Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Contents

General information

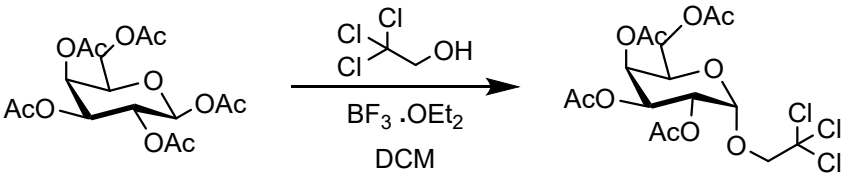
All the chemicals and solvents were provided from commercial suppliers and used without further purification. Dry DCM, acetonitrile, toluene, DMF and THF were obtained with an Innovative Technology PSMD-05 solvent drying system. As for other solvents were deal with using 4Å molecular sieves. Thin layer chromatography (TLC) was carried out using aluminum sheets coated with silica gel (60F). TLC plates were visualized with UV-light or with a 10 % solution of H_2SO_4 in ethanol and heat. Column chromatography was conducted with using Kieselgel 230-400 mesh silica gel. Specific rotations were measured by an Anton Paar polarimeter.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 500 MHz Ultra Shield Plus spectrograph equipped with a cryo-probe. Chemical shifts were reported relative to TMS (δ 0.00) or solvent residual signals. High resolution mass spectra (HRMS) were obtained from a Bruker SolariX XR 7T E8I/MALDI-FT-ICRMS instrument using matrix-assisted laser desorption ionization (MALDI) with dithranol as the matrix.

Synthetic procedures and characterization of compounds

General procedure for galactose

Synthesis of 2,2,2-trichloroethyl 2,3,4,6-tetra-O-acetyl-α-D-galactopyranoside (S1)[1]

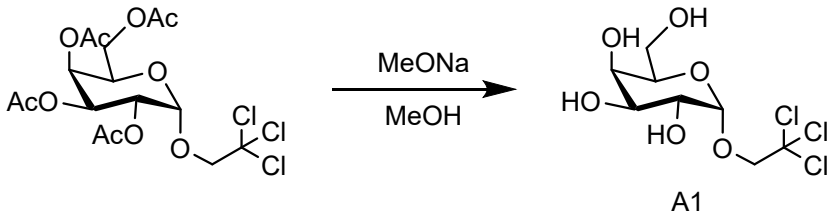


D-Galactose pentaacetate (9.75 g, 25 mmol) was dissolved in anhydrous DCM (20 mL). $BF_3{\cdot}Et_2O$ (10 mL) and $HOCH_2CCl_3$(10 mL) were sequentially added during stirring at room temperature. After 5 minutes the reaction was heated to reflux for 24 h. Then diluted with DCM (50 mL) and washed with aq. $NaHCO_3$ (100 mL). The organic flash was combined and dried with $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:5) to afford a white solid (9.37 g, 78%, α, Rf: 0.6 in Heptane/EtOAc=1/1); $[\alpha]_D^{25}$: 104(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{16}H_{21}Cl_3O_{10}Na^+$501.0093，found 501.0092

^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.45 – 5.41 (m, 1H, H2), 5.40 – 5.36 (m, 1H, H1), 5.36 – 5.30 (m, 1H, H3), 5.11 – 5.01 (m, 1H, H4), 4.25 (m 1H, H5), 4.19 – 4.14 (m, 1H, H6A), 4.05 (m, 2.3 Hz, 3H, H6B, -O-CH_2-), 2.09 – 2.06 (m, 3H, -Me), 2.02 – 1.99 (m, 3H, -Me), 1.99 – 1.96 (m, 3H, -Me), 1.95 – 1.91 (m, 3H, -Me).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.47, 170.24, 170.01, 169.88(-C=O), 96.89(C1), 96.86(-CCl_3), 79.44(-OCH_2), 67.62(C3, C5), 67.24(C2), 67.13(C4), 61.45(C6), 20.62(-Me), 20.57(-Me), 20.56(-Me), 20.50(-Me);

Synthesis of 2,2,2-trichloroethyl α-D-galactopyranoside (A1)



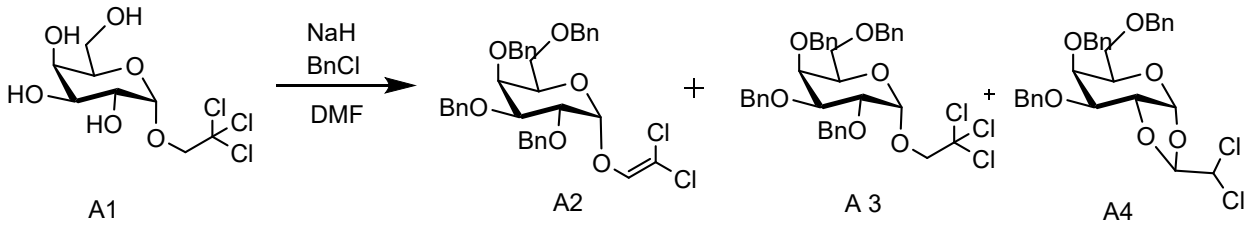
A1

Under N_2 atm., 2,2,2-trichloroethyl galactopyranoside **S1** (3.0 g, 6.25 mmol) was dissolved in dry methanol (40 mL), then added the CH_3ONa (68 mg, 1.25 mmol), and stirred for 1 h. Then the reaction was neutralized with Amberlite 120, filtered and concentrated in vacuo to give the product (Rf:0.13 in DCM/MeOH=10/1).

^{1}H NMR (500 MHz, MeOD) δ 5.12 (d, *J* = 3.5 Hz, 1H, H1), 4.37 (d, *J* = 11.5 Hz, 1H, -OCH_2-), 4.25 (d, *J* = 11.5 Hz, 1H-OCH_2), 3.98 (ddd, *J* = 6.7, 5.1, 1.3 Hz, 1H, H5), 3.95 (dd, *J* = 3.0, 1.4 Hz, 1H, H4), 3.86(qd, *J* = 10.2, 3.3 Hz, 2H, H2, H3), 3.74 (qd, *J* = 11.5, 6.0 Hz, 2H, H6A, H6B).

^{13}C NMR (126 MHz, MeOD) δ 101.21(C1), 80.70(-OCH_2), 73.54(C5), 71.23(C4), 71.02(C3), 70.08(C2), 62.73(C6).[1]

Synthesis of 2,2-dichloroethyl 3,4,6-tris-*O*-benzyl-α-D-galactopyranoside(A4)[2]



A1 A2 A 3 A4

The residue **A1** was dried and dissolved into anhydrous DMF (40 mL) under a N_2 atm., after that, NaH (1.5 g, 62 mmol) was added to the reaction. After keeping the reaction for 30 minutes, benzyl chloride (4.06 g 32.1 mmol) was added dropwise over 30 minutes. After reaction overnight, the reaction was quenched by methanol (2.0 mL), poured into ice water and extracted with EA (3×50 mL). The combined organic phases were then washed with water (2×50 mL) and concentrated. Purification by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:20 - 1/10) afforded a colorless oil **A3**(2.68 g, 62%, α, Rf:0.42 in Heptane/EtOAc=4/1) and the white solid byproduct **A2**, [α] : -10.2(c=0.98, $CHCl_3$), and the white solid

byproduct **A4** (1.34 g, 34%, α, [α] : 25(c=1, $CHCl_3$).) which will be major product on condition with NaH treatment for longer time.

In the same experimental setup, we lengthen the reaction time (NaH and the residue) from 30 minutes to 2 hours and only the main product **A4** (83%) and side product **A2** were isolated.

Product A2 (2,2-dichlorovinyl 2,3,4,6-tetra-O-benzyl-β-D-galactopyranoside)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 20H, arom-H), 6.89 (s, 1H, -CH=C-), 4.97 (dd, *J* = 10.1, 9.0 Hz, 2H, -$PhCH_2O$), 4.83 – 4.76 (m, 3H, -$PhCH_2O$), 4.68 – 4.62 (m, 2H, -$PhCH_2O$, H1), 4.50 – 4.43 (m, 2H, -$PhCH_2O$), 3.99 (dd, *J* = 9.8, 7.6 Hz, 1H, H2), 3.93 (d, *J* = 3.0 Hz, 1H, H3), 3.64 – 3.59 (m, 3H, H5, H6A, H6B), 3.56 (dd, *J* = 9.7, 2.9 Hz, 1H, H4).

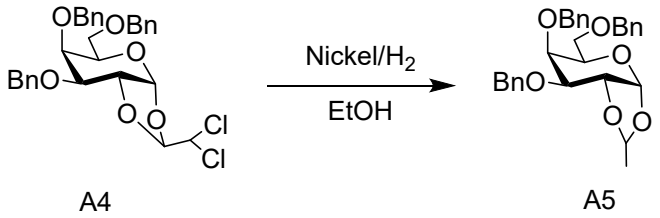
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.12(C=C), 138.37, 138.23, 138.10, 137.69, 128.50, 128.48, 128.45, 128.39, 128.29, 128.24, 127.96, 127.93, 127.84, 127.73, 127.70, 127.55(arom-C), 106.65(-CCl_2), 103.33(α-C1), 81.64(C4), 78.56(C2), 75.42(-$PhCH_2O$), 74.67(-$PhCH_2O$), 74.26(-$PhCH_2O$), 73.64(C5), 73.20(C3), 73.12(-$PhCH_2O$), 68.47(C6); HRMS(ESI): $[M+Na]^+$ calcd for $C_{36}H_{36}Cl_2O_6Na^+$657.1781，found 657.1775.

Product A4 (2,2-dichloroethyl 3,4,6-tris-*O*-Benzyl-α-D-galactopyranoside)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 – 7.16 (m, 15H，arom-H), 5.57 (d, *J* = 4.5 Hz, 1H, H1), 5.46 (d, *J* = 5.0 Hz, 1H, -O_2CH-), 5.18 (d, *J* = 4.9 Hz, 1H, -$CHCl_2$-), 4.83 (d, *J* = 11.4 Hz, 1H, -$PhCH_2O$), 4.72 (d, *J* = 12.1 Hz, 1H, -$PhCH_2O$), 4.61 (d, *J* = 12.1 Hz, 1H, -$PhCH_2O$), 4.53 (d, *J* = 11.5 Hz, 1H, -$PhCH_2O$), 4.38 (q, *J* = 11.8 Hz, 2H, -$PhCH_2O$), 4.31 (dd, *J* = 6.3, 4.5 Hz, 1H, H2), 4.00 (td, *J* = 6.7, 2.3 Hz, 1H, H5), 3.91 (t, *J* = 2.3 Hz, 1H, H4), 3.69 (dd, *J* = 6.3, 2.4 Hz, 1H, H3), 3.53 (dd, *J* = 6.7, 2.3 Hz, 2H, H6A, H6B).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.25, 137.93, 137.77, 128.44, 128.33, 128.02, 127.90, 127.83, 127.75, 127.66(arom-C), 103.06(-O_2CH-), 98.50(α-C1), 80.02(C3), 79.05(C2), 74.58(-$PhCH_2O$), 73.62(-$PhCH_2O$), 73.54(C5), 72.65(C4), 71.45(-$PhCH_2O$), 71.11C(-$CHCl_2$), 67.83(C6). HRMS(ESI): $[M+Na]^+$ calcd for $C_{29}H_{30}Cl_2O_6Na^+$567.1312，found 567.1305.

Synthesis of 1,2-O-ethylidene-3,4,6-tris-*O*-benzyl-α-D-galactopyranoside (A5)[3]



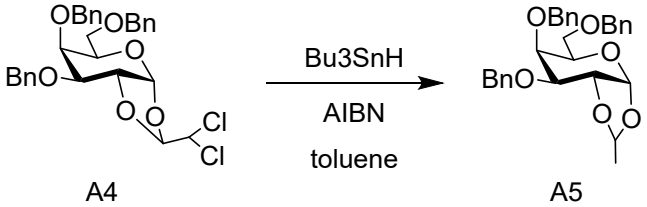
A4 A5

To a mixture of the starting material **A4** (150 mg, 0.28 mmol) in EtOH (10 mL) Raney-Ni (1.0 g) was added together with a H_2-atmosphere. The suspension was stirred for 8h at rt, triethylamine (1 mL) was then added and stirring was continued for another 8 h. Then the mixture was filtered through silica gel, and the filtrate was concentrated under vacuo. After column chromatographic purification (Heptane/EtOAc=1/1), afforded a colorless oil (82 mg, 63%, Rf:0.8 in Heptane/EtOAc=5/1); $[\alpha]_D^{25}$: 33(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{29}H_{32}O_6Na^+$ 499.2091，found 499.2104.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 15H, arom-H), 5.54 (d, *J* = 4.5 Hz, 1H. H1), 5.21 (q, *J* = 4.9 Hz, 1H. -O_2CH-), 4.96 (dd, *J* = 11.5, 2.1 Hz, 1H, -PhCH_2O), 4.85 – 4.81 (m, 1H,-PhCH_2O), 4.73 (dd, *J* = 12.1, 2.0 Hz, 1H, -PhCH_2O), 4.65 (d, *J* = 11.5 Hz, 1H, -PhCH_2O), 4.53 (d, *J* = 11.8 Hz, 1H, -PhCH_2O), 4.49 – 4.47 (m, 1H, -PhCH_2O), 4.23 (dd, *J* = 6.3, 4.5 Hz, 1H, H2), 4.12 (ddd, *J* = 7.8, 5.9, 2.3 Hz, 1H, H4), 4.04 (q, *J* = 3.0, 2.5 Hz, 1H, H5), 3.71 – 3.62 (m, 3H, H3, H6A, H6B), 1.44 (d, *J* = 4.9 Hz, 3H, -CH3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.51, 138.24, 137.96, 128.44, 128.42, 128.38, 128.30, 128.02, 128.00, 127.91, 127.86, 127.77, 127.75, 127.68, 127.66, 127.63, 127.57, 127.54(arom-C), 100.16(-O_2CH-), 98.00(C1), 80.91(C3), 77.53(C2), 74.48(-PhCH_2O), 73.48(-PhCH_2O), 73.13(C4), 72.80(C5), 71.50(-PhCH_2O), 68.18(C6), 21.25(CH_3). Signals missing possibly due to overlap. peaks are in agreement with previously reported spectra[4]

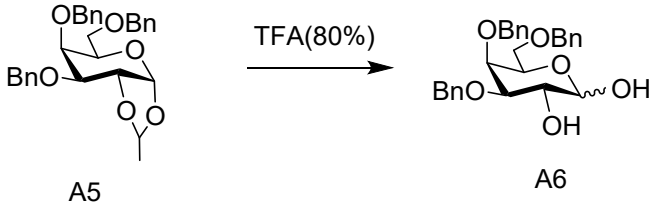
Synthesis of 1,2-O-ethylidene-3,4,6-tri-*O*-benzyl-α-D-galactopyranoside(A5)[5,6,7]



A4 A5

To a solution of starting materials **A4** (0.30 g, 0.55 mmol) in toluene (10 mL), Bu_3SnH (0.60 g, 0.6 ml, 2.06 mmol) and AIBN (0.02 g, 0.11 mmol) was added at 70 °C with stirring. After about 4 h the reaction was estimated finished (TLC control) and the mixture was shaken with 10% aq KF (10 mL) for 45 min. Thus, Bu_3SnF formed from the soluble chloride precipitated and was removed by filtration. The organic phase was washed with 3% aq $NaHSO_4$ (10 mL) and H_2O (2×10 mL), and concentrated under reduced pressure. The residue was purified by column (Heptane/EtOAc=20/1) to afford the colorless oil product (188 mg, 72%, Rf: 0.5 in Heptane/EtOAc=10/1)

Synthesis of 3,4,6-tris-O-benzyl-D-galactopyranose (A6) [6,8]



A5 A6

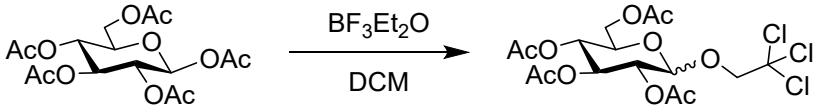
The starting material **A5** (1.0 g, 2.10 mmol) was dissolved by treatment with 80%, aqueous trifluoroacetic acid (10 mL) while stirring overnight at rt. After evaporation of the solvents under reduced pressure, the residue was purified by column chromatography(Heptane/EtOAc=3/1-2/1) to afford the colorless oil product (784 mg, 83%, α/β=3/1, Rf:0.4 in Heptane/EtOAc=1/2); $[\alpha]_D^{25}$: 48(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{27}H_{30}O_6Na^+$473.1940，found 473.1948.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 30H, arom-H), 5.33 (d, *J* = 3.8 Hz, 1H, αH1), 4.92 – 4.88 (m, 1H, -PhCH2O), 4.75 (d, *J* = 11.9 Hz, 1H, -PhCH2O), 4.72 – 4.66 (m, 2H, -PhCH2O), 4.59 (dd, *J* = 13.3, 11.4 Hz, 2H, -PhCH2O), 4.53 (d, *J* = 3.4 Hz, 1H, βH1), 4.50 (d, *J* = 3.1 Hz, 1H, -PhCH2O), 4.48 – 4.40 (m, 2H, -PhCH2O), 4.18 – 4.13 (m, 2H, αH2, βH5), 3.94 – 3.89 (m, 2H, αH4, βH2, βH4), 3.75 (dd, *J* = 10.0, 2.8 Hz, 1H, αH3), 3.63 – 3.51 (m, 3H, αH5, αH6A, βH6A), 3.49 – 3.39 (m, 2H, βH3, αH6B, βH6B), 2.71 (s, 2H, -OH, -OH);

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.34, 138.25, 138.14, 137.93, 137.62, 137.59(arom-C), 128.59, 128.51, 128.49, 128.45, 128.43, 128.37, 128.36, 128.35, 128.32, 128.29, 128.21, 128.16, 128.10, 127.95, 127.93, 127.88, 127.84, 127.78, 127.76, 127.65, 127.62(arom-C), 97.25(βC1), 92.67(αC1), 81.91(βC3), 79.13(αC3), 74.62(-PhCH2O), 74.60(-PhCH2O), 74.55(αC4), 73.88(βC2), 73.56(-PhCH2O), 73.52(-PhCH2O), 72.95(βC4), 72.45(-PhCH2O), 72.43(-PhCH2O), 69.53(αC2), 69.30(βC5), 68.98(αC6), 68.66(βC6). Signals missing possibly due to overlap. Peaks are in agreement with previously reported spectra.[9]

General experimental procedure for glucose

Synthesis of 2,2,2-trichloroethyl 2,3,4,6-tetra-O-acetyl-D-glucopyranoside (S2)

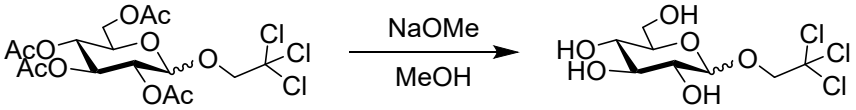


D-Glucose pentaacetate (5 g, 12.8 mmol) was dissolved in anhydrous DCM (80 mL), and $BF_3{\cdot}Et_2O$ (4 mL), $HOCH_2CCl_3$(4 mL) were sequentially added during the stirring at room temperature. After 5 minutes, the reaction was heated to reflux for 24 h., then diluted with DCM (100 mL) and washed with aq. $NaHCO_3$

(2×100 mL). The organic phase was combined and dried with $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Ethyl acetate / Heptane= 1/5-1/3) to afford a white solid (4.52 g, 73%, α/β=5:1, Rf: 0.4 in Heptane/EtOAc=2/1); [α] $^{25}_{D}$: 66(c=1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (dd, *J* = 10.2, 9.4 Hz, 1H, H3), 5.44 (d, *J* = 3.9 Hz, 1H, αH1), 5.10 (t, *J* = 9.8 Hz, 1H, H4), 4.90 (dd, *J* = 10.2, 3.8 Hz, 1H, H2), 4.29 – 4.24 (m, 2H, H6A, -CH_2CCl_3), 4.18 – 4.12 (m, 5H, H6B, H5, -CH_2CCl_3), 2.11 (s, 3H, -CH_3), 2.08 (s, 3H, -CH_3), 2.05 (s, 3H, -CH_3), 2.04 (s, 3H, -CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.61, 170.37, 170.08, 169.62(arom-C), 96.57(αC1), 95.90(-CCl_3), 79.63(-CH_2CCl_3), 70.48(C2), 69.79(C3), 68.32(C4), 68.22(C5), 61.64(C6), 20.71(-CH_3), 20.63(-CH_3), 20.60(-CH_3), 20.57(-CH_3). Signals missing possibly due to overlap. peaks are in agreement with previously reported spectra[10]

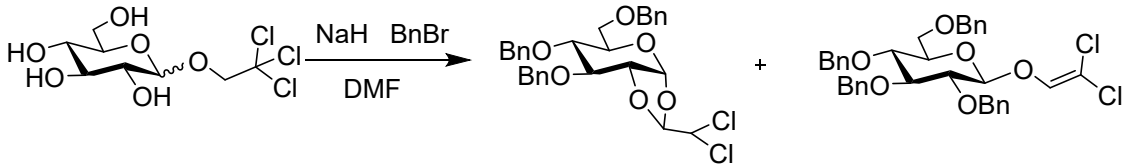
Synthesis of 2,2,2-trichloroethyl D-glucopyranoside (B1)



B1

N_2 protection, 2,2,2-trichloroethyl galactopyranoside S2 (2.0 g, 4.17 mmol) was dissolved in the dry methanol (40 mL), then added CH_3ONa (68 mg, 1.3 mmol) and left stirring for 1 h. Afterwards it was neutralized with Amberlite 120, filtered and washed with methanol, concentrated in vacuo and was used to next step reaction directly. HRMS(ESI): $[M+Na]^+$ calcd for $C_8H_{13}O_6Cl_3Na^+$332.9670，found 332.9669.

Synthesis of 1,2-O-(2,2-dichloroethyliden) 3,4,6-tris-*O*-Benzyl-α-D-glucopyranoside(B2)



B1 B2 B3

B1(1.0 g 3.2 mmol) was dried and dissolved in anhydrous DMF (20 mL) under a N_2 atmosphere, after that, NaH (308 mg, 12.8 mmol) was added to the reaction. After keeping the reaction for 2 h, benzyl chloride (2.47 g 14.4 mmol) was added dropwise into it over 30 minutes. After reaction overnight, the reaction was quenched by methanol (2.0 mL), poured into the ice water and extracted with EA (3×50 mL). The combined organic phases were washed with water (2×50 mL), concentrated and purified by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:20 - 1/10) to afford mixture colorless oil **B2** (1.19

g, 66%, α, [α] : 47(c=1, $CHCl_3$), Rf:0.5 in Heptane/EtOAc=5/1) and **B3** (0.25 g, 14%, β, [α] : 1.0($CHCl_3$), Rf:0.6 in Heptane/EtOAc=5/1)

Product B2 (1,2-O-(2,2-dichloroethylidene) 3,4,6-tris-*O*-benzyl-α-D-glucopyranoside)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 15H, arom-H), 5.78 (d, *J* = 5.1 Hz, 1H, H1), 5.68 (d, *J* = 4.6 Hz, 1H, -$CHCHCl_2$), 5.24 (d, *J* = 4.6 Hz, 1H, -$CHCl_2$), 4.82 (d, *J* = 11.8 Hz, 1H, -$PhCHO_2$), 4.75 (d, *J* = 11.2 Hz, 1H, -$PhCHO_2$), 4.70 (d, *J* = 11.7 Hz, 1H, -$PhCHO_2$), 4.62 (d, *J* = 12.1 Hz, 1H, -$PhCHO_2$), 4.52 (dd, *J* = 11.7, 6.2 Hz, 2H, -$PhCHO_2$), 4.28 (t, *J* = 4.7 Hz, 1H, H2), 4.06 – 4.00 (m, 2H, H3, H5), 3.81 – 3.77 (m, 1H, H4), 3.74 (d, *J* = 3.0 Hz, 2H, H6A, H6B).

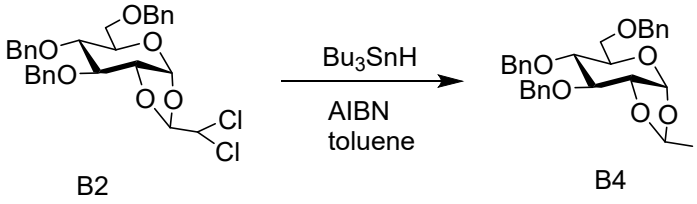
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.99, 137.94, 137.73, 128.66, 128.53, 128.48, 128.42, 128.40, 128.25, 128.05, 128.02, 127.93, 127.87, 127.82, 127.73（arom-H), 102.78(-$CHCl_2$), 98.60(C1), 80.57(C3), 78.16(C2), 74.40(C4), 73.83(-$PhCH_2O$-), 73.52(-$PhCH_2O$-), 72.44(-$PhCH_2O$-), 72.00(C5), 70.40(-O2CH-), 68.76(C6). HRMS(ESI): $[M+Na]^+$ calcd for $C_{29}H_{30}Cl_2O_6Na^+$567.1314，found 567.1302.

Product B3 (2,2-Dichlorovinyl 2,3,4,6-tetra-O-benzyl-β-D-glucopyranoside)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 18H, arom-H), 7.19 – 7.16 (m, 2H, arom-H), 6.91 (s, 1H, -$CH=CCl_2$), 4.98 (dd, *J* = 12.9, 10.8 Hz, 2H, -$PhCH_2$-), 4.83 (dd, *J* = 10.9, 3.7 Hz, 2H, -$PhCH_2$-), 4.77 (d, *J* = 10.7 Hz, 1H, -$PhCH_2$-), 4.71 (d, *J* = 7.6 Hz, 1H, -β-H1), 4.63 (d, *J* = 12.2 Hz, 1H, -$PhCH_2$-), 4.59 – 4.54 (m, 2H, -$PhCH_2$-), 3.76 (dd, *J* = 10.9, 2.1 Hz, 1H, -H6A), 3.73 – 3.71 (m, 1H, H6B), 3.69 – 3.65 (m, 2H, H3, H4), 3.64 – 3.60 (m, 1H, H2), 3.53 (ddt, *J* = 11.4, 7.8, 3.9 Hz, 1H, H5).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.19（-$CH=CCl_2$), 138.38, 137.88, 137.86, 137.81, 128.57, 128.51, 128.47, 128.45, 128.43, 128.40, 128.00, 127.95, 127.92, 127.87, 127.83, 127.81, 127.78, 127.71, 127.64(arom-C), 107.07(-CCl_2), 103.04(-β-C1), 84.14(C3), 81.29(C2), 77.20(C4), 75.74(-$PhCH_2$-), 75.55(C5), 75.12(-$PhCH_2$-), 75.02(-$PhCH_2$-), 73.55(-$PhCH_2$-), 68.41(C6). HRMS(ESI): $[M+Na]^+$ calcd for $C_{36}H_{36}Cl_2O_6Na^+$657.1781，found 657.1755.

Synthesis of 1,2-O-ethylidene-3,4,6-tris-*O*-benzyl-α-D-glucopyranoside(B4)

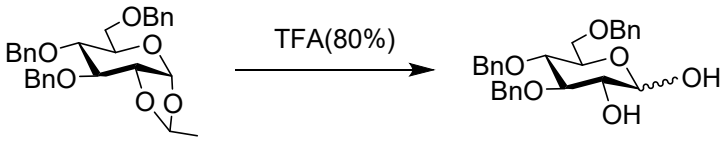


To a solution of starting materials **B2** (0.60 g, 1.1 mmol) in toluene (10 mL), Bu_3SnH (1.20 g, 1.2 ml, 4.12 mmol) and AIBN (0.04 g, 0.22 mmol) was added at 80 °C with stirring. After about 10 h the reaction was finished (TLC control) and the mixture was shaken with 10% aq. KF (20 mL) for 45 min. Thus, Bu_3SnF formed and was removed by filtration. The organic phase was washed with 3% aq. $NaHSO_4$ (10 mL) and H_2O (2×10 mL), and concentrated under reduced pressure. The residue was purified by column (Heptane/EtOAc=20/1) to afford the colorless oil product (398 mg, 76%, Rf:0.5 in Heptane/EtOAc=10/1); $[\alpha]_D^{25}$: 31 (c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{29}H_{32}O_6Na^+$499.2091，found 499.2110.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.17 (m, 15H, arom-H), 5.65 (d, *J* = 5.0 Hz, 1H, -H1), 5.13 (q, *J* = 4.8 Hz, 1H, -O_2CH-), 4.73 – 4.52 (m, 6H, -PhCH_2O), 4.18 – 4.14 (m, 1H, -H2), 4.00 – 3.95 (m, 2H, -H3, -H4), 3.82 – 3.78 (m, 1H, -H6A), 3.76 – 3.72 (m, 1H, -H5), 3.71 – 3.69 (m, 1H, -H6B), 1.51 (d, *J* = 4.9 Hz, 3H, -CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.17(arom-C), 137.90, 137.77, 128.66, 128.54, 128.51, 128.44, 128.42, 128.38, 128.35, 128.18, 128.12, 128.06, 128.00, 127.95, 127.87, 127.74, 127.63(arom-C), 100.74(-O_2CH), 97.30(-C1), 77.93(-C3), 75.70(-C2), 75.10(-C5), 73.36(-PhCH_2O-), 72.60(-PhCH_2O-), 71.80(-PhCH_2O-), 69.79(-C4), 69.07(-C6), 19.97(-CH_3).[11]

Synthesis of 3,4,6-tris-O-Benzyl-D-glucopyranose (B5)



B4 B5

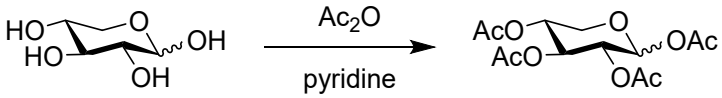
B4 (300 mg, 0.6 mmol) was dissolved in 80%, aqueous trifluoroacetic acid (10 mL) and stirred overnight at rt. After evaporation of the solvents under reduced pressure, the residue was purified by column chromatography (Heptane/EtOAc=3/1-2/1) to afford the colorless oil product (232 mg, 82%, α/β=5:2, Rf:0.4 in Heptane/EtOAc=1/2); $[\alpha]_D^{25}$: 40(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{27}H_{30}O_6Na^+$473.1935，found 473.1945.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.17 (m, 24H), 5.28 (d, *J* = 3.7 Hz, 1H, -α-H1), 4.94 – 4.82 (m, 5H，-α-PhCH2O-, -β-PhCH2O-), 4.61 (dd, *J* = 12.1, 6.3 Hz, 2H, -α-PhCH2O-, -β-PhCH2O-), 4.58 (d, *J* = 7.7 Hz, 1H, -β-PhCH2O-), 4.56 – 4.52 (m, 3H, ， -α-PhCH2O-, -β-PhCH2O-), 4.08 (dt, *J* = 9.9, 3.5 Hz, 1H, -α-H5), 3.82 (t, *J* = 9.1 Hz, 1H, -α-H3), 3.74 – 3.65 (m, 5H, -a-H2-, -α-H6A, -β-H6B,-b-H6A, -β-H6B), 3.61 – 3.53 (m, 3H, -α-H4,, -β-H3, -β-H4, β-H5), 3.51 – 3.47 (m, 1H, -β-H2).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.56, 138.49, 138.05, 137.91, 137.76, 137.69, 128.53, 128.44, 128.42, 128.05, 128.03, 127.98, 127.96, 127.92, 127.86, 127.82, 127.79(arom-C), 96.74(-b-H1), 92.42(-α-H1), 84.35(-b-H3), 82.47(-α-H3), 77.68(-α-H4), 77.57(-β-H4), 75.63(-β-H2), 75.35(-β-H5), 75.20(-α-PhCH2O), 74.97(-α-PhCH2O), 74.86(-β-PhCH2O), 73.57(-α-PhCH2O), 73.52((-β-PhCH2O), 72.76(-α-H2), 70.58(-α-H5), 68.84(-β-H6), 68.77(-α-H6). Signals missing possibly due to overlap. Peaks are in agreement with previously reported spectra.[12]

General experimental procedure for xylose

Synthesis of 1,2,3,4-tetra-O-acetyl-D-xylopyranose (S3)[13]



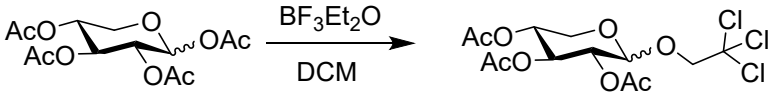
D-Xylose (10 g, 67.5 mmol) was dissolved in dry pyridine (50 mL), and Ac_2O (30 mL) was added at 0 °C, the resulting reaction mixture was stirred at rt overnight. The solvent was concentrated in vacuo, the residue was co-evaporated with toluene (3×20 mL), and poured into ice water and extracted with EA (3×50 mL). The combined organic phases were washed with water (2×50 mL), concentrated and purified by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:5 - 1/2) to afford the title product (21.3 g, 99%, α/β: 3/1, Rf: 0.5 in Heptane/EtOAc=1/1); [α] $^{25}_{D}$: 63(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{13}H_{18}O_9Na^+$ 341.0843，found 341.0853.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.27 (d, *J* = 3.6 Hz, 1H, -α-H1), 5.73 (d, *J* = 7.0 Hz, 0.3H, -β-H1), 5.49 (t, *J* = 9.8 Hz, 1H, -α-H3), 5.22 (t, *J* = 8.3 Hz, 0.3H, -β-H3), 5.09 – 4.96 (m, 3H, -α-H2, -α-H4, -β-H2, -β-H4), 4.17 (dd, *J* = 12.0, 5.0 Hz, 0.3H, -β-H5A), 3.96 (dd, *J* = 11.2, 5.9 Hz, 1H, -α-H5A), 3.73 (t, *J* = 11.0 Hz, 1H, -α-H5B), 3.54 (dd, *J* = 12.0, 8.5 Hz, 0.3H, -β-H5B), 2.20 (s, 3H, -α-CH3), 2.12 (d, *J* = 8.2 Hz, 2H, -β-CH3, -β-CH3), 2.08 (s, 1H, -CH3, -β-CH3) , 2.07 (t, *J* = 1.6 Hz, 7H, -α-CH3, -α-CH3, -β-CH3), 2.05 (s, 3H, -α-CH3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.23, 169.92, 169.86, 169.82, 169.40, 169.12(-C=O) , 92.01(-β-C1), 89.22(-α-C1), 70.96(-β-C3), 69.43(-β-C2), 69.31(-α-C2), 69.27(-α-C3), 68.66(-α-C4), 68.29(-β-C4),

62.80(-β-C6), 60.63(-α-C6), 20.95(-CH3), 20.89(-CH3), 20.81(-CH3), 20.75(-CH3), 20.68(-CH3), 20.57(-CH3).

Synthesis of 2,2,2-trichloroethyl 2,3,4-tris-O-acetyl-D-xylopyranoside (S4)[2]



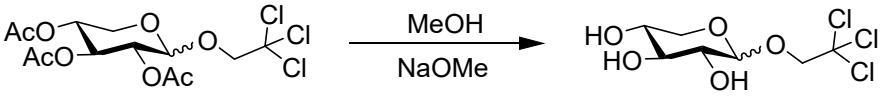
D-Xylose tetraacetate **S3** (10 g, 33 mmol) was dissolved in anhydrous DCM (80 mL) followed by the sequentially addition of $BF_3{\cdot}Et_2O$(10 mL) and $HOCH_2CCl_3$(10 mL) while stirring at room temperature. After 5 minutes the reaction was heated to reflux for 24 h, then diluted with DCM (200 mL) and washed with aq. $NaHCO_3$ (2×100 mL). The organic phases were combined and dried with $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Ethyl acetate / Heptane= 1/10-1/5) to afford a white solid (11.06 g, 82%, α/β: 5/2, Rf: 0.4 in Heptane/EtOAc=5/1); $[\alpha]_D^{25}$: 115(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{13}H_{17}Cl_3O_8Na^+$ 428.9881，found 428.9894.

2,2,2-trichloroethyl 2,3,4-tris-O-acetyl-α-D-xylopyranoside

^1H NMR (500 MHz, $CDCl_3$) δ 5.57 (t, *J* = 9.9 Hz, 1H, H3), 5.39 (d, *J* = 3.8 Hz, 1H, -α-H1), 5.00 (ddd, *J* = 10.7, 9.5, 5.9 Hz, 1H, H4), 4.84 (dd, *J* = 10.2, 3.7 Hz, 1H, H2), 4.25 (d, *J* = 11.9 Hz, 1H, $-CH_2CCl_3$), 4.10 (d, *J* = 11.9 Hz, 1H, $-CH_2CCl_3$), 3.87 (dd, *J* = 10.9, 5.9 Hz, 1H, H5A), 3.72 (t, *J* = 10.9 Hz, 1H, H5B), 2.08 (s, 3H, -CH3), 2.07 (s, 3H, -CH3), 2.06 (s, 3H, -CH3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.51, 170.06, 170.04(C=O), 96.64(-α-C1), 96.09($-CCl_3$), 79.42($-CH_2CCl_3$), 70.66(C2), 69.13(C3), 69.11(C4), 59.02(C5), 20.85(-CH3), 20.78(-CH3), 20.73(-CH3). Signals missing possibly due to overlap. Peaks are in agreement with previously reported spectra.[2]

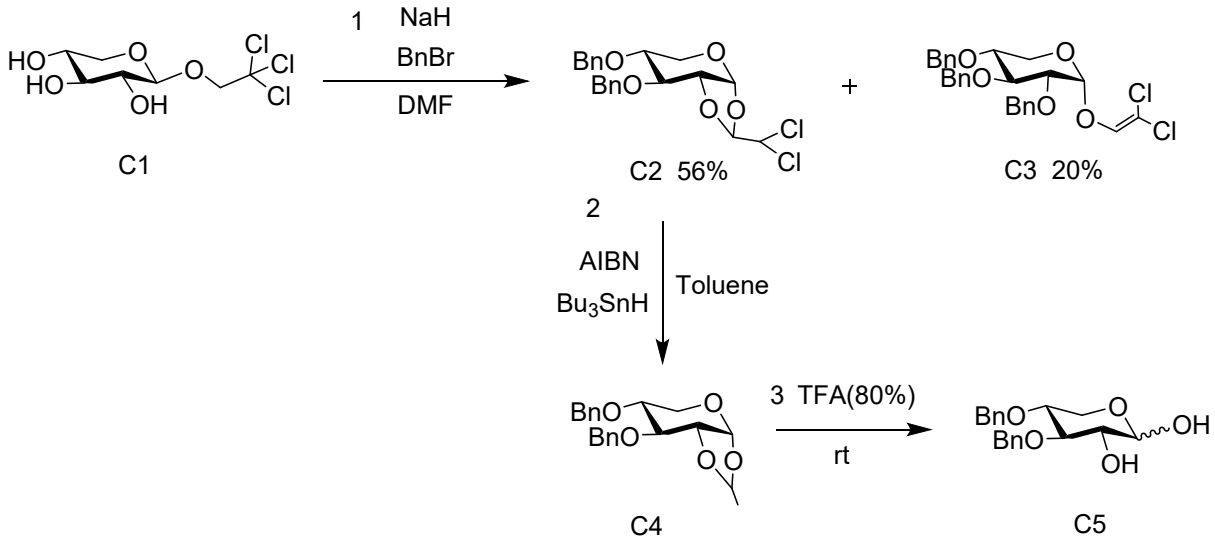
Synthesis of 2,2,2-trichloroethyl D-xylopyranoside (C1)



C1

Under a N_2 atmosphere, 2,2,2-trichloroethyl xylopyranoside **S4** (4.0 g, 9.8 mmol) was dissolved in dry methanol (20 mL) followed by the addition of CH_3ONa (106 mg, 1.96 mmol) and then stirred for 3 h. After this, it was neutralized with Amberlite 120, filtered and washed with methanol, concentrated in vacuo and used directly in the next step without purification. HRMS(ESI): $[M+Na]^+$ calcd for $C_7H_{11}Cl_3O_5Na^+$302.9564，found 302.9576.

Synthesis of 3,4-di-O-Benzyl-D-xylopyranose (C5)



1. The residue **C1** (2.76 g, 9.8 mmol) was dried and dissolved into anhydrous DMF (50 mL) under a N_2 atmosphere, after that, NaH (941 mg, 39.2 mmol) was added to the reaction. After keeping the reaction for 1 h, benzyl chloride (5.87 g 34.3 mmol) was added dropwise over 30 minutes. After stirring overnight, the reaction was quenched by methanol (2.0 mL), poured into ice water and extracted with EA (3×50 mL) and the combined organic phases were washed with water (3×50 mL). Then the organic phase was concentrated and the crude purified by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:20 - 1/10) to afford a mixture of **C2** and **C3** as a colorless oil (3.15 g, 76%, Rf: 0.5 in Heptane/EtOAc=10/1). Product **C2** $[\alpha]_D^{25}$: 21(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{21}H_{22}Cl_2O_5Na^+$447.0737，found 447.0758.

Product **C3** $[\alpha]_D^{25}$: 44(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{28}H_{28}Cl_2O_5Na^+$537.1206，found 537.1238.

2. The mixture (3.15 g) were dissolved into toluene (20 mL), Bu_3SnH (6.0 g, 22.2 mmol) and AIBN (180 mg, 1.6 mmol) was added at 100 °C with stirring. After about 4 h the reaction is finished (TLC control) and the mixture was shaken with 10% aq KF (50 mL) for 45 min. Thus, Bu_3SnF formed from the soluble chloride precipitated and was removed by filtration. The organic phase was washed with 3% aq. $NaHSO_4$ (50 mL) and H_2O (3×50 mL), and concentrated under reduced pressure to afford the colorless oil crude product (1.69 g, 64%, $[\alpha]_D^{25}$: 22 (c=1, $CHCl_3$).) which was used directly in the next step without purification.

3. The crude product (1.68 g) was treated with 80% aqueous trifluoroacetic acid (10 mL) under stirring overnight at rt. After evaporation of the solvents, under reduced pressure, the residue was purified by

column chromatography (Heptane/EtOAc=2/1-1/1) to afford a white solid (1.38g, 88%, α/β=2/1, Rf:0.3 in Heptane/EtOAc=1/1); [α] $^{25}_{D}$: 11(c=1, $CHCl_3$).

Product C3 (2,2-dichlorovinyl 2,3,4-tris-O-benzyl-α-D-xylopyranoside)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 10H, arom-H), 6.56 (s, 1H, -CH=CCl_2), 4.98 – 4.92 (m, 2H, -PhCH_2O), 4.90 – 4.83 (m, 2H, -PhCH_2O, H1), 4.78 (d, *J* = 11.6 Hz, 1H, -PhCH_2O), 4.66 (d, *J* = 11.9 Hz, 2H, -PhCH_2O), 4.03 – 3.96 (m, 1H, H3), 3.69 (dd, *J* = 5.0, 2.3 Hz, 1H, H5A), 3.65 – 3.58 (m, 2H, H5B, H4), 3.53 (dd, *J* = 9.6, 3.5 Hz, 1H, H2).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.08(-CH=CCl_2), 138.70, 138.10, 138.04, 128.55, 128.51, 128.41, 128.05, 128.03, 128.00, 127.93, 127.87, 127.69(arom-C), 107.89(-CH=CCl2), 98.86(C1), 80.95(C3), 79.04(C2), 77.47(C4), 75.90(-PhCH_2O), 73.73(-PhCH_2O), 73.65(-PhCH_2O), 61.31C5). HRMS(ESI): $[M+Na]^+$ calcd for $C_{28}H_{28}Cl_2O_5Na^+$ 537.1206，found 537.1238.

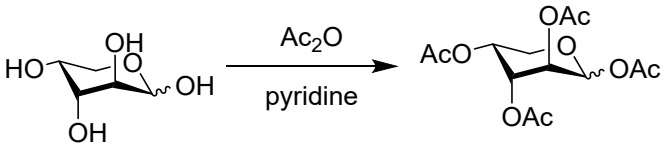
3,4-di-O-Benzyl-D-xylopyranose (C5)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (tq, *J* = 11.8, 4.4, 3.6 Hz, 20H, arom-H), 5.14 (d, *J* = 3.5 Hz, 1H， -α-H1), 4.88 (d, *J* = 3.9 Hz, 3H, -PhCH_2O-), 4.80 (d, *J* = 11.7 Hz, 1H, -PhCH_2O-), 4.74 (d, *J* = 11.7 Hz, 1H, -PhCH_2O-), 4.71 (t, *J* = 3.7 Hz, 1H, -PhCH_2O-), 4.69 – 4.63 (m, 3H, -PhCH_2O-,-β-H2), 3.98 (dd, *J* = 11.8, 4.1 Hz, 1H, -β-H5A), 3.88 (t, *J* = 8.6 Hz, 1H, -α-H3), 3.85 – 3.80 (m, 1H, -α-H5A), 3.70 (dd, *J* = 11.3, 5.2 Hz, 1H, -α-H5B), 3.66 – 3.62 (m, 1H, -β-H3, -α-H4), 3.57 (ddd, *J* = 10.2, 8.4, 5.2 Hz, 1H, -α-H4), 3.51 (dd, *J* = 8.8, 3.5 Hz, 1H, -α-H2), 3.36 – 3.28 (m, 1H, -β-H2, -β-H5B), 2.39(s, 2H, -OH, -OH).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.66, 138.51, 138.35, 138.25, 138.10, 137.83, 128.58, 128.53, 128.50, 128.46, 128.44, 128.40, 128.37, 128.11, 128.06, 128.03, 128.01, 127.98, 127.96, 127.90, 127.84, 127.82, 127.79, 127.73, 127.69(arom-C), 97.76(-β-C1), 91.50(-α-C1), 83.18(-β-C3), 82.31(-β-C2), 80.48(-α-C2), 79.47(-α-C3), 77.54(-β-C4), 77.48(-α-C4), 75.50(-PhCH_2O), 74.79(-PhCH_2O), 73.46(-PhCH_2O), 73.28(-PhCH_2O), 63.75(−β-C5), 60.42(-α-C5). HRMS(ESI): $[M+Na]^+$ calcd for $C_{19}H_{22}O_5Na^+$353.1359, found 353.1395. Signals missing possibly due to overlap. Peaks are in agreement with previously reported spectra.[14]

General experimental procedure for arabinose

Synthesis of 1,2,3,4-Tetra-O-acetyl-D-Arabinopyranose (S5)[15]

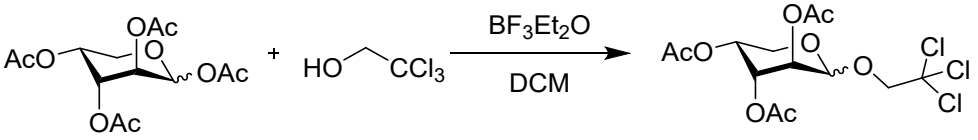


Arabinose (5.00 g, 33 mmol) was dissolved in dry pyridine (50 mL), and Ac_2O (30 mL) was added at 0 °C, the resulting reaction mixture was stirred at rt overnight. The reaction mixture was concentrated in vacuo, the residue was co-evaporated with toluene (3×20 mL), and poured into the ice water and extracted with EA (3×50 mL), which was then washed with water (2×50 mL). The organic phase was concentrated and purified by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:5-1/2) to afford the title product (9.6 g, 91%, α/β: 1/5 Rf: 0.6 in Heptane/EtOAc=1/1); $[\alpha]_D^{25}$: -89(c=1, $CHCl_3$).

^1H NMR (500 MHz, $CDCl_3$) δ 6.37 (d, *J* = 3.1 Hz, 1H, H1), 5.40 (dt, *J* = 3.2, 1.5 Hz, 1H, H4), 5.39 – 5.36 (m, 2H, H2, H3), 4.08 (dd, *J* = 13.4, 1.4 Hz, 1H, H5A), 3.85 (dd, *J* = 13.2, 2.0 Hz, 1H, H5B), 2.18 (s, 6H, -CH_3, -CH_3), 2.05 (s, 6H, CH_3, -CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.40, 170.26, 170.00, 169.25(-C=O), 90.15(C1), 68.42(C4), 66.99(C2), 66.62(C3), 62.78(C5), 20.99(-CH_3), 20.97(-CH_3), 20.79(-CH_3), 20.66(-CH_3).[16]

Synthesis of 2,2,2-trichloroethyl 2,3,4-tris-O-Acetyl-D-arabinopyranoside (S6)



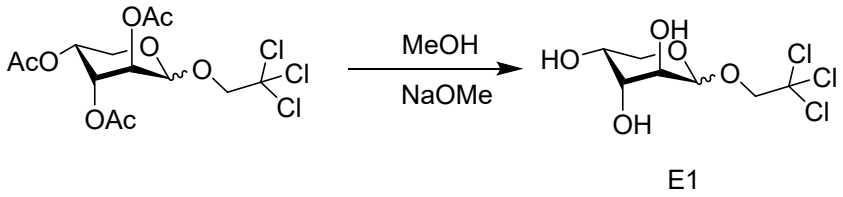
Arabinose tetraacetate **S5** (10 g, 33 mmol) was dissolved in anhydrous DCM (80 mL), and $BF_3{\cdot}Et_2O$ (10 mL), $HOCH_2CCl_3$(10 mL) were sequentially added during the stirring at room temperature. After 5 minutes, the reaction was heated to reflux and left for 24 h. The reaction mixture was diluted with DCM (200 mL) and washed with aq. $NaHCO_3$ (2×100 mL). The organic phases were combined and dried with $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Ethyl acetate / Heptane= 1/10-1/5) to afford the white solid (12.81 g, 96%, Rf: 0.7 in Heptane/EtOAc=1/1); $[\alpha]_D^{25}$: -105(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{13}H_{17}Cl_3O_8Na^+$428.9881，found 428.9906.

^1H NMR (500 MHz, $CDCl_3$) δ 5.46 (d, *J* = 3.6 Hz, 1H, -β-H1), 5.44 – 5.40 (m, 2H, H3, H4), 5.19 (ddd, *J* = 12.0, 3.7, 1.5 Hz, 1H, H2), 4.26 (d, *J* = 11.9 Hz, 1H, -CH_2CCl_3), 4.12 (d, *J* = 11.8 Hz, 1H, -CH_2CCl_3), 4.09 – 4.03 (m, 1H, H5A), 3.78 (dd, *J* = 13.1, 1.8 Hz, 1H, H5B), 2.16 (d, *J* = 4.9 Hz, 3H, -CH_3), 2.10 (s, 3H, -CH_3), 2.05 (s, 4H, -CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.69, 170.37, 170.15(-C=O), 97.37(-β-C1), 96.19(-CCl_3), 79.48(-

CH_2CCl_3), 68.69(C3), 67.90(C2), 66.92(C4), 61.12(C5), 21.00(-CH_3), 20.84(-CH_3), 20.82(-CH_3).[2]

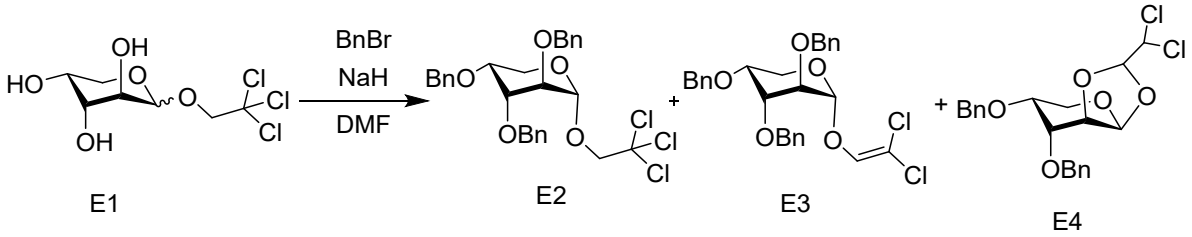
Synthesis of 2,2,2-trichloroethyl D-Arabinopyranoside (E1)



E1

Under an atmosphere of N_2 2,2,2-trichloroethyl arabinopyranoside **S6** (4.0 g, 9.8 mmol) was dissolved in the dry methanol (20 mL) followed by CH_3ONa (106 mg, 1.96 mmol) and then stirred for 3 h. The reaction was then neutralized with Amberlite 120, filtered and washed with methanol and concentrated in vacuo. The crude was used directly in the next step without purification. HRMS(ESI): $[M+Na]^+$ calcd for $C_7H_{11}Cl_3O_5Na^+$ 302.9564，found 302.9580.

Synthesis of 1,2-O-(2,2-dichloroethylidene) 3,4-di-*O*-Benzyl-D-arabinopyranoside(E4)



E1 E2 E3 E4

The residue **E1** was dried and dissolved in anhydrous DMF (50 mL) under a N_2 atmosphere, after that, NaH (941 mg, 39.2 mmol) was added to the reaction. After keeping the reaction for 2 h, benzyl chloride (5.87 g 34.3 mmol) was added dropwise into it over 30 minutes. After reaction overnight, the reaction was quenched by methanol (2.0 mL), poured into the ice water and extracted with EA (3×50 mL). The combined organic phases were then washed with water (3×50 mL), concentrated and purified by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:20 - 1/10) to afford a colorless oil Byproduct E2, Product **E3** (0.38g, 10%) HRMS(ESI): $[M+Na]^+$ calcd for $C_{28}H_{28}Cl_2O_5Na^+$537.1206, found 537.1225. A

colorless oil Product **E4** (2.26g, 61%, [α] : -37(c=1, $CHCl_3$).) HRMS(ESI): $[M+Na]^+$ calcd for $C_{21}H_{22}Cl_2O_5Na^+$447.0737, found 447.0754.

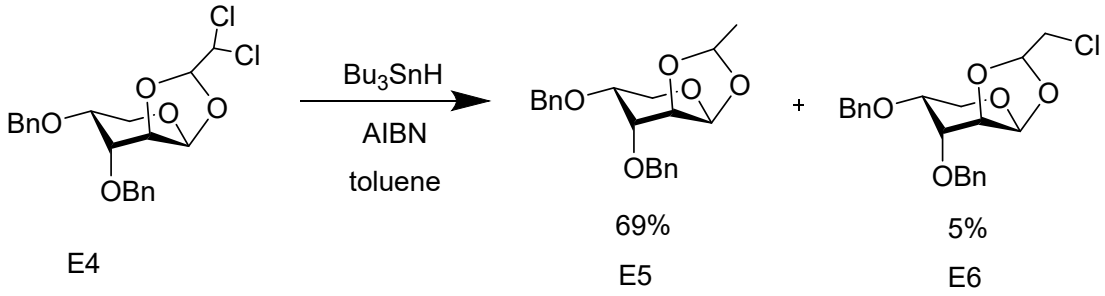
Product E4 1,2-O-(2,2-dichloroethylidene) 3,4-di-*O*-benzyl-D-arabinopyranoside

^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (ddt, *J* = 21.3, 10.1, 6.2 Hz, 10H, arom-H), 5.59 (d, *J* = 6.3 Hz, 1H, -CH-CCl_2H), 5.53 (d, *J* = 3.2 Hz, 1H, H1), 5.31 (d, *J* = 6.3 Hz, 1H, -CH-CCl_2H), 4.77 (d, *J* = 2.8 Hz, 2H, -

$PhCH_2O$), 4.70 – 4.63 (m, 2H, -$PhCH_2O$), 4.29 (dd, *J* = 4.6, 3.2 Hz, 1H, H2), 4.01 (dd, *J* = 4.8, 2.3 Hz, 1H, H3), 3.93 (dd, *J* = 12.9, 7.7 Hz, 1H, H5A), 3.87 (dtd, *J* = 9.8, 5.9, 4.8, 2.5 Hz, 2H, H5B, H4).

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.90, 137.87, 128.49, 128.47, 127.89, 127.86, 127.61(arom-C), 105.41(O_2C-CCl_2H), 97.24(C1), 80.25(C2),75.26(C3), 72.67(-$PhCH_2O$), 72.47(-$PhCH_2O$), 72.07(C4), 71.52(-CH-CCl_2H), 63.38(C5).

Synthesis of 1,2-O-ethylidene-3,4-di-*O*-Benzyl-D-Arabinopyranoside(E5)



The starting material **E4** (200 mg, 0.47 mmol) was dissolved in toluene (4 mL), Bu_3SnH (548 mg, 1.88 mmol) and AIBN (20 mg) was added at 100 °C while stirring. After about 8 h the reaction was finished (TLC control) and then shaken with 10% aq KF (50 mL) for 45 min. Thus, the Bu_3SnF formed from the soluble chloride precipitated and was removed by filtration. The organic phase was washed with 3% aq. $NaHSO_4$ (50 mL) and H_2O (3×50 mL), and concentrated under reduced pressure to afford the colorless oil mixture product (124 mg, 74%), which was used directly in the next step without purification.

1,2-O-Ethylidene-3,4-di-*O*-Benzyl-D-arabinopyranoside E5

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 10H，arom-H), 5.39 (d, *J* = 3.5 Hz, 1H, H1), 5.22 (q, *J* = 4.9 Hz, 1H, -CHCH3), 4.77 (s, 2H, -PhCH2O), 4.68 (d, *J* = 3.2 Hz, 2H, -PhCH2O), 4.12 (dd, *J* = 4.6, 3.4 Hz, 1H, H2), 3.96 – 3.93 (m, 1H, H3), 3.92 – 3.86 (m, 3H, H4, H5A, H6A), 1.47 (d, *J* = 4.9 Hz, 3H, -CH3).

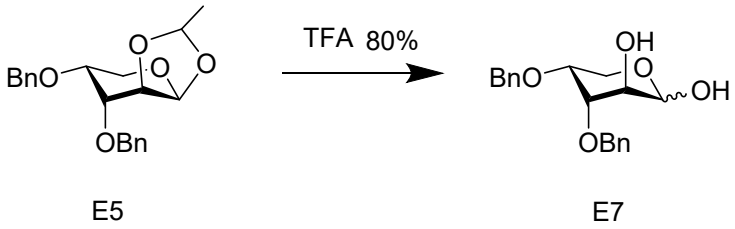
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.23, 138.21, 128.43, 128.40, 127.73, 127.72, 127.55(arom-C), 102.18(-CHCH3), 96.97(-C1), 78.72(-C2)), 76.03(-C3), 72.76(-C4), 72.53(-PhCH2O), 71.87(-PhCH2O), 63.31(-C5), 21.30(-CHCH3). HRMS(ESI): $[M+Na]^+$ calcd for $C_{21}H_{24}O_5Na^+$379.1516, found 379.1525.

1,2-O-(2-chloro-ethylidene)-3,4-di-*O*-benzyl-D-arabinopyranoside E6

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 10H), 5.47 (d, *J* = 3.3 Hz, 1H), 5.30 (t, *J* = 4.6 Hz, 1H, -CH-O2-), 4.80 – 4.74 (m, 2H, -PhCH2-), 4.67 (d, *J* = 2.7 Hz, 2H, -PhCH2-), 4.20 (dd, *J* = 4.6, 3.2 Hz, 1H, -H2), 4.00 (dd, *J* = 4.7, 2.5 Hz, 1H, -H3), 3.95 – 3.84 (m, 3H, -H4, -H5A, -H5B), 3.59 (qd, *J* = 11.6, 4.7 Hz, 2H, -CH_2Cl).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.05, 128.48, 128.46, 128.43, 127.82, 127.81, 127.79, 127.56(-arom-C), 103.32(-CH-O2), 97.00(C1), 79.06(C2), 75.41(-C3), 72.64(-PhCH2-), 72.53(-C4), 71.93(-PhCH2-), 63.06(-C5), 45.10(-CH2Cl). HRMS(ESI): $[M+Na]^+$ calcd for $C_{21}H_{23}ClO_5Na^+$413.1126, found 413.1140.

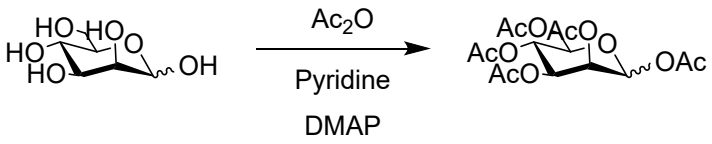
Synthesis of 3,4-di-O-Benzyl-D-arabinopyranose (E7)



The crude material **E5** (124 mg) was dissolved in 80%, aqueous trifluoroacetic acid (5 mL) and stirred overnight at rt. After evaporation of the solvents under reduced pressure, the residue was purified by column chromatography (Heptane/EtOAc=2/1-1/1) to afford a white solid (84.1 mg, 76%, α/β=1/5, Rf:0.3 in Heptane/EtOAc=1/1). HRMS(ESI): $[M+Na]^+$ calcd for $C_{19}H_{22}O_5Na^+$353.1359, found 353.1379.

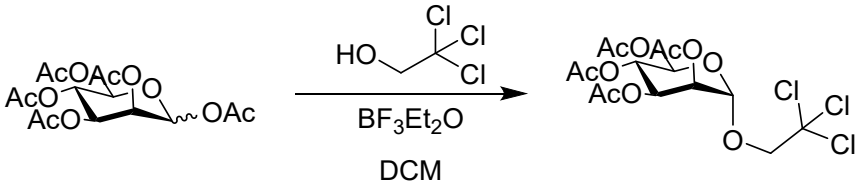
General experimental procedure for mannose 1

Synthesis of D-mannose pentaacetate (S7) [17,18]



D-Mannose (10 g, 55.5 mmol) was dissolved in dry pyridine (50 mL), DMAP (0.5 g, 4.9 mmol) and Ac_2O (50 mL) was added at 0 °C, the resulting reaction mixture was stirred at rt overnight. The solvent was removed in vacuo, the residue co-evaporated with toluene (2×20 mL) and then dried under vacuum to afford the title compound 4 (21.7 g crude, 97%, α/β=1/4, Rf:0.6 in Heptane/EtOAc=1/1), which was used directly in the next step without purification.

Synthesis of 2,2 ,2-Trichloroethyl 2,3,4,6-tetra-O-acetyI-α-D-mannopyranoside (S8) [19]



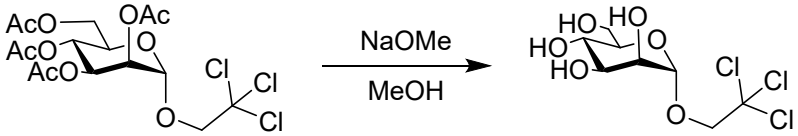
D-Mannose pentaacetate **S7** (5.0 g, 12.8mmol) was dissolved in anhydrous DCM (100 mL). $BF_3{\cdot}Et_2O$ (5 mL) and $HOCH_2CCl_3$(5 mL) were sequentially added during stirring at room temperature. After 5 minutes, the reaction was heated to reflux overnight. The reaction was quenched by aq. $NaHCO_3$ (50 mL), then diluted with DCM (100 mL) and washed with aq. $NaHCO_3$ (2×100 mL). The organic phases were combined

and dried with $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Ethyl acetate / Heptane 1/5-1/2) to afford the white solid (4.97 g, 81%, α, Rf: 0.3 in Heptane/EtOAc=5/1); $[\alpha]_D^{25}$: 50(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{16}H_{21}Cl_3O_{10}Na^+$501.0093，found 501.0126.

^1H NMR (500 MHz, $CDCl_3$) δ 5.47 – 5.40 (m, 2H, H2, H4), 5.33 (t, *J* = 9.8 Hz, 1H, H3), 5.12 (d, *J* = 1.6 Hz, 1H, H1), 4.33 – 4.25 (m, 2H, H6A, $-CH_2CCl_3$), 4.20 – 4.13 (m, 3H, H5, H6B, $-CH_2CCl_3$), 2.20 (d, *J* = 1.6 Hz, 3H, $-CH_3$), 2.13 (s, 3H, $-CH_3$), 2.08 (s, 3H, $-CH_3$), 2.03 (s, 3H, $-CH_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.54, 169.88, 169.74, 169.71(C=O), 98.13(C1), 95.60($-CCl_3$), 79.39(CH_2CCl_3), 69.63(C5), 69.08(C2), 68.67(C4), 65.93(C3), 62.26(C6), 20.85($-CH_3$), 20.72($-CH_3$), 20.69($-CH_3$), 20.65($-CH_3$). Signals missing possibly due to overlap. peaks are in agreement with previously reported spectra.

Synthesis of 2,2,2-Trichloroethyl-D-mannopyranoside (D1) [19]



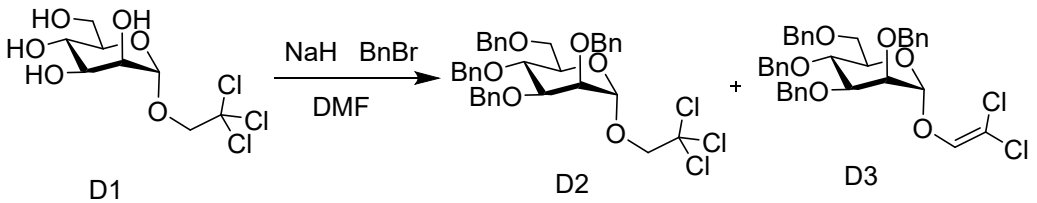
D1

Under N_2 protection, 2,2,2-trichloroethyl mannopyranoside **S8** (5.0 g, 10.4 mmol) was dissolved in dry methanol (40 mL), then added the CH_3ONa (113 mg, 2.1 mmol), and stirred overnight. Then the reaction was neutralized with Amberlite 120, filtered and concentrated in vacuo to give the crude product, and was used to next step reaction directly.

^1H NMR (500 MHz, MeOD) δ 5.07 (t, *J* = 1.4 Hz, 1H, H1), 4.36 (dd, *J* = 11.6, 1.2 Hz, 1H, $-CH_2CCl_3$), 4.24 (dd, *J* = 11.5, 1.2 Hz, 1H, $-CH_2CCl_3$), 3.96 (dt, *J* = 3.3, 1.4 Hz, 1H, H2), 3.89 (dt, *J* = 11.6, 1.5 Hz, 1H, H6A), 3.77 (ddd, *J* = 9.3, 3.4, 1.2 Hz, 1H, H3), 3.75 – 3.70 (m, 1H, H6B), 3.68 – 3.62 (m, 2H, H4, H5).

^{13}C NMR (126 MHz, MeOD) δ 102.33（C1）, 98.00（$-CCl_3$）, 80.15($-CH_2CCl_3$), 75.83(C4), 72.38(C3), 71.69(C2), 68.40(C5), 62.94(C6).

Synthesis of 2,2,2-trichloroethyl 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside(D2)[2]



D1 D2 D3

The residue **D1** was dried and dissolved into anhydrous DMF (40 mL) under N_2 atm. after that; NaH (1.25 g, 52 mmol) was added to the reaction. After keeping the reaction for 1 h, benzyl bromide (8.92 g 52 mmol) was added dropwise over 30 minutes. After reaction overnight, the reaction was quenched by methanol (2.0 mL), poured into ice water and extracted with EA (3×50 mL). The combined organic phases were then washed with water (2×50 mL) and concentrated. Purification by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:20 - 1/10) afforded a colorless oil byproduct D2 (420 mg, 6 %, Rf:0.82 in Heptane /EtOAc) and solid **D3** (4.38 g, 62%, Rf: 0.8 in Heptane/EtOAc=5/1). Product **D3** $[\alpha]_D^{25}$: 26(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{36}H_{36}Cl_2O_6Na^+$657.1781，found 657.1775.

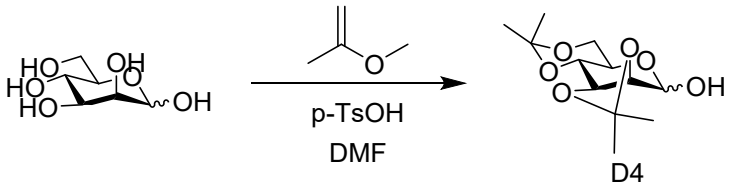
Product D3 (2,2-Dichlorovinyl 2,3,4,6-tetra-O-benzyl-β-D-mannopyranoside)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.19 (m, 20H), 6.74 (s, 1H, -CH=CCl2), 5.18 (d, *J* = 2.1 Hz, 1H, H1), 4.91 (dd, *J* = 10.8, 6.3 Hz, 1H, -$PhCH_2O$), 4.83 (d, *J* = 12.3 Hz, 1H, -$PhCH_2O$), 4.73 – 4.68 (m, 4H, -$PhCH_2O$), 4.57 – 4.53 (m, 2H, -$PhCH_2O$), 4.13 – 4.08 (m, 1H, H3), 4.00 – 3.95 (m, 1H, H4), 3.90 (dt, *J* = 5.2, 2.6 Hz, 1H, H2), 3.83 – 3.73 (m, 3H, H6A, H5, H6B).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.16(-CH=CCl2), 138.25, 138.22, 138.20, 137.96, 128.47, 128.40, 128.37, 128.06, 127.95, 127.94, 127.90, 127.86, 127.83, 127.79, 127.75, 127.72, 127.70, 127.60(arom-H), 107.24(=CCl2), 99.27(C1), 79.41(C4), 75.19(-$PhCH_2O$), 74.31(C3), 74.11(C2), 73.37(C5), 73.22(-$PhCH_2O$), 73.13(-$PhCH_2O$), 72.74(-$PhCH_2O$), 68.73(C6).

