Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Stereoselective Access to 2-Deoxy-2-trifluoromethyl Sugar Mimetics by Trifluoromethyl-Directed 1,2-*Trans* Glycosylation

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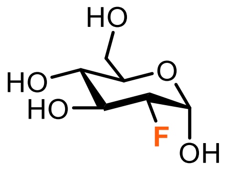
1. Materials and methods

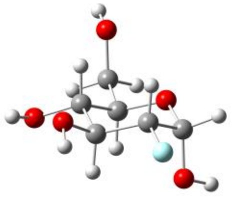
Proton (^{1}H NMR), carbon (^{13}C NMR), and fluorine (^{19}F NMR) nuclear magnetic resonance spectra were recorded on a Varian Mercury spectrometer or a Bruker Avance Ultrashield (400 MHz for ^{1}H), (100.6 MHz for ^{13}C), and (376.5 MHz for ^{19}F). Spectra were fully assigned using COSY, HSQC, HMBC, and NOESY. All chemical shifts are quoted on the δ scale in parts per million (ppm) using the residual solvent as the internal standard (^{1}H NMR: $CDCl_3$ = 7.26, CD_3OD = 3.31 and ^{13}C NMR: $CDCl_3$ = 77.16, CD_3OD = 49.0). Coupling constants (J) are reported in Hz with the following splitting abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and app = apparent. Infrared (IR) spectra were recorded on a FTIR–ATR spectrophotometer. Absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were recorded on an LC–MS system (UHPLC 1290 Infinity II Series coupled to a qTOF/MS 6550 Series, both Agilent Technologies (Agilent Technologies). For the ionization, an ESI operating on positive or negative ionization or an APCI operating on positive or negative ionization was used. Water and methanol with 0.05% formic acid were used as mobile phases. The quadrupole time of flight mass spectrometer (qTOF) operated in high-resolution MS scan mode between 100–1000 *m/z*. Nominal and exact *m/z* values are reported in Daltons. Thin layer chromatography (TLC) was carried out using commercial backed sheets coated with 60 Å F_{254} silica gel. Visualization of the silica plates was achieved using a UV lamp (λ_{max} = 254 nm), 6% H_2SO_4 in EtOH, cerium molybdate, and/or potassium permanganate staining solutions. Flash column chromatography was carried out using silica gel 60 Å CC (230–400 mesh). Mobile phases are reported in relative composition (*e.g.,* 1:1 EtOAc/hexane v/v). All reactions using anhydrous conditions were performed using oven-dried apparatus under an atmosphere of argon. Brine refers to a saturated solution of sodium chloride. Anhydrous sodium sulfate (Na_2SO_4) was used as drying agent after reaction work-up, as indicated. All reagents were purchased from Sigma Aldrich, Cymit, Carbosynth, Apollo Scientific, Fluorochem and Manchester Organics chemical companies. X-ray figures in the article were rendered with CyLview software.[1]

2. Electrostatic potential surface calculation

DFT calculations were performed using Gaussian 09.[2] Geometry optimization was conducted at the CPCM (water) B3LYP/6-311+G(d,p) level of theory. Frequencies were calculated at the same level of theory and used to verify the nature of all stationary points as minima.

2-Deoxy-2-fluoro-α-D-glucopyranose (S1)





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10	8	0	-0.504595	-1.423369	-0.342639
11	8	0	-1.138626	1.951853	0.915336
12	1	0	-0.709713	2.793141	0.721117
13	8	0	1.408350	2.232886	-0.340148
14	1	0	2.310537	2.381998	-0.040339
15	6	0	-2.627798	-0.514735	0.263842
16	1	0	-3.112353	0.178326	0.953754
17	1	0	-2.926471	-1.532786	0.524861
18	8	0	-2.983426	-0.215517	-1.087968
19	1	0	-3.940805	-0.259701	-1.163856
20	1	0	1.201227	-2.315840	-0.873656
21	8	0	1.302217	-1.787804	1.118603
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23	9	0	2.917613	-0.230763	-0.460956

Electrostatic potential surface:

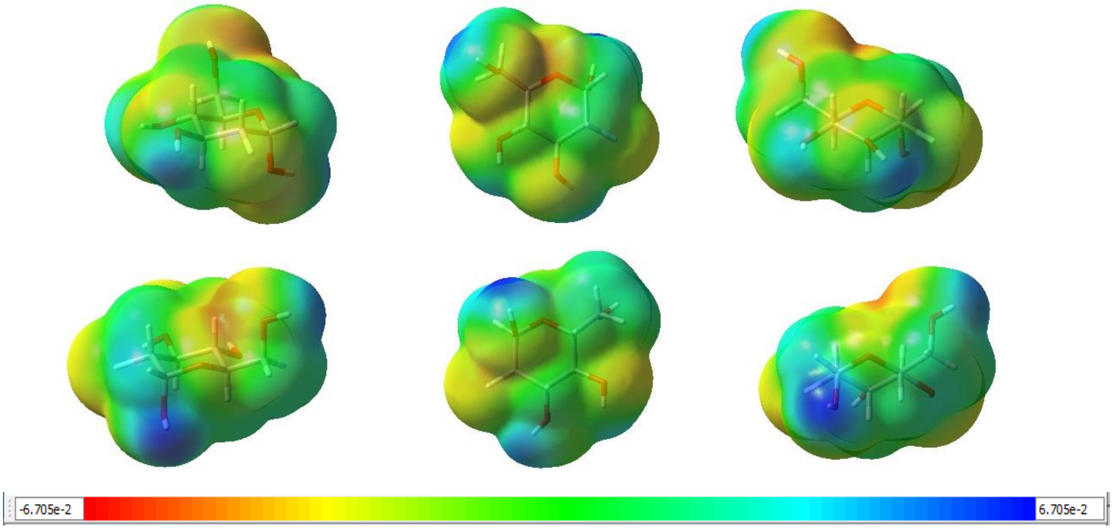
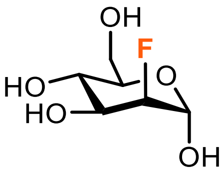
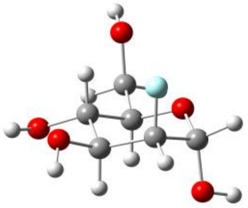


Figure S1. Different views of the electrostatic potential surface of 2-deoxy-2-fluoro-α-D-glucopyranose **S1**

2-Deoxy-2-fluoro-α-D-mannopyranose (S2)





Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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4	6	0	-1.122451	0.887283	-0.355559
5	6	0	-1.699996	-0.322315	0.366763
6	1	0	0.566209	1.183406	0.936152
7	1	0	-1.296817	0.745810	-1.424836
8	1	0	0.920969	-0.484977	-1.589240
9	8	0	0.460491	-1.425049	0.204686
10	8	0	0.946520	2.021957	-0.920992
11	1	0	0.421667	2.816359	-0.768958
12	8	0	-1.703956	2.115180	0.080105
13	1	0	-2.528205	2.263101	-0.393858
14	6	0	2.547136	-0.358461	-0.245774
15	1	0	3.023408	0.386849	-0.884901
16	1	0	2.928648	-1.345834	-0.516826
17	8	0	2.802158	-0.080570	1.133143
18	1	0	3.754246	-0.059362	1.264585
19	1	0	-1.206339	-2.395013	0.692180
20	8	0	-1.262829	-1.907786	-1.320996

21	1	0	-2.759128	-0.450340	0.151901
22	1	0	-0.929309	-2.789244	-1.521280
23	9	0	-1.583282	-0.141618	1.756799

Electrostatic potential surface:

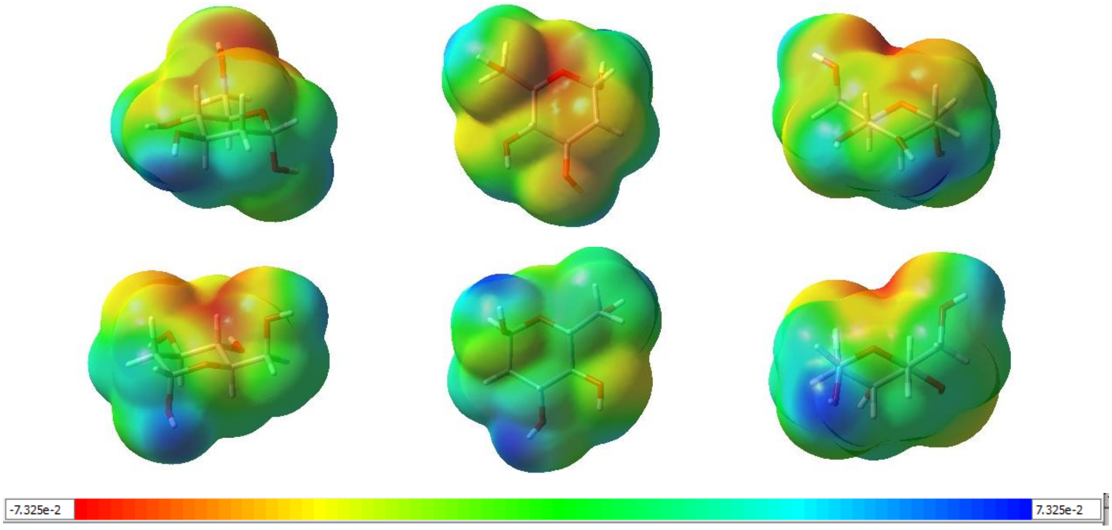
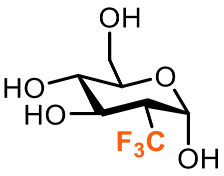
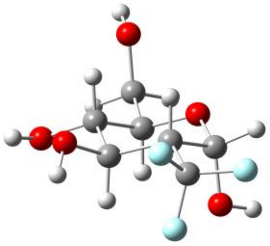


Figure S2. Different views of the electrostatic potential surface of 2-deoxy-2-fluoro-α-mannopyranoside **S2**

2-Deoxy-2-trifluoromethyl-α-D-glucopyranoside (S3)





Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
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3	6	0	-1.358260	0.953899	0.039466
4	6	0	0.144989	1.050419	0.289103
5	6	0	0.860385	-0.098440	-0.443548
6	1	0	-1.542242	1.125995	-1.024745
7	1	0	0.327583	0.978487	1.361463
8	1	0	0.704802	0.023175	-1.515755
9	1	0	-1.757603	-0.576723	1.491623
10	8	0	-1.155160	-1.436197	-0.300379
11	8	0	-2.052717	1.920131	0.819921
12	1	0	-1.640384	2.774269	0.645018

13	8	0	0.542233	2.338592	-0.186528
14	1	0	1.286349	2.662093	0.329759
15	6	0	2.369495	-0.081687	-0.248563
16	6	0	-3.360689	-0.623807	0.115338
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19	8	0	-3.617933	-0.361110	-1.265898
20	1	0	-4.563519	-0.445625	-1.417358
21	9	0	2.942373	-1.247120	-0.630422
22	9	0	2.952646	0.888979	-0.990968
23	9	0	2.747014	0.139822	1.028439
24	1	0	0.613595	-2.242046	-0.700793
25	8	0	0.541228	-1.715091	1.293169
26	1	0	0.292843	-2.625030	1.490546

Electrostatic potential surface:

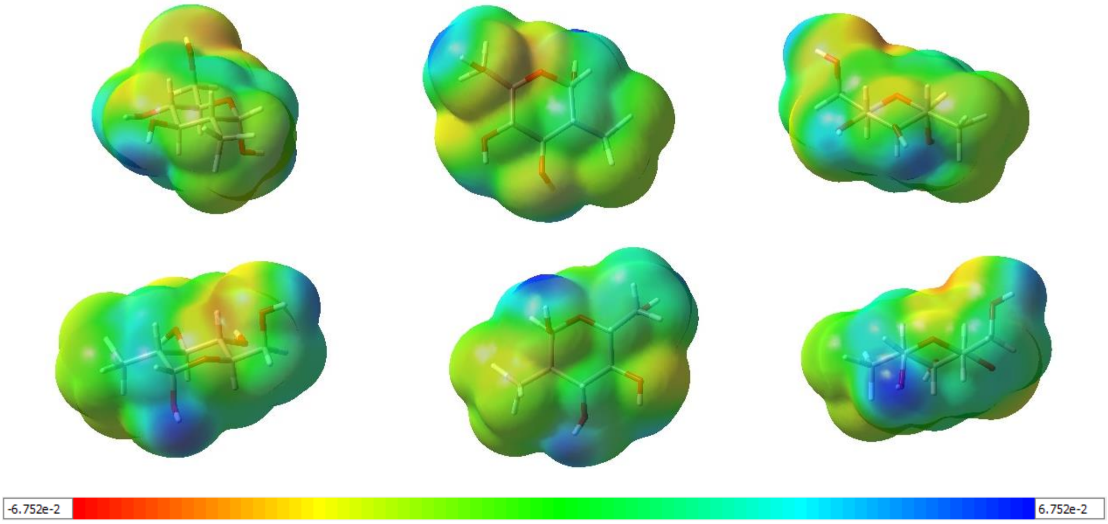
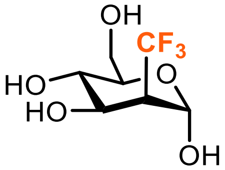
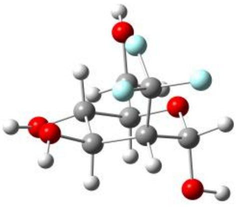


Figure S3. Different views of the electrostatic potential surface of 2-deoxy-2-trifluoromethyl-α-D-glucopyranose **S3**

2-Deoxy-2-trifluoromethyl-α-D-mannopyranose (S4)





Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
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4	6	0	0.240567	1.080435	0.894311
5	6	0	1.158200	-0.149081	0.688998
6	1	0	-0.840180	1.091981	-0.967985
7	1	0	-0.027818	1.092004	1.952073
8	1	0	-2.063840	-0.385535	1.393775
9	8	0	-0.845688	-1.427559	0.076278
10	8	0	-1.952065	2.023754	0.508609
11	1	0	-1.473431	2.858040	0.442959
12	8	0	0.845469	2.321992	0.540219
13	1	0	1.460259	2.589060	1.230879
14	6	0	-2.994661	-0.559235	-0.495052
15	1	0	-3.738408	0.183195	-0.200542
16	1	0	-3.390732	-1.554459	-0.279476
17	8	0	-2.675458	-0.433578	-1.882774
18	1	0	-3.487662	-0.528981	-2.388200
19	1	0	0.878163	-2.307092	0.509805
20	8	0	0.054943	-1.546738	2.240393
21	1	0	1.918932	-0.152959	1.469223
22	6	0	1.952805	-0.154643	-0.611325
23	9	0	2.589941	-1.339733	-0.792048
24	9	0	1.209135	0.048261	-1.719559
25	9	0	2.919167	0.787452	-0.610041
26	1	0	-0.348328	-2.406944	2.402965

Electrostatic potential surface:

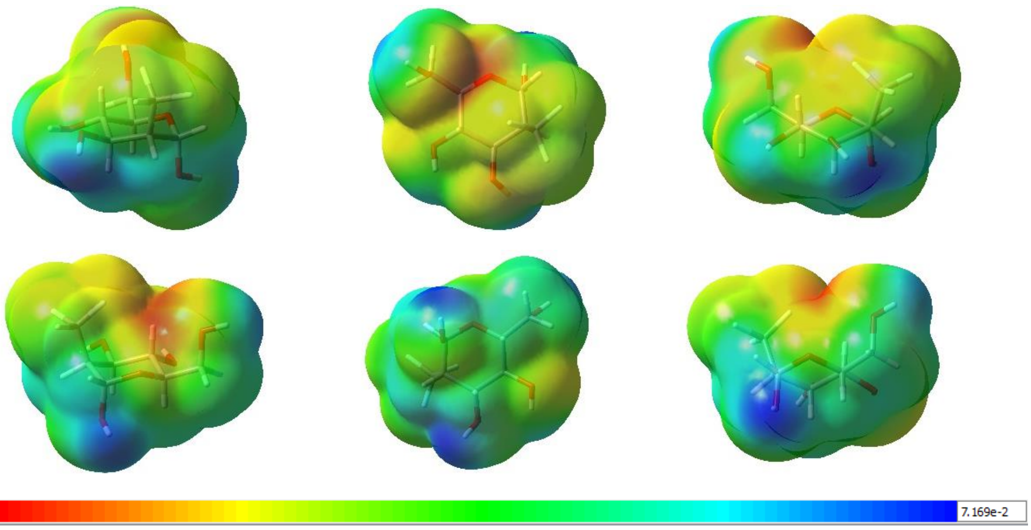
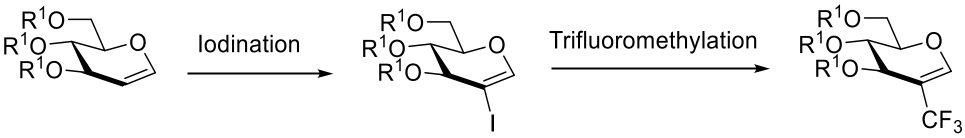


Figure S4. Different views of the electrostatic potential surface of 2-deoxy-2-trifluoromethyl-α-D-mannopyranose **S4**

3. Experimental section

3.1. Synthesis of 2-trifluoromethyl-D-glucals

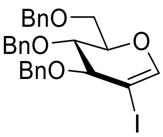


1a, R^1 = OBn
1b, R^1 = OAc

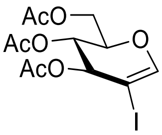
2a, R^1 = OBn
2b, R^1 = OAc

3a, R^1 = OBn
3b, R^1 = OAc

Scheme S1. Synthesis of protected 2-trifluoromethyl-D-glucals



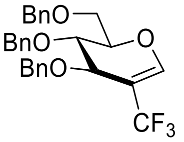
3,4,6-Tri-*O*-benzyl-2-iodo-D-glucal (2a). 3,4,6-Tri-*O*-benzyl-D-glucal **1a** (1 g, 2.40 mmol) was azeotropically dried with toluene and dissolved in dry acetonitrile (20 mL) under argon. To the reaction mixture was added azeotropically dried NIS (630 mg, 2.8 mmol) and AgNO$_3$ (81.6 mg, 0.48 mmol) and the reaction mixture was stirred under reflux for 1 h. The crude was then diluted with EtOAc and filtered through a short path of silica. The solvent was evaporated under vacuum and the residue was purified by column chromatography (1:9 EtOAc/Hexane) to afford **2a** (1.03 g, 79%) as a yellowish solid. **R$_f$** (1:9 EtOAc/hexane): 0.4; **^{1}H NMR** (CDCl$_3$, 400 MHz) δ in ppm: 7.43–7.19 (m, 15H, Ar), 6.74 (bs, 1H, H-1), 4.74–4.48 (m, 6H, 3CH$_2$Ph), 4.30 (m, 1H, H-5), 4.09 (d, $J_{3,4}$ = 4.8 Hz, 1H, H-3), 4.00 (dd, $J_{4,5}$ = 7.0 Hz, $J_{3,4}$ = 4.8 Hz, 1H, H-4), 3.79 (dd, $J_{6a,b}$ = 10.8 Hz, $J_{5,6a}$ = 5.5 Hz, 1H, H-6a), 3.71 (dd, $J_{6a,b}$ = 10.8 Hz, $J_{5,6b}$ = 3.8 Hz, 1H, H-6b); **^{13}C NMR** (CDCl$_3$, 100.6 MHz) δ in ppm: 148.4 (C-1), 137.8, 137.6, 137.6 (C, Ar), 128.5, 128.4, 128.4, 128.1, 127.9, 127.9, 127.7, 127.7 (CH, Ar), 78.9 (C-3), 76.5 (C-5), 73.4 (C-4), 73.4, 73.1, 72.2 (3xCH$_2$Ph), 70.4 (C-2), 67.8 (C-6). Spectroscopic data are in agreement with that reported.[3]



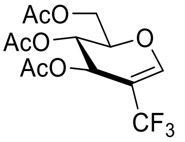
3,4,6-Tri-*O*-acetyl-2-iodo-D-glucal (2b). NIS (4.95 g, 22 mmol) and AgNO$_3$ (0.62 g, 3.65 mmol) were added under argon atmosphere to a solution of 3,4,6-Tri-*O*-acetyl-D-glucal **1b** (5.0 g, 18.36 mmol) in dry CH$_3$CN (50 mL) at room temperature. The reaction mixture was warmed up to 80 ^{o}C and stirred for 4 h. The crude was filtered through a short path of Silica and the solvent evaporated. The residue was purified by column chromatography using (2:8 EtOAc/hexane) to afford **2b** (4.3 g, 59%) as a colorless syrup. **R$_f$** (2:3 EtOAc/hexane): 0.46; **^{1}H NMR** (CDCl$_3$, 400 MHz) δ in ppm: 6.69 (d, $J_{1,3}$ = 1.1 Hz, 1H, H-1), 5.36 (d, $J_{3,4}$ = 5.1 Hz, 1H, H-3), 5.10 (appt, $J_{3,4}$ = $J_{4,5}$ = 6.4 Hz, 1H, H-4), 4.35–4.23 (m, 2H, H-6a, H-5), 4.07 (dd, $J_{6a,6b}$ = 14.6 Hz, $J_{5,6b}$ = 5.6 Hz, 1H, H-6b), 2.00, 1.96, 1.96 (s, 9H, 3CH$_3$, Ac); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.1, 169.6, 169.1 (3xC=O, Ac), 149.1 (C-1), 73.7 (C-5), 70.3 (C-3), 67.30 (C-4), 66.2 (C-2), 60.7 (C-6), 20.7, 20.6, 20.5 (3xCH_3, Ac). Spectroscopic data are in agreement with that reported.[4]

Preparation of $CuCF_3$. DMF (25 mL) and DMI (25 mL) were added to a flask containing KF (3.56 g, 61.3 mol) and CuBr (8.79 g, 61.3 mol) under argon. The suspension was vigorously stirred at 0 ºC. $TMSCF_3$ (8.8 mL, 59.5 mmol) was slowly added and the mixture stirred for 3 h at 0 ºC. An aliquot (0.6 mL) was transferred to an NMR tube under argon and 1,3-bis(trifluoromethyl)benzene (20 µL, 0.129 mmol) was added and the tube caped with a rubber septum. The $CuCF_3$ was produced in 89% yield as determined by quantitative ^{19}F NMR analysis. The freshly prepared solution of $CuCF_3$ was immediately used.

3,4,6-Tri-*O*-benzyl-2-trifluoromethyl-D-glucal (3a). A round-bottom flask containing **2a** (4.1 g, 7.55 mmol) was evacuated and backfilled with argon 3 times. DMI (18 mL) and $CuCF_3$ solution (18.2 mL, 15.1 mmol) were successively added and the mixture was shaken until complete homogeneity. The reaction was heated without stirring at 40 ºC for 17 h and then the temperature raised to 50 ºC for additional 16 h. Saturated aqueous NH_4Cl was slowly added at 0 ºC and the crude extracted with Et_2O, dried over $MgSO_4$ and the solvent was evaporated. Purification by column chromatography (1:15 EtOAc/hexane) gave **3a** (3.61 g, 98%) as a colorless syrup. **R_f** (1:4 EtOAc/hexane): 0.43; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.40–7.21 (m, 15H, Ar), 7.07 (bq, $J_{1,F}$ = 1.5 Hz, 1H, H-1), 4.59–4.44 (m, 7H, 3CH_2Ph, H-5), 4.10 (bs, 1H, H-3), 3.90 (appt, $J_{3,4} = J_{4,5}$ = 3.2 Hz, 1H, H-4), 3.78 (dd, $J_{6a,6b}$ = 10.5 Hz, $J_{5,6a}$ = 6.9 Hz, 1H, H-6a), 3.67 (dd, $J_{6a,6b}$ = 10.5 Hz, $J_{5,6b}$ = 5.1 Hz, 1H, H-6b); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.6 (s, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 148.1 (q, $J_{1,F}$ = 7.2 Hz, C-1), 137.8, 137.6, 137.4 (C, Ar), 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 128.1, 128.0 127.9, 127.8 (CH, Ar), 125.0 (q, $J_{C,F}$ = 269.9 Hz, CF_3), 103.6 (q, $J_{2,F}$ = 30.7 Hz, C-2), 76.5 (C-5), 73.4, 72.4, 72.2 (3xCH_2Ph), 71.2 (C-4), 68.9 (C-3), 71.2 (C-4), 68.9 (C-3), 67.7 (C-6); Spectroscopic data are in agreement with that reported.[5]



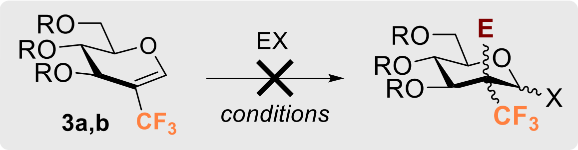
3,4,6-Tri-*O*-acetyl-2-trifluoromethyl-D-glucal (3b). A round-bottom flask containing **2b** (3.3 g, 8.29 mmol) was evacuated and backfilled with argon 4 times. DMI (20 mL) and $CuCF_3$ solution (20 mL, 16.6 mmol) were successively added and the mixture was shaken to complete homogeneity. The reaction was heated without stirring at 40 ºC for 17 h and then the



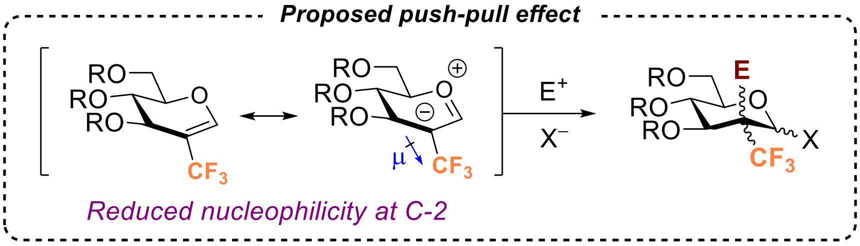
temperature raised to 50 ºC for additional 16 h. Saturated aqueous NH_4Cl was slowly added at 0 ºC and the crude extracted with Et_2O dried over $MgSO_4$ and the solvent evaporated. Purification by column chromatography (3:7 EtOAc/hexane) gave **3b** (2.62 g, 93%) as a colorless syrup. **R_f** (2:3 EtOAc/hexane): 0.47; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.17 (q, $J_{1,F}$ = 1.5 Hz, 1H, H-1), 5.57 (d, $J_{3,4}$ = 3.4 Hz, 1H, H-3), 5.16 (t, $J_{4,5}$ = $J_{4,3}$ = 3.5 Hz, 1H, H-4), 4.54–4.49 (m, 1H, H-5), 4.45 (dd, $J_{6a,b}$ = 12.0 Hz, $J_{6a,5}$ = 7.6 Hz, 1H, H-6a), 4.20 (dd, $J_{6b,a}$ = 12.0 Hz, $J_{6b,5}$ = 4.2 Hz, 1H, H-6b), 2.10, 2.10, 2.08 (s, 9H, $3CH_3$, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –63.6 (s, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.5, 169.4, 169.4 (3xC=O, Ac), 149.4 (q, J = 6.8 Hz, C-1), 123.9 (q, J = 270.1 Hz, CF_3), 102.1 (q, J = 32.0 Hz, C-2), 74.4 (C-5), 65.8 (C-4), 61.3 (C-3), 60.8 (C-6), 20.9, 20.8, 20.8 ($3xCH_3$, Ac); Spectroscopic data are in agreement with that reported.[6]

3.2. Synthesis of 2-deoxy-2-trifluoromethyl-D-hexopyranoses

3.2.1. Attempted activation of 3a,b



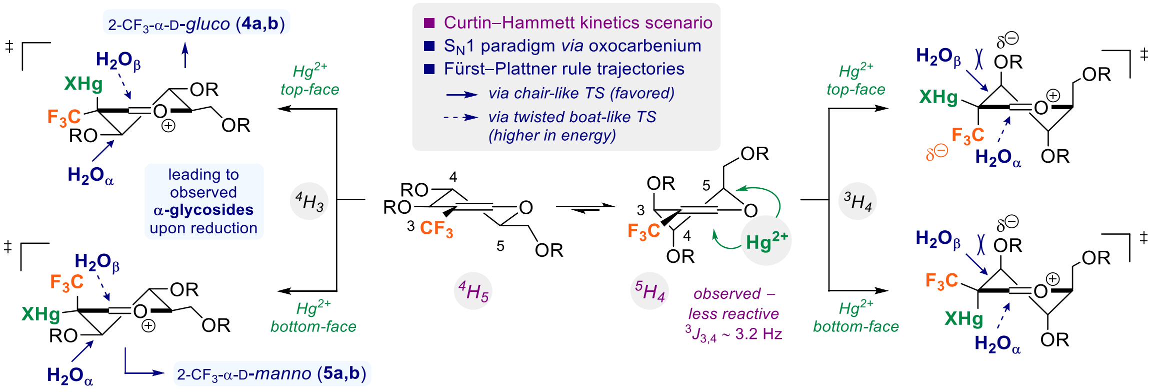
1) Epoxidation: a) Oxone, $NaHCO_3$, acetone in CH_2Cl_2/H_2O, b) MCPBA in MeOH
c) Oxone, $NaHCO_3$, CF_3COCH_3 in CH_2Cl_2/H_2O, d) DMDO in acetone
2) Halogenation: e) NaOCl in H_2O, f) PhIO in MeOH, g) NIS, CH_3CN/H_2O, rt to 80 °C
h) NIS/TfOH, CH_3CN/H_2O, i) NBS, CH_3CN/H_2O, rt to 80 °C
3) Hydroboration: j) $BH_3{\cdot}THF$, THF, 0 °C to rt
4) Hydroxylation: k) H_2O_2, NaOH, CH_2Cl_2, l) H_2SO_4, THF, rt to 85 °C
5) Hydroxymercuration: m) $Hg(OCOCH_3)_2$, THF/H_2O, $NaBH_4$
6) Hydration: n) LiBr, Amberlite IR-120, (1:1) CH_3CN/H_2O, rt, 40 °C, 80 °C, 100 °C
o) 48% HBr in H_2O, CH_3CN, rt, 40 °C, p) $HBr{\cdot}PPh_3$, (4:1) CH_3CN/H_2O, rt, 40 °C, 80 °C, 100 °C



Scheme S2. Attempted reactions for the activation of the double bond in **3a,b** (*top*). Proposed push-pull effect between the electron-donating oxygen group of the enol ether and the electron withdrawal of the CF_3 group, which makes the vinyl moiety considerable unreactive (*bottom*)

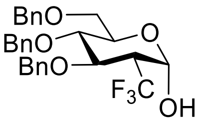
3.2.2. Mechanistic considerations of the hydroxymercuration-reduction of 3a,b.

Hydroxymercuration/demercuration of **3a,b** gave only α-isomers of the corresponding *gluco* and *manno* glycosides. Although 2-CF_3-D-glucals **3a,b** adopt an ‘inverted’ $^5H_4$ conformation from which a bottom-face attack of the Hg(II)-electrophile is expected,[3,7] the resulting final product distribution of 1:1.6 *gluco*/*manno* suggests a Curtin-Hammet kinetic scenario. Under these conditions, the ground state conformations are not determinant of the product distribution but rather the relative energies of the transition-state structures. In this particular case (for **3a,b**), the $^4H_5$ half-chair is not the most populated conformation but is the conformation that benefits from the greatest stabilization in the transition state (more reactive). Thus, we hypothesize this is the conformation that may react with the Hg(II)-electrophile and ultimately leads to the observed α-glycosides upon addition of water to the oxocarbenium ion intermediate followed by a reductive demercuration step (Scheme S3).

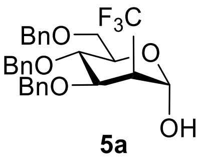


Scheme S3. Proposed selectivity model for the hydroxymercuration reaction.

3,4,6-Tri-*O*-benzyl-2-deoxy-2-trifluoromethyl-D-glucopyranose (4a) and 3,4,6-tri-*O*-benzyl-2-deoxy-2-trifluoromethyl-D-mannopyranose (5a). To a stirred solution of **3a** (32 mg, 0.066 mmol) in THF (1 mL) was added a solution of $Hg(OCOCF_3)_2$ (42.3 mg, 0.099 mmol) in water (0.3 mL) at 0 ºC. The mixture was stirred 36 h at room temperature. H_2O (0.2 mL) was then added followed by portionwise addition of $NaBH_4$ (16 mg, 0.416 mmol) at 0 ºC and the mixture stirred at this temperature for 20 min. The crude was concentrated under vacuum and diluted with 1:1 (v/v) EtOAc/H_2O (10 mL) and the aqueous phase extracted successively with EtOAc. The combined organic layers were dried with Na_2SO_4, filtered and the solvent evaporated. The crude was purified using column chromatography (1:4 EtOAc/hexane) to afford a chromatographically inseparable **4a**/**5a** (1:1.6) mixture (30 mg, 90%) as a white solid. The solid was dissolved in hot hexane and cooled to 4 ºC until precipitation ceased. The precipitate was separated and washed with cold hexane to afford **4a** as a white solid. The washings were combined with the previous mother liquor hexane solution, the solvent evaporated and the whole process was repeated five times to afford additional **4a** and pure fraction of **5a** as a colorless syrup. The purification afforded **4a** (9.9 mg, 30%) and **5a** (12.9 mg, 39%). Data for **4a**: **R_f** (3:7 EtOAc/hexane): 0.31; **m.p**: 151–153 ºC; **$[\alpha]^{D}_{25}$**: +18.1 (0.3, CH_2Cl_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.40–7.37 (m, 15H, Ar), 5.52 (appt, $J_{1,OH}$ = 3.5 Hz, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 4.85–4.48 (m, 6H, $3CH_2Ph$), 4.23 (dd, $J_{2,3}$ = 11.1 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H-3), 4.11 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.4 Hz, $J_{5,6b}$ = 2.3 Hz, 1H, H-5), 3.70 (dd, $J_{6a,b}$ = 10.6 Hz, $J_{5,6a}$ = 4.4 Hz, 1H, H-6a), 3.67–3.58 (m, 2H, H-6b, H-4), 2,83 (dd, $J_{1,OH}$ = 3.5 Hz, 1H, OH), 2.67 (m, 1H, H-2); **^{19}F**

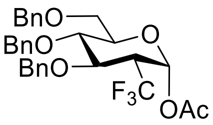


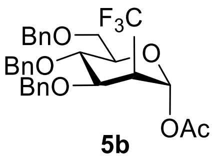
4a



5a

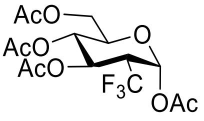
NMR ($CDCl_3$, 376.5 MHz) δ in ppm: –63.8 (d, J = 8.2 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 138.0, 137.9, 137.8 (C, Ar), 128.6, 128.6, 128.3, 128.1, 128.0, 128.0, 127.9 (CH, Ar), 125.2 (q, ^1J = 280.1 Hz, CF_3), 90.3 (q, ^3J = 4.1 Hz, C-1), 79.1 (C-4), 77.4 (CH_2Ph), 76.2 (C-3), 75.3, 73.7 ($2CH_2Ph$), 71.1 (C-5), 68.7 (C-6), 50.2 (q, ^2J = 24.9 Hz, C-2); **FT–IR** (neat) v in cm^{-1}: 3353, 2944, 2867, 1463, 1190, 1103, 881; **HRMS** (TOF ES^+) for $(M+Na)^+$ $C_{28}H_{29}F_3NaO_5^+$ (m/z): calc. 525.1859; found 525.1857. Data for **5a**: **R_f** (3:7 EtOAc/hexane): 0.31; **$[\alpha]^D_{25}$**: +14.3 (0.24, CH_2Cl_2); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.38–7.11 (m, 15H, Ar), 5.58 (appt, $J_{1,OH}$ = 3.4 Hz, 1H, H-1), 4.79–4.36 (m, 6H, $3CH_2Ph$), 4.20 (appt, $J_{2,3}$ = $J_{3,4}$ = 7.4 Hz, 1H, H-3), 4.07 (ddd, $J_{4,5}$ = 7.8 Hz, $J_{5,6a}$ = 5.7 Hz, $J_{5,6b}$ = 3.0 Hz, 1H, H-5), 3.74 (appt, $J_{3,4}$ = $J_{4,5}$ = 7.8 Hz, 1H, H-4), 3.65 (dd, $J_{6a,6b}$ = 10.2 Hz, $J_{5,6b}$ = 3.0 Hz, 1H, H-6b), 3.62 (dd, $J_{6a,6b}$ = 10.2 Hz, $J_{5,6a}$ = 5.7 Hz, 1H, H-6a), 3.03 (d, $J_{OH,1}$ = 3.4 Hz, 1H, OH), 2.95 (m, 1H, H-2); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.4 (d, J = 10.5 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 138.1, 138.0, 137.6 (C-Ar), 128.6, 128.5, 128.2, 128.1, 128.8, 128.0, 127.9, 127.8 (CH, Ar), 125.7 (q, ^1J = 281.3 Hz, CF_3), 90.4 (q, ^3J = 4.6 Hz, C-1), 75.9 (C-3), 74.6 (C-4), 74.5, 73.5, 72.3 ($3CH_2Ph$), 71.5 (C-5), 69.6 (C-6), 46.3 (q, ^2J = 24.2 Hz, C-2); **FT–IR** (neat) v in cm^{-1}: 3385, 3031, 2924, 1454, 1365, 1263, 1158, 1097; **HRMS** (TOF ES^+) for $(M+Na)^+$ $C_{28}H_{29}F_3NaO_5^+$ (m/z): calc. 525.1859; found 525.1864.


4b

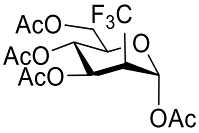

5b

1-*O*-Acetyl-3,4,6-tri-*O*-benzyl-2-deoxy-2-trifluoromethyl-D-glucopyranose (4b) and 1-*O*-acetyl-3,4,6-tri-*O*-benzyl-2-deoxy-2-trifluoromethyl-D-mannopyranose (5b): To a stirred solution of **3a** (3.23 g, 6.66 mmol) in THF (40 mL) was added a solution of $Hg(OCOCF_3)_2$ (4.26 g, 10 mmol) in H_2O (20 mL) at 0 ºC. The mixture was stirred 36 h at room temperature. Then, $NaBH_4$ (1.5 g, 40 mmol) was portionwise added at 0 ºC and the resulting mixture was stirred at this temperature for 20 min. The crude was concentrated under vacuum and diluted with 1:1 (v/v) EtOAc/H_2O (60 mL) and the aqueous phase extracted successively with EtOAc. The combined organic layers were dried with $MgSO_4$, filtered and the solvent evaporated. The crude was dissolved in pyridine (22.9 mL) and Ac_2O (2.26 mL) was added and the reaction mixture stirred at room temperature for 15 h. The solvent was then evaporated under vacuum and the residue dissolved in EtOAc and washed with saturated aqueous $CuSO_4$, NH_4Cl and NaCl. The organic phase was dried with $MgSO_4$, filtered, the solvent evaporated and the reaction crude was purified by flash column chromatography (1:9 EtOAc/hexane) to afford pure fractions of **4b** (1.26 g, 35%) and **5b** (1.67 g, 46%). Data for **4b**: White solid; **R_f** (1:4 EtOAc/hexane): 0.44; **m.p**: 114–116 ºC; **$[\alpha]^D_{25}$**: +74.9 (0.12, $CHCl_3$); **^{1}H**

NMR ($CDCl_3$, 400 MHz) δ in ppm: 7.40–7.15 (m, 15H, Ar), 6.44 (d, $J_{1,2}$ = 3.2 Hz, 1H, H-1), 4.89–4.81 (m, 2H, 2xCH-Ph), 4.77 (d, J = 10.2 Hz, 1H, CH-Ph), 4.63 (d, J = 12.0 Hz, 1H, CH-Ph), 4.58 (d, J = 10.7 Hz, 1H, CH-Ph), 4.50 (d, J = 12.0 Hz, 1H, CH-Ph), 4.22 (m, 1H, H-3), 3.90–3.78 (m, 3H, H-4, H-5, H-6a), 3.67 (bd, $J_{6a,6b}$ = 10.9 Hz, 1H, H-6b), 2.85 (m, 1H, H-2), 2.13 (s, 3H, CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –63.9 (d, J = 8.3 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 168.5 (C=O, Ac), 137.9, 137.8, 137.7 (C, Ar), 128.6, 128.6, 128.5, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9 (CH, Ar), 124.7 (q, $J_{C,F}$ = 281.0 Hz, CF_3), 88.7 (q, $J_{C1,F}$ = 4.7 Hz, C-1), 78.1 (C-4), 76.5 (C-3), 75.5, 75.4, 73.7 (3xCH_2Ph), 73.3 (C-5), 67.9 (C-6), 49.11 (q, $J_{C2,F}$ = 25.0 Hz, C-2), 20.9 (CH_3, Ac); **FTIR–ATR (neat)** ν in cm^{-1}: 3063, 3032, 2870, 2361, 2331, 1757, 1455, 1367, 1221, 1156, 1116, 954, 738; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{30}H_{31}F_3NaO_6^+$ (m/z): calc. 567.1965; found 567.1964. Data for **5b**: Colorless syrup; **R$_f$** (1:4 EtOAc/hexane): 0.35; **[α]$^{D}_{25}$**: +41.4 (1.0, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.45–7.15 (m, 15H, Ar), 6.53 (d, $J_{1,2}$ = 3.3 Hz, 1H, H-1), 4.75 (d, J = 11.0 Hz, 1H, CH-Ph), 4.74 (d, J = 11.1 Hz, 1H, CH-Ph), 4.63 (d, J = 12.0 Hz, 1H, CH-Ph), 4.59 (d, J = 11.1 Hz, 1H, CH-Ph), 4.53 (d, J = 12.0 Hz, 1H, CH-Ph), 4.47 (d, J = 11.0 Hz, 1H, CH-Ph), 4.17 (appt, $J_{2,3}$ = $J_{3,4}$ = 5.6 Hz, 1H, H-3), 4.01–3.90 (m, 2H, H-4, H-5), 3.75 (dd, $J_{6a,6b}$ = 11.0 Hz, $J_{6a,5}$ = 4.2 Hz, 1H, H-6a), 3.69 (dd, $J_{6a,6b}$ = 11.1 Hz, $J_{5,6b}$ = 2.3 Hz, 1H, H-6b), 2.99 (m, 1H, H-2), 2.10 (s, 3H, CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –69.6 (bs, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 168.8 (C=O, Ac), 138.2, 137.8, 137.3 (C, Ar), 128.6, 128.5, 128.4, 128.2, 128.2, 128.1, 127.8, 127.7 (CH, Ar), 125.2 (q, $J_{C,F}$ = 281.2 Hz, CF_3), 89.6 (q, $J_{C,F}$ = 4.4 Hz, C-1), 75.5 (C-3), 74.5 (CH_2Ph), 73.9 (C-5), 73.8 (C-4), 73.5, 72.4 (2xCH_2Ph), 68.9 (C-6), 45.12 (q, $J_{C,F}$ = 24.7 Hz, C-2), 21.0 (CH_3, Ac); **FTIR–ATR (neat)** ν in cm^{-1}: 3032, 2870, 2361, 1758, 1222, 1173, 1118, 1010, 954, 740, 698; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{30}H_{31}F_3NaO_6^+$ (m/z): calc. 567.1965; found 567.1964.

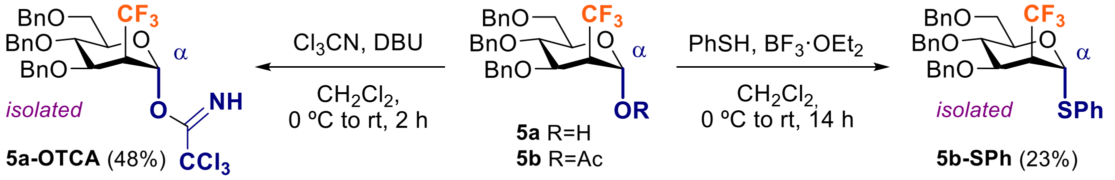


1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-trifluoromethyl-α-D-glucopyranose (4c). 10% Pd/C (33 mg, 0.03 mmol Pd) was added to a solution of **4b** (180 mg, 0.33 mmol) in dry and deoxygenated methanol (4 mL) at room temperature. The mixture was stirred under H_2 (1 atm) at the same temperature for 16 h, filtered through a short path of Celite® 545, and concentrated under reduced pressure. The crude was dissolved in pyridine (1 mL) and Ac_2O (0.23 mL) was added and the reaction stirred at room temperature overnight. Pyridine was then evaporated under vacuum and the residue dissolved in EtOAc and washed with saturated aqueous $CuSO_4$, NH_4Cl, and NaCl. The organic phase was dried with $MgSO_4$, filtered, the solvent evaporated and the crude purified using column chromatography (3:7 EtOAc/hexane) to afford **4c** (103 mg, 78%) as a white solid. **R$_f$** (3:7 EtOAc/hexane): 0.35; **m.p**: 94–96 ^{o}C; **$[\alpha]^{D}_{25}$** :+111.2 (0.24, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 6.45 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1), 5.70 (dd, $J_{3,2}$ = 11.4 Hz, $J_{3,4}$ = 9.3 Hz, 1H, H-3), 5.11 (appt, $J_{4,5}$ = $J_{3,4}$ = 9.5 Hz, 1H, H-4), 4.31 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 3.8 Hz, 1H, H-6a), 4.12–4.01 (m, 2H, H-5, H-6b), 3.04–2.92 (m, 1H, H-2), 2.16, 2.08, 2.05, 2.04 (s, 12H, 4CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.3 (d, J = 7.5 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.7, 169.7, 169.7, 168.1 (4xC=O, Ac), 123.7 (q, $J_{C,F}$ = 281.1 Hz, CF_3), 87.7 (q, $J_{C1,F}$ = 4.3 Hz, C-1), 69.7 (C-5), 68.3 (C-4), 66.7 (bq, $J_{C3,F}$ = 2.0 Hz, C-3), 61.5 (C-6), 47.7 (q, $J_{C2,F}$ = 26.2 Hz, C-2), 20.8, 20.7, 20.7 (4xCH_3, Ac); **FTIR–ATR (neat)** v in cm^{-1}: 2970, 1759, 1370, 1221, 1178, 1014, 938; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{15}H_{19}F_3NaO_9^+$ (m/z): calc. 423.0873; found 423.0880.

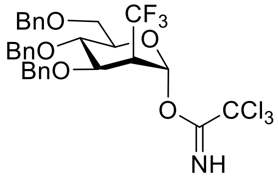


1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-trifluoromethyl-α-D-mannopyranose (5c). 10% Pd/C (124 mg, 0.11 mmol Pd) was added to a solution of **5b** (680 mg, 1.24 mmol) in dry and deoxygenated methanol (12 mL) at room temperature. The mixture was stirred under H_2 (1 atm) at the same temperature for 16 h, filtered through a short path of Celite® 545, and concentrated under reduced pressure. The crude was dissolved in pyridine (4.20 mL) and Ac_2O (0.9 mL) was added, and the reaction stirred at room temperature overnight. Pyridine was then evaporated under vacuum and the residue dissolved in EtOAc and washed with saturated aqueous $CuSO_4$, NH_4Cl and NaCl. The organic phase was dried with $MgSO_4$, filtered, the solvent evaporated, and the crude purified using column chromatography (3:7 EtOAc/hexane) to afford **5c** (400 mg, 80%) as a colorless syrup. **R$_f$** (3:7 EtOAc/hexane): 0.26; **$[\alpha]^{D}_{25}$** : +58.2 (0.27, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 6.45 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1), 5.47–5.31 (m, 2H, H-3, H-4), 4.20–4.10 (m, 2H, H-6a, H-6b), 4.03 (m, 1H, H-5), 3.14 (m, 1H, H-2), 2.16, 2.06, 2.06 (s, 12H, 4CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.8 (d, J = 9.3 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.7, 170.2, 169.4, 168.2 (4xC=O, Ac), 124.4 (q, $J_{C,F}$ = 281.3 Hz, CF_3), 88.9 (q, $J_{C1,F}$ = 4.5 Hz, C-1), 70.5 (C-5), 67.4 (C-3), 65.4 (C-4), 62.0 (C-6), 45.2 (q, $J_{C2,F}$ = 25.5 Hz, C-2), 20.9, 20.8, 20.7 (4xCH_3, Ac); **FTIR–ATR (neat)** v in cm^{-1}: 2969, 1749, 1371, 1220, 1159, 1125; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{15}H_{19}F_3NaO_9^+$ (m/z): calc. 423.0873; found 423.0872.

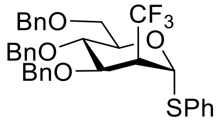
3.3. Synthesis of glycosyl donors



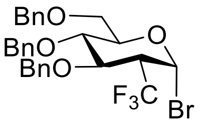
Scheme S4. Preliminary synthesis of OTCA and SPh glycosyl donors. Reactions performed at 0.03 M concentration unless otherwise indicated. Isolated yields after flash column chromatography. DBU = 1,8-diazabicyclo(5.4.0)undec-7-ene, TMS = trimethylsilyl, TCA = trichloroacetimidate.



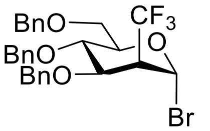
2-Deoxy-2-trifluoromethyl-3,4,6-tri-*O*-benzyl-α-D-mannosyl trichloroacetimidate (5a-OTCA). To a solution of **5a** (50 mg, 0.1 mmol) in dry CH_2Cl_2 (2 mL) was added Cl_3CCN (100 µL, 1 mmol) and DBU (1.5 µL, 0.1 mmol) at 0 °C. Reaction was let to warm up to room temperature and stirred for 2 h. Solvents were evaporated under reduced pressure and the crude was purified by flash column chromatography (from 100:5 hexane/EtOAc to 100:8 hexane/EtOAc) to afford **5a-OTCA** (63 mg, 48%) as a yellowish syrup. Compound **5a-OTCA** was straightway used in the subsequent reaction. Selected spectroscopic data for **5a-OTCA**: **R$_f$** (1:4 EtOAc/hexane): 0.50; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 8.63 (s, 1H, NH), 7.35–7.19 (m, 13H, Ar), 7.16–7.11 (m, 2H, Ar), 6.60 (d, $J_{1,2}$ = 3.1 Hz, 1H, H-1), 4.68 (d, J = 11.0 Hz, 1H, CH-Ph), 4.67 (d, J = 11.4 Hz, 1H, CH-Ph), 4.56 (d, J = 12.0 Hz, 1H, CH-Ph), 4.55 (d, J = 11.5 Hz, 1H, CH-Ph), 4.43 (d, J = 11.9 Hz, 1H, CH-Ph), 4.39 (d, J = 11.0 Hz, 1H, CH-Ph), 4.13 (appt, $J_{2,3}$ = $J_{3,4}$ = 4.7 Hz, 1H, H-3), 3.95 (m, 2H, H-4, H-5), 3.68 (dd, $J_{6a,6b}$ = 11.2 Hz, $J_{5,6a}$ = 3.3 Hz, 1H), 3.62 (d, $J_{6a,6b}$ = 11.0 Hz, 1H), 2.93 (qdd, $J_{2,CF3}$ = 9.1 Hz, $J_{2,3}$ = 5.0 Hz, $J_{1,2}$ = 3.0 Hz, 1H); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.5 (s, 3F, CF_3); **^{13}C NMR** (from HSQC) ($CDCl_3$, 100.6 MHz) δ in ppm: 128.0 (CH, Ar), 93.8 (C-1), 74.8 (C-3), 73.8 (C-5), 73.7 (CH_2Ph), 73.1 (CH_2Ph), 72.5 (CH_2Ph), 68.5 (C-6), 44.5 (C-2).



Phenyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-trifluoromethyl-1-thio-α-D-mannopyranose (5b-SPh). A solution of **5a** (102 mg, 0.19 mmol) and preactivated 3 Å MS in dry CH_2Cl_2 (1 mL) were stirred under argon for 30 min. Then, PhSH (58 µL, 0.56 mmol) was added and the mixture stirred under argon for 30 min. The reaction was cooled down to 0 °C and $BF_3\cdot Et_2O$ (70 µL, 0.56 mmol) was added dropwise. The reaction was let to warm up to room temperature and stirred for 14 h. The crude was diluted with EtOAc and organic layer was washed with $NaHCO_3$ and H_2O twice. Solvents were evaporated under reduced pressure and the crude was purified by flash column chromatography (from hexane to 95:5 hexane/EtOAc) to afford **5b-SPh** (25 mg, 23%) as a colorless syrup. Selected spectroscopic data for **5b-SPh**: **R_f** (1:9 EtOAc/hexane): 0.45; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.51–7.47 (m, 2H, Ar), 7.39–7.22 (m, 16H, Ar), 7.20–7.16 (m, 2H, Ar), 5.86 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1), 4.81 (d, J = 10.9 Hz, 1H, CH-Ph), 4.76 (d, J = 11.2 Hz, 1H, CH-Ph), 4.59 (d, J = 12.2 Hz, 1H, CH-Ph), 4.58 (d, J = 11.1 Hz, 1H, CH-Ph), 4.46 (d, J = 11.1 Hz, 1H, CH-Ph), 4.43 (d, J = 12.0 Hz, 1H, CH-Ph), 4.38 (ddd, $J_{4,5}$ = 9.2 Hz, $J_{5,6a}$ = 5.1 Hz, $J_{5,6b}$ = 1.9 Hz, 1H, H-5), 4.18 (appt, $J_{2,3}$ = $J_{3,4}$ = 7.2 Hz, 1H, H-3), 3.94 (t, $J_{3,4}$ = $J_{4,5}$ = 8.9 Hz, 1H, H-4), 3.75 (dd, $J_{6a,6b}$ = 10.9 Hz, $J_{5,6a}$ = 5.1 Hz, 1H, H-6a), 3.66 (dd, $J_{6a,6b}$ = 10.9 Hz, $J_{5,6b}$ = 2.0 Hz, 1H, H-6b), 2.93 (qdd, $J_{2,CF3}$ = 9.3 Hz, $J_{2,3}$ = 5.5 Hz, $J_{1,2}$ = 1.6 Hz, 1H, H-2); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –61.8 (d, J = 8.8 Hz, 3F, CF_3); **^{13}C NMR** (from HSQC) ($CDCl_3$, 100.6 MHz) δ in ppm: 132.0, 128.4, 128.2 (CH, Ar), 82.3 (C-1), 76.5 (C-3), 74.8 (CH_2Ph), 74.4 (C-5), 74.0 (CH_2Ph), 72.9 (C-4), 72.1 (CH_2Ph), 68.4 (C-6), 45.7 (C-2).

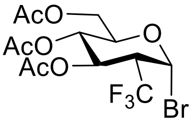


2-Deoxy-2-trifluoromethyl-3,4,6-tri-*O*-benzyl-α-D-glucosyl bromide (4b-Br). To a solution of **4b** (24 mg, 0.04 mmol) in dry CH_2Cl_2 (1,4 mL) was added 33% HBr in AcOH (90 µL) at 0 ºC. Reaction was stirred at 0 ºC for 3 h. The crude was then diluted with CH_2Cl_2 and washed with $NaHCO_3$ twice. Solvents were evaporated under reduced pressure and the crude was analyzed by ^{1}H NMR (85%). Product **4b-Br** (24 mg, 85%) was isolated as a colorless syrup and straightway used in the subsequent reaction. Selected spectroscopic data for **4b-Br** (crude): **R_f** (1:9 EtOAc/hexane): 0.47; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.36–7.29 (m, 13H, Ar), 7.21–7.17 (m, 2H, Ar), 6.82 (d, $J_{1,2}$ = 3.2 Hz, 1H, H-1), 4.84 (d, J = 10.3 Hz, 1H, CH-Ph), 4.83 (d, J = 10.8 Hz, 1H, CH-Ph), 4.78 (d, J = 10.2 Hz, 1H, CH-Ph), 4.59 (d, J = 12.2 Hz, 1H, CH-Ph), 4.56 (d, J = 11.0 Hz, 1H, CH-Ph), 4.48 (d, J = 12.1 Hz, 1H, CH-Ph), 4.28 (dd, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H-3), 4.10 (dt, $J_{4,5}$ = 10.1 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 2.3 Hz, 1H, H-5), 3.87 (dd, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 9.1 Hz, 1H, H-4), 3.82 (dd, $J_{6a,6b}$ = 11.1 Hz, $J_{5,6a}$ = 3.1 Hz, 1H, H-6a), 3.67 (d, $J_{6a,6b}$ = 11.1 Hz, $J_{5,6a}$ = 2.0 Hz, 1H, H-6b), 2.94 (dqd, $J_{2,3}$ = 11.0 Hz, $J_{2,CF3}$ = 7.6 Hz, $J_{1,2}$ = 3.5 Hz, 1H, H-2); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –63.5 (d, J = 7.9 Hz, 3F, CF_3); **^{13}C NMR** (from HSQC) ($CDCl_3$, 100.6 MHz) δ in ppm: 128.2, 127.8 (CH, Ar), 83.3 (C-1), 77.6 (C-4), 77.0 (C-3), 75.8 (CH_2Ph), 75.3 (C-5), 73.3 (CH_2Ph), 67.2 (C-6), 52.0 (C-2).



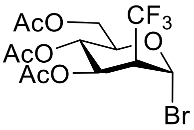
2-Deoxy-2-trifluoromethyl-3,4,6-tri-*O*-benzyl-α-D-mannosyl bromide (5b-Br). To a solution of **5b** (20 mg, 0.04 mmol) in dry CH_2Cl_2 (1,2 mL) was added 33% HBr in AcOH (75 µL) at 0 ºC. Reaction was stirred at 0 ºC for 3 h. The crude was then diluted with CH_2Cl_2 and washed with $NaHCO_3$ twice. Solvents were evaporated under reduced pressure and the crude was analyzed by ^{1}H NMR (95%). Product **5b-Br** (21 mg, 95%) was isolated as a colorless syrup and straightway used in the subsequent reaction. Selected spectroscopic data for **5b-Br**: **R$_f$** (1:9 EtOAc/hexane): 0.43; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.37–7.27 (m, 13H, Ar), 7.18–7.13 (m, 2H, Ar), 6.82 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1), 4.81 (d, J = 10.8 Hz, 1H, CH-Ph), 4.74 (d, J = 11.2 Hz, 1H, CH-Ph), 4.60 (d, J = 11.2 Hz, 1H, CH-Ph), 4.59 (d, J = 12.3 Hz, 1H, CH-Ph), 4.47 (d, J = 10.8 Hz, 1H, CH-Ph), 4.46 (d, J = 12.1 Hz, 1H, CH-Ph), 4.50–4.40 (m, 1H, H-3), 4.08–3.98 (m, 2H, H-4, H-5), 3.76 (dd, $J_{6a,6b}$ = 11.3 Hz, $J_{5,6a}$ = 3.9 Hz, 1H, H-6a), 3.65 (d, $J_{6a,6b}$ = 11.3 Hz, $J_{5,6b}$ = 1.8 Hz, 1H, H-6b), 2.93 (qdd, $J_{2,CF3}$ = 9.4 Hz, $J_{2,3}$ = 5.5 Hz, $J_{1,2}$ = 1.7 Hz, 1H, H-2); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.2 (s, 3F, CF_3); **^{13}C NMR** (from HSQC) ($CDCl_3$, 100.6 MHz) δ in ppm: 128.9, 128.4, 128.2 (CH, Ar), 83.2 (C-1), 76.4 (C-5), 76.2 (C-3), 75.0 (CH_2Ph), 73.5 (C-4), 73.0 (CH_2Ph), 72.7 (CH_2Ph), 67.8 (C-6), 51.0 (C-2).

2-Deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α-D-glucosyl bromide (4c-Br). To a



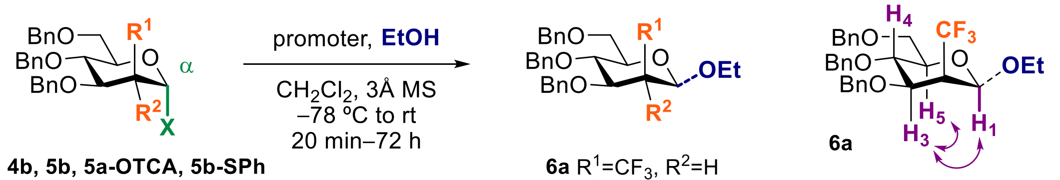
solution of **4c** (25 mg, 0.06 mmol) in dry CH_2Cl_2 (0.4 mL) was added 33% HBr in AcOH (0.4 mL) at 0 ºC. Reaction was stirred at room temperature for 3 h. The crude was then diluted with CH_2Cl_2 and washed with $NaHCO_3$ twice. Solvents were evaporated under reduced pressure and the crude was analyzed by ^{1}H NMR (>99%). Product **4c-Br** (26 mg, 99%) was isolated as a colorless syrup and straightway used in the subsequent reaction. Selected spectroscopic data for **4c-Br** (crude): **R$_f$** (2:3 EtOAc/hexane): 0.45; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 6.50 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 5.73 (dd, $J_{2,3}$ = 11.1 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 5.13 (dd, $J_{4,5}$ = 10.1 Hz, $J_{3,4}$ = 9.3 Hz, 1H, H-4), 4.38–4.27 (m, 2H, H-5, H-6a), 4.11 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6b}$ = 2.0 Hz, 1H, H-6b), 3.14 (dqd, $J_{2,3}$ = 10.9 Hz, $J_{2,CF3}$ = 7.4 Hz, $J_{1,2}$ = 3.5 Hz, 1H, H-2), 2.09, 2.06, 2.04 (s, 9H, CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –64.7 (d, J = 7.1 Hz, 3F, CF_3); **^{13}C NMR** (from HSQC) ($CDCl_3$, 100.6 MHz) δ in ppm: 80.7 (C-1), 72.5 (C-5), 67.6 (C-4), 67.2 (C-3), 60.8 (C-6), 50.4 (C-2), 20.5, 20.3 ($3CH_3$, Ac).

2-Deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α-D-mannosyl bromide (5c-Br). To a



solution of **5c** (32 mg, 0.08 mmol) in dry CH_2Cl_2 (0.5 mL) was added 33% HBr in AcOH (0.5 mL) at 0 ºC. Reaction was stirred at room temperature for 3 h. The crude was then diluted with CH_2Cl_2 and washed with $NaHCO_3$ twice. Solvents were evaporated under reduced pressure and the crude was analyzed by ^{1}H NMR (>99%). Product **5c-Br** (31 mg, 99%) was isolated as colorless crystals and straightway used in the subsequent reaction. Selected spectroscopic data for **5c-Br** (crude): **R$_f$** (4:6 EtOAc/hexane): 0.40; **^{1}H NMR** (CDCl$_3$, 400 MHz) δ in ppm: **^{1}H NMR** (CDCl$_3$, 400 MHz) δ in ppm: 6.72 (s, 1H, H-1), 5.66 (dd, $J_{3,4}$ = 8.5 Hz, $J_{2,3}$ = 6.2 Hz, 1H, H-3), 5.50 (t, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, 1H, H-4), 4.25–4.16 (m, 3H, H-5, H-6a, H-6b), 3.51 (qd, $J_{2,CF3}$ = 9.1 Hz, $J_{2,3}$ = 5.5 Hz, 1H, H-2), 2.09, 2.08, 2.07 (s, 9H, CH$_3$, Ac); **^{19}F NMR** (CDCl$_3$, 376.5 MHz) δ in ppm: –62.7 (d, J = 9.3 Hz, 3F); **^{13}C NMR** (from HSQC) (CDCl$_3$, 100.6 MHz) δ in ppm: 80.1 (C-1), 72.8 (C-5), 67.5 (C-4), 64.5 (C-3), 61.2 (C-6), 50.6 (C-2), 20.3 (CH$_3$, Ac).

3.4. Preliminary glycosylation reactions and solvent screening



4b, 5b, 5a-OTCA, 5b-SPh

6a R^1=CF$_3$, R^2=H
6b R^1=H, R^2=CF$_3$

entry[a]	donor	promoter	yield (%)[b]	α/β ratio[b]
1	**4b** OAc	TMSOTf	**6b** NR	–
2	**4b** OAc	BF$_3$·OEt$_2$	**6b** NR	–
3	**5b** OAc	TMSOTf	**6a** NR	–
4	**5a-OTCA**	TMSOTf	**6a** 69[c]	38:62
5[d]	**5b-SPh**	NIS/TfOH	**6a** 73	58:42

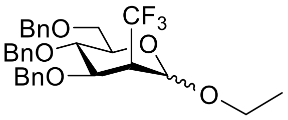
$^4C_1$ conformation

- *Key NOEs*
- $^3J_{1,2}$ ~ 2.0 Hz
- $^3J_{2,3}$ ~ 5.7 Hz
- $^3J_{3,4}$ ~ 8.0 Hz
- $^1J_{C1-H1}$ ~ 174.3 Hz (**6aα**)
- $^1J_{C1-H1}$ ~ 163.4 Hz (**6aβ**)

- OTCA, SPh (purification required, low yield, hydrolysis detected)
- OAc (unreactive for *Glc*/*Man* up to room temperature)

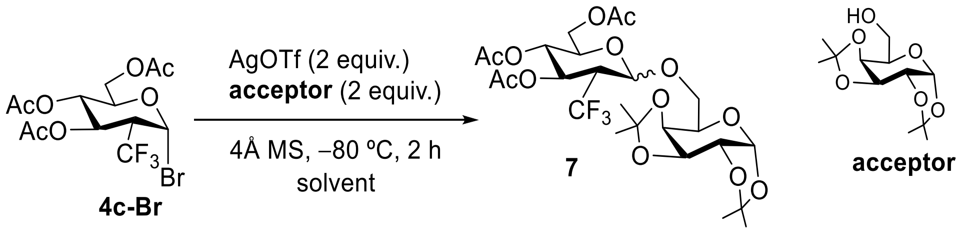
Scheme S5. Preliminary glycosylation results. [a] Reactions performed at 0.03 M concentration unless otherwise indicated. [b] Yield and selectivity determined by ^{19}F NMR of the crude reaction mixture using 1,4-difluorobenzene as internal standard unless otherwise indicated. [c] Isolated yield. [d] Reaction performed at 0.2 M concentration. TMS = trimethylsilyl, TCA = trichloroacetimidate, MS = molecular sieves, NIS = *N*-iodosuccinimide, THF = tetrahydrofuran, NR = no reaction.

1-*O*-Ethyl-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α/β-D-mannopyranose

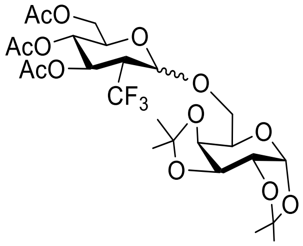


(6a). *Method A.* To a solution of **5a-OTCA** (28 mg, 0.04 mmol) and preactivated 4Å MS in CH$_2$Cl$_2$ (1.5 mL) at –78 ºC, were added EtOH (3.3 µL, 0.06 mmol) and TMSOTf (0.8 µL, 0.004 mmol). Reaction was stirred for 30 minutes at the same temperature. Then, the solvents were evaporated and the crude was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane to afford **6aα** (6 mg, 26%) as a colorless syrup and **6aβ** (10 mg, 43%) as a colorless syrup. *Method B.* A solution of **5b-SPh** (14 mg, 0.024 mmol), EtOH (8 µL, 0.071 mmol), and preactivated 3Å MS in CH$_2$Cl$_2$ (1.5 mL) was mixed for 30 min at room temperature. Then, the mixture was cooled down to –78 ºC and NIS (16.7 mg, 0.071 mmol) and TfOH (0.2 µL, 0.0024 mmol) were added. The reaction was maintained for 15 min at –78ºC and then slowly warmed up to 0 ºC for 3 h. The reaction was quenched with Et$_3$N and aqueous Na$_2$S$_2$O$_3$ and the product extracted with CH_2Cl_2. The organic phase was dried with Na_2SO_4, filtered, and the solvent evaporated under vacuum. Quantitative ^{19}F NMR analysis indicated an α/β ratio (1.41:1) and a combined yield (73%) using 1,4-difluorobenzene (5 µL, 0.049 mmol) as the internal standard. Selected data for **6aα**: **R$_f$** (1:4 EtOAc/hexane): 0.62; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.38–7.23 (m, 13H, Ar), 7.15–7.10 (m, 2H, Ar), 5.19 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1), 4.76 (d, J = 10.6 Hz, 1H, CH-Ph), 4.74 (d, J = 10.7 Hz, 1H, CH-Ph), 4.63 (d, J = 12.1 Hz, 1H, CH-Ph), 4.54 (d, J = 11.2 Hz, 1H, CH-Ph), 4.50 (d, J = 12.1 Hz, 1H, CH-Ph), 4.41 (d, J = 10.8 Hz, 1H, CH-Ph), 4.19 (t, $J_{3,4}$ = $J_{2,3}$ = 7.3 Hz, 1H, H-3), 3.88 (t, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, 1H, H-4), 3.81 (ddd, $J_{4,5}$ = 9.4 Hz, $J_{5,6a}$ = 4.6 Hz, $J_{5,6b}$ = 2.3 Hz, 1H, H-5), 3.79–3.67 (m, 2H, H-6a, H-7), 3.67 (dd, $J_{6a,6b}$ = 10.8 Hz, $J_{5,6b}$ = 2.3 Hz, 1H, H-6b), 3.48 (dq, $J_{7,7'}$ = 9.7 Hz, $J_{7',8}$ = 7.1 Hz, 1H, H-7', Et), 3.00 (qdd, $J_{2,CF3}$ = 10.1 Hz, $J_{2,3}$ = 5.6 Hz, $J_{1,2}$ = 2.1 Hz, 1H, H-2), 1.19 (t, J = 7.1 Hz, 3H, CH_3, Et); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.0 (d, J = 9.8 Hz, 3F, CF_3); **^{13}C NMR** (from HSQC) ($CDCl_3$, 100.6 MHz) δ in ppm: 128.0, 127.9, 127.8 127.6, 127.5 (CH, Ar), 95.2 (C-1), 76.4 (C-3), 74.5 (CH_2Ph), 74.3 (C-4), 73.1 (CH_2Ph), 71.9 (CH_2Ph), 70.9 (C-5), 68.8 (CH_2, Et), 62.9 (C-6), 45.7 (C-2), 14.3 (CH_3, Et). Data for **6aβ**: **R$_f$** (2:8 EtOAc/hexane): 0.49; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.35–7.25 (m, 13H, Ar), 7.22–7.18 (m, 2H, Ar), 4.88 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1), 4.65 (d, J = 11.6 Hz, 2H, CH-Ph), 4.55–4.44 (m, 4H, CH-Ph), 3.95–3.85 (m, 3H, H-7, H-4, H-5), 3.85–3.79 (m, 2H, H-6, H-6b), 3.75 (dd, $J_{3,4}$ = 9.6 Hz, $J_{2,3}$ = 5.3 Hz, 1H, H-3), 3.00 (dqd, $J_{2,CF3}$ = 9.4 Hz, $J_{2,3}$ = 4.4 Hz, $J_{1,2}$ = 2.2 Hz, 1H, H-2), 1.22 (t, J = 7.1 Hz, 3H, CH_3, Et); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –61.5 (s, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 138.3, 137.8, 137.4 (C-Ar), 128.4, 128.37, 128.3, 128.0, 127.9, 127.8 127.6, 127.5 (CH, Ar), 125.4 (q, J = 282.2 Hz, CF_3), 96.4 (C-1), 75.4 (C-3), 74.7 (C-5), 73.4 (CH_2Ph), 73.2 (CH_2Ph), 72.4 (C-4), 72.0 (CH_2Ph), 69.9 (CH_2, Et), 64.9 (C-6), 43.7 (q, J = 24.9 Hz, C-2), 14.7 (CH_3, Et).

3.4.1. Solvent Screening



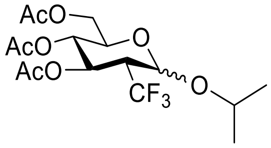
General procedure. To a solution of **4c** (0.10 mmol) in CH_2Cl_2 (0.5 mL) was added 33 % HBr in AcOH (0.5 mL) at 0 °C. The reaction mixture was then slowly allowed to warm up to room temperature and stirred for 4 h. The crude was diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ at 0 ºC. The two layers were separated, and the aqueous phase was successively extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered and the solvent evaporated to afford the crude bromopyranoside **4c-Br**, which was used in the next step without further purification. The resulting crude was azeotropically dried with toluene, maintained under vacuum for 3 h and redissolved in dry solvent (1 mL). The solution was transferred via cannula to a Schlenk flask containing azeotropically dried [1:2,3:4]-di-*O*-isopropylidene-α-D-galactopyranoside (52 mg, 0.2 mmol) and 4 Å MS under argon and maintained at –80 ºC for 30 minutes. A solution of azeotropically dried AgOTf (51.4 mg, 0.2 mmol) in the indicated solvent (1 mL) was transferred via cannula under argon. The reaction was stirred at –80 °C for 2 h, then diluted with CH_2Cl_2, filtered through a short path of silica and the solvent evaporated. The α/β ratio and reaction yield was determined quantitative ^{19}F NMR analysis using 1,4-difluorobenzene (20 μL, 0.194 mmol) as the internal standard.



3,4,6-Tri-*O*-benzyl-2-deoxy-2-trifluoromethyl-α-D-mannopyranosyl-(1 → 6)-[1:2,3:4]-di-*O*-isopropylidene-α-D-galactopyranoside (7). Product **7** was isolated following the general procedure above, starting from **4c** (97 mg, 0.242 mmol) in CH_2Cl_2 (1 mL) and 33% HBr in AcOH (1 mL) at 0 °C. After standard work-up and azeotropic drying, the bromopyranoside **4c-Br** was redissolved with dry CH_2Cl_2 (2.5 mL). The solution was transferred via cannula to a Schlenk flask containing azeotropically dried 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (126 mg, 0.484 mmol) and 4 Å MS under argon and maintained at –80 ºC for 30 minutes. A solution of azeotropically dried AgOTf (125 mg, 0.484 mmol) in dry toluene (2.5 mL) was transferred via cannula under argon. The reaction was stirred at –80 °C for 2 h, and then diluted with CH_2Cl_2, filtered through a short path of silica and the solvent evaporated. The residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **7β** (124 mg, 86%) as a white solid. **R_f** (2:3 EtOAc/hexane): 0.39; **m.p**: 148–150 ºC; **$[\alpha]^{D}_{25}$** : –20.7 (1.21, $CHCl_3$); **^1H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.49 (d, $J_{1',2'}$ = 5.0 Hz, 1H, H-1'), 5.42 (dd, $J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 8.9 Hz, 1H, H-3), 5.04 (dd, $J_{4,5}$ = 10.1 Hz, $J_{3,4}$ = 8.9 Hz, 1H, H-4), 4.86 (d, $J_{1,2}$ = 7.8 Hz, 1H, H-1), 4.59 (dd, $J_{3',4'}$ = 7.9 Hz, $J_{2',3'}$ = 2.4 Hz, 1H, H-3'), 4.30 (dd, $J_{1',2'}$ = 5.0 Hz, $J_{2',3'}$ = 2.4 Hz, 1H, H-2'), 4.28 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 5.1 Hz, 1H, H-6a), 4.20 (dd, $J_{3',4'}$ = 7.9 Hz, $J_{4',5'}$ = 1.8 Hz, 1H, H-4'), 4.10 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6b}$ = 2.5 Hz, 1H, H-6b), 4.01–3.94 (m, 2H, H-6a', H-5'), 3.79 (dd, $J_{6a',6b'}$ = 12.8 Hz, $J_{5',6b'}$ = 8.2 Hz, 1H, H-6b'), 3.71 (ddd, $J_{4,5}$ = 10.1 Hz, $J_{5,6a}$ = 5.1 Hz, $J_{5,6b}$ = 2.5 Hz, 1H, H-5), 2.68 (m, 1H, H-2), 2.07, 2.01, 2.01 (s, 9H, 3CH_3, Ac), 1.50, 1.43, 1.32 (s, 12H, 4CH_3); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.8 (d, *J* = 7.7 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.8, 169.8, 169.7 (3xC=O, Ac), 126.0 (q, $J_{C,F}$ = 282.0 Hz, CF_3), 109.5, 108.9 (2Cketal), 98.5 (q, $J_{C1,F}$ = 2.5 Hz, C-1), 96.4 (C-1'), 71.5 (C-5), 71.3 (C-4'), 70.7 (C-3'), 70.5 (C-2'), 69.0 (C-4), 68.6 (C-6'), 68.1 (q, $J_{C3,F}$ = 1.6 Hz, C-3), 67.7 (C-5'), 62.3 (C-6), 49.8 (q, $J_{C2,F}$ = 24.5 Hz, C-2), 26.1, 26.0, 25.1, 24.5 (4xCH_3'), 20.9, 20.7 (3xCH_3, Ac); **FTIR–ATR (neat)** ν in cm^{-1}: 2988, 1755, 1375, 1220, 1180, 1121, 1069, 747, 695; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{25}H_{27}F_{35}NaO_{13}^+$ (m/z): calc. 623.1922; found 623.1916.

3.5. Screening of CF_3 configuration, protecting groups, nucleophiles, concentration, stoichiometry, promoters, and comparison with 2-fluorosugars.

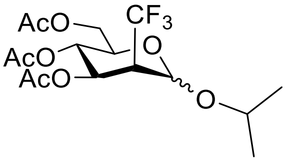
General procedure. To a solution of 2-fluoro or 2-trifluoromethylglycosyl acetate (0.10 mmol) in CH_2Cl_2 (0.5 mL) was added 33% HBr in AcOH (0.5 mL) at 0 °C. The reaction mixture was then slowly allowed to warm up to room temperature and stirred for 4 h. After completion of the reaction (TLC monitoring), the crude was diluted with CH_2Cl_2 and neutralized with saturated aqueous $NaHCO_3$ at 0 ºC. The two layers were separated, and the aqueous phase was successively extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, filtered and the solvent evaporated to afford the crude bromopyranoside, which was used in the next step without further purification. The resulting crude was azeotropically dried with toluene and maintained under vacuum for 3 h. Then, anhydrous CH_2Cl_2 (1 mL) was added to the crude bromopyranoside and the solution was transferred via cannula to a Schlenk flask containing 4 Å MS. Acceptor (0.2 mmol) was added under argon and the solution was stirred at –80 ºC for 30 minutes. Next, a solution of azeotropically dried AgOTf (0.2 mmol) in dry toluene (1 mL) was transferred via cannula under argon to the Schlenk flask and the reaction mixture was stirred at –80 °C for 2 h. The mixture was diluted with CH_2Cl_2, filtered through a short path of silica and the solvent evaporated. The α/β ratio and yield were determined by quantitative ^{19}F NMR using 1,4-difluorobenzene (20 μL, 0.194 mmol) as the internal standard. The residue was further purified by flash column chromatography to afford pure or enriched anomeric fractions for NMR characterization. In some cases, due to purification issues and prior to flash column chromatography, the remaining acceptor was submitted to acetylation conditions using Ac_2O (0.6 mmol) and pyridine (6 mmol) in CH_2Cl_2 (0.6 mL) for 16 h at room temperature. The crude was evaporated under reduced pressure, redissolved in CH_2Cl_2 (2 mL) and washed with $CuSO_4$ (x2), NH_4Cl (x2) and brine (x2). The combined organic layers were dried over $MgSO_4$ and the solvent evaporated.



1-*O*-Isopropyl-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α/β-D-glucopyranose (10). The title compound was prepared following the general procedure above, starting from **4c** (55 mg, 0.137 mmol), CH_2Cl_2 (1 mL) and 33% HBr in AcOH (1 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **4c-Br**, isopropyl alcohol (31 µL, 0.41 mmol), dry CH_2Cl_2 (1.4 mL), dry toluene (1.4 mL), 4 Å MS and AgOTf (70 mg, 0.27 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard workup, quantitative ^{19}F NMR analysis indicated an α/β ratio (33:67) and yield (61%) using 1,4-difluorobenzene (10 µL, 0.097 mmol) as the internal standard. The residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **10α** (5 mg, 9%) and a fraction containing an anomeric mixture of **10** (α/β, 1:7) (25 mg, 56%). Data for **10α**: Colorless syrup; **R$_f$** (1:4 EtOAc/hexane): 0.26; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.66 (dd, $J_{2,3}$ = 11.3 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 5.21 (d, J = 3.5 Hz, 1H, H-1), 5.01 (dd, $J_{4,5}$ = 10.2 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-4), 4.28 (dd, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6a}$ = 4.6 Hz, 1H, H-6a), 4.14 (ddd, $J_{4,5}$ = 10.2 Hz, $J_{5,6a}$ = 4.5 Hz, $J_{5,6b}$ = 2.3 Hz, 1H, H-5), 4.06 (dd, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6b}$ = 2.3 Hz, 1H, H-6b), 3.88 (sept, $J_{7,8}$ = 6.3 Hz, 1H, H-7), 2.78 (dqd, $J_{2,3}$ = 11.4 Hz, $J_{2,F}$ = 7.7 Hz, $J_{1,2}$ = 3.4 Hz, 1H, H-2), 2.08, 2.04, 2.02 (s, 9H, $3CH_3$, Ac), 1.24 (d, $J_{7,8}$ = 6.2 Hz, 3H, H-8), 1.17 (d, $J_{7,8}$ = 6.2 Hz, 3H, H-8'); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.03 (d, J = 8.1 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 169.9, 169.6 (3xC=O, Ac), 126.0 (q, $J_{C,F}$ = 280.8 Hz, CF_3), 93.9 (q, $J_{C1,F}$ = 4.0 Hz, C-1), 71.9 (C-7), 69.1 (C-4), 67.6 (C-5), 67.1 (q, $J_{C3,F}$ = 2.0 Hz, C-3), 62.0 (C-6), 48.9 (q, $J_{C2,F}$ = 25.6 Hz, C-2), 23.1 (C-8), 21.3 (C-8'), 20.7, 20.65, 20.60 ($3xCH_3$, Ac); **FTIR–ATR (neat)** ν in cm^{-1}: 2975, 2923, 2362, 1752, 1369, 1307, 1223, 1180, 1157, 1114, 1044, 1026, 924, 914; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{16}H_{23}F_3NaO_8^+$ (m/z): calc. 423.1237; found 423.1239. Data for **10β**: Colorless syrup; Inseparable mixture of **9** (α/β, 1:7). **R$_f$** (1:4 EtOAc/hexane): 0.23; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.43 (dd, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 8.9 Hz, 1H, H-3), 5.00 (dd, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H-4), 4.71 (d, $J_{1,2}$ = 8.2 Hz, 1H, H-1), 4.26 (dd, $J_{6a,b}$ = 12.2 Hz, $J_{5,6a}$ = 5.3 Hz, 1H, H-6a), 4.11 (dd, $J_{6a,b}$ = 12.2 Hz, $J_{5,6b}$ = 2.6 Hz, 1H, H-6b), 3.96 (sept, $J_{7,8}$ = 6.2 Hz, 1H, H-7), 3.68 (ddd, $J_{4,5}$ = 10.1 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.6 Hz, 1H, H-5), 2.66 (ddq, $J_{2,3}$ = 10.7 Hz, $J_{1,2}$ = 8.2 Hz, $J_{2,F}$ = 7.7 Hz, 1H, H-2), 2.07, 2.02, 2.02 (s, 9H, $3CH_3$, Ac), 1.25 (d, $J_{7,8}$ = 6.2 Hz, 3H, H-8), 1.17 (d, $J_{7,8}$ = 6.2 Hz, 3H, H-8'); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.69 (d, J = 7.6 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 169.7, 169.6 (3xC=O, Ac), 126.0 (q, $J_{C,F}$ = 281.8 Hz, CF_3), 97.1 (q, $J_{C1,F}$ = 2.5 Hz, C-1), 72.9 (C-7), 71.3 (C-5), 69.1 (C-4), 68.1 (q, $J_{C3,F}$ = 1.7 Hz, C-3), 62.2 (C-6), 49.9 (q, $J_{C2,F}$ = 23.9 Hz, C-2), 23.2 (C-8), 21.4 (C-8'), 21.2, 20.7, 20.6 ($3xCH_3$, Ac); **FTIR–ATR (neat)** ν in cm^{-}

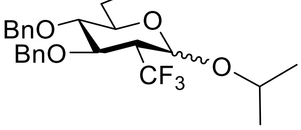
^{1}: 2977, 1750, 1668, 1433, 1372, 1328, 1223, 1182, 1122, 1072, 1031, 906; **HRMS (TOF ES^{+})** for (M+Na)$^{+}$ $C_{16}H_{23}F_3NaO_8^{+}$ (m/z): calc. 423.1237; found 423.1245.

1-*O*-Isopropyl-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α-D-mannopyranose



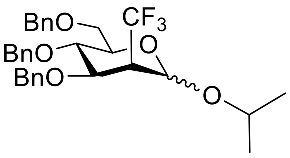
(11). The title compound was prepared following the general procedure above, starting from **5c** (25 mg, 0.062 mmol), CH_2Cl_2 (0.5 mL) and 33% HBr in AcOH (0.5 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **5c-Br**, isopropyl alcohol (4 μL, 0.186 mmol), dry CH_2Cl_2 (0.6 mL), dry toluene (0.6 mL), 4 Å MS and AgOTf (31.9 mg, 0.124 mmol). The reaction mixture was stirred under argon at –80 °C for 2 h. After standard workup, quantitative ^{19}F NMR analysis indicated an α/β ratio (>95:5) and yield (91%) using 1,4-difluorobenzene (10 μL, 0.097 mmol) as the internal standard. The residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **11α** (20 mg, 82%) as a colorless syrup. **R$_f$** (1:4 EtOAc/hexane): 0.18; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.41–4.31 (m, 2H, H-3, H-4), 5.26 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1), 4.17 (d, $J_{5,6}$ = 3.9 Hz, 2H, H-6a, H-6b), 4.02 (dt, $J_{4,5}$ = 8.9 Hz, $J_{5,6a}$ = 3.9 Hz, $J_{5,6b}$ = 1H, H-5), 3.92 (sept, $J_{7,8}$ = 6.2 Hz, 1H, H-7), 3.08 (qdd, $J_{2,F}$ = 9.8 Hz, $J_{2,3}$ = 5.5 Hz, $J_{1,2}$ = 1.6 Hz, 1H, H-2), 2.08, 2.07, 2.05 (s, 9H, 3CH_3, Ac), 1.24 (d, $J_{7,8}$ = 6.2 Hz, 3H, CH_3-8), 1.18 (d, $J_{7,8}$ = 6.2 Hz, 3H, CH_3-8'); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.64 (d, J = 9.8 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.7, 170.1, 169.5 (3xC=O, Ac), 124.7 (q, $J_{C,F}$ = 281.5 Hz, CF_3), 93.4 (q, $J_{C1,F}$ = 4.4 Hz, C-1), 70.6 (C-7), 68.2 (C-5), 67.9 (C-4), 66.0 (C-3), 62.4 (C-6), 46.6 (q, $J_{C2,F}$ = 24.6 Hz, C-2), 22.9 (C-8), 21.3 (C-8'), 20.6, 20.6, 20.5 (3xCH_3, Ac); **FTIR–ATR (neat)** ν in cm^{-1}: 2976, 1748, 1371, 1306, 1267, 1227, 1160, 1110, 1044, 977, 911; **HRMS (TOF ES^{+})** for (M+Na)$^{+}$ $C_{16}H_{23}F_3NaO_8^{+}$ (m/z): calc. 423.1237; found 423.1246.

1-*O*-Isopropyl-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranose

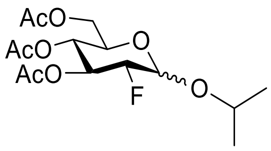


(12). The title compound was prepared following the general procedure above, starting from **4b** (56,5 mg, 0.104 mmol), CH_2Cl_2 (3 mL) and 33% HBr in AcOH (0.2 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **4b-Br**, isopropyl alcohol (32 μL, 0.421 mmol), dry CH_2Cl_2 (1 mL), dry toluene (1 mL), 4 Å MS and AgOTf (53.5 mg, 0.208 mmol). The reaction mixture was stirred under argon at –80 °C for 2 h. After standard workup, quantitative ^{19}F NMR analysis indicated an α/β ratio (3:97) and yield (72%) using 1,4-difluorobenzene (10 μL, 0.097 mmol) as the internal standard. The residue was purified by flash column chromatography (from hexane to 1:9 EtOAc/hexane) obtaining an inseparable mixture of the desired product **12β** (24 mg, 42%) and the elimination product 3,4,6-tri-*O*-benzyl-2-trifluoromethyl-D-glucal as a yellowish syrup. **R_f** (1:4 EtOAc/hexane): 0.35; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.35–7.27 (m, 13H, Ar), 7.22–7.18 (m, 2H, Ar), 4.79 (d, *J* = 10.2 Hz, 1H, CH-Ph), 4.78 (d, *J* = 11.0 Hz, 1H, CH-Ph), 4.71–4.65 (m, 2H, CH-Ph), 4.63–4.49 (m, 3H, 2xCH-Ph, H-1), 3.98 (sept, $J_{7,8}$ = 6.1 Hz, 1H, H-7), 3.83 (dd, $J_{4,5}$ = 9.6 Hz, $J_{3,4}$ = 8.6 Hz, 1H, H-4), 3.75–3.63 (m, 3H, H-3, H-6a, H-6b), 3.52 (ddd, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = 4.4 Hz, $J_{5,6b}$ = 2.9 Hz, 1H, H-5), 2.61 (qdd, $J_{2,CF3}$ = 8.2 Hz, $J_{2,3}$ = 5.3 Hz, $J_{1,2}$ = 2.4 Hz, 1H, H-2), 1.20 (d, $J_{7,8}$ = 6.3 Hz, 3H, CH_3-8), 1.15 (d, $J_{7,8}$ = 6.1 Hz, 3H, CH_3-8’); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –64.63 (d, *J* = 8.2 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 138.1, 137.9, 137.8 (C, Ar), 128.51, 128.48, 128.42, 128.38, 128.08, 127.94, 127.90, 127.87, 127.81, 127.75, 127.65 (CH, Ar), 125.5 (q, $J_{C,F}$ = 282.0 Hz, CF_3), 96.8 (q, $J_{F,1}$ = 2.6 Hz, C-1), 78.7 (C-3), 78.5 (C-4), 74.8 (CH_2Ph), 74.75 (CH_2Ph), 74.7 (C-5), 73.5 (CH_2Ph), 71.9 (C-7), 69.1 (C-6), 51.5 (q, $J_{F,2}$ = 22.9 Hz, C-2), 23.4 (CH_3-8), 21.4 (CH_3-8’); **FTIR–ATR (neat)** ν in cm^{-1}: 3031, 2973, 2921, 2866, 1497, 1454, 1383, 1356, 1329, 1308, 1290, 1245, 1212, 1174, 1124, 1101 1077, 1050, 1027, 912, 735, 697; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{31}H_{35}F_3NaO_5^+$ (m/z): calc. 567.2329; found 567.2330.

