Synthesis of 2-deoxy-2,2-difluoro-*α*-maltosyl fluoride and its X-ray structure in complex with *Streptomyces coelicolor* GlgEI-V279S

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Supplementary Information

COSY of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (**14**)
HMQC of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (**14**)
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (**14**)
^{1}H NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (**2**)
^{13} C NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (**2**)
^{13}C NMR (APT) of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (**2**)
COSY of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (**2**)
HMQC of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (**2**)
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (**2**) (Vxrs400 MHz)
^{1}H NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (**3**)
^{13} C NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (**3**)
COSY of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (**3**)
HMQC of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (**3**)
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (**3**) (Gemini 200MHz)
^{1}H NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α/β*-D-glucopyranose (**4**)
^{13}C NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α/β*-D-glucopyranose (**4**)
COSY of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α/β*-D-glucopyranose (**4**)
HMQC of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α/β*-D-glucopyranose (**4**)
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α/β*-D-glucopyranose (**4**)
^{1}H NMR of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (**5**)
^{13}C NMR of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (**5**)
COSY of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (**5**)
HMQC of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (**5**)

Enzyme substrate assay for α-MTF

MALDI-MS was performed to evaluate α-MTF incorporation into maltooligosaccharides via *Sco* GlgE-V279S and compared to a series of controls, (Fig S-1). The spectra of only maltohexaose (M6) in buffer, showed a single peak representing a sodiated M6, Fig S-1A. The addition of *Sco* GlgE1-V279S resulting in a series of higher molecular weight products which result from known background transglycosylation activity catalyzed by *Sco* GlgE1-V279S, Fig S-1B. We also prepared α-maltosyl fluoride (α-M1F), a substrate for *Sco* GlgE1. The use of M1F, M6 and *Sco* GlgE1-V279S, Fig S-1C, resulted in higher molecular weight peaks. A final experiment replaced M1F with α-MTF, which produced a spectrum identical to the control shown in Fig S-1B. Any production of longer maltooligosaccharides would be the result of GlgE activity and those products would have a molecular weight change resulting from the difluoromethylene unit.

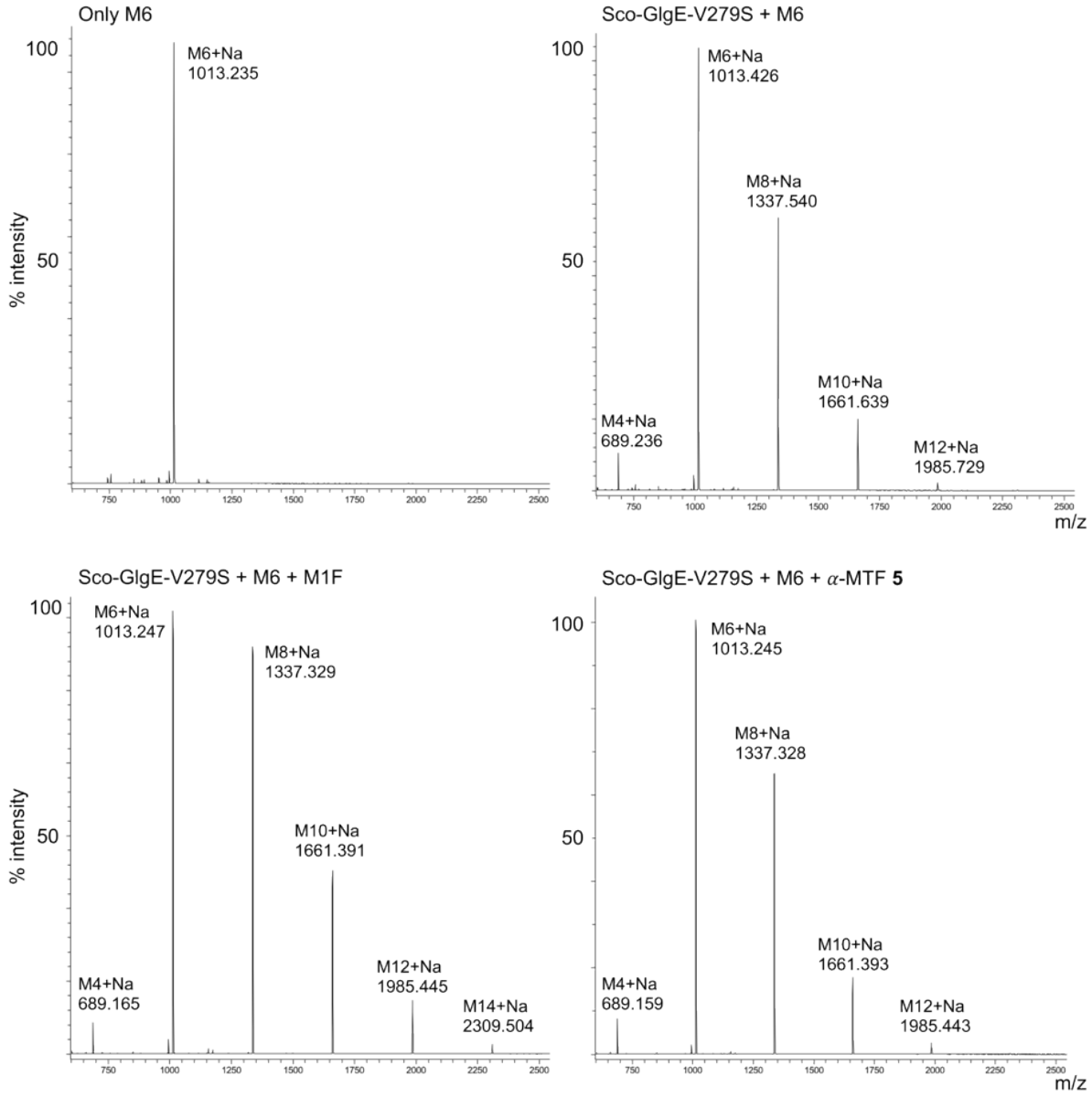
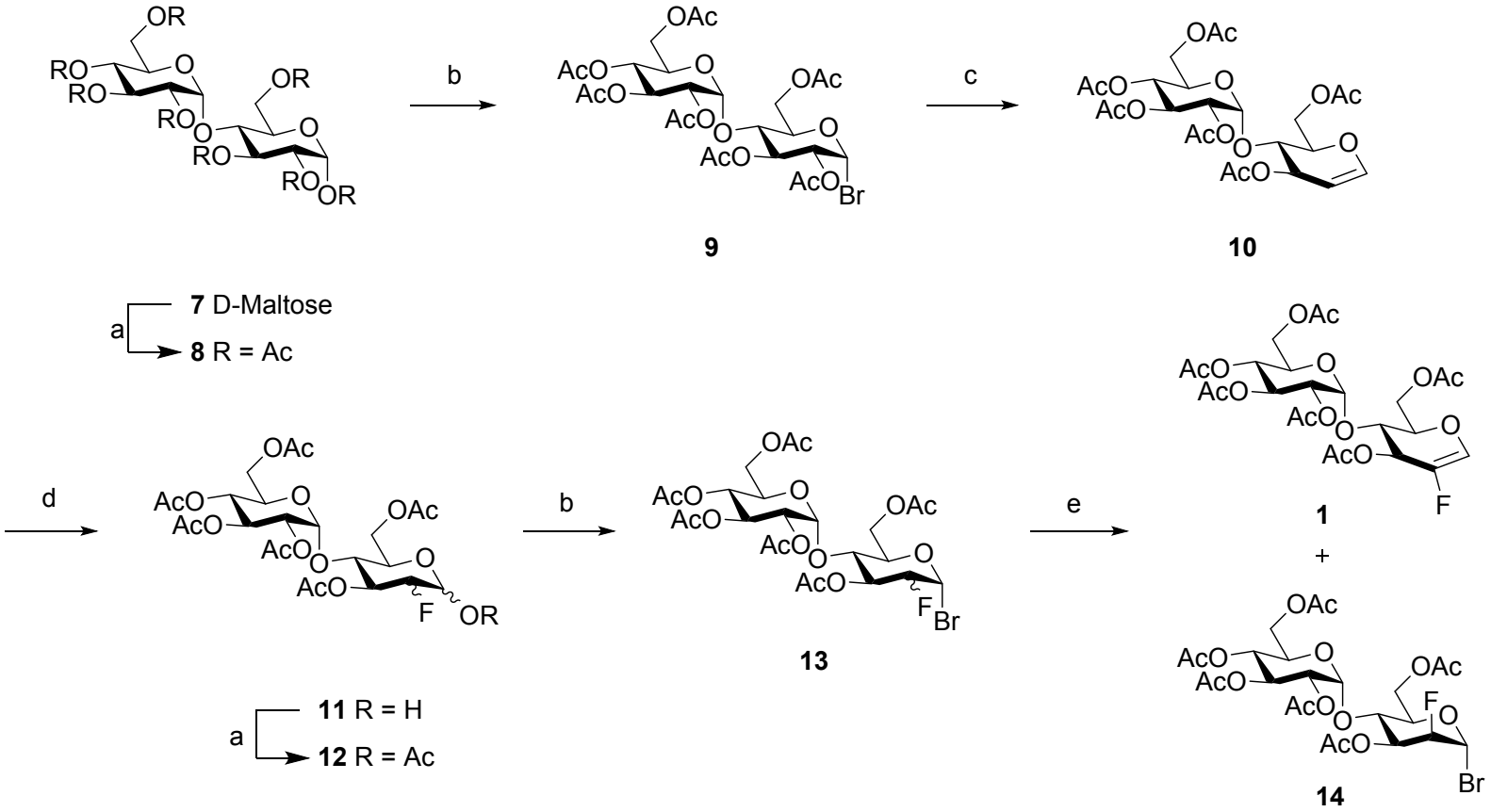


Fig S-1. Evaluation of α-MTF as a substrate for *Sco* GlgEI-V279S. (A) control 1: ESI-MS of maltohexaose (M6). (B) control 2: ESI-MS of M6 + *Sco* GlgEI-V279S. (C) control 3: ESI-MS of M6 + *Sco* GlgEI-V279S + α-M1F. (D) ESI-MS of M6 + *Sco* GlgEI-V279S + α-MTF. M4, M6, M8, M10, M12, and M14, represent 4, 6, 8, 10, 12, and 14 maltose units in the respective products. R = the continuation of the maltose repeat.

Synthesis of 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-glycal (1) and 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (14)

Synthesis of Peracetylated glycal (**10**) was performed the methods of Braitsch *et al.*[1] D-maltose **7** was peracetylated to obtain peracetyl maltose **8**. Maltose derivative **8** was brominated at the anomeric position using 33% hydrobromic acid in glacial acetic acid to obtain the corresponding *α*-maltosyl bromide (**9**), Scheme S-1. Maltosyl bromide **9** was subjected to a zinc-mediated *β*-elimination using activated zinc and *N*-methylimidazole to afford the glycal **10** in 53% yield.[1] Glycal **10** was dissolved in DMF:H_2O (3:1) and subjected to treatment with 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane ditetrafluoroborate (Selectfluor®) to afford an anomeric mixture of (*α*/*β*)-1-hydroxy-2-fluoro derivatives with gluco and manno (2:1 ratio, respectively) stereochemistry **11**.[2] This mixture **11** was acetylated using Ac_2O/Py. The resulting peracetylated mixture **12** was treated with 33% hydrobromic acid in glacial acetic acid at 0 °C to afford a mixture of 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-gluco/ D-mannopyranosyl bromides (**13**). The mixture **13** was subjected to a second elimination. Only the compound with gluco stereochemistry which has anti-periplanarity between C1'-bromo group and the C2' hydrogen eliminated to afford per-*O*-acetyl-2-fluoro-maltal (**1**).[3, 4] This result was confirmed by isolating 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (**14**) while purifying glycal (**1**).

Scheme S-1. Synthesis of 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-glycal (**1**) and 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (**14**).



Reagents and conditions: a) Ac_2O, pyridine, rt (99%); b) 33% HBr in AcOH, dry CH_2Cl_2 (88%); c) Zinc, *N*-methylimidazole, EtOAc, reflux (53%); d) Selectfluor®, DMF:H_2O (3:1), rt (53%) (2:1); e) CH_3CN, Et_3N, reflux (30%).

2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-1,2,3,6-tetra-*O*-acetyl-*α*-D-glucopyranose (8)[1]

To a solution of maltose monohydrate **7** (4.0 g, 11.1 mmol) in pyridine (12.5 mL, 133.2 mmol) was added acetic anhydride (14.3 mL, 178 mmol) drop wise at 0 °C. The solution was maintained at room temperature for 12 h. The pyridine was removed as an azeotrope with toluene by repeated coevaporation. The resulting clear syrup was dissolved in ethyl acetate and washed with 1 N HCl (25 mL) and saturated $NaHCO_3$ solution (50.0 mL). The organic layer was dried by passing through anhydrous Na_2SO_4. The solvent was evaporated under vacuum to afford a clear white foam compound **8**. Yield: 96% (7.2 g); silica gel TLC R_f = 0.56 (1:1 hexane-acetone); ^{1}H-NMR (600 MHz, $CDCl_3$): δ 5.75 (d, 1H, $^3J_{1,2}$ 8.07 Hz, H-1), 5.42 (d, 1H, $^3J_{1',2'}$ 4.03 Hz, H-3'), 5.36 (dd, 1H, $^3J_{3',4'}$ 9.9 Hz, $^3J_{3',2'}$ 10.27 Hz, H-3'), 5.30 (dd, 1H, $^3J_{3,2}$ 9.17 Hz, $^3J_{3,4}$ 8.80 Hz, H-3), 5.06 (dd, 1H, $^3J_{3',4'}$ 9.9 Hz, H-4'), 4.98 (dd, 1H, $^3J_{2,3}$ 8.80 Hz, H-2), 4.87 (dd, 1H, $^3J_{2',3'}$ 10.64 Hz, $^3J_{3',4'}$ 4.03 Hz, H-2'), 4.46 (dd, 1H, $^2J_{6a,6b}$ 12.10 Hz, $^3J_{6a,5}$ 1.83 Hz, H-6a), 4.26-4.22 (m, 2H, 6-a, 6-b), 4.06-4.03 (m, 2H, 6'b, H-4), 3.95-3.93 (m, 1H, H-5'), 3.86-3.83 (m, 1H, H-5), 2.23 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.01 (s, 3H, CH_3); ^{13}C-NMR (600 MHz, $CDCl_3$): 170.73 (C=O), 170.68 (C=O), 170.61 (C=O), 170.24 (C=O), 170.06 (C=O), 169.77 (C=O), 169.61 (C=O), 168.97 (C=O), 95.85 (C1'), 91.39 (C1), 75.40 (C3), 73.11 (C4), 72.50 (C5), 71.07 (C2), 70.13 (C2'), 69.43 (C3'), 68.71 (C5'), 68.06 (C4'), 62.64 (C6), 61.57 (C6'), 21.02 (CH_3), 20.97 (2 CH_3), 20.84 (CH_3), 20.75 (3 CH_3), 20.71 (CH_3) ppm; mass spectrum (ESIMS), *m/z* = 701.3 $(M+23)^+$ $C_{28}H_{38}O_{19}$ requires 701.19 $(M+23)^+$.

2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-2,3,6-tri-*O*-acetyl-*α*-D-glucopyranosyl bromide (9)[1]

Compound **8** (1.00 g, 1.47 mmol) was dissolved in dry methylene chloride (5.0 mL). To the solution was added acetic acid (5.0 mL). The solution was cooled to 0 °C 33% HBr in acetic acid (1.0 mL, 2.76 mmol) was added by drop wise addition. The reaction was maintained at 0 °C for 4 h. Ice cold water was added and the solution extracted with DCM (20.0 mL, 3 times). The combined DCM extracts were washed with cold distilled. H_2O and the organic layer dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to obtain a light yellow foam **9**, which was sensitive to light. Yield: 88.2% (0.908 g); silica gel TLC R_f = 0.42 (6:4 Hexanes-Acetone). ^{1}H-NMR (600 MHz, $CDCl_3$): δ 6.51 (d, 1H, $^3J_{1,2}$ 3.67 Hz, H-1), 5.63 (dd, 1H, $^3J_{3,2}$ 9.54 Hz, H-3), 5.44 (d, 1H, $^3J_{1',2'}$ 4.03 Hz, H-1'), 5.39 (dd, 1H, $^3J_{3',2'}$ 10.27 Hz, $^3J_{3',4'}$ 9.90 Hz, H-3), 5.09 (dd, 1H, $^3J_{4',3'}$ 9.90 Hz, H-4'), 4.88 (dd, 1H, $^3J_{1',2'}$ 4.03 Hz, $^3J_{2',3'}$ 10.64 Hz, H-2'), 4.73 (dd, 1H, $^3J_{1,2}$ 3.67 Hz, $^3J_{2,3}$ 9.90 Hz, H-2), 4.53 (dd, 1H, $^2J_{6a,6b}$ 13.94 Hz, $^3J_{6a,5}$ 4.55 Hz, H-6a), 4.29-4.25 (m, 3H, 6-a', 6-b, H-5), 4.10-4.05 (m, 2H, H-4, 6-b'), 3.96-3.95 (m, 1H, H-5'), 2.16 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.02 (s, 3H, CH_3) ppm; ^{13}C NMR ($CDCl_3$): 170.86 (C=O), 170.67 (C=O), 170.46 (C=O), 170.14 (2 C=O), 169.68 (C=O), 169.60 (C=O), 95.91 (C1'), 86.18 (C1), 72.66 (C5), 72.47 (C3), 71.64 (C4), 71.17 (C2), 70.15 (C2), 69.38 (C3'), 68.78 (C5), 68.01 (C4), 61.97 (C6), 61.45 (C6'), 21.03 (CH_3), 20.95 (CH_3), 20.86 (CH_3), 20.81 (CH_3), 20.77 (3 CH_3) ppm; mass spectrum (ESIMS), *m/z* = 722.38 $(M+23)^+$ $C_{28}H_{38}O_{19}$ requires 722.44 $(M+23)^+$.

2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-*α*-D-glycal (10)[1]

Compound **9** (2.10 g, 3.00 mmol) was dissolved in dry ethyl acetate (30 mL). To this solution was added Zn powder (1.9 g, 30.0 mmol), and *N*-methylimidazole (377 mg, 4.60 mmol). The solution was stirred vigorously, heated to reflux, and maintained at that temperature for 6 h. After the reaction was completed the Zn was removed by filtering through Celite. The Celite was washed twice with EtOAc (15 mL) for complete extraction. The filtrate was washed with saturated $NaHSO_4$ (20 mL) followed by $NaHCO_3$ (20 mL), and the ethyl acetate layer was dried over anhydrous Na_2SO_4. The dried ethyl acetate layer was concentrated under reduced pressure to obtain crude **10** which was purified by flash column chromatography on silica gel using a mobile phase of 25% acetone in hexanes. Compound **10** was obtained as a colorless solid. Yield: 53% (0.891 g); silica gel TLC R_f = 0.44 (6:4 hexanes-acetone); ^{1}H-NMR (600 MHz, CDCl3): δ 6.45 (d, 1H, $^3J_{1,2}$ 6.01 Hz, H-1), 5.52 (d, 1H, $^3J_{1',2'}$ 3.9 Hz, H-1'), 5.41 (dd, 1H, $^3J_{3',2'}$ 10.01 Hz, H-3'), 5.18 (m, 1H, H-3), 5.07 (t, 1H, $^3J_{3',4'}$ 10.01 Hz, $^3J_{4',5'}$ 9.77 Hz, H-4'), 4.84-4.82 (m, 2H, H-2', H-2), 4.39 (dd,1H, $^2J_{6a,6b}$ 11.96 Hz, $^3J_{6a,5}$ 3.42 Hz, H-6a), 4.35 (dd, 1H, $^2J_{6a,6b}$ 12.21 Hz, $^3J_{6a,5}$ 5.62 Hz, H-6b), 4.31-4.29 (m, 1H, H-5), 4.25 (dd, $^2J_{6'a,6'b}$ 12.45, $^3J_{6a,5}$ 3.91 Hz, 1H, H-6'a), 4.10 (dd, 1H, $^2J_{6'a,6'b}$ 12.45 Hz, $^3J_{6a,5}$ 1.71 Hz, H-6'b), 4.06-4.02 (m, 2H, H-4, H-5'), 2.13 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.02 (s, 3H, CH_3) ppm; ^{13}C NMR ($CDCl_3$): δ 170.8 (C=O), 170.71 (C=O), 170.71 (C=O), 170.61 (C=O), 170.26 (C=O), 170.78 (C=O), 145.78 (C1), 98.83 (C2), 95.97 (C1'), 74.25 (C5), 72.60 (C4), 70.59 (C2'), 69.826 (C3'), 69.82 (C3'), 69.74 (C3), 68.43 (C5'), 68.29 (C4), 62.03 (C6), 61.77 (C6'), 21.32 (CH_3),

21.03 (CH_3), 20.91 (CH_3), 20.89 (CH_3), 20.83 (CH_3), 20.77 (CH_3) ppm; mass spectrum (ESIMS), *m/z* = 583.3 $(M+23)^+$ $C_{24}H_{32}O_{16}$ requires 583.49 $(M+23)^+$.

2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α/β*-D-gluco-and D-mannopyranoses (11)[2]

To a solution of compound **10** (1.22 g, 2.17 mmol) in DMF (15.0 mL) was added H_2O (5.0 mL). The reagent Selectfluor® (1.90 g, 5.41 mmol) was added to the solution in two proportions. The second portion was added after 4 h of maintenance of the reaction at room temperature. The reaction was allowed to stir an additional 12 h at room temperature. The solution was diluted with EtOAc (60 mL) and washed with cold H_2O (50 mL 3 times). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure to obtain a light yellow syrup. The crude product was purified by flash column chromatography on silica gel by elution with acetone-hexanes (2:3). This yielded a mixture of compounds, (*α/β*)-1-hydroxy-2-fluoro derivatives, with gluco and manno stereochemistry **11**. Yield: 54% (695.0 mg); silica gel TLC R_f = 0.31 (6:4 hexanes -acetone); crude product used for next step without purification; mass spectrum (ESIMS), *m/z* = 619.25 $(M+23)^+$ $C_{24}H_{33}FO_{16}$ requires 619.16 $(M+23)^+$.

2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-1,3,6-tri-*O*-acetyl-2-deoxy-2-fluoro-*α/β*-D-gluco-and D-mannopyranoses (12)

To a solution compounds **11** (694 mg, 1.16 mmol) in pyridine was added acetic anhydride (329 μL, 3.49 mmol). The solution was maintained at room temperature for 8 h. The reaction was concentrated by evaporating the pyridine under reduced pressure to obtain

an oily liquid. This residue was diluted with EtOAc (20 mL). The EtOAc layer was washed with 0.5 N HCl (15 mL), followed by water (20 mL), and brine (20 mL). The organic layer dried over anhydrous Na_2SO_4 and the solvent evaporated under reduced pressure to obtain a colorless foam **12** as a mixture of *α*/*β*-2-fluoro derivatives with gluco and manno stereochemistry **12** (2.2:1, respectively). Yield: 99% (742 mg); silica gel TLC R_f = 0.48 (2:3 acetone-hexanes), the obtained compound was used in next step without purification; ^{19}F-NMR (Vxrs400 MHz, $CDCl_3$): 2-fluro gluco derivative: δ -203.3 (dd, $^2J_{F,2}$ 48.84 Hz, $J_{F,3}$ 12.21 Hz, F-2a); 2-fluoro manno derivative: δ -204.75 (ddd, $^2J_{F,2}$ 48.83 Hz, $^3J_{F,3}$ 27.47 Hz, $^3J_{F,1}$ 7.64 Hz, F-2e) ppm; mass spectrum (ESIMS), *m/z* = 661.18 $(M+23)^+$ $C_{26}H_{35}FO_{17}$ requires 661.17 $(M+23)^+$.

2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-gluco-and D-mannopyranosyl bromide (13)

The mixture of compounds **12** (784 mg, 1.23 mmol) was dissolved in methylene chloride (3.5 mL) and the solution was cooled to 0 °C. To the solution was added 33% HBr in acetic acid (4.5 mL) by drop-wise addition. The reaction was maintained at 18 °C for 8 h. After the reaction was complete, the solution was diluted with cold H_2O and extracted three times with DCM (25 mL). The organic layers were combined and washed with H_2O (15 mL), brine (15 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to obtain a colorless foam **13** as a mixture of *α*-1-bromo-2-fluoro derivatives with gluco and manno stereochemistry. Yield: 98% (807.0 mg); The crude material was used for next step without purification; ^{19}F-NMR of compounds *α*-bromo-2-fluoro derivatives with gluco and manno stereochemistry: δ -183 (m, F-2), -190.5 (m, F-

2) ppm; mass spectrum (ESIMS), *m/z* = 681.09 $(M+23)^+$ $C_{24}H_{32}BrFO_{15}$ requires 681.08 $(M+23)^+$.

2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-glycal (1)[4]

Mixture **13** (808 mg, 1.23 mmol) was dissolved in acetonitrile (10.0 mL) and triethylamine (304 µL, 3.68 mmol) was added. The reaction mixture was heated to 65-70° C for 6 h. The solution was concentrated under reduced pressure and purified by gravity column chromatography on silica gel using a mobile phase consisting of 7% acetone in DCM to obtain pure compound **1**. Yield: 33% (230.0 mg); silica gel TLC R_f = 0.19 (3:97 acetone-dichloromethane), and compound **14**. Yield: 30% (207.0 mg); silica gel TLC R_f = 0.28 (3:97 acetone-dichloromethane); (**1**): ^{1}H-NMR (600 MHz, $CDCl_3$): δ 6.77 (d, 1H, $^3J_{1,2}$ 4.77 Hz, H-1), 5.44-5.41 (m, 2H, H-1', H-3'), 5.37 (dd, 1H, $^3J_{3,4}$ 5.87 Hz, $^3J_{3,1}$ 1.47 Hz, H-3), 5.05 (t, 1H, $^3J_{3,4}$ 9.9 Hz, H-4'), 4.85 (dd, 1H, $^3J_{2',3'}$ 10.27 Hz, $^3J_{2',1'}$ 4.03 Hz, H-2'), 4.47 (m, 1H, H-5), 4.37 (dd, 1H, $^2J_{6a,6b}$ 11.74 Hz, $^3J_{6a,5}$ 7.70 Hz, H-6a), 4.20 (dd, 1H, $^2J_{6'a,6'b}$ 12.47 Hz, $^3J_{6'a,5'}$ 4.77 Hz, H-6a'), 4.16 (dd, 1H, $^2J_{6a,6b}$ 11.74 Hz, $^3J_{6b,5}$ 4.4 Hz, H-6b), 4.13 (dd, 1H, $^2J_{6'b,6'a}$ 12.47 Hz, $^3J_{6'b,5'}$ 2.20 Hz, H-6b'), 4.09-4.06 (m, 1H, H-5), 4.00-3.98 (m, 1H, H-4), 2.11 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.03 (s, 3H, CH_3) ppm; ^{13}C-NMR ($CDCl_3$): δ 170.59 (C=O), 170.47 (C=O), 170.31 (C=O), 170.68 (C=O), 169.97 (C=O), 169.59 (C=O), 142.12 (d, $^1J_{2,2F}$ 239.99 Hz, C2), 132.09 (d, $^2J_{1,2F}$ 39.61 Hz, C1), 96.88 (C1'), 74.50 (d, $^3J_{4,2F}$ 7.70 Hz, C4), 73.99 (C5), 70.54 (C2'), 69.87 (C3'), 68.38 (C4', C5'), 65.79 (d, $^2J_{3,2F}$ 23.11 Hz, C3), 61.91 (C6'), 60.62 (C6), 20.76 (s, 6H, 2 CH_3), 20.71 (s, 3H, CH_3), 20.68 (s, 3H, CH_3), 20.62 (s, 3H, CH_3), 20.55 (s, 3H,

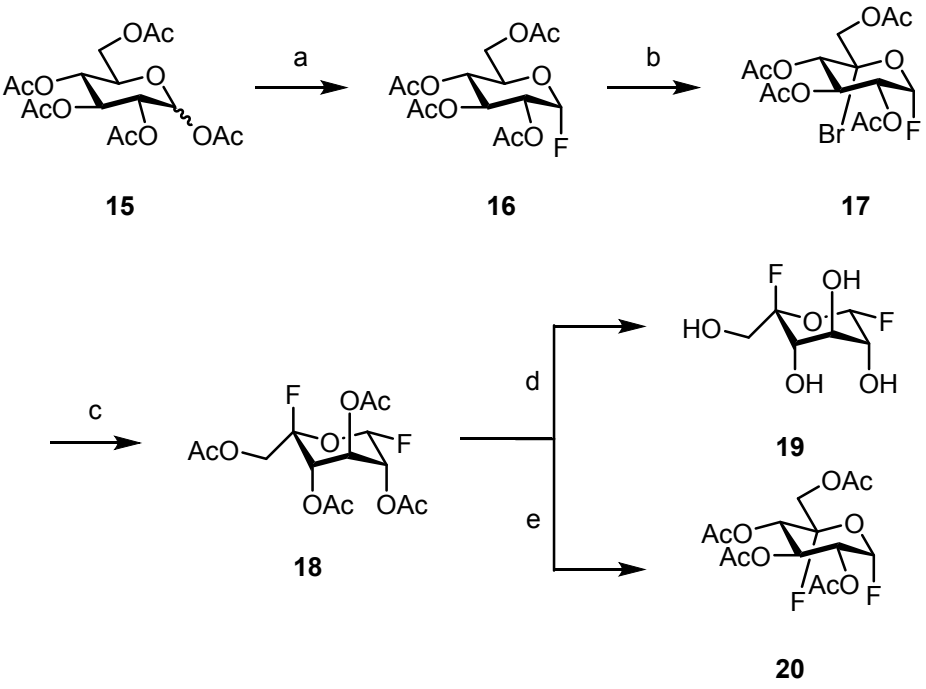
CH_3) ppm; ^{19}F NMR (Vxrs400 MHz, $CDCl_3$): δ -164.51 (dd ,1F, $^3J_{F,1}$ 6.11 Hz, $^3J_{3,F}$ 4.58 Hz, F-2) ppm; mass spectrum (ESIMS), *m/z* = 601.14 $(M+23)^+$ $C_{24}H_{33}FO_{16}$ requires 601.15 $(M+23)^+$.