General experimental procedure for mannose 2

Synthesis of 2,3:4,6-di-O-isopropylidene-D-mannopyranose(D4) [17,20]



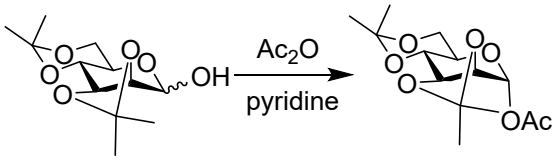
D-Mannose (20 g, 111 mmol) was dissolved in anhydrous DMF (40 mL) and cooled to 0°C. p-TsOH (100 mg, 0.6 mmol) and 2-methoxypropene (10 mL) were added to the resulting solution. The reaction mixture was stirred at 0°C for 3 h, after which 2-methoxypropene (8 mL) was added. The mixture was allowed to warm to rt overnight. The reaction mixture was neutralized by addition of Et_3N (2 mL) and extracted with ether (2×200 mL). The combined organic layers were washed with water (2×200 mL) and dried using $MgSO_4$. After filtration and concentration in vacuo, the product was isolated from the resulting gum by crystallization using ethyl acetate/PE to afford the desired product (21.9 g, 76%, Rf: 0.6 in

Heptane/EtOAc=3/1) as a white solid containing a mixture of anomers; $[\alpha]_D^{25}$: 9.0(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{12}H_{20}O_6Na^+$283.1152，found 283.1159.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.40 (d, *J* = 1.7 Hz, 1H, -H1), 4.83 (dd, *J* = 5.9, 3.6 Hz, 1H, -H3), 4.64 (d, *J* = 5.9 Hz, 1H, -H2), 4.45 – 4.40 (m, 1H, -H5), 4.21 (dd, *J* = 7.1, 3.6 Hz, 1H, -H4), 4.13 – 4.04 (m, 2H, H6A, -H6B), 3.00 – 2.94 (m, 1H, -OH), 1.48 (d, *J* = 3.8 Hz, 6H, $-CH_3$), 1.40 (s, 3H, $-CH_3$), 1.35 (s, 3H, $-CH_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 112.66(-O2C-), 109.10, -O2C-), 101.28(-C1), 85.48(-C2), 80.29(-C4), 79.64(-C3), 73.27(-C5), 66.569(-C6) 26.84($-CH_3$), 25.85($-CH_3$), 25.17(-CH3), 24.46($-CH_3$).

Synthesis of 1-O acetyl-2,3:4,6-di-O-isopropylidene-D-mannopyranose(D5)[17]



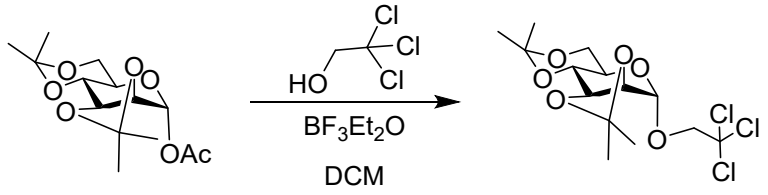
D4 D5

On an ice bath, hemiacetals **D4** (3.0 g, 11.53 mmol) were dissolved in dry pyridine (20 mL). To the resulting mixture was added Ac_2O (3.0 mL) and the reaction mixture was stirred overnight at rt. The solution was concentrated under high-vacuum and co-evaporated with toluene (3×10 mL) to afford a residue, which was purified by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:10 - 1/5) to afford a colorless oil (2.91 g, 84%, α, Rf: 0.7 in Heptane/EtOAc=4/1); $[\alpha]_D^{25}$: 47 (c=1, $CHCl_3$). HRMS (ESI): $[M+Na]^+$ calcd for $C_{14}H_{22}O_7Na^+$325.1258，found 325.1268.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.13 (s, 1H, H1), 4.86 (dd, *J* = 5.9, 3.6 Hz, 1H, H3), 4.71 (d, *J* = 5.9 Hz, 1H, H2), 4.41 (ddd, *J* = 7.9, 6.1, 4.2 Hz, 1H, H5), 4.11 (dd, *J* = 8.9, 6.2 Hz, 1H, H6A), 4.07 – 4.02 (m, 2H, H6B, H4), 2.08 (s, 3H, $-COCH_3$), 1.49 (s, 3H, $-CH_3$), 1.47 (s, 3H, $-CH_3$), 1.39 (s, 3H, $-CH_3$), 1.35 (s, 3H, $-CH_3$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.40(-C=O), 113.26($-O_2C$-), 109.34($-O_2C$-), 100.809-C1), 85.07(-C2), 82.23(-C4), 79.31(-C3), 72.89(-C5), 66.82(-C6), 27.00($-CH_3$), 25.95($-CH_3$), 25.13($-CH_3$), 24.67($-CH_3$), 21.07($-CH_3$).

Synthesis of 2,2,2-trichloroethyl 2,3:4,6-di-O-Isopropylidene-D-mannopyranoside(D6)



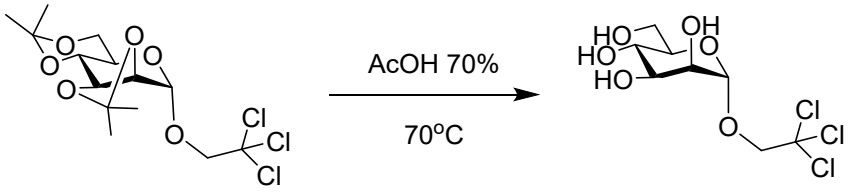
D5 D6

The starting material **D5** (1.0 g, 3.3 mmol) was dissolved in anhydrous DCM (20 mL). $BF_3{\cdot}Et_2O$ (1 mL) and $HOCH_2CCl_3$(1 mL) were then sequentially added during stirring at room temperature. After 5 minutes, the reaction was heated to reflux and left overnight. The reaction was quenched by aq. $NaHCO_3$ (50 mL), then diluted with DCM (3×50 mL) and washed with aq. $NaHCO_3$ (2×50 mL). The organic phases were combined and dried with $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (Ethyl acetate / Heptane 1/20-1/10) to afford the white solid (0.72 g, 55%, α, Rf: 0.8 in Heptane/EtOAc=4/1). HRMS(ESI): $[M+Na]^+$ calcd for $C_{14}H_{21}Cl_3O_6Na^+$413.0296，found 413.0307.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.28 (s, 1H, -H1), 4.88 (dd, *J* = 5.9, 3.6 Hz, 1H, -H3), 4.80 (d, *J* = 5.9 Hz, 1H, -H2), 4.44 (ddd, *J* = 7.6, 6.3, 4.4 Hz, 1H, H5), 4.21 (d, *J* = 11.5 Hz, 1H, -CH_2-), 4.14 (d, *J* = 2.3 Hz, 1H, -CH_2-), 4.11 (dd, *J* = 8.1, 3.3 Hz, 2H, -H6A, -H4), 4.05 (dd, *J* = 8.8, 4.4 Hz, 1H, -H6B), 1.50 (s, 3H, -CH_3), 1.47 (s, 3H, -CH_3), 1.41 (s, 3H, -CH_3), 1.36 (s, 3H, -CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 112.91(-O2C-), 109.33(-O_2C-), 106.81(-C1), 96.43(-CCl3-), 84.85(-C2), 81.13(-C4), 79.36(-C3), 78.80(-CH_2), 72.97(-C5), 66.82(-C6), 26.90(-CH_3), 25.85(-CH_3), 25.18(-CH_3), 24.49(-CH_3).

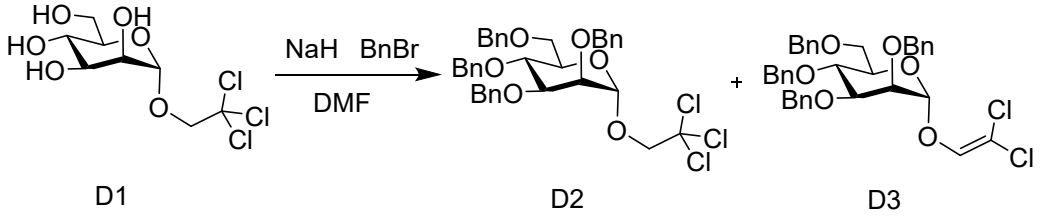
Synthesis of 2,2,2-trichloroethyl-D-mannopyranoside(D1)



D6 D1

The starting material **D6** (1.0 g, 2.55 mmol) was dissolved in a 70% aqueous AcOH solution (5.0 mL). The resulting solution was stirred at 70°C for 5 h and the mixture was then concentrated under vacuum and co-evaporated with toluene (3×10 mL). The residue was dried under high vacuum to yield the crude product, which was used directly in the next step.

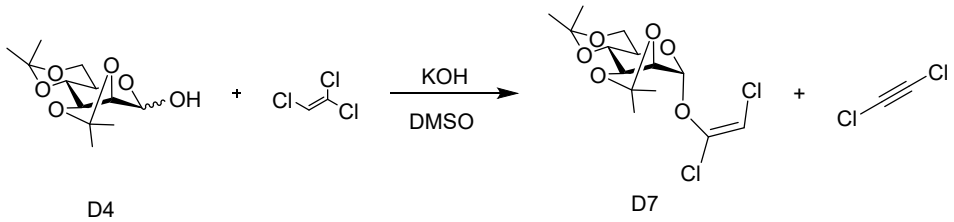
Synthesis of 2,2,2-trichloroethyl 2,3,4,6-tetra-O-benzyl-α-D-mannopyranoside (D2)[2]



The residue was dried and dissolved into anhydrous DMF (10 mL) under N_2 atm. after that; NaH (308 mg, 12.84 mmol) was added to the reaction. After keeping the reaction for 1 h, benzyl bromide (1.98 g 11.56 mmol) was added dropwise over 30 minutes. The reaction was left overnight and then quenched by methanol (1.0 mL), poured into ice water and extracted with EA (3×50 mL). The combined organic phases were then washed with water (2×50 mL) and concentrated. Purification by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:20 - 1/10) afforded a colorless oil (1.22 g, 75%, α, Rf: 0.8 in Heptane/EtOAc=5/1).

General experimental procedure for mannose using trichloroethylene

Synthesis of 1,2-Dichlorovinyl 2,3:4,6-di-O-isopropylidene-D-mannopyranoside (D7)



Attention! The byproduct 1,2-dichloroethyne is a dangerous gas, which has to be removed continuously.

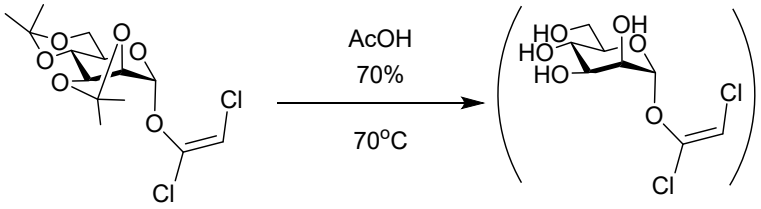
The starting materials **D4** (0.5 g, 1.92 mmol) was dissolved into DMSO (10 mL), and at the same time, KOH (350 mg, 5.76 mmol) was added. Keeping the reaction overnight, then trichloroethylene (406 mg, 3.8 mmol) was added dropwise over 30 minutes. The product was formed along with a dangerous gas, so the reaction mixture was kept overnight without septum and then purged with nitrogen gas flowing for at least half an hour. After that, the reaction was poured into ice water and extracted by EA (3×50 mL). The combined organic phases were then washed with water (3×50 mL) and concentrated. Purification by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:20) afforded a colorless oil (0.61 g, 90%, α, Rf: 0.6 in Heptane/EtOAc=10/1); $[\alpha]_D^{25}$: 2.8(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{14}H_{20}Cl_2O_6Na^+$377.0529，found 377.0538.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.69 (d, *J* = 5.3 Hz, 2H, H1, CCl=CHCl), 4.93 (dd, *J* = 5.8, 3.5 Hz, 1H, H3), 4.86 (d, *J* = 5.8 Hz, 1H, H2), 4.44 (ddd, *J* = 8.3, 6.2, 4.3 Hz, 1H, H5), 4.26 (dd, *J* = 8.3, 3.5 Hz, 1H, H4),

4.13 (dd, *J* = 8.7, 6.2 Hz, 1H, H6A), 4.04 (dd, *J* = 8.8, 4.3 Hz, 1H, H6B), 1.51 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.39 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.64(-OCCl=CHCl), 113.28(-O2C-), 109.58(-O2C-), 105.69(-C1), 101.42(=CHCl), 84.72(-C2), 82.74(-C4), 79.24(-C3), 72.60(-C5), 67.04(-C6), 26.90(-CH_3), 25.95(-CH_3), 25.32(-CH_3), 24.66(-CH_3).

Synthesis of 1,2-Dichlorovinyl α-D-mannopyranoside(D8) [21]

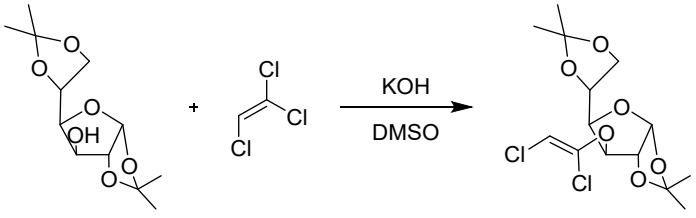


D7 D8

The starting material D7 (140 mg, 0.4 mmol) was dissolved in 1.4 mL acetic acid and 0.35 mL water. The reaction was then stirred at room temperature for 10 hours. The reaction was diluted with toluene and concentrated at reduced pressure to afford a crude product. Although the group is stable under alkaline conditions, it is very unstable under acidic conditions, and only very small amounts of the product could be isolated.

General experimental procedure for the introduction on secondary alcohols.

Synthesis of 1,2-dichlorovinyl 1,2:4,6-di-O-isopropylidene-D-Glucofuranose(F2)[22]



F1 F2

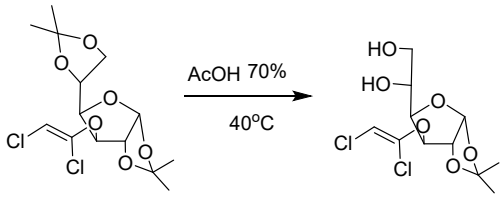
Diacetone glucose (1.0 g, 3.84 mmoL) was dissolved into DMSO (10 mL), and at the same time, KOH (323 mg, 5.76 mmol) was added. After keeping the reaction overnight, trichloroethylene (656 mg, 4.99 mmol) was added dropwise over 30 minutes. The product is formed together with a dangerous gas, so the reaction was kept overnight without a septum and then it was purged with nitrogen gas for at least half an hour. After that, the reaction was poured into ice water and extracted by EA (3×50 mL). The combined organic

phases were then washed with water (3×50 mL) and concentrated. Purification by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:20) afforded a colorless oil (1.26 g, 93%, α, Rf: 0.5 in Heptane/EtOAc=10/1); $[\alpha]_D^{25}$: -6.5($CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{14}H_{20}Cl_2O_6Na^+$377.0529，found 377.0534.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.99 (d, *J* = 3.7 Hz, 1H, H1), 5.64 (d, *J* = 1.5 Hz, 1H, -CHCl)), 4.82 (d, *J* = 2.9 Hz, 1H, H3), 4.65 (d, *J* = 3.7 Hz, 1H, H2), 4.41 (ddd, *J* = 7.7, 6.2, 5.1 Hz, 1H, H5), 4.25 (dd, *J* = 7.7, 2.9 Hz, 1H, H4), 4.14 (dd, *J* = 8.7, 6.2 Hz, 1H, -H6A), 4.10 – 4.03 (m, 1H, -H6B).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.76(-CClO=C), 112.48(-C(CH3)2, 109.32(-C(CH3)2, 105.34(-C1), 99.70(-CHCl), 82.51(-C3), 81.82(-C2), 80.21(-C4), 72.14(-C5), 67.15(-C6), 26.85(-CH3), 26.76(-CH3), 26.27(-CH3), 25.21(-CH3).

Synthesis of 1,2-dichlorovinyl 1,2-di-O-isopropylidene-D-glucofuranose(F3)[23,24]



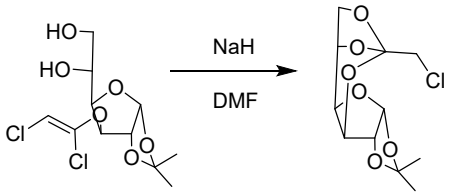
F2 F3

The protected carbohydrate derivative **F2** was dissolved in 70% AcOH and stirred for a period of 3h at rt. Then heated to 40°C for 2h. Upon completion of the reaction, the solvent was removed under reduced pressure and the obtained product was dried under high vacuum. HRMS (ESI): $[M+Na]^+$ calcd for $C_{11}H_{16}Cl_2O_6Na^+$337.0216，found 337.0237.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.01 (d, *J* = 3.8 Hz, 1H, H1), 5.69 (s, 1H, =CHCl), 4.89 (d, *J* = 2.9 Hz, 1H, H3), 4.68 (d, *J* = 3.7 Hz, 1H, H2), 4.31 (dd, *J* = 8.7, 2.9 Hz, 1H, H4), 4.11 (ddd, *J* = 8.6, 5.2, 3.3 Hz, 1H, H5), 3.92 (dd, *J* = 11.4, 3.3 Hz, 1H, H6A), 3.81 (dd, *J* = 11.5, 5.2 Hz, 1H, H6B), 2.38 (s, 2H, -2OH), 1.54 (s, 3H, -CH3), 1.36 (s, 3H, -CH3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.85(=COCl), 112.54(-CO2), 105.32(-C1), 100.13(=CHCl), 83.02(C3), 81.67(C2), 79.29(C4), 68.46(C5), 64.26(C6), 26.72(-CH3), 26.27(-CH3).

Synthesis of 1,2-O-isopropylidene-3,5,6-O-chloromethyl-α-D-glucofuranose(F4)



F3 F4

Under a N_2 atmosphere, the crude starting material **F3** was dissolved in DMF (10 mL) and NaH (98 mg, 4.1 mmol) was added into the reaction. TLC indicated full conversion after 1 h. and the reaction was poured into ice water and extracted by EA (3×20 mL). The combined organic phases were then washed with water (3×30 mL) and concentrated. Purification by flash column chromatography on silica gel (Ethyl acetate / Heptane 1:20-1:10) afforded a white solid (381 mg, 96%, Rf: 0.7 in Heptane/EtOAc=10/1); $[\alpha]_D^{25}$: -47.5(c=1, $CHCl_3$). HRMS(ESI): $[M+Na]^+$ calcd for $C_{11}H_{15}ClO_6Na^+$301.0449，found 301.0426.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.09 (d, *J* = 3.5 Hz, 1H, H1), 4.89 (dd, *J* = 4.8, 2.1 Hz, 1H, H5), 4.61 (d, *J* = 3.5 Hz, 1H, H3), 4.44 (d, *J* = 3.1 Hz, 1H, H2), 4.17 – 4.11 (m, 2H, H4, -H6A), 4.05 (dd, *J* = 7.9, 4.8 Hz, 1H, -H6B), 3.72 (d, *J* = 3.1 Hz, 2H, -CH2Cl), 1.52 (s, 3H, -CH3), 1.36 (d, *J* = 3.1 Hz, 3H, -CH3).

^{13}C NMR (126 MHz, $CDCl_3$) δ 116.87(-CO3), 112.16(-CO2), 106.25(-C1), 83.46(-C2), 75.27(-C3), 74.91(-C4), 74.21(-C5), 67.72(-C6), 42.90(-CH2Cl), 26.98(-CH3), 26.24(-CH3).

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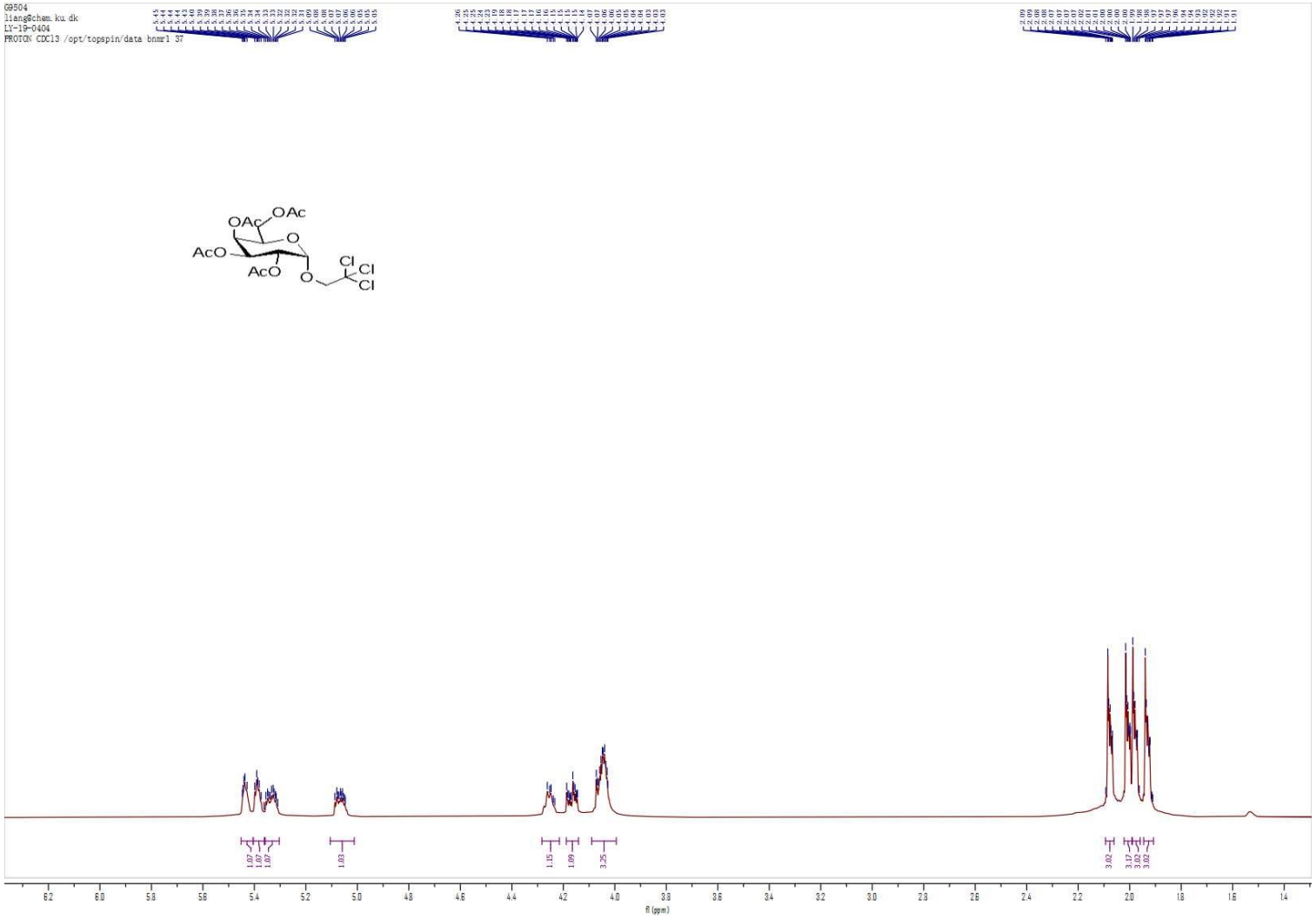
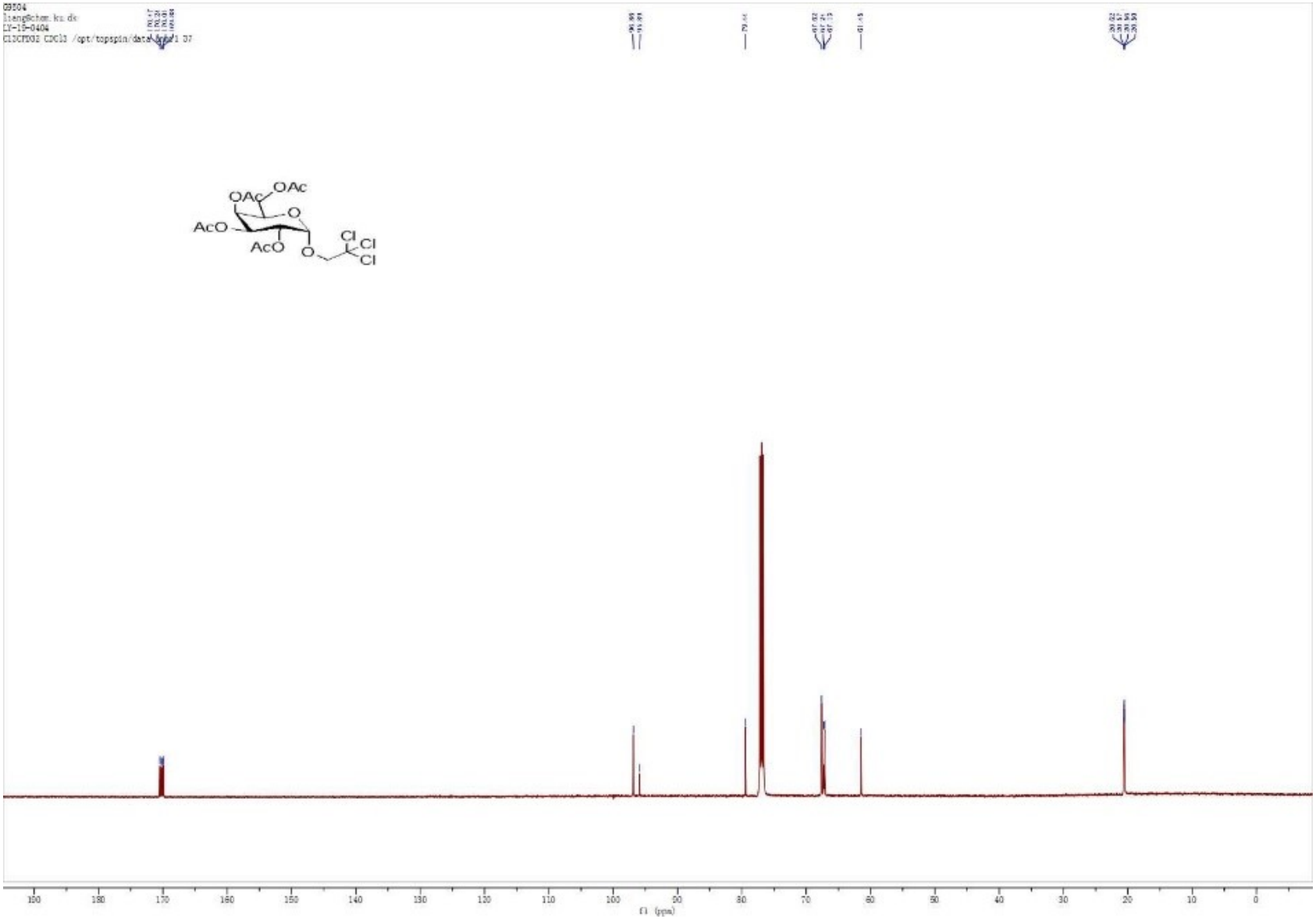
Copies of NMR spectra

2,2,2-trichloroethyl 2,3,4,6-tetra-O-acetyl-α-D-galactopyranoside S1

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



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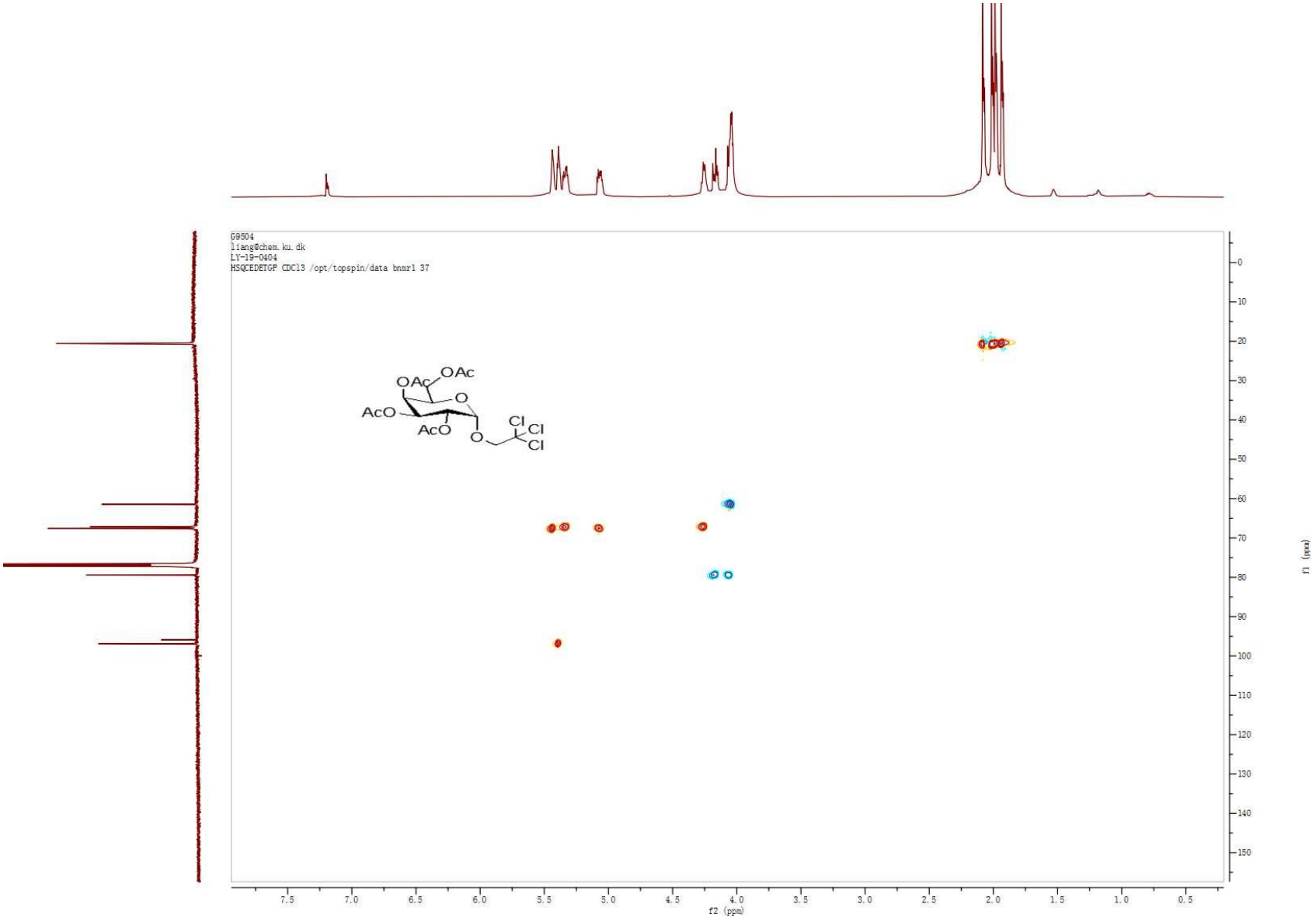
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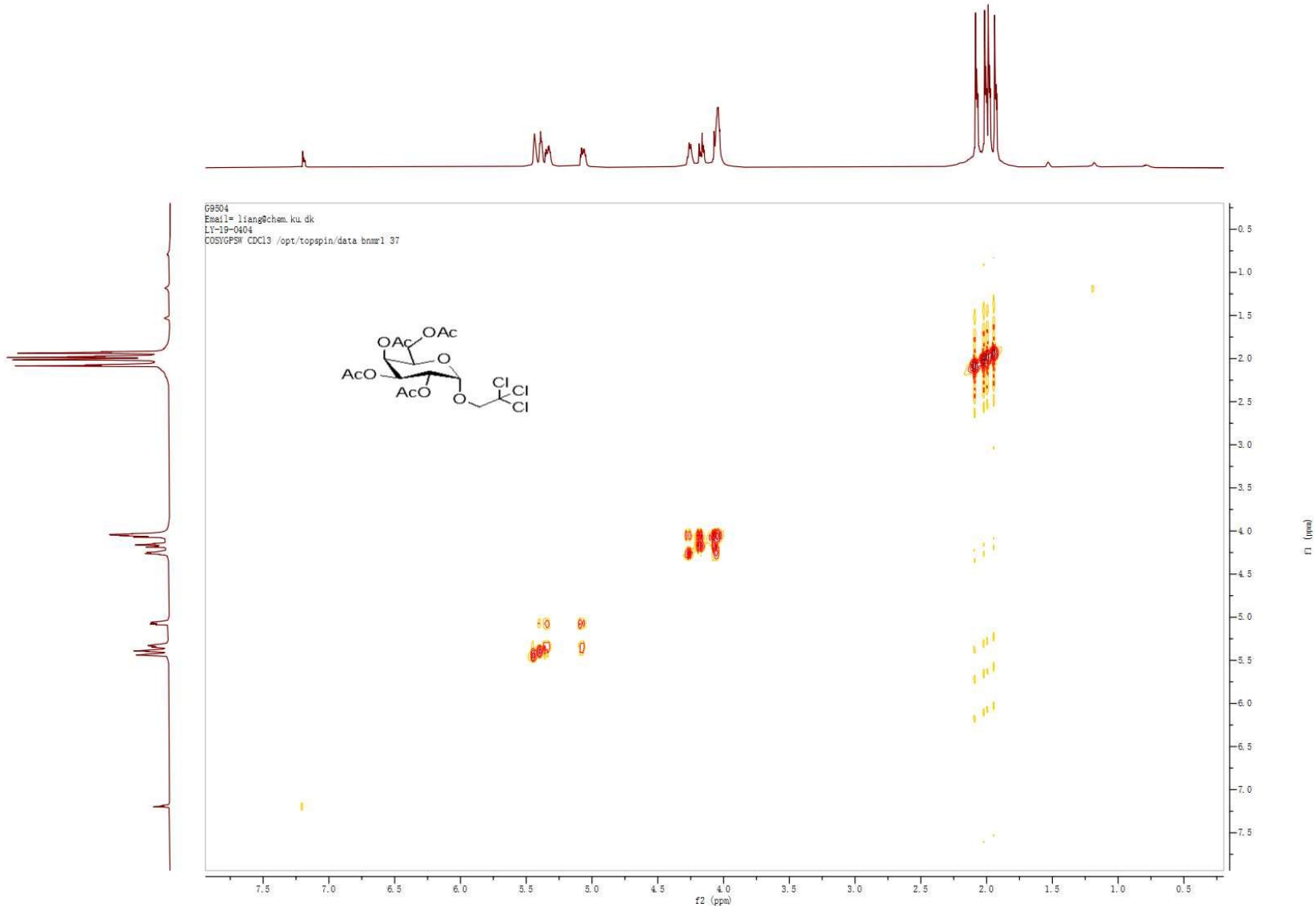
f1 (ppm)

H-H COSY NMR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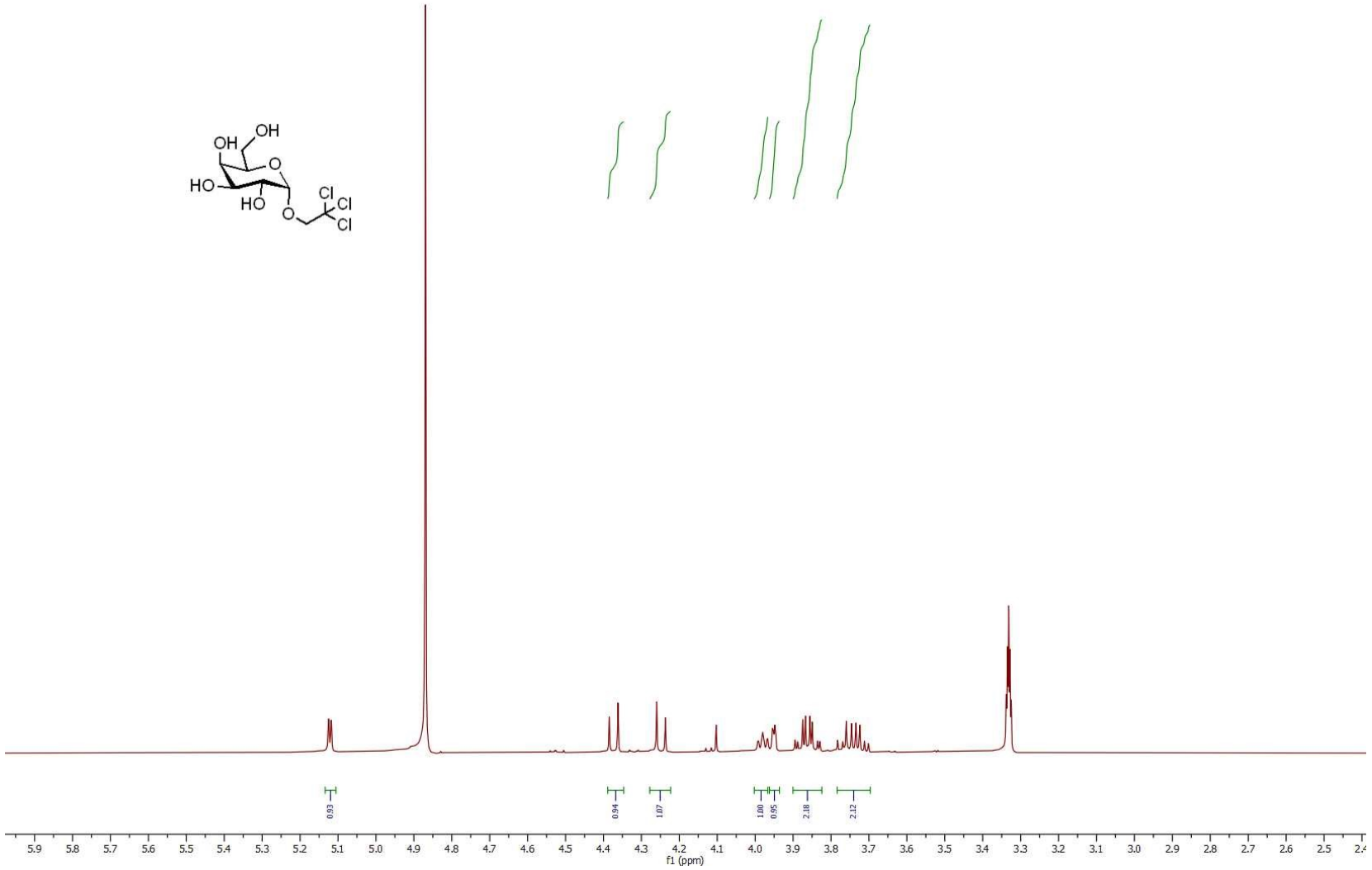
2,2,2-trichloroethyl-α-D-galactopyranoside(A1)

^{1}H NMR (500 MHz, $CDCl_3$)



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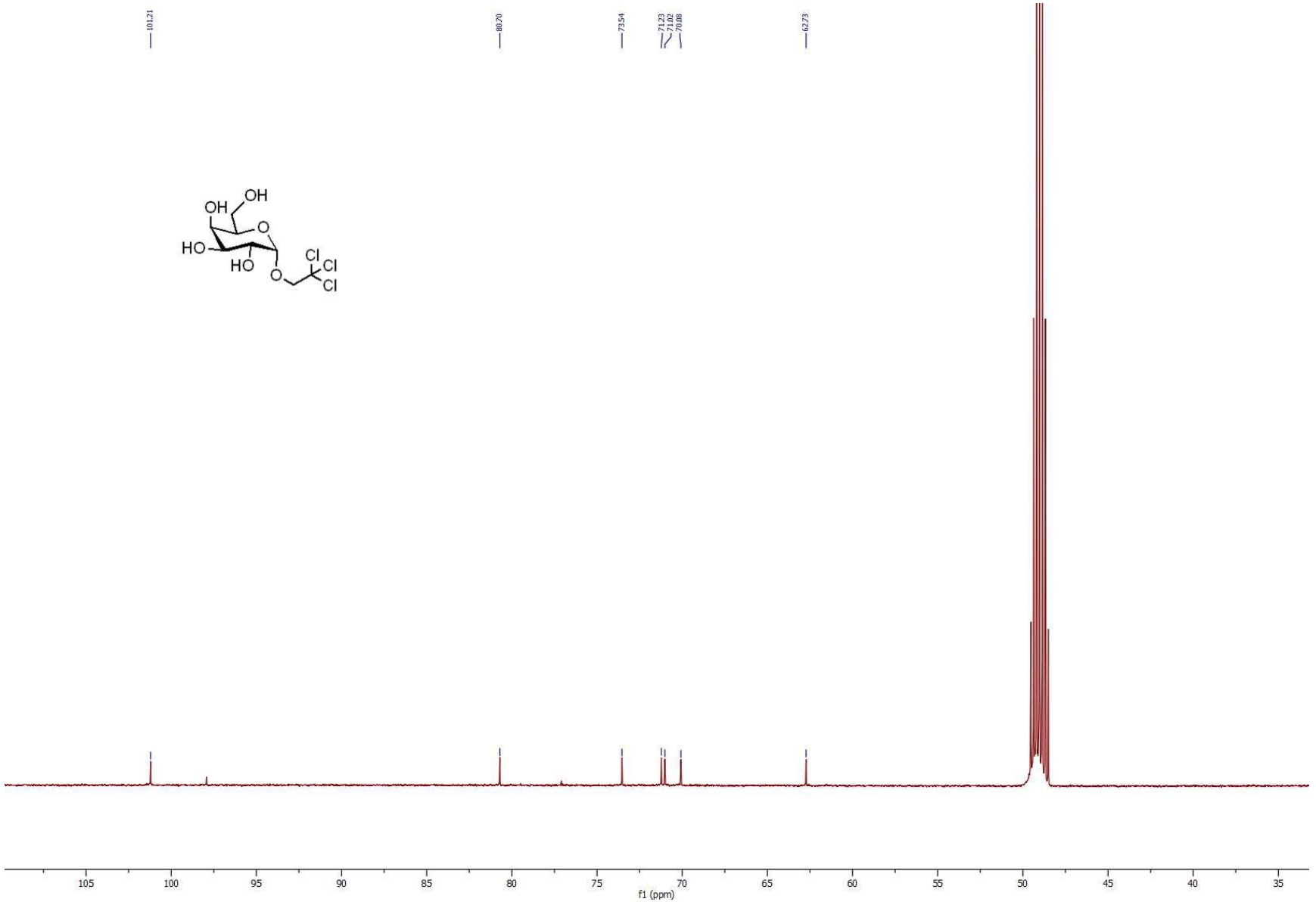

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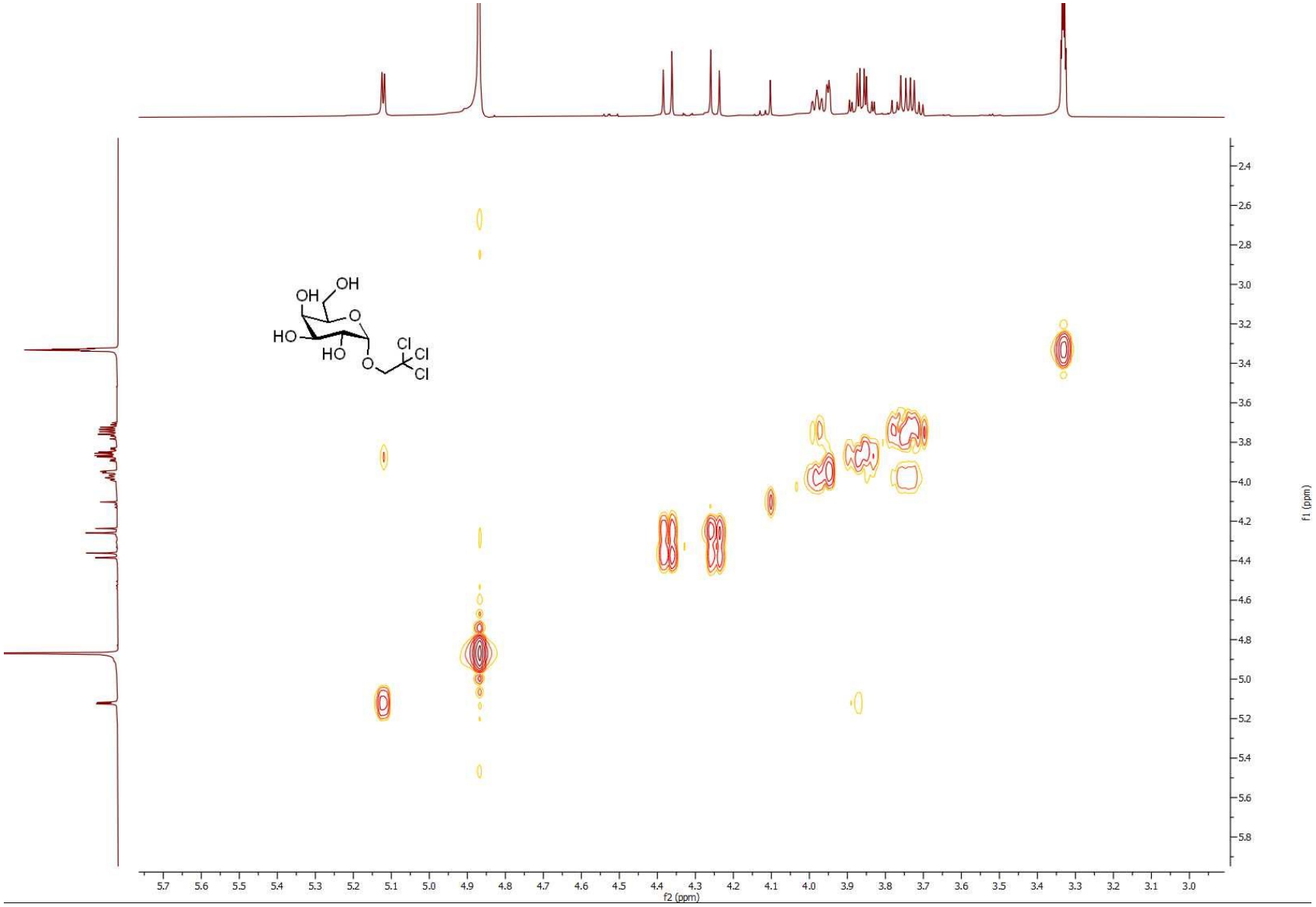

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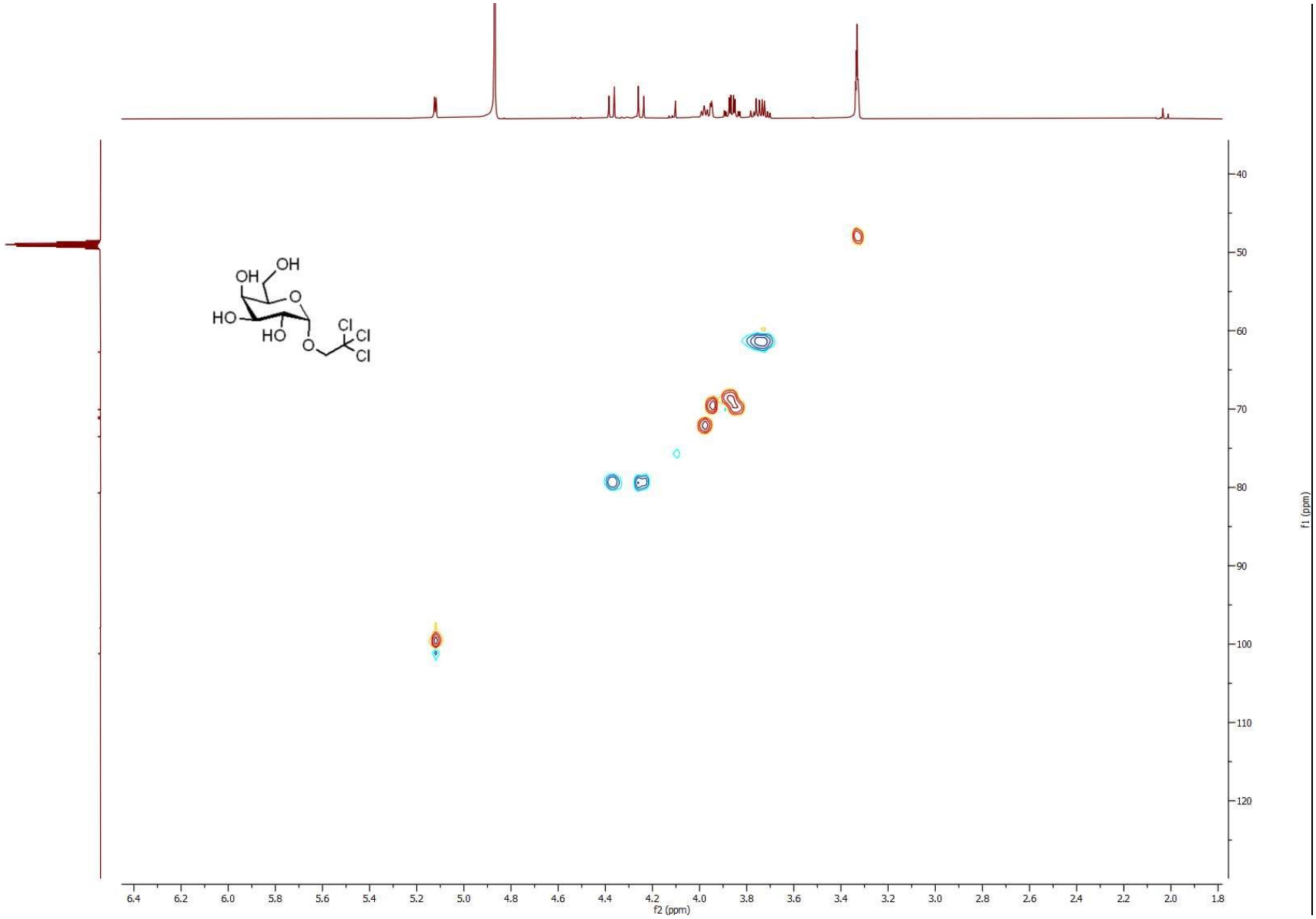
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2.2
2.0
1.8
f2 (ppm)

Product (2,2-Dichlorovinyl 2,3,4,6-tetra-O-Benzyl-α-D-galactopyranoside)(A2)

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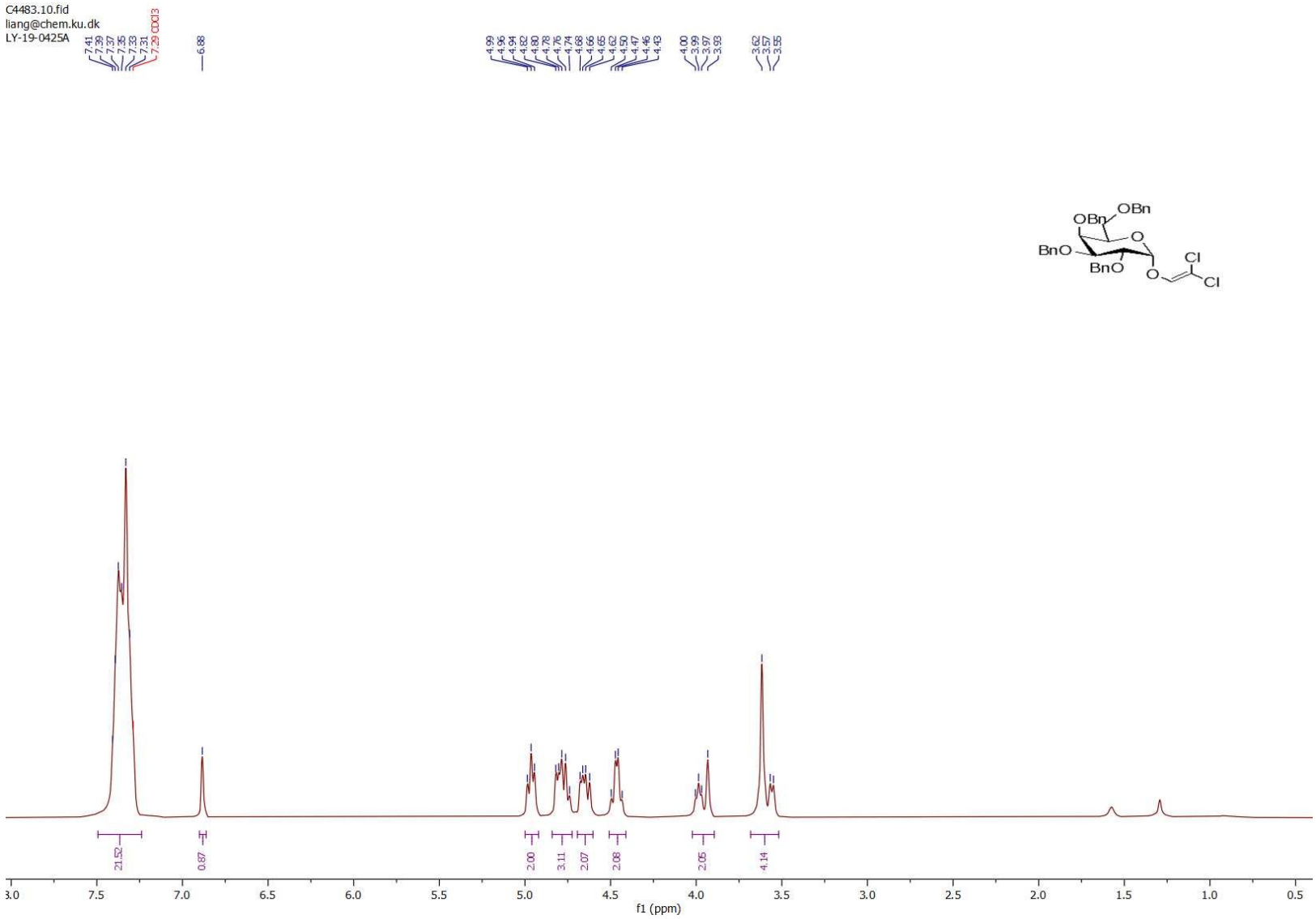

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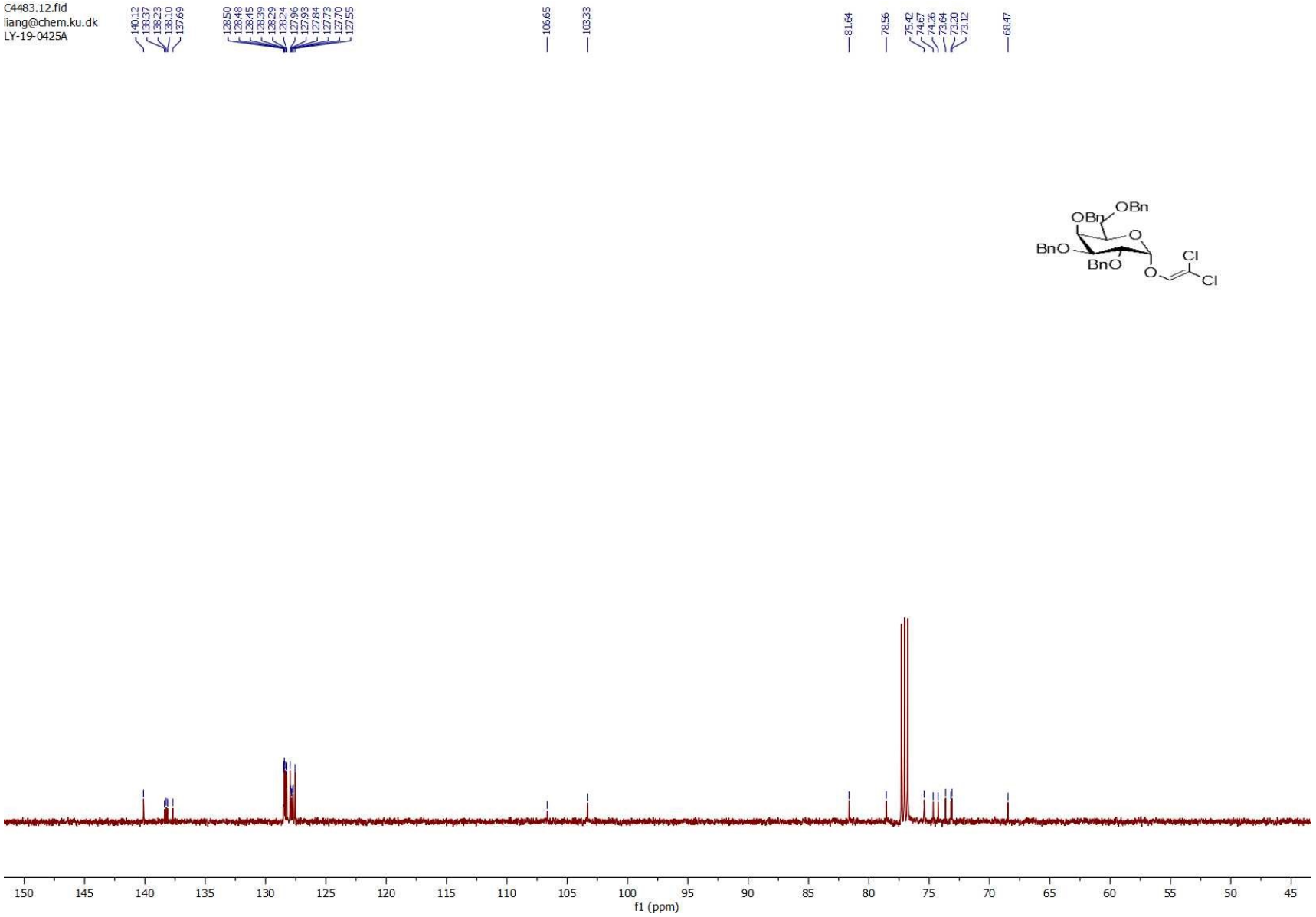

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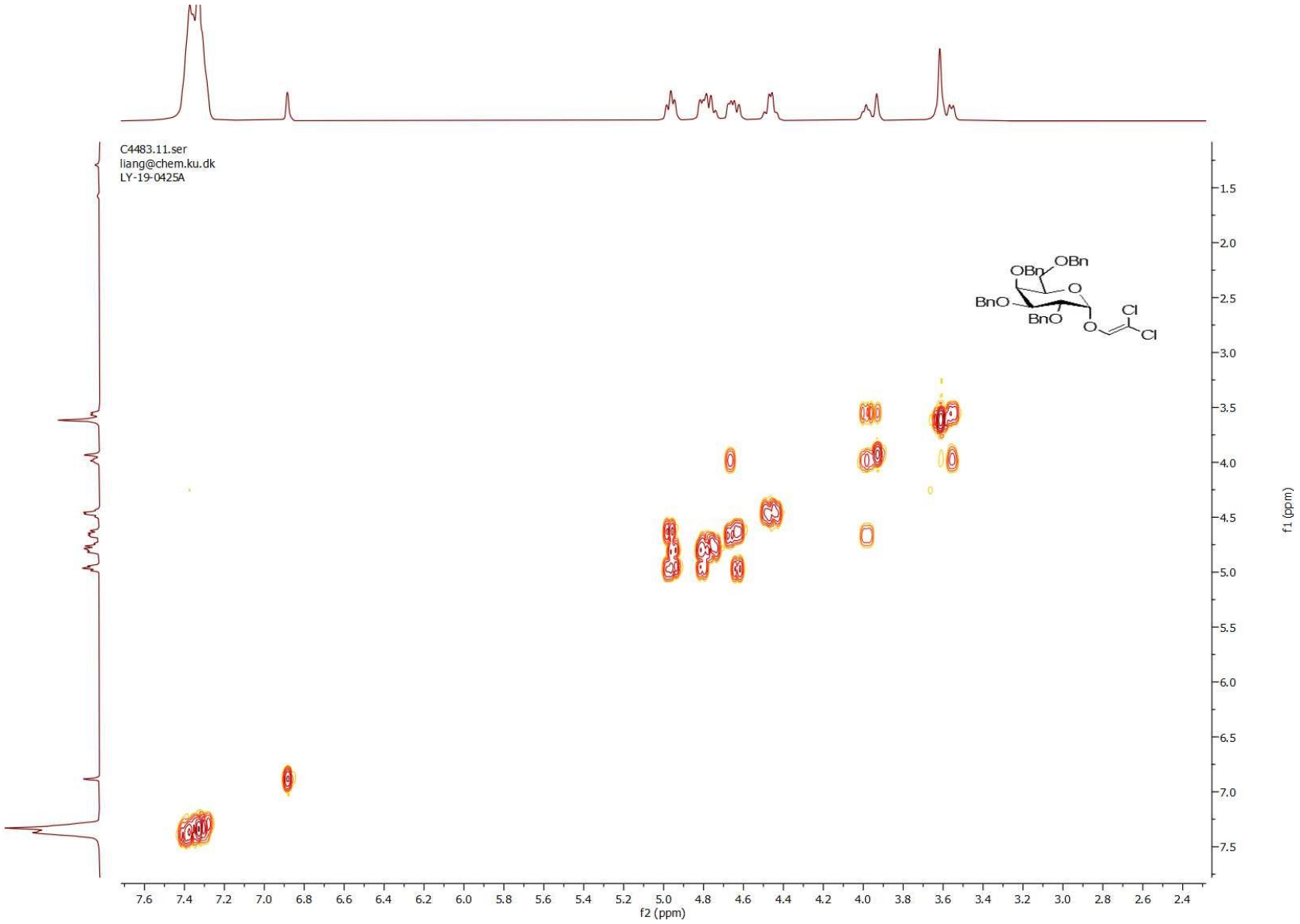
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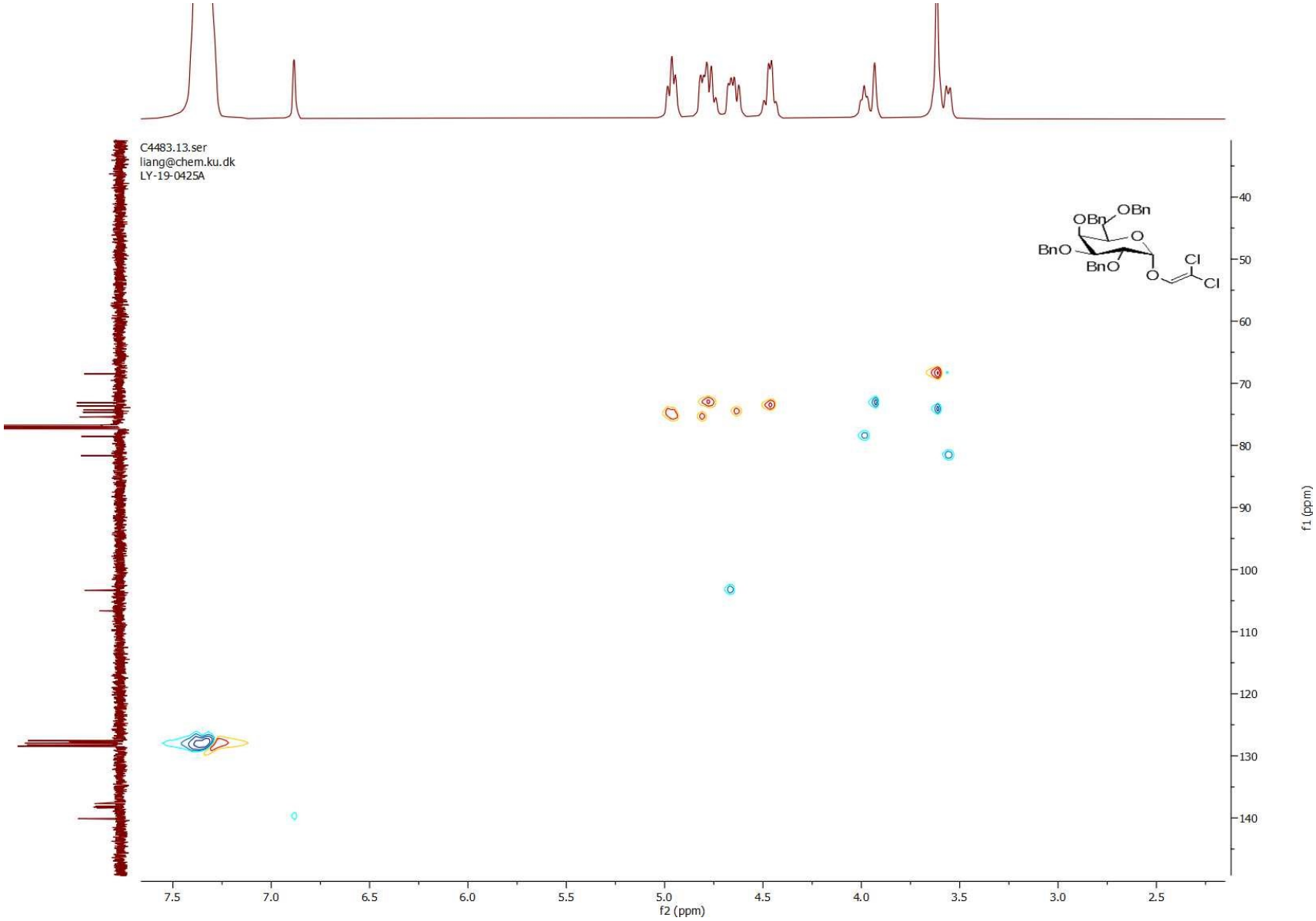
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2.5
f2 (ppm)
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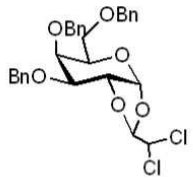
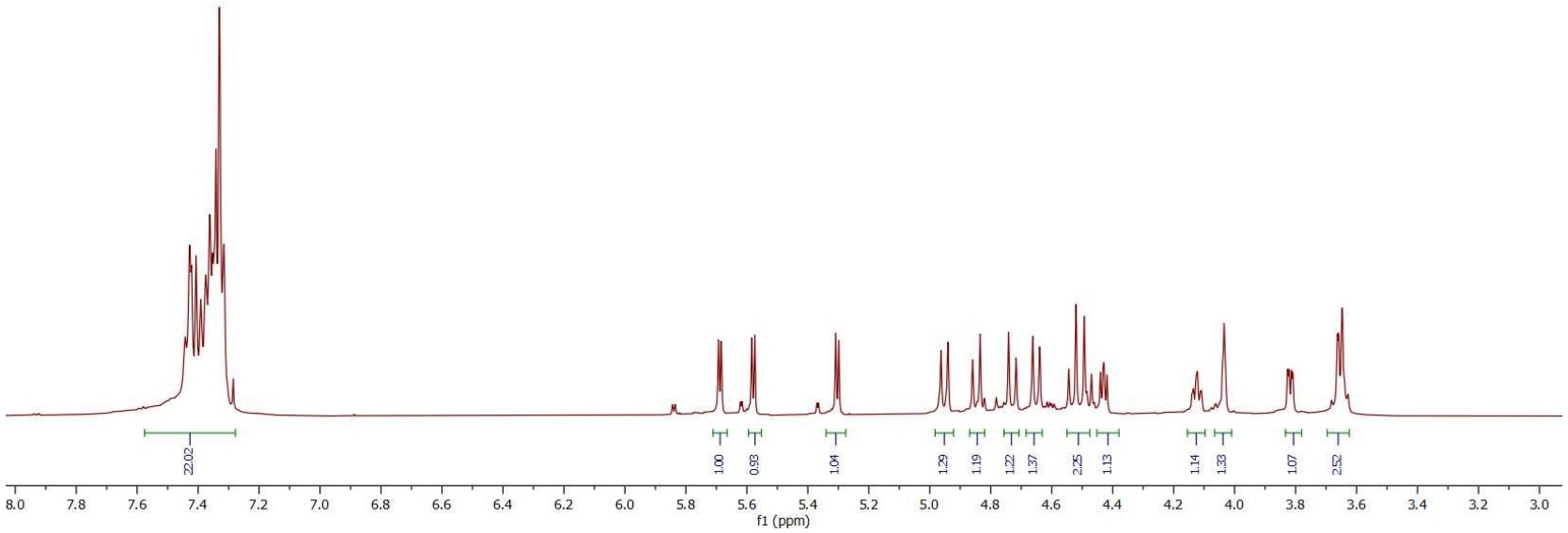
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

