Supporting information for

Glycosylation of vicinal di-and trifluorinated glucose and galactose donors

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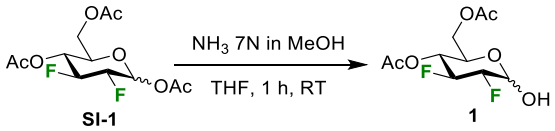
1 General information

Chemical reagents were obtained from commercial sources and used without further purification, unless stated otherwise. All air/moisture sensitive reactions were carried out under inert atmosphere (argon) in flame-dried glassware. Anhydrous bottles of THF, isopropanol, 1-propanol and CH_2Cl_2, bought from commercial sources, were used for the reactions unless stated as redistilled, in which case toluene was redistilled with sodium as a drying agent and CH_2Cl_2 with calcium hydride. When appropriate, other reagents and solvents were purified by standard techniques. Reactions were monitored by TLC (MERCK Kieselgel 60 F_{254}, aluminium sheet), visualised under UV light (254 nm), and by staining with sugar dip (0.3% (w/v) of *N*-(1-naphthyl)ethylenediamine and 5% (v/v) conc. H_2SO_4 in methanol). Column chromatography were performed using a Biotage Isolera One instrument with the described solvent system, prepacked Biotage column stated and dry loaded on silica gel (MERCK Geduran 60 Å, particle size 40-63 µm) when required. All reported solvent mixtures are volume measured. ^1H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ using a BRUKER AV400 (400, 101 and 376 MHz respectively) and AV500 (500, 126 and 471 MHz respectively) spectrometers. ^1H and ^{13}C chemical shifts (δ) are quoted in ppm relative to residual solvent peaks as appropriate. The coupling constants (J) were recorded in Hertz (Hz). The coupling constants have not been averaged. The signals are shown as s for singlet, d for doublet, t for triplet, q for quadruplet, quin for quintuplet and m for multiplet. dd means doublet of doublet and dt doublet of triplet etc. Fourier-transform infrared (FT-IR) spectra are reported in wavenumbers (cm^{-1}) and were recorded as neat films on a Thermo Scientific Nicolet iS5 spectrometer using neat samples (solid or liquid). Electrospray mass spectra were obtained from a Waters 2700 sample manager ESI and recorded in m/z (abundance). HRMS was obtained from a Bruker APEX III FT-ICR-MS. Samples were run in HPLC methanol or MeCN. Optical rotations were recorded on an Optical Activity POLAAR 2001 at 589 nm, samples were pre-equilibrated for 24 h when required.

2 Synthesis and characterisation of the glycosylation donors

2.1 Precursor syntheses

2.1.1 4,6-Di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-D-glucopyranose (**1**)

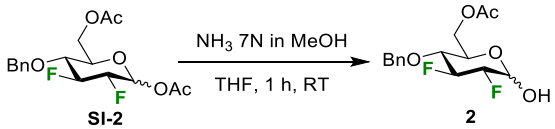


SI-1 **1**

To a solution of **SI-1** (4.86 g, 15.7 mmol, 1.0 equiv) in THF (100 mL) at 0 °C was slowly added a 7N ammonia solution in MeOH (37.0 mL, 314 mmol, 20 equiv). After 15 min the reaction mixture was warmed up to rt and stirred for 2 h. The mixture was concentrated in *vacuo* and the crude was purified by flash column chromatography (50 g, hexane/EtOAc 90:10 to 50:50) to afford product **1** as a white solid (3.96 g, 14.8 mmol, 94% yield). R_f 0.43 (hexane/EtOAc 50:50); mp 95–97 °C (EtOAc); $[\alpha]_D^{20}$ +65.2 (c 0.25, $CHCl_3$); IR (neat) 3447 (br), 2970 (w), 2360 (w), 1748 (s), 1373 (w), 1239 (s), 1155 (w), 1033 (s), 763 (w), 553 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, α/β 83:17) (COSY/HMBC/HSQC) δ 5.50 (1H, t, *J* = 3.7 Hz, $H_{1\alpha}$), 5.18 (1H, dd, *J* = 23, 9.7 Hz, $H_{4\alpha}$), 4.96 (1H, ddt, *J* = 54.2, 13.3, 8.3 Hz, $H_{3\alpha}$), 4.85 (1H, dd, *J* = 7.7, 3.2 Hz, $H_{1\beta}$), 4.68 (1H, ddt, *J* = 52.5, 15.3, 8.8 Hz, $H_{3\beta}$), 4.61

(1H, dddd, *J* = 50.1, 13.0, 9.0, 3.9 Hz, $H_{2\alpha}$), 4.40 (1H, dddd, *J* = 51.1, 14.5, 8.5, 7.7 Hz, $H_{2\beta}$), 4.24 (1H, dd, *J* = 11.9, 4.1 Hz, $H_{6\alpha}$), 4.16–4.24 (1H, m, $H_{5\alpha}$), 4.13 (1H, dt, *J* = 11.6, 2.0 Hz, $H_{6'\alpha}$), 3.74 (1H, br. s, H_{OH}), 3.68 (1H, dddd, *J* = 10.2, 5.0, 2.5, 1.2 Hz, $H_{5\beta}$), 2.13 (3H, s, H_{CH3}), 2.10 (3H, s, H_{CH3}) ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ -196.2 (1F, d, *J* = 53.3, 12.9 Hz, $F_{3\beta}$), -199.7 (1F, dtd, *J* = 50.3, 15.6, 3.5 Hz, $F_{2\beta}$), -201.2 (1F, dt, *J* = 50.3, 12.1 Hz, $F_{3\alpha}$), -201.8 (1F, dqd, *J* = 53.8, 13.9, 3.5 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$) δ -196.2 (1F, d, *J* = 13.9 Hz, $F_{3\beta}$), -199.7 (1F, d, *J* = 13.9 Hz, $F_{2\beta}$), -201.2 (1F, d, *J* = 13.9 Hz, $F_{3\alpha}$), -201.8 (1F, d, *J* = 12.1 Hz, $F_{2\alpha}$) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.9 ($C_{\underline{C}OCH3\alpha}$), 170.9 ($C_{\underline{C}OCH3\beta}$), 169.5 ($C_{\underline{C}OCH3\alpha}$), 169.4 ($C_{\underline{C}OCH3\beta}$), 94.2 (dd, *J* = 23.5, 11.0 Hz, $C_{1\beta}$), 91.8 (dd, *J* = 190, 19.8 Hz, $C_{2\beta}$), 90.9 (dd, *J* = 189.3, 17.6 Hz, $C_{3\beta}$), 90.5 (dd, *J* = 21.3, 10.3 Hz, $C_{1\alpha}$), 89.8 (dd, *J* = 187.8, 19.8 Hz, $C_{2\alpha}$), 88.0 (dd, *J* = 191.5, 16.9 Hz, $C_{3\alpha}$), 71.1 (d, *J* = 7.3 Hz, $C_{5\beta}$), 67.84 (dd, *J* = 18.7, 7.7 Hz, $C_{4\alpha}$), 67.0 (d, *J* = 19.1, 7.3 Hz, $C_{5\alpha}$), 61.7 (C_6), 20.7 (C_{CH3}), 20.7 (C_{CH3}) ppm; HRMS (ESI+) for $C_{10}H_{14}F_2NaO_6$ $[M + Na]^+$ calcd 291.0651 found 291.0653 (-0.9 ppm error).

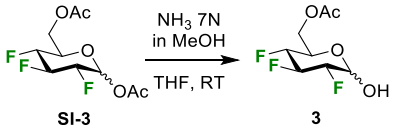
2.1.26-*O*-Acetyl-4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-D-glucopyranose (**2**)



SI-2 **2**

To a solution of **SI-2** (11.0 g, 30.7 mmol, 1.0 equiv) in THF (150 mL) at 0 °C was slowly added a 7 N ammonia solution in MeOH (87.5 mL, 614 mmol, 20 equiv). After 15 min the reaction mixture was warmed up to rt and stirred for 1 h. The mixture was concentrated in *vacuo* and the crude was purified by flash column chromatography (100 g, hexane/EtOAc 90:10 to 70:30) to afford product **2** as a pale-yellow solid (10.2 g, 32.4 mmol, quant.). R_f 0.09 (hexane/EtOAc 80:20); $[\alpha]_D^{20}$ +94.6 (c 0.44, $CHCl_3$); mp 85–87 °C (CH_2Cl_2); IR (neat) 3420 (br), 2935 (s), 2866 (s), 2359 (w), 1743 (s), 1456 (w), 1368 (w), 1237 (s), 1040 (s), 750 (w), 699 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, α/β 77:23) (COSY/HMBC/HSQC) δ 7.46–7.30 (5H, m, H_{Ar}), 5.42 (1H, t, *J* = 3.6 Hz, $H_{1\alpha}$), 5.11 (1H, ddt, *J* = 54.7, 13.9, 8.8 Hz, $H_{3\alpha}$), 4.91 (1H, d, *J* = 11.1 Hz, $H_{CH2OBn\alpha}$), 4.90 (1H, d, *J* = 11.3 Hz, $H_{CH2OBn\beta}$), 4.85 (1H, dd, *J* = 7.83, 2.81 Hz, $H_{1\beta}$), 4.64 (1H, d, *J* = 11.4 Hz, $H_{CH2OBn\alpha}$), 4.63 (1H, d, *J* = 11.3 Hz, $H_{CH2OBn\beta}$), 4.55 (1H, dddd, *J* = 50.3, 13.1, 8.8, 3.9 Hz, $H_{2\alpha}$), 4.33 (1H, dt, *J* = 12.0, 2.0 Hz, $H_{6\alpha}$), 4.24 (1H, br. dd, *J* = 12.0, 4.0 Hz, $H_{6'\alpha}$), 4.12 (1H, br. d, *J* = 9.7 Hz, $H_{5\alpha}$), 3.63 (1H, ddd, *J* = 14.0, 9.8, 8.4 Hz, $H_{4\alpha}$), 2.01 (3H, s, H_{CH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -191.3 (1F, ddd, *J* = 52.5, 13.4, 5.2 Hz, $F_{3\beta}$), -196.8 (1F, dq, *J* = 55.1, 12.9 Hz, $F_{3\alpha}$), -199.6 (1F, dd, *J* = 52.0, 15.6 Hz, $F_{2\beta}$), -201.1 (1F, dd, *J* = 50.3, 13.9, 12.1 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -191.3 (1F, dt, *J* = 10.4, 5.2 Hz, $F_{3\beta}$), -196.8 (1F, d, *J* = 12.1, 3.5 Hz, $F_{3\alpha}$), -199.6 (1F, d, *J* = 13.9 Hz, $F_{2\beta}$), -201.1 (1F, d, *J* = 12.1 Hz, $F_{2\alpha}$) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.8 ($C_{\underline{C}OCH3}$), 137.1 (C_{Ar}), 128.5 (C_{Ar}), 128.4 (C_{Ar}), 128.1 (C_{Ar}), 93.9 (ddd, *J* = 183.4, 16.9, 2.2 Hz, C_3), 90.3 (ddd, *J* = 18.3, 9.5, 2.2 Hz, C_1), 88.2 (dd, *J* = 192.2, 17.6 Hz, C_2), 74.7 (dd, *J* = 16.9, 6.6 Hz, C_4), 74.2 (d, *J* = 2.9 Hz, C_{CH2OBn}), 67.6 (d, *J* = 8.1 Hz, C_5), 62.4 (d, *J* = 5.1 Hz, C_6), 20.8 (C_{CH3}) ppm; HRMS (ESI+) for $C_{15}H_{18}F_2NaO_5$ $[M + Na]^+$ calcd 339.1015 found 339.1018 (-1.1 ppm error).

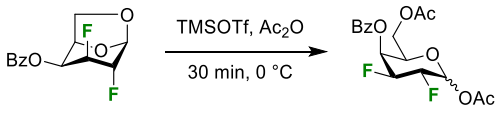
2.1.3 1,6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-D-glucopyranose (**3**)



SI-3 **3**

To a solution of **SI-3** (100 mg, 0.37 mmol, 1.0 equiv) in THF (2 mL) at 0 °C was slowly added a 7 N ammonia solution in MeOH (1.13 mL, 7.4 mol, 20 equiv). The reaction mixture was warmed up to rt and stirred for 16 h. The mixture was concentrated in *vacuo* and the crude was purified by flash column chromatography (100 g, cyclohexane/EtOAc 100:0 to 50:50) to afford product **3** as a non-separable mixture of the α- and β-anomers as a colourless oil (64 mg, 0.28 mmol, 75% yield). R_f 0.16 (hexane/EtOAc 70:30); $[\alpha]_D^{22.5}$ +64.9 (c 2.75, $CHCl_3$); IR (neat) 3425 (br), 2962 (w), 1738 (s), 1375 (w), 1240 (s), 1032 (s), 1007 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, α/β 4.72:1) (COSY/HMBC/HSQC) δ 5.46 (1H, br s, $H_{1\alpha}$), 5.08 (1H, dddt, *J* = 54.9, 16.3, 13.7, 8.5 Hz, $H_{3\alpha}$), 4.89 (1H, dd, *J* = 7.7, 3.1 Hz, $H_{1\beta}$), 4.81 (1H, dddd, *J* = 53.1, 24.3, 16.6, 8.5 Hz, $H_{3\beta}$), 4.41–4.66 (3H, m, $H_{2\alpha}$, $H_{4\alpha}$, H_6), 4.20–4.31 (2H, m H_6, $H_{5\alpha}$), 3.74 (1H, m, $H_{5\beta}$), 3.70 (1H, br s, H_{OH}), 2.12 (3H, s, $H_{CH3\alpha}$ and $H_{CH3\beta}$) ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ -195.3 (1F, dquind, *J* = 53.3, 13.6, 1.1 Hz, $F_{3\beta}$), -199.0 (1F, dtsxt, *J* = 51.1, 14.7, 1.8 Hz, $F_{4\alpha}$), -199.8 (1F, dddt, *J* = 50.8, 15.9, 13.0, 2.9 Hz, $F_{2\beta}$), -200.2 (1F, dtspt, *J* = 50.8, 14.7, 14.7, 1.8 Hz, $F_{4\beta}$), -201.1 (1F, dquindd, *J* = 54.7, 12.9, 1.8, 0.7 Hz, $F_{3\alpha}$), -201.5 (1F, dtd, *J* = 50.1, 13.6, 2.1 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$) δ -195.3 (1F, t, *J* = 12.9 Hz, $F_{3\beta}$), -199.0 (1F, dd, *J* = 12.7, 2.0 Hz, $F_{4\alpha}$), -199.8 (1F, dd, *J* = 13.2, 2.9 Hz, $F_{2\beta}$), -200.2 (1F, dd, *J* = 12.9, 2.9 Hz, $F_{4\beta}$), -201.1 (1F, t, *J* = 12.9 Hz, $F_{3\alpha}$), -201.5 (1F, dd, *J* = 13.2, 2.1 Hz, $F_{2\alpha}$) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.9 ($C_{C=O\alpha}$), 170.9 ($C_{C=O\beta}$), 94.0 (ddd, *J* = 23.1, 10.5, 1.0 Hz, $C_{1\beta}$), 91.9 (dt, *J* = 190.5, 20.0 Hz, $C_{3\beta}$) 90.3 (ddd, *J* = 21.2, 9.8, 1.2 Hz, $C_{1\alpha}$), 90.0 (dt, *J* = 186.8, 19.4 Hz, $C_{3\alpha}$), 87.5 (ddd, *J* = 193.6, 17.6, 7.6 Hz, C_2), 86.6 (ddd, *J* = 187.4, 18.7, 7.7 Hz, C_4), 70.4 (dd, *J* = 23.6, 7.4 Hz, $C_{5\beta}$), 66.3 (ddd, *J* = 23.4, 6.7, 0.5 Hz, $C_{5\alpha}$), 61.8 (C_6), 20.7 (C_{CH3}), 20.7 (C_{CH3}) ppm; HRMS (ESI+) for $C_8H_{11}F_3NaO_4$ $[M + Na]^+$ calcd 251.0502 found 251.0508 (-0.6 ppm error).

2.1.4 1,6-Di-*O*-acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α/β-D-galactopyranoside (**SI-5**)

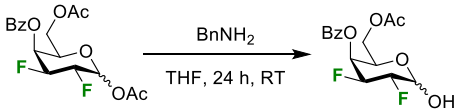


SI-4 **SI-5**

To a solution of **SI-4** (7.0 g, 26.0 mmol, 1.0 equiv) in Ac_2O (65 mL) at 0 °C was slowly added TMSOTf (0.94 mL, 5.2 mmol, 0.2 equiv). After 30 min the reaction mixture was warmed up to rt and stirred for an extra 30 min. The mixture was diluted with CH_2Cl_2 (150 mL) and slowly neutralised with a solution of sat. aq. $NaHCO_3$ (250 mL). The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL); the combined organic phases were washed with sat. aq. $NaHCO_3$ (150 mL), H_2O (150 mL), dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The crude was purified by flash column chromatography (100 g, hexane/acetone 90:10 to 70:30) to afford product **SI-5** as a non-separable mixture of the α- and β-anomers as a pale-yellow oil (8.8 g, 23.7 mmol, 91% yield, α/β 84:16). R_f 0.38 (hexane/acetone 70:30); mp 75–77 °C ($CDCl_3$); IR (neat) 2361 (w), 2343 (w), 1734 (s), 1374 (w), 1268 (s), 1223 (s), 1081 (s), 1038 (w), 713 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, α/β 84:16)

(COSY/HMBC/HSQC) δ 8.06 (2H, dd, *J* = 8.5, 1.3 Hz, H_{Ar}), 7.63 (1H, tt, *J* = 7.5, 1.3 Hz, H_{Ar}), 7.50 (2H, t, *J* = 8.0 Hz, H_{Ar}), 6.58 (1H, t, *J* = 4.2 Hz, $H_{1\alpha}$), 5.96 (1H, dtd, *J* = 7.0, 3.3, 1.2 Hz, $H_{4\alpha}$), 5.90 (1H, dddd, *J* = 5.2, 3.9, 2.5, 1.1 Hz, $H_{4\beta}$), 5.82 (1H, dd, *J* = 7.7, 4.2 Hz, $H_{1\beta}$), 5.25–5.03 (2H, m, $H_{2\alpha}$,$H_{3\alpha}$), 5.03–4.75 (2H, m, $H_{2\beta}$,$H_{3\beta}$), 4.38 (1H, t, *J* = 6.5 Hz, $H_{5\alpha}$), 4.19 (1H, q, *J* = 6.5 Hz, $H_{6\alpha}$), 4.17 (1H, d, *J* = 6.7 Hz, $H_{6'\alpha}$), 2.21 (3H, s, H_{CH3}), 2.03 (3H, s, H_{CH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -200.6 (1F, dtd, *J* = 48.5, 13.0, 6.9 Hz, $F_{3\beta}$), -204.7 (1F, ddtt, *J* = 48.6, 12.1, 6.9, 5.2 Hz, $F_{3\alpha}$), -208.1 (1F, dtt, *J* = 53.7, 10.4, 3.5 Hz, $F_{2\beta}$), -209.7 (1F, dtd, *J* = 48.5, 13.9, 3.5 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -200.6 (1F, d, *J* = 13.9 Hz, $F_{3\beta}$), -204.7 (1F, d, *J* = 13.9 Hz, $F_{3\alpha}$), -208.1 (1F, d, *J* = 13.9 Hz, $F_{2\beta}$), -209.7 (1F, d, *J* = 13.9 Hz, $F_{2\alpha}$) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.3 ($C_{C=O}$), 168.6 ($C_{C=O}$), 165.2 ($C_{C=O}$), 133.8 (C_{Ar}), 129.9 (C_{Ar}), 128.7 (C_{Ar}), 89.2 (dd, *J* = 22.7, 9.5 Hz, C_1), 86.4 (dd, *J* = 192.9, 18.3 Hz, C_2), 85.3 (dd, *J* = 191.8, 19.4 Hz, C_3), 68.8 (d, *J* = 4.4 Hz, C_5), 68.4 (dd, *J* = 16.9, 8.1 Hz, C_4), 61.4 (C_6), 20.8 (C_{CH3}), 20.6 (C_{CH3}) ppm; HRMS (ESI+) for $C_{17}H_{18}F_2NaO_7$ $[M + Na]^+$ calcd 395.0913 found 395.0914 (-0.4 ppm error).

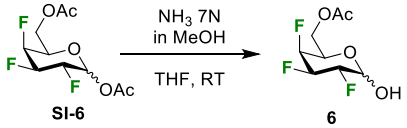
2.1.5 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-D-galactopyranose (**5**)



SI-5 **5**

To a solution of **SI-5** (8.12 g, 21.8 mmol, 1.0 equiv) in THF (100 mL) was slowly added an $BnNH_2$ (3.57 mL, 32.7 mmol, 1.5 equiv). The mixture was stirred at rt for 30 h. The mixture was concentrated in *vacuo* and the crude was purified by flash column chromatography (100 g, hexane/EtOAc 95:5 to 70:30) to afford product **5** as a non-separable mixture of the α- and β-anomers as a pale-yellow oil (6.02 g, 18.2 mmol, 83% yield). R_f 0.40 (cyclohexane/EtOAc 60:40); $[\alpha]_D^{20}$ +66.3 (c 0.80, $CHCl_3$); IR (neat) 3447 (br), 2361 (w), 1730 (s), 1268 (s), 1069 (s), 713 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, α/β 77:23) (COSY/HMBC/HSQC) δ 8.11–8.03 (2H, m, H_{Ar}), 7.67–7.58 (1H, m, H_{Ar}), 7.52–7.44 (2H, m, H_{Ar}), 5.92 (1H, dtd, *J* = 7.2, 3.1, 1.2 Hz, $H_{4\alpha}$), 5.86 (1H, dddd, *J* = 5.2, 3.9, 2.6, 1.0 Hz, $H_{4\beta}$), 5.82 (1H, dd, *J* = 7.8, 4.1 Hz, $H_{1\beta}$), 5.64 (1H, t, *J* = 4.2 Hz, $H_{1\alpha}$), 5.19 (1H, dddd, *J* = 48.9, 12.0, 9.5, 3.9 Hz, $H_{3\alpha}$), 5.00 (1H, dddd, *J* = 50.6, 11.7, 9.1, 3.6 Hz, $H_{2\alpha}$), 4.59–4.97 (2H, m, $H_{2\beta}$, $H_{3\beta}$), 4.55 (1H, t, *J* = 6.2 Hz, $H_{5\alpha}$), 4.25–4.17 (2H, m, $H_{6\alpha}$), 2.03 (3H, s, H_{CH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -200.9 (1F, dtd, *J* = 47.2, 13.7, 5.2 Hz, $F_{3\beta}$), -206.6 (1F, dtt, *J* = 49.2, 11.8, 5.2 Hz, $F_{3\alpha}$), -206.9 (1F, dtt, *J* = 52.0, 13.9, 3.5 Hz, $F_{2\beta}$), -208.0 (1F, br. dt, *J* = 50.3, 13.9 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -200.9 (1F, d, *J* = 15.6 Hz, $F_{3\beta}$), -206.6 (1F, d, *J* = 13.9 Hz, $F_{3\alpha}$), -206.9 (1F, d, *J* = 13.9 Hz, $F_{2\beta}$), -208.0 (1F, d, *J* = 13.9 Hz, $F_{2\alpha}$) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.6 ($C_{C=O}$), 165.4 ($C_{C=O}$), 133.7 (C_{Ar}), 129.9 (C_{Ar}), 128.6 (C_{Ar}), 91.1 (dd, *J* = 21.3, 9.5 Hz, C_1), 87.5 (dd, *J* = 58.0, 18.3 Hz, C_2), 85.6 (dd, *J* = 59.8, 18.7 Hz, C_3), 69.3 (dd, *J* = 16.9, 8.1 Hz, C_4), 66.7 (d, *J* = 5.1 Hz, C_5), 62.0 (C_6), 20.7 (C_{CH3}) ppm; HRMS (ESI+) for $C_{15}H_{16}F_2NaO_6$ $[M + Na]^+$ calcd 353.0807 found 353.0816 (-2.4 ppm error).

2.1.6 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-D-galactopyranose (**6**)

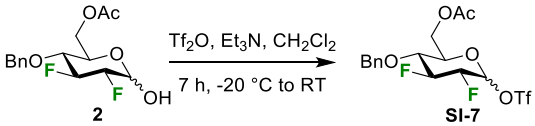


SI-6 **6**

To a solution of **SI-6** (13.57 g, 50.3 mmol, 1.0 equiv) in THF (250 mL) at 0 °C was slowly added a 7 N ammonia solution in MeOH (153.6 mL, 1.0 mol, 20 equiv). After 15 min the reaction mixture was warmed up to rt and stirred for 1 h. The mixture was concentrated in *vacuo* and the crude was purified by flash column chromatography (200 g, cyclohexane/EtOAc 80:20 to 60:40) to afford product **6** as a non-separable mixture of the α- and β-anomers as a white solid (9.01 g, 39.5 mmol, 78% yield). R_f 0.46 (cyclohexane/EtOAc 50:50); mp 127–129 °C (EtOAc); $[\alpha]_D^{25}$ +77.9 (c 0.63, $CHCl_3$); IR (neat) 3411 (w, br), 2961 (w), 2360 (s), 2342 (s), 1734 (w), 1238 (w), 1041 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, α/β 84:16) (COSY/HMBC/HSQC) δ 5.56 (1H, t, *J* = 4.1 Hz, $H_{1\alpha}$), 4.81–5.12 (4H, m, $H_{2\alpha}$, $H_{3\alpha}$, $H_{4\alpha}$, $H_{1\beta}$), 4.25–4.37 (3H, m, $H_{6\alpha}$, $H_{6'\alpha}$, $H_{5\alpha}$), 3.20 (1H, br. s, H_{OH}), 2.11 (3H, s, H_{CH3}) ppm; $^1H\{^{19}F\}$ NMR (500 MHz, $CDCl_3$) δ 5.56 (1H, d, *J* = 3.8 Hz, $H_{1\alpha}$), 5.04 (1H, d, *J* = 2.8 Hz, $H_{4\alpha}$), 5.01 (1H, dd, *J* =9.4, 2.9 Hz, $H_{3\alpha}$), 4.90 (1H, dd, *J* = 9.4, 3.8 Hz, $H_{2\alpha}$), 4.84 (1H, d, *J* = 7.0 Hz, $H_{1\beta}$), 4.30 (2H, d, *J* = 6.6 Hz, $H_{6\alpha}$), 4.30 (1H, dd, *J* = 23.9 3.7 Hz, $H_{5\alpha}$), 3.20 (1H, br. s, H_{OH}), 2.11 (3H, s, H_{CH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -202.6 (1F, ddd, *J* = 45.5, 13.4, 5.2 Hz, $F_{3\beta}$), -207.9 (1F, tt, *J* = 13.9, 3.5 Hz, $F_{2\beta}$), -208.1 (1F, ddtd, *J* = 40.2, 27.2, 13.1, 5.2 Hz, $F_{3\alpha}$), -209.3 (1F, dtd, *J* = 5 0.3, 12.1, 3.5 Hz, $F_{2\alpha}$), -217.6 (1F, dtd, *J* = 52.0, 26.0, 15.6 Hz, $F_{4\beta}$), -220.3 (1F, dddt, *J* = 39.9, 29.5, 26.0, 13.9 Hz, $F_{4\alpha}$); $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -202.6 (1F, t, *J* = 13.9 Hz, $F_{3\beta}$), -208.0 (1F, d, *J* = 13.9 Hz, $F_{2\beta}$), -208.1 (1F, t, *J* = 13.9 Hz, $F_{3\alpha}$), -209.3 (1F, d, *J* = 12.1 Hz, $F_{2\alpha}$), -217.6 (1F, d, *J* = 15.6 Hz, $F_{4\beta}$), -220.3 (1F, d, *J* = 13.9 Hz, $F_{4\alpha}$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.5 ($C_{C=O}$), 94.3 (dd, *J* = 23.5, 10.6 Hz, $C_{1\beta}$), 90.9 (dd, *J* = 21.5, 9.5 Hz, $C_{1\alpha}$), 87.5 (ddd, *J* = 186.2, 16.7, 8.6 Hz, $C_{4\alpha}$), 86.2 (dt, *J* = 191.7, 16.9 Hz, $C_{3\alpha}$), 86.1 (ddt, *J* = 191.0, 18.4, 1.9, 1.9 Hz, $C_{2\alpha}$), 66.8 (ddd, *J* = 17.9, 5.0, 0.7 Hz, $C_{5\alpha}$), 61.6 (dd, *J* = 6.3, 1.8 Hz, C_6), 20.7 (C_{CH3}) ppm; HRMS (ESI+) for $C_8H_{11}F_3NaO_4$ $[M + Na]^+$ calcd 251.050 found 2251.0501 (0.2 ppm error).

2.2 Triflate

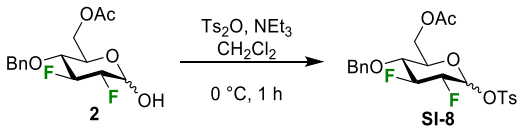
2.2.1 6-*O*-Acetyl-4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-α/β-D-glucopyranosyl triflate (**SI-7**)



To a solution of **2** (100 mg, 0.32 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) at –20 °C was slowly added NEt_3 (0.1 mL, 0.35 mmol, 2.0 equiv). The mixture was stirred at –20 °C for 10 min and Tf_2O 1M in CH_2Cl_2 (1.33 mL, 0.64 mmol, 2.0 equiv) was added and the mixture was stirred at –20 °C for 1.5 h. The RM was allowed to warm up to rt and diluted in CH_2Cl_2 (20 mL) and filtered through a pad of silica. The mixture was concentrated in *vacuo.* The NMR of the crude showed trace of the desired product and the product decomposed overnight.

2.3 Tosylate

2.3.1 Tosyl 6-*O*-acetyl-4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-α/β-D-glucopyranoside (**SI-8**)



To a solution of **2** (100 mg, 0.32 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) at 0 °C was slowly added NEt_3 (0.1 mL, 0.35 mmol, 2.0 equiv). The mixture was stirred at 0 °C for 10 min and Ts_2O (209 mg, 0.64 mmol, 2.0 equiv) was added. The mixture was stirred at 0 °C for 1 h. The RM was allowed to warm up to rt and diluted in CH_2Cl_2 (20 mL) and 1 M HCl (20 mL). The phases were separated, and the organic was washed with brine (20 mL). The aqueous was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in *vacuo* to give 196 mg of crude. The crude was purified by flash column chromatography (10 g, cyclohexane/EtOAc, 100:0 to 60:40) to afford product **SI-8** as a colourless oil (103 mg, 0.22 mmol, 68% yield). R_f 0.8 (cyclohexane/EtOAc 60:40); IR (neat) 2955 (w), 2360 (w), 1741 (s), 1366 (s), 1178 (s), 1058 (s), 832 (s), 560 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, α/β 97:3) (COSY/HMBC/HSQC) δ 7.82 (2H, d, *J* = 8.2 Hz, H_{Ar}), 7.32-7.38 (5H, m, H_{Ar}), 7.28-7.32 (2H, m, H_{Ar}), 6.08 (1H, t, *J* = 3.7 Hz, $H_{1\alpha}$), 5.71 (1H, dd, *J* = 8.2, 3.1 Hz, $H_{1\beta}$), 4.98 (1H, ddt, *J* = 53.9, 13.0, 8.4 Hz, $H_{3\alpha}$), 4.84 (1H, d, *J* = 11.1 Hz, H_{CH2OBn}), 4.61 (1H, dddd, *J* = 48.9, 13.2, 8.9, 3.9 Hz, $H_{2\alpha}$), 4.57 (1H, d, *J* = 11.0 Hz, H_{CH2OBn}), 4.10 (1H, dd, *J* = 12.3, 2.9 Hz, $H_{6\alpha}$), 3.84 (1H, dt, *J* = 12.3, 1.8 Hz, $H_{6'\alpha}$), 3.69 (1H, d, *J* = 4.9 Hz, $H_{5\alpha}$), 3.66 (1H, d, *J* = 7.8 Hz, $H_{4\alpha}$), 2.46 (3H, s, H_{CH3}), 1.96 (3H, s, H_{COCH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -191.0 (1F, dq, *J* = 50.3, 12.1 Hz, $F_{3\beta}$), -196.0 (1F, dq, *J* = 53.8, 12.7 Hz, $F_{3\alpha}$), -200.1 (1F, dt, *J* = 53.8, 13.9 Hz, $F_{2\beta}$), -202.1 (1F, dt, *J* = 48.5, 13.9 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -191.0 (1F, d, *J* = 10.4 Hz, $F_{3\beta}$), -196.0 (1F, d, *J* = 12.1 Hz, $F_{3\alpha}$), -200.1 (1F, d, *J* = 13.9 Hz, $F_{2\beta}$), -202.1 (1F, d, *J* = 13.9 Hz, $F_{2\alpha}$) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.2 ($C_{C=O}$), 145.5 (C_{Ar}), 136.6 (C_{Ar}), 133.7 (C_{Ar}), 129.9 (C_{Ar}), 128.5 (C_{Ar}), 128.5 (C_{Ar}), 128.3 (C_{Ar}), 127.8 (C_{Ar}), 95.9 (dd, *J* = 22.4, 10.6 Hz, C_1), 93.1 (dd, *J* = 186.3, 18.3 Hz, C_3), 86.0 (dd, *J* = 198.1, 19.1 Hz, C_2), 74.4 (d, *J* = 2.9 Hz, C_{CH2OBn}), 73.3 (dd, *J* = 16.9, 6.6 Hz, C_4), 70.1 (d, *J* = 8.1 Hz, C_5), 61.0 (C_6), 21.6 (C_{CH3}), 20.6 (C_{COCH3}) ppm; HRMS (ESI+) for $C_{22}H_{24}F_2NaO_7S$ $[M + Na]^+$ calcd 493.1103 found 493.1110 (-1.5 ppm error).

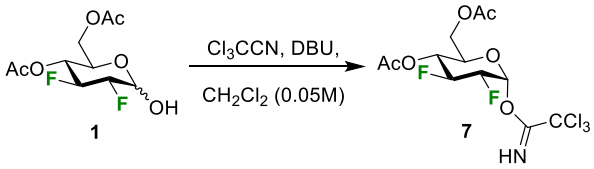
2.4 Trichloroacetimidates

2.4.1 General procedure

The trichloroacetimidates were synthesised according to a procedure published by Gilmour et al.[1]

General procedure A: DBU (0.1 equiv) was added to a solution of Cl_3CCN (10 equiv) and the reducing sugar substrate (1.0 equiv) in dry CH_2Cl_2 at 0 °C under an atmosphere of Ar. After 5–10 min the ice bath was removed, and the solution stirred for 2–18 h. The solvents were evaporated and purification by flash column chromatography was performed.

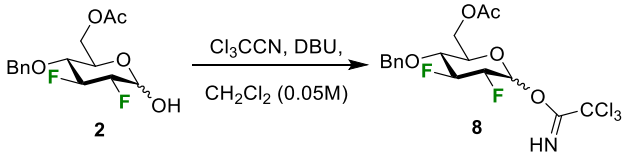
2.4.2 4,6-Di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α-D-glucopyranosyl trichloroacetimidate (**7**)



According to the general procedure A, **1** (250 mg, 0.93 mmol, 1.0 equiv) was reacted at 0 ˚C for 10 min before being stirred at rt for 18 h. The resultant crude material was purified by flash column chromatography (10 g, hexane/EtOAc 90:10 to 60:40) to afford product **7** as a colourless oil (351 mg, 0.854 mmol, 91% yield, α only). R_f 0.56 (hexane/EtOAc 50:50); $[\alpha]_D^{22}$ +77.1 (c 0.46, $CHCl_3$); IR (neat) 3342 (br), 2959 (br), 2360 (br), 2331 (br), 1745

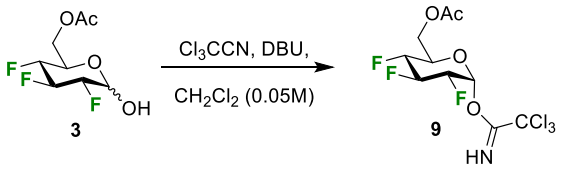
(w), 1679 (w), 1234 (w), 1034 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.83 (1H, s, H_{NH}), 6.63 (1H, t, *J* = 3.7 Hz, H_1), 5.30 (1H, dt, *J* = 12.7, 9.6 Hz, H_4), 5.03 (1H, ddt, *J* = 53.7, 13.1, 9.1 Hz, H_3), 4.83 (1H, dddd, *J* = 48.8, 13.0, 8.9, 4.2 Hz, H_2), 4.27 (1H, dd, *J* = 13.1, 4.9 Hz, H_6), 4.10–4.17 (2H, m, H_5 and H_6), 2.15 (3H, s, H_{CH3}), 2.08 (3H, s, H_{CH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -200.5 (1F, dqd, *J* = 53.8, 12.7, 3.5 Hz, F_3), -203.2 (1F, dt, *J* = 48.6, 13.9 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -200.5 (1F, d, *J* = 13.9 Hz, F_3), -203.2 (1 F, d, *J*=13.9 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.5 (C_{COCH3}), 169.2 (C_{COCH3}), 160.3 ($C_{C=N}$), 92.6 (dd, *J* = 22.0, 9.5 Hz, C_1), 90.5 (C_{CCl3}), 89.7 (dd, *J* = 190.0, 20.5 Hz, C_3), 86.8 (dd, *J* = 196.6, 18.3 Hz, C_2), 69.7 (d, *J* = 7.3 Hz, C_5), 67.0 (dd, *J* = 18.7, 7.7 Hz, C_4), 61.1 (C_6), 20.6 ($2C_{CH3}$) ppm; HRMS (ESI+) for $C_{12}H_{14}Cl_3F_2NNaO_6$ $[M + Na]^+$ calcd 433.9747 found 433.9748 (-0.3 ppm error).

2.4.3 6-*O*-Acetyl-4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-α/β-D-glucopyranosyl trichloroacetimidate (**8**)



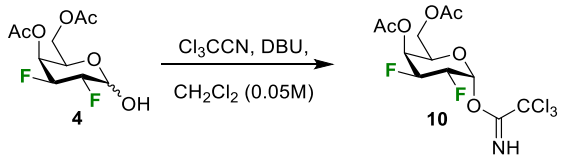
According to the general procedure A, **2** (250 mg, 0.79 mmol, 1.0 equiv) was reacted at 0 ˚C for 5 min before being stirred at rt for 18 h. The resultant crude material was purified by flash column chromatography (10 g, hexane/EtOAc 90:10 to 60:40) to afford product **8** as a non-separable mixture of the α- and β-anomers as a colourless oil (342 mg, 0.745 mmol, 94% yield, α/β 10:1). R_f 0.45 (hexane/EtOAc 60:40); IR (neat) 3342 (br), 2956 (br), 2359 (w), 2341 (w), 1742 (s), 1676 (s), 1368 (w), 1283 (w), 1238 (s), 1061 (s), 1015 (w), 796 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, α/β 10:1) (COSY/HMBC/HSQC) δ 8.77 (1H, s, H_{NH}), 7.29–7.43 (5H, m, H_{Ar}), 6.57 (1H, t, *J* = 3.7 Hz, $H_{1\alpha}$), 5.90 (1H, dd, *J* = 7.8, 3.4 Hz, $H_{1\beta}$), 5.15 (1H, ddt, *J* = 53.9, 13.4, 9.2, 9.2 Hz, H_3), 4.91 (1H, d, *J* = 11.1 Hz, H_{CH2OBn}), 4.76 (1H, dddd, *J* = 49.5, 12.8, 8.9, 3.9 Hz, H_2), 4.65 (1H, d, *J* = 11.2 Hz, H_{CH2OBn}), 4.27–4.30 (2H, m, H_5 and $H_{6'}$), 4.05 (1H, dt, *J* = 10.1, 2.7 Hz, H_6), 3.75 (1H, ddd, *J* = 13.3, 10.1, 8.4 Hz, H_4), 2.05 (3H, s, H_{CH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.5 (1F, dq, *J* = 52.0, 13.3 Hz, $F_{3\beta}$), -195.9 (1F, ddd, *J* = 53.8, 26.0, 12.1 Hz, $F_{3\alpha}$), -200.1 (1F, dddd, *J* = 52.0, 17.0, 12.1, 3.5 Hz, $F_{2\beta}$), -203.4 (1F, dt, *J* = 49.4, 12.6 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -190.5 (1F, d, *J* = 12.1 Hz, $F_{3\beta}$), -195.9 (1F, d, *J* = 12.1 Hz, $F_{3\alpha}$), -200.1 (1F, d, *J* = 12.1 Hz, $F_{2\beta}$), -203.4 (1F, d, *J* = 12.1 Hz, $F_{2\alpha}$) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4 (C_{COCH3}), 160.5 ($C_{C=N}$),136.8 (C_{Ar}), 128.6 (C_{Ar}), 128.4 (C_{Ar}), 93.7 (dd, *J* = 188.5, 18.3 Hz, C_3), 92.8 (dd, *J* = 26.4, 7.3 Hz, C_1), 90.5 (C_{CCl3}), 86.9 (dd, *J* = 195.9, 18.3 Hz, C_2), 74.5 (d, *J* = 3.7 Hz, C_{CH2OBn}), 73.8 (dd, *J* = 17.2, 7.0 Hz, C_4), 70.5 (d, *J* = 8.8 Hz, C_5), 61.9 (C_6), 21.0 (C_{CH3}) ppm; HRMS (ESI+) for $C_{17}H_{18}Cl_3F_2NNaO_5$ $[M + Na]^+$ calcd 482.0111 found 482.0110 (0.2 ppm error).

2.4.4 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α-D-glucopyranosyl trichloroacetimidate (**9**)



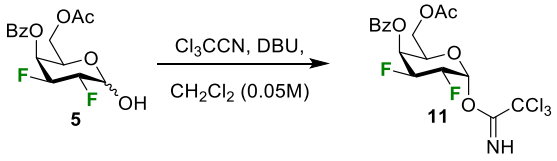
According to the general procedure A, **3** (1.00 g, 4.38 mmol, 1.0 equiv) was reacted at 0 ˚C for 10 min before being stirred at rt for 18 h. The resultant crude material was purified by flash column chromatography (25 g, cyclohexane/EtOAc 100:0 to 60:40) to afford product **9** as a colourless oil (1.16 g, 3.12 mmol, 72% yield, α only). R_f 0.52 (hexane/EtOAc 60:40); $[\alpha]_D^{22}$ +88.5 (c 0.84, $CHCl_3$); IR (neat) 3344 (w), 2963 (w), 2360 (w), 2334 (w), 1743 (s), 1679 (s), 1281 (s), 1251 (s), 1088 (s), 1020 (s), 836 (s), 795 (s), 646 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.85 (1H, s, H_{NH}), 6.60 (1H, q, *J* = 3.3 Hz, H_1), 5.14 (1H, dddt, *J* = 54.2, 16.0, 13.6, 8.6 Hz, H_3), 4.77 (1H, dddd, *J* = 48.4, 13.0, 9.0, 4.2 Hz, H_2), 4.68 (1H, dddd, *J* = 50.4, 14.7, 10.0, 8.4 Hz, H_4), 4.44 (1H, dq, *J* = 12.4, 1.8 Hz, H_6), 4.28 (1H, ddd, *J* = 12.3, 4.4, 1.5 Hz, H_6), 4.20 (1H, dtd, *J* = 10.0, 4.4, 2.2 Hz, H_5), 2.10 (3H, s, H_{CH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -199.8 (1F, dt, *J* = 49.9, 13.9 Hz, F_4), -200.0 (1F, dquin, *J* = 54.6, 13.9, Hz, F_3), -203.8 (1F, dt, *J* = 49.0, 12.6 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -199.8 (1F, d, *J* = 13.0 Hz, F_4), -200.0 (1F, t, *J* = 12.6 Hz, F_3), -203.8 (1F, dd, *J* = 12.6, 1.3 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.3 (C_{COCH3}), 160.2 ($C_{C=N}$), 92.3 (dd, *J* = 22.0, 9.5 Hz, H_1), 90.3 (C_{CCl3}), 89.9 (dt, *J* = 187.8, 18.3 Hz, C_3), 86.4 (ddd, *J* = 196.6, 18.3, 8.1 Hz, C_2), 86.0 (ddd, *J* = 189.0, 19.8, 7.3 Hz, C_4), 68.9 (dd, *J* = 23.8, 6.2 Hz, C_5), 61.2 (C_6), 20.6 (C_{COCH3}) ppm; HRMS (ESI+) for $C_{10}H_{11}Cl_3F_3NNaO_4$ $[M + Na]^+$ calcd 393.9598 found 393.9600 (-0.4 ppm error).

2.4.5 4,6-Di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranosyl trichloroacetimidate (**10**)



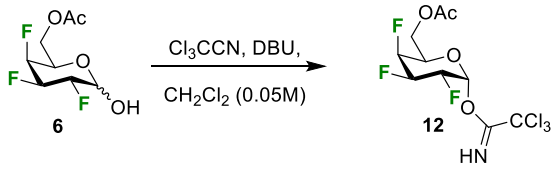
According to the general procedure A, **4** (1.00 g, 3.73 mmol, 1.0 equiv) was reacted at 0 ˚C for 10 min before being stirred at rt for 18 h. The resultant crude material was purified by flash column chromatography (25 g, cyclohexane/EtOAc 100:0 to 60:40) to afford product **10** as a white powder (1.34 g, 3.24 mmol, 87% yield, α only). R_f 0.41 (hexane/EtOAc 60:40); $[\alpha]_D^{22}$ +126.3 (c 0.30, $CHCl_3$); mp 73–75 ˚C (CH_2Cl_2); IR (neat) 3341 (w), 2972 (w), 2360 (w), 2334 (w), 1747 (s), 1677 (s), 1372 (s), 1254 (s), 1083 (s), 1021 (s), 794 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.81 (1H, s, H_{NH}), 6.67 (1H, t, *J* = 4.1 Hz, $H_{1\alpha}$), 5.73 (1H, dtd, *J* = 6.0, 3.7, 1.2 Hz, H_4), 4.94–5.25 (2H, m, H_3 and H_2), 4.39 (1H, tt, *J* = 6.5, 1.2 Hz, H_5), 4.20 (1H, dd, *J* = 11.5, 6.2 Hz, H_6), 4.07 (1H, ddd, *J* = 11.5, 6.8, 1.1 Hz, H_6), 2.17 (3H, s, H_{CH3}), 2.03 (3H, s, H_{CH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -205.2 (1F, dtt, *J* = 48.1, 12.6, 5.2 Hz, F_3), -210.2 (1F, dtd, *J* = 48.0, 13.4, 3.5 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -205.2 (1F, d, *J* =13.9 Hz, F_3), -210.2 (1F, d, *J* = 13.9 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.2 (C_{COCH3}), 169.5 (C_{COCH3}), 160.4 ($C_{C=N}$), 93.2 (dd, *J* = 22.4, 9.9 Hz, C_1), 90.6 (C_{CCl3}), 86.1 (dd, *J* = 192.9, 19.1 Hz, C_2), 85.4 (dd, *J* = 192.2, 19.8 Hz, C_3), 69.0 (d, *J* = 4.4 Hz, C_5), 67.8 (dd, *J* = 16.9, 8.1 Hz, C_4), 61.1 (d, *J* = 1.5 Hz, C_6), 20.6 (C_{CH3}), 20.5 (C_{CH3}) ppm; HRMS (ESI+) for $C_{12}H_{14}Cl_3F_2NNaO_6$ $[M + Na]^+$ calcd 433.9747 found 433.9753 (-1.3 ppm error).

2.4.6 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranosyl trichloroacetimidate (**11**)



According to the general procedure A, **5** (1.00 g, 3.03 mmol, 1.0 equiv) was reacted at 0 ˚C for 10 min before being stirred at rt for 18 h. The resultant crude material was purified by flash column chromatography (25 g, cyclohexane/EtOAc 100:0 to 60:40) to afford product **11** as a white powder (1.18 g, 2.49 mmol, 81% yield, α only). R_f 0.45 (hexane/EtOAc 60:40); $[\alpha]_D^{22}$ +94.0 (c 0.31, $CHCl_3$); mp 132–134 ˚C (CH_2Cl_2); IR (neat) 3340 (w), 2972 9 (w), 2361 (w), 2334 (w), 1734 (s), 1677 (s), 1264 (s), 1083 (s), 1068 (s), 1025 (s), 970 (w), 795 (w), 712 (w)cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.84 (1H, s, H_{NH}), 8.04–8.09 (2H, m, H_{Ar}), 7.61–7.67 (1H, m, H_{Ar}), 7.47–7.54 (2H, m, H_{Ar}), 6.77 (1H, t, *J* = 4.1 Hz, H_1), 6.01 (1H, dtd, *J* = 6.0, 3.5, 1.2 Hz, H_4), 5.07–5.40 (2H, m, H_3 and H_2), 4.51 (1H, tt, *J* = 6.3, 1.1 Hz, H_5), 4.24 (1H, dd, *J* = 11.7, 5.7 Hz, H_6), 4.17 (1H, ddd, *J* = 11.5, 6.8, 0.9 Hz, H_6), 2.00 (3H, s, H_{CH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -204.7 (1F, dtt, *J* = 48.1, 13.4, 5.2 Hz, F_3), -209.8 (1F, dddd, *J* = 52.5, 13.0, 9.1, 3.0 Hz, F_2) ppm; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -204.7 (1F, d, *J* = 13.4 Hz, F_3), -209.8 (1F, d, *J* = 13.4 Hz, F_2) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.3 (C_{COCH3}), 165.2 (C_{COCH3}), 160.5 ($C_{C=N}$), 133.8 (C_{Ar}), 129.9 (C_{Ar}), 128.7 (C_{Ar}), 93.2 (dd, *J* = 22.7, 9.5 Hz, C_1), 90.6 (C_{CCl3}), 86.4 (dd, *J* = 193.7, 19.0 Hz, C_2), 85.6 (dd, *J* = 192.9, 19.8 Hz, C_3), 69.4 (d, *J* = 4.4 Hz, C_5), 68.5 (dd, *J* = 16.9, 8.1 Hz, C_4), 61.5 (d, *J* = 2.2 Hz, C_6), 20.6 (C_{CH3}) ppm; HRMS (ESI+) for $C_{17}H_{16}Cl_3F_2NNaO_6$ $[M + Na]^+$ calcd 495.9903 found 495.9903 (0.1 ppm error).

2.4.7 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α-D-galactopyranosyl trichloroacetimidate (**12**)



According to the general procedure A, **6** (1.00 g, 4.38 mmol, 1.0 equiv) was reacted at 0 ˚C for 10 min before being stirred at rt for 18 h. The resultant crude material was purified by flash column chromatography (25 g, hexane/EtOAc 100:0 to 60:40) to afford product **12** as a white solid (953 mg, 2.57 mmol, 59% yield, α only). R_f 0.59 (hexane/EtOAc 60:40); $[\alpha]_D^{22}$ +98.6 (c 0.32, $CHCl_3$); mp 70–72 ˚C (CH_2Cl_2); IR (neat) 3343 (w), 2970 (w), 2360 (w), 2333 (w), 1743 (s), 1678 (s), 1230 (s), 1088 (s), 1055 (s), 1025 (s), 969 (s), 834 (s), 794 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.83 (1H, s, H_{NH}), 6.69 (1H, t, *J* = 4.0 Hz, H_1), 4.97–5.21 (3H, m, H_2, H_3 and H_4), 4.23–4.35 (3H, m, H_6 and H_5), 2.08 (3H, s, H_{CH3}) ppm; ^{1}H{^{19}F} NMR (500 MHz, $CDCl_3$) δ 8.83 (1H, s, H_{NH}), 6.69 (1H, d, *J* = 3.8 Hz, H_1), 5.12 (1H, dd, *J* = 9.5, 3.7 Hz, H_2), 5.12 (1H, d, *J* = 2.8 Hz, H_4), 5.08 (1H, dd, *J* = 9.4, 2.9 Hz, H_3), 4.26–4.35 (3H, m, H_6 and H_5), 2.08 (3H, s, H_{CH3}) ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ -206.0 (1F, dttt, *J* = 48.3, 13.9, 7.5, 4.7 Hz, F_3), -210.9 (1F, dddd, *J* = 52.2, 13.2, 8.6, 3.6 Hz, F_2), -219.7 (1F, dtd, *J* = 50.4, 26.8, 14.6 Hz, F_4) ppm; ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ -206.0 (1F, dd, *J* = 14.7, 13.2 Hz, F_3), -210.9 (1F, d, *J* = 13.2 Hz, F_2), -219.7 (1F, d,

J = 14.3 Hz, F_4) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.3 (C_{COCH3}), 160.3 ($C_{C=N}$), 93.0 (dd, *J* = 22.5, 9.4 Hz, C_1), 90.5 (C_{CCl3}), 86.9 (ddd, *J* = 186.9, 16.9, 8.6 Hz, C_4), 86.3 (ddd, *J* = 193.1, 19.5, 17.6 Hz, C_3), 84.9 (ddd, *J* = 193.4, 19.6, 2.6 Hz, C_2), 69.2 (ddd, *J* = 18.4, 5.2, 0.7 Hz, C_5), 61.1 (dd, *J* = 6.0, 1.7 Hz, C_6), 20.6 (C_{CH3}) ppm; HRMS (ESI+) for $C_{10}H_{11}Cl_3F_3NNaO_4$ $[M + Na]^+$ calcd 393.9598 found 393.9600 (-0.5 ppm error).

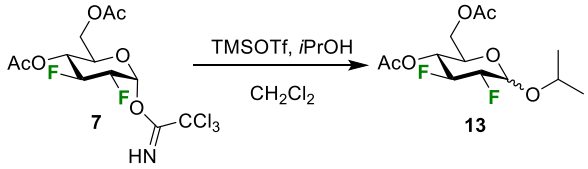
3 Glycosidation reactions

3.1 General procedure for isopropyl glycoside formation

General procedure B: The trichloroacetimidate (1.0 equiv) was co-evaporated with redistilled toluene (3 ×) and redistilled CH_2Cl_2 (1 ×), dried under high vacuum. Freshly activated molecular sieves (3 Å) were added, the trichloroacetimidate was dissolved in redistilled CH_2Cl_2 under argon. The mixture was stirred at room temperature for 30 min. The reaction vessel was cooled to the stated temperature (–50 ˚C – 0 ˚C). Isopropanol (1.2 equiv) and TMSOTf (0.2 equiv) were added and the reaction mixture was stirred for the stated time at the same temperature. The reaction was followed by $^{19}F\{^1H\}$ NMR. After completion, the mixture was diluted with CH_2Cl_2, quenched by the addition of NEt_3 (0.5 mL), and filtered through a pad of Celite. The solvents were removed under reduced pressure, and the crude product was purified by flash column chromatography. The ratios were obtained by $^{19}F\{^1H\}$ NMR of the crude reaction mixture with a delay time (D1) of 3 s.

3.2 Isopropyl 4,6-di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α/β-D-glucopyranoside (**13**)

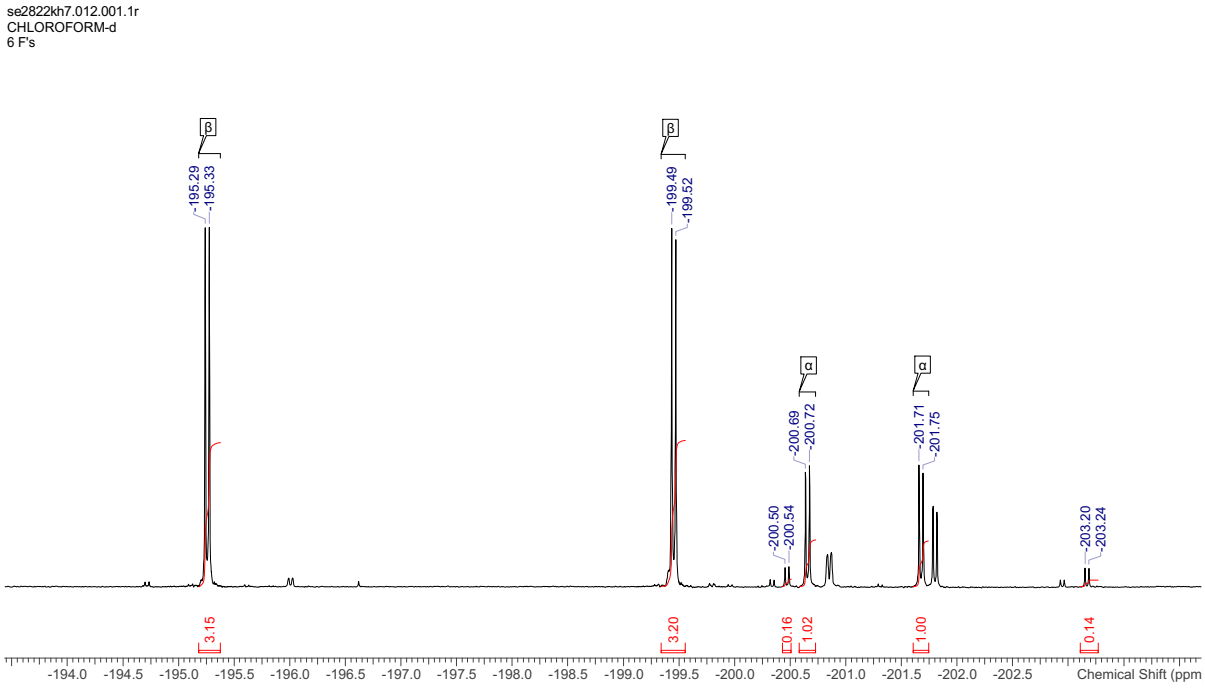
3.2.1 Glycosidation (Table 2, entry 1)



According to general procedure B, **7** (108 mg, 0.27 mmol, 1.0 equiv) was reacted at –30 ˚C for 3.5 h. The resultant crude material (α/β 1:3.20) was purified by flash column chromatography (10 g, hexane/EtOAc 90:10 to 60:40) to collect **13** as a mixture of α- and β-anomers as a colourless oil (87 mg, 0.281 mmol, quant.). An analytical sample was purified to separate the anomers using flash column chromatography (10 g, hexane/EtOAc 90:10 to 60:40). Anomers assignment was based on the chemical shift and coupling constant values of the anomeric protons.

3.2.2 Ratio determination, crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:3.20, no hydrolysis of the trichloroacetimidate was observes as no peak corresponding to the hemiacetal **1** is present however the peaks integrating for 0.16 and 0.14 correspond to unreacted trichloroacetimidate **7**.



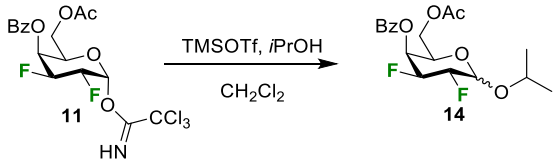
3.2.3 Characterisation of the glycosides (pure anomers)

Data for **13α**: R_f 0.24 (hexane/EtOAc 80:20); $[\alpha]_D^{22.5}$ +89.5 (c 0.57, $CHCl_3$); IR (neat) 2976 (br), 2933 (br), 2360 (br), 2332 (br), 1745 (s), 1370 (w), 1233 (s), 1028 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 5.16 (1H, t, *J* = 3.6 Hz, H_1), 5.15 (1H, ddd, *J* = 13.6, 10.1, 9.1 Hz, H_4), 4.89 (1H, ddt, *J* = 54.3, 13.1, 9.1 Hz, H_3), 4.55 (1H, dddd, *J* = 50.3, 13.0, 8.9, 4.0 Hz, H_2), 4.24 (1H, dd, *J* = 12.3, 4.8 Hz, H_6), 4.10 (1H, dt, *J* = 12.2, 1.7 Hz H_6), 4.03 (1H, ddd, *J* = 10.2, 4.9, 2.3 Hz, H_5), 3.93 (1H, spt, *J* = 6.2 Hz, H_{iPr}), 2.13 (3H, s, H_{CH3}), 2.09 (3H, s, H_{CH3}), 1.27 (3H, d, *J* = 6.1 Hz, H_{CH3iPr}), 1.22 (3H, d, *J* = 6.1 Hz, H_{CH3iPr}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -200.7 (1F, dq, *J* = 54.6, 14.2 Hz, F_3), -201.7 (1F, dt, *J* = 50.3, 13.0 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -200.7 (1F, d, *J* = 15.6 Hz, F_3), -201.7 (1F, d, *J* = 13.9 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.6 ($C_{C=O}$), 169.4 ($C_{C=O}$), 94.9 (dd, *J* = 20.5, 9.5 Hz, C_1), 90.1 (dd, *J* = 187.1, 18.2 Hz, C_3), 87.4 (dd, *J* = 193.7, 17.6 Hz, C_2), 72.1 (C_{CHiPr}), 68.1 (dd, *J* = 19.1, 7.3 Hz, C_4), 67.0 (d, *J* = 6.6 Hz, C_5), 61.8 (C_6), 23.1 (C_{CH3iPr}), 21.6 (C_{CH3iPr}), 20.7 (C_{CH3}) ppm; HRMS (ESI+) for $C_{13}H_{20}F_2NaO_6$ $[M + Na]^+$ calcd 333.1120 found 333.1127 (-2.0 ppm error).

Data for **13β**: R_f 0.54 (hexane/EtOAc 50:50); $[\alpha]_D^{22.5}$ -16.5 (c 3.67, $CHCl_3$); IR (neat) 3367 (br), 3319 (br), 3244 (br), 3143 (br), 2360 (w), 2342 (w), 1744 (s), 1691 (s), 1374 (s), 1030 (s), 831 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 5.16 (1H, dt, *J* = 12.7, 9.6 Hz, H_4), 4.65 (1H, ddt, *J* = 52.5, 15.8, 8.4 Hz, H_3), 4.58 (1H, dd, *J* = 7.7, 3.3 Hz, H_1), 4.38 (1H, ddt, *J* = 51.0, 14.2, 8.3 Hz, H_2), 4.25 (1H, dd, *J* = 12.5, 5.1 Hz, H_6), 4.09–4.18 (1H, m, H_6), 4.01 (1H, spt, *J* = 6.2 Hz, H_{iPr}), 3.61 (1H, dddd, *J* = 10.1, 5.2, 2.6, 1.3 Hz, H_5), 2.12 (3H, s, H_{CH3}), 2.09 (3H, s, H_{CH3}), 1.28 (3H, d, *J* = 6.2 Hz, H_{CH3iPr}), 1.23 (3H, d, *J* = 6.1 Hz, H_{CH3iPr}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -195.3 (1F, dq, *J* = 52.2, 13.8 Hz, F_3), -199.5 (1F, dtd, *J* = 50.3, 15.6, 3.5 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -195.3 (1F, d, *J* = 13.9 Hz, F_3), -199.5 (1F, d, *J* =13.9 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 169.3 ($C_{C=O}$), 163.6 ($C_{C=O}$), 98.4 (dd, *J* = 22.7, 11.0 Hz, C_1), 92.1 (dd, *J* = 190.0, 19.8 Hz, C_3), 89.8 (dd, *J* = 189.6, 18.0 Hz, C_2), 73.1 (C_{CHiPr}), 70.7 (d, *J* = 7.3 Hz, C_5), 68.1 (dd, *J* = 18.7, 7.7 Hz, C_4), 61.9 (C_6), 23.2 (C_{CH3iPr}), 21.8 (C_{CH3iPr}), 20.7 (C_{CH3}), 20.7 (C_{CH3}) ppm; HRMS (ESI+) for $C_{13}H_{20}F_2NaO_6$ $[M + Na]^+$ calcd 333.1120 found 333.1121 (-0.4 ppm error).

3.3 Isopropyl 6-*O*-acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α/β-D-galactopyranoside (**14**)

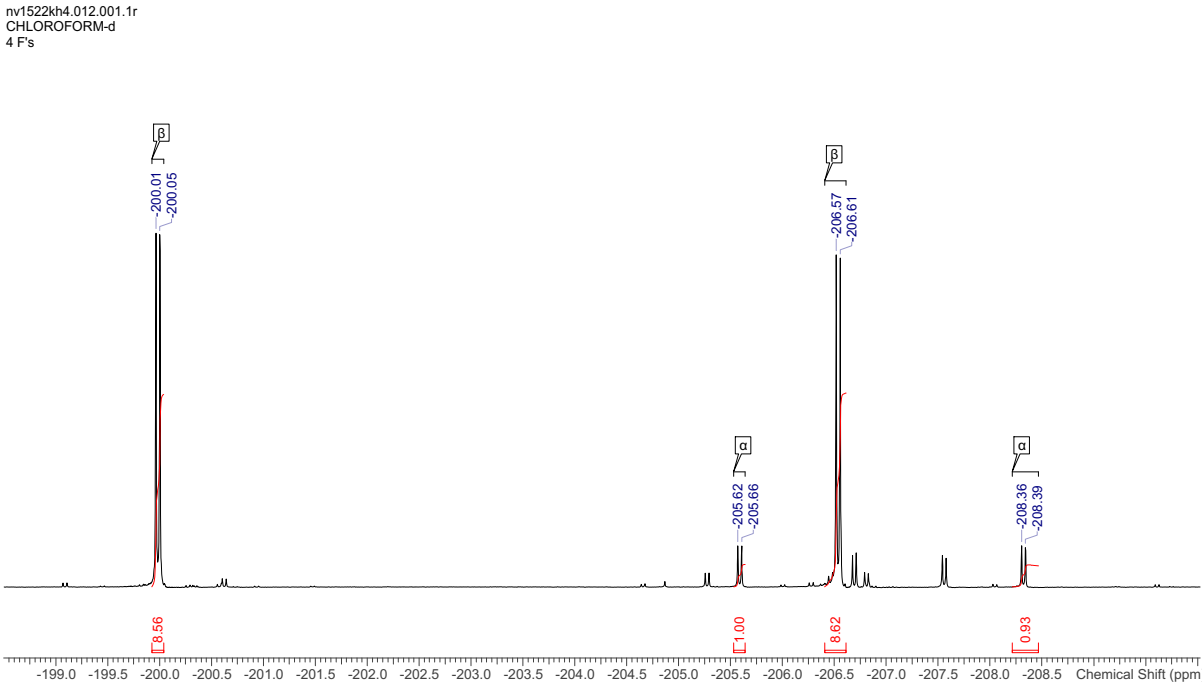
3.3.1 Glycosylation (Table 2, entry 5)



According to general procedure B, **11** (109 mg, 0.23 mmol, 1.0 equiv) was reacted at –50 ˚C for 4 h. The resultant crude material (α/β 1:8.56) was purified by flash column chromatography (10 g, hexane/EtOAc 100:0 to 60:40) to collect **14** as a mixture of α- and β-anomers (83 mg, 0.22 mmol, 97% yield). An analytical sample was purified to separate the anomers using flash column chromatography (10 g, hexane/EtOAc 100:0 to 60:40). Anomers assignment was based on the chemical shift and coupling constant values of the anomeric protons.

3.3.2 Ratio determination, crude reaction mixture, $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^{1}H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:8.56, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **5** is present and no unreacted trichloroacetimidate **11** is observed in the crude reaction mixture.



3.3.3 Characterisation of the glycosides (both anomers)

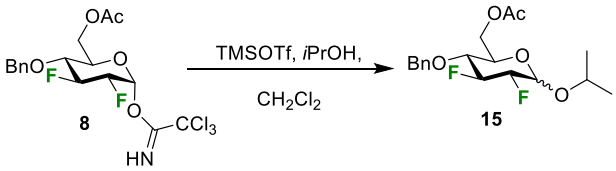
Data for **14α**: colourless oil; R_f 0.57 (hexane/EtOAc 60:40); IR (neat) 2975 (w), 2931 (w), 1728 (s), 1265 (s), 1229 (s), 1069 (s), 1069 (s), 1024 (s), 712 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.06 (2H, br dd, *J* = 8.4, 1.3 Hz, H_{Ar}), 7.61 (1H, ddt, *J* = 7.9, 6.8, 1.2 Hz, H_{Ar}), 7.48 (2H, br t, *J* = 7.9 Hz, H_{Ar}), 5.89 (1H, m, H_4), 5.30 (1H, t, *J* = 4.1 Hz, H_1), 5.13 (1H, dddd, *J* = 49.0, 11.5, 9.7, 3.9 Hz, H_3), 4.94 (1H, dddd, *J* = 50.6, 11.6, 9.5, 4.0 Hz, H_2),

4.38 (1H, ddt, *J* = 6.8, 5.6, 1.1 Hz, H_5), 4.18 (1H, d, *J* = 5.5 Hz, H_6), 4.17 (1H, d, *J* = 7.0 Hz, H_6), 3.96 (1H, spt, *J* = 6.2 Hz, H_{CHiPr}), 2.02 (3H, s, H_{COCH3}), 1.29 (3H, d, *J* = 6.2 Hz, H_{CH3iPr}), 1.25 (3H, d, *J* = 6.2 Hz, H_{CH3iPr}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -205.7 (1F, dtt, *J* = 49.0, 12.6, 4.8 Hz, F_3), -208.4 (1F, dtd, *J* = 50.7, 12.8, 2.6 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -205.7 (1F, d, *J* = 13.9 Hz, F_3), -208.4 (1F, br d, *J* = 12.1 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4 ($C_{C=O}$), 165.4 ($C_{C=O}$), 133.6 (C_{Ar}), 129.9 (C_{Ar}), 129.0 (C_{Ar}), 128.5 (C_{Ar}), 95.6 (dd, *J* = 20.5, 8.8 Hz, C_1), 86.6 (dd, *J* = 192.0, 19.0 Hz, C_2), 86.3 (dd, *J* = 191.5, 17.6 Hz, C_3), 72.2 (C_{CHiPr}), 69.4 (dd, *J* = 16.9, 8.1 Hz, C_4), 66.6 (d, *J* = 4.4 Hz, C_5), 62.1 (d, *J* = 2.2 Hz, C_6), 23.1 (C_{CH3iPr}), 21.7 (C_{CH3iPr}), 20.6 (C_{COCH3}) ppm; HRMS (ESI+) for $C_{18}H_{22}F_2NaO_6$ $[M + Na]^+$ calcd 395.1277 found 395.1287 (-2.6 ppm error).

Data for **14β**: white solid; R_f 0.48 (hexane/EtOAc 60:40); $[\alpha]_D^{22}$ -11.4 (c 0.53, $CHCl_3$); mp 95–97 ˚C (CH_2Cl_2); IR (neat) 2976 (w), 1723 (s), 1372 (w), 1269 (s), 1069 (s), 1026 (s), 827 (s), 712 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.08 (2H, dd, *J* = 8.4, 1.3 Hz, H_{Ar}), 7.61 (1H, ddt, *J* = 7.9, 7.0, 1.3 Hz, H_{Ar}), 7.48 (2H, t, *J* = 7.8 Hz, H_{Ar}), 5.84 (1H, dddd, *J* = 5.1, 3.8, 2.6, 1.0 Hz, H_4), 4.70–4.94 (1H, m, H_3), 4.63 (1H, d, *J* = 7.7 Hz, H_1), 4.53–4.81 (1H, m, H_2), 4.25 (1H, ddd, *J* = 11.2, 7.0, 0.9 Hz, H_6), 4.17 (1H, dd, *J* = 11.4, 6.1 Hz, H_6), 4.06 (1H, spt, *J* = 6.2 Hz, H_{CHiPr}), 3.95 (1H, tt, *J* = 6.4, 1.3 Hz, H_5), 2.05 (3H, s, H_{COCH3}), 1.33 (3H, d, *J* = 6.2 Hz, H_{CH3iPr}), 1.28 (3H, d, *J* = 6.5 Hz, H_{CH3iPr}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -199.9 (1F, dtd, *J* = 47.4, 13.4, 5.2 Hz, F_3), -206.4 (1F, br dt, *J* = 52.9, 15.2 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -199.9 (1F, d, *J* = 14.3 Hz, F_3), -206.4 (1F, d, *J* = 14.3 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4 ($C_{C=O}$), 165.4 ($C_{C=O}$), 133.7 (C_{Ar}), 130.0 (C_{Ar}), 128.8 (C_{Ar}), 128.5 (C_{Ar}), 98.9 (dd, *J* = 22.7, 11.0 Hz, C_1), 89.2 (dd, *J* = 187.1, 19.1 Hz, C_3), 89.3 (dd, *J* = 194.4, 19.1 Hz, C_2), 73.3 (C_{CHiPr}), 70.1 (d, *J* = 5.9 Hz, C_5), 68.2 (dd, *J* = 16.5, 8.4 Hz, C_4), 61.6 (d, *J* = 2.2 Hz, C_6), 23.3 (C_{CH3iPr}), 21.9 (C_{CH3iPr}), 20.6 (C_{COCH3}) ppm; HRMS (ESI+) for $C_{18}H_{22}F_2NaO_6$ $[M + Na]^+$ calcd 395.1277 found 395.1282 (-1.4 ppm error).

3.4 Isopropyl 6-*O*-acetyl-4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-α/β-D-glucopyranoside (**15**)

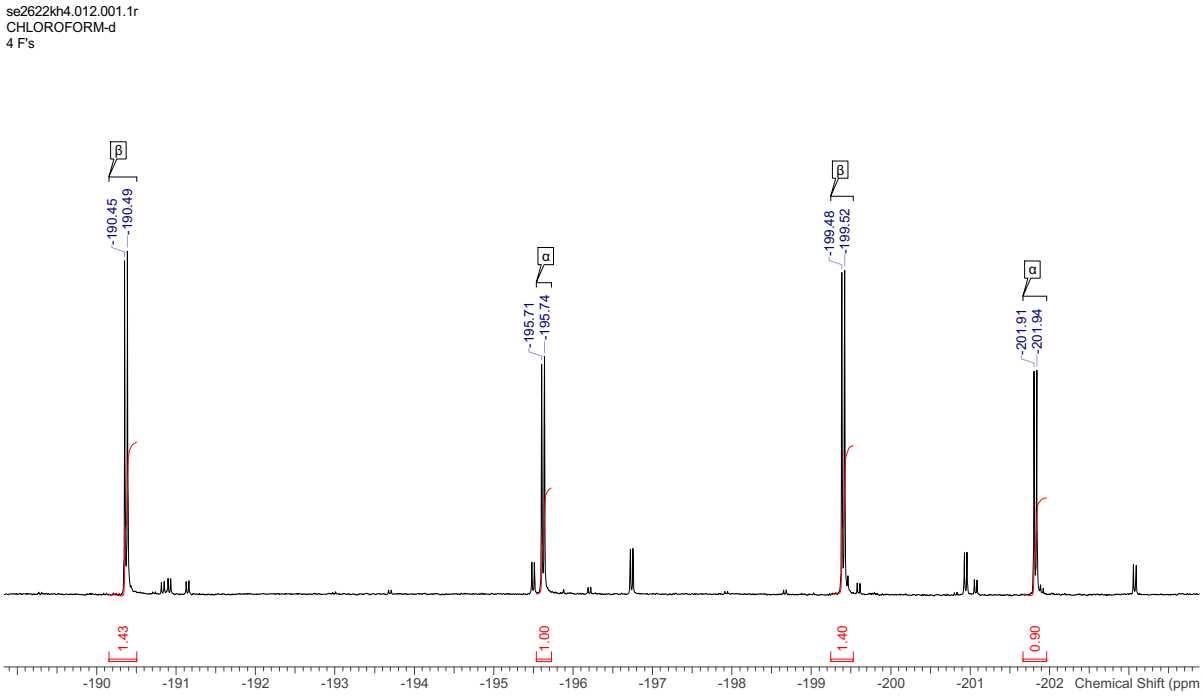
3.4.1 Glycosidation (Table 2, entry 2)



According to general procedure B, **8** (109 mg, 0.24 mmol, 1.0 equiv) was reacted at –30 ˚C for 3.5 h. The resultant crude material (α/β 1:1.43) was purified by flash column chromatography (10 g, hexane/EtOAc 100:0 to 70:30) to afford **15** as a non-separable mixture of α- and β-anomers as a colourless oil (73.2 mg, 0.204 mmol, 86% yield).

3.4.2 Ratio determination, crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:1.43, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **2** is present and no unreacted trichloroacetimidate **8** is observed in the crude reaction mixture.

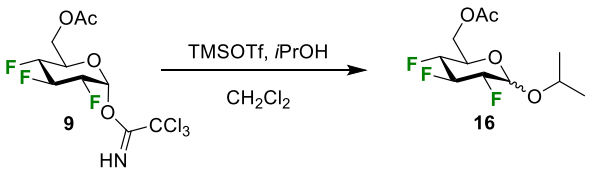


3.4.3 Characterisation of the glycosides (as anomeric mixture)

R_f 0.46 (hexane/EtOAc 70:30); IR (neat) 3342 (br), 2956 (br), 2359 (w), 2341 (w), 1742 (s), 1676 (s), 1368 (w), 1283 (w), 1238 (s), 1061 (s), 1015 (w), 796 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, α/β 1:1.07) (COSY/HMBC/HSQC) δ 7.29–7.40 (10H, m, $H_{Ar\alpha}$ and $H_{Ar\beta}$), 5.12 (1H, t, *J* = 3.5 Hz, $H_{1\alpha}$), 5.04 (1H, ddt, *J* = 55.0, 13.3, 8.9 Hz, $H_{3\alpha}$), 4.89 (1H, d, *J* = 11.1 Hz, $H_{CH2OBn\alpha}$), 4.87 (1H, d, *J* = 11.4 Hz, $H_{CH2OBn\beta}$), 4.77 (1H, ddt, *J* = 52.8, 16.8, 8.4 Hz, $H_{3\beta}$), 4.61 (1H, d, *J* = 11.1 Hz, $H_{CH2OBn\alpha}$), 4.61 (1H, d, *J* = 11.1 Hz, $H_{CH2OBn\beta}$), 4.53 (1H, dd, *J* = 7.8, 2.9 Hz, $H_{1\beta}$), 4.18–4.44 (4H, m, $H_{6\alpha}$ and $H_{6\beta}$), 3.99 (1H, spt, *J* = 6.1 Hz, $H_{i\mathrm{Pr}\beta}$), 3.90 (1H, spt, *J* = 6.1 Hz, $H_{i\mathrm{Pr}\alpha}$), 3.65 (1H, ddd, *J* = 13.3, 10.0, 8.4 Hz, $H_{4\beta}$), 3.61 (1H, ddd, *J* = 14.1, 10.1, 8.4 Hz, $H_{4\alpha}$), 3.48–3.54 (1H, m, H_5), 2.02 (3H, s, H_{CH3}), 1.25 (6H, dd, *J* = 16.1, 6.2 Hz, $H_{CH3i\mathrm{Pr}\beta}$), 1.22 (6H, dd, *J* = 13.7, 6.2 Hz, $H_{CH3i\mathrm{Pr}\alpha}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.5 (1F, dq, *J* = 52.0, 13.9 Hz, $F_{3\beta}$), -195.7 (1F, dq, *J* = 54.8, 12.9 Hz, $F_{3\alpha}$), -199.5 (1F, dddd, *J* = 52.0, 15.6, 12.1, 3.5 Hz, $F_{2\beta}$), -201.9 (1F, dt, *J* = 50.3, 13.0 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -190.5 (1F, d, *J* = 13.9 Hz, $F_{3\beta}$), -195.7 (1F, d, *J* = 12.1 Hz, $F_{3\alpha}$), -199.5 (1F, d, *J* = 13.9 Hz, $F_{2\beta}$), -201.9 (1F, d, *J* = 12.1 Hz, $F_{2\alpha}$) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.6 ($C_{C=O}$), 137.1 ($C_{Ar\alpha}$), 137.0 ($C_{Ar\beta}$), 128.5 ($C_{Ar\alpha}$ and $C_{Ar\beta}$), 128.4 ($C_{Ar\alpha}$), 128.4 ($C_{Ar\beta}$), 128.2 ($C_{Ar\beta}$), 128.2 ($C_{Ar\alpha}$), 98.4 (dd, *J* = 23.5, 10.3 Hz, $C_{1\beta}$), 96.2 (dd, *J* = 186.3, 18.5 Hz, $C_{3\beta}$), 94.8 (dd, *J* = 28.6, 18.3 Hz, $C_{1\alpha}$), 89.9 (dd, *J* = 190.7, 19.1 Hz, $C_{2\beta}$), 87.6 (dd, *J* = 194.4, 18.3 Hz, $C_{2\alpha}$), 75.0 (dd, *J* = 16.9, 7.3 Hz, C_4), 74.2–74.4 (C_{CH2OBn}), 72.9 ($C_{CHi\mathrm{Pr}\beta}$), 71.7 ($C_{CHi\mathrm{Pr}\alpha}$), 71.6 (d, *J* = 10.3 Hz, $C_{5\beta}$), 67.8 (d, *J* = 7.3 Hz, $C_{5\alpha}$), 62.2–63.0 ($C_{6\alpha}$ and $C_{6\beta}$), 23.3 ($C_{CH3i\mathrm{Pr}\beta}$), 23.1 ($C_{CH3i\mathrm{Pr}\alpha}$), 21.9 ($C_{CH3i\mathrm{Pr}\beta}$), 21.6 ($C_{CH3i\mathrm{Pr}\alpha}$), 20.8 ($C_{CH3\beta}$), 20.7 ($C_{CH3\alpha}$) ppm; HRMS (ESI+) for $C_{17}H_{18}Cl_3F_2NNaO_5$ $[M + Na]^+$ calcd 482.0111 found 482.0110 (0.2 ppm error).

3.5 Isopropyl 6-*O*-acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α/β-D-glucopyranoside (**16**)

3.5.1 Glycosylation (Table 2, entry 3)



According to general procedure B, **9** (104 mg, 0.280 mmol, 1.0 equiv) was reacted at 0 ˚C for 5 h. The resultant crude material (α/β 1:2.10) was purified by flash column chromatography (10 g, hexane/EtOAc 90:10 to 60:40) to afford **16** as a non-separable mixture of α- and β-anomers as a colourless oil (26 mg, 0.096 mmol, 34% yield).

3.5.2 Ratio determination, crude reaction mixture, $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^{1}H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:2.10, no hydrolysis of the trichloroacetimidate was observes as no peak corresponding to the hemiacetal **3** is present however peaks integrating for ~1 correspond to unreacted trichloroacetimidate **9**.

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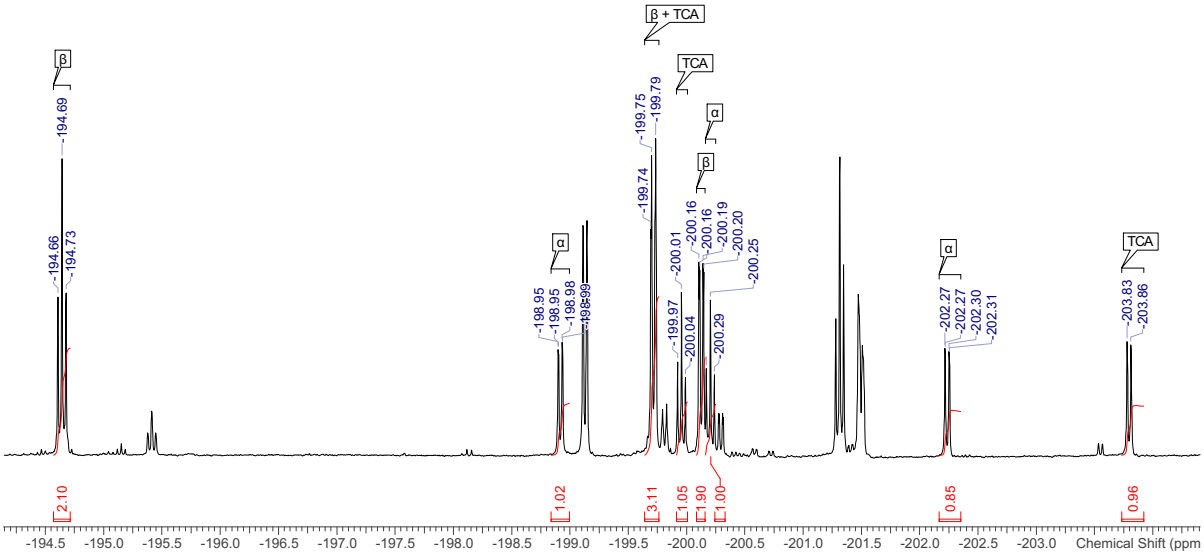
8 F's



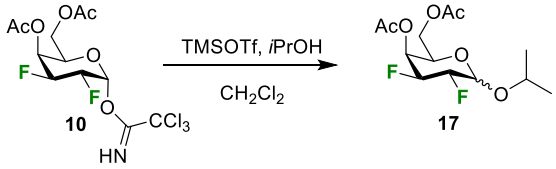
3.5.3 Characterisation of the glycosides (as anomeric mixture)

R_f 0.71 (hexane/EtOAc 60:40); IR (neat) 2978 (w), 2363 (s), 1745 (s), 1373 (w), 1236 (s), 1081 (s), 1030 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, α/β 1.24:1) (COSY/HMBC/HSQC) δ 5.13 (1H, q, *J* = 3.2 Hz, $H_{1\alpha}$), 5.01 (1H, dddt, *J* = 55.3, 16.6, 13.4, 8.6 Hz, $H_{3\alpha}$), 4.77 (1H, dtt, *J* = 53.1, 16.4, 8.3 Hz, $H_{3\beta}$), 4.60 (1H, dd, *J* = 7.8, 3.2 Hz, $H_{1\beta}$), 4.36–4.47 (2H, m, H_6), 4.36–4.65 (3H, m, $H_{4\alpha}$, $H_{4\beta}$, $H_{2\alpha}$), 4.21–4.33 (2H, m, H_6), 4.19–4.47 (1H, m, $H_{2\beta}$), 4.10 (1H, dtd, *J* = 10.0, 4.4, 2.4 Hz, $H_{5\alpha}$), 4.00 (1H, spt, *J* = 6.1 Hz, $H_{CHiPr\beta}$), 3.93 (1H, spt, *J* = 6.1 Hz, $H_{CHiPr\alpha}$), 3.67 (1H, ddtd, *J* = 9.8, 5.1, 2.6, 1.1 Hz, $H_{5\beta}$), 2.11 (3H, s, $H_{COCH3\beta}$), 2.11 (3H, s, $H_{COCH3\alpha}$), 1.27 (6H, d, *J* = 6.2 Hz, $2H_{CH3iPr}$), 1.23 (3H, d, *J* = 6.1 Hz, $H_{CH3iPr\beta}$), 1.22 (3H, d, *J* = 6.1 Hz, $H_{CH3iPr\alpha}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -194.7 (1F, dquin, *J* = 53.5, 13.8 Hz, $F_{3\beta}$), -199.0

(1F, dt, *J* = 51.3, 14.5 Hz, $F_{4\alpha}$), -199.8 (1F, dtt, *J* = 50.7, 15.2, 2.2 Hz, $F_{2\beta}$), -200.5–-200.0 (2F, m, $F_{4\beta}$ and $F_{3\alpha}$), -202.3 (F, dt, *J* = 50.1, 13.3 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -194.7 (1F, t, *J* = 13.0 Hz, $F_{3\beta}$), -199.0 (1F, dd, *J* = 12.6, 1.3 Hz, $F_{4\alpha}$), -199.8 (1F, dd, *J* = 13.4, 2.6 Hz, $F_{2\beta}$), -200.2 (1F, dd, *J* = 12.6, 2.6 Hz, $F_{4\beta}$), -200.3 (1F, t, *J* = 13.0 Hz, $F_{3\alpha}$), -202.3 (1F, dd, *J* = 13.2, 1.5 Hz, $F_{2\alpha}$) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.5 ($C_{C=O}$), 98.4 (dd, *J* = 23.5, 10.3 Hz, $C_{1\beta}$), 94.8 (dd, *J* = 20.5, 9.5 Hz, $C_{1\alpha}$), 92.3 (dt, *J* = 189.3, 20.5 Hz, $C_{3\beta}$), 90.3 (dt, *J* = 187.1, 19.8 Hz, $C_{3\alpha}$), 89.5 (ddd, *J* = 190.7, 18.7, 7.7 Hz, $C_{2\beta}$), 85.6–88.2 (m, $C_{4\alpha}$, $C_{4\beta}$ and $C_{2\alpha}$), 73.2 ($C_{CH\textit{i}Pr\beta}$), 72.3 ($C_{CH\textit{i}Pr\alpha}$), 70.0 (dd, *J* = 23.1, 7.7 Hz, $C_{5\beta}$), 66.4 (dd, *J* = 23.8, 7.0 Hz, $C_{5\alpha}$), 61.9 ($C_{6\beta}$), 61.8 ($C_{6\alpha}$), 23.2 ($C_{CH3\textit{i}Pr\beta}$), 23.0 ($C_{CH3\textit{i}Pr\alpha}$), 21.8 ($C_{CH3\textit{i}Pr\beta}$), 21.6 ($C_{CH3\textit{i}Pr\alpha}$), 20.7 ($C_{COCH3\beta}$), 20.7 ($C_{COCH3\alpha}$) ppm; HRMS (ESI+) for $C_{11}H_{17}F_3NaO_4$ $[M + Na]^+$ calcd 293.0971 found 293.0969 (0.6 ppm error).

3.6 Isopropyl 4,6-di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α/β-D-galactopyranoside (**17**)

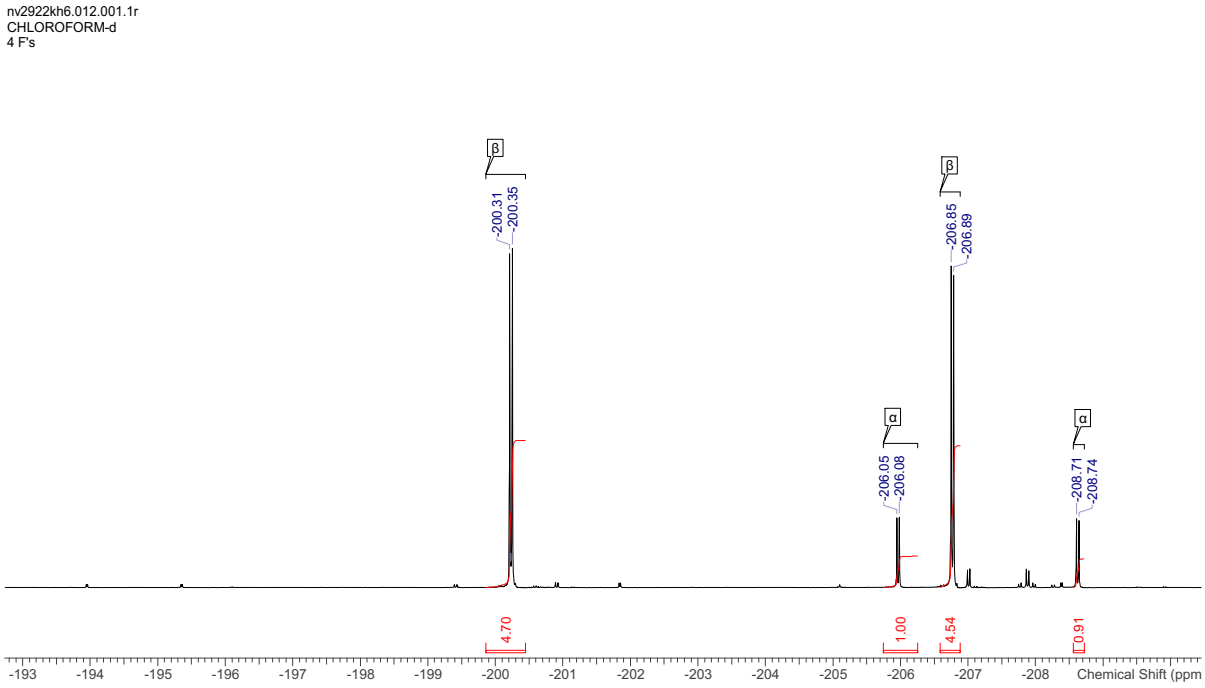
3.6.1 Glycosylation (Table 2, entry 4)



According to general procedure B, **10** (106 mg, 0.258 mmol, 1.0 equiv) was reacted at –30 ˚C for 3.5 h. The resultant crude material (α/β 1:4.70) was purified by flash column chromatography (10 g, hexane/EtOAc 80:20 to 60:40) to collect **17** as a mixture of α- and β-anomers (80 mg, 0.258 mmol, quant.). An analytical sample was purified to isolate the β-anomer using flash column chromatography (10 g, hexane/EtOAc 80:20 to 60:40).

3.6.2 Ratio determination, crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:4.70, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **4** is present and no unreacted trichloroacetimidate **10** is observed in the crude reaction mixture.

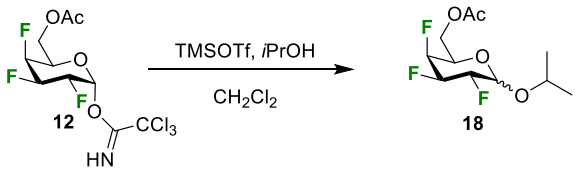


3.6.3 Characterisation of the glycosides (beta anomer only)

Data for **17β**: colourless crystal; R_f 0.57 (hexane/EtOAc 60:40); $[\alpha]_D^{22}$ +0.58 (c 0.34, $CHCl_3$); mp 125–127 ˚C (hexane); IR (neat) 2977 (w), 2360 (w), 2334 (w), 1744 (s), 1372 (s), 1331 (s), 1070 (s), 1035 (s), 730 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 5.56 (1H, dddd, *J* = 5.2, 3.9, 2.6, 1.0 Hz, H_4), 4.71 (1H, dddd, *J* = 47.9, 14.2, 8.9, 4.0 Hz, H_3), 4.55 (1H, d, *J* = 9.9 Hz, H_1), 4.43–4.70 (1H, m, H_2), 4.16 (1H, ddd, *J* = 11.5, 6.8, 0.9 Hz, H_6), 4.12 (1H, dd, *J* = 11.2, 6.4 Hz, H_6), 4.00 (1H, spt, *J* = 6.2 Hz, H_{CHiPr}), 3.84 (1H, tt, *J* = 6.5, 1.5 Hz, H_5), 2.14 (3H, s, H_{COCH3}), 2.05 (3H, s, H_{COCH3}), 1.28 (3H, d, *J* = 6.1 Hz, H_{CH3iPr}), 1.23 (3H, d, *J* = 6.1 Hz, H_{CH3iPr}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -200.3 (1F, dtd, *J* = 47.8, 13.6, 5.2 Hz, F_3), -206.9 (1F, dt, *J* = 53.0, 14.3 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -200.3 (1F, d, *J* = 14.3 Hz, F_3), -206.9 (1F, d, *J* = 14.7 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4 ($C_{C=O}$), 169.9 ($C_{C=O}$), 98.7 (dd, *J* = 22.7, 11.0 Hz, C_1), 89.1 (dd, *J* = 193.7, 19.1 Hz, C_2), 89.0 (dd, *J* = 186.3, 19.8 Hz, C_3), 73.2 (C_{CHiPr}), 69.7 (d, *J* = 5.9 Hz, C_5), 67.5 (dd, *J* = 16.1, 8.1 Hz, C_4), 61.2 (d, *J* = 2.9 Hz, C_6), 23.2 (C_{CH3iPr}), 21.8 (C_{CH3iPr}), 20.6 (C_{COCH3}), 20.5 (C_{COCH3}) ppm; HRMS (ESI+) for $C_{13}H_{20}F_2NaO_6$ $[M + Na]^+$ calcd 333.1120 found 333.1129 (-2.6 ppm error).

3.7 Isopropyl 6-*O*-acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α/β-D-galactopyranoside (**18**)

3.7.1 Glycosylation (Table 2, entry 6)

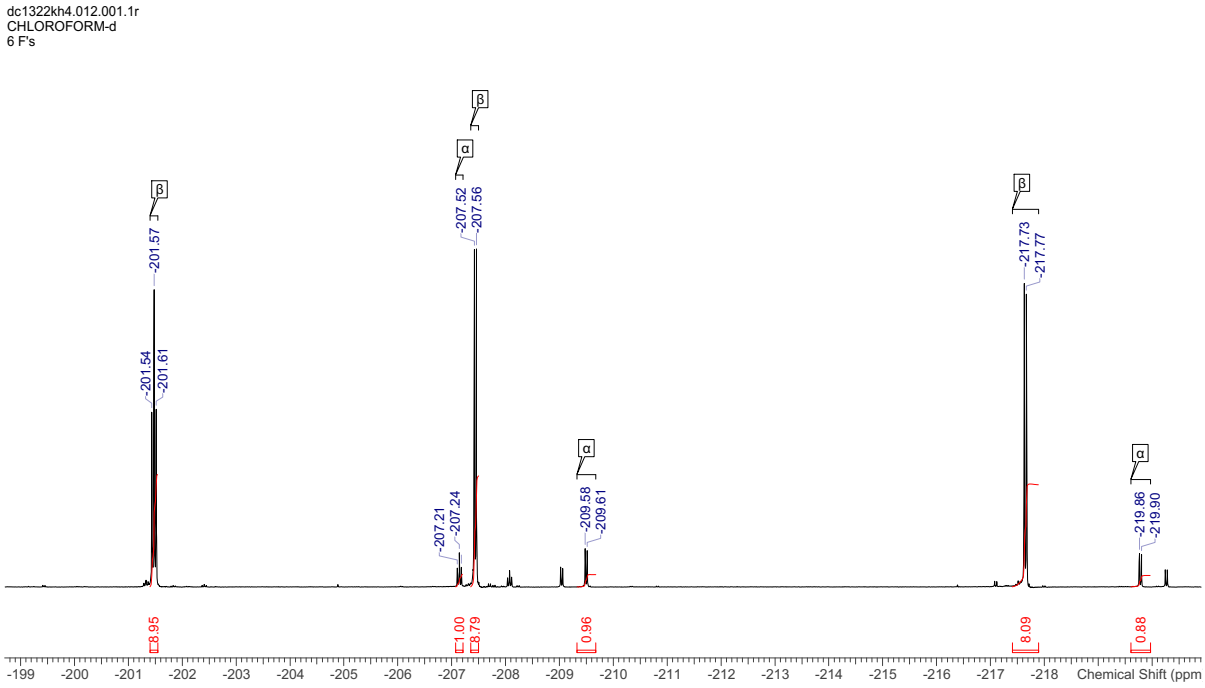


According to general procedure B, **12** (112 mg, 0.302 mmol, 1.0 equiv) was reacted at –30 ˚C for 4 h. The resultant crude material (α/β 1:8.95) was purified by flash column chromatography (10 g, hexane/EtOAc 80:20 to 60:40) to collect **18** as a mixture of α- and β-anomers as a colourless oil (81 mg, 0.302 mmol, quant.). An analytical

sample was purified to isolate the β-anomer using flash column chromatography (10 g, hexane/EtOAc 90:10 to 60:40).

3.7.2 Ratio determination, crude reaction mixture, $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^{1}H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:8.95, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **6** is present and no unreacted trichloroacetimidate **12** is observed in the crude reaction mixture.



3.7.3 Characterisation of the glycosides (beta anomer only)

Data for **18β**: R_f 0.41 (hexane/EtOAc 60:40); $[\alpha]_D^{22}$ -23.2 (c 0.59, $CHCl_3$); mp 67–69 ˚C (CH_2Cl_2); IR (neat) 2977 (w), 1739 (s), 1373 (s), 1233 (s), 1070 (s), 1055 (s), 1035 (s), 826 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 4.94 (1H, ddt, *J* = 50.4, 6.5, 2.6 Hz, H_4), 4.57 (1H, d, *J* = 7.2 Hz, H_1), 4.50–4.78 (2H, m, H_2 and H_3), 4.39 (1H, ddt, *J* = 11.2, 6.6, 1.1 Hz, H_6), 4.24 (1H, dd, *J* = 11.4, 6.7 Hz, H_6), 4.02 (1H, spt, *J* = 6.2 Hz, H_{CHiPr}), 3.74 (1H, dtd, *J* = 25.4, 6.6, 1.7 Hz, H_5), 2.10 (3H, s, H_{CH3}), 1.29 (3H, d, *J* = 6.2 Hz, H_{CH3iPr}), 1.23 (3H, d, *J* = 6.2 Hz, H_{CH3iPr}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -201.6 (1F, ddsxt, *J* = 45.5, 13.9, 6.1 Hz, F_3), -207.5 (1F, dtd, *J* = 55.5, 14.3, 2.6 Hz, F_2), -217.7 (1F, dtd, *J* = 49.9, 26.4, 16.0 Hz, F_4) ppm; $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -201.6 (1F, t, *J* = 14.7 Hz, F_3), -207.5 (1F, d, *J* = 13.9 Hz, F_2), -217.7 (1F, d, *J* = 15.2 Hz, F_4) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.5 ($C_{C=O}$), 98.6 (dd, *J* = 22.7, 11.0 Hz, C_1), 89.3 (ddd, *J* = 193.7, 19.8, 18.3 Hz, C_3), 88.6 (dd, *J* = 186.3, 19.1 Hz, C_2), 86.3 (ddd, *J* = 187.1, 16.5, 9.2 Hz, C_4), 73.0 (C_{CHiPr}), 69.7 (dd, *J* = 18.0, 6.2 Hz, C_5), 61.2 (dd, *J* = 5.9, 2.9 Hz, C_6), 23.3 (C_{CH3iPr}), 21.8 (C_{CH3iPr}), 20.7 (C_{COCH3}) ppm; HRMS (ESI+) for $C_{11}H_{17}F_3NaO_4$ calcd 293.0971 found 293.0968 (1.1 ppm error).

4 Glycosylation reactions

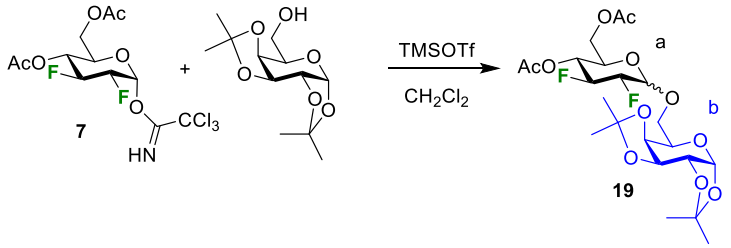
4.1 General procedure

General procedure C: The trichloroacetimidate (1.0 equiv) and the acceptor (1.2 equiv.) were co-evaporated separately with redistilled toluene (3 ×) and redistilled CH_2Cl_2 (1 ×), dried under high vacuum. Freshly activated molecular sieves (3 Å) were added to both flasks, the trichloroacetimidate and the acceptor were dissolved separately in redistilled CH_2Cl_2 under argon. The mixtures were stirred at room temperature for 30 min. The reaction vessel containing the trichloroacetimidate was cooled to the stated temperature (–50 ˚C – 0 ˚C). TMSOTf (0.2 equiv) was added, followed by addition of the acceptor solution, and the reaction mixture was stirred for the stated time at the same temperature. The reaction was followed by $^{19}F\{^1H\}$ NMR. After completion, the mixture was diluted with CH_2Cl_2, quenched by the addition of NEt_3 (0.5 mL), and filtered through a pad of Celite. The solvents were removed under reduced pressure, and the crude product was purified by flash column chromatography. The ratios were obtained by $^{19}F\{^1H\}$ NMR of the crude reaction mixture with a delay time (D1) of 3 s.

4.2 Glycosylation with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose

4.2.1 4,6-Di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α/β-D-glucopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**19**)

4.2.1.1 Glycosylation (Table 3, entry 1)



According to general procedure C, **7** (110 mg, 0.266 mmol, 1.0 equiv) was reacted at –30 ˚C for 3.5 h. The resultant crude material (α/β 1:1.14) was purified by flash column chromatography (10 g, hexane/EtOAc 90:10 to 60:40) to collect **19** as a mixture of α- and β-anomers as a colourless oil (135 mg, 0.266 mmol, quant.). An analytical sample was purified to separate the anomers using flash column chromatography (25 g, hexane/EtOAc 80:20 to 60:40). Anomers assignment was based on the chemical shift and coupling constant values of the anomeric protons.

4.2.1.2 Ratio determination, crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:1.14, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **1** is present and no unreacted trichloroacetimidate **7** is observed in the crude reaction mixture.

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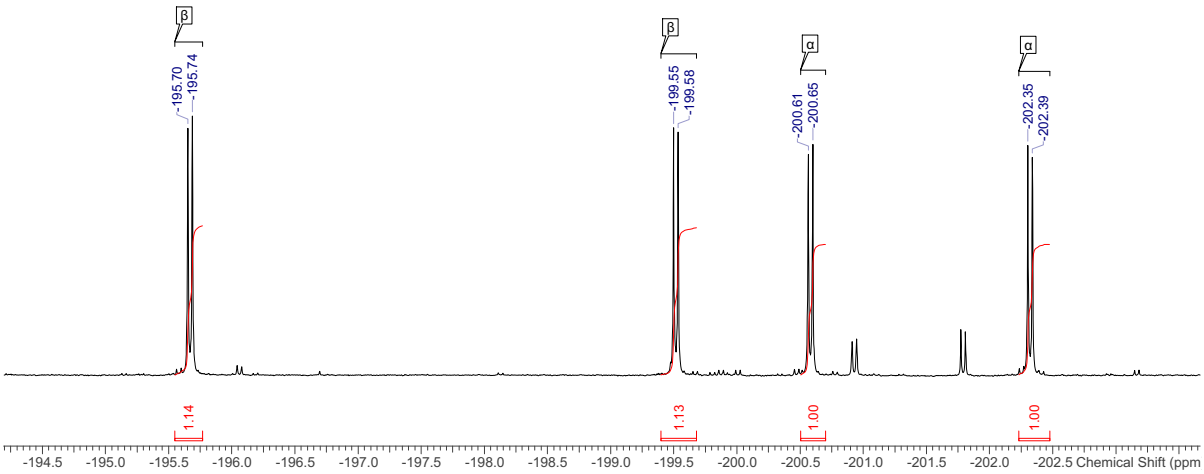
CHLOROFORM-d
4 F's



4.2.1.3 Characterisation of the disaccharides (pure anomers)

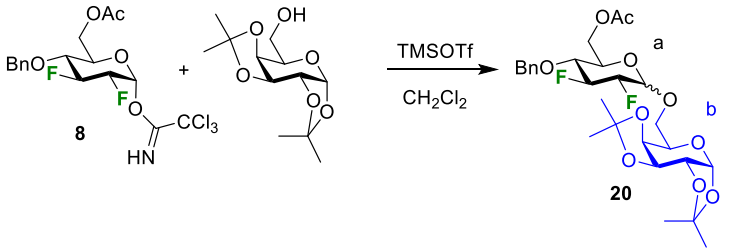
Data for **19α**: Colourless oil; Rf 0.50 (hexane/EtOAc 50:50); $[\alpha]_D^{22.5}$ +5.0 (c 2.17, $CHCl_3$); IR (neat) 2980 (br, s), 2360 (s), 2342 (s), 1734 (s), 1717 (s), 1374 (w), 1214 (w), 1070 (s), 1034 (s), 1007 (w), 827 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 5.49 (1H, d, *J* = 5.0 Hz, H_{1b}), 5.07–5.20 (2H, m, H_{1a} and H_{4a}), 4.87 (1H, ddt, *J* = 54.5, 13.1, 8.9 Hz, H_{3a}), 4.60 (1H, dd, *J* = 7.9, 2.4 Hz, H_{3b}), 4.56 (1H, dddd, *J* = 49.9, 13.1, 8.4, 4.0 Hz, H_{2a}), 4.30 (1H, dd, *J* = 4.9, 2.4 Hz, H_{2b}), 4.19–4.29 (2H, m, H_{4b}, H_{6a}), 4.02–4.15 (2H, m, H_{6a}, H_{5a}), 3.98 (1H, ddd, *J* = 6.7, 5.2, 1.7 Hz, H_{5b}), 3.81 (1H, dd, *J* = 10.9, 7.0 Hz, H_{6b}), 3.76 (1H, dd, *J* = 11.2, 5.1 Hz, H_{6b}), 2.10 (3H, s, $H_{CH3(a)}$), 2.07 (3H, s, $H_{CH3(a)}$), 1.52 (3H, s, $H_{CH3(b)}$), 1.41 (3H, s, $H_{CH3(b)}$), 1.32 (3H, s, $H_{CH3(b)}$), 1.31 (3H, s, $H_{CH3(b)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -200.6 (1F, dq, *J* = 55.5, 12.1 Hz, F_3), -202.4 (1F, dt, *J* = 50.3, 13.0 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -200.6 (1F, d, *J* = 12.1 Hz, F_3), -202.4 (1F, d, *J* = 12.1 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.6 ($C_{\underline{C}OCH3}$), 169.4 ($C_{\underline{C}OCH3}$), 109.4 ($C_{C(CH3)2(b)}$), 108.6 ($C_{\underline{C}(CH3)2(b)}$), 96.4 (dd, *J* = 19.8, 9.5 Hz, C_{1a}), 96.2 (C_{1b}), 90.0 (dd, *J* = 187.8, 19.8 Hz, C_{3a}), 87.6 (dd, *J* = 194.8, 17.2 Hz, C_{2a}), 70.9 (C_{4b}), 70.5 (C_{3b}), 70.4 (C_{2b}), 68.1 (C_{6b}), 67.7 (dd, *J* = 18.3, 7.3 Hz, C_{4a}), 66.9 (d, *J* = 6.6 Hz, C_{5a}), 66.8 (C_{5b}), 61.5 (C_{6a}), 26.0 ($C_{CH3(b)}$), 25.9 ($C_{CH3(b)}$), 24.9 ($C_{CH3(b)}$), 24.3 ($C_{CH3(b)}$), 20.6 ($C_{CH3(a)}$), 20.6 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{22}H_{32}F_2NaO_{11}$ $[M + Na]^+$ calcd 533.1805 found 533.1817 (err -2.2 ppm).

Data for **19β**: Colourless oil; R_f 0.40 (hexane/EtOAc 50:50); $[\alpha]_D^{23}$ -74 (c 0.36, $CHCl_3$); IR (neat) 2988 (w), 1749 (s), 1717 (s), 1375 (w), 1214 (s), 1069 (s), 1033 (s), 1008 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 5.53 (1H, d, *J* = 5.0 Hz, H_{1b}), 5.18 (1H, dt, *J* = 13.0, 9.2 Hz, H_{4a}), 4.74 (1H, dd, *J* = 7.6, 3.0 Hz, H_{1a}), 4.66 (1H, ddt, *J* = 52.6, 16.0, 8.7 Hz, H_{3a}), 4.61 (1H, dd, *J* = 7.9, 2.5 Hz, H_{3b}), 4.32 (1H, dd, *J* = 4.9, 2.4 Hz, H_{2b}), 4.42 (1H, ddt, *J* = 51.2, 14.5, 8.2 Hz, H_{2a}), 4.28 (1H, dd, *J* = 12.2, 4.9 Hz, H_{6a}), 4.26 (1H, dd, *J* = 7.9, 1.7 Hz, H_{4b}), 4.09–4.17 (1H, m, H_{6a}), 3.98–4.07 (2H, m, H_{5b} and H_{6b}), 3.80–3.89 (1H, m, H_{6b}), 3.61 (1H, dddt, *J* = 10.0, 3.7, 2.4, 1.1 Hz, H_{5a}), 2.11 (3H, s, $H_{CH3(a)}$), 2.09 (3H, s, $H_{CH3(a)}$), 1.54 (3H, s, $H_{CH3(b)}$), 1.45 (3H, s, $H_{CH3(b)}$), 1.34 (6H, s, $2H_{CH3(b)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -195.6 (1F, dq, *J* = 52.6, 13.7 Hz, F_3), -199.4 (1F, dtd, *J* = 51.6, 13.9, 3.0 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376

MHz, $CDCl_3$) δ -195.6 (1F, d, *J* = 13.9 Hz, F_3), -199.4 (1F, d, *J* = 13.9 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.6 ($C_{\underline{C}OCH3}$), 169.2 ($C_{\underline{C}OCH3}$), 109.4 ($C_{\underline{C}(CH3)2(b)}$), 108.8 ($C_{\underline{C}(CH3)2(b)}$), 99.7 (dd, *J* = 22.7, 11.0 Hz, C_{1a}), 96.2 (C_{1b}), 92.1 (dd, *J* = 190.0, 20.5 Hz, C_{3a}), 89.6 (dd, *J* = 190.4, 18.7 Hz, C_{2a}), 71.2 (C_{4b}), 70.8 (d, *J* = 8.1 Hz, C_{5a}), 70.6 (C_{3b}), 70.4 (C_{2b}), 68.8 (C_{6b}), 67.9 (C_{5b}), 67.9 (dd, *J* = 19.1, 7.3 Hz, C_{4a}), 61.7 (C_{6a}), 26.0 ($C_{CH3(b)}$), 25.9 ($C_{CH3(b)}$), 24.9 ($C_{CH3(b)}$), 24.3 ($C_{CH3(b)}$), 20.7 ($C_{CH3(a)}$), 20.6 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{22}H_{32}F_2NaO_{11}$ $[M + Na]^+$ calcd 533.1805 found 533.1816 (err -2.1 ppm).

4.2.2 6-*O*-Acetyl-4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-α/β-D-glucopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**20**)

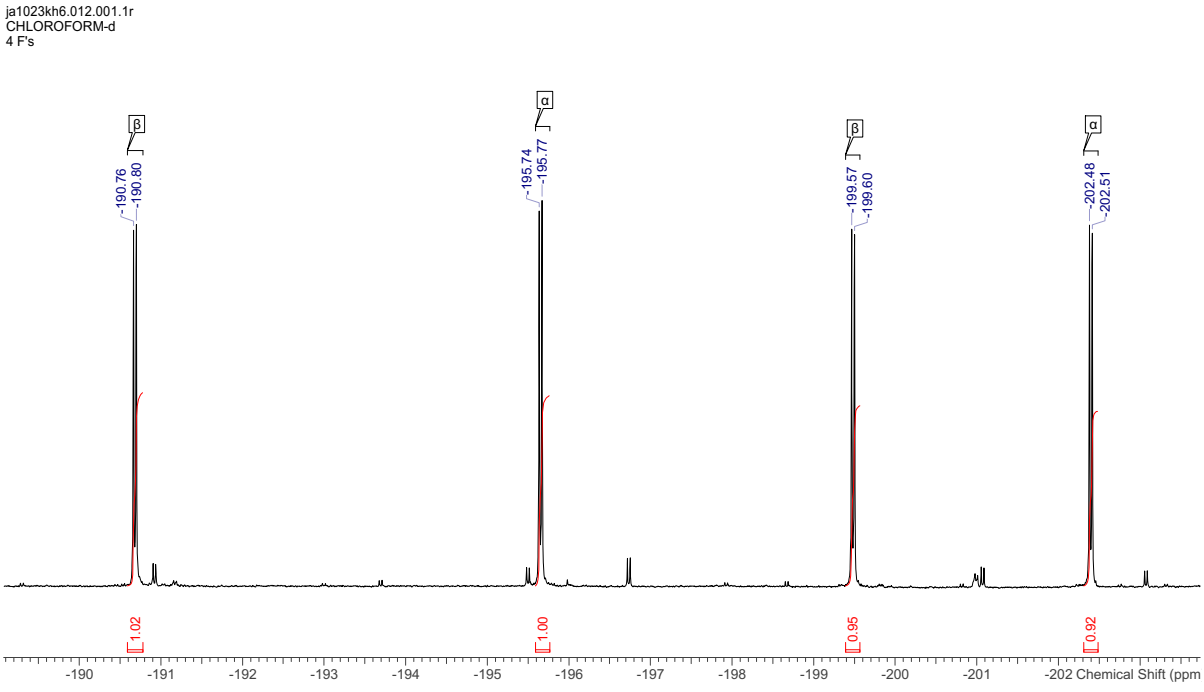
4.2.2.1 Glycosylation (Table 3, entry 2)



According to general procedure C, **8** (101 mg, 0.233 mmol, 1.0 equiv) was reacted at –30 ˚C for 4 h. The resultant crude material (α/β 1:1.02) was purified by flash column chromatography (10 g, hexane/EtOAc 100:0 to 60:40) to afford **20** as a non-separable mixture of α- and β-anomers as a colourless oil (124 mg, 0.223 mmol, quant.).

4.2.2.2 Ratio determination, crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:1.02, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **2** is present and no unreacted trichloroacetimidate **8** is observed in the crude reaction mixture.

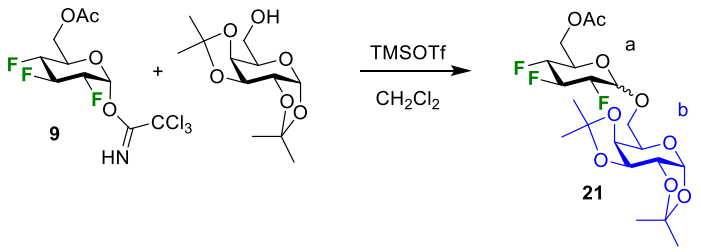


4.2.2.3 Characterisation of the disaccharides (as anomeric mixture)

R_f 0.45 (hexane/EtOAc 60:40); IR (neat) 2981 (br), 2937 (br), 2360 (s), 2342 (br), 1734 (w), 1069 (br) cm^{-1}; $^1H\{^{19}F\}$ NMR (500 MHz, $CDCl_3$, α/β 1/1.53) (COSY/HMBC/HSQC) δ 7.29–7.40 (10H, m, $H_{Ar\alpha}$, $H_{Ar\beta}$), 5.53 (1H, d, *J* = 5.0 Hz, $H_{1b\beta}$), 5.50 (1H, d, *J* = 5.0 Hz, $H_{1b\alpha}$) 5.09 (1H, d, *J* = 4.0 Hz, $H_{1a\alpha}$), 5.04 (1H, t, *J* = 8.6 Hz, $H_{3a\alpha}$), 4.87 (2H, dd, *J* = 11.2, 2.6 Hz, $H_{CH2OBn(a)\alpha}$, $H_{CH2OBn(a)\beta}$), 4.79 (1H, t, *J* = 8.4 Hz, $H_{3a\beta}$), 4.67 (1H, d, *J* = 7.8 Hz, $H_{1a\beta}$), 4.58–4.64 (4H, m, $H_{CH2OBn(a)\alpha}$, $H_{CH2OBn(a)\beta}$, H_{3b}), 4.52 (1H, dd, *J* = 8.9, 4.0 Hz, $H_{2a\alpha}$), 4.37 (1H, t, *J* = 8.0 Hz, $H_{2a\beta}$), 4.21–4.35 (8H, m, $H_{6a\alpha}$, $H_{6a\beta}$, H_{2b}, H_{4b}), 3.94–4.05 (4H, m, H_{6b}, H_{5b}), 3.81 (2H, ddd, *J* = 10.4, 6.5, 5.6 Hz, H_{6b}), 3.75 (1H, dd, *J* = 10.5, 5.9 Hz, H_{6b}), 3.67 (1H, dd, *J* = 10.0, 8.3 Hz, $H_{4a\beta}$), 3.62 (1H, dd, *J* = 10.0, 8.3 Hz, $H_{4a\alpha}$), 3.52 (1H, ddd, *J* = 9.9, 4.6, 2.1 Hz, H_{5a}), 2.02 (3H, s, $H_{CH3(a)}$), 2.01 (3H, s, $H_{CH3(a)}$), 1.54 (3H, s, $H_{CH3(b)}$), 1.53 (3H, s, $H_{CH3(b)}$), 1.44 (3H, s, $H_{CH3(b)}$), 1.43 (3H, s, $H_{CH3(b)}$) ppm; ^1H NMR (500 MHz, $CDCl_3$) δ 7.29–7.39 (10H, m, $H_{Ar\alpha}$ and $H_{Ar\beta}$), 5.53 (1H, d, *J* = 5.0 Hz, $H_{1b\beta}$), 5.50 (1H, d, *J* = 5.0 Hz, $H_{1b\alpha}$), 5.09 (1H, t, *J* = 3.4 Hz, $H_{1a\alpha}$), 5.04 (1H, ddt, *J* = 54.8, 13.5, 8.7 Hz, $H_{3a\alpha}$), 4.87 (2H, dd, *J* = 12.2, 2.5 Hz, $H_{CH2OBn(a)\alpha}$, $H_{CH2OBn(a)\beta}$), 4.79 (1H, ddt, *J* = 52.8, 16.6, 8.5 Hz, $H_{3a\beta}$), 4.67 (1H, dd, *J* = 7.8, 2.6 Hz, $H_{1a\beta}$), 4.58–4.64 (4H, m, $H_{CH2OBn(a)\alpha}$, $H_{CH2OBn(a)\beta}$, H_{3b}), 4.52 (1H, dddd, *J* = 50.1, 13.4, 9.0, 3.9 Hz, $H_{2a\alpha}$), 4.21–4.37 (8H, m, $H_{6a\alpha}$, $H_{6a\beta}$, H_{2b}, H_{4b}), 3.95–4.07 (4H, m, H_{6b}, H_{5b}), 3.81 (2H, ddd, *J* = 10.4, 6.5, 5.6 Hz, H_{6b}), 3.75 (1H, dd, *J* = 10.5, 6.0 Hz, H_{6b}), 3.67 (1H, ddd, *J* = 13.5, 10.0, 8.2 Hz, $H_{4a\beta}$), 3.62 (1H, ddd, *J* = 13.5, 10.0, 8.5 Hz, $H_{4a\alpha}$), 3.52 (1H, dddd, *J* = 9.7, 4.8, 2.2, 1.4 Hz, H_{5a}), 2.02 (3H, s, $H_{CH3(a)}$), 2.01 (3H, s, $H_{CH3(a)}$), 1.54 (3H, s, $H_{CH3(b)}$), 1.53 (3H, s, $H_{CH3(b)}$), 1.44 (3H, s, $H_{CH3(b)}$), 1.43 (3H, s, $H_{CH3(b)}$) ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ -190.6 (1F, dq, *J* = 52.9, 14.0 Hz, $F_{3\beta}$), -195.5 (1F, dq, *J* = 54.4, 13.6 Hz, $F_{3\alpha}$), -199.3 (1F, dddd, *J* = 51.5, 16.1, 13.2, 2.5 Hz, $F_{2\beta}$), -202.3 (1F, dt, *J* = 50.1, 13.2 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$) δ -190.6 (1F, d, *J* = 12.9 Hz, $F_{3\beta}$), 195.5 (1F, d, *J* = 12.9 Hz, $F_{3\alpha}$), -199.3 (1F, d, *J* = 12.9 Hz, $F_{2\beta}$), -202.3 (1F, d, *J* = 12.9 Hz, $F_{2\alpha}$) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.6 ($C_{\underline{C}OCH3(a)\alpha}$), 170.6 ($C_{\underline{C}OCH3(a)\beta}$), 128.5 ($C_{Ar\beta}$), 128.5 $C_{Ar\beta}$), 128.4 ($C_{Ar\alpha}$ and $C_{Ar\beta}$), 128.2 ($C_{Ar\alpha}$), 128.1 ($C_{Ar\alpha}$), 109.4 ($C_{C(CH3)2(b)}$), 109.3 ($C_{C(CH3)2(b)}$), 108.8 ($C_{C(CH3)2(b)}$), 108.7 ($C_{C(CH3)2(b)}$), 99.7 (dd, *J* = 22.8, 11.6 Hz, $C_{1a\beta}$), 96.6 (dd, *J* = 20.3, 10.3 Hz, $C_{1a\alpha}$), 96.2 (C_{1b}), 96.2 (C_{1b}), 96.2 (dd, *J* = 186.2, 18.6 Hz, $C_{3a\beta}$), 94.0 (dd, *J* = 184.3, 17.9 Hz, $C_{3a\alpha}$), 89.8 (dd, *J* = 190.7, 18.4 Hz, $C_{2a\beta}$), 87.8 (dd, *J* = 194.3, 17.6 Hz, $C_{2a\alpha}$), 74.7 (ddd, *J* = 27.5, 16.9, 6.7 Hz, C_{4a}), 74.1 (dd, *J* = 28.9, 3.1 Hz, $C_{CH2OBn(a)}$), 71.7 (d, *J* = 10.3 Hz, C_{5a}), 70.3 - 71.2 (m, C_{2b}, C_{4b}, C_{3b}), 68.8 (C_{6b}), 67.8 (d, *J* = 1.0 Hz, C_{6b}), 67.7 (C_{5b}), 66.5 (C_{5b}), 62.4 (d, *J* = 6.2 Hz, C_{6a}), 25.9 ($C_{CH3(b)}$), 20.8 ($C_{CH3(a)\beta}$), 20.4 ($C_{CH3(a)\alpha}$) ppm; HRMS (ESI+) for $C_{27}H_{36}F_2NaO_{10}$ $[M + Na]^+$ calcd 581.2169 found 581.2176 (err -1.3 ppm).

4.2.3 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α/β-D-glucopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**21**)

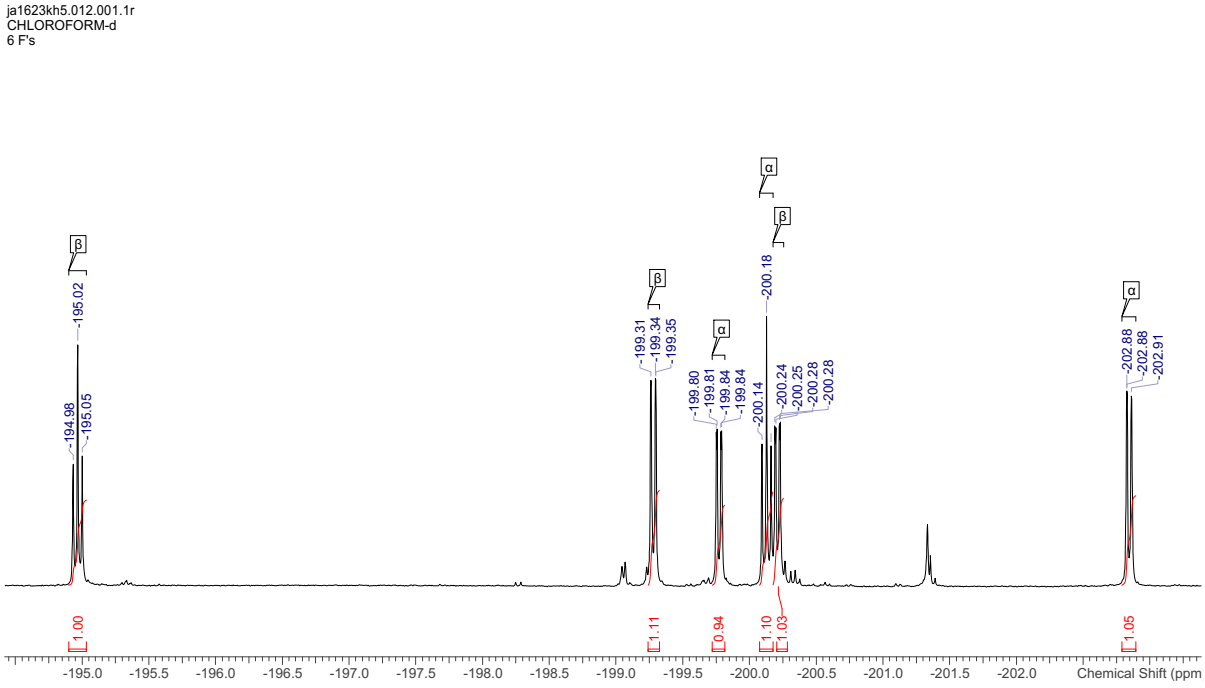
4.2.3.1 Glycosylation (Table 3, entry 3)



According to general procedure C, **9** (110 mg, 0.297 mmol, 1.0 equiv) was reacted at –30 ˚C for 3 h. The resultant crude material (α/β 1:1) was purified by flash column chromatography (10 g, hexane/EtOAc 80:20 to 60:40) to afford **21** as a non-separable mixture of α- and β-anomers as a colourless oil (139 mg, 0.297 mmol, quant.).

4.2.3.2 Ratio determination, crude reaction mixture, $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^{1}H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:1, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **3** is present and no unreacted trichloroacetimidate **9** is observed in the crude reaction mixture.



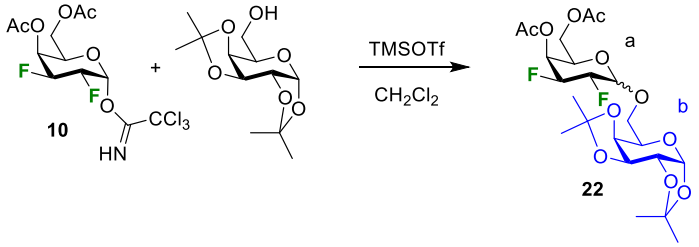
4.2.3.3 Characterisation of the disaccharides (as anomeric mixture)

R_f 0.47 (hexane/EtOAc 60:40); IR (neat) 2989 (br), 2360 (w), 1735 (w), 1212 (w), 1068 (s), 1032 (s), 1066 (s) 909 (s), 729 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, α/β 1/1) (COSY/HMBC/HSQC) δ 5.52 (1H, d, *J* = 5.0 Hz, H_{1b}), 5.50 (1H, d, *J* = 5.0 Hz, H_{1b}), 5.08 (1H, q, *J* = 3.2 Hz, $H_{1a\alpha}$), 4.75 (1H, dd, *J* = 7.7, 2.9 Hz, $H_{1a\beta}$), 4.64–5.18 (2H, m, $H_{3a\alpha}$, $H_{3a\beta}$), 4.61 (1H, dd, *J* = 7.9, 2.4 Hz, H_{3b}), 4.60 (1H, dd, *J* = 7.9, 2.4 Hz, H_{3b}), 4.34 - 4.51 (2H, m, H_{6a}), 4.31 (1H, dd, *J* = 5.0, 2.4 Hz, H_{2b}), 4.29–4.69 (4H, m, $H_{2a\alpha}$, $H_{2a\beta}$, $H_{4a\alpha}$, $H_{4a\beta}$), 4.23 (1H, dd, *J* = 7.8, 2.0 Hz, H_{4b}), 4.16–4.28 (5H, m, H_{2b}, H_{6a}, $H_{5a\alpha}$, H_{4b}), 3.95–4.05 (3H, m, H_{5b}, $2H_{6b}$), 3.77–3.88 (3H, m, H_{5b}, $2H_{6b}$), 3.68 (1H, ddtd, *J* = 9.9, 5.1, 2.5, 1.0 Hz, $H_{5a\beta}$), 2.10 (3H, s, $H_{CH3(a)}$), 2.10 (3H, s, $H_{CH3(a)}$), 1.52 (6H, s, $2H_{CH3(b)}$), 1.43 (3H, s, $H_{CH3(b)}$), 1.42 (3H, s, $H_{CH3(b)}$), 1.32 (9H, s, $3H_{CH3(b)}$), 1.32 (3H, s, $H_{CH3(b)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -194.9 (1F, dquin, *J* = 53.0, 13.8 Hz, $F_{3\beta}$), -199.2 (1F, dt, *J* = 51.1, 14.3 Hz, $F_{4\alpha}$), -199.7 (1F, br dt, *J* = 50.7, 13.4 Hz, $F_{2\beta}$), -200.4–-199.8 (2F, m, $F_{3\alpha}$, $F_{4\beta}$), -202.7 (1F, dt, *J* = 49.9, 13.2 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -194.9 (1F, t, *J* = 13.0 Hz, $F_{3\beta}$), -199.2 (1F, dd, *J* = 12.6, 1.3 Hz, $F_{4\alpha}$), -199.7 (1F, dd, *J* = 13.0, 2.2 Hz, $F_{2\beta}$), -200.0 (1F, t, *J* = 12.8 Hz, $F_{3\alpha}$), -200.2 (1F, dd, *J* = 12.6, 2.2 Hz, $F_{4\beta}$), -202.7 (1F, dd, *J* = 13.2, 1.1 Hz, $F_{2\alpha}$) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.5 ($C_{\underline{C}OCH3(a)}$), 170.5 ($C_{\underline{C}OCH3(a)}$), 109.4 ($C_{C(CH3)2(b)}$), 108.8 ($C_{C(CH3)2(b)}$), 108.7 ($C_{C(CH3)2(b)}$), 99.6 (dd, *J* = 22.7, 10.3 Hz, $C_{1a\beta}$), 96.2 (C_{1b}), 96.2 (C_{1b}), 96.2 (dd, *J* = 19.8, 10.3 Hz, $C_{1a\alpha}$), 92.1 (dt, *J* = 188.5, 20.5 Hz, C_{3a}), 90.3 (dt, *J* = 187.1, 19.8 Hz, C_{3a}), 89.3 (ddd, *J* = 191.5, 19.1, 8.1 Hz, C_{2a}), 87.2 (ddd, *J* = 195.9, 17.6, 8.1 Hz, C_{2a}), 86.7 (ddd, *J* = 187.8, 19.0, 8.1 Hz, C_{4a}), 86.6

(ddd, *J* = 187.8, 18.3, 8.1 Hz, C_{4a}), 71.2 (C_{4b}), 70.9 (C_{4b}), 70.6 (C_{3b}), 70.6 (C_{3b}), 70.4 (C_{2b}), 70.3 (C_{2b}), 70.0 (dd, *J* = 23.5, 7.3 Hz, $C_{5a\beta}$), 68.9 (C_{6b}), 68.4 (C_{6b}), 67.8 (C_{5b}), 66.8 (C_{5b}), 66.2 (dd, *J* = 23.5, 6.6 Hz, $C_{5a\alpha}$), 61.8 (C_{6a}), 61.7 (C_{6a}), 25.9 ($C_{CH3(b)}$), 25.9 ($C_{CH3(b)}$), 24.9 ($C_{CH3(b)}$), 24.3 ($C_{CH3(b)}$), 20.7 ($C_{CH3(a)}$), 20.7 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{20}H_{29}F_3NaO_9$ $[M + Na]^+$ calcd 493.1656 found 493.1664 (err -1.3 ppm).

4.2.4 4,6-Di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α/β-D-galactopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**22**)

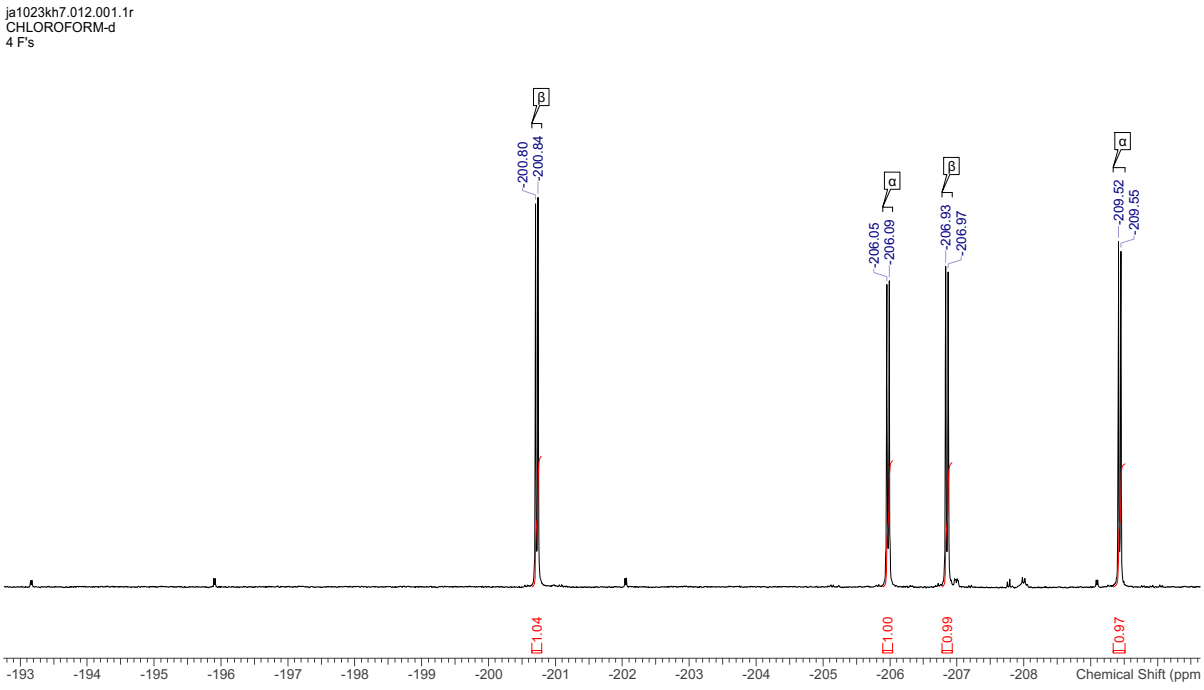
4.2.4.1 Glycosylation (Table 3, entry 4)



According to general procedure C, **10** (104 mg, 0.252 mmol, 1.0 equiv) was reacted at –30 ˚C for 4 h. The resultant crude material (α/β 1:1.04) was purified by flash column chromatography (10 g, hexane/EtOAc 80:20 to 60:40) to collect **22** as a mixture of α- and β-anomers (128 mg, 0.252 mmol, quant.). An analytical sample was purified to isolate both anomer using flash column chromatography (25 g, hexane/EtOAc 80:20 to 60:40).

4.2.4.2 Ratio determination, crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:1.04, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **4** is present and no unreacted trichloroacetimidate **10** is observed in the crude reaction mixture.



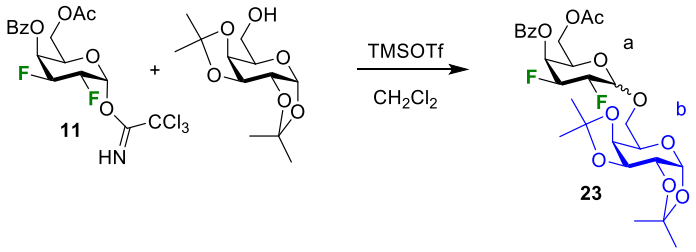
4.2.4.3 Characterisation of the disaccharides (both anomers)

Data for **22α**: Colourless oil; R_f 0.38 (hexane/EtOAc 60:40); IR (neat) 2988 (br, w), 1725 (s), 1373 (w), 1214 (s), 1067 (s), 1005 (w), 826 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 5.64 (1H, dqd, *J* = 4.0, 3.1, 1.2 Hz, H_{4a}), 5.51 (1H, d, *J* = 5.0 Hz, H_{1b}), 5.16 (1H, t, *J* = 4.0 Hz, H_{1a}), 5.03 (1H, dddd, *J* = 49.3, 11.7, 9.7, 4.0 Hz, H_{3a} or H_{2a}), 4.83 (1H, dddd, *J* = 50.5, 11.7, 9.3, 4.0 Hz, H_{3a} or H_{2a}), 4.62 (1H, dd, *J* = 7.9, 2.4 Hz, H_{3b}), 4.36 (1H, br t, *J* = 6.4 Hz, H_{5a}), 4.32 (1H, dd, *J* = 5.0, 2.4 Hz, H_{2b}), 4.24 (1H, dd, *J* = 7.9, 1.9 Hz, H_{4b}), 4.04–4.20 (2H, m, H_{6a}), 4.00 (1H, ddd, *J* = 7.0, 4.9, 1.8 Hz, H_{5b}), 3.84 (1H, dd, *J* = 10.6, 7.2 Hz, H_{6b}), 3.76 (1H, dd, *J* = 10.4, 4.8 Hz, H_{6b}), 2.15 (3H, s, $H_{CH3(a)}$), 2.06 (3H, s, $H_{CH3(a)}$), 1.54 (3H, s, $H_{CH3(b)}$), 1.44 (3H, s, $H_{CH3(b)}$), 1.34 (3H, s, $H_{CH3(b)}$), 1.34 (3H, s, $H_{CH3(b)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -206.0 (1F, dtt, *J* = 49.4, 12.6, 6.1 Hz, F_3), -209.5 (1F, dtd, *J* = 50.3, 12.7, 3.0 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -206.1 (1F, d, *J* = 13.9 Hz, F_3), -209.5 (1F, d, *J* = 13.4 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4 ($C_{\underline{C}OCH3(a)}$), 169.8 ($C_{\underline{C}OCH3(a)}$), 109.4 ($C_{C(CH3)2(b)}$), 108.7 ($C_{C(CH3)2(b)}$), 96.6 (dd, *J* = 20.5, 9.5 Hz, C_{1a}), 96.2 (C_{1b}), 86.5 (dd, *J* = 190.7, 5.1 Hz, C_{3a} or C_{2a}), 86.3 (dd, *J* = 190.7, 5.1 Hz, C_{3a} or C_{2a}), 71.0 (C_{4b}), 70.7 (C_{3b}), 70.5 (C_{2b}), 68.7 (dd, *J* = 16.5, 7.7 Hz, C_{4a}), 67.7 (C_{6b}), 66.8 (C_{5b}), 66.4 (d, *J* = 5.1 Hz, C_{5a}), 61.5 (d, *J* = 2.2 Hz, C_{6a}), 26.0 ($C_{CH3(b)}$), 25.9 ($C_{CH3(b)}$), 24.9 ($C_{CH3gal(b)}$), 24.3 ($C_{CH3(b)}$), 20.7 ($C_{CH3(a)}$), 20.6 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{22}H_{32}F_2NaO_{11}$ $[M + Na]^+$ calcd 533.1805 found 533.1819 (err -2.6 ppm).

Data for **22β**: White powder; R_f 0.30 (hexane/EtOAc 60:40); mp 132–134 (CH_2Cl_2) °C; $[\alpha]_D^{23}$ -46 (c 0.83, $CHCl_3$); IR (neat) 2987 (br, w), 1749 (s), 1374 (w), 1216 (s), 1068 (s), 1008 (w), 733 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 5.56 (1H, dddd, *J* = 5.1, 3.8, 2.5, 0.9 Hz, H_{4a}), 5.52 (1H, d, *J* = 5.0 Hz, H_{1b}), 4.73 (1H, dd, *J* = 7.6, 3.8 Hz, H_{1a}), 4.71 (1H, ddtd, *J* = 47.2, 13.9, 8.8, 3.9 Hz, H_{3a}), 4.60 (1H, dd, *J* = 7.9, 2.4 Hz, H_{3b}), 4.58 (1H, dddd, *J* = 51.0, 13.7, 9.0, 7.7 Hz, H_{2a}), 4.31 (1H, dd, *J* = 5.0, 2.5 Hz, H_{2b}), 4.25 (1H, dd, *J* = 7.9, 1.7 Hz, H_{4b}), 4.14 (2H, d, *J* = 6.6 Hz, H_{6a}), 3.97 - 4.08 (2H, m, H_{6b}, H_{5b}), 3.81 - 3.90 (2H, m, H_{6b} and H_{5a}), 2.14 (3H, s, $H_{CH3(a)}$), 2.06 (3H, s, $H_{CH3(a)}$), 1.54 (3H, s, $H_{CH3(b)}$), 1.44 (3H, s, $H_{CH3(b)}$), 1.33 (6H, br. s, $2H_{CH3(b)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -200.8 (1F, dtd, *J* = 47.4, 13.9, 13.9, 5.0 Hz, F_3), -207.0 (1F, br dt, *J* = 50.7, 14.3 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -200.8 (1F, d, *J* = 13.9 Hz, F_3), -207.0 (1F, d, *J* = 14.3 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.3 ($C_{\underline{C}OCH3(a)}$), 169.7 ($C_{\underline{C}OCH3(a)}$), 109.4 ($C_{C(CH3)2(b)}$), 108.8 ($C_{C(CH3)2(b)}$), 100.0 (dd, *J* = 22.7, 11.0 Hz, C_{1a}), 96.2 (C_{1b}), 89.0 (dd, *J* = 192.9, 19.1 Hz, C_{3a}), 88.8 (dd, *J* = 187.8, 19.8 Hz, C_{2a}), 71.3 (C_{4b}), 70.6 (C_{3b}), 70.4 (C_{2b}), 69.8 (d, *J* = 5.9 Hz, C_{5a}), 68.8 (C_{6b}), 68.0 (C_{5b}), 67.4 (dd, *J* = 16.9, 8.8 Hz, C_{4a}), 61.0 (d, *J*=2.2 Hz, C_{6a}), 25.9 ($C_{CH3(b)}$), 25.9 ($C_{CH3(b)}$), 24.9 ($C_{CH3(b)}$), 24.3 ($C_{CH3(b)}$), 20.6 ($C_{CH3(a)}$), 20.5 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{22}H_{32}F_2NaO_{11}$ $[M + Na]^+$ calcd 533.1805 found 533.1809 (err -0.8 ppm).

4.2.5 6-*O*-Acetyl-*O*-4-benzoyl-2,3-dideoxy-2,3-difluoro-α/β-D-galactopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**23**)

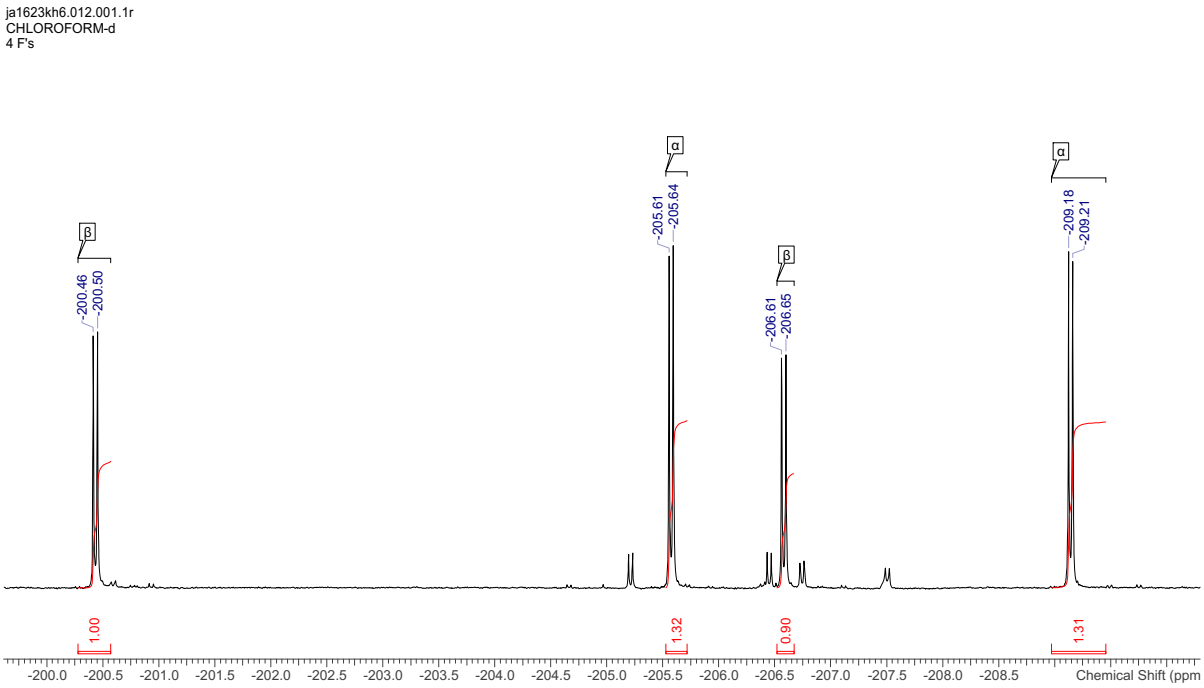
4.2.5.1 Glycosylation (Table 3, entry 5)



According to general procedure C, **11** (102 mg, 0.216 mmol, 1.0 equiv) was reacted at –50 ˚C for 4 h. The resultant crude material (α/β 1.32/1) was purified by flash column chromatography (25 g, hexane/EtOAc 100:0 to 60:40) to collect **23** as a mixture of α- and β-anomers (110 mg, 0.193 mmol, 89% yield). An analytical sample was purified to separate the anomers using flash column chromatography (10 g, hexane/EtOAc 100:0 to 60:40). Anomers assignment was based on the chemical shift and coupling constant values of the anomeric protons.

4.2.5.2 Ratio determination, crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1.32:1, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **5** is present and no unreacted trichloroacetimidate **11** is observed in the crude reaction mixture.



4.2.5.3 Characterisation of the disaccharides (both anomers)

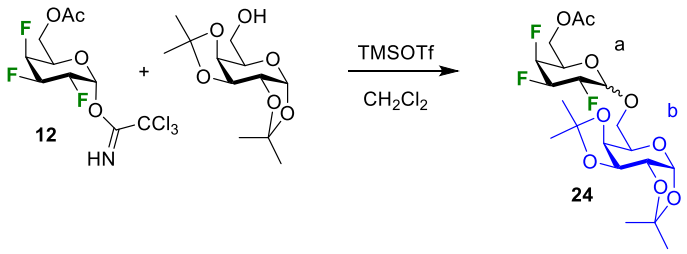
Data for **23α**: Colourless crystals; R_f 0.45 (hexane/EtOAc 60:40); IR (neat) 2982 (br, s), 2360 (w), 2342 (w), 1726 (s), 1372 (w), 1255 (s), 1066 (s), 1004 (s), 730 (s), 711 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 7.99–8.09 (2H, m, H_{Ar}), 7.54–7.64 (1H, m, H_{Ar}), 7.42–7.52 (2H, m, H_{Ar}), 5.90 (1H, dt, J = 5.9, 2.9 Hz, H_{4a}), 5.52 (1H,

d, *J* = 5.0 Hz, H_{1b}), 5.25 (1H, t, *J* = 4.0 Hz, H_{1a}), 5.14 (1H, dddd, *J* = 48.8, 11.6, 9.3, 4.2 Hz, H_{3a}), 4.97 (1H, dddd, *J* = 50.3, 11.6, 9.8, 3.7 Hz, H_{2a}), 4.62 (1H, dd, *J* = 7.9, 2.4 Hz, H_{3b}), 4.46 (1H, br t, *J* = 6.1 Hz, H_{5a}), 4.33 (1H, dd, *J* = 5.0, 2.4 Hz, H_{2b}), 4.26 (1H, dd, *J* = 7.9, 1.9 Hz, H_{4b}), 4.21 (1H, dd, *J* = 11.5, 5.4 Hz, H_{6a}), 4.15 (1H, dd, *J* = 11.6, 6.8 Hz, H_{6a}), 4.02 (1H, ddd, *J* = 6.9, 4.9, 1.8 Hz, H_{5b}), 3.88 (1H, dd, *J* = 10.5, 7.1 Hz, H_{6b}), 3.79 (1H, dd, *J* = 10.8, 4.8 Hz, H_{6b}), 2.00 (3H, s, $H_{CH3(a)}$), 1.55 (3H, s, $H_{CH3(b)}$), 1.44 (3H, s, $H_{CH3(b)}$), 1.34 (3H, s, $H_{CH3(b)}$), 1.34 (3H, s, $H_{CH3(b)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -205.5 (1F, dtt, *J* = 48.5, 12.1, 5.6 Hz, F_3), -209.1 (1F, dtd, *J* = 50.3, 13.0, 3.0 Hz, F_2) ppm; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -205.5 (1F, d, *J* = 13.9 Hz, F_3), -209.1 (1F, d, *J* = 13.9 Hz, F_2) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.4 ($C_{\underline{C}OCH3(a)}$), 165.4 ($C_{\underline{C}OCH3(a)}$), 133.6 (C_{Ar}), 129.8 (C_{Ar}), 129.0 (C_{Ar}), 128.5 (C_{Ar}), 109.4 ($C_{C(CH3)2(b)}$), 108.7 ($C_{C(CH3)2(b)}$), 96.7 (dd, *J* = 20.5, 8.8 Hz, C_{1a}), 96.2 (C_{1b}), 86.5 (dd, *J* = 191.5, 19.1 Hz, C_{3a}), 86.5 (dd, *J* = 191.5, 18.3 Hz, C_{2a}), 70.9 (C_{4b}), 70.6 (C_{3b}), 70.4 (C_{2b}), 69.4 (dd, *J* = 16.5, 7.7 Hz, C_{4a}), 67.8 (C_{6b}), 66.8 (C_{5b}), 66.7 (d, *J* = 4.4 Hz, C_{5a}), 61.9 (d, *J* = 2.2 Hz, C_{6a}), 26.0 ($C_{CH3(b)}$), 25.9 ($C_{CH3(b)}$), 24.9 ($C_{CH3(b)}$), 24.3 ($C_{CH3(b)}$), 20.6 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{27}H_{34}F_2NaO_{11}$ $[M + Na]^+$ calcd 595.1961 found 595.1975 (err -2.2 ppm).

Data for **23β**: colourless oil; R_f 0.36 (hexane/EtOAc 60:40); $[\alpha]_D^{23}$ -45 (c 1.4, $CHCl_3$); IR (neat) 2982 (br, w), 2360 (w), 2342 (w), 1733 (s), 1373 (w), 1255 (s), 1212 (s), 1065 (s), 1004 (s), 908 (s), 730 (s), 711 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.07 (2H, dd, *J* = 8.5, 1.3 Hz, H_{Ar}), 7.58–7.64 (1H, m, H_{Ar}), 7.41–7.50 (2H, m, H_{Ar}), 5.79–5.86 (1H, m, H_{4a}), 5.55 (1H, d, *J* = 4.9 Hz, H_{1b}), 4.80 (1H, dd, *J* = 7.7, 3.2 Hz, H_{1a}), 4.63 (1H, dd, *J* = 7.9, 2.4 Hz, H_{3b}), 4.58–4.96 (2H, m, H_{2a}, H_{3a}), 4.33 (1H, dd, *J* = 5.0, 2.4 Hz, H_{2b}), 4.29 (1H, dd, *J* = 7.9, 1.6 Hz, H_{4b}), 4.24 (1H, ddd, *J* = 11.4, 6.7, 0.9 Hz, H_{6a}), 4.17 (1H, dd, *J* = 11.4, 6.4 Hz, H_{6a}), 4.02–4.11 (2H, m, H_{5b}, H_{6b}), 3.96 (1H, tt, *J* = 6.5, 1.5 Hz, H_{5a}), 3.92 (1H, m, *J* = 4.8 Hz could be extracted, H_{6b}), 2.05 (3H, s, $H_{CH3(a)}$), 1.56 (3H, s, $H_{CH3(b)}$), 1.46 (3H, s, $H_{CH3(b)}$), 1.35 (3H, s, $H_{CH3(b)}$), 1.35 (3H, s, $H_{CH3(b)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -200.3 (1F, dtd, *J* = 47.2, 13.8, 4.3 Hz, F_3), -206.5 (1F, dtd, *J* = 49.0, 13.0, 5.6 Hz, F_2) ppm; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -200.3 (1F, d, *J* = 14.3 Hz, F_3), -206.5 (1F, d, *J* = 14.3 Hz, F_2) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.4 ($C_{\underline{C}OCH3(a)}$), 165.3 ($C_{\underline{C}OCH3(a)}$), 133.7 (C_{Ar}), 130.0 (C_{Ar}), 128.8 (C_{Ar}), 128.5 (C_{Ar}), 109.4 ($C_{C(CH3)2(b)}$), 108.8 ($C_{C(CH3)2(b)}$), 100.2 (dd, *J* = 23.1, 10.6 Hz, C_{1a}), 96.3 (C_{1b}), 89.0 (dd, *J* = 187.8, 19.1 Hz, C_{2a}), 89.2 (dd, *J* = 193.7, 19.1 Hz, C_{3a}), 71.3 (C_{4b}), 70.7 (C_{3b}), 70.4 (C_{2b}), 70.2 (d, *J* = 5.1 Hz, C_{5a}), 68.9 (C_{6b}), 68.1 (dd, *J* = 16.9, 8.1 Hz, C_{4a}), 68.0 (C_{5b}), 61.5 (d, *J* = 2.9 Hz, C_{6a}), 26.0 ($C_{CH3(b)}$), 25.9 ($C_{CH3(b)}$), 25.0 ($C_{CH3(b)}$), 24.4 ($C_{CH3(b)}$), 20.6 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{27}H_{34}F_2NaO_{11}$ $[M + Na]^+$ calcd 595.1961 found 595.1968 (err -1.1 ppm).