2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (14)

^1H-NMR (600 MHz, $CDCl_3$): δ 6.37 (d, 1H, $^3J_{1,2}$ 9.54 Hz, H-1), 5.57 (d, 1H, $^3J_{1',2'}$ 4.04 Hz, H-1'), 5.54 (dd, 1H, $^3J_{3,F}$ 26.04 Hz, $^3J_{3,4}$ 9.54 Hz, $^3J_{3,2}$ 2.20 Hz, H-3), 5.40 (t, 1H, $^3J_{3',4'}$ 9.90 Hz, H-3'), 5.10 (t, 1H, $^3J_{3'4'}$ 9.90 Hz, H-4'), 4.95 (d, 1H, $^2J_{F,2}$ 48.78 Hz, H-2), 4.89 (dd, 1H, $^3J_{2',3'}$ 11.00 Hz, $^3J_{2'1'}$ 4.03 Hz, H-2'), 4.52 (dd, 1H, $^2J_{6a,6b}$ 12.47 Hz, $^3J_{6a,5}$ 1.83 Hz, H-6a), 4.32-4.29 (m, 2H, H-4, H-6b), 4.27 (dd, 1H, $^2J_{6'a,6'b}$ 12.47 Hz, $^3J_{6'a,5'}$ 3.30 Hz, H-6a), 4.20-4.18 (m, 1H, H-5), 4.08 (dd, 1H, $^2J_{6'a,6'b}$ 12.47 Hz, $^3J_{6'b,5'}$ 2.20 Hz, H-6b'), 3.99-3.97 (m, 1H, H-5') ppm; ^{13}C-NMR ($CDCl_3$): δ 170.70 (C=O), 170.57 (C=O), 170.51 (C=O), 170.17 (C=O), 170.12 (C=O), 169.61 (C=O), 95.98 (C1'), 88.59 (dd, $^1J_{2F,2}$ 185.76 Hz, C2), 82.16 (d, $^2J_{2F,1}$ 26.14 Hz, C1), 72.98 (C5), 71.99 (C3), 71.88 (C2), 70.38 (C2'), 69.50 (C3'), 69.46 (C4), 68.74 (C5'), 68.03 (C4'), 62.03 (C5'), 61.49 (C6'), 21.07 (CH_3), 20.91 (CH_3), 20.84 (CH_3), 20.78 (CH_3), 20.75 (CH_3), 20.67 (CH_3) ppm; ^{19}F NMR: δ -183 (m, F-2) ppm; *m/z* = 681.0806 $(M+Na)^+$, $C_6H_{10}F2O_5$ requires 658.0909.

Synthesis of 5-fluoro-*β*-D-idosyl fluoride (19): 5-Fluoro-glycosyl fluorides have also been reported to inhibit of glycoside hydrolases.[5] We synthesized 5-fluoro-*β*-idosyl fluoride (**19**) and trace 5-fluoro-*α*-glycosyl fluoride (**20**). [6, 7] We envisioned fluoride **19** as a key intermediate on route to fluoride **20**, Scheme S-2. The known approach to access C5**'** fluoro glycosides has been to photo-brominate the C5**'** position of the glycoside followed by displacement of the bromide using a fluoride source.[8, 9] We explored the photo-bromination of per-*O*-acetyl-*α*-glycosyl fluoride (**16**) to access 2,3,4,6-tetra-*O*-acetyl-5-bromo-1-fluoro-*α*-glycosyl fluoride (**17**) (Figure S-2). Glycosyl fluoride **17** was treated with AgF or $AgBF_4$; however, only undesired epimeric 2,3,4,6-tetra-*O*-acetyl-5-fluoro-*β*-L-idosyl fluoride **18** was formed.[8-10] We investigated methods for equilibrating **18** to the D-gluco configuration **20**. We examined: i) longer reaction times, ii) higher tempratures, and iii) addition of HF-pyridine to equilibriate the L-idosyl fluoride **18** to the D-glucosyl fluoride **20**.[9] However, these efforts did not prove to be helpful in our case. Other strategies to epimerize from the L-idose to the D-glucose configuration were to treat the L-idosyl fluoride with Lewis acids e.g., i) $BF_3.OEt_2$, ii) $BF_3.OEt_2$ + TMSOTf, iii) $BF_3.OEt_2$ + HF-pyridine, and iv) $Cp_2(Zr)Cl_2$ + AgOTf, respectively. [9, 11-13] $BF_3.OEt_2$ worked with trace yields in our hands to produce the 2,3,4,6-tetra-*O*-acetyl-5-fluoro-*α*-glycosyl fluoride (**20**) in an equilbium favoring starting material **18**.[6] Fluoride **18** was deacetylated with NH_3-MeOH to afford **19**. Since we could only produce **20** in only trace ammounts and since the structure of the GlgE 2-deoxy-2-fluoro-*α*-maltosyl fluoride (*α*-MDF) in complex with *Sco* GlgEI-E423A[14] was reported, there was no need to further pursue this target. Our reaction apparatus description and detailed conditions to produce **17** may be helpful to other researchers.

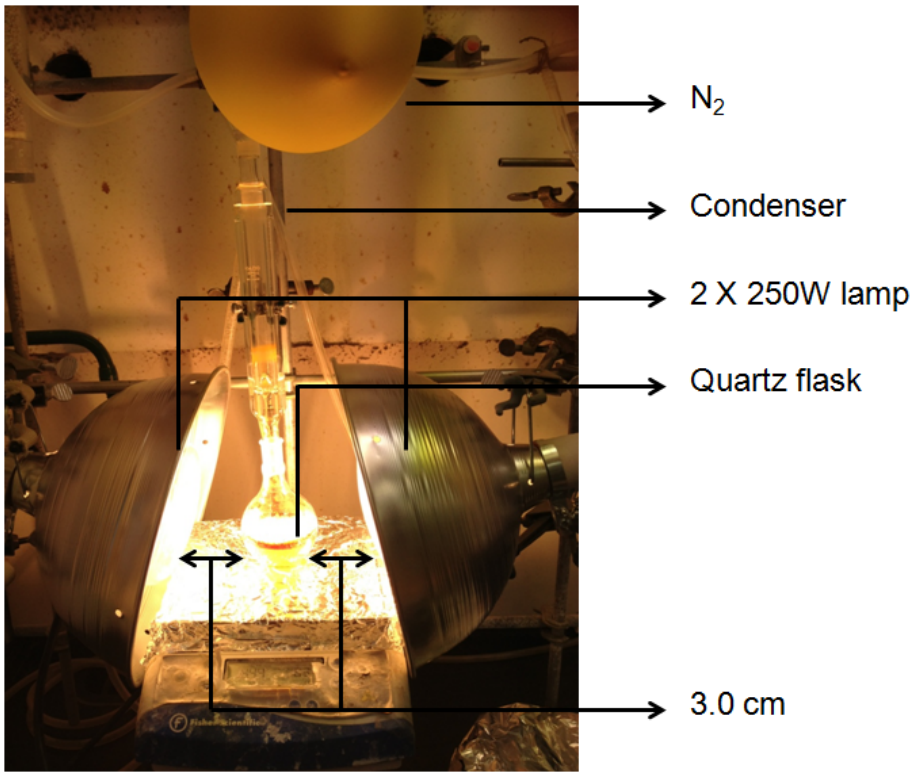
Scheme S-2. Synthesis of 2,3,4,6-tetra-*O*-acetyl-5-fluoro-*β*-D-idosyl fluoride (**19**) and 2,3,4,6-tetra-*O*-acetyl-5-fluoro-*α*-glycosyl fluoride (**20**)



15 **16** **17** **18** **19** **20**

Reagents and conditions: a) HF-Pyridine, 83 %; b) *N*-bromosuccinamide, AIBN, CCl_4, 2x250W flood lamp (50 %); c) AgF, CH_3CN (68 %); d) NH_3-MeOH, quantitative; e) $BF_3.OEt_2$ (low).

Figure S-2. Reaction assembly set-up for photobromination of C5 position of glycosyl compounds



1,2,3,4,6-penta-*O*-acetyl-*α*/*β*-D-glucopyranoside (15):[15] Compound **15** (10.0 g, 0.055 mol), was dissolved in pyridine (48.2 g, 0.61 mol) and acetic anhydride (62.2 g, 0.61 mol). DMAP (10 mg) was added to the reaction flask and reaction stirred for a period of 4 h. Completion of the reaction was monitored by TLC using ethyl acetate-hexanes (3:7). The reaction was concentrated under reduced pressure to obtain colorless residue. The residue was dissolved in toluene and concentrated under reduced pressure to remove most of the pyridine and residual acetic acid generated during the reaction. The residue was diluted with ethyl acetate and was washed with 1 N HCl followed by saturated aqueous sodium bicarbonate. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material **15** was obtained as white amorphous solid. Yield: 99% (21.0 g). The characterization data for compound **15** matches the previously reported data.

2,3,4,6-penta-*O*-acetyl-*α*-D-glycosyl fluoride (16)[16] HF-pyridine (~70% hydrogen fluoride in ~30% pyridine) (15 mL) was added to compound **15** (2.0 g, 5.1 mmol) in a polypropylene tube. The mixture was stirred to dissolution at room temperature. The reaction was further stirred for 7 h. Completion of the reaction was monitored by TLC using hexanes-acetone (6:4). The reaction was diluted with excess of dichloromethane. The solution was neutralized with saturated aqueous sodium bicarbonate cooled over an ice-bath. The organic layer was extracted with saturated aqueous sodium bicarbonate solution (3 × 100 mL) to remove residual acid. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude material was purified using flash column chromatography on silica gel using 25% acetone in hexanes to obtain *α*-glucosyl fluoride, compound **16** as white amorphous solid. Yield: 75% (1.32 g); silica gel TLC R_f = 0.50 (99:2 ethyl acetate-dichloromethane). The characterization data for compound

16 matches the previously reported data; ^{1}H NMR (600 MHz, CD_3OD): δ (600 MHz, $CDCl_3$) 5.76 (dd, 1H, $^{2}J_{H1,F}$ = 53.4 Hz, $^{3}J_{H1,H2}$ = 2.4Hz, H-1), 5.49 (m, 1H, H-3), 5.15 (m, 1H, H-4), 4.95 (dddd, 1H, $^{3}J_{H2,F}$ = 24 Hz, $^{3}J_{H2,H3}$ = 10.2 Hz, $^{3}J_{H2,H1}$ = 2.4 Hz, H-2), 4.29 (dd, 1H, $^{3}J_{H6a,H5}$ = 12.6 Hz, $^{3}J_{H6a,H6b}$ = 3.6 Hz, H-6a), 4.19 (m, 1H, H-5), 4.15 (dd, 1H, $^{3}J_{H6b,H5}$ = 12.6 Hz, $^{3}J_{H6a,H6b}$ = 2.4 Hz, H-6b), 2.11 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.03 (s, 3H, CH_3) ppm; mass spectrum (ESIMS), *m/z* = 373.09 $(M+23)^+$ $C_{14}H_{19}FO_9$ requires 373.09 $(M+23)^+$.

2,3,4,6-penta-*O*-acetyl-5-bromo-*α*-D-glycosyl fluoride (17)[8] Compound **16** (1.80 g, 5.14 mmol) was stirred in 80.0 mL anhydrous CCl_4 at room temperature, in a quartz flask attached to a reflux assembly under nitrogen atmosphere. *N*-Bromosuccinimide (3.65 g, 20.6 mmol) and AIBN (83 mg, 0.51 mmol) was added to the reaction vessel. The reaction was stirred under refluxing conditions using 2x250 Watts (120V) heat lamps stationed at a distance of 3.0 cm on either side of the reaction vessel. Completion of reaction was monitored using ^{1}H-NMR and TLC using ethyl acetate: dichloromethane (0.2:9.9). The reaction was stirred under reflux for 18.0 h. The reaction was concentrated under reduced pressure to obtain a brown colored residue. The residue was diluted with dichloromethane (100 mL) and washed sequentially with water (1 × 50 mL), saturated sodium bicarbonate (1 × 50 mL) and brine solution (1 × 50 mL). The organic layer was dried over anhydrous MgSO4 and concentrated under reduced pressure. The crude material was purified using silica gel flash column chromatography using 1 % ethyl acetate in dichloromethane to obtain 5-bromo-*α*-glucosyl fluoride, compound **17**. Yield: 47% (1.03 g); silica gel TLC R_f = 0.55 (99:2 ethyl acetate-dichloromethane). The characterization data for compound **17** matches the previously reported data. ^{1}H NMR (600 MHz, CD_3OD): δ 5.93 (dd, 1H, $^{2}J_{H1,F}$ = 52.8 Hz, $^{3}J_{H1,H2}$ = 3.0 Hz, H-1), 5.86 (t, 1H, H-3), 5.21 (d, 1H, $^{3}J_{H4,H3}$ = 10.2 Hz, H-

4), 5.06 (dddd, 1H, $^{3}J_{H2,F}$ = 24 Hz, $^{3}J_{H2,H3}$ = 10.8 Hz, $^{3}J_{H2,H1}$ = 3.6 Hz, H-2) 4.43 (dd, 2H, H-6a,H-6b), 2.13 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.10 (s, 3H, CH_3) 2.05 (s, 3H, CH_3) ppm; mass spectrum (ESIMS), *m/z* = 451.00 $(M+23)^+$ $C_{14}H_{18}BrFO_9$ requires 451.00 $(M+23)^+$.

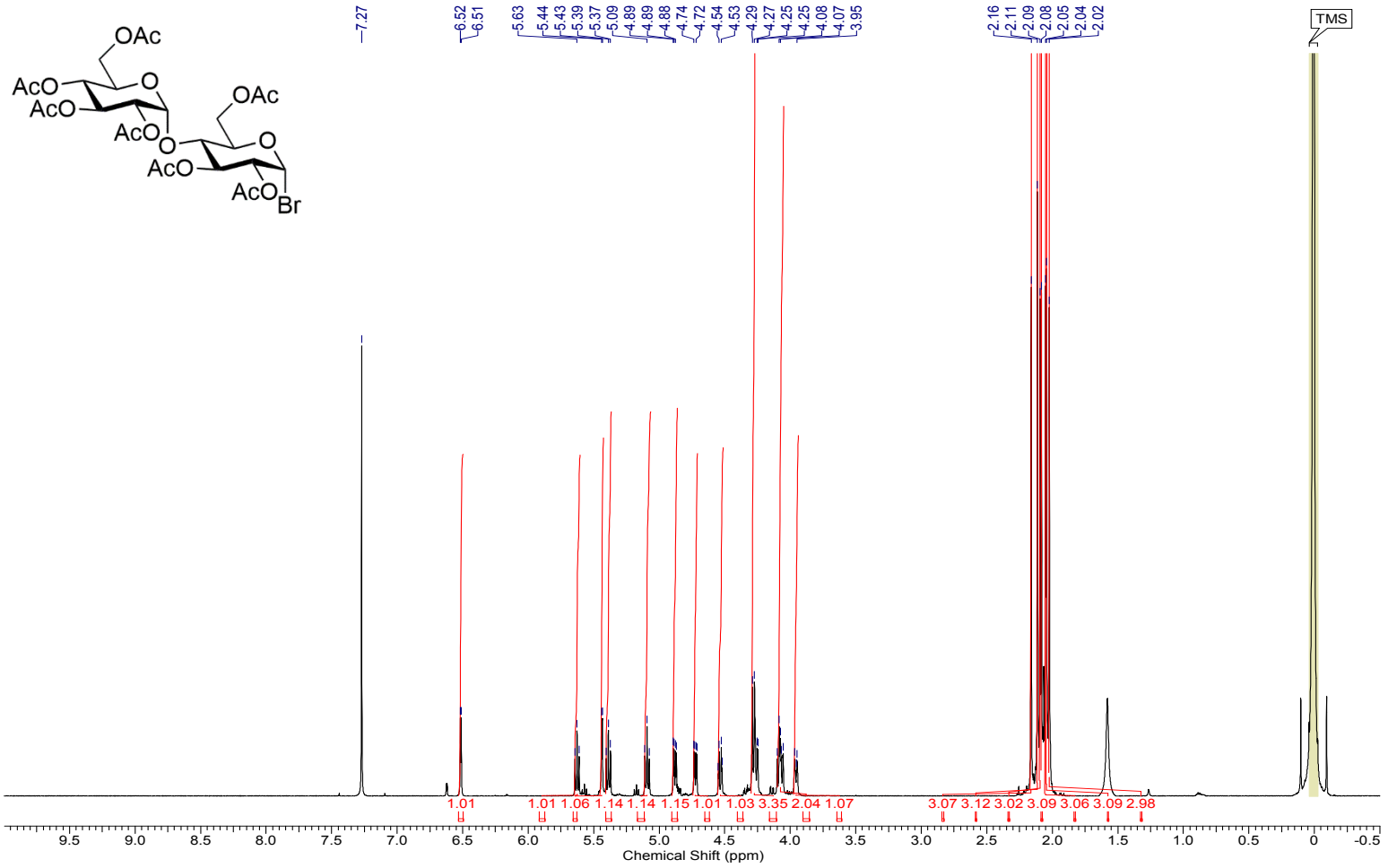
2,3,4,6-*O*-acetyl-5-fluoro-*β*-D-idosyl fluoride (18):[8] Compound **17** (1.0 g, 2.2 mmol) was dissolved in 15 mL of anhydrous acetonitrile under nitrogen atmosphere. The reaction flask was covered with aluminum foil and the reaction carried out in the dark. Silver (I) fluoride (0.70 g, 5.5 mmol) was added to the flask under nitrogen atmosphere and the reaction stirred at room temperature. The reaction was stirred for 4 h. Completion of the reaction was monitored by TLC using ethyl acetate-hexane (3:97). The reaction was filtered and the filtrate was concentrated under reduced pressure to obtain a light brown residue. The residue was dissolved in ethyl acetate (50 mL) and washed sequentially with water (1 × 50 mL) and brine solution (1 × 50 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude material was purified using silica gel flash column chromatography using 1 % ethyl acetate in diethyl ether to obtain 5-fluoro-*β*-L-idosyl fluoride, compound **18.** Yield: 68% (0.55 g); silica gel TLC R_f = 0.38 (3:97 ethyl acetate-hexanes). ^{1}H NMR (600 MHz, CD_3OD): δ 5.78 (d, 1H, $^{2}J_{F,1H}$ = 60.04, H-1), 5.39 (dd, 1H, $^{3}J_{H2,F}$ = 30.0 Hz, $^{3}J_{H2,H3}$ = 12.0 Hz, H-2), 5.28 (m, 2H, H-3, H-4), 4.43 (dd, 2H, $^{2}J_{H6a,H6b}$ = 24.0 Hz, $^{3}J_{H6a,H5}$ = 12.0 Hz, H-6a), 4.18 (t, 1H, $^{2}J_{H6a,H6b}$ = 24.0 Hz, H-6b), 2.13 (s, 3H, CH_3), 2.12 (s, 6H, $2CH_3$), 2.09 (s, 3H, CH_3) ppm; mass spectrum (ESIMS), *m/z* = 391.07 $(M+23)^+$ $C_{14}H_{18}F_2O_9$ requires 391.08 $(M+23)^+$.

5-Fluoro-*β*-D-idosyl fluoride (19):[6] Compound **18** (8.6 mg) was dissolved in MeOH (1.5 mL) and the reaction mixture was cooled to -10 °C using dry ice in acetone. Ammonia gas was

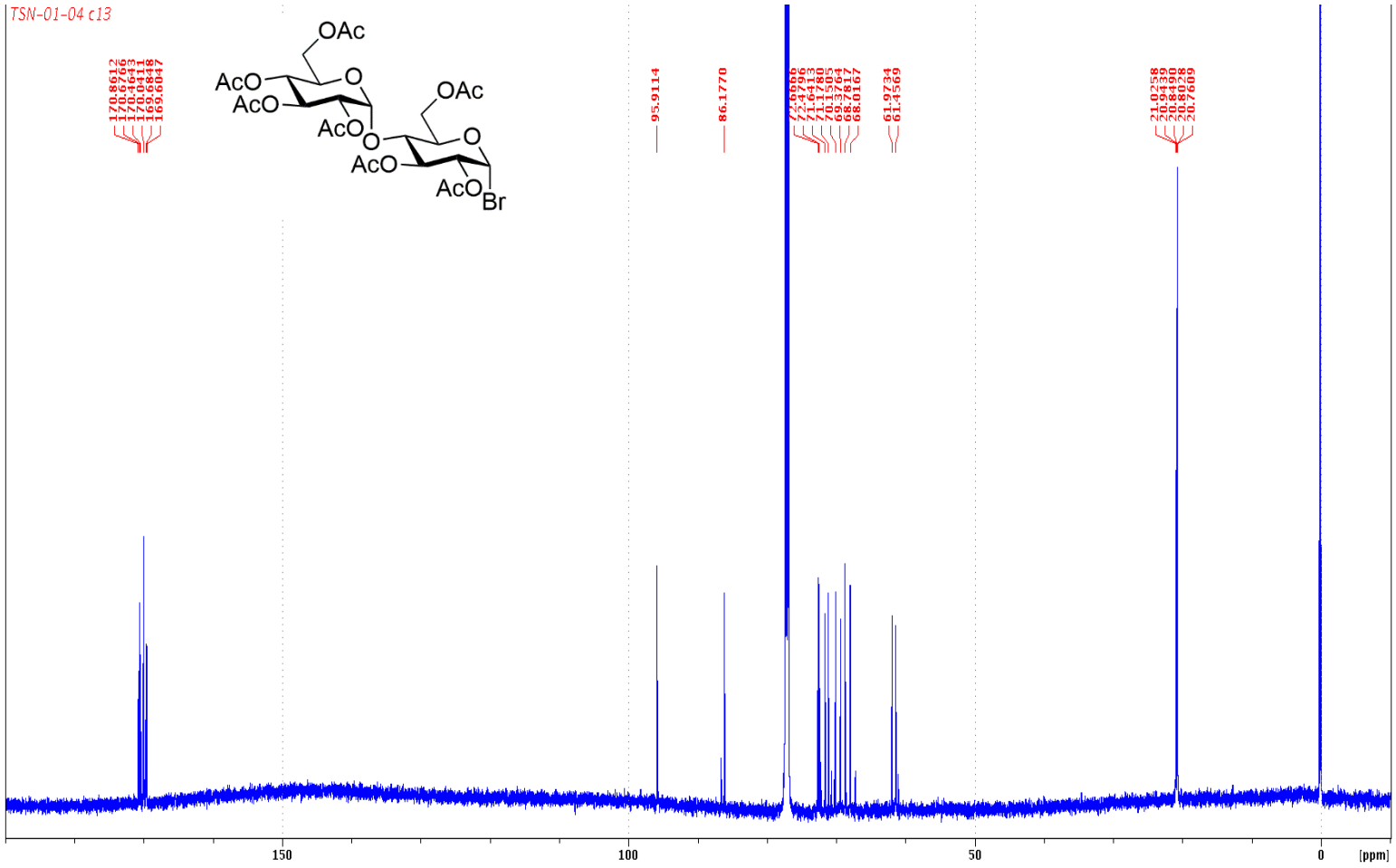
bubbled into the solution for 10 min. The outlet of the reaction apparatus was connected to a bent finger trap cooled to -78 °C to trap any escaping ammonia gas. The reaction was maintained at room temperature for 2 h. The reaction was concentrated to obtain an oily liquid of crude compound **19**, the crude compound was dissolved in minimum amount of H_2O purified by C-18 chromatography (2% methanol in H_2O), to obtain pure compound **19**. ^{1}H NMR (600 MHz, CD_3OD): δ 5.65 (d, 1H, $^2J_{F,1H}$ = 56.12, H-1), 3.93 (m, 1H, H-2), 3.78 (m, 3H), 3.66 (m, 1H) ppm; mass spectrum (HRMS), *m/z* = 223.0401 $(M+Na)^+$, $C_6H_{10}F2O_5$ requires 223.0394 $(M+Na)^+$.

5-Fluoro-*α*-D-glycosyl fluoride (20):[17] Compound **19** (69.0 mg, 188 µM) was dissolved in anhydrous CH_2Cl_2 (1.0 mL) under nitrogen atmosphere. The solution was cooled to 0 °C and $BF_3.OEt_2$ (0.007 mL) was added. The reaction was maintained at 0 °C for another 10 minutes and allowed to room temperature. The progress of reaction was monitored by ^{1}H NMR. After 4 h reaction was complete. The reaction was quenched with saturated aqueous $NaHCO_3$ (5.0 mL). The product was extraced from the aqueous layer by CH_2Cl_2 (5.0 mL). The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The CH_2Cl_2 layer was concentrated under reduced pressure and purifed by flash column chromatography on silica gel using 5% ethyl acetate in dichloromethane as an eluent. The product was obtaind as mixture with 5-fluoro-*β*-D-idosyl fluoride **(19)** and **(20)**. ^{1}H NMR (600 MHz, CD_3OD): δ 5.85 (d, 1H, $^2J_{F,1H}$ = 53.0, H-1), 5.0 (dd, 1H, $^3J_{H2,F}$ = 24.0 Hz, H-2), 5.77 (t, 1H, $^3J_{F,2H}$ = 10.2, H-3), 5.23 (dd, 1H, $^3J_{H4,F5}$ = 22.2 Hz, H-4), 4.3 (dd, 1H, $^2J_{H6a,H6b}$ = 12.0 Hz, H-6a), 4.0 (dd, 1H, $^2J_{H6a,H6b}$ = 12.3 Hz, H-6b); mass spectrum (ESIMS), *m/z* = 391.27 $(M+Na)^+$, $C_6H_{10}F2O_5$ requires 391.27 $(M+Na)^+$.

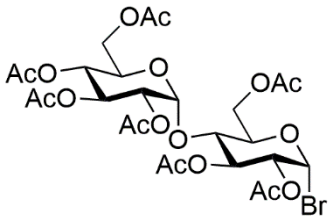
^{1}H NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-2,3,6-tri-*O*-acetyl-*α*-D-glucopyranosyl bromide (9):

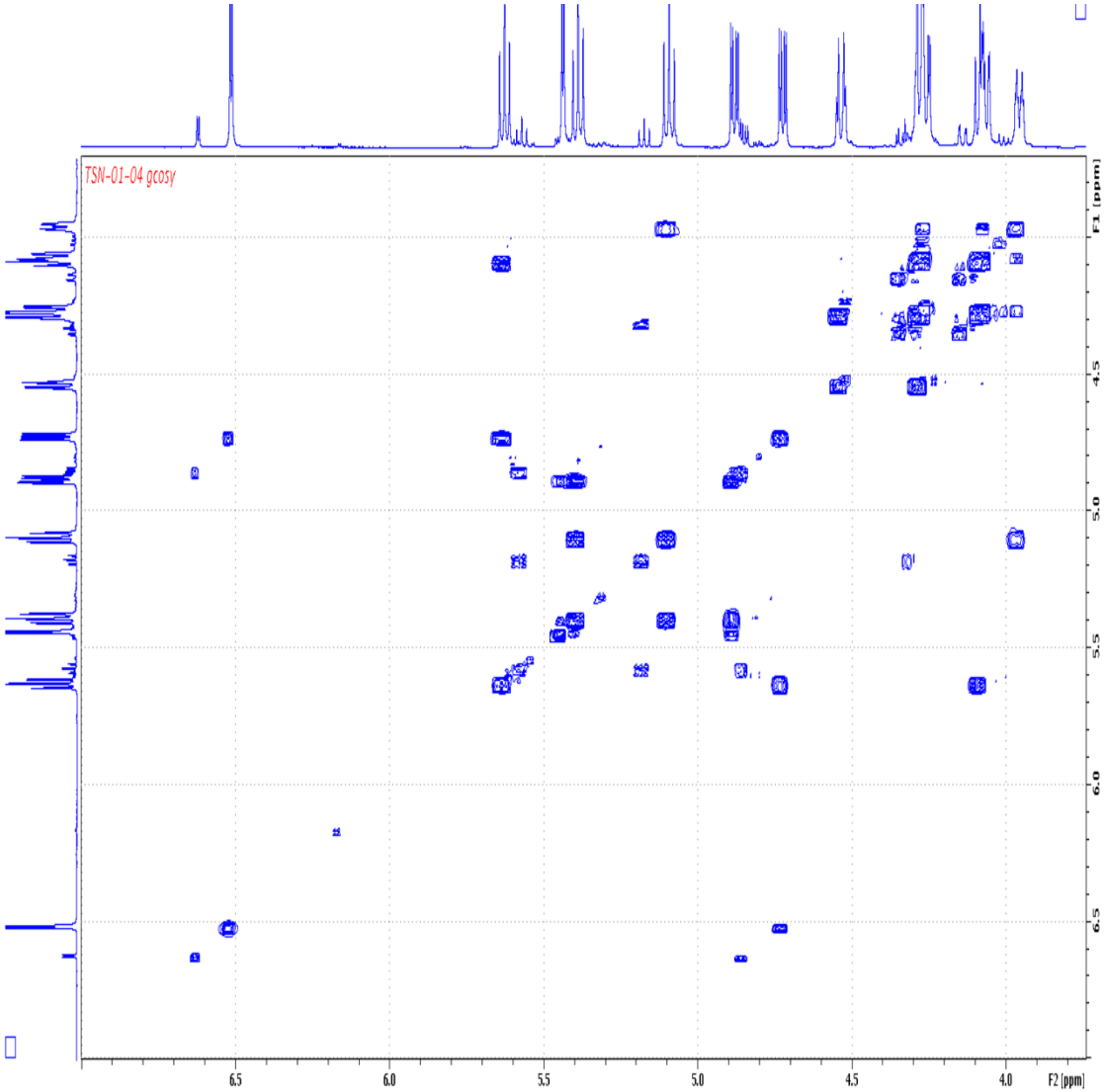


^{13}C NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-2,3,6-tri-*O*-acetyl-*α*-D-glucopyranosyl bromide (9)

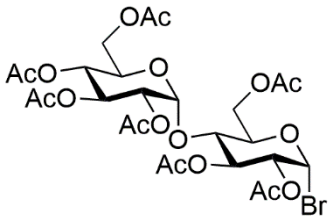


COSY of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-2,3,6-tri-*O*-acetyl-*α*-D-glucopyranosyl bromide (9)