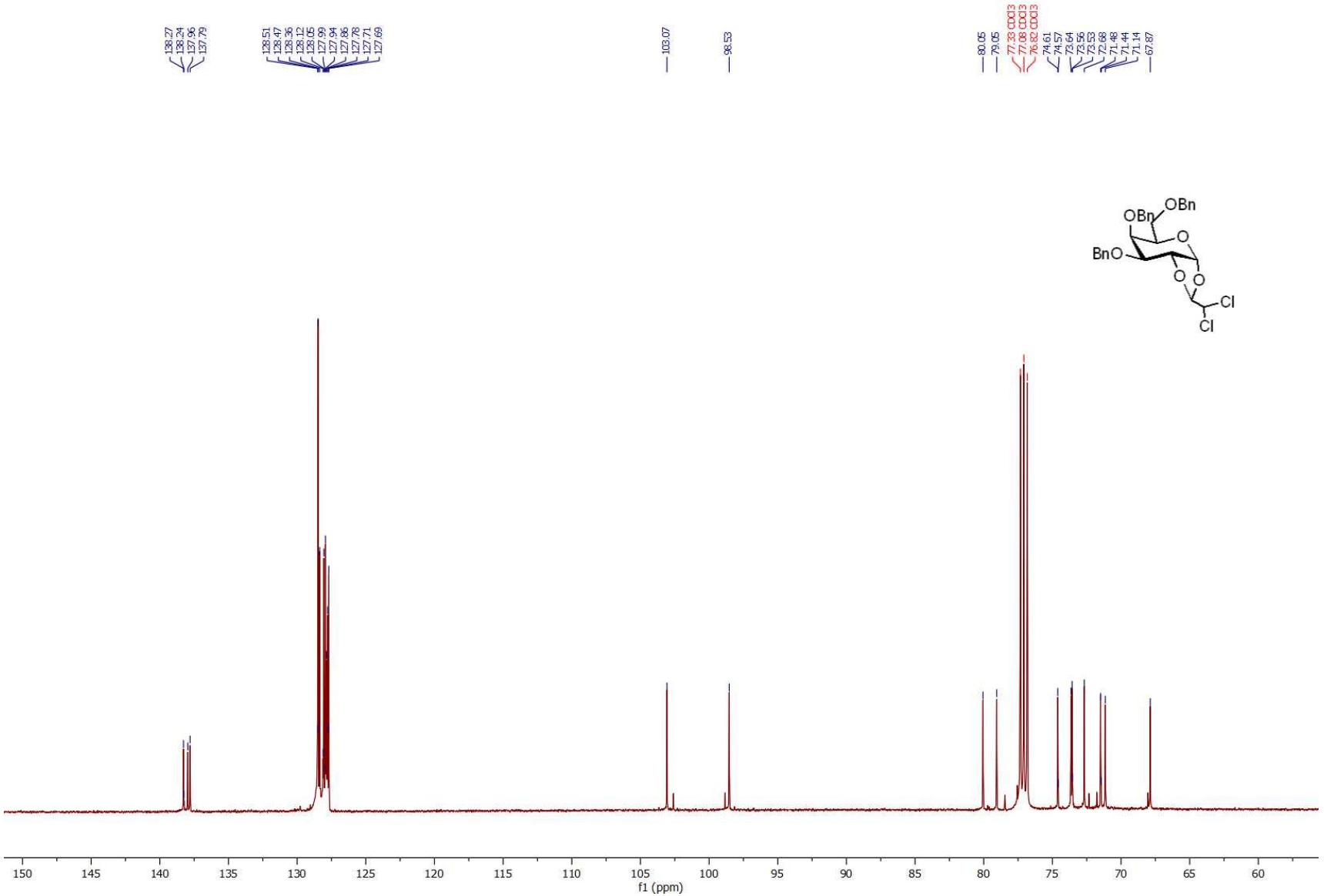
Product (2,2-dichloroethyl 3,4,6-tris-*O*-benzyl-α-D-galactopyranoside)(A4)

^{1}H NMR (500 MHz, $CDCl_3$)

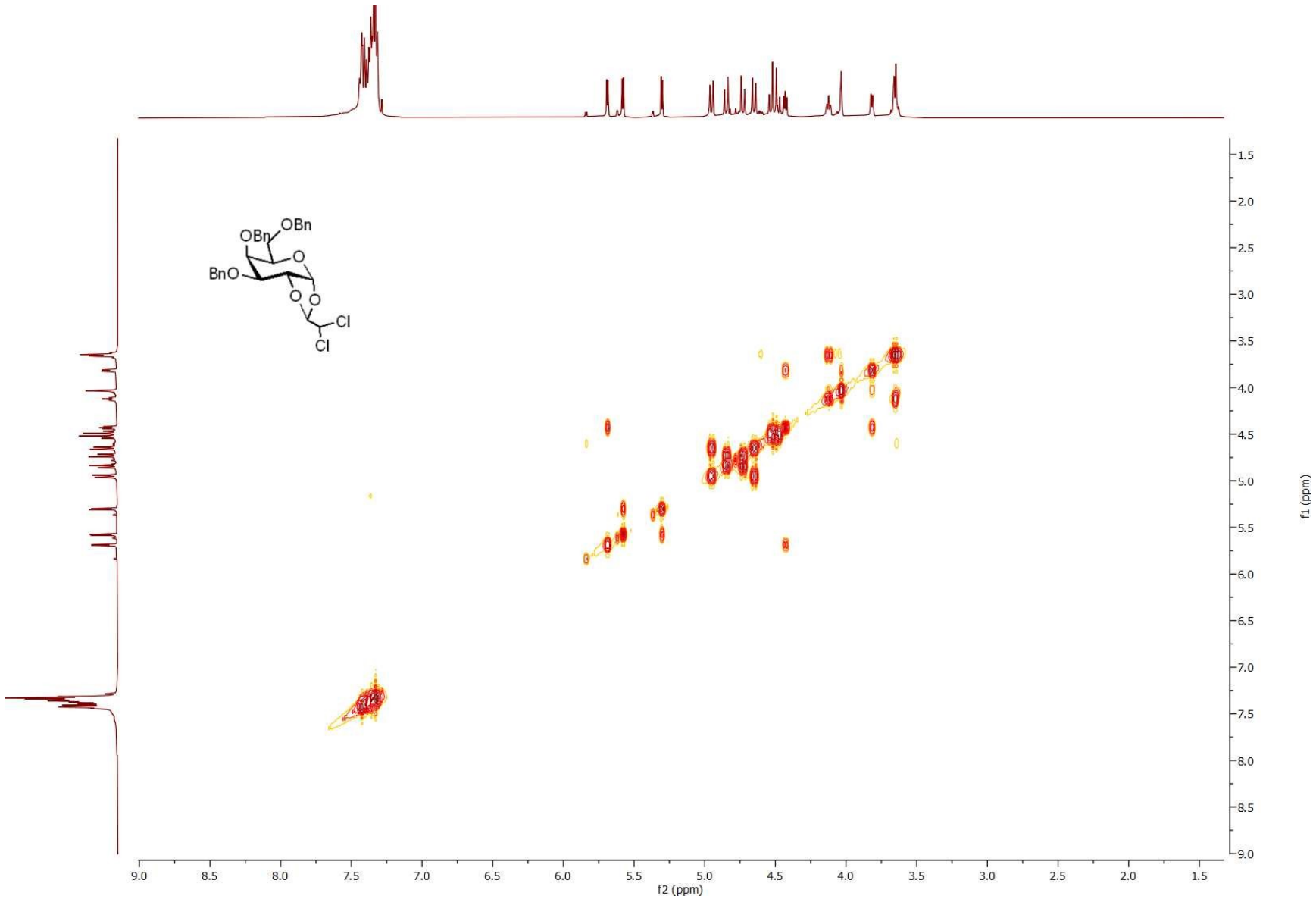




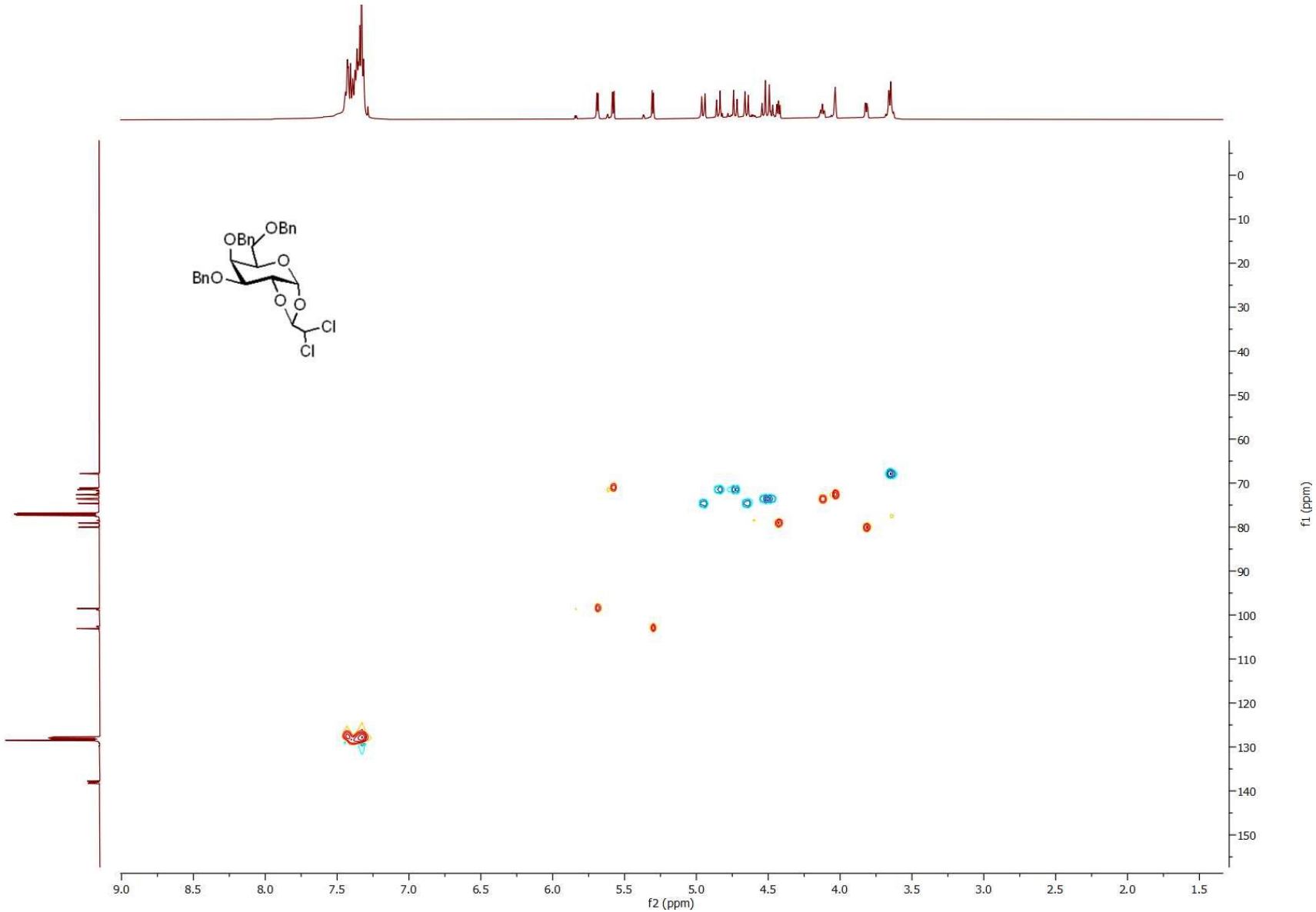
^{13}C NMR (126 MHz, $CDCl_3$)



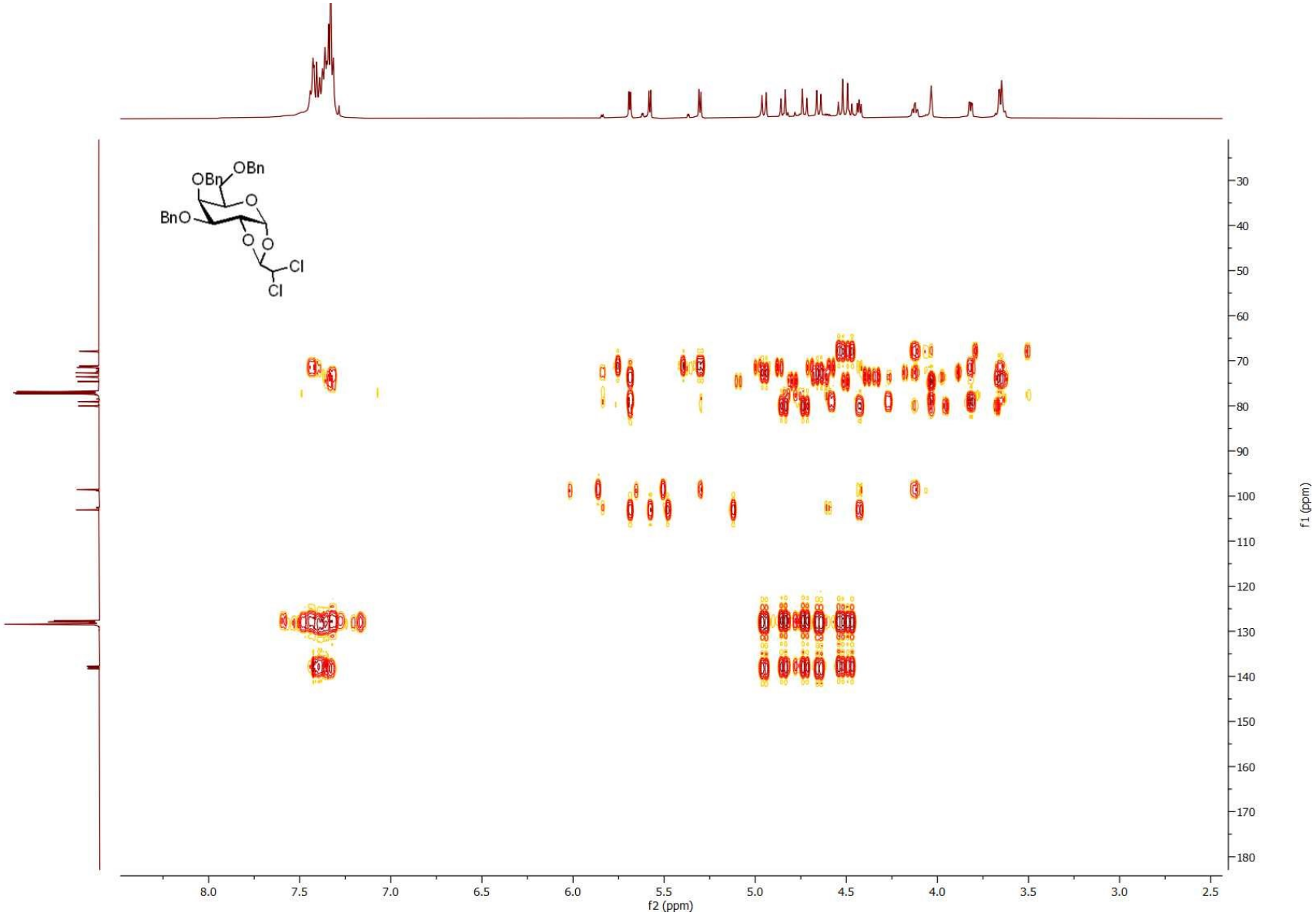
H-H COSY NMR



HSQC NMR



HMBC NMR


OBn
OBn
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O
O
Cl
Cl
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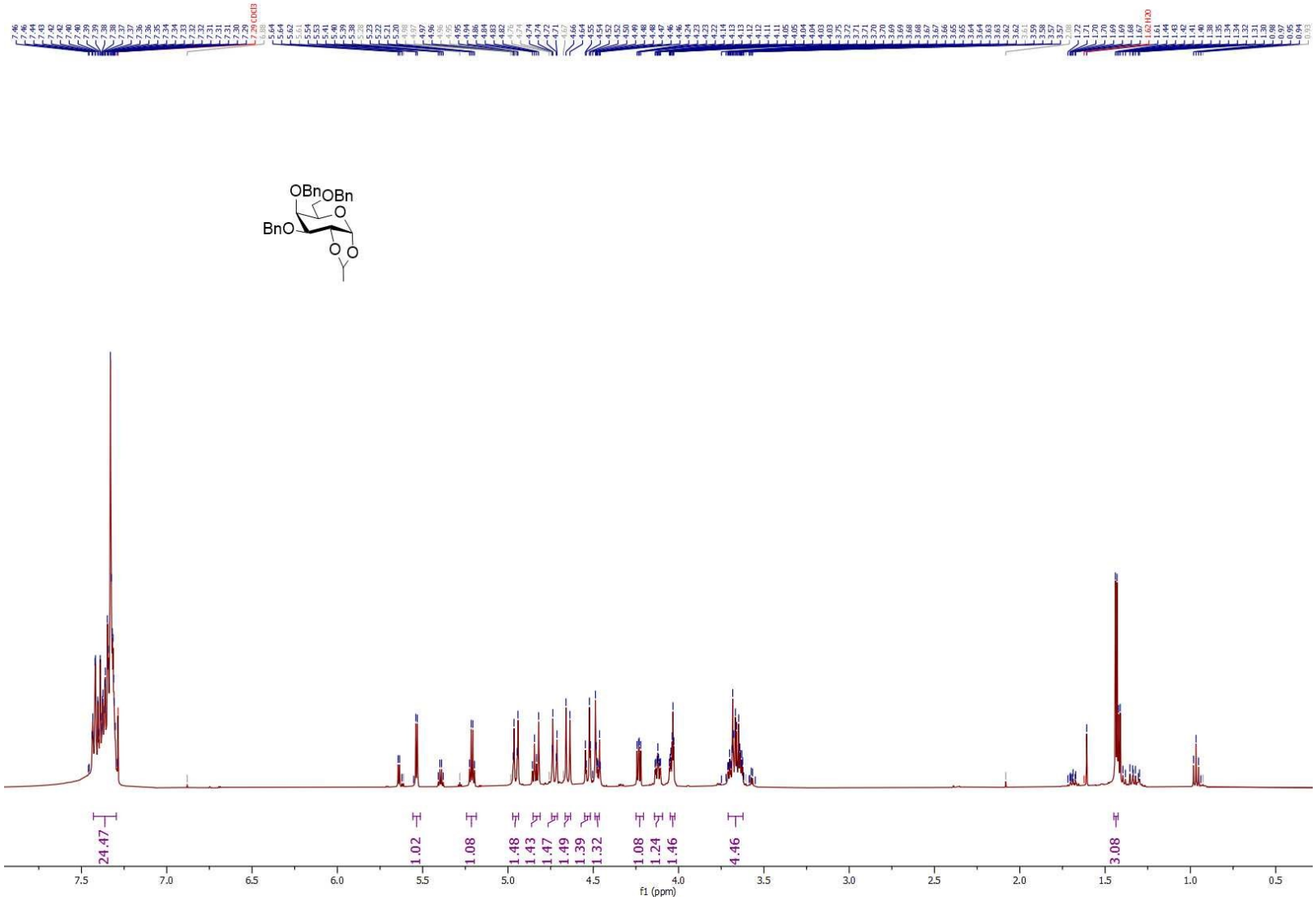
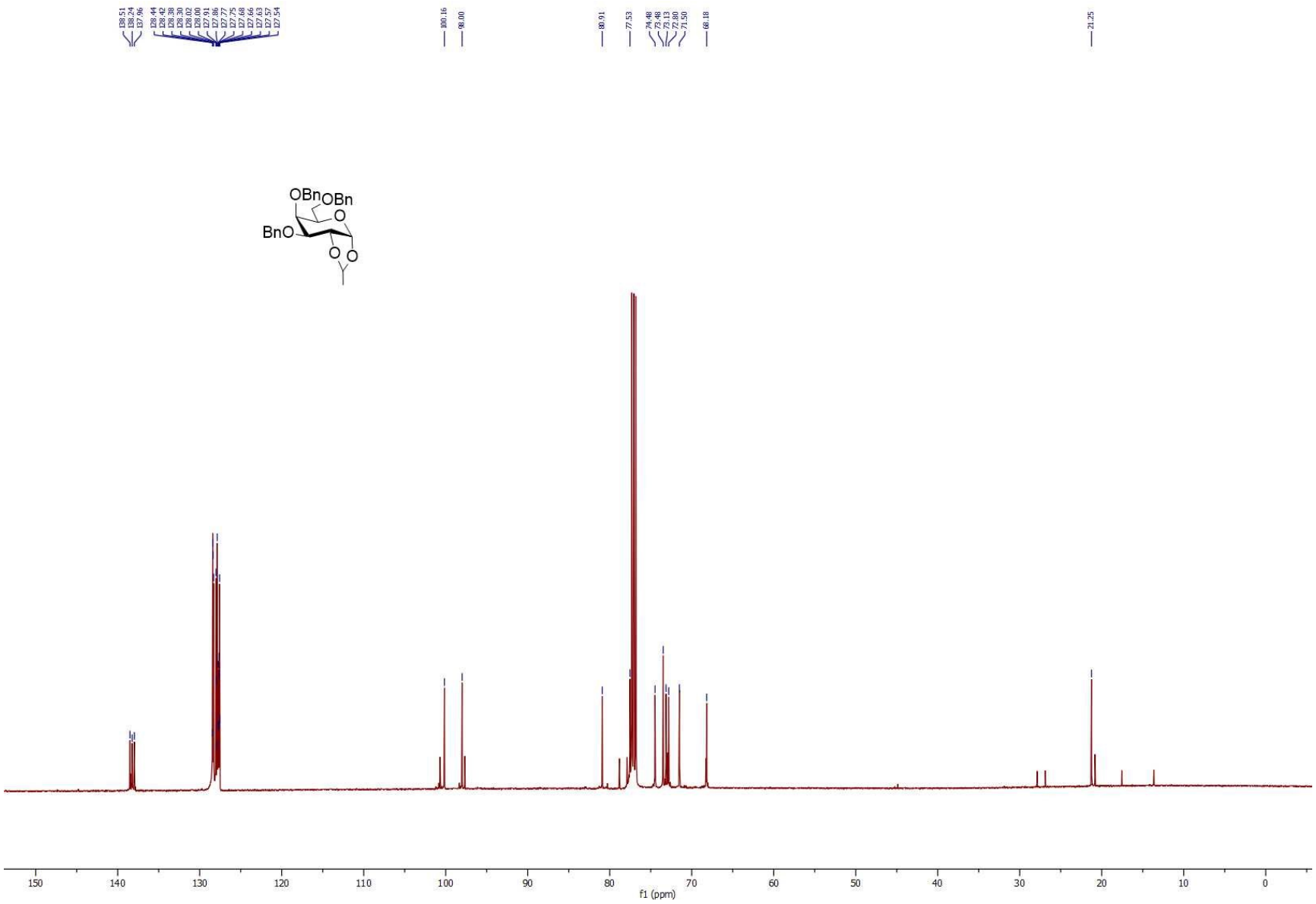
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

1,2-O-ethylidene-3,4,6-tris-*O*-benzyl-α-D-galactopyranoside(A5)

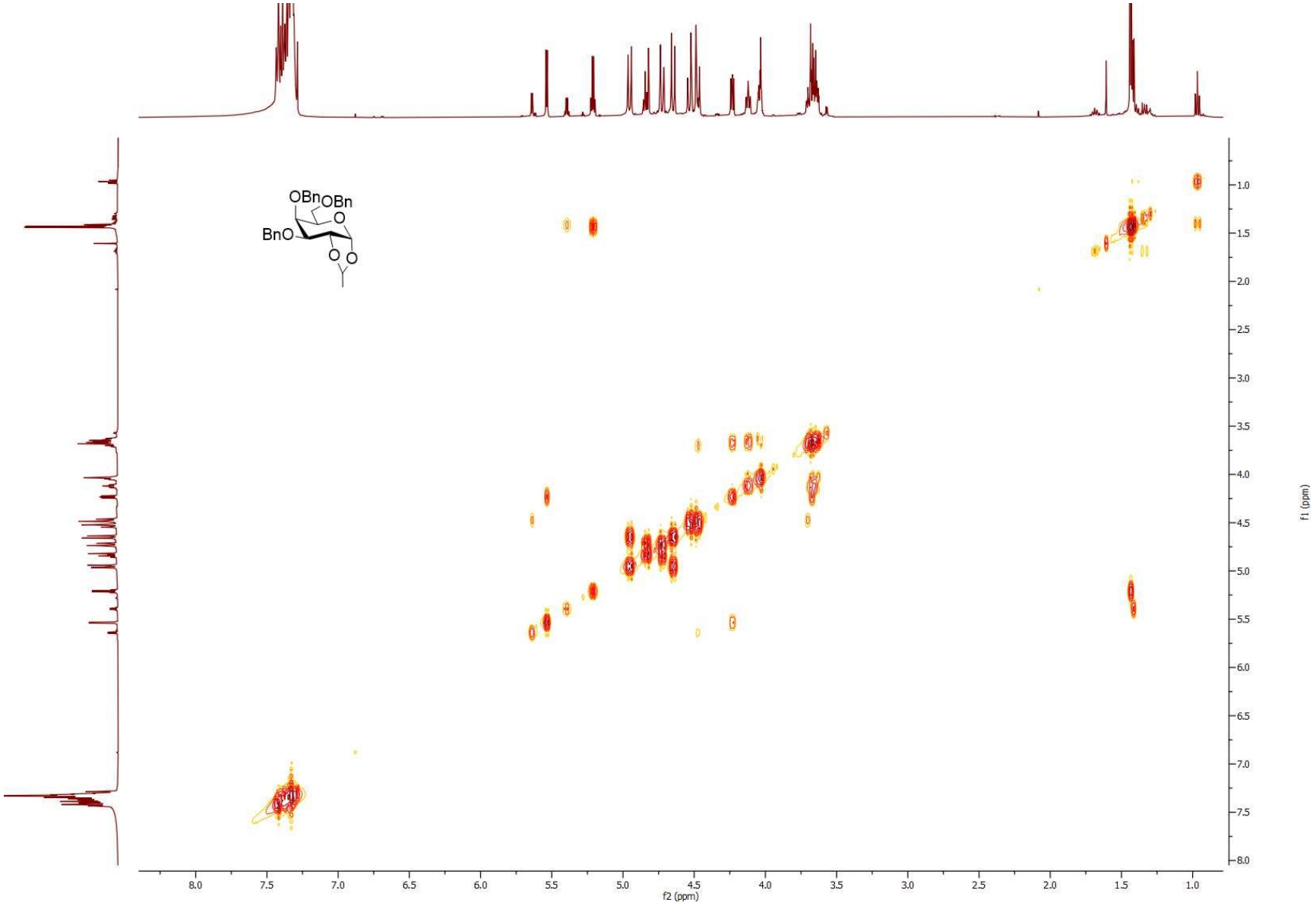
^{1}H NMR (500 MHz, $CDCl_3$)



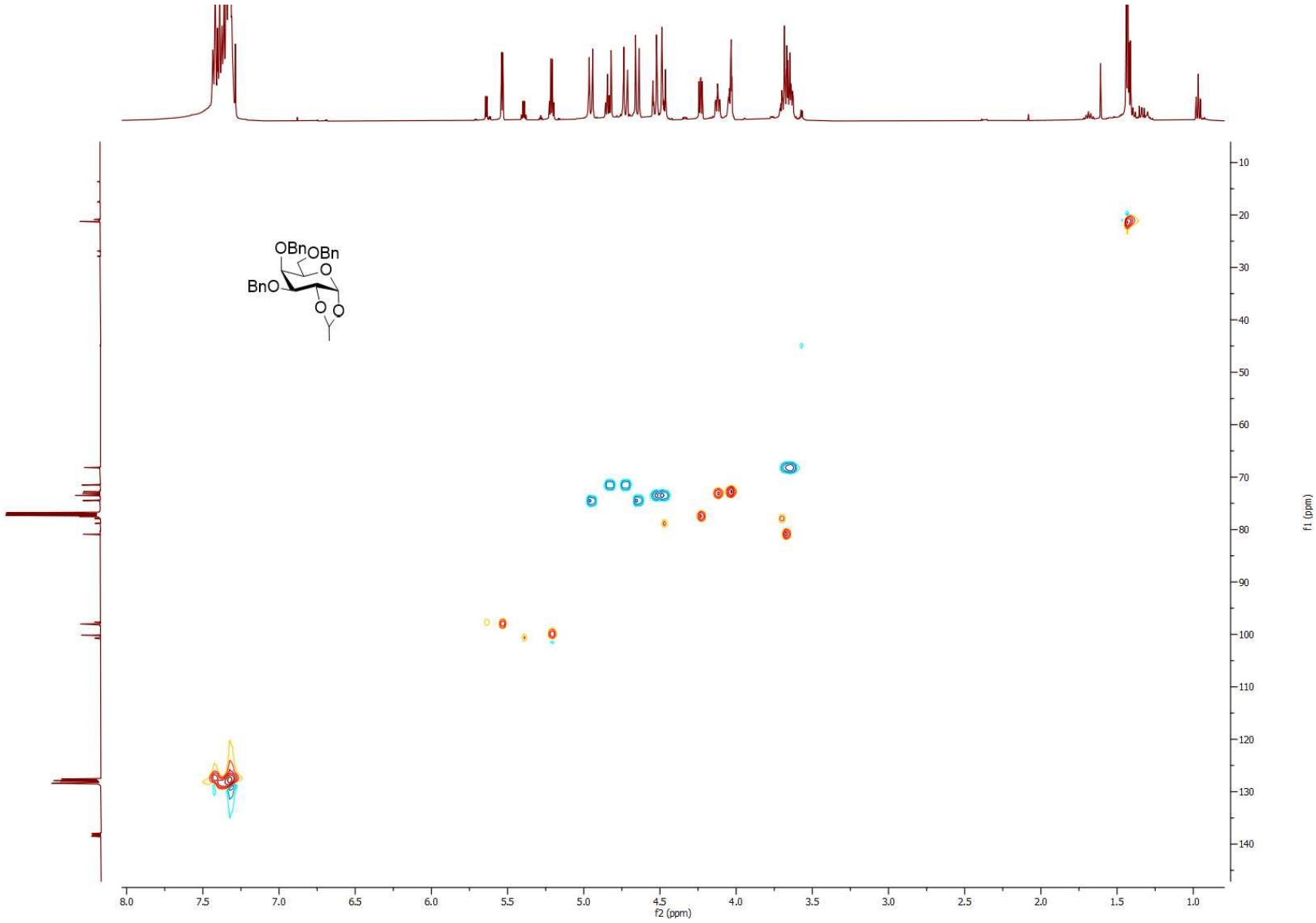
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR



HSQC NMR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OBn
BnO
O
O
O
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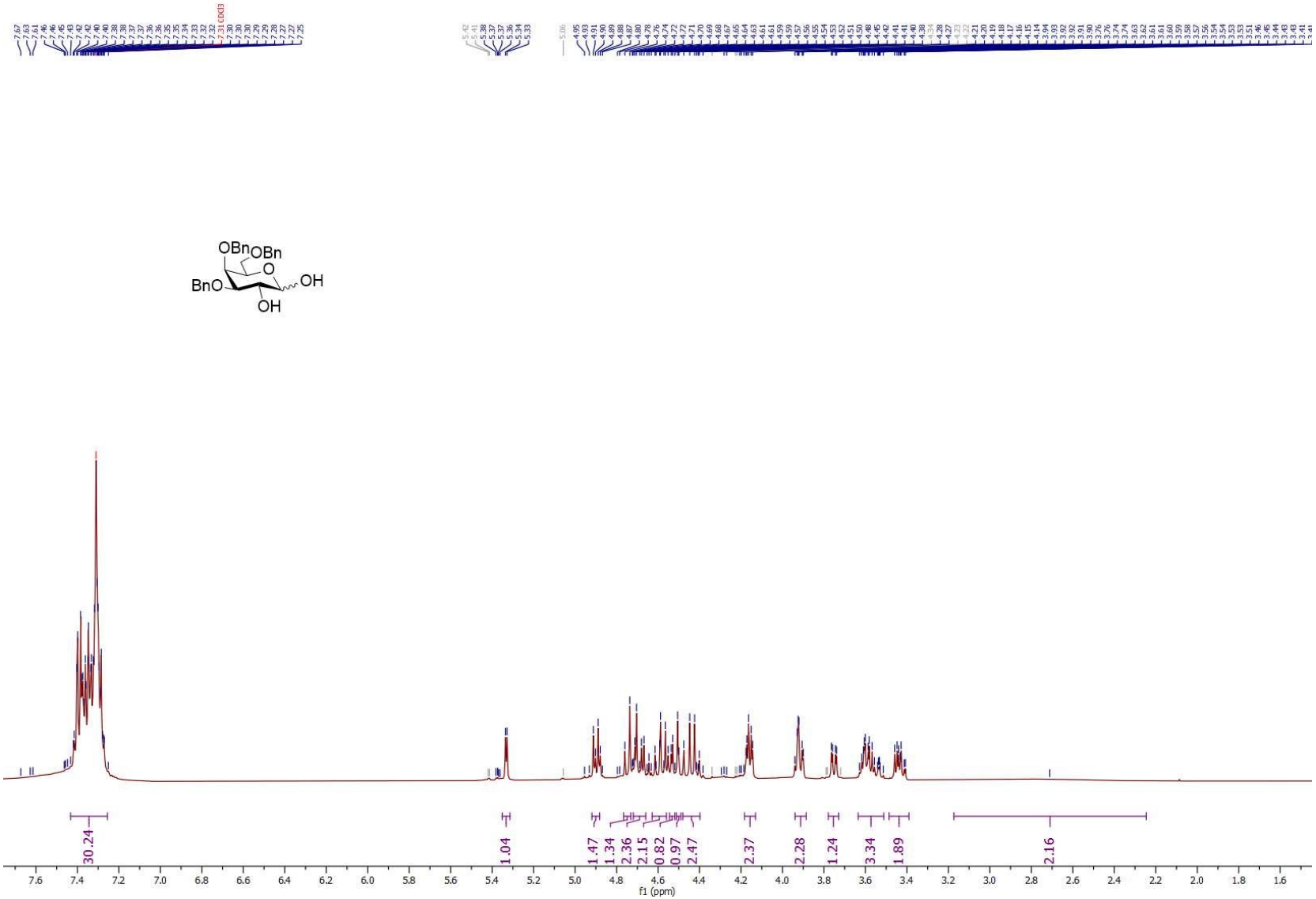
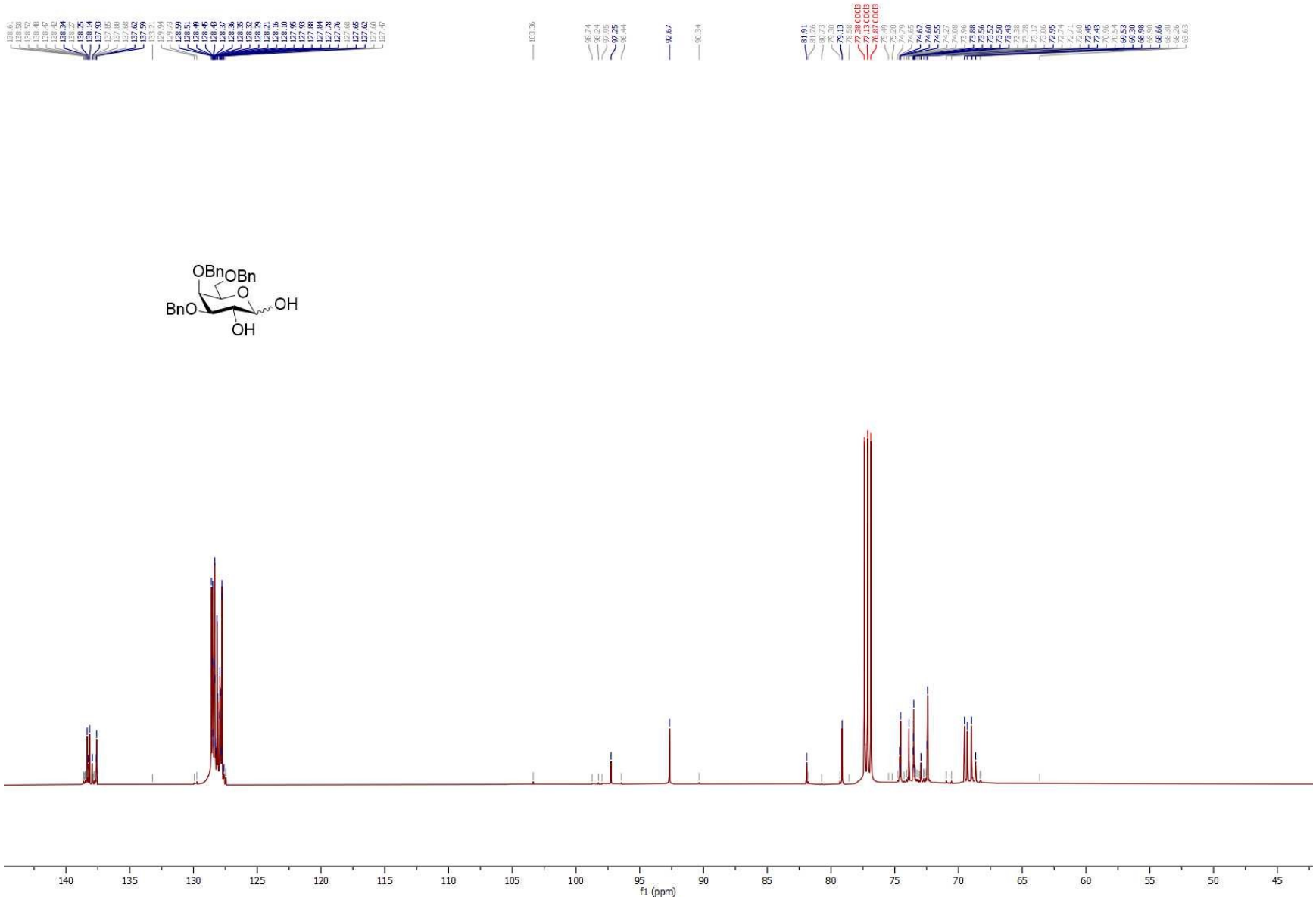
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

3,4,6-Tris-O-Benzyl-D-galactopyranose (A6)

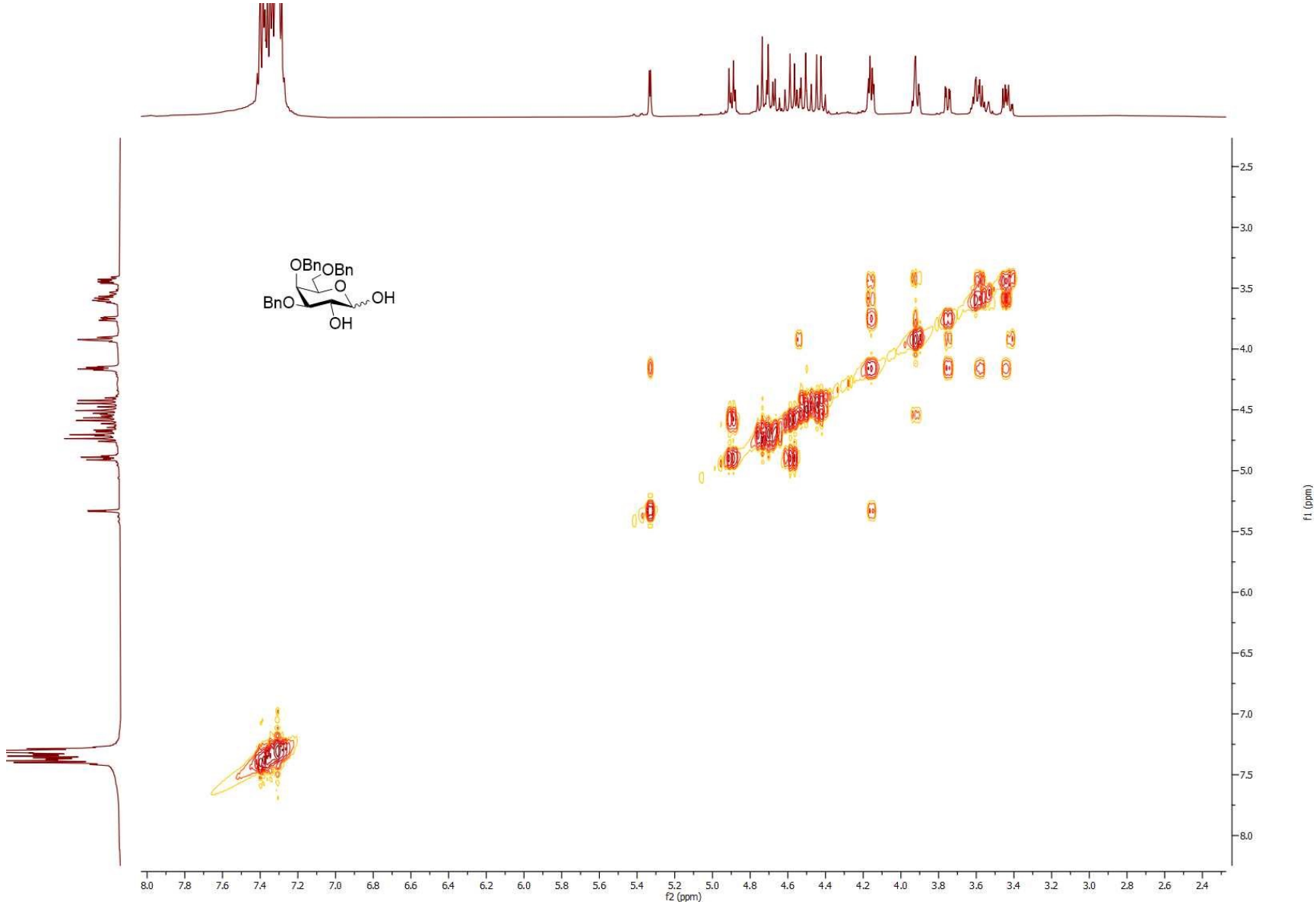
^{1}H NMR (500 MHz, $CDCl_3$)



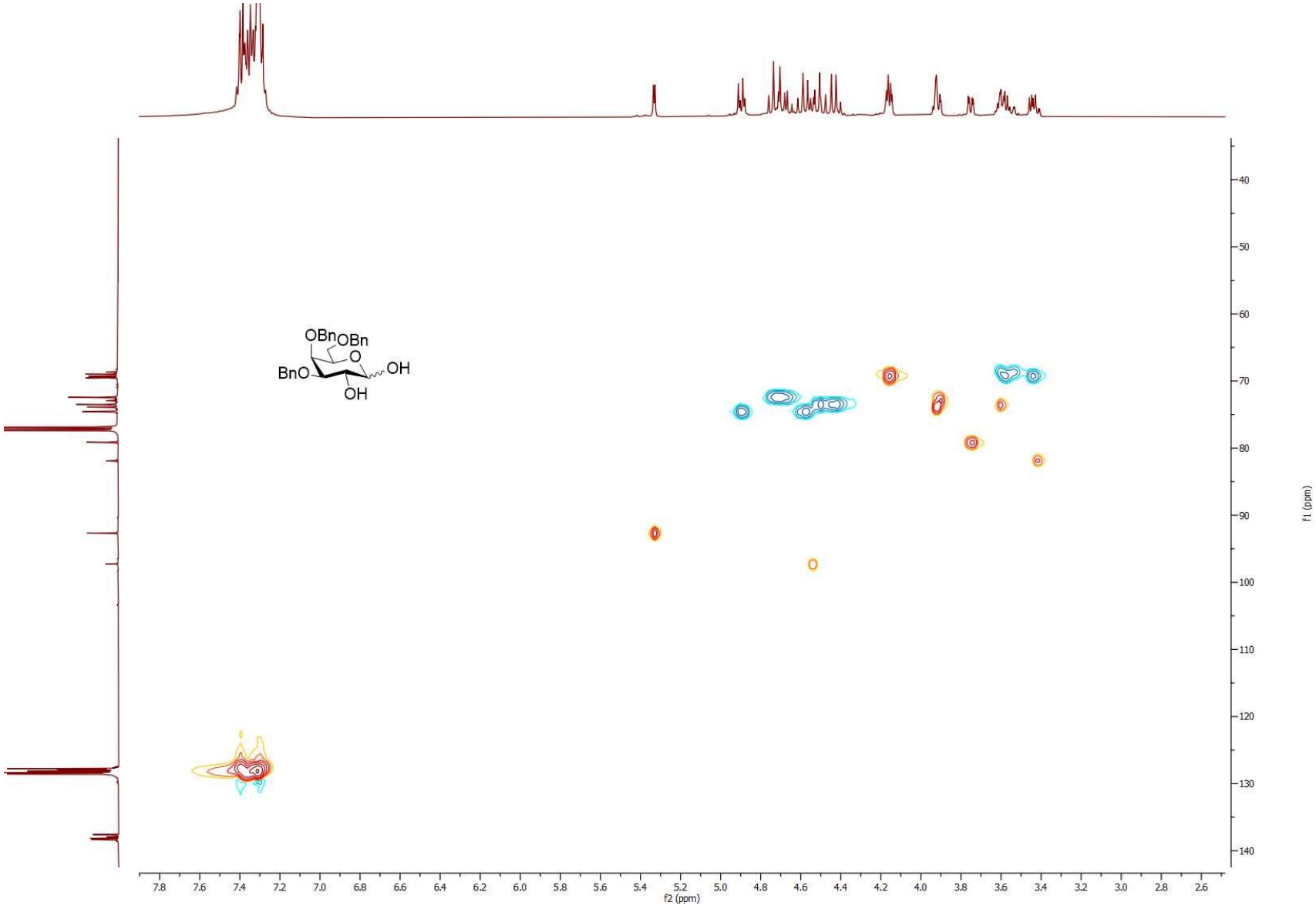
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR



HSQC NMR


OBn
OBn
O
BnO
OH
OH
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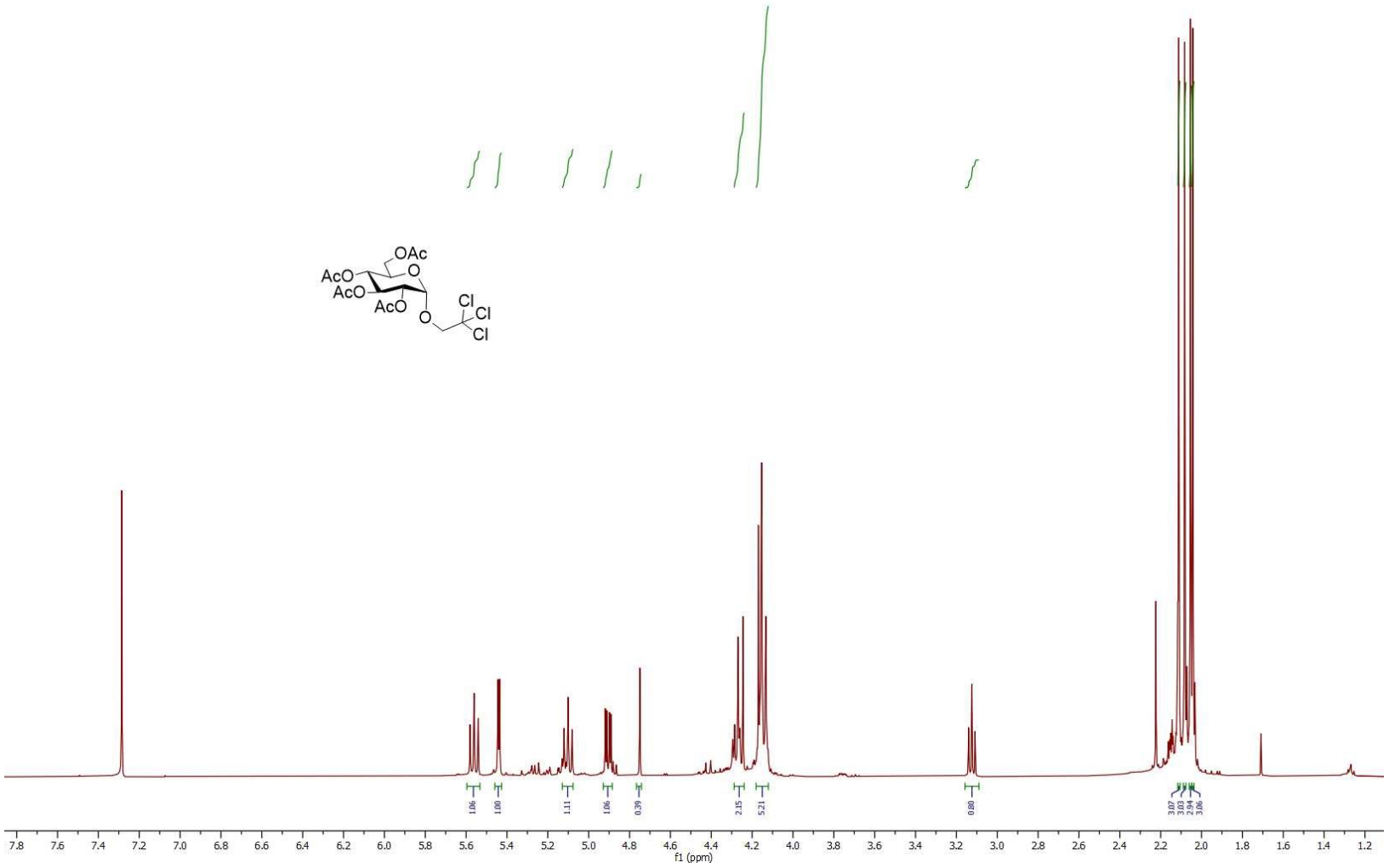
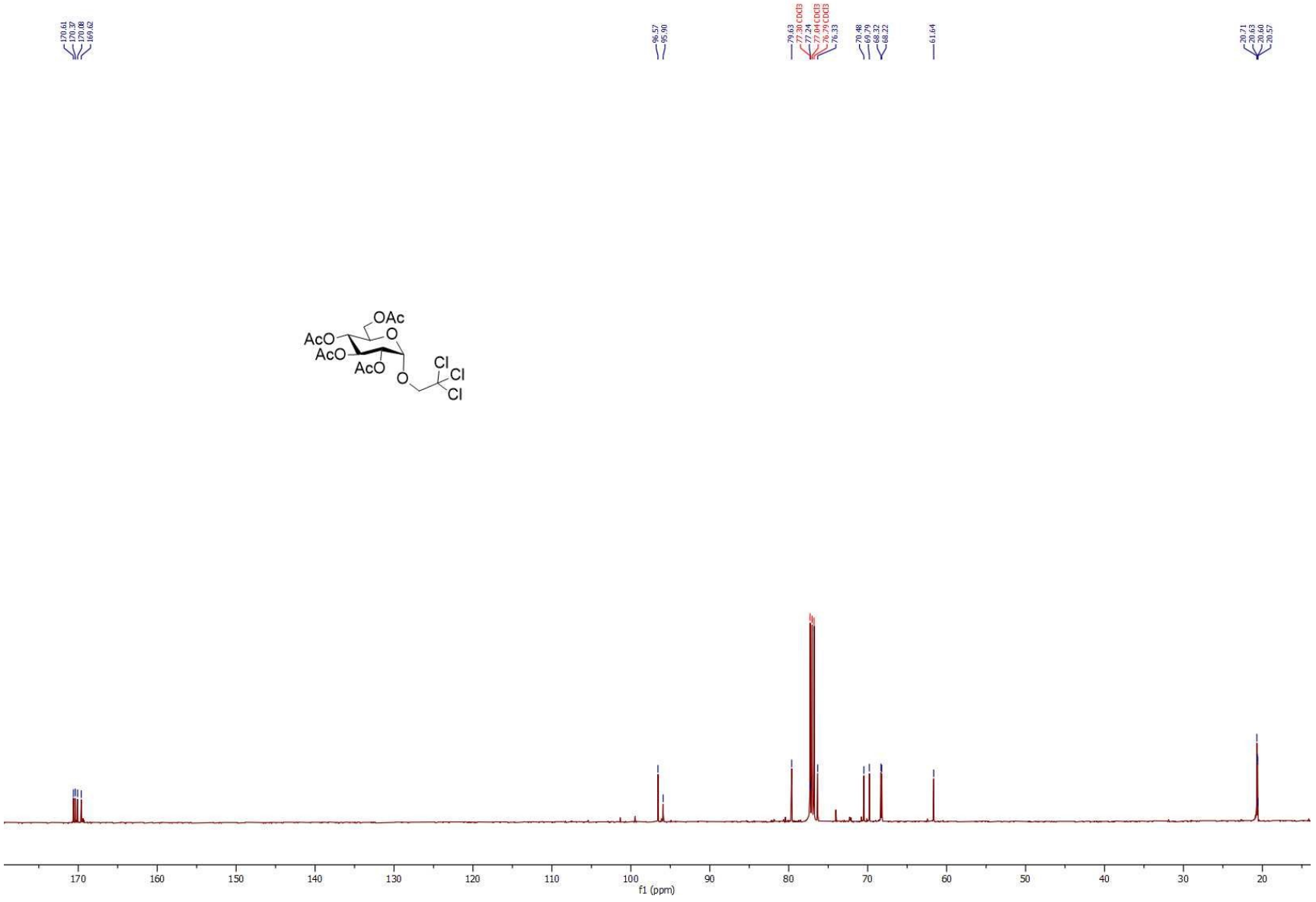
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
f2 (ppm)
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

2,2,2-trichloroethyl 2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside S2

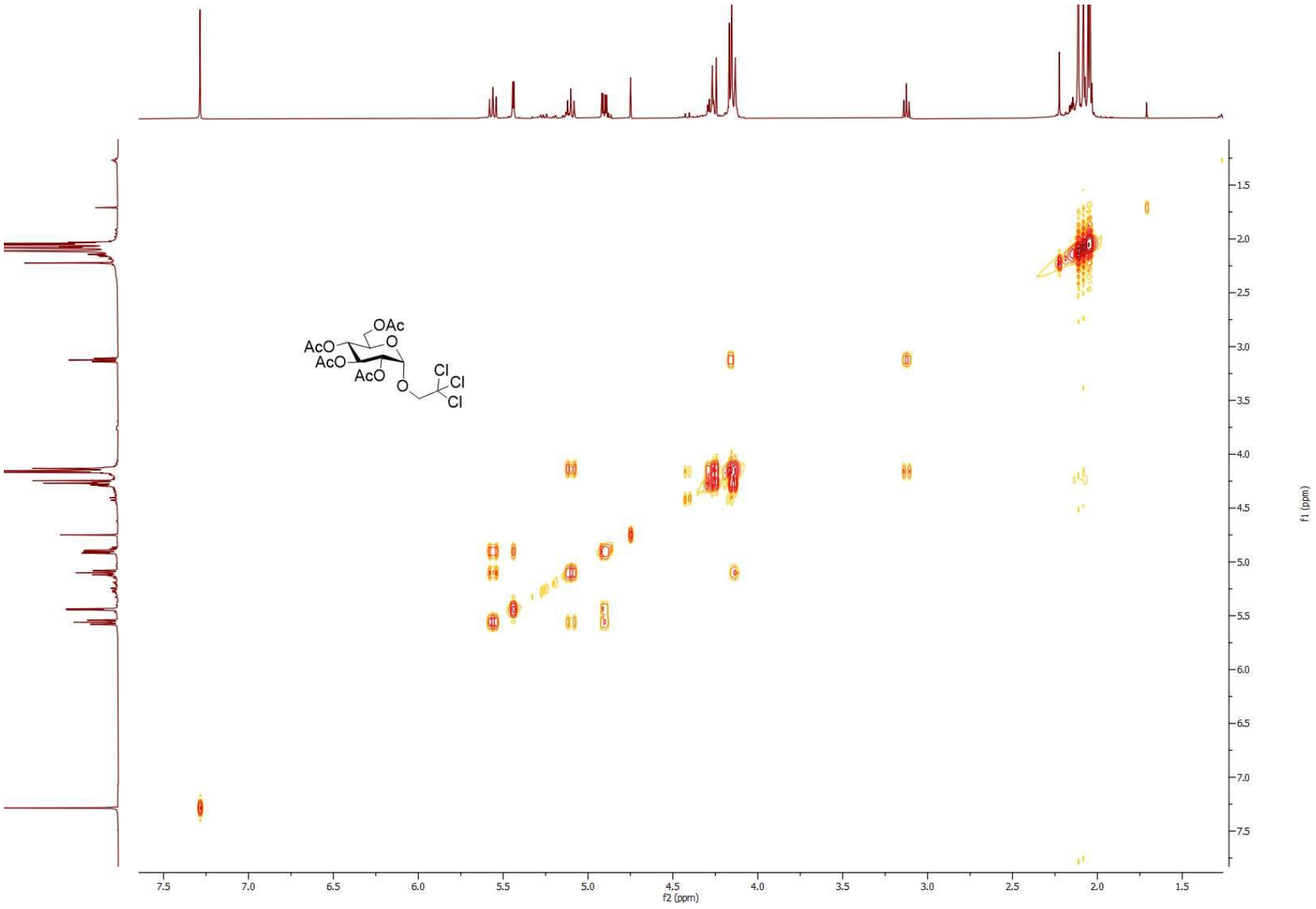
^{1}H NMR (500 MHz, $CDCl_3$)



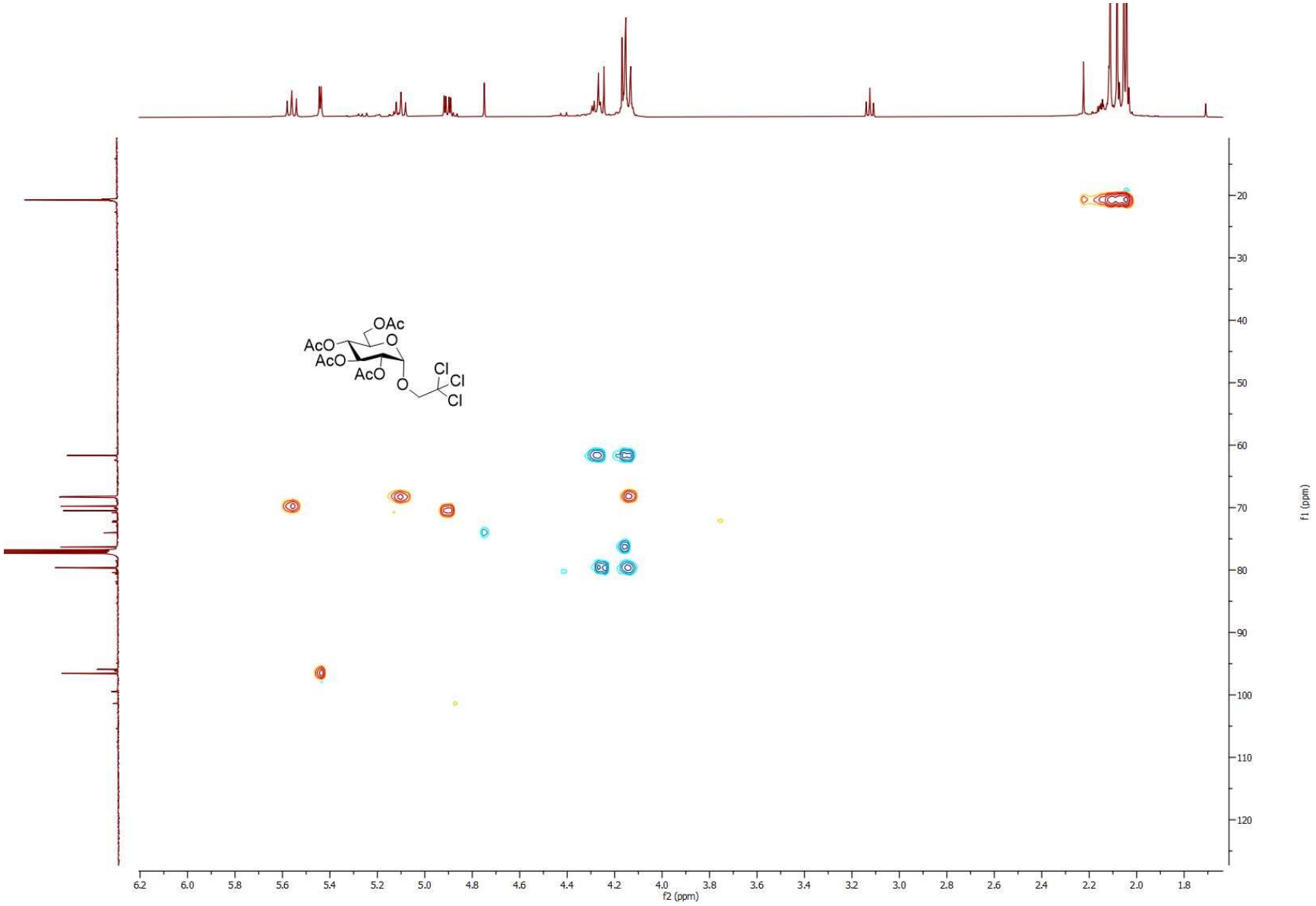
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

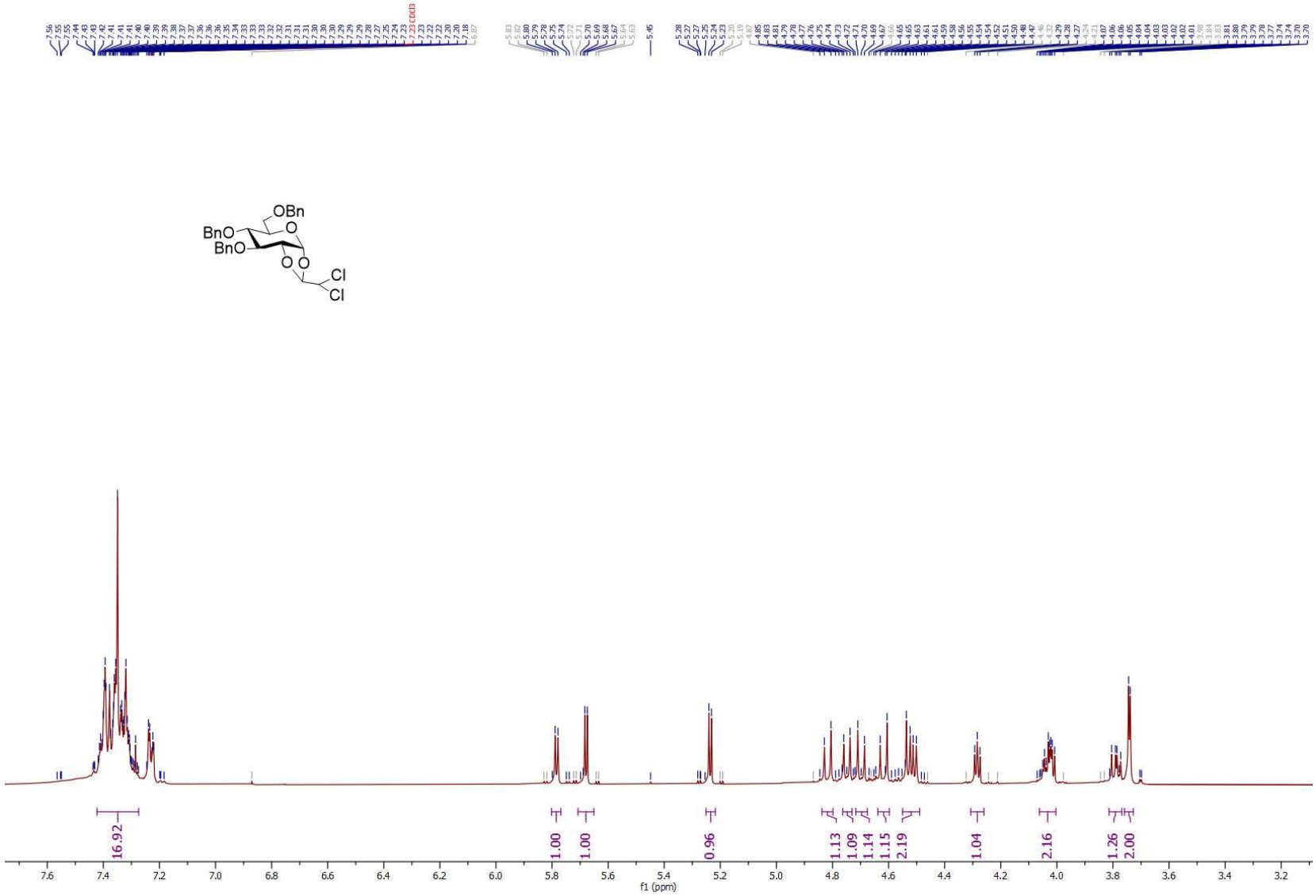


HSQC NMR

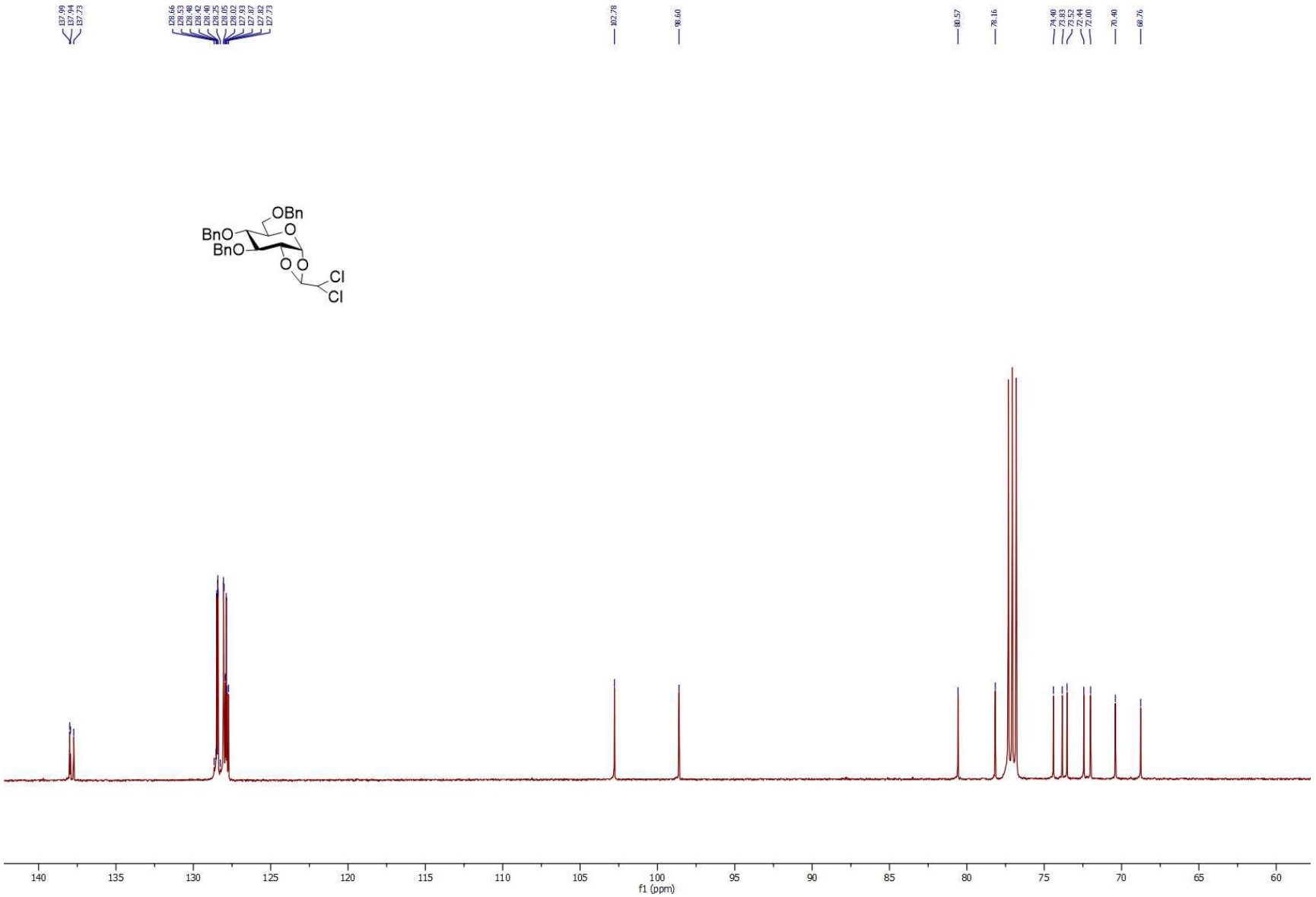


Product (2,2-dichloroethyl 3,4,6-tris-*O*-benzyl-α-D-glucopyranoside) (B2)