4.2.6 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α/β-D-galactopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**24**)

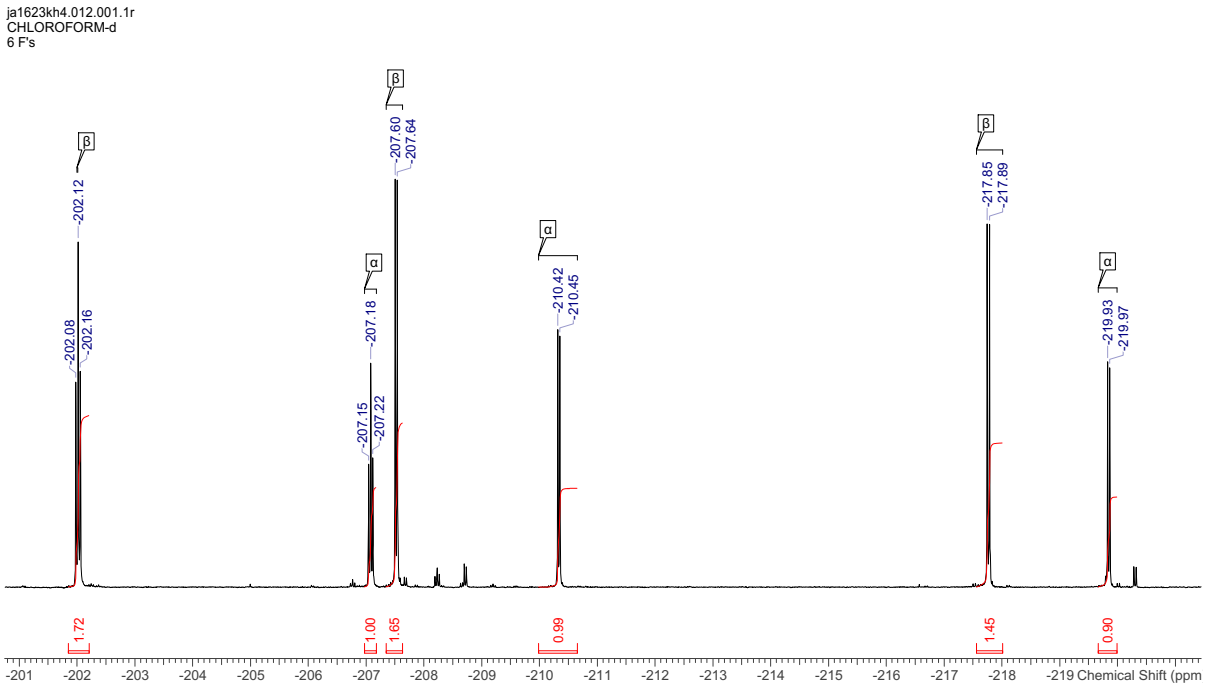
4.2.6.1 Glycosylation (Table 3, entry 3)



According to general procedure C, **12** (110 mg, 0.277 mmol, 1.0 equiv) was reacted at –30 ˚C for 4 h. The resultant crude material (α/β 1:1.72) was purified by flash column chromatography (25 g, hexane/EtOAc 90:10 to 60:40) to collect **24** as a mixture of α- and β-anomers as a colourless oil (75 mg, 0.277 mmol, quant.). An analytical sample was purified to isolate the pure anomers using flash column chromatography (25 g, hexane/EtOAc 80:20 to 60:40).

4.2.6.2 Ratio determination, crude reaction mixture, $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^{1}H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:1.72, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **6** is present and no unreacted trichloroacetimidate **16** is observed in the crude reaction mixture.



4.2.6.3 Characterisation of the disaccharides (both anomers)

Data for **24α**: Colourless crystals; R_f 0.42 (hexane/EtOAc 60:40); IR (neat) 2988 (br, w), 1726 (s), 1373 (w), 1254 (w), 1213 (w), 1069 (s), 1004 (w), 8276 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 5.50 (1H, d, *J* = 5.0 Hz, H_{1b}), 5.17 (1H, t, *J* = 4.0 Hz, H_{1a}), 4.76–5.12 (3H, m, H_{2a}, H_{3a}, H_{4a}), 4.62 (1H, dd, *J* = 7.9, 2.4 Hz, H_{3b}), 4.32 (1H, dd, *J* = 5.0, 2.4 Hz, H_{2b}), 4.20–4.31 (3H, m, $2H_{6a}$ and H_{5a}), 4.23 (1H, dd, *J* = 7.9, 1.9 Hz, H_{4b}), 3.99 (1H, ddd, *J* = 7.0, 4.6, 1.8 Hz, H_{5b}), 3.85 (1H, dd, *J* = 10.4, 7.3 Hz, H_{6b}), 3.76 (1H, dd, *J* = 10.6, 4.5 Hz, H_{6b}), 2.10 (3H, s, $H_{CH3(a)}$), 1.53 (3H, s, $H_{CH3(b)}$), 1.44 (3H, s, $H_{CH3(b)}$), 1.34 (6H, s, $2H_{CH3(b)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -207.2 (1F, dddt, *J* = 48.1, 16.0, 13.9, 8.2 Hz, F_3), -210.4 (1F, dtd, *J* = 49.4, 13.4, 3.5 Hz, F_2), -219.9 (1F, dddd, *J* = 50.3, 29.5, 26.9, 14.7 Hz, F_4) ppm; $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -207.2 (1F, t, *J* = 13.9 Hz, F_3), -210.4 (1F, d, *J* = 13.4 Hz, F_2), -219.9 (1F, d, *J* = 14.3 Hz, F_4) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4 ($C_{COCH3(a)}$), 109.4 ($C_{C(CH3)2(b)}$), 108.7 ($C_{C(CH3)2(b)}$), 96.4 (dd, *J* = 20.5, 9.5 Hz, C_{1a}), 96.2 (C_{1b}), 84.4–89.2 (C_{2a}, C_{3a}, C_{4a}), 71.0 (C_{4b}), 70.7 (C_{3b}), 70.4 (C_{2b}), 67.8 (C_{6b}), 66.9 (C_{5b}), 66.8 (dd, *J* = 17.6, 4.4 Hz, C_{5a}), 61.6 (dd, *J* = 5.9, 2.2 Hz, C_{6a}), 26.0 ($C_{CH3(b)}$), 25.9 ($C_{CH3(b)}$), 24.9

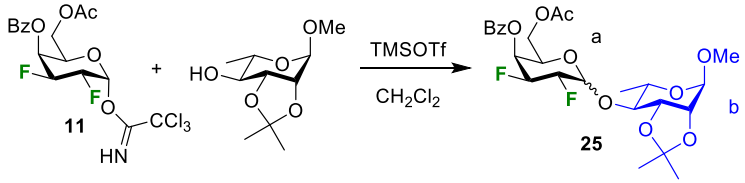
($C_{CH3(b)}$), 24.3 ($C_{CH3(b)}$), 20.7 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{20}H_{29}F_3NaO_9$ $[M + Na]^+$ calcd 493.1656 found 493.1664 (err -1.7 ppm).

Data for **24β**: White powder; R_f 0.25 (hexane/EtOAc 60:40); mp 136–138 ˚C (CH_2Cl_2); $[\alpha]_D^{23}$ -61 (c 0.55, $CHCl_3$); IR (neat) 2987 (br, w), 1743 (s), 1373 (w), 1212 (w), 1066 (s), 1004 (w), 899 (w), 731 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 5.52 (1H, d, *J* = 5.0 Hz, H_{1b}), 4.94 (1H, ddt, *J* = 50.6, 6.7, 2.6 Hz, H_{4a}), 4.61 (1H, dd, *J* = 7.9, 2.4 Hz, H_{3b}), 4.50–4.77 (3H, m, H_{1a}, H_{2a}, H_{3a}), 4.38 (1H, dd, *J* = 11.4, 6.5 Hz, H_{6a}), 4.31 (1H, dd, *J* = 4.9, 2.4 Hz, H_{2b}), 4.26 (1H, dd, *J* = 7.8, 1.7 Hz, H_{4b}), 4.24 (1H, ddd, *J* = 11.4, 6.8, 0.4 Hz, H_{6a}), 3.99–4.08 (2H, m, H_{5b} and H_{6b}), 3.85 (1H, dd, *J* = 10.4, 5.9 Hz, H_{6b}), 3.75 (1H, dtd, *J* = 25.6, 6.6, 1.8 Hz, H_{5a}), 2.10 (3H, s, $H_{CH3(a)}$), 1.54 (3H, s, $H_{CH3(b)}$), 1.45 (3H, s, $H_{CH3(b)}$), 1.34 (3H, s, $H_{CH3(b)}$), 1.34 (3H, s, $H_{CH3(b)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -202.0 (1F, dqd, *J* = 45.5, 13.9, 5.6 Hz, F_3), -207.5 (1F, dtdd, *J* = 52.0, 13.4, 4.3, 2.6 Hz, F_2), -217.7 (1F, dtd, *J* = 49.9, 26.5, 15.2 Hz, F_4) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -202.0 (1F, t, *J* = 14.7 Hz, F_3), -207.5 (1F, d, *J* = 13.9 Hz, F_2), -217.7 (1F, d, *J* = 15.2 Hz, F_4) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4 ($C_{COCH3(a)}$), 109.4 ($C_{C(CH3)2(b)}$), 108.8 ($C_{C(CH3)2(b)}$), 99.8 (dd, *J* = 23.1, 10.6 Hz, C_{1a}), 96.2 (C_{1b}), 89.2 (dt, *J* = 194.4, 19.1 Hz, C_{3a}), 88.4 (dd, *J* = 187.8, 19.1 Hz, C_{2a}), 86.3 (ddd, *J* = 187.8, 17.6, 8.8 Hz, C_{4a}), 71.2 (C_{4b}), 70.6 (C_{3b}), 70.4 (C_{2b}), 69.9 (dd, *J* = 18.3, 5.9 Hz, C_{5a}), 68.7 (C_{6b}), 68.0 (C_{5b}), 61.1 (dd, *J* = 5.5, 2.6 Hz, C_{6a}), 25.9 ($C_{CH3(b)}$), 25.9 ($C_{CH3(b)}$), 24.9 ($C_{CH3(b)}$), 24.3 ($C_{CH3(b)}$), 20.7 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{20}H_{29}F_3NaO_9$ $[M + Na]^+$ calcd 493.1656 found 493.1661 (err -1.1 ppm).

4.3 Glycosylation with methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside

4.3.1 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α/β-D-galactopyranosyl-(1,4)-methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**25**)

4.3.1.1 Glycosylation to **25** (Figure 2)

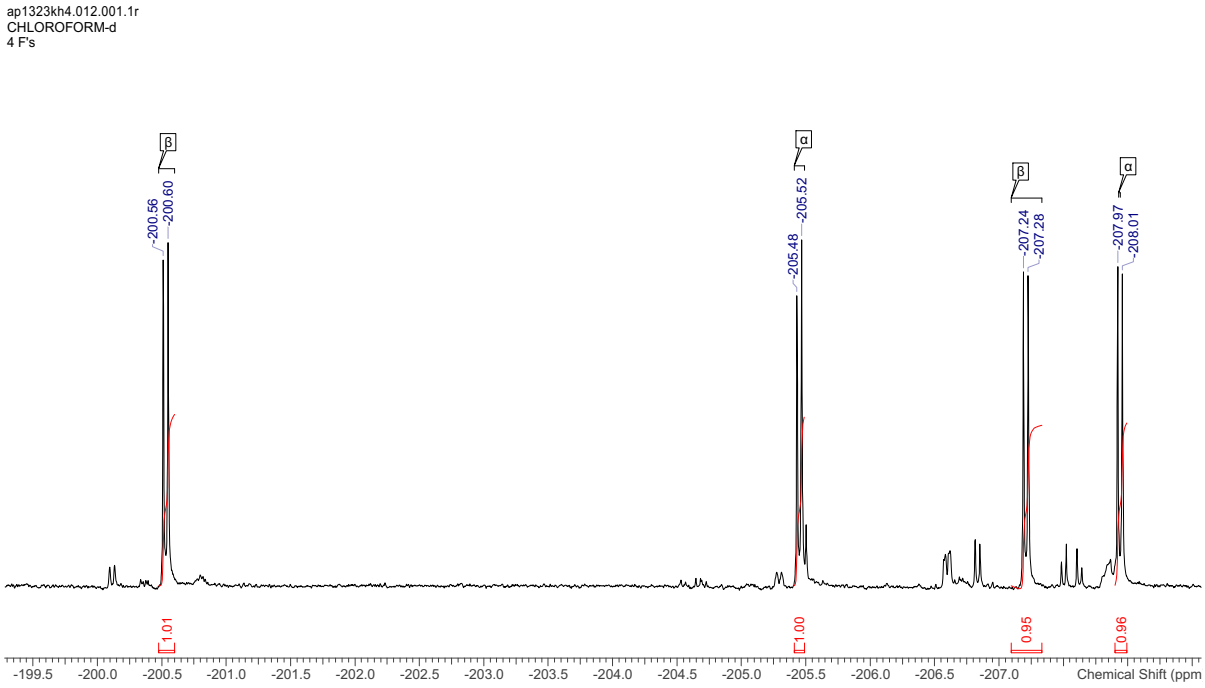


According to general procedure C, **11** (107 mg, 0.226 mmol, 1.0 equiv) was reacted at –30 ˚C for 4 h. The resultant crude material (α/β 1/1) was purified by flash column chromatography (25 g, hexane/EtOAc 100:0 to 60:40) to collect **25** as a mixture of α- and β-anomers (107 mg, 0.202 mmol, 89% yield). An analytical sample was purified to separate the anomers using flash column chromatography (25 g, hexane/EtOAc 100:0 to 60:40).

Anomers assignment was based on the chemical shift and coupling constant values of the anomeric protons.

4.3.1.2 Ratio determination, crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:1, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **5** is present and no unreacted trichloroacetimidate **11** is observed in the crude reaction mixture.



4.3.1.3 Characterisation of the disaccharides (both anomers)

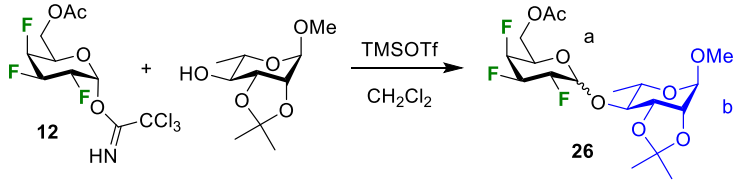
Data for **25α**: White powder; R_f 0.49 (hexane/EtOAc 60:40); IR (neat) 2938 (br, w), 2359 (w), 2342 (w), 1727 (s), 1372 (w), 1267 (s), 1256 (s), 1222 (s), 1092 (s), 1070 (s), 1044 (s), 1023 (s), 909 (w), 856 (w), 829 (w), 730 (s), 711 (s) cm^{-1}; ^1H NMR (α enriched) (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.05 (2H, dd, *J* = 8.4, 1.3 Hz, H_{Ar}), 7.60 (1H, tt, *J* = 7.4, 1.3 Hz, H_{Ar}), 7.46 (2H, br t, *J* = 7.9 Hz, H_{Ar}), 5.94 (1H, dt, *J* = 5.9, 2.9 Hz, H_{4a}), 5.34 (1H, t, *J* = 3.9 Hz, H_{1a}), 5.11 (1H, dddd, *J* = 48.4, 11.6, 9.7, 3.8 Hz, H_{3a}), 4.98 (1H, dddd, *J* = 51.8, 11.7, 9.5, 4.0 Hz, H_{2a}), 4.87 (1H, s, H_{1b}), 4.54 (1H, br t, *J* = 6.6 Hz, H_{5a}), 4.27 (1H, ddd, *J* = 11.1, 5.1, 1.2 Hz, H_{6a}), 4.10–4.16 (3H, m, H_{6a}, H_{2b}, H_{3b}), 3.73 (1H, dq, *J* = 10.1, 6.3 Hz, H_{5b}), 3.34–3.45 (4H, m, H_{4b}, $H_{C\underline{H}3O}$), 1.96 (3H, s, H_{CH3a}), 1.55 (3H, s, H_{CH3b}), 1.35 (3H, s, H_{CH3b}), 1.34 (3H, d, *J* = 6.5 Hz, H_{6b}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -205.4 (1F, br d, *J* = 48.1 Hz, F_3), -207.9 (1F, dtd, *J* = 49.4, 13.0, 2.2 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -205.4 (1F, br d, *J* = 13.4 Hz, F_3), -207.9 (1F, br d, *J* = 13.9 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.3 ($C_{\underline{C}OCH3a}$), 165.3 ($C_{\underline{C}OCH2Ph}$), 133.5 (C_{Ar}), 129.8 (C_{Ar}), 129.1 (C_{Ar}), 128.5 (C_{Ar}), 109.5 ($C_{(CH3)2b}$), 97.8 (C_{1b}), 97.6 (dd, *J* = 20.5, 9.5 Hz, C_{1a}), 86.6 (dd, *J* = 191.5, 19.1 Hz, C_{2a}), 86.5 (dd, *J* = 192.2, 19.1 Hz, C_{3a}), 82.1 (C_{4b}), 76.7 (C_{3b}), 76.0 (C_{2b}), 69.0 (dd, *J* = 16.5, 7.7 Hz, C_{4a}), 66.4 (d, *J* = 5.1 Hz, C_{5a}), 64.4 (C_{5b}), 60.9 (C_{6a}), 54.8 (C_{MeOb}), 28.0 ($C_{(\underline{C}H3)2b}$), 26.2 ($C_{(\underline{C}H3)2b}$), 20.6 (C_{CH3a}), 17.1 (C_{6b}) ppm; HRMS (ESI+) for $C_{25}H_{32}F_2NaO_{10}$ $[M + Na]^+$ calcd 553.1856 found 553.1863 (err -1.4 ppm).

Data for **25β**: colourless oil; R_f 0.47 (hexane/EtOAc 60:40); $[\alpha]_D^{23}$ -34.0 (c 0.41, $CHCl_3$); IR (neat) 2937 (br, w), 1729 (s), 1371 (w), 1267 (s), 1223 (s), 1088 (s), 1067 (s), 1020 (s), 860 (w), 730 (w), 712 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.05 (2H, dd, *J* = 8.4, 1.3 Hz, H_{Ar}), 7.62 (1H, tt, *J* = 7.6, 1.3 Hz, H_{Ar}), 7.48 (2H, t, *J* = 7.8 Hz, H_{Ar}), 5.82 (1H, dt, *J* = 5.9, 2.9 Hz, H_{4a}), 5.14 (1H, dd, *J* = 7.7, 3.2 Hz, H_{1a}), 4.88 (1H, s, H_{1b}), 4.86 (1H, dddd, *J* = 47.7, 14.1, 8.8, 4.0 Hz, H_{3a}), 4.64 (1H, dddd, *J* = 52.0, 13.6, 8.9, 7.9 Hz, H_{2a}), 4.29 (1H, t, *J* = 6.2 Hz, H_{3b}), 4.19 (2H, d, *J* = 6.1 Hz, $2H_{6a}$), 4.13 (1H, dd, *J* = 5.6, 0.6 Hz, H_{2b}), 3.93 (1H, t, *J* = 6.3 Hz, H_{5a}), 3.67–3.77 (2H, m, H_{5b}, H_{4b}), 3.39 (3H, s, $H_{C\underline{H}3O}$), 2.03 (3H, s, H_{CH3a}), 1.55 (3H, s, H_{CH3b}), 1.37 (3H, s, H_{CH3b}), 1.35 (3H, d, *J* = 5.7 Hz, H_{6b}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -200.6 (1F, dtd, *J* = 47.8, 13.5, 4.6 Hz, F_3), -207.2 (1F, dt, *J* = 52.0, 14.1 Hz, F_2) ppm;

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -200.6 (1F, d, *J* = 13.9 Hz, F_3), -207.2 (1F, d, *J* = 13.9 Hz, F_2) ppm; $^{13}C\ \{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4 (C_{COCH3}), 165.3 ($C_{COCH2Ph}$), 133.7 (C_{Ar}), 129.9 (C_{Ar}), 128.8 (C_{Ar}), 128.6 (C_{Ar}), 109.4 ($C_{(CH3)2b}$), 97.8 (C_{1b}), 98.0 (dd, *J* = 22.7, 11.0 Hz, C_{1a}), 89.2 (dd, *J* = 194.4, 19.1 Hz, C_{2a}), 89.4 (dd, *J* = 187.8, 19.1 Hz, C_{3a}), 78.7 (C_{4b}), 77.9 (C_{3b}), 76.0 (C_{2b}), 70.3 (d, *J* = 5.1 Hz, C_{5a}), 68.4 (dd, *J* = 16.5, 8.4 Hz, C_{4a}), 63.7 (C_{5b}), 61.8 (d, *J* = 2.9 Hz, C_{6a}), 54.8 (C_{MeOb}), 27.9 ($C_{(CH3)2b}$), 26.3 ($C_{(CH3)2b}$), 20.6 (C_{CH3a}), 17.6 (C_{6b}) ppm; HRMS (ESI+) for $C_{25}H_{32}F_2NaO_{10}$ [M + Na]$^+$ calcd 553.1856 found 553.1862 (err -1.1 ppm).

4.3.2 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α/β-D-galactopyranosyl-(1,4)-methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**26**)

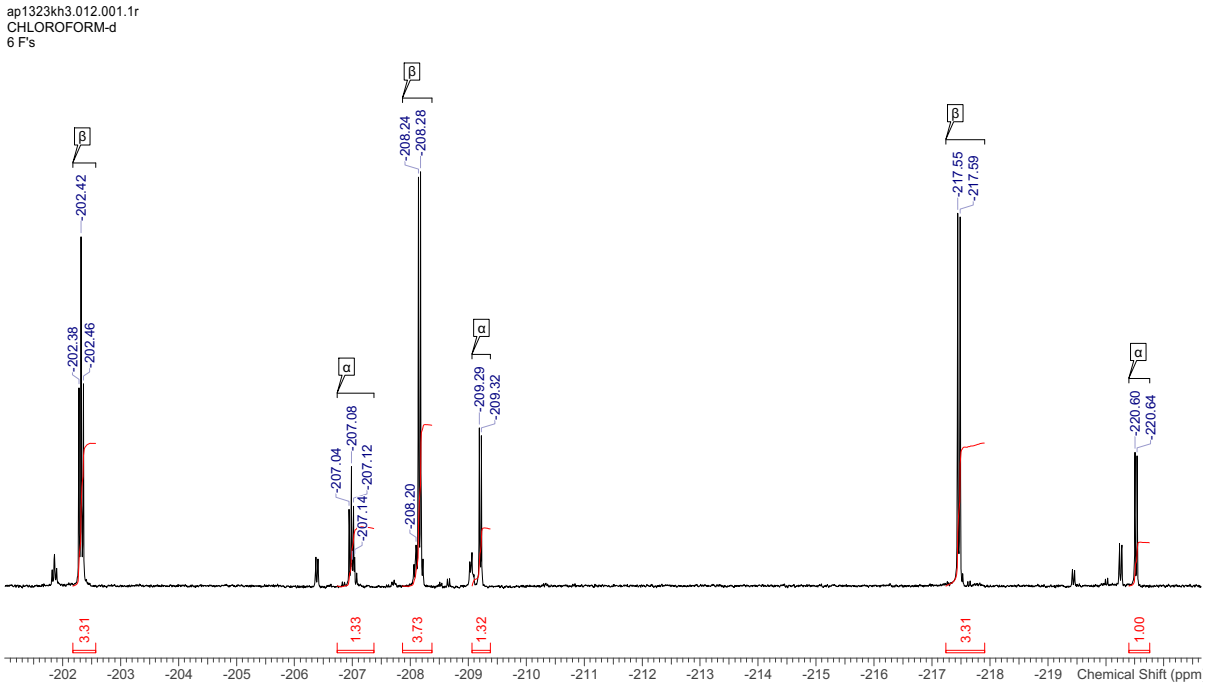
4.3.2.1 Glycosylation to **26** (Figure 2)



According to general procedure C, **12** (105 mg, 0.282 mmol, 1.0 equiv) was reacted at –30 ˚C for 4 h. The resultant crude material (α/β 1:3.31) was purified by flash column chromatography (25 g, hexane/EtOAc 100:0 to 60:40) to collect **26** as a mixture of α- and β-anomers as a colourless oil (120 mg, 0.282 mmol, quant.). An analytical sample was purified to separate the anomers using flash column chromatography (25 g, hexane/EtOAc 100:0 to 60:40).

4.3.2.2 Ratio determination, crude reaction mixture, $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^{1}H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:3.31, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **6** is present and no unreacted trichloroacetimidate **16** is observed in the crude reaction mixture.



4.3.2.3 Characterisation of the disaccharides (both anomers)

Data for **26α**: Colourless crystals; R_f 0.49 (hexane/EtOAc 60:40); $[\alpha]_D^{23}$ +75.0 (c 0.26, $CHCl_3$); IR (neat) 2939 (br, w), 1749 (w), 1373 (w), 1242 (w), 1223 (w), 1139 (w), 1076 (s), 1044 (s), 1024 (s), 977 (w), 859 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 5.24 (1H, t, *J* = 3.9 Hz, H_{1a}), 4.86 (1H, s, H_{1b}), 4.78–5.15 (3H, m, H_{2a}, H_{3a}, H_{4a}), 4.26–4.49 (2H, m, H_{5a}, H_{6a}), 4.04–4.15 (3H, m, H_{2b}, H_{3b}, H_{6a}), 3.70 (1H, dq, *J* = 10.1, 6.3 Hz, H_{5b}), 3.33–3.42 (4H, m, H_{4b}, $H_{C\underline{H}3O}$), 2.10 (3H, s, H_{CH3a}), 1.56 (3H, s, H_{CH3b}), 1.35 (3H, s, H_{CH3b}), 1.32 (3H, d, *J* = 6.4 Hz, H_{6b}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -207.1 (1F, ddd, *J* = 53.3, 12.1, 5.6 Hz, F_3), -209.3 (1F, dtd, *J* = 49.0, 13.0, 3.5 Hz, F_2), -220.6 (1F, dtd, *J* = 49.4, 27.7, 14.7 Hz, F_4) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -207.1 (1F, t, *J* = 14.1 Hz, F_3), -209.3 (1F, d, *J* = 13.4 Hz, F_2), -220.6 (1F, d, *J* = 14.7 Hz, F_4) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.1 ($C_{\underline{C}OCH3a}$), 109.5 ($C_{(CH3)2b}$), 97.8 (C_{1b}), 97.3 (dd, *J* = 19.8, 9.5 Hz, C_{1a}), 87.3 (ddd, *J* = 186.3, 16.9, 8.8 Hz, C_{4a}), 86.4 (dt, *J* = 192.2, 19.1 Hz, C_{3a}), 86.0 (ddd, *J* = 191.5, 18.3, 2.2 Hz, C_{2a}), 81.6 (C_{4b}), 76.7 (C_{3b}), 76.0 (C_{2b}), 66.5 (dd, *J* = 18.3, 5.1 Hz, C_{5a}), 64.5 (C_{5b}), 60.2 (br d, *J* = 5.9 Hz, C_{6a}), 54.8 (C_{MeOb}), 28.0 ($C_{(\underline{C}H3)2b}$), 26.2 ($C(_{\underline{C}H3)2b}$), 20.7 (C_{CH3a}), 17.1 (C_{6b}) ppm; HRMS (ESI+) for $C_{18}H_7F_2NaO_8$ $[M + Na]^+$ calcd 451.1550 found 451.1559 (err -1.9 ppm).

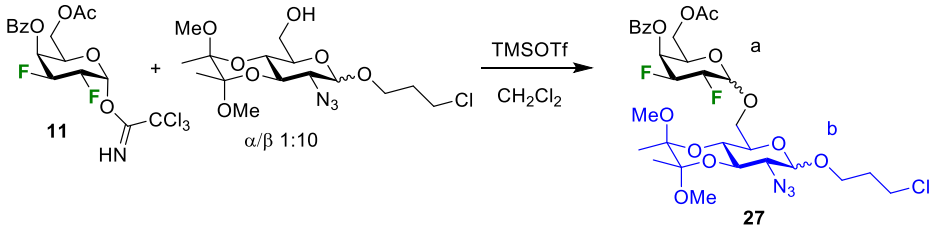
Data for **26β**: Colourless oil; R_f 0.41 (hexane/EtOAc 60:40); $[\alpha]_D^{23}$ -49.3 (c 0.41, $CHCl_3$); IR (neat) 2987 (br, w), 2938 (br, w), 1742 (w), 1372 (w), 1222 (w), 1086 (s), 1069 (s), 1019 (s), 977 (w), 860 (w), 733 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.07 (1H, dd, *J* = 7.7, 3.3 Hz, H_{1a}), 4.93 (1H, ddt, *J* = 50.6, 6.2, 2.8 Hz, H_{4a}), 4.86 (1H, s, H_{1b}), 4.46–4.80 (2H, m, H_{2a}, H_{3a}), 4.34 (1H, br dd, *J* = 11.4, 6.7 Hz, H_{6a}), 4.26 (1H, dd, *J* = 11.6, 6.4 Hz, H_{6a}), 4.21–4.30 (1H, m, H_{3b}), 4.10 (1H, dd, *J* = 5.6, 0.6 Hz, H_{2b}), 3.62–3.78 (3H, m, H_{5b}, H_{4b}, H_{5a}), 3.37 (3H, s, $H_{C\underline{H}3O}$), 2.08 (3H, s H_{CH3a}), 1.52 (3H, s, H_{CH3b}), 1.35 (3H, s, H_{CH3b}), 1.29 (3H, d, *J* = 5.7 Hz, H_{6b}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -202.4 (1F, dqd, *J* = 46.0, 14.7, 6.1 Hz, F_3), -208.3 (1F, br dt, *J* = 51.6, 13.9 Hz, F_2), -217.6 (1F, dtd, *J* = 50.9, 26.0, 15.0 Hz, F_4) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -202.4 (1F, t, *J* = 14.5 Hz, F_3), -208.3 (1F, d, *J* = 13.9 Hz, F_2), -217.6 (1F, d, *J* = 14.7 Hz, F_4) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.4 ($C_{\underline{C}OCH3a}$), 109.3 ($C_{(CH3)2b}$), 97.8 (C_{1b}), 97.7 (dd, *J* = 22.7, 11.0 Hz, C_{1a}), 89.2 (dt, *J* = 194.4, 18.3 Hz), 88.7 (dd, *J* = 187.8, 19.1 Hz), 86.5 (ddd, *J* = 187.1, 16.5, 9.2 Hz),

78.5 (C_{4b}), 78.0 (C_{3b}), 76.0 (C_{2b}), 70.0 (dd, *J* = 18.3, 5.9 Hz, C_{5a}), 63.6 (C_{5b}), 61.4 (dd, *J* = 5.9, 2.9 Hz, C_{6a}), 54.8 (C_{MeOb}), 27.9 ($C_{(\underline{C}H3)2b}$), 26.3 ($C_{(\underline{C}H3)2b}$), 20.6 (C_{CH3a}), 17.5 (C_{6b}) ppm, HRMS (ESI+) for $C_{18}H_{27}F_3NaO_8$ $[M + Na]^+$ calcd 451.1550 found 451.1558 (err -1.8 ppm).

4.4 Glycosylation with 3-chloropropyl 2-deoxy-2-azido-3,4-*O*-[(2'S,3'S)-2',3'-dimethoxybutane-2',3'-diyl]-D-glucopyranoside

4.4.1 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α/β-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-3,4-*O*-[(2'S,3'S)-2',3'-dimethoxybutane-2',3'-diyl]-D-glucopyranoside (**27**)

4.4.1.1 Glycosylation to **27** (Figure 2)



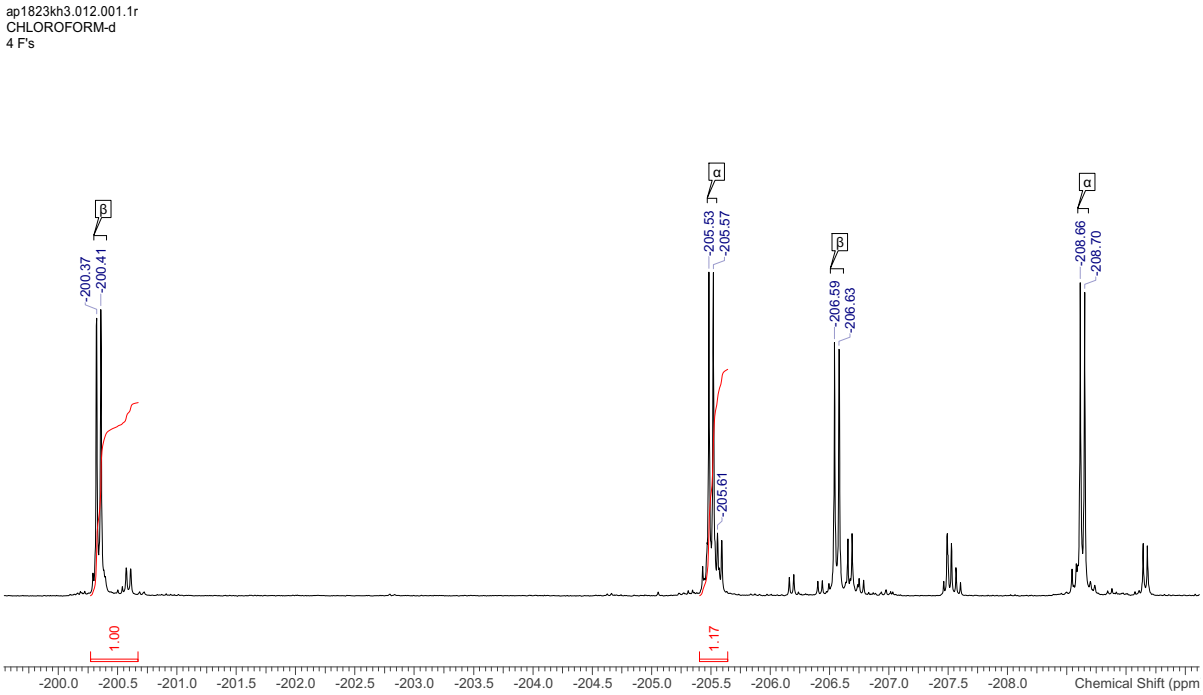
According to general procedure C, **11** (102 mg, 0.216 mmol, 1.0 equiv) was reacted with the acceptor[2] (which consisted of an 1:10 α/β-mixture of anomers) at –30 ˚C for 3.5 h. The resultant crude material (α/β 1.2:1) was purified by flash column chromatography (25 g, hexane/EtOAc 100:0 to 60:40) to collect **27α** (58.4 mg, 0.0826 mmol, 38% yield) and **27β** (13.4 mg, 0.0189 mmol, 9% yield).

Anomers assignment was based on the chemical shift and coupling constant values of the anomeric protons.

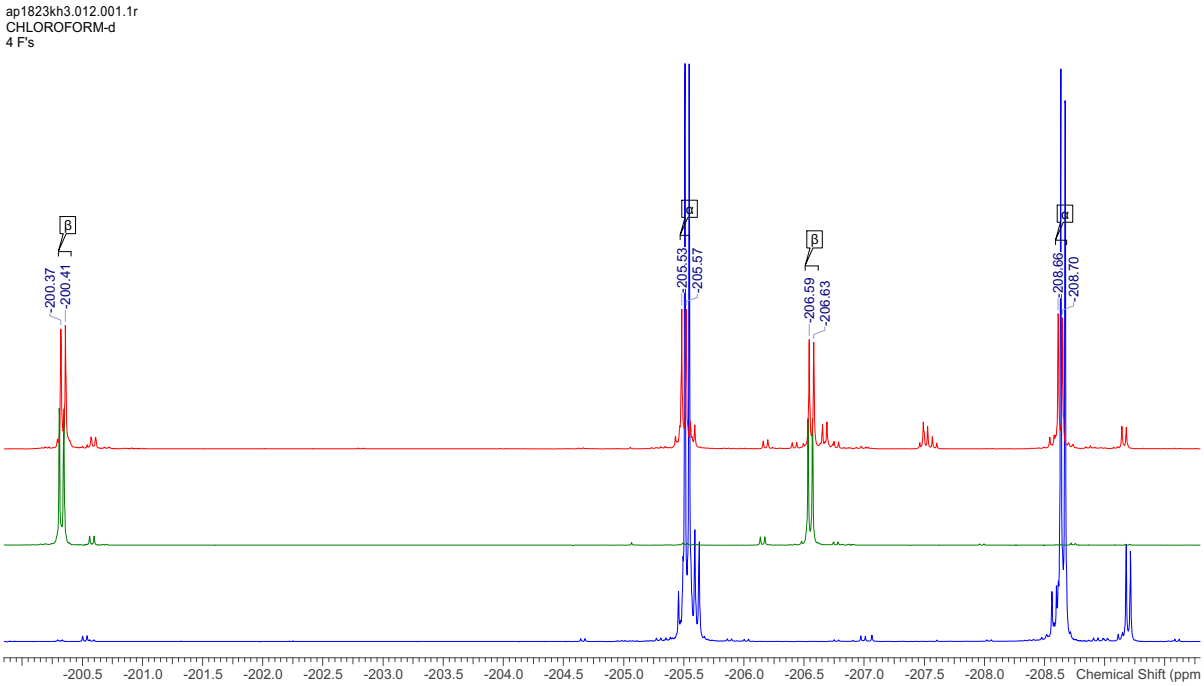
4.4.1.2 Ratio determination, crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1.2:1, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **5** is present and no unreacted trichloroacetimidate **11** is observed. This crude reaction mixture shows the α and the β anomers, they both contain α/β 1:10 of chloropropyl chain and a mixture of BDA isomerisation products. The chloropropyl anomers could not be separated, but the disaccharide anomers were separable, each obtained as a mixture of BDA isomers, and chloropropyl anomers. Removal of the BDA group then led to just a mixture of the chloropropyl anomers (see below).

$^{19}F\{^1H\}$ NMR of the crude reaction mixture with the integration:



Overlay of the $^{19}F\{^{1}H\}$ NMRs of the crude reaction mixture (in red) with that of the isolated mixtures of alfa-anomer (in blue) and the beta anomer (in green) indicated suitable integration ranges.



4.4.1.3 Characterisation of the disaccharides (both anomers)

Data for **27α**, ^{1}H and ^{19}F NMR could be assigned: ^{1}H NMR (400 MHz, $CDCl_3$, major anomer) δ 8.04 (2H, br dd, *J* = 8.4, 1.3 Hz, H_{Ar}), 7.61 (1H, tt, *J* = 7.5, 1.3 Hz, H_{Ar}), 7.47 (2H, br t, *J* = 8.1 Hz, H_{Ar}), 5.88 (1H, dt, *J* = 5.9, 2.9 Hz, H_{4a}), 5.38 (1H, t, *J* = 3.9 Hz, H_{1a}), 5.28 (1H, t, *J* = 3.9 Hz, $H_{1\alpha O(CH2)3Cl}$), 4.84–5.18 (2H, m, H_{2a}, H_{3a}), 4.29–4.36 (1 H, m, H_{6a}), 4.31 (1H, d, *J* = 7.7 Hz, H_{1b}), 4.08–4.25 (2H, m, H_{5a}, H_{6a}), 4.03 (1H, ddd, *J* = 9.8, 6.1, 5.4 Hz, $H_{OCHHCH2}$), 3.93 (1H, dd, *J* = 11.6, 1.8 Hz, H_{6b}), 3.84 (1H, dd, *J* = 12.0, 5.5 Hz, H_{6b}), 3.53–3.79 (5H, m, $H_{OCHHCH2}$, H_{4b}, $H_{CH2CH2Cl}$, H_{3b}, H_{5b}), 3.44

(1H, dd, *J* = 10.3, 7.8 Hz, H_{2b}), 3.31 (3H, s, H_{OMe}), 3.27 (3H, s, H_{Ome}), 2.10 (2H, td, *J* = 5.8, 2.5 Hz, $H_{OCH2C\underline{H}2}$), 2.01 (3H, s, $H_{CH3(a)}$), 1.35 (3H, s, $H_{CH3(b)}$), 1.31 (3H, s, $H_{CH3(b)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$, major anomer) δ -205.6 (1F, dtt, *J* = 48.6, 12.6, 5.6 Hz, F_3), -208.7 (1F, dtd, *J* = 50.3, 13.0, 2.2 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, major anomer) δ -205.6 (1F, d, *J* = 13.9 Hz, F_3), -208.7 (1F, d, *J* = 13.4 Hz, F_2) ppm.

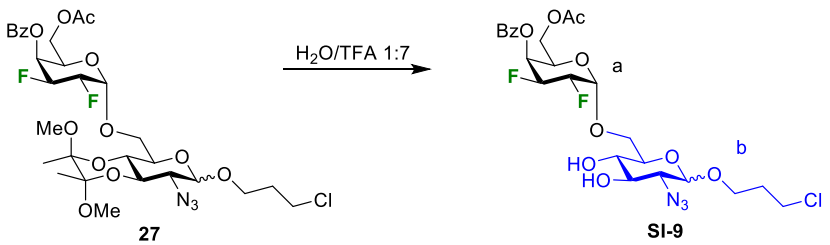
Data for **27β**, ^1H, ^{19}F and ^{13}C NMR could be assigned: ^1H NMR (500 MHz, $CDCl_3$, major anomer) (COSY/HMBC/HSQC) δ 8.07 (2H, dd, *J* = 8.4, 1.5 Hz, H_{Ar}), 7.62 (1H, tt, *J* = 7.4, 1.3 Hz, H_{Ar}), 7.49 (2H, br t, *J* = 8.1 Hz, H_{Ar}), 5.84 (1H, dt, *J* = 5.9, 2.9 Hz, H_{4a}), 4.74 (1H, dd, *J* = 7.6, 2.3 Hz, H_{1a}), 4.62 – 4.90 (2H, m, H_{3a}, H_{2a}), 4.34 (1H, d, *J* = 7.9 Hz, H_{1b}), 4.25 (1H, ddd, *J* = 11.4, 6.4, 0.7 Hz, H_{6a}), 4.21 (1H, dd, *J* = 11.6, 1.7 Hz, H_{6b}), 4.17 (1H, dd, *J* = 11.7, 6.4 Hz, H_{6a}), 4.08 (1 H, ddt, *J* = 10.1, 6.3, 5.3 Hz, $H_{OC\underline{H}HCH2}$), 3.95 (1H, tt, *J* = 6.5, 1.4 Hz, H_{5a}), 3.80 (1H, dd, *J* = 11.7, 6.9 Hz, H_{6b}), 3.75 (1H, dt, *J* = 6.4, 5.2 Hz, $H_{OC\underline{H}HCH2}$), 3.71 (2H, t, *J* = 6.3 Hz, $H_{OC\underline{H}HCH2}$), 3.68–3.73 (1H, m, H_{5b}), 3.59–3.65 (2H, m, H_{3b}, H_{4b}), 3.45 (1H, dd, *J* = 10.4, 7.9 Hz, H_{2b}), 3.32 (3H, s, H_{Ome}), 3.25 (3H, s, H_{Ome}), 2.07 – 2.13 (2H, m, $H_{OCH2C\underline{H}2}$), 2.05 (3H, s, $H_{CH3(a)}$), 1.35 (3H, s, $H_{CH3(b)}$), 1.30 (3H, s, $H_{CH3(b)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$, major anomer) δ -200.4 (1F, dtd, *J* = 48.1, 13.4, 4.8 Hz, F_3), -206.6 (1F, dt, *J* = 54.2, 13.9 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, major anomer) δ -200.4 (1F, d, *J* = 14.3 Hz, F_3), -206.6 (1F, d, *J* = 14.3 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, major anomer) δ 170.4 ($C_{COCH3(a)}$), 165.3 ($C_{COPh(a)}$), 133.7 (C_{Ar}), 130.0 (C_{Ar}), 128.8 (C_{Ar}), 128.6 (C_{Ar}), 102.6 (C_{1b}), 100.8 (dd, *J* = 22.9, 10.7 Hz, C_{1a}), 100.1 ($C_{CH3(b)}$), 99.8 ($C_{CH3(b)}$), 89.2 (dd, *J* = 194.8, 19.8 Hz, C_{3a}), 89.2 (dd, *J* = 187.2, 19.8 Hz, C_{2a}), 73.9 (C_{5b}), 70.7 (C_{3b}), 70.2 (d, *J* = 6.0 Hz, C_{5a}), 68.2 (C_{6b}), 68.0 (dd, *J* = 16.7, 8.6 Hz, C_{4a}), 66.6 (C_{4b}), 66.5 ($C_{O\underline{C}H2CH2}$), 62.7 (C_{2b}), 61.4 (d, *J* = 2.4 Hz, C_{6a}), 48.08 ($C_{CH3(b)}$), 48.06 ($C_{CH3(b)}$), 41.7 ($C_{CH2\underline{C}H2Cl}$), 32.5 ($C_{OCH2\underline{C}H2}$), 20.6 ($C_{CH3(a)}$), 17.6 ($C_{CH3(b)}$), 17.5 ($C_{CH3(b)}$) ppm.

4.4.2 BDA protecting group removal.

The BDA protecting group in **27** was removed to show that it indeed was present as a mixture of BDA-anomers: the $^{19}F\{^1H\}$ spectrum of the crude reaction mixtures indeed showed the ~9:1 ratio of the chloropropyl anomers.

General procedure D:[2] A suspension of the BDA protected starting material in H_2O/TFA (1:7, 0.3 M) at 0 ˚C was warmed up to rt and stirred for 45 min. The solvents were removed under reduced pressure, and the crude product was purified by flash column chromatography.

4.4.2.1 BDA removal of the alfa anomer: 6-*O*-acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-D-glucopyranoside (**SI-9**)

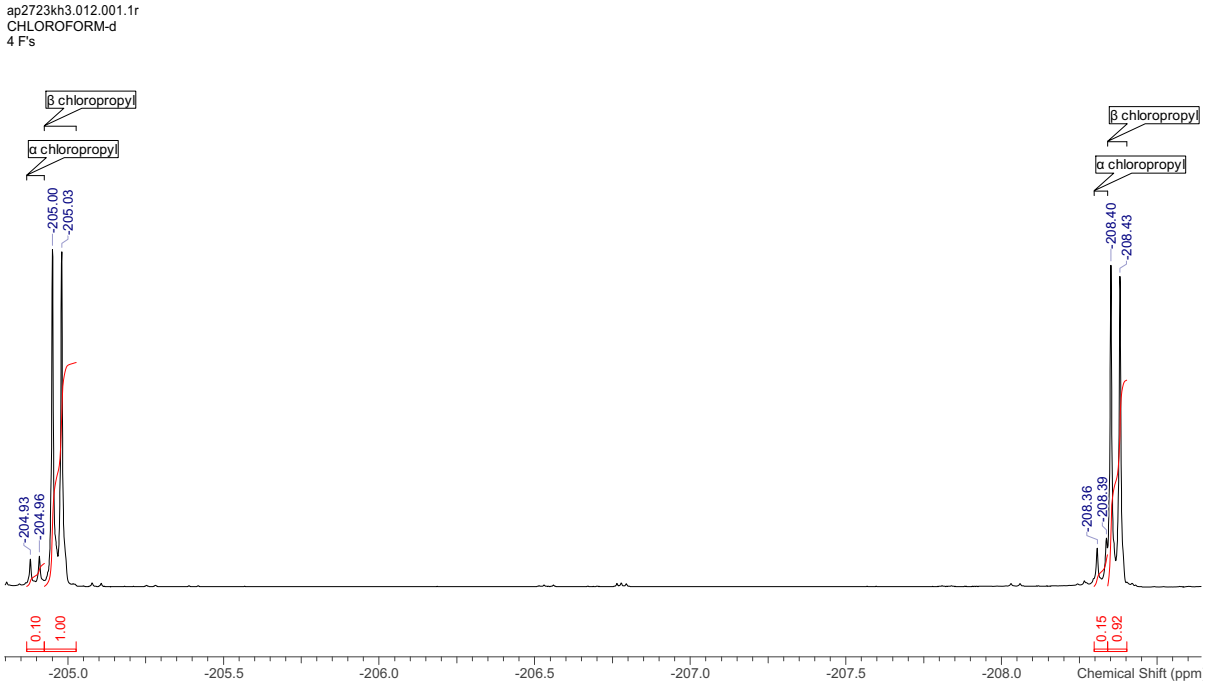


27 **SI-9**

According to general procedure D, **27α** (41 mg, 0.0579 mmol, 1.0 equiv) was reacted with H_2O/TFA (0.19 mL). The resultant crude material was purified by flash column chromatography (10 g, $CHCl_3$/Acetone 100:0 to 60:40) to collect **SI-9** as a colourless oil (32 mg, 0.0539 mmol, 93% yield).

4.4.2.2 Crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows no more a mixture of BDA isomerisation products, as the BDA protecting group was removed. The only two products present are the α disaccharide with β chloropropyl chain (major) and the α disaccharide with α chloropropyl chain (minor).

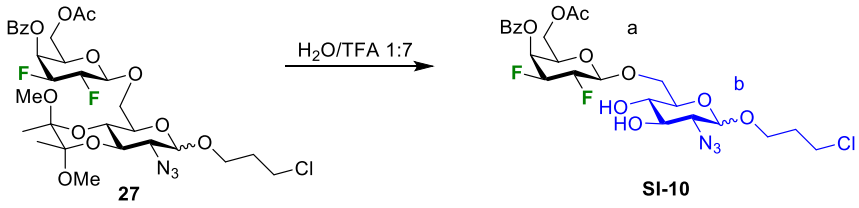


4.4.2.3 Characterisation of the disaccharide

R_f 0.30 ($CHCl_3$/acetone 70:30); IR (neat) 3447 (br, w), 2926 (br, w), 2360 (w), 2342 (w), 2111 (s), 1730 (s), 1266 (s), 1071 (s), 1026 (s), 173 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major anomer) (COSY/HMBC/HSQC) δ 8.05 (2H, dd, *J* = 8.4, 1.3 Hz, H_{Ar}), 7.61 (1H, tt, *J* = 7.5, 1.5 Hz, H_{Ar}), 7.48 (2H, br t, *J* = 7.9 Hz, H_{Ar}), 5.89 (1H, dt, *J* = 5.8, 3.0 Hz, H_{4a}), 5.34 (1H, t, *J* = 4.0 Hz, H_{1a}), 5.16 (1H, dddd, *J* = 48.9, 12.0, 9.7, 3.9 Hz, H_{2a} or H_{3a}), 4.99 (1H, dddd, *J* = 50.1, 12.0, 9.5, 4.2 Hz, H_{2a} or H_{3a}), 4.37 (1H, d, *J* = 7.8 Hz, H_{1b}), 4.32–4.40 (1H, m, H_{5a}), 4.22 (1H, dd, *J* = 11.5, 5.9 Hz, H_{6a}), 4.16 (1H, dd, *J* = 11.6, 6.7 Hz, H_{6a}), 4.06 (1H, ddd, *J* = 9.9, 6.2, 5.1 Hz, $H_{OC\underline{H}HCH2}$), 3.99 (1H, dd, *J* = 11.2, 5.0 Hz, H_{6b}), 3.90 (1H, dd, *J* = 11.3, 2.5 Hz, H_{6b}), 3.76 (1H, ddd, *J* = 9.9, 7.0, 5.3 Hz, $H_{OC\underline{H}HCH2}$), 3.71 (2H, t, *J* = 6.2 Hz, $H_{CH2C\underline{H}2Cl}$), 3.60 (1H, t, *J* = 9.2 Hz, H_{4b}), 3.49 (1H, ddd, *J* = 9.4, 4.9, 2.3 Hz, H_{3b}), 3.28–3.44 (2H, m, H_{5b}, H_{2b}), 2.05–2.15 (2H, m, $H_{OCH2C\underline{H}2}$), 2.02 (3H, s, $H_{CH3(a)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$, major anomer) δ -205.3 (1F, br dt, *J* = 48.9, 12.6 Hz, F_3), -208.7 (1F, dtd, *J* = 50.3, 13.4, 13.4, 2.6 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -205.2 (1F, d, *J* = 13.9 Hz, $F_{3α}$), -205.3 (1F, d, *J* = 13.9 Hz, $F_{3β}$), -208.6 (1F, d, *J* = 13.9 Hz, $F_{2α}$) -208.7 (1F, d, *J* = 13.9 Hz, $F_{2β}$) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, major anomer) δ 170.7 ($C_{COCH3(a)}$), 165.3 ($C_{COPh(a)}$), 133.7 (C_{Ar}), 129.9 (C_{Ar}), 128.9 (C_{Ar}), 128.6 (C_{Ar}), 102.2 (C_{1b}), 96.7 (dd, *J* = 20.5, 9.5 Hz, C_{1a}), 86.5 (dd, *J* = 191.7, 18.9 Hz, C_{3a} or C_{2a}), 86.4 (dd, *J* = 191.5, 18.3 Hz, C_{3a} or C_{2a}), 74.9 (C_{5b}), 74.4 (C_{3b}), 70.2 (C_{4b}), 69.1 (dd, *J* = 16.9, 8.1 Hz, C_{4a}), 67.0 (C_{6b}), 66.7

(d, *J* = 5.1 Hz, C_{5a}), 66.4 ($C_{OCH2CH2}$), 65.9 (C_{2b}), 61.9 (d, *J* = 1.5 Hz, C_{6b}), 41.6 ($C_{CH2CH2Cl}$), 32.5 ($C_{OCH2CH2}$), 20.6 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{24}H_{30}ClF_2N_3NaO_{10}$ $[M + Na]^+$ calcd 616.1480 found 616.1482 (err -0.3 ppm).

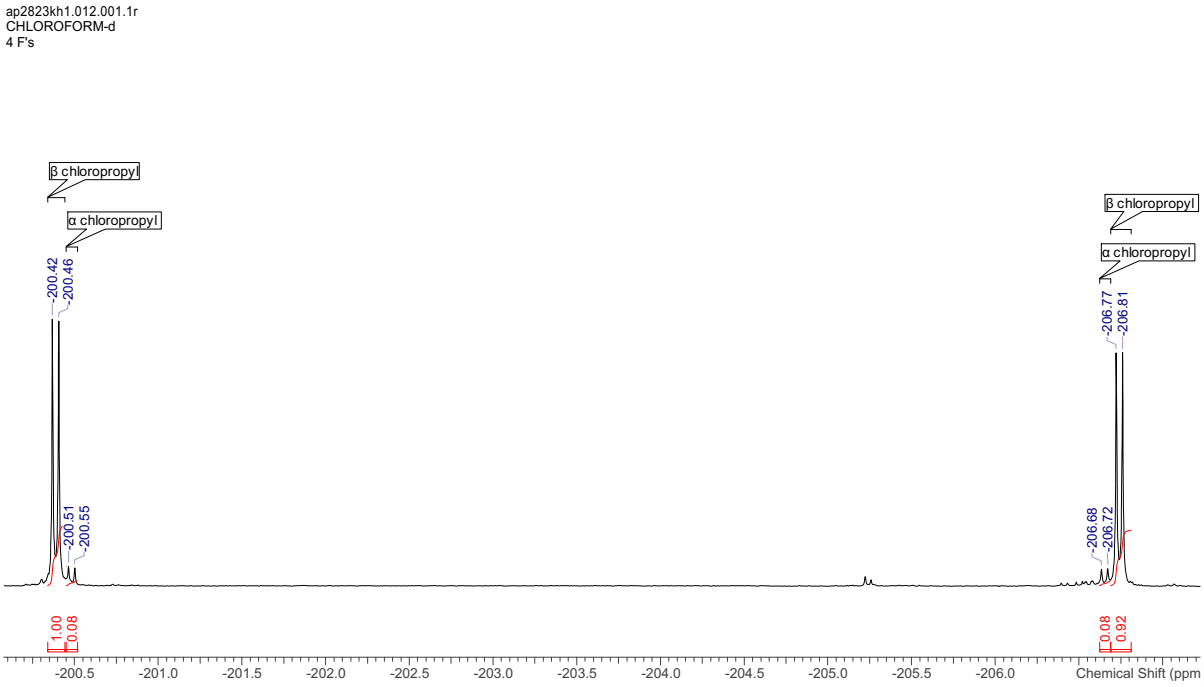
4.4.2.4 BDA removal of the beta-anomer: 6-*O*-acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-β-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-D-glucopyranoside (**SI-10**)



According to general procedure D, **27β** (8 mg, 0.0113 mmol, 1.0 equiv) was reacted with H_2O/TFA (0.038 mL). The resultant crude material was purified by flash column chromatography (5 g, $CHCl_3$/Acetone 100:0 to 50:50) to collect **SI-10** as a colourless oil (3 mg, 0.00505 mmol, 44% yield).

4.4.2.5 Crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows no more a mixture of BDA isomerisation products, as the BDA protecting group was removed. The only two products present are the β disaccharide with β chloropropyl chain (major) and the β disaccharide with α chloropropyl chain (minor).



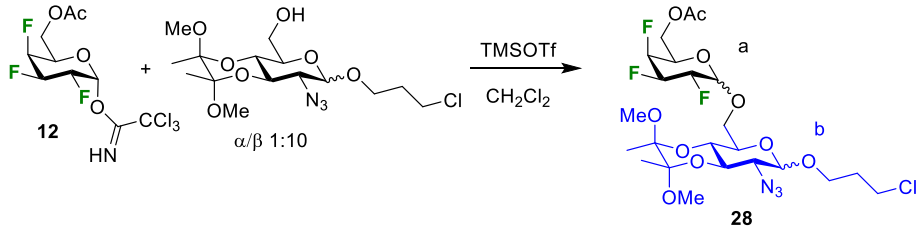
4.4.2.6 Characterisation of the disaccharide

R_f 0.19 ($CHCl_3$/acetone 70:30); IR (neat) 3447 (br, w), 2925 (br, w), 2360 (w), 2342 (w), 2111 (s), 1730 (s), 1269 (s), 1070 (s), 174 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, major anomer) (COSY/HMBC/HSQC) δ 8.07 (2H, dd, *J* = 8.4, 1.3 Hz, H_{Ar}), 7.62 (1H, tt, *J* = 7.5, 1.3 Hz, H_{Ar}), 7.49 (2H, br t, *J* = 8.0 Hz, H_{Ar}), 5.84 (1H, dt, *J* = 5.8, 3.0 Hz, H_{4a}), 4.75 (1H, dd, *J* = 7.6, 2.3 Hz, H_{1a}), 4.65–4.91 (2H, m, H_{3a}, H_{2a}), 4.39 (1H, d, *J* = 7.8 Hz, H_{1b}), 4.25 (1H, dd, *J* = 11.3, 6.1

Hz, H_{6a}), 4.21–4.29 (1H, m, H_{6b}), 4.20 (1H, dd, *J* = 11.6, 6.0 Hz, H_{6a}), 4.10 (1H, ddd, *J* = 10.0, 6.1, 5.3 Hz, $H_{OCHHCH2}$), 3.96 (1H, tt, *J* = 5.9, 1.3 Hz, H_{5a}), 3.93 (1H, dd, *J* = 11.6, 5.7 Hz, H_{6b}), 3.73–3.80 (1H, m, $H_{OCHHCH2}$), 3.71 (2H, t, *J* = 6.3 Hz, $H_{OCHHCH2}$), 3.55–3.61 (2H, m, H_{3b}, H_{4b}), 3.37–3.42 (1H, m, H_{5b}), 3.32 (1H, dd, *J* = 9.7, 7.7 Hz, H_{2b}), 2.73 (1H, br s, H_{OH}), 2.11 (2H, qd, *J* = 5.9, 1.1 Hz, $H_{OCH2CH2}$), 2.05 (3H, s, $H_{CH3(a)}$), 1.60 (1H, br s, H_{OH}) ppm; ^{19}F NMR (471 MHz, $CDCl_3$, major anomer) δ -200.2 (1F, dtd, *J* = 47.9, 12.9, 12.9, 5.4 Hz, F_3), -206.5 (1F, dt, *J* = 52.6, 15.7 Hz, F_2) ppm; ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ -200.2 (1F, d, *J* = 14.3 Hz, $F_{3\beta}$), -200.3 (1F, d, *J* = 14.3 Hz, $F_{3\alpha}$), -206.45 (1F, d, *J* = 13.9 Hz, $F_{2\alpha}$), -206.54 (1F, d, *J* = 14.3 Hz, $F_{2\beta}$) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.5 ($C_{COCH3(a)}$), 165.3 ($C_{COPh(a)}$), 133.8 (C_{Ar}), 130.0 (C_{Ar}), 128.6 (C_{Ar}), 102.2 (C_{1b}), 101.0 (dd, *J* = 23.0, 10.8 Hz, C_{1a}), 89.1 (dd, *J* = 186.7, 19.6 Hz, C_{2a}), 89.1 (dd, *J* = 194.5, 18.4 Hz, C_{3a}), 74.9 (C_{5b}), 74.8 (C_{3b}), 70.6 (C_{4b}), 70.4 (d, *J* = 5.7 Hz, C_{5a}), 69.6 (C_{6b}), 68.1 (dd, *J* = 16.8, 8.5 Hz, C_{4a}), 66.6 ($C_{OCH2CH2}$), 65.9 (C_{2b}), 61.5 (d, *J* = 2.4 Hz, C_{6a}), 41.7 ($C_{CH2CH2Cl}$) 32.5 ($C_{OCH2CH2}$), 20.7 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{24}H_{30}ClF_2N_3NaO_{10}$ $[M + Na]^+$ calcd 616.1480 found 616.1486 (err -0.9 ppm).

4.4.3 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α/β-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-3,4-*O*-[(2'S,3'S)-2',3'-dimethoxybutane-2',3'-diyl]-D-glucopyranoside (**28**)

4.4.3.1 Glycosylation to **28** (Figure 2)



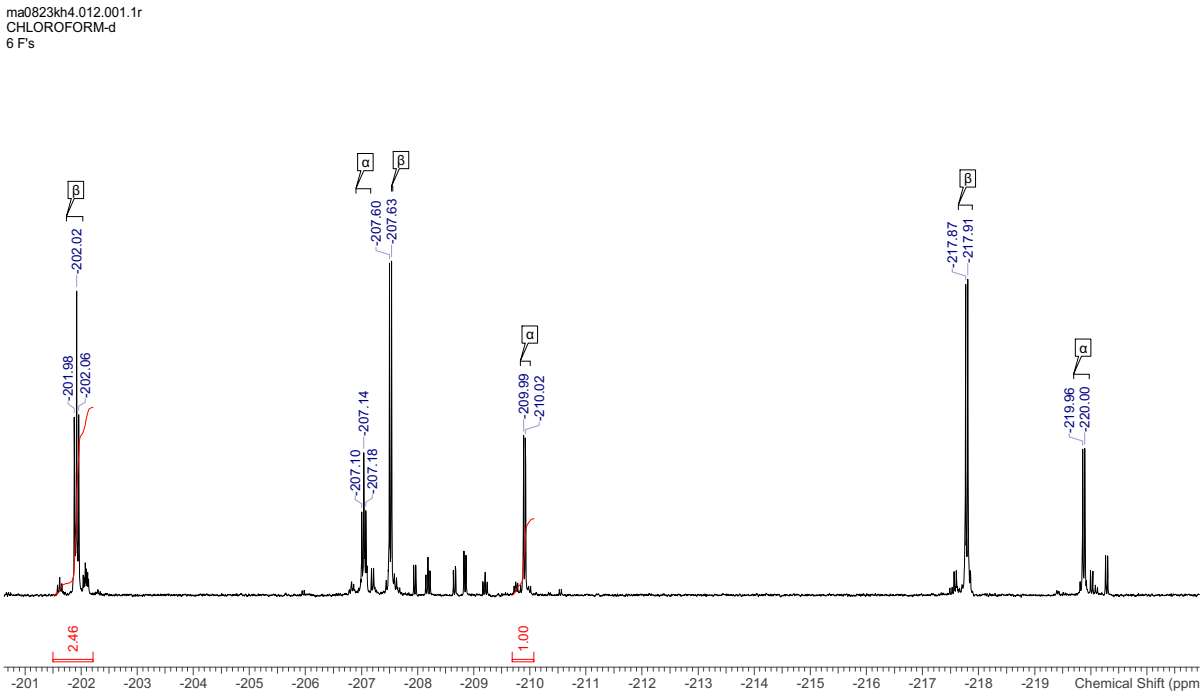
According to general procedure C, **12** (142 mg, 0.280 mmol, 1.0 equiv) was reacted with the acceptor[2] (which consisted of an 1:10 α/β-mixture of anomers) at 0 ˚C for 5 h. The resultant crude material (α/β 1:2.5) was purified by flash column chromatography (10 g, hexane/EtOAc 100:0 to 60:40) to collect **28α** (44 mg, 0.0728 mmol, 26% yield) and **28β** (106 mg, 0.175 mmol, 63% yield).

Anomers assignment was based on the chemical shift and coupling constant values of the anomeric protons.

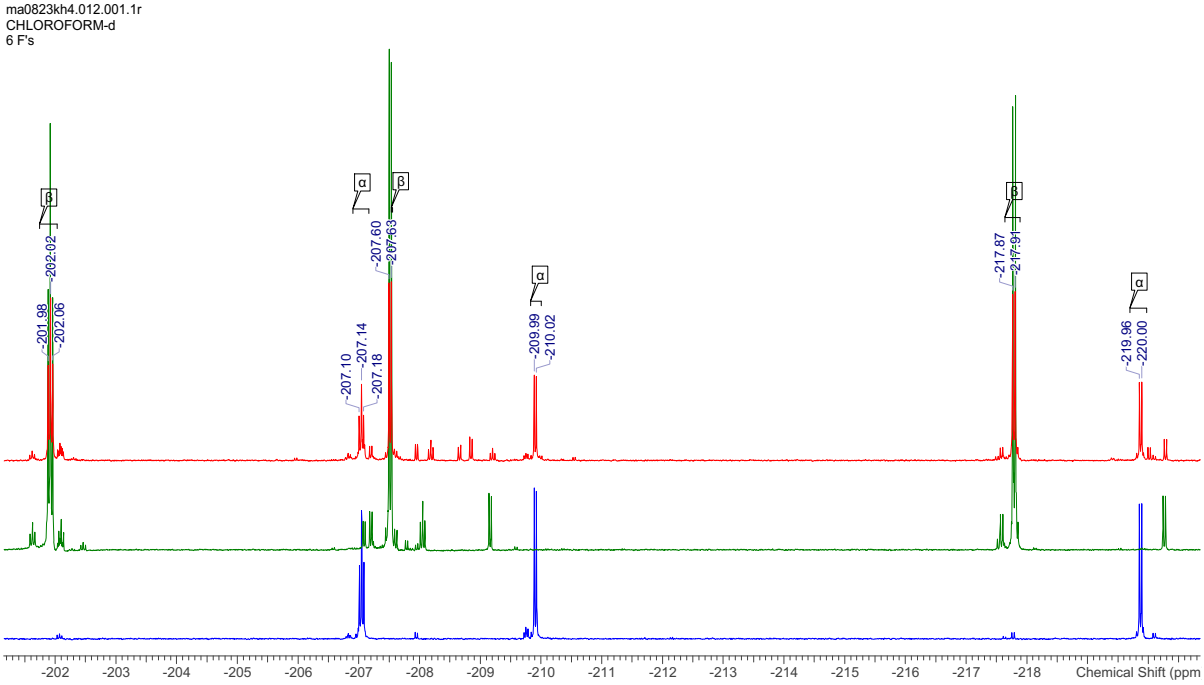
4.4.3.2 Ratio determination, crude reaction mixture, ^{19}F{^{1}H} NMR, 376 MHz, $CDCl_3$

The ^{19}F{^{1}H} NMR of the crude reaction mixture shows a ratio of α/β 1:2.5, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **6** is present and no unreacted trichloroacetimidate **12** is observed. This crude reaction mixture shows the α and the β anomers, they both contain α/β 1:10 of chloropropyl chain and a mixture of BDA isomerisation products. The chloropropyl anomers could not be separated, but the disaccharide anomers were separable, each obtained as a mixture of BDA isomers, and chloropropyl anomers. Removal of the BDA group then led to just a mixture of the chloropropyl anomers (see below).

^{19}F{^{1}H} NMR of the crude reaction mixture with the integration:



Overlay of the $^{19}F\{^{1}H\}$ NMRs of the crude reaction mixture (in red) with that of the isolated mixtures of alfa-anomer (in blue) and the beta anomer (in green) indicated suitable integration ranges.



4.4.3.3 Characterisation of the disaccharides (both anomers)

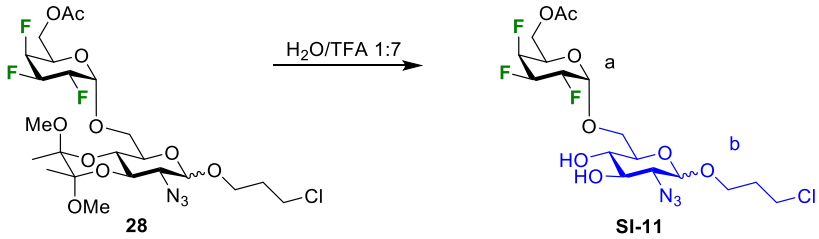
Data for **28α**, ^{1}H, ^{19}F and ^{13}C NMR could be assigned: ^{1}H NMR (α major) (500 MHz, $CDCl_3$, major anomer) (COSY/HMBC/HSQC) δ 5.28 (1H, t, *J* = 3.9 Hz, H_{1a}), 4.76–5.07 (3H, m, H_{2a}, H_{3a}, H_{4a}), 4.29 (H, d, *J* = 7.8 Hz, H_{1b}), 4.28 (2H, t, *J* = 6.2 Hz, $2H_{6a}$), 4.04–4.15 (1H, m, H_{5a}), 3.99 (1H, ddd, *J* = 9.8, 6.1, 5.4 Hz, $H_{OCHHCH2}$), 3.90 (1H, dd, *J* = 11.9, 1.7 Hz, H_{6b}), 3.79 (1H, dd, *J* = 11.8, 5.4 Hz, H_{6b}), 3.66 (5H, m, $H_{OCHHCH2}$, H_{4b}, $H_{CH2CH2Cl}$, H_{3b}, H_{5b}), 3.41 (1H, dd, *J* = 10.1, 7.8 Hz, H_{2b}), 3.30 (3H, s, H_{OMe}), 3.24 (3H, s, H_{OMe}), 2.09 (3H, s, $H_{CH3(a)}$), 2.05–2.11 (2H, m, $H_{OCH2CH2}$), 1.34 (3H, s, $H_{CH3(b)}$), 1.29 (3H, s, $H_{CH3(b)}$) ppm; ^{19}F NMR (471 MHz, $CDCl_3$, major anomer) δ -206.9 (1F, dddt, *J* = 48.1,

16.0, 13.9, 8.2 Hz, F_3), -209.8 (1F, dtd, *J* = 49.4, 13.6, 3.6 Hz, F_2), -219.8 (1F, dtdd, *J* = 50.3, 27.5, 14.7, 2.9 Hz, F_4) ppm; $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$, major anomer) δ -206.9 (1F, t, *J* = 13.9 Hz, F_3), -209.8 (1F, d, *J* = 13.6 Hz, F_2), -219.8 (1F, d, *J* = 14.3 Hz, F_4) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, major anomer) δ 170.3 ($C_{COCH3(a)}$), 102.5 (C_{1b}), 100.0 ($C_{CH3(b)}$), 99.8 ($C_{CH3(b)}$), 96.7 (dd, *J* = 20.7, 9.3 Hz, C_{1a}), 87.4 (ddd, *J* = 186.0, 16.9, 8.1 Hz, C_{4a}), 86.4 (ddd, *J* = 191.2, 19.6, 17.6 Hz, C_{3a}), 85.7 (ddd, *J* = 191.7, 18.5, 2.0 Hz, C_{2a}), 73.6 (C_{5b}), 70.6 (C_{3b}), 66.8 (dd, *J* = 18.1, 5.0 Hz, C_{5a}), 66.4 ($C_{OCH2CH2}$), 66.2 (C_{4b}), 65.9 (C_{6b}), 62.6 (C_{2b}), 61.4 (dd, *J* = 6.1, 1.8 Hz, C_{6a}), 48.04 ($C_{CH3(b)}$), 47.97 ($C_{CH3(b)}$), 41.6 ($C_{CH2CH2Cl}$), 32.4 ($C_{OCH2CH2}$), 20.7 ($C_{CH3(a)}$), 17.5 ($C_{CH3(b)}$), 17.5 ($C_{CH3(b)}$) ppm.

Data for **28β**, ^{19}F NMR could be assigned: ^{19}F NMR (376 MHz, $CDCl_3$, major anomer) δ -202.0 (1F, dtt, *J* = 52.6, 14.1, 7.0 Hz, F_3), -207.6 (1F, br dt, *J* = 52.5, 13.4 Hz, F_2), -217.9 (1F, dtd, *J* = 50.5, 25.9, 15.6 Hz, F_4) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$, major anomer) δ -202.0 (1F, t, *J* = 14.5 Hz, F_3), -207.6 (1F, d, *J* = 13.9 Hz, F_2), -217.9 (1F, d, *J* = 15.6 Hz, F_4) ppm

4.4.4 BDA removal

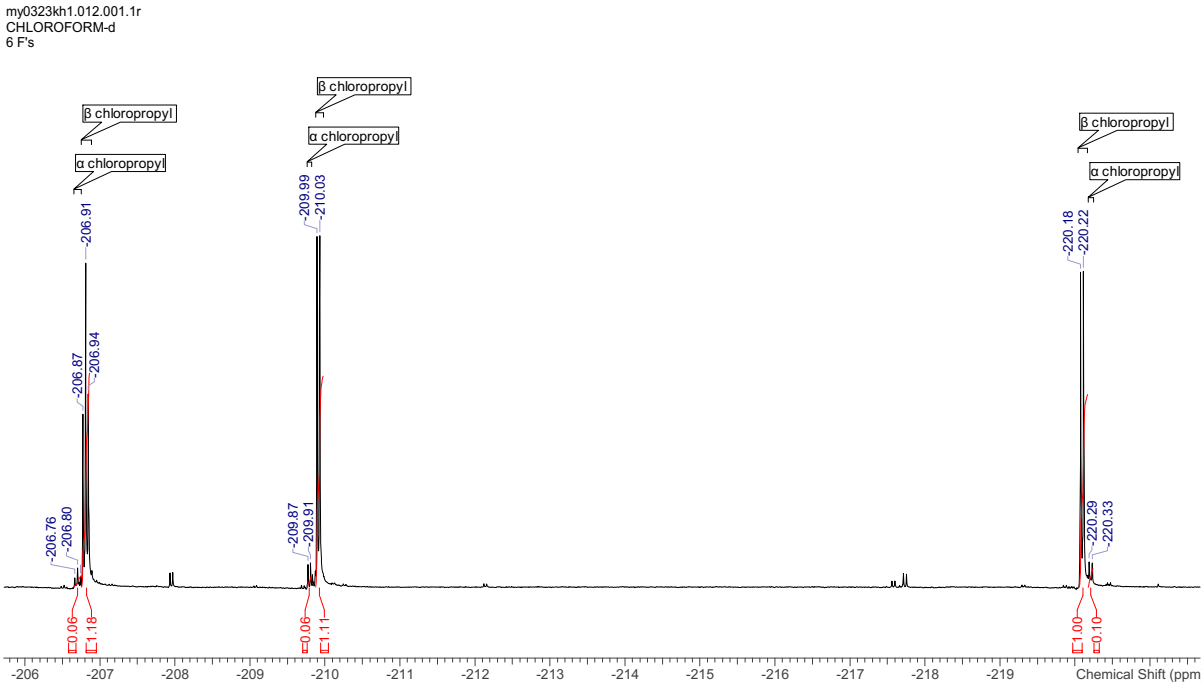
4.4.4.1 BDA removal of the alpha anomer: 6-*O*-acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-D-glucopyranoside (**SI-11**)



According to general procedure D, **28α** (40.3 mg, 0.0666 mmol, 1.0 equiv) was reacted with H_2O/TFA (0.22 mL). The resultant crude material was purified by flash column chromatography (10 g, $CHCl_3$/Acetone 100:0 to 60:40) to collect **SI-11** as a yellow oil (21.6 mg, 0.0440 mmol, 66% yield).

4.4.4.2 Crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

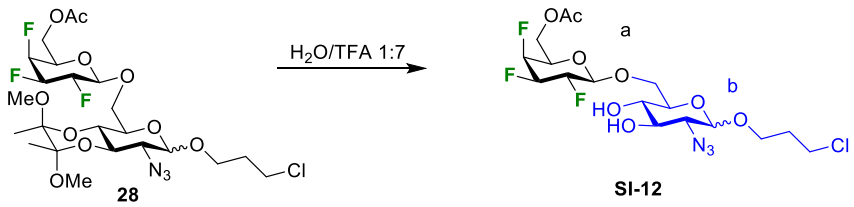
The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows no more a mixture of BDA isomerisation products, as the BDA protecting group was removed. The only two products present are the α disaccharide with β chloropropyl chain (major) and the α disaccharide with α chloropropyl chain (minor).



4.4.4.3 Characterisation of the disaccharide

R_f 0.21 ($CHCl_3$/acetone 70:30); IR (neat) 3441 (br, w), 2925 (br, w), 2360 (w), 2342 (w), 2111 (s), 1734 (s), 1254 (w), 1075 (s), 1027 (s), 174 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, major anomer) (COSY/HMBC/HSQC) δ 5.25 (1H, t, *J* = 4.0 Hz, H_{1a}), 4.80–5.09 (3H, m, H_{2a}, H_{3a}, H_{4a}), 4.35 (1H, d, *J* = 7.9 Hz, H_{1b}), 4.32 (1H, dd, *J* = 11.4, 7.0 Hz, H_{6a}), 4.27 (1H, dd, *J* = 11.4, 6.5 Hz, H_{6a}), 4.13 (1H, dt, *J* = 28.4, 6.3 Hz, H_{5a}), 4.03 (1H, ddd, *J* = 9.8, 6.2, 5.3 Hz, $H_{OC\underline{H}HCH2}$), 3.95 (1H, dd, *J* = 11.2, 5.0 Hz, H_{6b}), 3.87 (1H, dd, *J* = 11.2, 2.5 Hz, H_{6b}), 3.75 (1H, ddd, *J* = 9.8, 6.8, 5.2 Hz, $H_{OC\underline{H}HCH2}$), 3.70 (2H, t, *J* = 6.3 Hz, $H_{CH2C\underline{H}2Cl}$), 3.56 (1H, dd, *J* = 9.7, 7.8 Hz, H_{4b}), 3.46 (1H, ddd, *J* = 9.6, 4.9, 2.6 Hz, H_{3b}), 3.37 (1H, dd, *J* = 10.2, 8.7 Hz, H_{5b}), 3.29 (1H, dd, *J* = 9.8, 7.9 Hz, H_{2b}), 3.03 (2H, br s, $2H_{OH}$), 2.11 (3H, s, $H_{CH3(a)}$), 2.06–2.12 (2H, m, $H_{OCH2C\underline{H}2}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$, major anomer) δ -206.9 (1F, br d, *J* = 47.7 Hz, F_3), -210.0 (1F, dtd, *J* = 48.1, 13.4, 13.4, 3.5 Hz, F_2), -220.2 (1F, dtd, *J* = 51.3, 26.9, 14.5 Hz, F_4) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -206.8 (1F, t, *J* = 14.1 Hz, $F_{3\alpha}$), -206.9 (1F, t, *J* = 14.1 Hz, $F_{3\beta}$), -209.9 (1F, d, *J* = 14.3 Hz, $F_{2\alpha}$), -210.0 (1F, d, *J* = 13.4 Hz, $F_{2\beta}$), -220.15 (1F, d, *J* = 14.7 Hz, $F_{4\beta}$), -220.24 (1F, d, *J* = 14.3 Hz, $F_{4\alpha}$) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, major anomer) δ 170.7 (C_{COCH3}), 102.2 (C_{1b}), 96.6 (dd, *J* = 20.6, 9.4 Hz, C_{1a}), 87.4 (ddd, *J* = 186.4, 16.7, 8.3 Hz, C_{4a}), 86.4 (ddd, *J* = 191.7, 19.1, 17.4 Hz, C_{3a}), 85.8 (ddd, *J* = 191.7, 18.6, 2.1 Hz, C_{2a}), 75.0 (C_{5b}), 74.3 (C_{3b}), 70.2 (C_{4b}), 67.1 (C_{6b}), 66.7 (dd, *J* = 18.1, 5.2 Hz, C_{5a}), 66.5 ($C_{O\underline{C}H2CH2}$), 65.9 (C_{2b}), 61.4 (dd, *J*=6.1, 1.8 Hz, C_{6a}), 41.6 ($C_{CH2\underline{C}H2Cl}$), 32.5 ($C_{OCH2\underline{C}H2}$), 20.7 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{17}H_{25}ClF_3N_3NaO_8$ $[M + Na]^+$ calcd 514.1174 found 514.1179 (err -0.9 ppm).

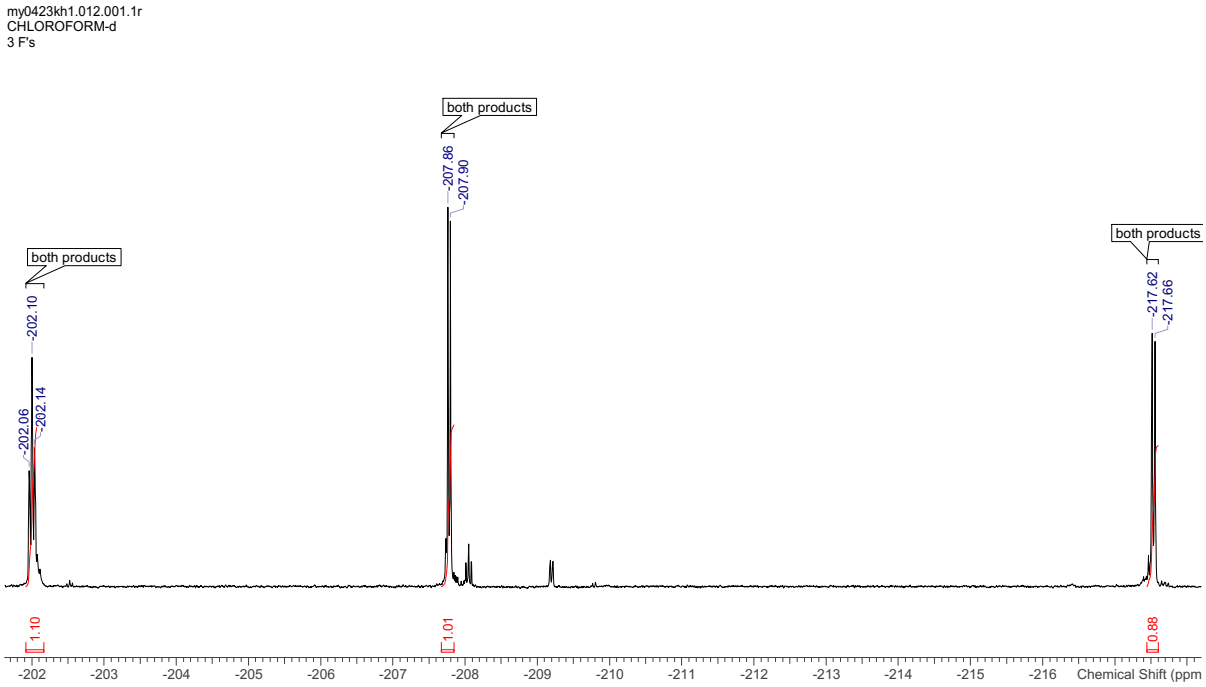
4.4.4.4 BDA removal of the beta anomer: 6-*O*-acetyl-2,3,4-trideoxy-2,3,4-trifluoro-β-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-D-glucopyranoside (**SI-12**)



According to general procedure D, **28β** (90.6 mg, 0.150 mmol, 1.0 equiv) was reacted with H_2O/TFA (0.50 mL). The resultant crude material was purified by flash column chromatography (10 g, $CHCl_3$/Acetone 100:0 to 50:50) to collect **SI-12** as a yellow oil (51.1 mg, 0.104 mmol, 69% yield).

4.4.4.5 Crude reaction mixture, $^{19}F\{^1H\}$ NMR, 376 MHz, $CDCl_3$

The $^{19}F\{^1H\}$ NMR of the crude reaction mixture shows no more a mixture of BDA isomerisation products, as the BDA protecting group was removed. The only two products present are the α disaccharide with β chloropropyl chain (major) and the α disaccharide with α chloropropyl chain (minor). In that case both product overlap in the $^{19}F\{^1H\}$ NMR.



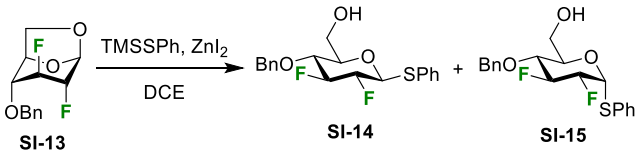
4.4.4.6 Characterisation of the disaccharide

R_f 0.22 ($CHCl_3$/acetone 70:30); IR (neat) 3421 (br, w), 2925 (br, w), 2360 (w), 2342 (w), 2110 (s), 1742 (s), 1238 (s), 1040 (s), 172 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, major anomer) (COSY/HMBC/HSQC) δ 4.95 (1H, ddd, *J* = 51.0, 6.9, 3.3 Hz, H_{4a}), 4.67 (1H, dd, *J* = 7.6, 2.3 Hz, H_{1a}), 4.54–4.78 (2H, m, H_{3a}, H_{2a}), 4.38 (1H, dd, *J* = 11.3, 6.4 Hz, H_{6a}), 4.35 (1H, d, *J* = 7.8 Hz, H_{1b}), 4.24 (1H, dd, *J* = 11.4, 6.7 Hz, H_{6a}), 4.19 (1H, dd, *J* = 11.5, 1.5 Hz, H_{6b}), 4.04 (1H, ddd, *J* = 9.8, 6.1, 5.3 Hz, $H_{OC\underline{H}HCH_2}$), 3.86 (1H, dd, *J* = 11.6, 5.4 Hz, H_{6b}), 3.73 (1H, ddd, *J* = 9.9, 6.6, 5.4 Hz, $H_{OC\underline{H}HCH_2}$), 3.76 (1H, dtd, *J* = 25.7, 6.5, 6.5, 1.4 Hz, H_{5a}), 3.69 (2H, t, *J* = 6.3 Hz, $H_{OC\underline{H}HCH_2}$), 3.46–3.54 (2H, m, H_{4b} and H_{3b}), 3.36

(1H, br t, *J* = 10.0 Hz, H_{5b}), 3.29 (1H, dd, *J* = 10.0, 7.8 Hz, H_{2b}), 2.63 (1H, s, H_{OH}), 2.18 (1H, s, H_{OH}), 2.10 (3H, s, $H_{CH3(a)}$), 2.05–2.12 (2H, m, $H_{OCH2CH2}$) ppm; ^{19}F NMR (471 MHz, $CDCl_3$, major anomer) δ -201.8 (1F, br ddd, *J* = 46.5, 15.0, 6.1 Hz, F_3), -207.4 (1F, br dt, *J* = 54.4, 13.4 Hz, F_2), -217.5 (1F, dtd, *J* = 50.5, 25.7, 15.4 Hz, F_4) ppm; ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$) δ -201.8 (1F, t, *J* = 14.7 Hz, $F_{3\beta}$), -201.9 (1F, t, *J* = 14.5 Hz, $F_{3\alpha}$), -207.2 (1F, d, *J* = 13.9 Hz, $F_{2\alpha}$),-207.4 (1F, d, *J* = 14.0 Hz, $F_{2\beta}$), -217.5 (1F, br d, *J* = 15.0 Hz, F_4) ppm;^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, major anomer) δ 170.6 ($C_{COCH3(a)}$), 102.1 (C_{1b}), 100.6 (dd, *J* = 23.0, 10.8 Hz, C_{1a}), 89.0 (dt, *J* = 194.1, 18.4 Hz, C_{3a}), 88.6 (dd, *J* = 186.9, 19.3 Hz, C_{2a}), 86.3 (ddd, *J* = 187.1, 16.6, 9.2 Hz, C_{4a}), 74.9 (C_{5b}), 74.8 (C_{3b}), 70.4 (C_{4b}), 70.0 (dd, *J* = 18.1, 5.7 Hz, C_{5a}), 69.3 (C_{6b}), 66.5 ($C_{OCH2CH2}$), 65.9 (C_{2b}), 61.1 (dd, *J* = 5.5, 2.4 Hz, C_{6a}), 41.7 ($C_{CH2CH2Cl}$), 32.4 ($C_{OCH2CH2}$), 20.7 ($C_{CH3(a)}$) ppm; HRMS (ESI+) for $C_{17}H_{25}ClF_3N_3NaO_8$ [M + Na]$^+$ calcd 514.1174 found 514.1178 (err -0.7 ppm).

4.5 Glycosylation with phenyl 4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-1-thio-α-D-glucopyranose

4.5.1 Synthesis of phenyl 4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-1-thio-α-D-glucopyranose donor (**SI-15**)



To a solution of **SI-13**[3, 4] (5.21 g, 20.35 mmol, 1.0 equiv) in DCE (67.8 mL) was sequentially added PhSTMS (11.6 mL, 61.25 mmol, 3.0 equiv) and ZnI_2 (11.5 g, 36.63 mmol, 1.8 equiv). The mixture was stirred protected from light, at rt for 18 h. The mixture was diluted with CH_2Cl_2 (100 mL) and H_2O (200 mL). The phases were separated and aqueous was extracted with CH_2Cl_2 (3 × 150 mL), the combined organic phases were dried over $MgSO_4$, filtered, and concentrated in *vacuo*. The residue was dissolved in MeOH (200 mL), AcOH (20 mL was added and the solution was stirred at room temperature for 1 h. The mixture was concentrated in *vacuo* to give 8.0 g of crude. The crude was purified by flash column chromatography (100 g, hexane/EtOAc 100:0 to 0:100) to afford product **SI-14** and **SI-15** as a separable mixture of α- and β- anomers: **SI-14** (485 mg, 1.32 mmol, 7%) and **SI-15** (2.36 g, 6.44 mmol, 32%) as colourless oils.

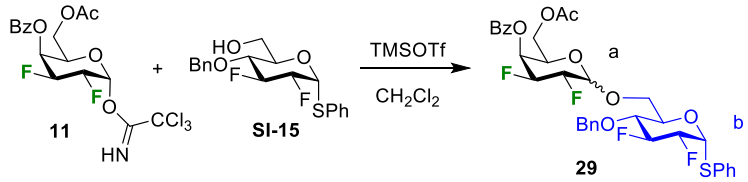
Data for **SI-15**: R_f 0.65 (hexane/EtOAc 80:20); $[\alpha]_D^{22.5}$ +24.8 (c 0.46, $CHCl_3$); m.p.: 76–78˚C (EtOAc); IR (neat) 2981 (w), 2884 (w), 2360 (s), 2342 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.53 (2 H, m, H_{Ar}), 7.29–7.43 (8 H, m, H_{Ar}), 5.71 (1H, br dt, *J* = 5.7, 2.1 Hz, H_1), 4.92 (1H, d, *J* = 11.1 Hz, H_7), 4.98 (1H, ddt, *J* = 53.8, 13.7, 8.9 Hz, H_3), 4.84 (1H, dddd, *J* = 50.7, 13.6, 9.0, 6.1 Hz, H_2), 4.68 (1H, d, *J* = 11.1 Hz, H_7), 4.26 (1H, dt, *J* = 9.9, 3.1 Hz, H_5), 3.80–3.84 (1H, m, H_6), 3.77 (1H, ddd, *J* = 14.1, 9.9, 8.4 Hz, H_4) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -191.0 (1F, dt, *J* = 50.7, 14.5 Hz, $F_{2\alpha}$), -193.0 (1F, dq, *J* = 53.8, 13.9 Hz, $F_{3\alpha}$) ppm; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -191.0 (1F, d, *J* = 13.9 Hz, F_2), -193.0 (1 F, d, *J* = 13.9 Hz, $F_{3\alpha}$) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.3 (C_{Ar}), 132.6 (C_{Ar}), 132.4 (C_{Ar}), 129.2 (C_{Ar}), 128.6 (C_{Ar}), 128.3 (C_{Ar}), 128.2 (C_{Ar}), 128.2 (C_{Ar}), 94.2 (dd, *J* = 186.3, 17.6 Hz, C_3), 87.5 (dd, *J* = 195.1, 18.3 Hz,

C_2), 85.8 (dd, *J* = 21.6, 8.4 Hz, C_1), 74.8 (dd, *J* = 16.5, 6.2 Hz, C_4), 74.6 (d, *J* = 2.9 Hz, C_7), 71.2 (d, *J* = 6.6 Hz, C_5), 61.2 (C_6) ppm; HRMS (ESI+) for $C_{26}H_{26}F_2NaO_3S$ $[M + Na]^+$ calcd 479.1463 found 479.1470 (-1.6 ppm error).

Data for **SI-14:** R_f 0.65 (hexane/EtOAc 80:20); $[\alpha]_D^{22.5}$ +21.9 (c 0.47, $CHCl_3$);IR (neat) 2981 (w), 2884 (w), 2360 (s), 2342 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.60 (2H, m, H_{Ar}), 7.29–7.42 (8H, m, H_{Ar}), 4.86 (1H, d, *J* = 11.5 Hz, H_7), 4.79 (1H, ddt, *J* = 53.4, 16.0, 8.3, 8.3 Hz, H_3), 4.67 (1H, dd, *J* = 1.4, 0.73 Hz, H_1), 4.63 (1H, d, *J* = 11.1, H_7), 4.26 (1H, dddd, *J* = 49.6, 13.6, 9.8, 8.2 Hz, H_2), 3.92 (1H, dddd, *J* = 12.1, 6.0, 2.6, 1.8 Hz, H_6), 3.72 (1H, ddd, *J* = 12.3, 7.6, 4.3 Hz, H_6), 3.67 (1H, ddd, *J* = 13.2, 9.7, 8.6 Hz, H_4), 3.42 (1H, dddd, *J* = 9.8, 4.3, 2.8, 1.2 Hz, H_5) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -188.36 (1F, dq, *J* = 53.8, 13.9 Hz, $F_{3\beta}$), -190.50 (1F, dt, *J* = 50.3, 15.6 Hz, $F_{2\beta}$) ppm; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -188.36 (1F, d, *J* = 13.9 Hz, $F_{3\beta}$), -190.50 (1F, br d, *J* = 13.9 Hz, $F_{2\beta}$) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.2 (C_{Ar}), 133.8 (C_{Ar}), 130.5 (C_{Ar}), 129.2 (C_{Ar}), 128.8 (C_{Ar}), 128.5 (C_{Ar}), 128.2 (C_{Ar}), 96.6 (dd, *J* = 189.3, 19.1 Hz, C_3), 87.7 (dd, *J* = 191.1, 19.4 Hz, C_2), 83.8 (dd, *J* = 23.5, 8.1 Hz, C_1), 78.4 (d, *J* = 8.1 Hz, C_5), 74.9 (dd, *J* = 16.9, 6.6 Hz, C_4), 74.6 (d, *J* = 2.9 Hz, C_7), 61.7 (C_6) ppm; HRMS (ESI+) for $C_{19}H_{20}F_2NaO_3S$ $[M + Na]^+$ calcd 389.0993 found 389.0998 (-1.1 ppm error).

4.5.2 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α/β-D-galactopyranosyl-(1,6)-phenyl 4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-1-thio-α-D-glucopyranose (**29**)

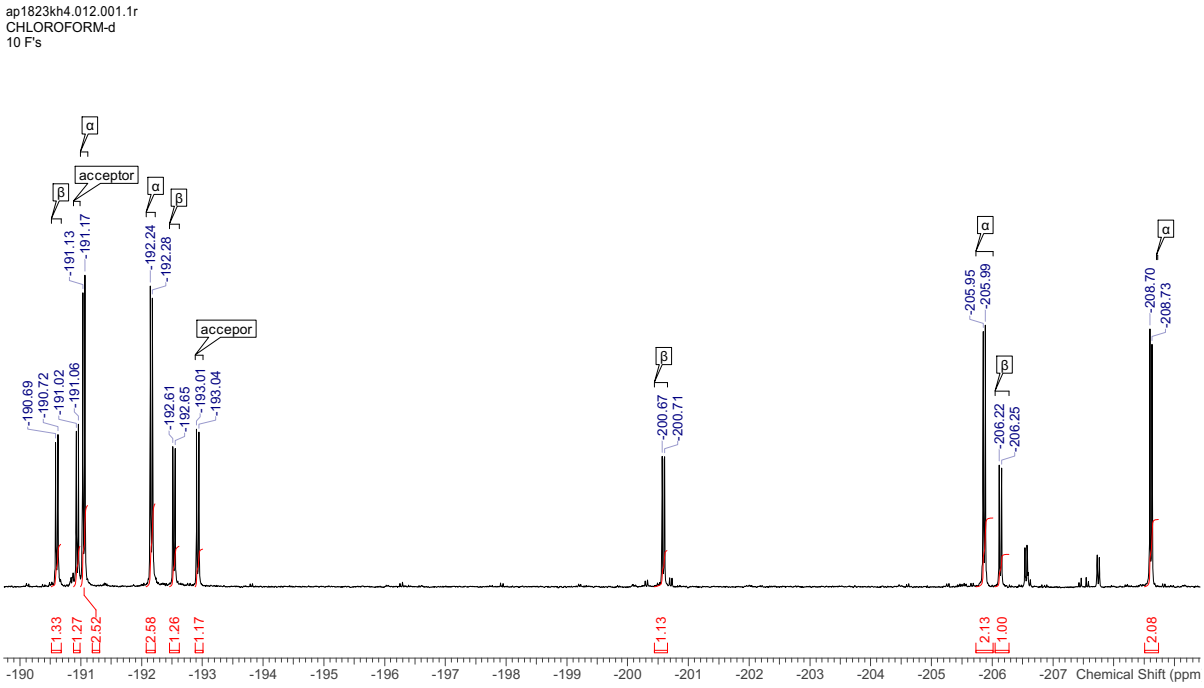
4.5.2.1 Glycosylation to **29** (Figure 2)



According to general procedure C, **11** (109 mg, 0.230 mmol, 1.0 equiv) was reacted at –30 ˚C for 3.5 h. The resultant crude material (α/β 2/1) was purified by flash column chromatography (25 g, hexane/EtOAc 100:0 to 60:40) to collect **29** as a mixture of α- and β-anomers (119 mg, 0.176 mmol, 77% yield). An analytical sample was purified to separate the anomers using flash column chromatography (25 g, hexane/EtOAc 100:0 to 60:40). Anomers assignment was based on the chemical shift and coupling constant values of the anomeric protons.

4.5.2.2 Ratio determination, crude reaction mixture, ^{19}F{^{1}H} NMR, 376 MHz, $CDCl_3$

The ^{19}F{^{1}H} NMR of the crude reaction mixture shows a ratio of α/β 2:1, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **5** is present and no unreacted trichloroacetimidate **11** is observed in the crude reaction mixture.



4.5.2.3 Characterisation of the disaccharides (both anomers)

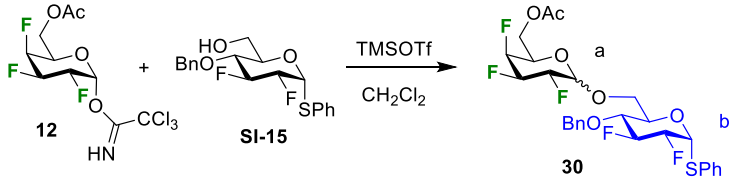
Data for **29α**: Colourless crystals; R_f 0.80 (hexane/EtOAc 60:40); $[\alpha]_D^{23}$ +151.4 (c 0.58, $CHCl_3$); IR (neat) 2360 (w), 2342 (w), 1730(s), 1366 (w), 1265 (s), 1025 (s), 908 (s), 730 (s), 712 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.03 (2H, dd, *J* = 8.6, 1.5 Hz, H_{Ar}), 7.61 (1H, tt, *J* = 7.5, 1.3 Hz, H_{Ar}), 7.50–7.55 (2H, m, H_{Ar}), 7.47 (2H, t, *J* = 7.8 Hz, H_{Ar}), 7.34–7.42 (8H, m, H_{Ar}), 5.78 (1H, dt, *J* = 5.6, 2.1 Hz, H_{1b}), 5.68 (1H, dt, *J* = 6.1, 3.3 Hz, H_{4a}), 5.23 (1H, t, *J* = 4.0 Hz, H_{1a}), 5.01 (2H, ddt, *J* = 53.5, 13.8, 8.9 Hz, H_{3b}), 4.96 (1H, d, *J* = 11.5 Hz, H_{CH2OBn}), 4.69–5.00 (3H, m, H_{3a}, H_{2b}, H_{2a}), 4.66 (1H, d, *J* = 11.4 Hz, H_{CH2OBn}), 4.46 (1H, dt, *J* = 9.9, 3.5 Hz, H_{5b}), 4.00–4.14 (3H, m, $2H_{6a}$, H_{5a}), 3.84 (2H, d, *J* = 4.0 Hz, $2H_{6b}$), 3.71 (1H, ddd, *J* = 14.4, 10.0, 8.3 Hz, H_{4b}), 1.98 (3H, s, H_{CH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -191.1 (1F, dt, *J* = 50.6, 13.9 Hz, F_{2b}), -192.2 (1F, dq, *J* = 53.5, 13.8 Hz, F_{3b}), -205.9 (1F, dtt, *J* = 48.6, 12.6, 4.3 Hz, F_{3a}), -208.6 (1F, dtd, *J* = 50.3, 12.6, 2.2 Hz, F_{2a}) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -191.1 (1F, br d, *J* = 13.9 Hz, F_{2b}), -192.2 (1F, d, *J* = 13.4 Hz, F_{3b}), -205.9 (1F, br d, *J* = 13.9 Hz, F_{3a}), -208.6 (1F, br d, *J* = 13.4 Hz, F_{2a}) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.2 (C_{COCH3}), 165.3 ($C_{COCH2Ph}$), 137.2 (C_{Ar}), 133.6 (C_{Ar}), 132.7 (C_{Ar}), 132.0 (C_{Ar}), 129.8 (C_{Ar}), 129.2 (C_{Ar}), 128.8 (C_{Ar}), 128.5 (C_{Ar}), 128.5 (C_{Ar}), 128.3 (C_{Ar}), 128.2 (C_{Ar}), 128.1 (C_{Ar}), 96.7 (dd, *J* = 20.5, 9.5 Hz, C_{1a}), 94.2 (dd, *J* = 187.1, 17.6 Hz, C_{3b}), 87.3 (dd, *J* = 195.1, 18.3 Hz, C_{2b}), 86.3 (dd, *J* = 191.5, 18.3 Hz, C_{3a}), 86.2 (dd, *J* = 192.2, 19.1 Hz, C_{2a}), 85.3 (dd, *J* = 21.3, 8.8 Hz, C_{1b}), 75.1 (dd, *J* = 16.9, 5.9 Hz, C_{4b}), 74.3 (d, *J* = 2.9 Hz, C_{CH2OBn}), 70.4 (d, *J* = 8.1 Hz, C_{5b}), 69.0 (dd, *J* = 16.9, 8.1 Hz, C_{4a}), 66.5 (d, *J* = 5.1 Hz, C_{5a}), 66.4 (C_{6b}), 61.7 (d, *J* = 2.2 Hz, C_{6a}), 20.6 (C_{CH3}) ppm; HRMS (ESI+) for $C_{34}H_{34}F_4NaO_8S$ $[M + Na]^+$ calcd 701.1803 found 701.1802 (err 0.1 ppm).

Data for **29β**: colourless oil; R_f 0.40 (hexane/EtOAc 60:40); $[\alpha]_D^{23}$ +151 (c 0.70, $CHCl_3$); IR (neat) 2360 (w), 1731 (s), 1266 (s), 1039 (s), 1025 (s), 732 (s), 711 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 8.05 (2H, dd, *J* = 8.4, 1.3 Hz, H_{Ar}), 7.61 (1H, tt, *J* = 7.4, 1.3 Hz, H_{Ar}), 7.53 (2H, dd, *J* = 8.0, 1.6 Hz, H_{Ar}), 7.46 (2H, t, *J* = 8.1 Hz, H_{Ar}), 7.36–7.41 (4H, m, H_{Ar}), 7.28–7.36 (4H, m, H_{Ar}), 5.82 (1H, br dt, *J* = 5.6, 2.1 Hz, H_{4a}), 5.77 (1H, dt, *J* = 5.7, 2.2 Hz, H_{1b}), 4.98 (1H, d, *J* = 11.1 Hz, H_{CH2OBn}), 4.67 (1H, d, *J* = 11.3 Hz, H_{CH2OBn}), 4.63–5.10 (4H, m, H_{3b}, H_{2b}, H_{3a}, H_{2a}),

4.47 (1H, dd, *J* = 10.0, 3.5 Hz, H_{5b}), 4.41 (1H, dd, *J* = 7.4, 3.8 Hz, H_{1a}), 4.15–4.24 (2H, m, $H_{6a,}$ H_{6b}), 4.16 (1H, dd, *J* = 11.4, 6.2 Hz, H_{6a}), 3.90 (1H, dd, *J* = 11.2, 3.9 Hz, H_{6b}), 3.81–3.95 (2H, m, H_{4b}, H_{5a}), 2.04 (3H, s, H_{CH3}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.7 (1F, dt, *J* = 51.7, 13.4 Hz, F_{2b}), -192.6 (1F, dq, *J* = 54.5, 13.3 Hz, F_{3b}), -200.7 (1F, dtd, *J* = 45.5, 15.2, 5.2 Hz, F_{3a}), -206.2 (1F, br dt, *J* = 51.6, 14.3 Hz, F_{2a}) ppm; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -190.7 (1F, d, *J* = 13.4 Hz, F_{2b}), -192.6 (1F, d, *J* = 13.9 Hz, F_{3b}), -200.7 (1F, d, *J* = 13.9 Hz, F_{3a}), -206.2 (1F, d, *J* = 13.9 Hz, F_{2a}) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.3 ($C_{\underline{C}OCH3}$), 165.3 ($C_{\underline{C}OCH2Ph}$), 137.7 (C_{Ar}), 133.7 (C_{Ar}), 132.8 (C_{Ar}), 132.2 (C_{Ar}), 130.0 (C_{Ar}), 129.2 (C_{Ar}), 128.7 (C_{Ar}), 128.6 (C_{Ar}), 128.5 (C_{Ar}), 128.04 (C_{Ar}), 128.03 (C_{Ar}), 127.97 (C_{Ar}), 100.9 (dd, *J* = 22.8, 10.8 Hz, C_{1a}), 94.3 (dd, *J* = 186.9, 17.6 Hz, C_{3b}), 89.0 (dd, *J* = 194.1, 19.6 Hz, C_{2b}), 89.0 (dd, *J* = 187.9, 19.3 Hz, C_{3a}), 87.3 (dd, *J* = 195.5, 18.6 Hz, C_{2a}), 86.0 (dd, *J* = 21.5, 8.3 Hz, C_{1b}), 75.1 (dd, *J* = 16.9, 6.2 Hz, C_{4b}), 74.6 (d, *J* = 2.1 Hz, $C_{\underline{C}H2OBn}$), 70.3 (d, *J* = 5.5 Hz, C_{5a}), 70.2 (d, *J* = 7.9 Hz, C_{5b}), 68.7 (C_{6b}), 68.0 (dd, *J* = 16.7, 8.6 Hz, C_{4a}), 61.4 (d, *J* = 2.4 Hz, C_{6a}), 20.6 (C_{CH3}) ppm; HRMS (ESI+) for $C_{34}H_{34}F_4NaO_8S$ $[M + Na]^+$ calcd 701.1803 found 701.1809 (err -0.9 ppm).

4.5.3 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α/β-D-galactopyranosyl-(1,6)-phenyl 4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-1-thio-α-D-glucopyranose (**30**)

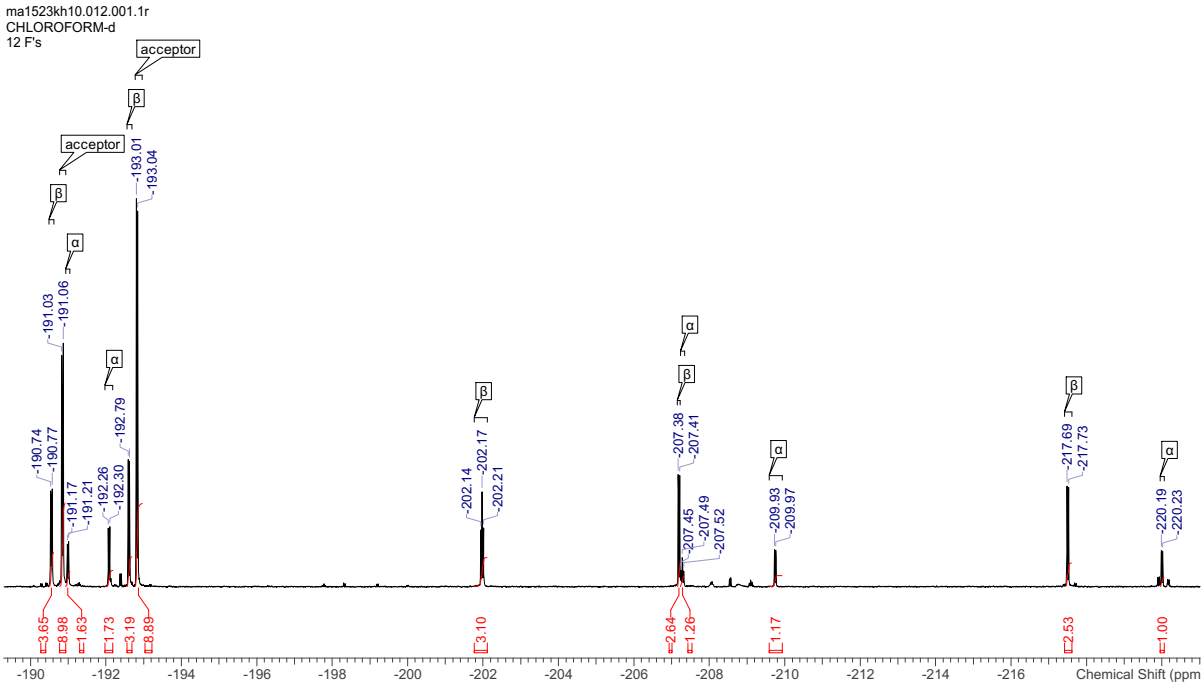
4.5.3.1 Glycosylation to **30** (Figure 2)



According to general procedure C, **12** (111 mg, 0.299 mmol, 1.0 equiv) was reacted at –30 ˚C for 4 h. The resultant crude material (α/β 1:2.53) was purified by flash column chromatography (25 g, hexane/EtOAc 100:0 to 60:40) to collect **30** as a mixture of α- and β-anomers as a colourless oil (62.7 mg, 0.108 mmol, 36% yield). An analytical sample was purified to separate the anomers using flash column chromatography (25 g, hexane/EtOAc 100:0 to 60:40).

4.5.3.2 Ratio determination, crude reaction mixture, ^{19}F{^{1}H} NMR, 376 MHz, $CDCl_3$

The ^{19}F{^{1}H} NMR of the crude reaction mixture shows a ratio of α/β 1:2.53, no hydrolysis of the trichloroacetimidate occurred as no peak corresponding to the hemiacetal **6** is present and no unreacted trichloroacetimidate **16** is observed in the crude reaction mixture.



4.5.3.3 Characterisation of the disaccharides (both anomer)

Data for **30α**: Colourless crystals; R_f 0.54 (hexane/EtOAc 60;40); $[\alpha]_D^{23}$ +210.8 (c 0.51, $CHCl_3$); IR (neat) 1731 (s), 1367 (w), 1233 (w), 1078 (s), 1027 (s), 825 (w), 736 (s), 692 (s), 603 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 7.45–7.54 (2H, m, H_{Ar}), 7.29–7.43 (8H, m, H_{Ar}), 5.75 (1H, br. dt, *J* = 5.8, 2.2 Hz, H_{1b}), 5.13 (1H, t, *J* = 4.1 Hz, H_{1a}), 5.00 (1H, ddt, *J* = 53.8, 13.7, 8.9 Hz, H_{3b}), 4.94 (1H, d, *J* = 10.9 Hz, H_{CH2OBn}), 4.69–4.98 (3H, m, H_{2b}, H_{2a}, H_{4a}), 4.63 (1H, d, *J* = 11.3 Hz, H_{CH2OBn}), 4.44–4.68 (1H, m, H_{3a}), 4.43 (1H, dt, *J* = 9.9, 3.7 Hz, H_{5b}), 4.22 (1H, dd, *J* = 11.4, 6.8 Hz, H_{6a}), 4.16 (1H, dd, *J* = 11.6, 6.4 Hz, H_{6a}), 3.74–3.88 (3H, m, $2H_{6b}$, H_{5a}), 3.67 (1H, ddd, *J* = 14.4, 10.0, 8.3 Hz, H_{4b}), 2.08 (3H, s, H_{CH3}) ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ -191.0 (1F, dtd, *J* = 50.8, 13.9, 1.8 Hz, F_{2b}), -192.1 (1F, dq, *J* = 54.4, 13.9 Hz, F_{3b}), -207.2 (1F, dddd, *J* = 48.3, 16.0, 13.9, 11.8, 3.6 Hz, F_{3a}), -209.7 (1F, dddd, *J* = 50.4, 13.6, 11.8, 3.6 Hz, F_{2a}), -220.0 (1F, dtd, *J* = 51.1, 27.2, 14.3 Hz, F_{4a}) ppm; $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$) δ -191.0 (1F, d, *J* = 13.6 Hz, F_{2b}), -192.1 (1F, d, *J* = 13.6 Hz, F_{3b}), -207.3 (1F, t, *J* = 13.9 Hz, F_{3a}), -209.7 (1F, d, *J* = 13.6 Hz, F_{2a}), -220.0 (1F, d, *J* = 14.7 Hz, F_{4a}) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.2 (C_{COCH3}), 137.2 (C_{Ar}), 132.8 (C_{Ar}), 132.1 (C_{Ar}), 129.2 (C_{Ar}), 128.5 (C_{Ar}), 128.2 (C_{Ar}), 128.2 (C_{Ar}), 128.1 (C_{Ar}), 96.6 (dd, *J* = 20.5, 9.3 Hz, C_{1a}), 94.2 (dd, *J* = 186.7, 17.6 Hz, C_{3b}), 87.330 (dd, *J* = 195.0, 17.9 Hz, C_{2b}), 87.333 (br dd, *J* = 177.4, 16.7 Hz, C_{4a}), 86.2 (br dt, *J* = 191.0, 18.5 Hz, C_{3a}), 85.7 (ddd, *J* = 191.9, 19.3, 2.9 Hz, C_{2a}), 85.2 (dd, *J* = 21.1, 8.5 Hz, C_{1b}), 75.1 (dd, *J* = 16.9, 6.2 Hz, C_{4b}), 74.3 (d, *J* = 3.1 Hz, C_{CH2OBn}), 70.3 (d, *J* = 7.4 Hz, C_{5b}), 66.50 (C_{6b}), 66.52 (dd, *J* = 17.9, 5.6 Hz, C_{5a}), 61.3 (dd, *J* = 6.2, 1.7 Hz, C_{6a}), 20.7 (C_{CH3}) ppm; HRMS (ESI+) for $C_{27}H_{29}F_5NaO_6S$ $[M + Na]^+$ calcd 599.1497 found 599.1511 (err -2.3 ppm).

Data for **30β**: Colourless oil; R_f 0.46 (hexane/EtOAc 60:40); $[\alpha]_D^{23}$ +192.5 (c 1.1, $CHCl_3$); IR (neat) 1743 (w), 1230 (w), 1040 (br, s), 908 (s), 729 (s), 698 (s), 609 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (COSY/HMBC/HSQC) δ 7.49–7.53 (2H, m, H_{Ar}), 7.28–7.41 (8H, m, H_{Ar}), 5.75 (1H, dt, *J* = 5.9, 2.3 Hz, H_{1b}), 4.96 (1H, d, *J* = 11.2 Hz, H_{CH2OBn}), 4.62–5.06 (4H, m, H_{3b}, H_{4a}, H_{2b}, H_{2a}), 4.65 (1H, d, *J* = 11.1 Hz, H_{CH2OBn}), 4.47–4.70 (1H, m, H_{3a}), 4.44 (1H, dd, *J* = 10.0, 3.9 Hz, H_{5b}), 4.39 (1H, dd, *J* = 7.3, 3.5 Hz, H_{1a}), 4.35 (1H, dd, *J* = 11.4, 6.4 Hz, H_{6a}), 4.23 (1H, dd, *J* = 11.3, 6.8 Hz, H_{6a}),

4.13 (1H, dt, *J* = 11.1, 1.7 Hz, H_{6b}), 3.87 (1H, dd, *J* = 11.0, 4.1 Hz, H_{6b}), 3.86 (1H, ddd, *J* = 14.3, 10.0, 8.4 Hz, H_{4b}), 3.67 (1H, dtd, *J* = 25.4, 6.3, 1.5 Hz, H_{5a}), 2.09 (3H, s, H_{CH3}) ppm; ^{19}F NMR (471 MHz, $CDCl_3$) δ -190.5 (1F, dtd, *J* = 50.4, 13.6, 1.8 Hz, F_{2b}), -192.6 (1F, dq, *J* = 54.1, 13.7 Hz, F_{3b}), -201.9 (1F, dqd, *J* = 47.3, 14.1, 6.4 Hz, F_{3a}), -207.2 (1F, dtt, *J* = 51.7, 14.0, 3.2 Hz, F_{2a}), -217.5 (1F, dtd, *J* = 50.1, 25.8, 15.4 Hz, F_{4a}) ppm; $^{19}F\{^1H\}$ NMR (471 MHz, $CDCl_3$) δ -190.5 (1F, d, *J* = 14.0 Hz, F_{2b}), -192.6 (1F, d, *J* = 13.6 Hz, F_{3b}), -201.9 (1F, t, *J* = 14.5 Hz, F_{3a}), -207.2 (1F, d, *J* = 13.9 Hz, F_{2a}), -217.5 (1F, d, *J* = 15.0 Hz, F_{4a}) ppm; $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.3 (C_{COCH3}), 137.7 (C_{Ar}), 132.7 (C_{Ar}), 132.2 (C_{Ar}), 129.2 (C_{Ar}), 128.5 (C_{Ar}), 128.0 (C_{Ar}), 128.0 (C_{Ar}), 127.9 (C_{Ar}), 100.4 (dd, *J* = 22.9, 10.7 Hz, C_{1a}), 94.2 (dd, *J* = 186.9, 17.6 Hz, C_{3b}), 88.9 (dt, *J* = 194.5, 18.4 Hz, C_{3a}), 88.4 (dd, *J* = 187.4, 19.6 Hz, C_{2a}), 87.2 (dd, *J* = 195.7, 18.4 Hz, C_{2b}), 85.9 (dd, *J* = 21.0, 8.3 Hz, C_{1b}), 86.1 (ddd, *J* = 187.2, 16.7, 9.1 Hz, C_{4a}), 75.2 (dd, *J* = 17.2, 6.2 Hz, C_{4b}), 74.5 (d, *J* = 2.4 Hz, C_{CH2OBn}), 70.0 (br d, *J* = 8.8 Hz, C_{5b}), 70.0 (dd, *J* = 18.1, 6.0 Hz, C_{5a}), 68.5 (C_{6b}), 61.0 (dd, *J* = 5.7, 2.4 Hz, C_{6a}), 20.6 (C_{CH3}) ppm; HRMS (ESI+) for $C_{27}H_{29}F_5NaO_6S$ $[M + Na]^+$ calcd 599.1497 found 599.1503 (err -1.0 ppm).

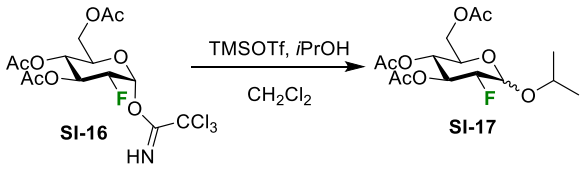
5 Control experiments

5.1 Control experiment: glycosylation of 3,4,6-tri-*O*-acetyl-2-deoxy-2-fluorogalactosyl trichloroacetimidate

5.1.1 Introduction

The Gilmour group reported the glycosidation of 2-deoxy-2-fluoro-3,4,6-tri-*O*-acetyl-D-glucopyranosyl trichloroacetimidate with 2-propanol at -30 ˚C for 2 h. Their reaction was done with 35 mg (77 μmol) of trichloroacetimidate, and they reported 22 mg of product, 81% yield (α/β = 1:1.7). In our hands, using our optimised protocol, when the reaction was executed with ~100 mg (~0.22 mmol) of trichloroacetimidate at -30 ˚C, the reaction never reached completion, even after 4-5 h. The α/β ratio could be reproduced at this temperature. In order to reach completion, the temperature was raised to -20 ˚C for 5 h. The reaction was performed twice and gave 85% yield (α/β ratio: 1/1.22) and 83% yield (α/β ratio: 1/1.15).

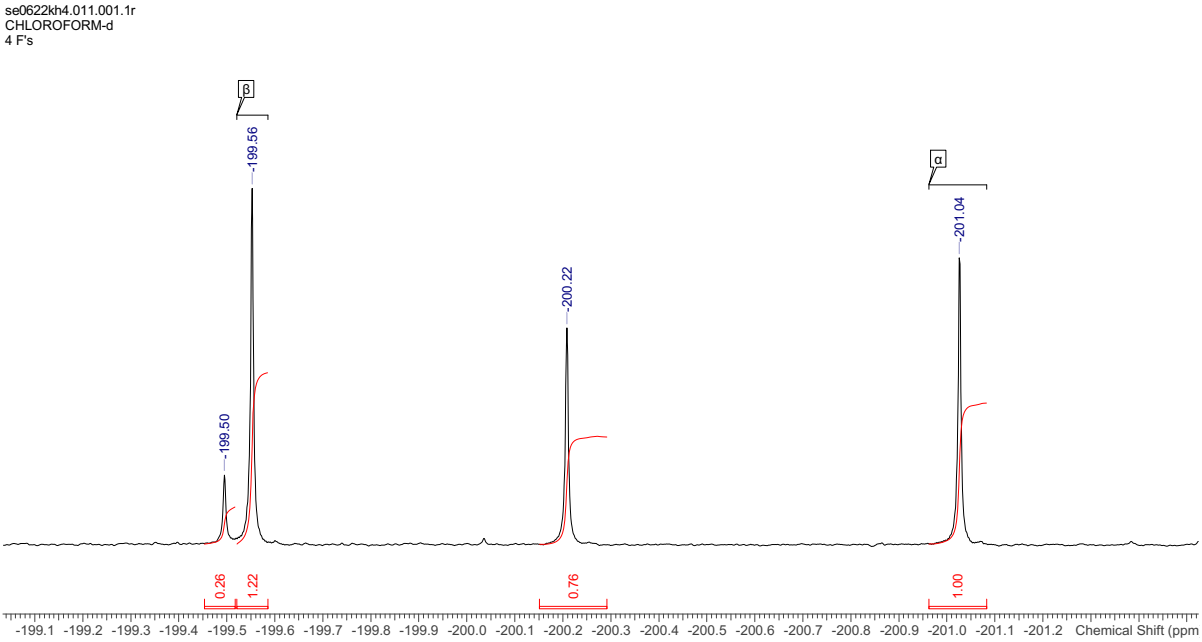
5.1.2 Glycosidation



According to general procedure B, **SI-16** (105 mg, 0.234 mmol, 1.0 equiv) was reacted at –20 ˚C for 5 h. The resultant crude material (α/β 1:1.22) was purified by flash column chromatography (10 g, hexane/EtOAc 70:30 to 60:40) to collect **SI-17** as a mixture of α- and β-anomers as a colourless oil (70 mg, 0.20 mmol, 85% yield). Anomers assignment was based on the chemical shift and coupling constant values of the anomeric protons.

5.1.3 Ratio determination, crude reaction mixture, $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

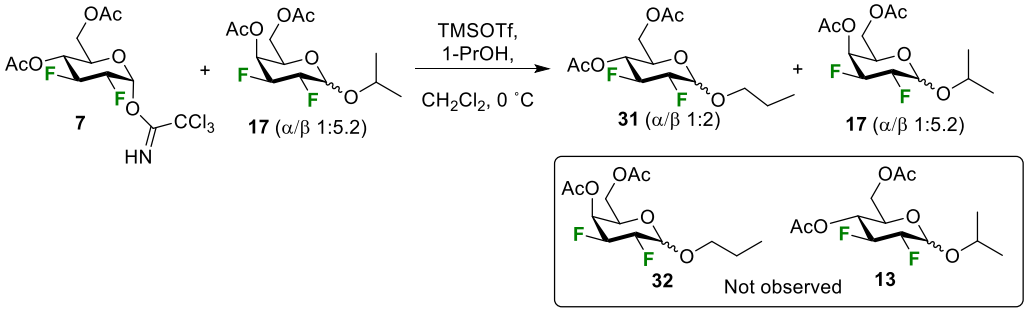
The $^{19}F\{^{1}H\}$ NMR of the crude reaction mixture shows a ratio of α/β 1:1.22, hydrolysis of the trichloroacetimidate was observed: the peaks at 199.50 and 200.22 ppm correspond to the α/β hemiacetal.



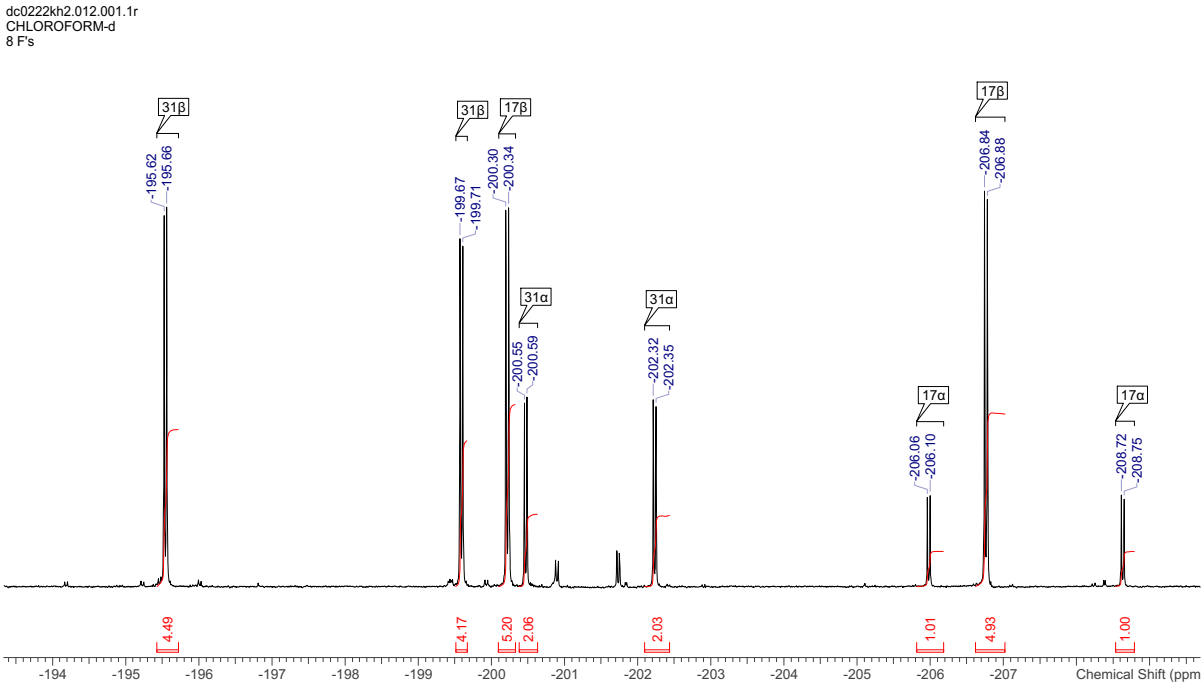
5.1.4 Characterisation of the glycosides as a mixture of both anomers

R_f 0.56 (hexane/EtOAc 50:50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (1H, dt, *J* = 11.8, 9.5 Hz, $H_{3\alpha}$), 5.32 (1H, dt, *J* = 14.5, 9.3 Hz, $H_{3\beta}$), 5.16 (1H, d, *J* = 3.9 Hz, $H_{1\alpha}$), 5.00 (1H, t, *J* = 9.7 Hz, $H_{4\beta}$), 5.02 (1H, t, *J* = 9.7 Hz, $H_{4\alpha}$), 4.63 (1H, dd, *J* = 7.7, 2.8 Hz, $H_{1\beta}$), 4.47 (1H, ddd, *J* = 49.6, 9.9, 4.2 Hz, $H_{2\alpha}$), 4.28 (1H, d, *J* = 4.3 Hz, H_6), 4.25 (1H, d, *J* = 4.3 Hz, H_6), 4.26 (1H, ddd, *J* = 51.0, 8.9, 7.7 Hz, $H_{2\beta}$), 4.08 - 4.15 (3H, m, $H_{6\alpha}$, $H_{6\beta}$, $H_{5\alpha}$), 4.02 (1H, spt, *J* = 6.2 Hz, $H_{CH\textit{i}Pr(\beta)}$), 3.94 (1H, spt, *J* = 6.2 Hz, $H_{CH\textit{i}Pr(\alpha)}$), 3.71 (1H, ddd, *J* = 10.1, 5.1, 2.4 Hz, $H_{5\beta}$), 2.09 (3H, s, $H_{COCH3(\alpha)}$), 2.08 (3H, s, $H_{COCH3(\beta)}$), 2.07 (3H, s, $H_{COCH3(\alpha)}$), 2.05 (3H, s, $H_{COCH3(\beta)}$), 2.05 (3H, s, $H_{COCH3(\alpha)}$), 2.04 (3H, s, $H_{COCH3(\beta)}$), 1.29 (6H, d, *J* = 6.2 Hz, $H_{CH3\textit{i}Pr(\alpha+\beta)}$), 1.23 (3H, d, *J* = 6.1 Hz, $H_{CH3\textit{i}Pr(\beta)}$), 1.23 (3H, d, *J* = 6.2 Hz, $H_{CH3\textit{i}Pr(\alpha)}$) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -199.6 (1F, ddd, *J* = 50.7, 14.3, 2.2 Hz, $F_{2\beta}$), -201.0 (1F, dd, *J* = 49.6, 11.9 Hz, $F_{2\alpha}$) ppm; $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -199.6 (1F, s, $F_{2\beta}$), -201.0 (1F, s, $F_{2\alpha}$) ppm; $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 170.63 ($C_{C=O}$), 170.61 ($C_{C=O}$), 170.1 ($C_{C=O}$), 169.7 ($C_{C=O}$), 169.5 ($C_{C=O}$), 99.0 (d, *J* = 22.7 Hz, $C_{1\beta}$), 94.6 (d, *J* = 20.5 Hz, $C_{1\alpha}$), 89.4 (d, *J* = 190.7 Hz, $C_{2\beta}$), 87.0 (d, *J*=195.1 Hz, $C_{2\alpha}$), 72.98 (d, *J* = 19.8 Hz, $C_{3\beta}$), 72.97 ($C_{CH\textit{i}Pr(\beta)}$), 72.0 ($C_{CH\textit{i}Pr(\alpha)}$), 71.7 ($C_{5\beta}$), 70.9 (d, *J* = 19.8 Hz, $C_{3\alpha}$), 68.4 (br d, *J* = 7.3 Hz, $C_{4\beta}$), 68.3 (d, *J* = 6.6 Hz, $C_{4\alpha}$), 67.2 ($C_{5\alpha}$), 62.0 ($C_{6\beta}$), 61.9 ($C_{6\alpha}$), 23.2 ($C_{CH3\textit{i}Pr(\beta)}$), 23.1 ($C_{CH3\textit{i}Pr(\alpha)}$), 21.8 ($C_{CH3\textit{i}Pr(\beta)}$), 21.7 ($C_{CH3\textit{i}Pr(\alpha)}$), 20.8 ($C_{CH3(\alpha)}$), 20.71 ($C_{CH3(\beta)}$), 20.68 ($C_{CH3(\alpha+\beta)}$), 20.61 ($C_{CH3(\alpha)}$), 20.57 ($C_{CH3(\beta)}$) ppm. Data in agreement with literature.[1]

5.2 Control experiment in Scheme 2



The trichloroacetimidate **7** (119 mg, 0.289 mmol, 1.0 equiv) and isopropyl glycoside **17** (α/β 1:5.2) (90 mg, 0.289 mmol, 1.0 equiv) were co-evaporated together with redistilled toluene (3 ×) and redistilled CH_2Cl_2 (1 ×), dried under high vacuum. Freshly activated molecular sieves (3 Å) were added, the mixture was dissolved in redistilled CH_2Cl_2 under argon. The mixture was stirred at room temperature for 30 min. The reaction vessel was cooled to 0 ˚C, 1-propanol (52 µL, 0.694 mmol, 2.4 equiv) and TMSOTf (21 µL, 0.116 mmol, 0.4 equiv) were added and the reaction mixture was stirred for 4 h at 0 ˚C. The reaction was followed by $^{19}F\{^1H\}$ NMR. After completion, the mixture was diluted with CH_2Cl_2, quenched by the addition of NEt_3 (1.0 mL), and filtered through a pad of Celite. The solvents were removed under reduced pressure, and the crude product was purified by flash column chromatography (10 g, hexane/EtOAc 80:20 to 60:40). The 4 products were recovered as a mixture (179 mg, 0.578 mmol, quant.), **31** (α/β 1:2) and **17** (α/β 1:5.2). The ratios were obtained by $^{19}F\{^1H\}$ NMR of the crude reaction mixture with a delay time (D1) of 3 s.



Data for propyl 4,6-di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α-D-glucopyranoside **31α**: Colourless oil; R_f 0.50 (hexane/EtOAc 60:40); IR (neat) 2966 (w), 1747 (s), 1370 (w), 1236 (s), 1033 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.16 (1H, ddd, *J* = 13.5, 10.2, 9.1 Hz, H_4), 5.08 (1H, t, *J* = 3.6 Hz, H_1), 4.92 (1H, ddt, *J* = 54.3, 13.2, 8.8 Hz, H_3), 4.58 (1H, dddd, *J* = 50.0, 13.1, 8.9, 3.8 Hz, H_2), 4.25 (1H, dd, *J* = 12.5, 4.6 Hz, H_6), 4.11 (1H, dt, *J* = 12.3, 2.0 Hz, H_6), 3.96 (1H, ddd, *J* = 10.3, 4.7, 2.3 Hz, H_5), 3.68 (1H, dtd, *J* = 9.5, 6.7, 0.6 Hz, H_{CH2OPr}), 3.50 (1H, dt, *J* = 9.6, 6.5 Hz,

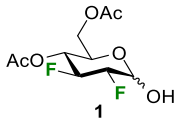
H_{CH2OPr}), 2.13 (3H, s, H_{CH3}), 2.10 (3H, s, H_{CH3}), 1.68 (2H, sxt, *J* = 7.2 Hz, H_{CH2OPr}), 0.97 (3H, t, *J* = 7.4 Hz, H_{CH3OPr}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -200.6 (1F, dq, *J* = 54.3, 13.1 Hz, F_3), -202.3 (1F, dt, *J* = 50.0, 13.4 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -200.6 (1F, d, *J* = 13.4 Hz, F_3), -202.3 (1F, d, *J* = 13.4 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.6 (C_{COCH3}), 169.4 (C_{COCH3}), 96.2 (dd, *J* = 20.2, 9.9 Hz, C_1), 90.1 (dd, *J* = 187.8, 19.8 Hz, C_3), 87.6 (dd, *J* = 194.4, 16.9 Hz, C_2), 70.7 (C_{CH2OPr}), 68.0 (dd, *J* = 18.3, 7.3 Hz, C_4), 67.0 (d, *J* = 6.6 Hz, C_5), 61.7 (C_6), 22.6 (C_{CH2OPr}), 20.68 (C_{COCH3}), 20.67 (C_{COCH3}), 10.5 (C_{CH3OPr}) ppm; HRMS (ESI+) for $C_{13}H_{20}F_2NaO_6$ $[M + Na]^+$ calcd 333.1120 found 333.1122.

Data for propyl 4,6-di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-β-D-glucopyranoside **31β**: Colourless crystals; R_f 0.43 in hexane/EtOAc 60:40; $[\alpha]_D^{23}$ = -24.3 (c 2.64, $CHCl_3$); IR (neat) 2967 (w), 1723 (s), 1372 (w), 1234 (s), 1068 (s), 1028 (s), 826 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.18 (1H, dt, *J* = 12.8, 9.5 Hz, H_4), 4.65 (1H, dddd, *J* = 52.6, 15.7, 9.3, 8.2 Hz, H_3), 4.51 (1H, dt, *J* = 7.7, 3.5 Hz, H_1), 4.42 (1H, dddd, *J* = 50.6, 14.9, 8.2, 7.8 Hz, H_2), 4.27 (1H, dd, *J* = 12.3, 4.9 Hz, H_6), 4.14 (1H, ddd, *J* = 12.2, 2.6, 1.5 Hz, H_6), 3.87 (1H, dt, *J* = 9.4, 6.7 Hz, H_{CH2OPr}), 3.61 (1H, dddd, *J* = 10.1, 4.9, 2.6, 1.2 Hz, H_5), 3.54 (1H, dt, *J* = 9.4, 6.8 Hz, H_{CH2OPr}), 2.12 (3H, s, H_{CH3}), 2.09 (3H, s, H_{CH3}), 1.67 (2H, sxt, *J* = 7.2 Hz, H_{CH2OPr}), 0.95 (3H, t, *J* = 7.4 Hz, H_{CH3OPr}) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -195.6 (1F, dq, *J* = 52.5, 13.6 Hz, F_3), -199.7 (1F, dtd, *J* = 50.7, 15.0, 3.5 Hz, F_2) ppm; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -195.6 (1F, d, *J* = 13.4 Hz, F_3), -199.7 (1F, d, *J* = 13.9 Hz, F_2) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 170.7 (C_{COCH3}), 169.2 (C_{COCH3}), 99.9 (dd, *J* = 23.1, 10.6 Hz, C_1), 92.1 (dd, *J* = 190.0, 19.8 Hz, C_3), 89.8 (dd, *J* = 190.0, 18.3 Hz, C_2), 72.2 (C_{CH2OPr}), 70.8 (d, *J* = 8.1 Hz, C_5), 68.0 (dd, *J* = 18.7, 7.7 Hz, C_4), 61.7 (C_6), 22.7 (C_{CH2OPr}), 20.7 (C_{COCH3}), 20.6 (C_{COCH3}), 10.2 (C_{CH3OPr}) ppm; HRMS (ESI+) for $C_{13}H_{20}F_2NaO_6$ $[M + Na]^+$ calcd 333.1120 found 333.1124 (err -1.3 ppm).