HMQC of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-2,3,6-tri-*O*-acetyl-*α*-D-glucopyranosyl bromide (9)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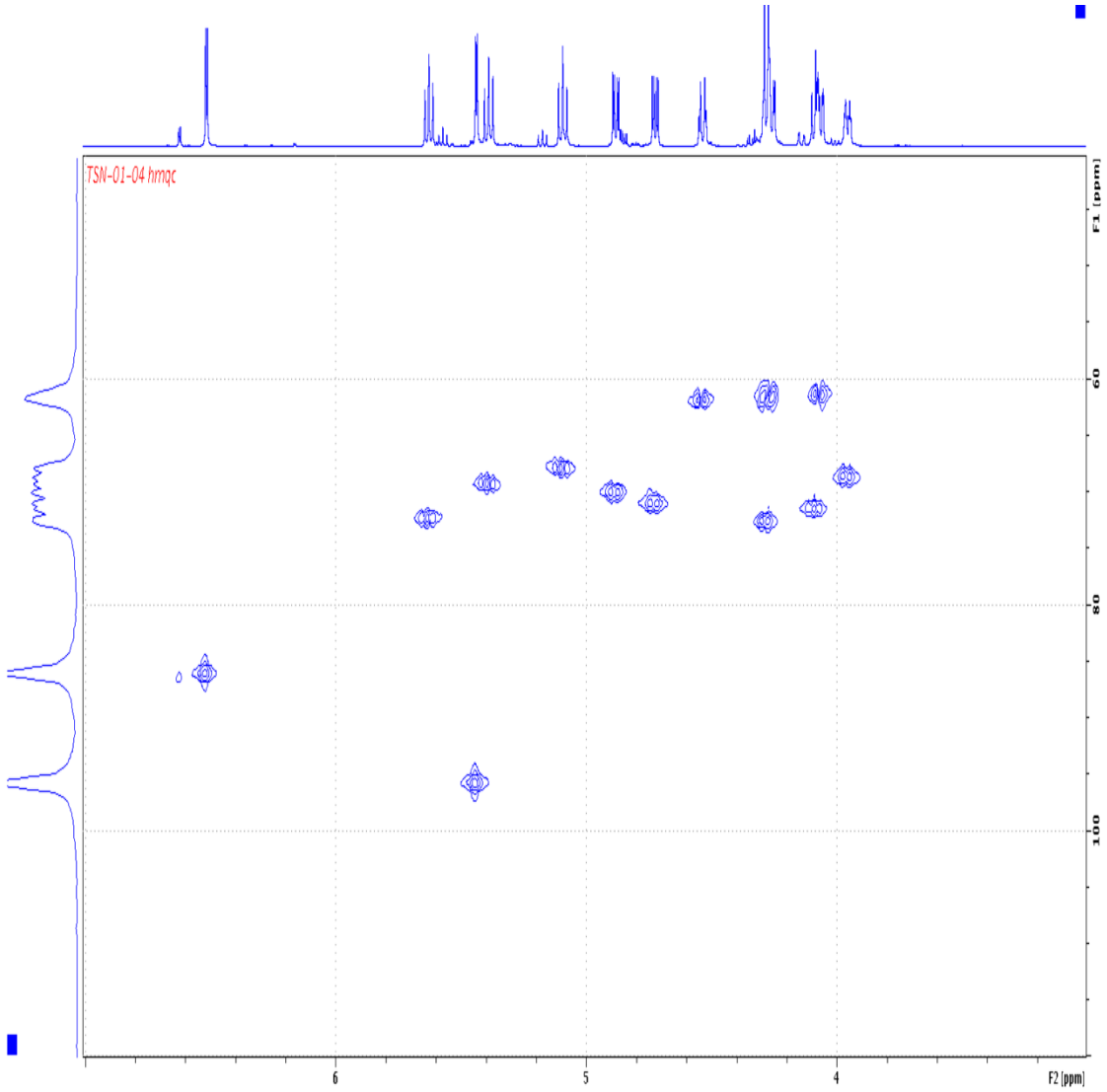
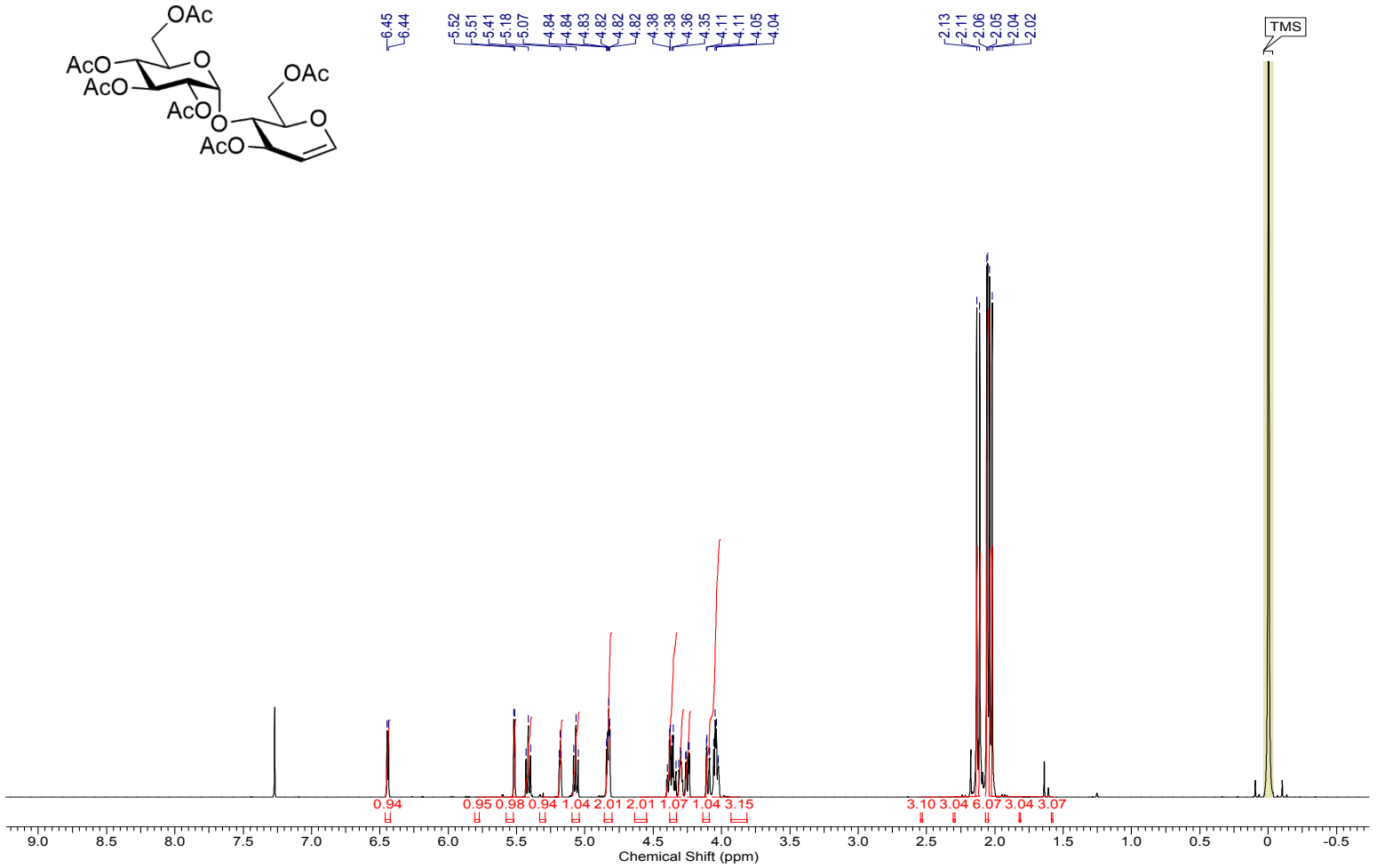
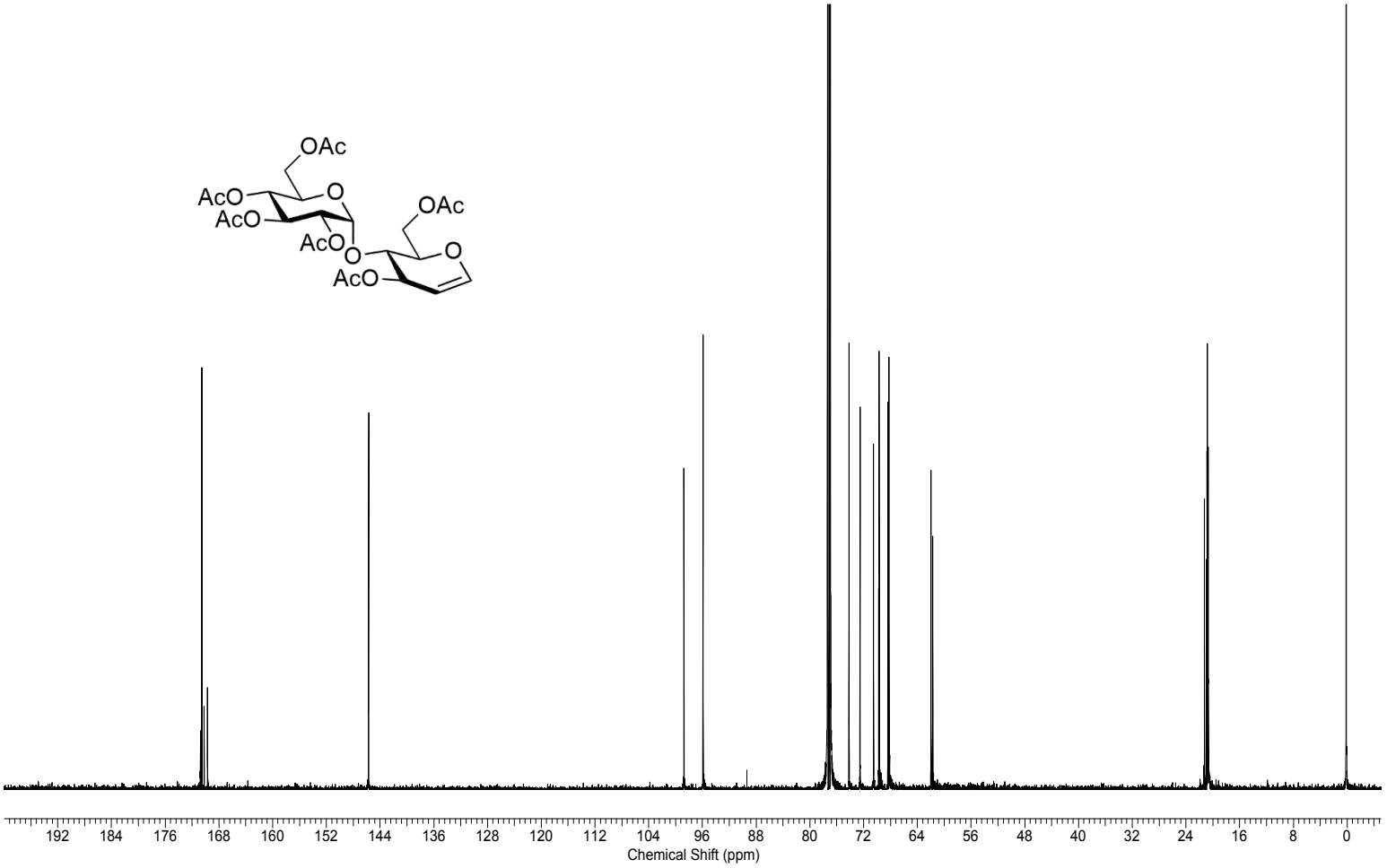
AcO
AcO
O
AcO
O
OAc
O
AcO
AcO
Br


TSN-01-04 hmqc
F1 [ppm]
60
80
100
6
5
4
F2 [ppm]

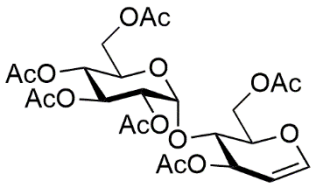
^{1}H NMR of 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-*α*-D-glycal (10)

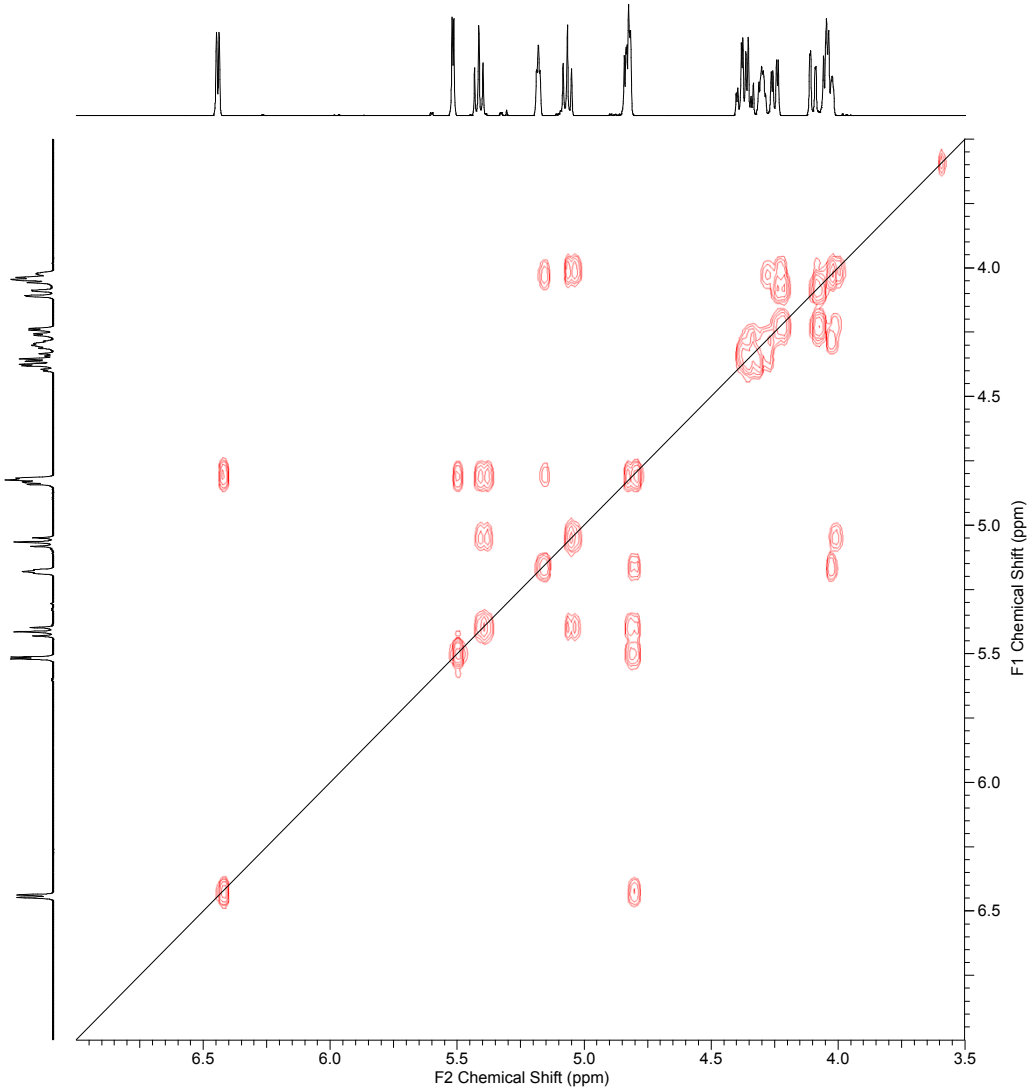


^{13}C NMR of 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-*α*-D-glycal (10):

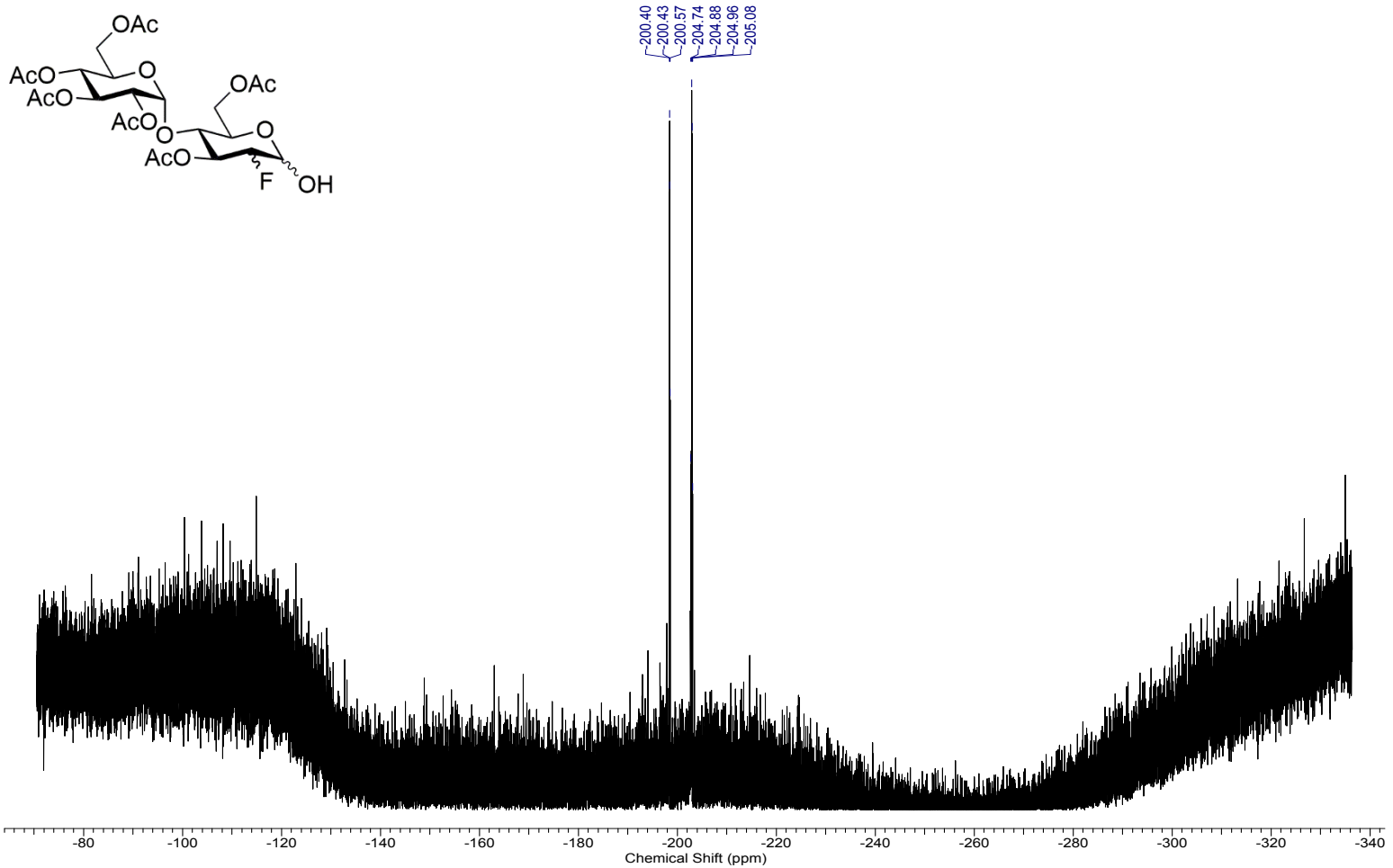


COSY of 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-*α*-D-glycal (10)

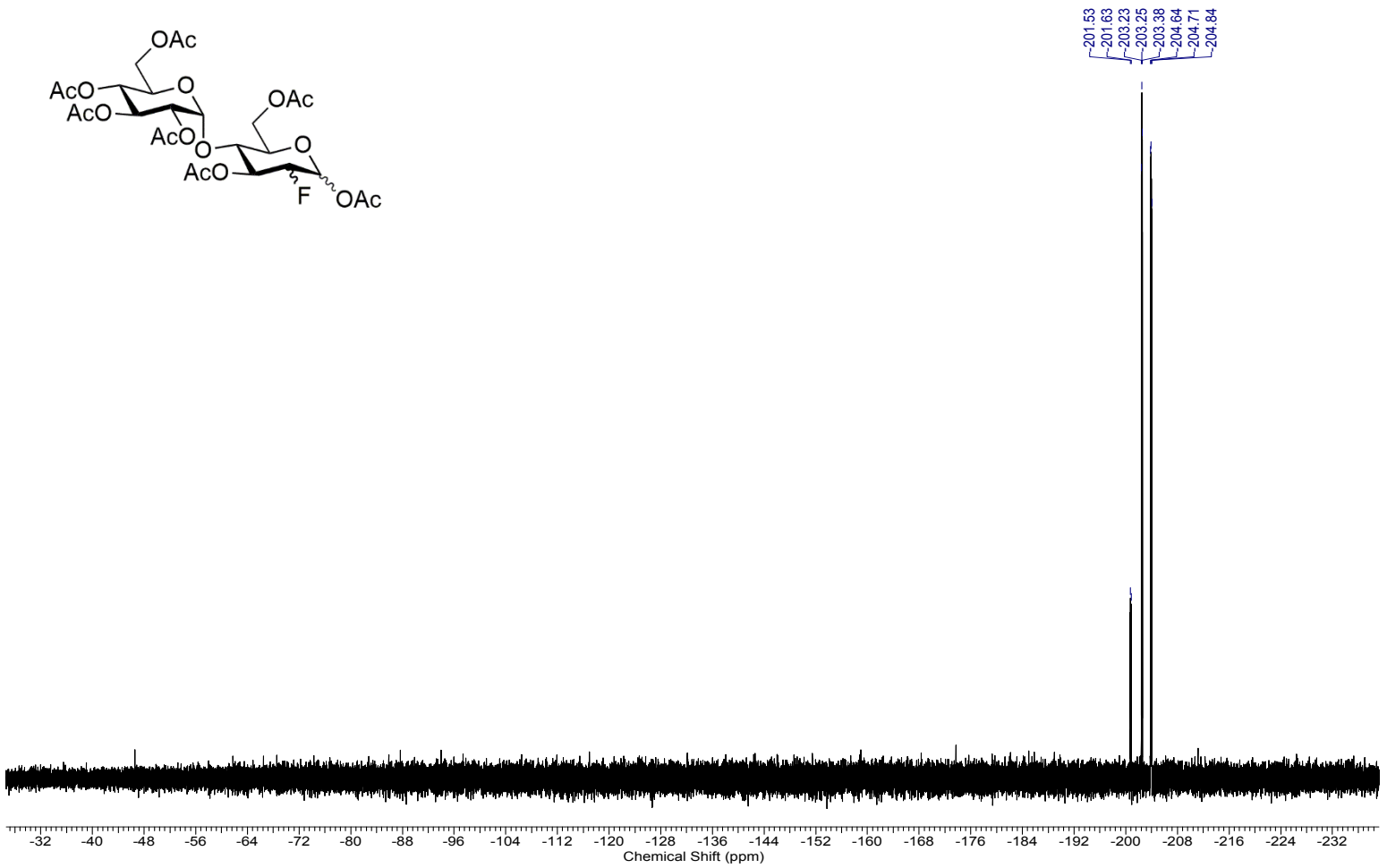




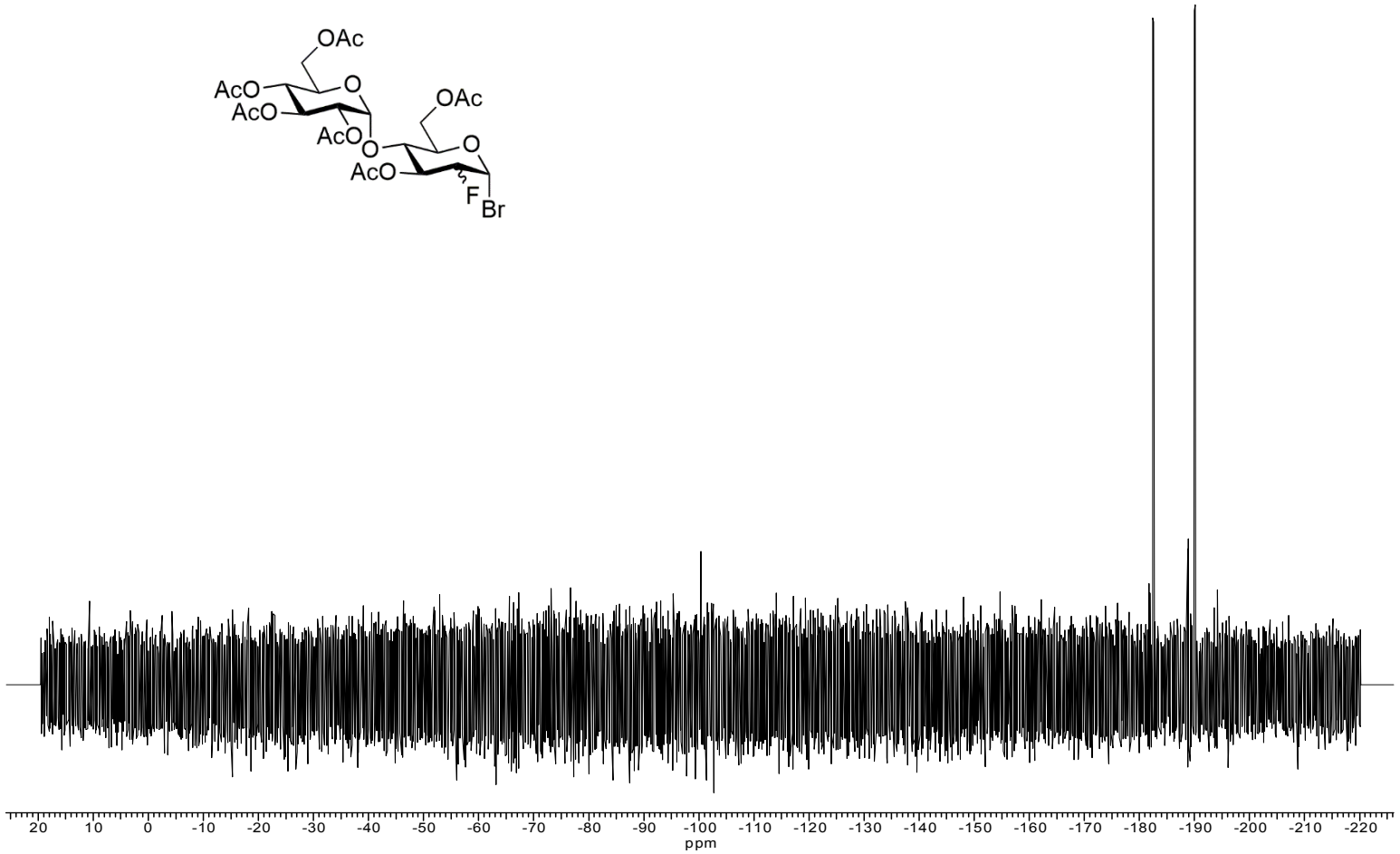
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α/β*-D-gluco-and D-mannopyranoses (11)



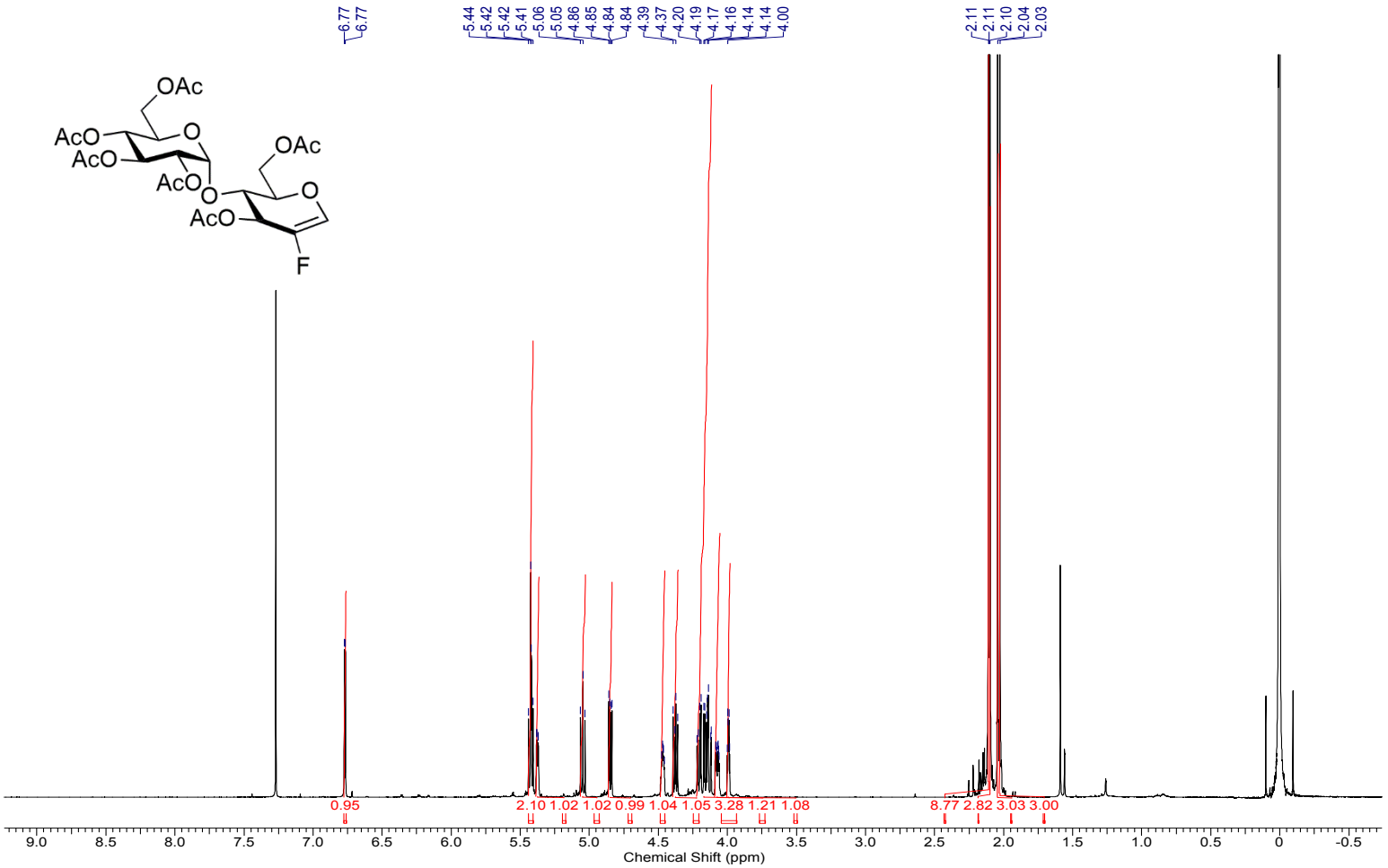
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-1,3,6-tri-*O*-acetyl-2-deoxy-2-fluoro-*α/β*-D-gluco-and D-mannopyranoses (12)



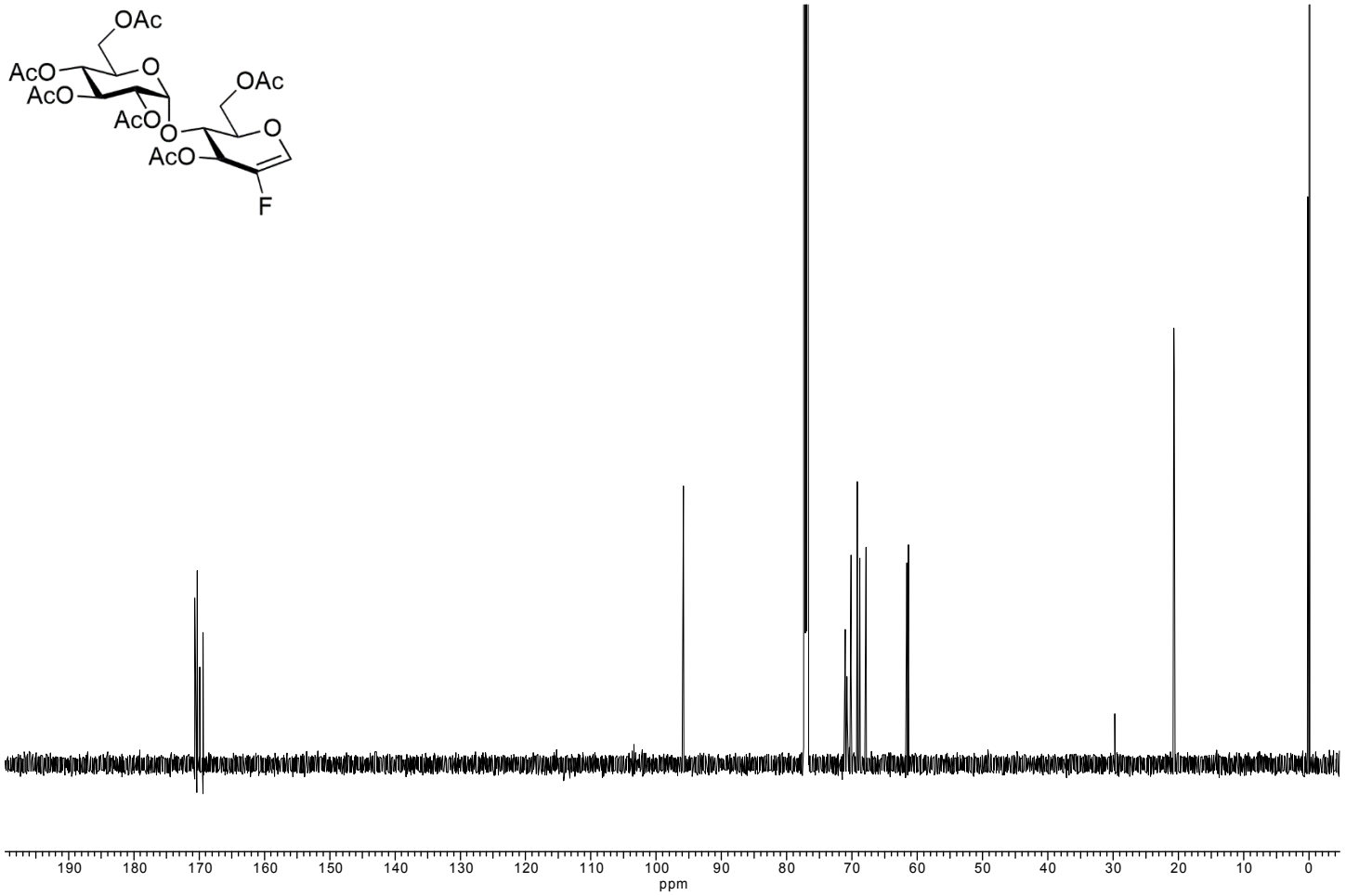
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-gluco-and D-mannopyranosyl bromide (13)