1-*O*-Isopropyl-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-benzyl-α/β-D-mannopyranose (13). The title compound was prepared following the general procedure above, starting from **5b** (65.5 mg, 0.120 mmol), CH_2Cl_2 (3.6 mL) and 33% HBr in AcOH (0.2 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **5b-Br**, isopropyl alcohol (28 µL, 0.360 mmol), dry CH_2Cl_2 (1.2 mL), dry toluene (1.2 mL), 4 Å MS and AgOTf (61.7 mg, 0.240 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard workup, quantitative ^{19}F NMR analysis indicated an α/β ratio (79:21) and yield (62%) using 1,4-difluorobenzene (10 µL, 0.097 mmol) as the internal standard. The residue was purified by flash column chromatography (from hexane to 1:9 EtOAc/hexane) to afford **13α** (26 mg, 40%) and **13β** (9 mg, 14%) as yellowish syrups and containing the elimination product 3,4,6-tri-*O*-benzyl-2-trifluoromethyl-D-glucal. Data for **13α**: Inseparable mixture of α and elimination product. Yellowish syrup. **R_f** (1:9 EtOAc/hexane): 0.45; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.40–7.24 (m, 13H, Ar), 7.19–7.13 (m, 2H, Ar), 5.31 (d, $J_{1,2}$ = 2.4 Hz, 1H, H-1), 4.74 (d, *J* = 10.9 Hz, 1H, CH-Ph), 4.73 (d, *J* = 11.2 Hz, 1H, CH-Ph), 4.63 (d, *J* = 12.1 Hz, 1H, CH-Ph), 4.54 (d,

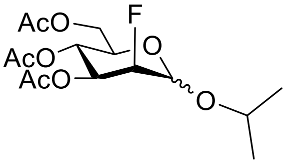


J = 11.2 Hz, 1H, CH-Ph), 4.49 (d, *J* = 12.1 Hz, 1H, CH-Ph), 4.40 (d, *J* = 10.9 Hz, 1H, CH-Ph), 4.18 (appt, $J_{2,3}$ = $J_{3,4}$ = 5.4 Hz, 1H, H-3), 3.93 (sept, $J_{7,8}$ = 6.1 Hz, 1H, H-7), 3.88 (m, 2H, H-4, H-5), 3.71 (dd, $J_{6a,6b}$ = 10.8 Hz, $J_{5,6a}$ = 3.2 Hz, 1H, H-6a), 3.66 (dd, $J_{6a,6b}$ = 10.8 Hz, $J_{5,6b}$ = 1.5 Hz, 1H, H-6b), 2.93 (qdd, $J_{2,CF3}$ = 9.9 Hz, $J_{2,4}$ = 5.3 Hz, $J_{1,2}$ = 2.4 Hz, 1H, H-2), 1.20 (d, $J_{7,8}$ = 6.3 Hz, 3H, CH$_3$-8), 1.15 (d, $J_{7,8}$ = 6.1 Hz, 3H, CH$_3$-8'); **^{19}F NMR** (CDCl$_3$, 376.5 MHz) δ in ppm: –62.2 (d, *J* = 9.9 Hz, 3F, CF$_3$); **^{13}C NMR** CDCl$_3$, 100.6 MHz) δ in ppm: 138.3, 138.1, 137.8 (C, Ar), 128.4, 128.35, 128.1, 128.0, 127.85, 127.8, 127.6, 127.5, (CH, Ar), 125.6 (q, $J_{C,F}$ = 281.3 Hz, CF$_3$), 93.6 (q, $J_{F,1}$ = 4.6 Hz, C-1), 76.5 (C-3), 74.6 (CH$_2$Ph), 73.3 (CH$_2$Ph), 72.2 (C-5), 71.3 (CH$_2$Ph), 69.6 (C-7), 69.2 (C-6), 46.6 (q, $J_{F,2}$ = 23.7 Hz, C-2), 23.2 (CH$_3$-8), 21.3 (CH$_3$-8'); **FTIR–ATR (neat)** ν in cm^{-1}: 3031, 2971, 2927, 2864, 1497, 1454, 1375, 1365, 1326, 1297, 1268, 1228, 1220, 1159, 1104, 1048, 1027, 922, 735, 718, 697; **HRMS (TOF ES$^+$)** for (M+Na)$^+$ $C_{31}H_{35}F_3NaO_5^+$ (m/z): calc. 567.2329; found 567.2336. Data for **13β**: Inseparable mixture of β and the elimination product 3,4,6-tri-*O*-benzyl-2-trifluoromethyl-D-glucal. Yellowish syrup. **R$_f$** (1:9 EtOAc/hexane): 0.40; **^{1}H NMR** (CDCl$_3$, 400 MHz) δ in ppm: 7.39–7.20 (m, 15H, Ar), 4.88 (d, $J_{1,2}$ = 2.0 Hz, H-1), 4.68 (d, *J* = 11.4 Hz, 1H, CH-Ph), 4.66 (d, *J* = 11.6 Hz, 1H, CH-Ph), 4.54 (d, *J* = 11.4 Hz, 1H, CH-Ph), 4.53 (d, *J* = 11.6 Hz, 1H, CH-Ph), 4.50 (d, *J* = 12.0 Hz, 1H, CH-Ph), 4.46 (d, *J* = 12.0 Hz, 1H, CH-Ph), 4.02–3.79 (m, 5H, H-3, H-4, H-5, H-6a, H-7), 3.73 (dd, $J_{6a,6b}$ = 9.9 Hz, $J_{5,6a}$ = 5.3 Hz, 1H, H-6b), 2.93 (qdd, $J_{2,CF3}$ = 9.4 Hz, $J_{2,3}$ = 4.3 Hz, $J_{1,2}$ = 3.2 Hz, 1H, H-2), 1.23 (d, $J_{7,8}$ = 6.2 Hz, 3H, CH$_3$-8), 1.16 (d, $J_{7,8}$ = 6.1 Hz, 3H, CH$_3$-8'); **^{19}F NMR** (CDCl$_3$, 376.5 MHz) δ in ppm: –61.5 (s, 3F, CF$_3$); **^{13}C NMR** (CDCl$_3$, 100.6 MHz) δ in ppm: 138.3, 137.9, 137.6 (C, Ar), 128.4, 128.35, 128.3, 128.0, 127.8, 127.7 127.65, 127.6, 127.5 (CH, Ar), 125.48 (q, $J_{C,F}$ = 281.8 Hz, CF$_3$), 94.5 (C-1), 75.7 (C-3), 74.7 (CH$_2$Ph), 73.4 (CH$_2$Ph), 73.2 (CH$_2$Ph), 72.5 (C-4), 71.9 (C-5), 70.7 (C-7), 70.1 (C-6), 44.9 (q, $J_{F,2}$ = 24.4 Hz, C-2), 23.1 (CH$_3$-8), 21.0 (CH$_3$-8'); **FTIR–ATR (neat)** ν in cm^{-1}: 3031, 2972, 2924, 2866, 2360, 1496, 1454, 1382, 1361, 1284, 1245, 1225, 1178, 1149, 1111, 1071, 1048, 1027, 1013, 942, 888, 735, 697; **HRMS (TOF ES$^+$)** for (M+Na)$^+$ $C_{31}H_{35}F_3NaO_5^+$ (m/z): calc. 567.2329; found 567.2337.



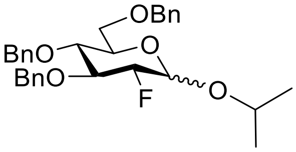
1-*O*-Isopropyl-2-deoxy-2-fluoro-3,4,6-tri-*O*-acetyl-α/β-D-glucopyranose (14). The title compound was prepared following the general procedure above, starting from 2-deoxy-2-fluoro-3,4,6-tri-*O*-acetyl-glycopyranose **8a** (100 mg, 0.28 mmol), CH$_2$Cl$_2$ (2 mL) and 33% HBr in AcOH (2 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **8a-Br**, isopropyl alcohol (59.4 µL, 0.776 mmol), dry CH_2Cl_2 (2.5 mL), dry toluene (2.5 mL), 4 Å MS and AgOTf (168.1 mg, 0.576 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard workup, quantitative ^{19}F NMR analysis indicated an α/β ratio (24:76) and yield (95%) using 1,4-difluorobenzene (10 μL, 0.097 mmol) as the internal standard. Selected data for **14α/β: ^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –199.4 (ddd, $J_{F,2}$ = 50.6 Hz, $J_{F,3}$ = 14.5 Hz, $J_{F,1}$ = 2.6 Hz, 1F, β-anomer), –200.9 (dd, $J_{F,2}$ = 49.6 Hz, $J_{F,3}$ = 11.8 Hz, 1F, α-anomer). Spectroscopic data are in agreement with that reported.[8]

1-*O*-Isopropyl-2-deoxy-2- fluoro-3,4,6-tri-*O*-acetyl-α/β-D-mannopyranose (15).



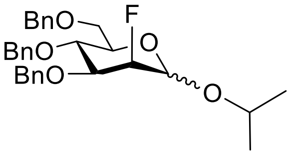
The title compound was prepared following the general procedure above, starting from 2-deoxy-2-fluoro-3,4,6-tri-*O*-acetyl-mannopyranose **9a** (50 mg, 0.14 mmol), CH_2Cl_2 (1 mL) and 33% HBr in AcOH (1 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **9a-Br**, isopropyl alcohol (27.9 μL, 0.363 mmol), dry CH_2Cl_2 (1.2 mL), dry toluene (1.2 mL), 4 Å MS and AgOTf (62.2 mg, 0.242 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard workup, quantitative ^{19}F NMR analysis indicated an α/β ratio (95:5) and yield (84%) using 1,4-difluorobenzene (10 μL, 0.097 mmol) as the internal standard. Selected data for **15α/β: ^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –203.1 to –203.5 (m, 1F, α-anomer). Spectroscopic data are in agreement with that reported.[8]

1-*O*-Isopropyl-2-deoxy-2- fluoro-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranose (16). The



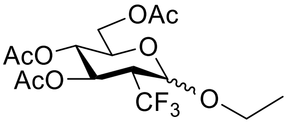
title compound was prepared following the general procedure above, starting from 2-deoxy-2-fluoro-3,4,6-tri-*O*-benzyl-glucopyranose **8b** (13.5 mg, 0.027 mmol), CH_2Cl_2 (0.3 mL) and 33% HBr in AcOH (82 μL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **8b-Br**, isopropyl alcohol (6.4 μL, 0.082 mmol), dry CH_2Cl_2 (0.3 mL), dry toluene (0.3 mL), 4 Å MS and AgOTf (14.0 mg, 0.054 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard workup, quantitative ^{19}F NMR analysis indicated an α/β ratio (4:96) and yield (78%) using 1,4-difluorobenzene (5 μL, 0.048 mmol) as the internal standard. Selected data for **16α/β: ^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –195.1 (ddd, $J_{F,2}$ = 50.8 Hz, $J_{F,3}$ = 15.1 Hz, $J_{F,1}$ = 2.2 Hz, 1F, β-anomer), –198.4 (dd, $J_{F,2}$ = 49.8 Hz, $J_{F,3}$ = 12.1 Hz, 1F, α-anomer). Spectroscopic data are in agreement with that reported.[9]

1-*O*-Isopropyl-2-deoxy-2- fluoro-3,4,6-tri-*O*-benzyl-α/β-D-mannopyranose (17).



The title compound was prepared following the general procedure above, starting from 2-deoxy-2-fluoro-3,4,6-tri-*O*-benzyl-mannopyranose **9b** (13.2 mg, 0.026 mmol), CH_2Cl_2 (0.27 mL) and 33% HBr in AcOH (80 µL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **9b-Br**, isopropyl alcohol (6.0 µL, 0.080 mmol), dry CH_2Cl_2 (0.27 mL), dry toluene (0.27 mL), 4 Å MS and AgOTf (13.7 mg, 0.053 mmol). The reaction mixture was stirred under argon at –80 °C for 2 h. After standard workup, quantitative ^{19}F NMR analysis indicated an α/β ratio (20:80) and yield (65%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard. Selected data for **17α/β:** **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –219.3 (ddd, $J_{F,2}$ = 51.3 Hz, $J_{F,3}$ = 28.7 Hz, $J_{F,1}$ = 18.8 Hz, 1F, β-anomer), –203.2 to –203.5 (m, 1F, α-anomer). Spectroscopic data are in agreement with that reported.[8]

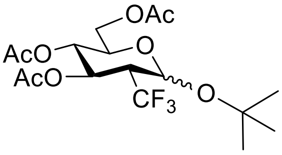
1-*O*-Ethyl-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α/β-D-glucopyranose (18).



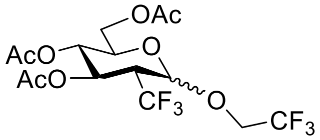
The title compound was prepared following the general procedure above, starting from **4c** (17 mg, 0.0425 mmol), CH_2Cl_2 (0.25 mL) and 33% HBr in AcOH (0.25 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **4c-Br**, ethanol (7.4 µL, 0.126 mmol), dry CH_2Cl_2 (0.4 mL), dry toluene (0.4 mL), 4 Å MS and AgOTf (21.6 mg, 0.084 mmol). The reaction mixture was stirred under argon at –80 °C for 2 h. After standard workup, quantitative ^{19}F NMR analysis indicated an α/β ratio (22:78) and yield (78%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard. The residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford an inseparable anomeric mixture of **18** (α/β, 1:5) (12 mg, 73%) along with elimination product 3,4,6-tri-*O*-acetyl-2-trifluoromethyl-D-glucal as a colorless syrup. **R_f** (1:4 EtOAc/hexane): 0.25; **FTIR–ATR (neat)** ν in cm^{-1}: 2916, 2848, 2369, 2356, 2310, 1220, 1186, 1129, 1037; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{15}H_{21}F_3NaO_8^+$ (m/z): calc. 409.1081; found 409.1088. Data for **18α:** **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.67 (dd, $J_{2,3}$ = 11.3 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 5.11 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1), 5.03 (appt, $J_{4,5}$ = $J_{3,4}$ = 9.6 Hz, 1H, H-4), 4.28 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6}$ = 4.1 Hz, 1H, H-6a), 4.12–4.04 (m, 2H, H-5, H-6b), 3.75 (dq, $J_{7,7'}$ = 9.8 Hz, $J_{7,8}$ = 7.1 Hz, 1H, H-7), 3.54 (dq, $J_{7,7'}$ = 9.8 Hz, $J_{7',8}$ = 7.1 Hz, 1H, H-7'), 2.80 (dqd, $J_{2,3}$ = 11.1 Hz, $J_{2,CF3}$ = 7.7 Hz, $J_{1,2}$ = 3.4 Hz, 1H, H-2), 2.09, 2.04, 2.02 (s, 9H, $3CH_3$, Ac), 1.24 (d, $J_{7,8}$ = $J_{7',8}$ = 7.1, 3H, CH_3-8); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.11 (d, *J* = 7.7 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.3, 169.8, 169.3 (3C=O, Ac), 95.0 (q, $J_{C1,F}$ = 3.7 Hz, C-1), 67.5 (C-5), 67.0 (q, $J_{C3,F}$ = 1.5 Hz, C-

3), 65.7 (C-4), 64.3 (C-7), 62.0 (C-6), 48.7 (q, $J_{C2,F}$ = 25.6 Hz, C-2), 20.7 (OAc), 20.64 (OAc), 20.63 (OAc), 14.7 (C-8). Data for **18β:** **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.43 (dd, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H-3), 5.04 (dd, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 8.9 Hz, 1H, H-4), 4.67 (d, J = 8.0 Hz, 1H, H-1), 4.29 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6}$ = 5.0 Hz, 1H, H-6a), 4.12 (dd, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6b}$ = 2.6 Hz, 1H, H-6b), 3.95 (dq, $J_{7,7'}$ = 9.5 Hz, $J_{7,8}$ = 7.1 Hz, 1H, H-7), 3.71 (ddd, $J_{4,5}$ = 10.1 Hz, $J_{5,6b}$ = 5.0 Hz $J_{5,6b}$ = 2.6 Hz, 1H, H-5), 3.61 (dq, $J_{7,7'}$ = 9.5 Hz, $J_{7',8}$ = 7.1 Hz, 1H, H-7'), 2.69 (ddq, $J_{2,3}$ = 10.5 Hz, $J_{1,2}$ = 8.0 Hz, $J_{2,CF3}$ = 7.7 Hz, 1H, H-2), 2.08, 2.03, 2.02 (s, 9H, 3CH_3, Ac), 1.24 (d, $J_{7,8}$ = $J_{7',8}$ = 7.1, 3H, CH_3-8); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.9 (d, J = 7.7 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 169.7, 169.6 (3C=O, Ac), 126.0 (q, $J_{C,F}$ = 281.5 Hz, CF_3), 98.3 (q, $J_{C1,F}$ = 2.7 Hz, C-1), 71.5 (C-7), 69.0 (C-4), 68.0 (q, $J_{C3,F}$ = 1.7 Hz, C-3), 65.9 (C-5), 62.2 (C-6), 49.8 (q, $J_{C2,F}$ = 24.2 Hz, C-2), 20.7 (OAc), 20.6 (2xOAc), 14.8 (C-8).

1-*O*-Tert-butyl-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α/β-D-glucopyranose



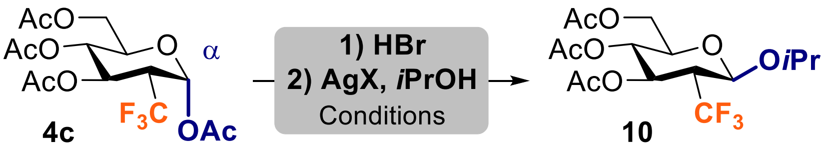
(19). The title compound was prepared following the general procedure above, starting from **4c** (28 mg, 0.07 mmol), CH_2Cl_2 (0.4 mL) and 33% HBr in AcOH (0.4 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **4c-Br**, tert-butyl alcohol (28.5 µL, 0.3 mmol), dry CH_2Cl_2 (1 mL), dry toluene (1 mL), 4 Å MS and AgOTf (38 mg, 0.15 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard workup, quantitative ^{19}F NMR analysis indicated an α/β ratio (42:58) and yield (58%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard. The residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **19α** (9 mg, 31%) and a fraction containing an anomeric mixture of **19** (α/β, 1:7) (5 mg, 18%) as colorless syrups. Data for **19α**: Colorless syrup. **R_f** (1:4 EtOAc/hexane): 0.22; **$[\alpha]^D_{25}$**: +93.5 (0.29, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.68 (dd, $J_{2,3}$ = 11.3 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 5.43 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1), 5.00 (dd, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 9.3 Hz, 1H, H-4), 4.29 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6a}$ = 4.9 Hz, 1H, H-6a), 4.23 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 2.1 Hz, 1H, H-5), 4.03 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6b}$ = 2.1 Hz, 1H, H-6b), 2.80 (dqd, $J_{2,3}$ = 11.1 Hz, $J_{2,CF3}$ = 7.6 Hz, $J_{1,2}$ = 3.4 Hz, 1H, H-2), 2.07, 2.04, 2.02 (s, 9H, 3CH_3, Ac), 1.27 (s, 9H, 3CH_3, ^{t}Bu); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –64.9 (d, J = 7.7 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 169.9, 169.6 (3C=O, Ac), 124.0 (q, $J_{C,F}$ = 281.4 Hz, CF_3), 90.0 (q, $J_{C1,F}$ = 3.9 Hz, C-1), 69.3 (C-4), 67.2 (q, $J_{C3,F}$ = 2.0 Hz, C-3), 67.1 (C-5), 62.1 (C-6), 49.2 (q, $J_{C2,F}$ = 25.1 Hz, C-2), 28.1 (3xC-8), 20.69 (OAc), 20.68 (OAc), 20.64 (OAc); **FTIR–ATR (neat)** ν in cm^{-1}: 2978, 2914, 2370, 2355, 2310, 1750, 1222, 1174, 1138, 1042; 907; **HRMS (TOF ES$^+$)** for $(M+NH_4)^+$ $C_{17}H_{29}F_3NO_8^+$ (m/z): calc. 432.1840; found 432.1851. Data for **19β**: Colorless syrup. Inseparable mixture of α/β (1:7). **R$_f$** (1:4 EtOAc/hexane): 0.18; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.44 (dd, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 8.8 Hz, 1H, H-3), 4.95 (dd, $J_{4,5}$ = 10.1 Hz, $J_{3,4}$ = 8.8 Hz, 1H, H-4), 4.83 (d, $J_{1,2}$ = 8.2 Hz, 1H, H-1), 4.22 (dd, $J_{6a,6b}$ = 12.1 Hz, $J_{5,6}$ = 6.1 Hz, 1H, H-6a), 4.09 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6b}$ = 2.6 Hz, 1H, H-6), 3.69 (ddd, $J_{4,5}$ = 10.2 Hz, $J_{5,6b}$ = 6.1 Hz, $J_{5,6b}$ = 2.6 Hz, 1H, H-5), 2.69 (ddq, $J_{2,3}$ = 10.7 Hz, $J_{1,2}$ = 8.2 Hz, $J_{2,CF3}$ = 7.7 Hz, 1H, H-2), 2.06, 2.02, 2.02 (s, 9H, $3CH_3$, Ac), 1.26 (s, 9H, $3CH_3$, ^{t}Bu); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.4 (d, J = 7.7 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 169.8, 169.7 (3C=O, Ac), 127.1 (q, $J_{C,F}$ = 281.8 Hz, CF_3), 93.5 (q, $J_{C1,F}$ = 2.2 Hz, C-1), 71.1 (C-5), 69.4 (C-4), 68.3 (q, $J_{C3,F}$ = 1.5 Hz, C-3), 62.5 (C-6), 50.2 (q, $J_{C2,F}$ = 23.4 Hz, C-2), 28.4 (3xC-8), 20.7 (OAc), 20.65 (2xOAc); **FTIR–ATR (neat)** ν in cm^{-1}: 2978, 2917, 2850, 2369, 2356, 2310, 1750, 1367, 1221, 1180, 1131, 1081, 1031, 910; **HRMS (TOF ES$^+$)** for $(M+NH_4)^+$ $C_{17}H_{29}F_3NO_8^+$ (m/z): calc. 432.1840; found 432.1849.



1-*O*-Trifluoroethyl-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α/β-D-glucopyranose (20). The title compound was prepared following the general procedure above, starting from **4c** (45 mg, 0.107 mmol), CH_2Cl_2 (1 mL) and 33% HBr in AcOH (1 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **4c-Br**, trifluoroethanol (23.2 μL, 0.321 mmol), dry CH_2Cl_2 (1.1 mL), dry toluene (1.1 mL), 4 Å MS and AgOTf (55.0 mg, 0.21 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard workup, quantitative ^{19}F NMR analysis indicated an α/β ratio (72:28) and yield (62%) using 1,4-difluorobenzene (5 μL, 0.048 mmol) as the internal standard. The residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford an inseparable anomeric mixture of **20** (α/β, 10:1) (21 mg, 44%) as a colorless syrup. **R$_f$** (3:7 EtOAc/hexane): 0.25; **FTIR–ATR (neat)** ν in cm^{-1}: 2955, 2917, 2850, 2363, 1748,1368, 1282, 1221, 1181, 1155, 1128, 1078, 1030, 970, 916, 901; **HRMS (TOF ES$^+$)** for $(M+NH_4)^+$ $C_{15}H_{22}F_3NO_8^+$ (m/z): calc. 458.1244; found 458.1249. Data for **20α**: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.66 (dd, $J_{2,3}$ = 11.4 Hz, $J_{3,4}$ = 9.3 Hz, 1H, H-3), 5.22 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 5.06 (dd, $J_{4,5}$ = 10.1 Hz, $J_{3,4}$ = 9.3 Hz, 1H, H-4), 4.28 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6}$ = 4.5 Hz, 1H, H-6a), 4.11 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 2.3 Hz, 1H, H-6b), 4.06 (ddd, $J_{4,5}$ = 10.2 Hz, $J_{5,6a}$ = 4.6 Hz, $J_{5,6b}$ = 2.3 Hz, 1H, H-5), 3.98 (q, $J_{7',CF3'}$ = 8.2 Hz, 2H, CH_2-7'), 2.88 (ddq, $J_{2,3}$ = 11.1 Hz, $J_{2,CF3}$ = 7.6 Hz, $J_{1,2}$ = 3.6 Hz, 1H, H-2), 2.09, 2.05, 2.03 (s, 9H, $3CH_3$, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.22 (d, $J_{CF3,2}$ = 7.5 Hz, 3F, CF_3), –74.08 (d, J $J_{CF3,7}$ = 8.4 Hz, 3F, CF_3'); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm:

170.5, 169.7, 169.4 (3C=O, Ac), 123.6 (q, $J_{C,F}$ = 280.9 Hz, CF_3), 123.1 (q, $J_{C,F}$ = 278.4 Hz, $CF_{3'}$), 95.9 (q, $J_{C1,F}$ = 4.2 Hz, C-1), 68.5 (C-5), 68.45 (C-4), 66.4 (q, $J_{C3,F}$ = 2.0 Hz, C-3), 65.3 (q, $J_{C2,F}$ = 35.8 Hz, C-7'), 61.6 (C-6), 48.3 (q, $J_{C2,F}$ = 26.7 Hz, C-2), 20.65 (OAc), 20.55 (2xOAc). Selected data for **20β**: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.45 (dd, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 8.9 Hz, 1H, H-3), 5.08 (dd, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 8.9 Hz, 1H, H-4), 4.82 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1), 4.28 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6}$ = 4.9 Hz, 1H, H-6a), 4.14 (dd, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6b}$ = 2.5 Hz, 1H, H-6b), 4.00 (q, $J_{7,CF3'}$ = 8.3 Hz, 2H, CH_2-7'), 3.75 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 5.0 Hz, $J_{5,6b}$ = 2.5 Hz, 1H, H-5), 2.76 (dp, $J_{2,3}$ = 10.2 Hz, $J_{2,CF3}$ = $J_{1,2}$ = 7.7 Hz, 1H, H-2), 2.04, 2.04, 2.02 (s, 9H, $3CH_3$, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: – 66.35 (d, $J_{CF3,2}$ = 7.6 Hz, 3F, CF_3), – 74.25 (d, $J_{CF3,7}$ = 8.5 Hz, 3F, CF_3').

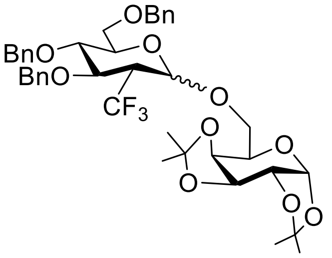
Table S1. Effect of concentration, stoichiometry, and promoter in the glycosylation reaction.[a]



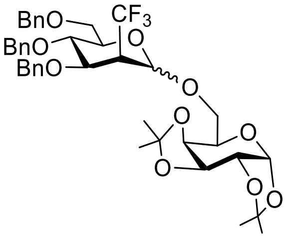
entry	concentration (M)	donor:acceptor ratio	promoter (equiv)	yield (%)[b]	α/β ratio[b]
1	0.05	1:2	AgOTf (2)	61	33:67
2	0.1	1:2	AgOTf (2)	62	30:70
3	0.05	1:1	AgOTf (2)	29[c]	36:64
4	0.05	1:15	AgOTf (2)	67	29:71
5	0.05	1:2	$AgBF_4$ (2)	45[c]	18:82
6	0.05	1:2	$AgSbF_6$ (2)	67[c]	20:80

[a] *General conditions*: 1) pyranose **4c** (1 equiv), 33 wt. % HBr in AcOH, 0 ºC to rt, 1–3 h; 2) glycosyl donor **4c-Br** (1 equiv), *i*PrOH, and promoter (2 equiv) in 1:1 (v/v) CH_2Cl_2/toluene, –80 ºC, 3 h unless otherwise indicated. Variable amounts of elimination side-reactions to the parent 2-CF_3-D-glucal (9–32%) were detected by ^{19}F NMR except for entry 5 (only 1%). [b] Determined by ^{19}F NMR analysis of the crude reaction mixture using 1,4-difluorobenzene as internal standard. [c] Substantial amounts of unidentified byproducts were detected.

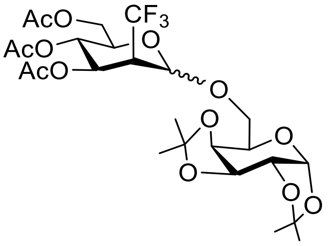
3.6. Glycosylation scope



3,4,6-Tri-*O*-benzyl-2-deoxy-2-trifluoromethyl-β-D-glucopyranosyl-(1→6)-[1:2,3:4]-di-*O*-isopropylidene-α-D-galactopyranoside (21). The title compound was prepared following the general procedure above, starting from **4b** (26 mg, 0.0477 mmol), CH_2Cl_2 (1.4 mL) and 33% HBr in AcOH (83 µL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **4b-Br**, [1:2,3:4]-di-*O*-isopropylidene-α-D-galactopyranoside (37 mg, 0.142 mmol), dry CH_2Cl_2 (0.5 mL), dry toluene (0.5 mL), 4 Å MS and AgOTf (24 mg, 0.095 mmol). The reaction mixture was stirred under argon at –80 ^{o}C for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (6:94). The residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford pure **21β** (25 mg, 70%) as a colorless syrup. **R_f** (1:4 EtOAc/hexane): 0.42; **$[\alpha]^{D}_{25}$**: +44.5 (1.76, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.36–7.15 (m, 15H, Ar), 5.52 (d, $J_{1',2'}$ = 5.0 Hz, 1H, H-1'), 4.81 (d, $J_{1,2}$ = 6.9 Hz, 1H, H-1), 4.81–4.52 (m, 7H, 3CH_2Ph, H-3'), 4.30 (dd, $J_{1',2}$ = 4.9 Hz, $J_{2',3'}$ = 2.4 Hz, 1H, H-2'), 4.12 (dd, $J_{3',4'}$ = 8.0 Hz, $J_{4',5'}$ = 1.7 Hz, 1H, H-4'), 4.03 (dd, $J_{6a,6b}$ = 11.0 Hz, $J_{5,6a}$ = 4.7 Hz, 1H, H-6a), 3.96 (m, 1H, H-5'), 3.89–3.80 (m, 2H, H-3, H-4), 3.77–3.68 (m, 3H, H-6b, H-6a', H-6b'), 3.56 (m, 1H, H-5), 2.68 (m, 1H, H-2), 1.52, 1.43, 1.33, 1.31 (s, 12H, 4CH_3); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –61.2 (d, $J_=$ 8.5 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 138.2, 138.1, 137.9 (C, Ar), 128.6, 128.5, 128.5, 128.0, 127.9, 127.9, 127.8, (CH, Ar), 125.6 (q, $J_{C,F}$ = 281.7 Hz, CF_3), 109.4, 108.8 (2Cketal), 98.2 (q, $J_{C1,F}$ = 2.7 Hz, C-1), 96.4 (C-1'), 78.3 (C-3), 78.2 (C-4), 75.0 (C-5), 74.8, 74.5, 73.6 (3xCH_2Ph), 71.3 (C-4'), 70.8 (C-3'), 70.6 (C-2'), 69.1 (C-6), 68.1 (C-6'), 67.6 (C-5'), 51.3 (q, $J_{C2,F}$ = 23.6 Hz, C-2), 26.1, 26.0, 25.2, 24.5 (4xCH_3'); **FTIR–ATR (neat)** ν in cm^{-1}: 3032, 2987, 2903, 1497, 1455, 1373, 1252, 1210, 1173, 1068, 1005, 900, 738, 698; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{40}H_{47}F_3NaO_{10}^+$ (m/z): calc. 767.3014; found 767.3008.

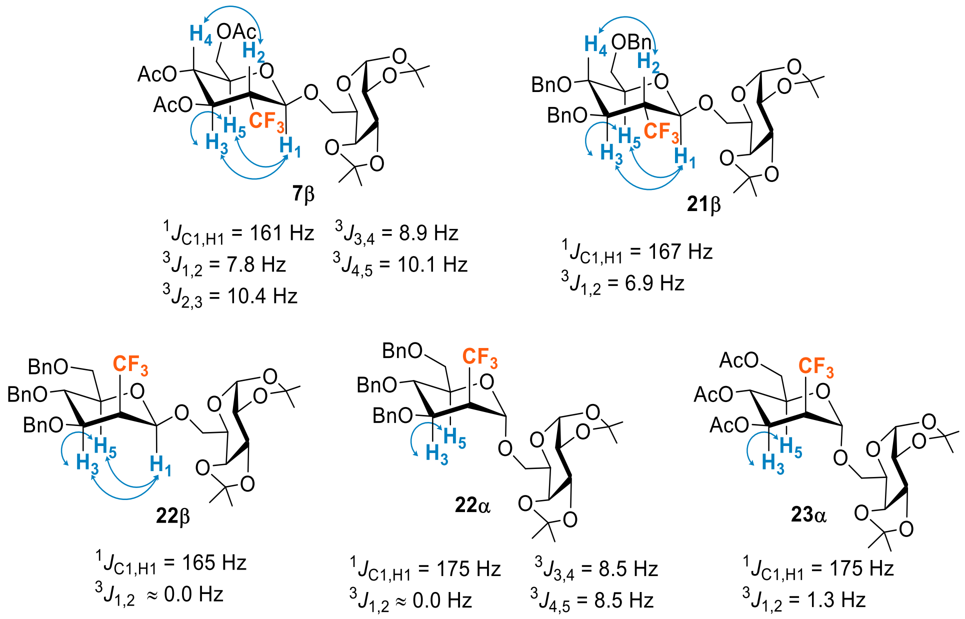


3,4,6-Tri-*O*-benzyl-2-deoxy-2-trifluoromethyl-α/β-D-mannopyranosyl-(1 → 6)-[1:2,3:4]-di-*O*-isopropylidene-α-D-galactopyranoside (22). The title compound was prepared following the general procedure above, starting from **5b** (89 mg, 0.163 mmol), CH_2Cl_2 (4.8 mL) and 33% HBr in AcOH (260 µL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **5b-Br**, [1:2,3:4]-di-*O*-isopropylidene-α-D-galactopyranoside (127 mg, 0.489 mmol), dry CH_2Cl_2 (1.6 mL), dry toluene (1.6 mL), 4 Å MS and AgOTf (83.7 mg, 0.33 mmol). The reaction mixture was stirred under argon at –80 °C for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (80:20). The residue was purified by flash column chromatography (from hexane to 1:9 EtOAc/hexane) to afford **22α** (19 mg, 16%) and **22β** (73 mg, 60%). Data for **22α**: Colorless syrup. **R$_f$** (1:4 EtOAc/hexane): 0.37; **[α]$^{D}_{25}$**: +15.2 (1.21, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.42–7.02 (m, 15H, Ar), 5.53 (d, $J_{1',2'}$ = 4.99 Hz, 1H, H-1’), 5.28 (bs, 1H, H-1), 4.78–4.35 (m, 7H, 3CH_2Ph, H-3’), 4.32 (dd, $J_{1',2'}$ = 5.0 Hz, $J_{2',3'}$ = 2.4 Hz, 1H, H-2’), 4.21–4.13 (m, 2H, H-4’, H-3), 3.98 (appt, $J_{5,6a}$ = $J_{5,6b}$ = 6.6 Hz, 1H, H-5’), 3.92 (appt, $J_{3,4}$ = $J_{4,5}$ = 8.5 Hz, 1H, H-4), 3.88–3.76 (m, 2H, H-6a’, H-5), 3.75–3.62 (m, 3H, H-6b’, H-6a, H-6b), 3.03 (m, 1H, H-2), 1.52, 1.44, 1.33 (s, 12H, 4CH_3); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.2 (bd, J = 7.7 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 138.4, 138.2, 137.8 (C, Ar), 128.5, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.8, 127.6 (CH, Ar), 125.6 (q, $J_{C,F}$ = 281.0 Hz, CF_3), 109.5, 108.7 (2Cketal), 97.4 (C-1’), 95.3 (q, $J_{C1,F}$ = 4.5 Hz, C-1), 76.4 (C-3), 74.6 (CH_2Ph), 74.4 (C-4), 73.4, 72.3 (2CH_2Ph), 71.5 (C-5), 71.0 (C-4’), 70.7 (C-3’), 70.7 (C-2’), 69.0 (C-6), 65.8 (C-6’), 65.4 (C-5’), 43.9 (q, $J_{C2,F}$ = 24.0 Hz, C-2), 26.1, 26.1, 25.0, 24.5 (4xCH_3’); **FTIR–ATR (neat)** v in cm^{-1}: 3031, 2988, 2934, 1497, 1455, 1382, 1256, 1211, 1160, 1115, 1070, 1005, 906, 737, 698; **HRMS (TOF ES^{+})** for $(M+Na)^+$ $C_{40}H_{47}F_3NaO_{10}^+$ (m/z): calc. 767.3014; found 767.3024. Data for **22β**: Colorless syrup. **R$_f$** (1:4 EtOAc/hexane): 0.31; **[α]$^{D}_{25}$**: –60.2 (0.49, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.38–7.14 (m, 15H, Ar), 5.52 (d, $J_{1',2'}$ = 4.9 Hz, 1H, H-1’), 4.88 (bs, 1H, H-1), 4.70 (d, J = 11.2 Hz, 1H, CH-Ph), 4.66 (d, J = 11.6 Hz, 1H, CH-Ph), 4.57 (dd, $J_{3',4'}$ = 8.0 Hz, $J_{2',3'}$ = 2.4 Hz, 1H, H-3’), 4.55–4.45 (m, 4H, 2CH_2Ph), 4.30 (dd, $J_{1',2'}$ = 4.9 Hz, $J_{2',3'}$ = 2.3 Hz, 1H, H-2’), 4.19 (bd, $J_{3',4'}$ = 8.0 Hz, 1H, H-4’), 4.07–4.01 (m, 2H, H-5’, H-6a’), 3.95–3.84 (m, 3H, H-6a, H-3, H-4), 3.80–3.72 (m, 2H, H-6b, H-5), 3.66 (dd, $J_{6a',6b'}$ = 11.9 Hz, $J_{5',6'}$ = 8.2 Hz, 1H, H-6b’), 3.17 (m, 1H, H-2), 1.53, 1.43, 1.34, 1.28 (s, 12H, 4CH_3); **^{19}F NMR** (CDCl3, 376.5 MHz) δ in ppm: –60.6 (bs, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 138.5, 138.0, 137.5 (C, Ar), 128.2, 128.4, 128.1, 128.1, 128.0, 127.9, 127.7, 127.6 (CH, Ar), 125.6 (q, $J_{C,F}$ = 282.1 Hz, CF_3), 109.5, 109.0 (2C_{ketal}), 97.9 (C-1), 96.4 (C-1’), 76.4 (C-3), 75.1 (C-5), 73.8, 73.3 (2CH_2Ph), 72.7 (C-4), 72.0 (CH_2Ph), 71.5 (C-4’), 70.8 (C-3’), 70.7 (C-2’), 69.8 (C-6), 69.1 (C-6’), 68.3 (C-5’), 43.9 (q, $J_{C2,F}$ = 24.4 Hz, C-2), 26.1, 26.0, 25.2, 24.5 (4xCH_3’); **FTIR–ATR (neat)** *v* in cm^{-1}: 3025, 2970, 1483, 1466, 1377, 1220, 1155, 1110, 1080, 1008, 743, 701; **HRMS (TOF ES^{+})** for $(M+Na)^+$ $C_{40}H_{47}F_3NaO_{10}^+$ (m/z): calc. 767.3014; found 767.3014.



3,4,6-Tri-*O*-acetyl-2-deoxy-2-trifluoromethyl-α-D-mannopyranosyl-(1 → 6)-[1:2,3:4]-di-*O*-isopropylidene-α-D-galactopyranoside (23). The title compound was prepared following the general procedure above, starting from **5c** (47 mg, 0.117 mmol), CH_2Cl_2 (0.47 mL) and 33% HBr in AcOH (0.47 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **5c-Br**, [1:2,3:4]-di-*O*-isopropylidene-α-D-galactopyranoside (91.7 mg, 0.35 mmol), dry CH_2Cl_2 (1.7 mL), dry toluene (1.7 mL), 4 Å MS and AgOTf (60 mg, 0.235 mmol). The reaction mixture was stirred under argon at –80 °C for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (94:6). The crude was purified by column chromatography (1:7 EtOAc/hexane) to afford **23α** (56 mg, 80%) as a colorless syrup. **R_f** (2:3 EtOAc/hexane): 0.41; **$[\alpha]^{D}_{25}$** : +7.4 (0.59, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.51 (d, $J_{1',2'}$ = 5.0 Hz, 1H, H-1’), 5.42–5.32 (m, 2H, H-4, H-3), 5.23 (d, $J_{1,2}$ = 1.3 Hz, 1H, H-1), 4.62 (dd, $J_{3',4'}$ = 7.9 Hz, $J_{2',3'}$ = 2.5 Hz, 1H, H-3’), 4.33 (dd, $J_{1',2'}$ = 5.0 Hz, $J_{2',3'}$ = 2.5 Hz, 1H, H-2’), 4.24–4.13 (m, 3H, H-4’, H-6a, H-6b), 4.07 (ddd, $J_{4,5}$ = 9.1 Hz, $J_{5,6a}$ = 4.5 Hz, $J_{5,6b}$ = 2.4 Hz, 1H, H-5), 3.98 (td, $J_{5',6a'}$ = $J_{5',6b'}$ = 6.4 Hz, $J_{4',5'}$ = 1.8 Hz, 1H, H-5’), 3.81 (dd, $J_{6a',6b'}$ = 10.6 Hz, $J_{5',6a'}$ = 6.4 Hz, 1H, H-6a’), 3.72 (dd, $J_{6a',6b'}$ = 10.6 Hz, $J_{5',6b'}$ = 6.4 Hz, 1H, H-6b’), 3.19 (m, 1H, H-2), 2.09, 2.06, 2.05 (s, 9H, $3CH_3$, Ac), 1.54 (s, 3H, CH_3’), 1.43 (s, 3H, CH_3’), 1.33 (s, 3H, CH_3’), 1.33 (s, 3H, CH_3’); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.6 (d, J = 9.7 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.9, 170.3, 169.6 (3xC=O, Ac), 124.8 (q, $J_{C,F}$ = 281.0 Hz, CF_3), 109.6, 108.8 (2Cketal), 96.4 (C-1’), 95.5 (q, $J_{C1,F}$ = 4.5 Hz, C-1), 71.0 (C-4’), 70.7 (C-3’), 70.6 (C-2’), 68.5 (C-5), 68.0 (C-3), 67.1 (C-6’), 66.1 (C-5’), 65.8 (C-4), 62.4 (C-6), 46.2 (q, $J_{C2,F}$ = 24.9 Hz, C-2), 26.2, 26.1, 25.1, 24.5 ($4xCH_3$’), 20.9, 20.8 ($3xCH_3$, Ac); **FTIR–ATR (neat)** v in cm^{-1}: 2922, 2850, 1747, 1457, 1372, 1225, 1163, 1119, 1067, 1007; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{25}H_{27}F_{35}NaO_{13}^+$ (m/z): calc. 623.1922; found 623.1923.

3.6.1. Conformational analysis of compounds 7, 21, 22, and 23.



7β: $^1J_{C1,H1}$ = 161 Hz, $^3J_{1,2}$ = 7.8 Hz, $^3J_{2,3}$ = 10.4 Hz, $^3J_{3,4}$ = 8.9 Hz, $^3J_{4,5}$ = 10.1 Hz

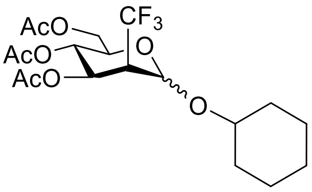
21β: $^1J_{C1,H1}$ = 167 Hz, $^3J_{1,2}$ = 6.9 Hz

22β: $^1J_{C1,H1}$ = 165 Hz, $^3J_{1,2}$ ≈ 0.0 Hz

22α: $^1J_{C1,H1}$ = 175 Hz, $^3J_{1,2}$ ≈ 0.0 Hz, $^3J_{3,4}$ = 8.5 Hz, $^3J_{4,5}$ = 8.5 Hz

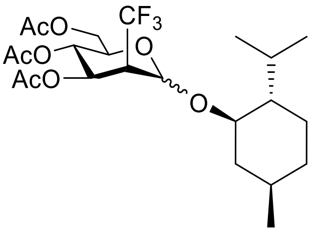
23α: $^1J_{C1,H1}$ = 175 Hz, $^3J_{1,2}$ = 1.3 Hz

Figure S5. Conformational analysis of **7β**, **21β**, **22α**, **22β**, and **23α**. Key NOE signals are indicated by blue arrows

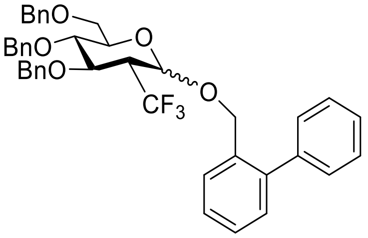


1-*O*-Cyclohexyl-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α/β-D-mannopyranose (24). The title compound was prepared following the general procedure above, starting from **5c** (23.5 mg, 0.059 mmol), CH_2Cl_2 (0.3 mL) and 33% HBr in AcOH (0.3 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **5c-Br**, cyclohexanol (18.8 µL, 0.18 mmol), dry CH_2Cl_2 (0.6 mL), dry toluene (0.6 mL), 4 Å MS and AgOTf (30.8 mg, 0.12 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (97:3) and yield (74%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard. The residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford pure **24α** (18 mg, 67%) as a colorless syrup. Data for **24α**: Colorless syrup**. R$_f$** (1:4 EtOAc/hexane): 0.27; **$[\alpha]^{D}_{25}$** : +61.7 (0.76, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.42–5.31 (m, 2H, H-3, H-4), 5.30 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1), 4.19 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 3.1 Hz, 1H, H-6a), 4.14 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6b}$ = 4.8 Hz, 1H, H-6b), 4.04 (ddd, $J_{4,5}$ = 9.2 Hz, $J_{5,6}$ = 4.8 Hz, $J_{5,6}$ = 3.1 Hz, 1H, H-5), 3.59 (m, 1H, H-7’), 3.09 (qdd, $J_{2,CF3}$ = 9.8 Hz, $J_{2,3}$ = 5.7 Hz, $J_{1,2}$ = 1.6 Hz, 1H, H-2), 2.07, 2.06, 2.04 (s, 9H, $3CH_3$, Ac), 1.92–1.83 (m, 2H, CH_2’), 1.79–1.62 (m, 2H, CH_2’), 1.60–1.48 (m, 1H, CH_2’), 1.46–1.11 (m, 5H, CH_2’); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.6 (d, J = 9.8 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 170.1, 169.5 (3C=O, Ac), 126.0 (q, $J_{C,F}$ = 281.5 Hz, CF_3), 93.4 (q, $J_{C1,F}$ = 4.6 Hz, C-1), 76.5 (C-7'), 68.3 (C-5), 68.0 (C-4), 66.1 (q, $J_{C3,F}$ = 1.6 Hz, C-3), 62.5 (C-6), 46.8 (q, $J_{C2,F}$ = 24.8 Hz, C-2), 33.1 (CH_2'), 31.3 (CH_2'), 25.4 (CH_2'), 24.1 (CH_2'), 23.8 (CH_2'), 20.72 (OAc), 20.71 (OAc), 20.60 (OAc); **FTIR–ATR (neat)** ν in cm^{-1}: 2934, 2857 1749, 1454, 1369,1267, 1228, 1177, 1159, 1114, 1047; **HRMS (TOF ES$^+$)** for $(M+NH_4)^+$ $C_{19}H_{31}F_3NO_8^+$ (m/z): calc. 458.1996; found 458.2001.

1-*O*-Menthyl-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α-D-mannopyranose

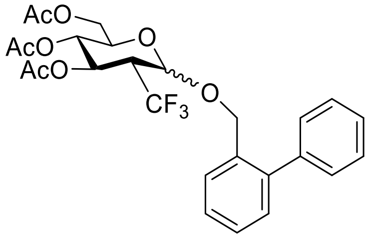


(25). The title compound was prepared following the general procedure above, starting from **5c** (21.6 mg, 0.054 mmol), CH_2Cl_2 (0.3 mL) and 33% HBr in AcOH (0.3 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **5c-Br**, (-)-menthol (25.3 mg, 0.162 mmol), dry CH_2Cl_2 (0.6 mL), dry toluene (0.6 mL), 4 Å MS and AgOTf (27.8 mg, 0.108 mmol). The reaction mixture was stirred under argon at –80 °C for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (95:5) and yield (83%) using 1,4-difluorobenzene (5 μL, 0.048 mmol) as the internal standard. The residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **25α** (21 mg, 78%) as a colorless syrup. Data for **25α**: Colorless syrup. **R$_f$** (1:4 EtOAc/hexane): 0.37; **$[\alpha]^D_{25}$** : +21.7 (0.96, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.43–5.29 (m, 2H, H-3, H-4), 5.31 (d, $J_{1,2}$ = 1.3 Hz, 1H, H-1), 4.25–4.07 (m, 3H, H-5, H-6a, H-6b), 3.40 (td, $J_{1'2'}$ = $J_{1'6'}$ = 10.7 Hz, $J_{1'6''}$ = 4.4 Hz, 1H, H-1'), 3.13 (qdd, $J_{2,CF3}$ = 9.8 Hz, $J_{2,3}$ = 5.7 Hz, $J_{1,2}$ = 1.3 Hz, 1H, H-2), 2.16–2.09 (m, 1H, H-6''), 2.09, 2.08, 2.06 (s, 9H, $3CH_3$, Ac), 2.04–1.97 (m, 1H, H-7'), 1.69–1.60 (m, 2H, H-3', H-4'), 1.48–1.30 (m, 1H, H-5'), 1.34–1.21 (m, 1H, H-2'), 1.05 (q, $J_{5',6'}$ = $J_{1',6'}$ = $J_{6',6''}$ = 12.0 Hz, 1H, H-6'), 1.03–0.94 (m, 1H, H-3''), 0.92 (d, $J_{7',8'}$ = 7.0 Hz, 3H, CH_3-8), 0.90 (d, $J_{5',10'}$ = 6.5 Hz, 3H, CH_3-10), 1.03–0.94 (m, 1H, H-4''), 0.77 (d, $J_{7',9'}$ = 7.0 Hz, 3H, CH_3-9); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.6 (d, *J* = 9.8 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 170.2, 169.5 (3C=O, Ac), 124.7 (q, $J_{C,F}$ = 281.0 Hz, CF_3), 97.2 (q, $J_{C1,F}$ = 4.5 Hz, C-1), 83.0 (C-1'), 68.5 (C-5), 67.9 (C-4), 66.0 (q, $J_{C3,F}$ = 1.7 Hz, C-3), 62.7 (C-6), 49.3 (C-2'), 46.8 (q, $J_{C2,F}$ = 24.8 Hz, C-2), 42.6 (C-6'), 34.1 (C-3'), 31.6 (C-5'), 25.9 (C-7'), 23.2 (C-4'), 22.3 (CH_3-10), 21.0 (CH_3-8), 20.7 (OAc), 20.67 (2xOAc), 16.0 (CH_3-9); **FTIR–ATR (neat)** ν in cm^{-1}: 2956, 2922, 2871, 1750, 1456, 1370, 1267, 1227, 1163, 1114, 1044; **HRMS (TOF ES$^+$)** for $(M+NH_4)^+$ $C_{23}H_{39}F_3NO_8^+$ (m/z): calc. 514.2622; found 514.2633.



1-*O*-(2-Biphenylmethan)-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-benzyl-α/β-D-glucopyranose (26). The title compound was prepared following the general procedure above, starting from **4b** (21.9 mg, 0.0402 mmol), CH_2Cl_2 (1.2 mL) and 33% HBr in AcOH (1.2 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **4b-Br**, 2-biphenylmethanol (14.8 mg, 0.0804 mmol), dry CH_2Cl_2 (0.4 mL), dry toluene (0.4 mL), 4 Å MS and AgOTf (20.7 mg, 0.0804 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (8:92) and yield (68%) using 1,4-difluorobenzene (5 μL, 0.048 mmol) as the internal standard. The crude was purified by column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **26α** (2 mg, 5%) and **26β** (15 mg, 56%). Selected data for **26α:** Colorless syrup. **R_f** (1:9 EtOAc/hexane): 0.15; Selected spectroscopic data: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.54–7.50 (m, 1H, Ph), 7.42–7.24 (m, 21H, Ph), 7.22–7.15 (m, 2H, Ph), 5.12 (d, $J_{1,2}$ = 3.3 Hz, 1H, H-1), 4.80 (d, J = 10.9 Hz, 1H, CH-Ph), 4.78 (d, J = 10.3 Hz, 1H, CH-Ph), 4.72 (d, J = 10.2 Hz, 1H, CH-Ph), 4.65 (d, J = 11.2 Hz, 1H, CH-Ph), 4.58 (d, J = 12.1 Hz, 1H, CH-Ph), 4.51 (d, J = 11.0 Hz, 1H, CH-Ph), 4.45 (d, J = 12.1 Hz, 1H, CH-Ph), 4.46 (d, J = 11.3 Hz, 1H, CH-Ph), 4.18 (dd, $J_{2,3}$ = 11.1 Hz, $J_{3.4}$ = 8.5 Hz, 1H, H-3), 3.78–3.64 (m, 3H, H-4, H-5, H-6a), 3.50 (dd, $J_{6a,6b}$ = 10.7 Hz, $J_{5,6b}$ = 1.6 Hz, 1H, H-6b), 2.70 (ddq, $J_{2,3}$ = 11.1 Hz, $J_{2,CF3}$ = 8.2 Hz, $J_{1,2}$ = 3.3 Hz, 1H, H-2); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –63.4 (d, J = 8.2 Hz, 3F, CF_3); **FTIR–ATR (neat)** ν in cm^{-1}: 2917, 2883, 2850, 2370, 2339, 2311, 1262, 1173, 1152, 1132, 1122, 1108, 1047, 795, 749, 700; **HRMS (TOF ES$^+$)** for $(M+NH_4)^+$ $C_{41}H_{43}F_3NO_5^+$ (m/z): calc. 686.3088; found 686.3051. Data for **26β:** White solid. **R_f** (1:9 EtOAc/hexane): 0.18; **m.p**: 100–102 ºC; **$[\alpha]^{D}_{25}$** : –23.8 (0.24, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.58–7.50 (m, 1H, Ph), 7.40–7.27 (m, 21H, Ph), 7.22–7.15 (m, 2H, Ph), 4.84 (d, J = 11.6 Hz, 1H, CH-Ph), 4.78 (d, J = 11.0 Hz, 1H, CH-Ph), 4.77 (d, J = 10.4 Hz, 1H, CH-Ph), 4.68 (d, J = 10.4 Hz, 1H, CH-Ph), 4.63 (d, $J_{1,2}$ = 6.9 Hz, 1H, H-1), 4.59 (d, J = 11.0 Hz, 1H, CH-Ph), 4.54 (d, J = 11.6 Hz, 1H, CH-Ph), 4.53 (d, J = 12.1 Hz, 1H, CH-Ph), 4.46 (d, J = 12.1 Hz, 1H, CH-Ph), 3.88–3.76 (m, 2H, H-3, H-4), 3.65 (dd, $J_{6a,6b}$ = 10.8 Hz, $J_{5,6a}$ = 4.5 Hz, 1H, H-6a), 3.59 (dd, $J_{6a,6b}$ = 10.8 Hz, $J_{5,6b}$ = 2.3 Hz, 1H, H-6b), 3.67 (ddd, $J_{4,5}$ = 8.9 Hz, $J_{5,6a}$ = 4.5 Hz, $J_{5,6b}$ = 2.3 Hz, 1H, H-5), 2.73 (h, $J_{2,3}$ = $J_{2,CF3}$ = $J_{1,2}$ = 8.3 Hz, 1H, H-2); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.19 (d, J = 8.5 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 141.9, 140.6, 138.0, 137.9, 137.8, 134.1, 130.4, 129.9, 129.6, 128.5, 128.42, 128.39, 128.12, 127.9, 127.8, 127.78, 127.76, 127.66, 127.5, 127.1 (CH, Ar), 125.5 (q, $J_{C,F}$ = 282.2 Hz, CF_3), 97.0 (d, $J_{C1,F}$ = 2.9 Hz, C-1), 78.2 (C-3, C-4), 74.9 (C-5), 74.85 (CH_2-

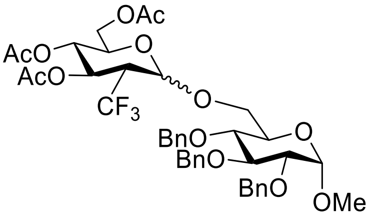
Ph), 74.5 (CH_2-Ph), 73.5 (CH_2-Ph), 68.9 (C-6), 68.4 (CH_2-Ph), 51.4 (q, $J_{C,F}$ = 23.5 Hz, C-2); **FTIR–ATR (neat)** ν in cm^{-1}: 2916, 2881, 2850, 2367, 2347, 2337, 1175, 1099, 1035, 1028, 748, 700; **HRMS (TOF ES$^+$)** for $(M+NH_4)^+$ $C_{41}H_{43}F_3NO_5^+$ (m/z): calc. 686.3088; found 686.3082.



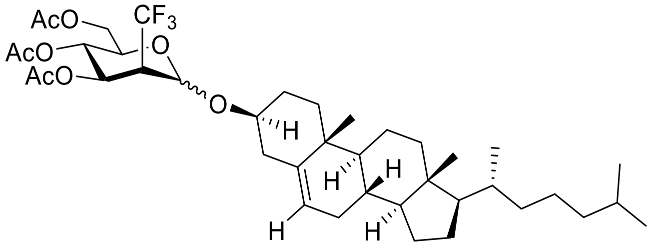
1-*O*-(2-Biphenylmethan)-2-deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α/β-D-glucopyranose (27). The title compound was prepared following the general procedure above, starting from **4c** (44.7 mg, 0.112 mmol), CH_2Cl_2 (0.8 mL) and 33% HBr in AcOH (0.8 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **4c-Br**, 2-biphenylmethanol (41.4 mg, 0.224 mmol), dry CH_2Cl_2 (1.2 mL), dry toluene (1.2 mL), 4 Å MS and AgOTf (57.7 mg, 0.224 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (18:82) and yield (45%) using 1,4-difluorobenzene (5 μL, 0.048 mmol) as the internal standard. The residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **27α** (4 mg, 7%) and an inseparable anomeric mixture of **27** (α/β, 1:13) (19 mg, 32%). Selected data for **27α:** Colorless syrup. **R$_f$** (1:4 EtOAc/hexane): 0.23; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.59–7.51 (m, 1H, Ph), 7.45–7.27 (m, 8H, Ph), 5.63 (dd, $J_{2,3}$ = 11.3 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 5.14 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1), 5.03 (d, $J_{4,5}$ = 10.2 Hz, $J_{3,4}$ = 9.3 Hz, 1H, H-4), 4.67 (d, J = 11.2 Hz, 1H, CH-Ph), 4.38 (d, J = 11.2 Hz, 1H, CH-Ph), 4.17 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 4.5 Hz, 1H, H-6a), 3.87 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 2.2 Hz, 1H, H-6b), 3.79 (ddd, $J_{4,5}$ = 10.2 Hz, $J_{5,6a}$ = 4.5 Hz, $J_{5,6b}$ = 2.2 Hz, 1H, H-5), 2.73 (dqd, $J_{2,3}$ = 11.6 Hz, $J_{2,CF3}$ = 7.9 Hz, $J_{1,2}$ = 3.7 Hz, 1H, H-2), 2.10 (s, 3H, CH_3, Ac), 2.10 (s, 3H, CH_3, Ac), 2.03 (s, 3H, CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –64.8 (d, J = 7.8 Hz, 3F, CF_3), **FTIR–ATR (neat)** ν in cm^{-1}: 1753, 1455, 1436, 1368, 1323, 1222, 1180, 1131, 1041, 908, 749, 704; **HRMS (TOF ES$^+$)** for $(M+NH_4)^+$ $C_{26}H_{31}F_3NO_8^+$ (m/z): calc. 542.1996; found 542.2007. Data for **27β:** Sticky solid. Inseparable mixture of α/β (1:13). **R$_f$** (1:4 EtOAc/hexane): 0.20; **m.p**: 79–81 ºC; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.59–7.51 (m, 1H, Ph), 7.45–7.27 (m, 8H, Ph), 5.39 (dd, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H-3), 5.03 (d, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H-4), 4.83 (d, J = 11.4 Hz, 1H, CH-Ph), 4.63 (d, $J_{1,2}$ = 7.9 Hz, 1H, H-1), 4.59 (d, J = 11.4 Hz, 1H, CH-Ph), 4.23 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 5.0 Hz, 1H, H-6a), 3.97 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6b}$ = 2.5 Hz, 1H, H-6b), 3.67 (ddd, $J_{4,5}$ = 10.1 Hz, $J_{5,6a}$ = 5.0 Hz, $J_{5,6b}$ = 2.5 Hz, 1H, H-5), 2.73 (dp, $J_{2,3}$ = 10.5 Hz, $J_{2,CF3}$ = $J_{1,2}$ = 7.8 Hz, 1H, H-2), 2.03 (s, 3H, CH_3, Ac), 2.02 (s, 3H, CH_3, Ac), 2.01 (s, 3H, CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.7 (d, J = 7.7 Hz, 3F,

CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 169.7, 169.6 (C=O, OAc), 142.0, 140.5, 133.3, 130.0, 129.8, 129.3, 128.3, 128.2, 128.1, 127.6, 127.3 (CH, Ar), 124.4 (q, $J_{C,F}$ = 282.0 Hz, CF_3), 97.1 (q, $J_{C1,F}$ = 2.5 Hz, C-1), 71.4 (C-5), 68.9 (C-4), 68.7 (CH_2-Ph), 68.0 (q, $J_{C1,F}$ = 1.8 Hz, C-3), 62.0 (C-6), 49.7 (q, $J_{C,F}$ = 24.4 Hz, C-2), 20.7, 20.6 (2xCH_3, OAc); **FTIR–ATR (neat)** ν in cm^{-1}: 1750, 1668, 1369, 1327, 1222, 1180, 1151, 1128, 1025, 911, 754, 704; **HRMS (TOF ES$^+$)** for $(M+NH_4)^+$ $C_{26}H_{31}F_3NO_8^+$ (m/z): calc. 542.1996; found 542.2006.

2-Deoxy-2-trifluoromethyl-3,4,6-tri-*O*-acetyl-α-D-glucosyl-(1→6)-1-*O*-methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranose (28). The title compound was prepared following the general procedure above, starting from **5c** (27.1 mg, 0.067 mmol), CH_2Cl_2 (0.35 mL) and 33% HBr in AcOH (0.35 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **5c-Br**, 1-*O*-methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranose (62.9 mg, 0.135 mmol), dry CH_2Cl_2 (0.7 mL), dry toluene (0.7 mL), 4 Å MS and AgOTf (34.8 mg, 0.135 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (5:95) and yield (62%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard. The residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford pure **28β** (25 mg, 48) as a colorless syrup. **R$_f$** (2:3 EtOAc/hexane): 0.35; **[α]^D$_{25}$** : +12.8 (0.9, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.39–7.23 (m, 15H, Ph), 5.42 (dd, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H-3), 5.04 (d, $J_{4,5}$ = 10.1 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H-4), 4.99 (d, J = 10.8 Hz, 1H, CH-Ph), 4.93 (d, J = 11.1 Hz, 1H, CH-Ph), 4.80 (d, J = 10.8 Hz, 1H, CH-Ph), 4.79 (d, J = 12.2 Hz, 1H, CH-Ph), 4.69–4.60 (m, 3H, H-1, H-1’, CH-Ph), 4.53 (d, J = 11.1 Hz, 1H, CH-Ph), 4.25 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 4.9 Hz, 1H, H-6a), 4.15–4.05 (m, 2H, H-6b, H-6a’), 3.99 (t, $J_{3,4}$ = $J_{2,3}$ = 9.3 Hz, 1H, H-3’), 3.78 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 4.0 Hz, $J_{5,6a}$ = 1.8 Hz, 1H, H-5’), 3.71 (dd, $J_{6a,6b}$ = 10.8 Hz, $J_{5,6b}$ = 4.4 Hz, 1H, H-6b’), 3.67 (ddd, $J_{4,5}$ = 10.1 Hz, $J_{5,6a}$ = 4.9 Hz, $J_{5,6a}$ = 2.5 Hz, 1H, H-5), 3.53 (dd, $J_{2,3}$ = 9.7 Hz, $J_{1,2}$ = 3.5 Hz, 1H, H-2’), 3.50 (dd, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 8.8 Hz, 1H, H-4’), 3.37 (s, 3H, CH_3-O), 2.76 (dp, $J_{2,3}$ = 10.5 Hz, $J_{2,CF3}$ = $J_{1,2}$ = 7.8 Hz, 1H, H-2), 2.05 (s, 3H, CH_3, Ac), 2.02 (s, 3H, CH_3, Ac), 2.02 (s, 3H, CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.35 (d, J = 7.8 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 169.6, 169.6 (C=O, OAc) 138.6, 138.3, 138.1, 128.5, 128.4(x2), 128.1, 128.0, 127.9, 127.72, 127.6, 127.5 (CH, Ar), 124.5 (q, $J_{C,F}$ = 281.9 Hz, CF_3), 98.5 (d, $J_{C1,F}$ = 2.6 Hz, C-1), 98.2 (C-1’), 82.1 (C-3’), 79.7 (C-2’), 77.4 (C-4’), 75.8 (CH_2Ph), 74.8 (CH_2Ph), 73.4 (CH_2Ph), 71.5 (C-5), 69.4

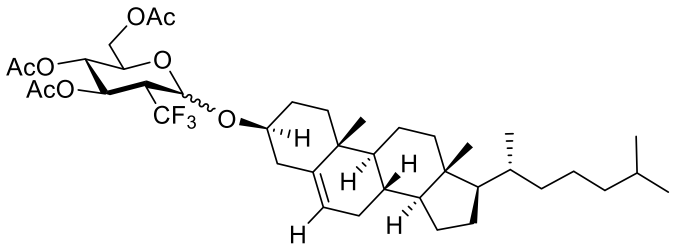


(C-5’), 68.8 (C-4), 68.2 (C-6’), 67.9 (C-3), 62.0 (C-6), 55.3 (CH_3-O), 49.5 (q, $J_{C,F}$ = 24.1 Hz, C-2), 20.7, 20.6 (x2) (CH_3, OAc); **FTIR–ATR (neat)** ν in cm^{-1}: 2929, 1753, 1454, 1364, 1223, 1183, 1131, 1086, 1072, 1046, 739, 699; **HRMS (TOF ES$^+$)** for $(M+NH_4)^+$ $C_{41}H_{51}F_3NO_{13}^+$ (m/z): calc. 822.3307; found 822.3307.



1-*O*-Cholesteryl-3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoromethyl-α/β-D-mannoyranose (29). The title compound was prepared following the general procedure above, starting from **5c** (22.2 mg, 0.055 mmol), CH_2Cl_2 (0.4 mL) and 33% HBr in AcOH (0.4 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **5c-Br**, cholesterol (42.6 mg, 0.11 mmol), dry CH_2Cl_2 (0.6 mL), dry toluene (0.6 mL), 4 Å MS and AgOTf (28.3 mg, 0.11 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (85:15) and yield (75%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard. Due to purification issues, the remaining cholesterol was submitted to acetylation conditions using Ac_2O (62.4 µL, 0.66 mmol) and pyridine (0.6 mL, 6.6 mmol) in CH_2Cl_2 (0.6 mL) for 16 h at room temperature. After standard work-up, the residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **29α** (30 mg, 57%) and a fraction containing an inseparable anomeric mixture of **29** (α/β, 2.2:1) (5 mg, 10%). Data for **29α:** Colorless syrup. **R_f** (1:9 EtOAc/hexane): 0.13; **$[\alpha]^{D}_{25}$** : +38.5 (1.15, $CHCl_3$) **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.43–5.30 (m, 4H, H-1, H-3, H-4, H-6’), 4.20 (dd, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6a}$ = 2.9 Hz, 1H, H-6a), 4.15 (dd, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6b}$ = 4.9 Hz, 1H, H-6b), 4.06 (ddd, $J_{4,5}$ = 8.2 Hz, $J_{5,6b}$ = 4.9 Hz, $J_{5,6a}$ = 2.9 Hz, 1H, H-5), 3.48 (m, 1H, H-3’), 2.68 (qdd, $J_{2,CF3}$ = 9.6 Hz, $J_{2,3}$ = 5.7 Hz, $J_{1,2}$ = 1.7 Hz, 1H, H-2), 2.42–2.27 (m, 2H, H-4’, H-7’), 2.07 (s, 3H, CH_3, Ac), 2.07 (s, 3H, CH_3, Ac), 2.05 (s, 3H, CH_3, Ac), 2.11–1.79 (m, 4H, H-4’’, H7’’, H-15’, H-16’), 1.64–0.85 (m, 22H), 1.01 (s, 3H, CH_3-18), 0.91 (d, $J_{20,21}$ = 6.5 Hz, 3H, CH_3-21), 0.87 (d, $J_{25,26}$ = 6.6 Hz, 3H, CH_3-26), 0.86 (d, $J_{25,27}$ = 6.6 Hz, 3H, CH_3-27), 0.68 (s, 3H, CH_3-19); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.6 (d, J = 9.6 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 170.0, 169.5 (3xC=O, Ac), 140.2 (C-5’), 124.7 (q, $J_{C,F}$ = 280.9 Hz, CF_3), 122.2 (C-6’), 93.5 (q, $J_{C1,F}$ = 4.1 Hz, C-1), 78.2 (C-3’), 68.3 (C-4), 67.9 (C-5), 66.0 (C-3), 62.5 (C-6), 56.7, 56.1, 50.0, 48.6 (q, $J_{C2,F}$ = 24.6 Hz, C-3), 42.3, 39.75, 39.7, 39.5, 36.9, 36.6, 36.1, 35.8, 31.9, 31.8, 28.2, 28.0, 27.6, 24.2, 23.8, 22.8, 22.5 (C-26, C-27), 21.0, 20.7 (2xCH_3, Ac), 20.6 (CH_3, Ac), 19.3

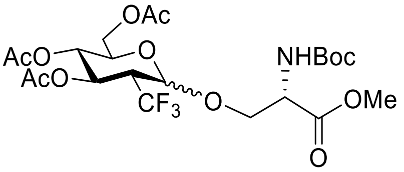
(C-18), 18.7 (C-21), 11.8 (C-19); **FTIR–ATR (neat)** v in cm^{-1}: 2938, 2868, 1751, 1456, 1436, 1370, 1267, 1229, 1177, 1159, 1114, 1047; **HRMS (TOF ES^{+})** for (M+Na)$^{+}$ $C_{40}H_{61}F_3NaO_8^{+}$ (m/z): calc. 749.4211; found 749.4219. Selected data for **29β:** Inseparable mixture of α/β (2.2:1). White solid. **R$_f$** (1:9 EtOAc/hexane): 0.10; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.36 (m, 1H, H-6'), 5.30 (dd, $J_{3,4}$ = 6.0 Hz, $J_{2,3}$ = 4.3 Hz, 1H, H-3), 5.15 (t, $J_{3,4}$ = $J_{4,5}$ = 5.8 Hz, 1H, H-4), 5.10 (d, $J_{1,2}$ = 3.2 Hz, 1H, H-1), 4.48 (dd, $J_{6a,6b}$ = 11.6 Hz, $J_{5,6a}$ = 6.1 Hz, 1H, H-6a), 4.34 (dd, $J_{6a,6b}$ = 11.6 Hz, $J_{5,6b}$ = 6.1 Hz, 1H, H-6b), 3.90 (q, $J_{4,5}$ = $J_{5,6a}$ = $J_{5,6b}$ = 5.8 Hz, 1H, H-5), 3.61–3.50 (m, 1H, H-3'), 3.07–2.97 (m, 1H, H-2), 2.39–2.27 (m, 2H, H-4', H-7'), 2.09 (s, 3H, CH_3, Ac), 2.09 (s, 3H, CH_3, Ac), 2.08 (s, 3H, CH_3, Ac), 2.21–1.79 (m, 4H, H-4'', H7'', H-15', H-16'), 1.64–0.80 (m, 22H), 1.01 (s, 3H, CH_3-18'), 0.91 (d, $J_{20,21}$ = 6.5 Hz, 3H, CH_3-21'), 0.87 (d, $J_{25,26}$ = 6.6 Hz, 3H, CH_3-26'), 0.86 (d, $J_{25,27}$ = 6.6 Hz, 3H, CH_3-27'), 0.68 (s, 3H, CH_3-19'); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –63.1 (d, J = 9.6 Hz, 3F, CF_3); **FTIR–ATR (neat)** v in cm^{-1}: 2927, 2851, 1750, 1456, 1431, 1370, 1230, 1159, 1114, 1047; **HRMS (TOF ES^{+})** for (M+Na)$^{+}$ $C_{40}H_{61}F_3NaO_8^{+}$ (m/z): calc. 749.4211; found 749.4212.



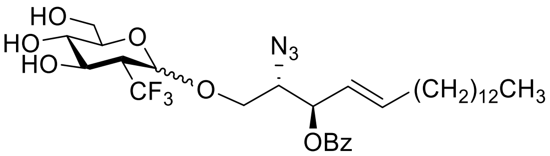
1-*O*-Cholesteryl-3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoromethyl-α/β-D-glucopyranose (30). The title compound was prepared following the general procedure above, starting from **4c** (25.7 mg, 0.064 mmol), CH_2Cl_2 (0.35 mL) and 33% HBr in AcOH (0.35 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **4c-Br**, cholesterol (74.3 mg, 0.192 mmol), dry CH_2Cl_2 (0.6 mL), dry toluene (0.6 mL), 4 Å MS and AgOTf (60 mg, 0.235 mmol). The reaction mixture was stirred under argon at –80 °C for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (21:79) and yield (69%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard. Due to purification issues, the remaining cholesterol was submitted to acetylation conditions using Ac_2O (0.1 mL, 1.15 mmol) and pyridine (1 mL, 11.5 mmol) in CH_2Cl_2 (1 mL) for 16 h at room temperature. After standard work-up, the residue was purified by column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **30α** (4 mg, 8%) and **30β** (26 mg, 56%) as white solids. Data for **30α**: White solid. **R$_f$** (1:4 EtOAc/hexane): 0.35; **m.p**: 172–174 °C; **$[\alpha]^{D}_{25}$** : –22.1 (0.20, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.67 (dd, $J_{2,3}$ = 11.3 Hz, $J_{3,4}$ = 9.2 Hz, 1H, H-3), 5.35 (d, $J_{6,7}$ = 4.9 Hz, 1H, H-6'), 5.24 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1), 5.00 (dd, $J_{4,5}$ = 10.1 Hz, $J_{3,4}$ = 9.4 Hz, 1H, H-4), 4.27 (dd, $J_{6a,6b}$ = 12.1 Hz, $J_{5,6a}$ = 4.8 Hz, 1H, H-6a) 4.17 (ddd, $J_{4,5}$ = 10.1 Hz, $J_{5,6a}$ = 4.7 Hz, $J_{5,6b}$

= 2.2 Hz, 1H, H-5), 4.09 (dd, $J_{6a,6b}$ = 12.1 Hz, $J_{5,6b}$ = 2.2 Hz, 1H, H-6b), 3.46 (m, 1H, H-3'), 2.79 (dqd, $J_{2,3}$ = 11.3 Hz, $J_{2,CF3}$ = 7.7 Hz, $J_{1,2}$ = 3.4 Hz, 1H, H-2), 2.43–2.24 (m, 2H, H-4', H-7'), 2.08 (s, 3H, CH_3, Ac), 2.04 (s, 3H, CH_3, Ac), 2.02 (s, 3H, CH_3, Ac), 2.12–1.73 (m, 4H, H-4'', H7'', H-15', H-16'), 1.60–0.80 (m, 22H), 1.01 (s, 3H, CH_3-18), 0.91 (d, $J_{20,21}$ = 6.5 Hz, 3H, CH_3-21), 0.86 (d, $J_{25,26}$ = 6.6 Hz, 3H, CH_3-26), 0.85 (d, $J_{25,27}$ = 6.6 Hz, 3H, CH_3-27), 0.68 (s, 3H, CH_3-19); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.00 (d, $J_=$ 7.4 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 169.8, 169.6 (3xC=O, Ac), 140.3 (C-5'), 122.2 (C-6'), 93.9 (m, C-1), 79.3 (C-3'), 69.0 (C-4), 67.6 (C-5), 66.9 (q, $J_{C3,F}$ = 2.2 Hz, C-3), 62.3 (C-6), 56.7, 56.1, 50.0, 48.6 (q, $J_{C2,F}$ = 27.2 Hz, C-2), 42.3, 40.0, 39.7, 39.5, 36.9, 36.6, 36.1, 35.8, 31.9, 31.8, 28.2, 28.0, 27.5, 24.3, 23.8, 22.8, 22.6 (C-26, C-27), 21.0, 20.7, 20.63, 20.62 (3xCH_3, Ac), 19.3 (C-18), 18.7 (C-21), 11.8 (C-19); **FTIR–ATR (neat)** ν in cm^{-1}: 2933, 2867, 2850, 1748, 1465, 1456, 1436, 1378, 1365, 1233, 1185, 1159, 1142, 1125, 1087, 1044, 1030; **HRMS (TOF ES$^+$)** for $(M+NH_4)^+$ $C_{40}H_{65}F_3NO_8^+$ (m/z): calc. 744.4657; found 744.4676.

Data for **30β:** White solid. **R$_f$** (1:4 EtOAc/hexane): 0.28; **m.p**: 170–172 °C; **$[\alpha]^{D}_{25}$** : +48.1 (0.30, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.43 (dd, $J_{2,3}$ = 10.7 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H-3), 5.37 (d, $J_{6',7'}$ = 5.2 Hz, 1H, H-6'), 5.01 (t, $J_{4,5}$ = 10.0 Hz, $J_{3,4}$ = 9.1 Hz, 1H, H-4), 4.76 (d, $J_{1,2}$ = 8.2 Hz, 1H, H-1), 4.28 (dd, $J_{6a,6b}$ = 12.2, $J_{5,6a}$ = 5.1 Hz, 1H, H-6a), 4.09 (dd, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6b}$ = 2.6 Hz, 1H, H-6b), 3.68 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6a}$ = 5.1 Hz, $J_{5,6b}$ = 2.6 Hz, 1H, H-5), 3.54 (m, 1H, H-3'), 2.68 (dp, $J_{2,3}$ = 10.7 Hz, $J_{1,2}$ = $J_{2,CF3}$ = 7.7 Hz, 1H, H-2), 2.34–2.22 (m, 2H, H-4', H-7'), 2.07 (s, 3H, CH_3, Ac), 2.02 (s, 3H, CH_3, Ac), 2.02 (s, 3H, CH_3, Ac), 2.11–1.76 (m, 4H, H-4'', H7'', H-15', H-16'), 1.60–0.8 (m, 22H), 1.00 (s, 3H, CH_3-18), 0.90 (d, $J_{20,21}$ = 6.5 Hz, 3H, CH_3-21), 0.86 (d, $J_{25,26}$ = 6.6 Hz, 3H, CH_3-26), 0.85 (d, $J_{25,27}$ = 6.6 Hz, 3H, CH_3-27), 0.68 (s, 3H, CH_3-19); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.53 (d, J = 7.4 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 169.7, 169.65 (3xC=O, Ac), 140.1 (C-5'), 122.2 (C-6'), 97.0 (q, $J_{C1,F}$ = 1.8 Hz, C-1), 80.0 (C-3'), 71.2 (C-5), 69.0 (C-4), 68.1 (q, $J_{C3,F}$ = 2.5 Hz, C-3), 62.1 (C-6), 56.7, 56.1, 50.0, 49.7 (m, C-2), 42.3, 39.7, 39.5, 38.2, 37.1, 36.7, 36.1, 35.7, 31.9, 31.8, 29.7, 29.4, 28.2, 28.0, 24.3, 23.8, 22.8, 22.6 (C-26, C-27), 21.0, 20.7 (CH_3, Ac), 20.6 (2xCH_3, Ac), 19.3 (C-18), 18.7 (C-21), 11.8 (C-19); **FTIR–ATR (neat)** ν in cm^{-1}: 2933, 2867, 2852, 1755, 1464, 1436, 1376, 1364, 1294, 1220, 1185, 1132, 1080, 1045, 906; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{40}H_{61}F_3NaO_8^+$ (m/z): calc. 749.4211; found 749.4214.



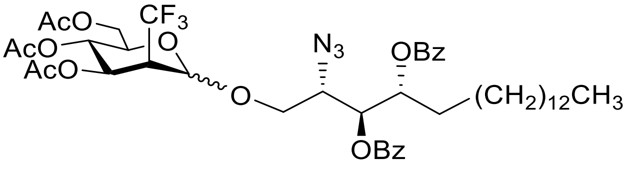
1-*O*-(*N*-tert-butoxycarbonyl)-L-serine methyl ester-3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoromethyl-β-D-glucopyranose (31). The title compound was prepared following the general procedure above, starting from **4c** (15.6 mg, 0.039 mmol), CH_2Cl_2 (0.3 mL) and 33% HBr in AcOH (0.3 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **4c-Br**, Boc-Serine-OMe (17.1 mg, 0.078 mmol), dry CH_2Cl_2 (0.4 mL), dry toluene (0.4 mL), 4 Å MS and AgOTf (20 mg, 0.078 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (5:95) and yield (35%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard.). Due to purification issues, the remaining acceptor was submitted to acetylation conditions using Ac_2O (44.5 µL, 0.47 mmol) and pyridine (0.35 mL, 4.67 mmol) in CH_2Cl_2 (0.35 mL) for 16 h at room temperature. After standard work-up, the residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **31β** (5 mg, 24%) as a white solid. **R_f** (1:4 EtOAc/hexane): 0.10; **m.p**: 130–132 ºC; **$[\alpha]^D_{25}$**: +74.0 (0.28, $CHCl_3$); **^1H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 5.58 (dd, $J_{2,3}$ = 11.2 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H-3), 5.45 (d, $J_{NH,2'}$ = 8.0 Hz, 1H, NH-Boc), 5.08 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-1), 5.02 (dd, $J_{4,5}$ = 10.2 Hz, $J_{3,4}$ = 9.5 Hz, 1H, H-4), 4.50 (dt, $J_{NH,2'}$ = 8.0 Hz, $J_{1',2'}$ = 3.1 Hz, 1H, H-2'), 4.29 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 4.5 Hz, 1H, H-6a), 4.07 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6a}$ = 2.2 Hz, 1H, H-6b), 4.03–3.96 (m, 2H, H-1', H-5), 3.93 (dd, $J_{1',1''}$ = 10.1 Hz, $J_{1'',2'}$ = 3.0 Hz, 1H, H-1''), 3.76 (s, 3H, COO-CH_3), 2.81 (dqd, $J_{2,3}$ = 11.3 Hz, $J_{2,CF3}$ = 7.8 Hz, $J_{1,2}$ = 3.6 Hz, 1H, H-2), 2.09 (s, 3H, CH_3, Ac), 2.05 (s, 3H, CH_3, Ac), 2.02 (s, 3H, CH_3, Ac), 1.48 (s, 9H, 3xCH_3, Boc); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –65.25 (d, J = 7.6 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.8, 170.0, 169.7, 169.4 (4xC=O, Ac, CO_2Me), 95.8 (q, $J_{C1,F}$ = 2.8 Hz, C-1), 69.4 (C-1'), 68.5 (C-4), 67.9 (C-5), 66.7 (C-3), 61.6 (C-6), 53.7 (C-2), 52.7 (CH_3, CO_2Me), 48.3 (q, $J_{C2,F}$ = 24.1 Hz, C-2), 28.3 (CH_3, Boc), 20.7, 20.6 (3xCH_3, Ac); **FTIR–ATR (neat)** ν in cm^{-1}: 2957, 2918, 2850, 1748, 1715, 1516, 1456, 1437, 1367, 1347, 1225, 1180, 1159, 1140, 1040; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{22}H_{32}F_3NNaO_{12}^+$ (m/z): calc. 582.1769; found 582.1767.



(2*S*,3*S*,4*E*)-2-azido-3-*O*-benzoyl-1-*O*-(2-deoxy-2-trifluoromethyl-α/β-D-glucopyranosyl)-4-octadecene-1,3-diol (32). The title compound was prepared following the general procedure above, starting from **4c** (25.7 mg, 0.064 mmol), CH_2Cl_2 (0.35 mL) and 33% HBr in AcOH (0.35 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **4c-Br**, (2*S*,3*S*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol (74.3 mg, 0.192 mmol), dry CH_2Cl_2 (0.6 mL), dry toluene (0.6 mL), 4 Å MS and AgOTf (32.9 mg, 0.128 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (49:51) and yield (24%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard. Due to purification issues, the crude **32a** was directly deacetylated using NaOMe (2 mg, 0.027 mmol) in MeOH (1 mL). After 6 h mixing at room temperature, it was neutralized with Dowex 50W-X8 ion exchange resin, the resin was filtered and washed with MeOH twice. The solvent was removed under the reduced pressure and the crude was purified by preparative TLC using a mixture of CH_2Cl_2/MeOH (10:0.5) to afford an anomeric mixture **32b** (α/β, 1.6:1), (10 mg, 18%) as an a colorless syrup. Data for **32bα/β: R_f** (9:1 CH_2Cl_2/MeOH): 0.39; **FTIR–ATR (neat)** v in cm^{-1}: 3363, 2924, 2853, 2096, 1724, 1634, 1453, 1316, 1264, 1170, 1122, 1068, 1026, 711; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{32}H_{48}F_3N_3NaO_7^+$ (m/z): calc. 666.3337; found 666.3312. Data for **32bα: ^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 8.09–8.02 (m, 2H, Ar, Bz), 7.68–7.62 (m, 1H, Ar, Bz), 7.52–7.42 (m, 2H, Ar, Bz), 6.01–5.88 (m, 1H, H-11'), 5.63–5.51 (m, 2H, H-9', H-10'), 5.09 (d, $J_{1,2}$ = 3.3 Hz, 1H, H-1), 4.20 (dd, $J_{2,3}$ = 10.8 Hz, $J_{3,4}$ = 8.9 Hz, 1H, H-3), 3.93–3.56 (m, 5H, H-5, H-6a, H-6b, H-7', H-8'), 3.60 (t, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, 1H, H-4), 3.49 (dd, $J_{7',7''}$ = 10.5 Hz, $J_{7'',8'}$ = 7.3 Hz, 1H, H-7''), 2.63–2.46 (m, 1H, H-2), 2.14–2.03 (m, 2H, CH_2-11'), 1.41–1.19 (m, 24H, CH_2-12'-23'), 0.88 (t, *J* = 6.9 Hz, 3H, CH_3-24'); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –64.20 (m, 3F, CF_3); **^{19}F NMR** (CD_3OD, 376.5 MHz) δ in ppm: –65.50 (d, *J* = 8,3 Hz, 3F); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 165.2 (C=O, Bz), 139.3 (C-11'), 133.4, 129.8, 129.75, 128.5 (CH, Ar, Bz), 122.8 (C-10'), 124.5 (q, $J_{C,F}$ = 281.0 Hz, CF_3), 96.3 (q, $J_{C1,F}$ = 3.9 Hz, C-1), 74.6 (C-9'), 71.6 (C-5), 71.4 (C-4), 68.4 (C-3), 67.3 (C-7'), 63.9 (C-8'), 62.2 (C-6), 50.0 (q, $J_{C2,F}$ = 24.8 Hz, C-2), 32.4 (C-11'), 31.9, 29.69, 29.68, 29.66, 29.6, 29.4, 29.3, 29.2, 29.1, 28.7, 28.68, 22.7 (C-24').

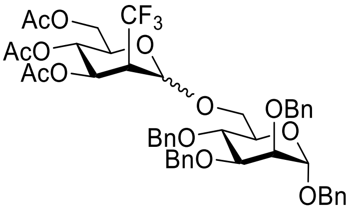
Data for **32bβ**: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 8.09–8.02 (m, 2H, Ar, Bz), 7.68–7.62 (m, 1H, Ar, Bz), 7.52–7.42 (m, 2H, Ar, Bz), 6.01–5.88 (m, 1H, H-11'), 5.74 (dd, $J_{9',10'}$ = 8.1 Hz, $J_{8',9'}$ = 4.6 Hz, 1H, H-9'), 5.63–5.51 (m, 1H, H-10'), 4.62 (d, $J_{1,2}$ = 8.2 Hz, 1H, H-1), 3.96 (td, $J_{7',8'}$ = $J_{7'',8'}$ = 6.1 Hz, $J_{8',9'}$ = 4.6 Hz, 1H, H-8'), 3.93–3.56 (m, 6H, H-3, H-4, H-6a, H-6b, H-7', H-7''), 3.34 (dt, $J_{4,5}$ = 9.9 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 3.7 Hz, 1H, H-5), 2.63–2.46 (m, 1H, H-2), 2.14–2.03 (m, 2H, CH_2-11'), 1.41–1.19 (m, 24H, CH_2-12'-23'), 0.88 (t, *J* = 6.9 Hz, 3H, CH_3-24'); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –64.20 (m, 3F, CF_3); **^{19}F NMR** (CD_3OD, 376.5 MHz) δ in ppm: –65.29 (d, *J* = 8,2 Hz, 3F); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 165.5 (C=O, Bz), 139.4 (C-11'), 133.4, 129.9, 128.5 (CH, Ar, Bz), 122.4 (C-10'), 124.5 (q, $J_{C,F}$ = 281.0 Hz, CF_3), 98.7 (q, $J_{C1,F}$ = 2.9 Hz, C-

1), 74.9 (C-5), 74.7 (C-9'), 70.9 (C-3), 70.3 (C-4), 68.6 (C-7'), 63.3 (C-8'), 61.8 (C-6), 51.5 (m, C-2), 32.4 (C-11'), 31.9, 29.69, 29.68, 29.66, 29.6, 29.4, 29.3, 29.2, 29.1, 28.7, 28.68, 22.7 (C-24').

