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Supporting Information

for

Comparison of glycosyl donors: a supramer approach

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Copies of NMR spectra for all new compounds, single crystal X-ray analysis data for compound 7 (CCDC 1843708)

Table of contents

Single crystal X-ray analysis of methyl (phenyl 3,5-dideoxy-2-thio-4,9-bis-*O*-chloroacetyl-5-trifluoroacetamido-D-glycero-β-D-galacto-nonulopyranosid)onate (7)

Single crystals of methyl (phenyl 3,5-dideoxy-2-thio-4,9-bis-*O*-chloroacetyl-5-trifluoroacetamido-D-glycero-β-D-galacto-nonulopyranosid)onate water solvate (**7**·H_2O) were grown from acetone-d_6 in an NMR tube. A suitable crystal was selected and the XRD analysis was performed on a Bruker SMART APEX2 DUO CCD diffractometer (Cu K_α radiation, λ = 1.54178 Å). The crystal was kept at 120 K during data collection. The data set was corrected for absorption with SADABS [1], the structure was solved with the ShelXT [2,3] structure solution program using Direct Methods and refined with the ShelXL [2,3] refinement package using Least Squares minimization (Olex2 [4] was used as an interface to ShelXT and ShelXL packages). Non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water molecules, amino and hydroxy groups were localized in the difference-Fourier maps and refined isotropically with X-H distances fixed at values 0.84 Å for O–H and 0.95 Å for N–H bonds. The other hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [Uiso(H) = 1.2 Ueq(C)].

Crystal Data for $6C_{22}H_{24}Cl_2F_3NO_{10}S\cdot 3H_2O$ [$C_{132}H_{150}Cl_{12}F_{18}N_6O_{63}S_6$] ($M$ = 3788.23 g·mol^{-1}): hexagonal, space group $P6_1$ (no. 169), a = 22.9311(10) Å, c = 27.2831(12) Å, V = 12424.4(12) Å^3, Z = 3, T = 120 K, μ(CuKα) = 3.520 mm^{-1}, D_{calc} = 1.519 g·cm^{-3}, 78997 reflections measured (4.45° ≤ 2Θ ≤ 146.052°), 15162 unique (R_{int} = 0.0838, R_{sigma} = 0.0608) which were used in all calculations. The final R_1 was 0.0531 (I > 2σ(I)) and wR_2 was 0.1498 (all data). Crystal structure has been deposited with Cambridge Crystallographic Data Center (CCDC reference number 1843708).

Crystal unit of methyl (phenyl 3,5-dideoxy-2-thio-4,9-bis-*O*-chloroacetyl-5-trifluoroacetamido-D-glycero-β-D-galacto-nonulopyranosid)onate (further, carbohydrate) water solvate constitutes of three independent carbohydrate molecules and 1.5 water molecules. The main conformation of one of the carbohydrate molecules is shown in Figure S5. A superposition of the main conformations of all three independent carbohydrate molecules is shown in Figure S6.

Two of the carbohydrate molecules are well ordered (with slightly disordered CH_2Cl, CF_3 and Ph groups) and have very similar conformations (Figure S5). They are connected by hydrogen bonds (both direct and through a complete water molecule) to form an infinite helix (Helix 1 on Figure S8). The period of this helix is 27.2831(12) Å and consists of 6 carbohydrate molecules.

The third carbohydrate molecule is strongly disordered (Figure S7, shift between parts is about 0.55–0.75 Å) with identical occupancies of both parts. This molecule has a conformation different from the first two (Figures S6, S7). It is bonded by hydrogen bonds to its symmetrical images in neighboring cells to form another infinite helix (Helix 2 on Figure S8). The period of this helix is identical to that of the first helix (27.2831(12) Å) and also consists of 6 carbohydrate molecules. Given the identical occupancies of the disordered parts, it is likely that they alternate in the helix.

Overall, the crystal structure consists of two independent infinite helixes, and a disordered halfly occupied water molecules residing between them.

Table S1. Conditions and results of sialylation of glycosyl acceptor **3** with sialyl donors **1** and **2** at 0.05 and 0.15 mol·L^{-1} concentrations (*c*).

entry	sialyl donor	R	*c* (mol·L^{-1})	α/β	yield (%)	time (h)
1[a]	**1**	TFA	0.05	16:1	55	2.5
2	**1**	TFA	0.15	12:1	66	3
3	**2**	ClAc	0.05	13:1	57	2
4	**2**	ClAc	0.15	18:1	62	1

[a] Data taken from [5].

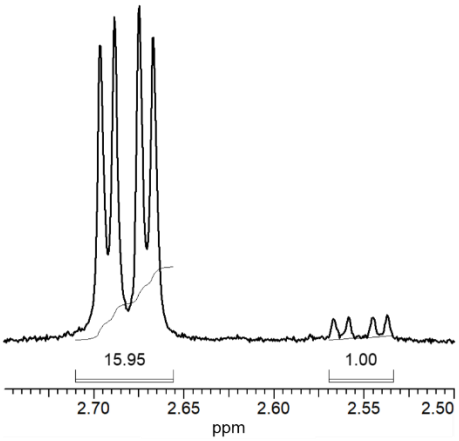


Figure S1. A part of ^{1}H NMR spectrum of disaccharide fraction (Entry 1 in Table S1) showing the signals of α-H-3eq and β-H-3eq of Neu5Ac residue of **4**.

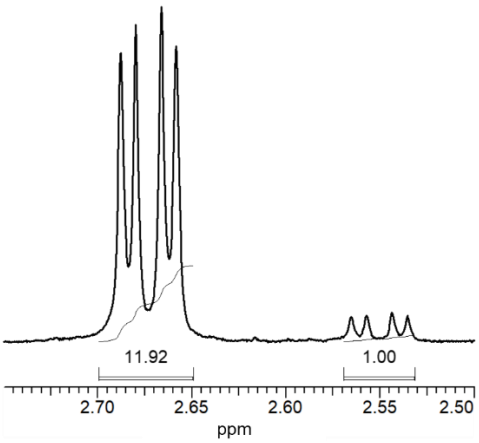


Figure S2. A part of ^{1}H NMR spectrum of disaccharide fraction (Entry 2 in Table S1) showing the signals of α-H-3eq and β-H-3eq of Neu5Ac residue of **4**.

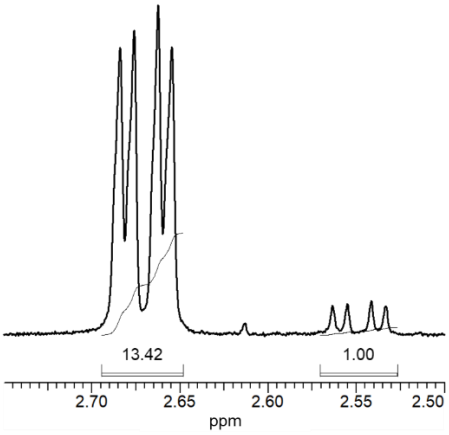


Figure S3. A part of ^{1}H NMR spectrum of disaccharide fraction (Entry 3 in Table S1) showing the signals of α-H-3eq and β-H-3eq of Neu5Ac residue of **4**.

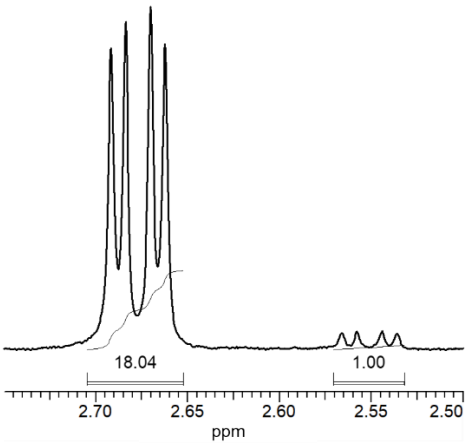


Figure S4. A part of ^{1}H NMR spectrum of disaccharide fraction (Entry 4 in Table S1) showing the signals of α-H-3eq and β-H-3eq of Neu5Ac residue of **4**.