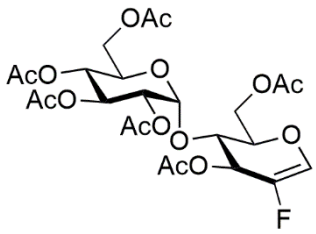
^{1}H NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-glycal (1)

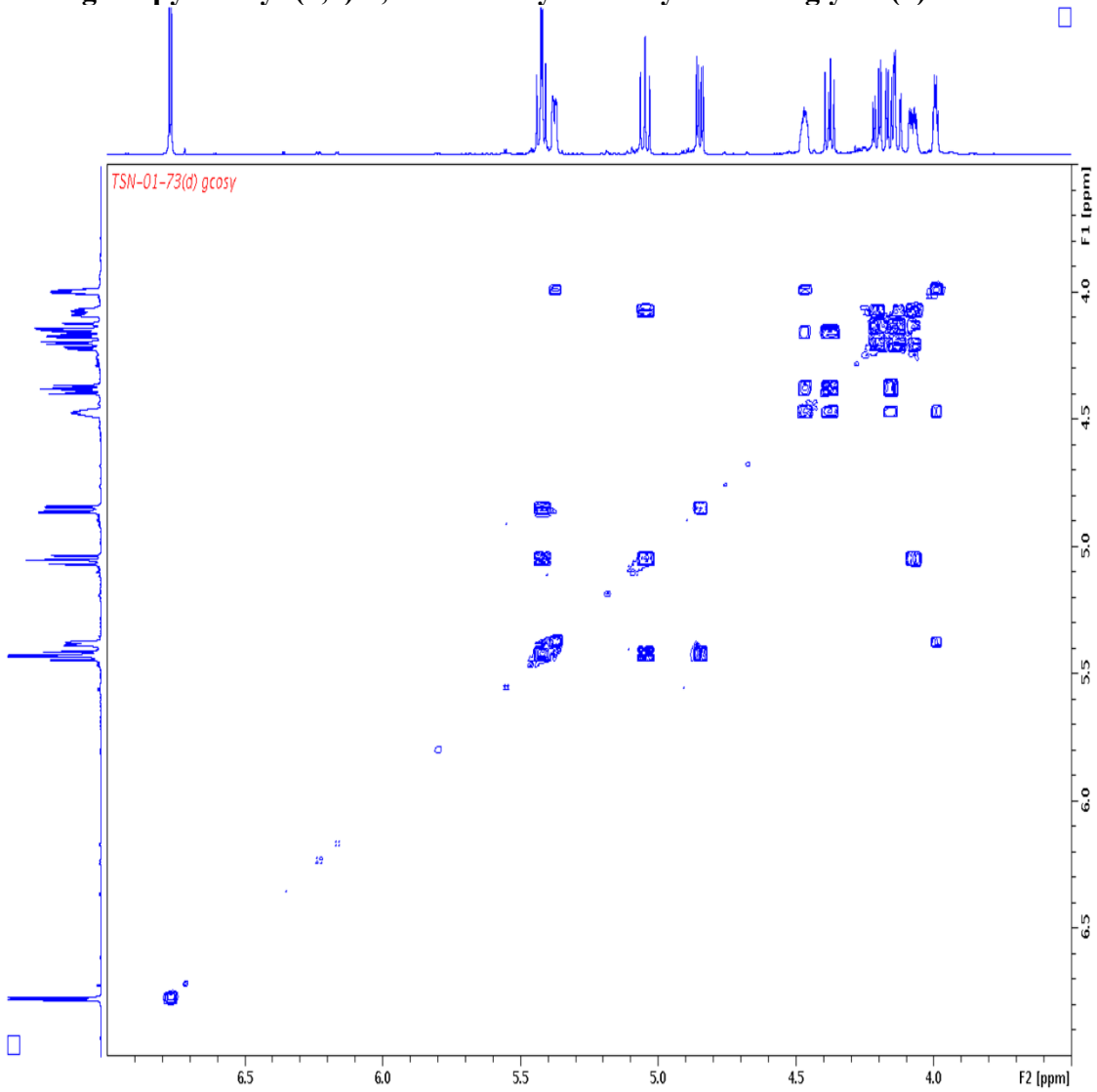


^{13}C NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-glycal (1)

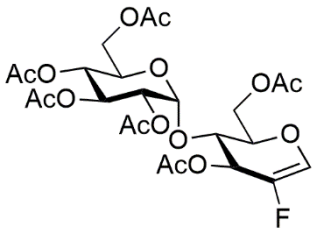


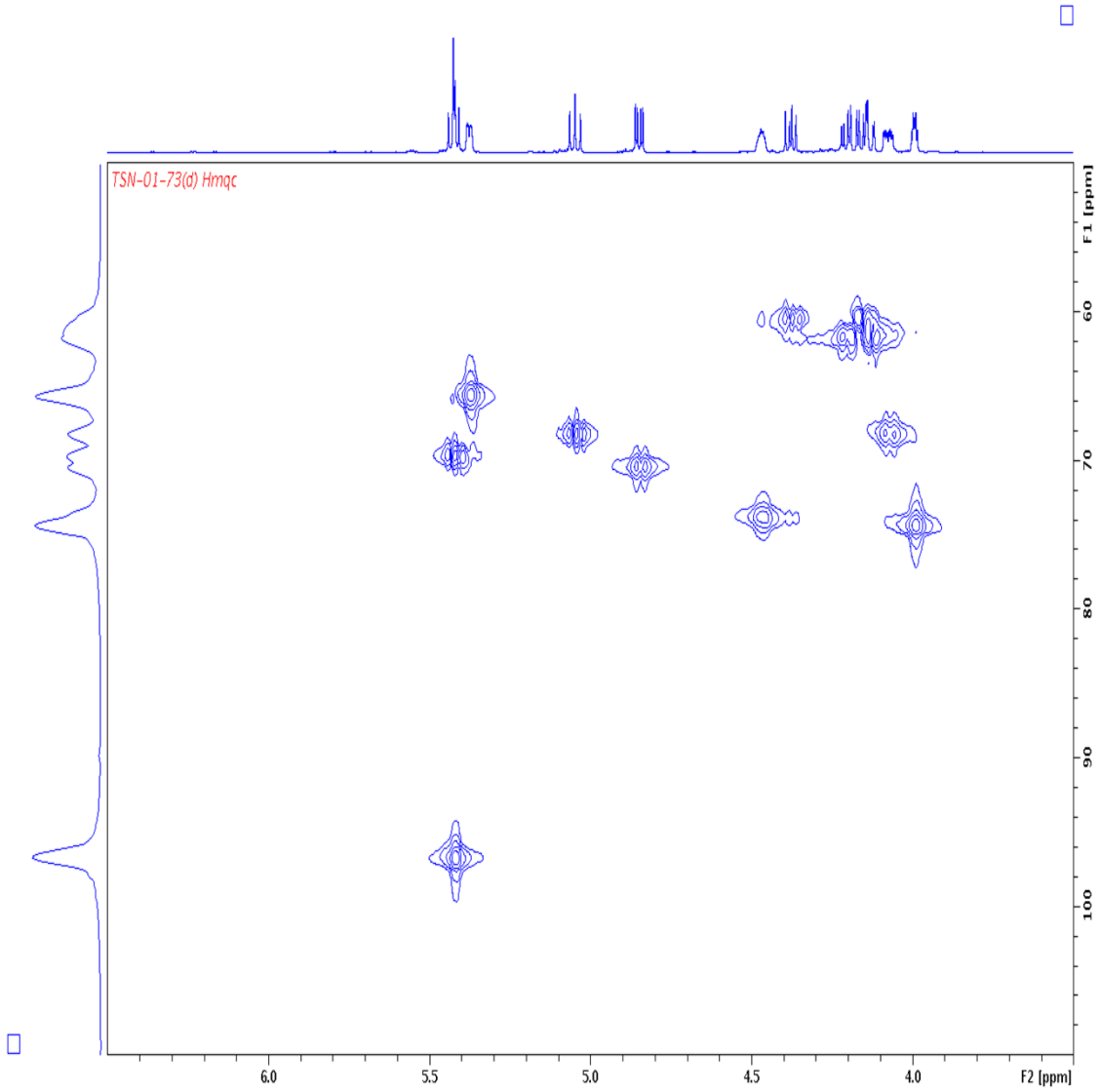
COSY of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-glycal (1)



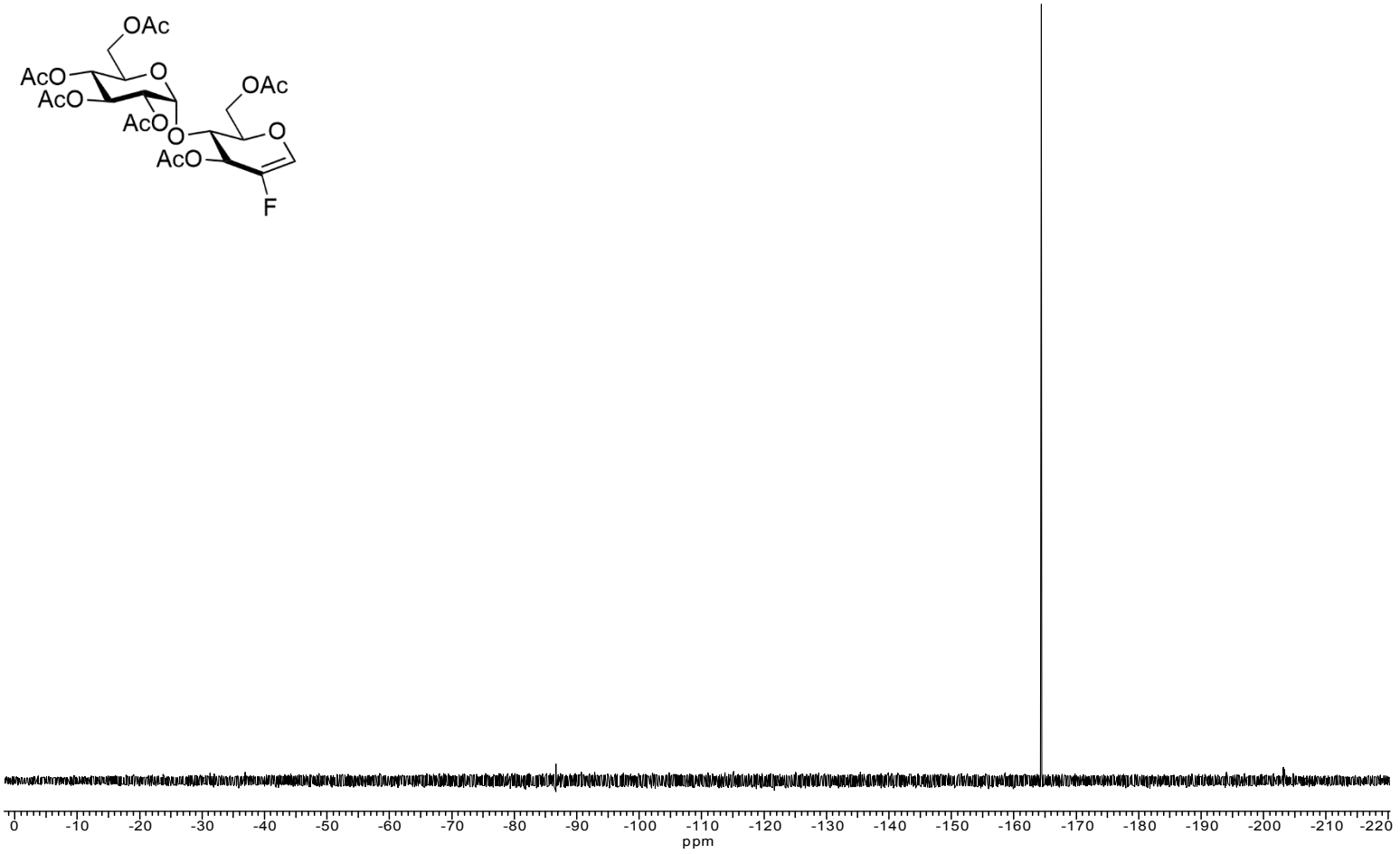


HMQC of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-glycal (1)

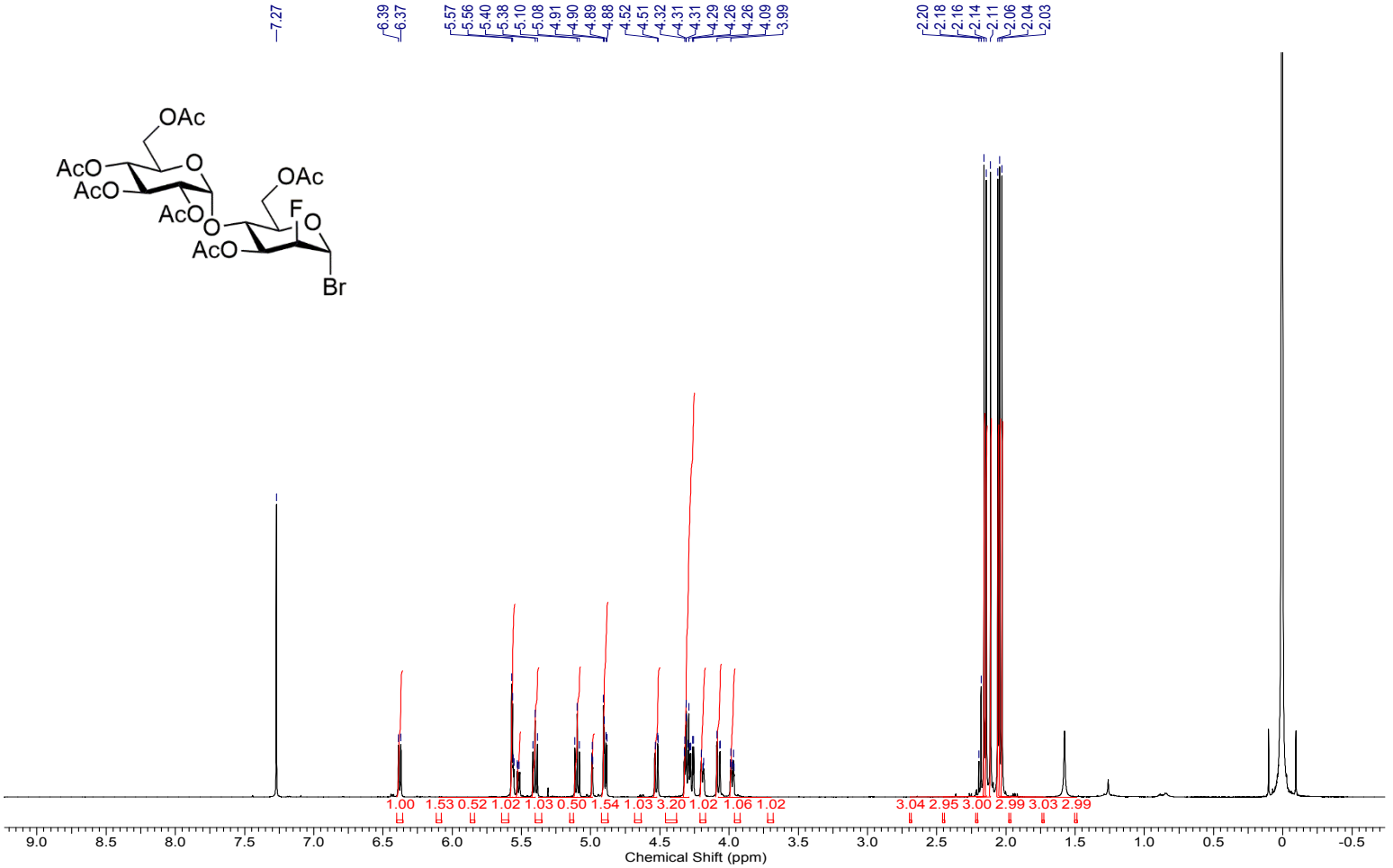




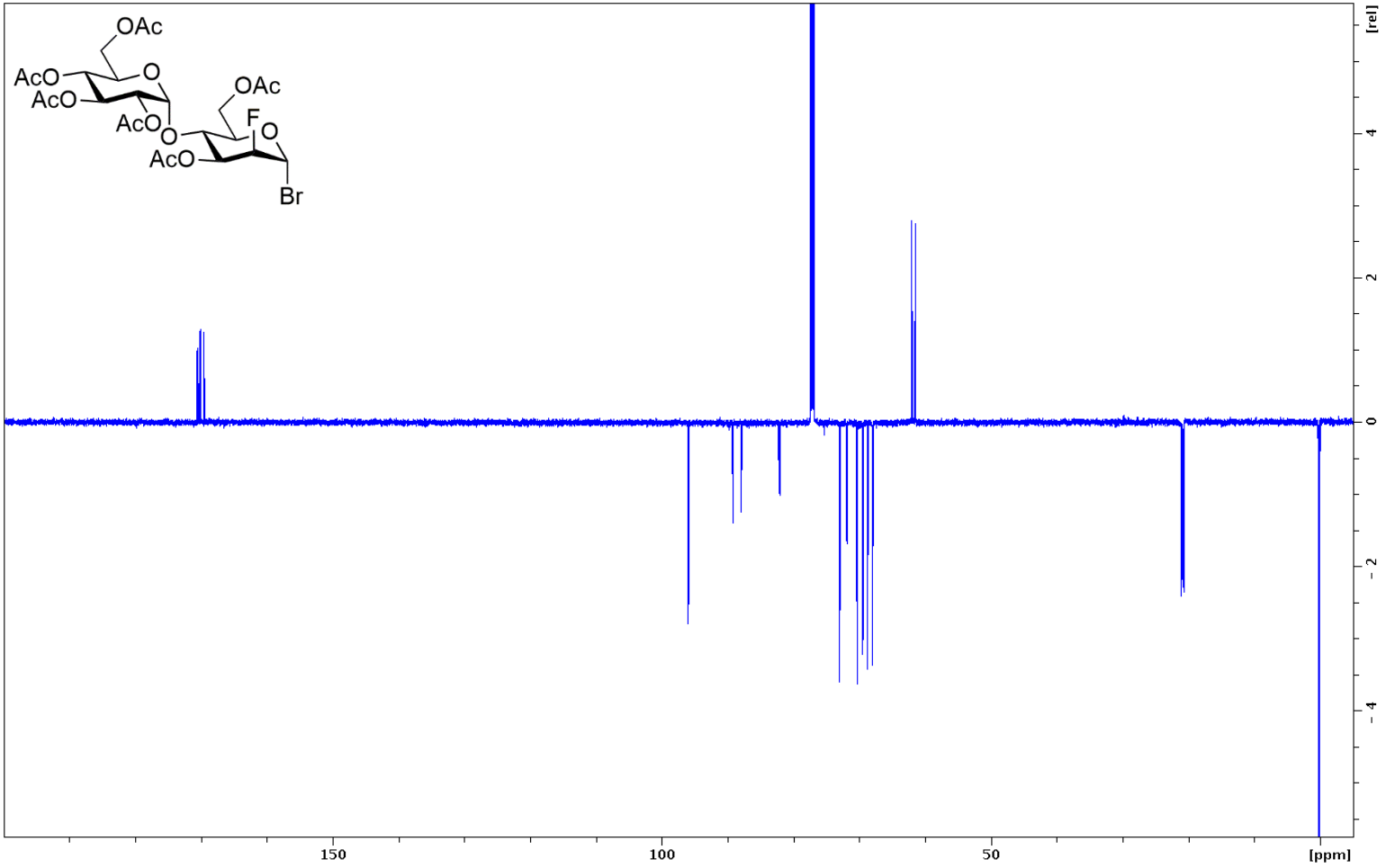
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-glycal (1)



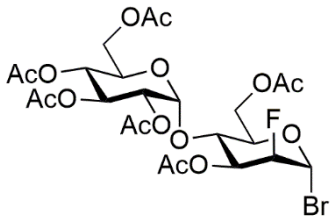
^{1}H NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (14)

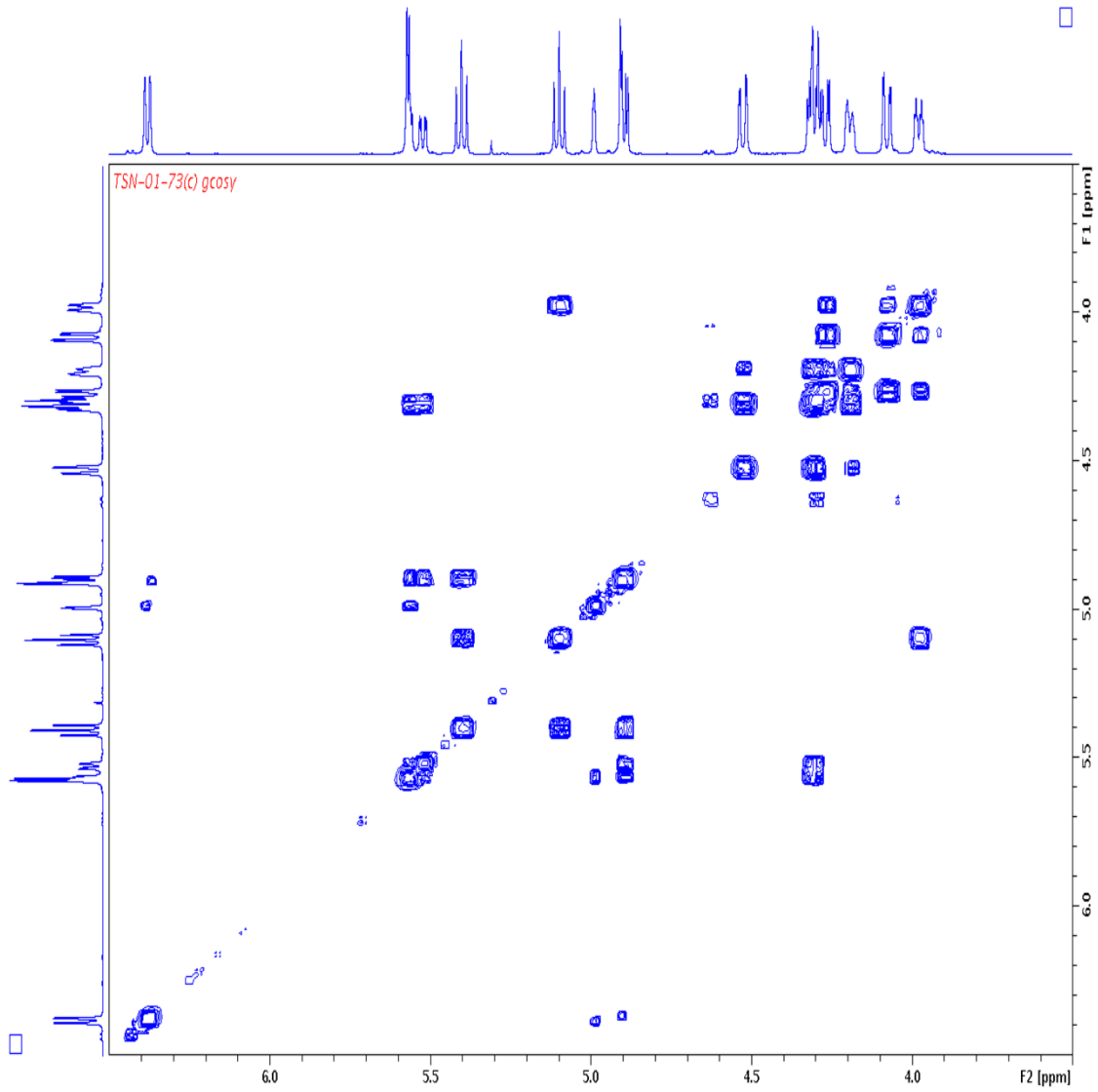


^{13}C NMR attached protein test (APT) experiment of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (14)

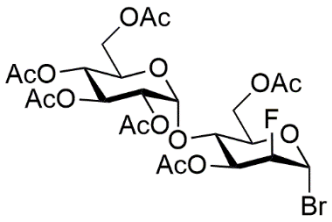


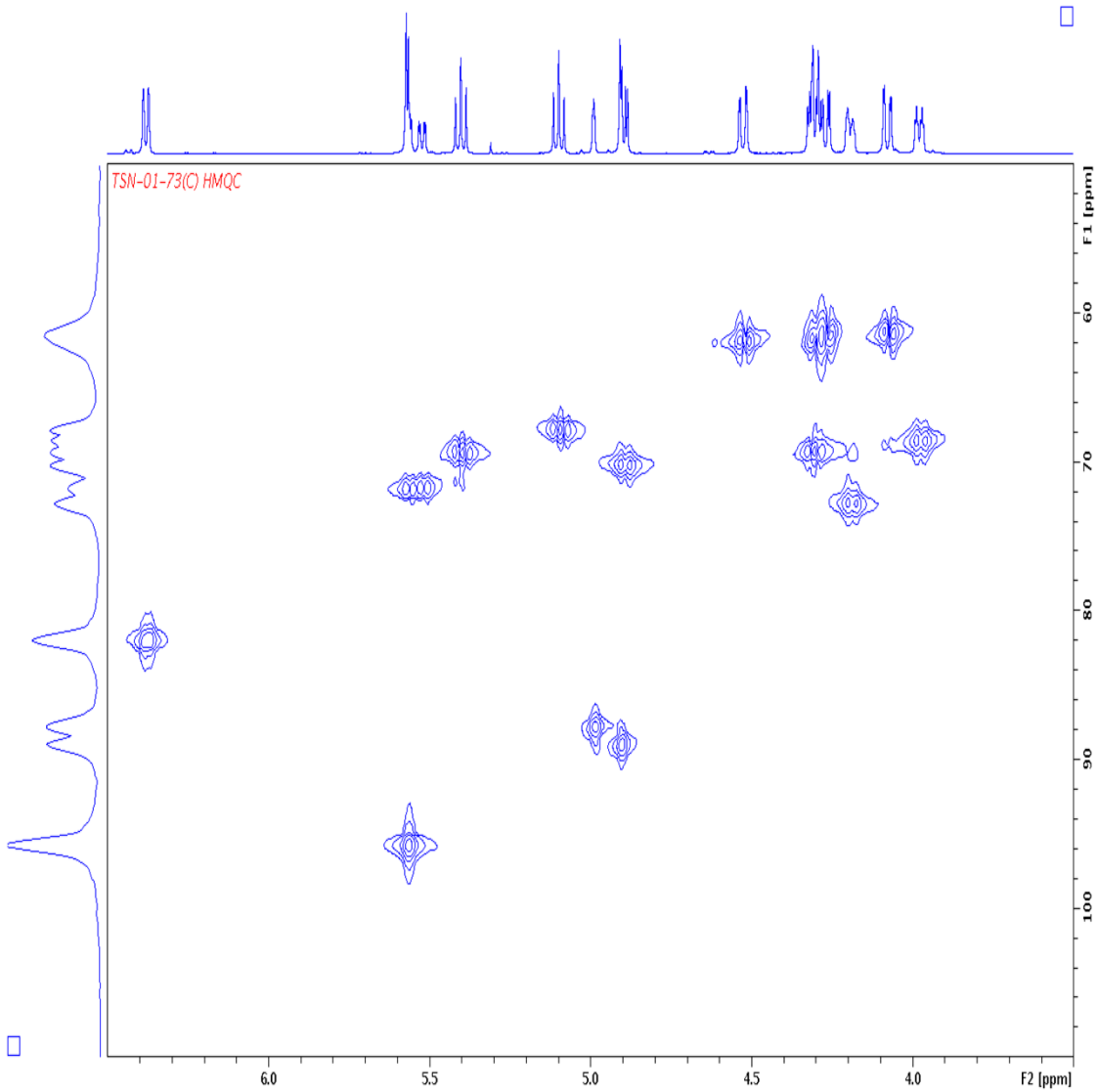
COSY of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (14)



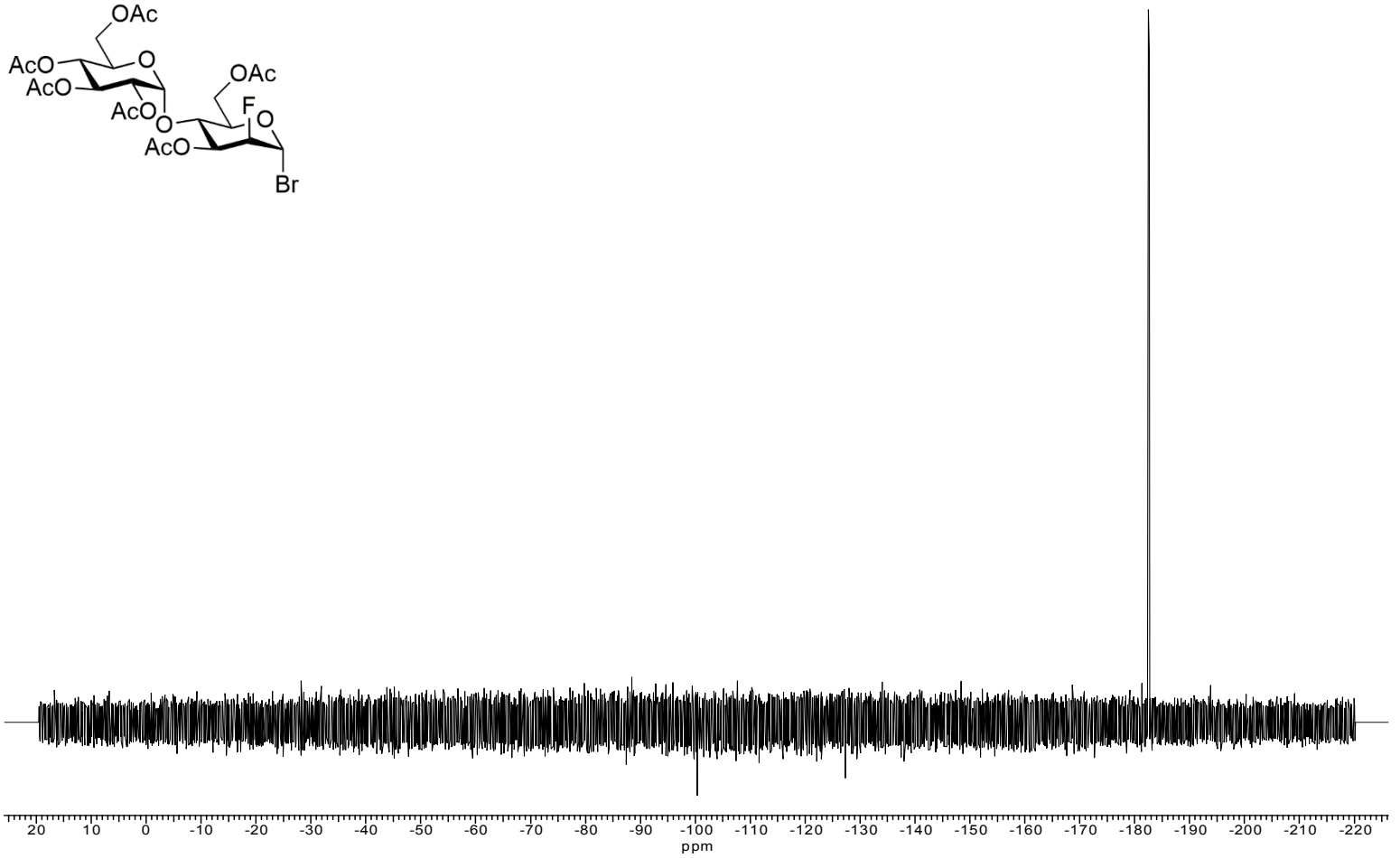


HMQC of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (14)

