Electronic Supplementary Material (ESI) for ChemComm.

Pd Catalyzed Synthesis of Hetero 1,2-Interlinked *C*-Disaccharides by Coupling of *iodo* Glycals with Glycals

Bisma Rasool[a,b], Irshad Ahmad Zargar[a,b], Nazar Hussain*[c], Debaraj Mukherjee*[a,b]

[a]Natural Products and Medicinal Chemistry Division, Indian Institute of Integrative Medicine (CSIR-IIIM), Jammu-180001, India.

[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.

[c]Department of Medicinal Chemistry Institute of Medical Sciences Banaras Hindu University/221005 Varanasi (India)

[d] Department of Chemical Sciences, Bose Institute Kolkata, EN 80, Sector V, Bidhan Nagar, Kolkata-700091, WB, India

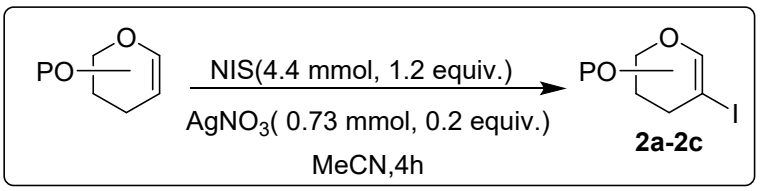
Table of Contents	
1. General Consideration	**S3**
2. General procedures	**S3-S4**
3. Characterization data: products	**S4-S15**
4. NMR spectra	**S16-S56**

1. General Consideration:

All reagents were purchased from commercial sources and used without treatment. Silica gel-coated aluminium plates were used for TLC. The products were purified by column chromatography on silica gel (60-120 mesh) using hexane-ethyl acetate as the eluent. ^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer in CDCl3 and Acetone-D_6, using CDCl3 (for ^{1}H, δ = 7.26) and acetone-d_6 (for ^{1}H, δ = 2.05) as the internal standard. ^{13}C NMR (101 MHz) spectra were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ using $CDCl_3$ (for ^{13}C, δ = 77.0) and acetone-d_6 (for ^{13}C, δ = 29.8) as the internal standard. Chemical shifts are expressed in parts per million (δ ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of the doublet, dt = doublet of triplet, m = multiplet, s br = singlet broad. The exact mass of all products was analysed by using HRMS having a QTOF analyser.

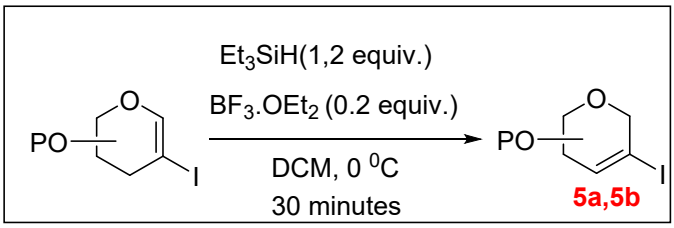
2. General procedures

2.1 General procedure for the Synthesis of 2-iodo glycals[1]



By taking Tri-*O*-acetyl-D-glucal as an example, To a stirred solution of Tri-*O*-acetyl-D-glucal (1 g) in dry CH_3CN (10 mL) at 80 °C under N_2 atmosphere was added successively NIS (991 mg, 4.4 mmol) and $AgNO_3$ (124 mg, 0.73 mmol) and stirred for 4 h. On consumption of starting material (TLC monitoring), the reaction mixture was filtered through sintered funnel and the filtrate was evaporated to give a crude product which was purified by silica gel column chromatography (30% of EtOAc/hexane) to obtain the resulting 2-*iodo* glycal.

2.2 Procedure for the Synthesis of C2-C3 unsaturated 2-iodo glycals:



To a stirred solution of 2-*iodo* glycal (1 equiv.) in DCM at 0 °C, add Et_3SiH (1.2 equiv.) and $BF_3.OEt_2$ (0.2 equiv.) and stir for 30 minutes. On consumption of starting material (TLC monitoring), the reaction mixture was quenched with triethyl amine and then diluted with ethyl acetate and washed with brine (20 mL). The organic layer was dried over magnesium sulphate

and then evaporated to dryness. The residue was purified by column chromatography over silica gel (60-120 mesh) with hexane/ ethyl acetate as eluent to afford the desired compound.

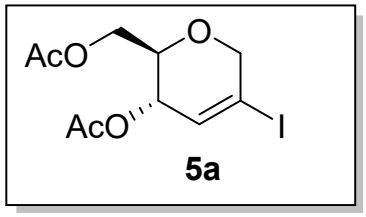
2.3 General experimental procedure for the synthesis of C2-C1 linked disaccharides (A):

To a solution of glycal (1 equiv.) in DMF (3 mL) taken in an oven dried sealed tube charged with magnetic bead, 2-*iodo* glycal (1.5 equiv.), $Pd(OAc)_2$ (0.10 equiv.) and PPh_3 (0.10 equiv.) were added. In the same solution, AgOAc (2 equiv.) was added and the reaction mixture was allowed to stir at 80 °C for 6 h. After the completion of the reaction, the reaction mixture was passed through celite, then filtered and extracted using ethyl acetate and washed with 20 mL of brine. The organic layer was dried over magnesium sulphate and evaporated to dryness. The residue was purified by column chromatography over silica gel (60-120 mesh) with hexane/ ethyl acetate as eluent to afford the desired compound.

2.4 General experimental procedure for the ring opening C2-C1 linked disaccharides (B):

To a stirred solution of C2-C1 linked disaccharide (1 equiv.) in DCM at 0 °C, add $BF_3.OEt_2$ (0.2 equiv.) and stir for 30 minutes. On consumption of starting material (TLC monitoring), the reaction mixture was quenched with triethyl amine and then diluted with ethyl acetate and washed with brine (20 mL). The organic layer was dried over magnesium sulphate and then evaporated to dryness. The residue was purified by column chromatography over silica gel (60-120 mesh) with hexane/ ethyl acetate as eluent to afford the desired compound.

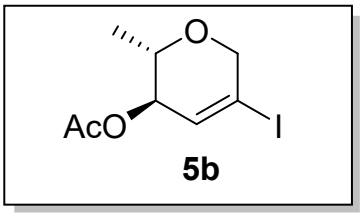
3. Characterization of the products:



5a

Prepared by general procedure **3.2** using Tri-*O*-acetyl-2-*iodo*-D-glucal (200 mg, 0.5 mmol), Et_3SiH (1.2 equiv.) and $BF_3.OEt_2$ (0.2 equiv.) in solvent DCM. The reaction mixture was stirred at 0 °C for 30 minutes and then quenched with triethyl amine. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 80:20) to afford **5a** as yellow oil in 71 % yield, 120 mg.

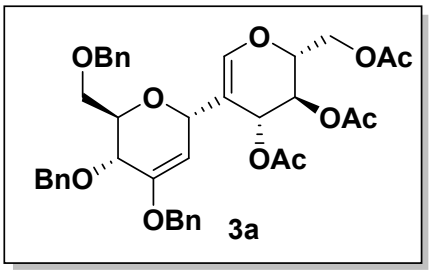
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (dd, J = 4.2, 2.2 Hz, 1H), 5.25 (dq, J = 8.1, 2.4 Hz, 1H), 4.24 (dd, J = 3.1, 2.2 Hz, 2H), 4.21 (d, J = 2.8 Hz, 1H), 4.19 – 4.15 (m, 1H), 3.80 (ddd, J = 8.4, 5.7, 2.9 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.80 (Cq), 170.04 (Cq), 133.46 (CH), 97.78 (Cq), 73.32 (CH), 72.98 (CH), 67.34 (CH), 62.87 (CH), 20.93 (CH_3), 20.81 (CH_3). **HRMS (ESI)** calcd for $C_{10}H_{17}INO_5$ $[M+NH_4]^+$:358.0151, found 358.0153



5b

Prepared by general procedure **3.2** using Tri-*O*-acetyl-2-*iodo*-D-glucal (200 mg, 0.5 mmol), Et_3SiH (1.2 equiv.) and $BF_3.OEt_2$ (0.2 equiv.) in solvent DCM. The reaction mixture was stirred at 0 °C for 30 minutes and then quenched with triethyl amine. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 85:15) to afford **5b** as yellow oil in 70 % yield, 98 mg.

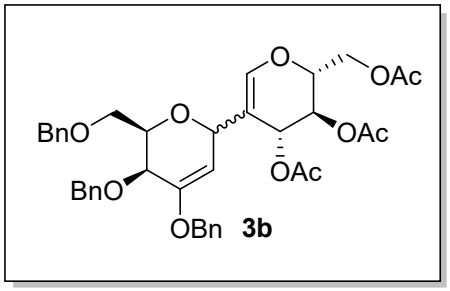
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (dd, J = 4.6, 2.1 Hz, 1H), 5.00 (ddd, J = 7.3, 5.0, 2.4 Hz, 1H), 4.18 (t, J = 2.2 Hz, 2H), 3.71 (dd, J = 7.2, 6.4 Hz, 1H), 2.09 (s, 3H), 1.24 (d, J = 6.4 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.30, 133.58, 98.62, 72.54, 72.35, 71.49, 21.03, 17.51 **HRMS (ESI)** calcd for $C_8H_{12}IO_3$ $[M+H]^+$: 281.9753, found 281.9755.



3a

Prepared by general procedure **A** using Tri-*O*-benzyl-D-glucal (50 mg, 0.12 mmol), $Pd(OAc)_2$ (0.006 mmol, 0.05 equiv.), PPh_3 (0.012 mmol, 0.10 equiv.), Tri-*O*-acetyl-2-*iodo*-D-glucal (0.179 mmol, 1.5 equiv.) and AgOAc (0.24 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 80:20) to afford **3a** as yellow oil in 75 % yield, 61.85 mg.

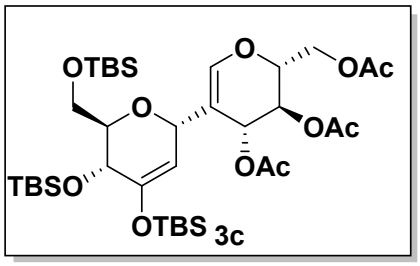
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.37 (m, 4H), 7.35 – 7.31 (m, 5H), 7.27 – 7.24 (m, 4H), 7.19 (dt, J = 6.6, 2.4 Hz, 2H), 6.41 (s, 1H), 5.63 – 5.54 (m, 1H), 5.19 (dd, J = 6.5, 5.0 Hz, 1H), 4.87 (s, 3H), 4.74 (d, J = 4.1 Hz, 1H), 4.60 (d, J = 12.2 Hz, 1H), 4.48 (d, J = 4.2 Hz, 1H), 4.45 (d, J = 2.8 Hz, 1H), 4.38 (dd, J = 12.0, 6.3 Hz, 1H), 4.25 – 4.18 (m, 2H), 4.11 (dd, J = 12.0, 3.5 Hz, 1H), 3.75 (ddd, J = 8.6, 3.9, 2.6 Hz, 1H), 3.65 (dd, J = 10.5, 4.1 Hz, 1H), 3.60 (dd, J = 10.5, 2.5 Hz, 1H), 2.06 (s, J = 1.9 Hz, 3H), 2.04 (s, 3H), 1.96 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.6 (Cq), 170.2 (Cq), 169.6 (Cq), 155.2 (Cq), 146.4 (CH), 138.2 (Cq), 138.2 (Cq), 136.7 (Cq), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.0 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.2 (CH), 109.5 (Cq), 95.7 (CH), 74.8 (CH_2), 73.6 (CH), 73.4 (CH_2), 71.5 (CH), 70.7 (CH), 69.2 (CH_2) , 69.0 (CH_2), 68.8 (CH), 67.4 (CH), 66.0 (CH), 61.3 (CH_2), 20.9 (CH_3), 20.8 (CH_3), 20.75 (CH_3). 6 CH resonances are missing in ^{13}C NMR due to the overlap. **HRMS (ESI)** calcd for $C_{39}H_{43}O_{11}$ $[M+H]^+$:687.2805, found 687.2808.



3b

Prepared by general procedure **A** using Tri-*O*-benzyl-D-galactal (50 mg, 0.12 mmol), $Pd(OAc)_2$ (0.006 mmol, 0.05 equiv.), PPh_3 (0.012 mmol, 0.10 equiv.),Tri-*O*-acetyl-2-*iodo*-D-glucal (0.179 mmol, 1.5 equiv.) and AgOAc (0.24 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 80:20) to afford **3b** as yellow oil as (α/β;4/1) mixture in 70 % yield, 57 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 4H), 7.25 – 7.23 (m, 5H), 7.21 – 7.18 (m, 6H), 6.19 (s, 1H), 5.56 (d, J = 5.2 Hz, 1H), 5.12 (dd, J = 6.8, 5.2 Hz, 1H), 4.89 (d, J = 3.6 Hz, 1H), 4.83 (d, J = 11.9 Hz, 1H), 4.77 (d, J = 11.7 Hz, 2H), 4.73 (d, J = 4.0 Hz, 1H), 4.58 (d, J = 11.7 Hz, 1H), 4.49 (d, J = 11.7 Hz, 1H), 4.41 (s, 1H), 4.31 (dd, J = 12.0, 6.1 Hz, 1H), 4.16 (dd, J = 6.5, 3.3 Hz, 1H), 4.05 (dd, J = 12.1, 3.3 Hz, 1H), 3.80 (dd, J = 6.2, 2.2 Hz, 1H), 3.75 (d, J = 2.2 Hz, 1H), 3.69 (dd, J = 9.7, 6.2 Hz, 1H), 3.57 (dd, J = 9.7, 6.2 Hz, 1H), 2.00 (s, 3H), 1.96 (s, 3H), 1.84 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.6 (Cq), 170.1 (Cq), 169.8 (Cq), 154.1 (Cq), 145.4 (CH), 138.5 (Cq), 138.3 (Cq), 136.5 (Cq), 128.6 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 127.3 (CH), 109.4 (Cq), 97.0 (CH), 73.7 (CH), 73.7 (CH_2), 73.1 (CH_2), 71.6 (CH), 70.6 (CH), 69.5 (CH_2), 69.2 (CH_2), 68.4 (CH), 67.4 (CH), 66.1 (CH), 61.3 (CH_2), 20.8 (CH_3), 20.7 (CH_3), 20.6 (CH_3). 4 CH resonances are missing in ^{13}C NMR due to the overlap. **HRMS(ESI)** calcd for $C_{39}H_{43}O_{11}$ $[M+H]^+$: 687.2805, found 687.2813.

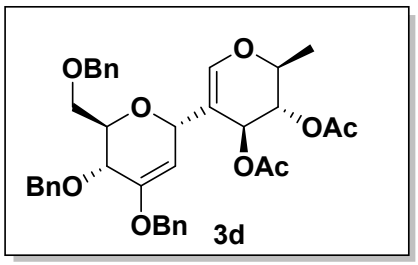


3c

Prepared by general procedure **A** using Tri-*O*-tertbutyldimethylsilyl-D-glucal (50 mg, 0.10 mmol), $Pd(OAc)_2$ (0.005 mmol, 0.05 equiv.), PPh_3 (0.01 mmol, 0.10 equiv.),Tri-*O*-acetyl-2-*iodo*-D-glucal (0.15 mmol,1.5 equiv.) and AgOAc (0.2 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over MgSO4 and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 90:10) to afford **3c** as yellow oil in 65 % yield, 49 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (s, 1H), 5.52 (d, *J* = 5.5 Hz, 1H), 5.12 (dd, *J* = 7.4, 5.5 Hz, 1H), 4.70 (d, *J* = 3.8 Hz, 1H), 4.61 (d, *J* = 3.7 Hz, 1H), 4.31 (dd, *J* = 12.0, 5.9 Hz, 1H), 4.21 –

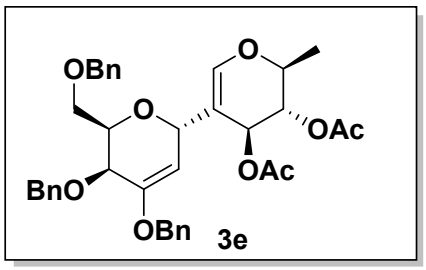
4.15 (m, 1H), 4.12 – 4.06 (m, 1H), 3.95 (dd, *J* = 7.0, 1.3 Hz, 1H), 3.64 (dd, *J* = 5.4, 4.4 Hz, 2H), 3.46 (dd, *J* = 7.0, 4.7 Hz, 1H), 2.00 (s, 3H), 1.95 (s, 2H), 1.95 (s, 3H), 0.86 (s, 9H), 0.80 (s, 9H), 0.79 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H), 0.01 (s, 3H), -0.00 (s, 3H), -0.04 (s, 3H), -0.05 (s, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.6 (Cq), 170.1 (Cq), 169.8 (Cq), 151.7 (Cq), 145.9 (CH), 110.5 (Cq), 102.7 (CH), 75.4 (CH), 73.8 (CH), 68.4 (CH), 67.6 (CH), 66.7 (CH), 66.6 (CH), 62.8 (CH_2), 61.5 (CH_2), 26.3 (CH_3), 26.0 (CH_3), 26.0 (CH_3), 25.8 (CH_3), 25.8 (CH_3), 24.7 (CH_3), 22.7 (CH_3), 20.9 (CH_3), 20.8 (CH_3), 20.8 (CH_3), 18.9 (Cq), 18.4 (Cq), 18.3 (Cq),-3.4 (CH_3), -4.6 (CH_3), -5.4 (CH_3), -5.4 (CH_3). 1 CH3 resonance is missing in ^{13}C NMR due to overlap. **HRMS** calcd for $C_{36}H_{67}O_{11}Si_3$ $[M+H]^+$: 759.3991, found 759.3994.



3d

Prepared by general procedure A using Tri-*O*-benzyl-D-glucal (50 mg, 0.12 mmol), $Pd(OAc)_2$ (0.002 mmol, 0.05 equiv.), PPh_3 (0.012 mmol, 0.10 equiv.), Di-*O*-acetyl-2-*iodo*-L- rhamnal (0.18 mmol,1.5 equiv.) and AgOAc (0.24 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 85:15) to afford **3d** as yellow oil in 68 % yield, 51 mg.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.38 (d, *J* = 4.5 Hz, 4H), 7.33 – 7.31 (m, 5H), 7.26 (d, *J* = 1.8 Hz, 4H), 7.22 (dd, *J* = 7.3, 2.4 Hz, 2H), 6.55 (s, 1H), 5.45 (d, *J* = 3.9 Hz, 1H), 4.94 (dd, *J* = 4.8, 4.1 Hz, 1H), 4.87 (d, *J* = 5.4 Hz, 2H), 4.86 – 4.83 (m, 2H), 4.74 (d, *J* = 3.8 Hz, 1H), 4.51 (d, *J* = 11.1 Hz, 1H), 4.47 (d, *J* = 4.1 Hz, 2H), 4.22 – 4.15 (m, 2H), 3.88 – 3.81 (m, 1H), 3.66 – 3.61 (m, 1H), 3.49 (dd, *J* = 10.4, 2.9 Hz, 1H), 2.07 (s, 3H), 1.90 (s, 3H), 1.29 (d, *J* = 6.7 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 170.6 (Cq), 169.9 (Cq), 154.3 (Cq), 146.7 (CH), 138.3 (Cq), 138.0 (Cq), 136.8 (Cq), 128.5 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.7 (CH), 127.4 (CH), 127.3 (CH), 107.5 (Cq), 97.1 (CH), 74.3 (CH_2), 73.3 (CH_2), 72.2 (CH), 71.9 (CH), 71.5 (CH), 71.2 (CH), 70.8 (CH), 69.1 (CH_2), 68.7 (CH_2), 67.6 (CH), 21.01 (CH_3),21.01 (CH_3),16.0 (CH_3). 4 CH resonances are missing in ^{13}C NMR due to overlap. **HRMS (ESI)** calculated $C_{37}H_{41}O_9$ $[M+H]^+$: 629.2751, Found:629.2755

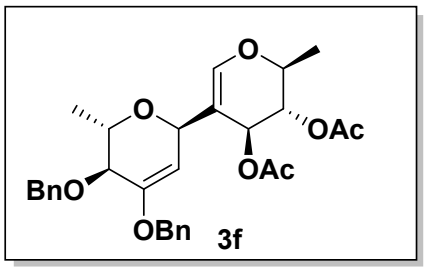


3e

Prepared by general procedure **A** using Tri-*O*-benzyl-D-galactal (50 mg, 0.12 mmol), $Pd(OAc)_2$ (0.002 mmol, 0.05 equiv.), PPh_3 (0.012 mmol, 0.10 equiv.),Di-*O*-acetyl-2-

iodo-L- rhamnal (0.18 mmol, 1.5 equiv.) and AgOAc (0.24 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 85:15) to afford **3e** as yellow oil in 70% yield, 52 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 4.5 Hz, 4H), 7.33 – 7.31 (m, 5H), 7.26 (d, J = 1.8 Hz, 4H), 7.24 – 7.21 (m, 2H), 6.55 (s, 1H), 5.45 (d, J = 3.9 Hz, 1H), 4.94 (dd, J = 4.8, 4.1 Hz, 1H), 4.87 (d, J = 5.4 Hz, 2H), 4.85 – 4.83 (m, 2H), 4.74 (d, J = 3.8 Hz, 1H), 4.52 (d, J = 6.5 Hz, 1H), 4.50 – 4.47 (m, 2H), 4.22 – 4.14 (m, 2H), 3.88 – 3.81 (m, 1H), 3.63 (dd, J = 10.4, 4.2 Hz, 1H), 3.49 (dd, J = 10.4, 2.9 Hz, 1H), 2.07 (s, 3H), 1.90 (s, 3H), 1.29 (d, J = 6.7 Hz, 3H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.6 (Cq), 169.9 (Cq), 153.5 (Cq), 145.9 (CH), 138.6 (Cq), 138.1 (Cq), 136.6 (Cq), 128.6 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 107.2 (Cq), 97.9 (CH), 73.3 (CH_2), 73.1 (CH_2), 71.95 (CH), 72.0 (CH), 71.7 (CH), 71.5 (CH), 70.2 (CH), 69.2 (CH_2), 69.0 (CH_2), 67.8 (CH), 21.0 (CH_3), 21.0 (CH_3), 16.1 (CH_3). 7 CH resonances are missing in ^{13}C NMR due to overlap. **HRMS (ESI)** calculated $C_{37}H_{41}O_9$ $[M+H]^+$: 629.2772, Found; 629.2774.

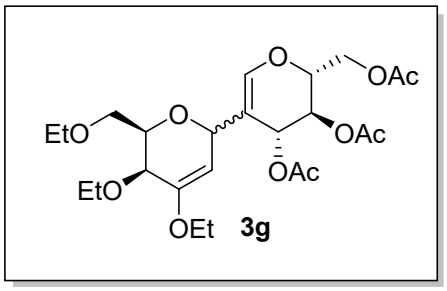


3f

Prepared by general procedure **A** using Di-*O*-benzyl-L-rhamnal (50 mg, 0.16 mmol), $Pd(OAc)_2$ (0.007 mmol, 0.05 equiv.), PPh_3 (0.016 mmol, 0.10 equiv.), Di-*O*-acetyl-2-*iodo*-L- rhamnal (0.24 mmol, 1.5 equiv.) and AgOAc (0.32 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 87:13) to afford **3f** as yellow oil in 72 % yield, 60 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 3.7, 1.8 Hz, 4H), 7.32 – 7.30 (m, 4H), 7.29 (dd, J = 2.7, 1.5 Hz, 1H), 7.26 (s, 1H), 6.36 (s, 1H), 5.56 (d, J = 5.5 Hz, 1H), 4.98 (dd, J = 7.3, 5.7 Hz, 1H), 4.91 (d, J = 11.0 Hz, 1H), 4.87 (d, J = 1.1 Hz, 2H), 4.76 (d, J = 3.9 Hz, 1H), 4.74 (d, J = 3.9 Hz, 1H), 4.61 (d, J = 11.1 Hz, 1H), 4.13 – 4.08 (m, 1H), 3.77 (dd, J = 7.6, 6.0 Hz, 1H), 3.75 – 3.72 (m, 1H), 2.06 (s, 2H), 2.03 (s, 2H), 1.28 (d, J = 6.6 Hz, 3H), 1.23 (d, J = 5.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.5 (Cq), 170.1 (Cq), 154.6 (Cq), 146.5 (CH), 138.3 (Cq), 136.8 (Cq), 128.6 (CH), 128.4 (CH), 128.4 (CH), 127.9 (CH), 127.8 (CH), 127.3 (CH),

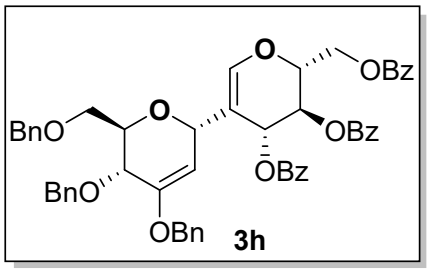
109.5 (Cq), 96.3 (CH), 77.3 (CH_2), 74.5 (CH_2), 72.3 (CH), 72.2 (CH), 69.1 (CH), 68.3 (CH), 67.2 (CH), 67.0 (CH), 20.9 (CH_3), 20.9 (CH_3), 18.3 (CH_3), 16.5 (CH_3). 4 CH resonances are missing in ^{13}C NMR due to overlapping. **HRMS (ESI)** calculated $C_{30}H_{35}O_8$ $[M+H]^+$: 523.2332, Found; 523.2335.



3g

Prepared by general procedure A using Tri-*O*-ethyl-D-glucal (50 mg, 0.21 mmol), $Pd(OAc)_2$ (0.010 mmol, 0.05 equiv.), PPh_3 (0.021 mmol, 0.10 equiv.),Tri-*O*-acetyl-2-*iodo*-D-glucal (0.31 mmol, 1.5 equiv.) and AgOAc (0.42 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 88:12) to afford **3g** as (α/β;4/1) as yellow oil in 75 % yield, 79 mg.