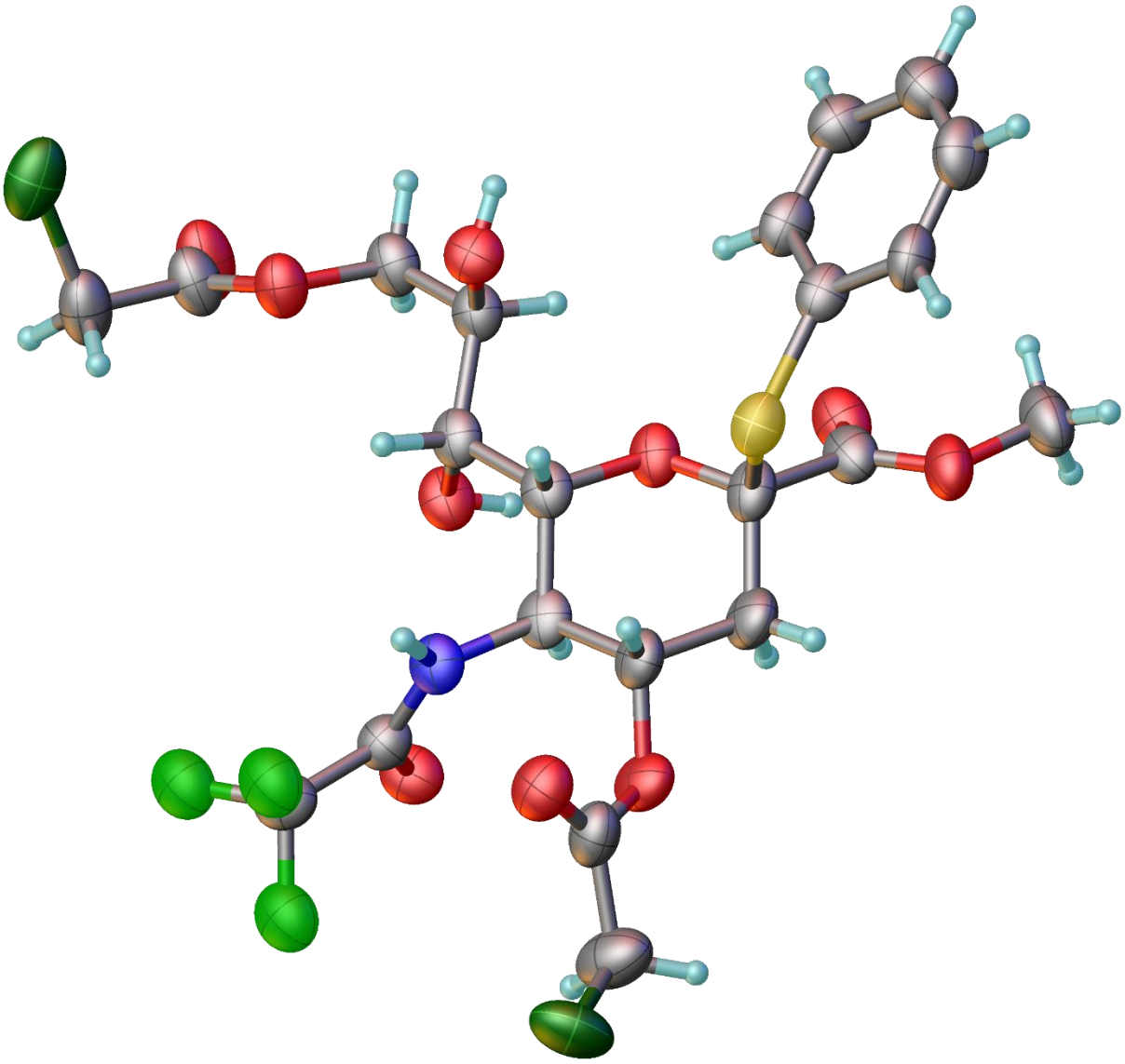


Figure S5. The general view of a molecule of **7** in the crystal in representation of atoms by thermal ellipsoids (p = 40%). Coloring: carbon – grey, oxygen – red, nitrogen – blue, fluorine – light green, sulphur – yellow, chlorine – dark green, hydrogen – sky blue.

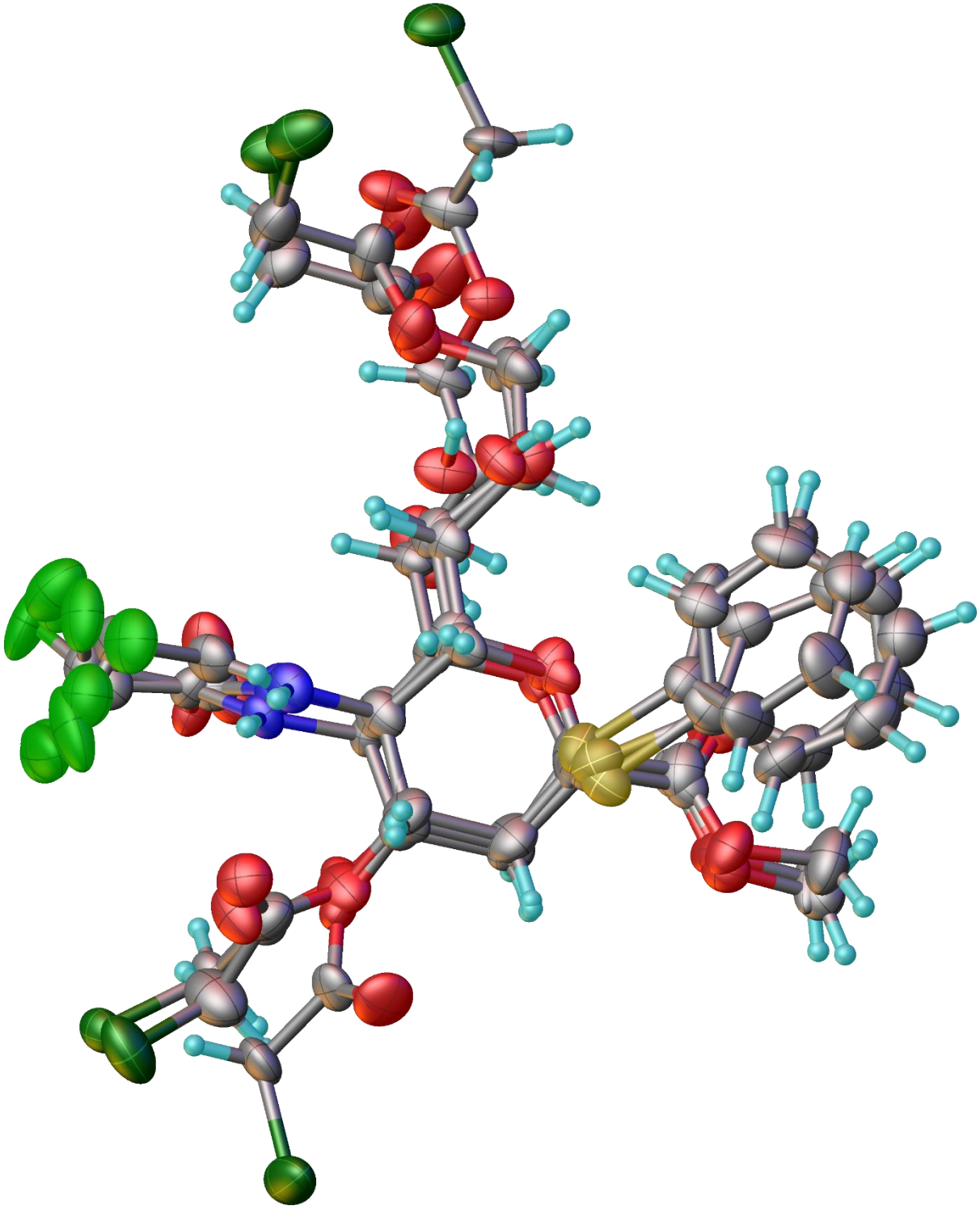


Figure S6. Superposition of the main conformations of the three independent molecules of **7** in the crystal in representation of atoms by thermal ellipsoids (p = 40%). Coloring: carbon – grey, oxygen – red, nitrogen – blue, fluorine – light green, sulphur – yellow, chlorine – dark green, hydrogen – sky blue.

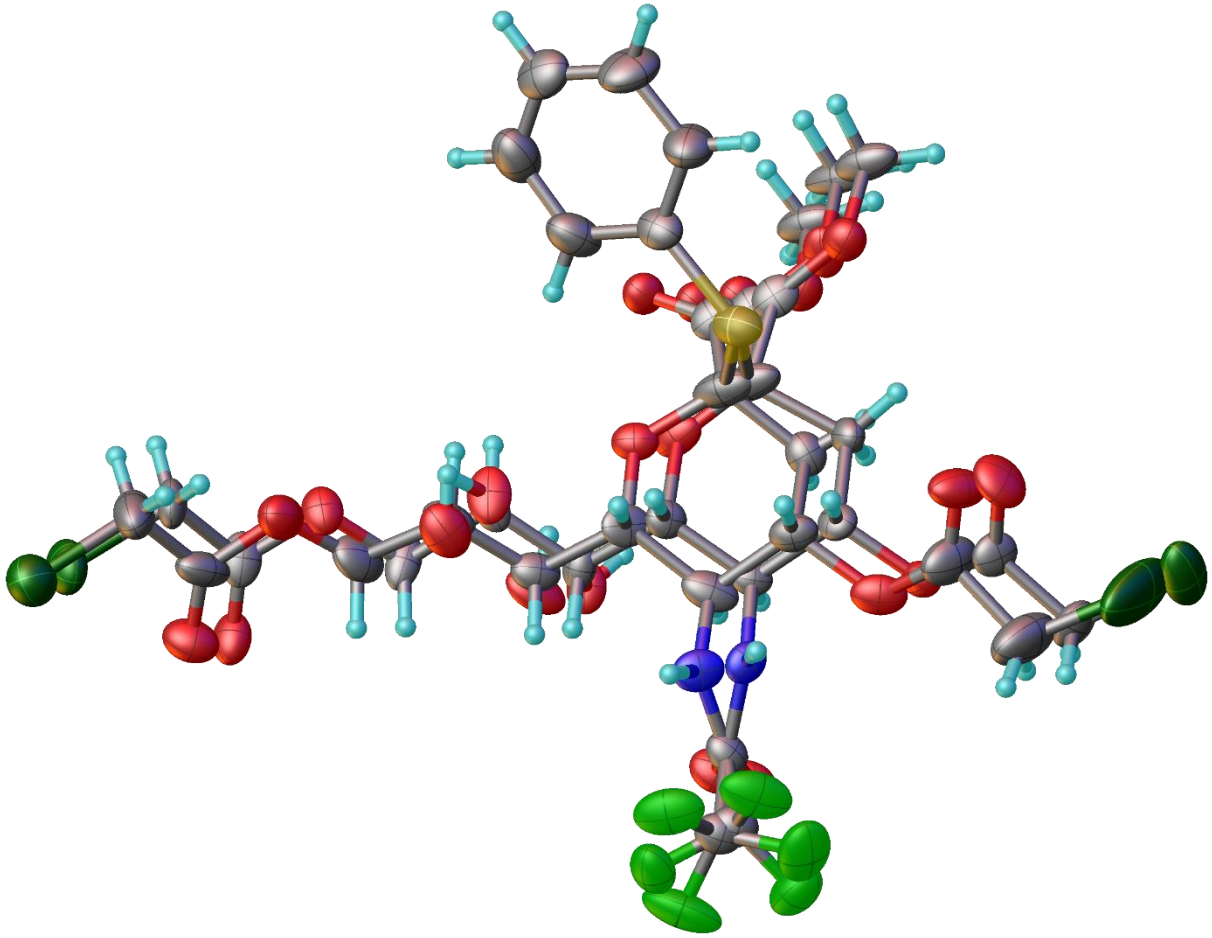


Figure S7. The general view of the disordered molecule of **7** in the crystal in representation of atoms by thermal ellipsoids (p = 40%). Coloring: carbon – grey, oxygen – red, nitrogen – blue, fluorine – light green, sulphur – yellow, chlorine – dark green, hydrogen – sky blue.