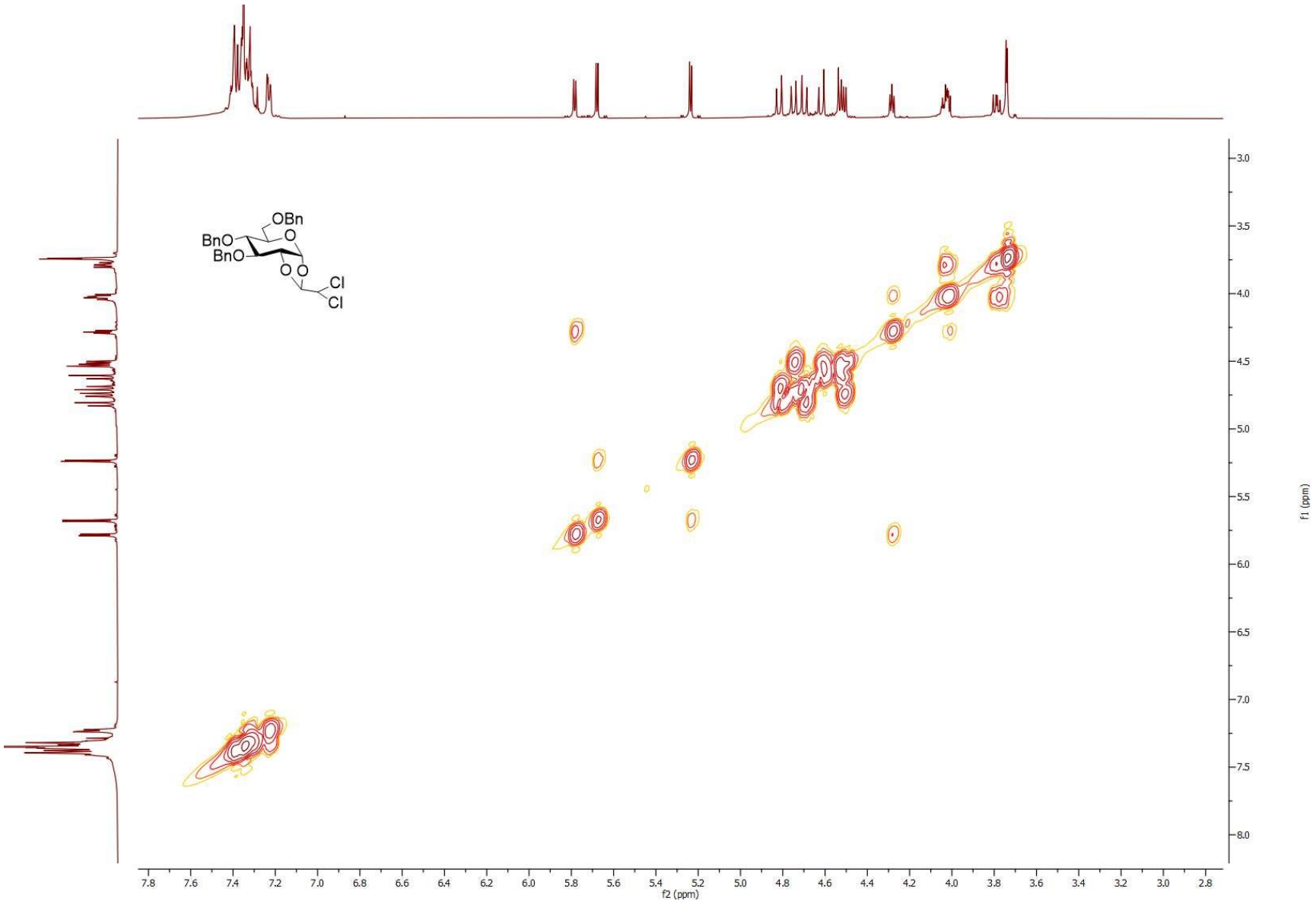
^{1}H NMR (500 MHz, $CDCl_3$)



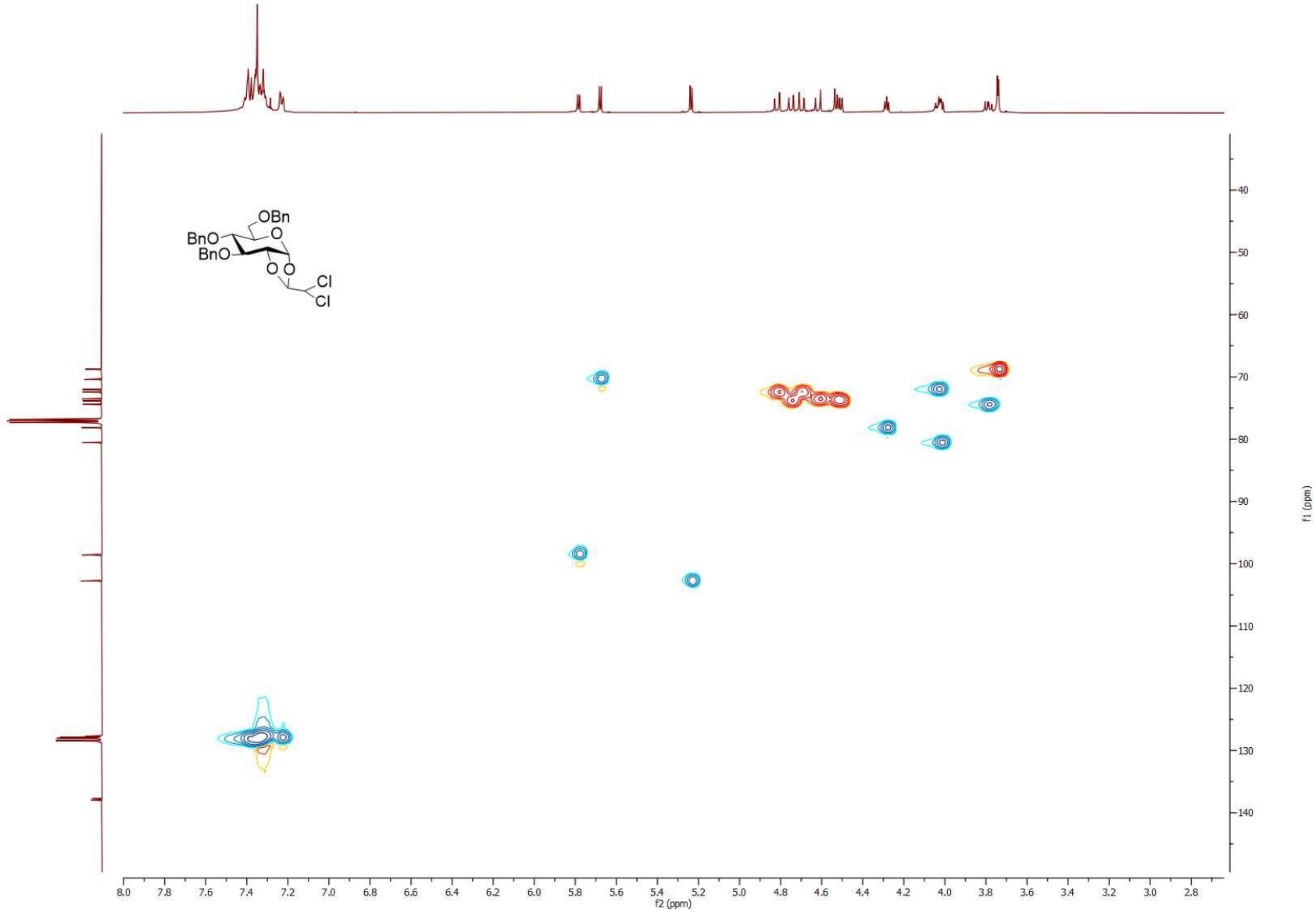
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

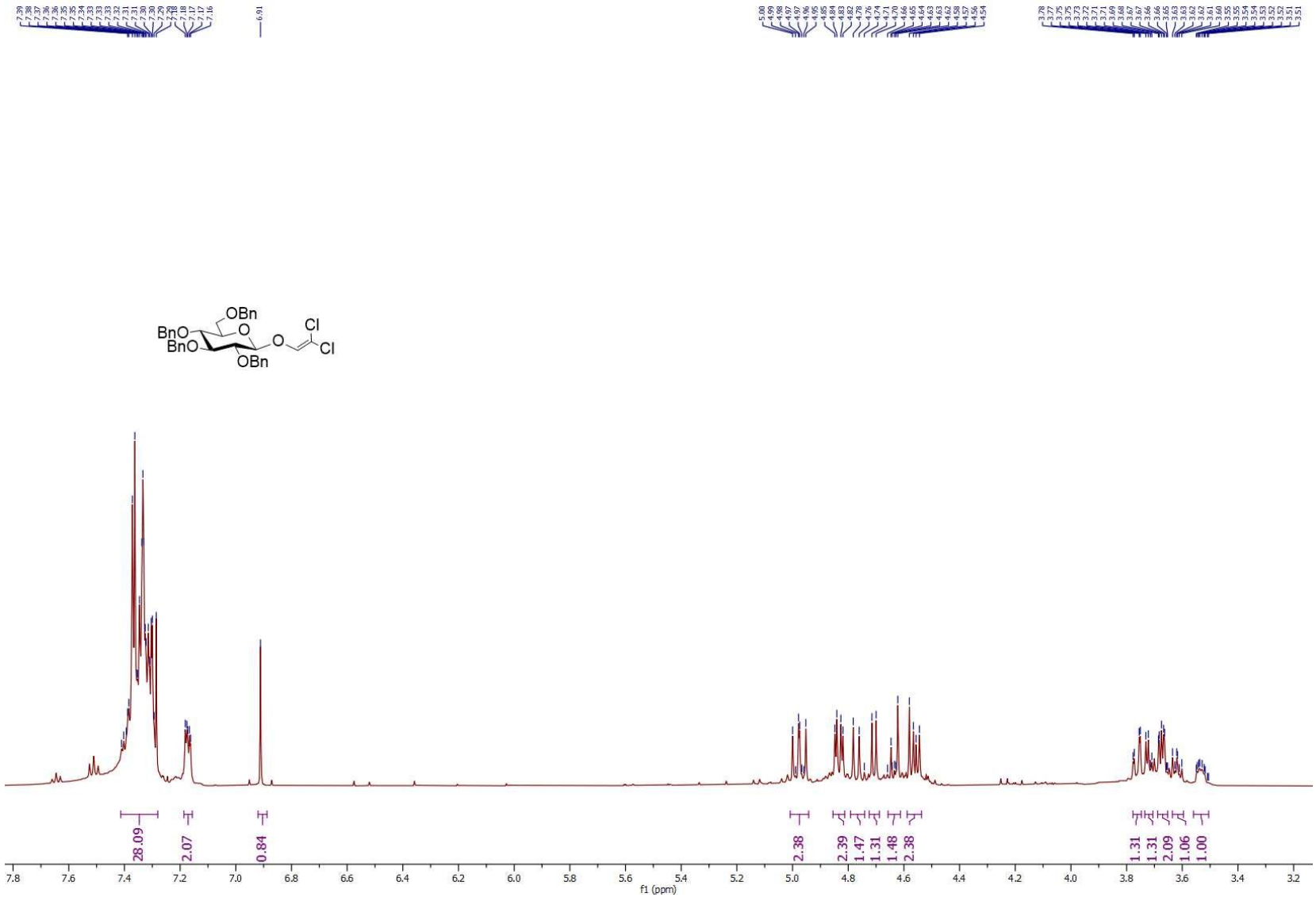


HSQC NMR

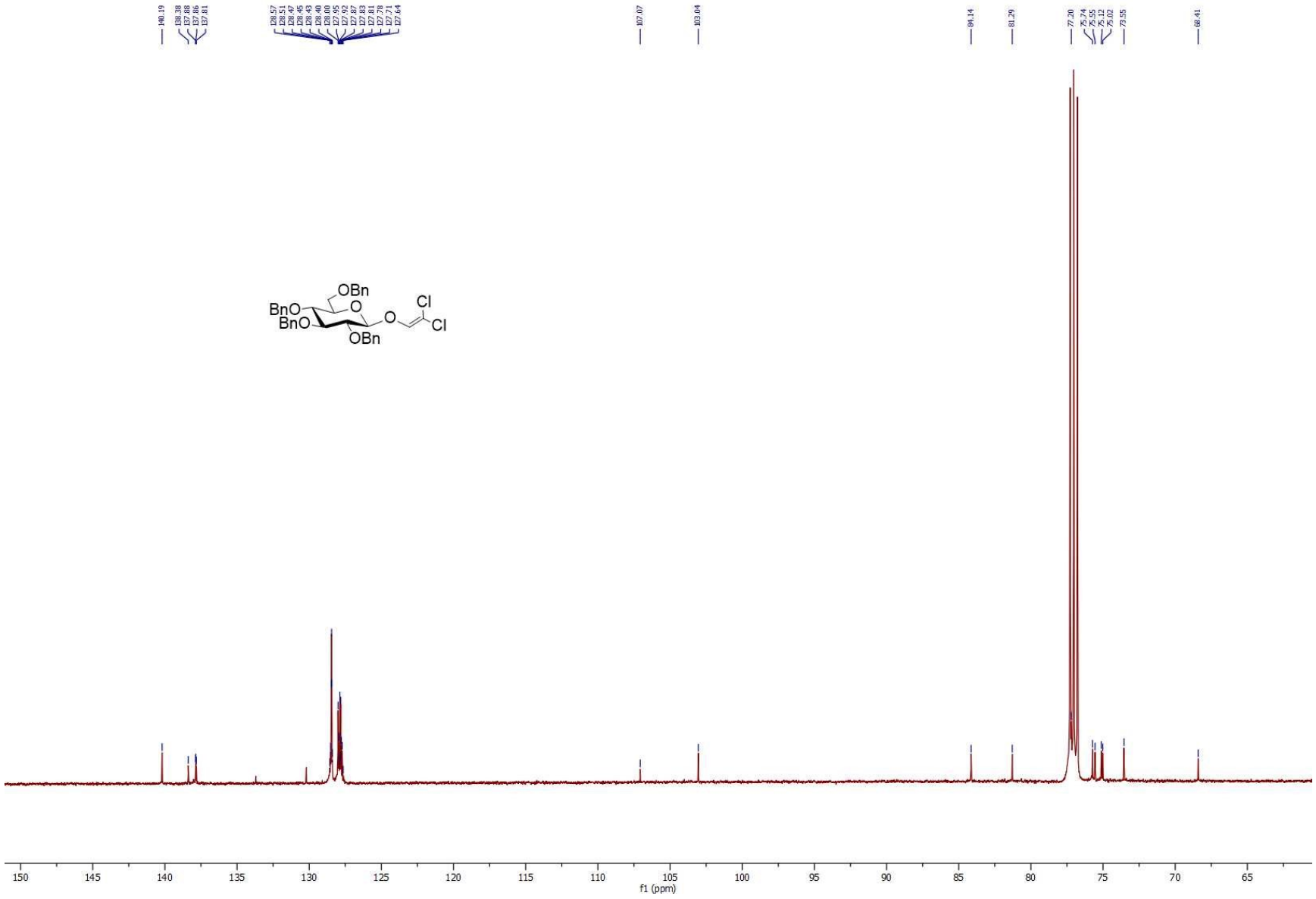

OBn
BnO
BnO
O
O
O
Cl
Cl
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
f2 (ppm)
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

Product (2,2-Dichlorovinyl 2,3,4,6-tetra-O-Benzyl-β-D-glucopyranoside) (B3)

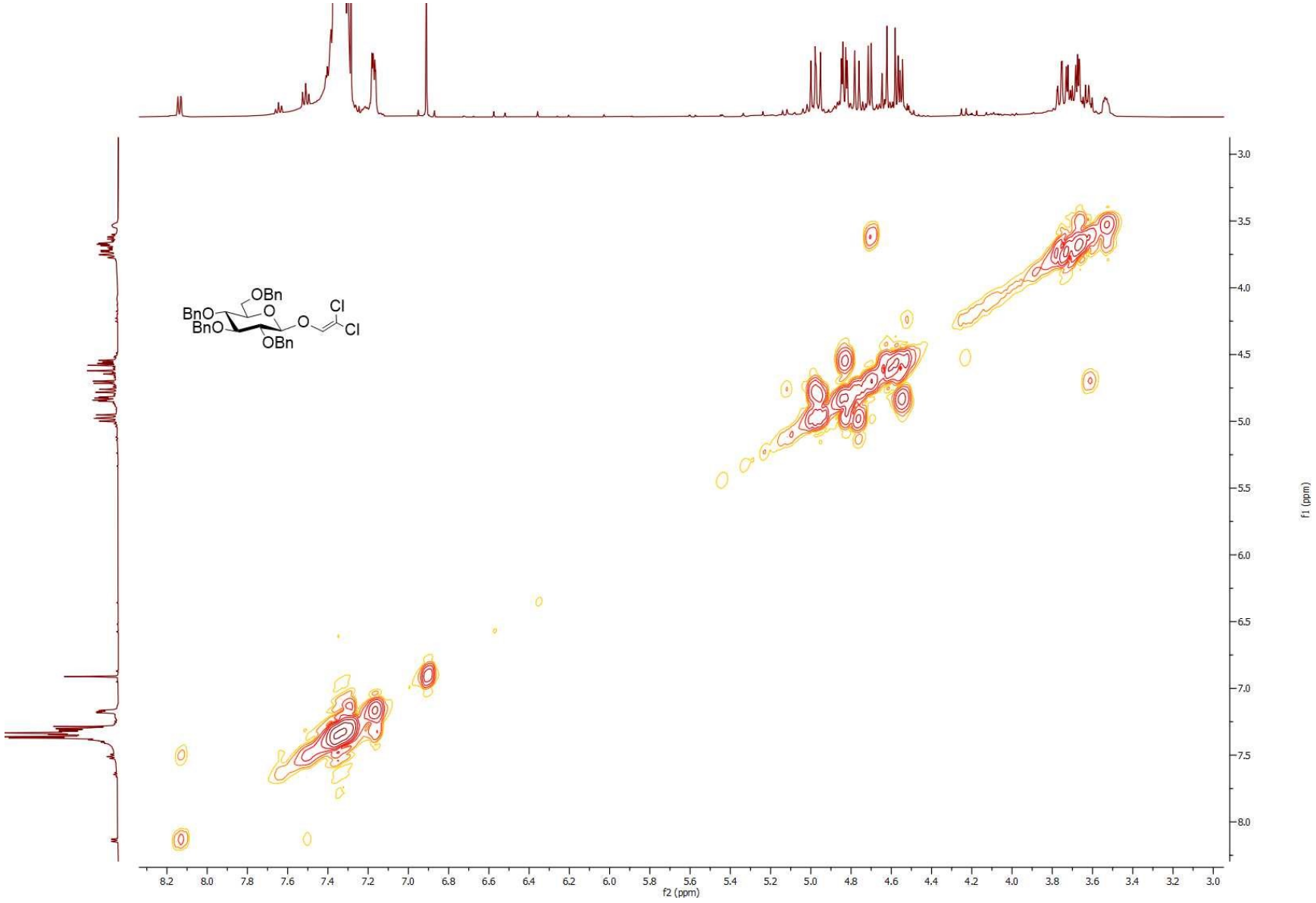
^{1}H NMR (500 MHz, $CDCl_3$)



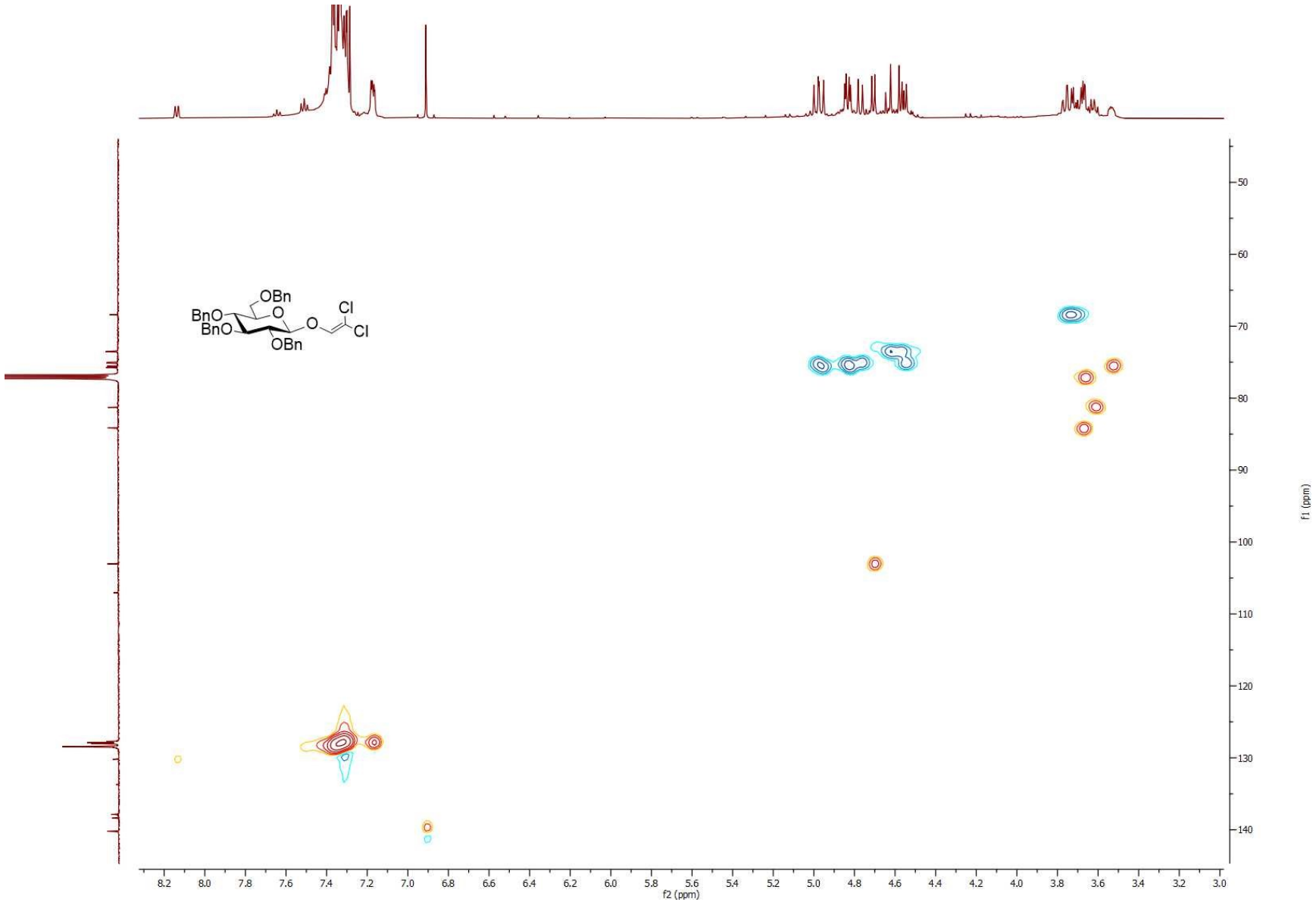
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

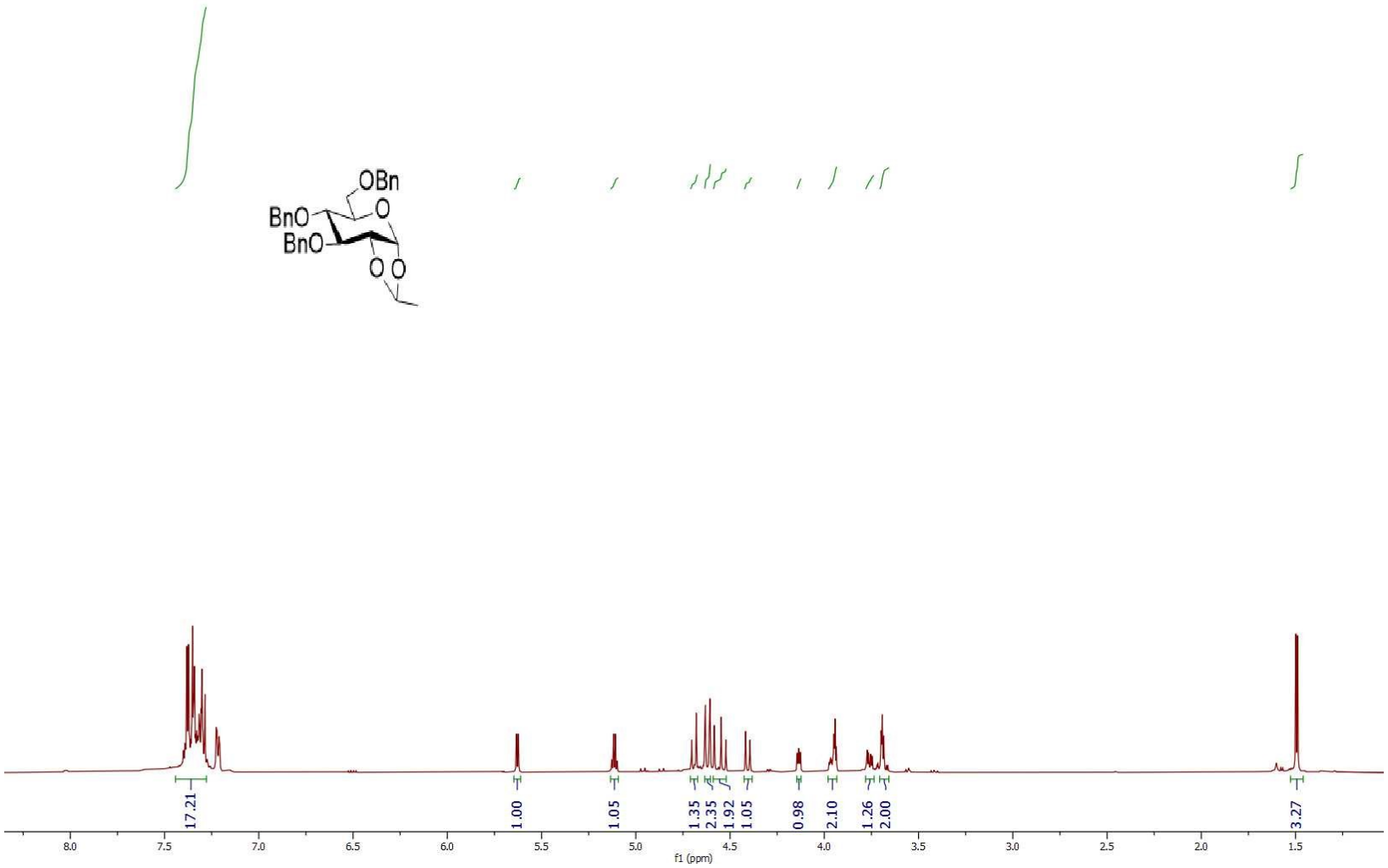


HSQC NMR

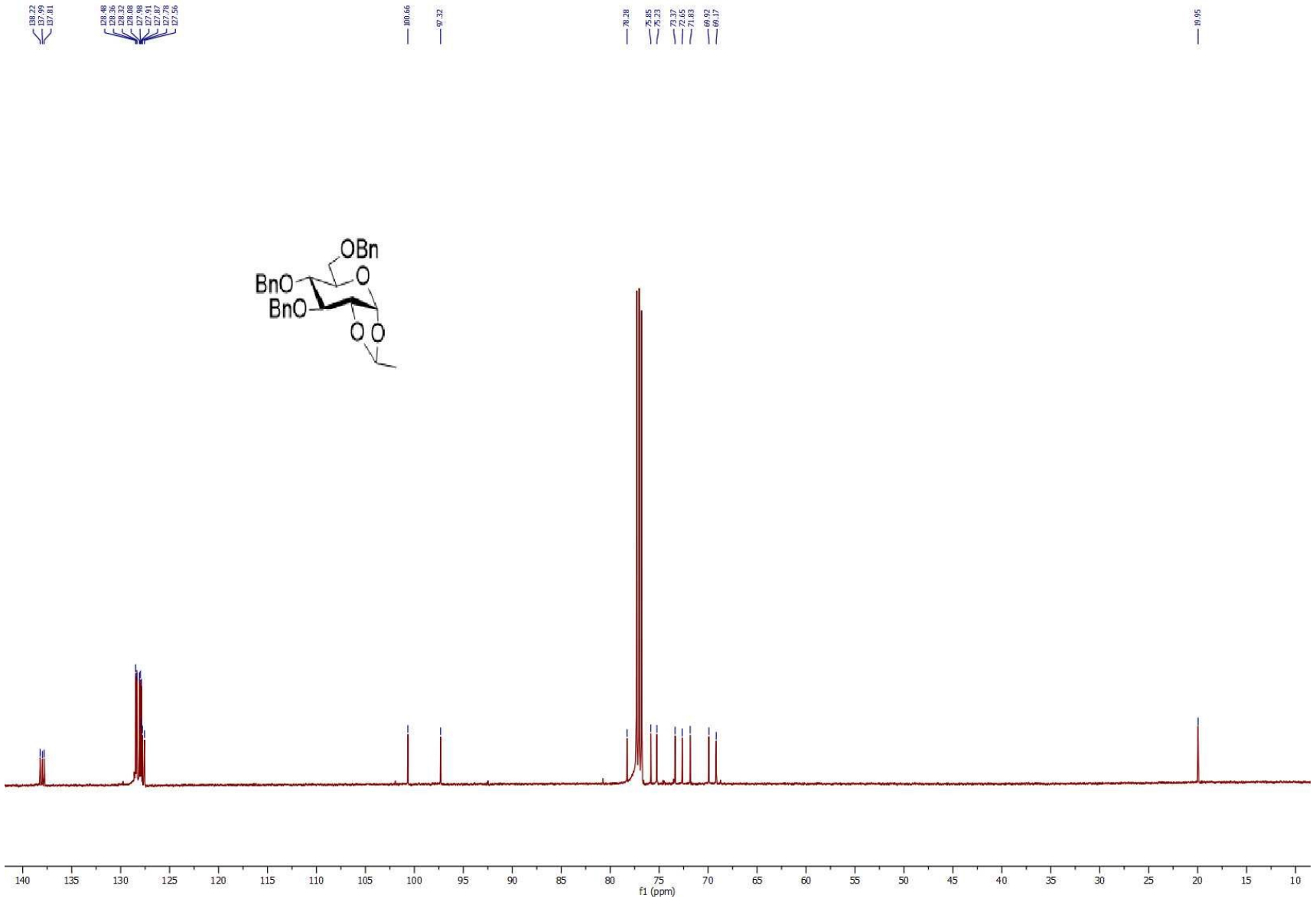

OBn
BnO
BnO
O
O
Cl
Cl
OBn
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
f2 (ppm)
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

1,2-O-ethylidene-3,4,6-tris-*O*-benzyl-α-D-glucopyranoside(B4)

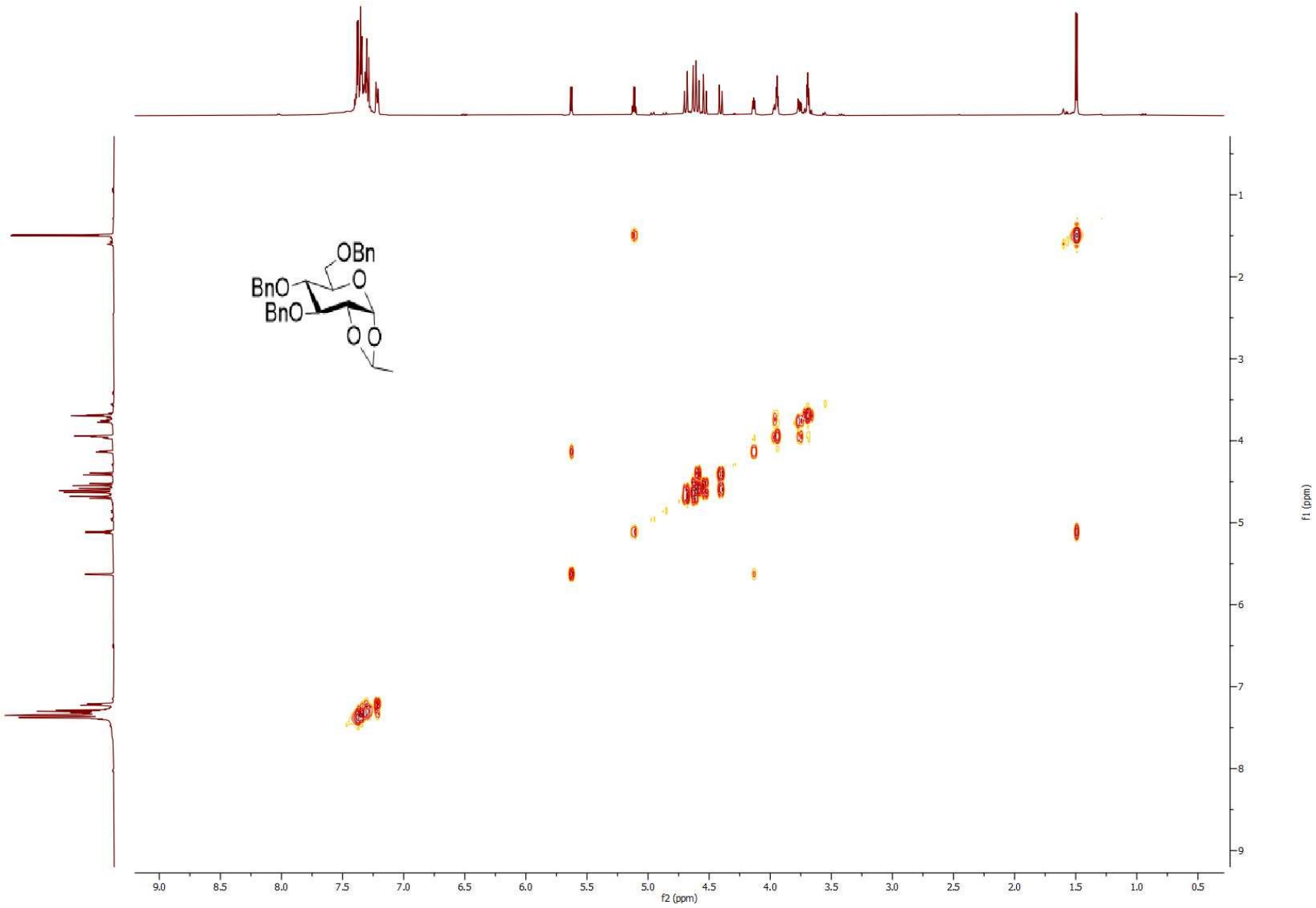
^{1}H NMR (500 MHz, $CDCl_3$)



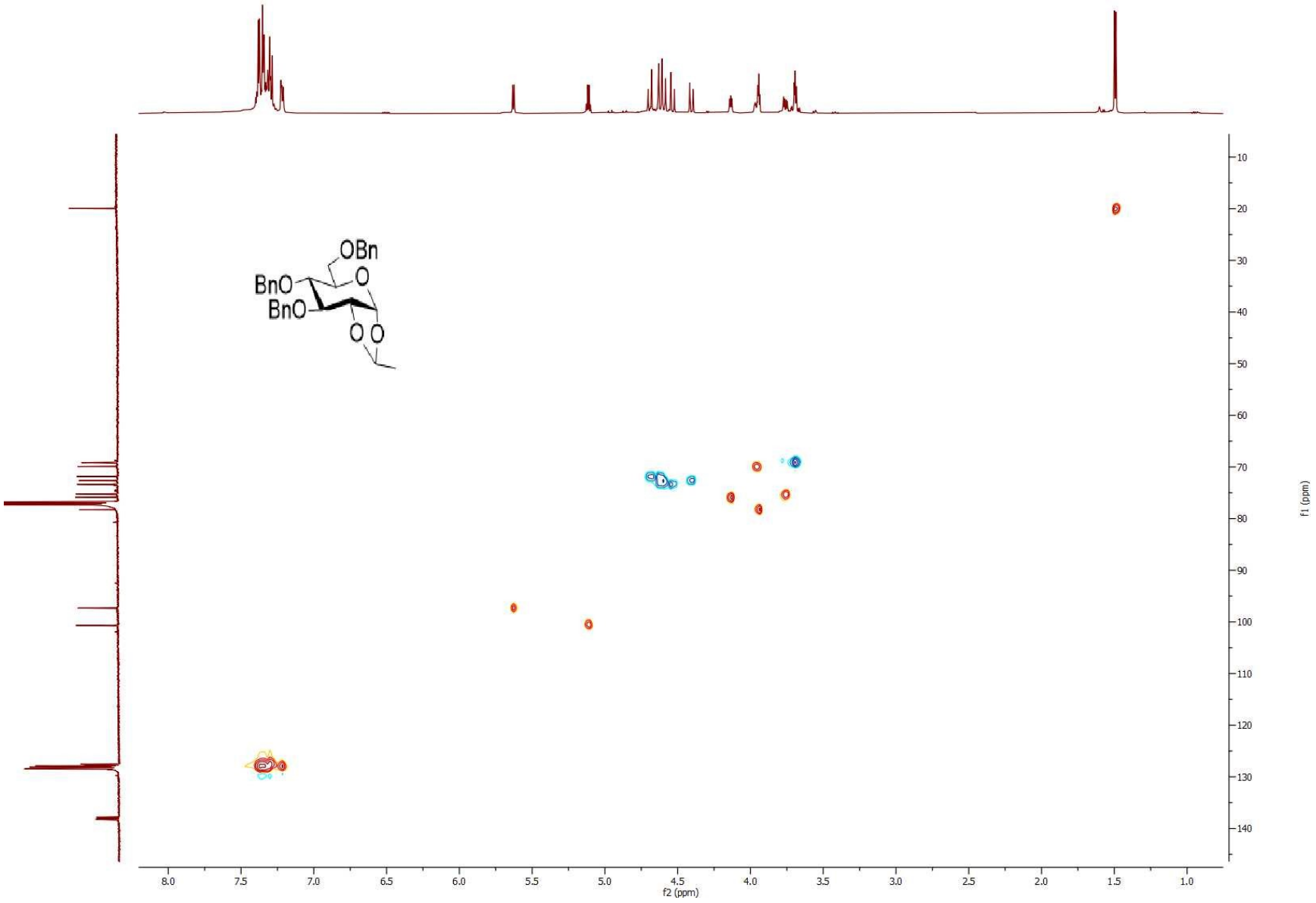
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

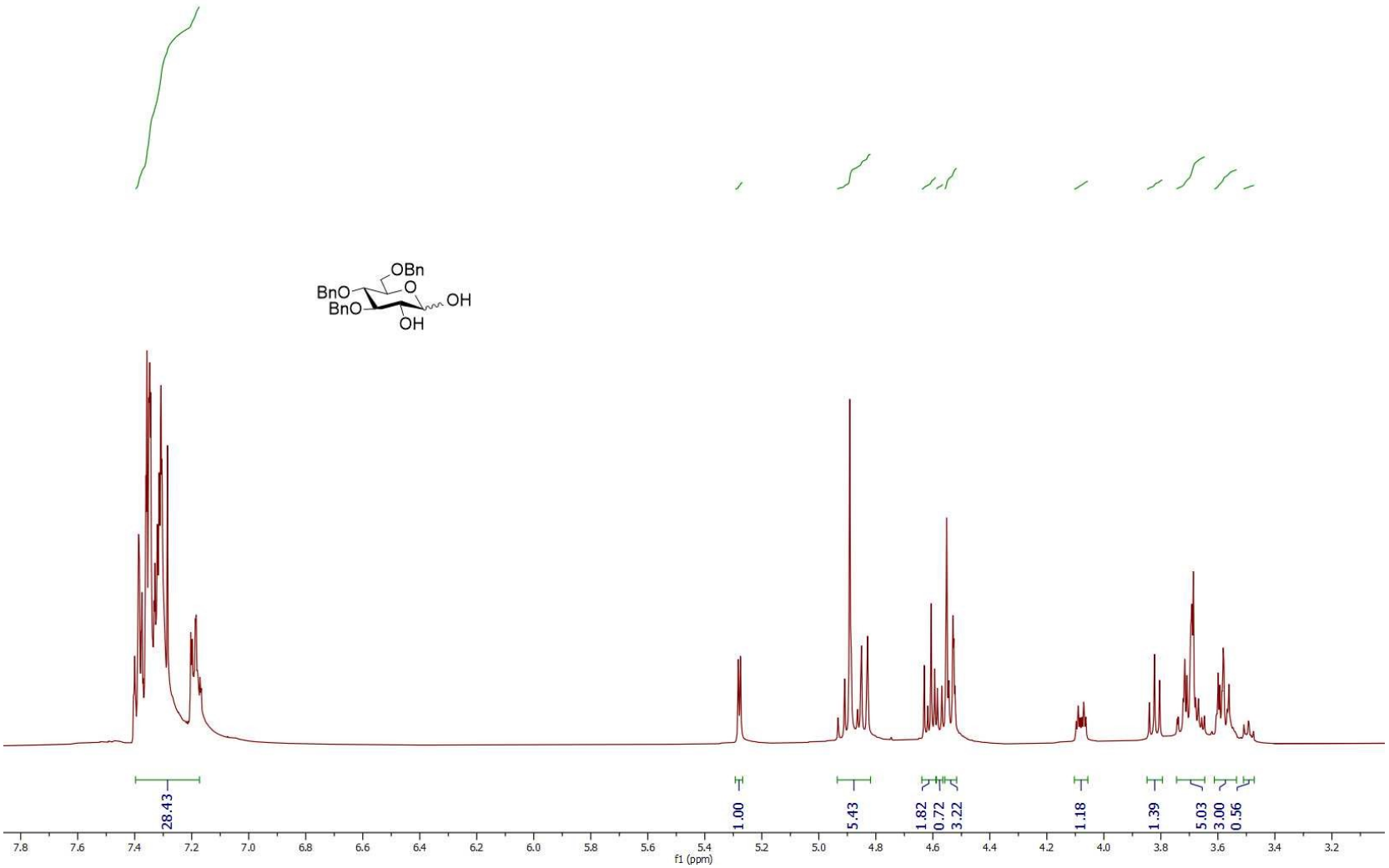


HSQC NMR

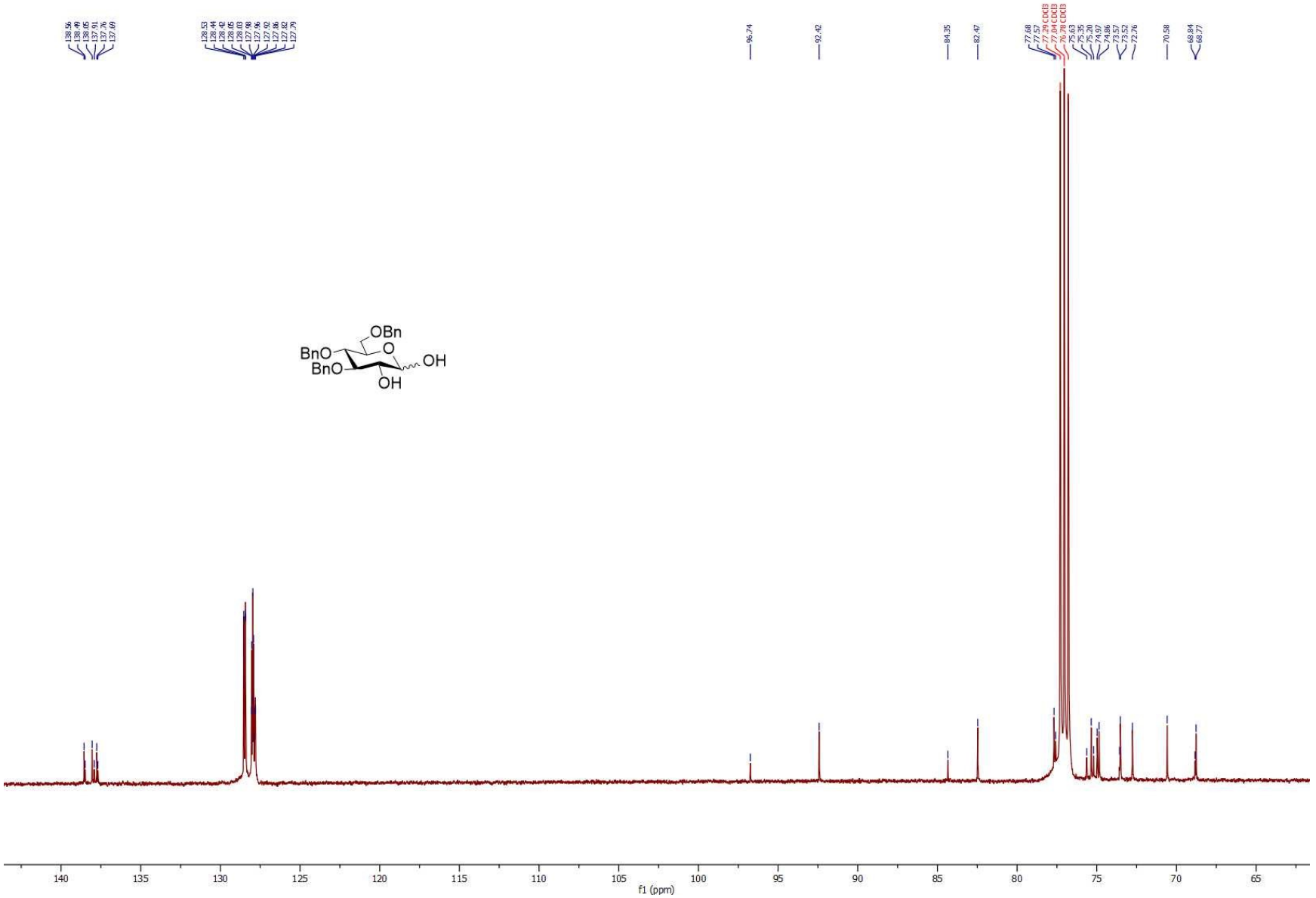


3,4,6-Tris-O-Benzyl-D-glucopyranose(B5)

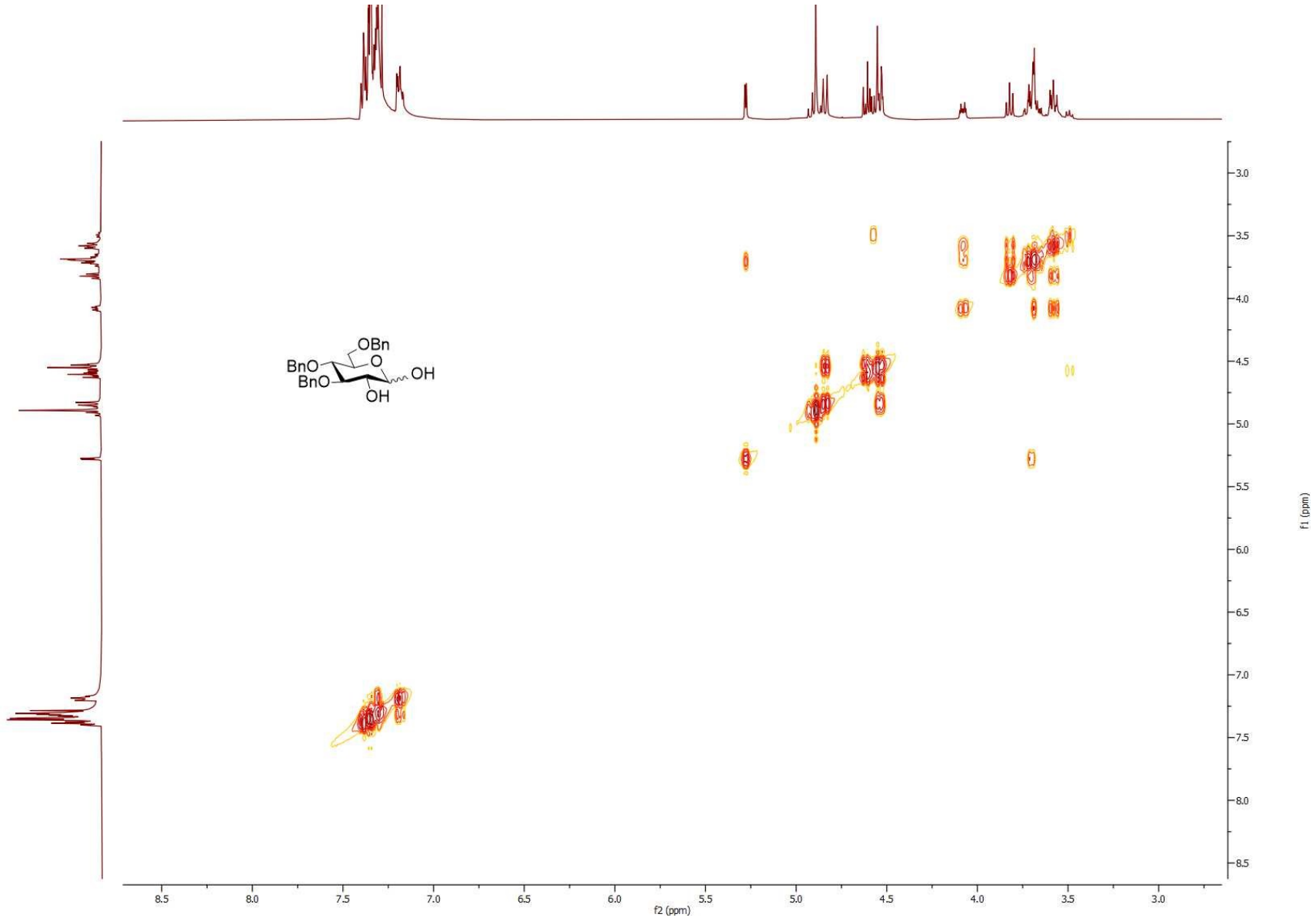
^{1}H NMR (500 MHz, $CDCl_3$)



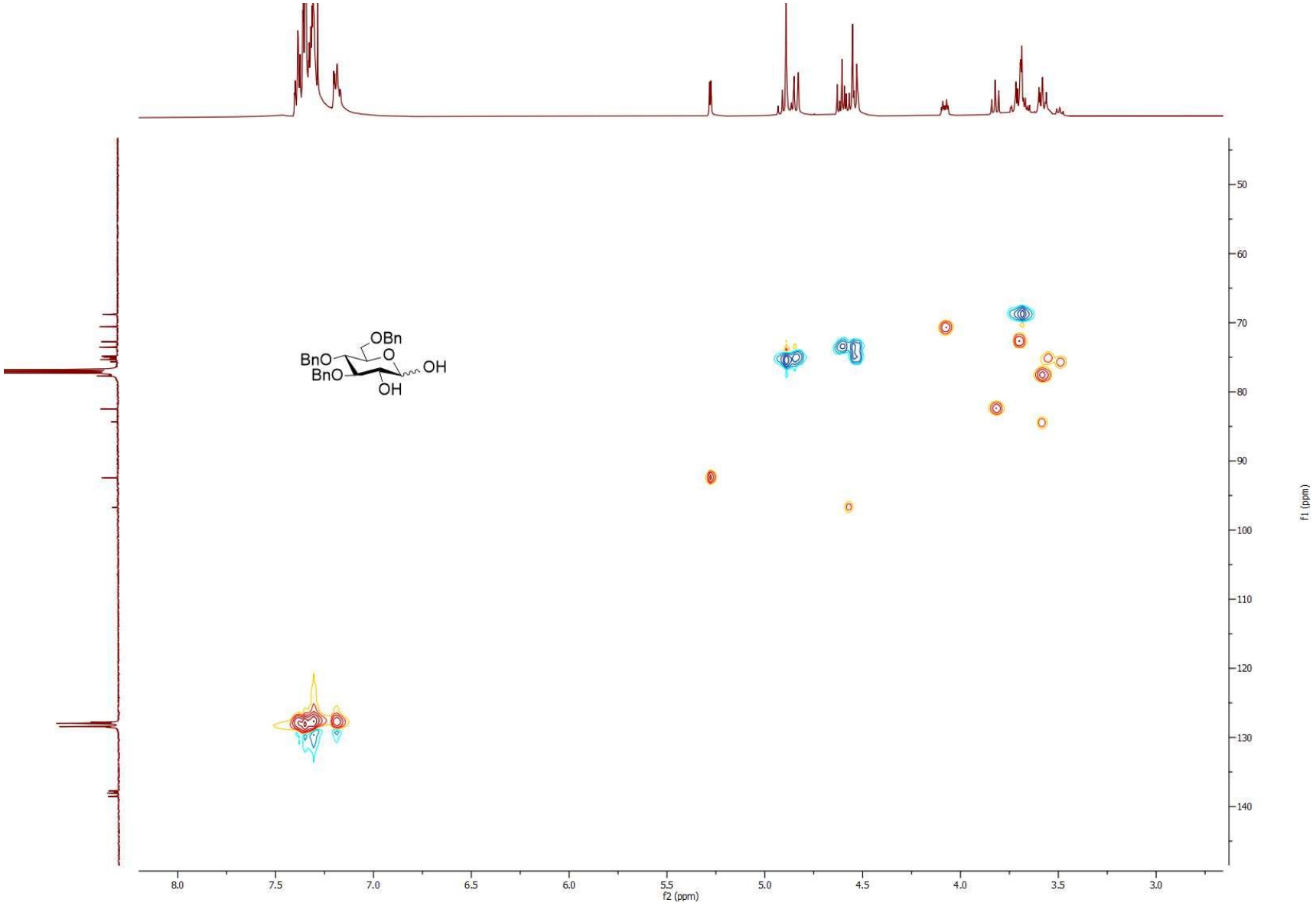
^{13}C NMR (126 MHz, $CDCl_3$)



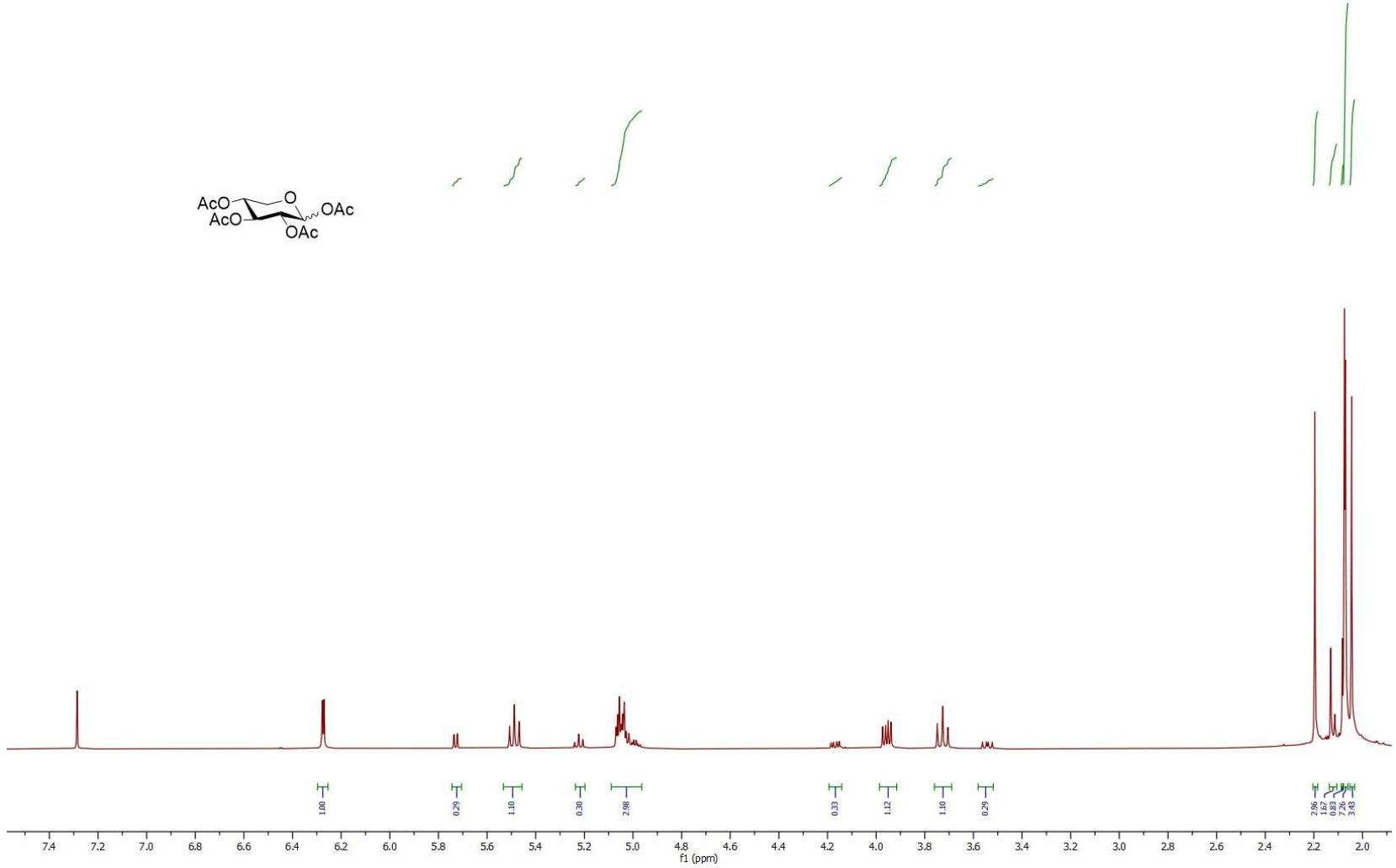
H-H COSY NMR



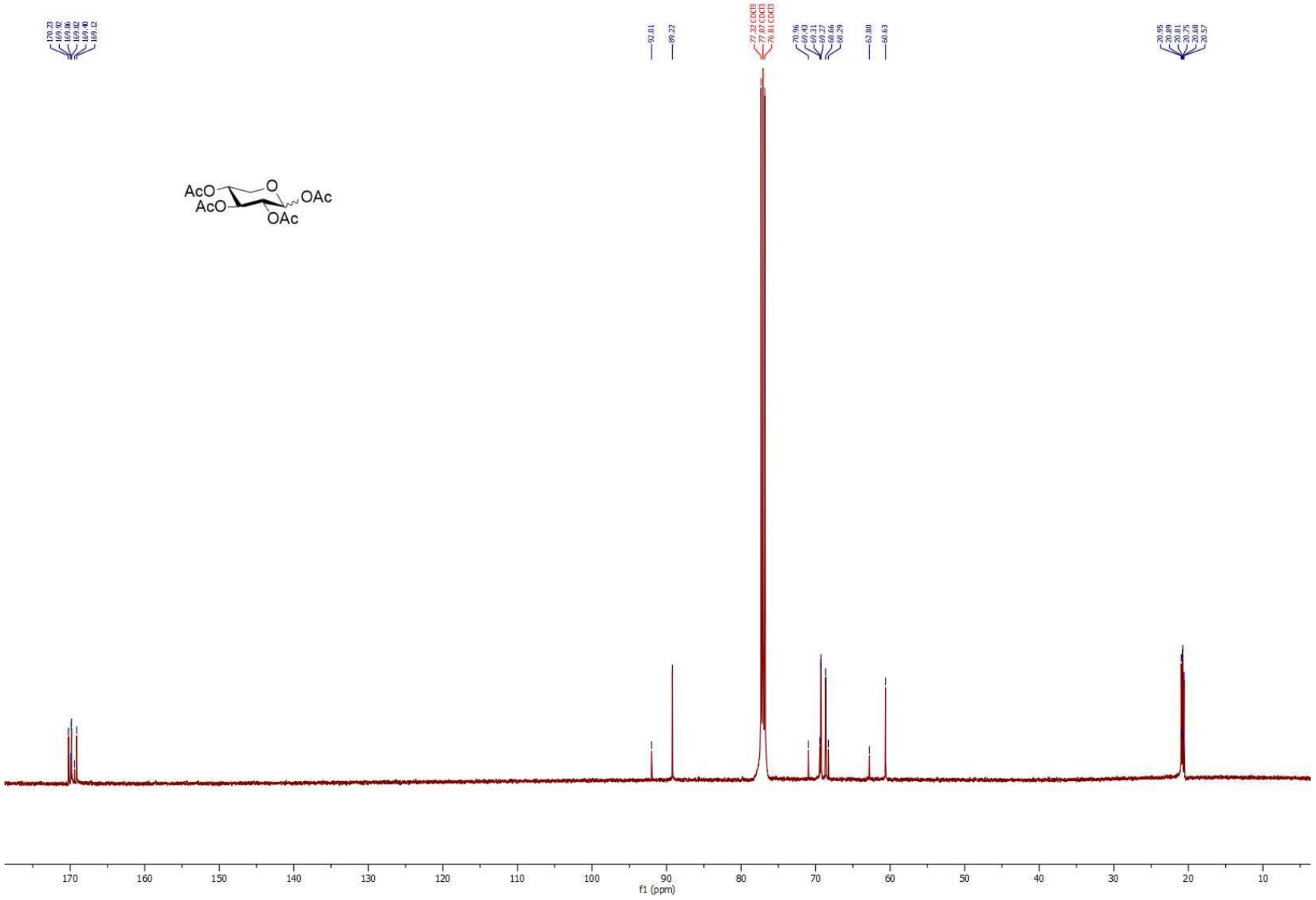
HSQC NMR


OBn
BnO
O
BnO
OH
OH
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

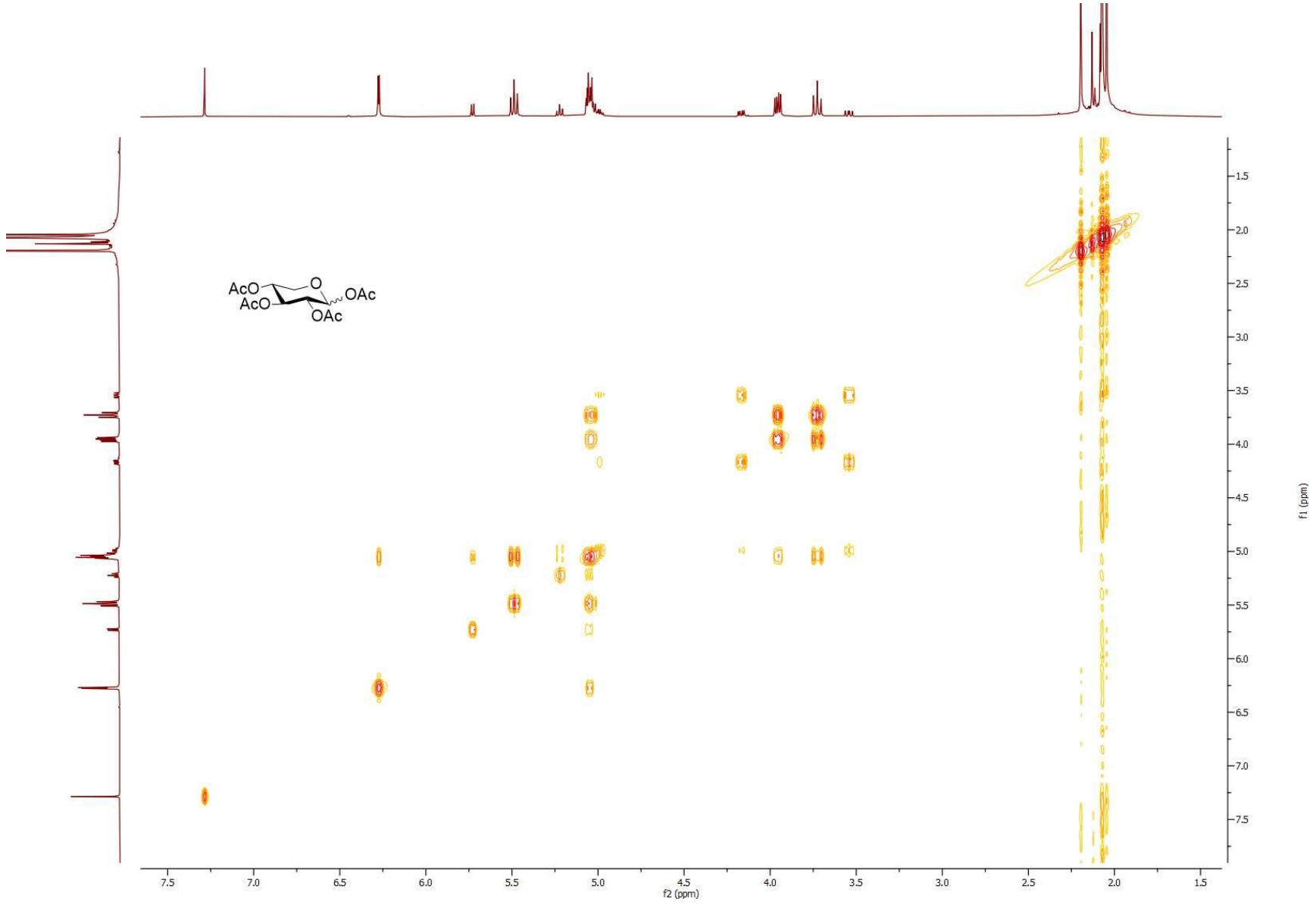
1,2,3,4-Tetra-O-acetyl-D-xylopyranose S3
^{1}H NMR (500 MHz, $CDCl_3$)



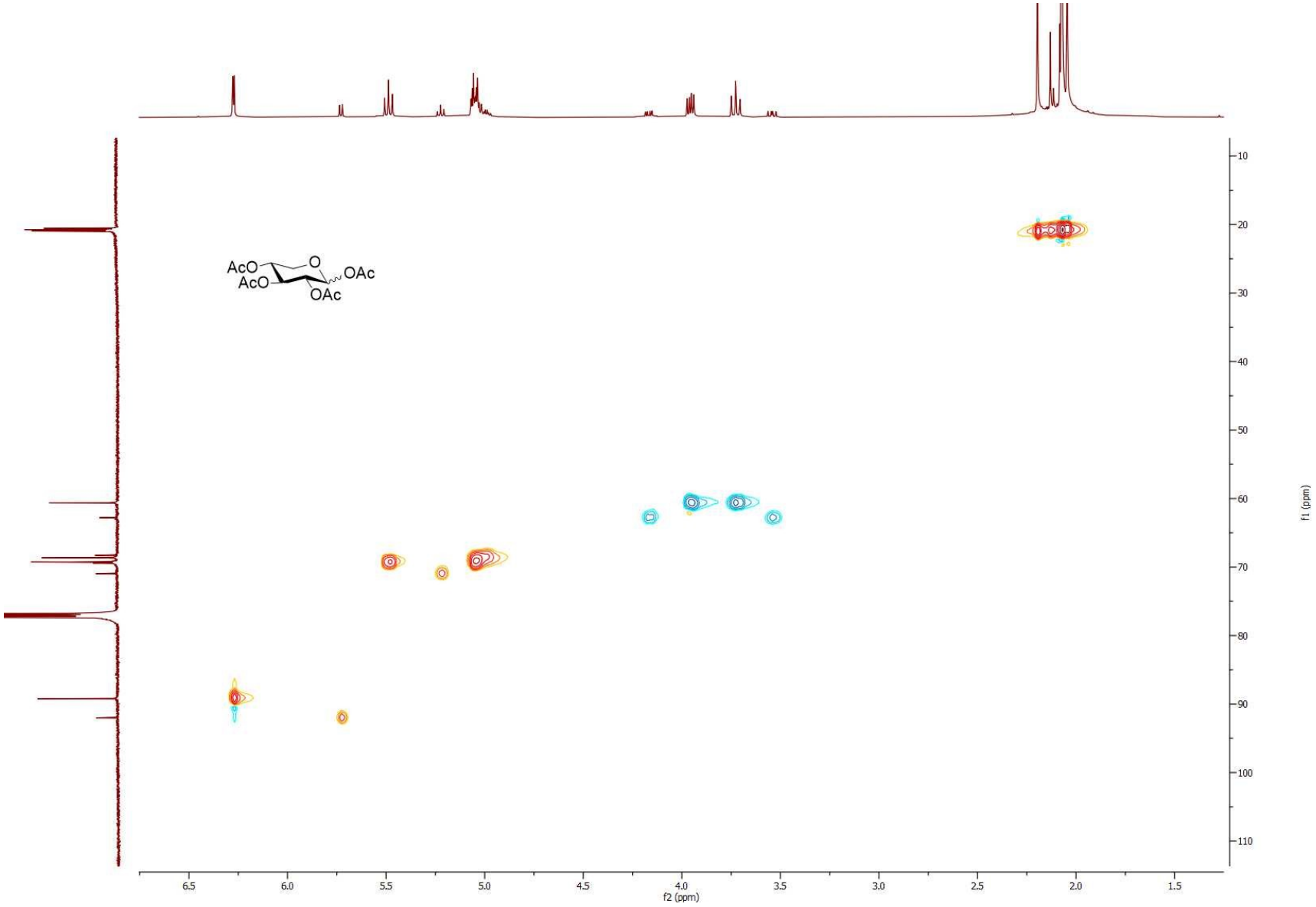
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

