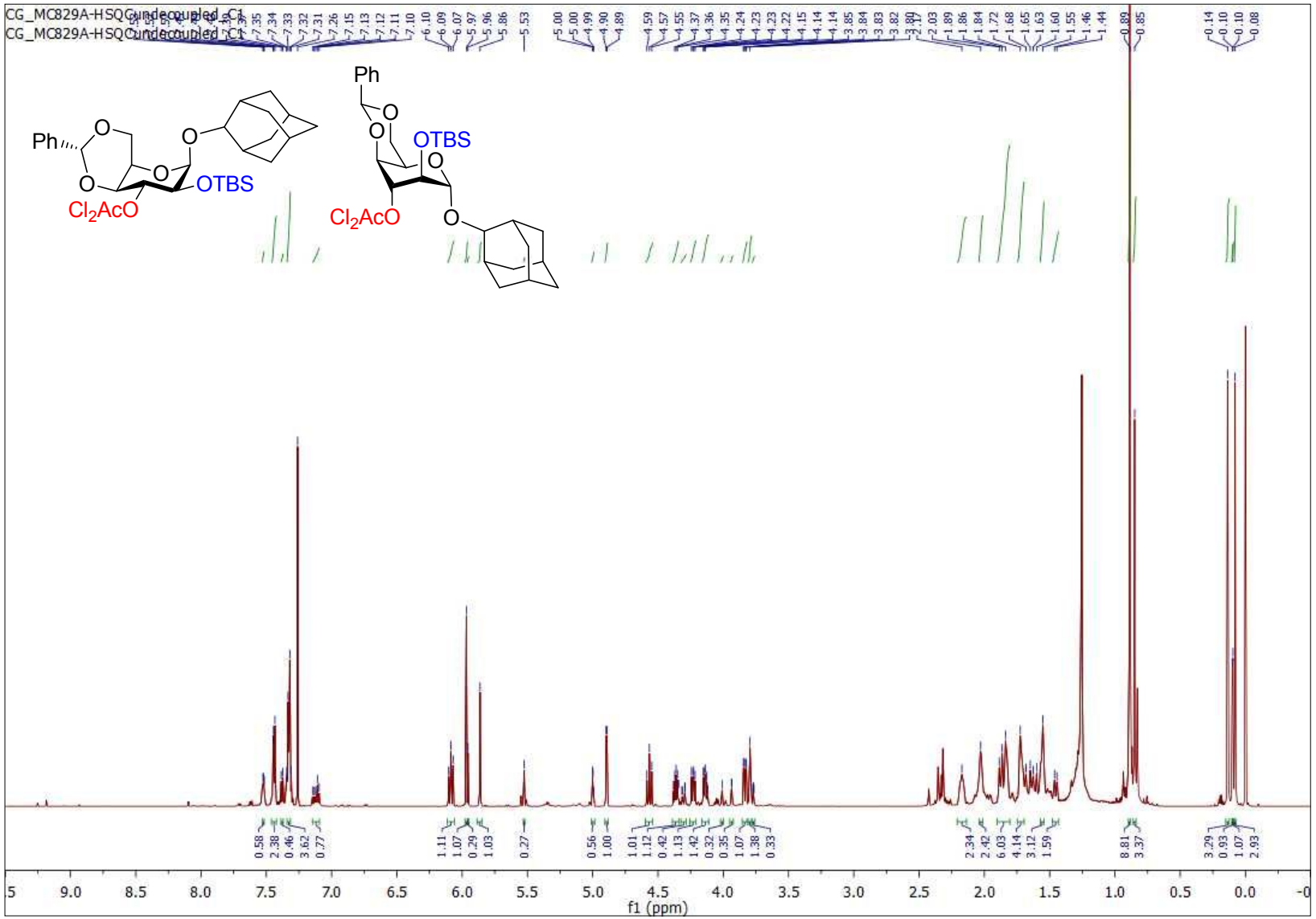


Figure S102. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*β*-D-idopyranoside (17b)** and **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*α*-D-idopyranoside (17c)**

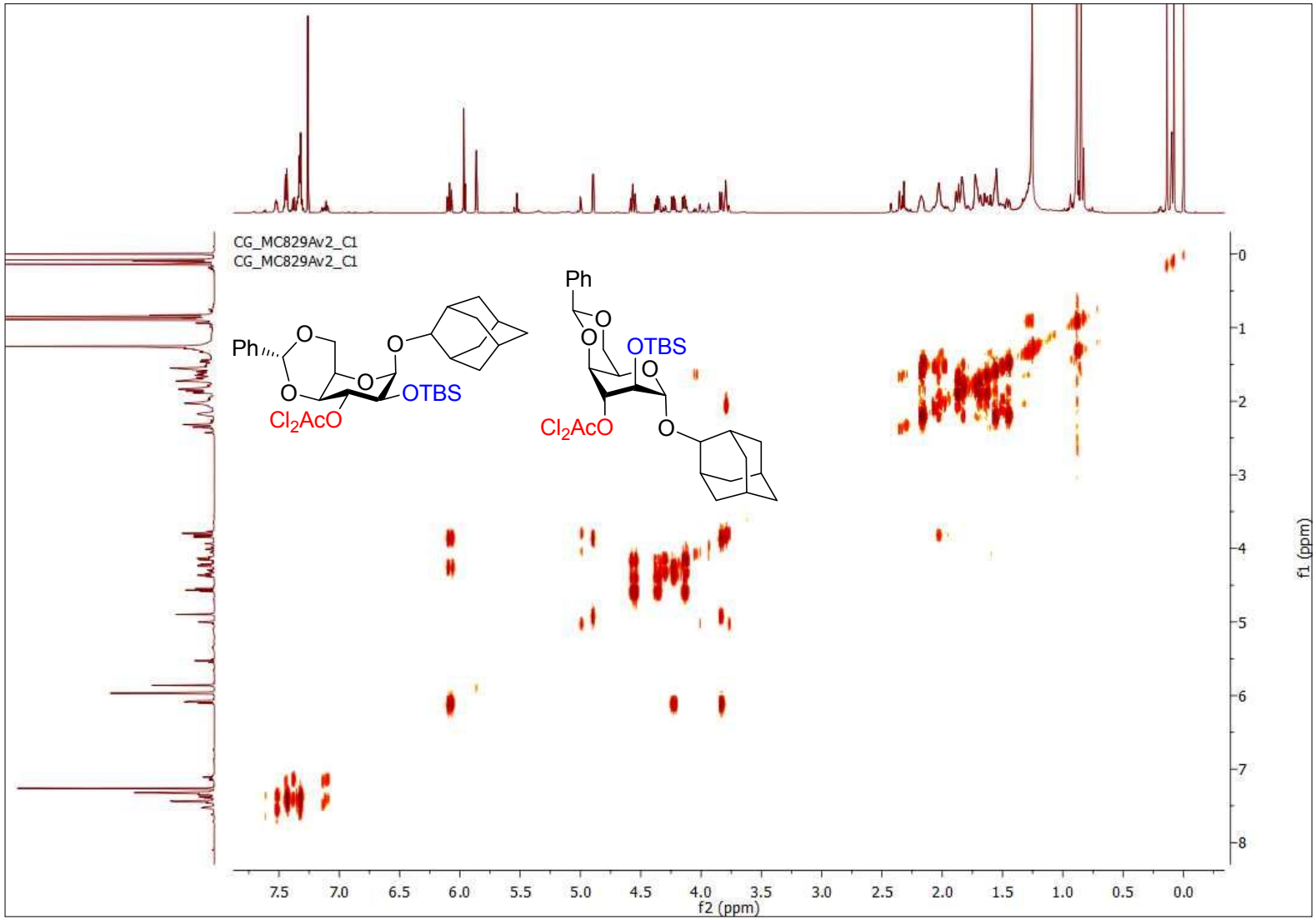


Figure S103. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*β*-D-idopyranoside (17b)** and **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*α*-D-idopyranoside (17c)**

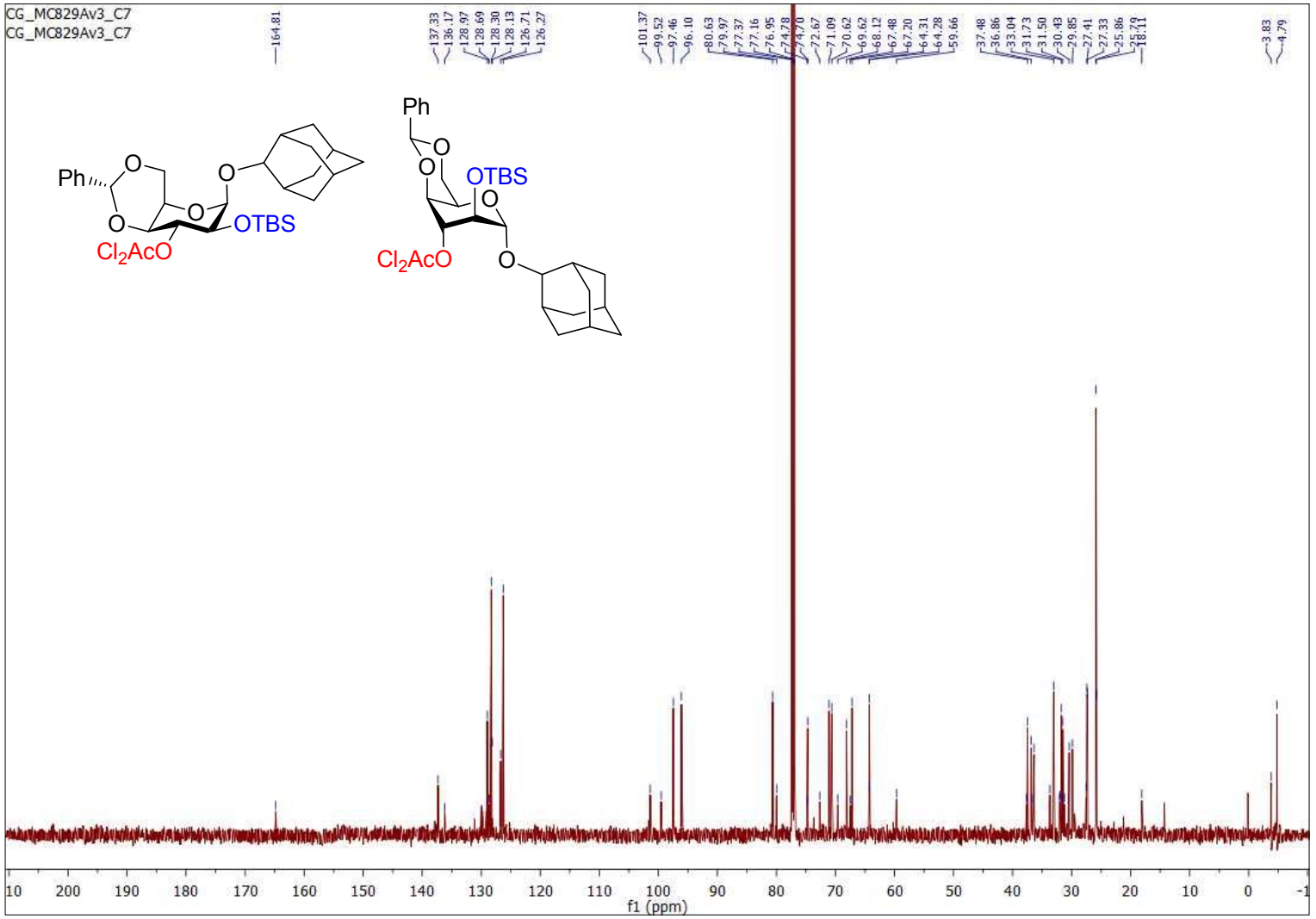


Figure S104. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*β*-D-idopyranoside (17b)** and **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*α*-D-idopyranoside (17c)**

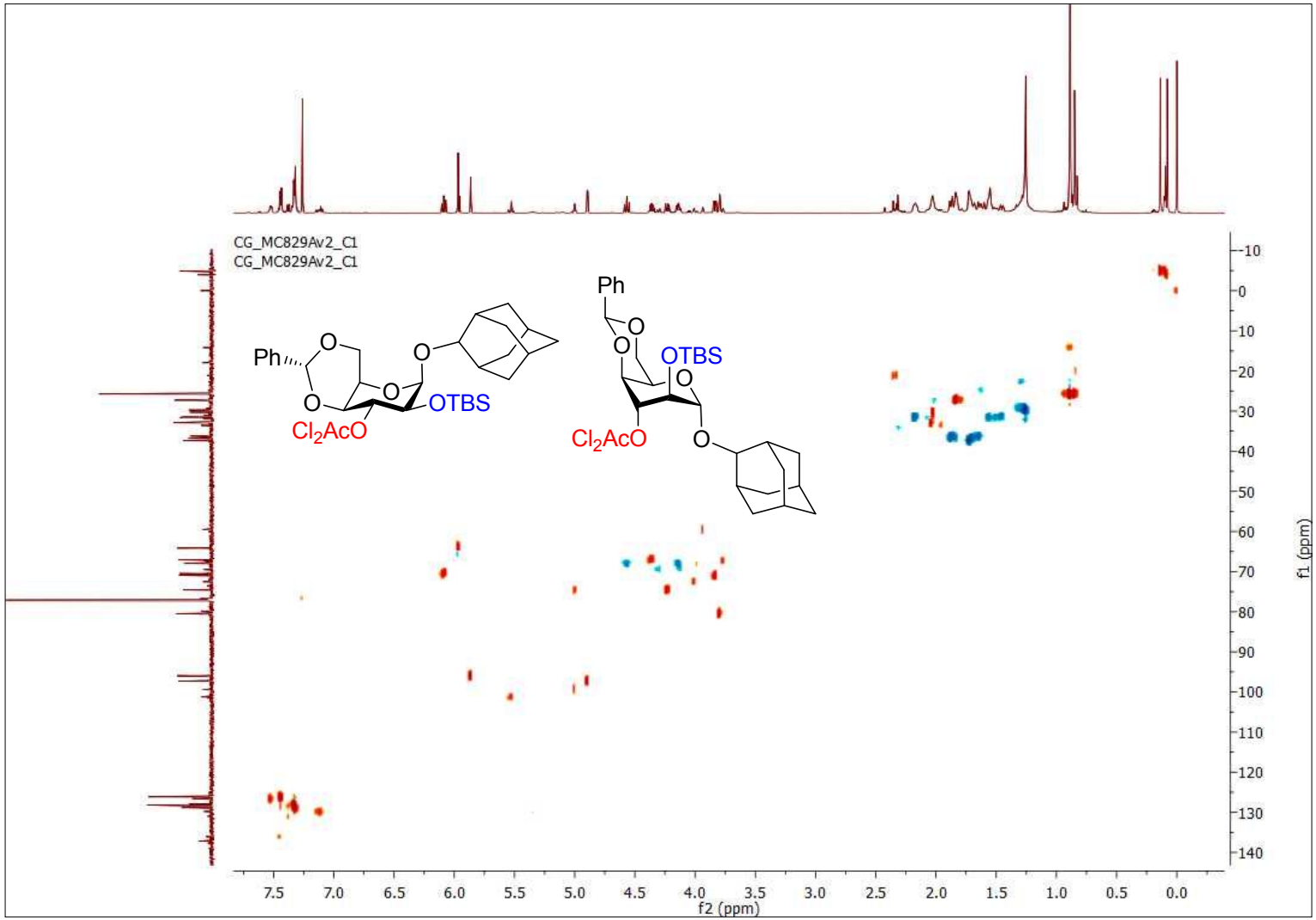


Figure S105. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*β*-D-idopyranoside (17b)** and **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-dichloroacetyl-*α*-D-idopyranoside (17c)**

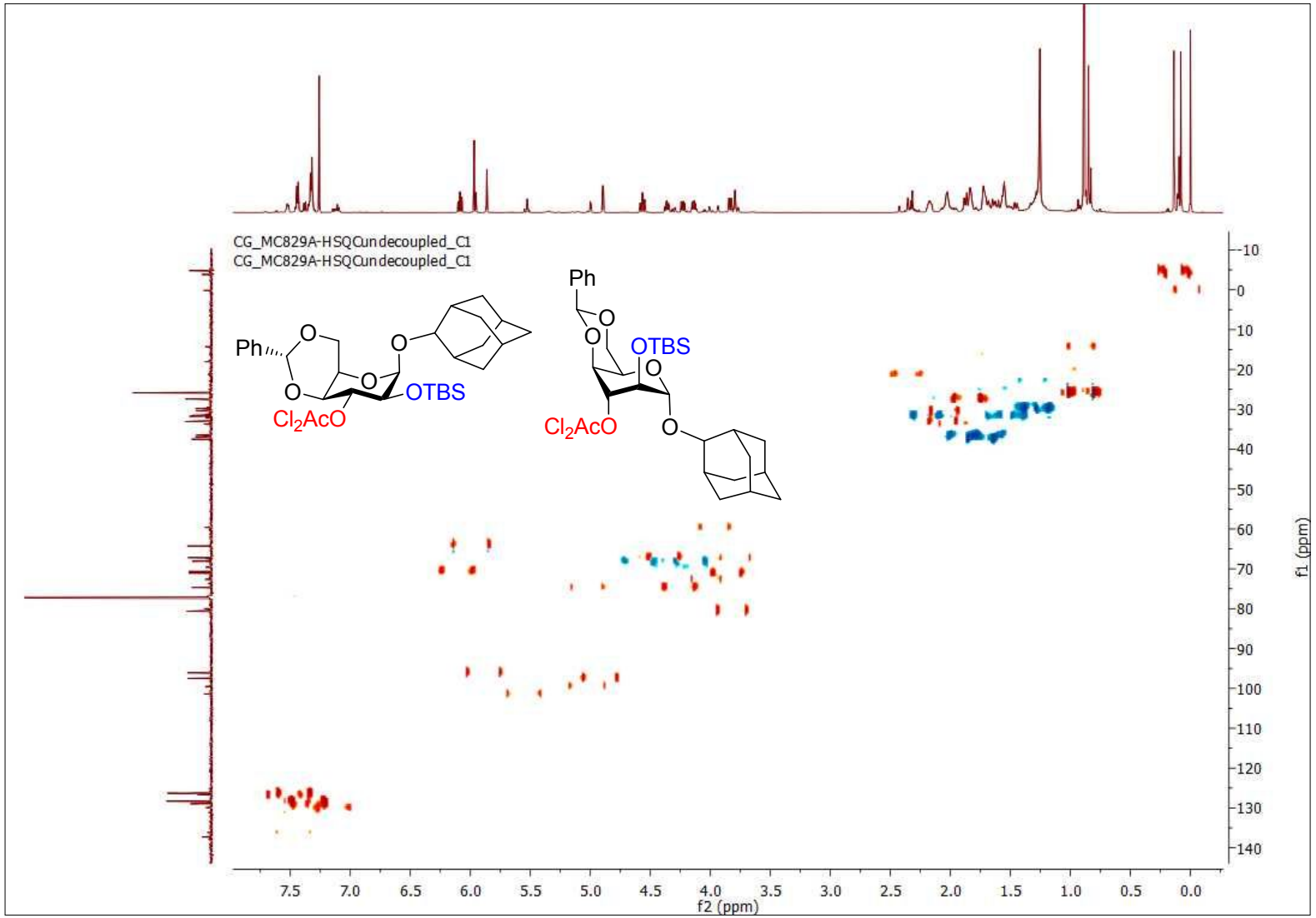


Figure S106. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (18a)**

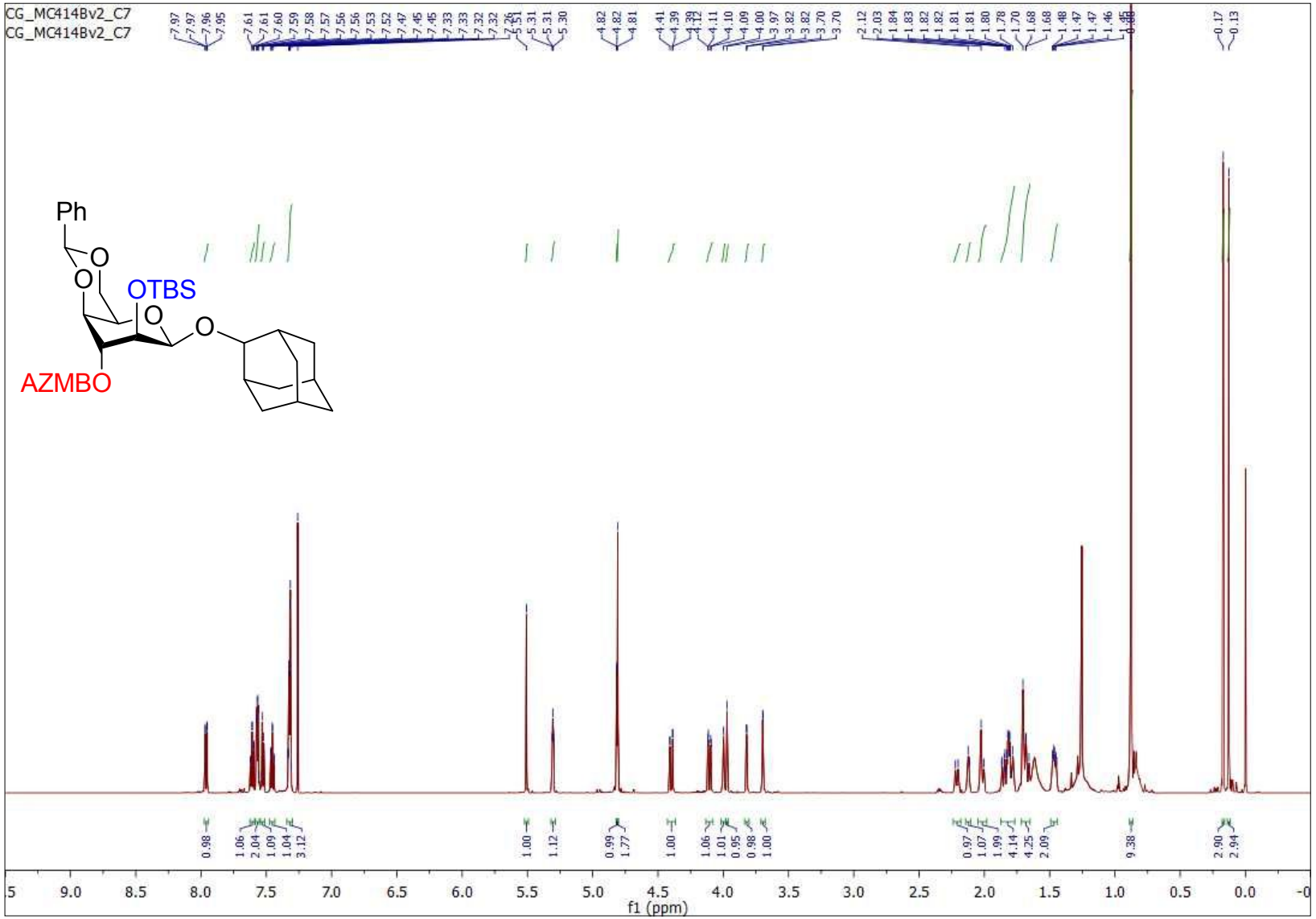


Figure S107. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (18a)**

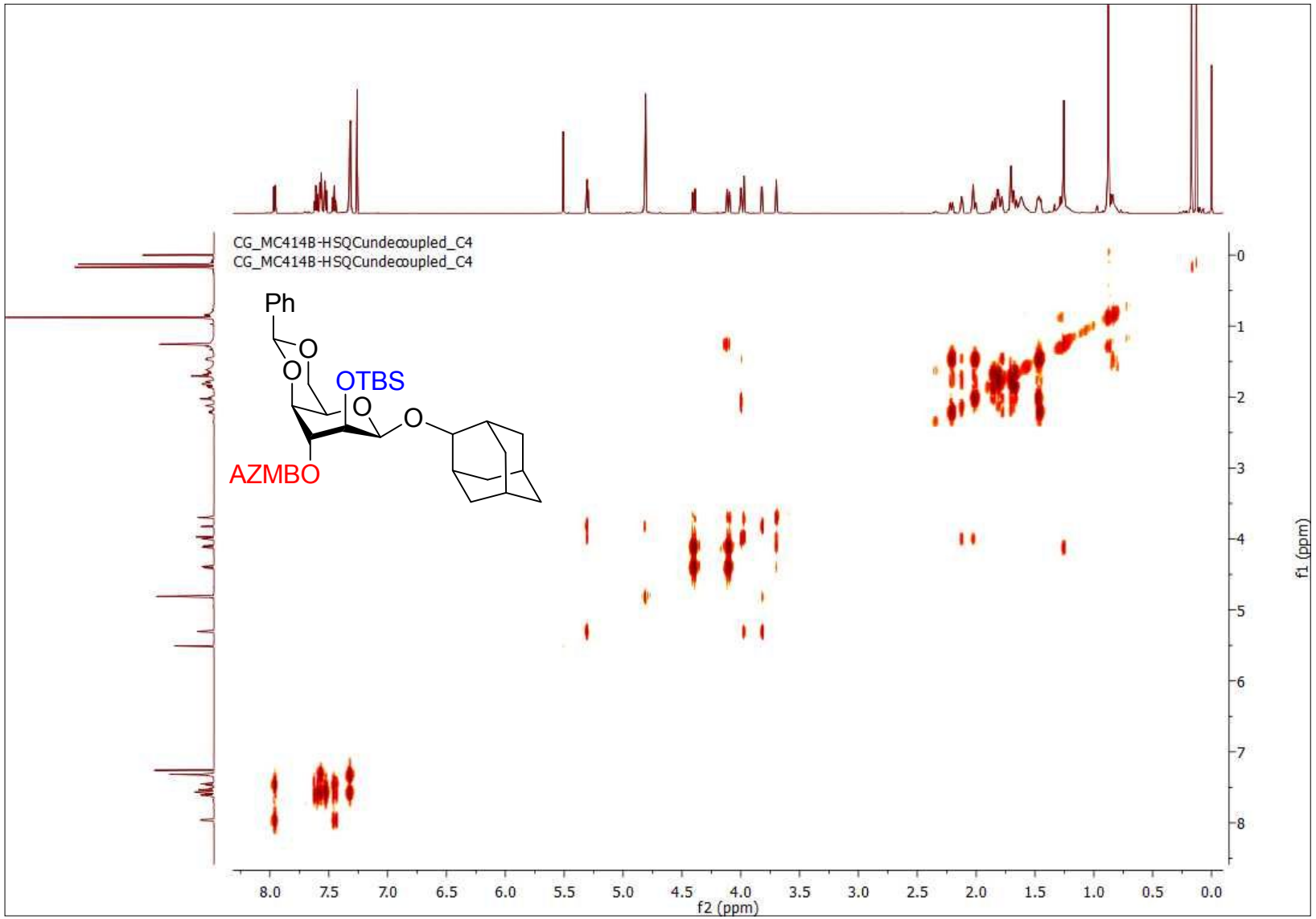


Figure S108. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (18a)**

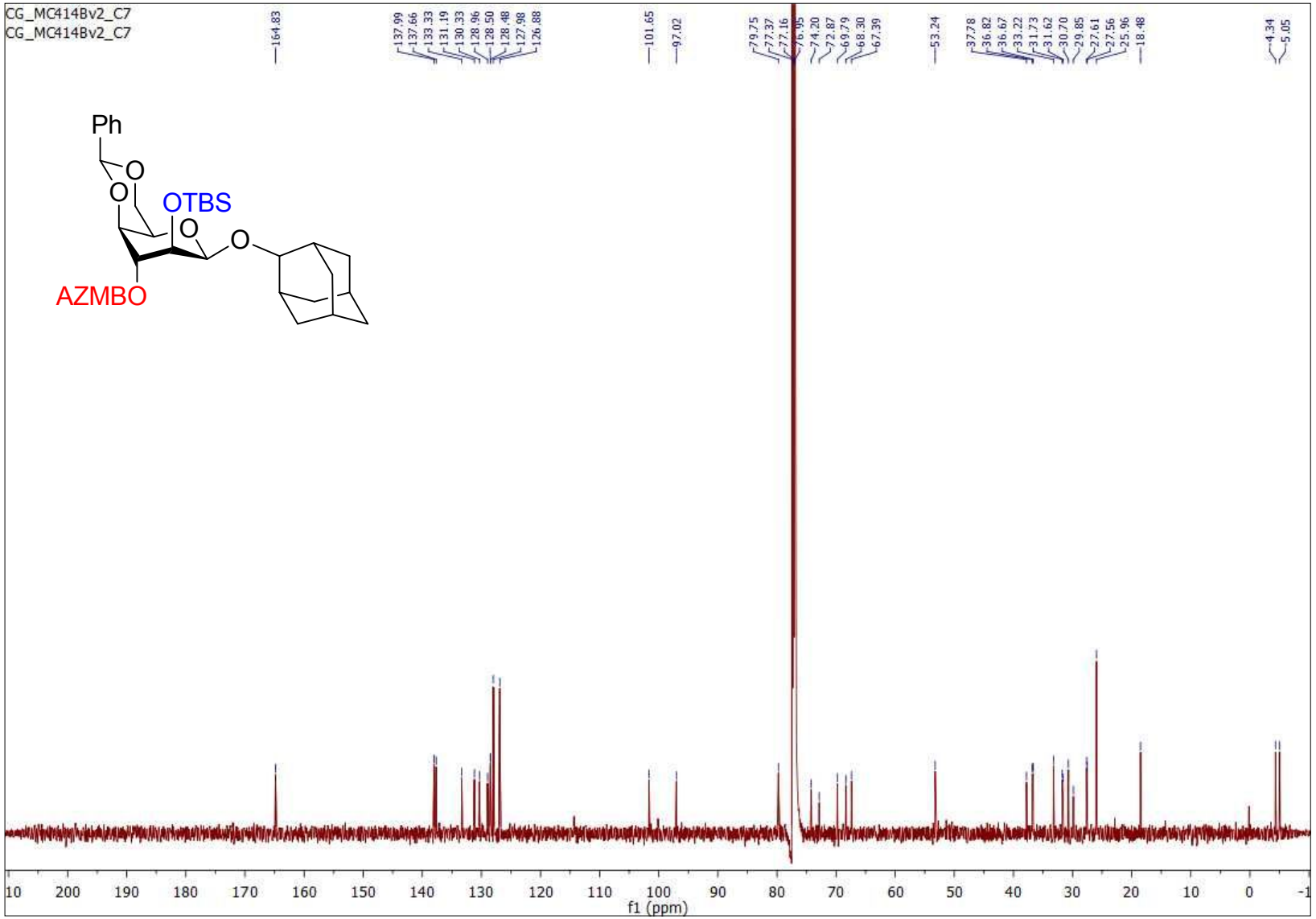


Figure S109. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (18a)**

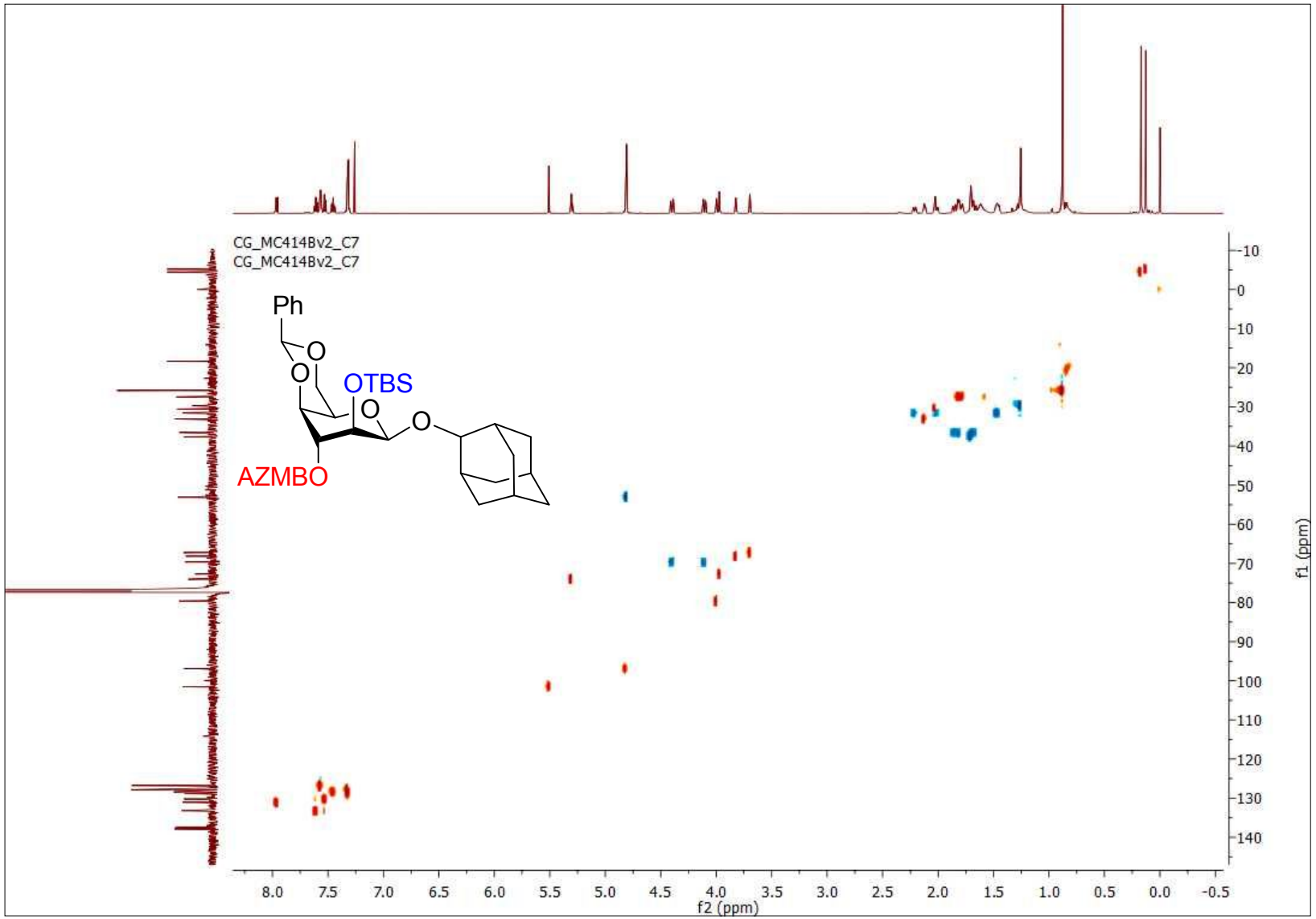


Figure S110. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (18a)**

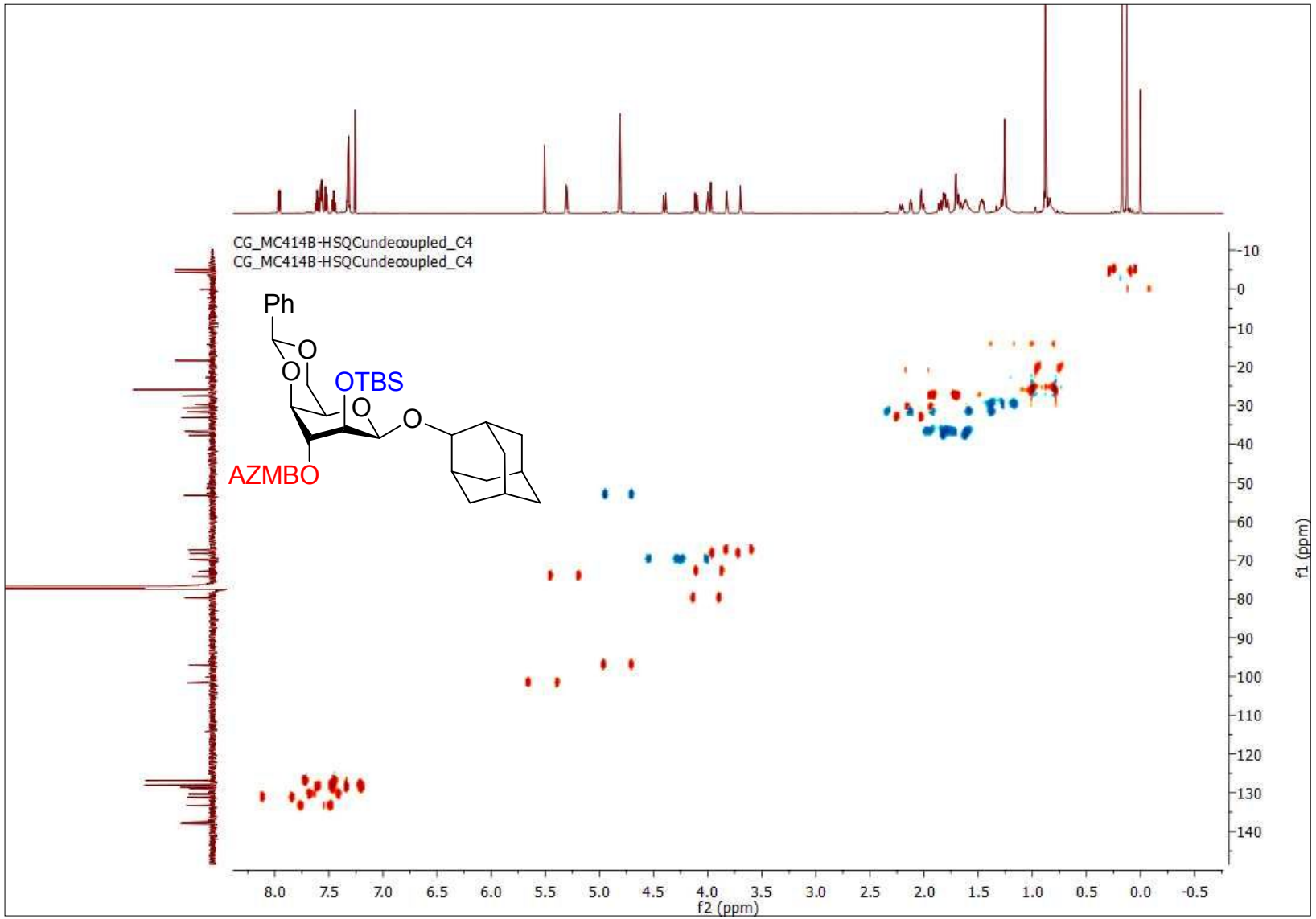


Figure S111. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (18b)** and **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (18c)**

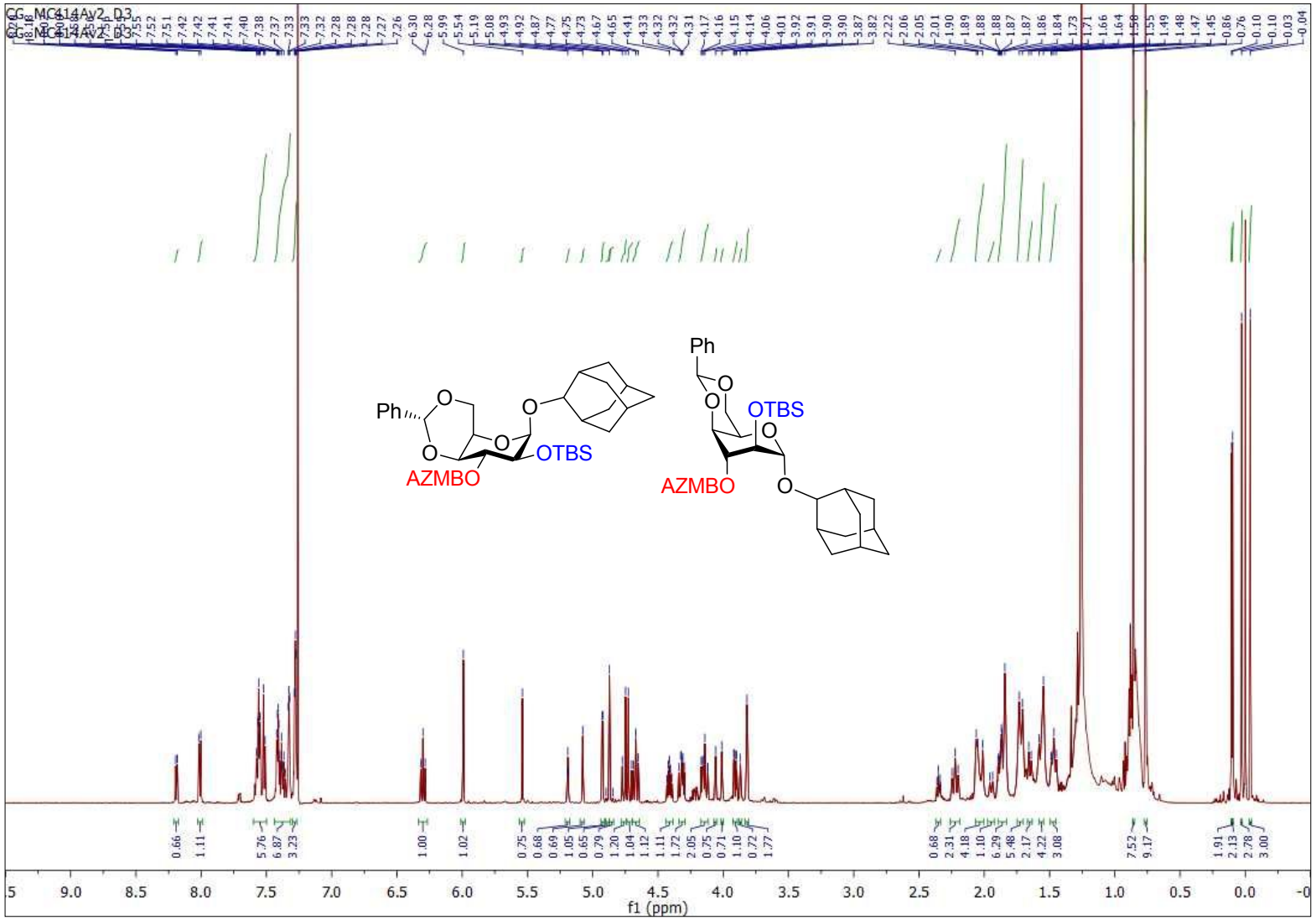


Figure S112. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (18b)** and **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (18c)**

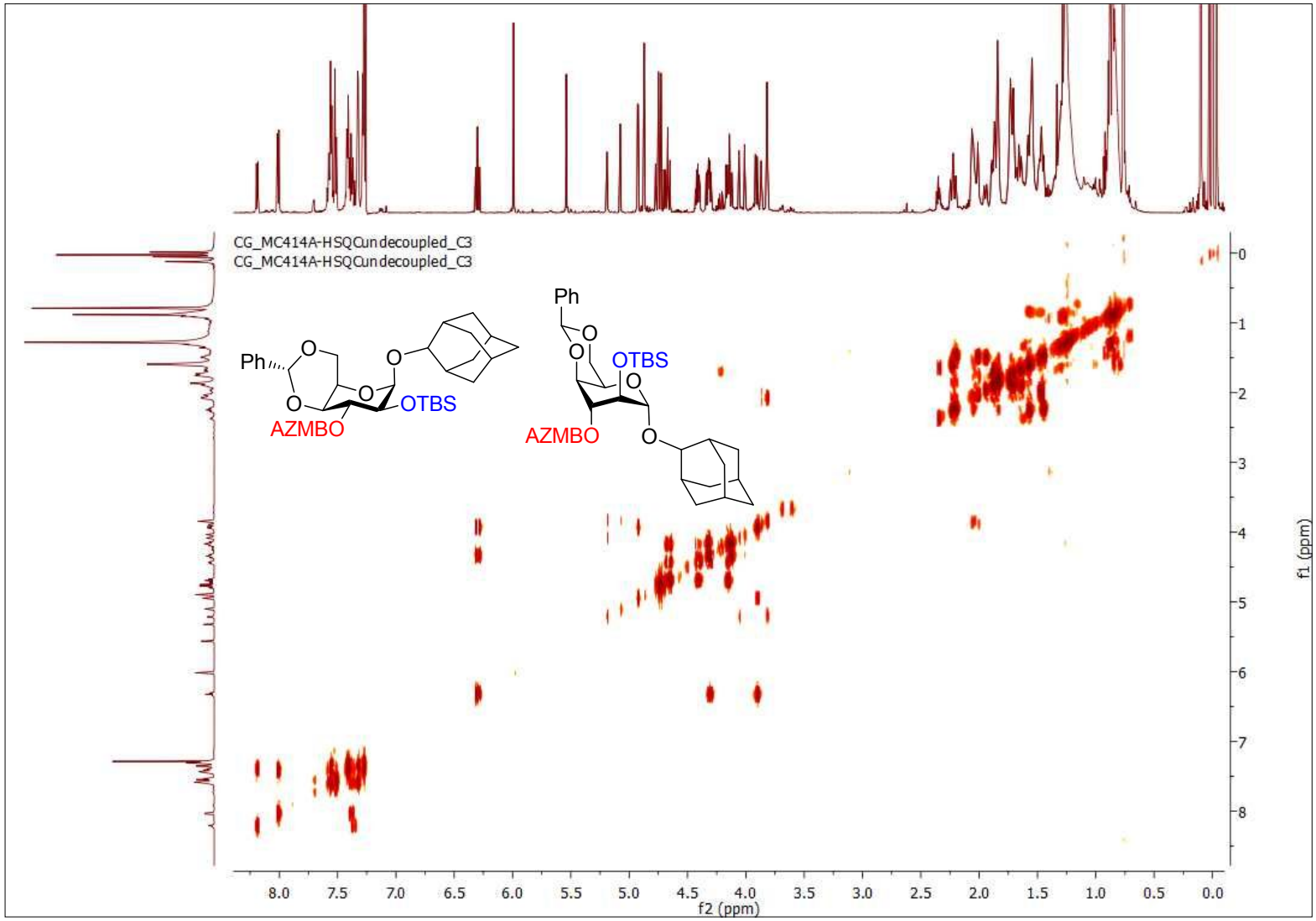


Figure S113. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (18b)** and **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (18c)**

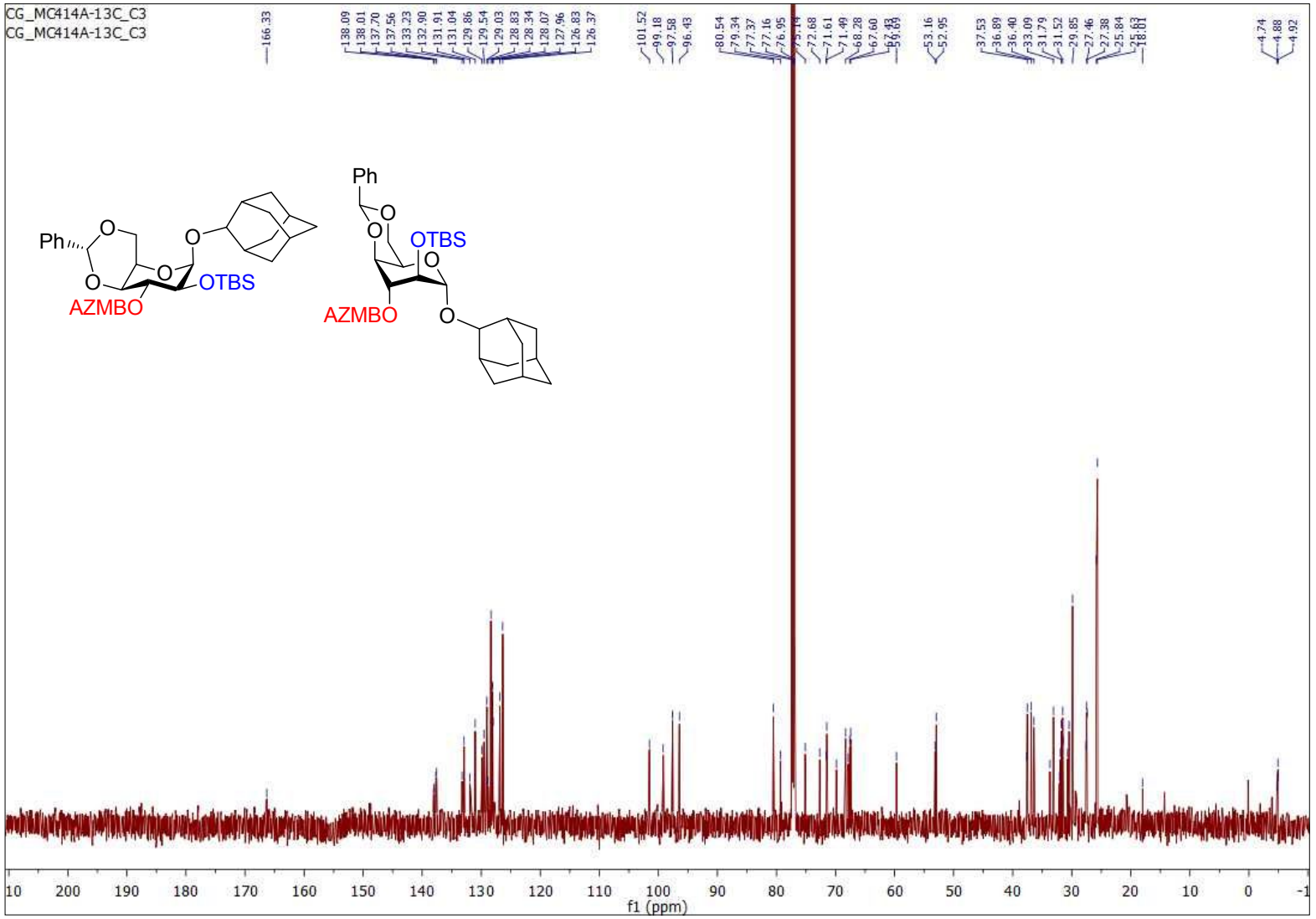


Figure S114. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (18b)** and **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (18c)**

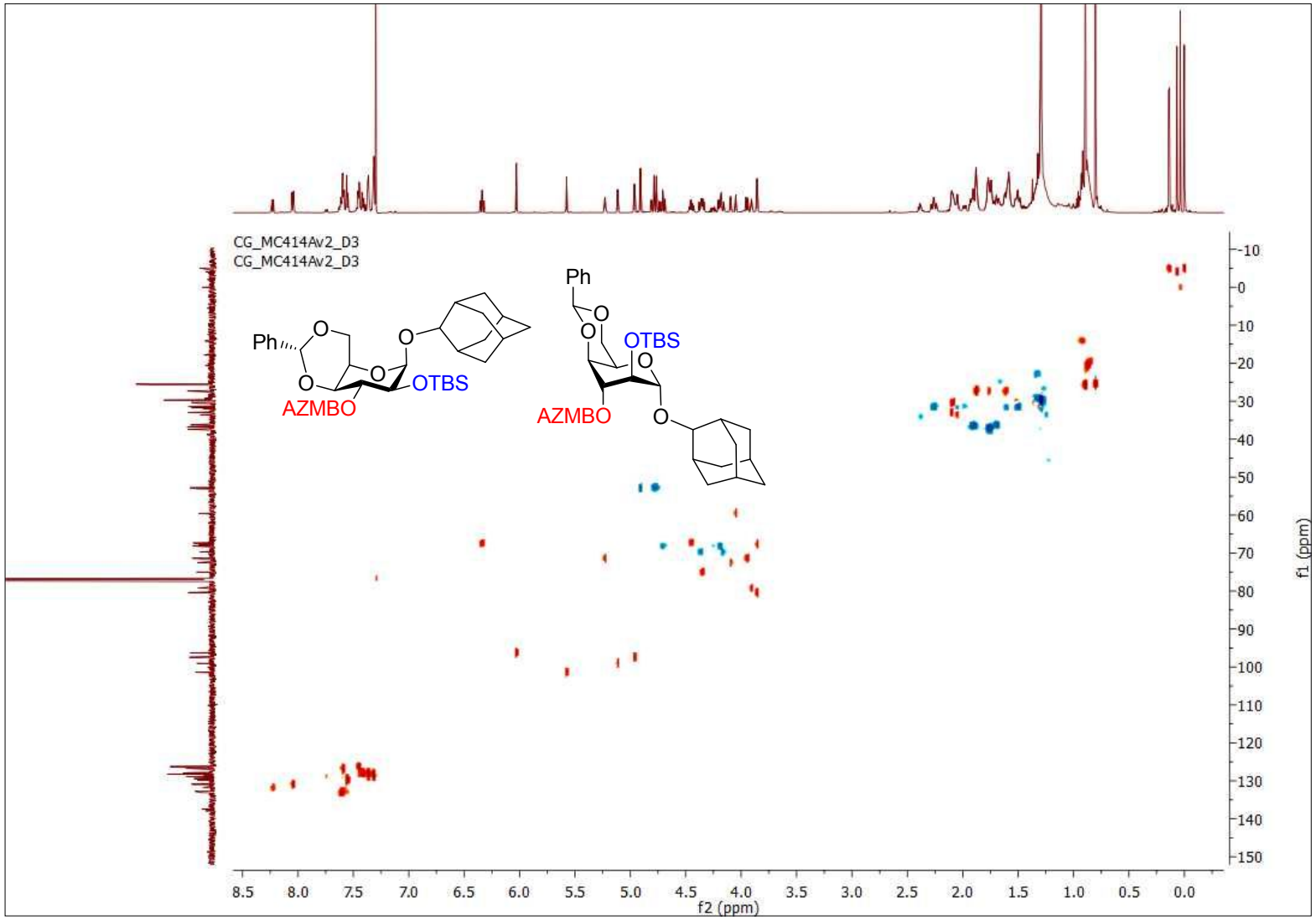


Figure S115. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (18b)** and **(2-adamantyl) 3-*O*-(2-azidomethyl)benzoyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranoside (18c)**

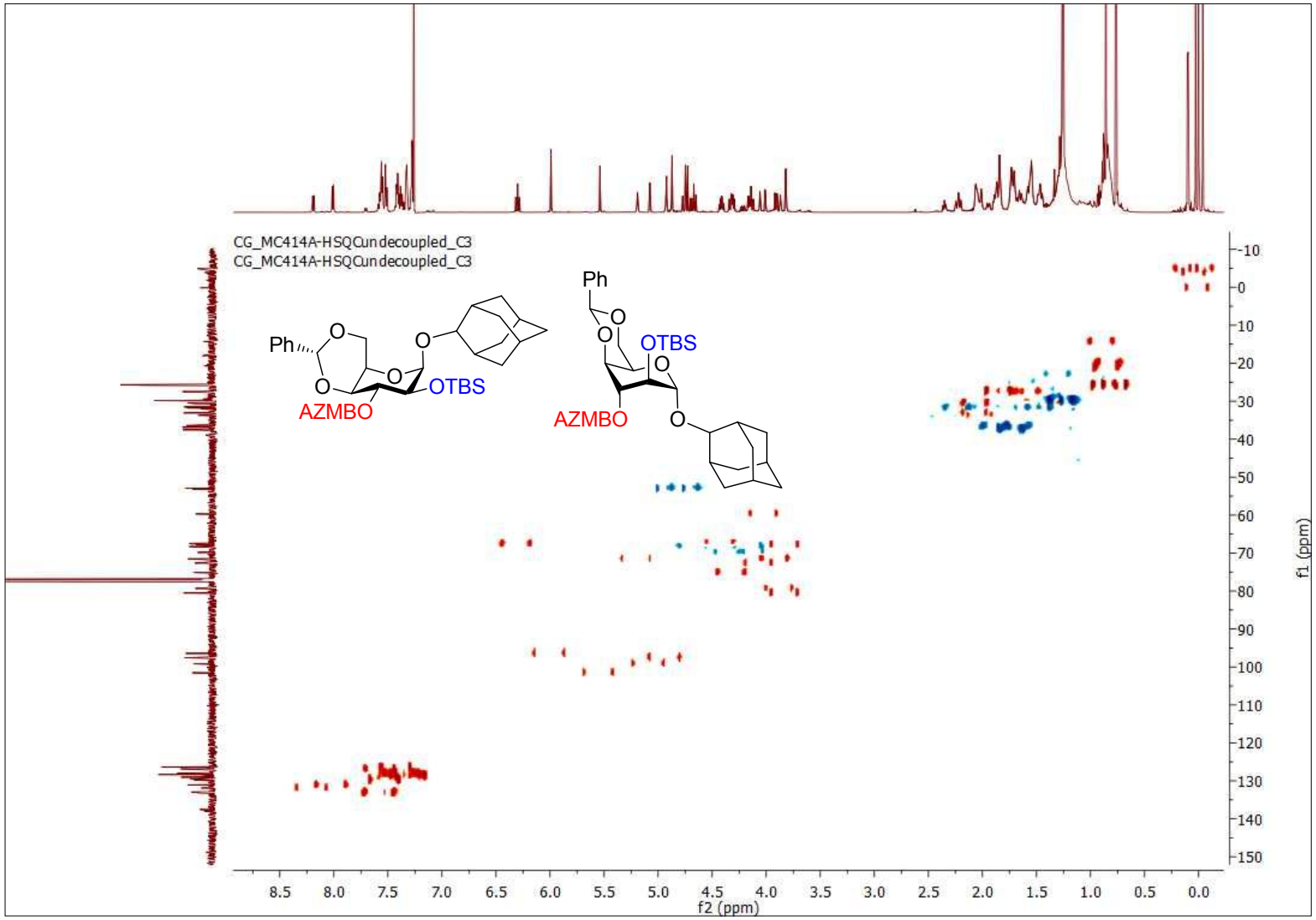


Figure S116. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*β*-D-idopyranoside (19a)**

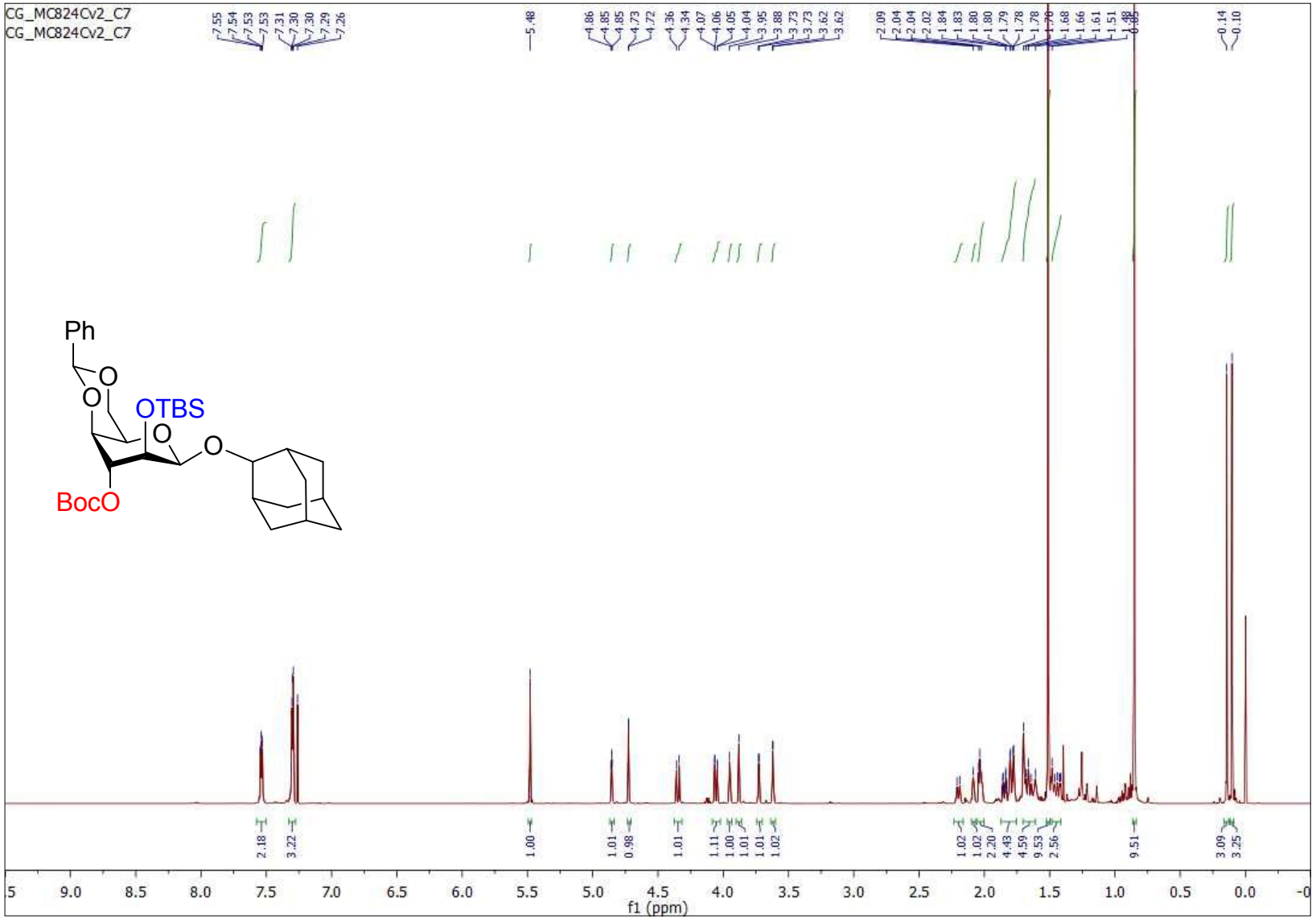


Figure S117. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*β*-D-idopyranoside (19a)**