Helix 1 (with incorporated water molecule)

Helix 2 (disordered)

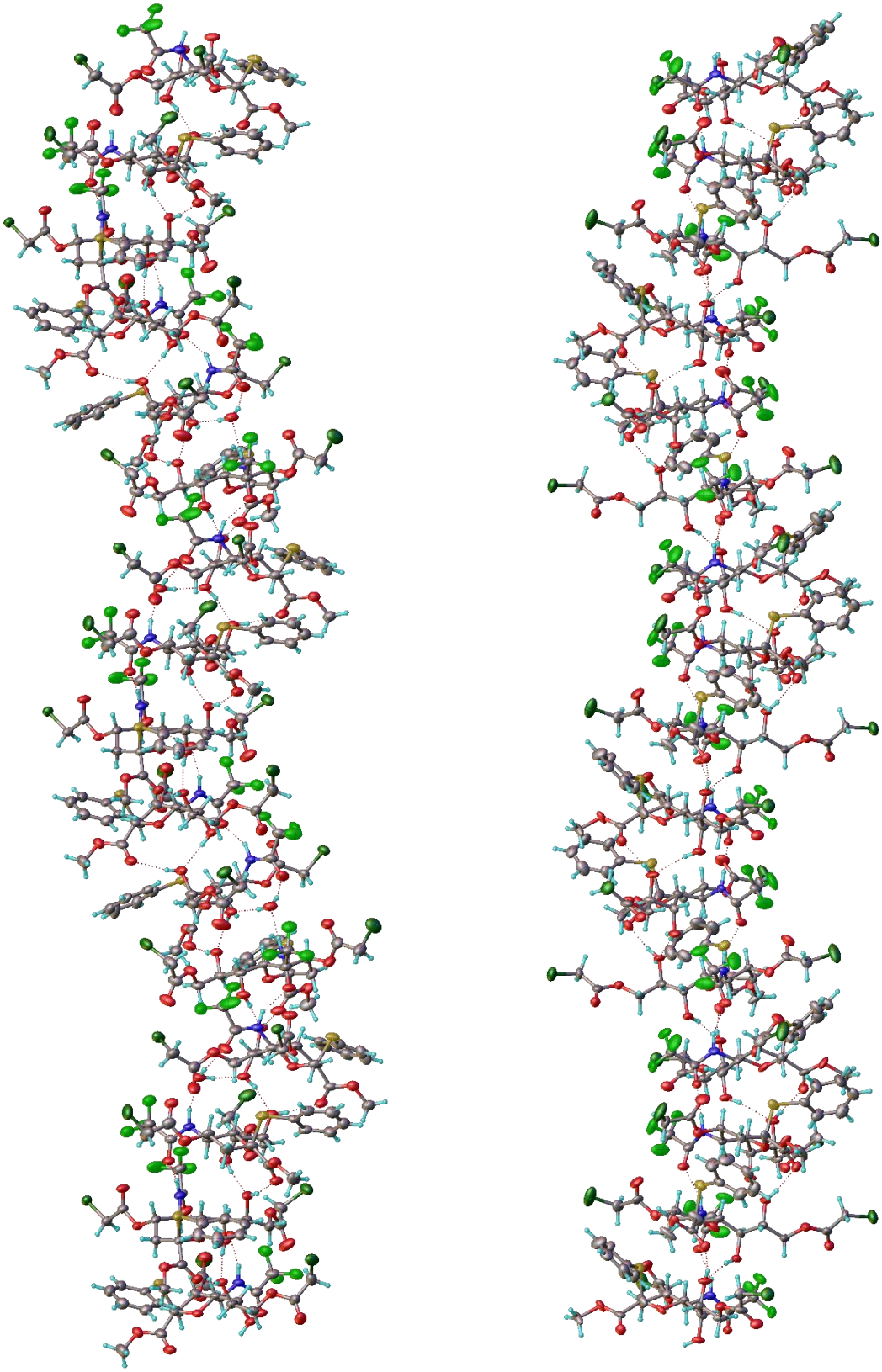
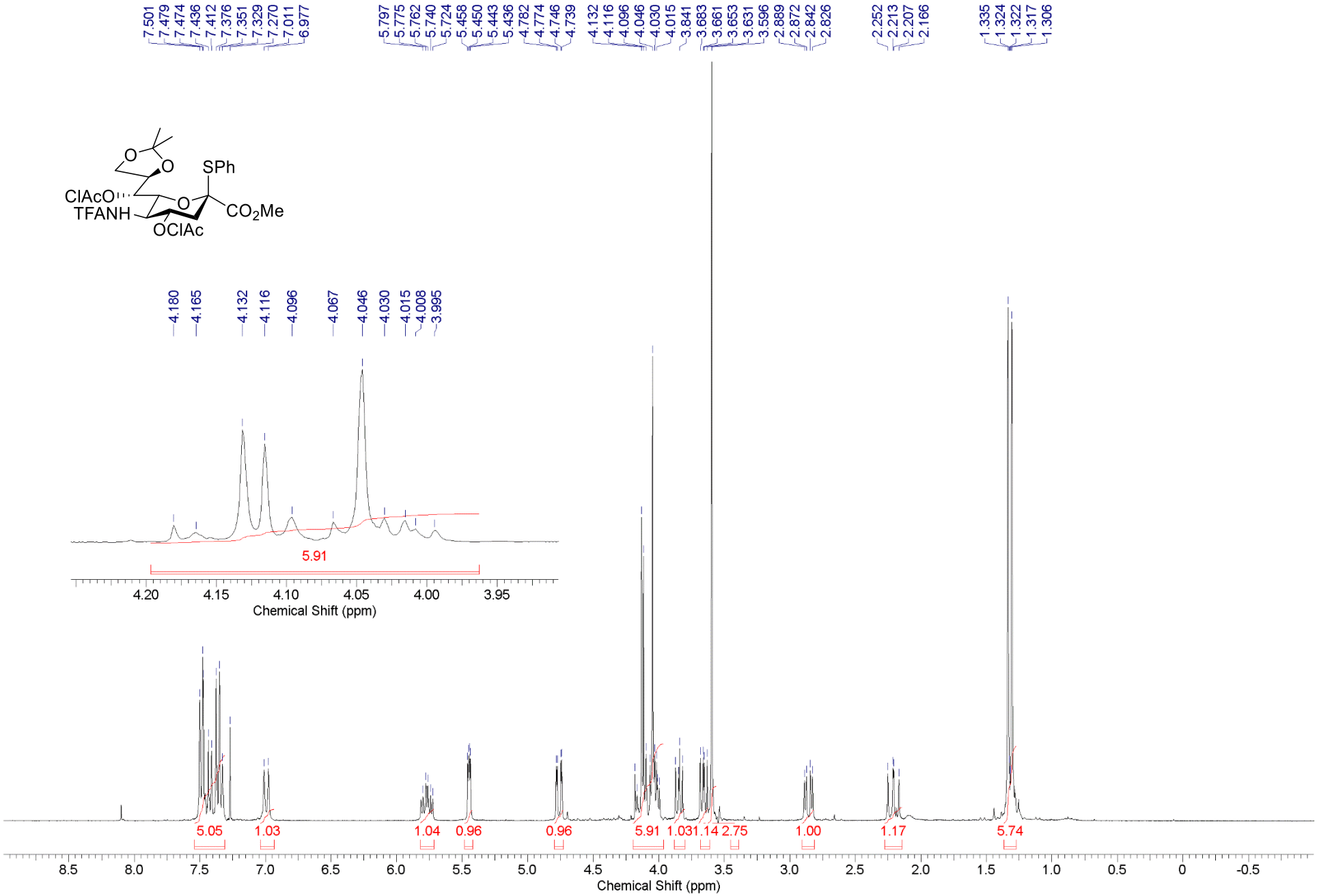
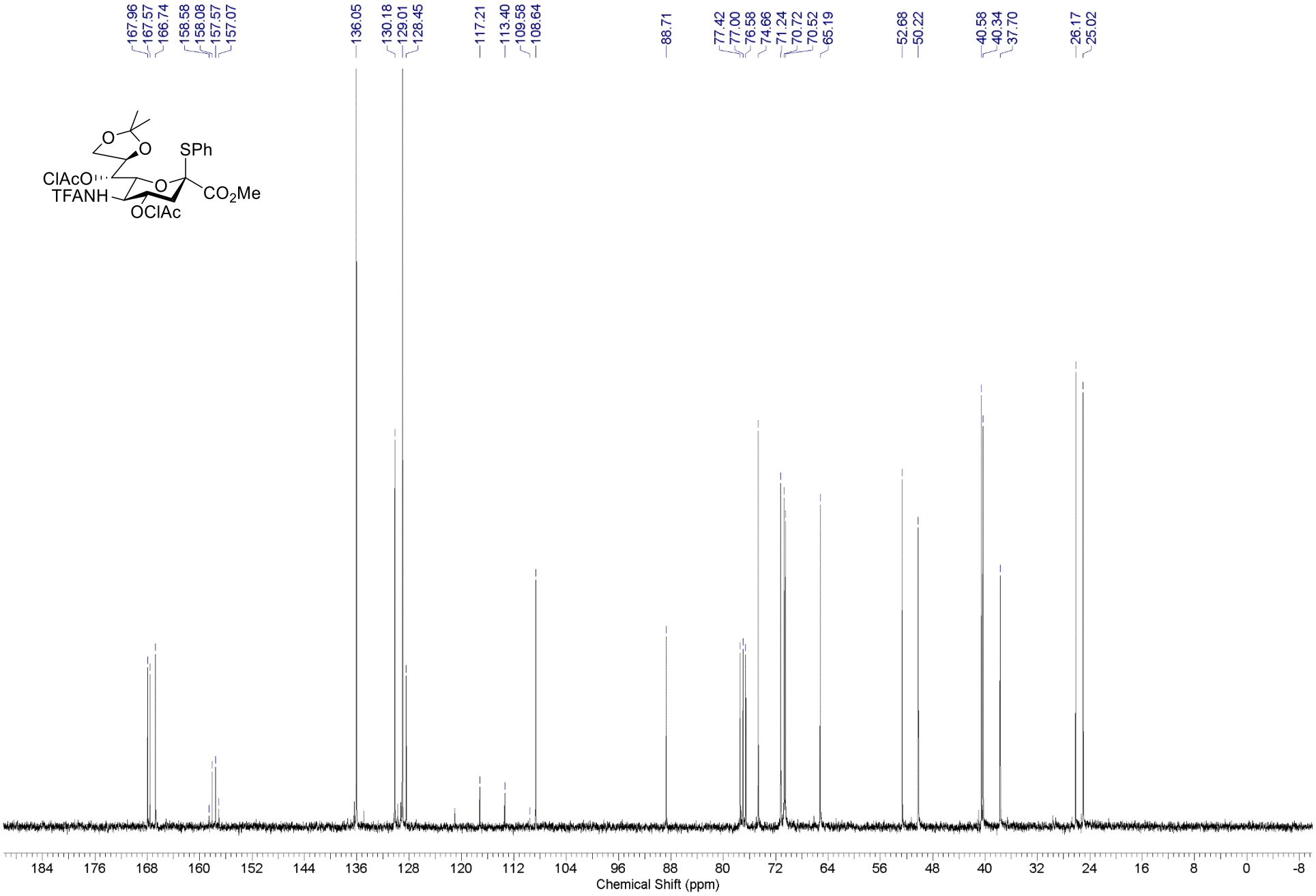