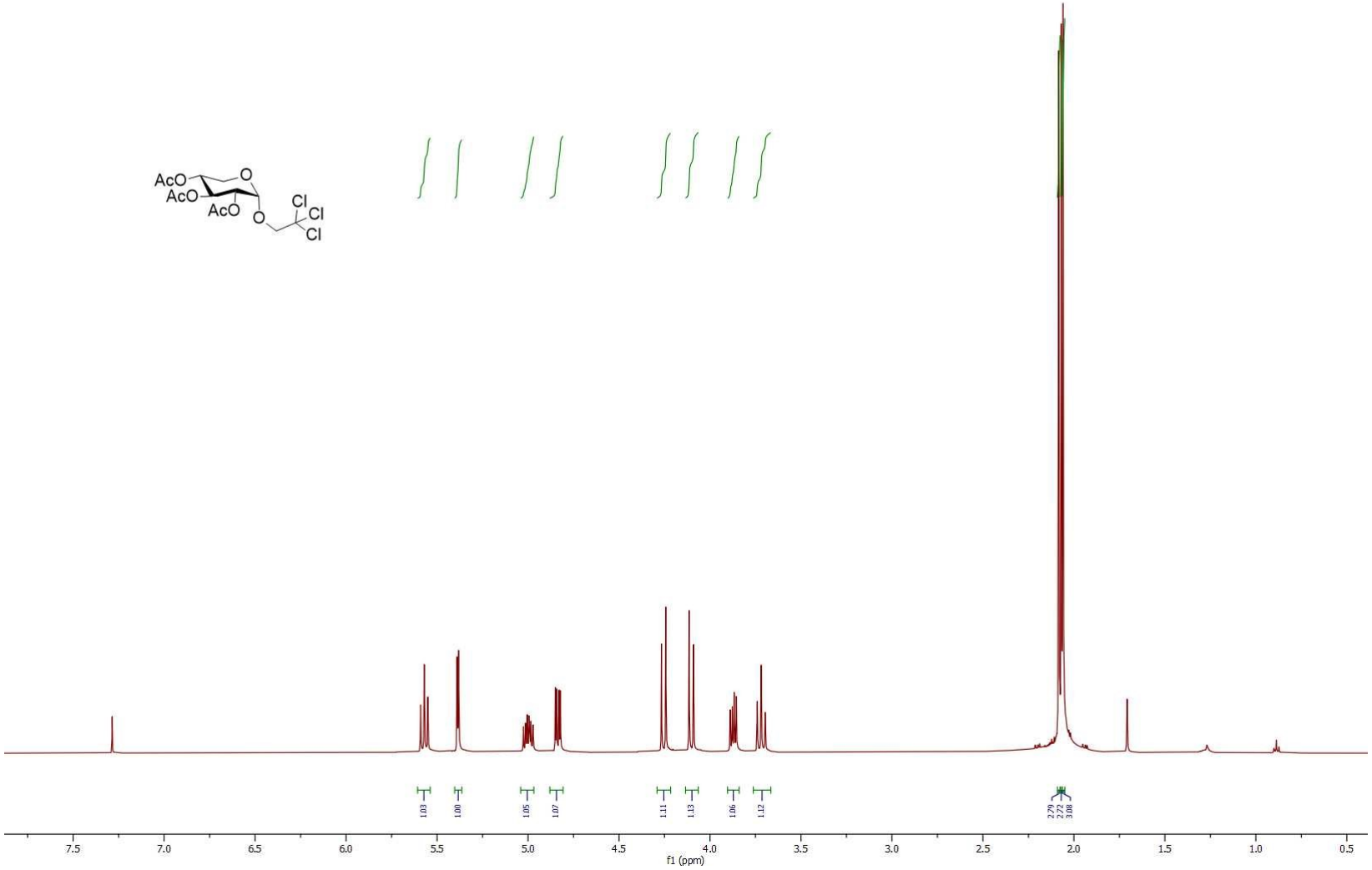


HSQC NMR

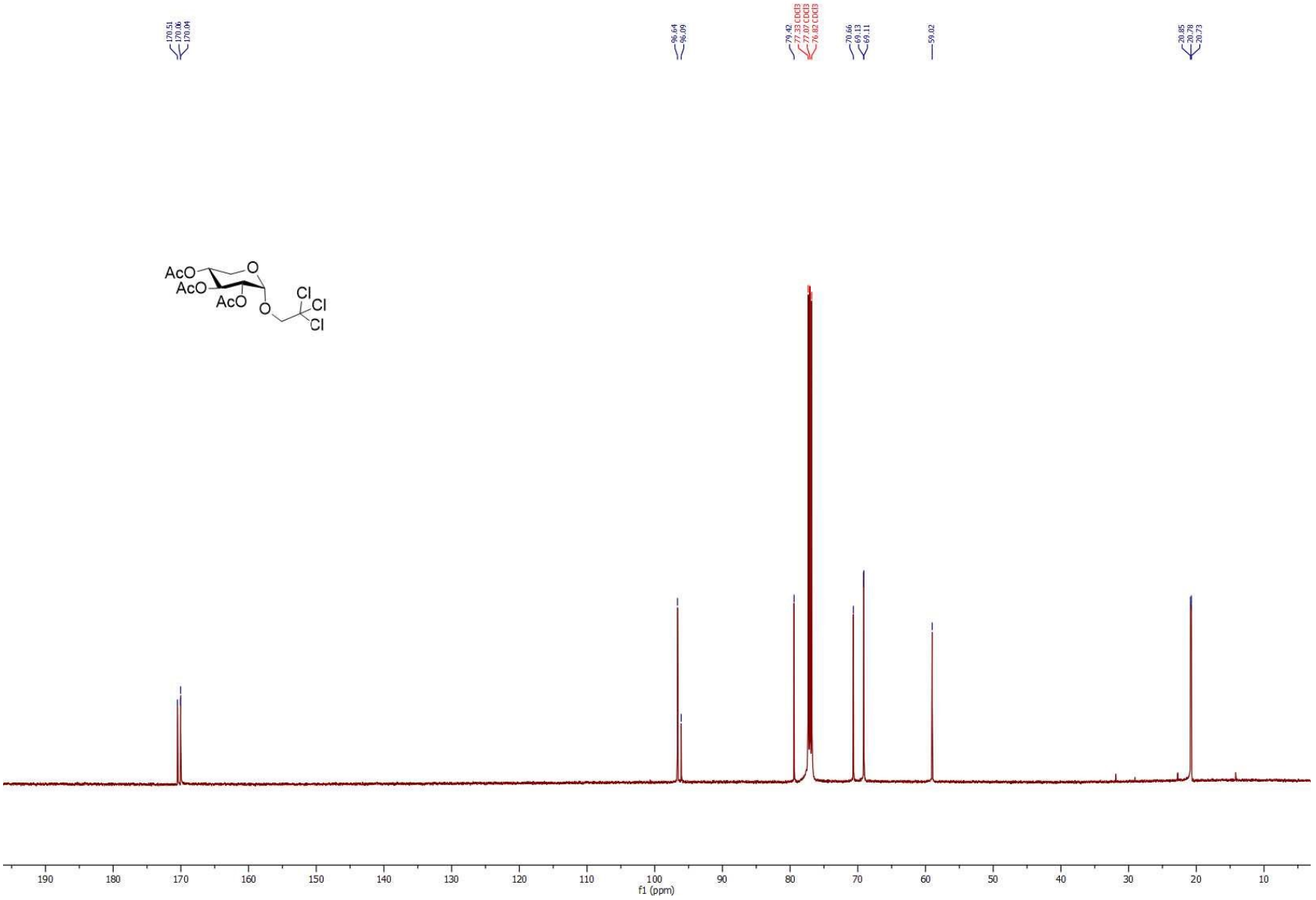

AcO
AcO
O
OAc
OAc
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

2,2,2-trichloroethyl 2,3,4-tris-O-Acetyl-D-xylopyranoside S4

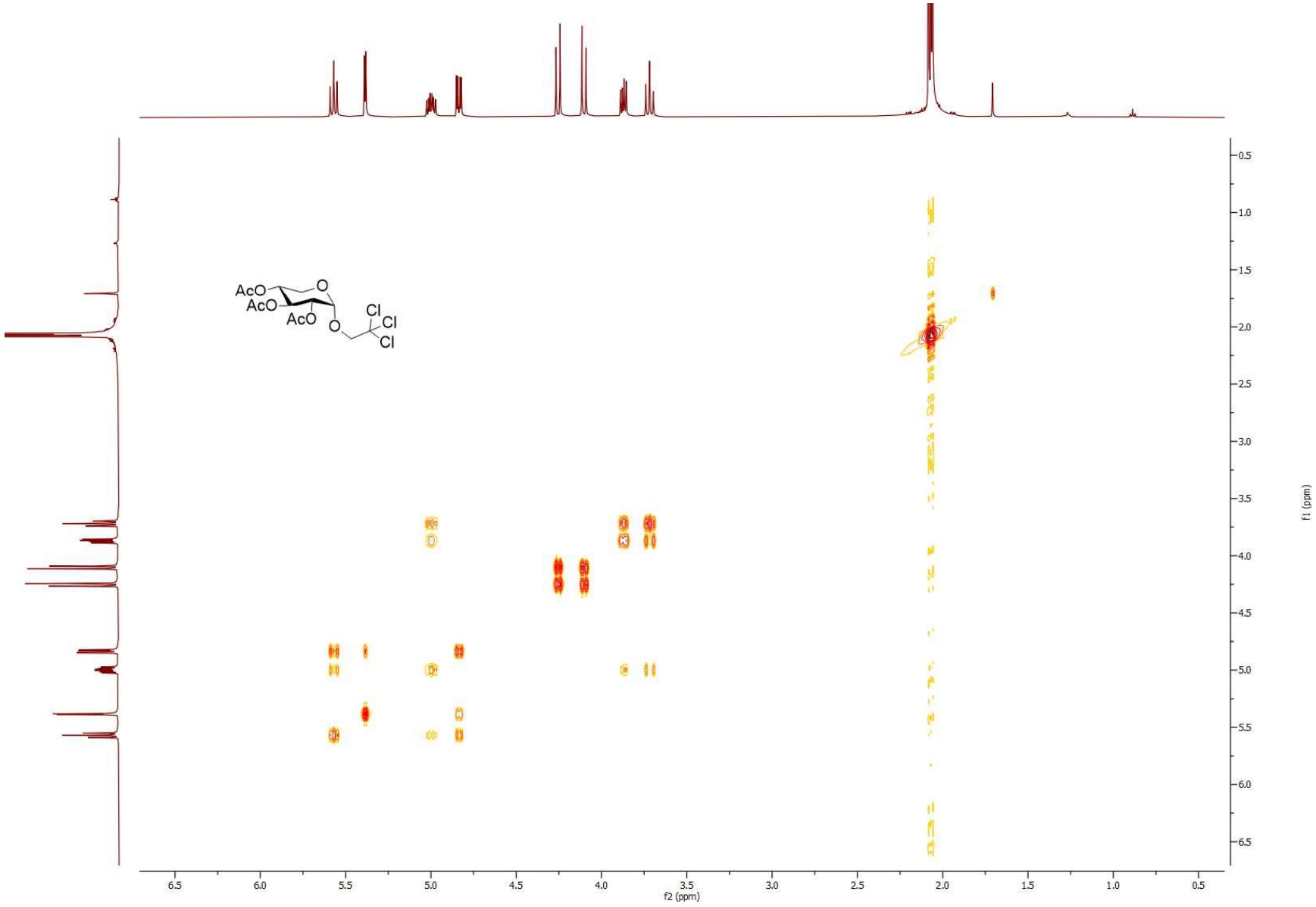
^{1}H NMR (500 MHz, $CDCl_3$)



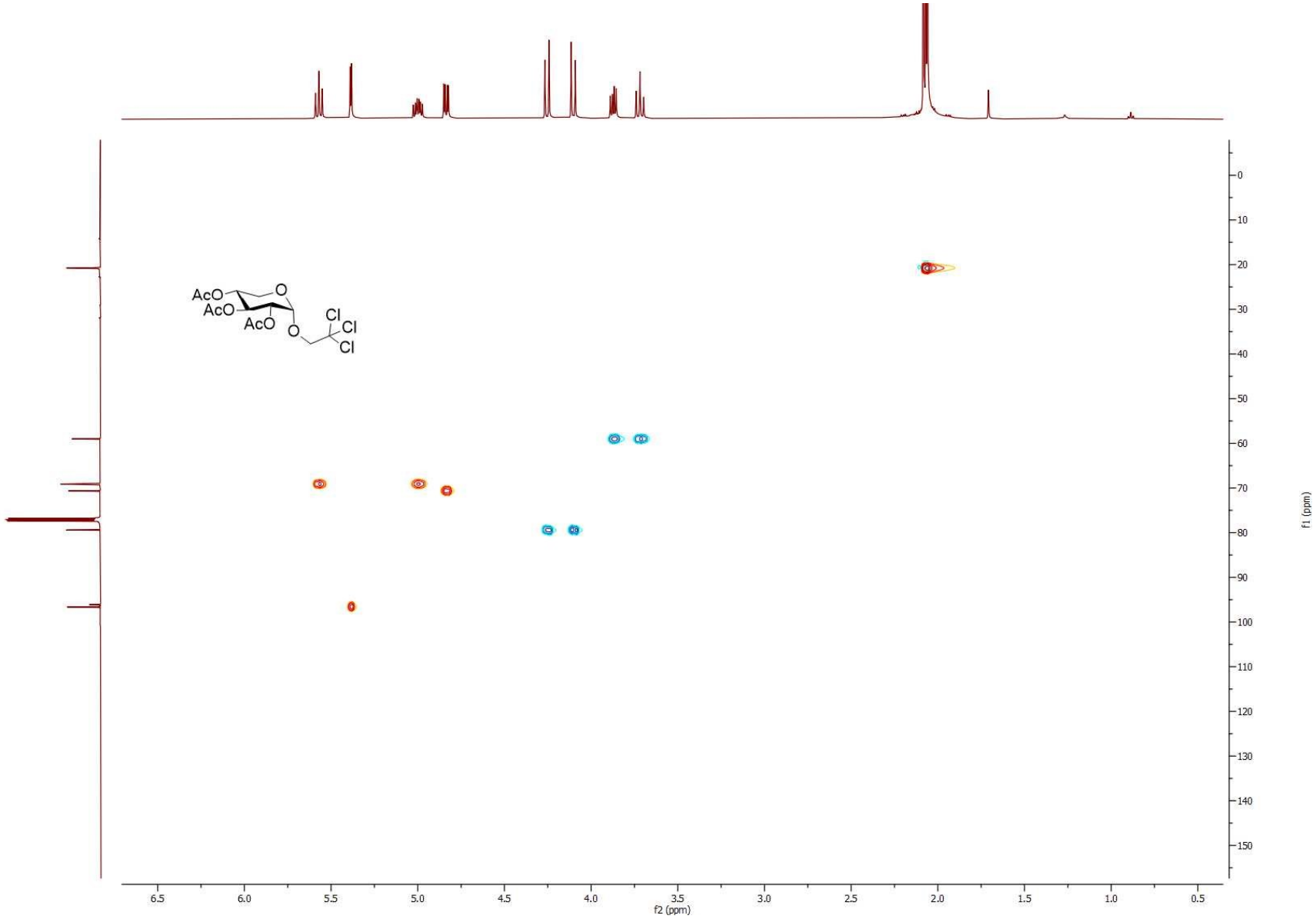
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

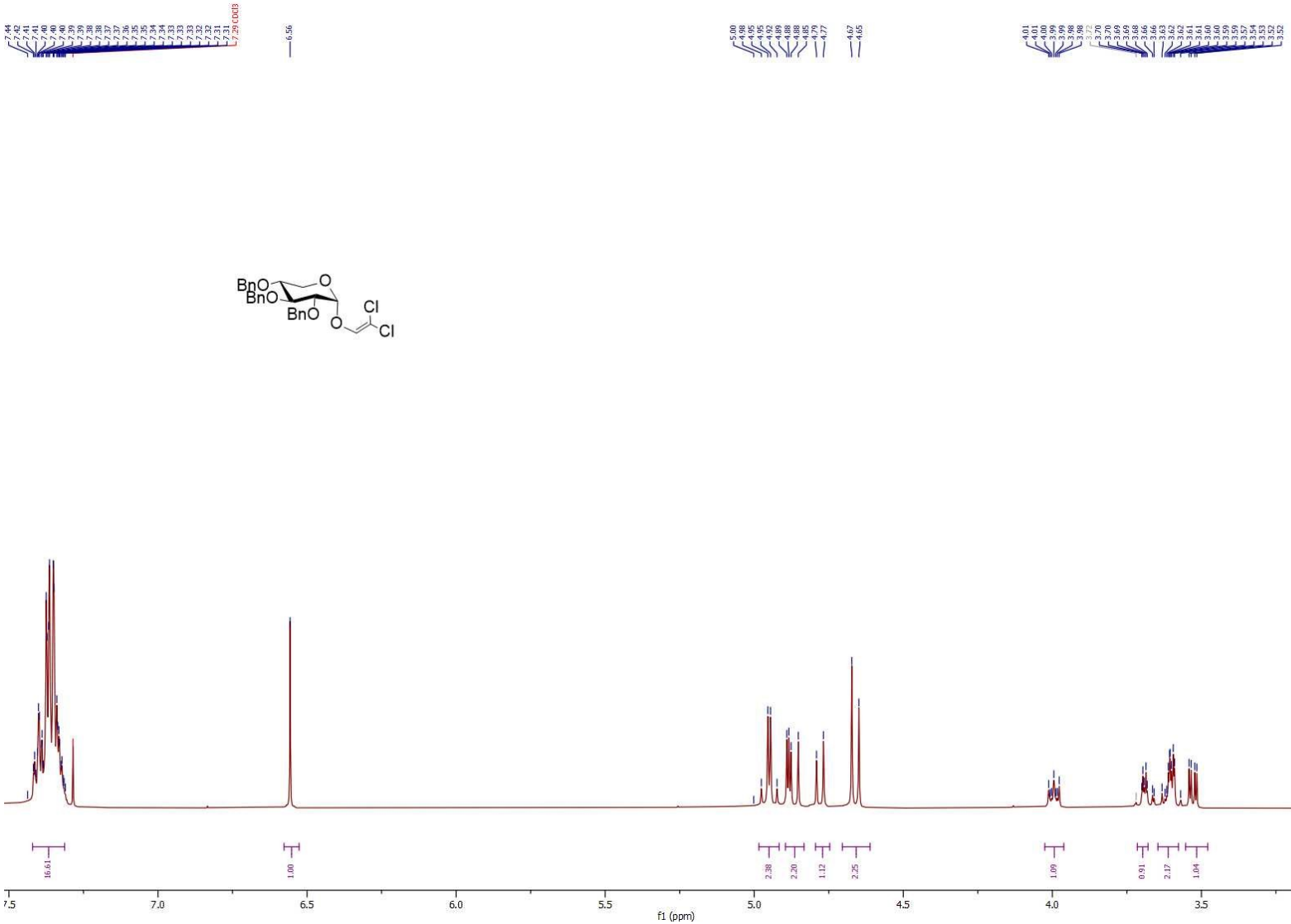


HSQC NMR

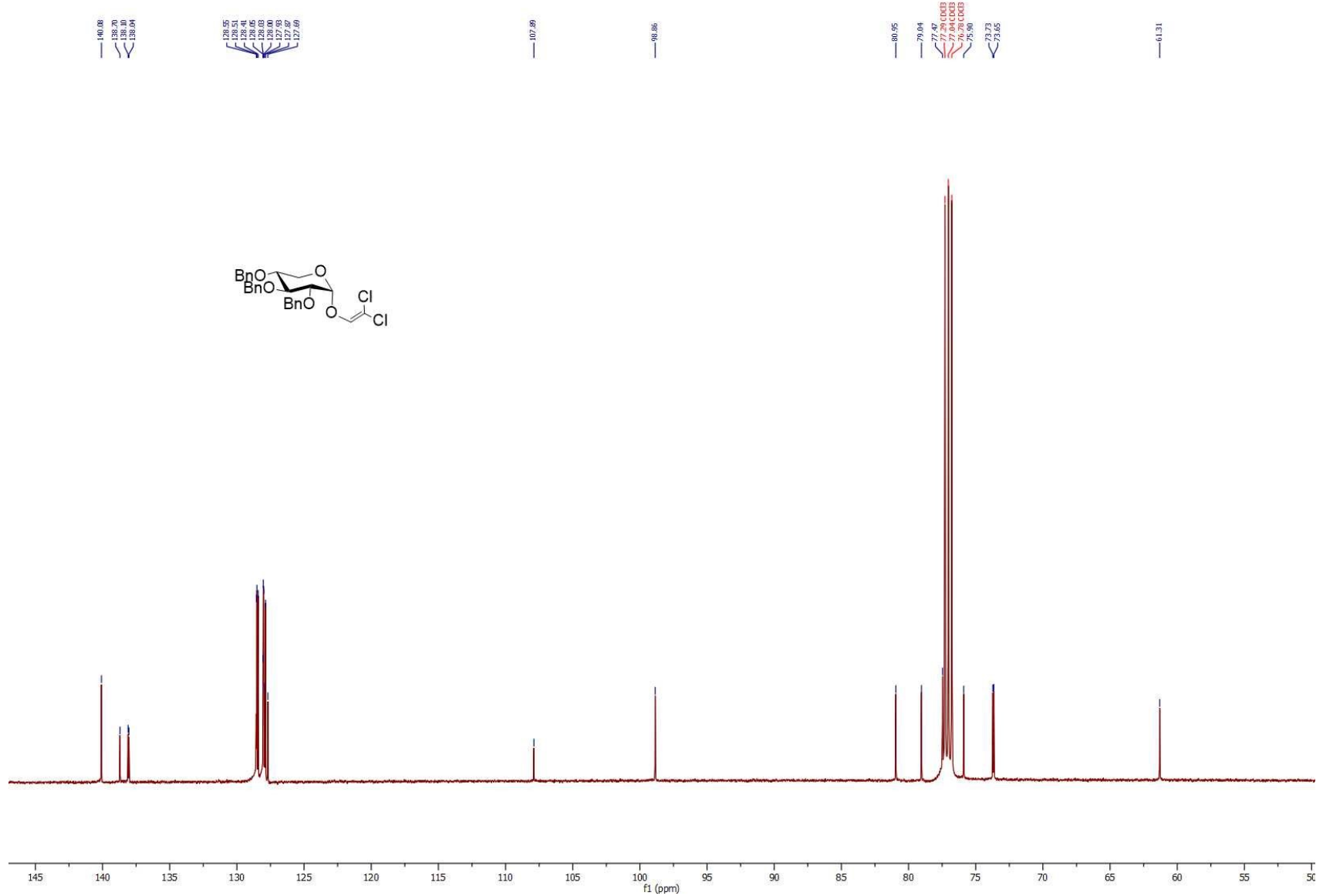

AcO
AcO
AcO
O
O
Cl
Cl
Cl
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

2,2-Dichlorovinyl 2,3,4-tris-O-Benzyl-β-D-xylopyranoside (C3)

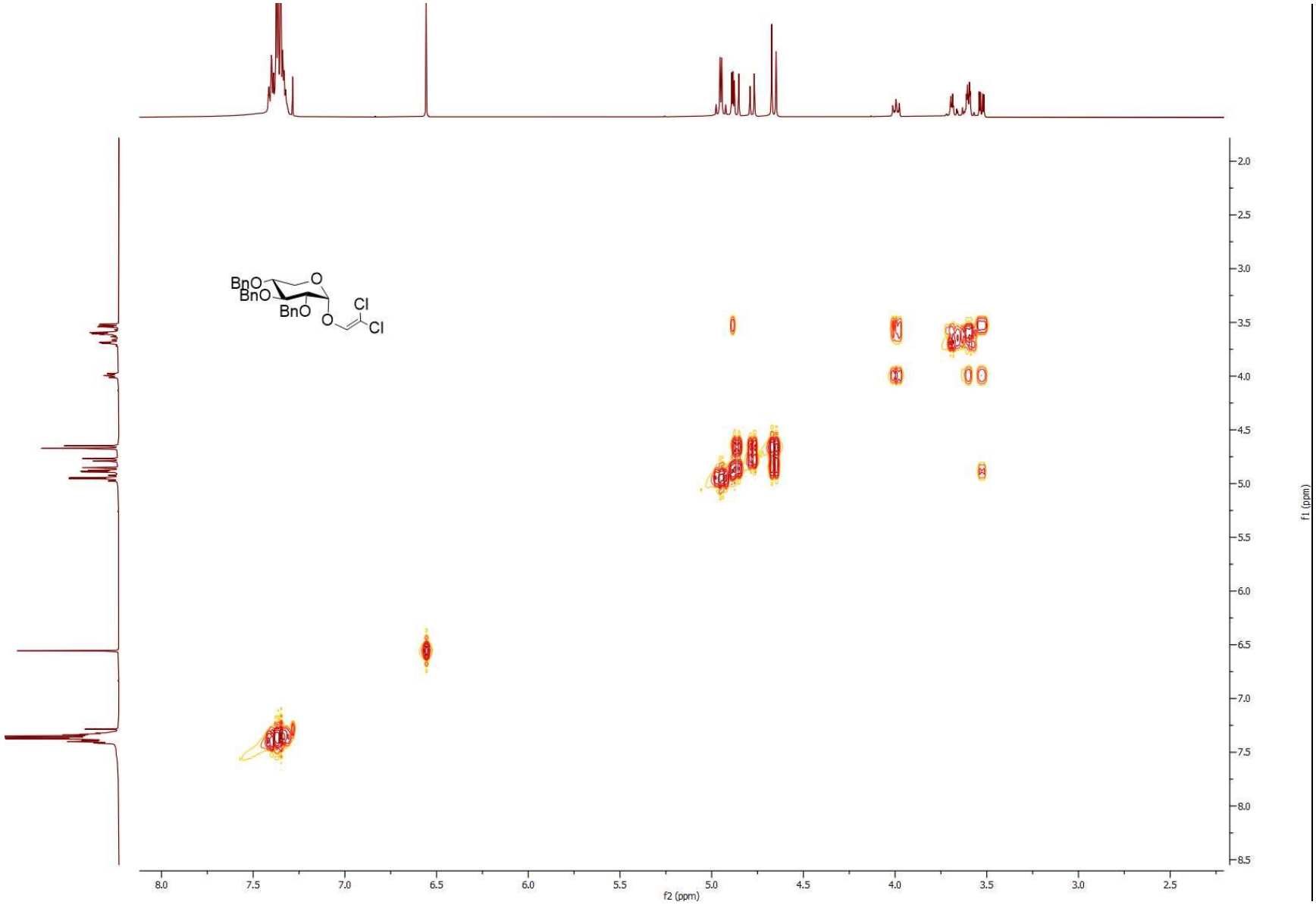
^{1}H NMR (500 MHz, $CDCl_3$)



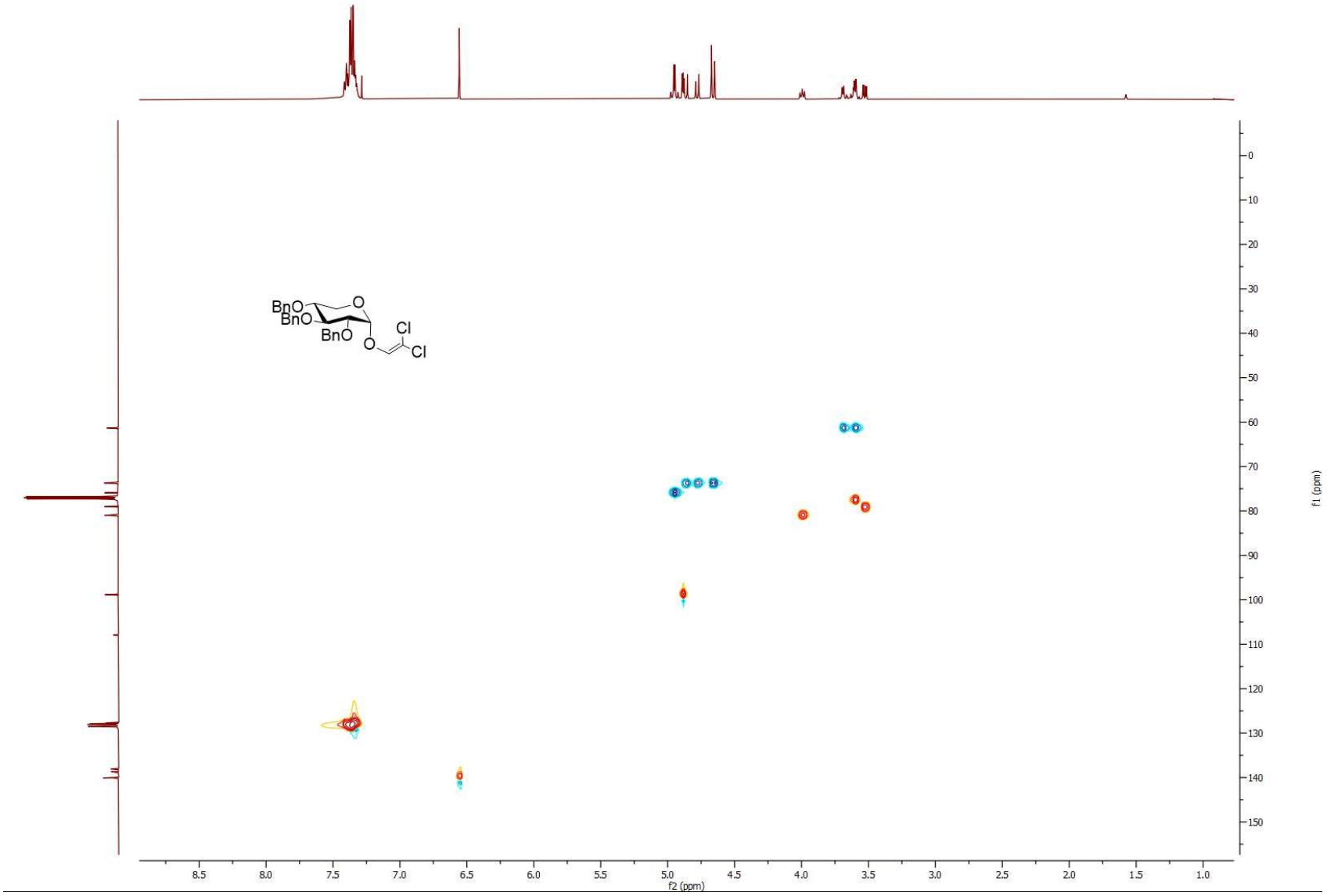
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

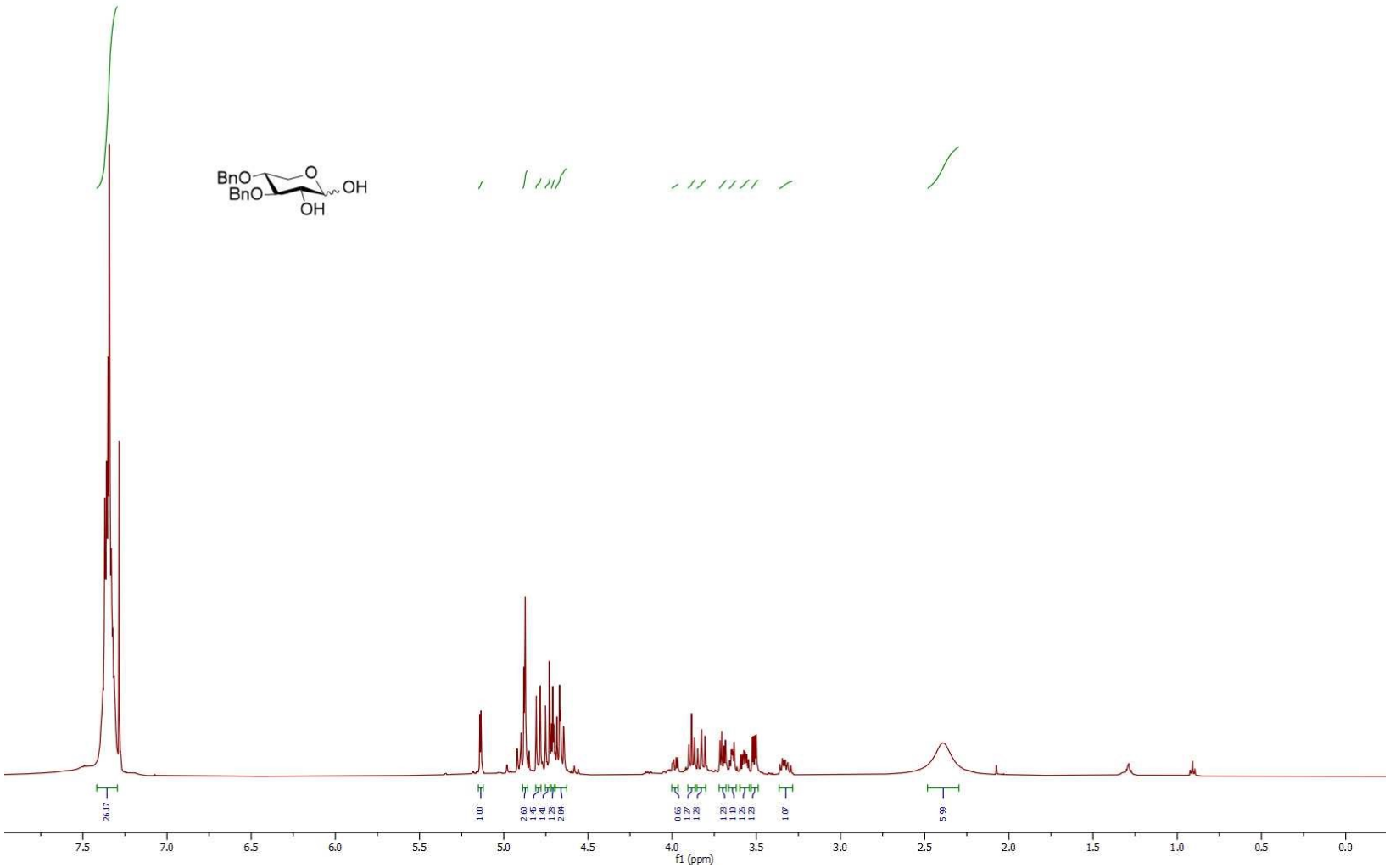

BnO
BnO
BnO
O
O
Cl
Cl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
f1 (ppm)

HSQC NMR

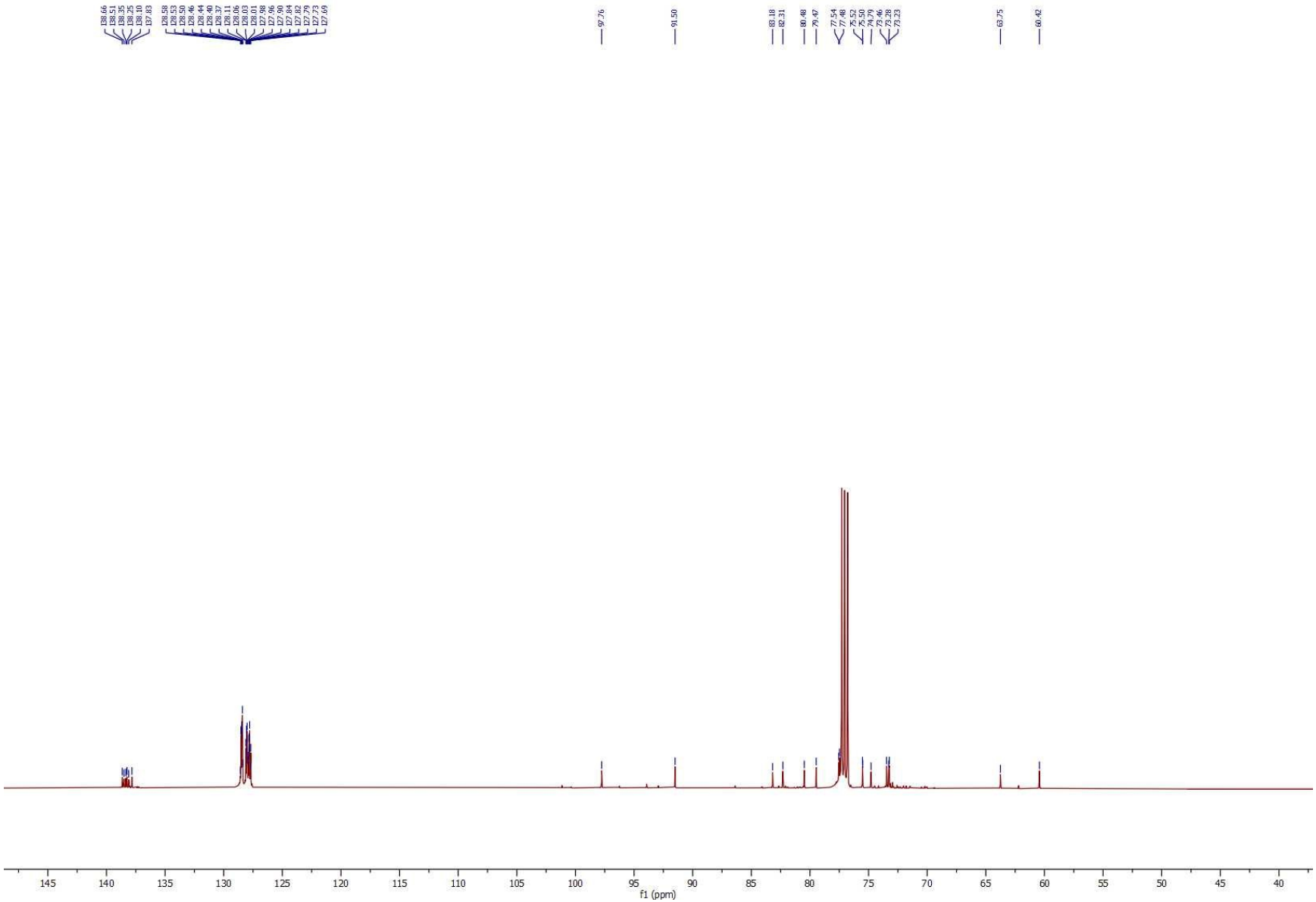


3,4-di-O-Benzyl-D-xylopyranose(C5)

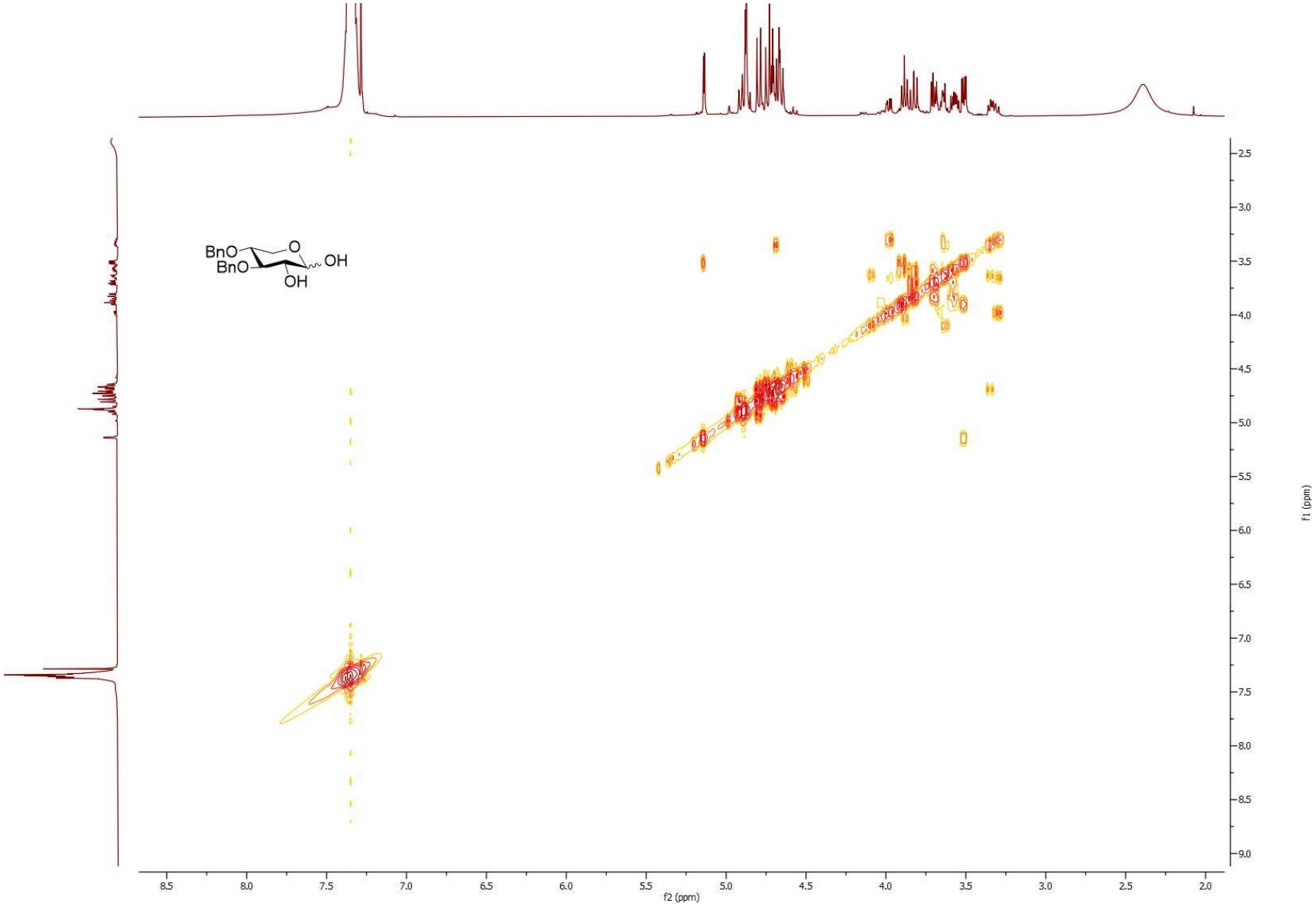
^{1}H NMR (500 MHz, $CDCl_3$)



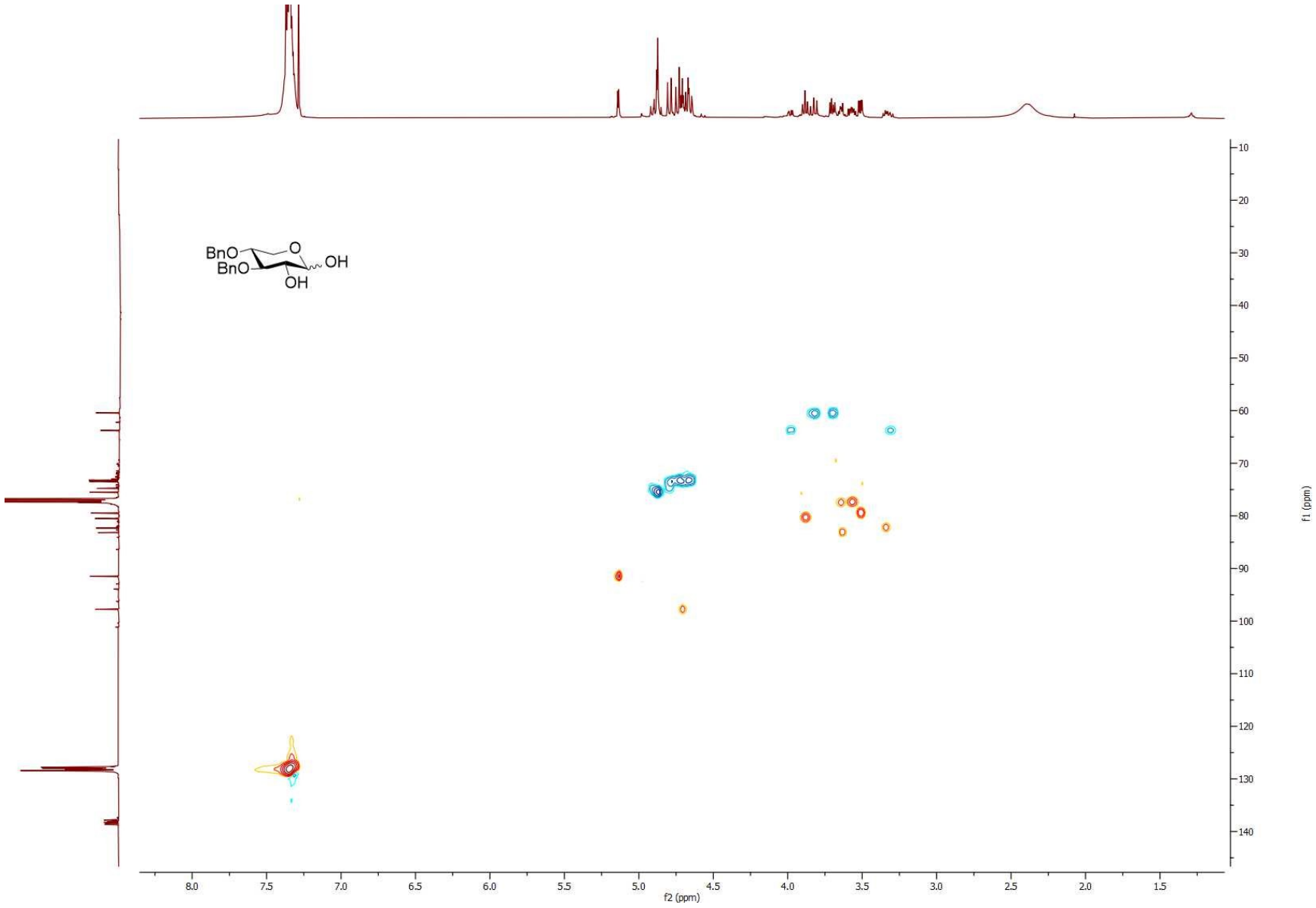
^{13}C NMR (126 MHz, $CDCl_3$)



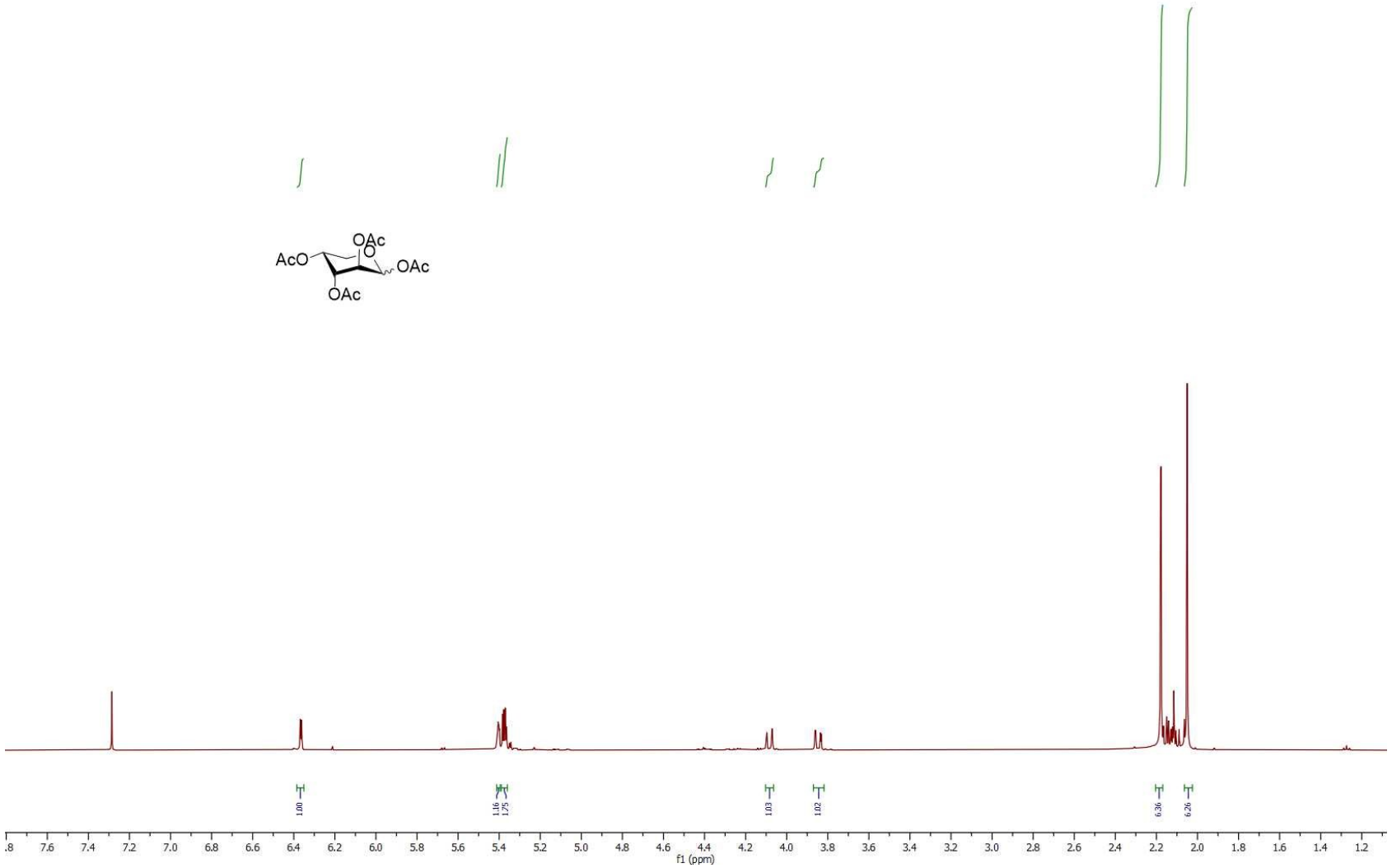
H-H COSY NMR


BnO
BnO
O
OH
OH
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
f1 (ppm)

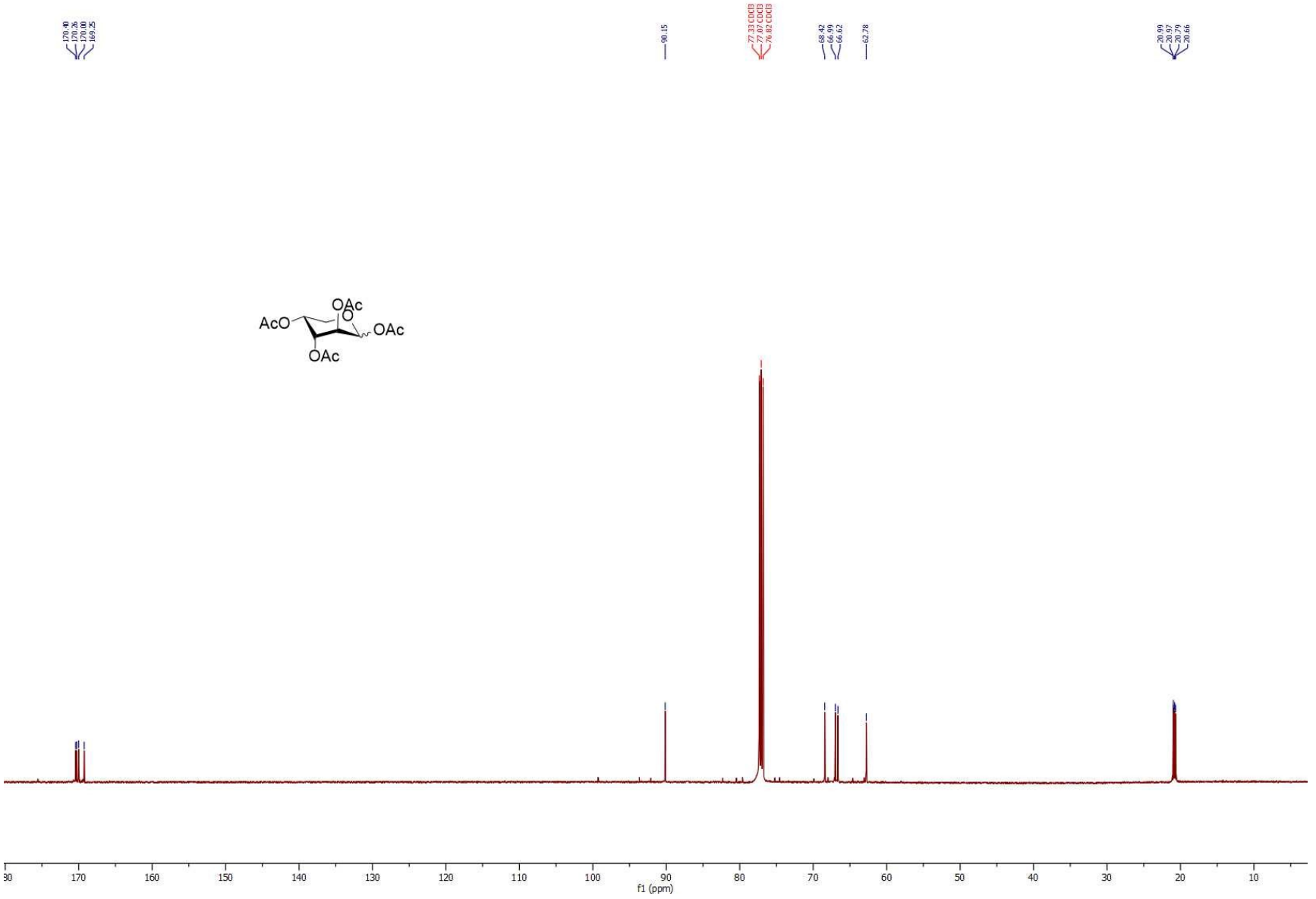
HSQC NMR



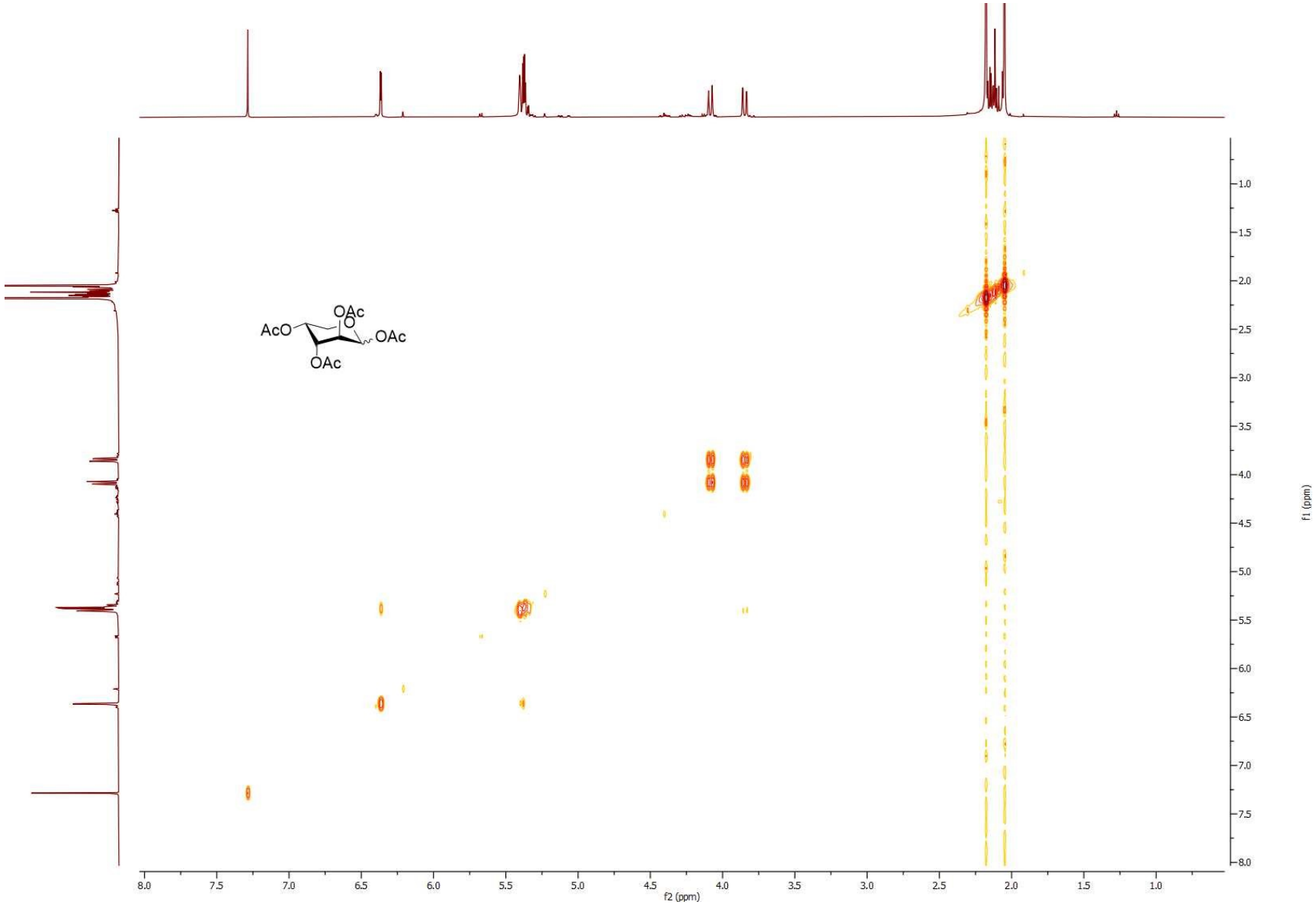
1,2,3,4-Tetra-O-Acetyl-D-Arabinopyranose S5
^{1}H NMR (500 MHz, $CDCl_3$)



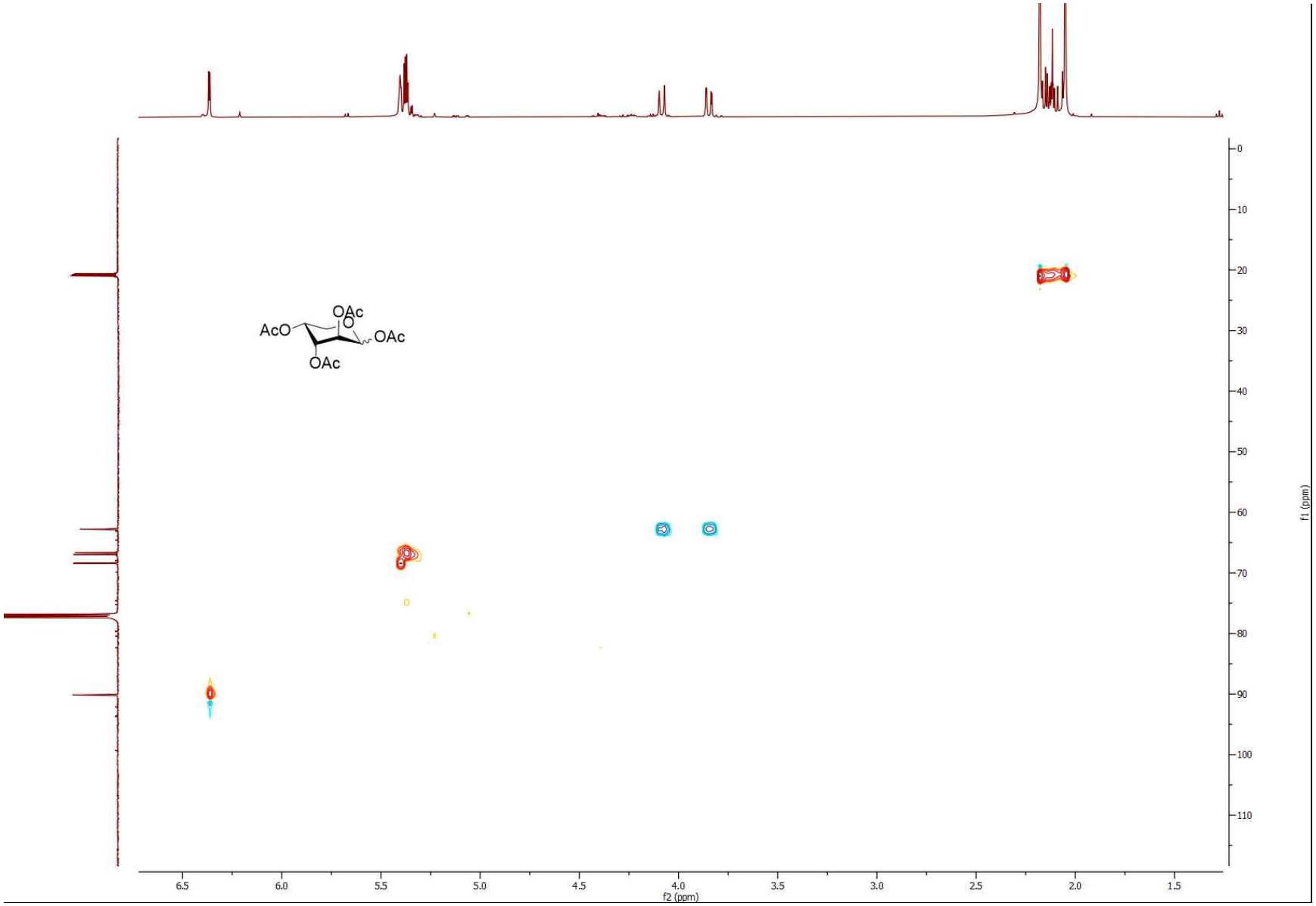
^{13}C NMR (126 MHz, $CDCl_3$)



COSY NMR

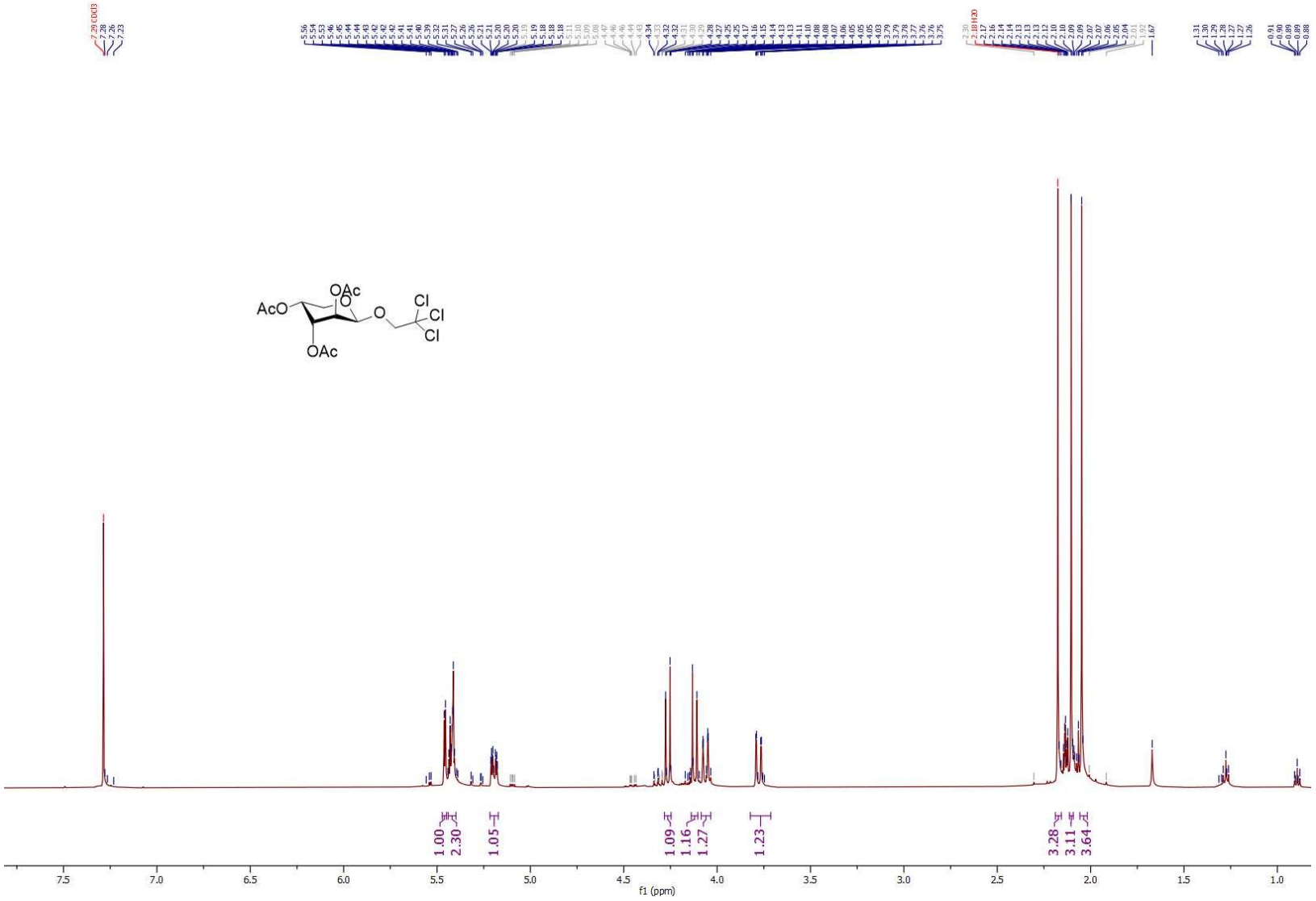

OAc
AcO
O
OAc
OAc
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

HSQC NMR

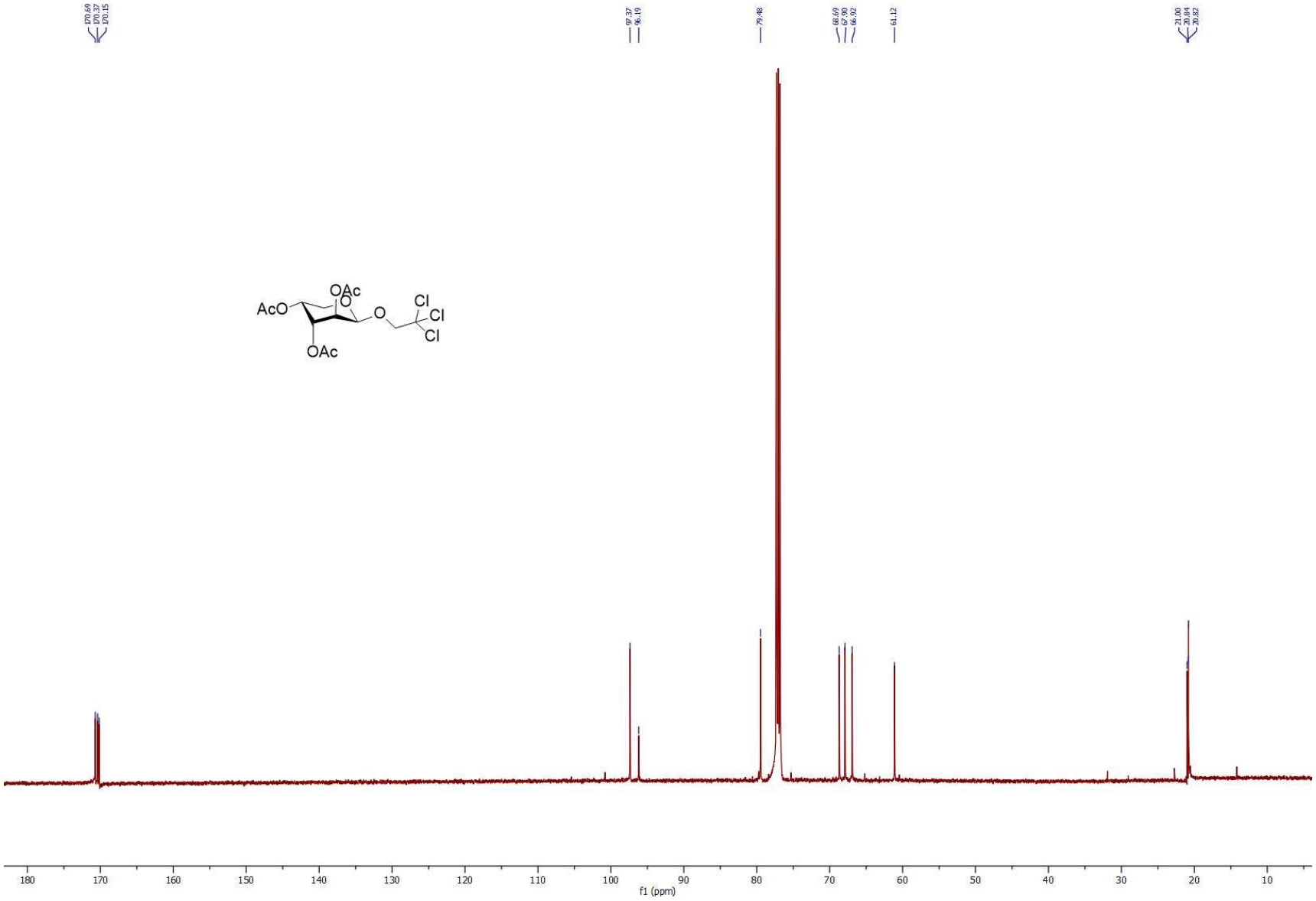

OAc
AcO
O
OAc
OAc
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
f1 (ppm)