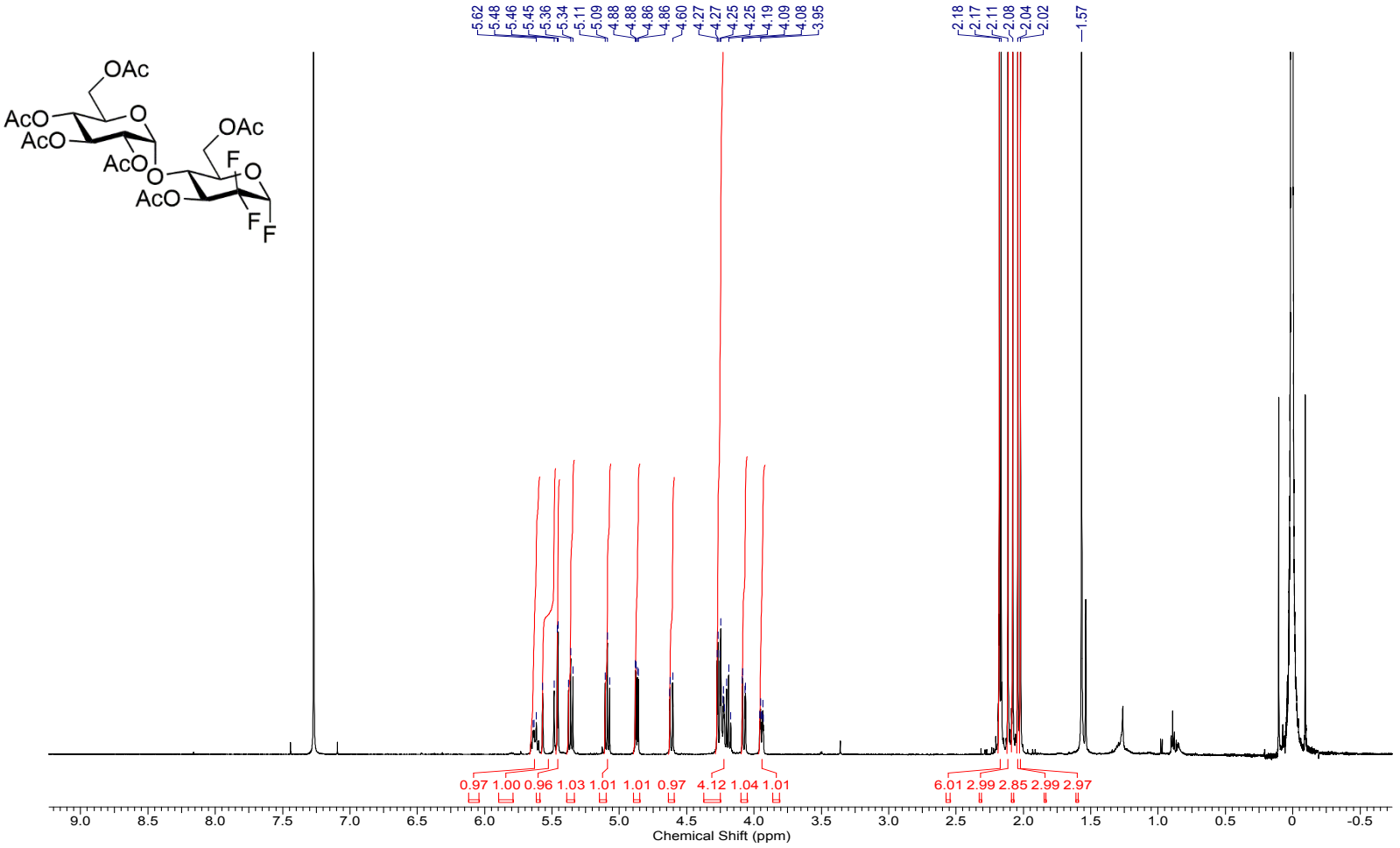




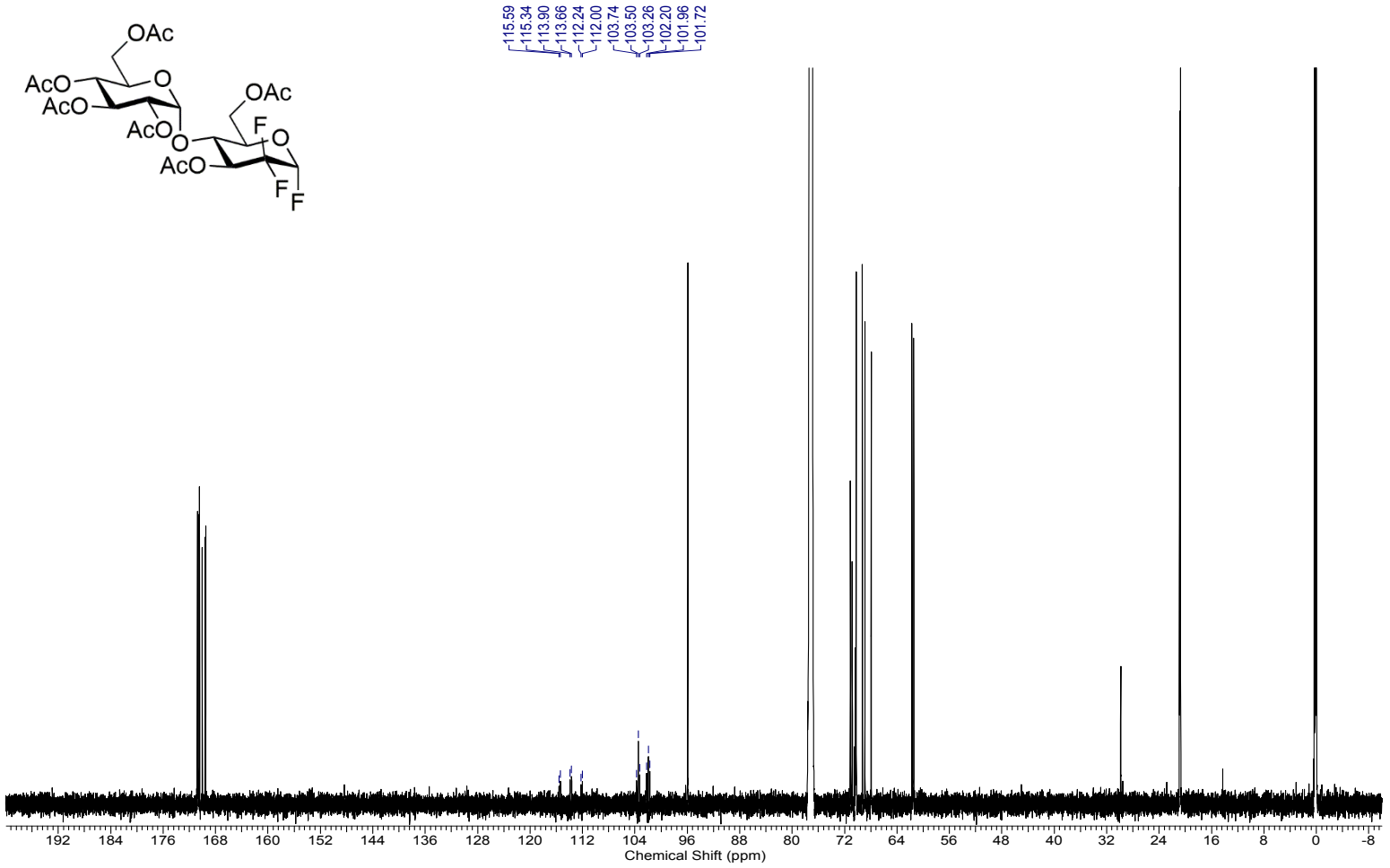
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2-fluoro-*α*-D-mannopyranosyl bromide (14)



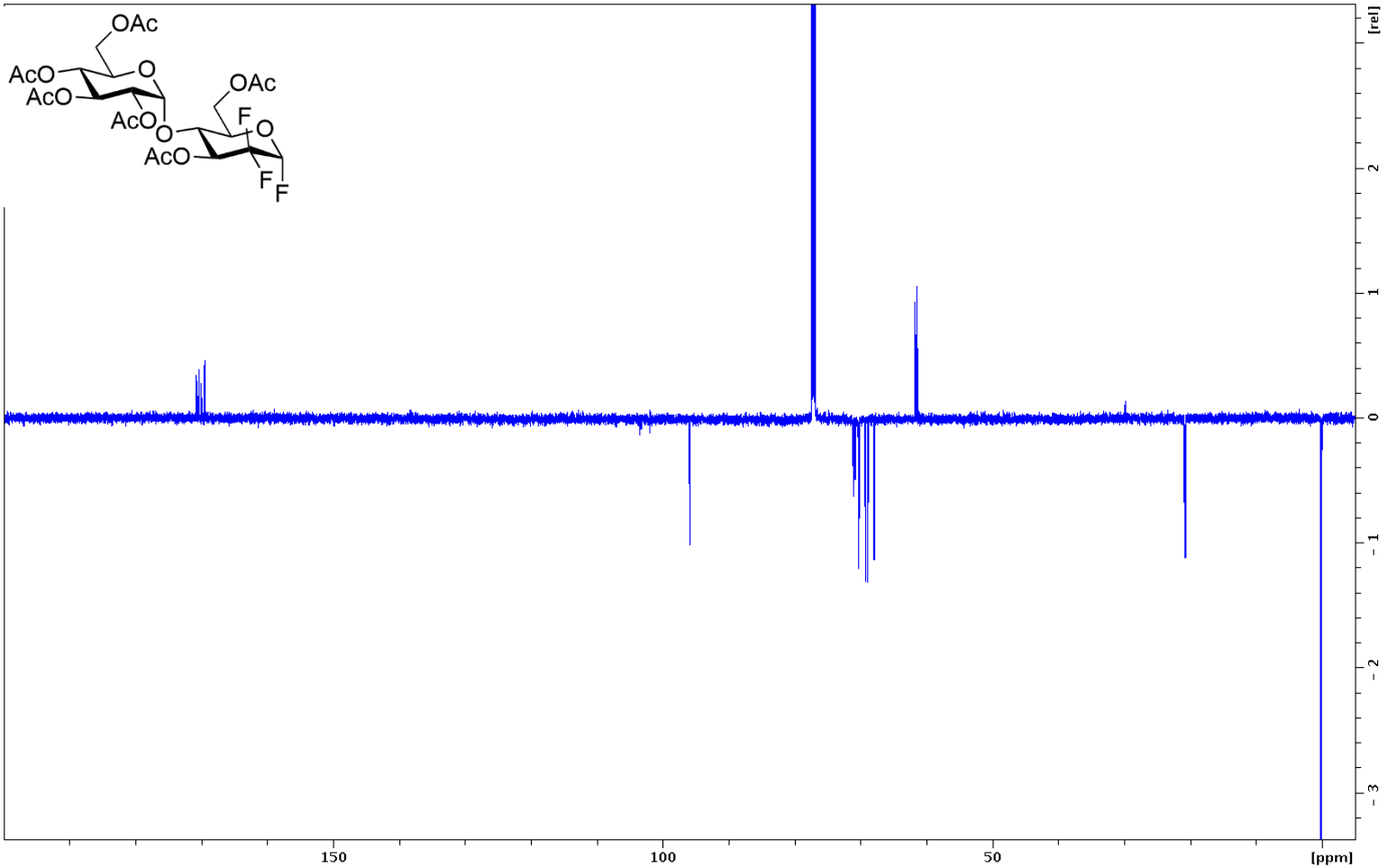
^{1}H NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (2)



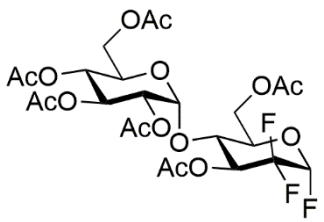
^{13} C NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (2)

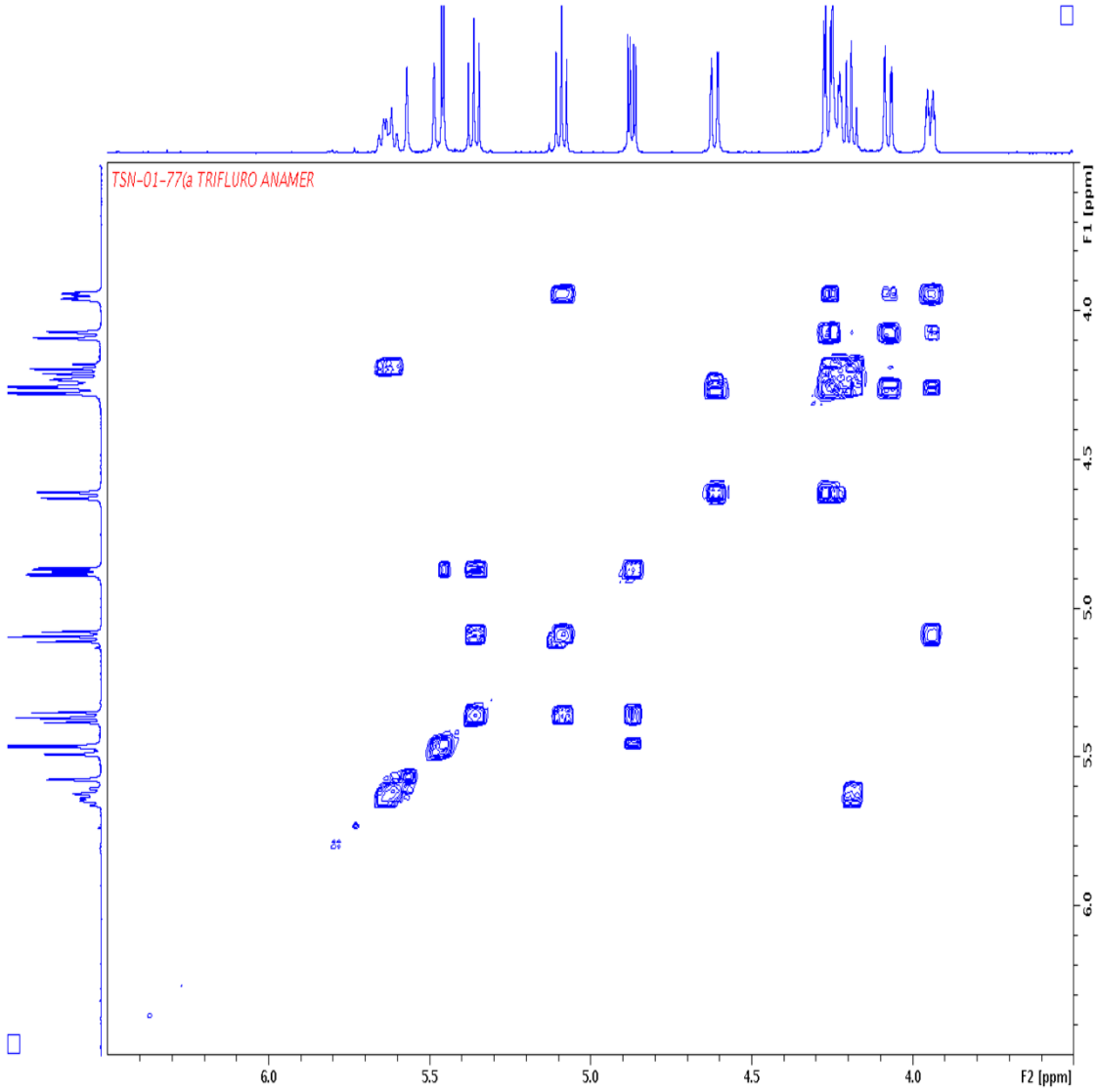


^{13}C NMR (APT) of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (2)

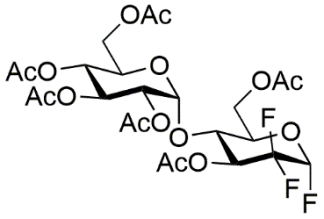


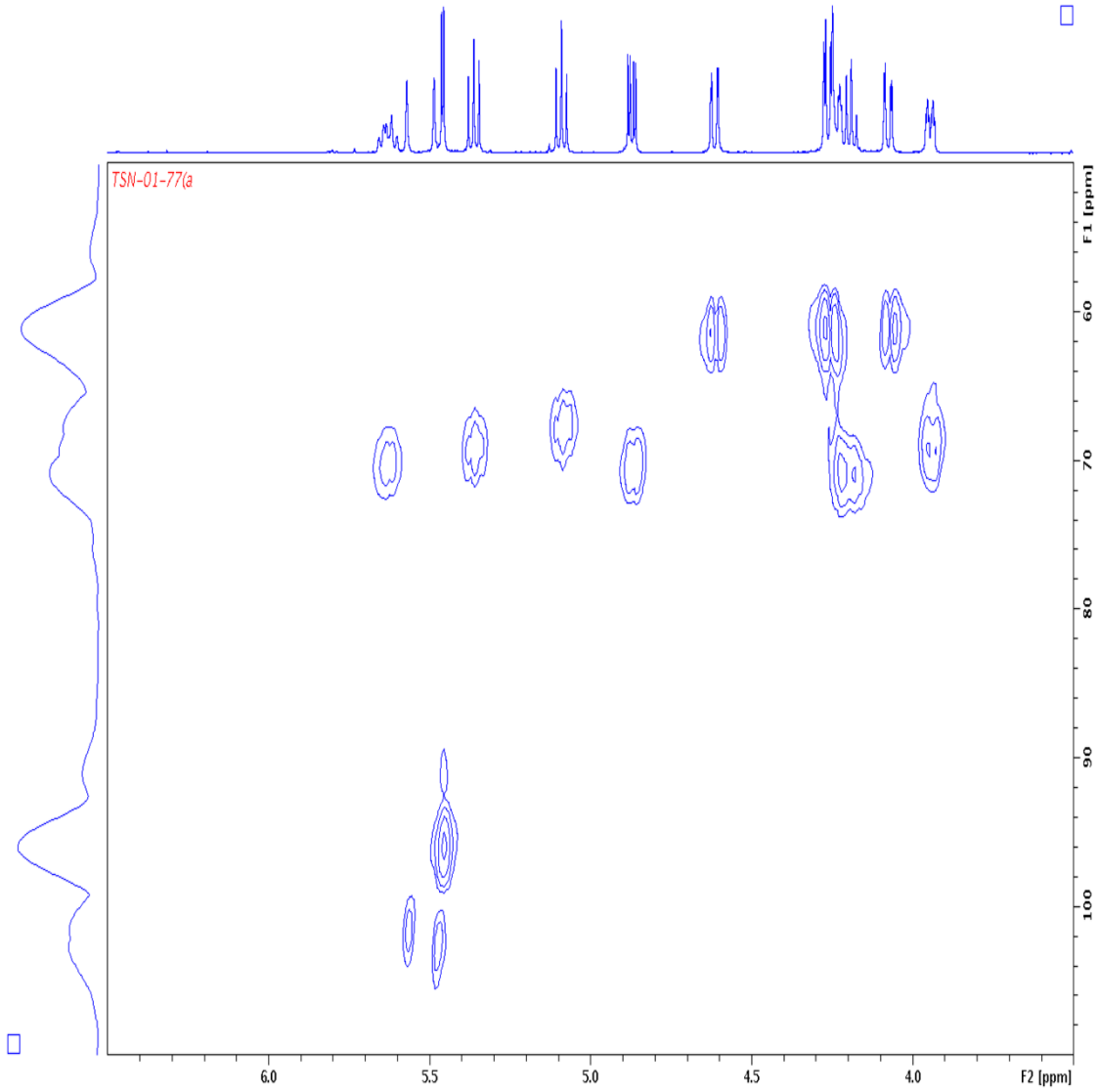
COSY of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (2)



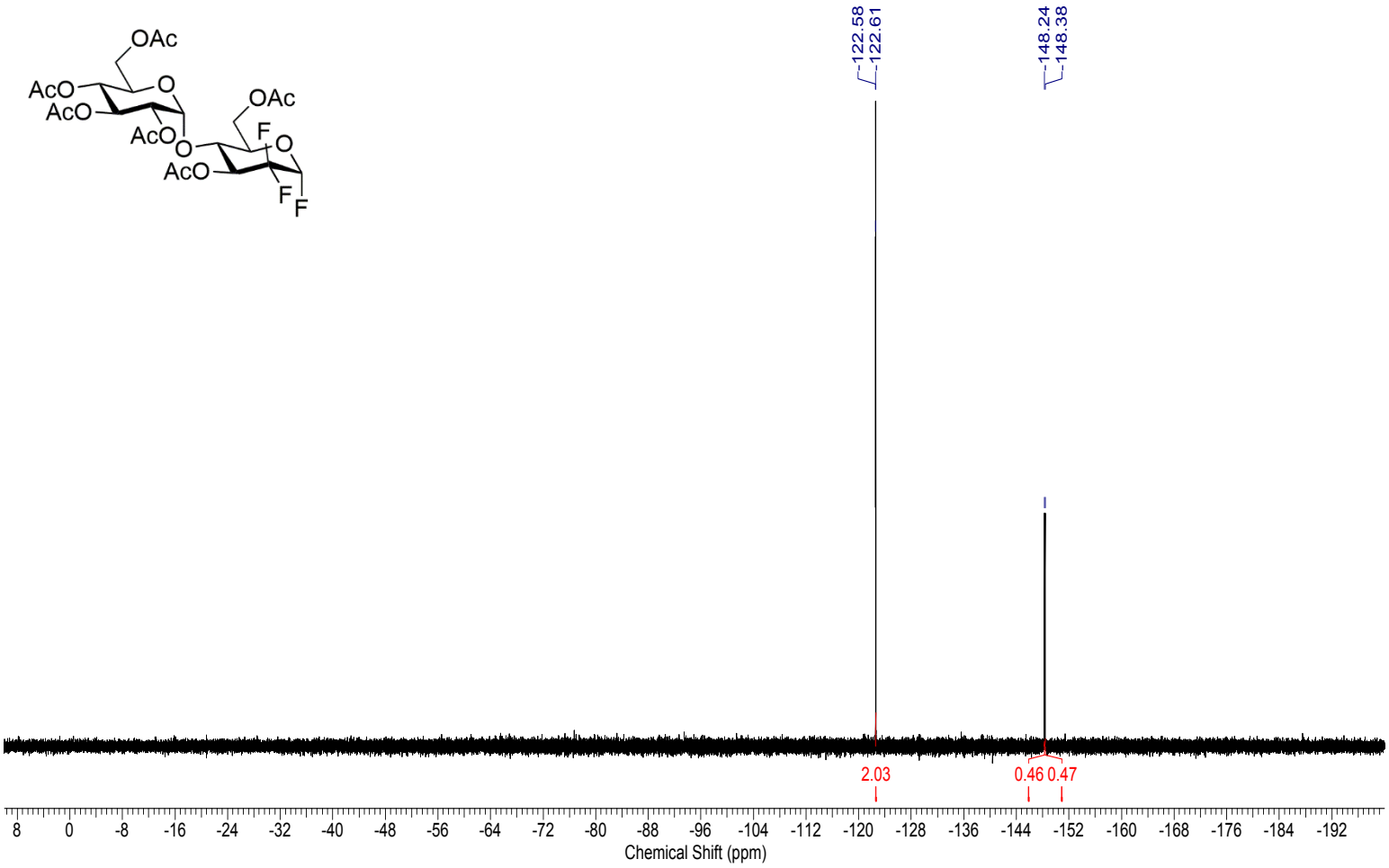


HMQC of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (2)

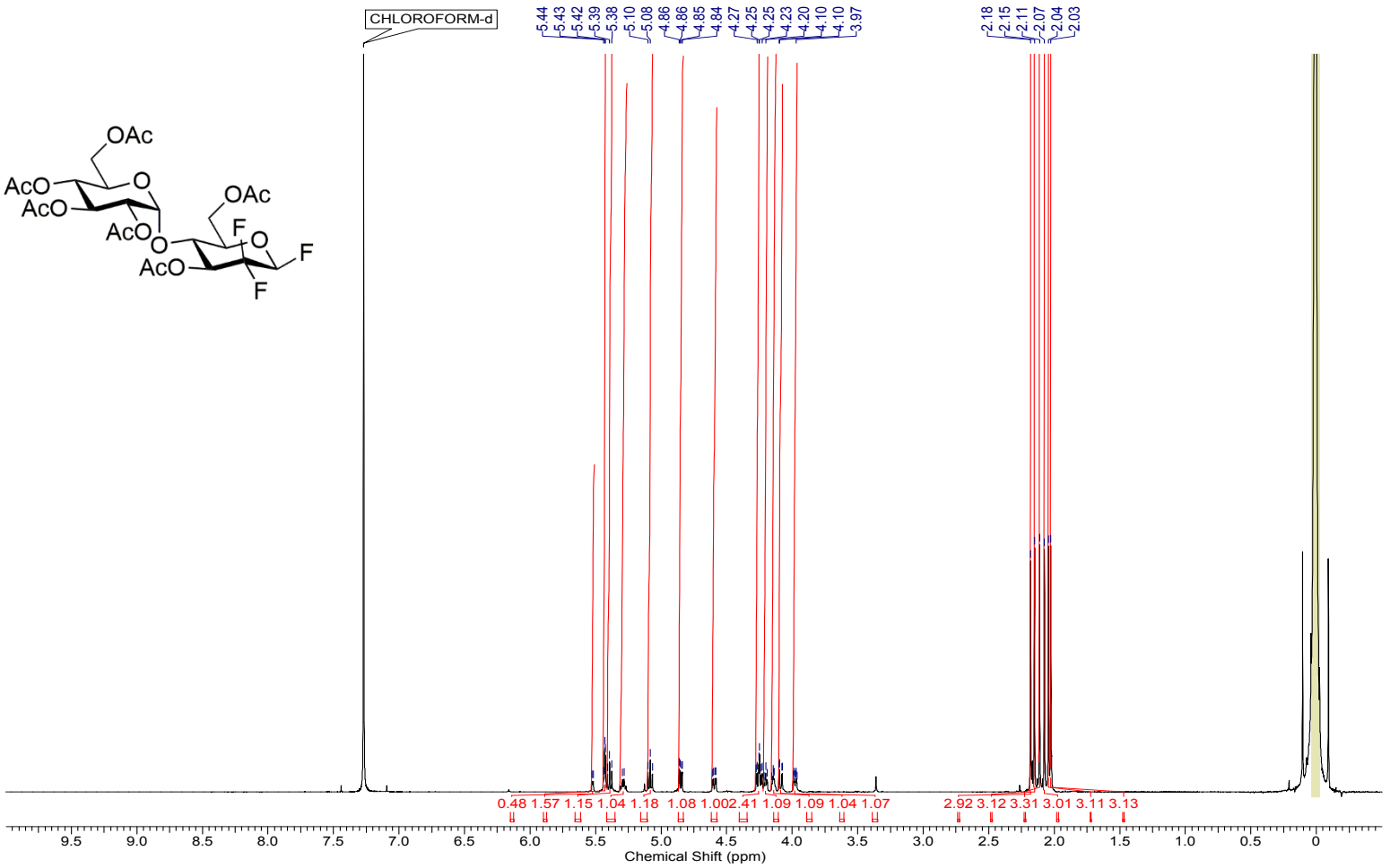




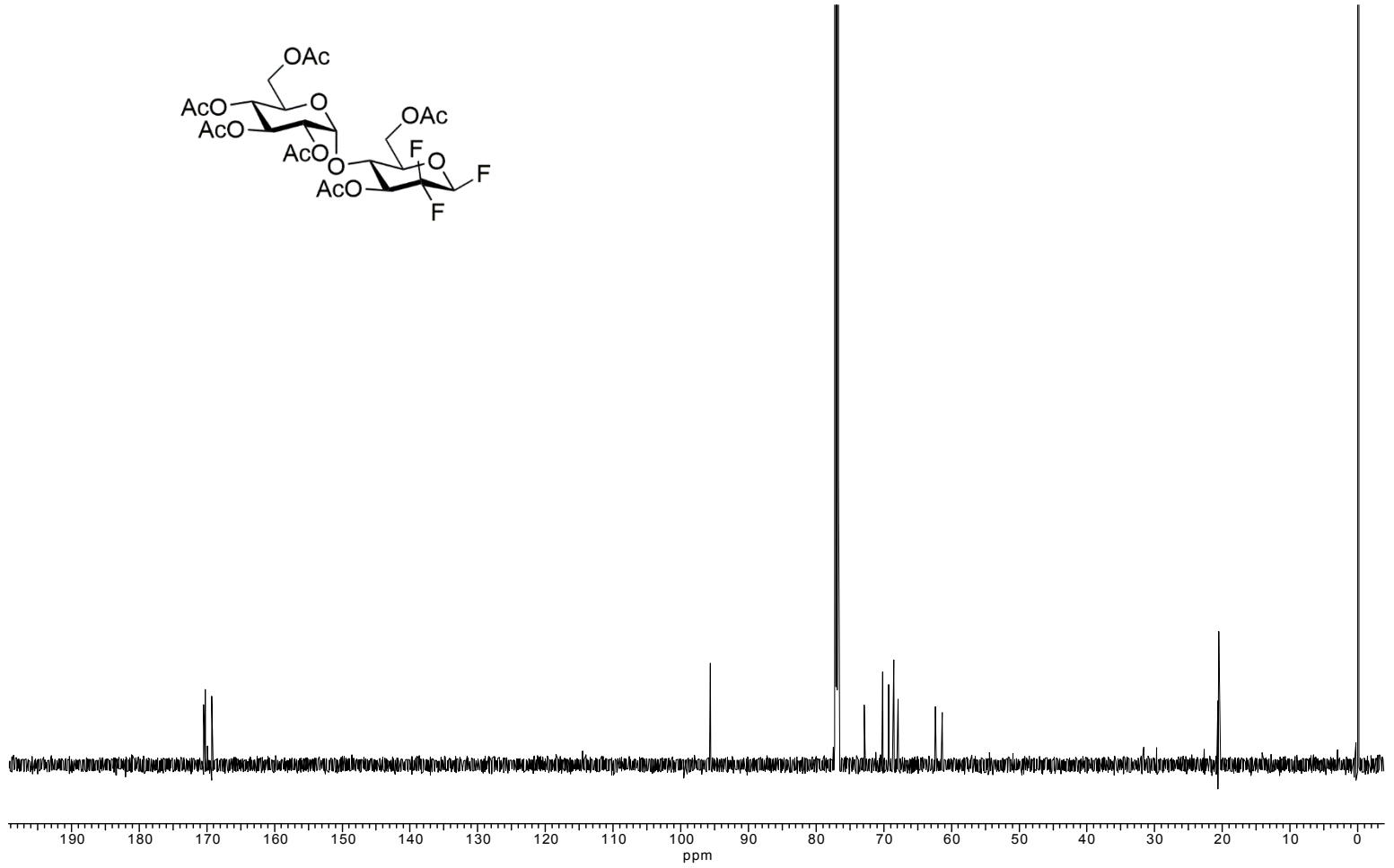
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (2) (Vxrs400 MHz)



