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Automated glycan assembly of highly branched heptadecasaccharide repeating unit of arabinogalactan polysaccharide HH1-1 from *Carthamus tinctorius* †

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1. General Information

All chemicals used were reagent grade and used as supplied unless otherwise noted. Automated syntheses were performed on a home-built synthesizer developed at the Max Planck Institute of Colloids and Interfaces.Merrifield resin LL (100-200 mesh, NovabiochemTM) was modified and used as solid support.[1] Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates (0.25 mm). Compounds were visualized by UV irradiation or dipping the plate in a *p*-anisaldehyde (PAA) solution. Flash column chromatography was carried out by using forced flow of the indicated solvent on Fluka Kieselgel 60 M (0.04 – 0.063 mm). Analysis and purification by normal and reverse phase HPLC were performed using an Agilent 1200 series. Products were lyophilized using a Christ Alpha 2-4 LD plus freeze dryer. ^{1}H, ^{13}C and HSQC NMR spectra were recorded on a Varian 400-MR (400 MHz), Varian 600-MR (600 MHz), or Bruker Biospin AVANCE700 (700 MHz) spectrometer. Spectra were recorded in $CDCl_3$ by using the solvent residual peak chemicalshift as the internal standard ($CDCl_3$: 7.26 ppm ^{1}H, 77.16 ppm ^{13}C) or in D_2O using the solvent as the internal standard in ^{1}H NMR (D_2O: 4.79 ppm ^{1}H) unless otherwise stated. High resolution mass spectra were obtained using a 6210 ESI-TOF mass spectrometer (Agilent) and a MALDI-TOF AutoflexTM (Bruker). MALDI and ESI mass spectra were run on IonSpec Ultima instruments.

Automated Synthesis

Solvents used for dissolving building blocks and preparing the activator, TMSOTf and capping solutions were taken from an anhydrous solvent system (jcmeyer-solvent systems). Other solvents used were HPLC grade. The building blocks were co-evaporated three times with toluene and dried under high vacuum before use. Activator, deprotection, acidic wash, capping and building block solutions were freshly prepared and kept under argon during the automation run. All yields of products obtained by AGA were calculated based on resin loading. Resin loading was determined by performing one glycosylation (Module C) with ten equivalents of building block followed by DBU promoted Fmoc-cleavage and determination of dibenzofulvene production by measuring its UV absorbance.

1. Preparation of Stock Solutions[2]

Building block: building block was dissolved in 1 mL dichloromethane (DCM).

Activator Solution 1 (for thioglycosides): Recrystallized NIS (1.58 g, 7.02 mmol) was dissolved in 45 mL of a 2:1 mixture of anhydrous CH2Cl2/dioxane, followed by addition of triflic acid (55 µL, 0.6 mmol). The solution was kept under ice-bath cooling for the duration of the automated run.

Activator Solution 2 (for glycosyl phosphates): TMSOTf (0.9 mL, 5.0 mmol) was added to 40 mL of anhydrous CH_2Cl_2.

Fmoc deprotection solution: A solution of 20% piperidine in dimethylformamide (DMF) (v/v) was prepared; or A solution of 5% DBU in dichloromethane (CH_2Cl_2) (v/v) was prepared.

TMSOTf solution: Trimethylsilyl trifluoromethanesulfonate (TMSOTf) (0.9 mL) wasadded to DCM (80 mL).

Capping solution: A solution of 10% acetic anhydride (Ac_2O) and 2% methanesulfunic acid (MsOH) in anhydrous CH_2Cl_2 (v/v) was prepared.

*Lev deprotection solution:*Hydrazine acetate (780 mg) was dissolved in a solution of 4:1:0.25 pyridine:AcOH:H2O (40 mL).

Modules for Automated Synthesis

3.1*Module A: Resin Preparation for Synthesis (20 min)*: All automated syntheses were performed on 140 µmol scale (40 mg). Resin was placed in the reaction vessel and swollen in DCM for 20 min at room temperature prior to synthesis. During this time, all reagent lines required for the synthesis were washed and primed. Before the first glycosylation, the resin was washed with DMF, tetrahydrofuran (THF), and CH_2Cl_2 (three times each with 2 mL for 25 s). This step is conducted as the first step for every synthesis.