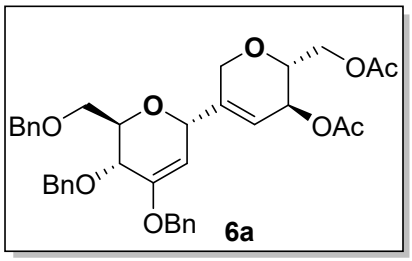
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (s, 1H), 5.49 (d, J = 3.5 Hz, 1H), 5.13 (ddd, J = 6.9, 5.1, 2.1 Hz, 1H), 4.77 (s, 1H), 4.55 – 4.51 (m, 1H), 4.37 – 4.30 (m, 2H), 4.19 (d, J = 2.3 Hz, 1H), 4.07 (dd, J = 12.1, 3.1 Hz, 1H), 3.90 (d, J = 7.7 Hz, 1H), 3.83 (ddd, J = 9.2, 4.8, 2.2 Hz, 1H), 3.70 – 3.66 (m, 2H), 3.53 (s, 3H), 3.48 – 3.42 (m, 2H), 2.01 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.18 (d, 3H), 1.14 (d, J = 1.9 Hz, 3H), 1.12 (d, J = 1.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.6 (Cq), 170.2 (Cq), 169.7 (Cq), 155.6 (Cq), 146.2 (CH), 109.9 (Cq), 94.0 (CH), 73.6 (CH), 71.5 (CH), 70.6 (CH), 69.4 (CH_2), 68.7 (CH), 67.9 (CH_2), 67.5 (CH), 67.0 (CH_2), 66.1 (CH), 62.7 (CH_2), 61.3 (CH_2), 20.9 (CH_2), 20.8 (CH_2), 20.7 (CH_2), 15.6 (CH_3), 15.1 (CH_3), 14.5 (CH_3). **HRMS (ESI)** calculated $C_{24}H_{37}O_{11}$ $[M+H]^+$: 501.2336, Found: 501.2338.



3h

Prepared by general procedure A using Tri-O-benzyl-D-glucal (50 mg, 0.12 mmol), Pd(OAc)2 (0.006 mmol, 0.05 equiv.), PPh3 (0.012 mmol, 0.10 equiv.),Tri-O-benzoyl-2-iodo-D-glucal (0.18 mmol, 1.5 equiv.) and AgOAc (0.24 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over MgSO4 and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 88:12) to afford 3h as yellow oil in 75 % yield, 92 mg.

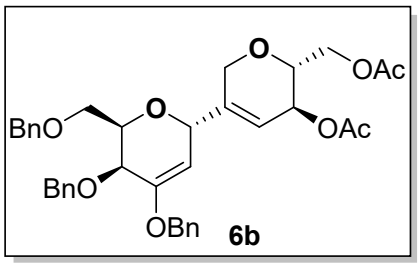
^{1}H NMR (400 MHz, Acetone d6) δ 7.93 – 7.82 (m, 7H), 7.53 – 7.47 (m, 3H), 7.38 – 7.31 (m, 7H), 7.31 – 7.22 (m, 4H), 7.19 – 7.12 (m, H), 6.62 (s, 1H), 5.97 (d, J = 4.1 Hz, 1H), 5.68 (t, J = 4.3 Hz, 1H), 4.97 (d, J = 4.1 Hz, 1H), 4.90 – 4.86 (m, 2H), 4.83 (d, J = 12.0 Hz, 1H), 4.78 (d, J = 11.2 Hz, 1H), 4.71 (dt, J = 11.2, 5.3 Hz, 2H), 4.52 (dd, J = 11.1, 3.7 Hz, 1H),4.33 (d, J = 12.3 Hz, 1H), 4.28 (d, J=12.3 Hz,1H), 3.99 (dd, J = 8.5, 1.0 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.45 – 3.42 (m, 1H). 13C NMR (101 MHz, Acetone d6) δ 164.5 (Cq), 164.7 (Cq),162.4 (Cq) 154.8 (Cq), 146.2 (CH), 138.9 (Cq), 138.8 (Cq), 137.4 (Cq), 138.9 (Cq), 138,8 (Cq), 137.4 (Cq), 133.4 (CH), 133.3 (CH), 133.2 (CH), 129.6 (CH), 129.5 (CH), 129.4 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 127.3 (CH), 127.1 (CH), 109.6 (Cq), 96.5 (CH), 73.5 (CH_2), 73.2 (CH), 72.8 (CH_2), 71.7 (CH), 71.2 (CH), 69.6 (CH_2), 68.9(CH), 68.8 (CH_2), 67.7 (CH), 65.2 (CH), 61.8 (CH_2). 14 CH resonances are missing in ^{13}C NMR due to overlapping. **HRMS (ESI)** calculated $C_{54}H_{49}O_{11}$ $[M+H]^+$: 872.3197, Found: 872.3198.



6a

Prepared by general procedure A using Tri-O-benzyl-D-glucal (50 mg, 0.12 mmol), Pd(OAc)2 (0.006 mmol, 0.05 equiv.), PPh3 (0.012 mmol, 0.10 equiv.), Di-O-acetyl-2-iodo-D- glucal (0.18 mmol,1.5 equiv.) and AgOAc (0.24 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 hrs. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over MgSO4 and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 85:15) to afford 6a as yellow oil in 75 % yield, 56 mg.

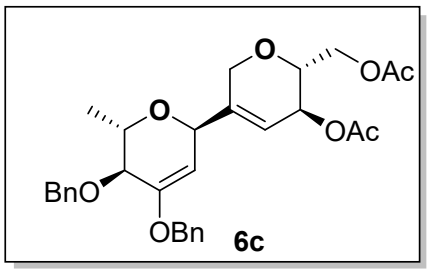
^{1}H NMR (400 MHz, CDCl3) δ 7.39 – 7.36 (m, 5H), 7.33 – 7.31 (m, 5H), 7.25 (d, J = 1.1 Hz, 3H), 7.22 – 7.18 (m, 2H), 5.63 (s, 1H), 5.29 (d, *J* = 8.5 Hz, 1H), 4.89 – 4.84 (m, 2H), 4.73 (d, *J* = 3.8 Hz, 1H), 4.70 (d, *J* = 3.6 Hz, 1H), 4.56 (d, *J* = 12.2 Hz, 1H), 4.46 (dd, *J* = 16.7, 11.8 Hz, 3H), 4.22 – 4.18 (m, 2H), 4.17 – 4.13 (m, 2H), 3.83 – 3.78 (m, 1H), 3.64 – 3.58 (m, 2H), 3.55 (dd, *J* = 10.4, 3.1 Hz, 1H), 2.10 (s, 3H), 2.07 (s, *J* = 3.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0 (Cq), 170.2 (Cq), 154.5 (Cq), 140.9 (Cq), 138.1 (Cq), 137.9 (Cq), 136.6 (Cq), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.3 (CH), 127.9 (CH), 127.9 (CH), 127.7 (CH), 127.3 (CH), 122.9 (CH), 96.0 (CH), 74.0 (CH_2), 73.9 (CH), 73.3 (CH_2), 72.3 (CH), 71.5 (CH), 71.1 (CH), 69.2 (CH_2), 68.5 (CH_2), 66.0 (CH_2), 65.3 (CH), 63.12 (CH_2), 21.1 (CH_3), 20.9 (CH_3). 7 CH resonances are missing in ^{13}C NMR due to overlapping. **HRMS (ESI)** calculated $C_{37}H_{44}NO_9$ $[M+NH_4]^+$: 646.3016, Found; 646.3017.



6b

Prepared by general procedure **A** using Tri-*O*-benzyl-D-galactal (50 mg, 0.12 mmol), $Pd(OAc)_2$ (0.006 mmol, 0.05 equiv.), PPh_3 (0.012 mmol, 0.10 equiv.),Di-*O*-acetyl-2-*iodo*-D- glucal (0.18 mmol, 1.5 equiv.) and AgOAc (0.24 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 85:15) to afford **6b** as yellow oil in 70 % yield, 53 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 15H), 5.52 (s, J = 9.7 Hz, 1H), 5.28 (d, J = 8.0 Hz, 1H), 4.91 (d, J = 11.9 Hz, 1H), 4.83 (dd, J = 15.5, 3.6 Hz, 3H), 4.77 (s, 1H), 4.65 (d, J = 11.6 Hz, 1H), 4.54 – 4.45 (m, 3H), 4.23 (dd, J = 11.6, 2.0 Hz, 1H), 4.17 (dd, J = 12.3, 5.6 Hz, 2H), 3.86 (td, J = 6.2, 2.0 Hz, 1H), 3.83 (d, J = 2.1 Hz, 1H), 3.71 – 3.60 (m, 3H), 2.10 (s, 3H), 2.08 (s, J = 0.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.0 (Cq), 170.3 (Cq), 154.0 (Cq), 140.6 (Cq), 138.4 (Cq), 138.1 (Cq), 136.5 (Cq), 128.6 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 127.6 (CH), 127.3 (CH), 122.6 (CH), 96.7 (CH), 73.9 (CH), 73.5 (CH_2), 73.2 (CH_2), 71.7 (CH), 71.4 (CH), 71.1 (CH), 69.2 (CH_2), 69.2 (CH_2), 66.3 (CH_2), 65.4 (CH), 63.1 (CH), 21.1 (CH_3), 20.9 (CH_3). 6 CH resonances are missing in ^{13}C NMR due to overlapping. **HRMS (ESI)** calculated $C_{37}H_{41}O_9$ $[M+H]^+$: 629.2751, Found; 629.2755.

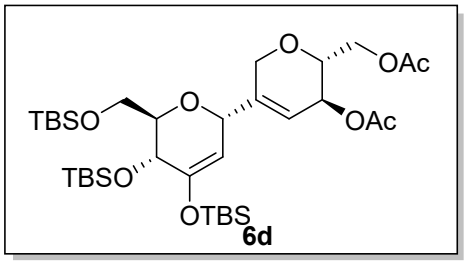


6c

Prepared by general procedure A using Di-*O*-benzyl-L-rhamnal (50 mg, 0.16 mmol), $Pd(OAc)_2$ (0.008 mmol, 0.05 equiv.), PPh_3 (0.016 mmol, 0.10 equiv.), Di-*O*-acetyl-2-*iodo*-D-glucal (0.192 mmol, 1.5 equiv.) and AgOAc (0.32 mol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 85:15) to afford **6c** as yellow oil in 72% yield, 60 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (ddd, J = 5.3, 3.7, 2.1 Hz, 4H), 7.32 – 7.26 (m, 6H), 5.67 – 5.64 (m, 1H), 5.29 – 5.24 (m, 1H), 4.87 – 4.83 (m, 3H), 4.78 (d, J = 3.4 Hz, 1H), 4.69 – 4.66 (m, 1H), 4.63 (d, J = 11.3 Hz, 1H), 4.27 (d, J = 1.7 Hz, 2H), 4.22 (dd, J = 12.1, 2.8 Hz, 1H),

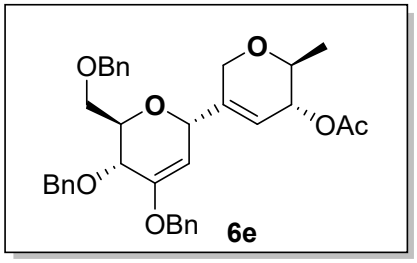
4.15 (dd, *J* = 12.1, 6.0 Hz, 1H), 3.91 – 3.86 (m, 1H), 3.72 (dd, *J* = 5.9, 1.3 Hz, 1H), 3.68 (ddd, *J* = 8.6, 6.0, 2.8 Hz, 1H), 2.10 (s, 3H), 2.08 (s, *J* = 1.5 Hz, 3H), 1.23 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 171.0 (Cq), 170.5 (Cq), 153.6 (Cq), 141.3 (Cq), 138.2 (Cq), 136.6 (Cq), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 127.4 (CH), 122.2 (CH), 96.3 (CH), 76.5 (CH), 74.0 (CH), 73.6 (CH_2), 71.4 (CH), 69.6 (CH), 69.1 (CH_2), 66.3 (CH_2), 65.4 (CH), 63.2 (CH_2), 21.2 (CH_3), 20.9 (CH_3), 17.6 (CH_3). **HRMS (ESI)** calculated $C_{30}H_{38}NO_8$ $[M+NH_4]^+$: 540.2597, Found; 540.2597.



6d

Prepared by general procedure A using Tri-O-tertbutyldimethylsilyl-D-glucal (50 mg, 0.10 mmol), Pd(OAc)2 (0.005 mmol, 0.05 equiv.), PPh3 (0.01 mmol, 0.10 equiv.), Di-O-acetyl-2-iodo-D- glucal (0.15 mmol, 1.5 equiv.) and AgOAc (0.2 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over MgSO4 and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 90:10) to afford **6d** as yellow oil in 65 % yield, 45 mg.

1H NMR (400 MHz, CDCl3) δ 5.62 (s, 1H), 5.20 – 5.14 (m, 2H), 4.56 (d, J = 2.8 Hz, 1H), 4.51 (s, 1H), 4.23 (d, J = 5.1 Hz, 1H), 4.20 – 4.19 (m, 1H), 4.15 (dd, *J* = 5.2, 2.3 Hz, 1H), 4.12 (d, *J* = 2.8 Hz, 1H), 4.09 (dd, *J* = 5.7, 1.4 Hz, 1H), 4.08 – 4.01 (m, 2H), 3.88 – 3.86 (m, 1H), 3.61 – 3.58 (m, 2H), 2.02 (s, 3H), 1.98 (s, 3H), 1.96 (s, 2H), 0.85 (s, 8H), 0.80 (s, 7H), 0.79 (s, 9H), 0.10 (d, *J* = 5.2 Hz, 6H), 0.00 (d, *J* = 2.8 Hz, 6H), -0.05 (d, *J* = 1.6 Hz, 6H).**^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 171.0 (Cq), 170.5 (Cq), 150.1 (Cq), 142.1 (Cq), 121.1 (CH), 103.0 (CH), 78.8 (CH), 74.0 (CH), 72.5 (CH), 67.4 (CH), 66.8 (CH), 65.7 (CH), 65.1 (CH_2), 63.3 (CH_2), 62.0 (CH_2), 31.6 (CH_3), 26.0 (CH_3), 25.9 (CH_3), 25.7 (CH_3), 22.7 (CH_3), 21.1 (CH_3), 20.9 (CH_3), 18.4 (Cq), 18.2 (Cq), 18.1 (Cq), 14.1 (CH_3), -3.9 (CH_3), -4.1 (CH_3), -4.1 (CH_3), -4.7 (CH_3), -5.4 (CH_3), -5.4 (CH_3). 3 CH_3 resonances are missing in ^{13}C NMR due to overlap. **HRMS (ESI)** calculated $C_{34}H_{65}O_9Si_3$ $[M+H]^+$: 701.3936, Found; 701.3937.

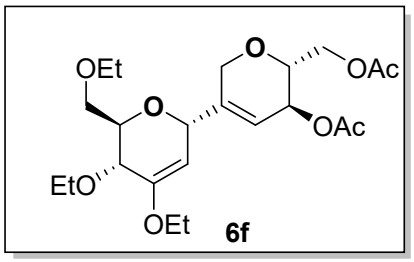


6e

Prepared by general procedure **A** using Tri-*O*-benzyl-D-glucal (50 mg, 0.12 mmol), $Pd(OAc)_2$ (0.006 mmol, 0.05 equiv.), PPh_3 (0.012 mmol, 0.10 equiv.), 4-*O*-acetyl-2-*iodo*-L-rhamnal (0.18 mmol, 1.5 equiv.) and AgOAc (0.24 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6

h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 90:10) to afford **6e** as yellow oil in 68 % yield, 46 mg.

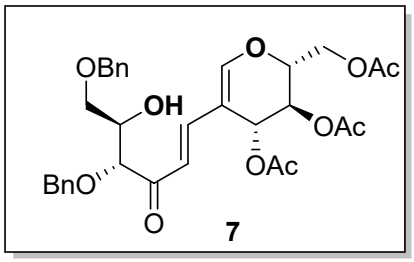
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 4H), 7.33 (d, J = 4.0 Hz, 5H), 7.26 (dd, J = 4.8, 2.0 Hz, 4H), 7.19 (dd, J = 6.7, 2.9 Hz, 2H), 5.61 (s, 1H), 5.05 – 5.00 (m, 1H), 4.87 – 4.84 (m, 2H), 4.81 (d, J = 1.9 Hz, 1H), 4.74 (s, 1H), 4.62 – 4.57 (m, 1H), 4.49 (d, J = 4.0 Hz, 1H), 4.34 – 4.29 (m, 1H), 4.20 – 4.16 (m, 1H), 4.15 – 4.11 (m, 3H), 3.82 (ddd, J = 7.6, 4.5, 3.1 Hz, 1H), 3.62 (d, J = 4.6 Hz, 1H), 3.60 – 3.55 (m, 2H), 2.05 (s, 3H), 1.22 (d, J = 6.3 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.8 (Cq), 154.3 (Cq), 140.9 (Cq), 138.0 (Cq), 138.0 (Cq), 136.6 (Cq), 128.5 (CH), 128.4 (CH), 128.4 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.4 (CH), 123.1 (CH), 96.0 (CH), 74.2 (CH_2), 73.4 (CH_2), 72.3 (CH), 72.1 (CH), 72.0 (CH), 71.4 (CH), 70.7 (CH), 69.2 (CH_2), 68.7 (CH_2), 65.9 (CH_2), 21.3 (CH_3), 17.7 (CH_3). 8 CH resonances are missing in ^{13}C NMR due to overlapping. **HRMS (ESI)** calculated $C_{35}H_{42}NO_7$ $[M+NH_4]^+$: 606.2961, Found; 606.2963.



6f

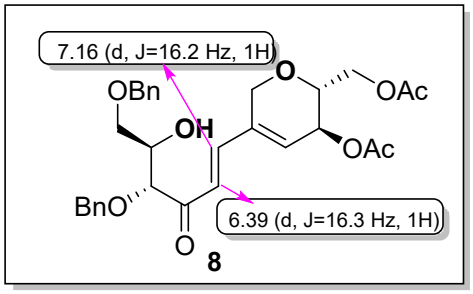
Prepared by general procedure **A** using Tri-*O*-ethyl-D-glucal (50 mg, 0.12 mmol), $Pd(OAc)_2$ (0.006 mmol, 0.05 equiv.), PPh_3 (0.012 mmol, 0.10 equiv.), Di-*O*-acetyl-2-*iodo*-D-glucal (0.18 mmol, 1.5 equiv.) and AgOAc (0.24 mmol, 2.0 equiv.). The reaction mixture was stirred at 80 °C for 6 h. The resulting mixture was extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 85:15) to afford **6f** as yellow oil in 65 % yield, 62 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (s, 1H), 5.30 (dd, J = 5.7, 2.4 Hz, 1H), 4.68 (d, J = 2.8 Hz, 1H), 4.60 (d, J = 3.8 Hz, 1H), 4.48 – 4.41 (m, 1H), 4.22 (dd, J = 5.3, 2.8 Hz, 1H), 4.19 (dd, J = 5.6, 4.5 Hz, 2H), 3.91 – 3.86 (m, 1H), 3.86 – 3.82 (m, 1H), 3.81 – 3.73 (m, 2H), 3.73 – 3.68 (m, 1H), 3.65 (ddd, J = 8.6, 5.6, 3.1 Hz, 1H), 3.60 – 3.56 (m, 3H), 3.55 – 3.45 (m, 2H), 2.11 (s, 3H), 2.08 (s, 3H), 1.34 (t, J = 7.0 Hz, 3H), 1.22 (t, J = 4.4 Hz, 3H), 1.19 (t, J = 5.9, 2.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.9 (Cq), 170.3 (Cq), 155.0 (Cq), 141.3 (Cq), 122.5 (CH), 94.4 (CH), 73.9 (CH), 72.3 (CH), 71.6 (CH), 71.4 (CH), 69.3 (CH_2), 67.1 (CH_2), 66.9 (CH_2), 66.0 (CH_2), 65.5 (CH), 63.2 (CH_2), 62.7 (CH_2), 21.1 (CH_3), 20.9 (CH_3), 15.6 (CH_3), 15.1 (CH_3), 14.5 (CH_3). **HRMS (ESI)** calculated $C_{22}H_{35}O_9$ $[M+H]^+$:444.2281, Found; 444.2283.



Prepared by general procedure **B** using **3a** (50 mg, 0.072 mmol), $BF_3.OEt_2$ (0.014 mmol, 0.20 equiv.). The reaction mixture was stirred at 0 °C for 30 minutes. The resulting mixture was quenched with Et_3N, and then extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 50:50) to afford **7** as gummy liquid in 76 % yield, 33 mg.

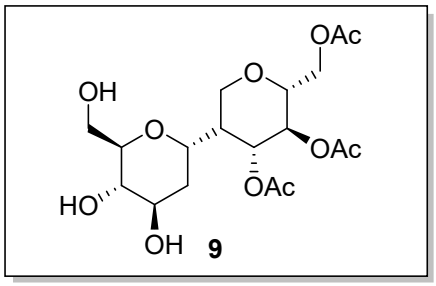
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.35 (m, 1H), 7.34 (d, *J* = 2.1 Hz, 1H), 7.33 – 7.32 (m, 2H), 7.30 (d, *J* = 2.8 Hz, 3H), 7.29 – 7.26 (m, 4H), 7.04 (s, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 5.65 – 5.60 (m, 1H), 5.19 – 5.14 (m, 1H), 4.70 – 4.61 (m, 1H), 4.54 – 4.51 (m, 1H), 4.51 – 4.48 (m, 2H), 4.46 (d, *J* = 3.4 Hz, 1H), 4.43 (dd, *J* = 7.6, 4.4 Hz, 1H), 4.19 (dd, *J* = 12.0, 4.2 Hz, 1H), 4.05 (t, *J* = 4.7 Hz, 1H), 4.01 (d, *J* = 6.1 Hz, 1H), 3.59 (d, *J* = 4.6 Hz, 2H), 2.10 (s, 3H), 2.09 (s, 3H), 2.00 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 199.0 (Cq), 170.4 (Cq), 170.0 (Cq), 169.4 (Cq), 154.0 (CH), 140.5 (CH), 137.8 (Cq), 137.2 (Cq), 129.1 (CH), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.8 (CH), 127.0 (CH), 118.1 (CH), 110.1 (Cq), 83.8 (CH), 74.6 (CH), 73.4 (CH_2), 72.9 (CH_2), 71.3 (CH), 70.2 (CH_2), 66.5 (CH), 62.7 (CH), 61.1 (CH_2), 20.8 (CH_3), 20.7 (CH_3), 20.6 (CH_3). **HRMS (ESI)** calculated $C_{32}H_{37}O_{11}$ $[M+H]^+$: 597.2336, Found; 597.2339.



Prepared by general procedure **B** using **6b** (50 mg, 0.079 mmol), $BF_3.OEt_2$ (0.015 mmol, 0.20 equiv.). The reaction mixture was stirred at 0 °C for 30 minutes. The resulting mixture was quenched with Et_3N, and then extracted with EtOAc and the combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (Hexane: EtOAc; 50:50) to afford **8** as gummy liquid in 70% yield, 30 mg.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 6H), 7.29 (dd, *J* = 6.1, 3.7 Hz, 5H), 7.16 (d, *J* = 16.2 Hz, 1H), 6.39 (d, *J* = 16.3 Hz, 1H), 6.12 (s, 1H), 5.39 (d, *J* = 6.5 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 3.5 Hz, 2H), 4.47 – 4.43 (m, 1H), 4.32 – 4.17 (m, 4H), 4.14 – 4.09 (m, 1H), 3.70 (ddd, *J* = 8.4, 5.7, 2.7 Hz, 1H), 3.54 (dd, *J* = 10.5, 4.8 Hz, 2H), 2.12 (s, 3H), 2.11 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 199.6 (Cq), 170.9 (Cq), 170.2 (Cq), 140.0 (CH), 137.7 (Cq), 136.8 (Cq), 136.7 (Cq), 133.2 (CH), 128.6 (CH), 128.4 (CH), 128.4 (CH), 128.3 (CH),

127.9 (CH), 127.8 (CH), 121.8 (CH), 83.5 (CH), 73.9 (CH), 73.5 (CH_2), 73.3 (CH_2), 71.4 (CH), 70.3 (CH_2), 65.5 (CH), 64.8 (CH_2), 63.0 (CH_2), 21.0 (CH_3), 20.8 (CH_3). 4 CH resonances are missing in ^{13}C NMR due to overlapping. **HRMS (ESI)** calculated $C_{30}H_{35}O_9$ $[M+H]^+$: 540.2306, Found; 540.2308.