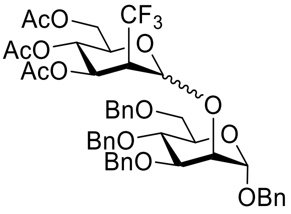


(2*S*,3*S*,4*R*)-2-azido-3,4-di-*O*-benzoyl-1-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-trifluoromethyl-α-D-mannopyranosyl)-1,3,4-octadecanetriol (33). The title compound was prepared following the general procedure above, starting from **5c** (23.2 mg, 0.058 mmol), CH$_2$Cl$_2$ (0.4 mL) and 33% HBr in AcOH (0.4 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **5c-Br**, (2*S*,3*S*,4*R*)-2-azido-3,4-di-*O*-benzoyl-1,3,4-octadecanetriol (63.9 mg, 0.116 mmol), dry CH$_2$Cl$_2$ (0.6 mL), dry toluene (0.6 mL), 4 Å MS and AgOTf (29.8 mg, 0.116 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (95:5) and yield (68%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard. Due to purification issues, the remaining acceptor was submitted to acetylation conditions using Ac$_2$O (66.3 µL, 0.69 mmol) and pyridine (0.56 mL, 6.69 mmol) in CH$_2$Cl$_2$ (0.56 mL) for 16h at room temperature. After standard work-up, the residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **33α** (33 mg, 64%) as a colorless syrup. **R$_f$** (1:4 EtOAc/hexane): 0.23; **$[\alpha]^{D}_{25}$**: +23.9 (0.35, CHCl$_3$); **^{1}H NMR** (CDCl$_3$, 400 MHz) δ in ppm: 8.05–7.97 (m, 4H, Ar, Bz), 7.66–7.54 (m, 2H, Ar, Bz), 7.52–7.40 (m, 4H, Ar, Bz), 5.53 (t, $J_{8',9'}$ = $J_{9',10'}$ = 5.4 Hz, 1H, H-9'), 5.51–5.44 (m, 1H, H-10'), 5.40–5.29 (m, 2H, H-3, H-4), 5.16 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1), 4.24–4.08 (m, 2H, H-7', H-6a), 4.06 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 4.7 Hz, 1H, H-6b), 3.99 (ddd, $J_{7'',8'}$ = 8.3 Hz, $J_{8',9'}$ = 5.4 Hz, $J_{7',8'}$ = 2.6 Hz, 1H, H-8'), 4.02–3.90 (m, 1H, H-5), 3.71 (dd, $J_{7,7'}$ = 10.6 Hz, $J_{7'',8'}$ = 8.3 Hz, 1H, H-7''), 3.19 (qdd, $J_{2,CF3}$ = 9.6 Hz, $J_{2,3}$ = 4.7 Hz, $J_{1,2}$ = 1.7 Hz, 1H, H-2), 2.06 (s, 3H, CH$_3$, Ac), 2.04 (s, 3H, CH$_3$, Ac), 2.00 (s, 3H, CH$_3$, Ac), 1.93–1.78 (m, 2H, CH$_2$-11'), 1.46–1.16 (m, 24H, CH$_2$-12'-23'), 0.87 (t, *J* = 6.9 Hz, 3H, CH$_3$-24'); **^{19}F NMR** (CDCl$_3$, 376.5 MHz) δ in ppm: –62.66 (d, *J* = 9.6 Hz, 3F, CF$_3$); **^{13}C NMR** (CDCl$_3$, 100.6 MHz) δ in ppm: 170.6, 169.9, 169.4 (3xC=O, Ac), 165.8, 165.1 (2xC=O, Bz) 133.7, 133.4, 129.8, 129.7, 129.55, 129.0, 128.7, 128.6 (CH, Ar, Bz), 124.5 (q, $J_{C,F}$ = 281.0 Hz, CF$_3$), 96.3 (q, $J_{C1,F}$ = 4.5 Hz, C-1), 72.7, 72.6 (C-9', C-10'), 68.8 (C-5), 68.5 (C-7'), 67.4 (C-4), 65.6 (C-3), 62.2 (C-6), 60.9 (C-8'), 45.9 (q, $J_{C2,F}$ = 25.0 Hz, C-2), 31.9, 30.2 (C-11'), 29.68, 29.66, 29.64, 29.58, 29.49, 29.39, 29.35, 29.33, 25.3, 22.7, 20.7, 20.6, 20.5 (3xCH$_3$, Ac), 14.1 (C-24'); **FTIR–ATR (neat)** ν in cm^{-1}: 2924, 2853, 2099, 1750, 1725, 1452, 1369, 1314, 1264, 1228, 1177, 1159, 1121, 1094, 1068, 1054, 1026, 712; **HRMS (TOF ES$^+$)** for (M+Na)$^+$ $C_{45}H_{60}F_3N_3NaO_{12}^+$ (m/z): calc. 914.4021; found 914.4016.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-trifluoromethyl-α/β-D-mannosyl-(1 → 2)-1,3,4,6-tetra-*O*-benzyl-α-D-mannopyranose (34). The title compound was prepared following the general procedure above, starting from **5c** (21.5 mg, 0.053 mmol), CH_2Cl_2 (0.38 mL) and 33% HBr in AcOH (0.38 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **5c-Br**, 1,2,3,4-tetra-*O*-benzyl-α-D-mannopyranose (55.8 mg, 0.106 mmol), dry CH_2Cl_2 (0.55 mL), dry toluene (0.55 mL), 4 Å MS and AgOTf (27.2 mg, 0.106 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (93:7) and yield (60%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard. Due to purification issues, the remaining acceptor was submitted to acetylation conditions using Ac_2O (60 µL, 0.64 mmol) and pyridine (0.5 mL, 6.36 mmol) in CH_2Cl_2 (0.5 mL) for 16h at room temperature. After standard work-up, the residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to obtain a fraction containing an anomeric mixture of **34** (α/β 10:1) (27 mg, 48%) as colorless syrup. Data for **34α/β: R$_f$** (1:9 EtOAc/hexane): 0.12; **FTIR–ATR (neat)** ν in cm^{-1}: 3031, 2928, 1749, 1496, 1455, 1435, 1367, 1307, 1267, 1227, 1178, 1154, 1119, 1092, 1051, 1027, 977, 913, 737, 699; **HRMS (TOF ES$^+$)** for (M+Na)$^+$ $C_{47}H_{51}F_3NaO_{13}^+$ (m/z): calc. 903.3174; found 903.3170. Data for **34α: ^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.35–7.20 (m, 20H, Ar), 5.39 (dd, $J_{3,4}$ = 9.7 Hz, $J_{2,3}$ = 5.4 Hz, 1H, H-3), 5.42–5.32 (m, 2H, H-1, H-4), 4.97 (d, J = 11.3 Hz, 1H, CH-Ph), 4.83 (d, $J_{1',2'}$ = 1,9 Hz, 1H, H-1'), 4.70–4.55 (m, 6H, 6xCH-Ph), 4.41 (d, J = 12.0 Hz, 1H, CH-Ph), 4.14 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6a}$ = 2.2 Hz, 1H, H-6a), 4.06 (dd, $J_{6a,6b}$ = 12.0 Hz, $J_{5,6b}$ = 4.7 Hz, 1H, H-6b), 4.02–3.99 (ddd, $J_{4,5}$ = 9.4 Hz, $J_{5,6b}$ = 4.7 Hz, $J_{5,6a}$ = 2.2 Hz, 1H, H-5), 3.97–3.87 (m, 2H, H-4', H-3'), 3.82 (dd, $J_{6a',6b'}$ = 12.0 Hz, $J_{5',6a'}$ = 4.8 Hz, 1H, H-6a'), 3.77 (d, $J_{1',2'}$ = 2.4 Hz, 1H, H-2'), 3.83-3.73 (m, 1H, H-5'), 3.72 (dd, $J_{6a',6b'}$ = 12.0 Hz, $J_{5',6b'}$ = 1.8 Hz, 1H, H-6b'), 3.23 (qdd, $J_{2,CF3}$ = 9.8 Hz, $J_{2,3}$ = 5.6 Hz, $J_{1,2}$ = 1.4 Hz, 1H, H-2), 2.04 (s, 3H, CH_3, Ac), 2.03 (s, 3H, CH_3, Ac), 2.02 (s, 3H, CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.32 (d, J = 9.8 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.8, 169.9, 169.5 (3xC=O, Ac), 138.3, 138.2, 138.0, 137.1, 128.45, 128.4, 128.35, 128.3, 127.8, 127.7, 127,68, 127.65, 127.6, 127.5 (Ar), 124.7 (q, $J_{C,F}$ = 281.0 Hz, CF_3), 97.2 (C-1'), 95.5 (q, $J_{C1,F}$ = 4.9 Hz, C-1), 80.2 (C-3'), 75.1 (CH_2Ph), 74.4 (C-4'), 74.3 (C-2'), 72.7 (CH_2Ph), 72.1 (CH_2Ph), 71.9 (C-5'), 69.0 (CH_2Ph), 68.2 (C-5), 67.7 (C-4), 66.7



(C-6'), 65.7 (C-3), 62.2 (C-6), 46.0 (q, $J_{C2,F}$ = 25.1 Hz, C-2), 20.7 (2xCH_3, Ac), 20.6 (CH_3, Ac). Selected data for **34β:** **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.38 (dd, J = 7.2 Hz, J = 2.2 Hz, 2H, Ar), 7.35–7.20 (m, 18H, Ar), 5.43–5.31 (m, 2H, H-3, H-4), 5.28 (s, 1H, H-1), 4.99–4.87 (m, 3H, 3xCH-Ph), 4.80 (d, J = 12.6 Hz, 1H, CH-Ph), 4.65–4.43 (m, 3H, 3xCH-Ph), 4.37 (s, 1H, H-1'), 4.36 (d, J = 12.1 Hz, 1H, CH-Ph), 4.18–4.10 (m, 1H, H-6a), 4.10–4.00 (m, 2H, H-5, H-6b), 3.92–3.70 (m, 3H, H-4', H-6a', H-6b'), 3.87 (d, $J_{2',3'}$ = 2.9 Hz, 1H, H-2'), 3.46 (dd, $J_{3',4'}$ = 9.3 Hz, $J_{2',3'}$ = 2.9 Hz, 1H, H-3'), 3.38 (ddd, $J_{4',5'}$ = 9.8 Hz, $J_{5',6a'}$ = 6.0 Hz, $J_{5',6b'}$ = 1.8 Hz, 1H, H-5'), 3.24 (qd, $J_{2,CF3}$ = 9.8 Hz, $J_{2,3}$ = 5.4 Hz, 1H, H-2), 2.01 (s, 3H, CH_3, Ac), 1.97 (s, 3H, CH_3, Ac), 1.87 (s, 3H, CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.22 (d, J = 9.8 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.7, 169.9, 169.5 (3xC=O, Ac), 138.6, 138.2, 137.9, 137.3, 128.5, 128.45, 128.40, 128.3, 128.1, 128.0, 127.95, 127.9, 127.8, 127.7, 127.65, 127.6, 127.4 (Ar), 124.71 (q, $J_{C,F}$ = 281.0 Hz, CF_3), 100.0 (C-1'), 96.7 (q, $J_{C1,F}$ = 4.5 Hz, C-1), 82.3 (C-3'), 75.10 (CH_2Ph, C-5'), 74.3 (C-4'), 73.9 (CH_2Ph), 73.8 (C-2'), 71.3 (CH_2Ph), 70.7 (CH_2Ph), 68.3 (C-5), 67.7 (C-4), 67.2 (C-6'), 65.7 (C-3), 62.1 (C-6), 46.2 (q, $J_{C2,F}$ = 24.7 Hz, C-2), 20.7, 20.6, 20.5 (3xCH_3, Ac).



3,4,6-Tri-*O*-acetyl-2-deoxy-2-trifluoromethyl-α/β-D-mannosyl-(1 → 2)-1,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranose (35). The title compound was prepared following the general procedure above, starting from **5c** (20.5 mg, 0.051 mmol), CH_2Cl_2 (0.36 mL) and 33% HBr in AcOH (0.36 mL). After standard work-up, glycosylation was carried out in a Schlenk flask using the crude bromopyranoside **5c-Br**, 1,3,4,6-tetra-*O*-benzyl-α-D-mannopyranose (53.7 mg, 0.102 mmol), dry CH_2Cl_2 (0.5 mL), dry toluene (0.5 mL), 4 Å MS and AgOTf (26.2 mg, 0.102 mmol). The reaction mixture was stirred under argon at –80 ºC for 2 h. Reaction was initiated by addition of AgOTf (26,2 mg, 0.102 mmol) solution in dry toluene (0.5 mL) and the reaction mixture was stirred under argon at –80 ºC for 2 h. After standard work-up, ^{19}F NMR analysis indicated an α/β ratio (86:14) and yield (54%) using 1,4-difluorobenzene (5 µL, 0.048 mmol) as the internal standard. Due to purification issues, the remaining acceptor was submitted to acetylation conditions using Ac_2O (58 µL, 0.61 mmol) and pyridine (0.5 mL, 6.12 mmol) in CH_2Cl_2 (0.5 mL) for 16 h at room temperature. After standard work-up, the residue was purified by flash column chromatography (from hexane to 1:4 EtOAc/hexane) to afford **33α** (20 mg, 45%) a **35β** (2 mg, 5%). Data for **35α:** Colorless syrup. **R_f** (1:9 EtOAc/hexane): 0.10; **$[\alpha]^D_{25}$**: +48.9 (0.66, $CHCl_3$); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.42–7.24 (m, 18H, Ar), 7.17–7.13

(m 2H, Ar), 5.42 (d, $J_{1,2}$ = 2.3 Hz, 1H, H-1), 5.40 (d, $J_{2,3}$ = 5.6 Hz, 1H, H-3), 5.30 (t, $J_{3,4}$ = $J_{4,5}$ = 8.8 Hz, 1H, H-4), 4.94 (d, $J_{1',2'}$ = 2.0 Hz, 1H, H-1’), 4.82 (d, J = 10.8 Hz, 1H, CH-Ph), 4.74 (d, J = 11.6 Hz, 1H, CH-Ph), 4.72 (d, J = 11.8 Hz, 1H, CH-Ph), 4.65 (d, J = 12.2 Hz, 1H, CH-Ph), 4.64 (d, J = 11.6 Hz, 1H, CH-Ph), 4.56 (d, J = 12.3 Hz, 1H, CH-Ph), 4.50 (d, J = 10.8 Hz, 1H, CH-Ph), 4.48 (d, J = 11.8 Hz, 1H, CH-Ph), 4.15–4.02 (m, 3H, H-5, H-6a, H-6b), 4.02 (t, $J_{1',2'}$ = $J_{2',3'}$ = 2.0 Hz, 1H, H-2’), 3.97 (dd, $J_{3'4'}$ = 9.1 Hz, $J_{2',3'}$ = 2.4 Hz, 1H, H-3’), 3.92 (t, $J_{3',4'}$ = $J_{4',5'}$ = 9.2 Hz, 1H, H-4’), 3.82 (ddd, $J_{4',5'}$ = 9.2 Hz, $J_{5',6a'}$ = 4.7 Hz, $J_{5',6b'}$ = 1.9 Hz, 1H, H-5’), 3.75 (dd, $J_{6a',6b'}$ = 10.6 Hz, $J_{5',6a'}$ = 4.7 Hz, 1H, H-6a’), 3.70 (dd, $J_{6a',6b'}$ = 10.6 Hz, $J_{5',6b'}$ = 1.9 Hz, 1H, H-6b’), 3.31 (qdd, $J_{2,CF3}$ = 9.6 Hz, $J_{2,3}$ = 5.6 Hz, $J_{1,2}$ = 2.5 Hz, 1H, H-2), 2.07 (s, 3H, CH_3, Ac), 2.07 (s, 3H, CH_3, Ac), 2.05 (s, 3H, CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.8 (d, J = 9.6 Hz, 3F, CF_3); **^{13}C NMR** ($CDCl_3$, 100.6 MHz) δ in ppm: 170.6, 169.8, 169.6 (3xC=O, Ac), 138.3, 138.1, 138.0, 137.0, 128.5, 128.45, 128.40, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.65, 127.6, 127.5 (Ar), 124.71 (q, $J_{C,F}$ = 280.8 Hz, CF_3), 97.7 (C-1’), 96.8 (q, $J_{C1,F}$ = 4.1 Hz, C-1), 79.8 (C-3’), 76.0 (C-2’), 75.3 (CH_2Ph), 74.9 (C-4’), 73.3 (CH_2Ph), 73.1 (CH_2Ph), 72.3 (C-5’), 69.1 (CH_2Ph), 69.0 (C-6’), 68.6 (C-5), 67.7 (C-3), 66.0 (C-4), 62.4 (C-6), 46.0 (q, $J_{C2,F}$ = 24.9 Hz, C-2), 20.7, 20.65, 20.6 (3xCH_3, Ac); **FTIR–ATR (neat)** ν in cm^{-1}: 2917, 2867, 1749, 1497, 1455, 1436, 1368, 1306, 1267, 1226, 1178, 1120, 1092, 1051, 978, 737, 699; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{47}H_{51}F_3NaO_{13}^+$ (m/z): calc. 903.3174; found 903.3173. Selected data for **35β:** Colorless syrup. **R$_f$** (1:9 EtOAc/hexane): 0.08; Selected spectroscopic data: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ in ppm: 7.37–7.19 (m, 18H, Ar), 7.15–7.11 (m, 2H, Ar), 5.78 (d, $J_{2,3}$ = 3.4 Hz, 1H, H-3), 5.77 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-1), 5.14 (ddd, $J_{4,5}$ = 9.5 Hz, $J_{5,6b}$ = 4.8 Hz, $J_{5,6a}$ = 2.4 Hz, 1H, H-5), 4.91 (d, $J_{1',2'}$ = 1,8 Hz, 1H, H-1), 4.79 (d, J = 10.8 Hz, 1H, CH-Ph), 4.72–4.68 (m, 3H, 3xCH-Ph), 4.65 (d, J = 12.0 Hz, 1H, CH-Ph), 4.53–4.45 (m, 3H, 3xCH-Ph), 4.43 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 2.5 Hz, 1H, H-6a), 4.30 (dd, $J_{3',4'}$ = 9.8 Hz, $J_{2',3'}$ = 3.1 Hz, 1H, H-3’), 4.06 (d, $J_{1',2'}$ = 2.5 Hz, 1H, H-2’), 3.97 (dd, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6b}$ = 2.1 Hz, 1H, H-6b), 3.98–3.93 (m, 1H, H-4), 3.92 (t, $J_{3',4'}$ = 9.5 Hz, 1H, H-4’), 3.80 (ddd, $J_{4',5'}$ = 9.6 Hz, $J_{5',6b'}$ = 4.5 Hz, $J_{5',6a'}$ = 1.9 Hz, 1H, H-5’), 3.73 (dd, $J_{6a',6b'}$ = 10.4 Hz, $J_{5',6a'}$ = 4.6 Hz, 1H, H-6a’), 3.67 (dd, $J_{6a',6b'}$ = 10.4 Hz, $J_{5',6b'}$ = 2.0 Hz, 1H, H-6b’), 2.68 (m, 1H, H-2), 2.04 (s, 3H, CH_3, Ac), 2.03 (s, 3H, CH_3, Ac), 2.02 (s, 3H, CH_3, Ac); **^{19}F NMR** ($CDCl_3$, 376.5 MHz) δ in ppm: –62.6 (d, J = 9.4 Hz, 3F, CF_3); **FTIR–ATR (neat)** ν in cm^{-1}: 2920, 2867, 1747, 1435, 1369, 1306, 1265, 1227, 1120, 1051, 740, 700; **HRMS (TOF ES$^+$)** for $(M+Na)^+$ $C_{47}H_{51}F_3NaO_{13}^+$ (m/z): calc. 903.3174; found 903.3167.

4. NMR Spectra

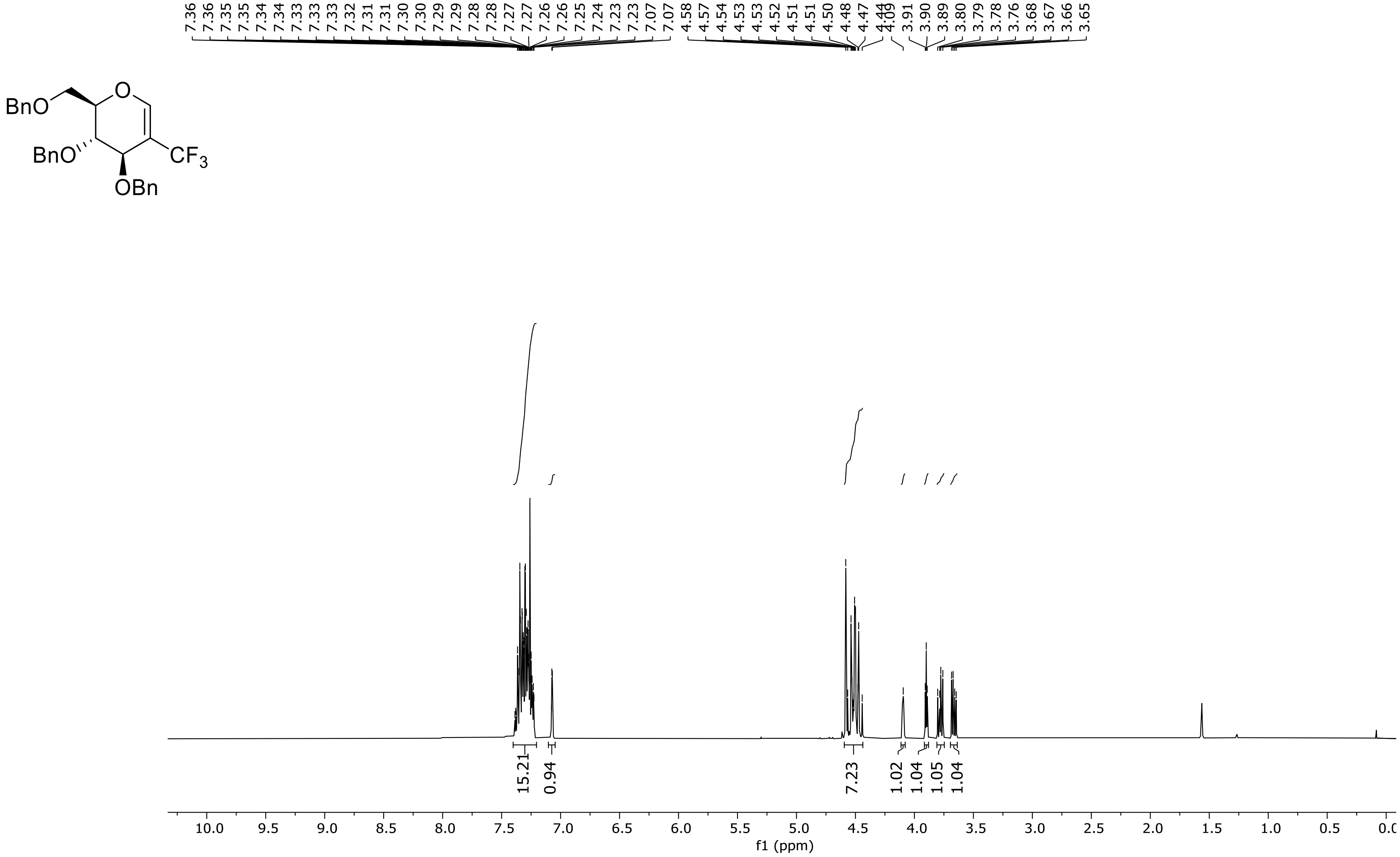


Figure S6. ^{1}H NMR ($CDCl_3$, 400 MHz) of **3a**

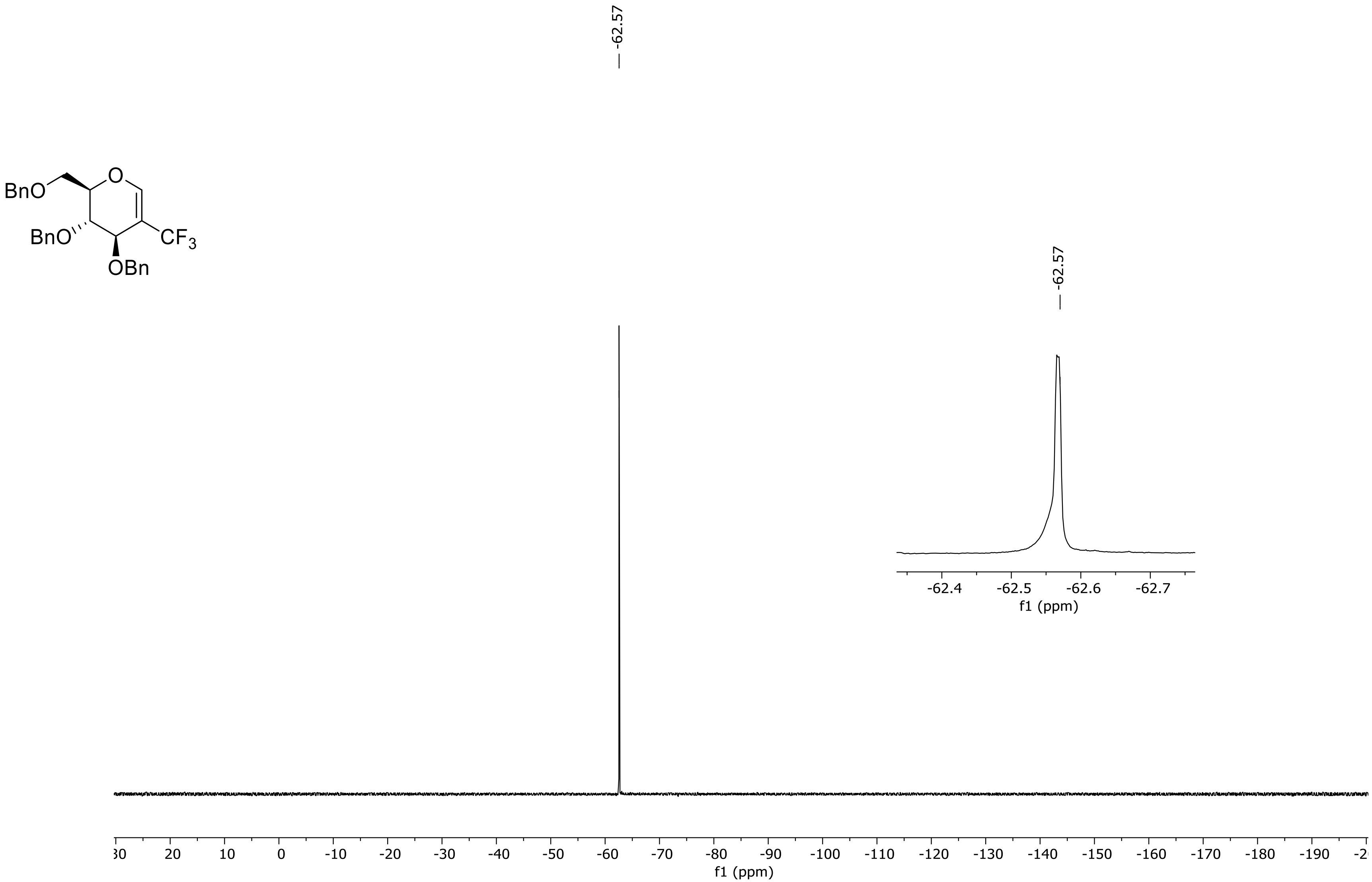


Figure S7. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **3a**

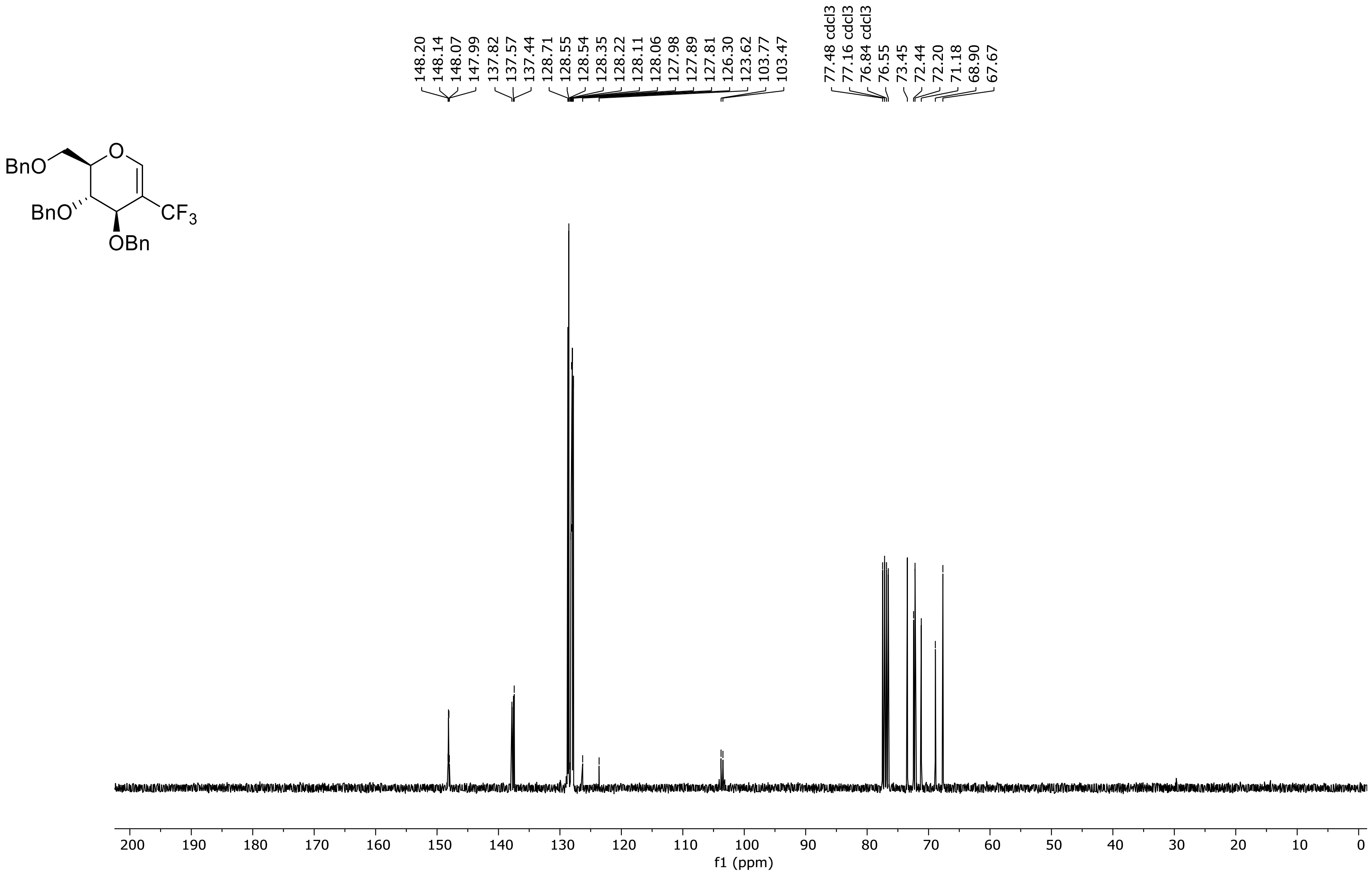


Figure S8. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **3a**

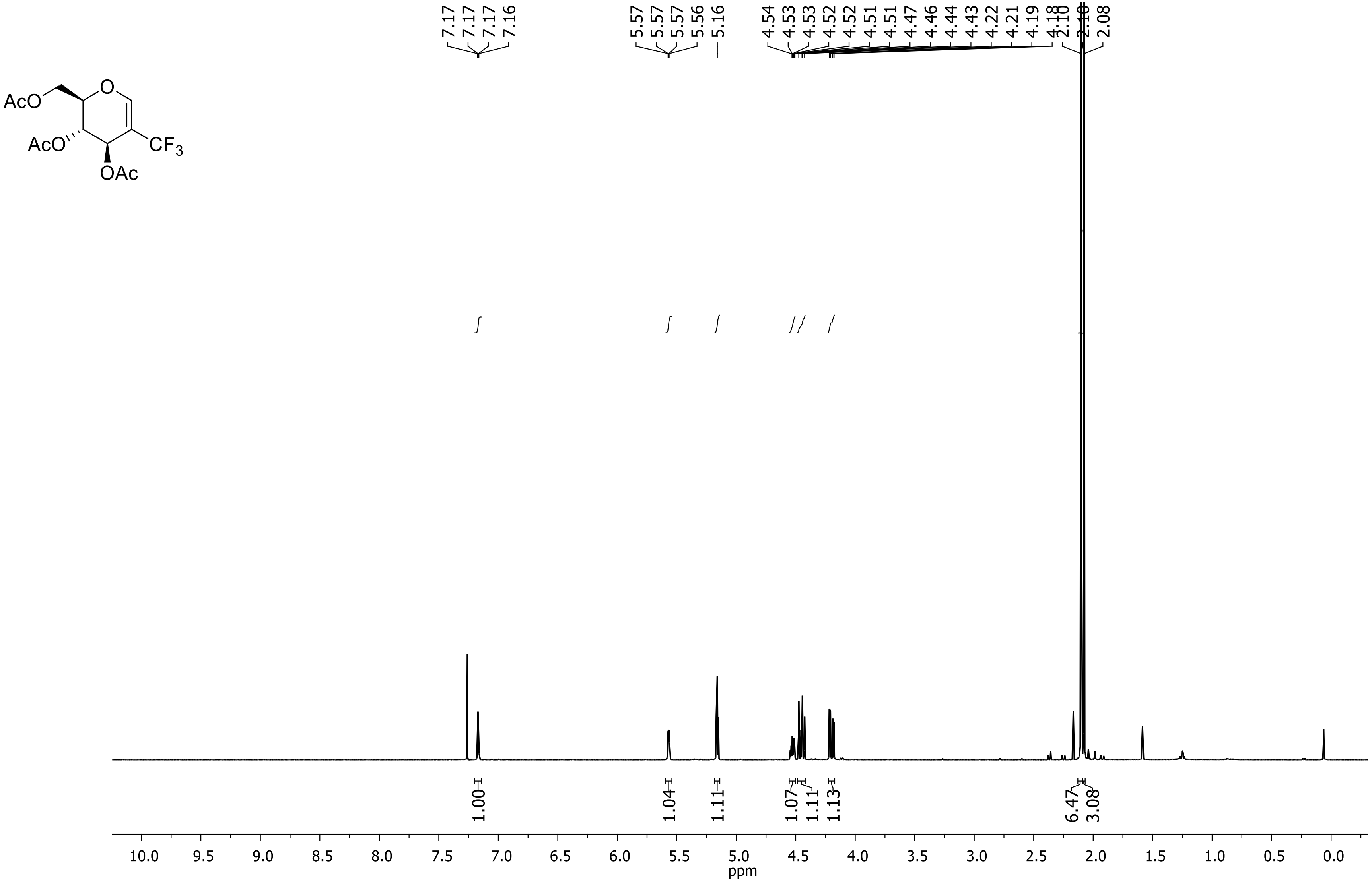


Figure S9. ^{1}H NMR ($CDCl_3$, 400 MHz) of **3b**

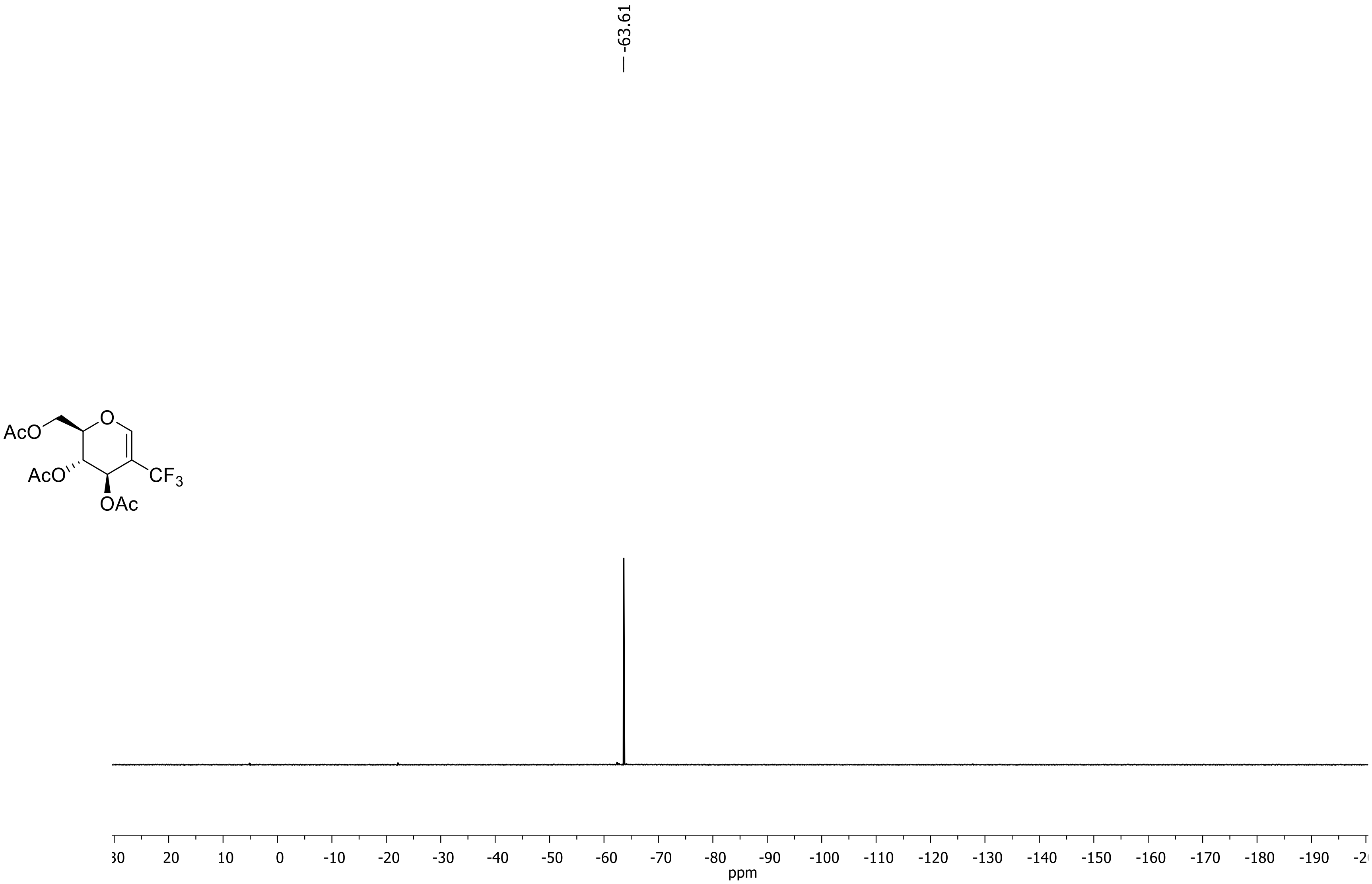


Figure S10. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **3b**

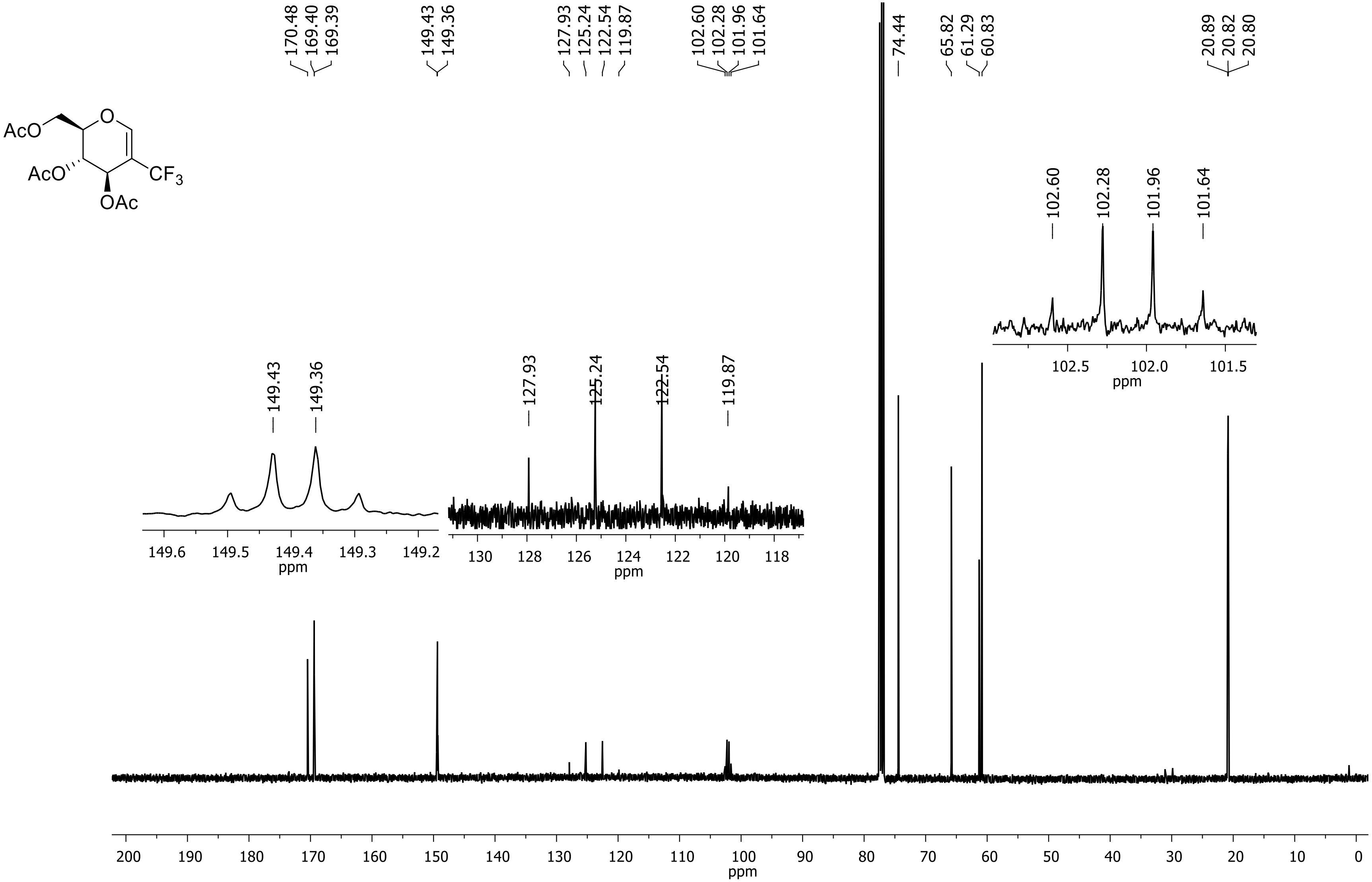
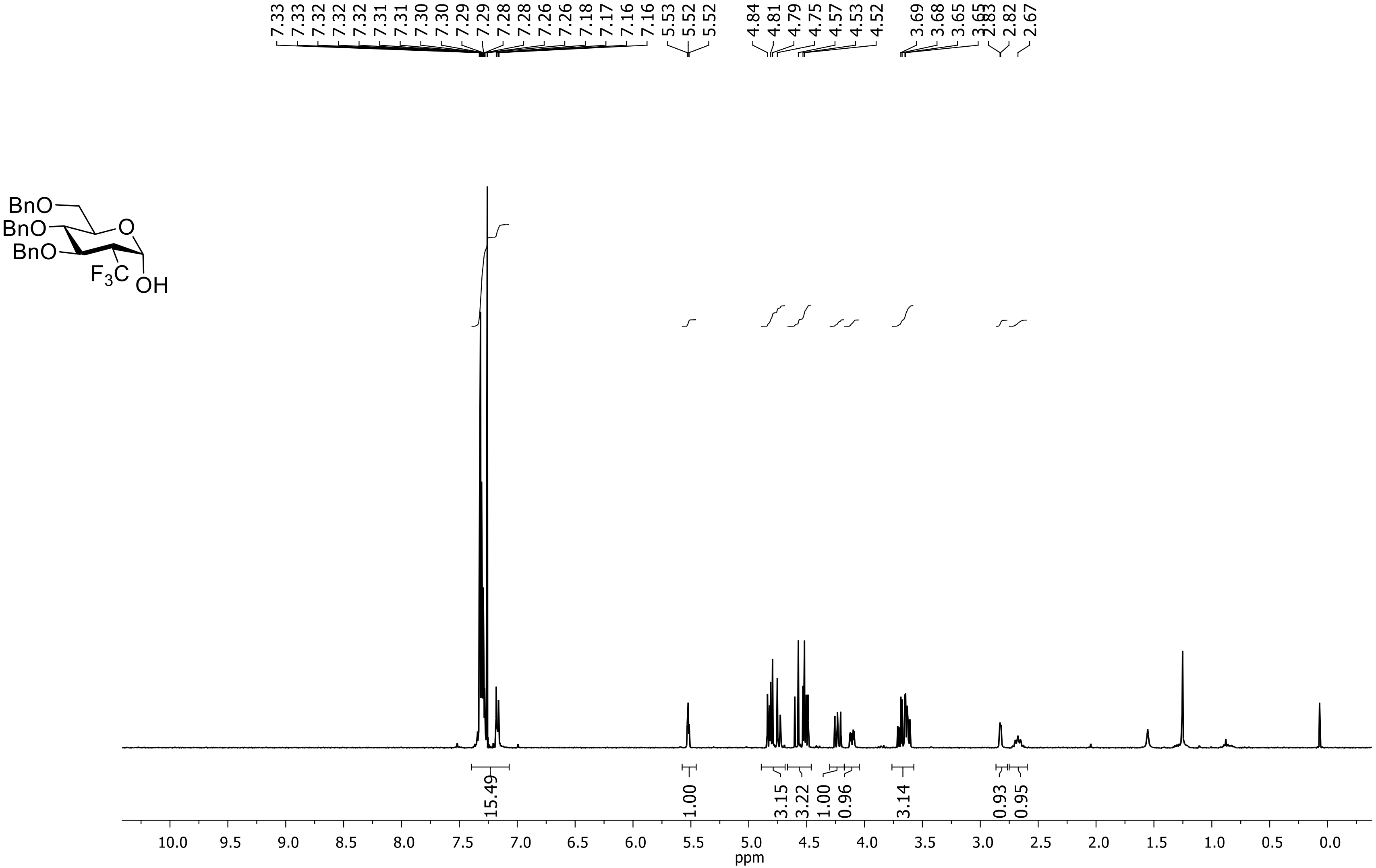


Figure S11. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **3b**



FigureS12. ^{1}H NMR (CDCl$_3$, 400 MHz) of **4a**

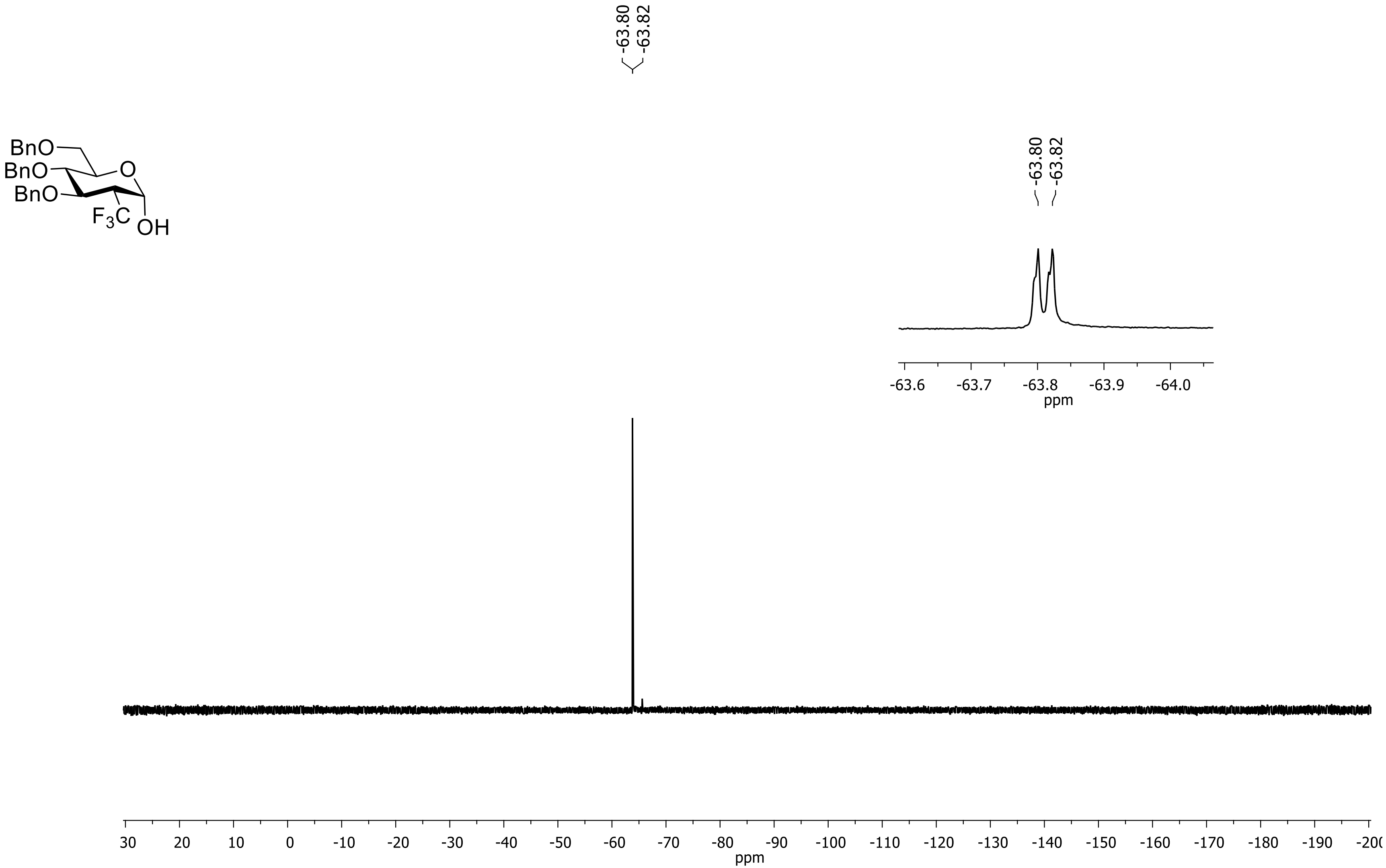


Figure S13. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **4a**

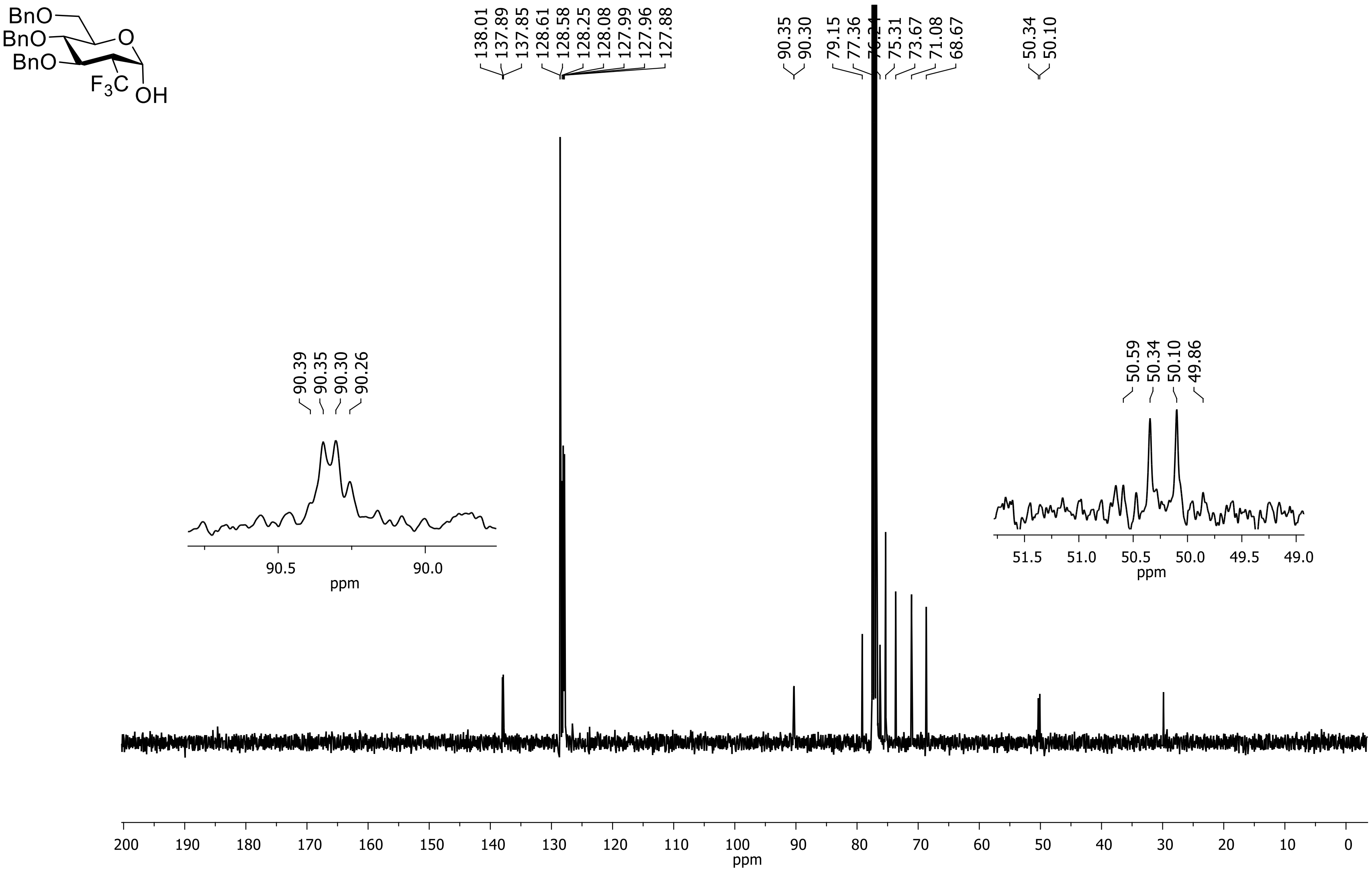


Figure S14. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **4a**

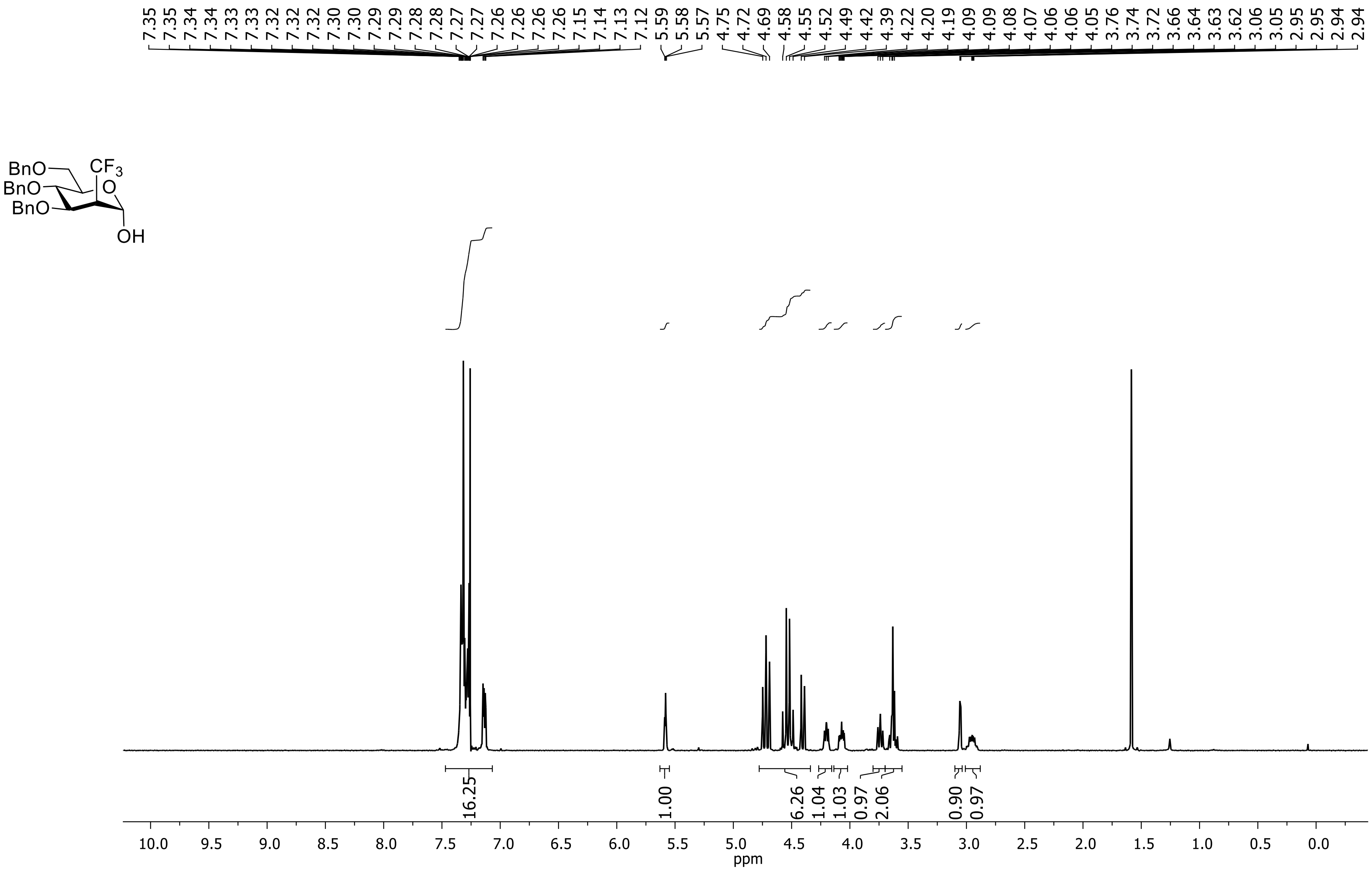


Figure S15. ^{1}H NM ($CDCl_3$, 400 MHz) of **5a**

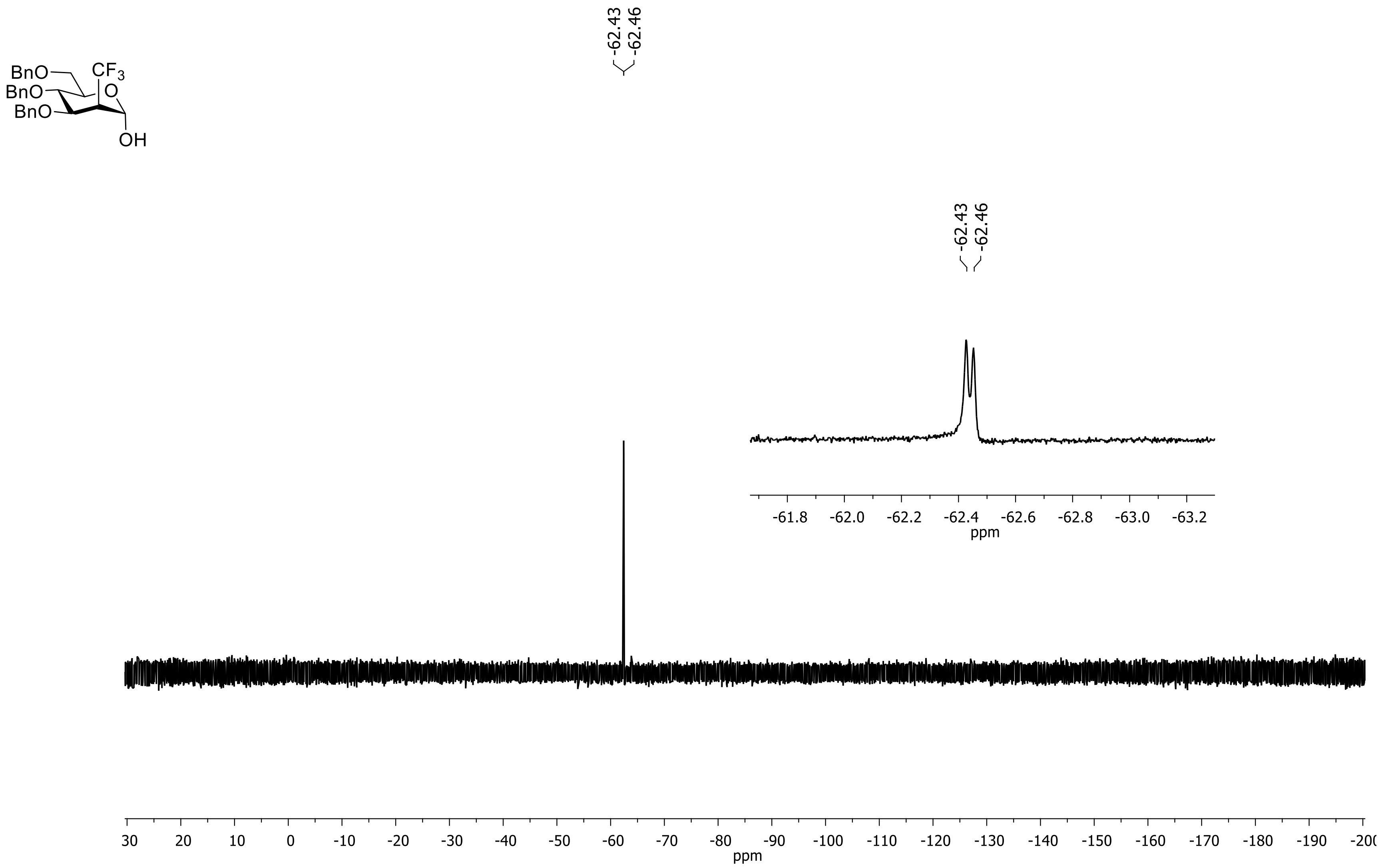
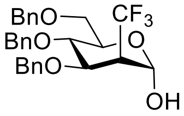


Figure S16. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **5a**



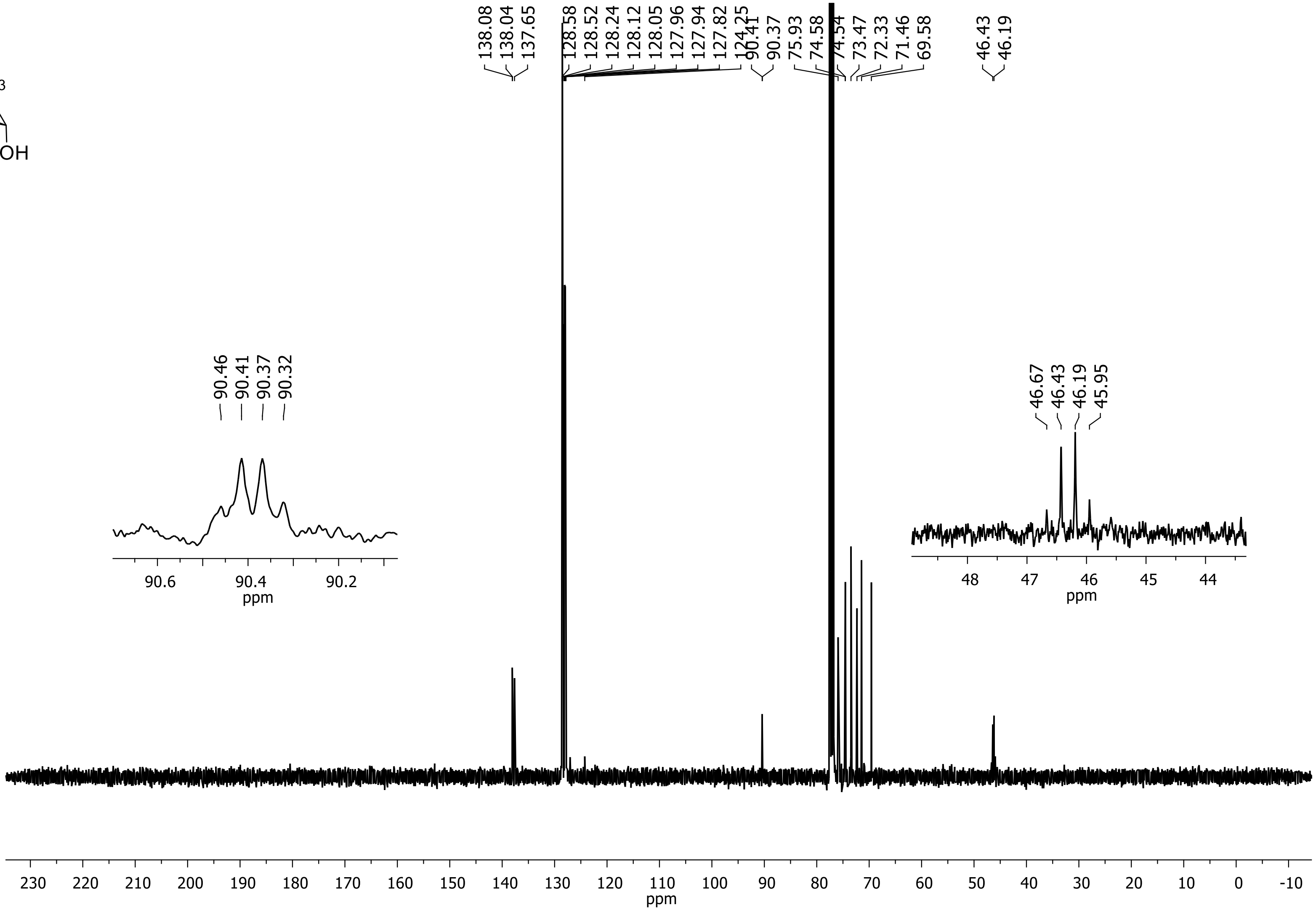


Figure S17. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **5a**

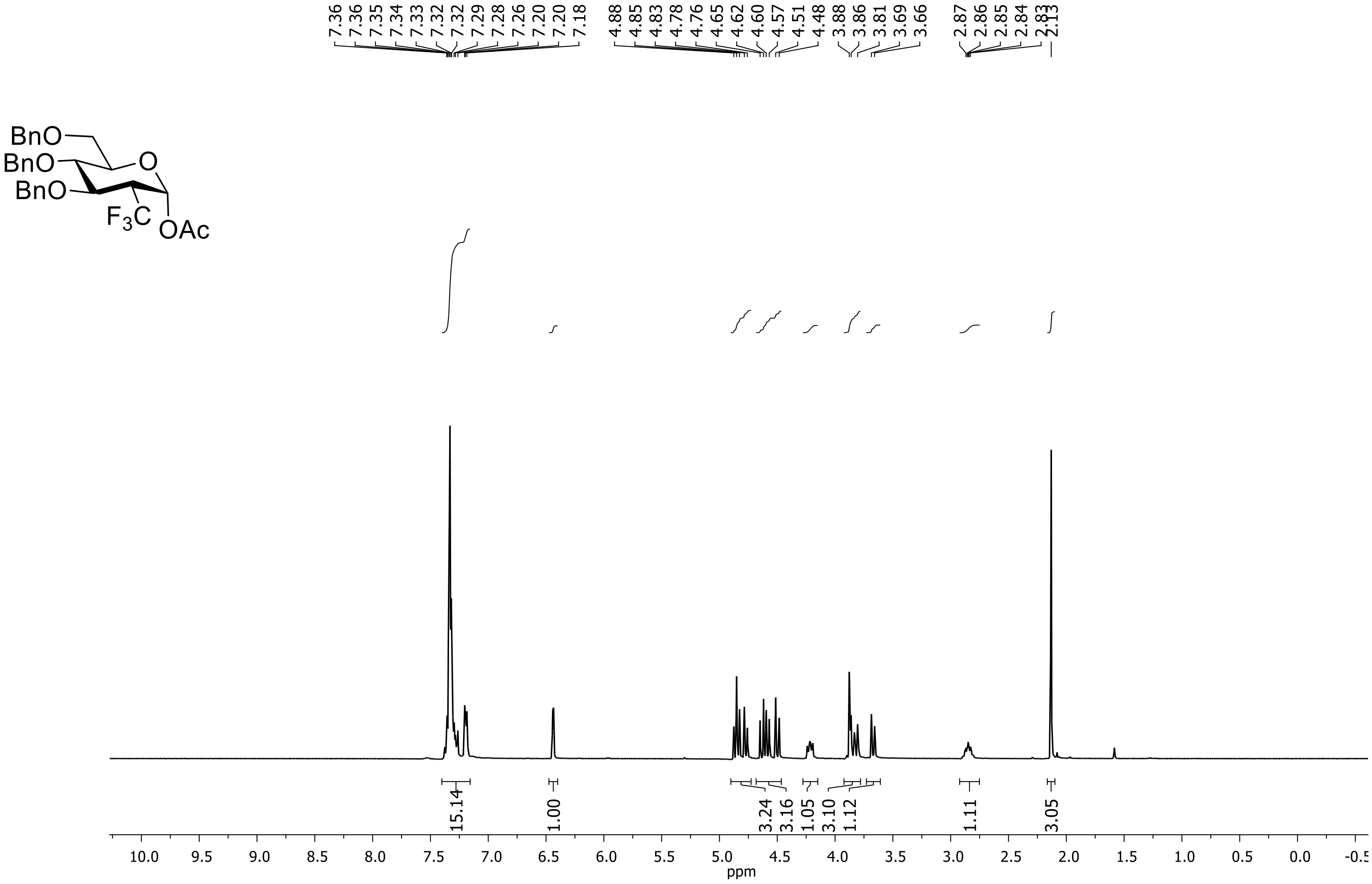


Figure S18. ^{1}H NMR ($CDCl_3$, 400 MHz) of **4b**

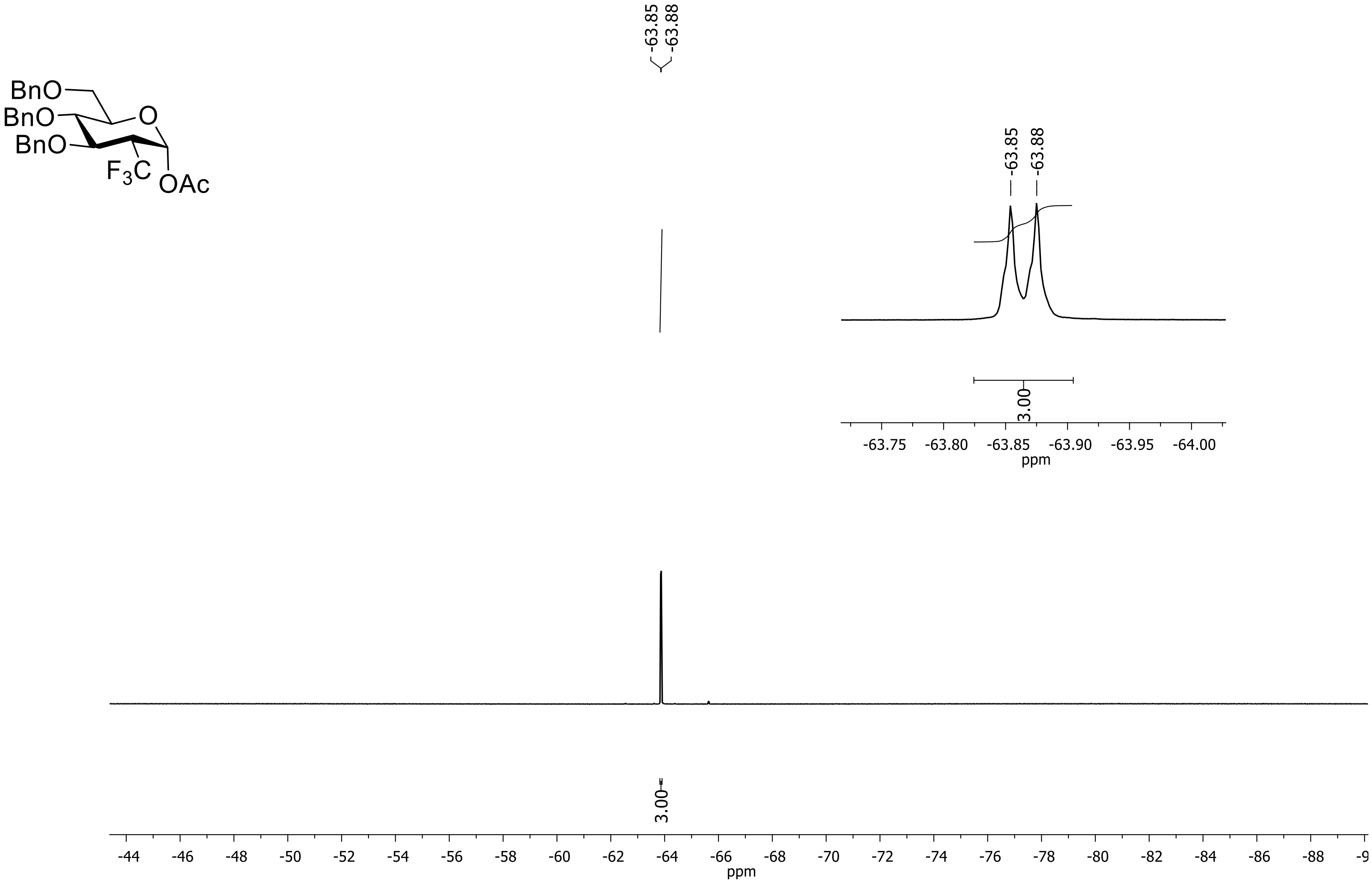


Figure S19. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **4b**

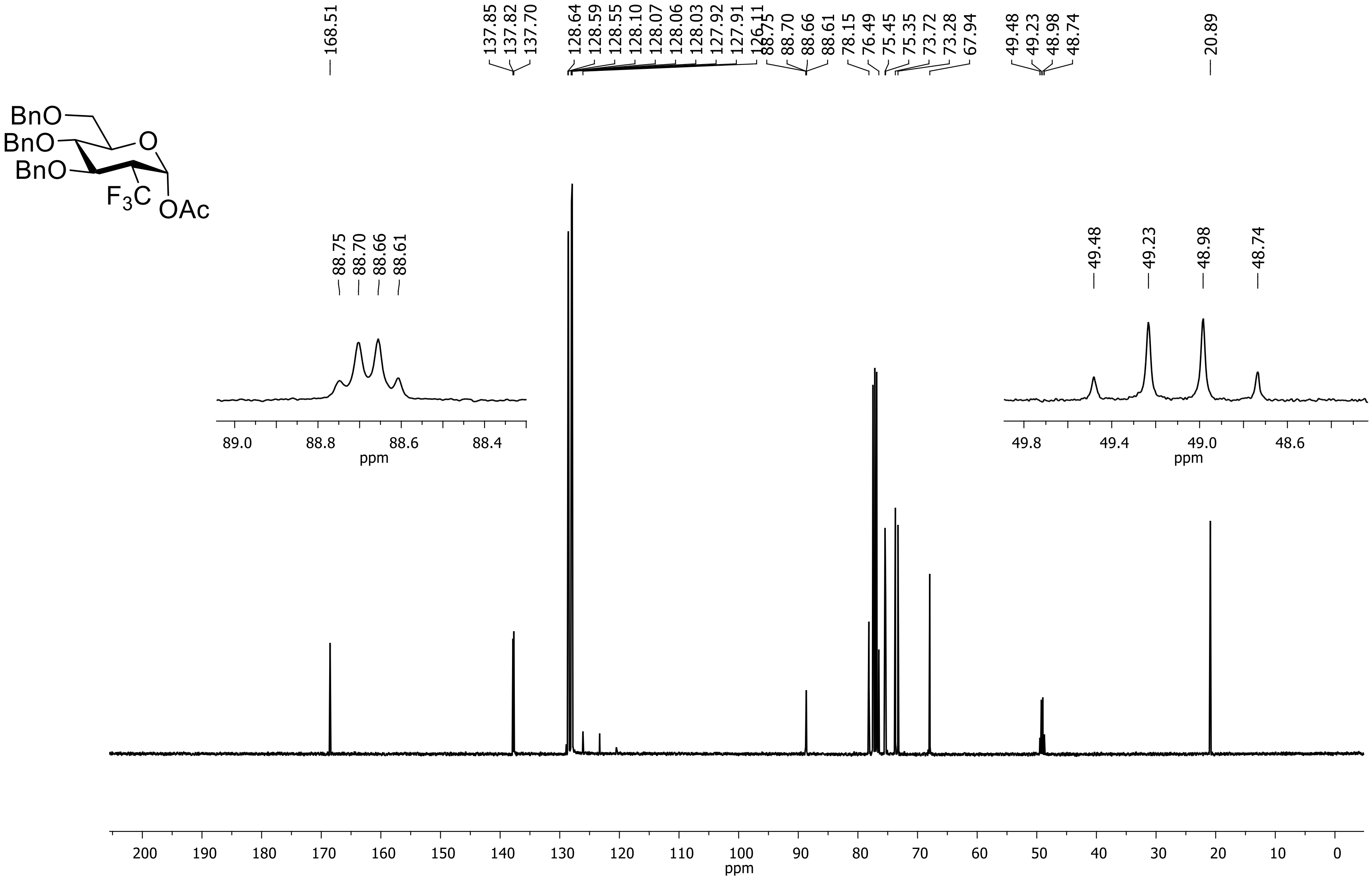


Figure S20. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **4b**

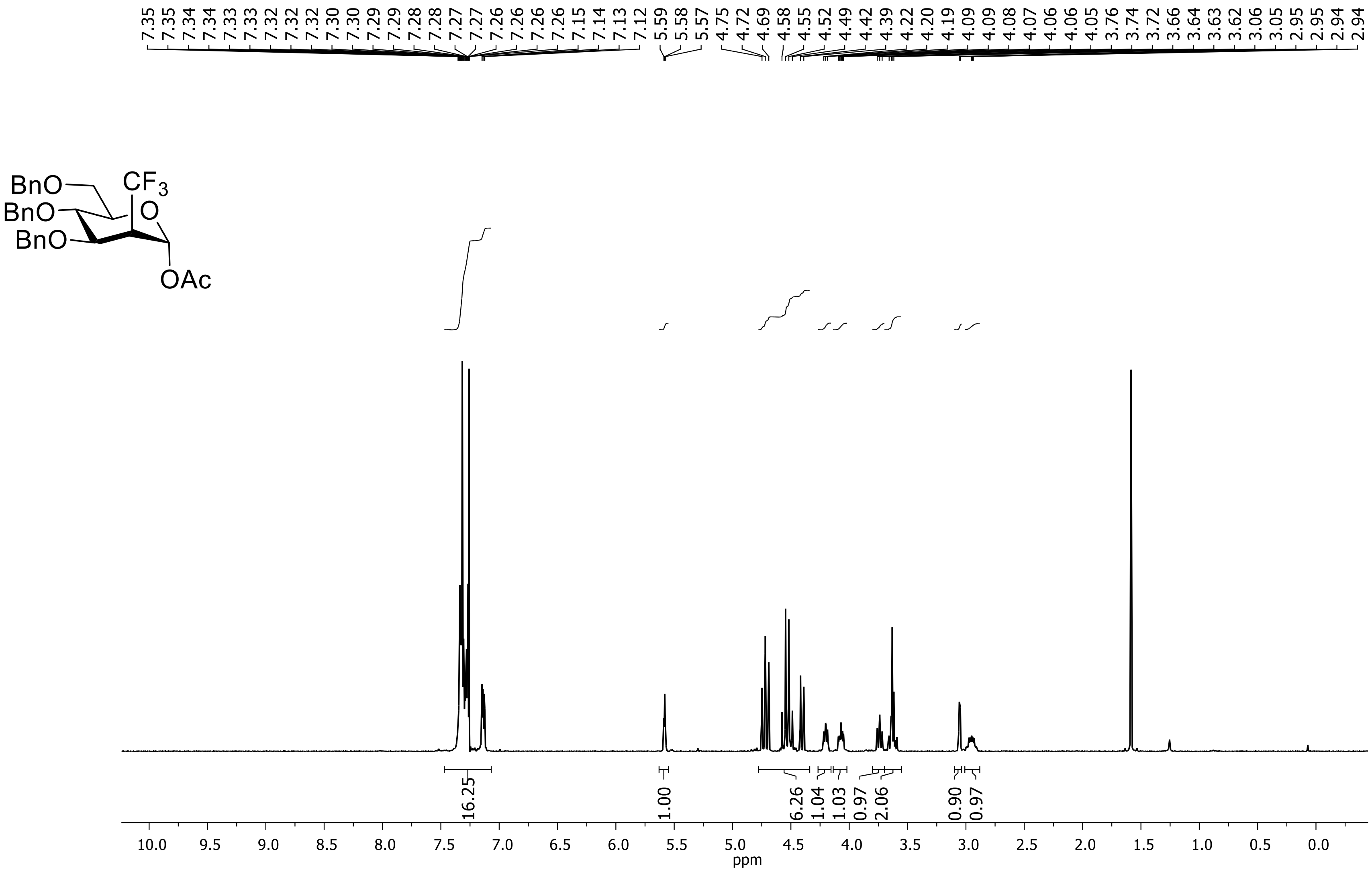


Figure S21. ^{1}H NMR ($CDCl_3$, 400 MHz) of **5b**

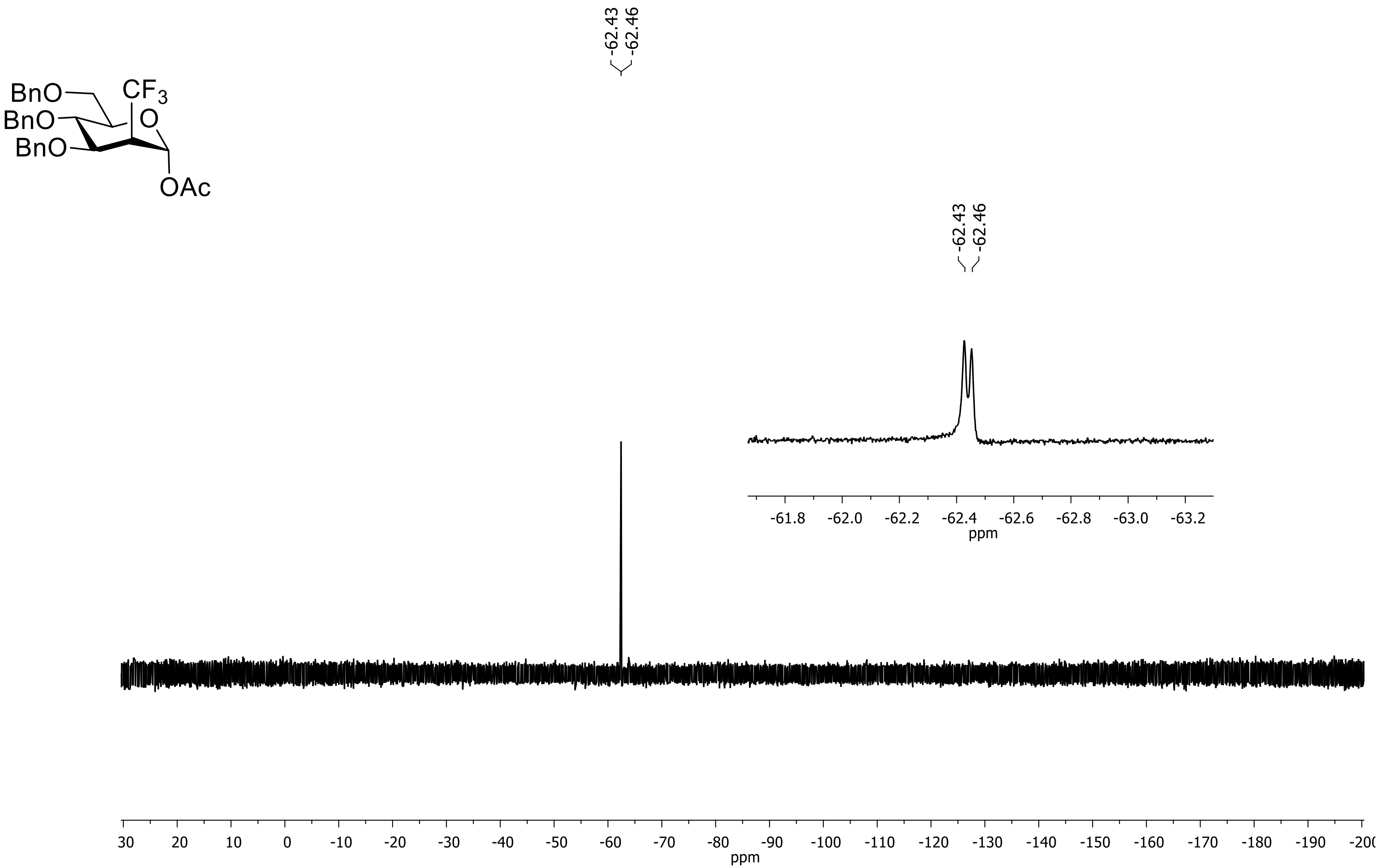


Figure S22. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **5b**

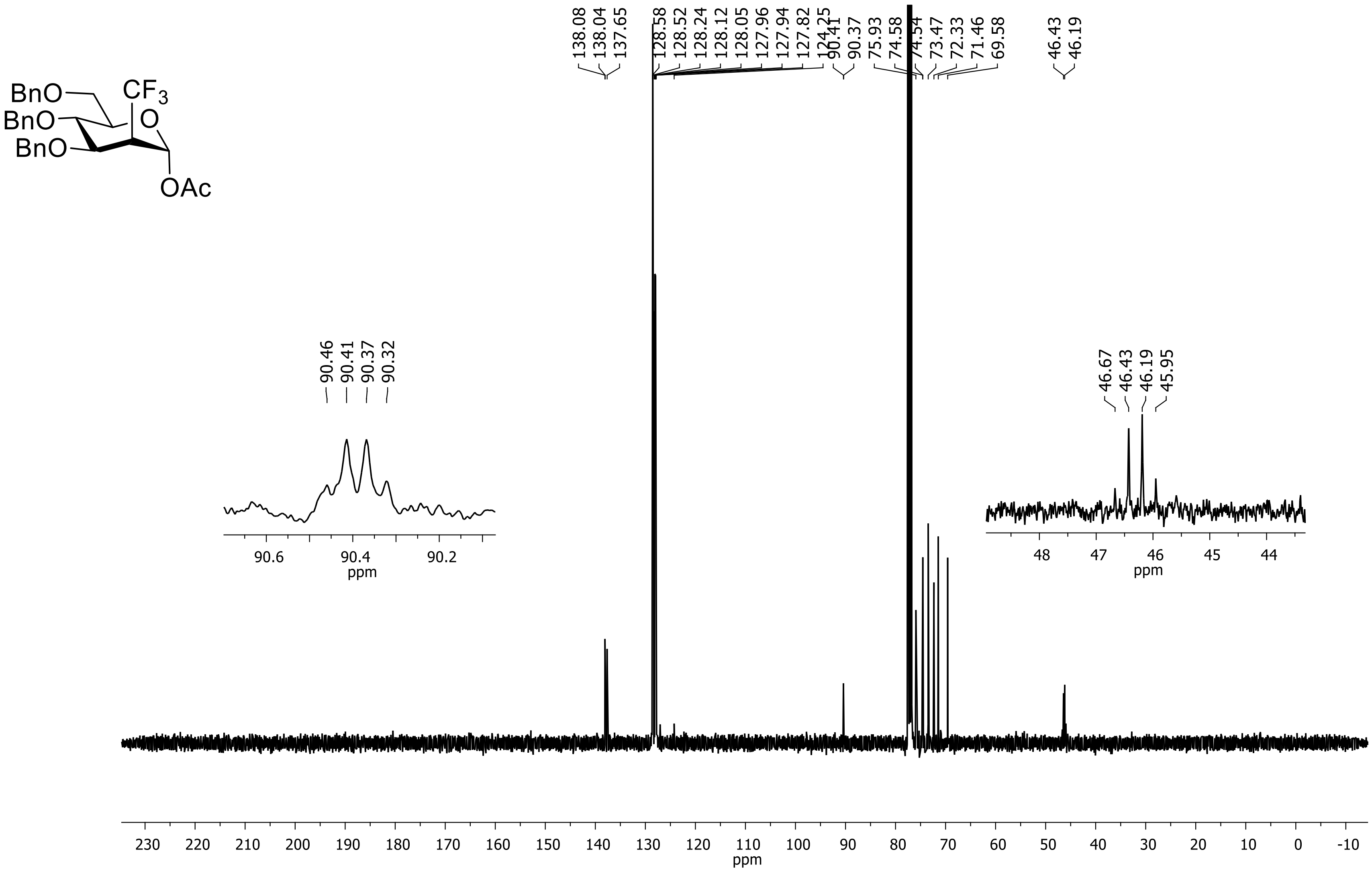
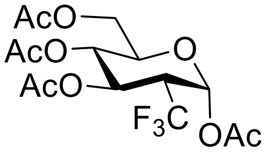