3.2 *Module B: Acidic Wash with TMSOTf Solution (20 min):* The resin was swollen in CH_2Cl_2 (2 mL) and the temperature of the reaction vessel was adjusted to -20 °C. Upon reaching the desired temperature, the TMSOTf solution (1 mL) was added

drop wise to the reaction vessel. After bubbling argon for 3 min, the acidic solution was drained and the resin was washed with 2 mL CH_2Cl_2 for 25 s.

3.3 *Module C: Thioglycoside Glycosylation (20-60 min):* The building block solution (0.095-0.123 mmol (5-6.5 equivalents) of BB in 1 mL of CH_2Cl_2 per glycosylation) was delivered to the reaction vessel. After the set temperature (-20 ^oC) was reached, the reaction was started by dropwise addition of the activator solution (1.0 mL, excess). The glycosylation was performed by increasing the temperature to 0 ^oC for 20-60 min (depending on oligosaccharide length). After completion of the reaction, the solution is drained and the resin was washed with CH_2Cl_2, CH_2Cl_2:Dioxane (1:2, 3 mL for 20 s) and CH_2Cl_2 (twice, each with 2 mL for 25 s). The temperature of the reaction vessel is increased to 25 °C for the next module.

3.4 *Module D: Capping (30 min)*: The resin was washed with DMF (twice with 2 mL for 25 s) and the temperature of the reaction vessel was adjusted to 25 °C. Pyridine solution (2 mL, 10% in DMF) was delivered into the reaction vessel. After 1 min, the reaction solution was drained and the resin washed with CH_2Cl_2 (three times with 3 mL for 25 s). The capping solution (4 mL) was delivered into the reaction vessel. After 20 min, the reaction solution was drained and the resin washed with CH_2Cl_2 (three times with 3 mL for 25 s).

3.5 *Module E: Fmoc Deprotection (14 min):* The resin was washed with DMF (three times with 2 mL for 25 s) and the temperature of the reaction vessel was adjusted to 25 °C. Fmoc deprotection solution (2 mL) was delivered into the reaction vessel. After 5 min, the reaction solution was drained and the resin washed with DMF (three times with 3 mL for 25 s) and CH_2Cl_2 (five times each with 2 mL for 25 s). The temperature of the reaction vessel is decreased to -20 °C for the next module.

3.6 *Module F: Lev Deprotection:*The resin was washed with DMF (3×30 sec) and DCM (1.3 mL) added to the reaction vessel. Solution F (0.8 mL) was added to the reaction vessel, and the temperature was adjusted to 25 °C. After 30 min, the reaction solution was drained and the entire cycle was repeated twice more. After Lev deprotection was complete, the resin was washed with DMF, THF and DCM.

Post-Synthesizer Manipulations

4.1 *Cleavage from the Solid Support:*After automated synthesis, the resin was removed from the reaction vessel, suspended in a 10:1 mixture of THF/water (20 mL), and photocleaved in a continuous-flow photoreactor. A Vapourtec E-Series easy-MedCHem, equipped with a UV-150 Photochemical reactor having a UV-150 LED lamp (365 nm) was used. A Pump 11 Elite Series (Harvard Apparatus syringe pump at a flow rate of 2 mL/min was used to pump the mixture through a FEP tubing (i.d. 3.0 inch, volume: 12 mL) at 20 °C. The reactor was washed with 20 mL of CH_2Cl_2at a flow rate of 2.0 mL/min. The output solution was filtered to remove the resin and the solvent was evaporated in vacuo. Crude was then analyzed by MALDI.[3,4]