6 Copies of spectra of the novel compounds

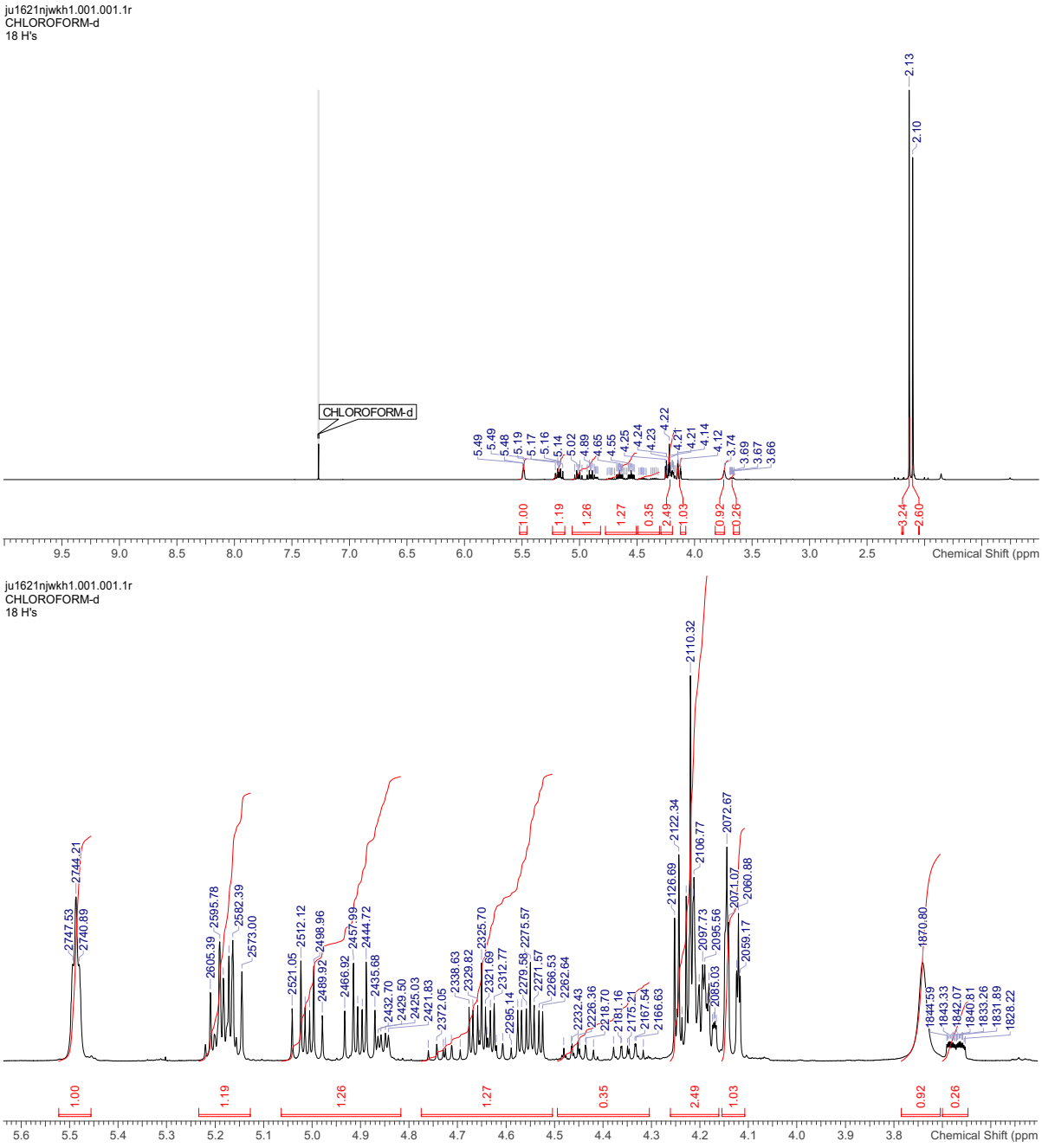
6.1 Copies of the spectra of the precursors

6.1.1 4,6-Di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-D-glucopyranose (**1**)

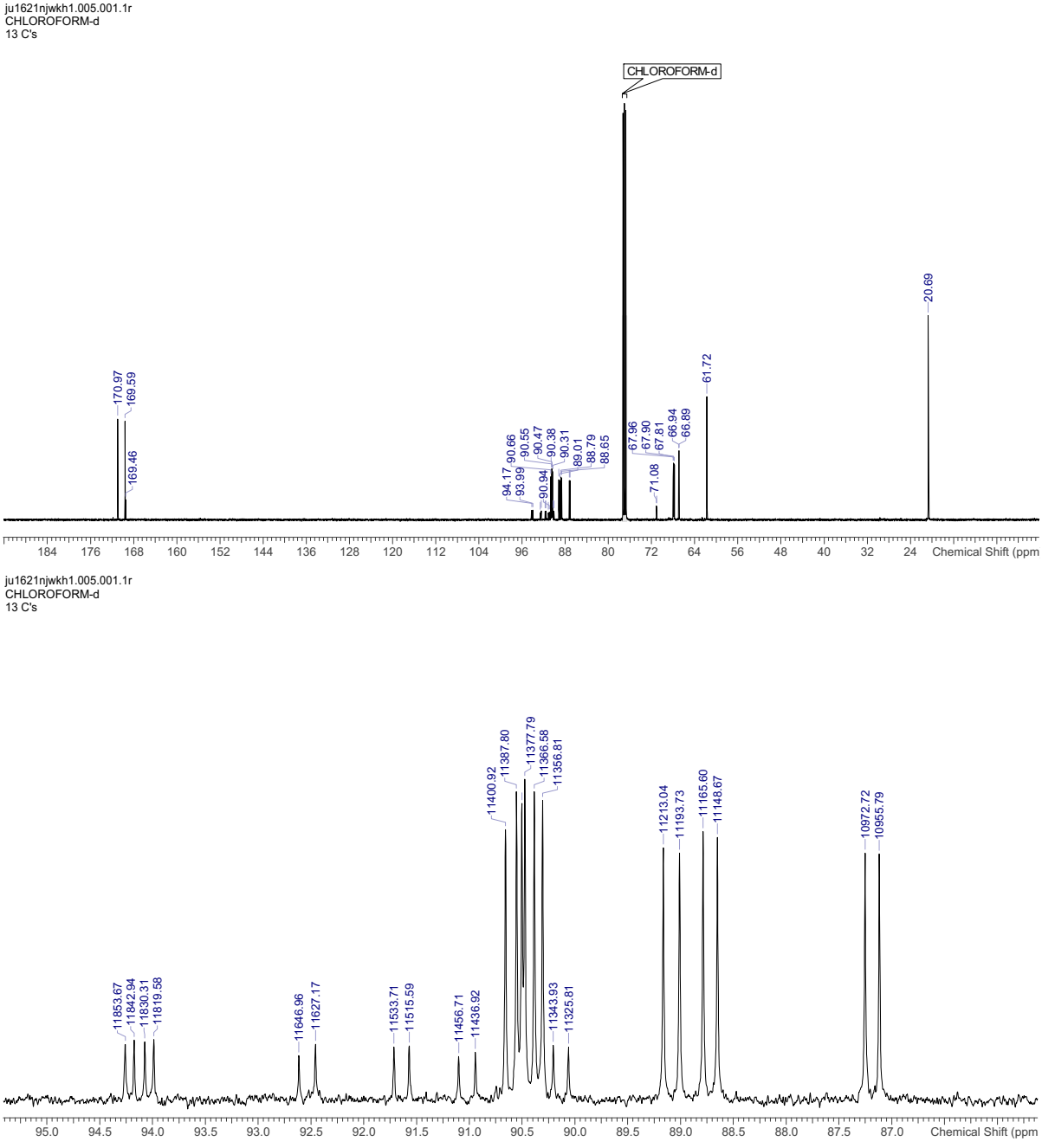


1

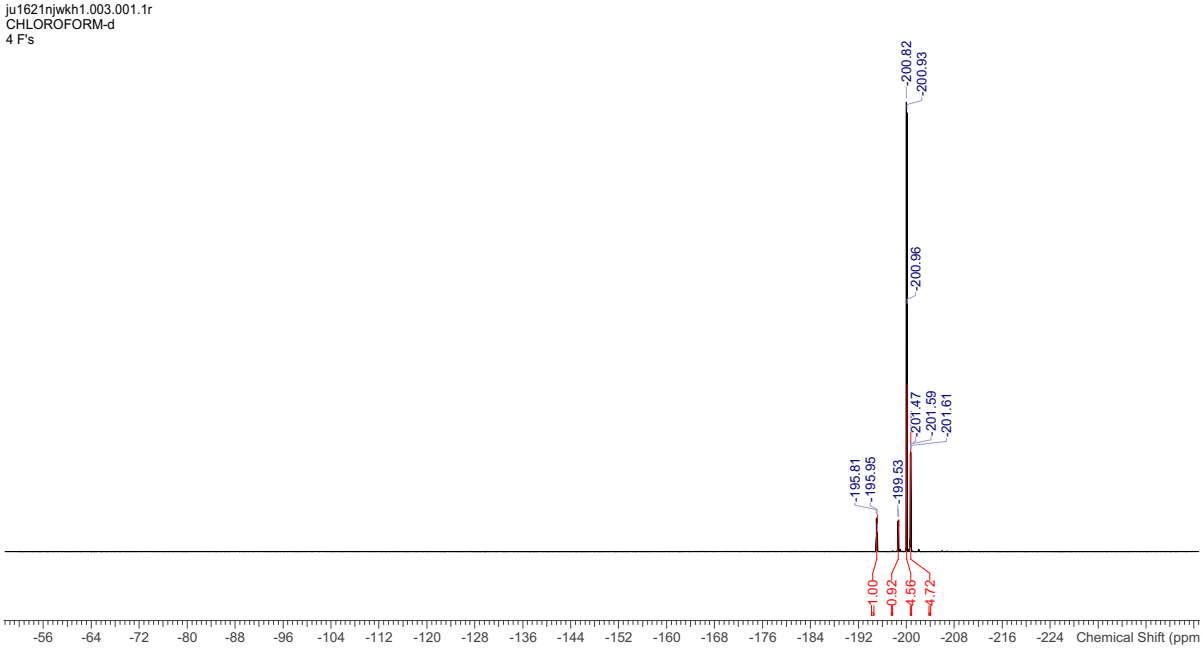
6.1.1.1 ^{1}H NMR, 500 MHz, $CDCl_3$

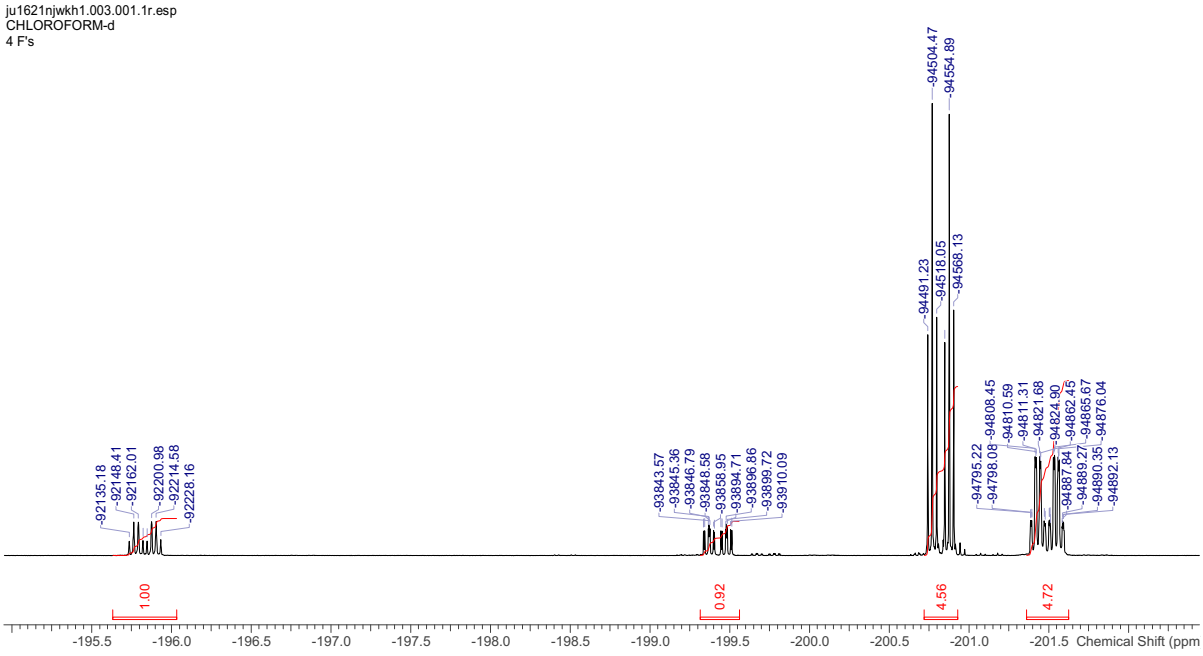


6.1.1.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

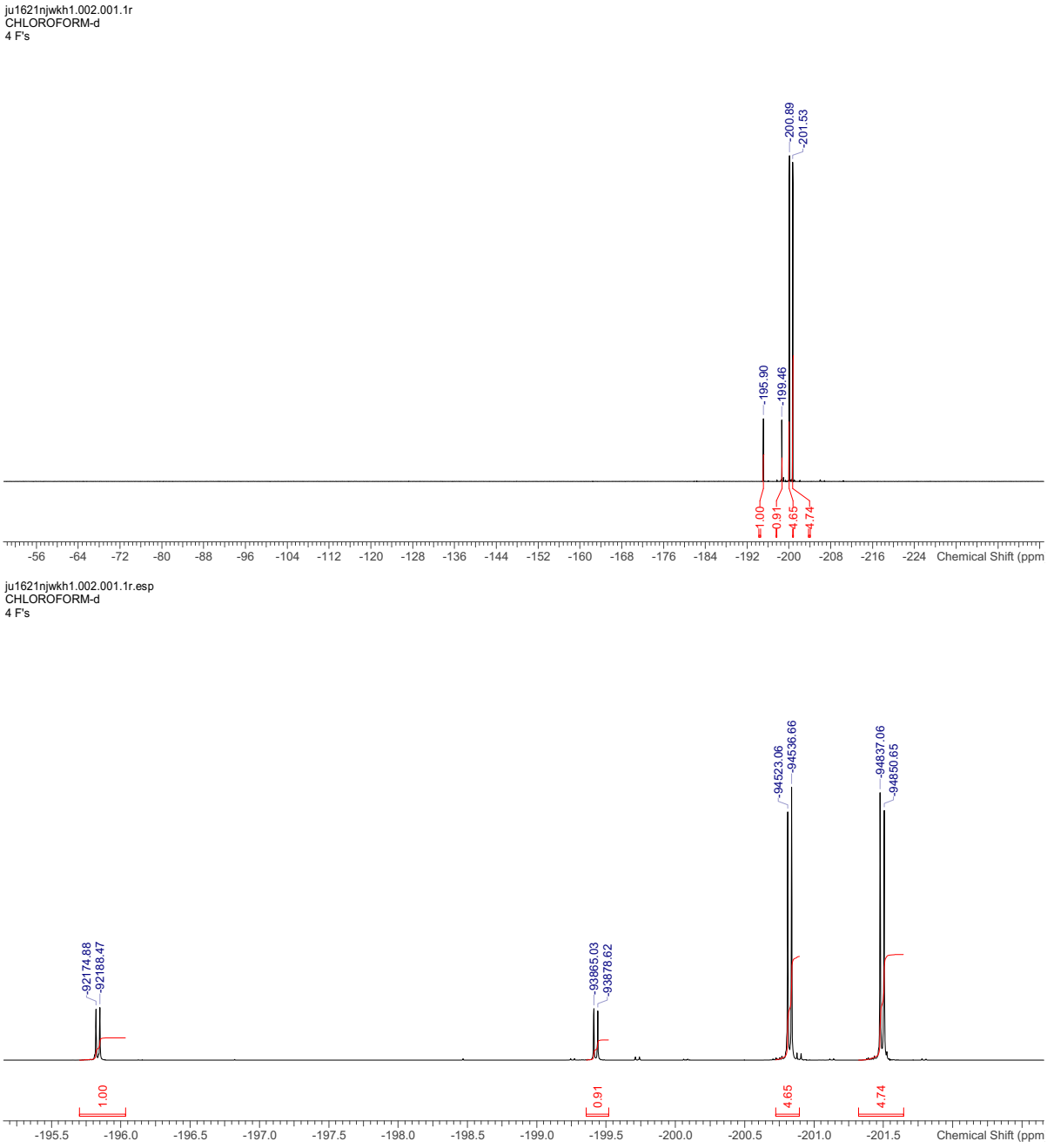


6.1.1.3 ^{19}F NMR, 471 MHz, $CDCl_3$

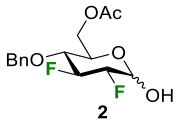




6.1.1.4 $^{19}F\{^{1}H\}$ NMR, 471 MHz, $CDCl_3$

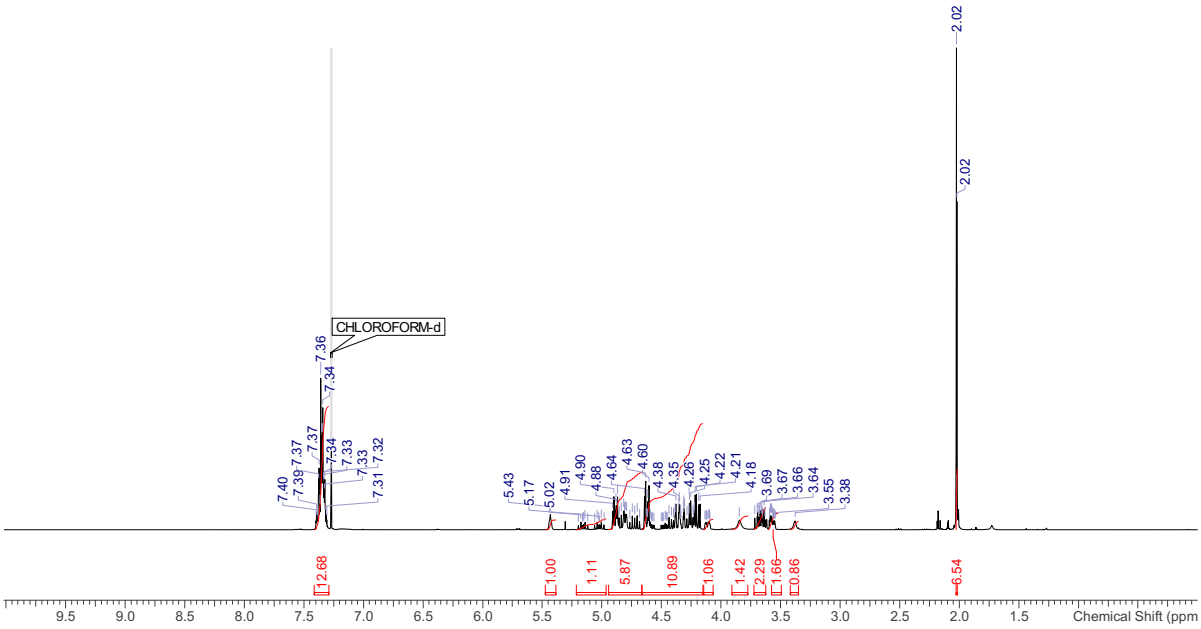


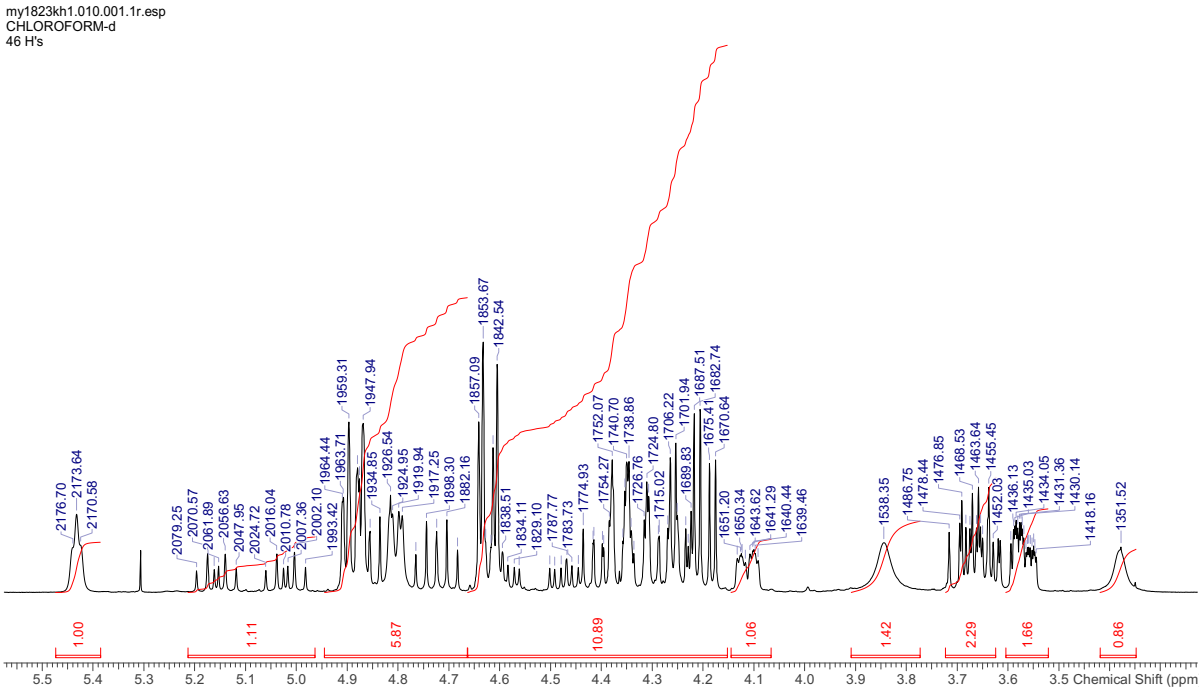
6.1.2 6-*O*-Acetyl-4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-D-glucopyranose (**2**)



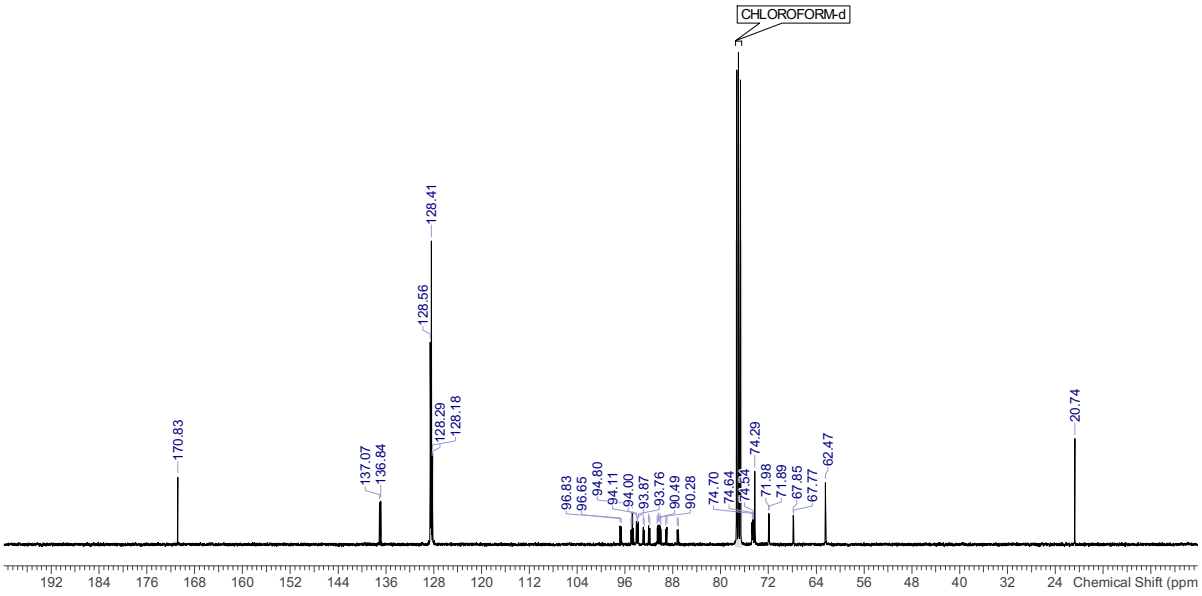
2

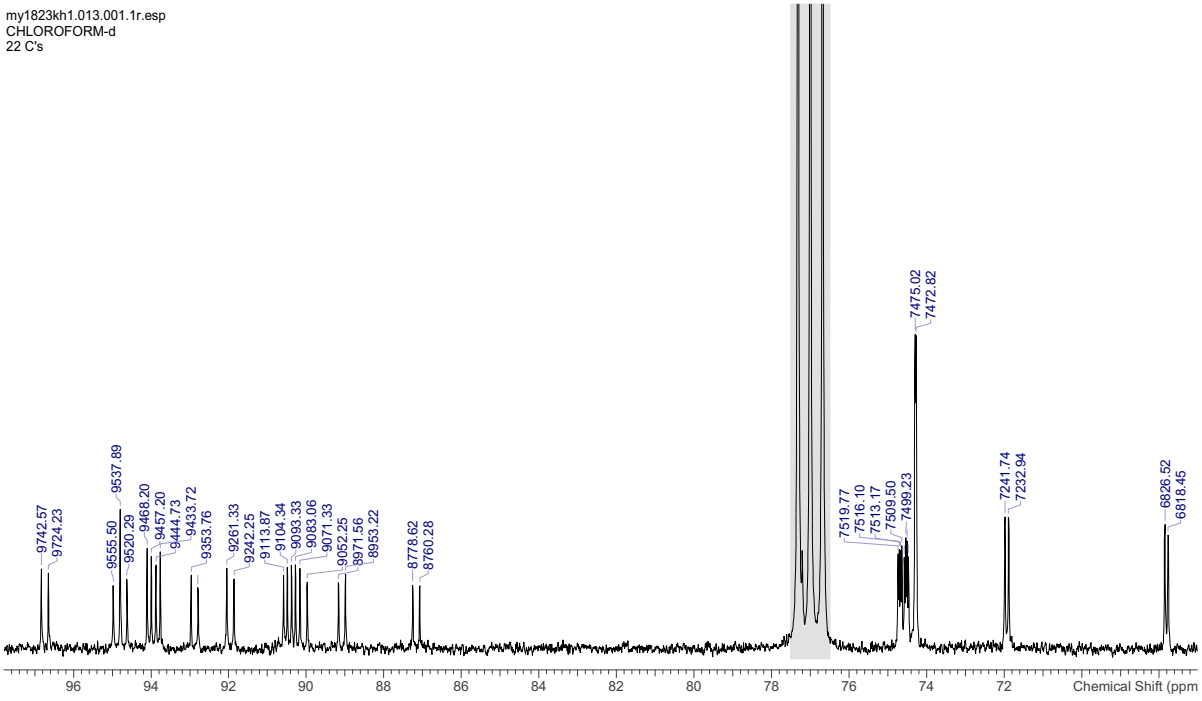
6.1.2.1 ^{1}H NMR, 400 MHz, $CDCl_3$





6.1.2.2 $^{13}C\{1H\}$ NMR, 101 MHz, $CDCl_3$





6.1.2.3 ^{19}F NMR, 376 MHz, $CDCl_3$

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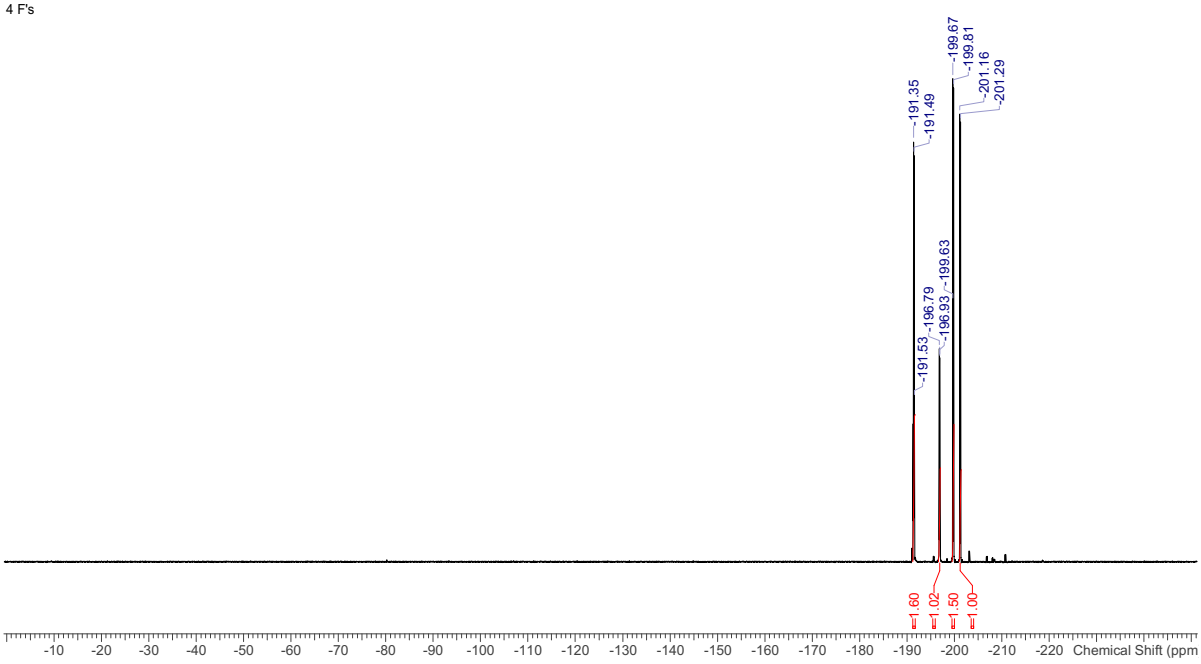
CHLOROFORM-d
4 F's



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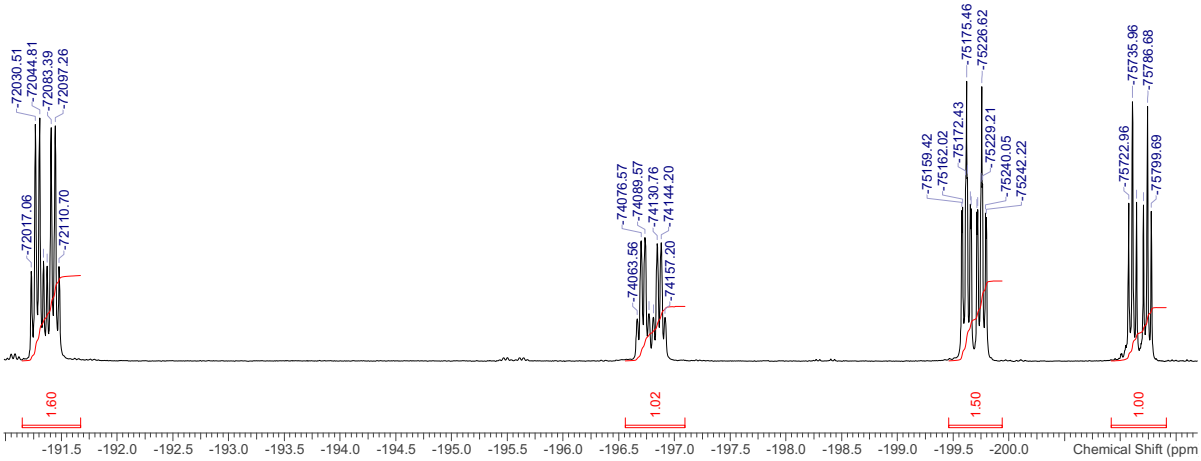
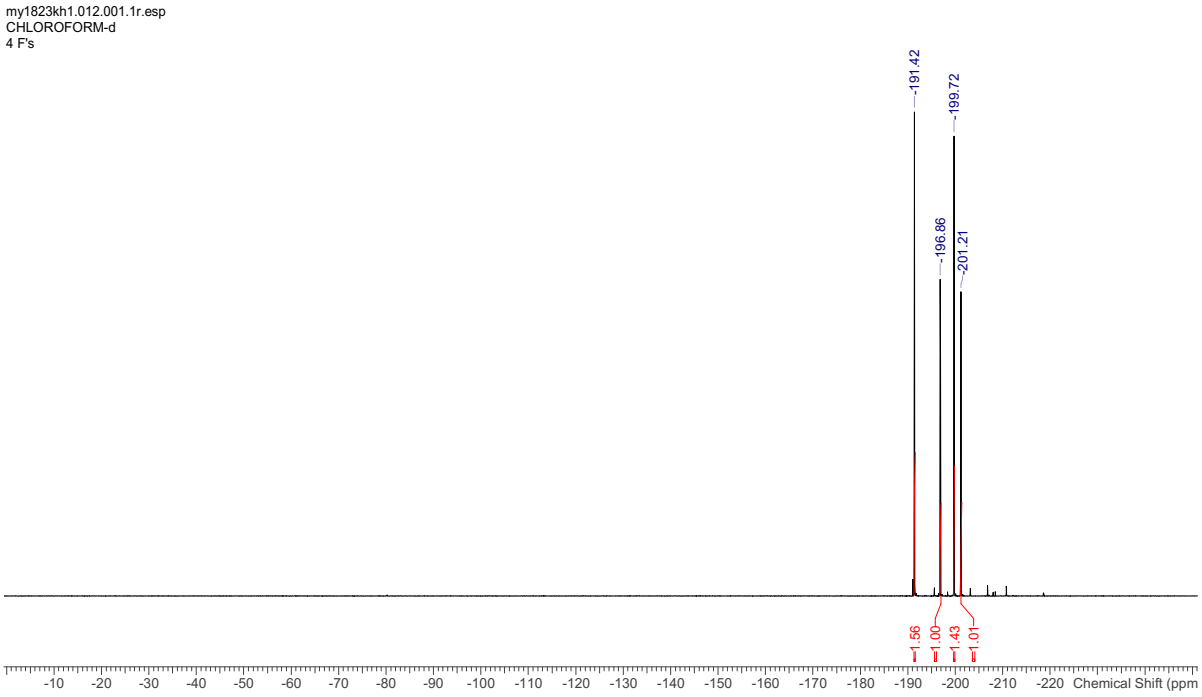
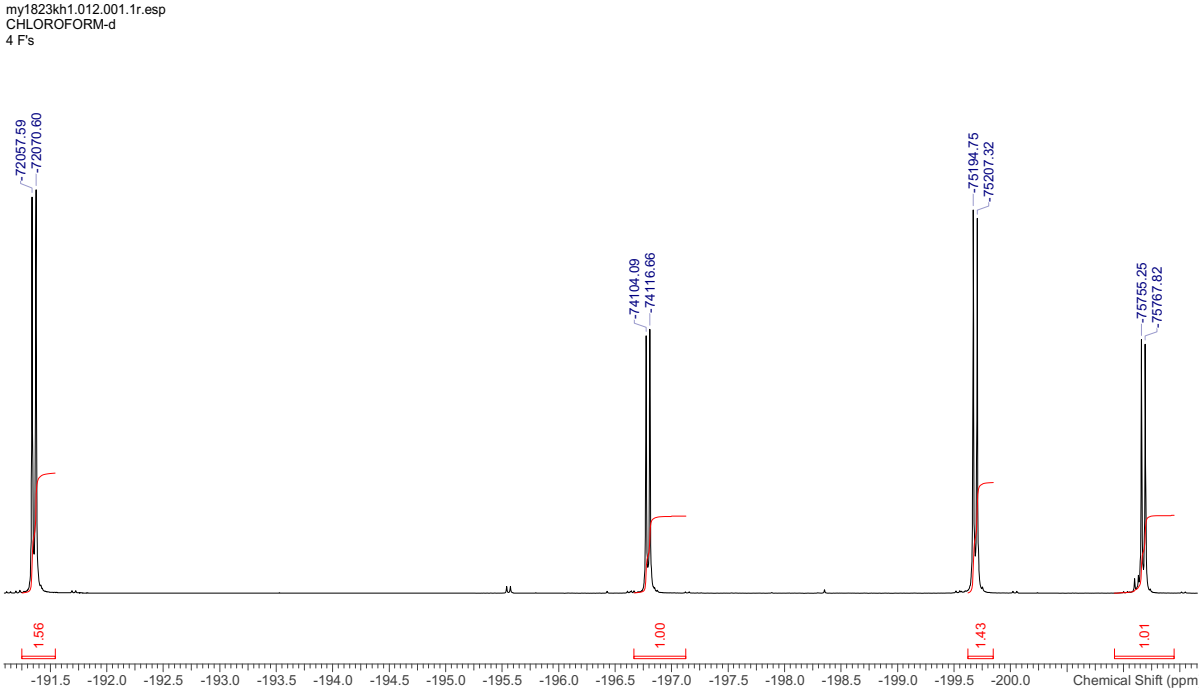
CHLOROFORM-d
4 F's

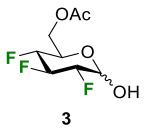


6.1.2.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$





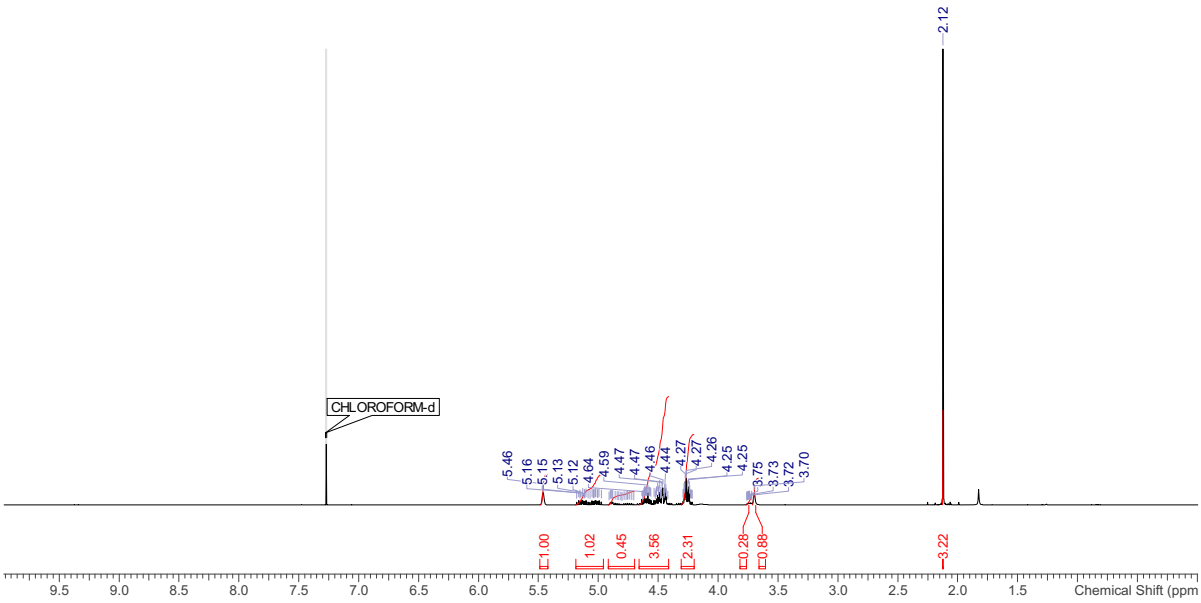
6.1.3 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-D-glucopyranose (**3**)



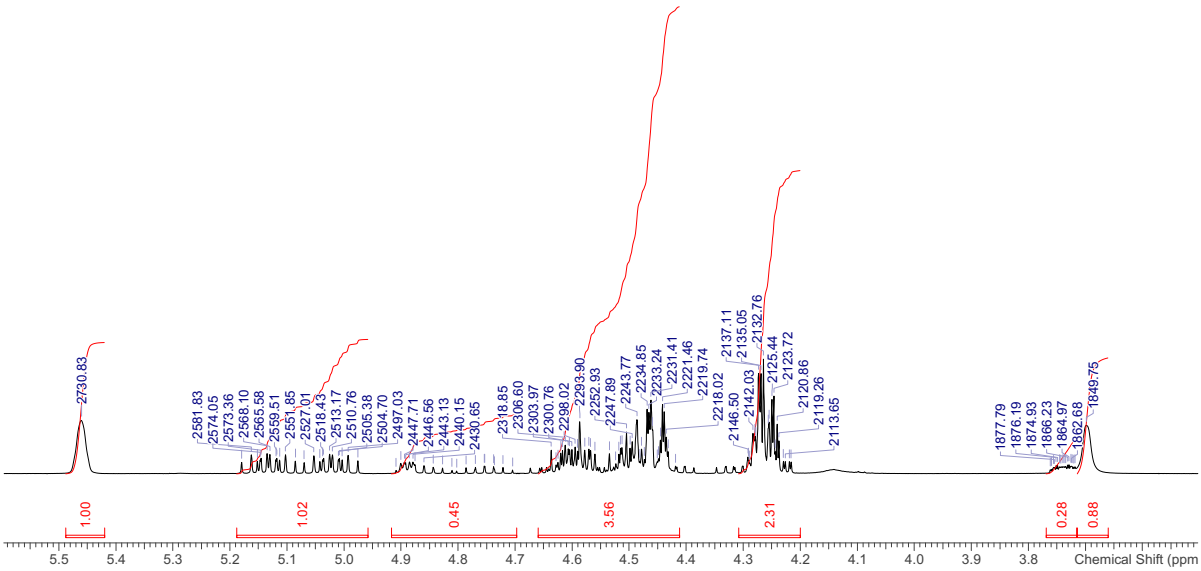
3

6.1.3.1 ^{1}H NMR, 500 MHz, $CDCl_3$

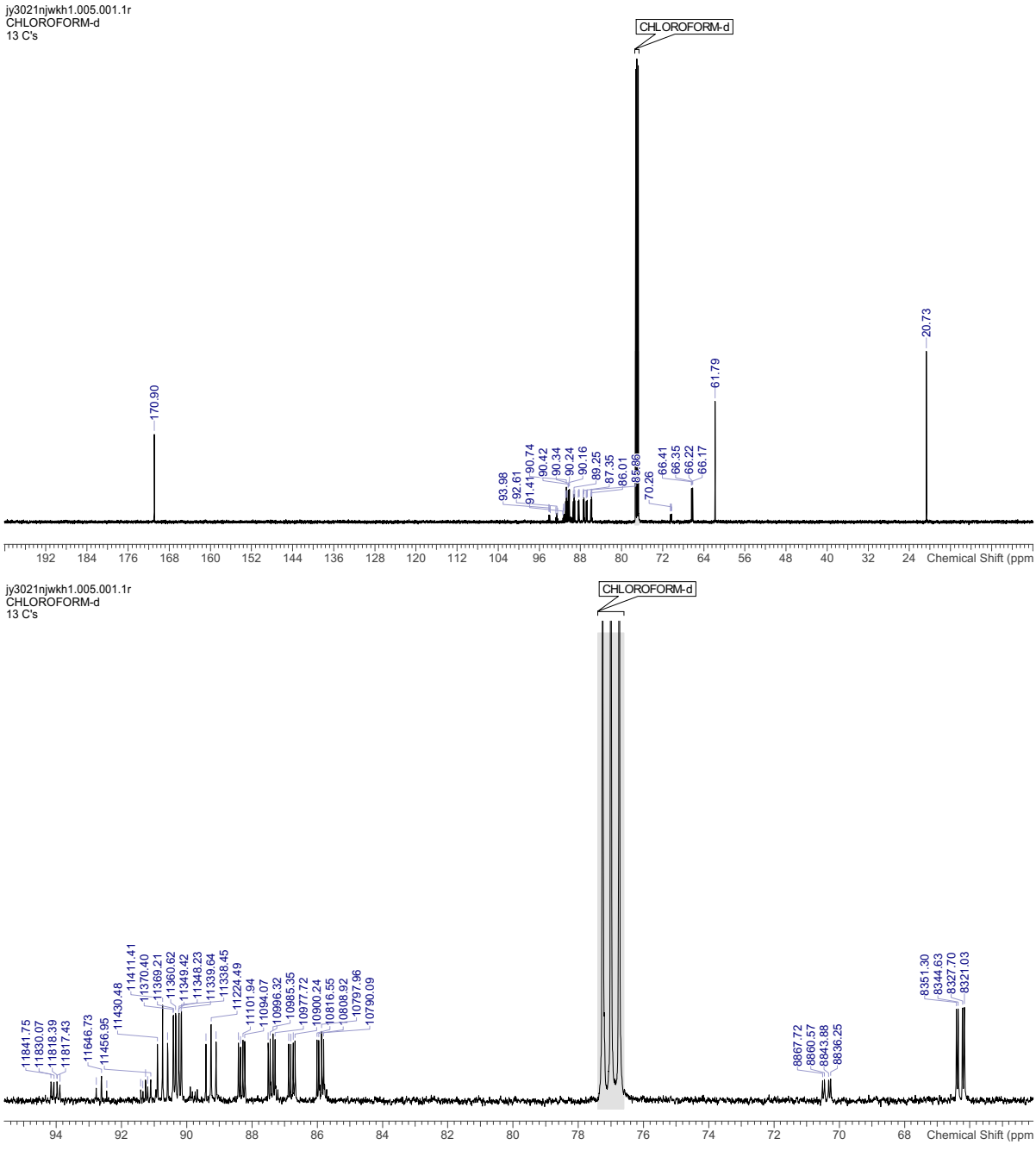
jy3021njwkh1.001.001.1r
CHLOROFORM-d
15 H's



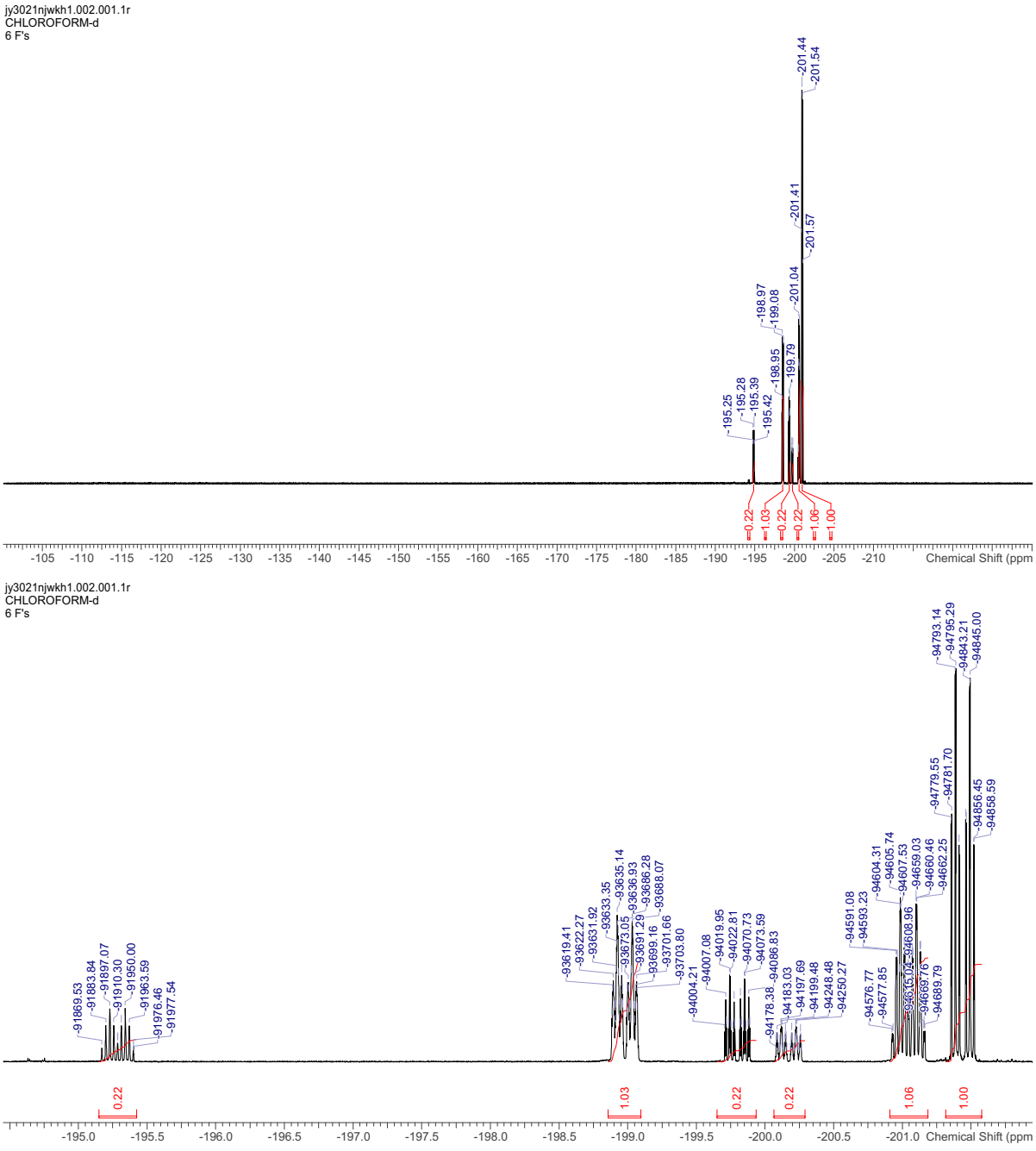
jy3021njwkh1.001.001.1r
CHLOROFORM-d
15 H's



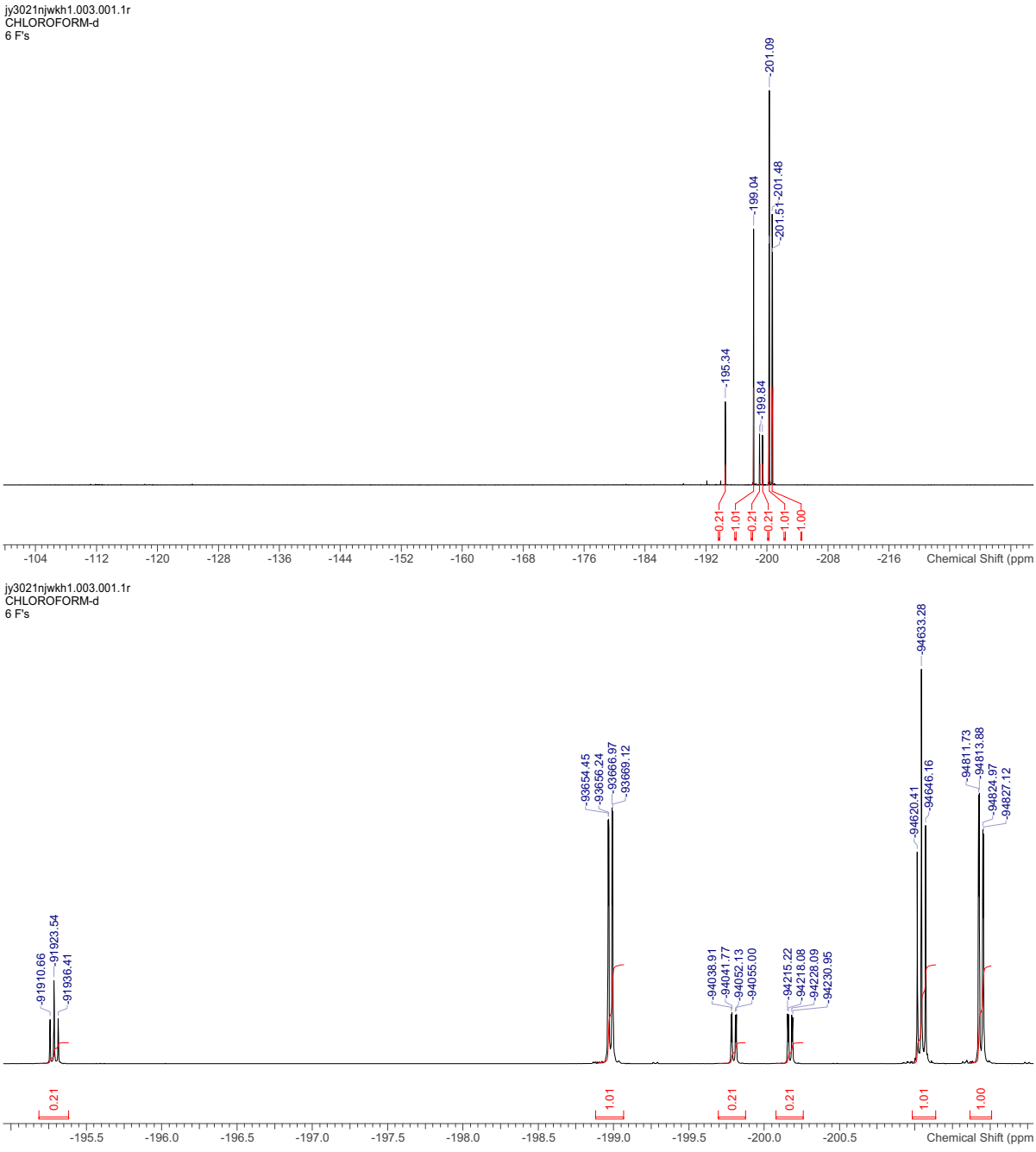
6.1.3.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$



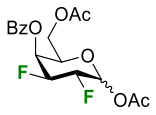
6.1.3.3 ^{19}F NMR, 471 MHz, $CDCl_3$



6.1.3.4 $^{19}F\{^{1}H\}$ NMR, 471 MHz, $CDCl_3$



6.1.4 1,6-Di-*O*-acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α/β-D-galactopyranoside (**SI-5**)



SI-5

6.1.4.1 ^{1}H NMR, 400 MHz, $CDCl_3$

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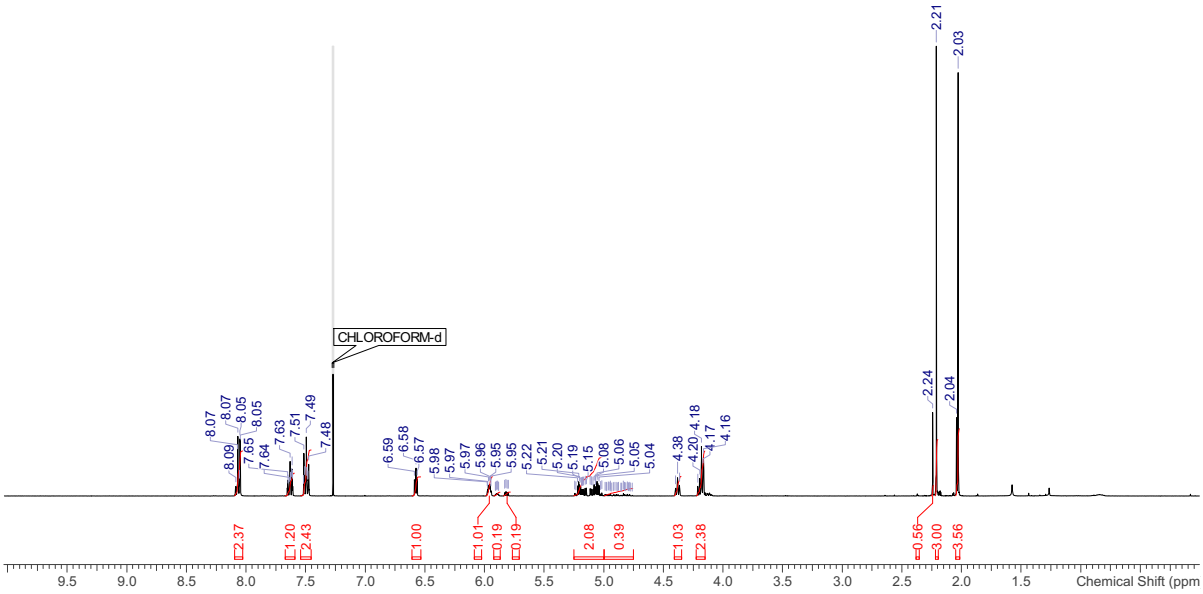
CHLOROFORM-d
23 H's



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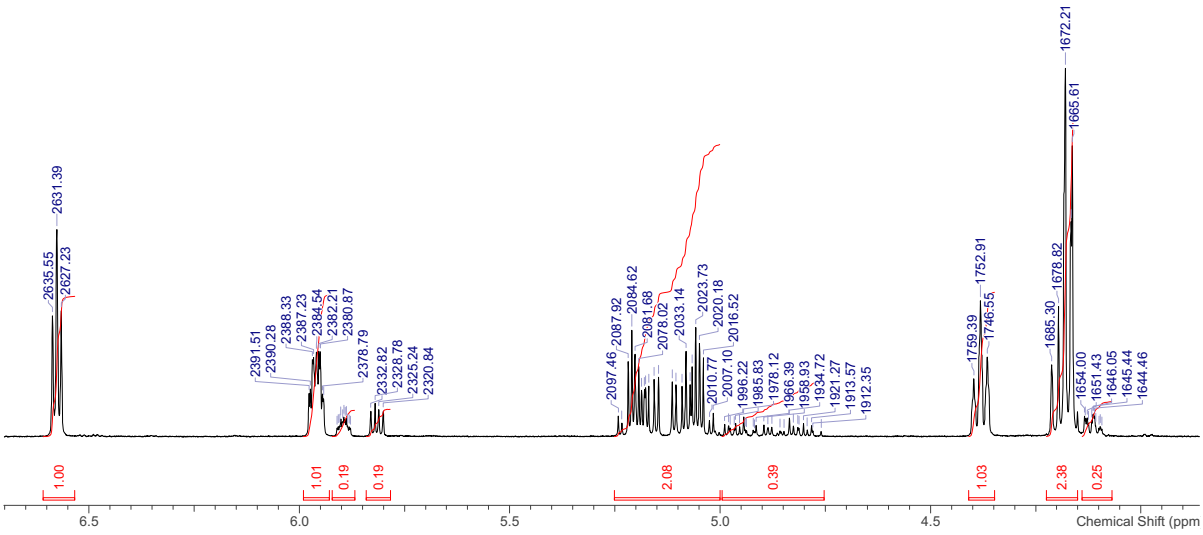
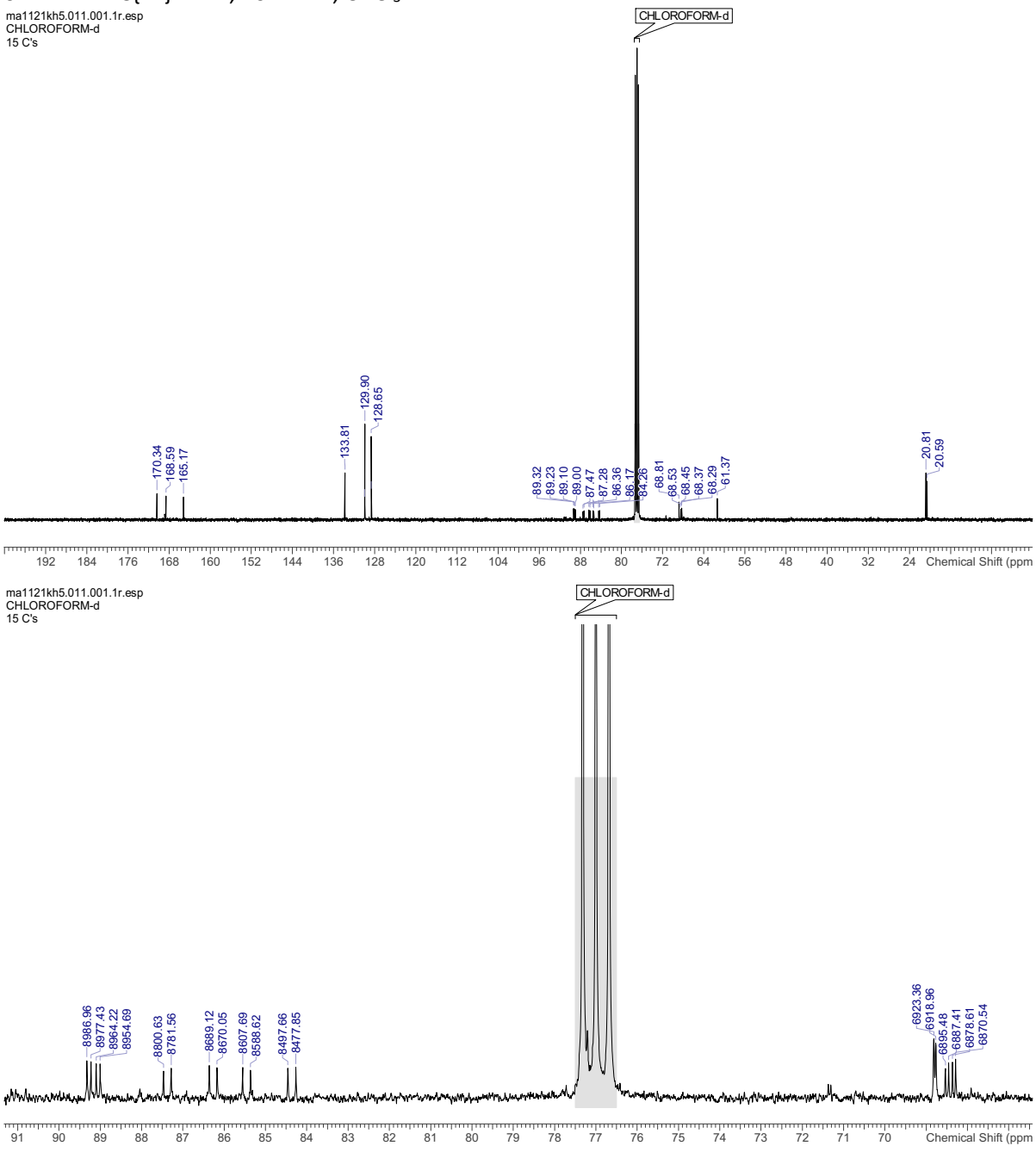
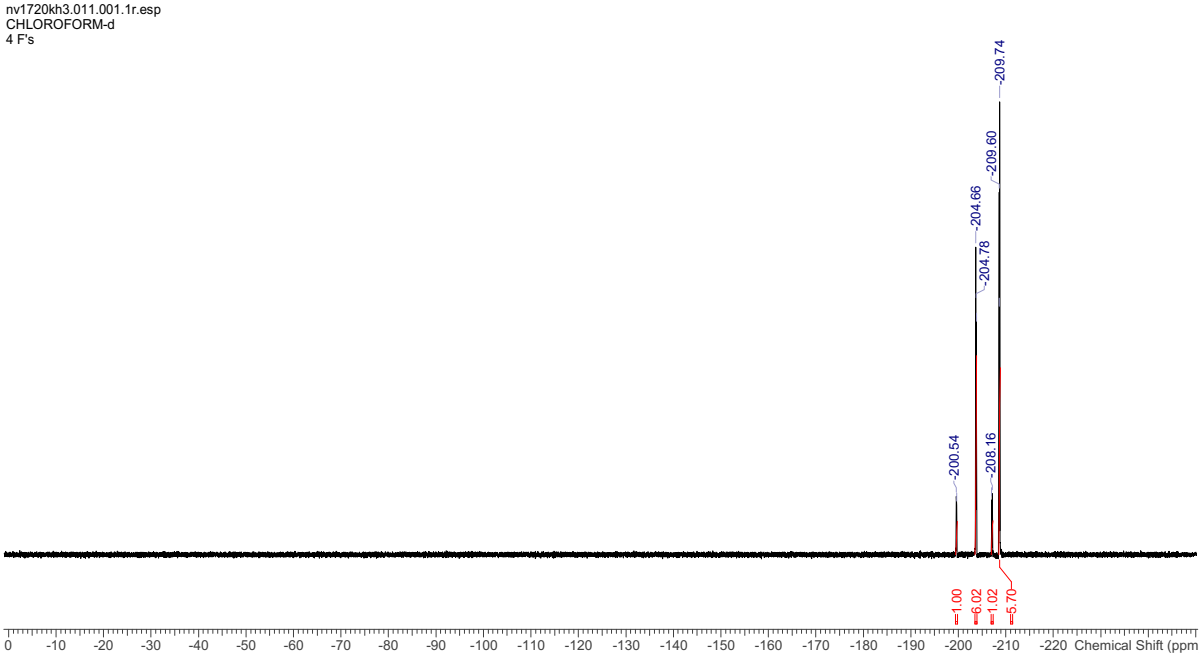
24 H's

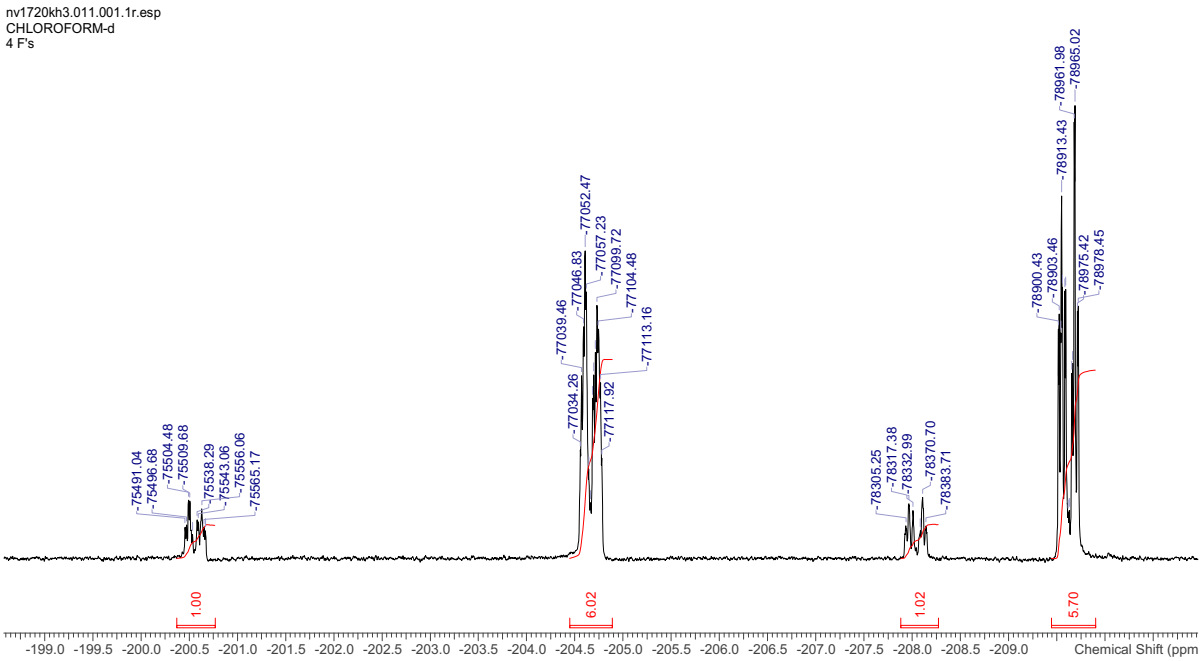


6.1.4.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

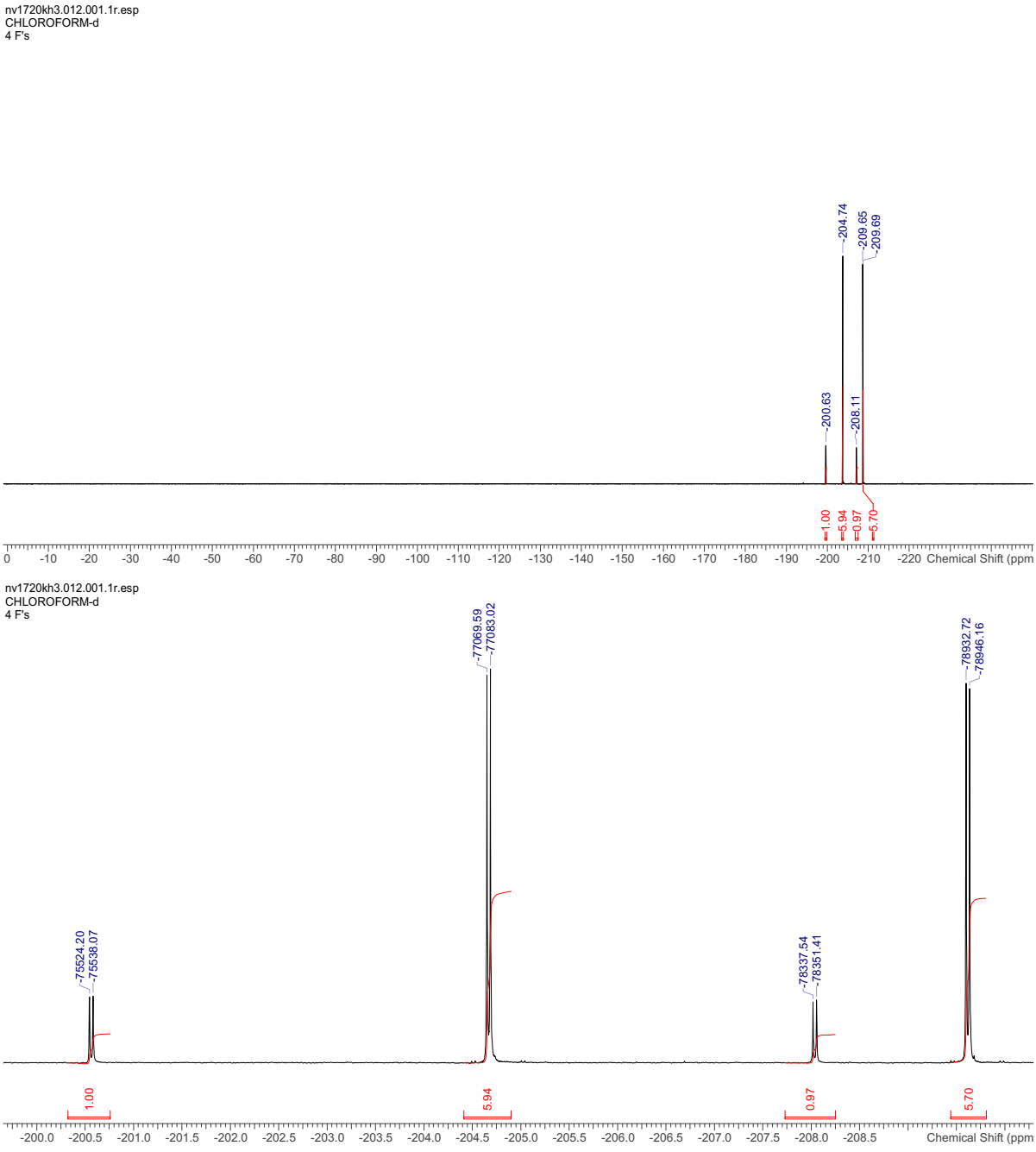


6.1.4.3 ^{19}F NMR, 376 MHz, $CDCl_3$

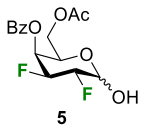




6.1.4.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



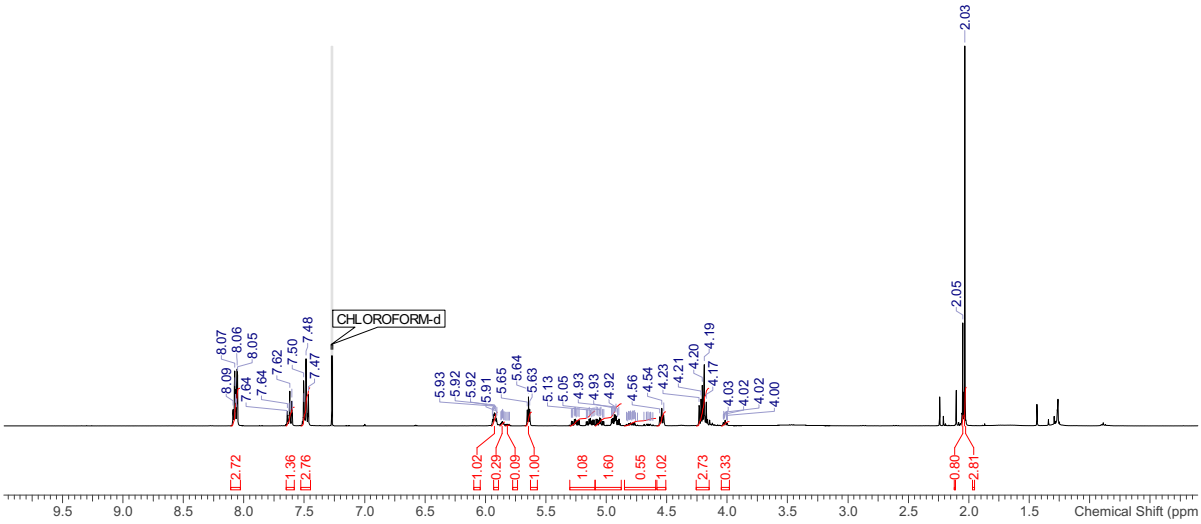
6.1.5 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-D-galactopyranose (**5**)



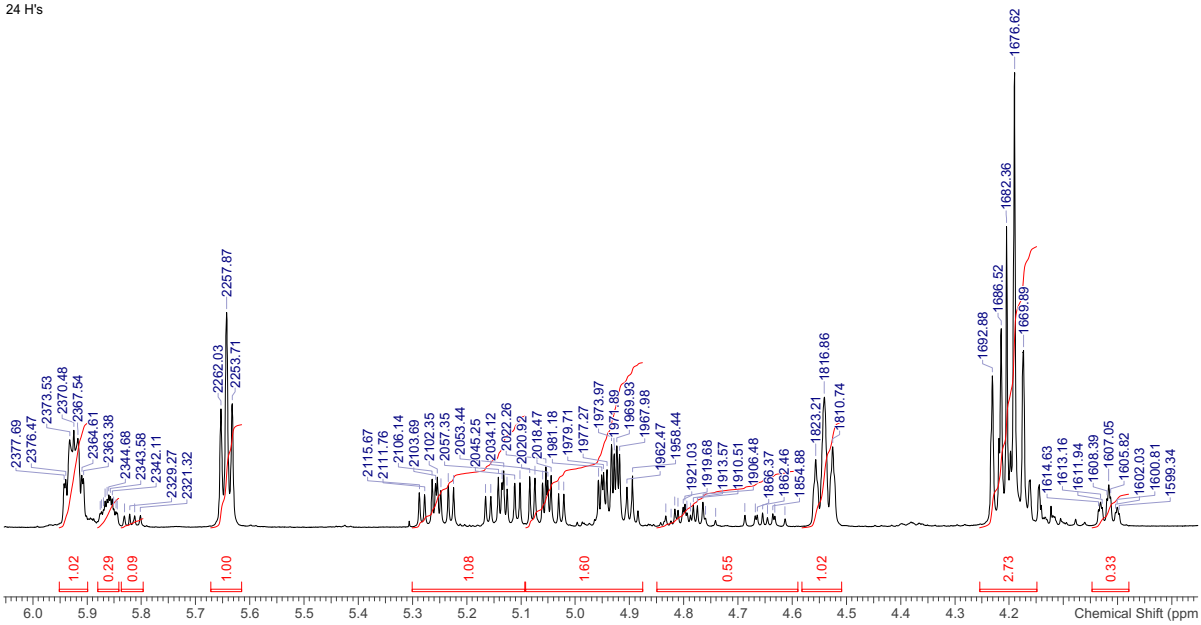
5

6.1.5.1 ^{1}H NMR, 400 MHz, $CDCl_3$

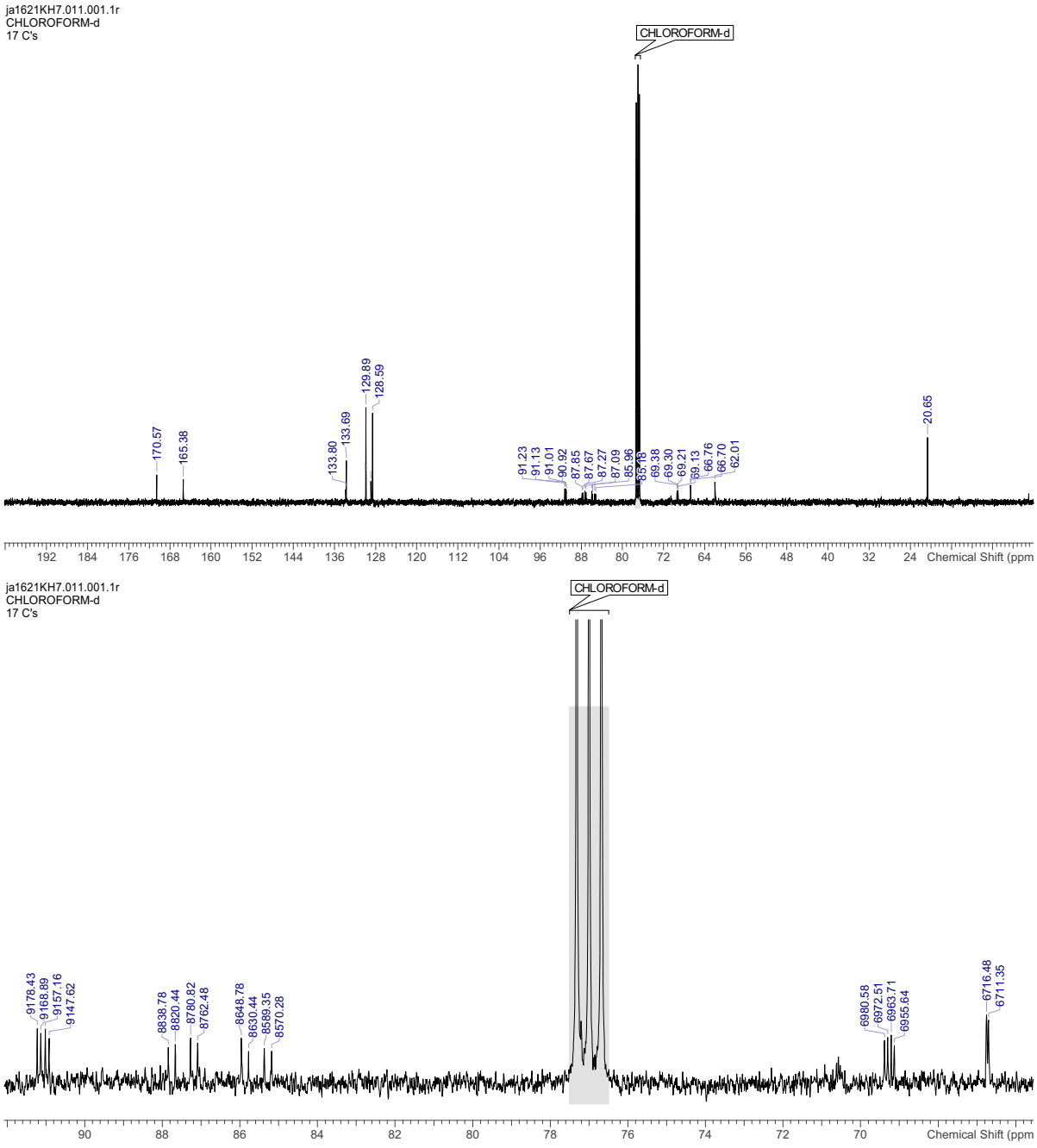
ja1621KH7.010.001.1r
CHLOROFORM-d
24 H's



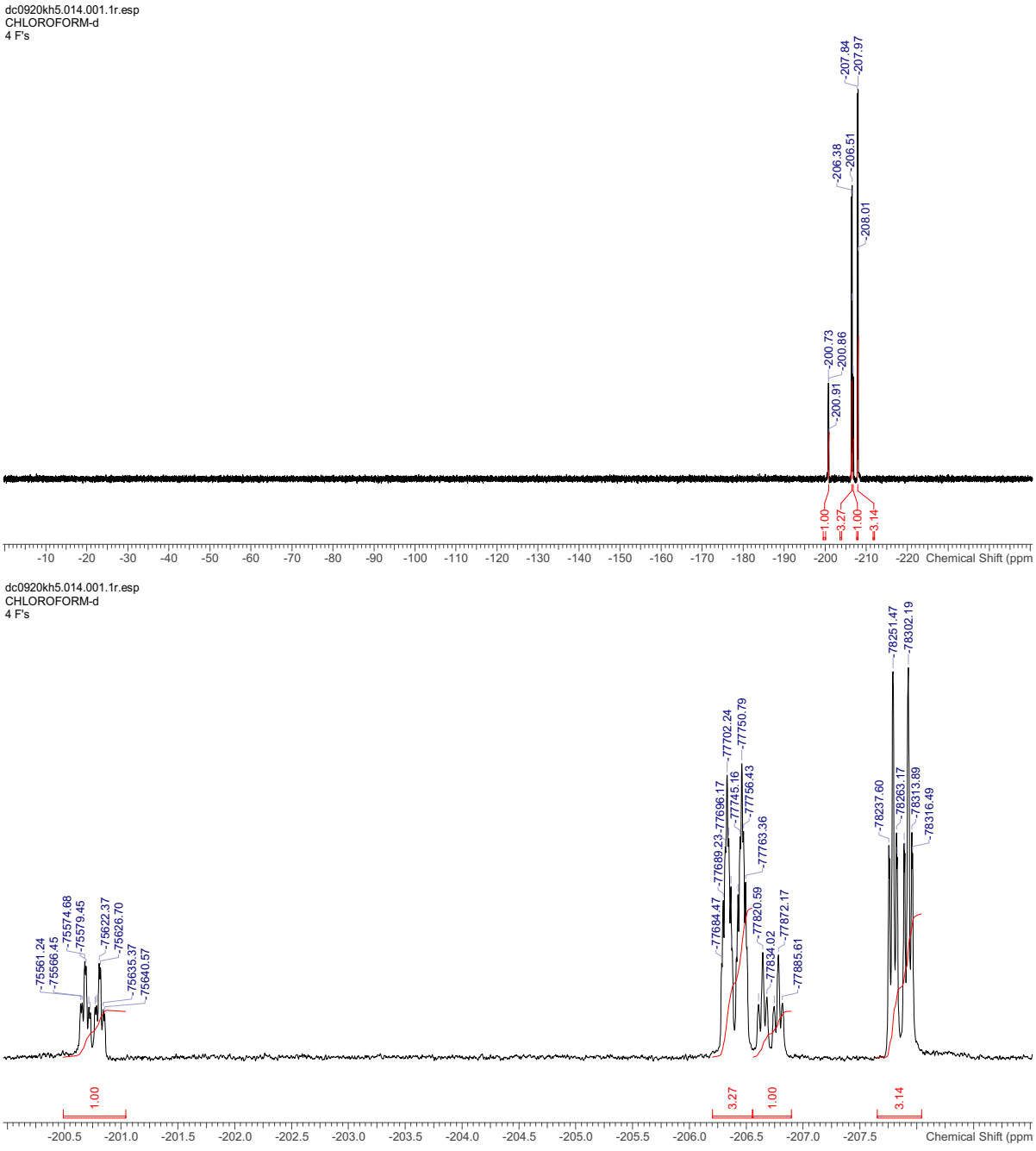
ja1621KH7.010.001.1r
CHLOROFORM-d
24 H's



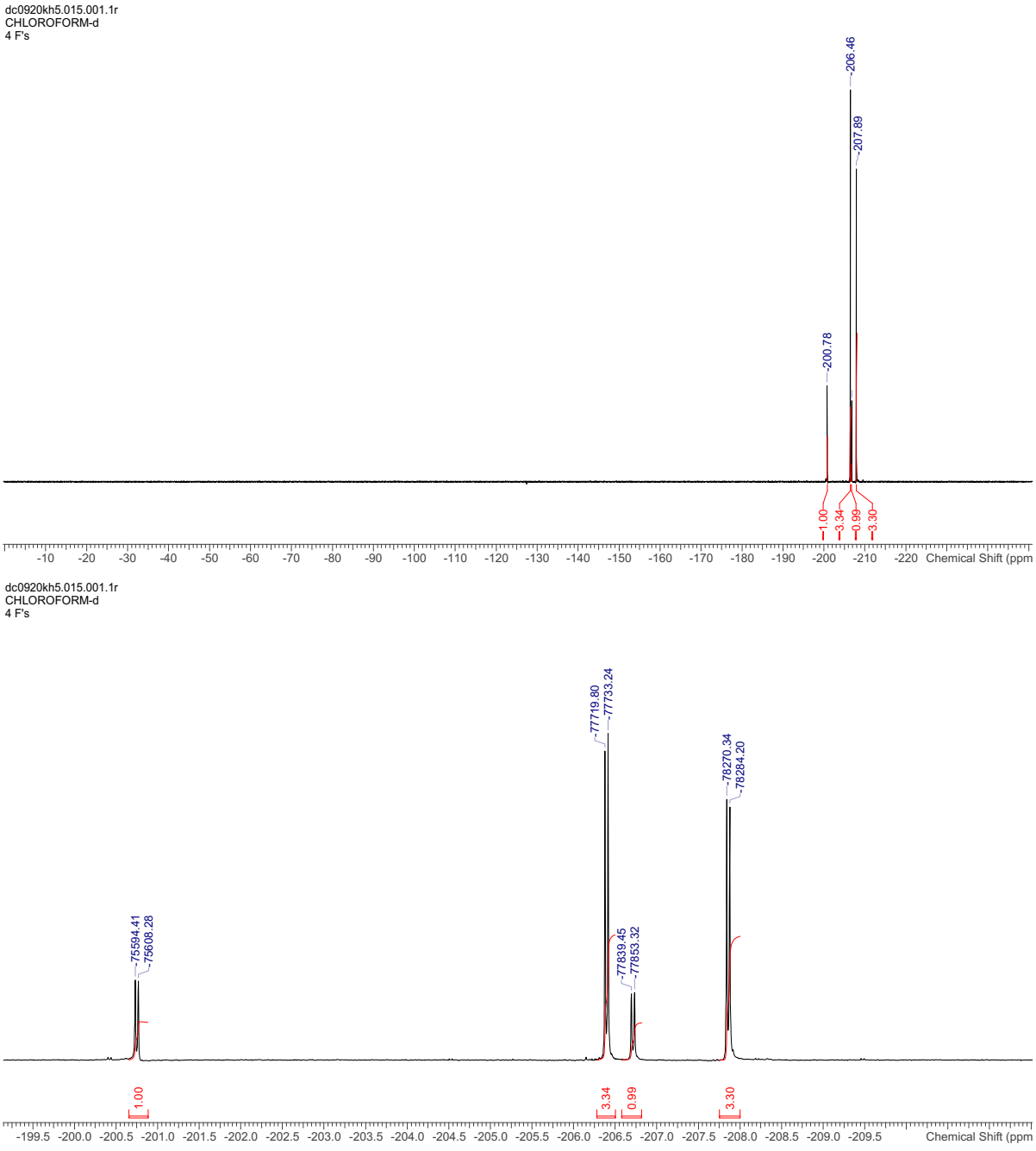
6.1.5.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$



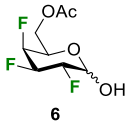
6.1.5.3 ^{19}F NMR, 376 MHz, $CDCl_3$



6.1.5.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



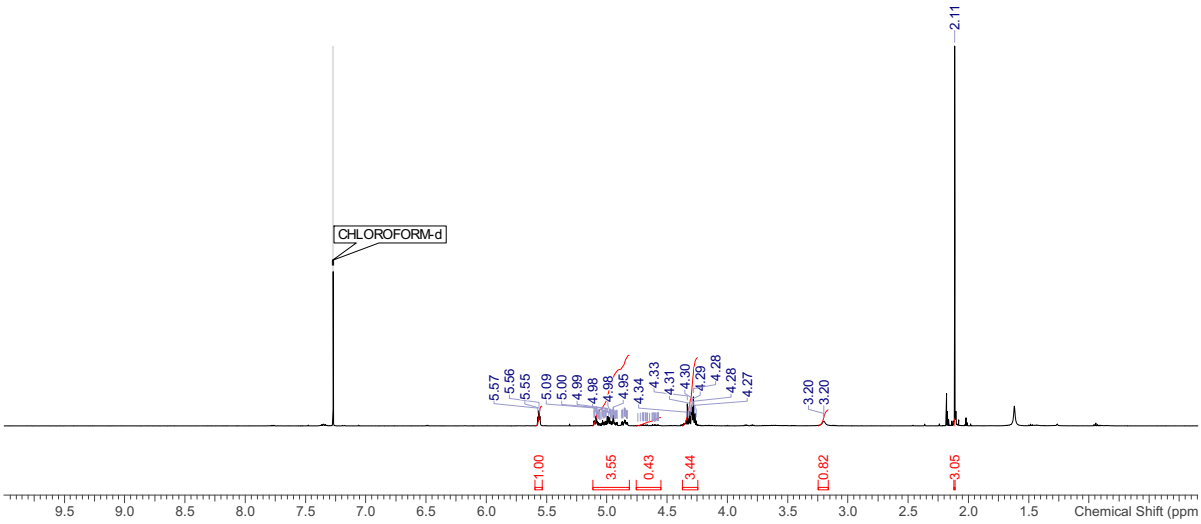
6.1.6 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-D-galactopyranose (**6**)



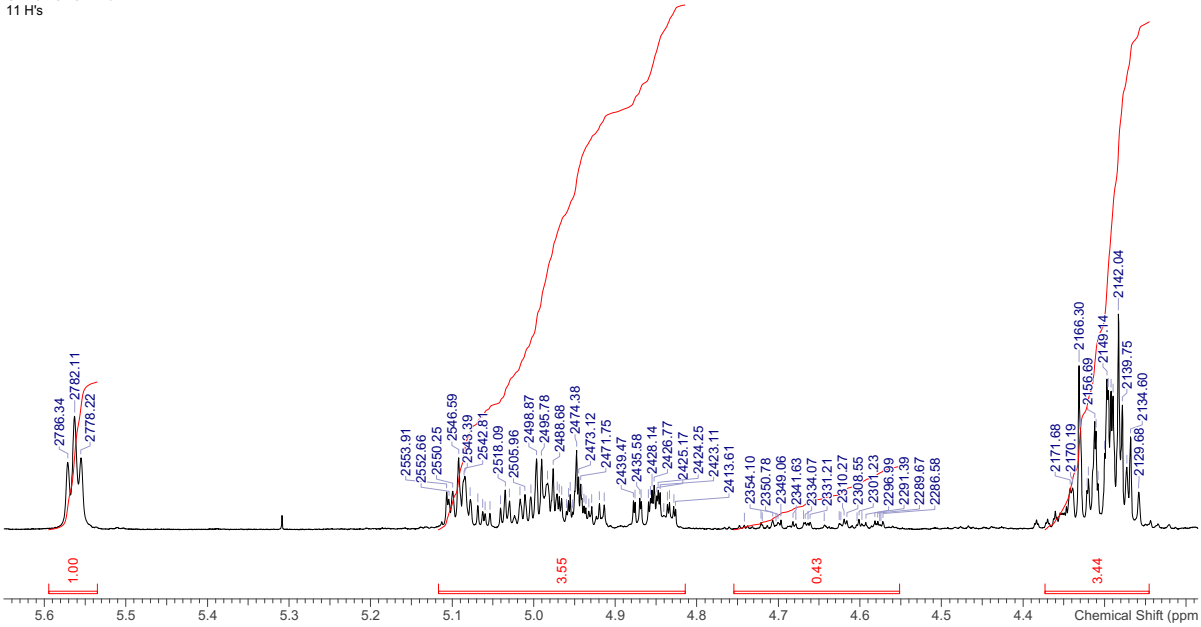
6

6.1.6.1 ^{1}H NMR, 500 MHz, $CDCl_3$

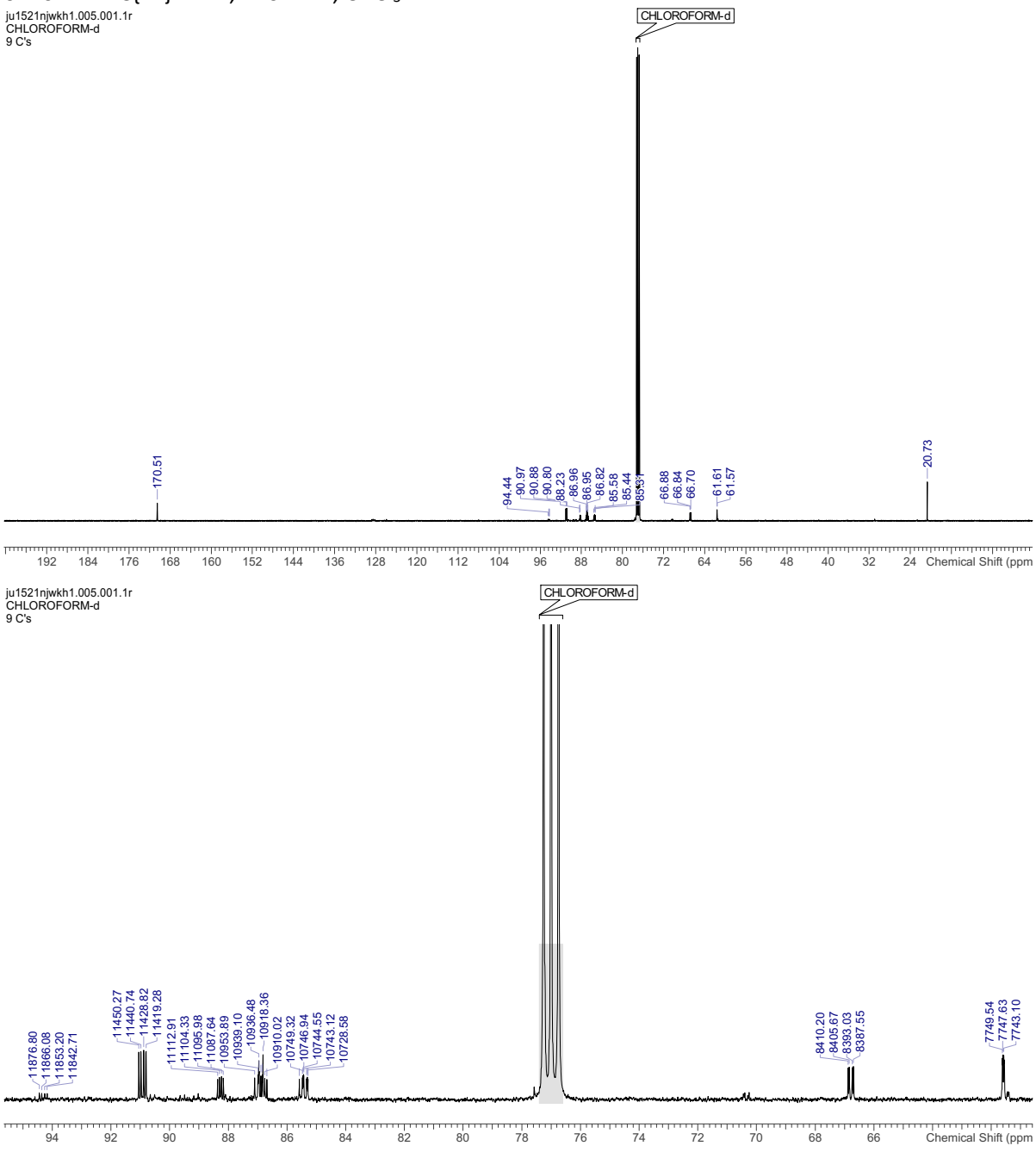
ju1521njwkh1.001.001.1r
CHLOROFORM-d
11 H's



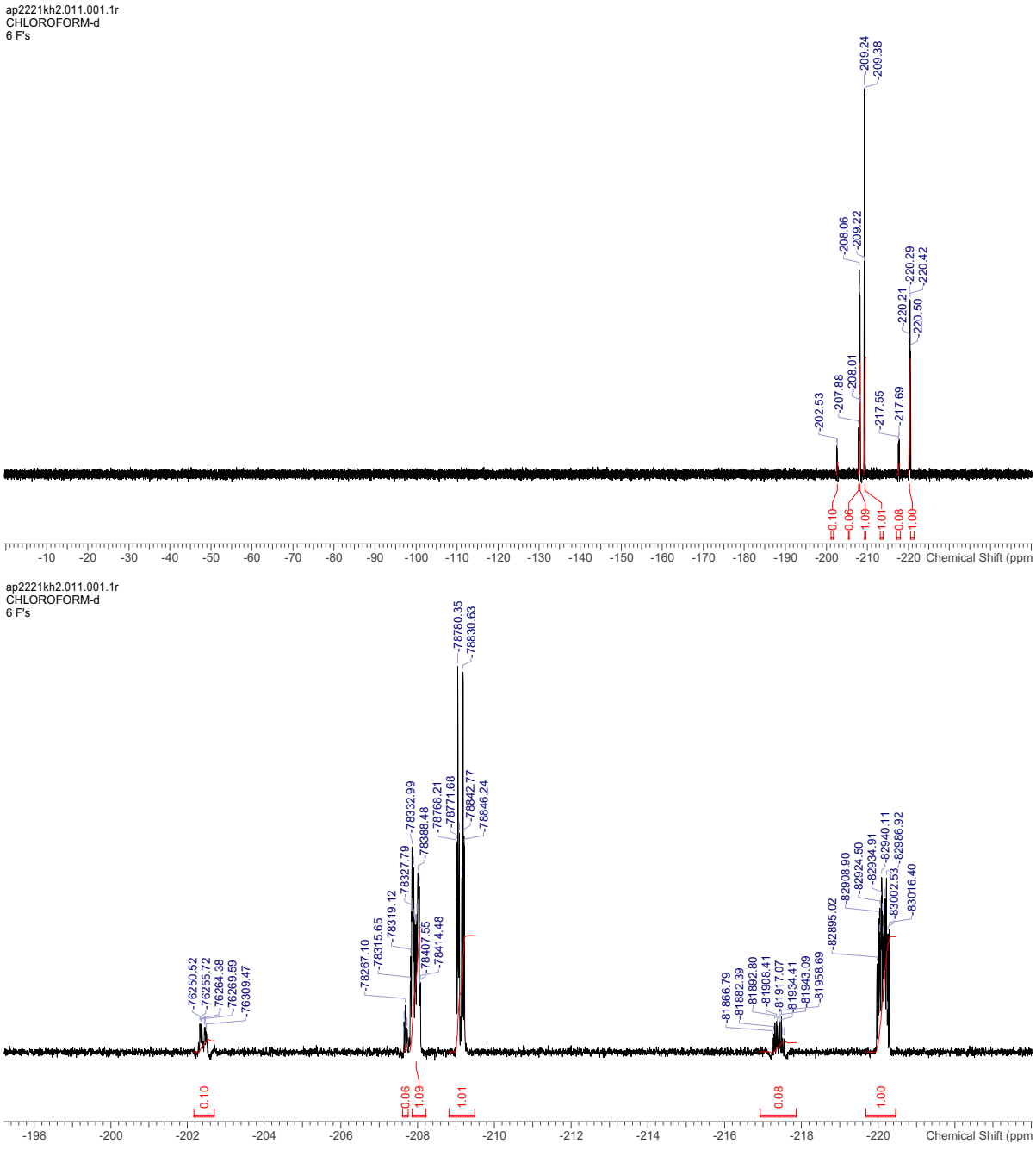
ju1521njwkh1.001.001.1r
CHLOROFORM-d
11 H's



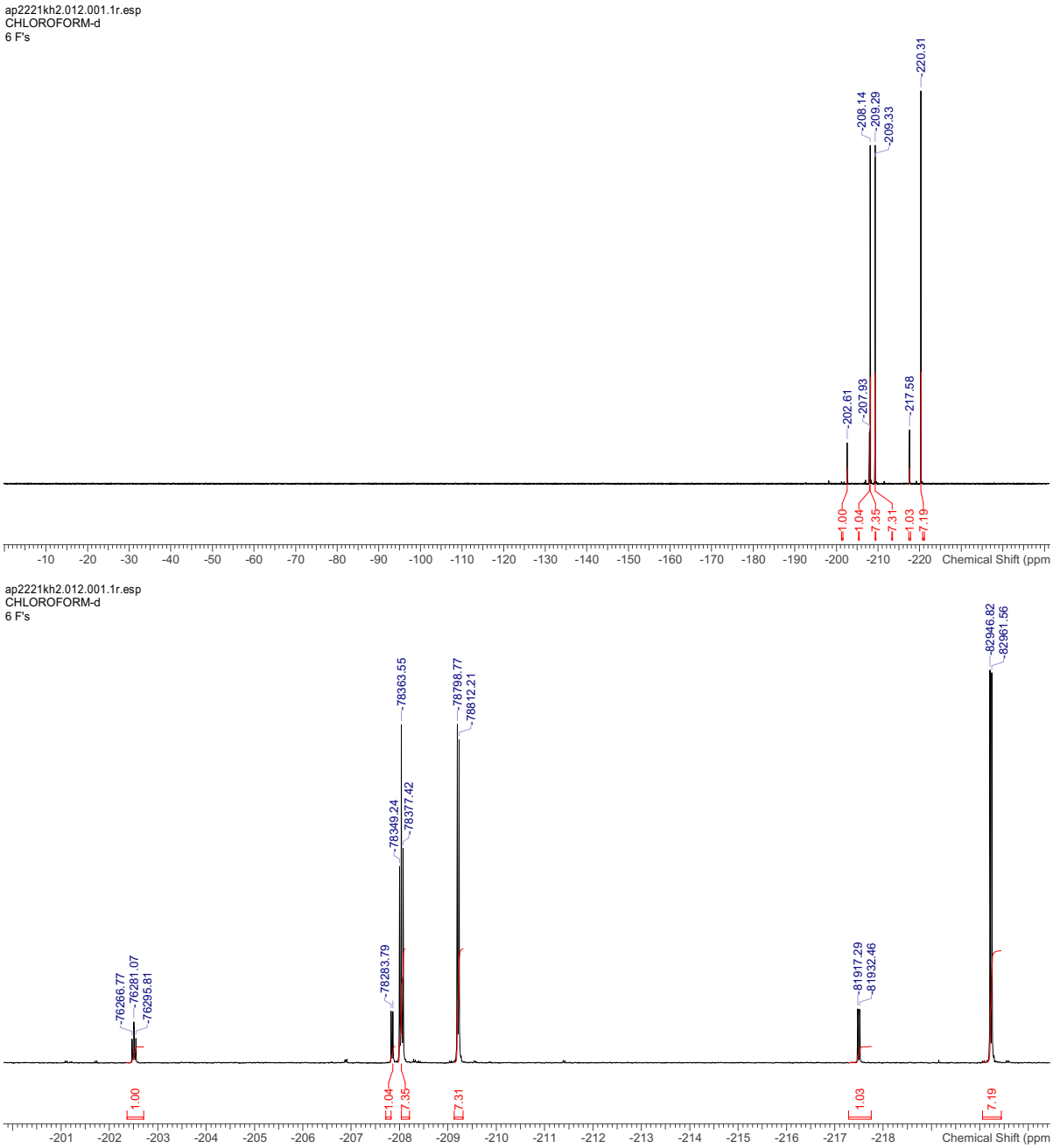
6.1.6.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$



6.1.6.3 ^{19}F NMR, 376 MHz, $CDCl_3$

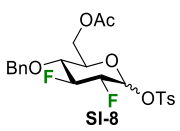


6.1.6.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



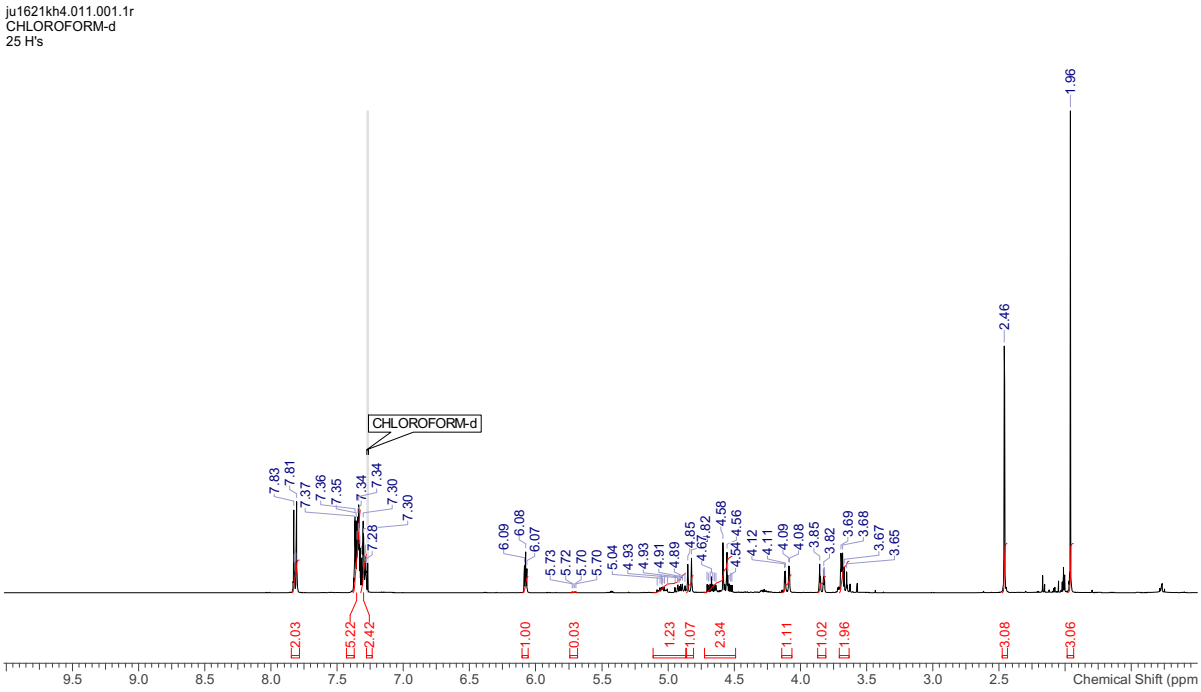
6.2 Copies of the spectra of the tosylates

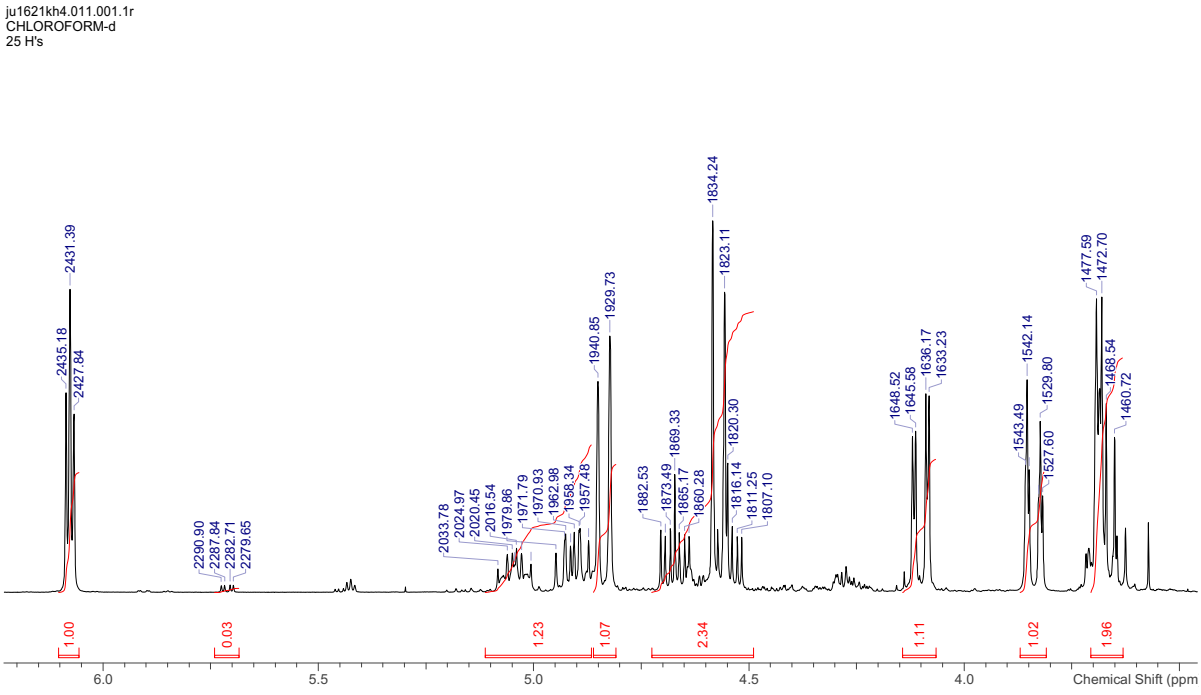
6.2.1 Tosyl 6-*O*-acetyl-4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-α/β-D-glucopyranoside (**SI-8**)



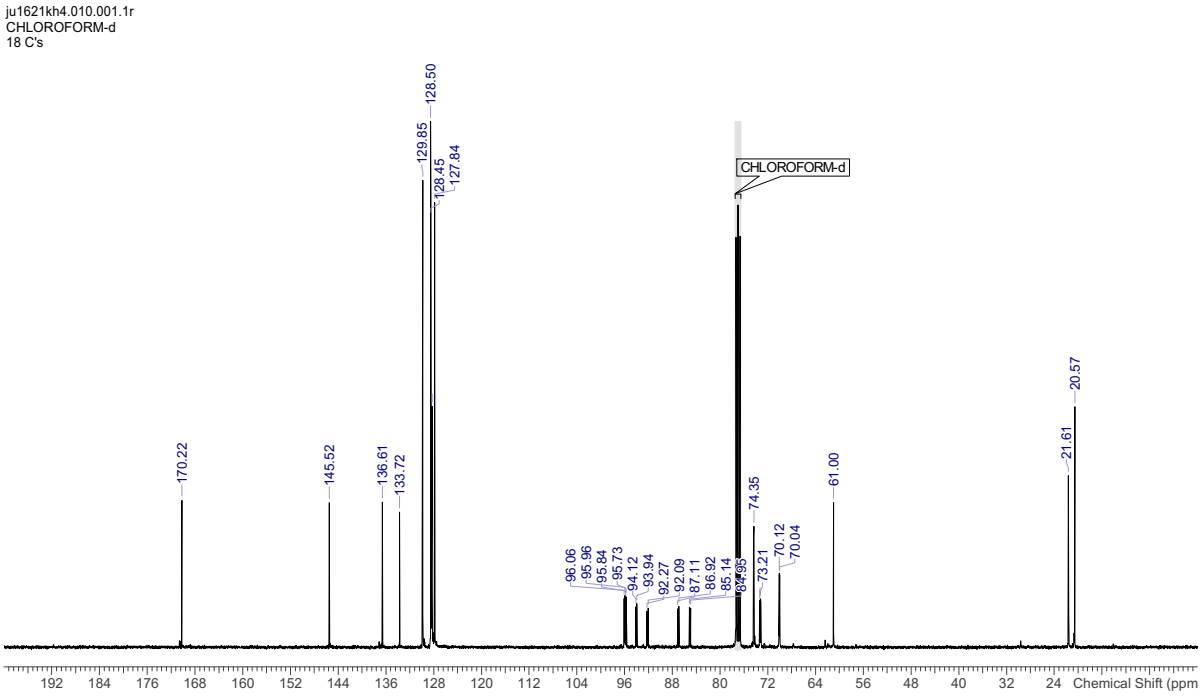
SI-8

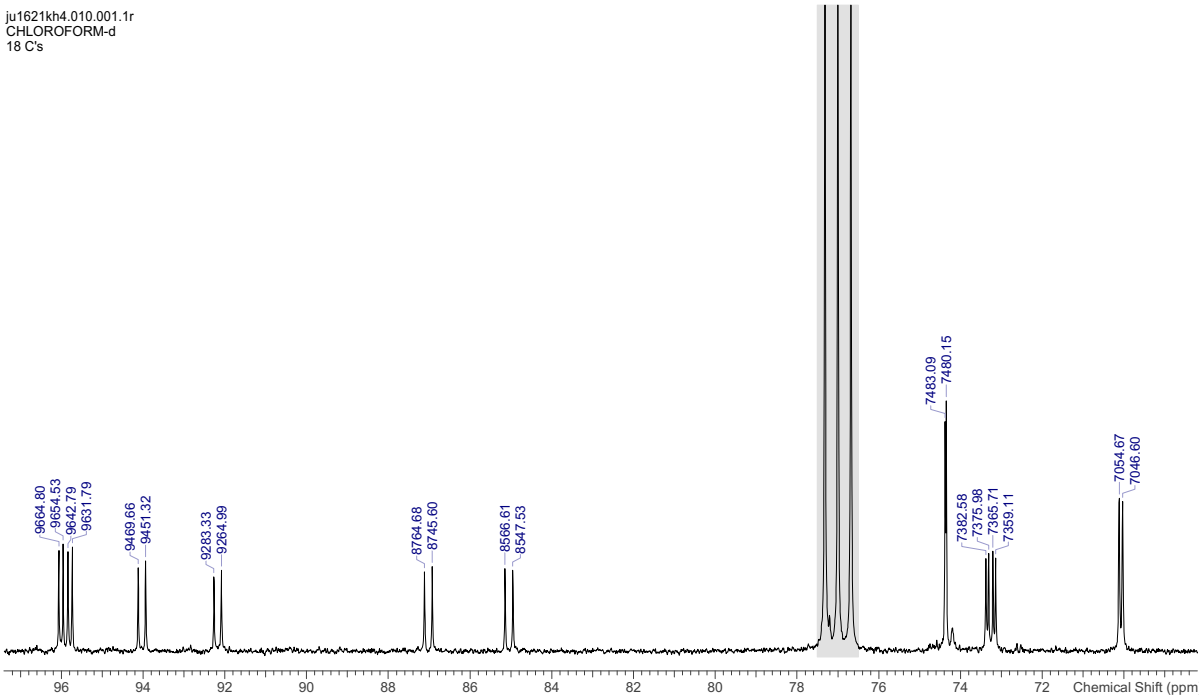
6.2.1.1 ^{1}H NMR, 400 MHz, $CDCl_3$



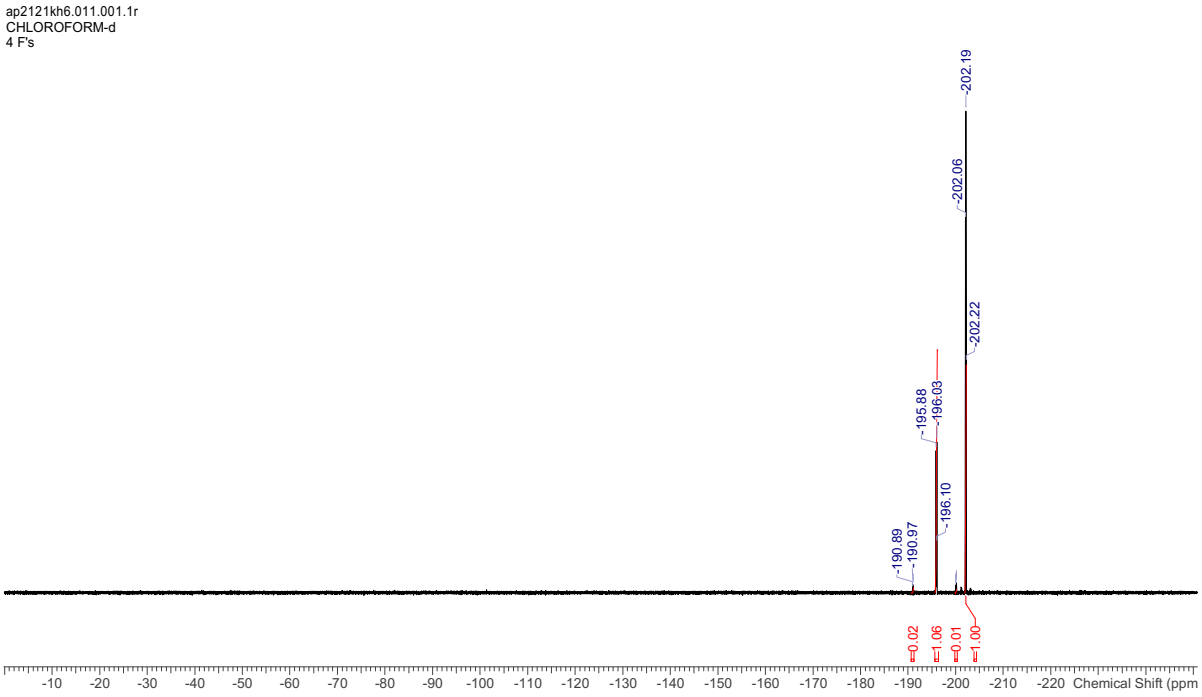


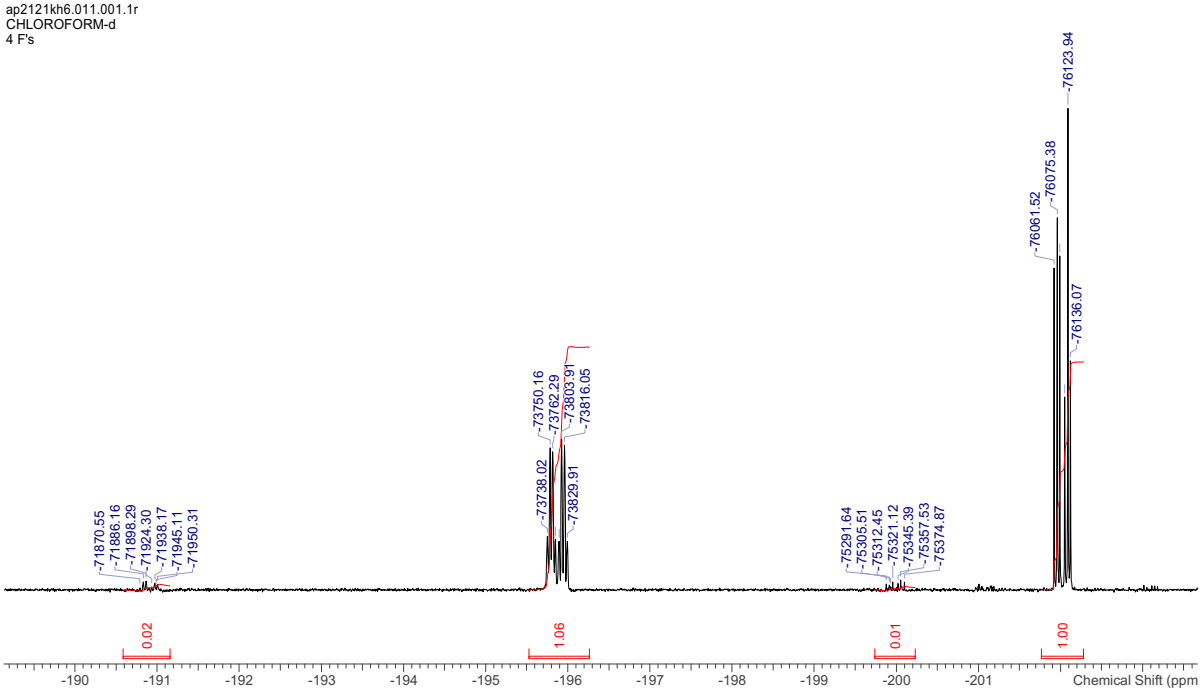
6.2.1.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$



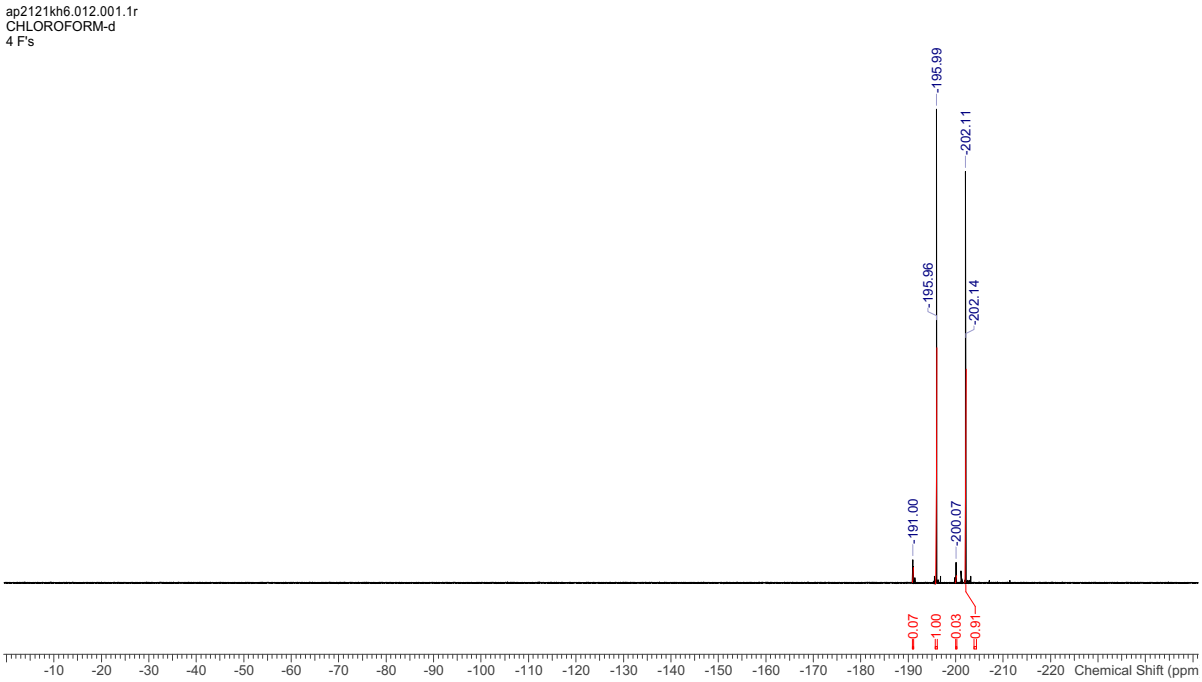


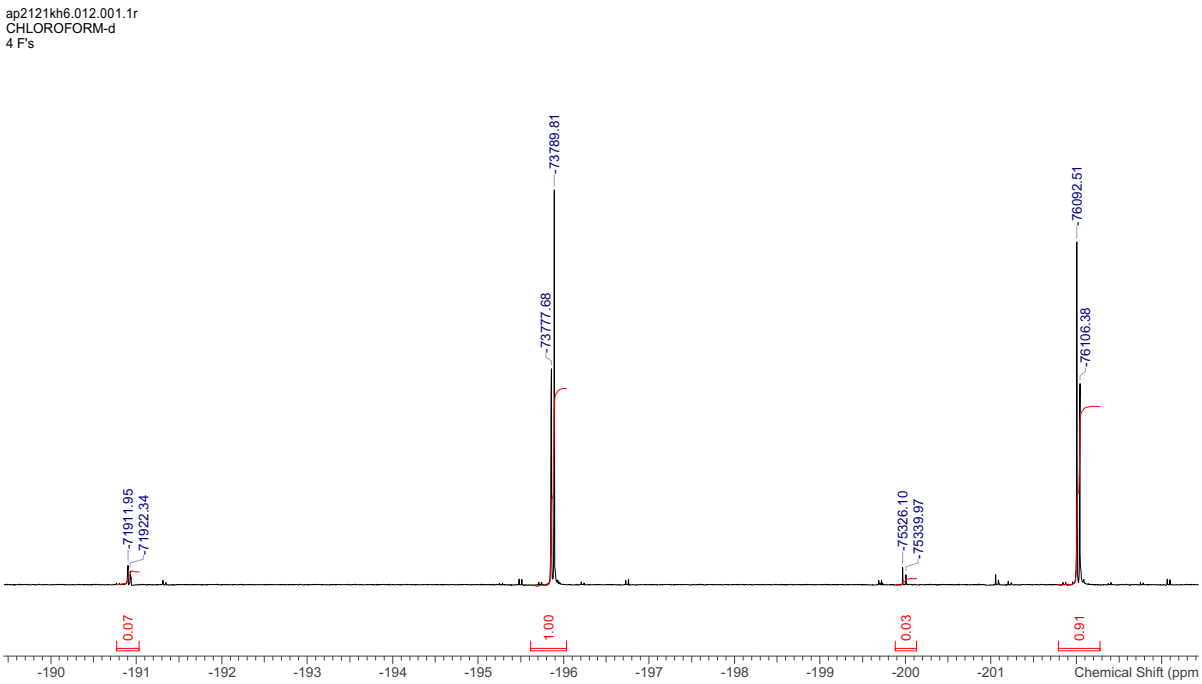
6.2.1.3 ^{19}F NMR, 376 MHz, $CDCl_3$





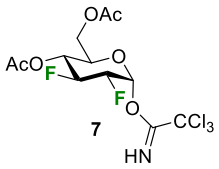
6.2.1.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$





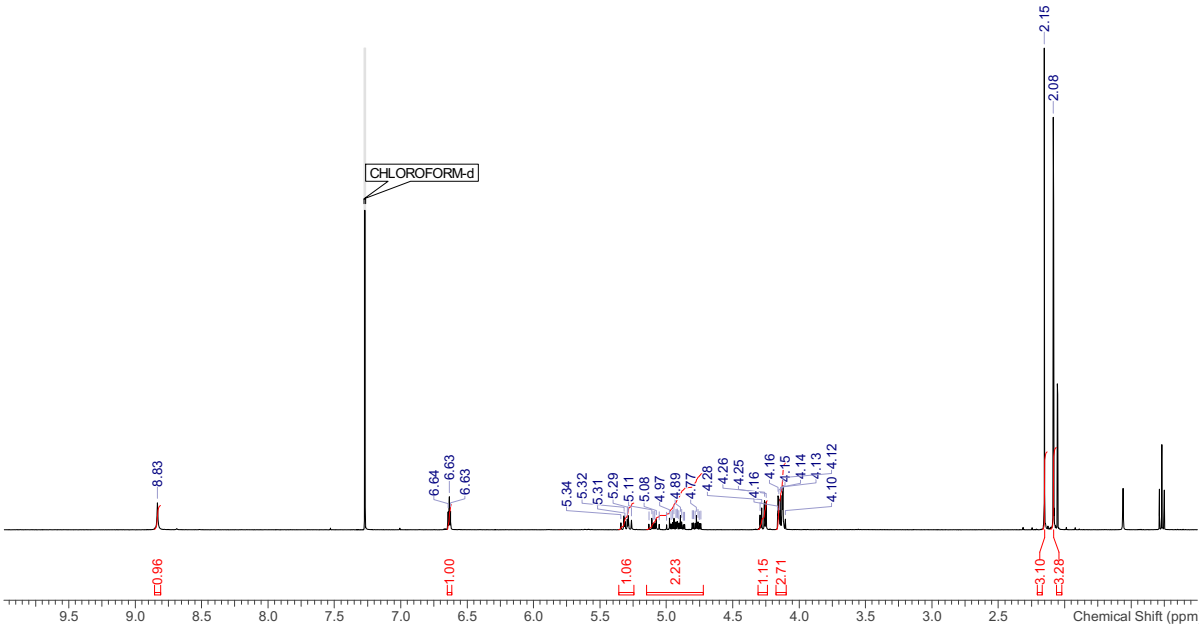
6.3 Copies of the spectra of the trichloroacetimidates

6.3.1 4,6-Di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α-D-glucopyranosyl trichloroacetimidate (**7**)

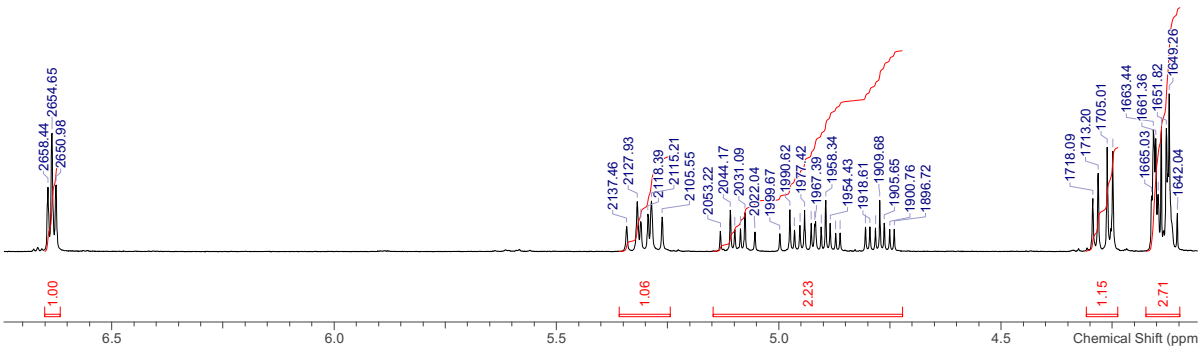


6.3.1.1 ^{1}H NMR, 400 MHz, $CDCl_3$

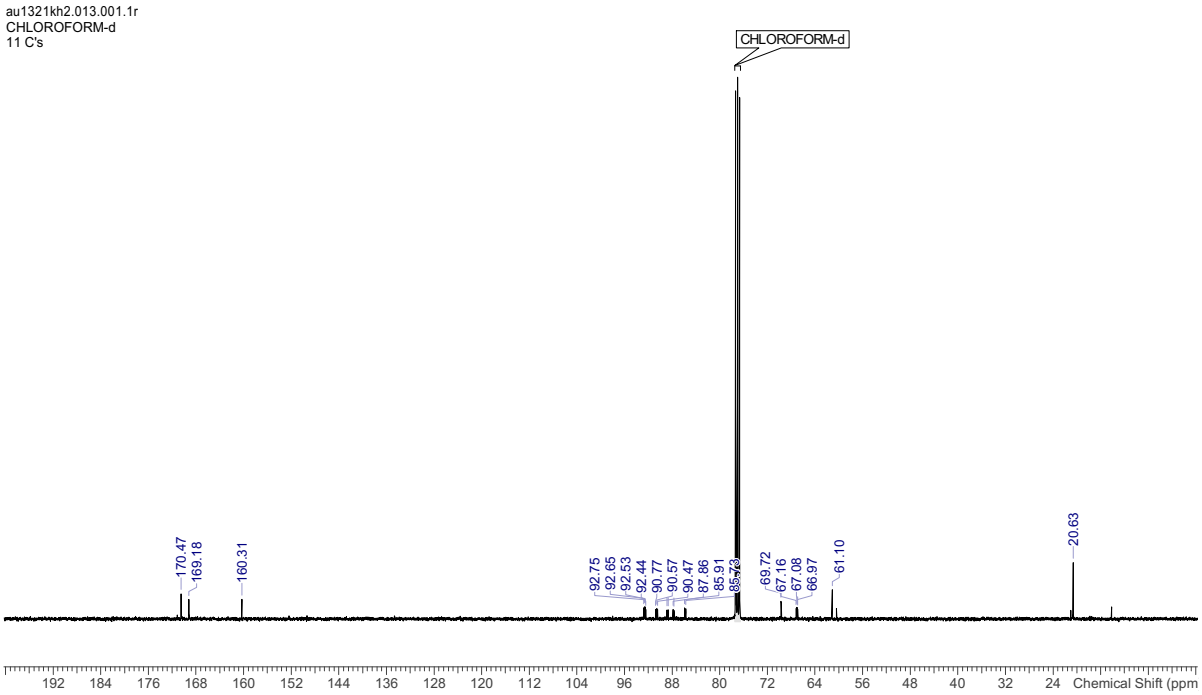
au1321kh2.010.001.1r
CHLOROFORM-d
15 H's

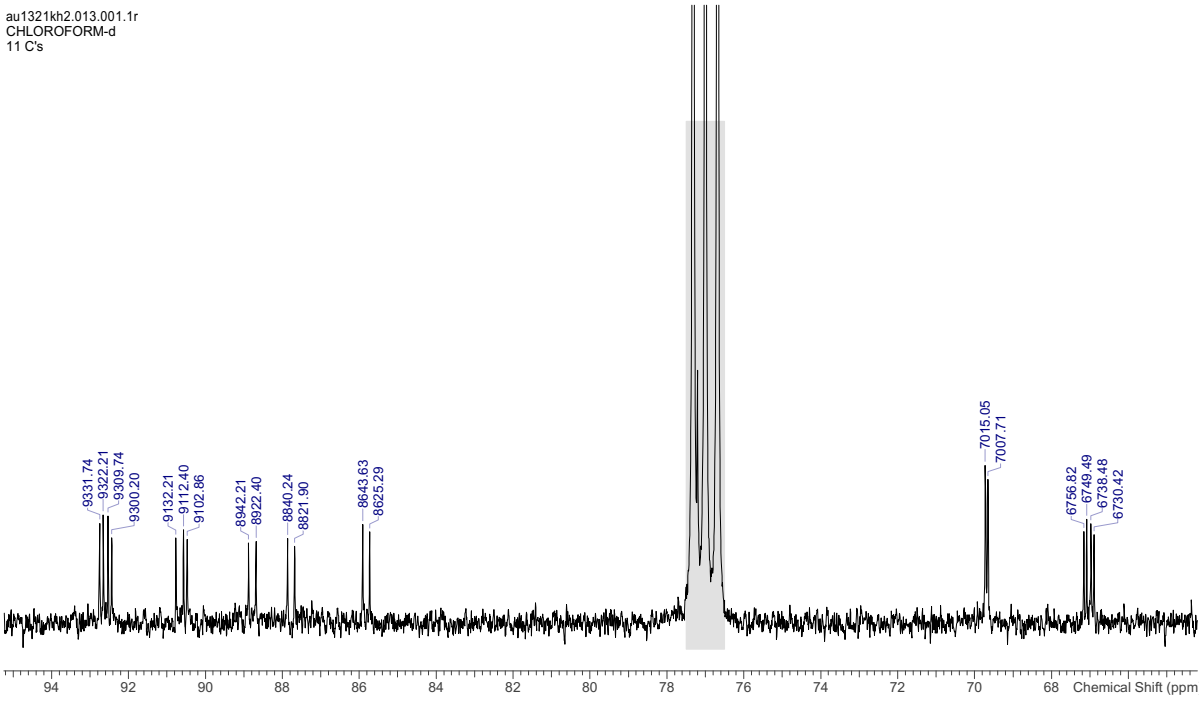


au1321kh2.010.001.1r
CHLOROFORM-d
15 H's

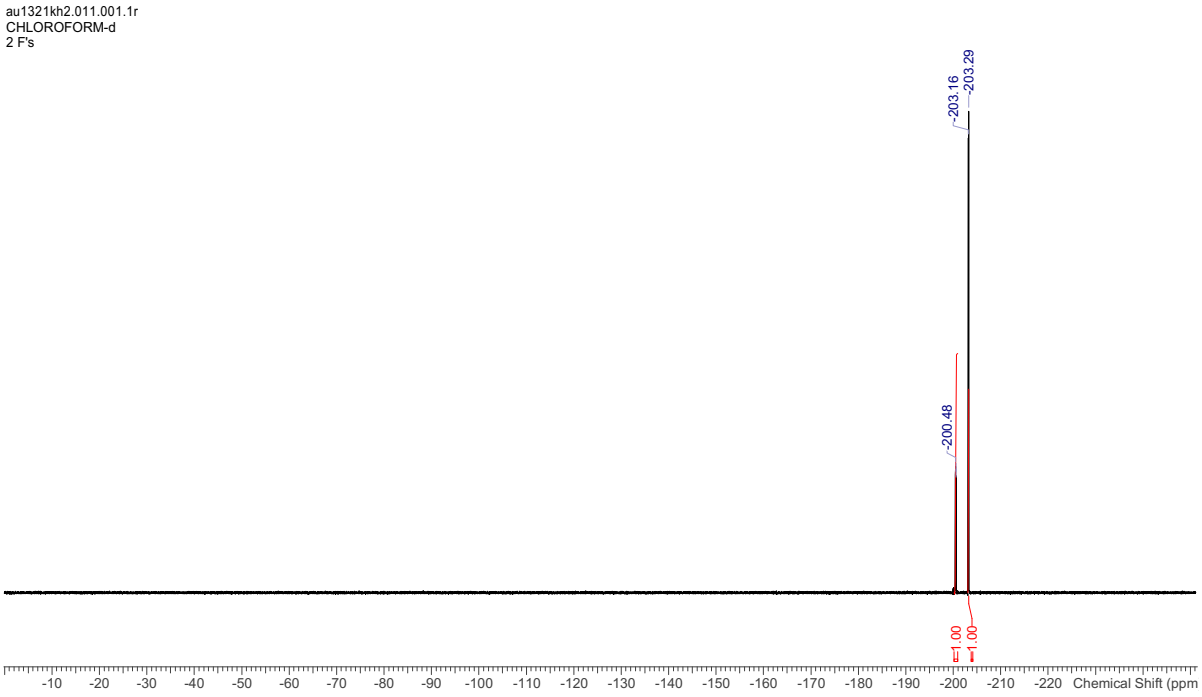


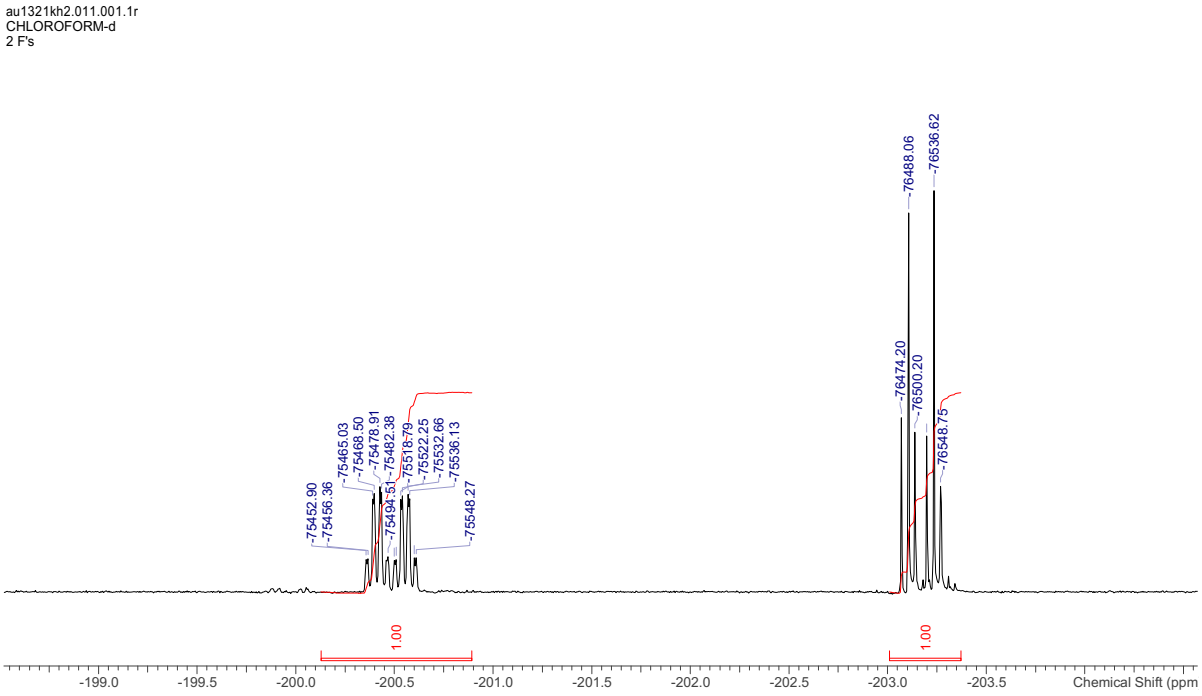
6.3.1.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$



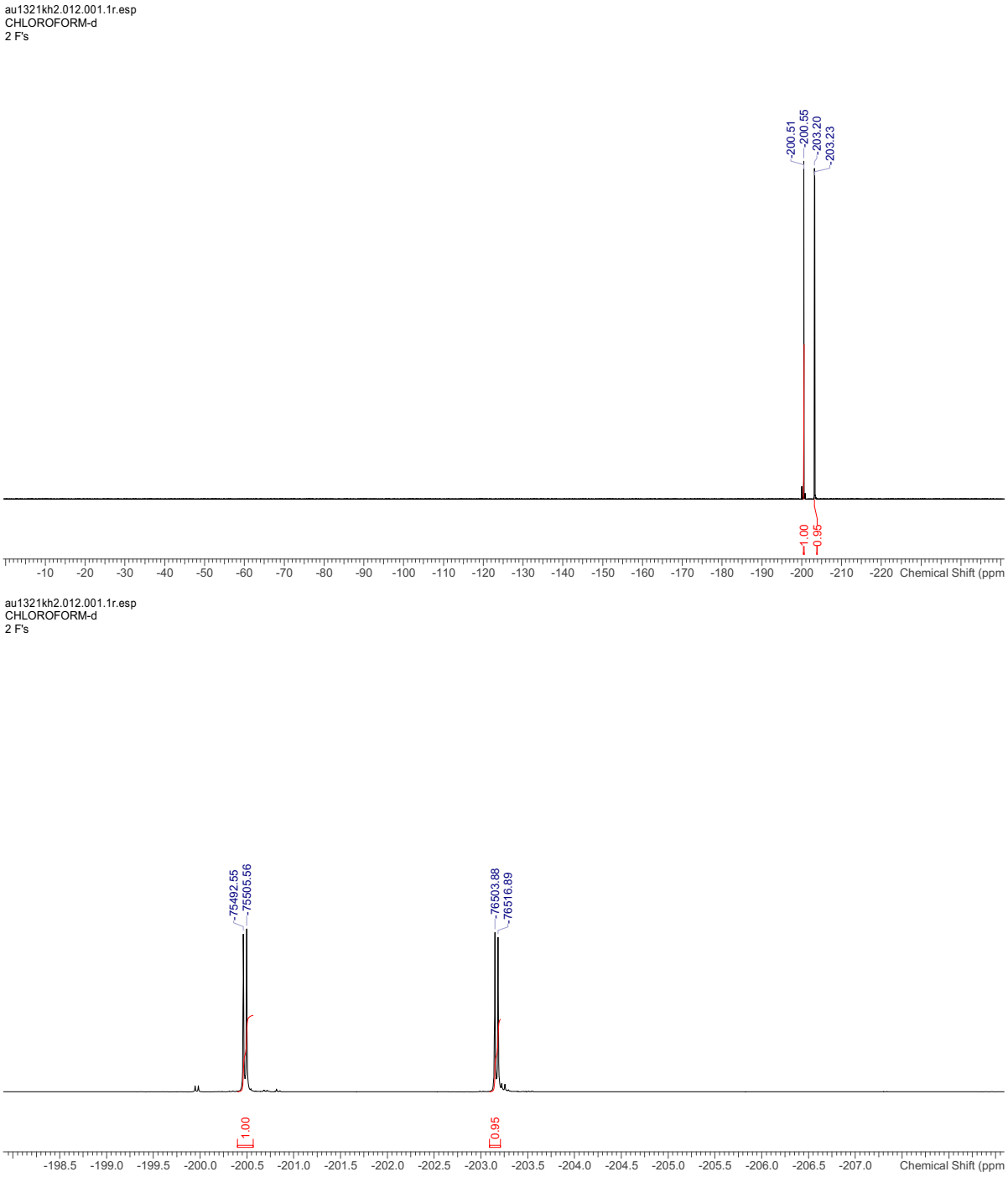


6.3.1.3 ^{19}F NMR, 376 MHz, $CDCl_3$

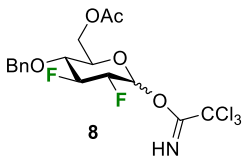




6.3.1.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



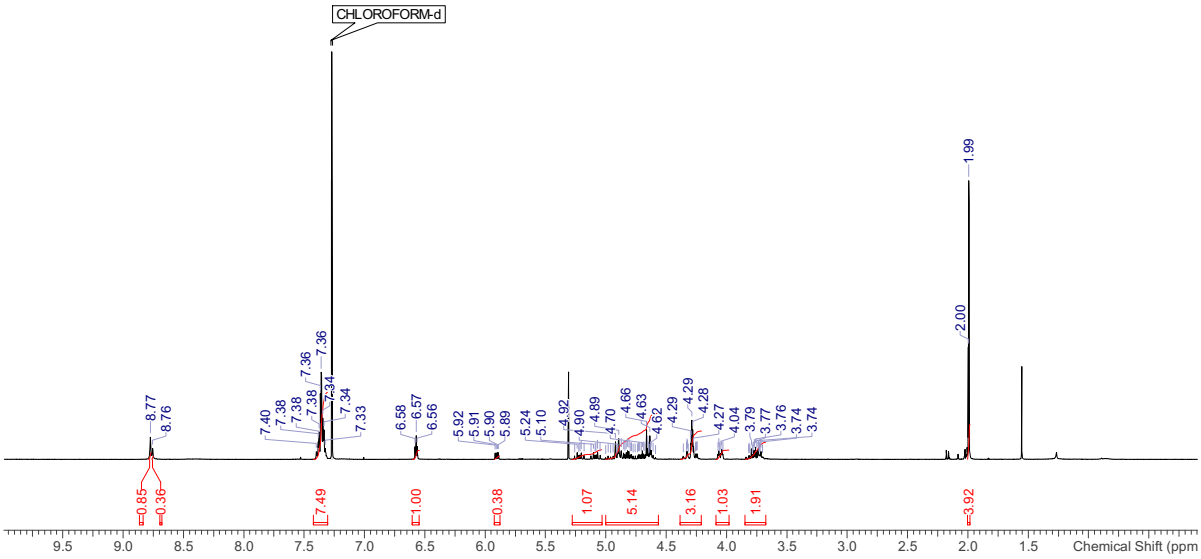
6.3.2 6-*O*-Acetyl-4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-α/β-D-glucopyranosyl trichloroacetimidate (**8**)



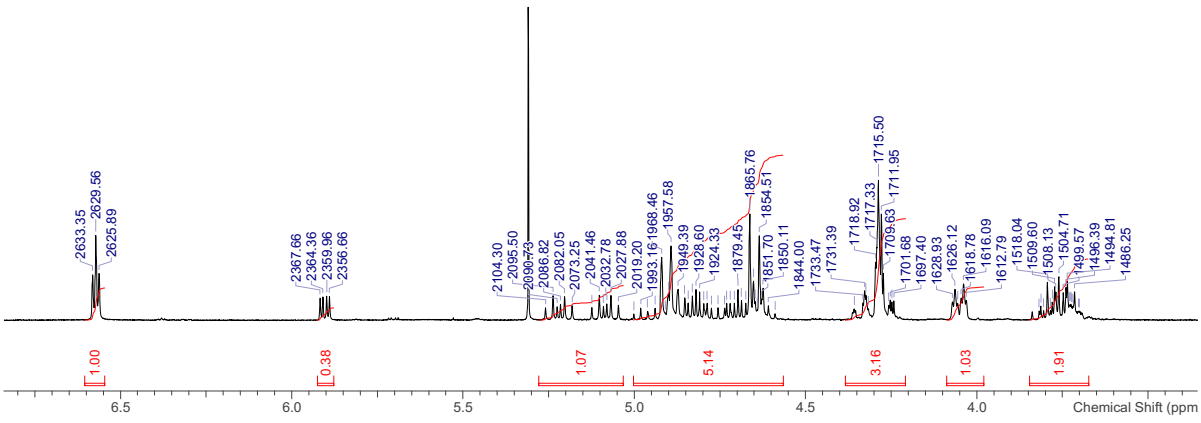
8

6.3.2.1 ^{1}H NMR, 400 MHz, $CDCl_3$

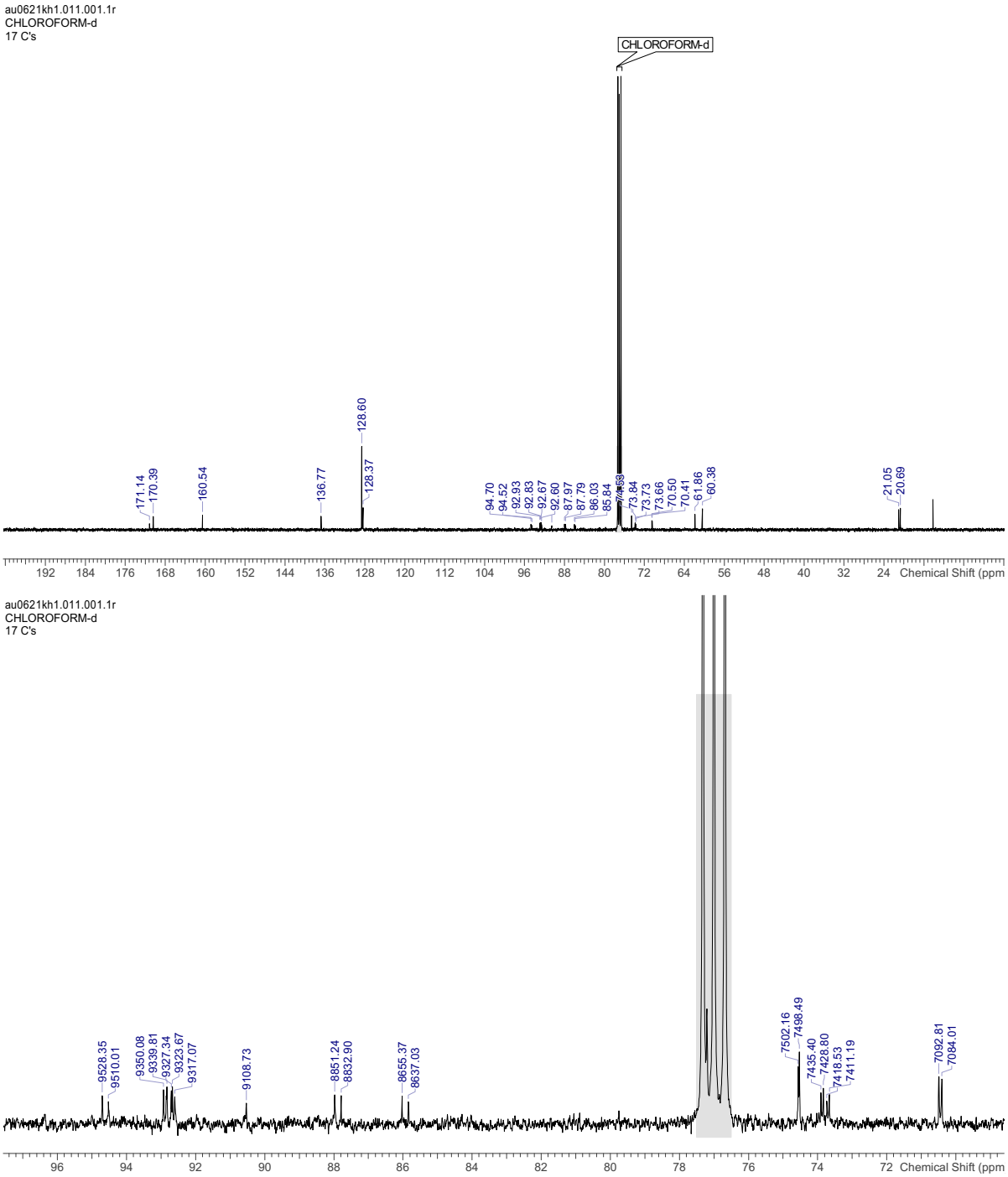
au2421kh1.010.001.1r
CHLOROFORM-d
27 H's



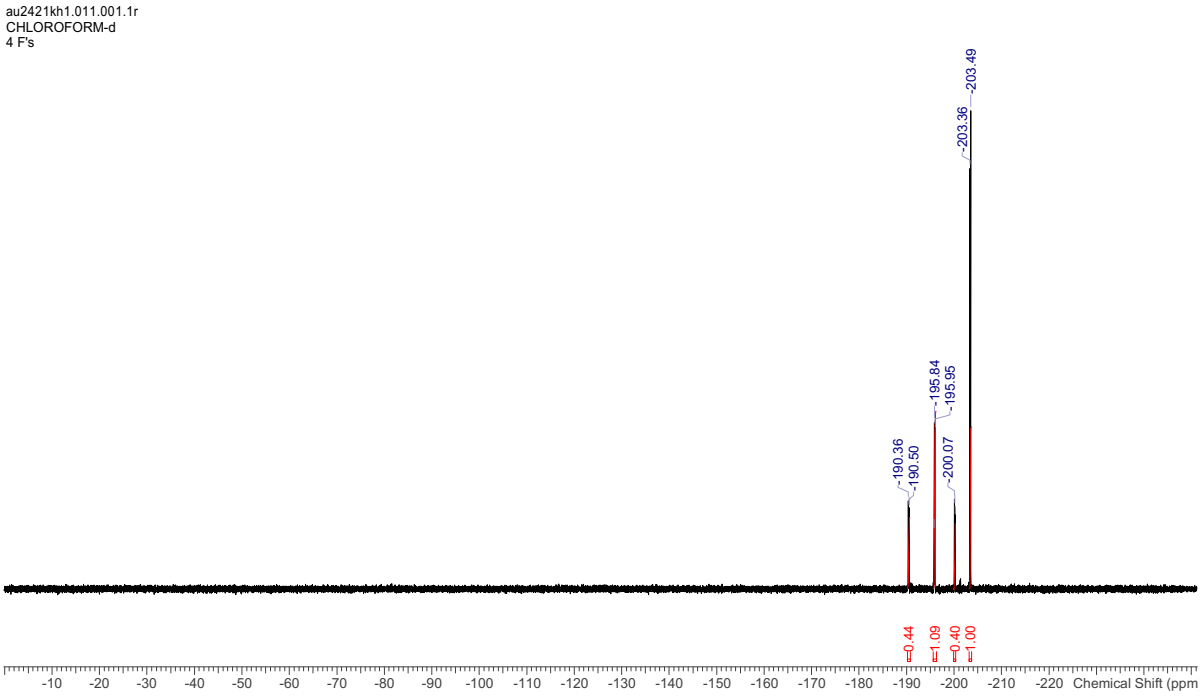
au2421kh1.010.001.1r
CHLOROFORM-d
27 H's

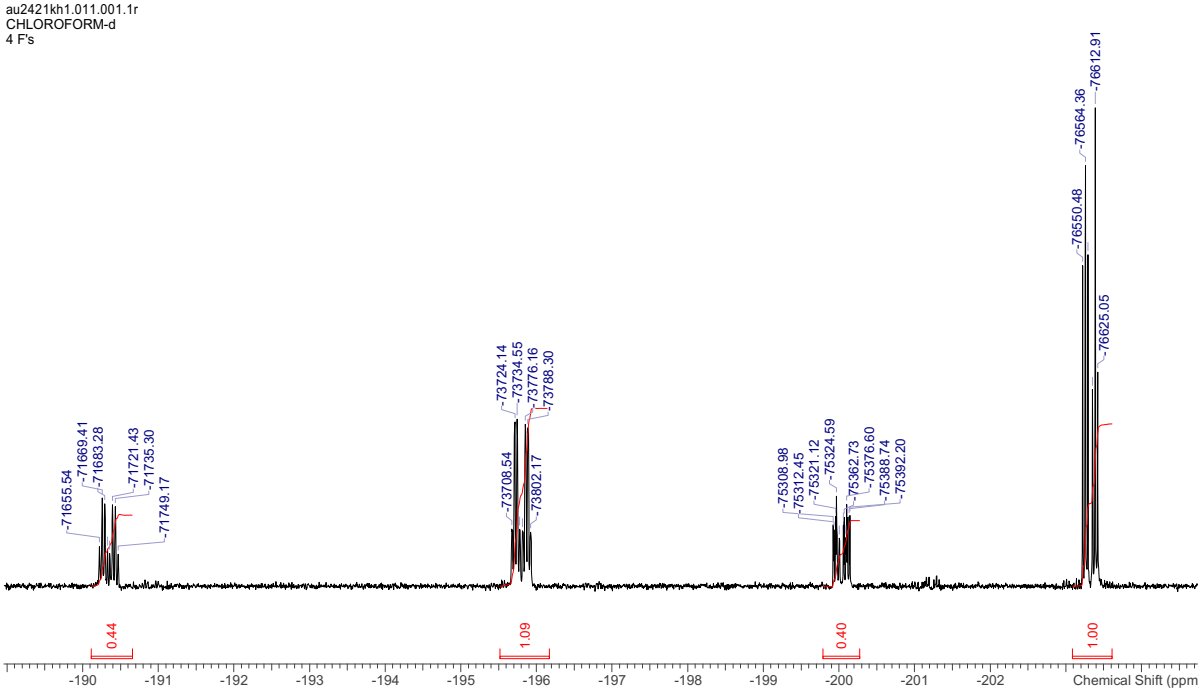


6.3.2.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

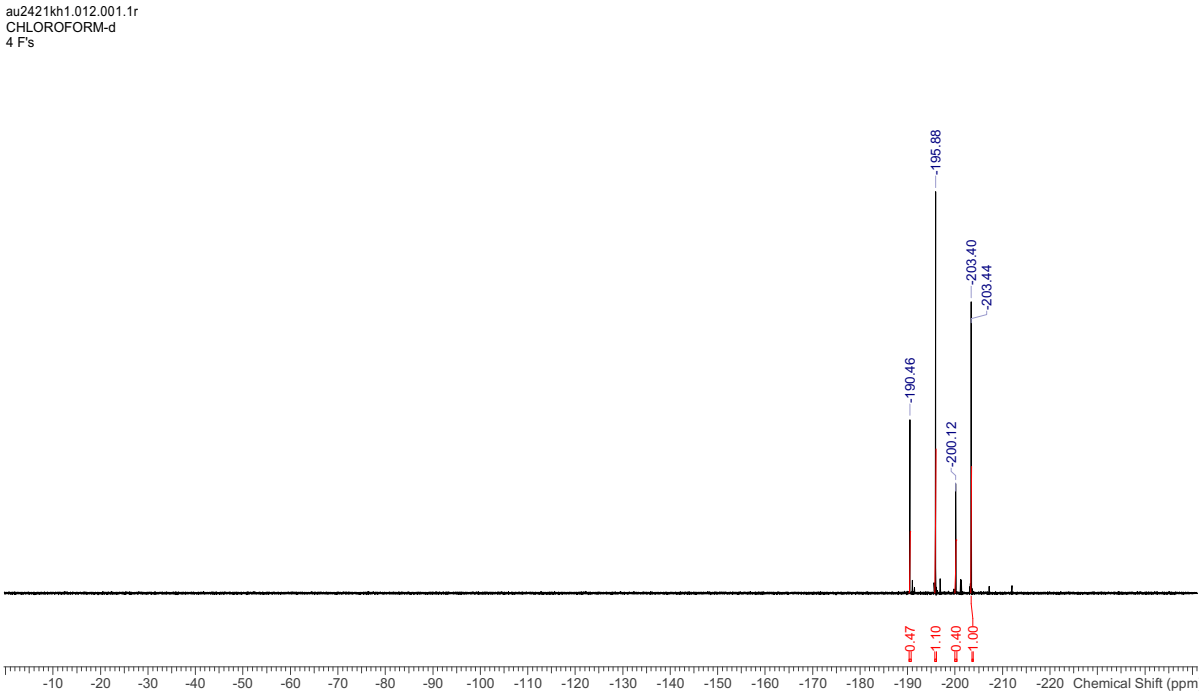


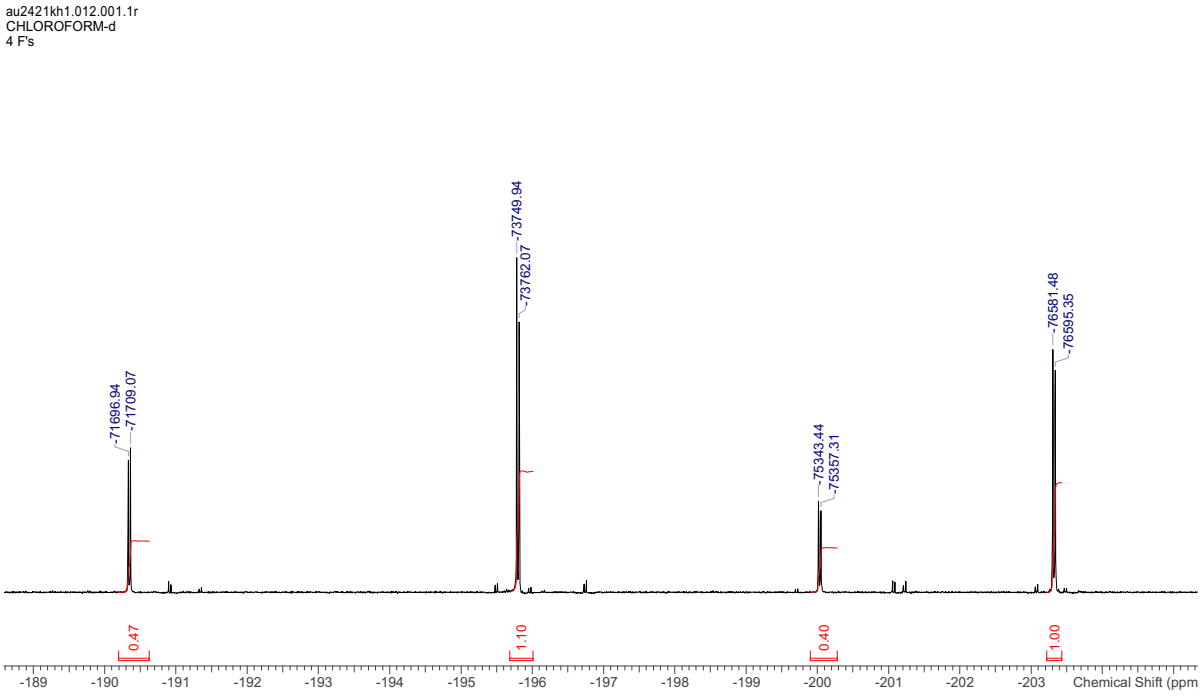
6.3.2.3 ^{19}F NMR, 376 MHz, $CDCl_3$



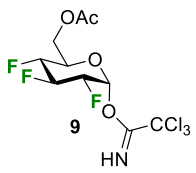


6.3.2.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



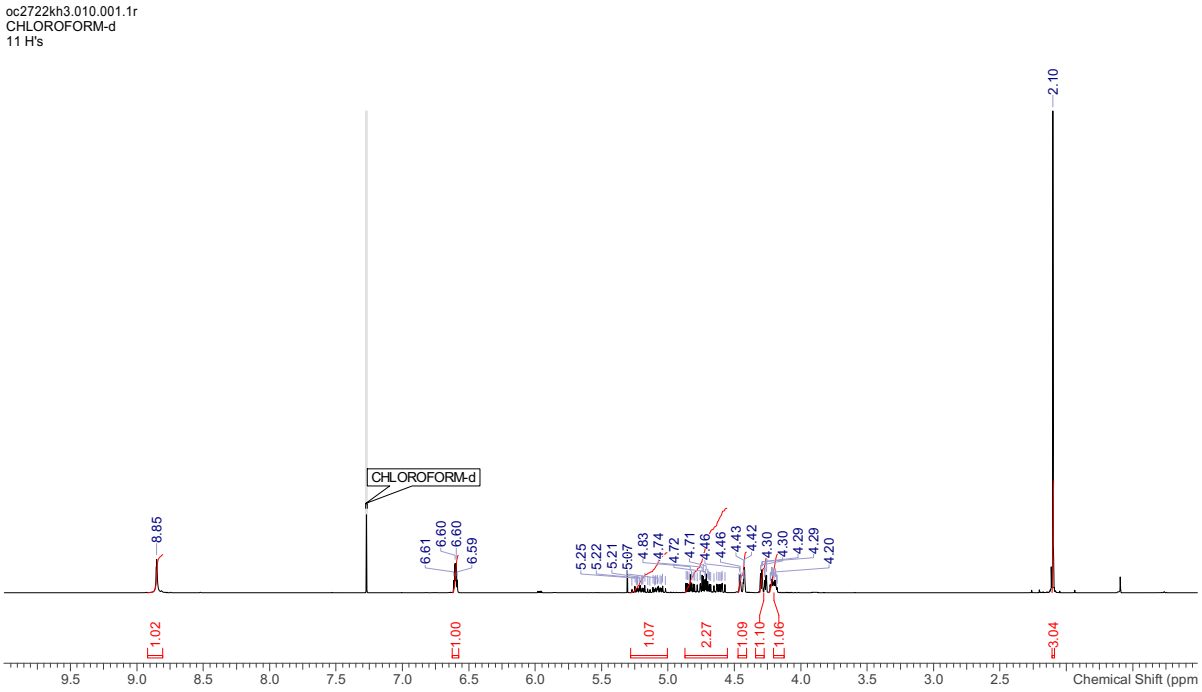


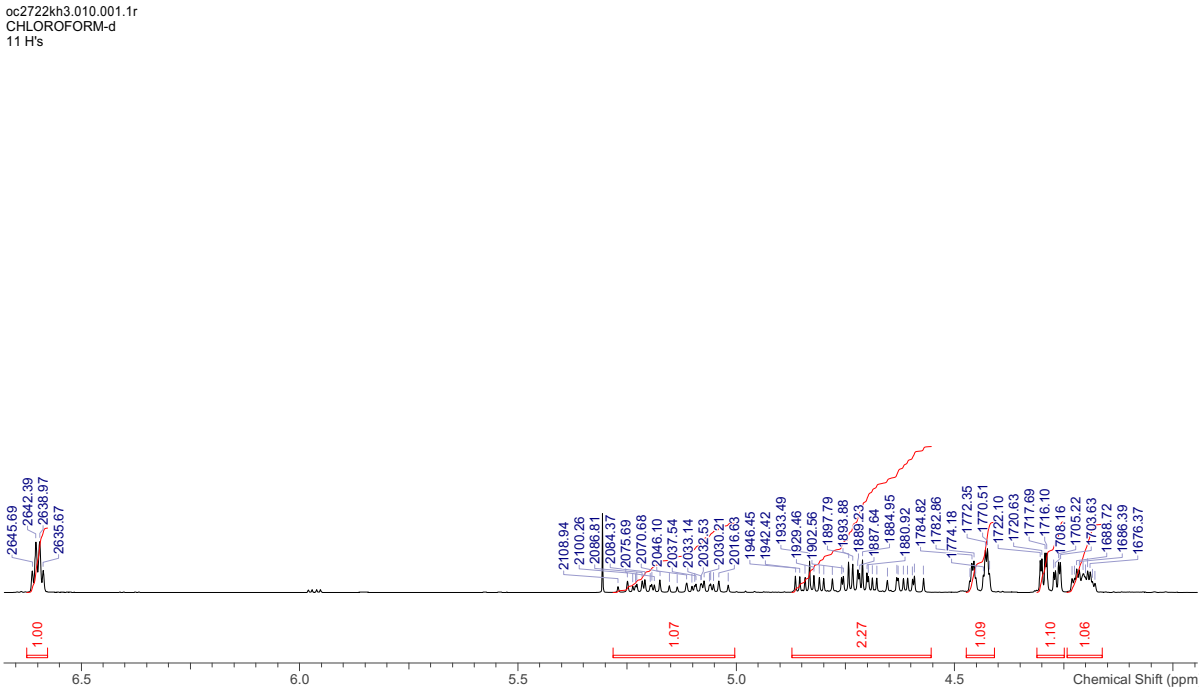
6.3.3 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α-D-glucopyranosyl trichloroacetimidate (**9**)