Figure S23. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **5b**



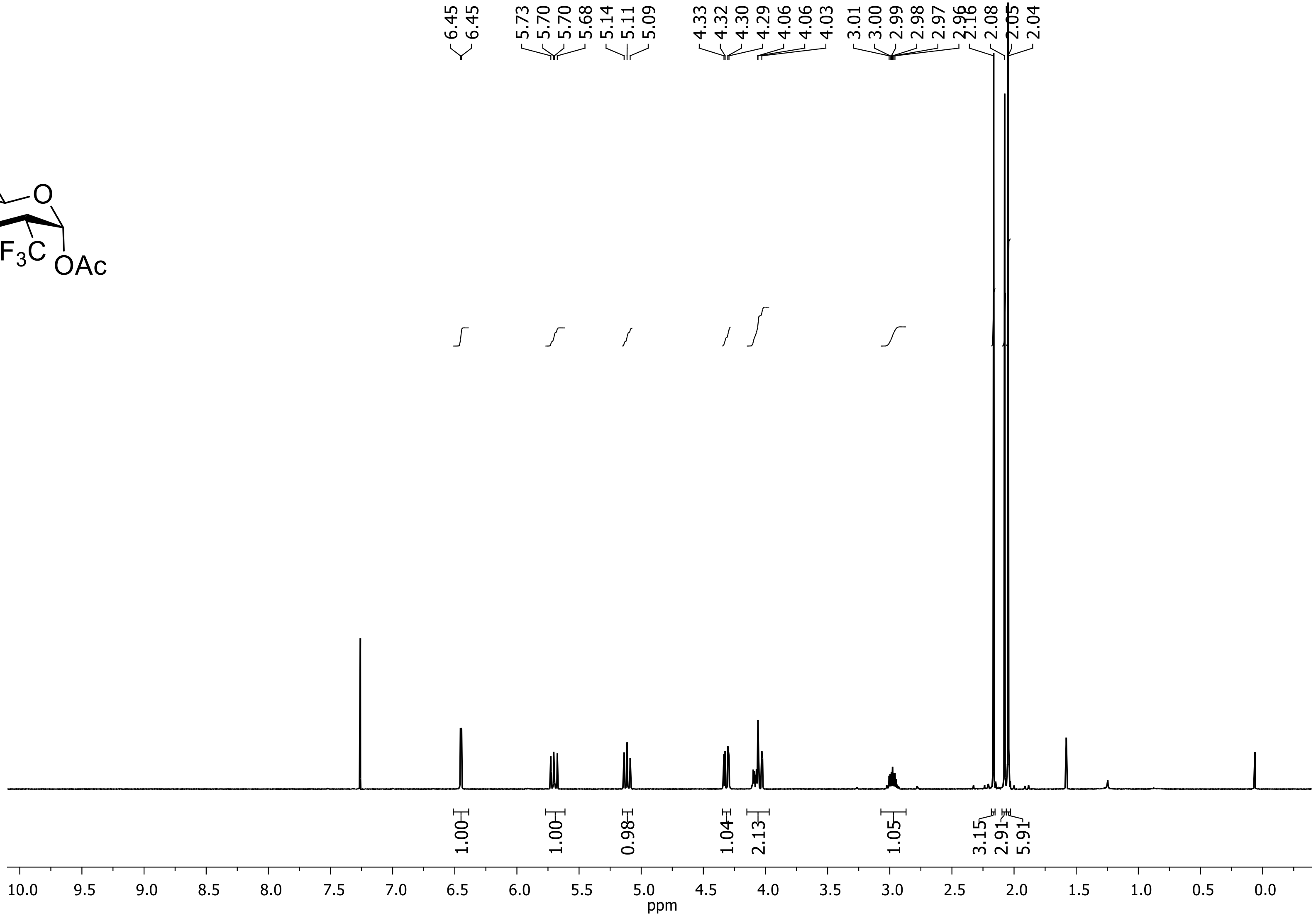


Figure S24. ^{1}H NMR (CDCl$_3$, 400 MHz) of **4c**

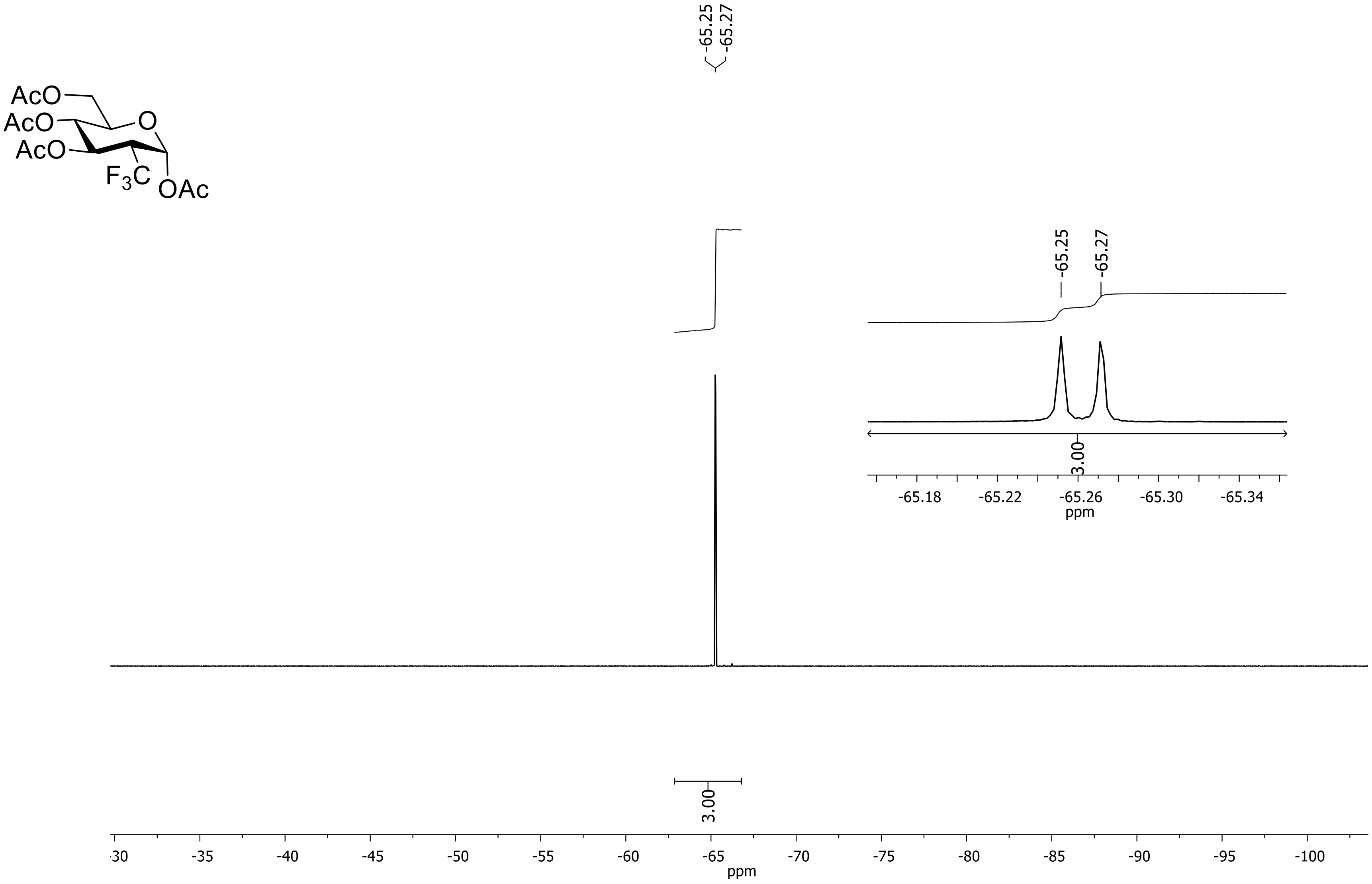


Figure S25. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **4c**

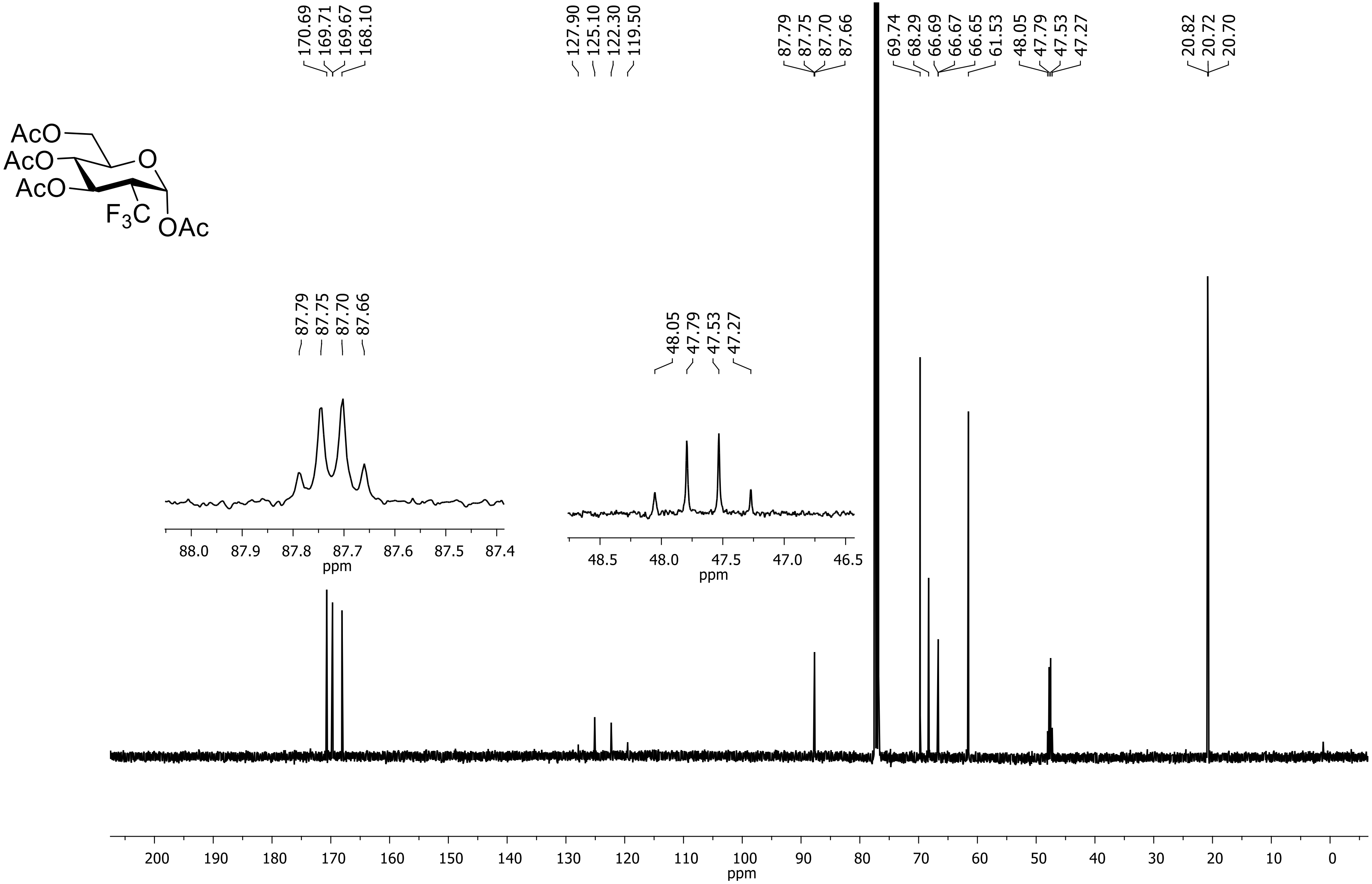


Figure S26. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **4c**

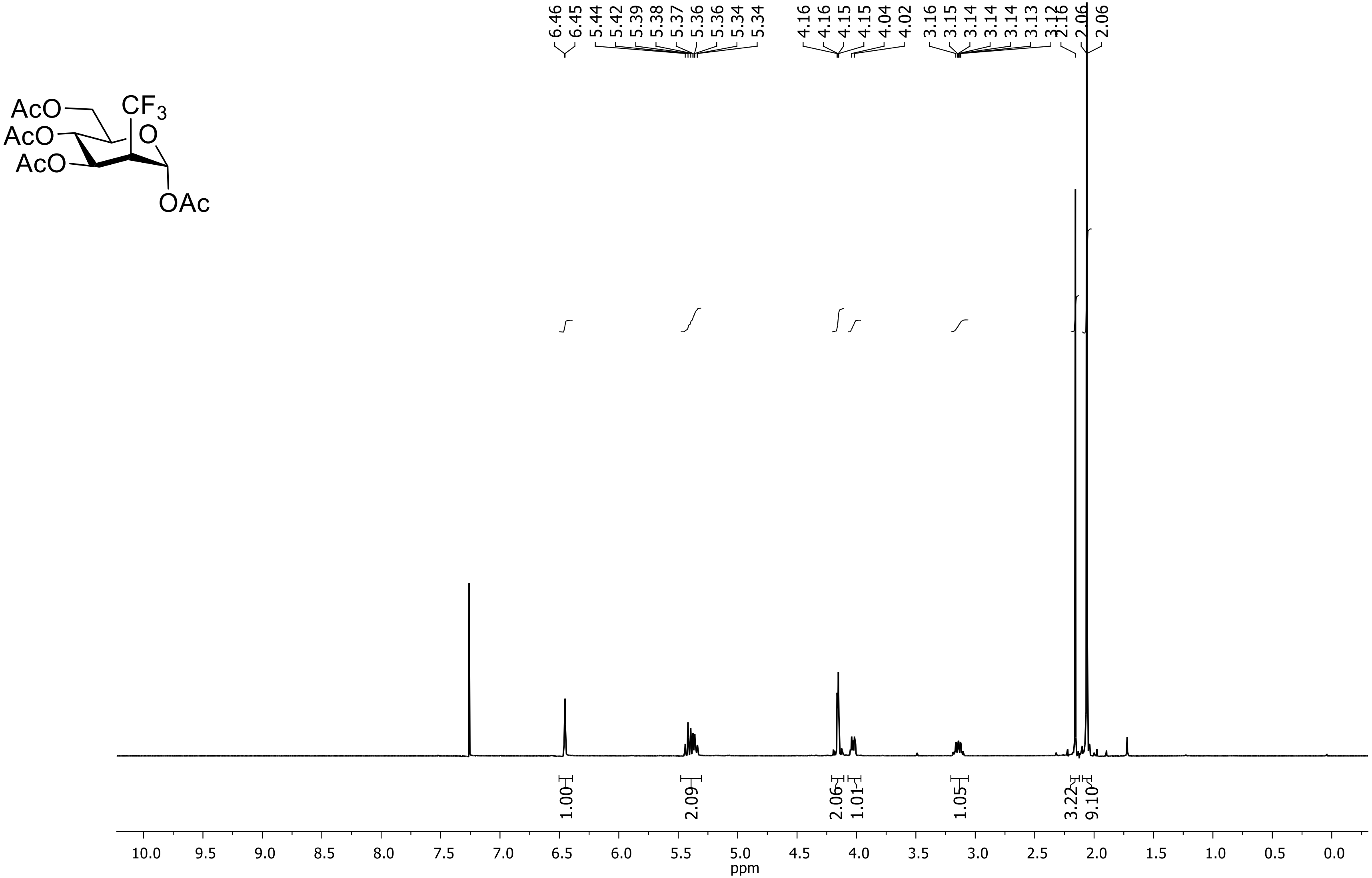


Figure S27. ^{1}H NMR ($CDCl_3$, 400 MHz) of **5c**

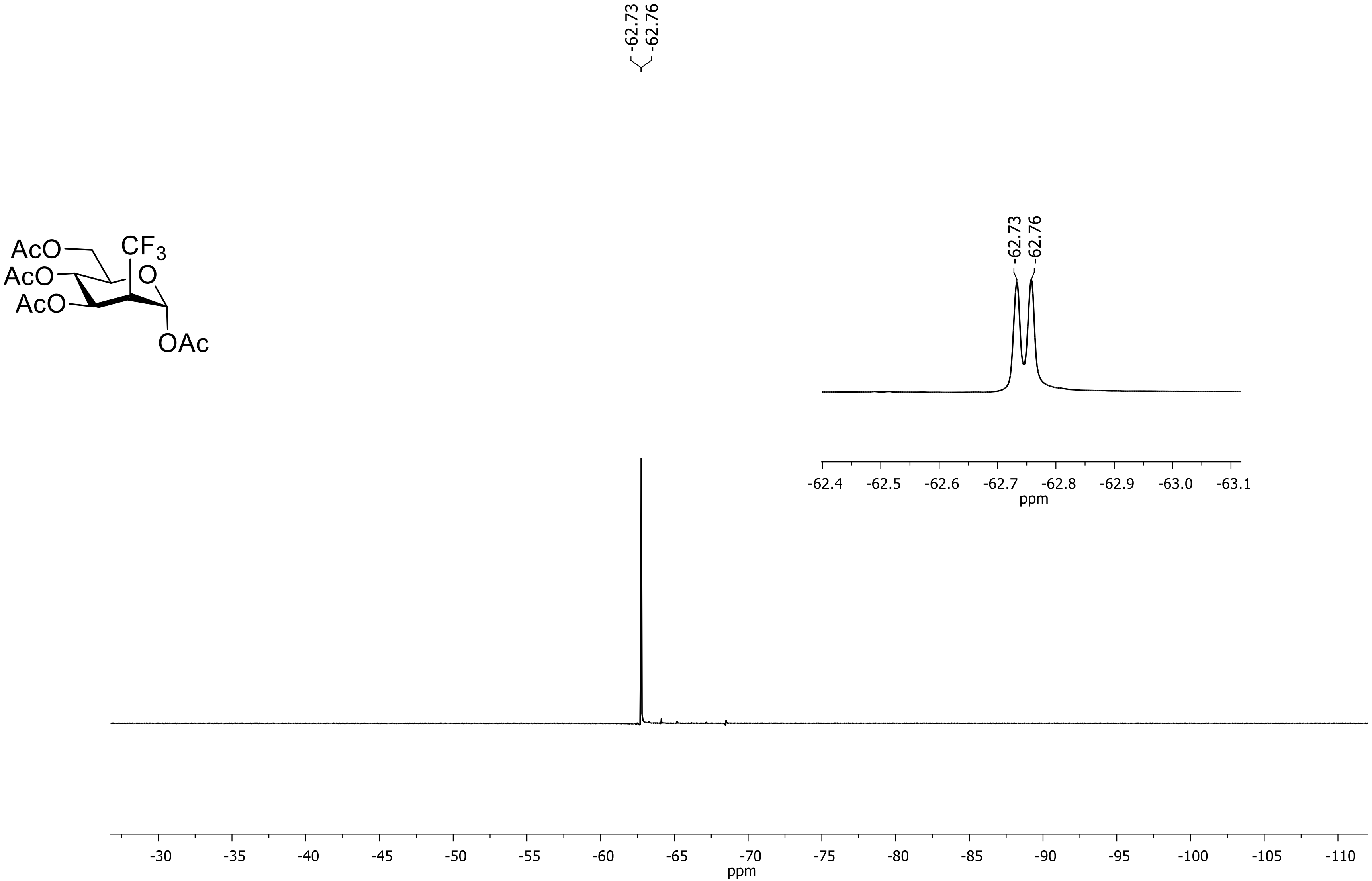


Figure S28. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **5c**

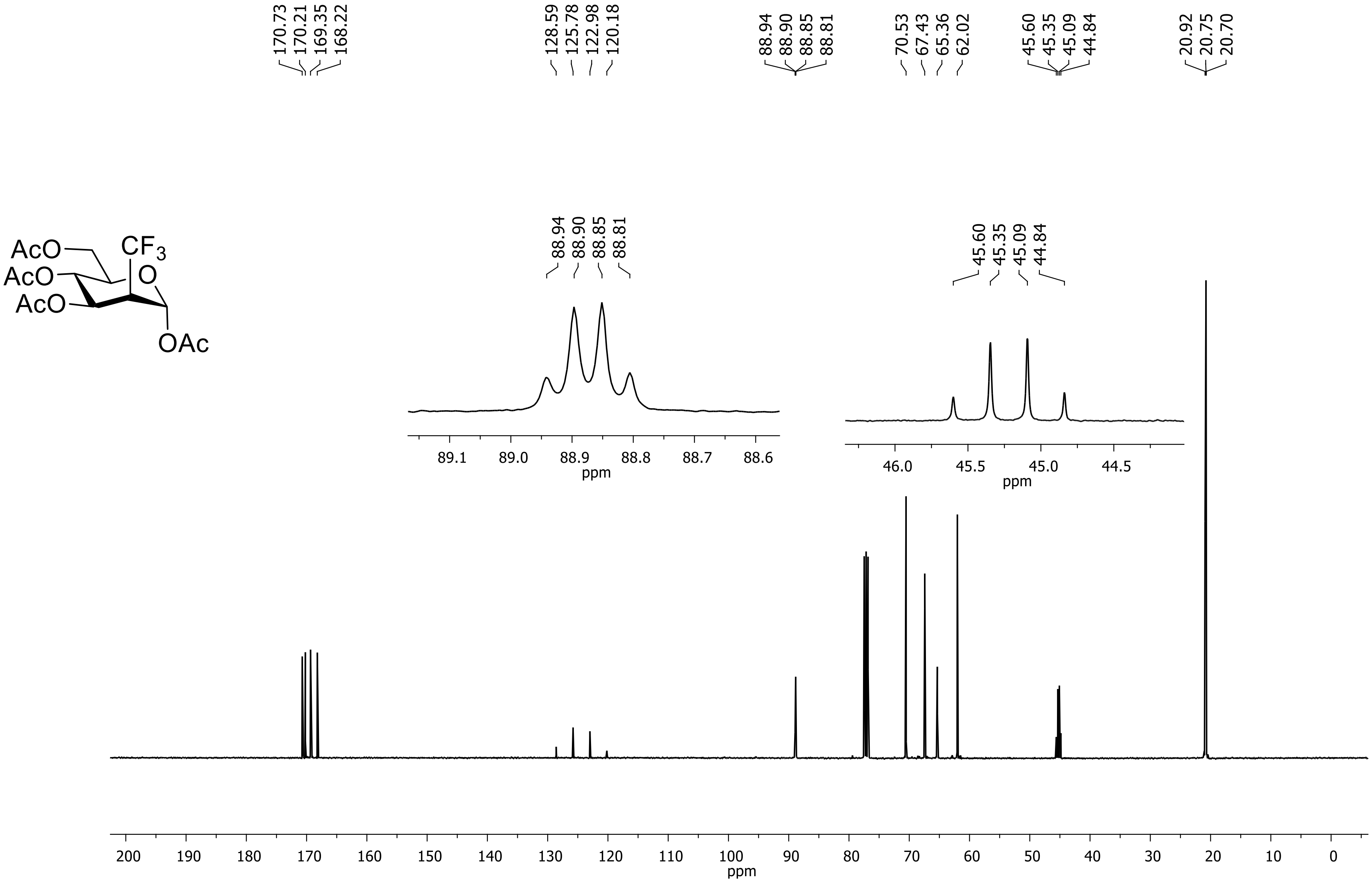


Figure S29. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **5c**

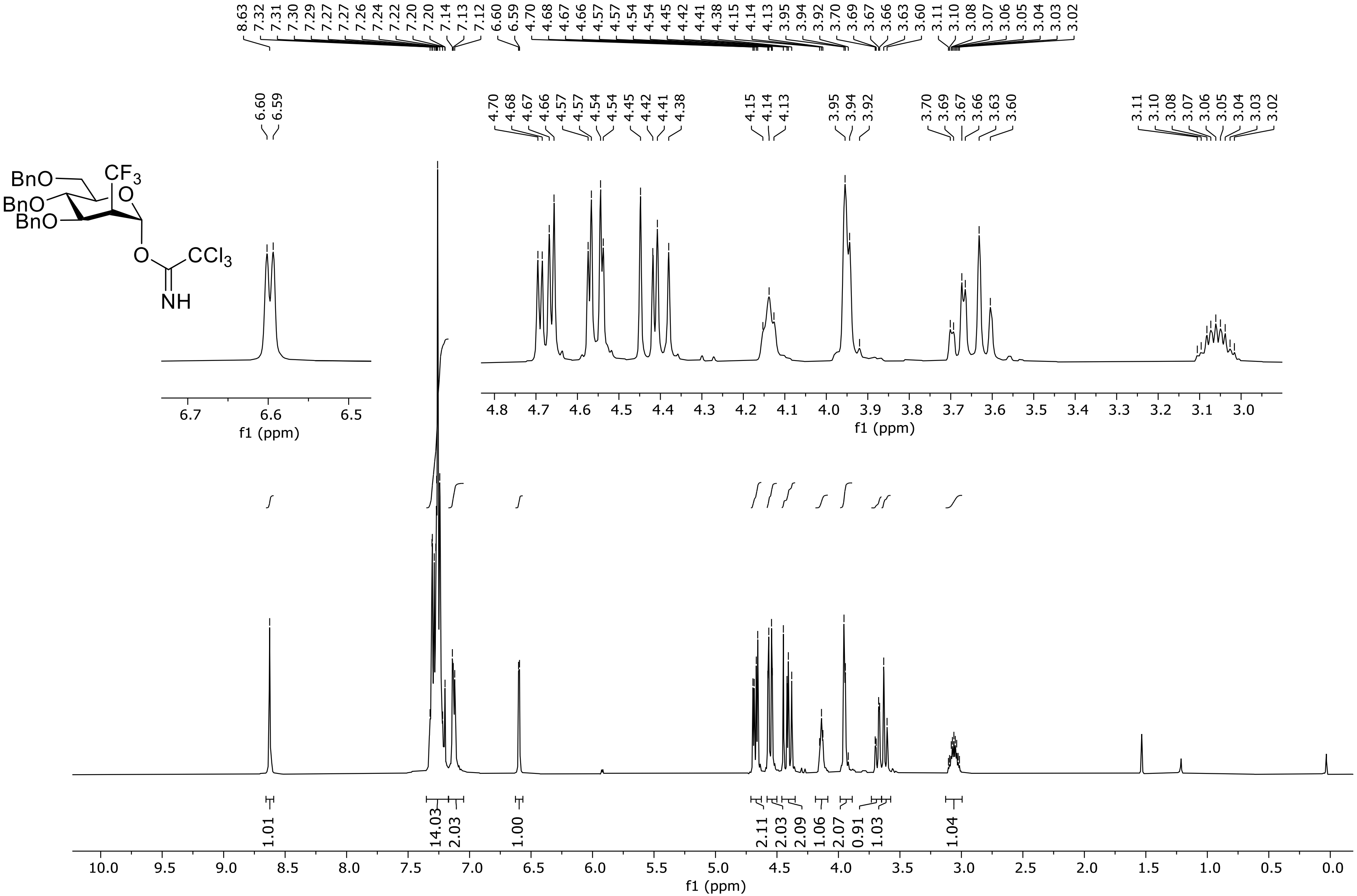


Figure S30. ^{1}H NMR (CDCl$_3$, 400 MHz) of **5a-OTCA**

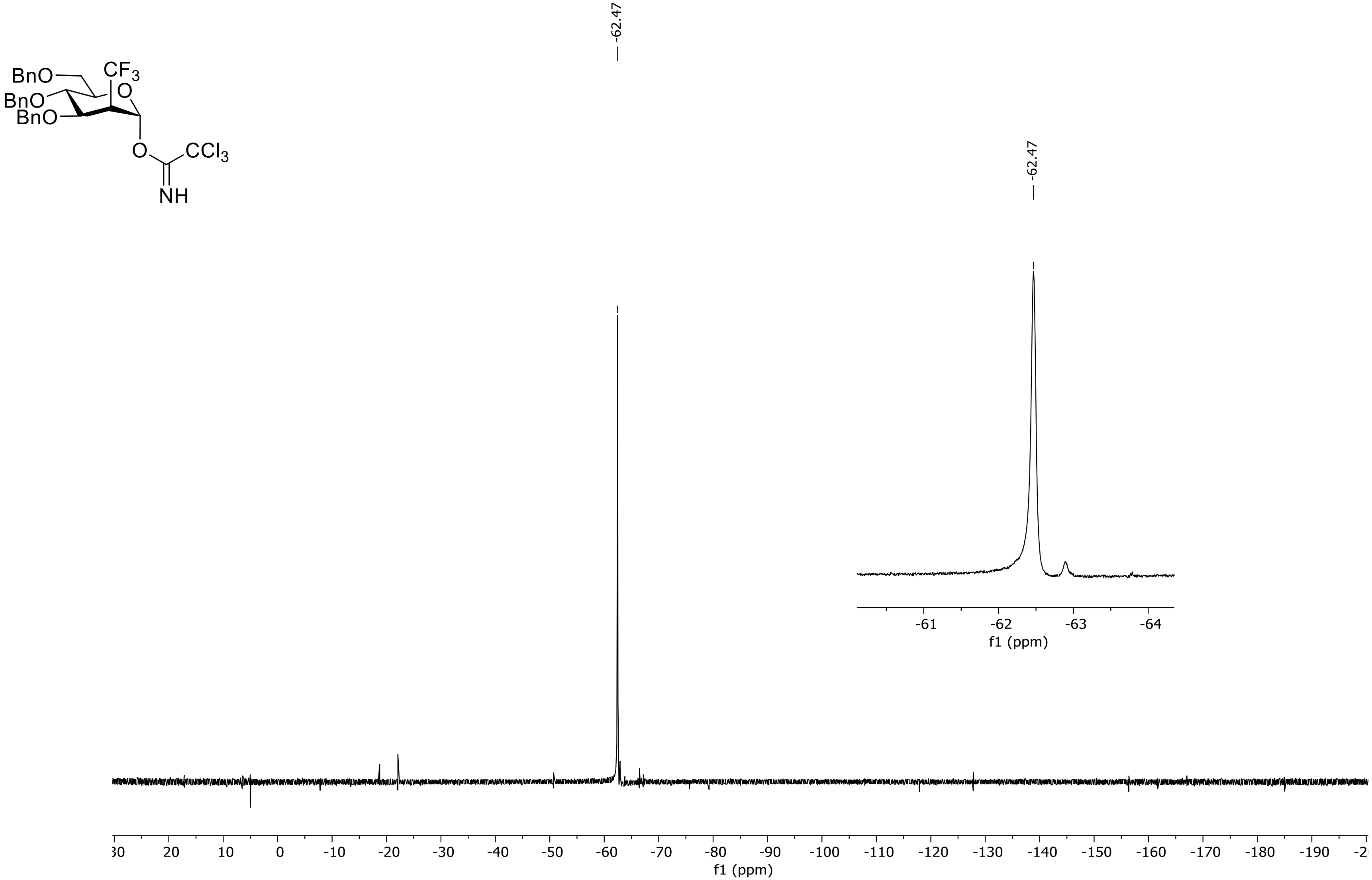


Figure S31. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **5a-OTCA**

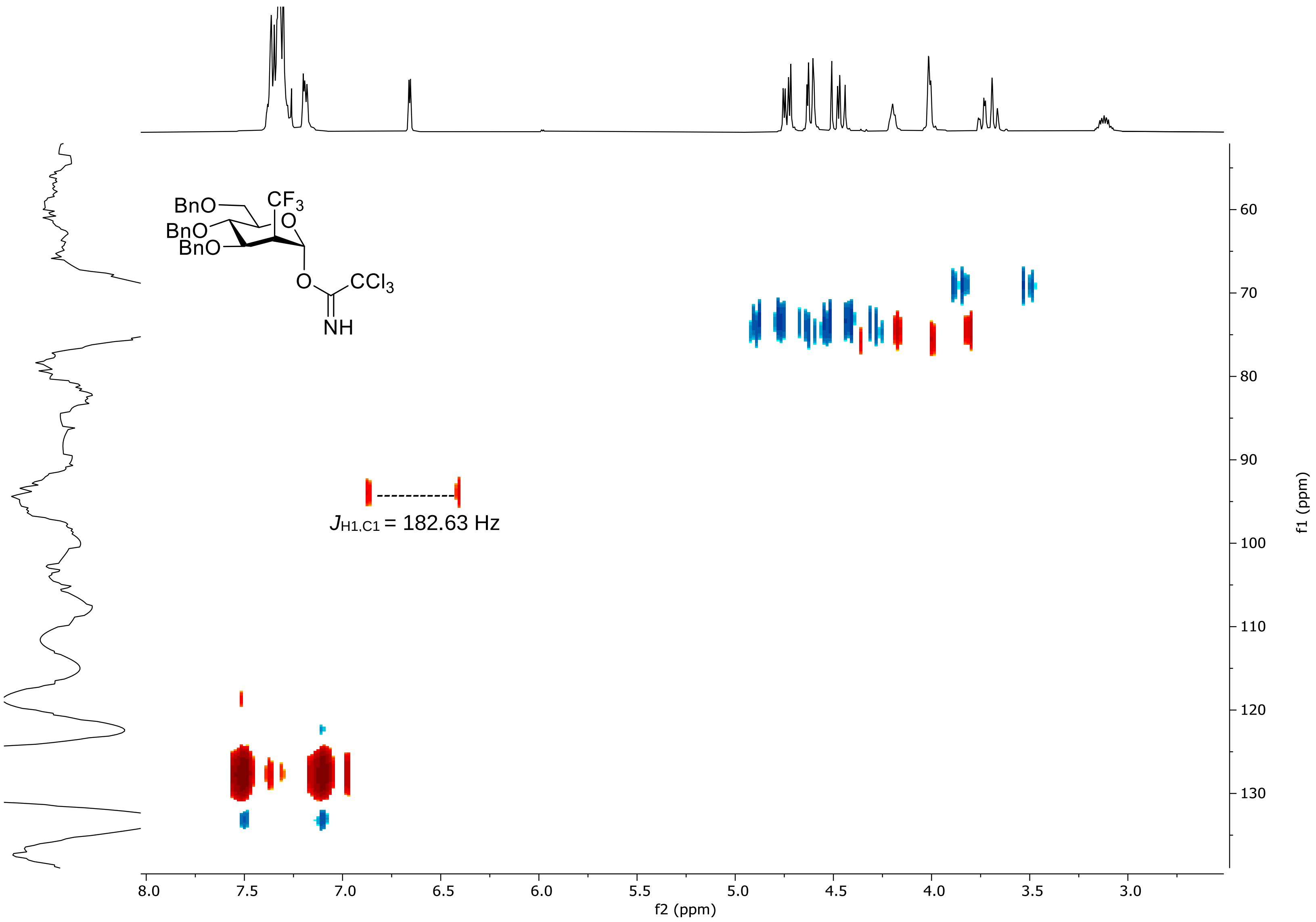


Figure S32. ^{1}H-coupled HSQC (CDCl$_3$, 400 MHz) of **5a-OTCA**

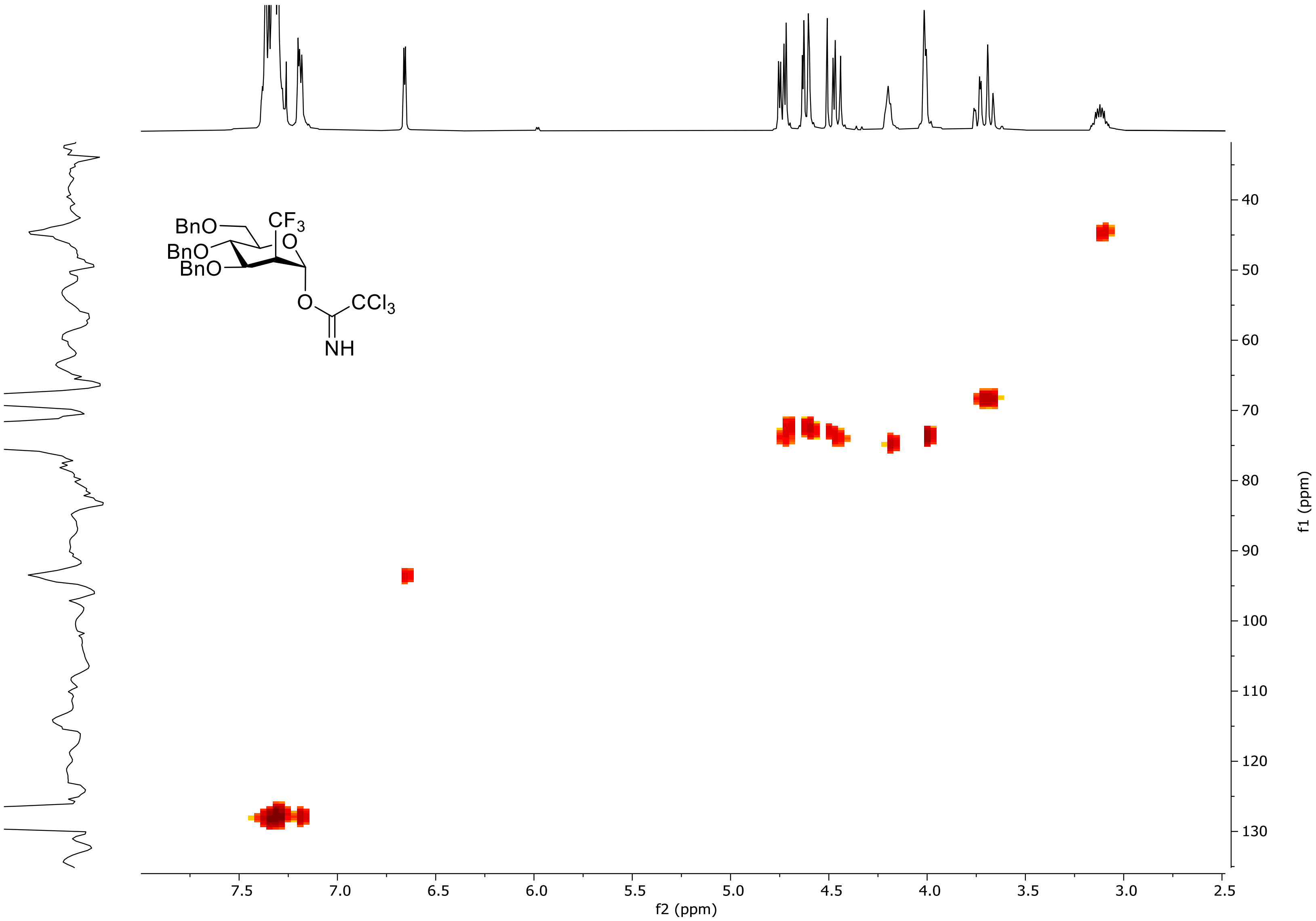


Figure S33. ^{1}H-decoupled HSQC (CDCl$_3$, 400 MHz) of **5a-OTCA**

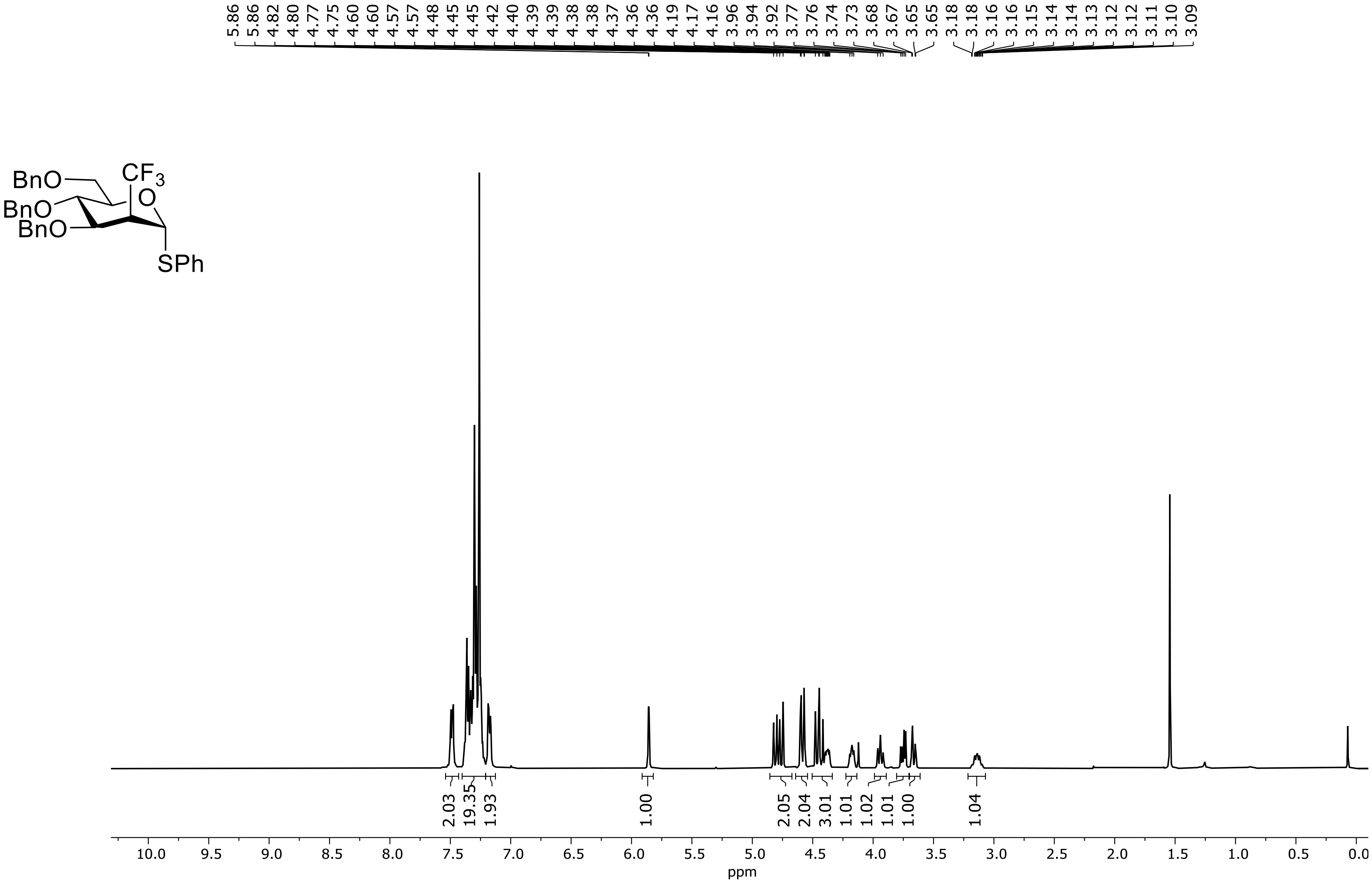


Figure S34. ^{1}H NMR ($CDCl_3$, 400 MHz) of **5b-SPh**

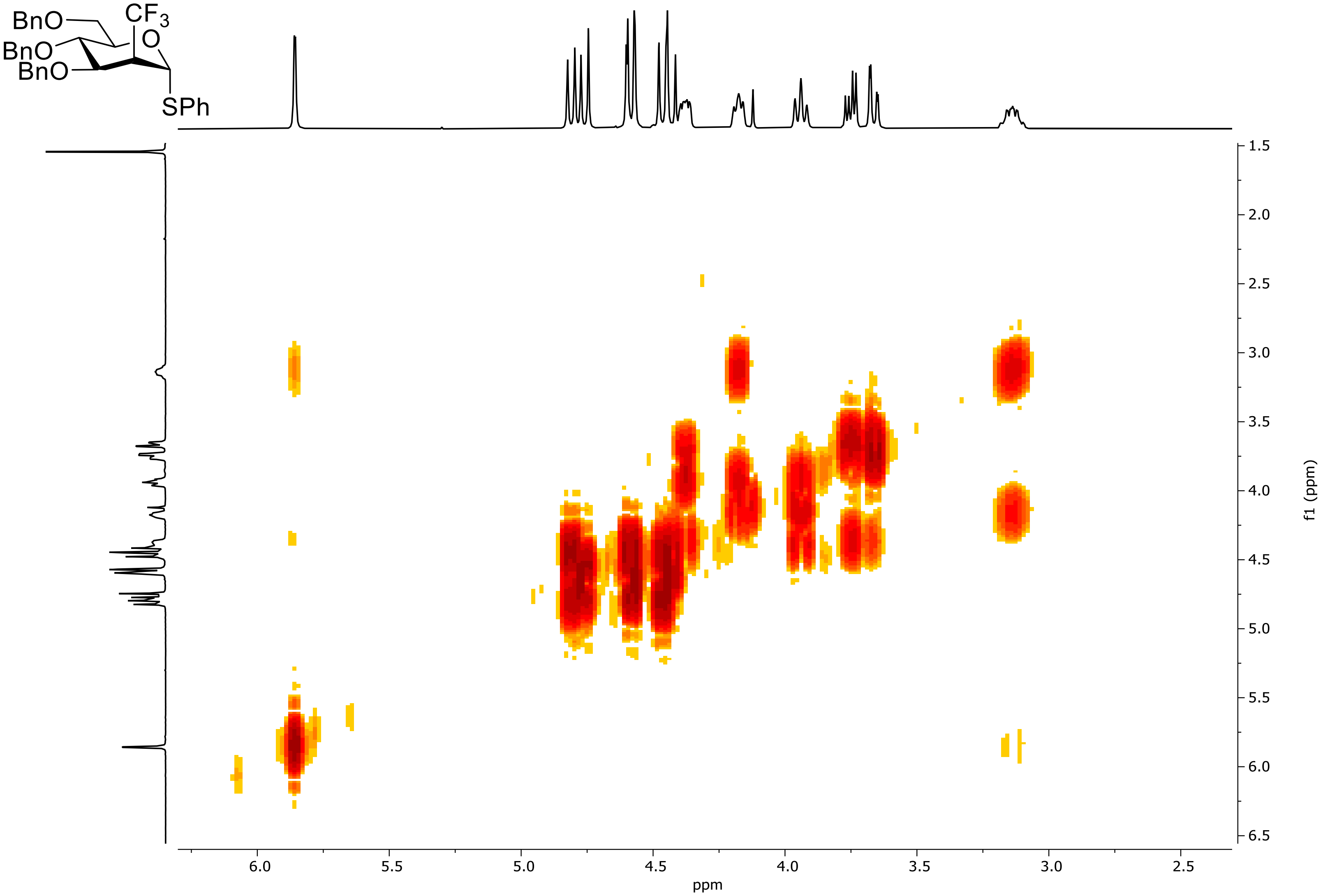
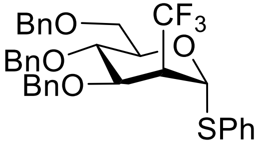


Figure S35. ^{1}H-^{1}H COSY (CDCl$_3$, 400 MHz) of **5b-SPh**



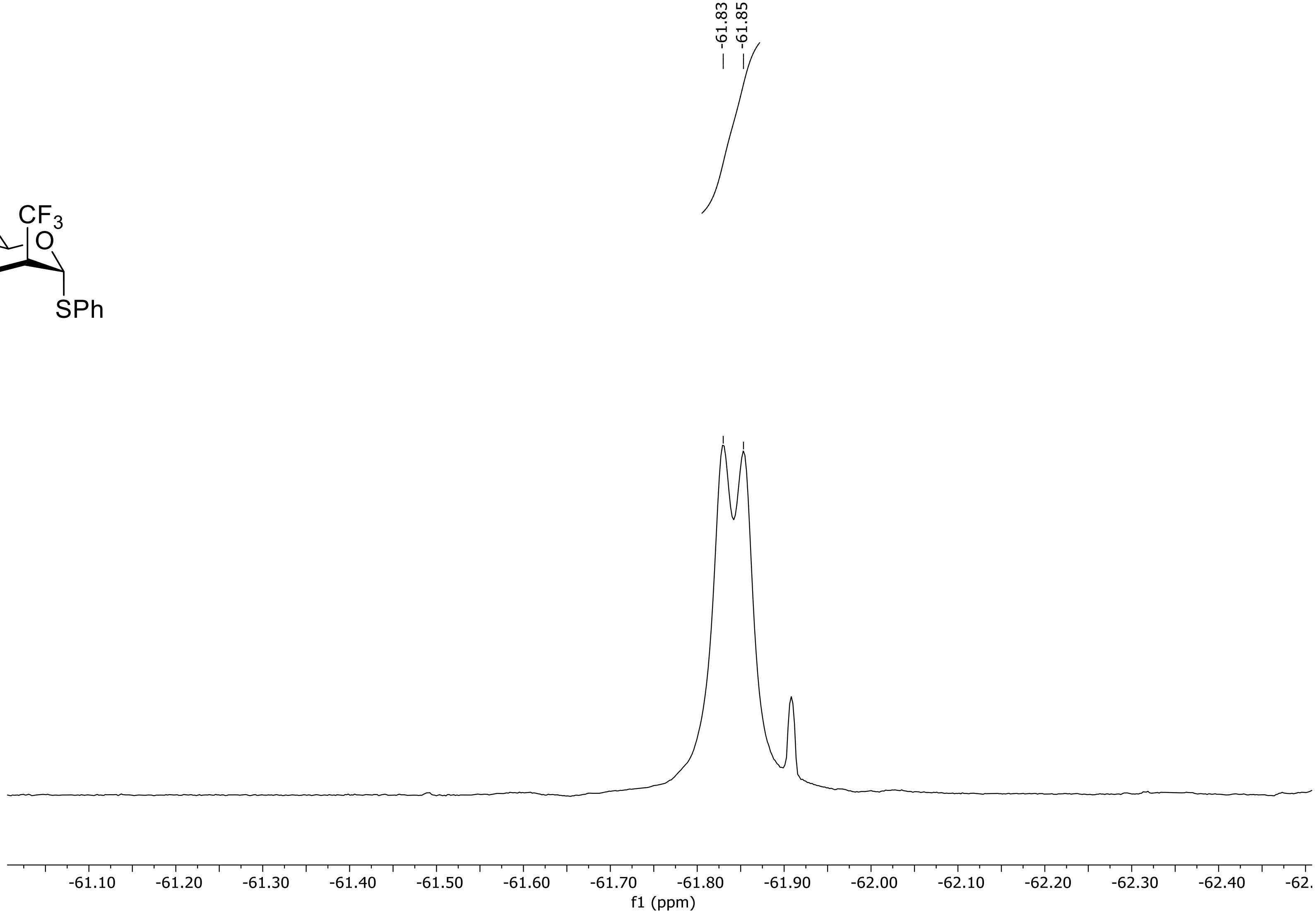


Figure S36. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **5b-SPh**

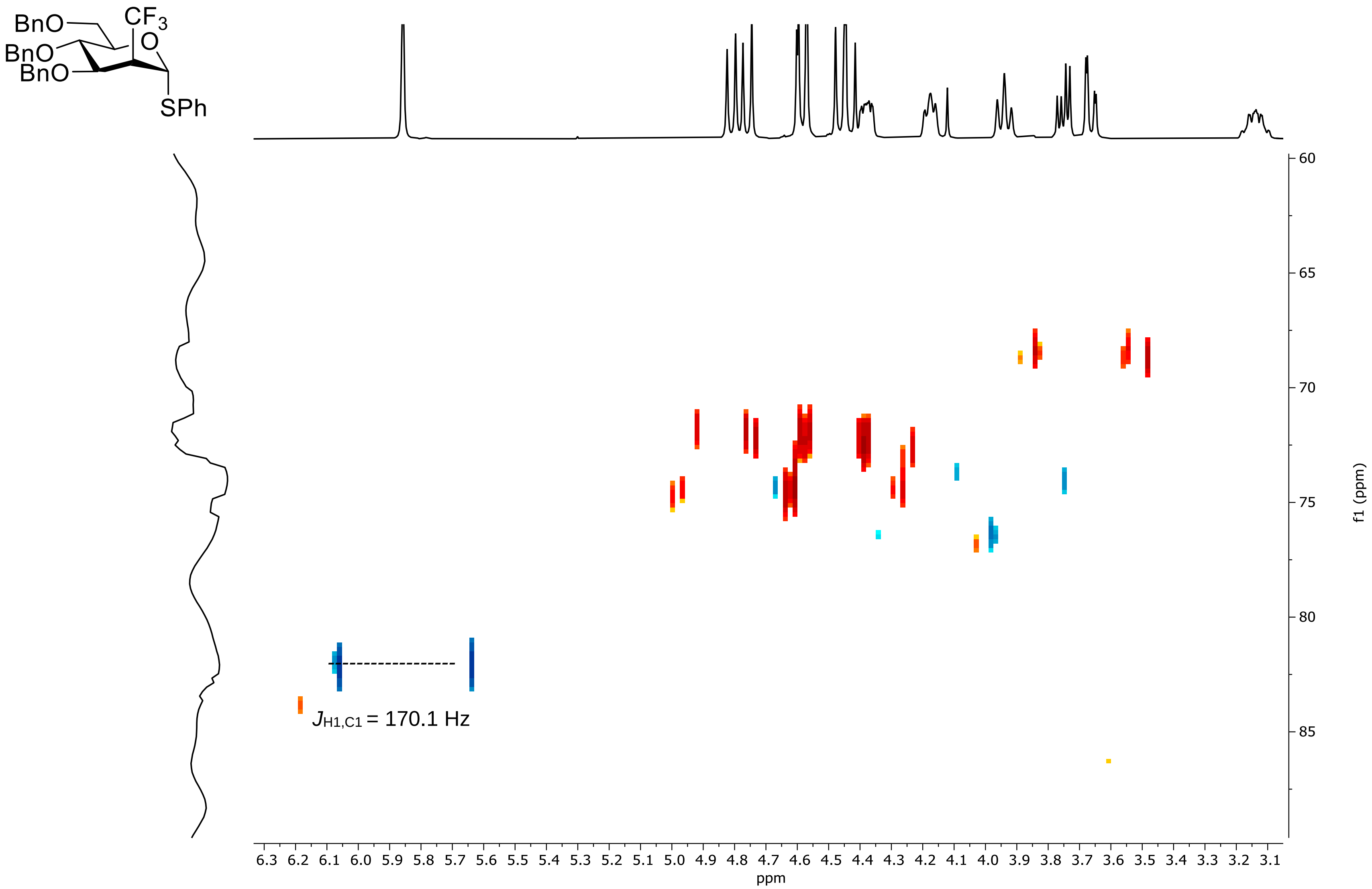


Figure S37. ^{1}H-coupled HSQC ($CDCl_3$, 400 MHz) of **5b-SPh**

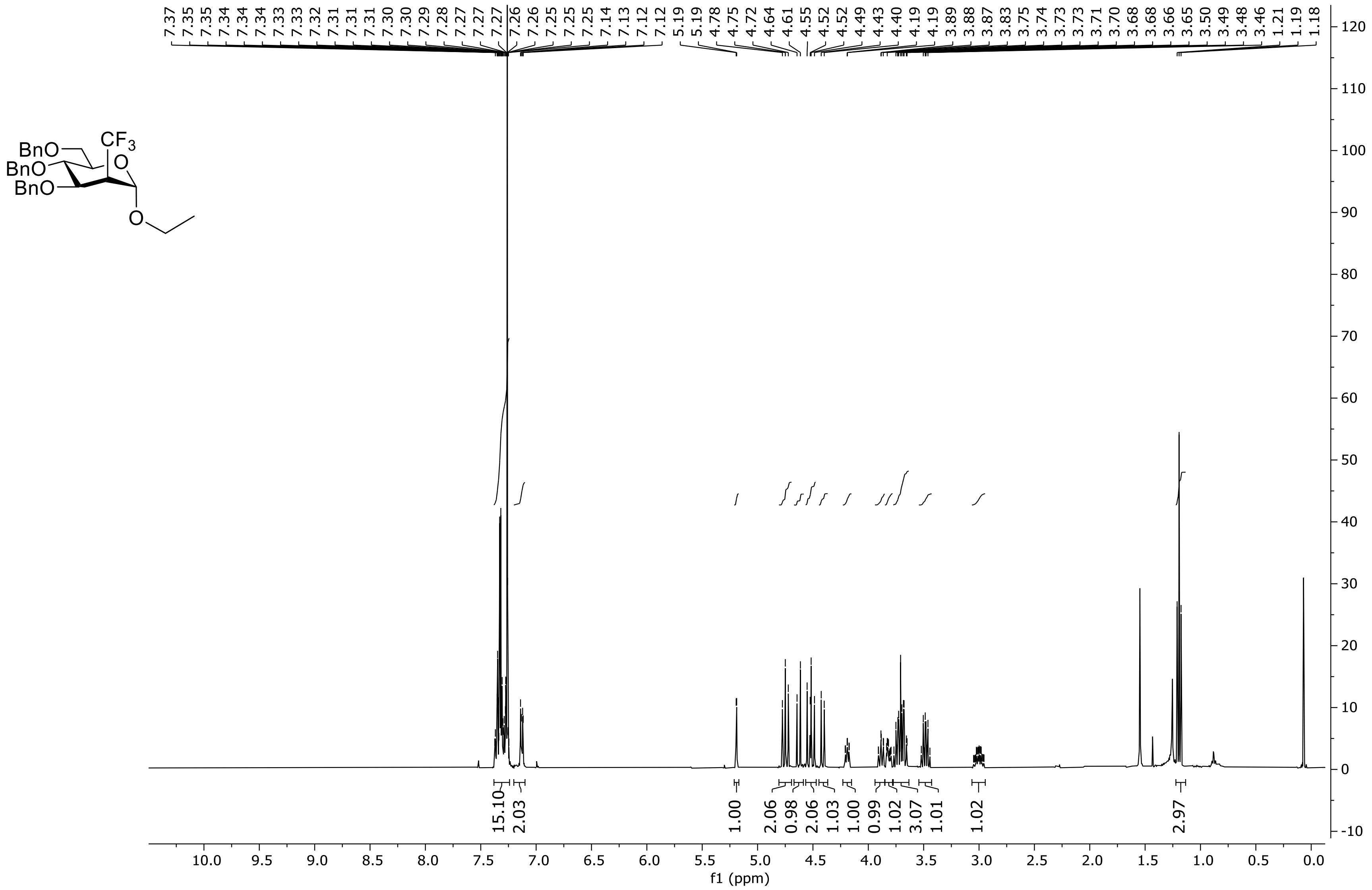


Figure S38. ^{1}H NMR (CDCl$_3$, 400 MHz) of **6aα**

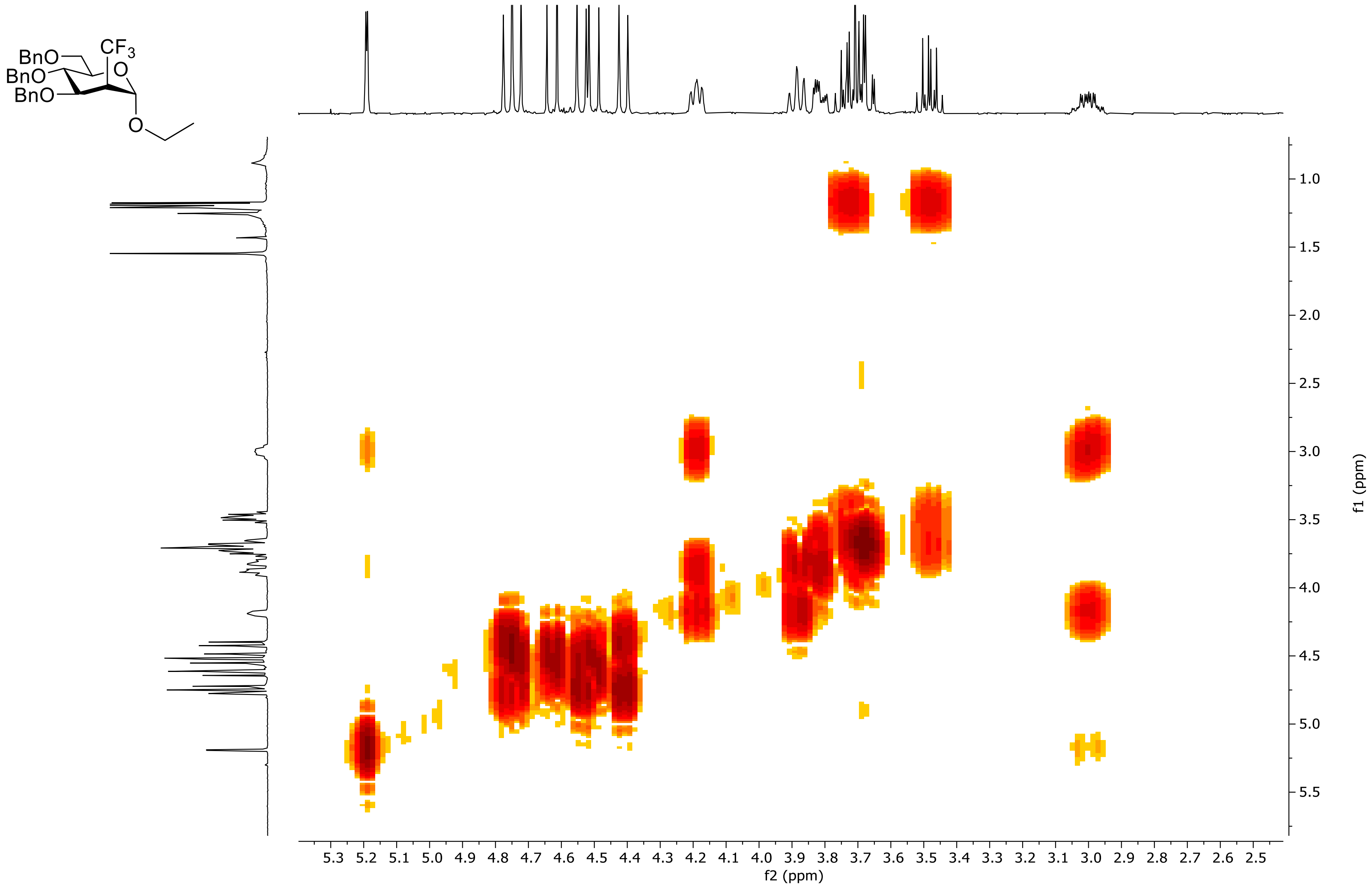


Figure S39. ^{1}H-^{1}H COSY ($CDCl_3$, 400 MHz) of **6aα**

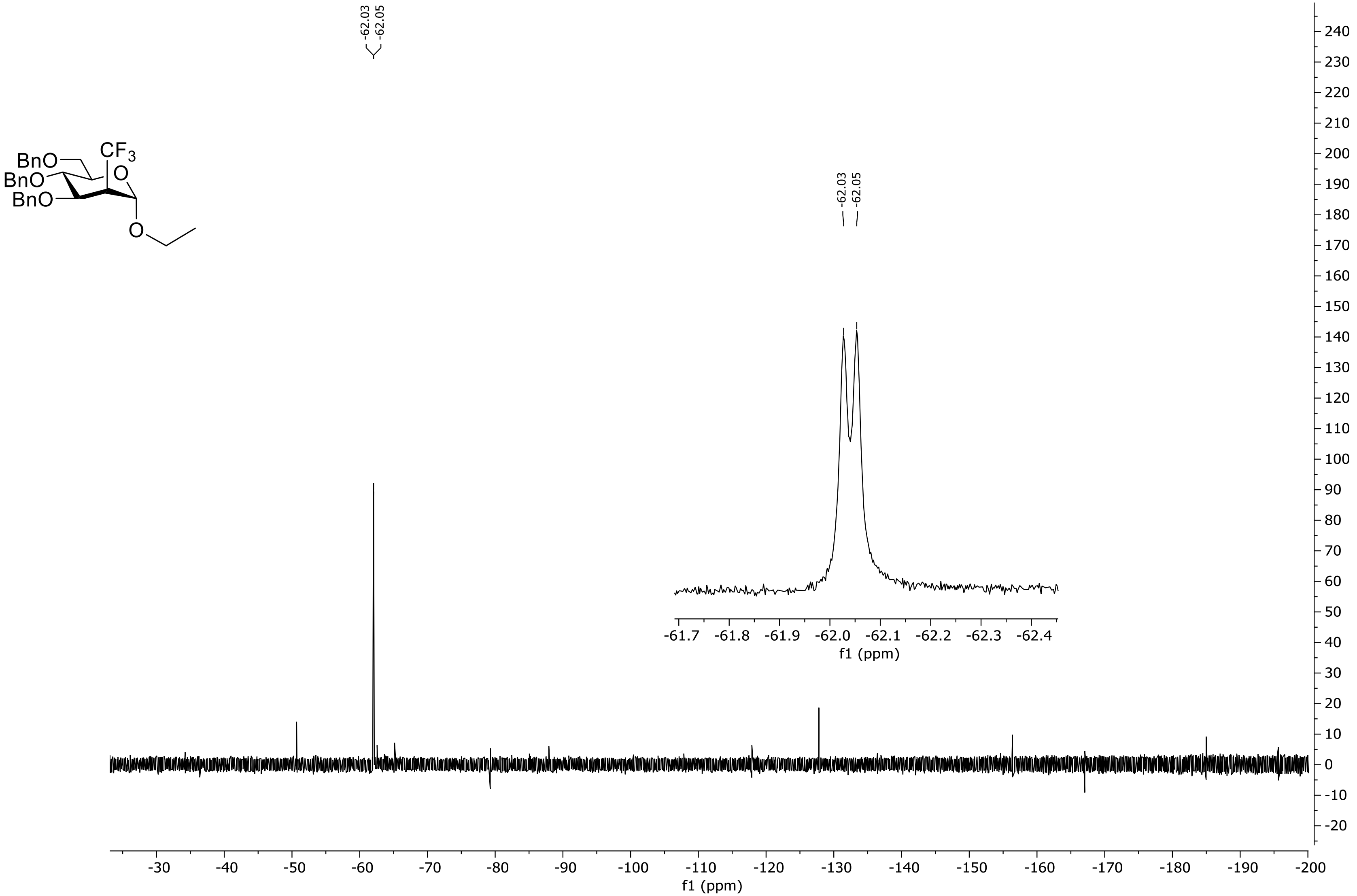


Figure S40. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **6aα**

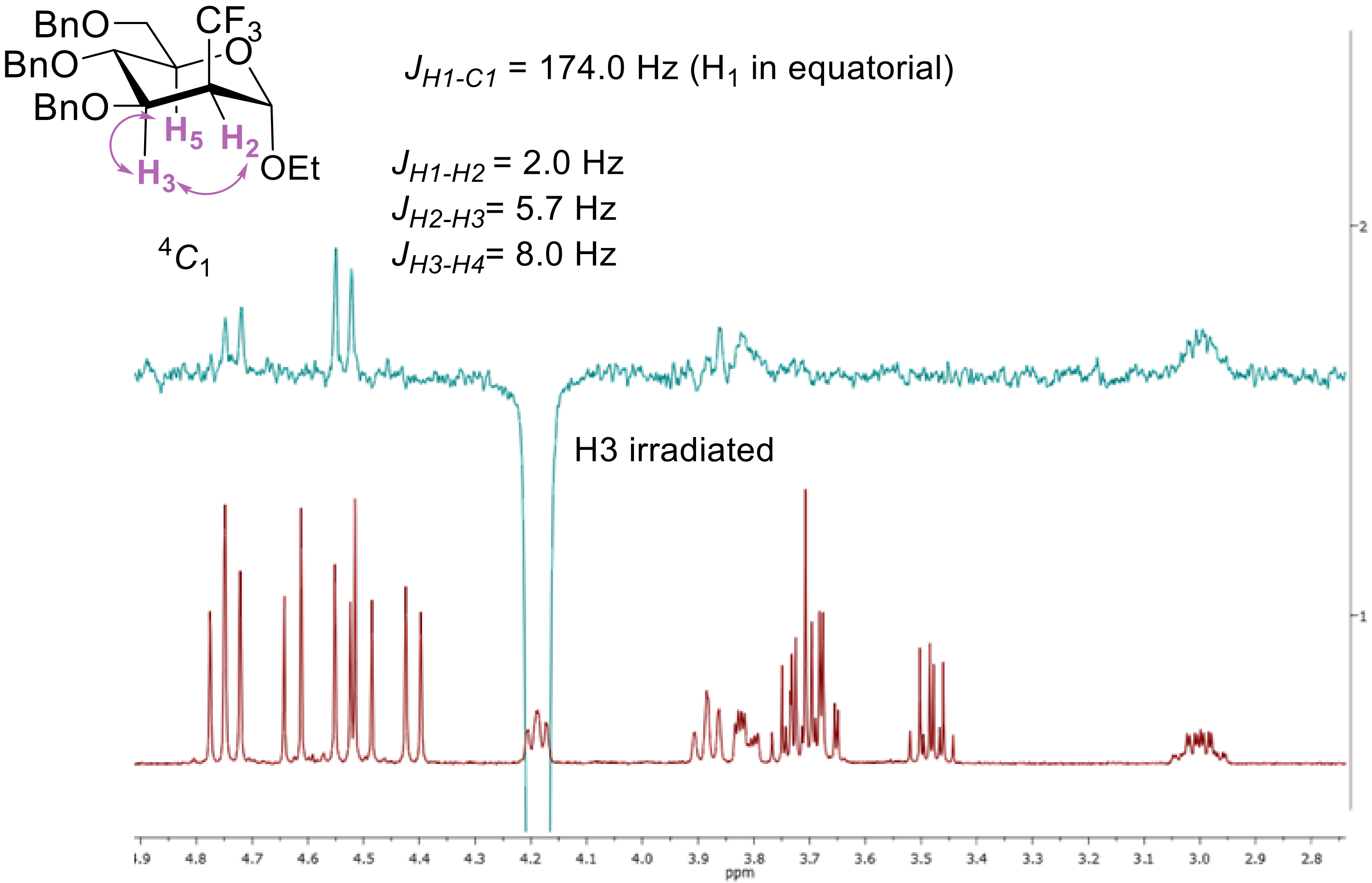


Figure S41 1D NOE ($CDCl_3$, 400 MHz) of **6aα**

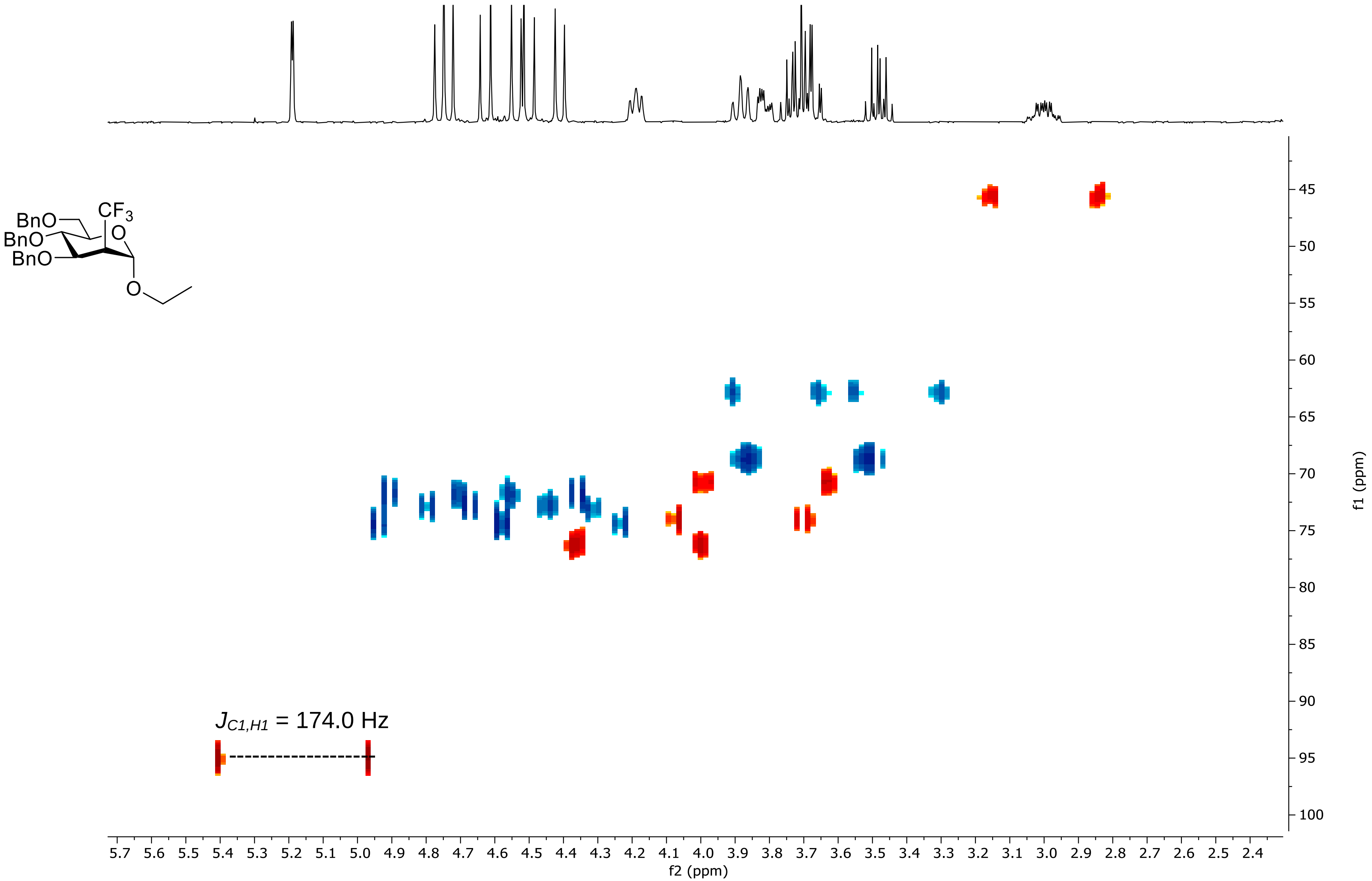


Figure S42. ^{1}H-coupled HSQC (CDCl$_3$, 400 MHz) of **6aα**

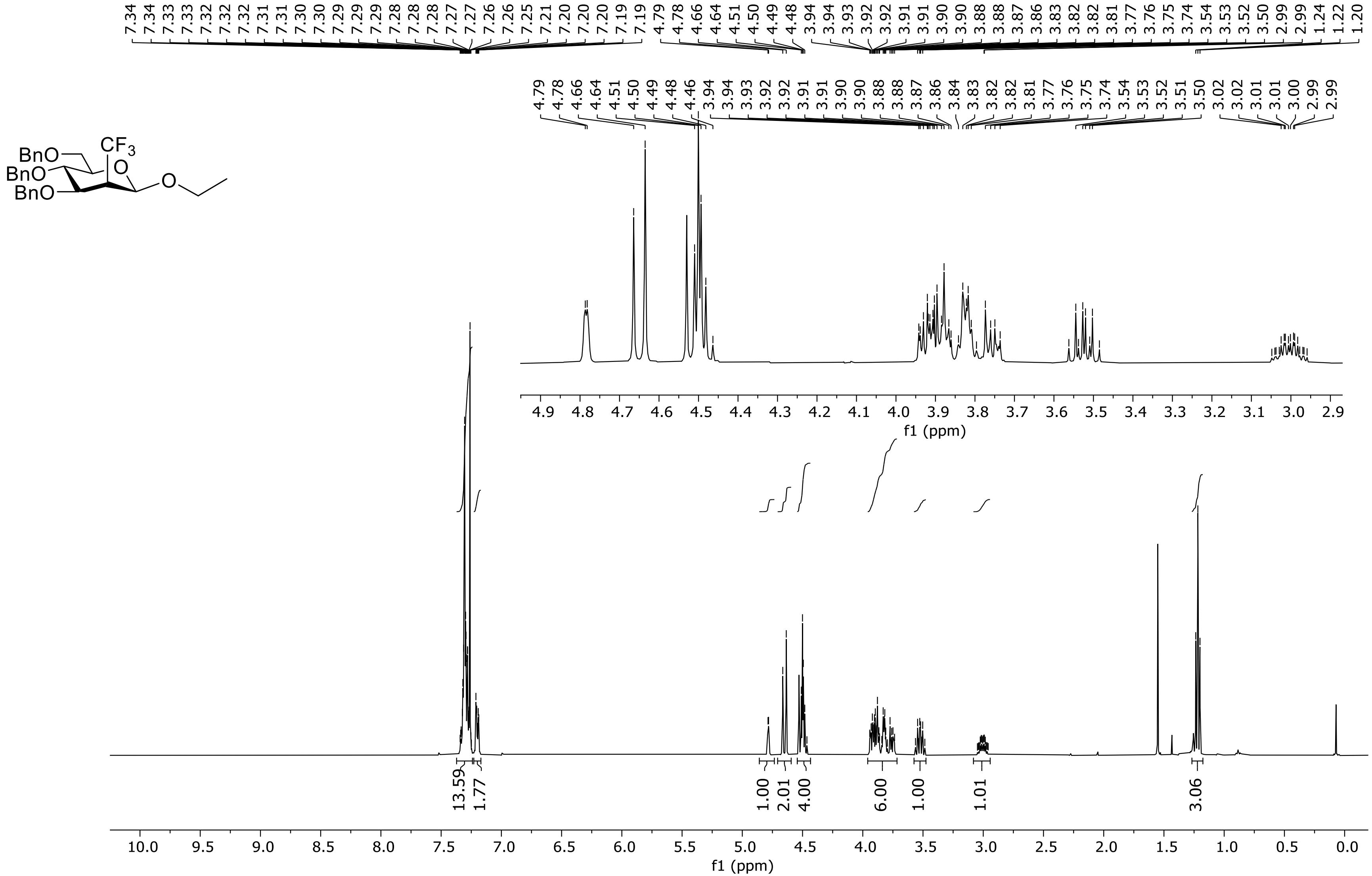


Figure S43. ^{1}H NMR ($CDCl_3$, 400 MHz) of **6aβ**

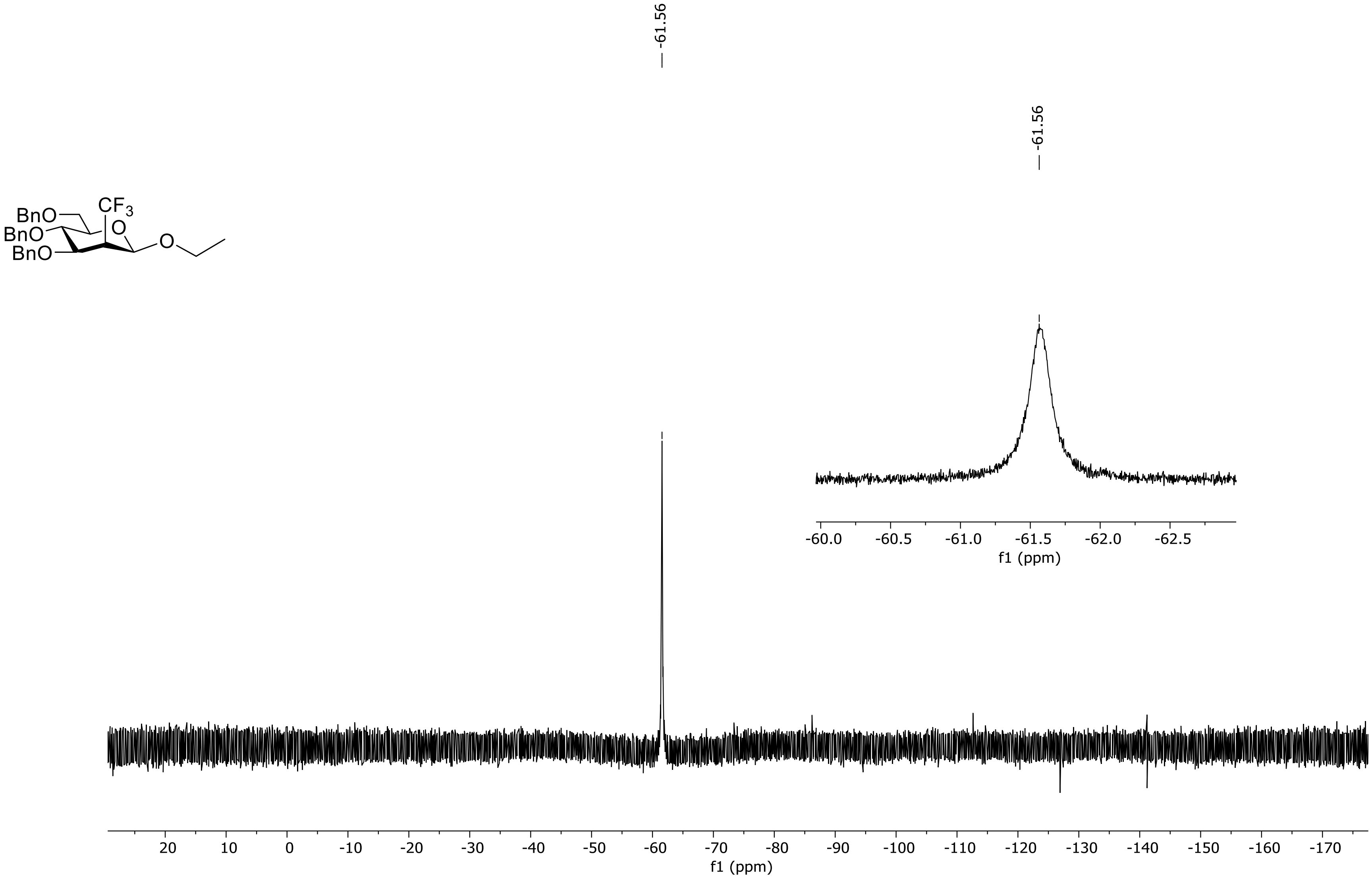


Figure S44. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **6aβ**

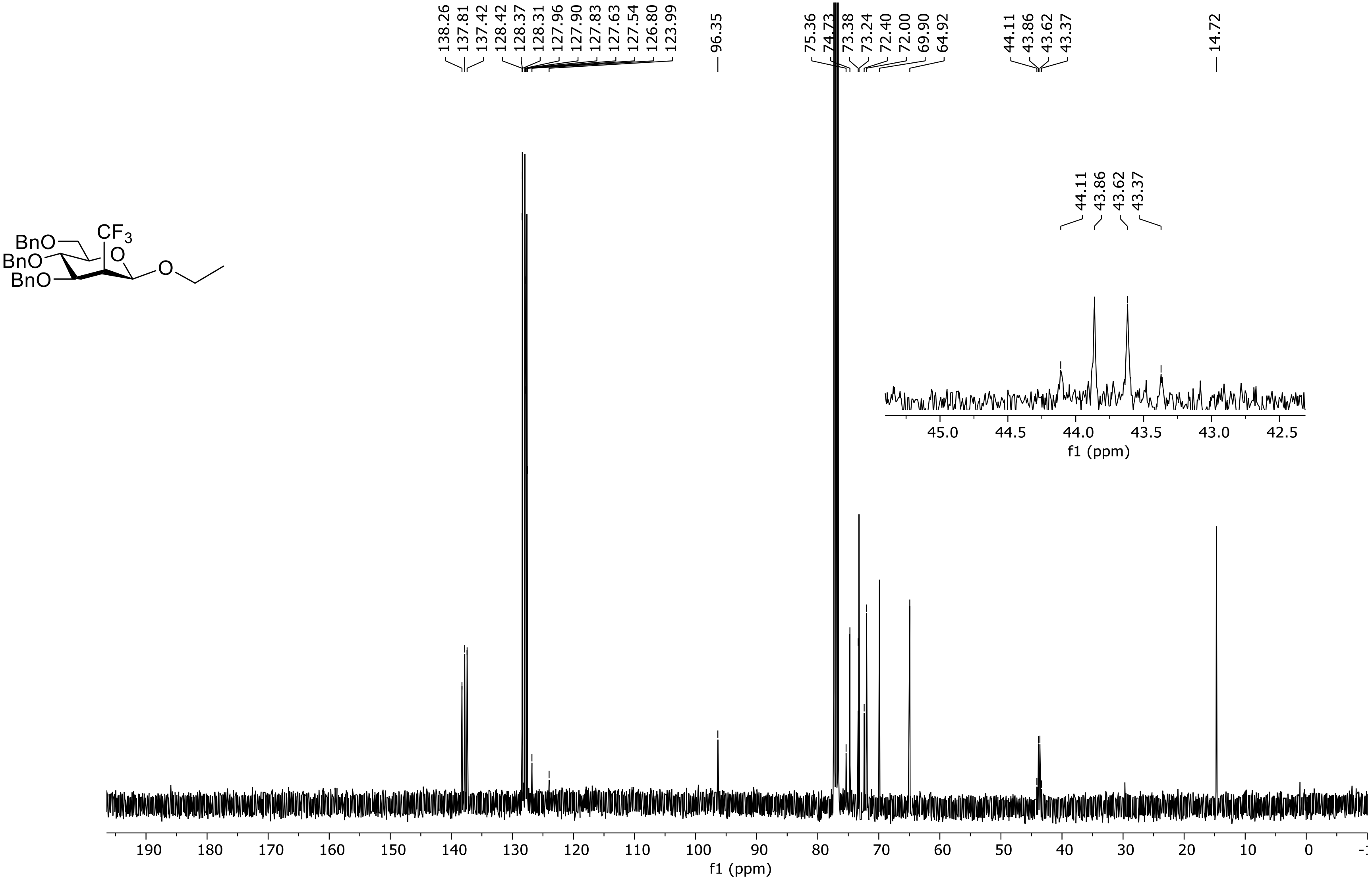


Figure S45. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **6aβ**

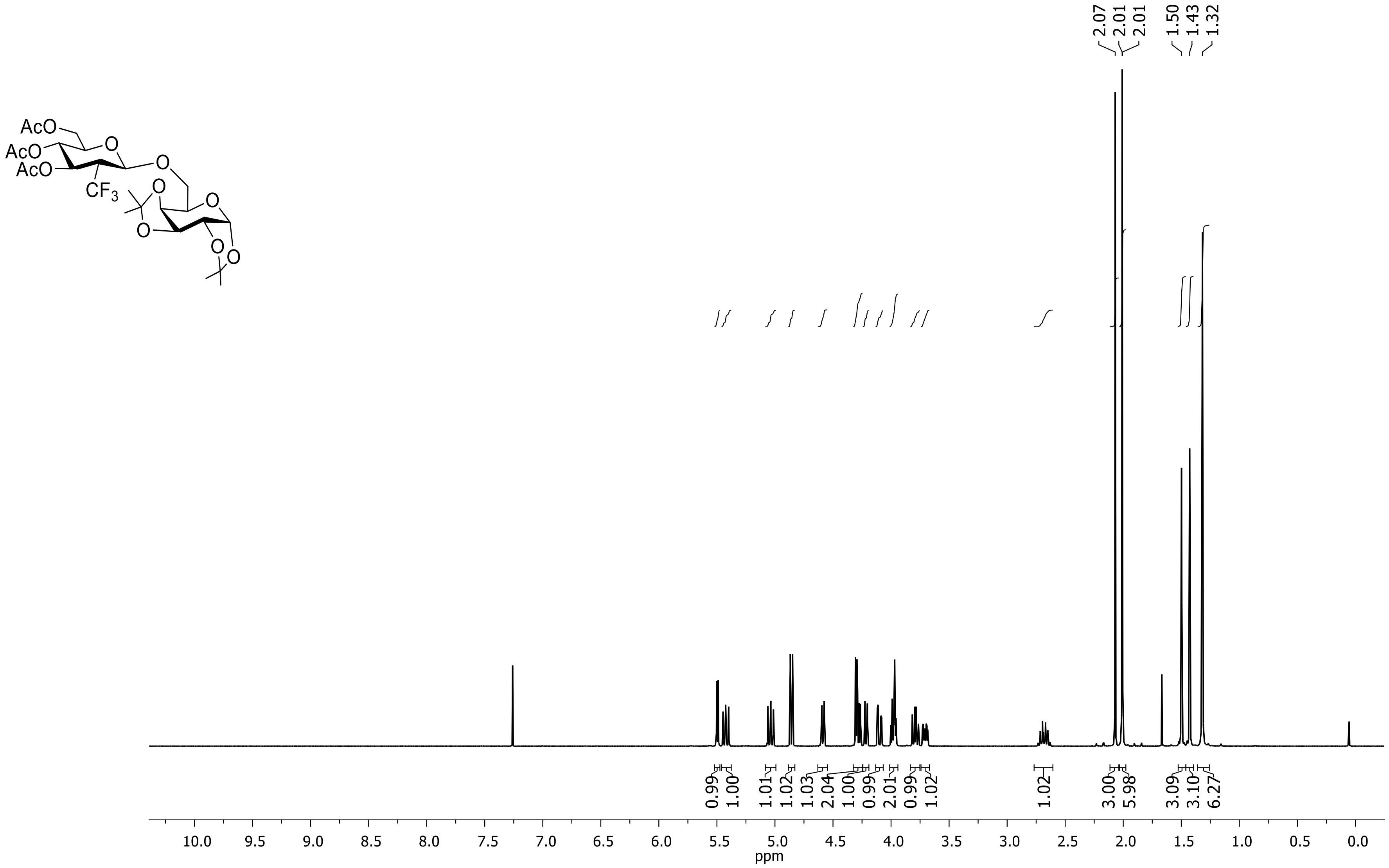


Figure S46. ^{1}H NMR ($CDCl_3$, 400 MHz) of **7β**

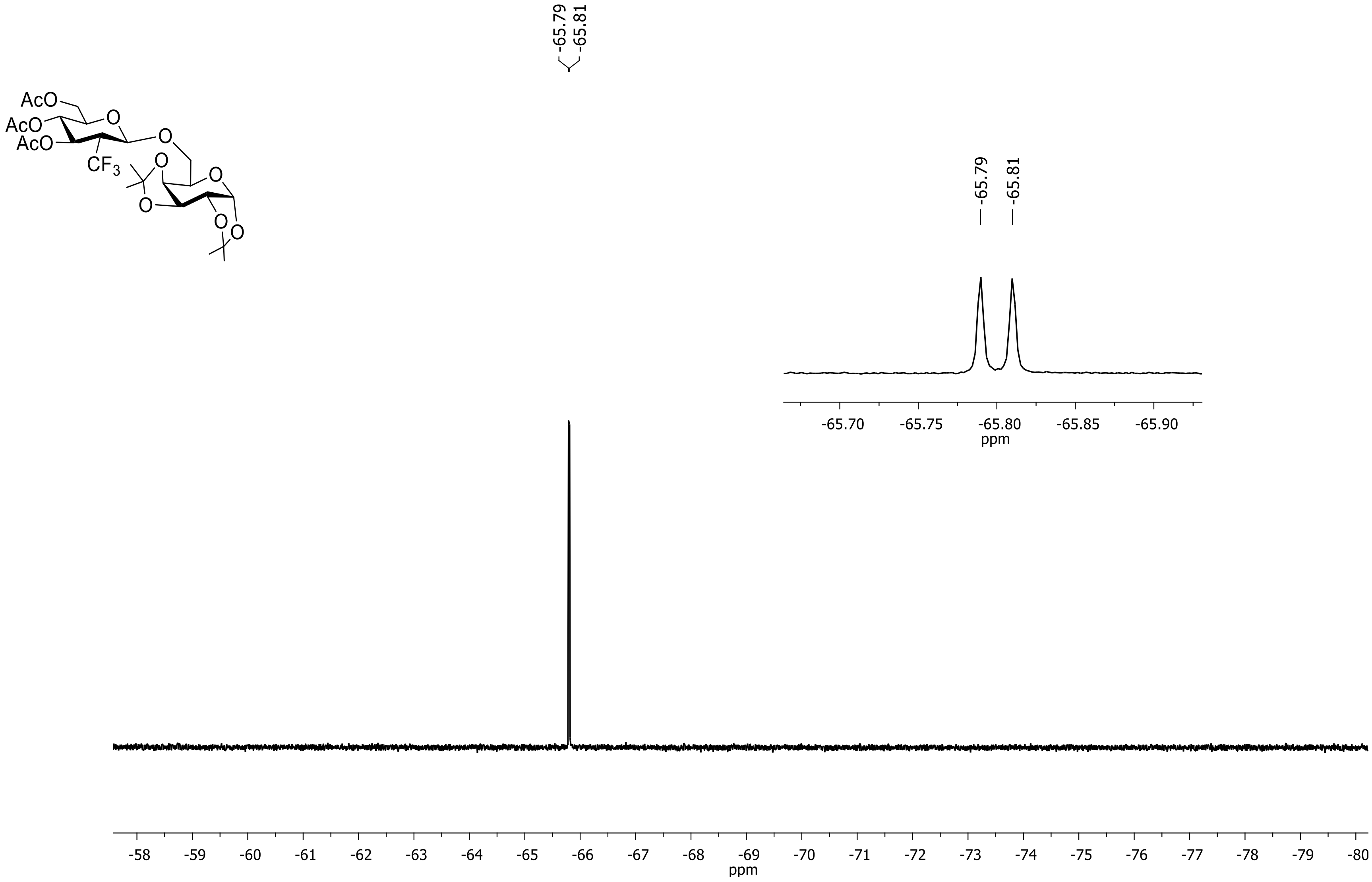


Figure S47. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **7β**

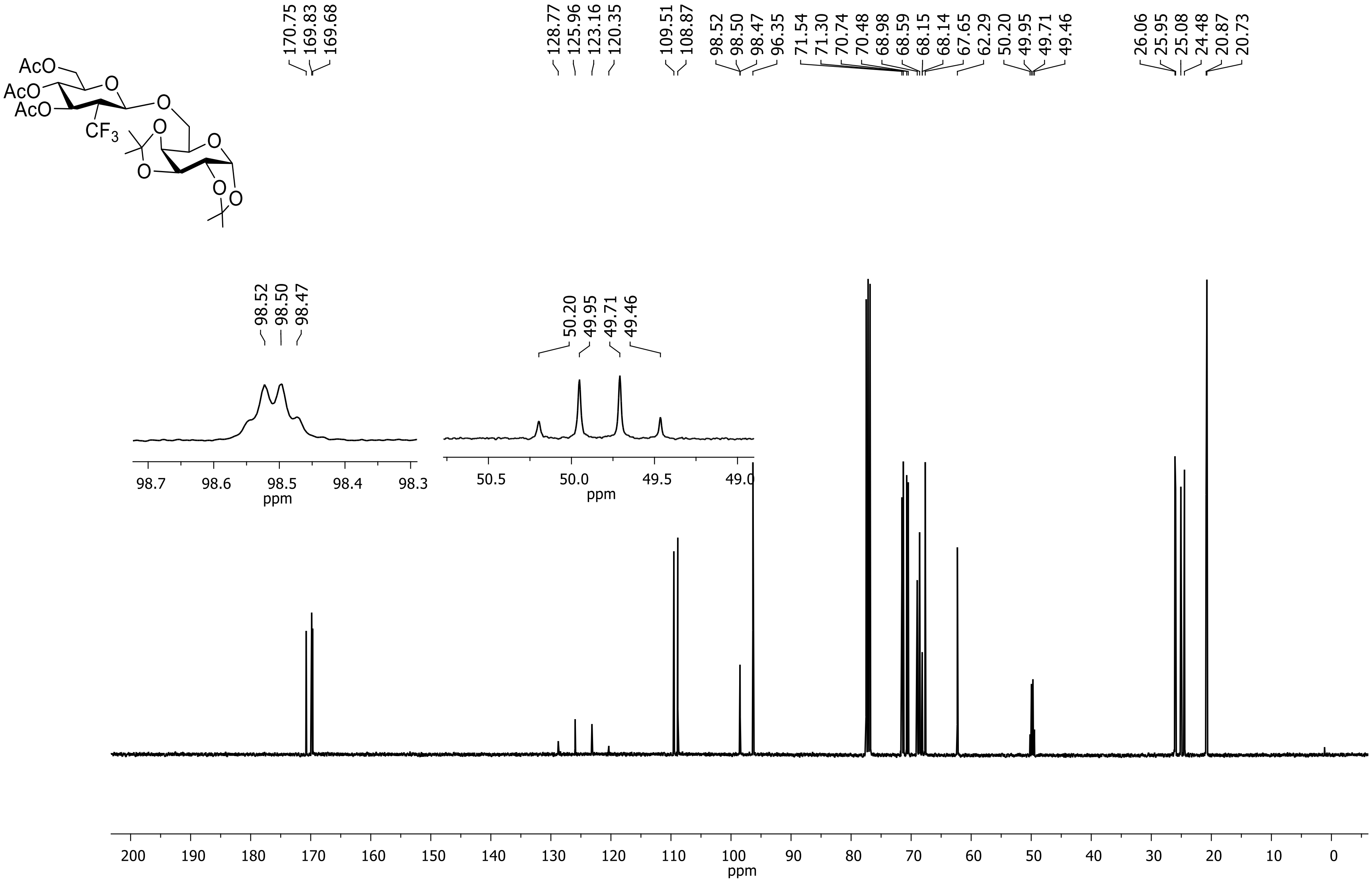


Figure S48. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **7β**

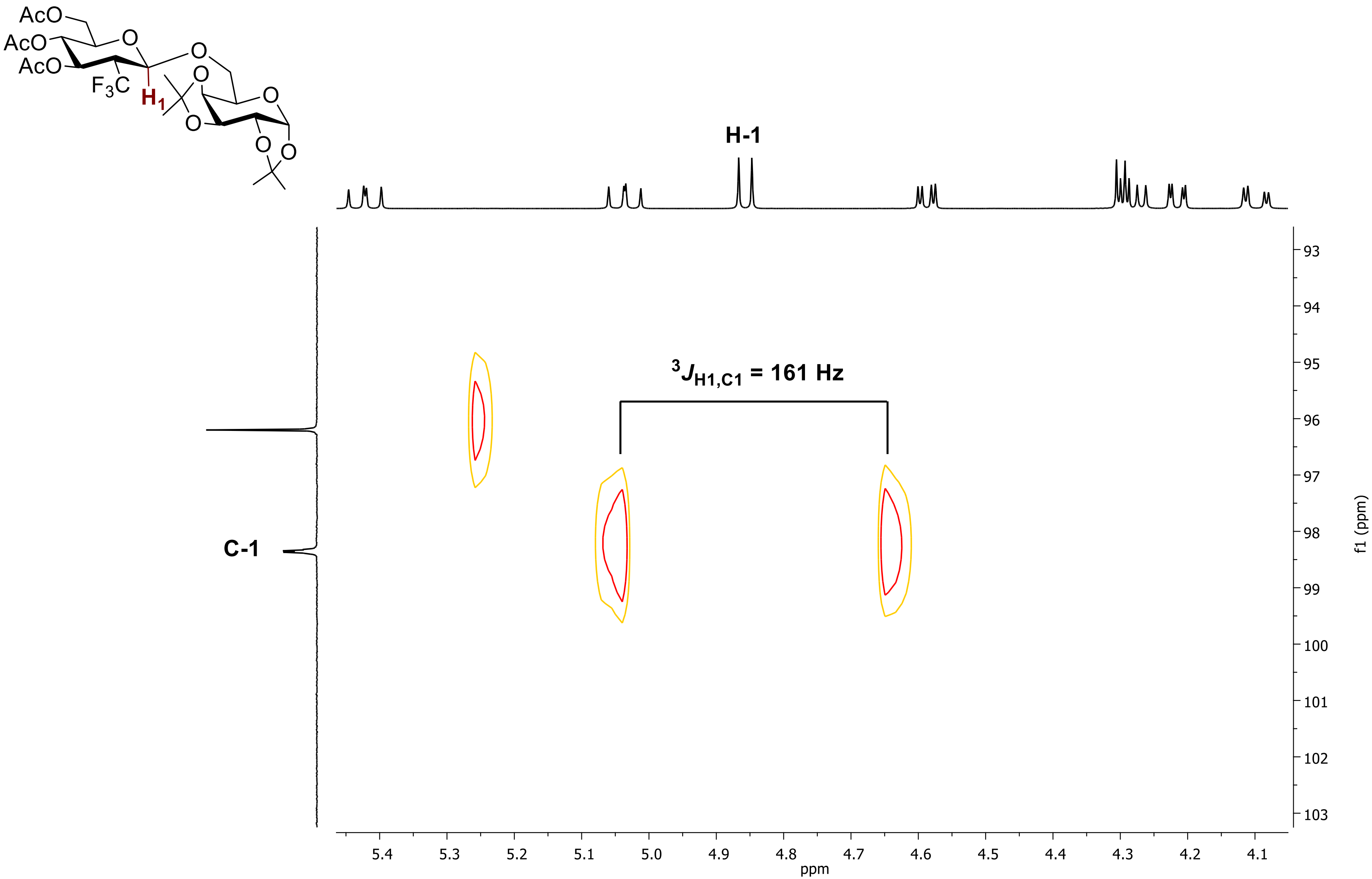


Figure S49. ^{1}H-coupled HSQC (CDCl$_3$, 400 MHz) of **7β**

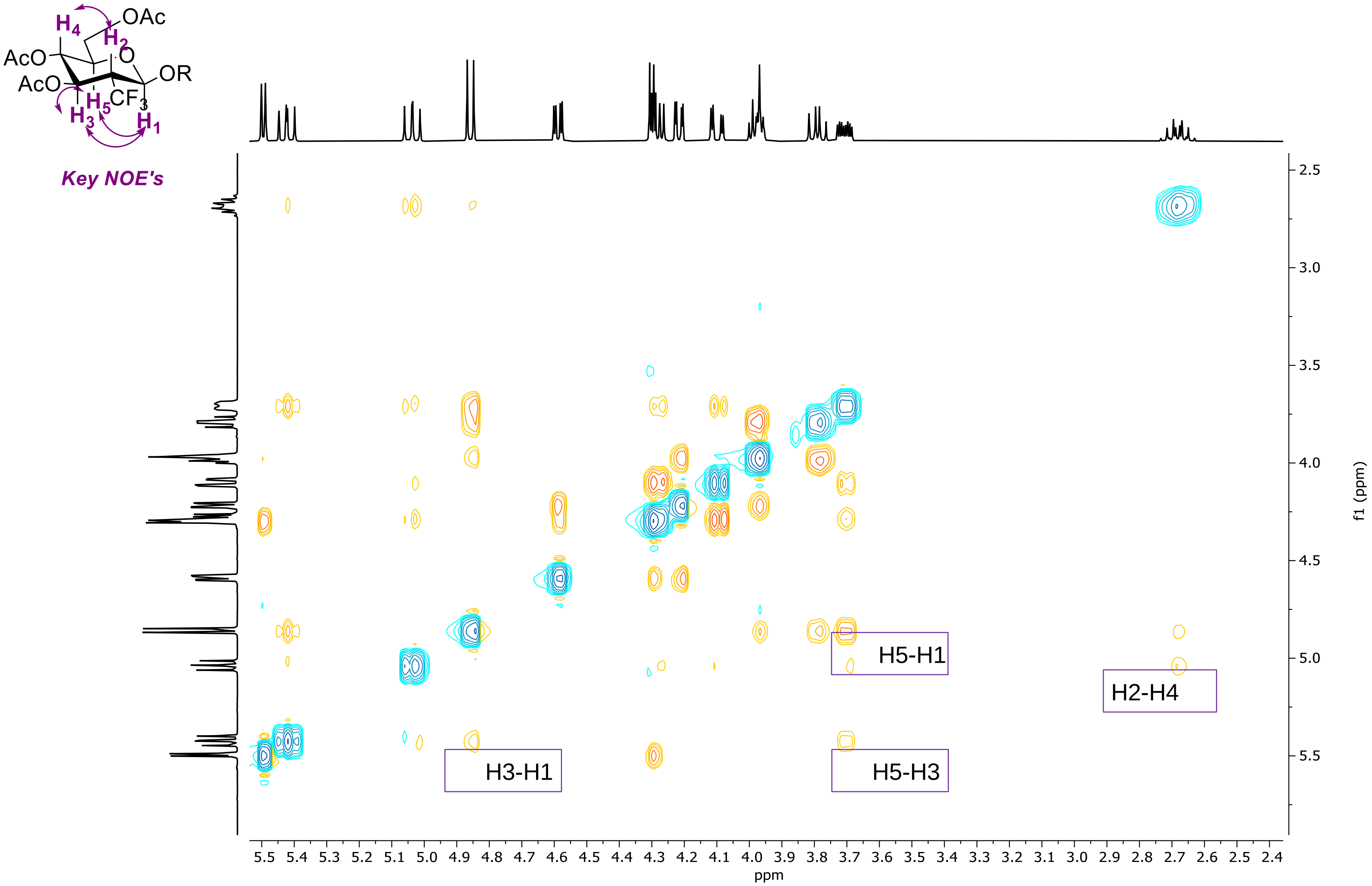
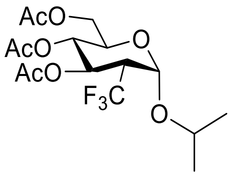