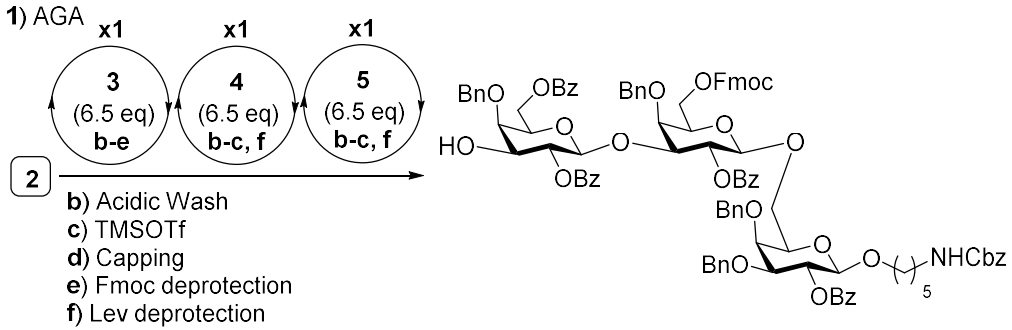
4.2 *Purification:* Solvent was evaporated in vacuo and the crude products were dissolved in a 1:1 mixture of hexanes and ethyl acetate and analyzed using analytical HPLC (DAD1F, 280 nm). Pure compounds were afforded by preparative HPLC (Agilent 1200 Series spectrometer).

Method A: (YMC-Diol-300 column, 150 x 4.6 mm) flow rate of 1.0 mL / min with Hex – 20% EtOAc as eluents [isocratic 20% EtOAc (5 min), linear gradient to 60% EtOAc (5 min), linear gradient to 60% EtOAc (30 min), linear gradient to 100% EtOAc (5 min)].

Method B:(Hypercarb, 150 x 10 mm) flow rate of 4.0 mL / min with water (0.1% formic acid) as eluents [isocratic (5 min), linear gradient to 10% ACN (30 min), linear gradient to 100% ACN (5 min)].

5. Automated Glycan Assembly of Heptadecasaccharide Repeating Unit of Arabinogalactan Polysaccharide HH1-1

5.1 Synthesis of trisaccharide repeating unit of arabinogalactan polysaccharide HH1-1 using building blocks 3, 4 and 5



Module	Conditions	Cycles
A: Resin Preparation for Synthesis		
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: Fmoc Deprotection	Building block **3** (6.5 equiv) -35°Cfor 20 min, -10 °C for 30 min	+
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **4** (6.5 equiv) -35°Cfor 20 min, -10 °Cfor 30 min	+

B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **5** (6.5 equiv) -35°Cfor 20 min, -10 °Cfor 30 min

The product was cleaved from the solid support as described in the post-synthesizer manipulations followed by purification using normal phase preparative HPLC with a (YMC-Diol-300 column, 150 x 4.6 mm) flow rate of 1.0 mL / min with Hex – 20% EtOAc as eluents [isocratic 20% EtOAc (5 min), linear gradient to 60% EtOAc (5 min), linear gradient to 60% EtOAc (30 min), linear gradient to 100% EtOAc (5 min)].