Figure S8. Infinite helixes formed in the crystal structure of **7**. Atoms are represented by thermal ellipsoids (p = 40%). Coloring: carbon – grey, oxygen – red, nitrogen – blue, fluorine – light green, sulphur – yellow, chlorine – dark green, hydrogen – sky blue.

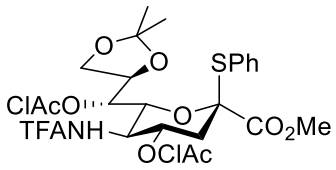
^{1}H NMR (300 MHz) spectrum of compound 6 in $CDCl_3$



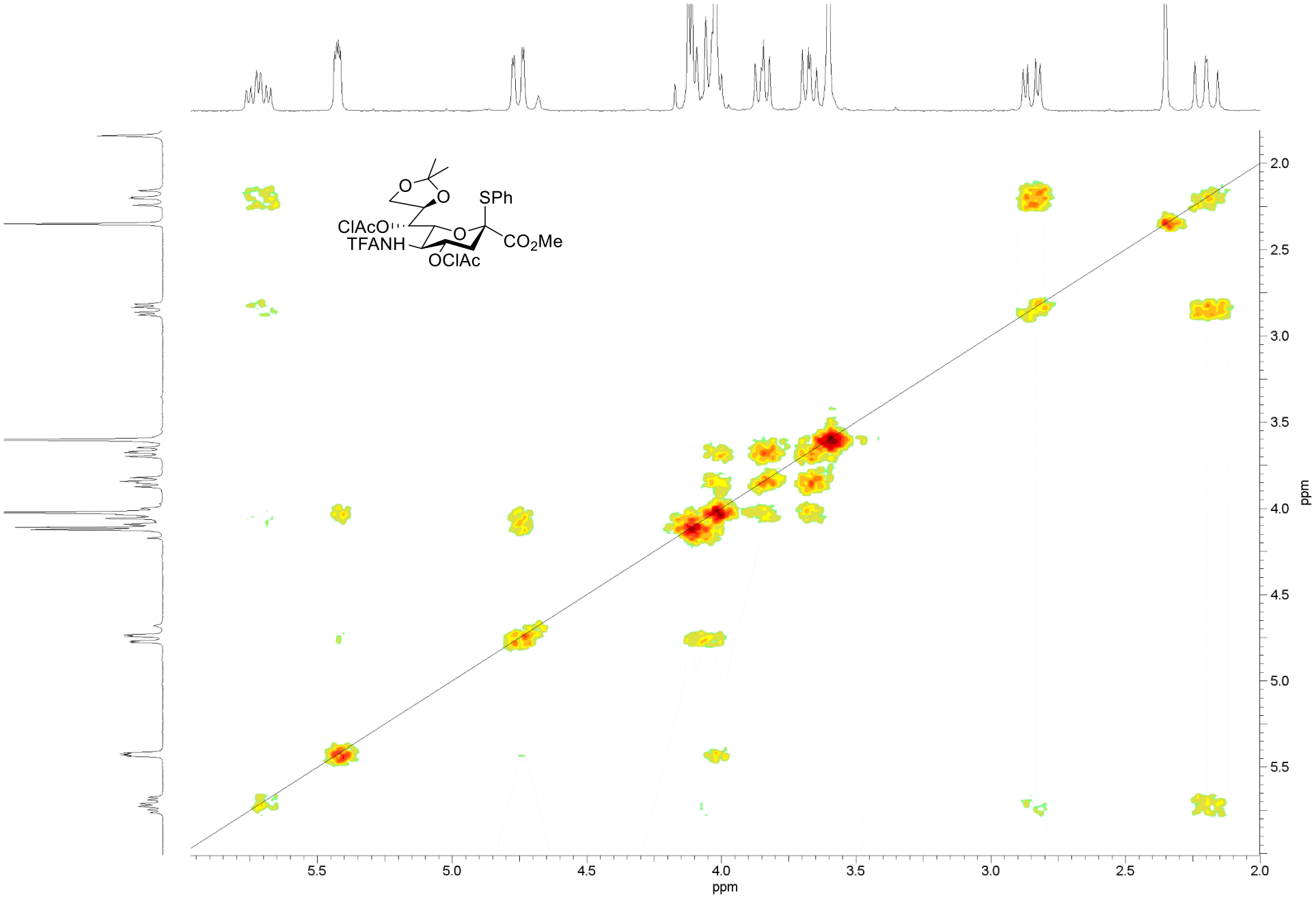
^{13}C NMR (75 MHz) spectrum of compound 6 in $CDCl_3$