2,2,2-trichloroethyl 2,3,4-tris-O-Acetyl-D-Arabinopyranoside S6

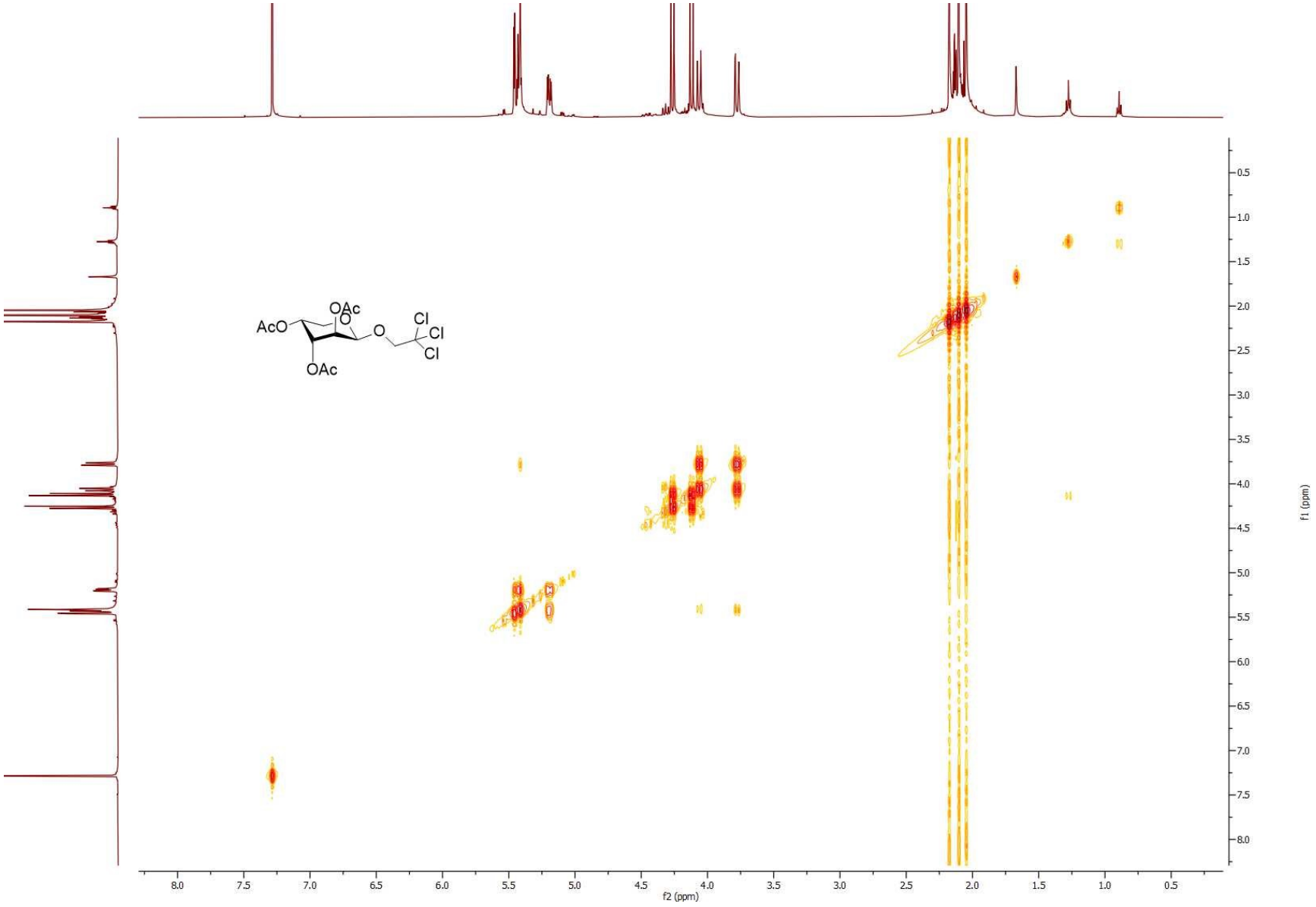
^{1}H NMR (500 MHz, $CDCl_3$)



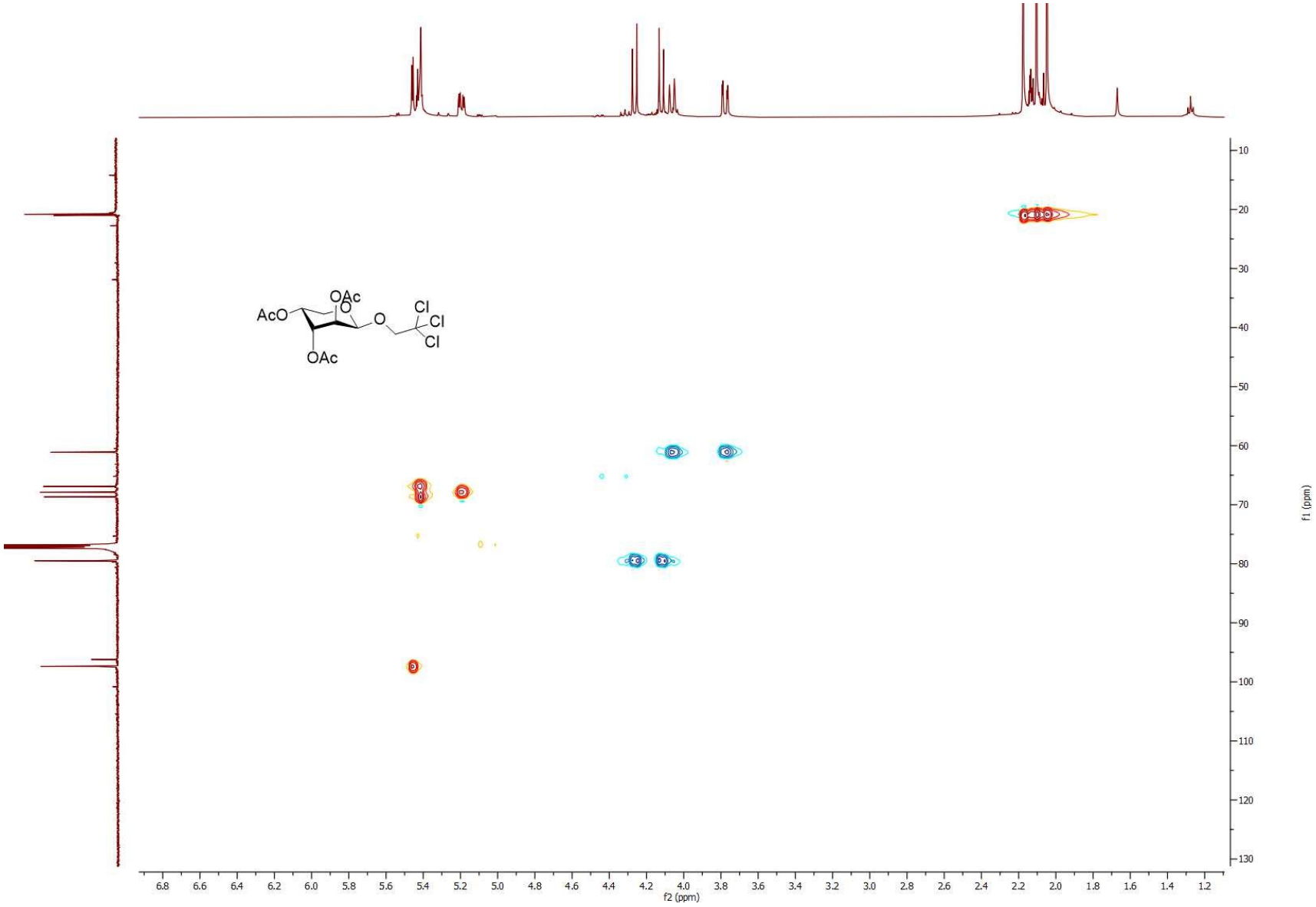
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

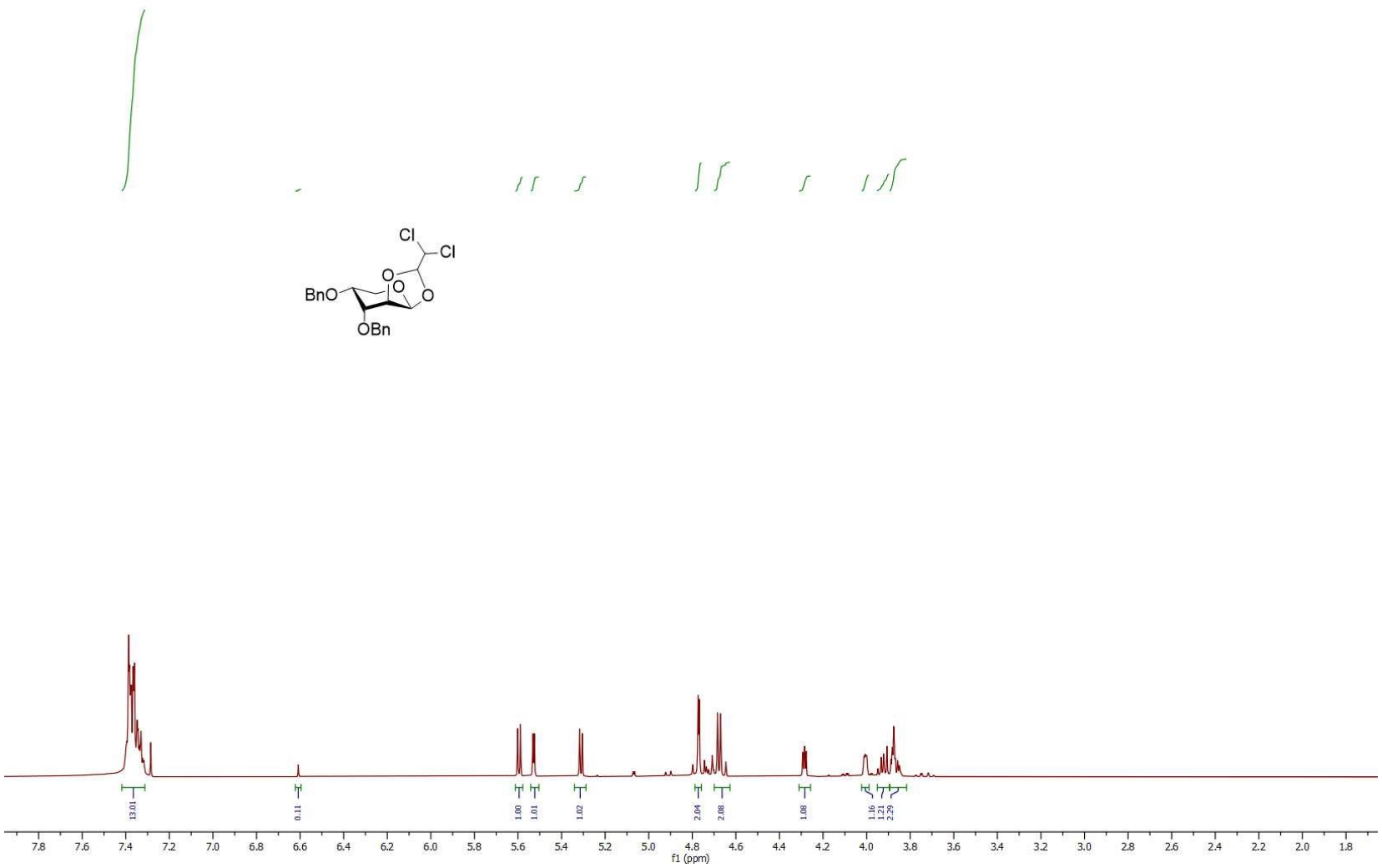


HSQC NMR

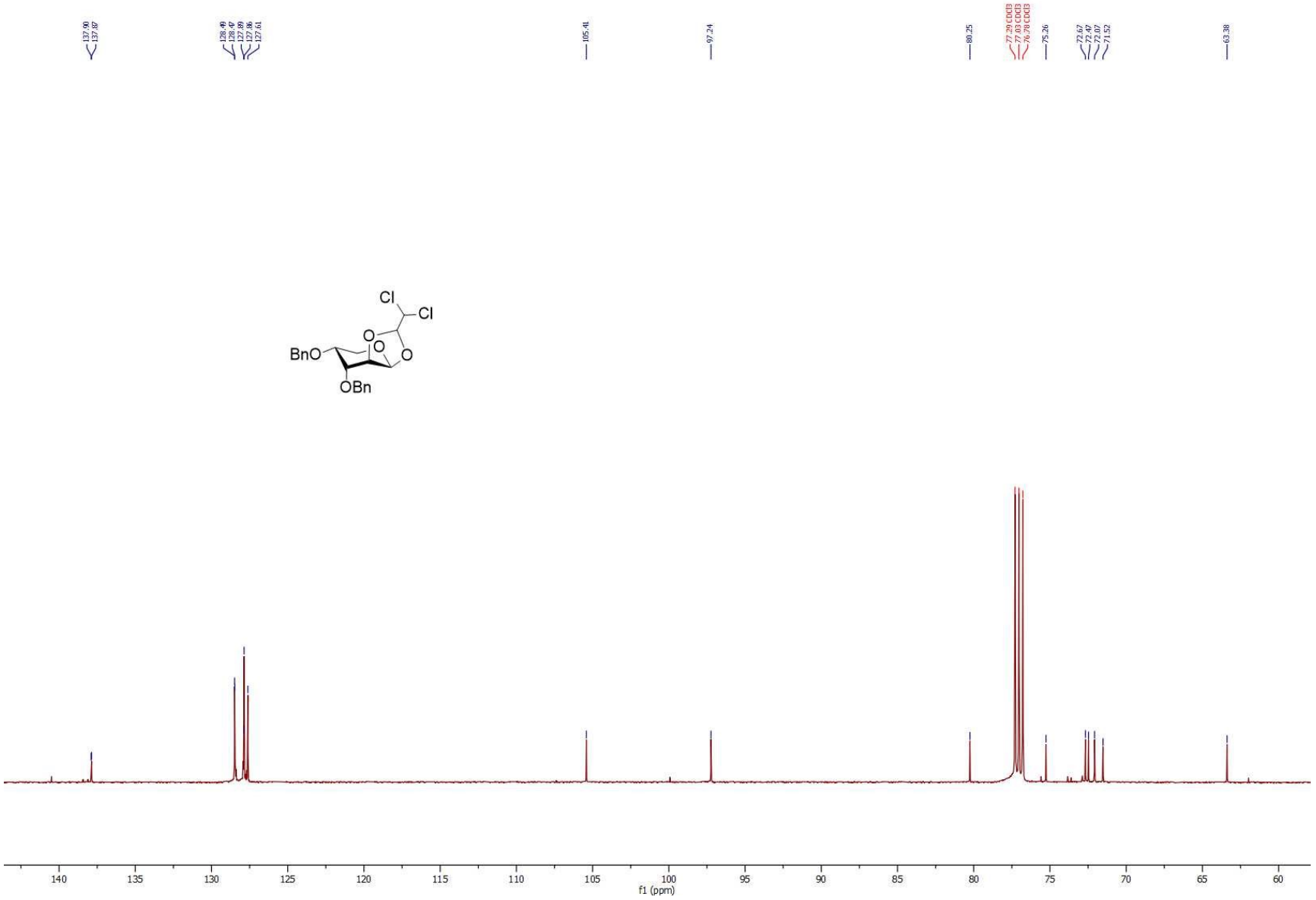


Product (2,2-dichloroethyl 3,4-di-*O*-Benzyl-D-Arabinopyranoside) (E4)

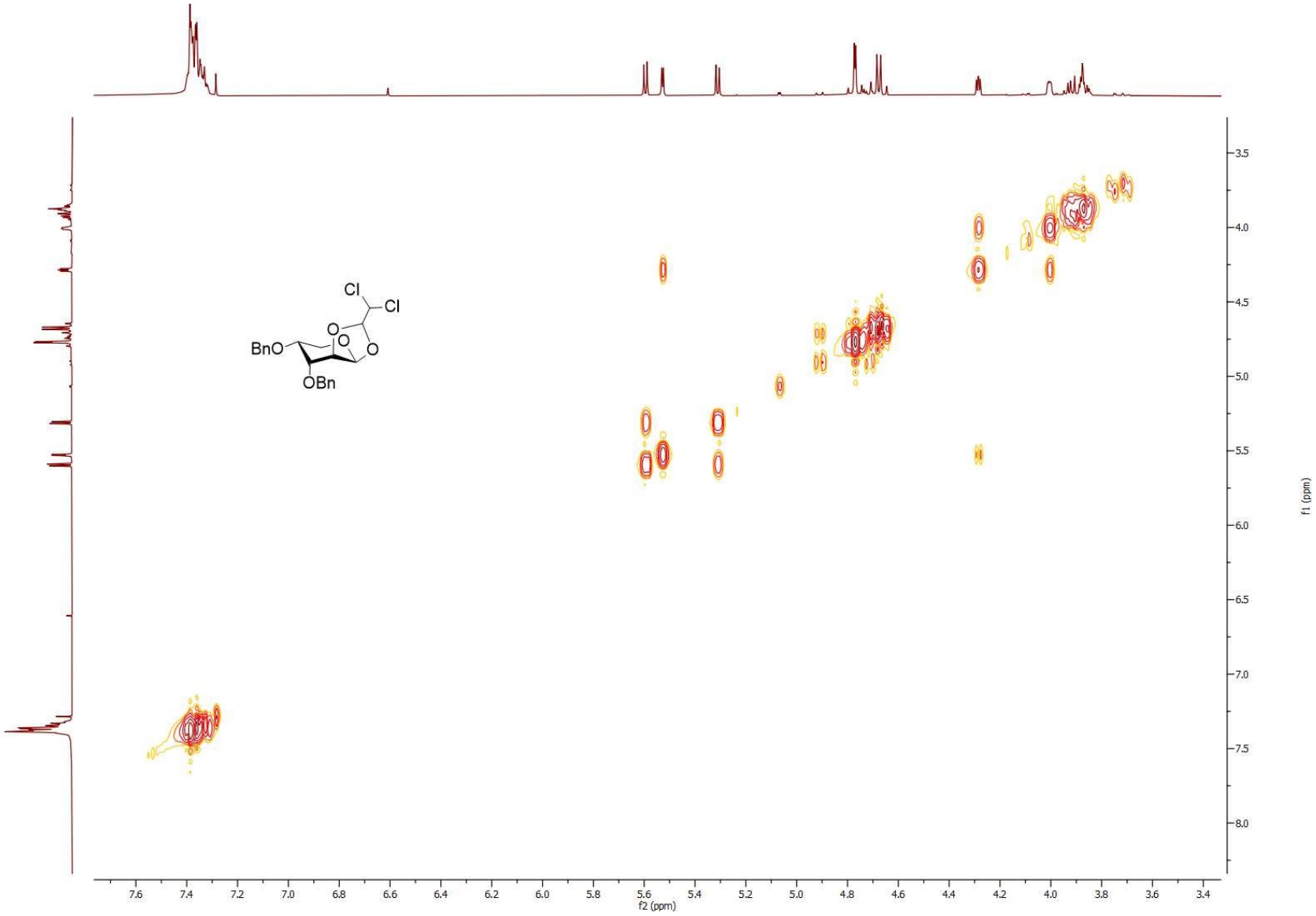
^{1}H NMR (500 MHz, $CDCl_3$)



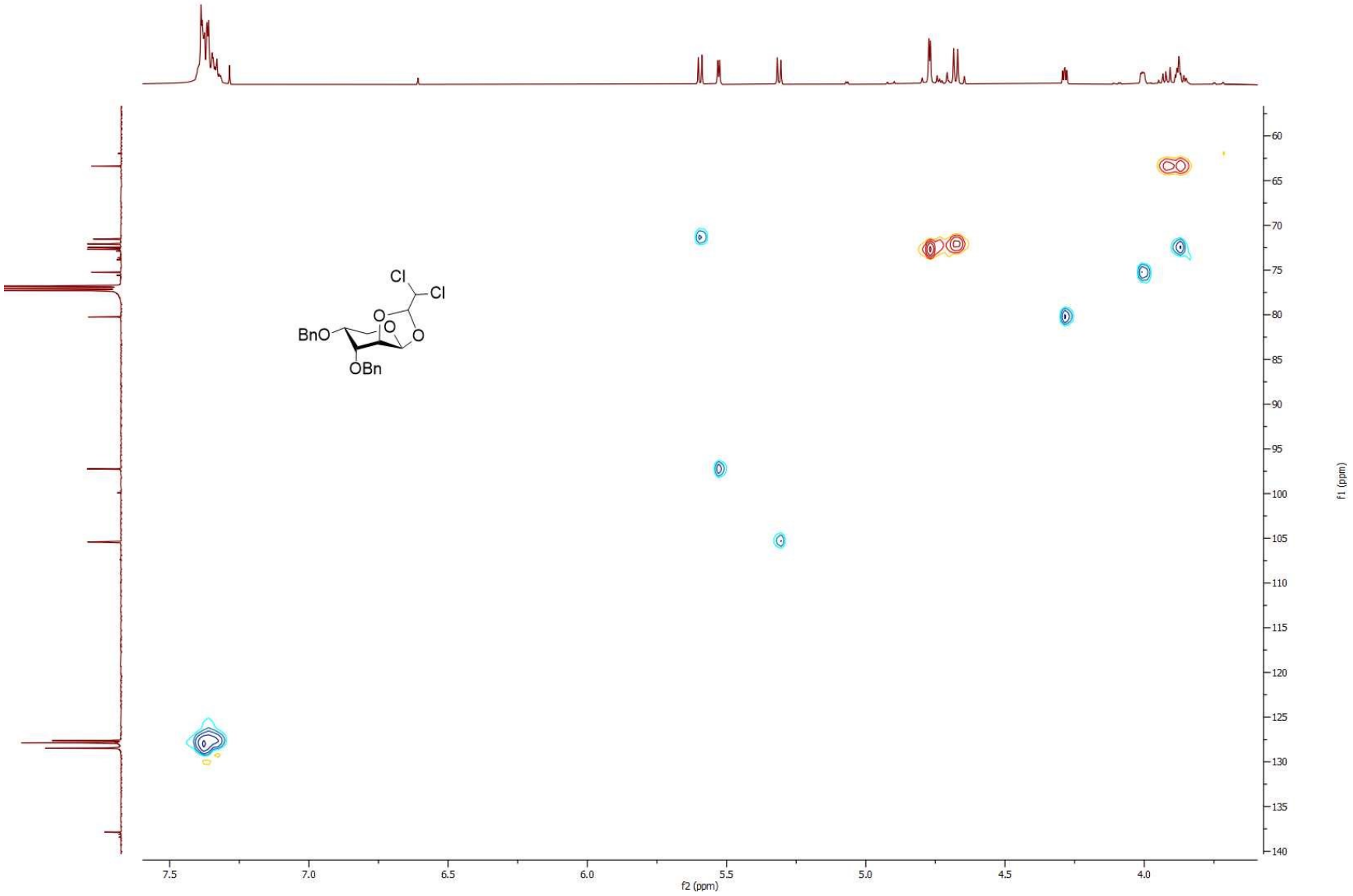
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

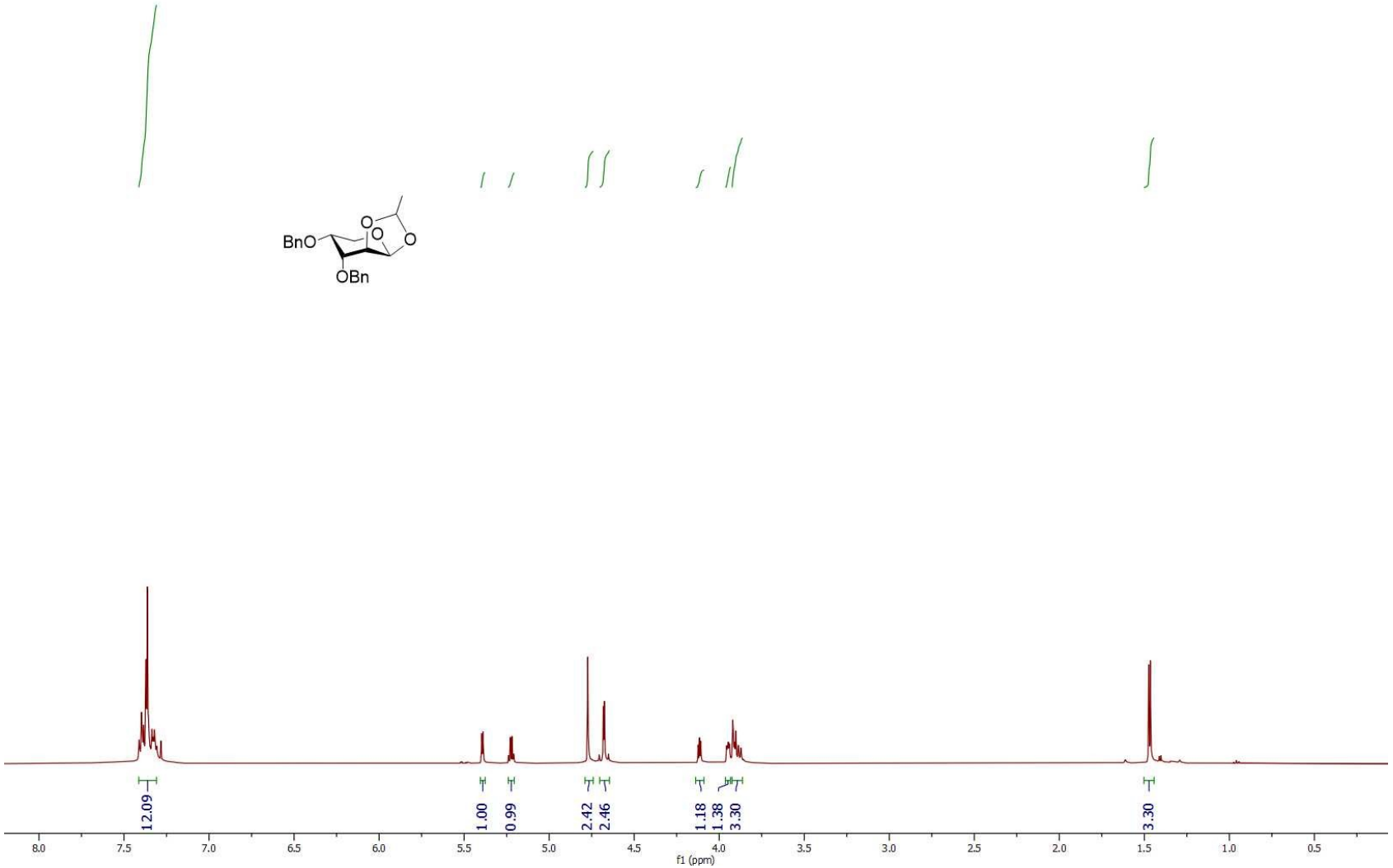

Cl
Cl
O
O
O
BnO
OBn
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
f2 (ppm)
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
f1 (ppm)

HSQC NMR

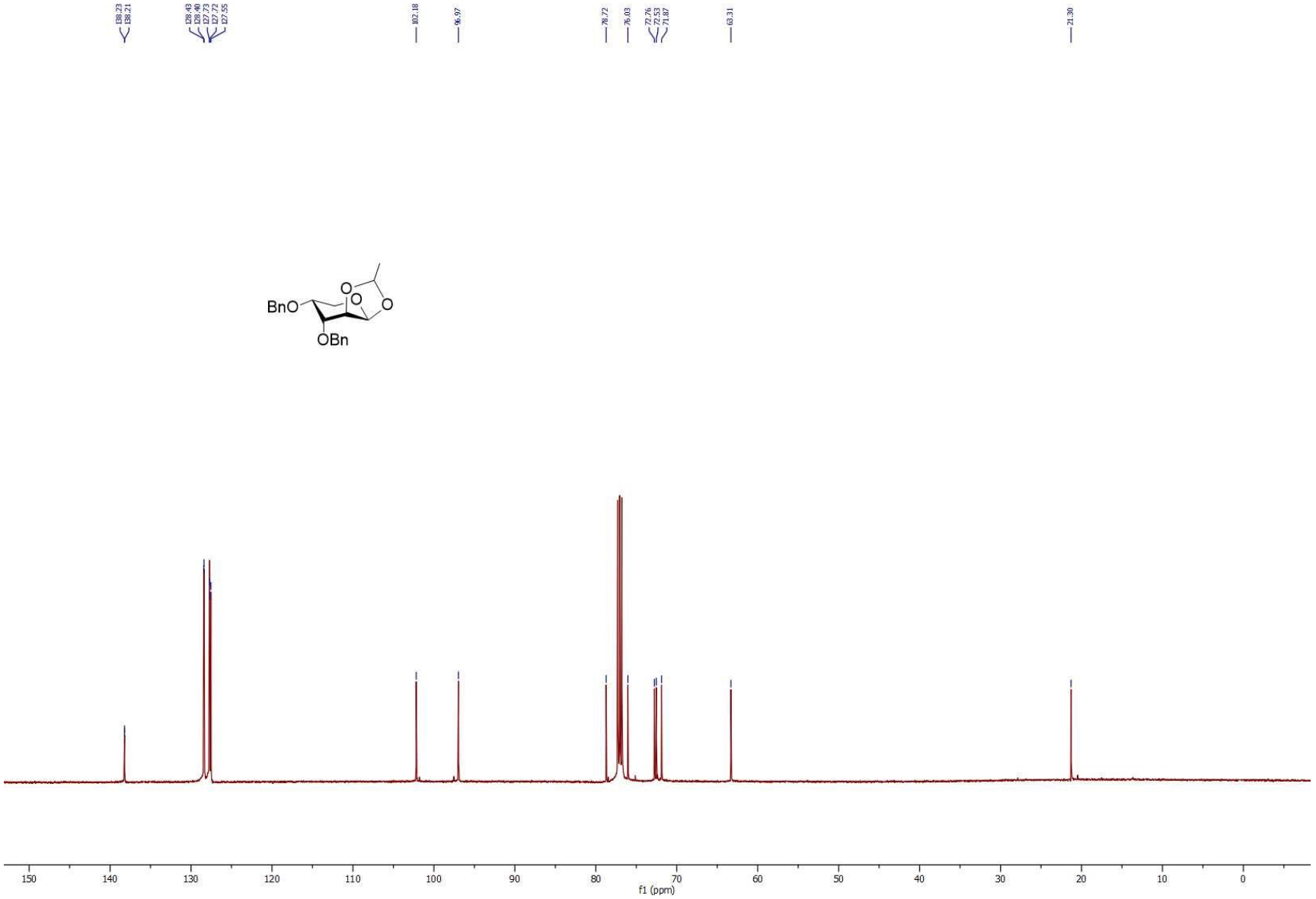

Cl
Cl
O
O
O
BnO
OBn
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f2 (ppm)
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
f1 (ppm)

1,2-O-ethylidene-3,4-di-*O*-Benzyl-D-Arabinopyranoside (E5)

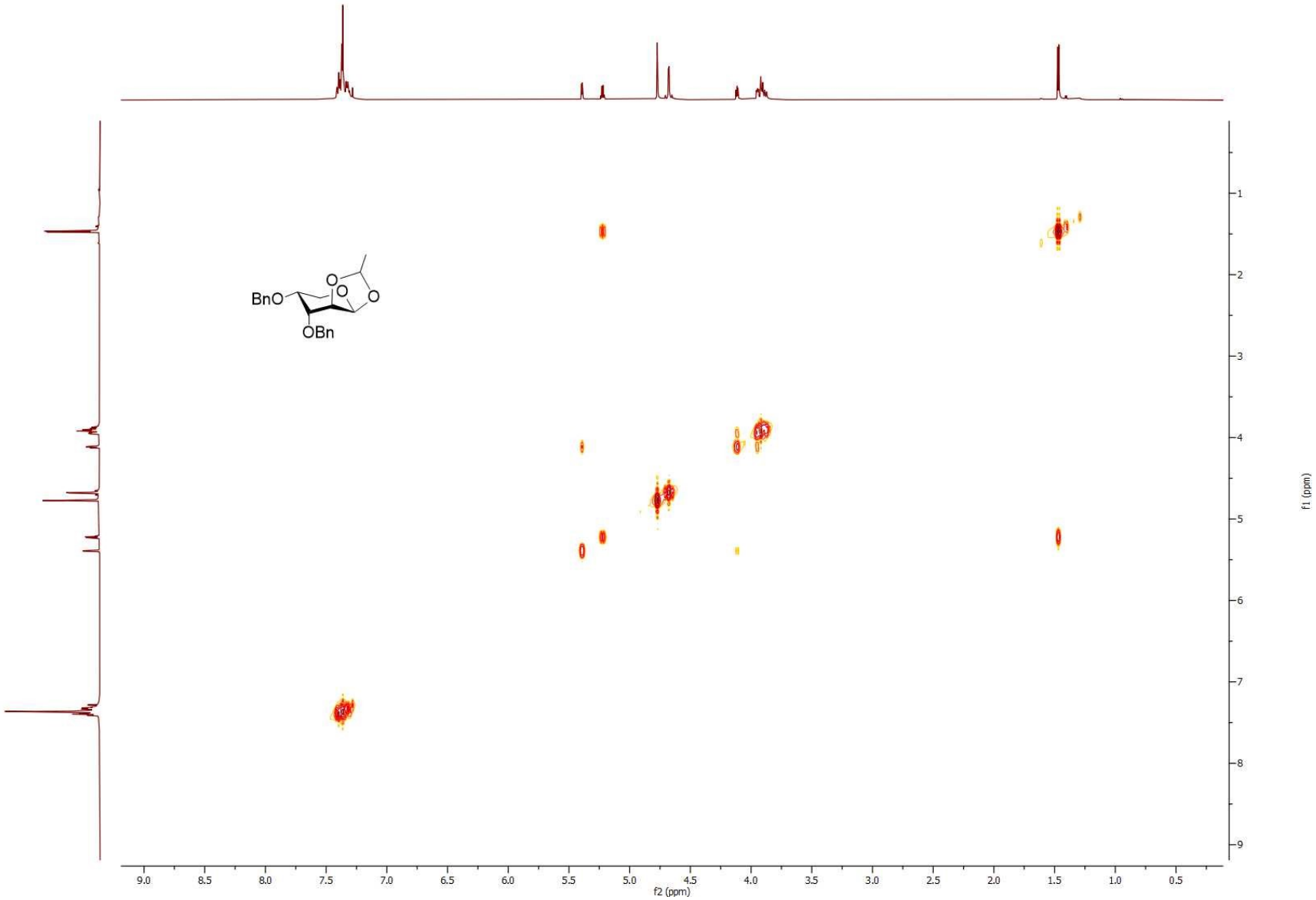
^{1}H NMR (500 MHz, $CDCl_3$)



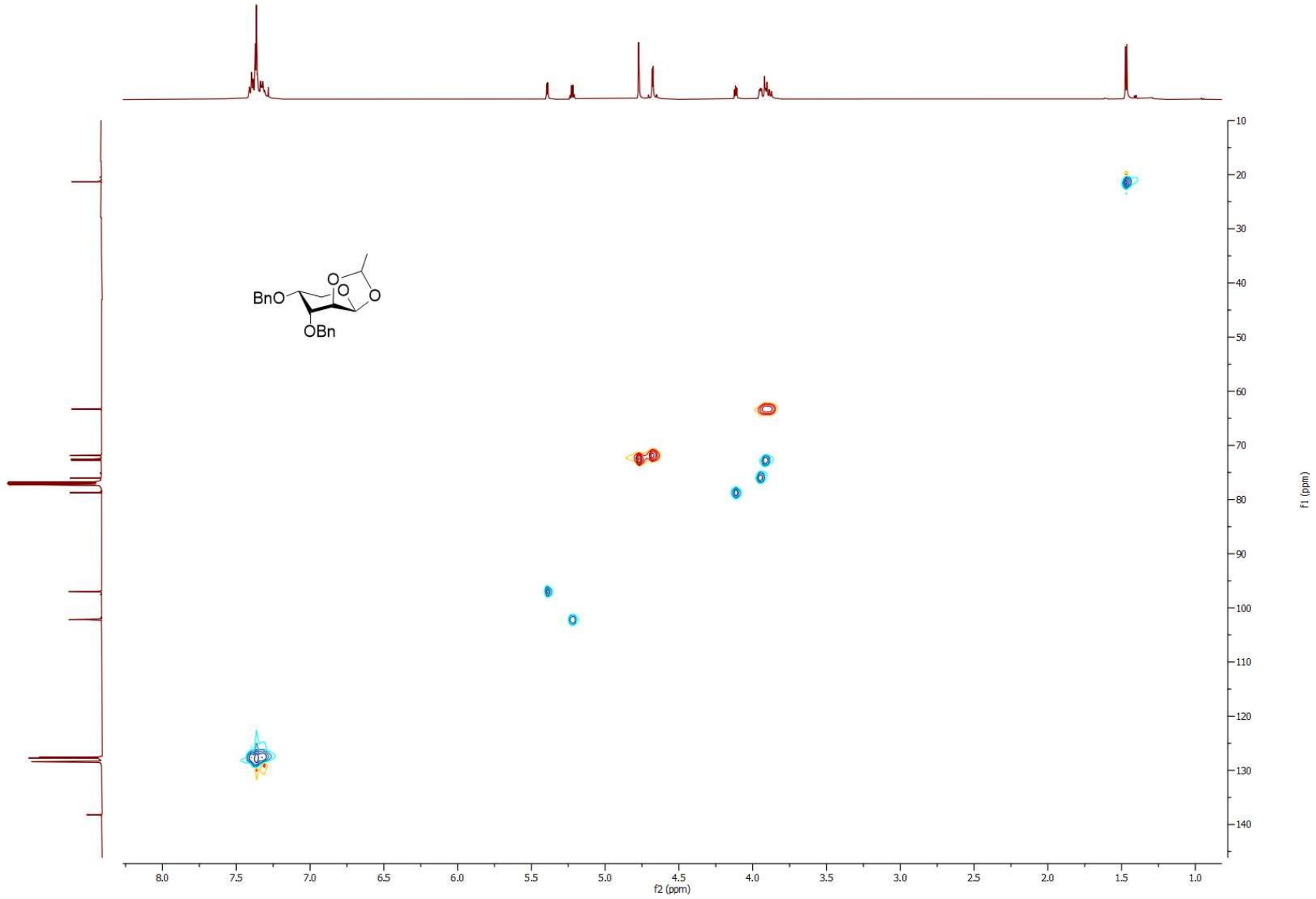
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

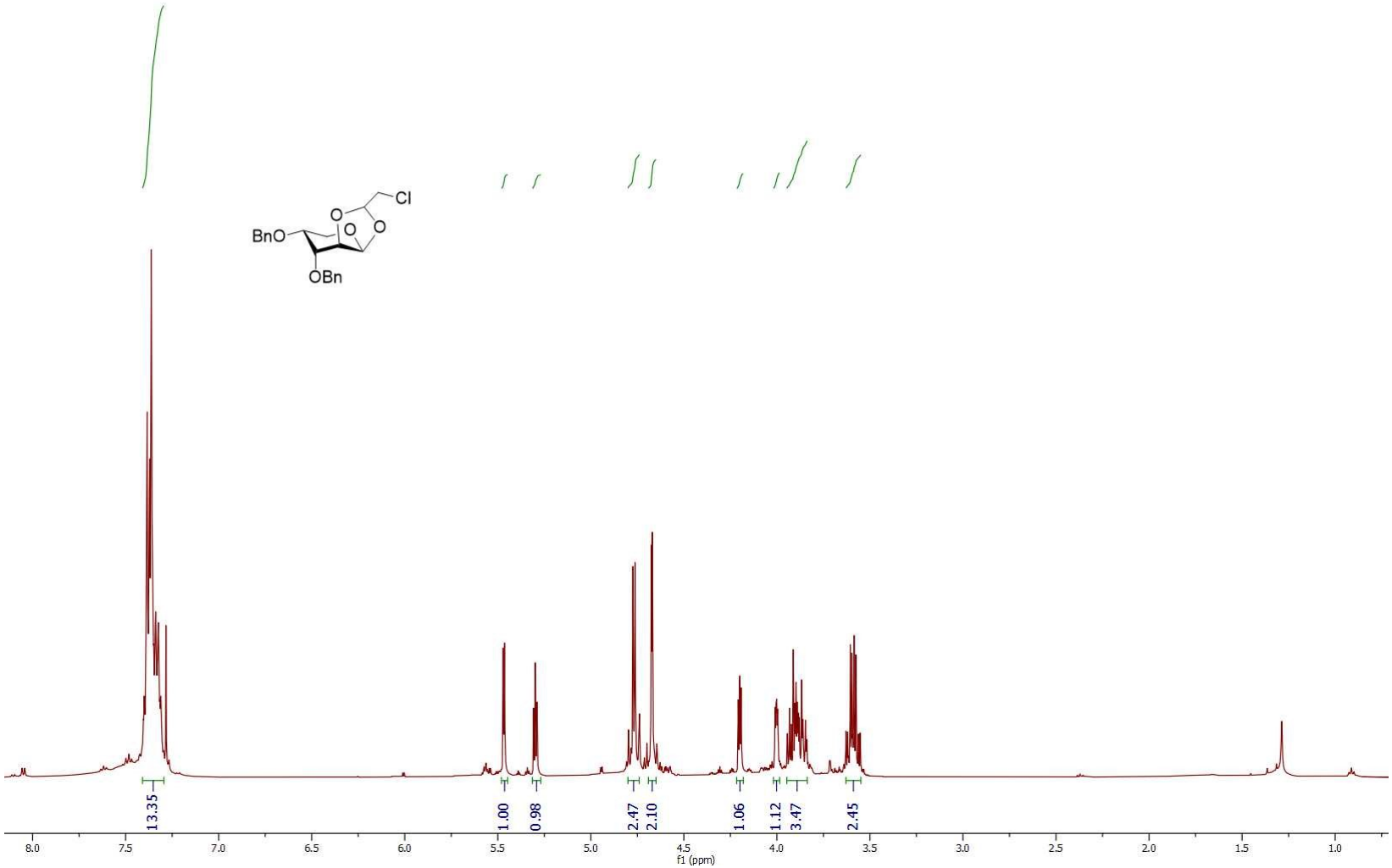

BnO
OBn
O
O
O
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
1
2
3
4
5
6
7
8
9
f1 (ppm)

HSQC NMR

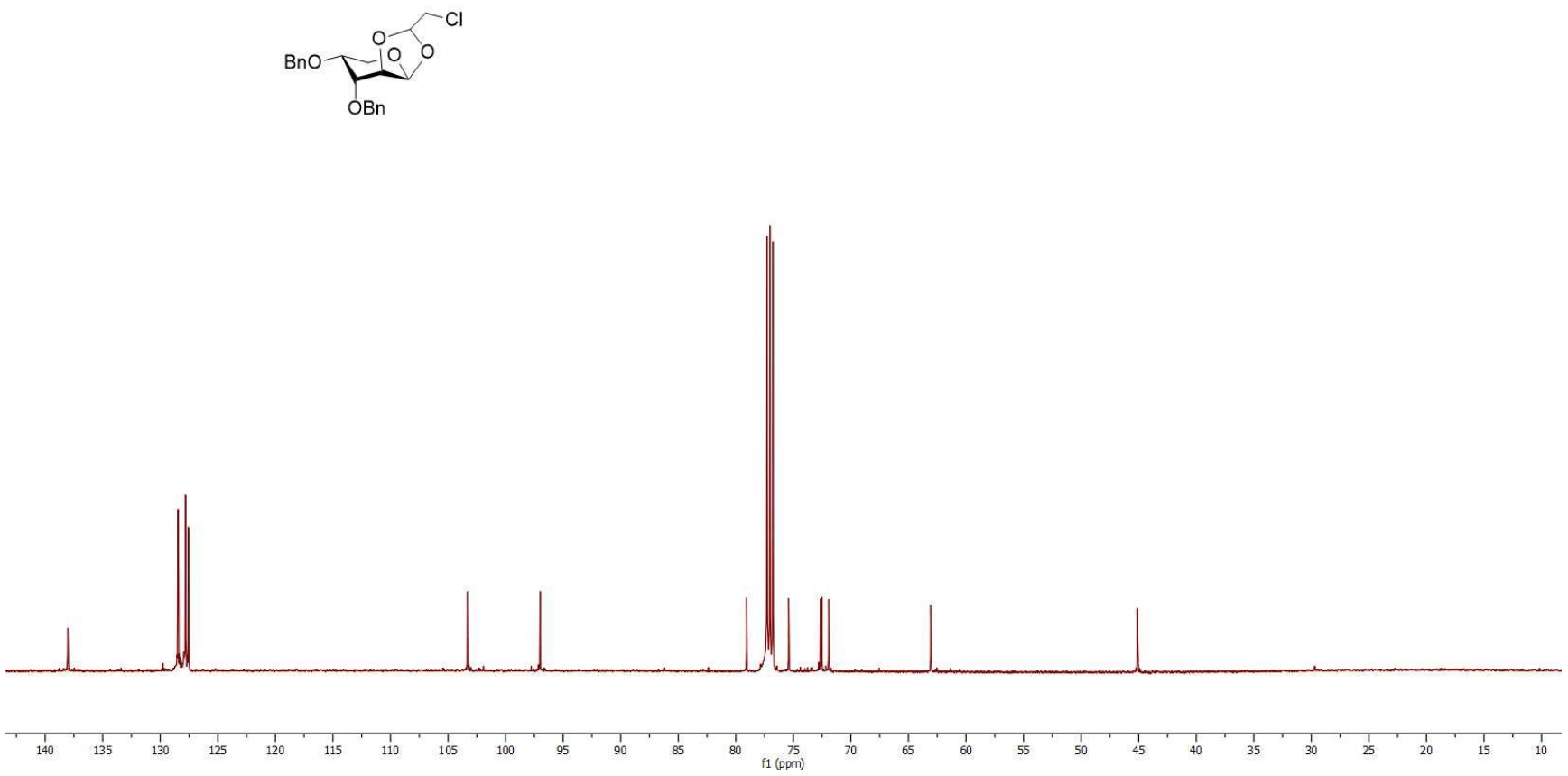


1,2-O-(2-chloro-ethylidene)-3,4-di-*O*-Benzyl-D-Arabinopyranoside(E6)

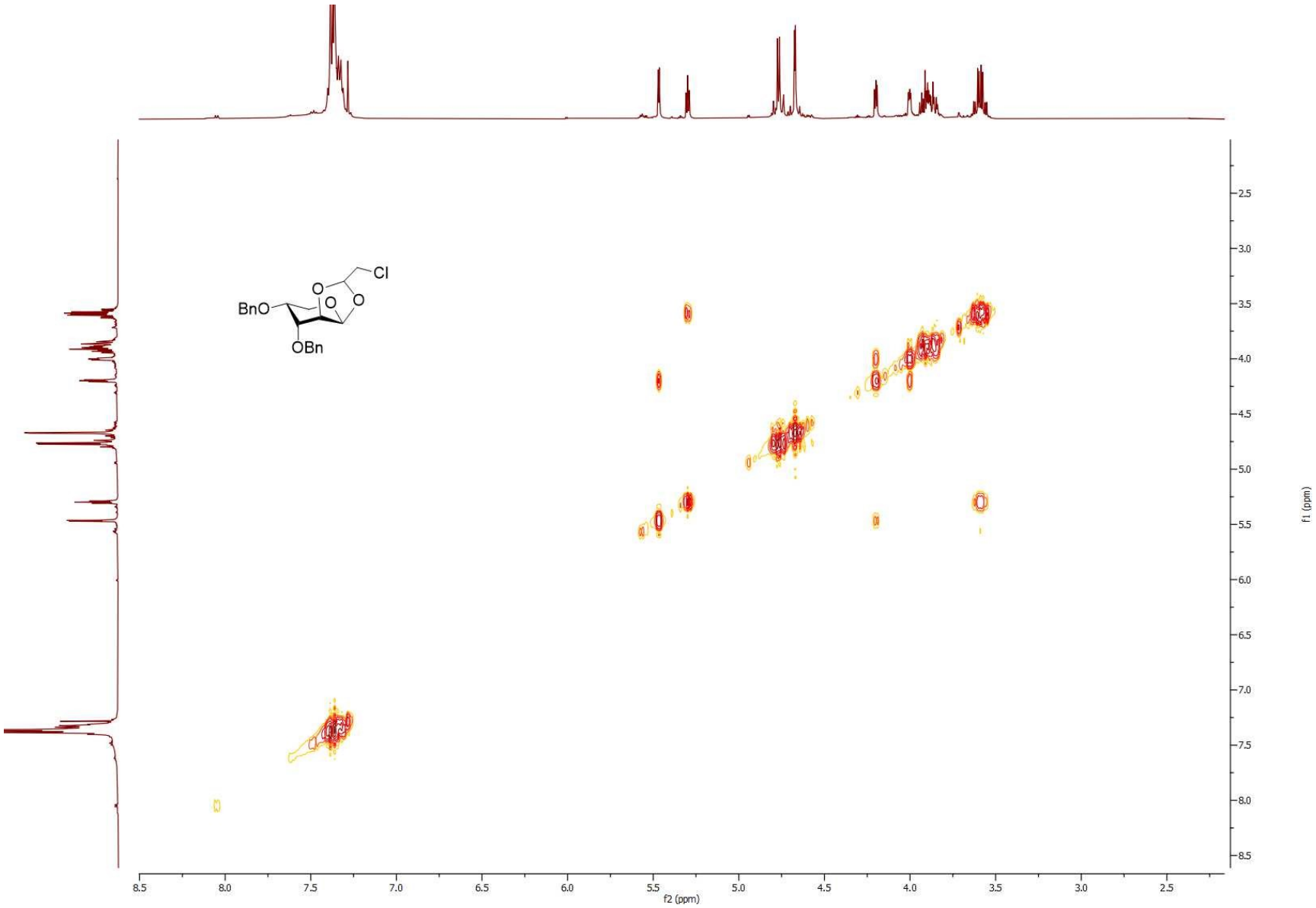
^{1}H NMR (500 MHz, $CDCl_3$)



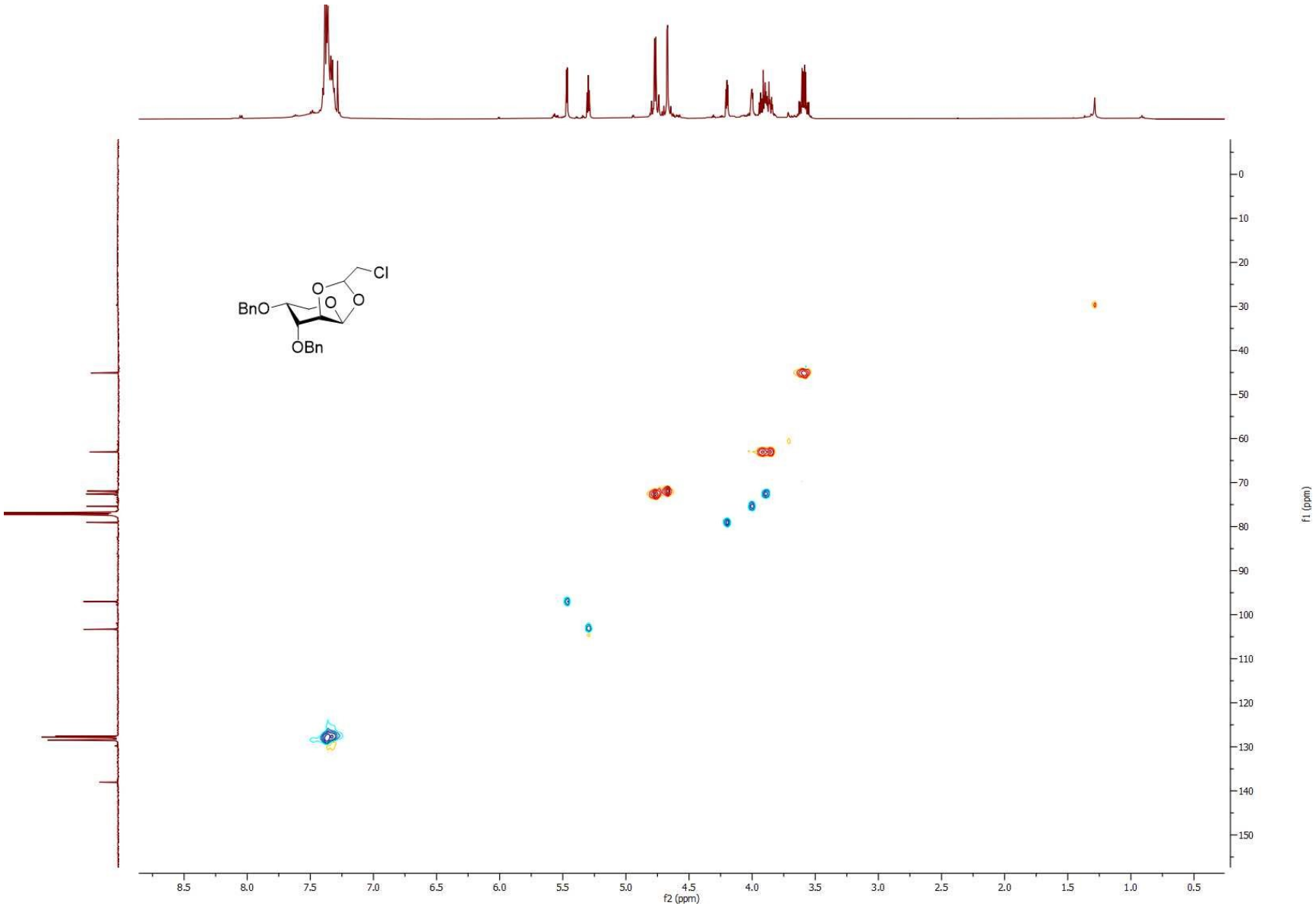
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

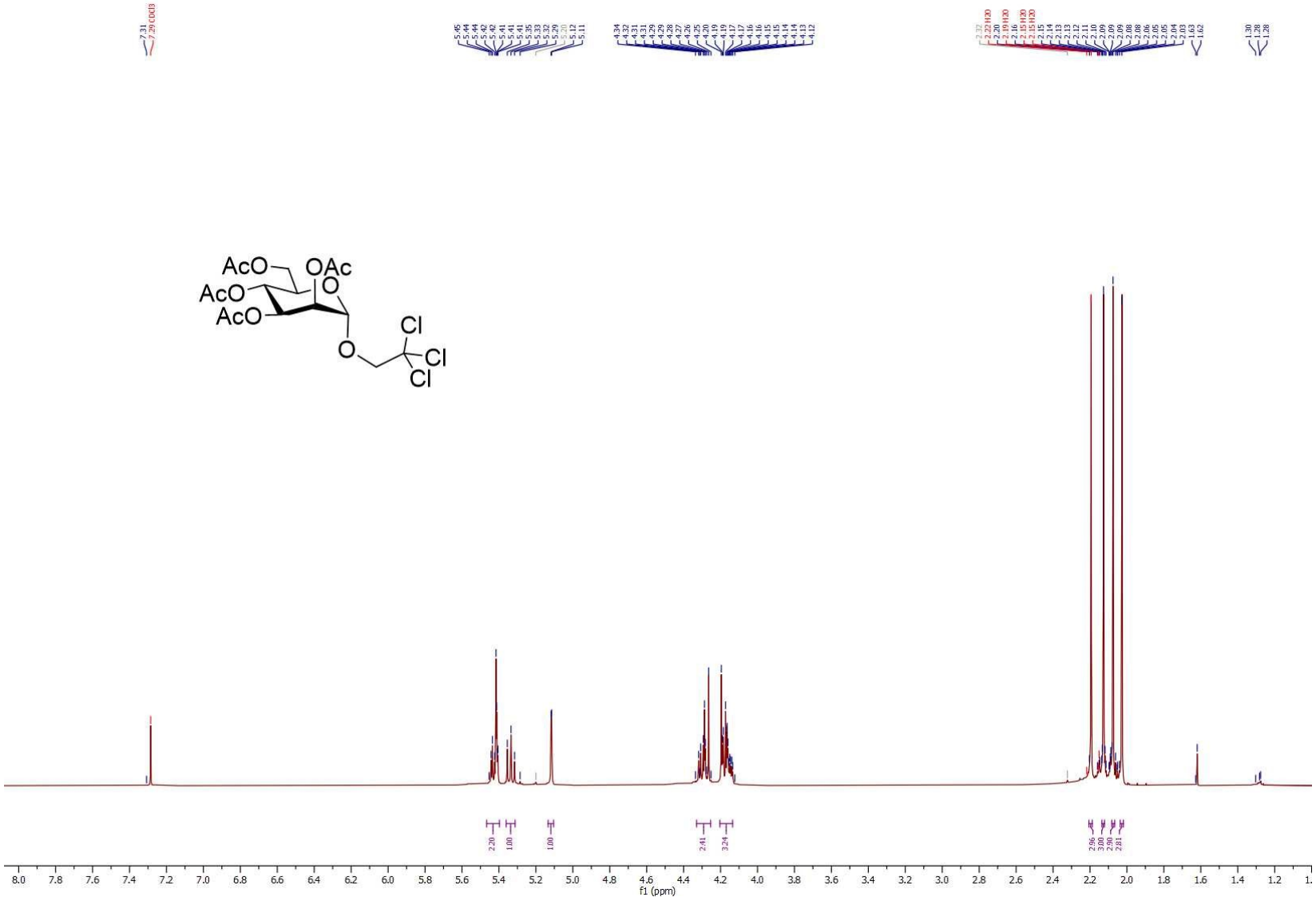


HSQC NMR

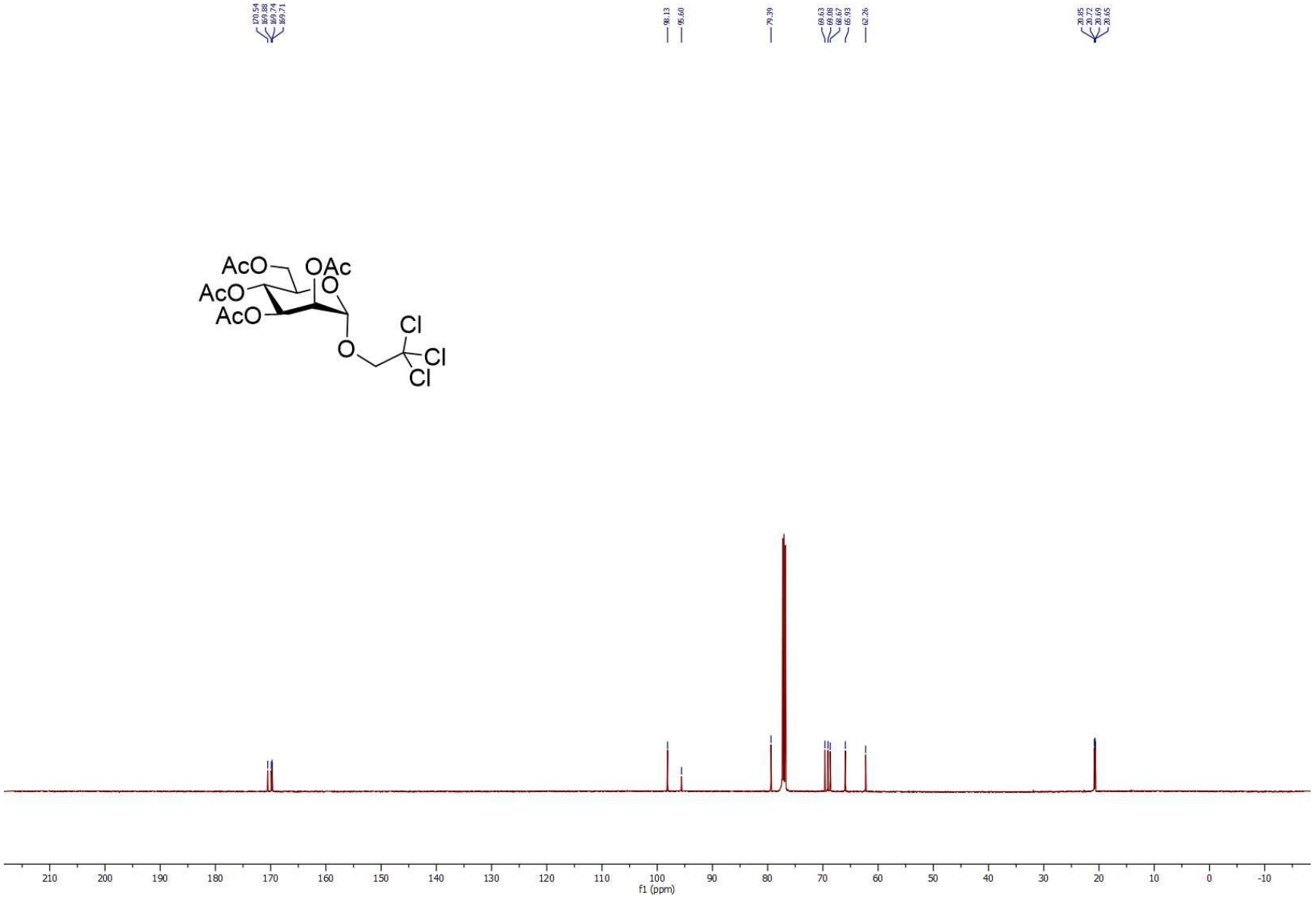


2,2 ,2-Trichloroethyl 2,3, 4,6-tetra-0-AcetyI-α-D-mannopyranoside S8

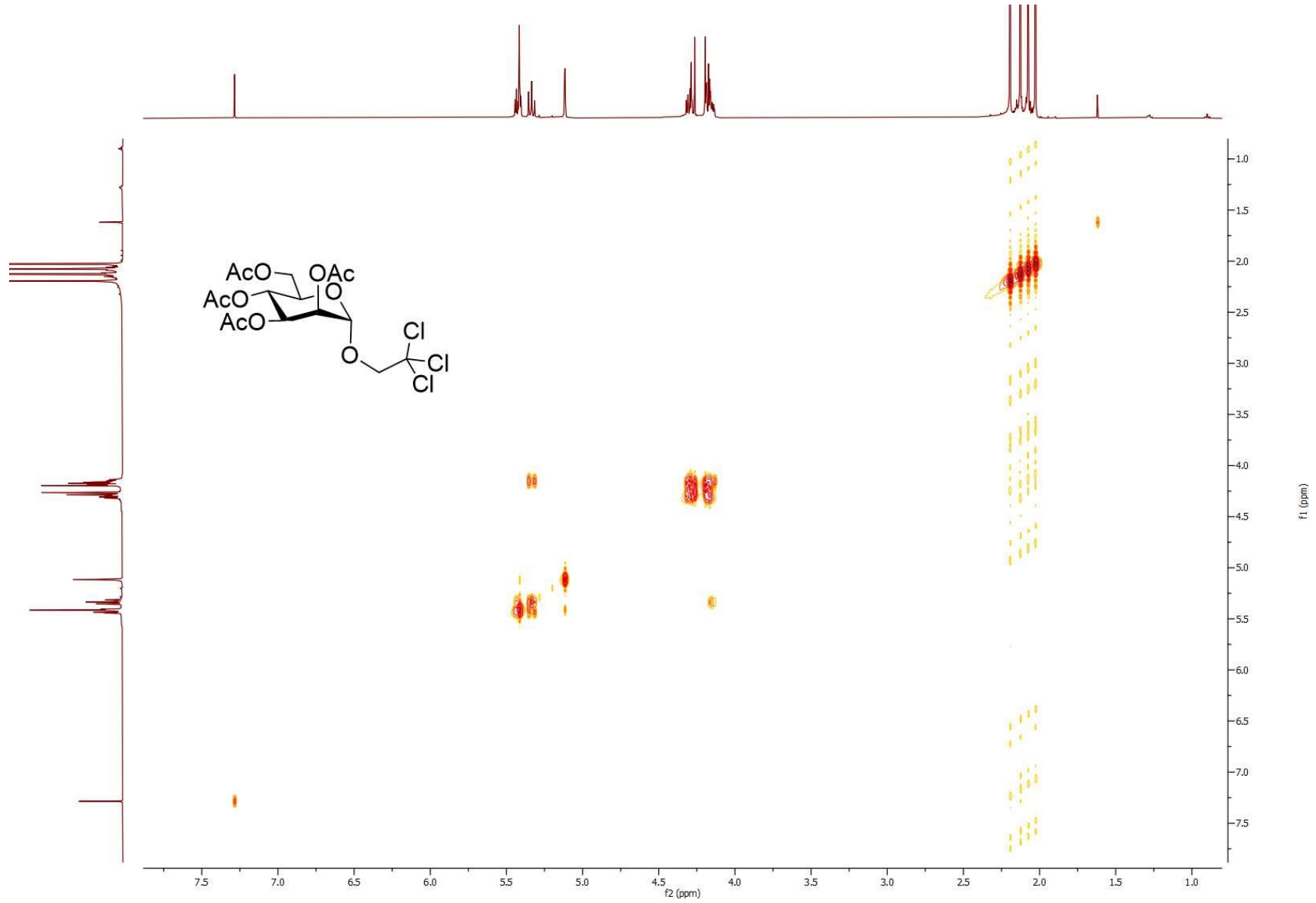
^{1}H NMR (500 MHz, $CDCl_3$)



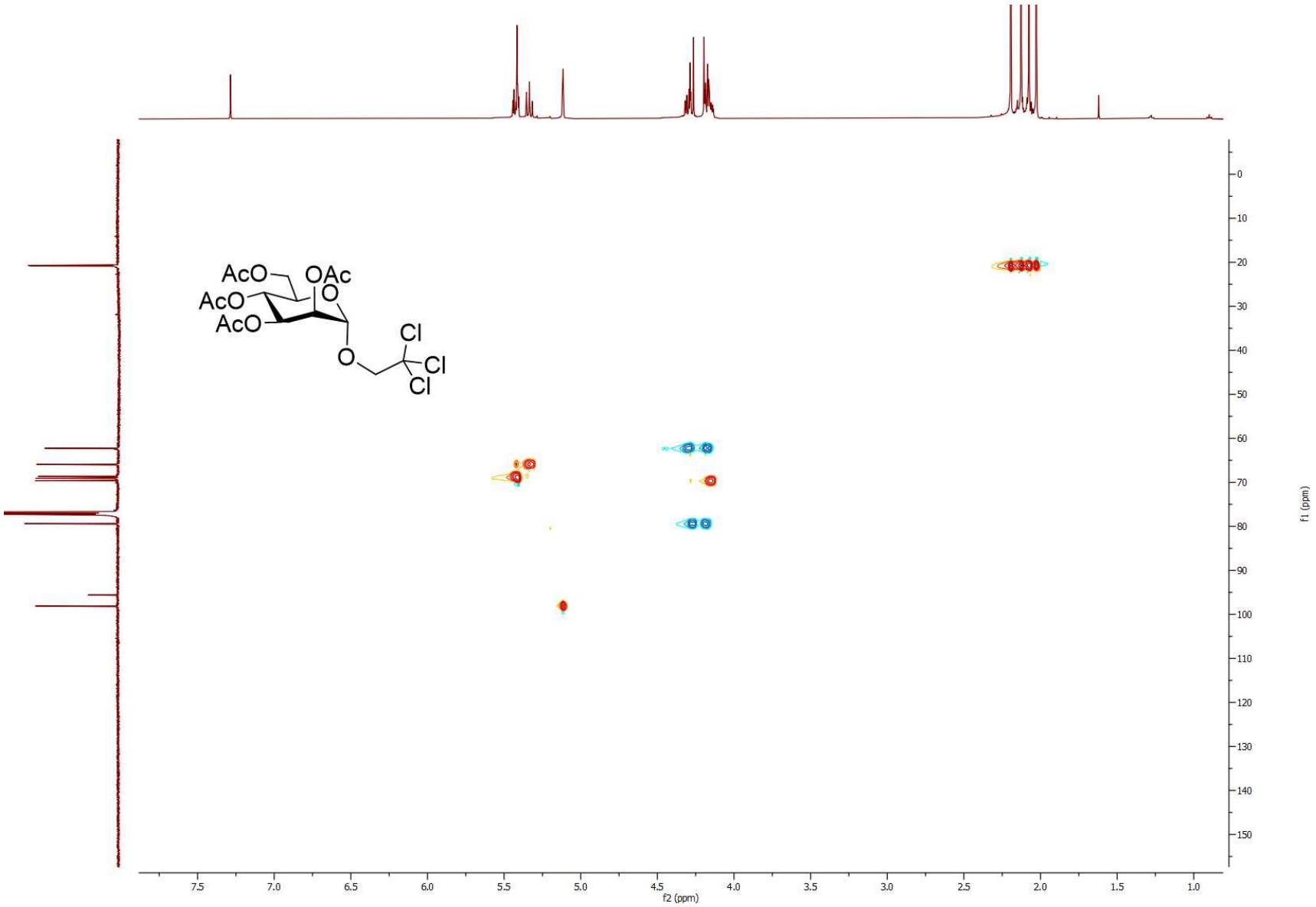
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