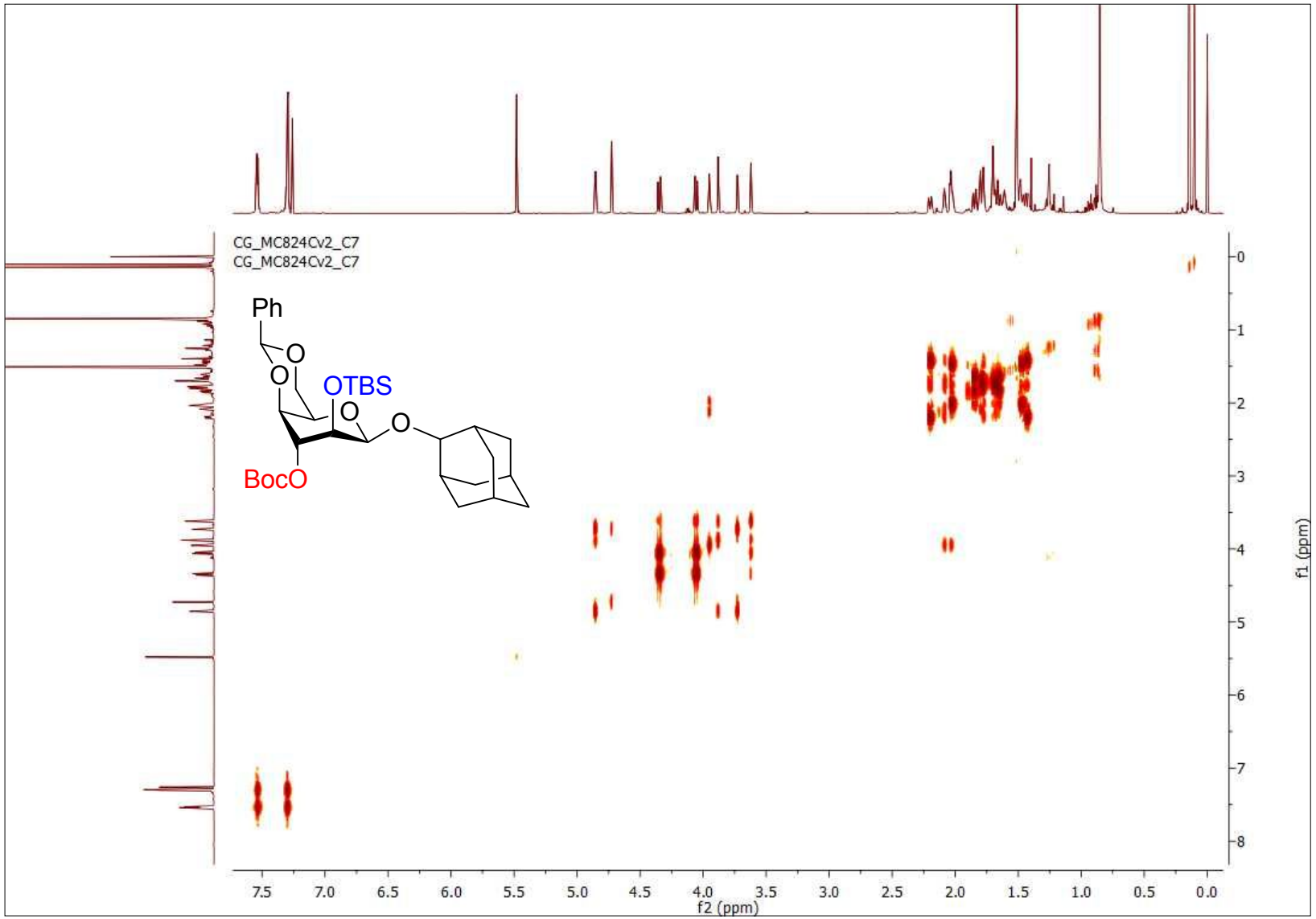


Figure S118. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*β*-D-idopyranoside (19a)**

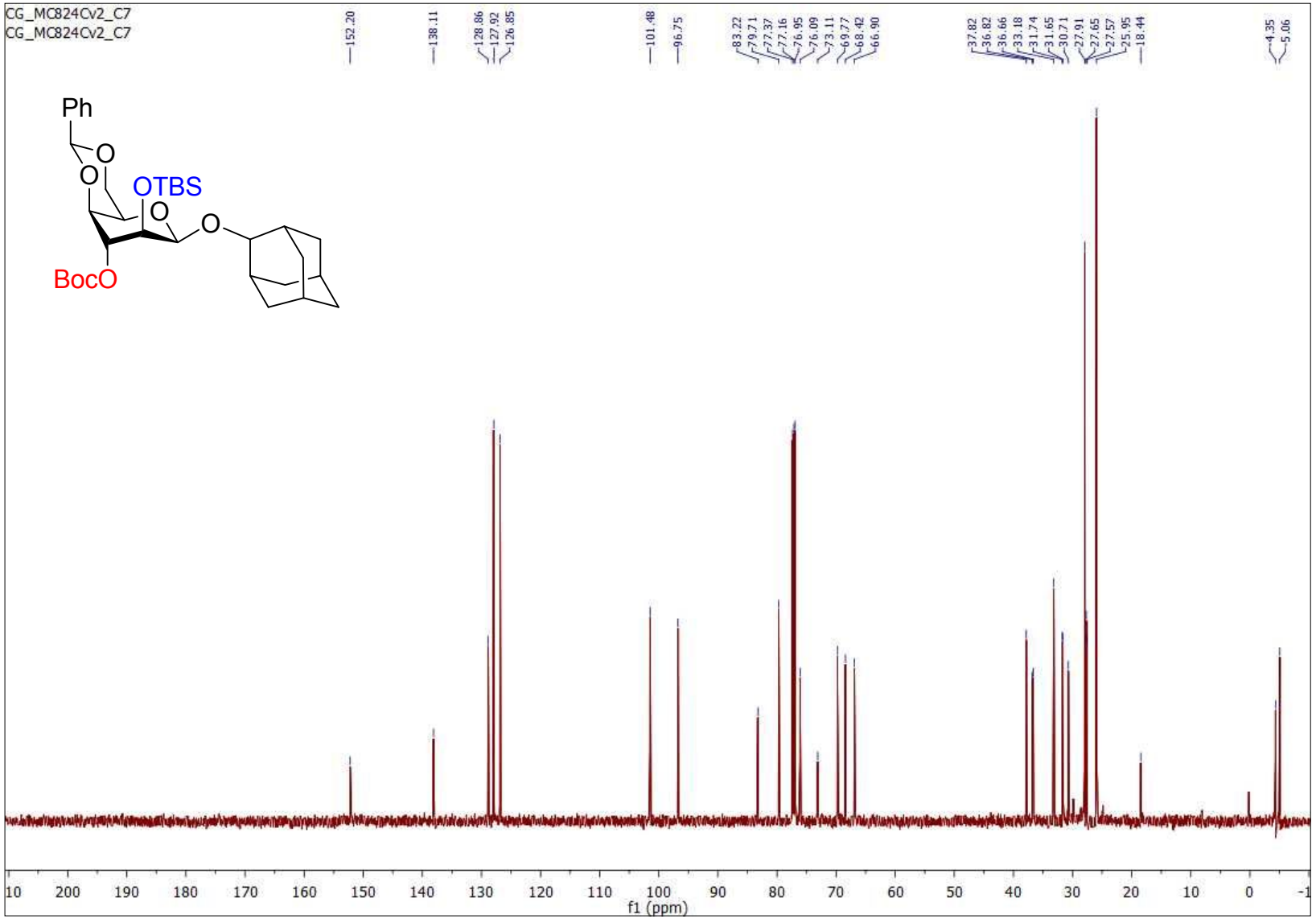


Figure S119. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*β*-D-idopyranoside (19a)**

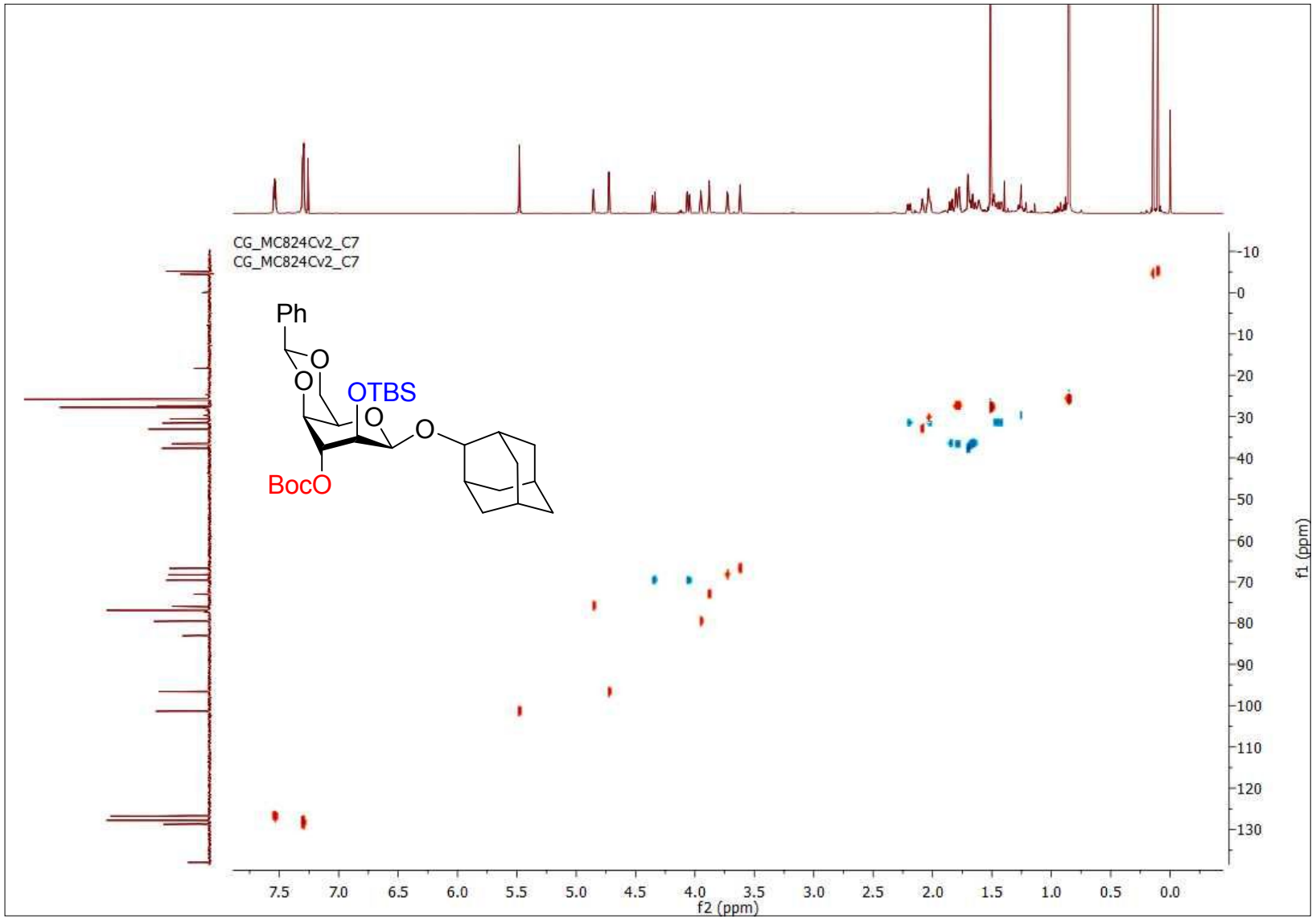


Figure S120. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*β*-D-idopyranoside (19a)**

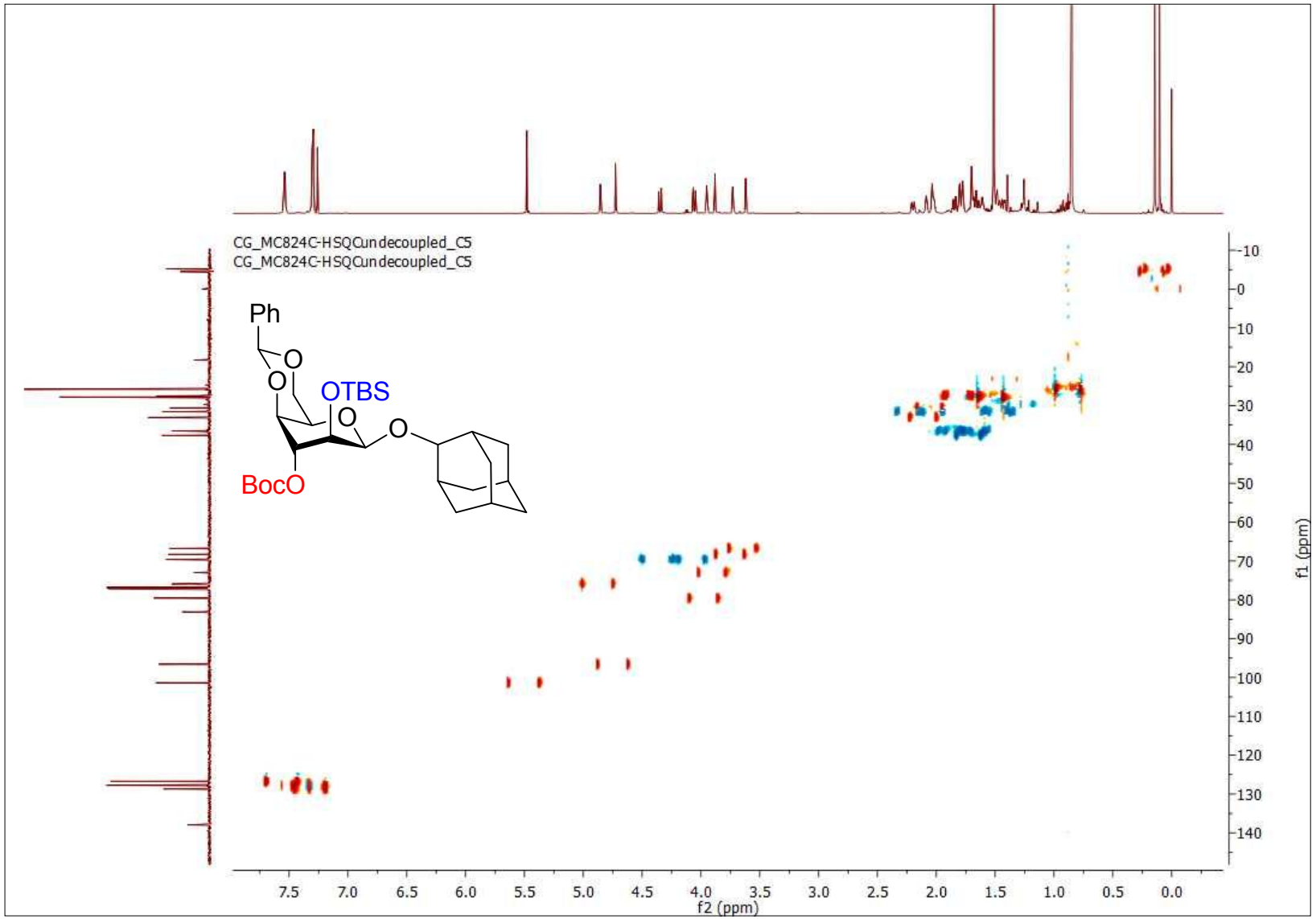


Figure S121. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*β*-D-idopyranoside (19b)** and **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*α*-D-idopyranoside (19c)**

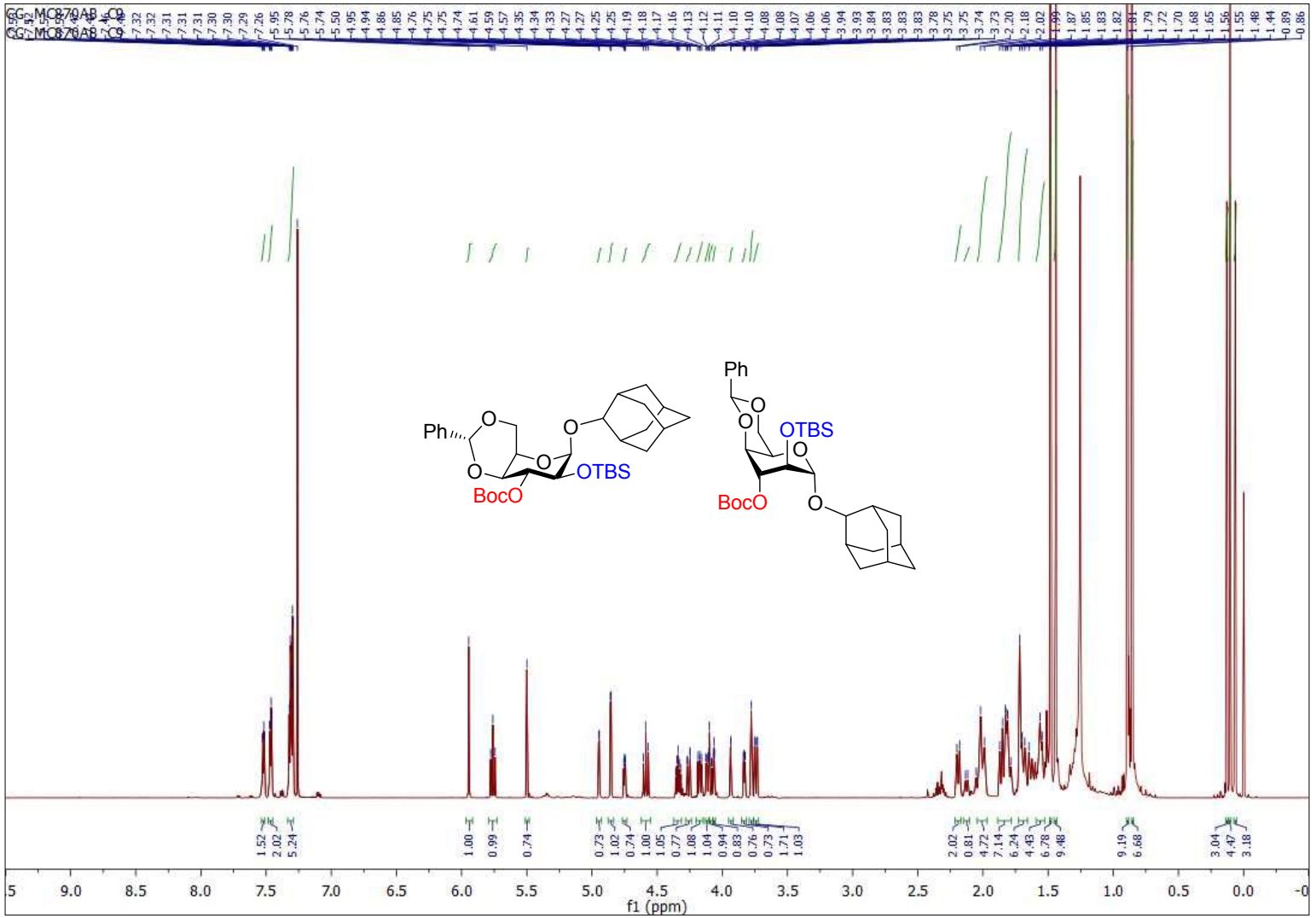


Figure S122. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*β*-D-idopyranoside (19b)** and **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*α*-D-idopyranoside (19c)**

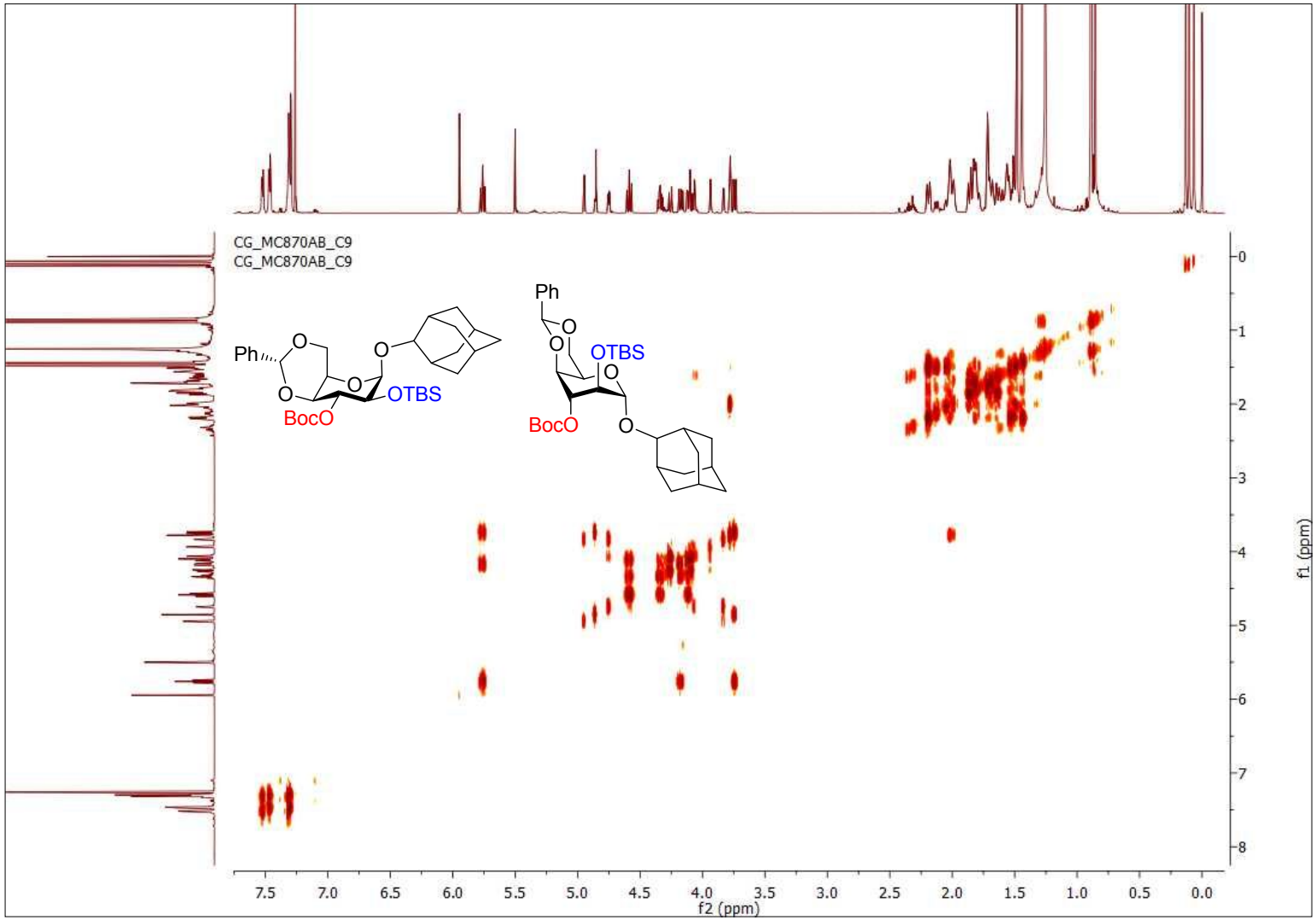


Figure S123. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*β*-D-idopyranoside (19b)** and **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*α*-D-idopyranoside (19c)**

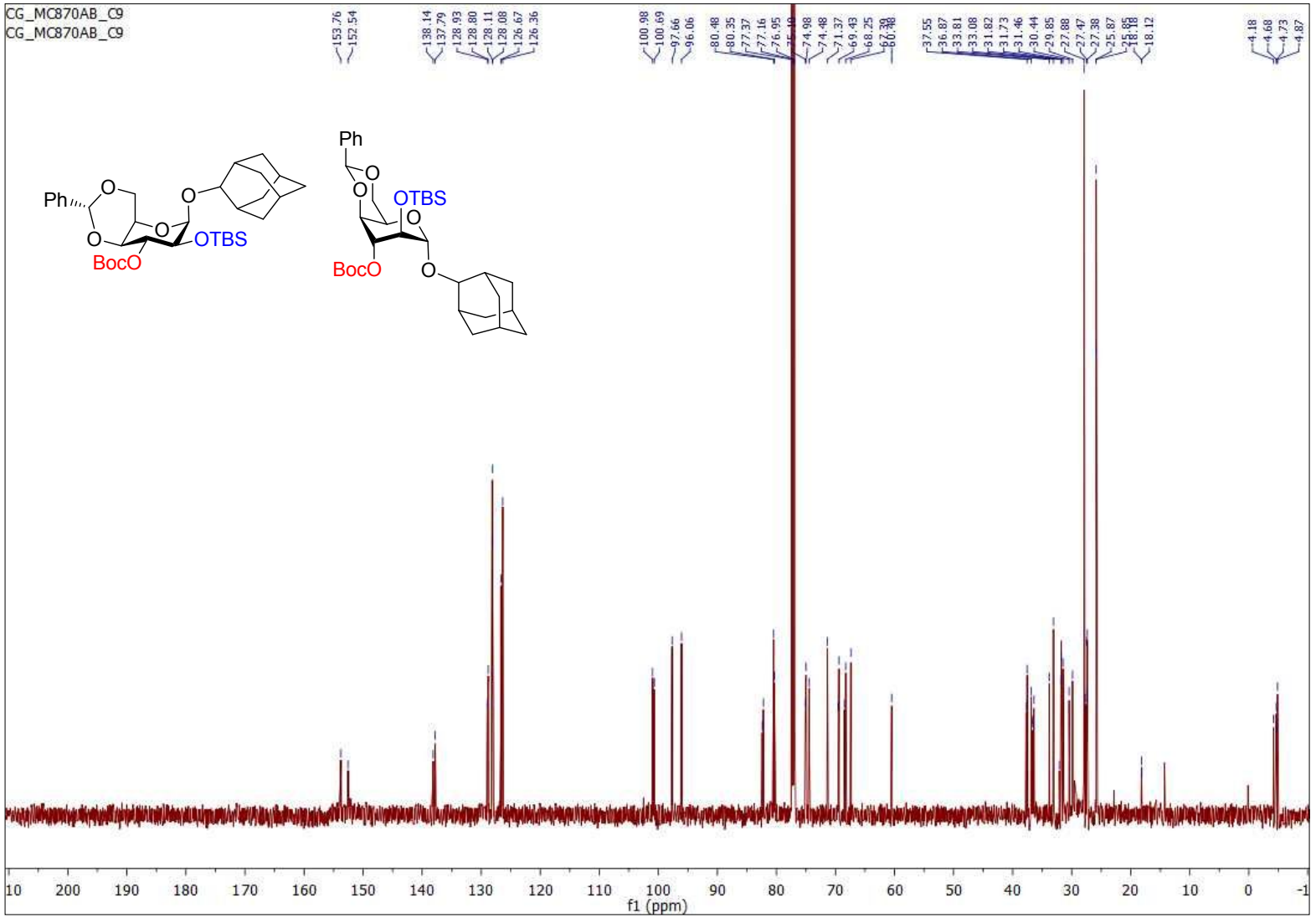


Figure S124. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*β*-D-idopyranoside (19b)** and **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*α*-D-idopyranoside (19c)**

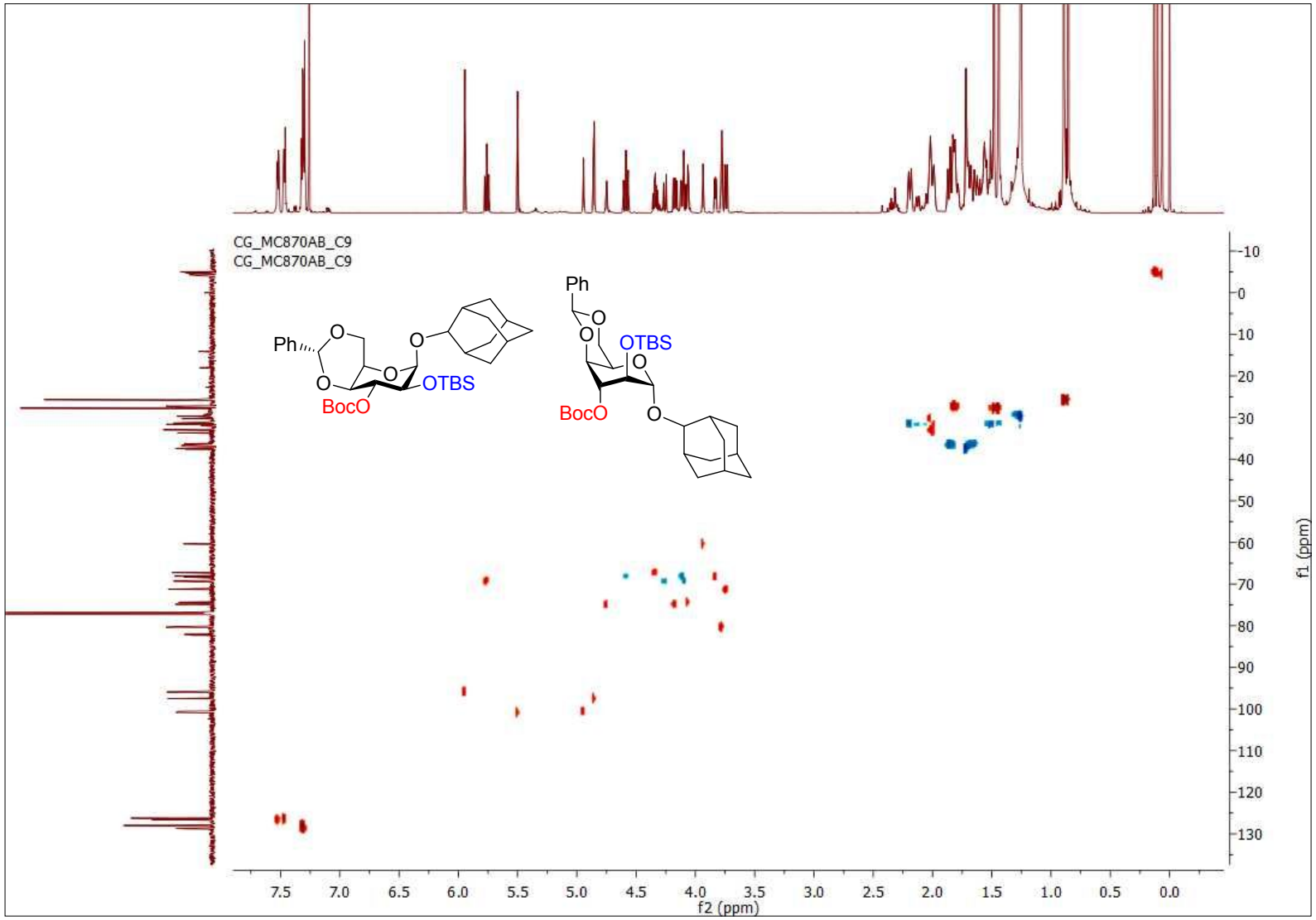


Figure S125. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*β*-D-idopyranoside (19b)** and **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-*tert*-butoxycarbonyl-*α*-D-idopyranoside (19c)**

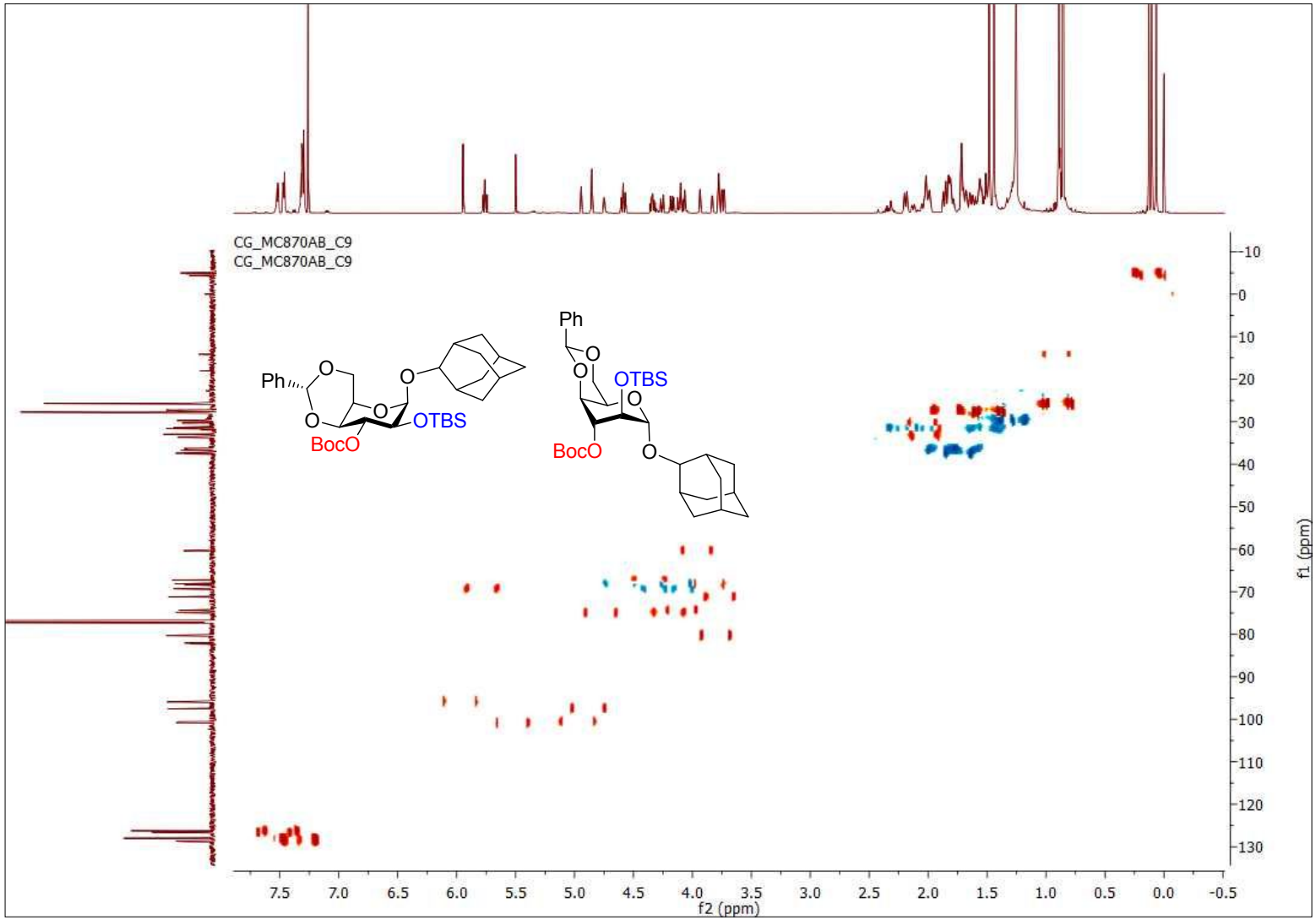


Figure S126. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-*β*-D-idopyranoside (20a)**

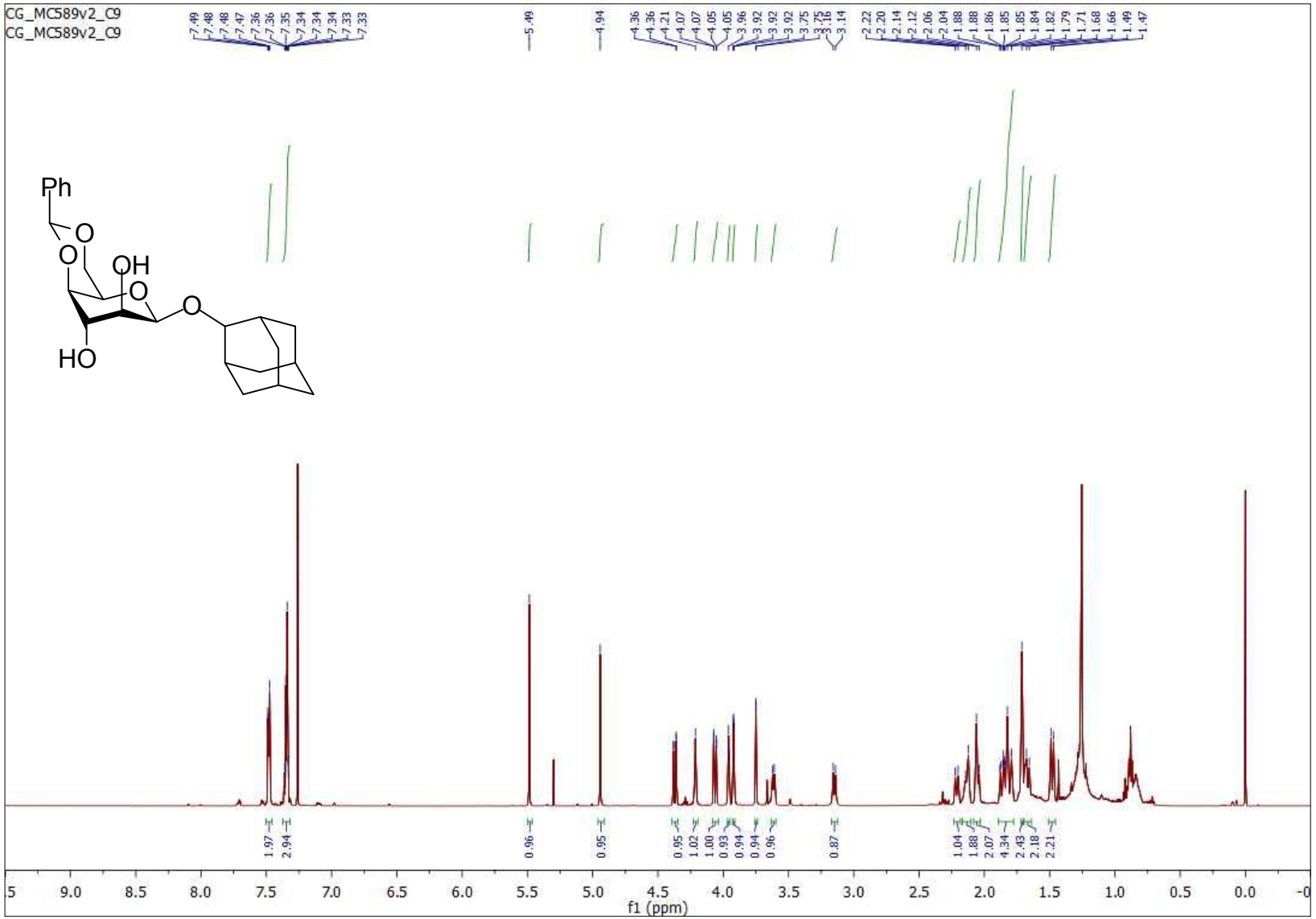


Figure S127. COSY NMR spectrum ($CDCl_3$, 500 MHz) of **(2-adamantyl) (S)-4,6-*O*-benzylidene-*β*-D-idopyranoside (20a)**

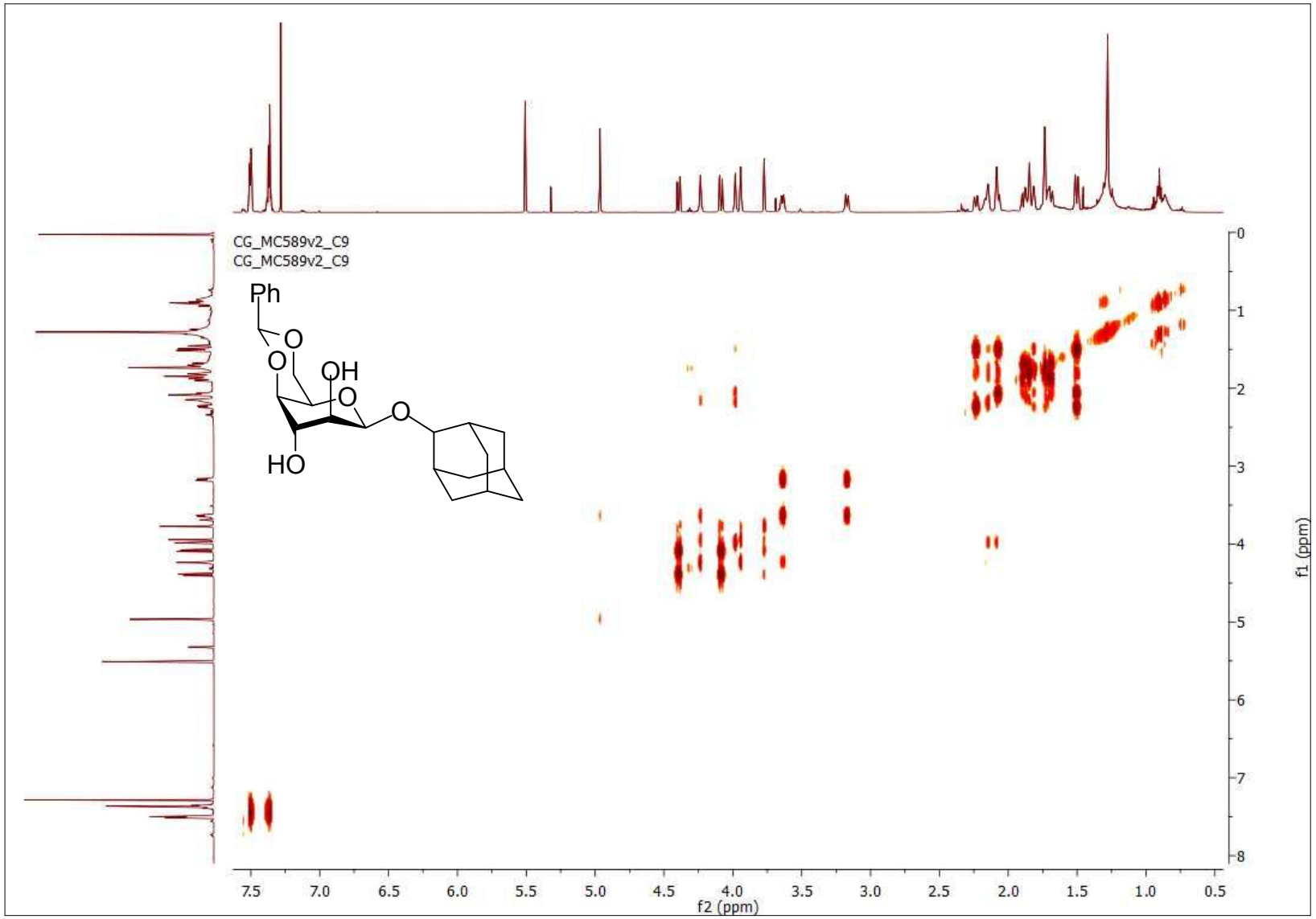


Figure S128. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz) of **(2-adamantyl) (S)-4,6-*O*-benzylidene-*β*-D-idopyranoside (20a)**

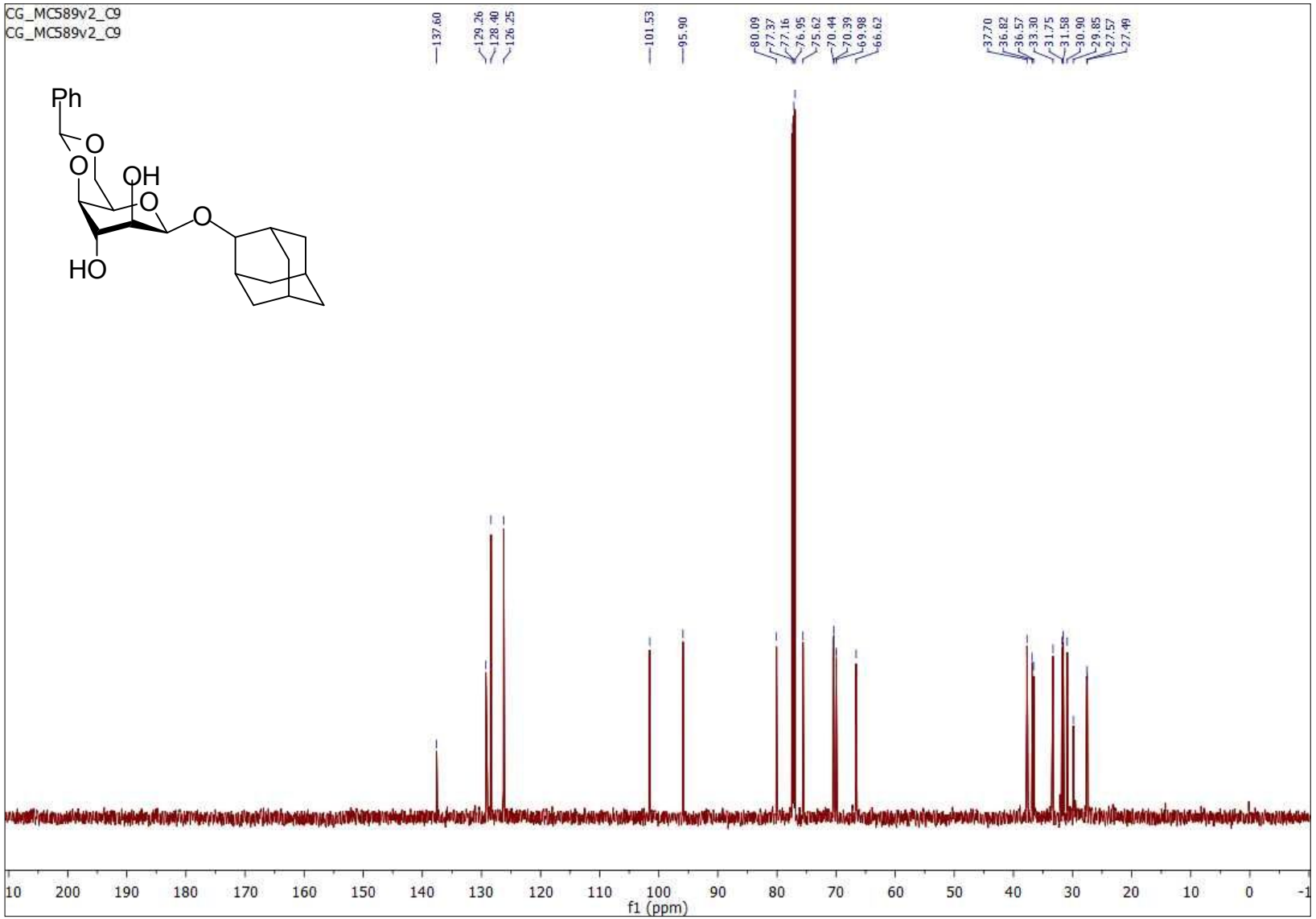


Figure S129. HSQC NMR spectrum ($CDCl_3$, 500 MHz) of **(2-adamantyl) (S)-4,6-*O*-benzylidene-*β*-D-idopyranoside (20a)**

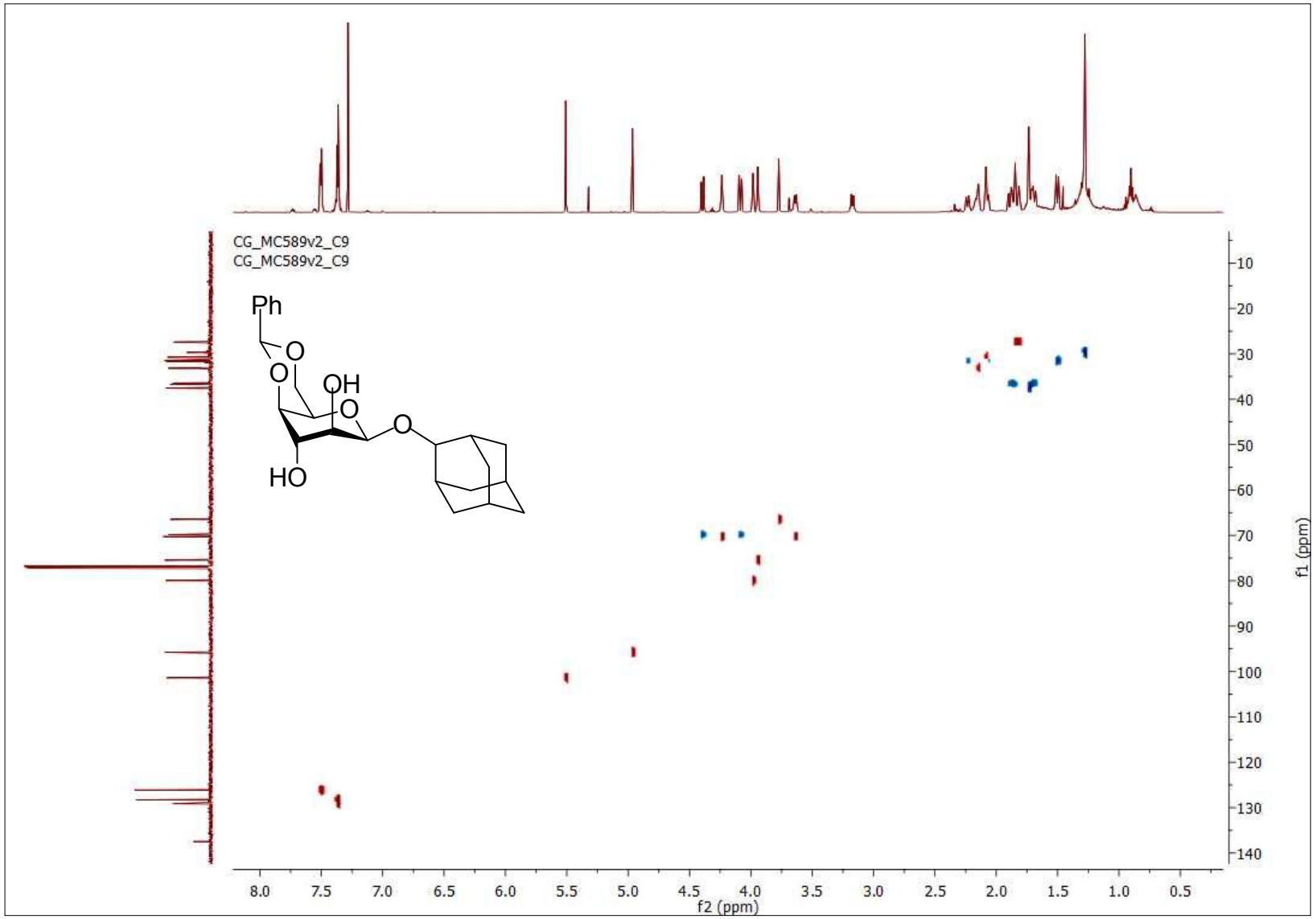


Figure S130. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-*β*-D-idopyranoside (20b)**

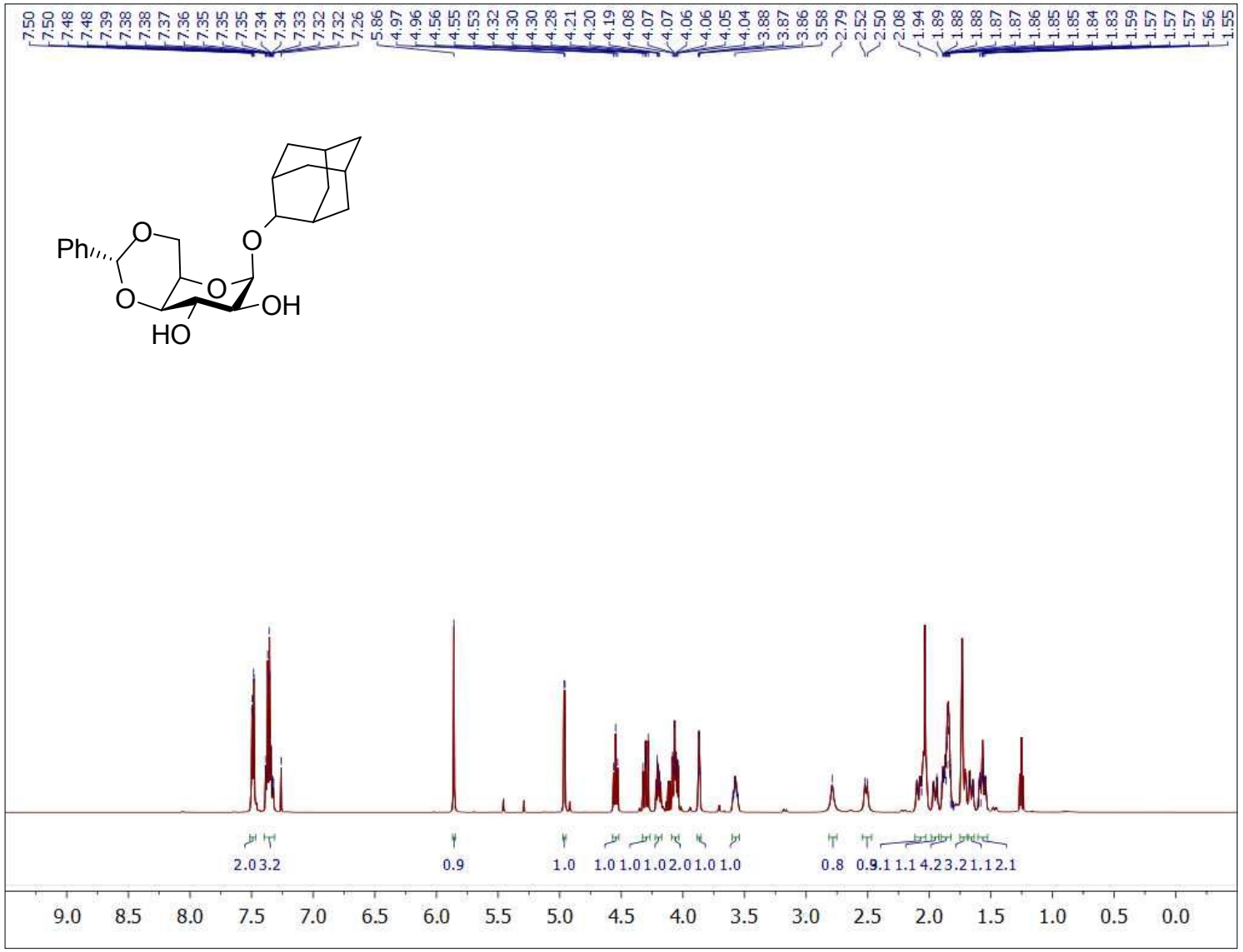


Figure S131. COSY NMR spectrum ($CDCl_3$, 500 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-*β*-D-idopyranoside (20b)**

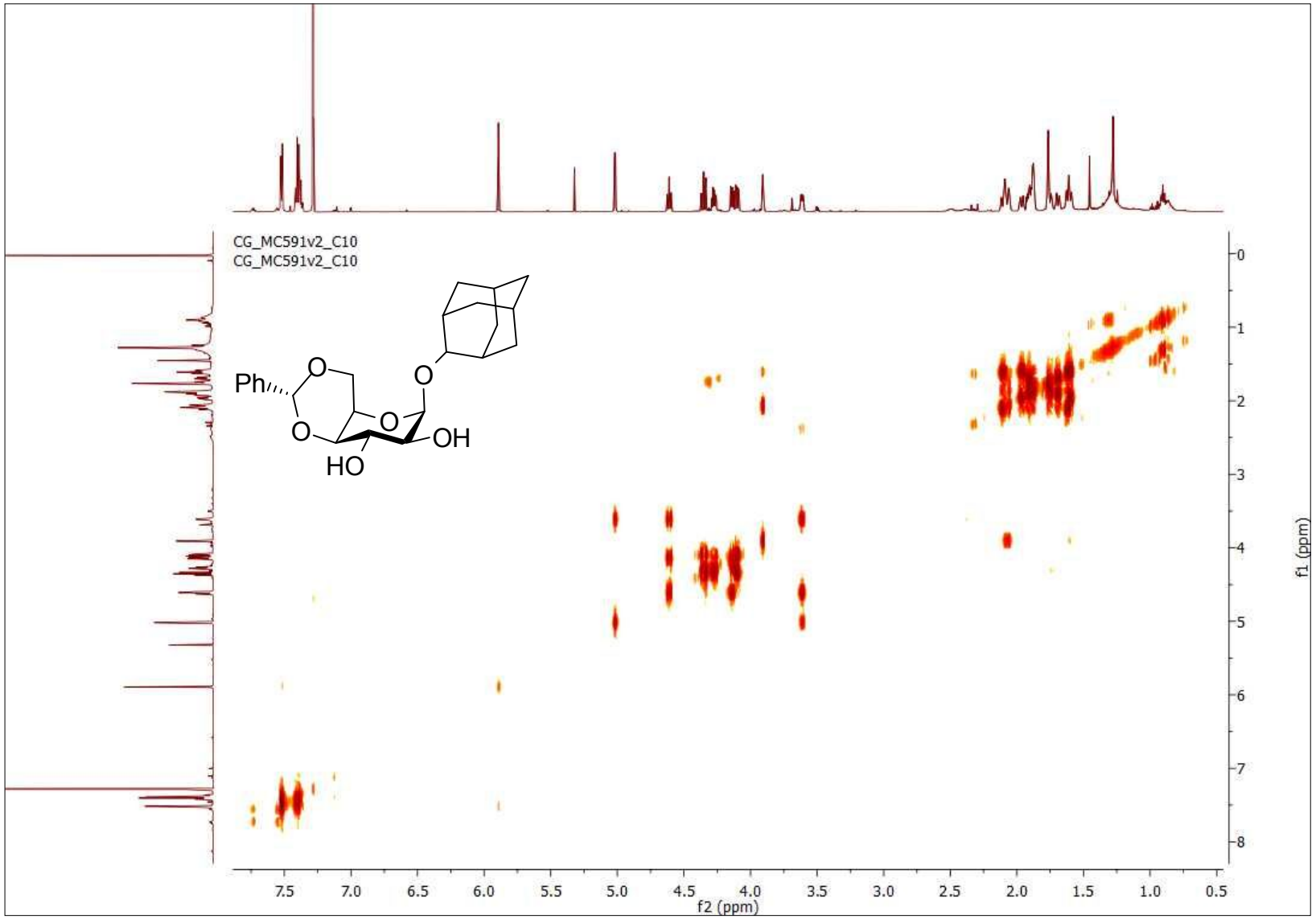


Figure S132. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-*β*-D-idopyranoside (20b)**