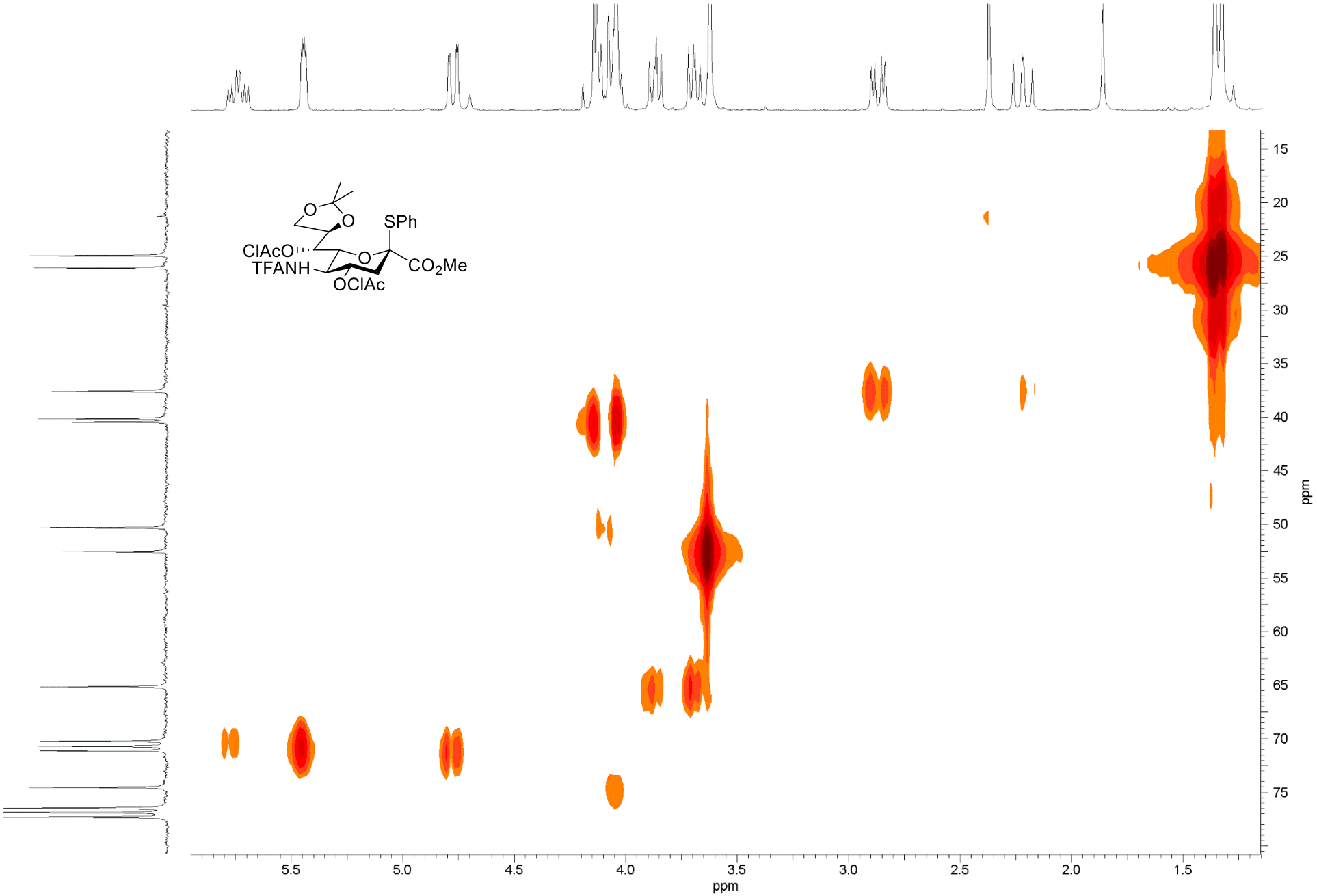
^{19}F NMR (282 MHz) spectrum of compound 6 in $CDCl_3$



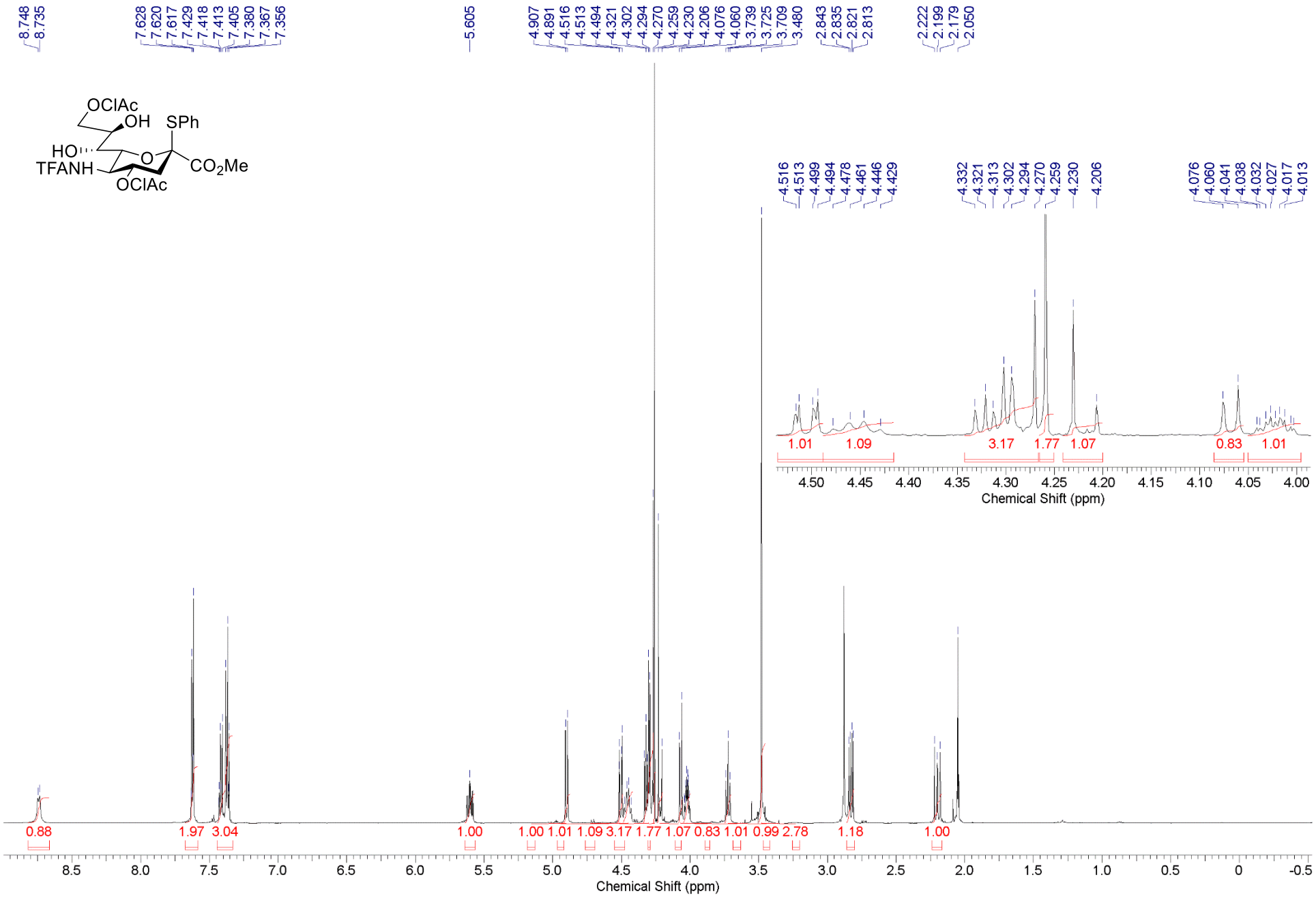
COSY (300 MHz) spectrum of compound 6 in $CDCl_3$



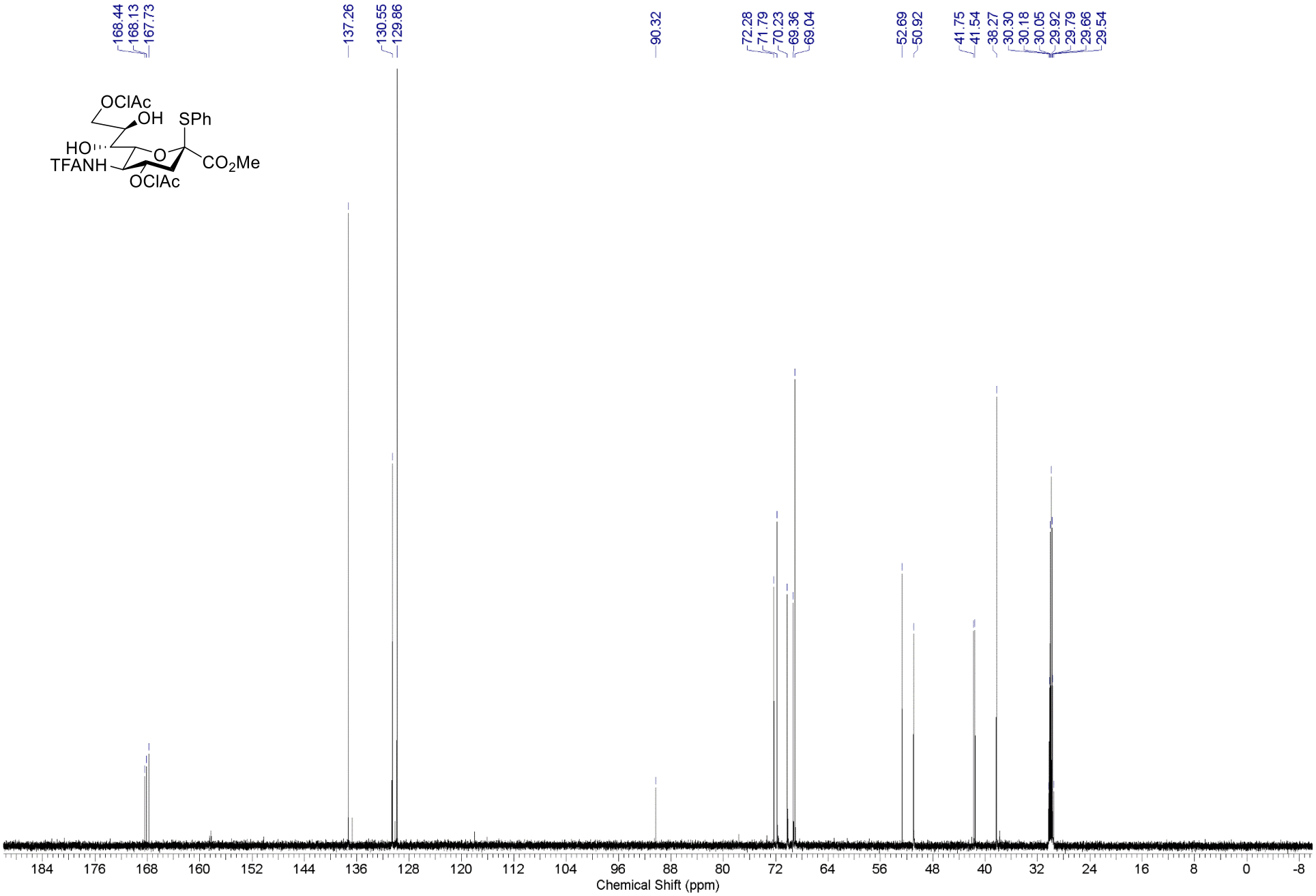
HSQC (300 MHz) spectrum of compound 6 in $CDCl_3$