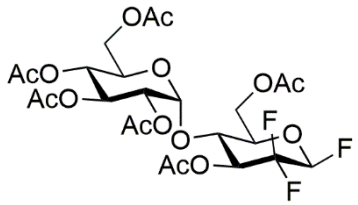
^{1}H NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (3)

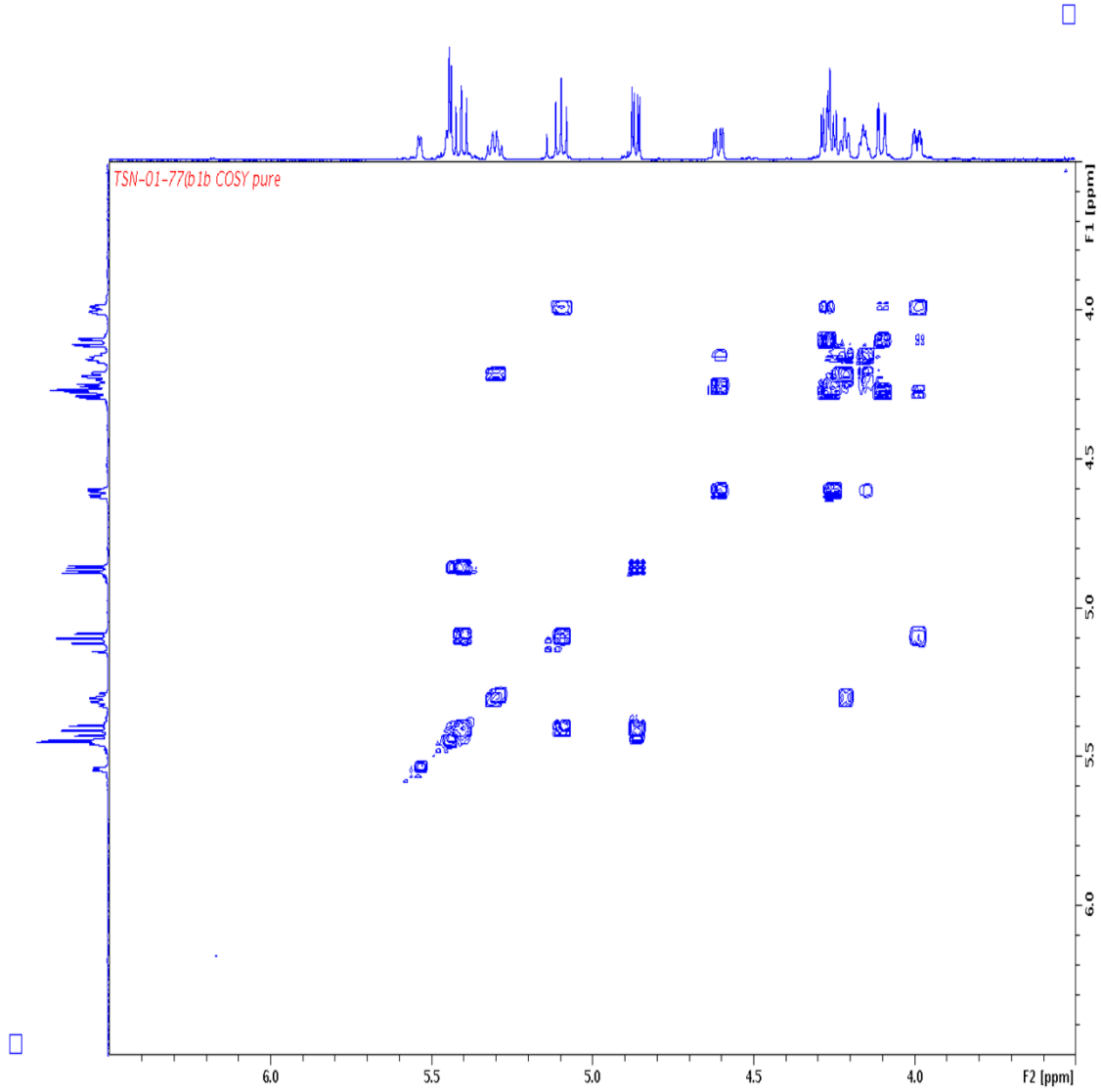


^{13} C NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (3)

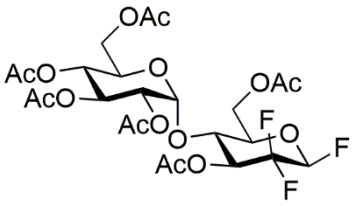


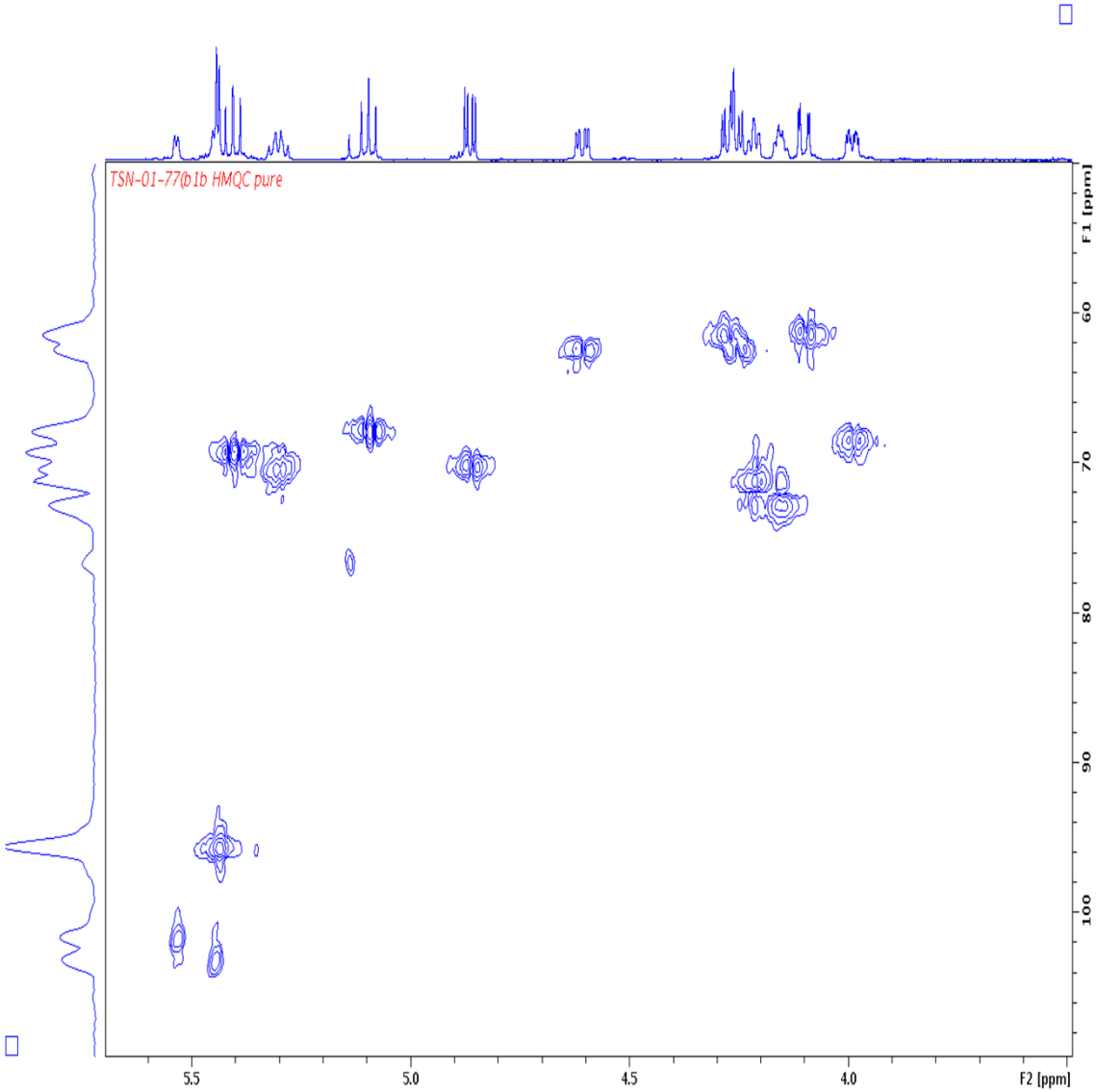
COSY of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (3)



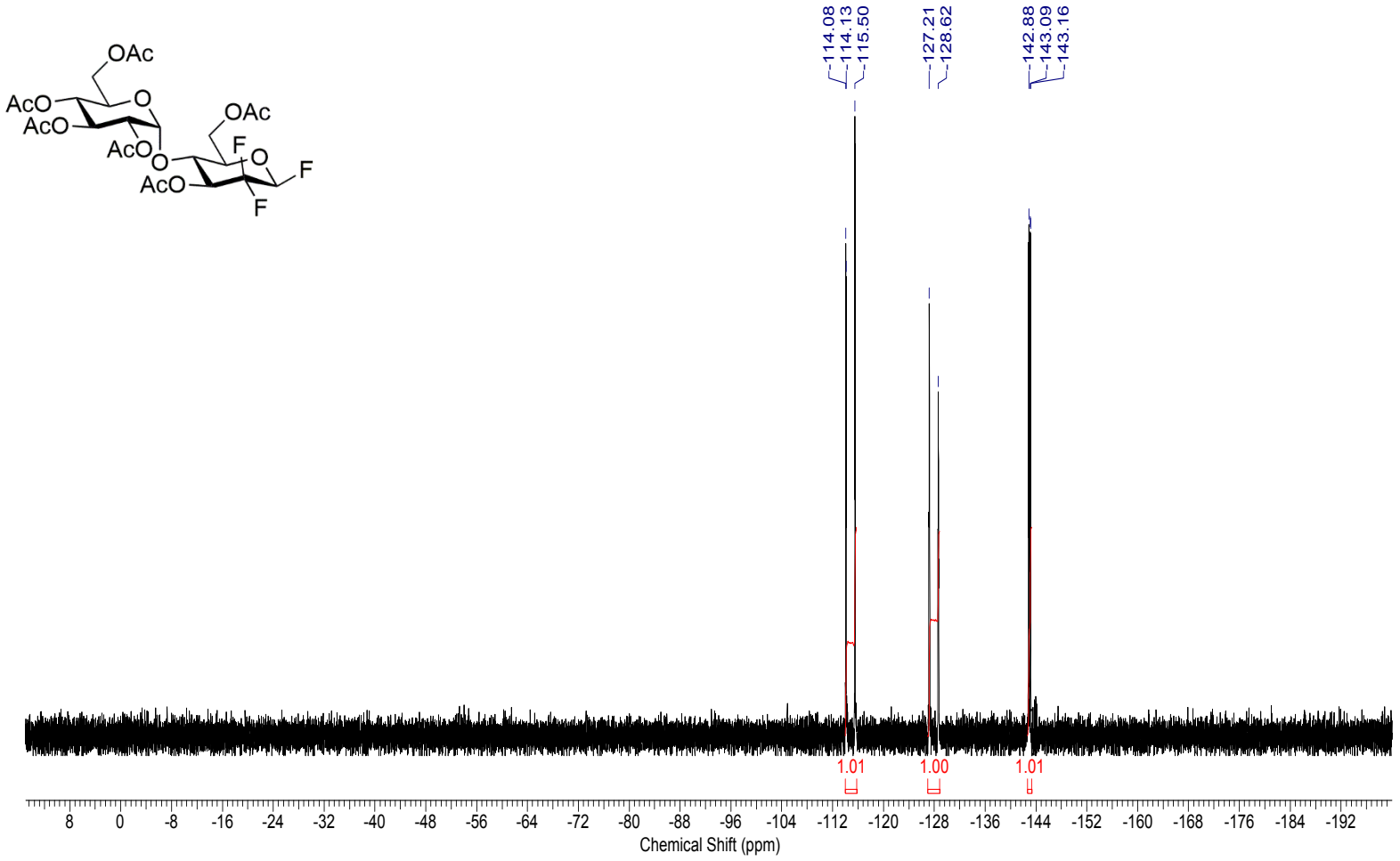


HMQC of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (3)

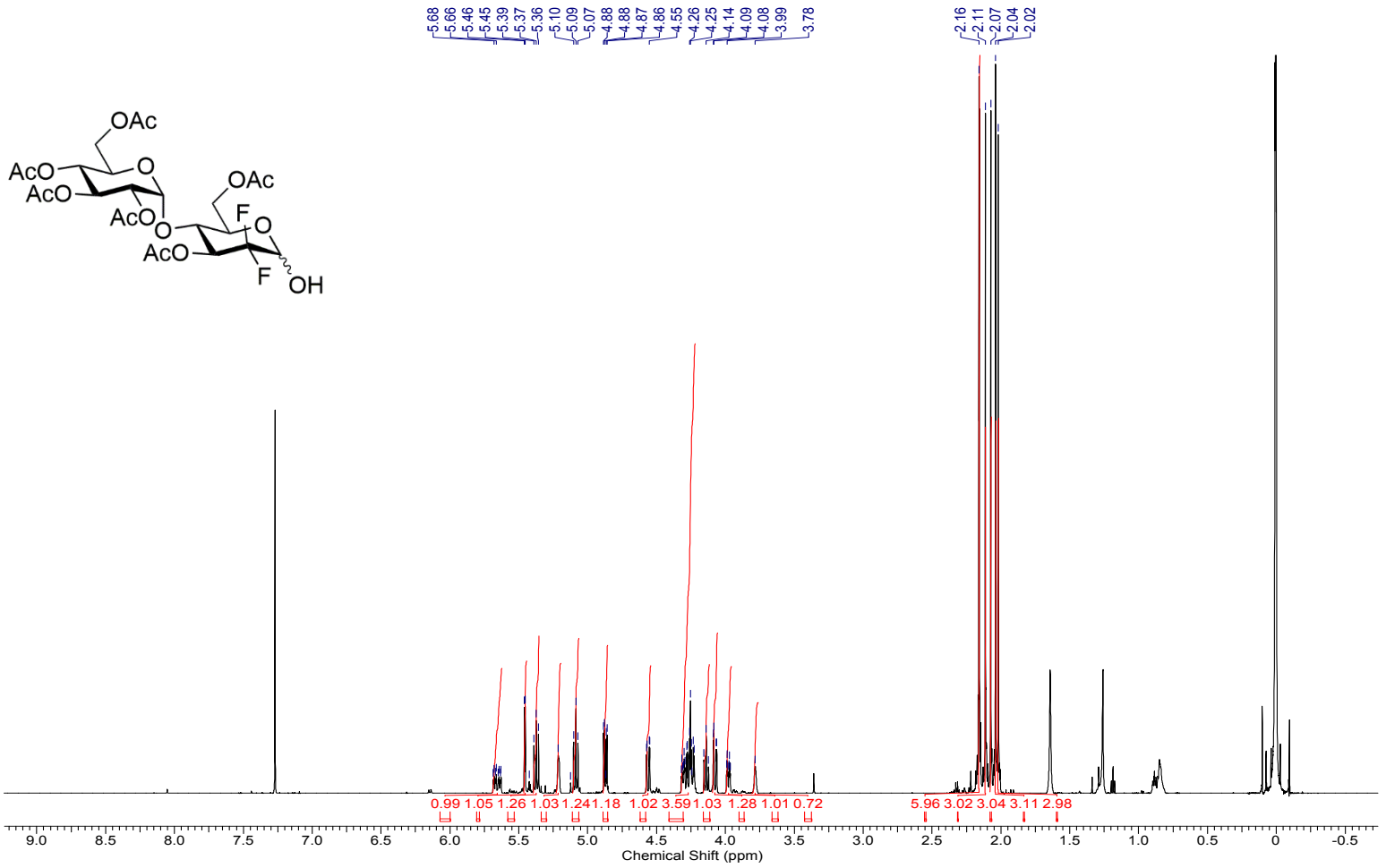




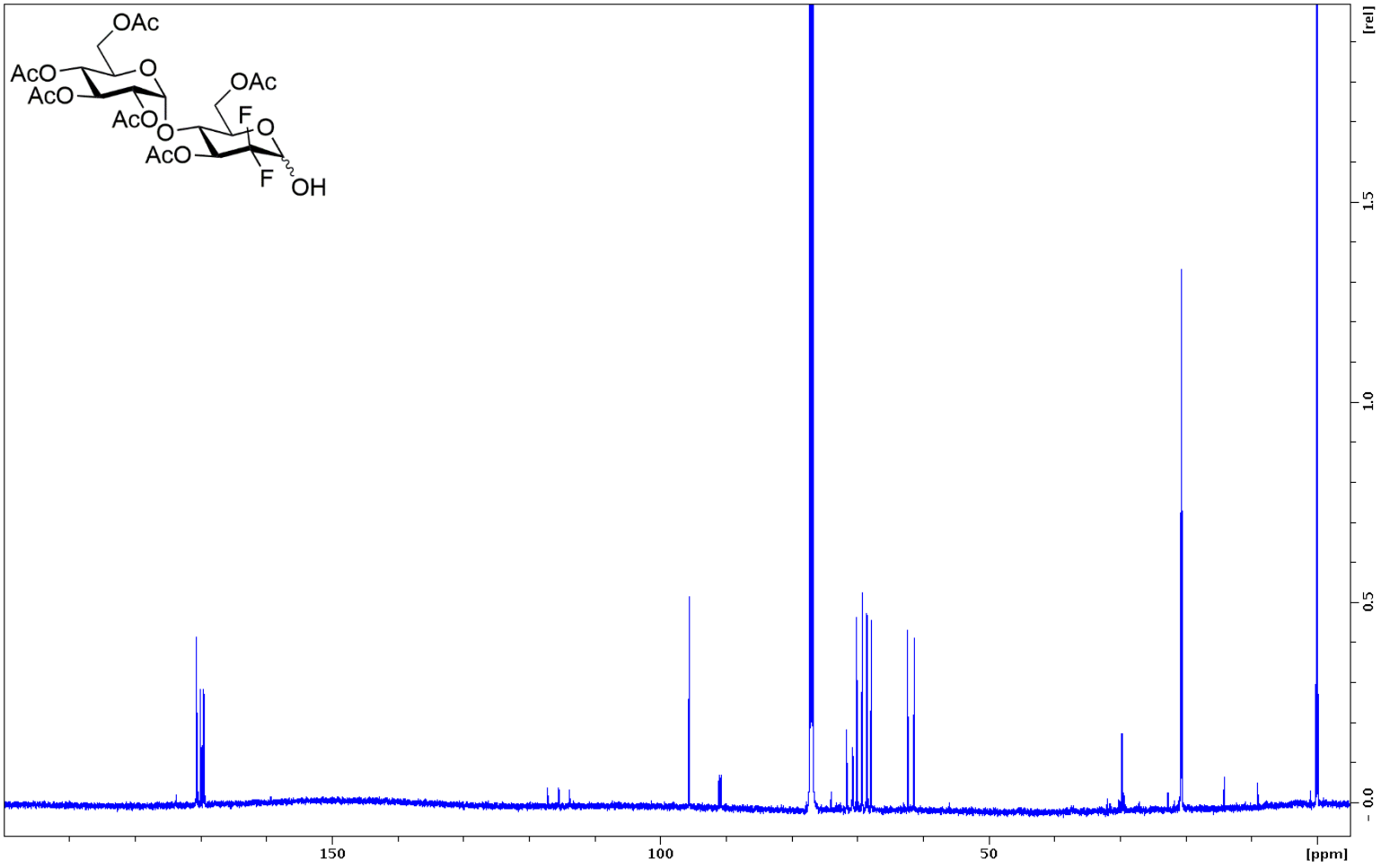
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (3) (Gemini 200MHz)



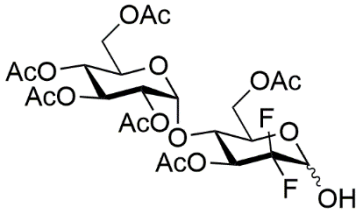
^{1}H NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro- *α/β*-D-glucopyranose (4)

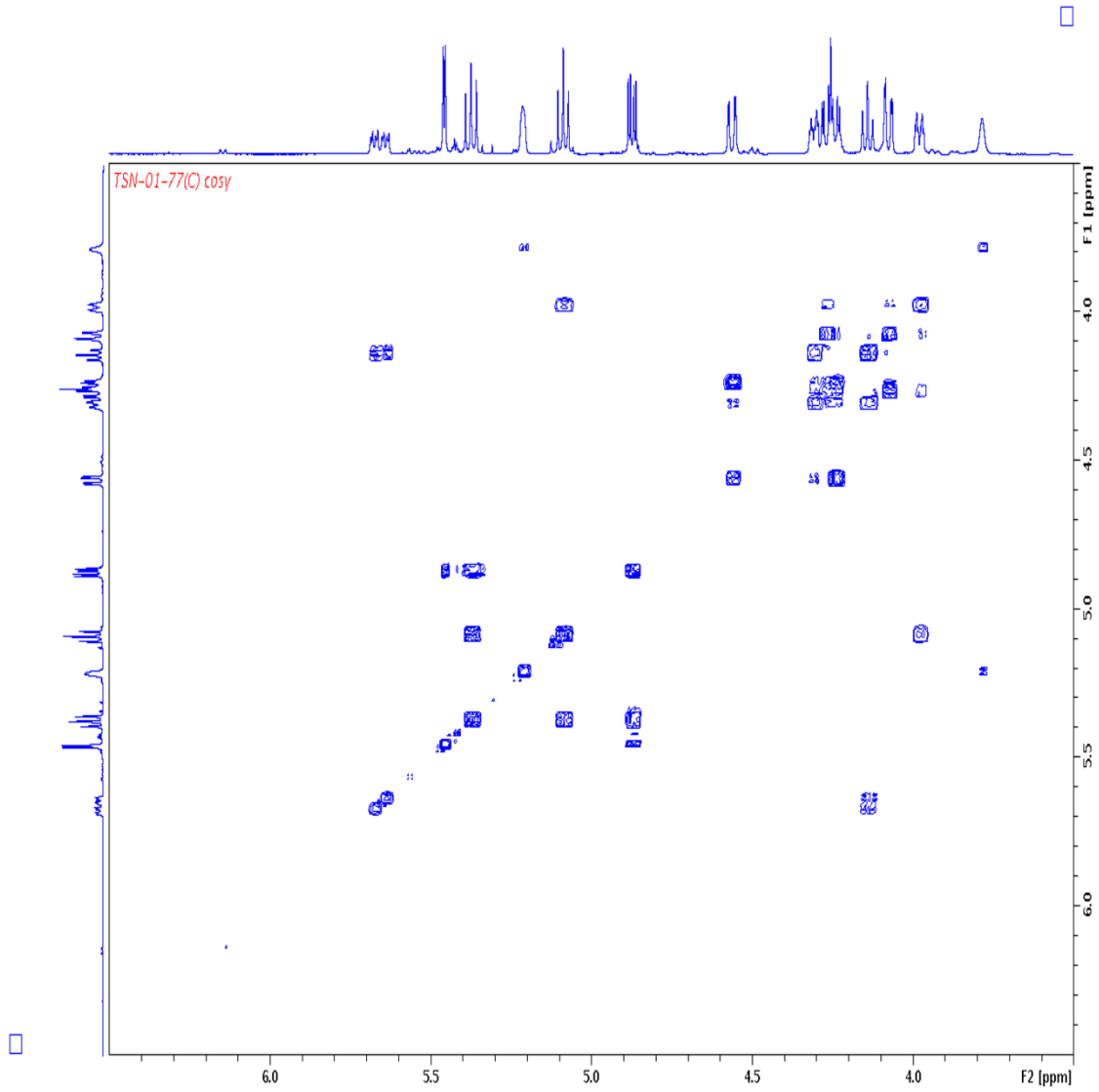


^{13}C NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro- *α/β*-D-glucopyranose (4)

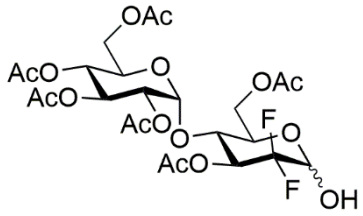


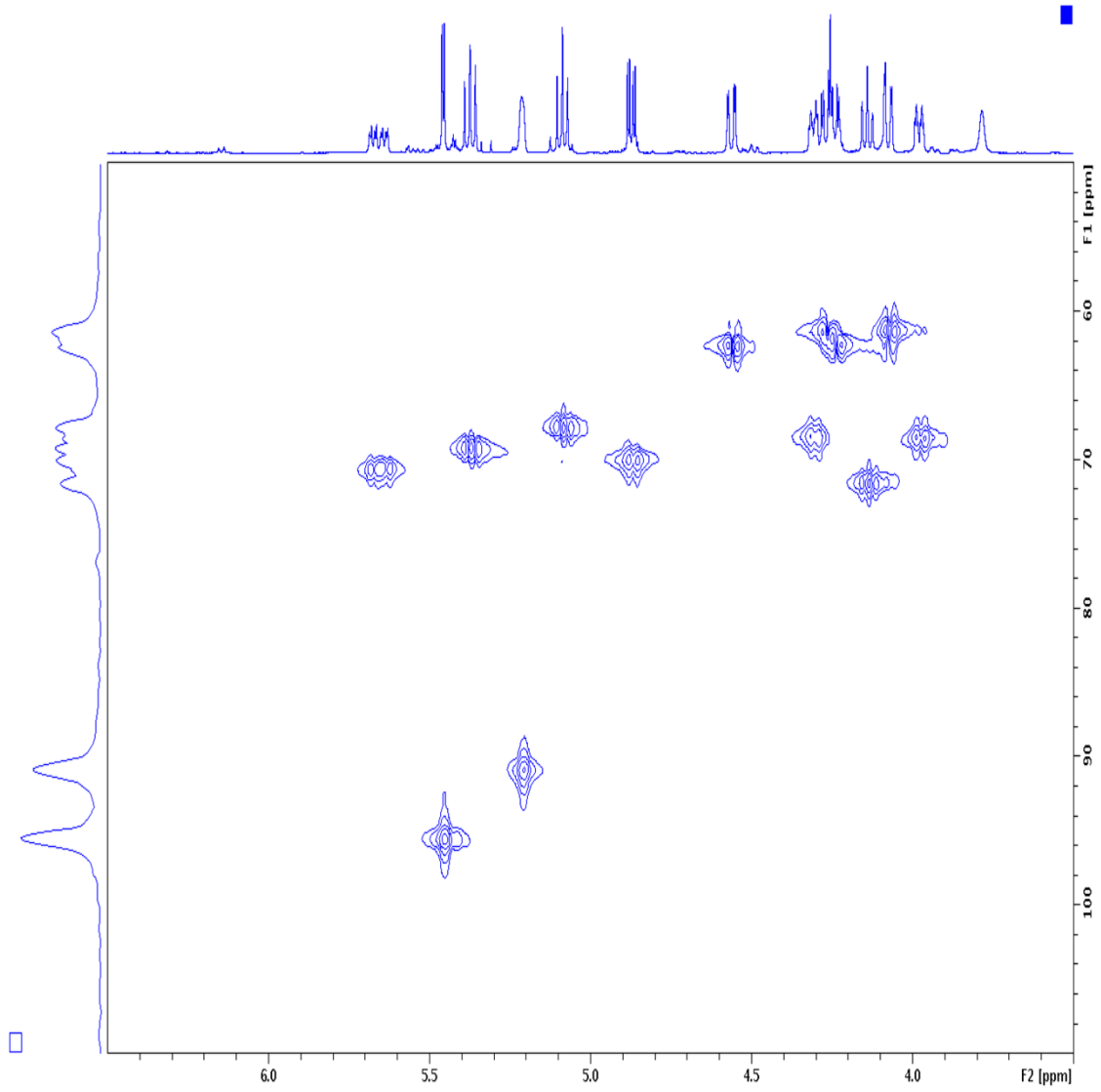
COSY of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro- *α/β*-D-glucopyranose (4)



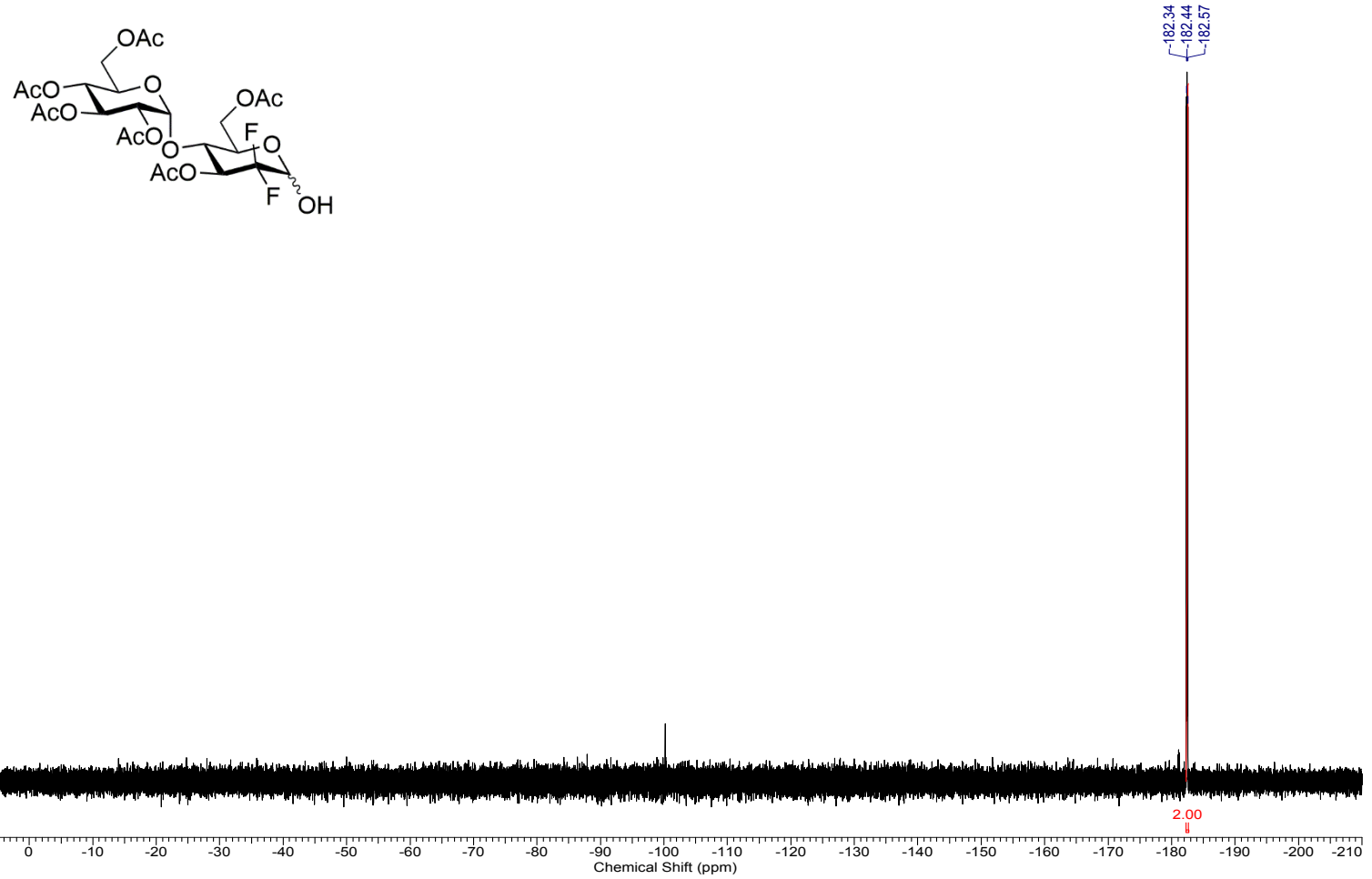


HMQC of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro- *α/β*-D-glucopyranose (4)