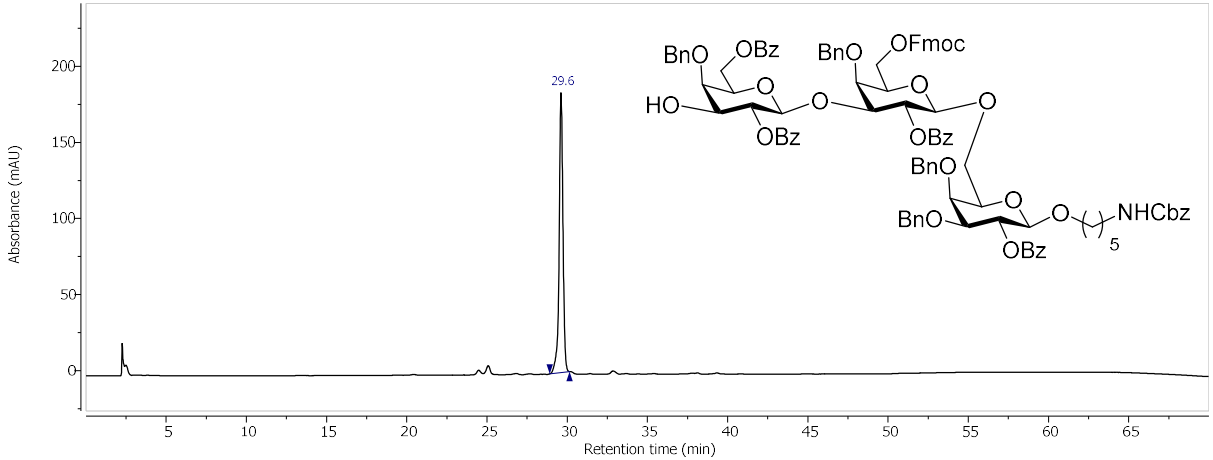
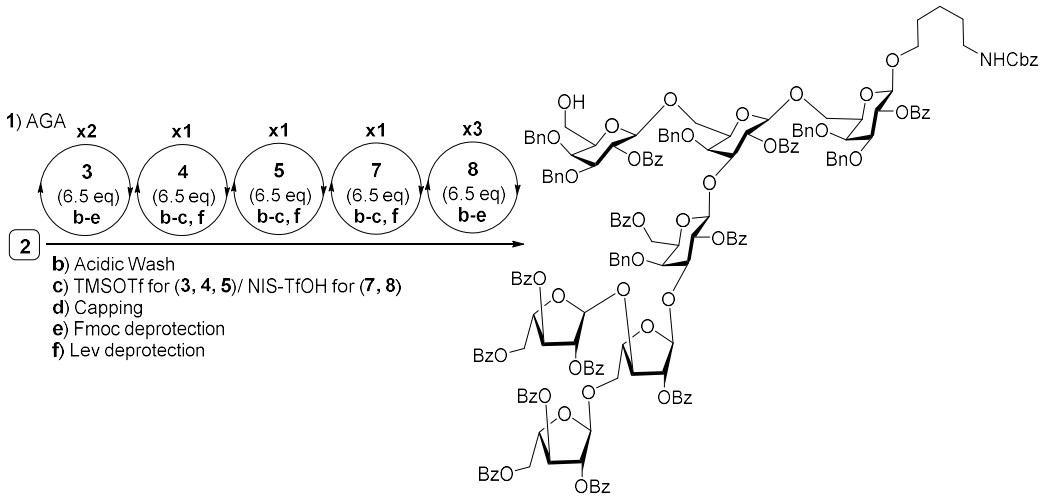


Figure S1. Analytical HPLC (Method A, 280 nm) of crude trisaccharide repeating unit of arabinogalactan polysaccharide HH1-1

5.2 Synthesis of heptasaccharide repeating unit of arabinogalactan polysaccharide HH1-1 using building blocks 3, 4, 5, 7 and 8



Module	Conditions	Cycles
A: Resin Preparation for Synthesis		
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: Fmoc Deprotection	Building block **3** (6.5 equiv) -35 °Cfor 20 min, -10 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **4** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1

B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **5** (6.5 equiv) -35 °C for 20 min, -10 °Cfor 30 min	1
B: Acidic Wash with TMSOTf Solution C: Thioglycoside Glycosylation D: Capping F: Lev Deprotection	Building block **7** (6.5 equiv) -40 °C for 20 min, -20 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Thioglycoside Glycosylation D: Capping E: FmocDeprotection	Building block **8** (6.5 equiv) -40 °C for 20 min, -20 °C for 30 min	3
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: Fmoc Deprotection	Building block **3** (6.5 equiv) -35 °Cfor 20 min, -10 °C for 30 min	1

The product was cleaved from the solid support as described in the post-synthesizer manipulations followed by purification using normal phase preparative HPLC with a (YMC-Diol-300 column, 150 x 4.6 mm) flow rate of 1.0 mL / min with Hex – 20% EtOAc as eluents [isocratic 20% EtOAc (5 min), linear gradient to 60% EtOAc (5 min), linear gradient to 60% EtOAc (30 min), linear gradient to 100% EtOAc (5 min)].