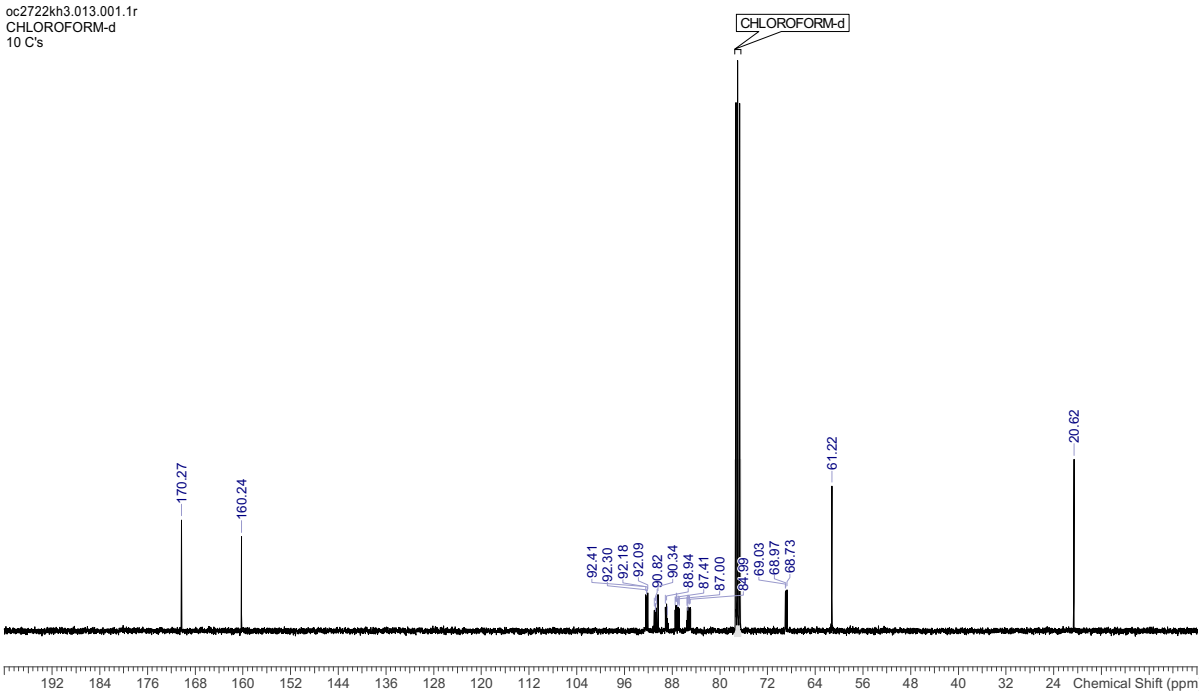
9

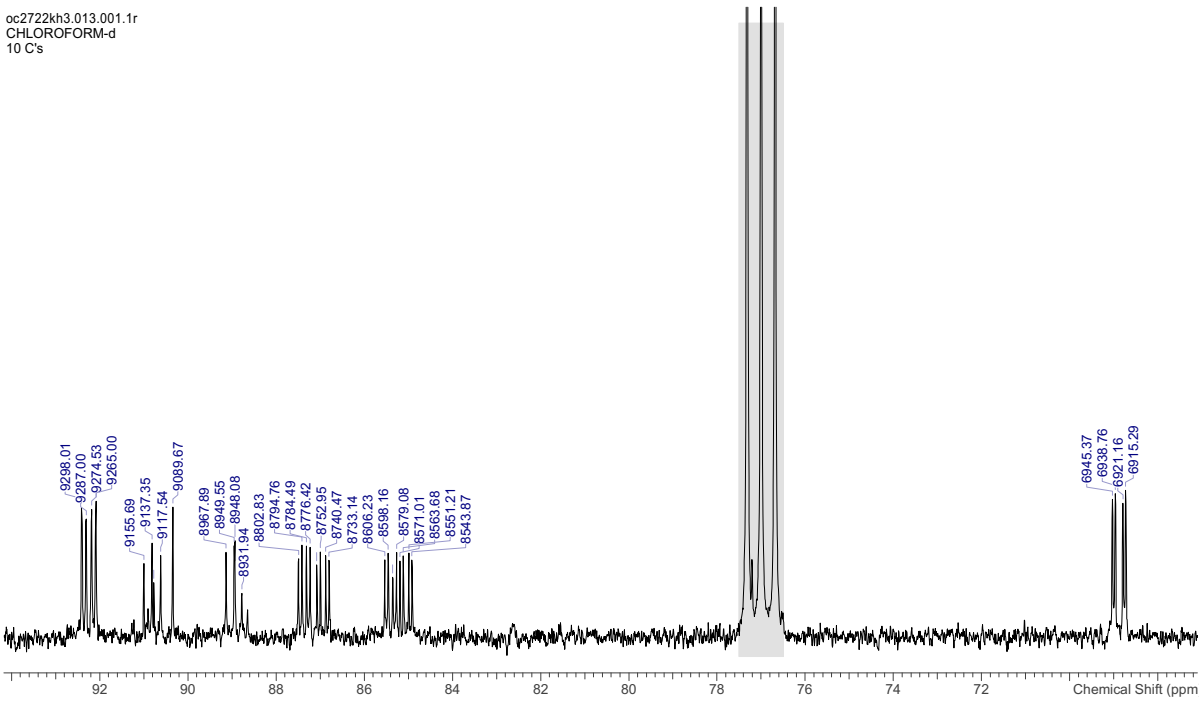
6.3.3.1 ^{1}H NMR, 400 MHz, $CDCl_3$



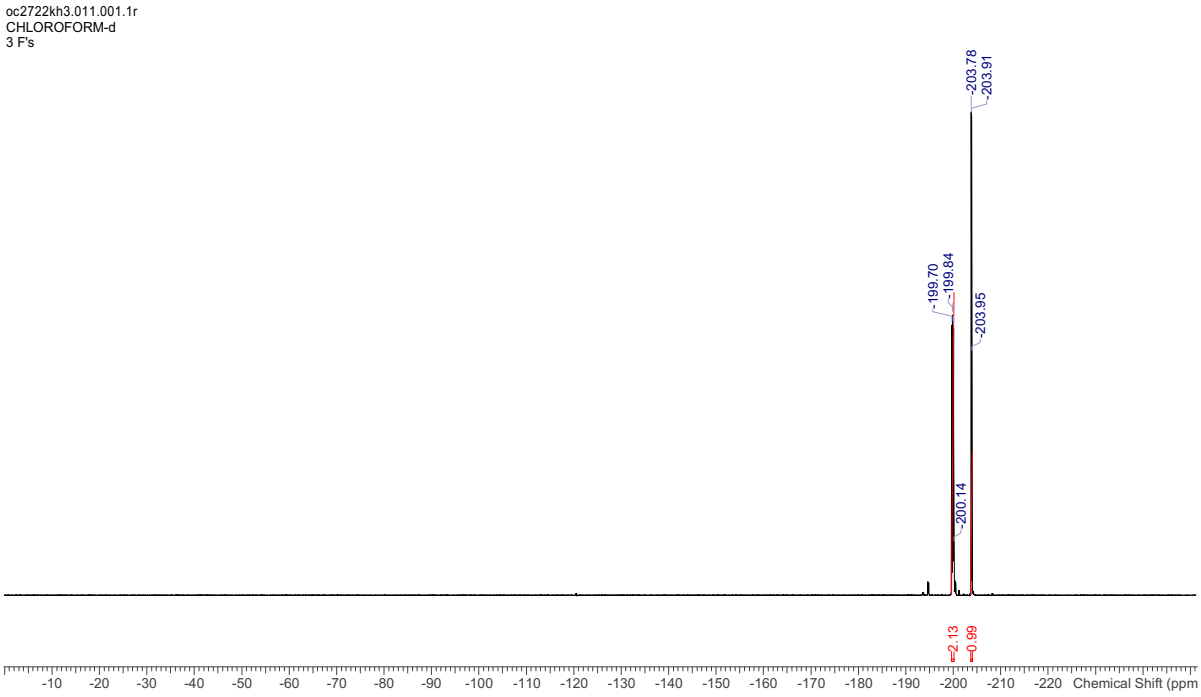


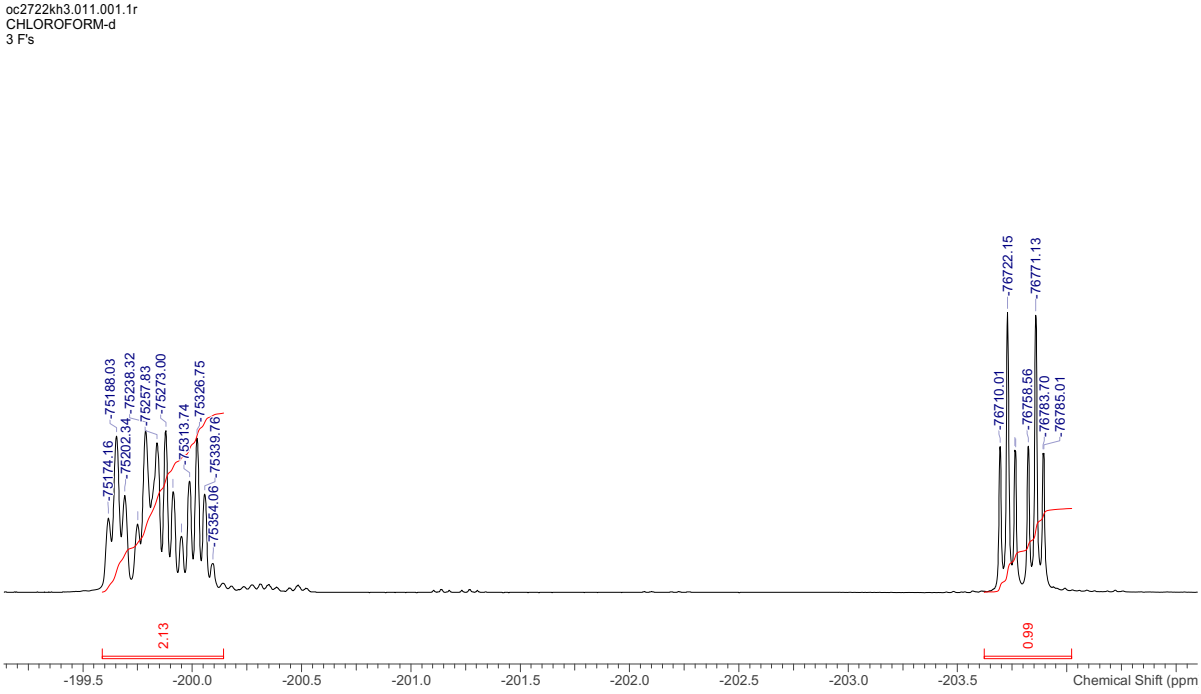
6.3.3.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$



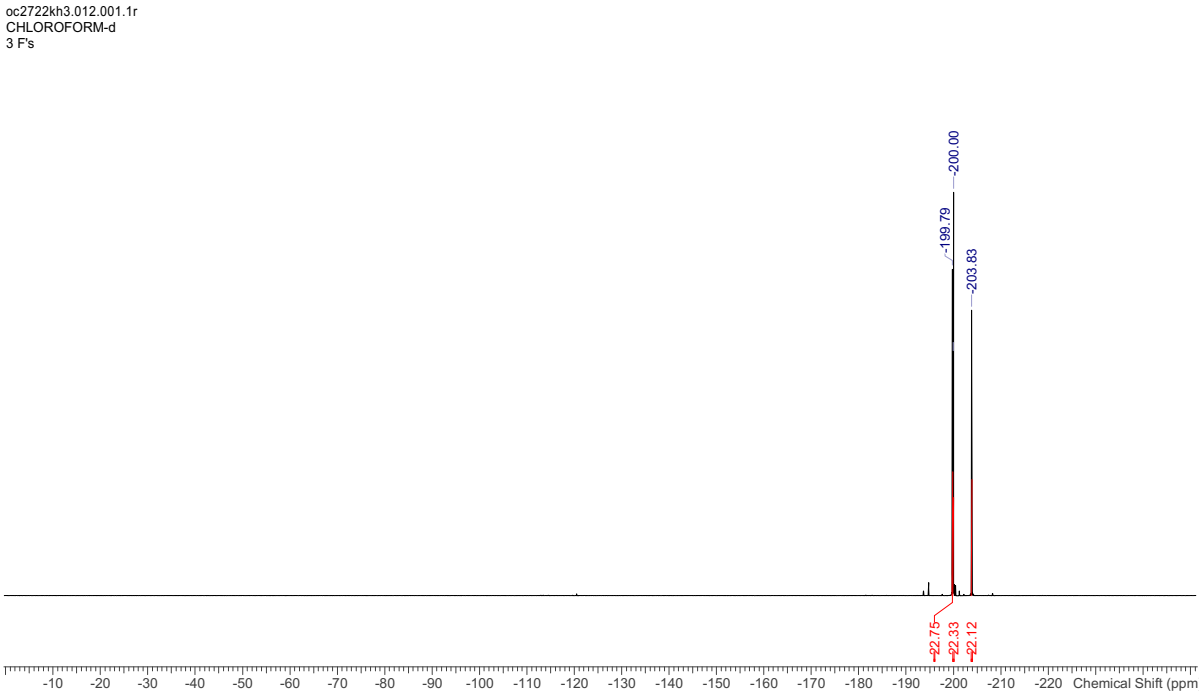


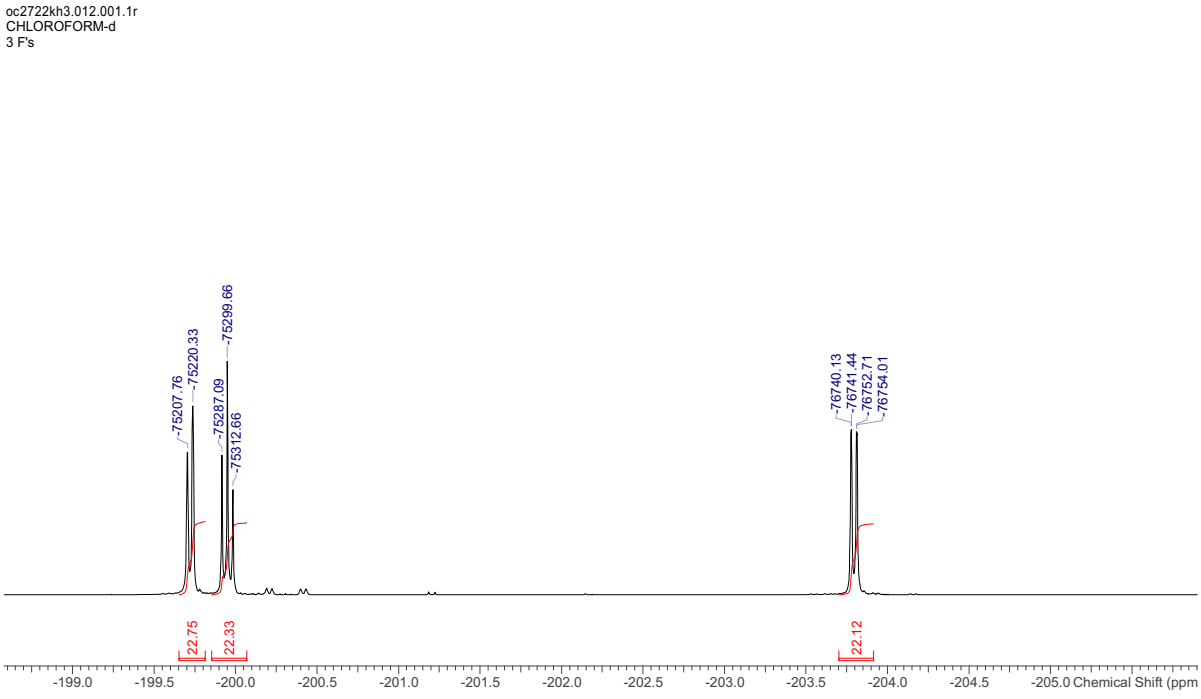
6.3.3.3 ^{19}F NMR, 376 MHz, $CDCl_3$



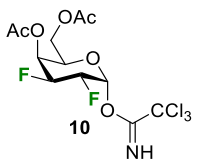


6.3.3.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



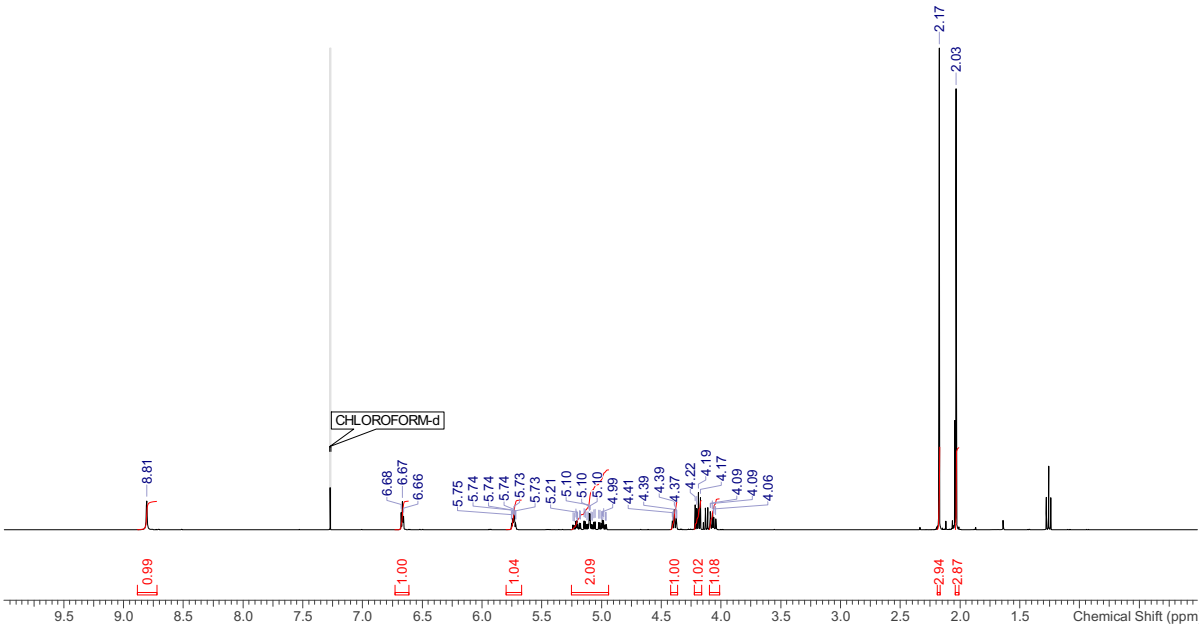


6.3.4 4,6-*O*-Acetyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranosyl trichloroacetimidate (**10**)

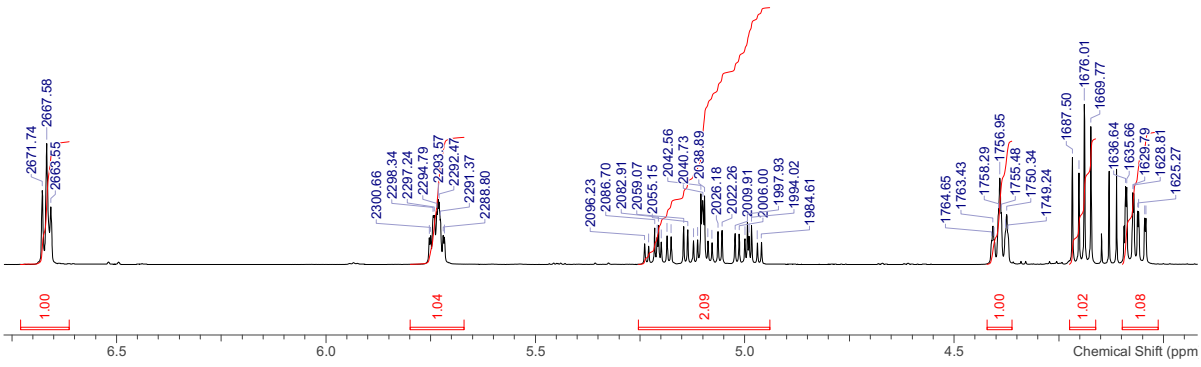


6.3.4.1 ^{1}H NMR, 400 MHz, $CDCl_3$

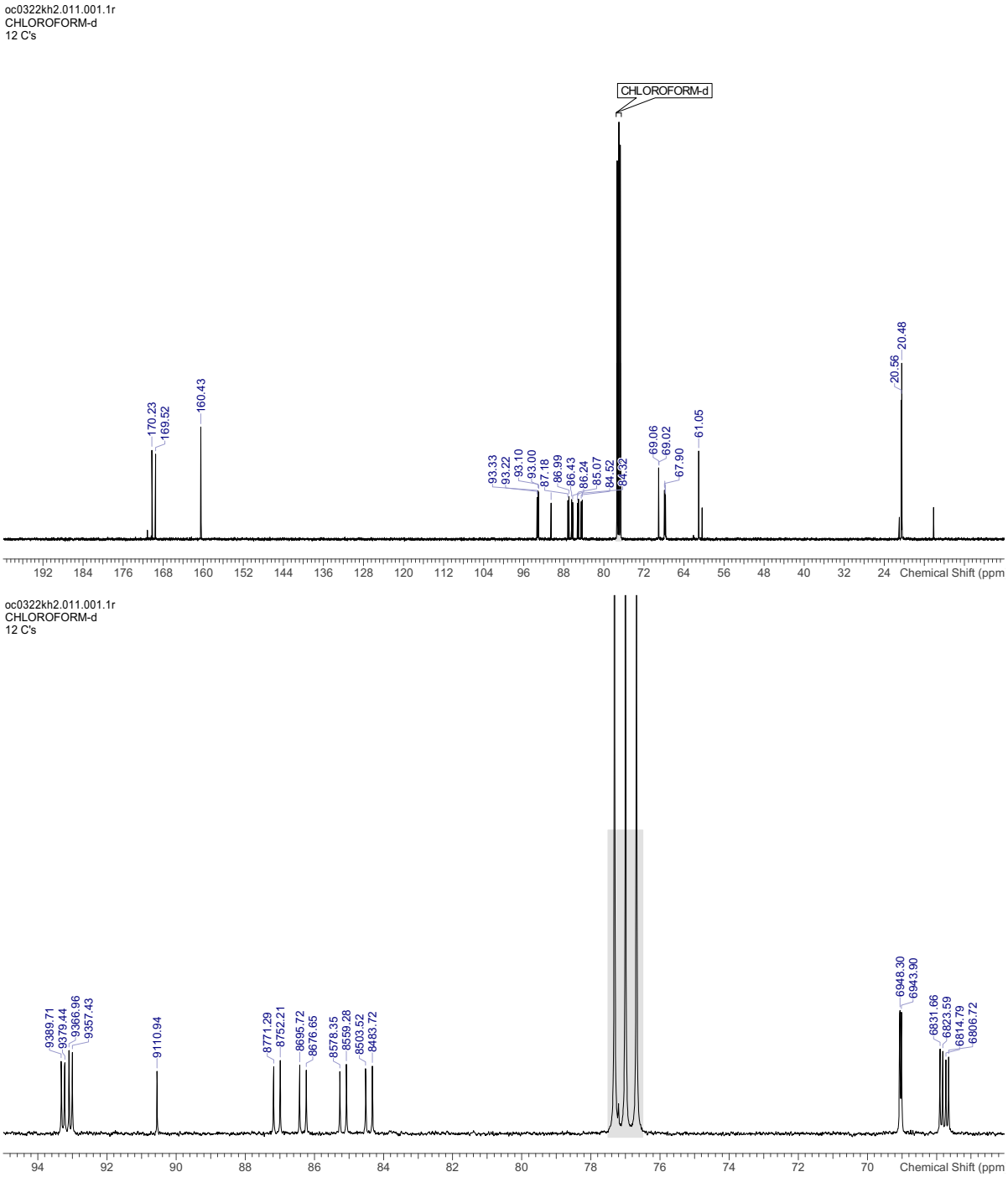
se3022kh6.010.001.1r
CHLOROFORM-d
14 H's



se3022kh6.010.001.1r
CHLOROFORM-d
14 H's

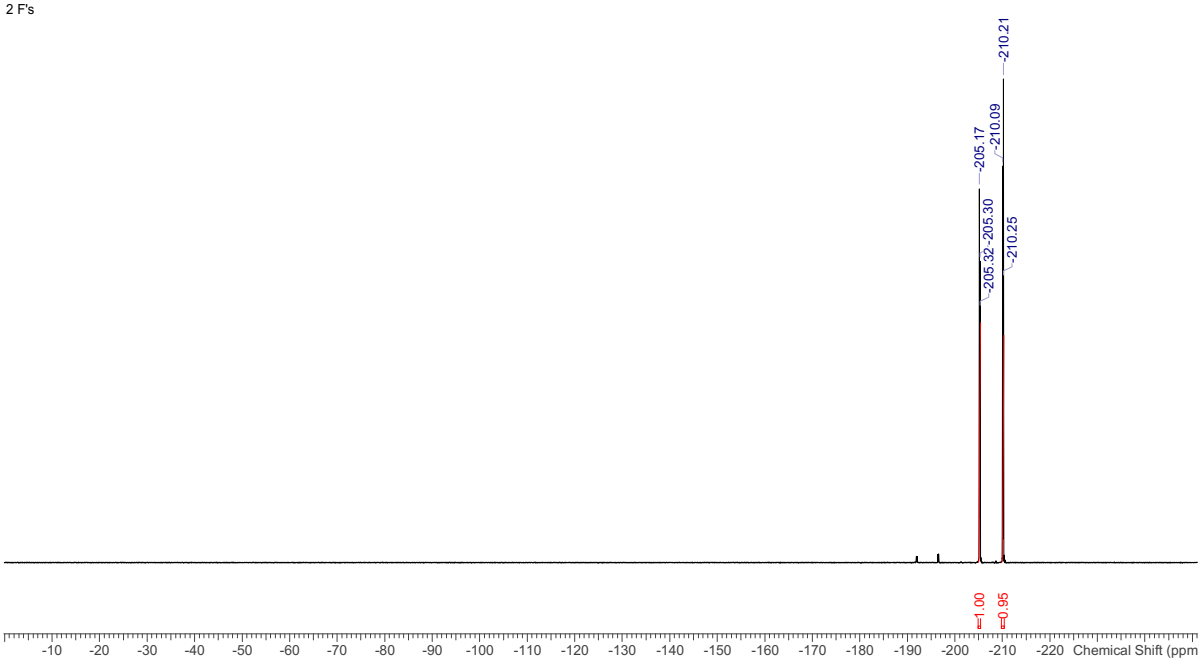


6.3.4.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

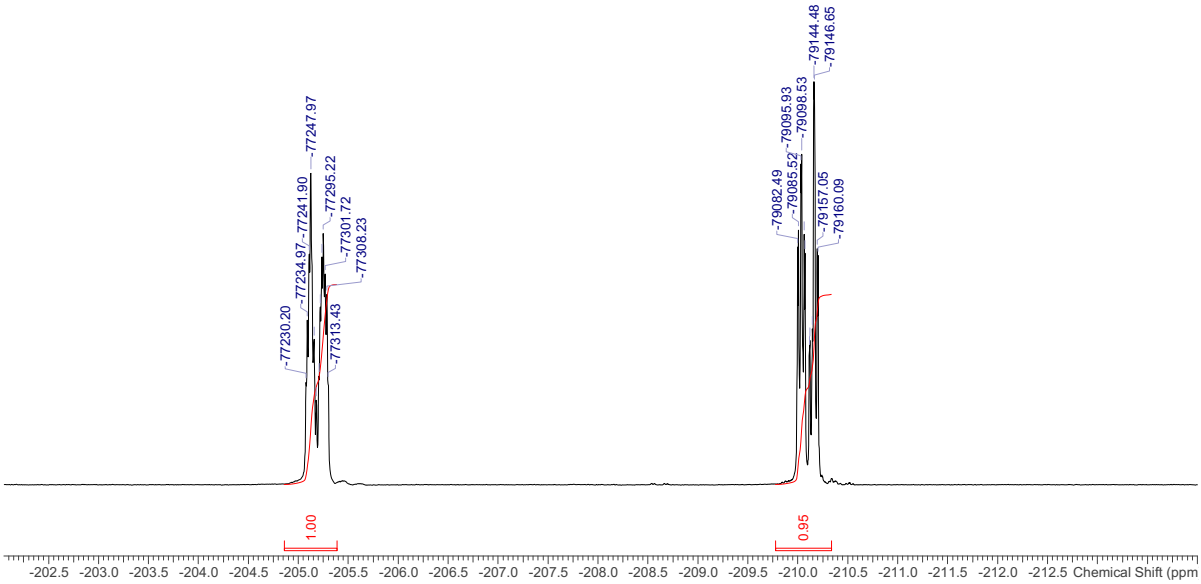


6.3.4.3 ^{19}F NMR, 376 MHz, $CDCl_3$

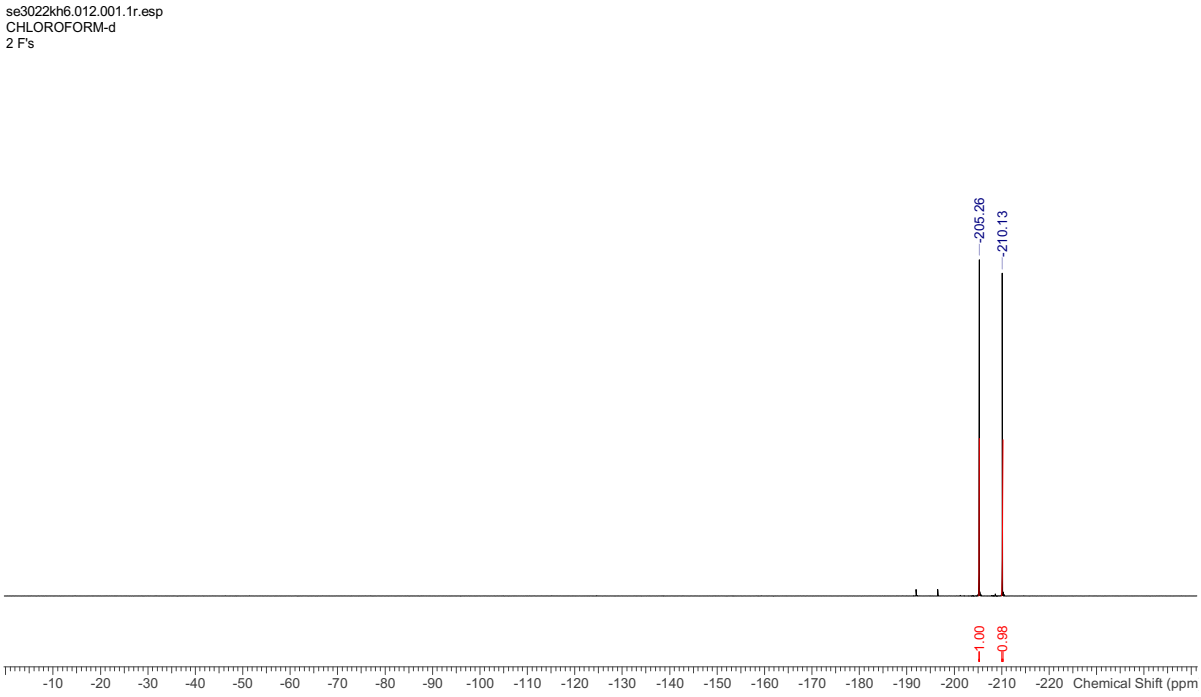
se3022kh6.011.001.1r
CHLOROFORM-d
2 F's

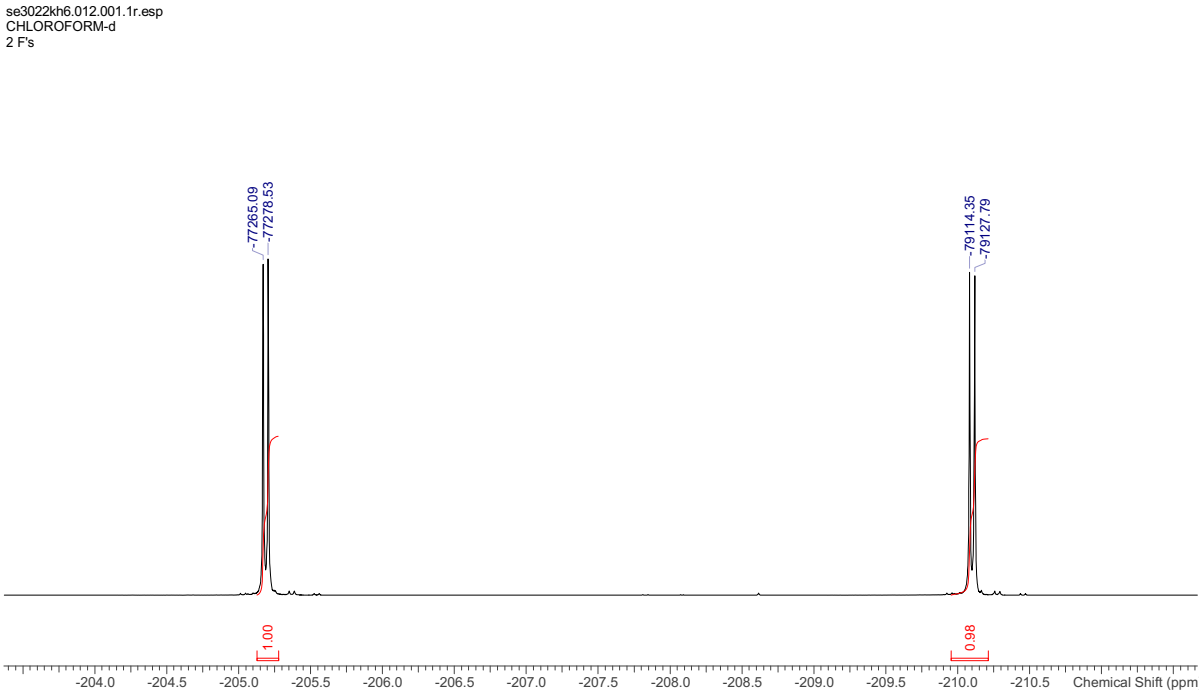


se3022kh6.011.001.1r
CHLOROFORM-d
2 F's

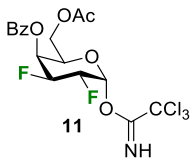


6.3.4.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



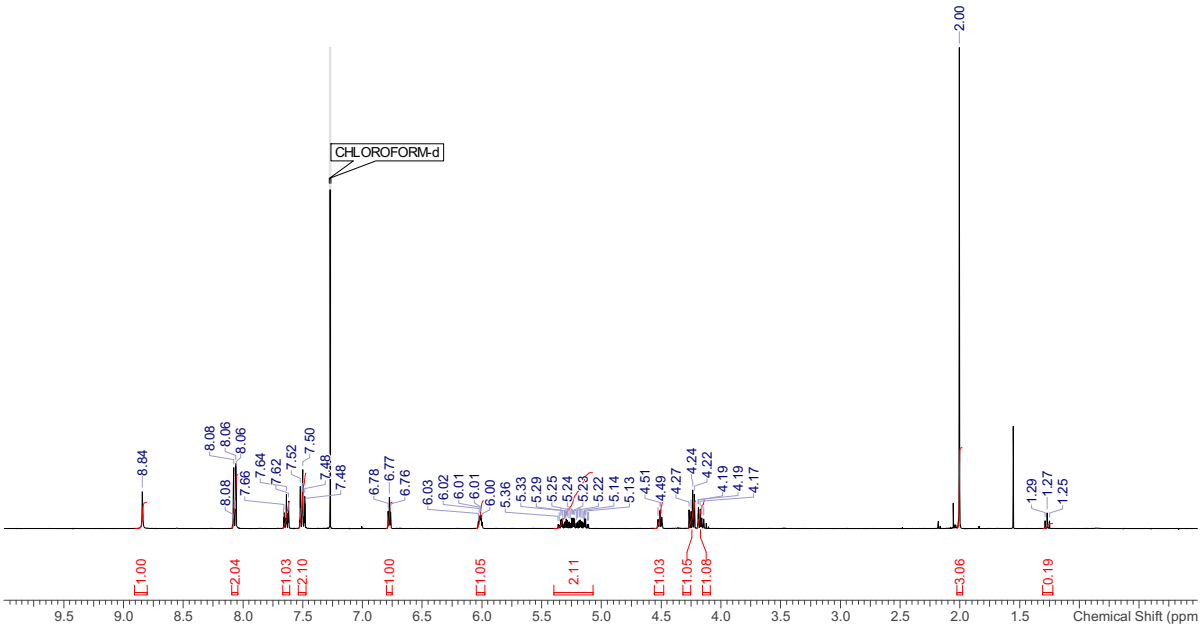


6.3.5 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranosyl trichloroacetimidate (**11**)

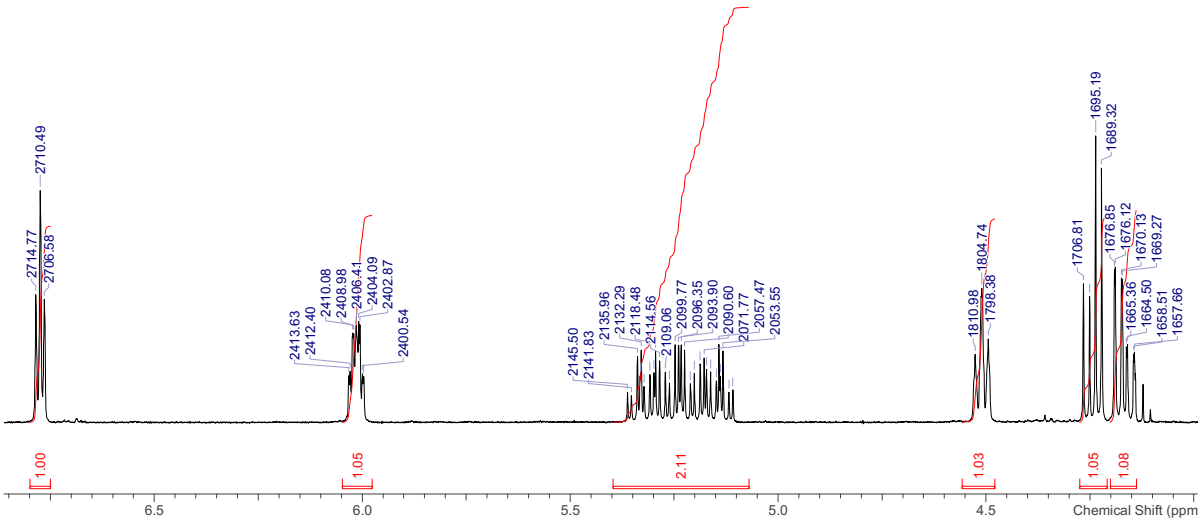


6.3.5.1 ^{1}H NMR, 400 MHz, $CDCl_3$

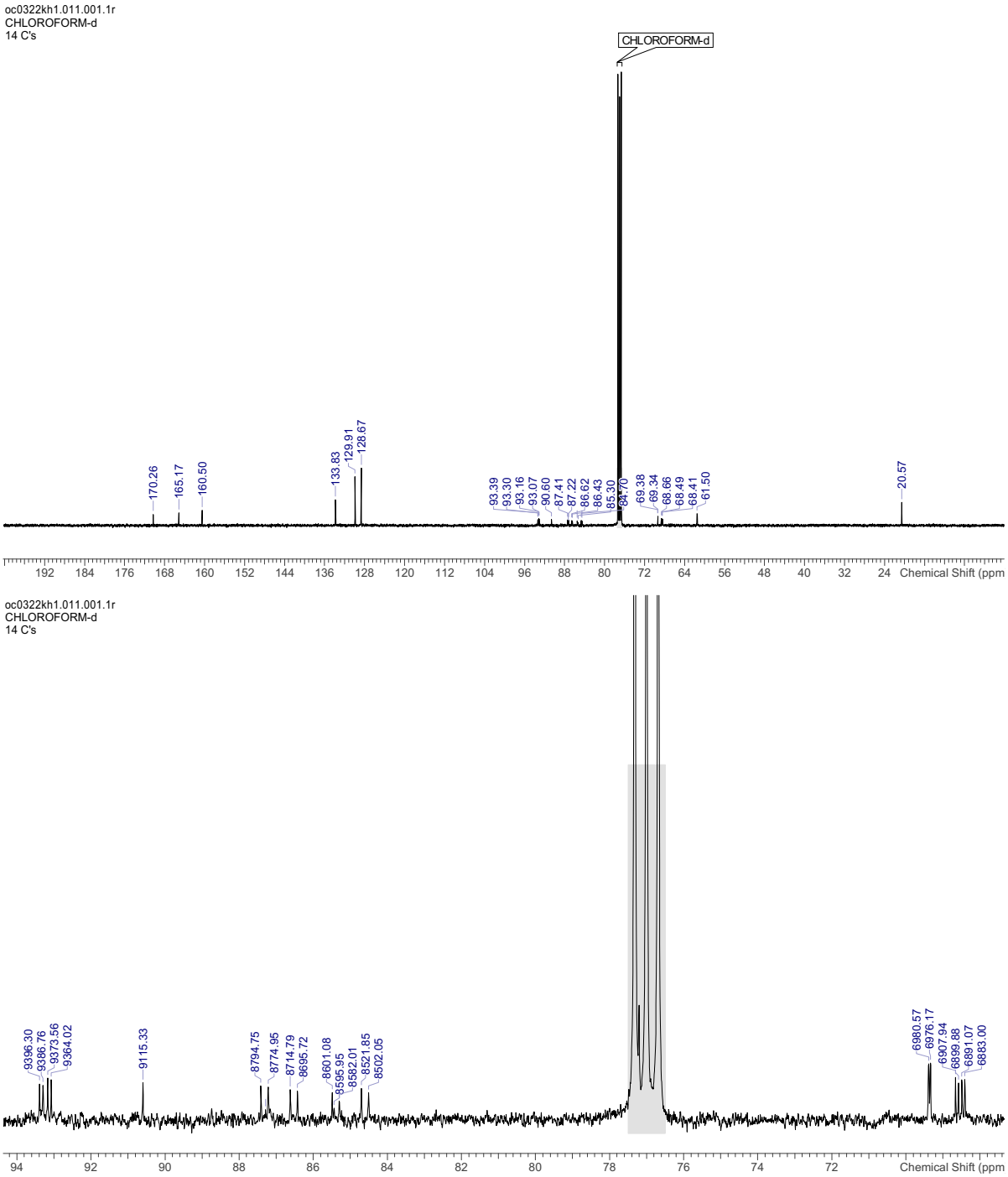
se3022kh4.010.001.1r
CHLOROFORM-d
17 H's



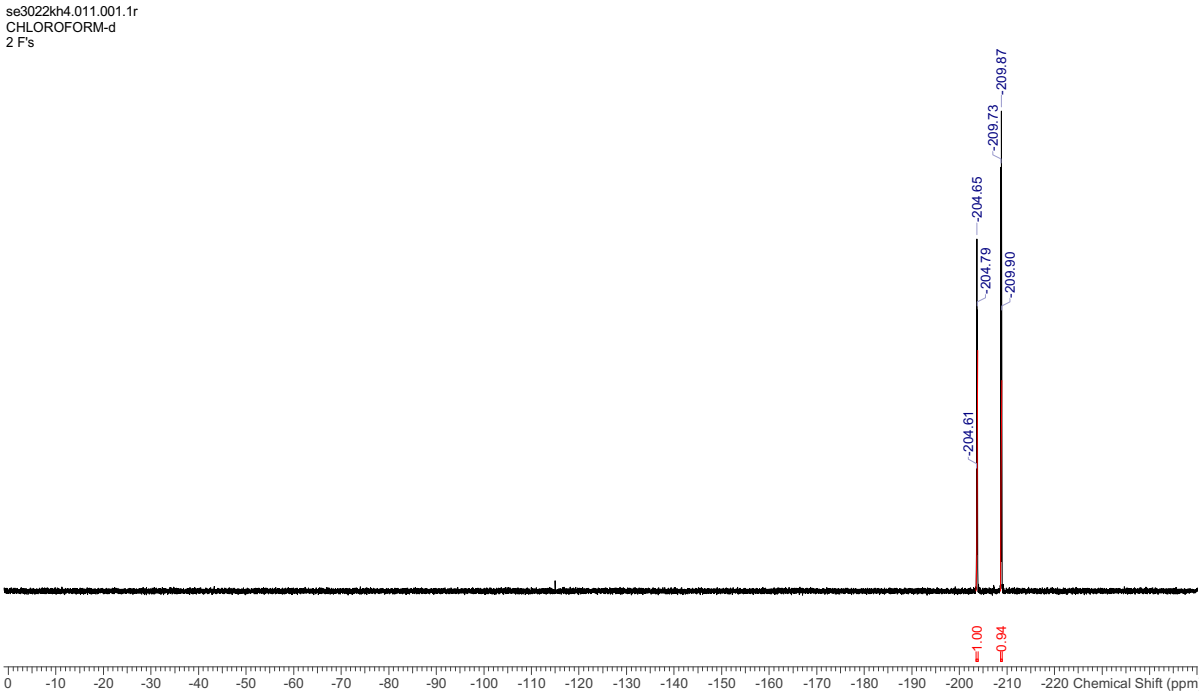
se3022kh4.010.001.1r
CHLOROFORM-d
17 H's

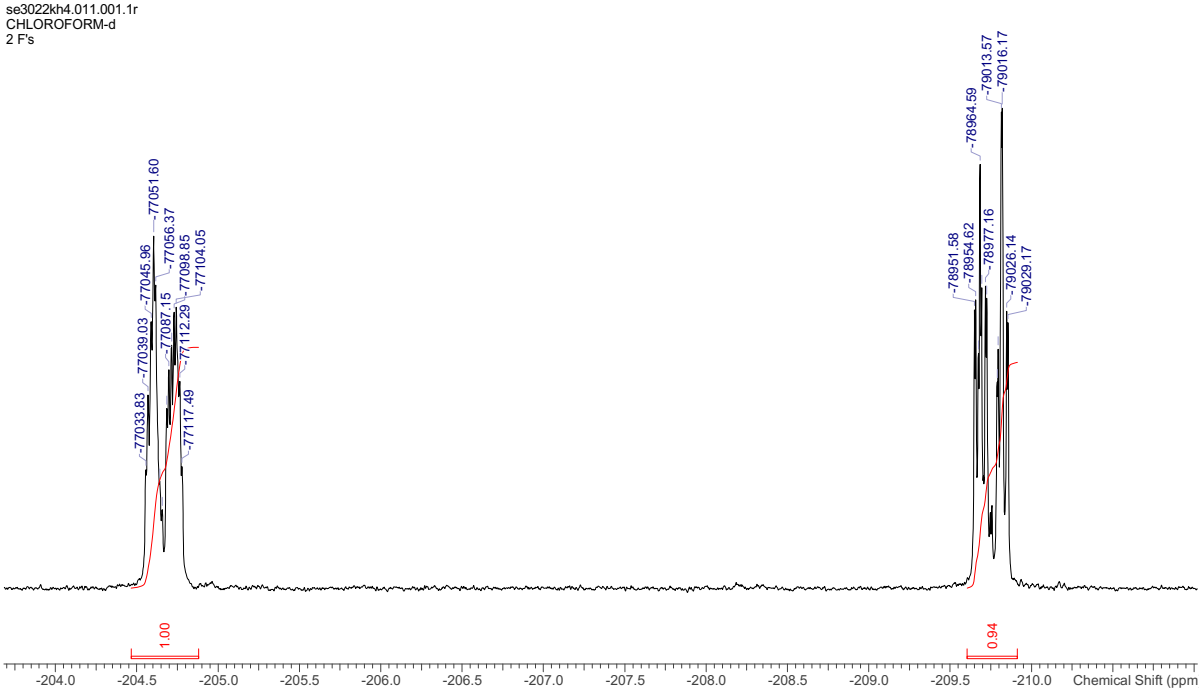


6.3.5.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

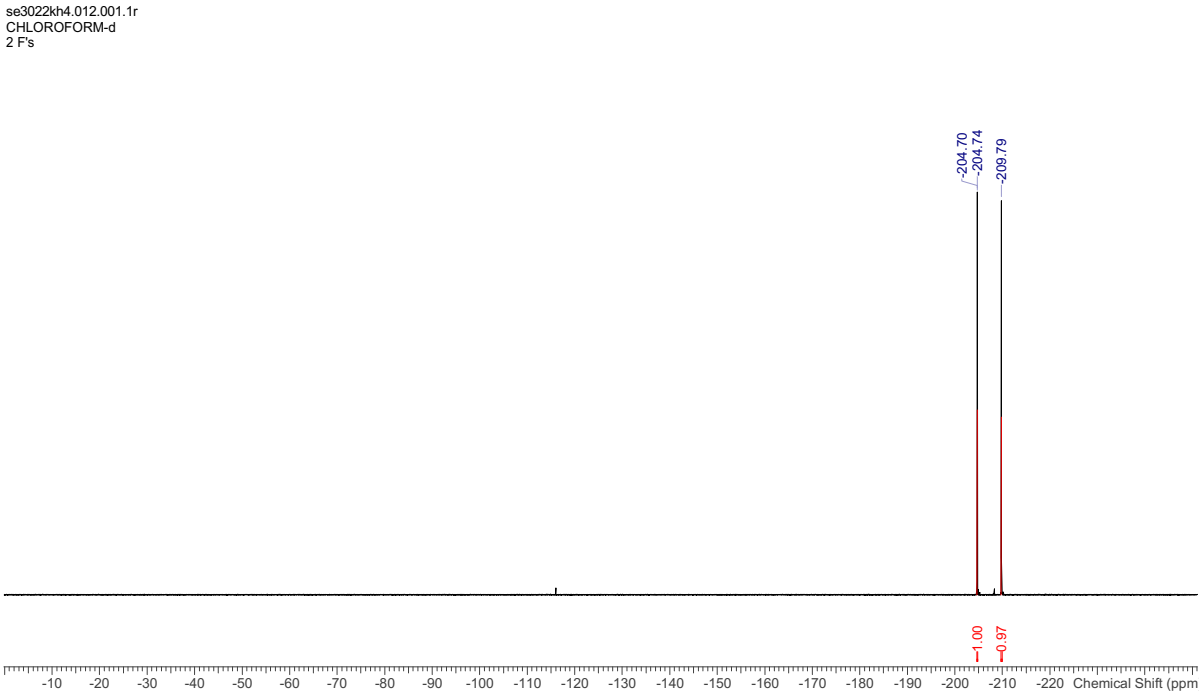


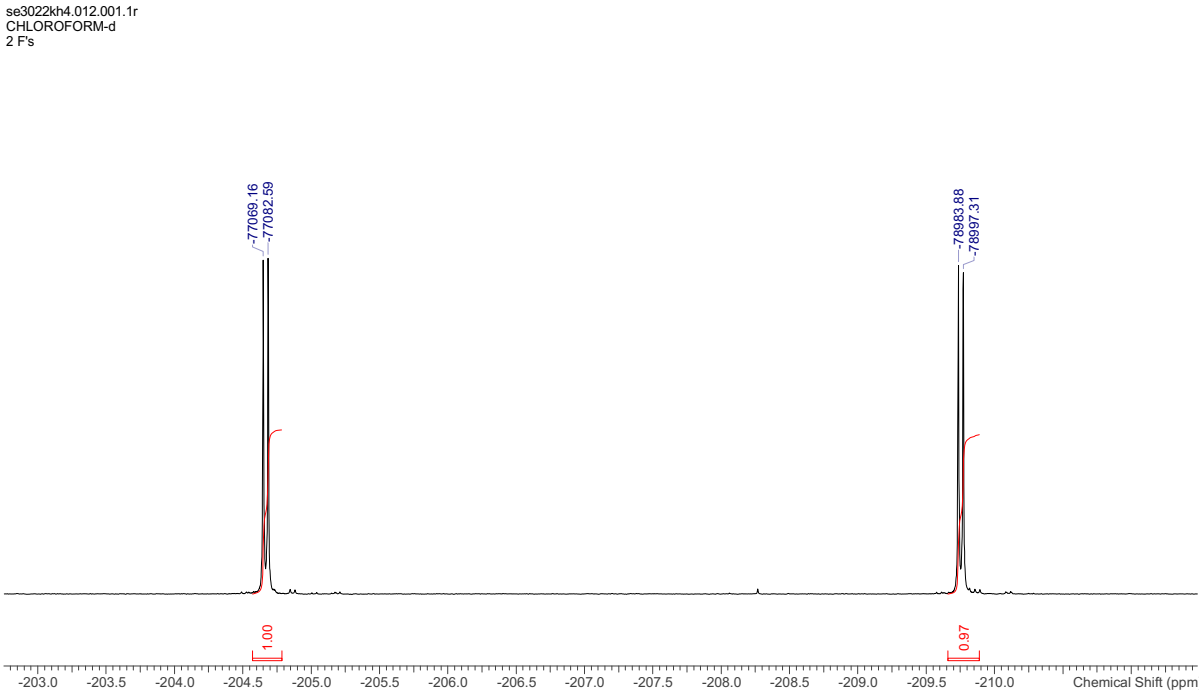
6.3.5.3 ^{19}F NMR, 376 MHz, $CDCl_3$



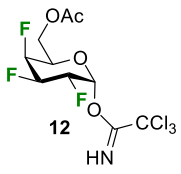


6.3.5.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



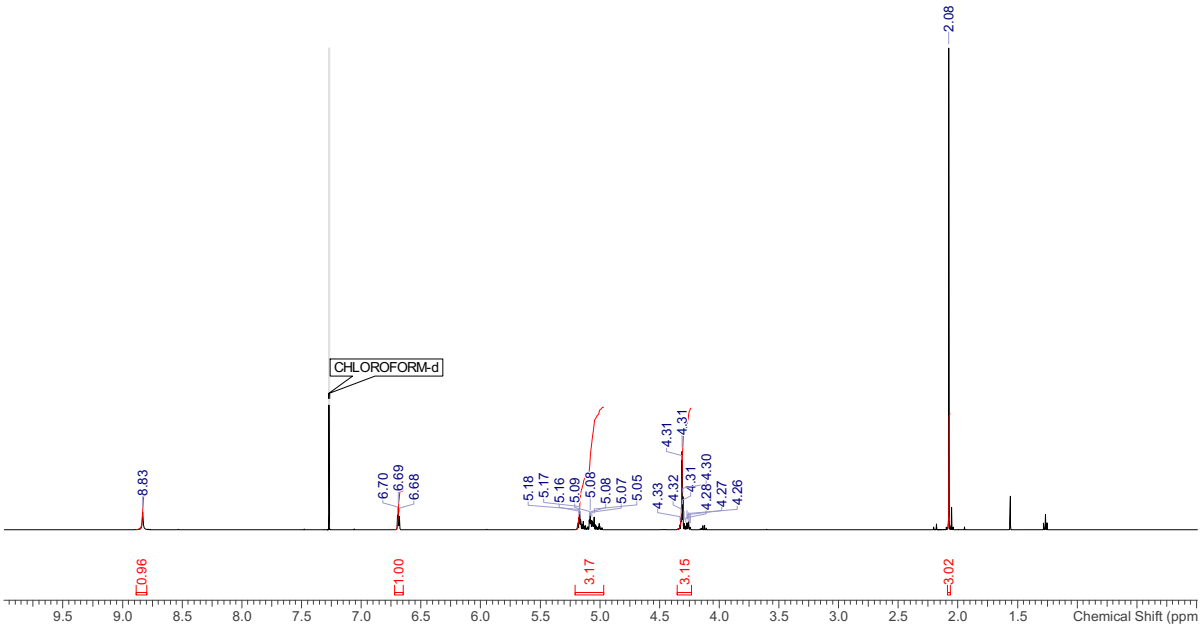


6.3.6 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α-D-galactopyranosyl trichloroacetimidate (**12**)

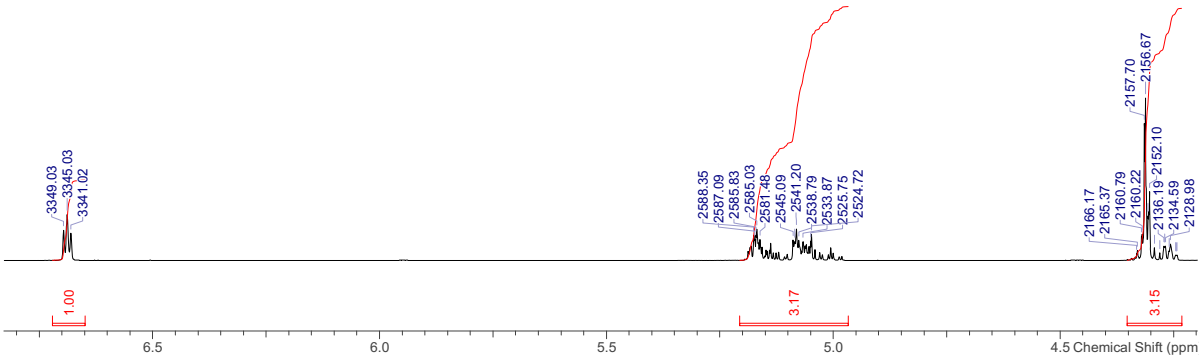


6.3.6.1 ^{1}H NMR, 500 MHz, $CDCl_3$

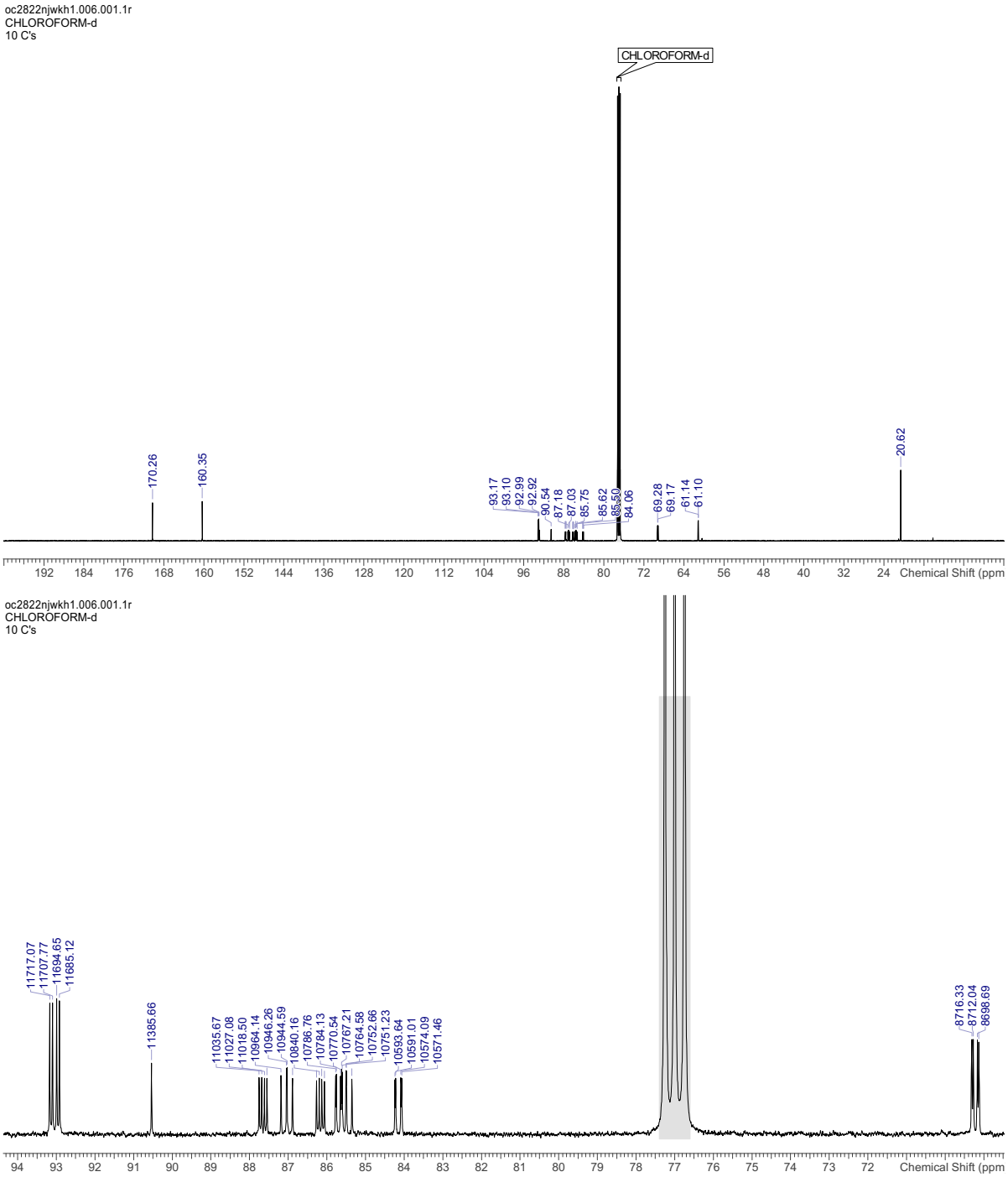
oc2822njwkh1.001.001.1r
CHLOROFORM-d
11 H's



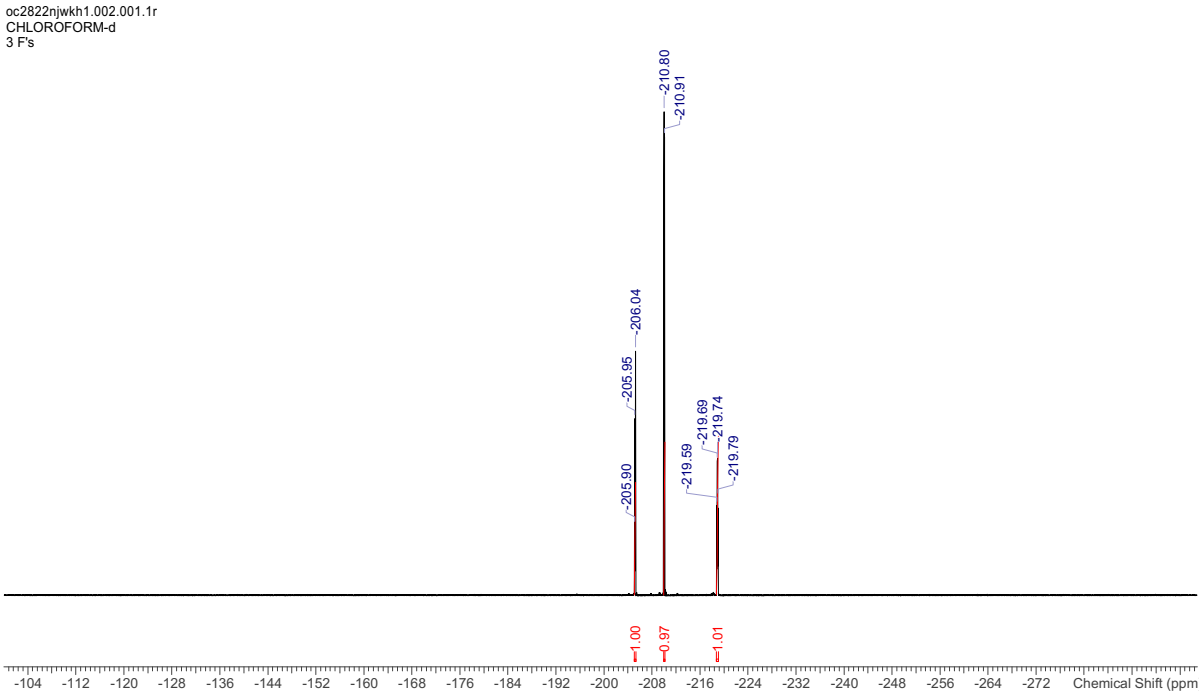
oc2822njwkh1.001.001.1r
CHLOROFORM-d
11 H's

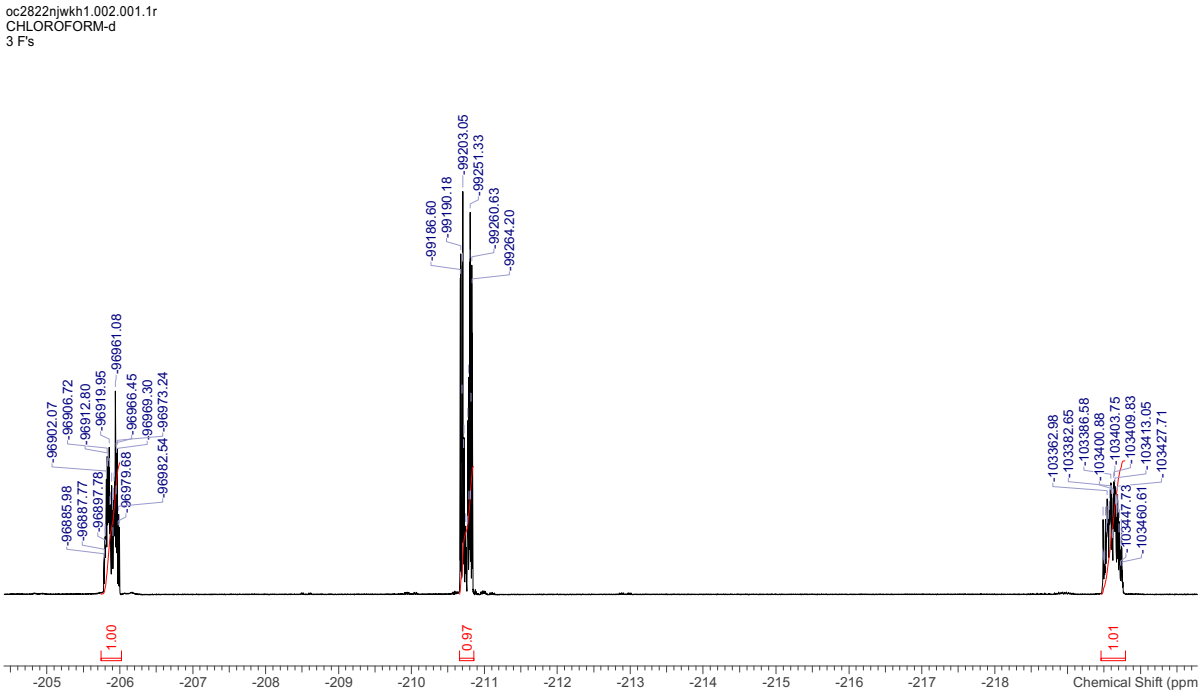


6.3.6.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

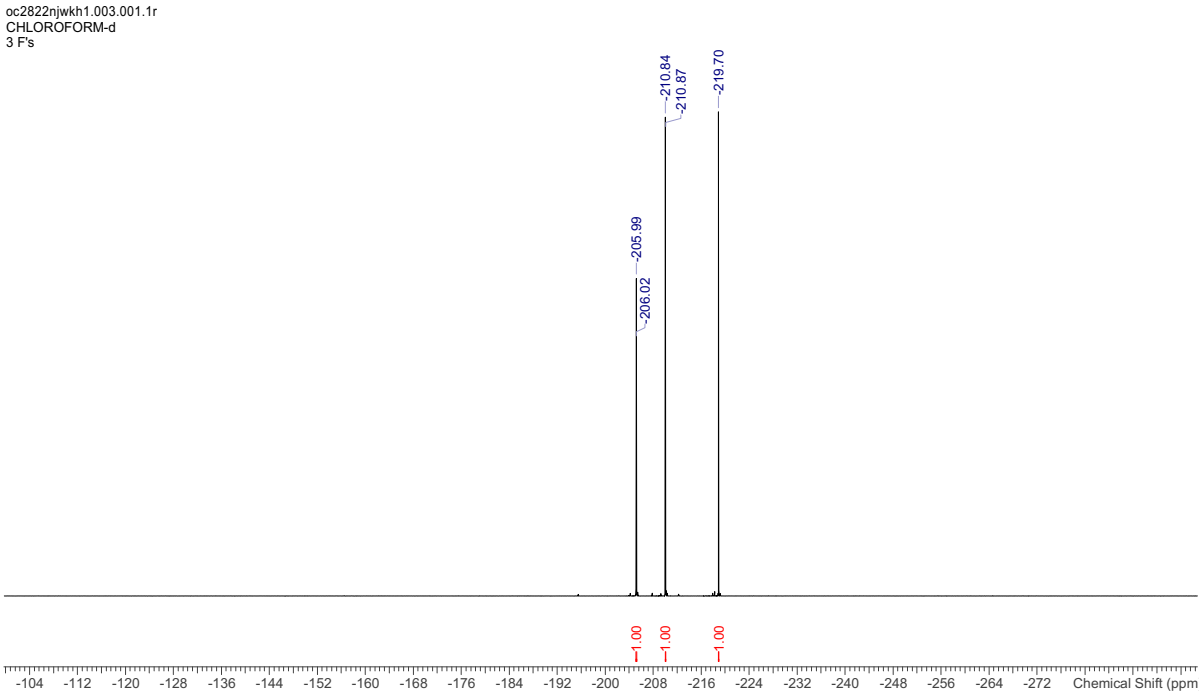


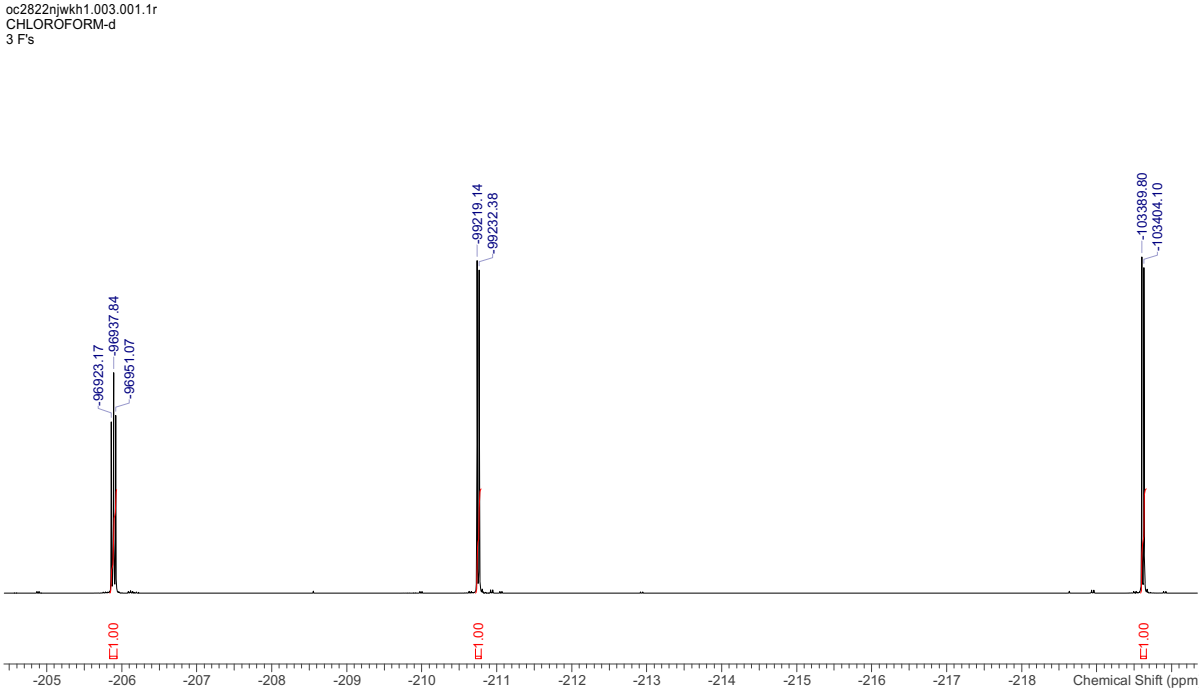
6.3.6.3 ^{19}F NMR, 471 MHz, $CDCl_3$





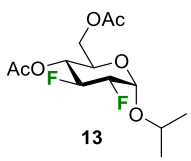
6.3.6.4 $^{19}F\{^{1}H\}$ NMR, 471 MHz, $CDCl_3$





6.4 Copies of the spectra of the isopropyl glycosides

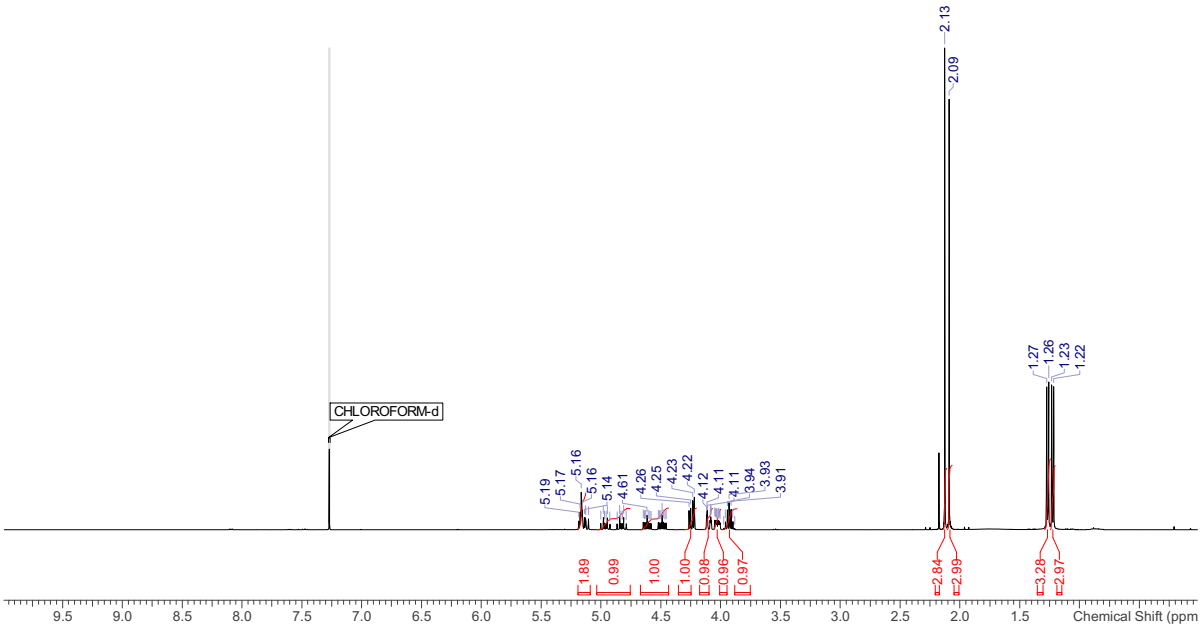
6.4.1 Isopropyl 4,6-di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α-D-glucopyranoside (**13α**)



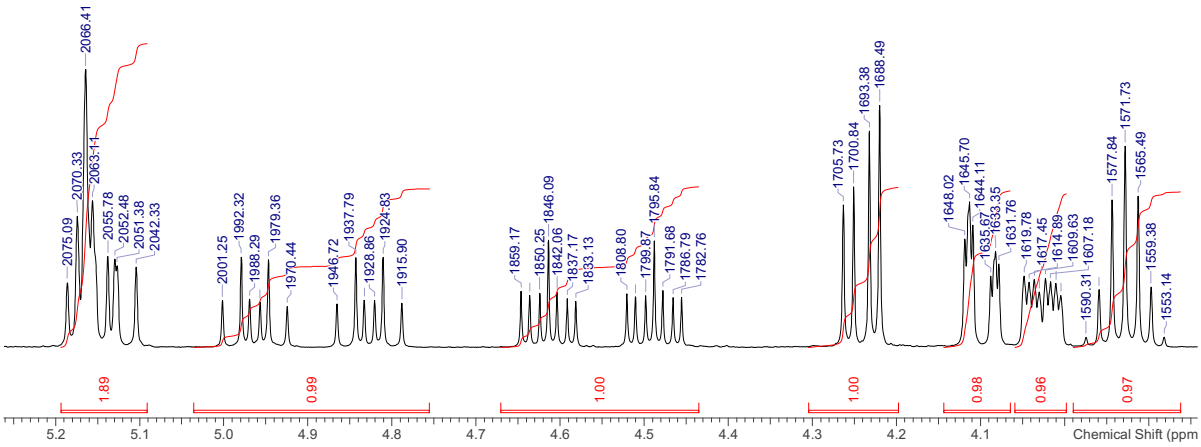
13

6.4.1.1 ^{1}H NMR, 400 MHz, $CDCl_3$

se0121kh2.010.001.1r
CHLOROFORM-d
20 H's

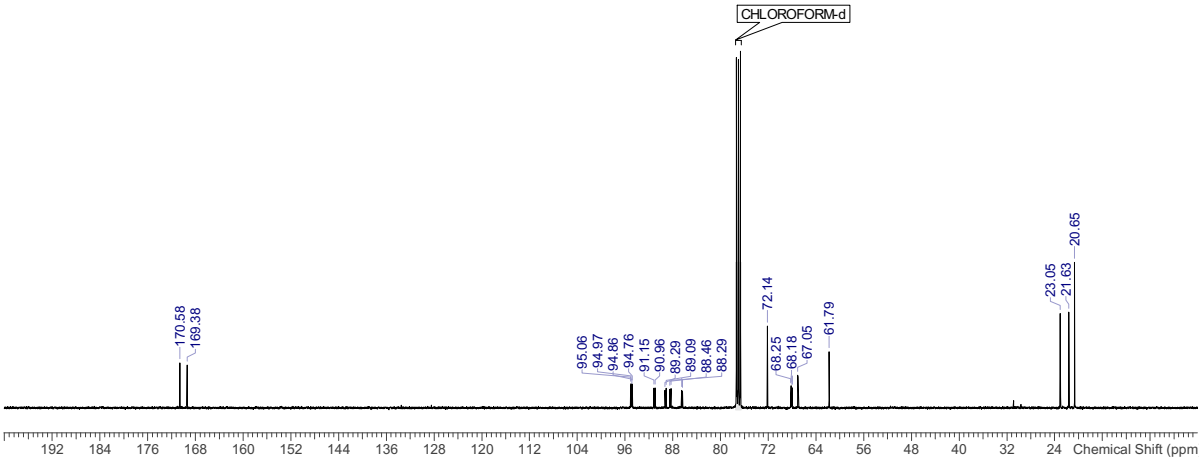


se0121kh2.010.001.1r
CHLOROFORM-d
20 H's

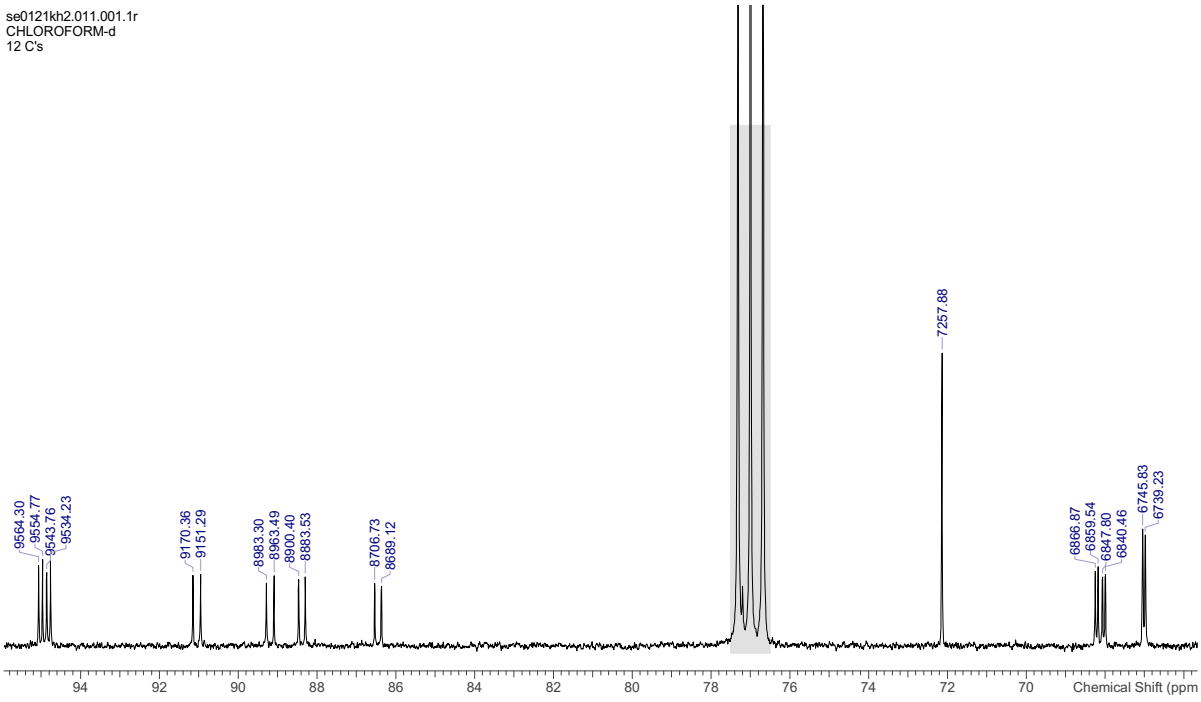


6.4.1.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

se0121kh2.011.001.1r
CHLOROFORM-d
12 C's

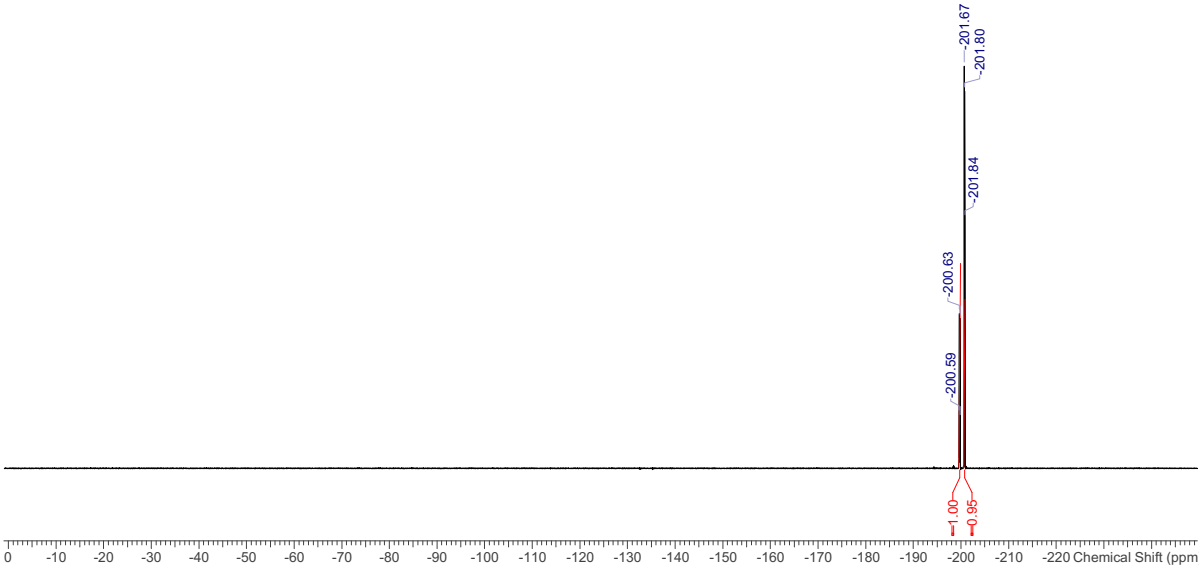


se0121kh2.011.001.1r
CHLOROFORM-d
12 C's

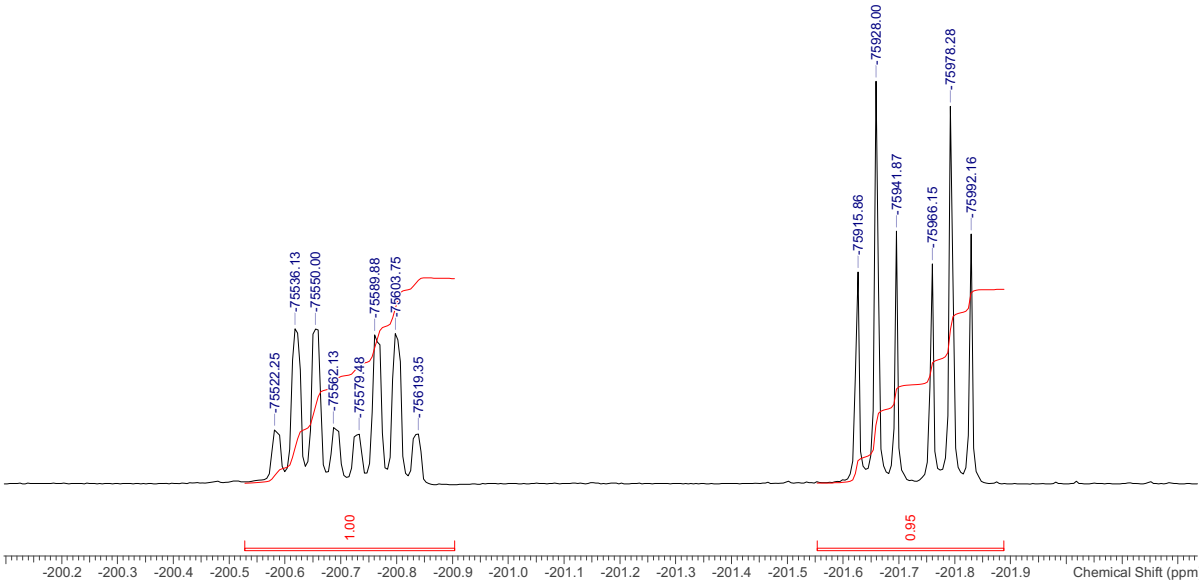


6.4.1.3 ^{19}F NMR, 376 MHz, $CDCl_3$

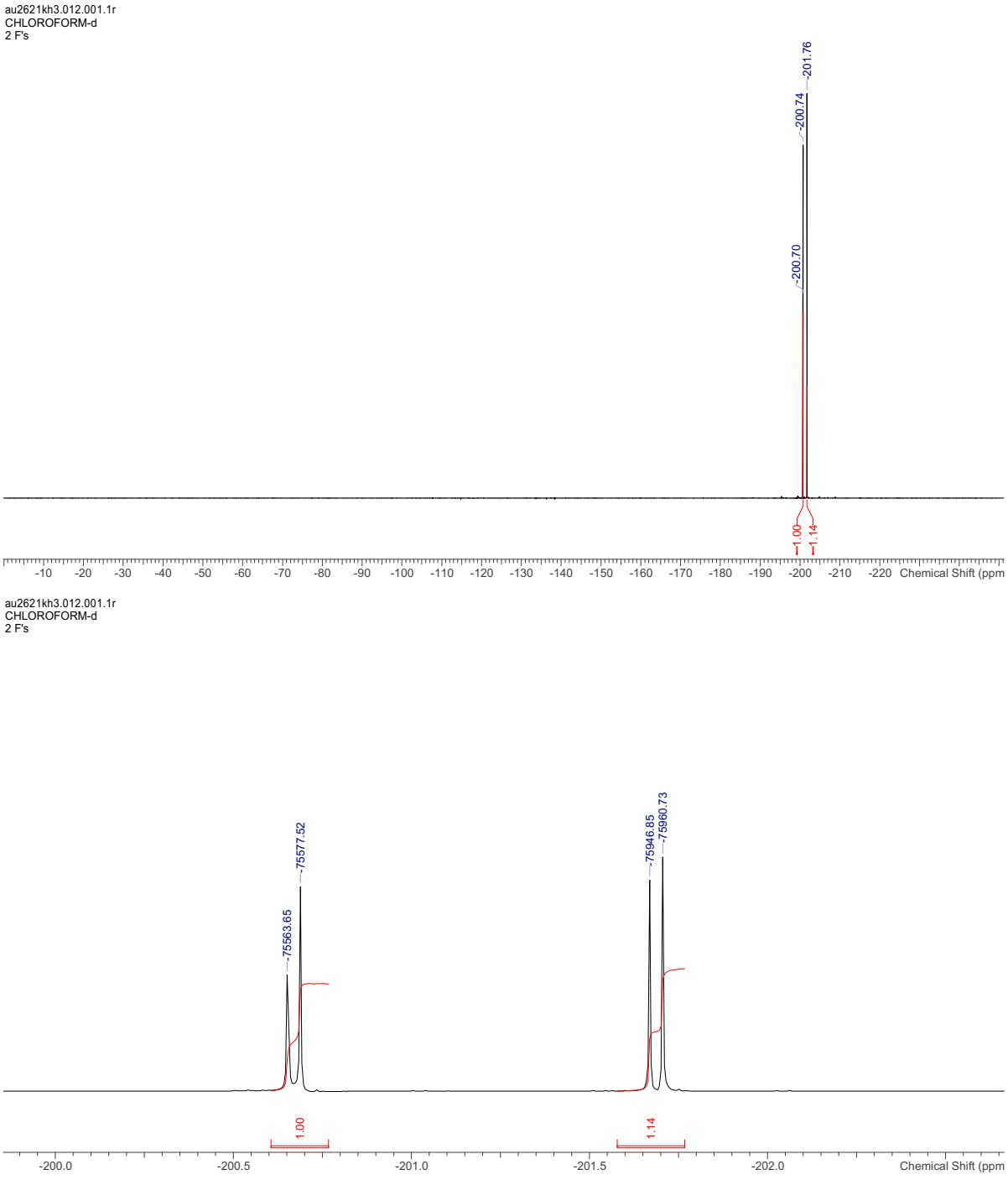
au2621kh3.011.001.1r
CHLOROFORM-d
2 F's



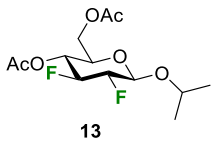
au2621kh3.011.001.1r
CHLOROFORM-d
2 F's



6.4.1.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



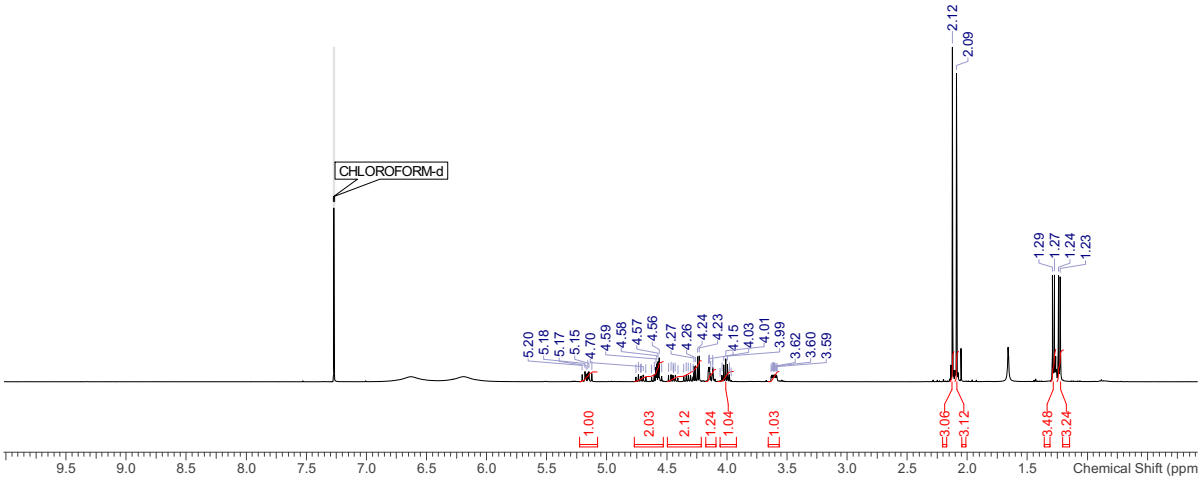
6.4.2 Isopropyl 4,6-di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-β-D-glucopyranoside (**13β**)



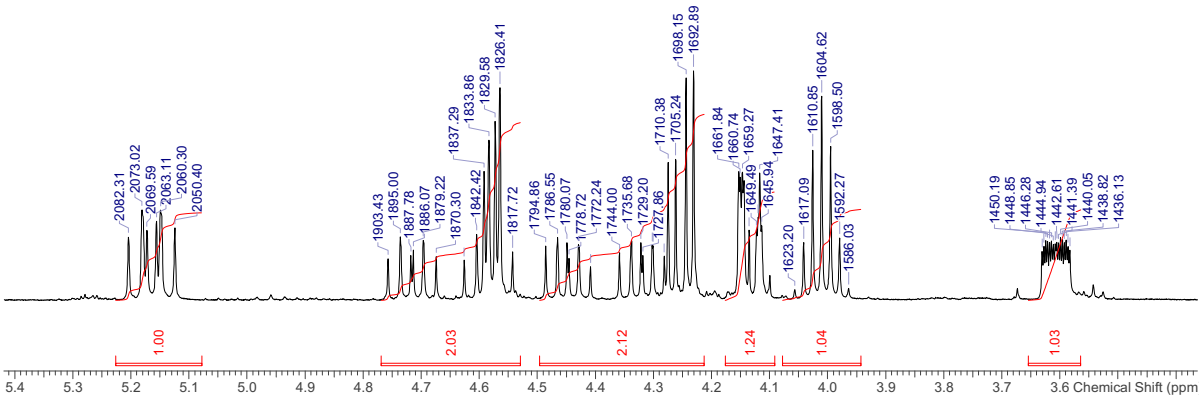
13

6.4.2.1 ^{1}H NMR, 400 MHz, $CDCl_3$

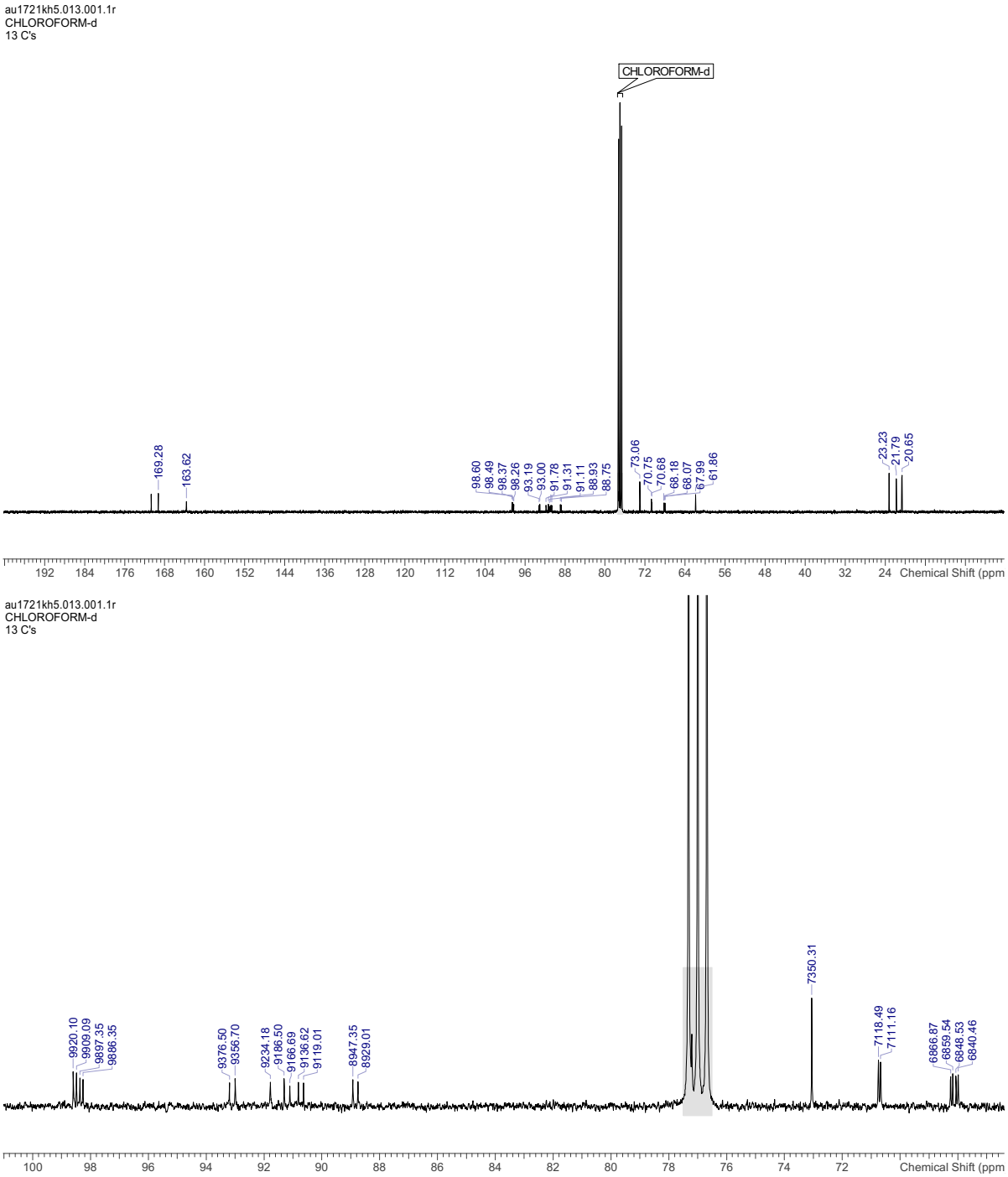
au1721kh5.010.001.1r
CHLOROFORM-d
20 H's



au1721kh5.010.001.1r
CHLOROFORM-d
20 H's

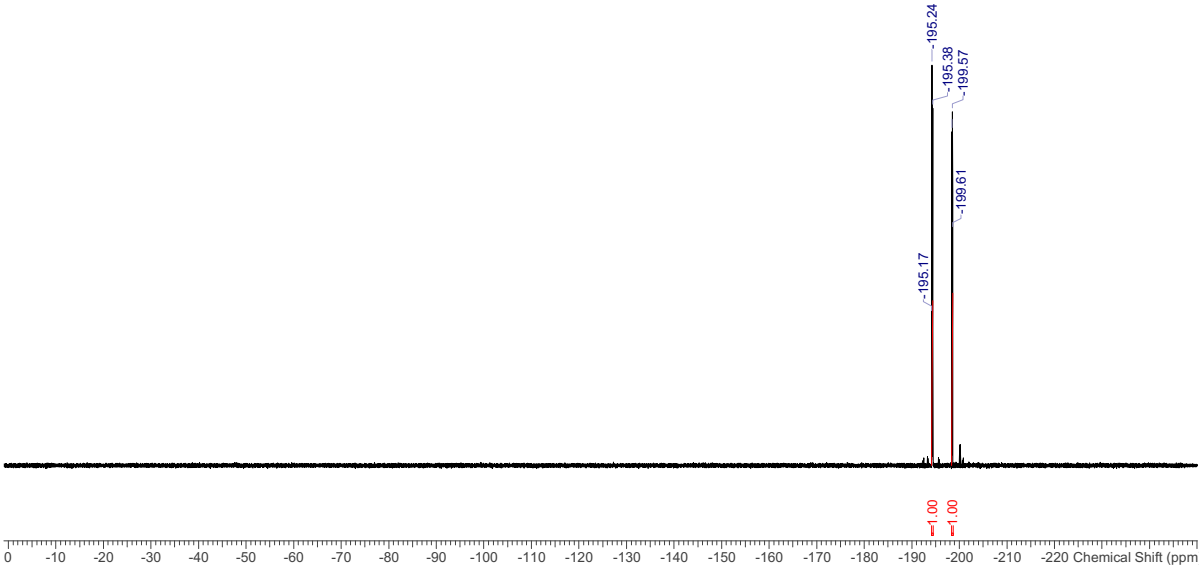


6.4.2.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

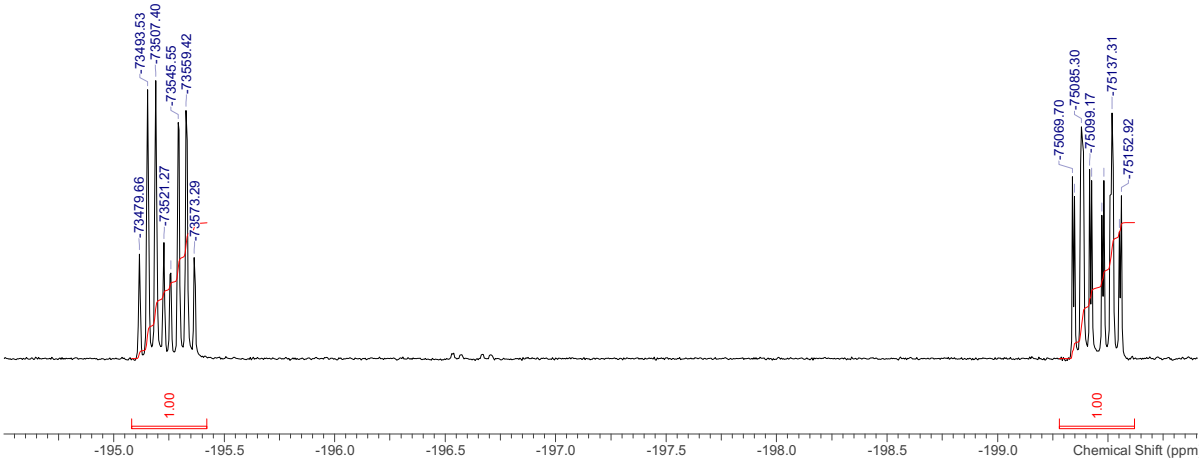


6.4.2.3 ^{19}F NMR, 376 MHz, $CDCl_3$

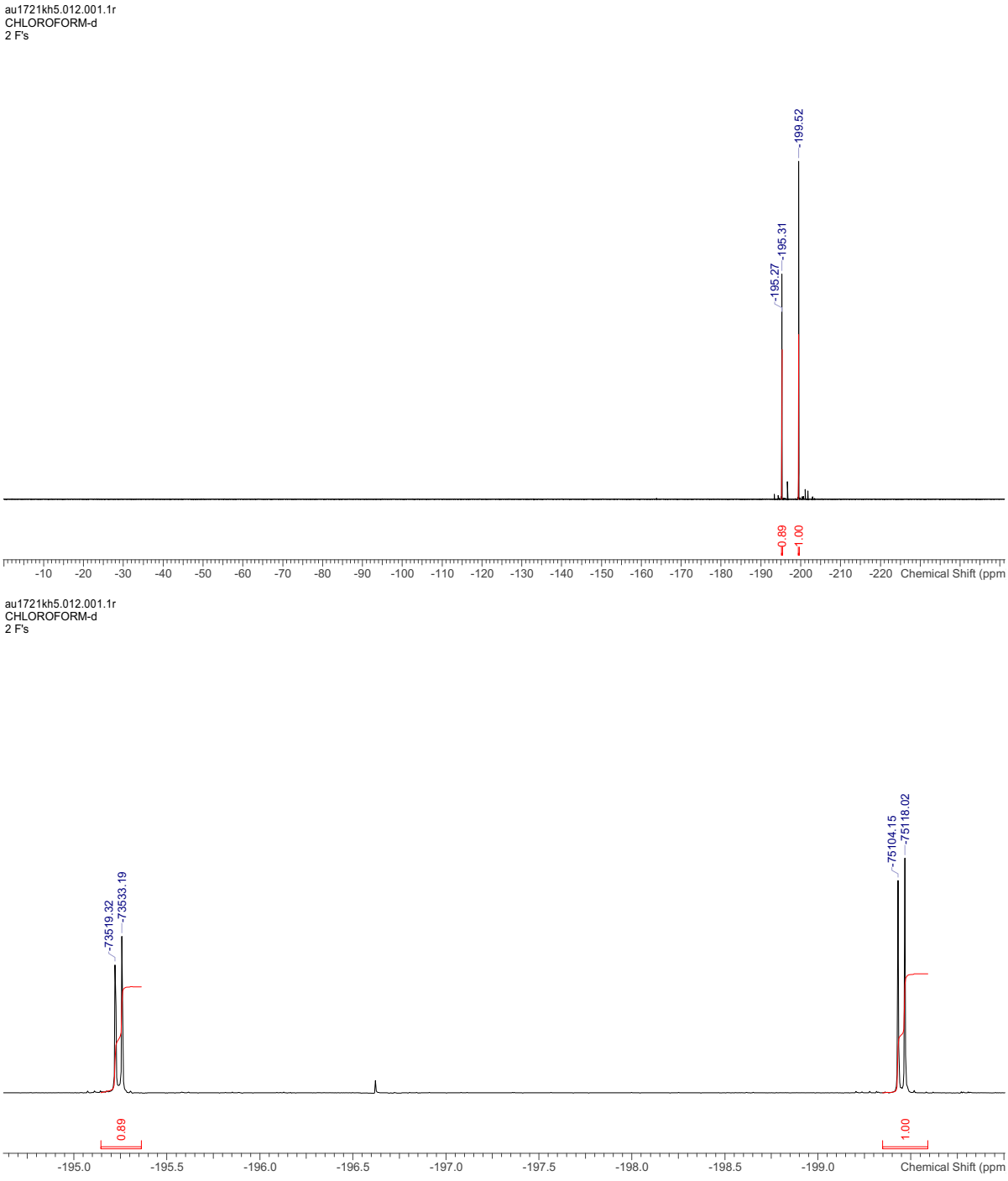
au1721kh5.011.001.1r
CHLOROFORM-d
2 F's



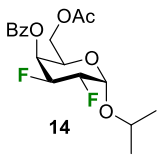
au1721kh5.011.001.1r
CHLOROFORM-d
2 F's



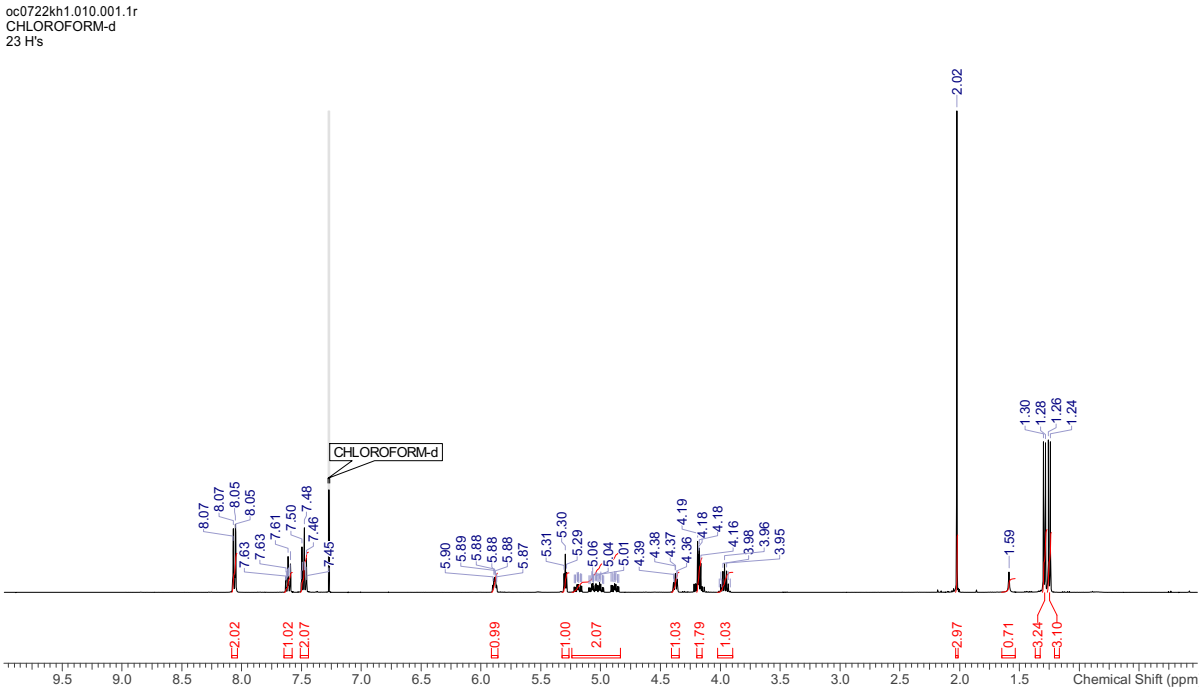
6.4.2.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

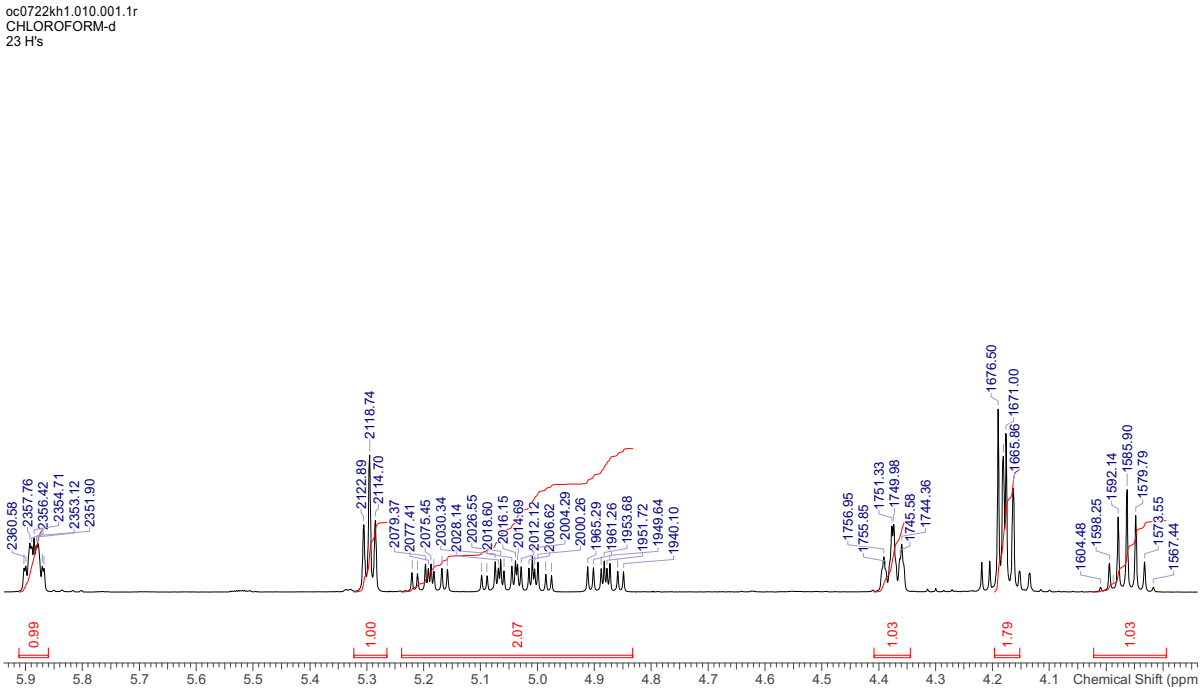


6.4.3 Isopropyl 6-*O*-acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranoside (**14α**)

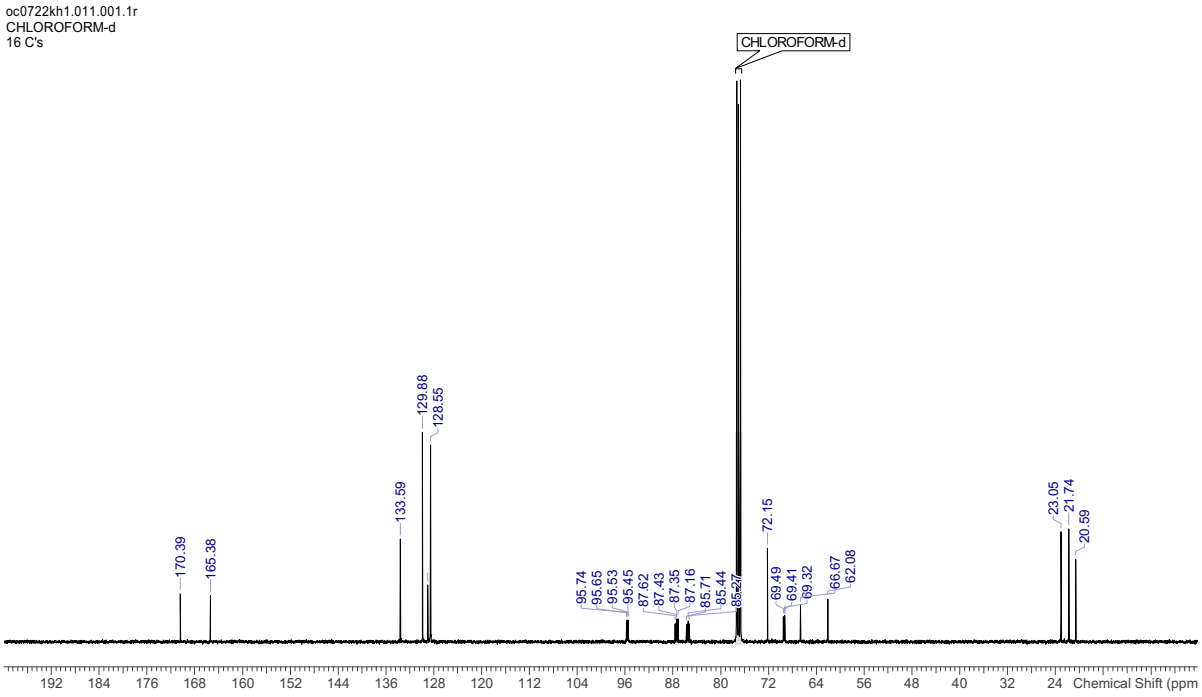


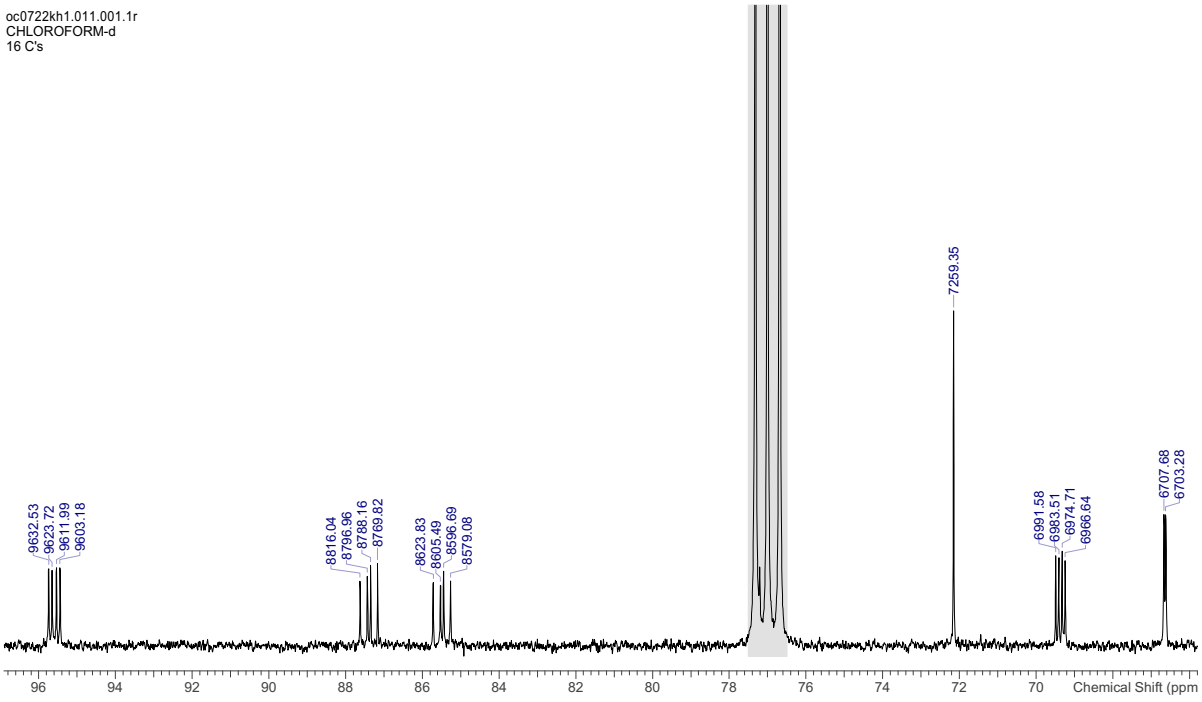
6.4.3.1 ^{1}H NMR, 400 MHz, $CDCl_3$





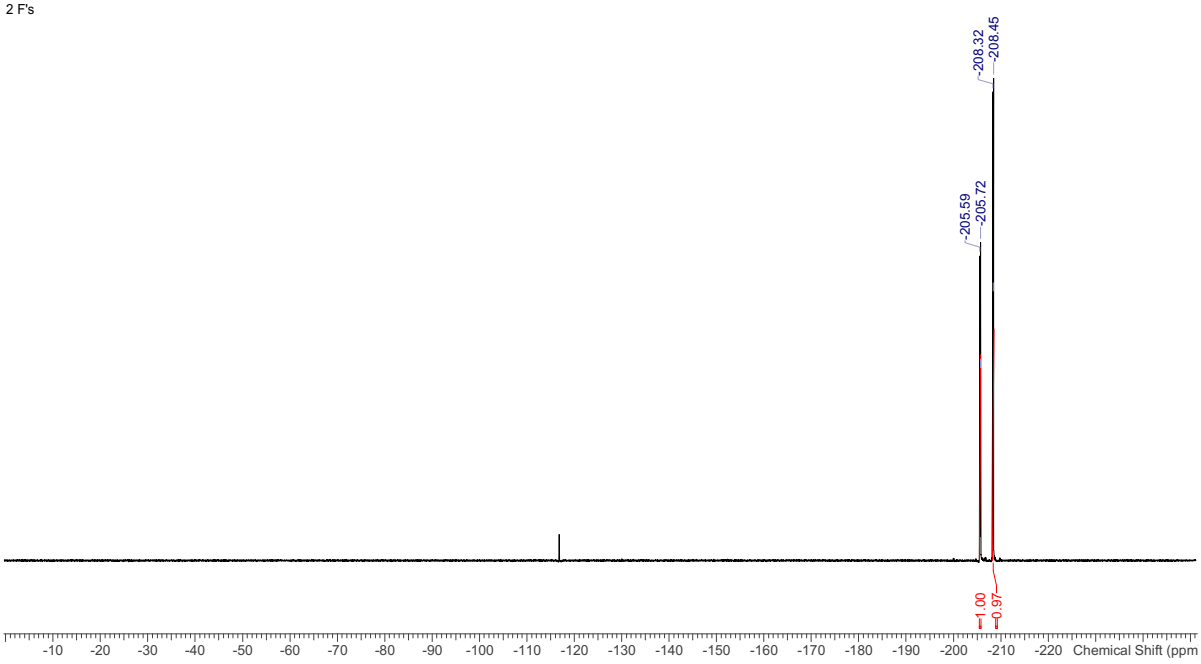
6.4.3.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$



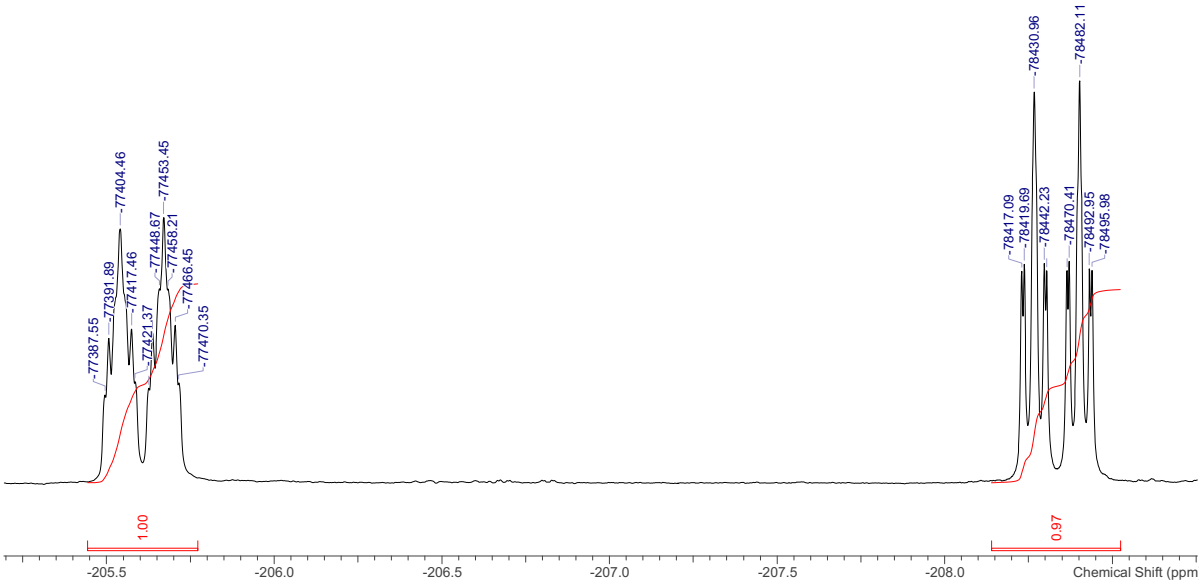


6.4.3.3 ^{19}F NMR, 376 MHz, $CDCl_3$

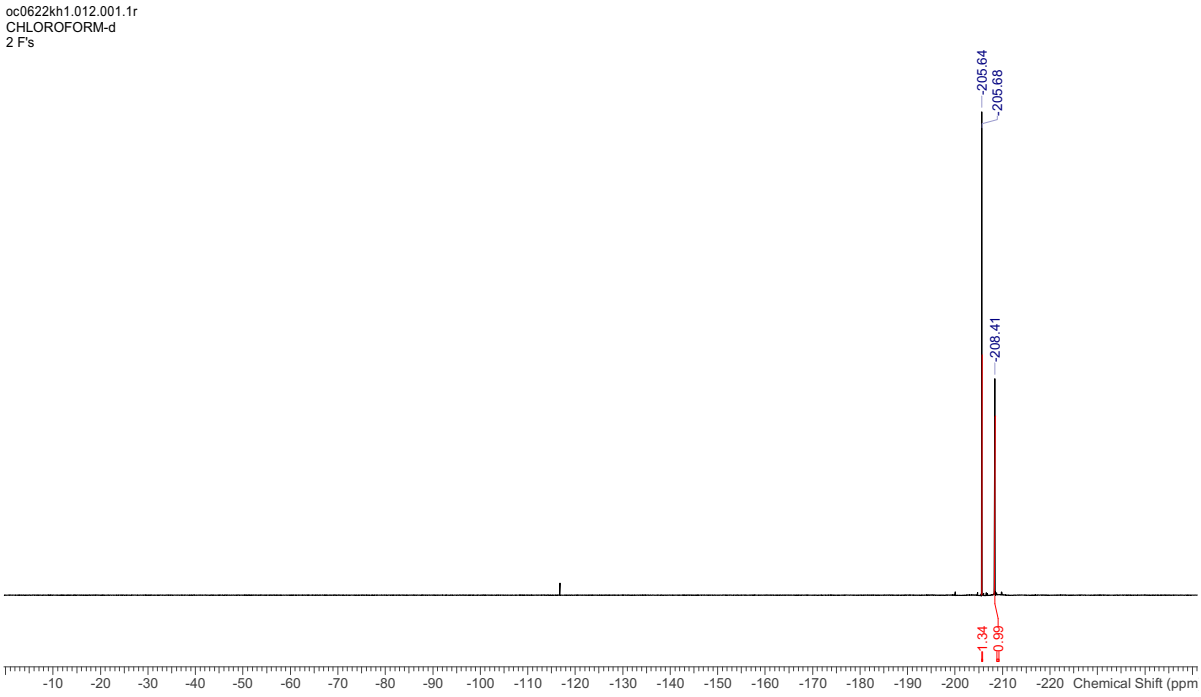
oc0622kh1.011.001.1r
CHLOROFORM-d
2 F's

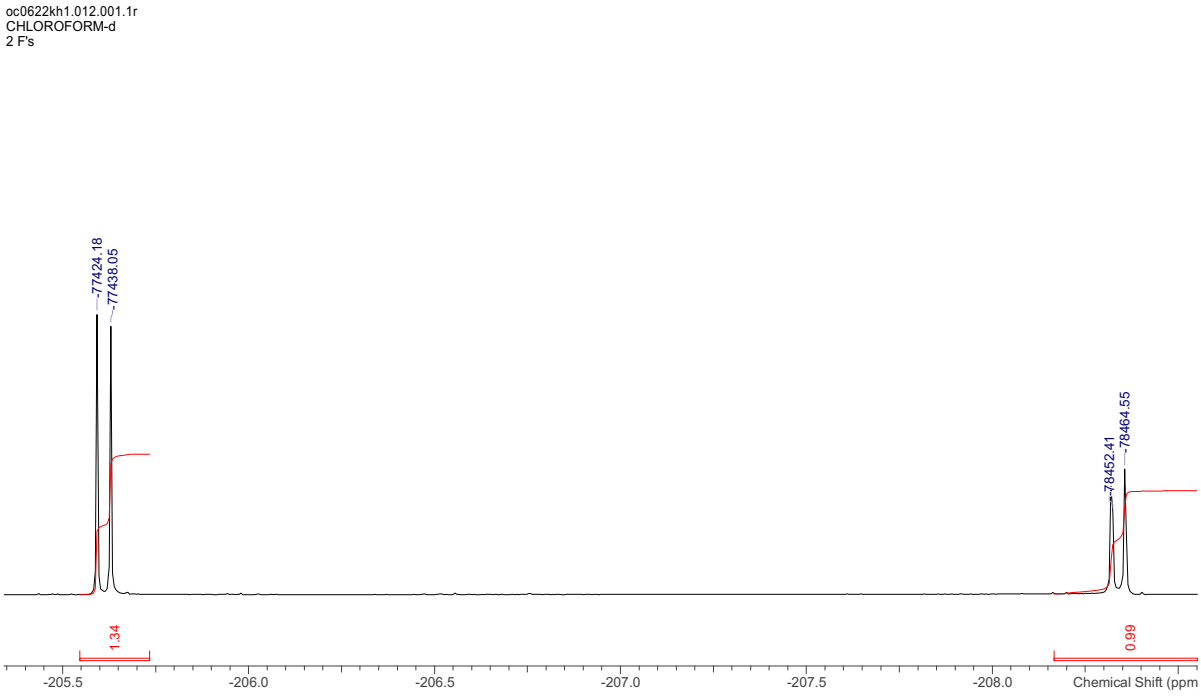


oc0622kh1.011.001.1r
CHLOROFORM-d
2 F's

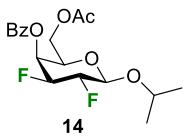


6.4.3.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$





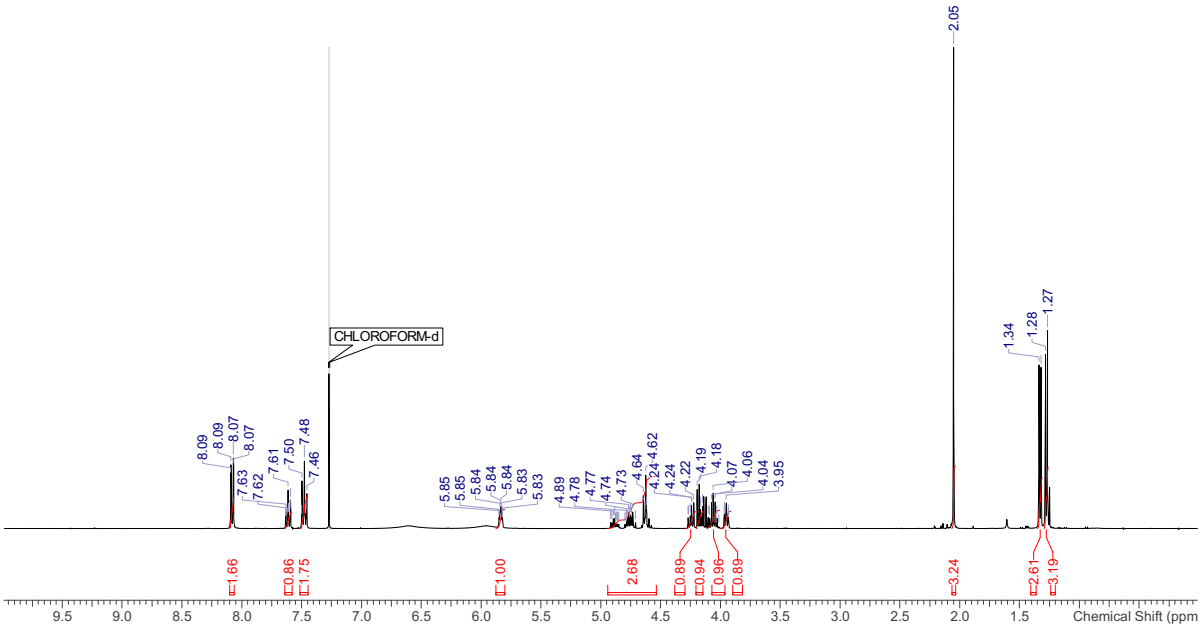
6.4.4 Isopropyl 6-*O*-acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-β-D-galactopyranoside (**14β**)



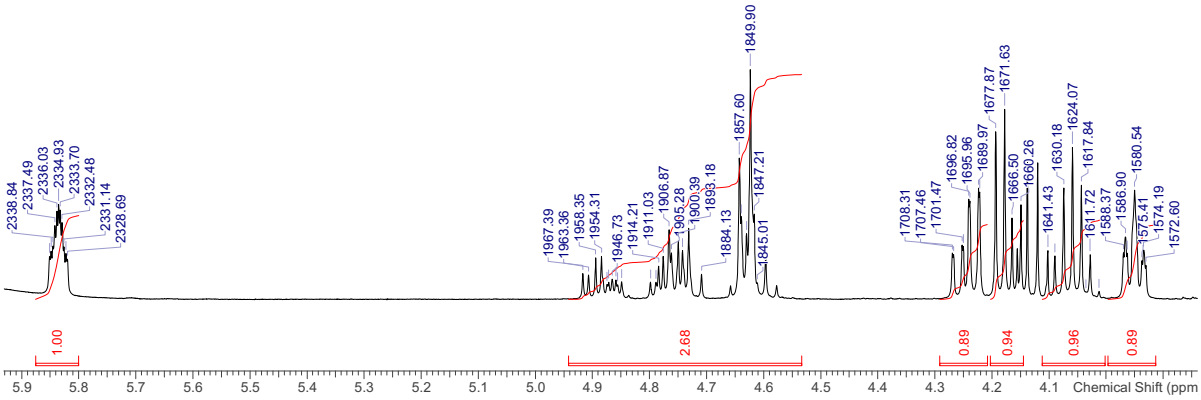
14

6.4.4.1 ^{1}H NMR, 400 MHz, $CDCl_3$

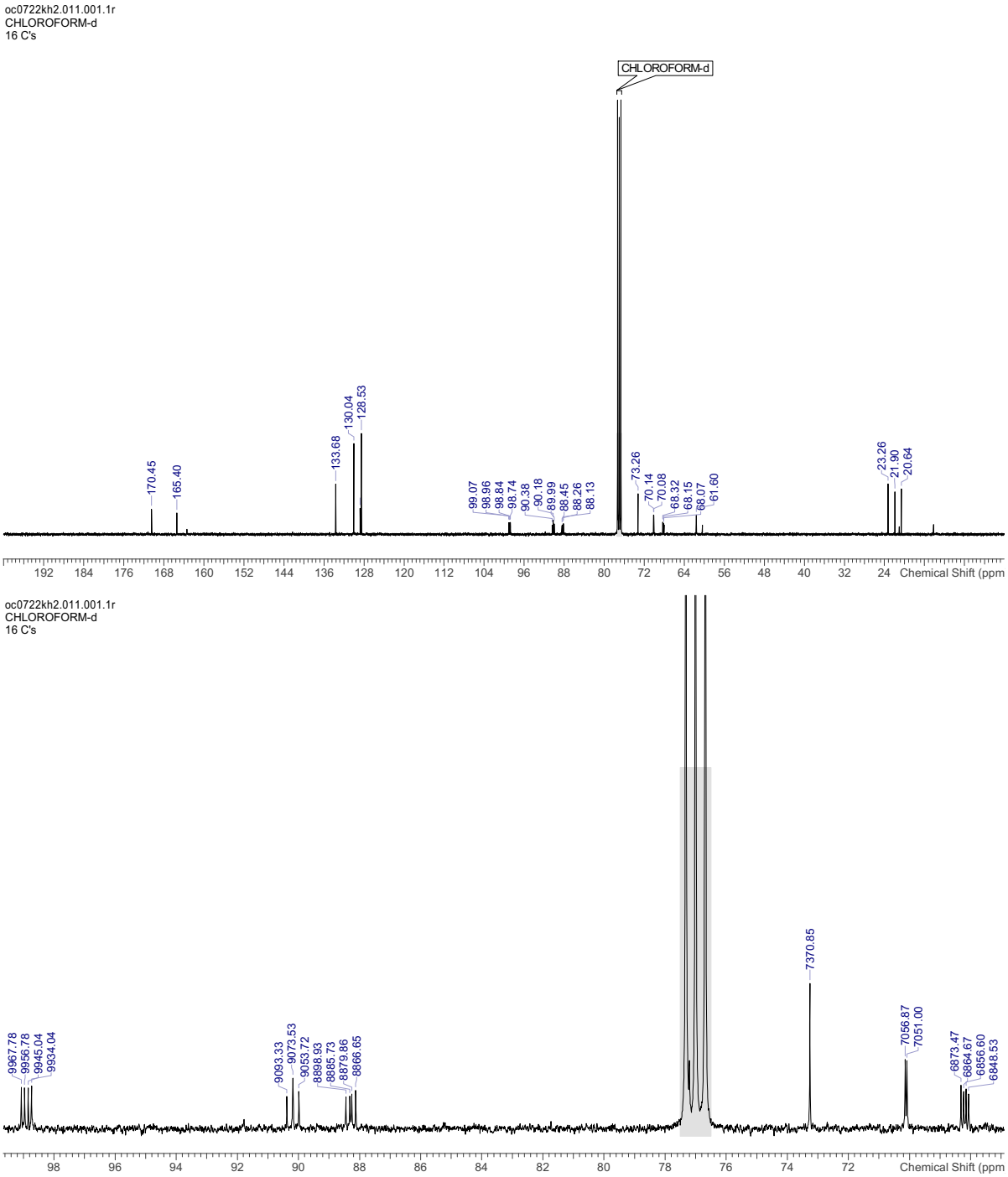
oc0722kh2.010.001.1r
CHLOROFORM-d
22 H's



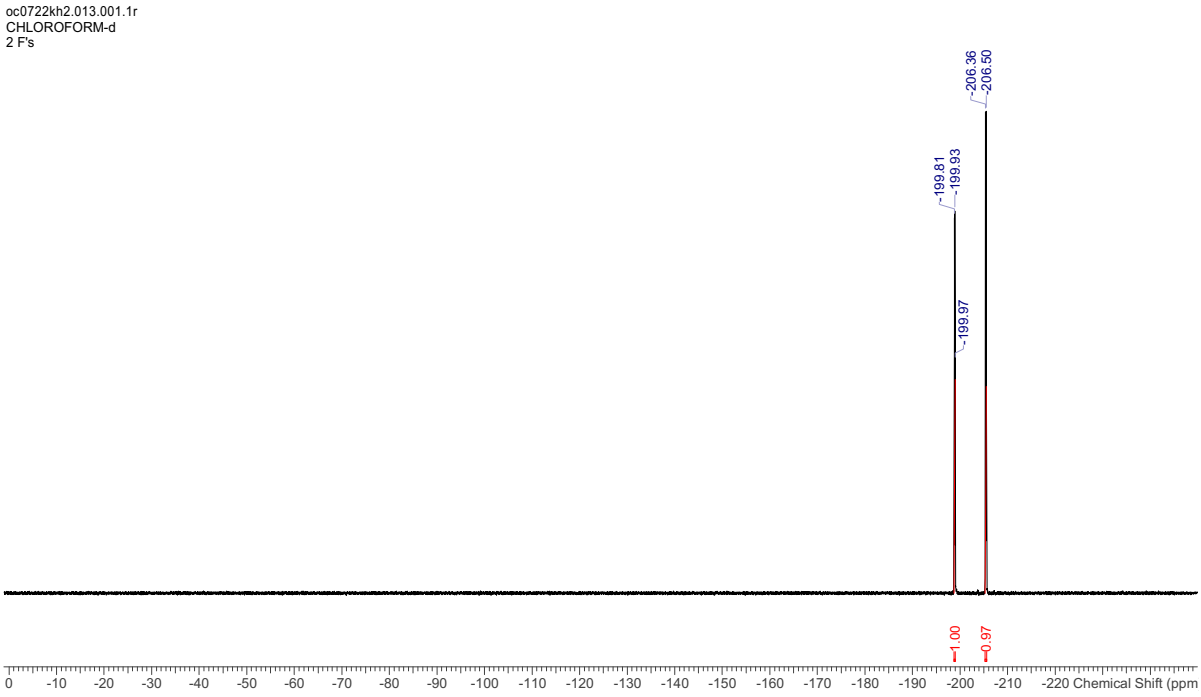
oc0722kh2.010.001.1r
CHLOROFORM-d
22 H's

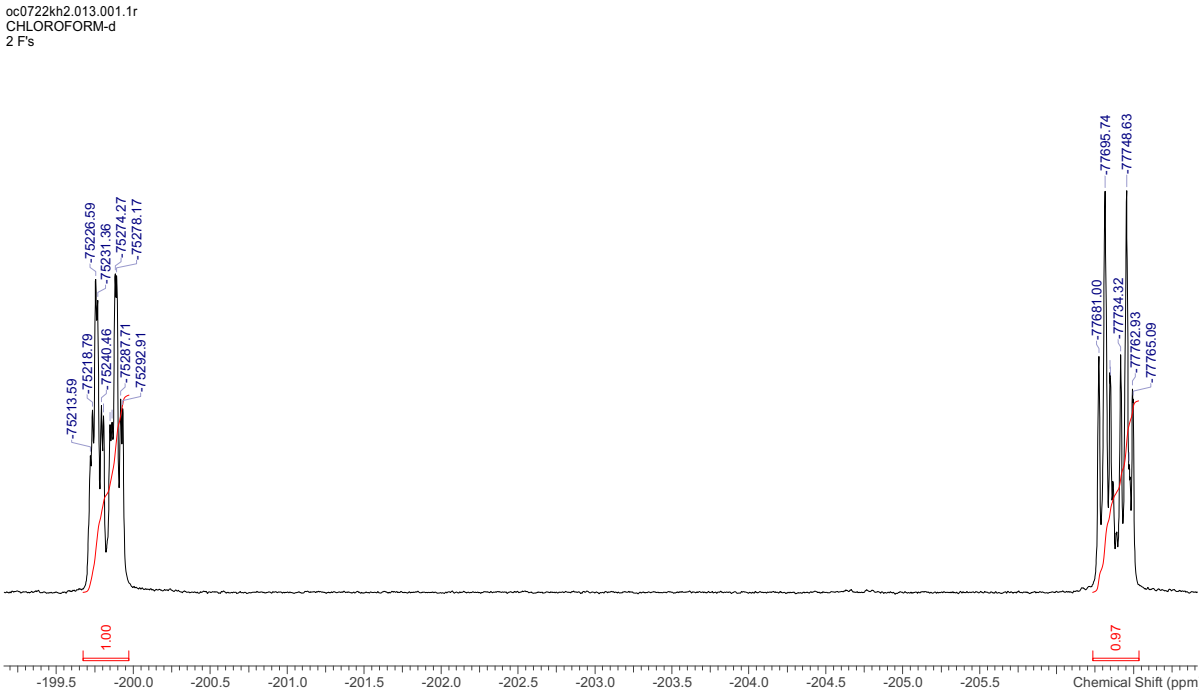


6.4.4.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

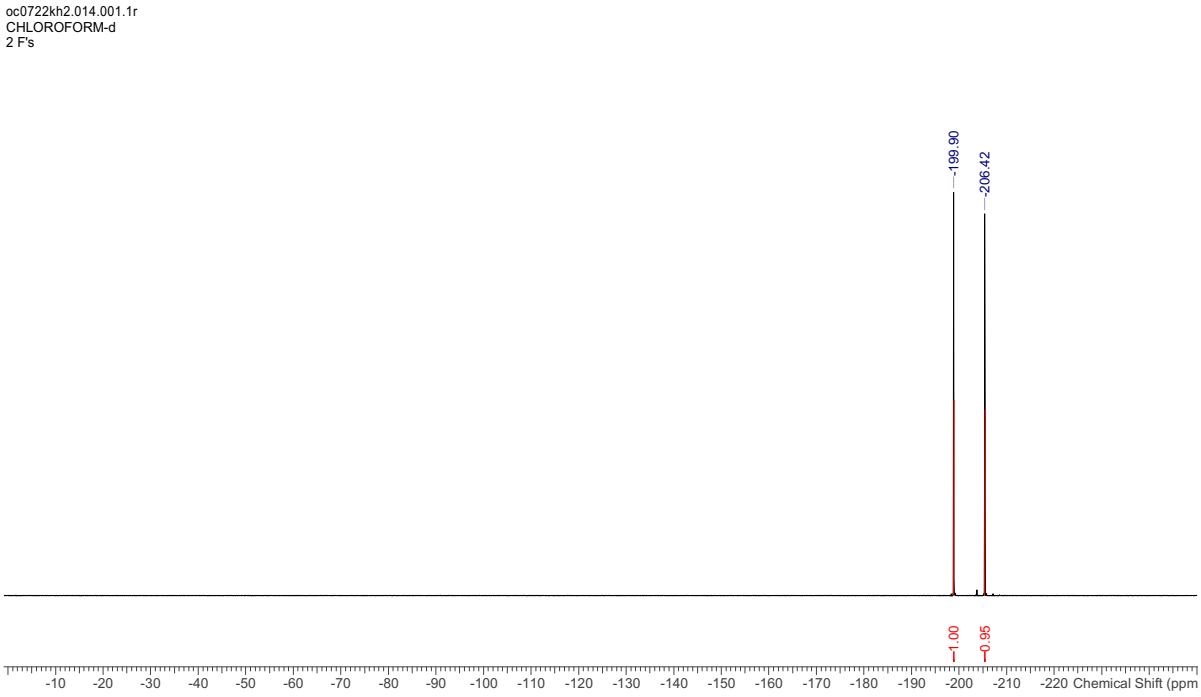


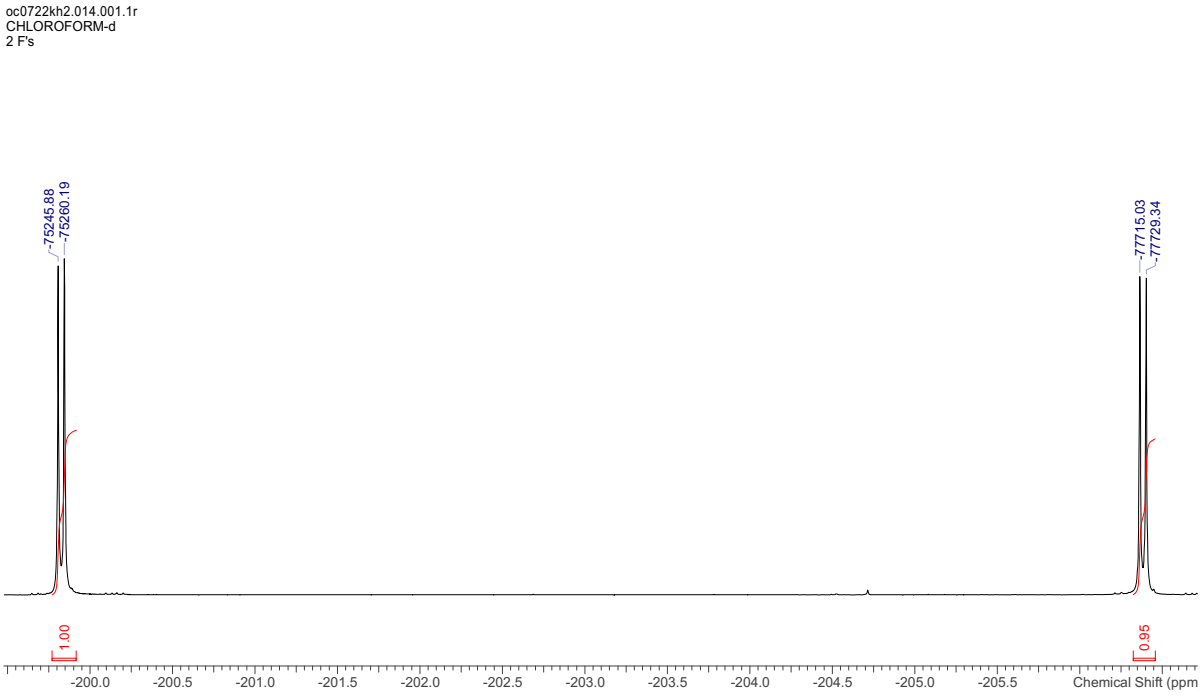
6.4.4.3 ^{19}F NMR, 376 MHz, $CDCl_3$



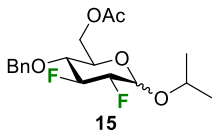


6.4.4.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$





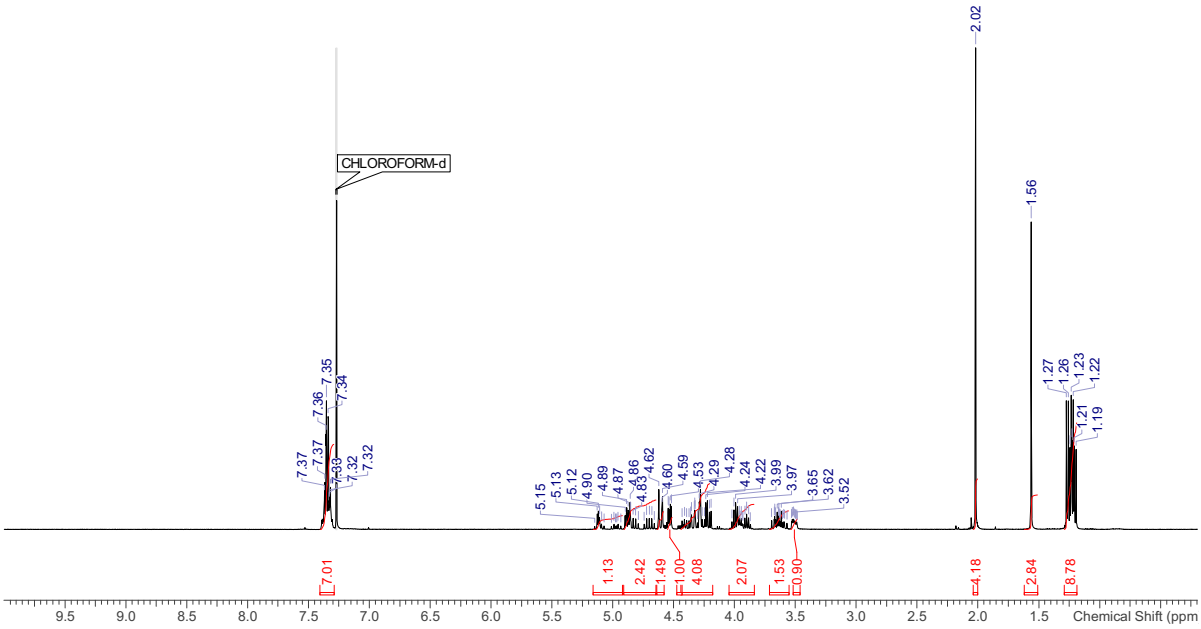
6.4.5 Isopropyl 4,6-di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α/β-D-glucopyranoside (**15**)



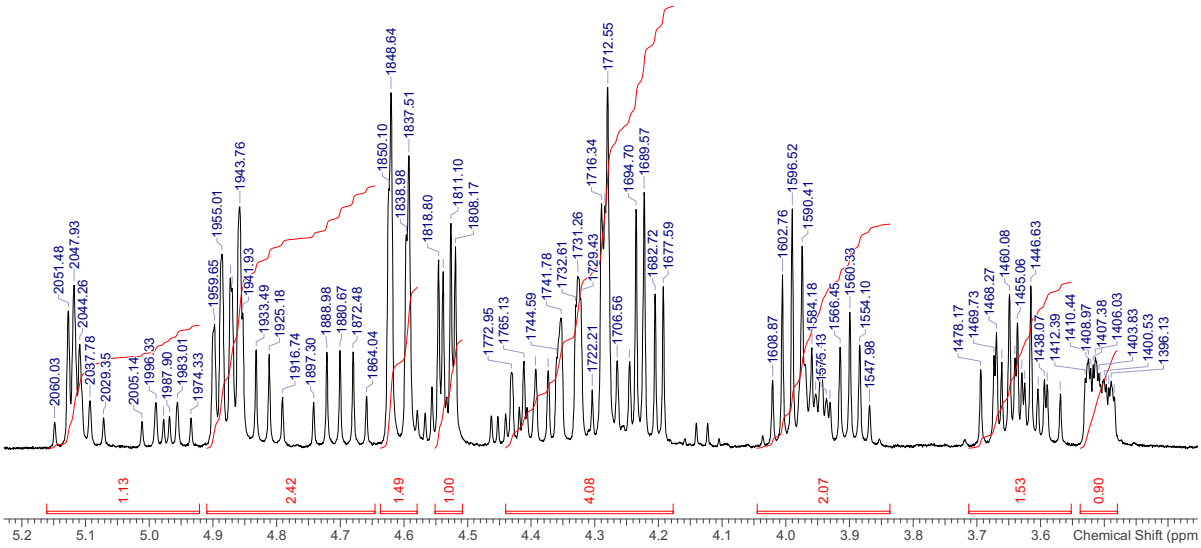
15

6.4.5.1 ^{1}H NMR, 400 MHz, $CDCl_3$

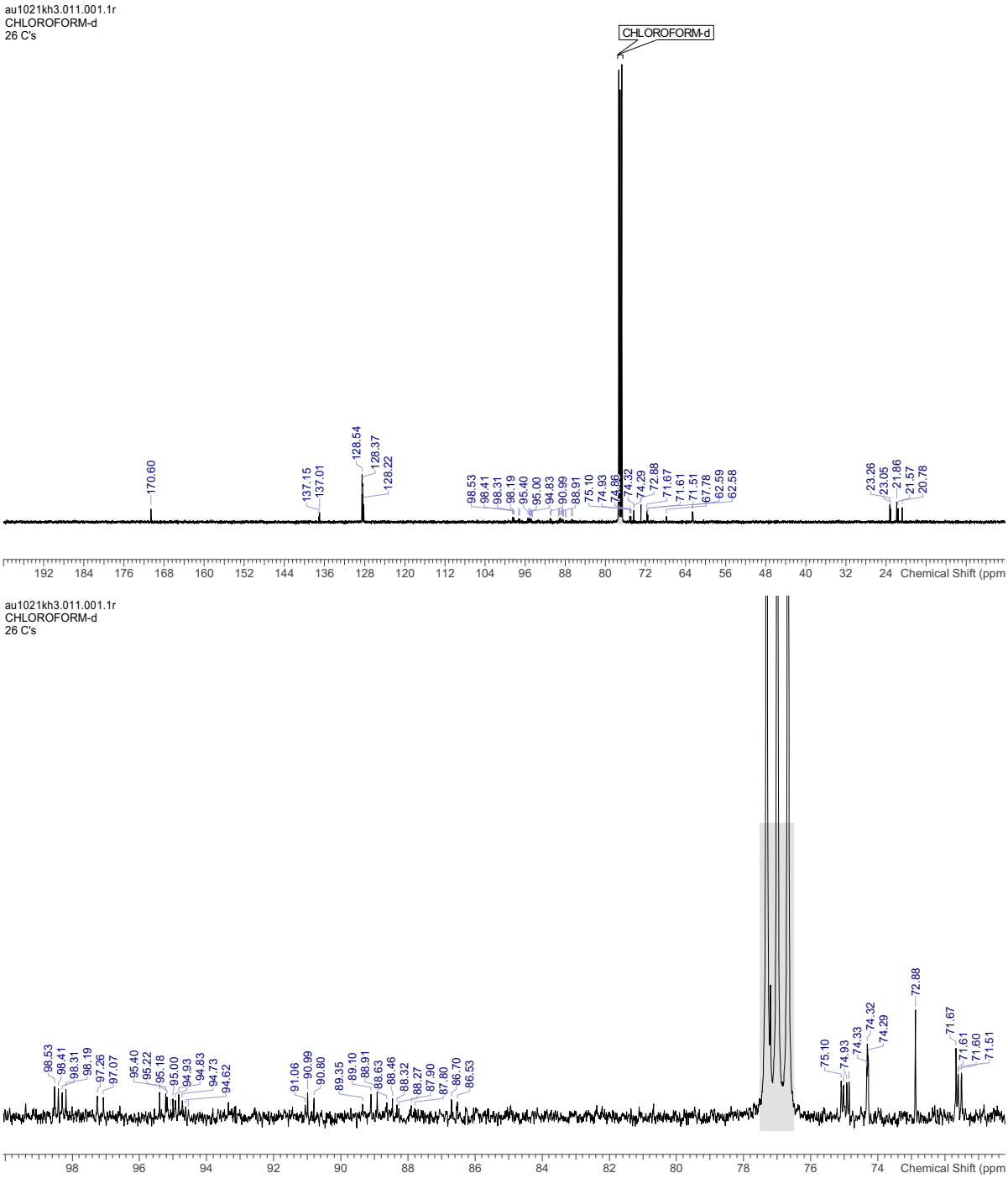
au1021kh3.010.001.1r
CHLOROFORM-d
40 H's



au1021kh3.010.001.1r
CHLOROFORM-d
40 H's

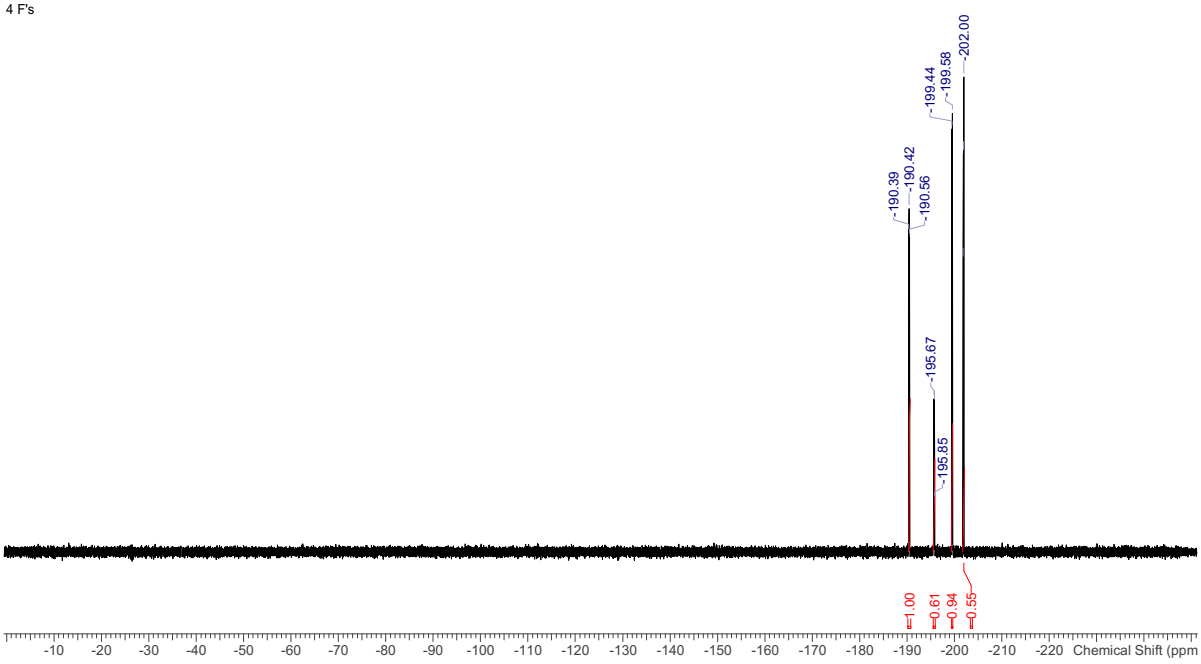


6.4.5.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

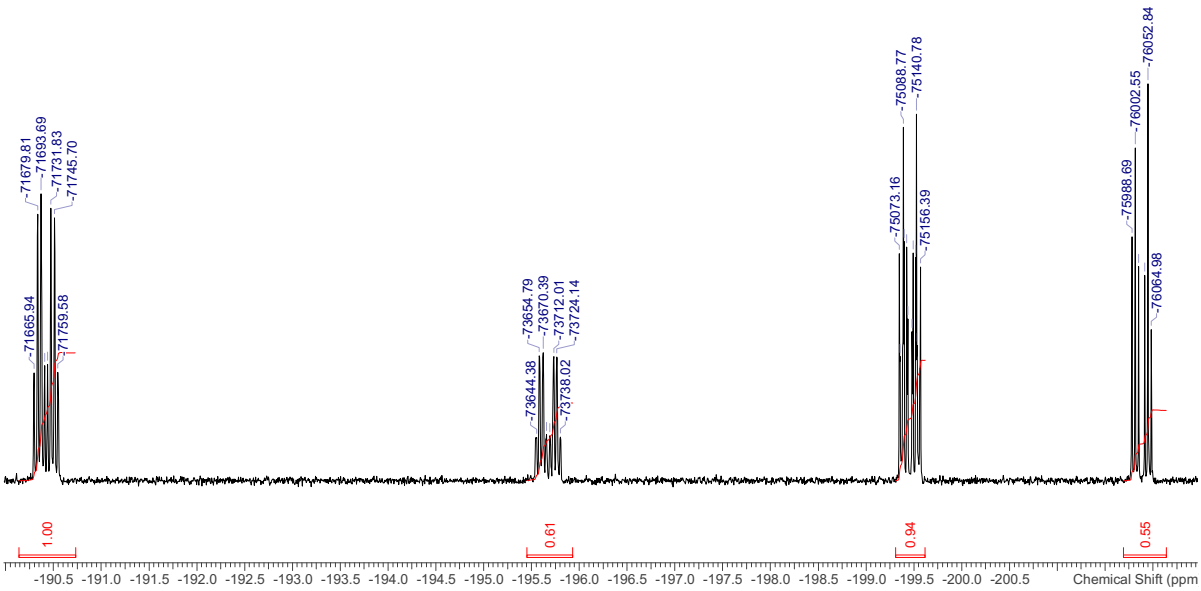


6.4.5.3 ^{19}F NMR, 376 MHz, $CDCl_3$

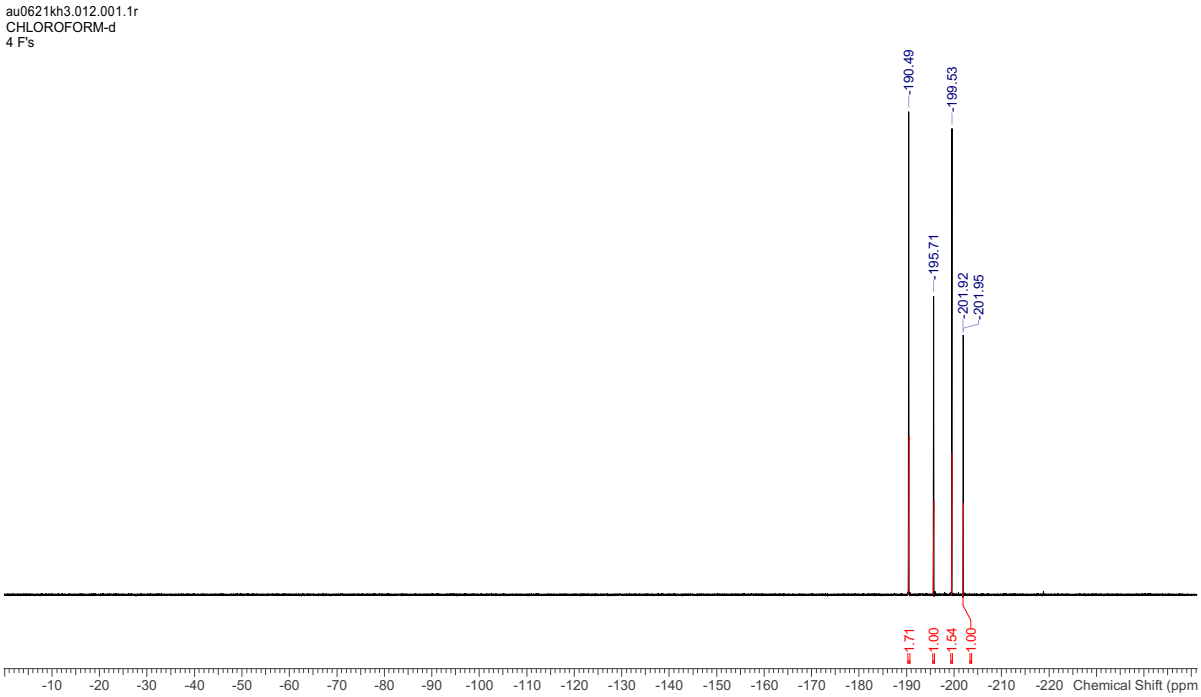
au0621kh3.011.001.1r
CHLOROFORM-d
4 F's

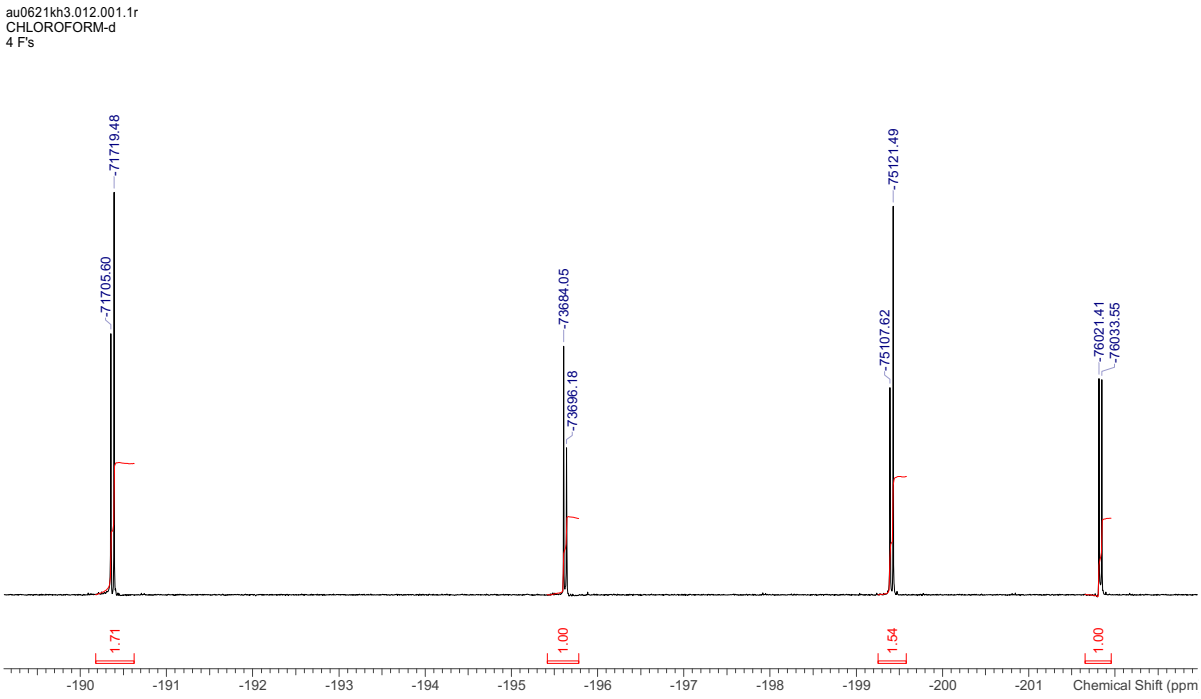


au0621kh3.011.001.1r
CHLOROFORM-d
4 F's

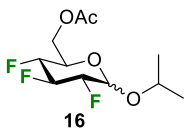


6.4.5.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$





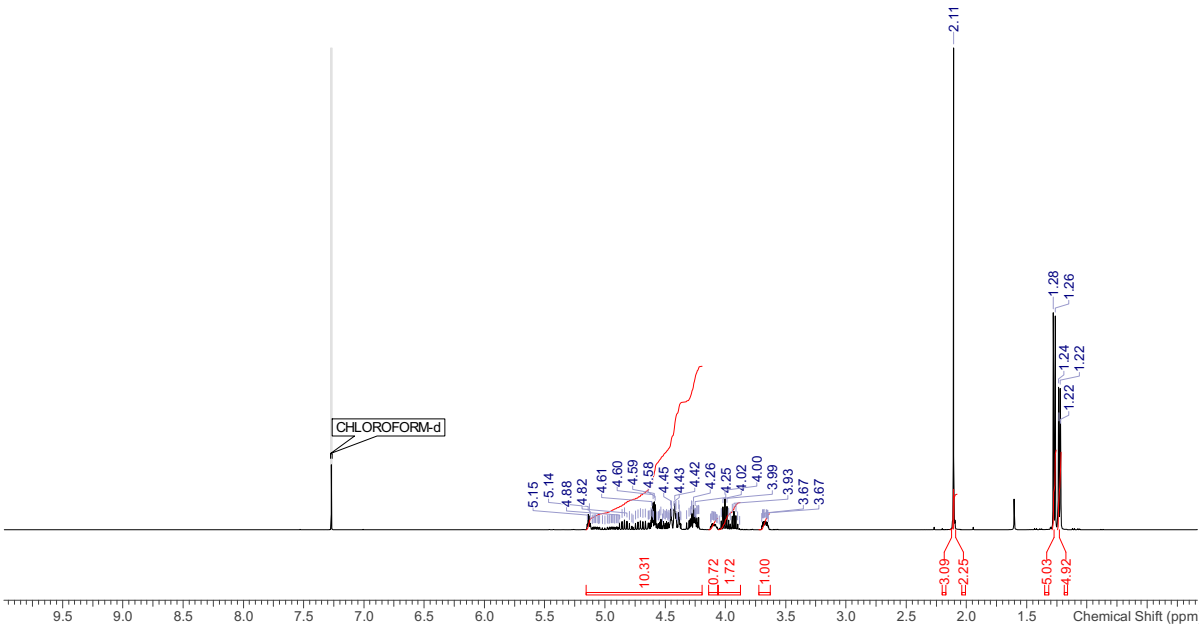
6.4.6 Isopropyl 6-*O*-acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α/β-D-glucopyranoside (**16**)