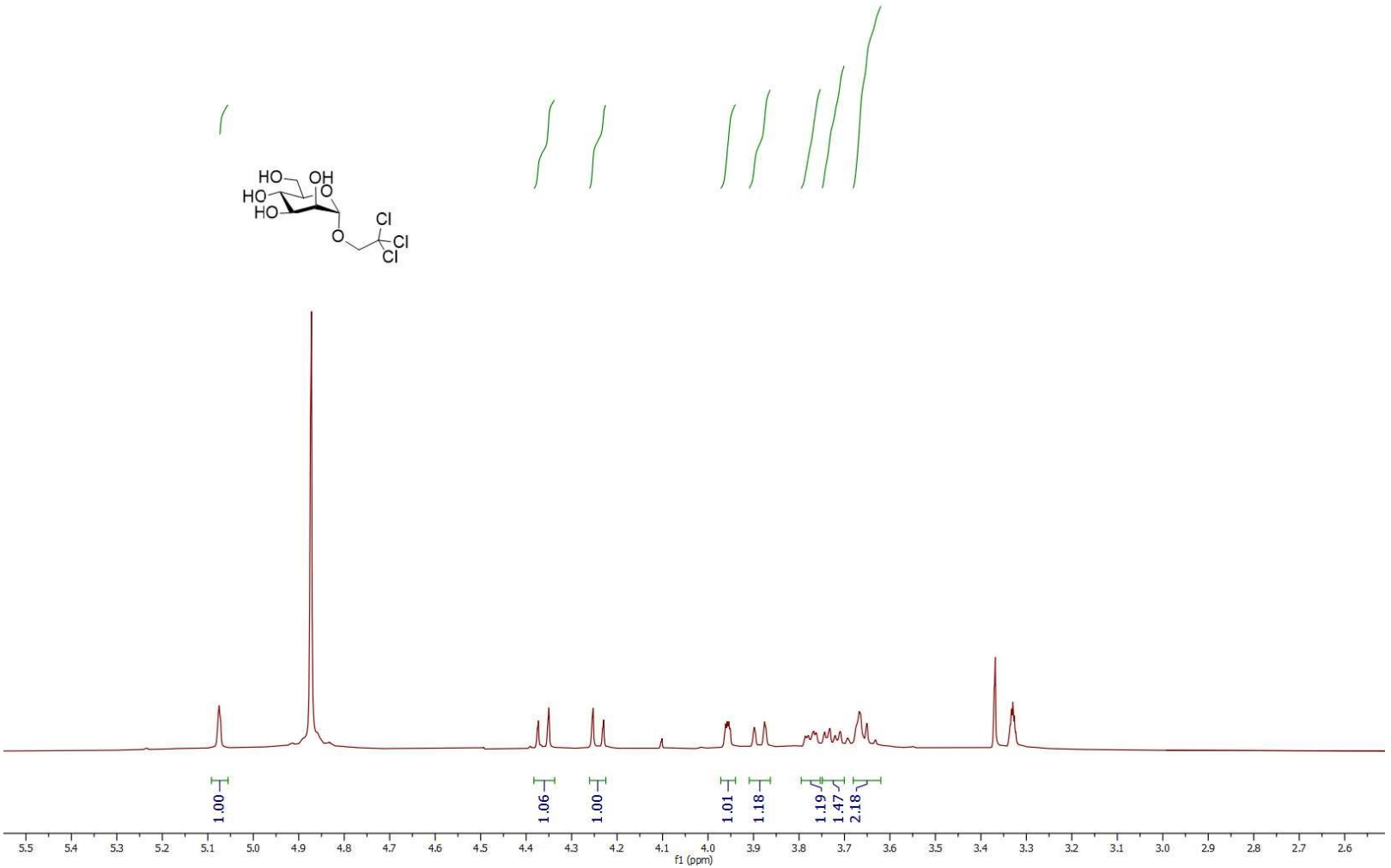


HSQC NMR

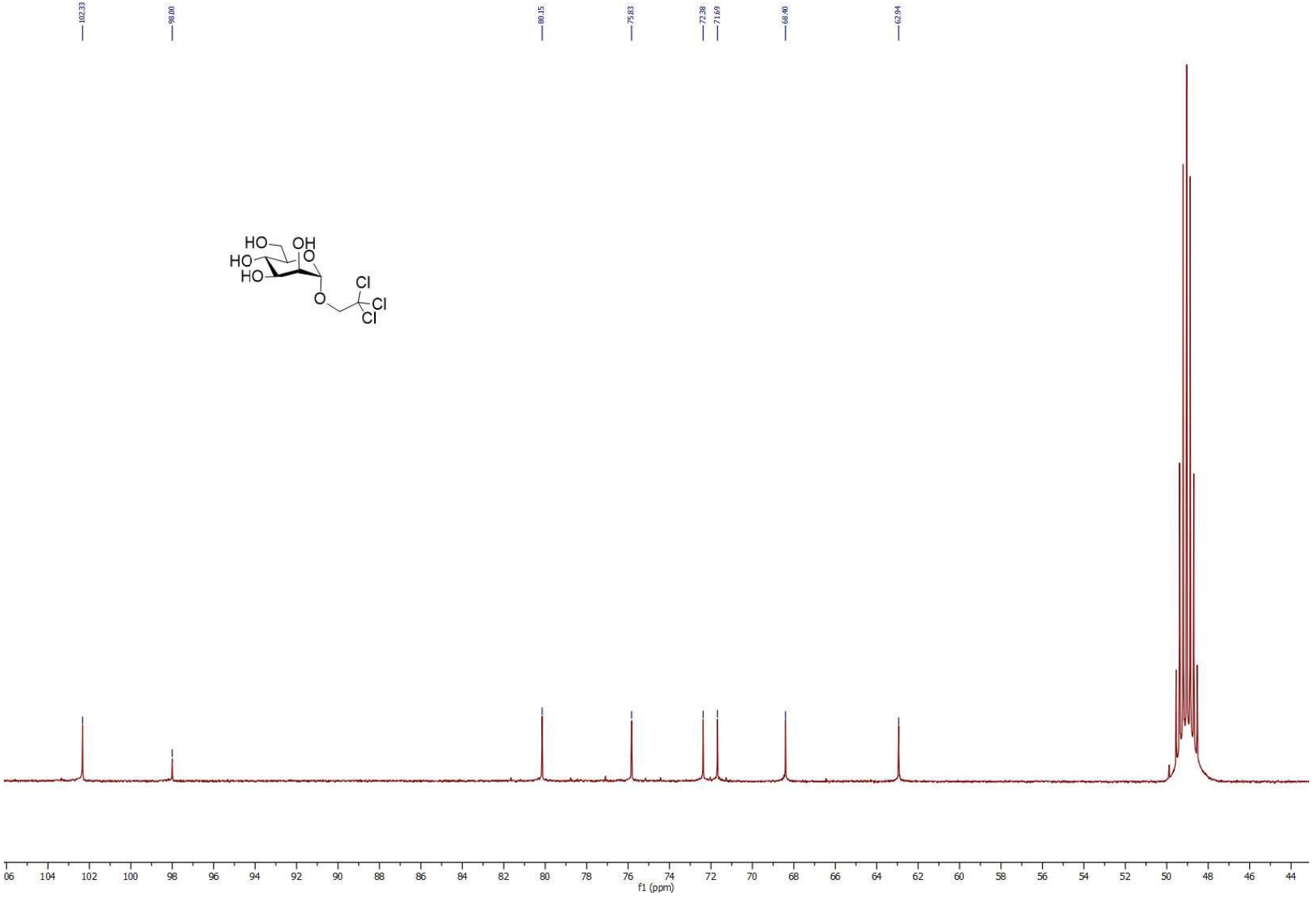


2,2,2-Trichloroethyl-D-mannopyranoside(D1)

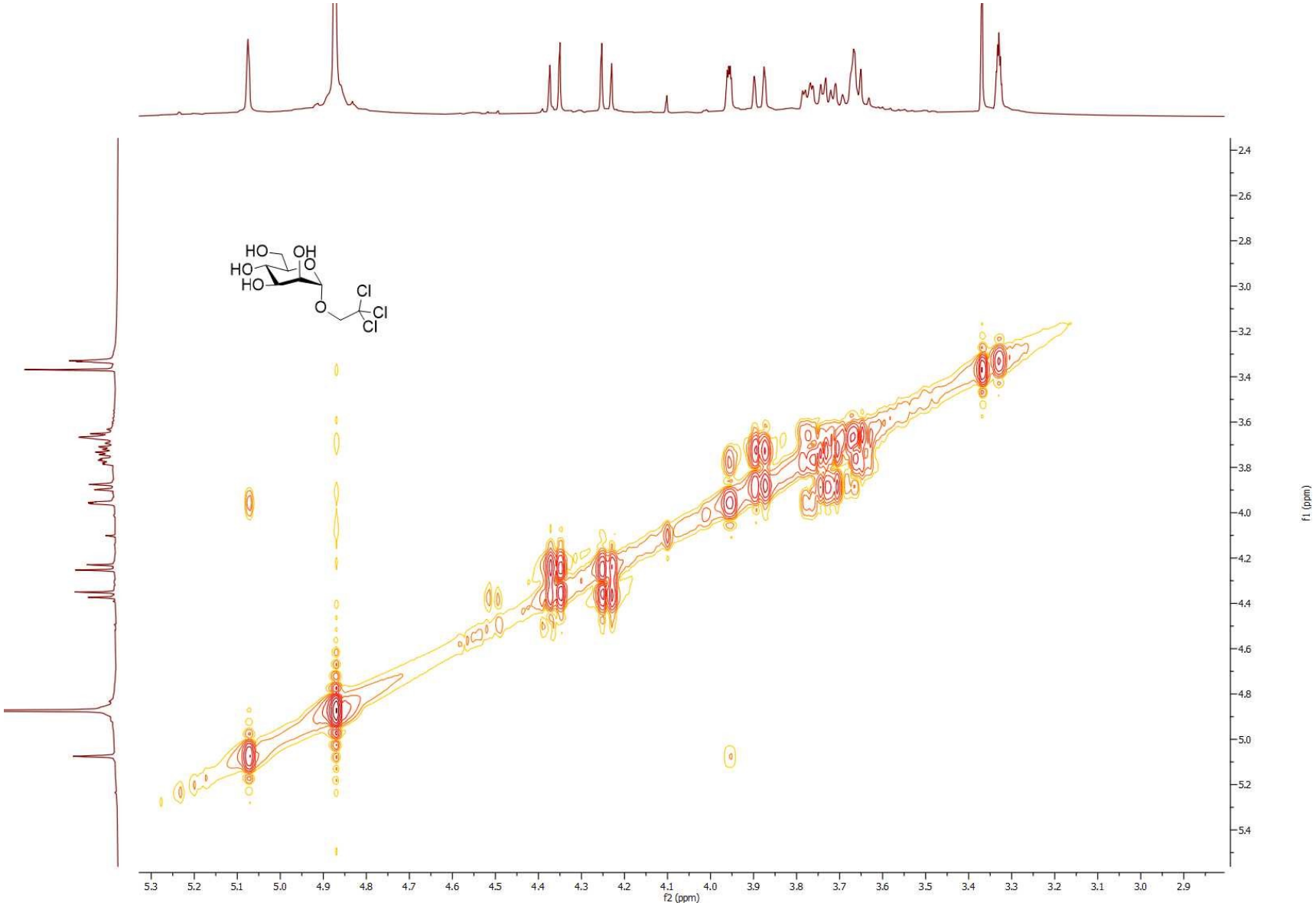
^{1}H NMR (500 MHz, $CDCl_3$)



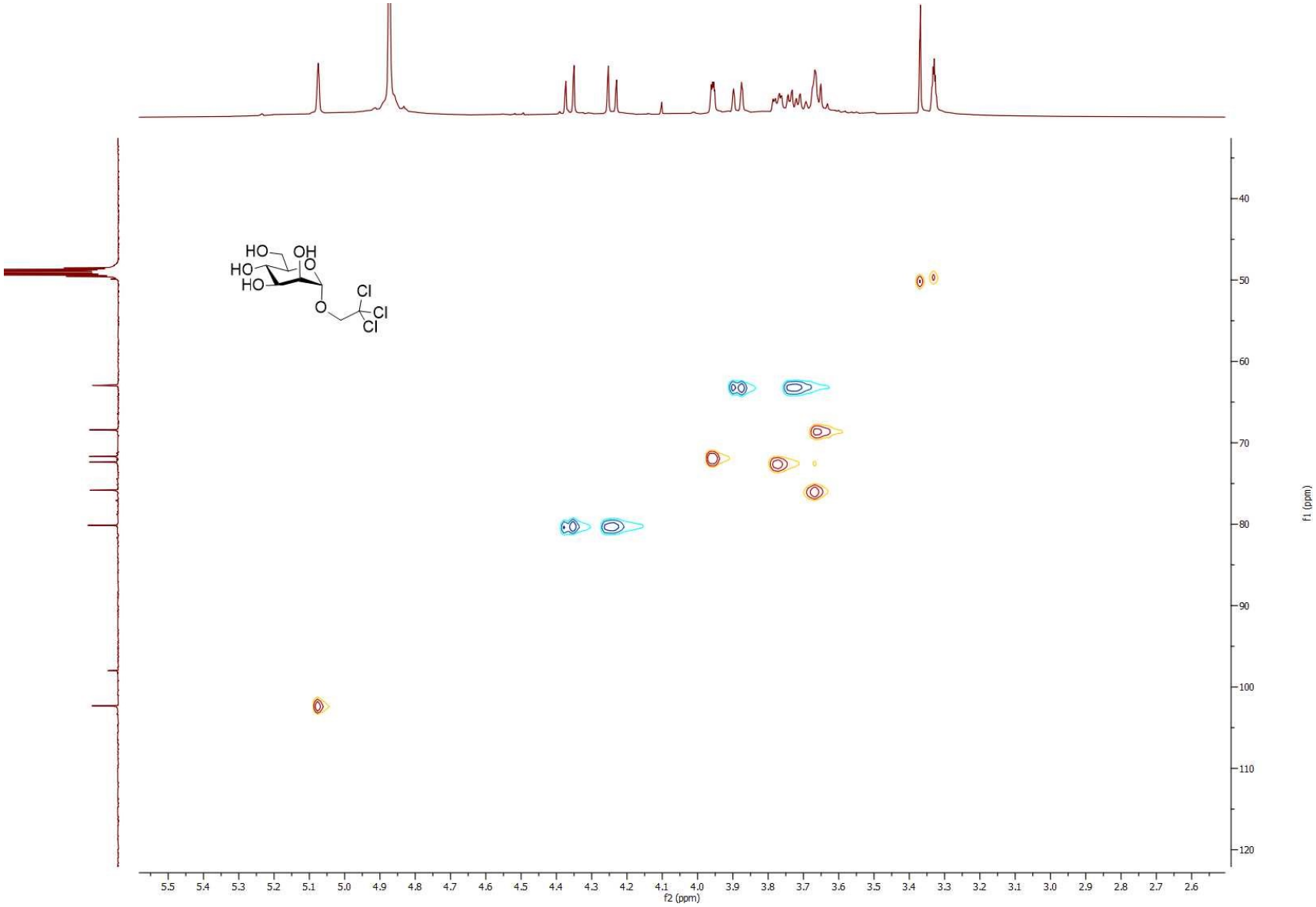
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

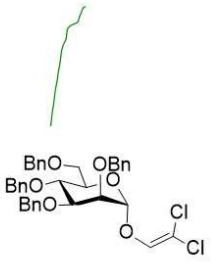


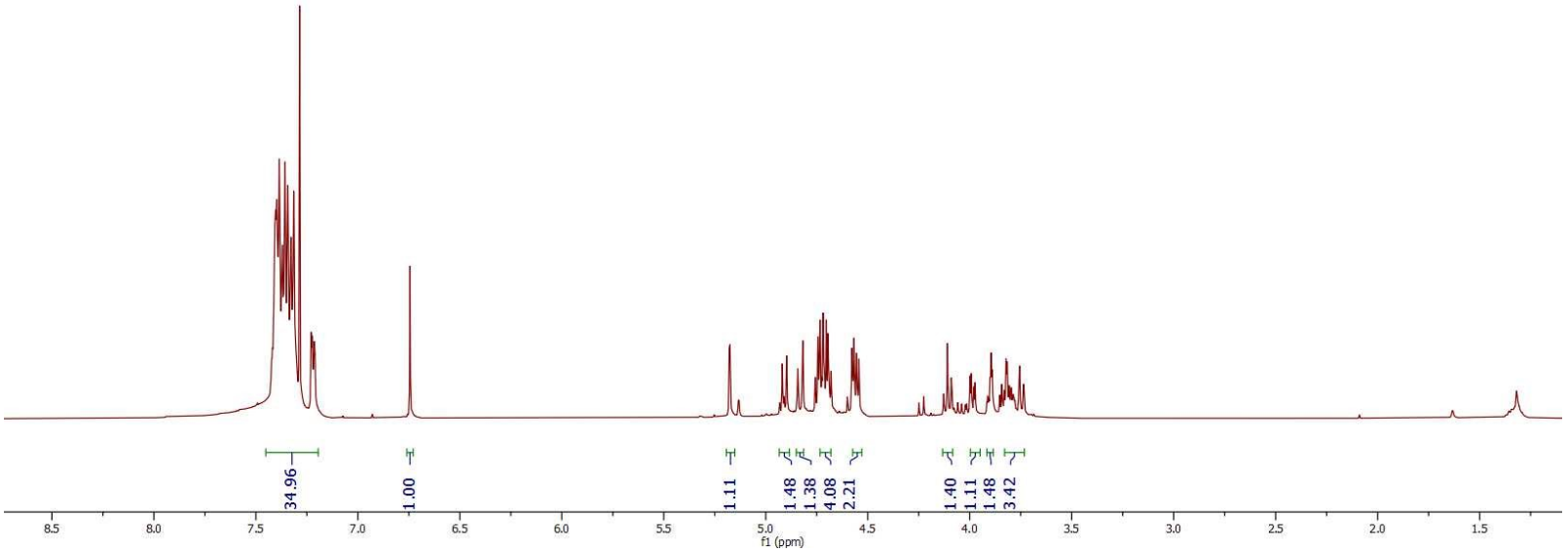
HSQC NMR


HO
OH
HO
HO
O
O
Cl
Cl
Cl
5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6
f2 (ppm)
40 50 60 70 80 90 100 110 120
f1 (ppm)

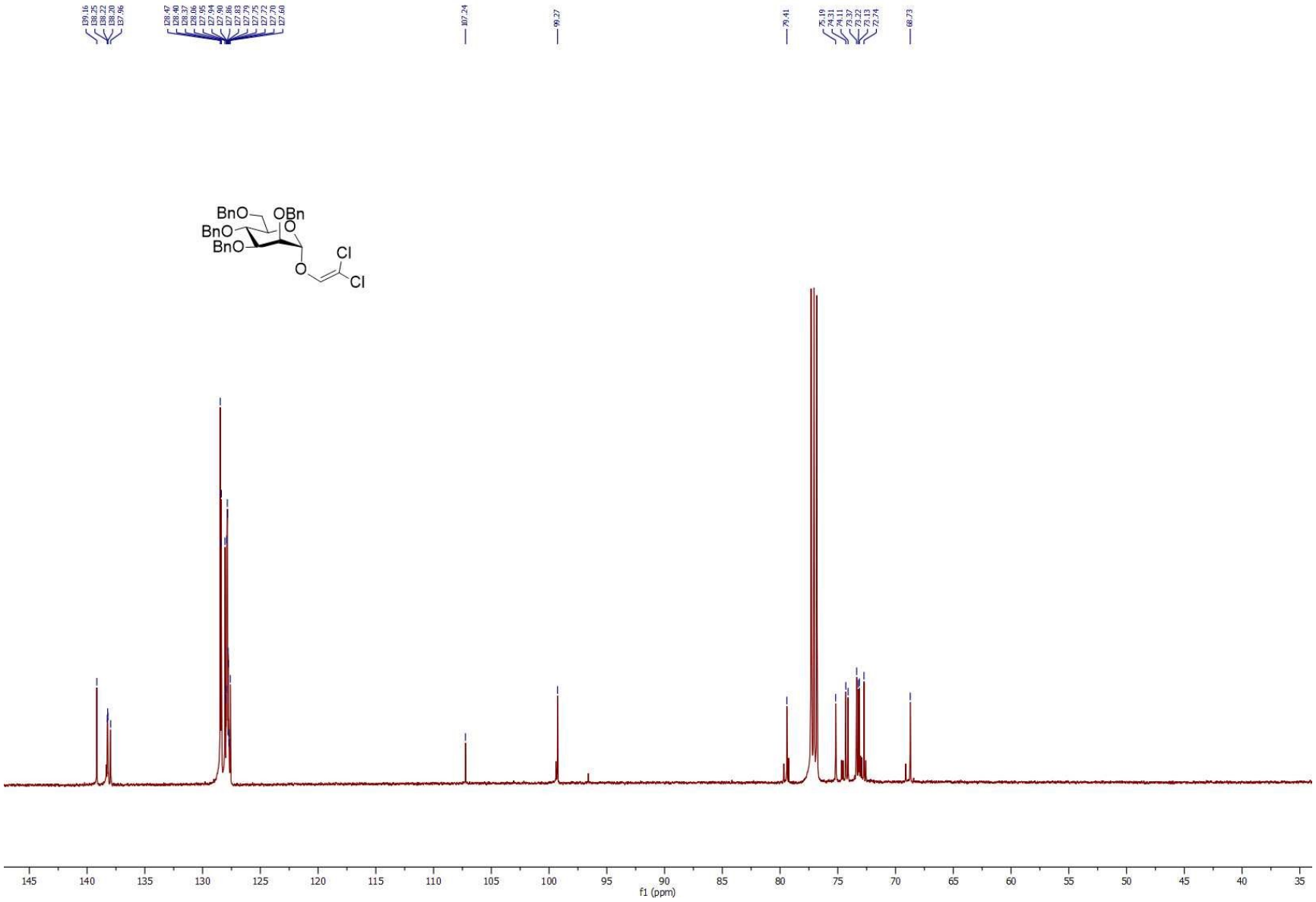
Product (2,2-Dichlorovinyl 2,3,4,6-tetra-O-Benzyl-α-D-mannopyranoside)(D3)

^{1}H NMR (500 MHz, $CDCl_3$)

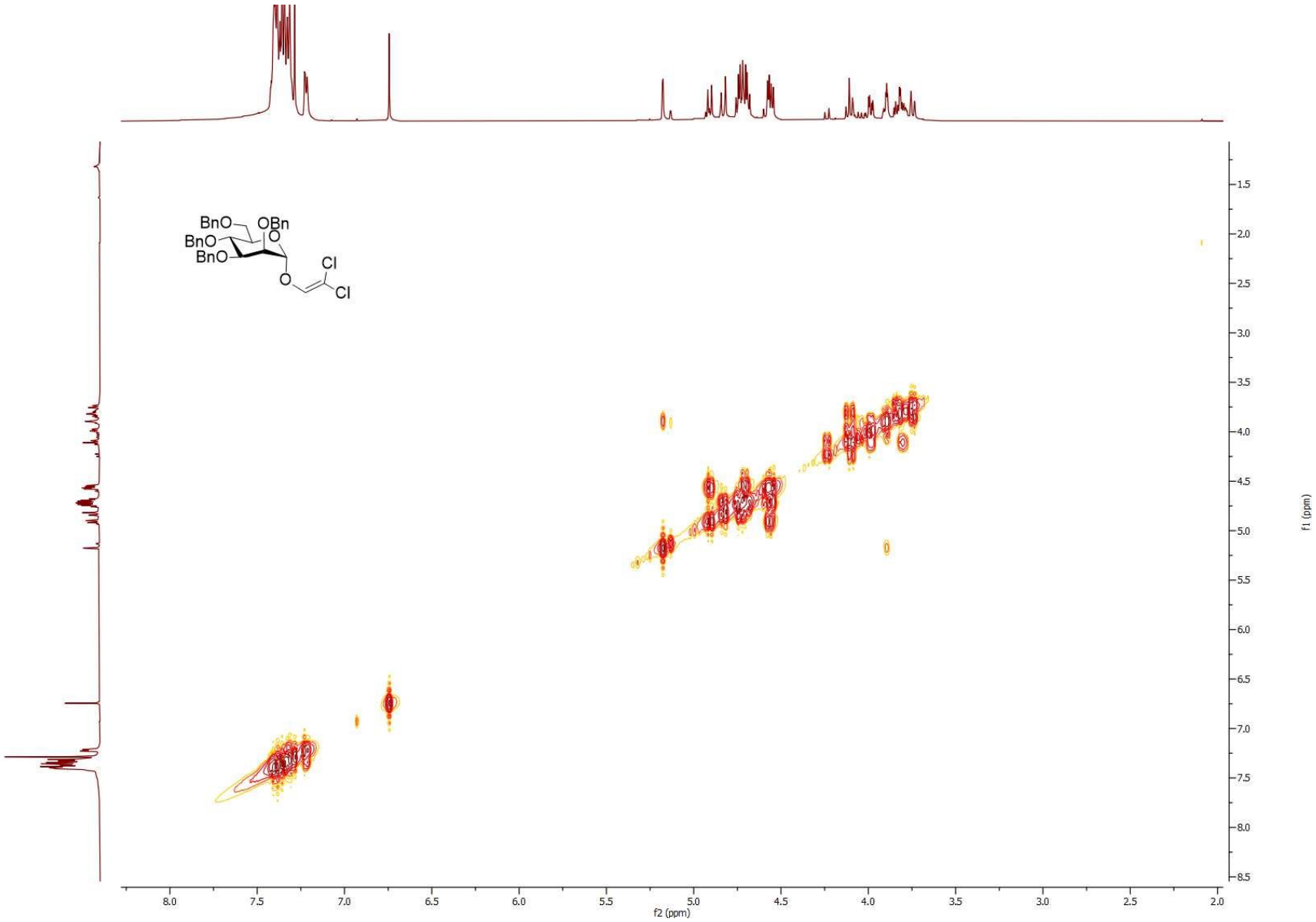




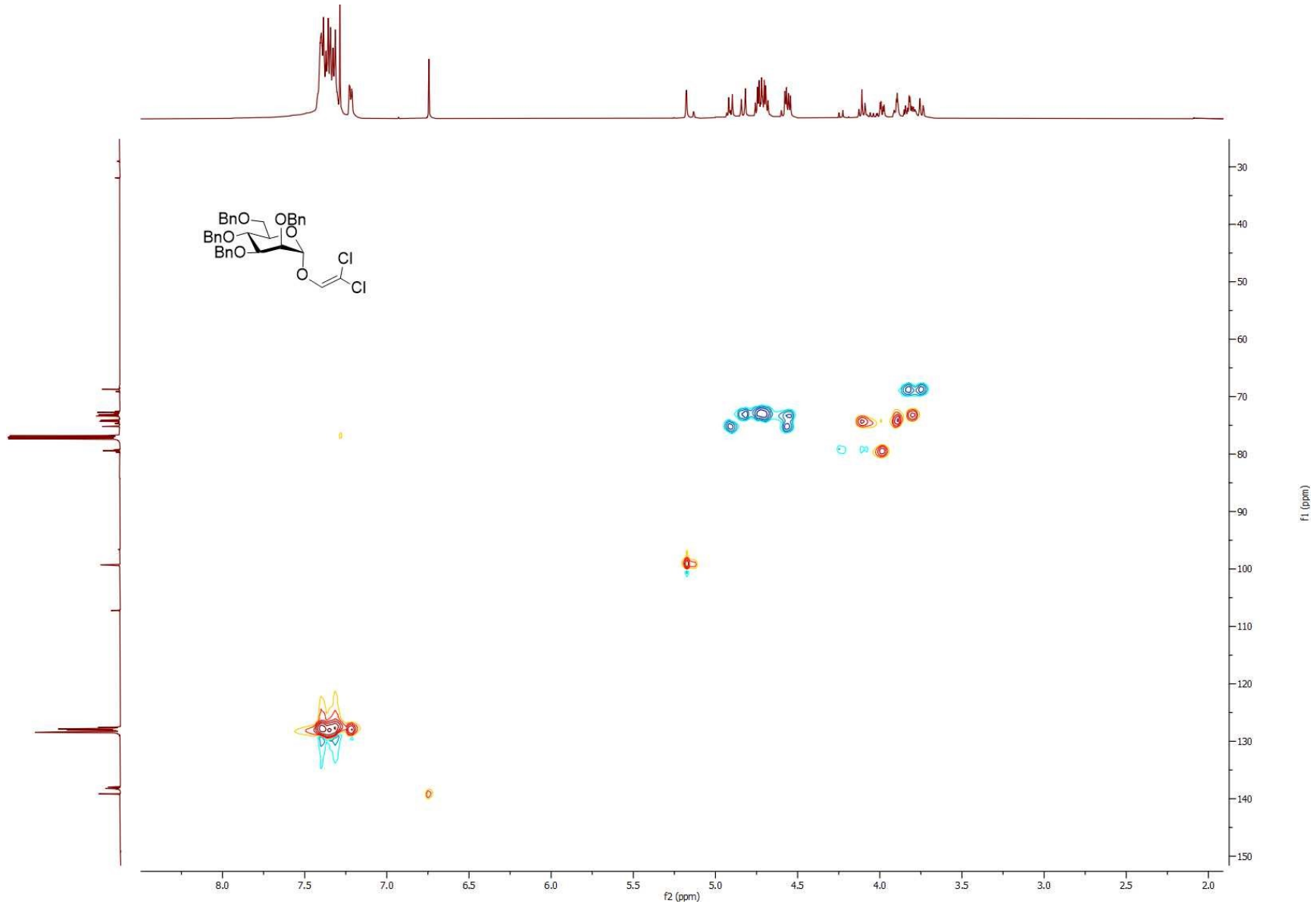
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

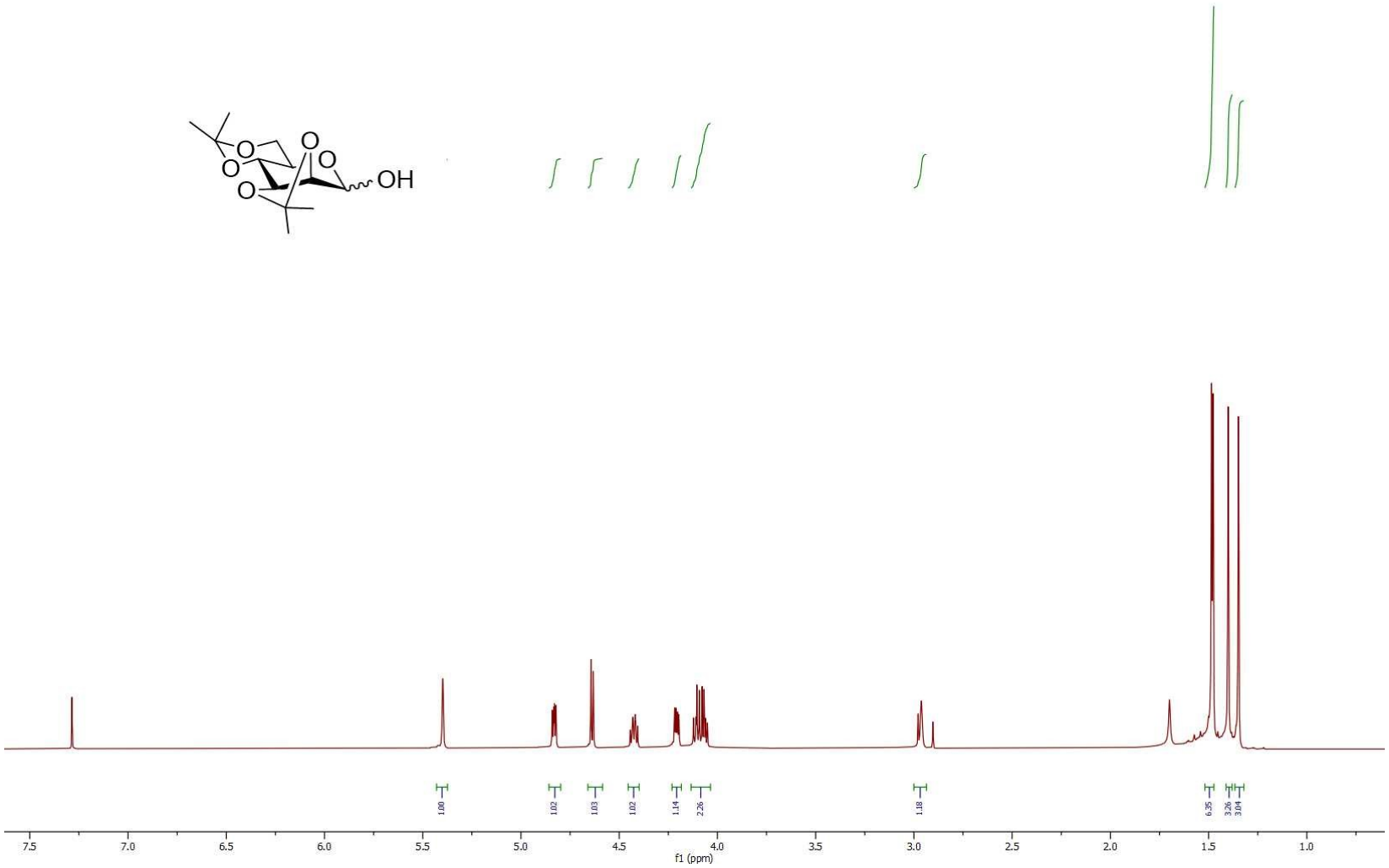

BnO
OBn
BnO
BnO
O
O
Cl
Cl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
f1 (ppm)

HSQC NMR

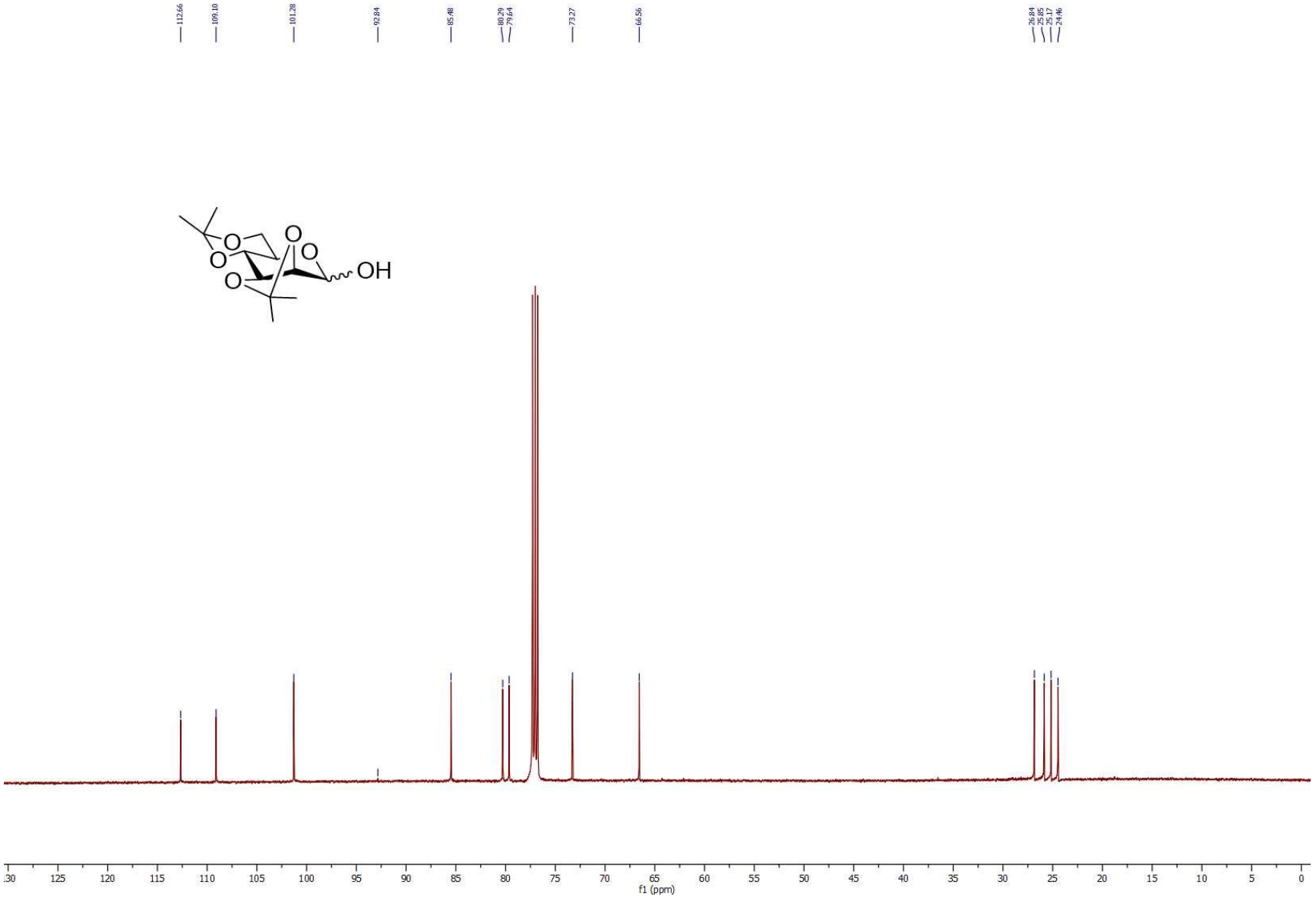

BnO
OBn
BnO
O
BnO
Cl
O
Cl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

2,3:4,6-di-O-Isopropylidene-D-mannopyranose(D4)

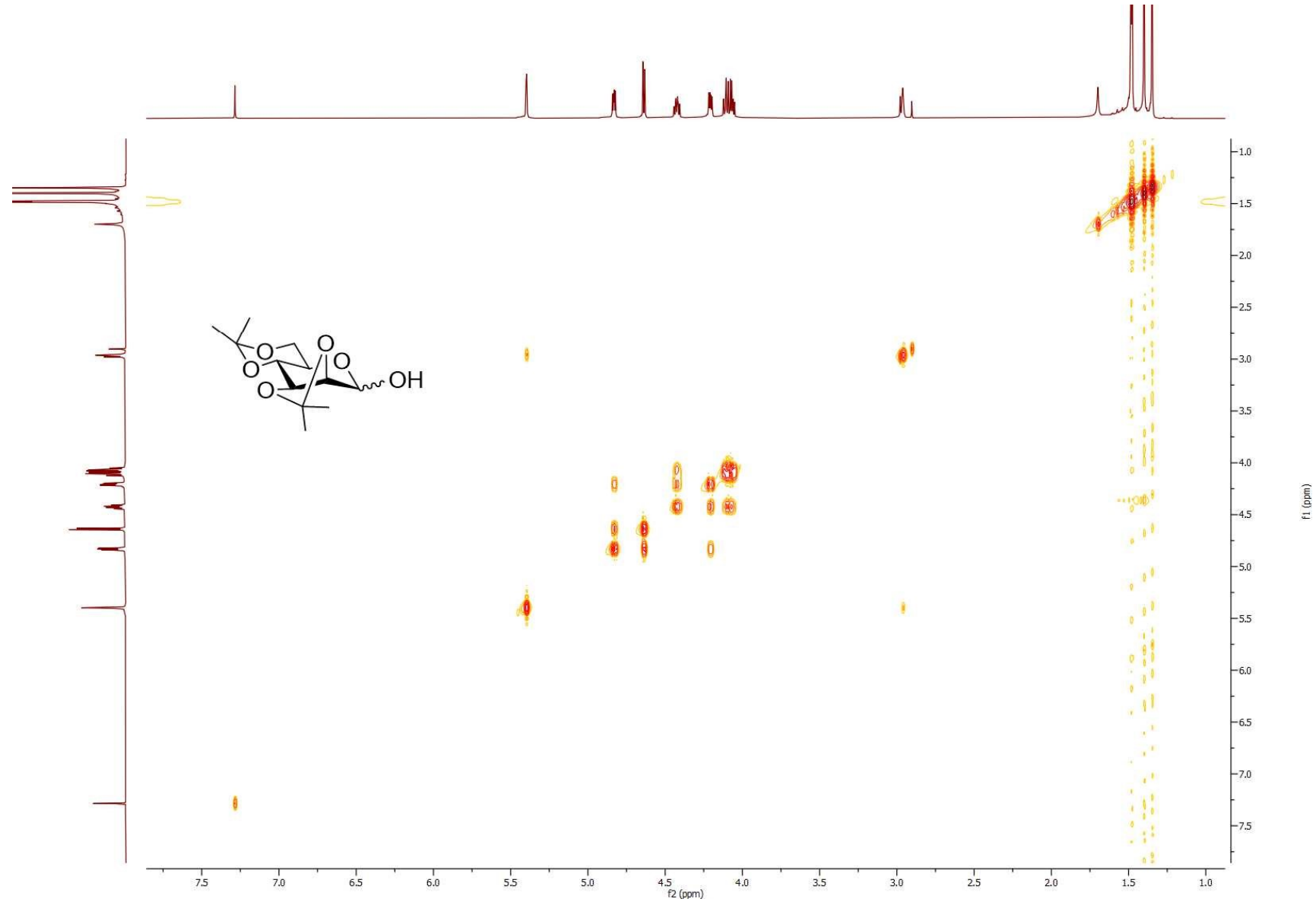
^{1}H NMR (500 MHz, $CDCl_3$)



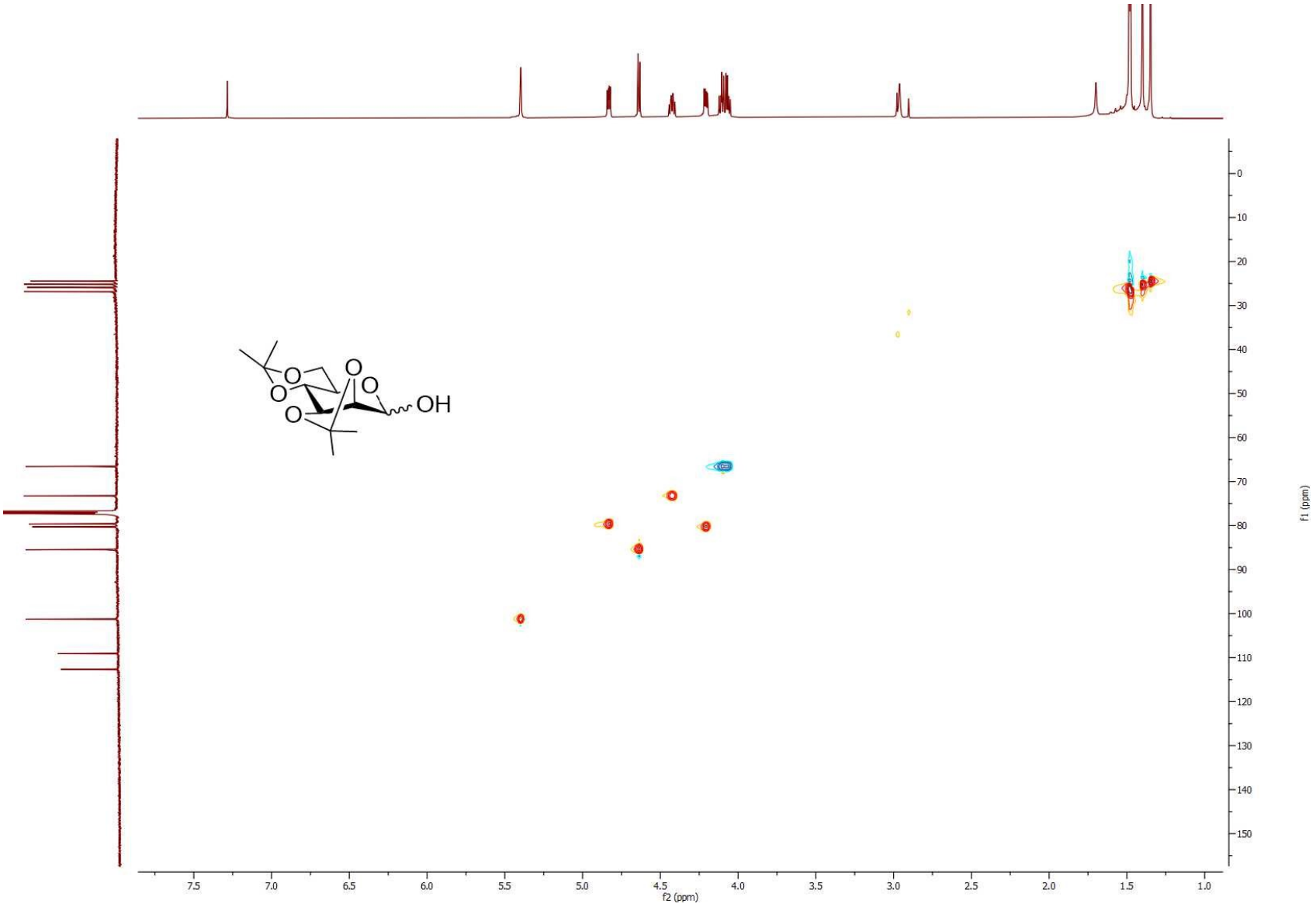
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

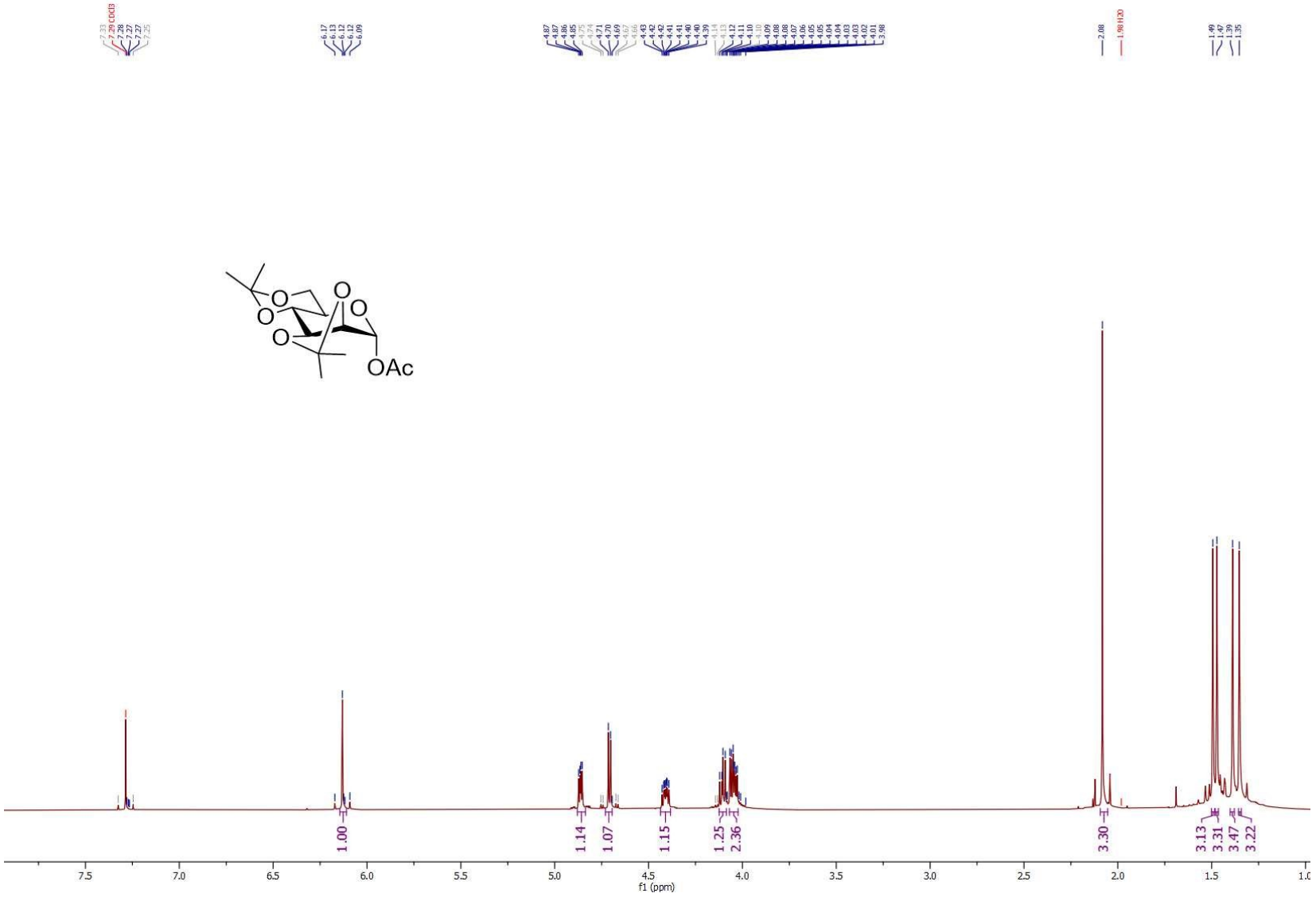


HSQC NMR

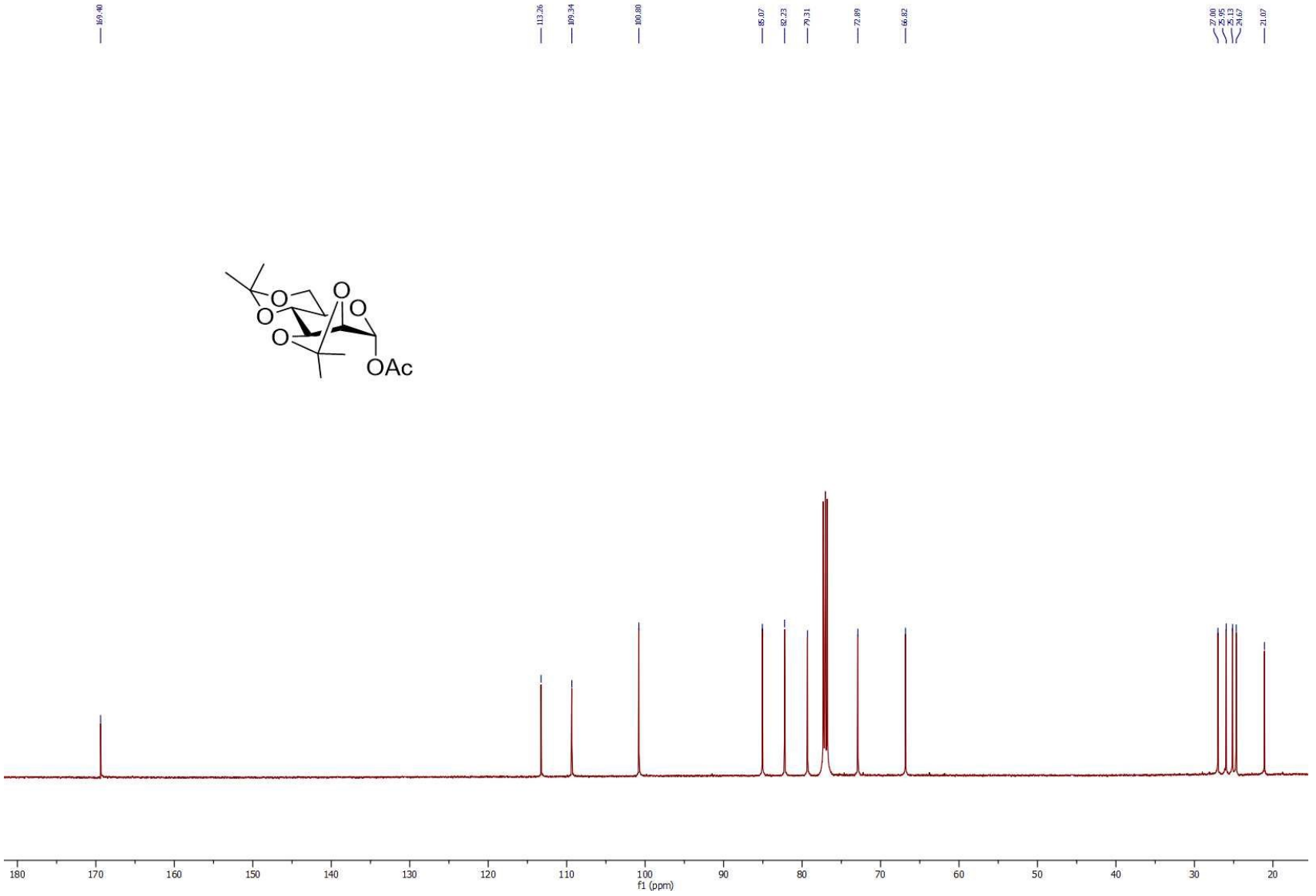

O
O
O
O
O
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

1-O Acetyl-2,3:4,6-di-O-Isopropylidene-D-mannopyranose(D5)

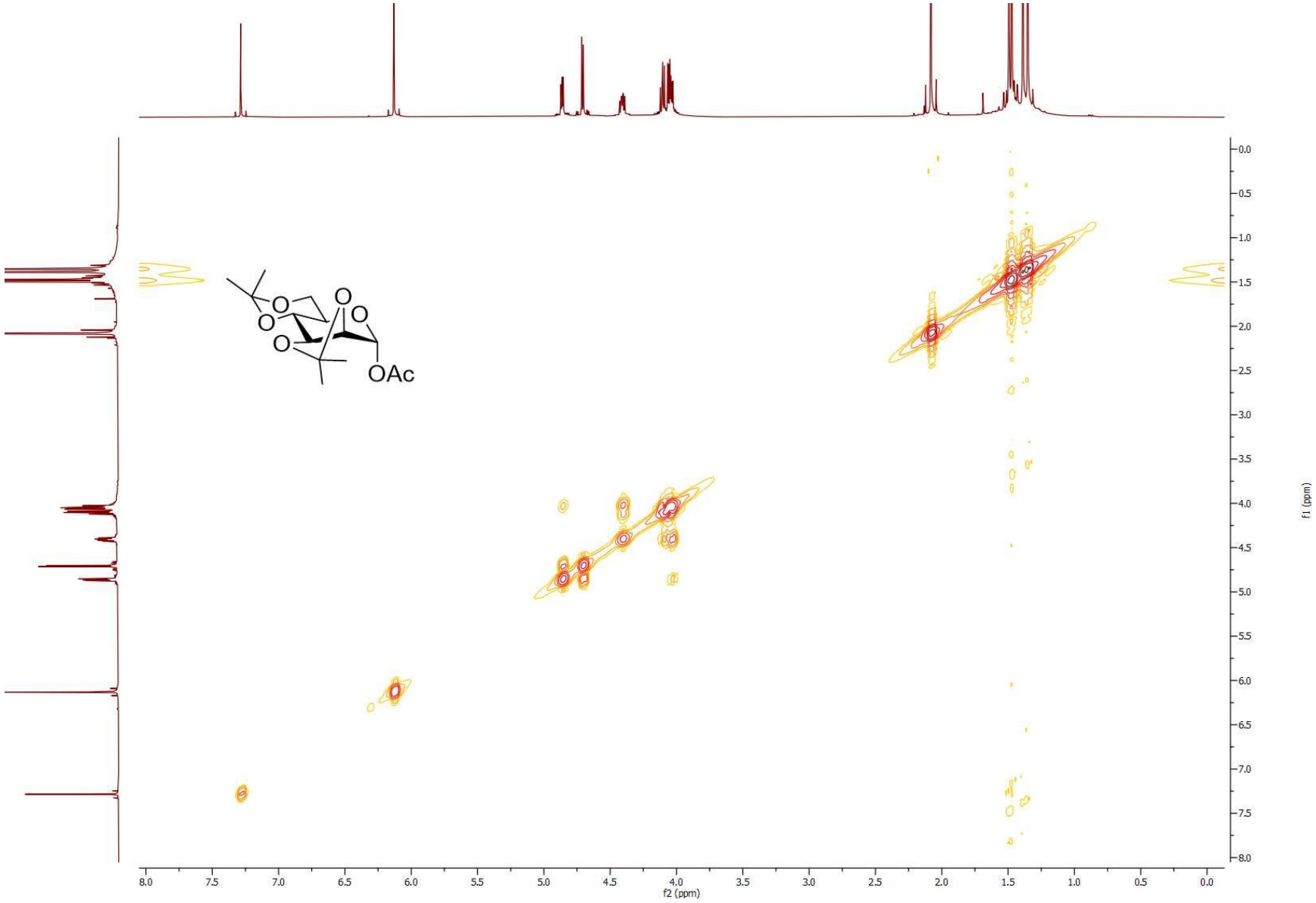
^{1}H NMR (500 MHz, $CDCl_3$)



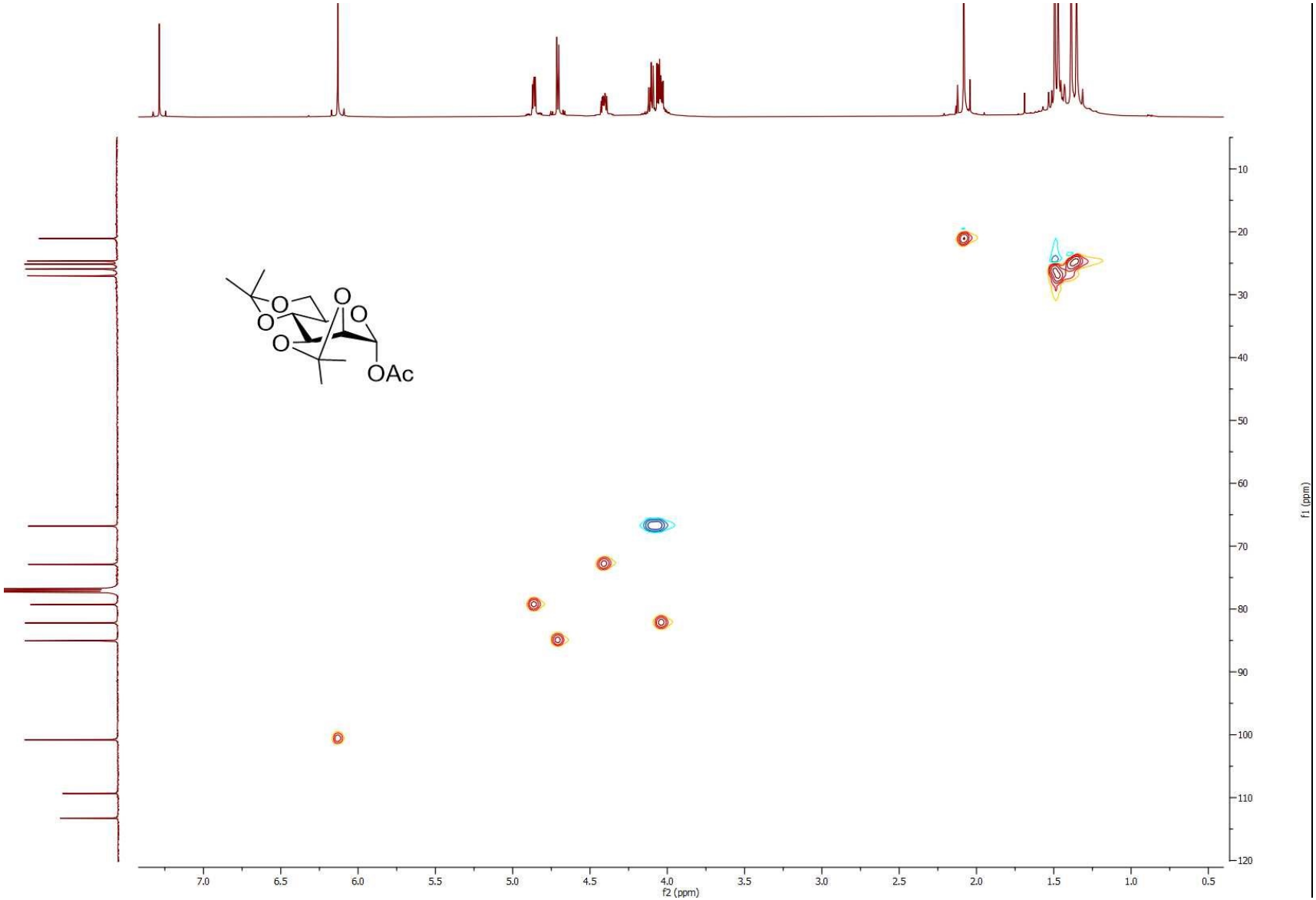
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

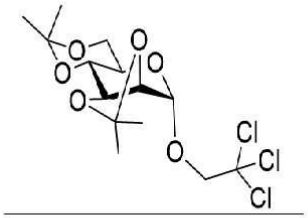


HSQC NMR

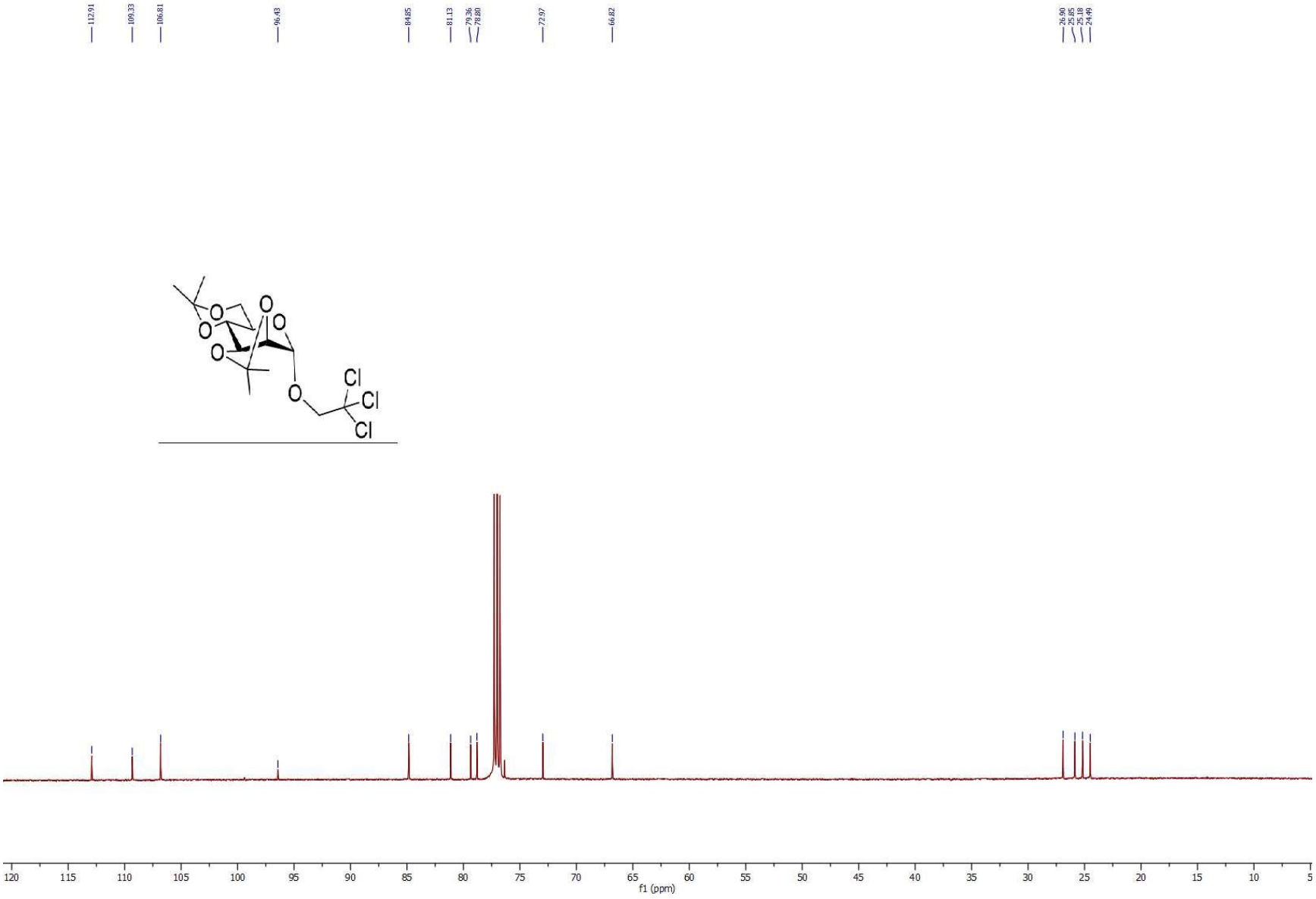

O
O
O
O
O
OAc
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
f1 (ppm)

2,2,2-trichloroethyl 2,3:4,6-di-O-Isopropylidene-D-mannopyranoside(D6)

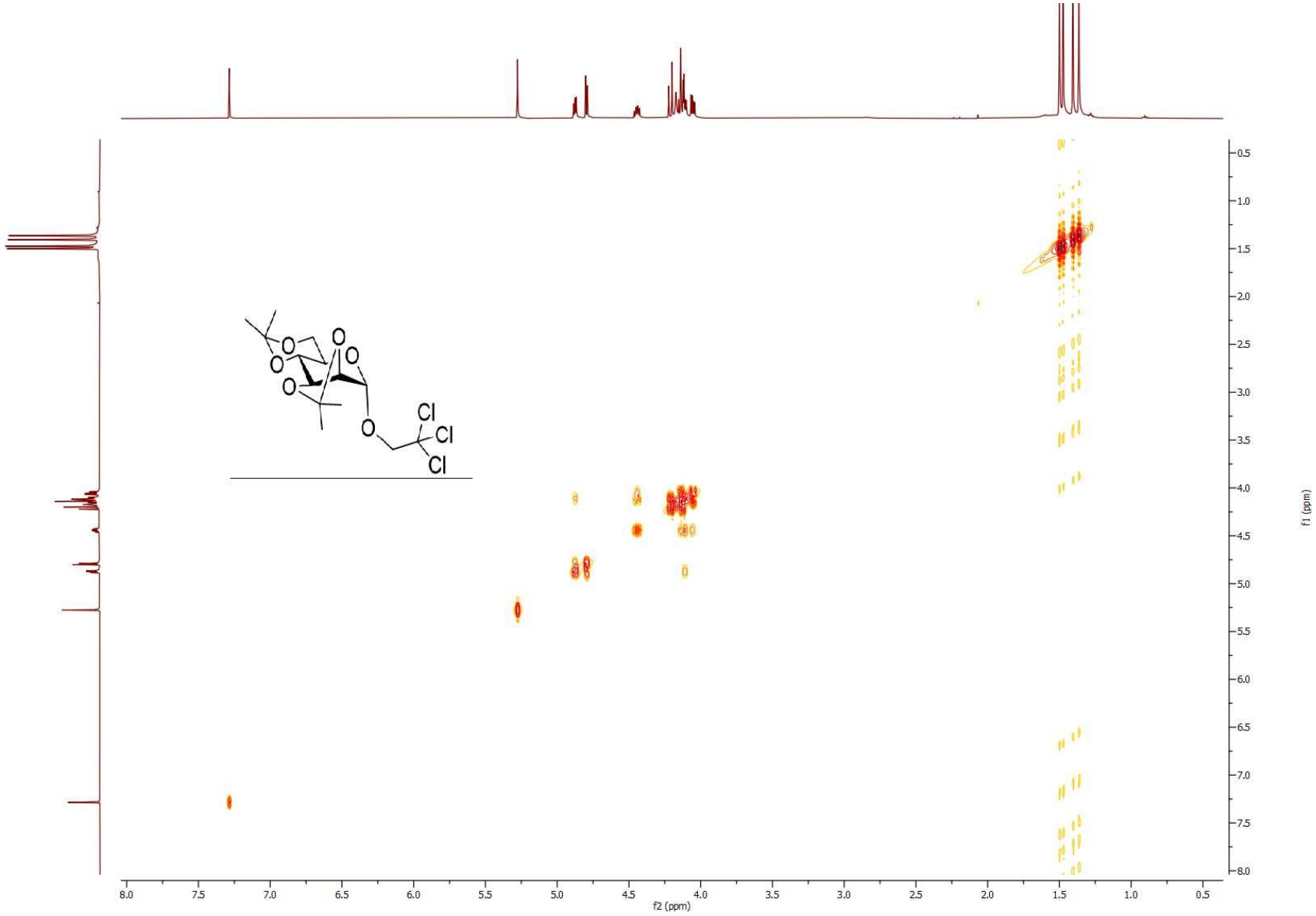
^{1}H NMR (500 MHz, $CDCl_3$)



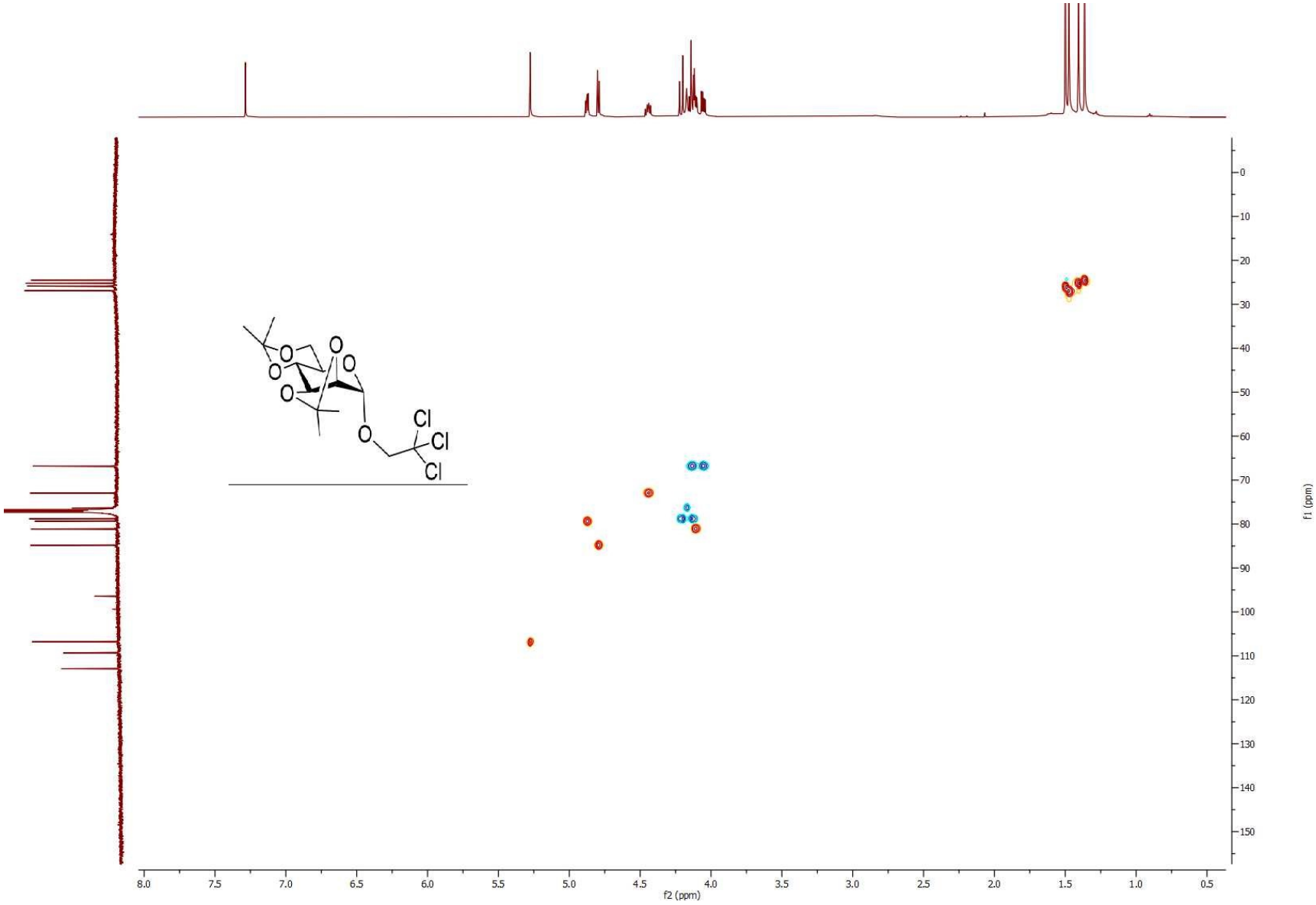
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