Figure S50. 2D NOESY (CDCl$_3$, 400 MHz) of **7β**



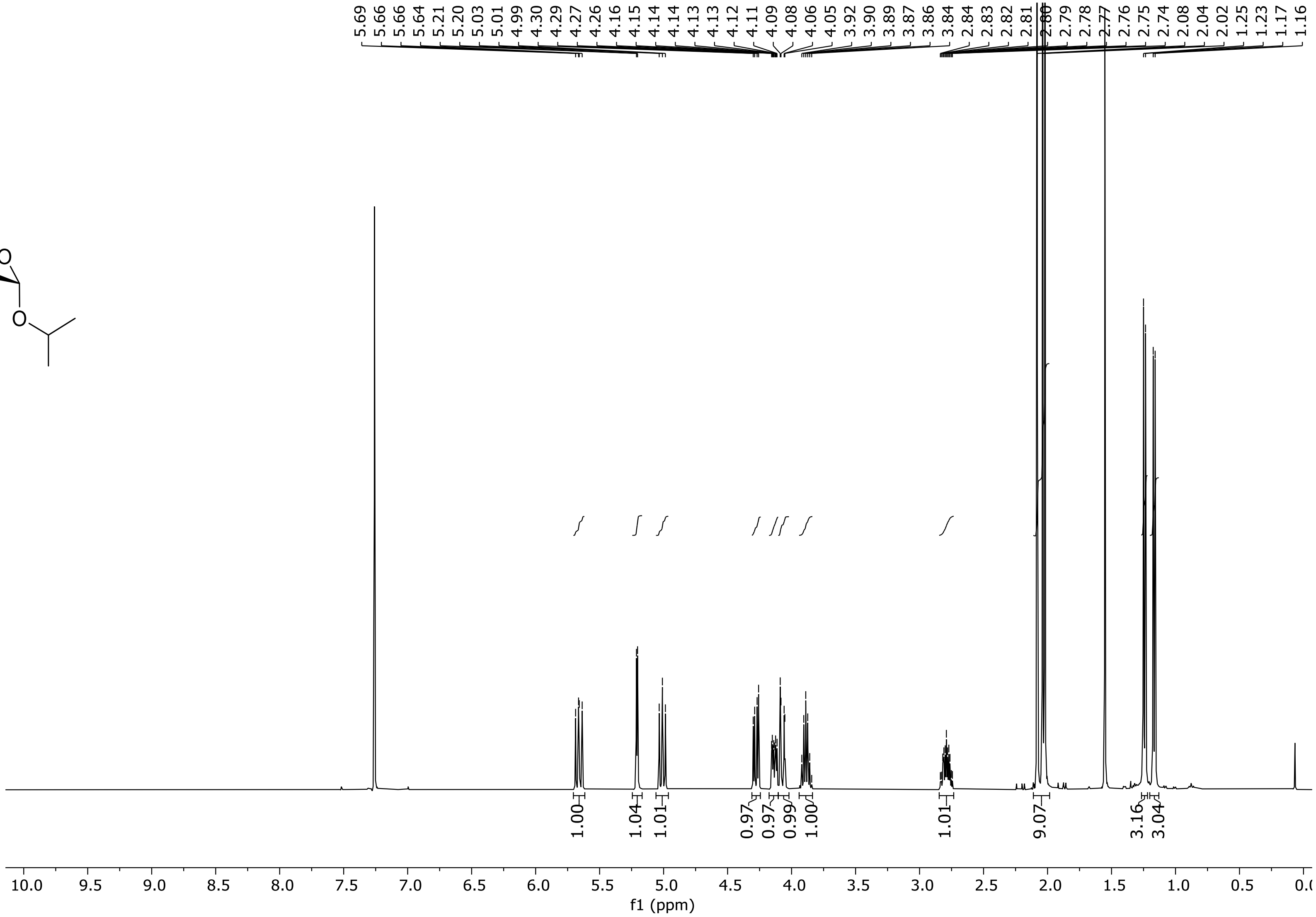


Figure S51: ^{1}H NMR ($CDCl_3$, 400 MHz) of **10α**

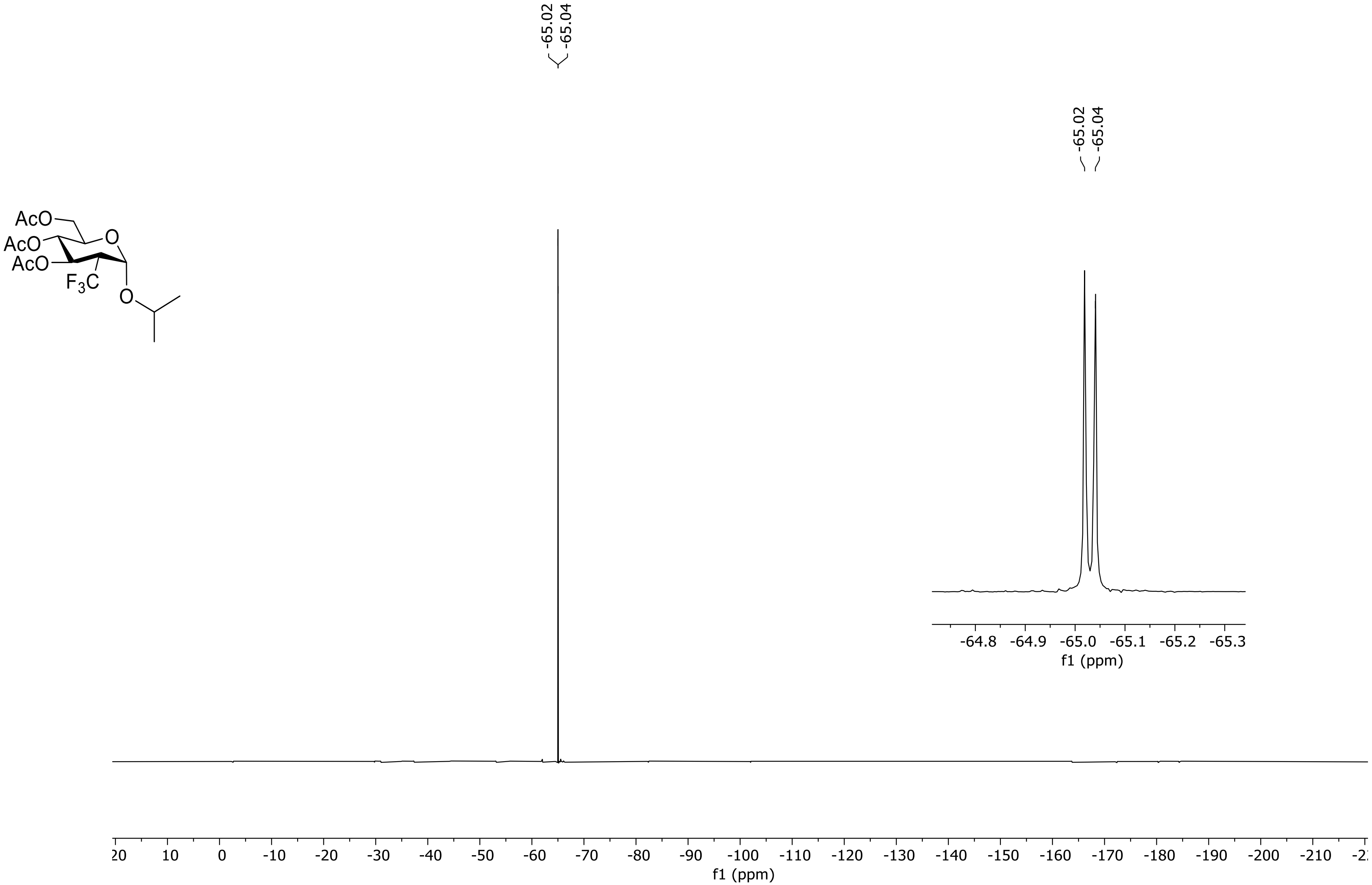


Figure S52. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **10α**

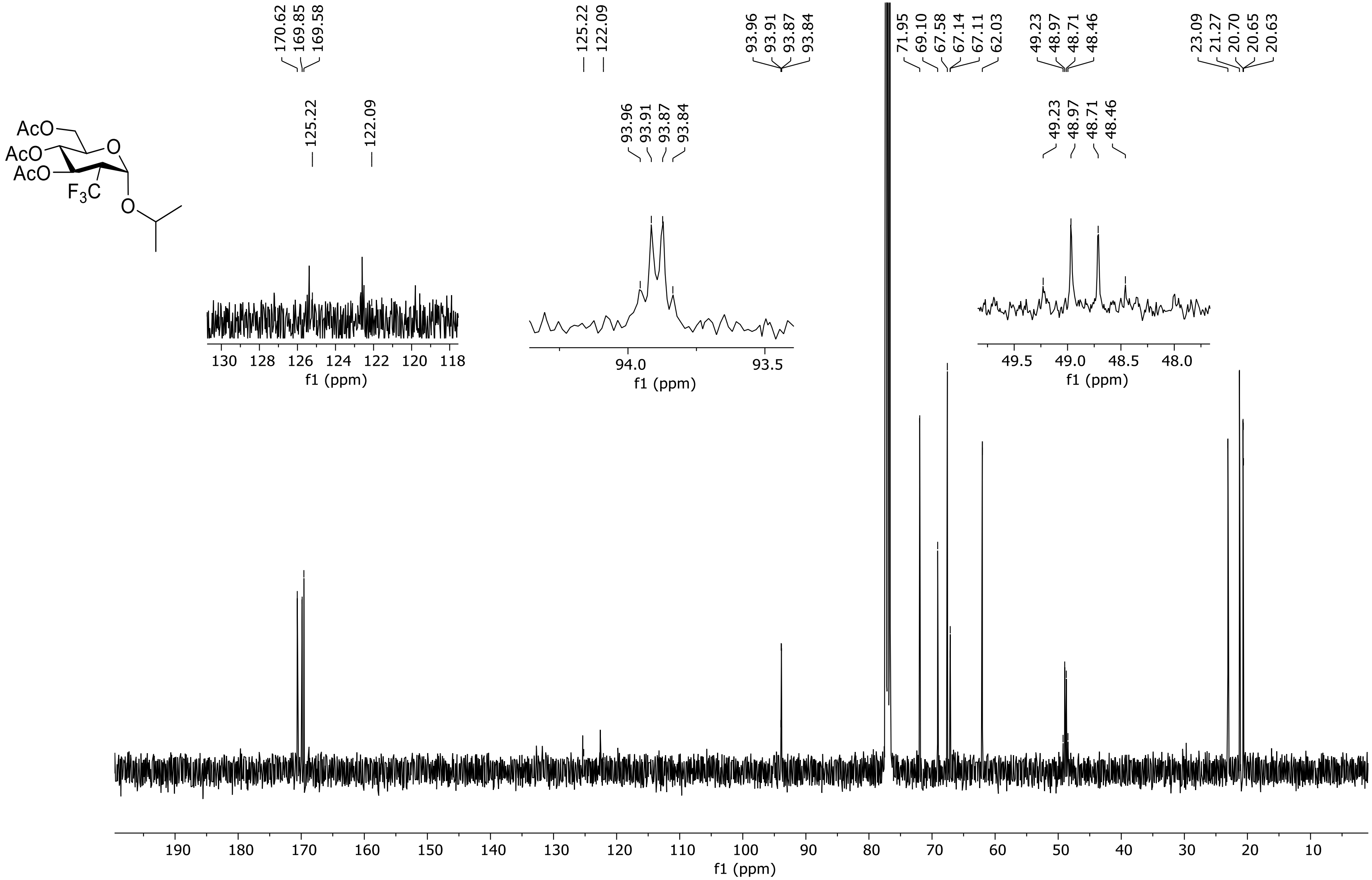


Figure S53. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **10α**

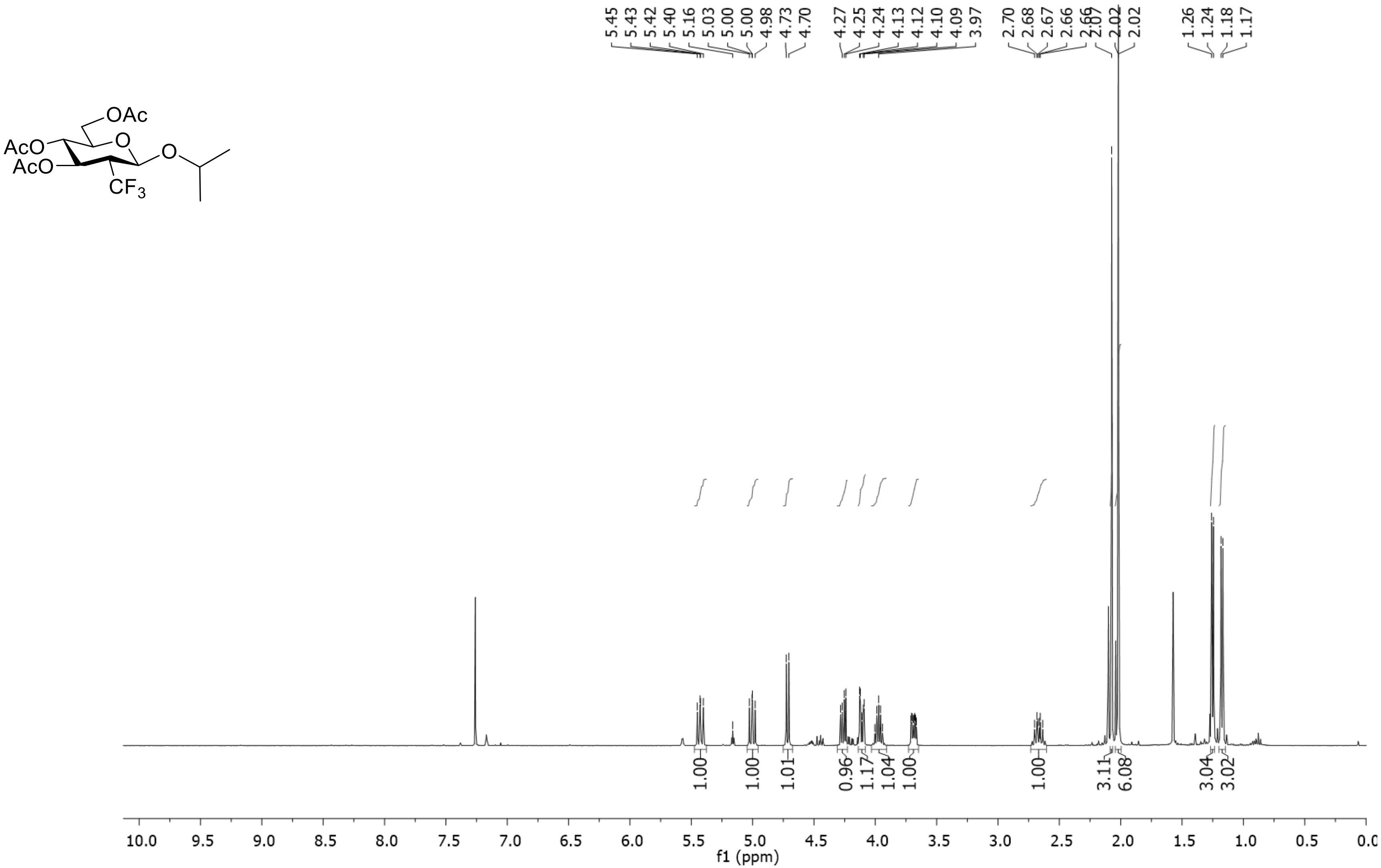


Figure S54. ^{1}H NMR ($CDCl_3$, 400 MHz) of **10α/β**

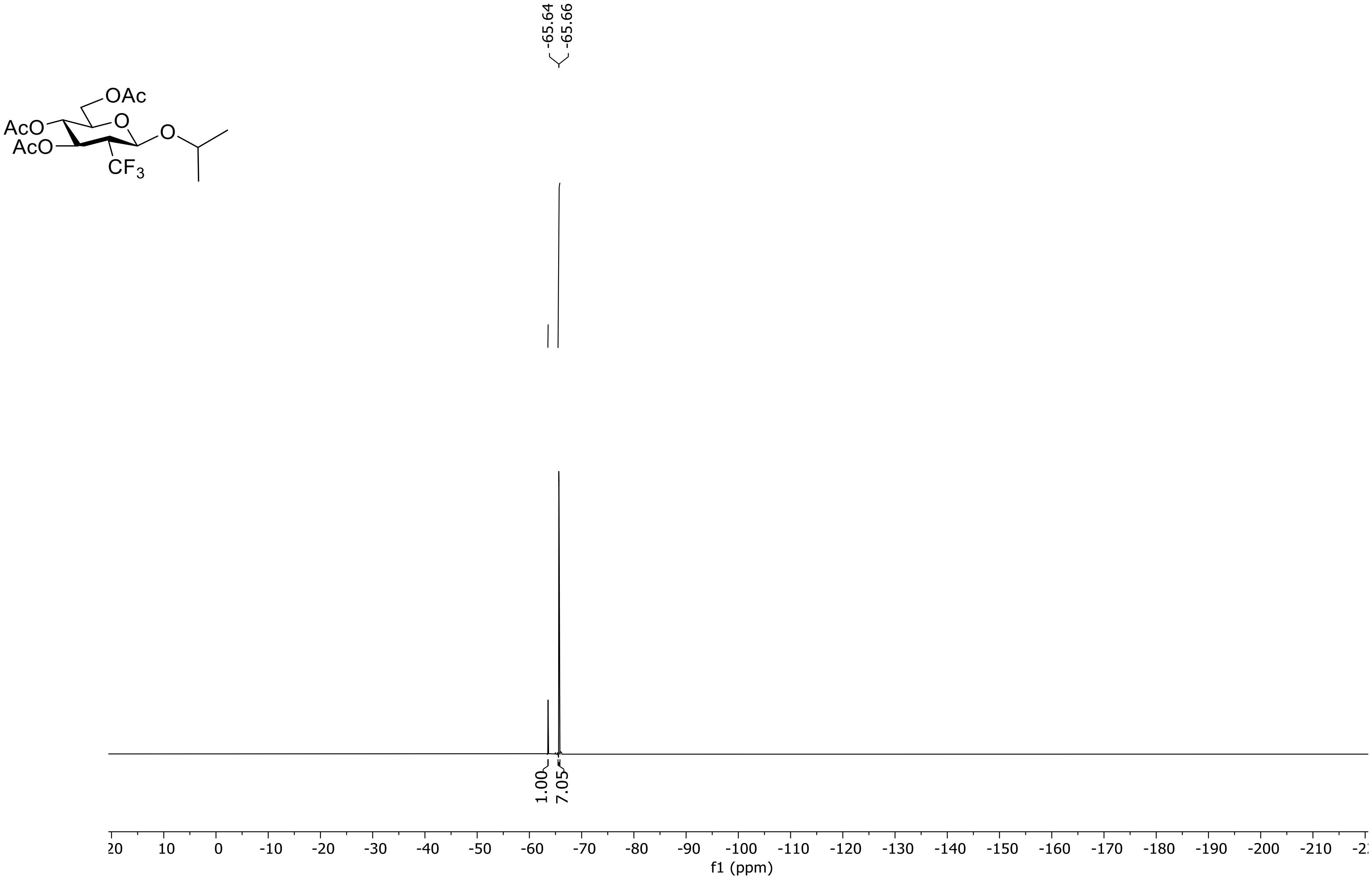


Figure S55. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **10α/β**

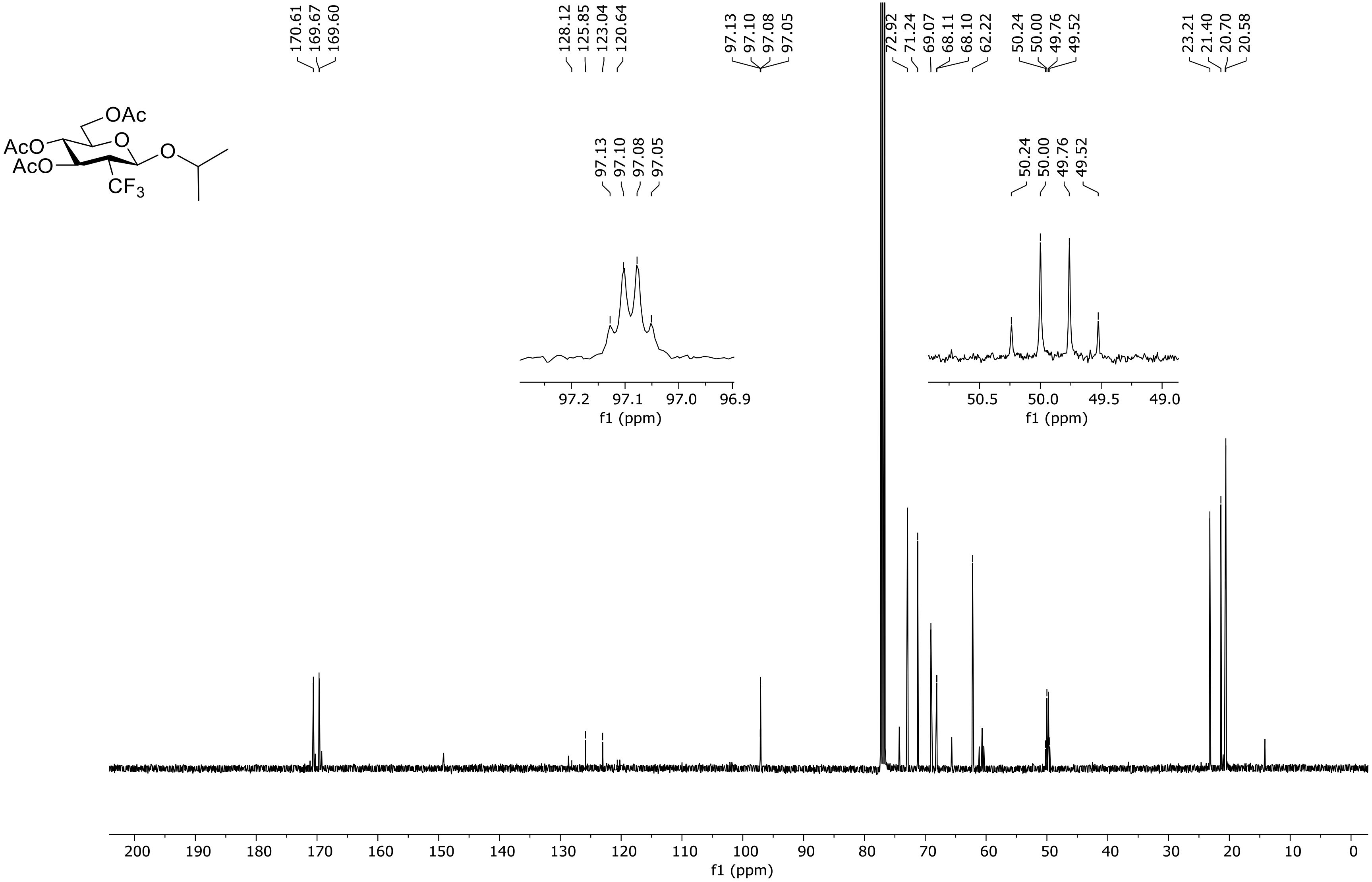


Figure S56. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **10α/β**

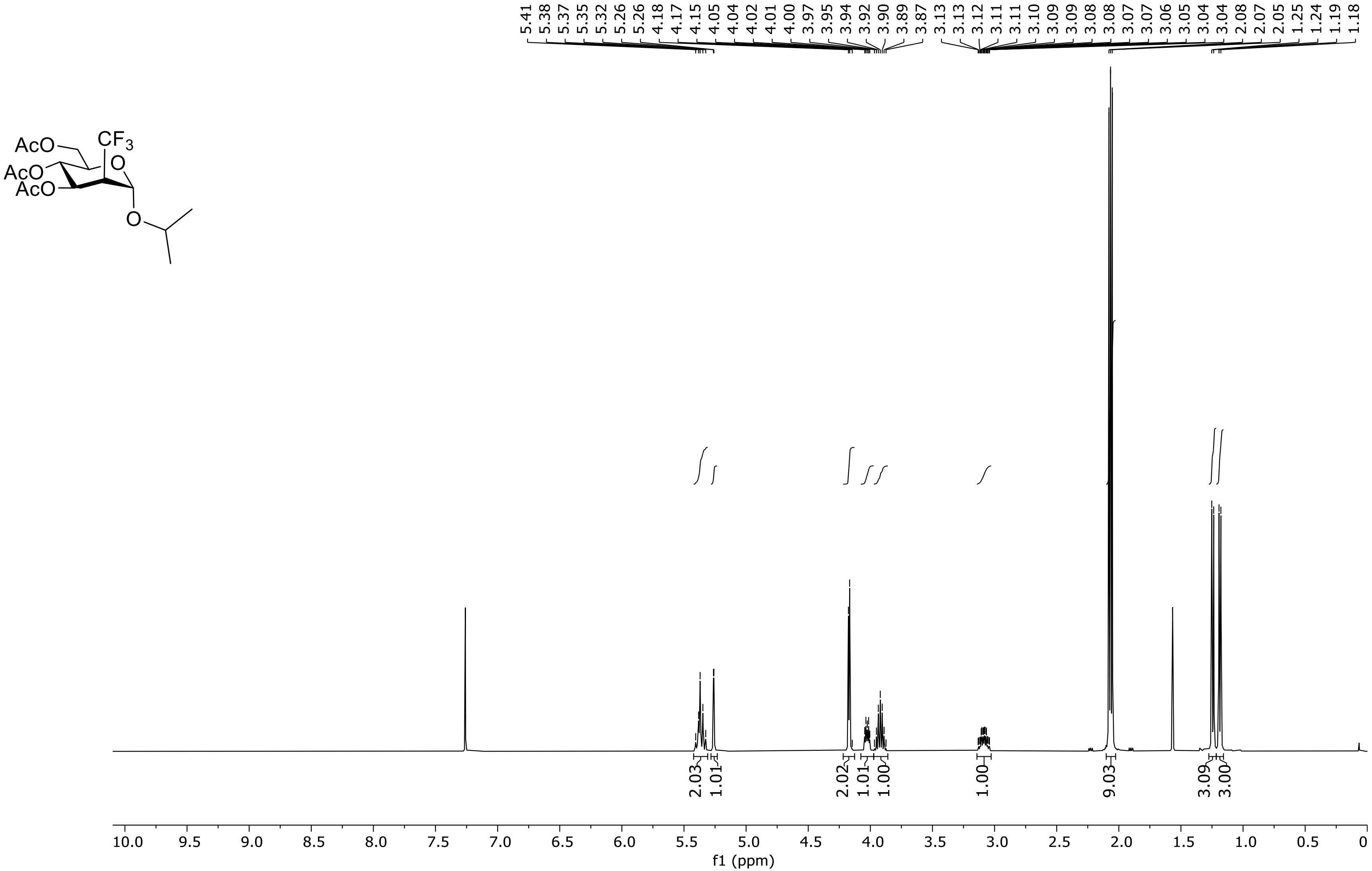


Figure S57: ^{1}H NMR (CDCl$_3$, 400 MHz) of **11α**

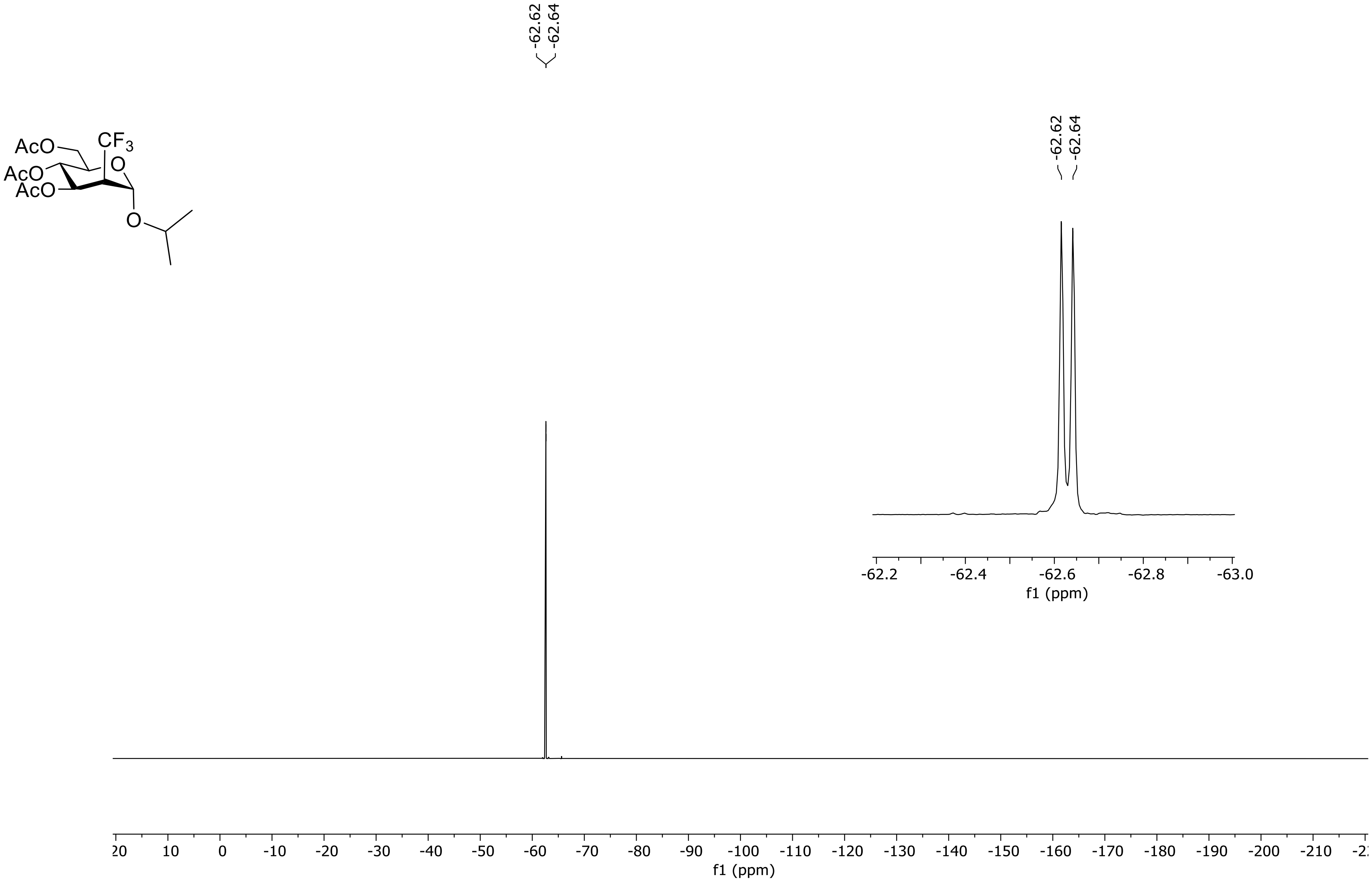


Figure S58. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **11α**

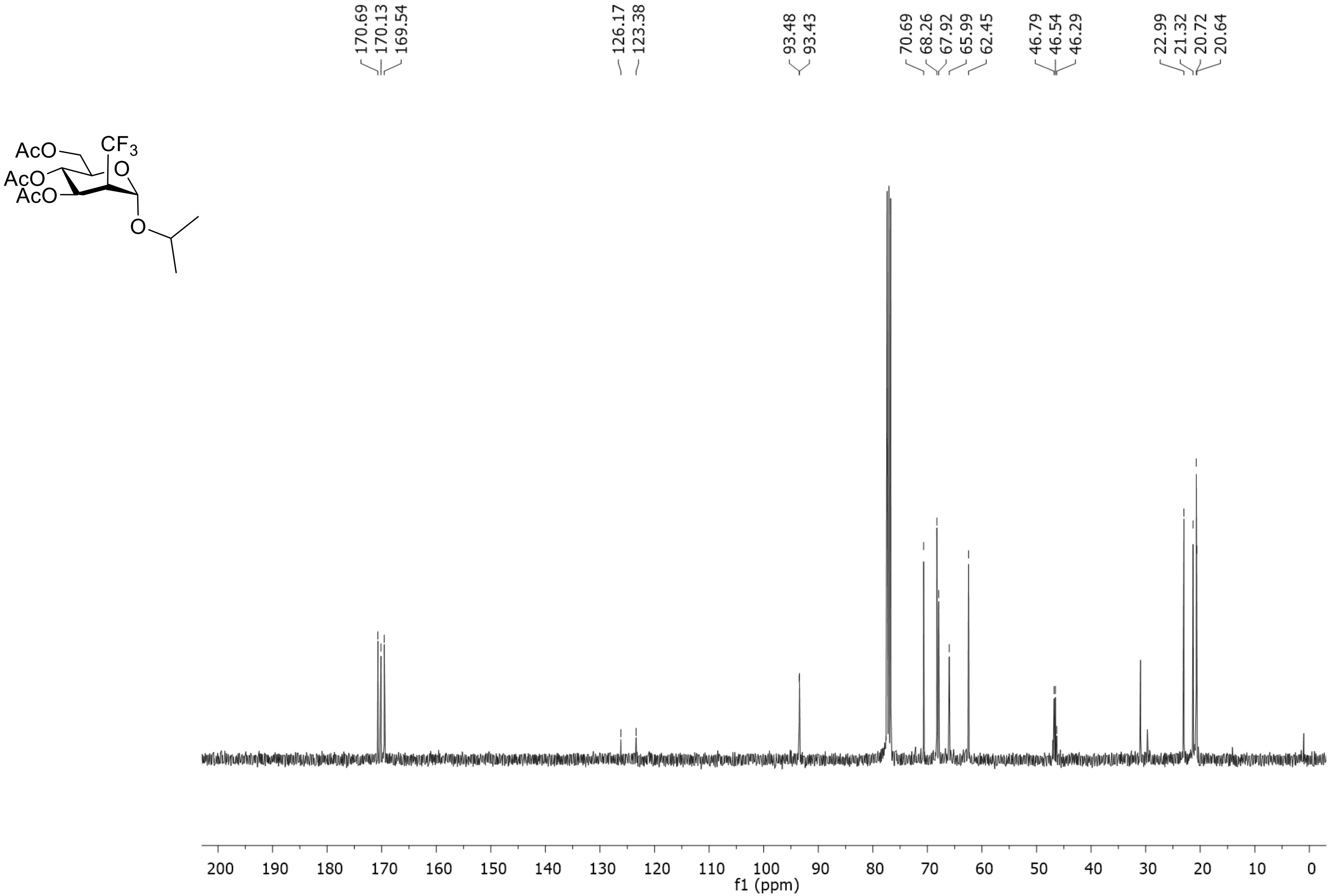


Figure S59. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **11α**

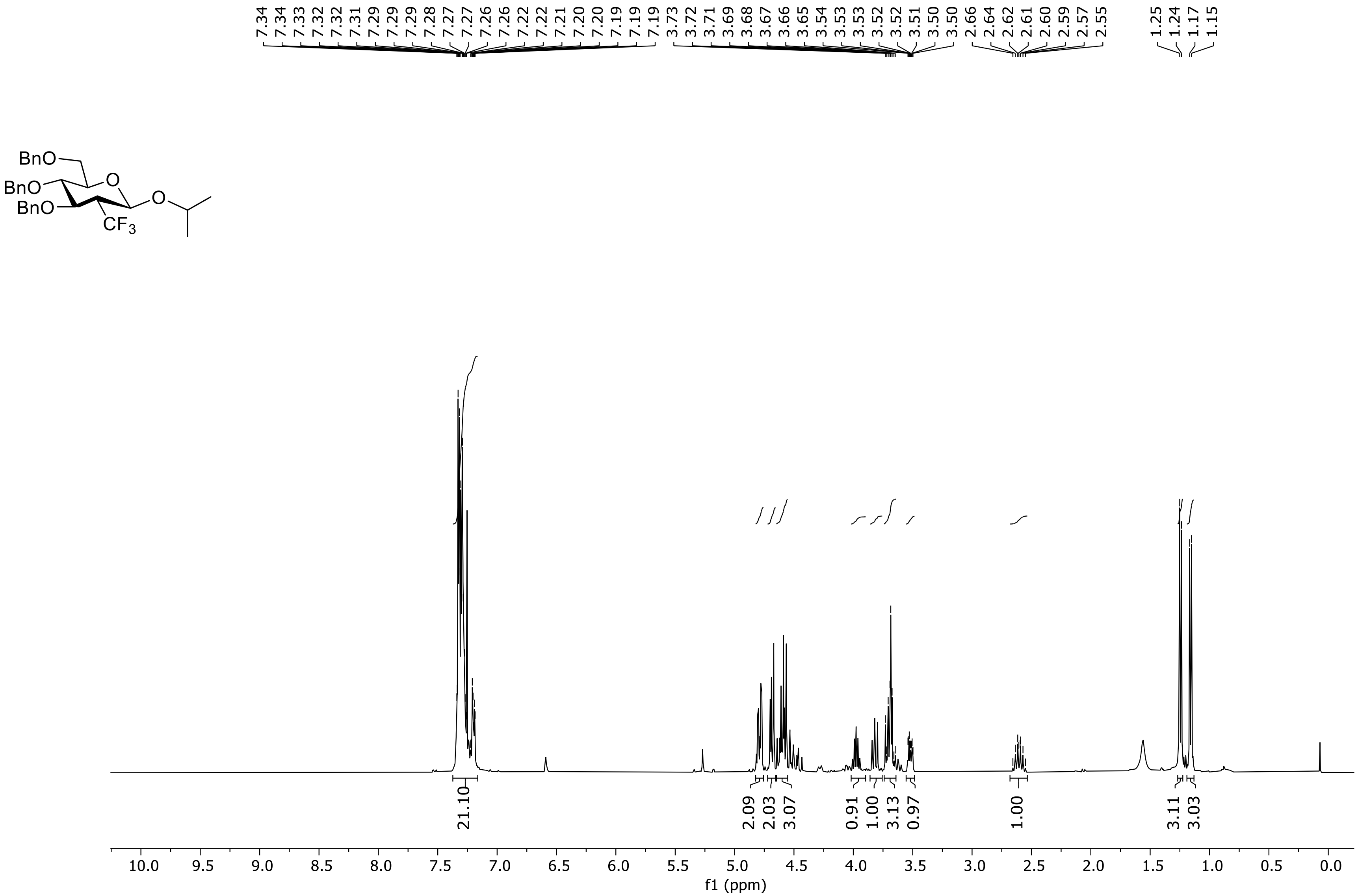


Figure S60. ^{1}H NMR ($CDCl_3$, 400 MHz) of **12β**

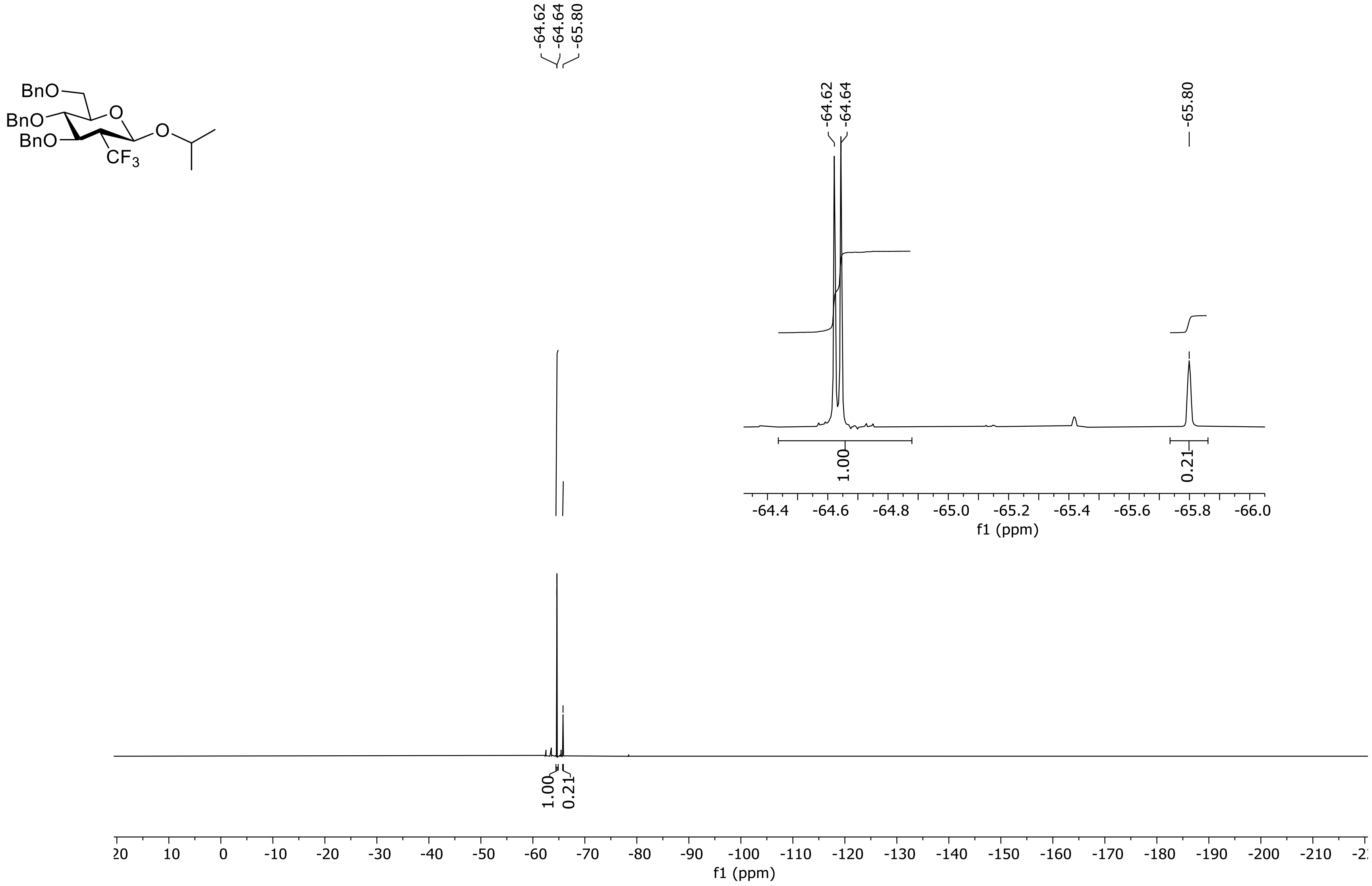


Figure S61. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **12β**

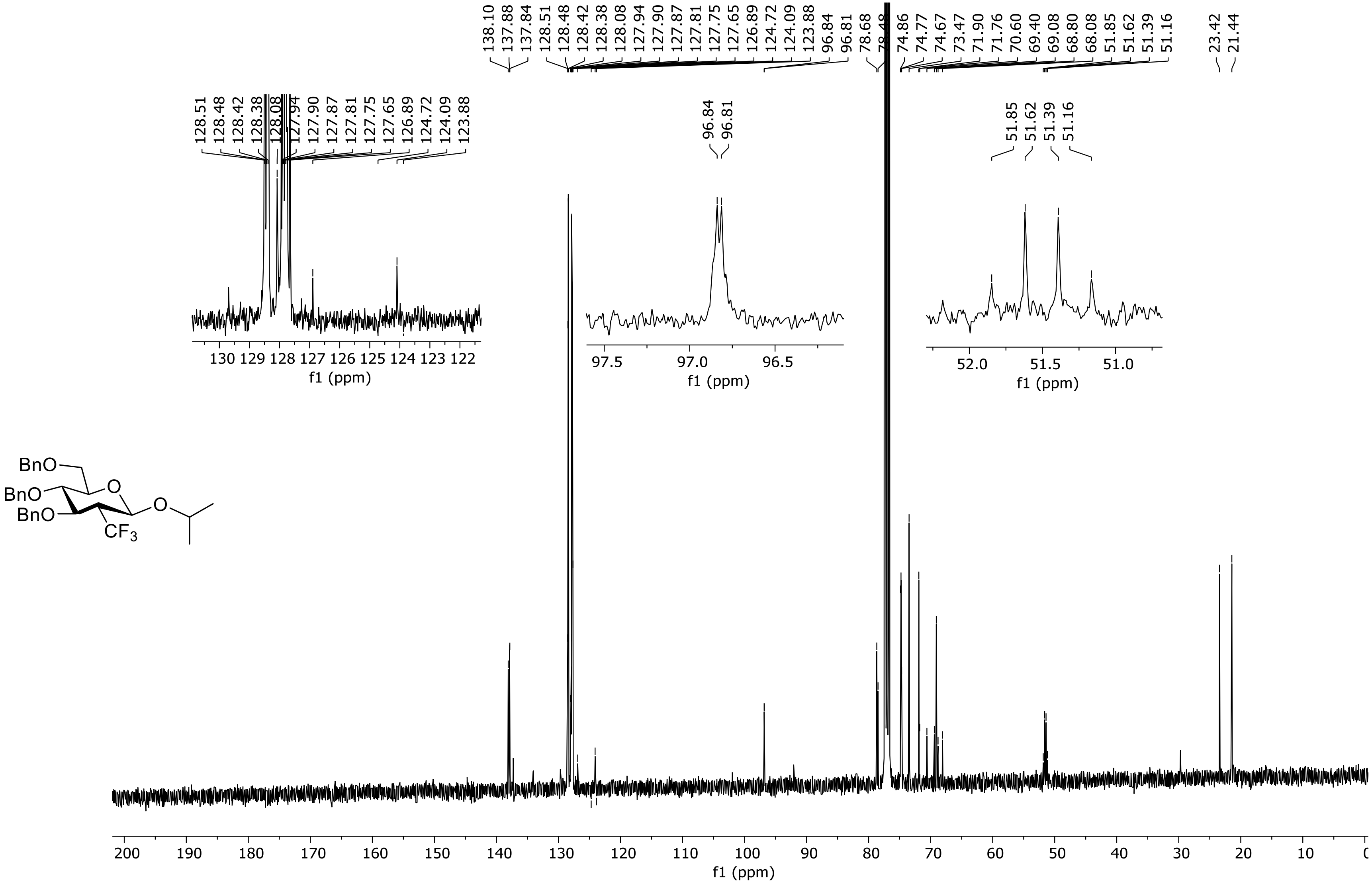
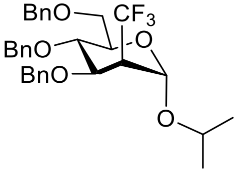