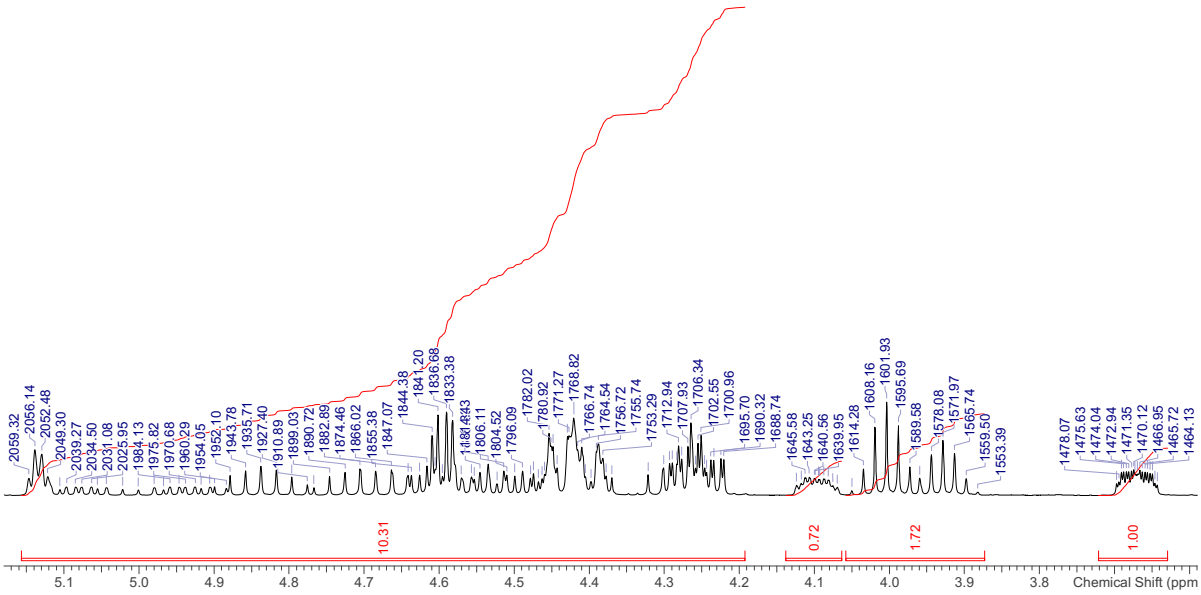
16

6.4.6.1 ^{1}H NMR, 400 MHz, $CDCl_3$

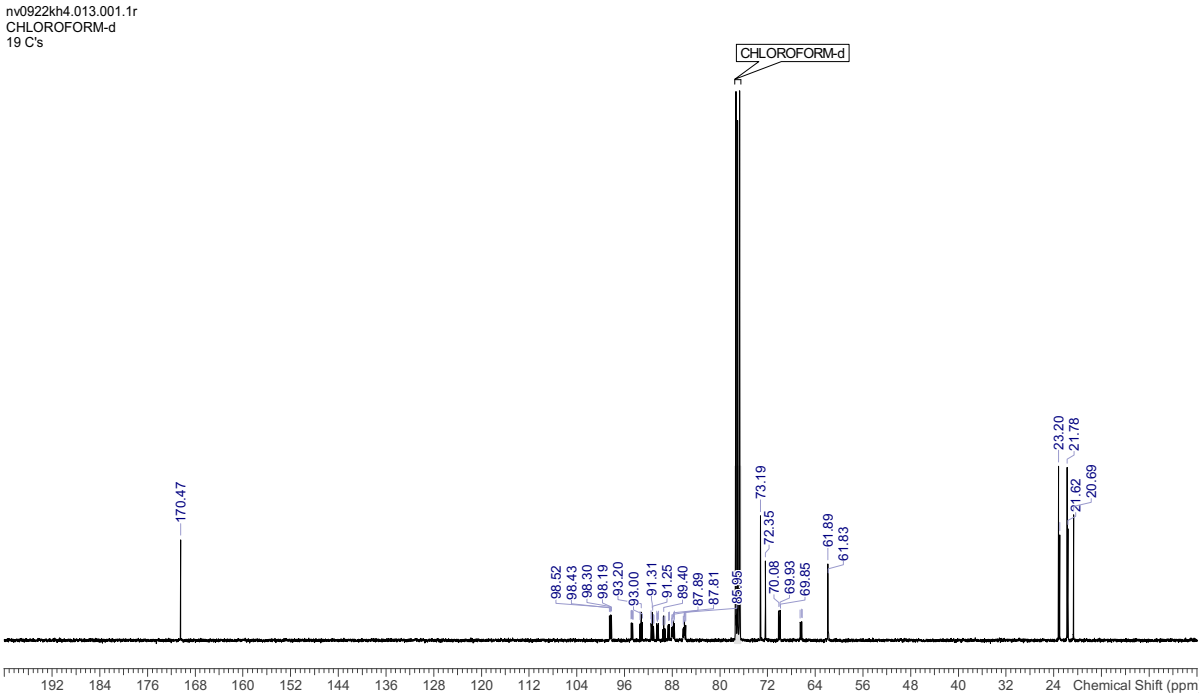
nv0922kh3.010.001.1r
CHLOROFORM-d
29 H's

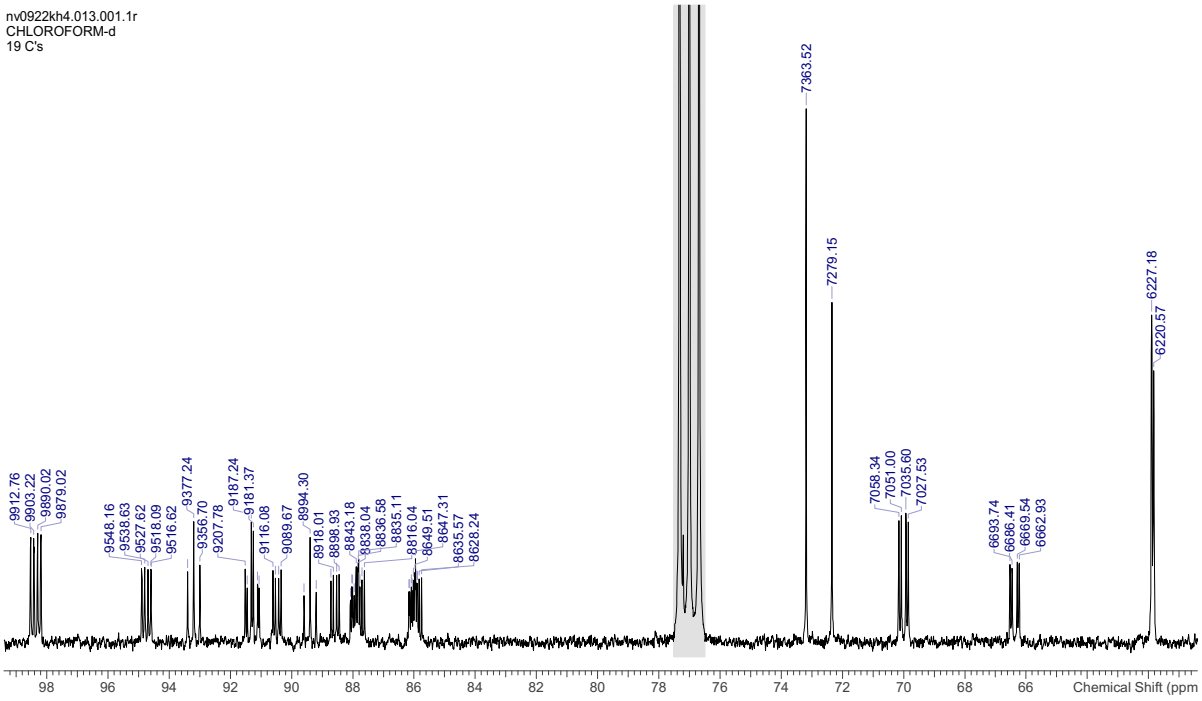


nv0922kh3.010.001.1r
CHLOROFORM-d
29 H's



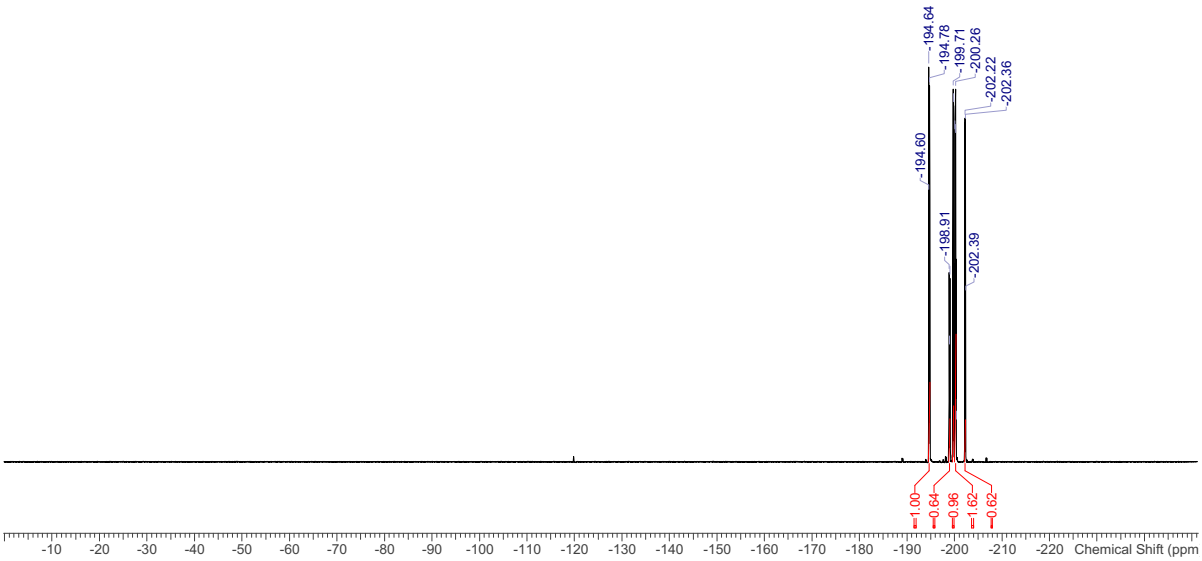
6.4.6.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$



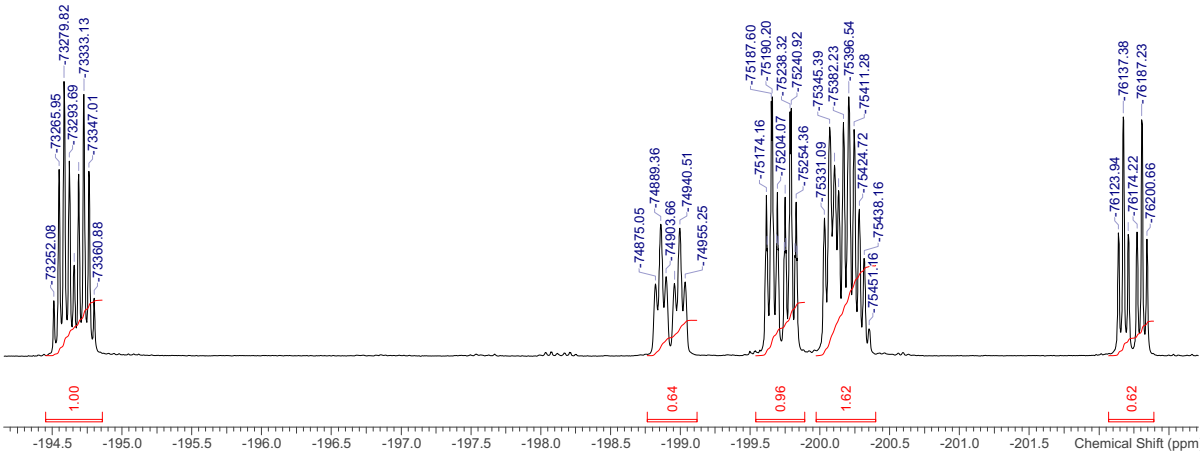


6.4.6.3 ^{19}F NMR, 376 MHz, $CDCl_3$

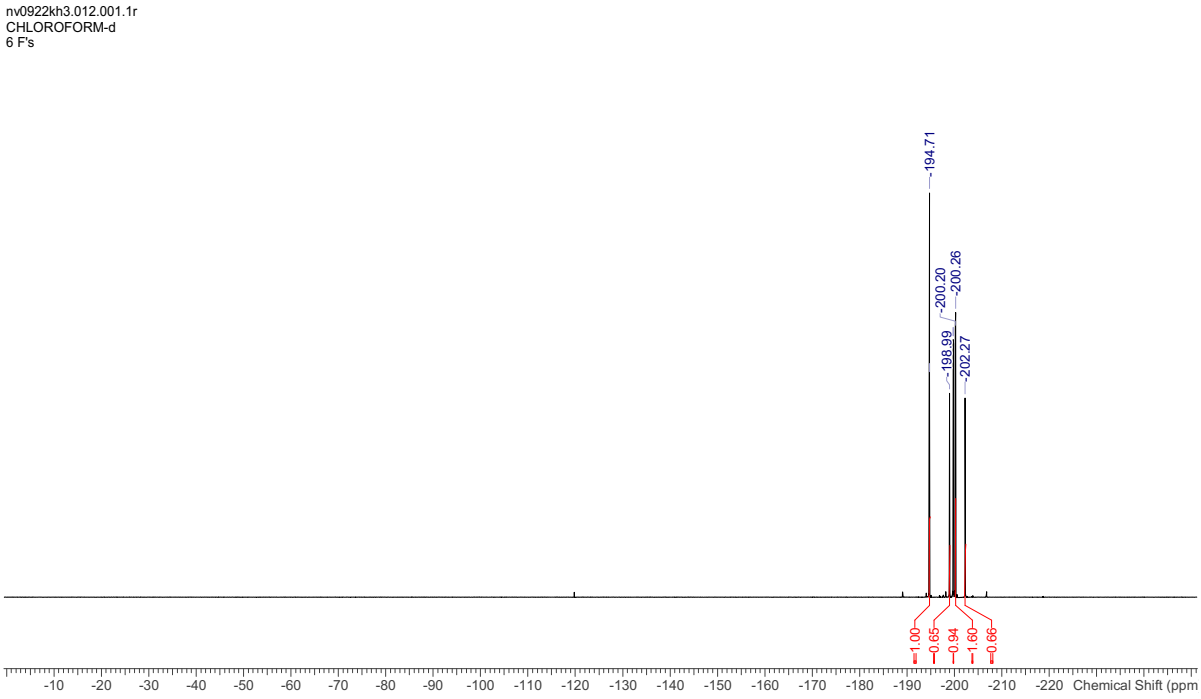
nv0922kh3.011.001.1r
CHLOROFORM-d
5 F's

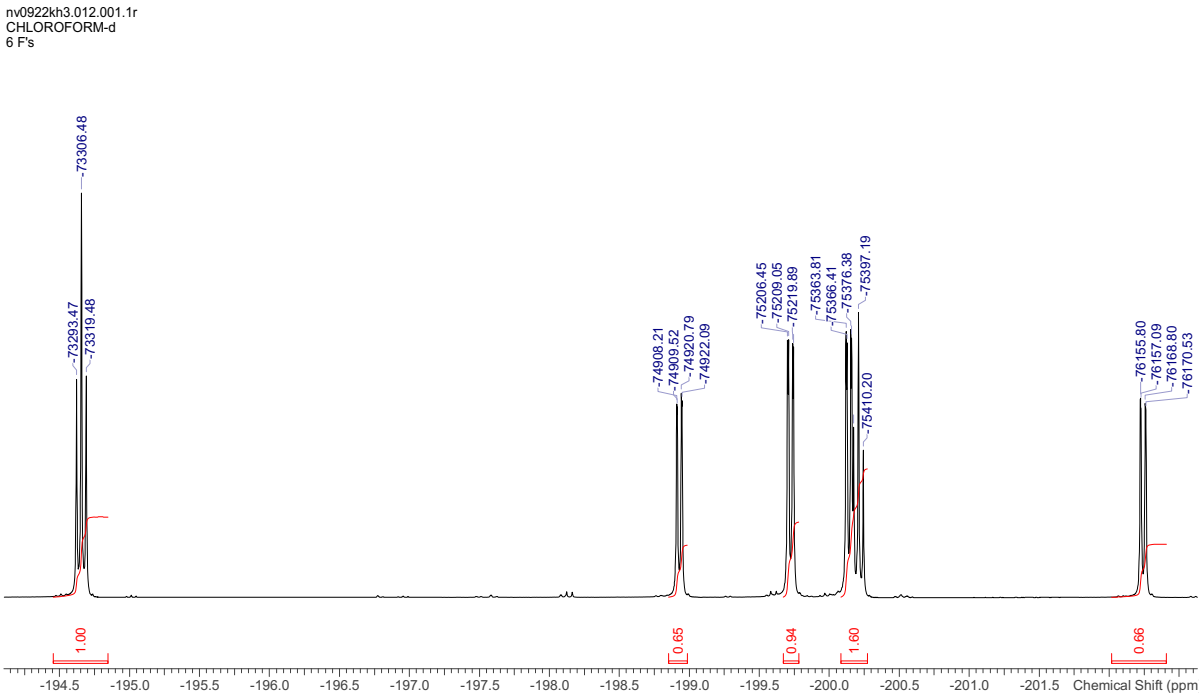


nv0922kh3.011.001.1r
CHLOROFORM-d
5 F's

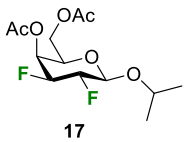


6.4.6.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



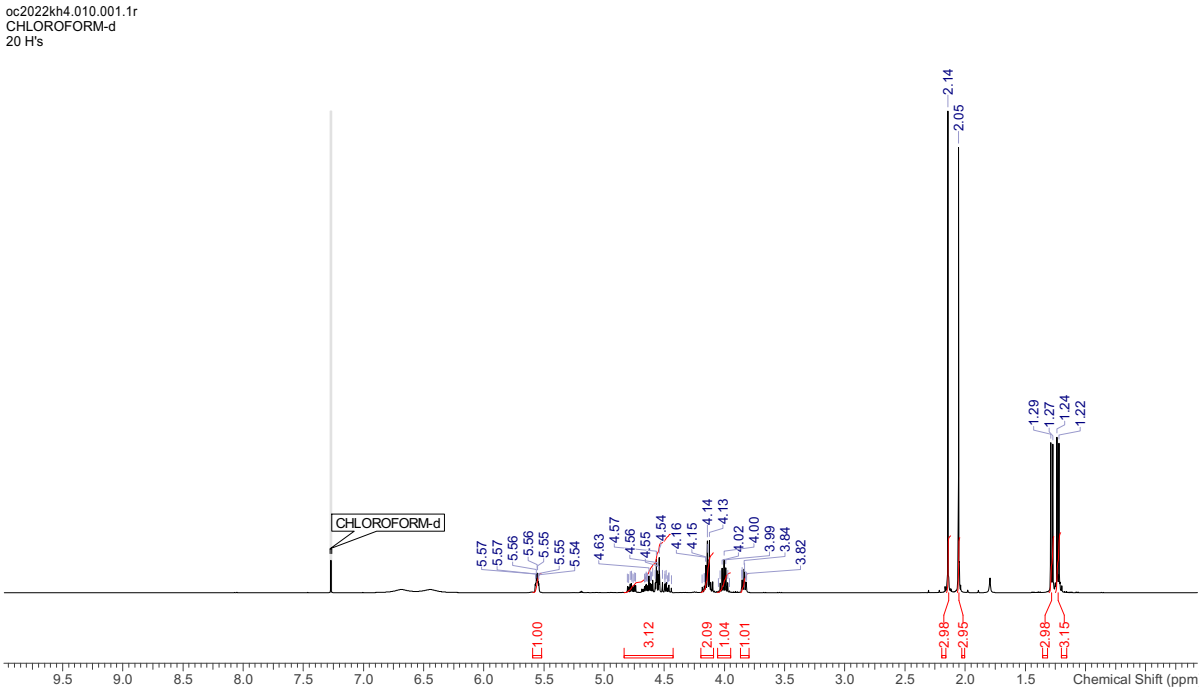


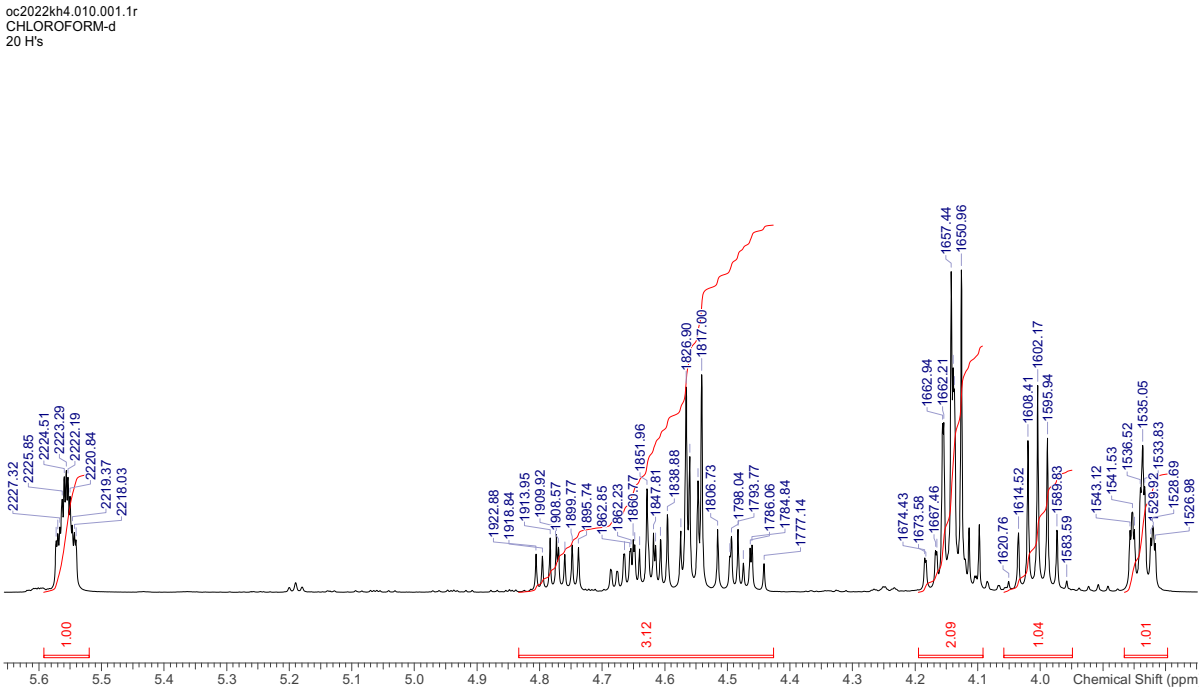
6.4.7 Isopropyl 4,6-di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-β-D-galactopyranoside (**17β**)



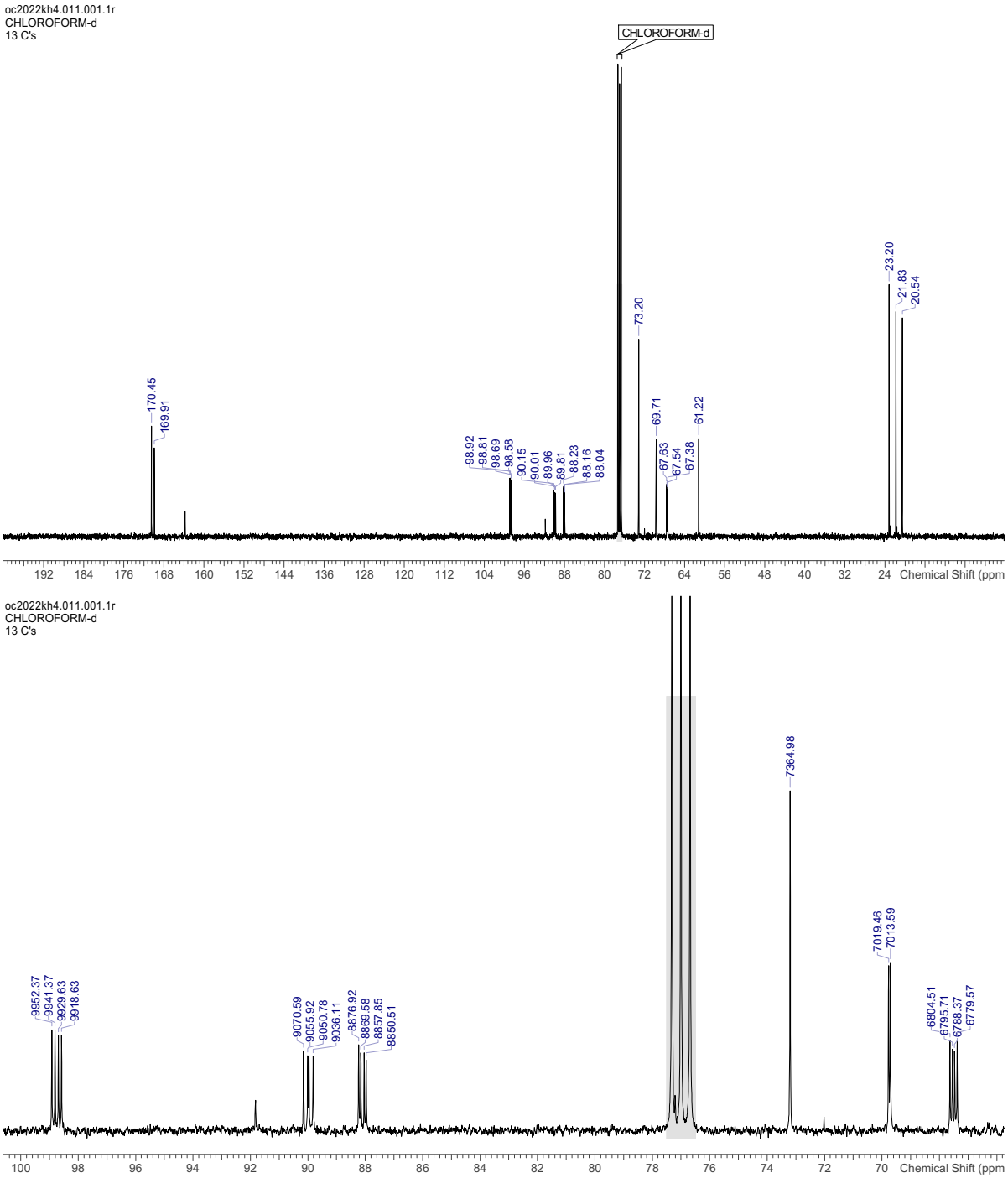
17

6.4.7.1 ^{1}H NMR, 400 MHz, $CDCl_3$

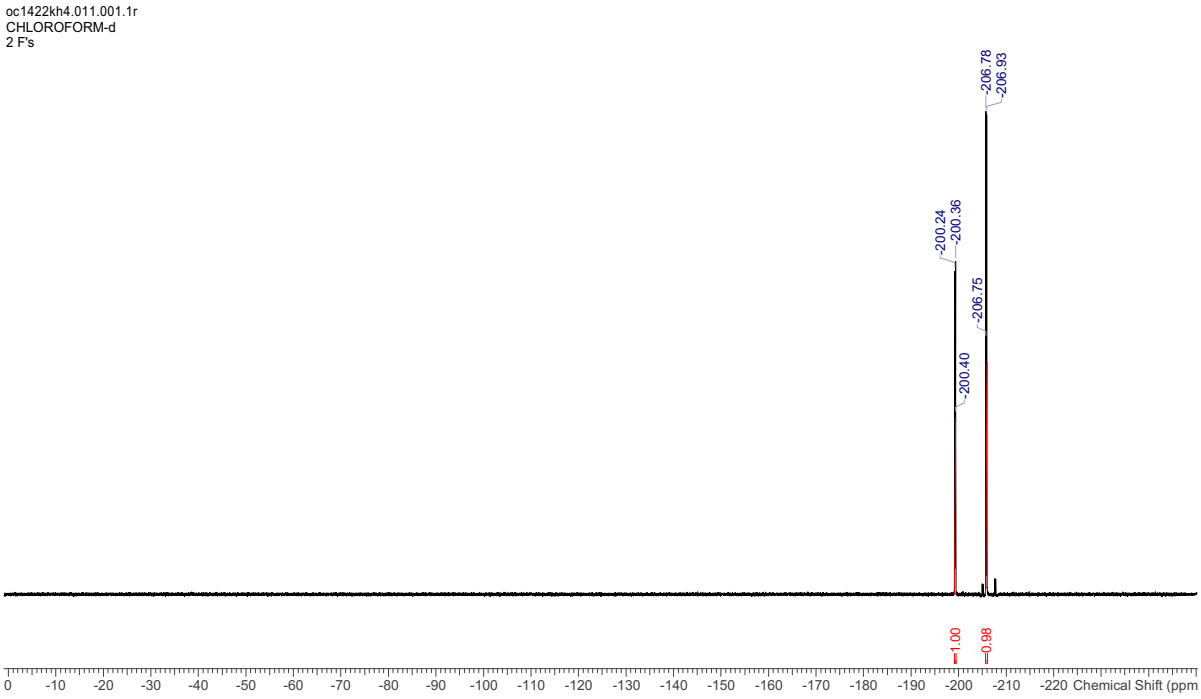


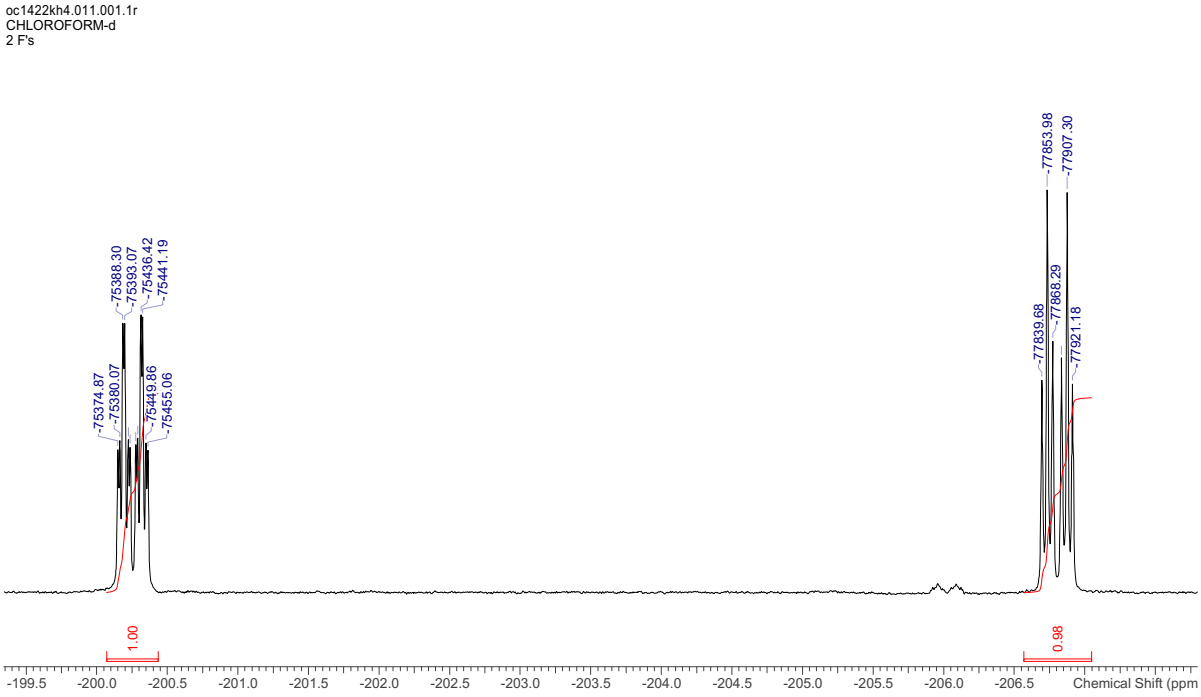


6.4.7.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

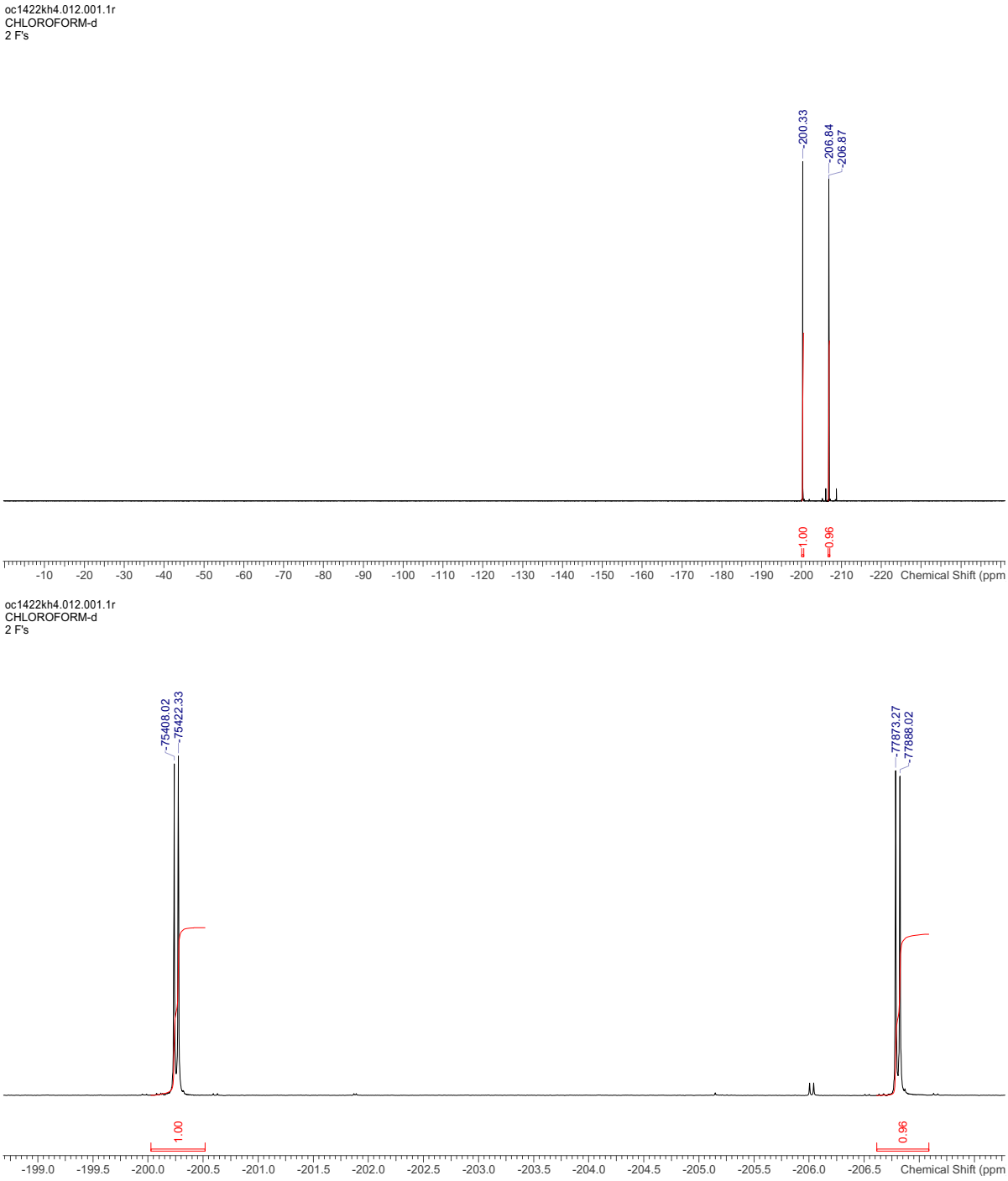


6.4.7.3 ^{19}F NMR, 376 MHz, $CDCl_3$

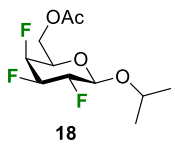




6.4.7.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



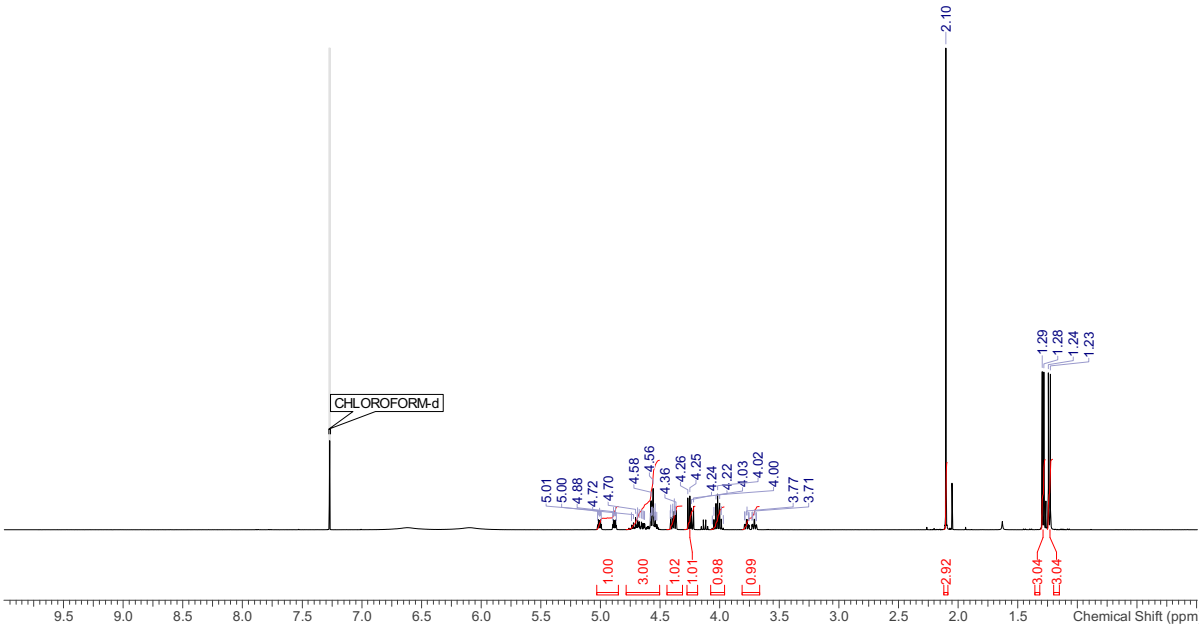
6.4.8 Isopropyl 6-*O*-acetyl-2,3,4-trideoxy-2,3,4-trifluoro-β-D-galactopyranoside (**18β**)



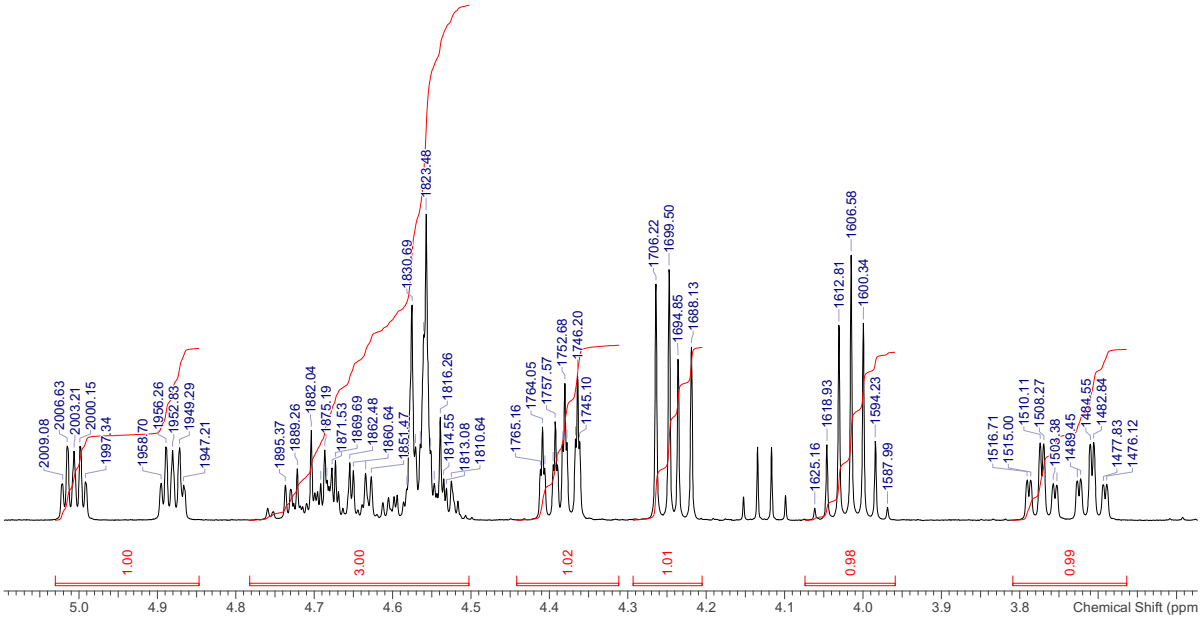
18

6.4.8.1 ^{1}H NMR, 400 MHz, $CDCl_3$

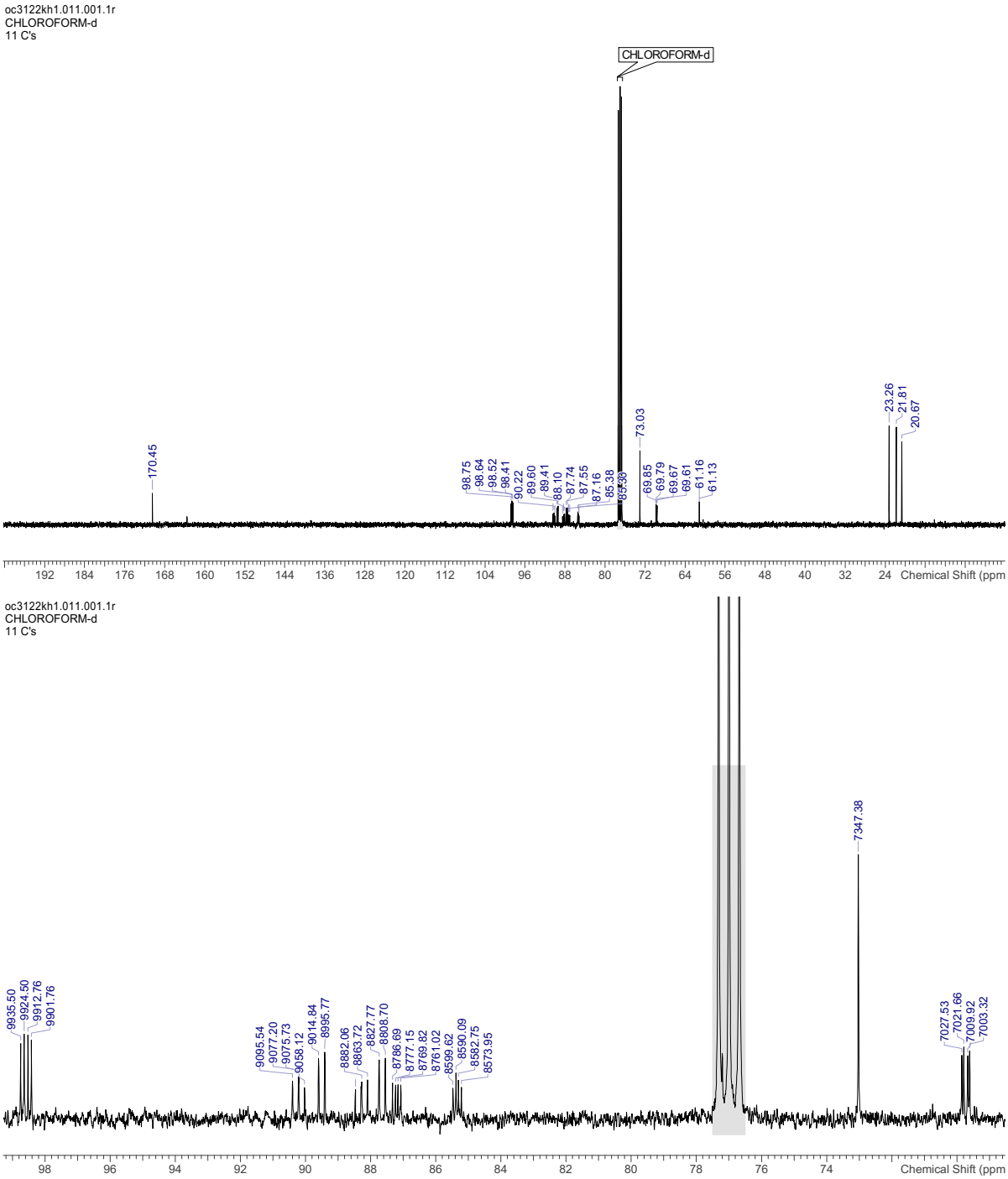
oc2922kh1.010.001.1r
CHLOROFORM-d
17 H's



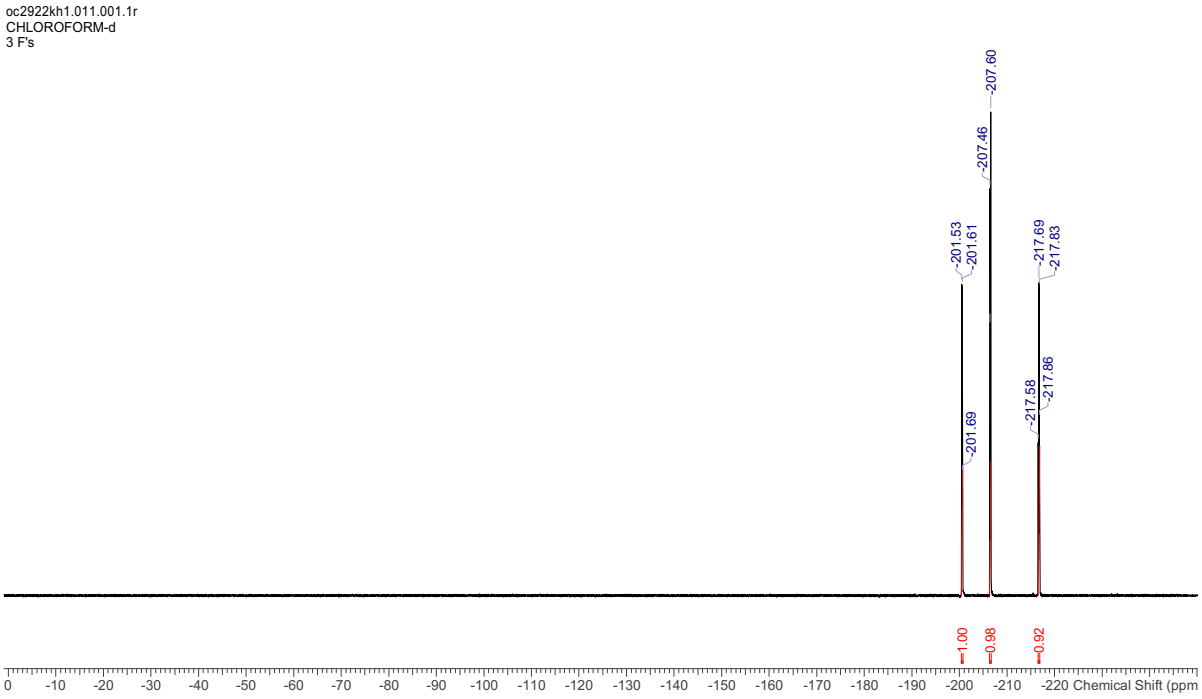
oc2922kh1.010.001.1r
CHLOROFORM-d
17 H's

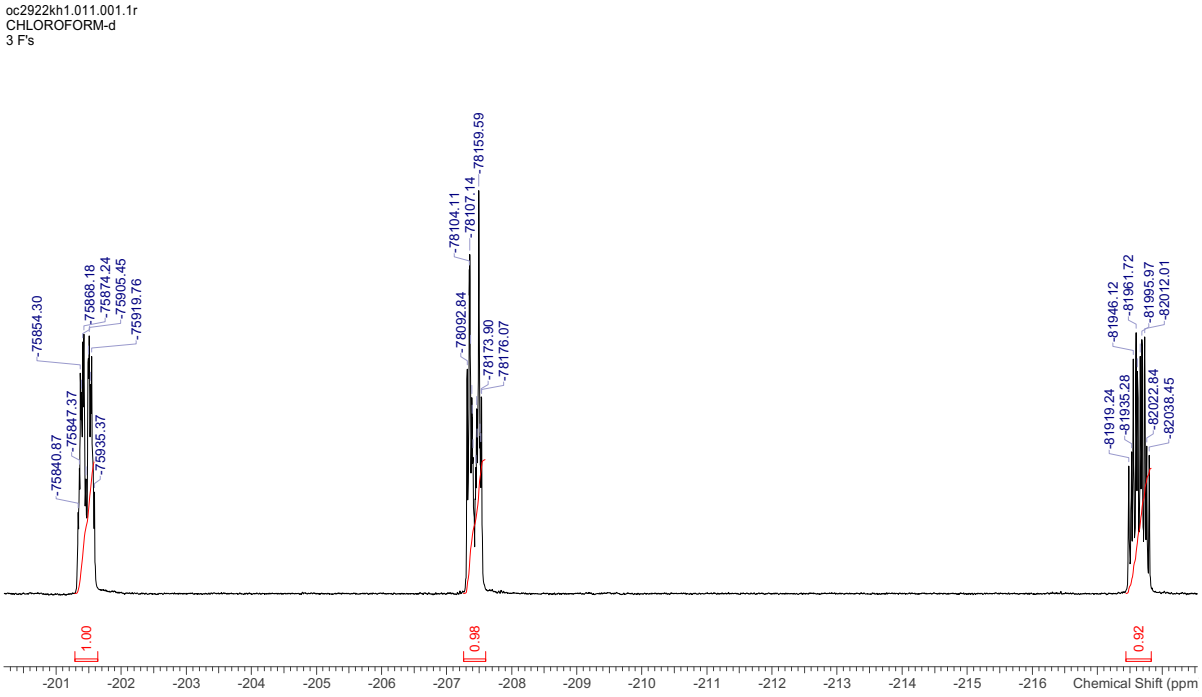


6.4.8.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

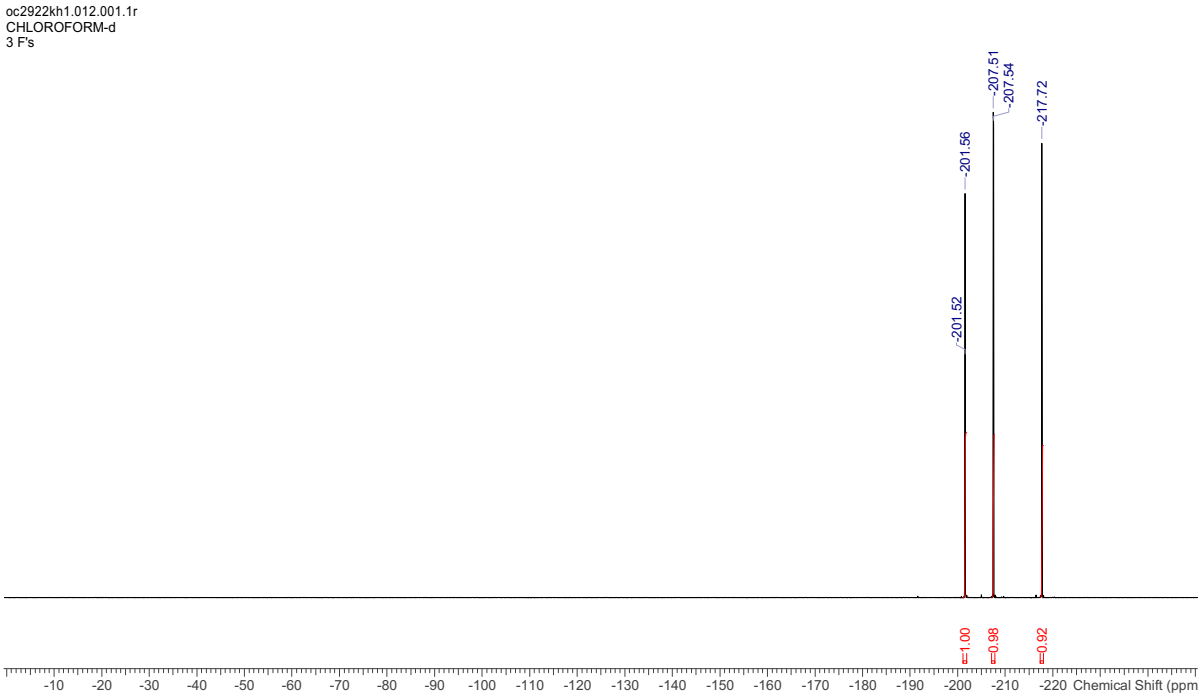


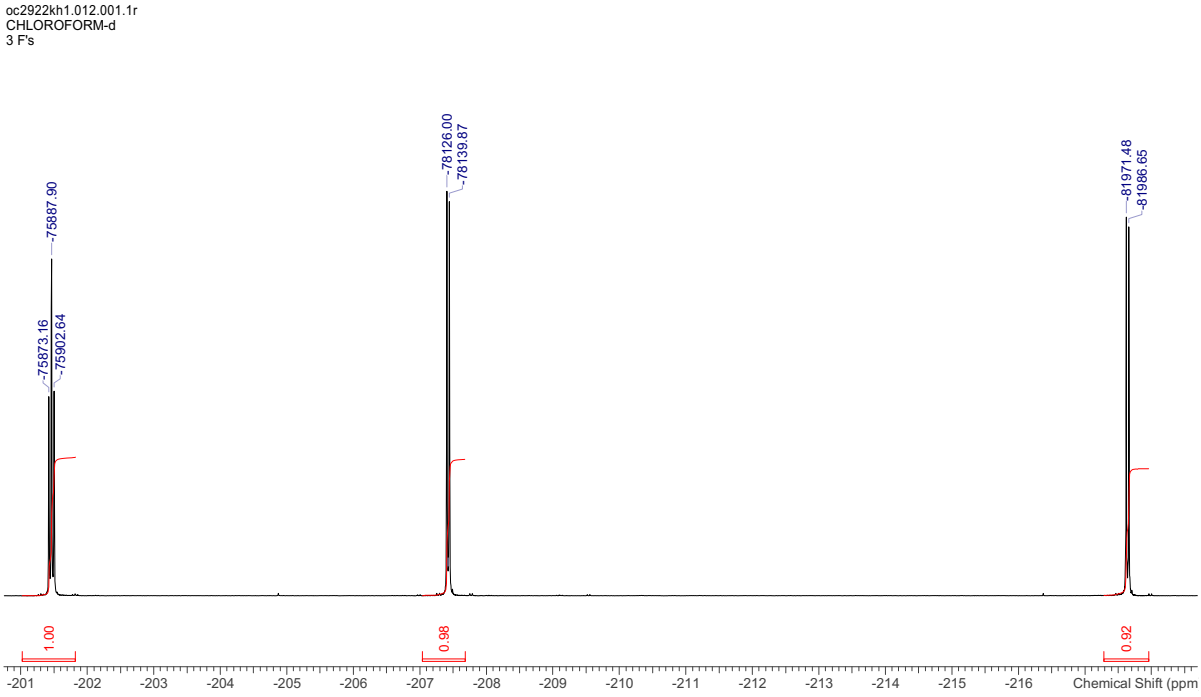
6.4.8.3 ^{19}F NMR, 376 MHz, $CDCl_3$





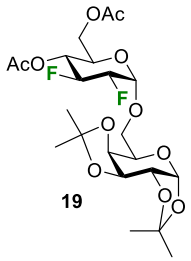
6.4.8.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



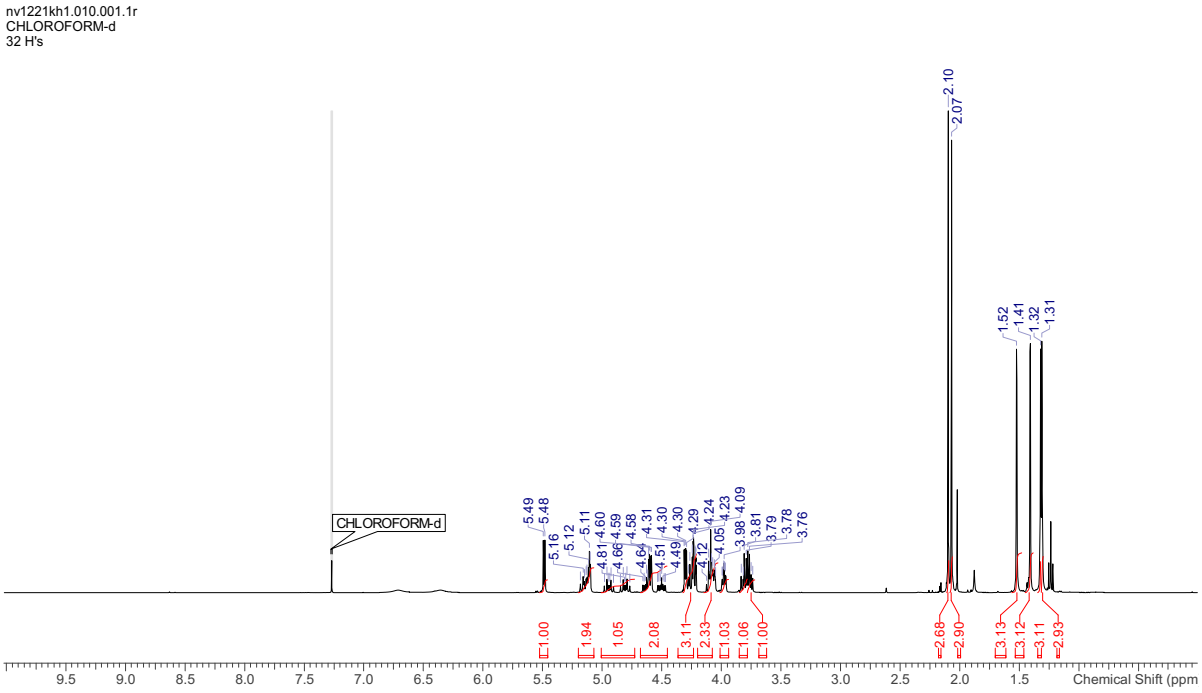


6.5 Copies of the spectra of the glycosylation product with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose

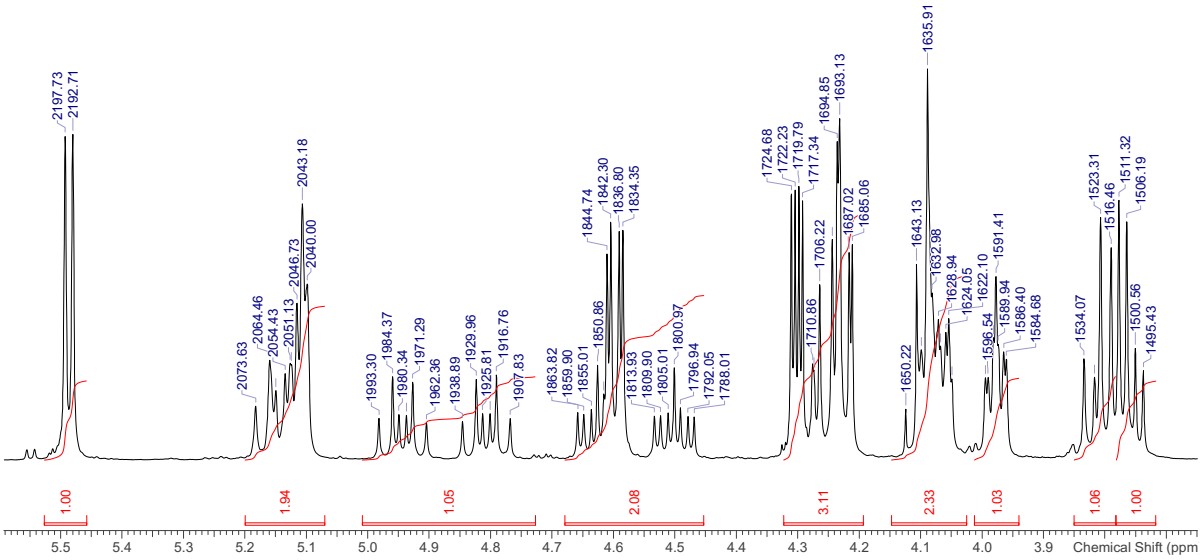
6.5.1 4,6-Di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α-D-glucopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**19α**)



6.5.1.1 ^{1}H NMR, 400 MHz, $CDCl_3$

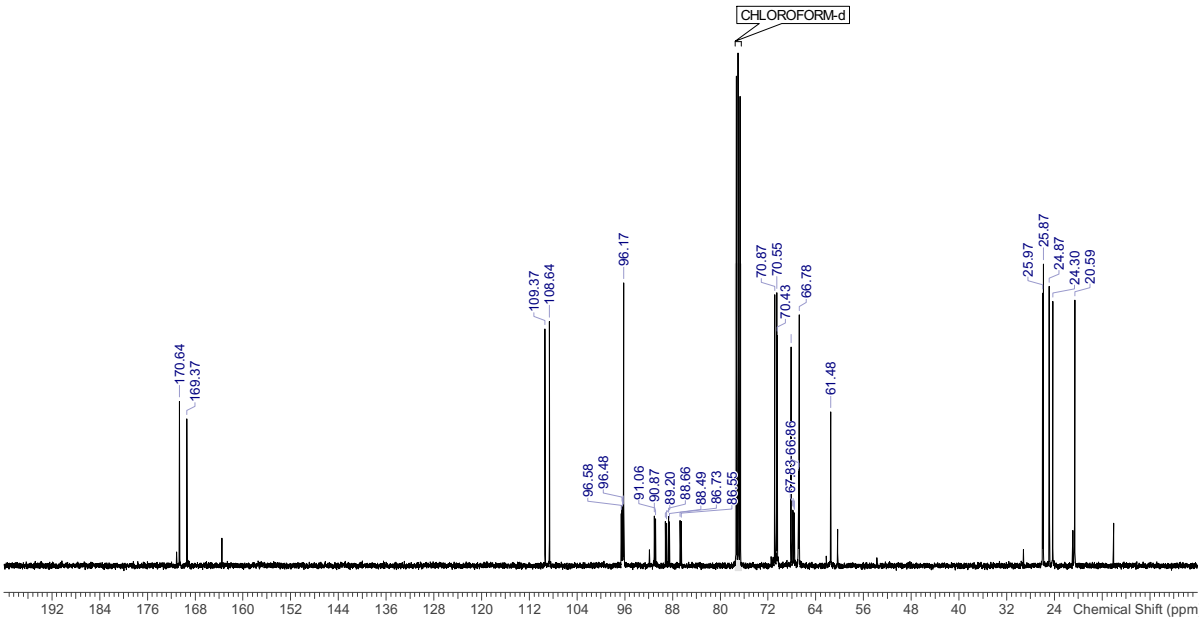


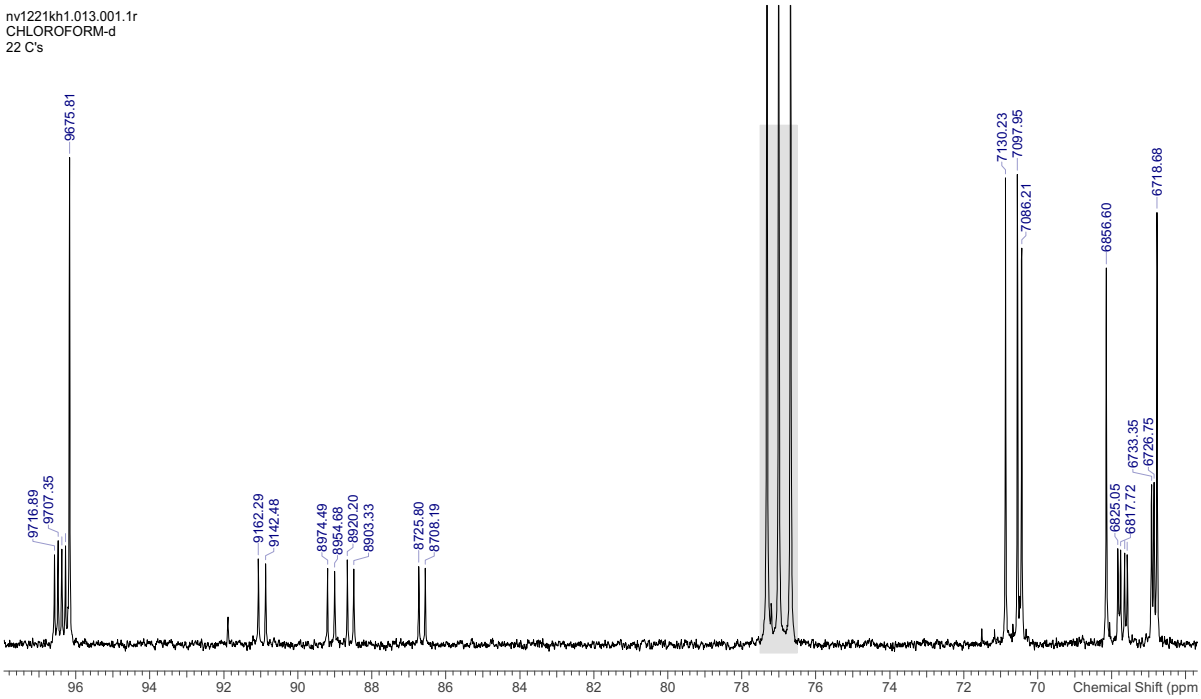
nv1221kh1.010.001.1r
CHLOROFORM-d
32 H's



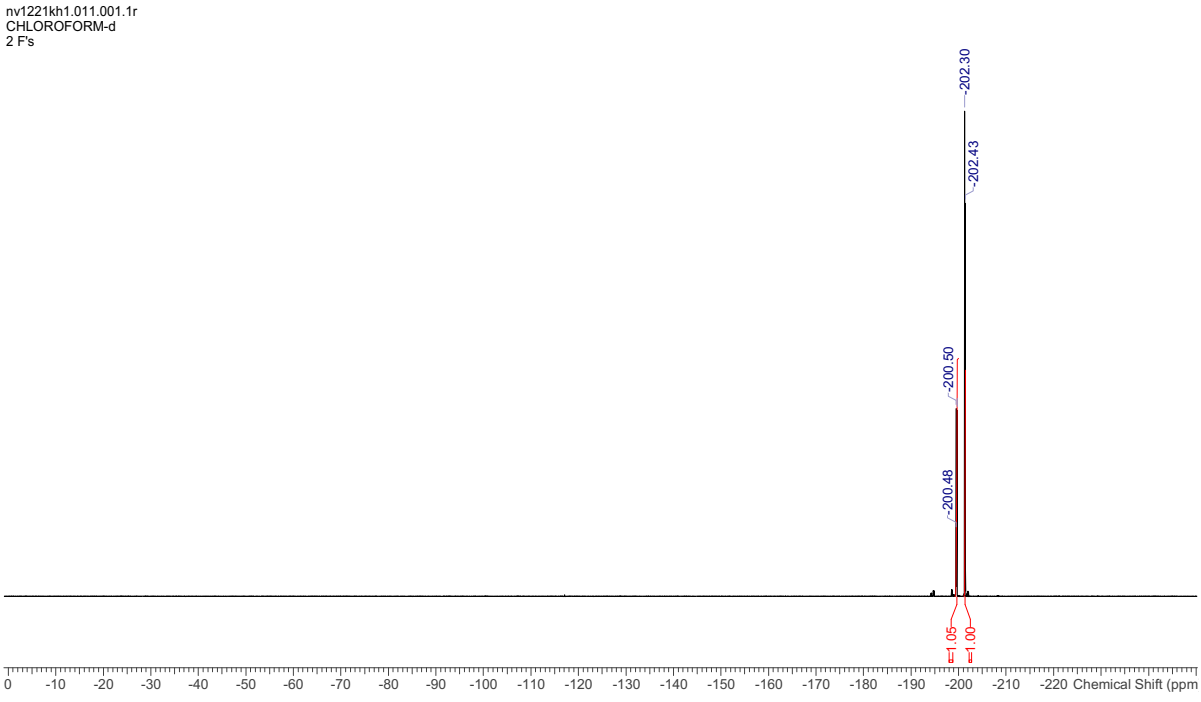
6.5.1.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

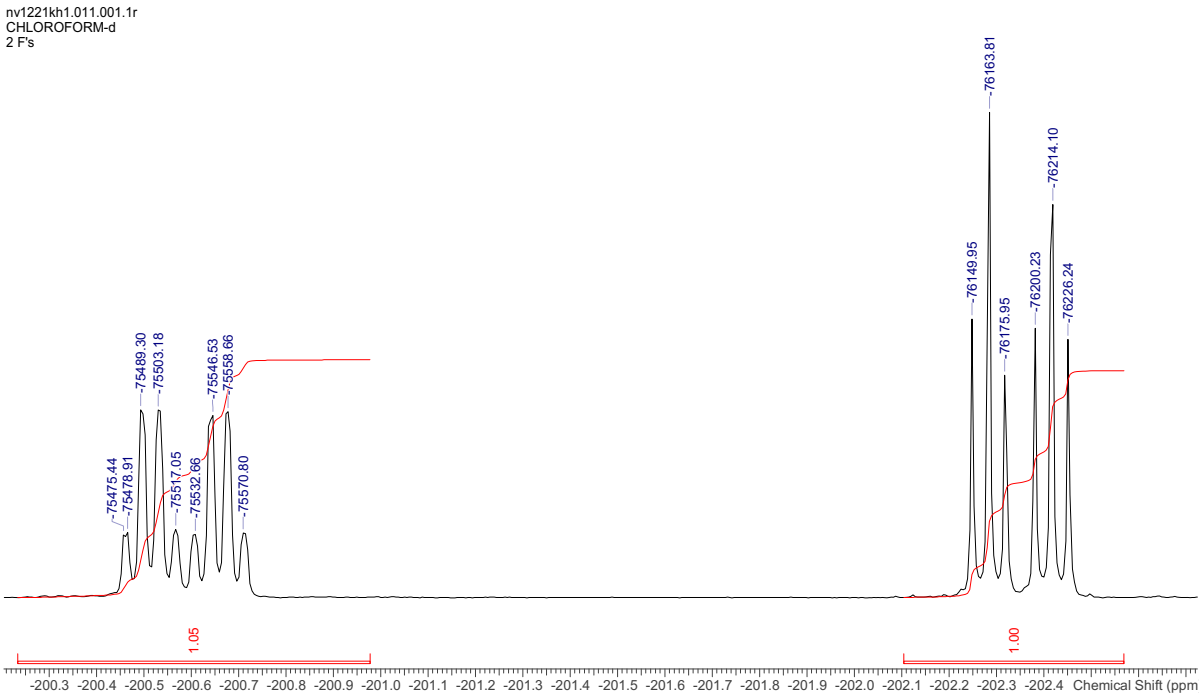
nv1221kh1.013.001.1r
CHLOROFORM-d
22 C's



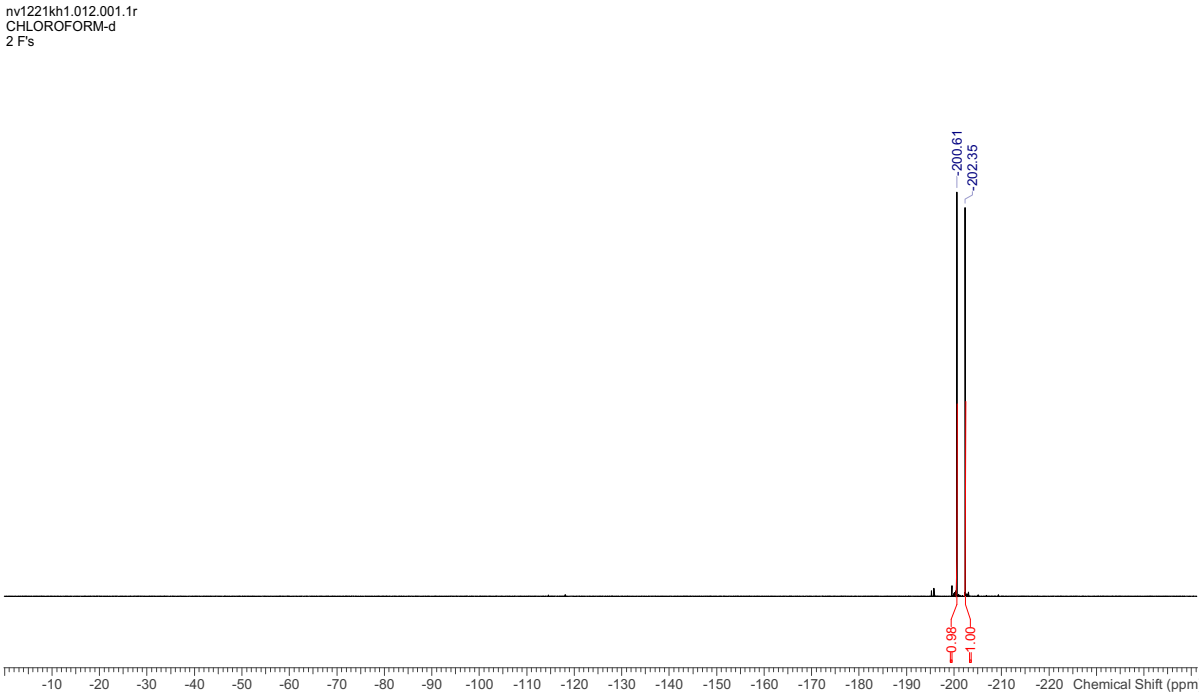


6.5.1.3 ^{19}F NMR, 376 MHz, $CDCl_3$

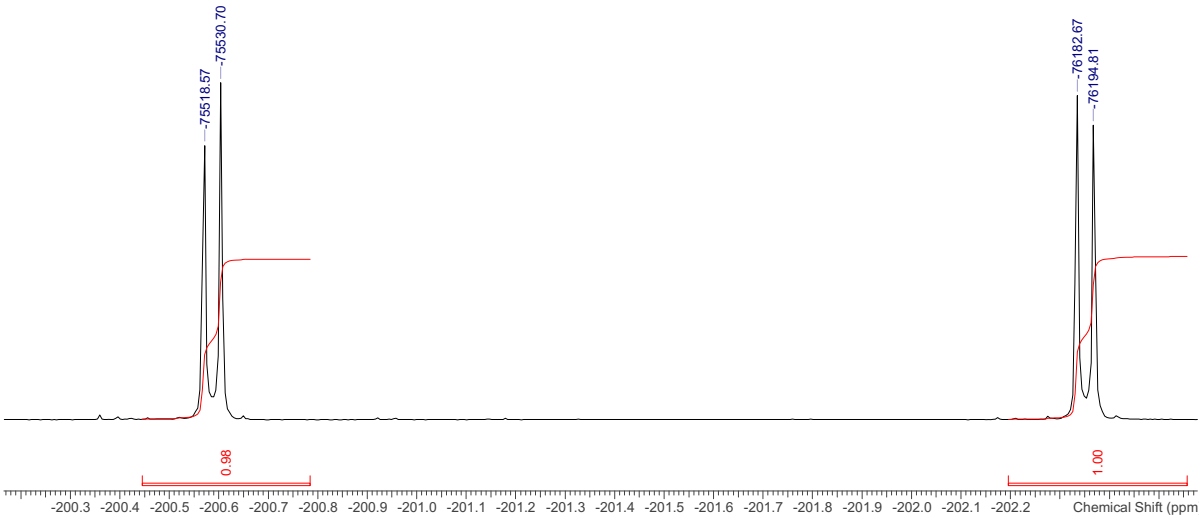




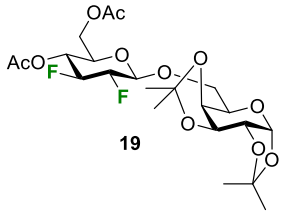
6.5.1.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



nv1221kh1.012.001.1r
CHLOROFORM-d
2 F's



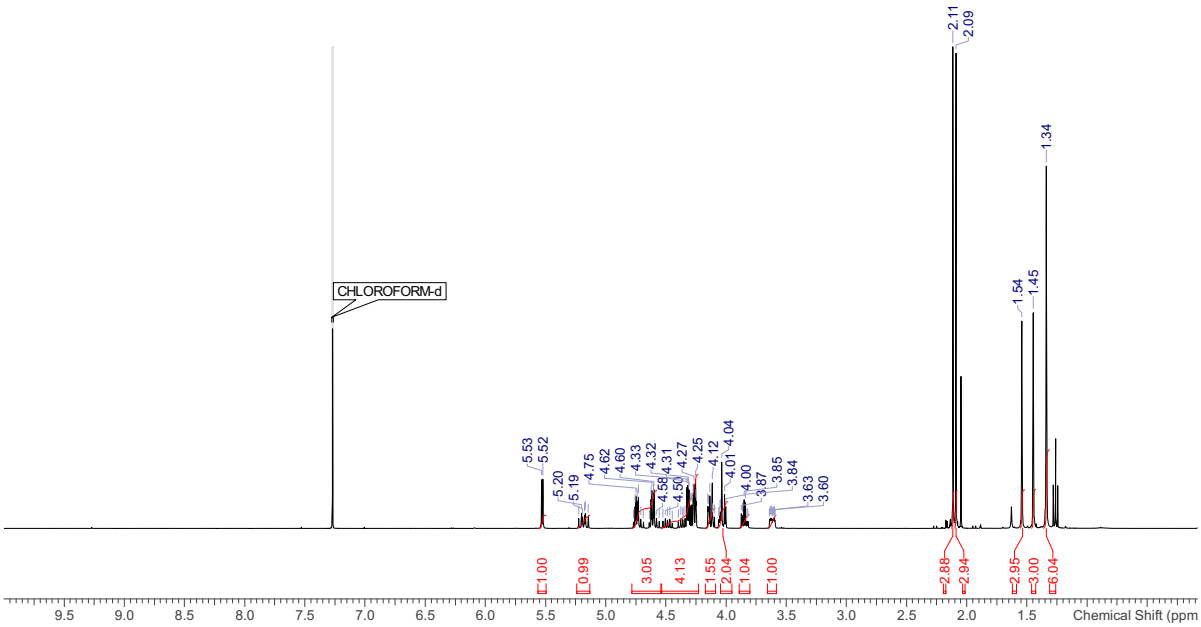
6.5.2 4,6-Di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-β-D-glucopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**19β**)



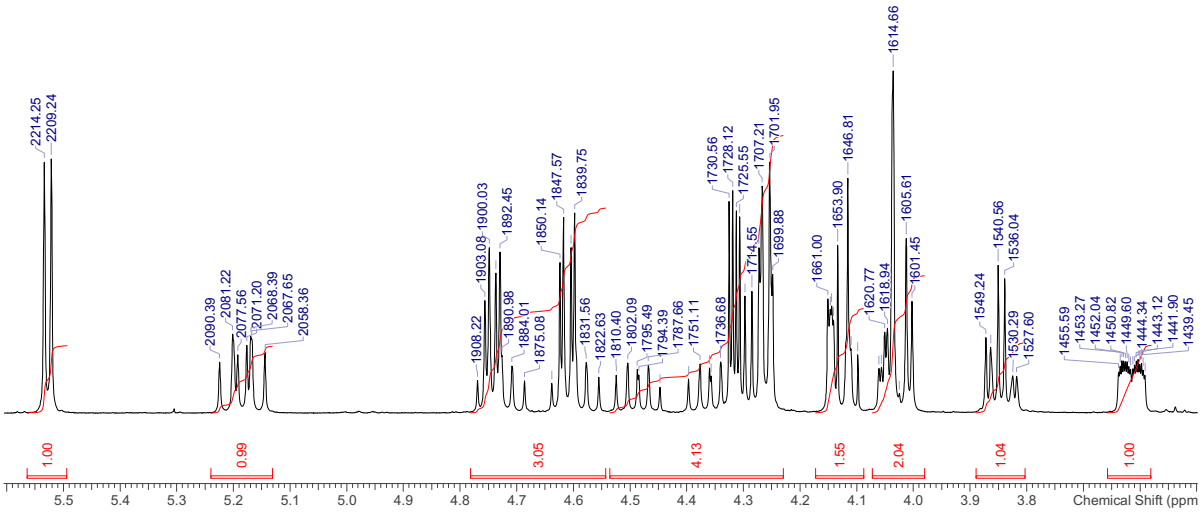
19

6.5.2.1 ^{1}H NMR, 400 MHz, $CDCl_3$

ja1923kh1.010.001.1r
CHLOROFORM-d
33 H's

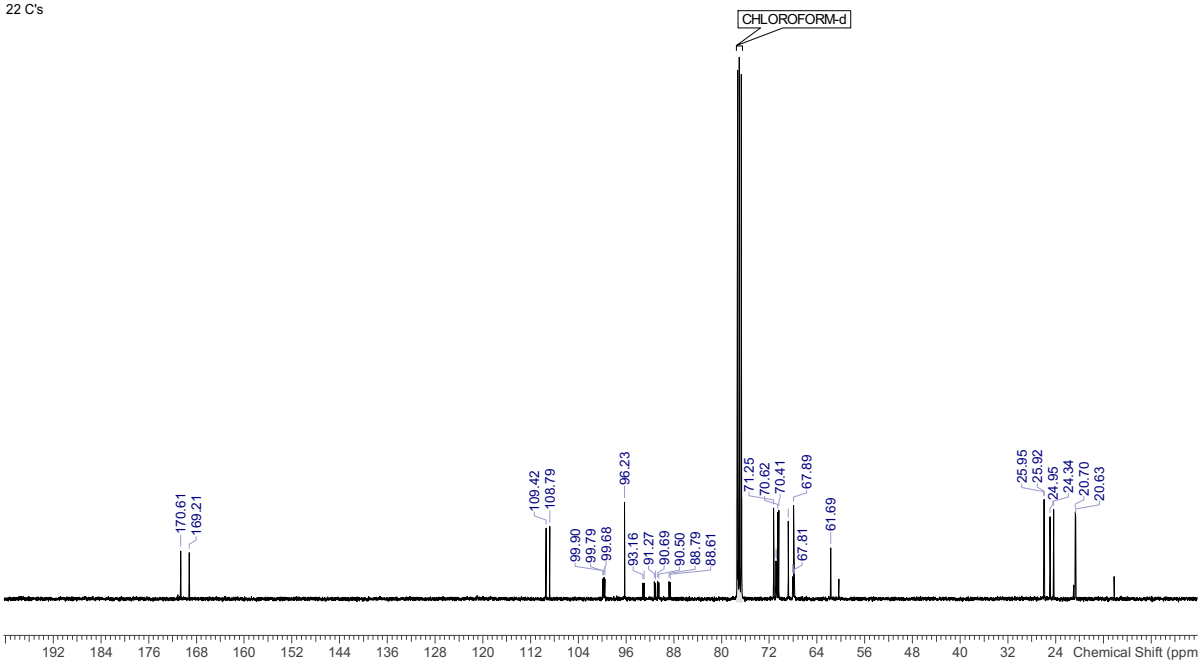


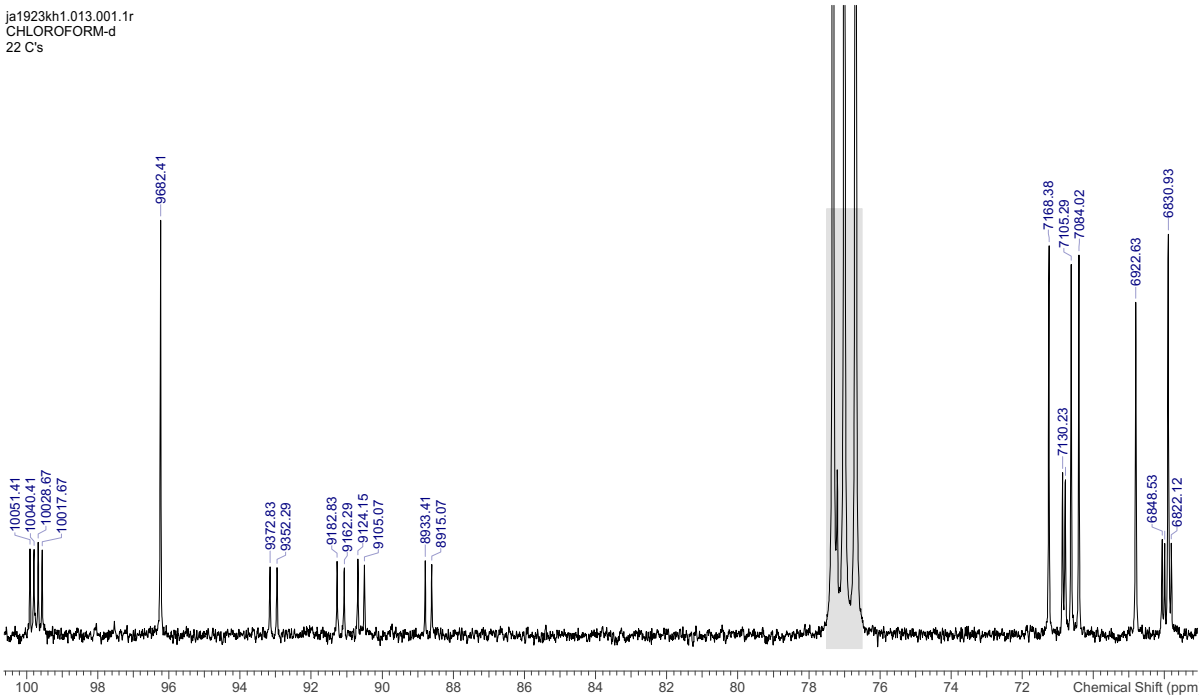
ja1923kh1.010.001.1r
CHLOROFORM-d
33 H's



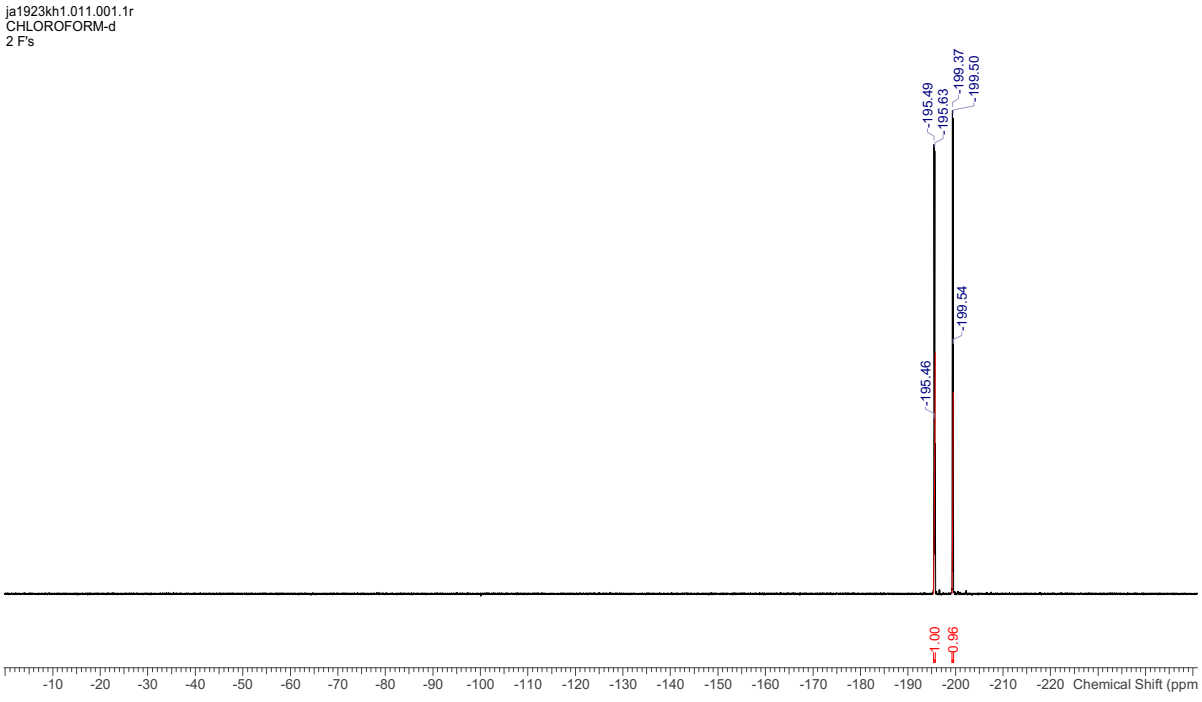
6.5.2.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

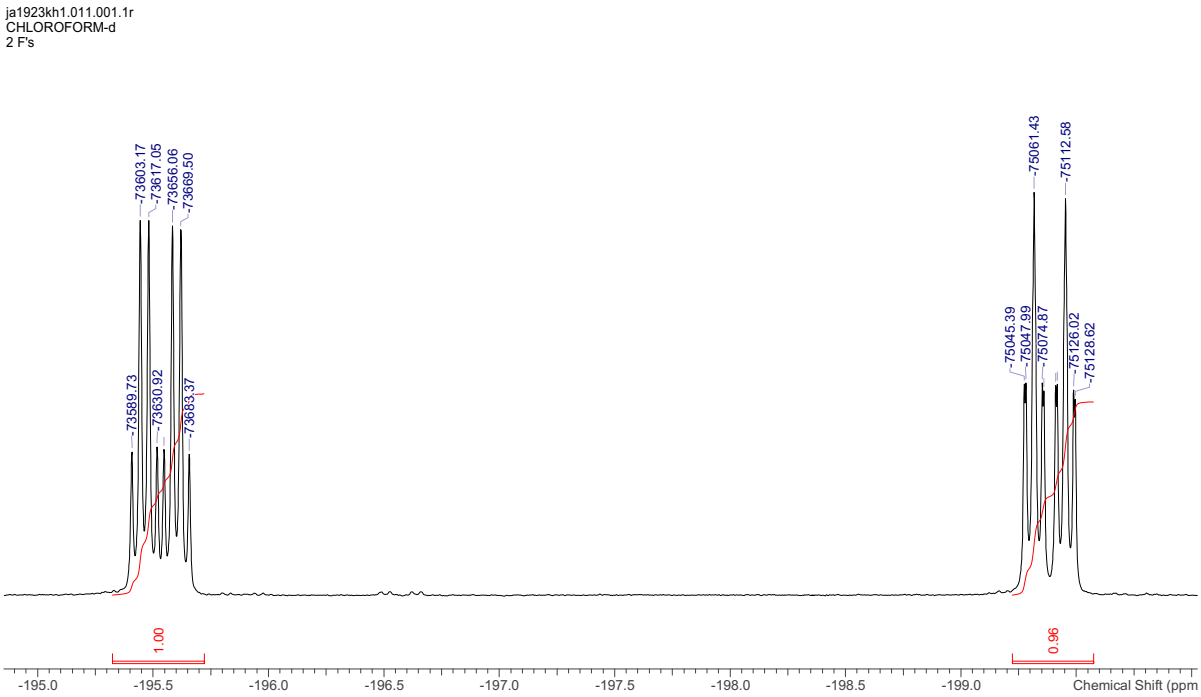
ja1923kh1.013.001.1r
CHLOROFORM-d
22 C's



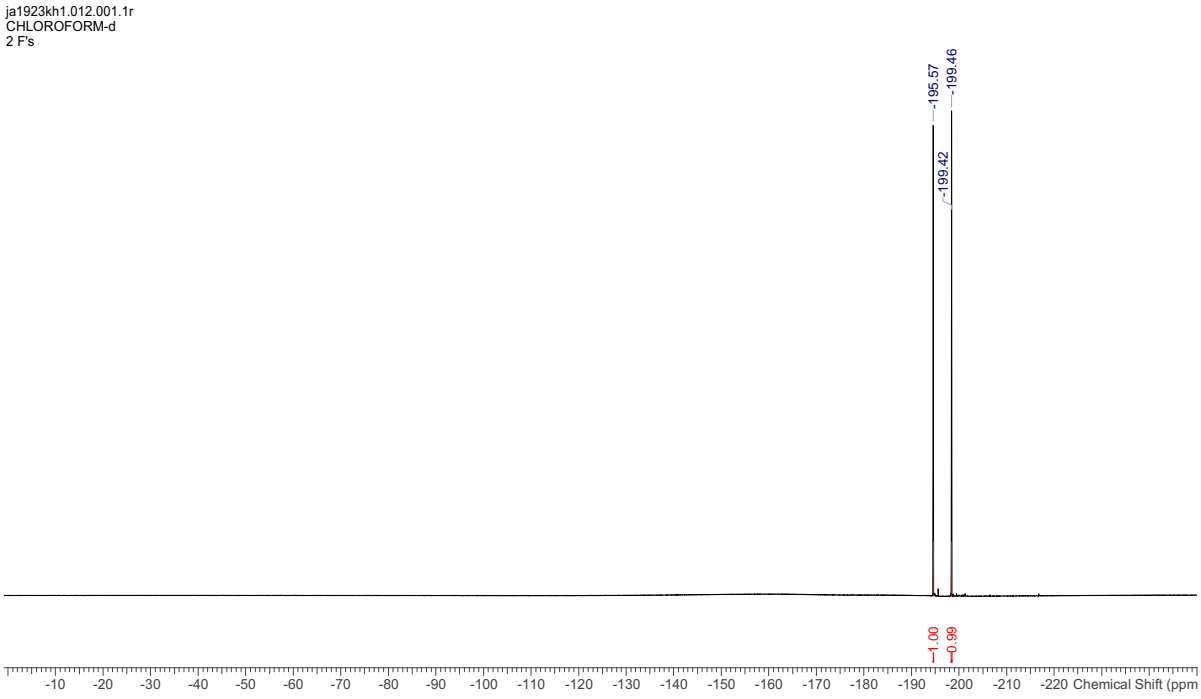


6.5.2.3 ^{19}F NMR, 376 MHz, $CDCl_3$

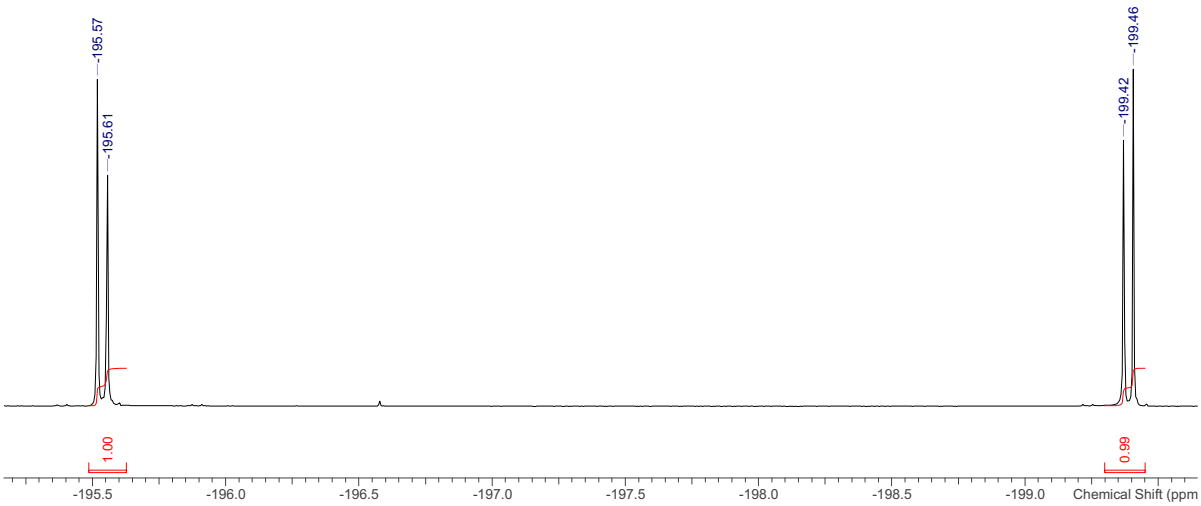




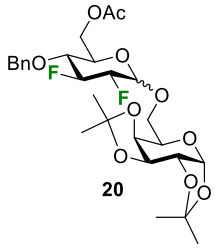
6.5.2.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



ja1923kh1.012.001.1r
CHLOROFORM-d
2 F's

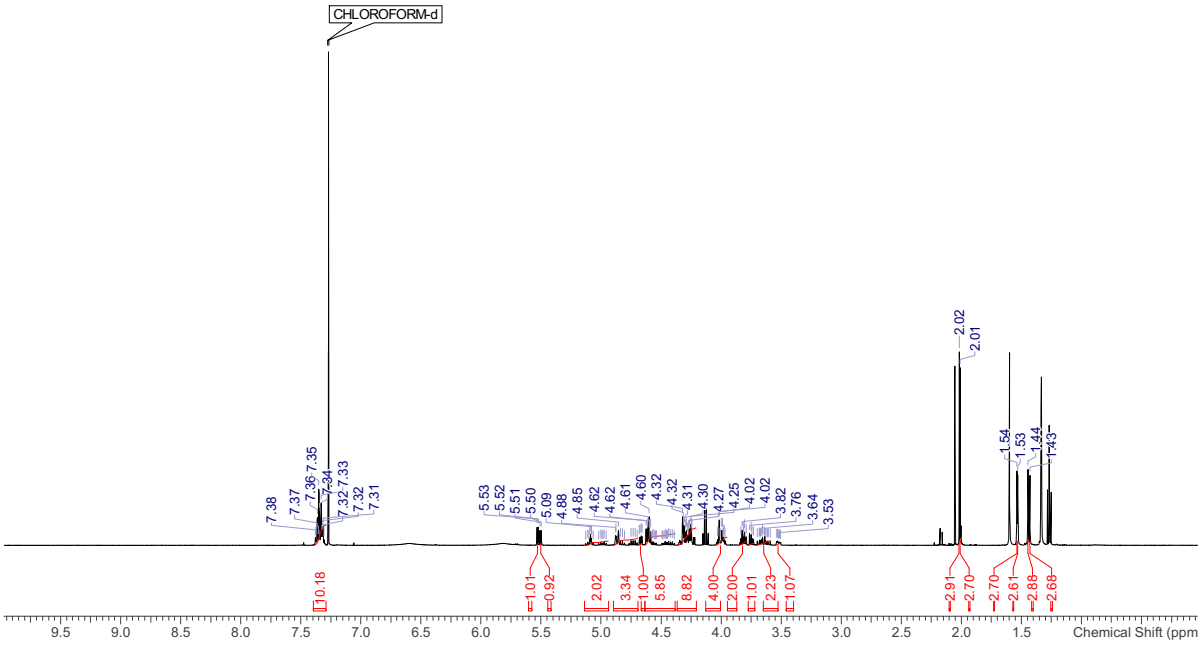


6.5.3 6-*O*-Acetyl-4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-α/β-D-glucopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**20**)

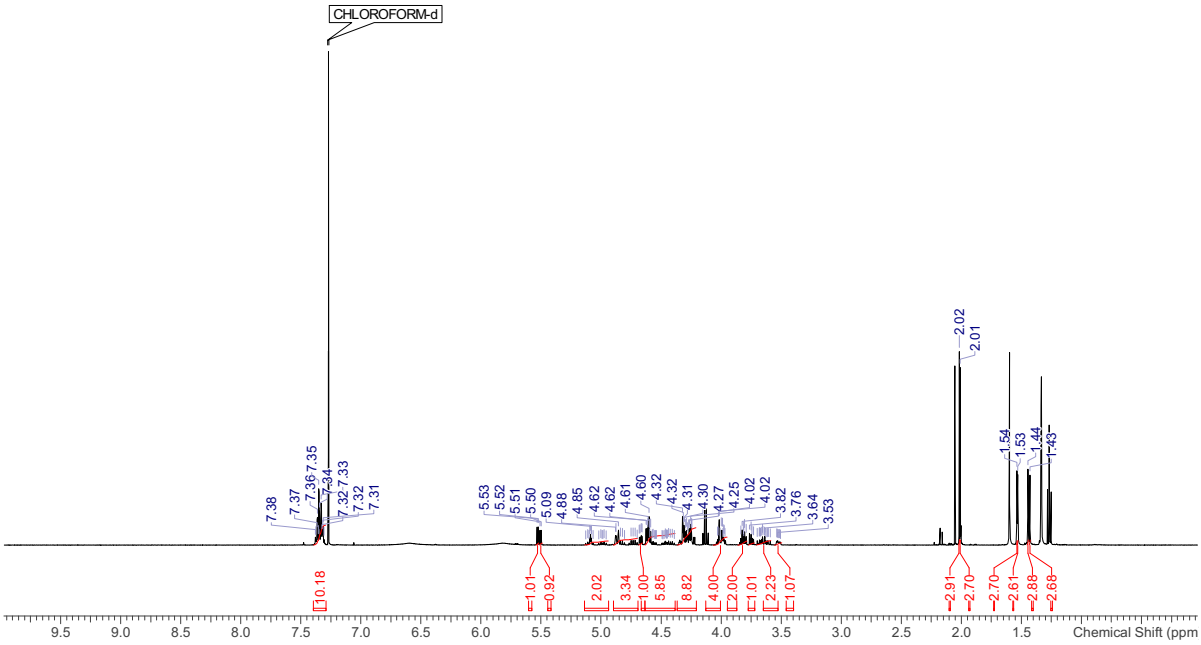


6.5.3.1 ^{1}H NMR, 500 MHz, $CDCl_3$

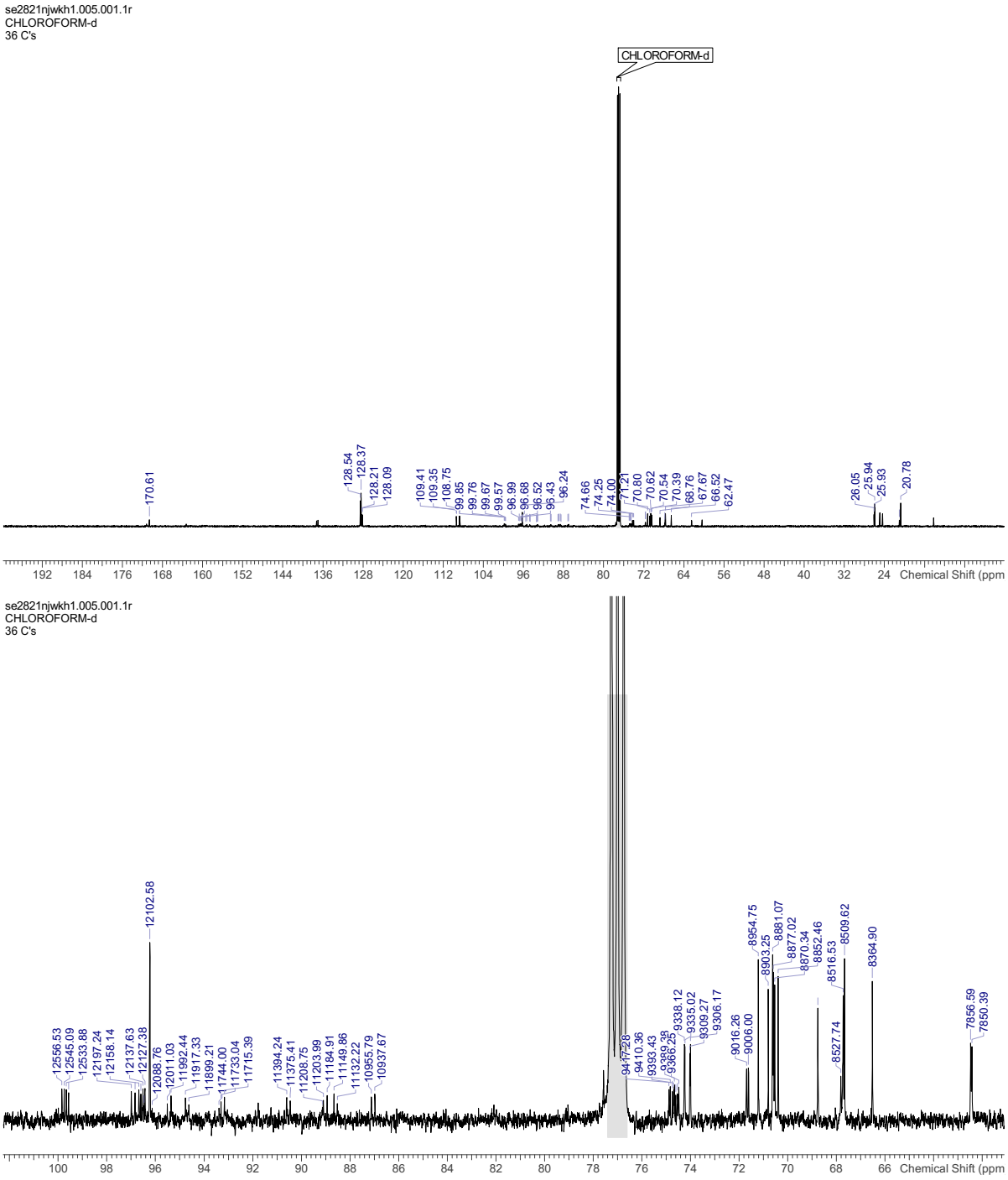
se2821njwkh1.001.001.1r
CHLOROFORM-d
61 H's



se2821njwkh1.001.001.1r
CHLOROFORM-d
61 H's

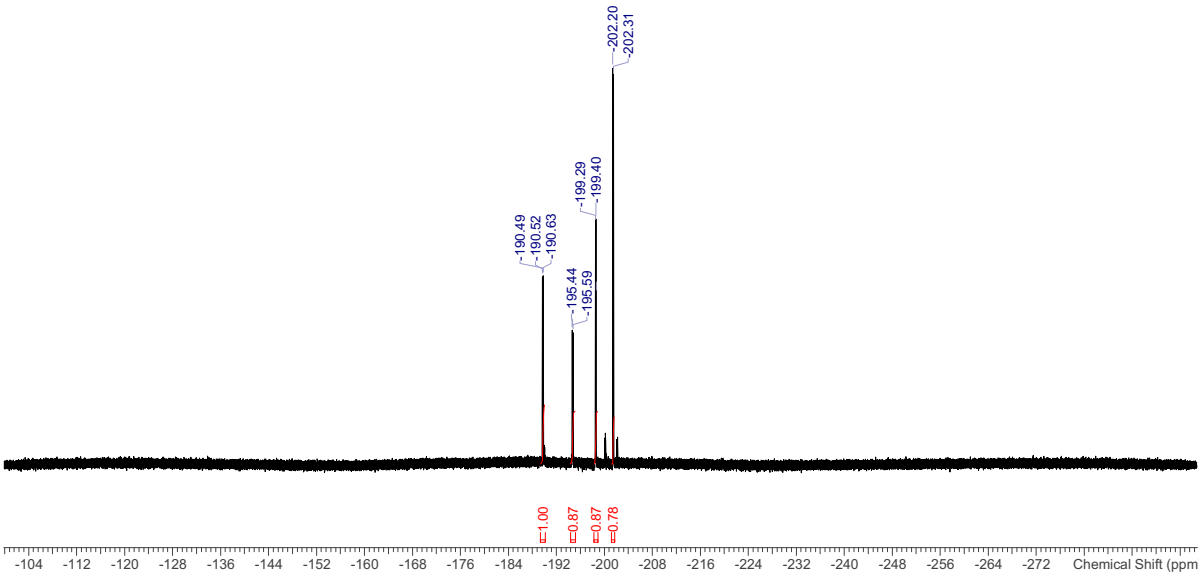


6.5.3.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

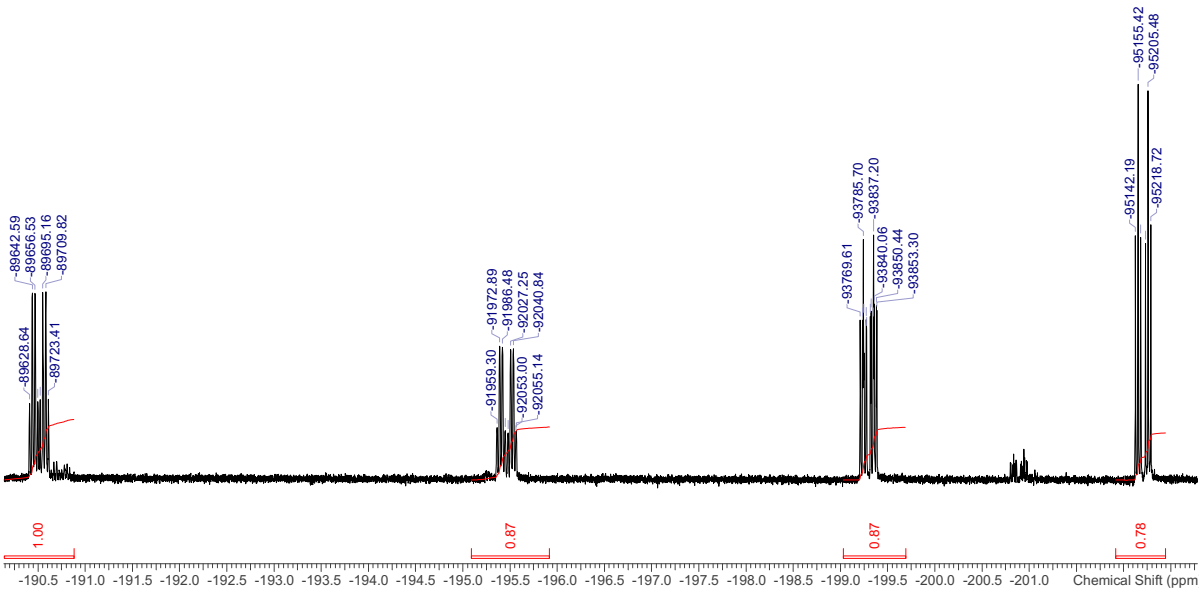


6.5.3.3 ^{19}F NMR, 471 MHz, $CDCl_3$

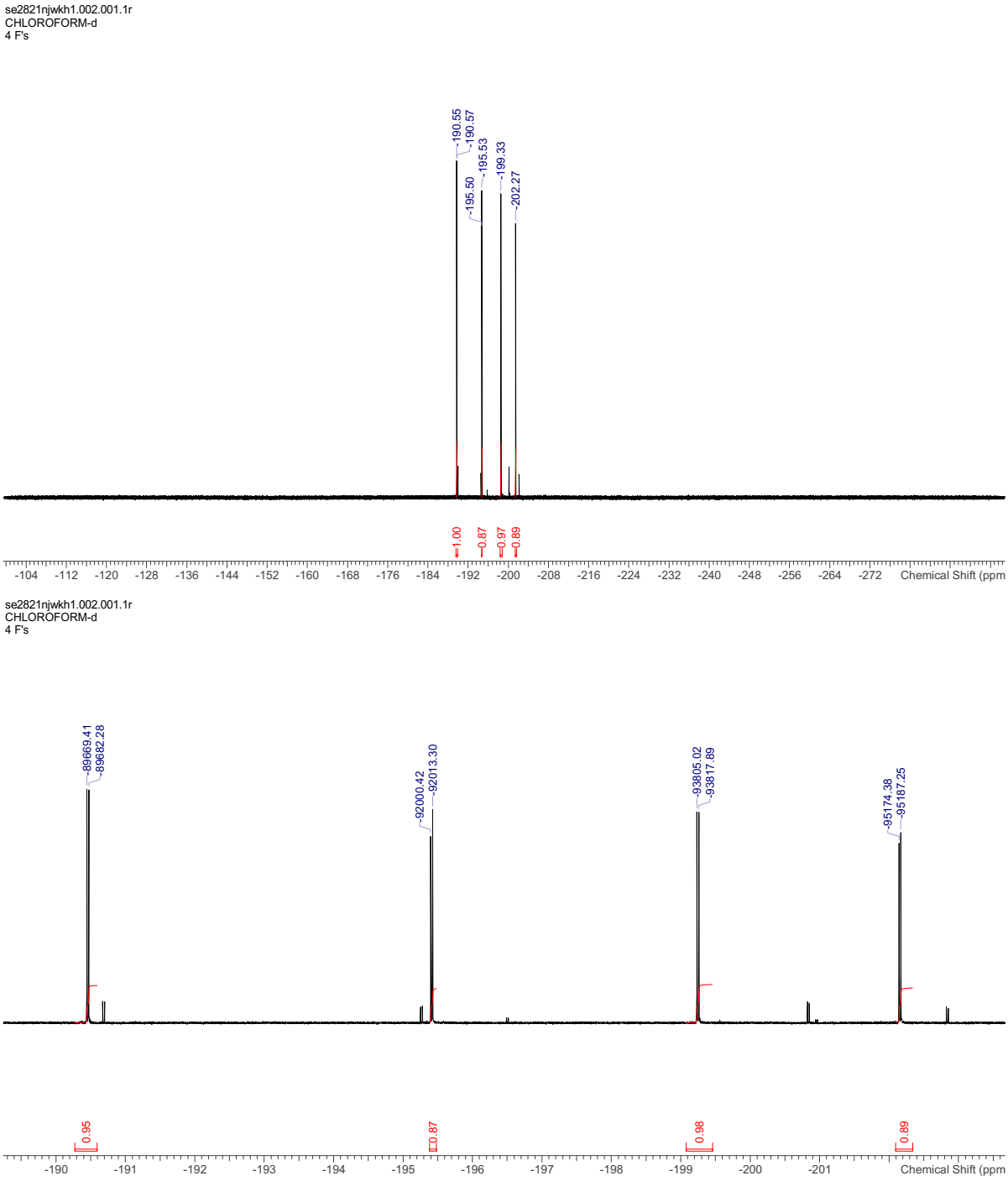
se2821njwkh1.003.001.1r
CHLOROFORM-d
4 F's



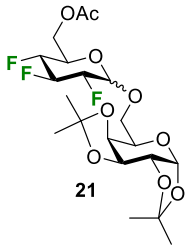
se2821njwkh1.003.001.1r
CHLOROFORM-d
4 F's



6.5.3.4 $^{19}F\{^{1}H\}$ NMR, 471 MHz, $CDCl_3$

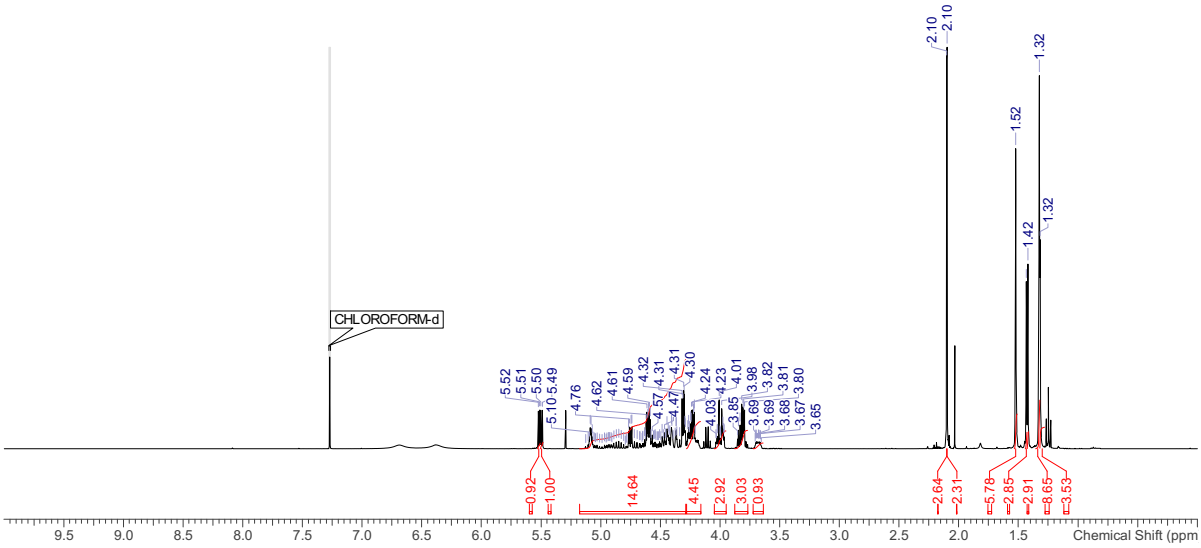


6.5.4 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α/β-D-glucopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**21**)

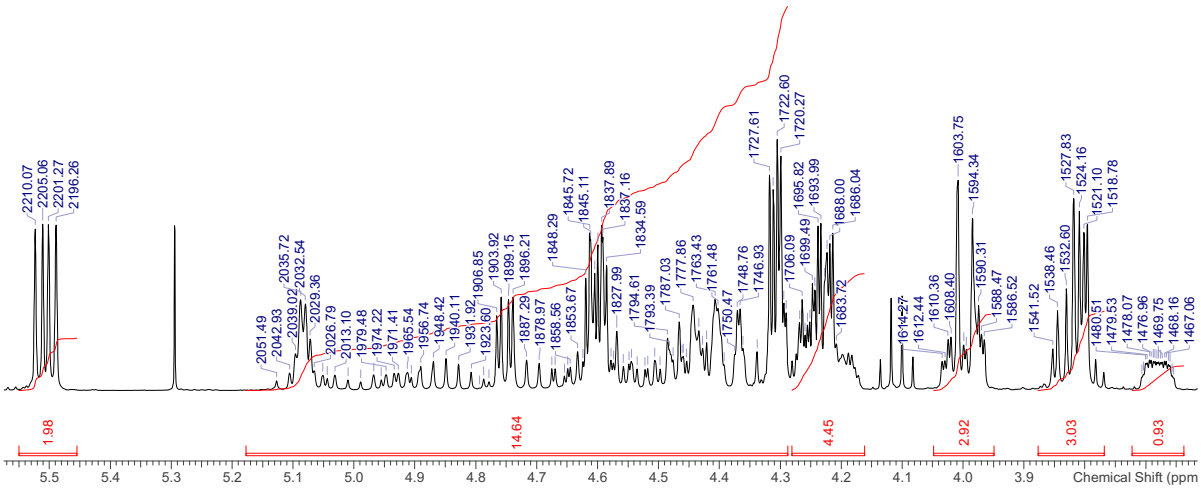


6.5.4.1 ^{1}H NMR, 400 MHz, $CDCl_3$

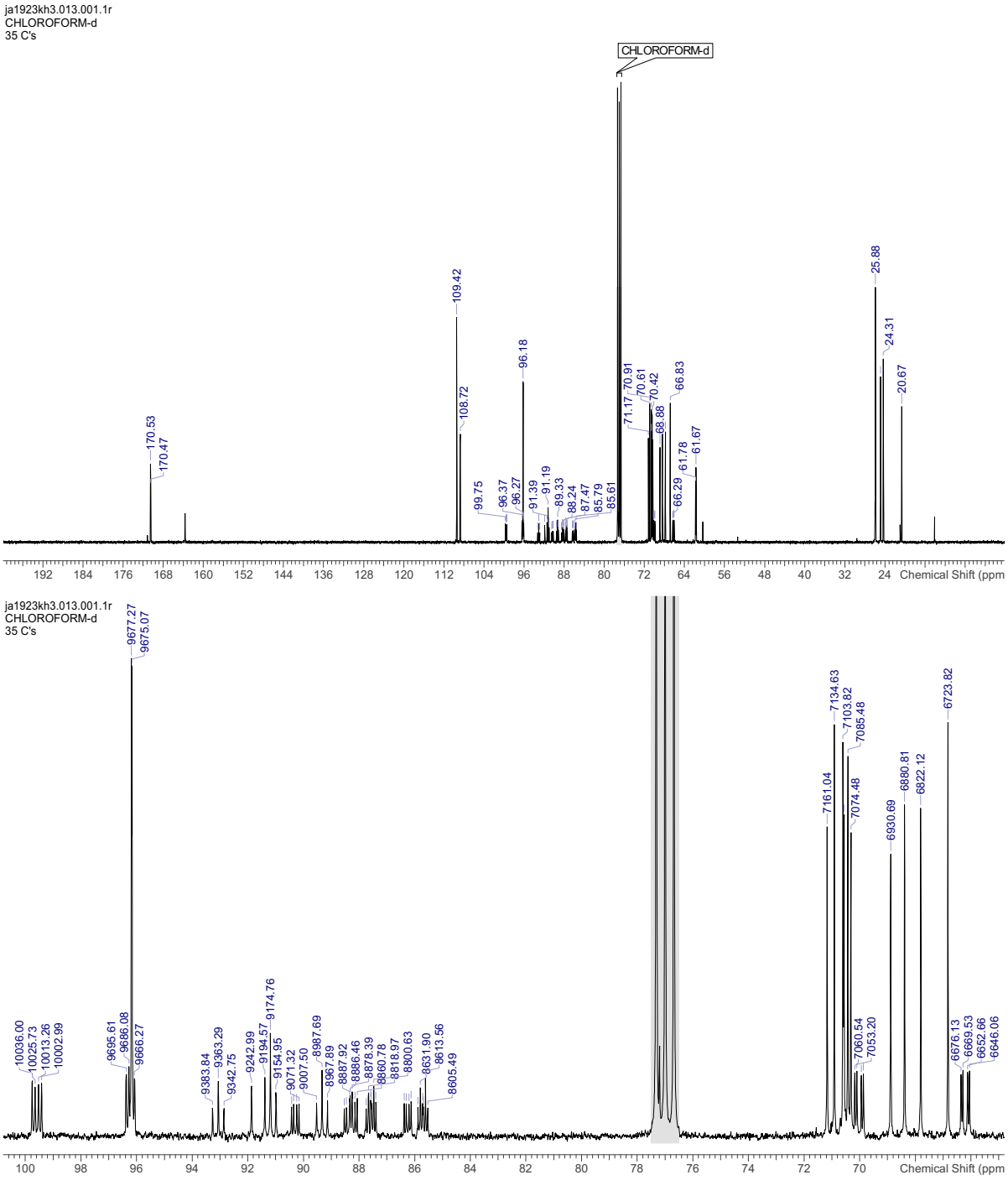
ja1923kh3.010.001.1r
CHLOROFORM-d
56 H's



ja1923kh3.010.001.1r
CHLOROFORM-d
57 H's

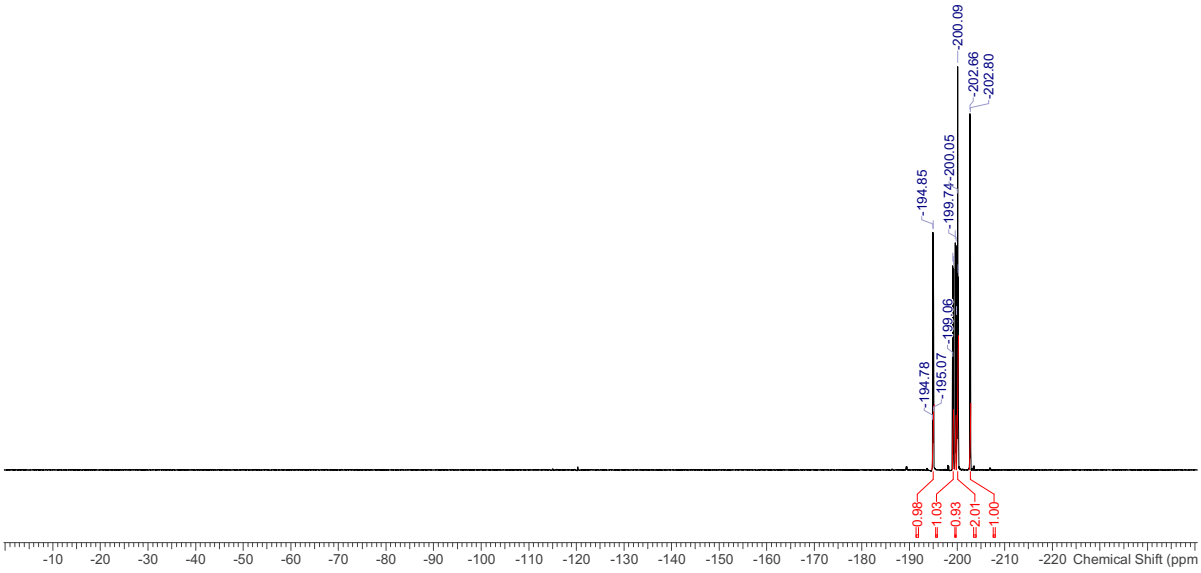


6.5.4.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

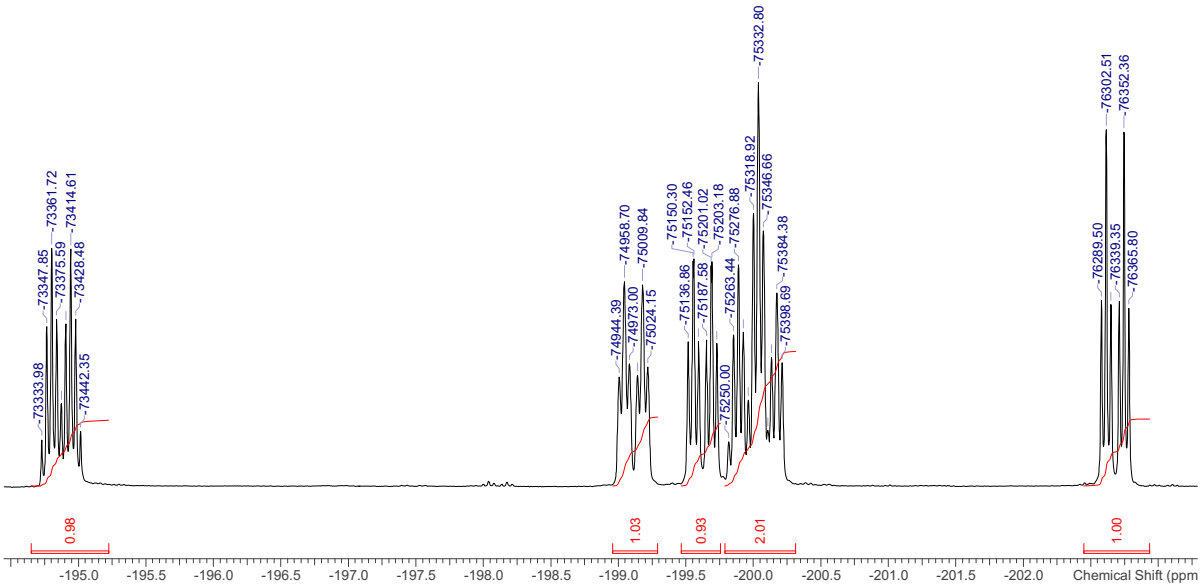


6.5.4.3 ^{19}F NMR, 376 MHz, $CDCl_3$

ja1923kh3.011.001.1r
CHLOROFORM-d
5 F's

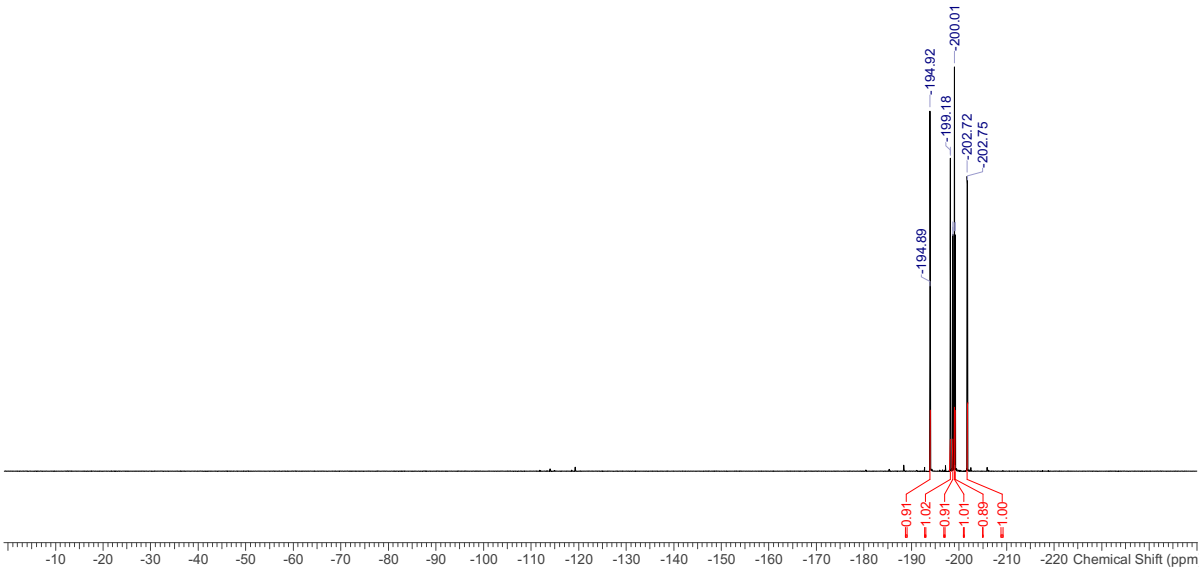


ja1923kh3.011.001.1r
CHLOROFORM-d
5 F's

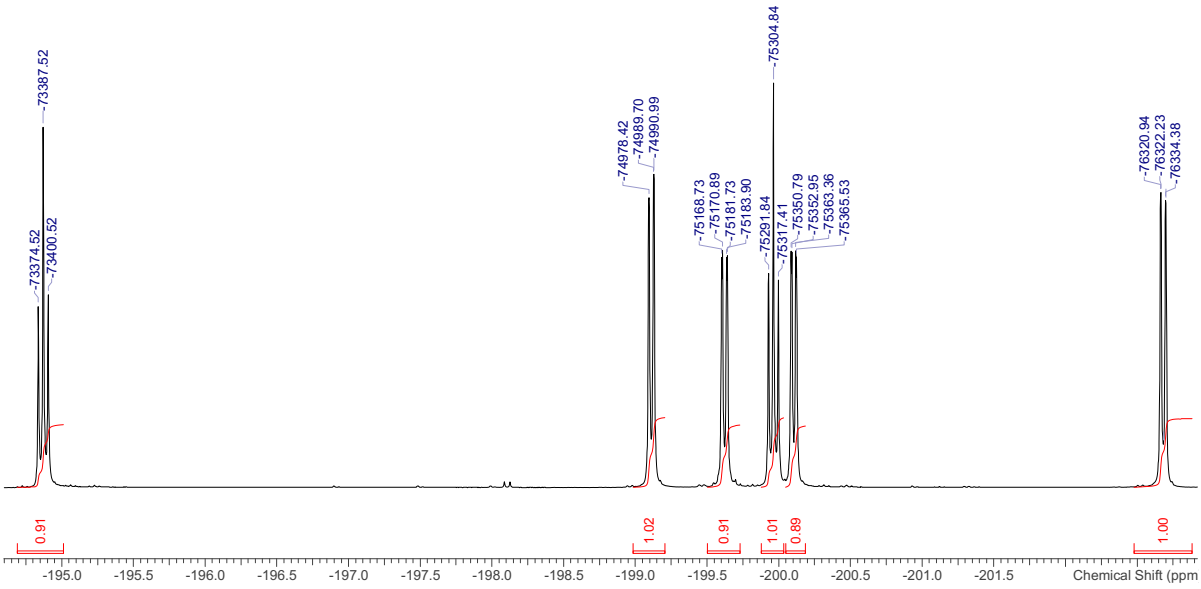


6.5.4.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

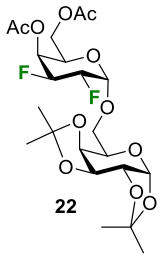
ja1923kh3.012.001.1r
CHLOROFORM-d
6 F's



ja1923kh3.012.001.1r
CHLOROFORM-d
6 F's

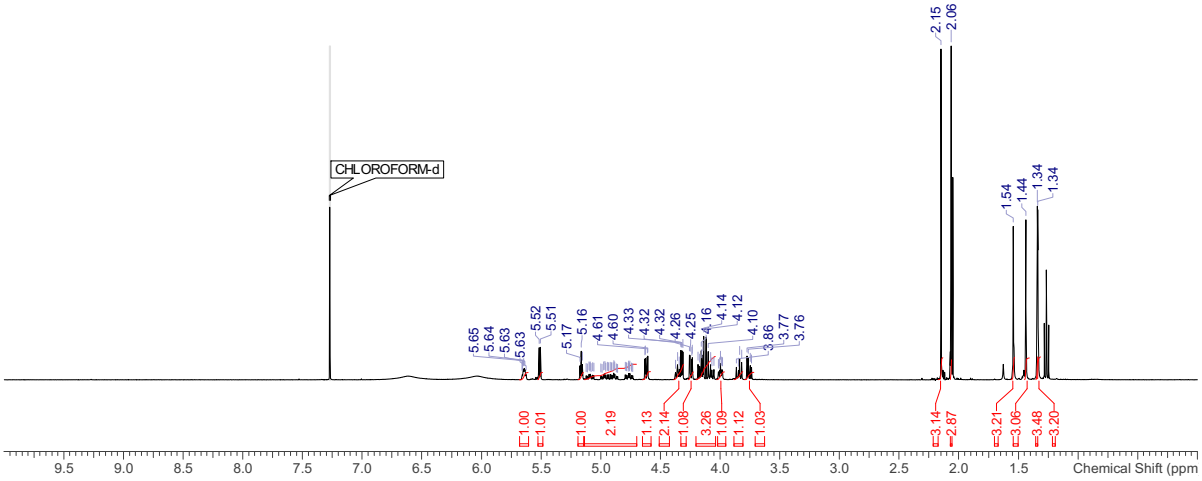


6.5.5 4,6-Di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**22α**)

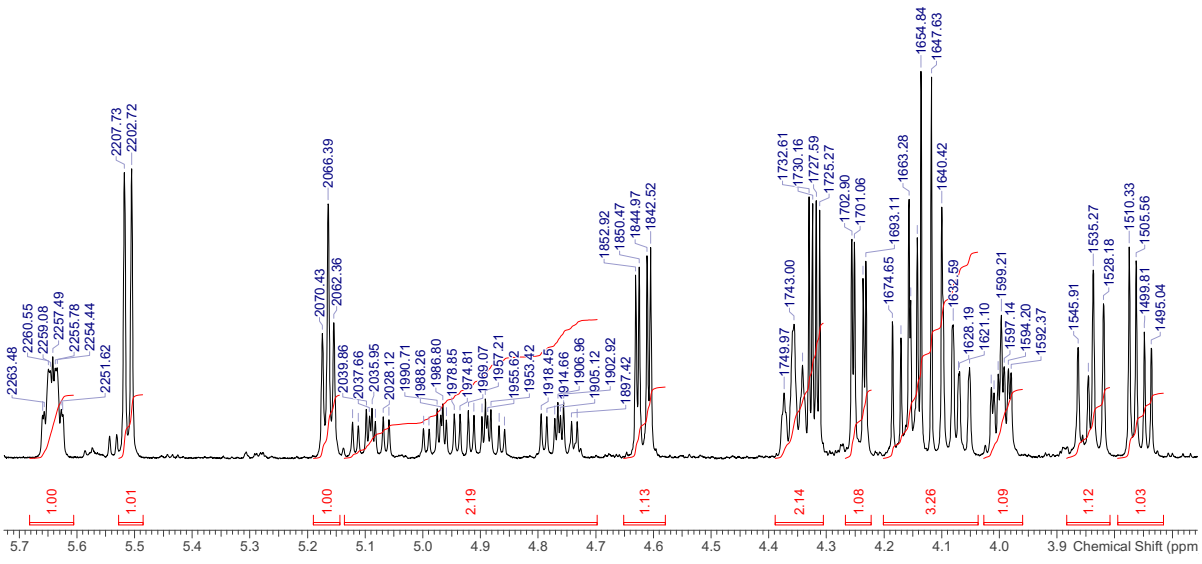


6.5.5.1 ^{1}H NMR, 400 MHz, $CDCl_3$

ja1123kh3.010.001.1r
CHLOROFORM-d
33 H's

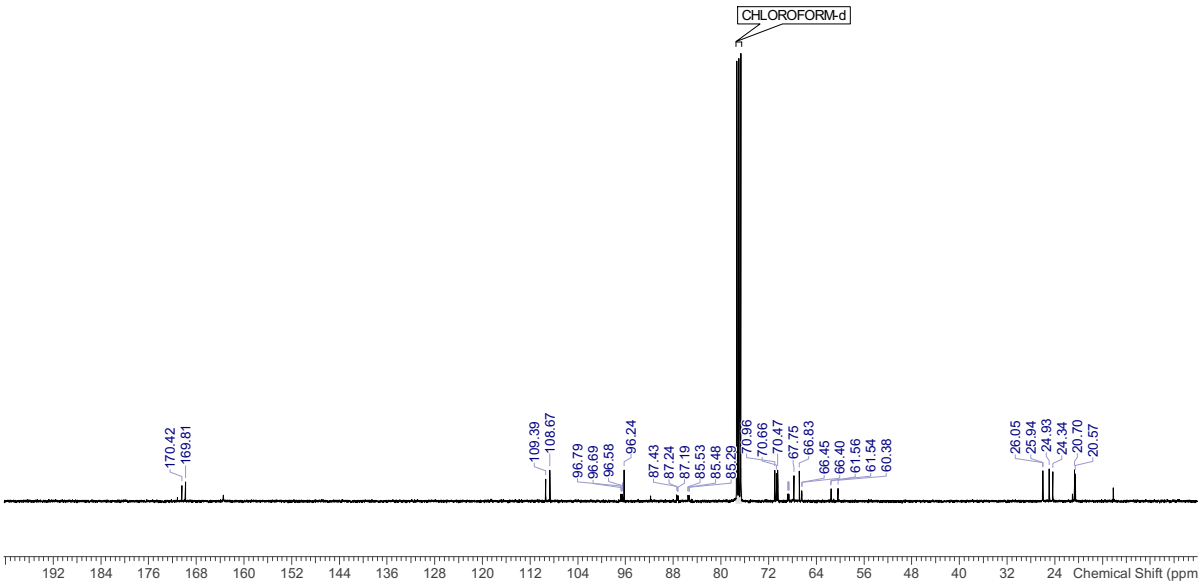


ja1123kh3.010.001.1r
CHLOROFORM-d
33 H's

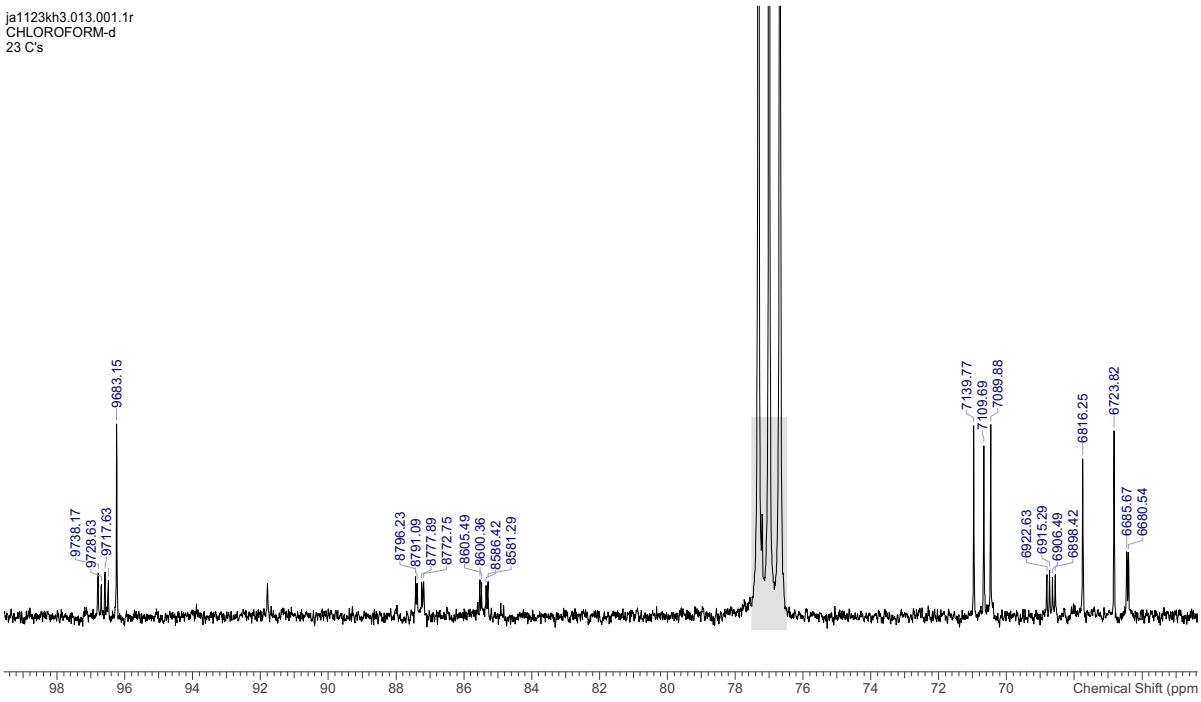


6.5.5.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

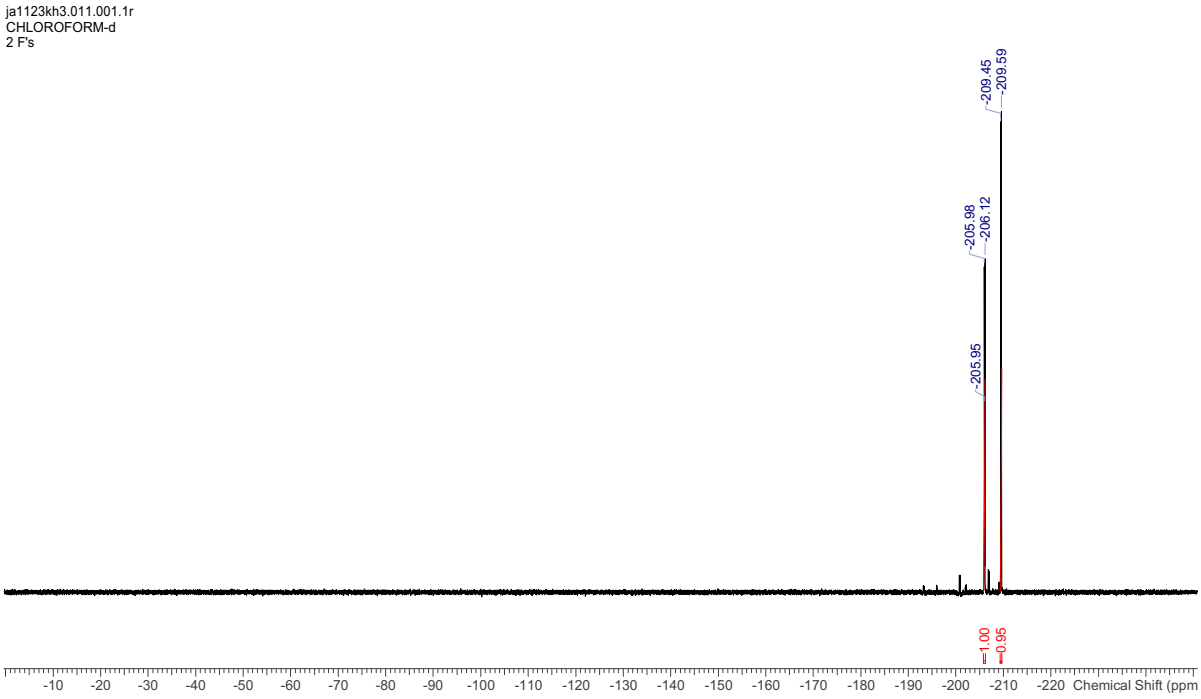
ja1123kh3.013.001.1r
CHLOROFORM-d
23 C's

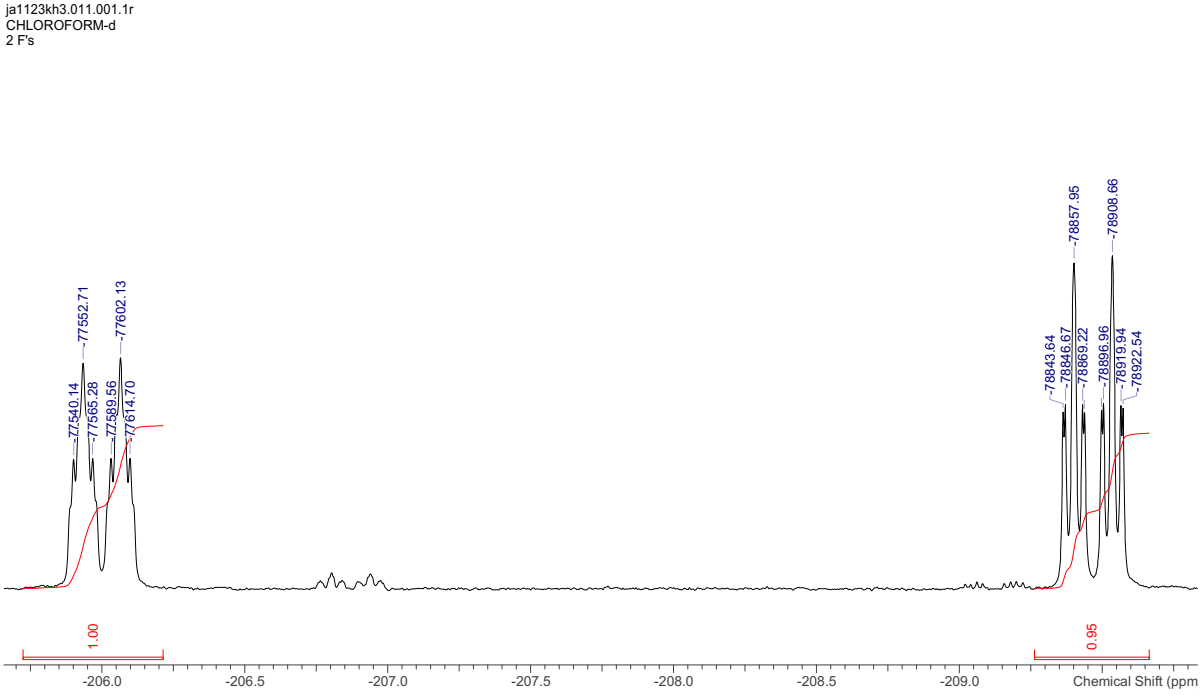


ja1123kh3.013.001.1r
CHLOROFORM-d
23 C's

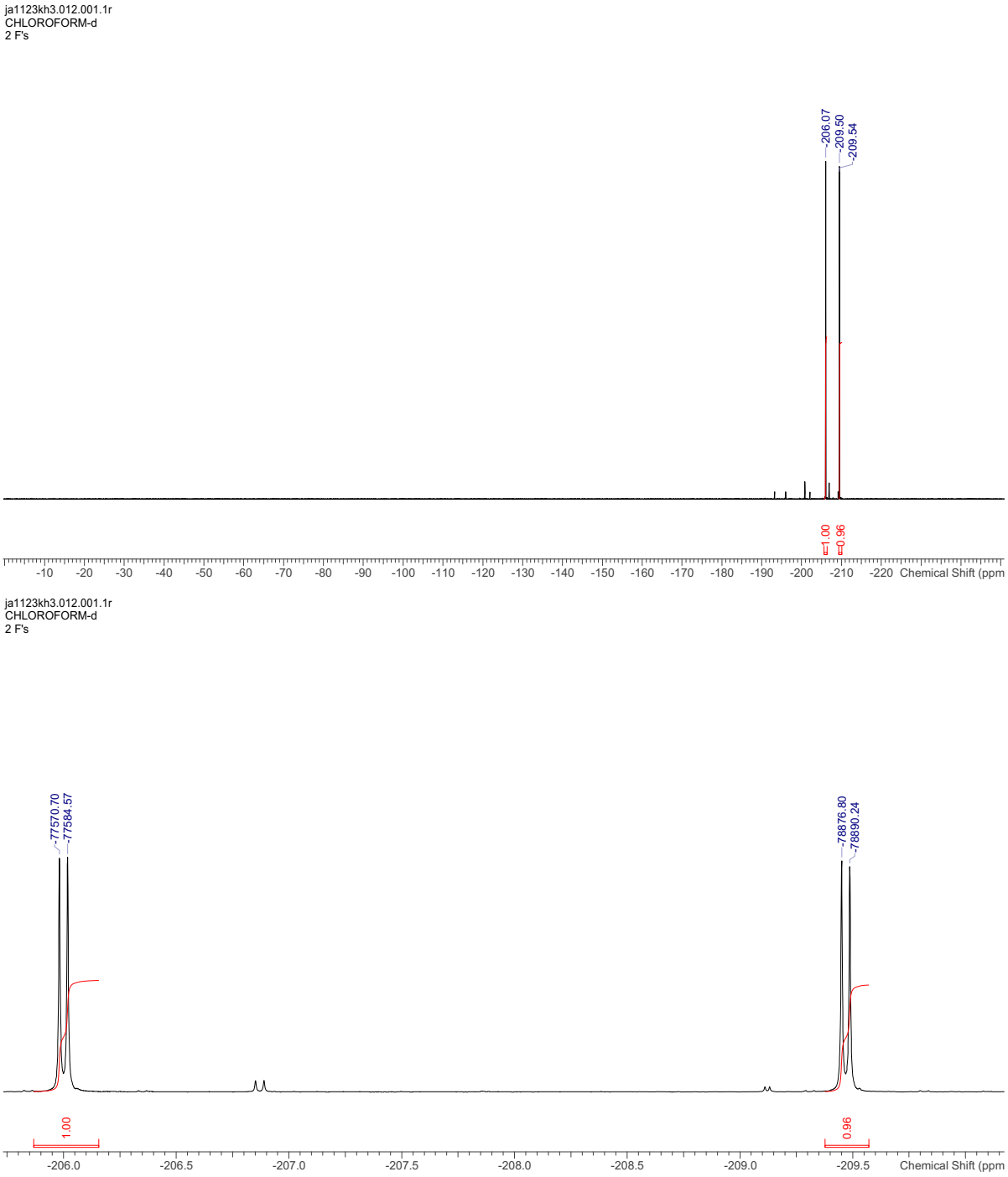


6.5.5.3 ^{19}F NMR, 376 MHz, $CDCl_3$

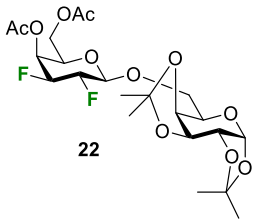




6.5.5.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



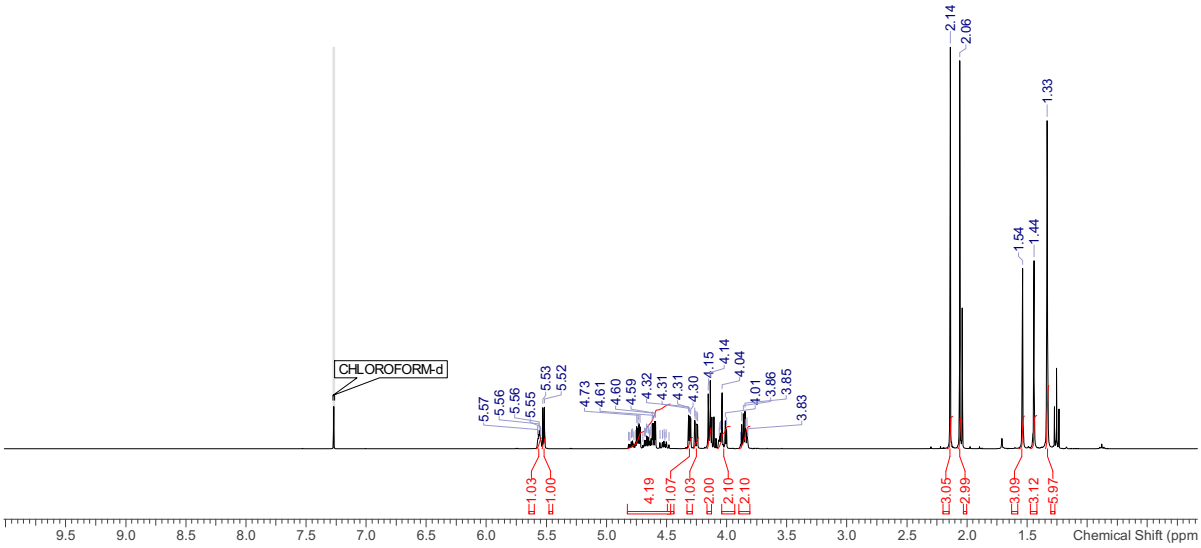
6.5.6 4,6-Di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-β-D-galactopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**22β**)