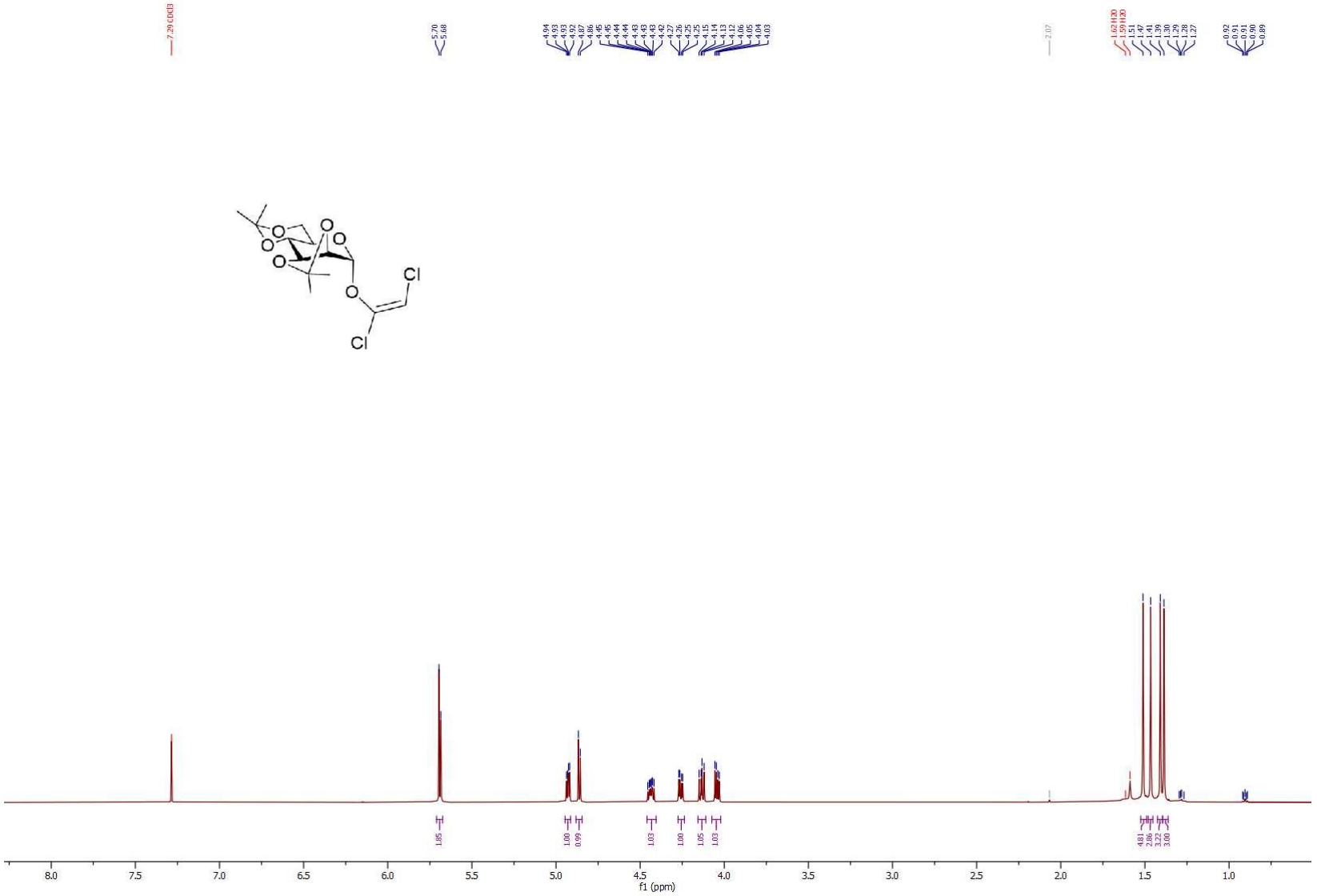

O
O
O
O
O
O
Cl
Cl
Cl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
f1 (ppm)

HSQC NMR

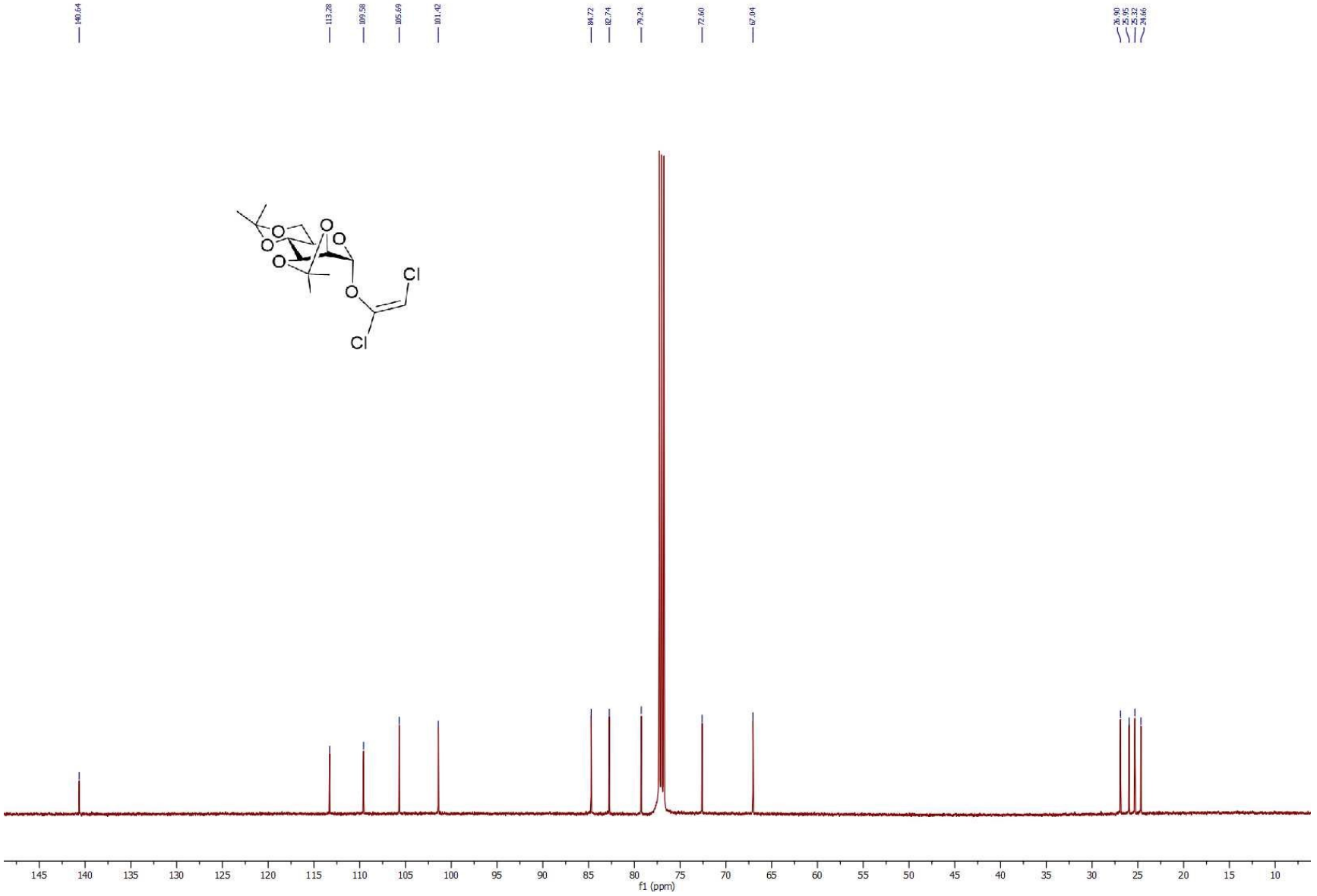

O
O
O
O
O
O
Cl
Cl
Cl
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

1,2-Dichlorovinyl 2,3:4,6-di-O-Isopropylidene-D-mannopyranoside (D7)

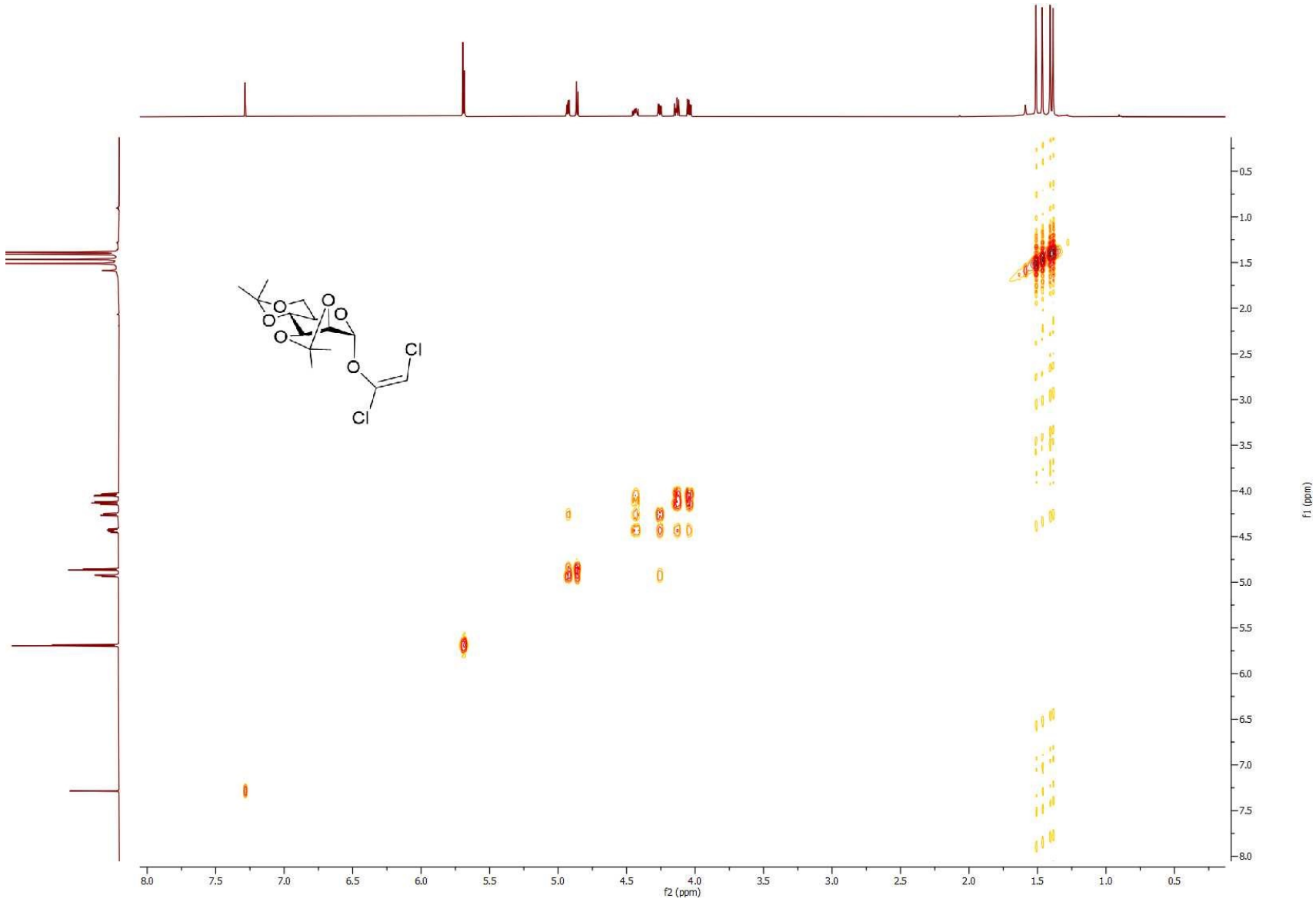
^{1}H NMR (500 MHz, $CDCl_3$)



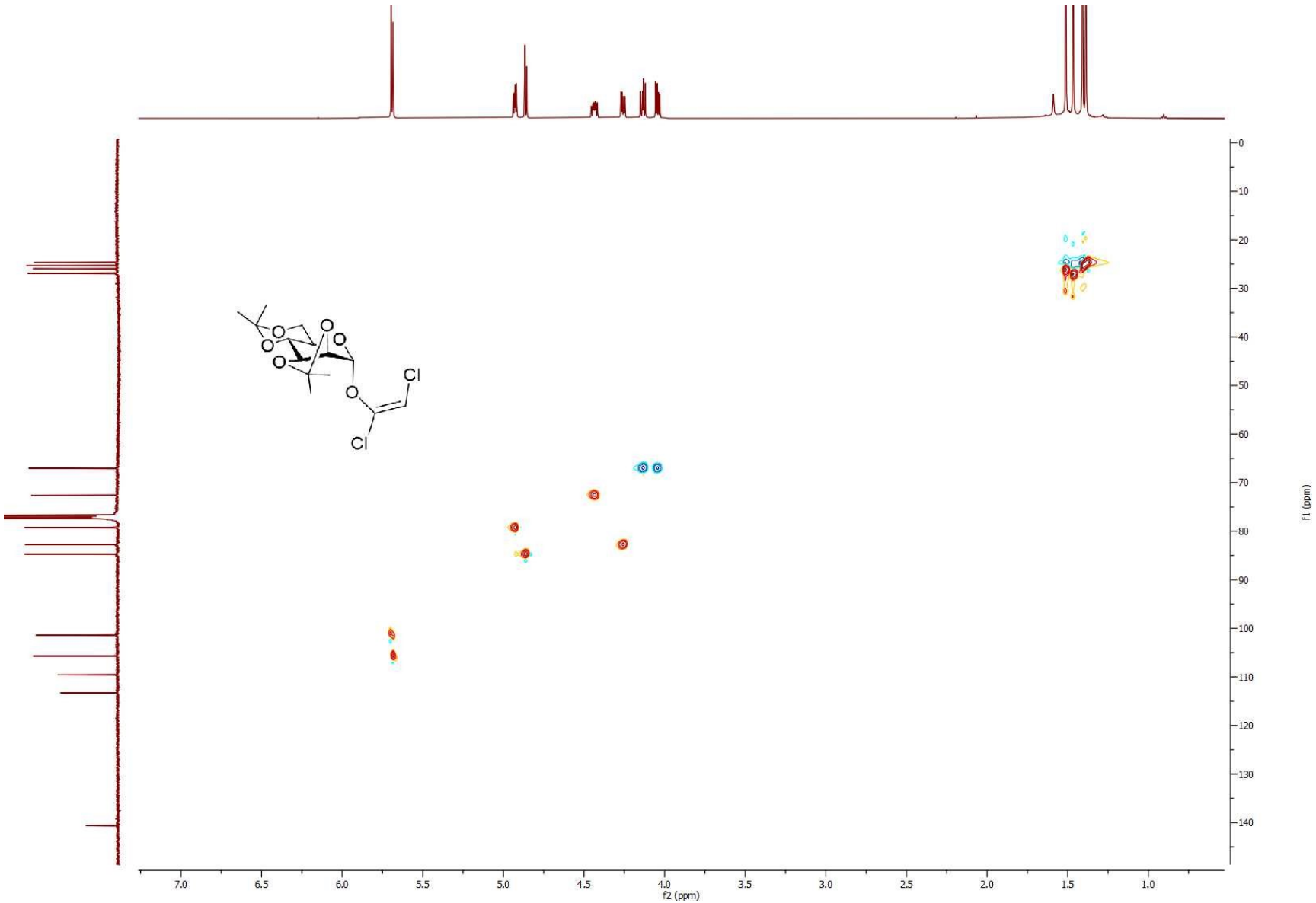
^{13}C NMR (126 MHz, $CDCl_3$)



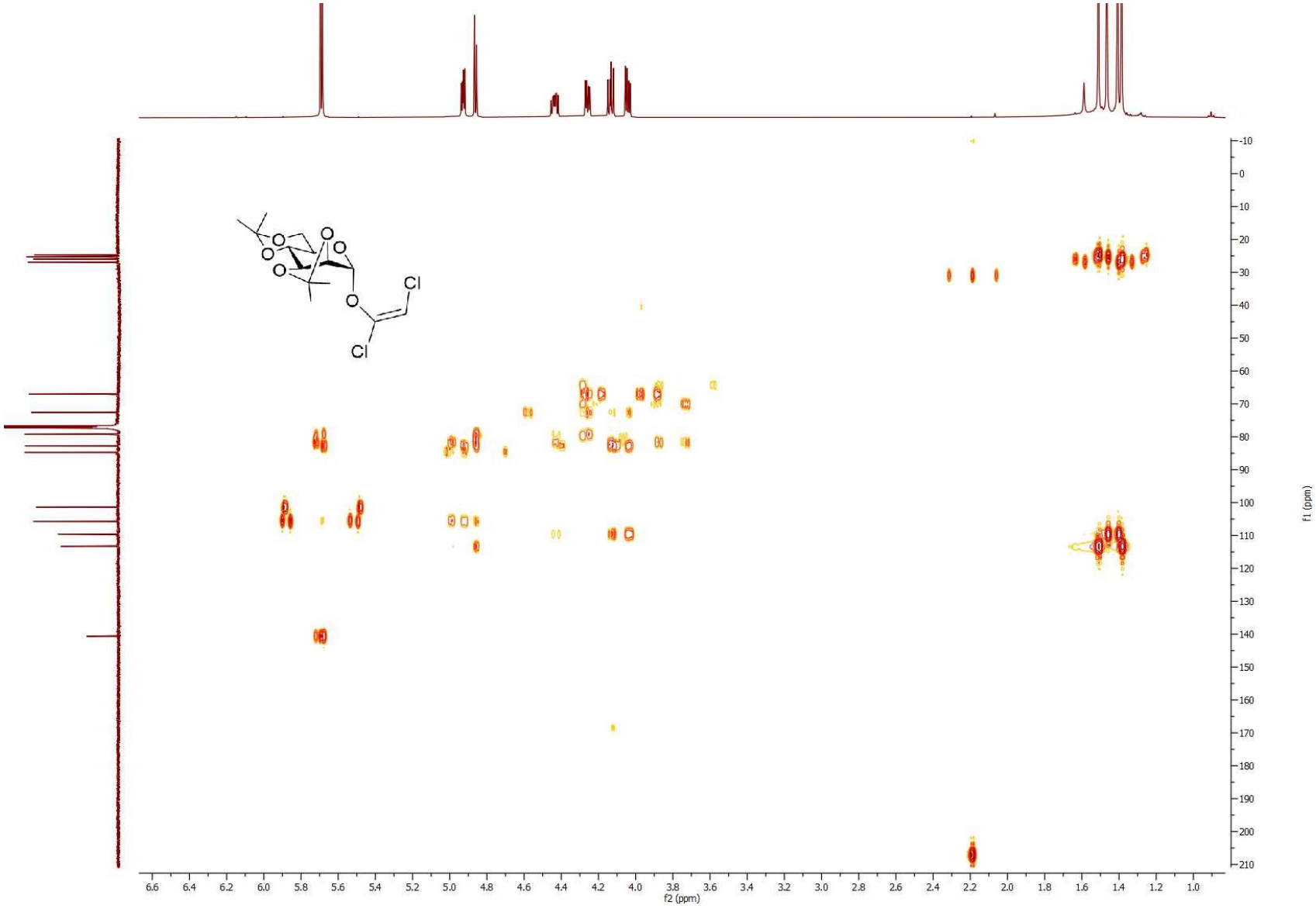
H-H COSY NMR



HSQC NMR

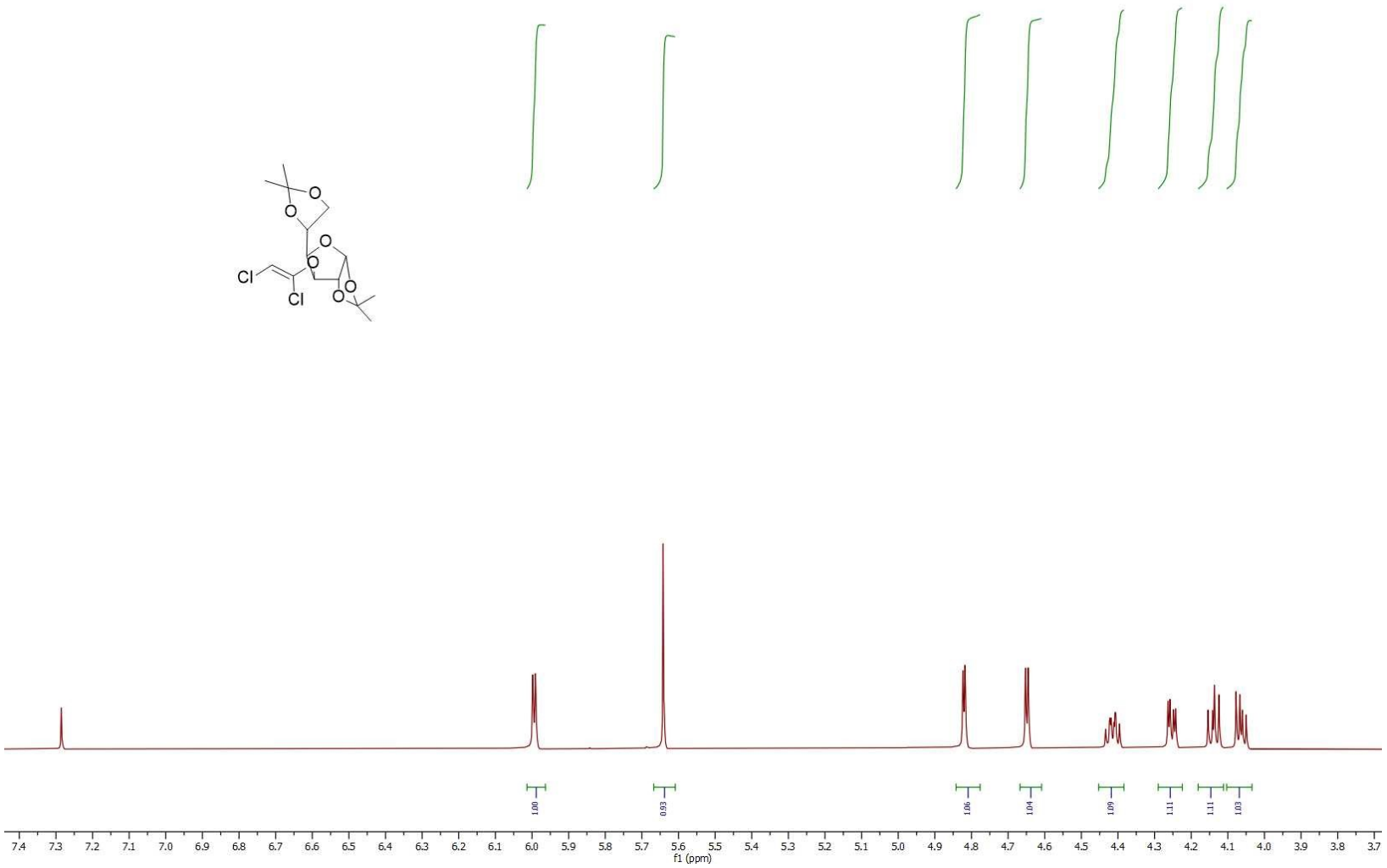

Cl
Cl
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

HMBC NMR

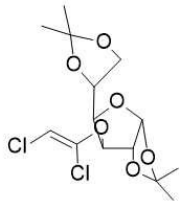


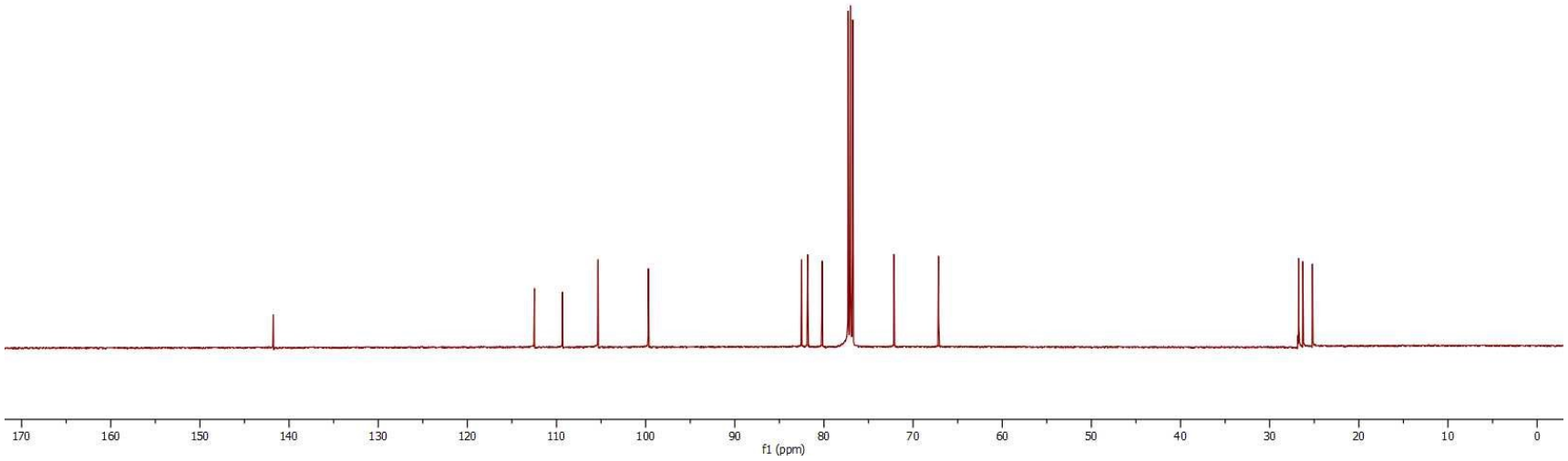
1,2-Dichlorovinyl 1,2:4,6-di-O-Isopropylidene- D-Glucofuranose (F2)

^{1}H NMR (500 MHz, $CDCl_3$)

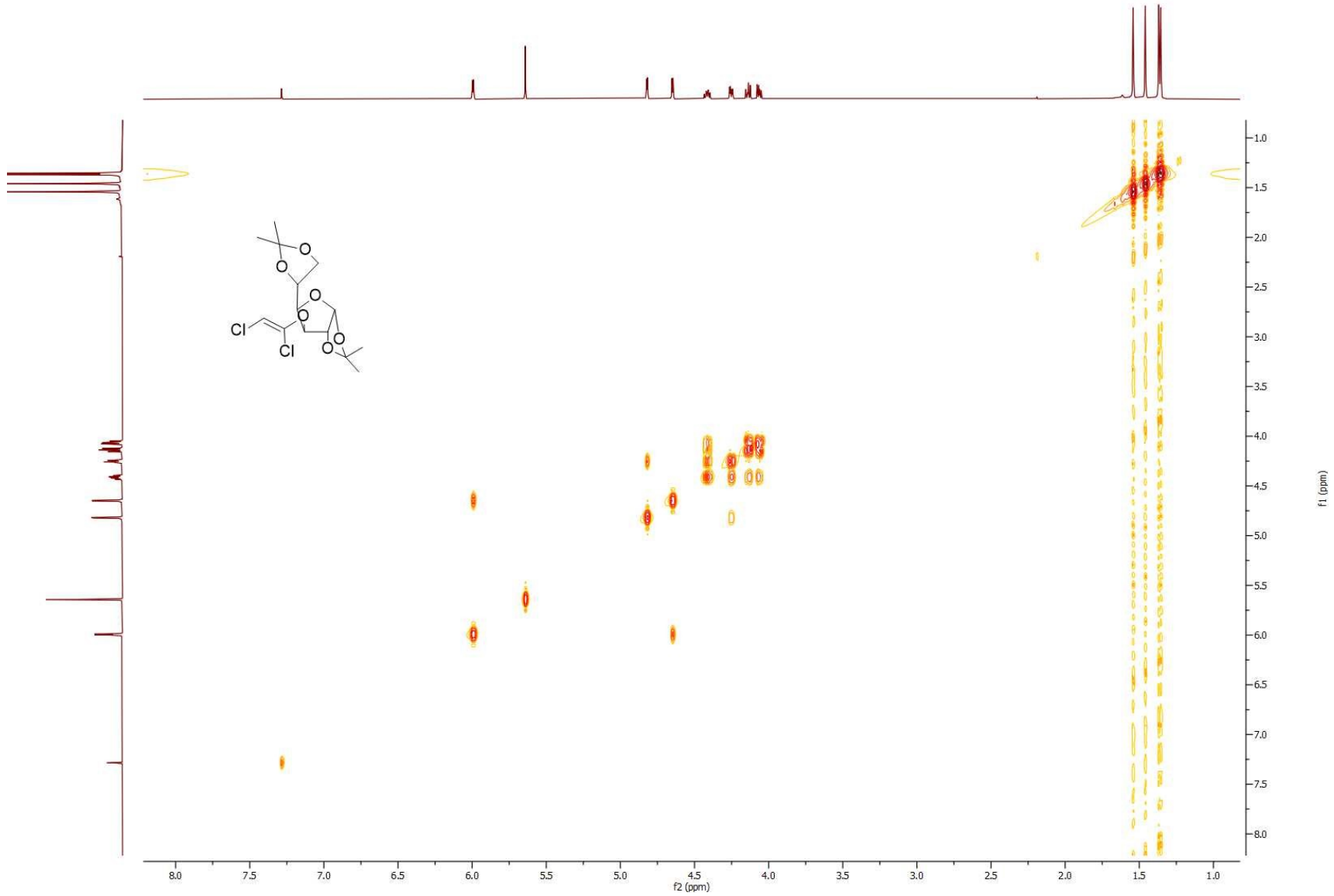


^{13}C NMR (126 MHz, $CDCl_3$)

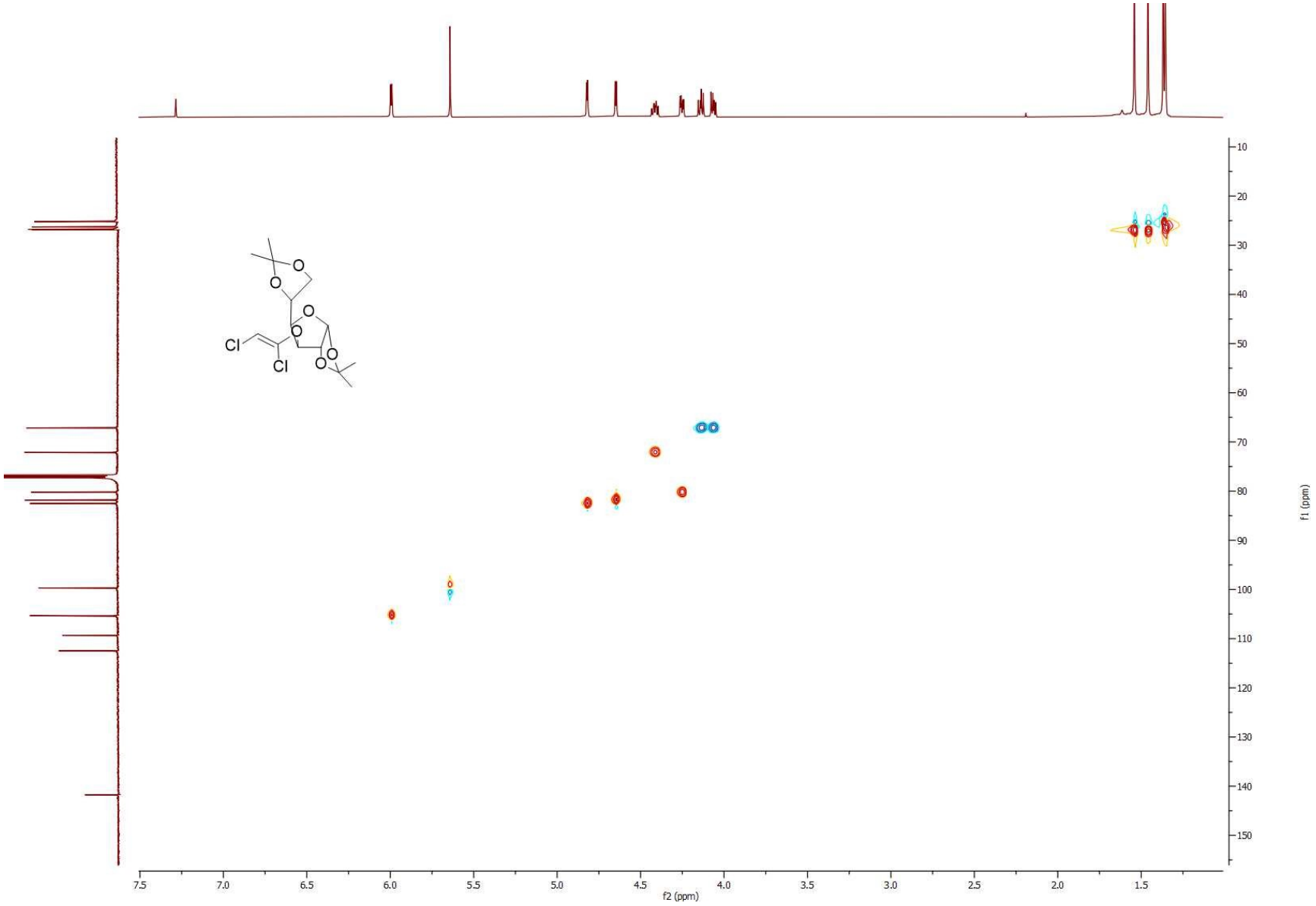




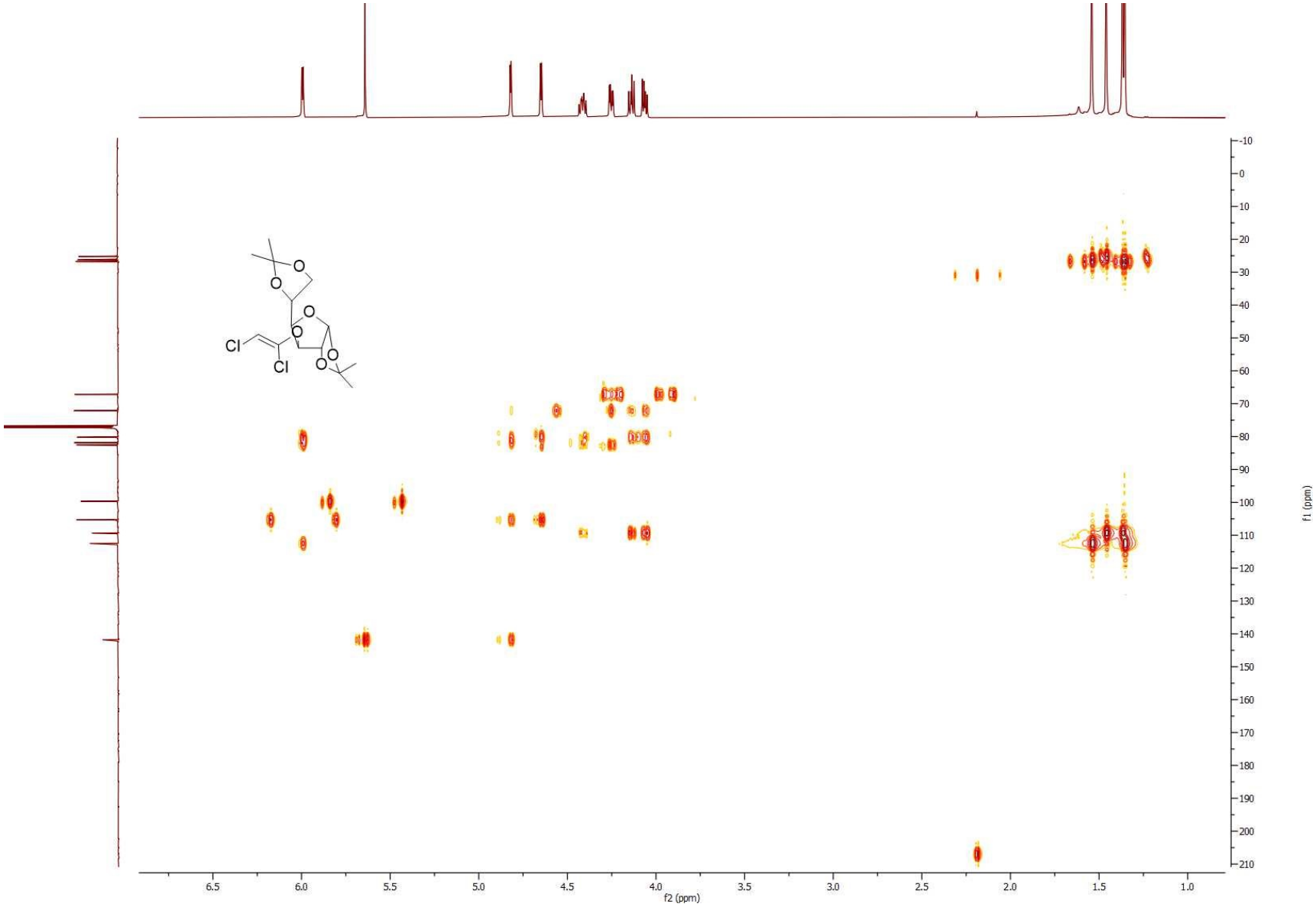
H-H COSY NMR



HSQC NMR

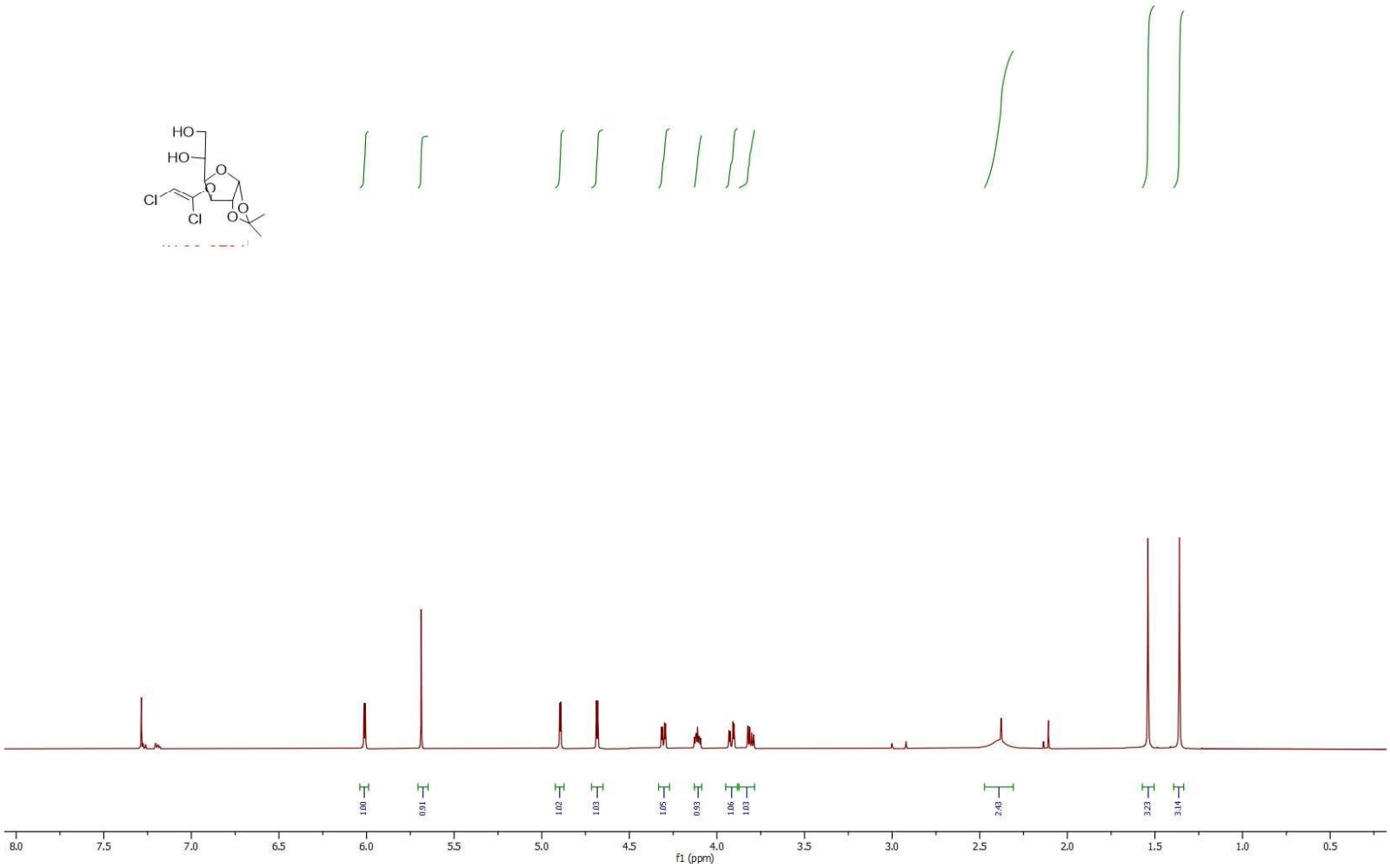

Cl
Cl
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

HMBC NMR

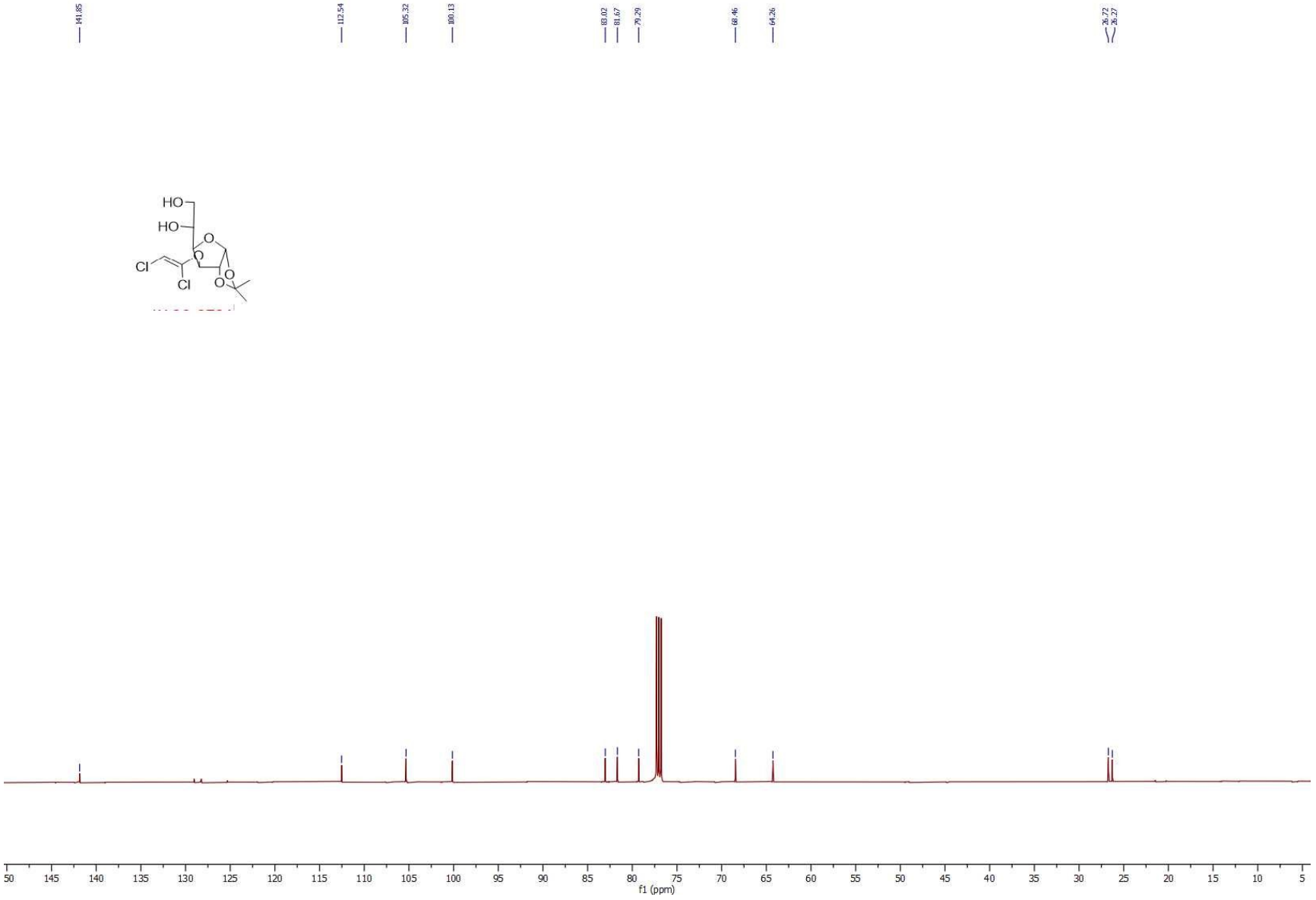


1,2-Dichlorovinyl 1,2-di-O-Isopropylidene- D-Glucofuranose (F3)

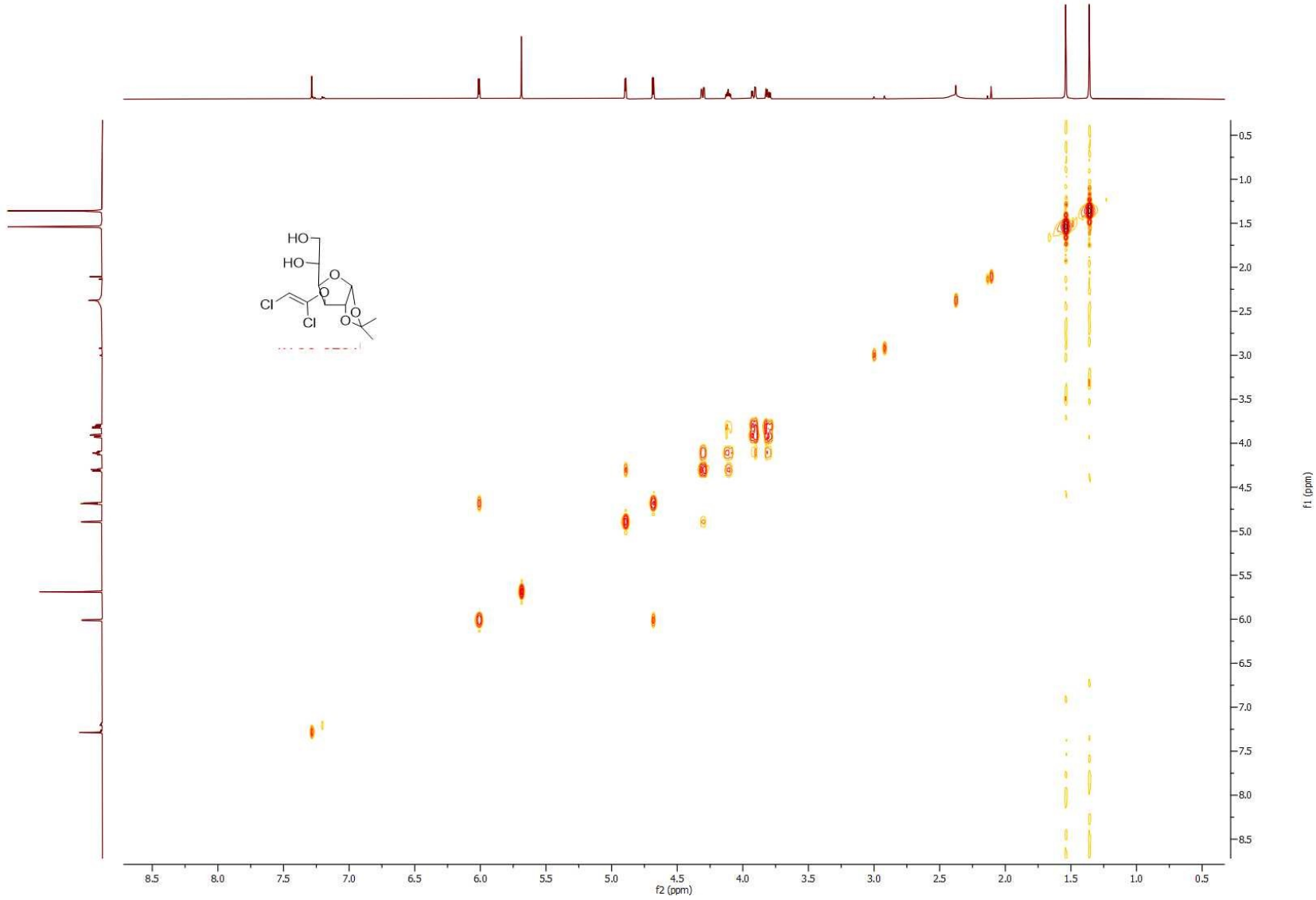
^{1}H NMR (500 MHz, $CDCl_3$)



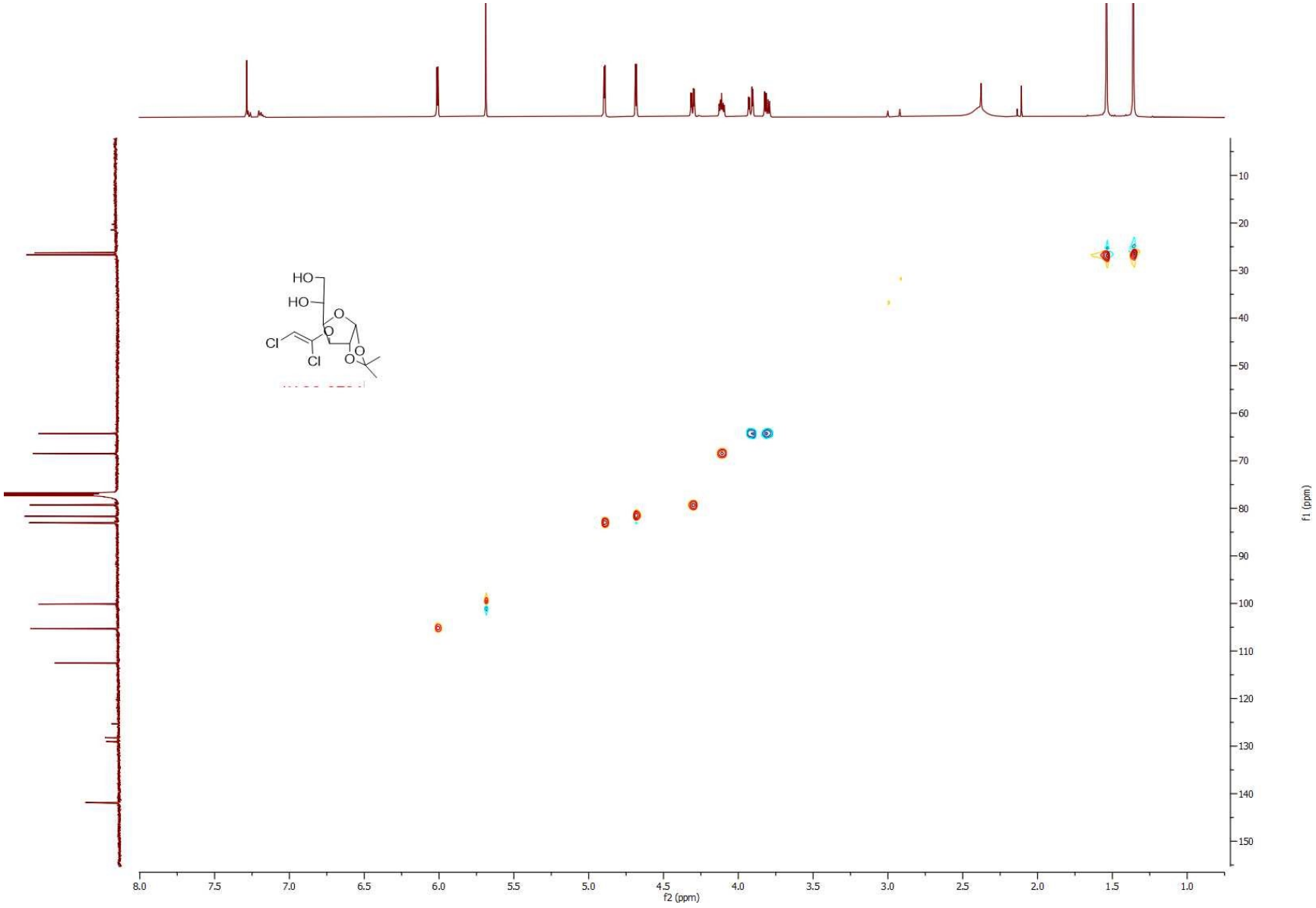
^{13}C NMR (126 MHz, $CDCl_3$)



H-H COSY NMR

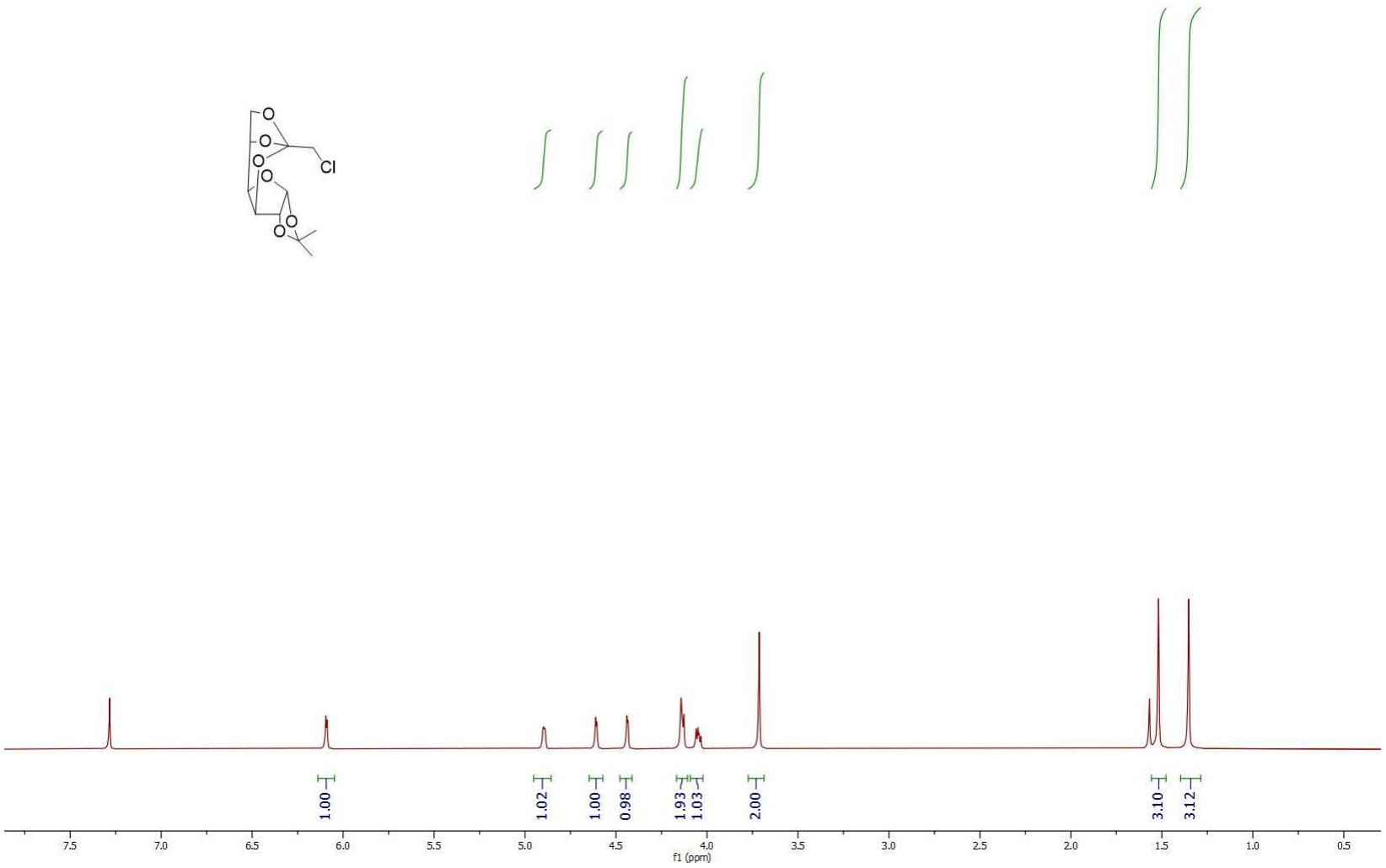

HO
HO
O
O
Cl
Cl
O
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
f1 (ppm)

HSQC NMR

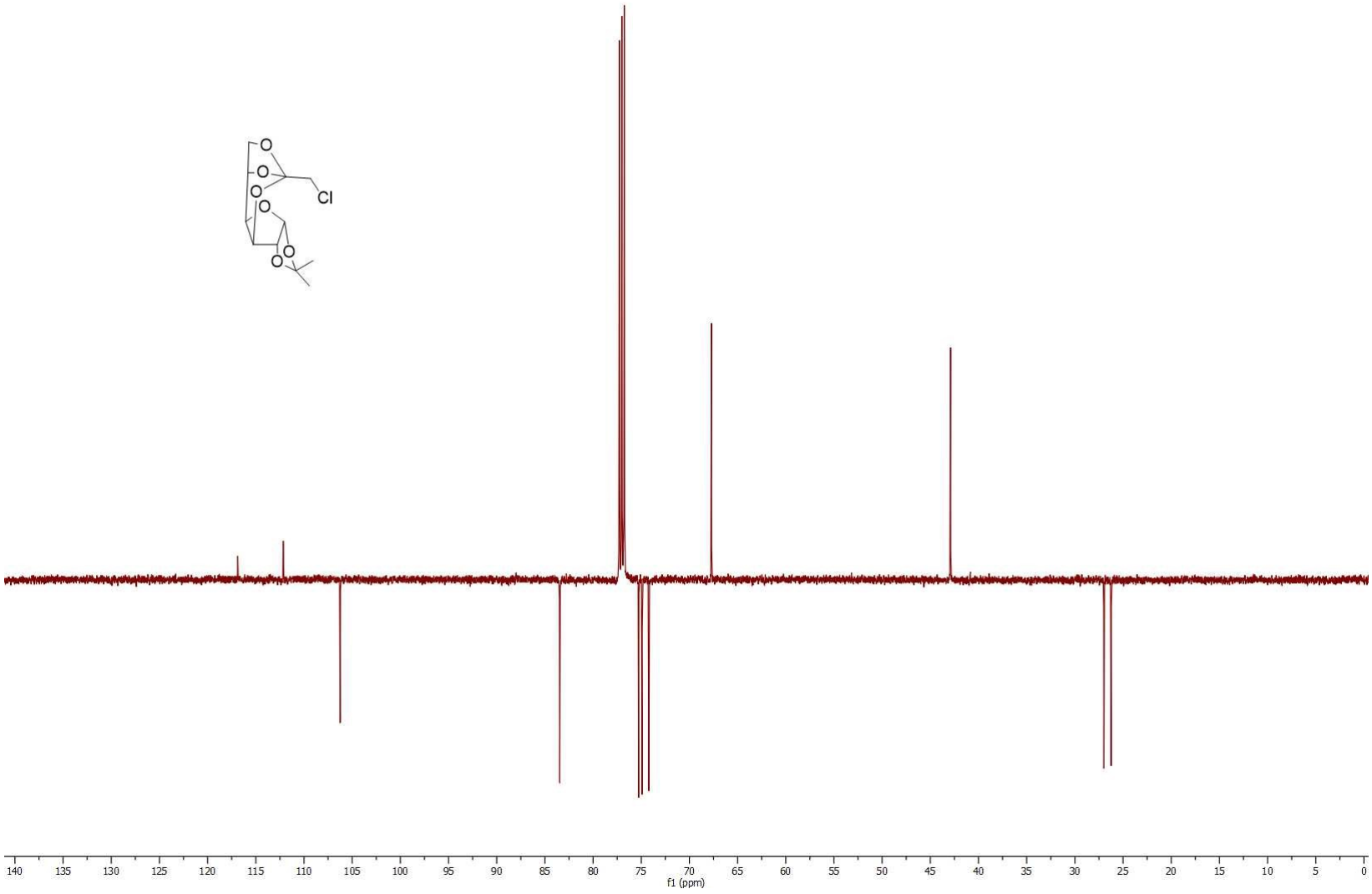

HO
HO
O
O
Cl
Cl
O
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

1,2-*O*-isopropylidene-3,5,6-*O*-chloromethyl-α-D-Glucofuranose(F4)

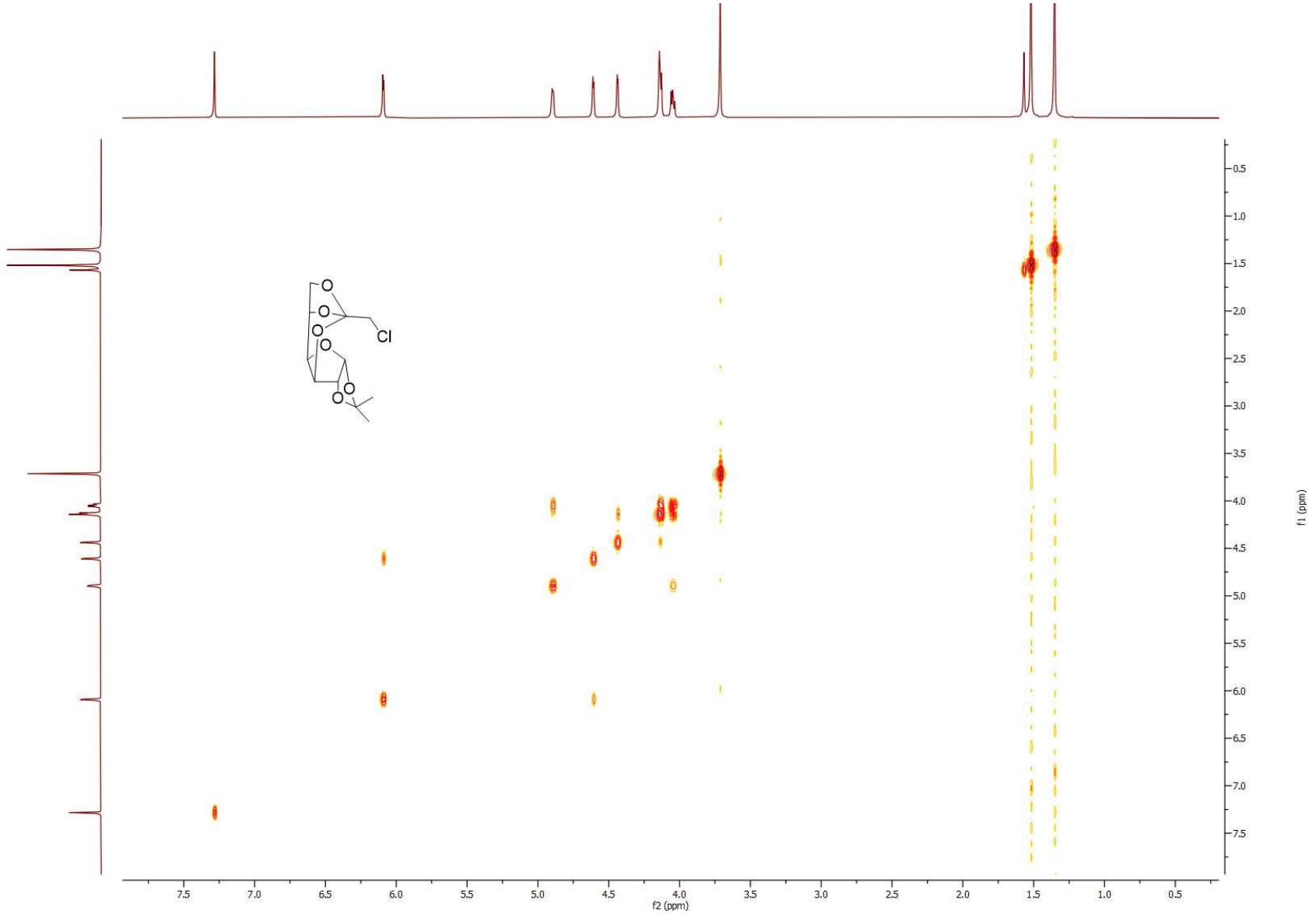
^{1}H NMR (500 MHz, $CDCl_3$)



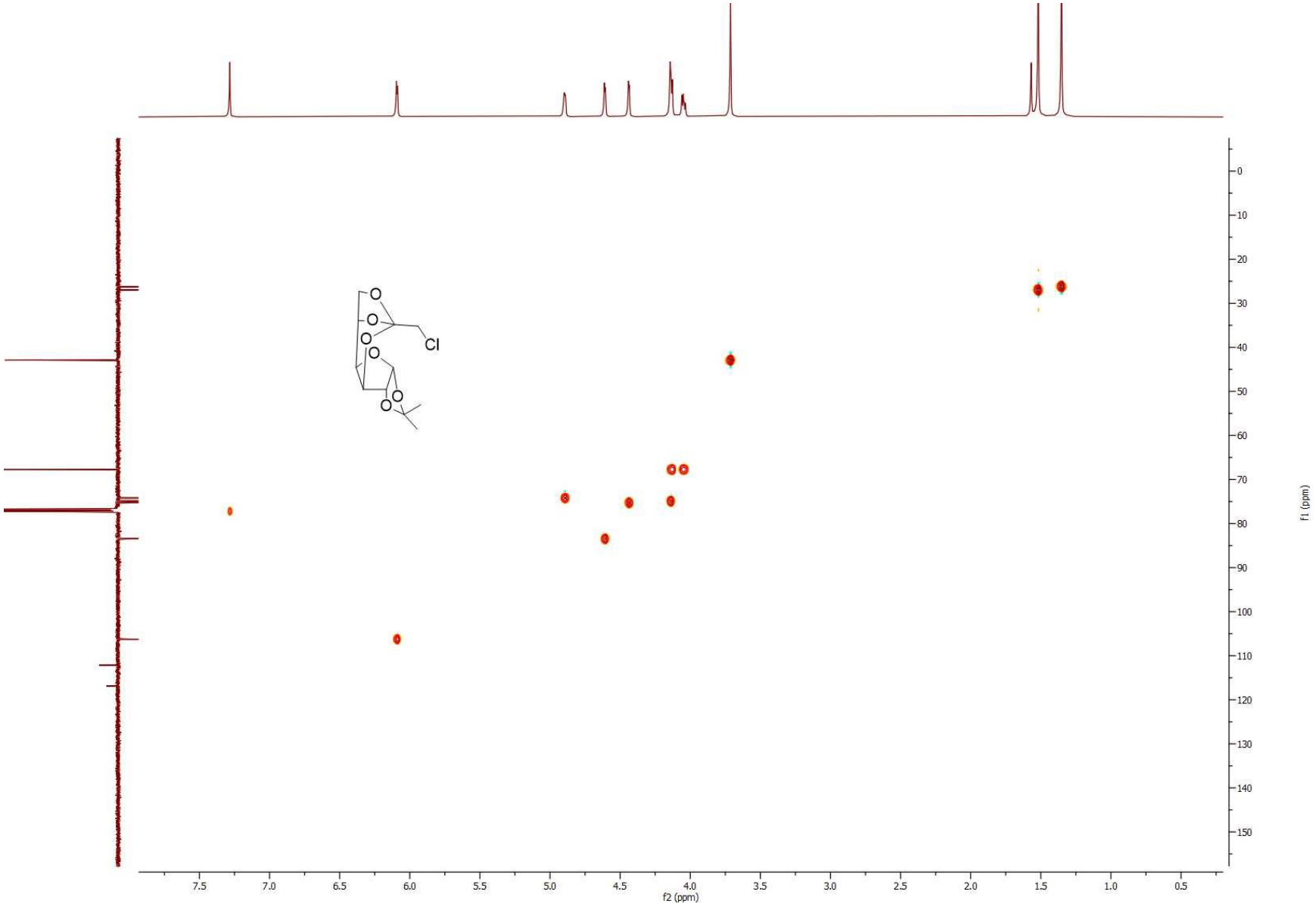
H-H COSY NMR


O
O
O
O
O
O
Cl
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

H-H COSY NMR


O
O
O
O
O
O
Cl
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)

HSQC NMR


O
O
O
O
O
O
Cl
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

HMBC NMR