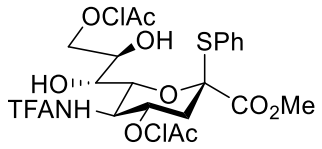
^{1}H NMR (600 MHz) spectrum of compound 7 in acetone-d_6



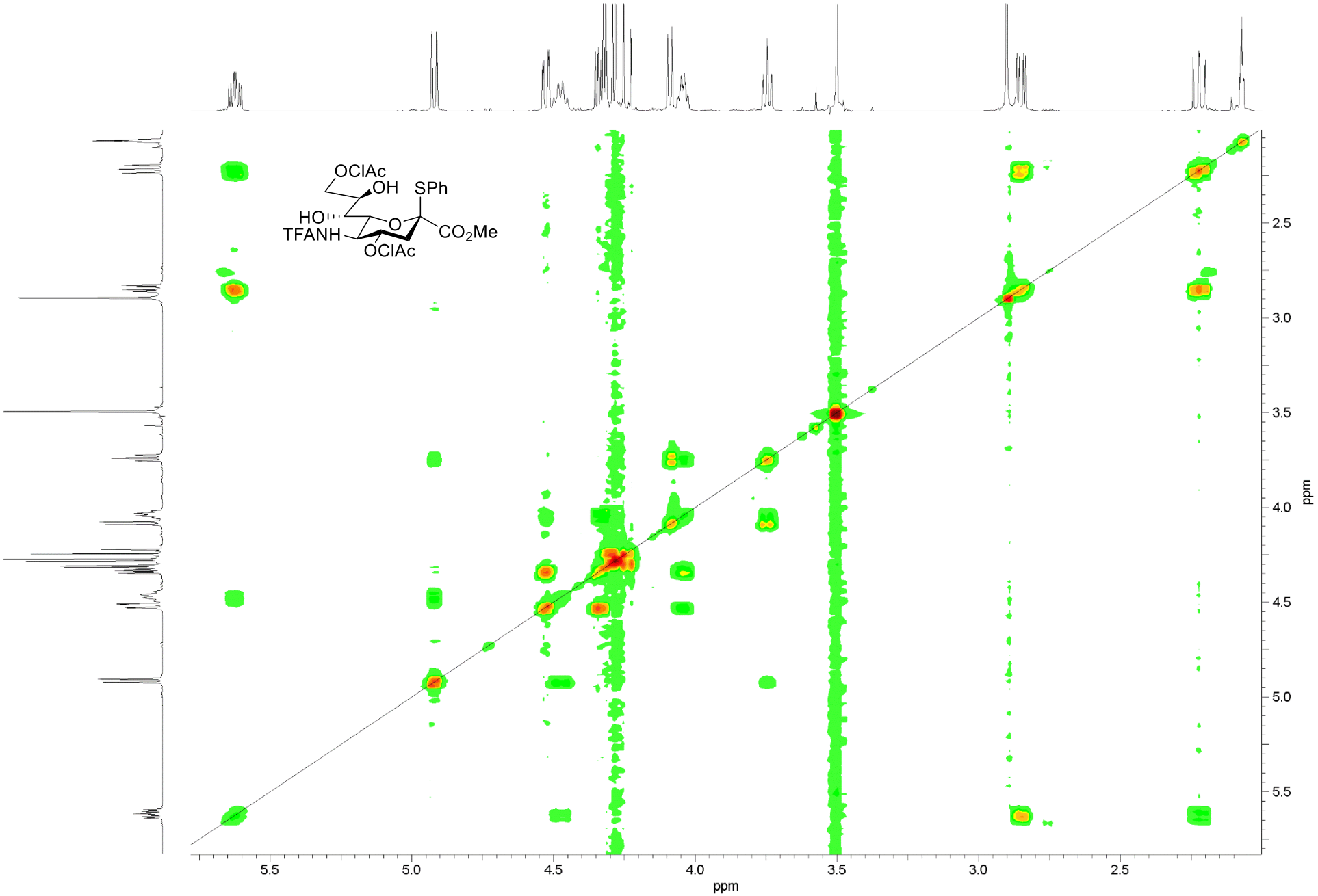
^{13}C NMR (151 MHz) spectrum of compound 7 in acetone-d_6



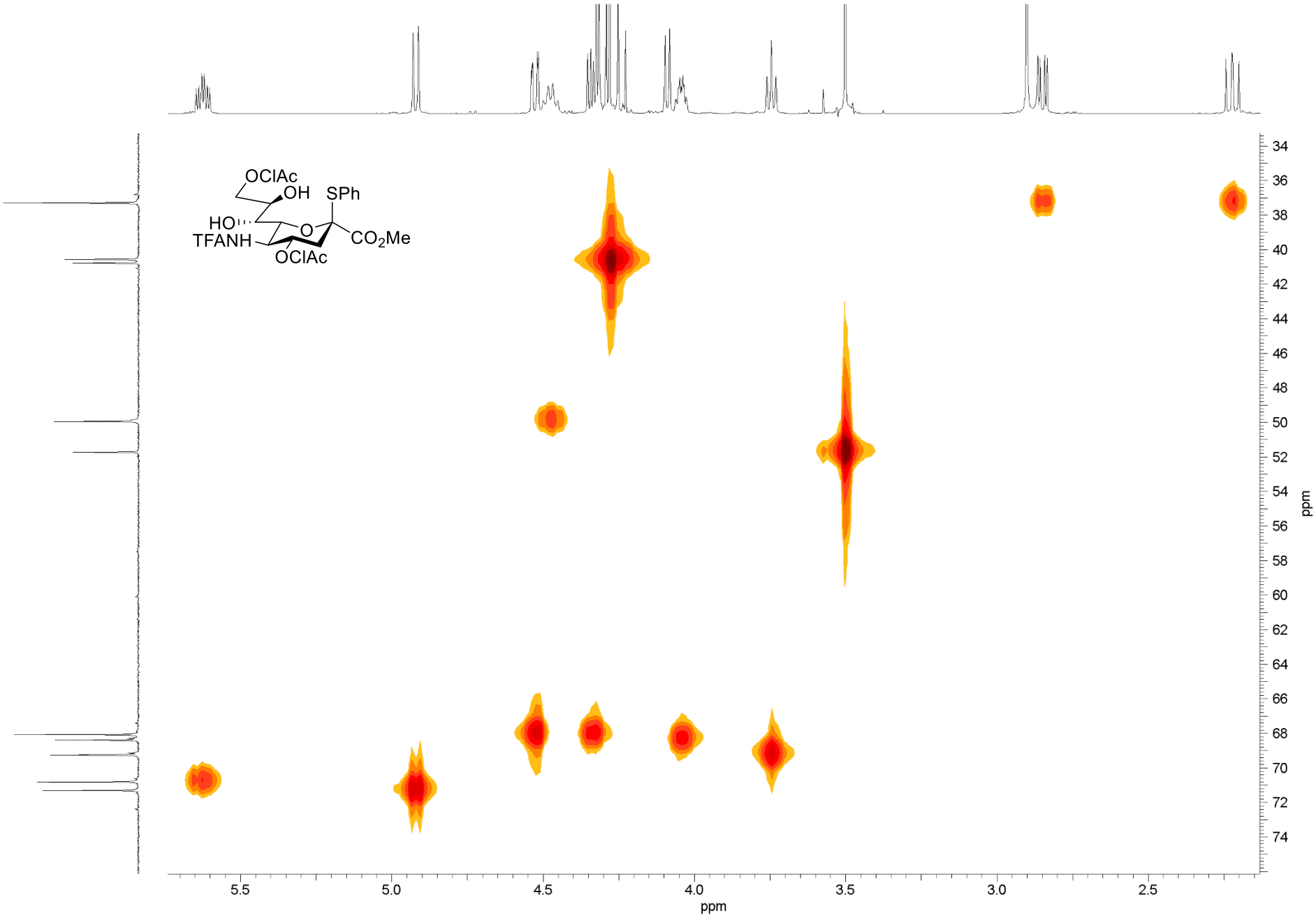
^{19}F NMR (282 MHz) spectrum of compound 7 in acetone-d_6