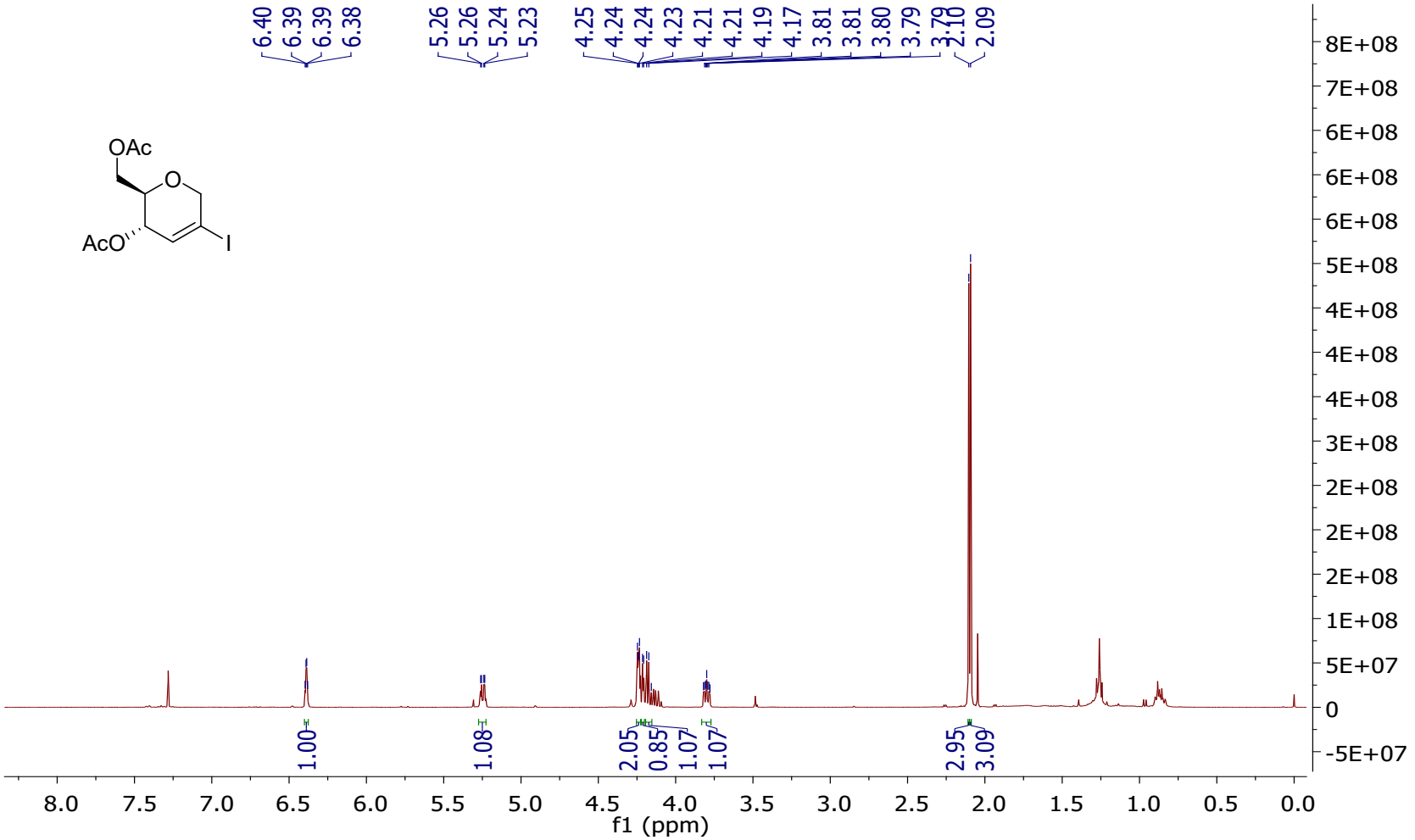
9

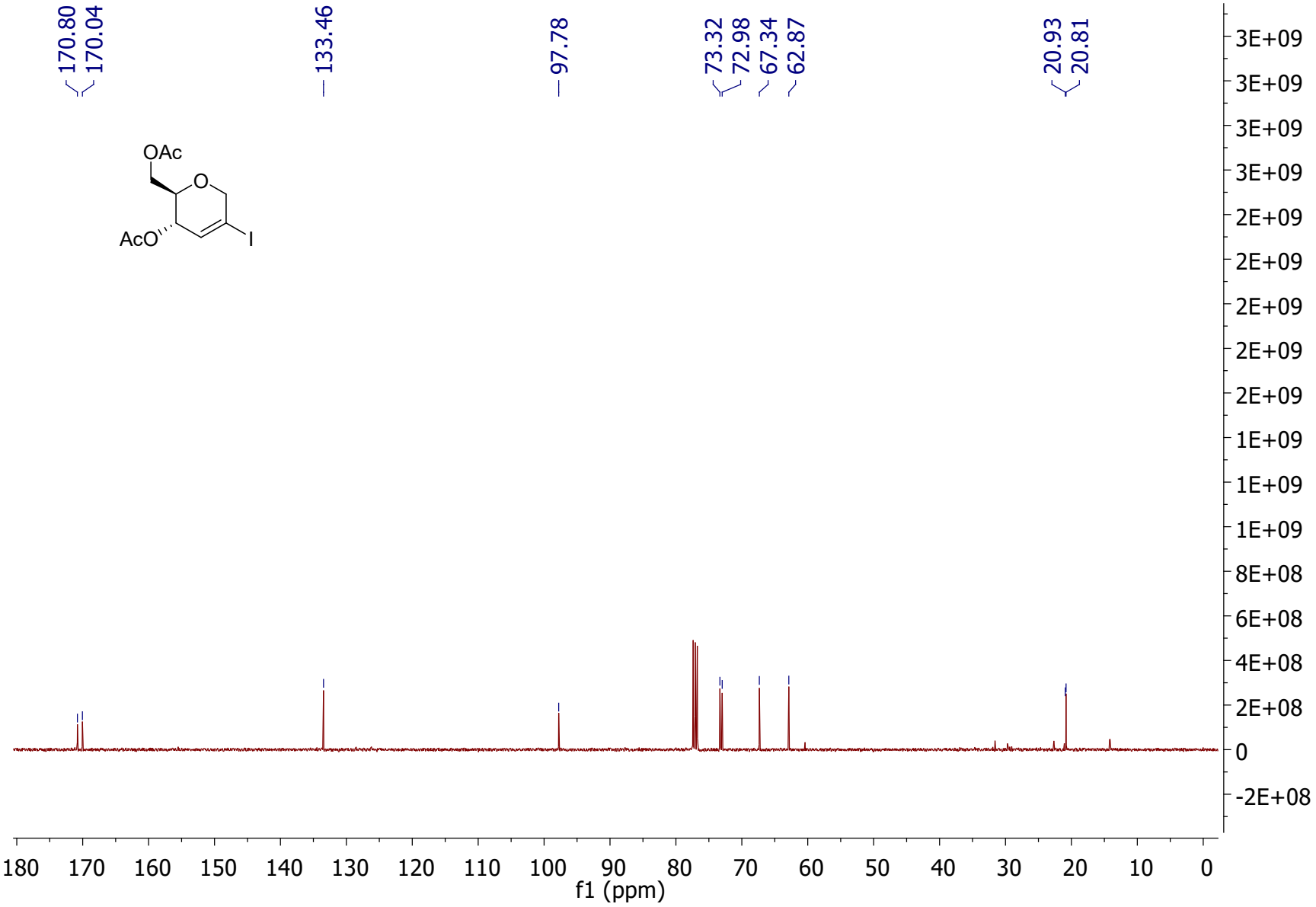
Compound 3a (50 mg, 0.072 mmol) was dissolved in MeOH (10 mL). To this solution 10 % Pd/C (60 mg) was added. The reaction was stirred under hydrogen atmosphere for 3 h. The reaction mixture was filtered through a Celite bed using methanol as eluent. Filtrate was concentrated under reduced pressure and dried under high vacuum to obtain **9** (27.5 mg, 90%) as white foam.

^{1}H NMR (400 MHz, MeOD) δ 5.06 – 4.95 (m, 2H), 4.47 (s, 1H), 4.11 (ddd, *J* = 12.1, 7.9, 3.4 Hz, 1H), 3.98 (tdd, *J* = 11.0, 6.7, 4.1 Hz, 1H), 3.86 (ddd, *J* = 9.7, 8.2, 1.9 Hz, 1H), 3.73 – 3.65 (m, 1H), 3.61 – 3.53 (m, 2H), 3.52 – 3.48 (m, 2H), 3.42 – 3.35 (m, 1H), 3.23 – 3.19 (m, 1H), 1.95 (s, 3H), 1.95 (s, *J* = 1.4 Hz, 3H), 1.93 (s, 3H), 1.76 – 1.63 (m, 1H), 1.60 – 1.46 (m, 2H).**^{13}C NMR (101 MHz, MeOD)** δ 171.2 (Cq), 170.6 (Cq), 170.4 (Cq), 76.6 (CH), 74.4(CH), 73.1 (CH), 72.1 (CH), 71.8 (CH), 66.8 (CH_2), 66.6 (CH), 63.3 (CH_2), 62.6 (CH_2), 48.5 (CH), 39.0 (CH), 29.4 (CH_2), 19.5 (CH_3), 19.4 (CH_3), 19.3 (CH_3).

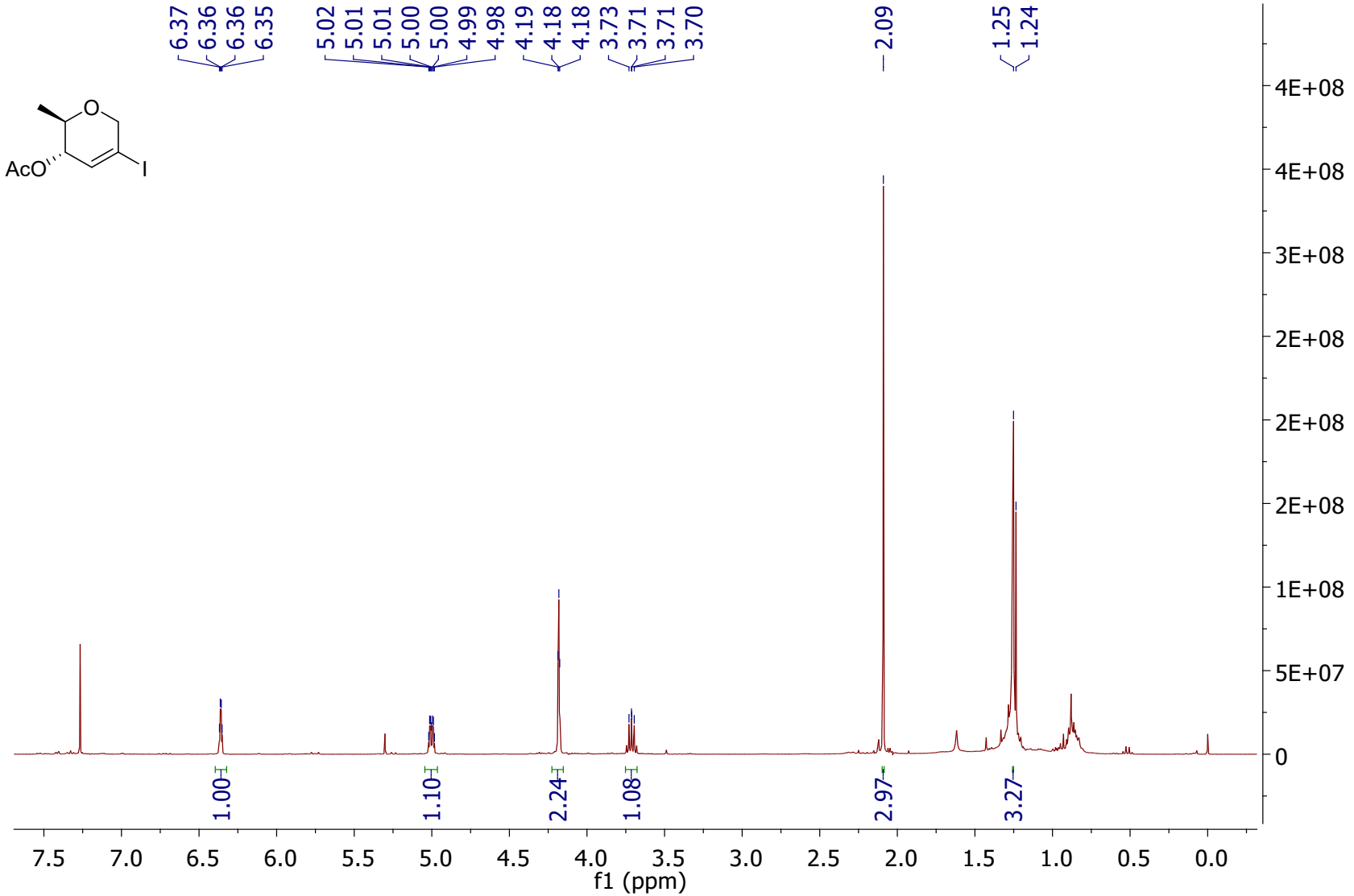
4. NMR Spectra:

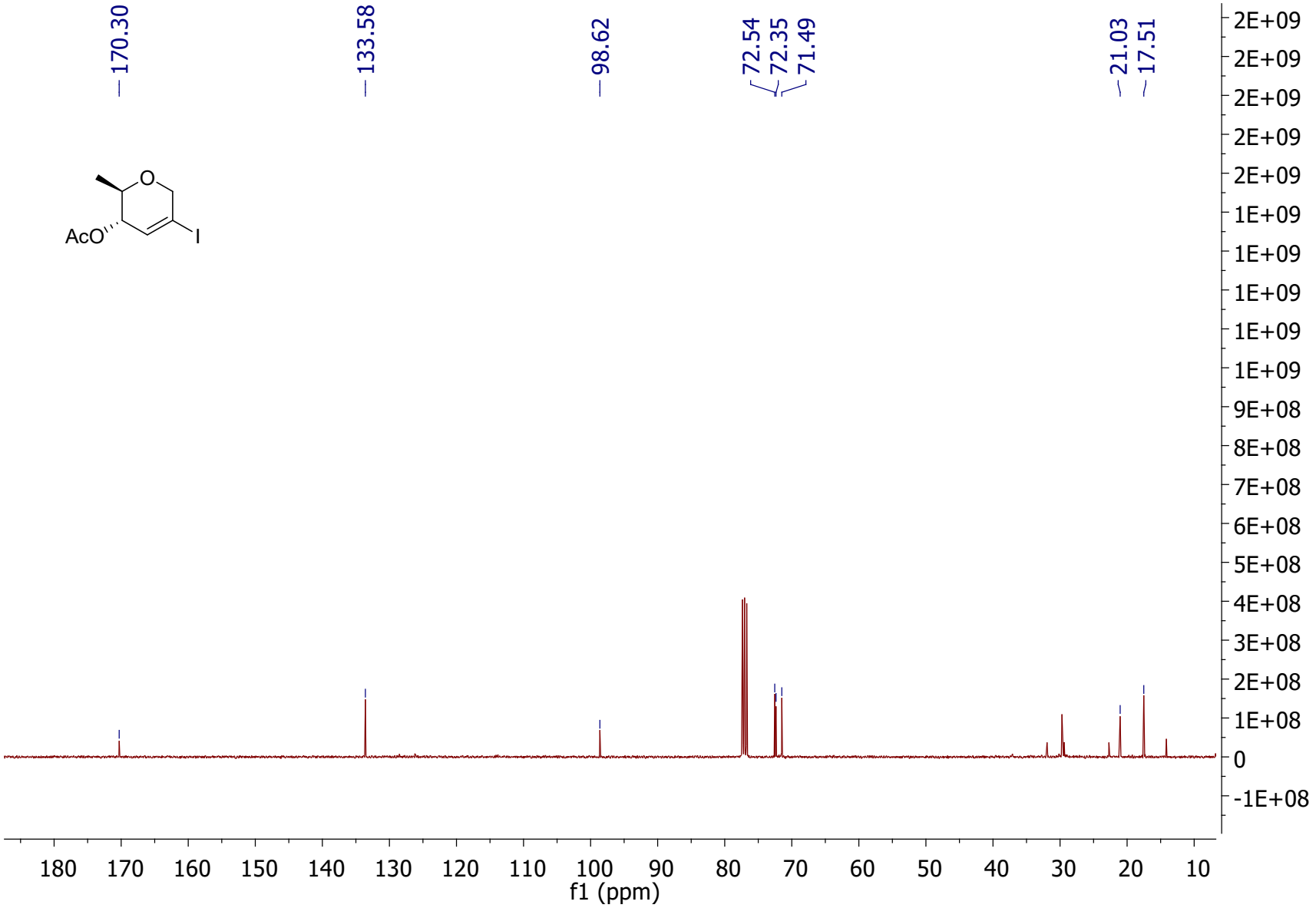
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5a



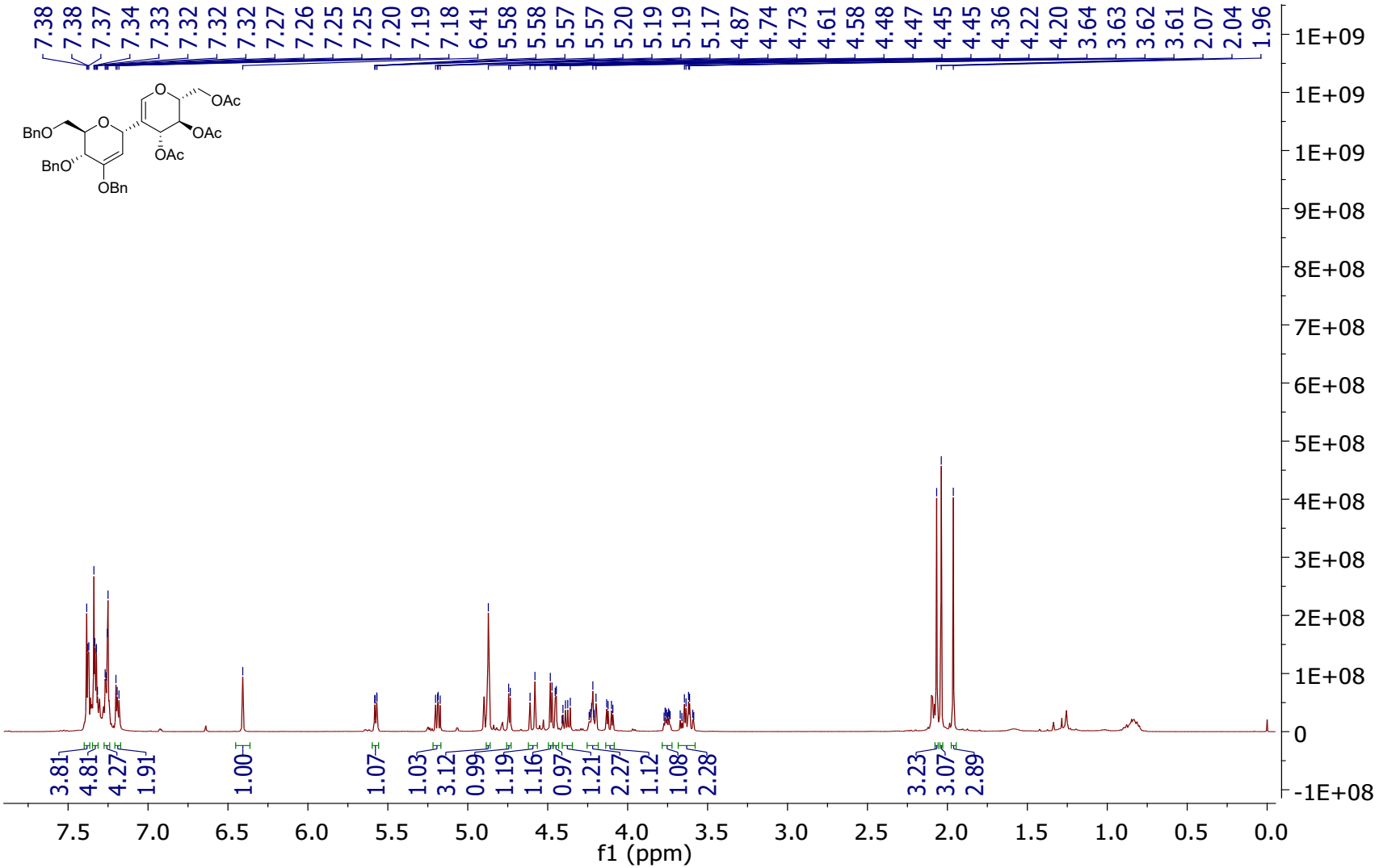

170.80
170.04
133.46
97.78
73.32
72.98
67.34
62.87
20.93
20.81
OAc
O
AcO
I
3E+09
3E+09
3E+09
3E+09
2E+09
2E+09
2E+09
2E+09
2E+09
2E+09
1E+09
1E+09
1E+09
8E+08
6E+08
4E+08
2E+08
0
-2E+08
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

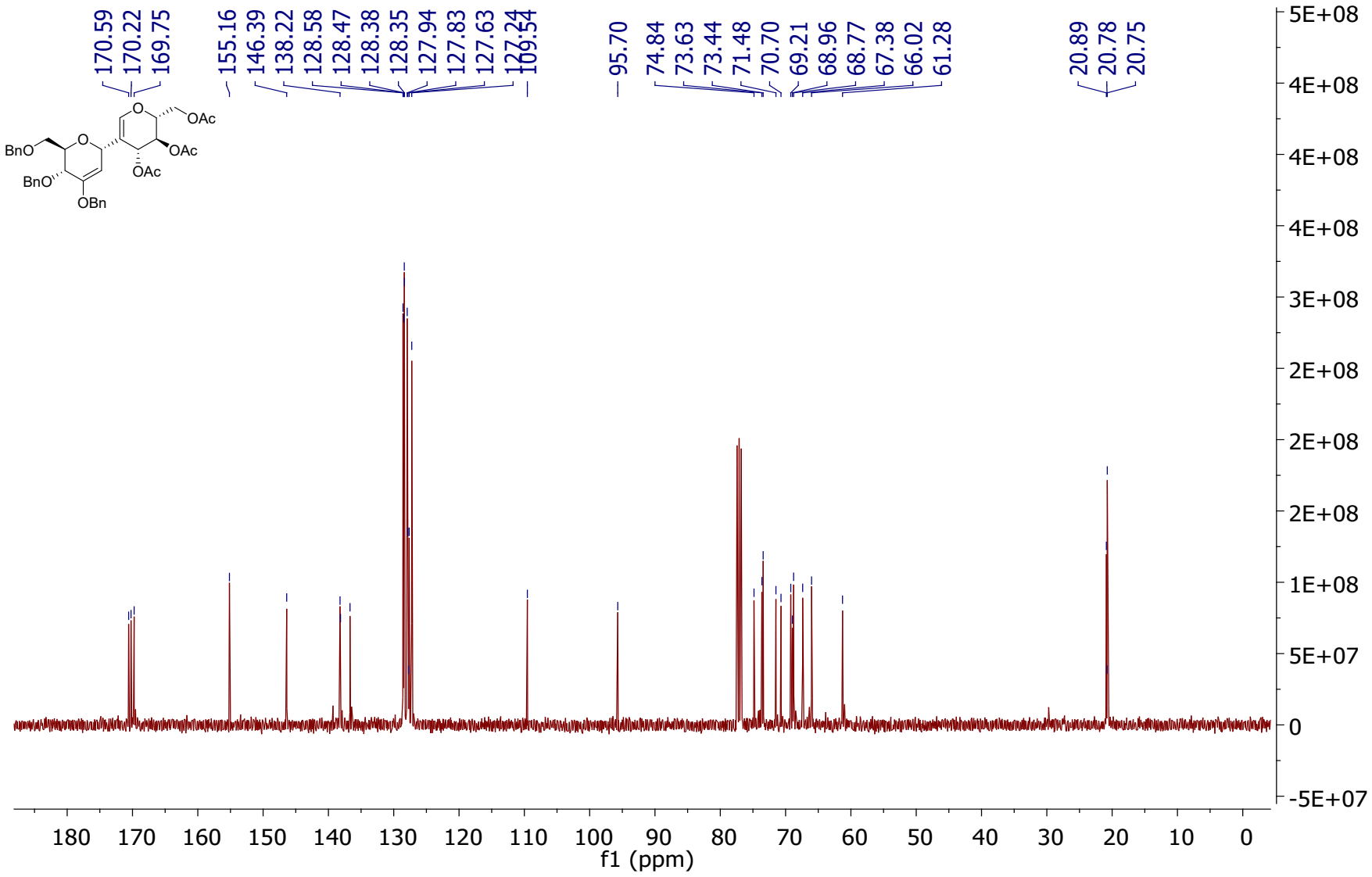
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 5b



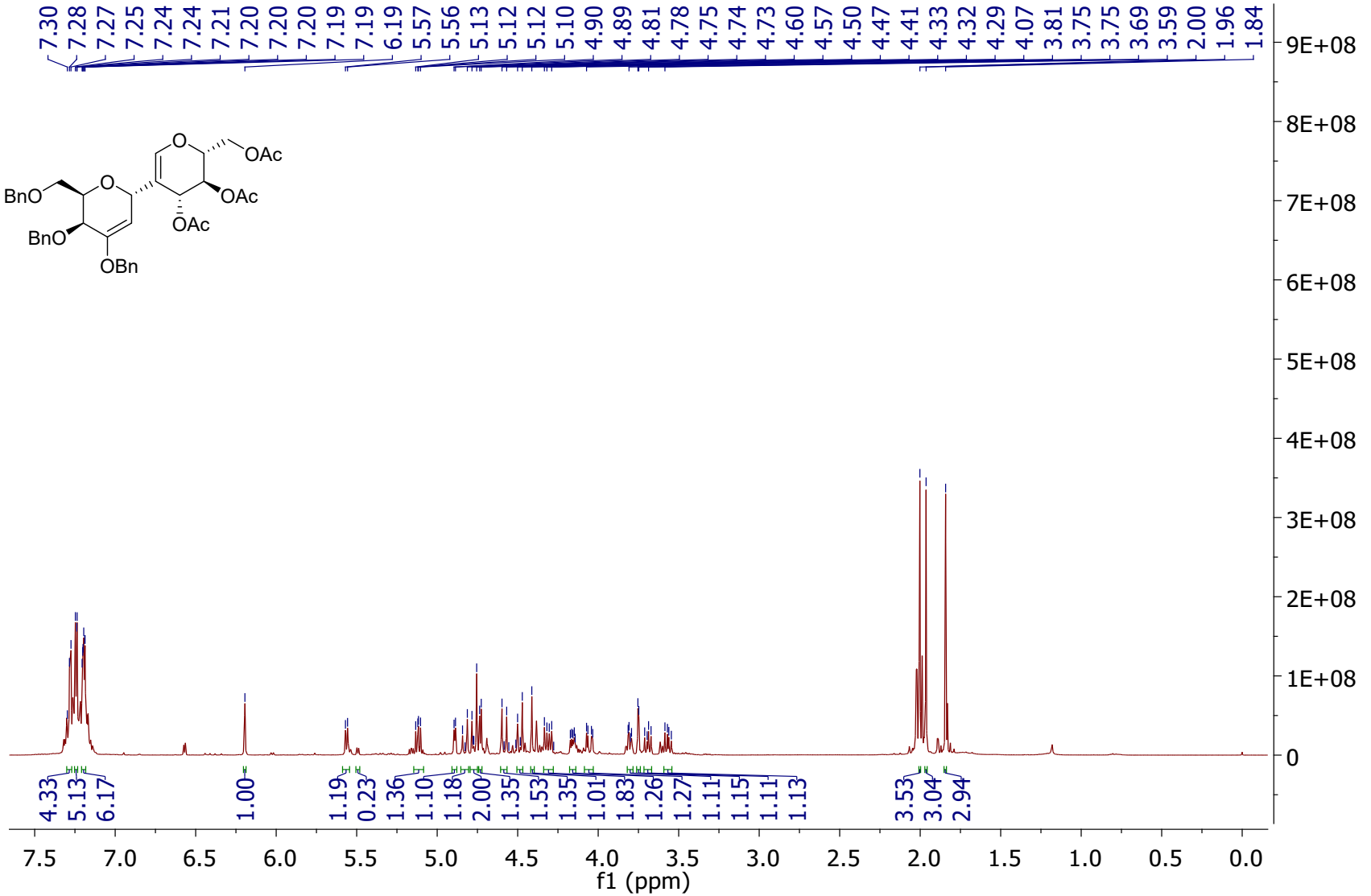

170.30
133.58
98.62
72.54
72.35
71.49
21.03
17.51
AcO
O
I
2E+09
2E+09
2E+09
2E+09
2E+09
1E+09
1E+09
1E+09
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