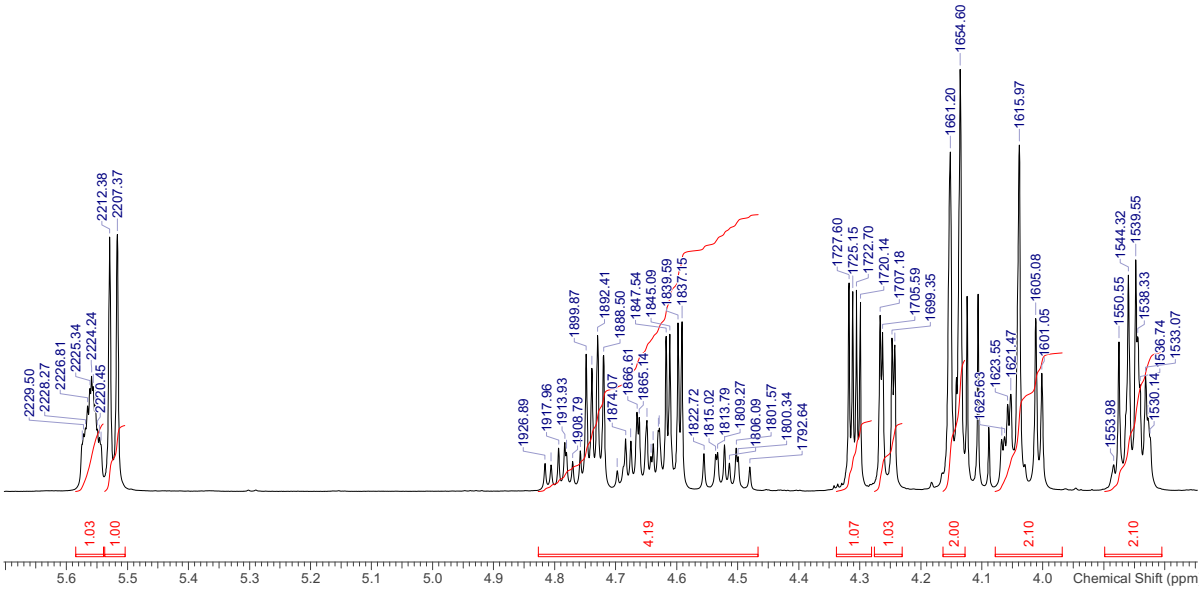
22

6.5.6.1 ^{1}H NMR, 400 MHz, $CDCl_3$

ja3023kh2.010.001.1r
CHLOROFORM-d
32 H's

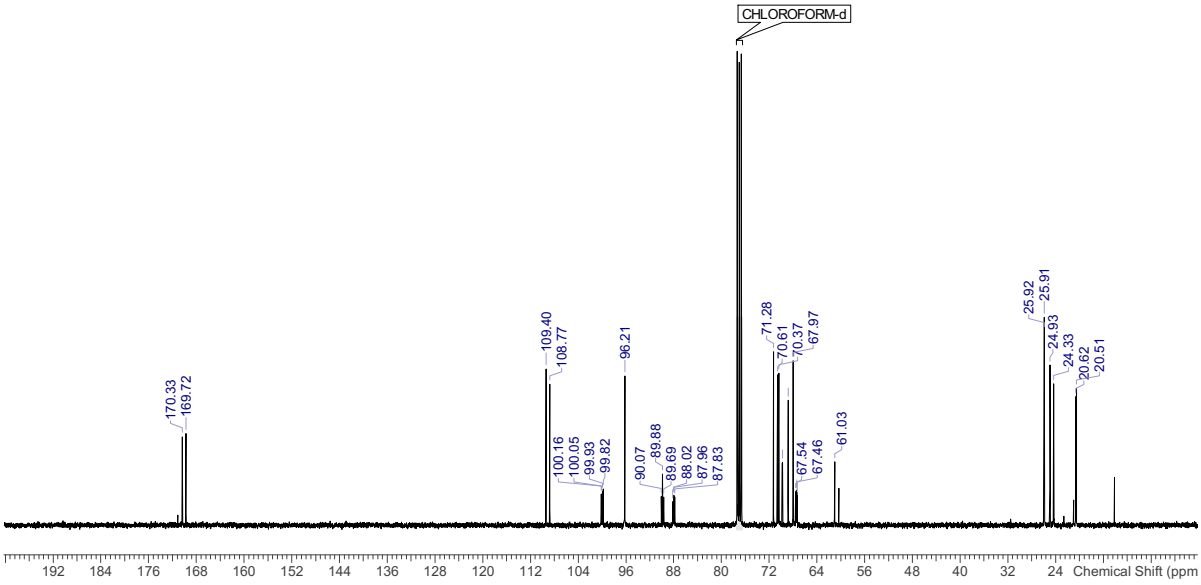


ja3023kh2.010.001.1r
CHLOROFORM-d
32 H's

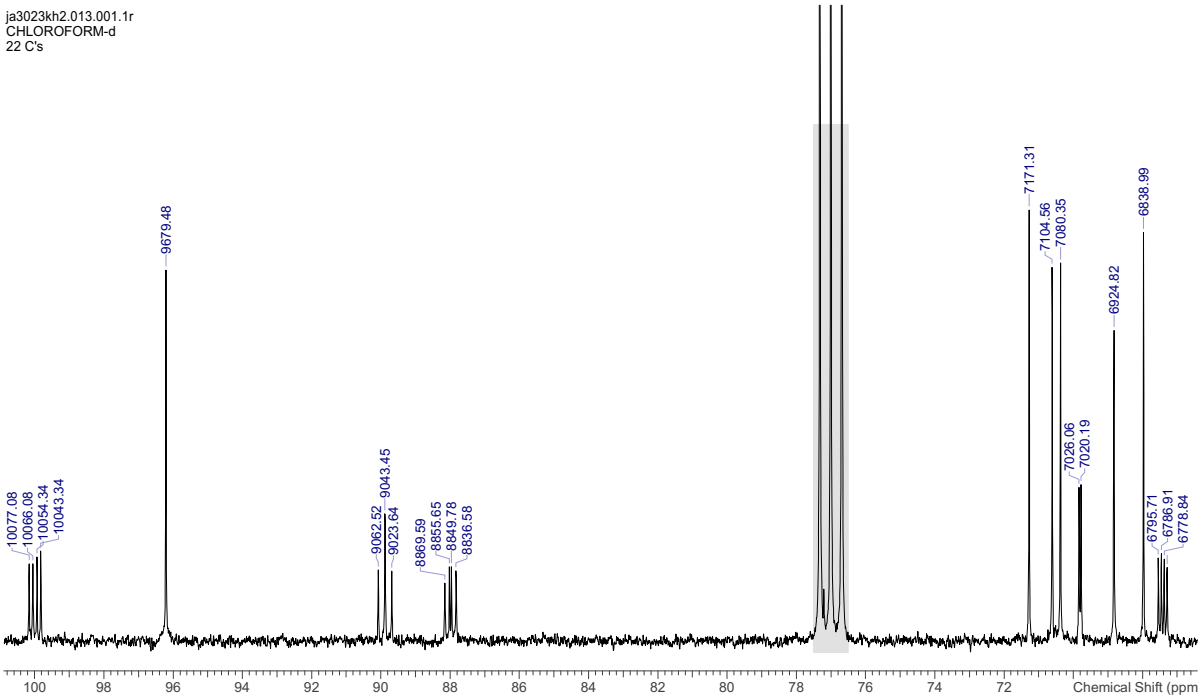


6.5.6.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

ja3023kh2.013.001.1r
CHLOROFORM-d
22 C's

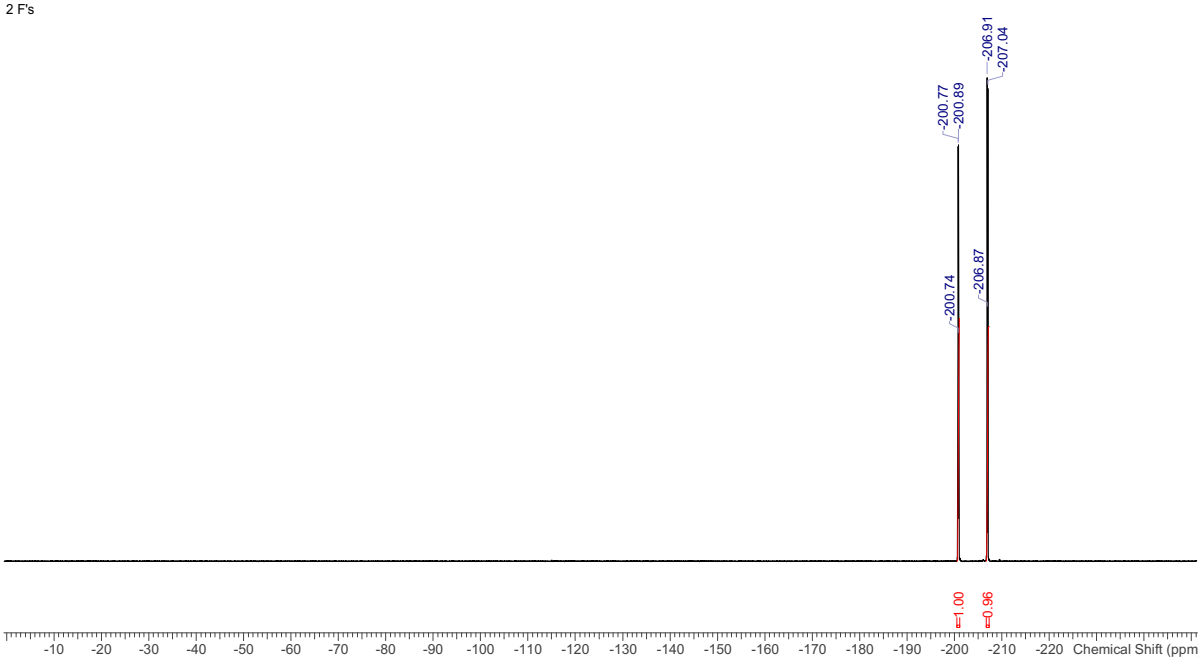


ja3023kh2.013.001.1r
CHLOROFORM-d
22 C's



6.5.6.3 ^{19}F NMR, 376 MHz, $CDCl_3$

ja3023kh2.011.001.1r.esp
CHLOROFORM-d
2 F's



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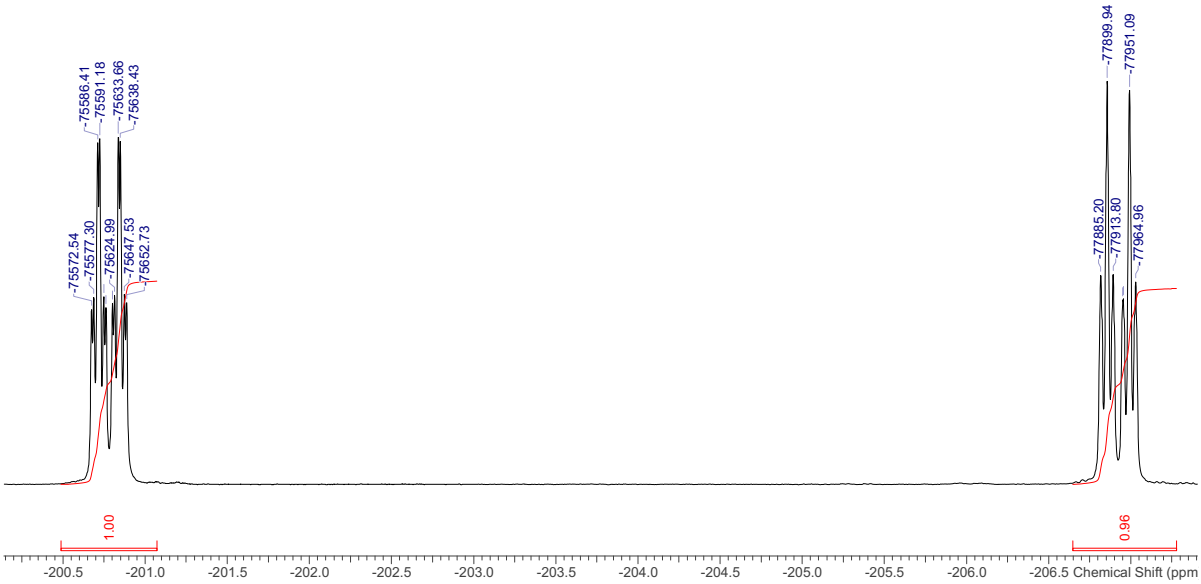
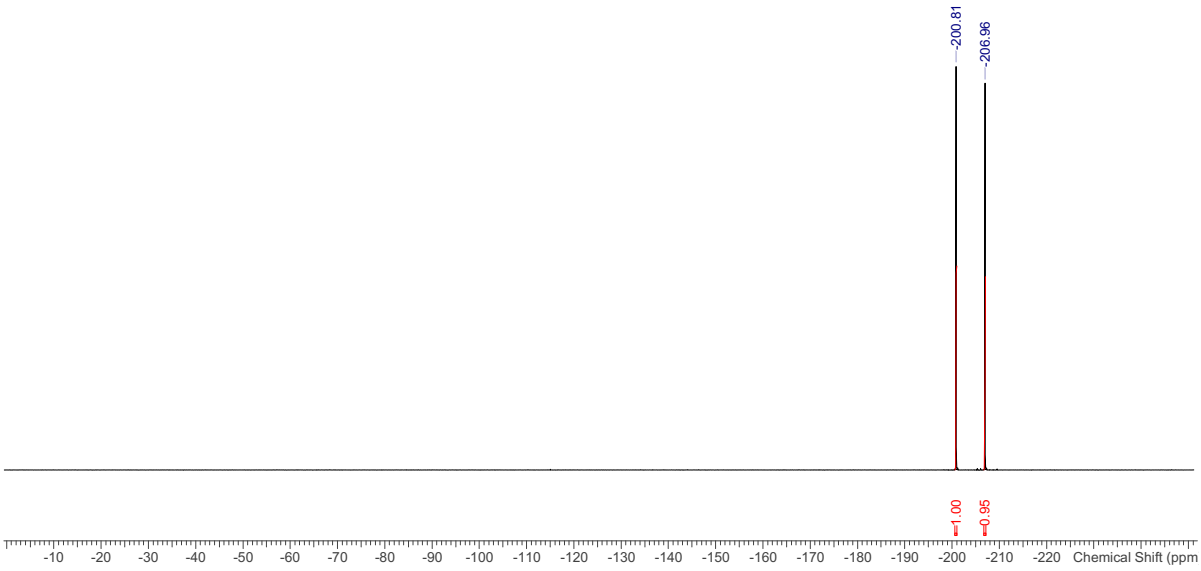
CHLOROFORM-d
2 F's



6.5.6.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

ja3023kh2.012.001.1r
CHLOROFORM-d
2 F's



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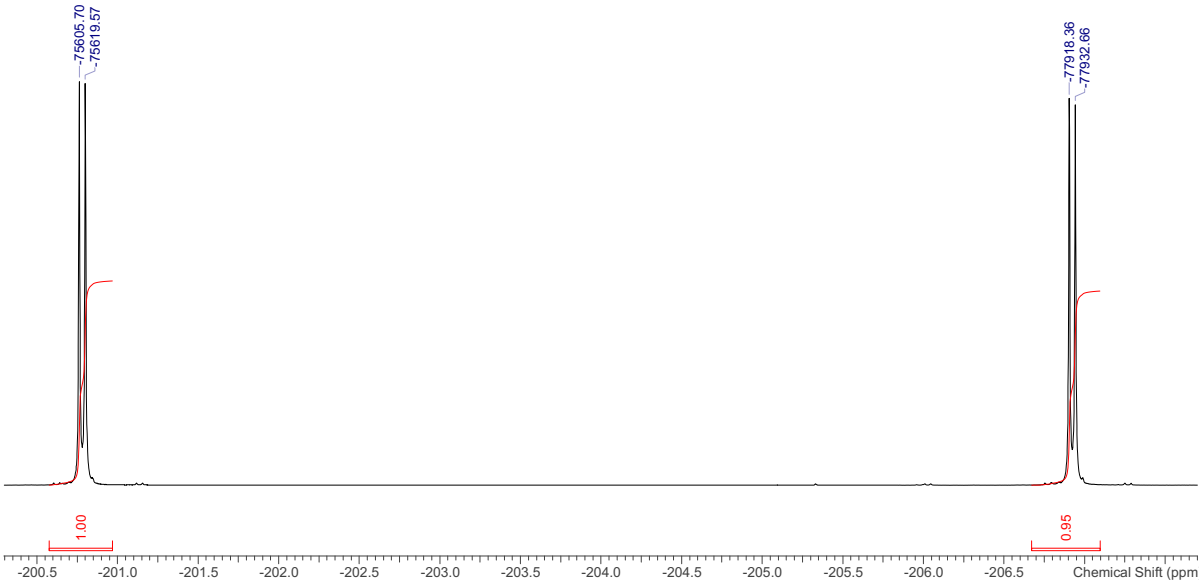
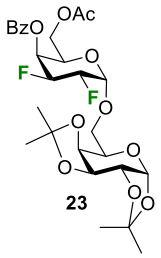
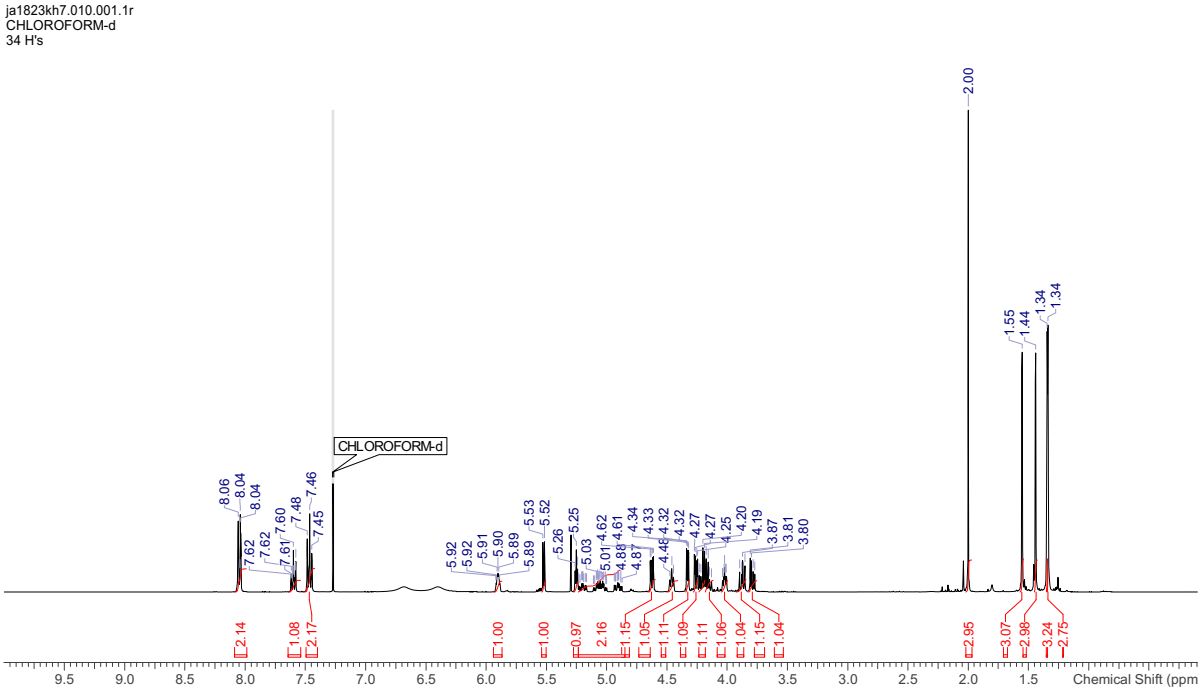
CHLOROFORM-d
2 F's

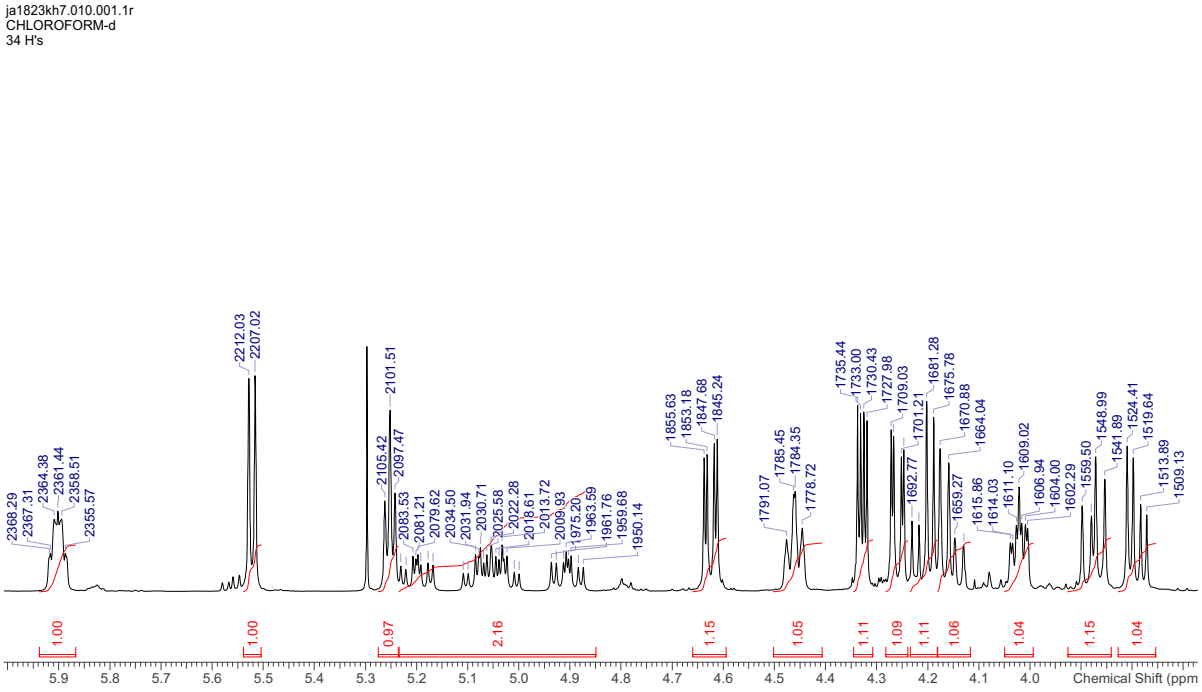


6.5.7 6-*O*-Acetyl-*O*-4-benzoyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**23α**)

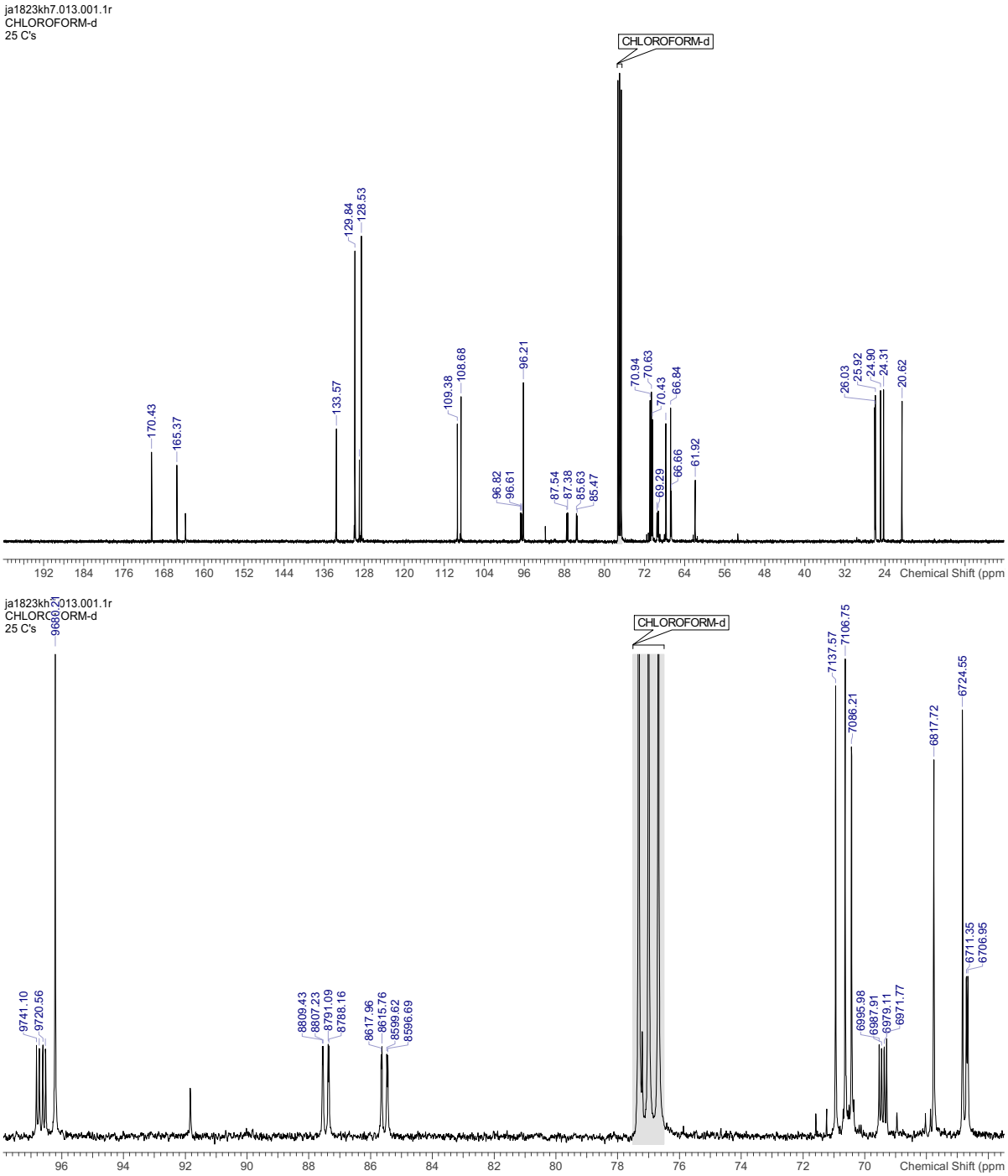


6.5.7.1 ^{1}H NMR, 400 MHz, $CDCl_3$

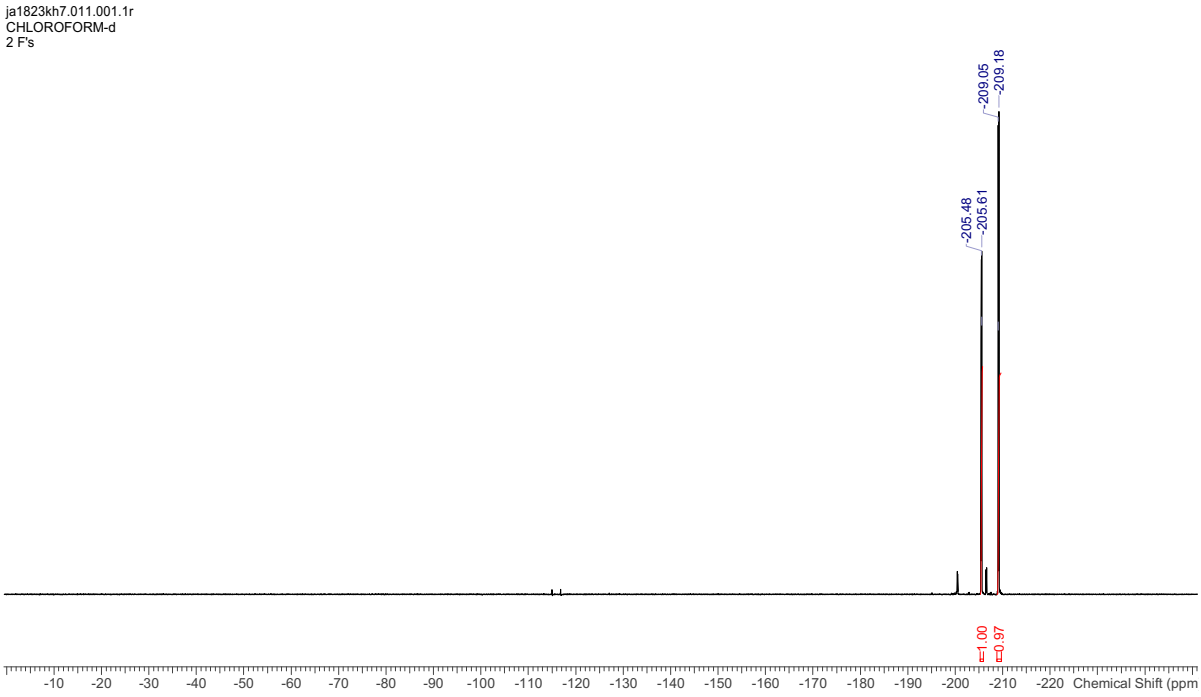


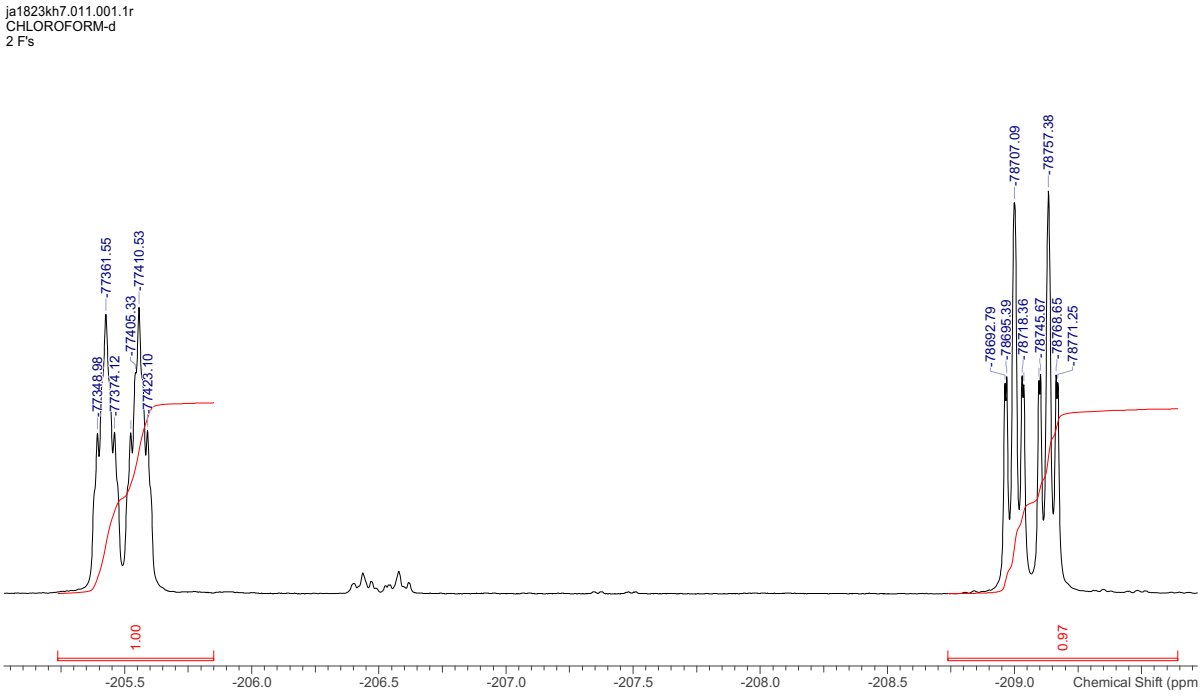


6.5.7.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

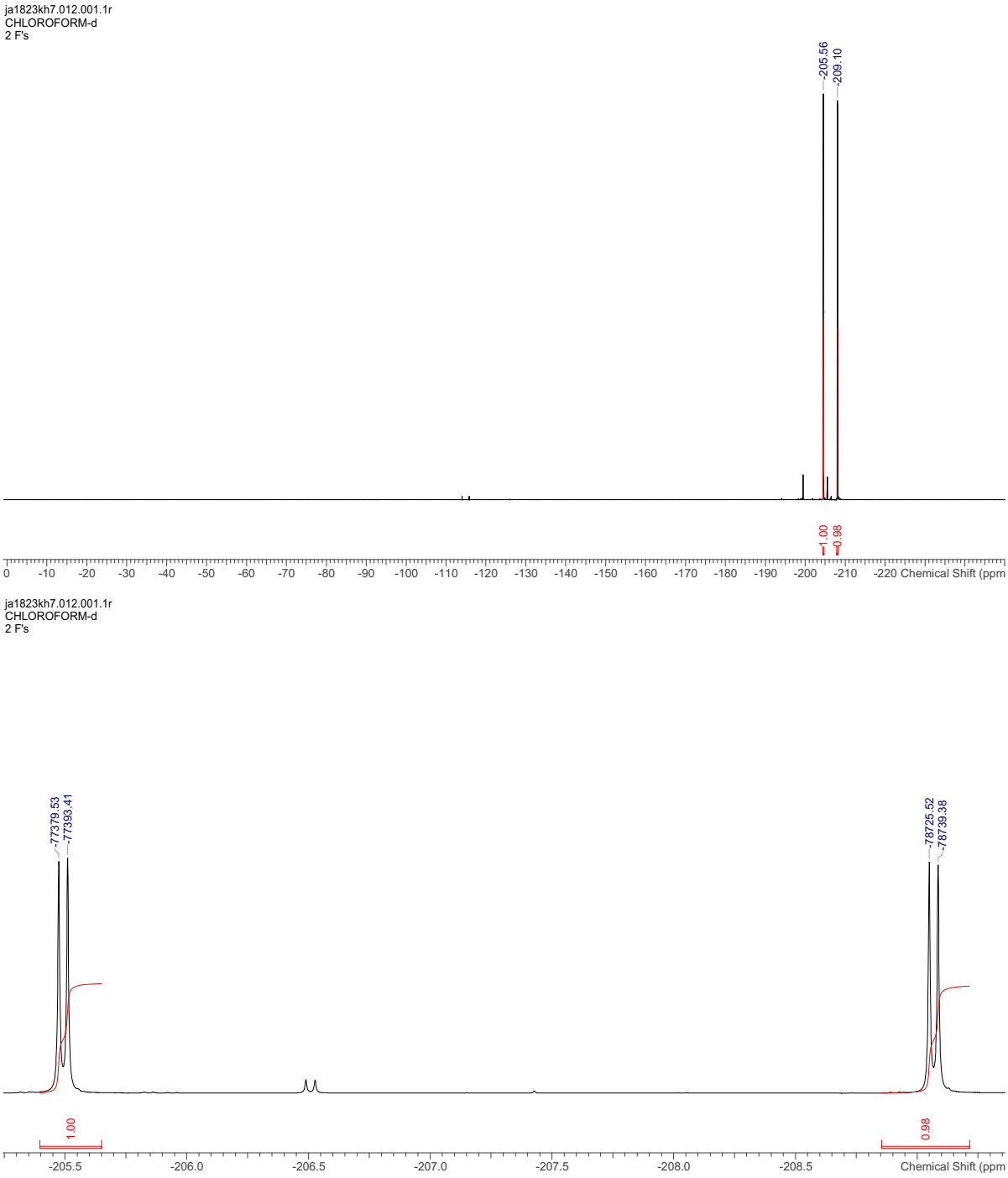


6.5.7.3 ^{19}F NMR, 376 MHz, $CDCl_3$

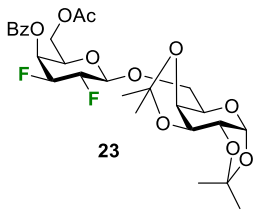




6.5.7.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



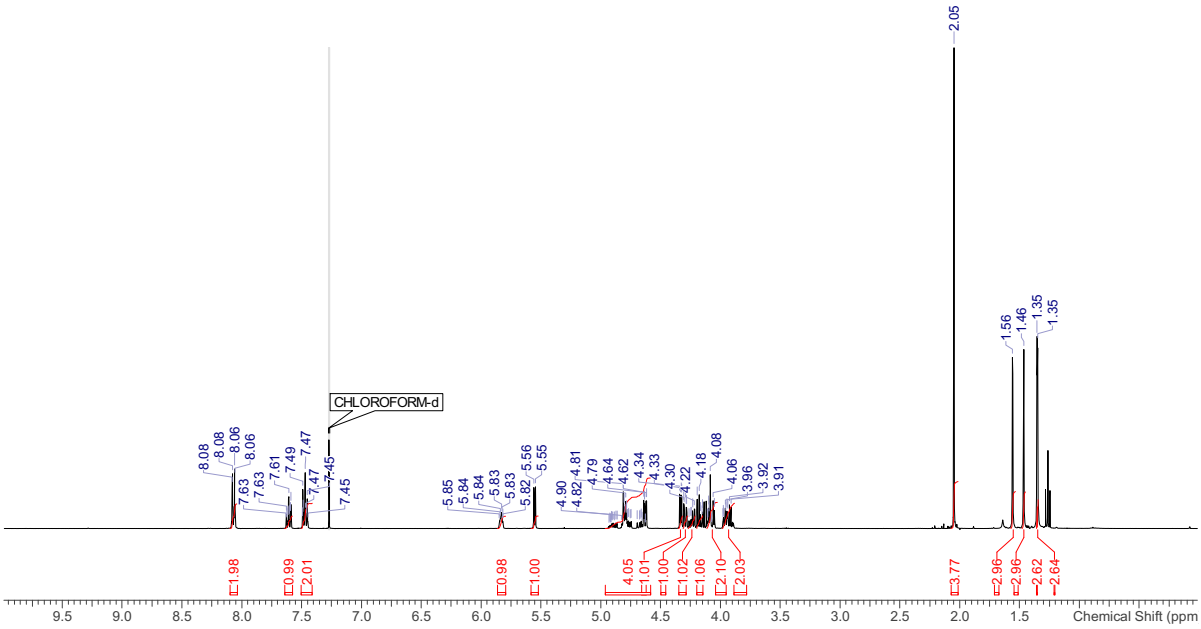
6.5.8 6-*O*-Acetyl-*O*-4-benzoyl-2,3-dideoxy-2,3-difluoro-β-D-galactopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**23β**)



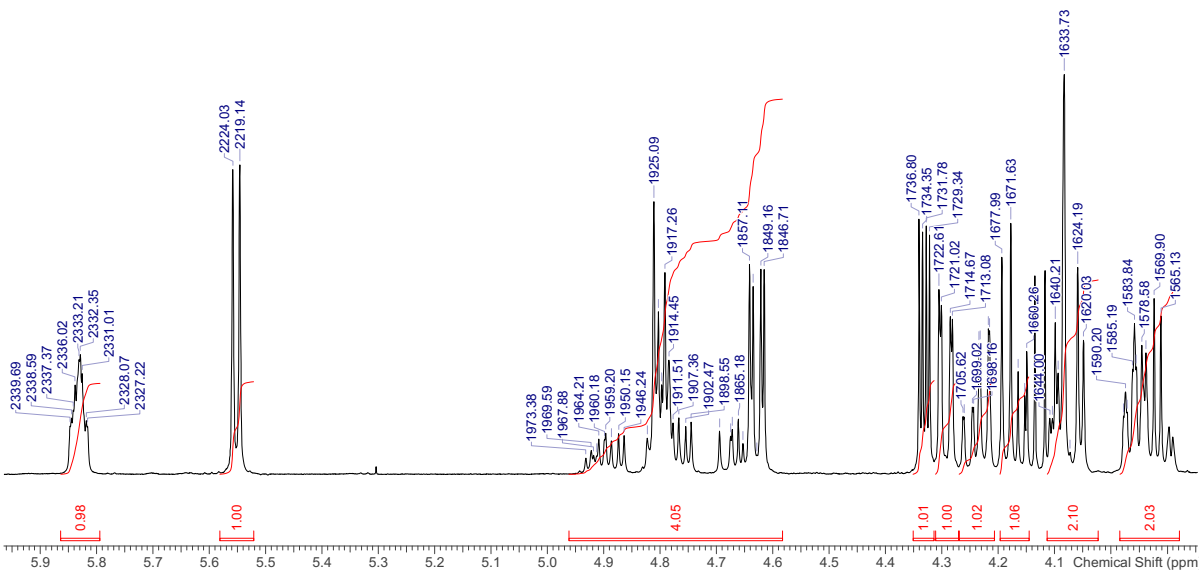
23

6.5.8.1 ^{1}H NMR, 400 MHz, $CDCl_3$

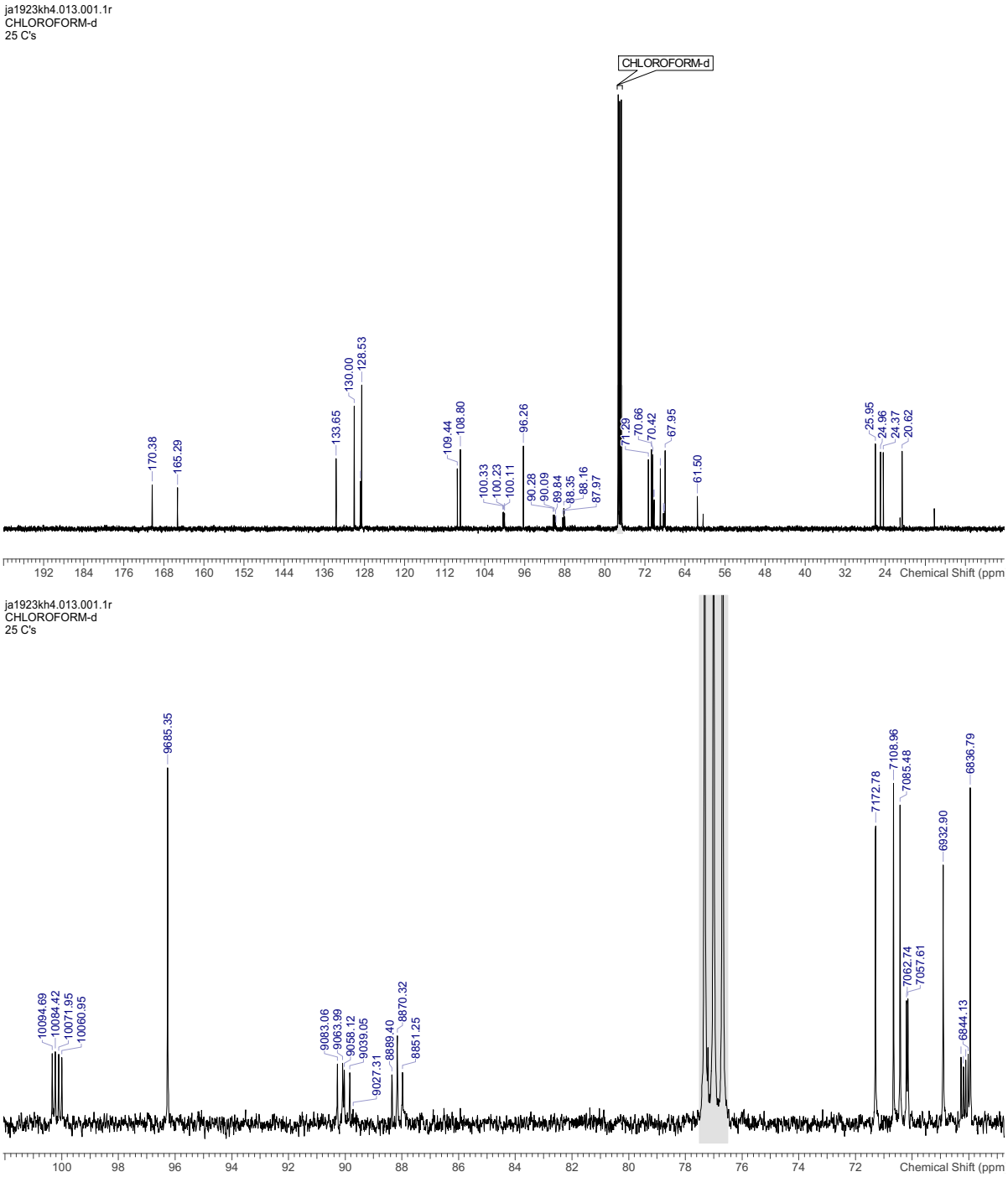
ja1923kh4.010.001.1r
CHLOROFORM-d
35 H's



ja1923kh4.010.001.1r
CHLOROFORM-d
35 H's

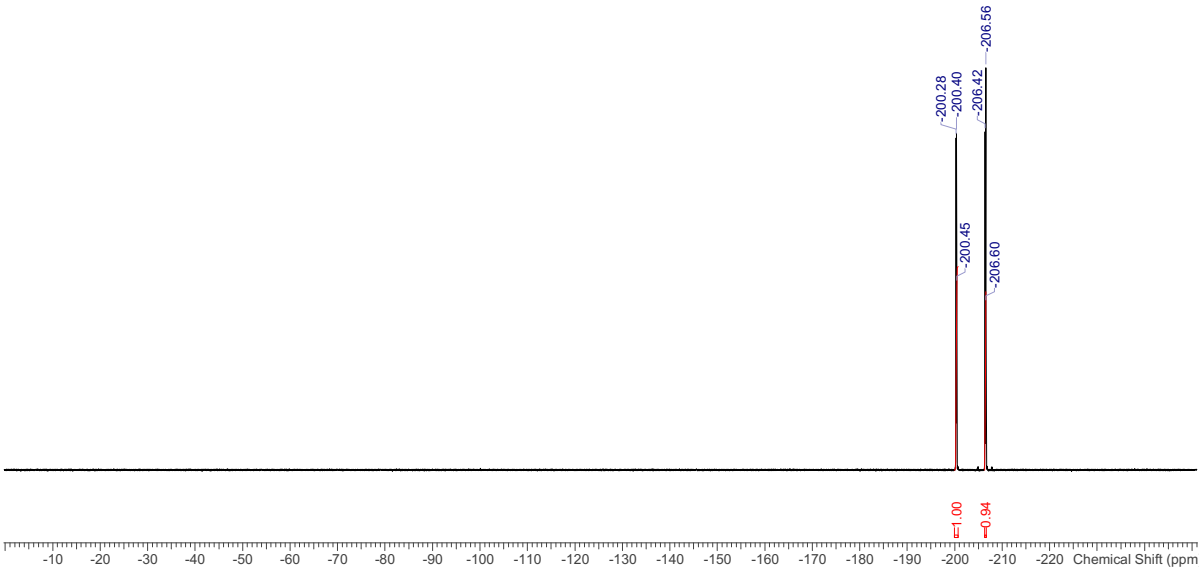


6.5.8.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

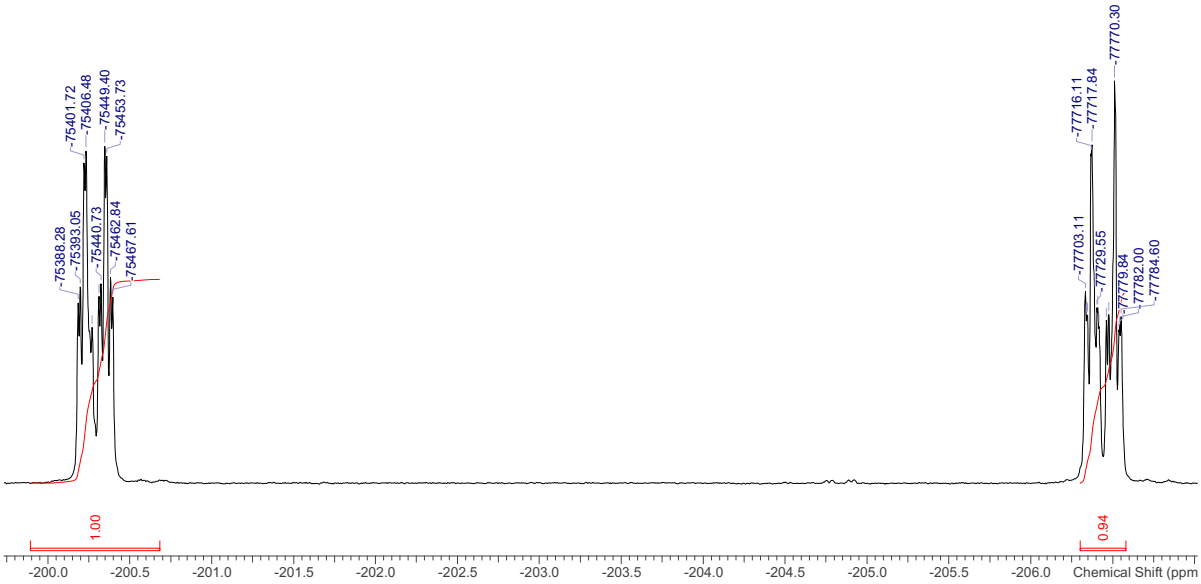


6.5.8.3 ^{19}F NMR, 376 MHz, $CDCl_3$

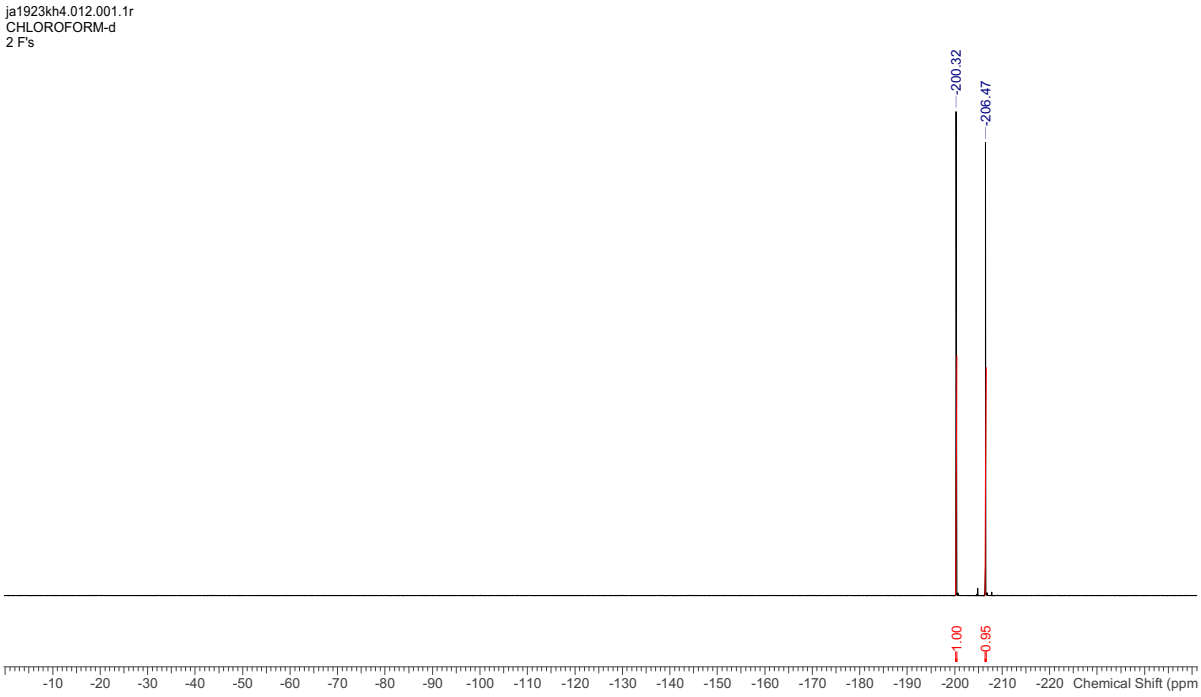
ja1923kh4.011.001.1r
CHLOROFORM-d
2 F's

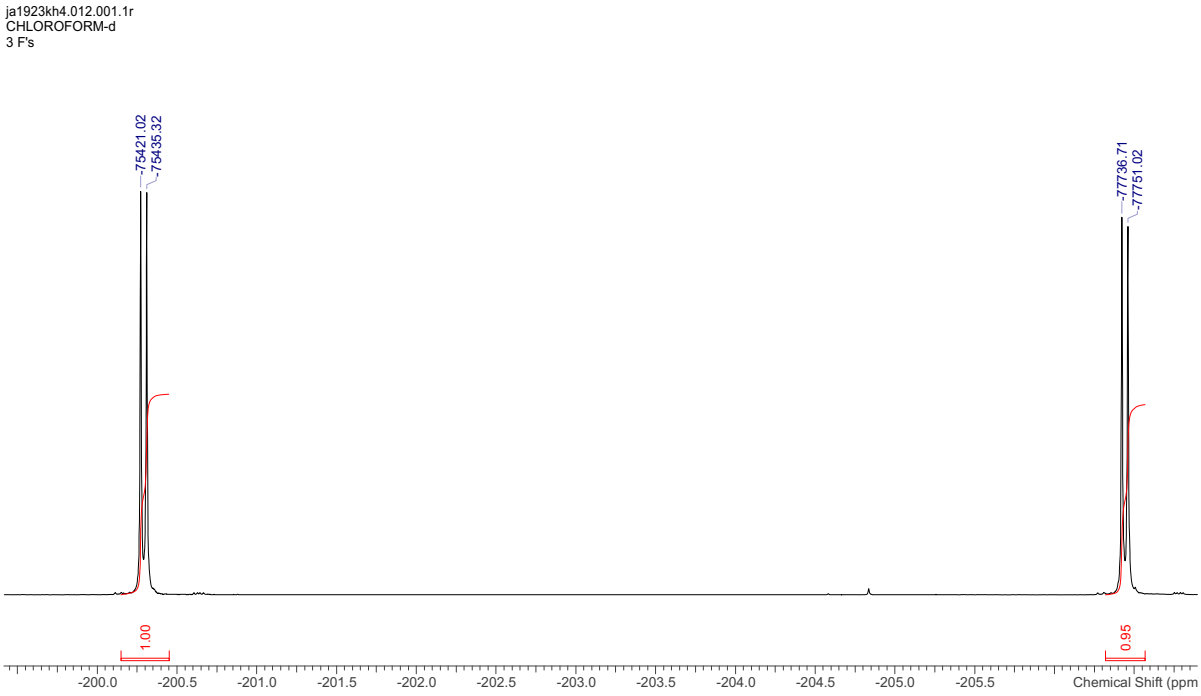


ja1923kh4.011.001.1r
CHLOROFORM-d
2 F's

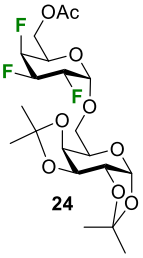


6.5.8.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

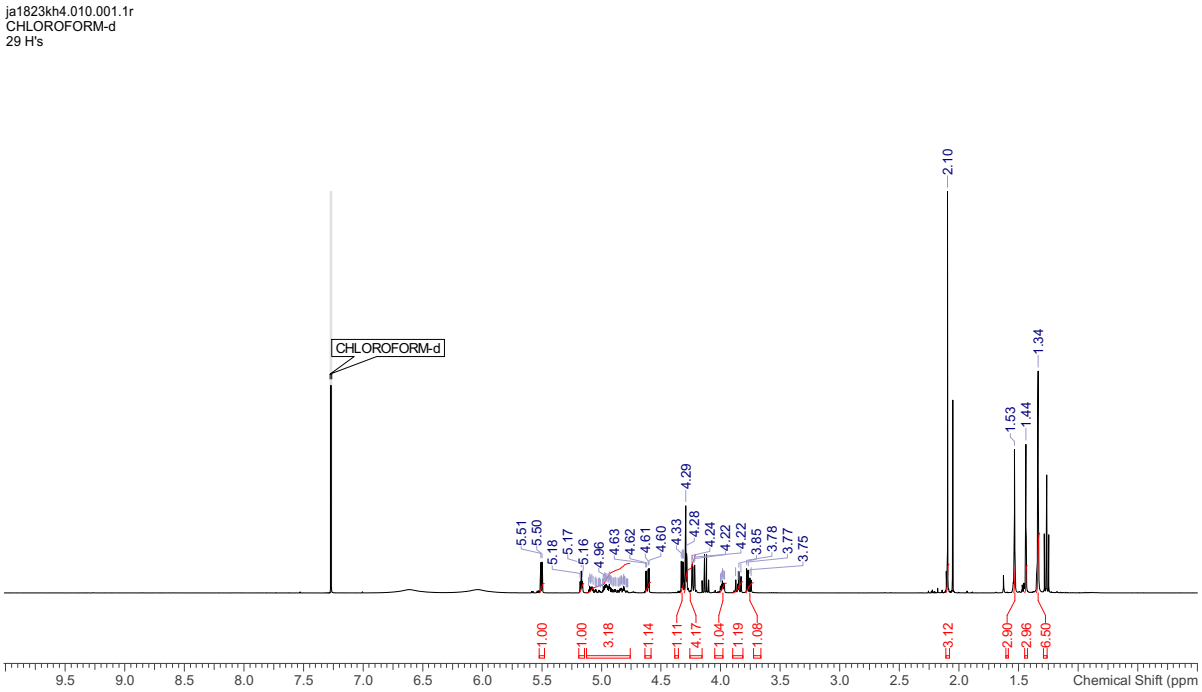


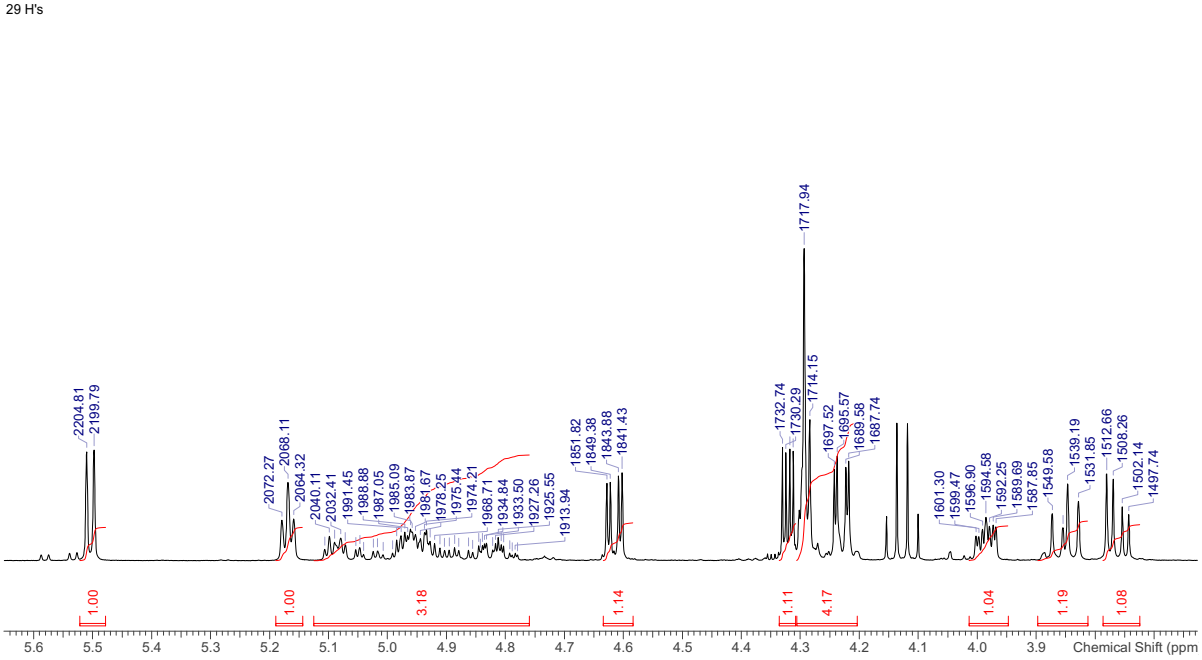


6.5.9 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α-D-galactopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**24α**)

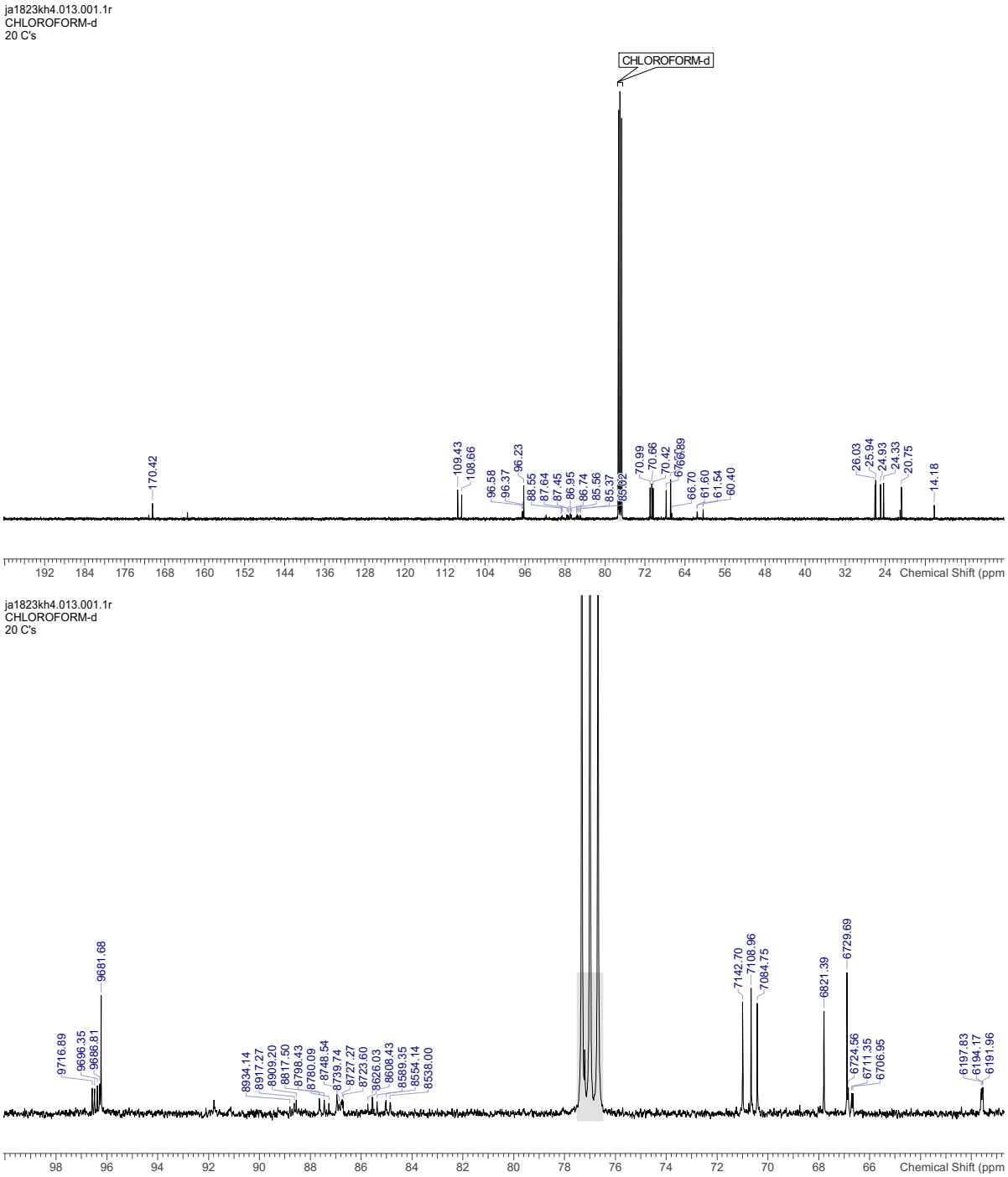


6.5.9.1 ^{1}H NMR, 400 MHz, $CDCl_3$

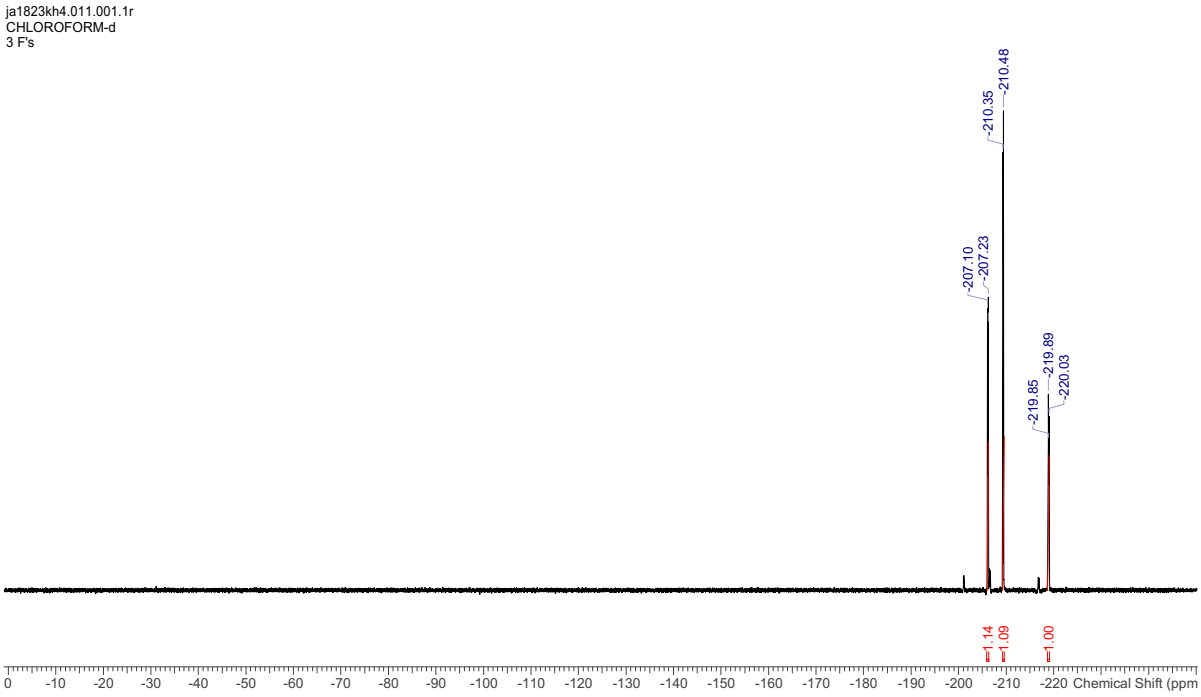


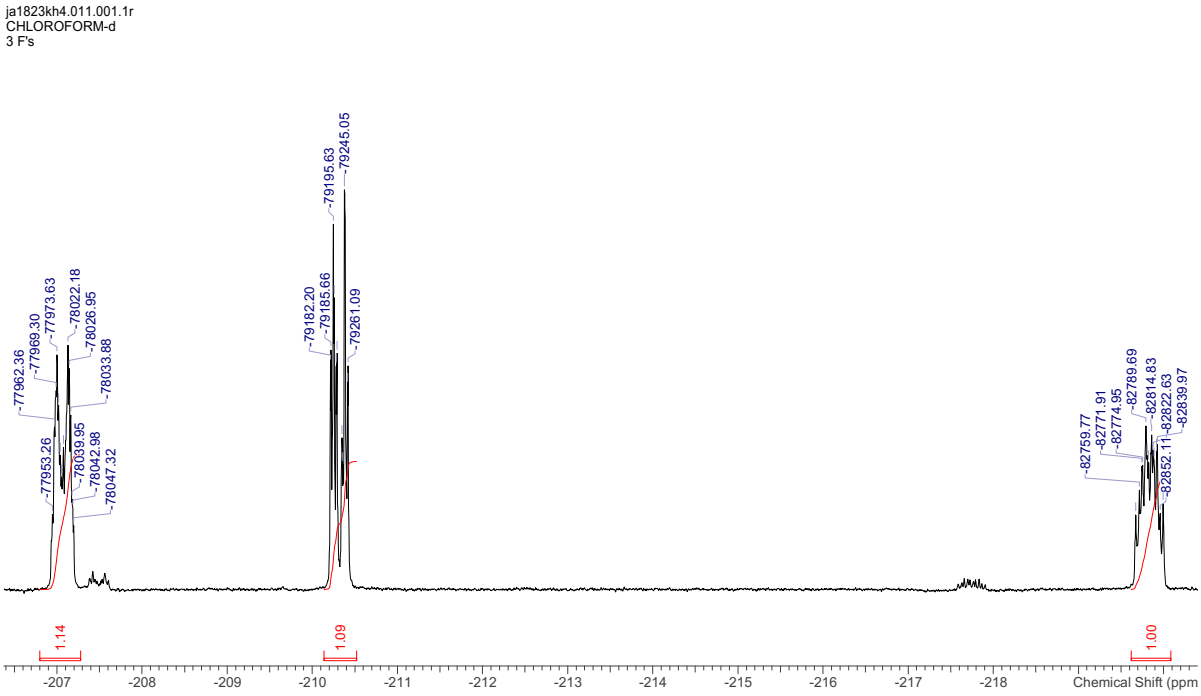


6.5.9.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

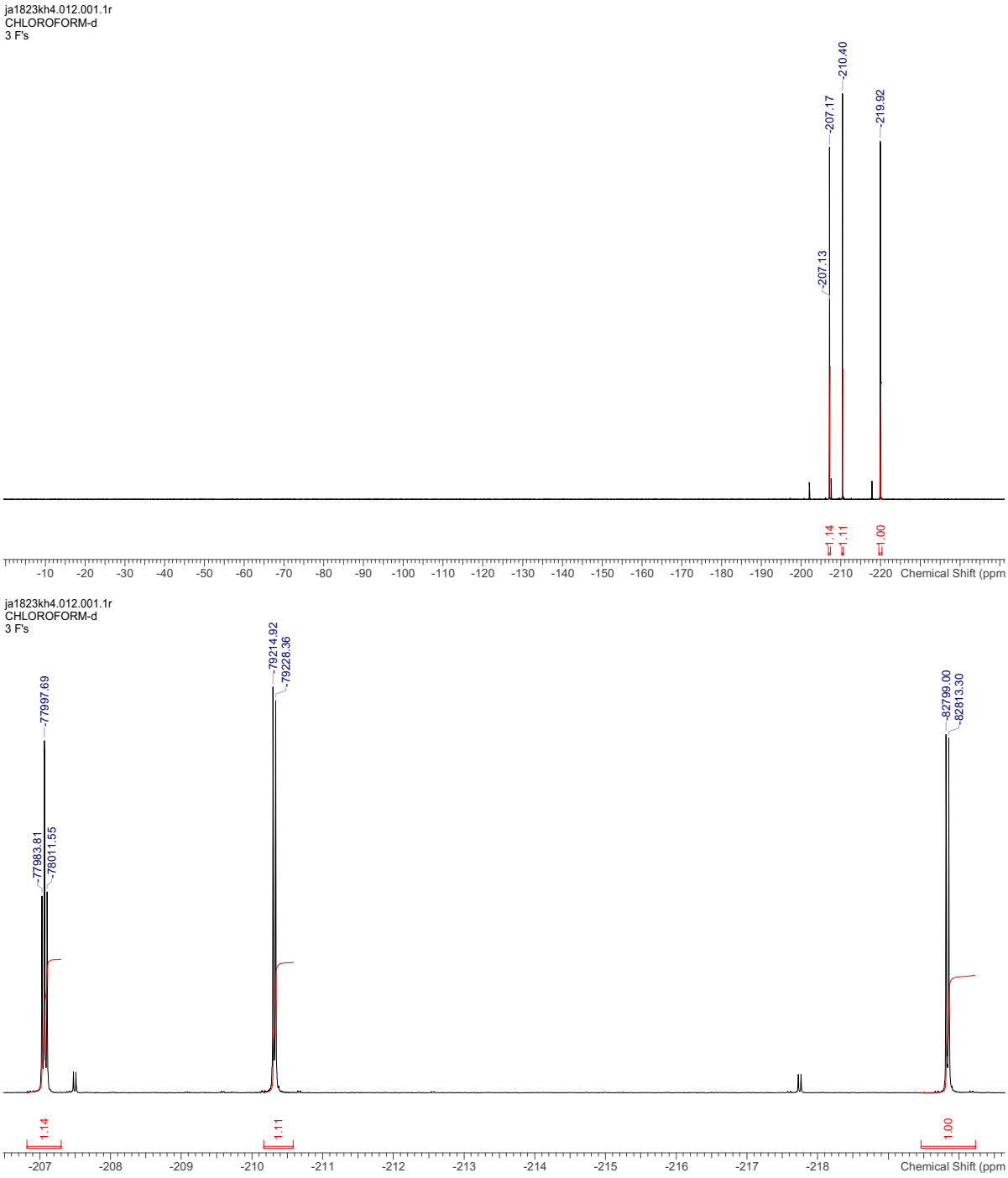


6.5.9.3 ^{19}F NMR, 376 MHz, $CDCl_3$

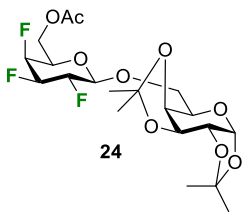




6.5.9.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



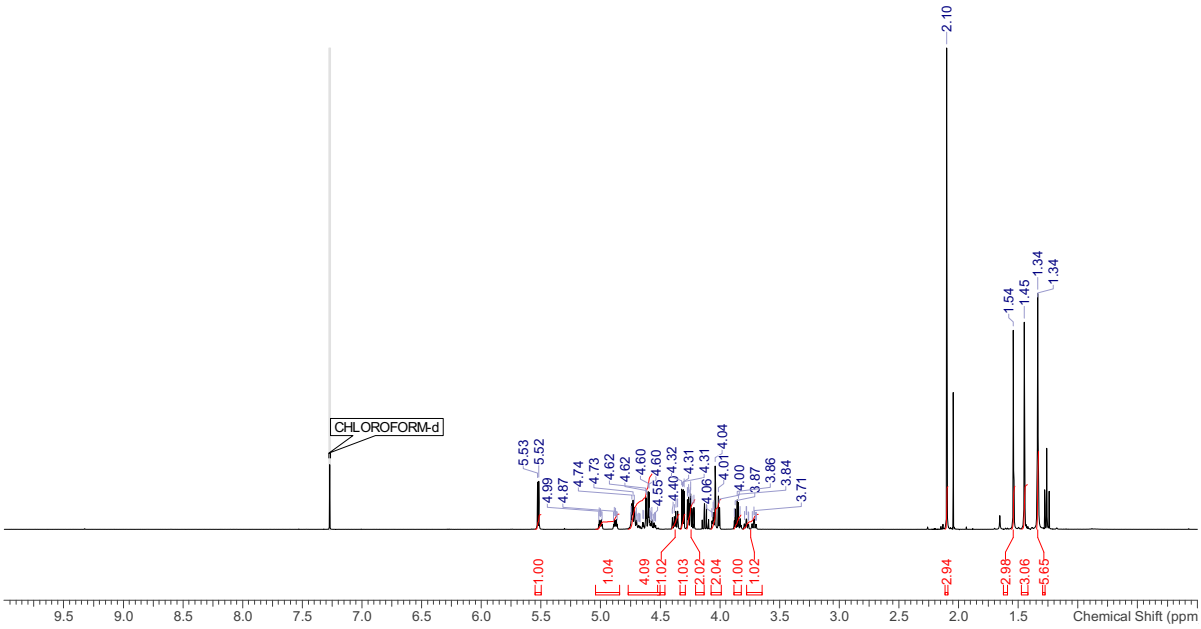
6.5.10 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-β-D-galactopyranosyl-1,2:3,4-di-*O*-isopropyliden-α-D-galactopyranoside (**24β**)



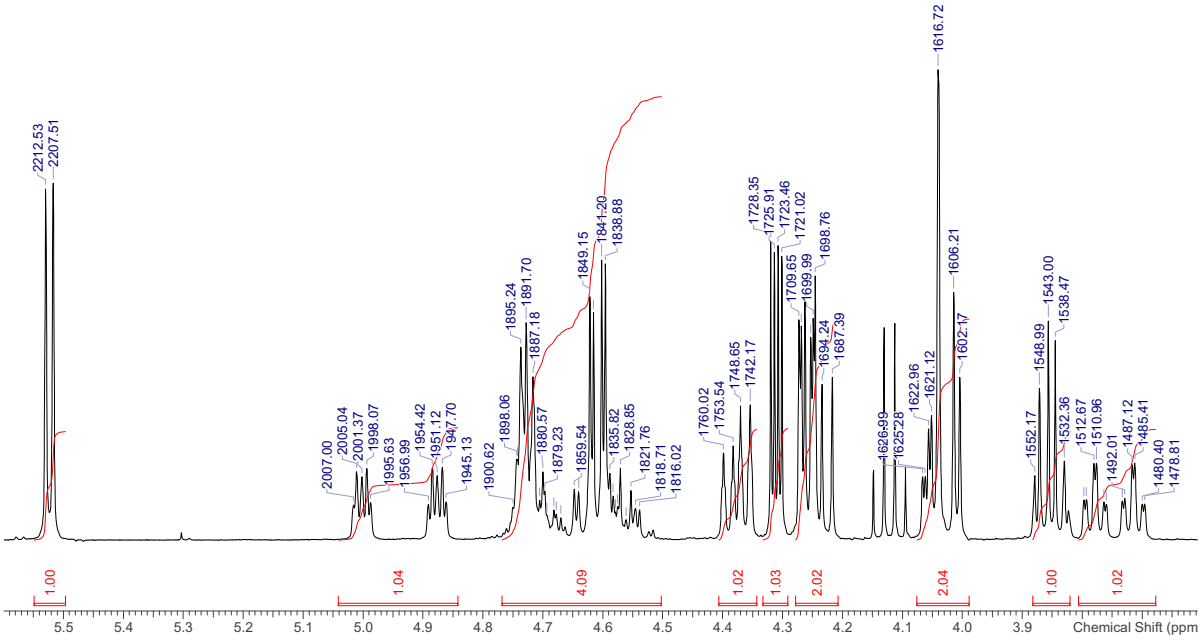
24

6.5.10.1 ^{1}H NMR, 400 MHz, $CDCl_3$

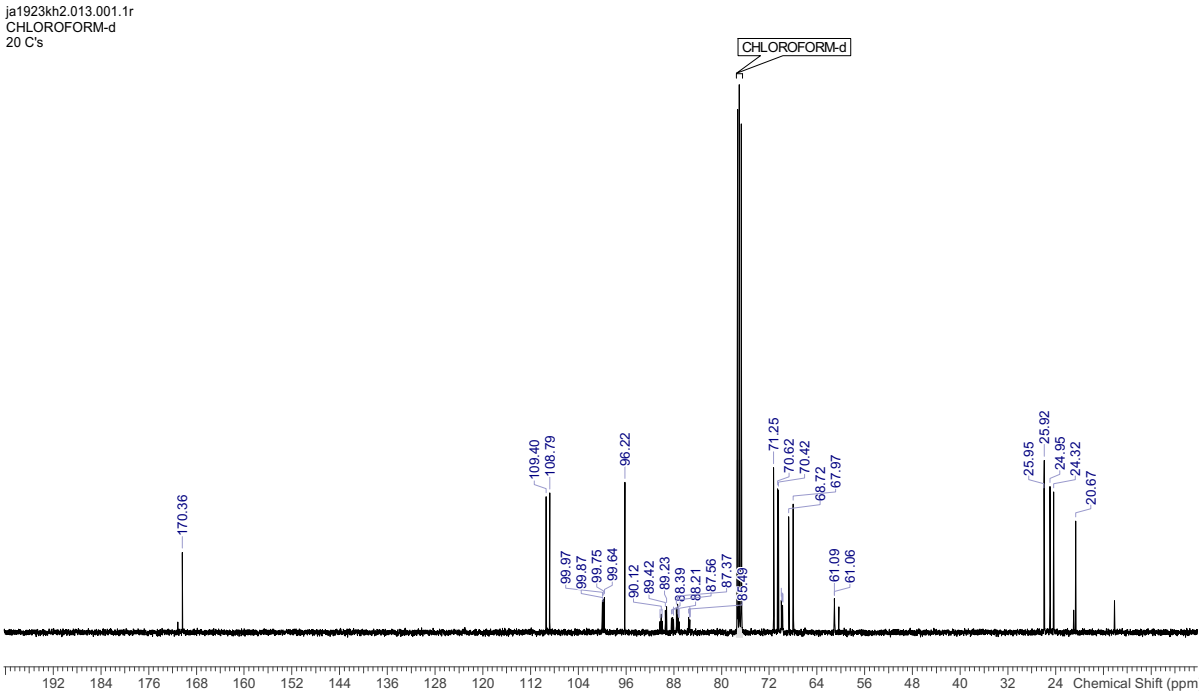
ja1923kh2.010.001.1r
CHLOROFORM-d
29 H's

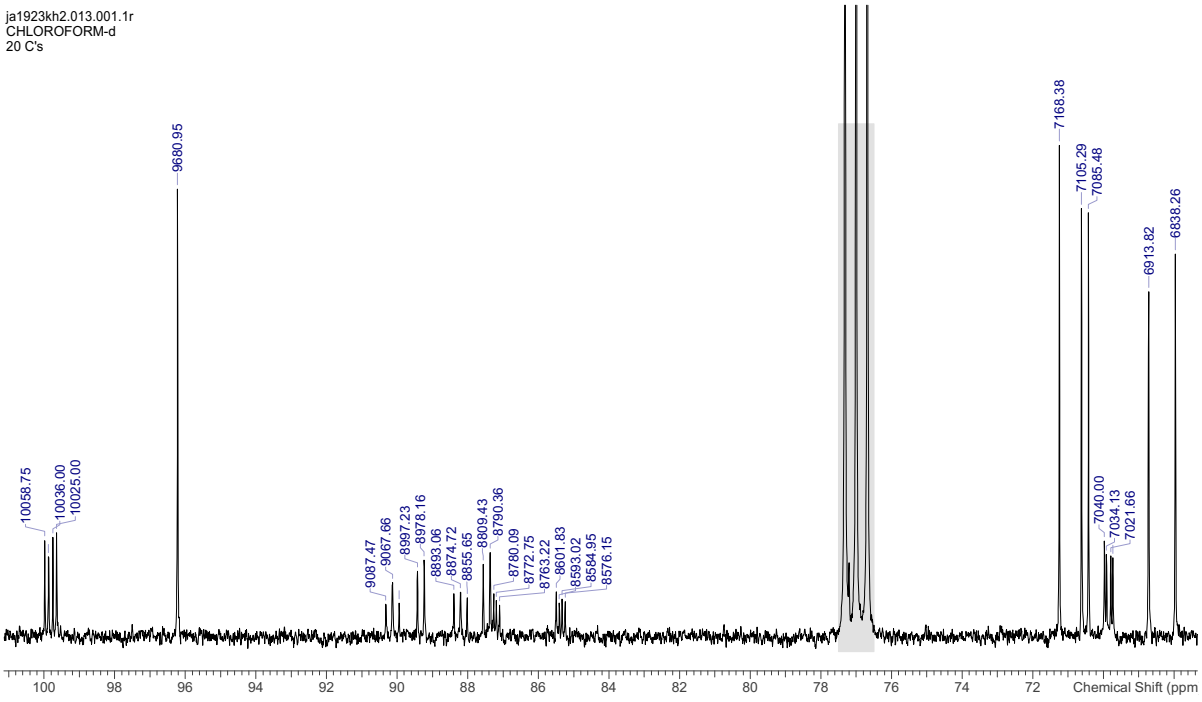


ja1923kh2.010.001.1r
CHLOROFORM-d
29 H's



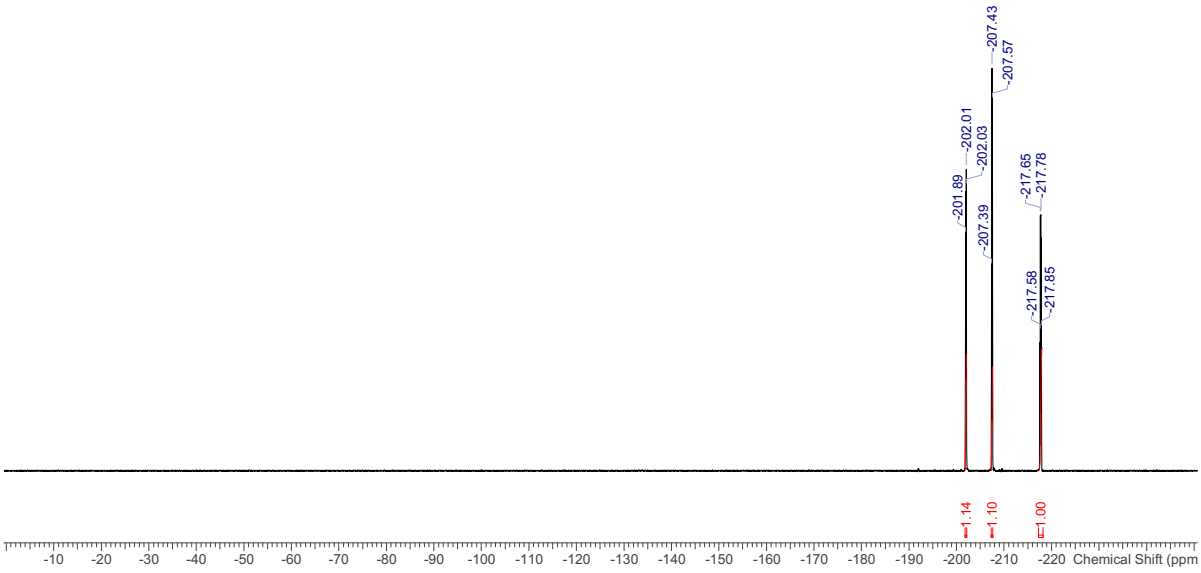
6.5.10.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$



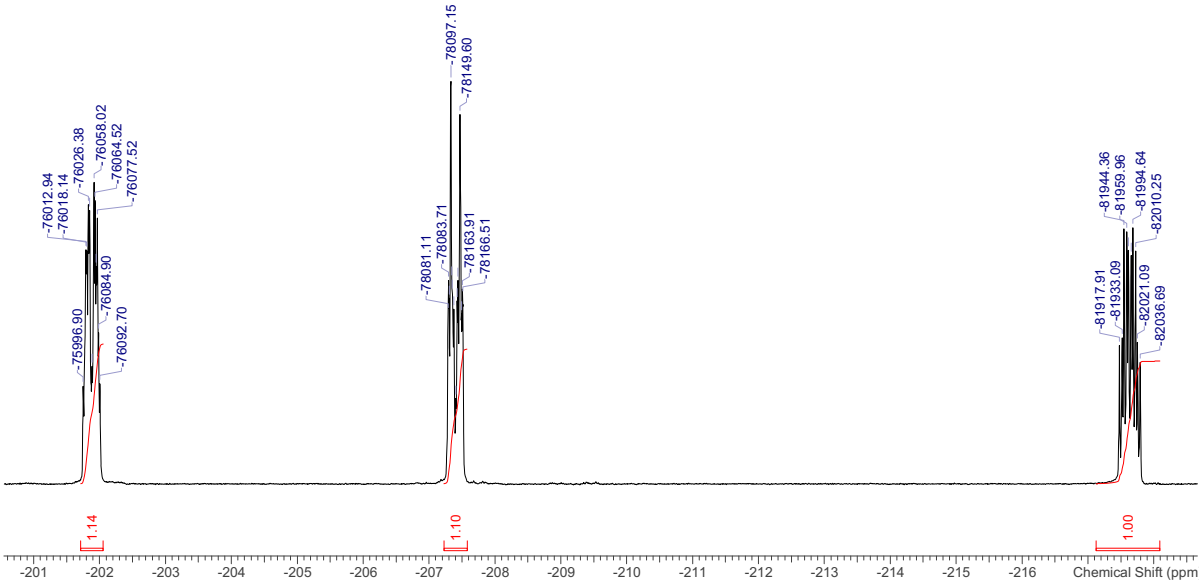


6.5.10.3 ^{19}F NMR, 376 MHz, $CDCl_3$

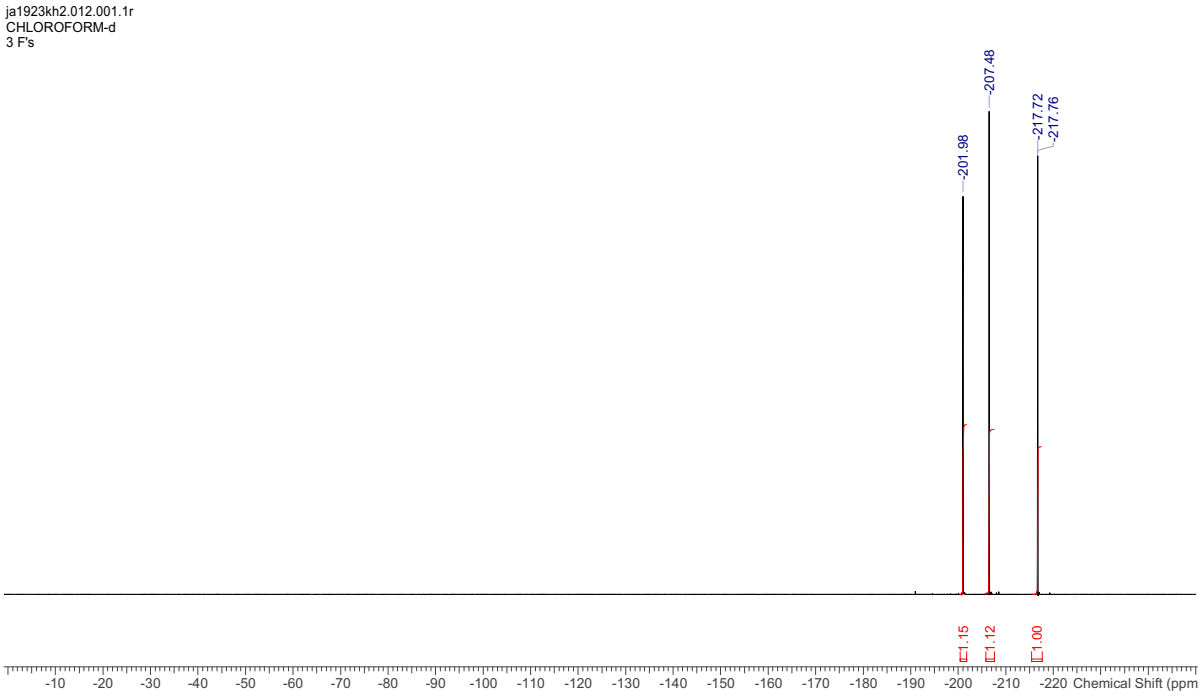
ja1923kh2.011.001.1r
CHLOROFORM-d
3 F's

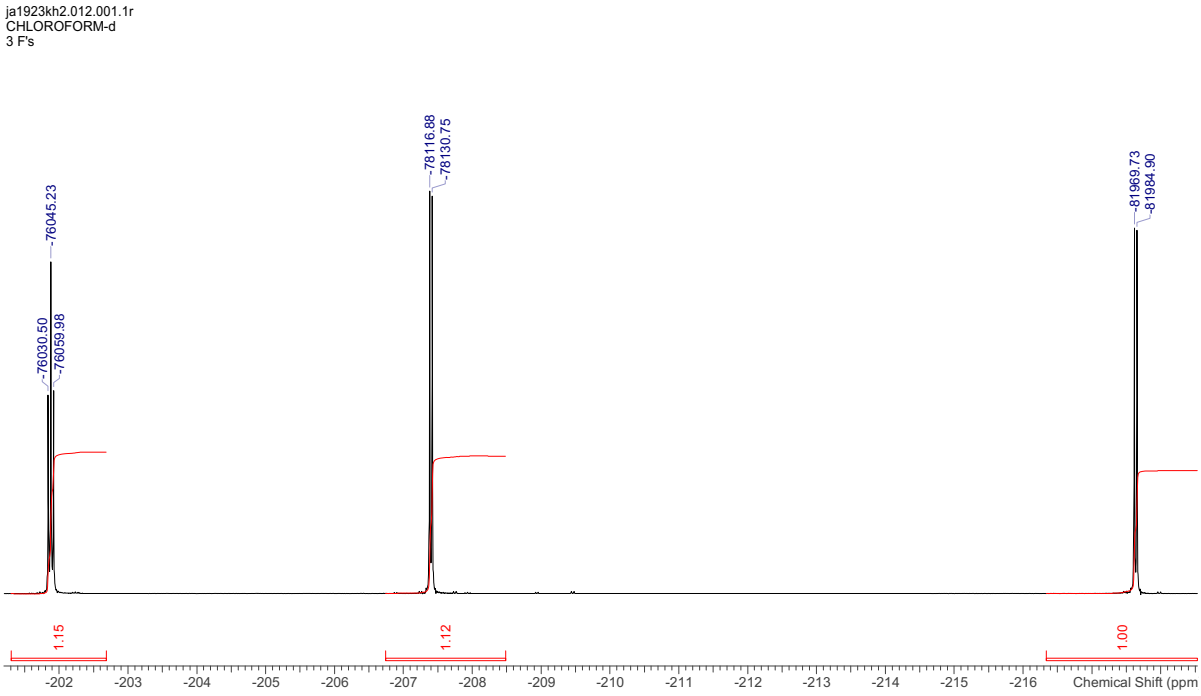


ja1923kh2.011.001.1r
CHLOROFORM-d
3 F's



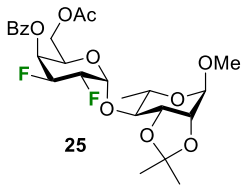
6.5.10.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$





6.6 Copies of the spectra of the glycosylation products with methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside

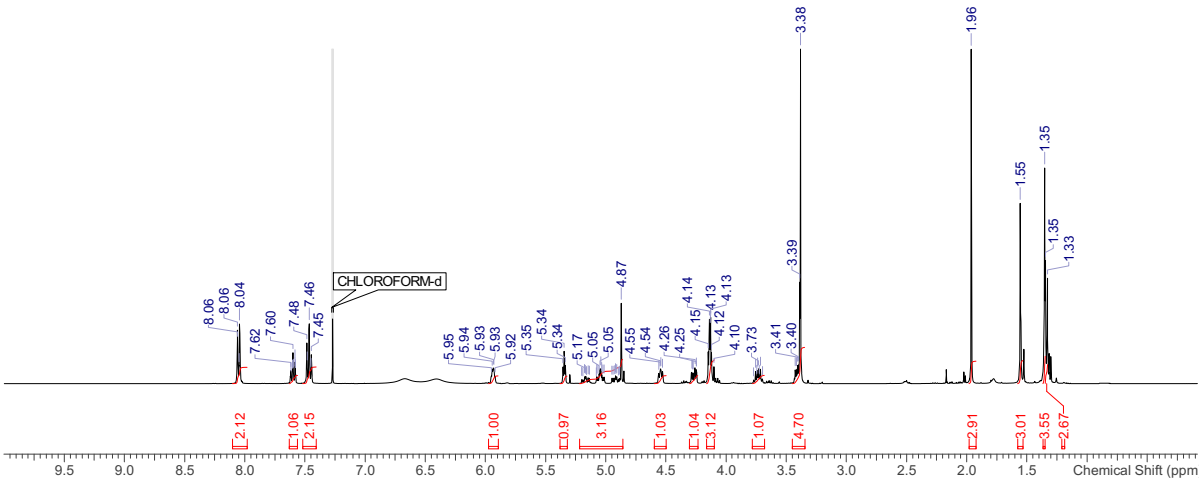
6.6.1 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranosyl-(1,4)-methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**25**)

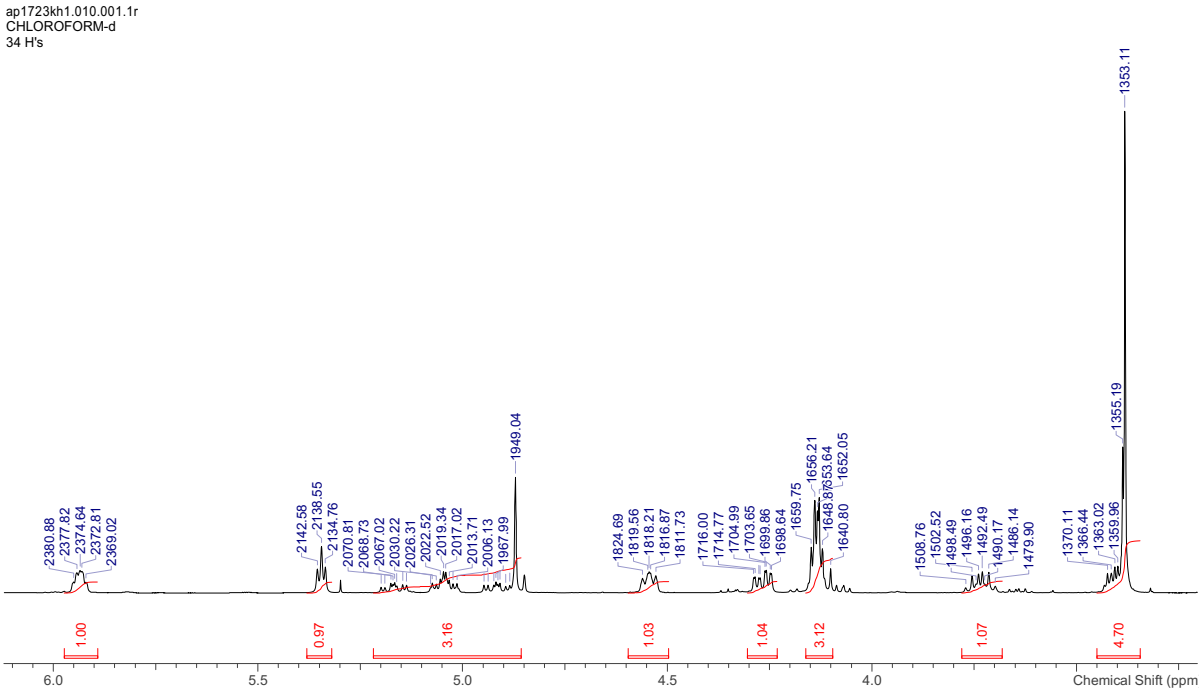


25

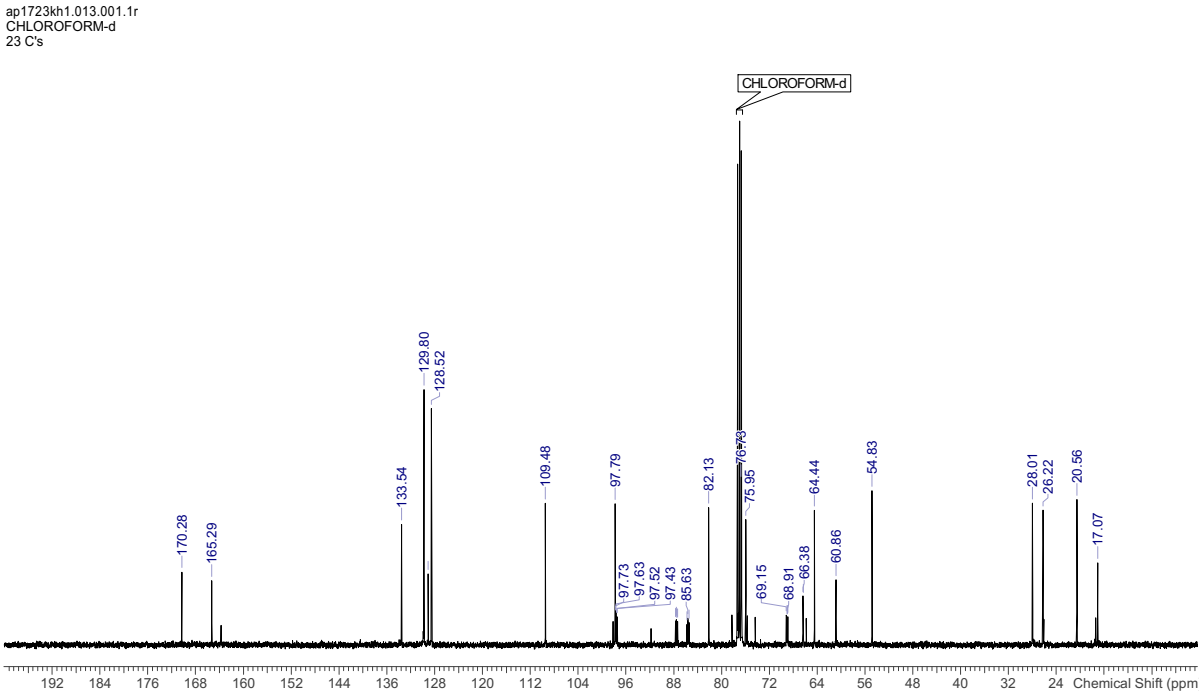
6.6.1.1 ^{1}H NMR, 400 MHz, $CDCl_3$

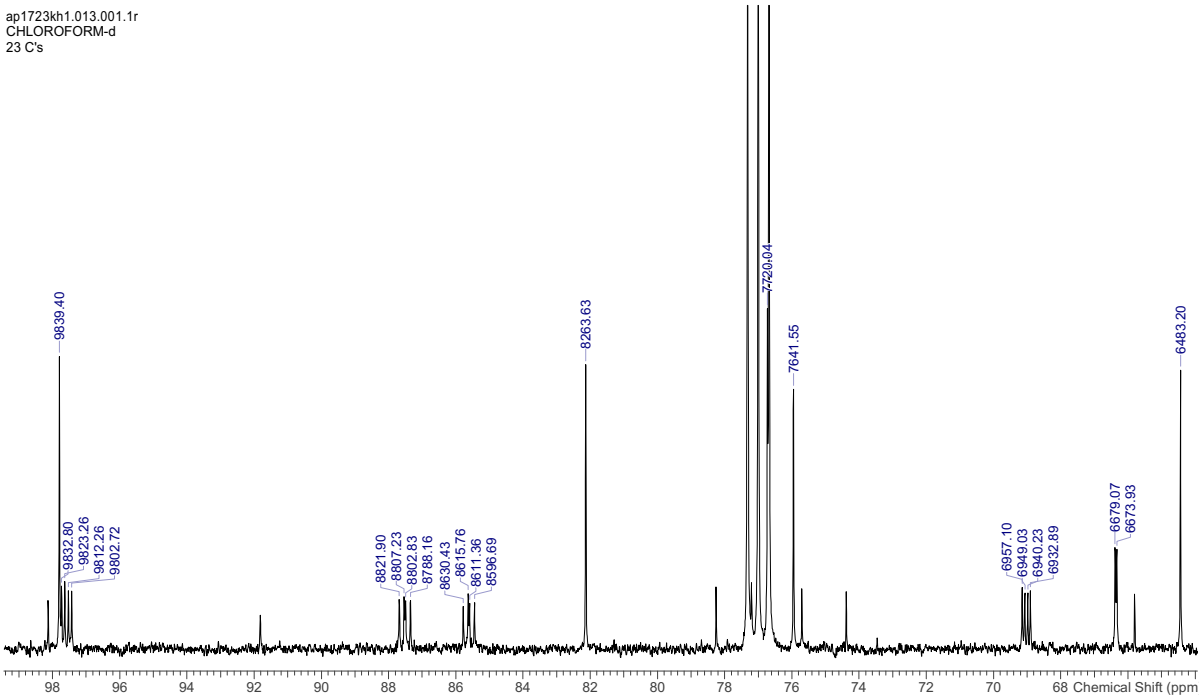
ap1723kh1.010.001.1r
CHLOROFORM-d
34 H's



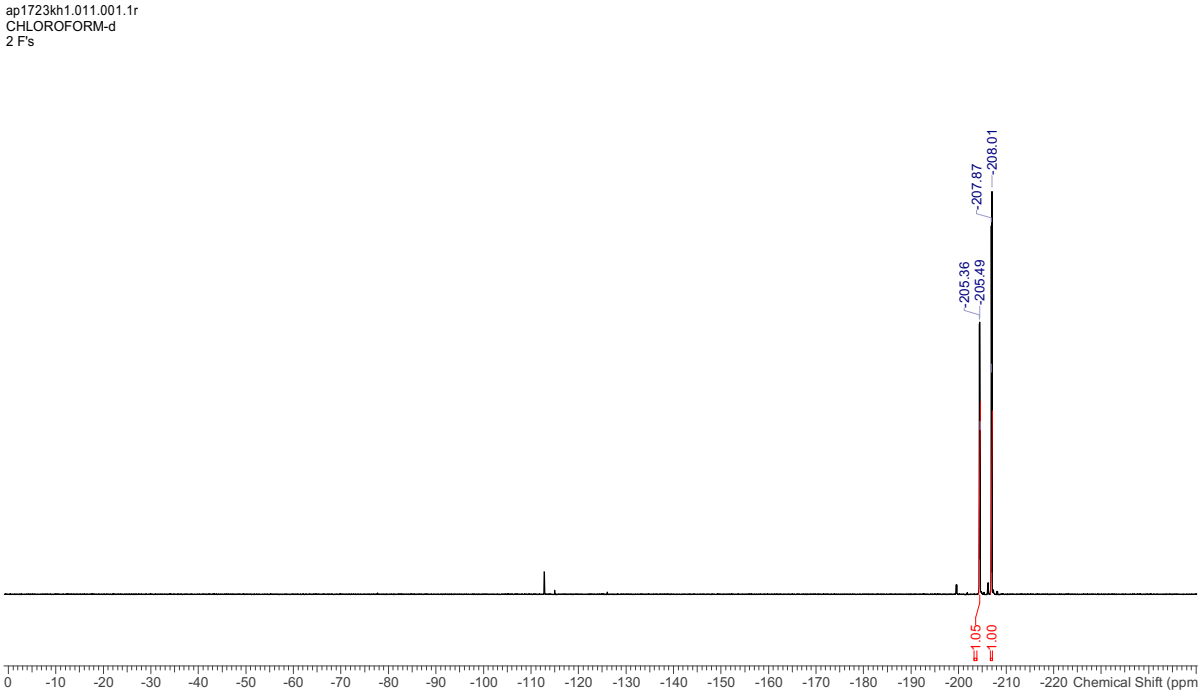


6.6.1.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

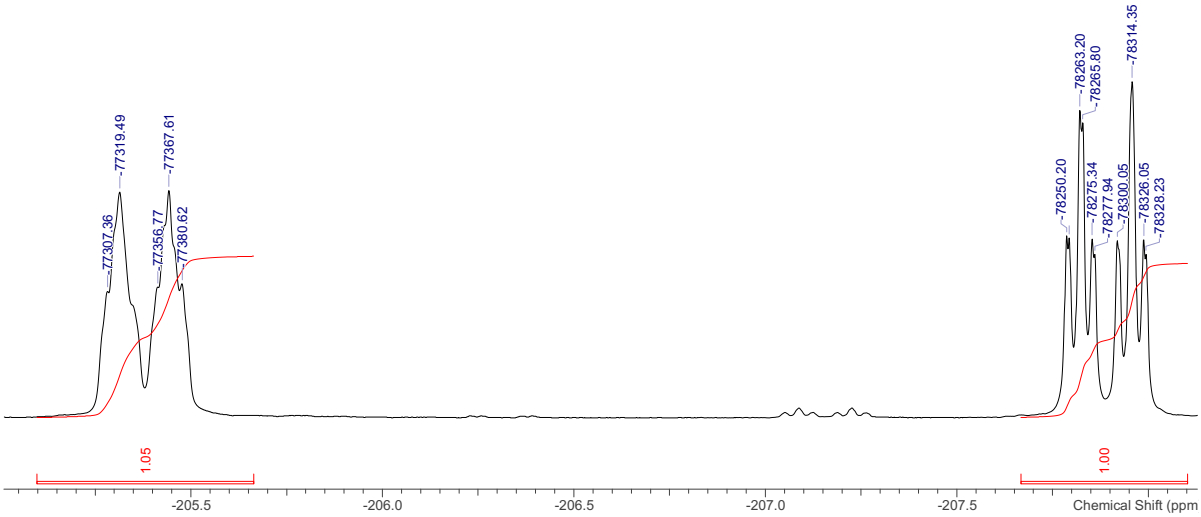




6.6.1.3 ^{19}F NMR, 376 MHz, $CDCl_3$



ap1723kh1.011.001.1r
CHLOROFORM-d
2 F's



6.6.1.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

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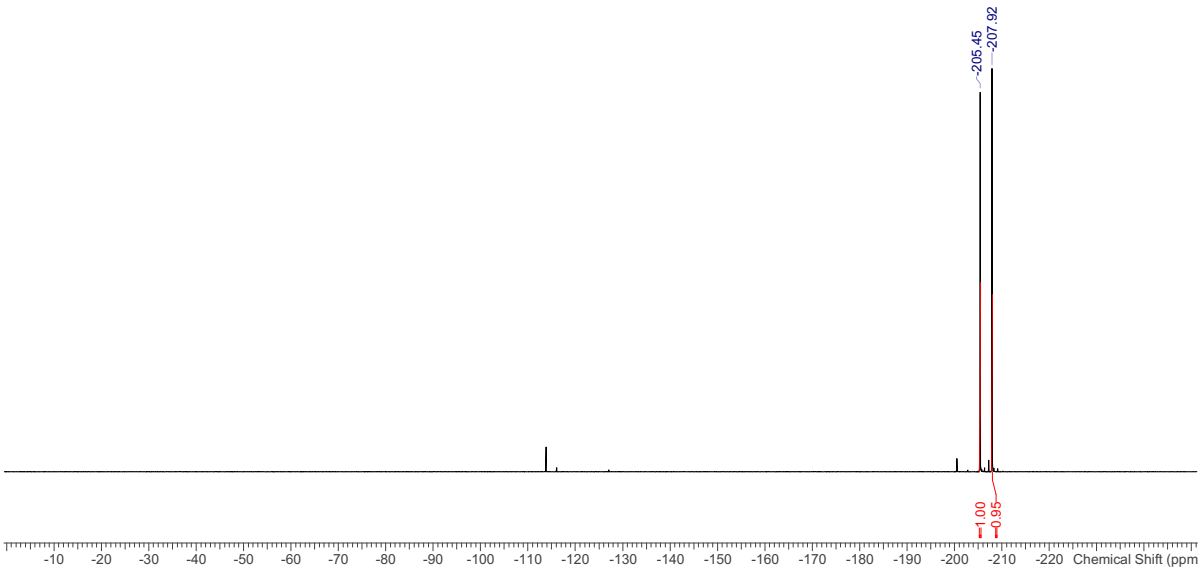
CHLOROFORM-d
2 F's



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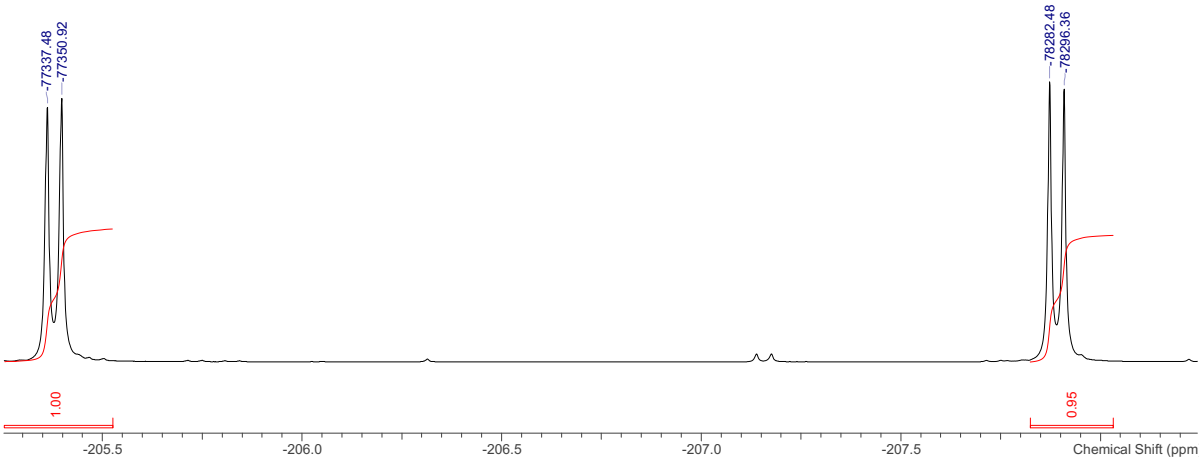
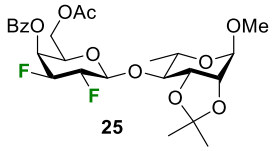
CHLOROFORM-d
2 F's



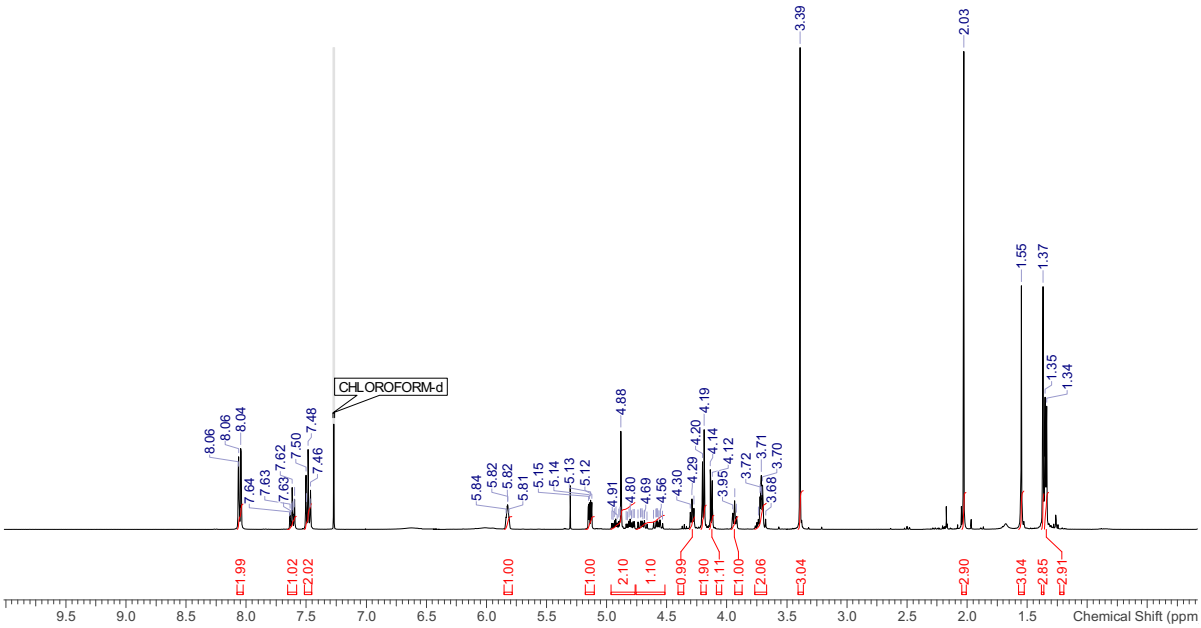
6.6.2 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-β-D-galactopyranosyl-(1,4)-methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**25β**)



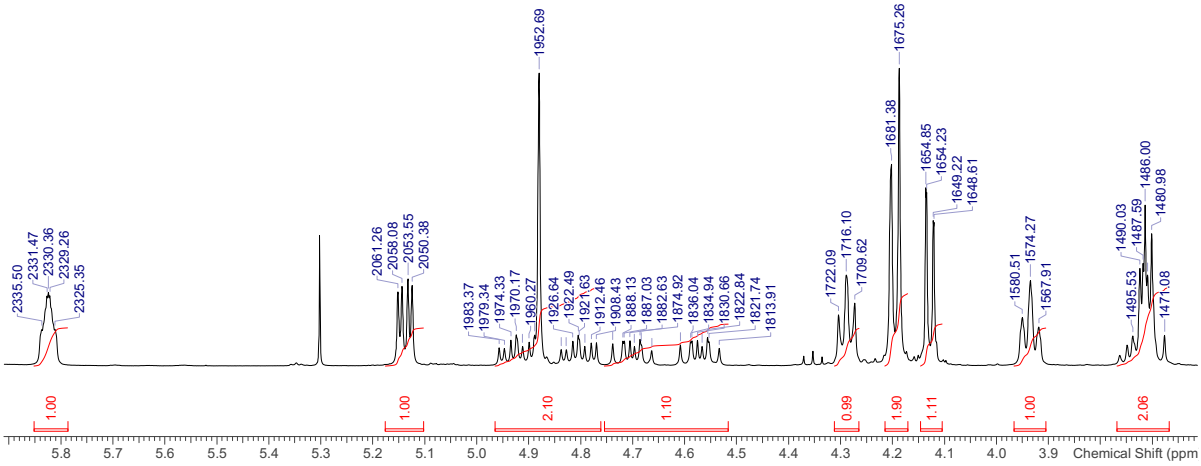
25

6.6.2.1 ^{1}H NMR, 400 MHz, $CDCl_3$

ap1723kh2.010.001.1r
CHLOROFORM-d
32 H's

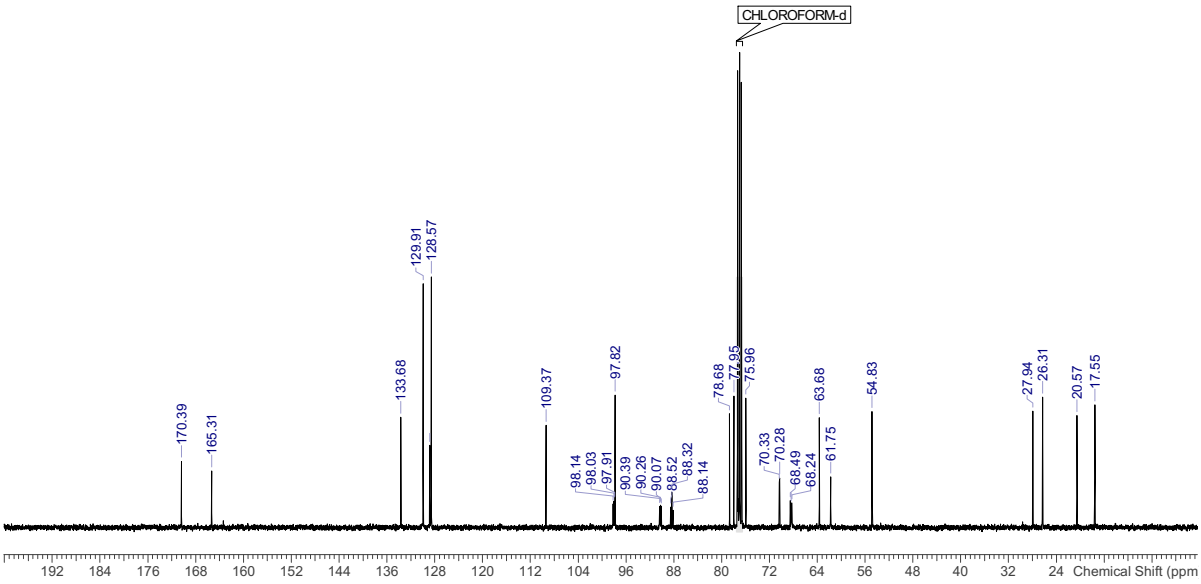


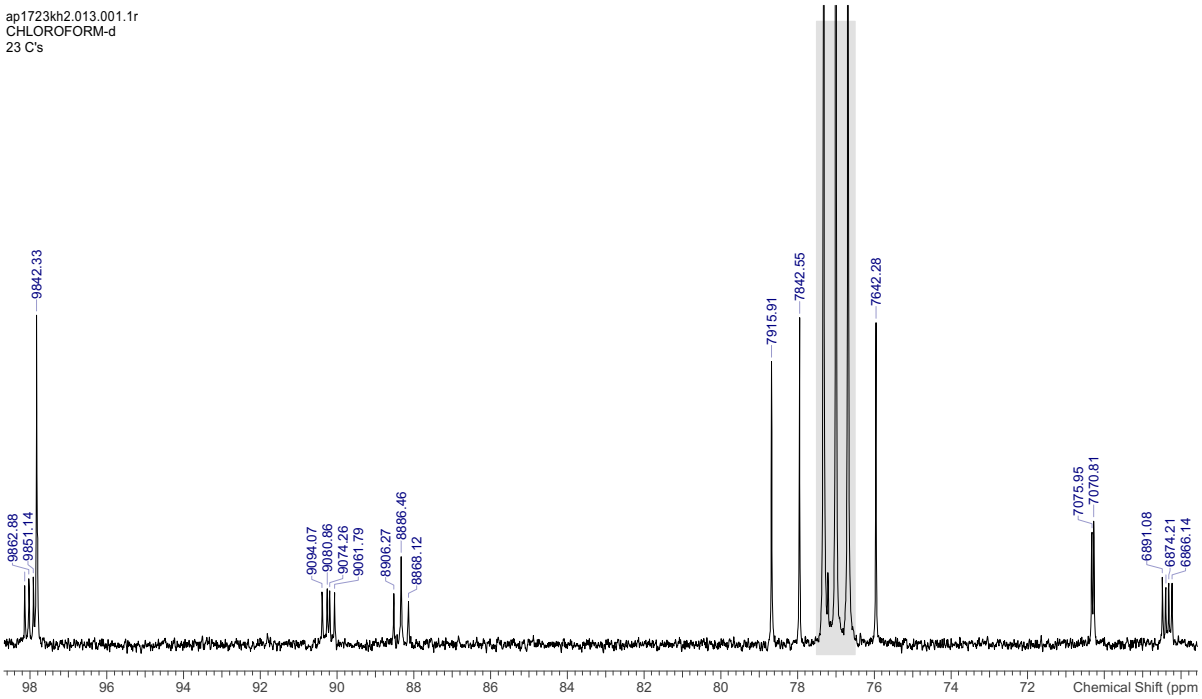
ap1723kh2.010.001.1r
CHLOROFORM-d
32 H's



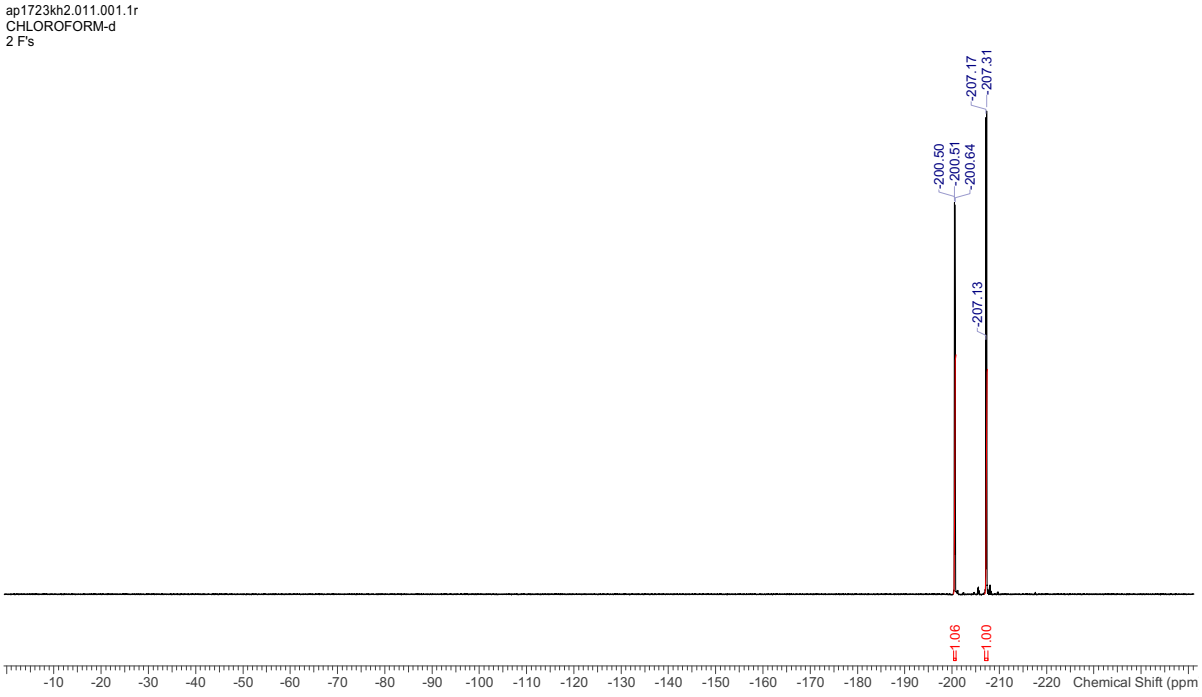
6.6.2.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

ap1723kh2.013.001.1r
CHLOROFORM-d
23 C's

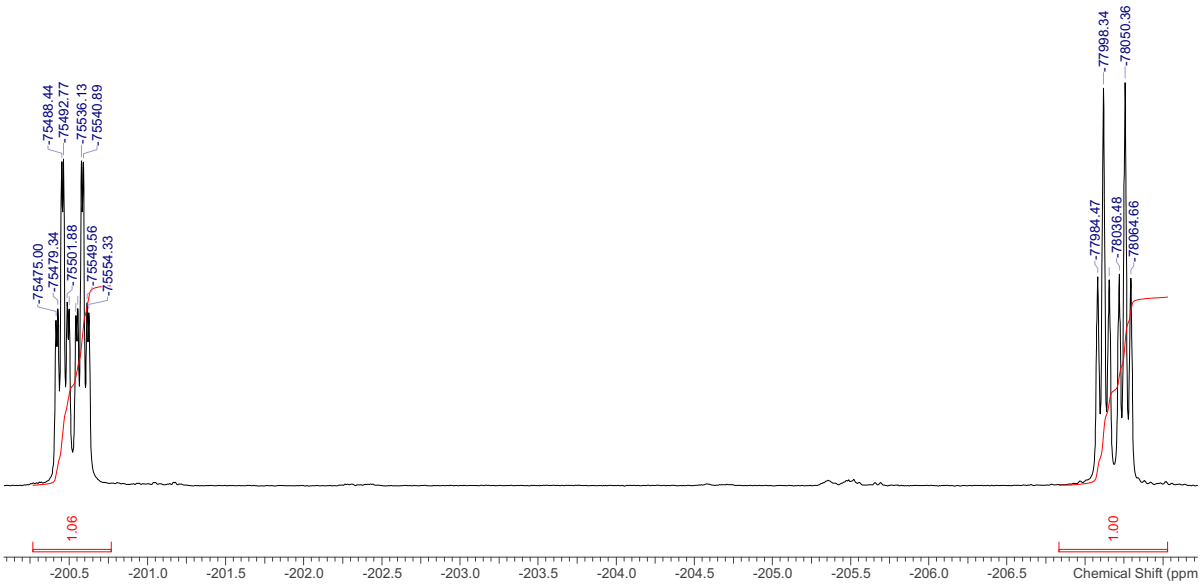




6.6.2.3 ^{19}F NMR, 376 MHz, $CDCl_3$



ap1723kh2.011.001.1r
CHLOROFORM-d
2 F's



6.6.2.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

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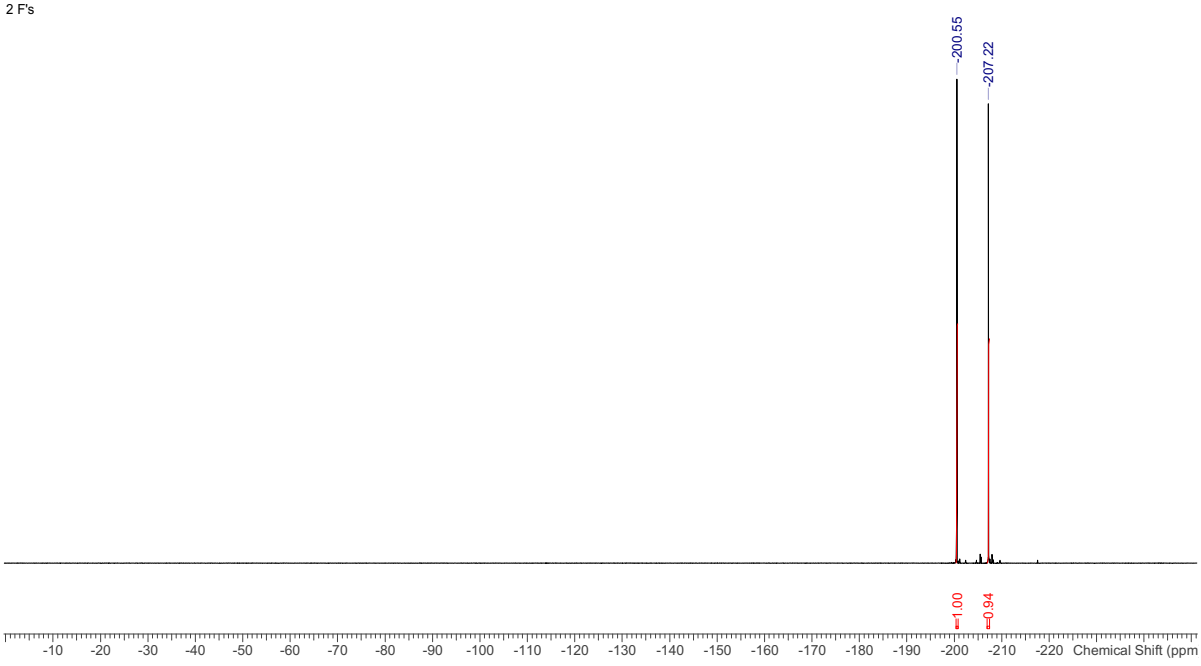
CHLOROFORM-d
2 F's



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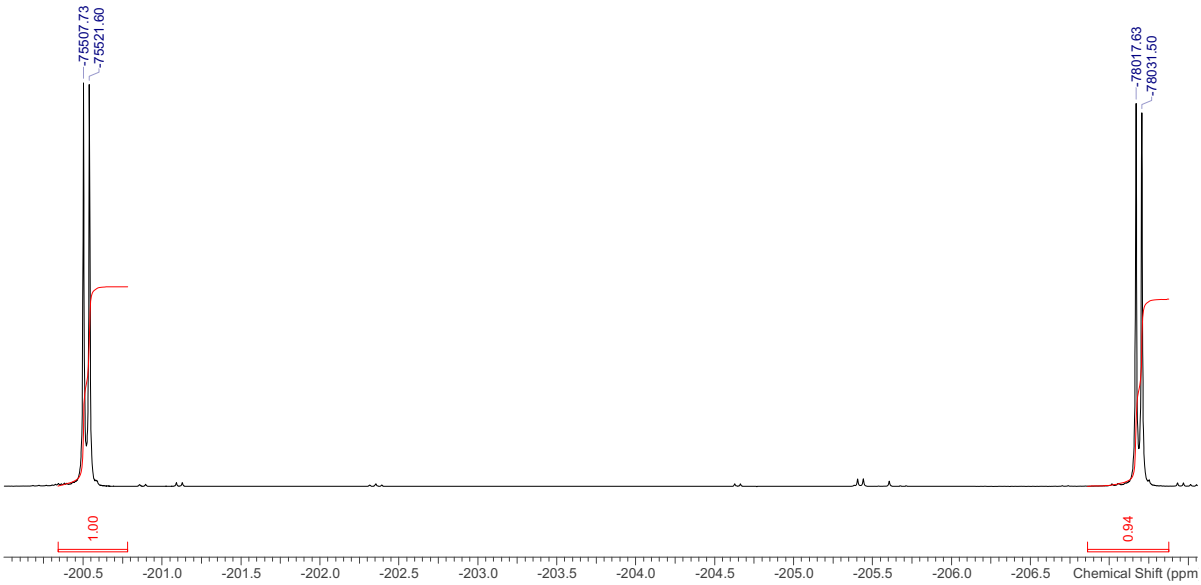
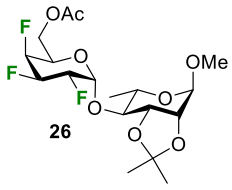
CHLOROFORM-d
2 F's



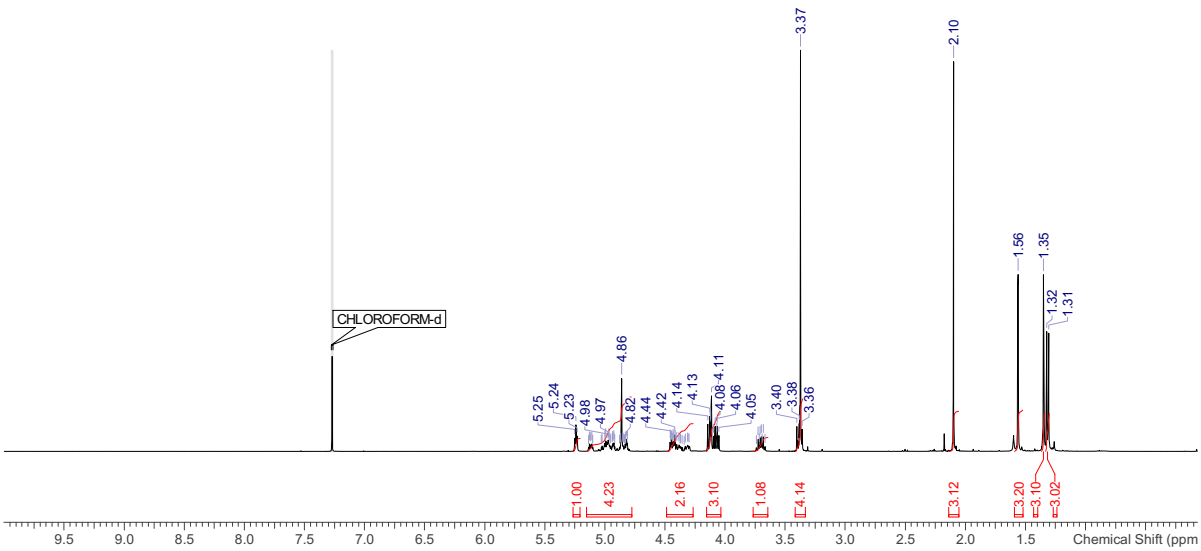
6.6.3 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α-D-galactopyranosyl-(1,4)-methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**26α**)

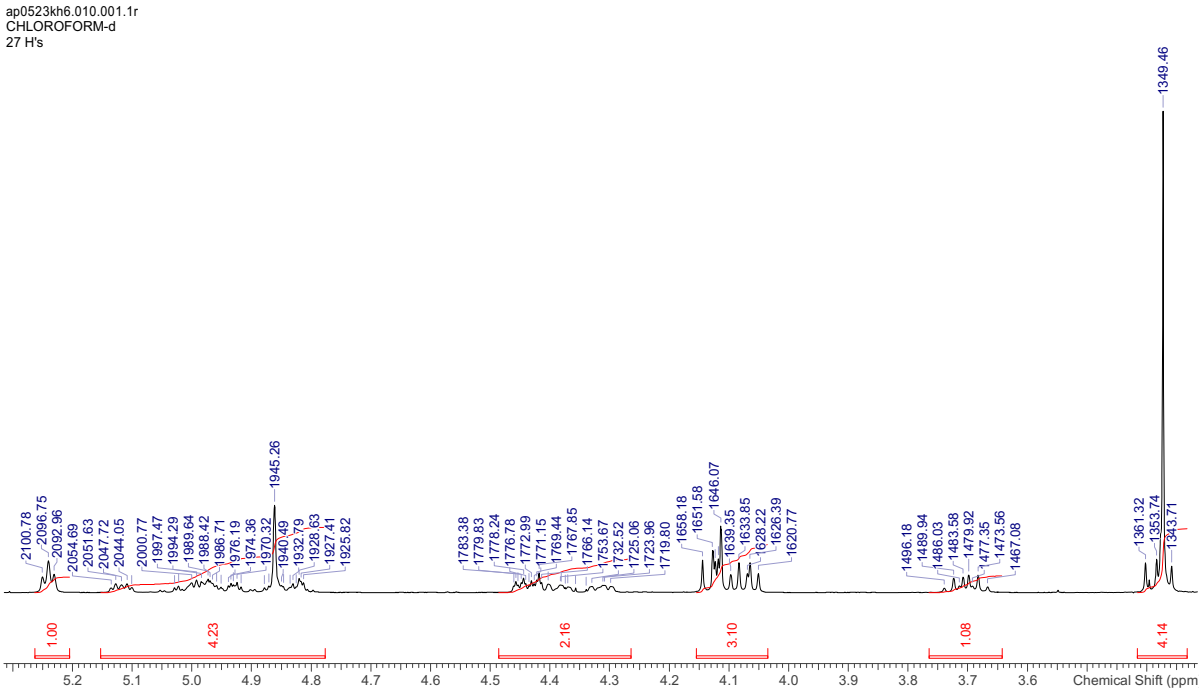


26

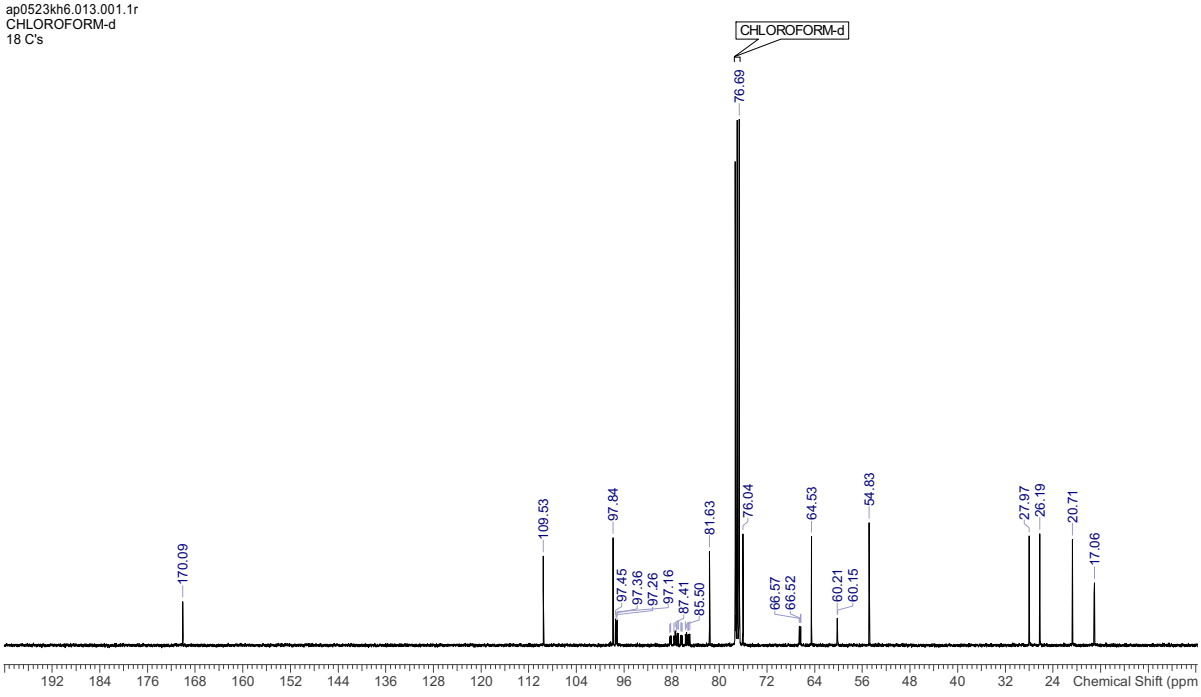
6.6.3.1 ^{1}H NMR, 400 MHz, $CDCl_3$

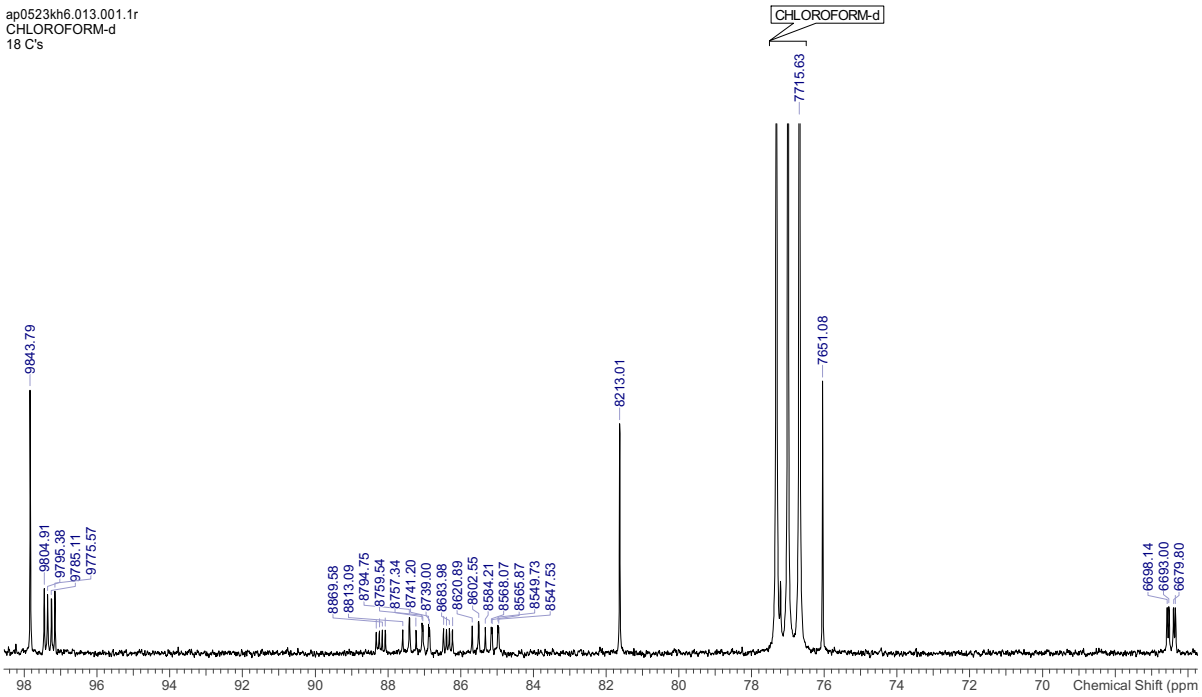
ap0523kh6.010.001.1r
CHLOROFORM-d
27 H's



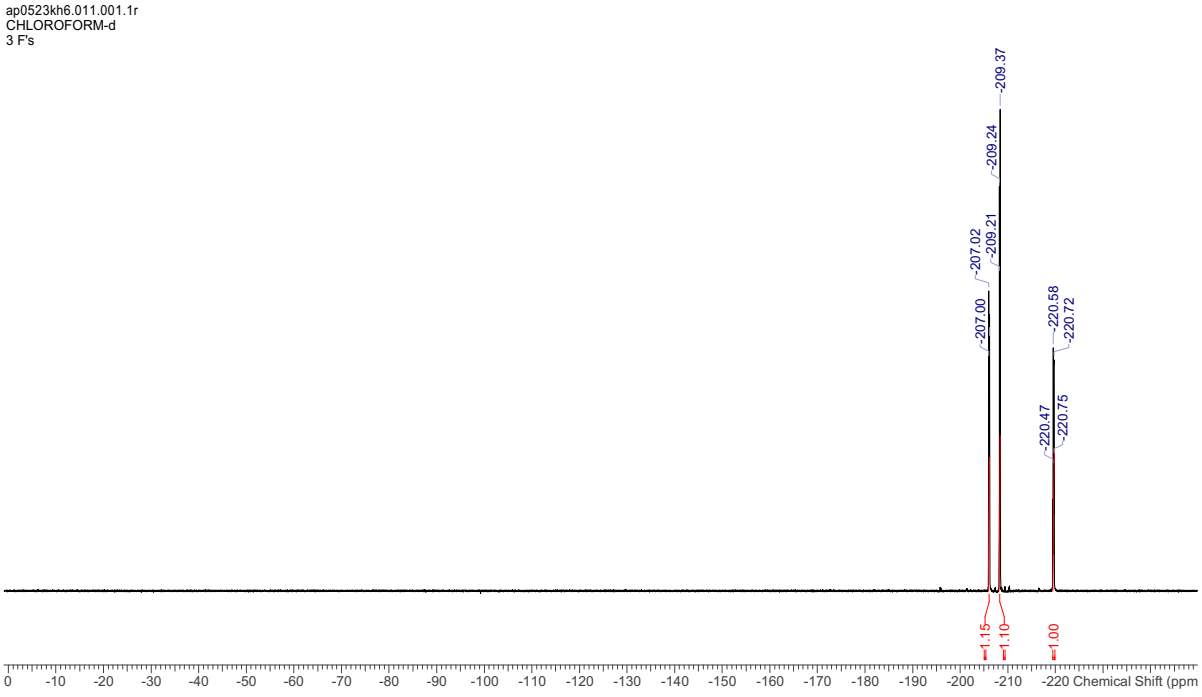


6.6.3.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

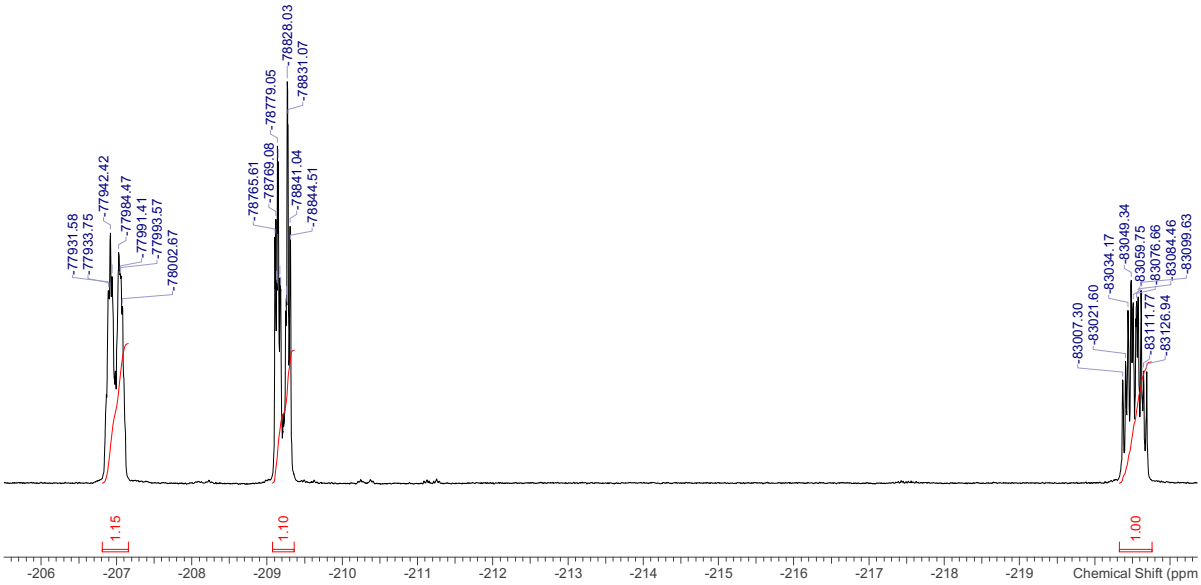




6.6.3.3 ^{19}F NMR, 376 MHz, $CDCl_3$



ap0523kh6.011.001.1r
CHLOROFORM-d
3 F's



6.6.3.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

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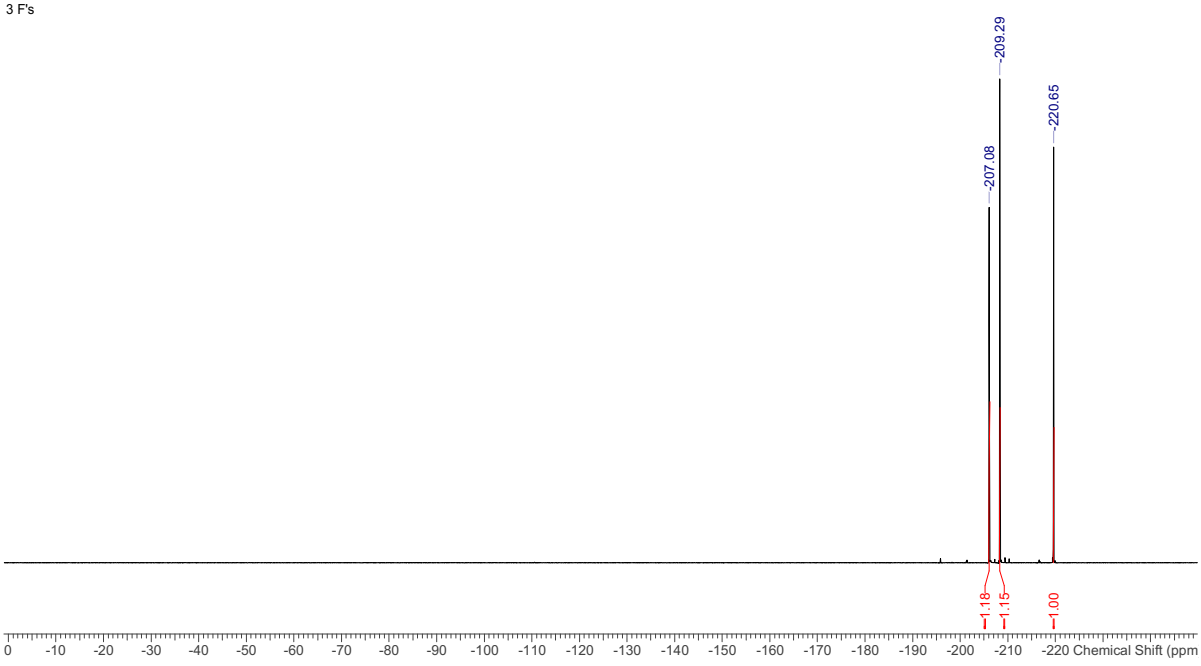
CHLOROFORM-d
3 F's



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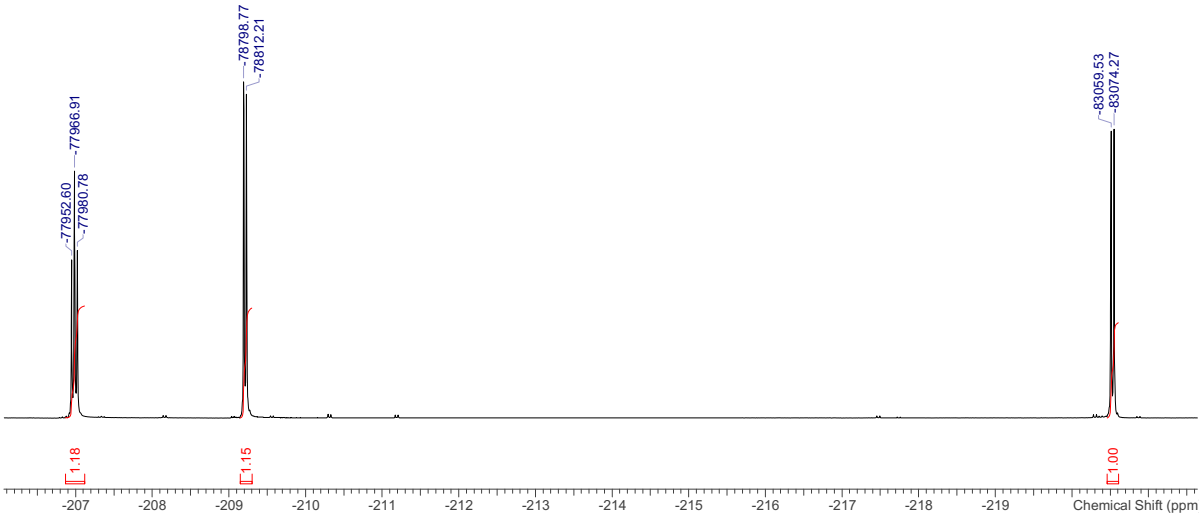
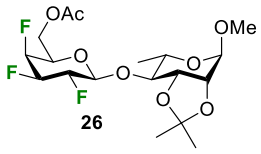
CHLOROFORM-d
3 F's