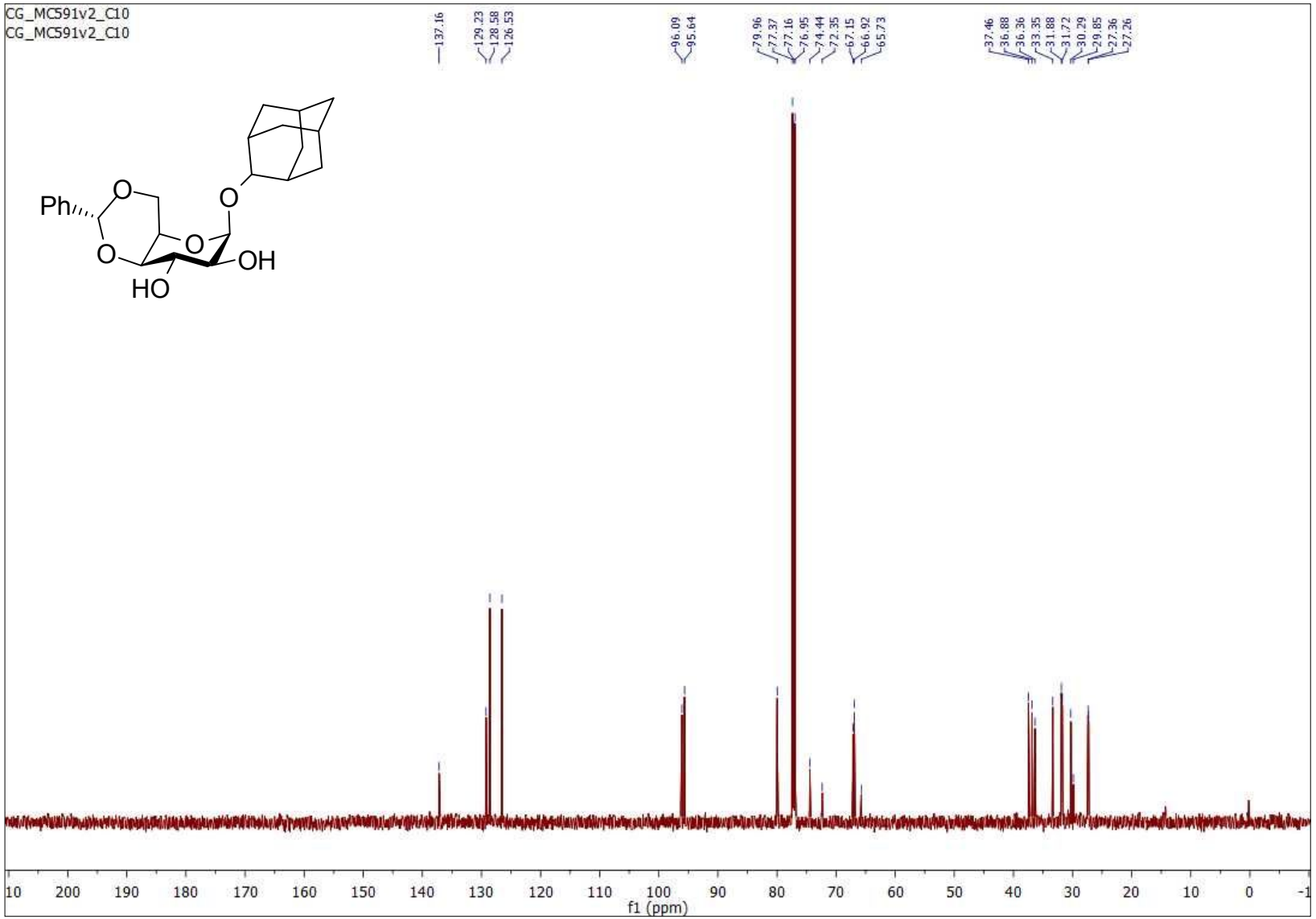


Figure S133. HSQC NMR spectrum ($CDCl_3$, 500 MHz) of **(2-adamantyl) (*R*)-4,6-*O*-benzylidene-*β*-D-idopyranoside (20b)**

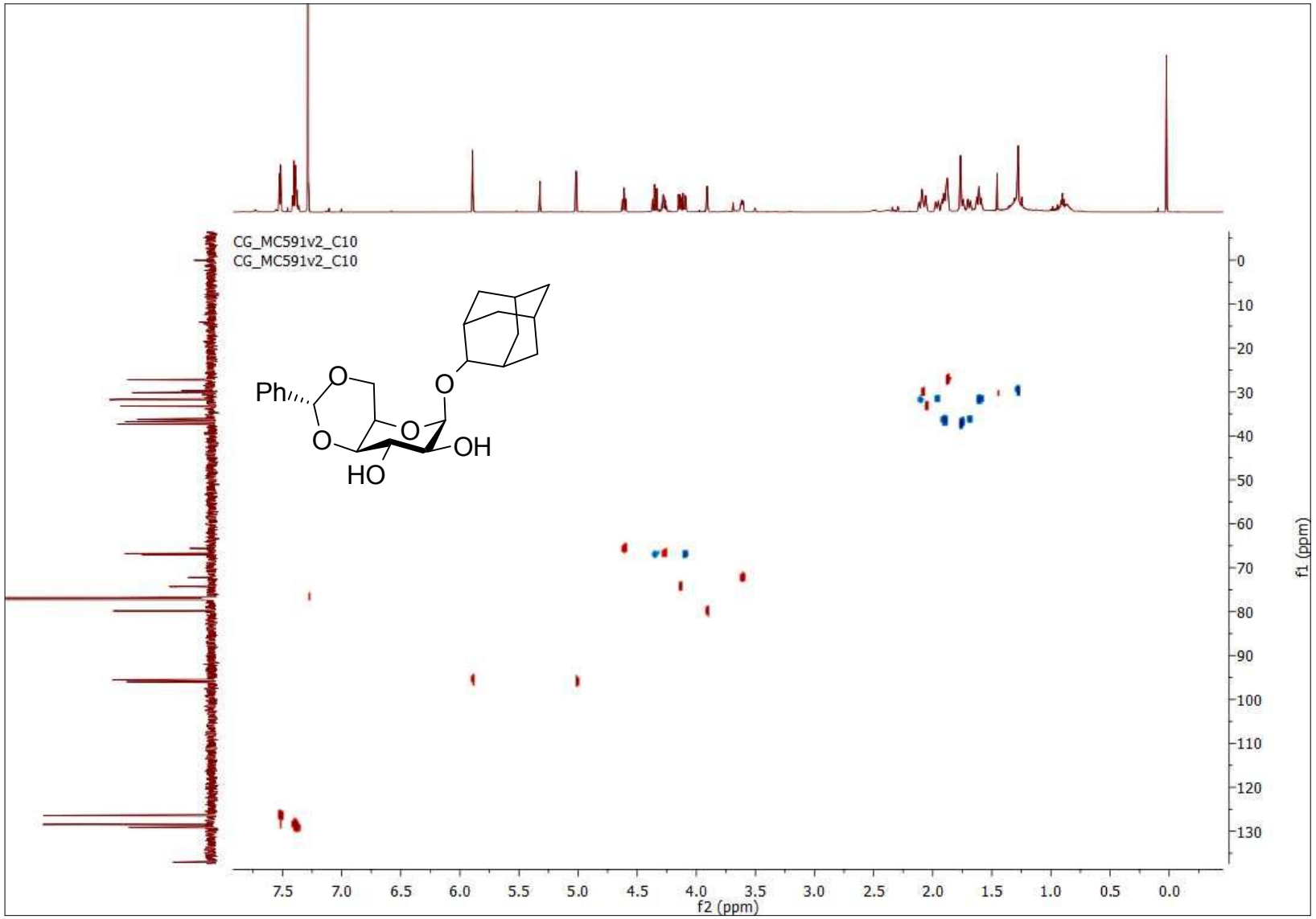


Figure S134. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-*α*-D-idopyranoside (20c)**

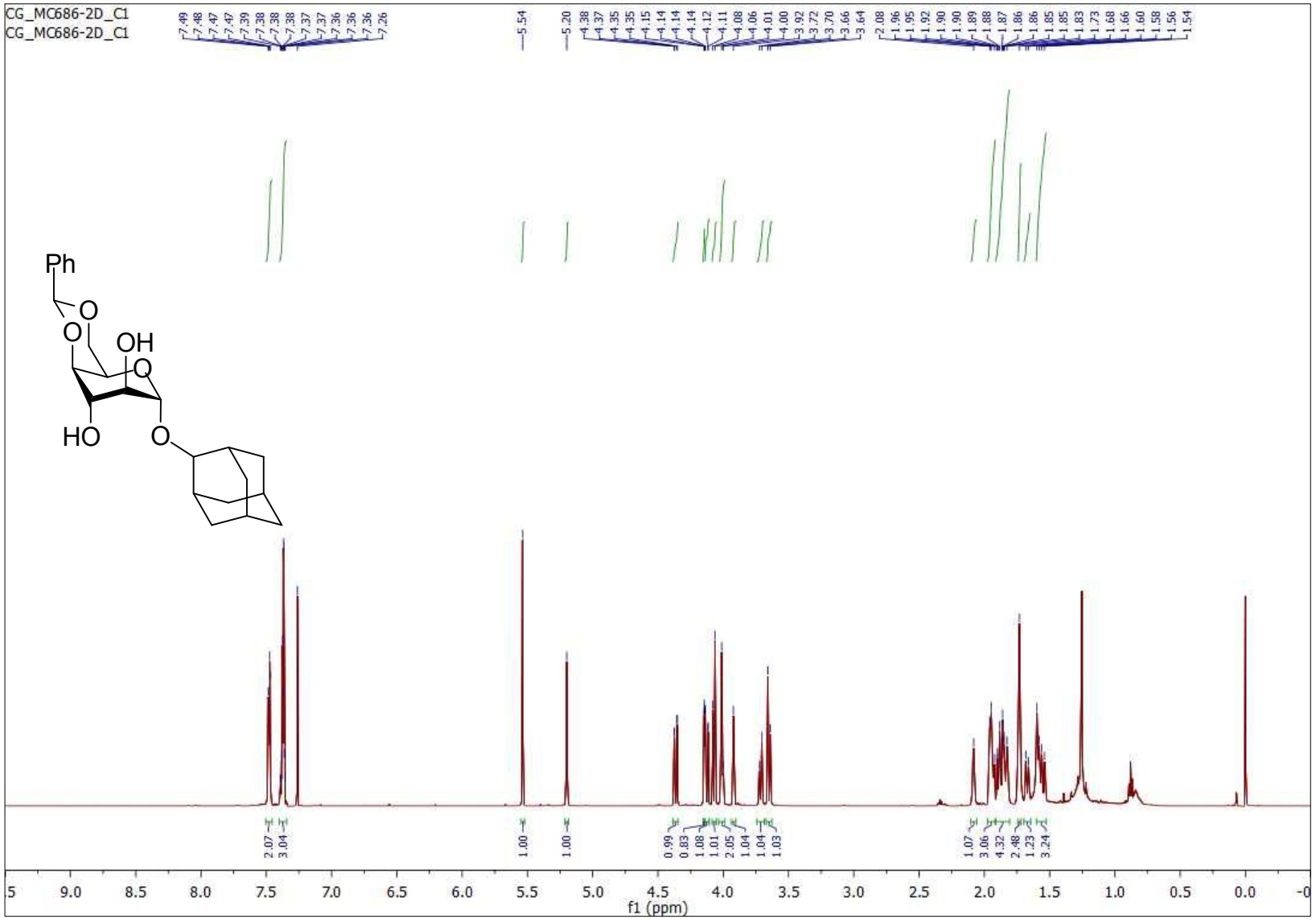


Figure S135. COSY NMR spectrum ($CDCl_3$, 500 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-*α*-D-idopyranoside (20c)**

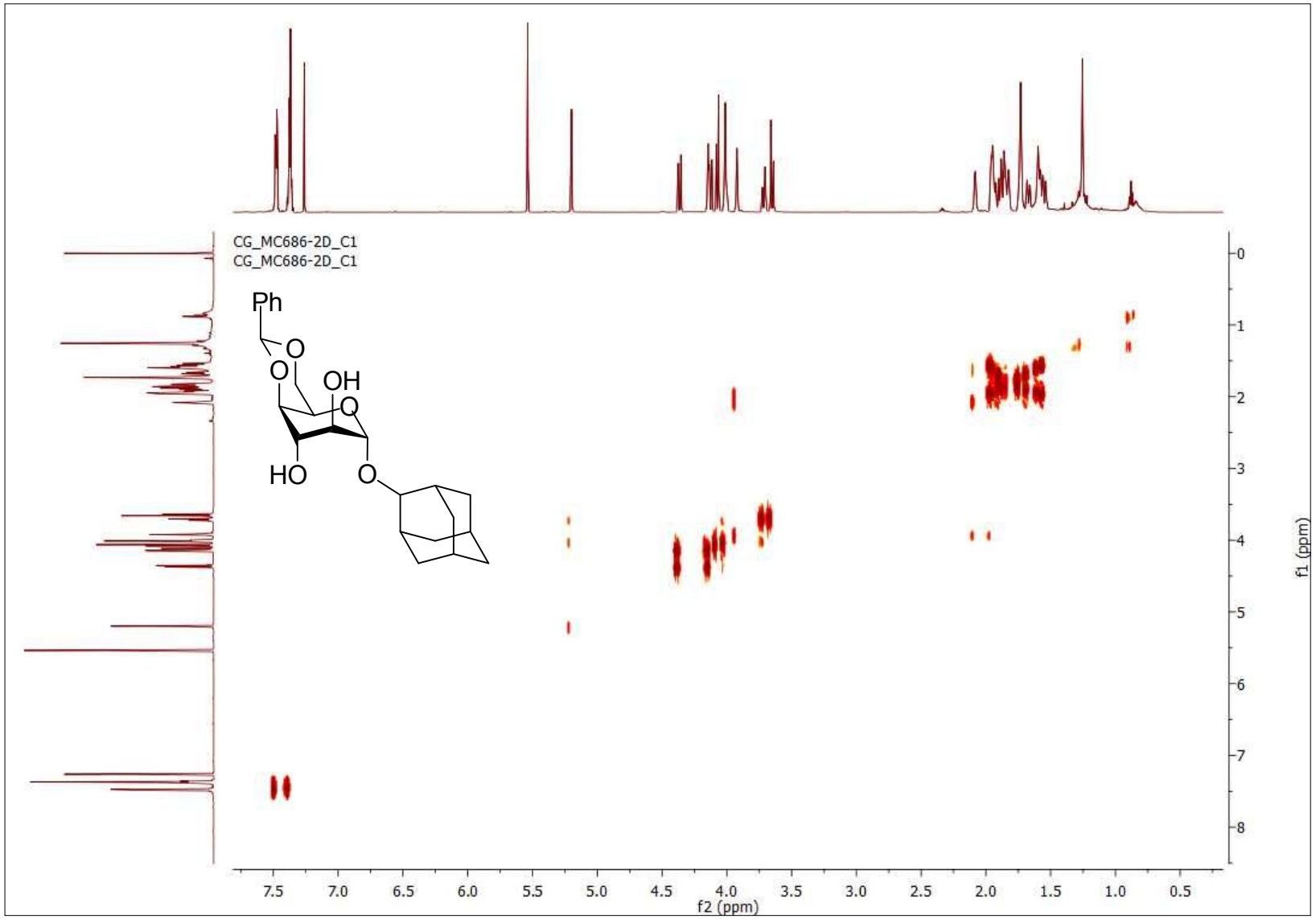


Figure S136. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-*α*-D-idopyranoside (20c)**

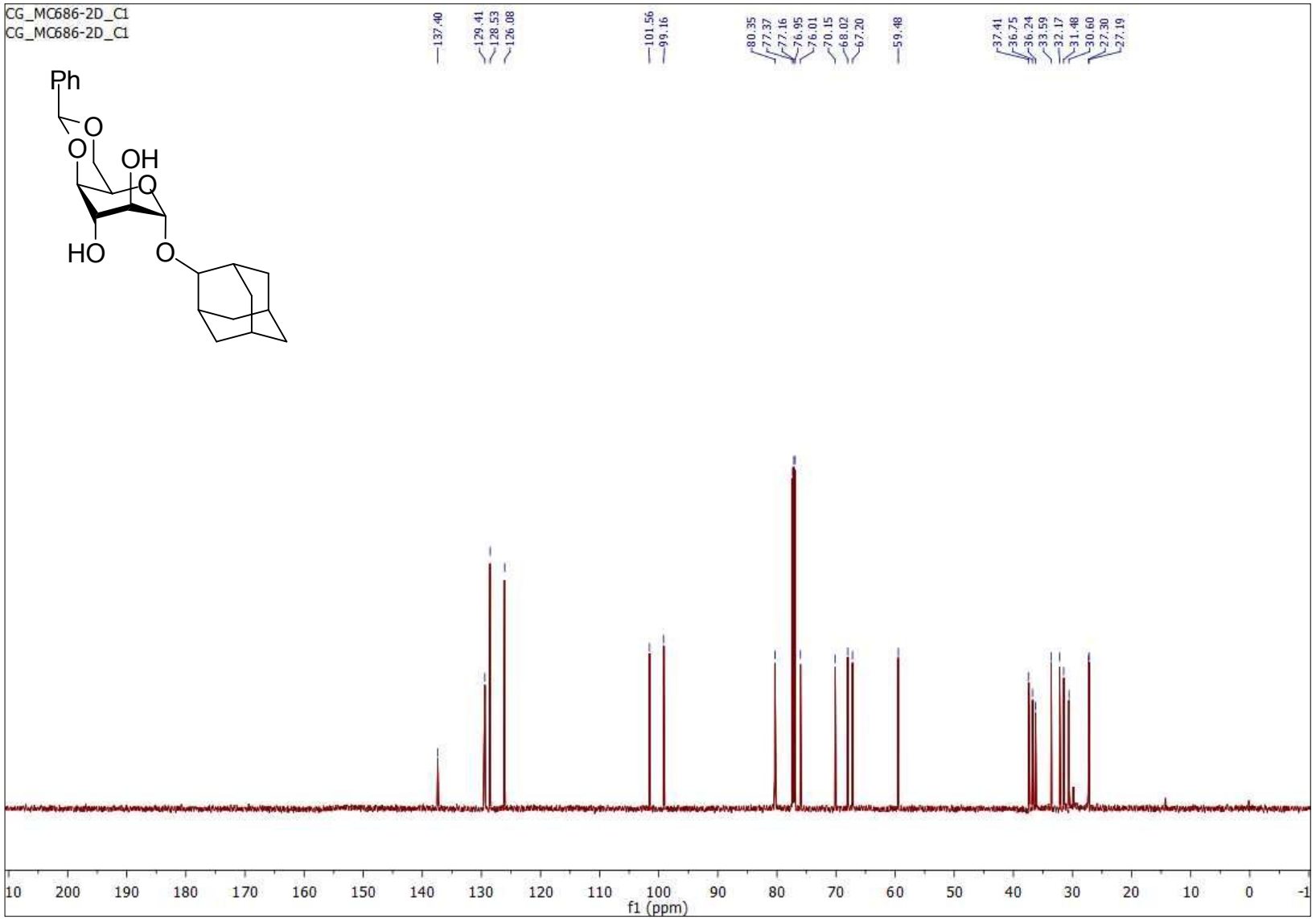


Figure S137. HSQC NMR spectrum ($CDCl_3$, 500 MHz) of **(2-adamantyl) (*S*)-4,6-*O*-benzylidene-*α*-D-idopyranoside (20c)**

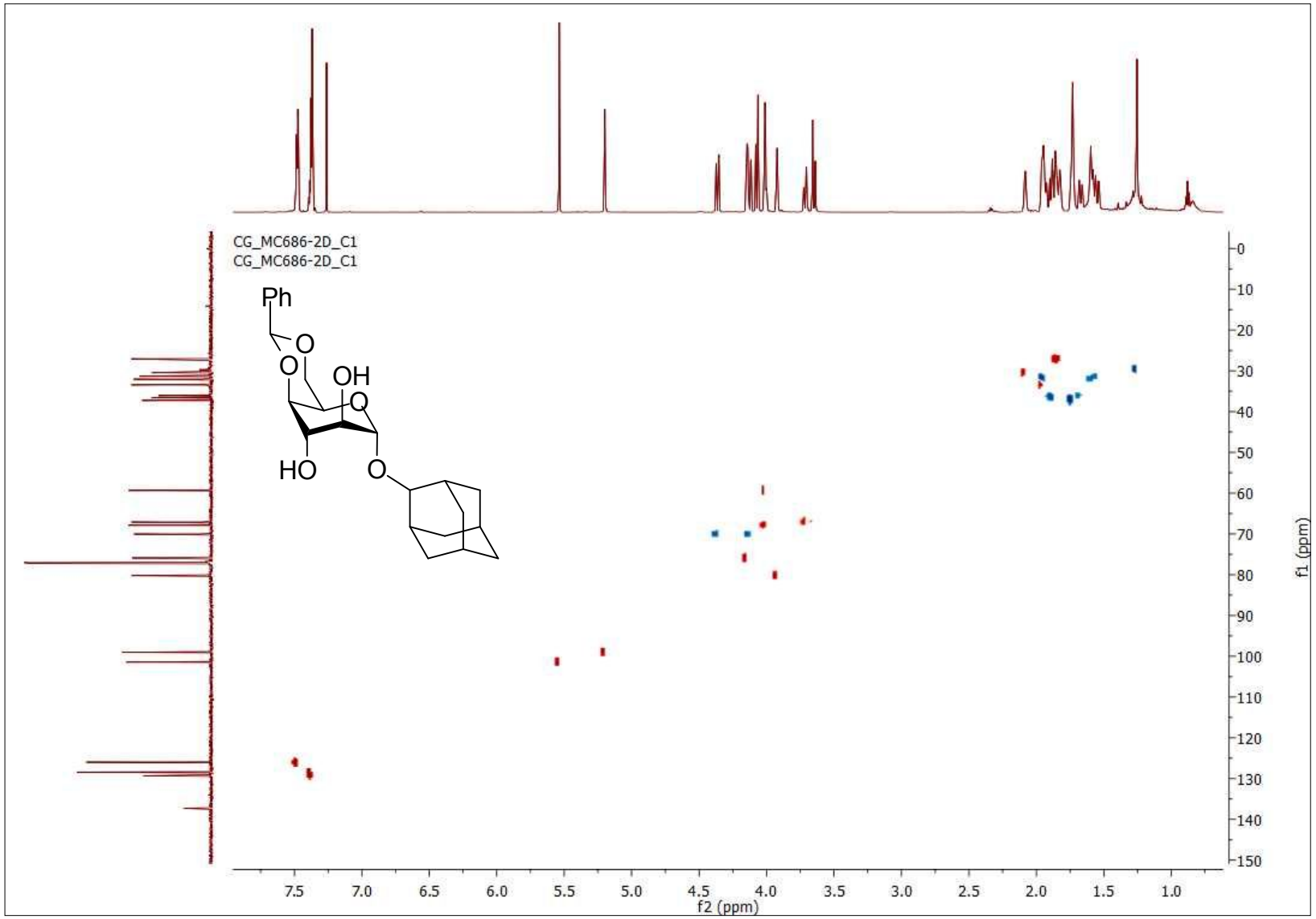


Figure S138. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (21)**

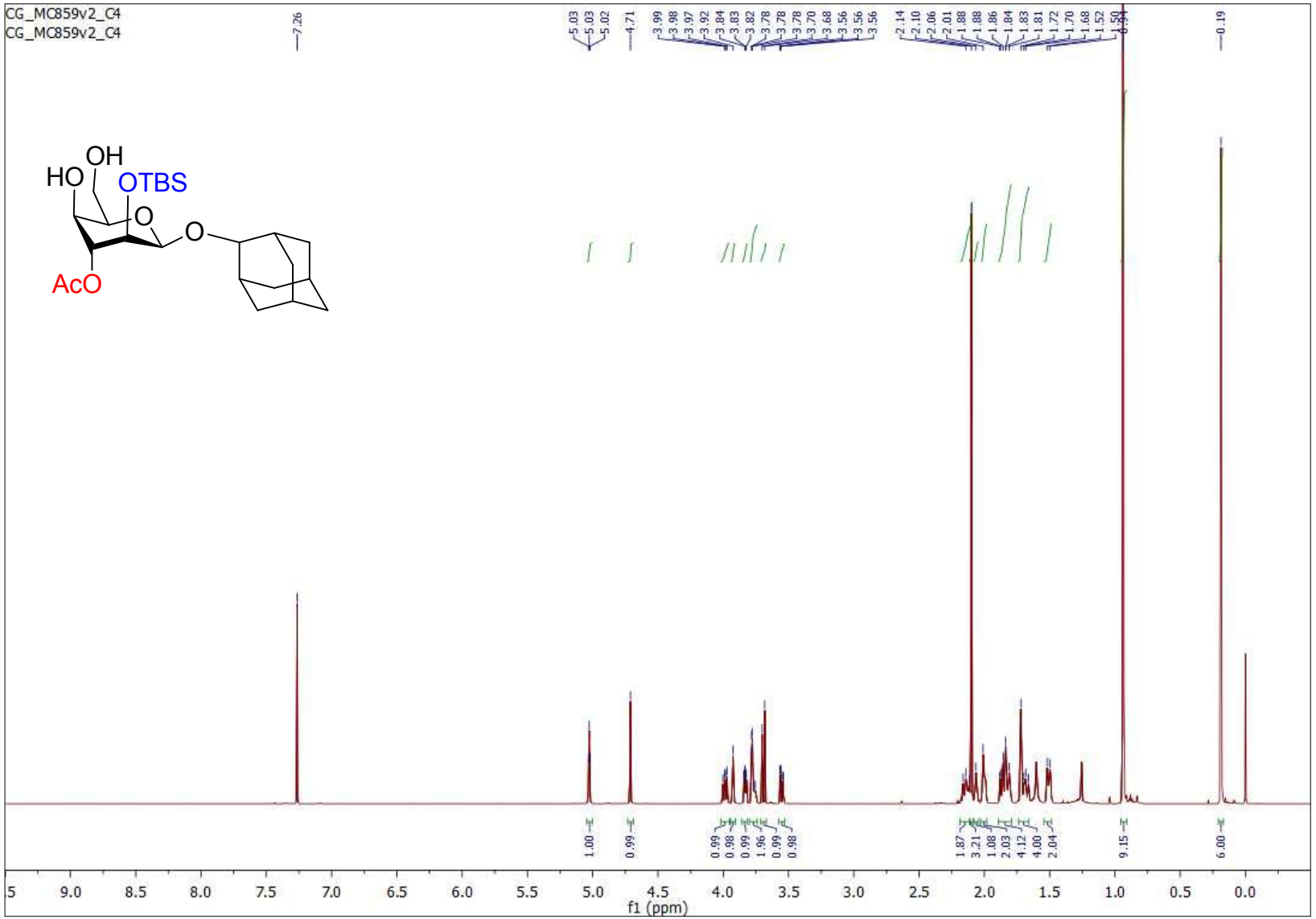


Figure S139. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (21)**

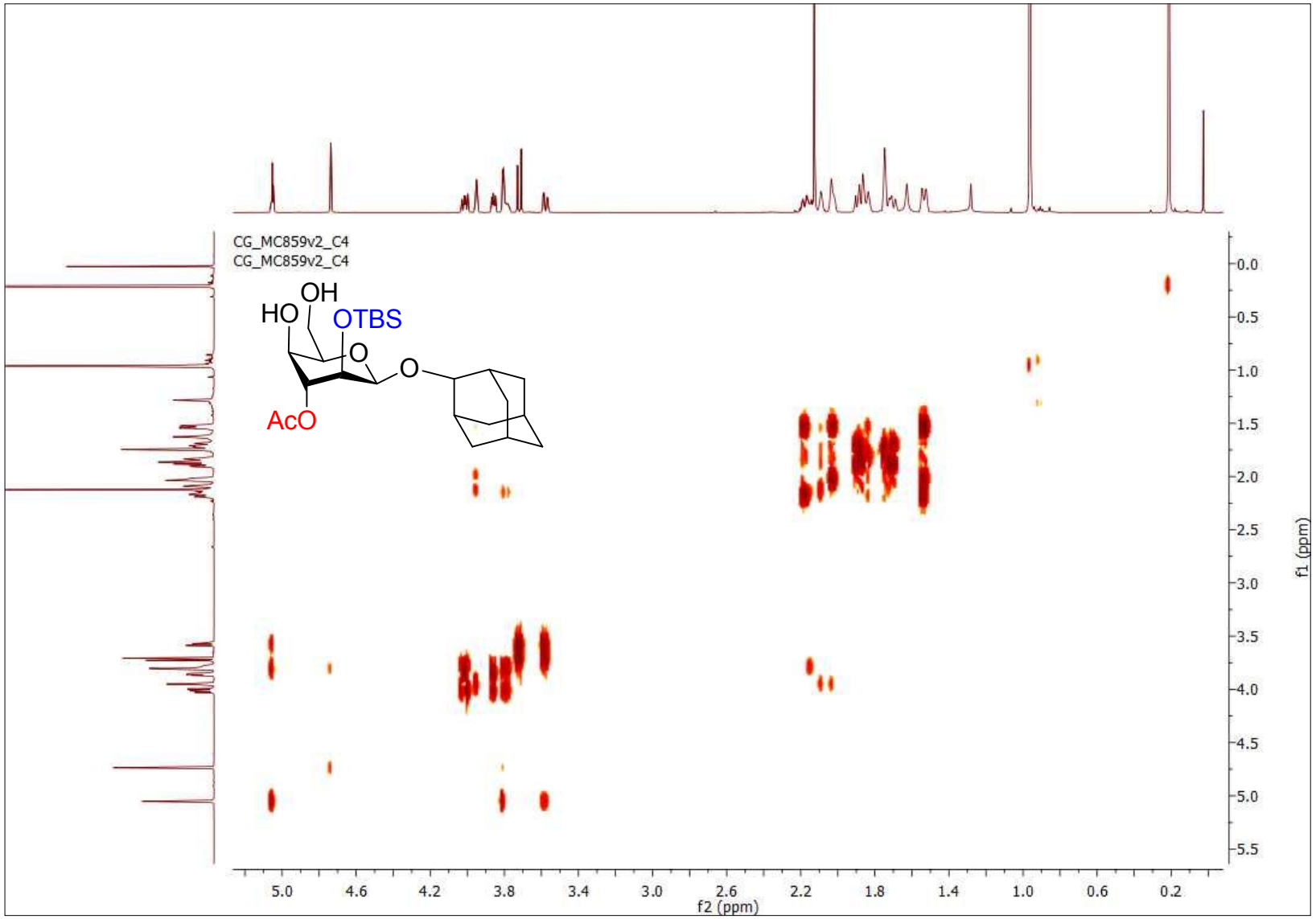


Figure S140. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) 3-*O*-acetyl-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (21)**

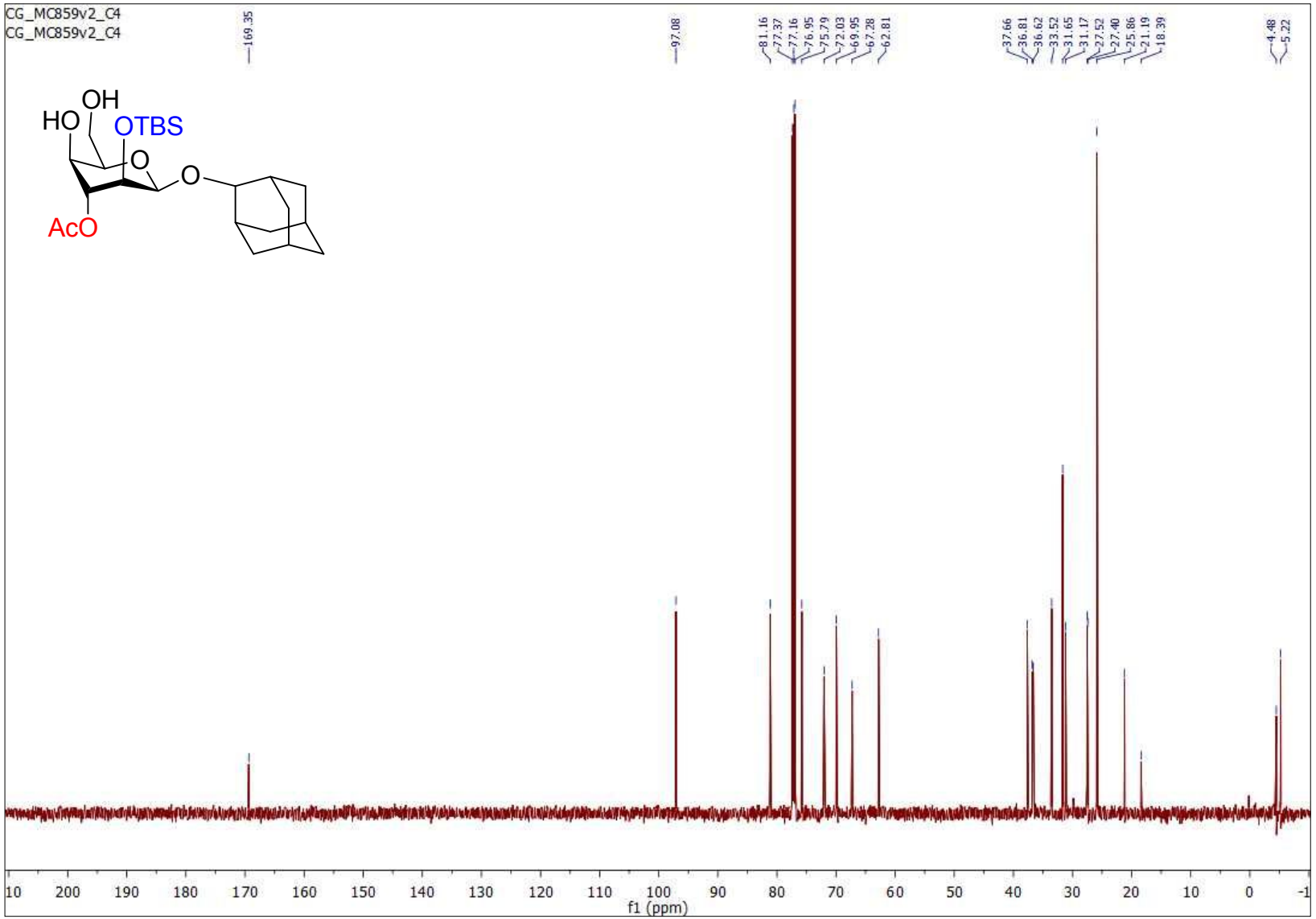


Figure S141. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (21)**

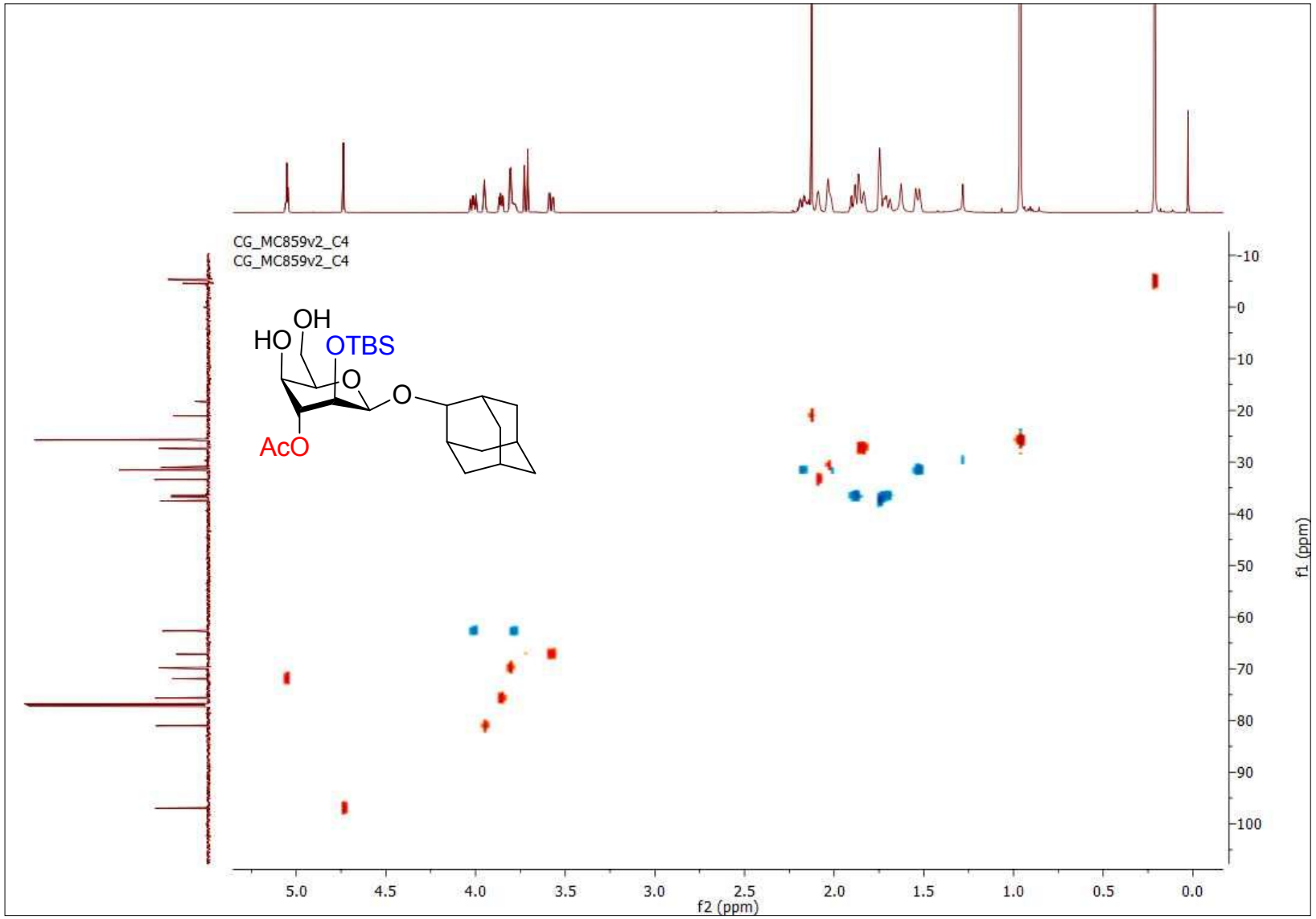


Figure S142. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (23)**

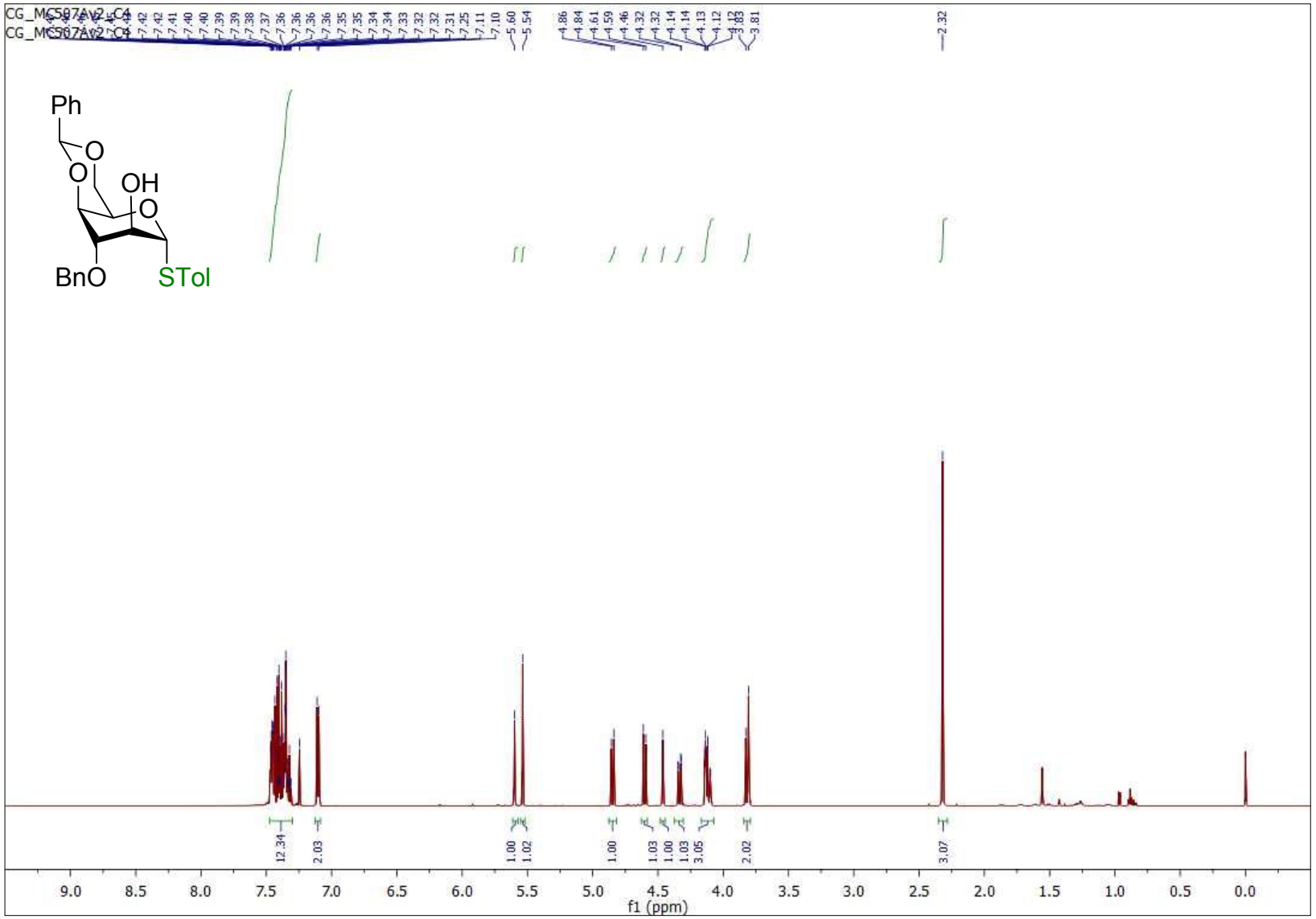


Figure S143. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (23)**

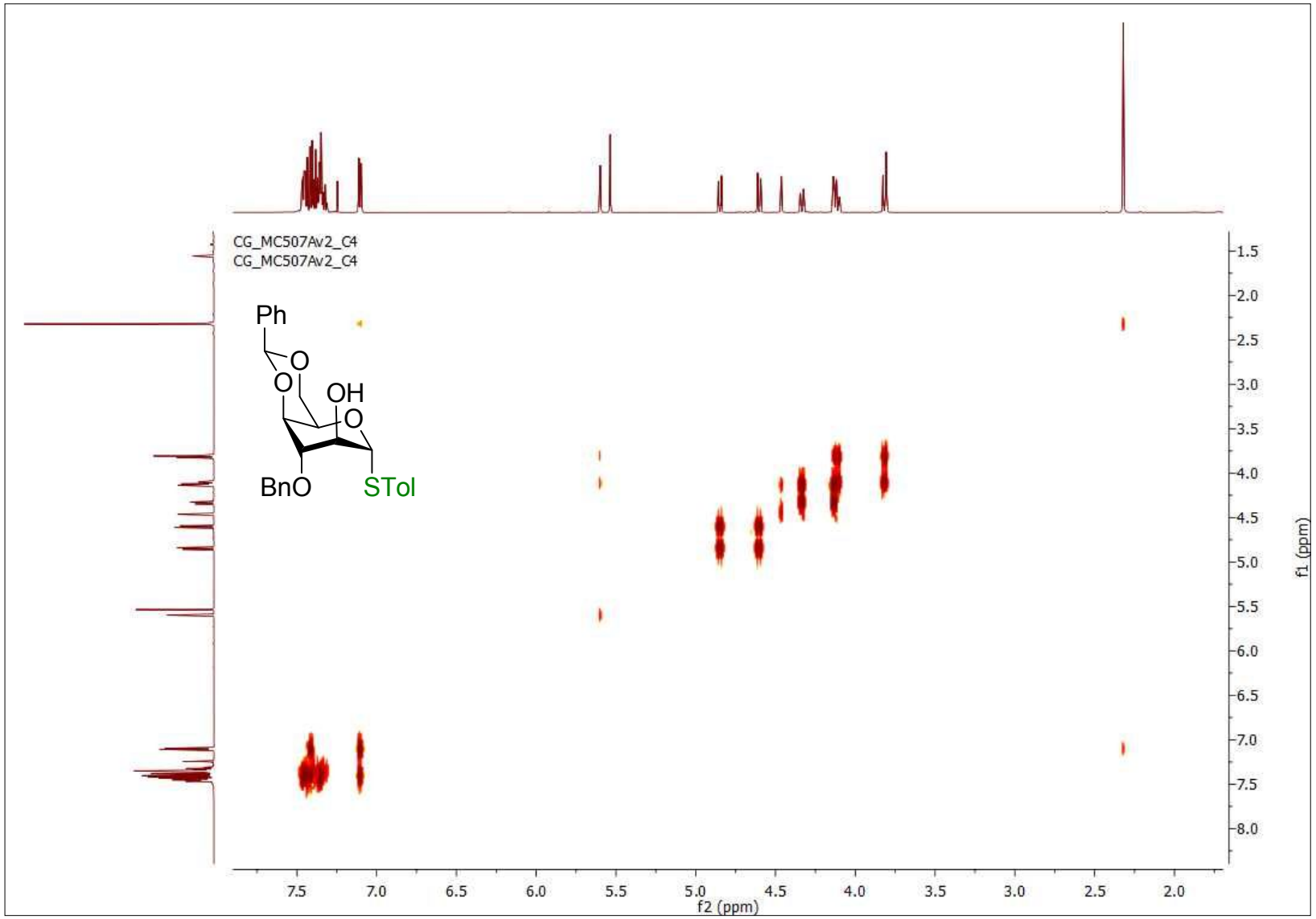


Figure S144. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***para*-methylphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (23)**

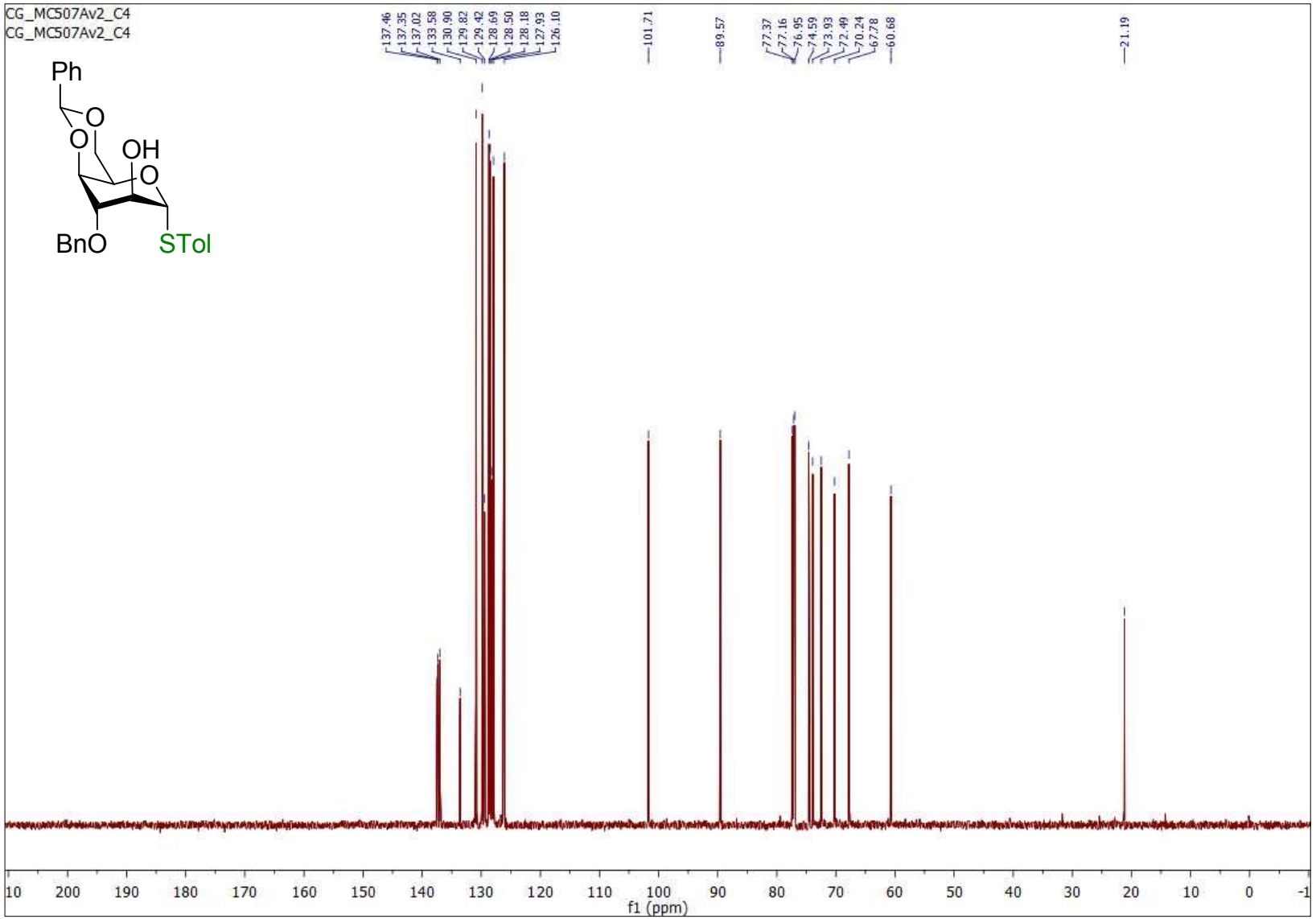


Figure S145. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*α*-D-idopyranoside (23)**

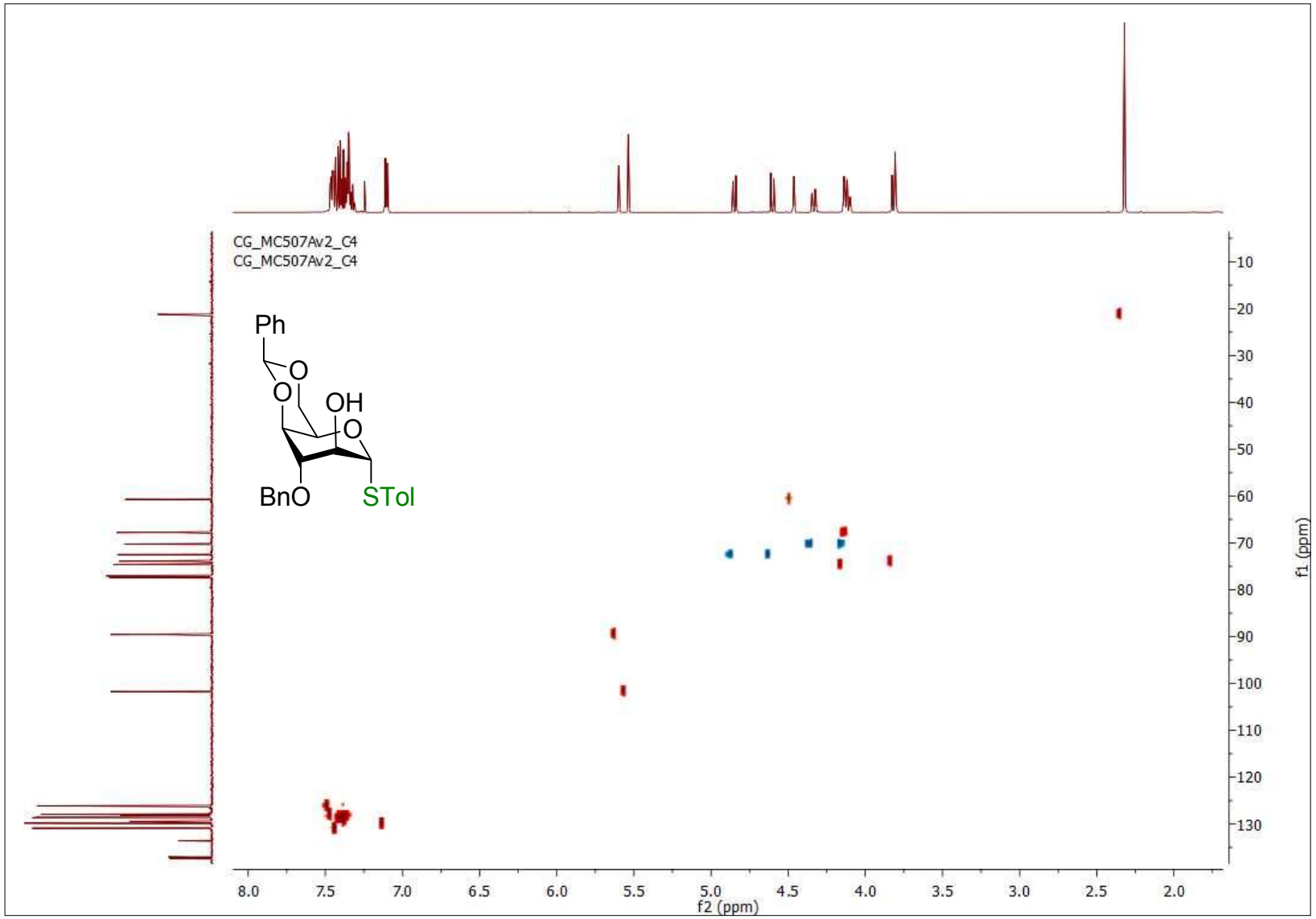


Figure S146. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-α-D-idopyranoside (24)**

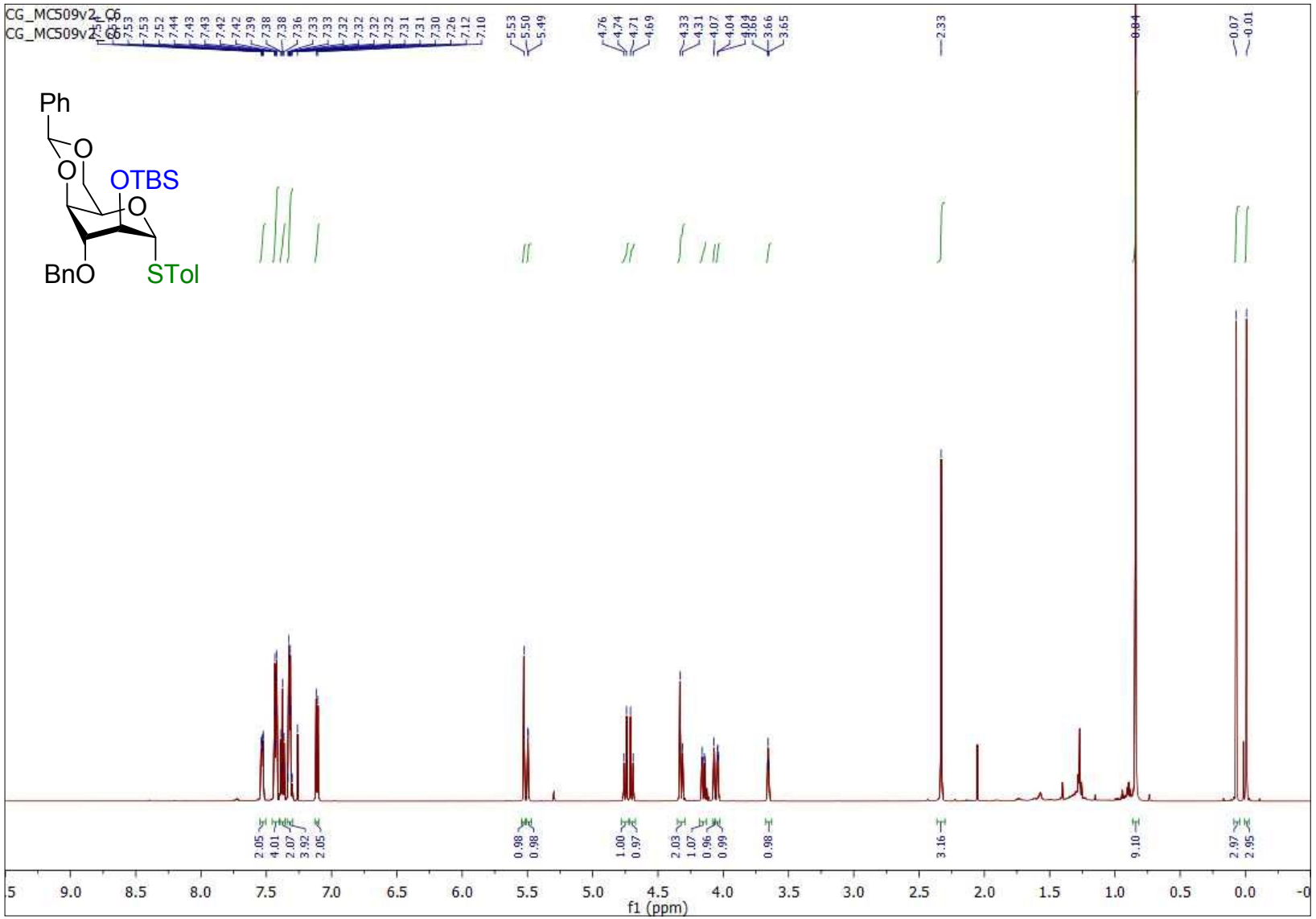


Figure S147. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (24)**

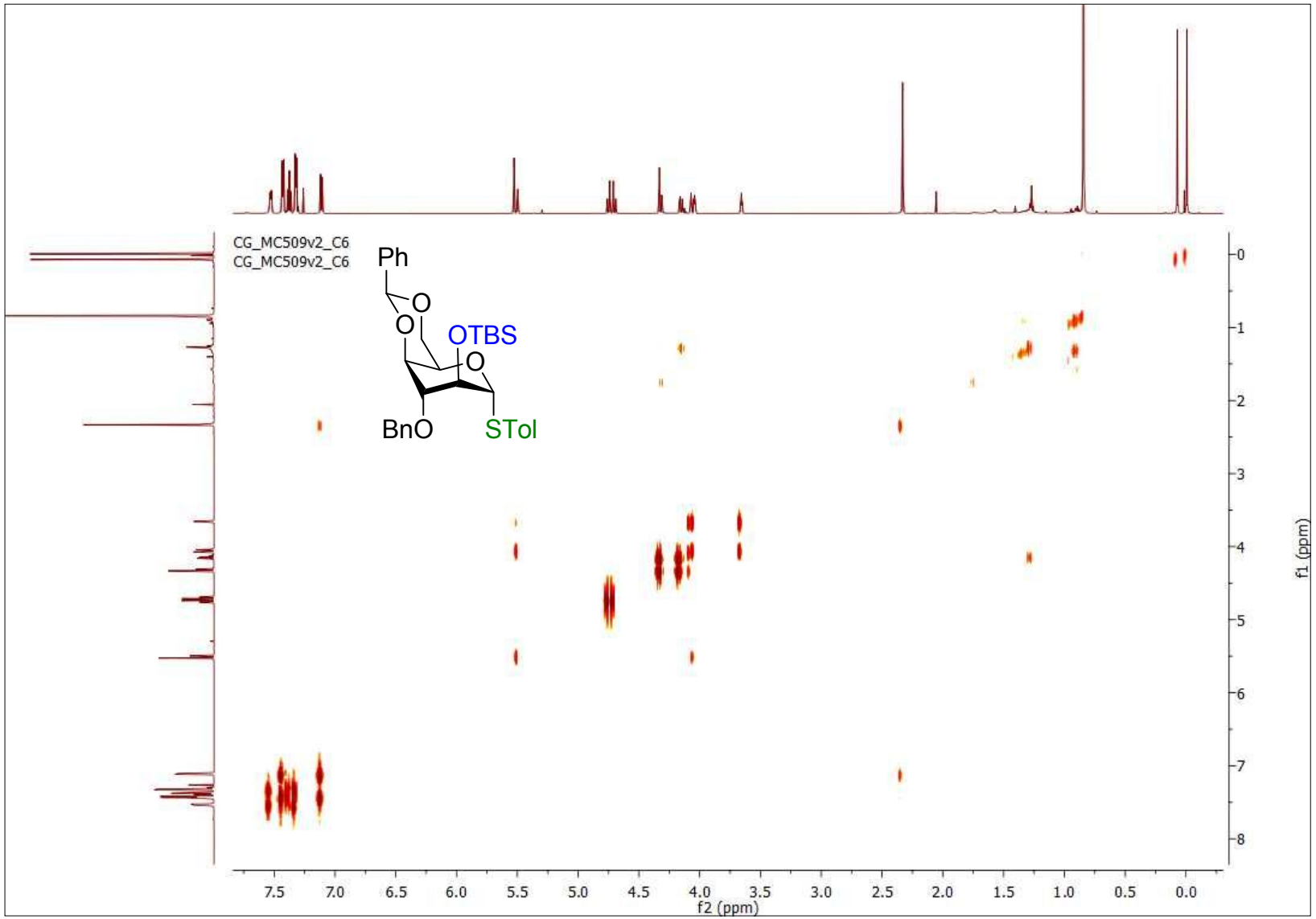


Figure S148. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***para*-methylphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (24)**