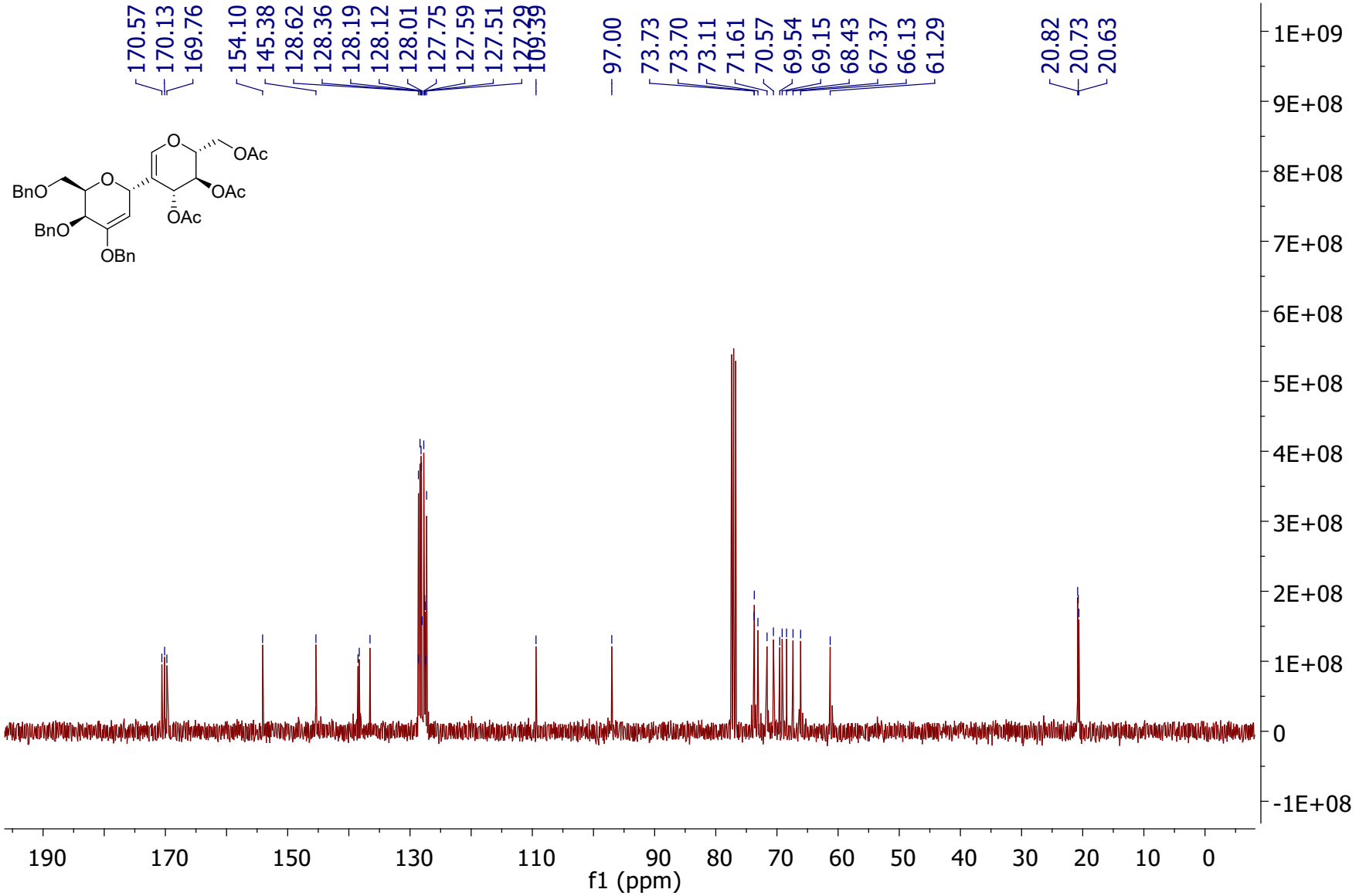
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3a:



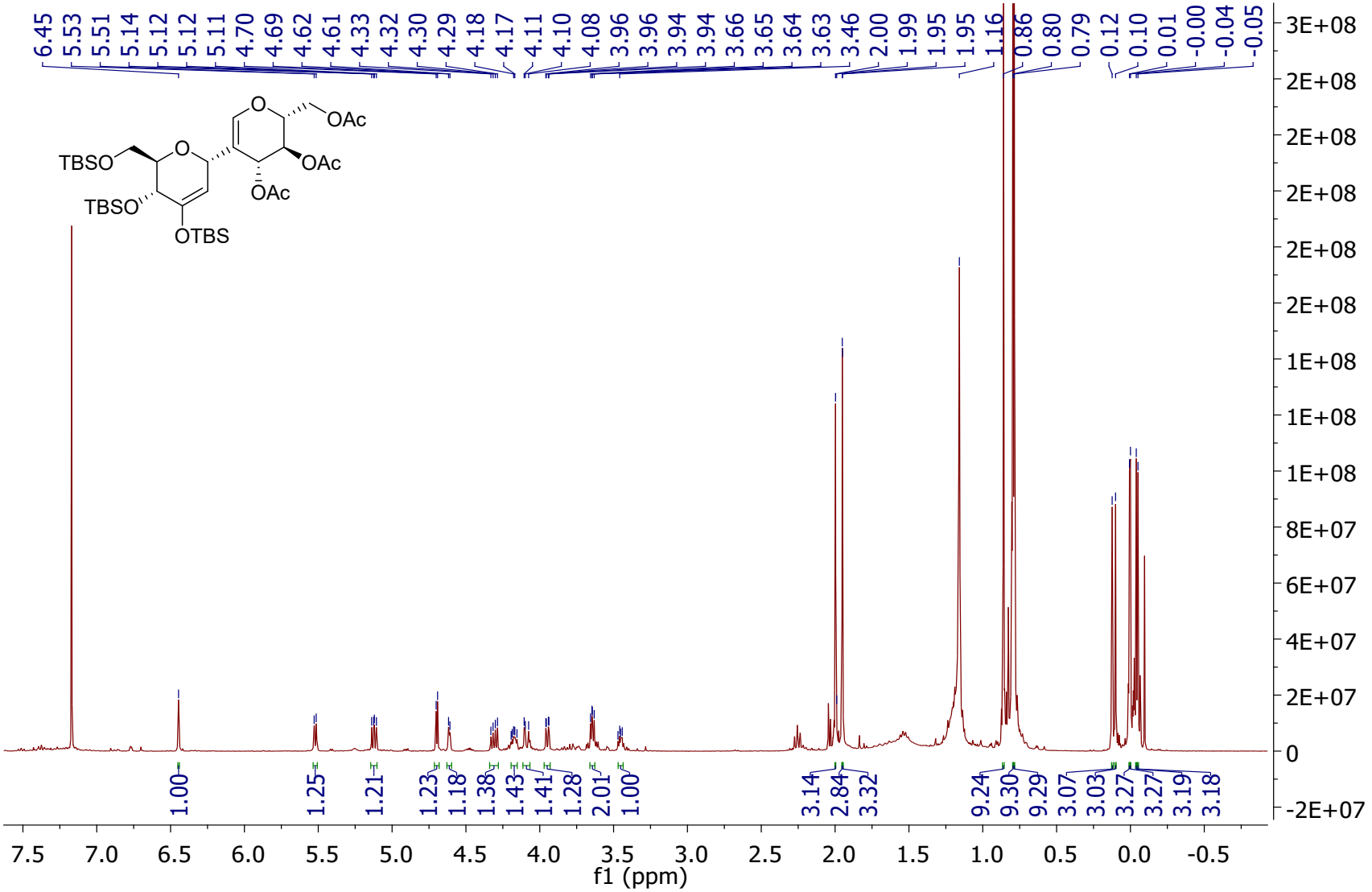

170.59
170.22
169.75
155.16
146.39
138.22
128.58
128.47
128.38
128.35
127.94
127.83
127.63
127.24
109.54
95.70
74.84
73.63
73.44
71.48
70.70
69.21
68.96
68.77
67.38
66.02
61.28
20.89
20.78
20.75
BnO
BnO
OBn
OAc
OAc
OAc
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

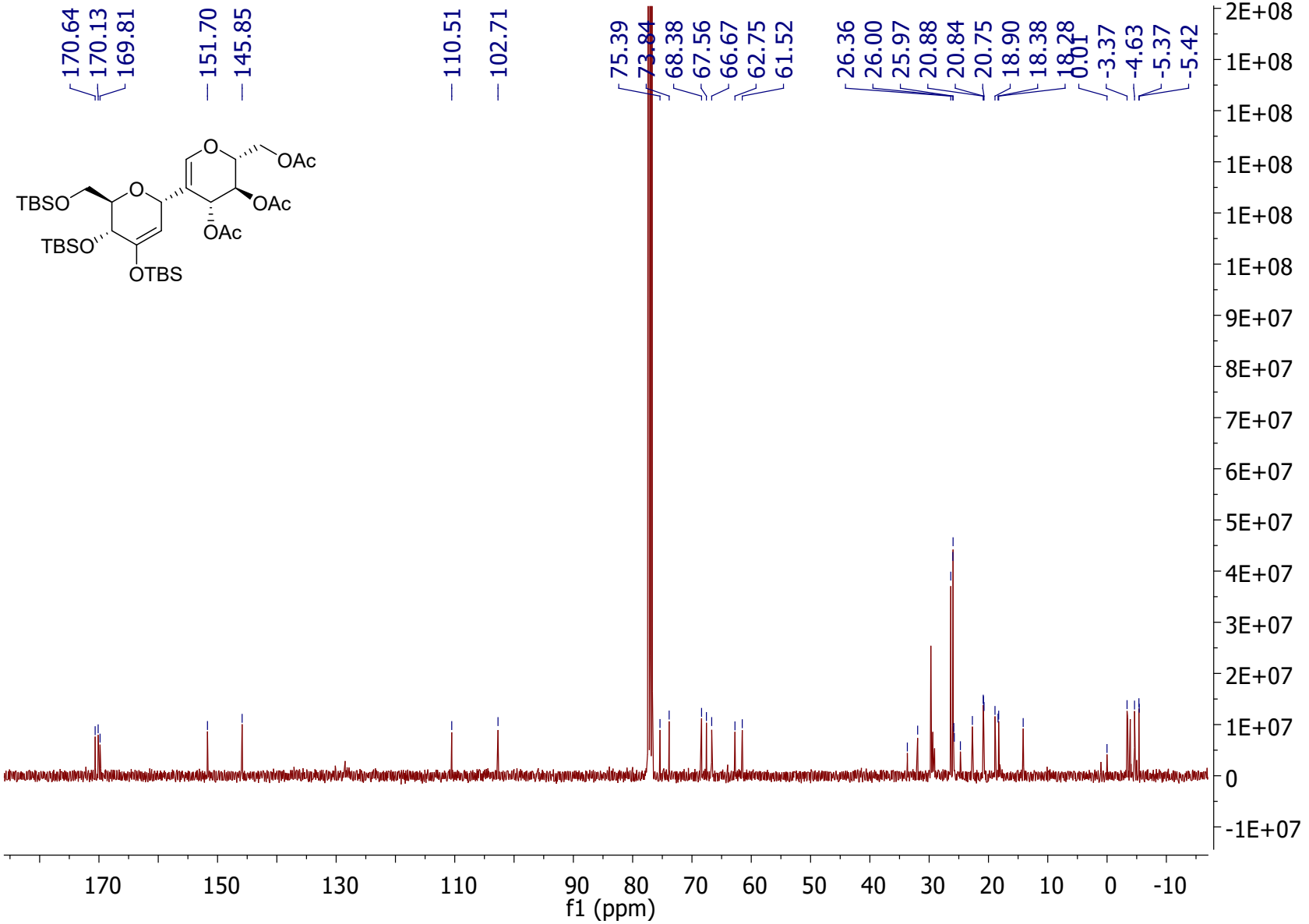
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3b (α/β; 4:1):



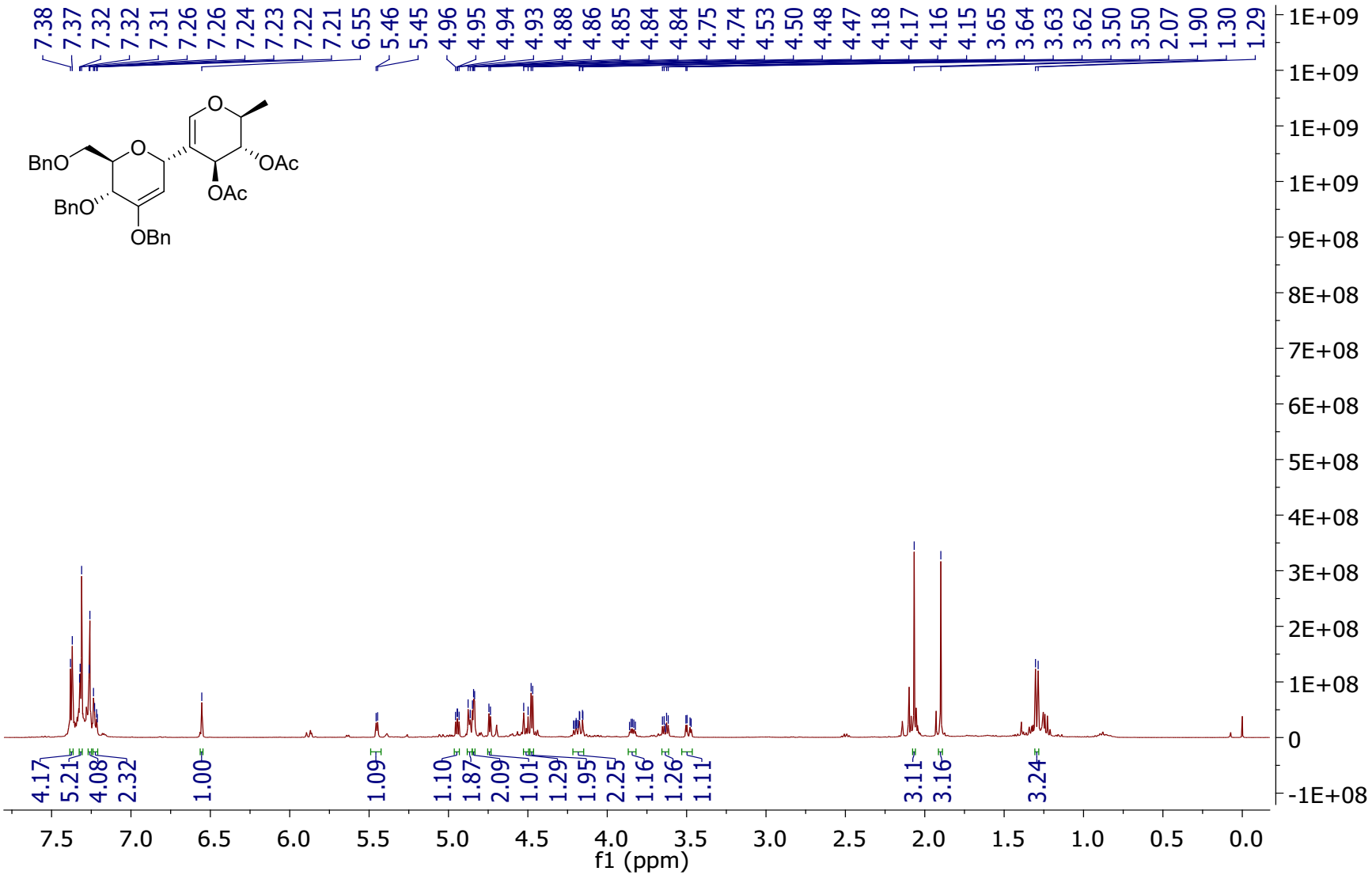

170.57
170.13
169.76
154.10
145.38
128.62
128.36
128.19
128.12
128.01
127.75
127.59
127.51
127.29
109.39
97.00
73.73
73.70
73.11
71.61
70.57
69.54
69.15
68.43
67.37
66.13
61.29
20.82
20.73
20.63
BnO
BnO
OBn
OAc
OAc
OAc
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

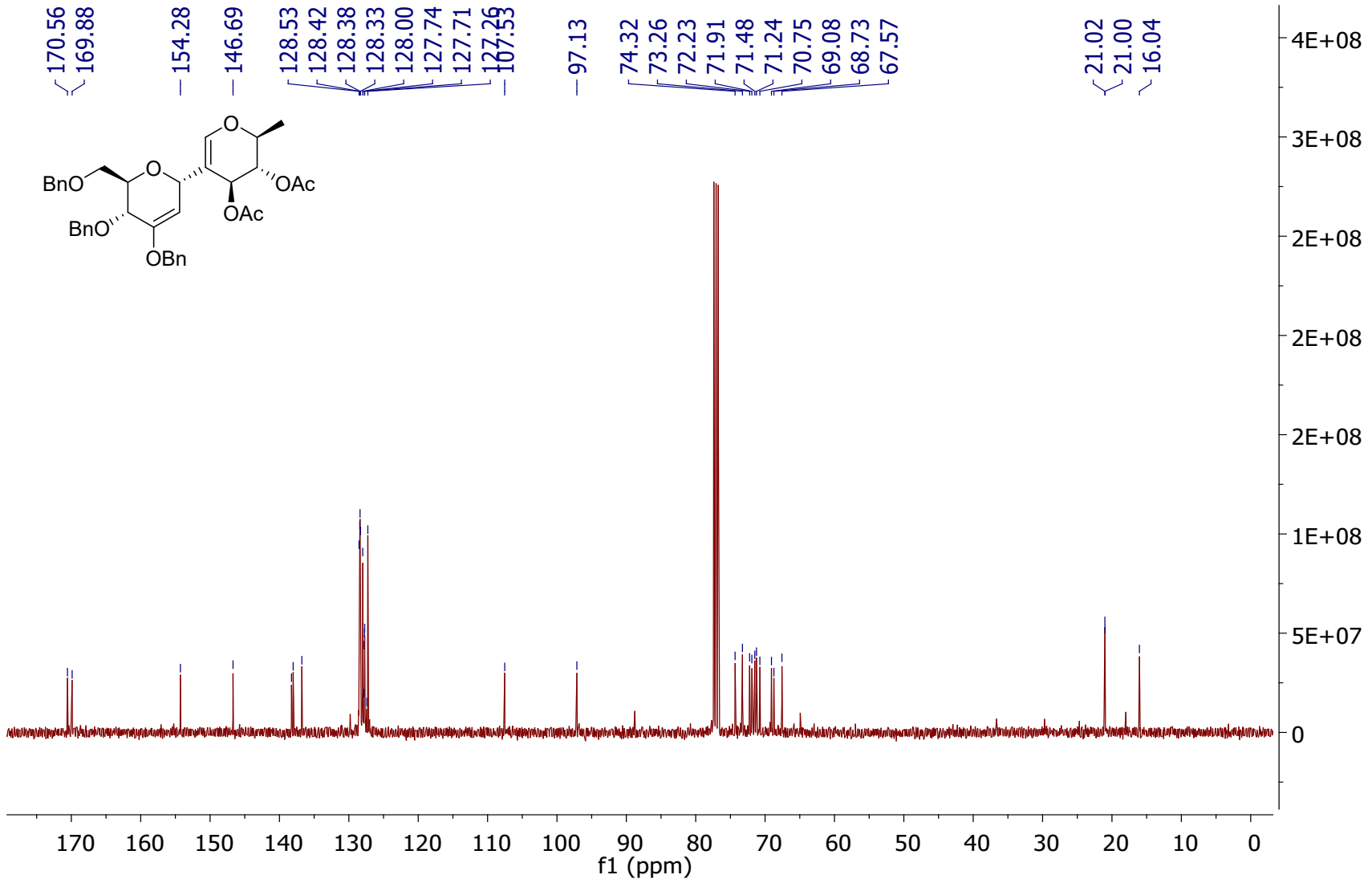
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3c:



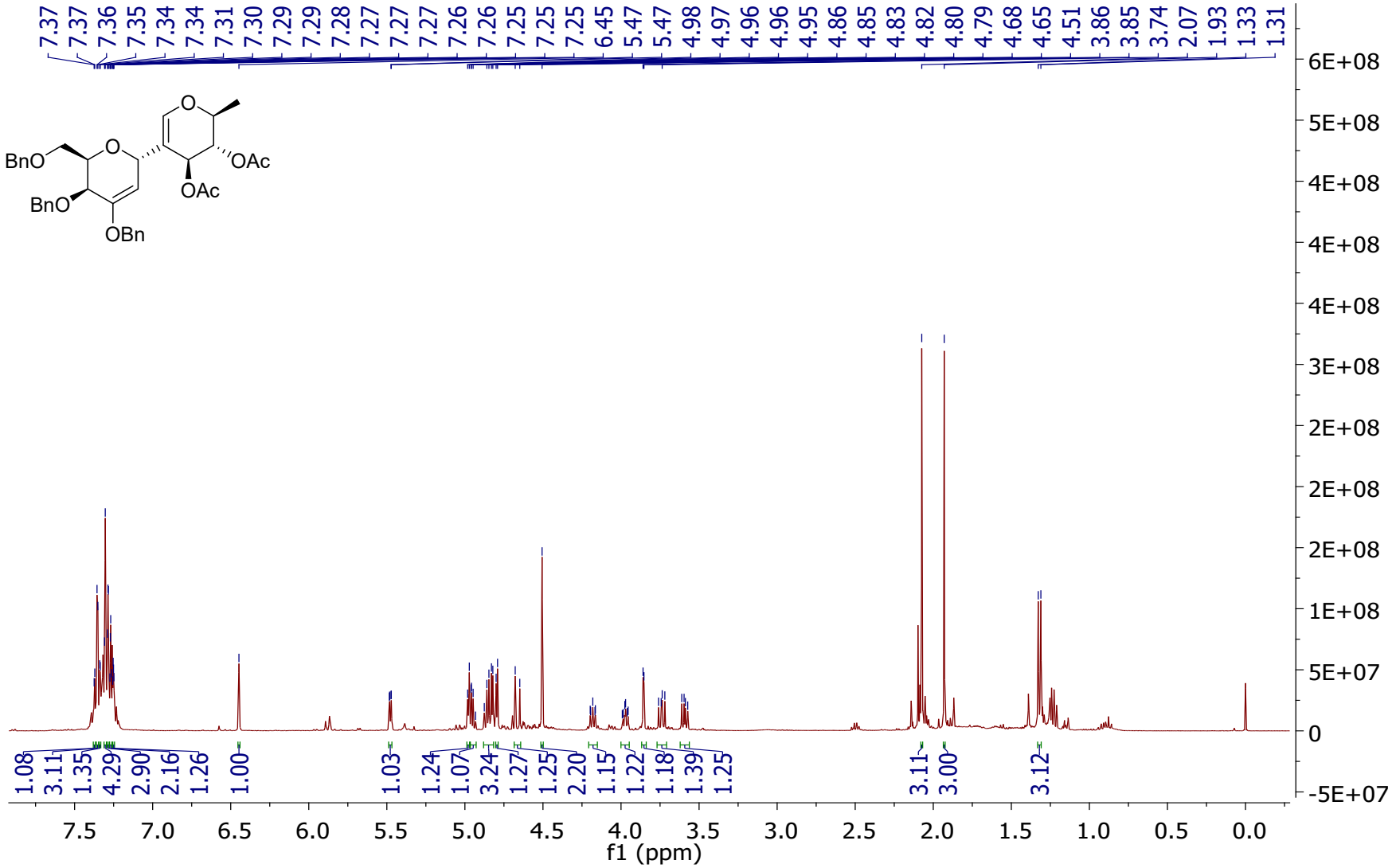

170.64
170.13
169.81
151.70
145.85
110.51
102.71
75.39
73.84
68.38
67.56
66.67
62.75
61.52
26.36
26.00
25.97
20.88
20.84
20.75
18.90
18.38
18.28
0.01
-3.37
-4.63
-5.37
-5.42
TBSO
TBSO
OTBS
OAc
OAc
OAc
2E+08
1E+08
1E+08
1E+08
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

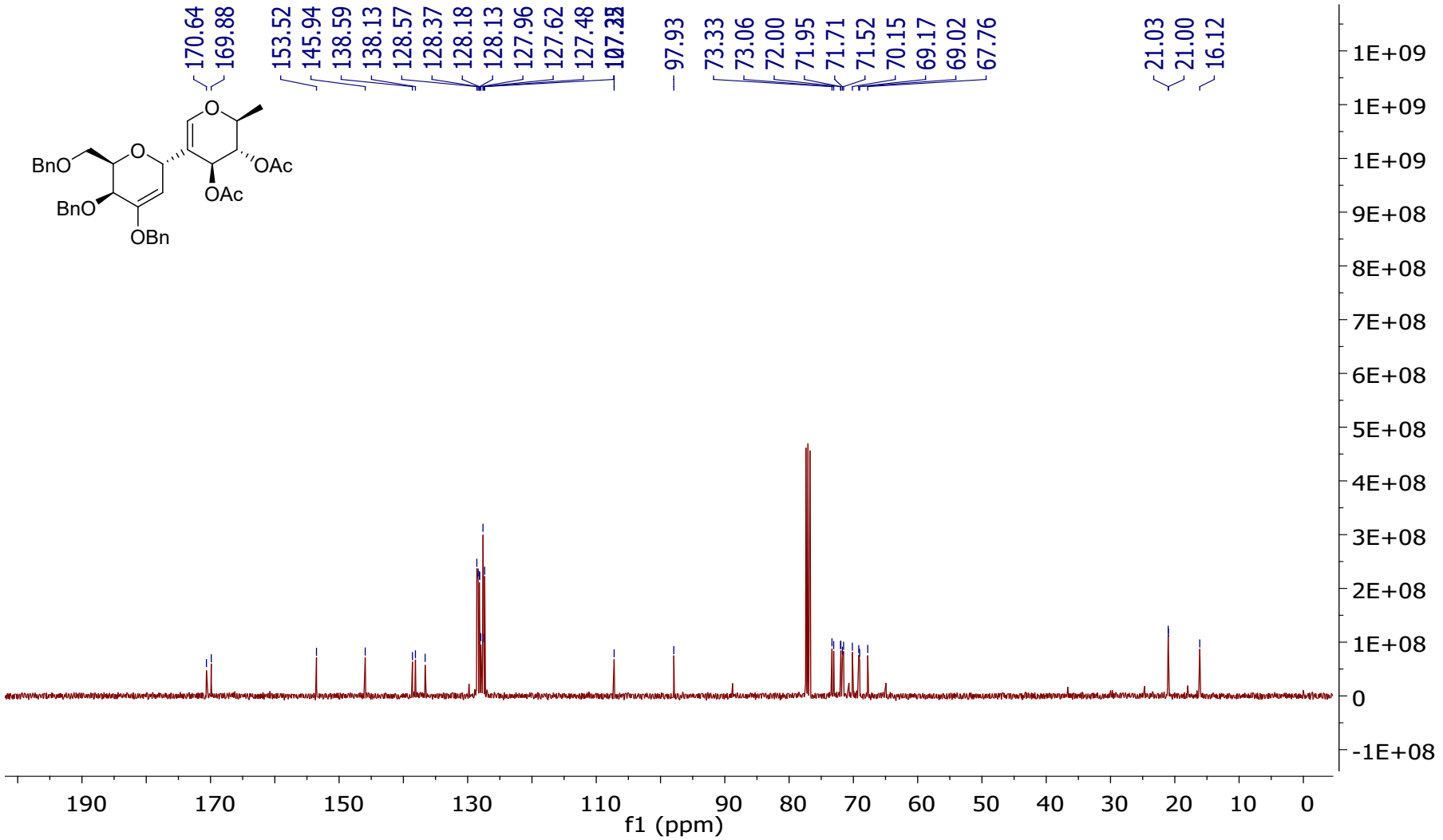
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3d:



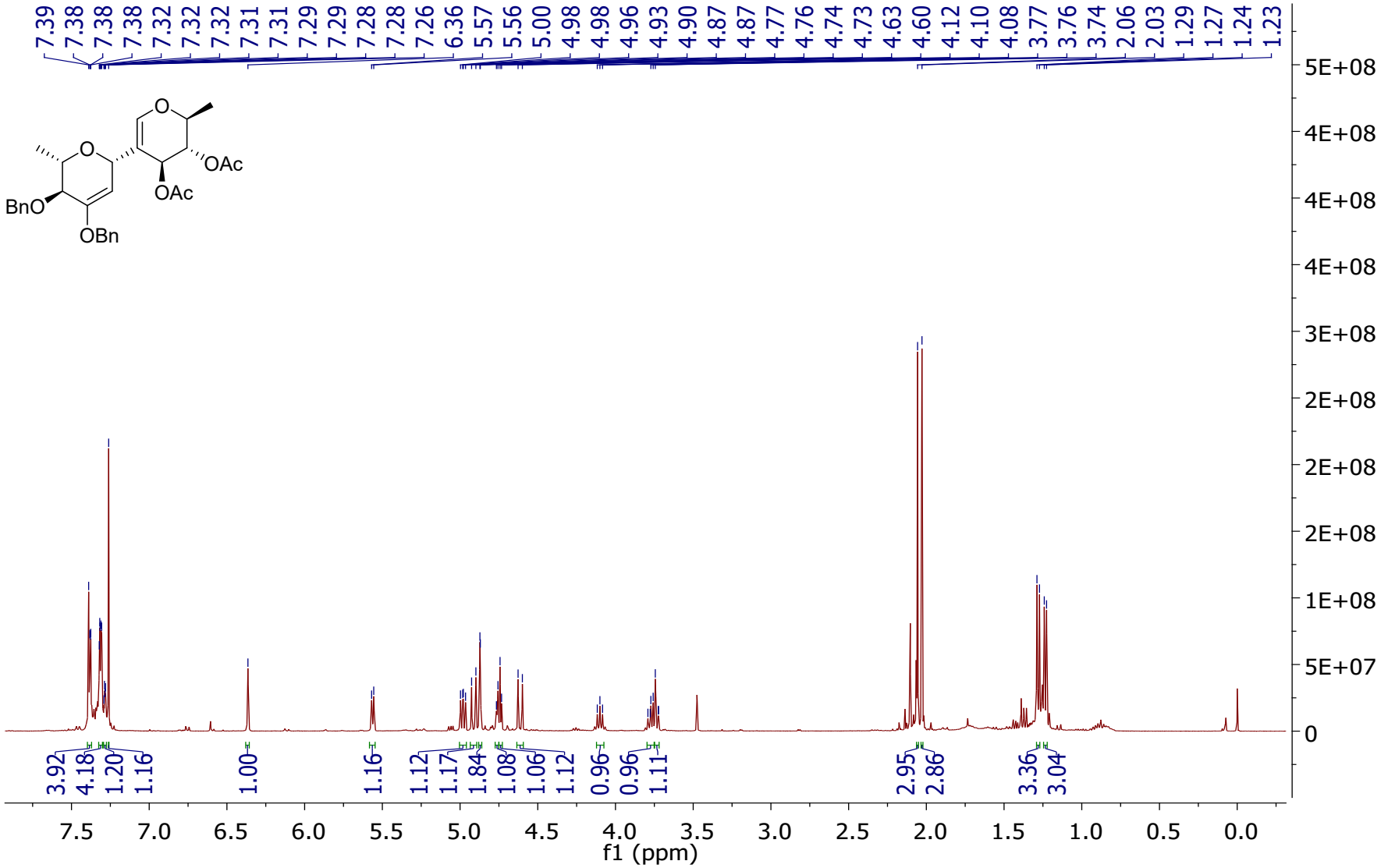

170.56
169.88
154.28
146.69
128.53
128.42
128.38
128.33
128.00
127.74
127.71
127.26
127.13
107.53
97.13
74.32
73.26
72.23
71.91
71.48
71.24
70.75
69.08
68.73
67.57
21.02
21.00
16.04
BnO
BnO
OBn
OAc
OAc
O
O
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

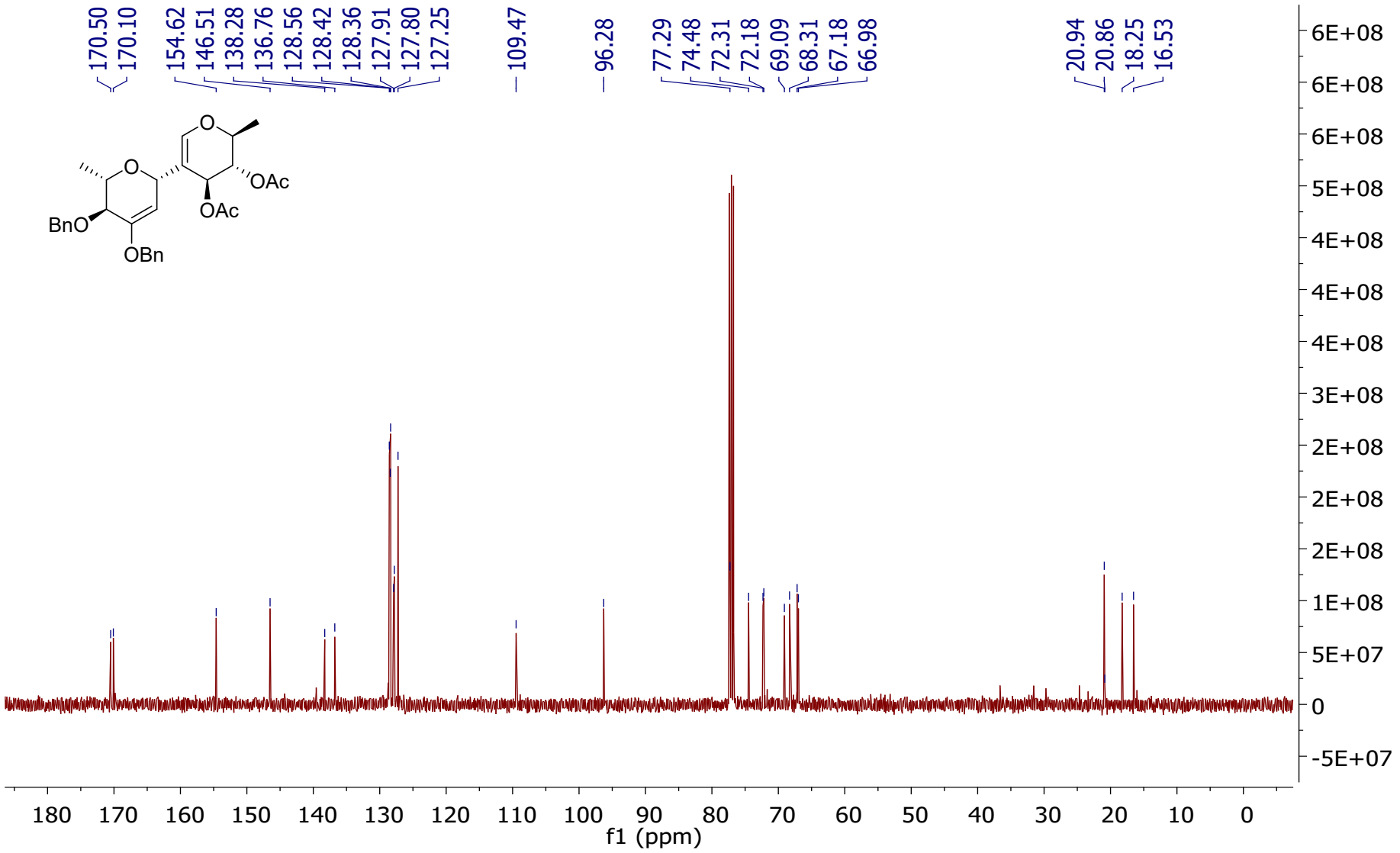
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3e:



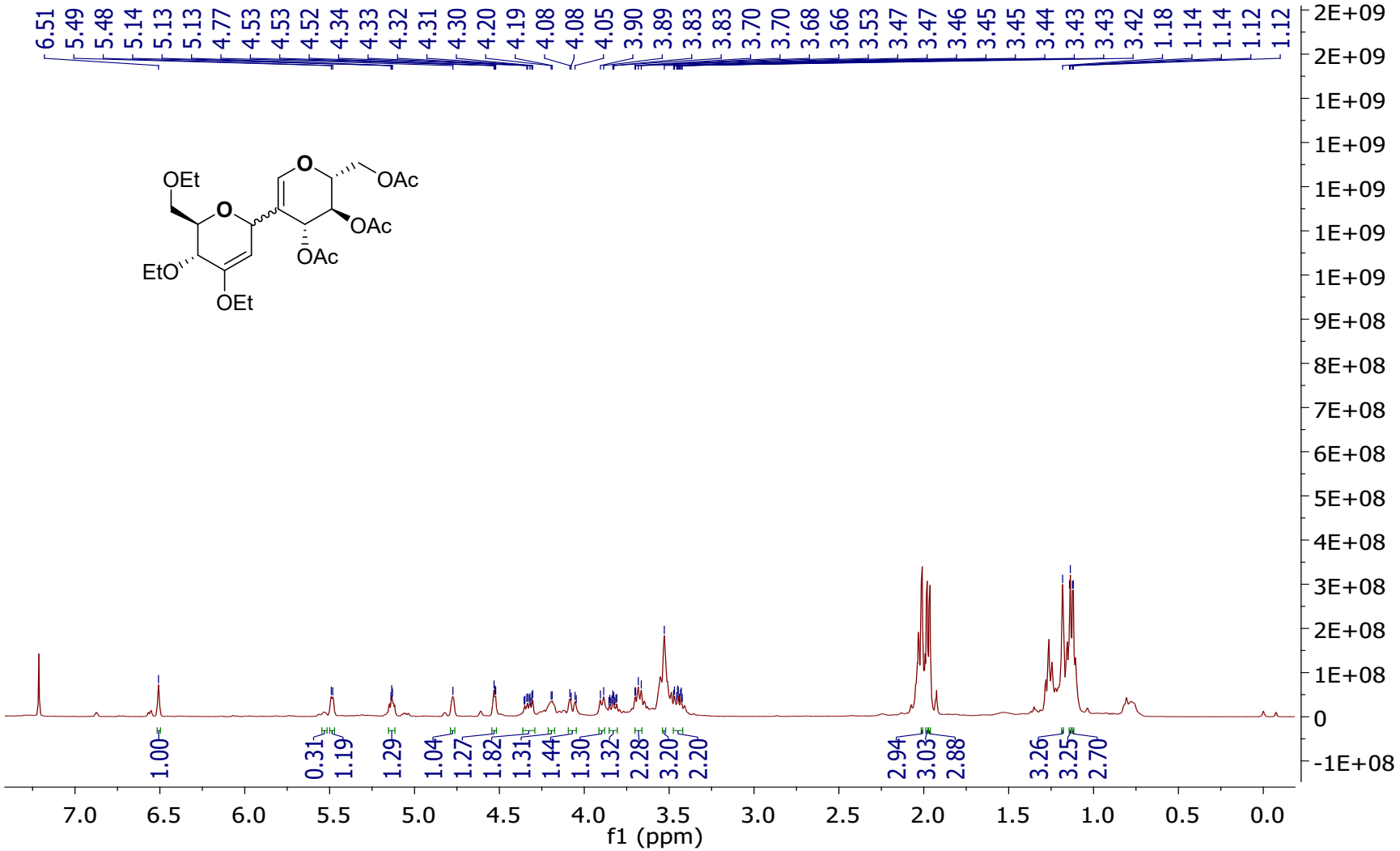

170.64
169.88
153.52
145.94
138.59
138.13
128.57
128.37
128.18
128.13
127.96
127.62
127.48
97.93
73.33
73.06
72.00
71.95
71.71
71.52
70.15
69.17
69.02
67.76
21.03
21.00
16.12
BnO
BnO
OBn
OAc
OAc
1E+09
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

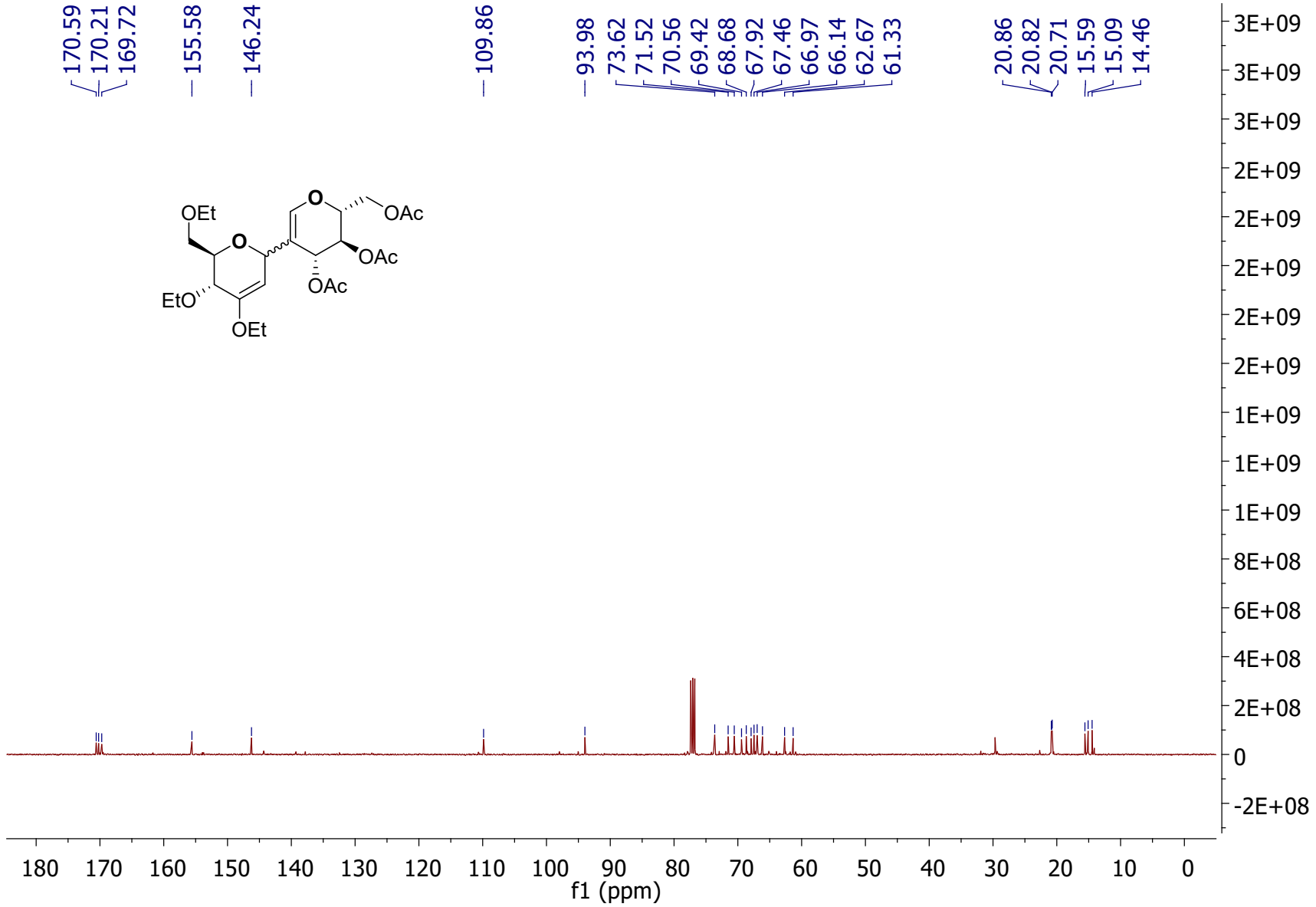
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) of compound 3f:



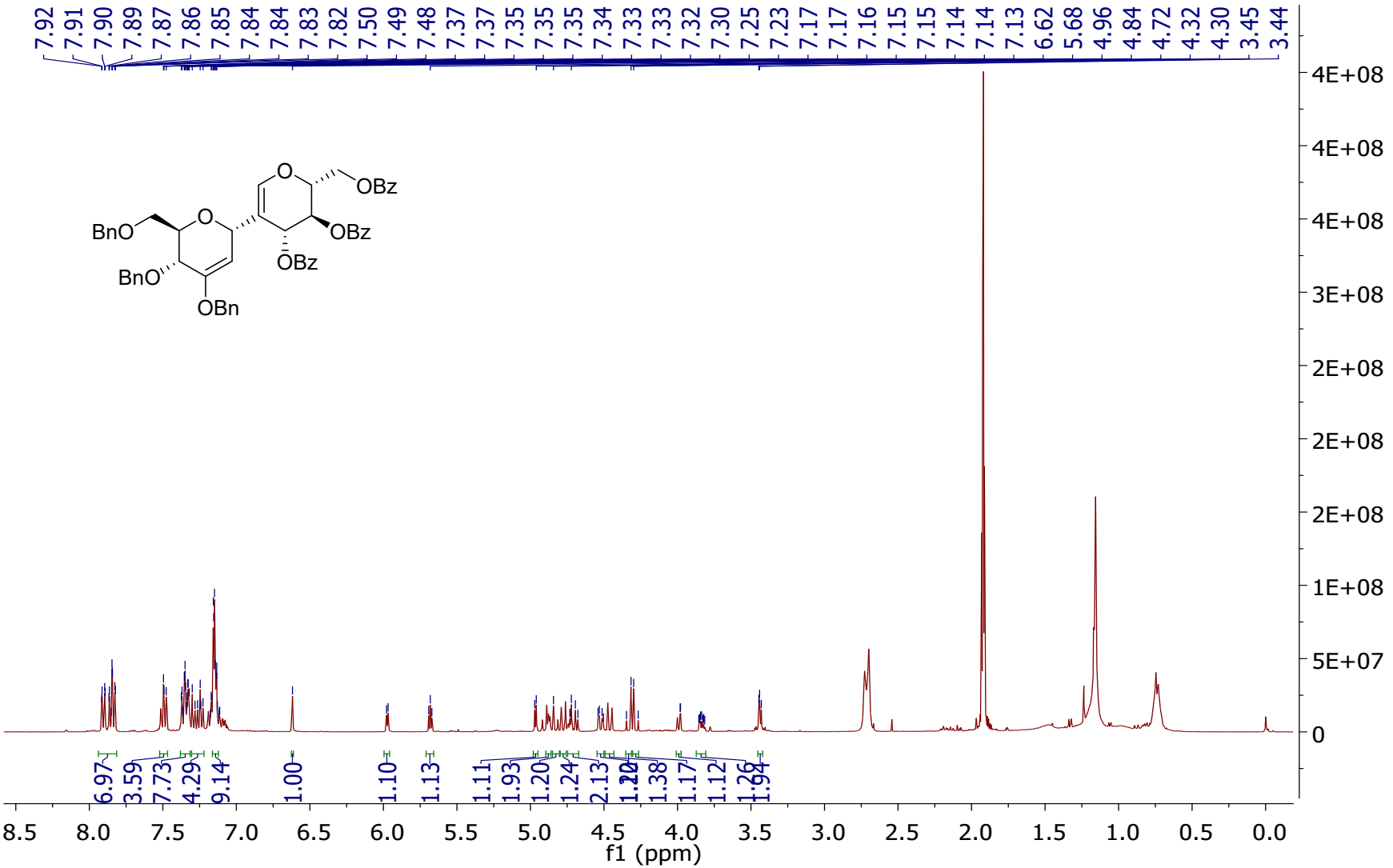

170.50
170.10
154.62
146.51
138.28
136.76
128.56
128.42
128.36
127.91
127.80
127.25
109.47
96.28
77.29
74.48
72.31
72.18
69.09
68.31
67.18
66.98
20.94
20.86
18.25
16.53
O
O
OAc
OAc
BnO
OBn
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

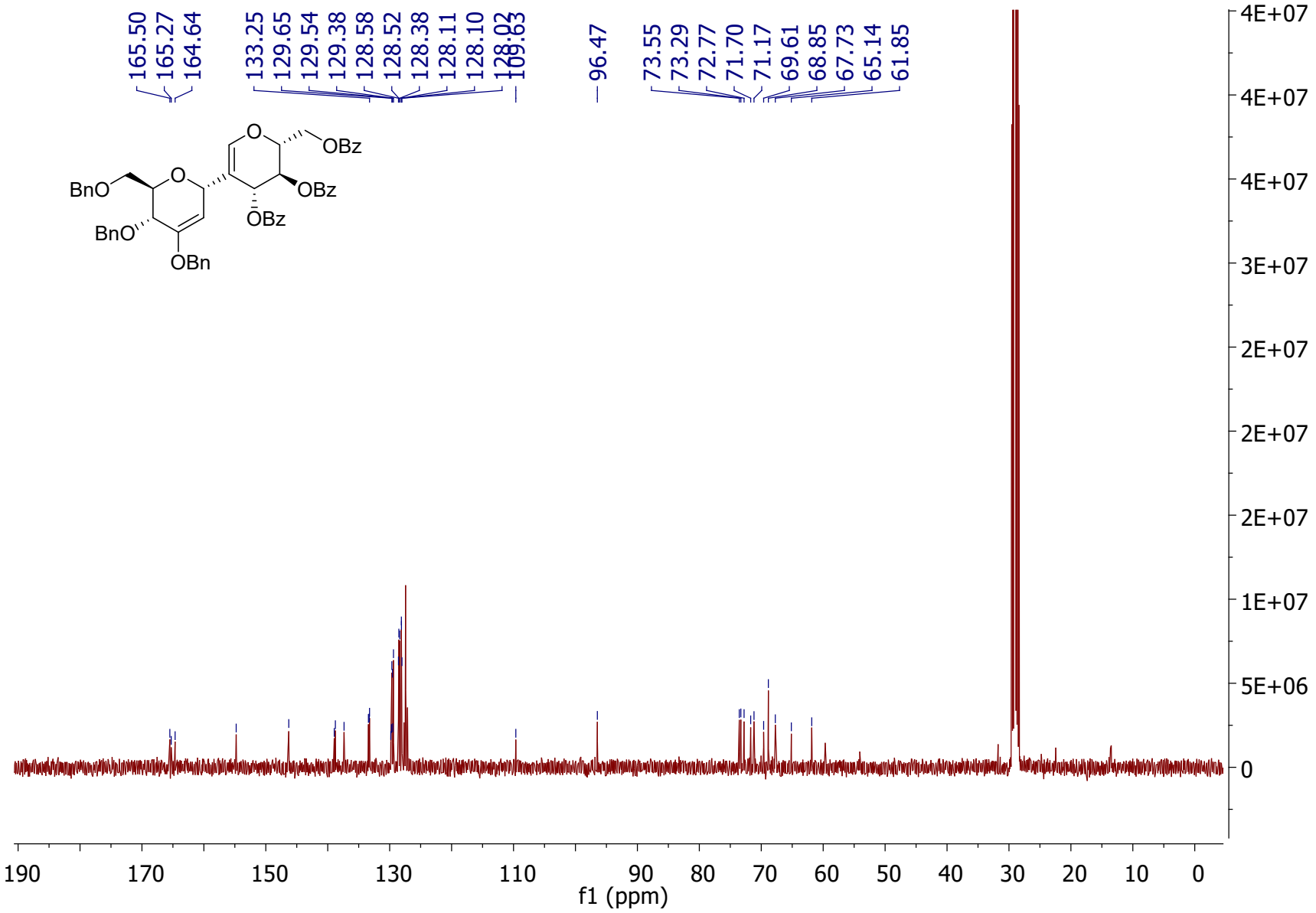
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 3g (α/β; 4:1):



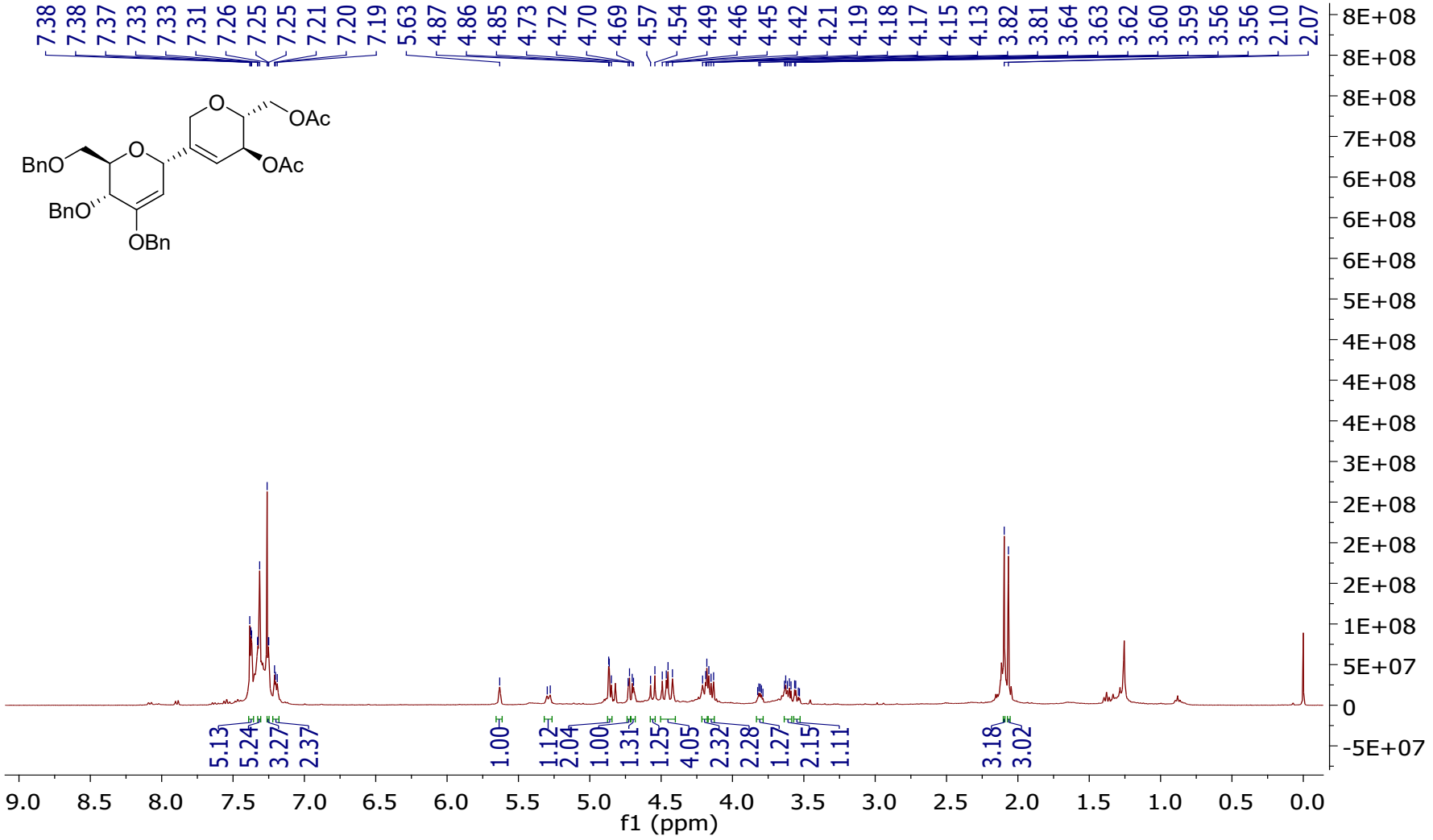

170.59
170.21
169.72
155.58
146.24
109.86
93.98
73.62
71.52
70.56
69.42
68.68
67.92
67.46
66.97
66.14
62.67
61.33
20.86
20.82
20.71
15.59
15.09
14.46
OEt
O
OAc
OAc
OAc
EtO
OEt
3E+09
3E+09
3E+09
2E+09
2E+09
2E+09
2E+09
2E+09
1E+09
1E+09
1E+09
8E+08
6E+08
4E+08
2E+08
0
-2E+08
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