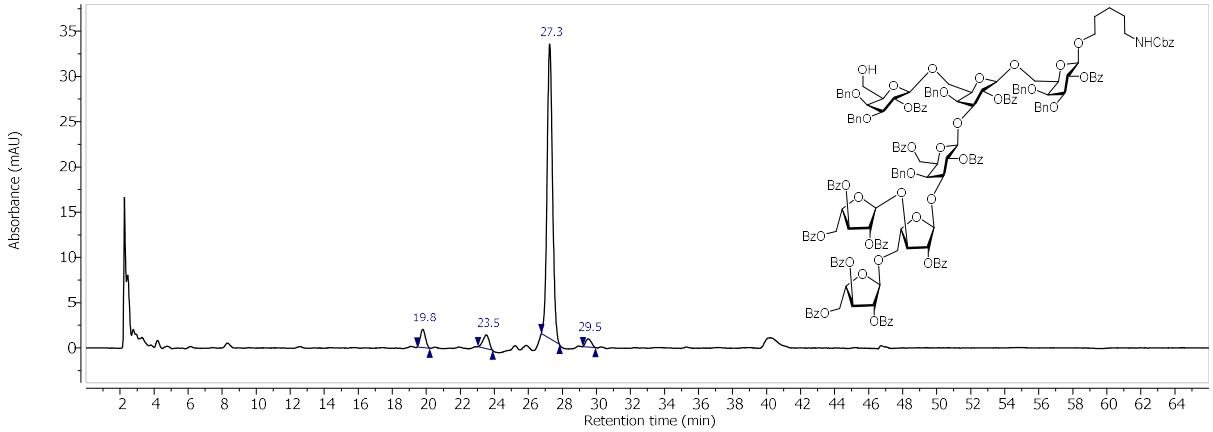
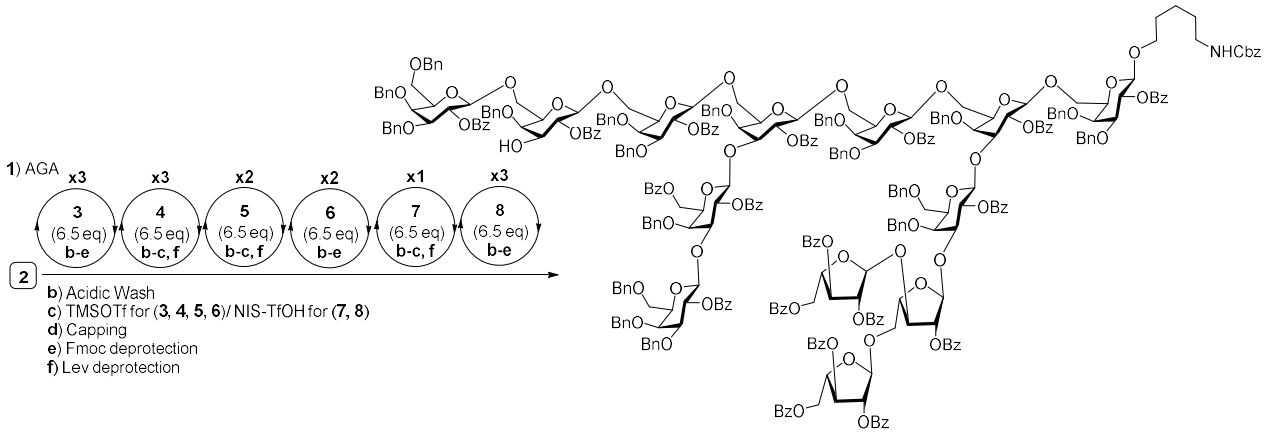


Figure S2. Analytical HPLC (Method A, 280 nm) of crude heptasaccharide repeating unit of arabinogalactan polysaccharide HH1-1

5.3 Synthesis of tridecasaccharide repeating unit of arabinogalactan polysaccharide HH1-1 using building blocks 3, 4, 5, 6, 7 and 8



Module	Conditions	Cycles
A: Resin Preparation for Synthesis		
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: Fmoc Deprotection	Building block **3** (6.5 equiv) -35 °Cfor 20 min, -10 °C for 30 min	+
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **4** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1