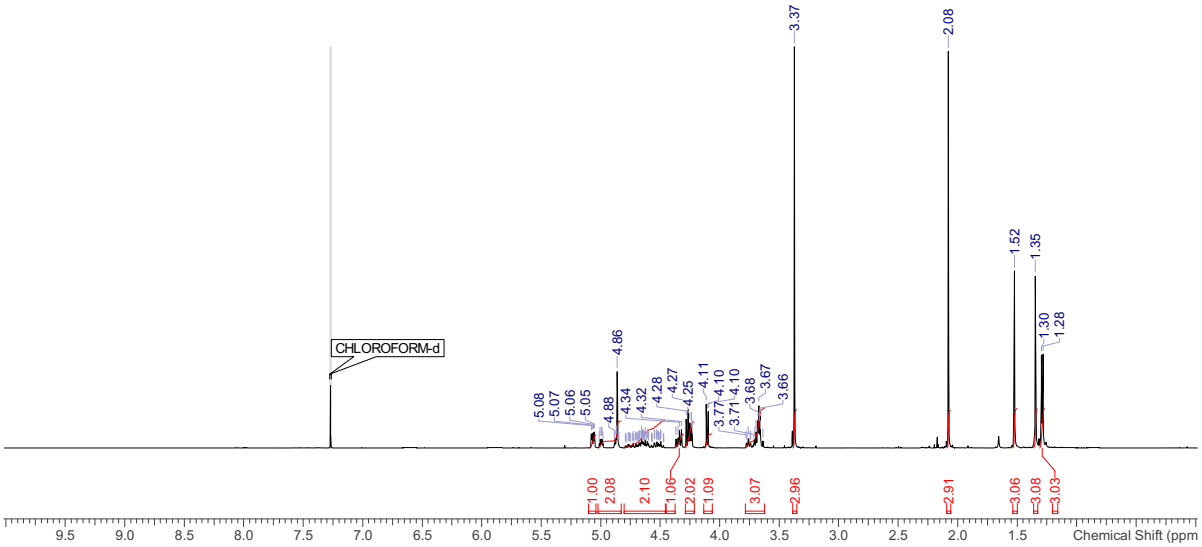
6.6.4 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-β-D-galactopyranosyl-(1,4)-methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**26β**)



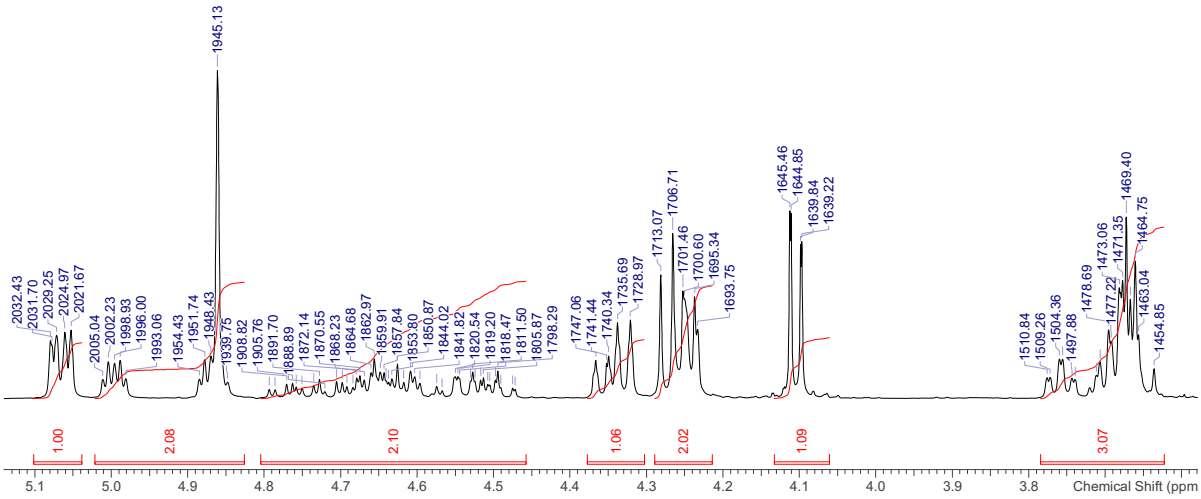
26

6.6.4.1 ^{1}H NMR, 400 MHz, $CDCl_3$

ap0523kh7.010.001.1r
CHLOROFORM-d
27 H's

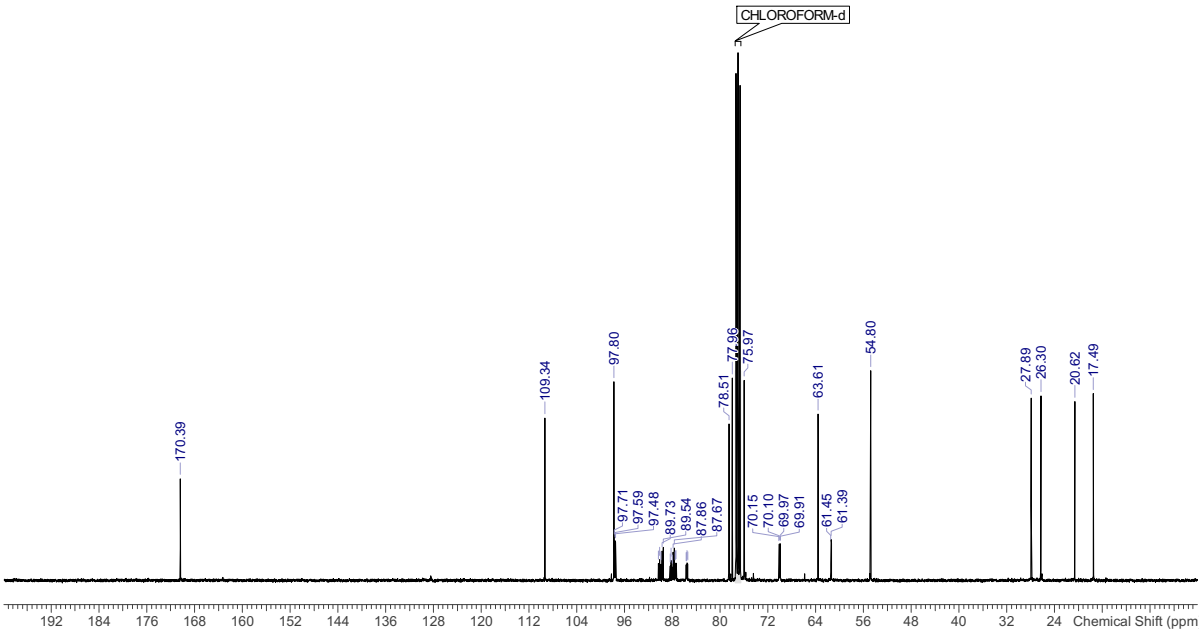


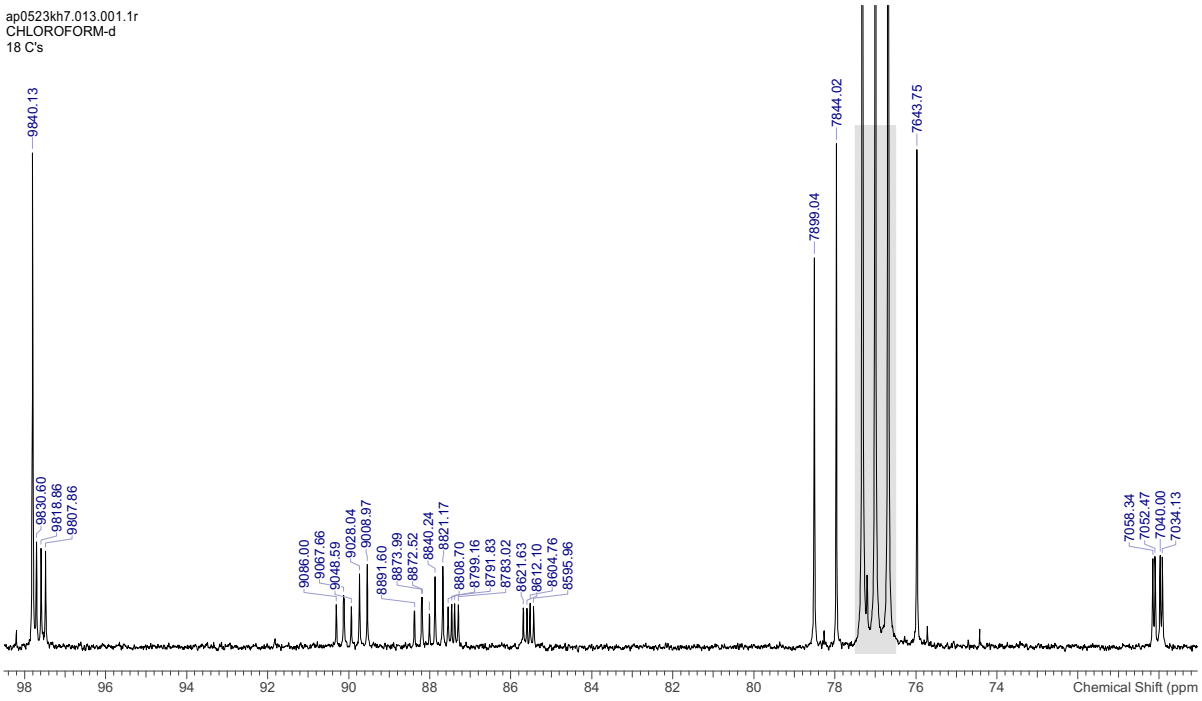
ap0523kh7.010.001.1r
CHLOROFORM-d
27 H's



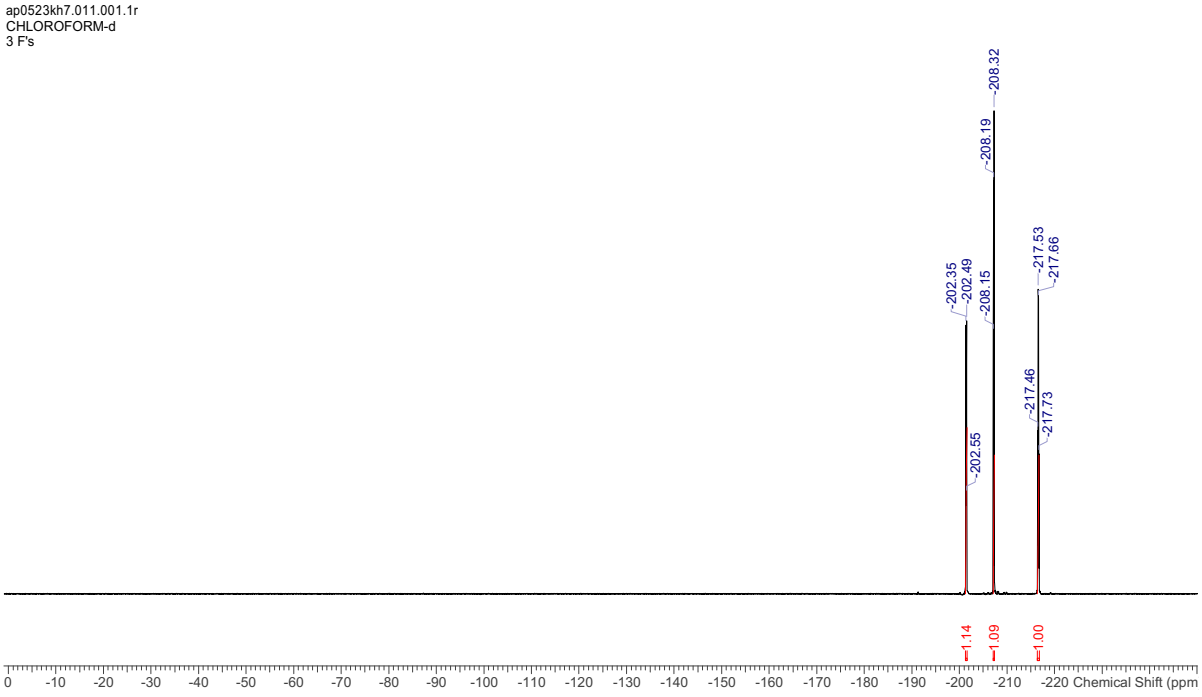
6.6.4.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

ap0523kh7.013.001.1r
CHLOROFORM-d
18 C's

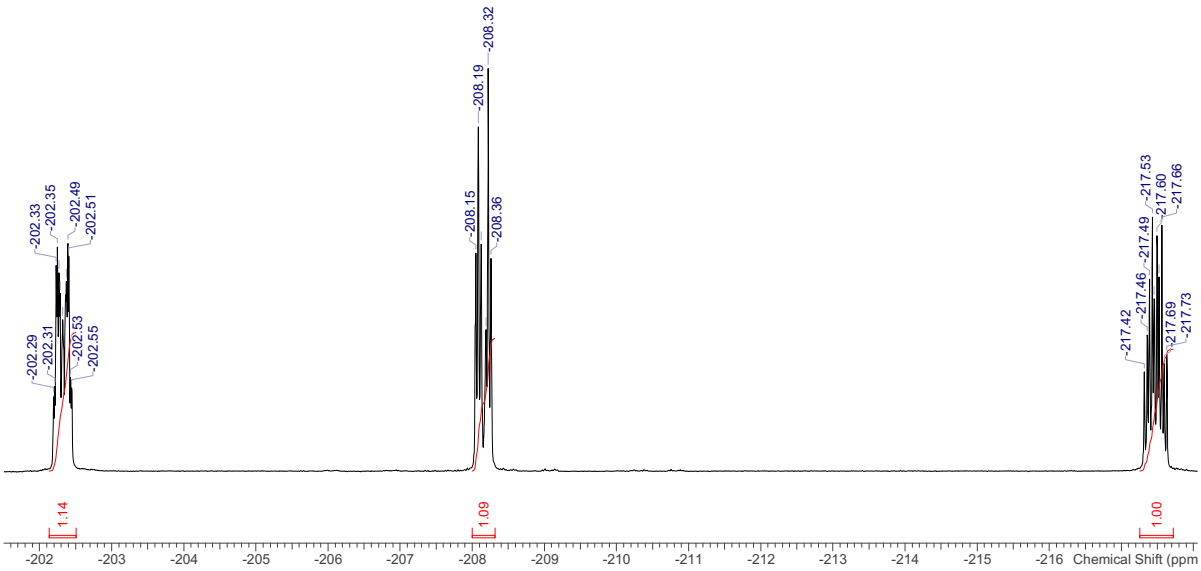




6.6.4.3 ^{19}F NMR, 376 MHz, $CDCl_3$

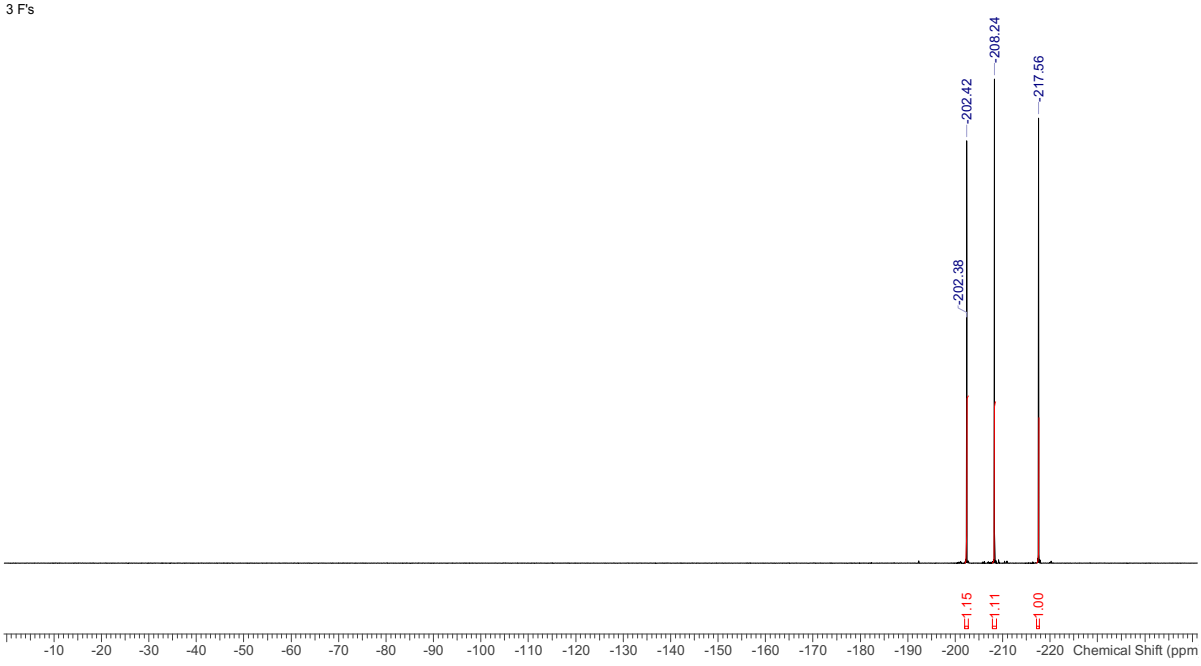


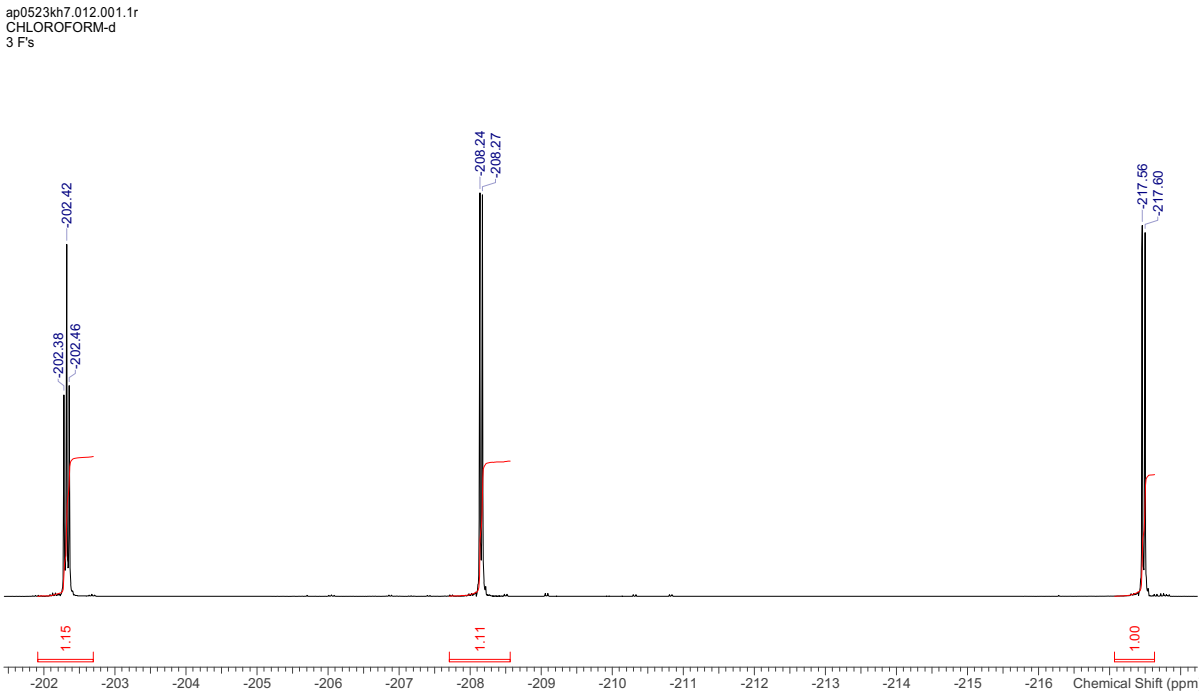
ap0523kh7.011.001.1r
CHLOROFORM-d
3 F's



6.6.4.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

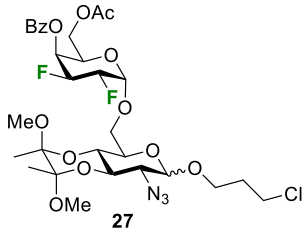
ap0523kh7.012.001.1r
CHLOROFORM-d
3 F's





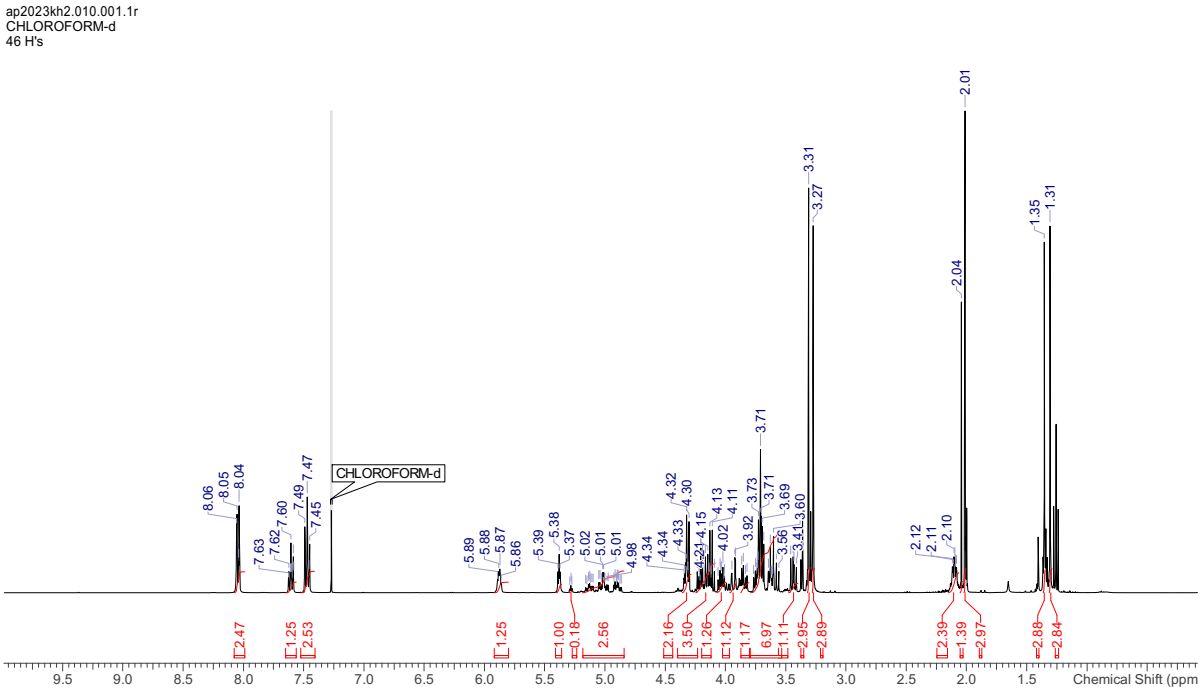
6.7 Copies of the spectra of the glycosylation products with 3-chloropropyl 2-deoxy-2-azido-3,4-*O*-[(2'S,3'S)-2',3'-dimethoxybutane-2',3'-diyl]-D-glucopyranoside

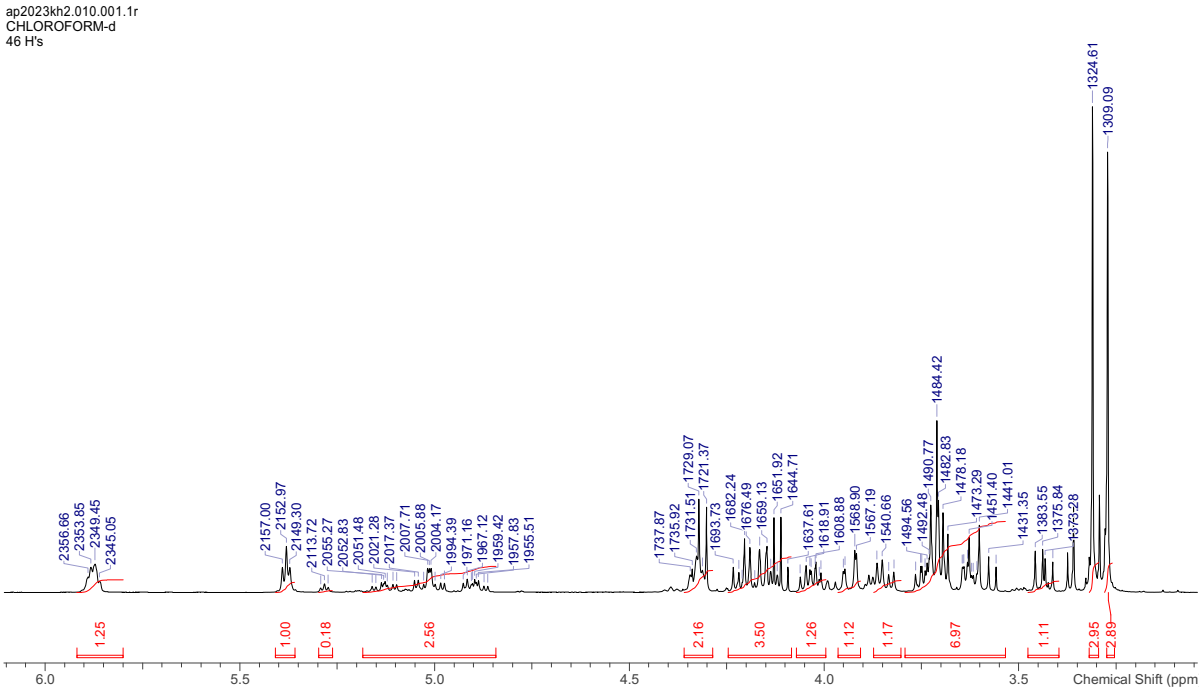
6.7.1 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-3,4-*O*-[(2'S,3'S)-2',3'-dimethoxybutane-2',3'-diyl]-D-glucopyranoside (**27α**)



27

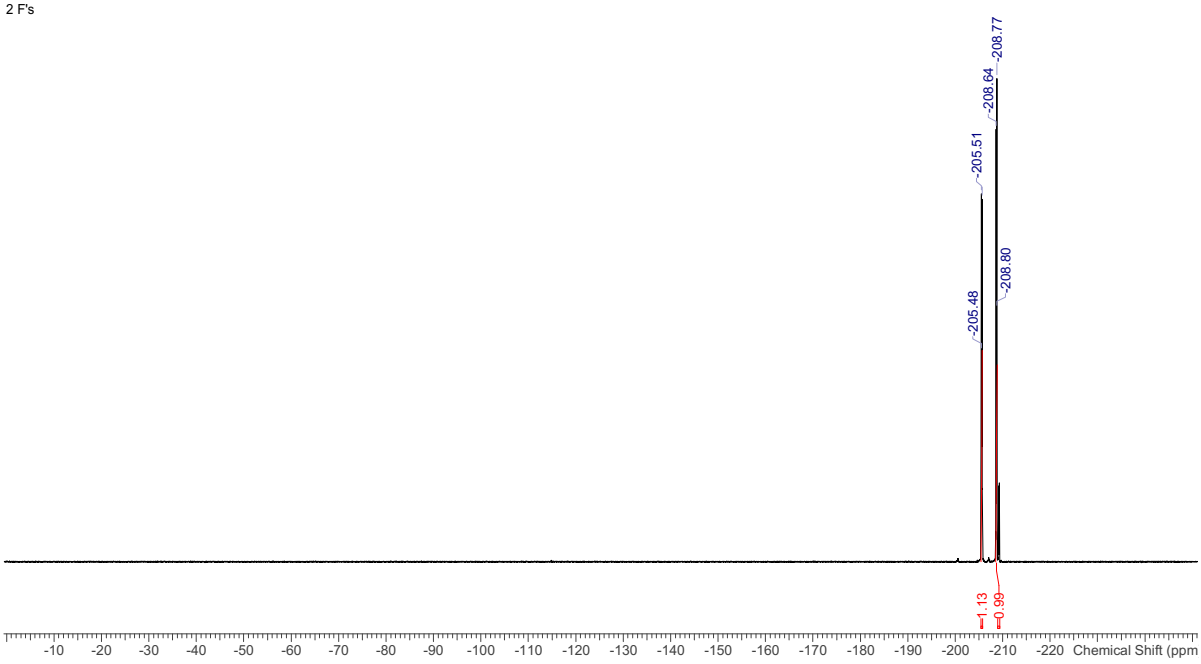
6.7.1.1 ^{1}H NMR, 400 MHz, $CDCl_3$



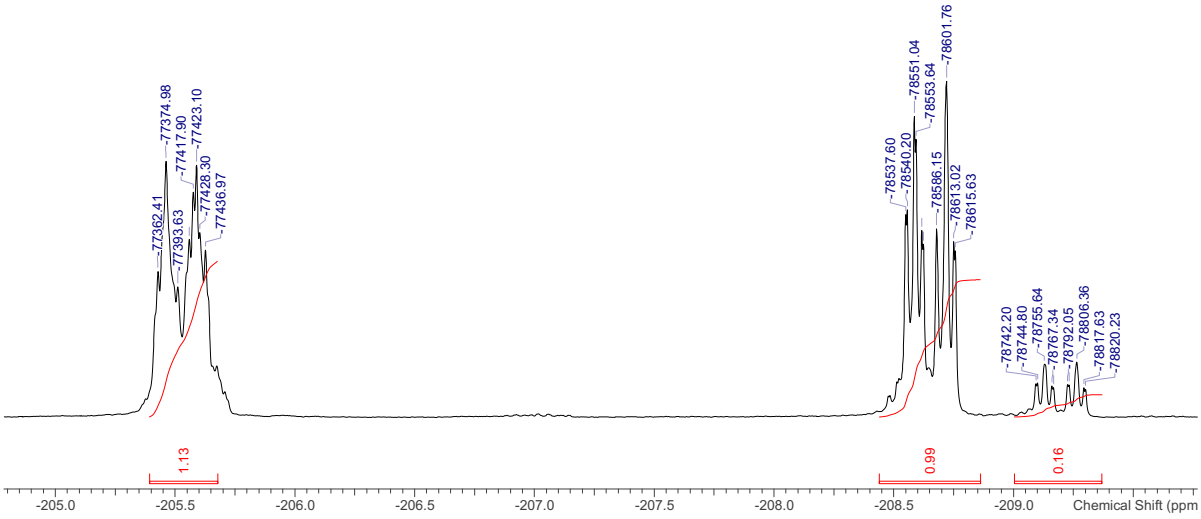


6.7.1.2 ^{19}F NMR, 376 MHz, $CDCl_3$

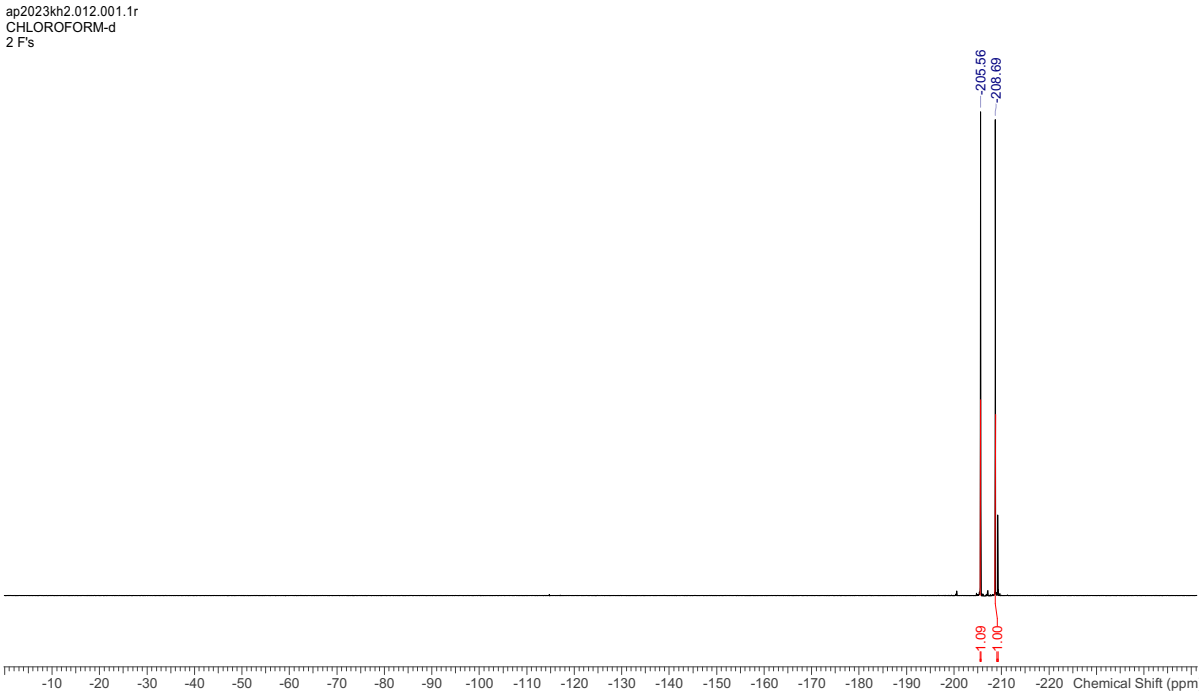
ap2023kh2.011.001.1r
CHLOROFORM-d
2 F's



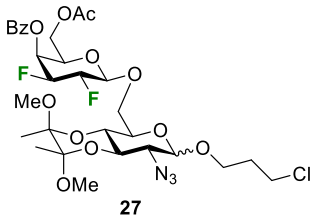
ap2023kh2.011.001.1r
CHLOROFORM-d
3 F's



6.7.1.3 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

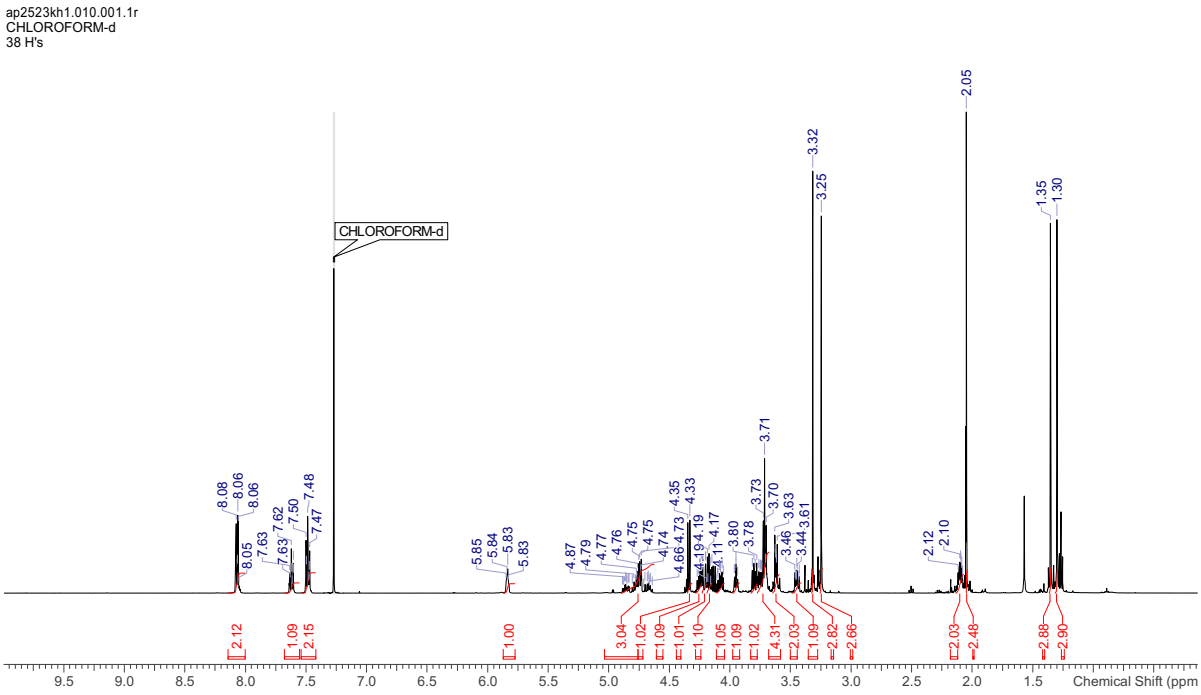


6.7.2 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-β-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-3,4-*O*-[(2'S,3'S)-2',3'-dimethoxybutane-2',3'-diyl]-D-glucopyranoside (**27β**)

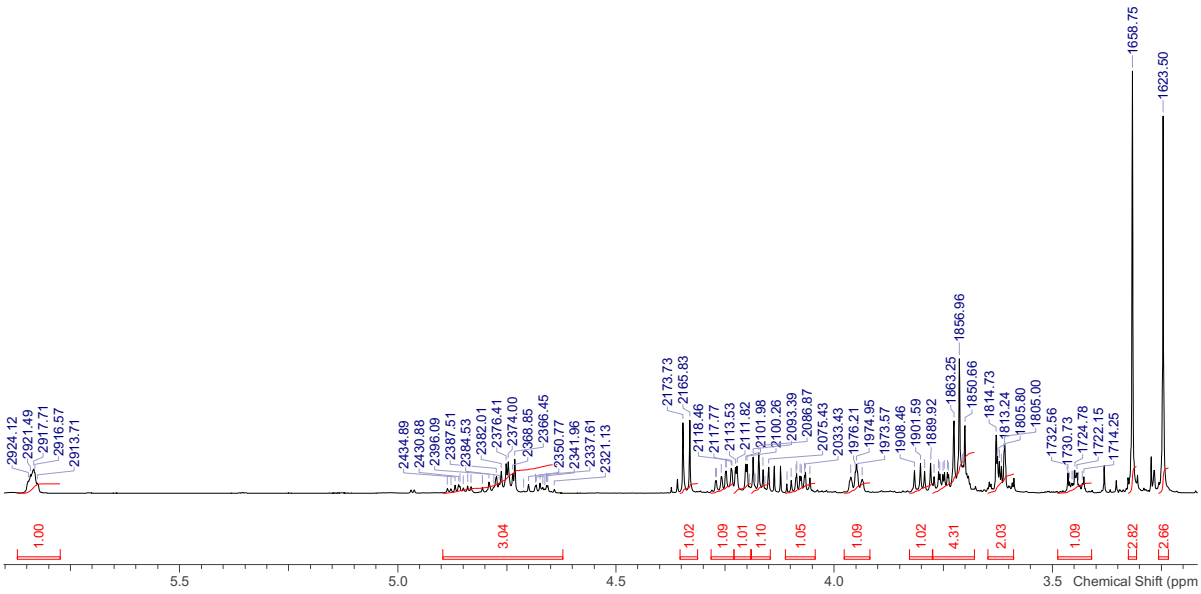


27

6.7.2.1 ^{1}H NMR, 500 MHz, $CDCl_3$

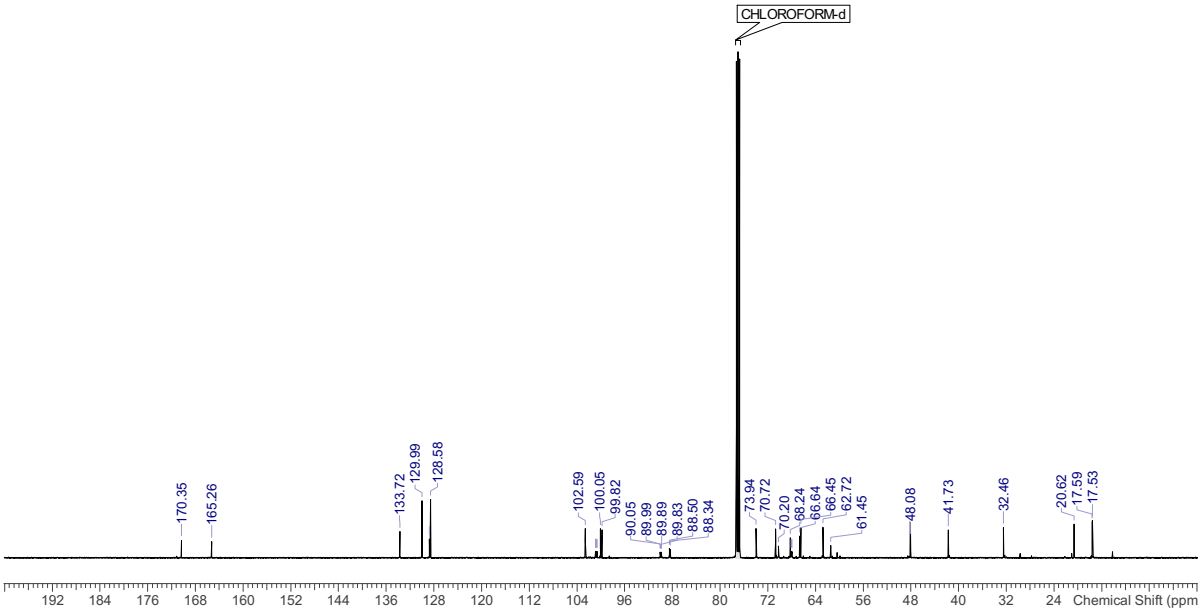


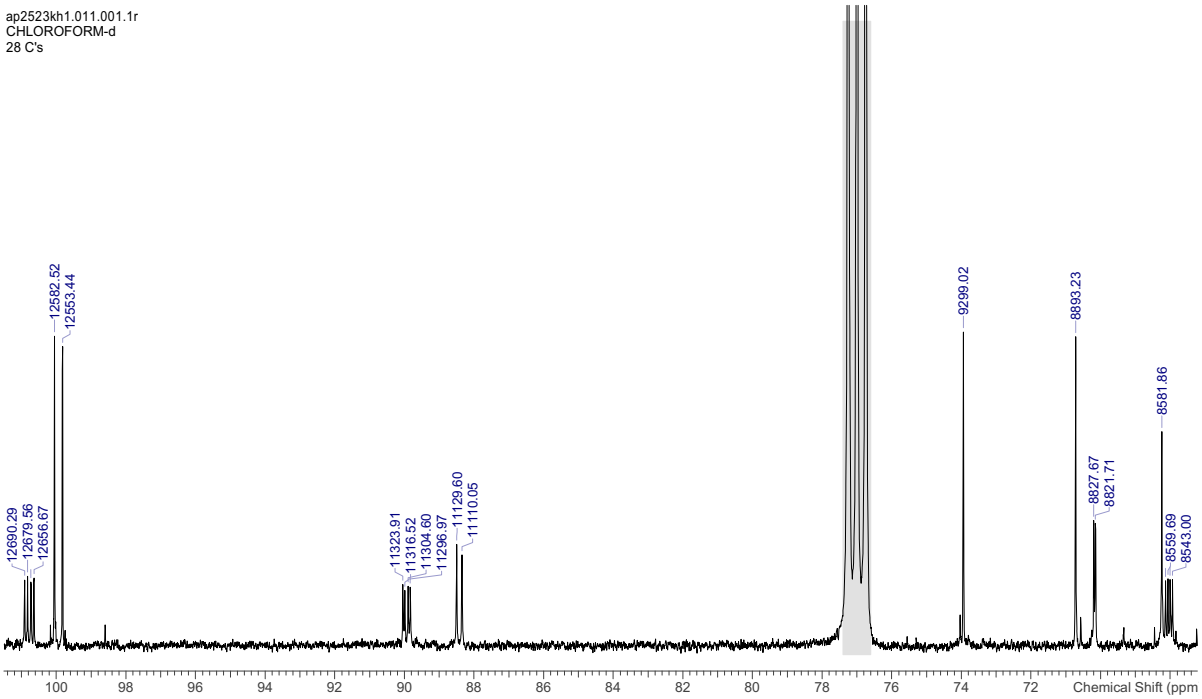
ap2523kh1.010.001.1r
CHLOROFORM-d
38 H's



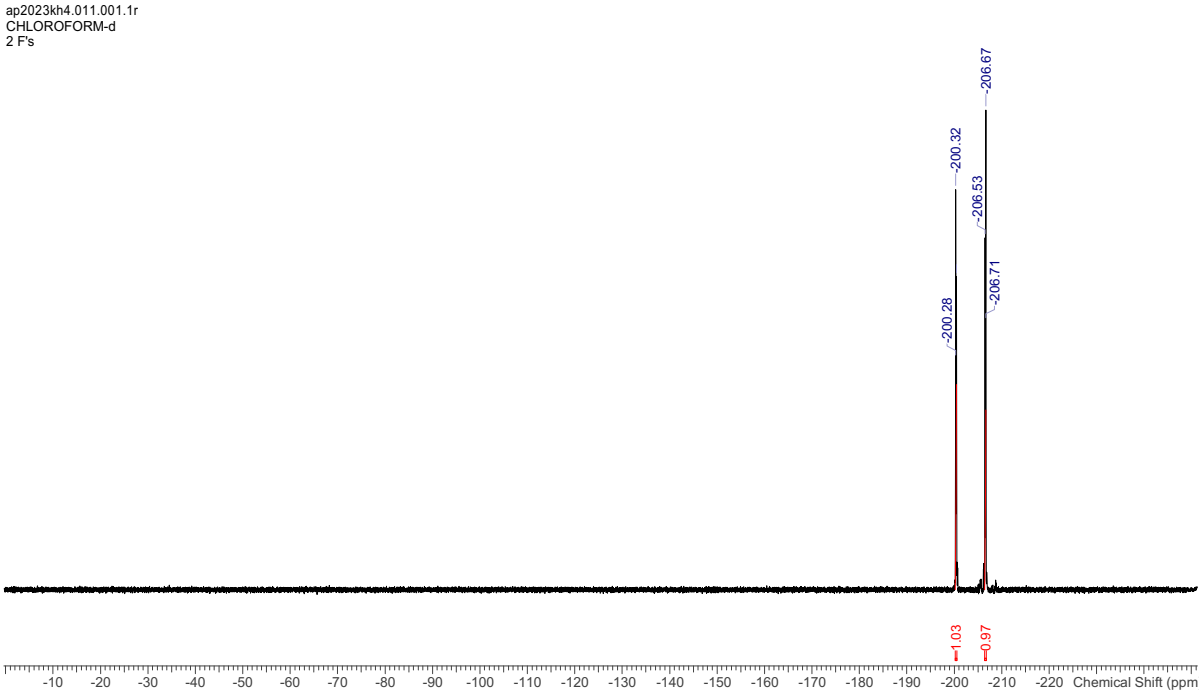
6.7.2.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

ap2523kh1.011.001.1r
CHLOROFORM-d
28 C's

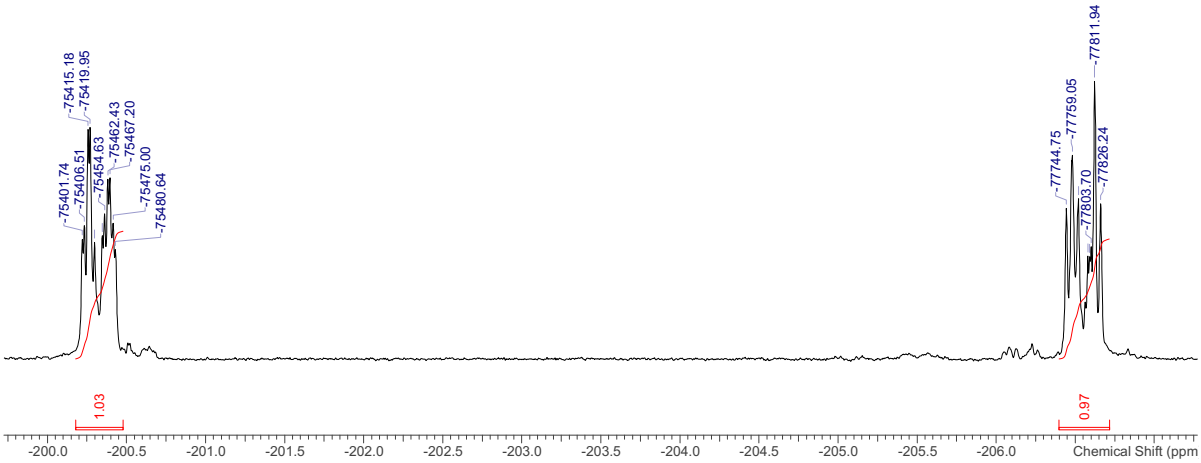




6.7.2.3 ^{19}F NMR, 376 MHz, $CDCl_3$

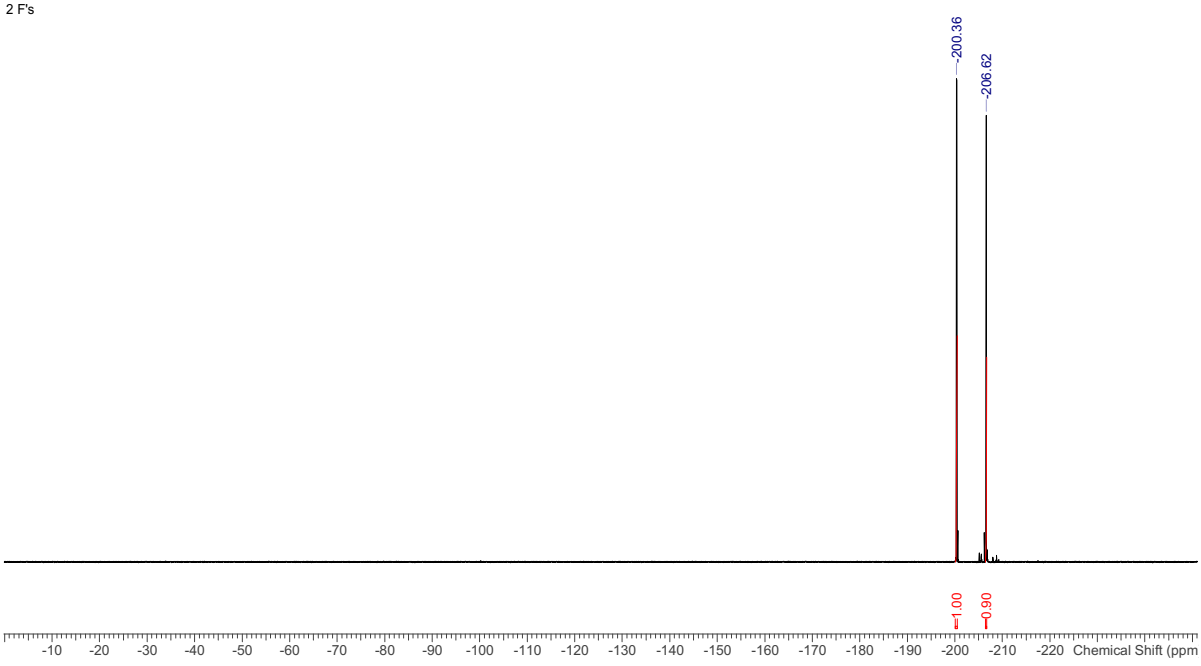


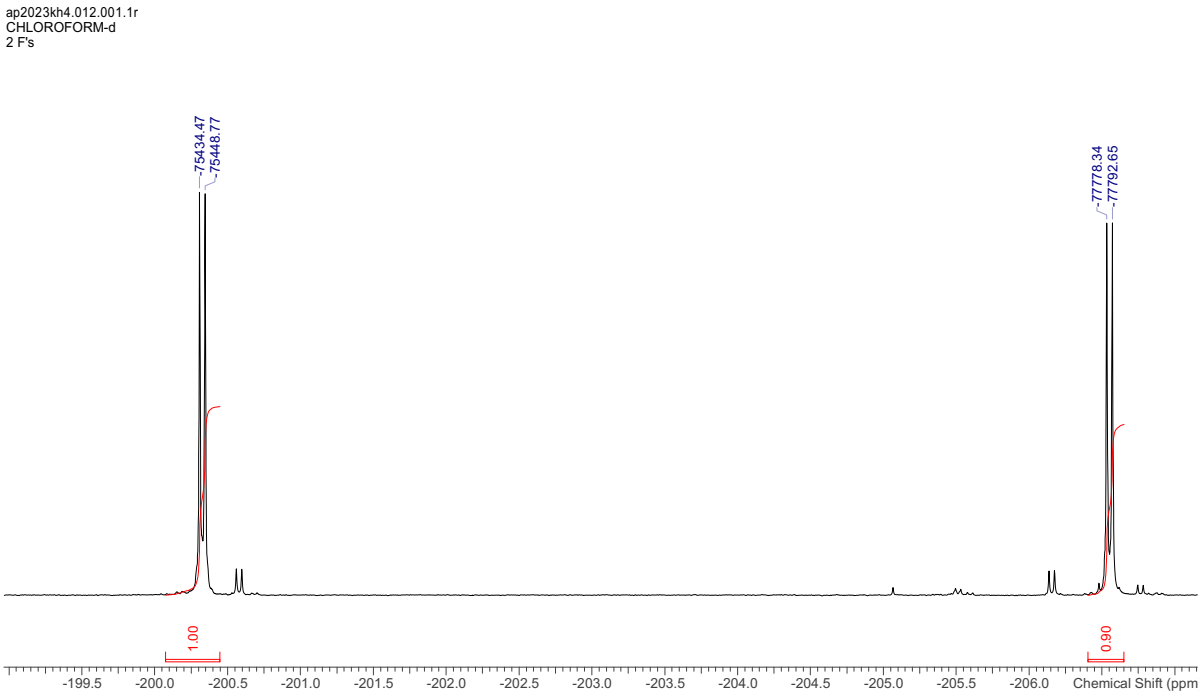
ap2023kh4.011.001.1r
CHLOROFORM-d
2 F's



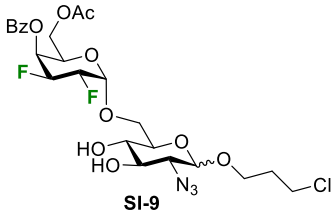
6.7.2.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$

ap2023kh4.012.001.1r
CHLOROFORM-d
2 F's





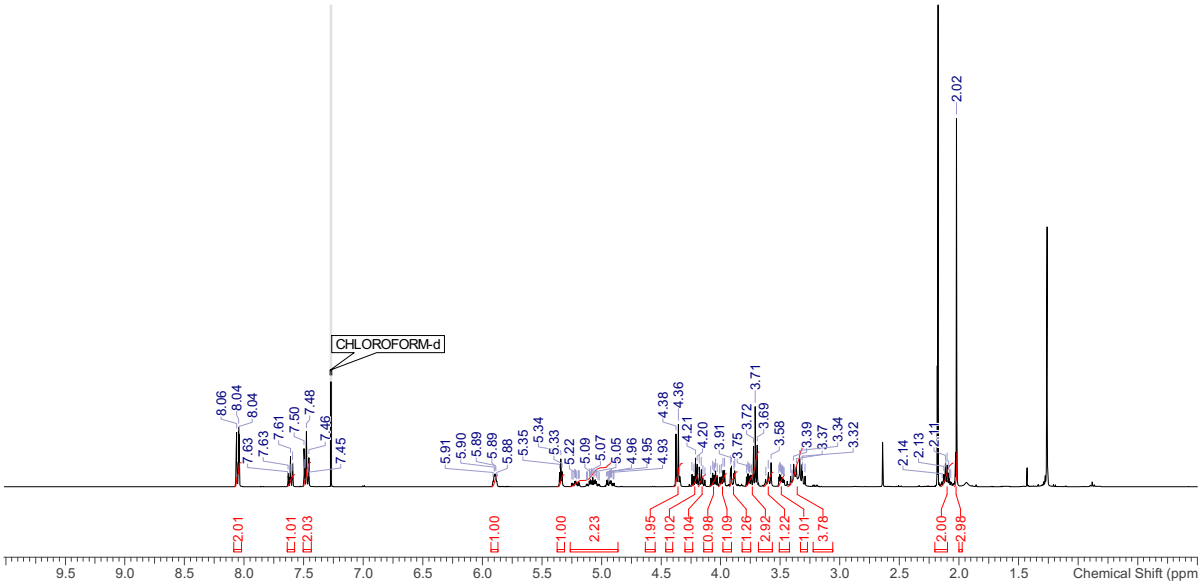
6.7.3 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-D-glucopyranoside (**SI-9**)



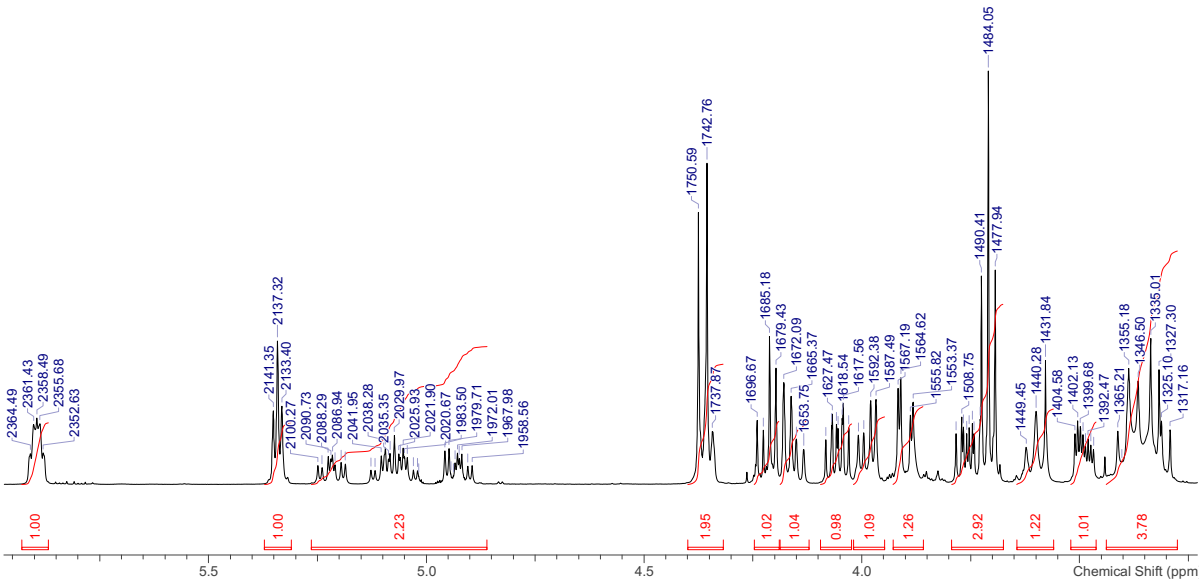
SI-9

6.7.3.1 ^{1}H NMR, 400 MHz, $CDCl_3$

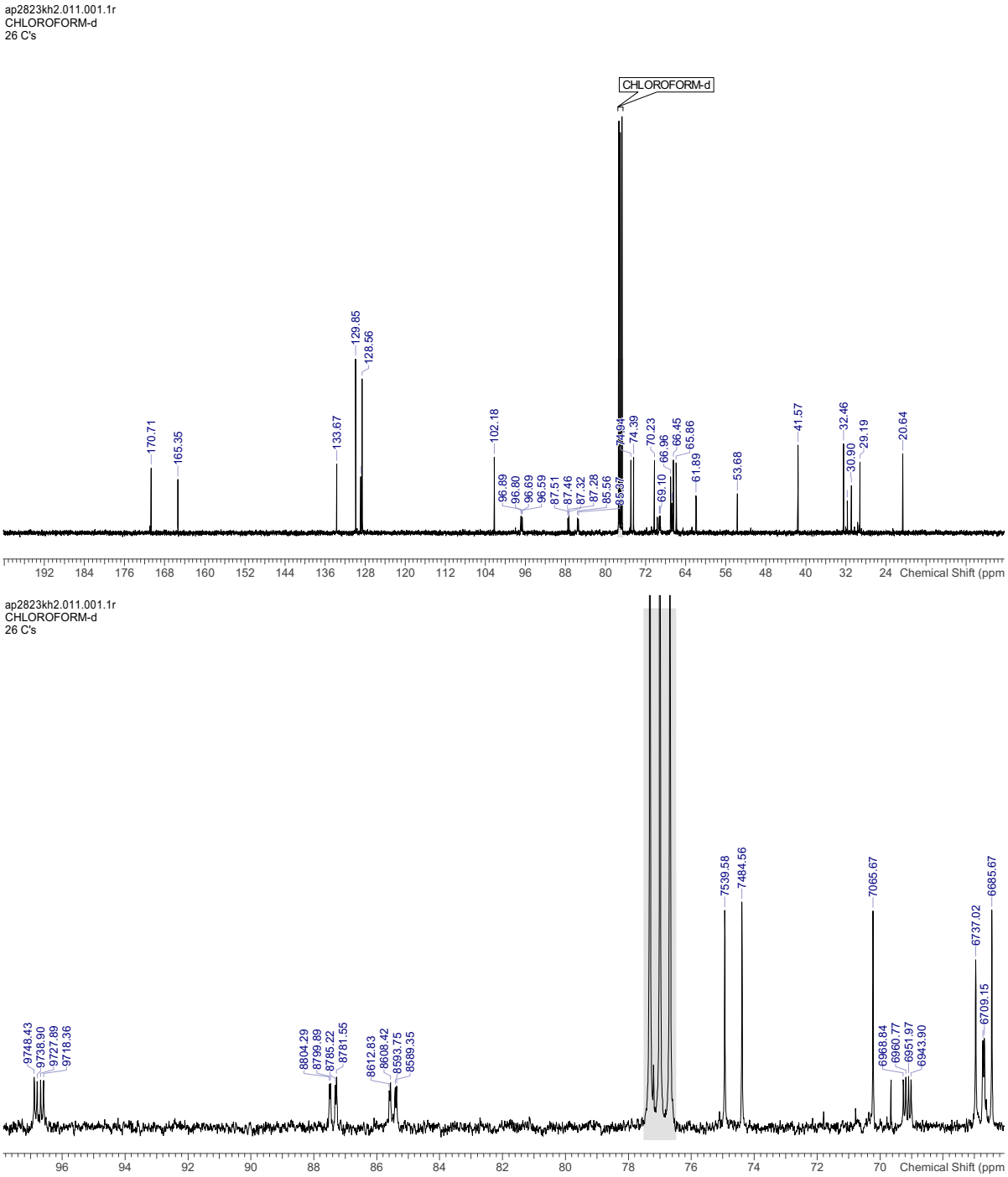
ap2823kh2.010.001.1r
CHLOROFORM-d
30 H's



ap2823kh2.010.001.1r
CHLOROFORM-d
30 H's

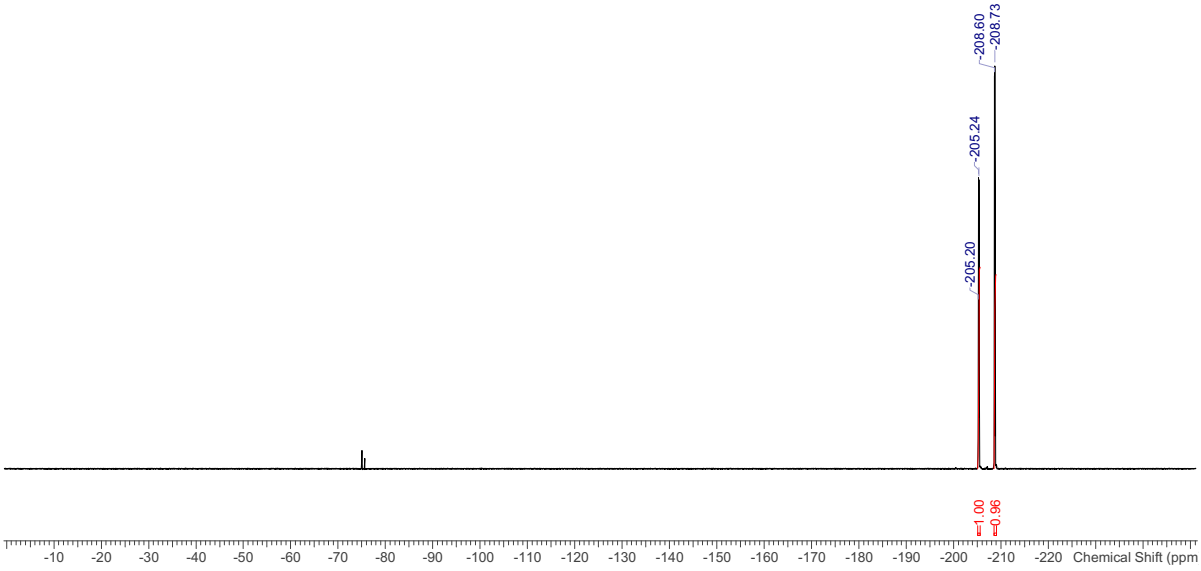


6.7.3.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$



6.7.3.3 ^{19}F NMR, 376 MHz, $CDCl_3$

ap2723kh4.011.001.1r
CHLOROFORM-d
2 F's



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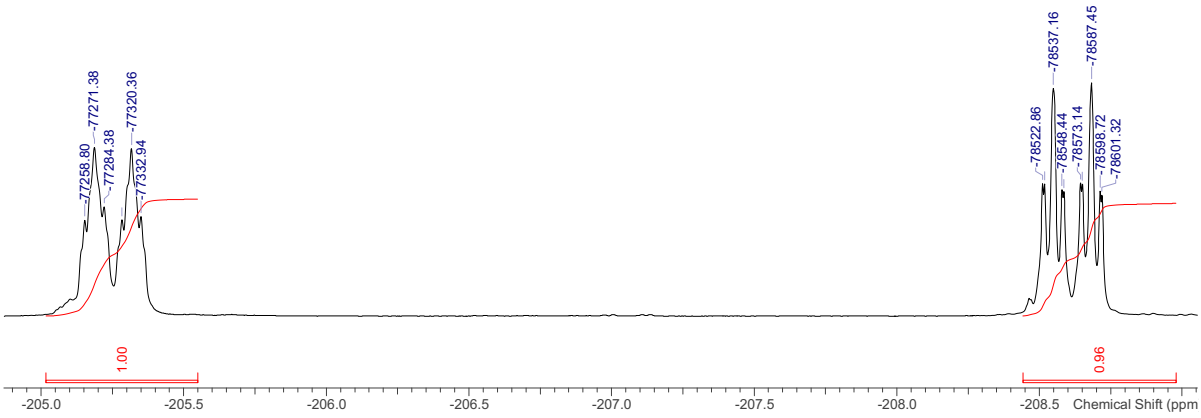
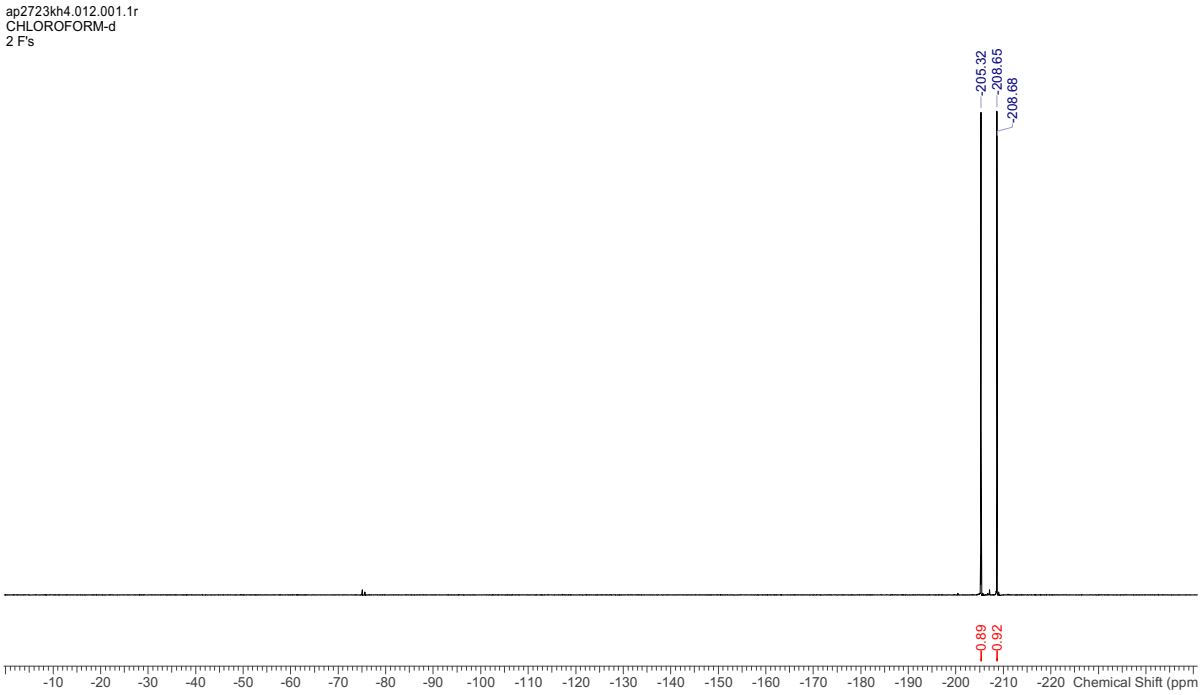
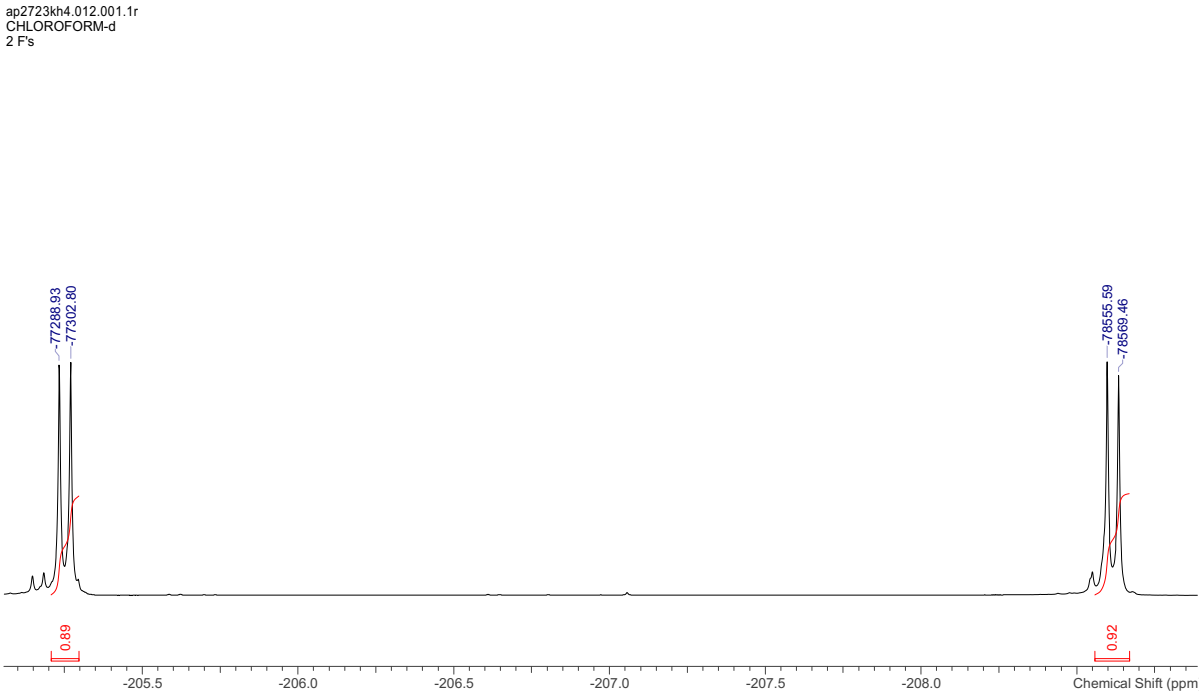
2 F's

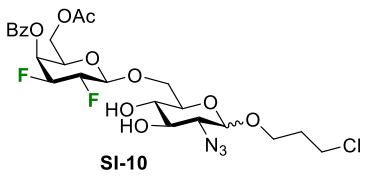


6.7.3.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



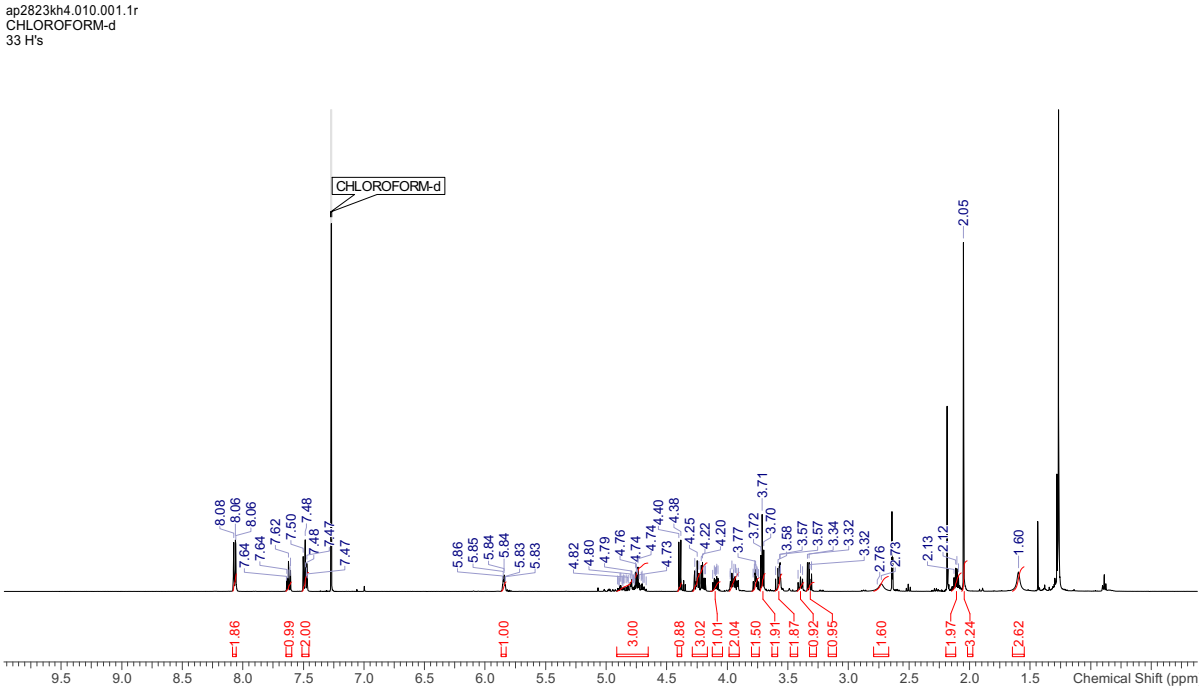


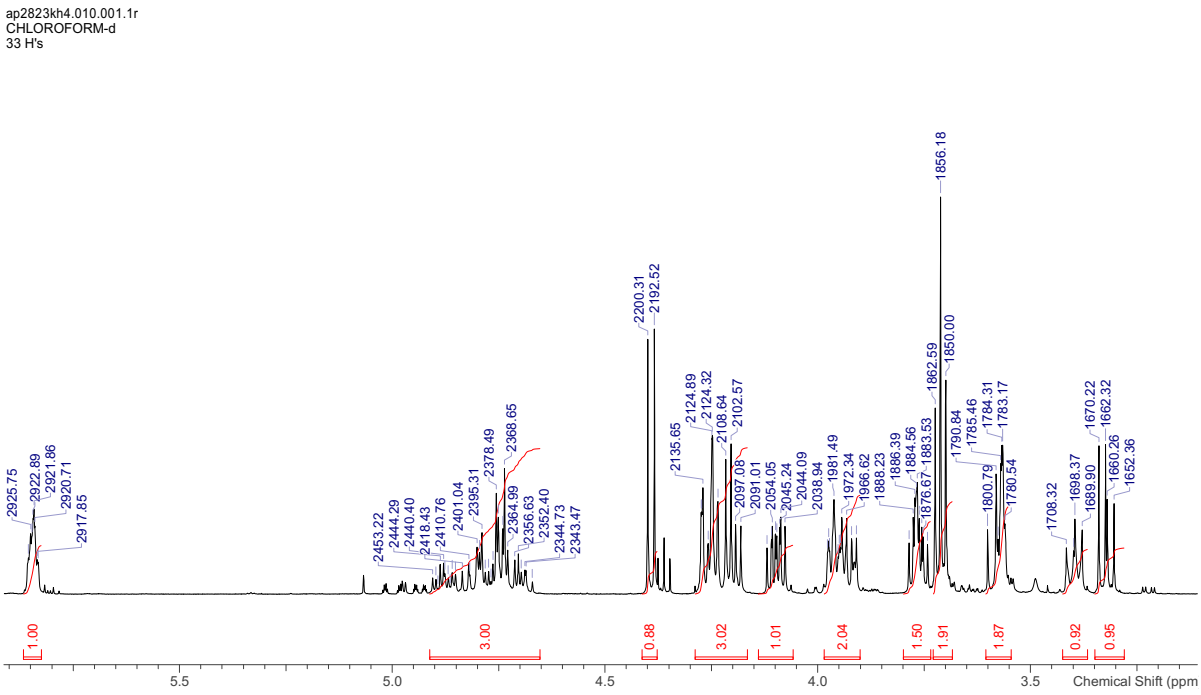
6.7.4 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-β-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-D-glucopyranoside (**SI-10**)



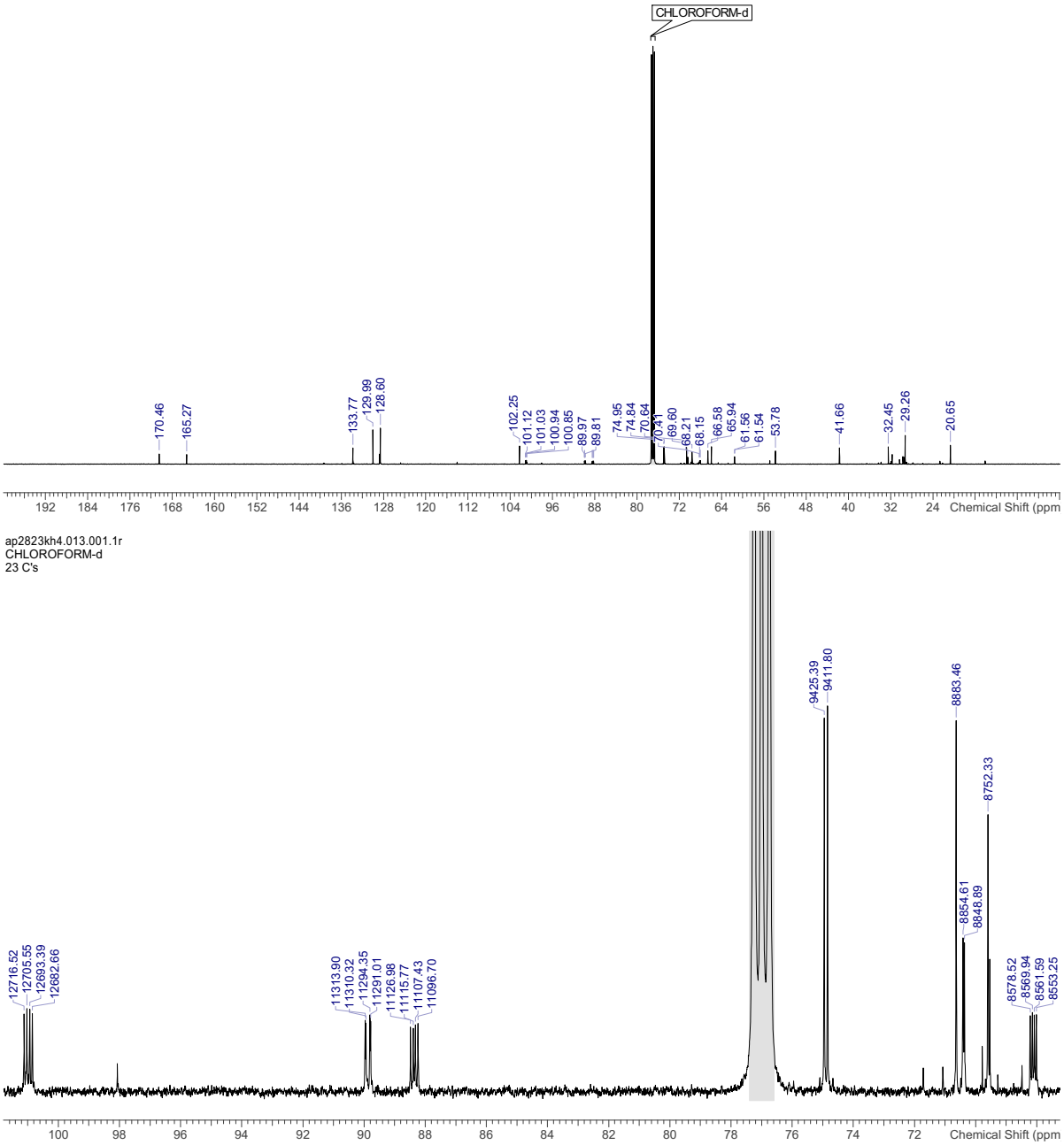
SI-10

6.7.4.1 ^{1}H NMR, 500 MHz, $CDCl_3$

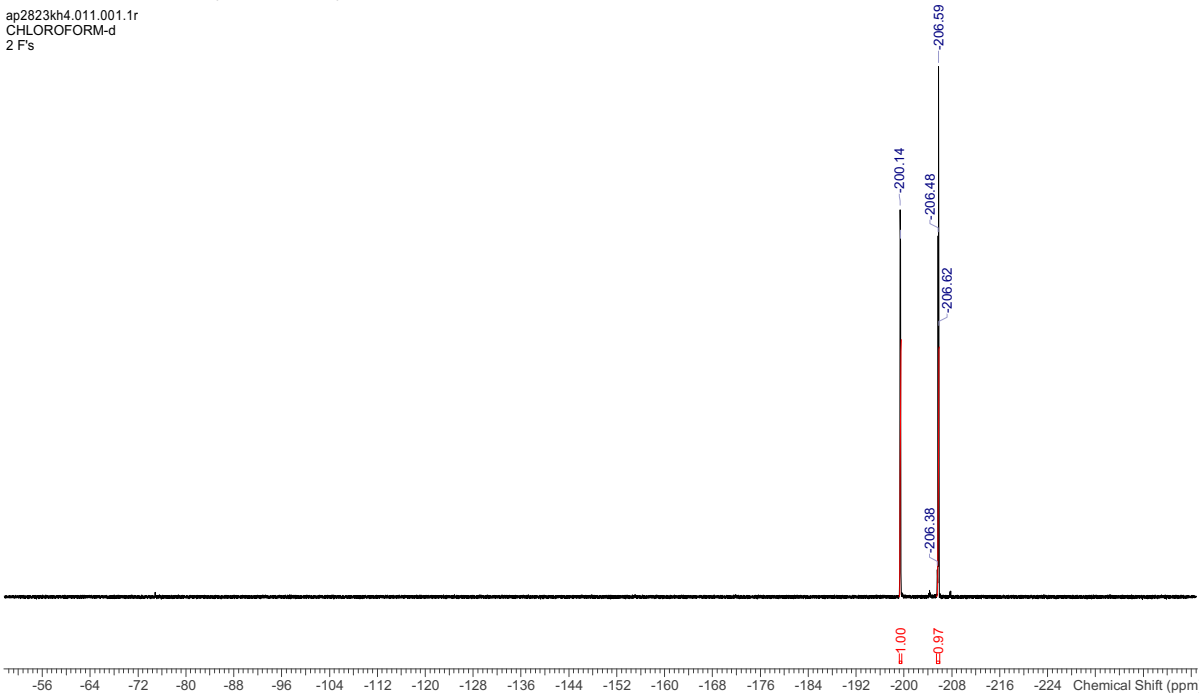


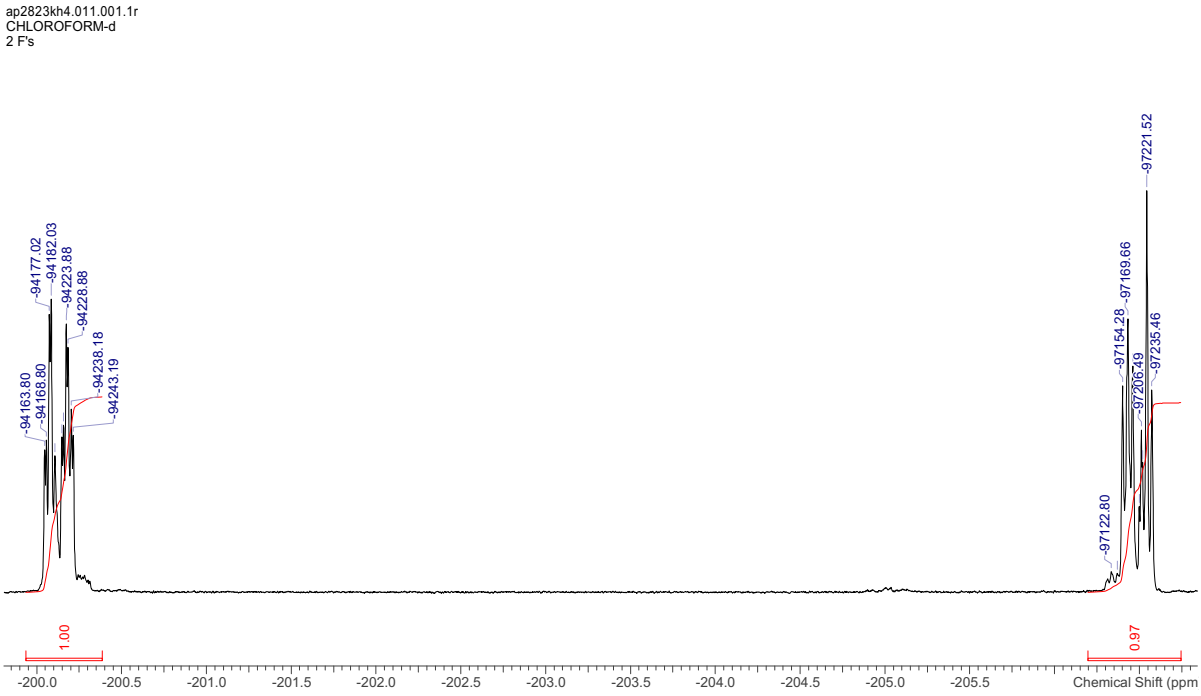


6.7.4.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

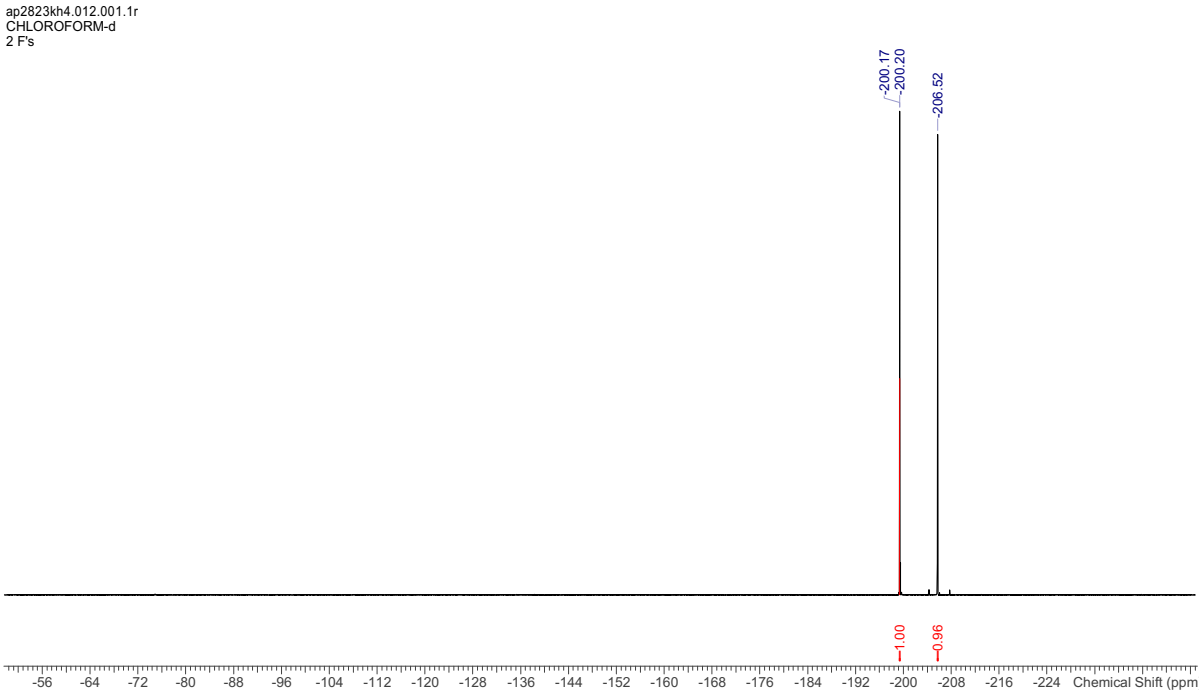


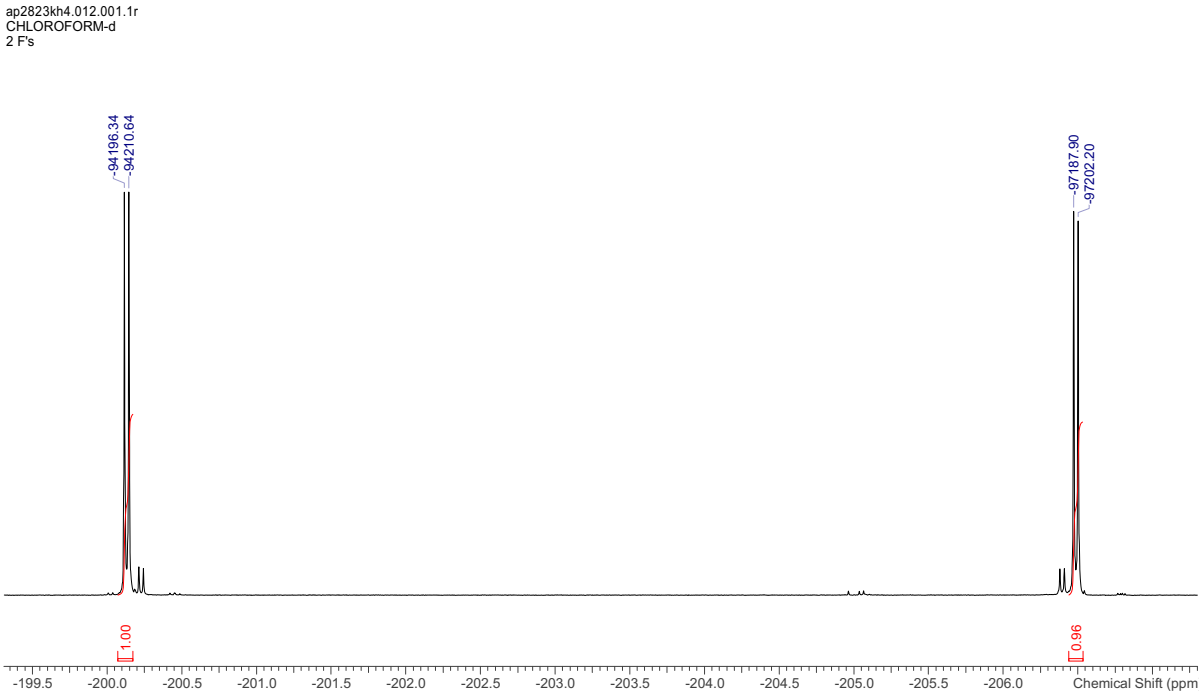
6.7.4.3 ^{19}F NMR, 471 MHz, $CDCl_3$



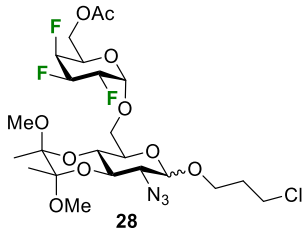


6.7.4.4 $^{19}F\{^{1}H\}$ NMR, 471 MHz, $CDCl_3$



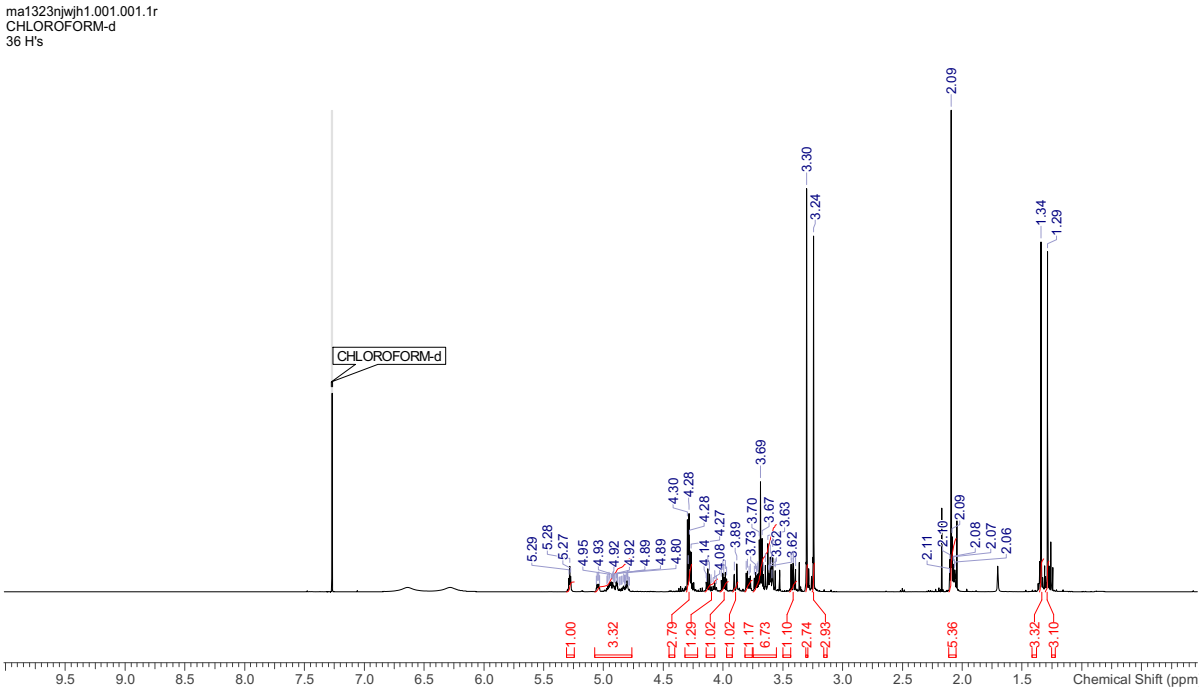


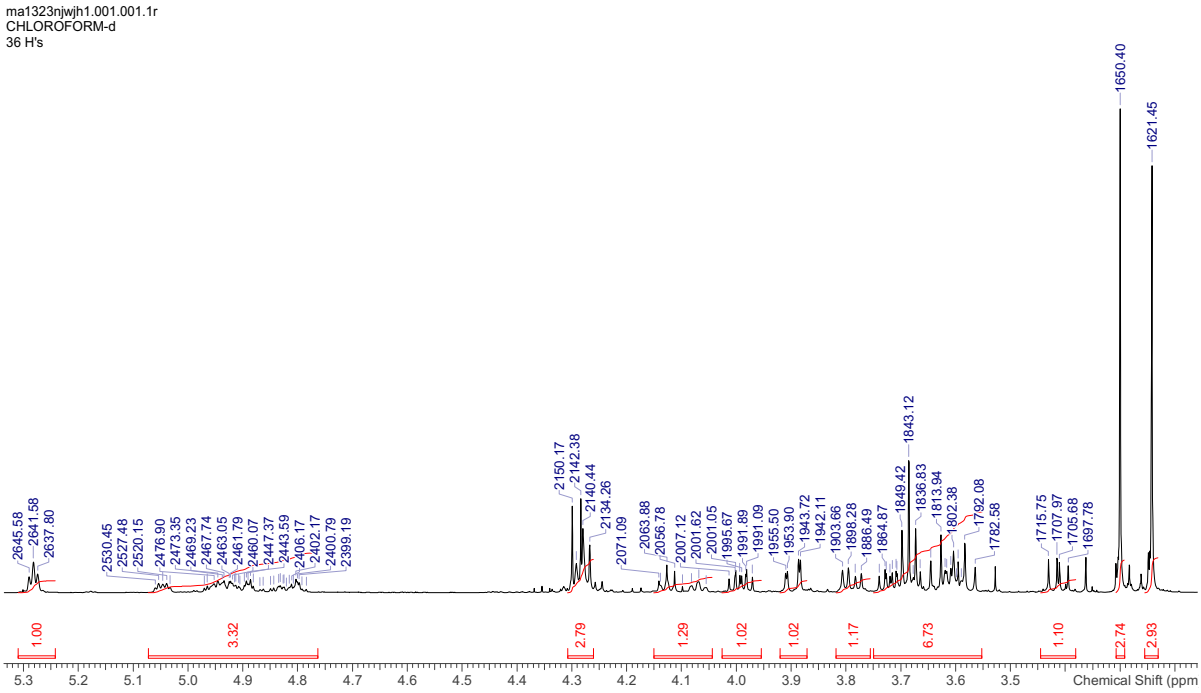
6.7.5 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-3,4-*O*-[(2'S,3'S)-2',3'-dimethoxybutane-2',3'-diyl]-D-glucopyranoside (**28α**)



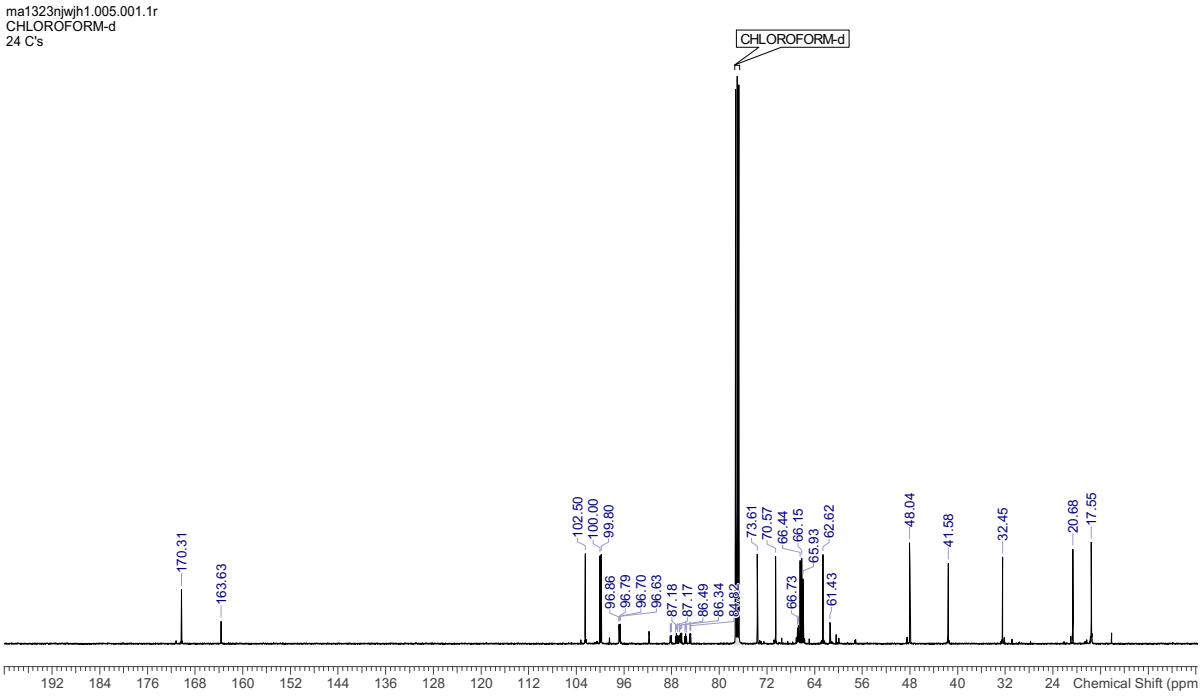
28

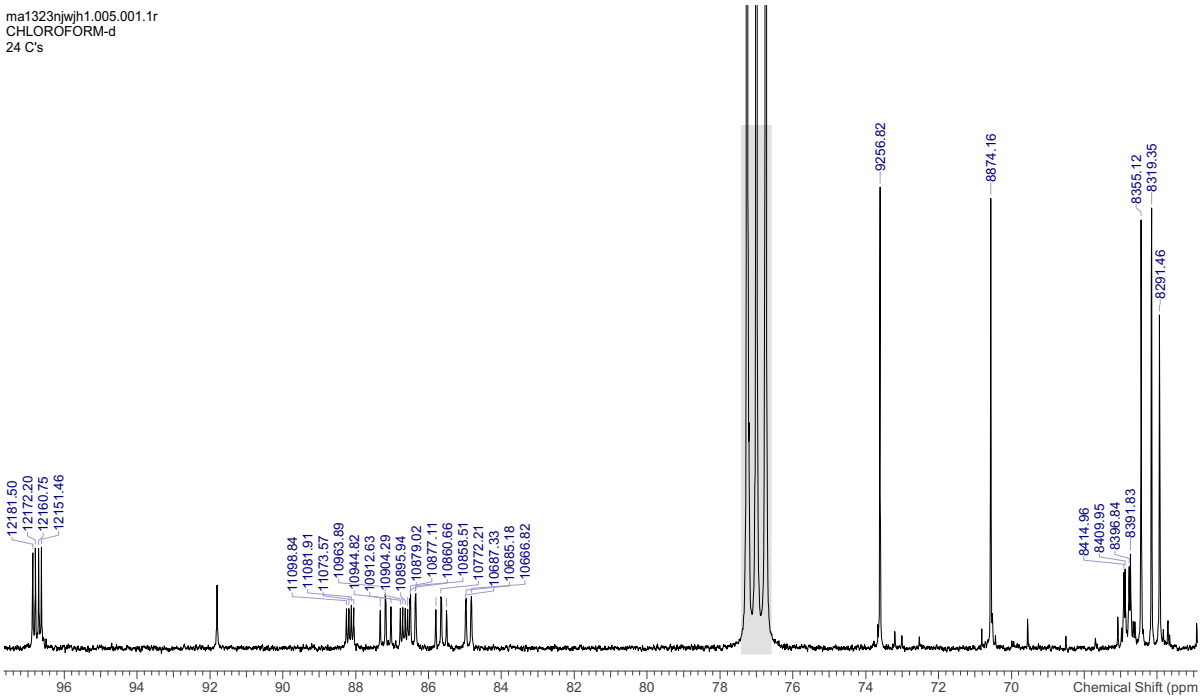
6.7.5.1 ^{1}H NMR, 500 MHz, $CDCl_3$



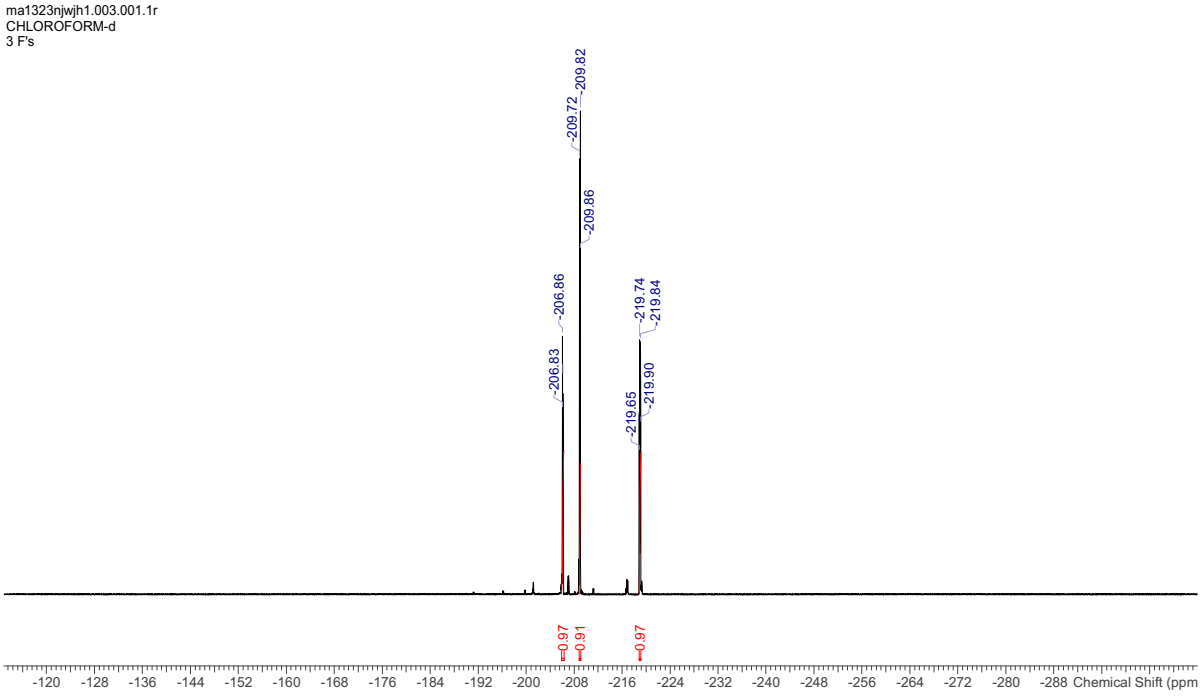


6.7.5.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

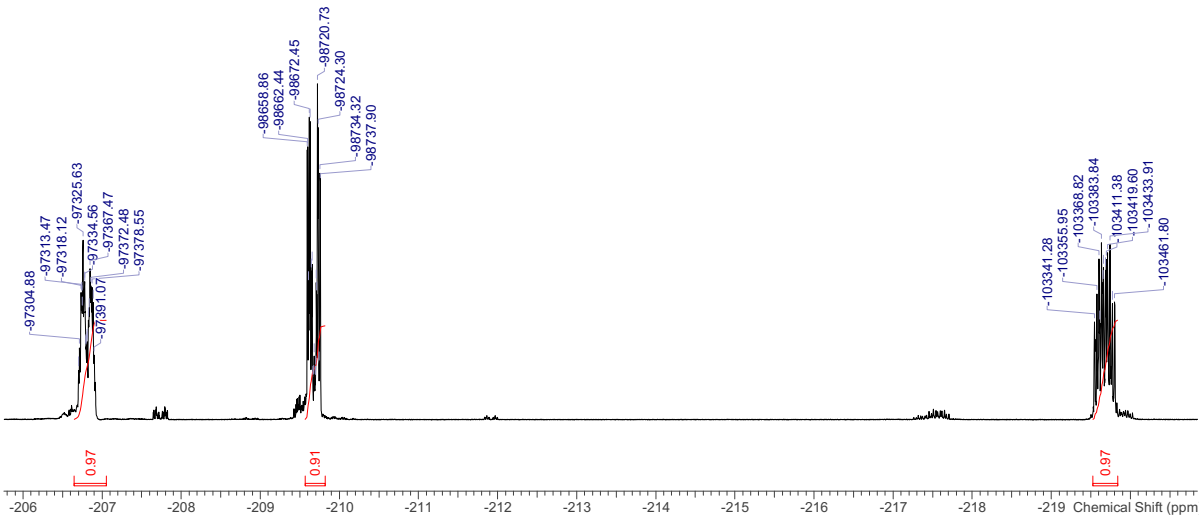




6.7.5.3 ^{19}F NMR, 471 MHz, $CDCl_3$



ma1323njwjh1.003.001.1r
CHLOROFORM-d
3 F's



6.7.5.4 $^{19}F\{^{1}H\}$ NMR, 471 MHz, $CDCl_3$

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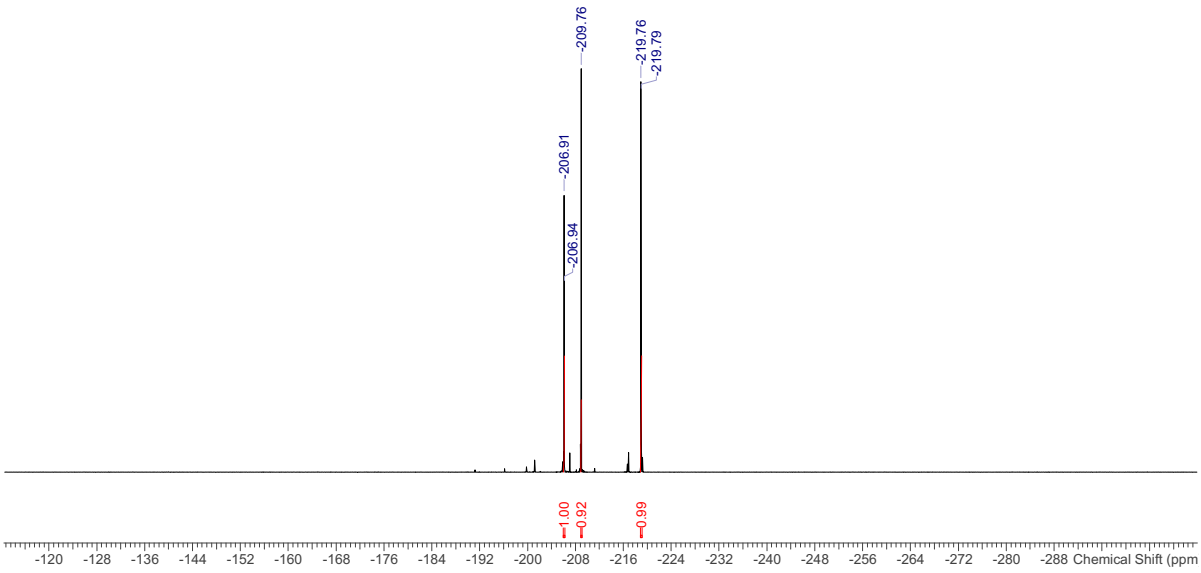
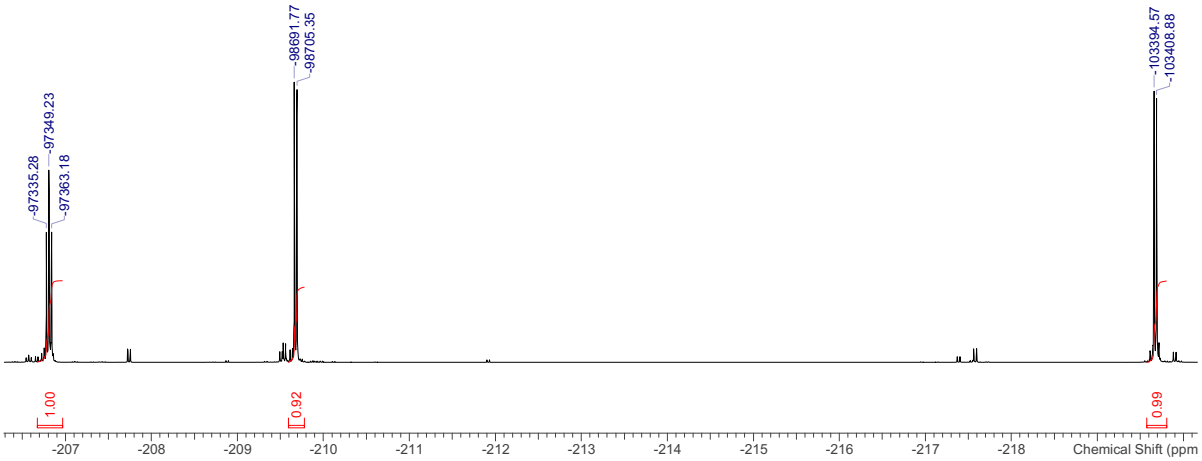
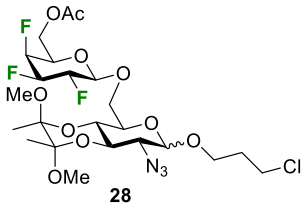
CHLOROFORM-d
3 F's



ma1323njwjh1.002.001.1r
CHLOROFORM-d
3 F's

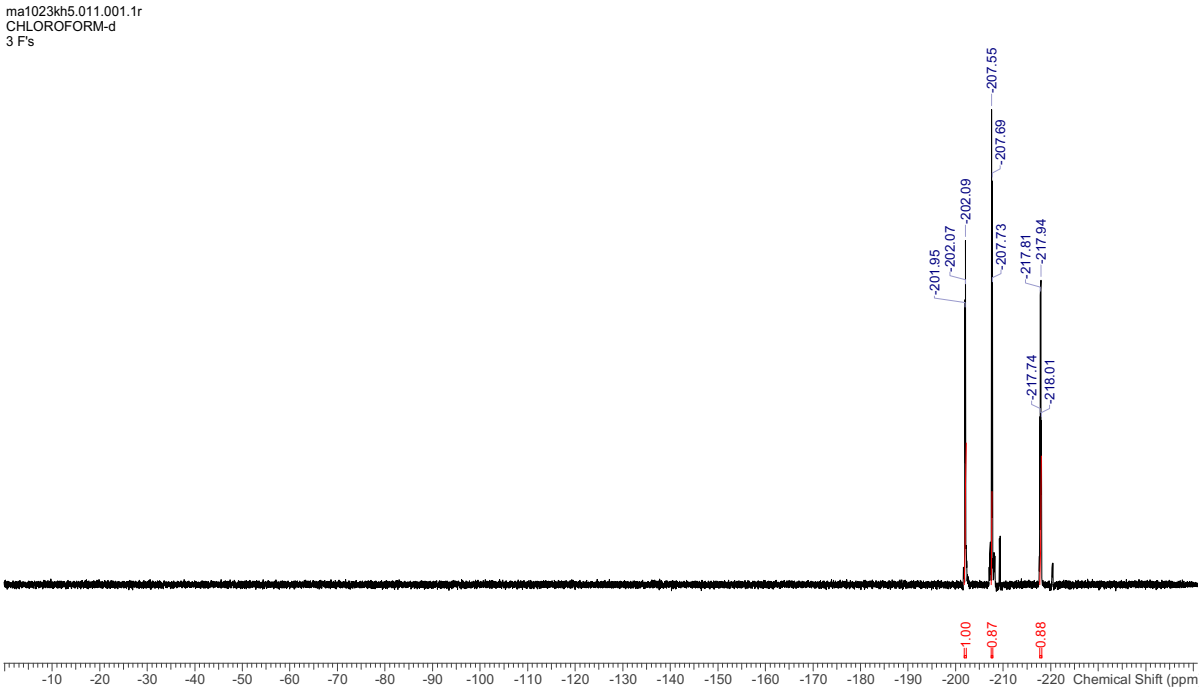


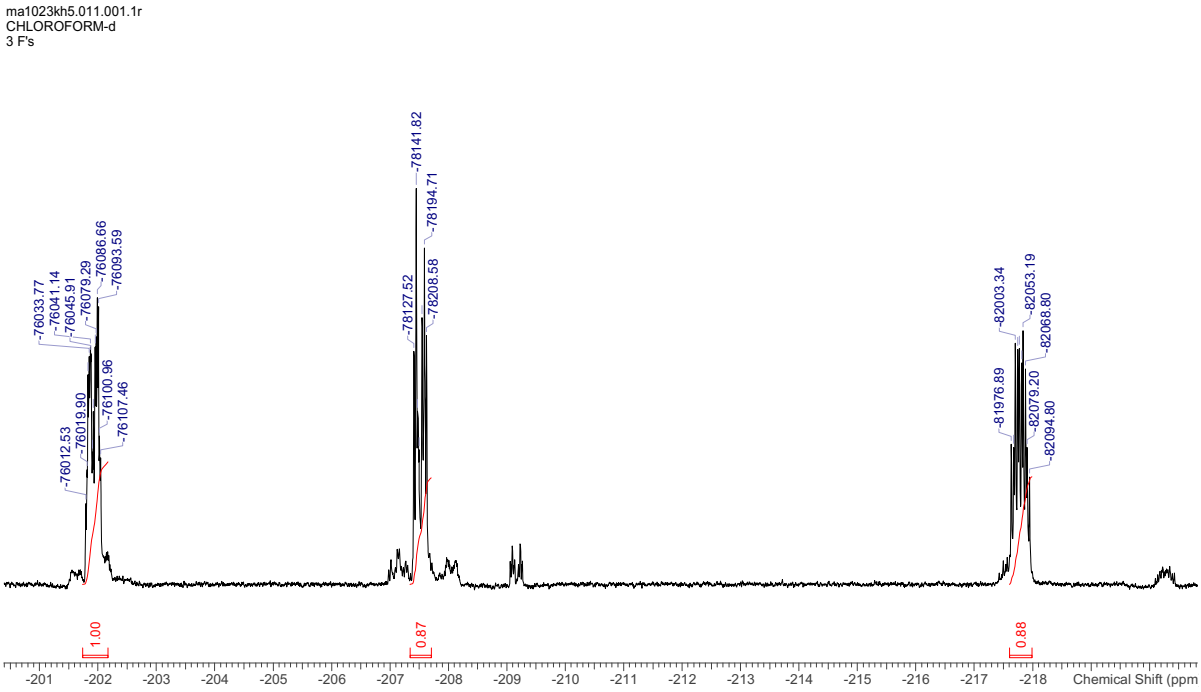
6.7.6 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-β-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-3,4-*O*-[(2'S,3'S)-2',3'-dimethoxybutane-2',3'-diyl]-D-glucopyranoside (**28β**)



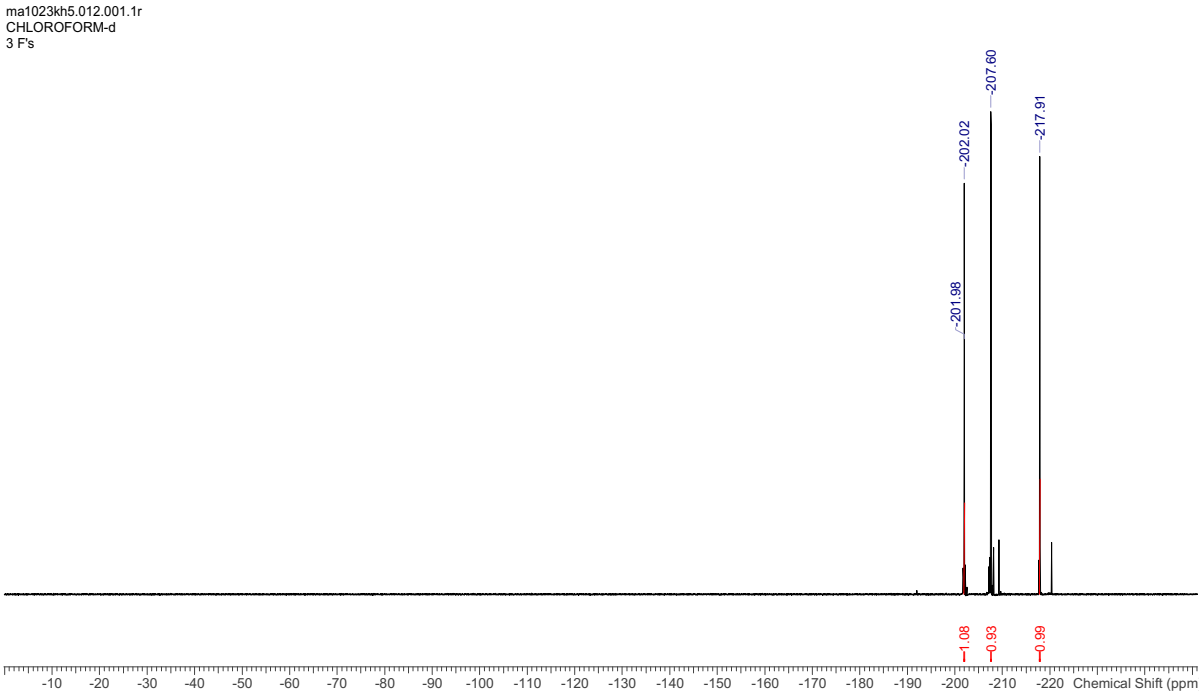
28

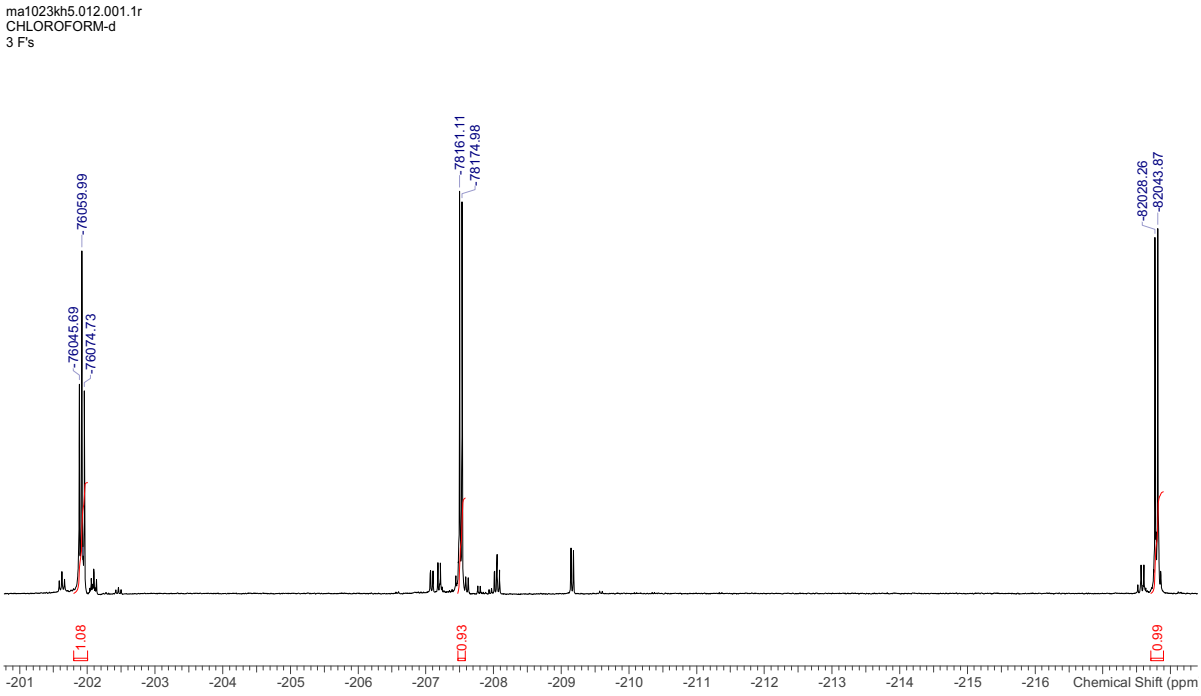
6.7.6.1 ^{19}F NMR, 376 MHz, $CDCl_3$



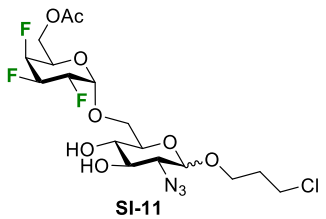


6.7.6.2 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$





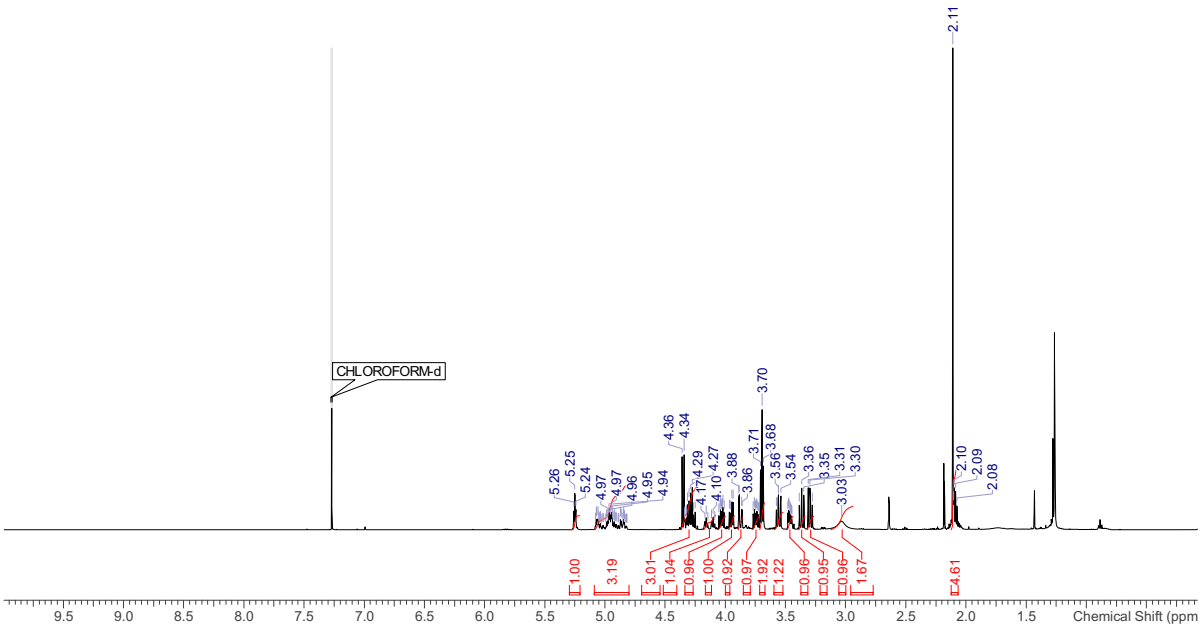
6.7.7 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-D-glucopyranoside (**SI-11**)



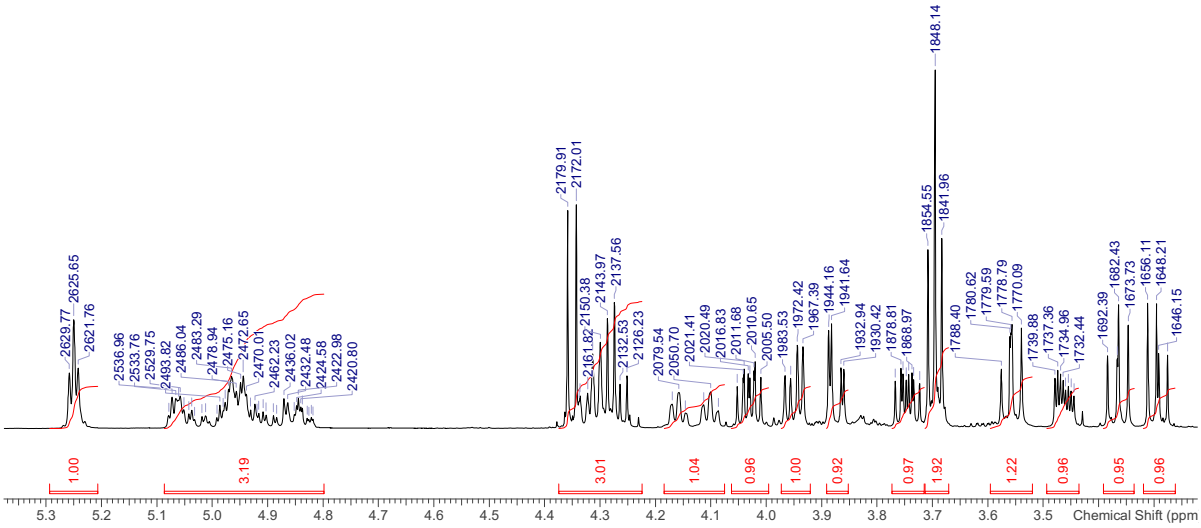
SI-11

6.7.7.1 ^{1}H NMR, 500 MHz, $CDCl_3$

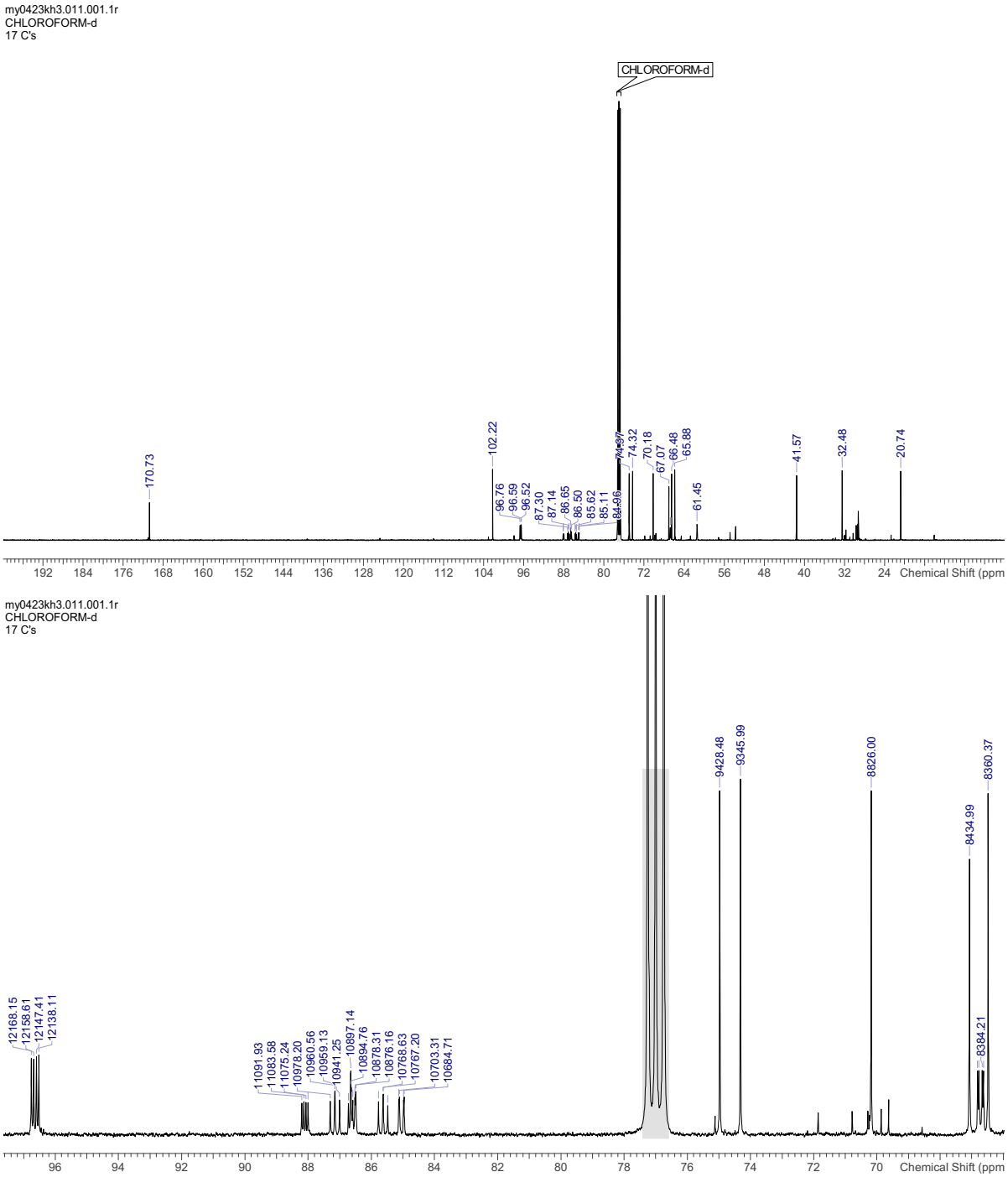
my0423kh3.010.001.1r
CHLOROFORM-d
24 H's



my0423kh3.010.001.1r
CHLOROFORM-d
24 H's

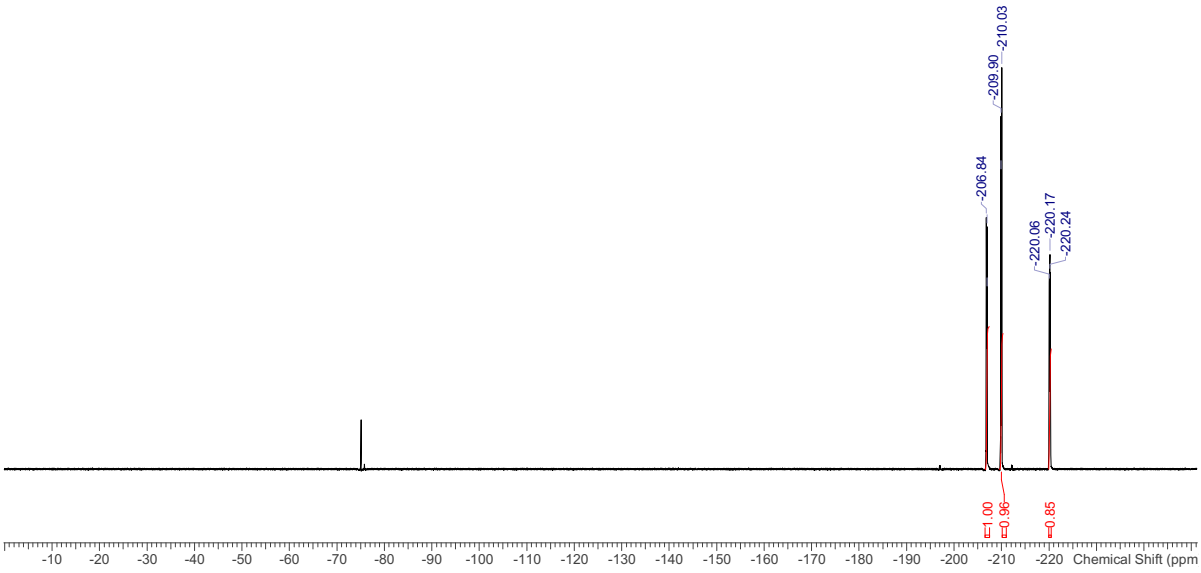


6.7.7.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

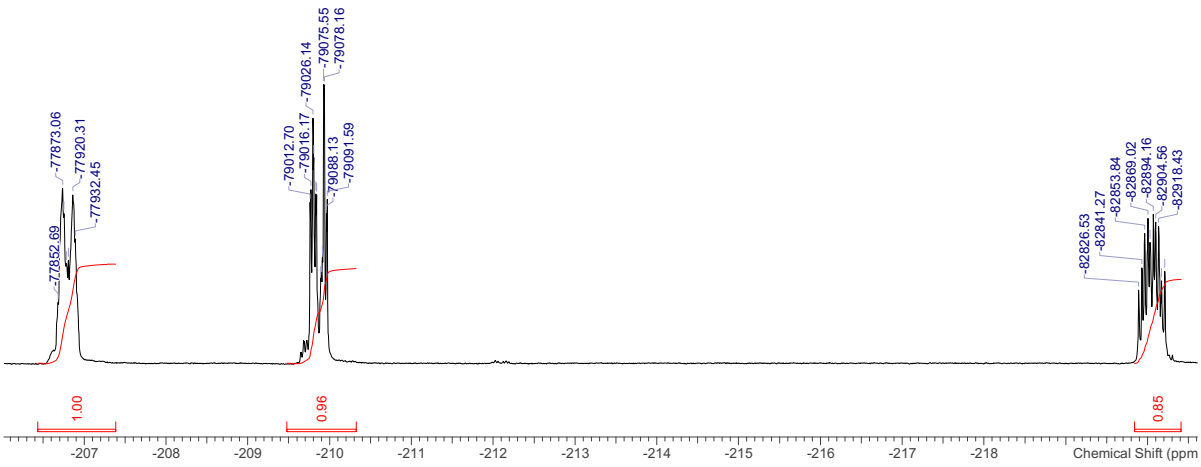


6.7.7.3 ^{19}F NMR, 376 MHz, $CDCl_3$

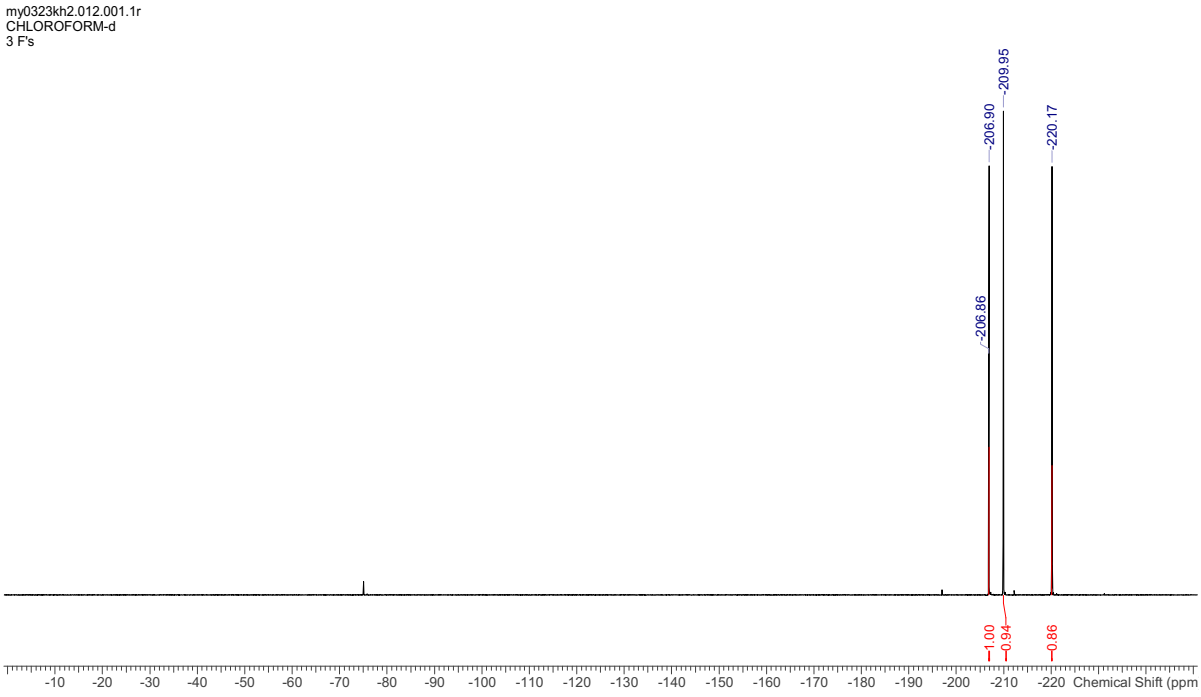
my0323kh2.011.001.1r
CHLOROFORM-d
3 F's

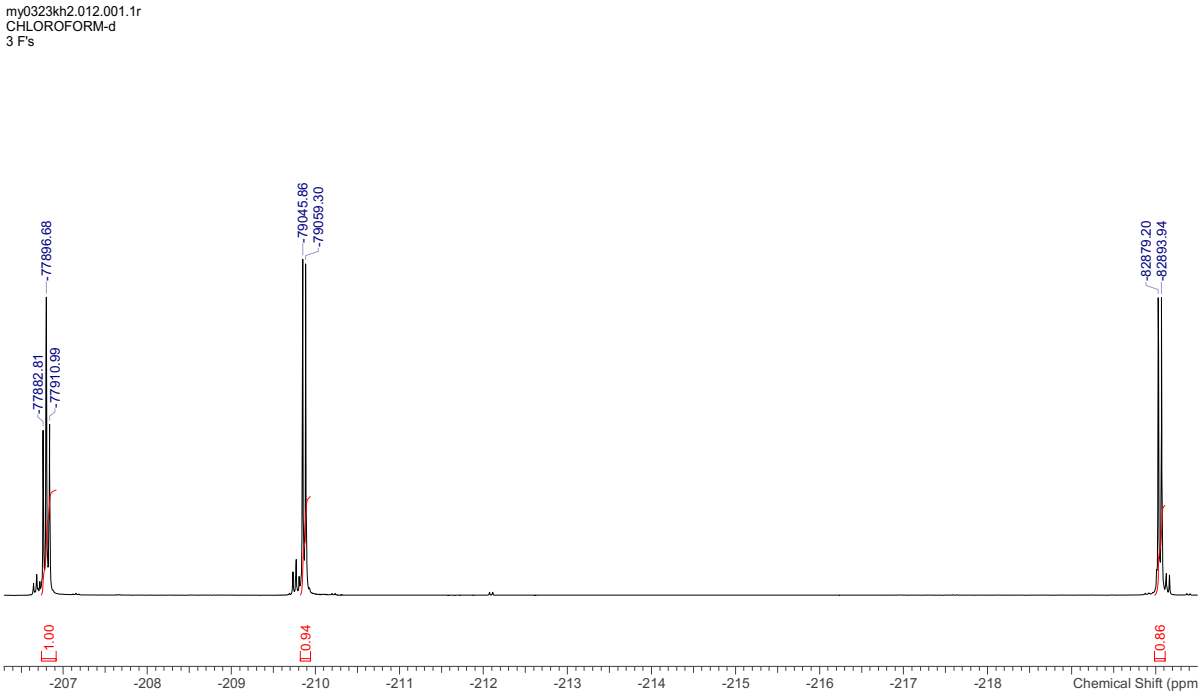


my0323kh2.011.001.1r
CHLOROFORM-d
3 F's

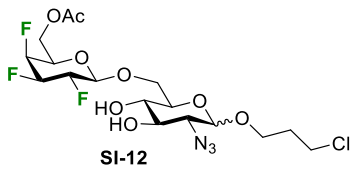


6.7.7.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



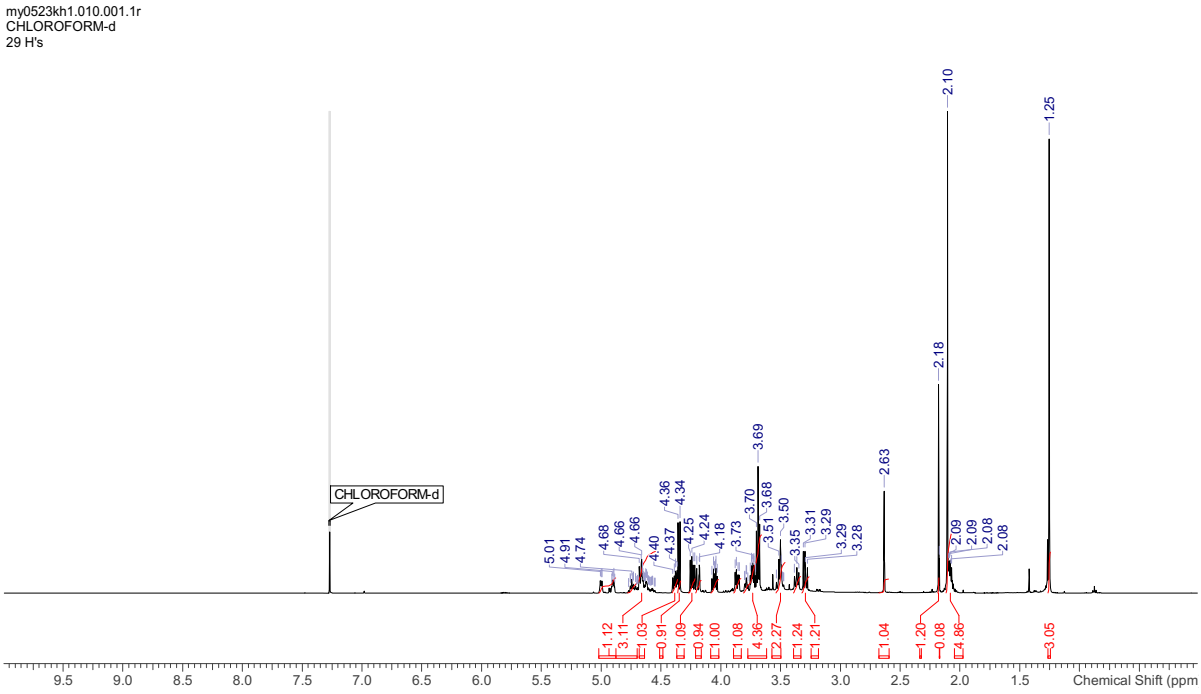


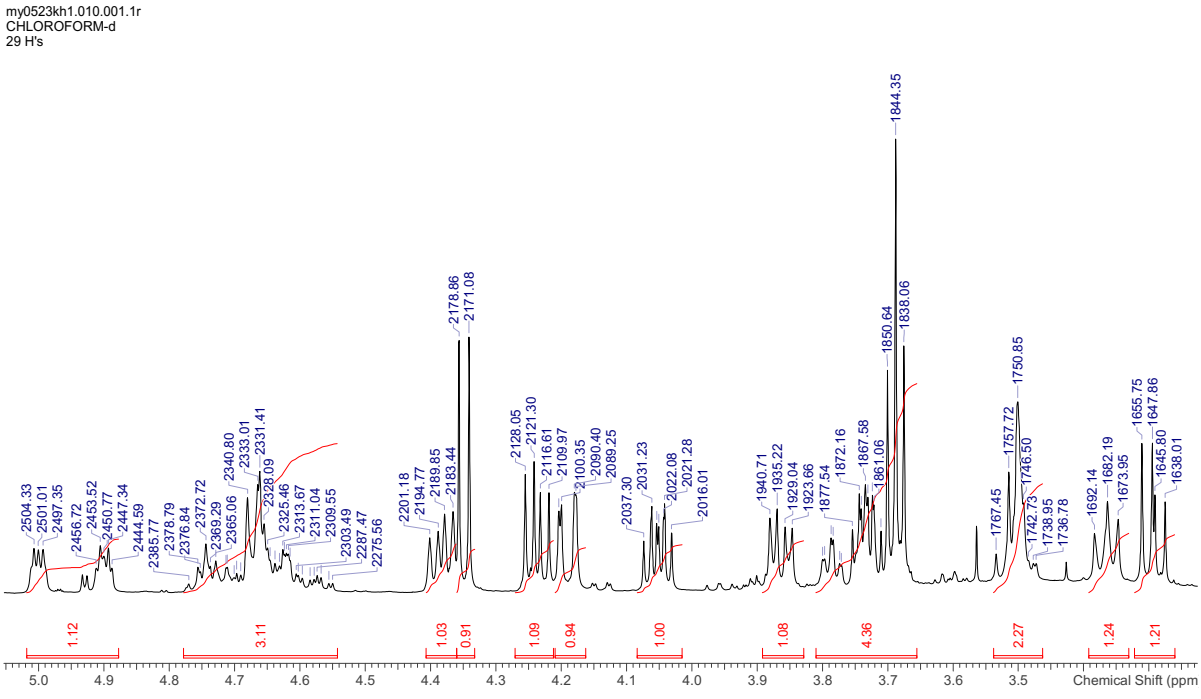
6.7.8 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-β-D-galactopyranosyl-(1,6)-3-chloropropyl 2-deoxy-2-azido-D-glucopyranoside (**SI-12**)



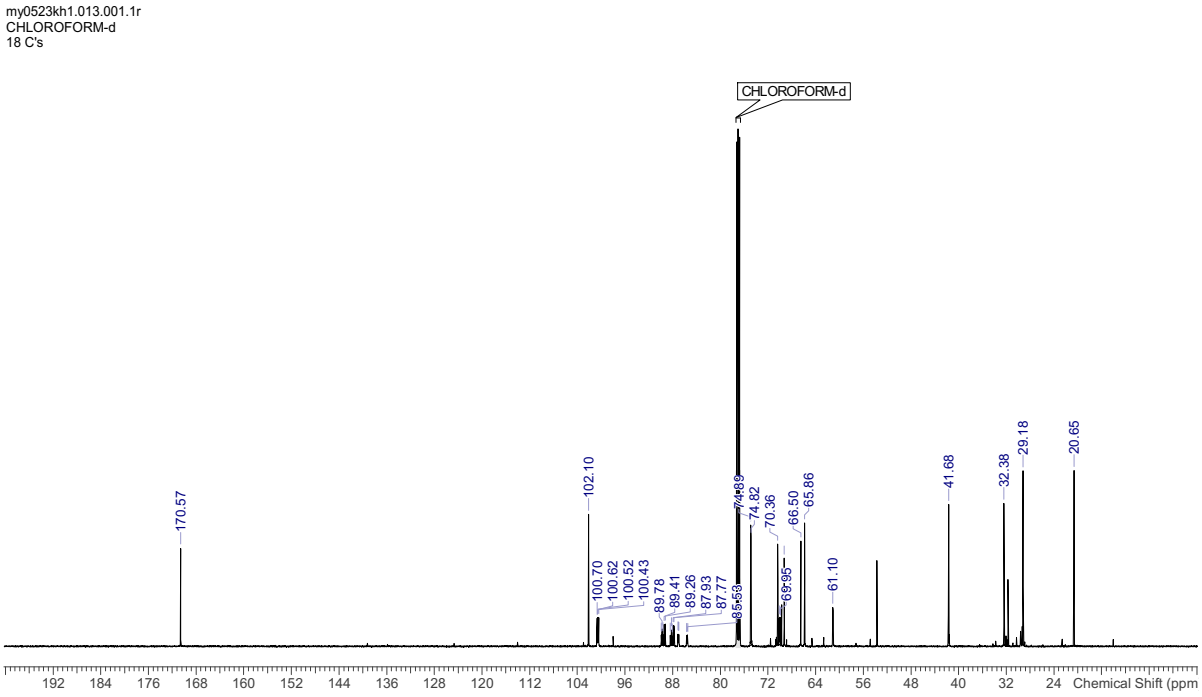
SI-12

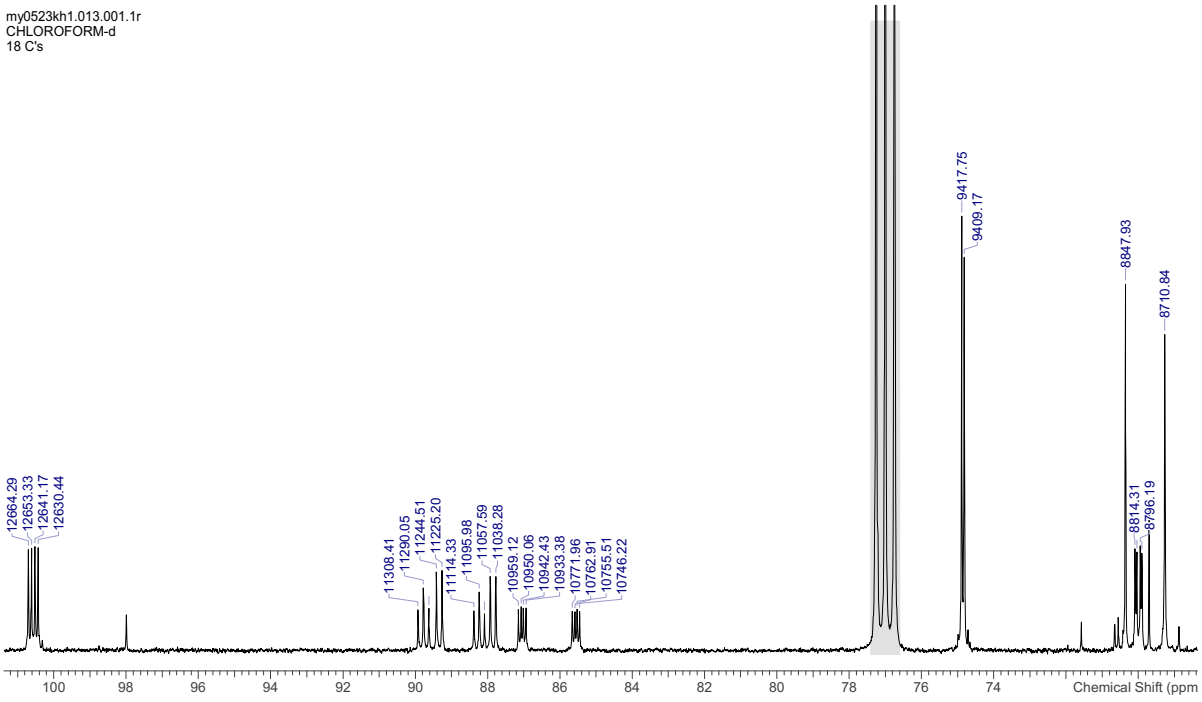
6.7.8.1 ^{1}H NMR, 500 MHz, $CDCl_3$





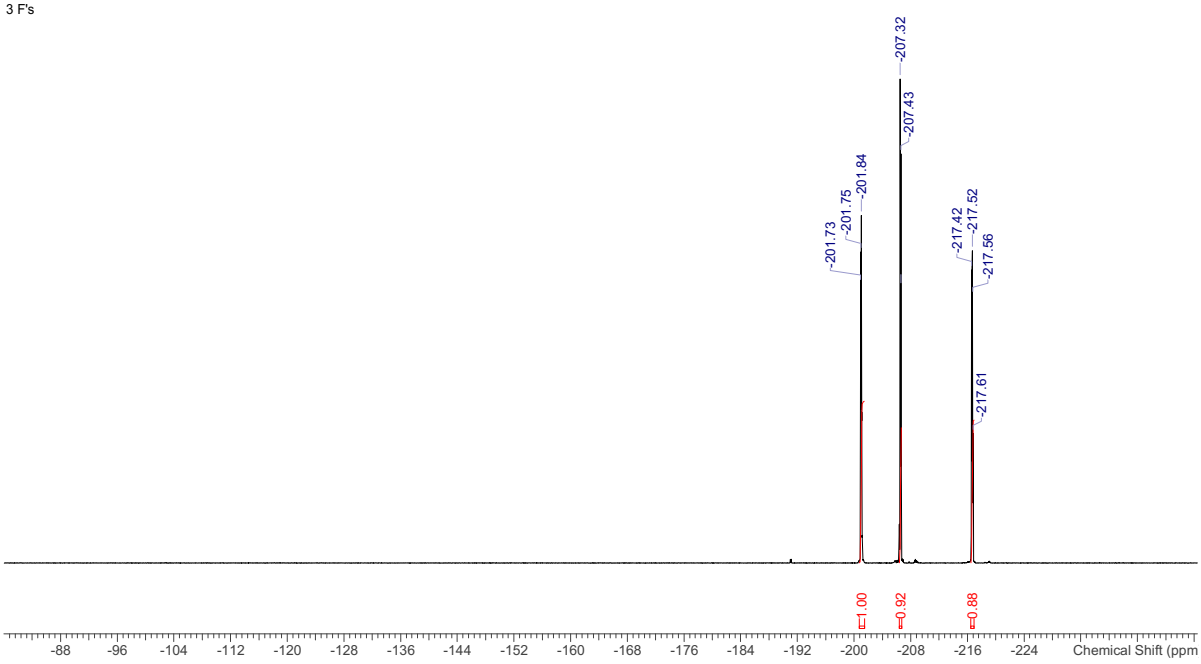
6.7.8.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$