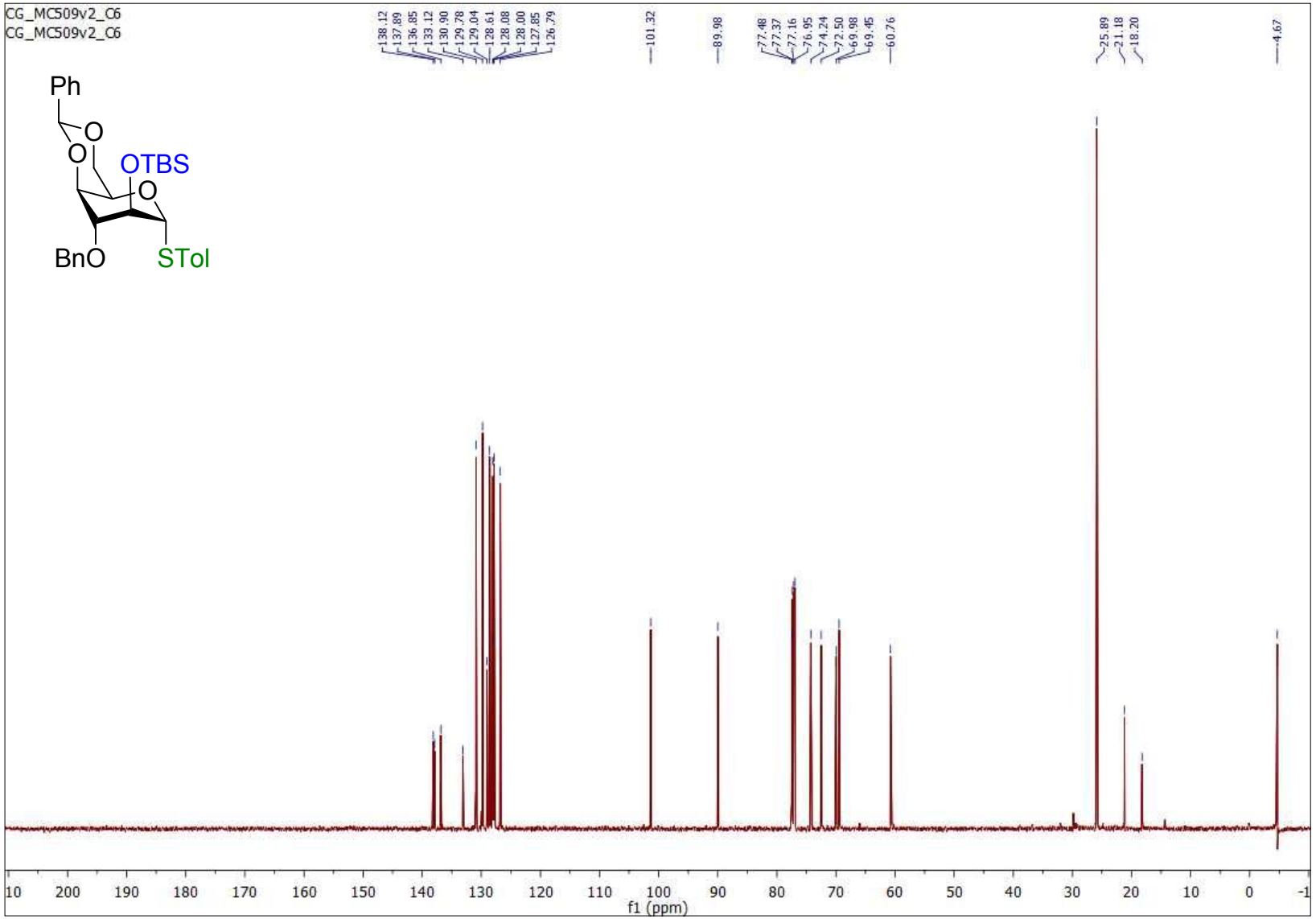


Figure S149. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***para*-methylphenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-idopyranoside (24)**

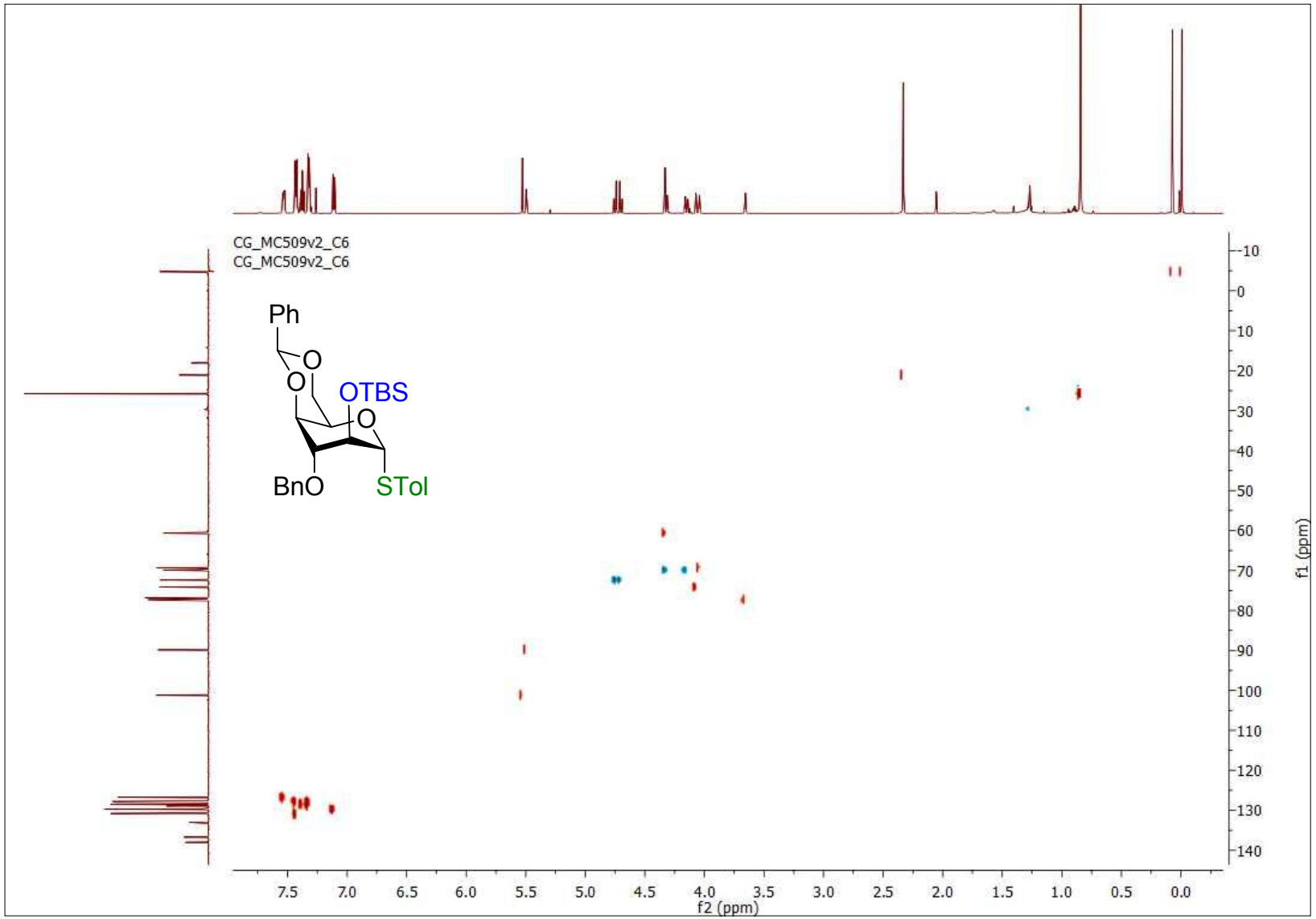


Figure S150. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **1,2,3,4,6-penta-*O*-acetyl *α*-D-talopyranose (26)**

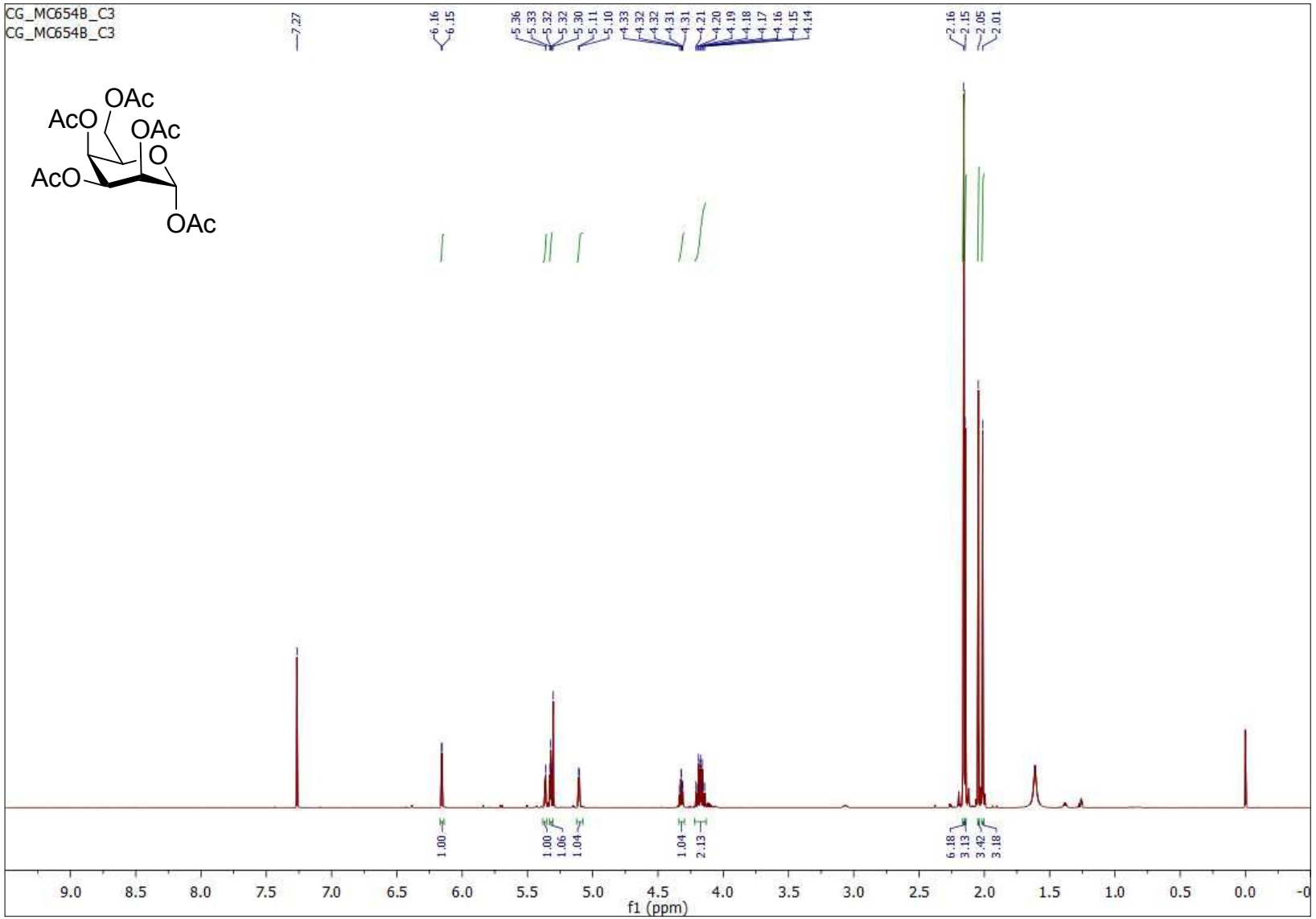


Figure S151. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-talopyranoside**

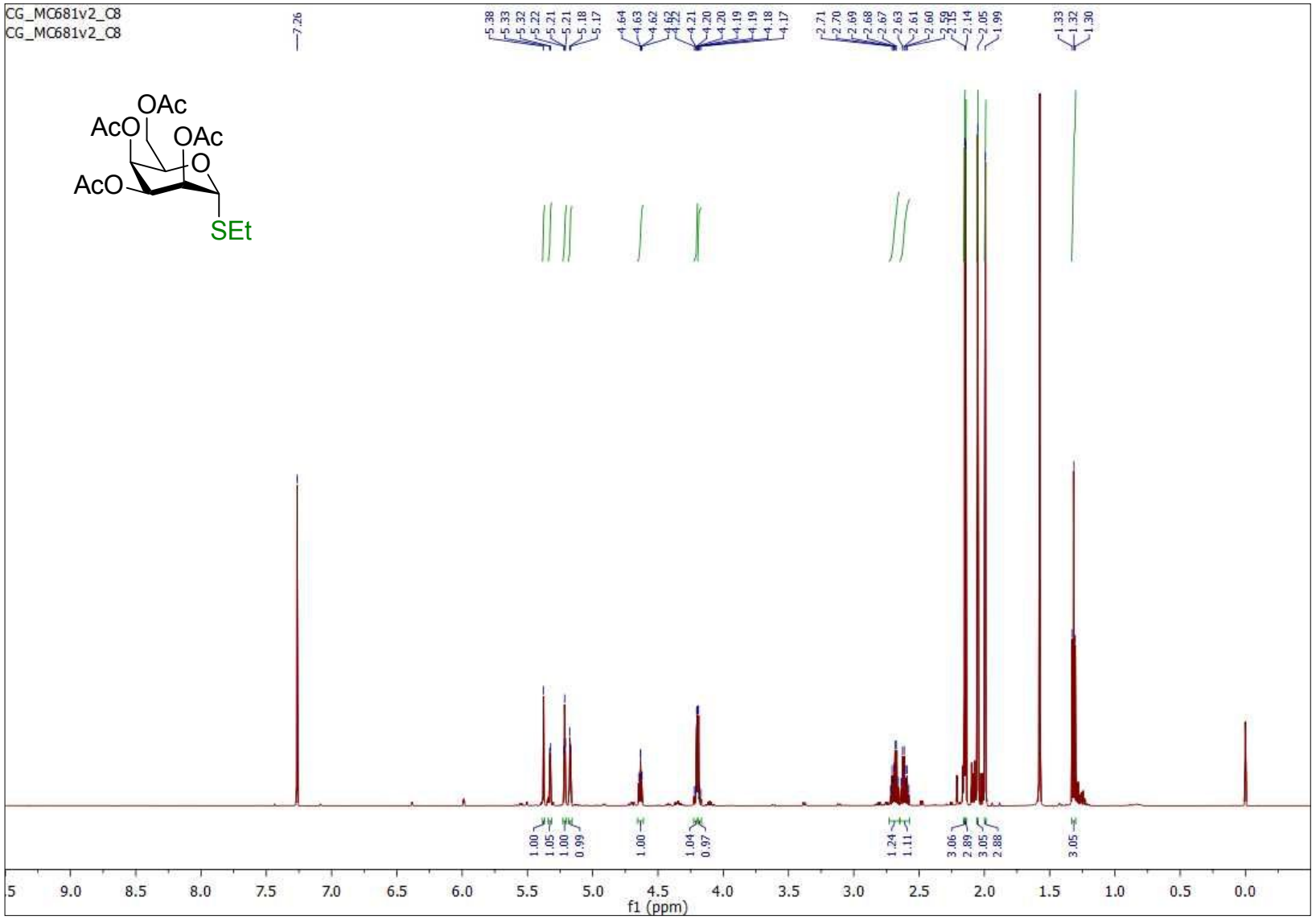


Figure S152. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-talopyranoside**

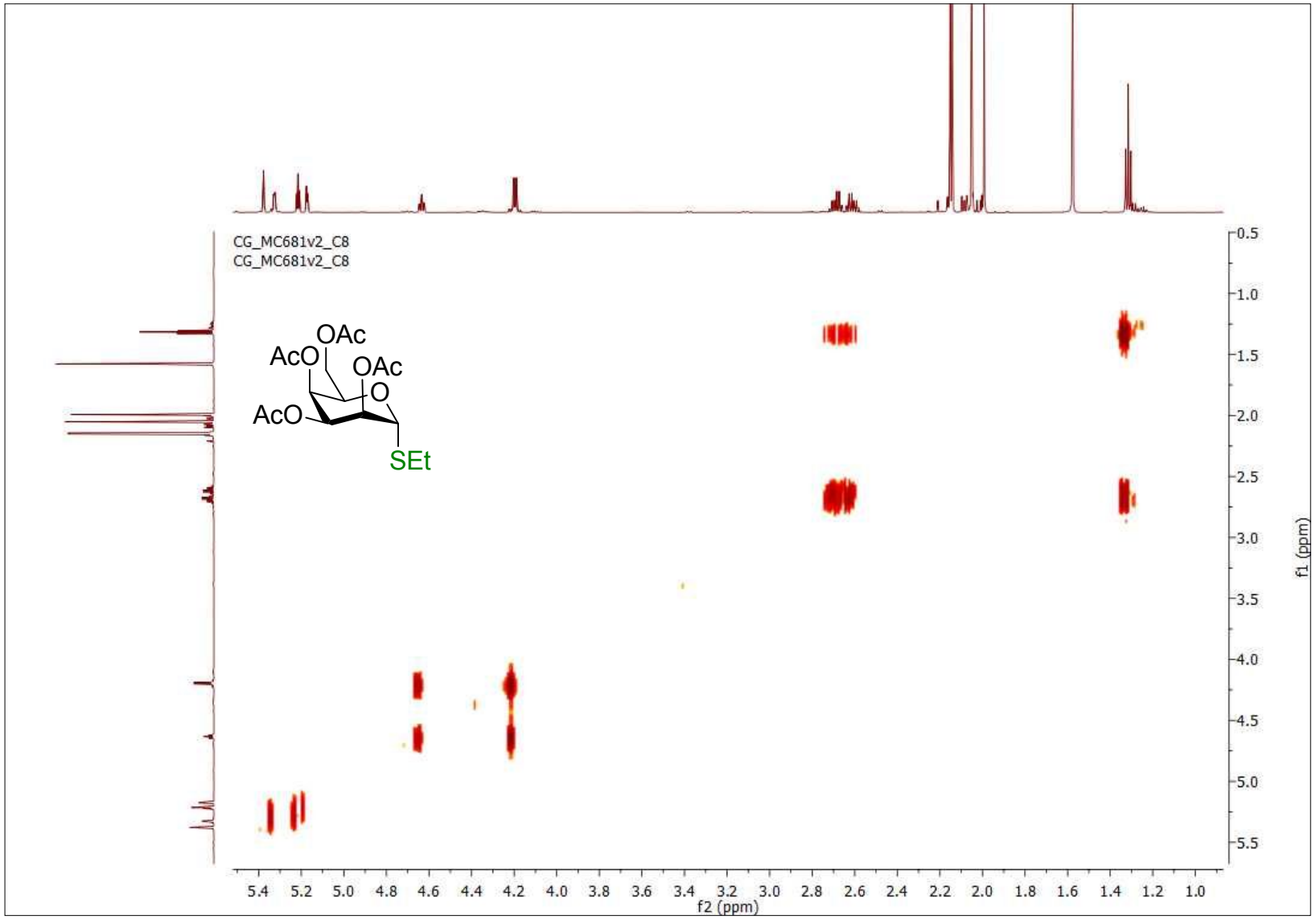


Figure S153. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-talopyranoside**

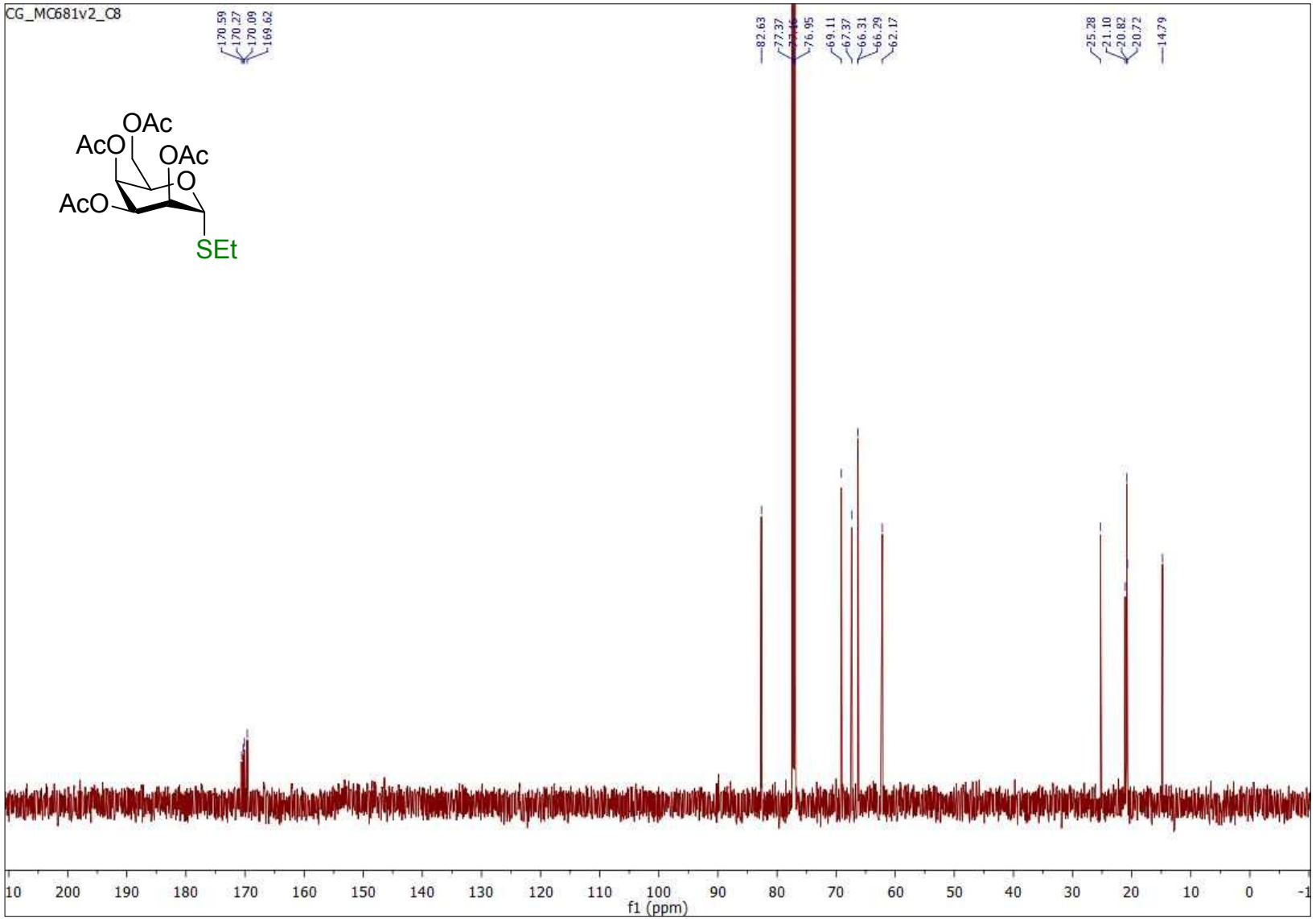


Figure S154. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-*α*-D-talopyranoside**

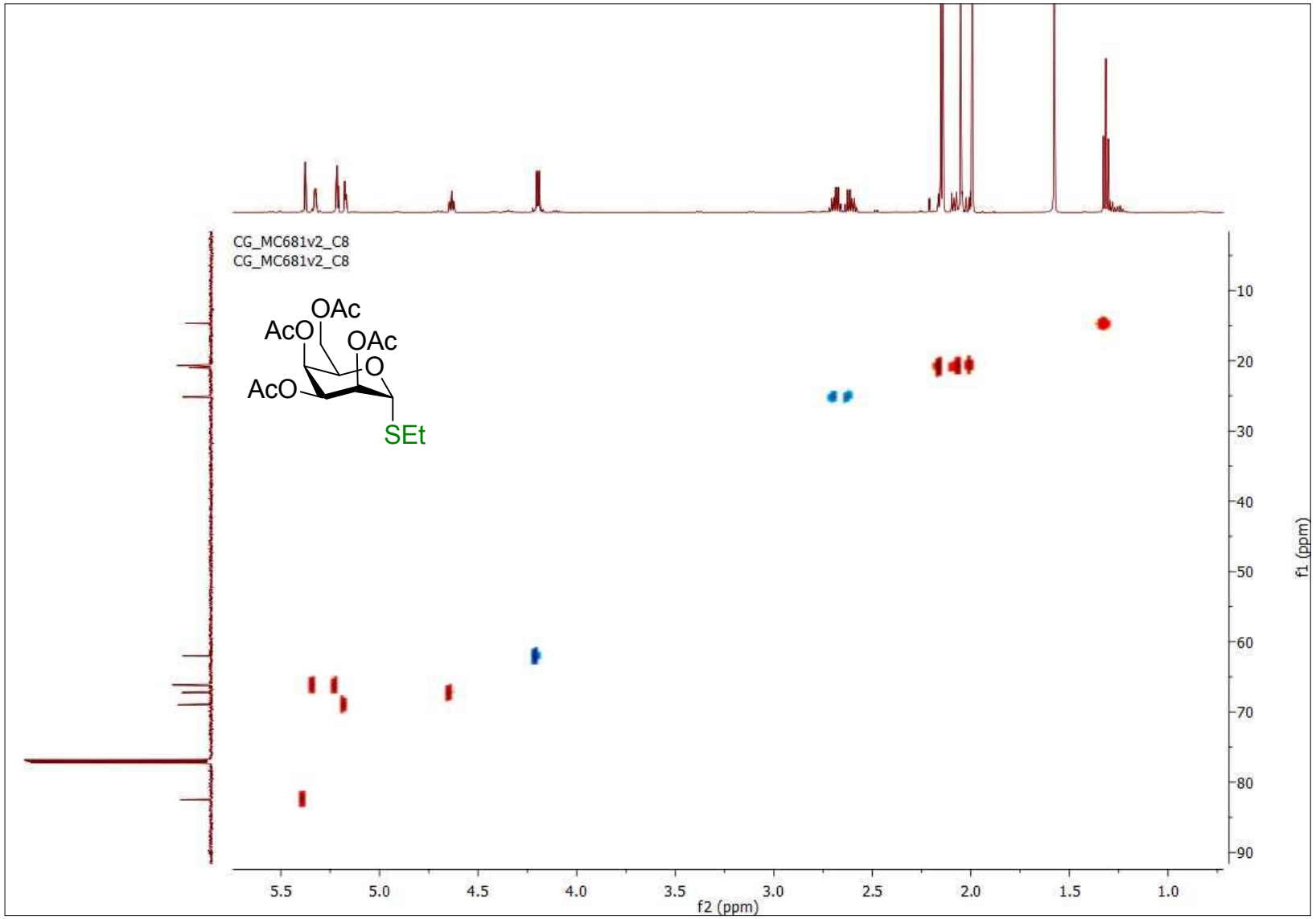


Figure S155. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-1-thio-*α*-D-talopyranoside (27)**

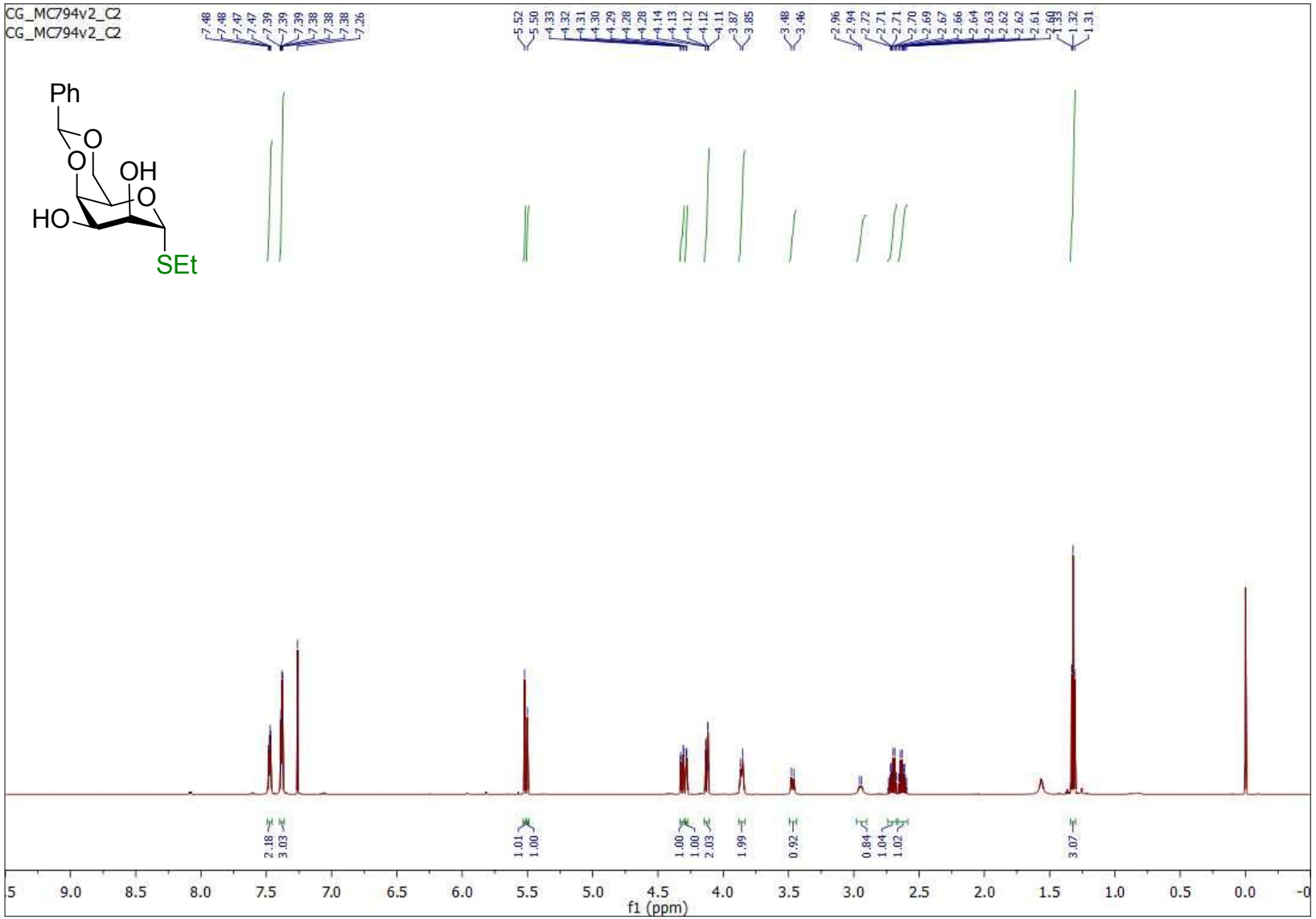


Figure S156. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-1-thio-*α*-D-talopyranoside (27)**

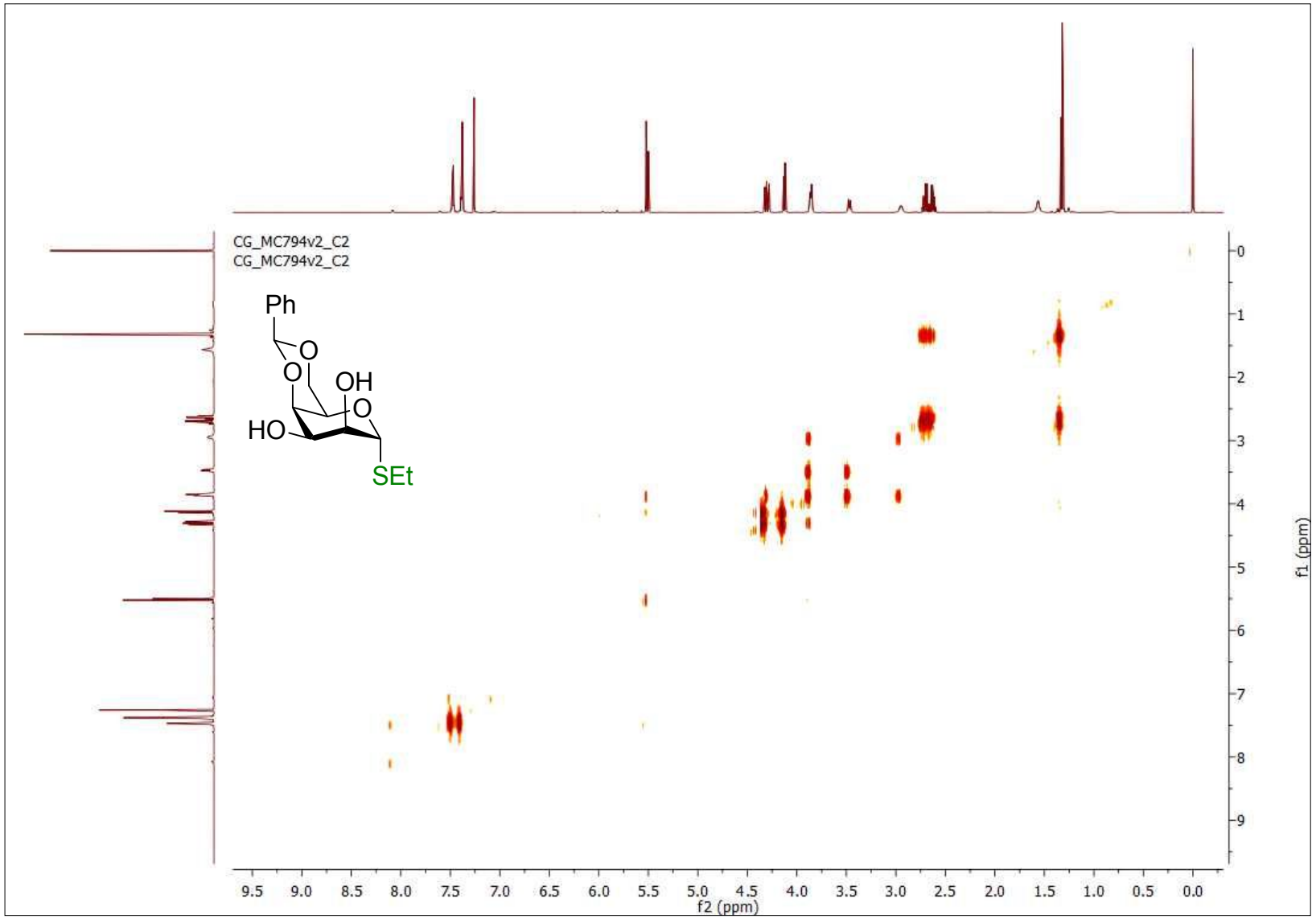


Figure S157. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **ethyl 4,6-*O*-benzylidene-1-thio-*α*-D-talopyranoside (27)**

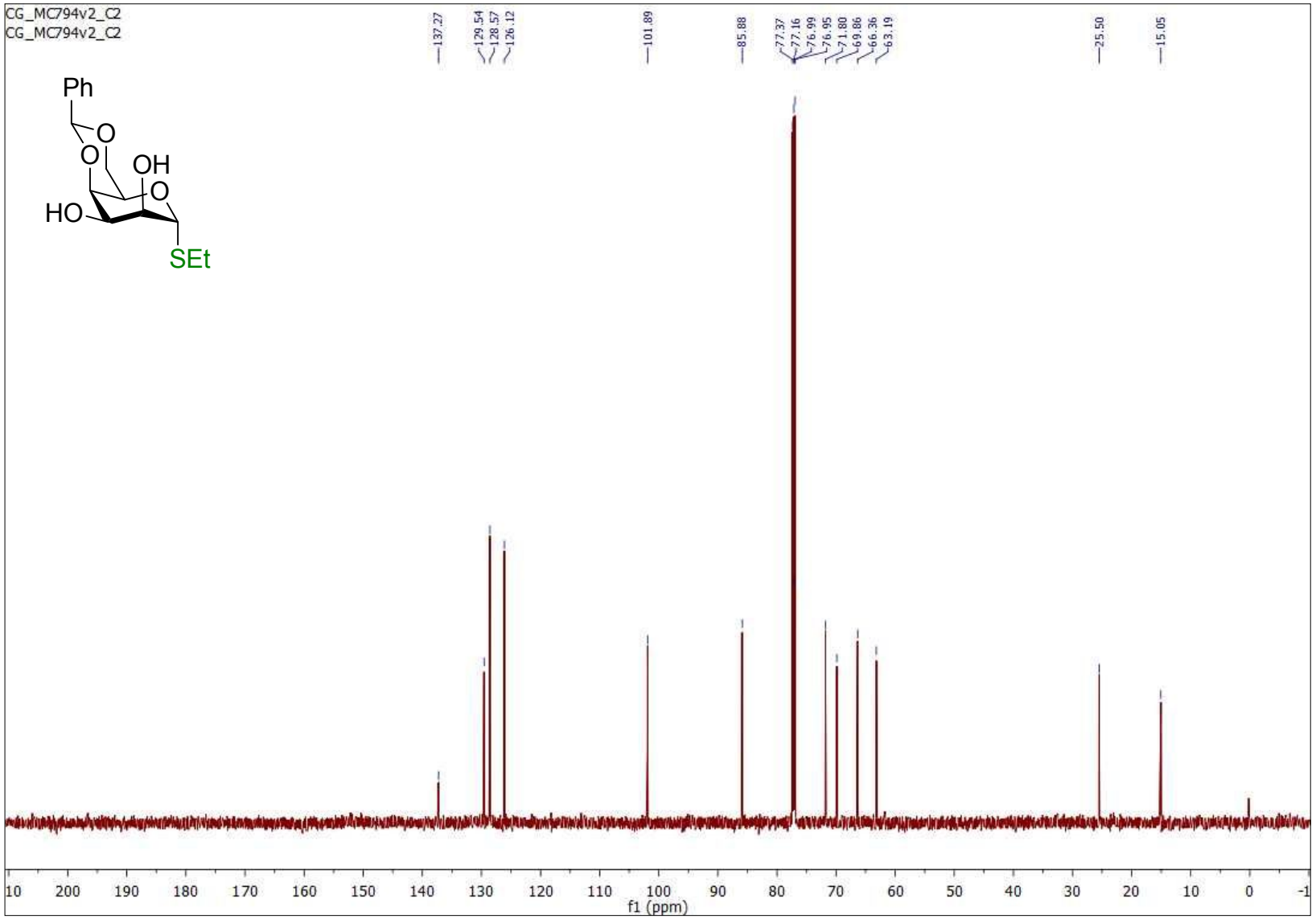


Figure S158. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 4,6-*O*-benzylidene-1-thio-*α*-D-talopyranoside (27)**

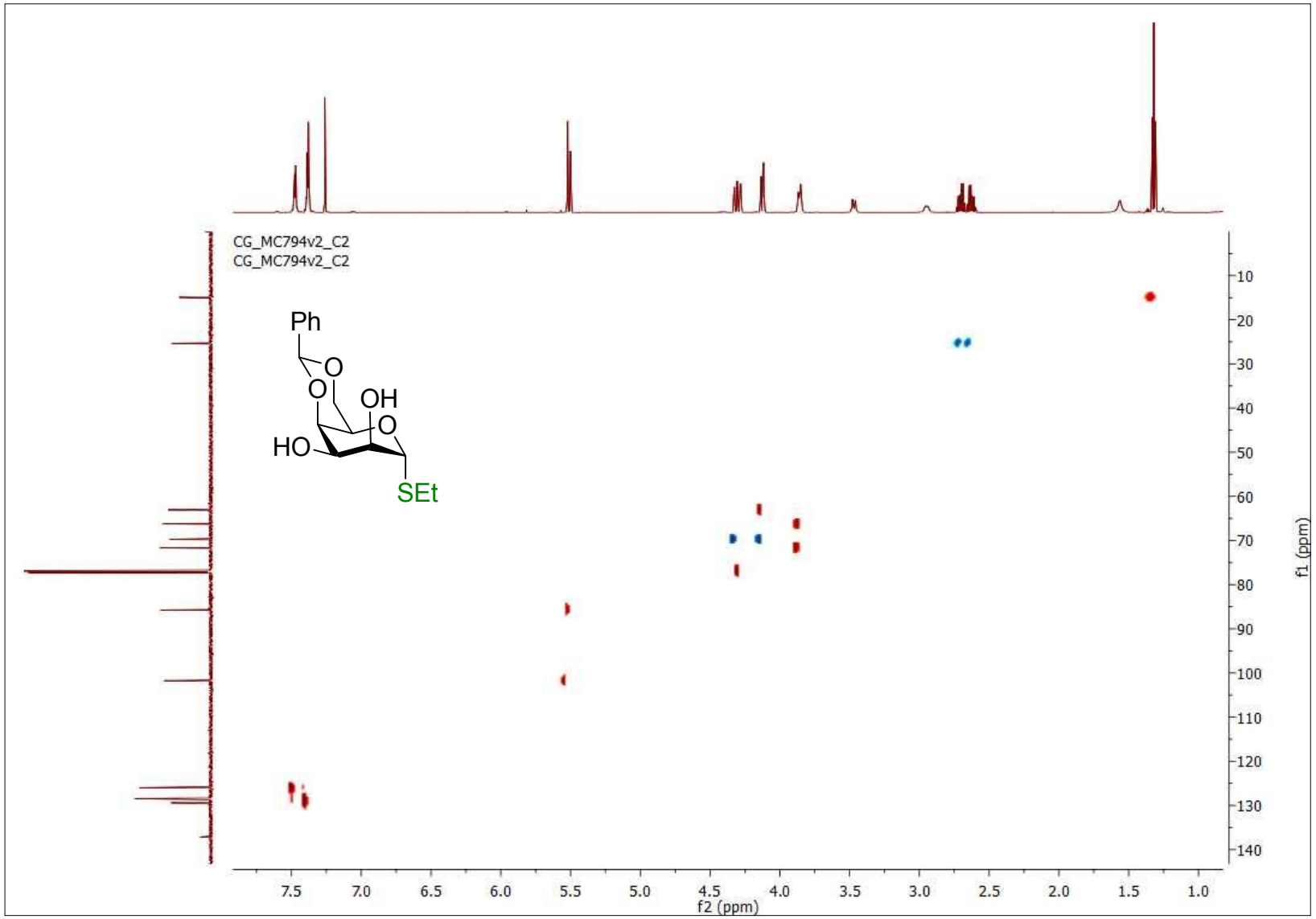


Figure S159. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-1-thio-*α*-D-talopyranoside**

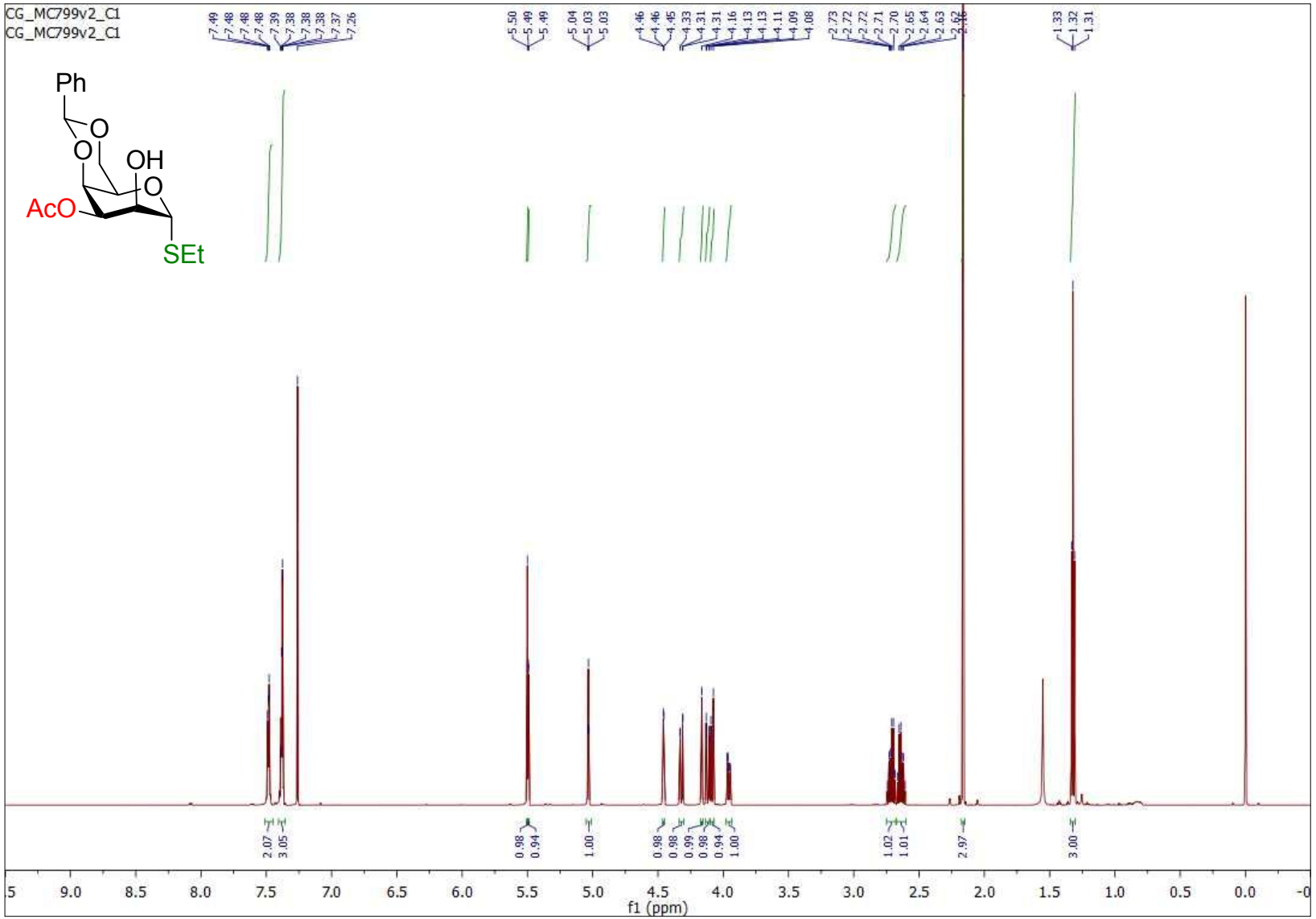


Figure S160. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-1-thio-*α*-D-talopyranoside**

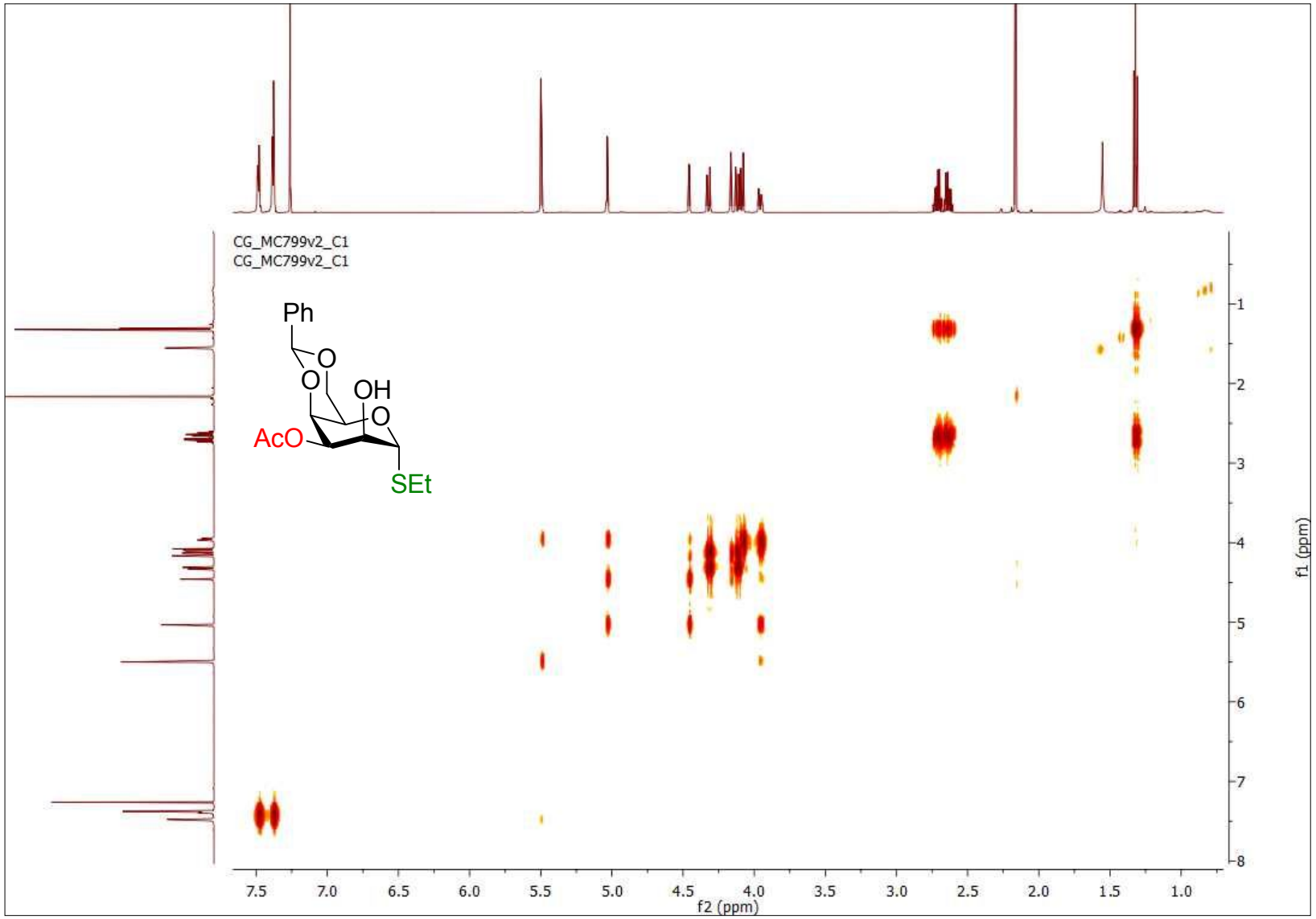


Figure S161. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-1-thio-*α*-D-talopyranoside**

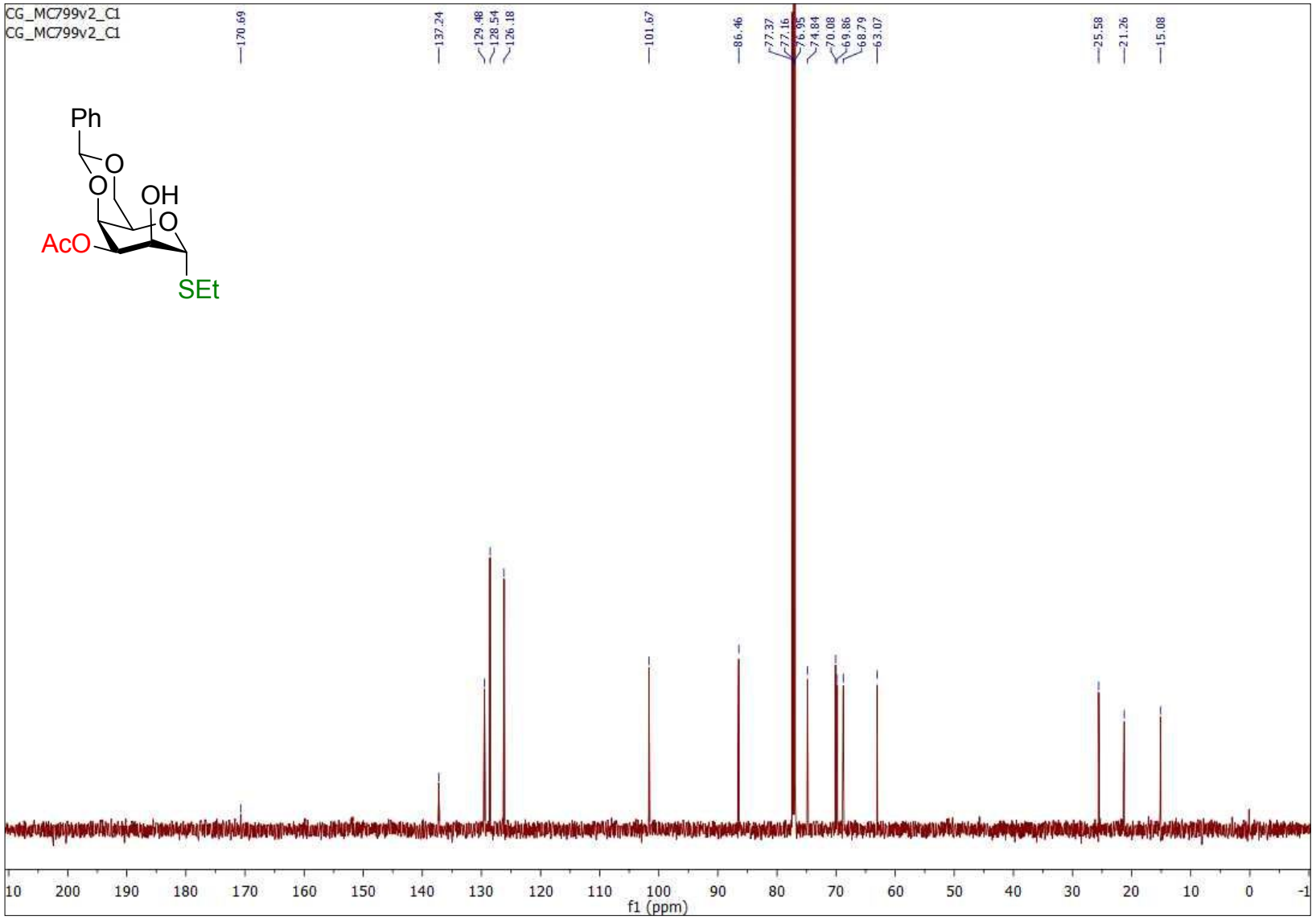


Figure S162. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-1-thio-*α*-D-talopyranoside**

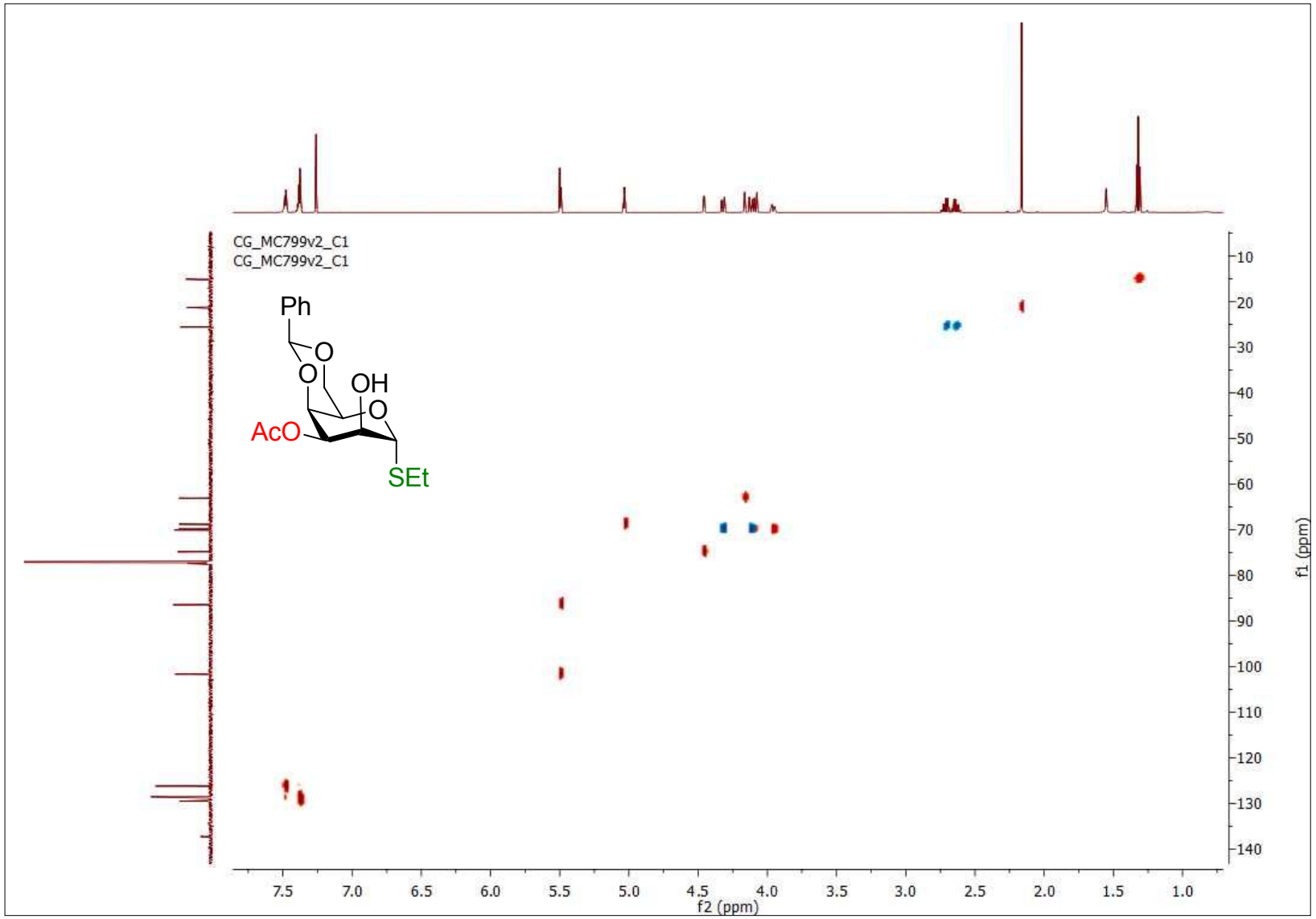


Figure S163. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-talopyranoside (28)**

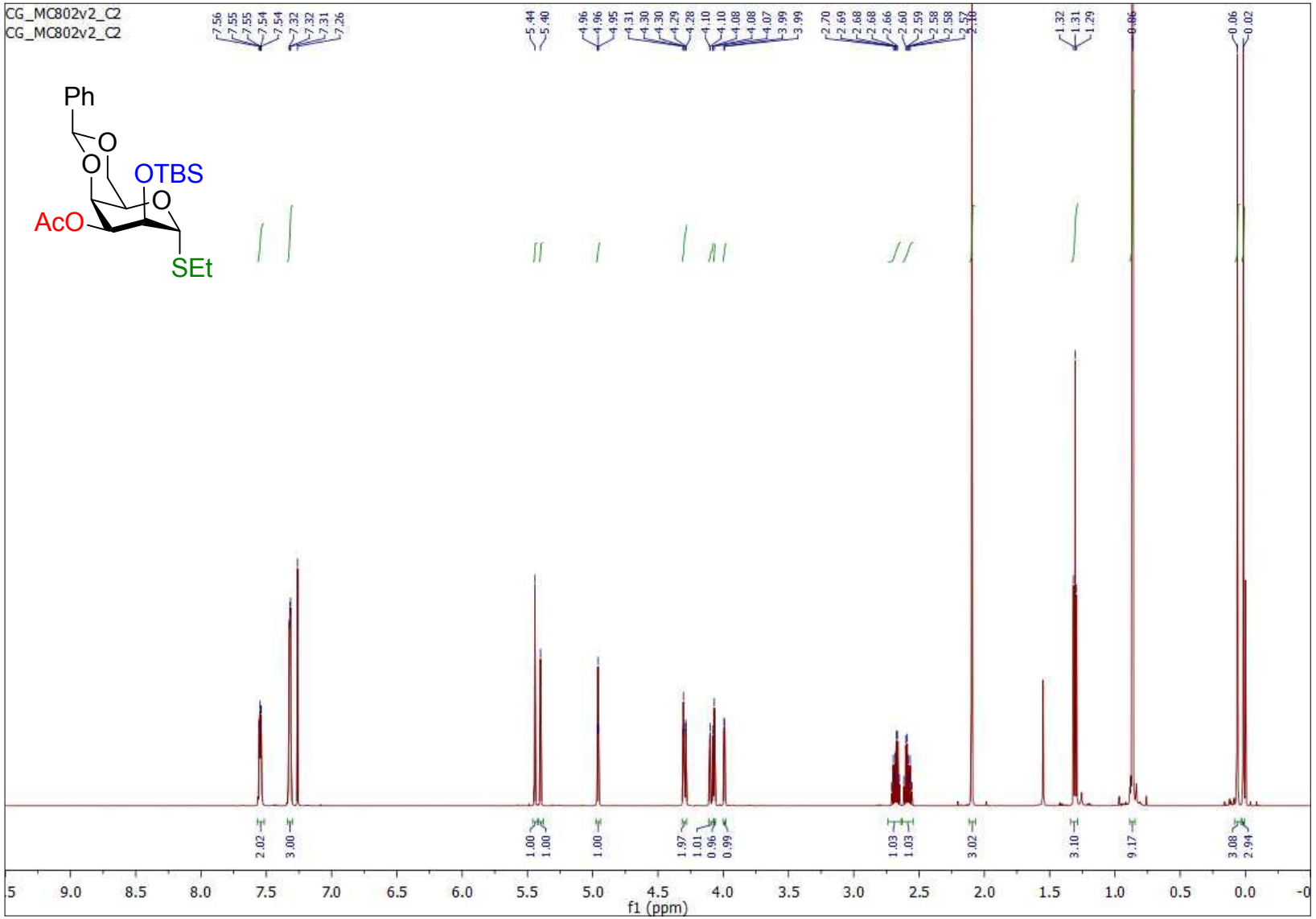


Figure S164. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-talopyranoside (28)**