B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **5** (6.5 equiv) -35 °C for 20 min, -10 °Cfor 30 min	1
B: Acidic Wash with TMSOTf Solution C: Thioglycoside Glycosylation D: Capping F: Lev Deprotection	Building block **7** (6.5 equiv) -40 °C for 20 min, -20 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Thioglycoside Glycosylation D: Capping E: Fmoc Deprotection	Building block **8** (6.5 equiv) -40 °C for 20 min, -20 °C for 30 min	3
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: Fmoc Deprotection	Building block **3** (6.5 equiv) -35 °Cfor 20 min, -10 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **4** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1

B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **5** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: FmocDeprotection	Building block **6** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: Fmoc Deprotection	Building block **3** (6.5 equiv) -35 °Cfor 20 min, -10 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **4** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1

B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation	Building block **6** (6.5 equiv) -35 °C for 20 min, -10 °C for	1
D: Capping F: Lev Deprotection	30 min	

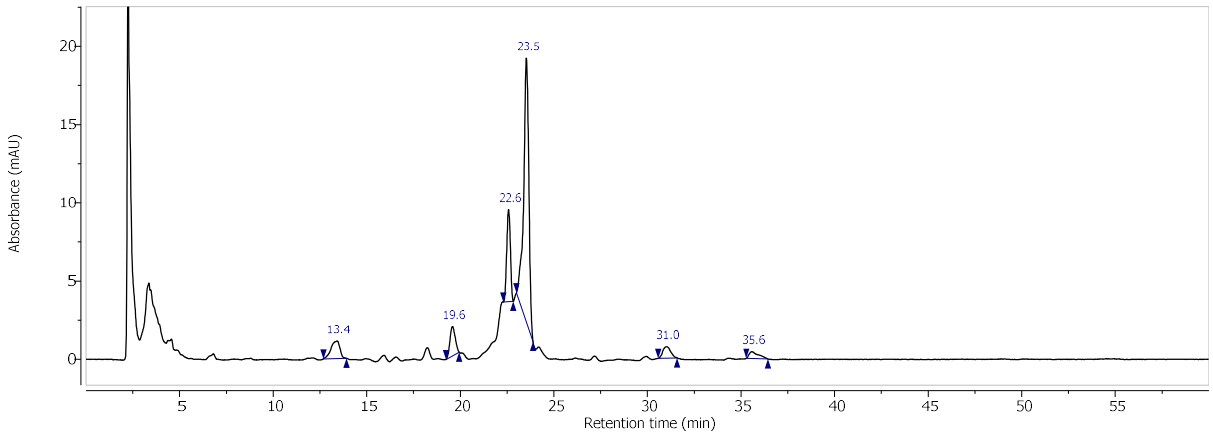
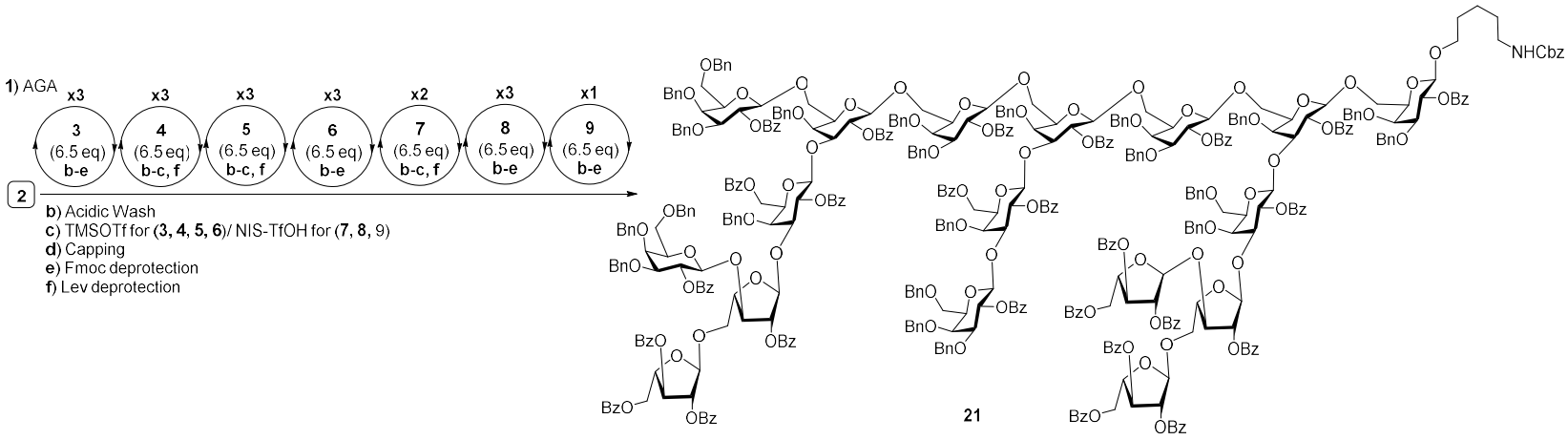