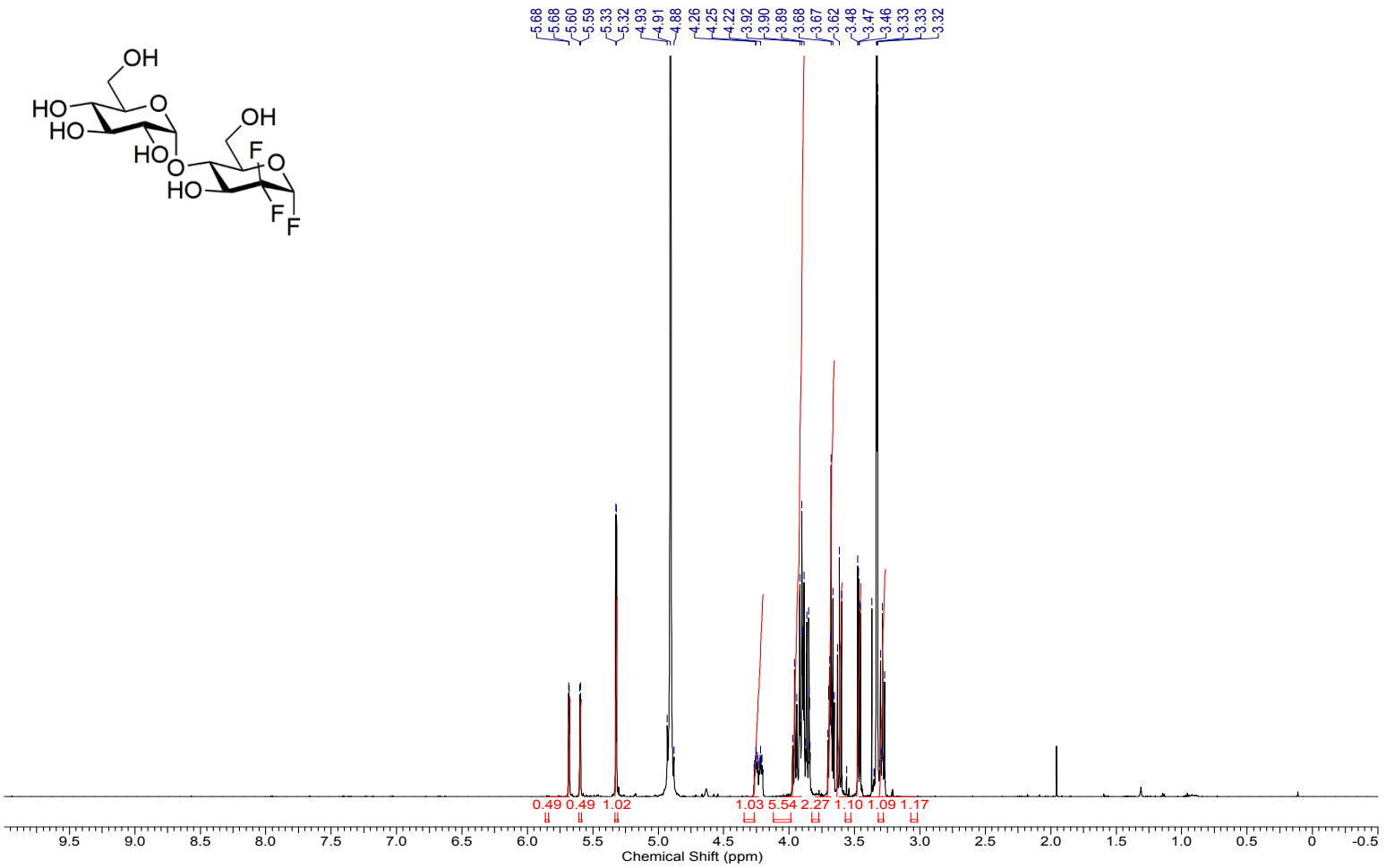




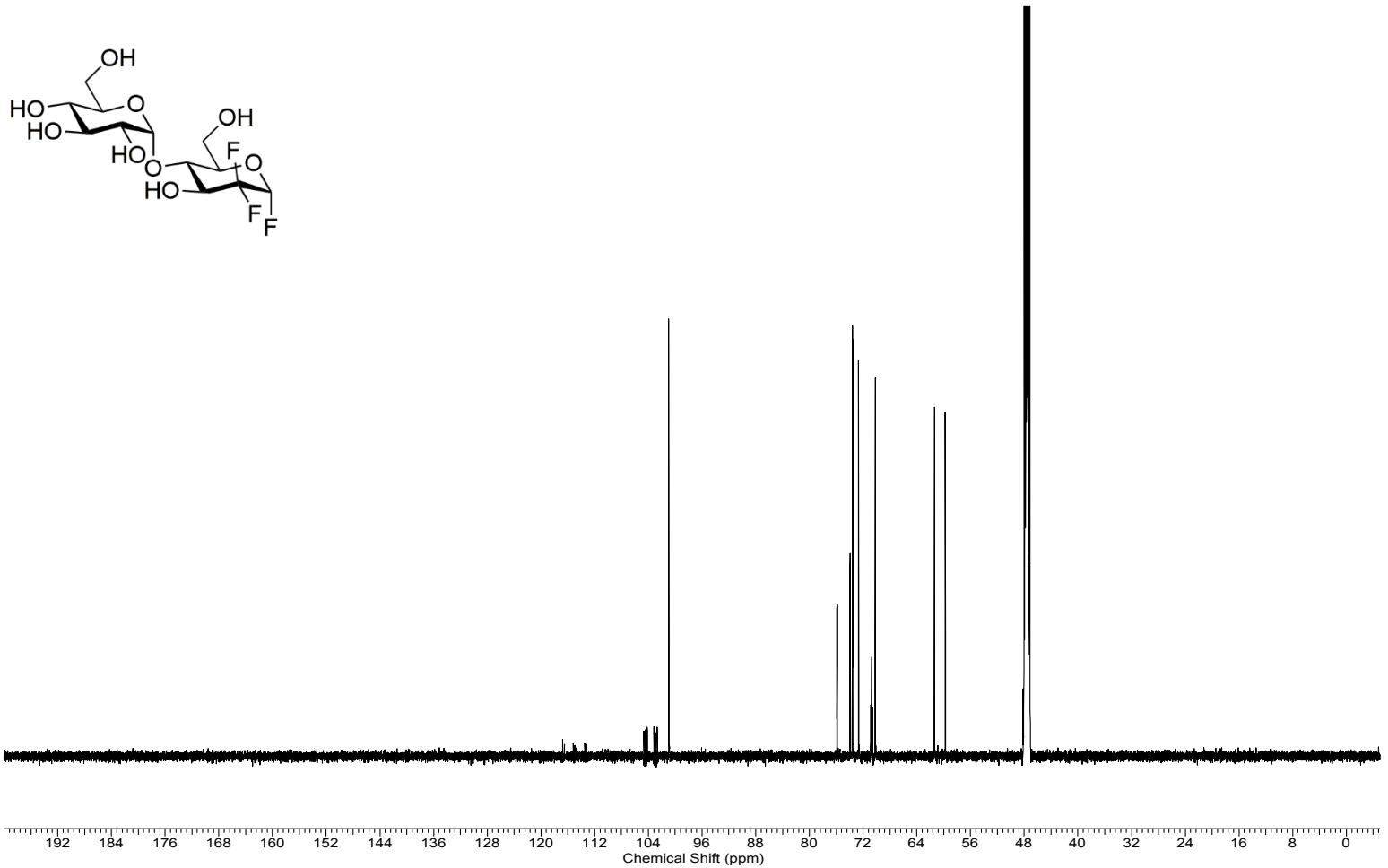
^{19}F NMR of compound 2',3',4',6'-Tetra-*O*-acetyl-*α*-D-glucopyranosyl-(1,4)-3,6-di-*O*-acetyl-2-deoxy-2,2-difluoro- *α/β*-D-glucopyranose (4)



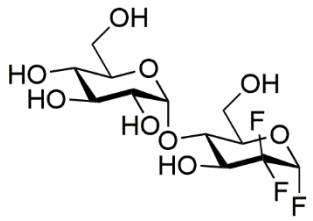
^{1}H NMR of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (5)

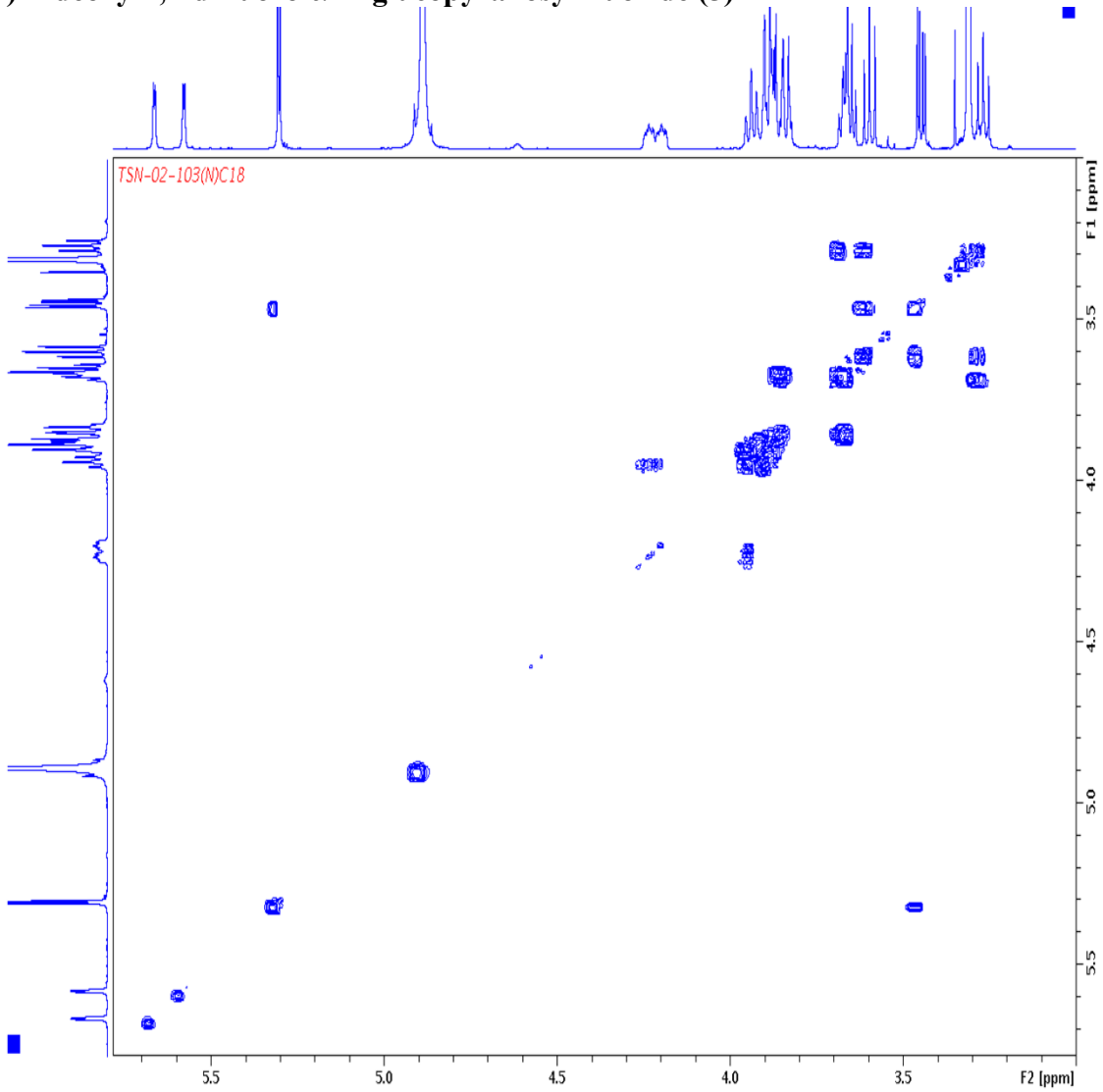


^{13}C NMR of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (5)

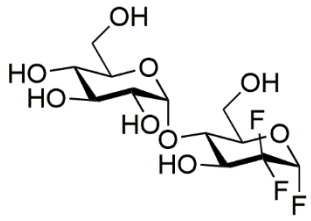


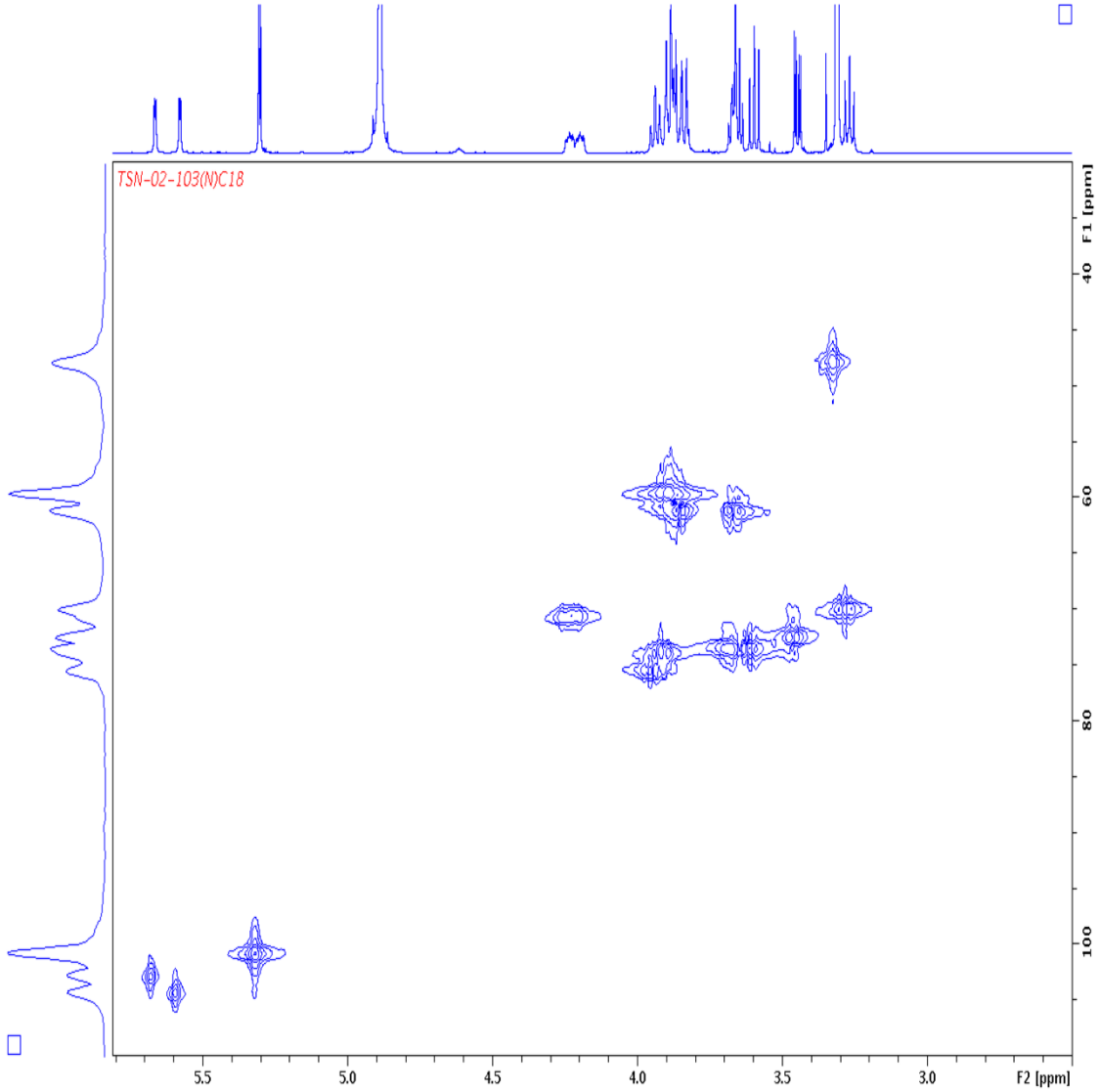
COSY of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (5)



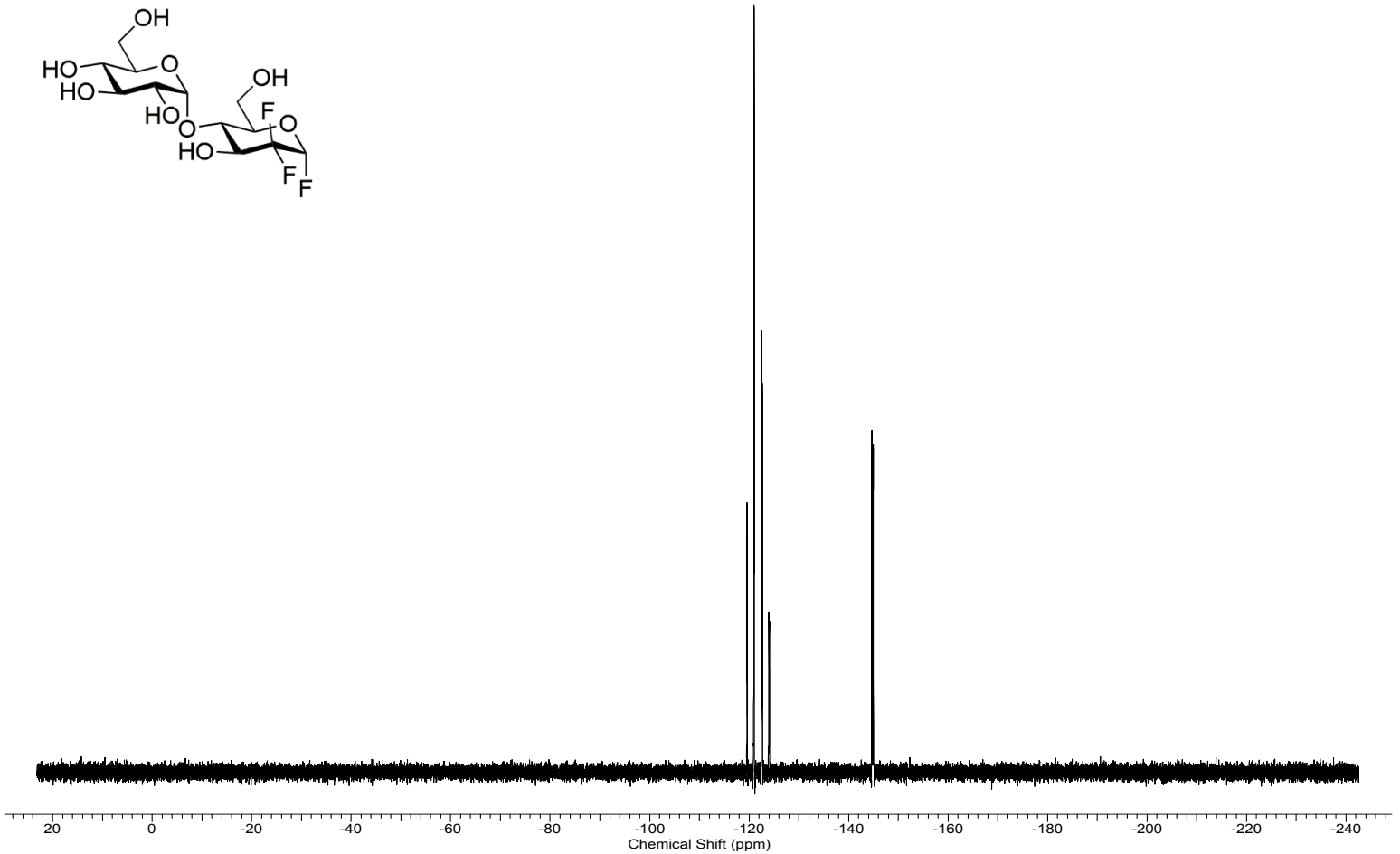


HMQC of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (5)

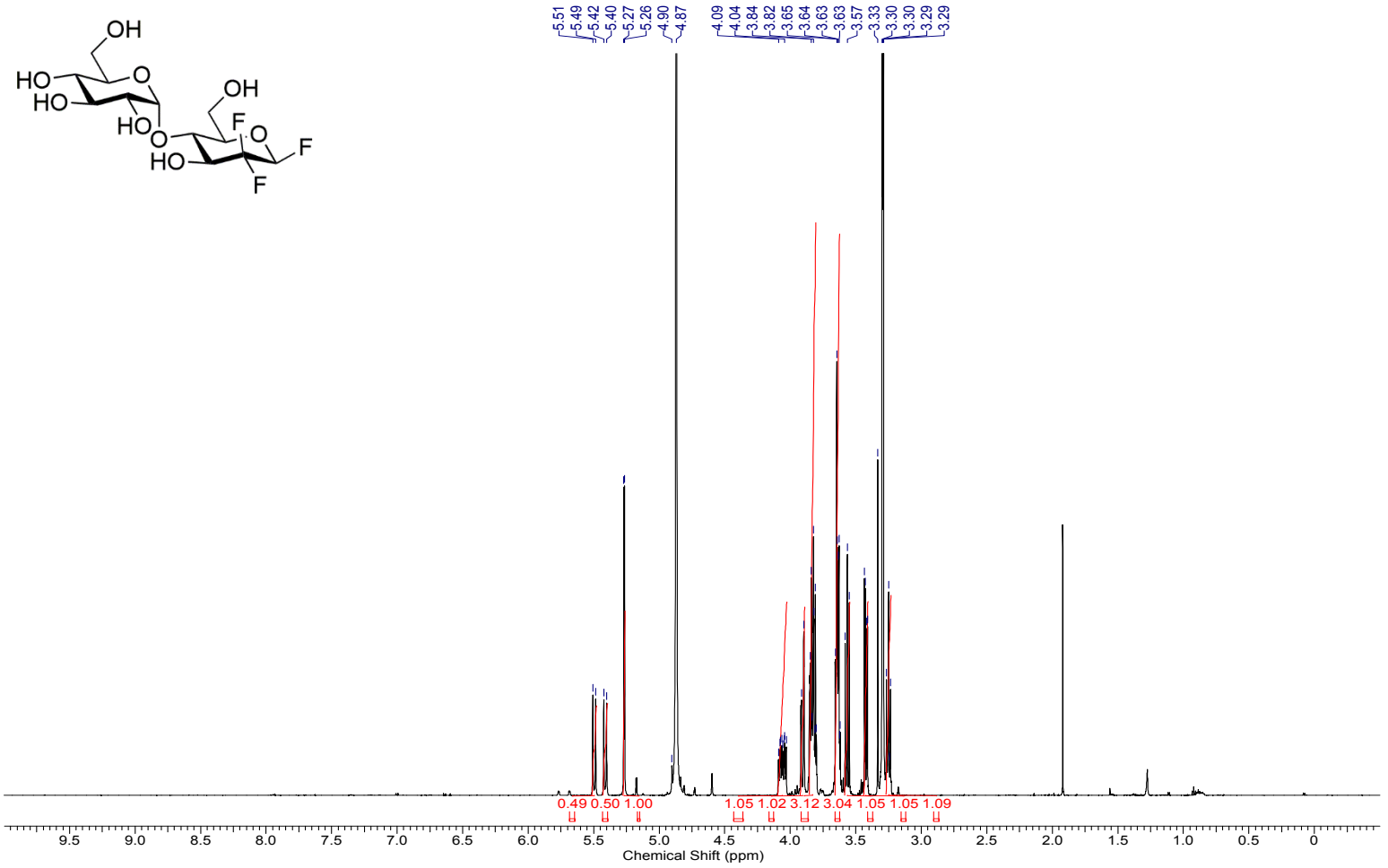




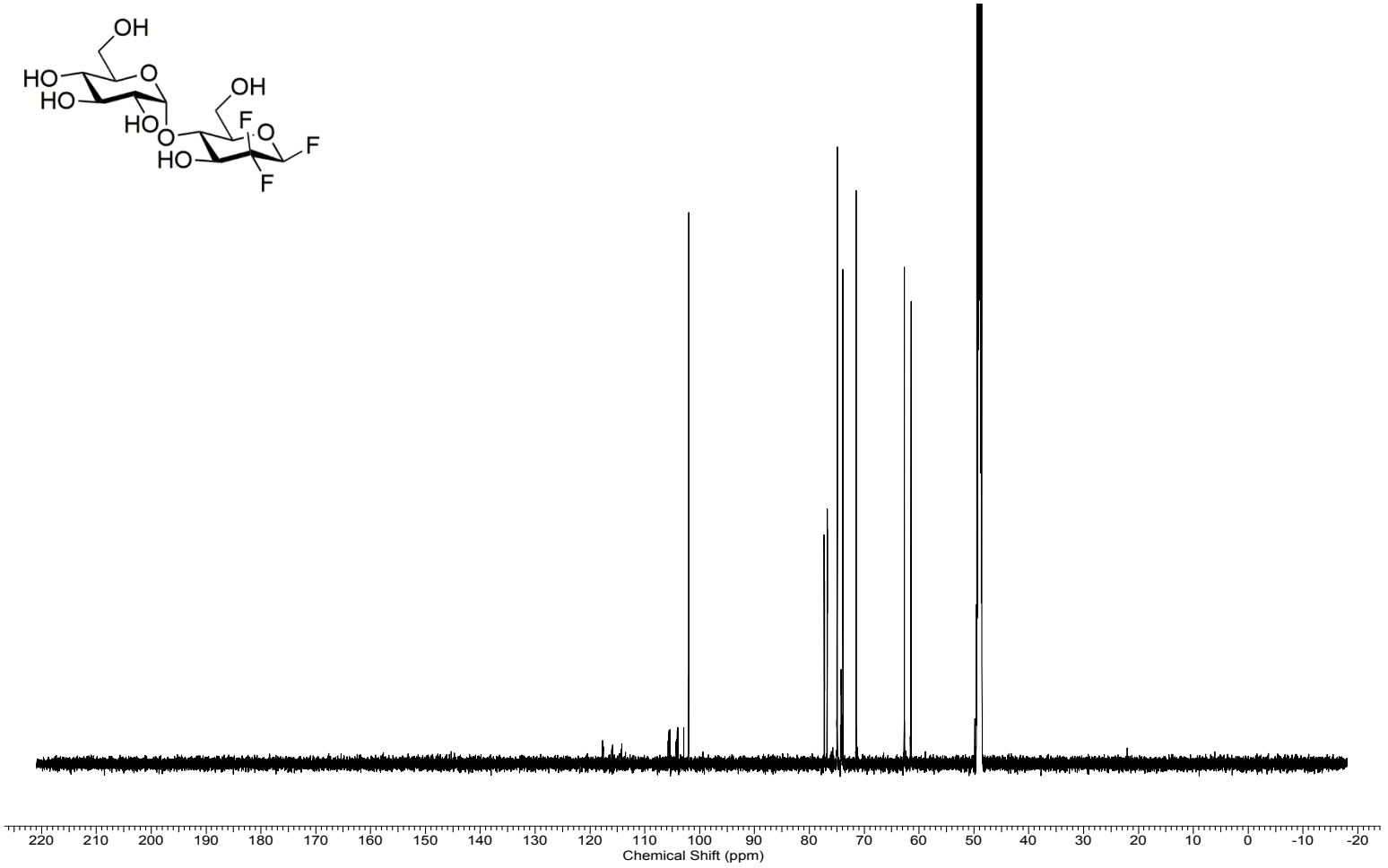
^{19}F of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*α*-D-glucopyranosyl fluoride (5)



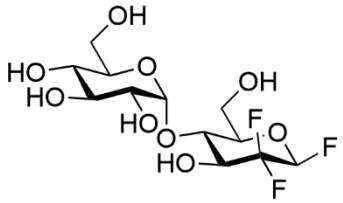
^{1}H NMR of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (6)

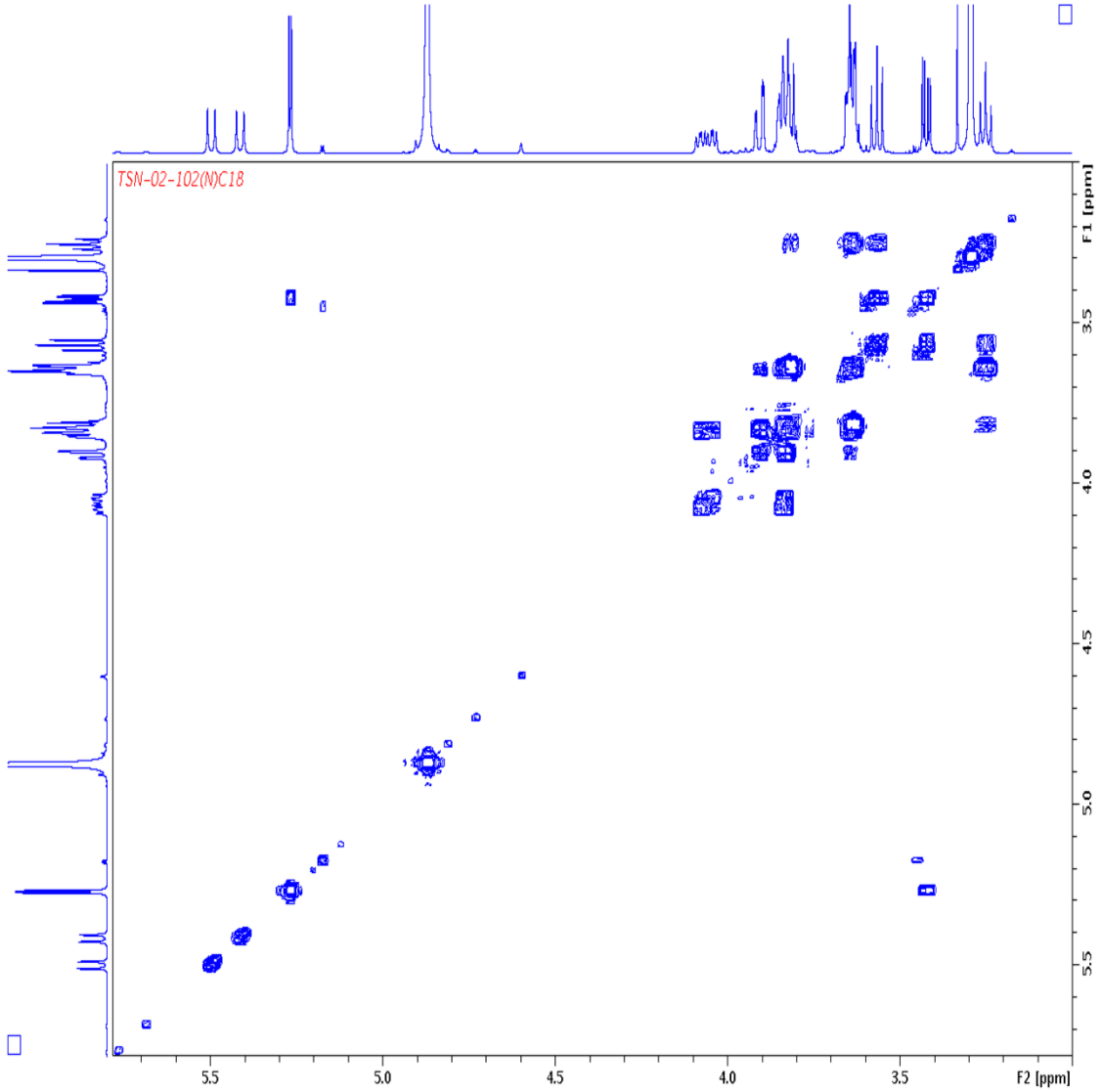


^{13}C NMR of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (6)