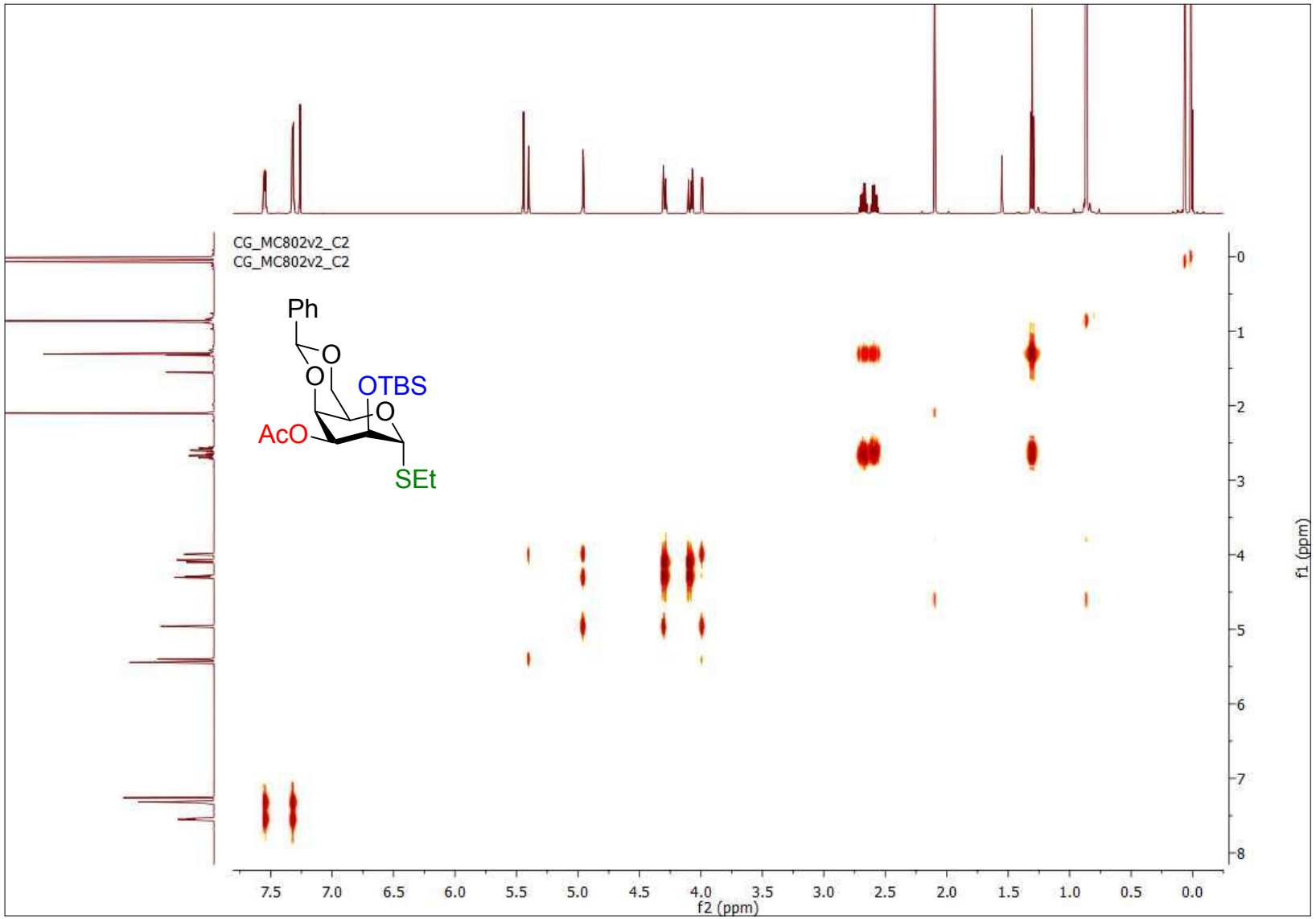


Figure S165. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-talopyranoside (28)**

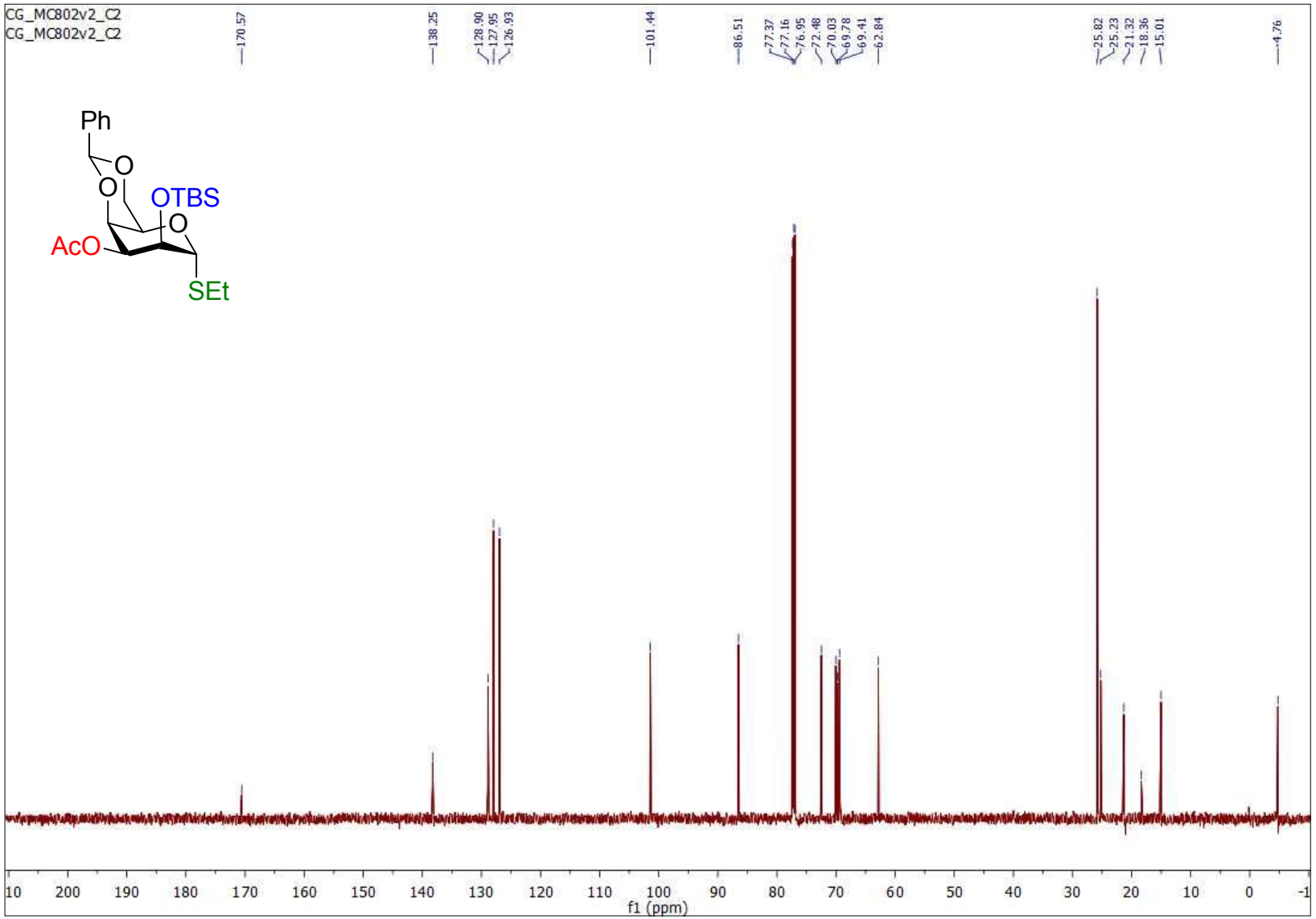


Figure S166. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **ethyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-1-thio-*α*-D-talopyranoside (28)**

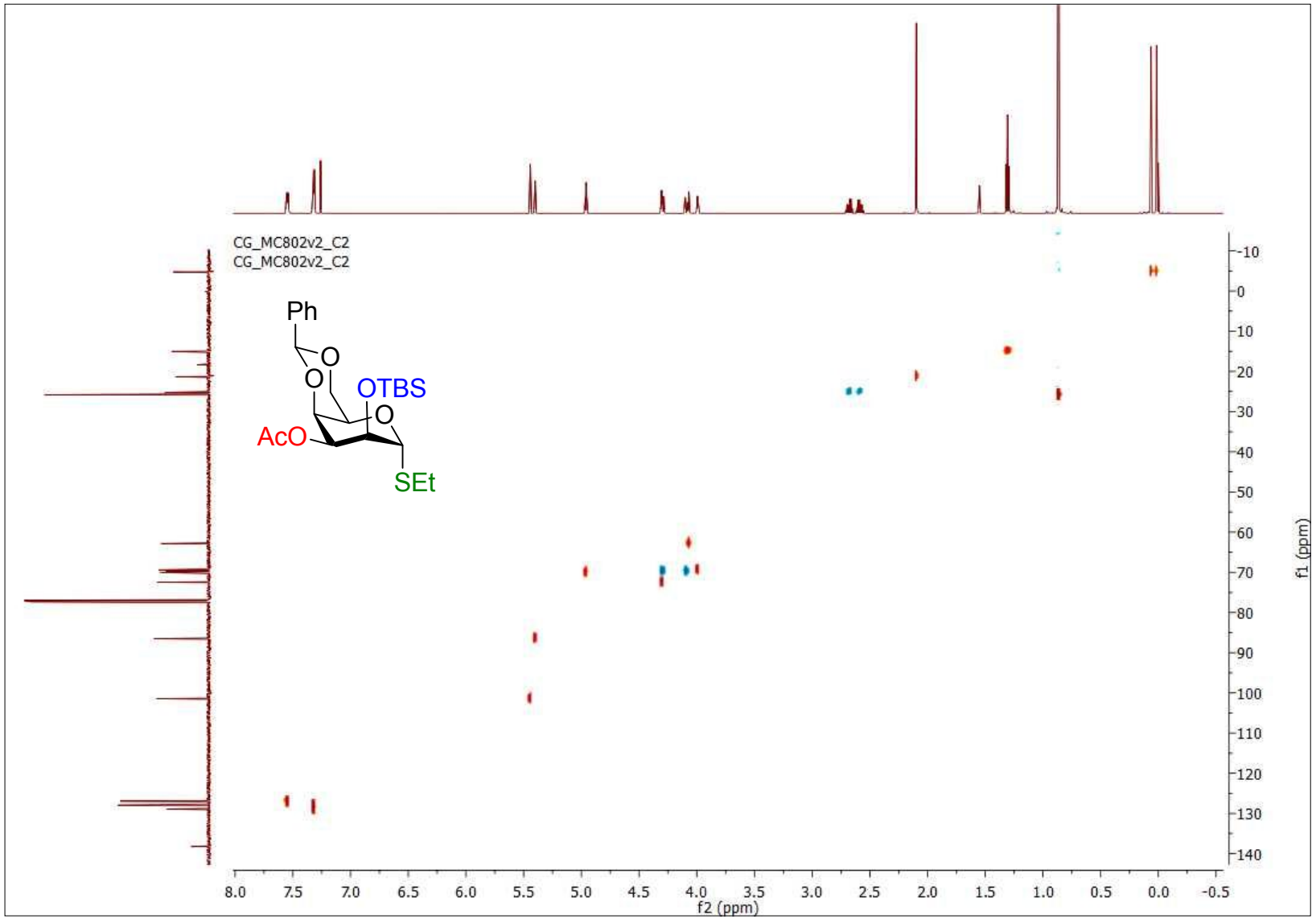


Figure S167. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (29)**

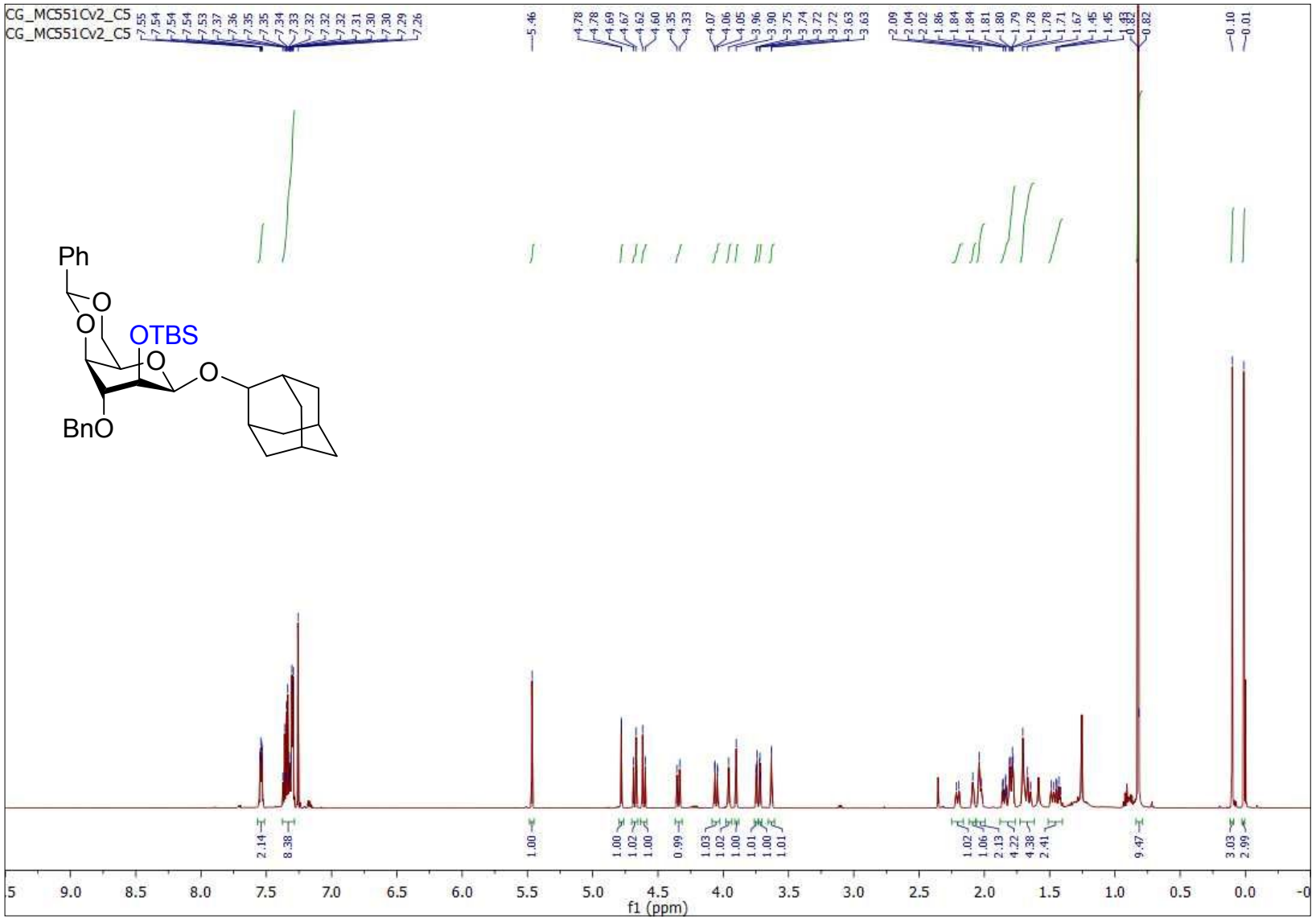


Figure S168. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (29)**

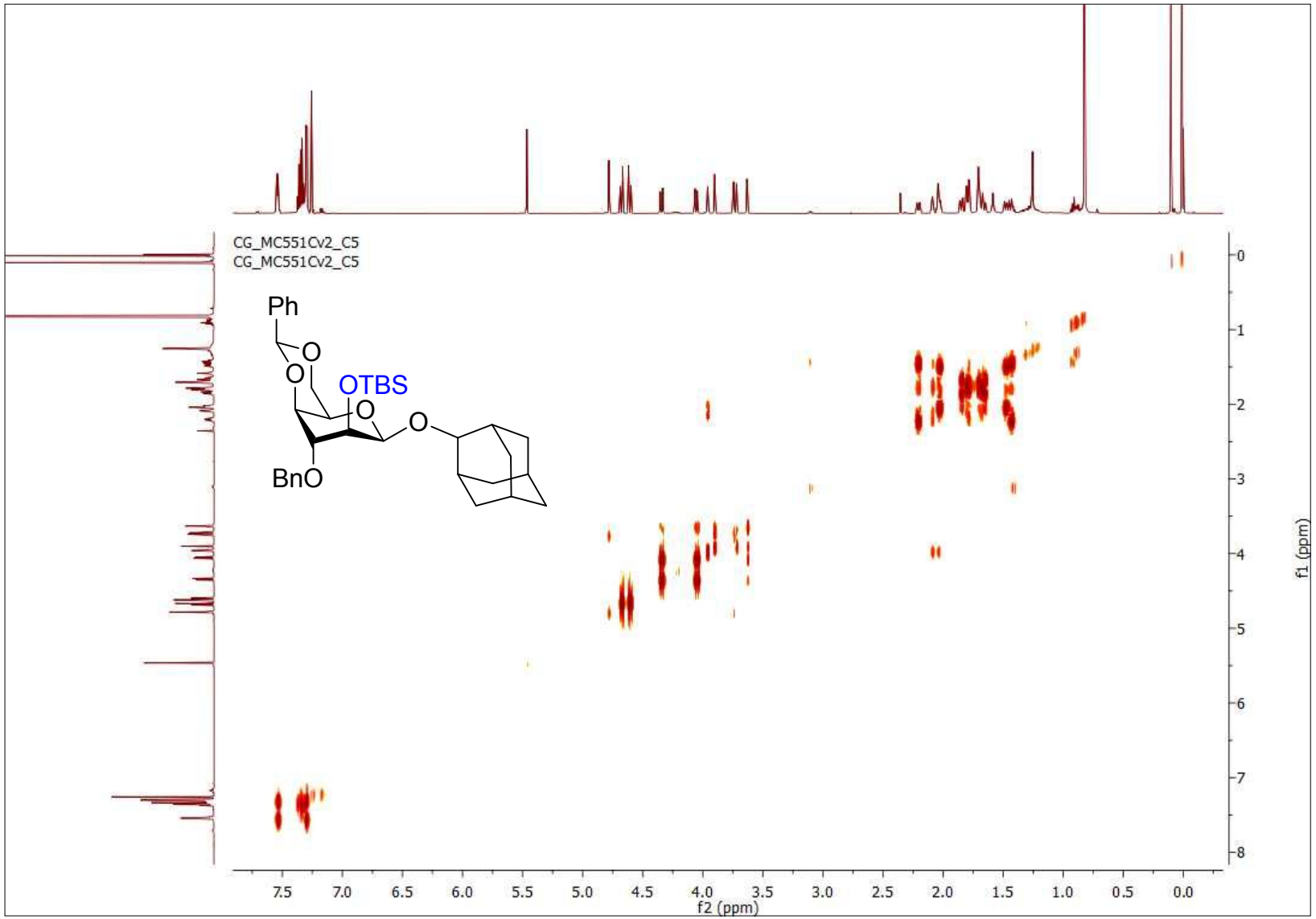


Figure S169. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (29)**

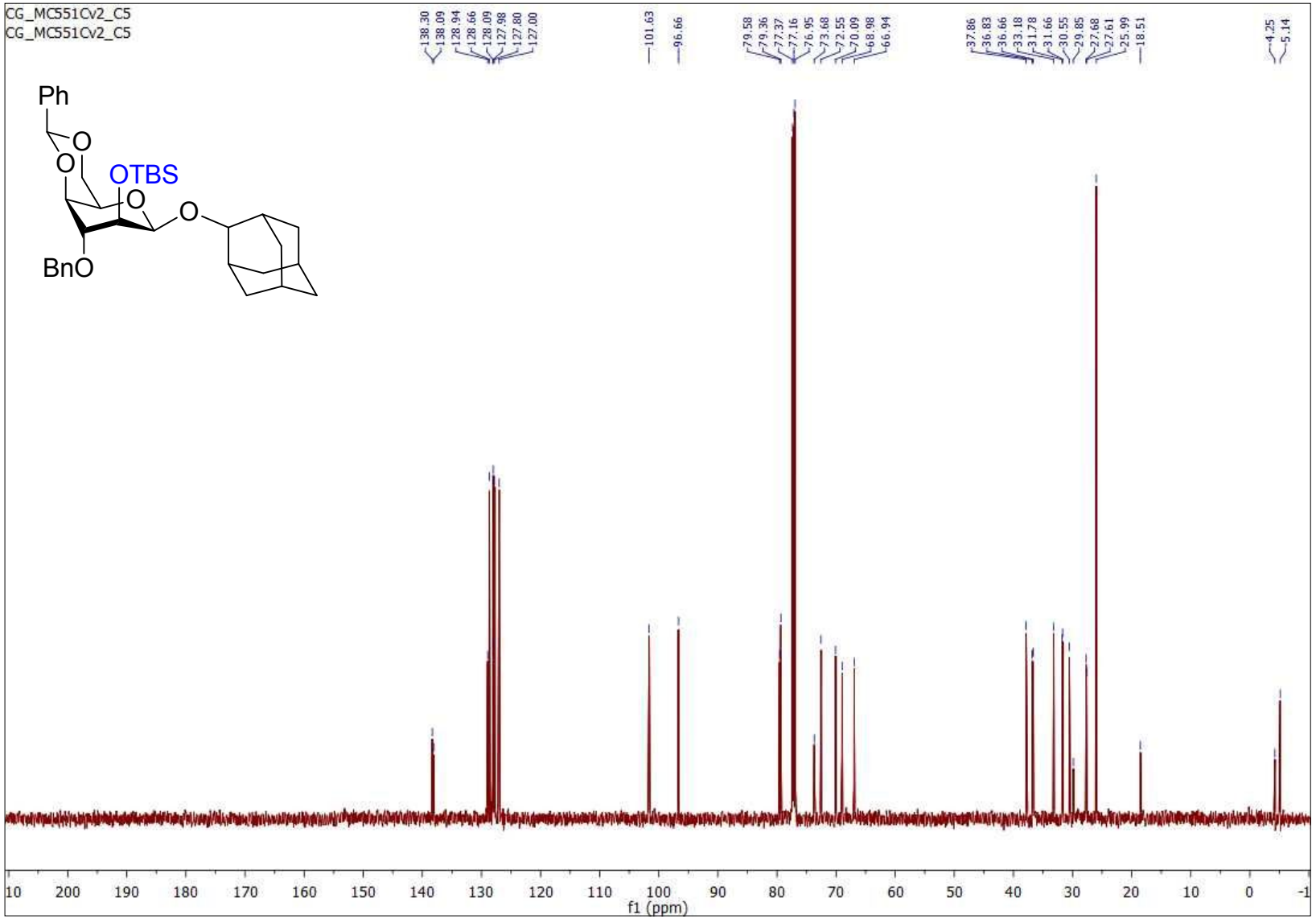


Figure S170. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (29)**

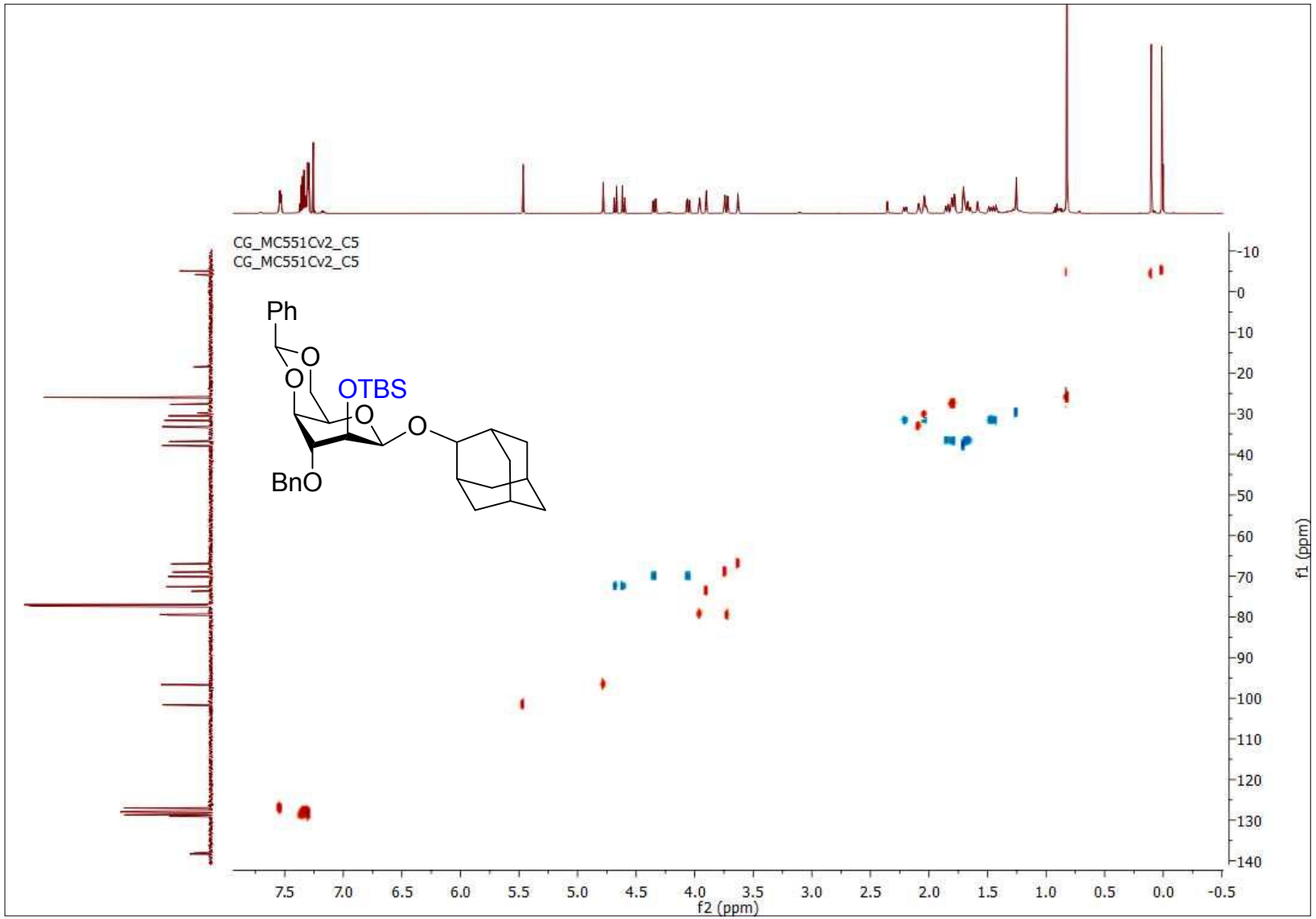


Figure S171. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranoside (29)**

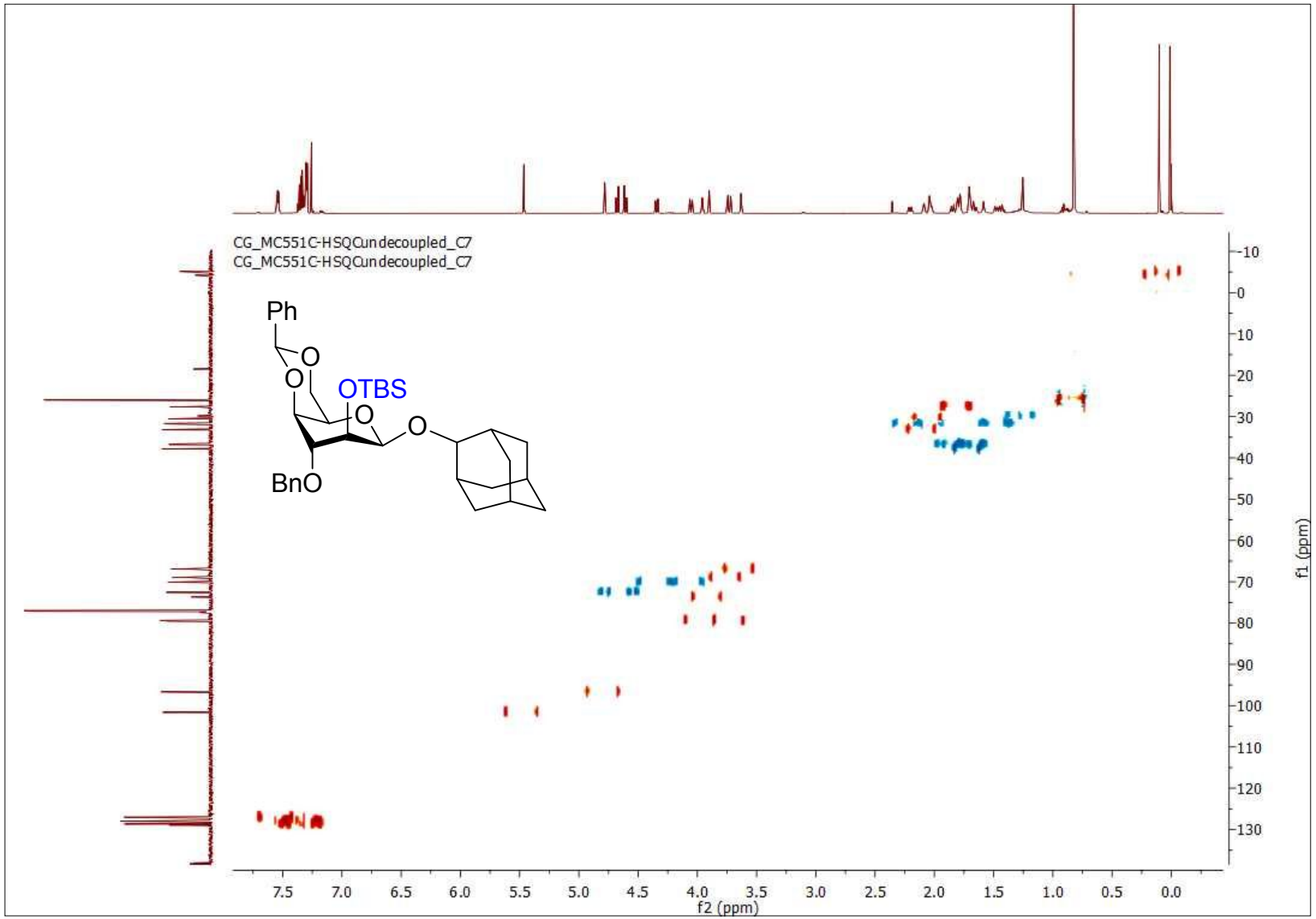


Figure S172. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-*β*-D-idopyranoside (31)**

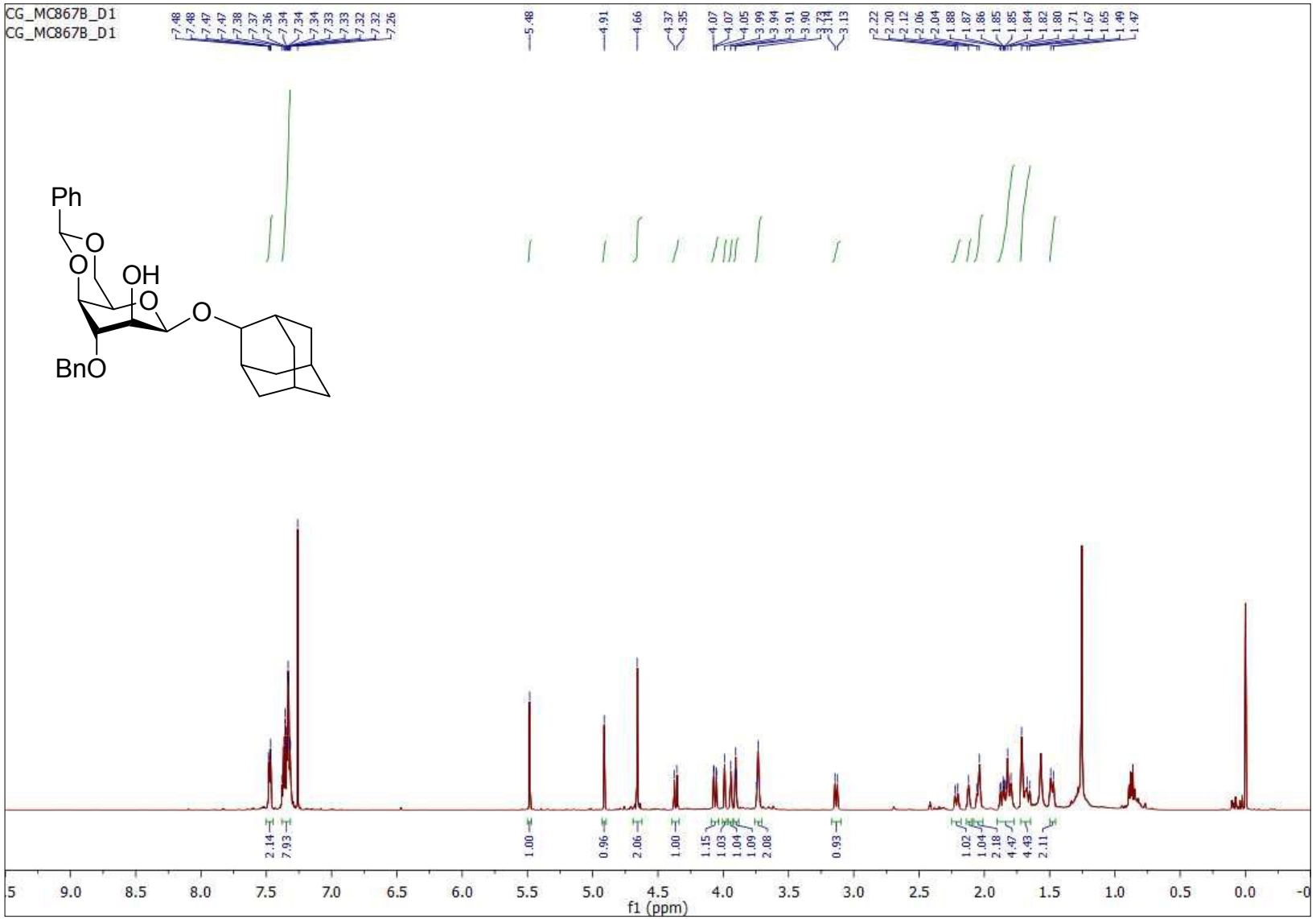


Figure S173. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-*β*-D-idopyranoside (31)**

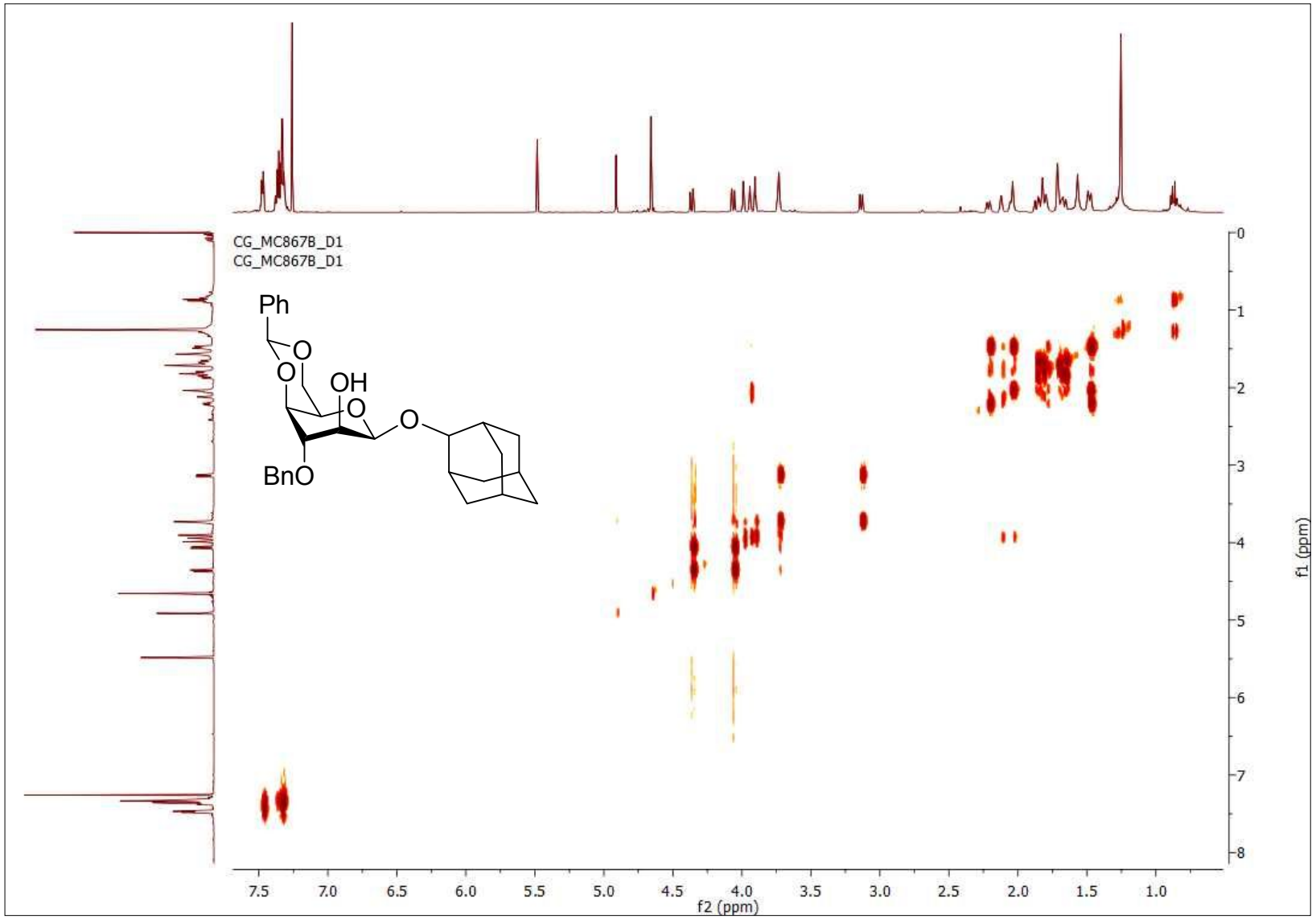


Figure S174. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-*β*-D-idopyranoside (31)**

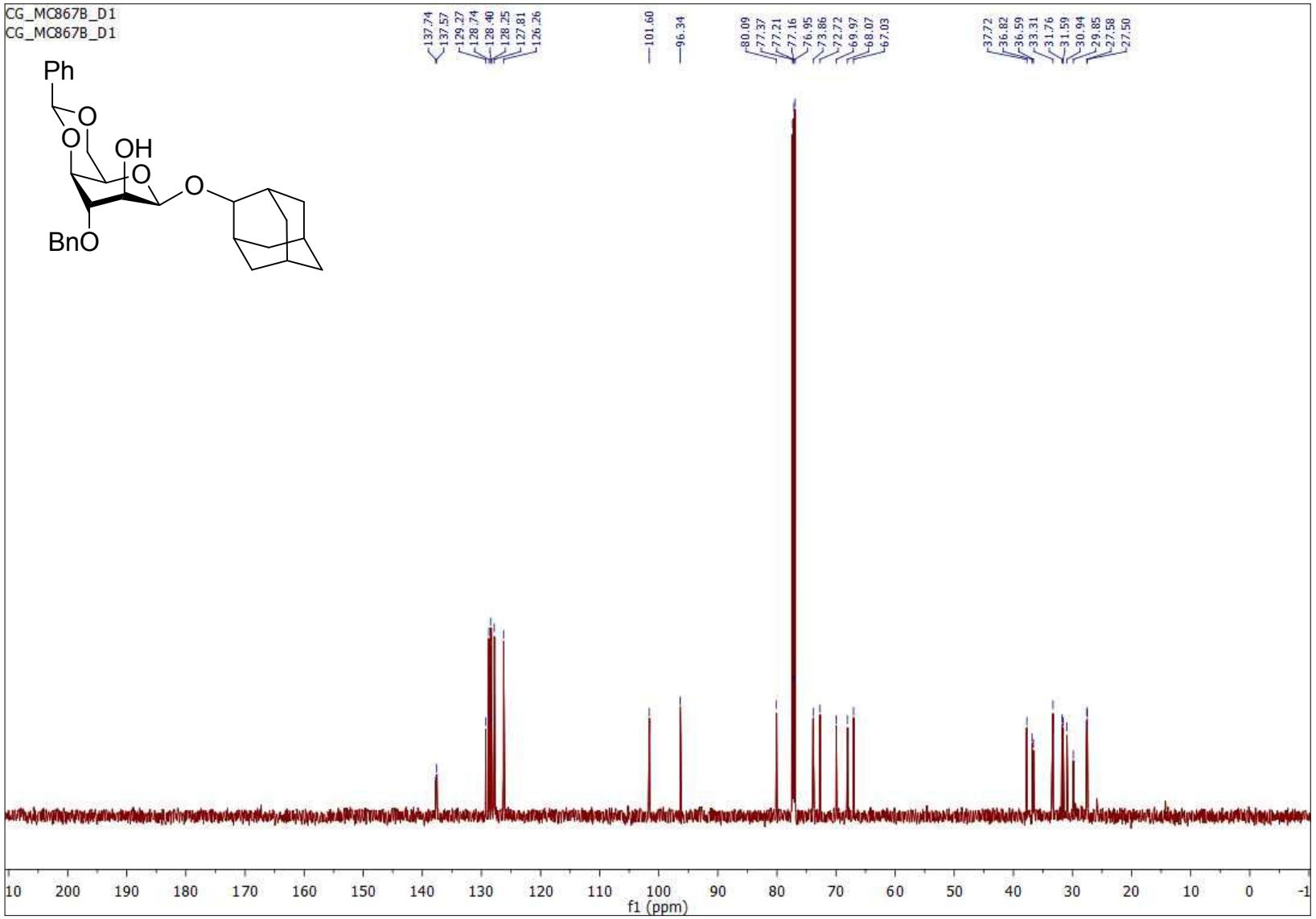


Figure S175. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-*β*-D-idopyranoside (31)**

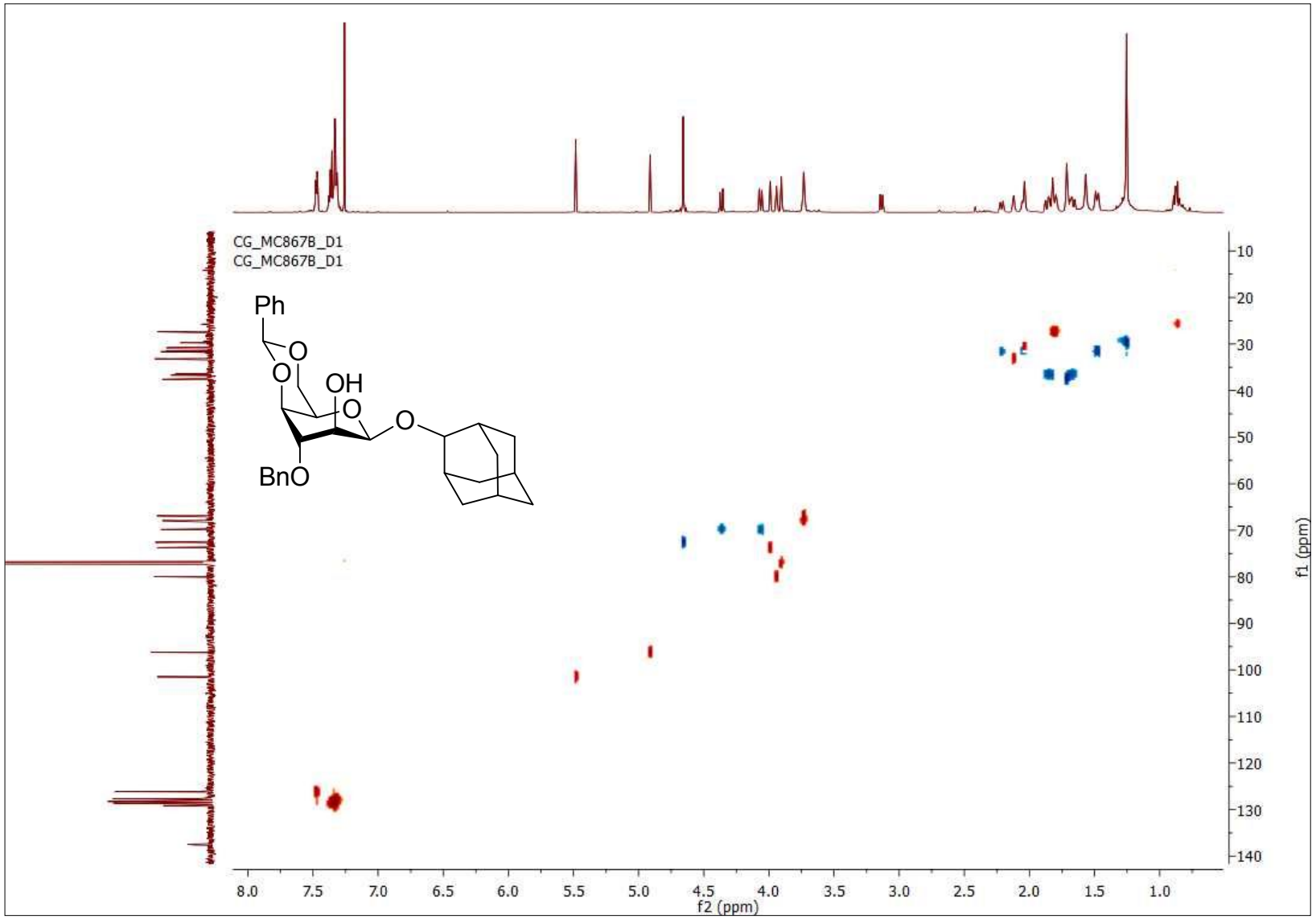


Figure S176. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-*β*-D-idopyranoside (31)**

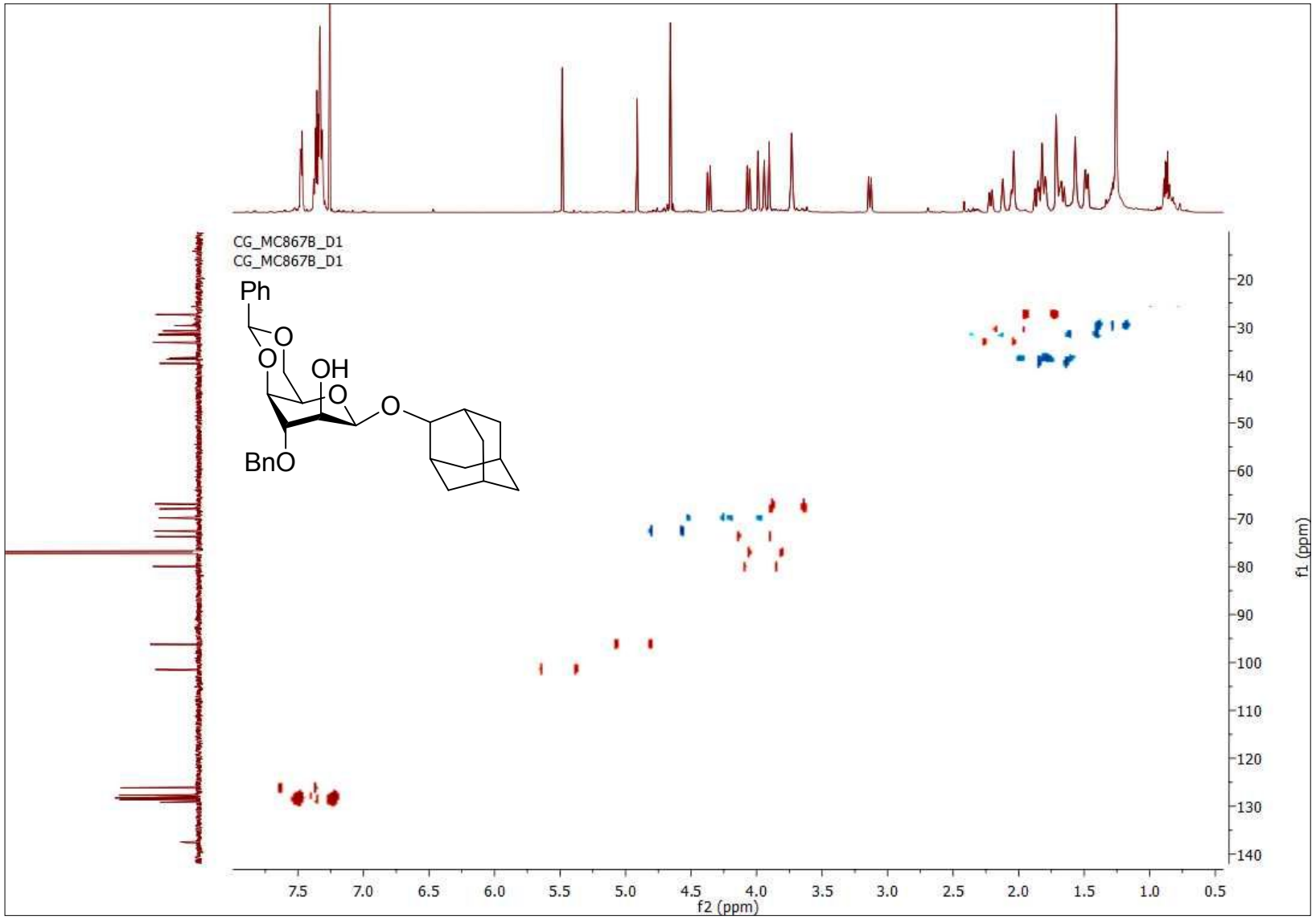


Figure S177. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-talopyranoside (30*α*)**

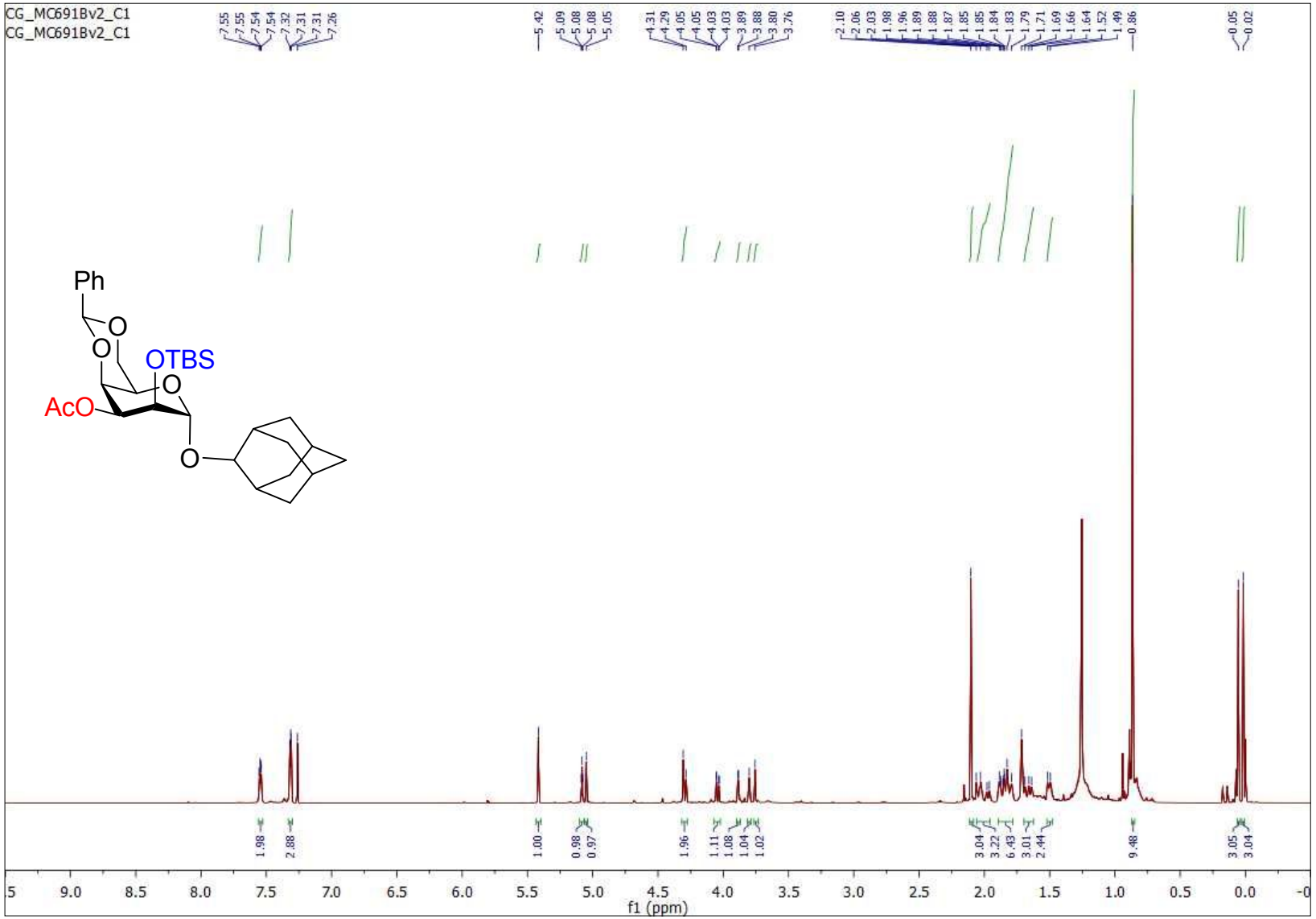


Figure S178. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-talopyranoside (30*α*)**

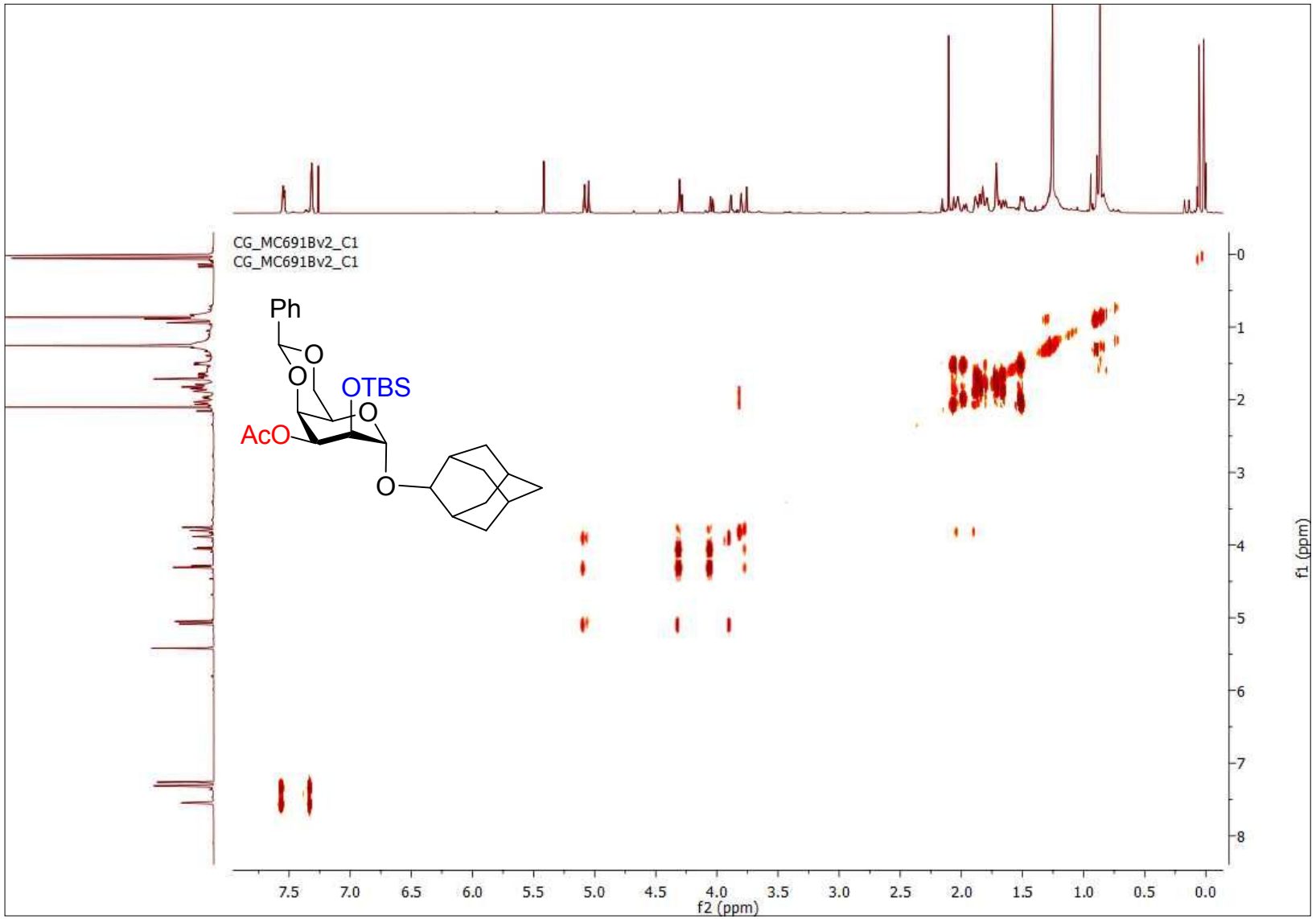


Figure S179. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-talopyranoside (30*α*)**

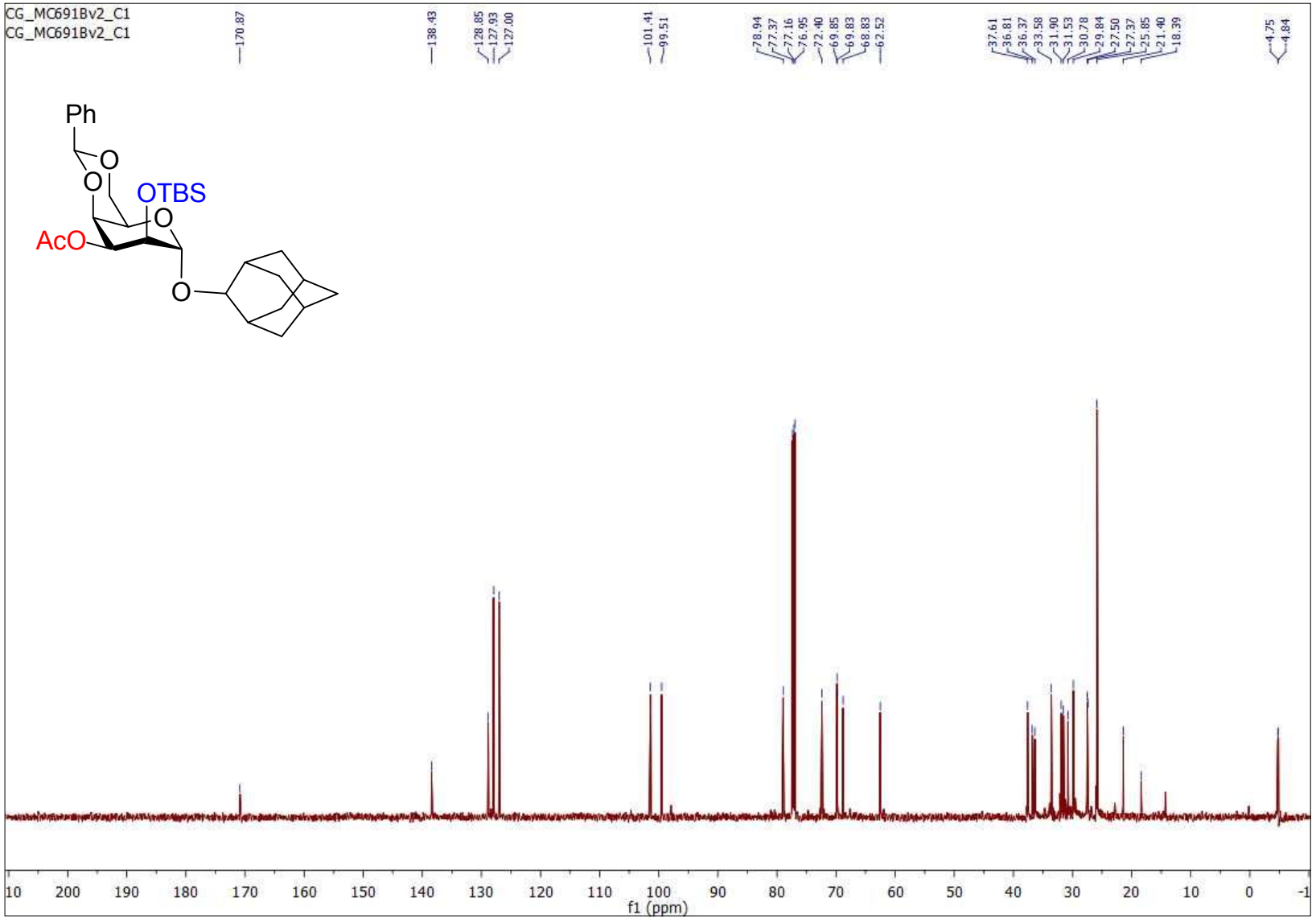


Figure S180. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-talopyranoside (30*α*)**