Figure S3. Analytical HPLC (Method A, 280 nm) of crude tridecasaccharide repeating unit of arabinogalactan polysaccharide HH1-1

5.4 Synthesis of heptadecasaccharide repeating unit of arabinogalactan polysaccharide HH1-1 (21) using building blocks 3, 4, 5, 6, 7, 8 and 9



Module	Conditions	Cycles
A: Resin Preparation for Synthesis		
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: Fmoc Deprotection	Building block **3** (6.5 equiv) -35 ^{o}Cfor 20 min, -10 ^{o}C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **4** (6.5 equiv) -35 ^{o}C for 20 min, -10 ^{o}C for 30 min	1

B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **5** (6.5 equiv) -35 °C for 20 min, -10 °Cfor 30 min	1
B: Acidic Wash with TMSOTf Solution C: Thioglycoside Glycosylation D: Capping F: Lev Deprotection	Building block **7** (6.5 equiv) -40 °C for 20 min, -20 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Thioglycoside Glycosylation D: Capping E: Fmoc Deprotection	Building block **8** (6.5 equiv) -40 °C for 20 min, -20 °C for 30 min	3
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: Fmoc Deprotection	Building block **3** (6.5 equiv) -35 °Cfor 20 min, -10 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **4** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1

B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **5** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: Fmoc Deprotection	Building block **6** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: Fmoc Deprotection	Building block **3** (6.5 equiv) -35 °Cfor 20 min, -10 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **4** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **6** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1

B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping F: Lev Deprotection	Building block **5** (6.5 equiv) -35 °C for 20 min, -10 °Cfor 30 min	1
B: Acidic Wash with TMSOTf Solution C: Thioglycoside Glycosylation D: Capping F: Lev Deprotection	Building block **9** (6.5 equiv) -40 °C for 20 min, -20 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Phosphate Donor Glycosylation D: Capping E: Fmoc Deprotection	Building block **6** (6.5 equiv) -35 °C for 20 min, -10 °C for 30 min	1
B: Acidic Wash with TMSOTf Solution C: Thioglycoside Glycosylation D: Capping	Building block **8** (6.5 equiv) -40 °C for 20 min, -20 °C for 30 min	1