Figure S62. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **12β**



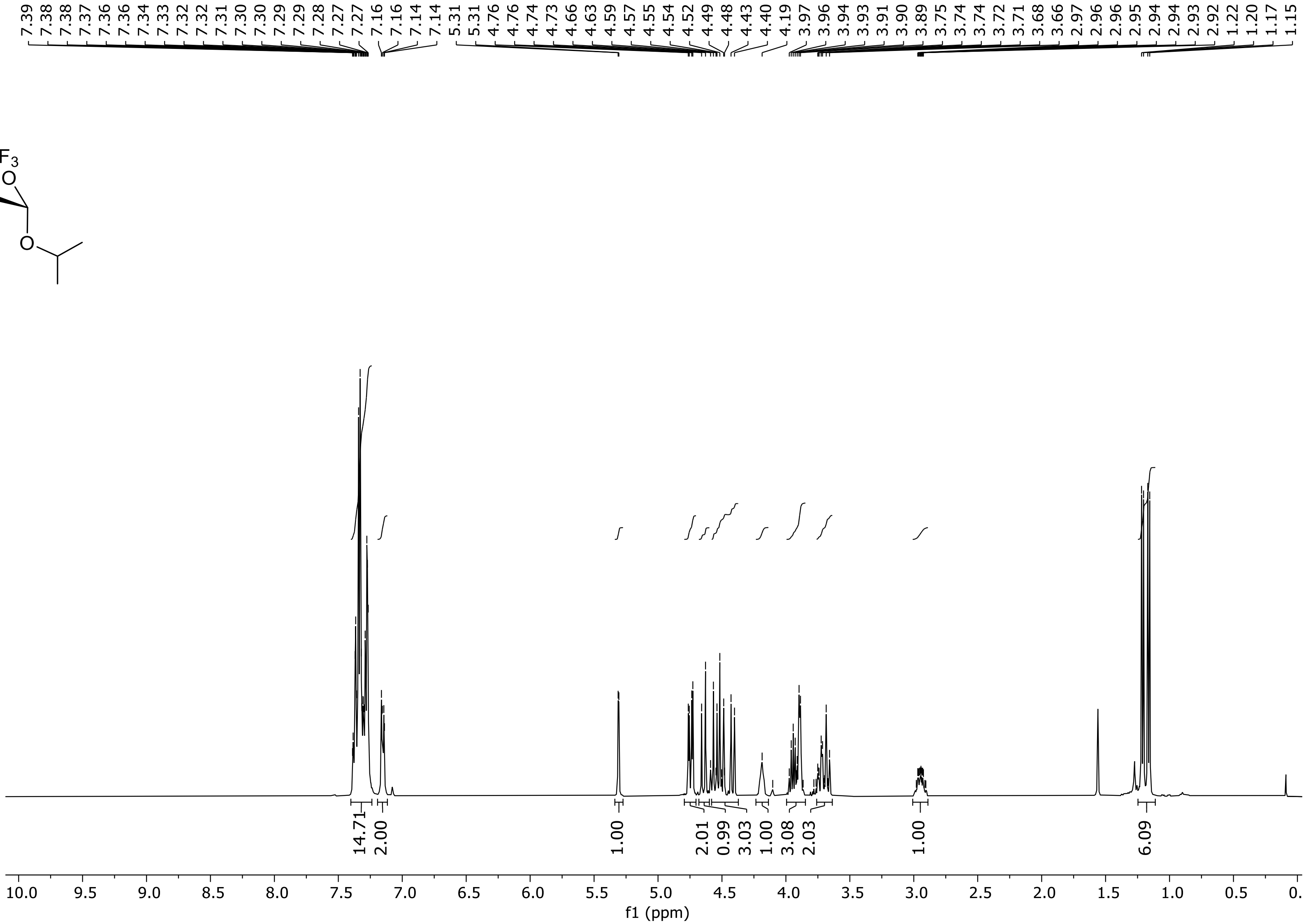


Figure S63. ^{1}H NMR (CDCl$_3$, 400 MHz) of **13α**

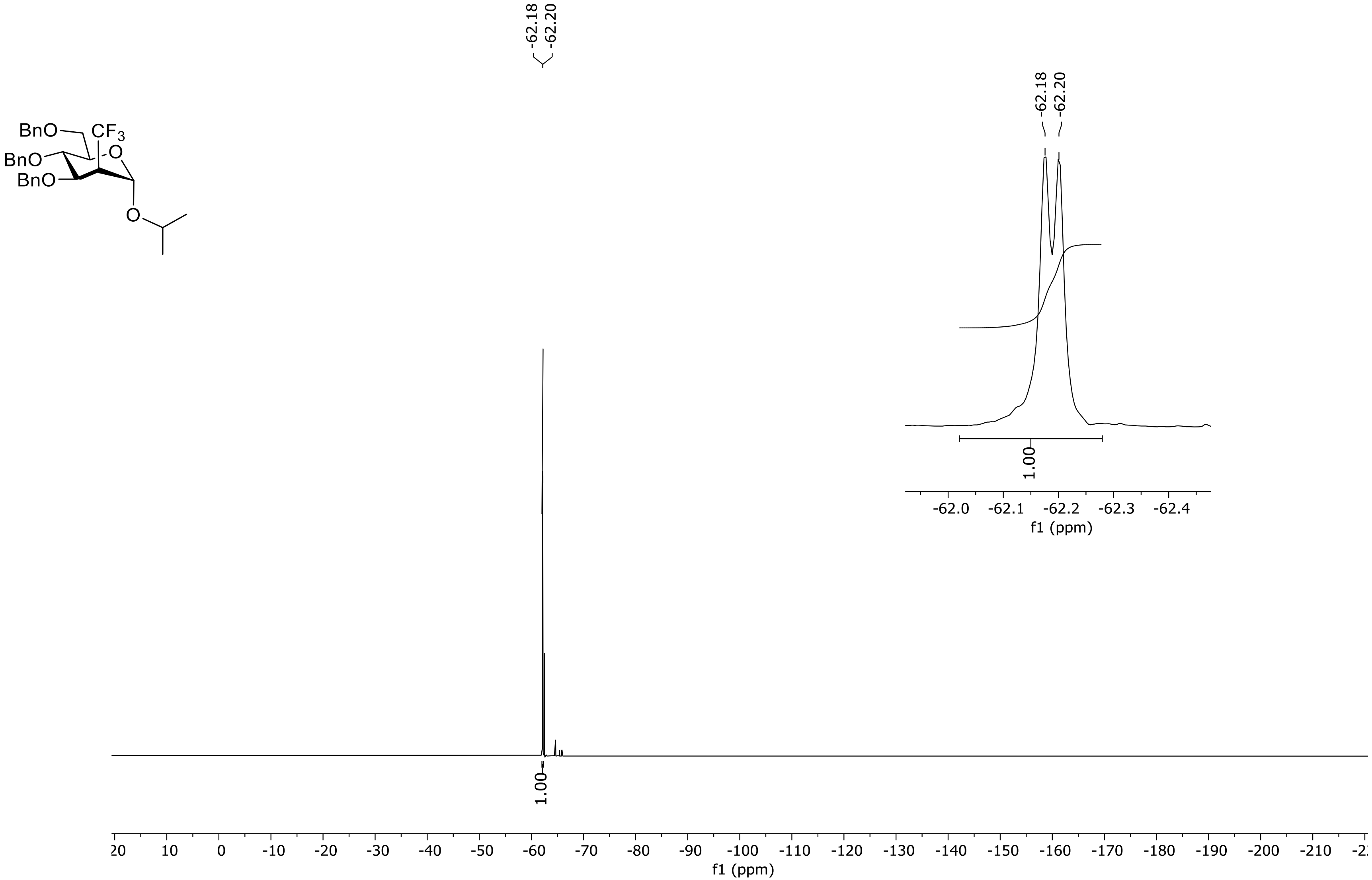


Figure S64. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **13α**

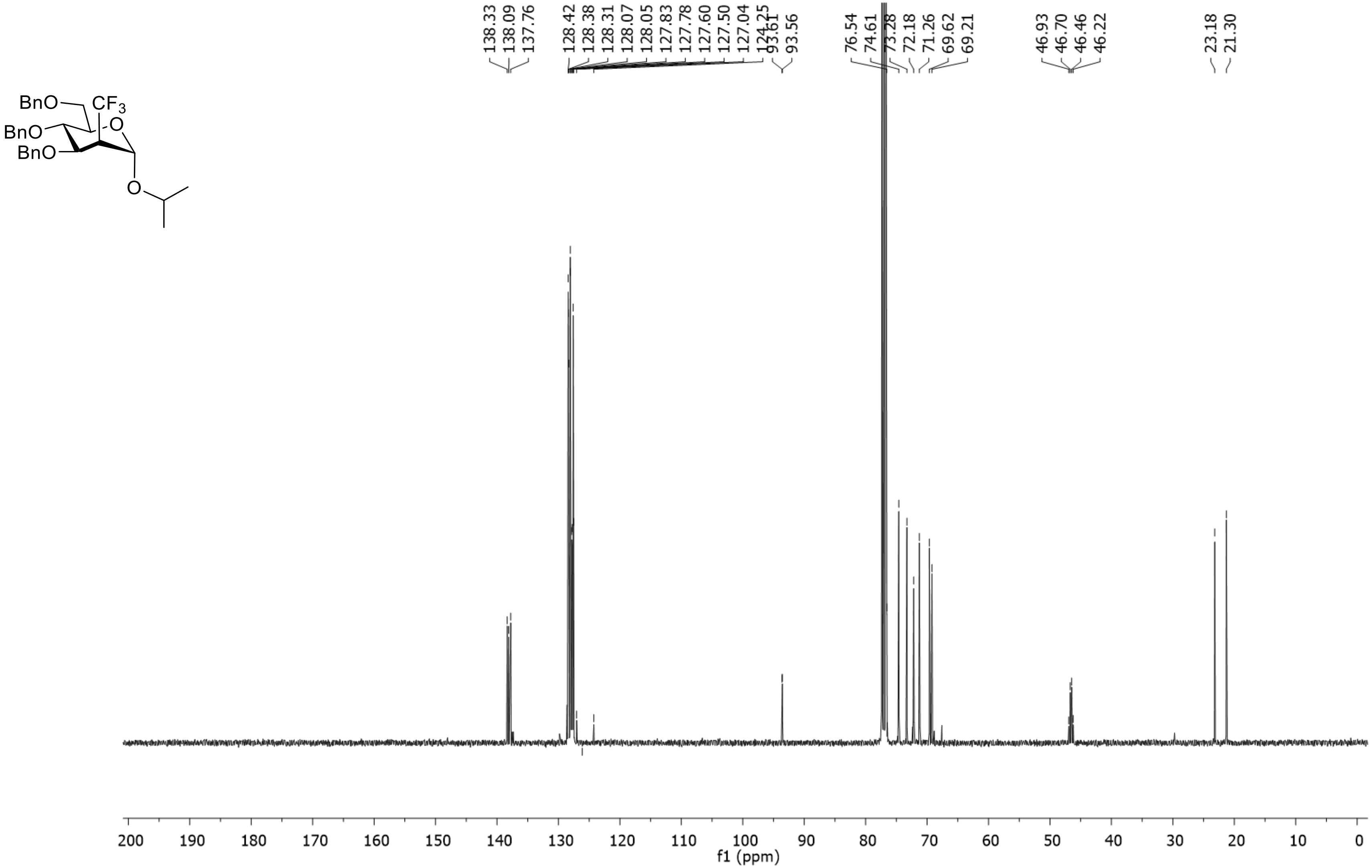


Figure S65. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **13α**

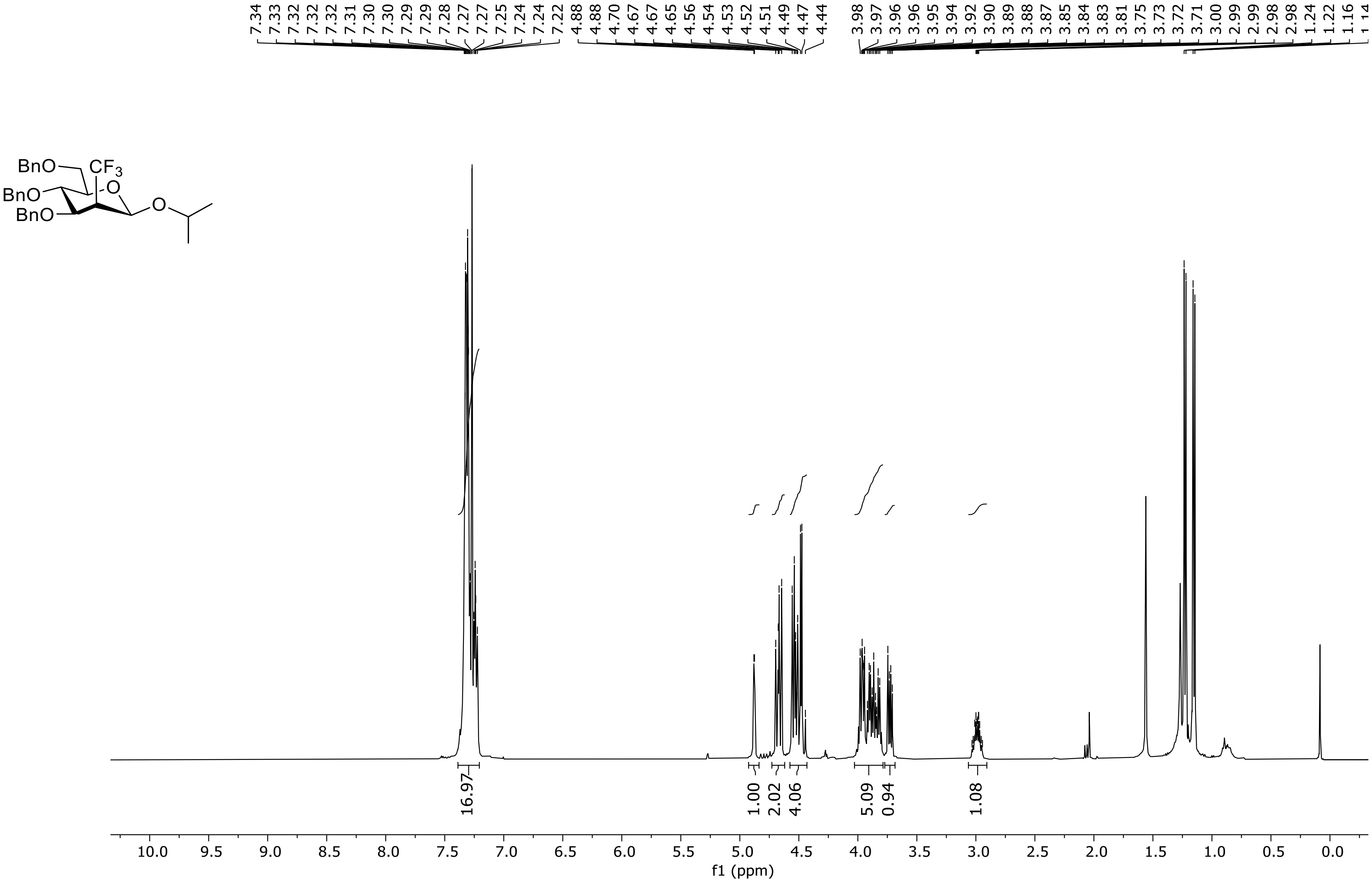


Figure S66. ^{1}H NMR (CDCl$_3$, 400 MHz) of **13β**

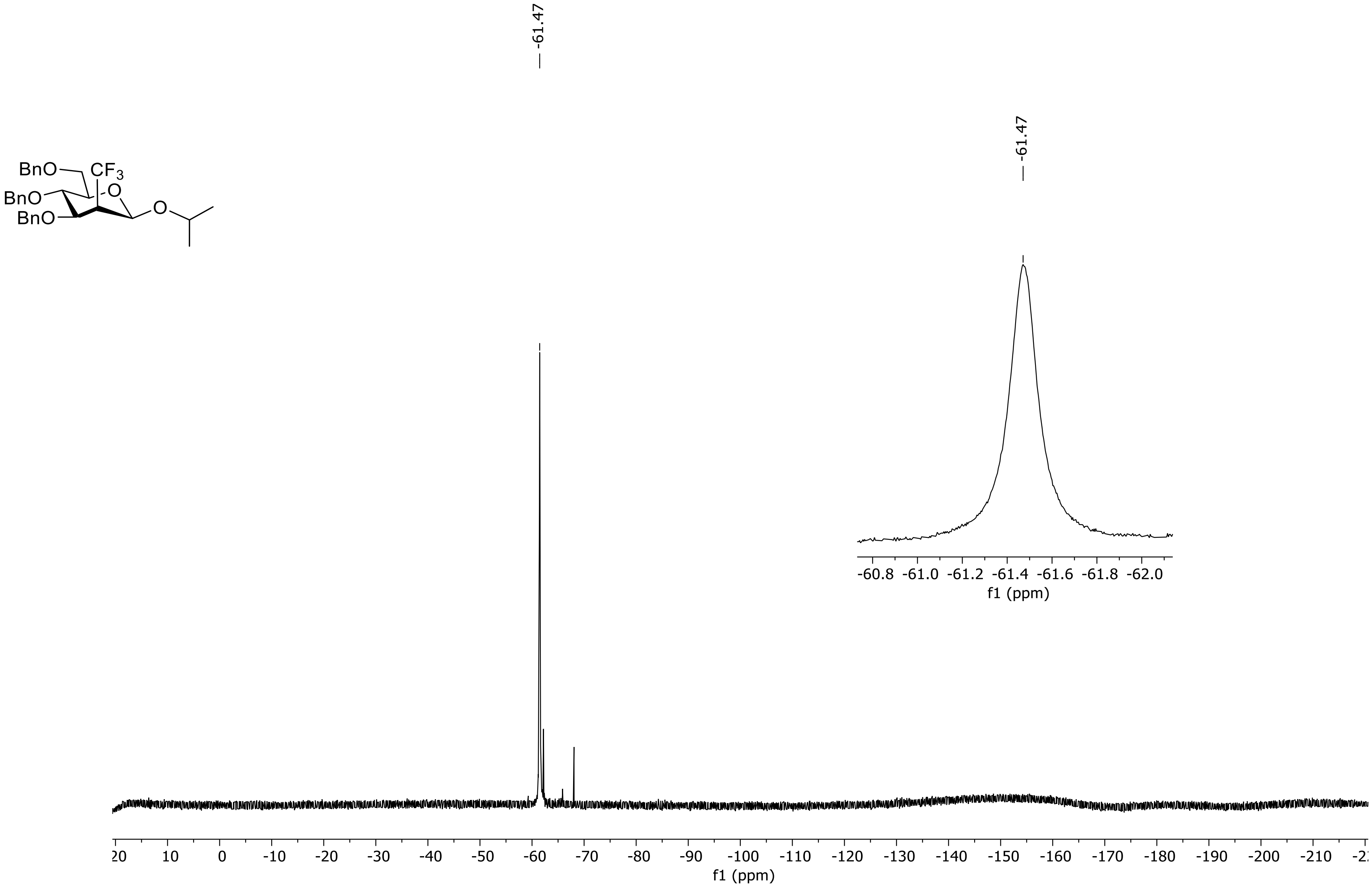


Figure S67. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **13β**

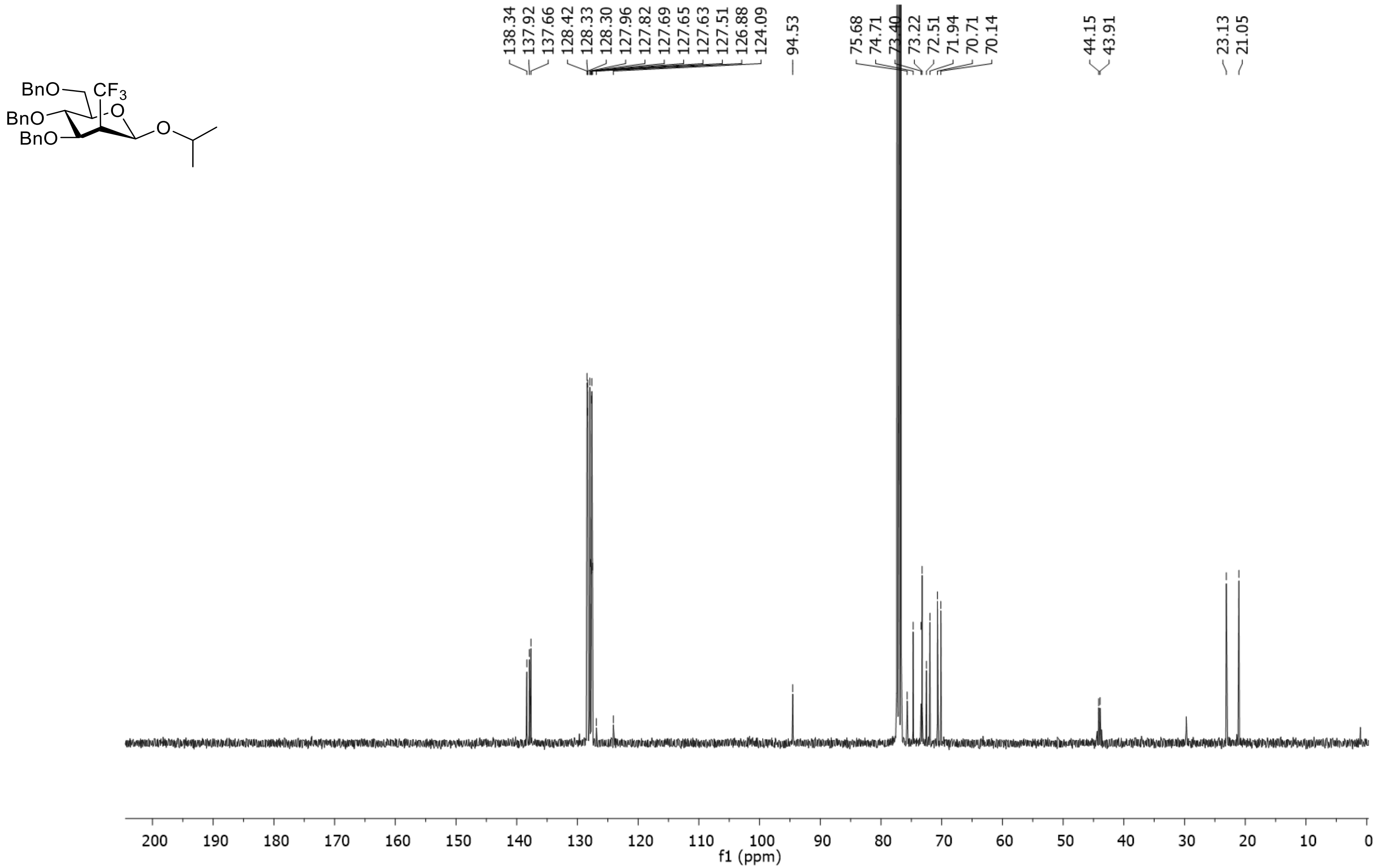


Figure S68. ^{13}C NMR ($CDCl_3$, 100.6 MHz) of **13β**

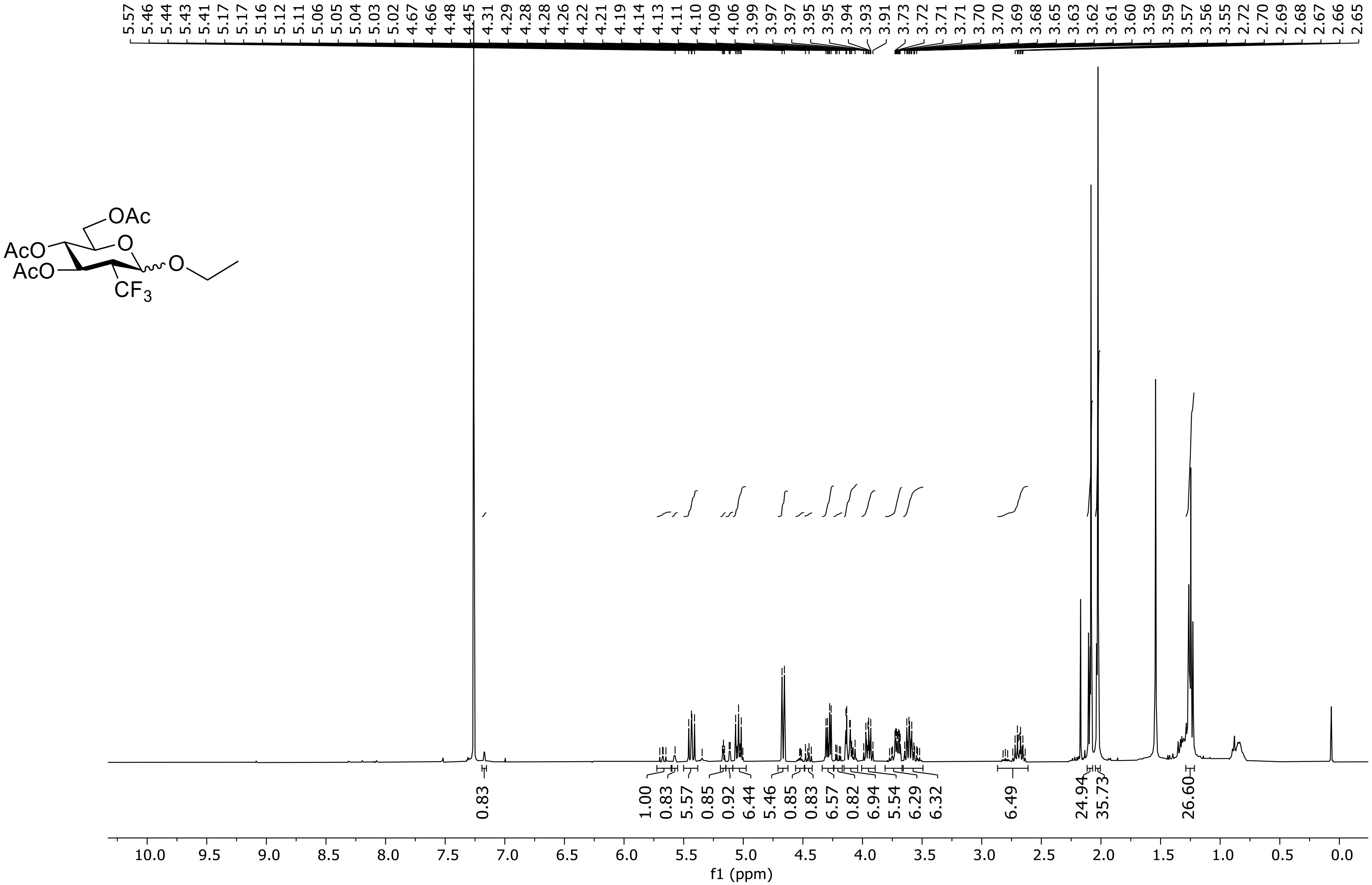


Figure S69. ^{1}H NMR (CDCl$_3$, 400 MHz) of **18α/β**

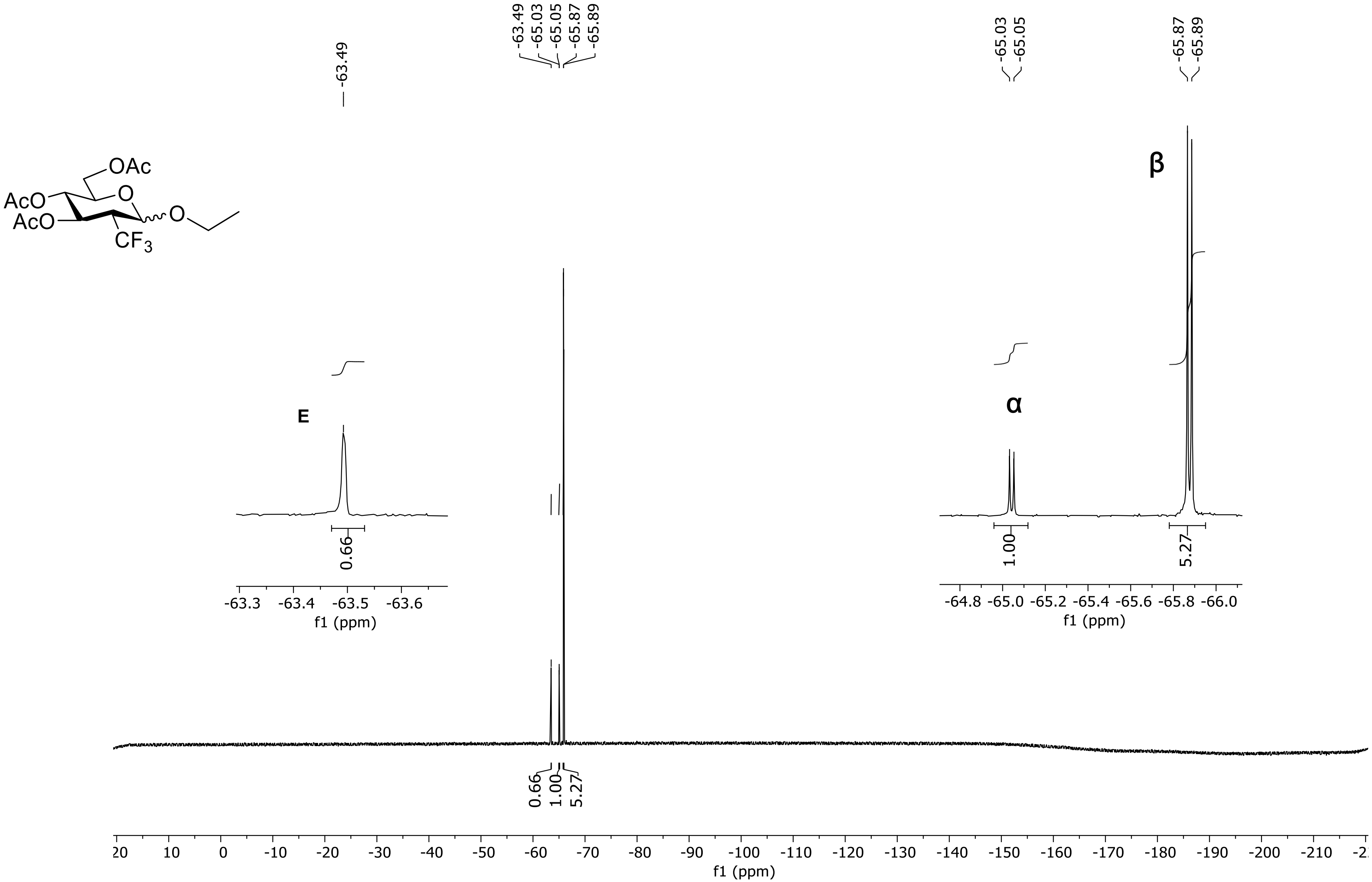


Figure S70. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **18α/β**

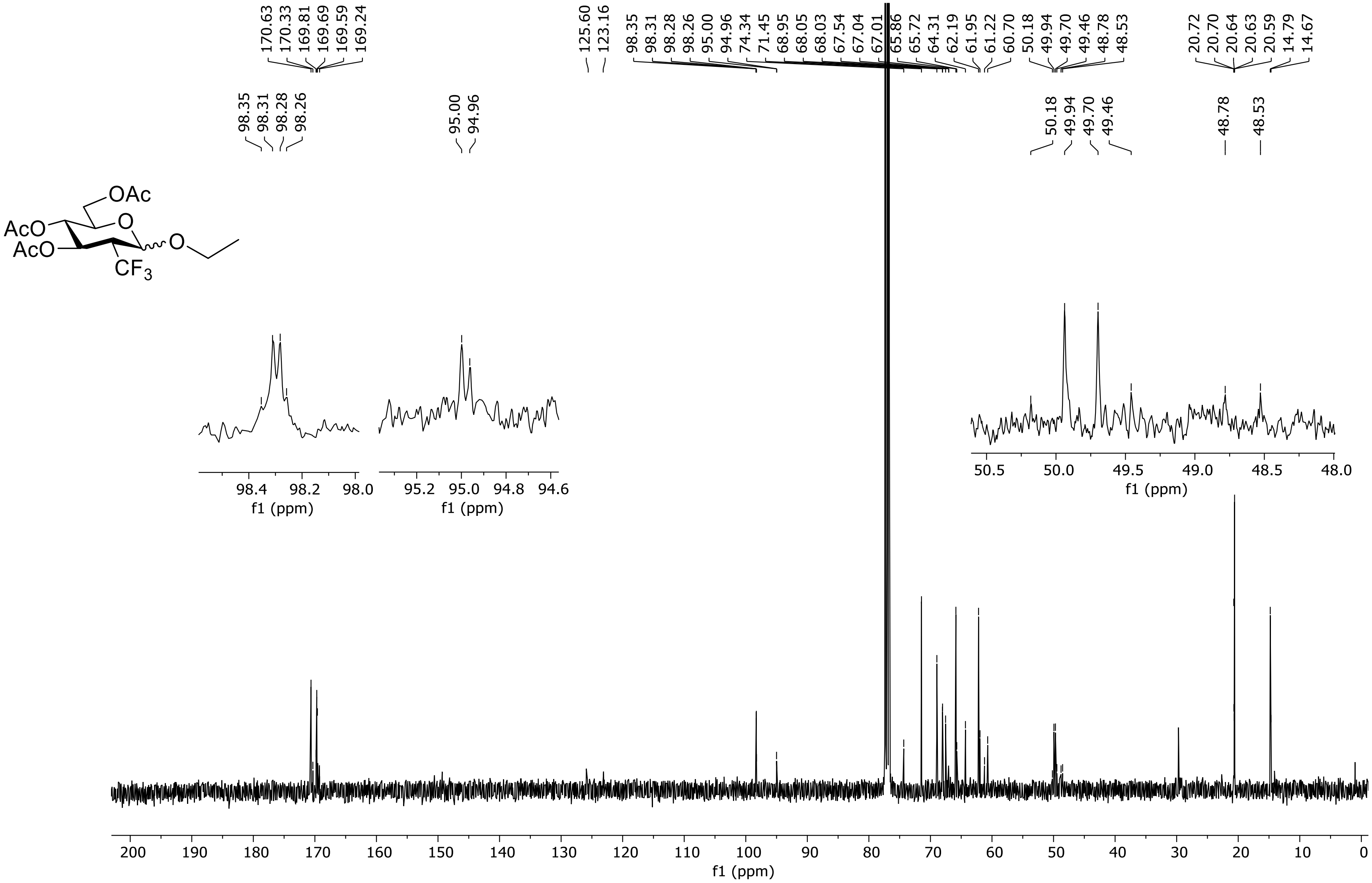


Figure S71. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **18α/β**

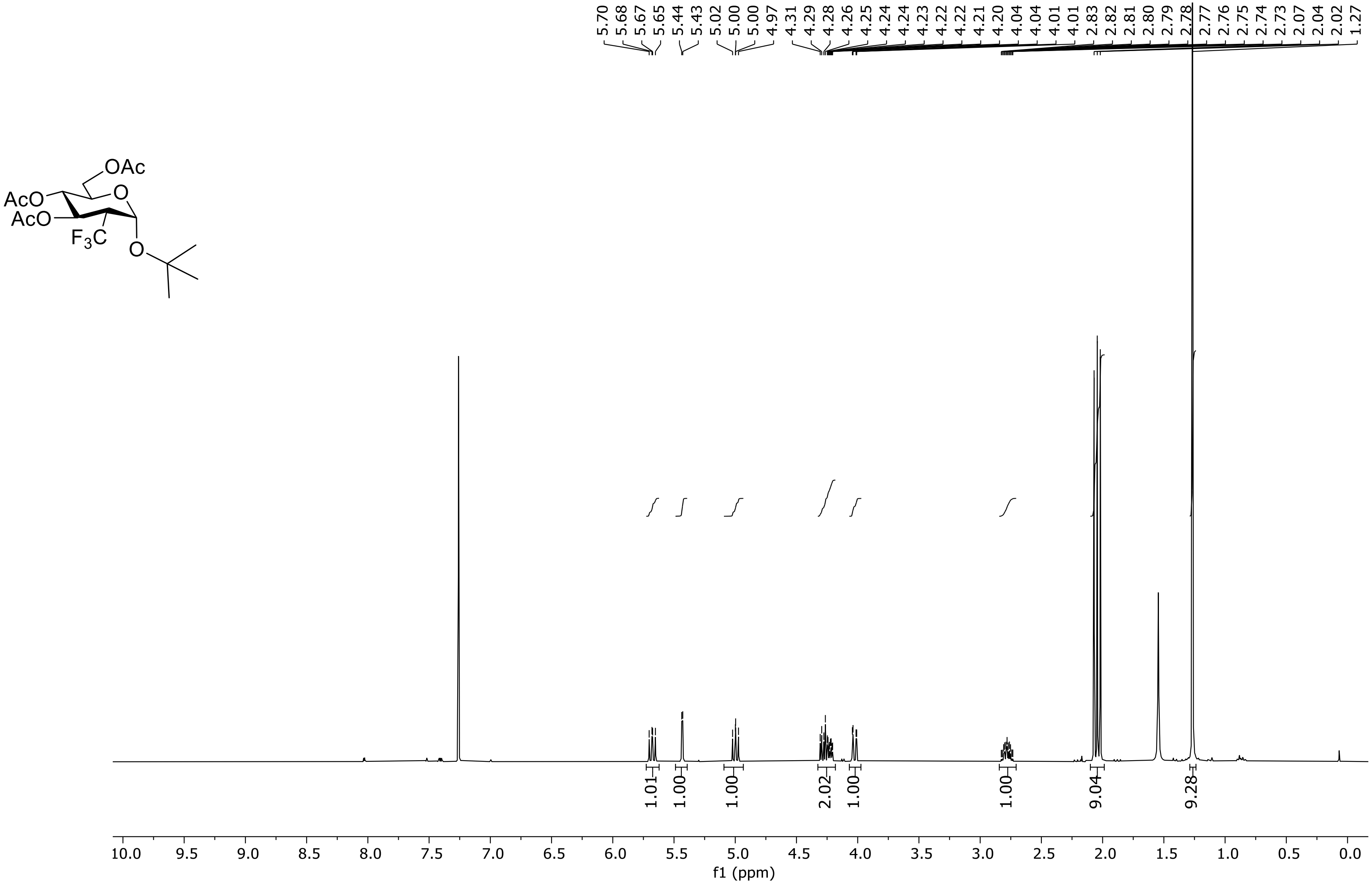


Figure S72. ^{1}H NMR (CDCl$_3$, 400 MHz) of **19α**

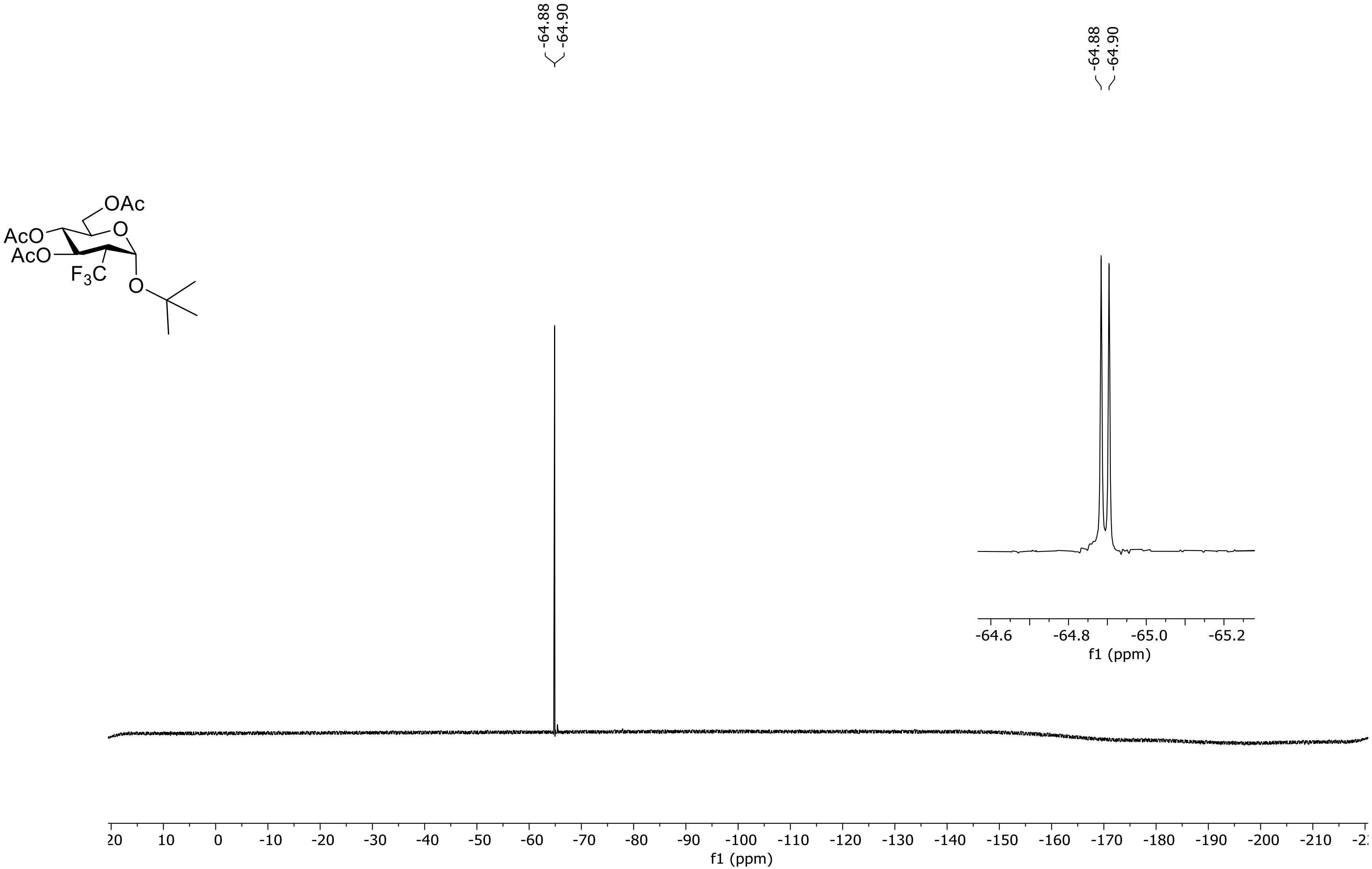


Figure S73. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **19α**

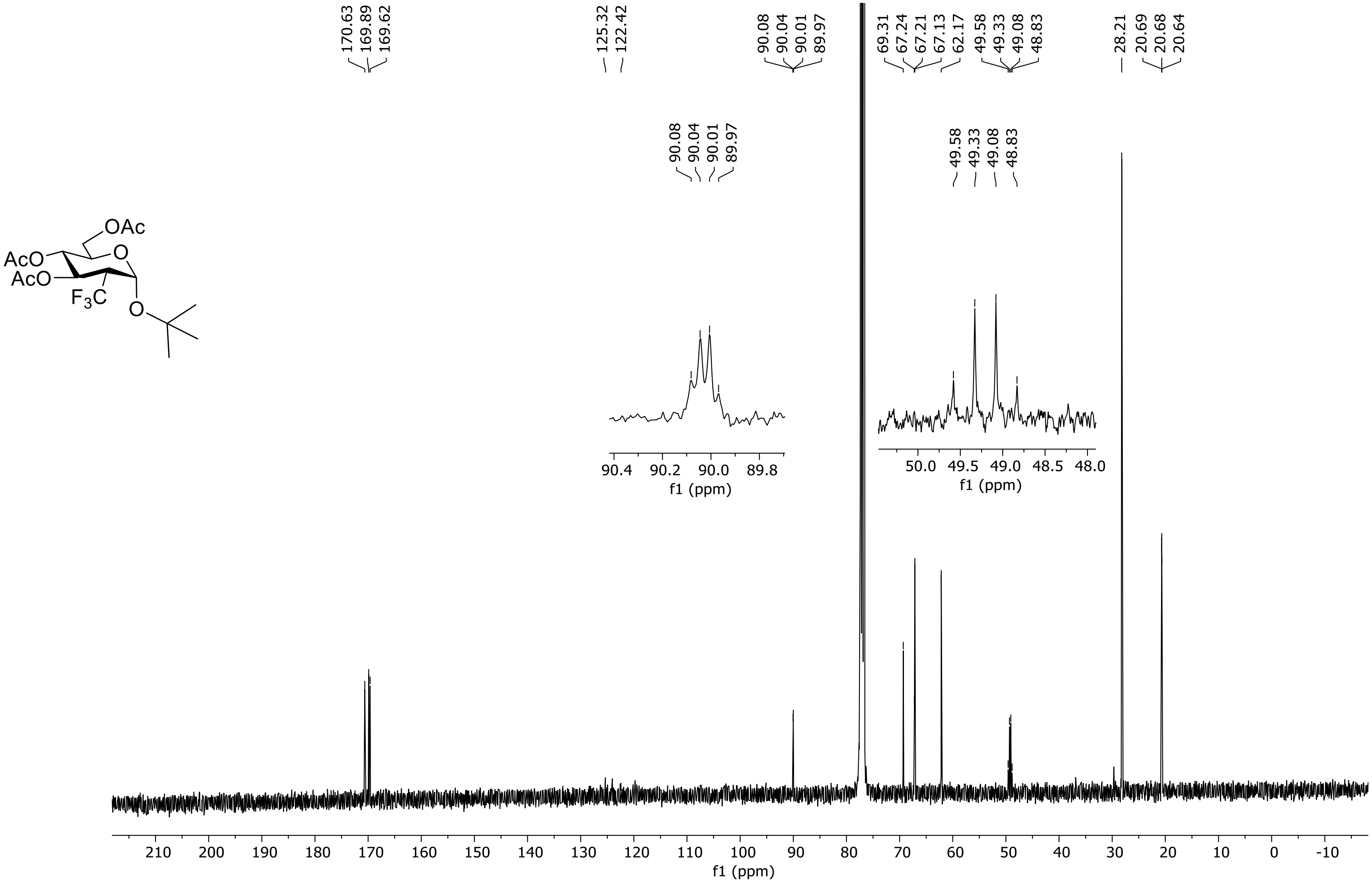


Figure S74. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **19α**

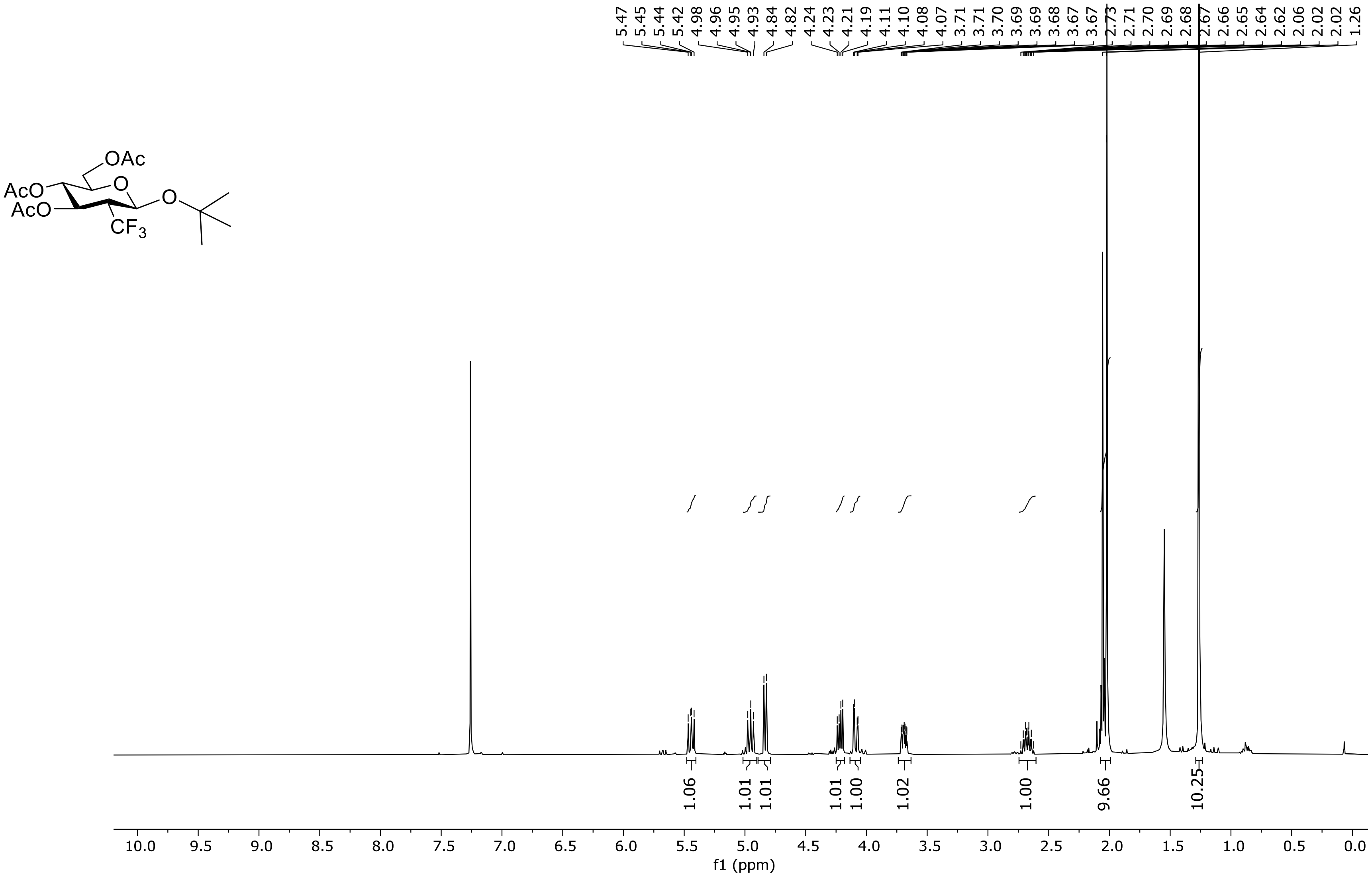


Figure S75. ^{1}H NMR (CDCl$_3$, 400 MHz) of **19α/β**

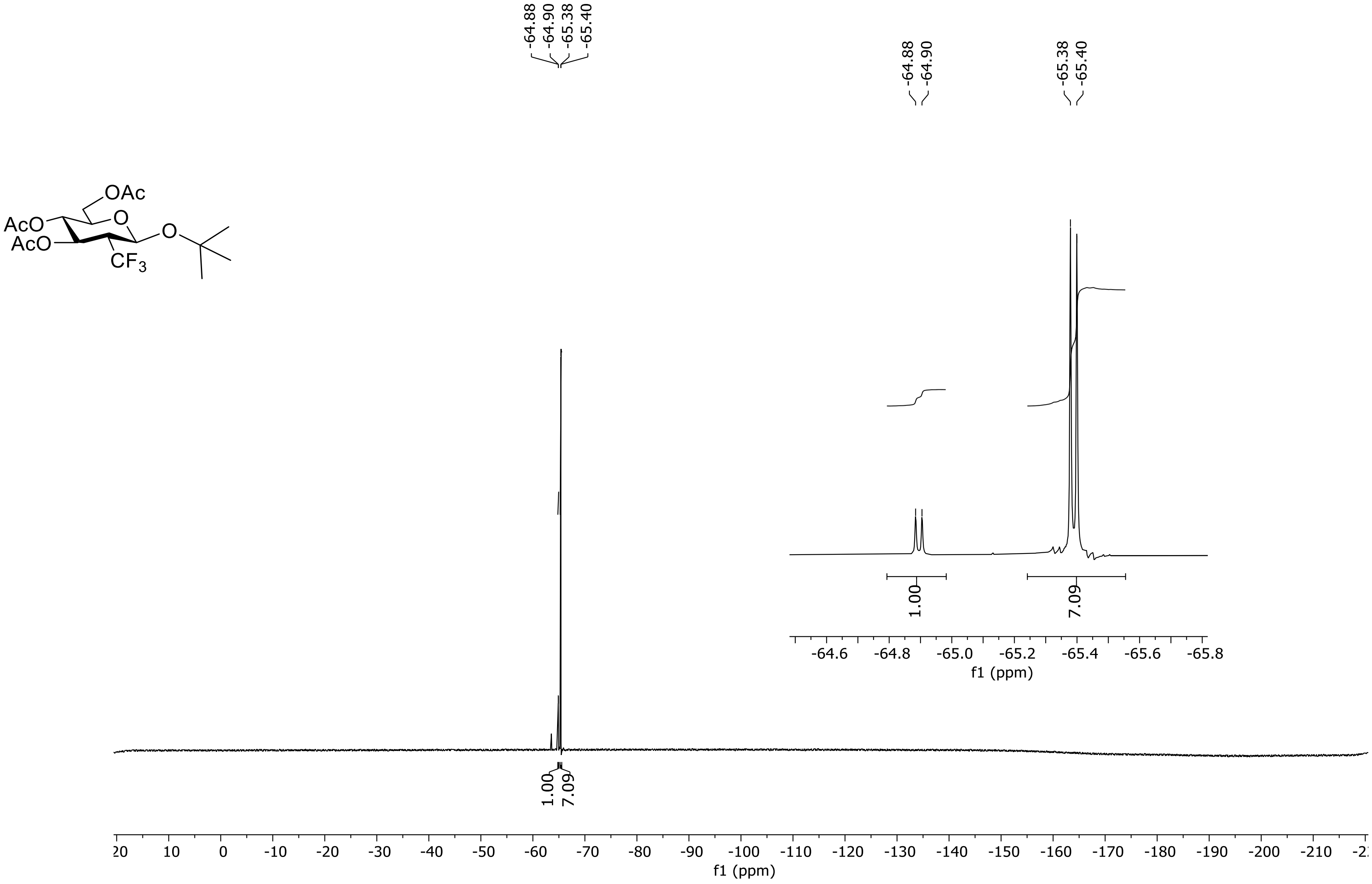


Figure S76. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **19α/β**

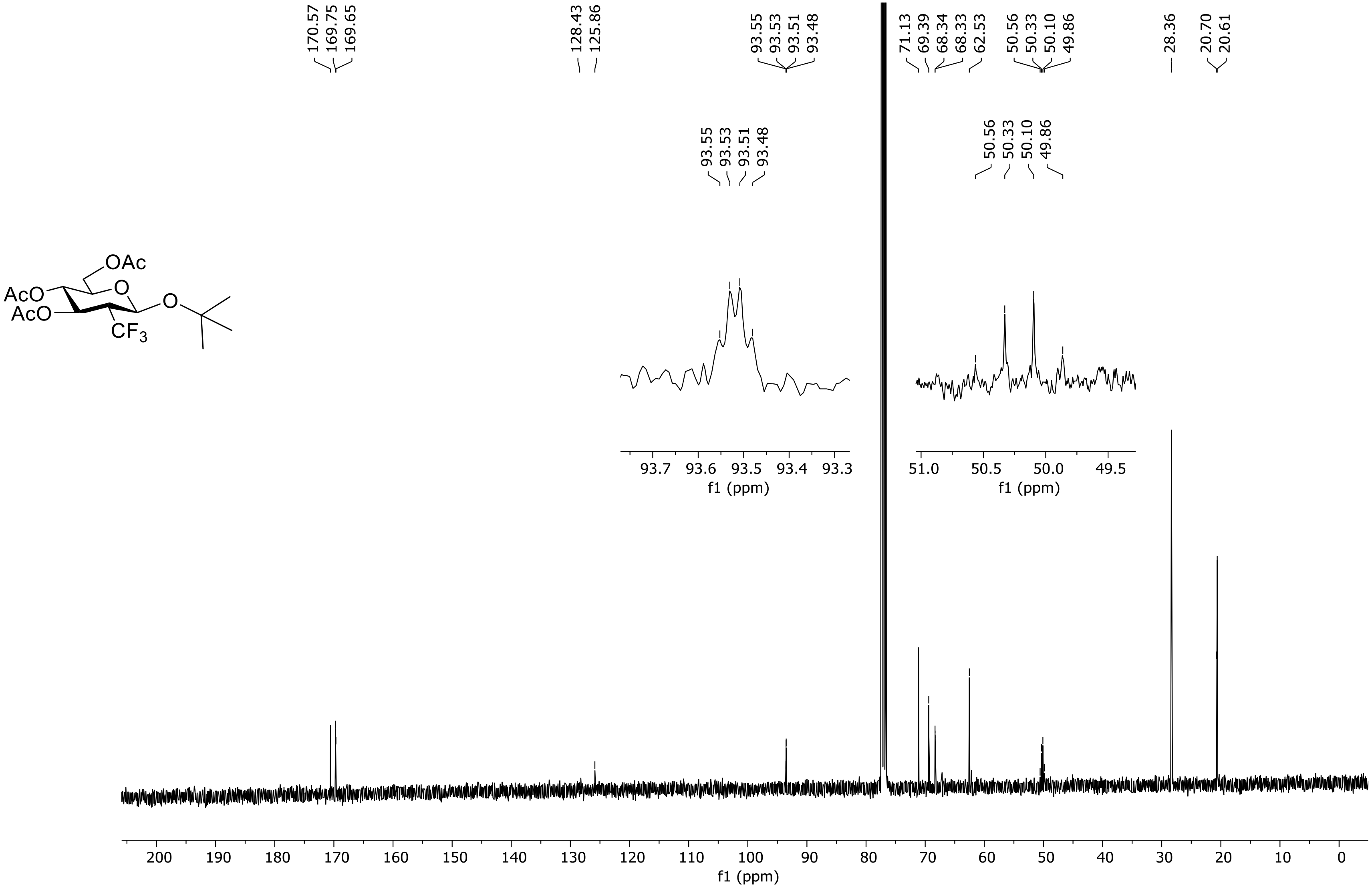


Figure S77. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **19α/β**

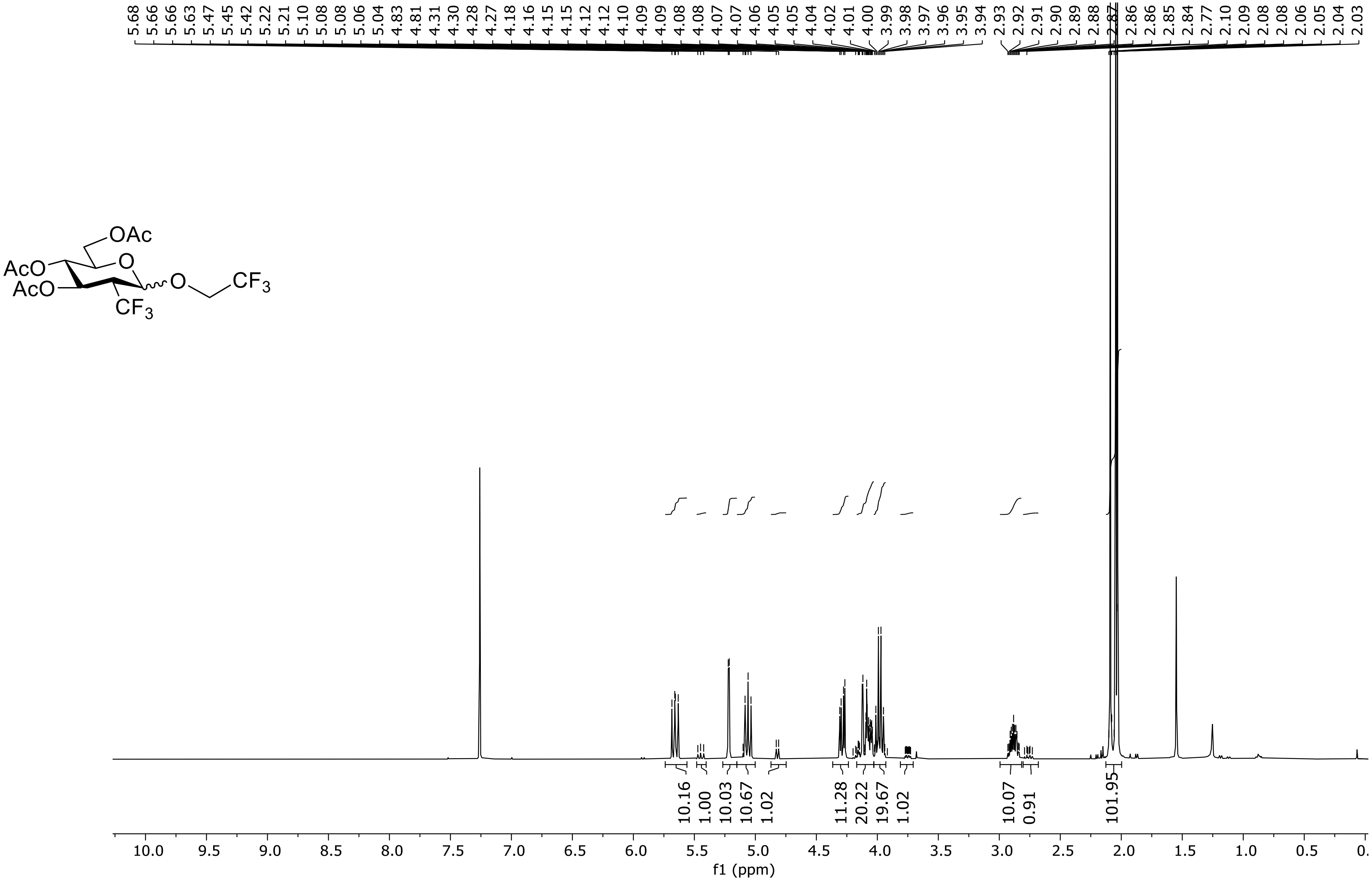


Figure S78. ^{1}H NMR (CDCl$_3$, 400 MHz) of **20α/β**

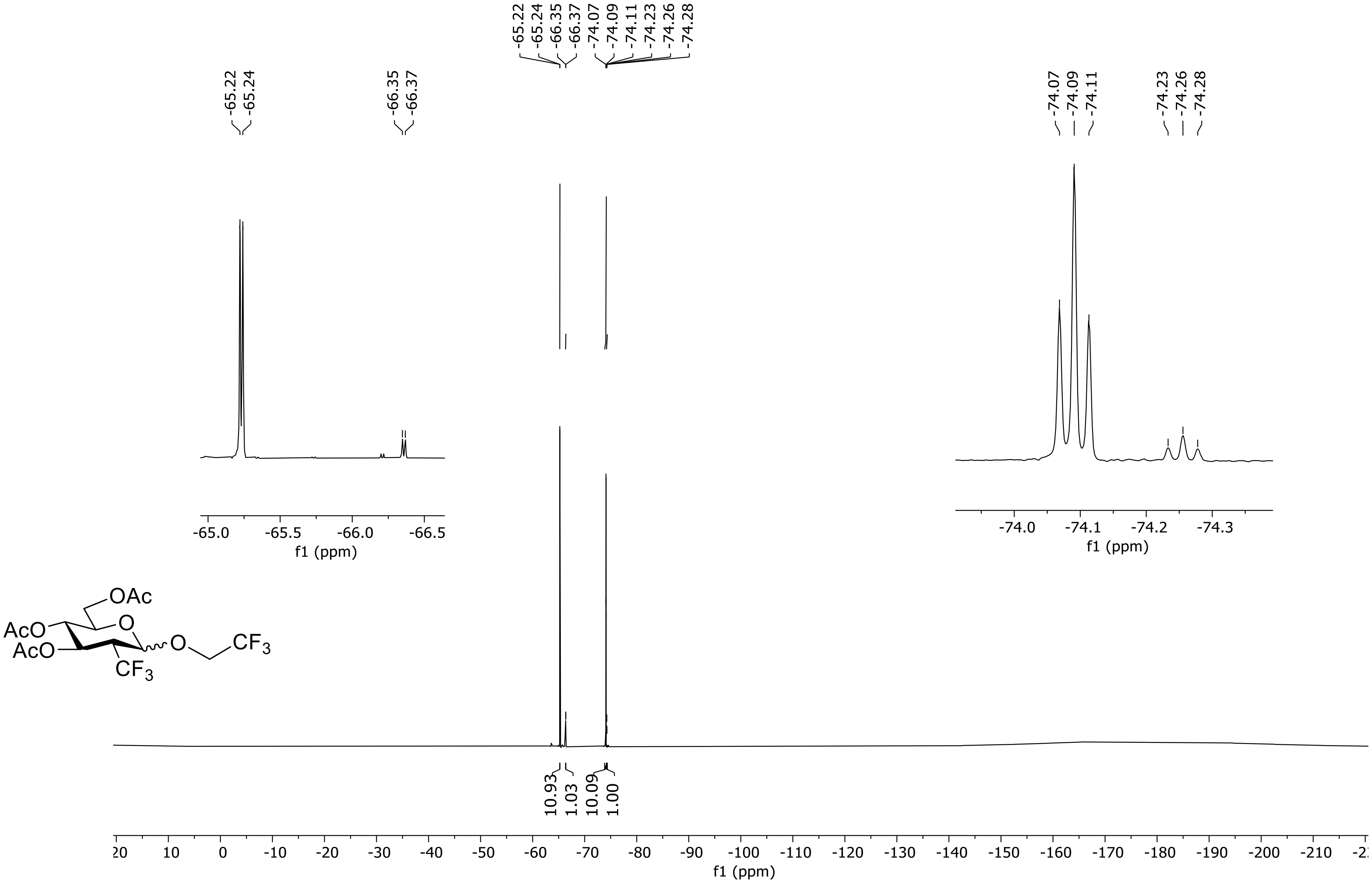


Figure S79. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **20α/β**

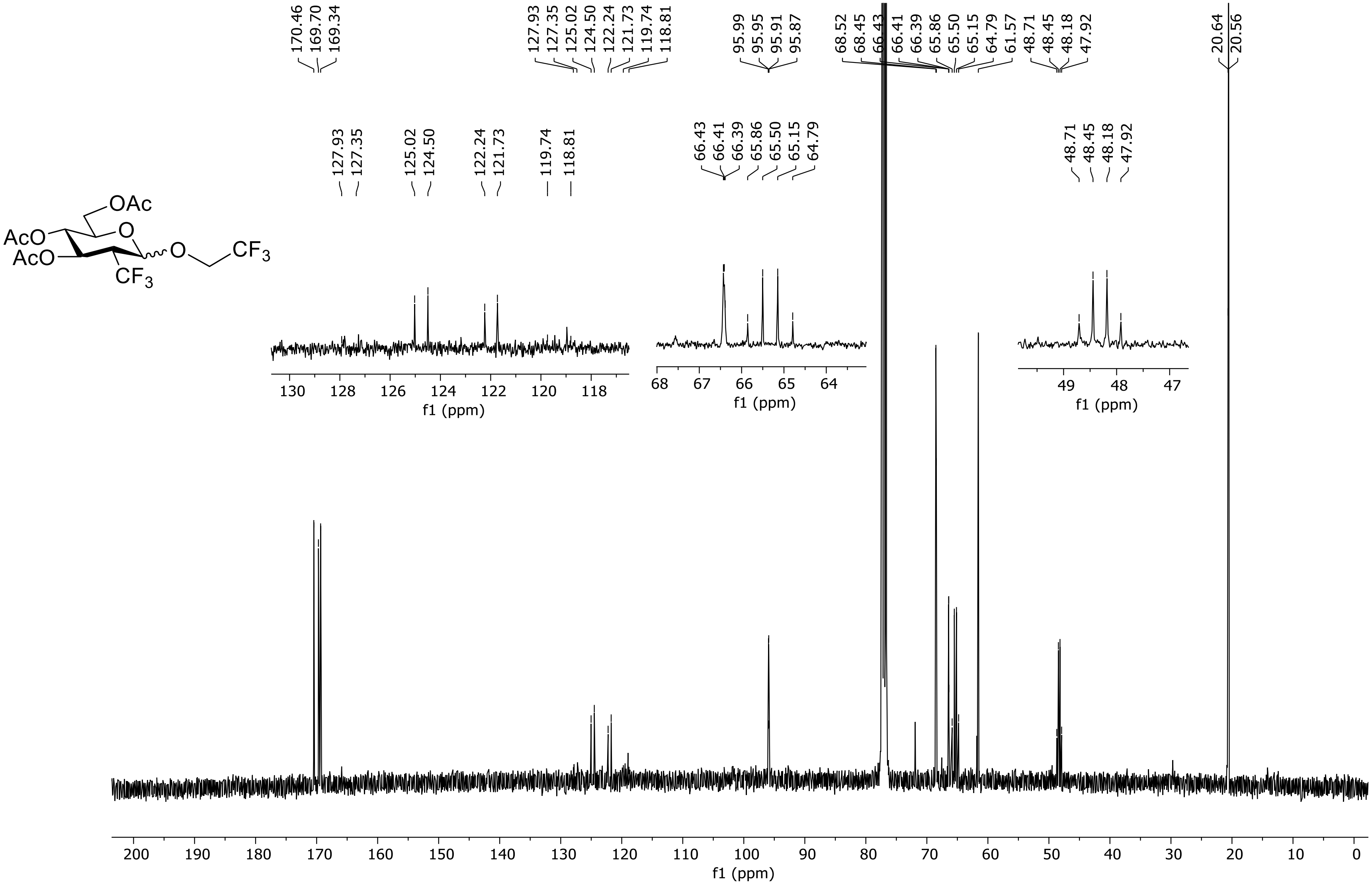


Figure S80. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **20α/β**

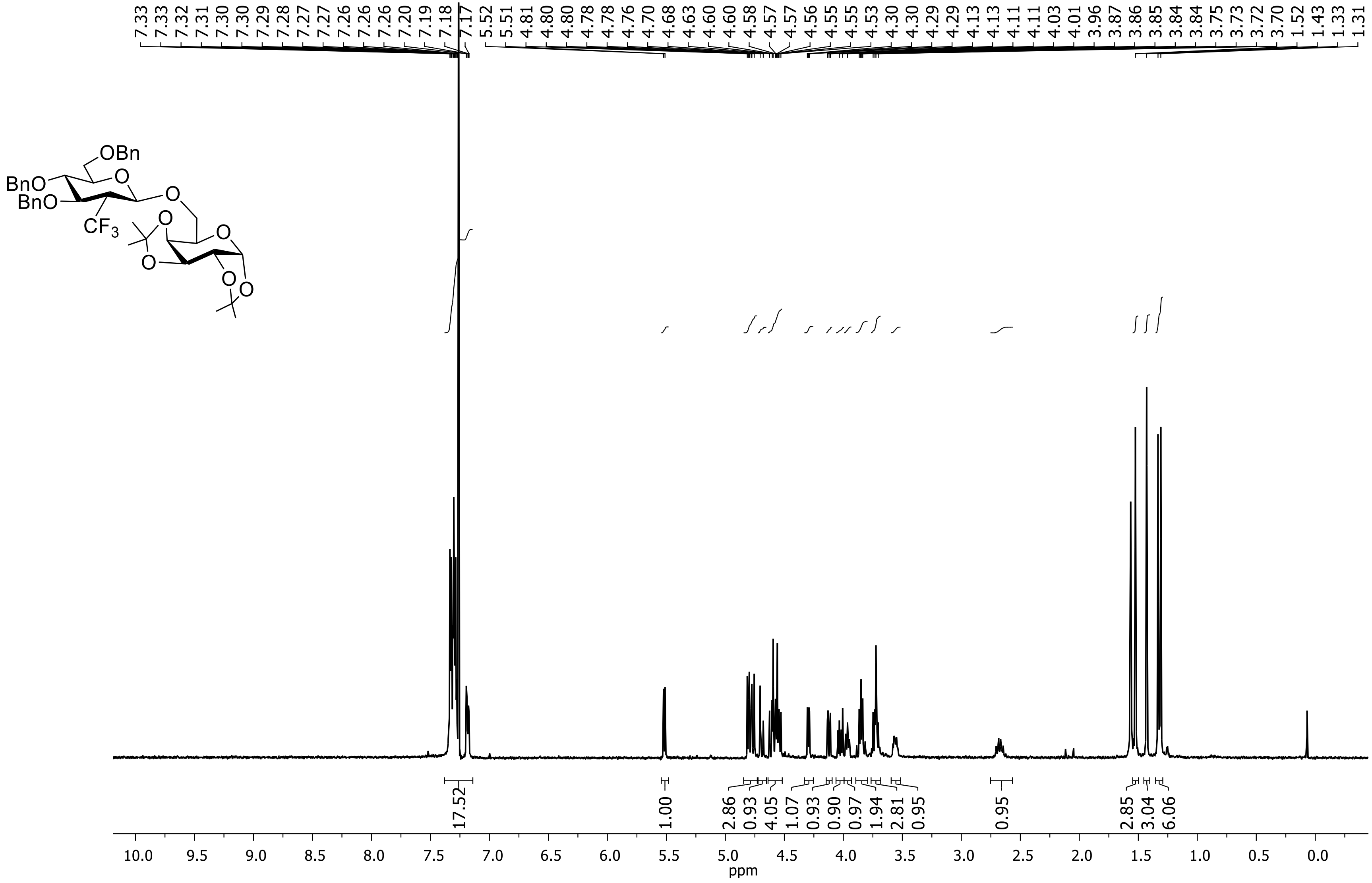


Figure S81. ^{1}H NMR ($CDCl_3$, 400 MHz) of **21β**

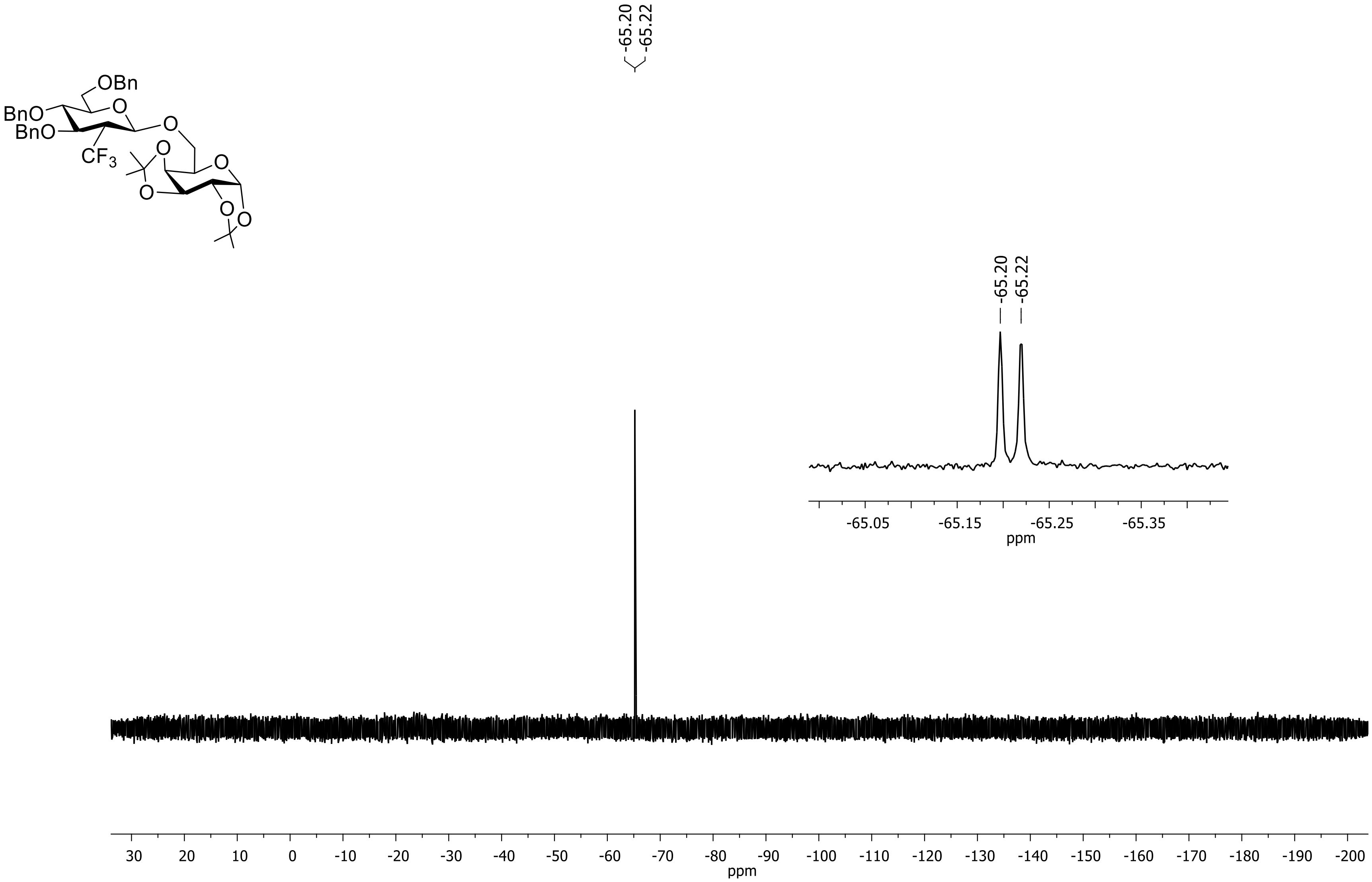


Figure S82. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **21β**

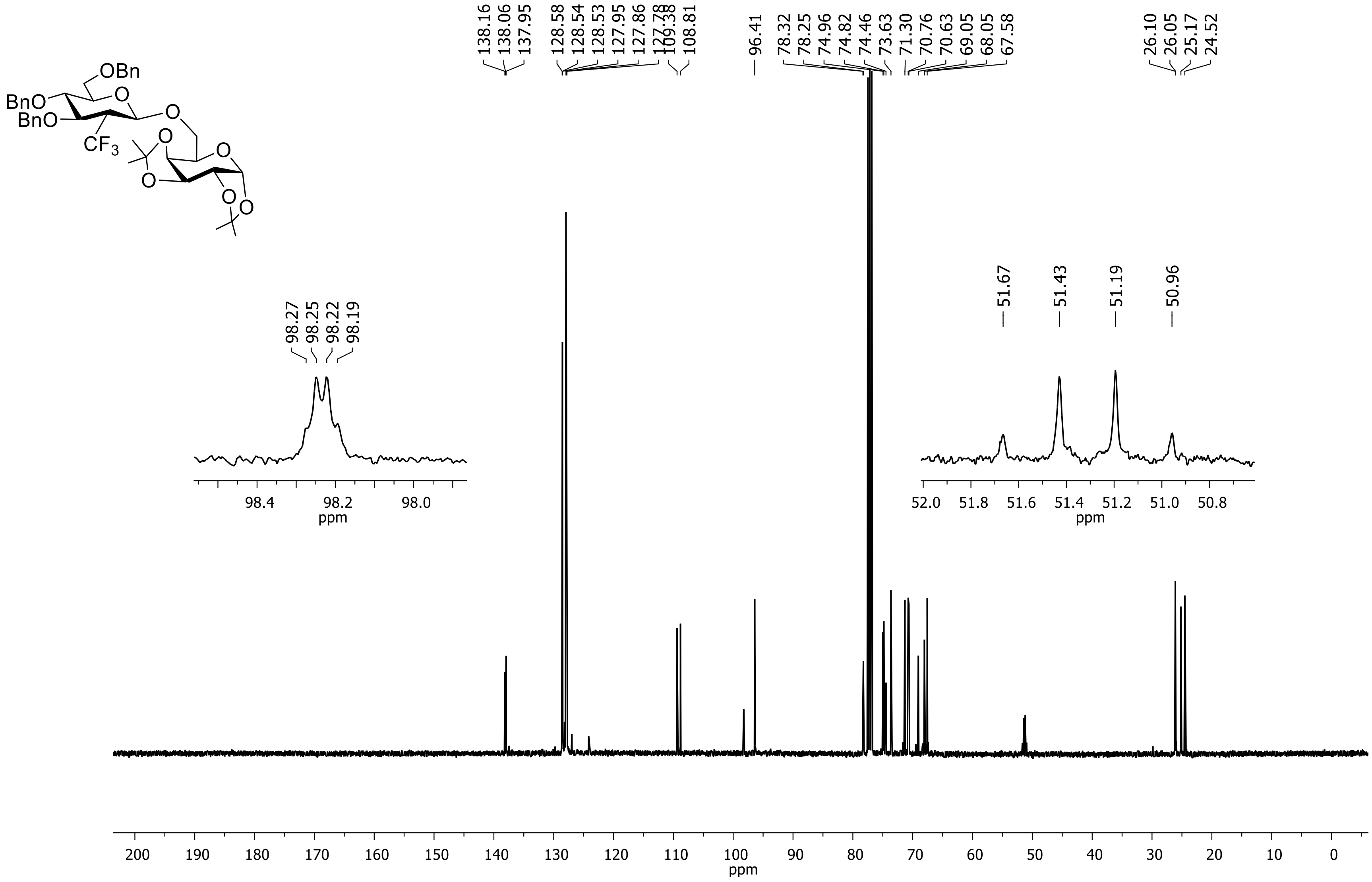


Figure S83. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **21β**

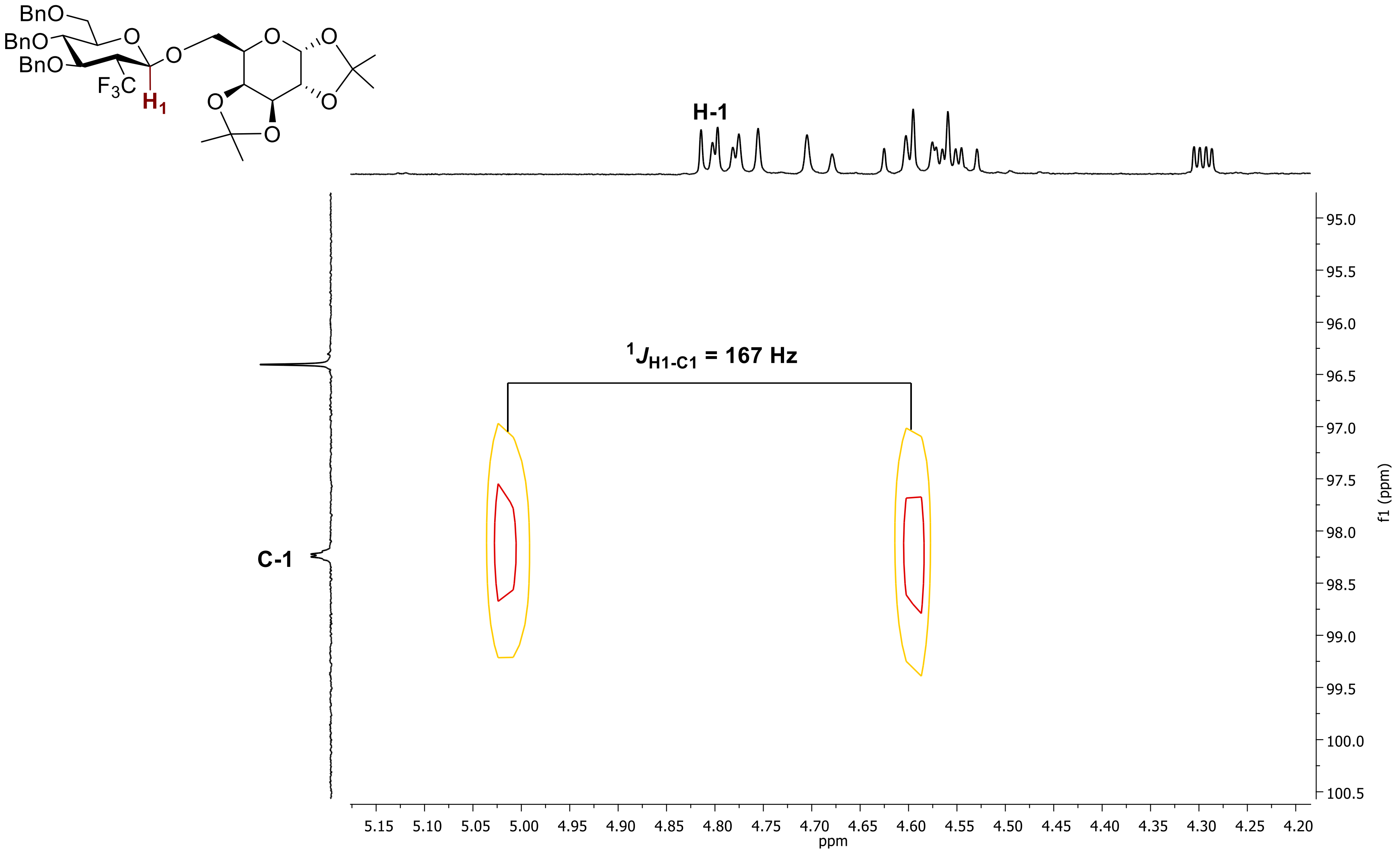


Figure S84. ^{1}H-coupled HSQC (CDCl$_3$, 400 MHz) of **21β**

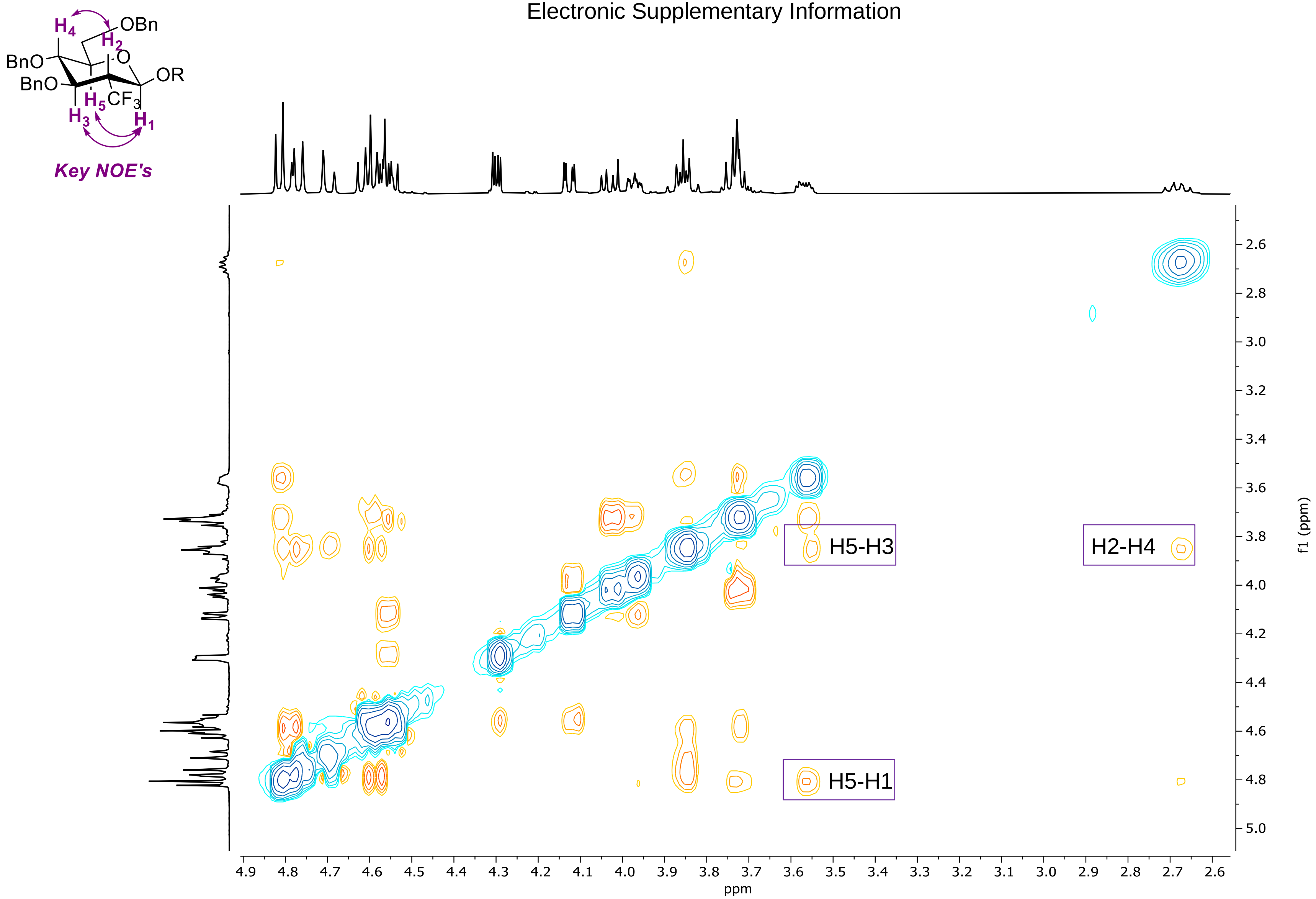


Figure S85. 2D NOESY ($CDCl_3$, 400 MHz) of **21**β

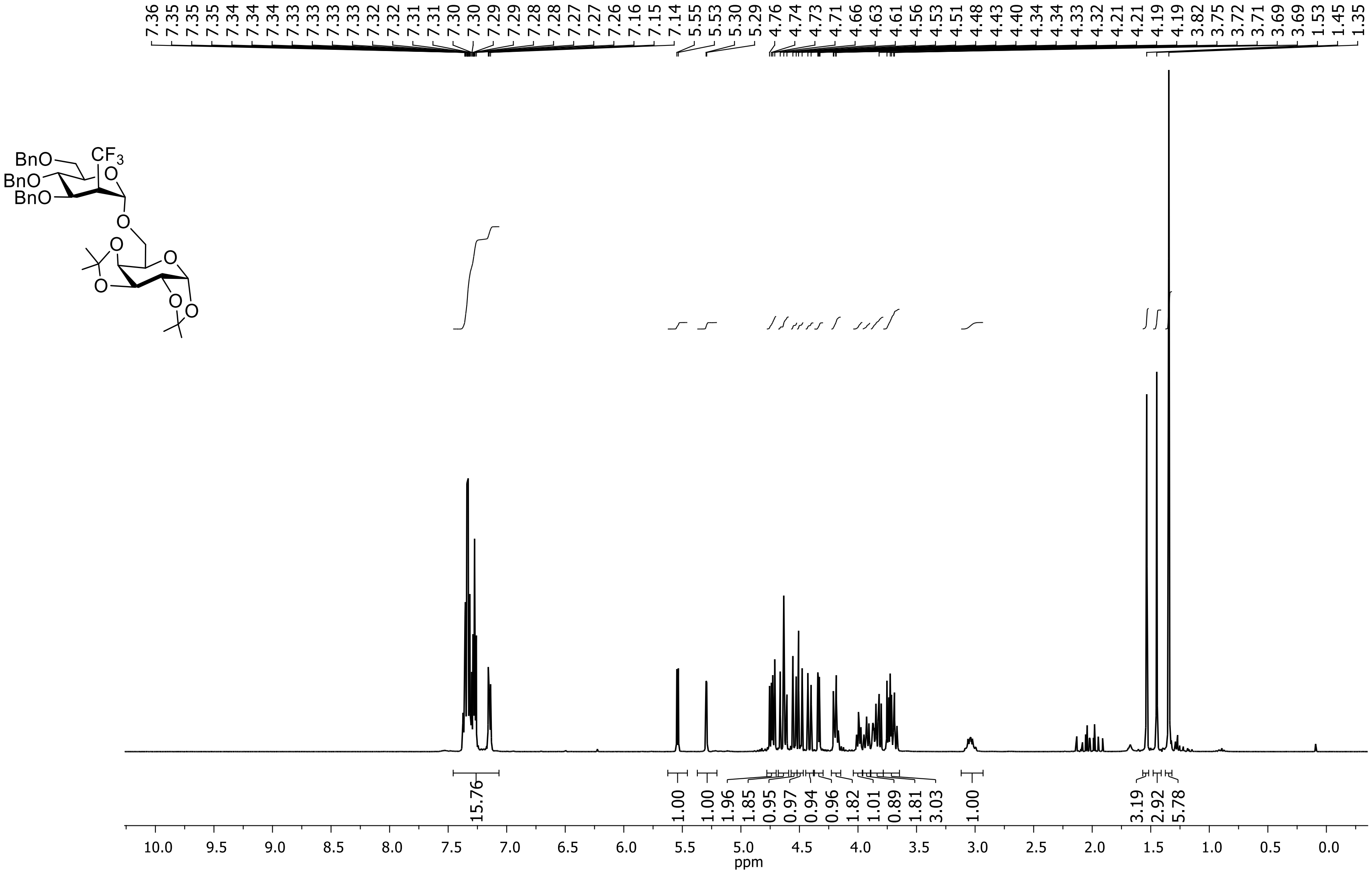


Figure S86. ^{1}H NMR (CDCl$_3$, 400 MHz) of **22α**

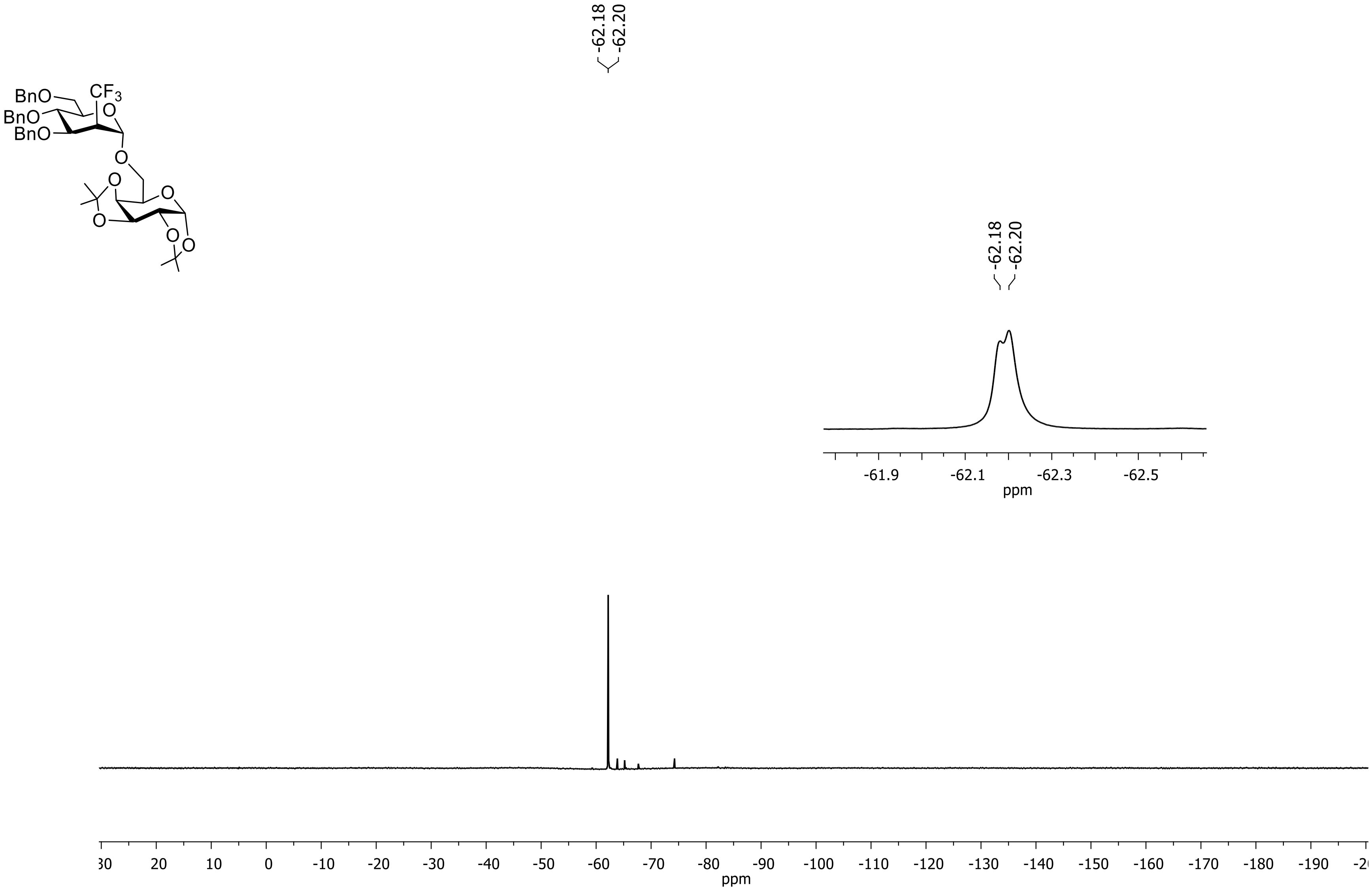


Figure S87. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **22α**

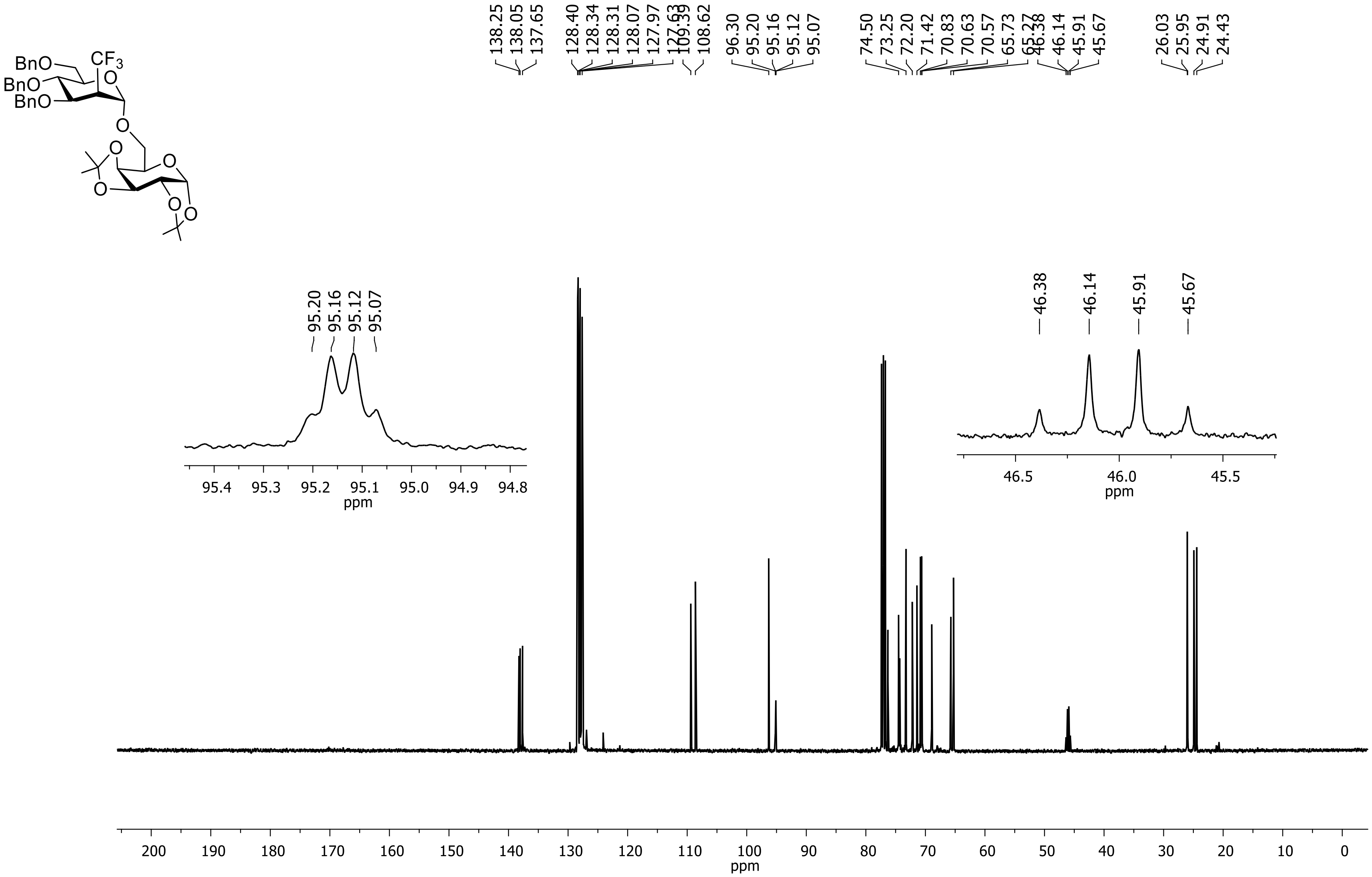


Figure S88. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **22α**

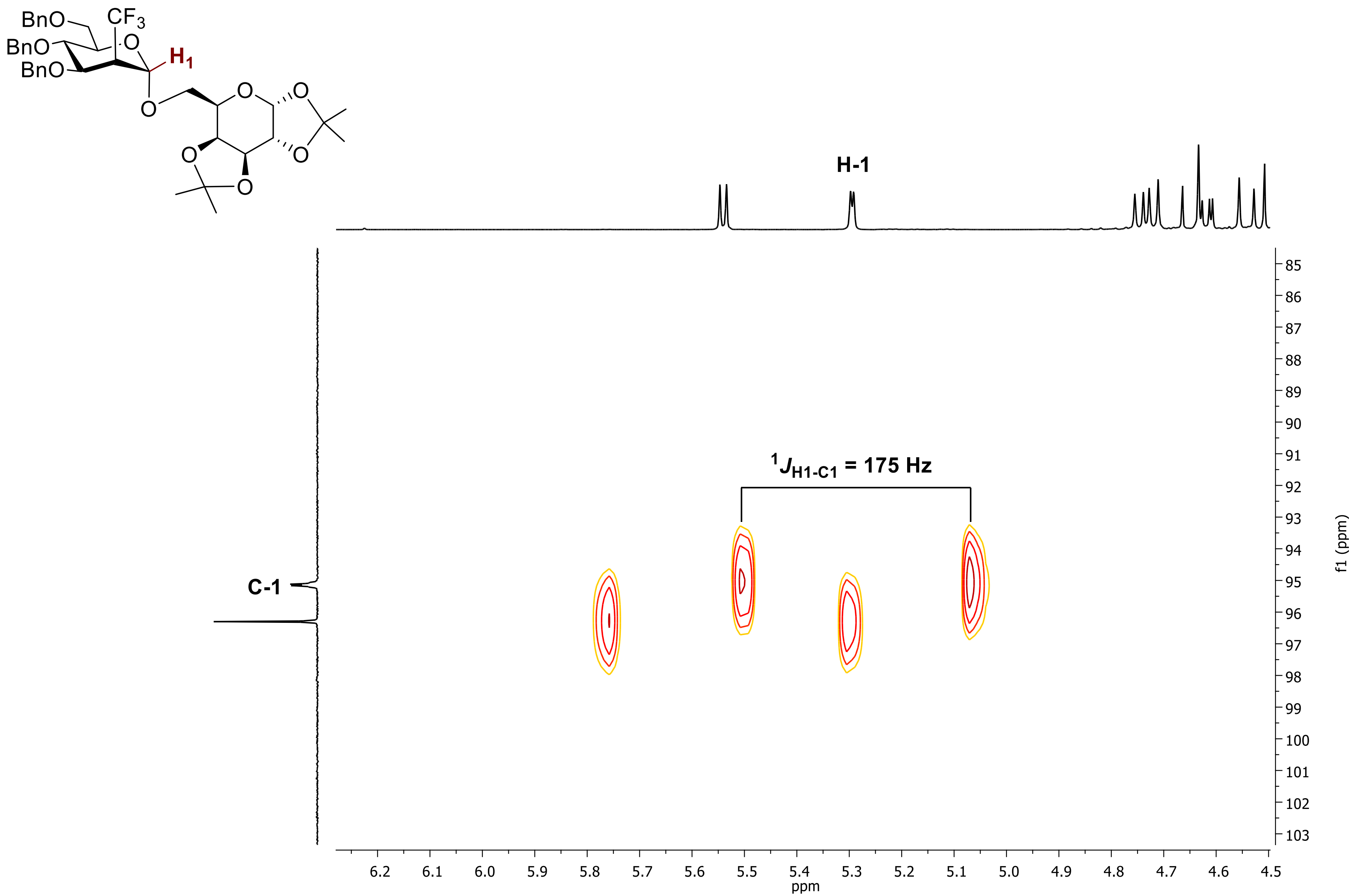


Figure S89. ^{1}H-coupled HSQC (CDCl$_3$, 400 MHz) of **22α**

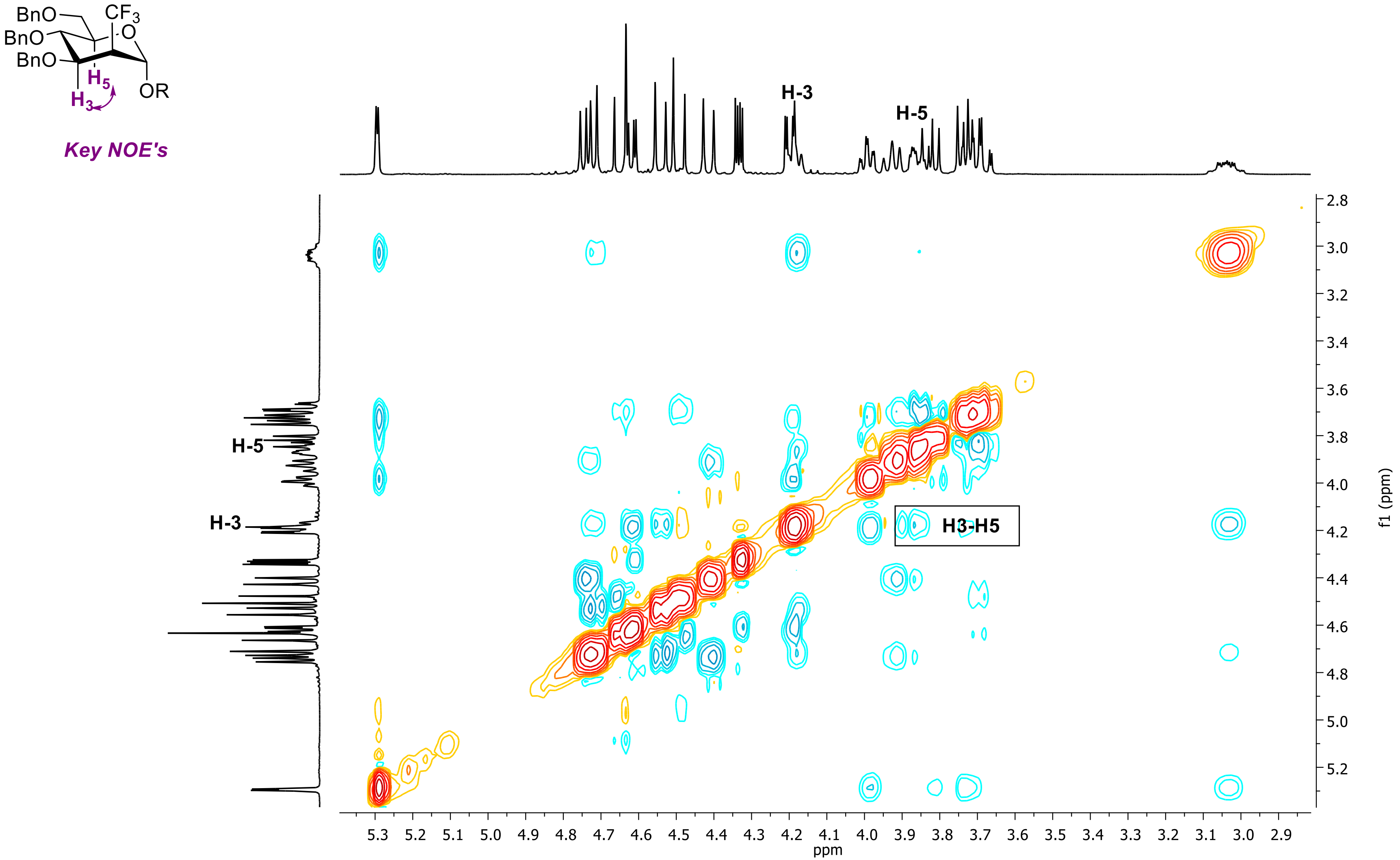


Figure S90 2D NOESY (CDCl$_3$, 400 MHz) of **22α**

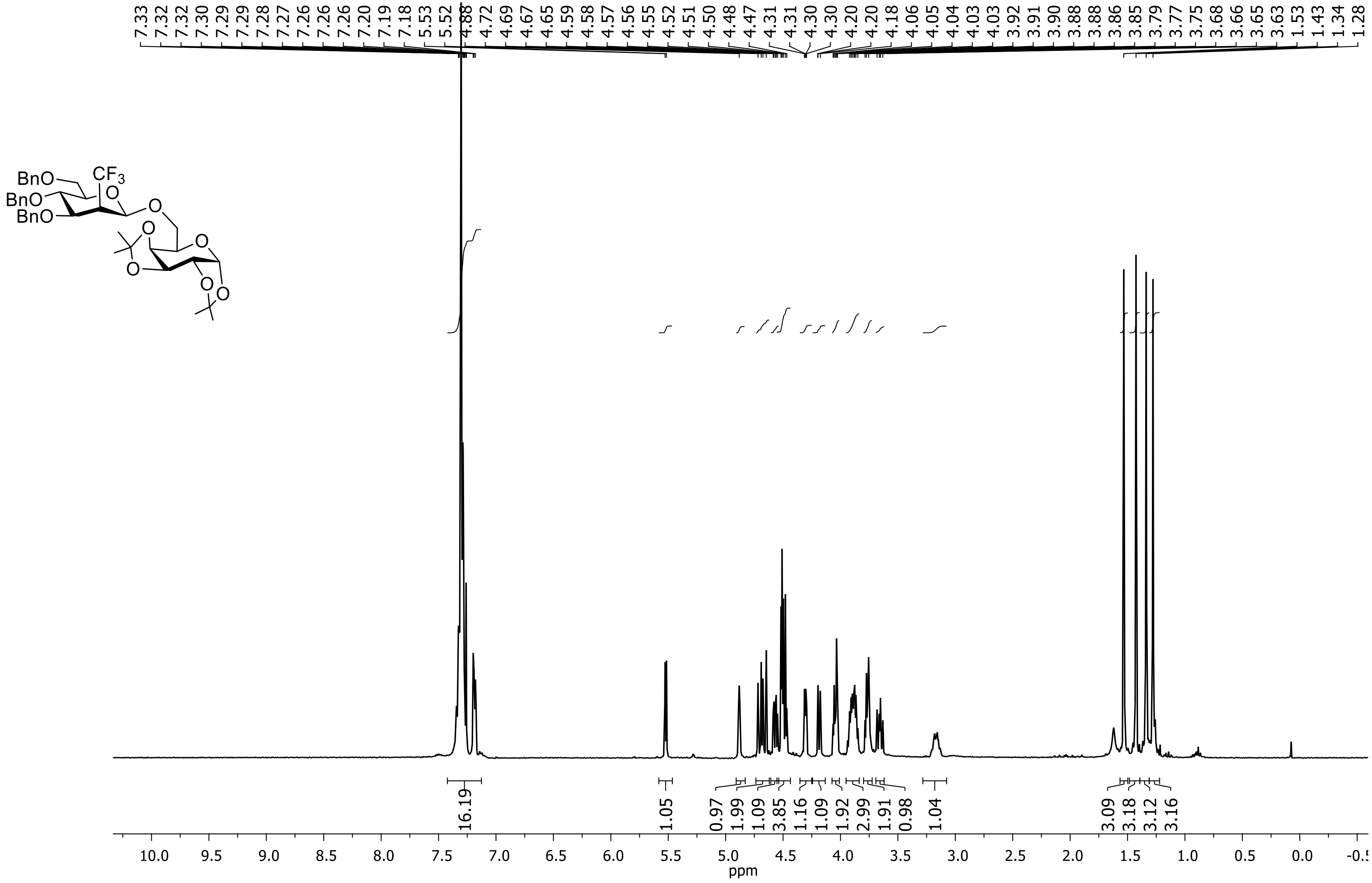


Figure S91. ^{1}H NMR ($CDCl_3$, 400 MHz) of **22β**

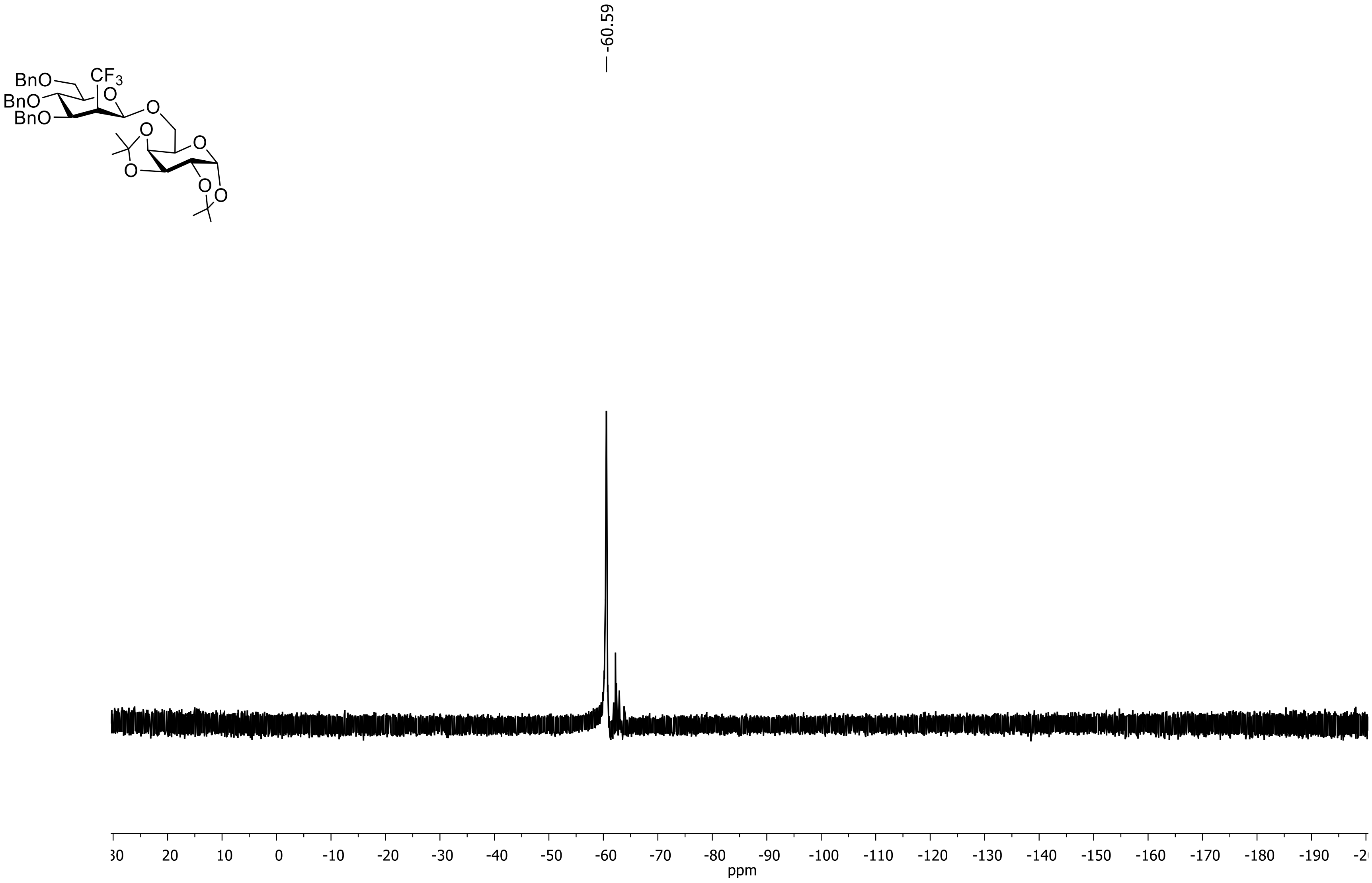


Figure S92. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **22β**

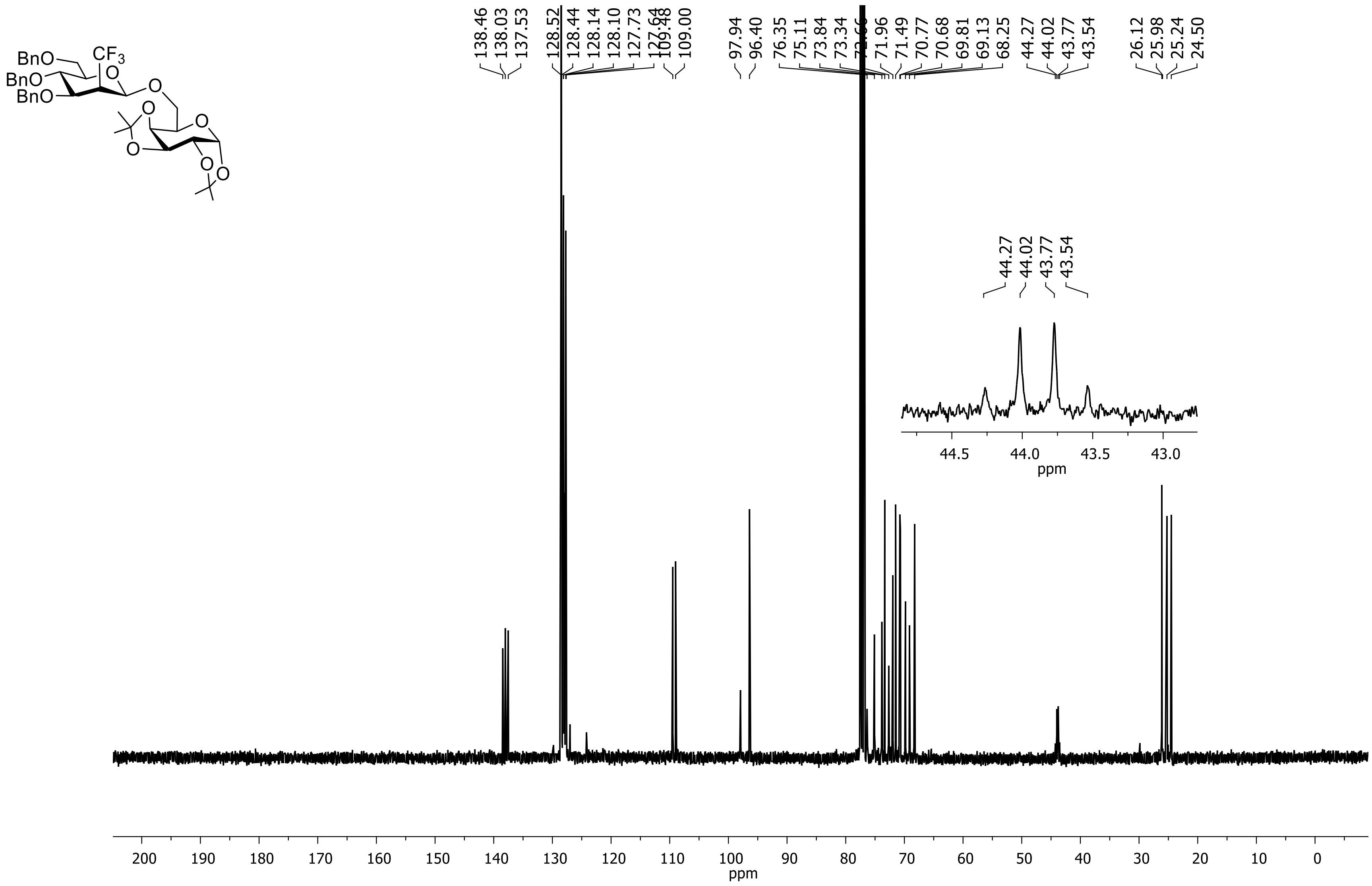


Figure S93. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **22β**

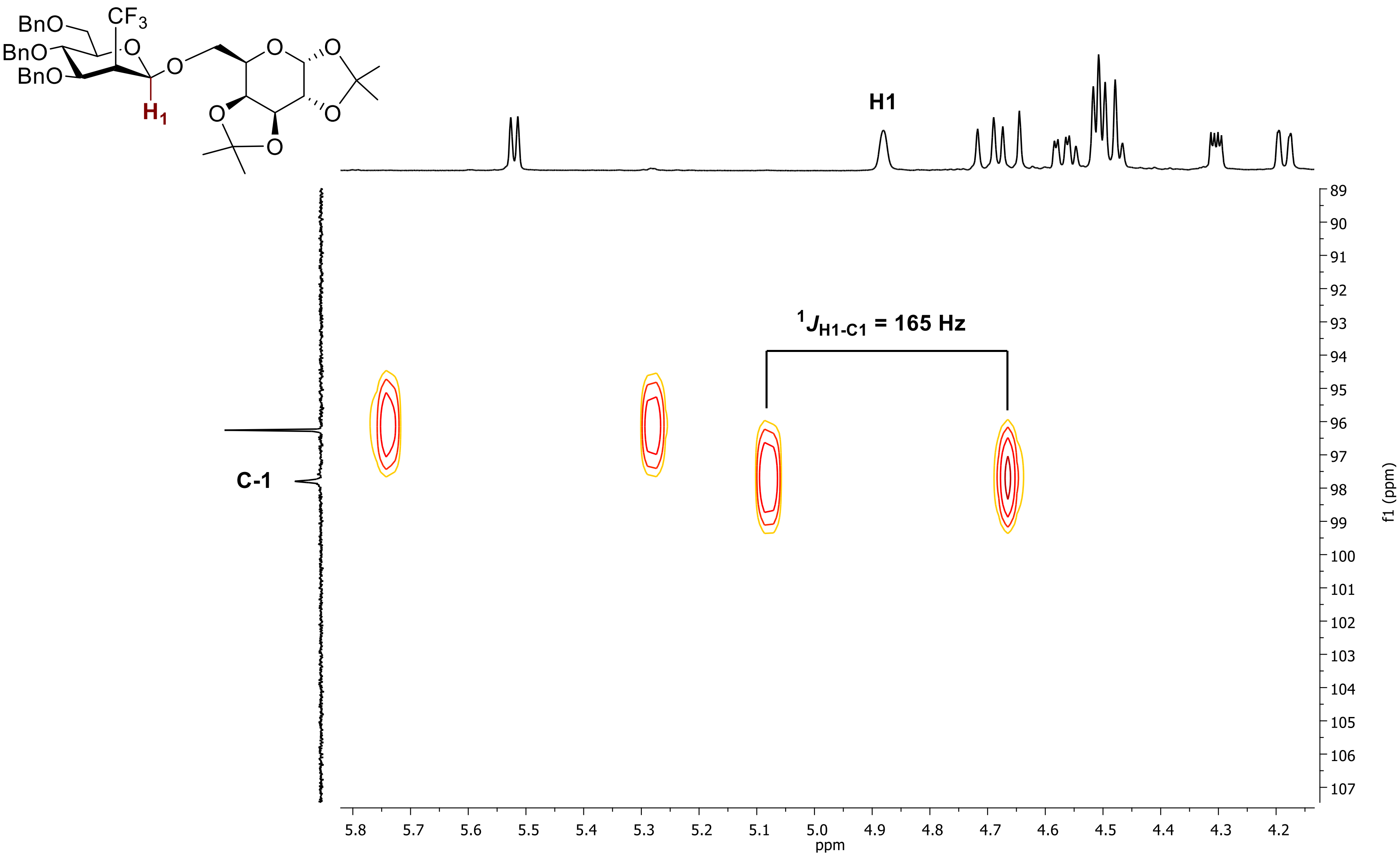


Figure S94. ^{1}H-coupled HSQC (CDCl$_3$, 400 MHz) of **22**β

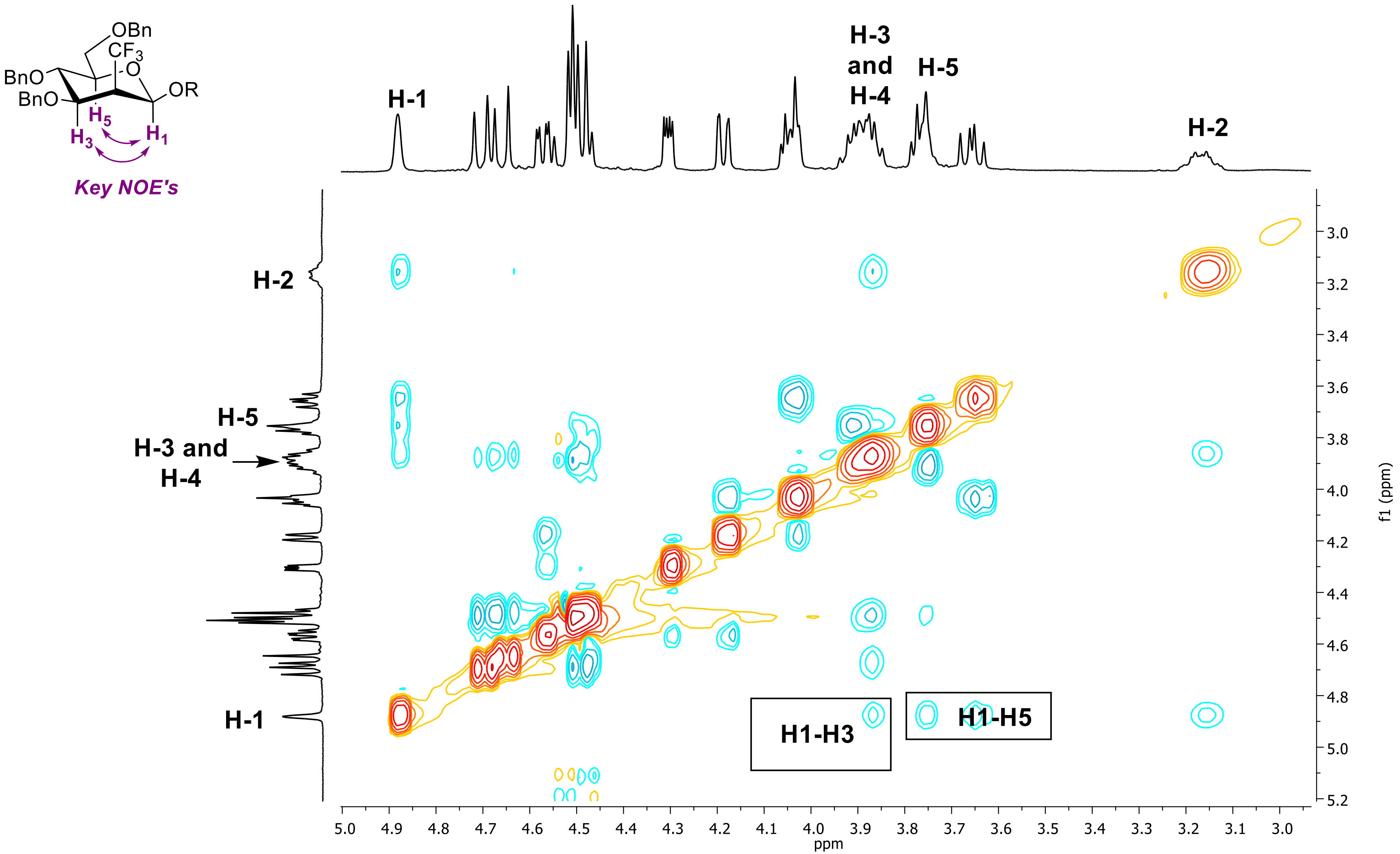


Figure S95. 2D NOESY ($CDCl_3$, 400 MHz) of **22**

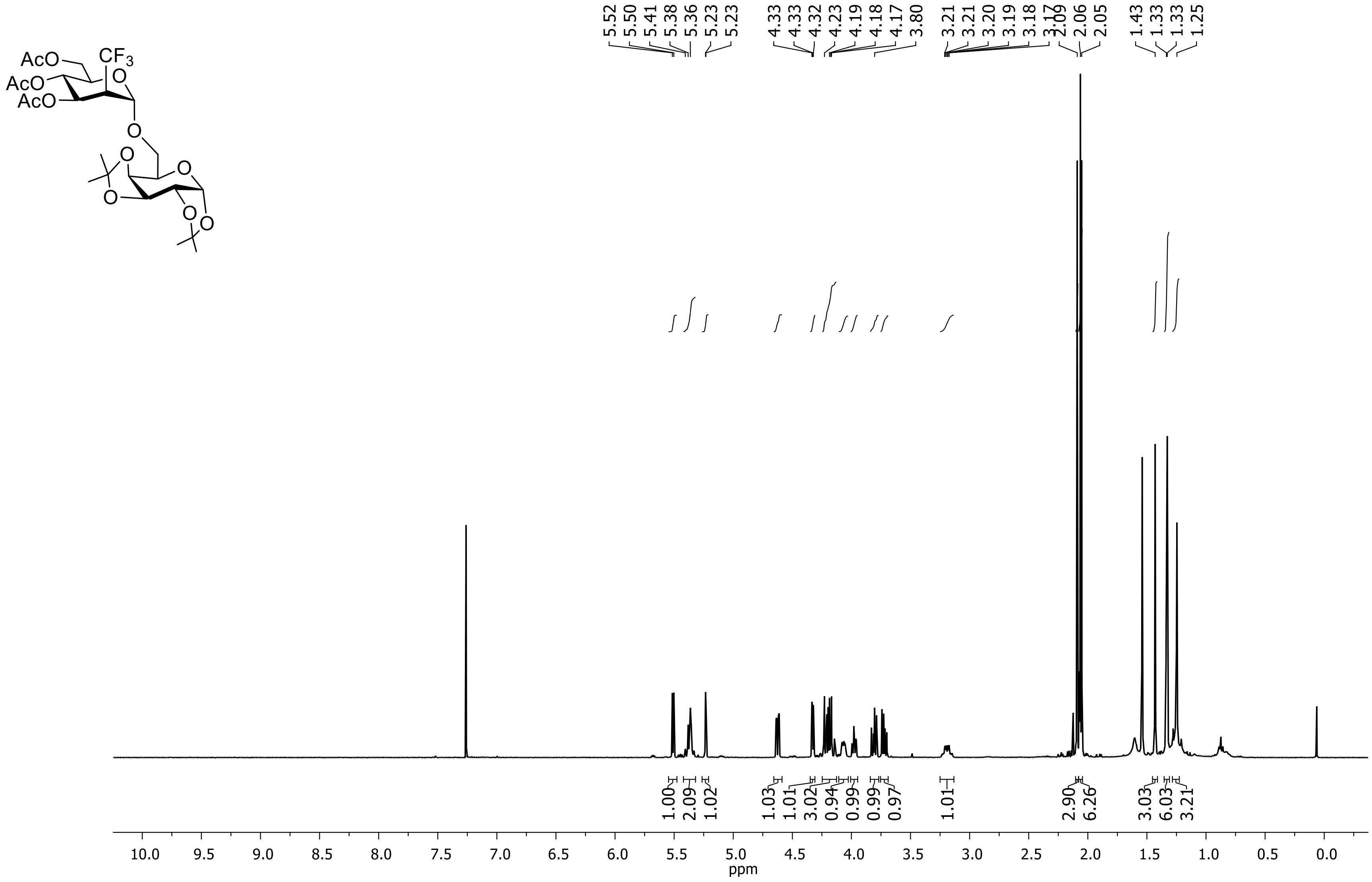


Figure S96. ^{1}H NMR ($CDCl_3$, 400 MHz) of **23α**

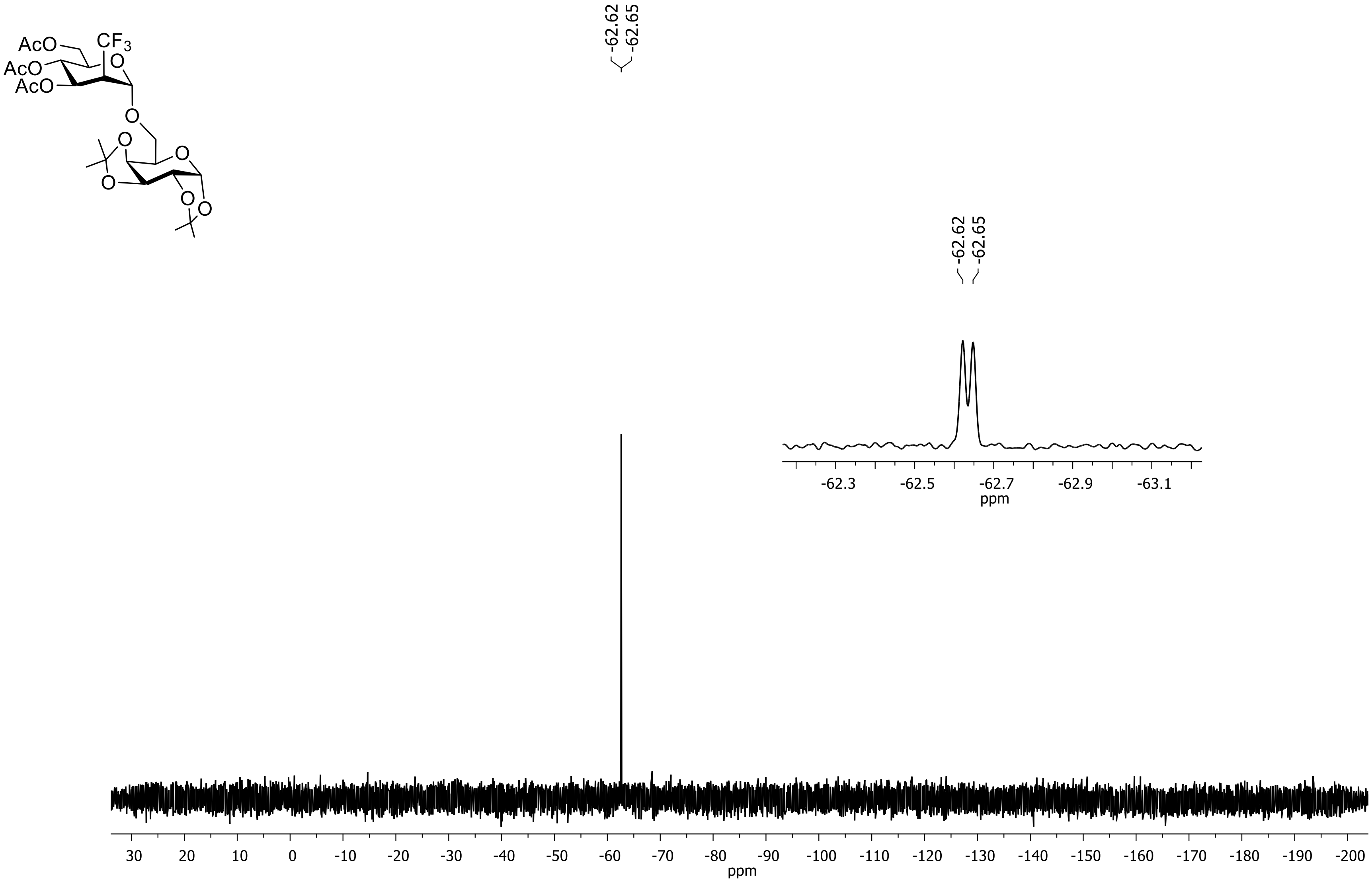


Figure S97. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **23α**

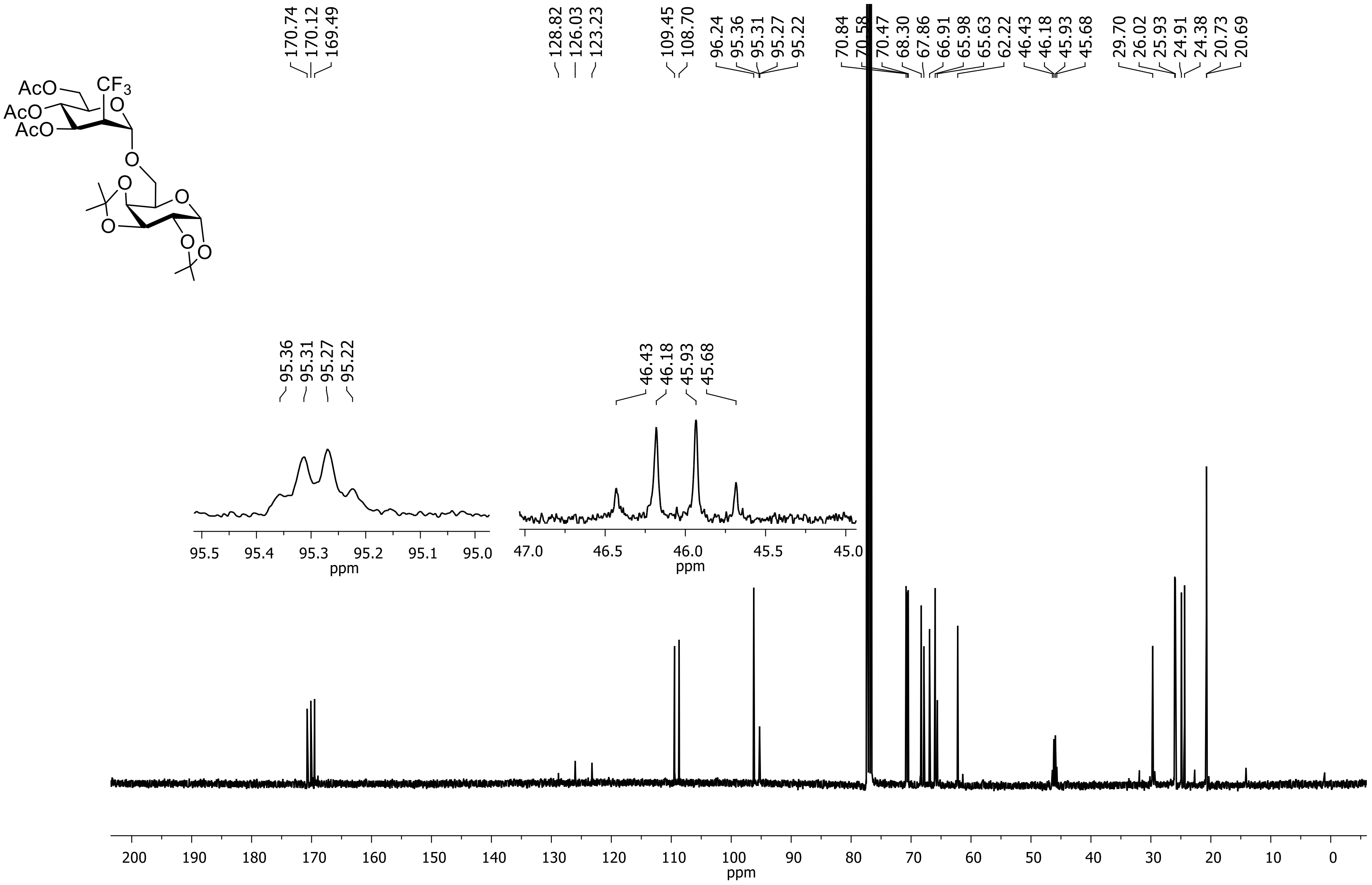
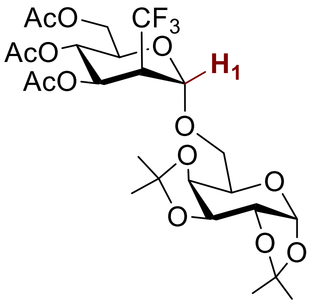