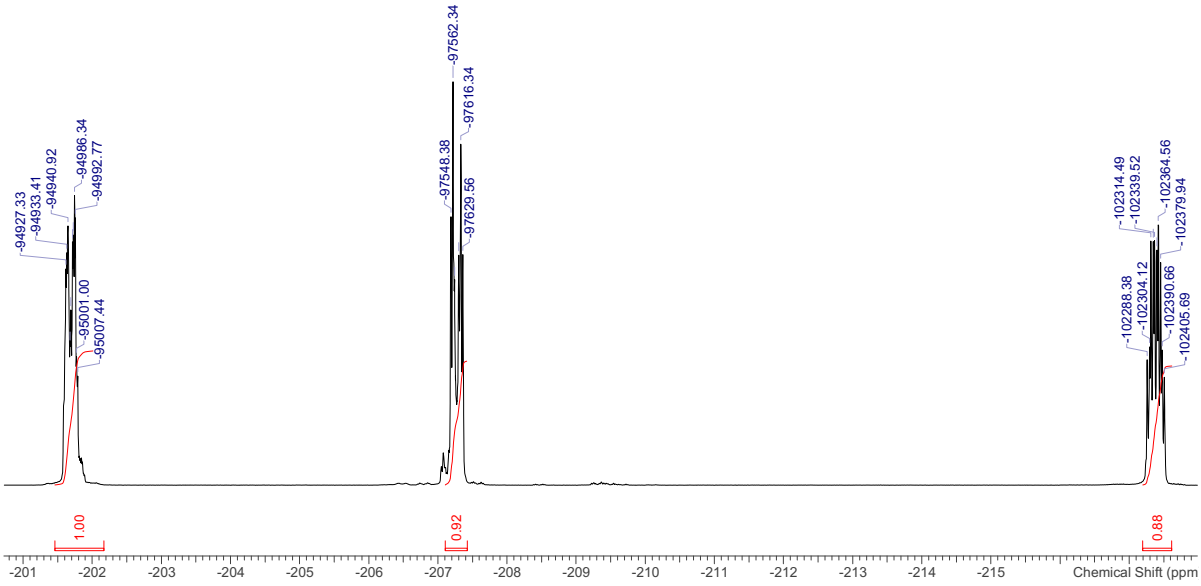


6.7.8.3 ^{19}F NMR, 471 MHz, $CDCl_3$

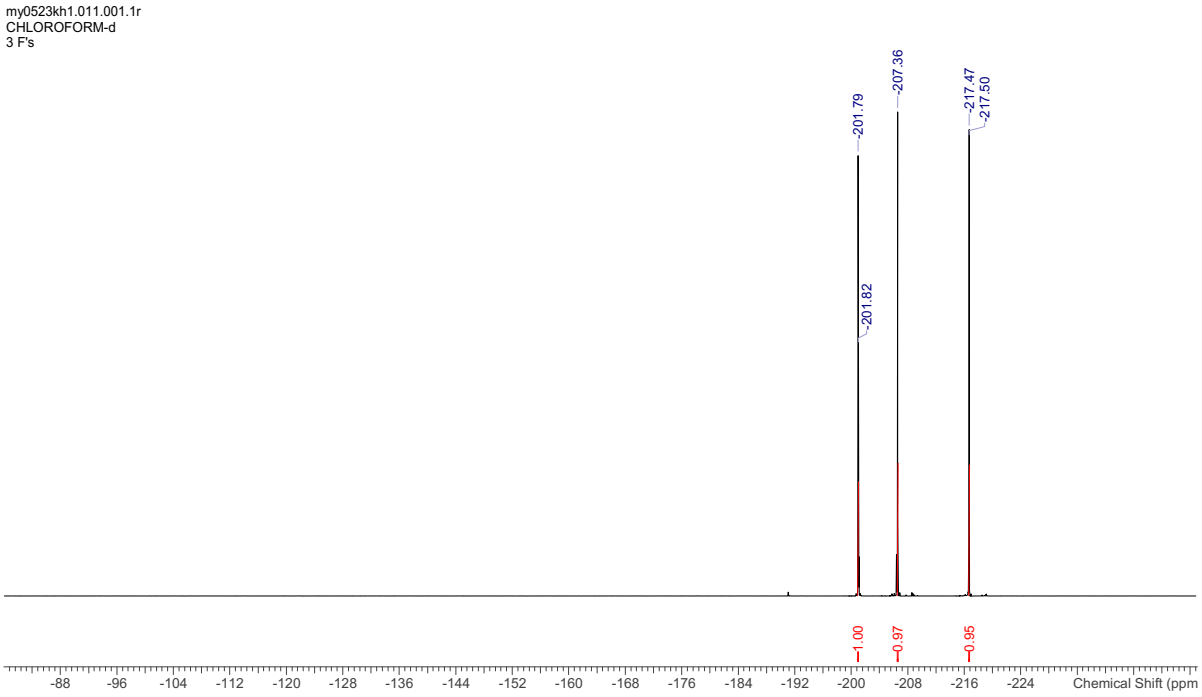
my0523kh1.012.001.1r
CHLOROFORM-d
3 F's

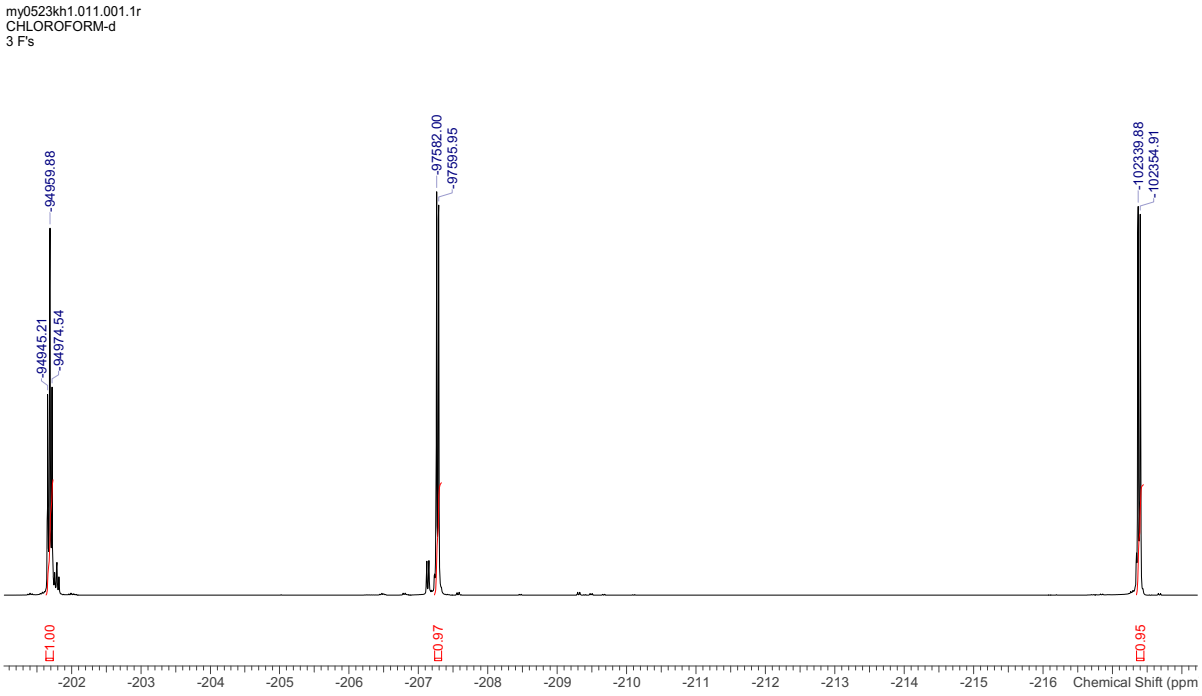


my0523kh1.012.001.1r
CHLOROFORM-d
3 F's



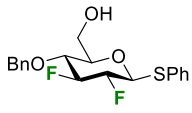
6.7.8.4 $^{19}F\{^{1}H\}$ NMR, 471 MHz, $CDCl_3$





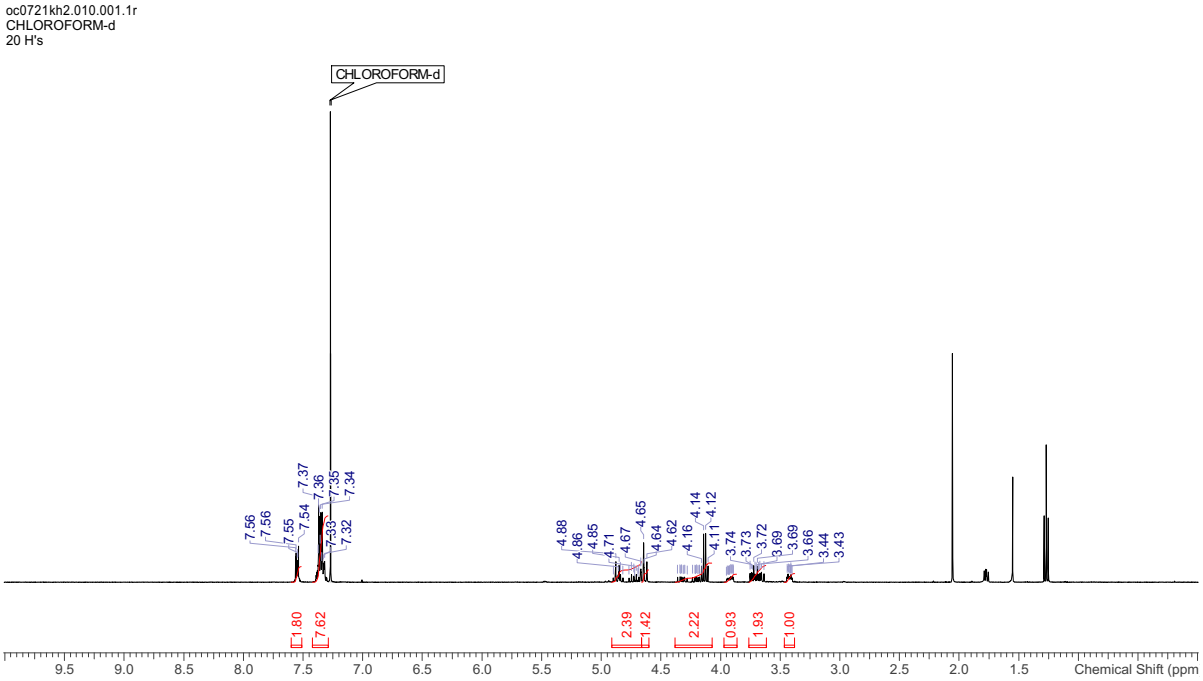
6.8 Copies of the spectra of the glycosylation products with phenyl 4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-1-thio-α-D-glucopyranose

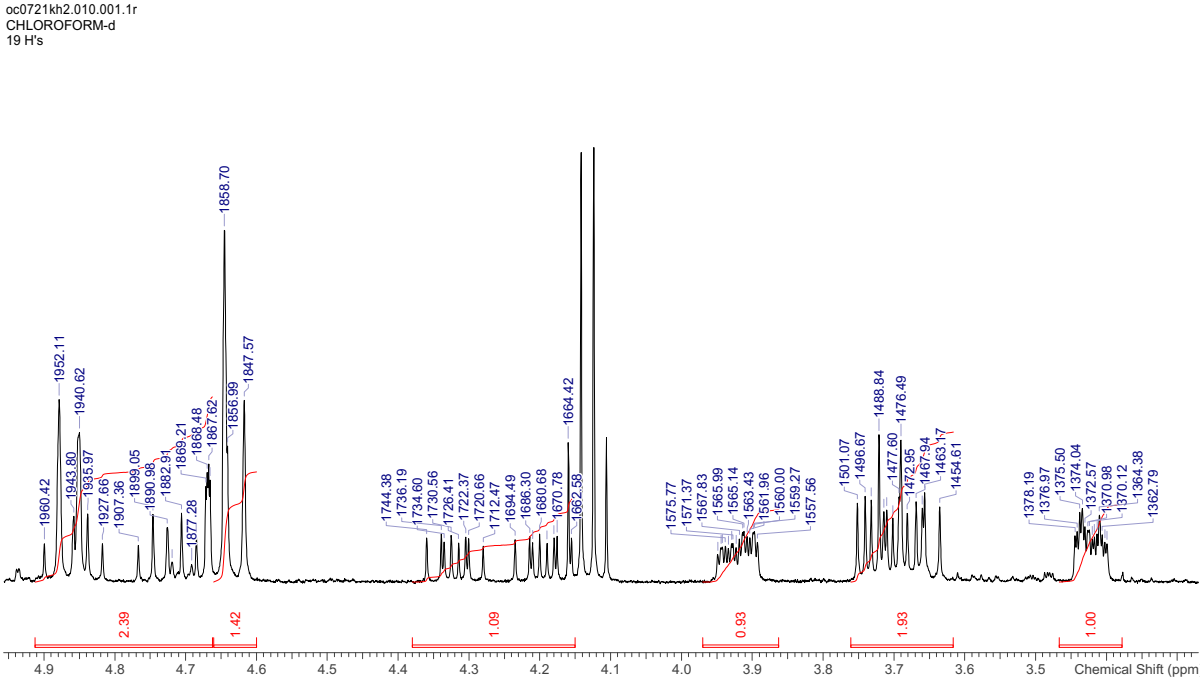
6.8.1 Phenyl 4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-1-thio-β-D-glucopyranose (**SI-14**)



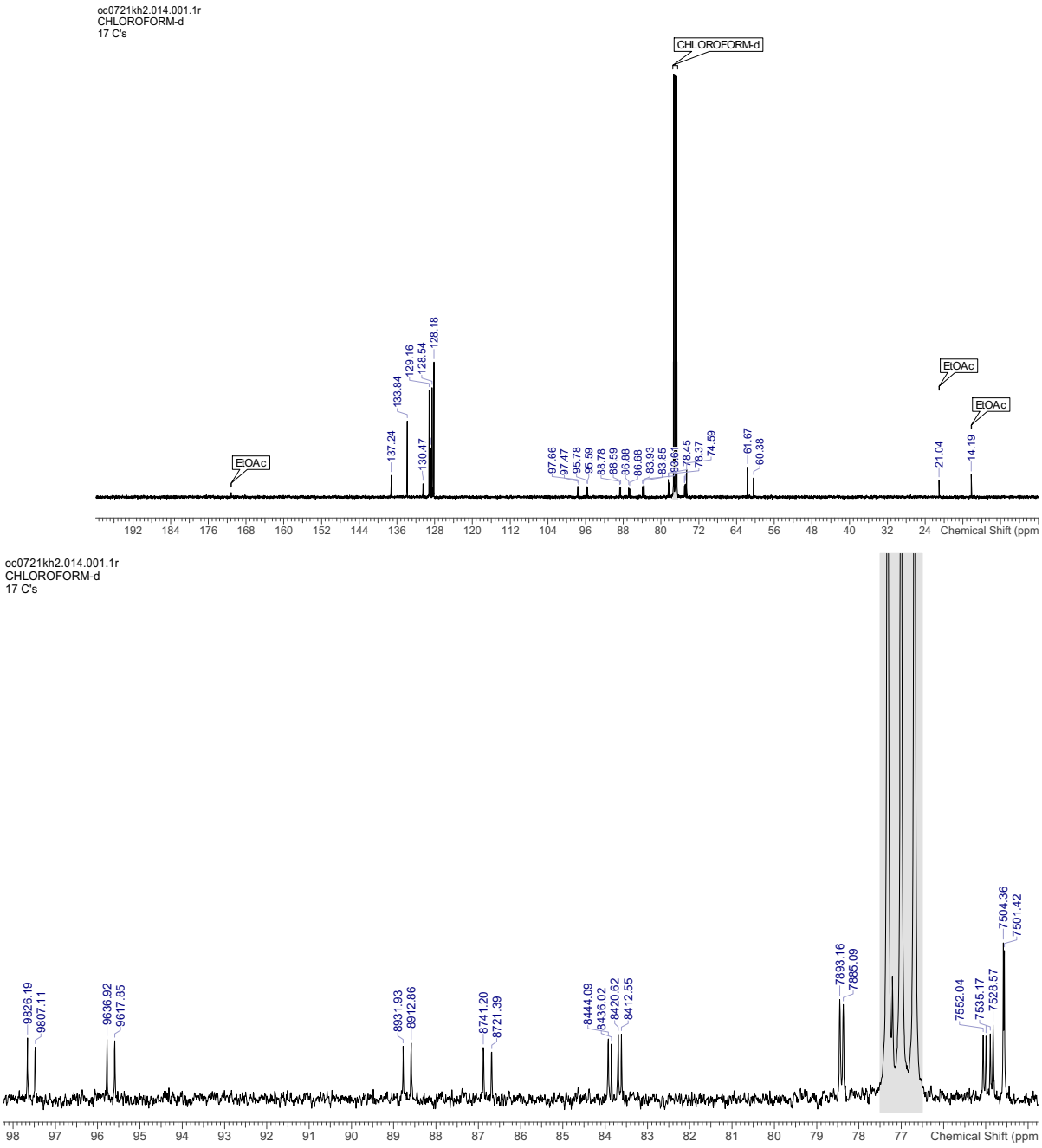
SI-14

6.8.1.1 ^{1}H NMR, 400 MHz, $CDCl_3$



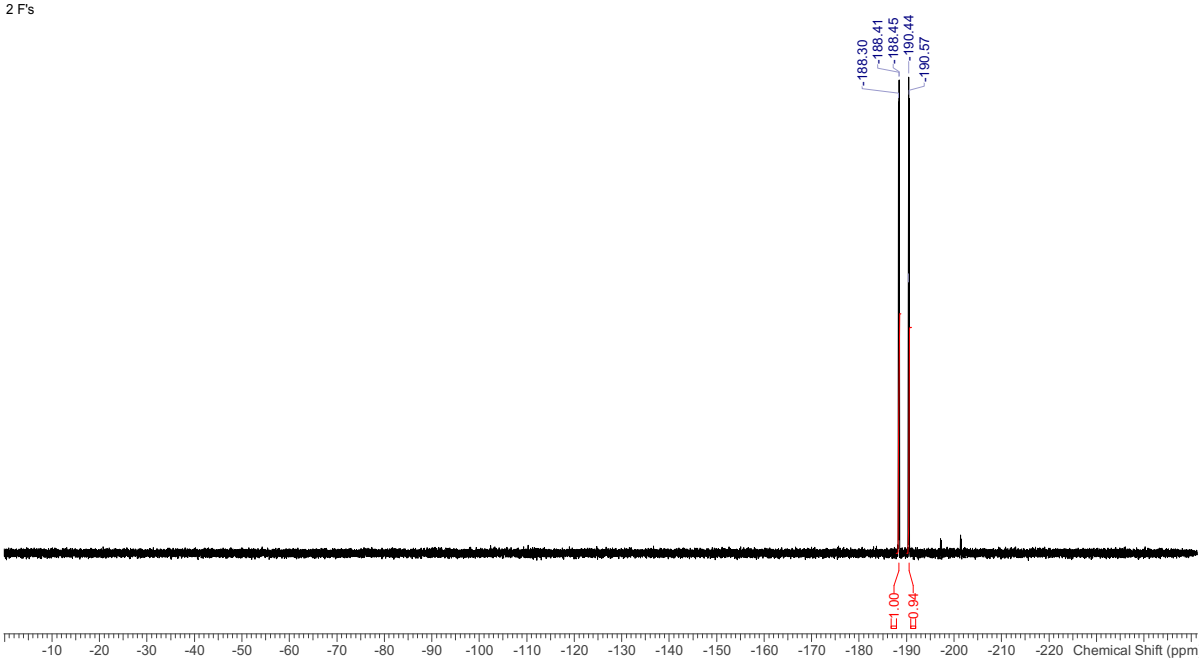


6.8.1.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

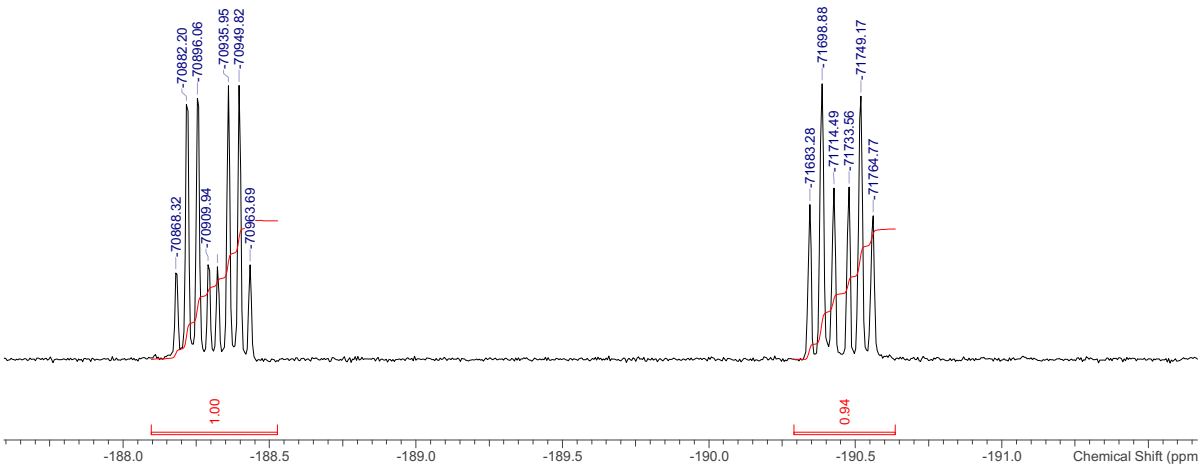


6.8.1.3 ^{19}F NMR, 376 MHz, $CDCl_3$

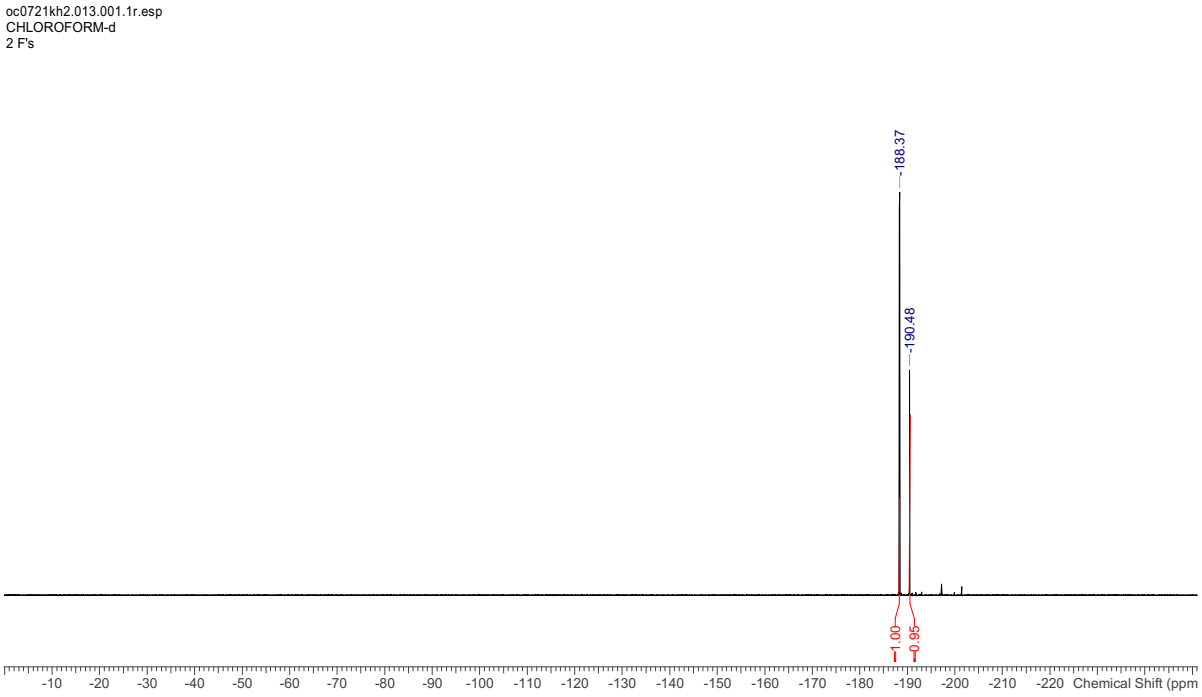
oc0721kh2.012.001.1r
CHLOROFORM-d
2 F's

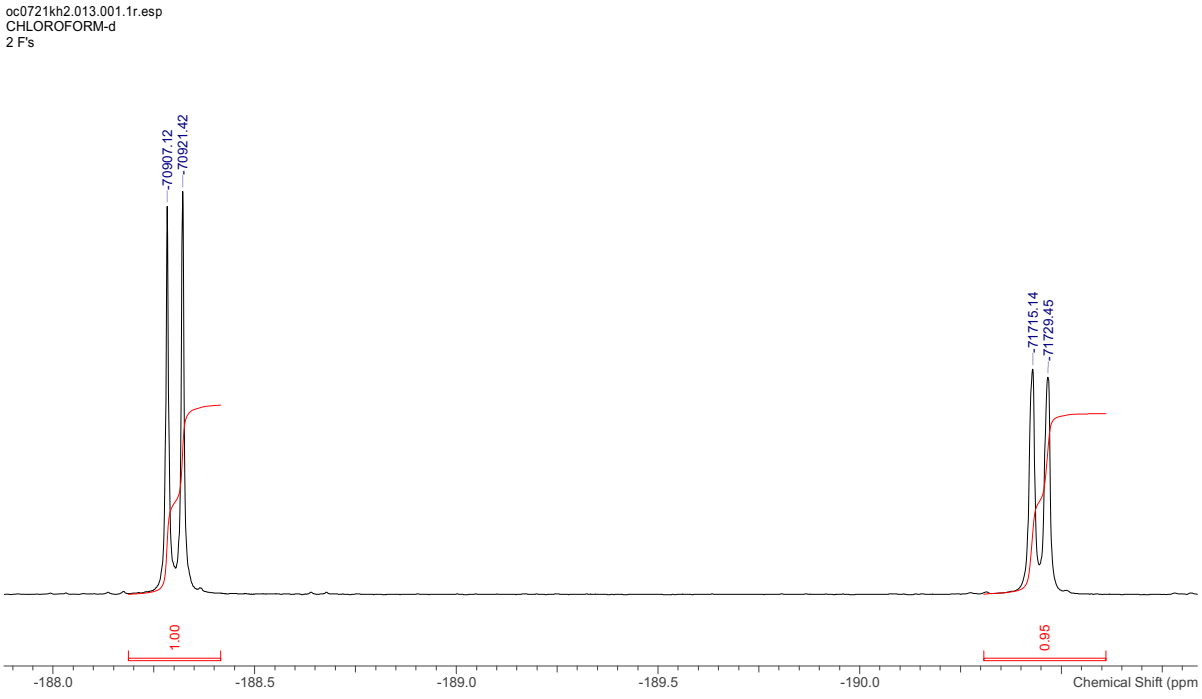


oc0721kh2.012.001.1r
CHLOROFORM-d
2 F's

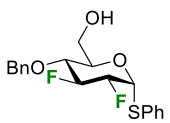


6.8.1.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$





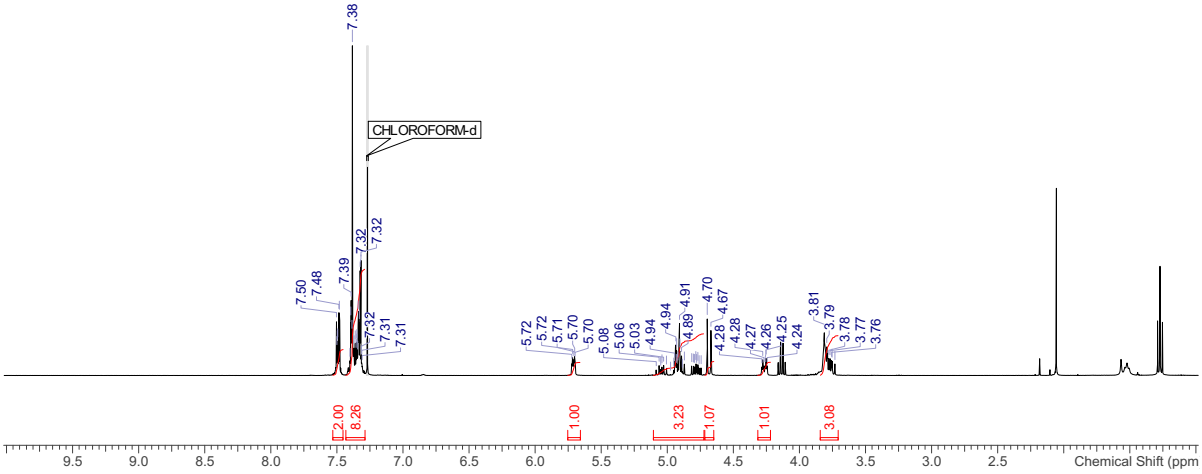
6.8.2 phenyl 4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-1-thio-α-D-glucopyranose (**SI-15**)



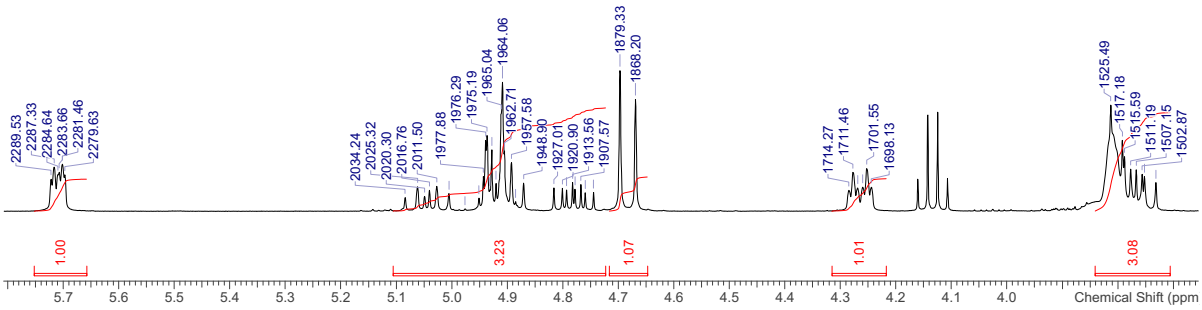
SI-15

6.8.2.1 ^{1}H NMR, 400 MHz, $CDCl_3$

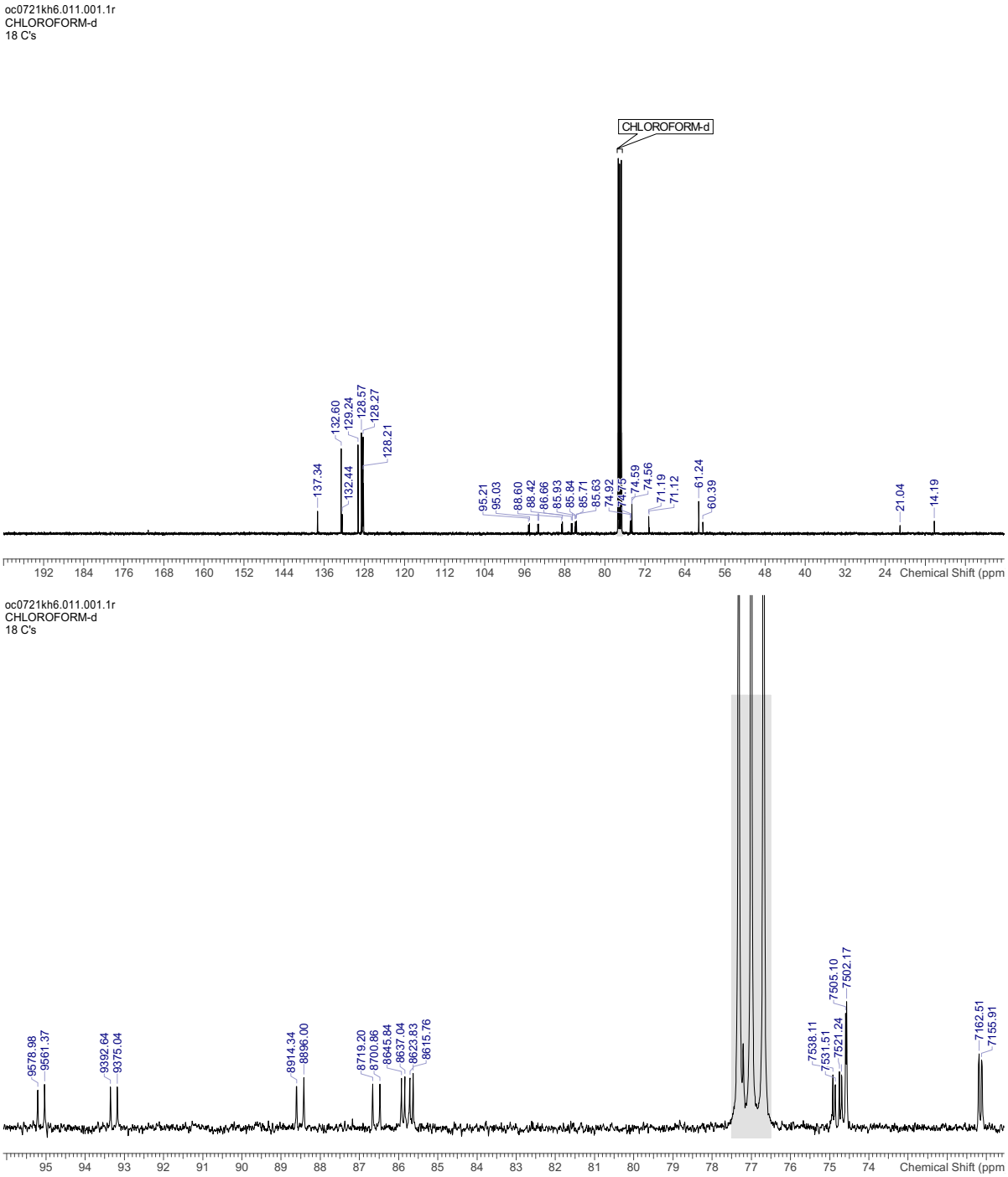
oc0721kh6.010.001.1r
CHLOROFORM-d
19 H's



oc0721kh6.010.001.1r
CHLOROFORM-d
19 H's

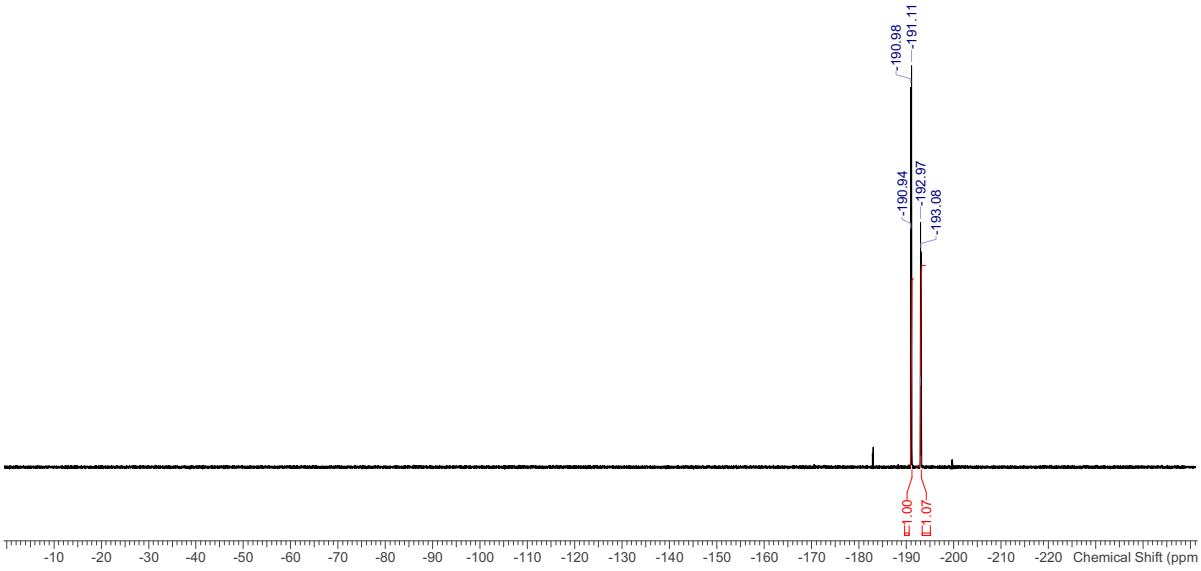


6.8.2.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

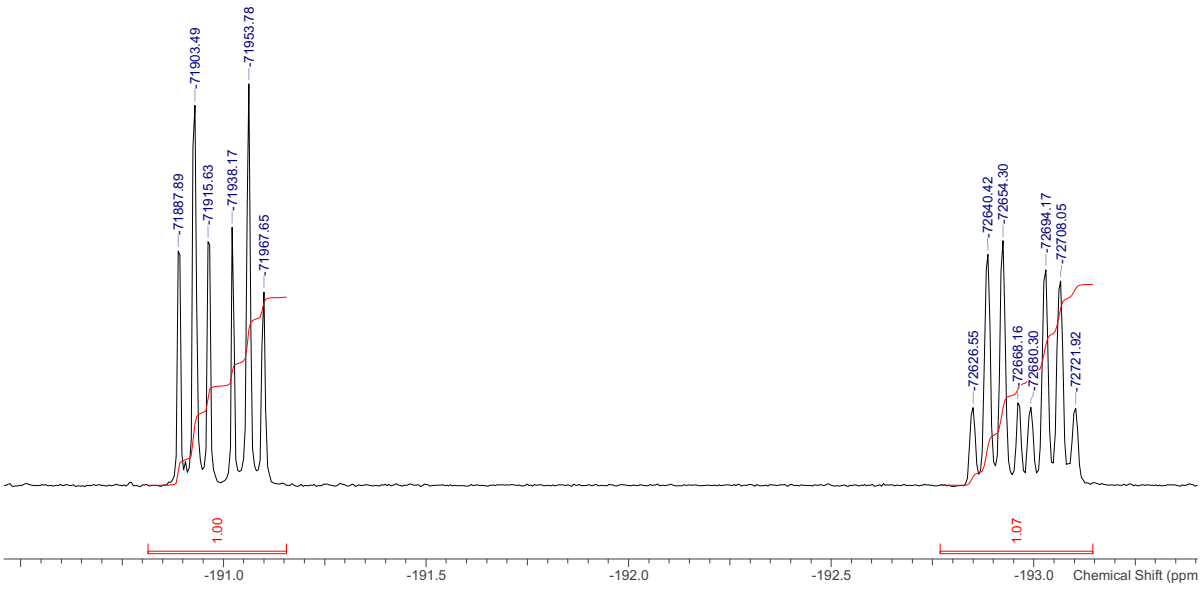


6.8.2.3 ^{19}F NMR, 376 MHz, $CDCl_3$

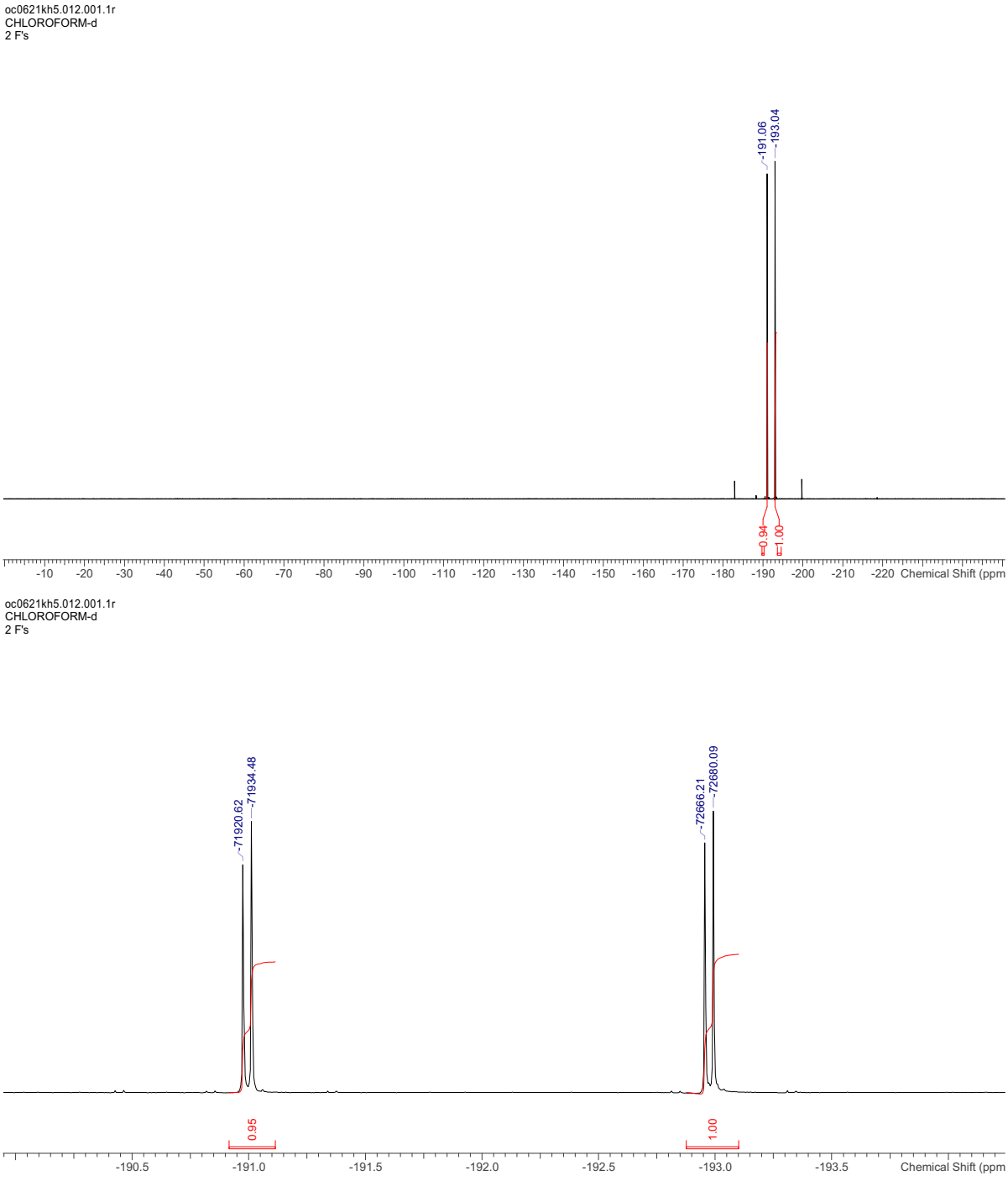
oc0621kh5.011.001.1r
CHLOROFORM-d
2 F's



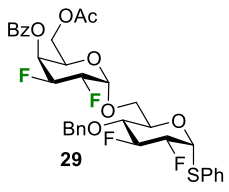
oc0621kh5.011.001.1r
CHLOROFORM-d
2 F's



6.8.2.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



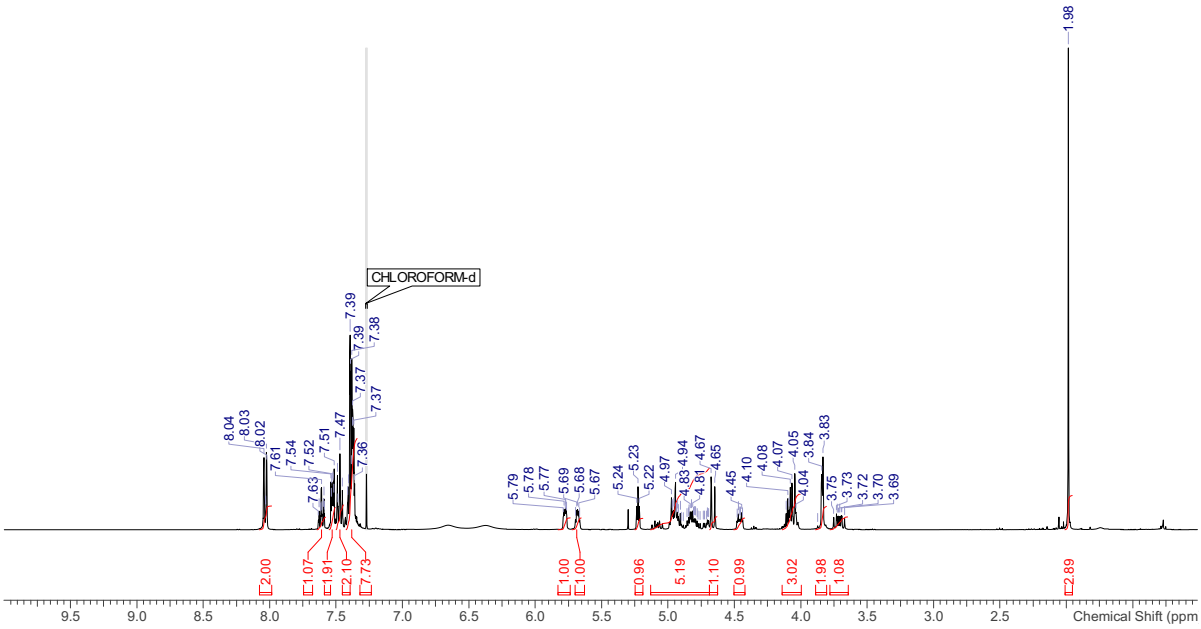
6.8.3 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-α-D-galactopyranosyl-(1,6)-phenyl 4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-1-thio-α-D-glucopyranose (**29α**)



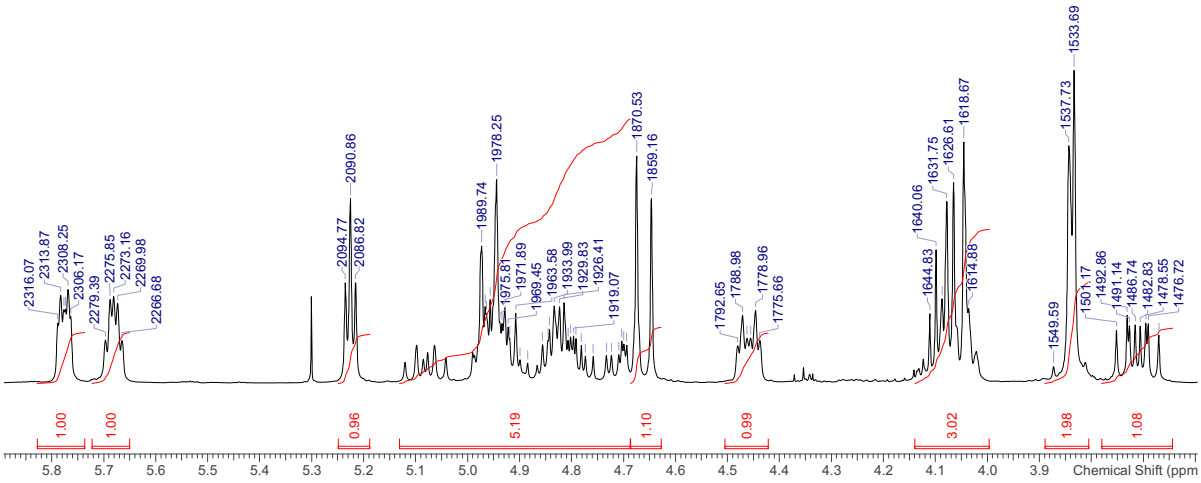
29

6.8.3.1 ^{1}H NMR, 400 MHz, $CDCl_3$

ap2423kh1.010.001.1r
CHLOROFORM-d
33 H's

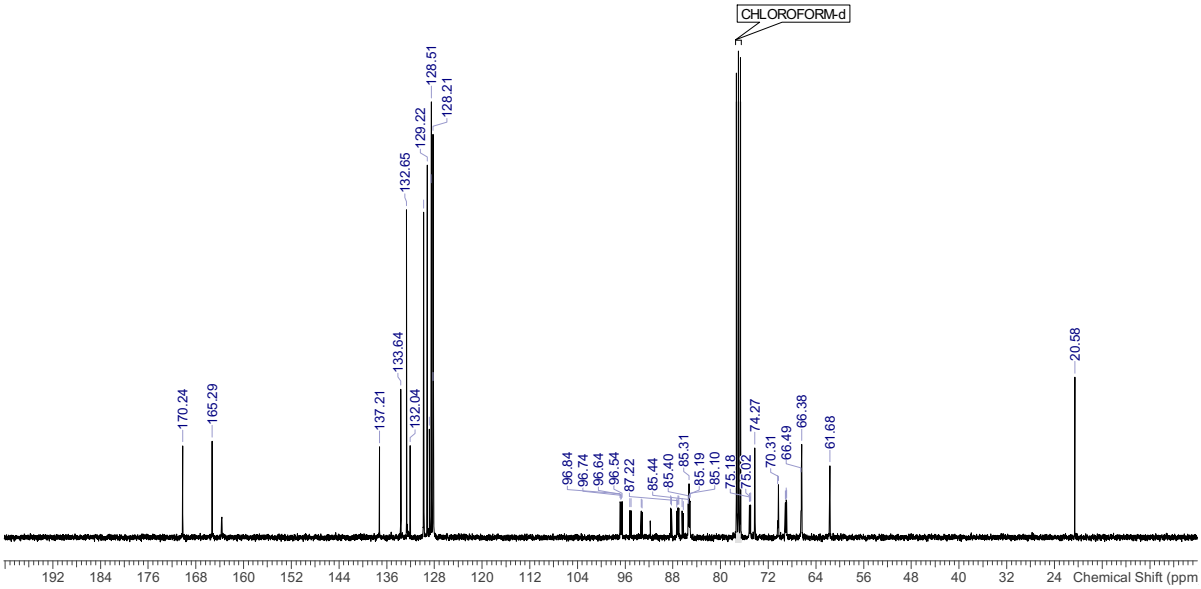


ap2423kh1.010.001.1r
CHLOROFORM-d
33 H's

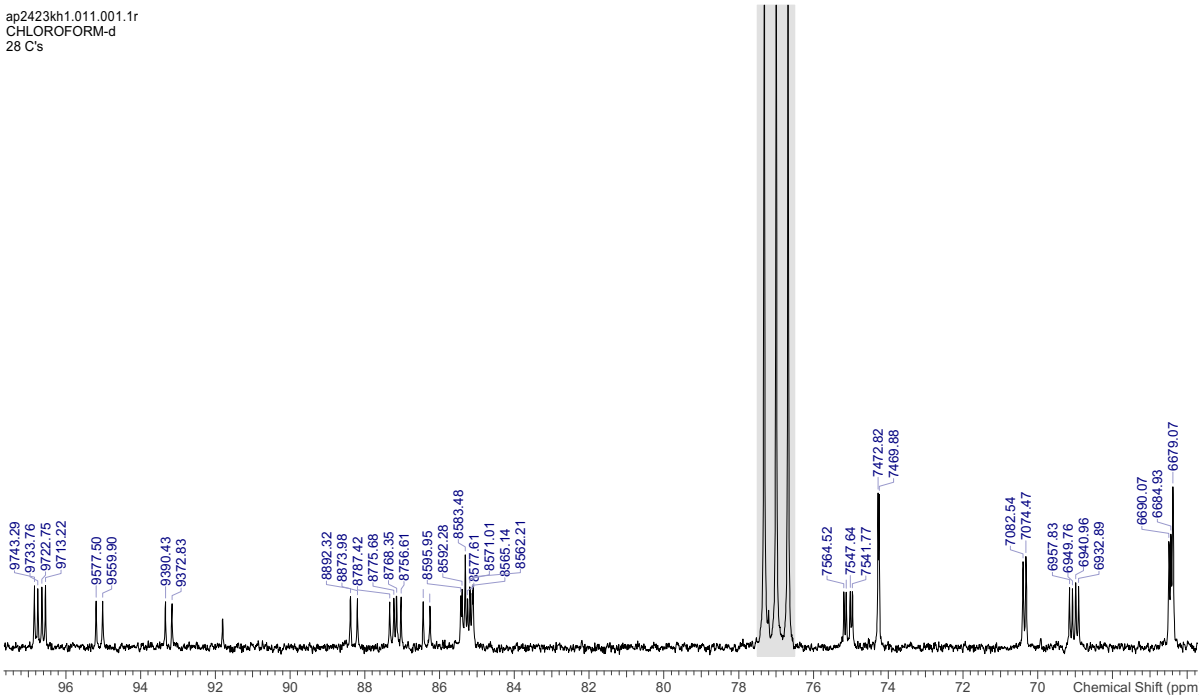


6.8.3.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

ap2423kh1.011.001.1r
CHLOROFORM-d
28 C's

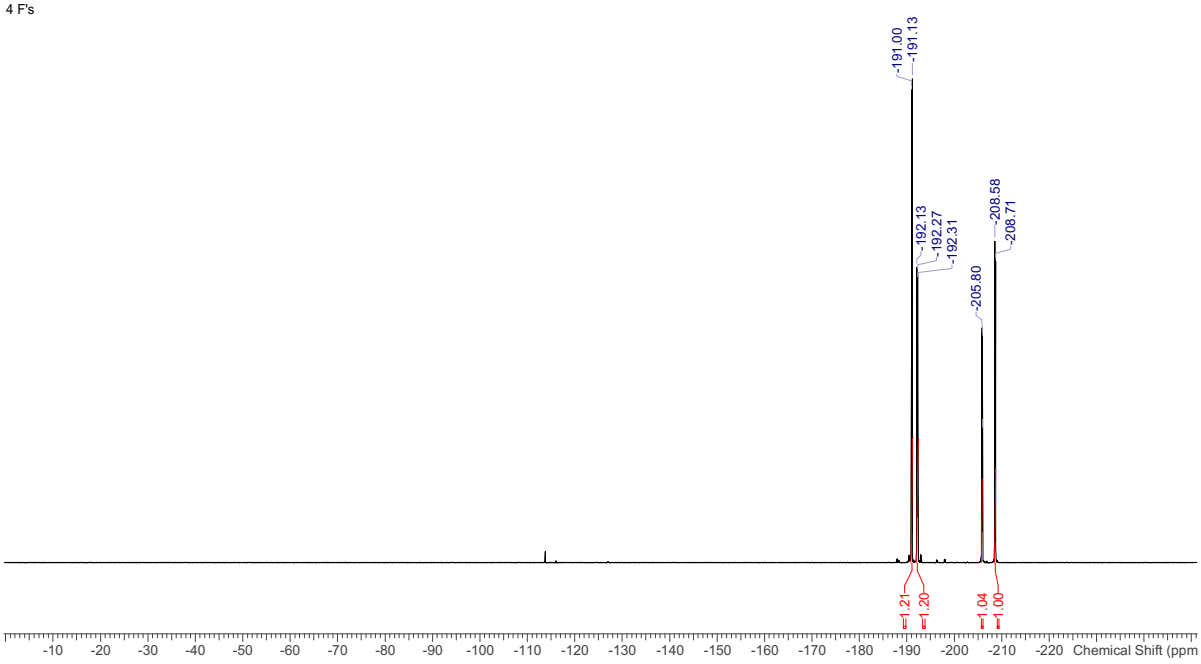


ap2423kh1.011.001.1r
CHLOROFORM-d
28 C's



6.8.3.3 ^{19}F NMR, 376 MHz, $CDCl_3$

ap2023kh1.011.001.1r
CHLOROFORM-d
4 F's



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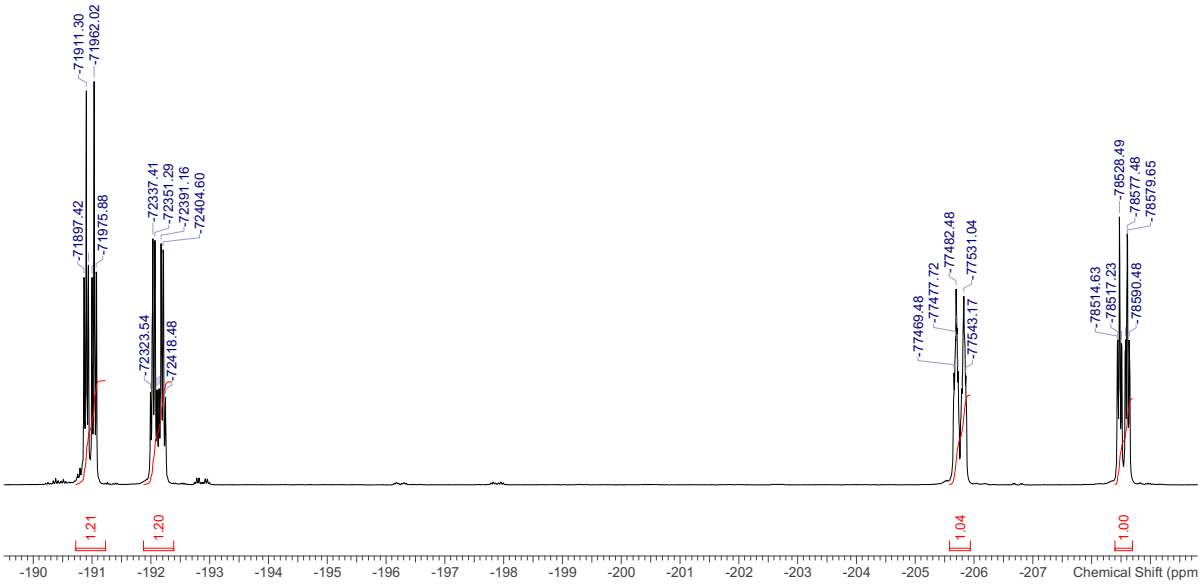
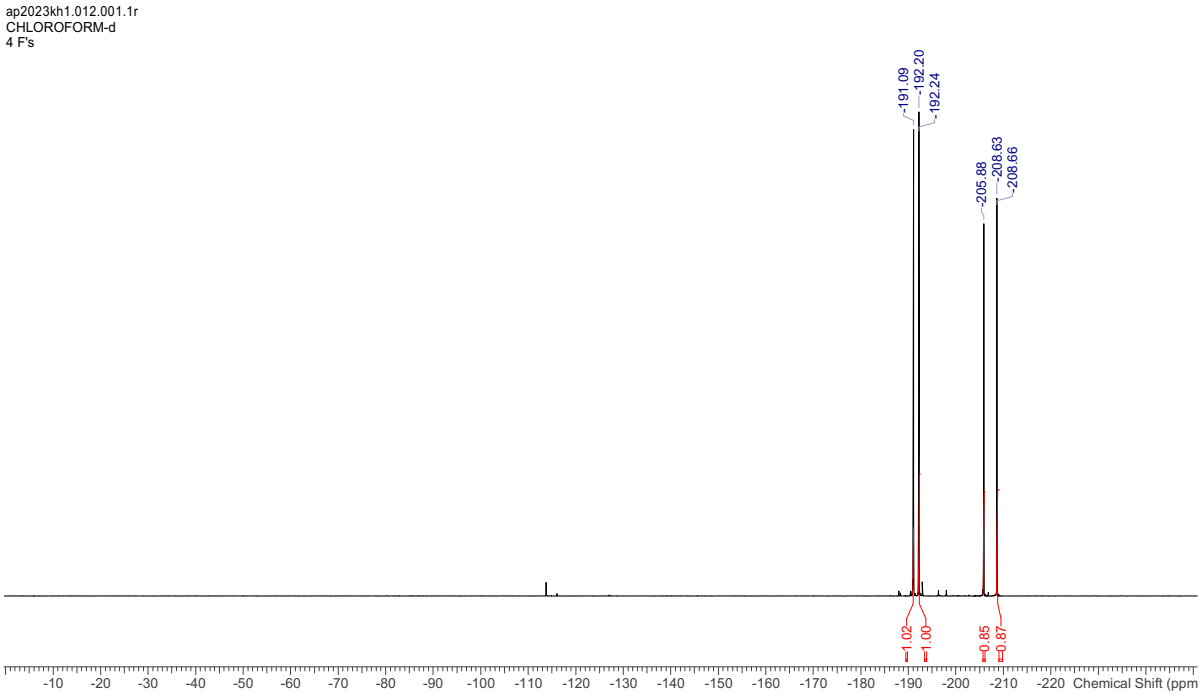
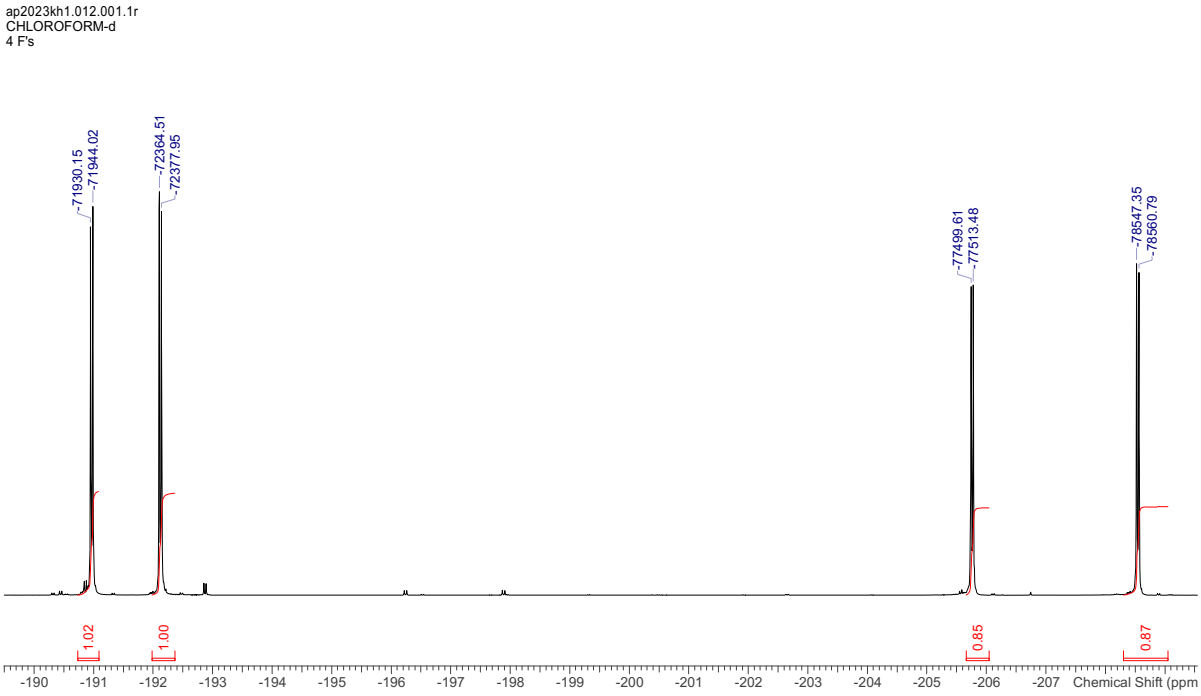
CHLOROFORM-d
4 F's

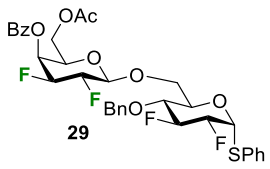


6.8.3.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$





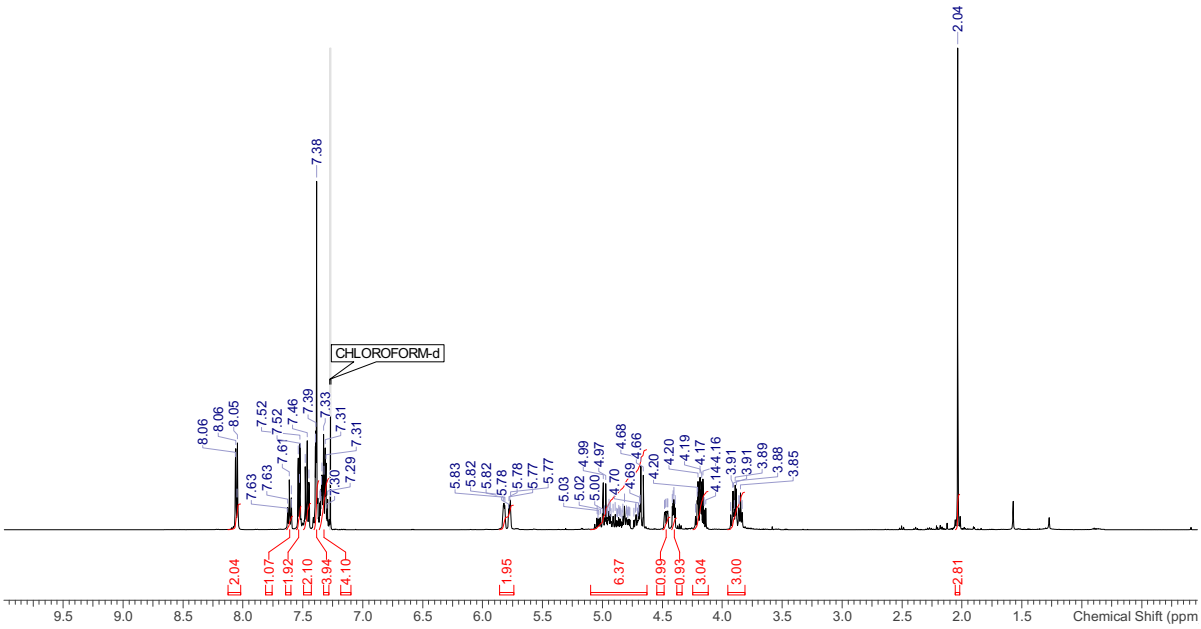
6.8.4 6-*O*-Acetyl-4-*O*-benzoyl-2,3-dideoxy-2,3-difluoro-β-D-galactopyranosyl-(1,6)-phenyl 4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-1-thio-α-D-glucopyranose (**29β**)



29

6.8.4.1 ^{1}H NMR, 400 MHz, $CDCl_3$

ap2523kh2.010.001.1r
CHLOROFORM-d
33 H's



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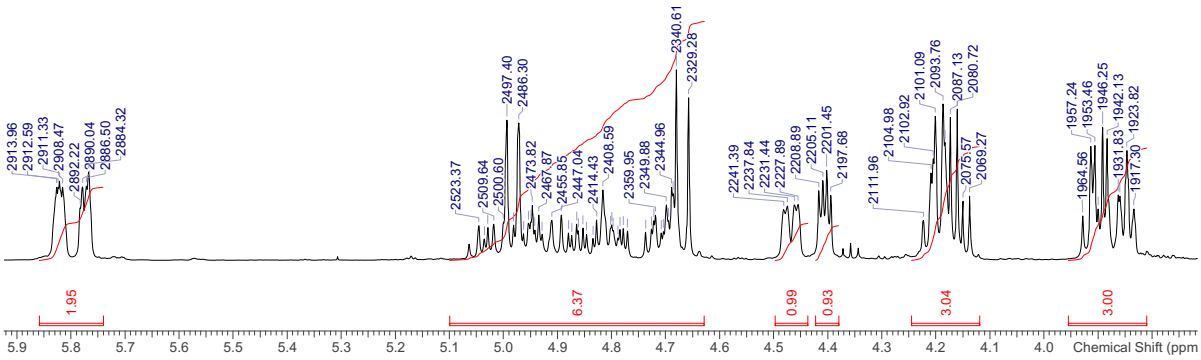
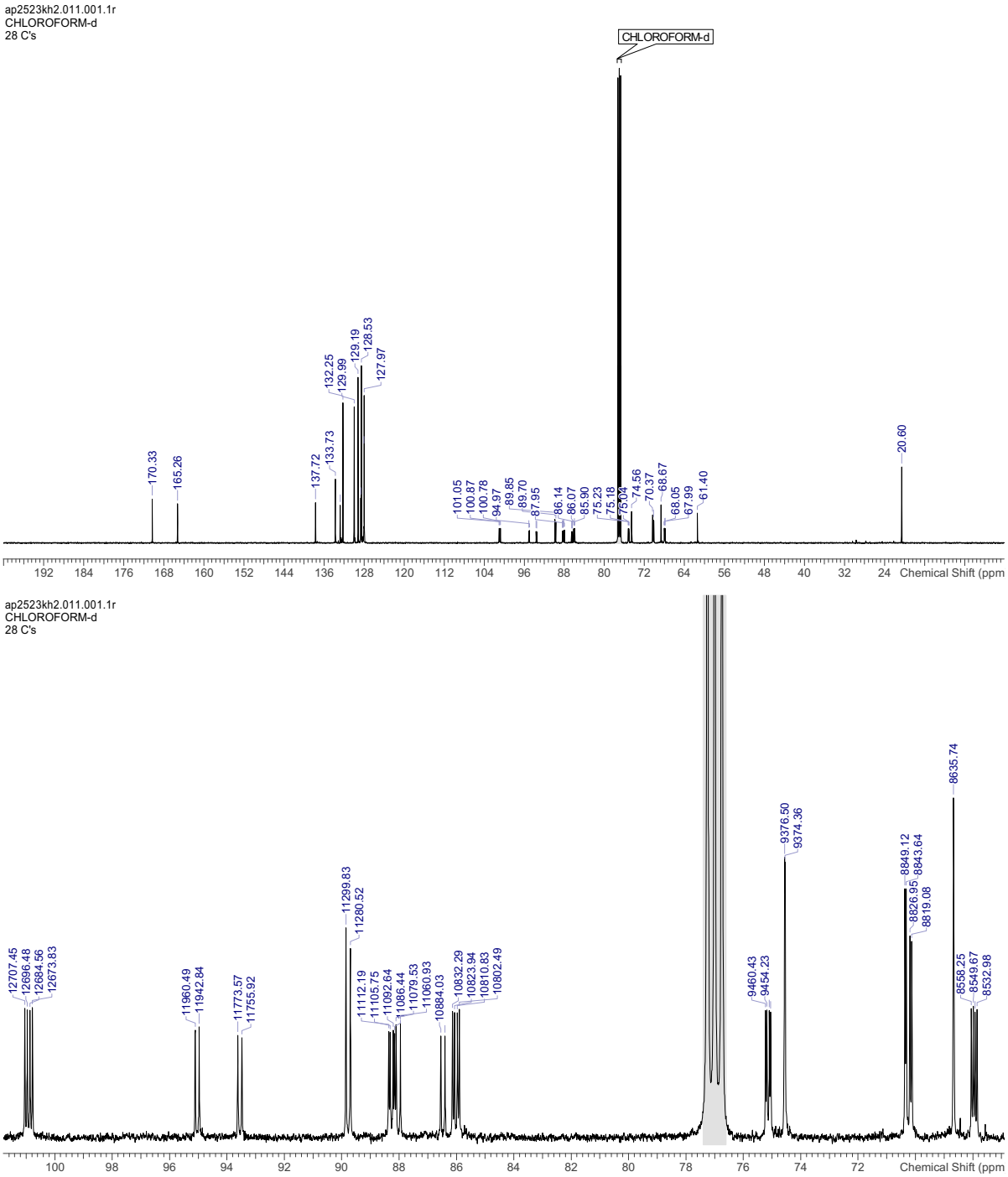
33 H's

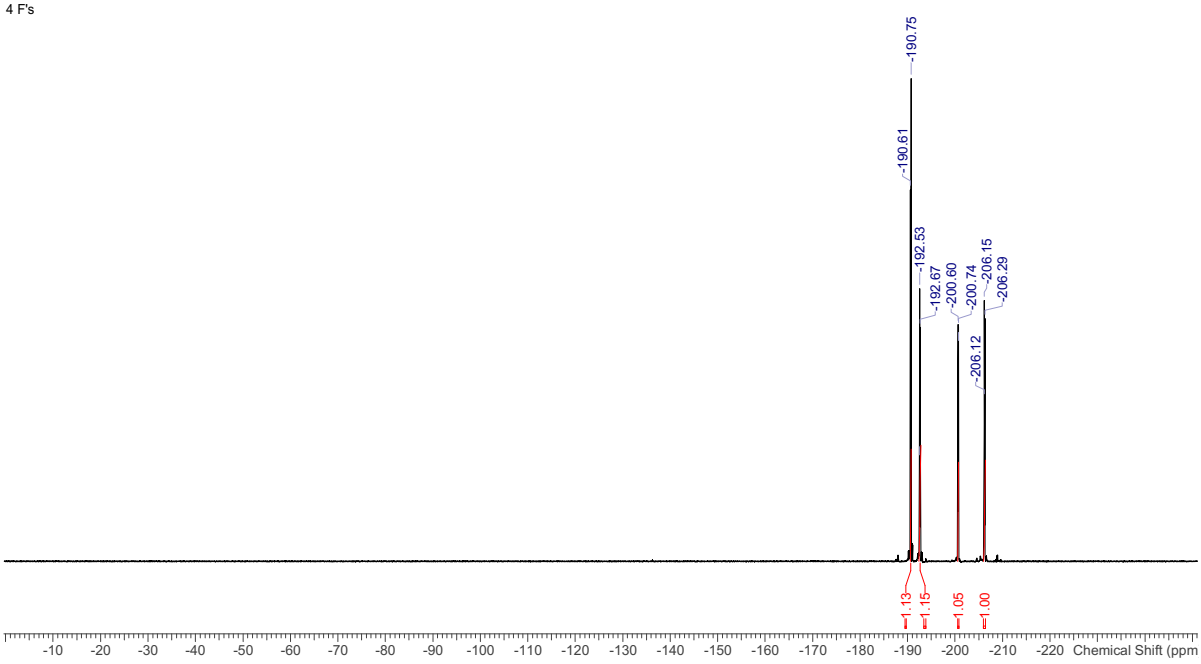


6.8.4.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$



6.8.4.3 ^{19}F NMR, 376 MHz, $CDCl_3$

ap2023kh9.011.001.1r
CHLOROFORM-d
4 F's



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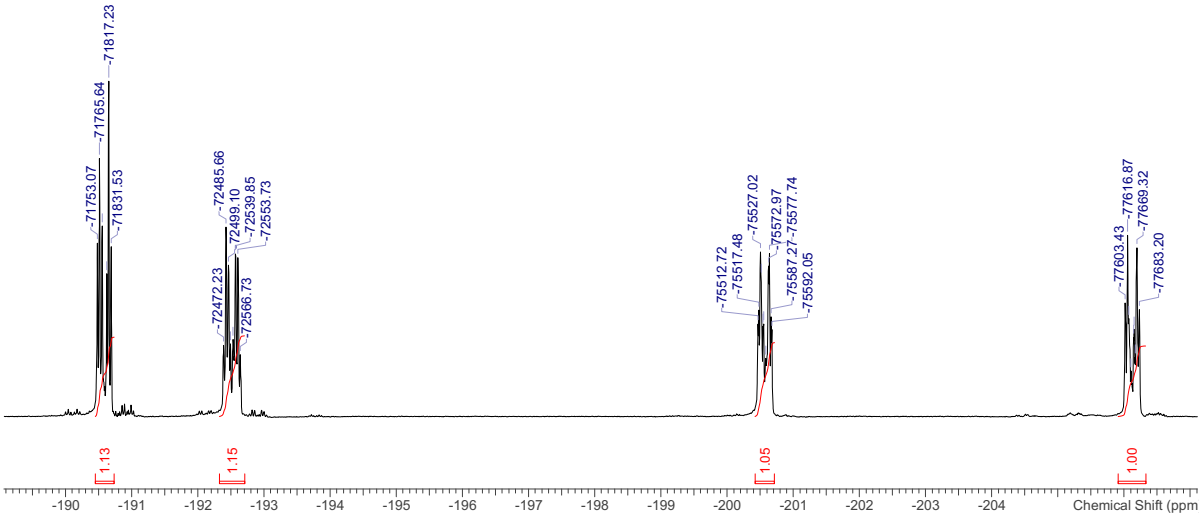
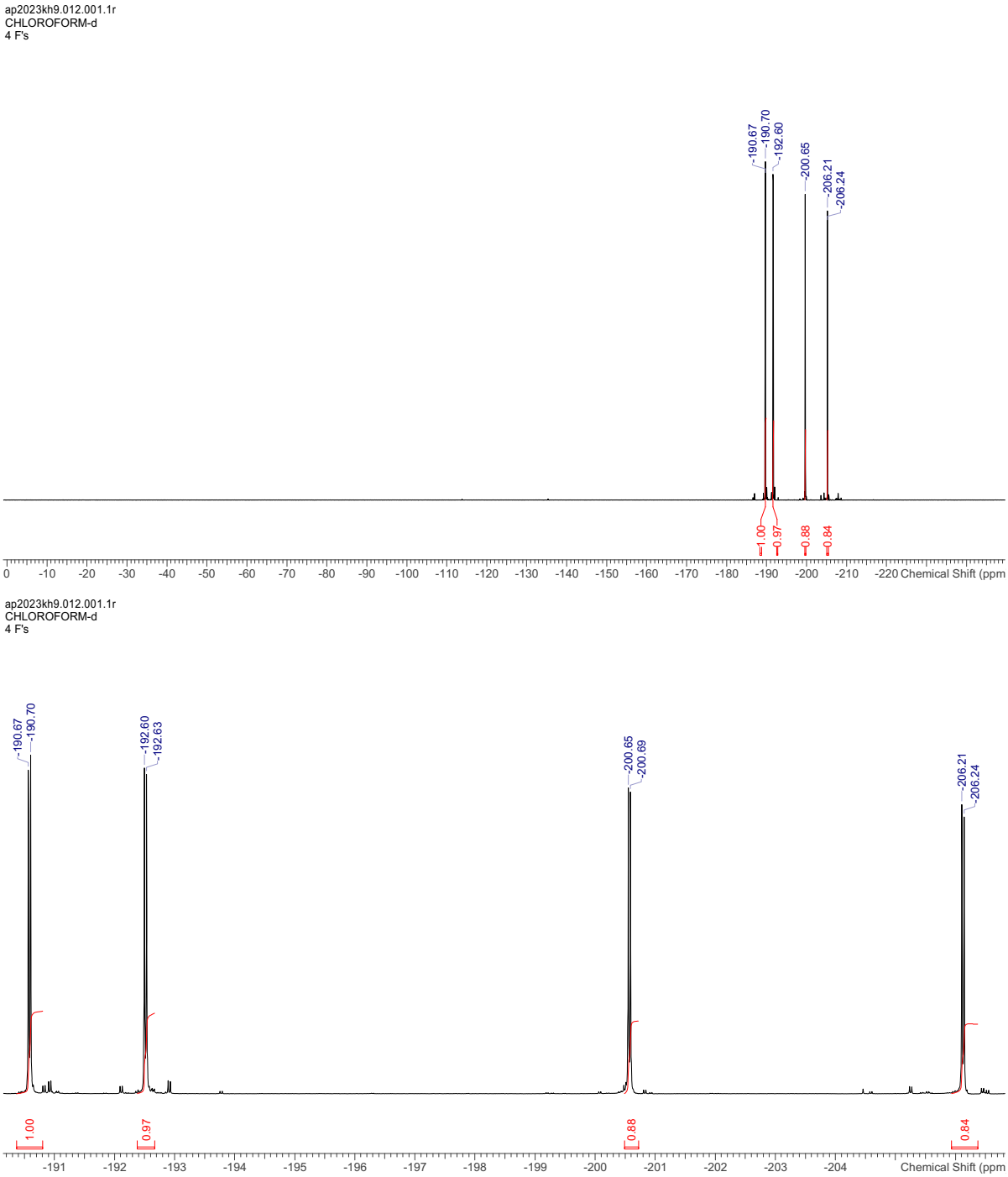
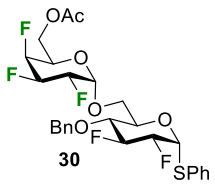
4 F's



6.8.4.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$



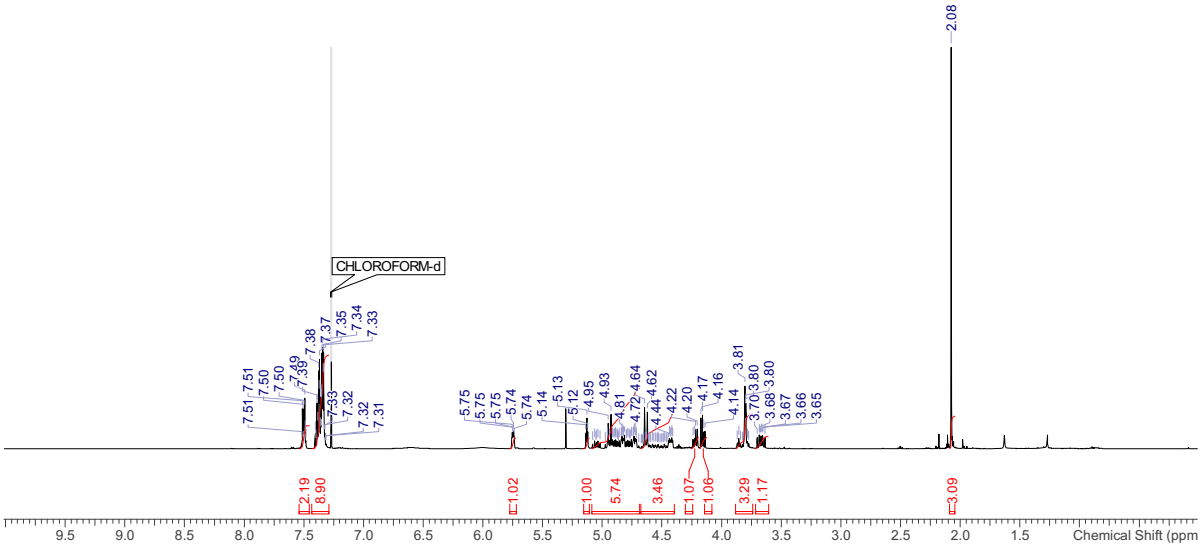
6.8.5 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-α-D-galactopyranosyl-(1,6)-phenyl 4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-1-thio-α-D-glucopyranose (**30α**)



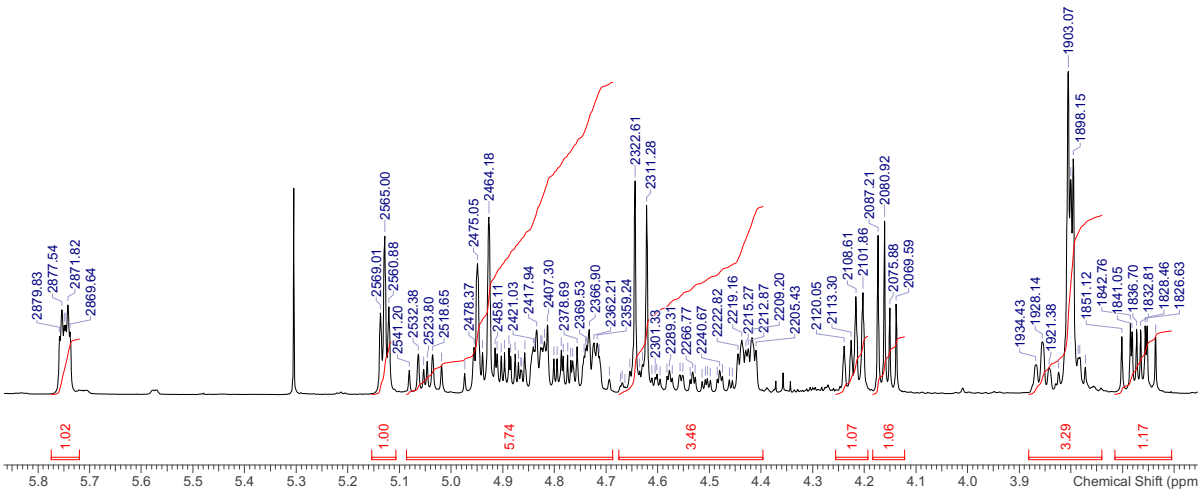
30

6.8.5.1 ^{1}H NMR, 500 MHz, $CDCl_3$

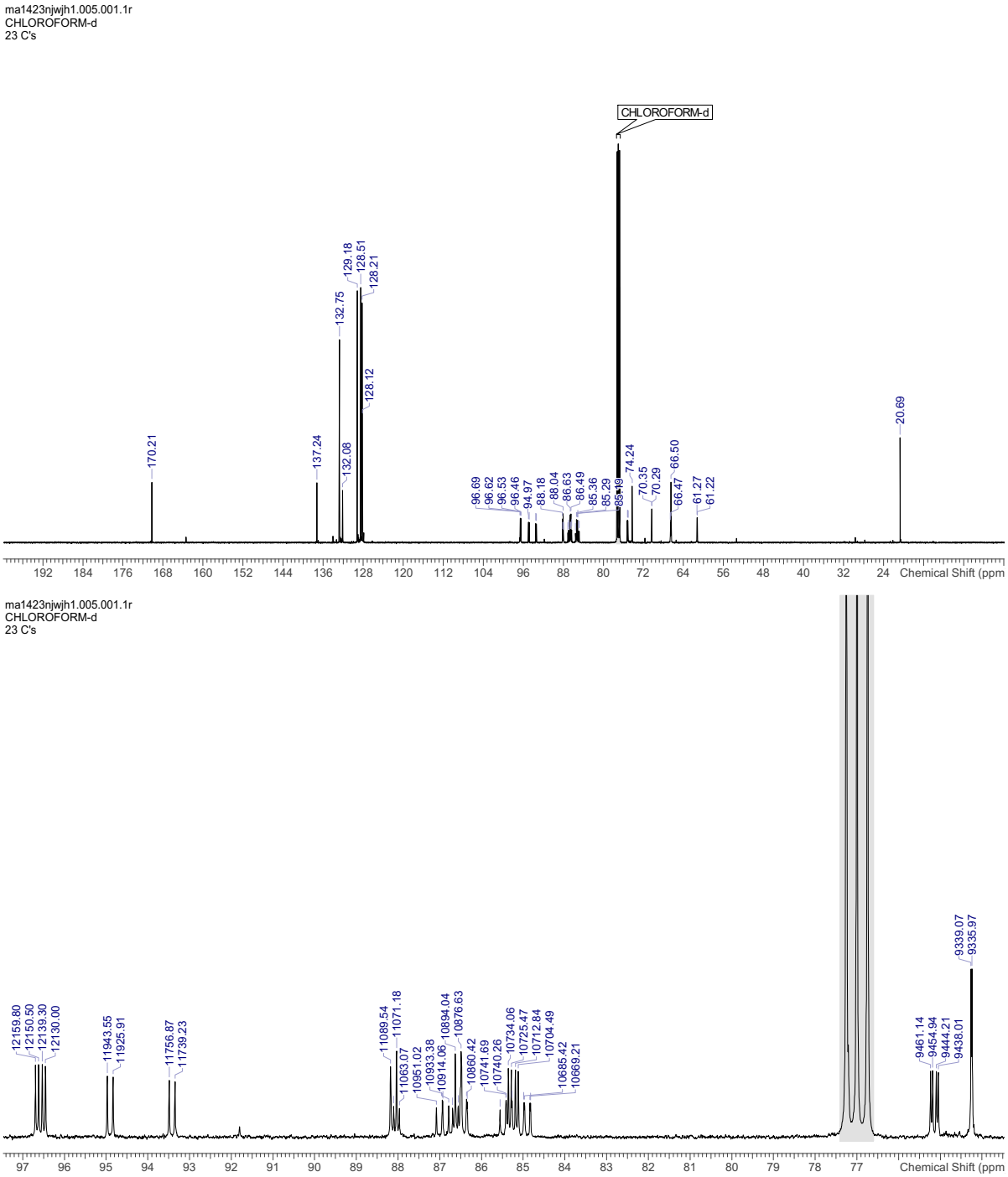
ma1423njwjh1.001.001.1r
CHLOROFORM-d
31 H's



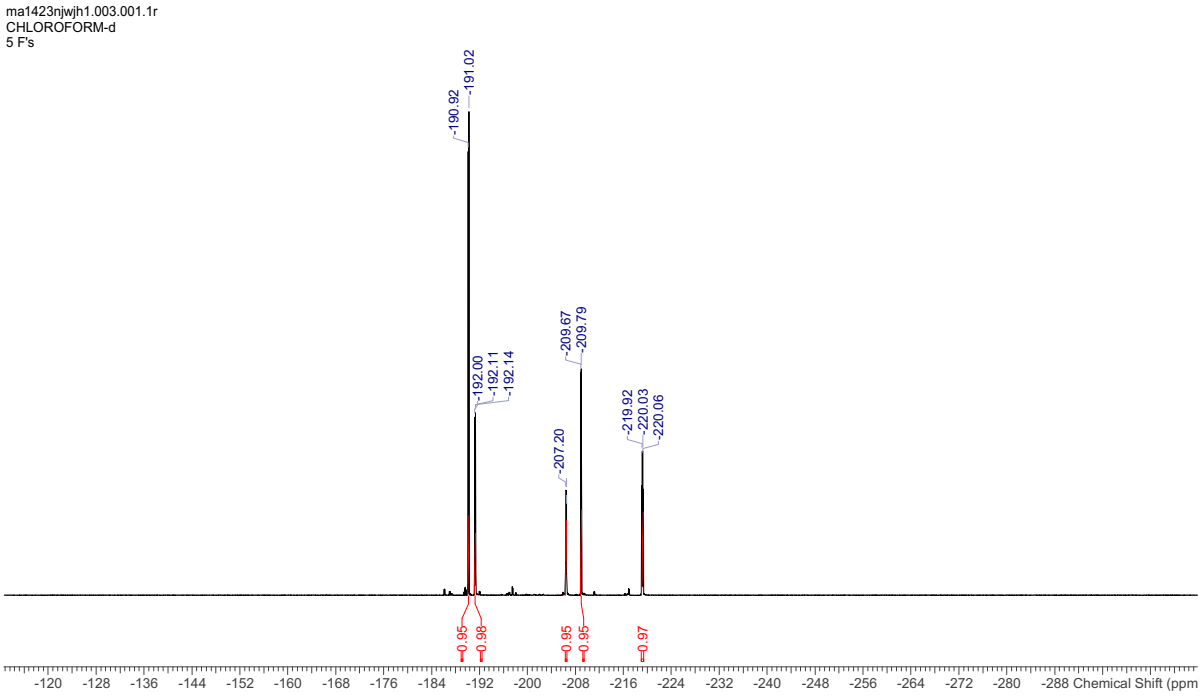
ma1423njwjh1.001.001.1r
CHLOROFORM-d
31 H's

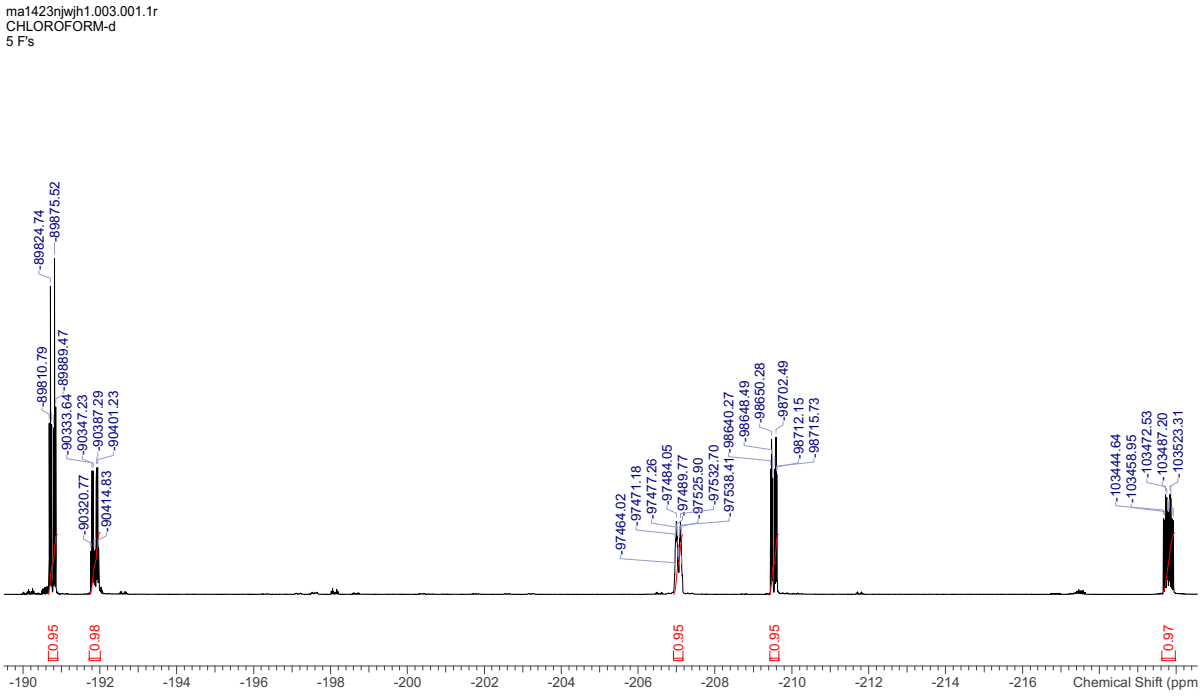


6.8.5.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$

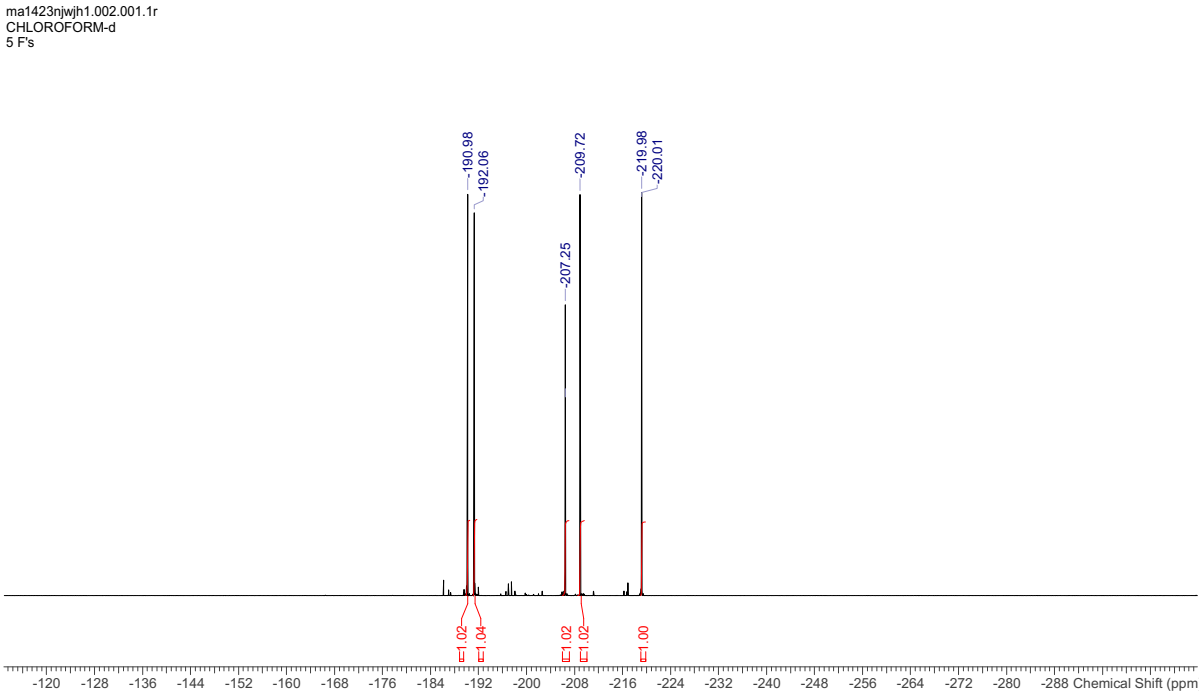


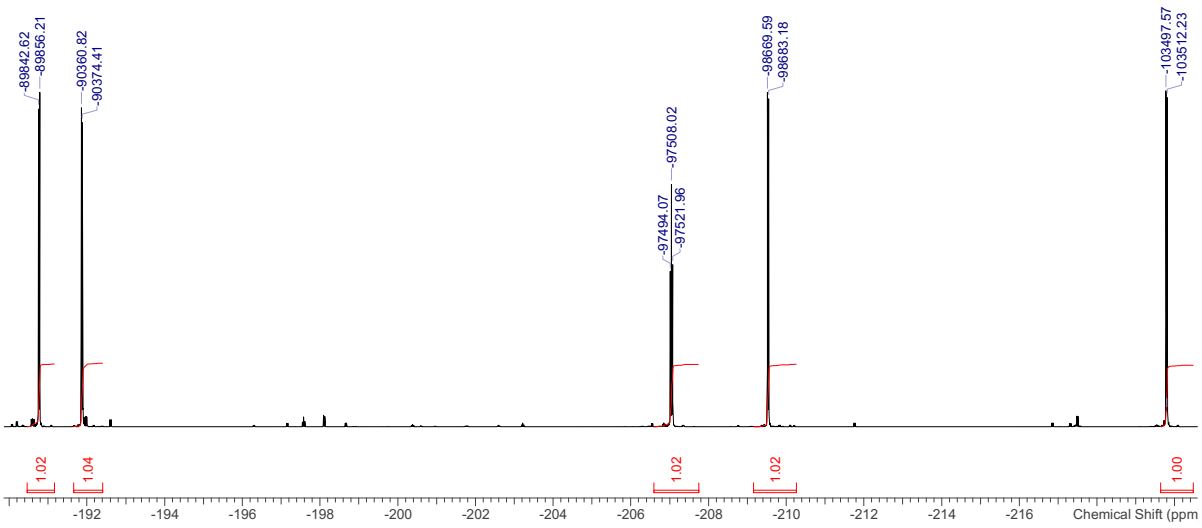
6.8.5.3 ^{19}F NMR, 471 MHz, $CDCl_3$



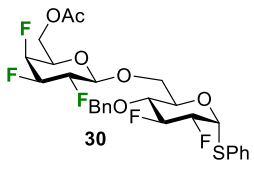


6.8.5.4 $^{19}F\{^{1}H\}$ NMR, 471 MHz, $CDCl_3$



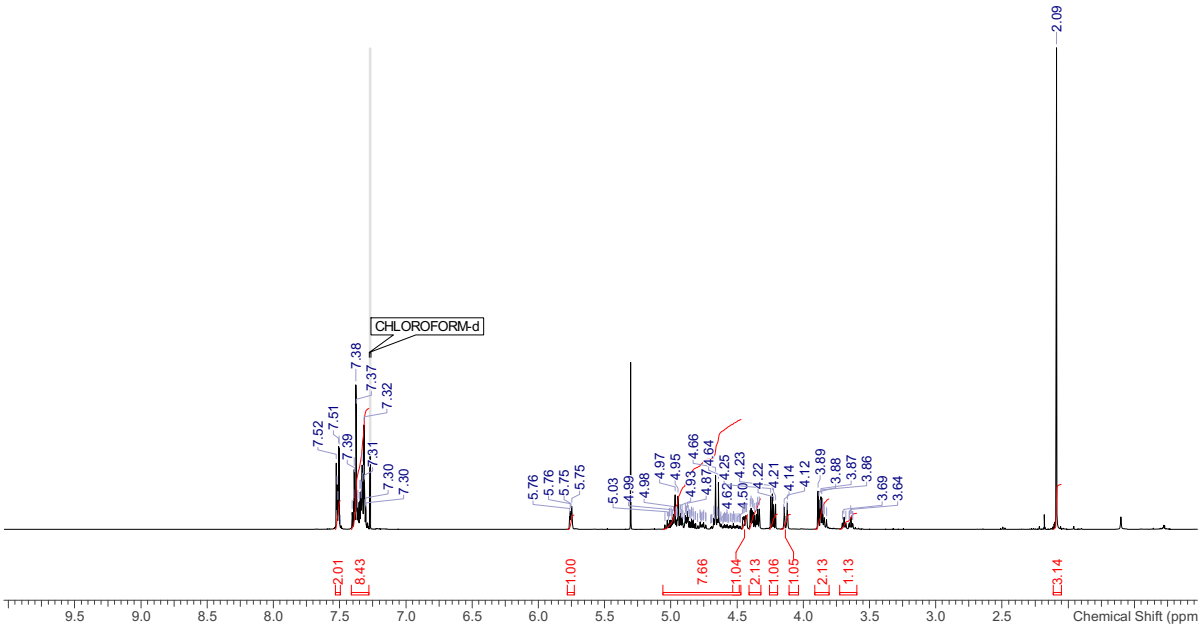


6.8.6 6-*O*-Acetyl-2,3,4-trideoxy-2,3,4-trifluoro-β-D-galactopyranosyl-(1,6)-phenyl 4-*O*-benzyl-2,3-dideoxy-2,3-difluoro-1-thio-α-D-glucopyranose (**30β**)



6.8.6.1 ^{1}H NMR, 500 MHz, $CDCl_3$

ma1423njwjh2.001.001.1r
CHLOROFORM-d
30 H's



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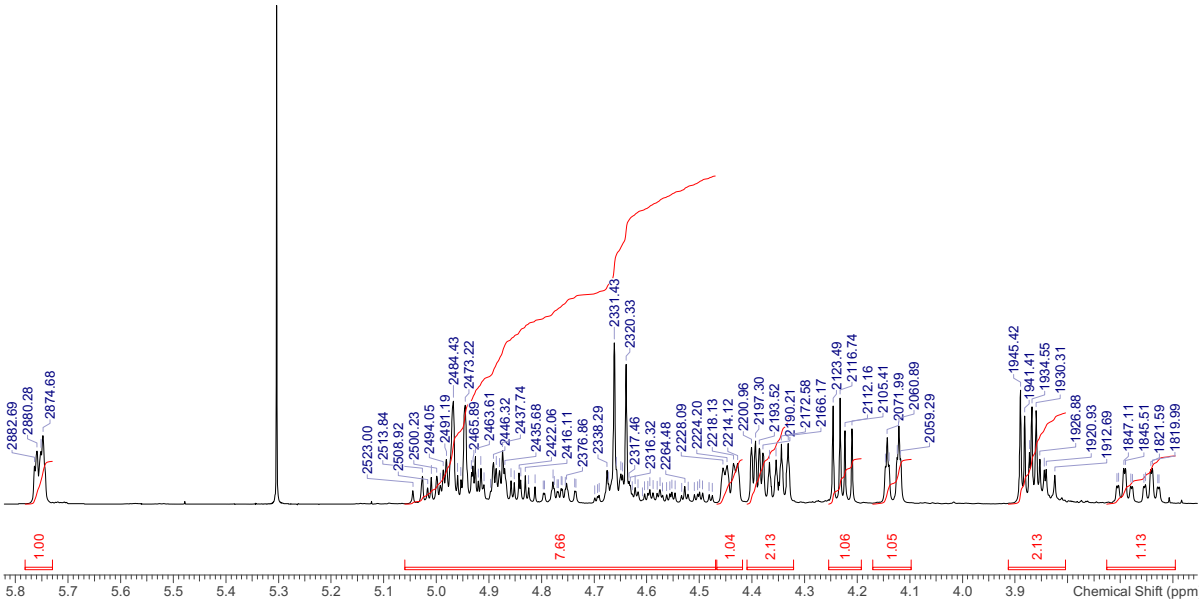
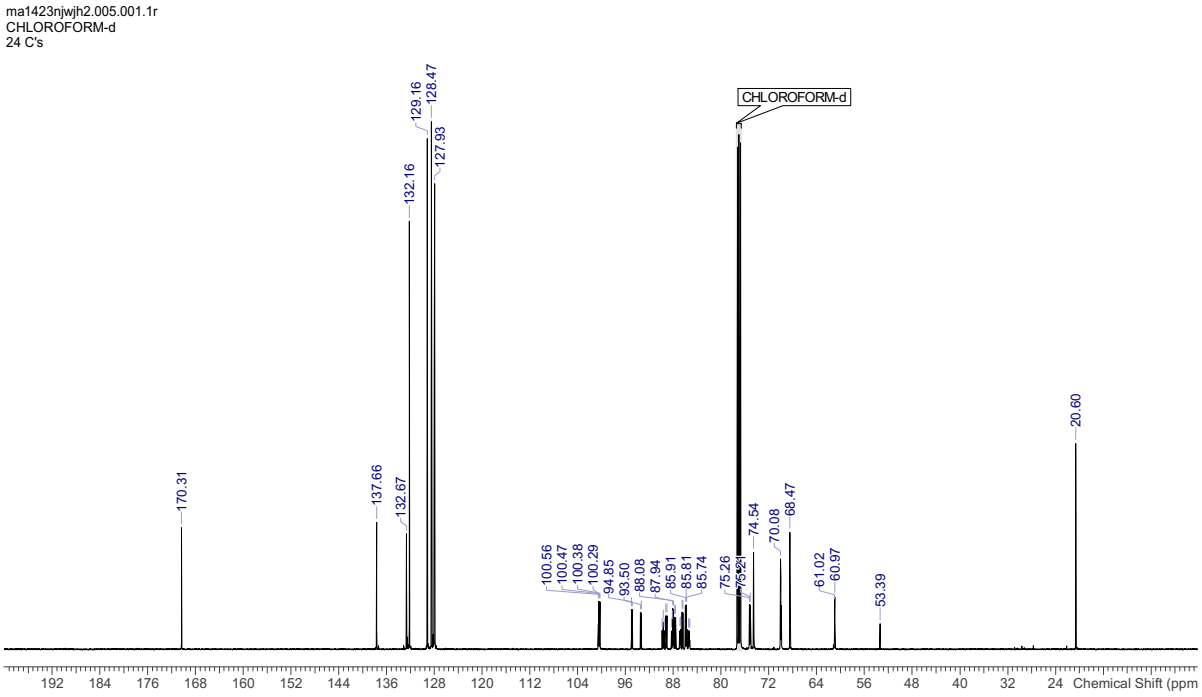
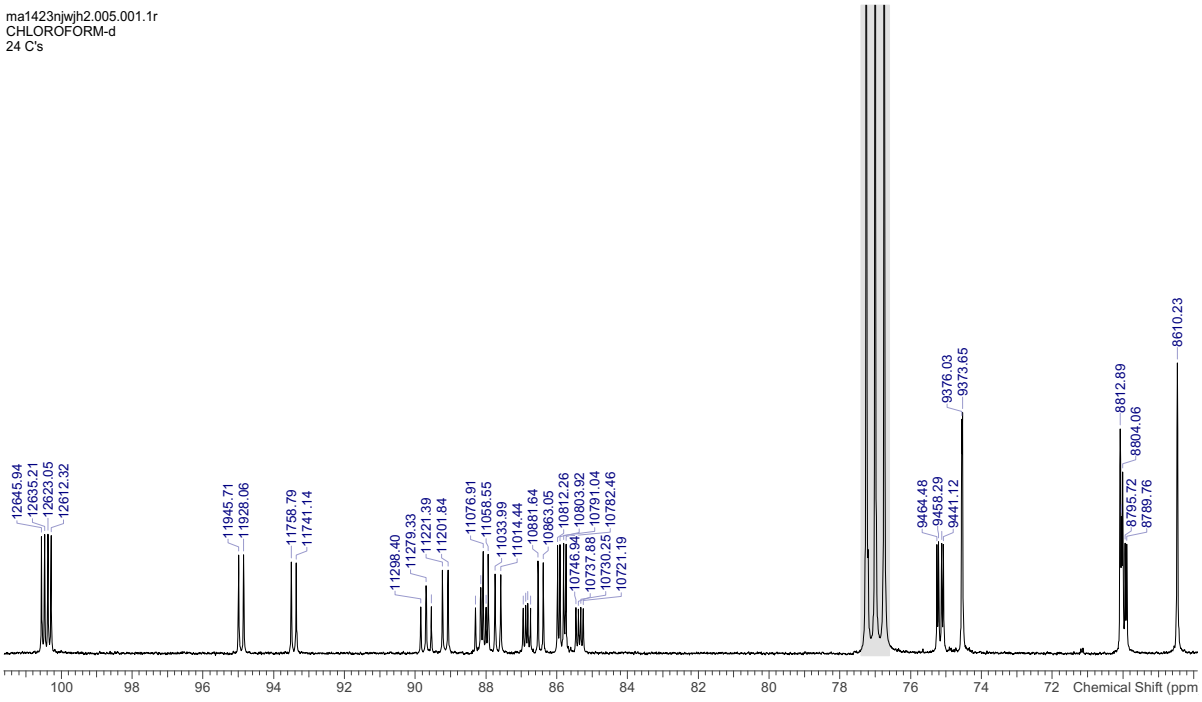
CHLOROFORM-d
30 H's

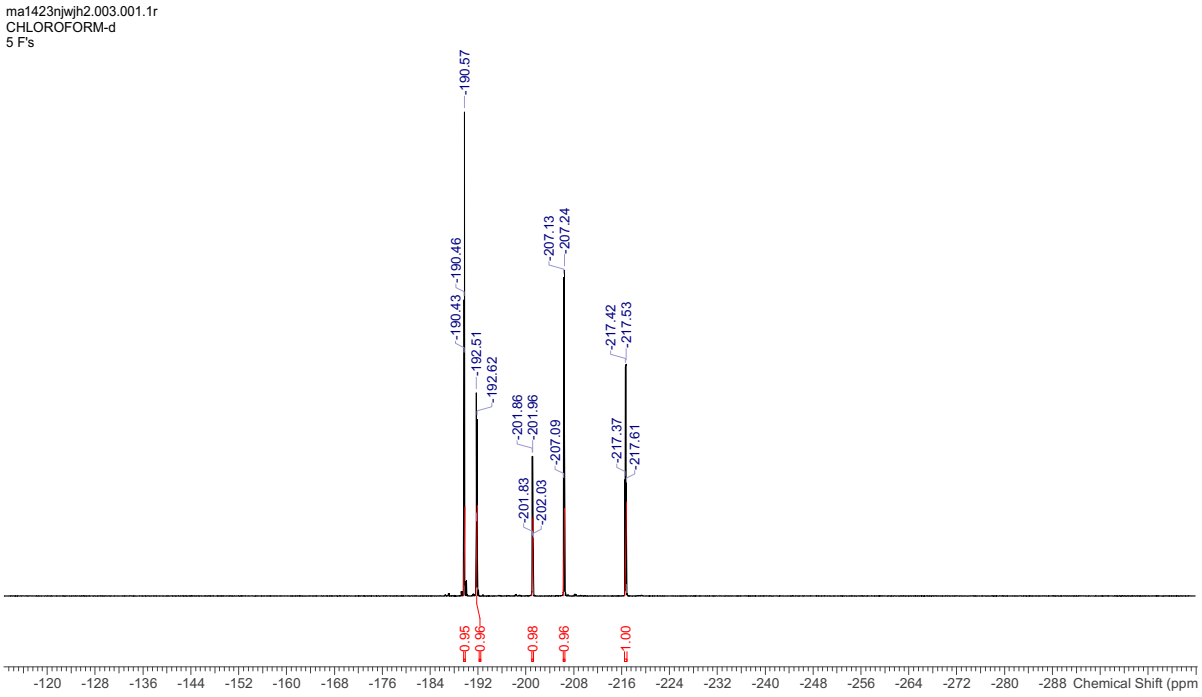


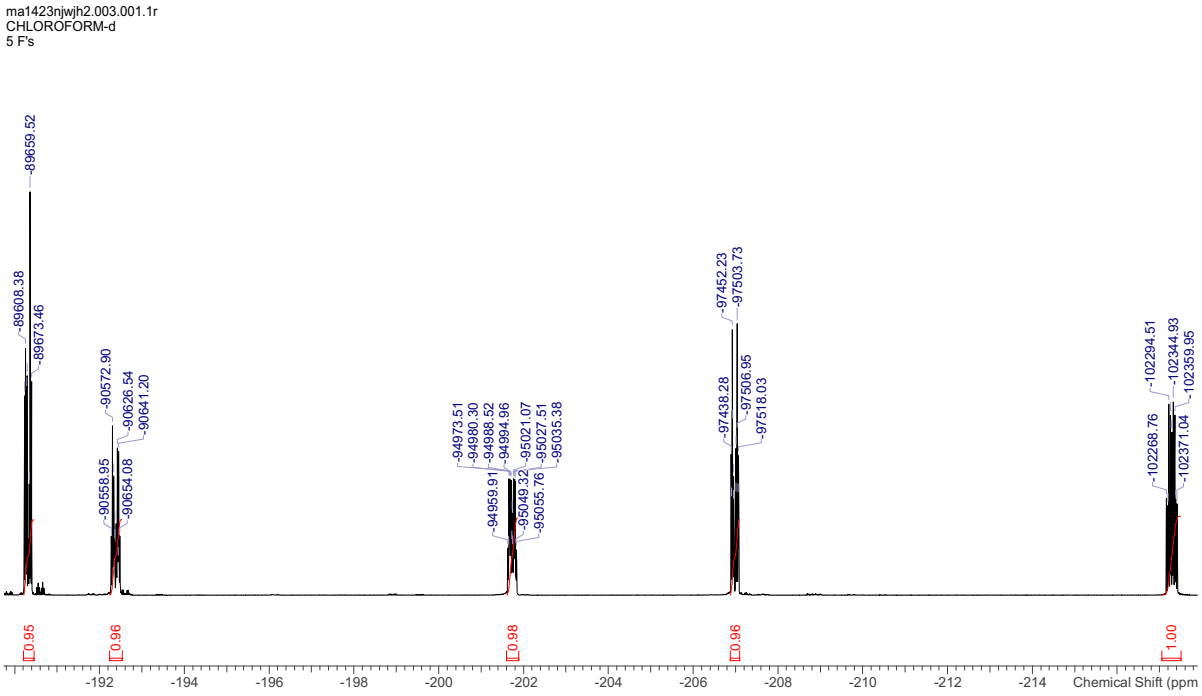
6.8.6.2 $^{13}C\{^{1}H\}$ NMR, 126 MHz, $CDCl_3$



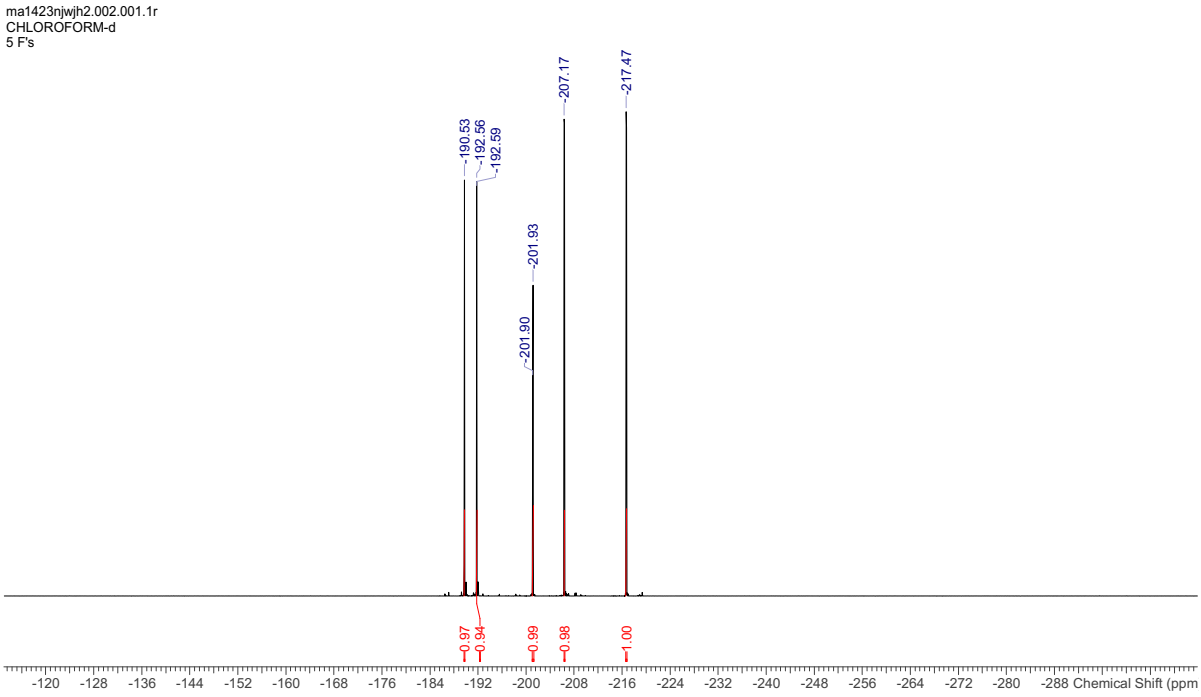


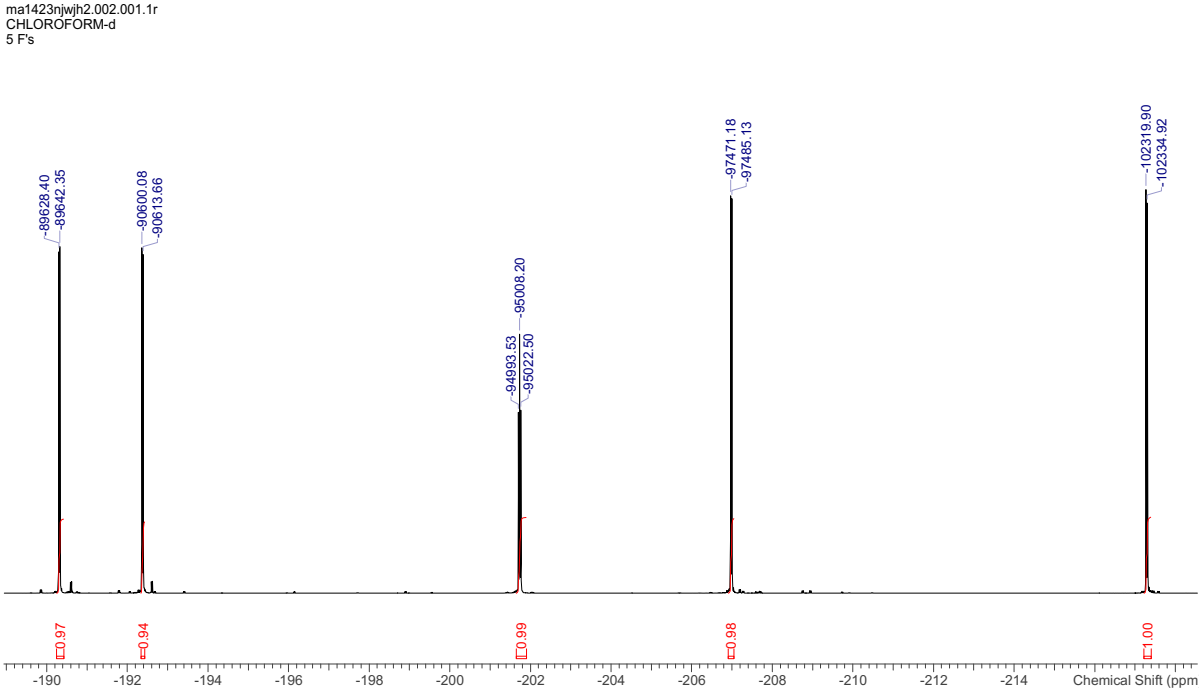
6.8.6.3 ^{19}F NMR, 471 MHz, $CDCl_3$





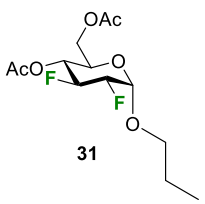
6.8.6.4 $^{19}F\{^{1}H\}$ NMR, 471 MHz, $CDCl_3$





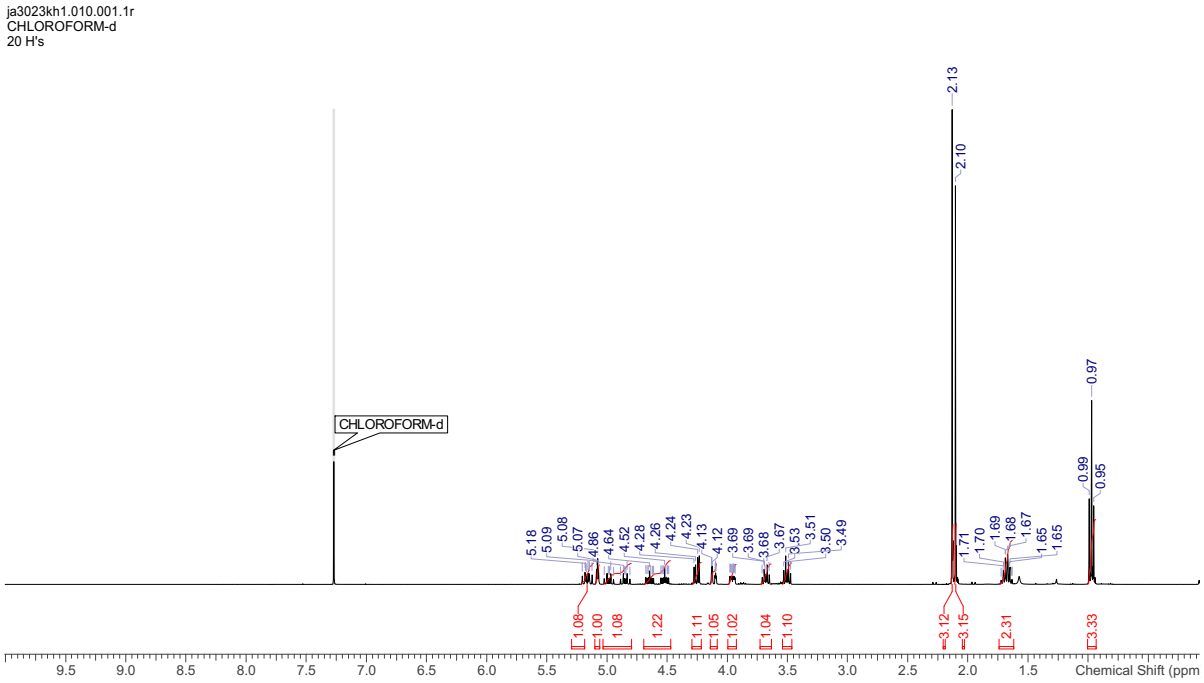
7 Copies of the spectra of the control experiments

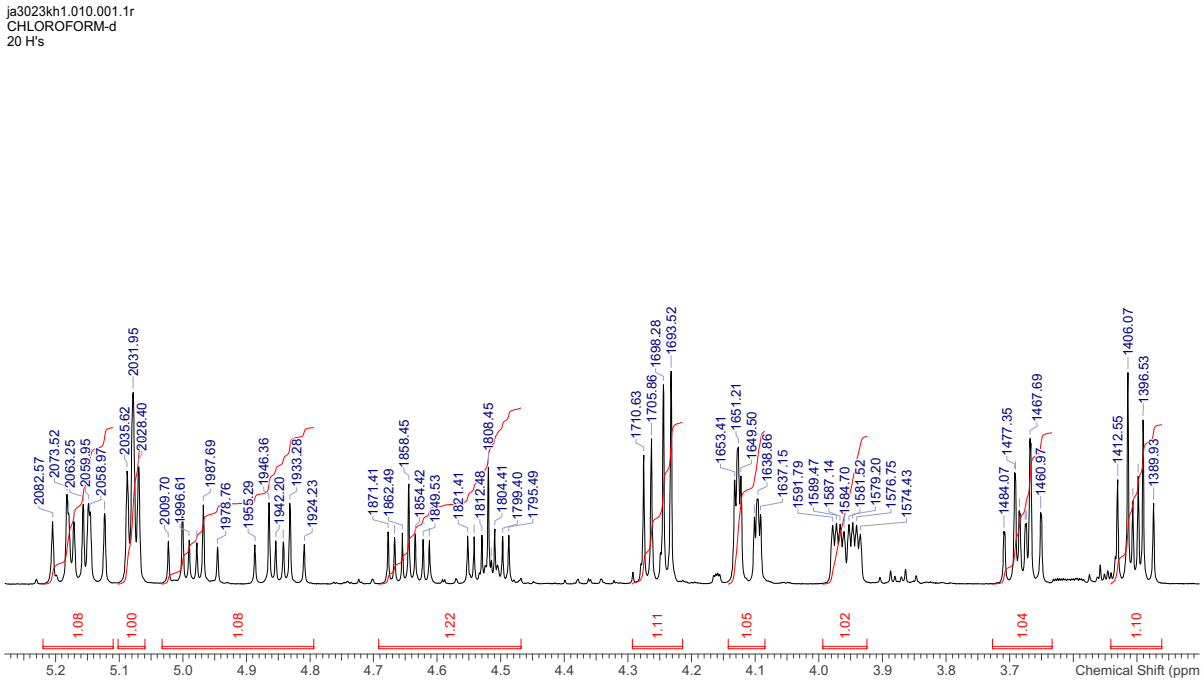
7.1 Propyl 4,6-di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-α-D-glucopyranoside (**31α**)



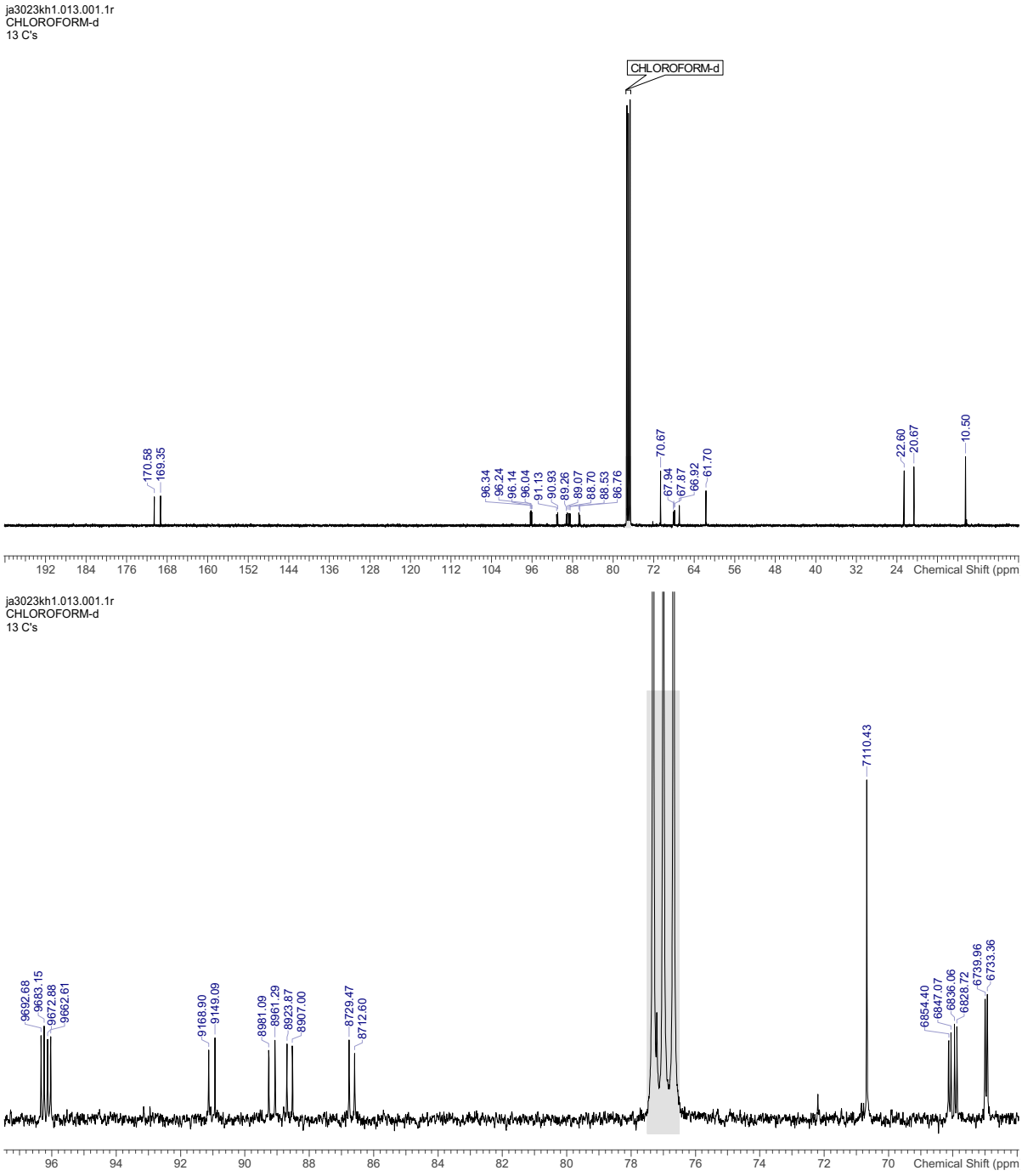
31

7.1.1 ^{1}H NMR, 400 MHz, $CDCl_3$

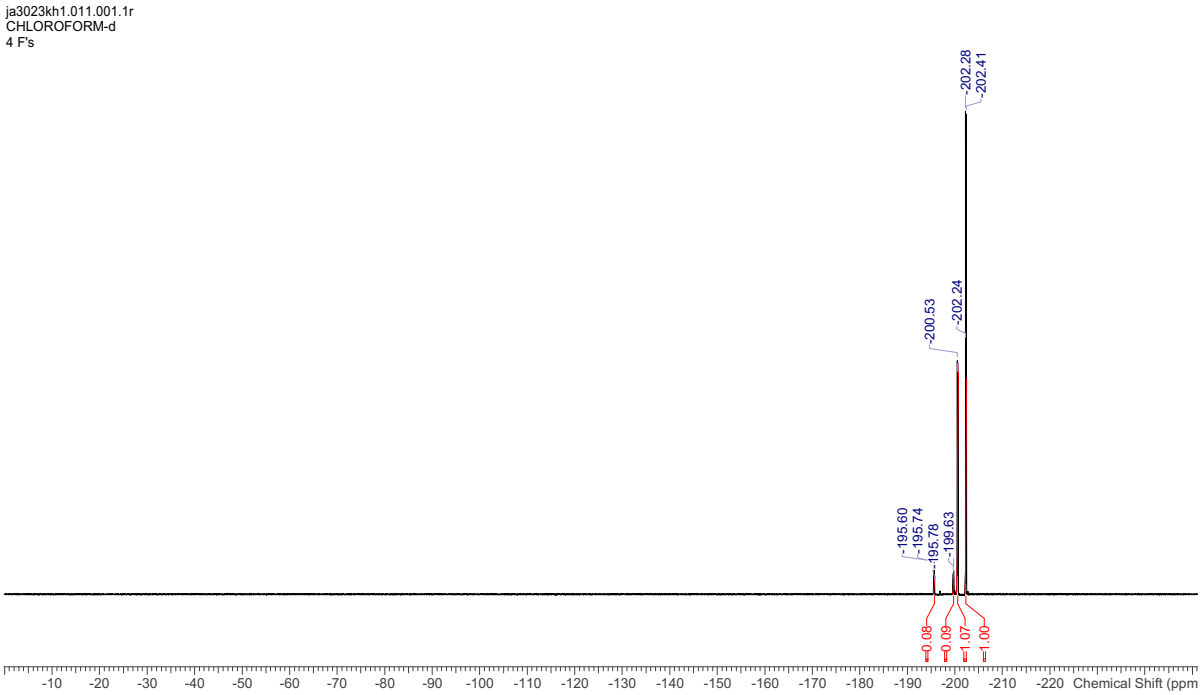


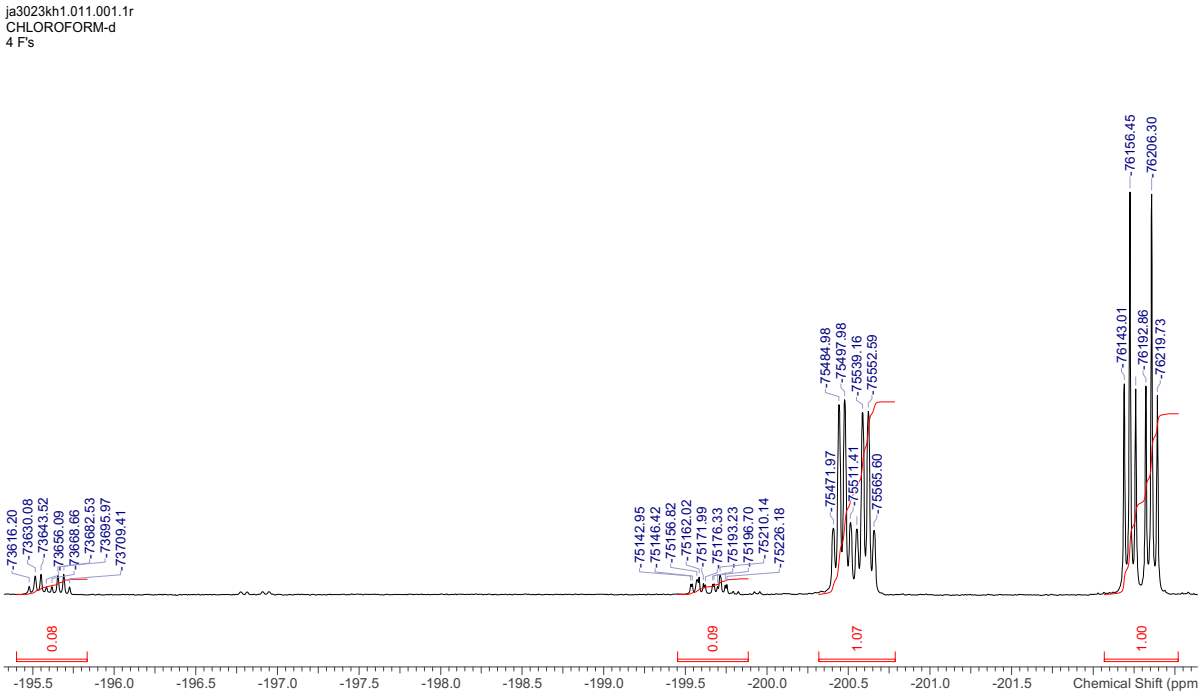


7.1.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

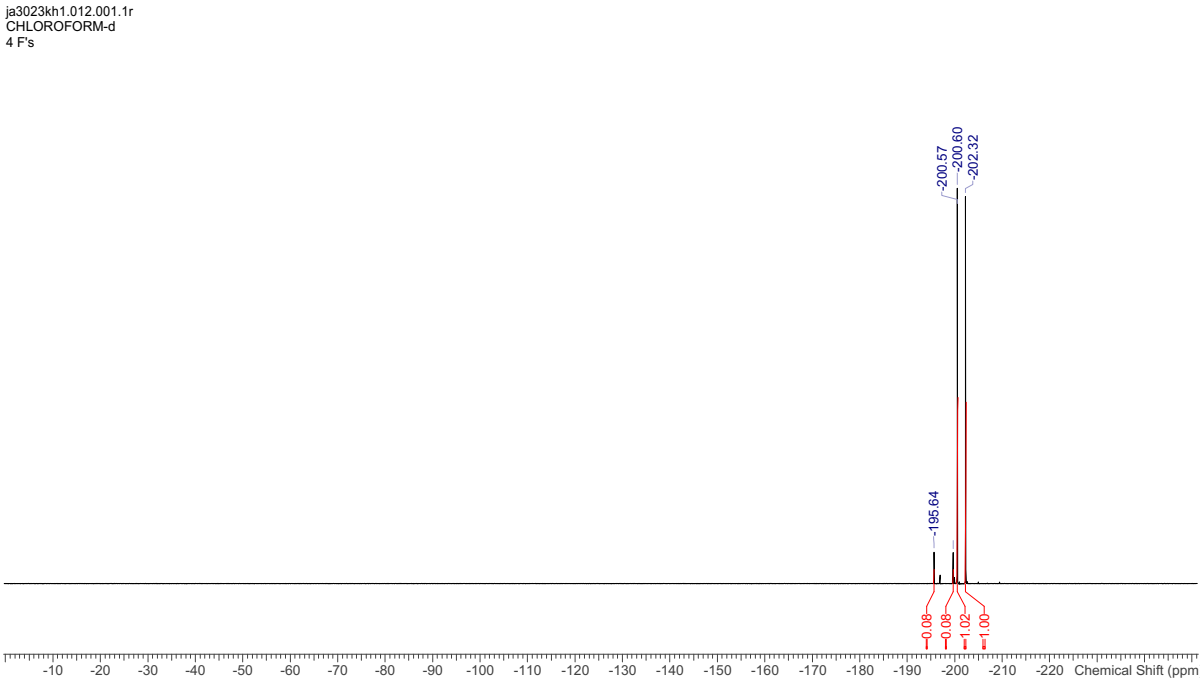


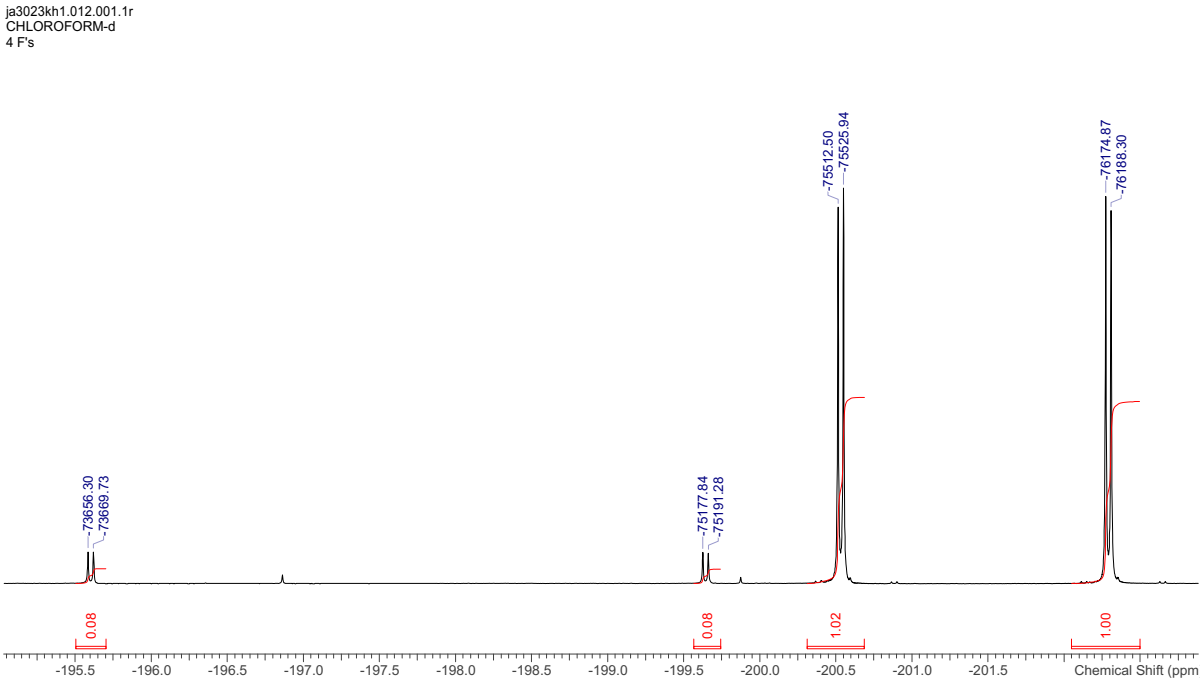
7.1.3 ^{19}F NMR, 376 MHz, $CDCl_3$



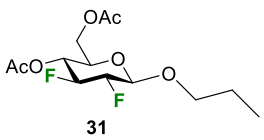


7.1.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$





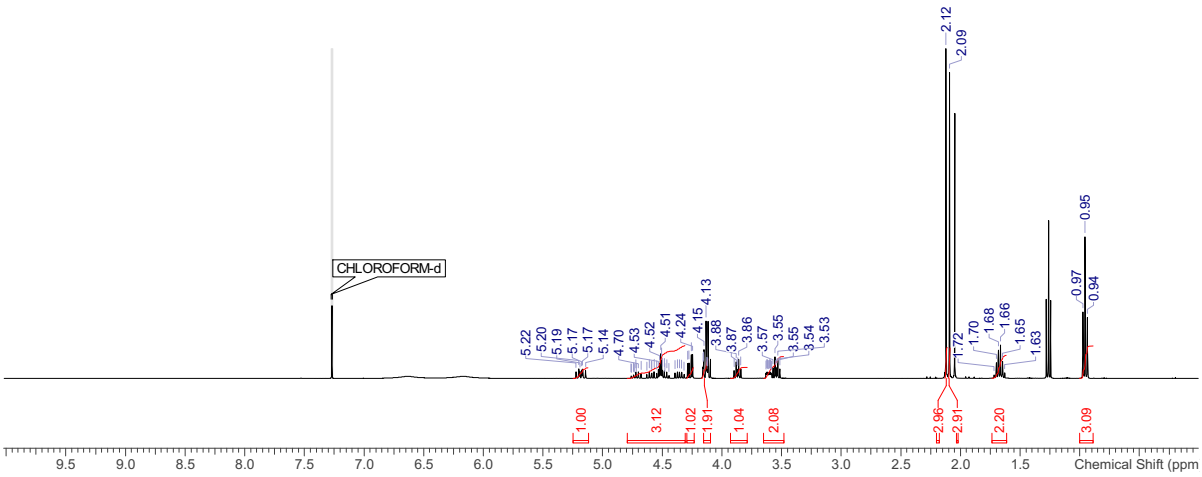
7.2 Propyl 4,6-di-*O*-acetyl-2,3-dideoxy-2,3-difluoro-β-D-glucopyranoside (**31β**)



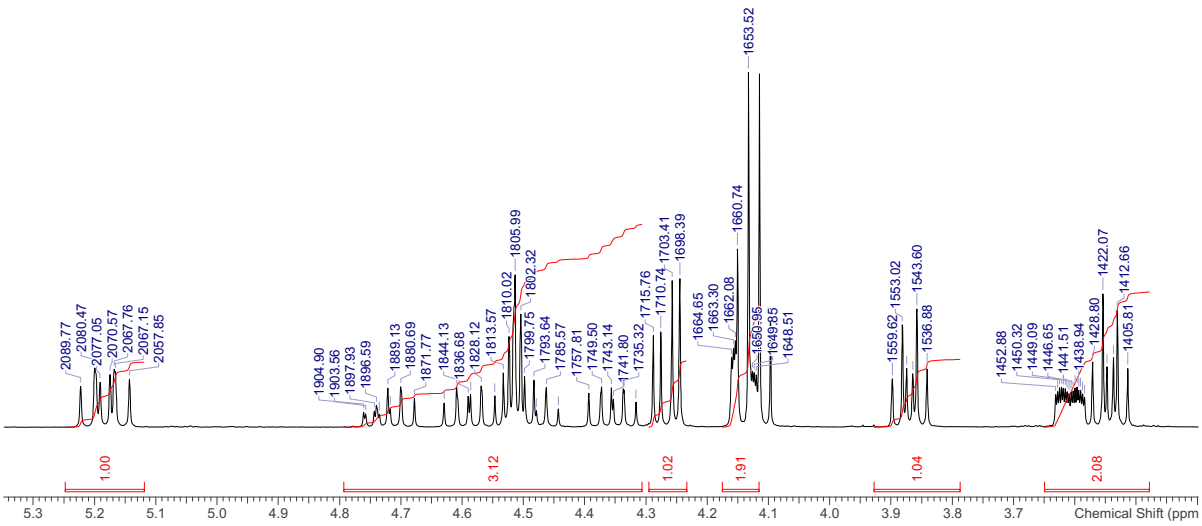
31

7.2.1 ^{1}H NMR, 400 MHz, $CDCl_3$

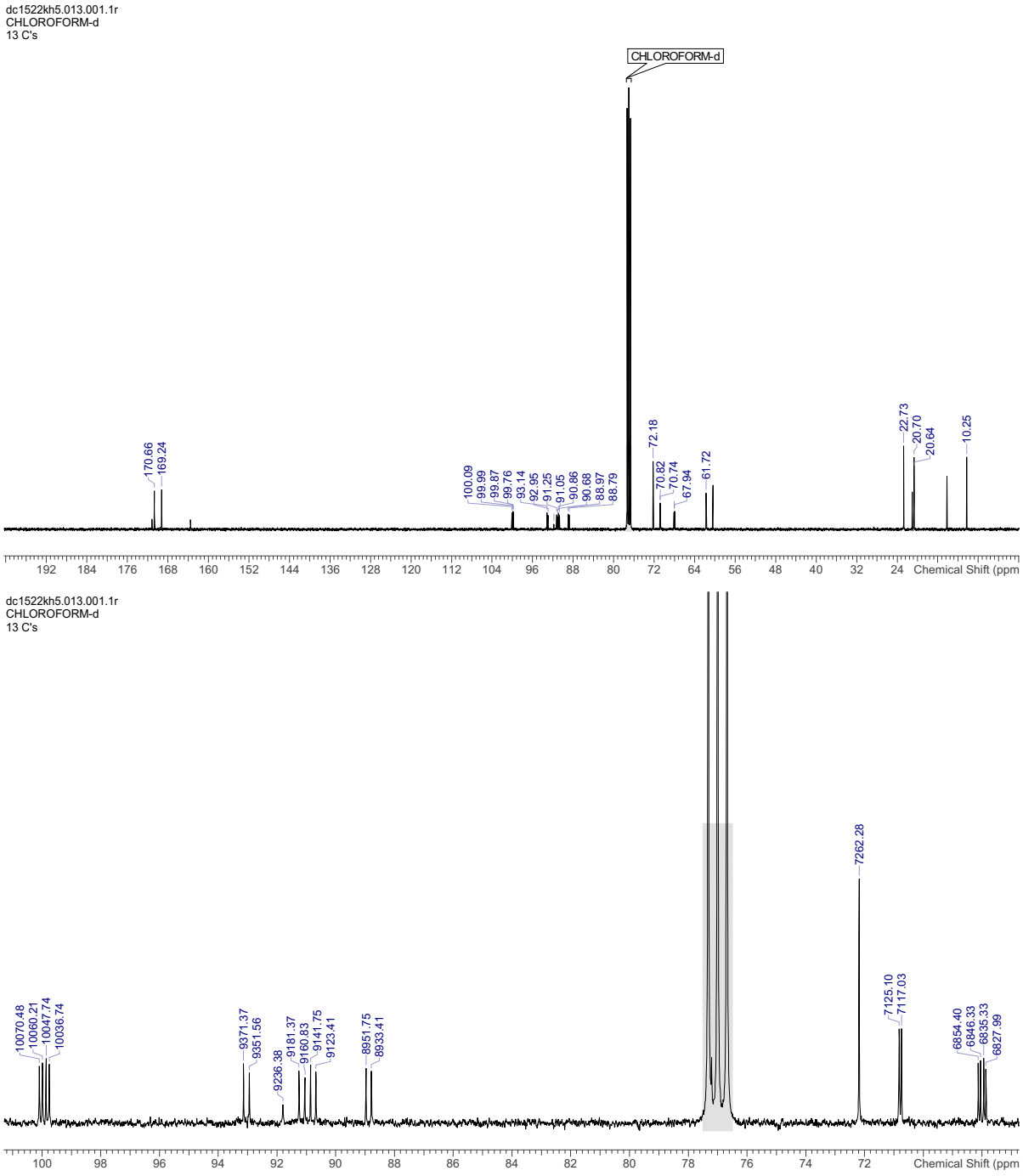
dc1522kh5.010.001.1r
CHLOROFORM-d
21 H's



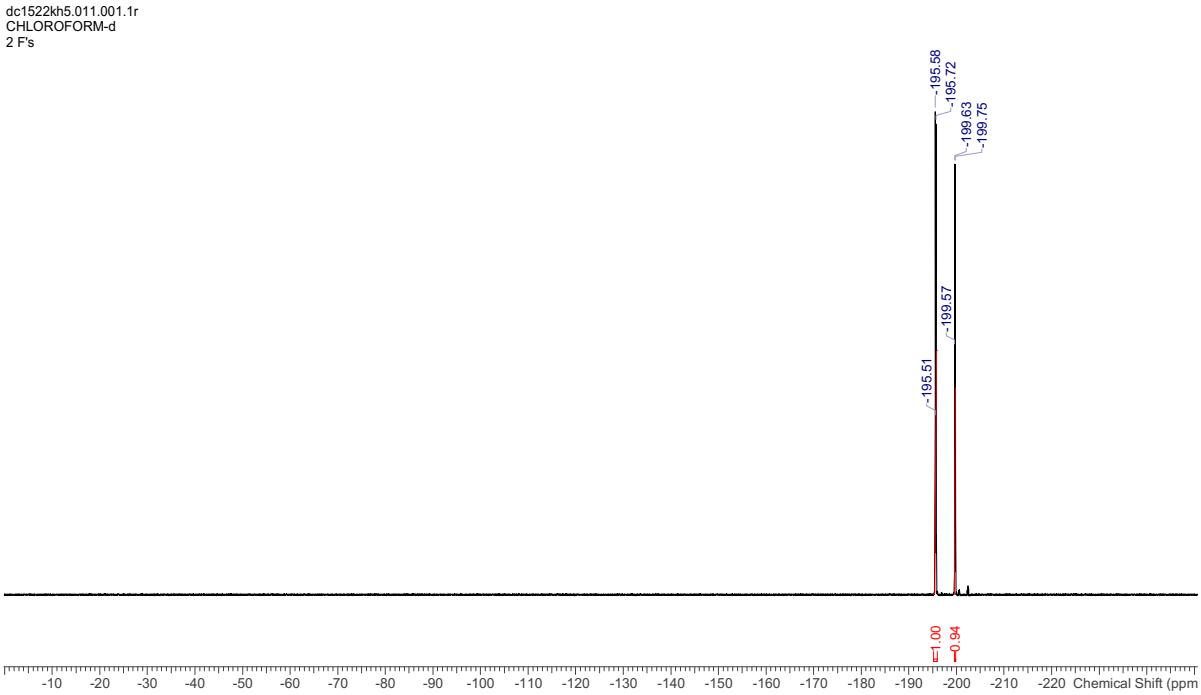
dc1522kh5.010.001.1r
CHLOROFORM-d
21 H's

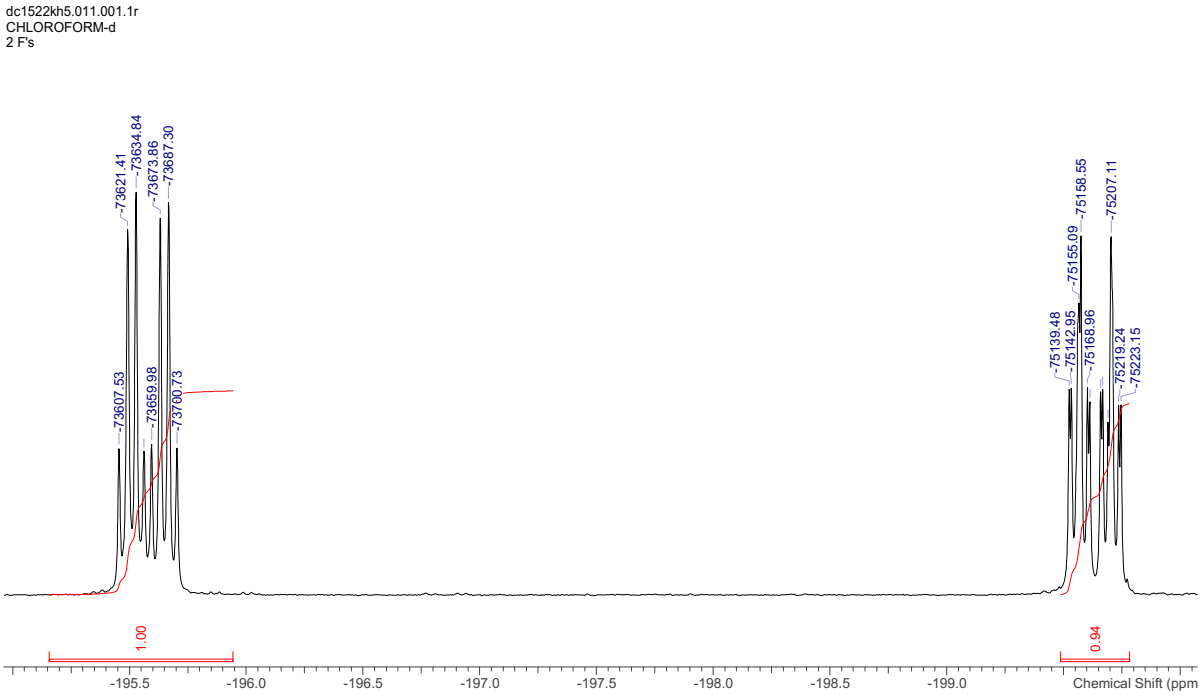


7.2.2 $^{13}C\{^{1}H\}$ NMR, 101 MHz, $CDCl_3$

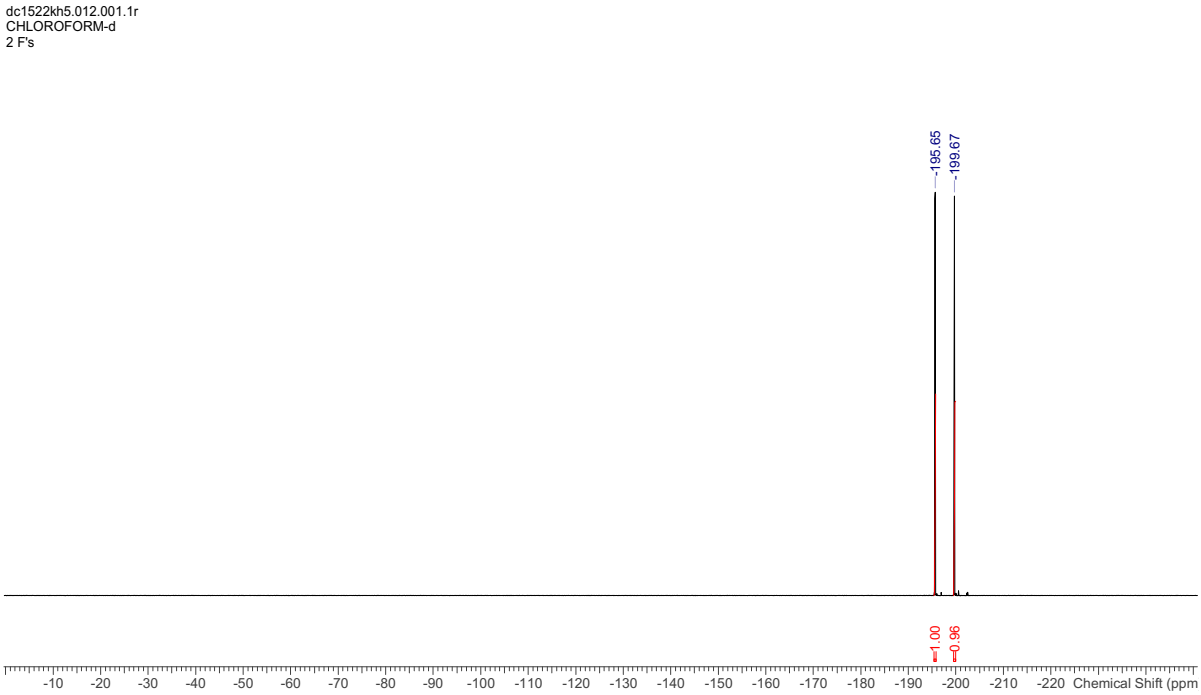


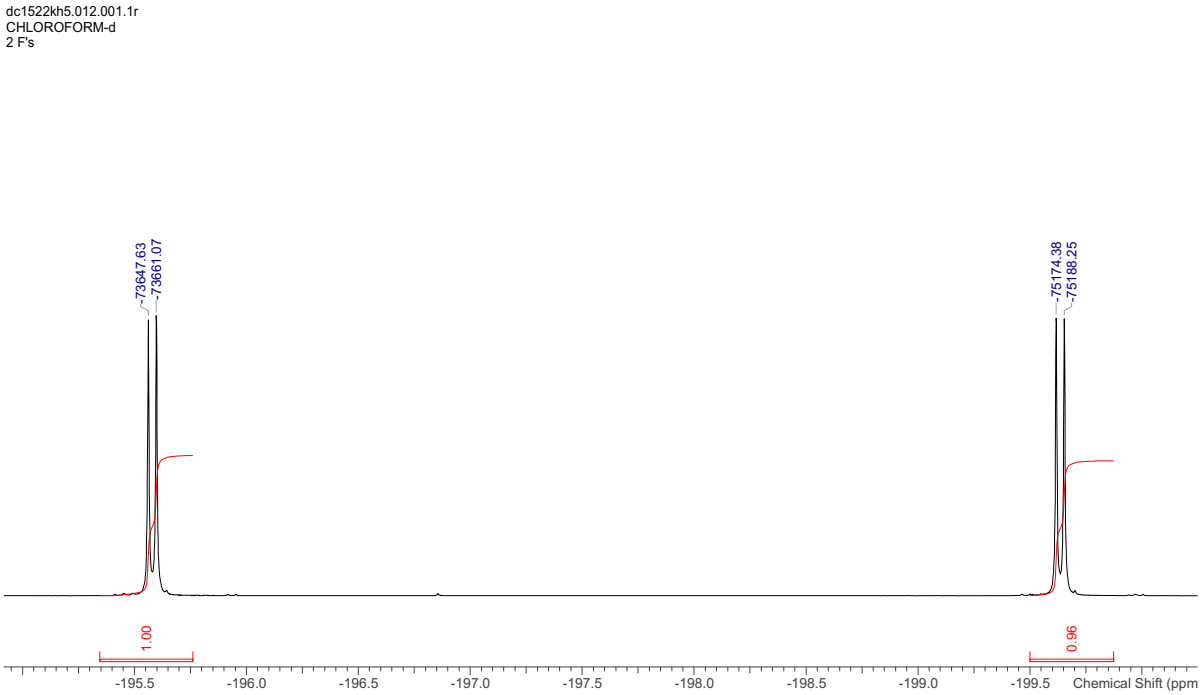
7.2.3 ^{19}F NMR, 376 MHz, $CDCl_3$





7.2.4 $^{19}F\{^{1}H\}$ NMR, 376 MHz, $CDCl_3$





8 References

1. C. Bucher and R. Gilmour, *Angew. Chem. Int. Ed.*, 2010, **49**, 8724-8728.
2. S.-J. Richards, T. Keenan, J.-B. Vendeville, D. E. Wheatley, H. Chidwick, D. Budhadev, C. E. Council, C. S. Webster, H. Ledru, A. N. Baker, M. Walker, M. C. Galan, B. Linclau, M. A. Fascione and M. I. Gibson, *Chem. Sci.*, 2021, **12**, 905-910.
3. L. Mtashobya, L. Quiquempoix and B. Linclau, *Journal of Fluorine Chemistry*, 2015, **171**, 92-96.
4. V. Denavit, D. Laine, C. Bouzriba, E. Shanina, E. Gillon, S. Fortin, C. Rademacher, A. Imberty and D. Giguere, *Chem. Eur. J.*, 2019, **25**, 4478-4490.