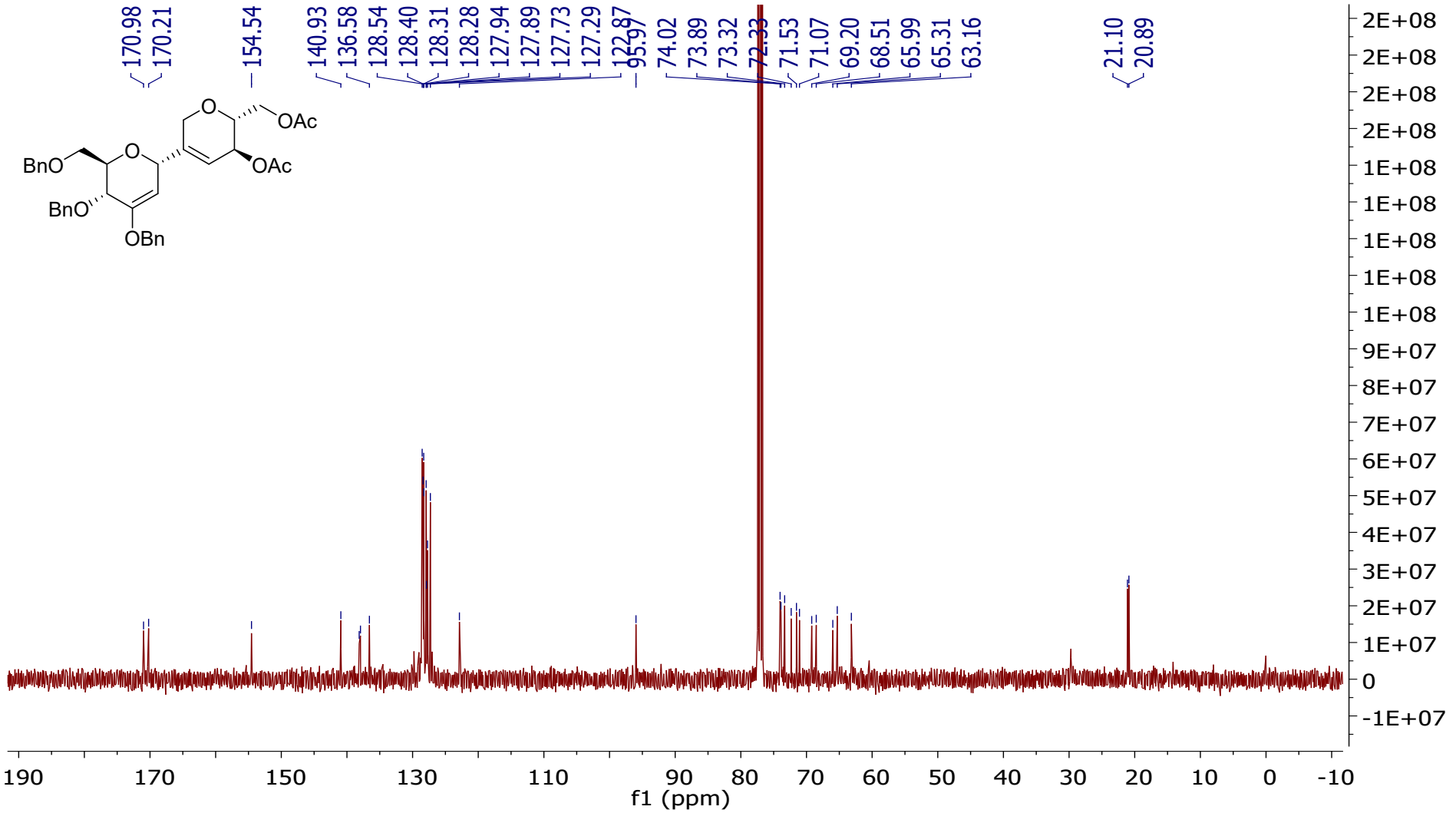
^{1}H NMR (400 MHz, acetone-d_6) and ^{13}C {^{1}H} NMR (101 MHz, acetone-d_6) of compound 3h



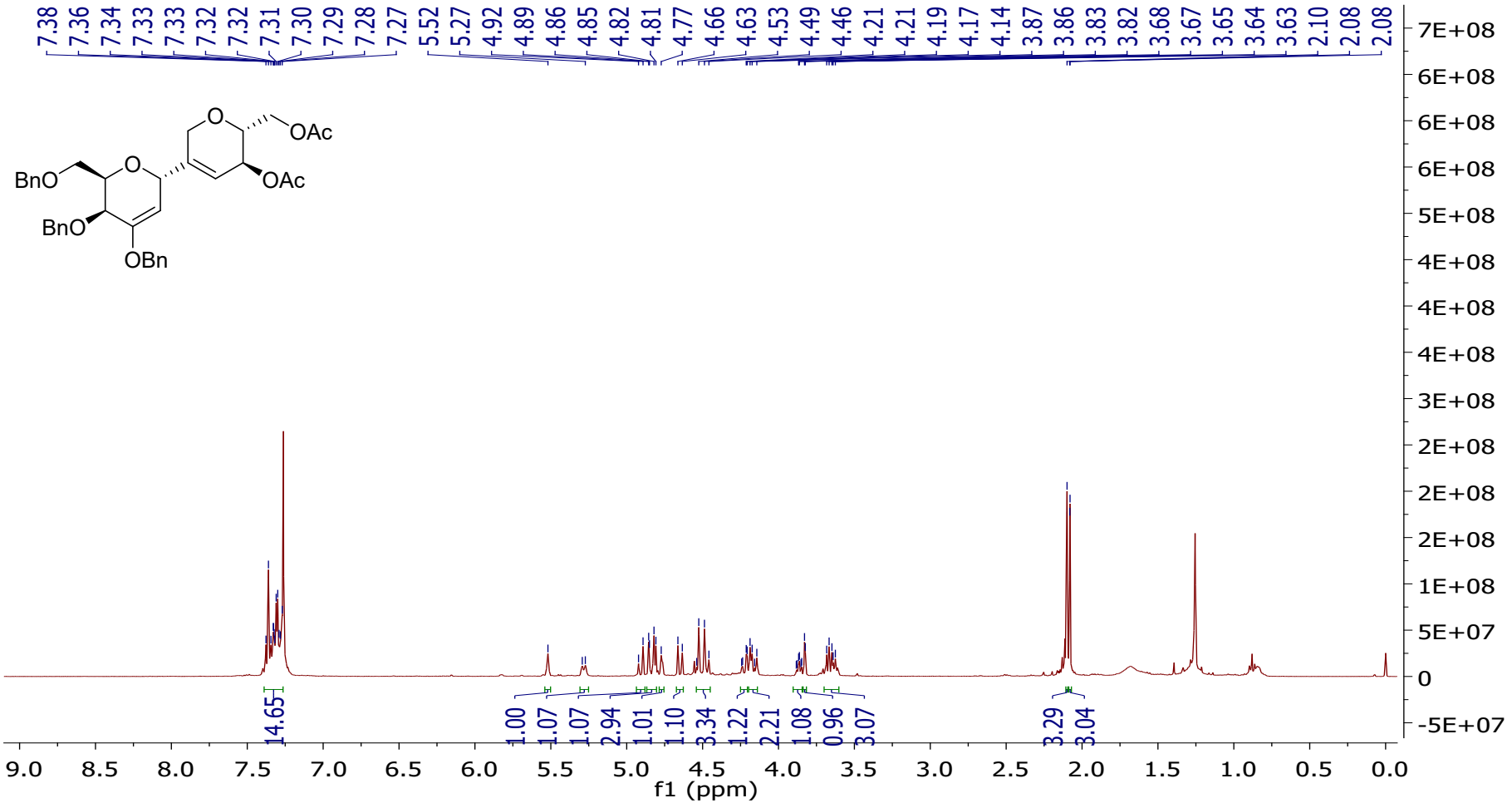

165.50
165.27
164.64
133.25
129.65
129.54
129.38
128.58
128.52
128.38
128.11
128.10
128.02
109.83
96.47
73.55
73.29
72.77
71.70
71.17
69.61
68.85
67.73
65.14
61.85
BnO
BnO
OBn
OBz
OBz
OBz
4E+07
4E+07
4E+07
3E+07
2E+07
2E+07
2E+07
1E+07
5E+06
0
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

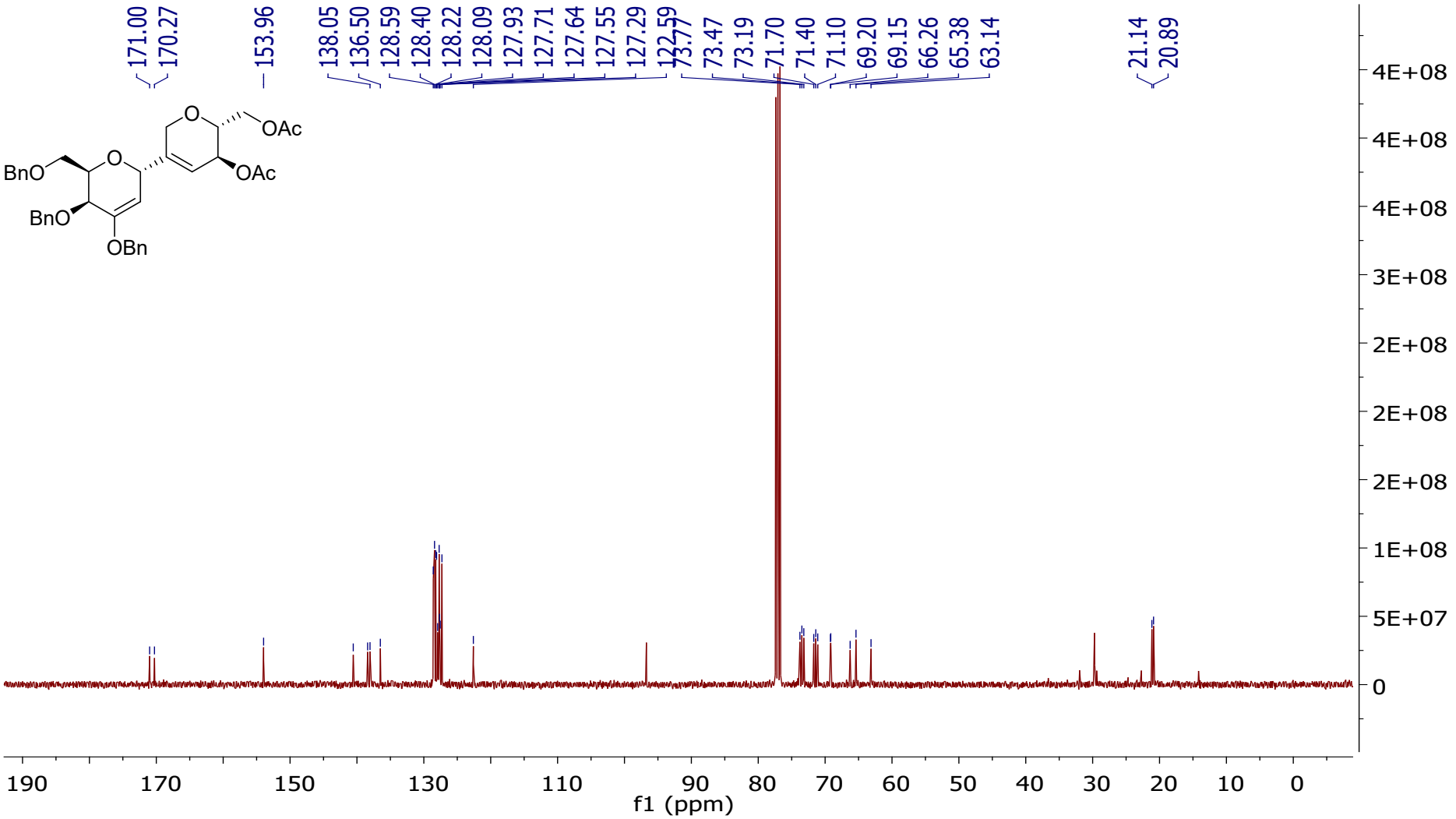
^{1}H NMR (400 MHz ,$CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 6a



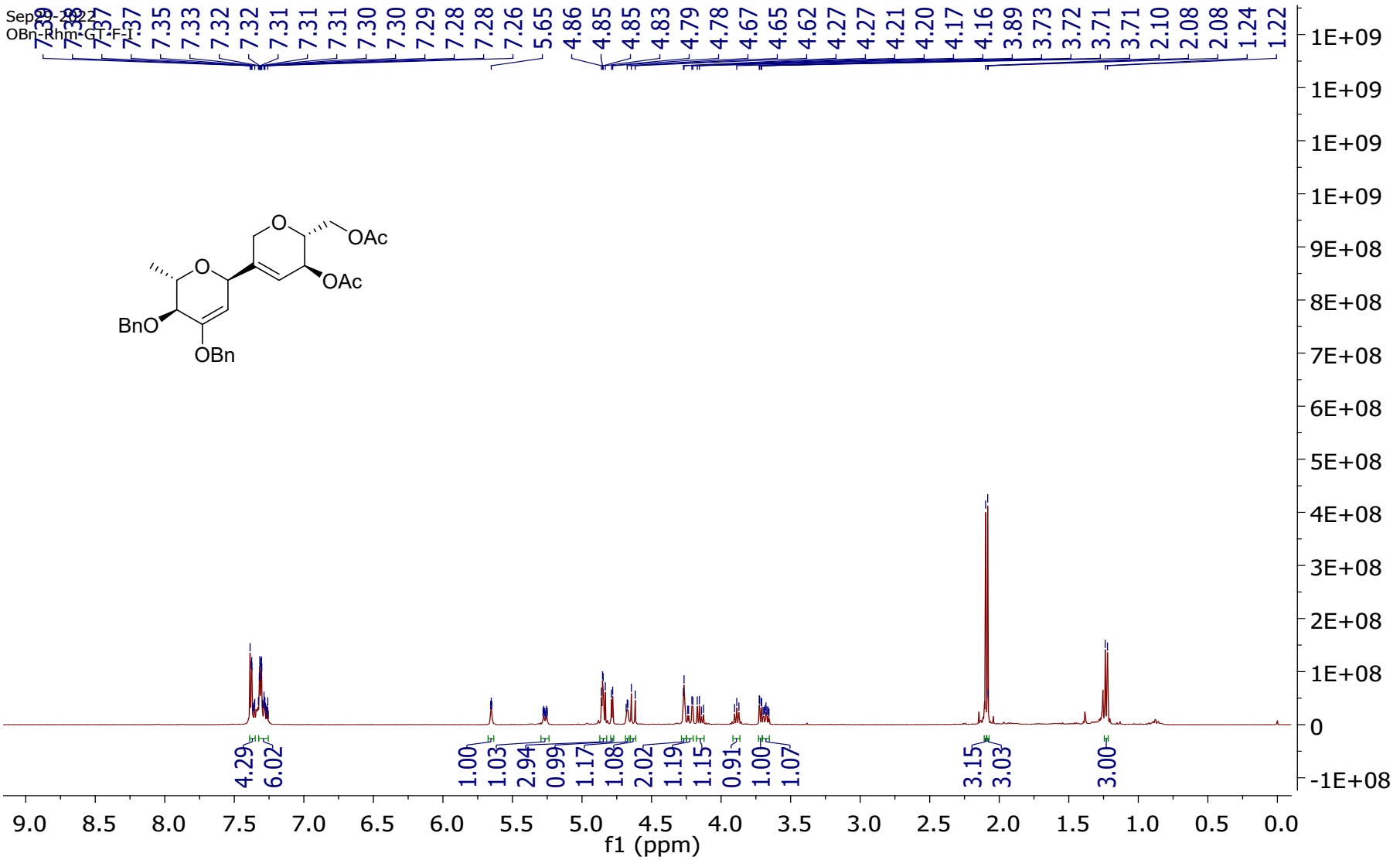

170.98
170.21
154.54
140.93
136.58
128.54
128.40
128.31
128.28
127.94
127.89
127.73
127.29
122.87
95.97
74.02
73.89
73.32
72.33
71.53
71.07
69.20
68.51
65.99
65.31
63.16
21.10
20.89
BnO
BnO
OBn
OAc
OAc
O
O
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
1E+08
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

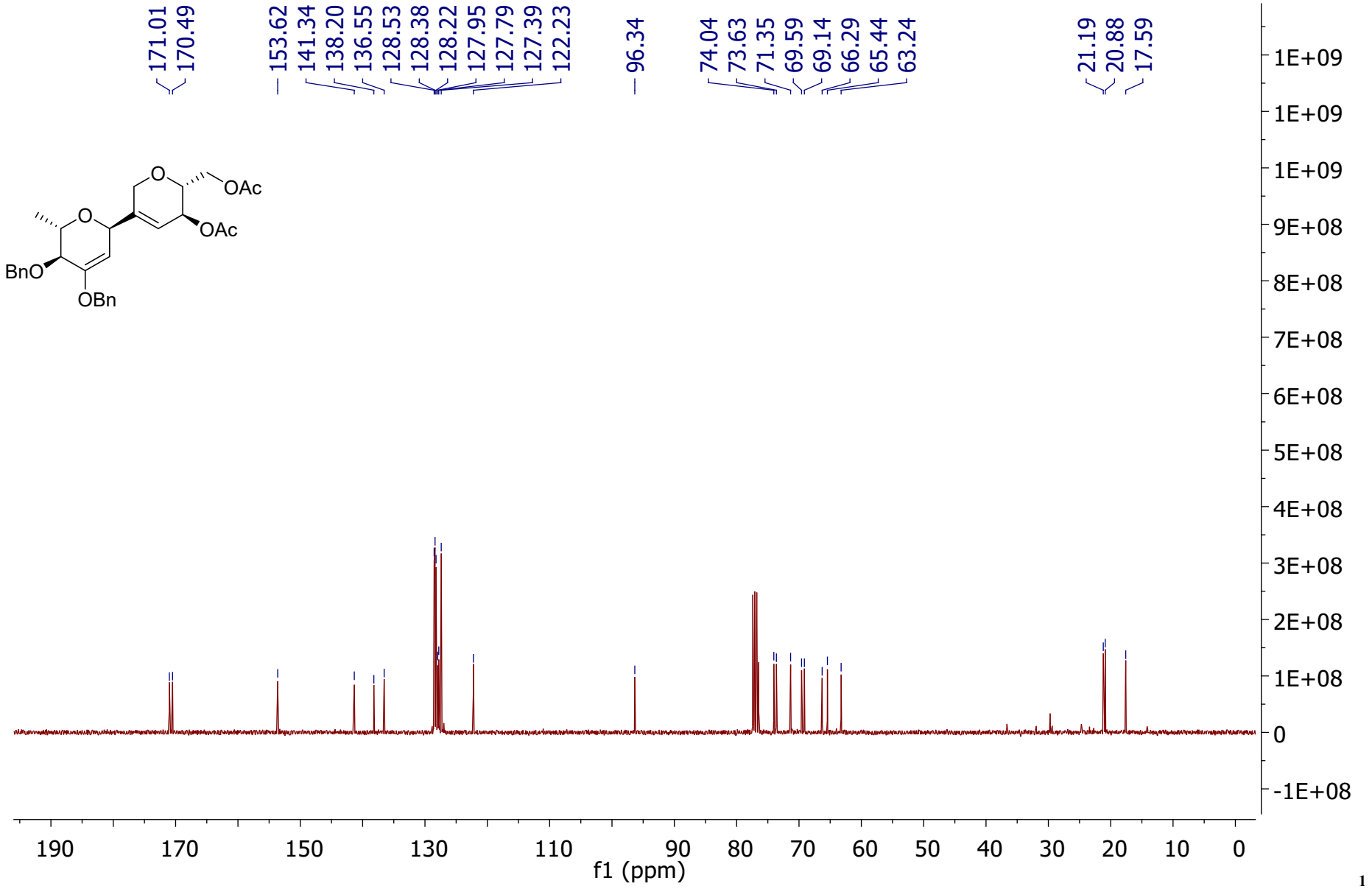
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 6b



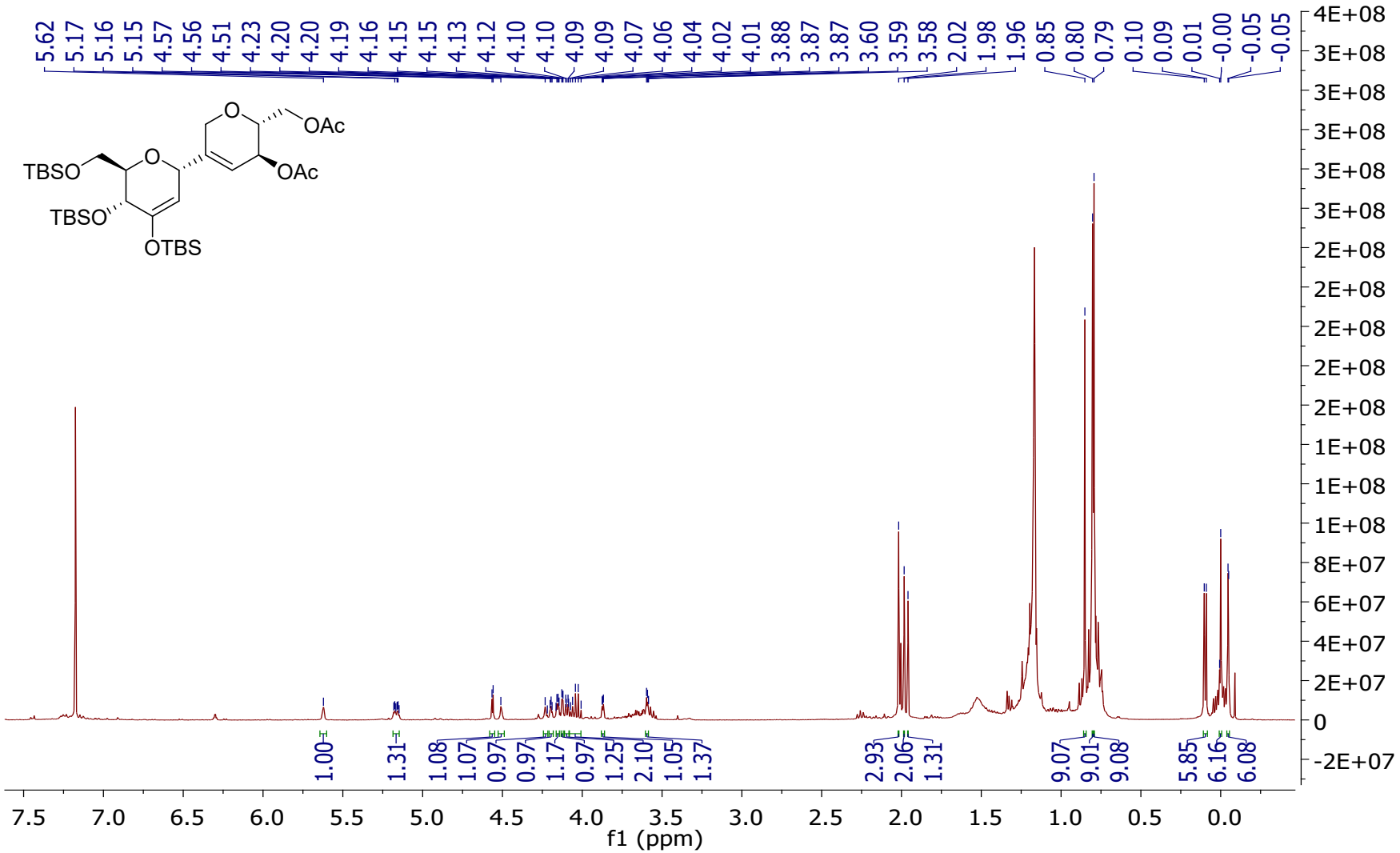

171.00
170.27
153.96
138.05
136.50
128.59
128.40
128.22
128.09
127.93
127.71
127.64
127.55
127.29
122.59
73.77
73.47
73.19
71.70
71.40
71.10
69.20
69.15
66.26
65.38
63.14
21.14
20.89
BnO
BnO
OBn
OAc
OAc
O
O
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