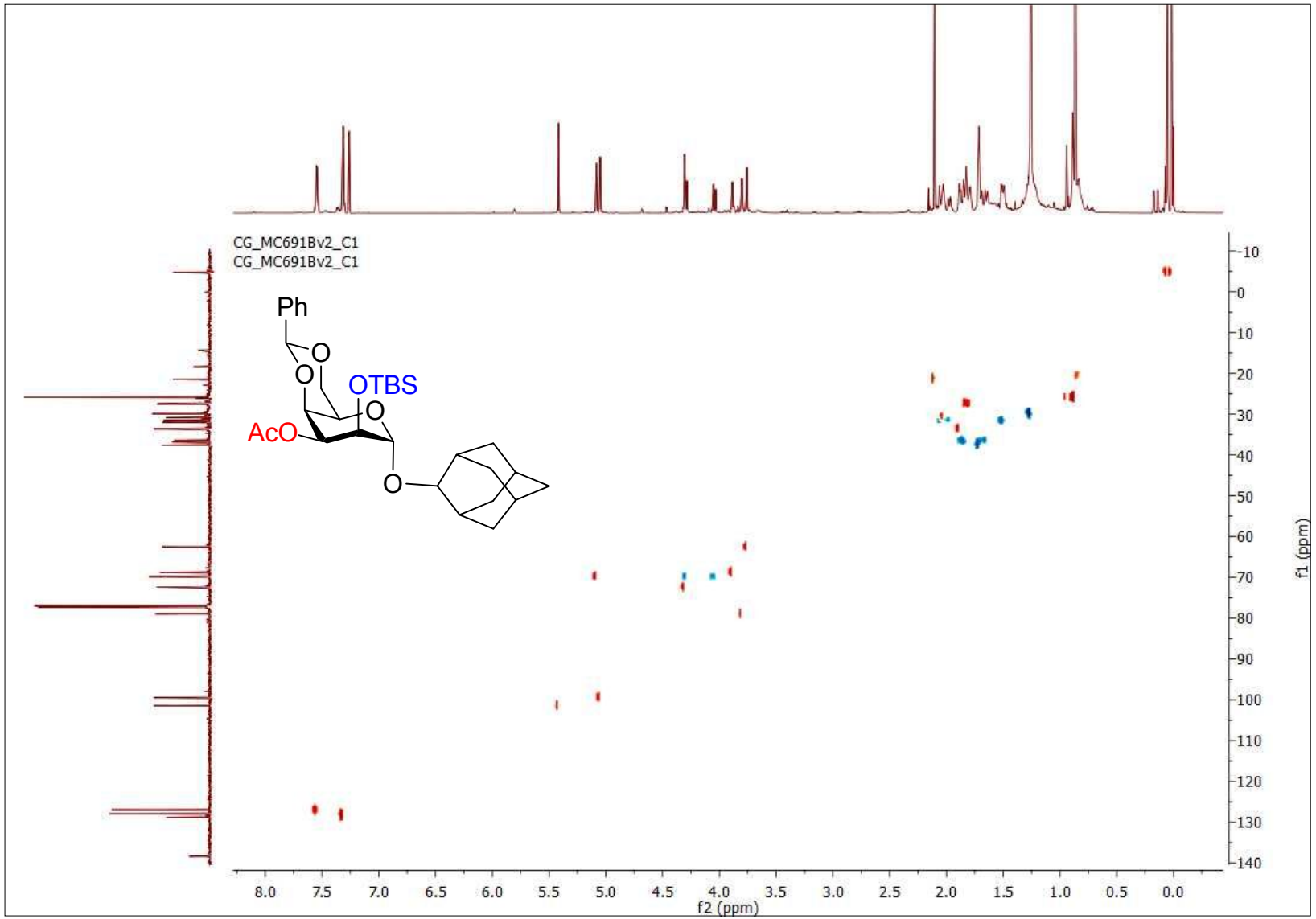


Figure S181. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-talopyranoside (30*α*)**

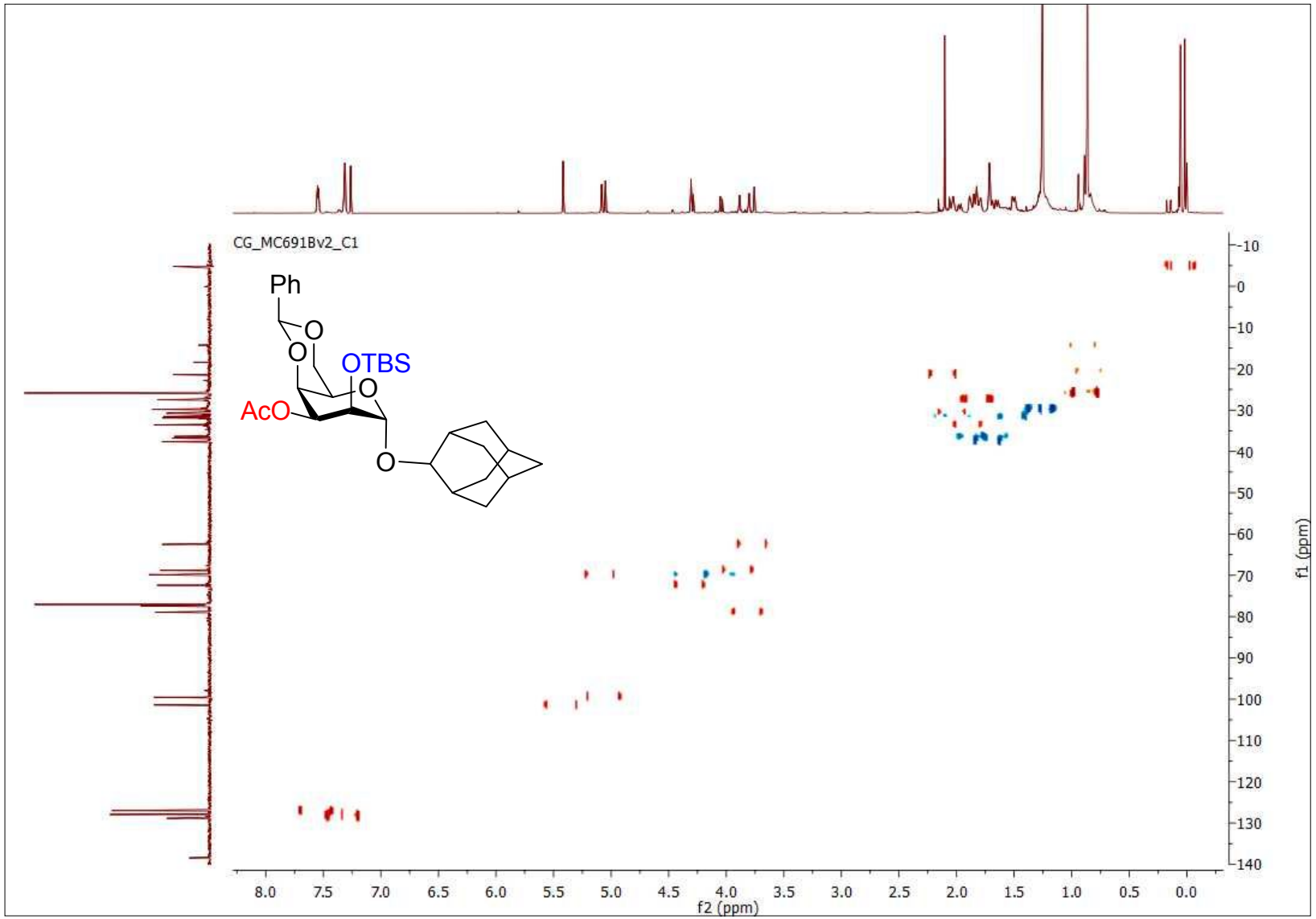


Figure S182. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-talopyranoside (30*β*)** and **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-*α*-D-talopyranoside (32)**

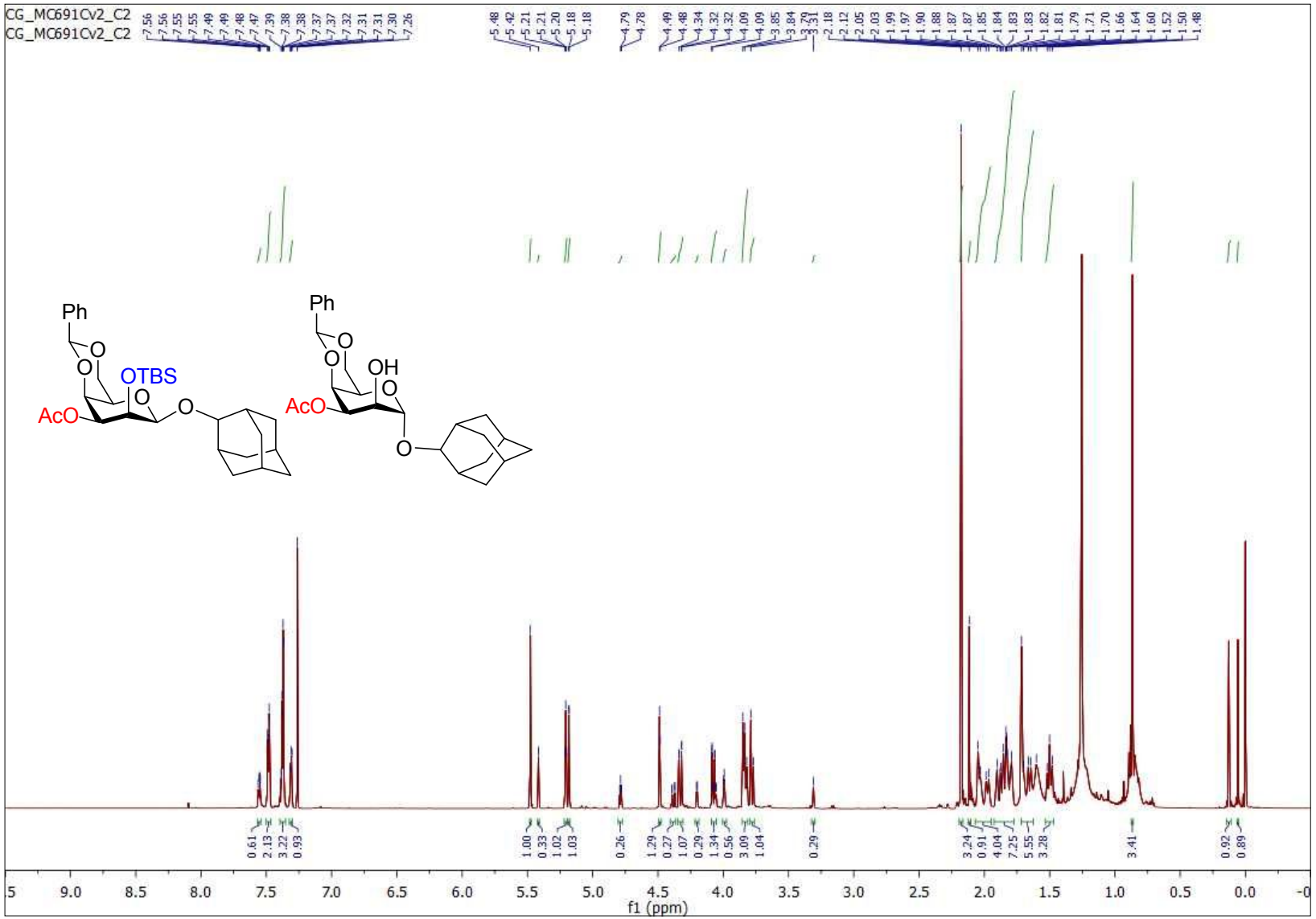


Figure S183. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-talopyranoside (30*β*)** and **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-*α*-D-talopyranoside (32)**

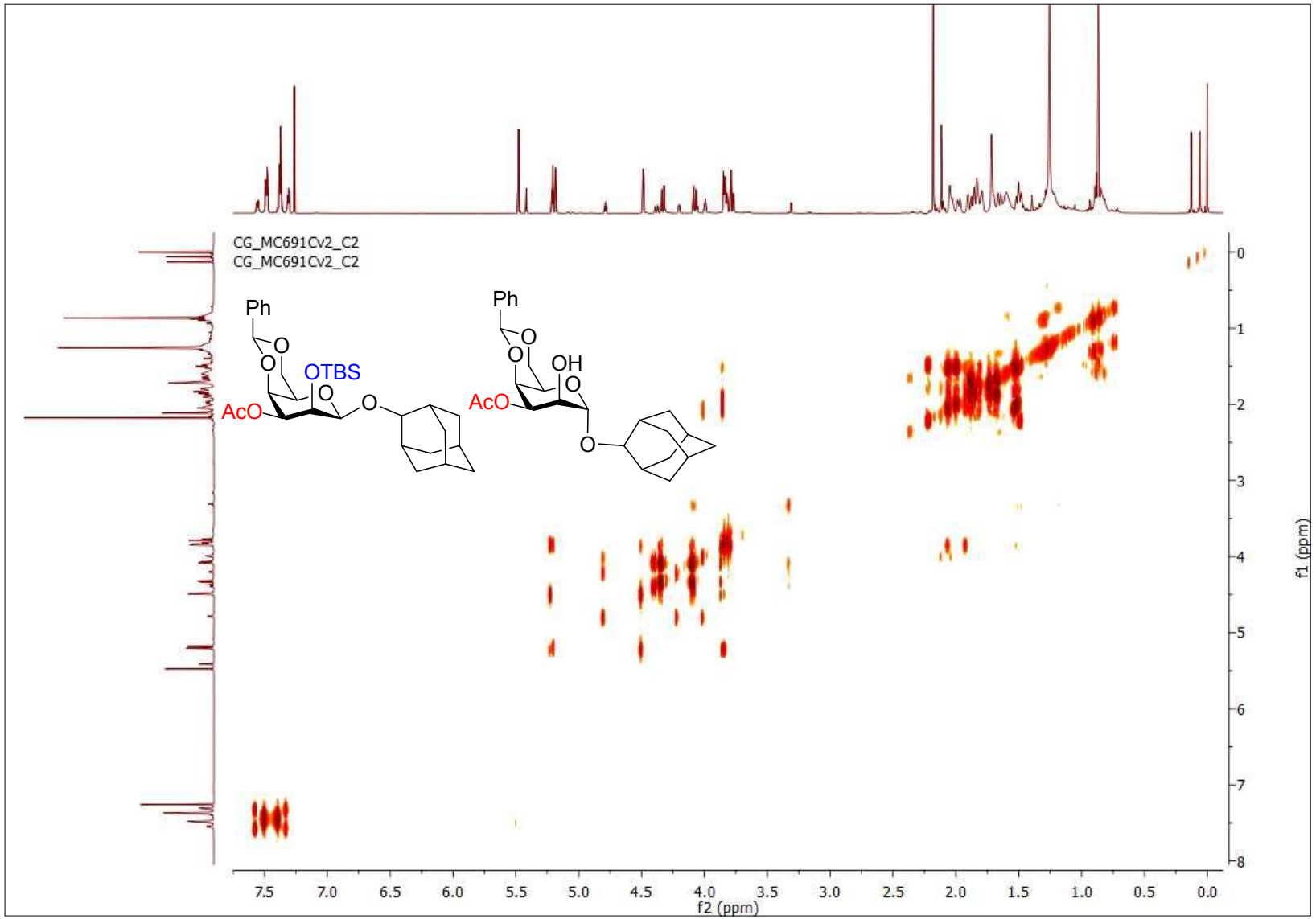


Figure S184. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-talopyranoside (30*β*)** and **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-*α*-D-talopyranoside (32)**

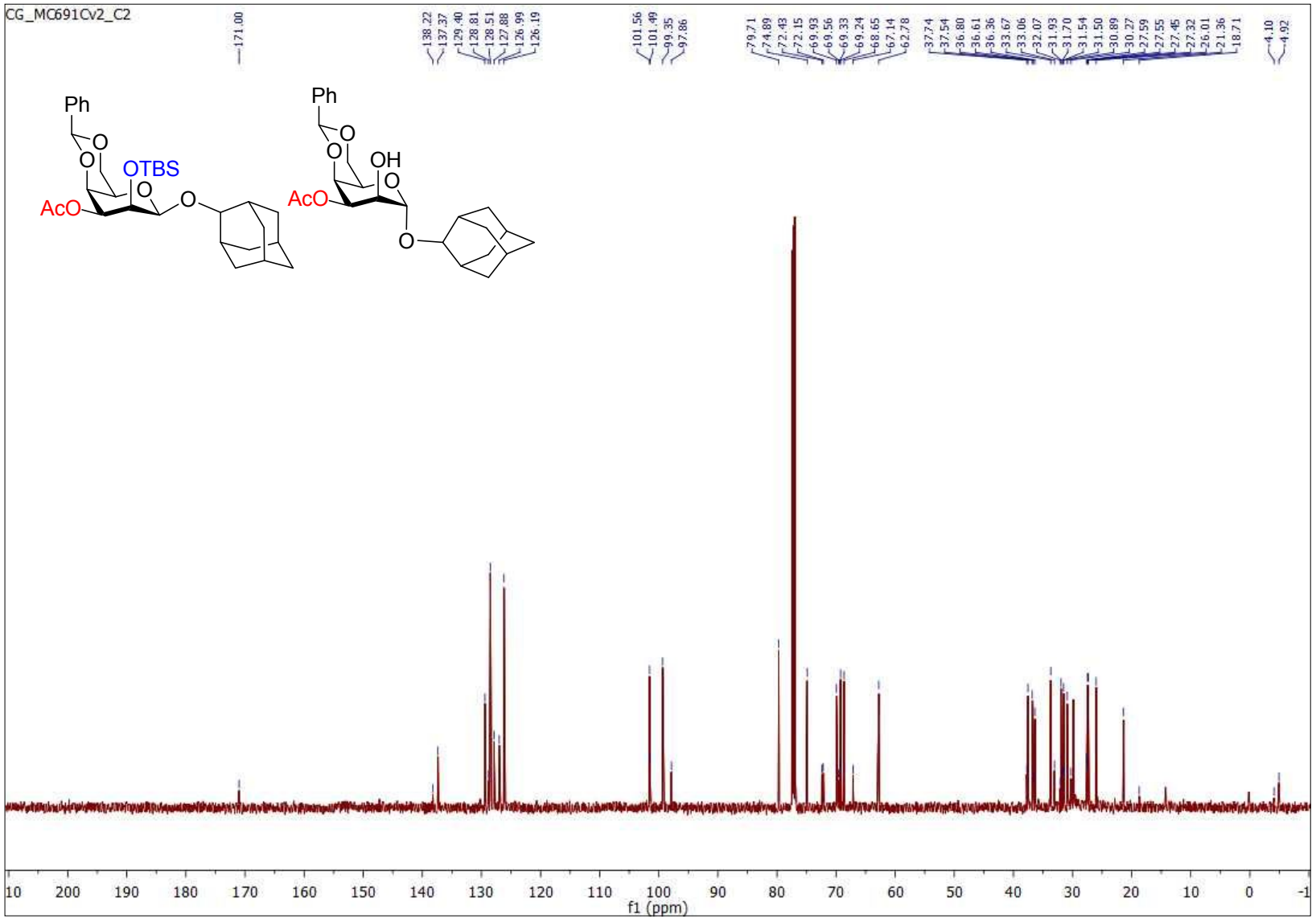


Figure S185. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-talopyranoside (30*β*)** and **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-*α*-D-talopyranoside (32)**

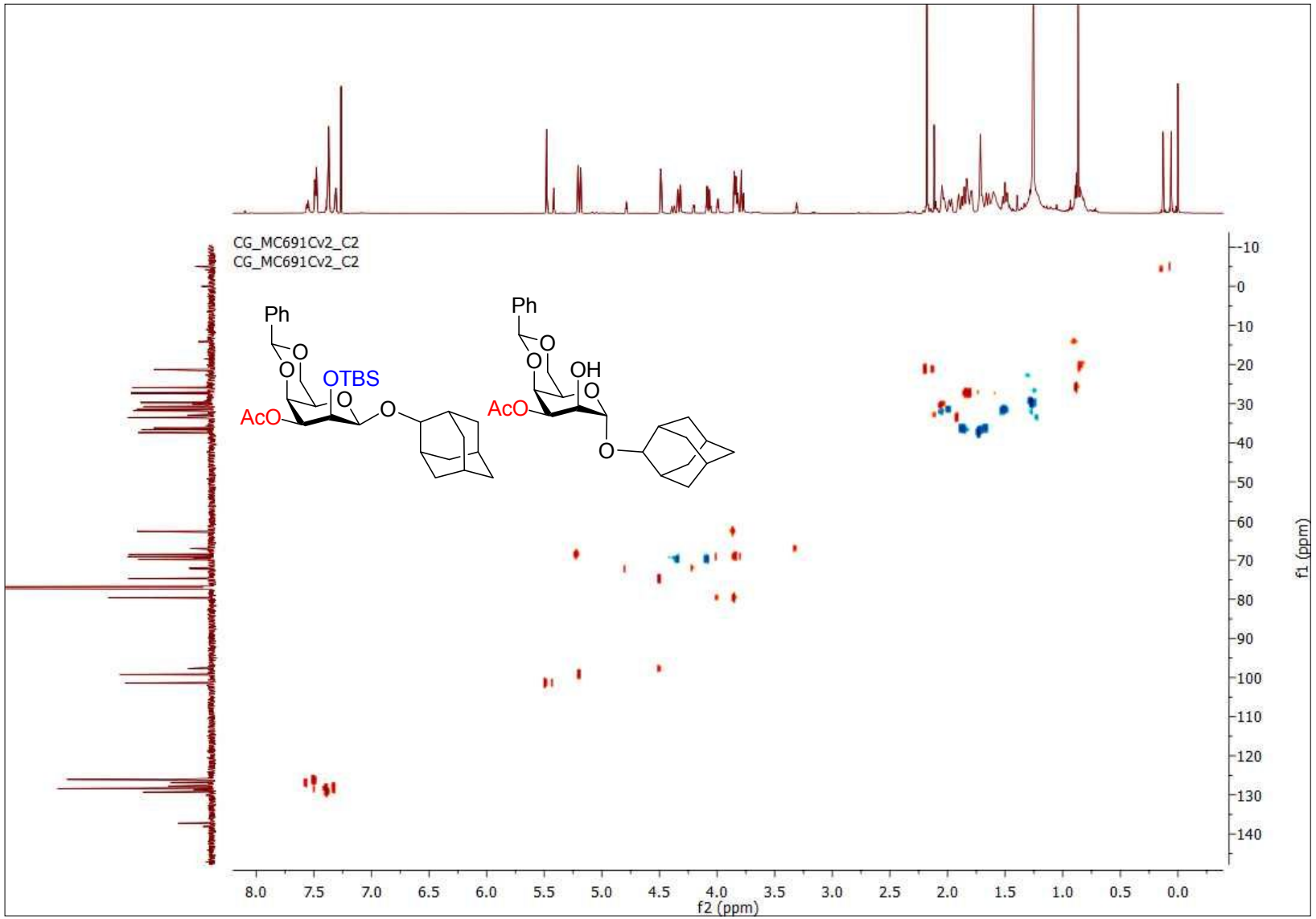


Figure S186. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-talopyranoside (30*β*)** and **(2-adamantyl) 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-*α*-D-talopyranoside (32)**

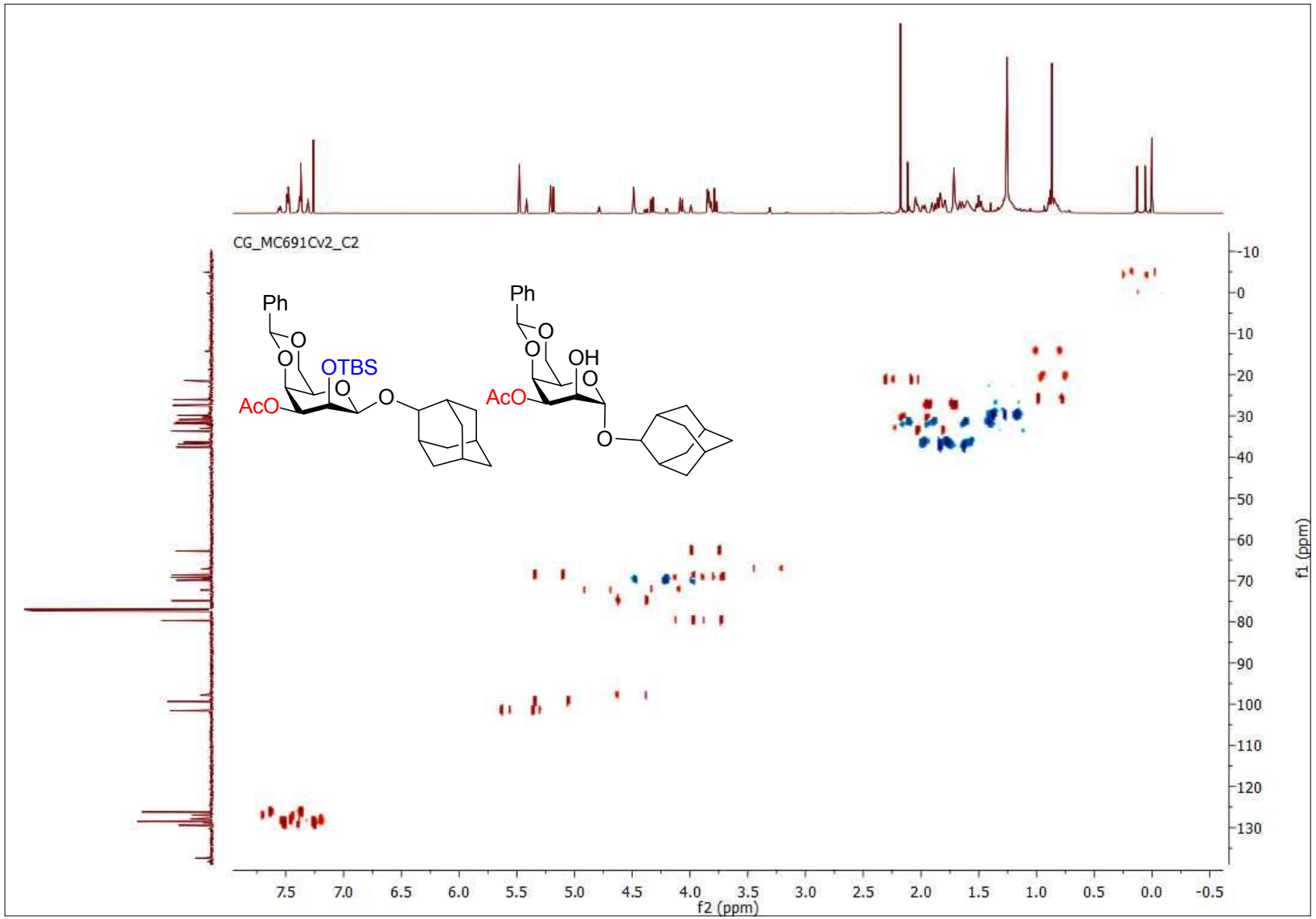


Figure S187. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-*para*-methoxybenzyl-*α*-D-glucopyranoside (37*α*)**

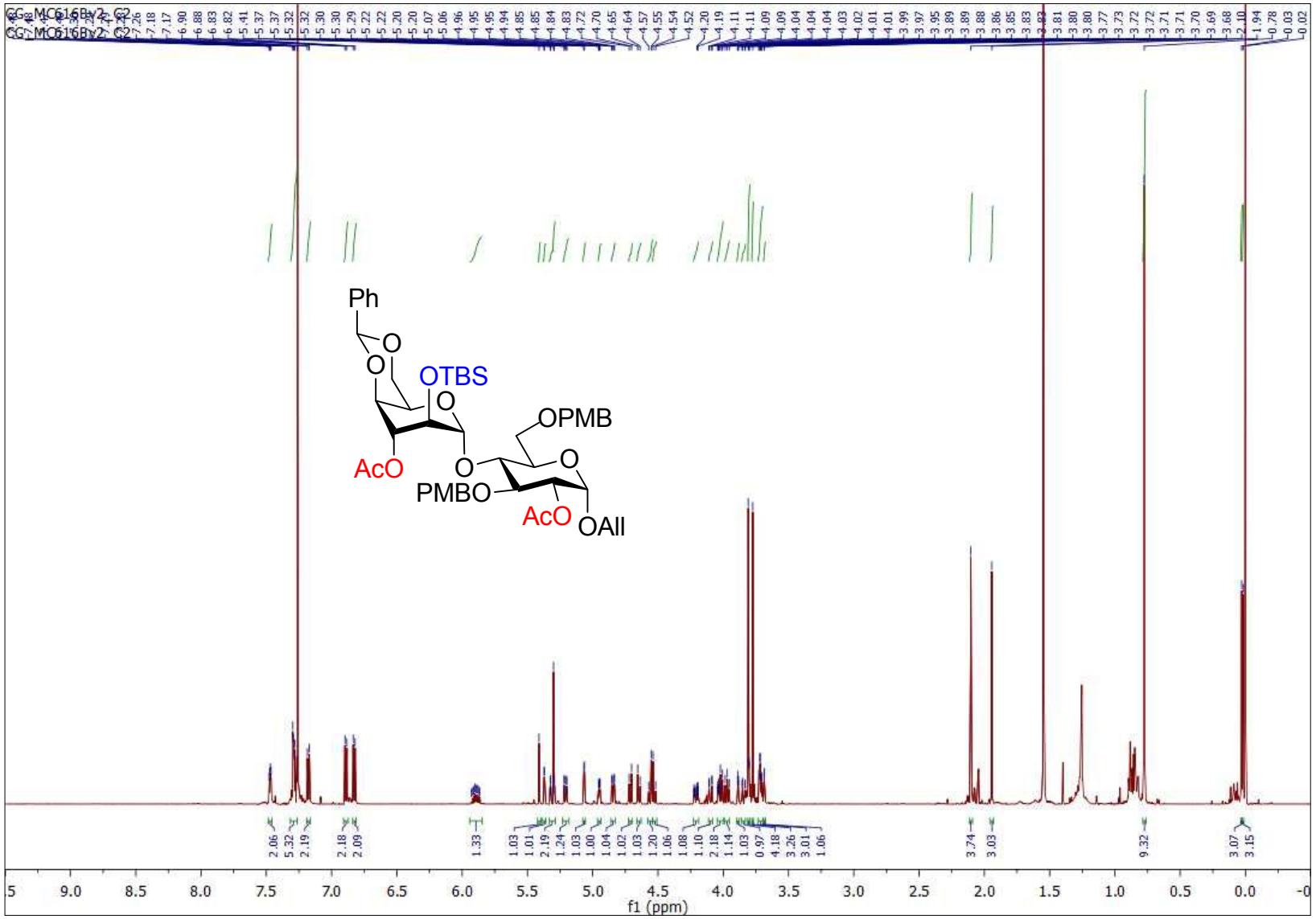


Figure S188. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-*para*-methoxybenzyl-*α*-D-glucopyranoside (37*α*)**

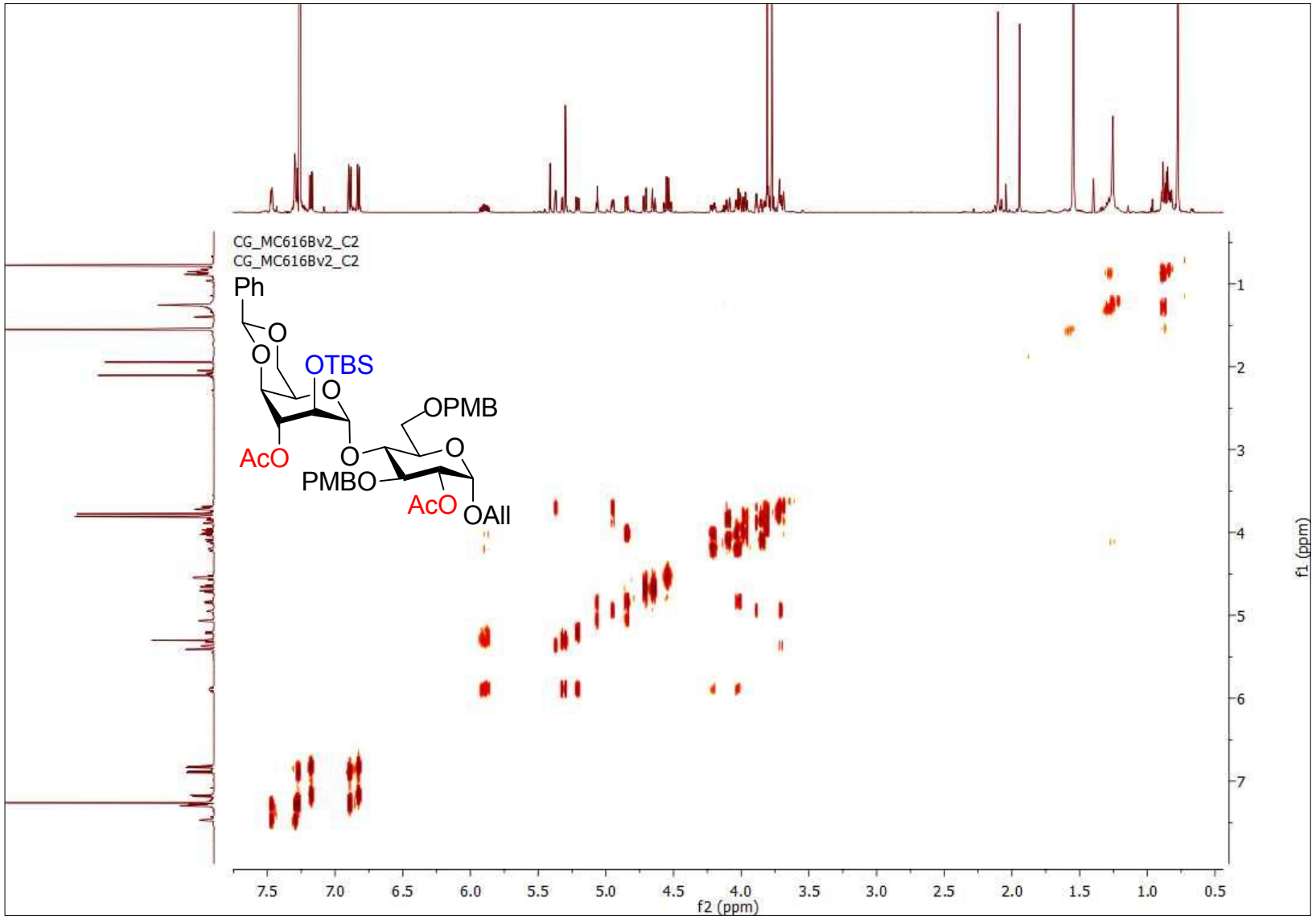


Figure S189. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-*para*-methoxybenzyl-*α*-D-glucopyranoside (37*α*)**

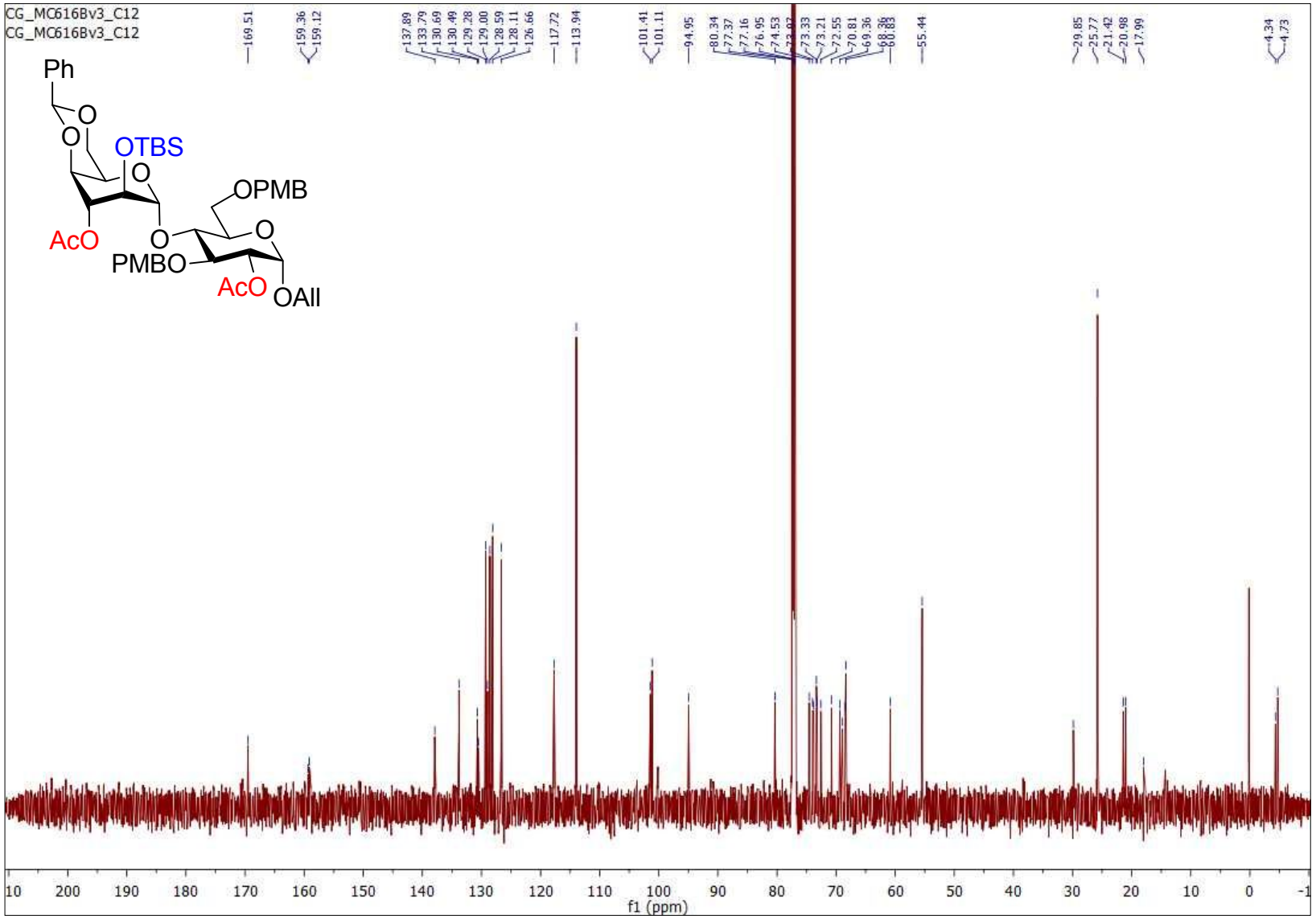


Figure S190. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-*para*-methoxybenzyl-*α*-D-glucopyranoside (37*α*)**

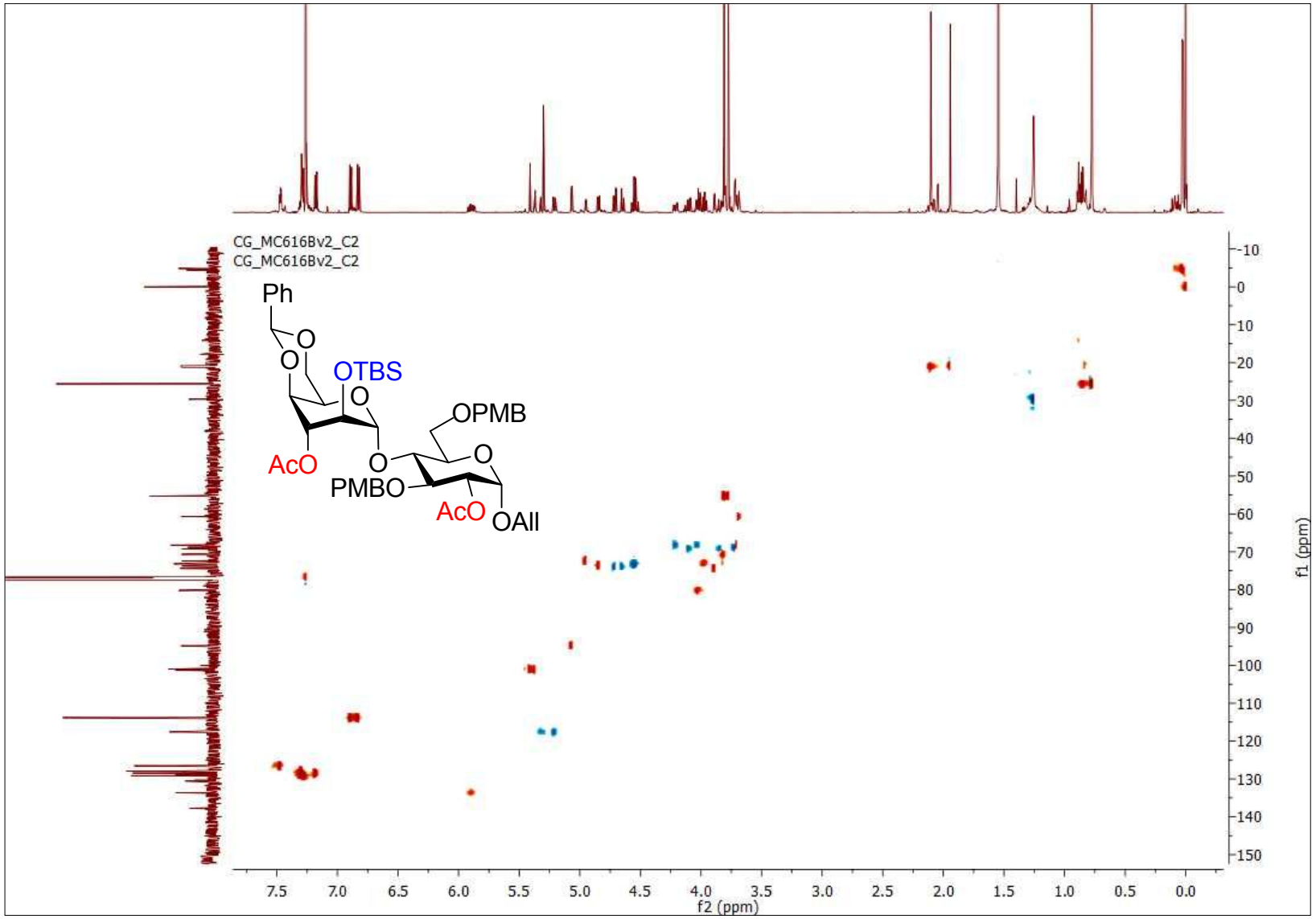


Figure S191. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-*para*-methoxybenzyl-*α*-D-glucopyranoside (37*α*)**

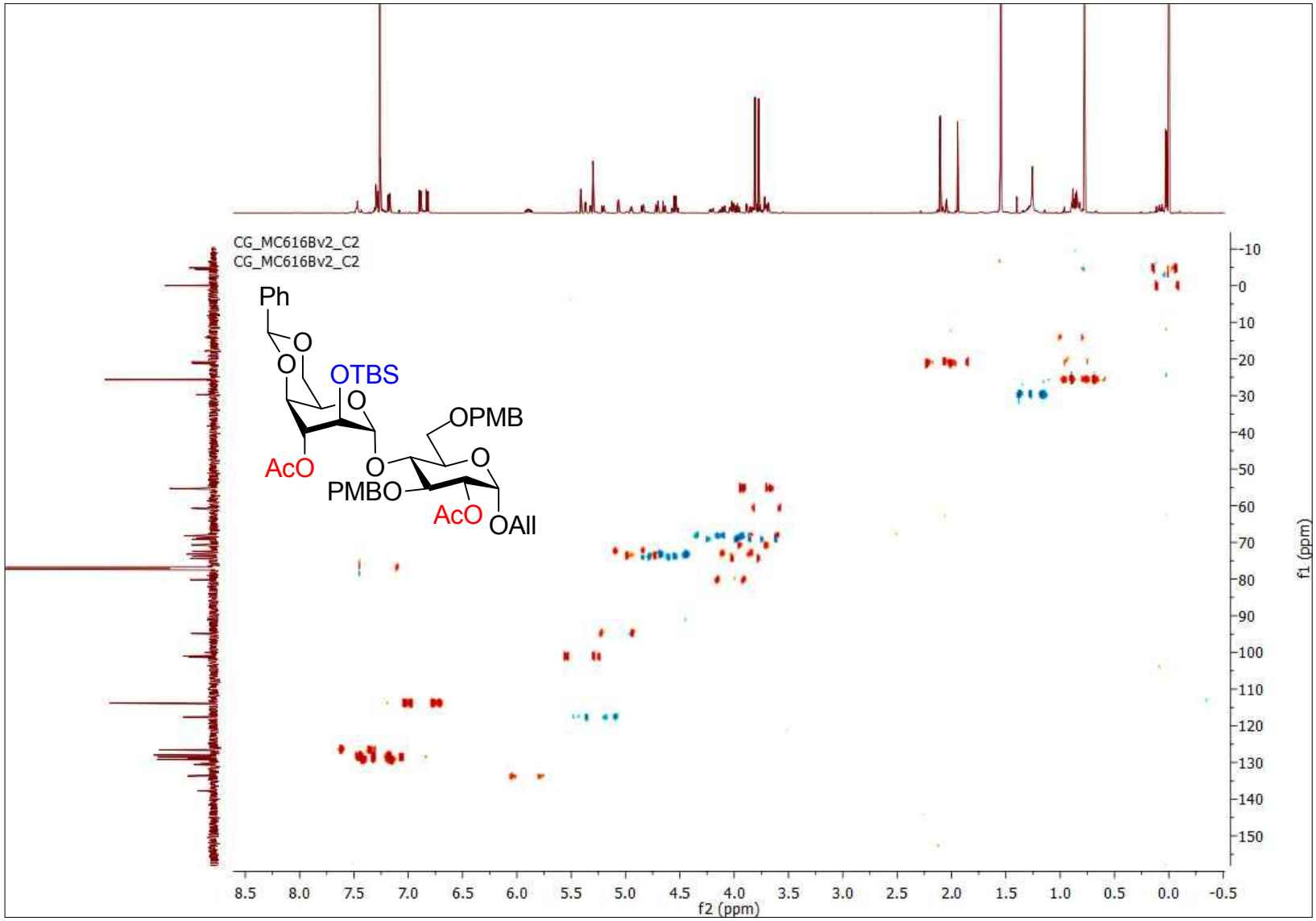


Figure S192. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-*para*-methoxybenzyl-*α*-D-glucopyranoside (37*β*)**

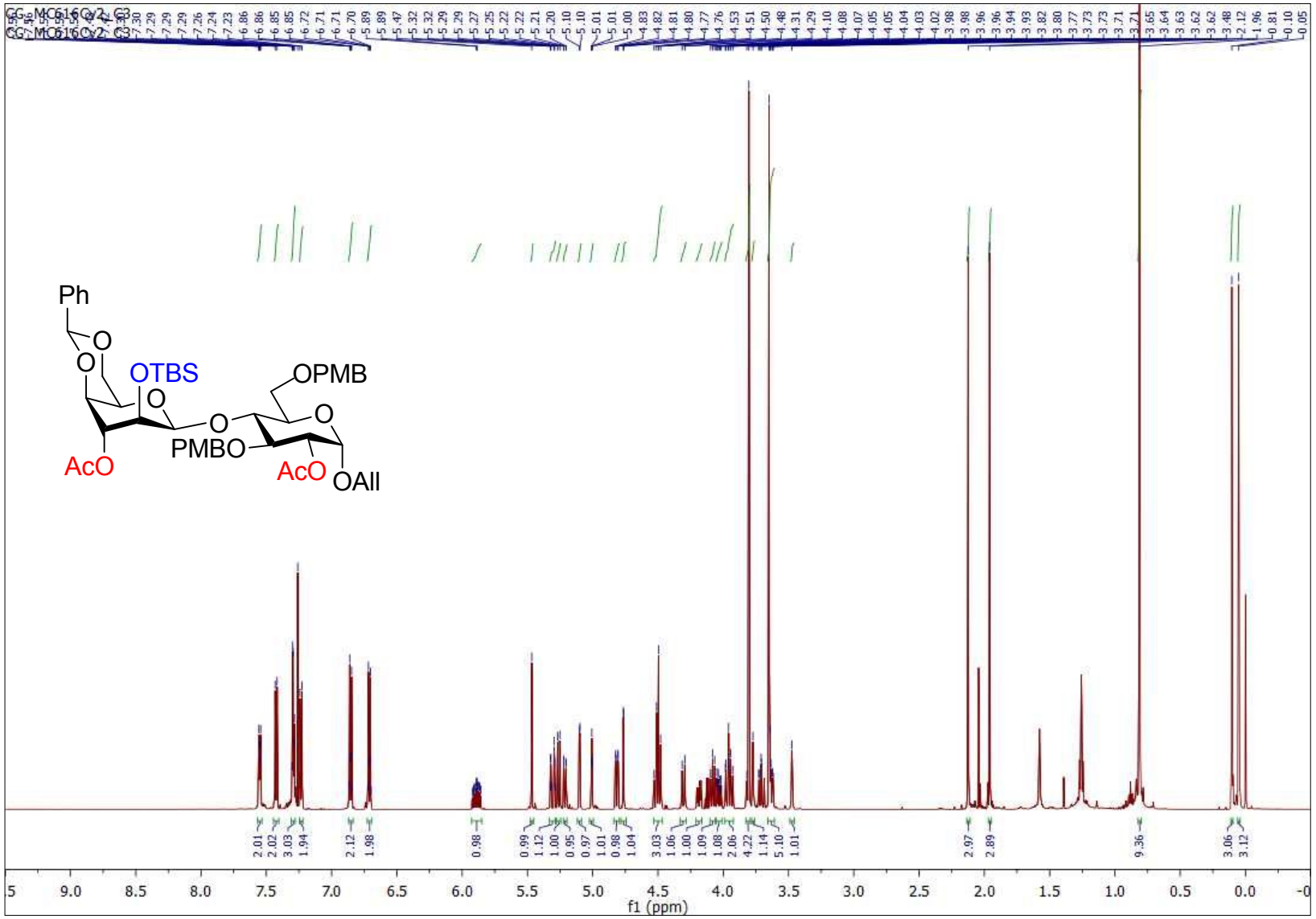


Figure S193. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-*para*-methoxybenzyl-*α*-D-glucopyranoside (37*β*)**

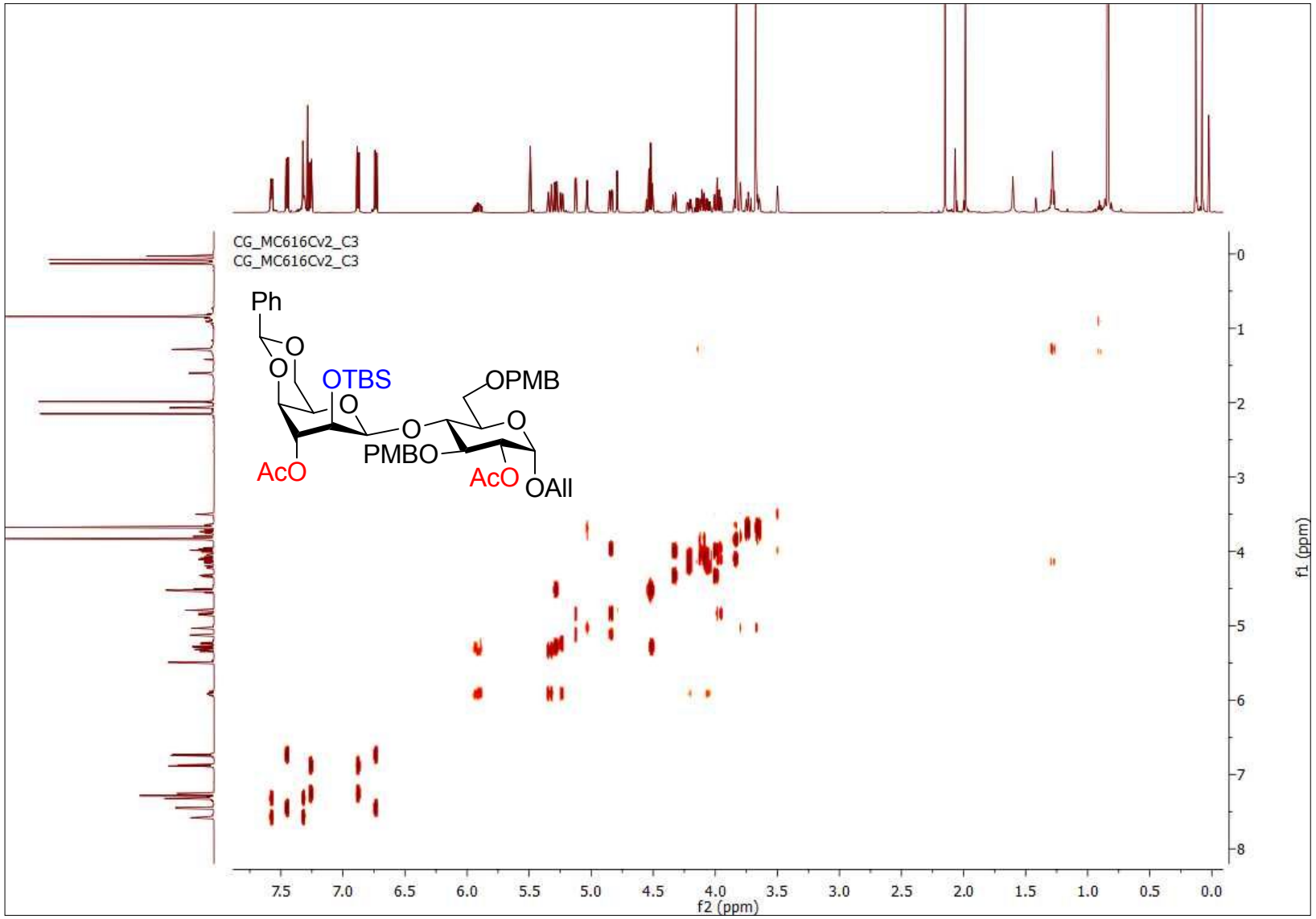


Figure S194. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-*para*-methoxybenzyl-*α*-D-glucopyranoside (37*β*)**

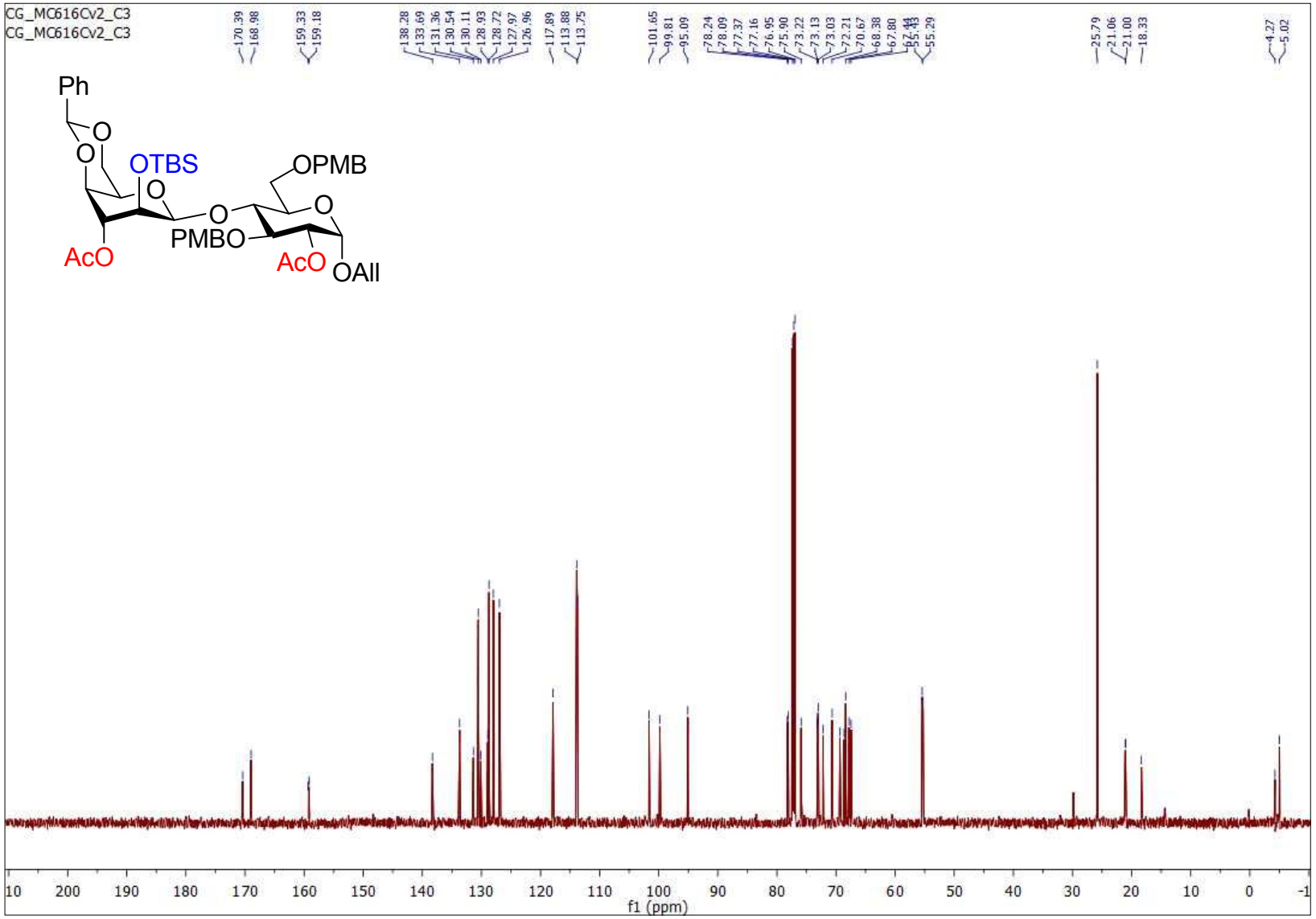


Figure S195. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-*para*-methoxybenzyl-*α*-D-glucopyranoside (37*β*)**

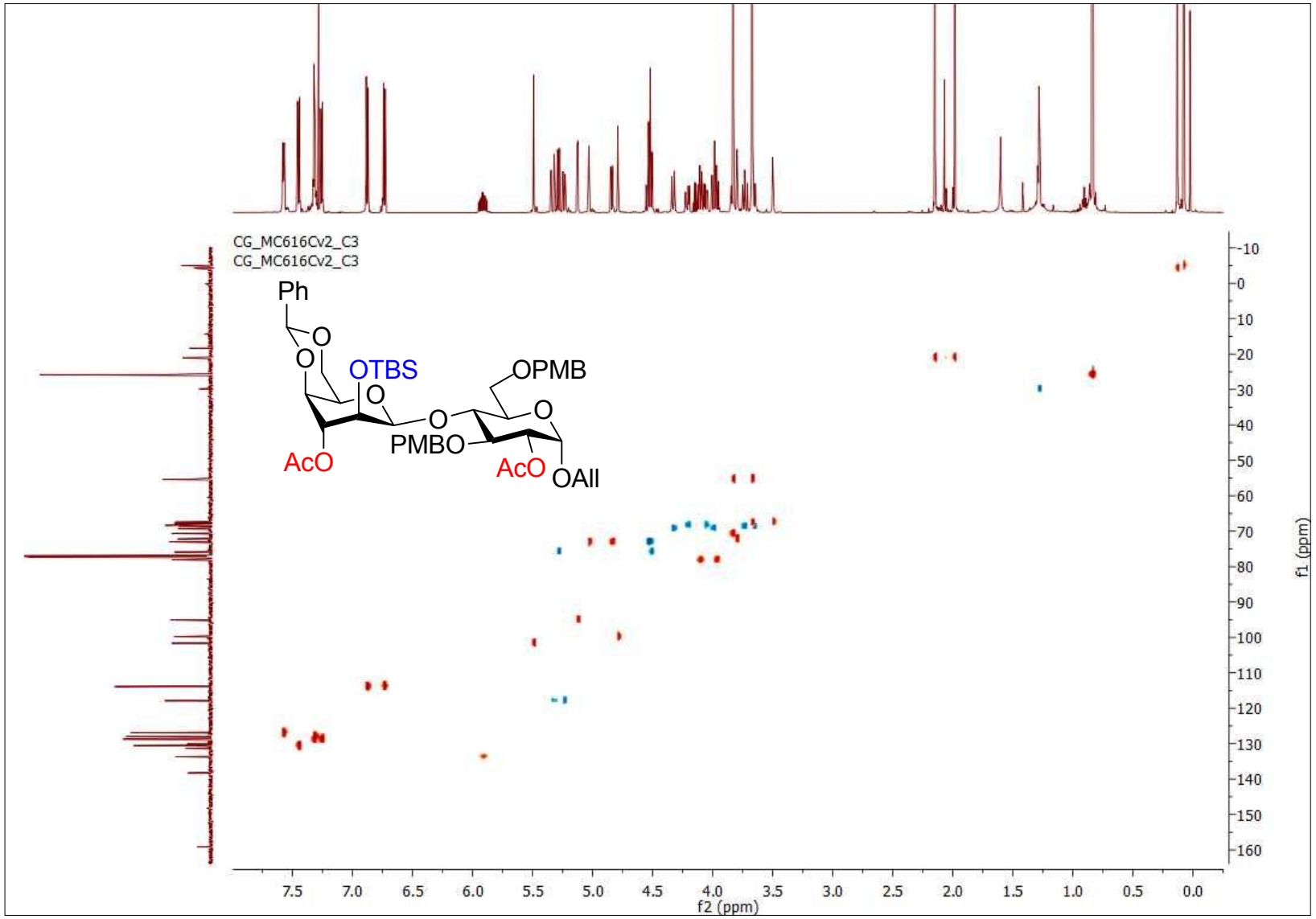


Figure S196. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-*para*-methoxybenzyl-*α*-D-glucopyranoside (37*β*)**