Figure S98. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **23α**



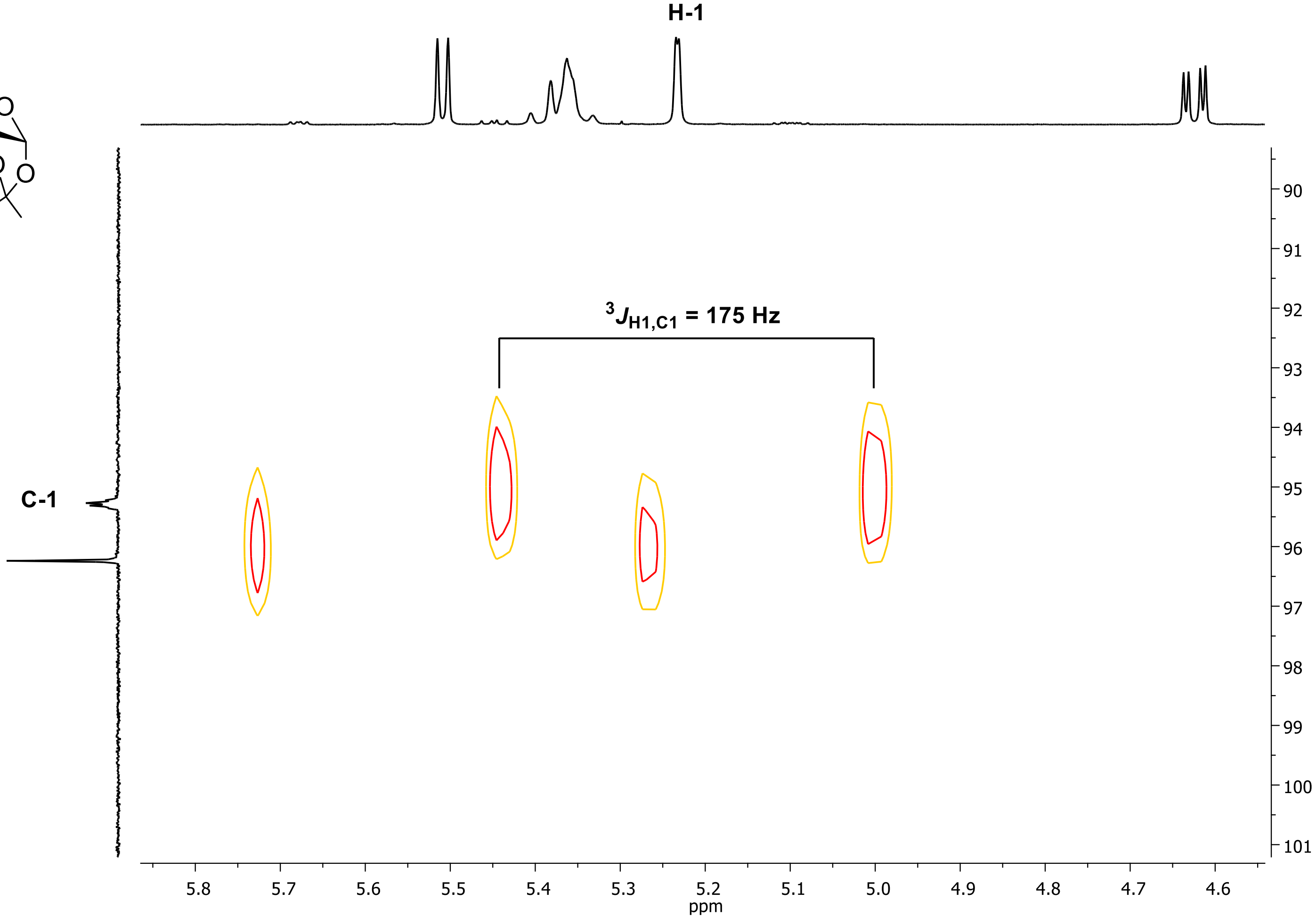


Figure S99. ^{1}H-coupled HSQC (CDCl$_3$, 400 MHz) of **23α**

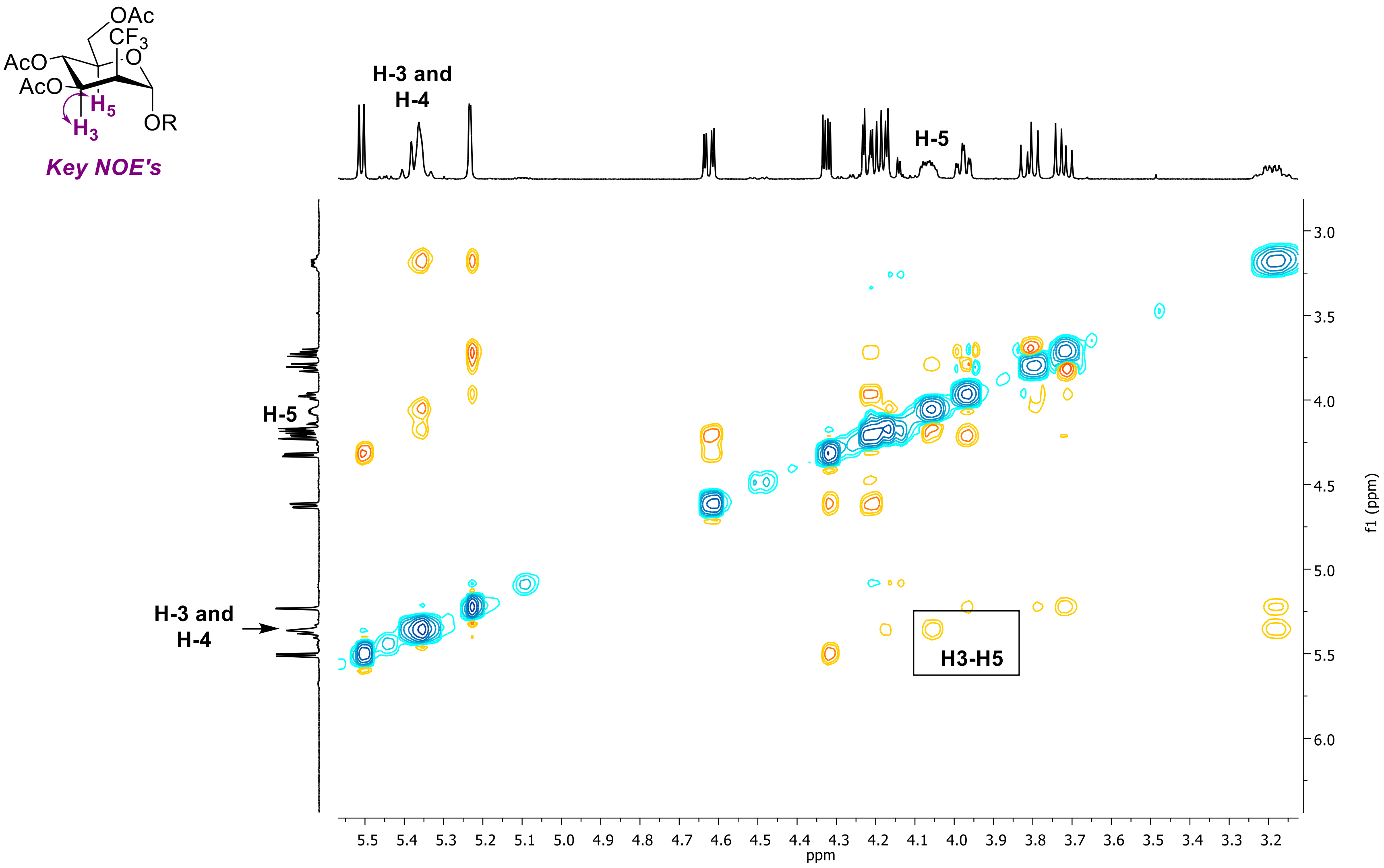


Figure S100. 2D NOESY ($CDCl_3$, 400 MHz) of **23α**

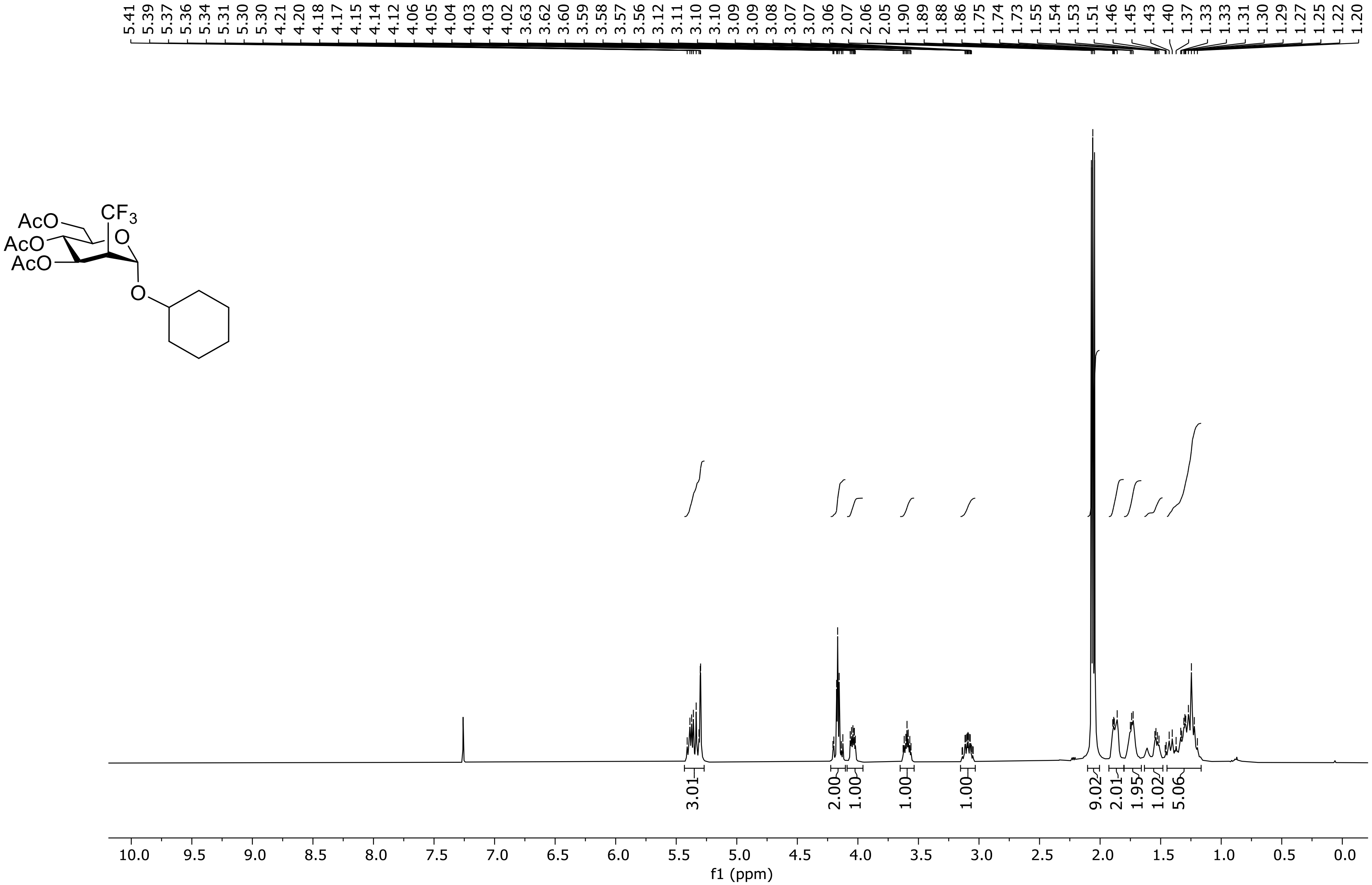


Figure S101. ^{1}H NMR ($CDCl_3$, 400 MHz) of **24α**

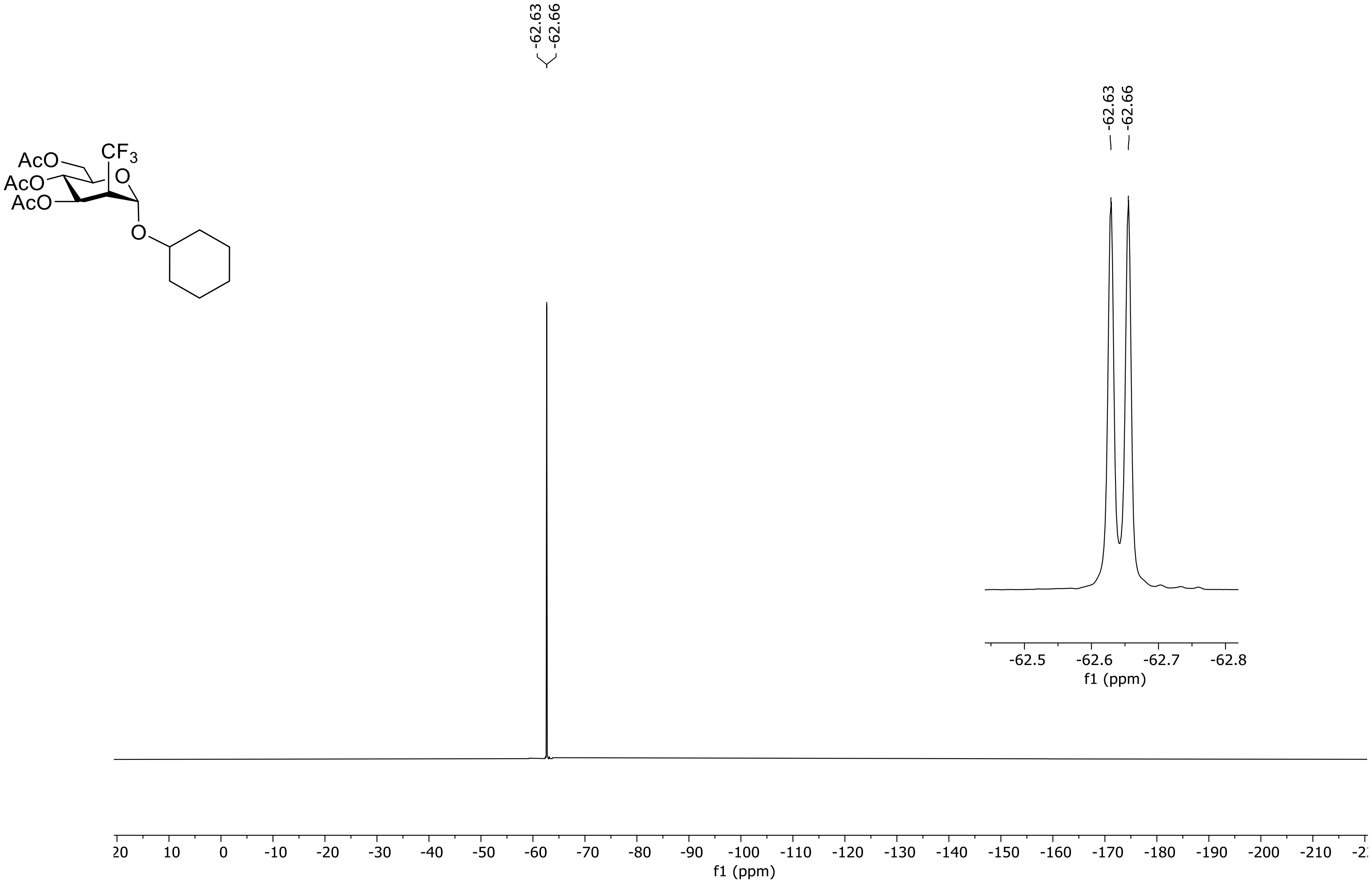


Figure S102. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **24α**

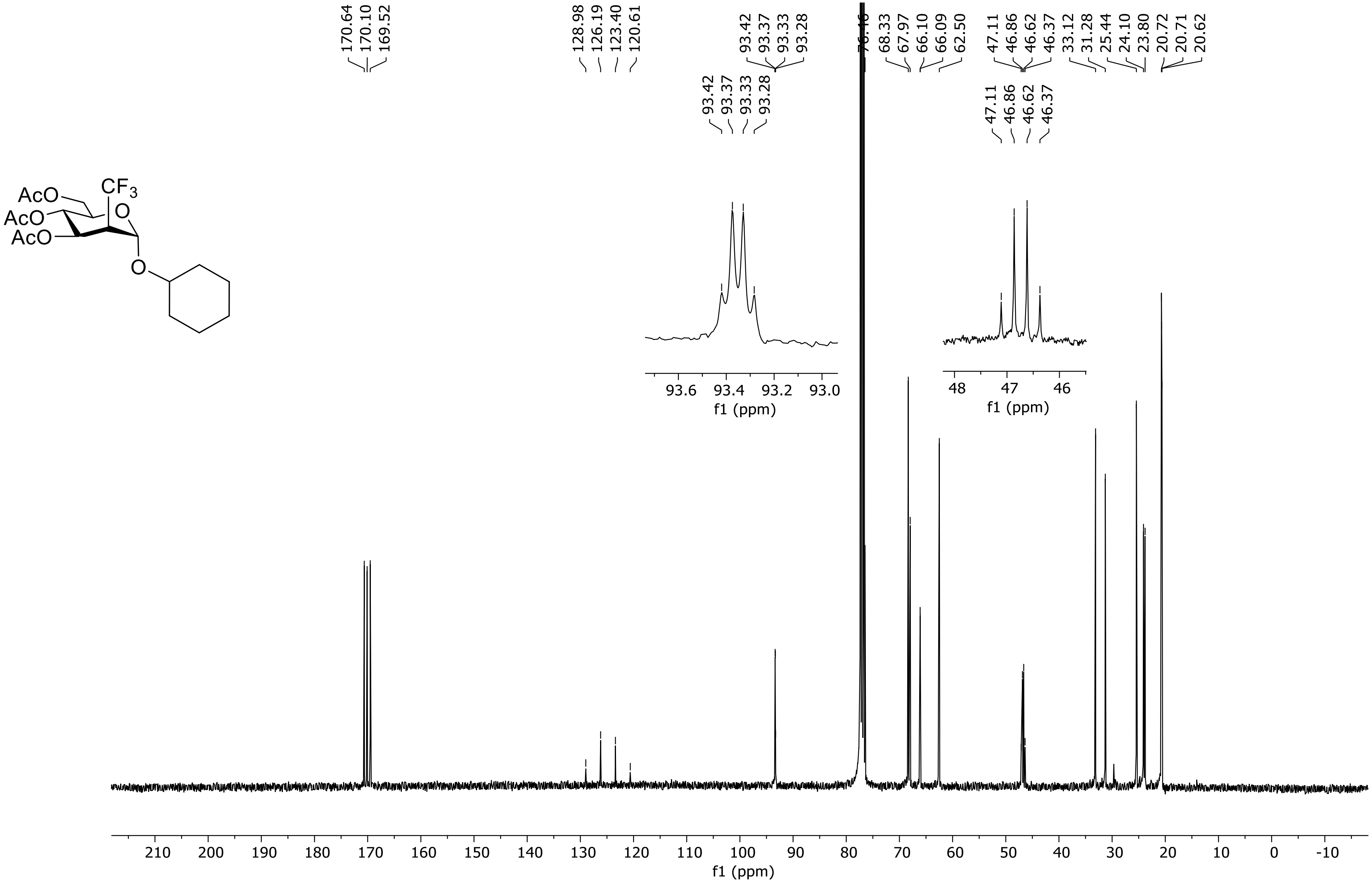


Figure S103. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **24α**

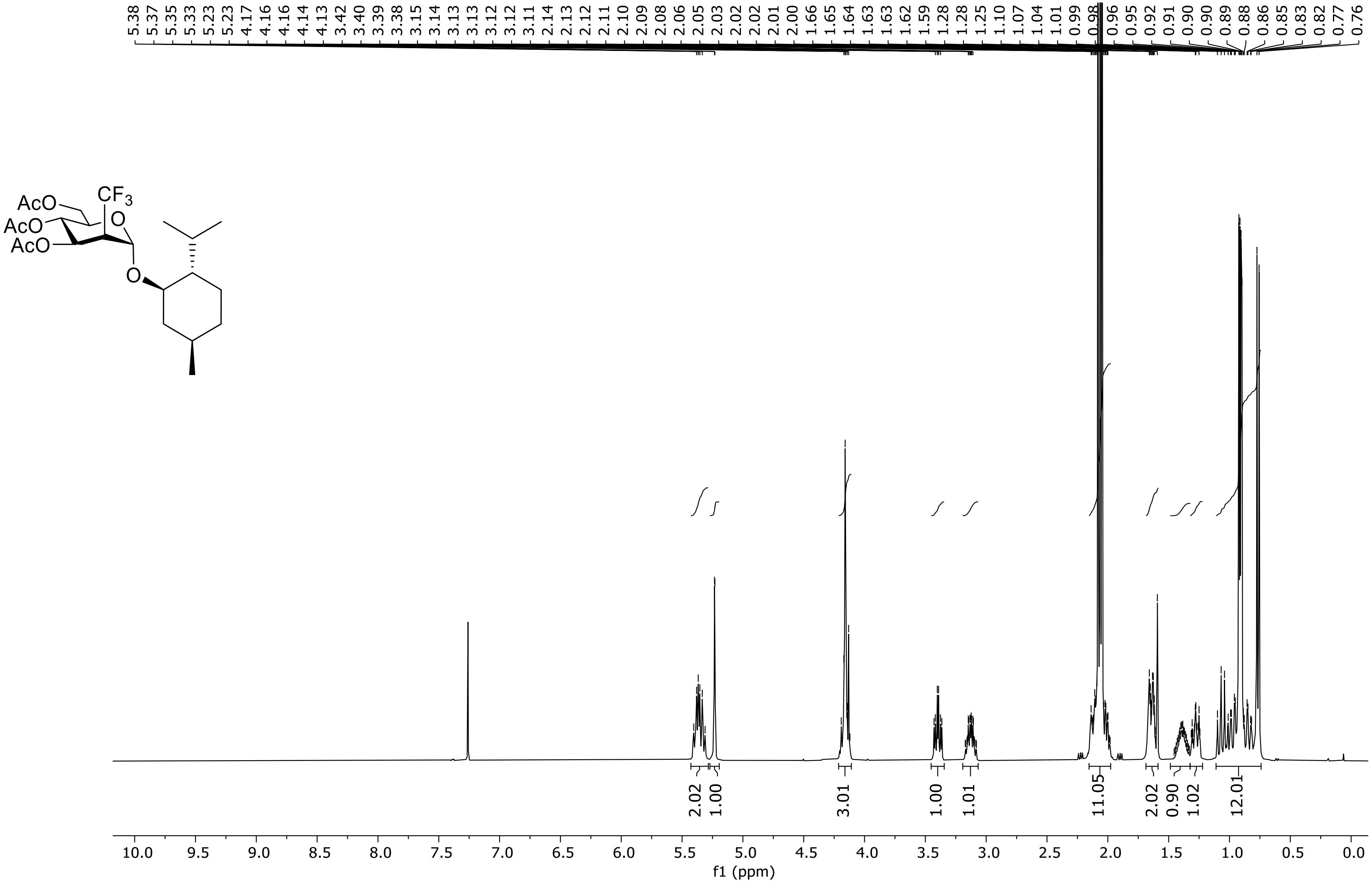


Figure S104. ^{1}H NMR (CDCl$_3$, 400 MHz) of **25α**

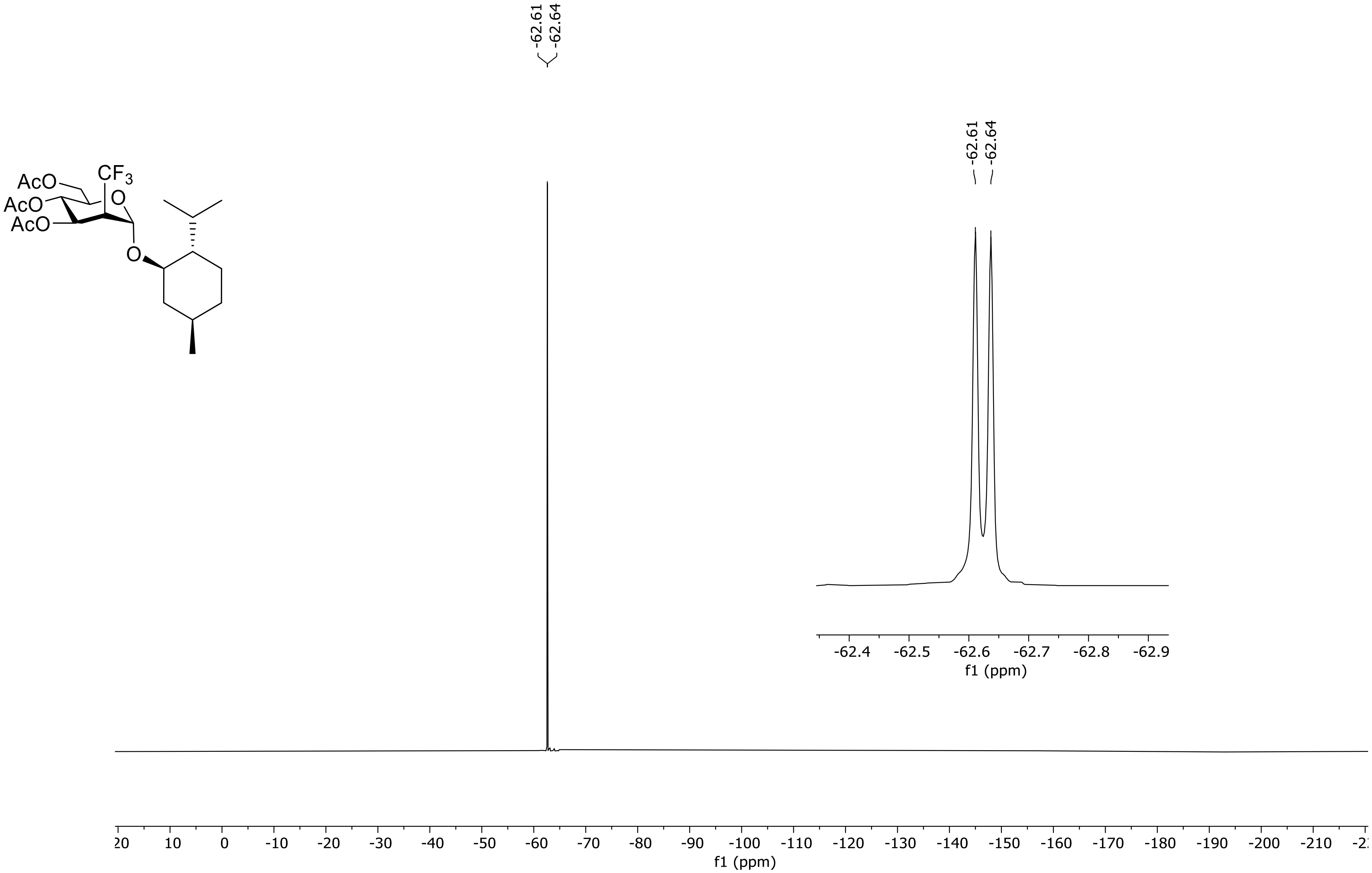


Figure S105. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **25α**

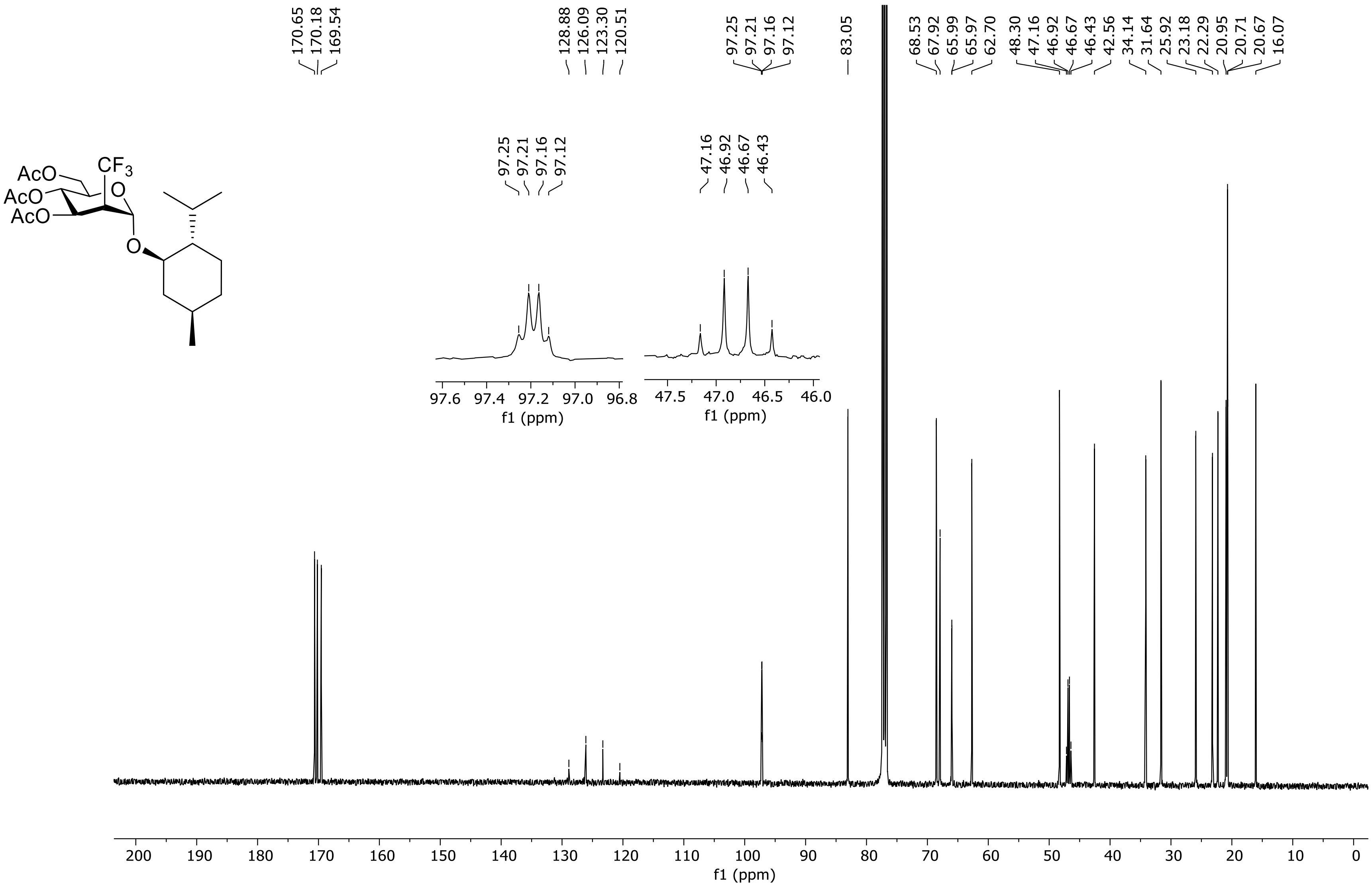


Figure S106. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **25α**

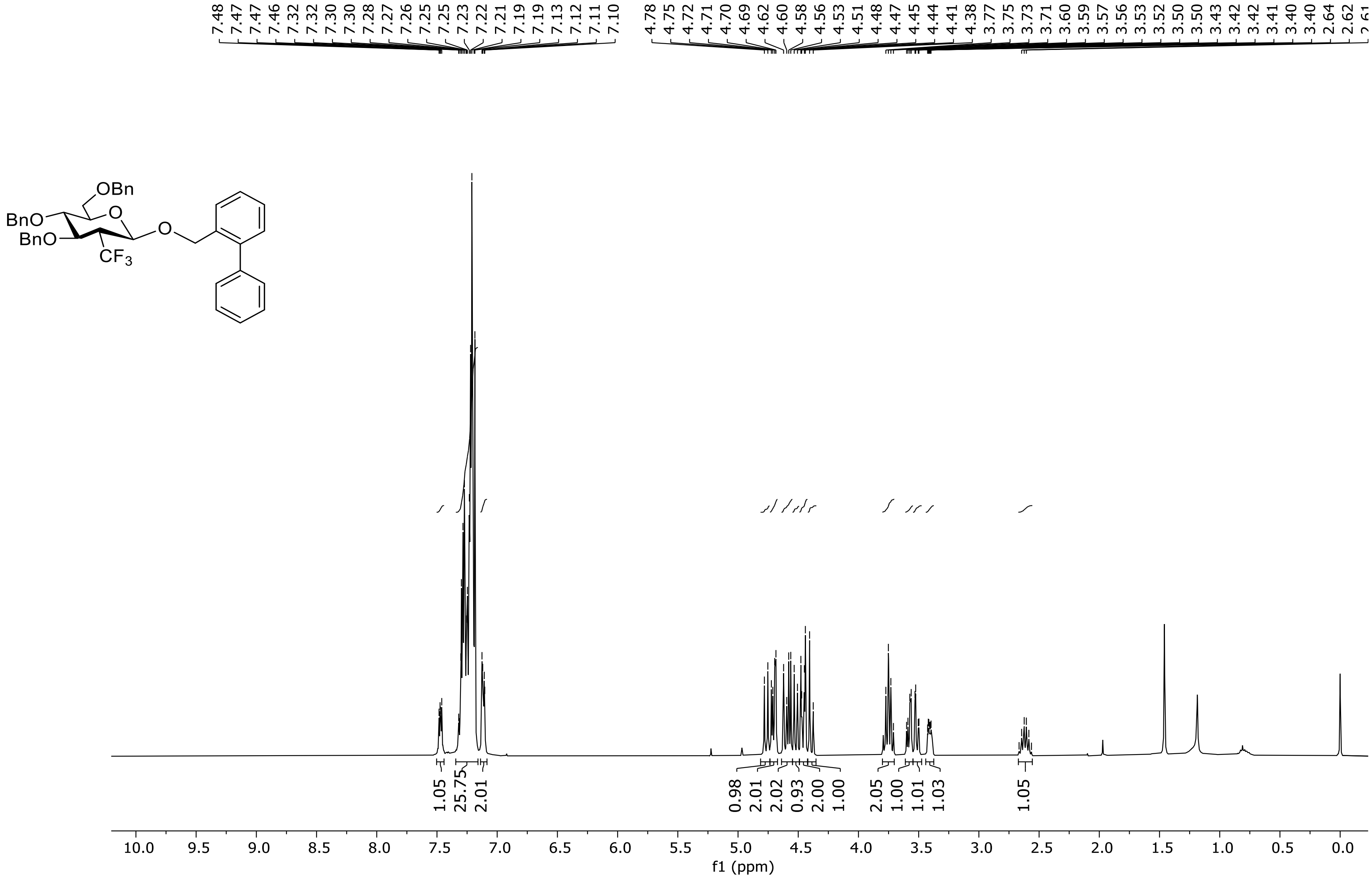


Figure S107. ^{1}H NMR ($CDCl_3$, 400 MHz) of **26β**

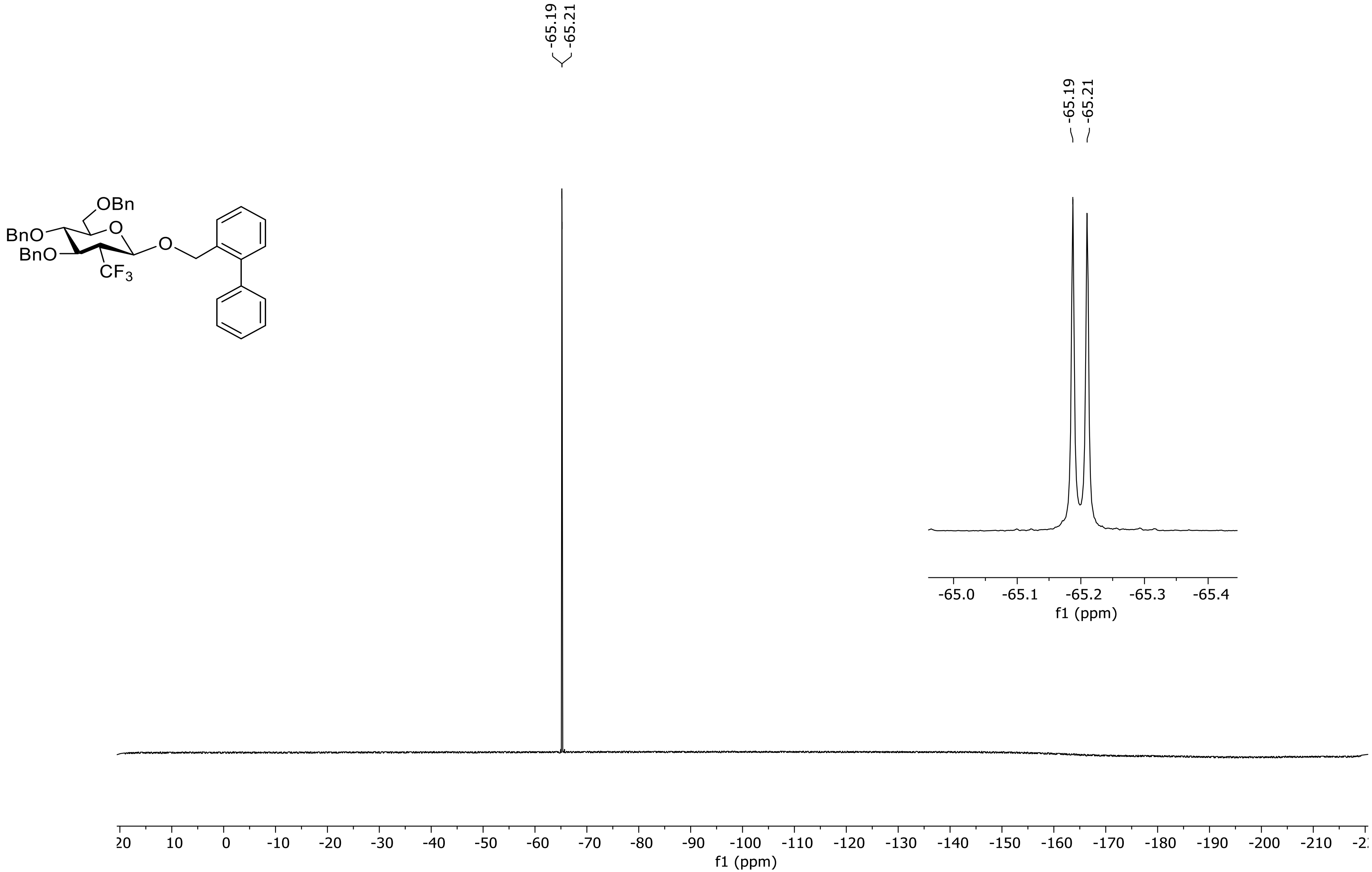


Figure S108. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **26β**

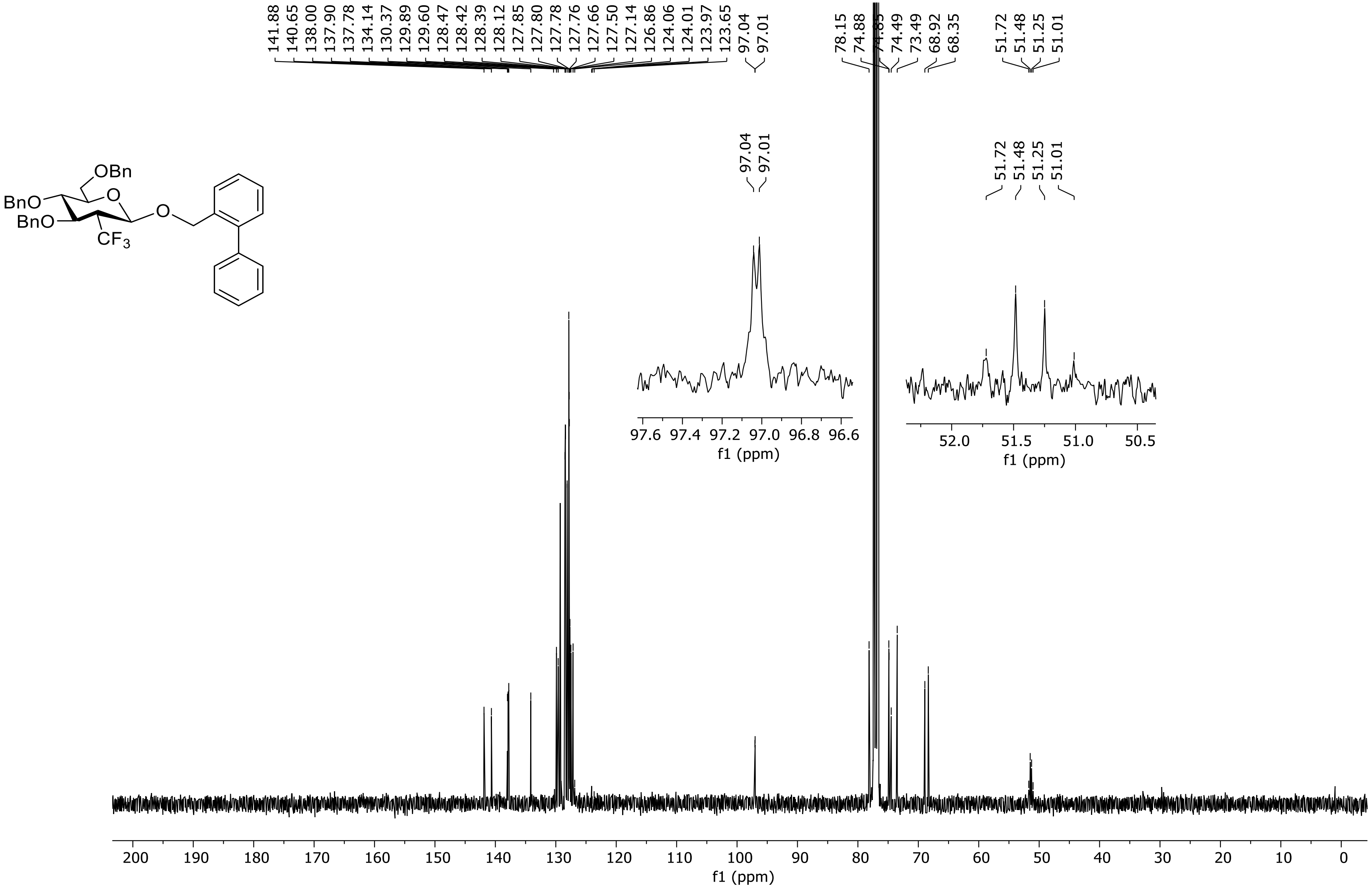


Figure S109. ^{13}C NMR CDCl$_3$, 100.6 MHz) of **26β**

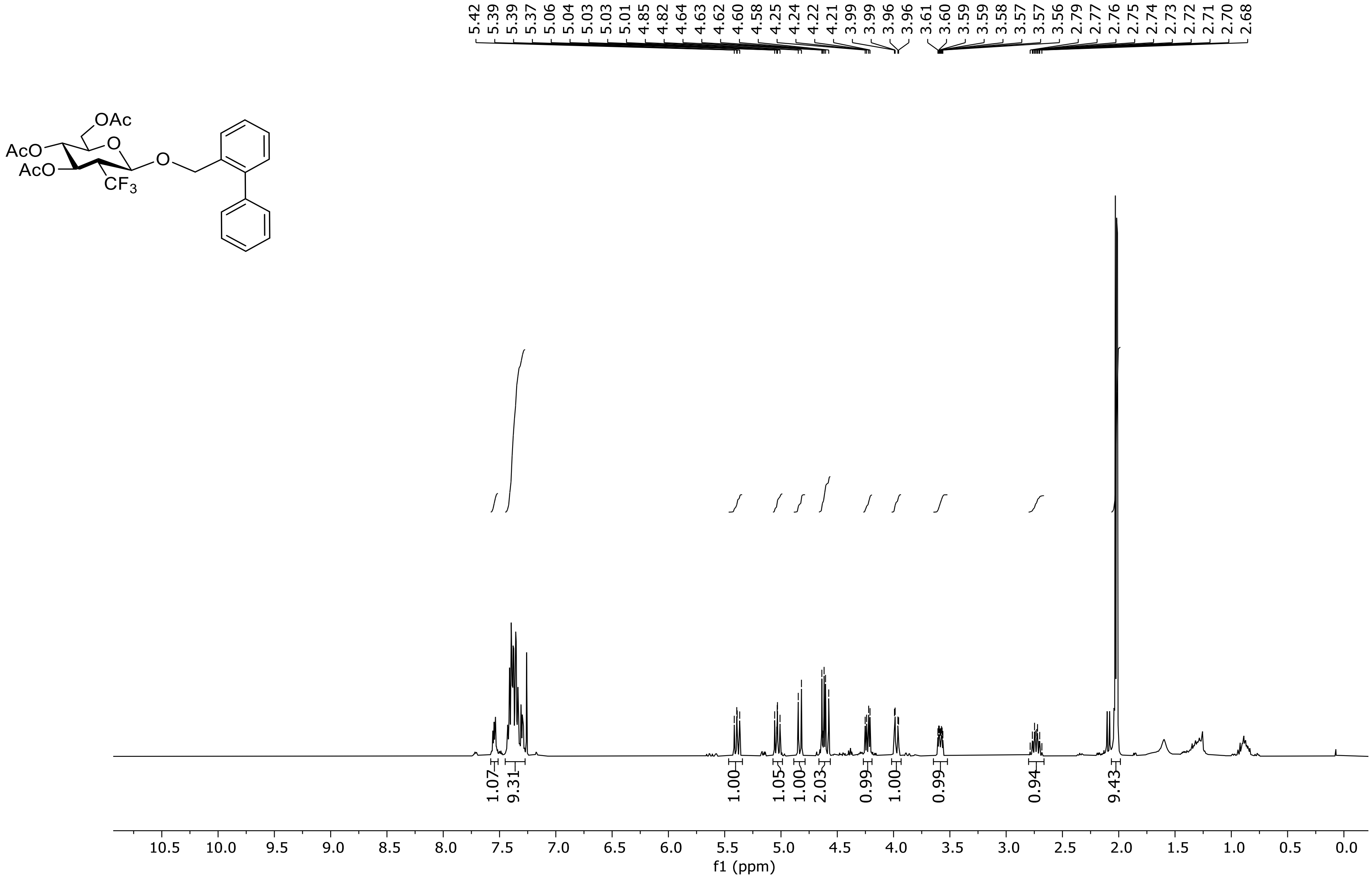


Figure S110. ^{1}H NMR (CDCl$_3$, 400 MHz) of **27β**

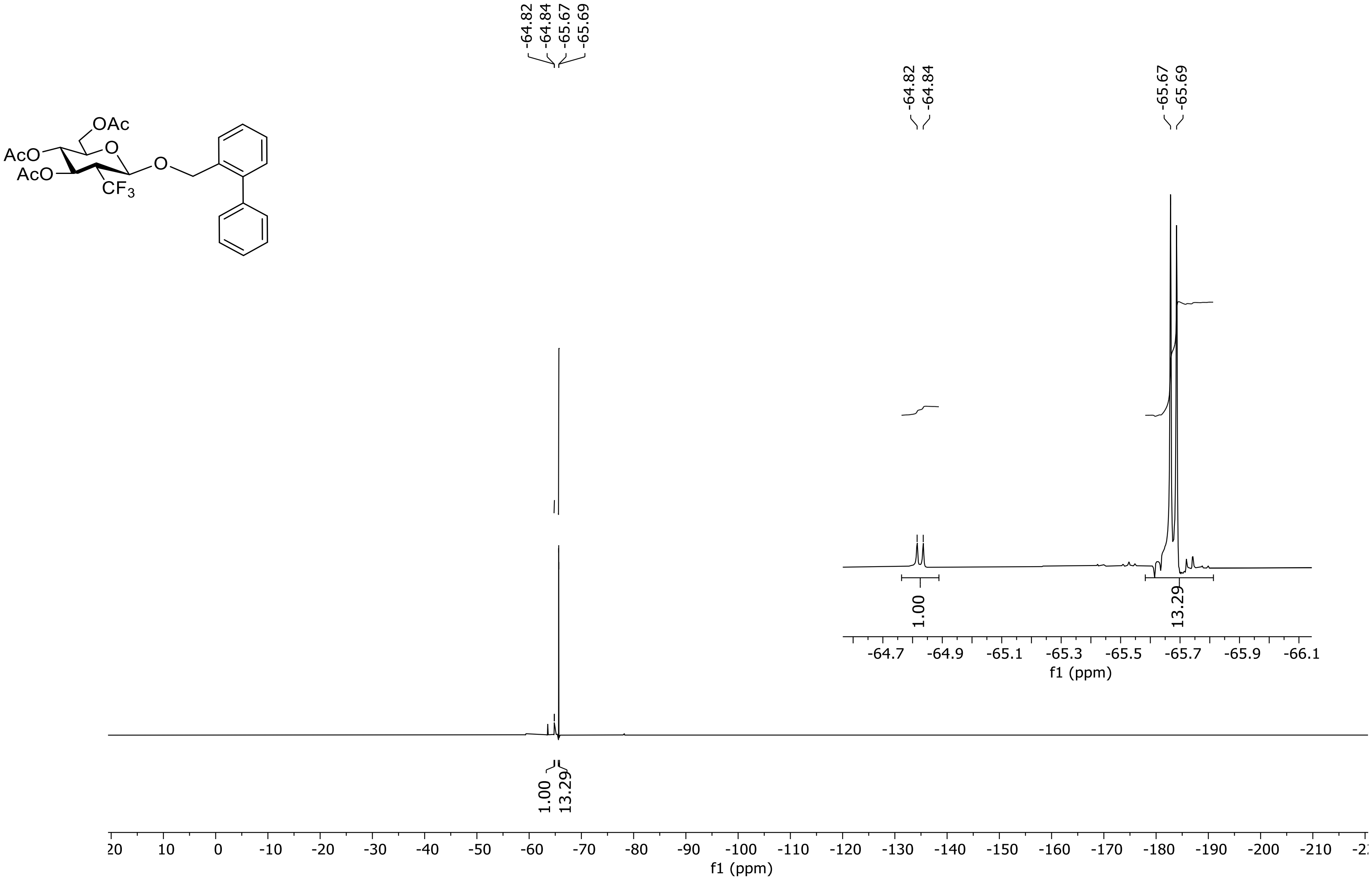


Figure S111. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **27β**

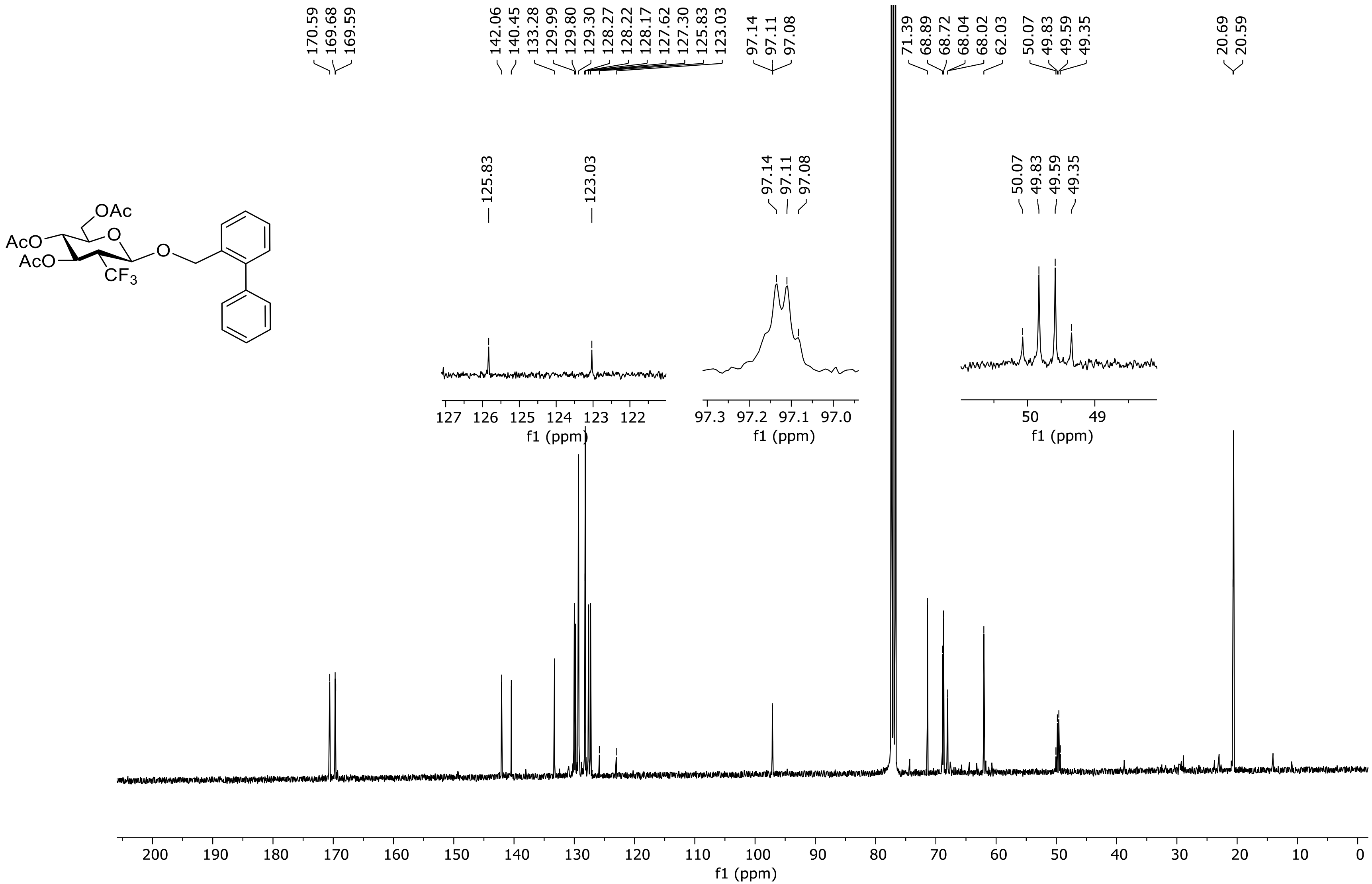


Figure S112. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **27β**

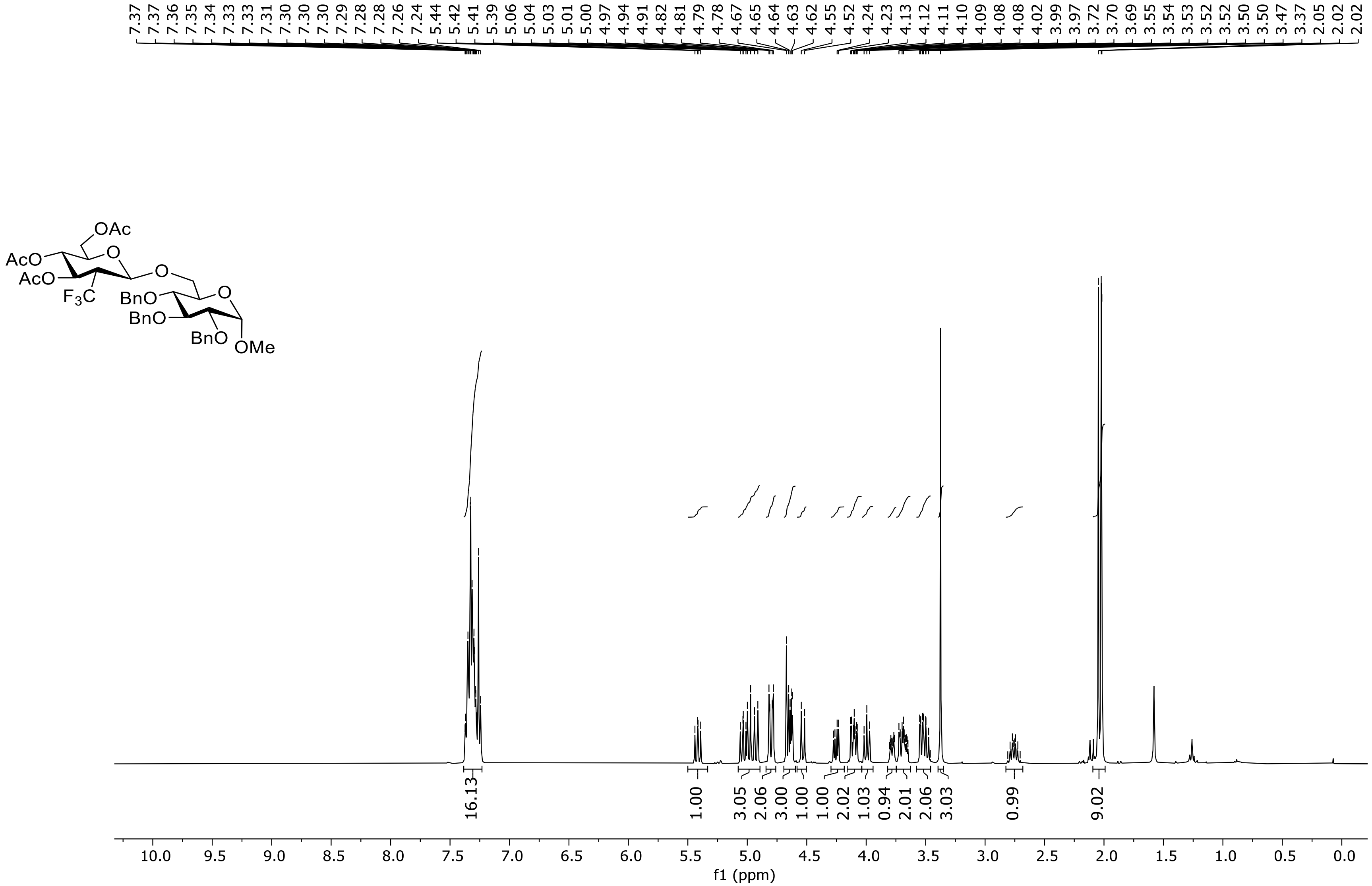


Figure S113. ^{1}H NMR (CDCl$_3$, 400 MHz) of **28β**

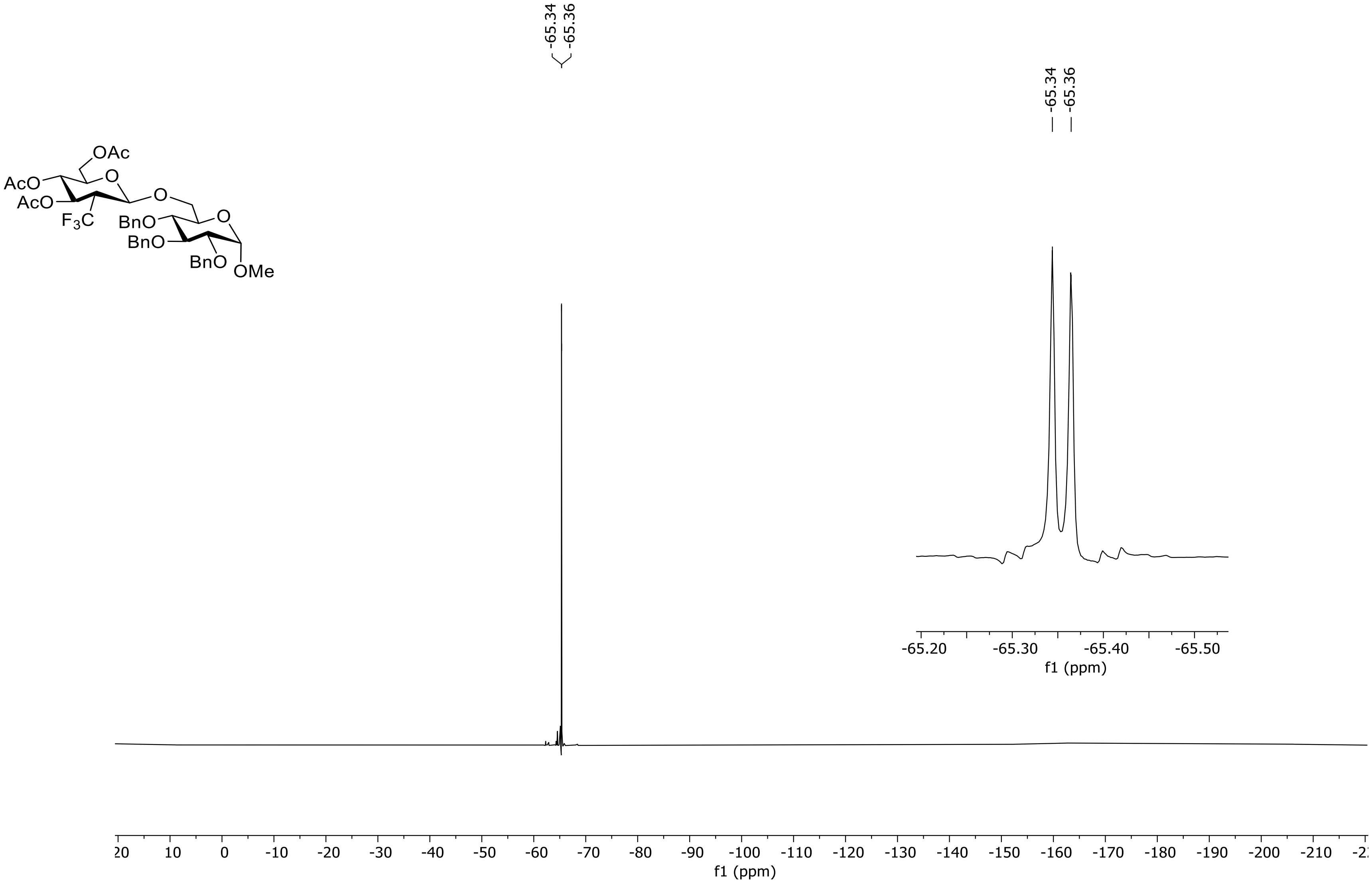


Figure S114. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **28β**

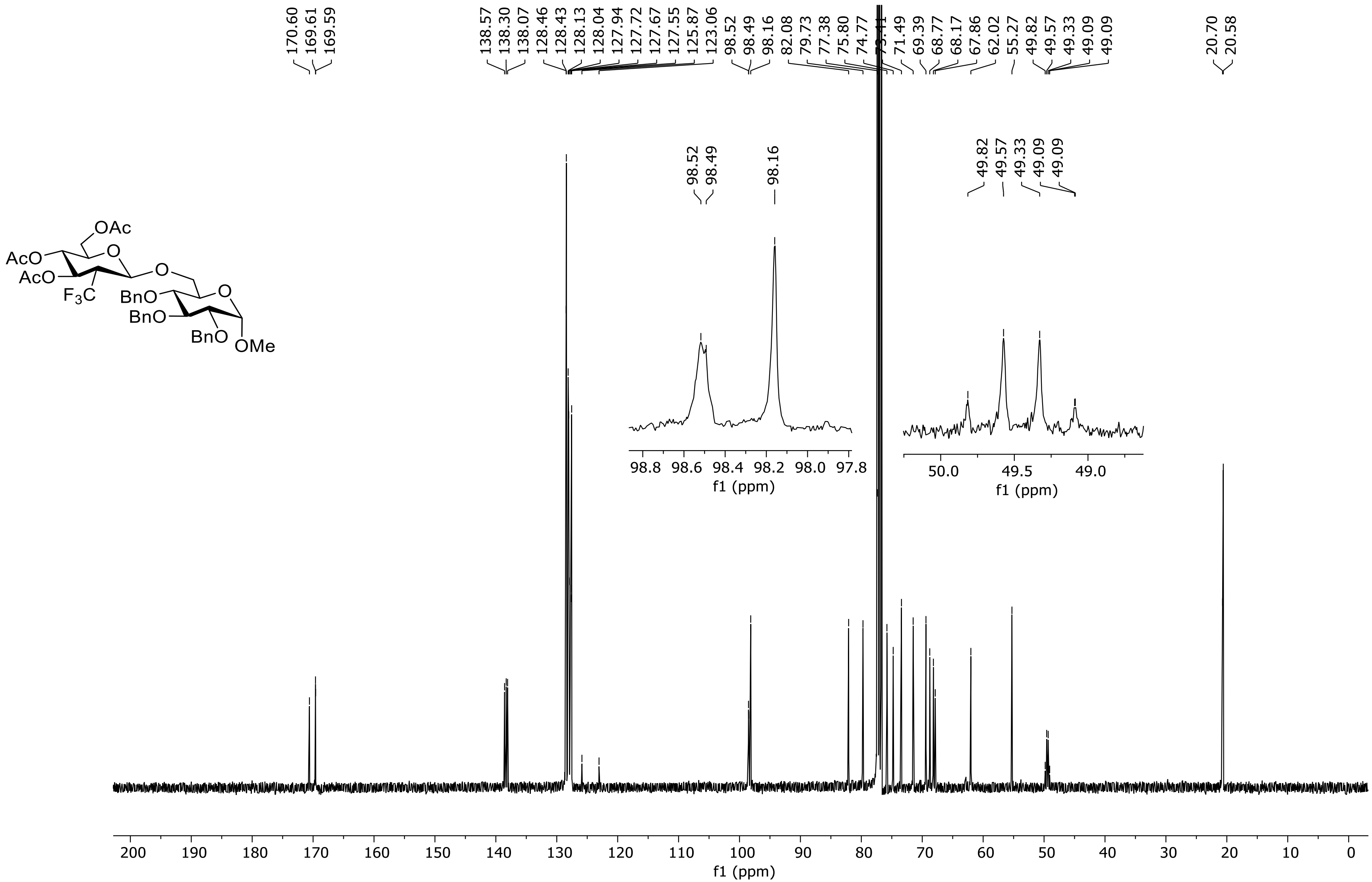


Figure S115. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **28β**

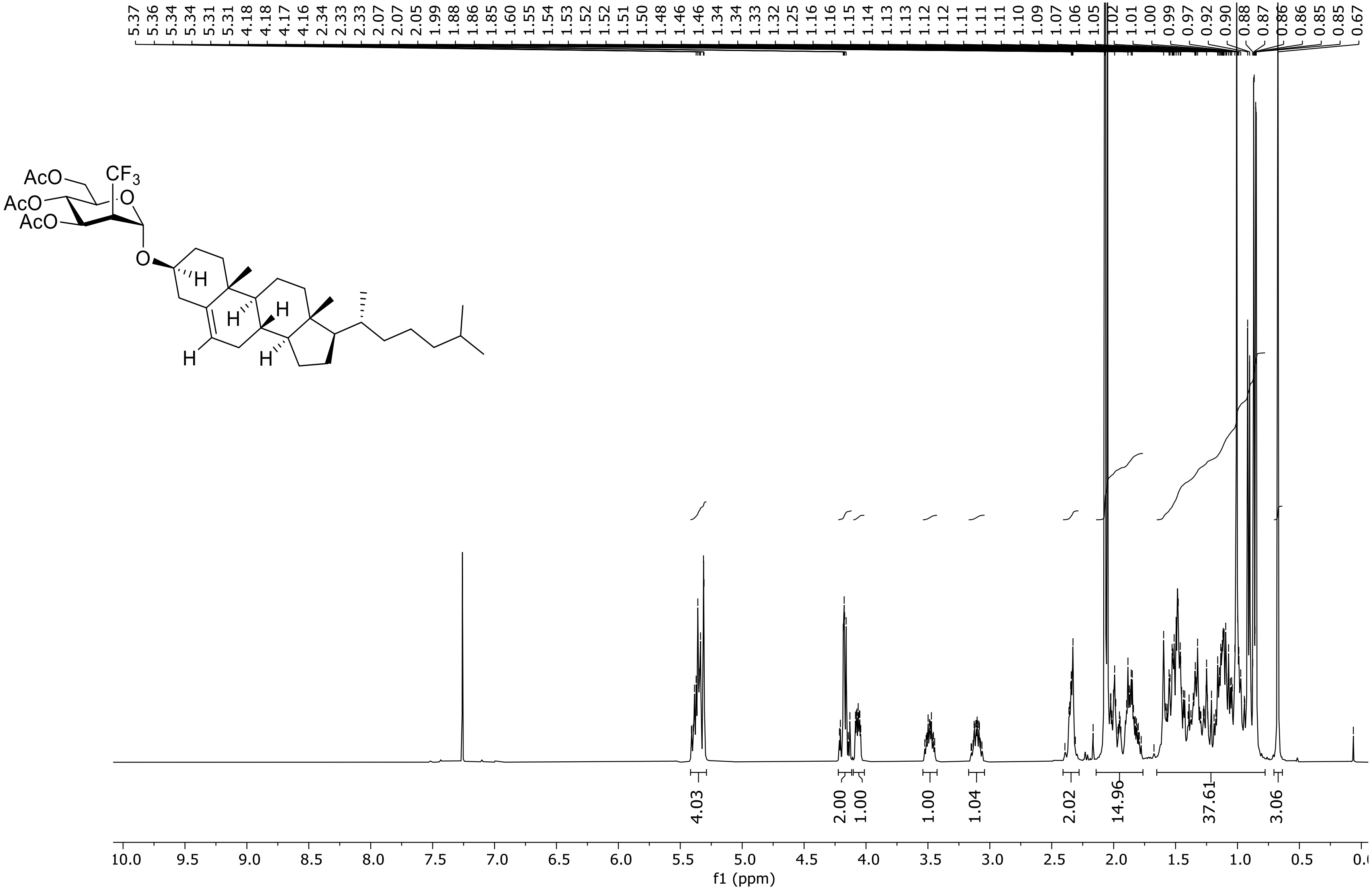


Figure S116. ^{1}H NMR ($CDCl_3$, 400 MHz) of **29α**

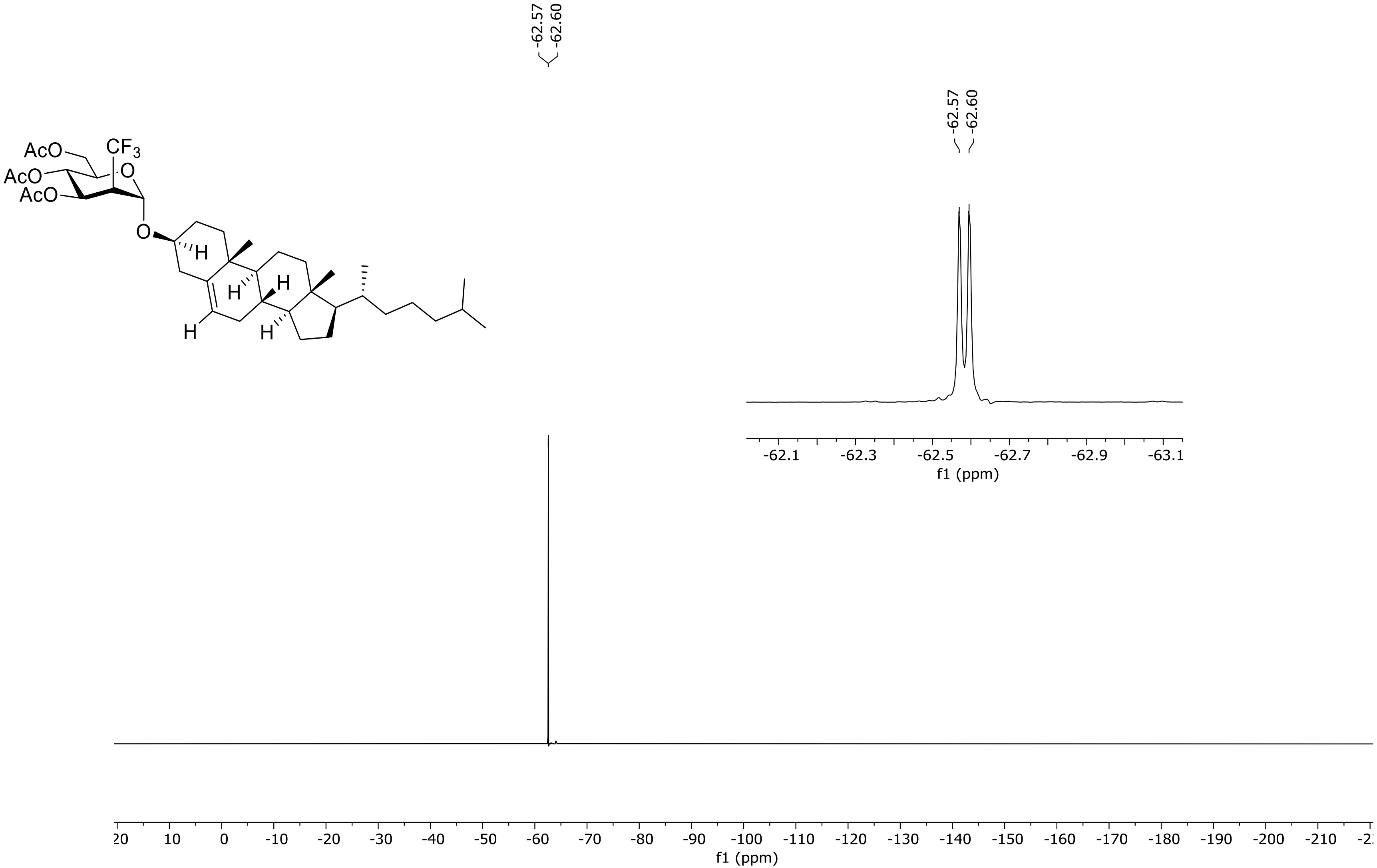


Figure S117. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **29α**

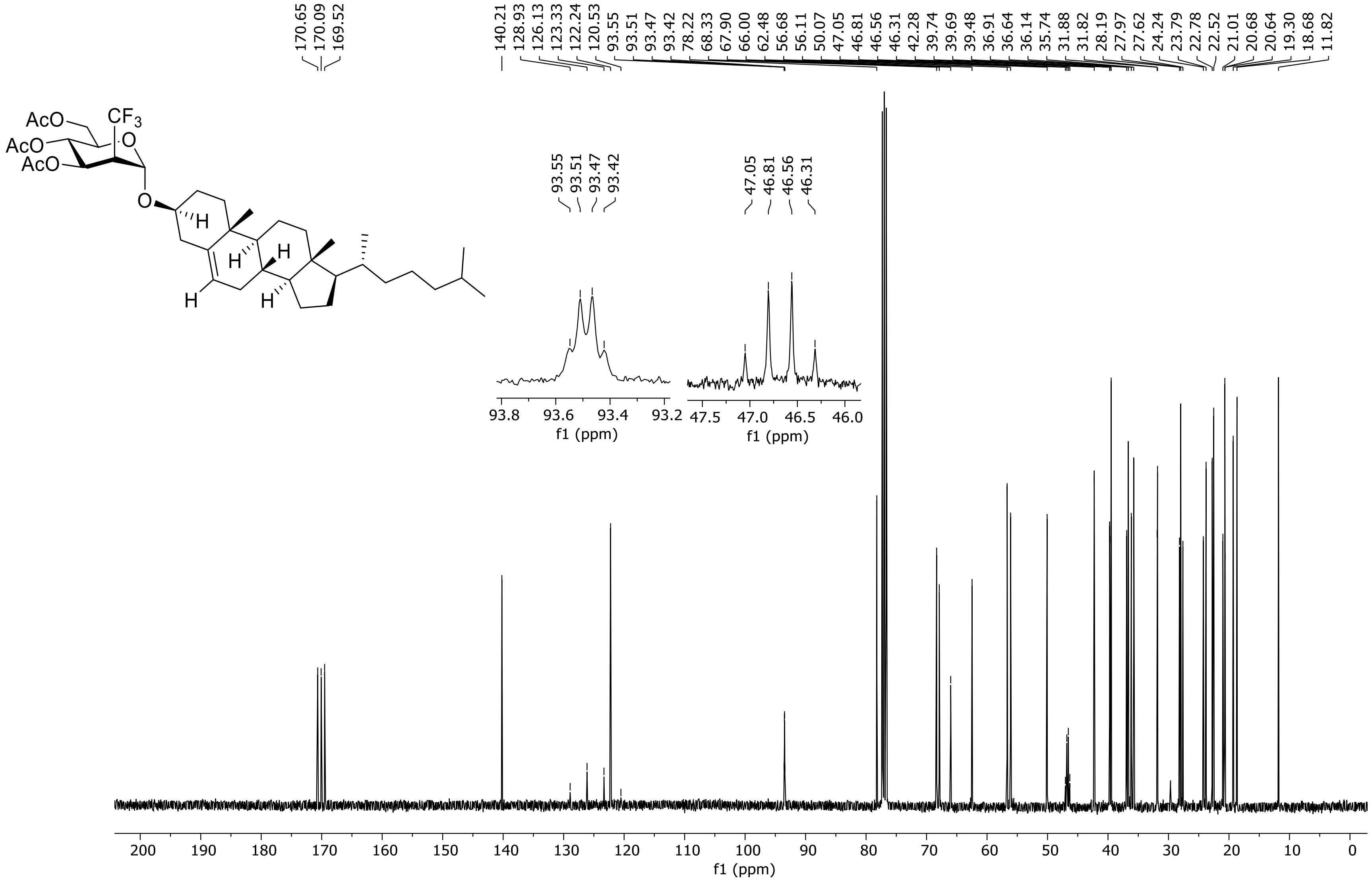


Figure S118. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **29α**

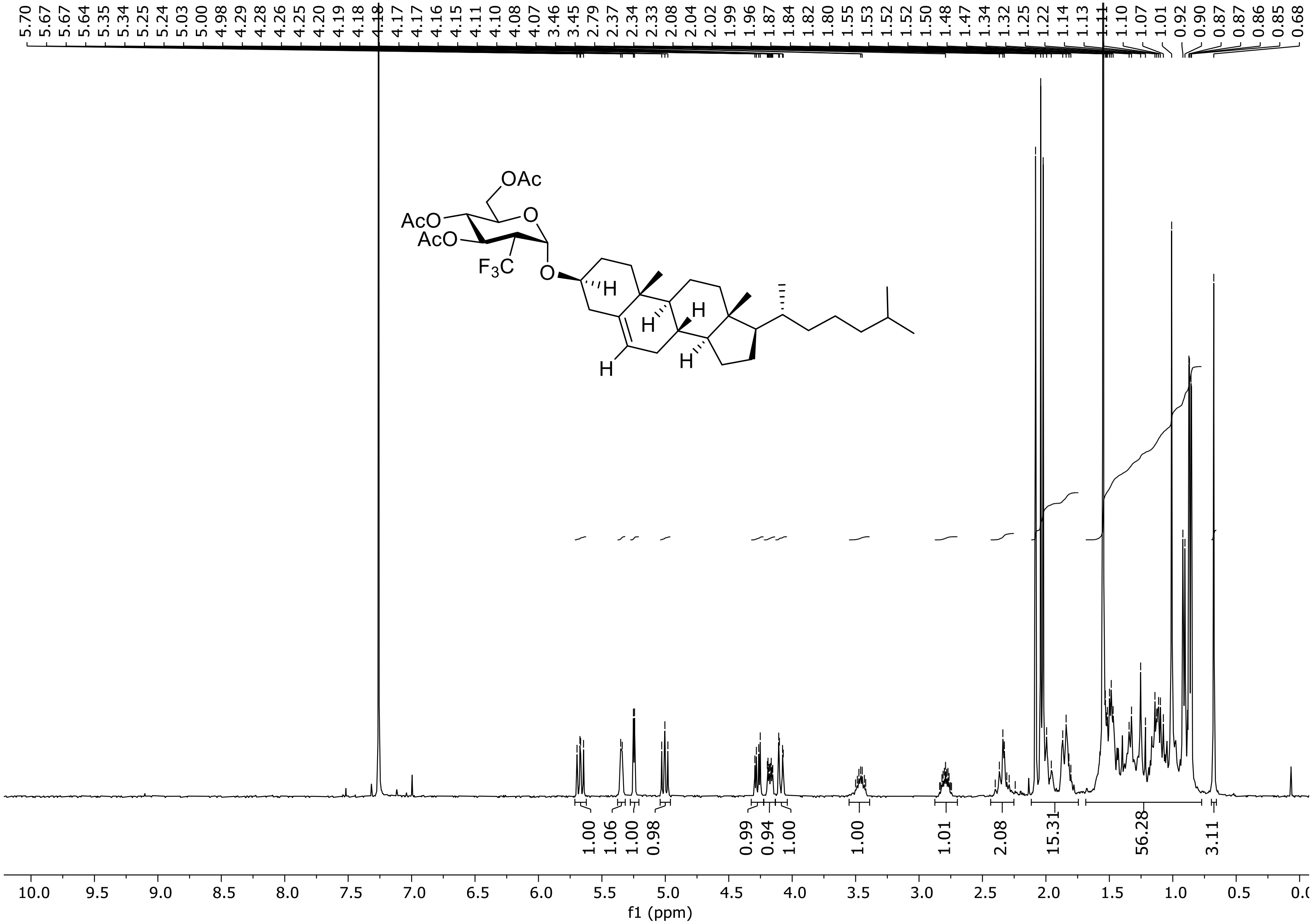


Figure S119. ^{1}H NMR ($CDCl_3$, 400 MHz) of **30α**

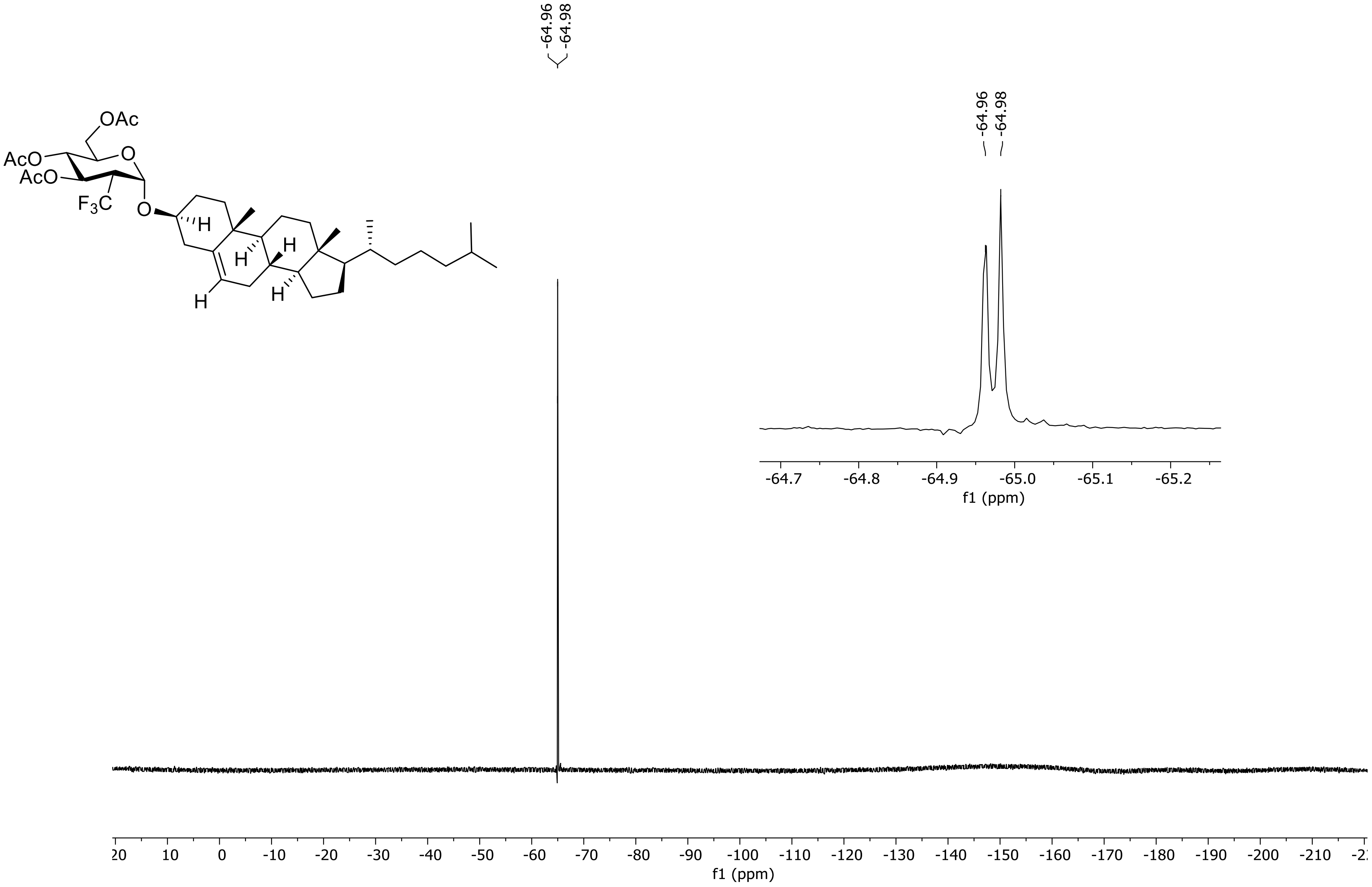


Figure S120. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **30α**

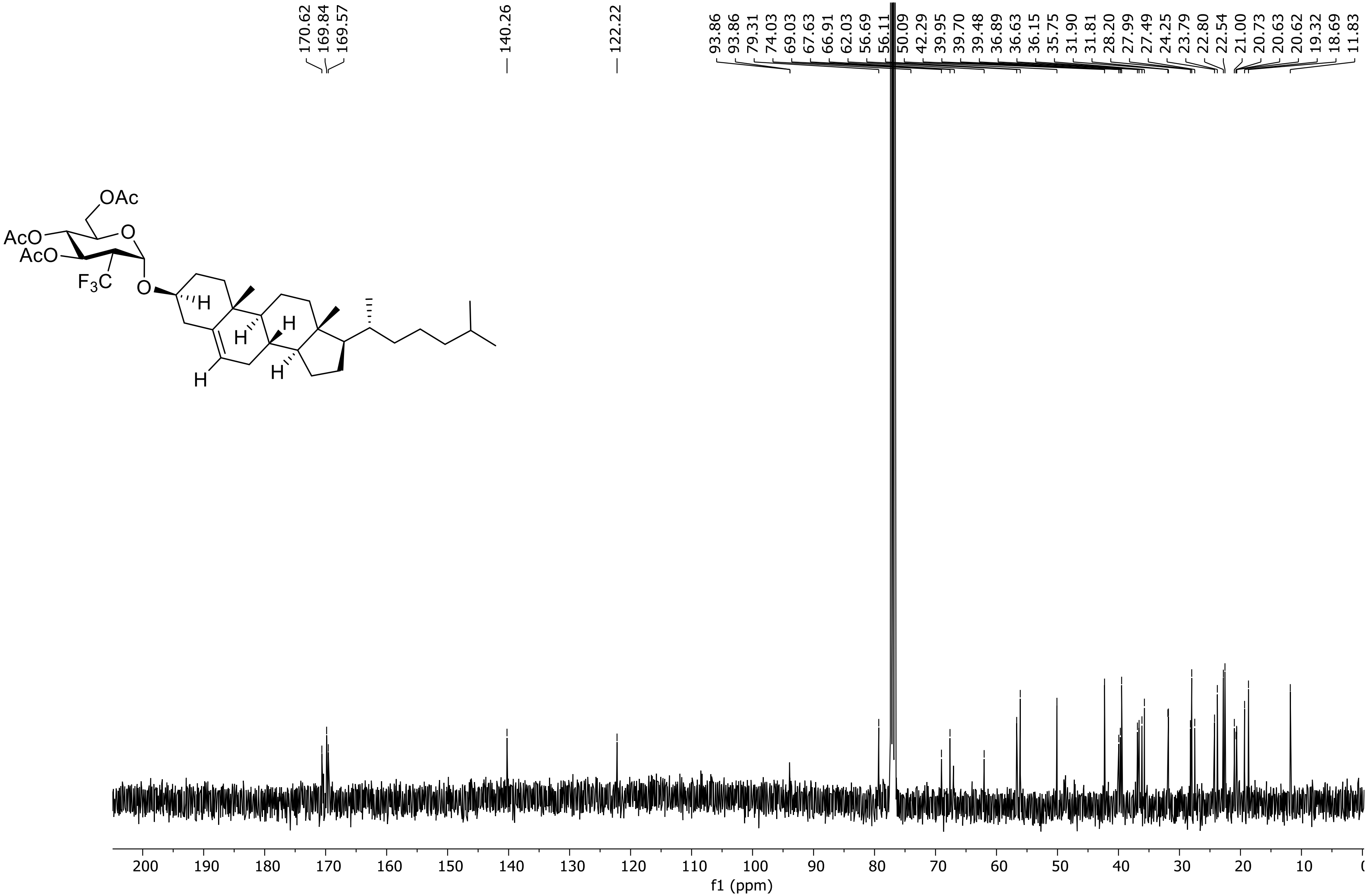


Figure S121. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **30α**

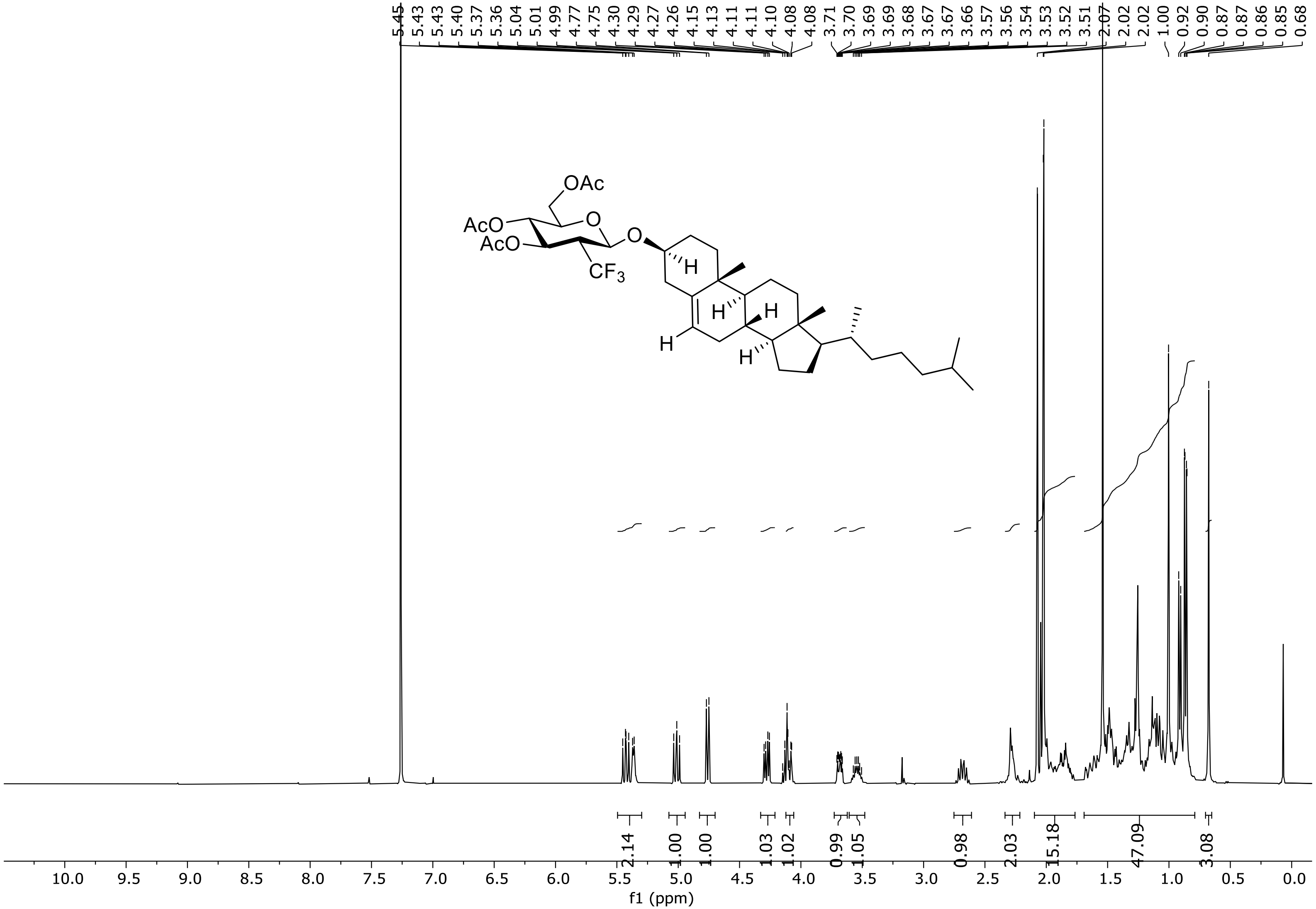


Figure S122. ^{1}H NMR (CDCl$_3$, 400 MHz) of **30β**

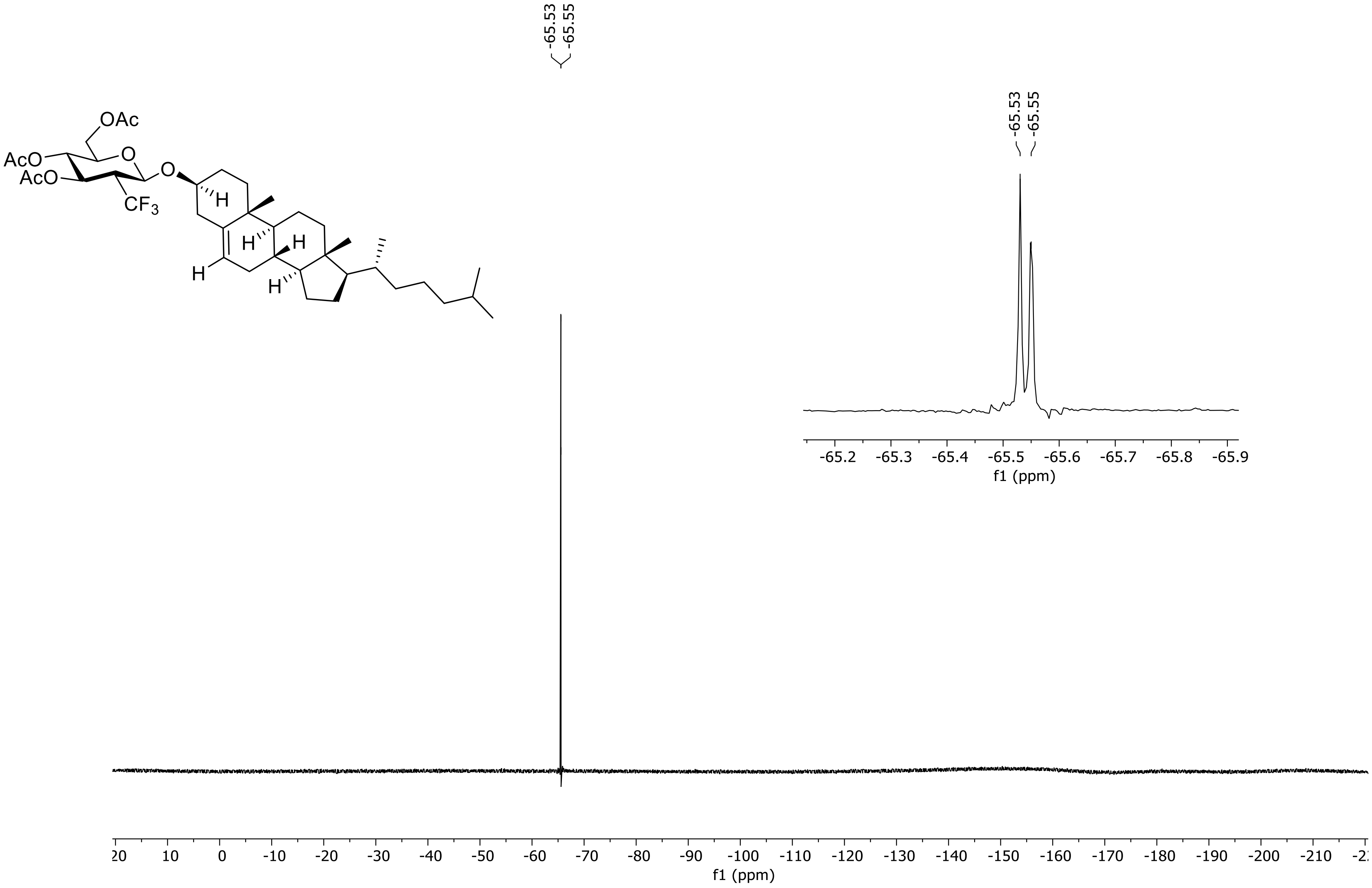


Figure S123. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **30β**

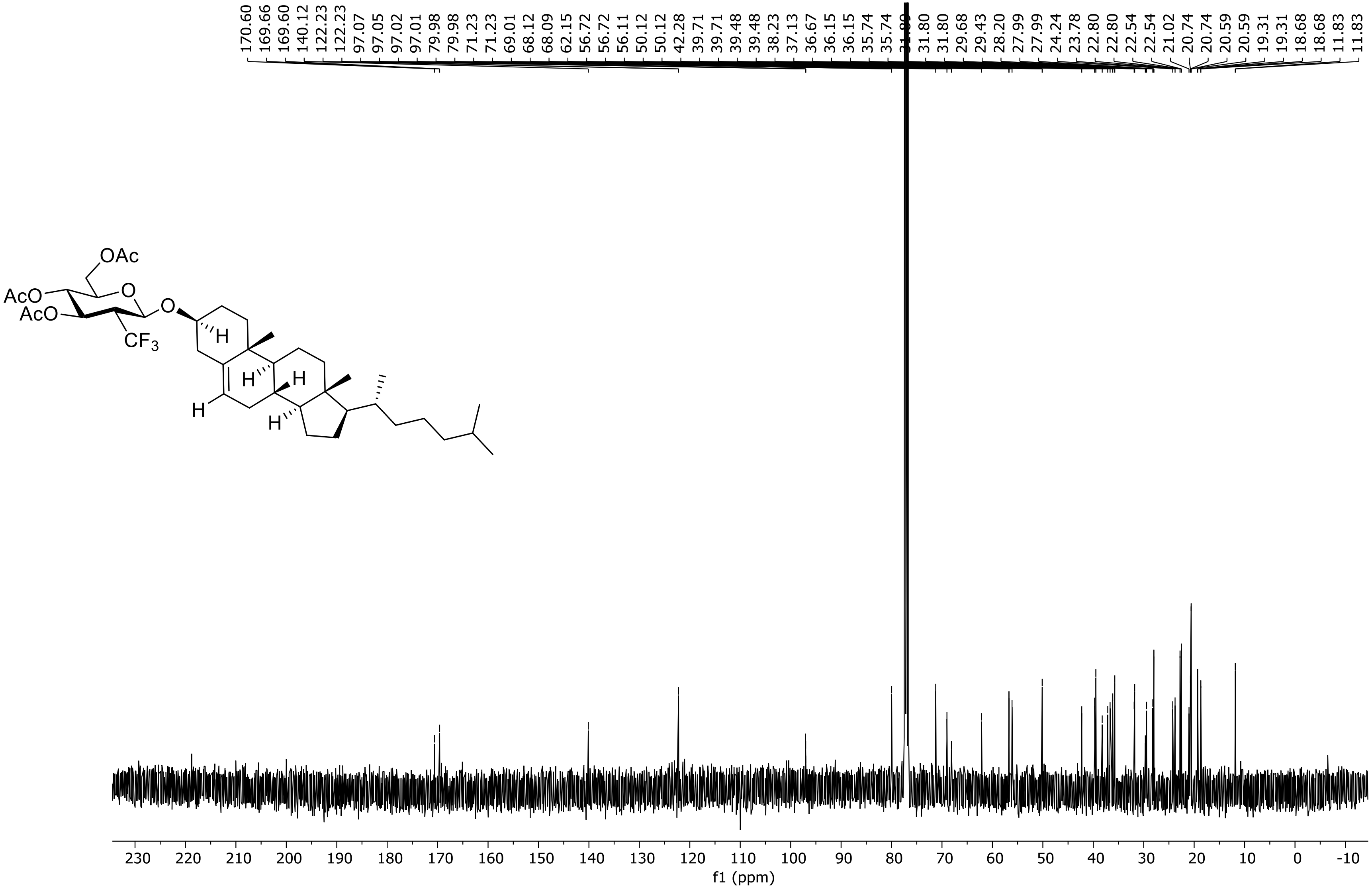


Figure S124. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **30β**

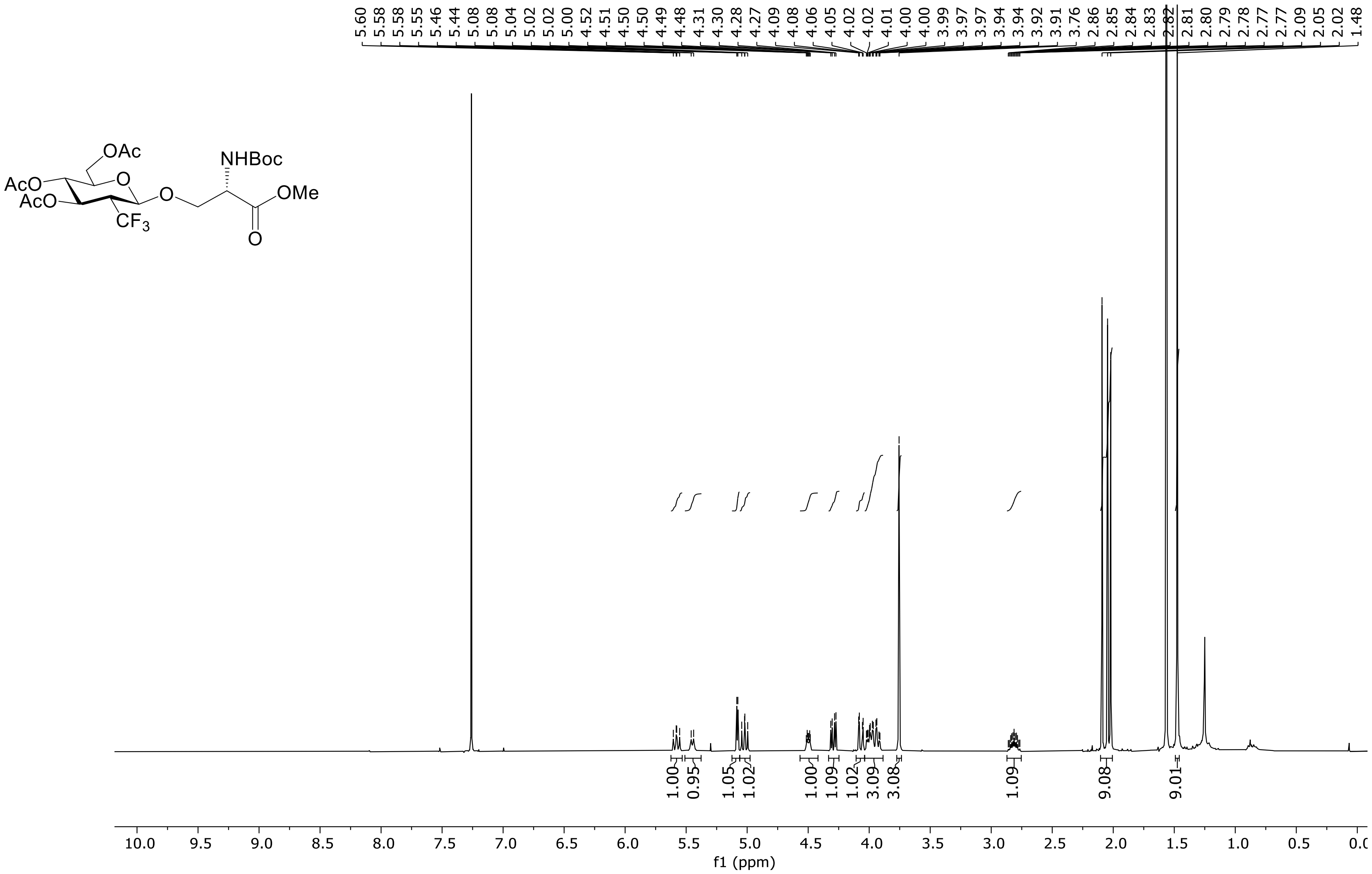


Figure S125. ^{1}H NMR (CDCl$_3$, 400 MHz) of **31β**

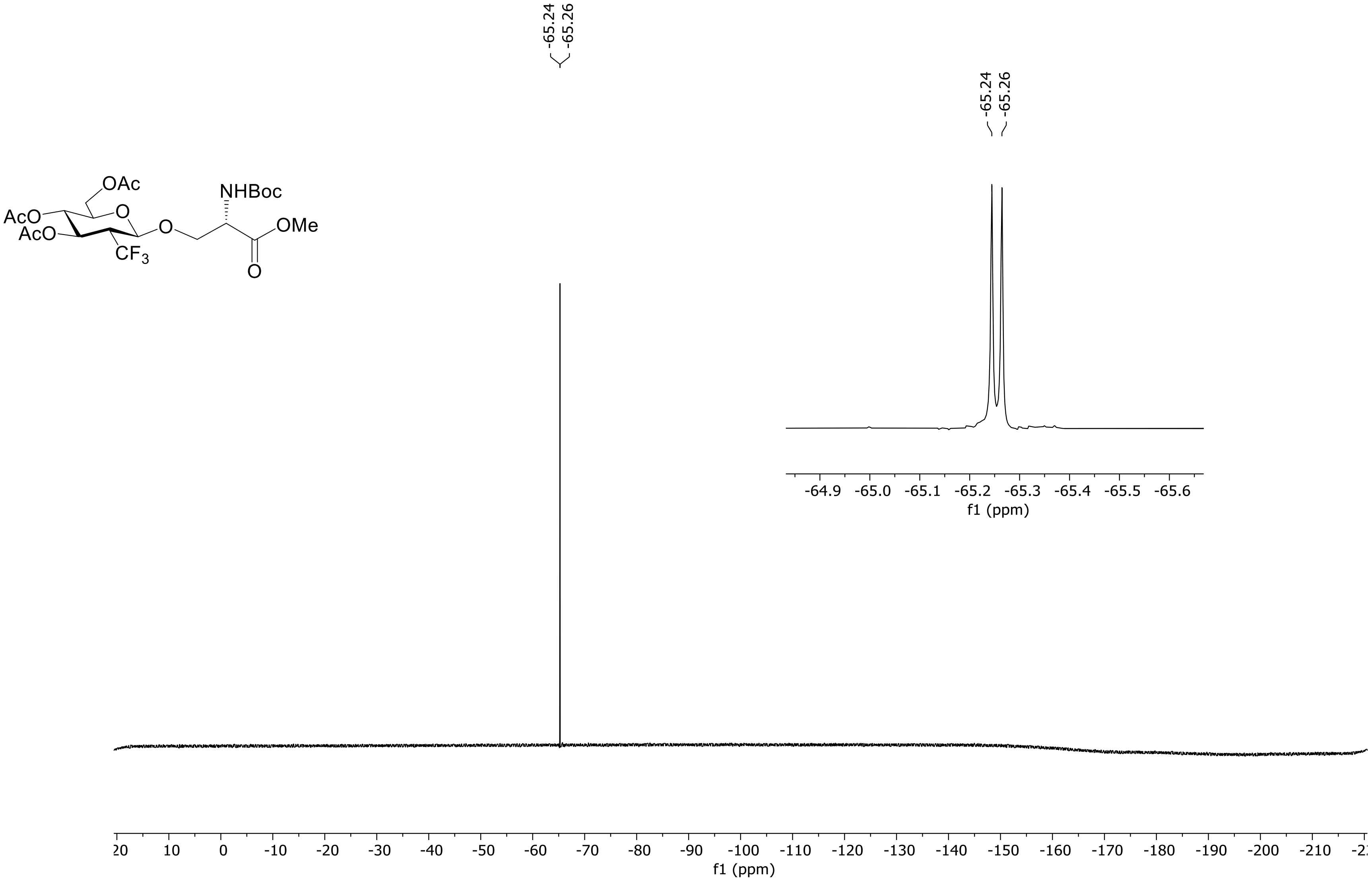


Figure S126. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **31β**

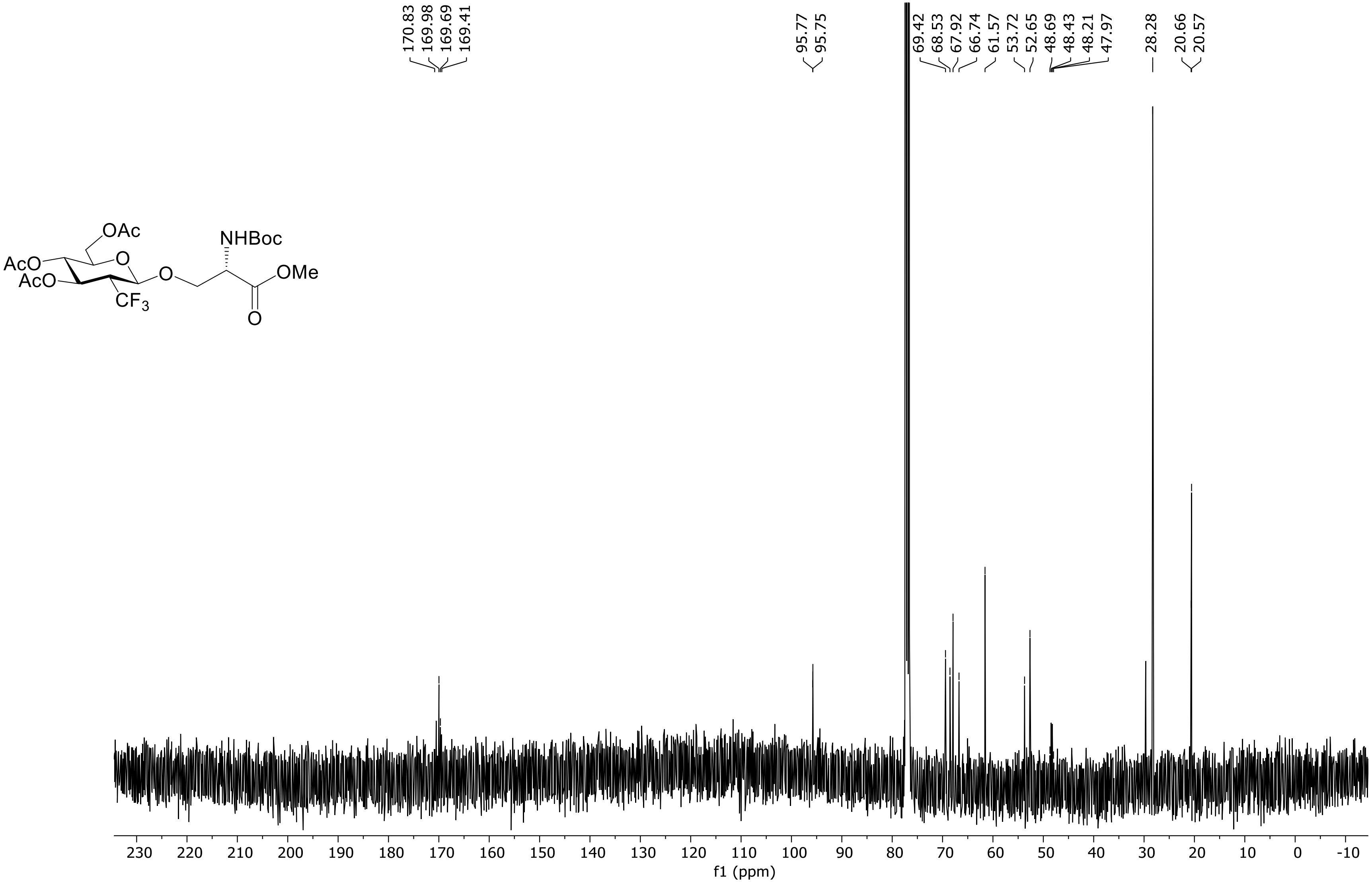


Figure S127. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **31β**

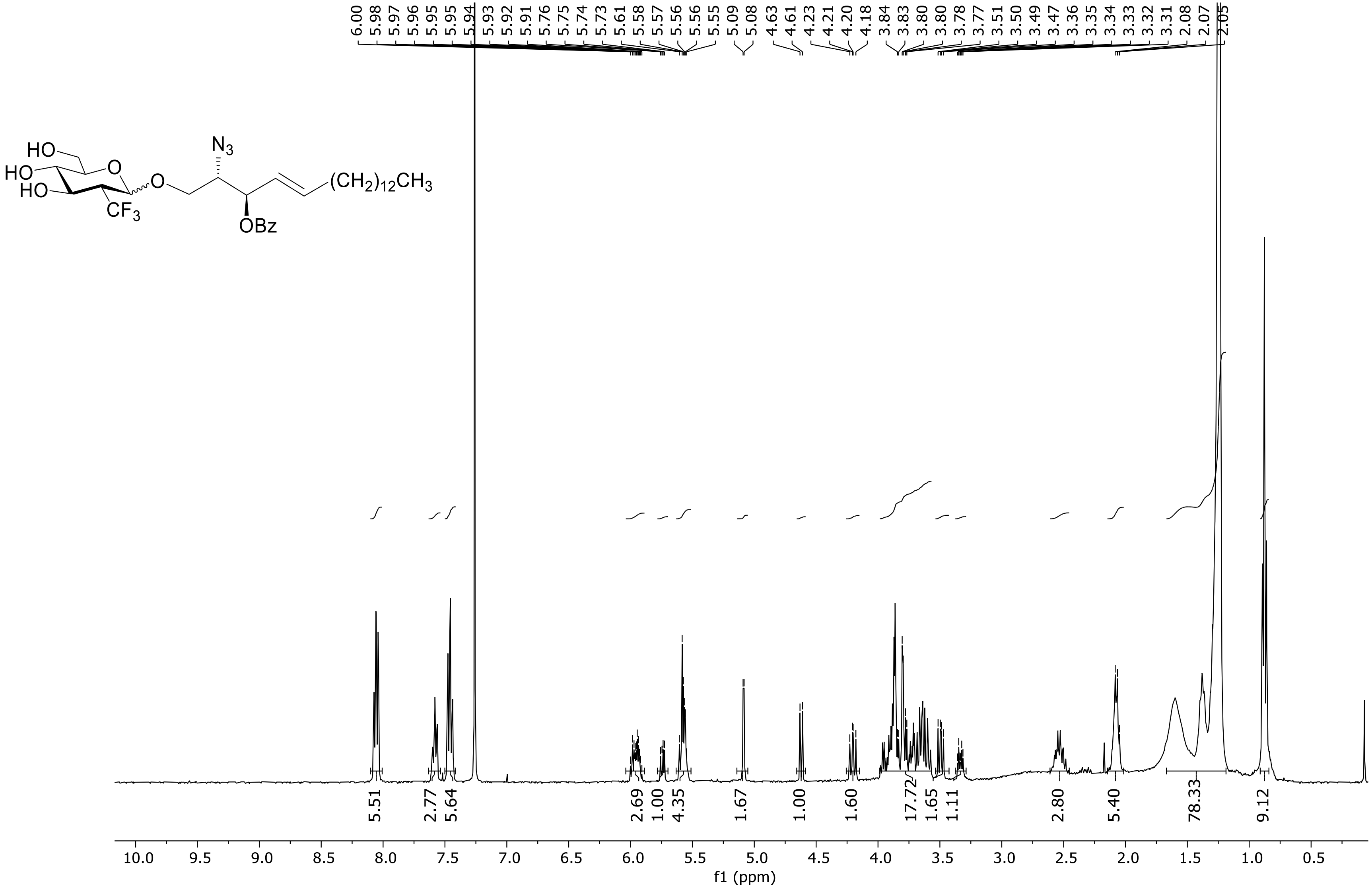


Figure S128. ^{1}H NMR ($CDCl_3$, 400 MHz) of **32bα/β**

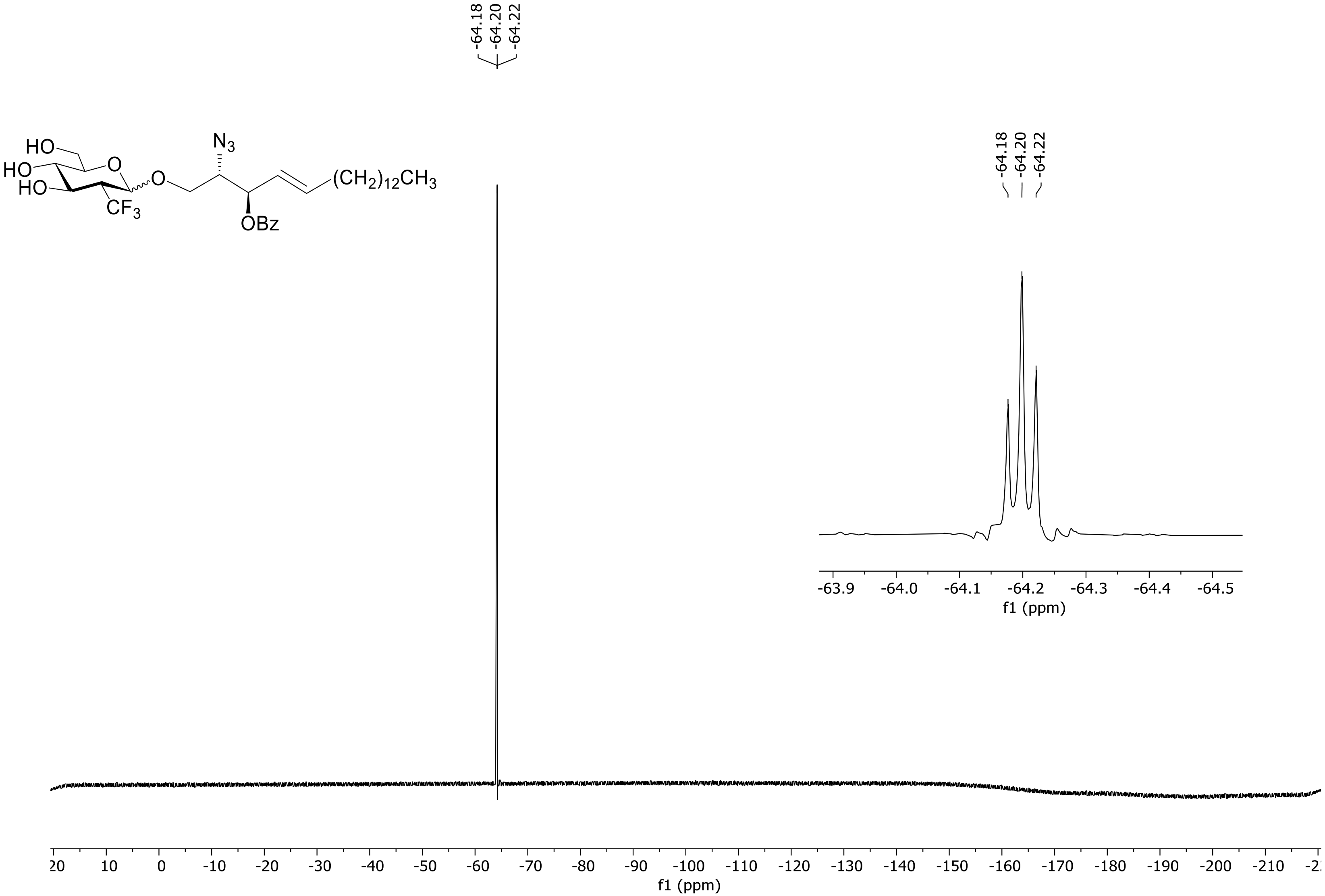


Figure S129. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **32bα/β**

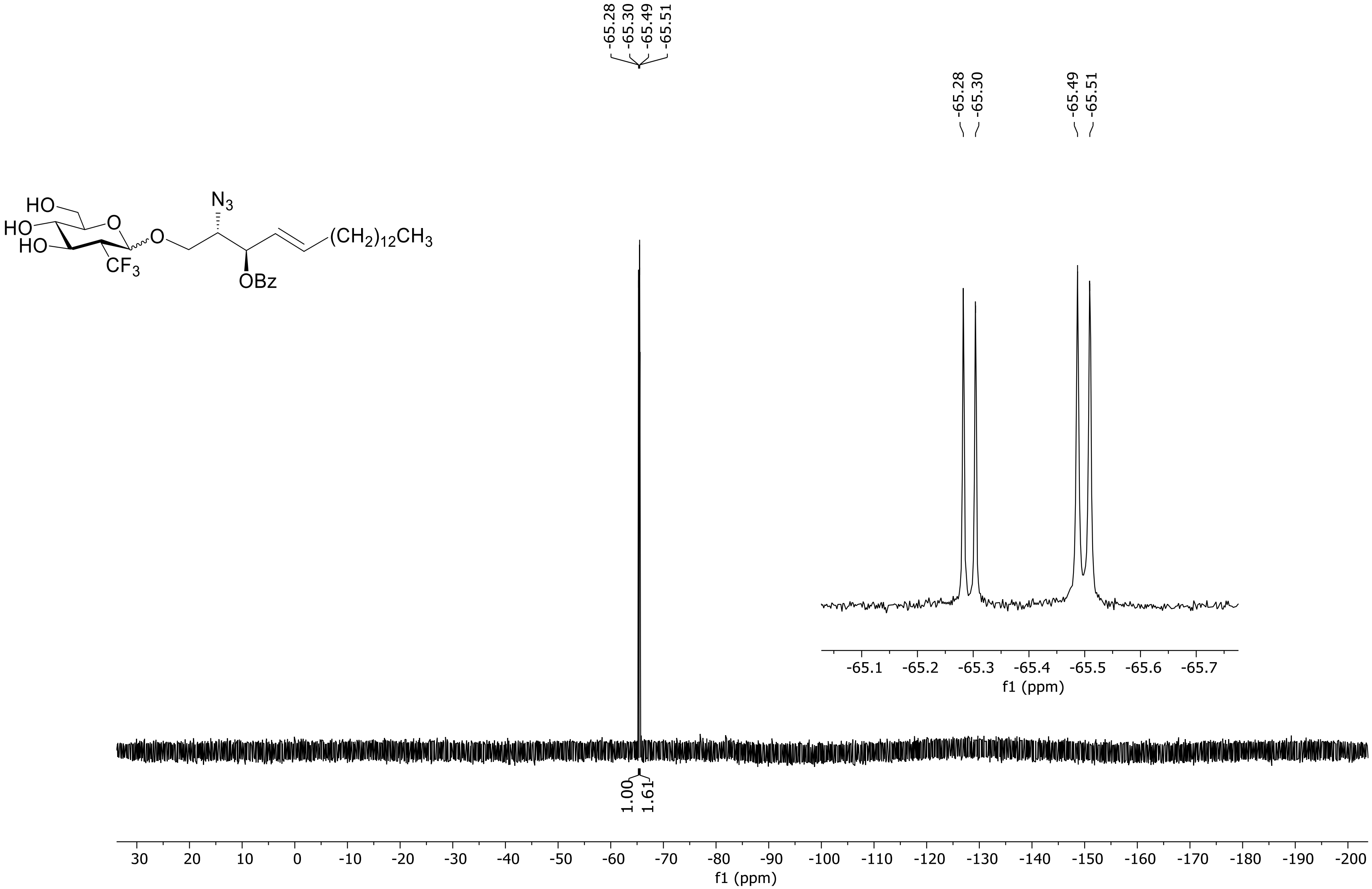


Figure S130. ^{19}F NMR (CD_3OD, 376.5 MHz) of **32bα/β**

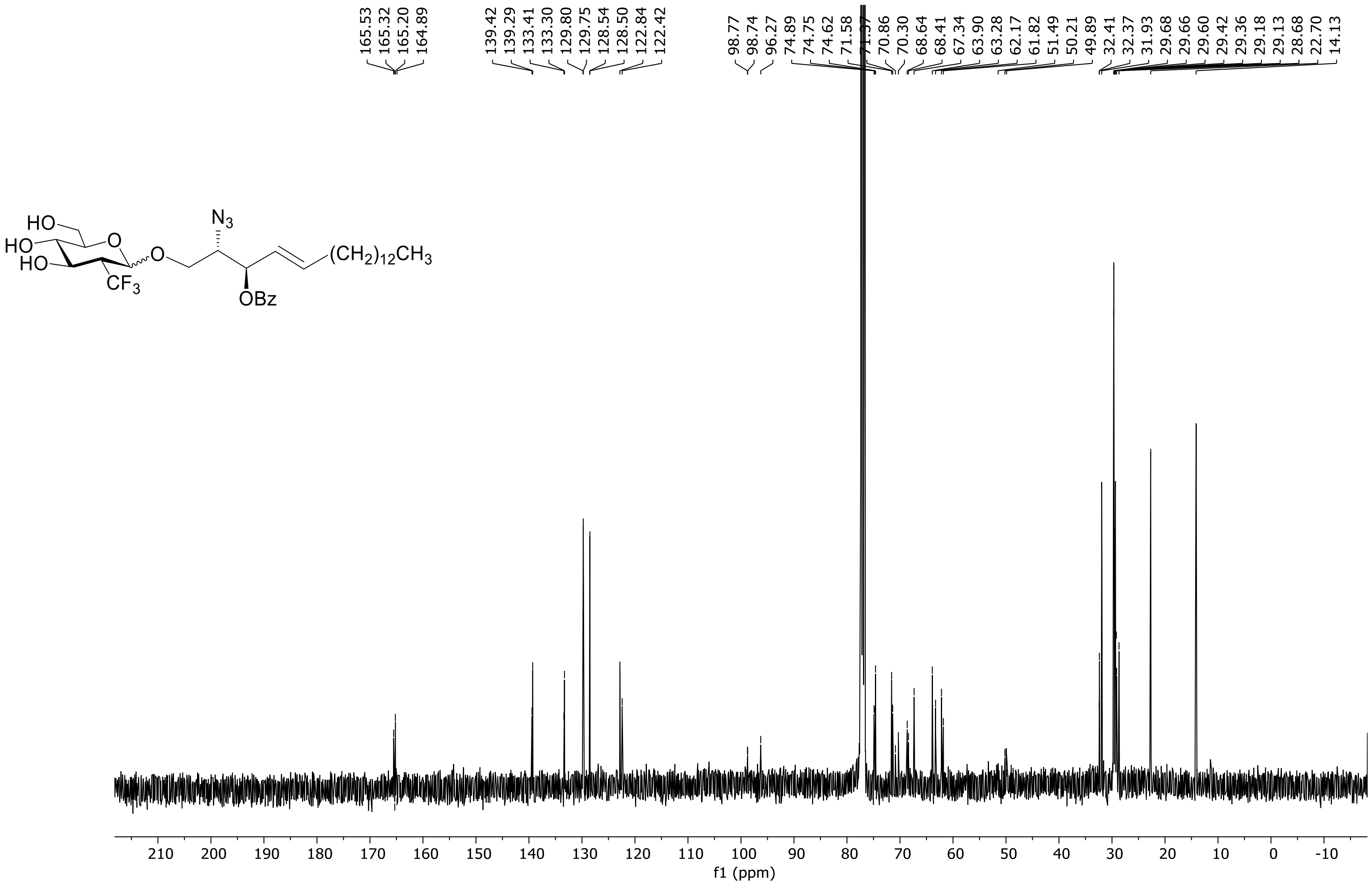