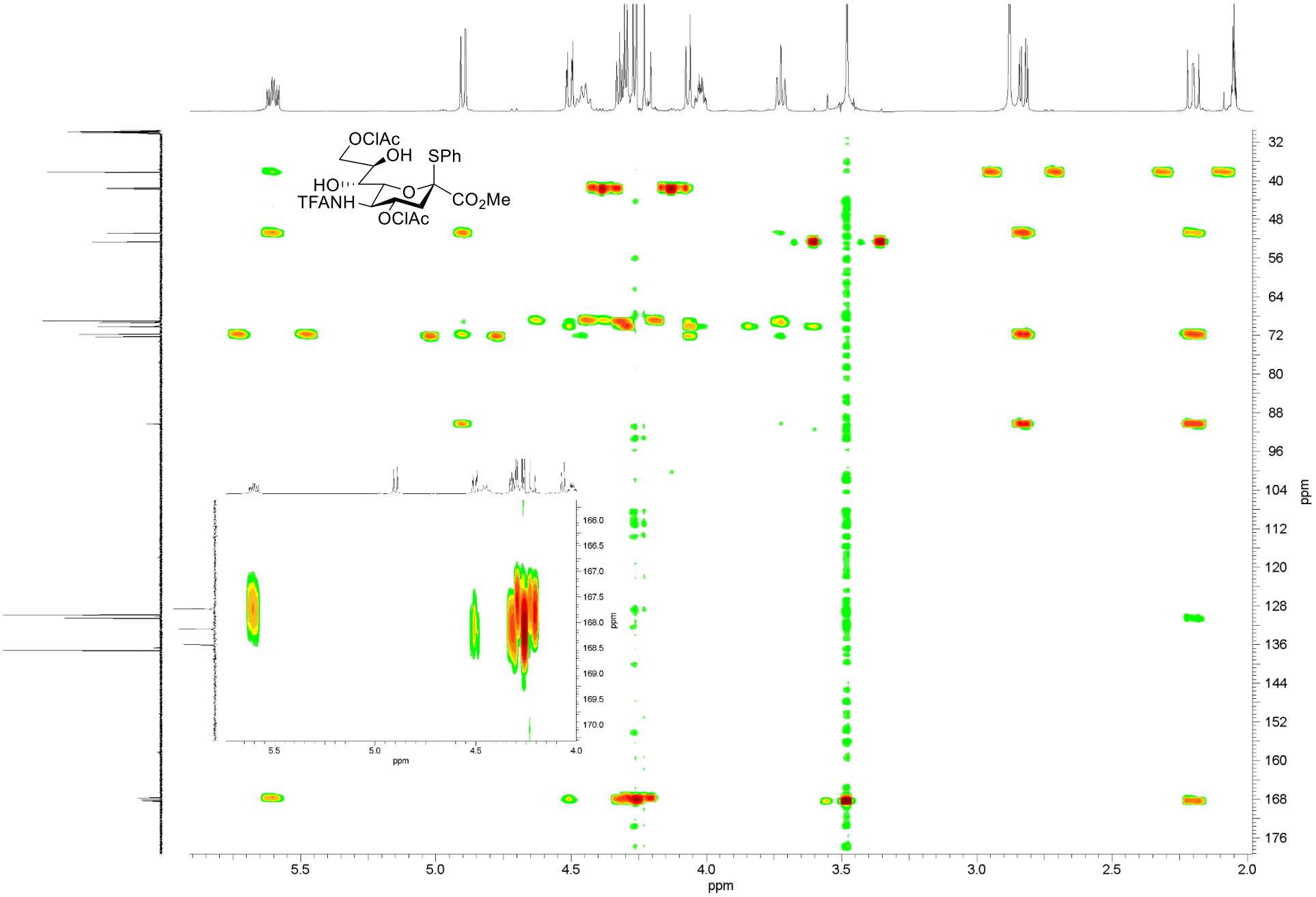
COSY (600 MHz) spectrum of compound 7 in acetone-d_6



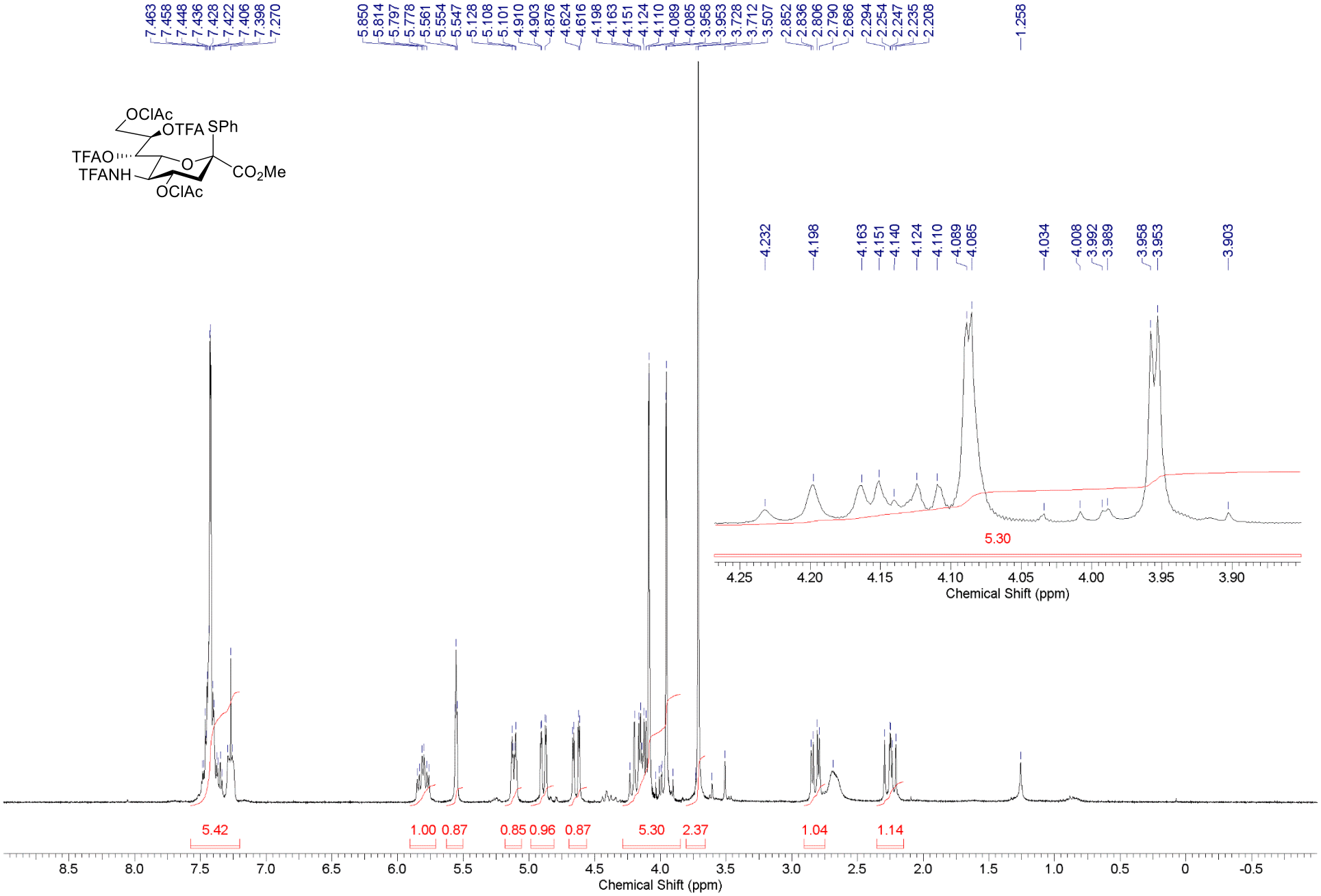
HSQC (600 MHz) spectrum of compound 7 in acetone-d_6



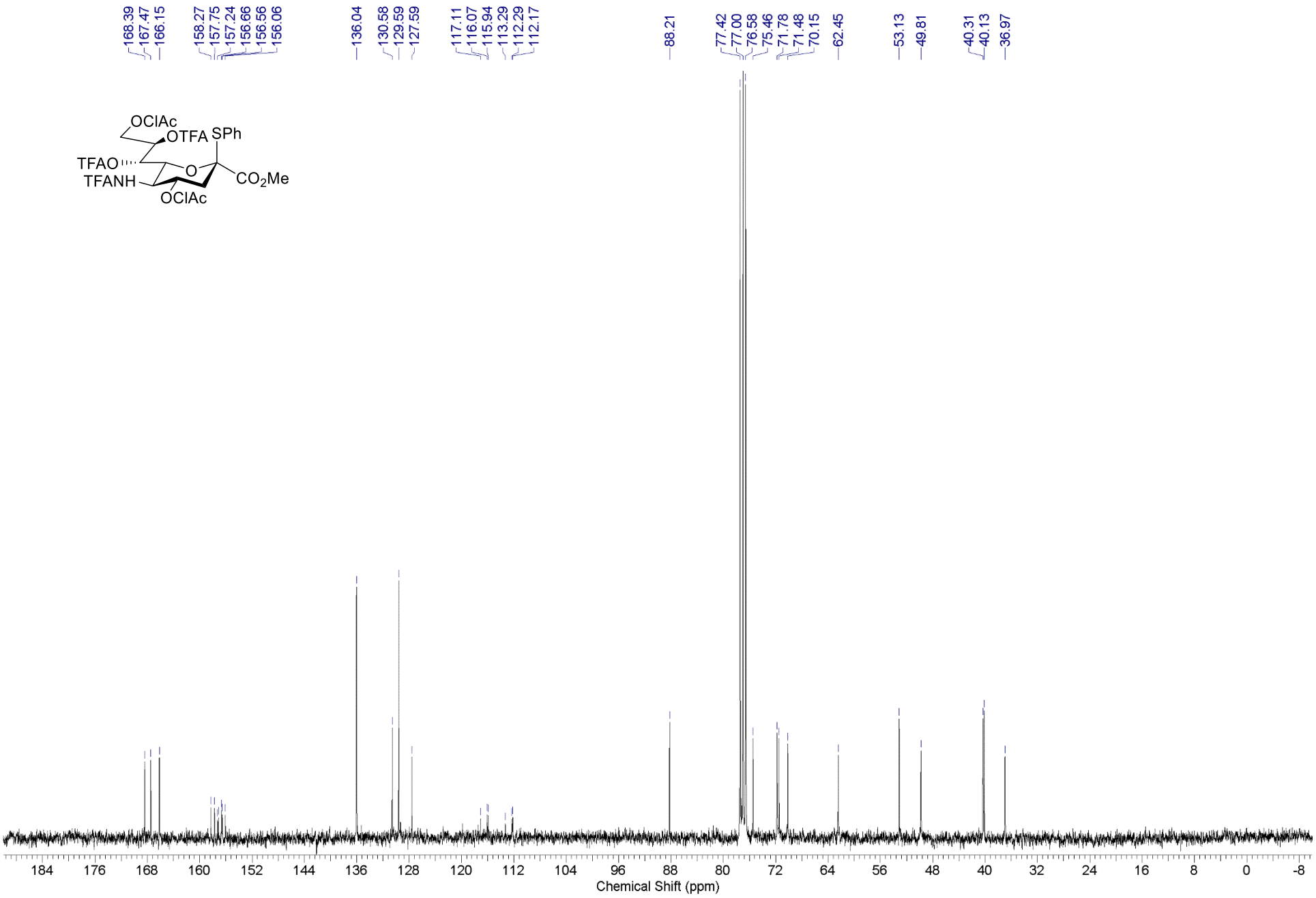
HMBC (600 MHz) spectrum of compound 7 in acetone-d_6