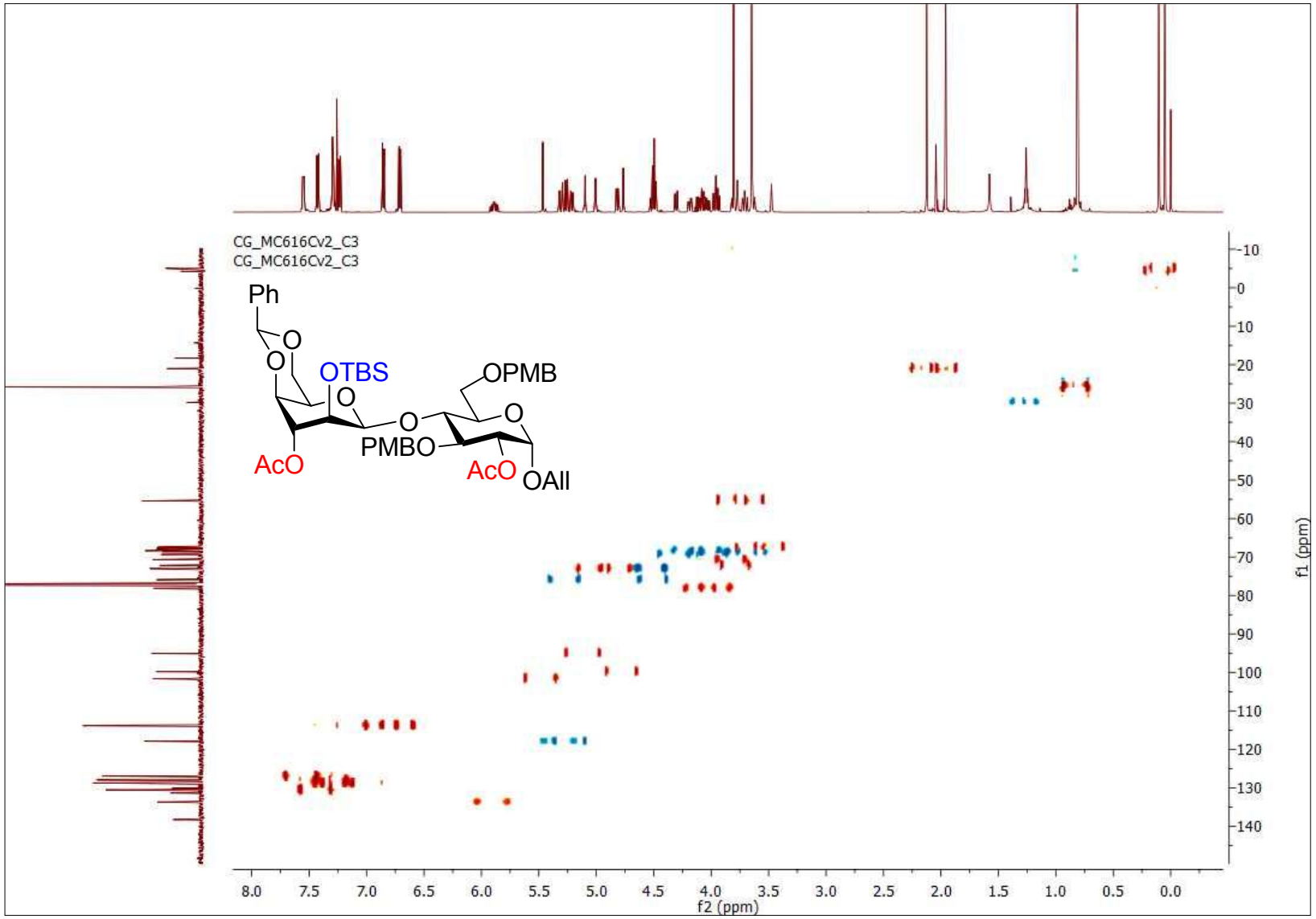


Figure S197. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→2)-3-*O*-*para*-methoxybenzyl-4,6-*O*-*para*-methoxybenzylidene-*α*-D-glucopyranoside (38)**

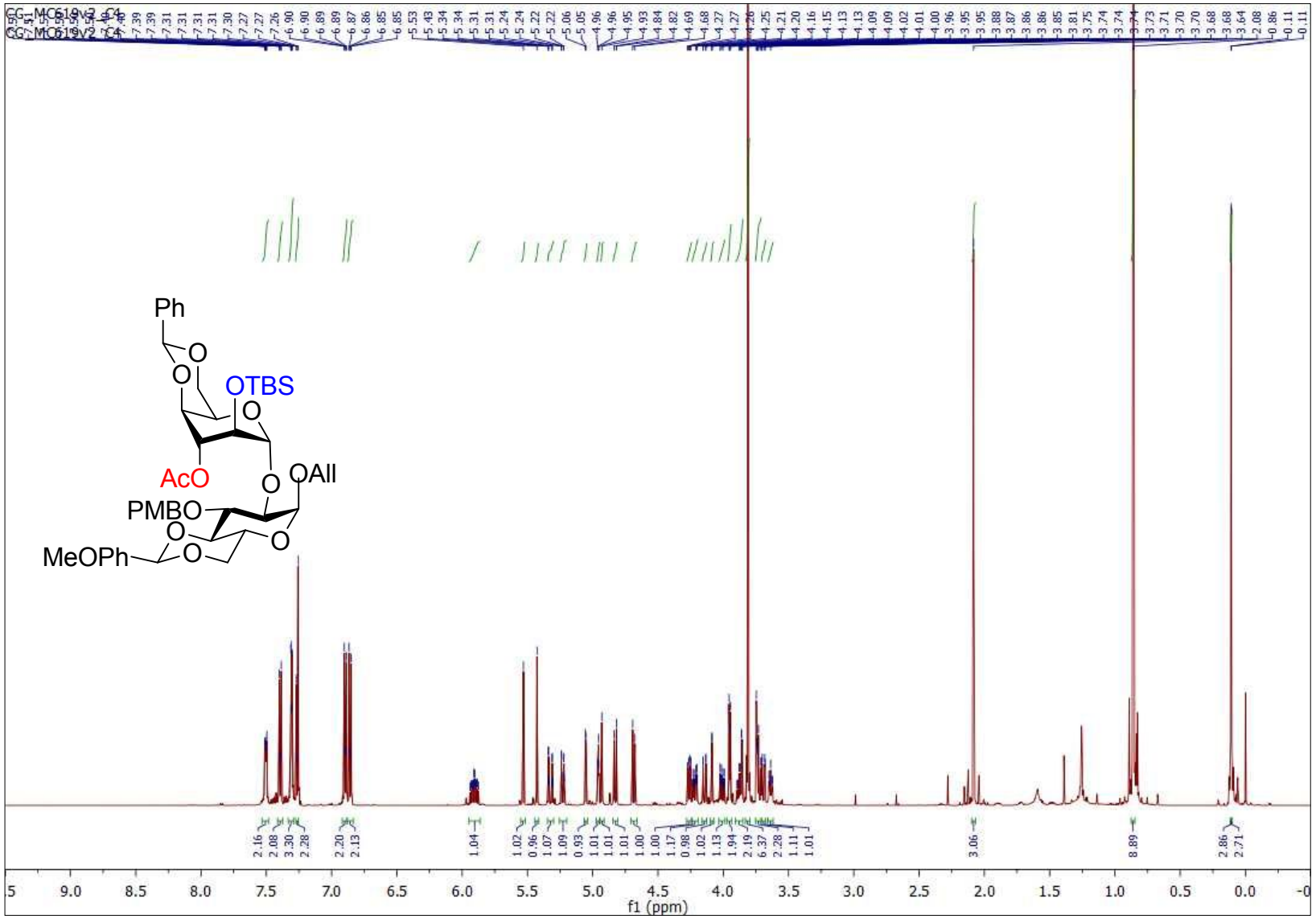


Figure S198. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→2)-3-*O*-*para*-methoxybenzyl-4,6-*O*-*para*-methoxybenzylidene-*α*-D-glucopyranoside (38)**

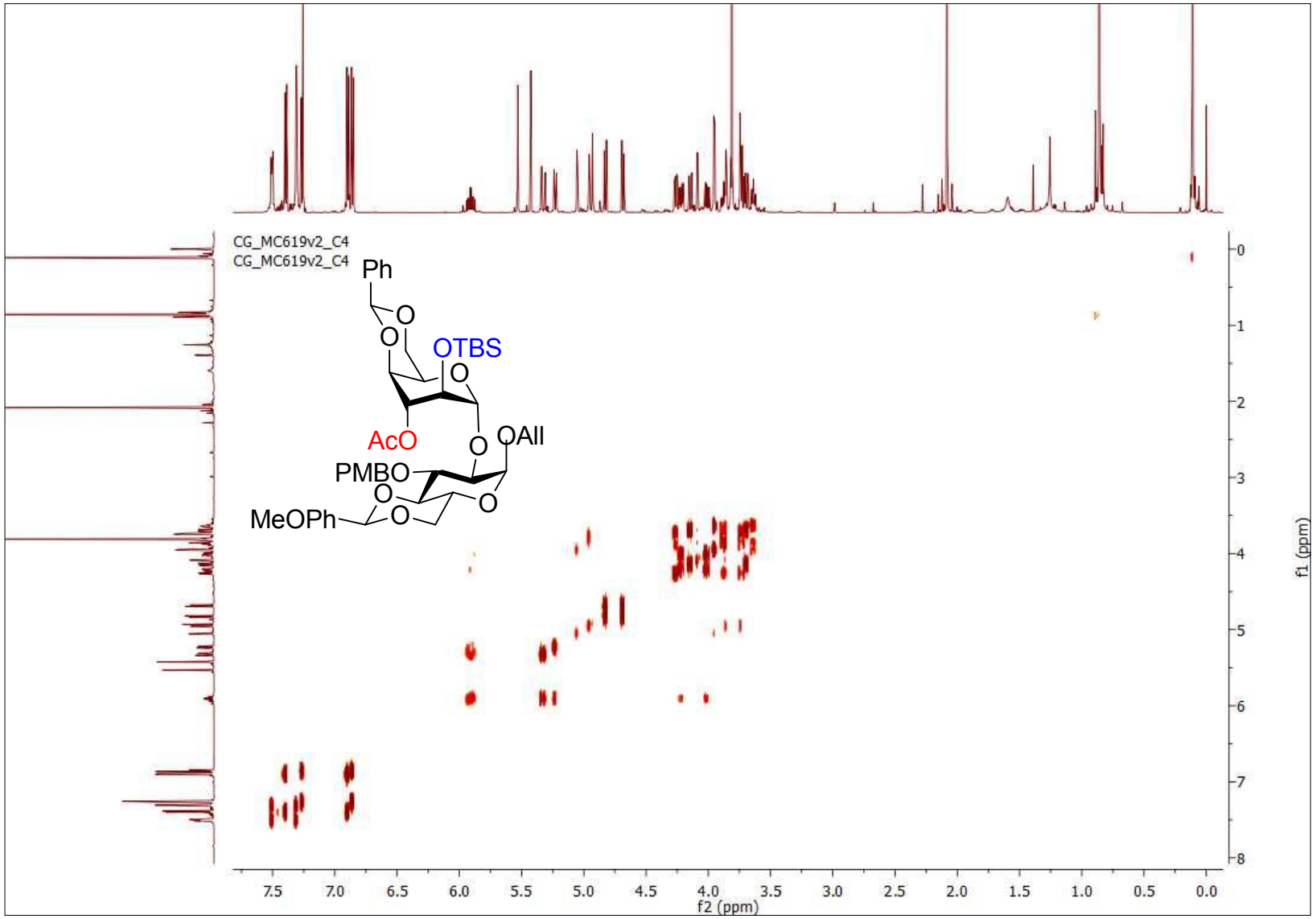


Figure S199. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→2)-3-*O*-*para*-methoxybenzyl-4,6-*O*-*para*-methoxybenzylidene-*α*-D-glucopyranoside (38)**

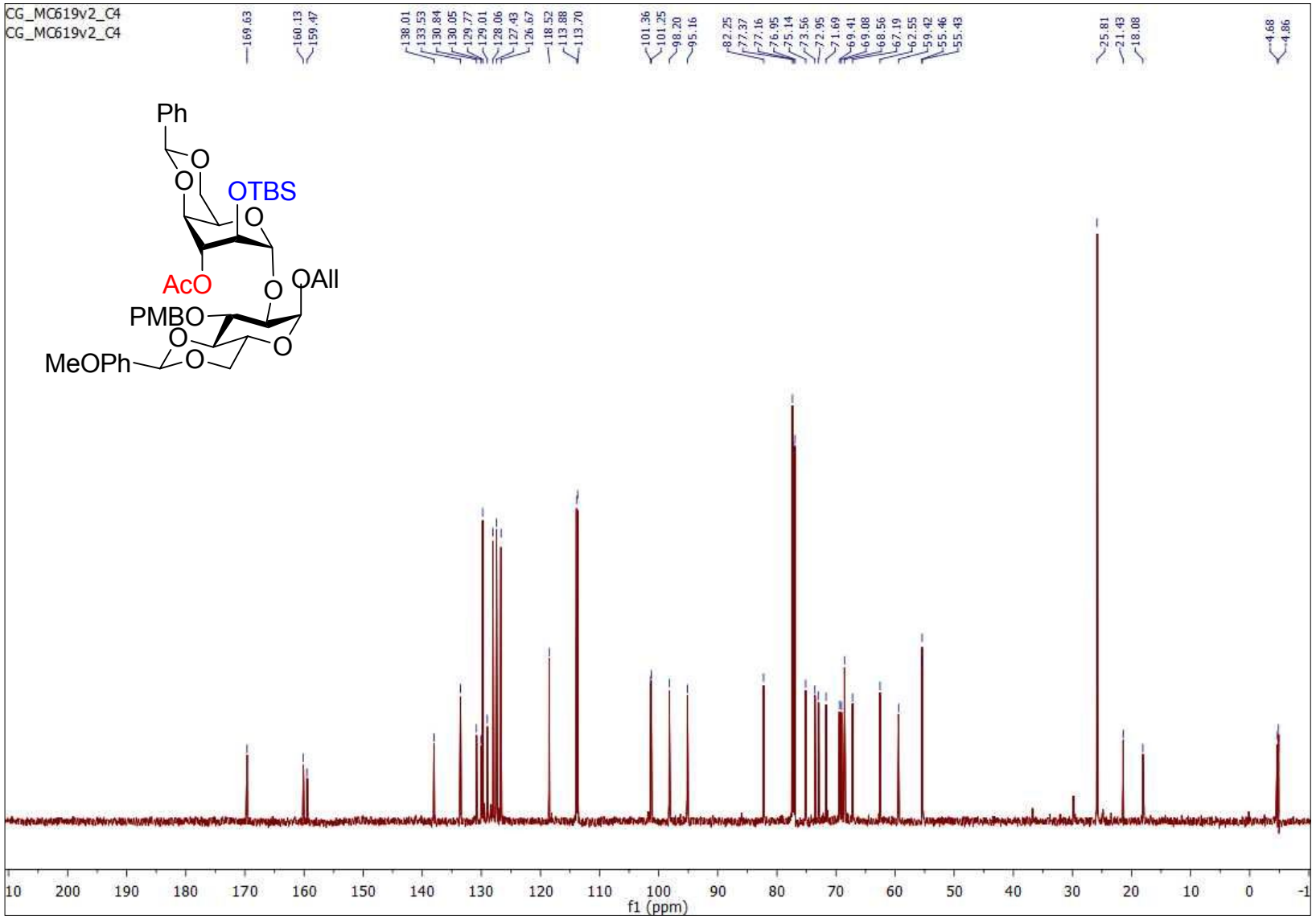


Figure S200. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→2)-3-*O*-*para*-methoxybenzyl-4,6-*O*-*para*-methoxybenzylidene-*α*-D-glucopyranoside (38)**

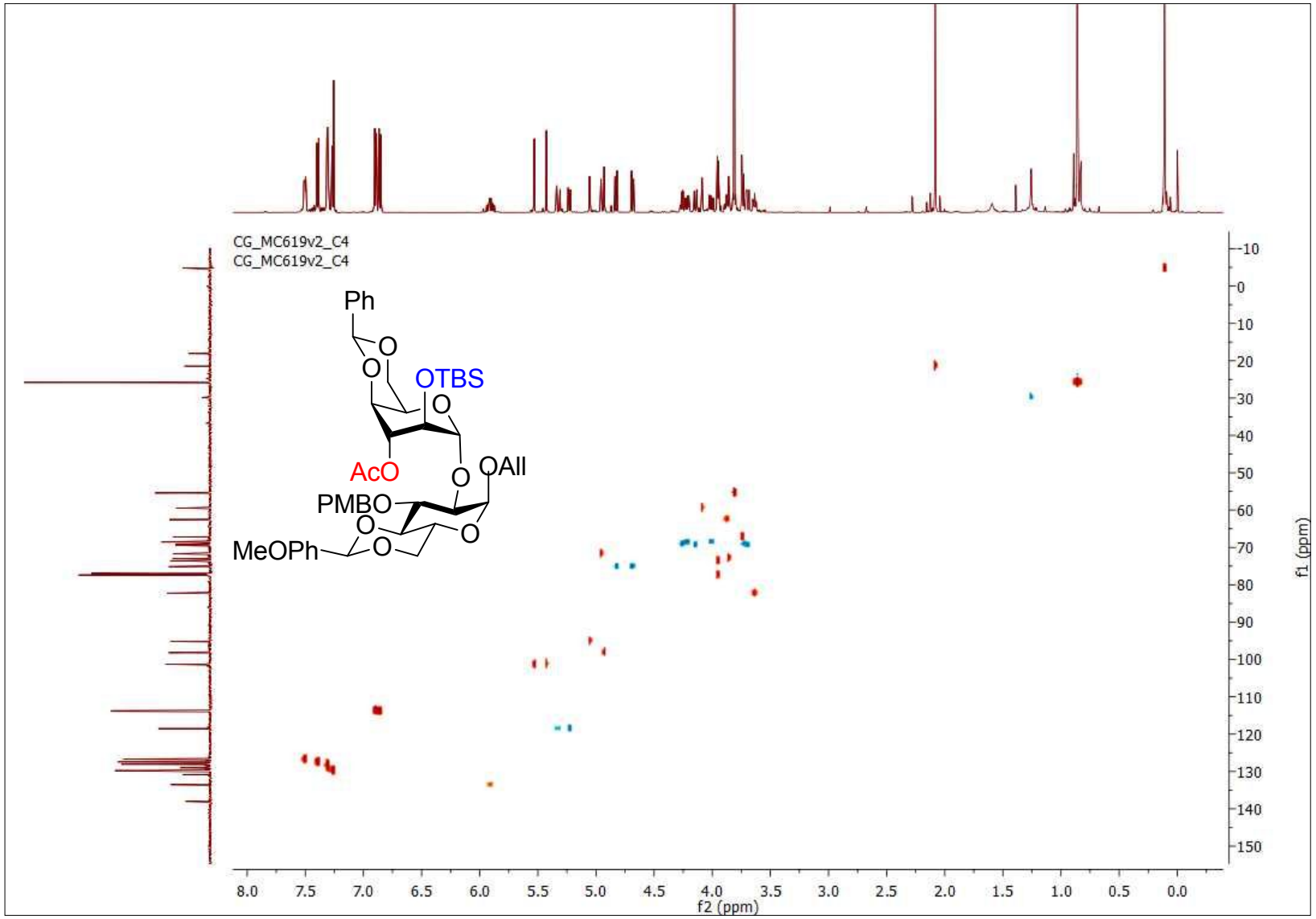


Figure S201. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→2)-3-*O*-*para*-methoxybenzyl-4,6-*O*-*para*-methoxybenzylidene-*α*-D-glucopyranoside (38)**

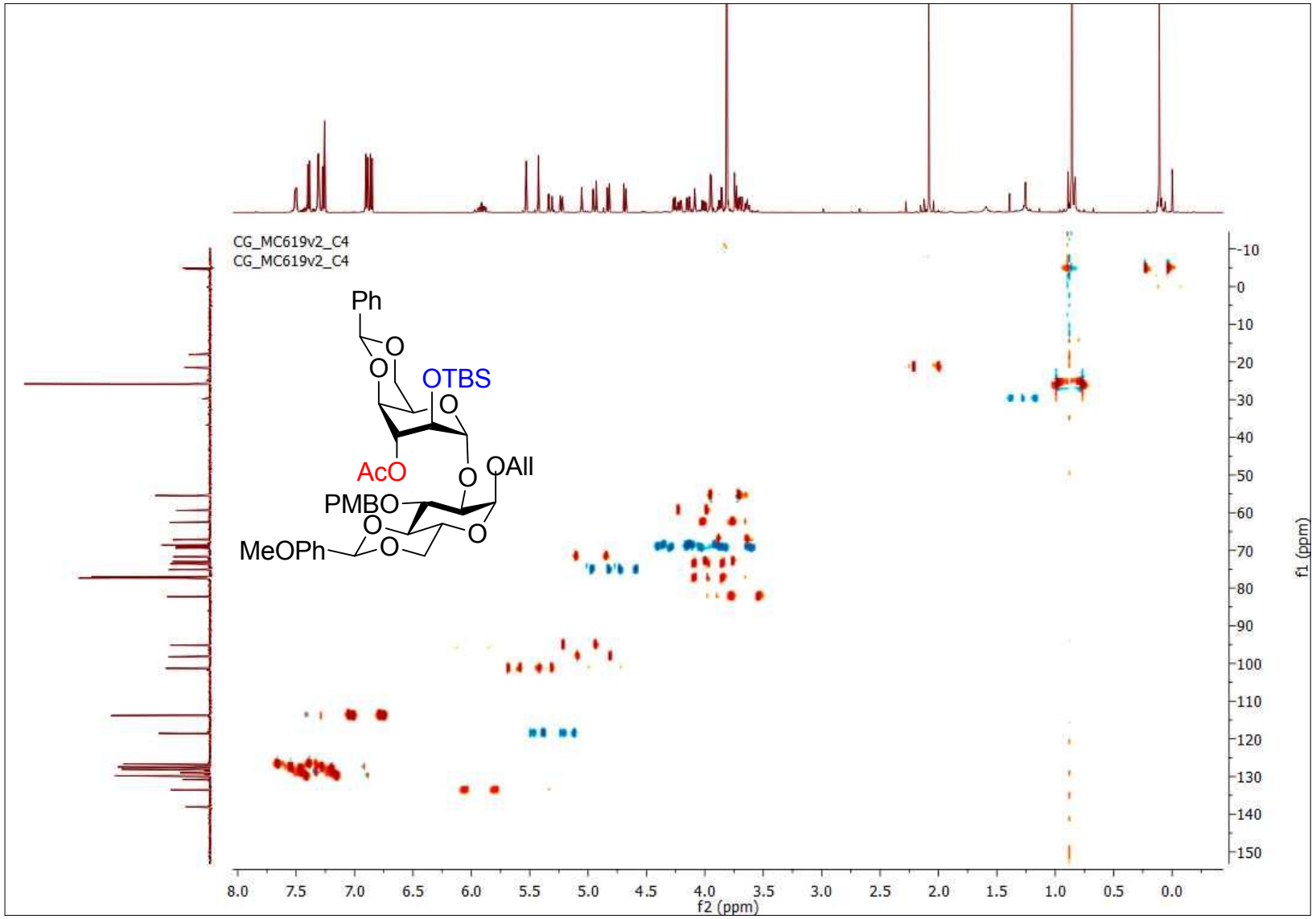


Figure S202. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (39a)**

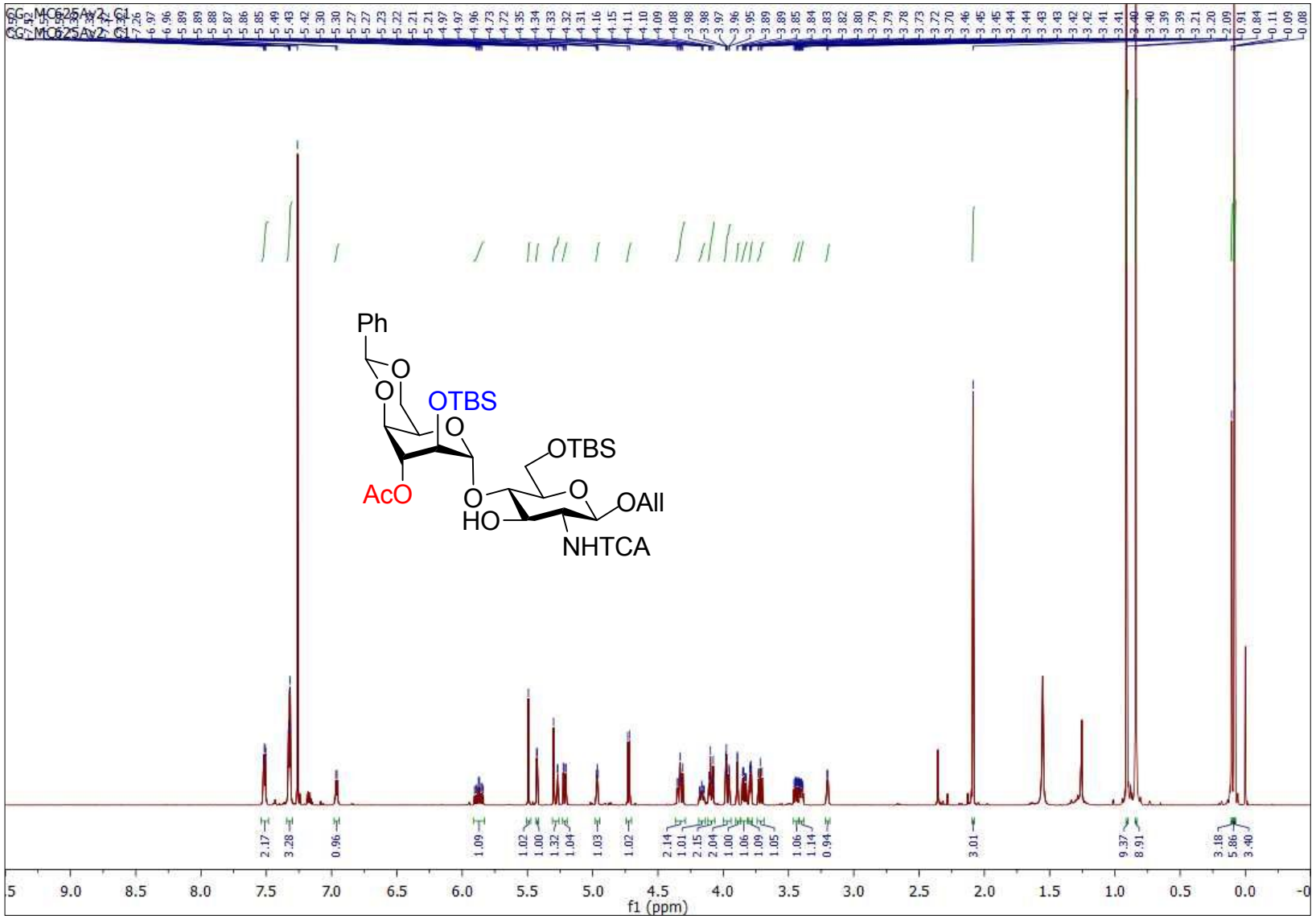


Figure S203. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (39a)**

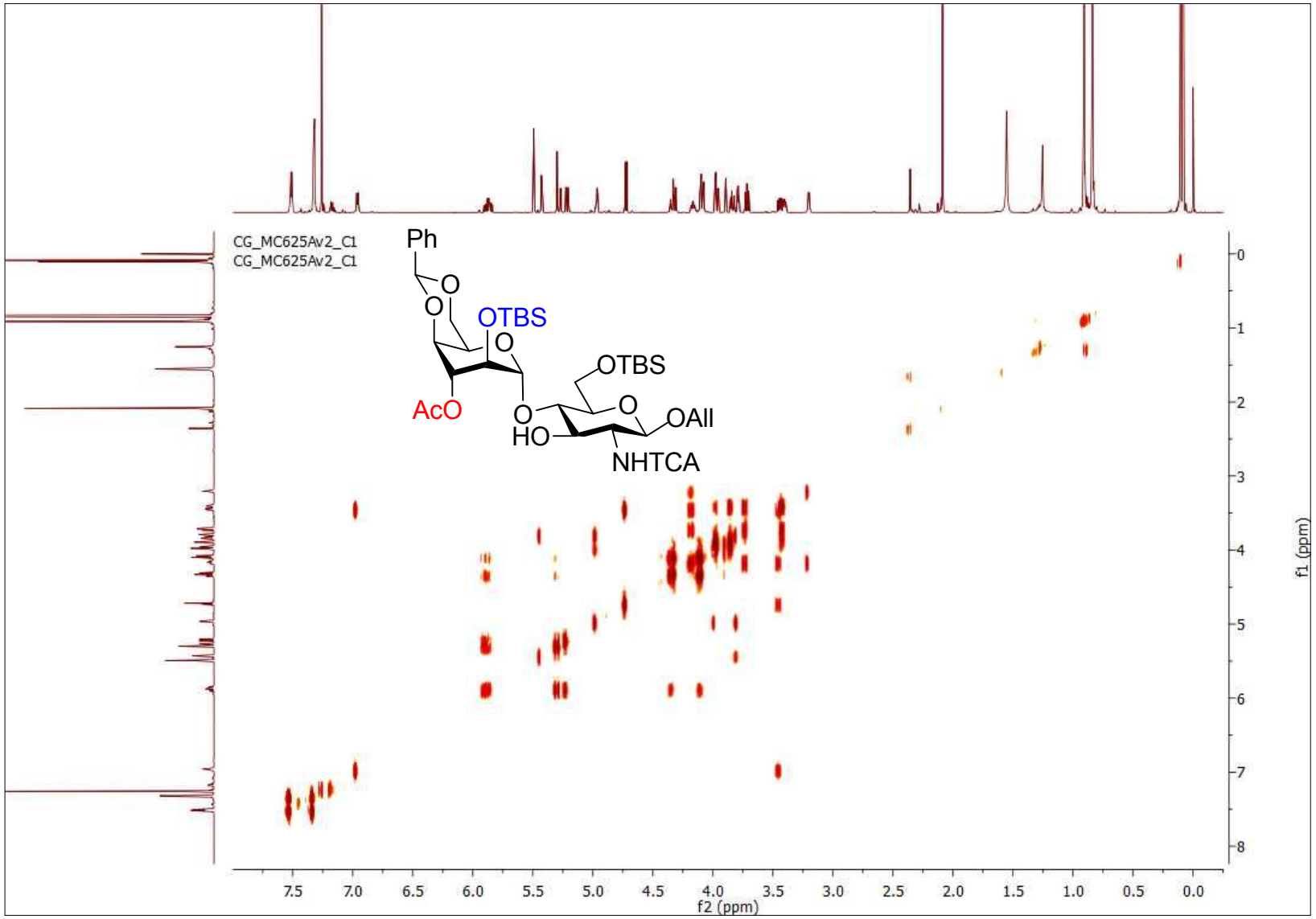


Figure S204. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (39a)**

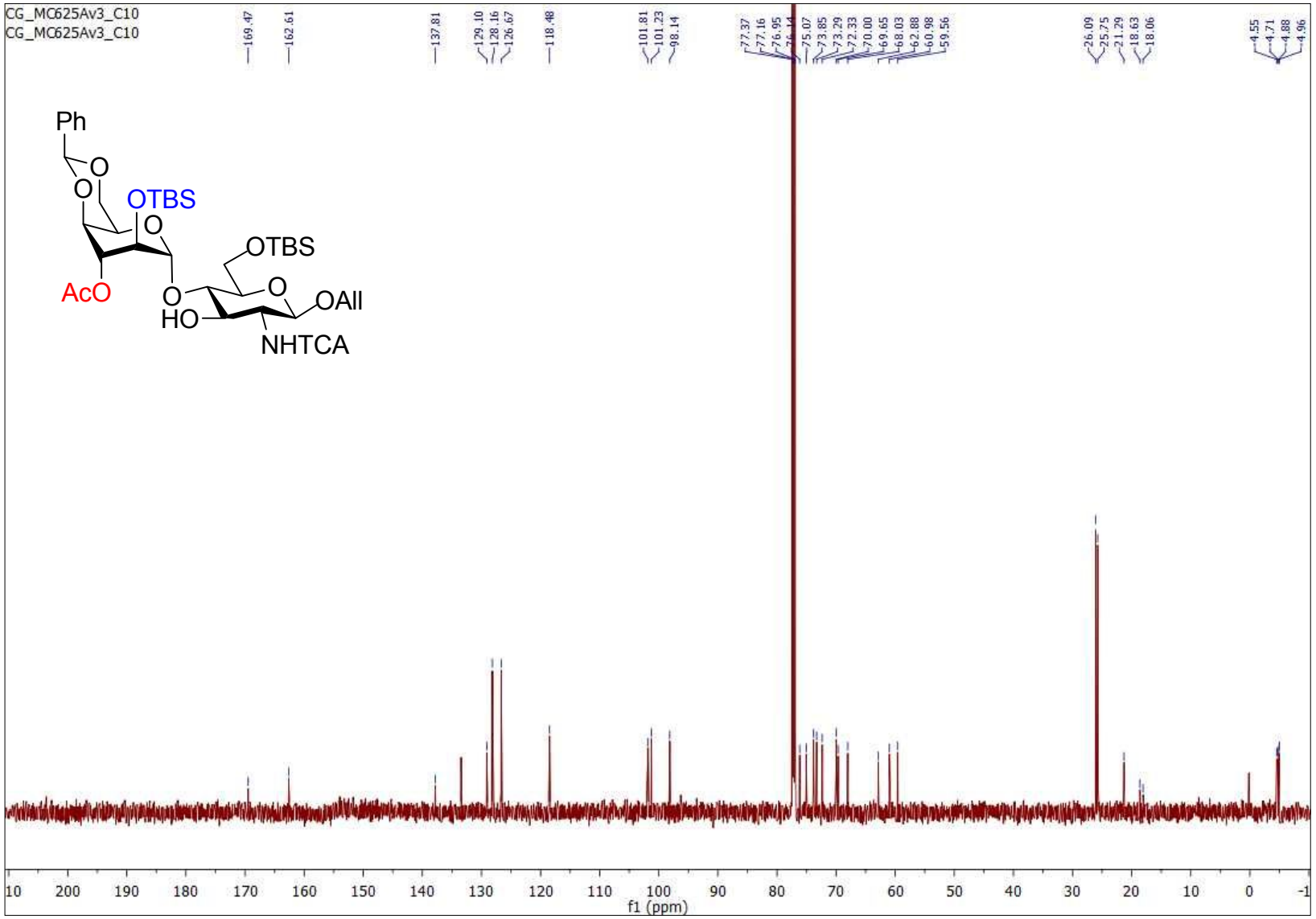


Figure S205. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (39a)**

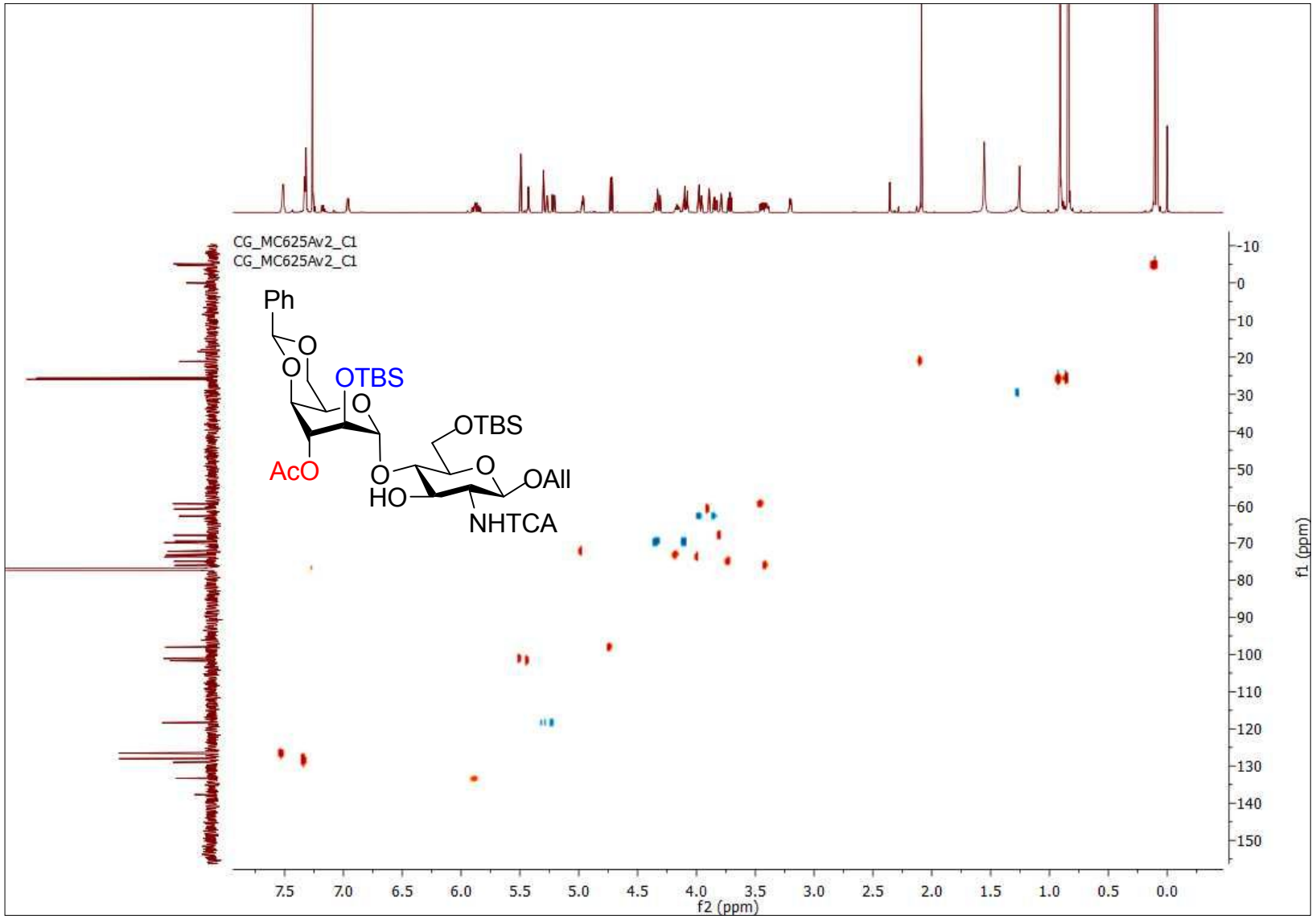


Figure S206. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (39a)**

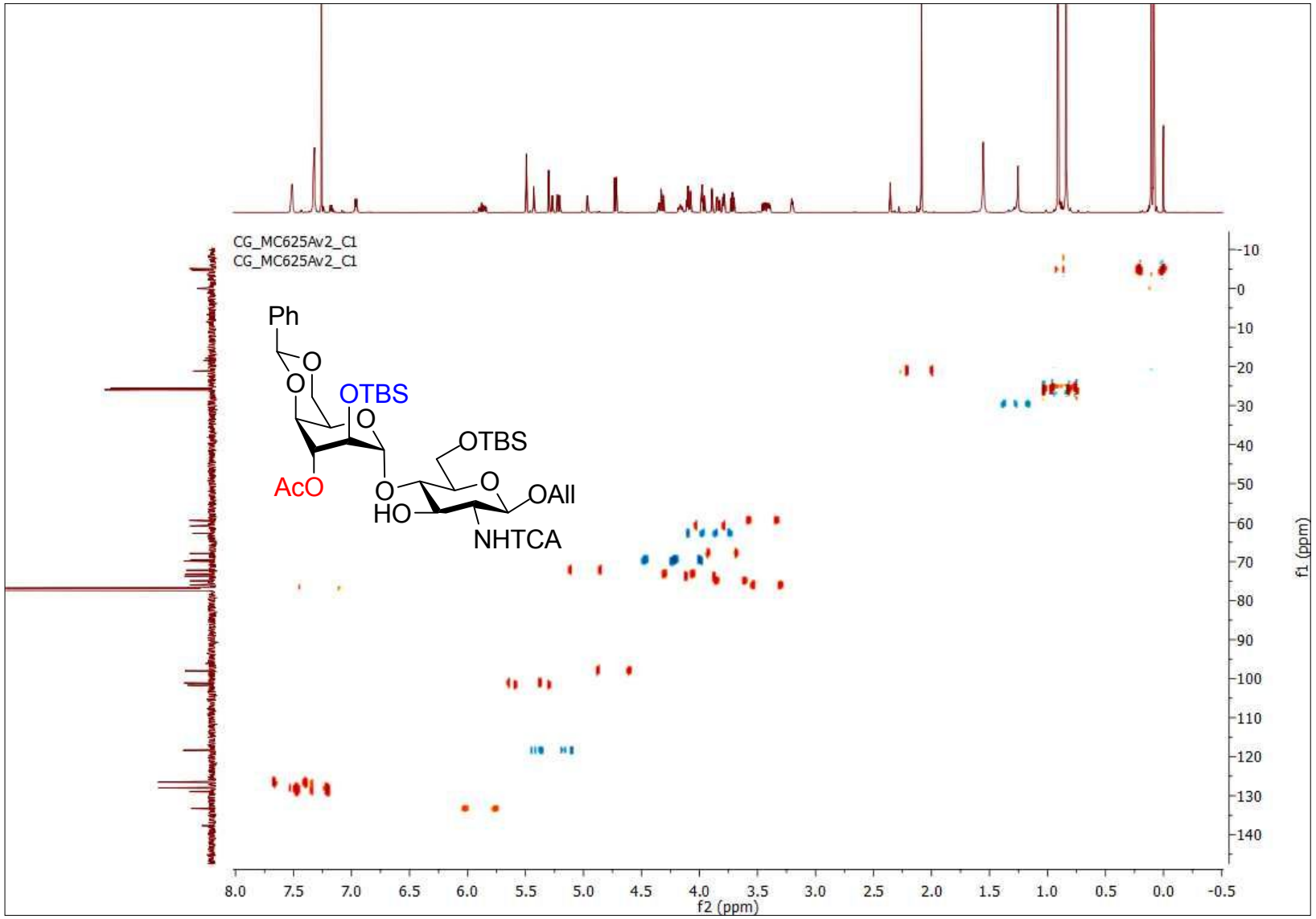


Figure S207. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→3)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (39b)**

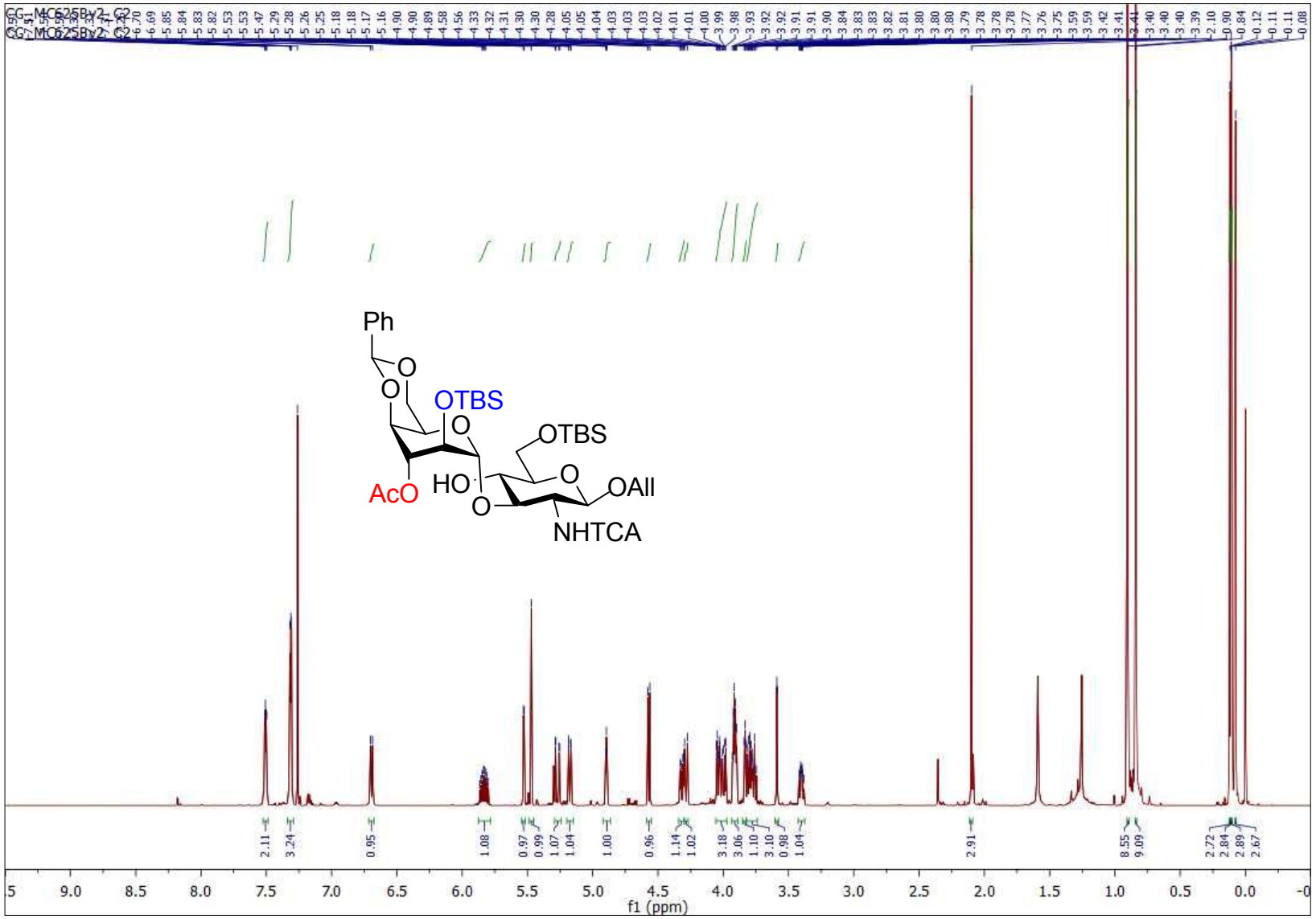


Figure S208. COSY NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→3)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (39b)**

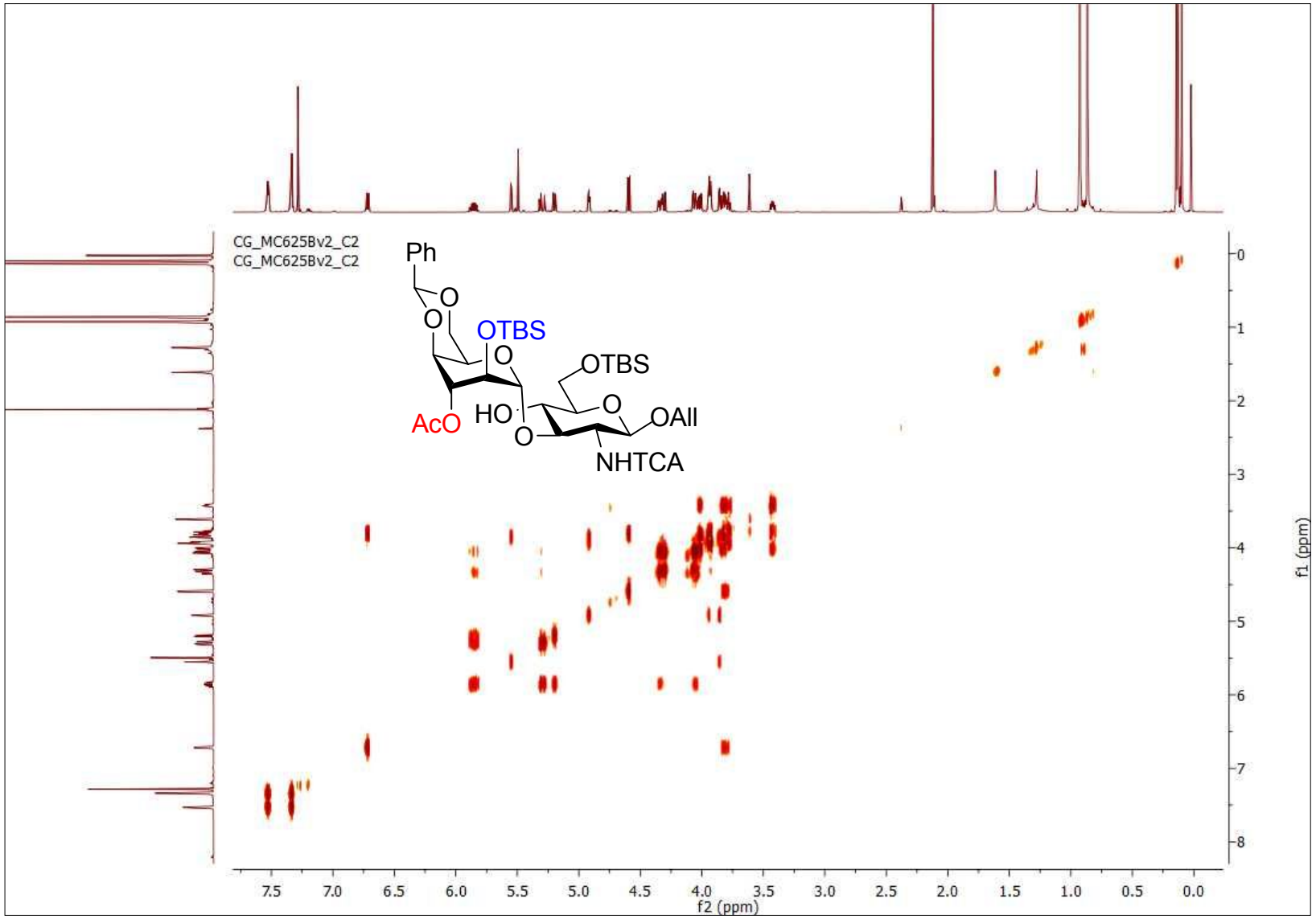


Figure S209. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→3)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (39b)**

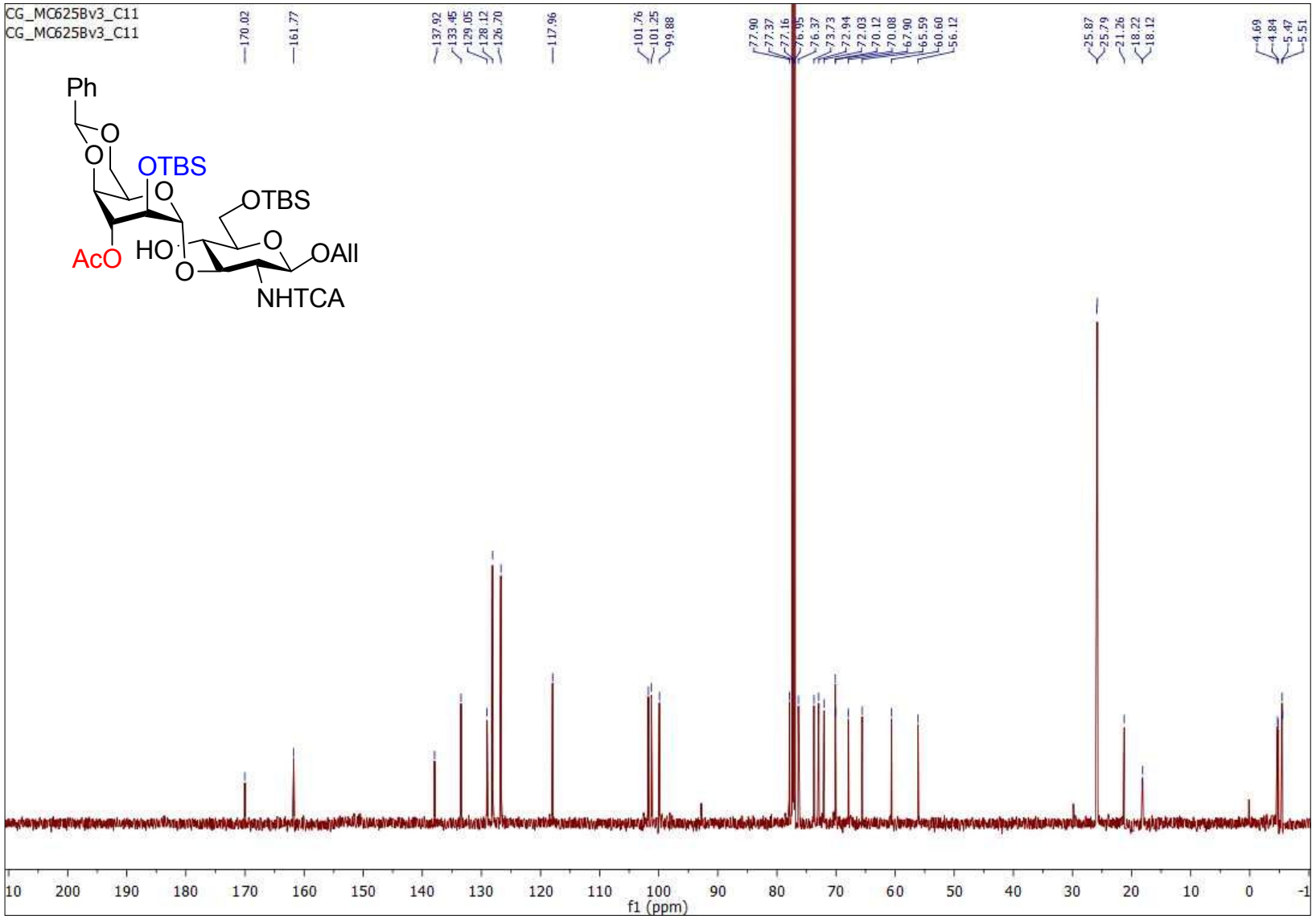


Figure S210. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→3)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (39b)**

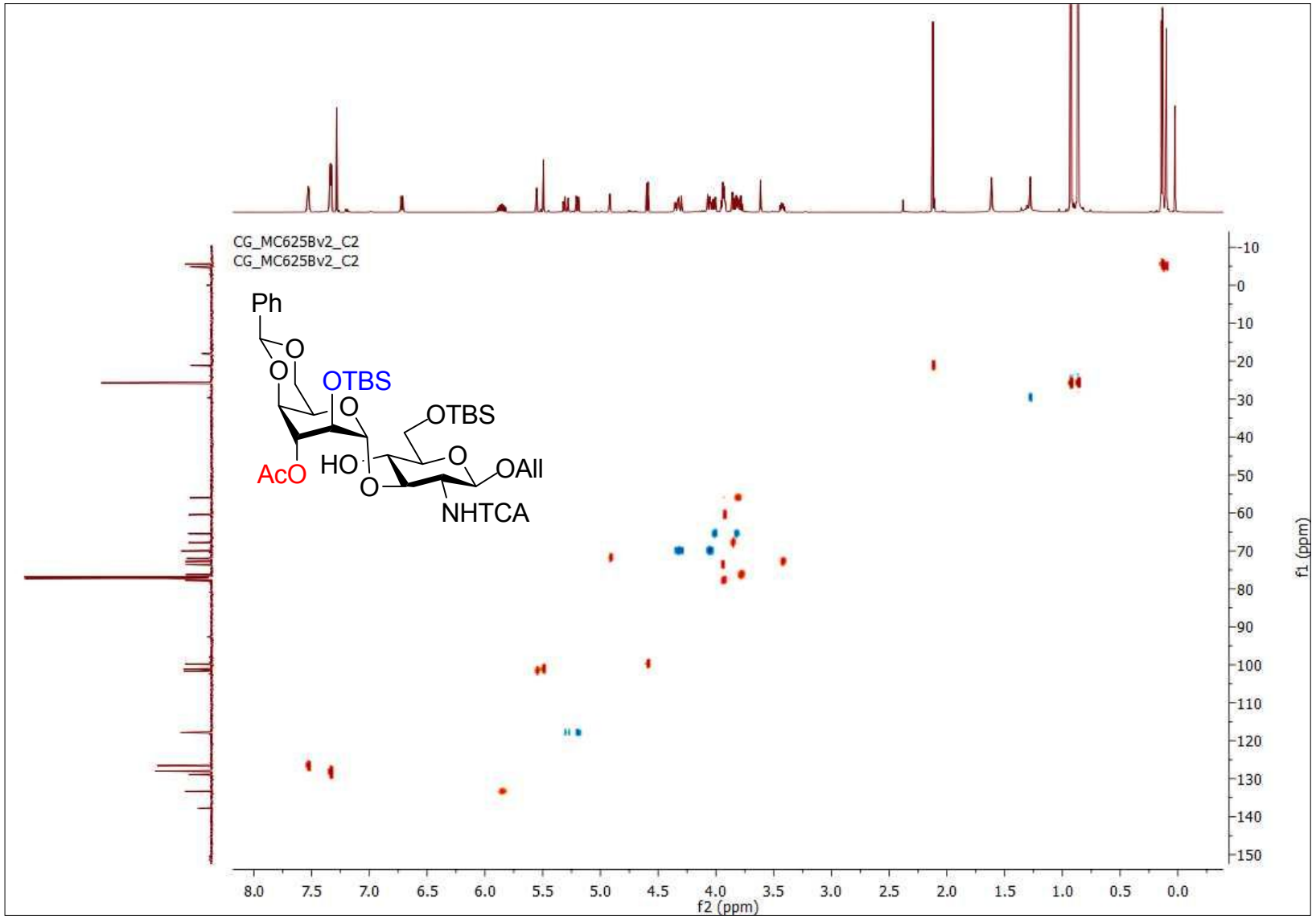


Figure S211. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of **allyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→3)-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (39b)**