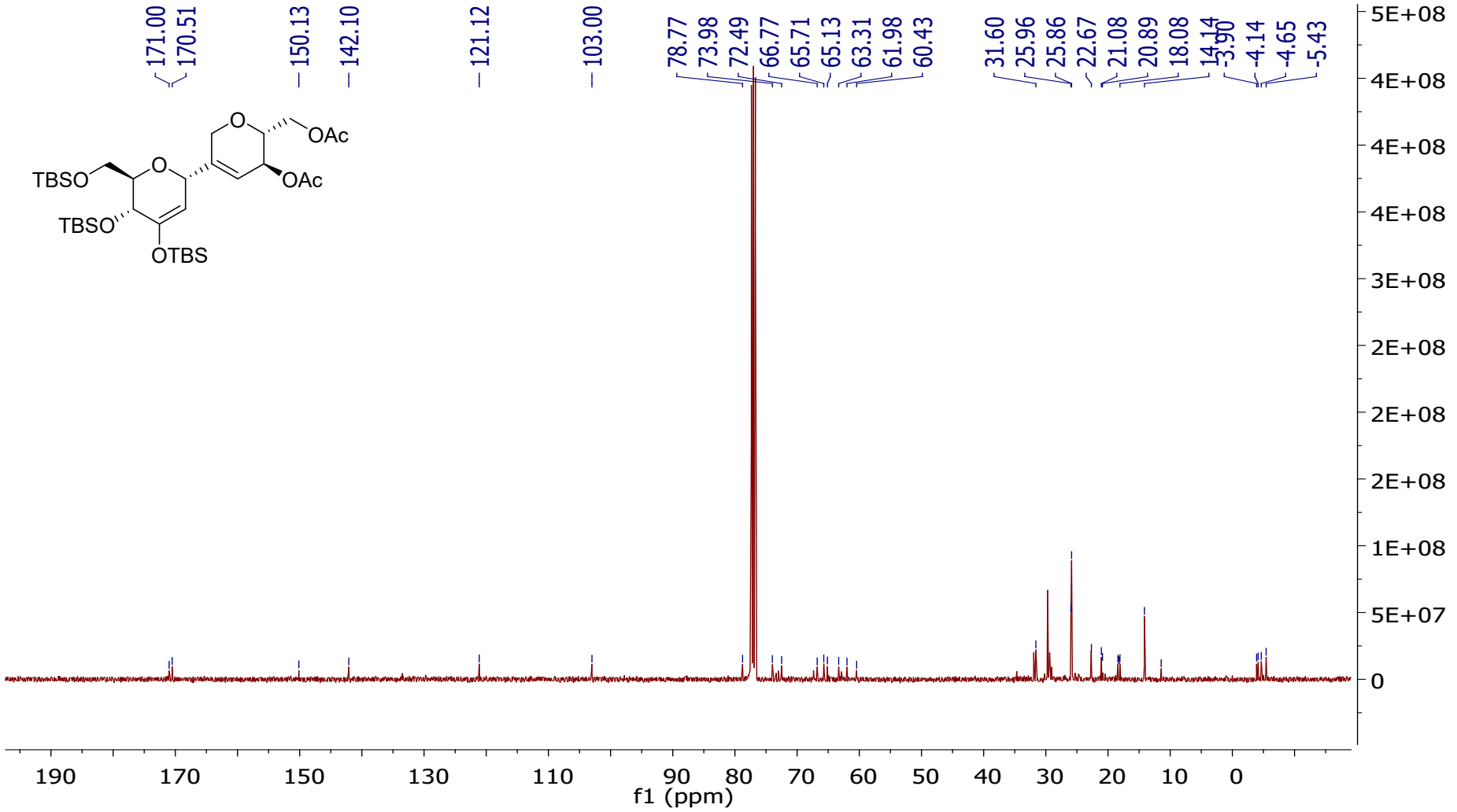
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 6c



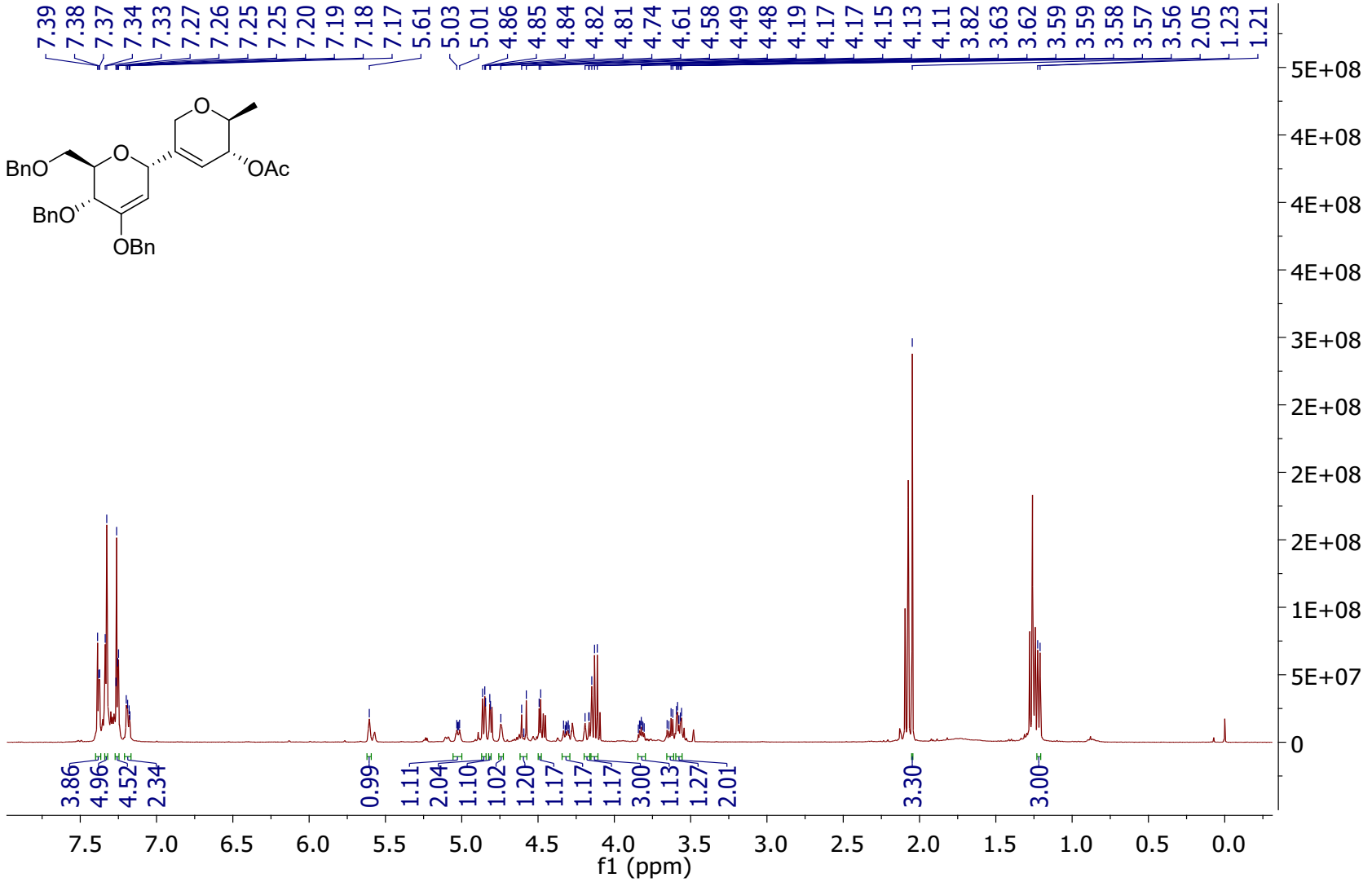

171.01
170.49
153.62
141.34
138.20
136.55
128.53
128.38
128.22
127.95
127.79
127.39
122.23
96.34
74.04
73.63
71.35
69.59
69.14
66.29
65.44
63.24
21.19
20.88
17.59
OAc
OAc
BnO
OBn
1E+09
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

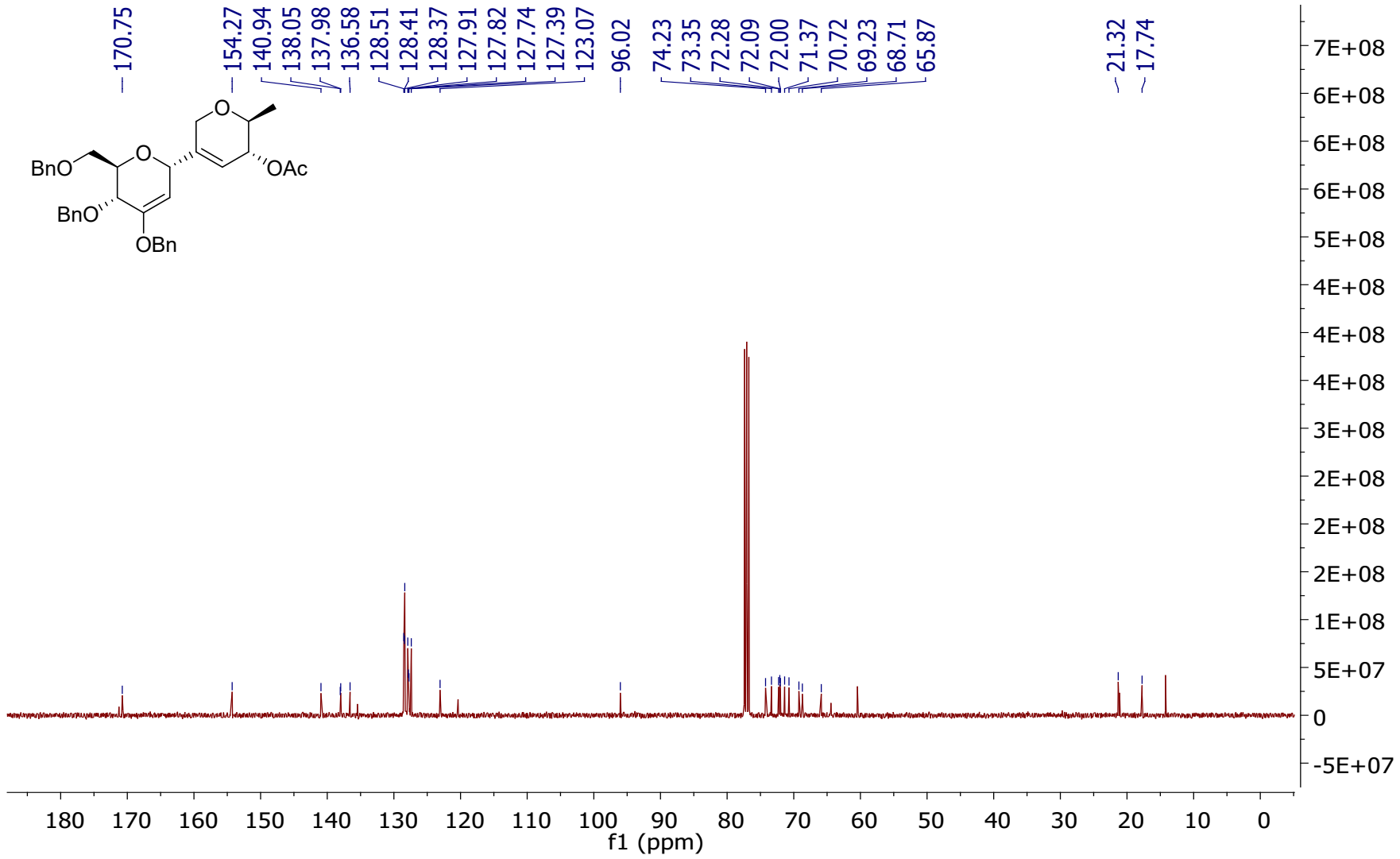
H NMR (400 MHz, $CDCl_3$) and ^{13}C {^1H} NMR (101 MHz, $CDCl_3$) of compound 6d



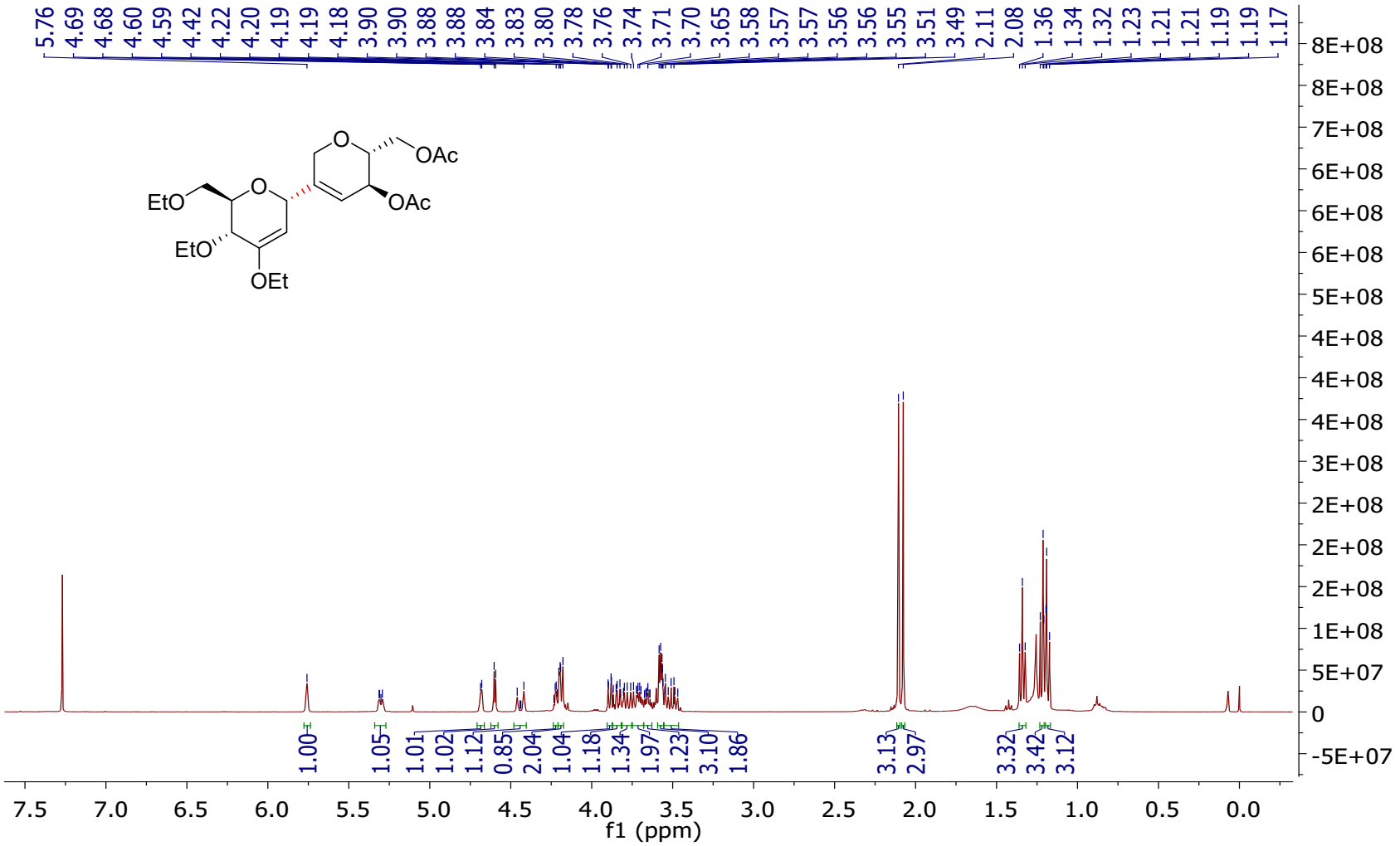

171.00
170.51
150.13
142.10
121.12
103.00
78.77
73.98
72.49
66.77
65.71
65.13
63.31
61.98
60.43
31.60
25.96
25.86
22.67
21.08
20.89
18.08
14.14
-3.90
-4.14
-4.65
-5.43
OAc
OAc
TBSO
TBSO
OTBS
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

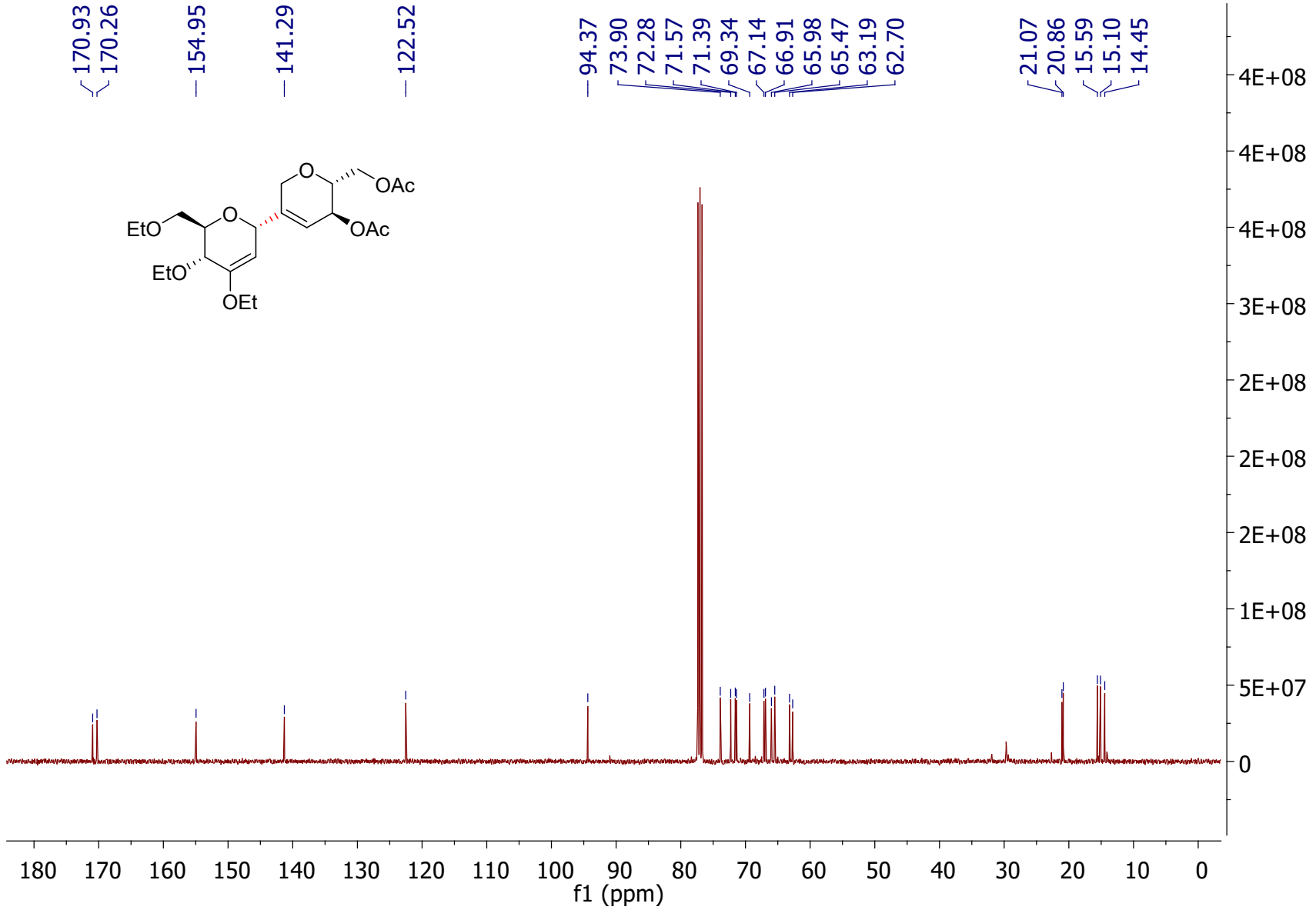
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 6e:



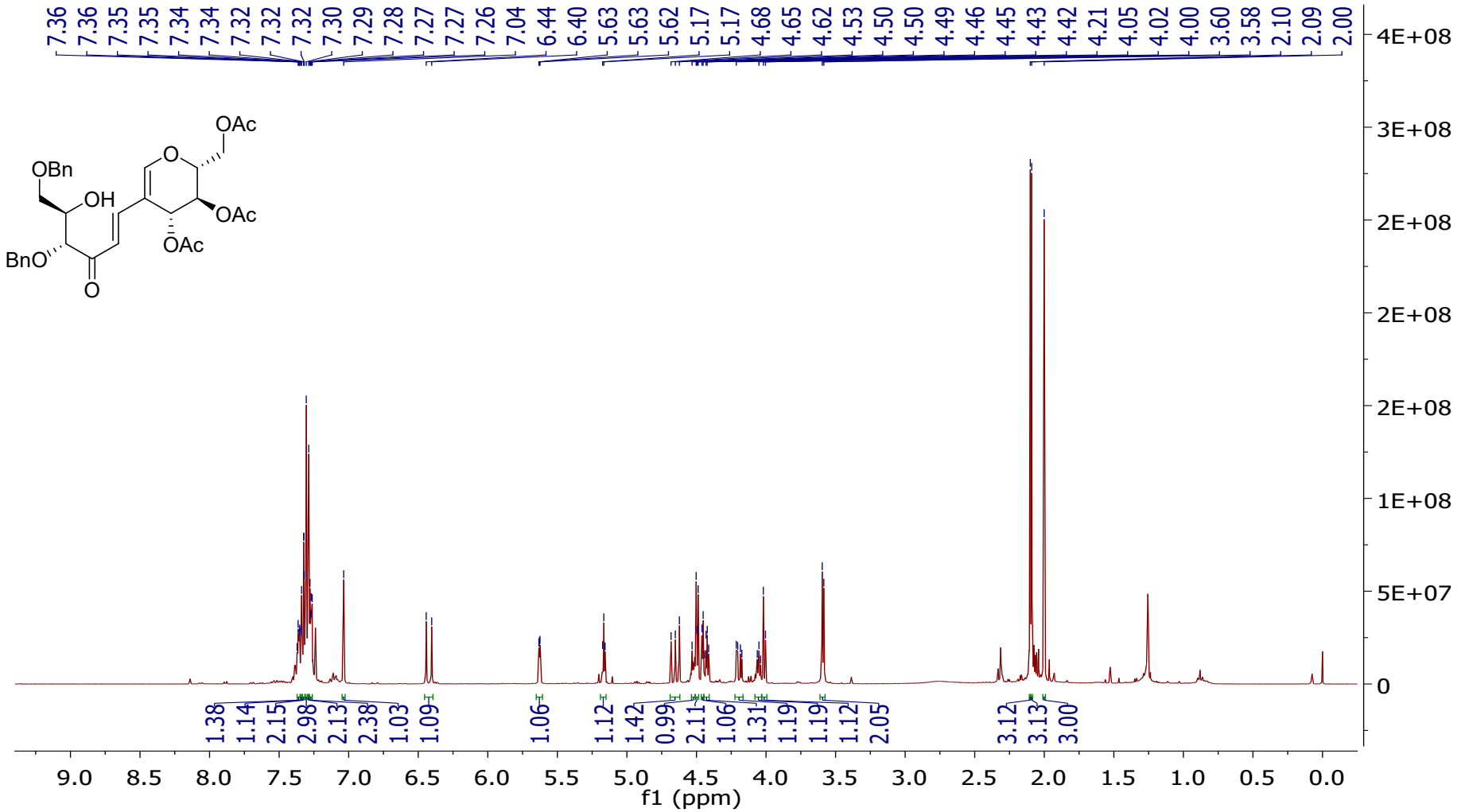

170.75
154.27
140.94
138.05
137.98
136.58
128.51
128.41
128.37
127.91
127.82
127.74
127.39
123.07
96.02
74.23
73.35
72.28
72.09
72.00
71.37
70.72
69.23
68.71
65.87
21.32
17.74
BnO
BnO
OBn
OAc
O
O
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

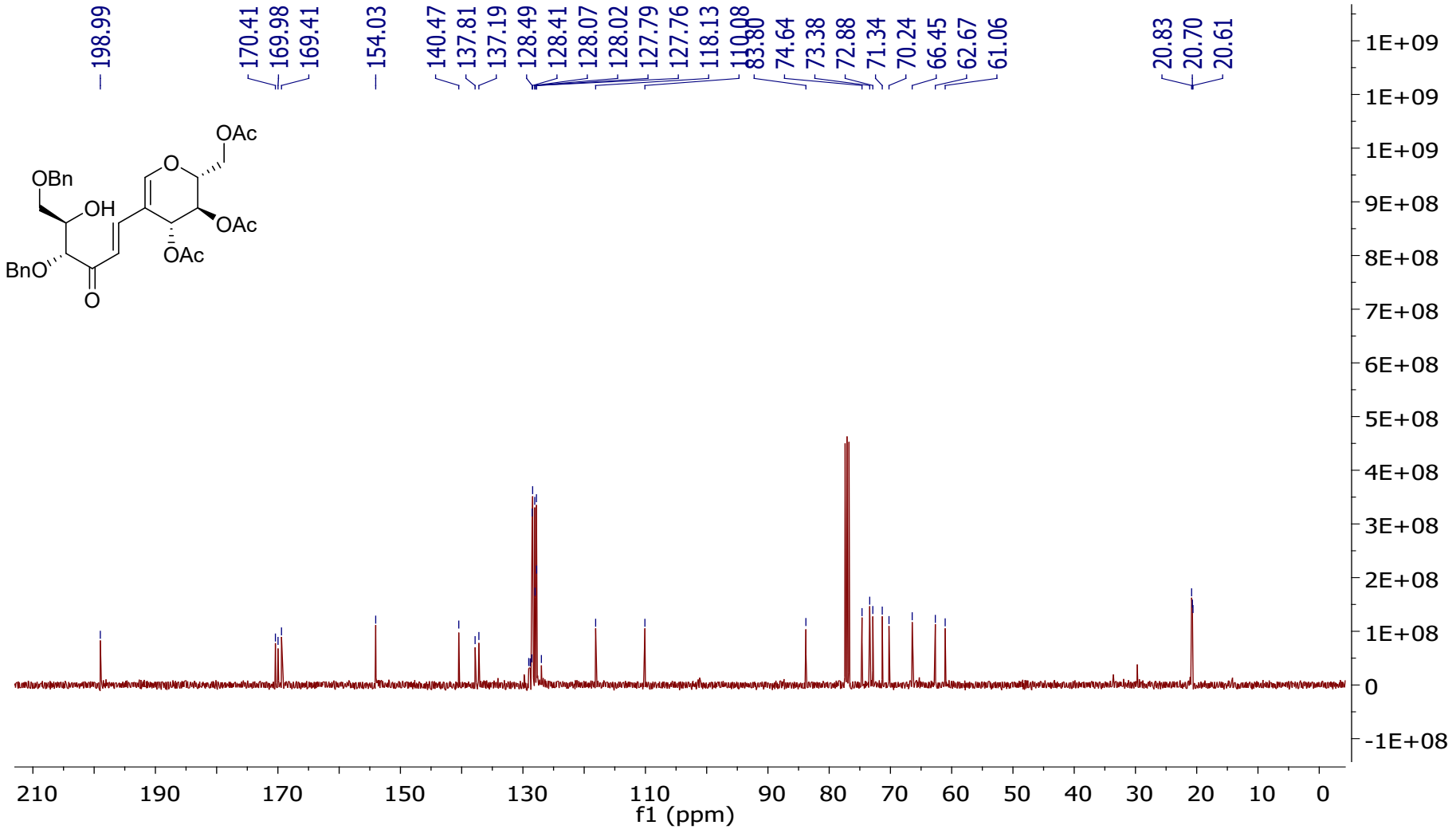
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) of compound 6f