Figure S131. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **32bα/β**

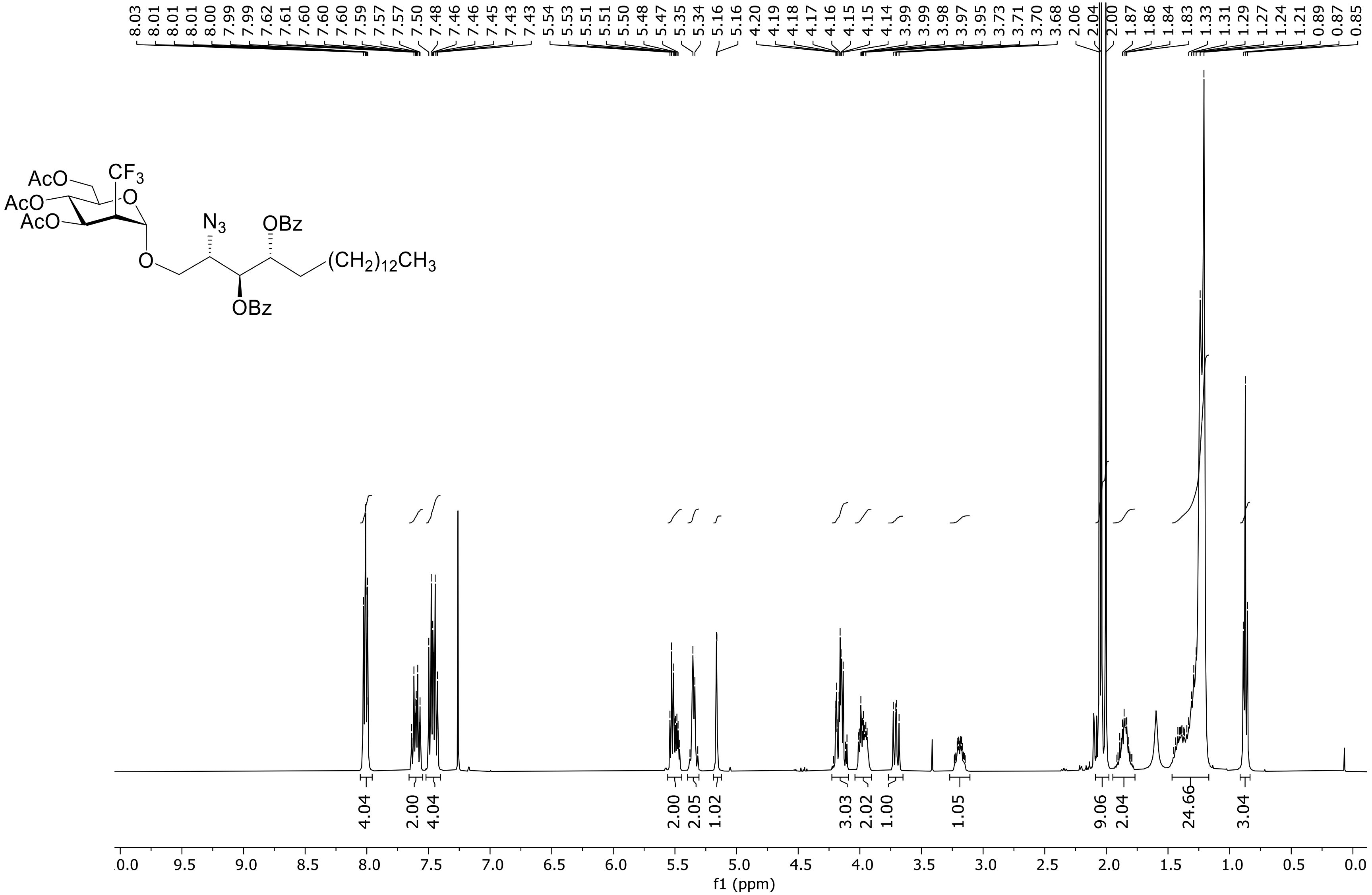


Figure S132. ^{1}H NMR ($CDCl_3$, 400 MHz) of **33α**

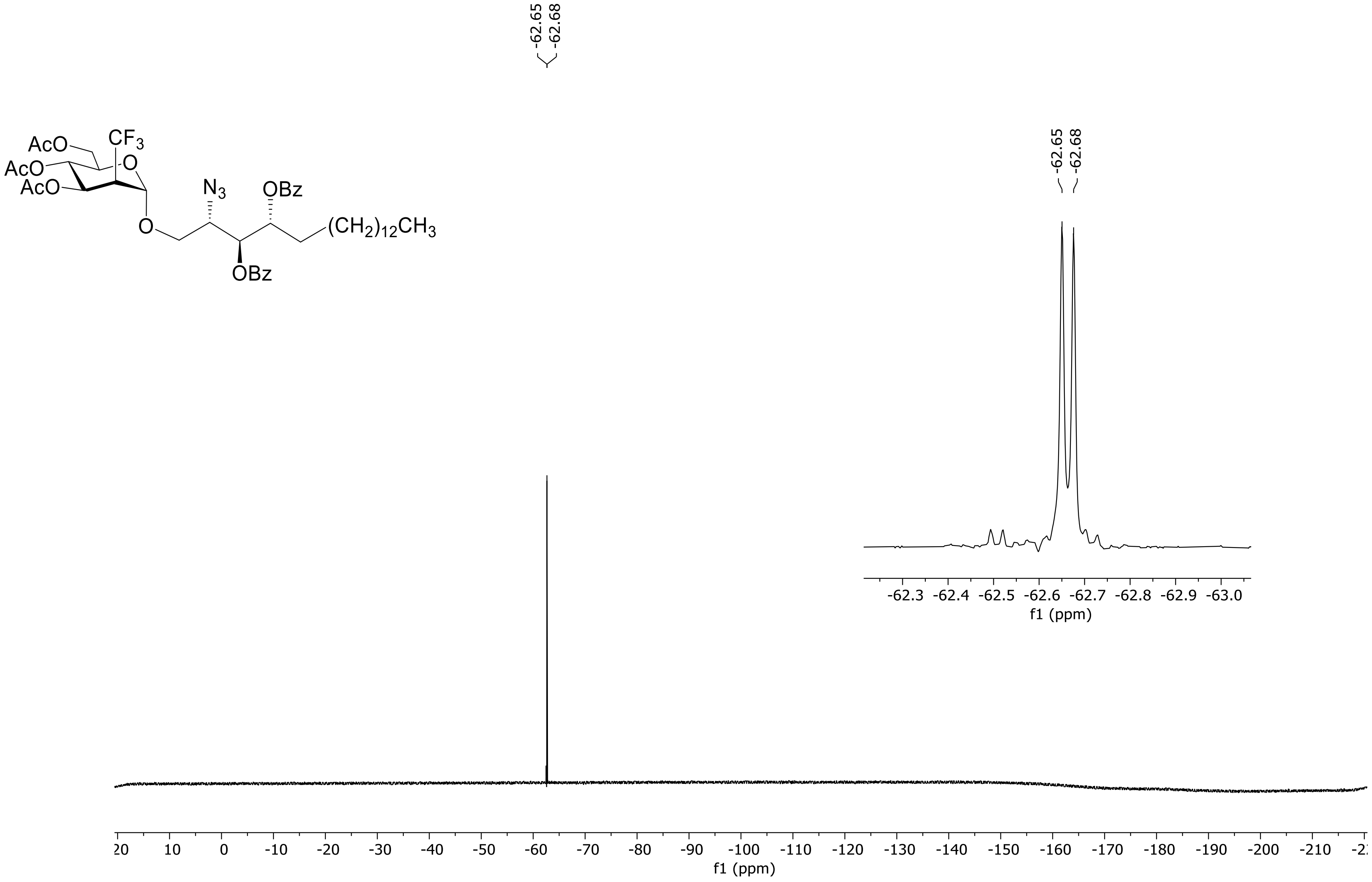


Figure S133. ^{19}F NMR ($CDCl_3$, 376.5 MHz) of **33α**

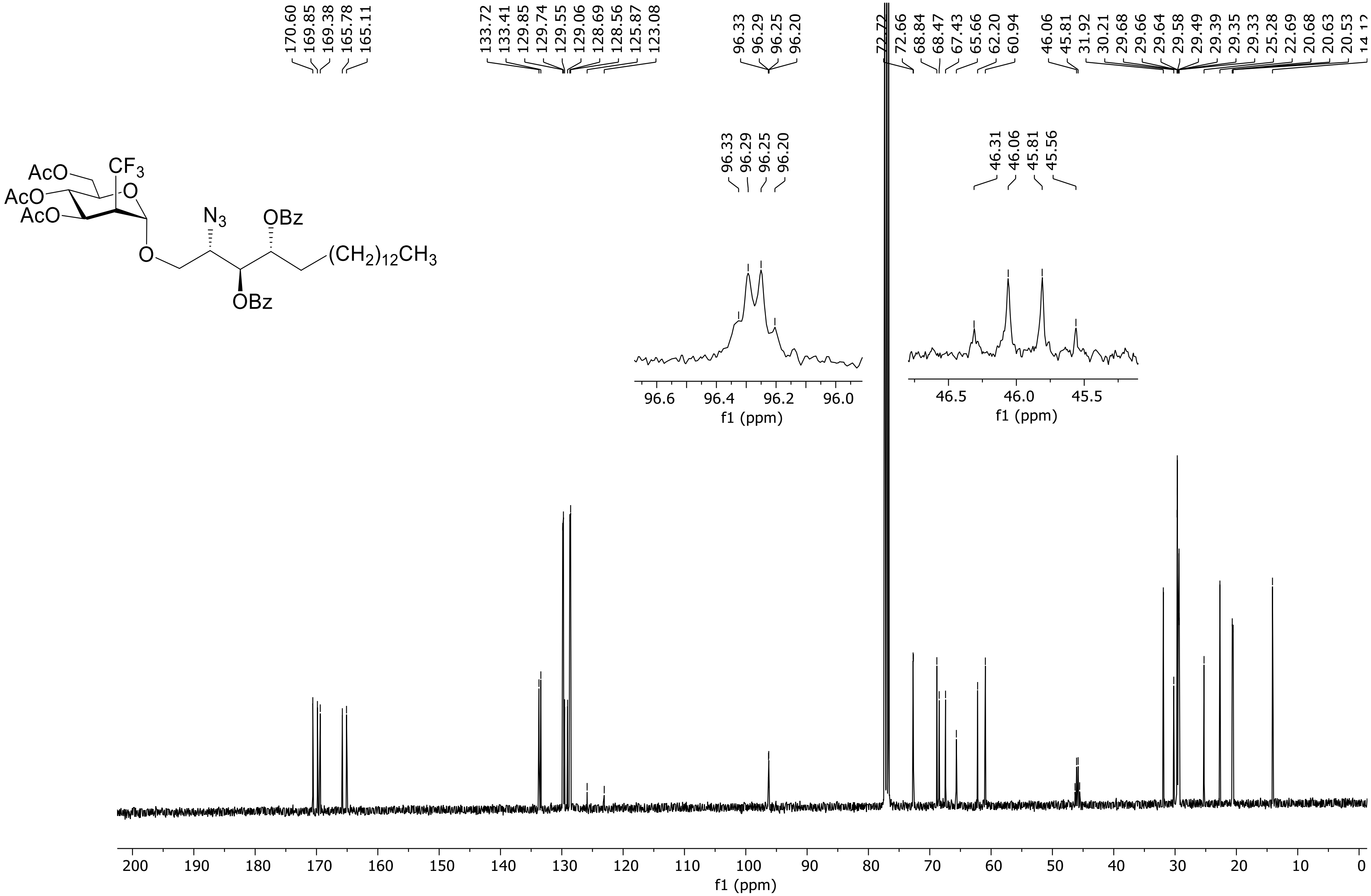


Figure S134. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **33α**

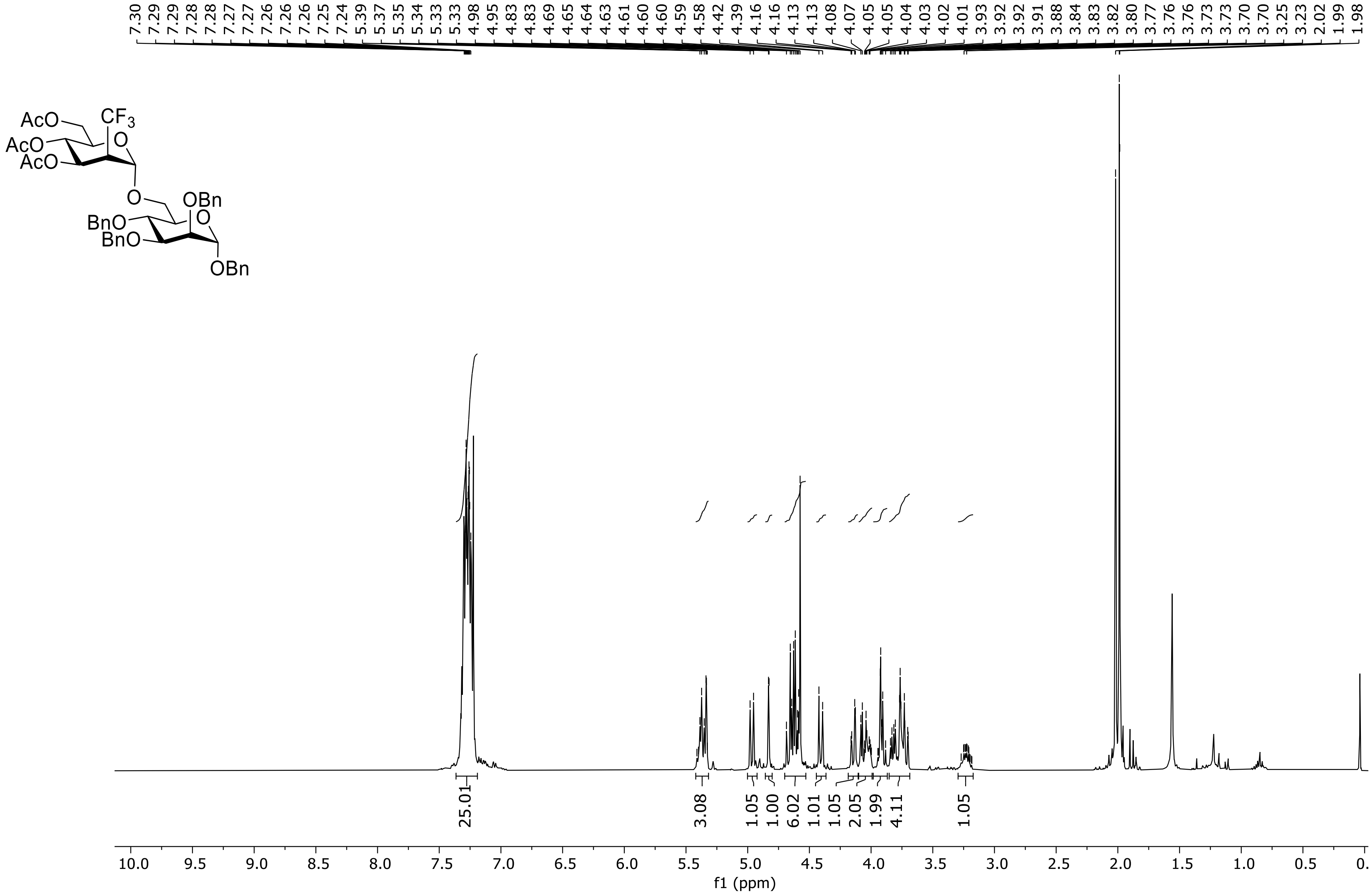


Figure S135. ^{1}H NMR (CDCl$_3$, 400 MHz) of **34α/β**

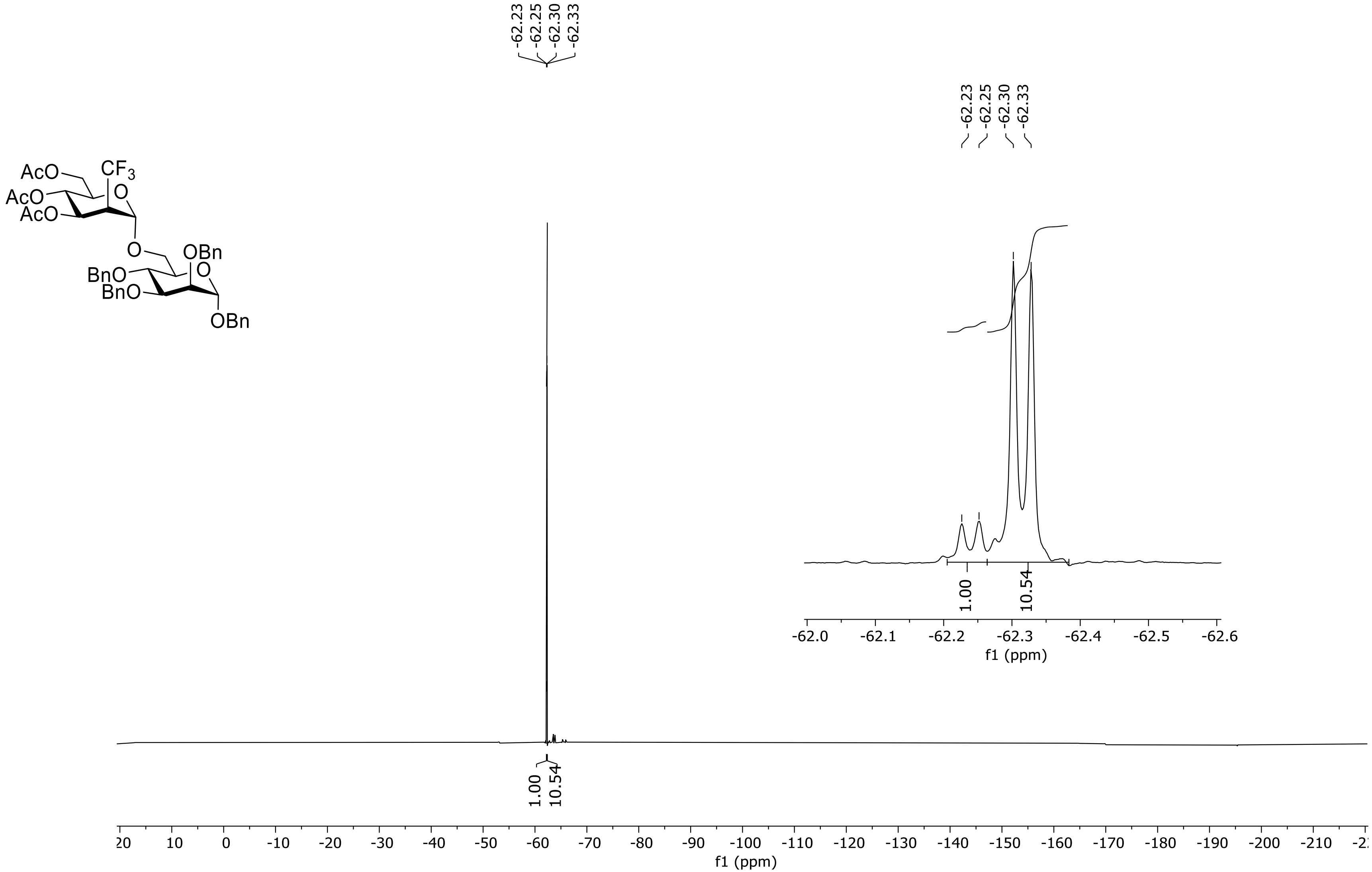


Figure S136. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **34α/β**

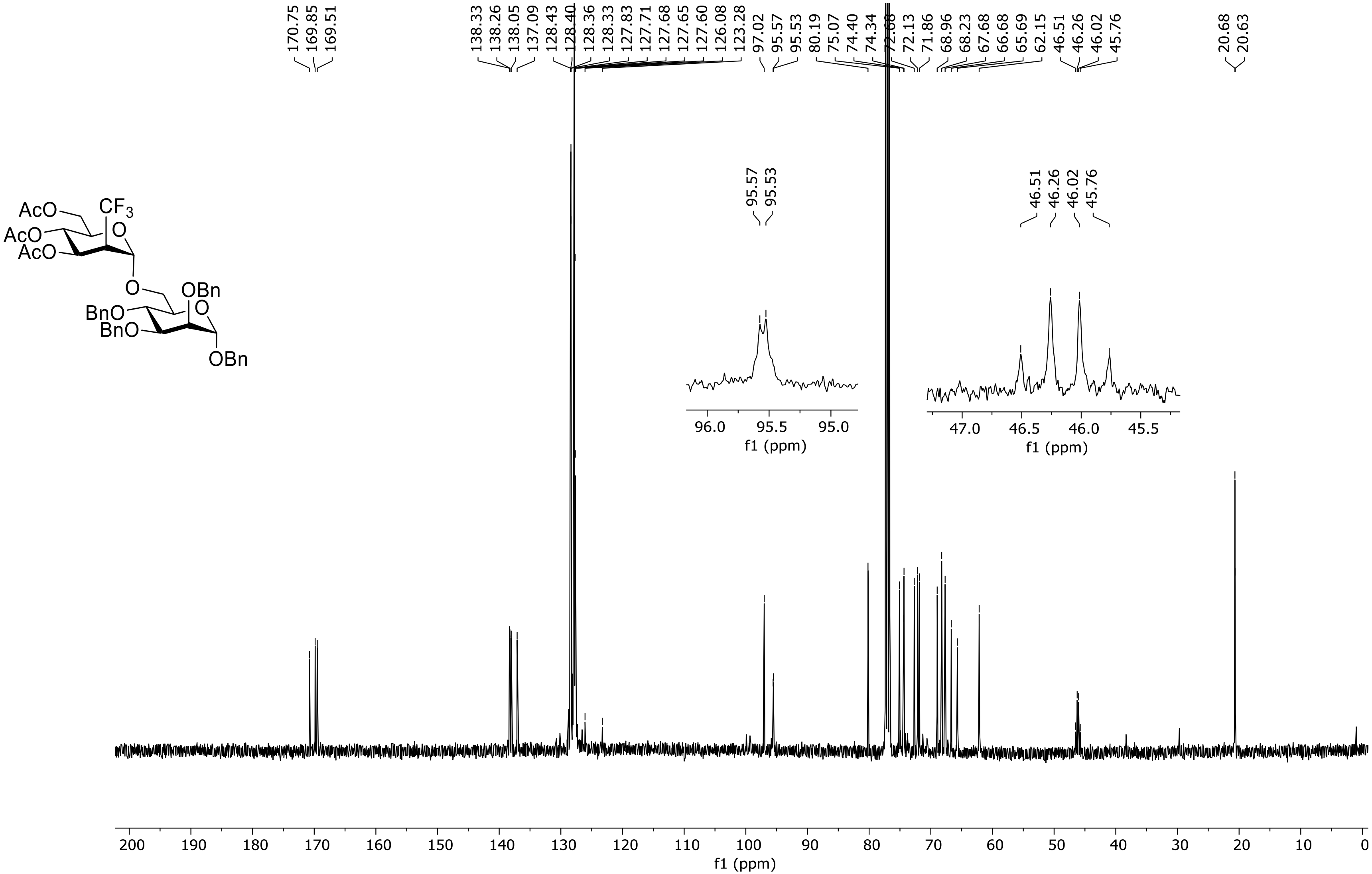


Figure S137. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **34α/β**

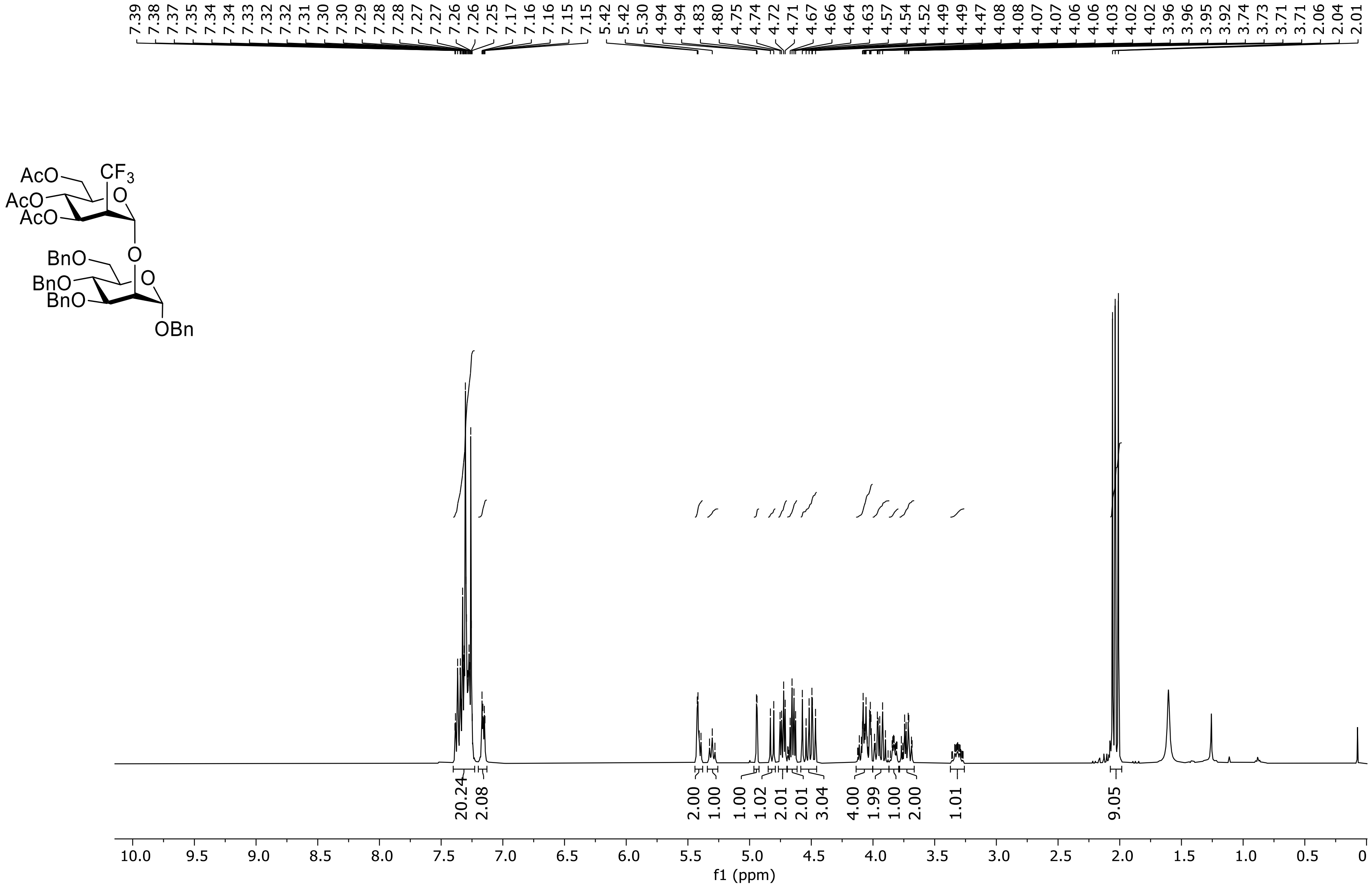


Figure S138. ^{1}H NMR ($CDCl_3$, 400 MHz) of **35α**

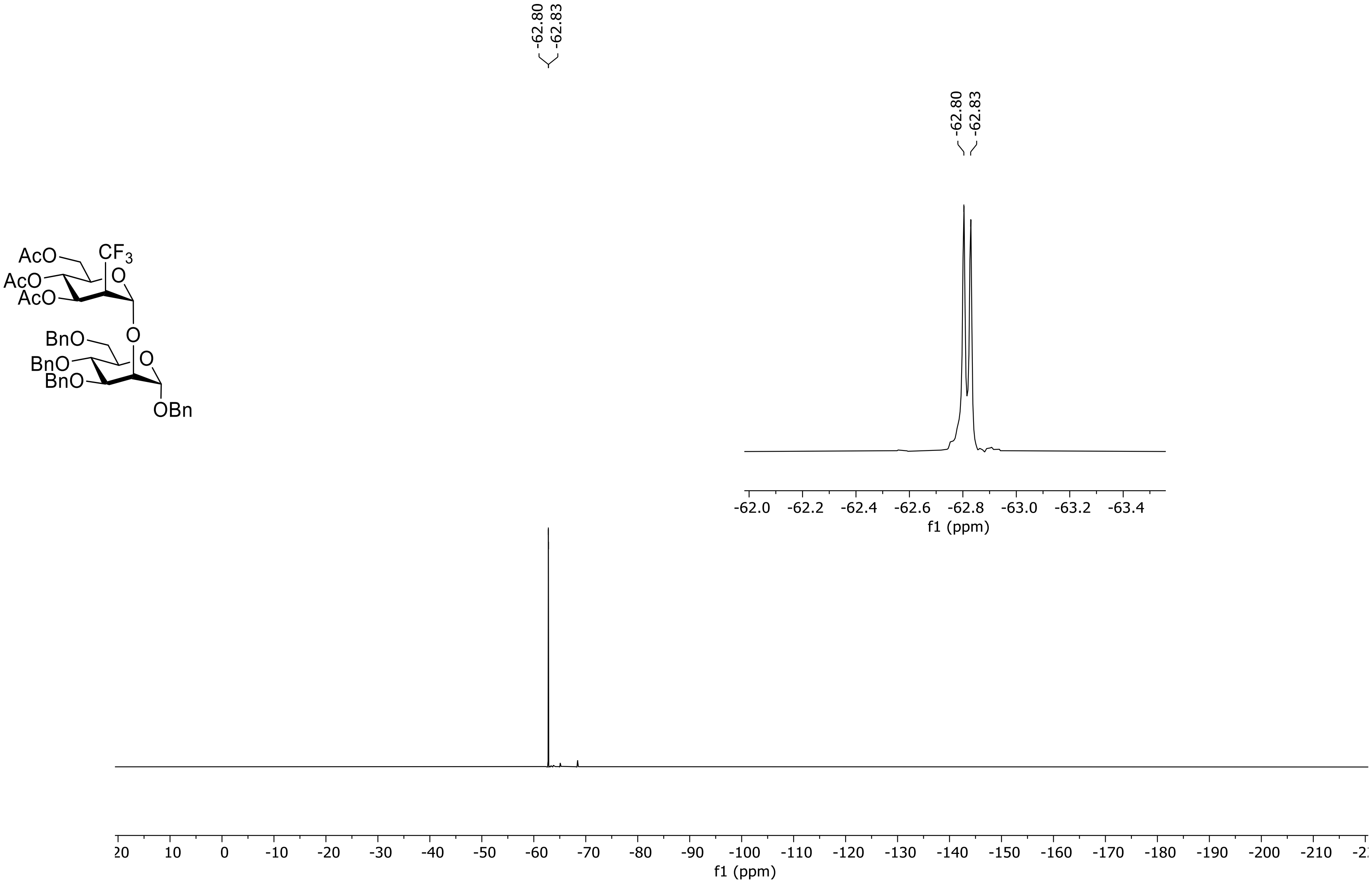


Figure S139. ^{19}F NMR (CDCl$_3$, 376.5 MHz) of **35α**

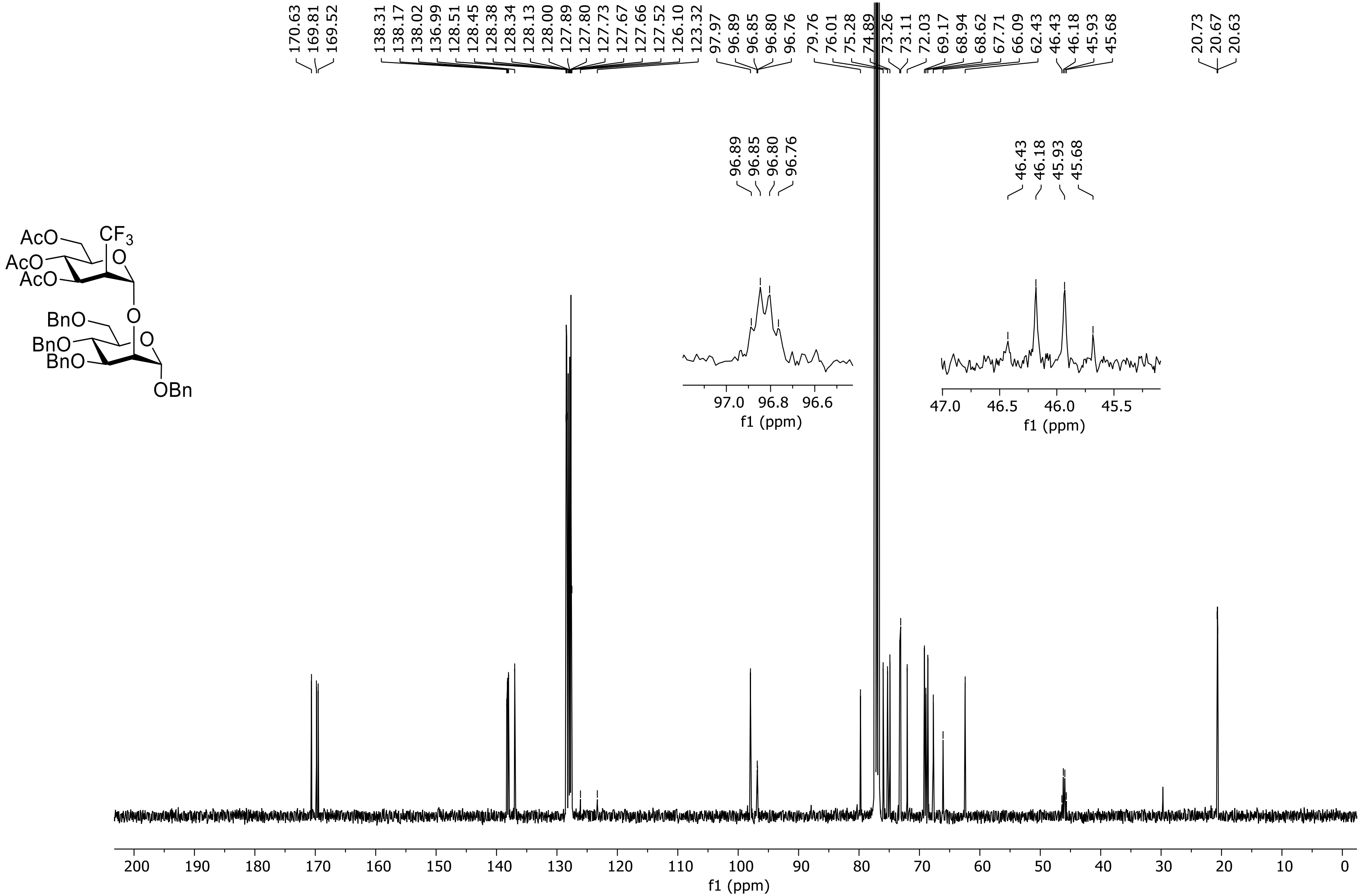


Figure S140. ^{13}C NMR (CDCl$_3$, 100.6 MHz) of **35α**

5. X-ray crystallographic data

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-trifluoromethyl-α-D-glucopyranose (4c)

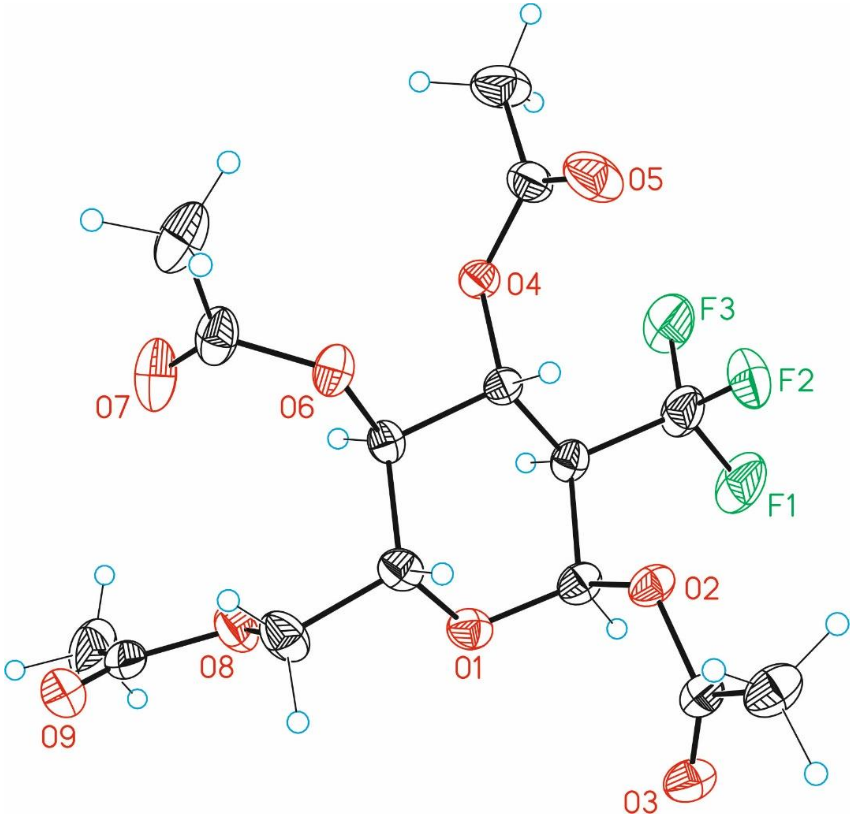


Figure S141. ORTEP diagram of compound **4c** with 50% probability ellipsoid:

Black = carbon, Red = oxygen, Blue = hydrogen, Green = fluorine

Table S2. Crystal data and structure refinement for **4c**

CCDC	2128832	
Empirical formula	$C_{15} H_{19} F_3 O_9$	
Formula weight	400.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	P3(2)	
Unit cell dimensions	a = 10.2792(4)Å	a= 90°.
	b = 10.2792(4)Å	b = 90°.
	c = 15.3888(6)Å	g = 120°.
Volume	1408.17(12) Å^3	
Z	3	
Density (calculated)	1.416 Mg/m^3	
Absorption coefficient	0.135 mm^{-1}	
F(000)	624	
Crystal size	0.40 x 0.40 x 0.20 mm^3	
Theta range for data collection	2.288 to 30.522°.	
Index ranges	-6<=h<=14,-14<=k<=9,-21<=l<=11	
Reflections collected	5160	
Independent reflections	3458[R(int) = 0.0148]	
Completeness to theta =30.522°	98.9%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.974 and 0.926	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3458/ 1/ 248	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0326, wR2 = 0.0819	
R indices (all data)	R1 = 0.0375, wR2 = 0.0852	
Flack parameter	x =-0.2(4)	
Largest diff. peak and hole	0.226 and -0.226 e.Å^{-3}	

3,4,6-Tri-*O*-benzyl-2-deoxy-2-trifluoromethyl-β-D-glucopyranosyl-(1→6)-[1:2,3:4]-di-*O*-isopropylidene-α-D-galactopyrano-side (7β)

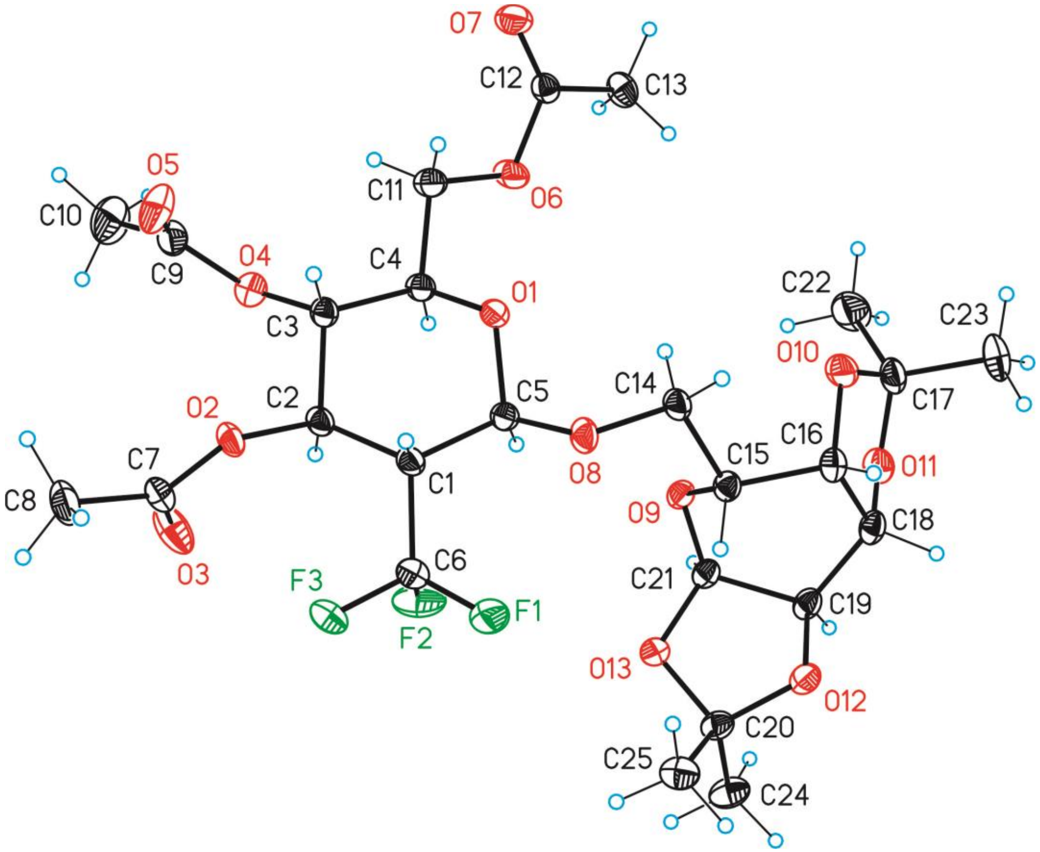


Figure S142. ORTEP diagram of compound **7β** with 50% probability ellipsoid:

Black = carbon, Red = oxygen, Blue = hydrogen, Green = fluorine

Table S3. Crystal data and structure refinement for **7β**

CCDC	2128831	
Empirical formula	$C_{25} H_{35} F_3 O_{13}$	
Formula weight	600.53	
Temperature	100(2)K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.4505(8)Å	a= 90°.
	b = 9.7494(7)Å	b = 108.262(2)°.
	c = 12.7672(8)Å	g = 90°.
Volume	1471.69(17) Å3	
Z	2	
Density (calculated)	1.355 Mg/m3	
Absorption coefficient	0.120 mm-1	
F(000)	632	
Crystal size	0.200 x 0.200 x 0.050 mm3	
Theta range for data collection	1.680 to 35.091°.	
Index ranges	-20<=h<=19,-15<=k<=15,-14<=l<=19	
Reflections collected	33703	
Independent reflections	11662[R(int) = 0.0233]	
Completeness to theta =35.091°	93.6%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.74 and 0.71	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	11662/ 1/ 377	
Goodness-of-fit on F2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0886	
R indices (all data)	R1 = 0.0413, wR2 = 0.0917	
Largest diff. peak and hole	0.344 and -0.198 e.Å	

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