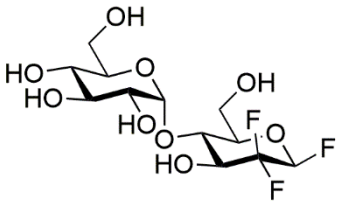


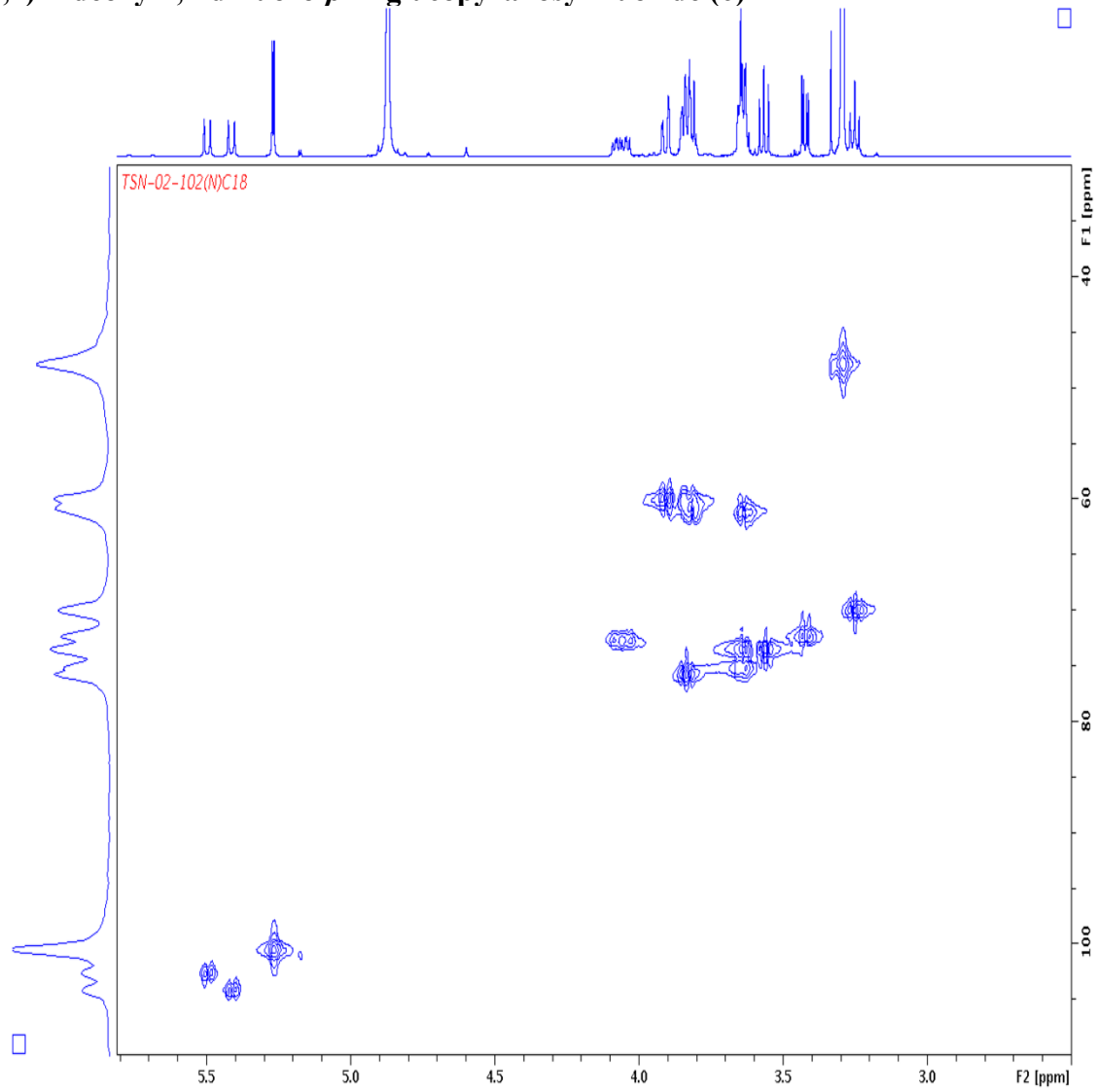
COSY of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (6)



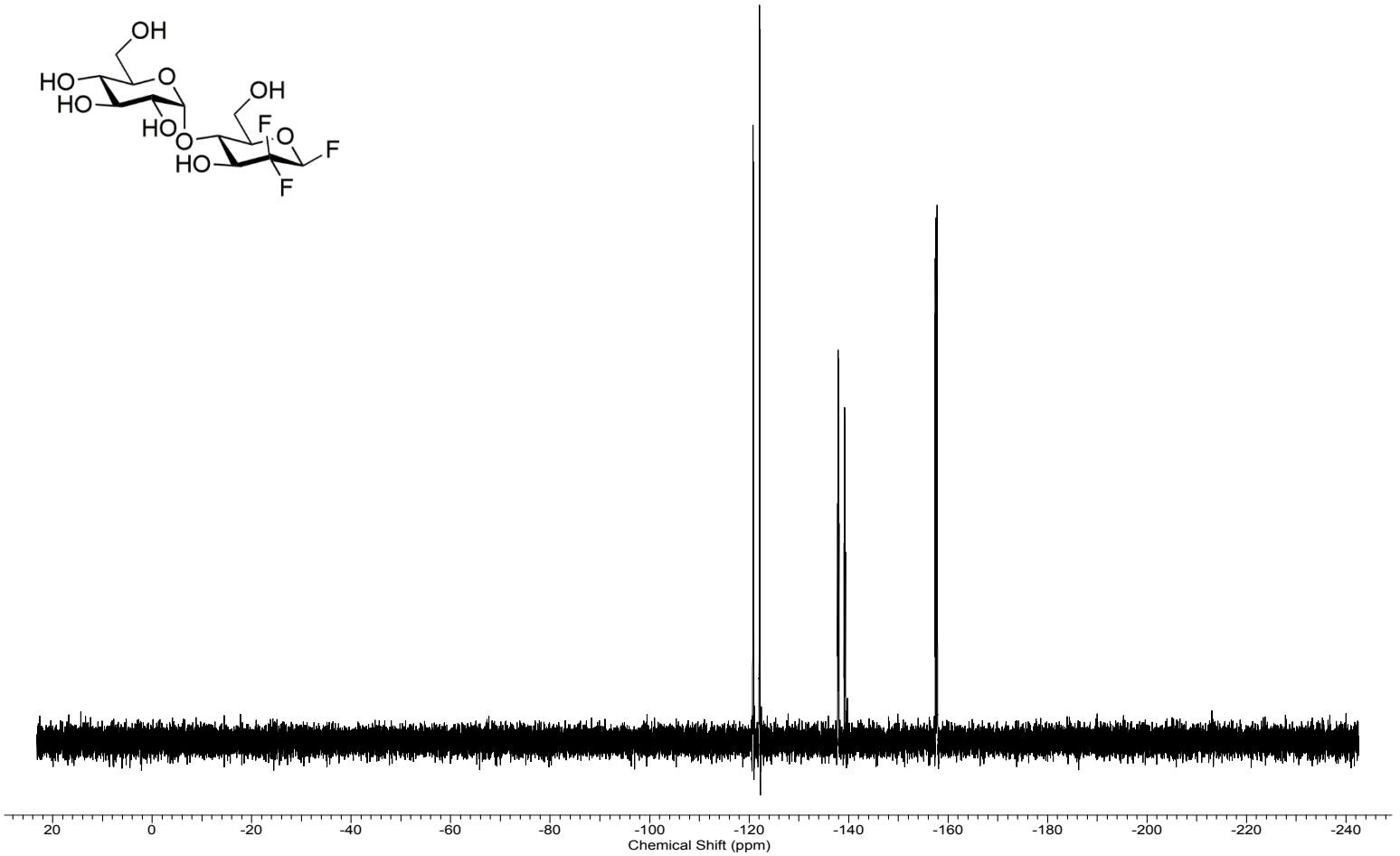


HMQC of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (6)

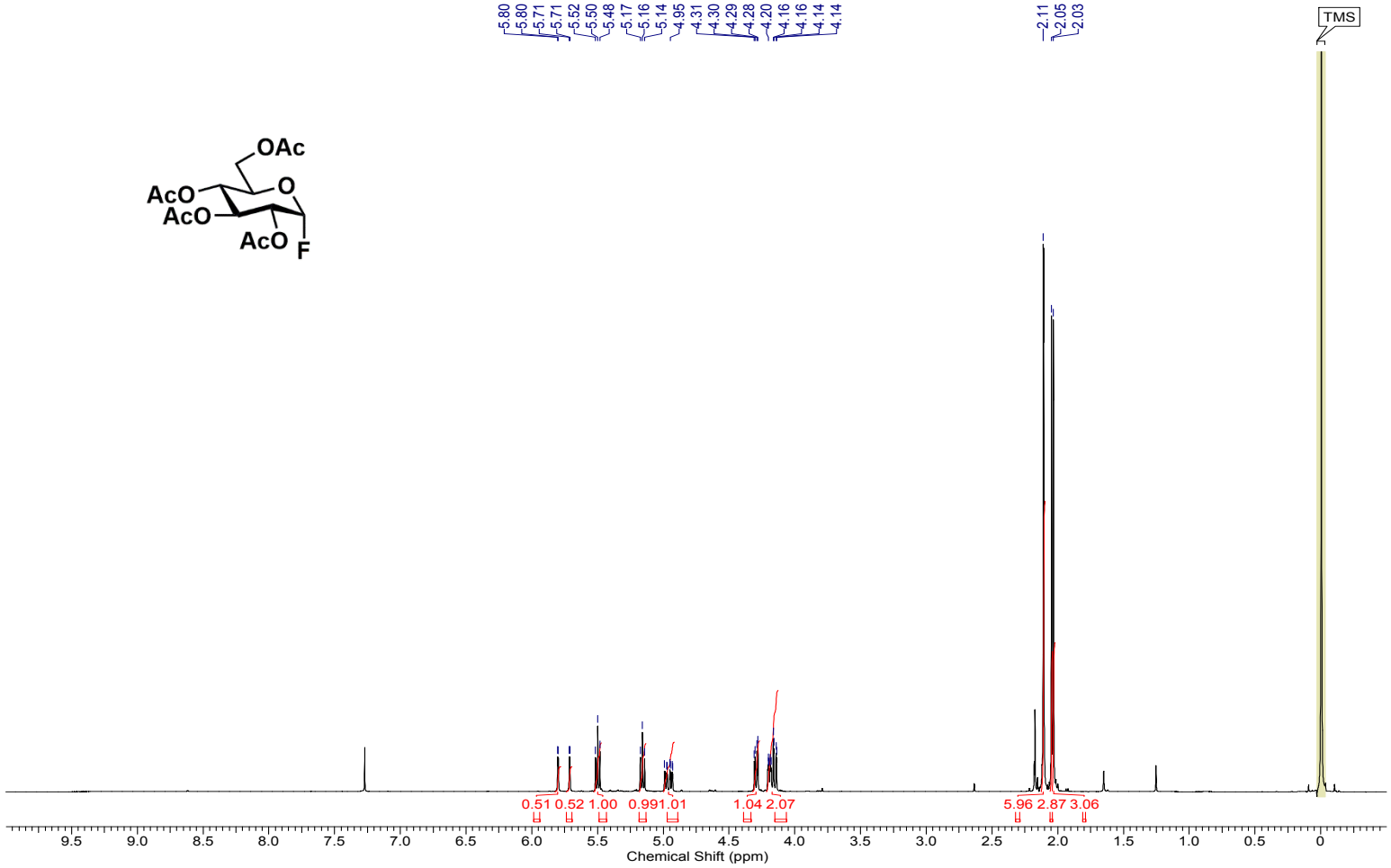




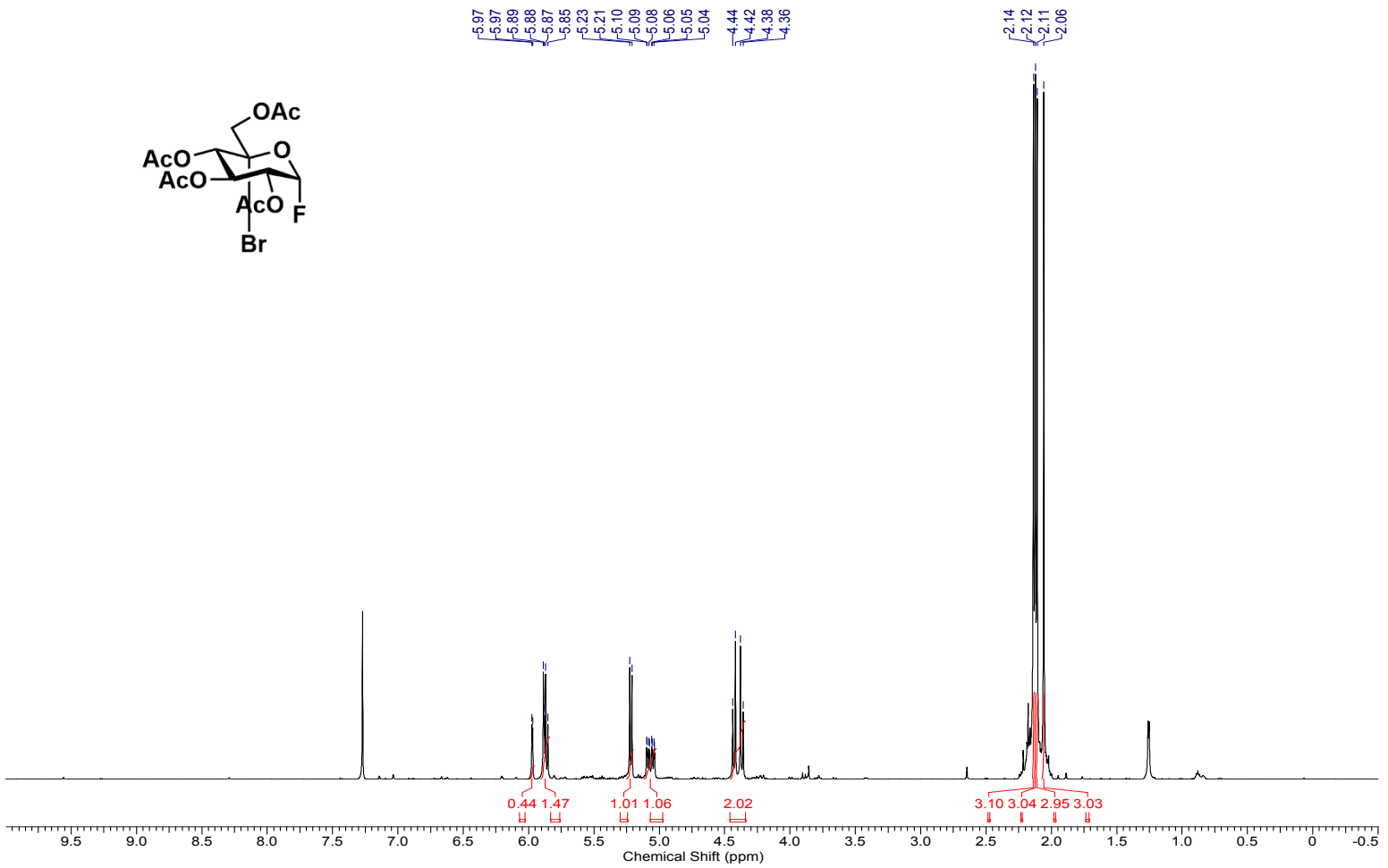
^{19}F of compound *α*-D-glucopyranosyl-(1,4)-2-deoxy-2,2-difluoro-*β*-D-glucopyranosyl fluoride (6)



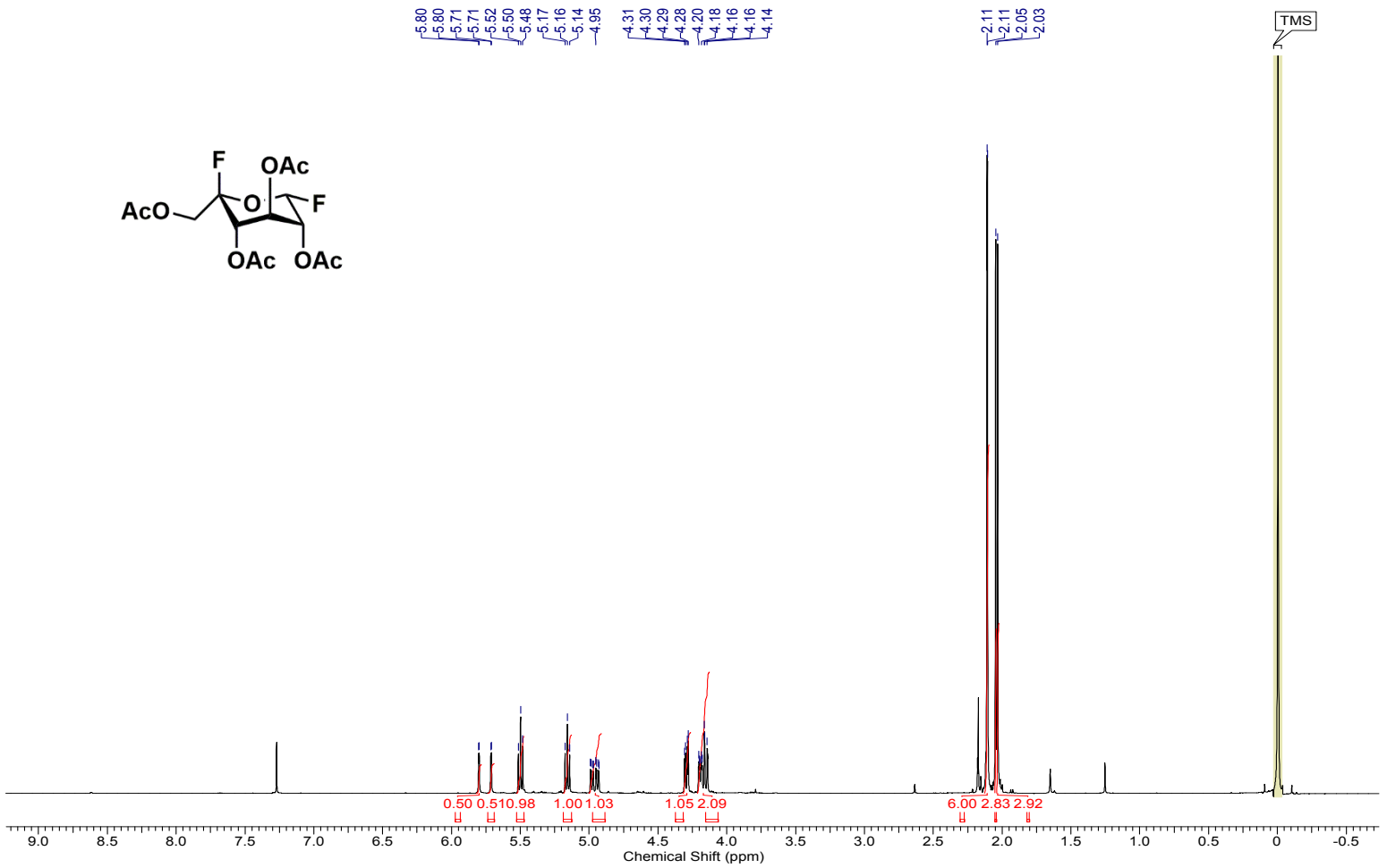
^{1}H NMR of compound 2,3,4,6-penta-*O*-acetyl-*α*-D-glycosyl fluoride (16)



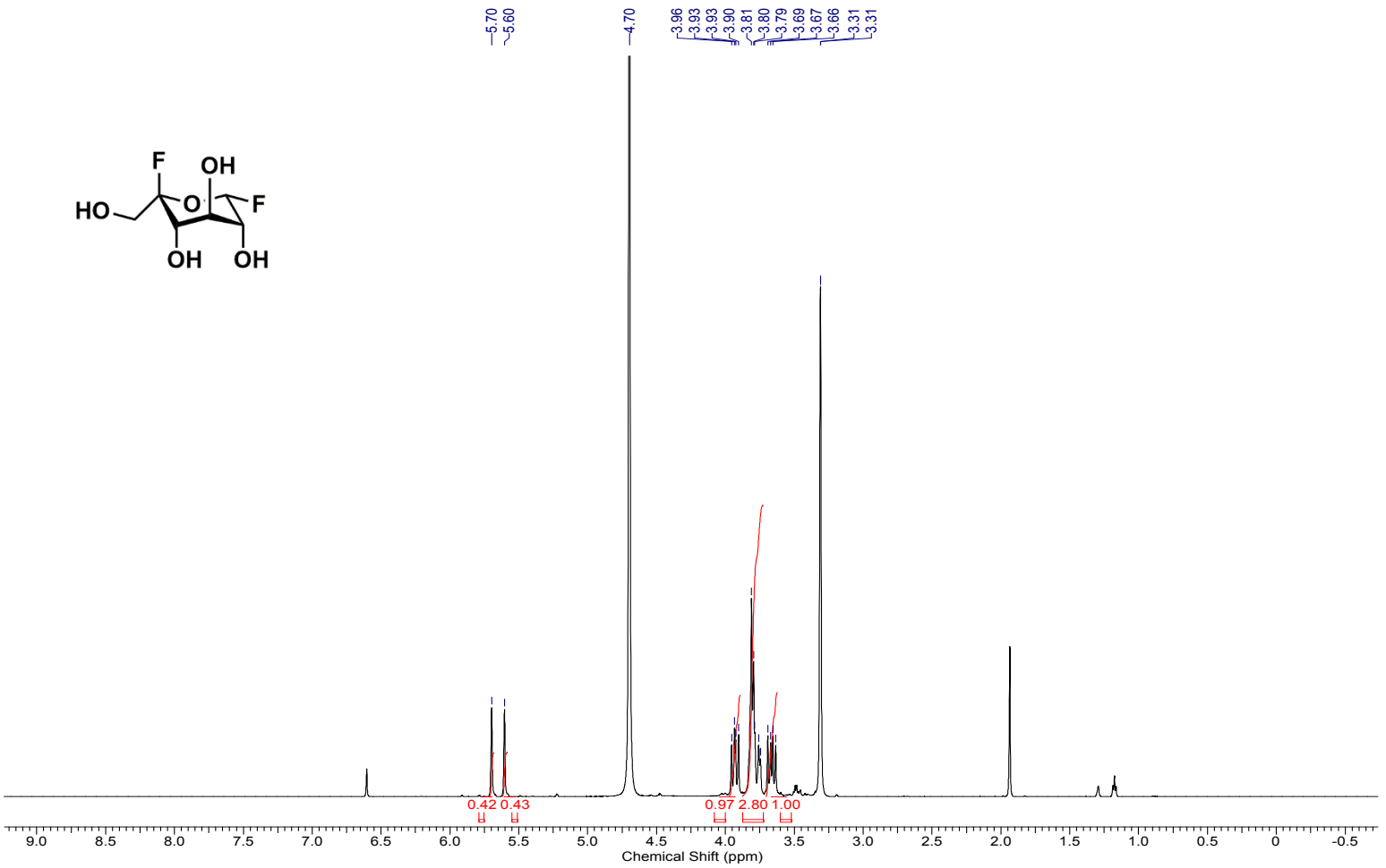
^{1}H NMR of compound 2,3,4,6-penta-*O*-acetyl-5-bromo-*α*-D-glycosyl fluoride (17)



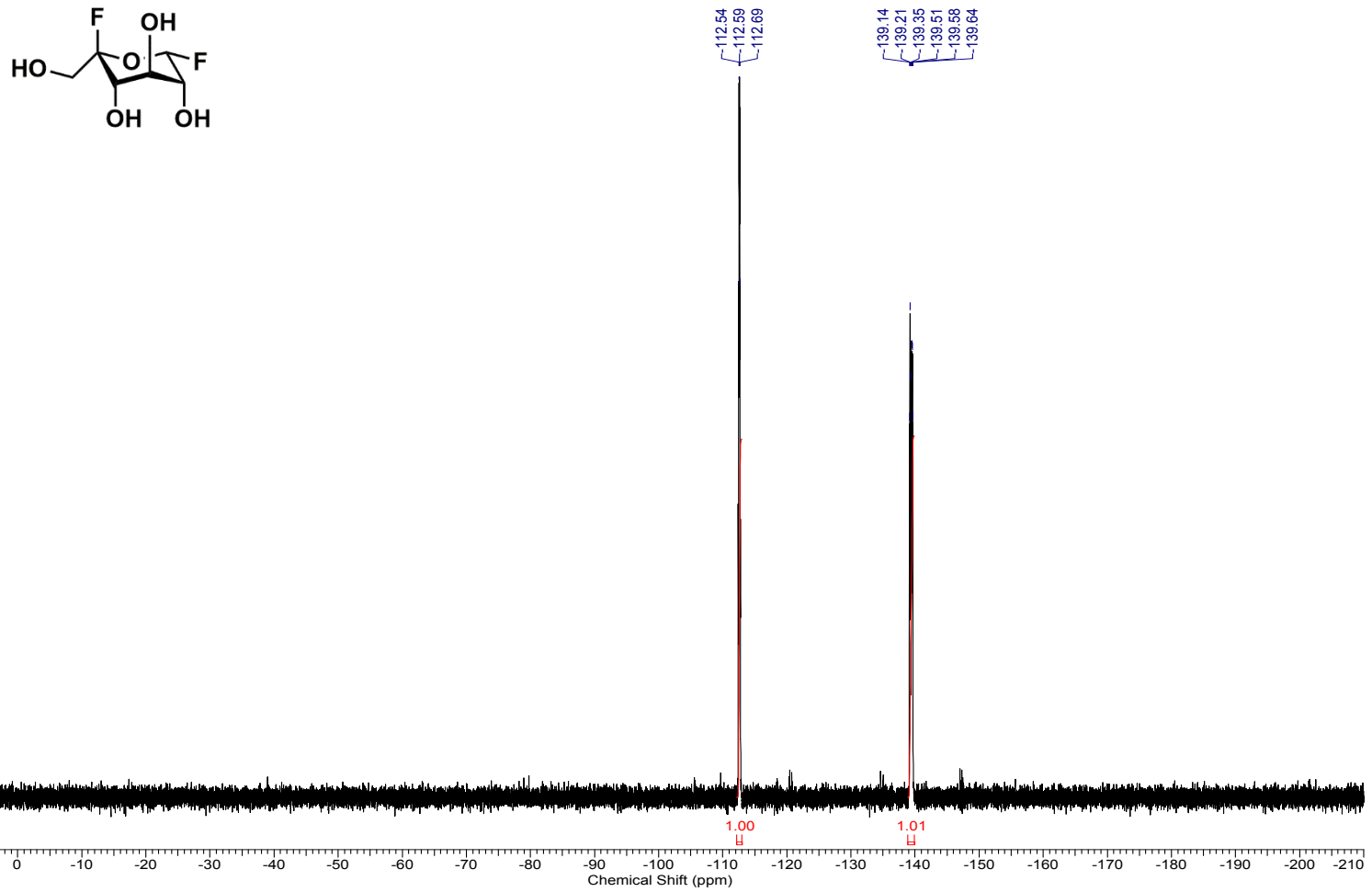
^{1}H NMR of compound 2,3,4,6-*O*-acetyl-5-fluoro-*β*-D-idosyl fluoride (18)



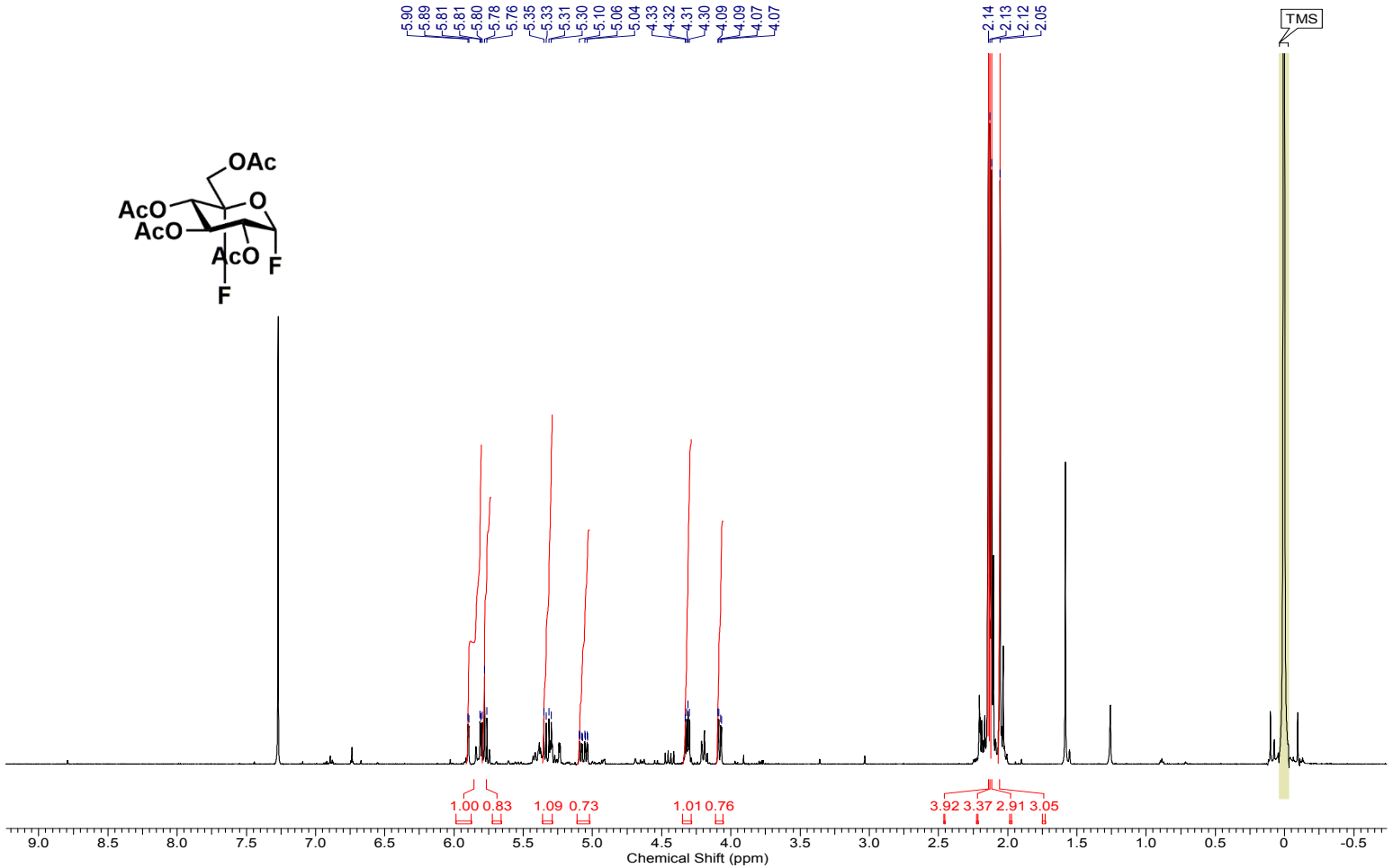
^{1}H NMR of compound 5-fluoro-*β*-D-idosyl fluoride (19)



^{19}F-NMR of compound 5-fluoro-*β*-D-iodosyl fluoride (19)



[1]H-NMR of compound per-*O*-acetyl-5-fluoro-*α*-glycosyl fluoride (20)



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