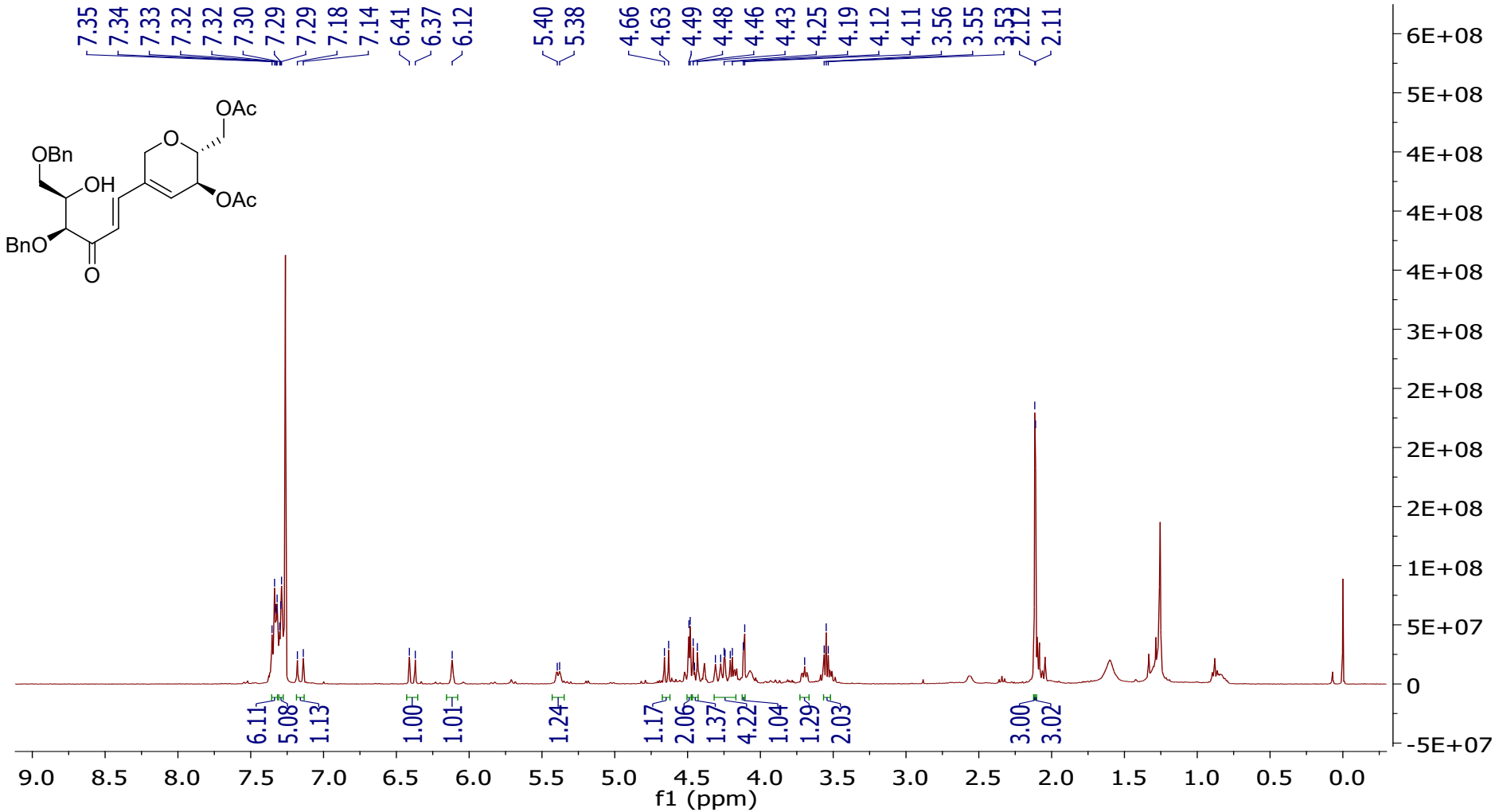

170.93
170.26
154.95
141.29
122.52
94.37
73.90
72.28
71.57
71.39
69.34
67.14
66.91
65.98
65.47
63.19
62.70
21.07
20.86
15.59
15.10
14.45
EtO
EtO
OEt
OAc
OAc
O
O
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

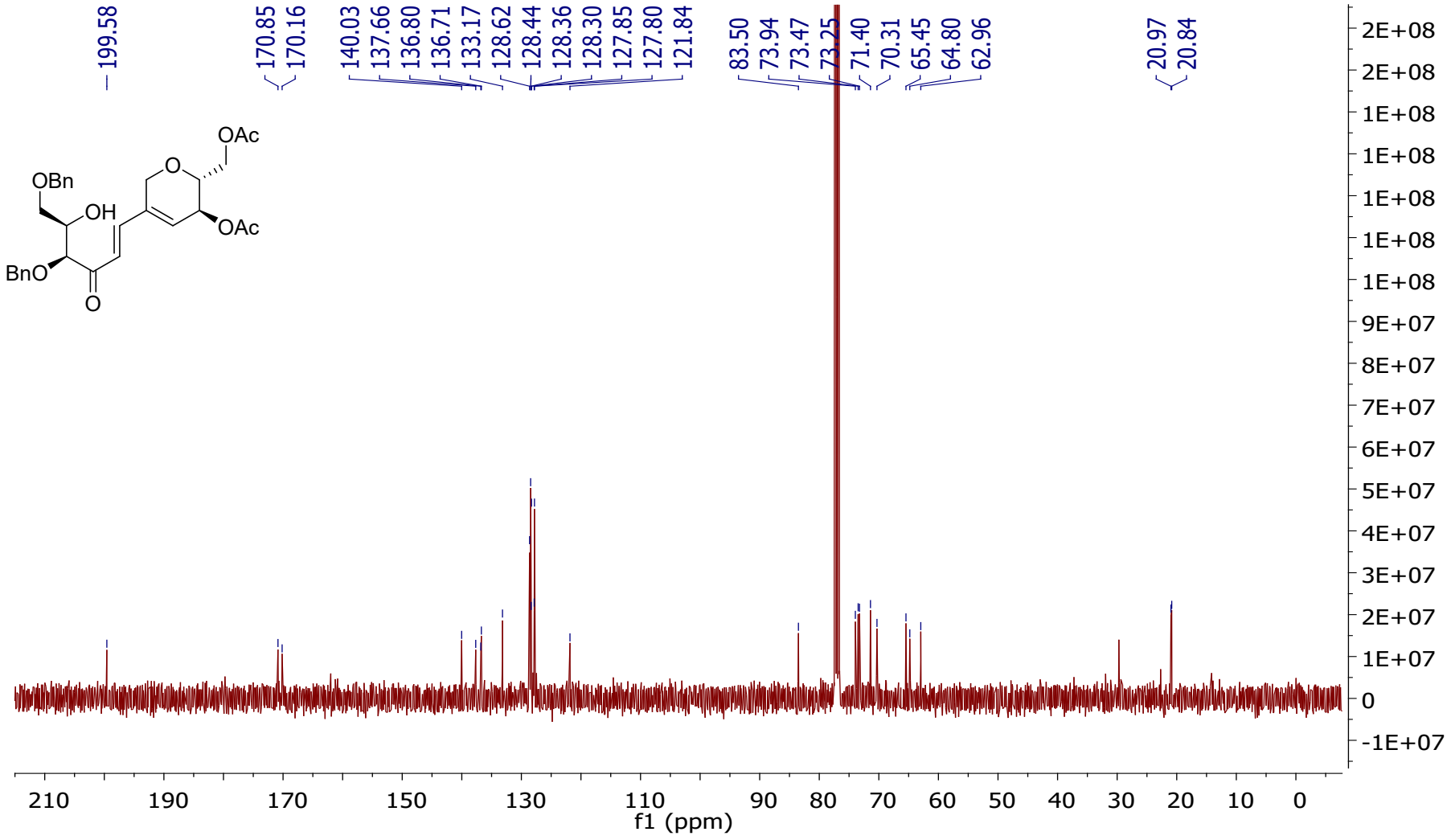
^{1}H (400 MHz, $CDCl_3$) & ^{13}C {^{1}H} (101 MHz, $CDCl_3$) NMR of compound 7



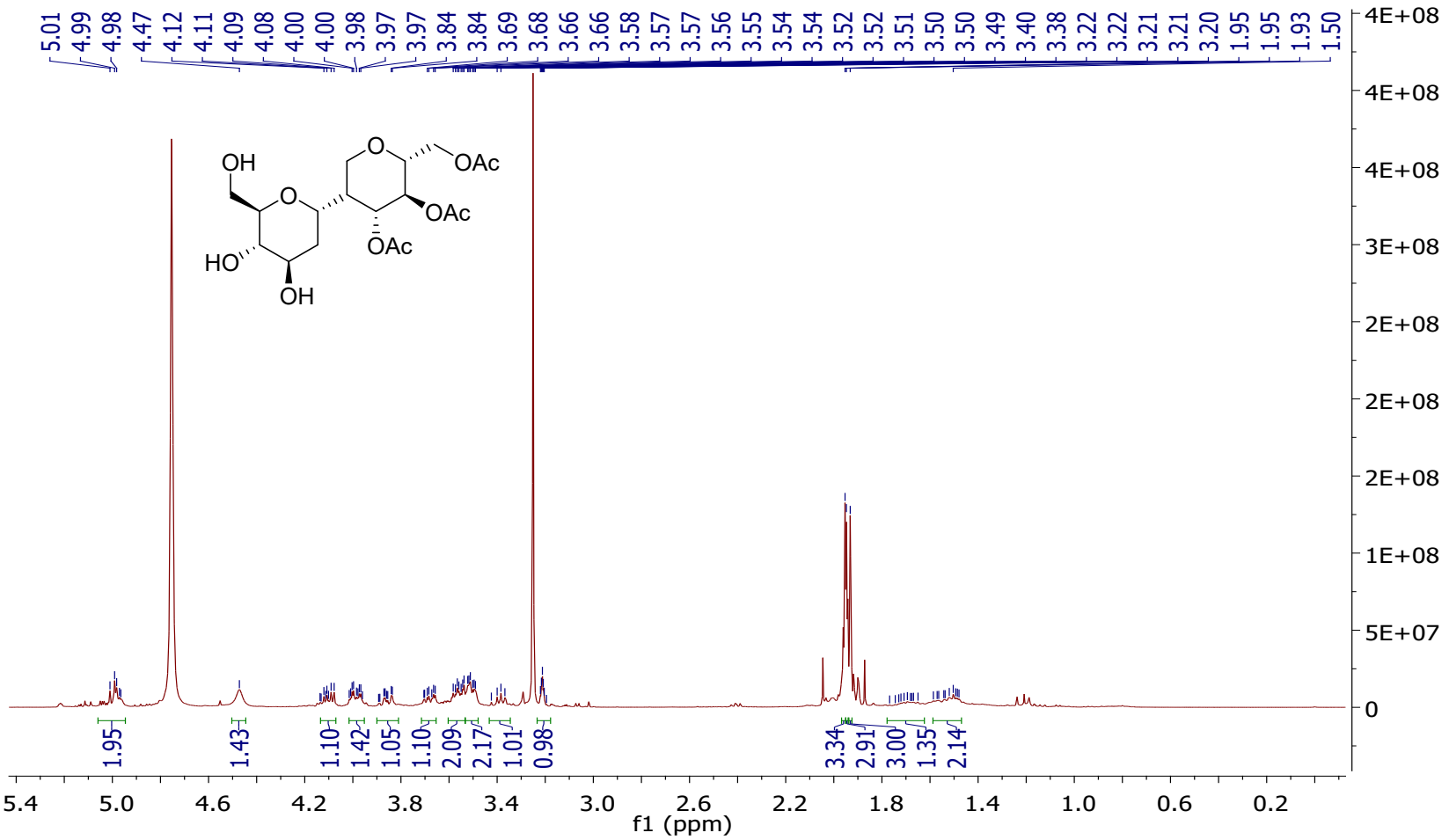

198.99
170.41
169.98
169.41
154.03
140.47
137.81
137.19
128.49
128.41
128.07
128.02
127.79
127.76
118.13
110.08
83.80
74.64
73.38
72.88
71.34
70.24
66.45
62.67
61.06
20.83
20.70
20.61
OAc
OBn
OH
O
OAc
BnO
OAc
O
1E+09
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

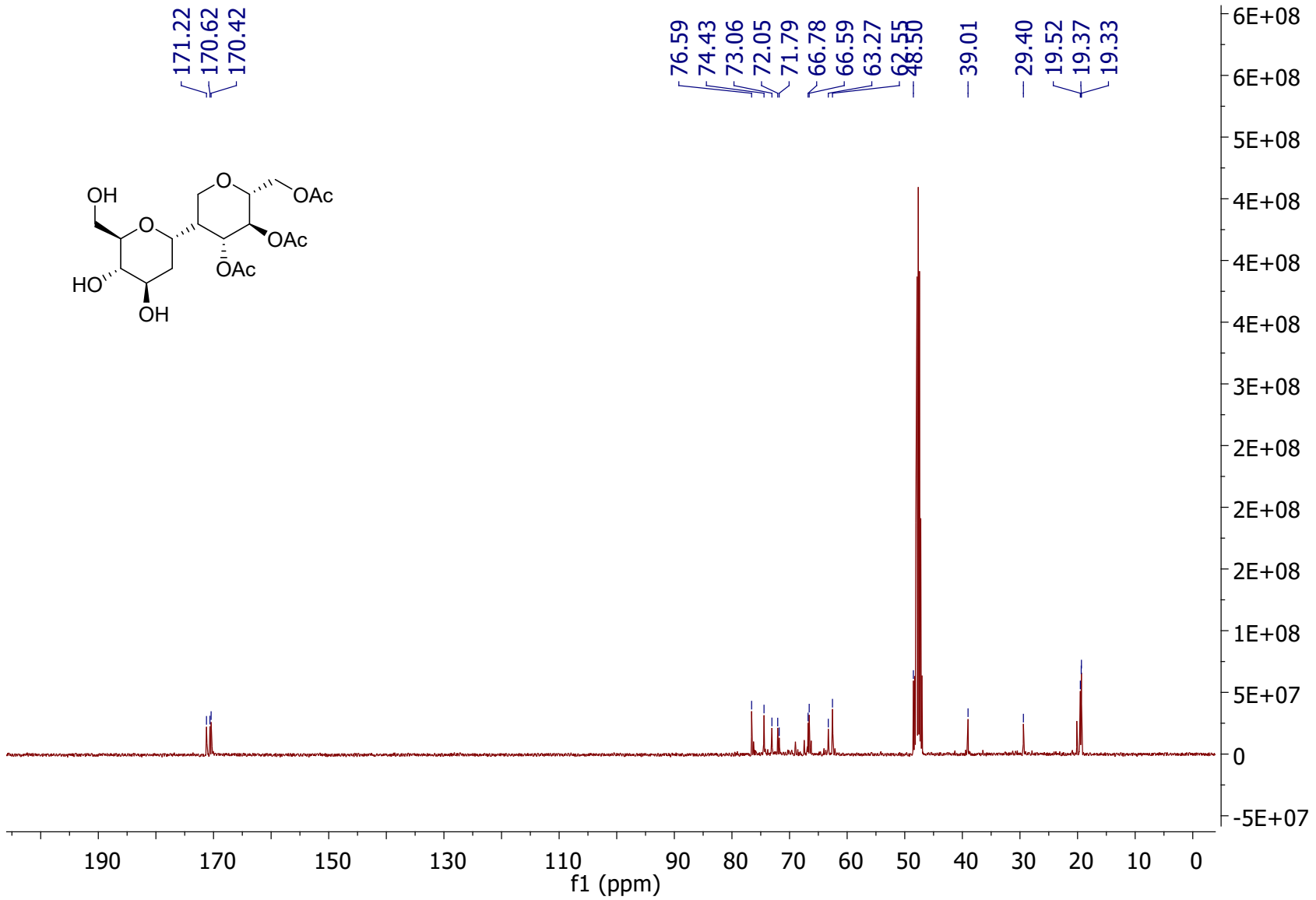
^{1}H (400 MHz, $CDCl_3$) & ^{13}C $\{^{1}H\}$ (101 MHz, $CDCl_3$) NMR of compound 8




199.58
170.85
170.16
140.03
137.66
136.80
136.71
133.17
128.62
128.44
128.36
128.30
127.85
127.80
121.84
83.50
73.94
73.47
73.25
71.40
70.31
65.45
64.80
62.96
20.97
20.84
OAc
OBn
OH
OAc
BnO
O
O
2E+08
2E+08
1E+08
1E+08
1E+08
1E+08
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

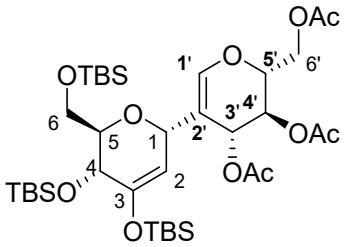
^{1}H (400 MHz, $CDCl_3$) & ^{13}C {^{1}H} (101 MHz, $CDCl_3$) NMR of compound 9

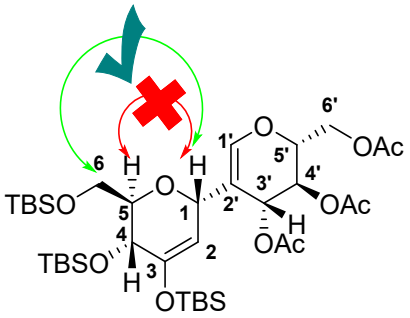



171.22
170.62
170.42
76.59
74.43
73.06
72.05
71.79
66.78
66.59
63.27
62.55
48.50
39.01
29.40
19.52
19.37
19.33
OH
O
OAc
OAc
OAc
HO
OH
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4.1 2D Data of Compound 3d:

4.1.1 Structure determination of compound 3d:

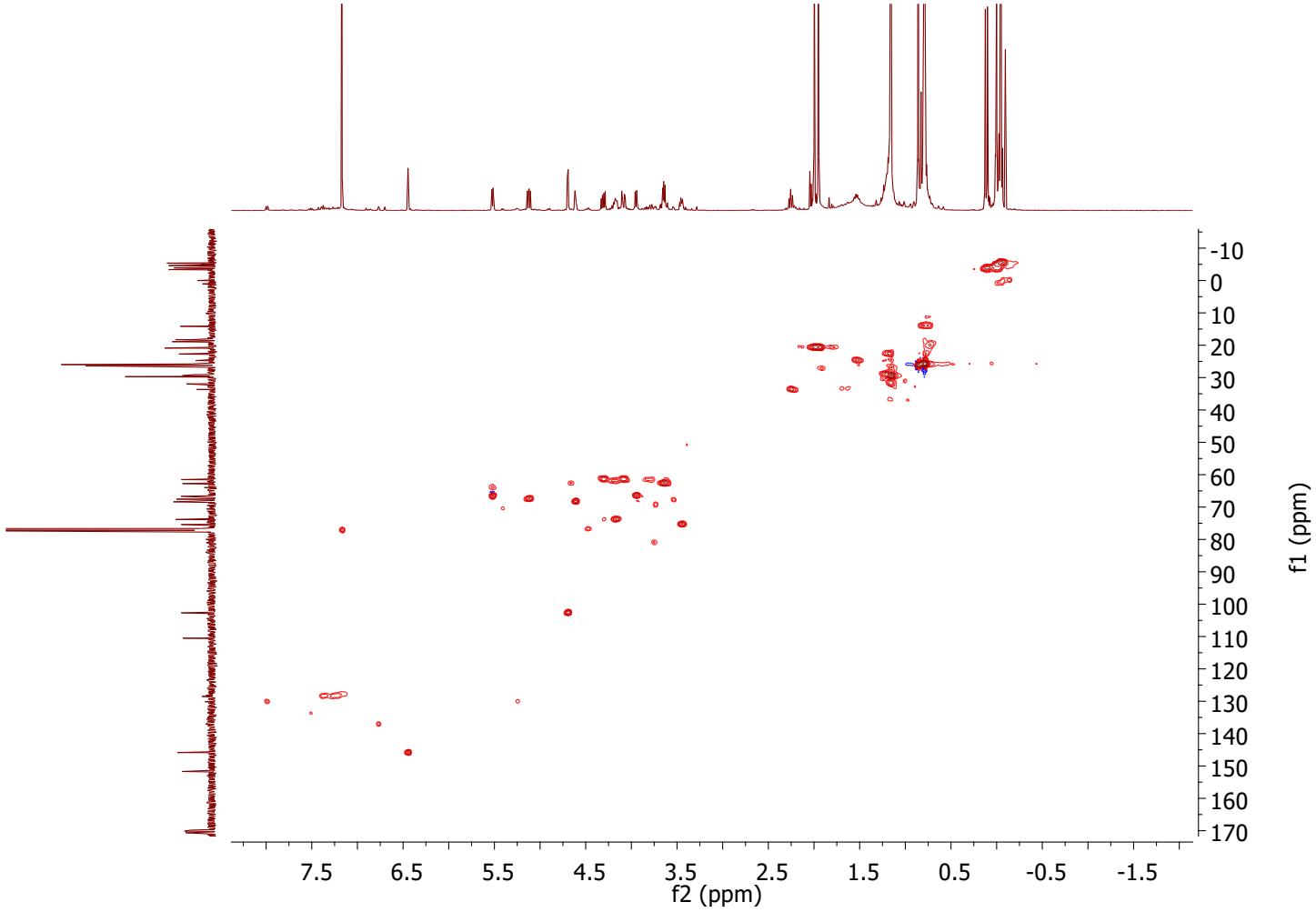




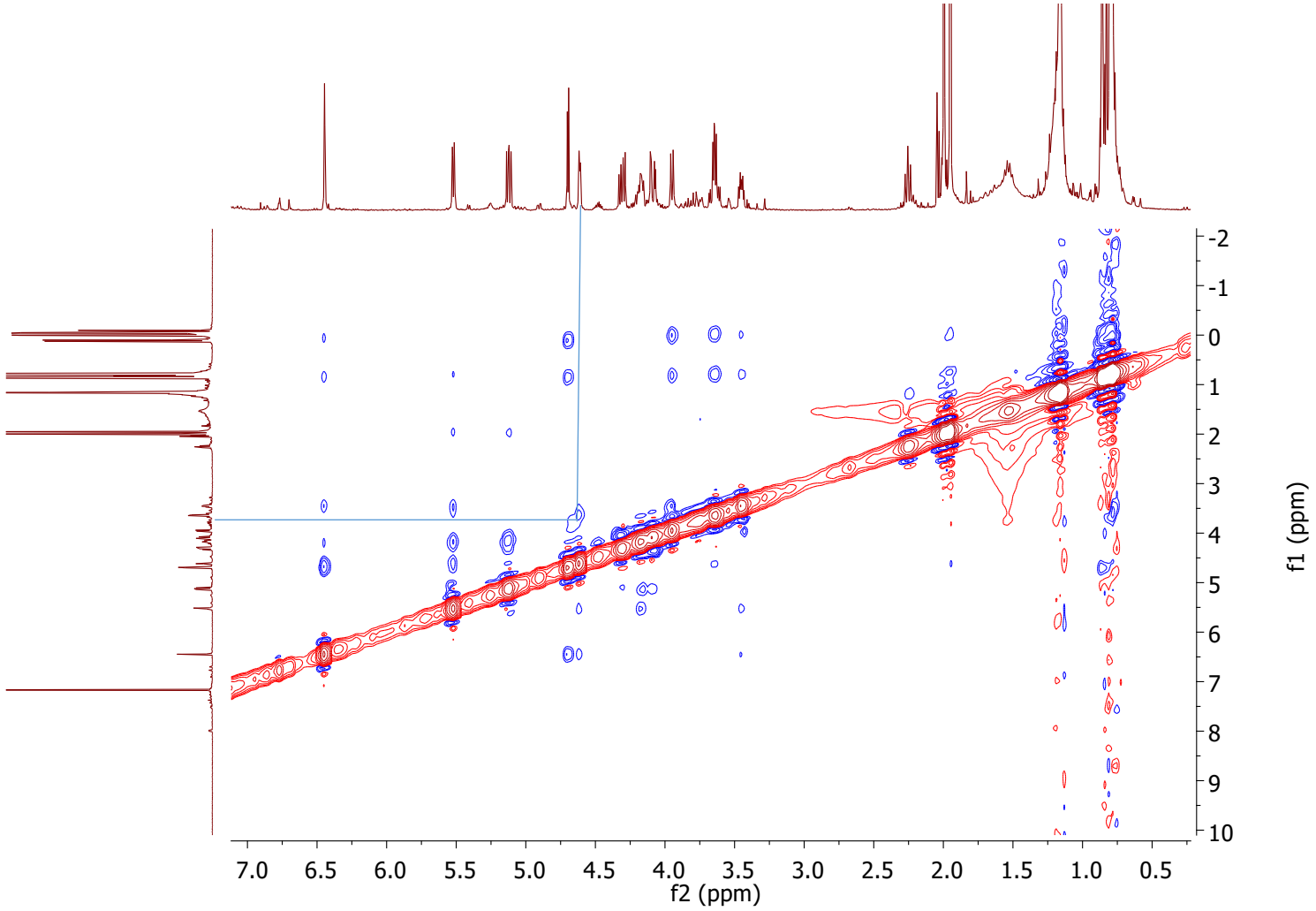
Atom Position	Type Of Atom	1H(ppm)	13C(ppm)
1	CH	4.61	68.4
2	CH	4.70	102.7
3	C		151.7
4	CH	3.95	66.56
5	CH	3.45	75.39
6	CH_2	3.64,3.65	62.8
1’	CH	6.45	145.9
2’	C		110.51
3’	CH	5.52	66.56
4’	CH	5.12	67.56
5’	CH	4.18	73.84
6’	CH_2	4.09,4.31	61.52

The structure of product 3d was confirmed by 2D NMR analysis. In NOESY experiment we observed the strong correlation between H1 and H6 but no correlation was seen between H1 and H5 which confirmed the alpha stereochemistry at anomeric carbon.

4.1.2 HSQC of 3d



4.1.3 NOESY of 3d:



5. References:

1 S. Dharuman and Y. D. Vankar, 2014, 1172–1175.