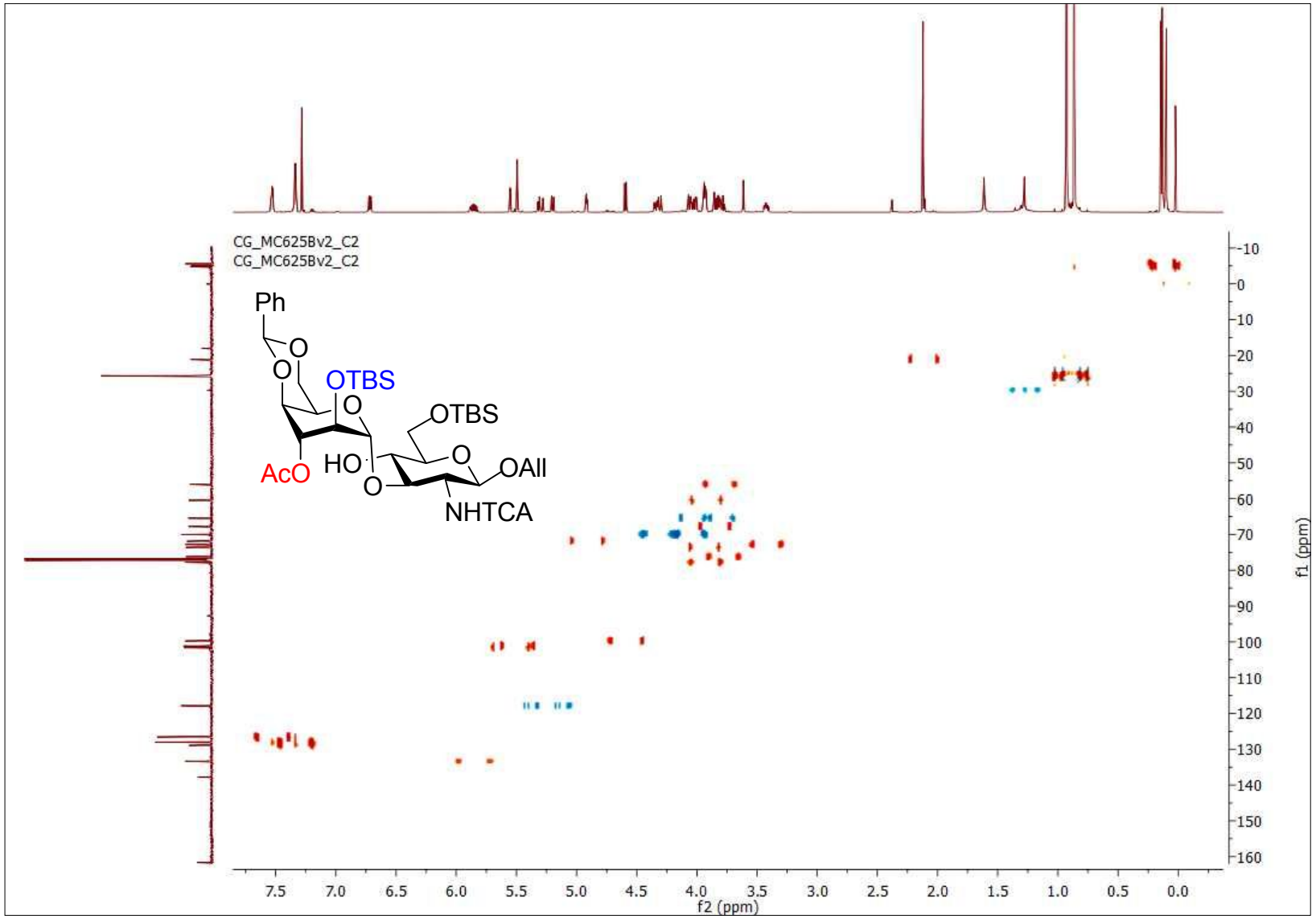


Figure S212. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (40)**

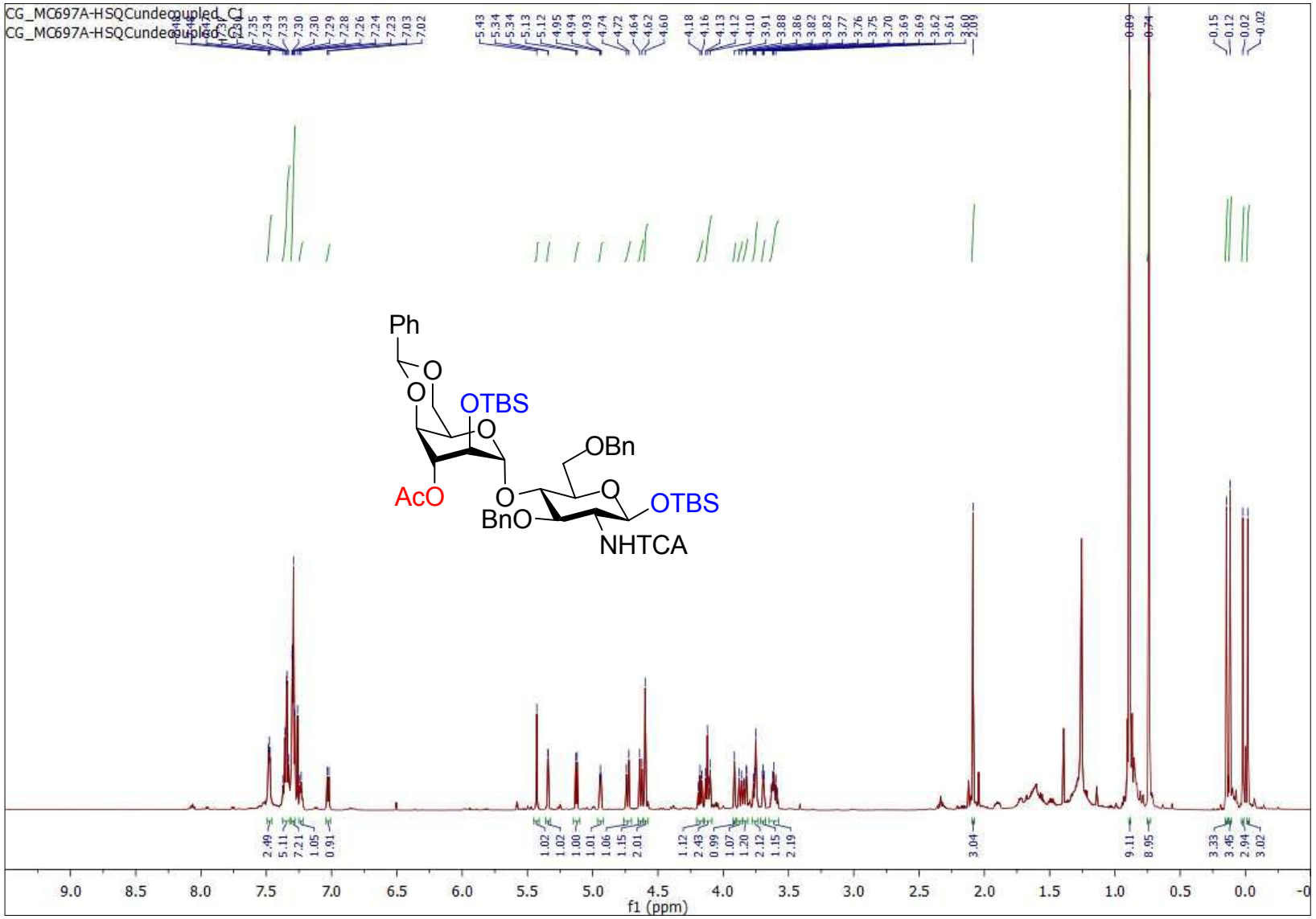


Figure S213. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (40)**

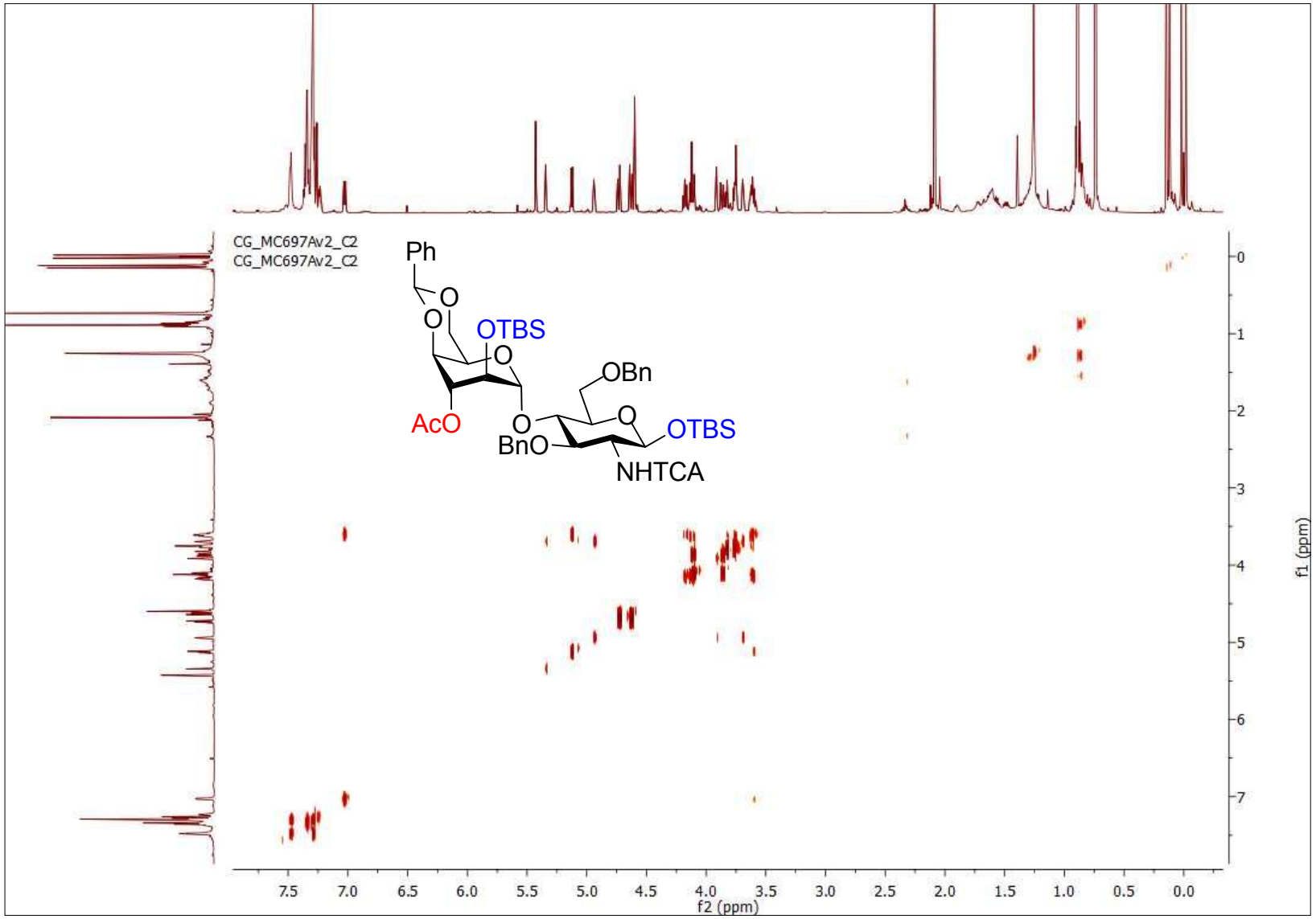


Figure S214. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***tert*-butyldimethylsilyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (40)**

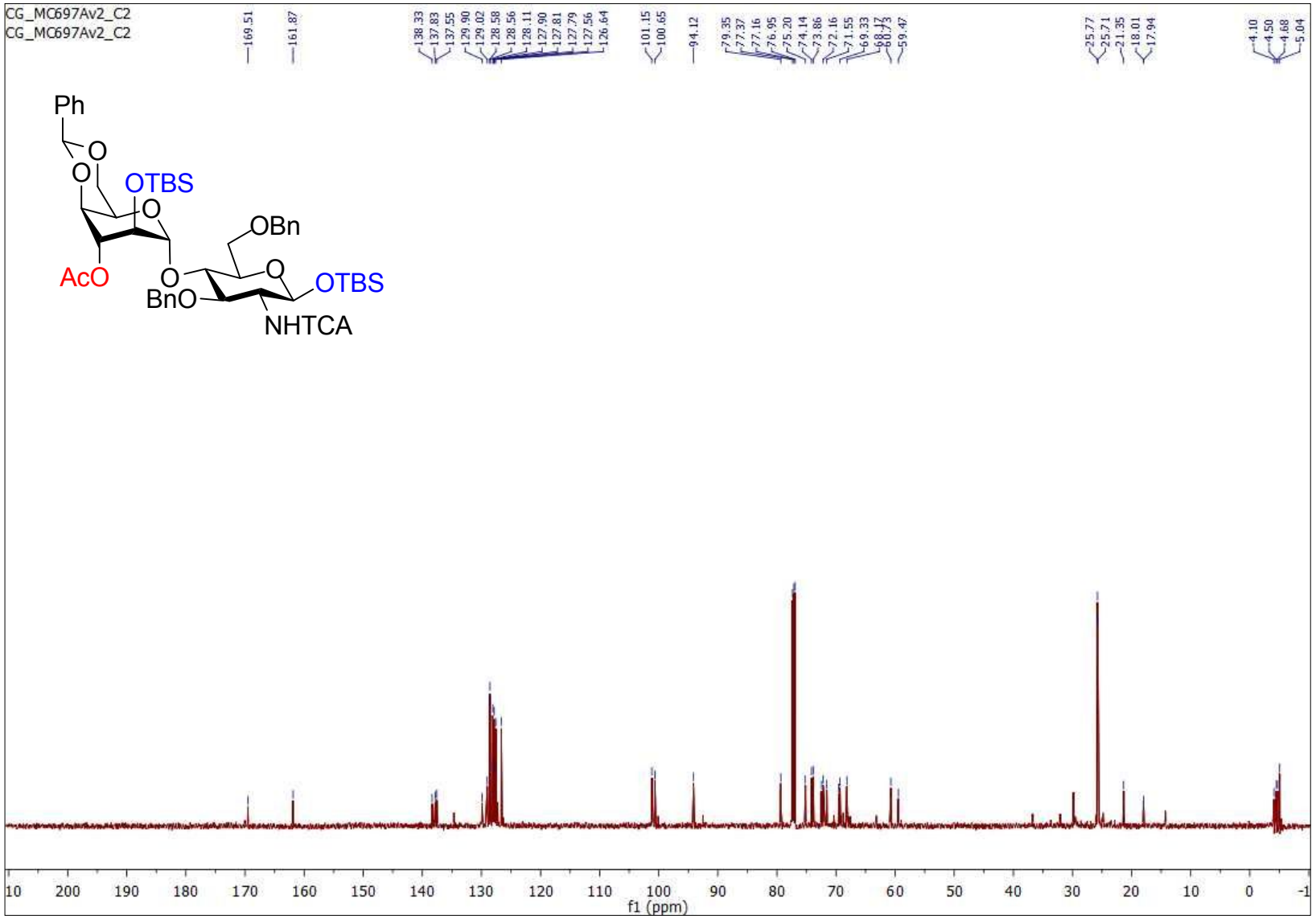


Figure S215. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (40)**

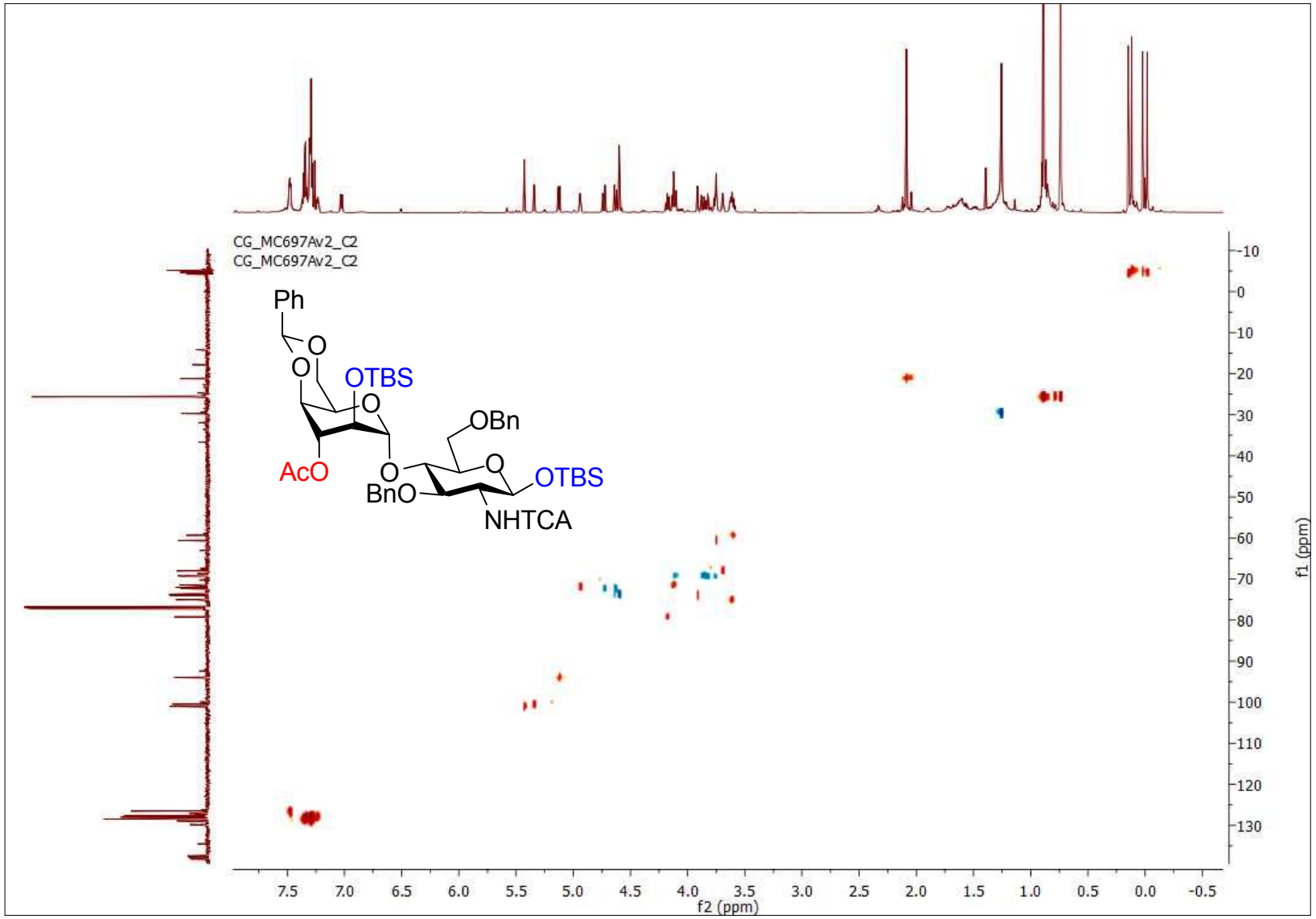


Figure S216. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-acetyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (40)**

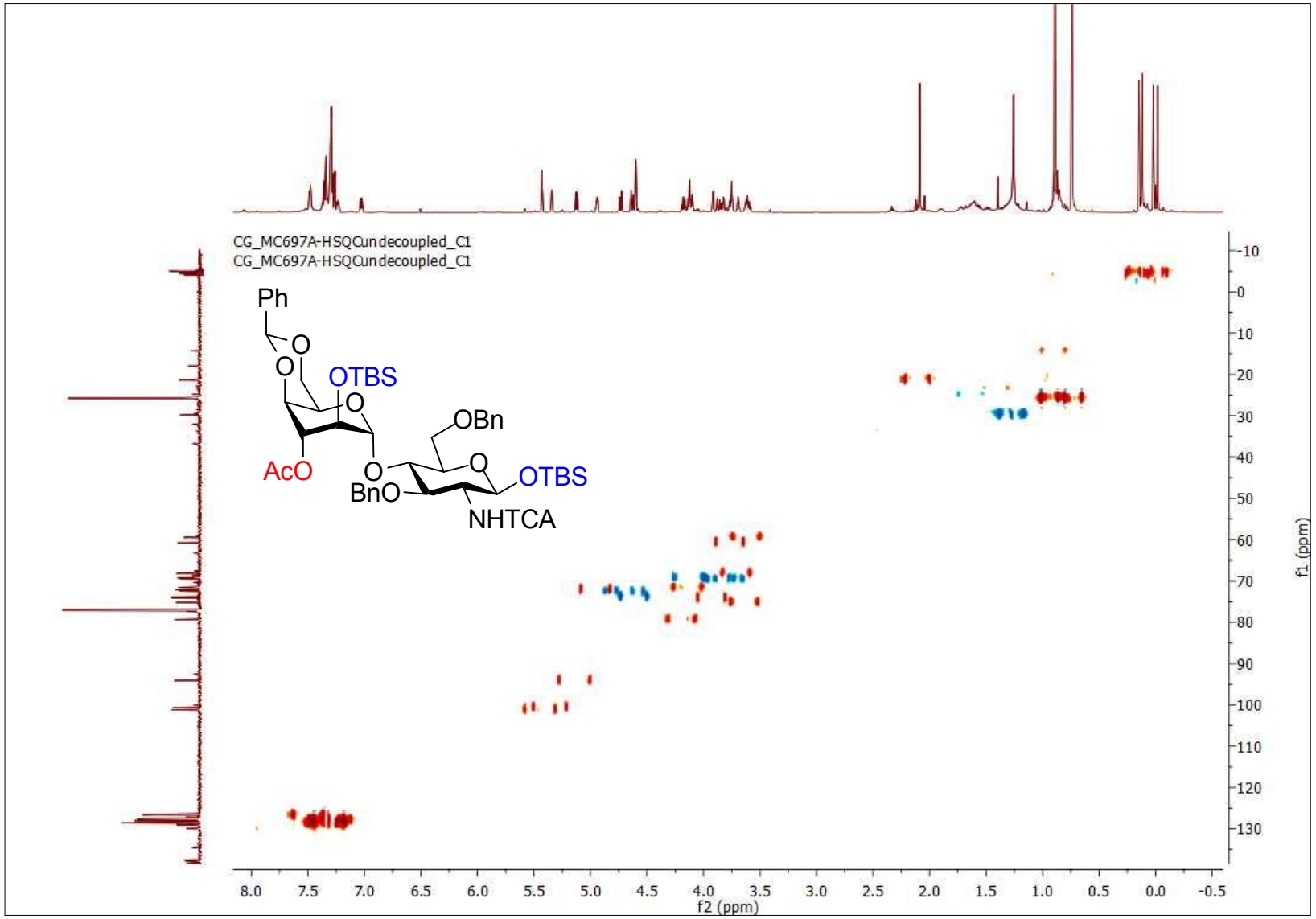


Figure S217. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (41*α*)**

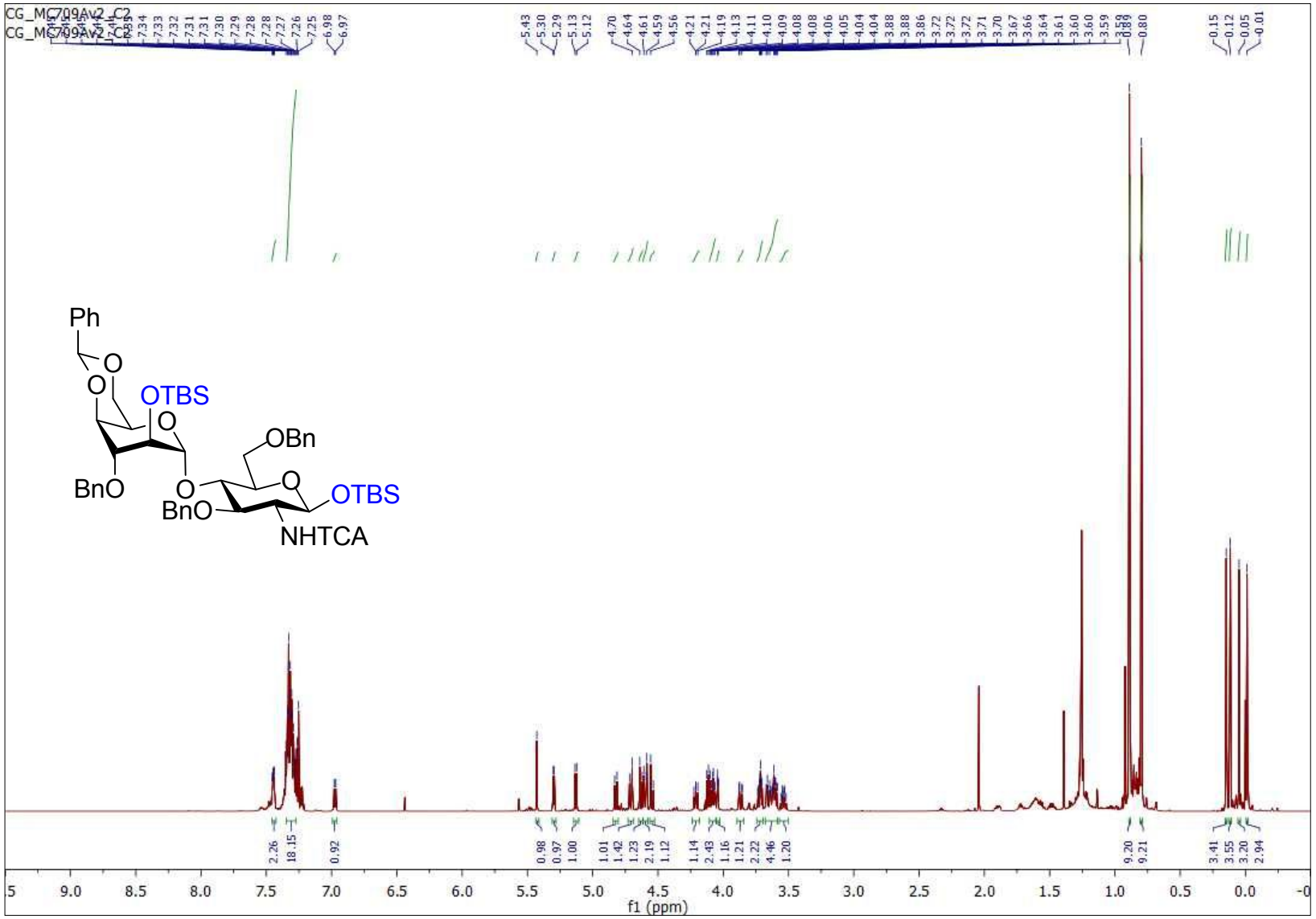


Figure S218. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (41*α*)**

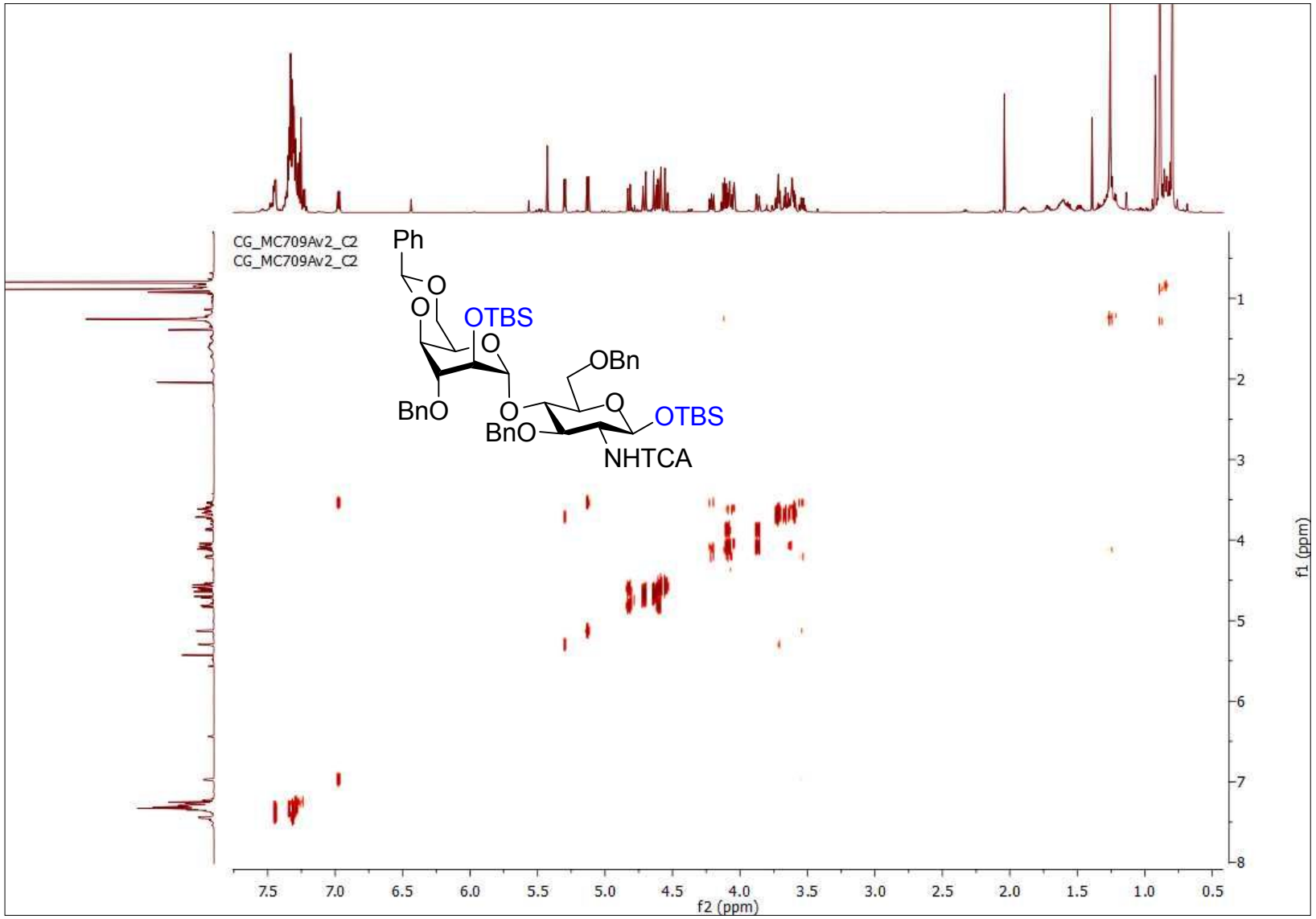


Figure S219. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***tert*-butyldimethylsilyl 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (41*α*)**

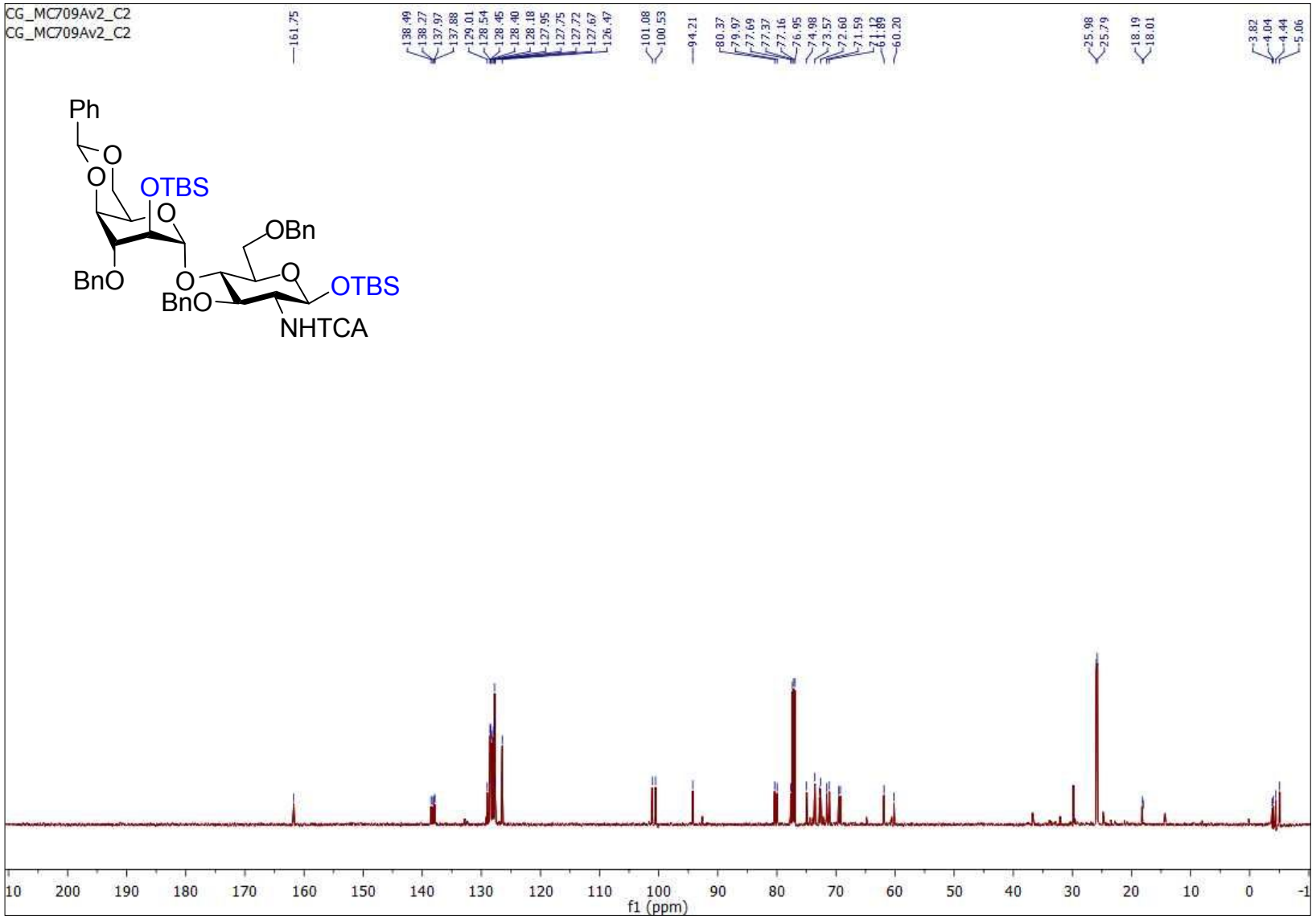


Figure S220. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (41*α*)**

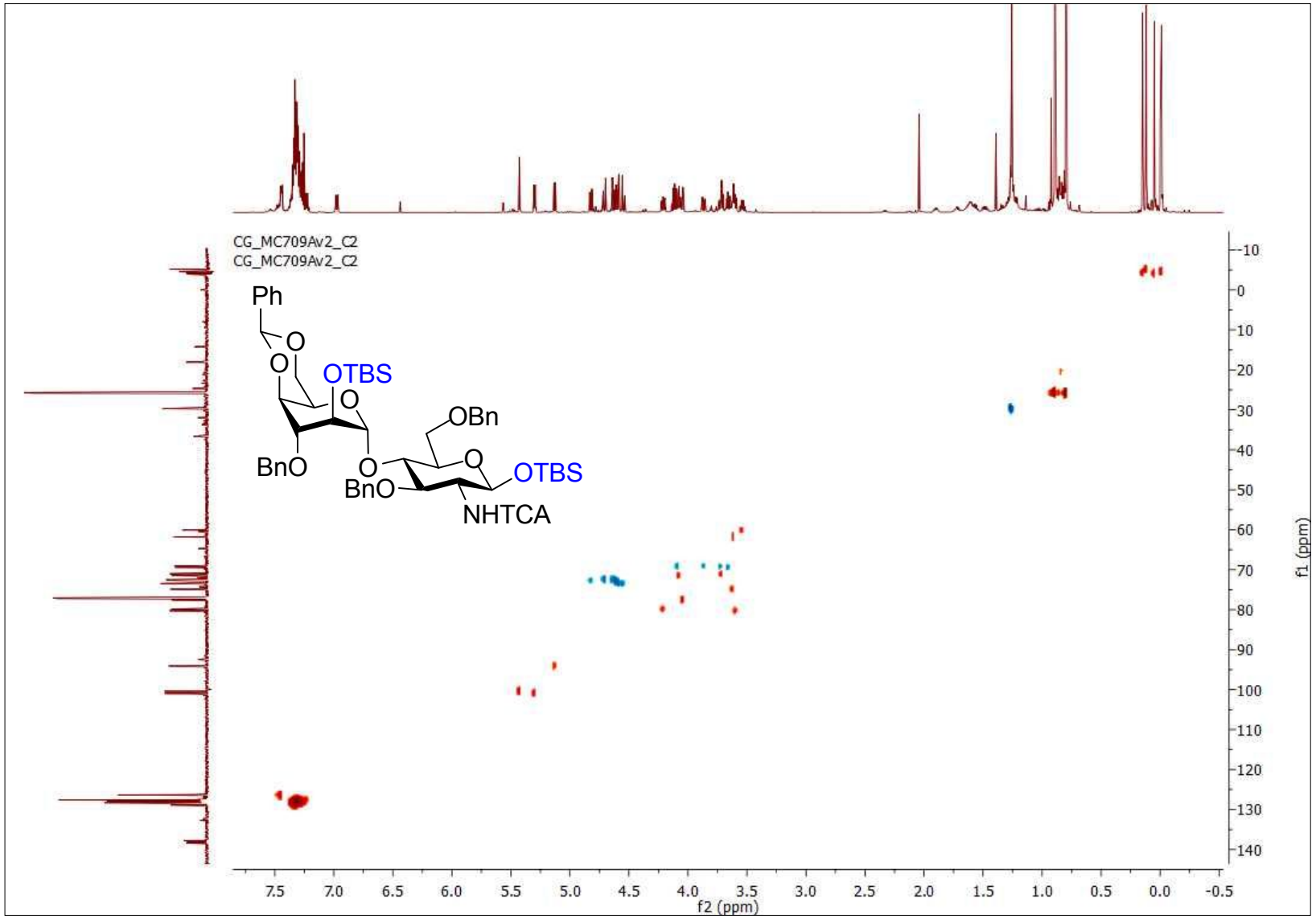


Figure S221. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*α*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (41*α*)**

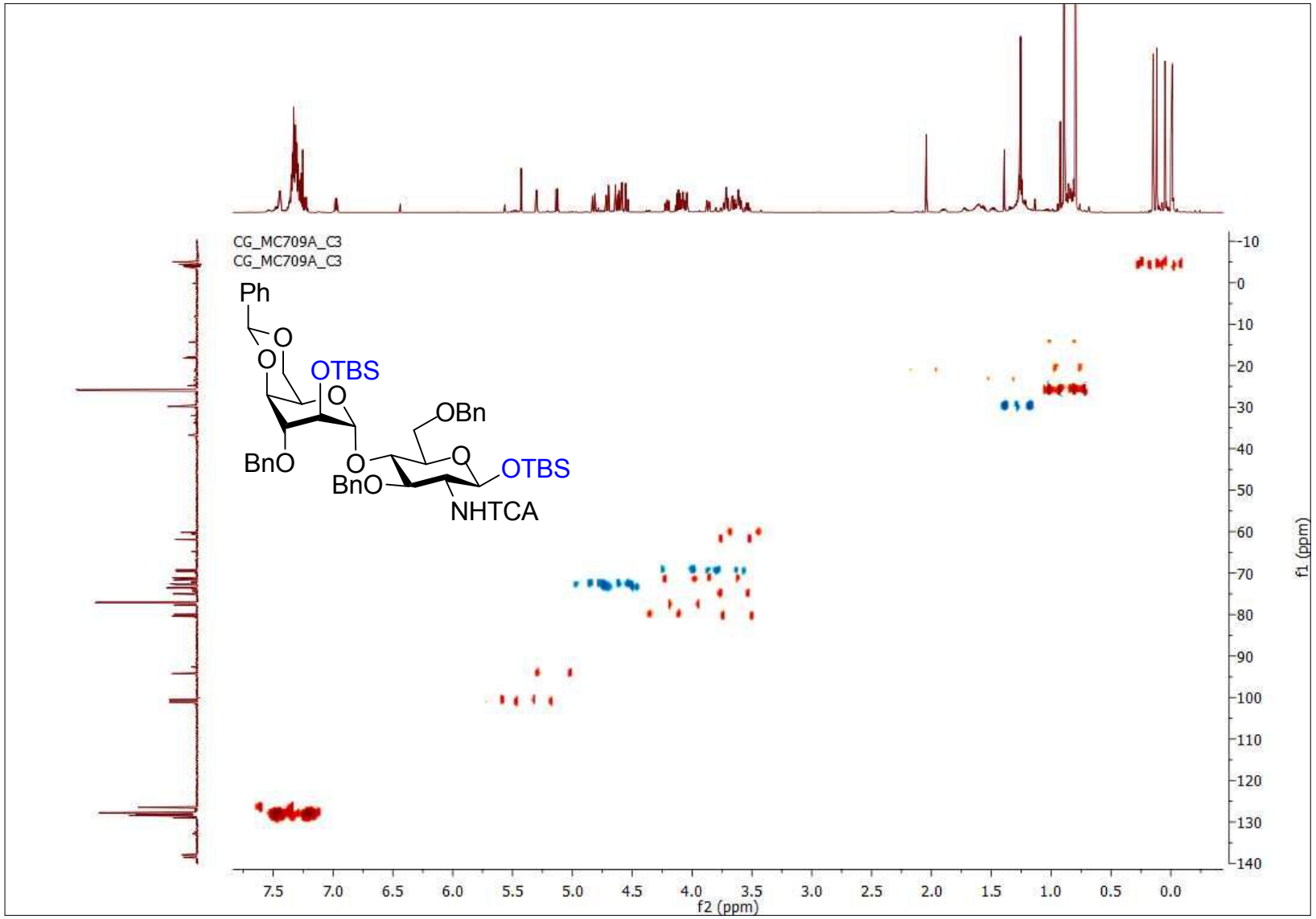


Figure S222. ^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (41*β*)**

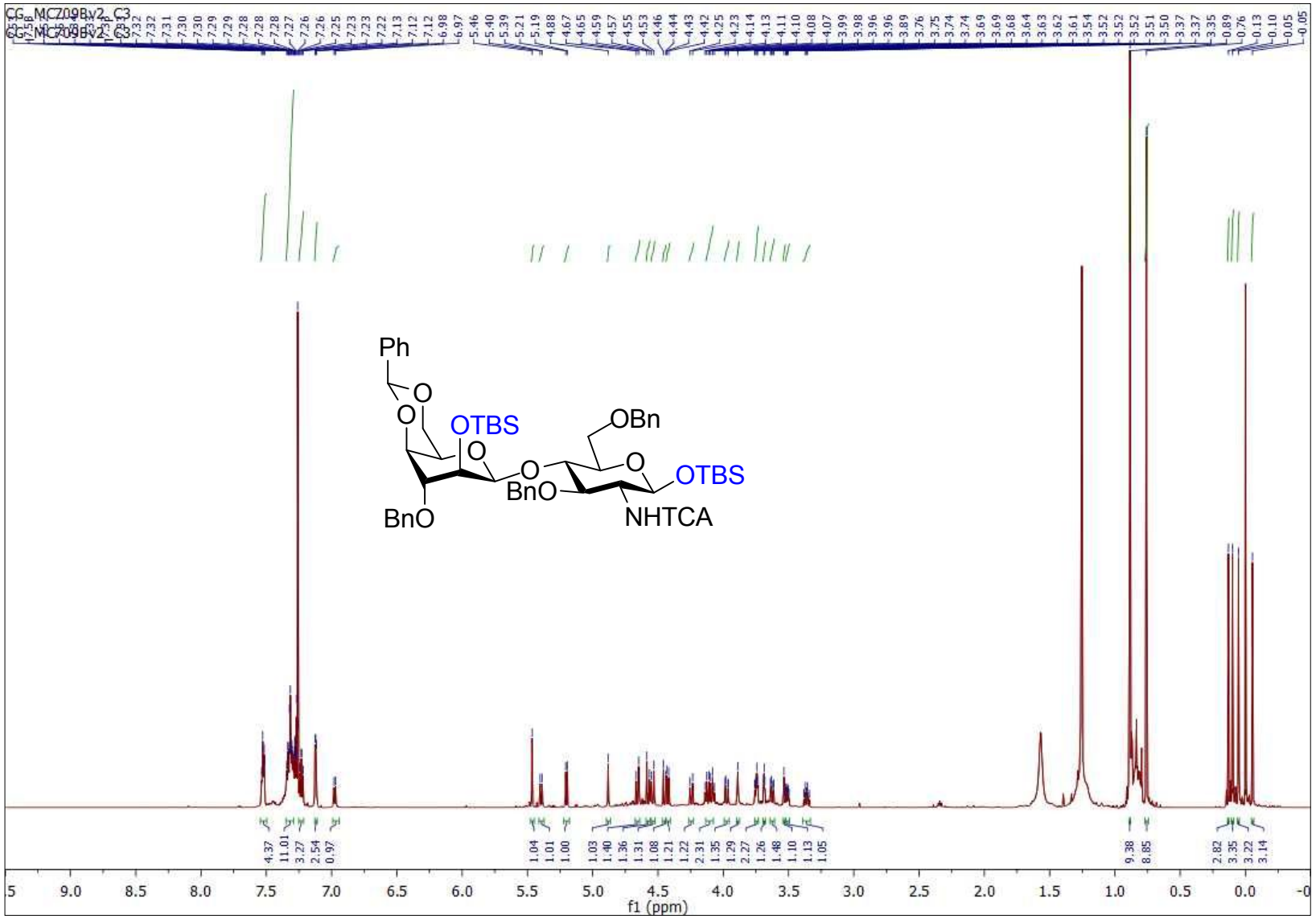


Figure S223. COSY NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (41*β*)**

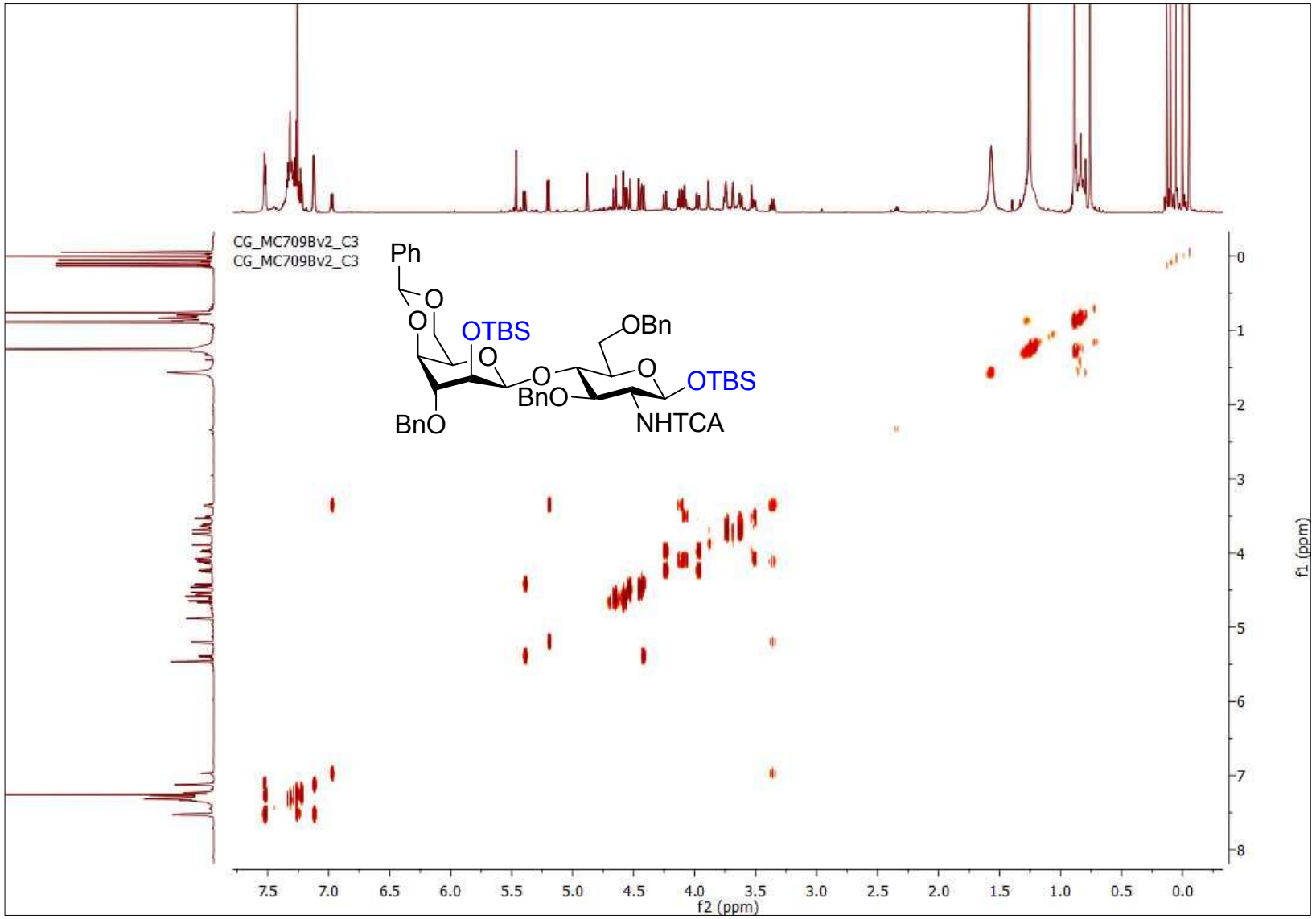


Figure S224. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***tert*-butyldimethylsilyl 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (41*β*)**

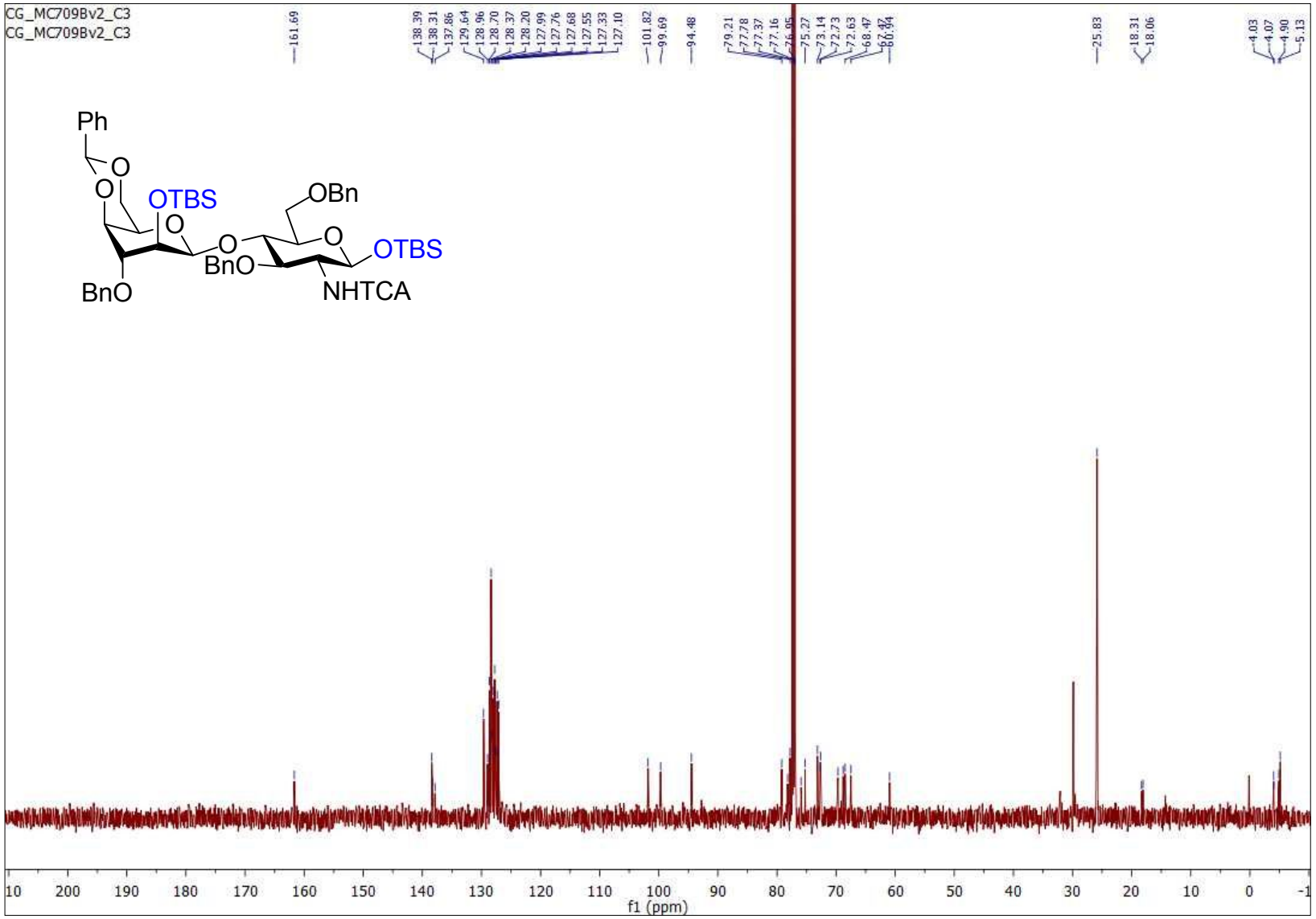


Figure S225. HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (41*β*)**

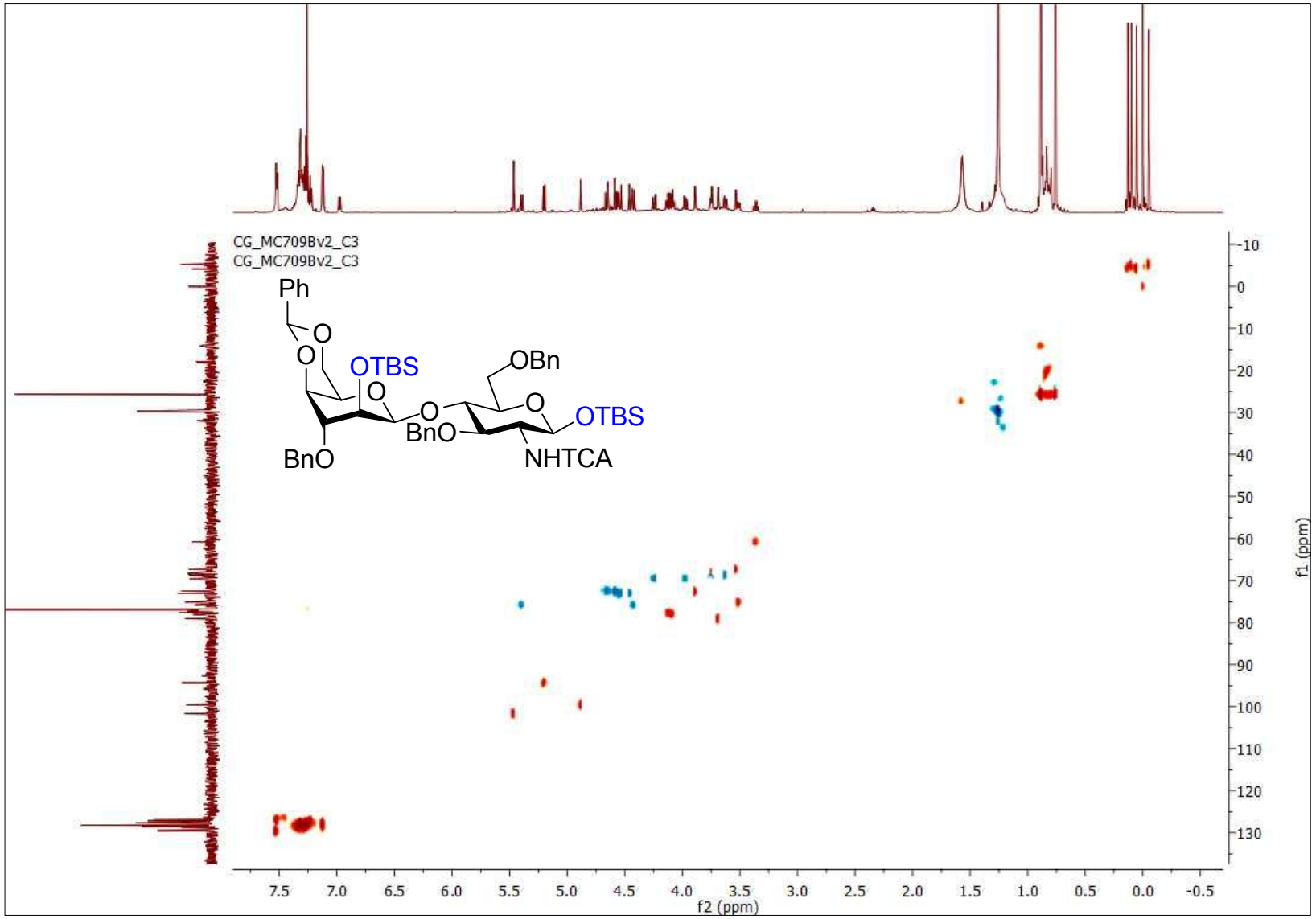
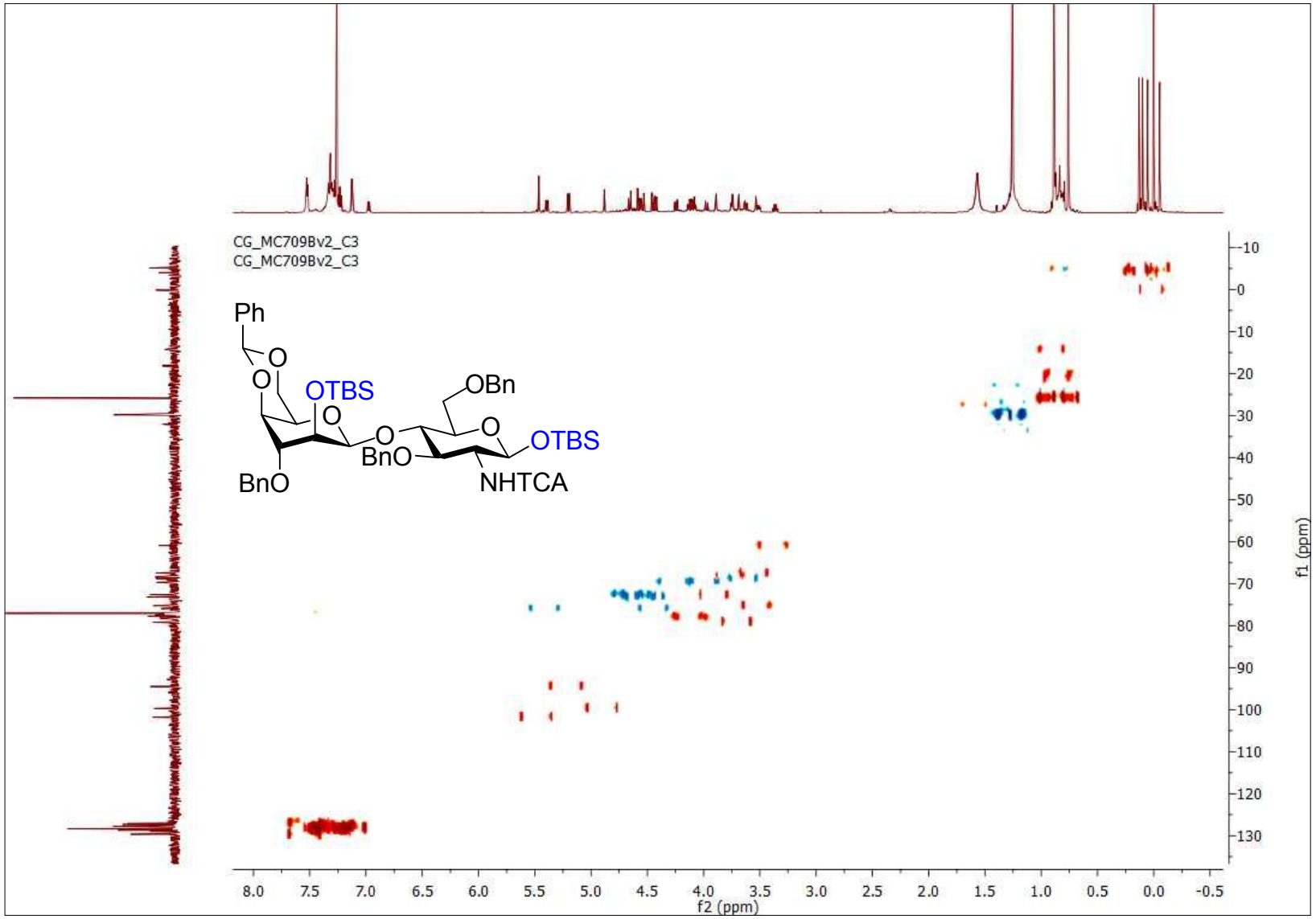


Figure S226. Coupled HSQC NMR spectrum ($CDCl_3$, 600 MHz) of ***tert*-butyldimethylsilyl 3-*O*-benzyl-(*S*)-4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-*β*-D-idopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-trichloroacetamido-*β*-D-glucopyranoside (41*β*)**



4. Supplementary references

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S2. Scheldrick, G., SHELXT-Integrated space-group and crystals-structure determination. *Acta Crystallogr., Sect. A: Found. Adv* **2015,** *71* (3).

S3. Sheldrick, G. M., SHELXL-97, Program for structure refinement. *University of Göttingen, Germany* **1997**.

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