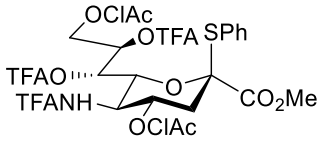
^{1}H NMR (300 MHz) spectrum of compound 2 in $CDCl_3$



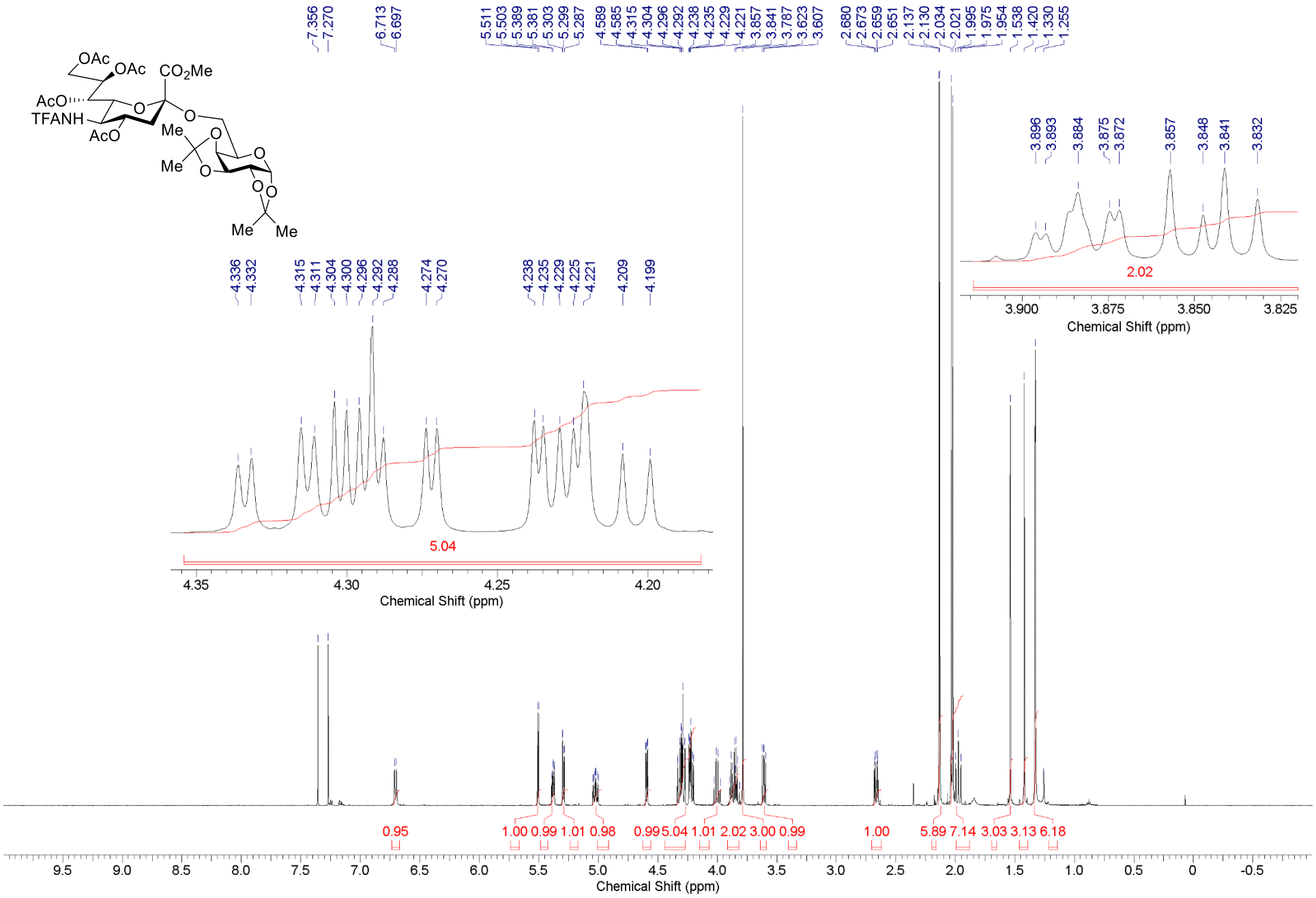
^{13}C NMR (75 MHz) spectrum of compound 2 in $CDCl_3$



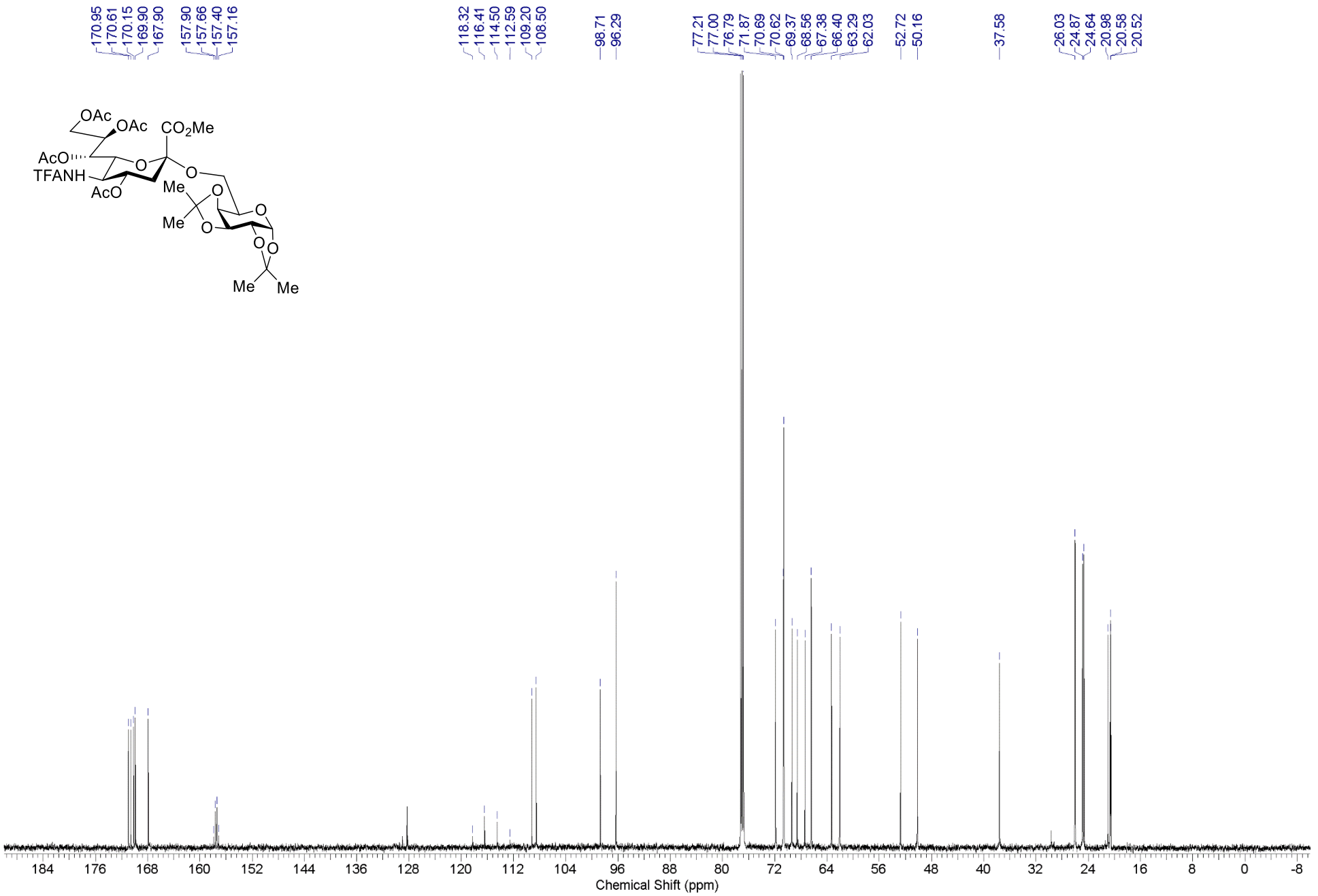
^{19}F NMR (282 MHz) spectrum of compound 2 in $CDCl_3$



^{1}H NMR (600 MHz) spectrum of compound α-4 in $CDCl_3$



^{13}C NMR (151 MHz) spectrum of compound α-4 in $CDCl_3$



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