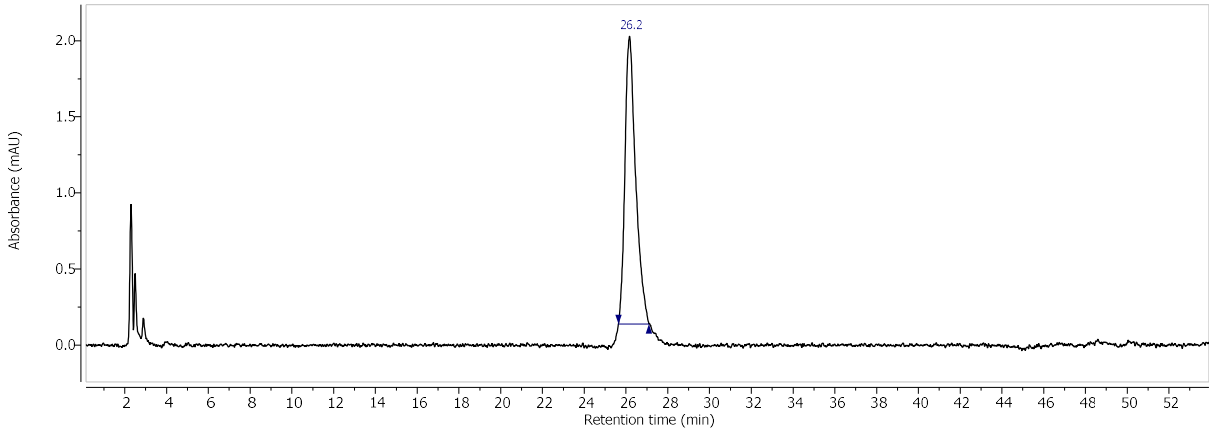
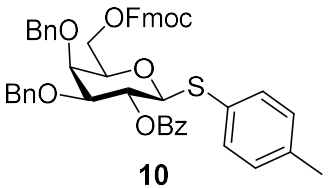


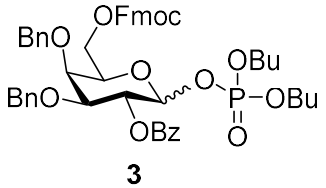
Figure S4. Analytical HPLC (Method A, 280 nm) of pure protected heptadecasaccharide repeating unit of arabinogalactan polysaccharide HH1-1 (**21**)

6. Chemical Synthesis and Characterization Data



10

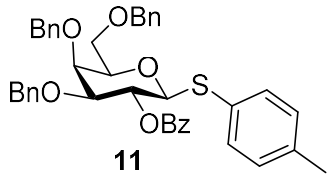
The building block **10** was purchased from GlycoUniverse. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.02 (m, 2H), 7.79 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.65 – 7.58 (m, 3H), 7.50 – 7.27 (m, 13H), 7.24 – 7.13 (m, 5H), 7.02 (d, *J* = 8.0 Hz, 2H), 5.68 (t, *J* = 9.8 Hz, 1H), 5.03 (d, *J* = 11.6 Hz, 1H), 4.75 – 4.61 (m, 3H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.49 – 4.36 (m, 3H), 4.30 – 4.17 (m, 2H), 3.97 (dd, *J* = 2.8, 1.1 Hz, 1H), 3.79 – 3.68 (m, 2H), 2.26 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 154.9, 143.4, 143.3, 141.4, 138.0, 137.9, 137.4, 133.2, 132.9, 130.1, 130.0, 129.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.86, 127.83, 127.3, 125.2, 120.2, 87.3, 81.1, 76.1, 74.3, 72.3, 72.2, 70.3, 70.1, 66.7, 46.8, 21.2; ESI HR-MS: m/z $[M+Na]^+$ calcd. for $C_{49}H_{44}NaO_8S$: 815.2655; Found 815.2670.



3

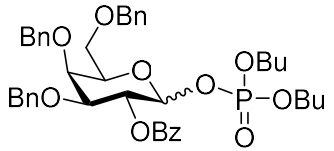
Anhydrous CH_2Cl_2 (40 mL) was added to a powdered, flame-dried 4 Å molecular sieves (3.5 g), followed by the addition of thioglycoside **10** (3.2 g, 4.0 mmol) and dibutyl phosphate (2.4 mL, 12.1 mmol). The reaction mixture was stirred for 30 min at roomtemperature and was then cooled to -15 °C. At this temperature, NIS (2.7 g, 12.0mmol) and TfOH (0.1 mL, 1.1 mmol) were added dropwise and continued the reaction to stir at -15^{o}C for 4 h. After completion of the reaction as indicted by TLC (ethyl acetate/*n*-hexanes: 2/8), the reaction was quenched with Et_3N, then filtered through pad of Celite® washed subsequently with sat. $Na_2S_2O_3$, water, brine,dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressureand crude compound subjected to

flash column chromatography to yield titled compound **3** (2.76 g,78%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.78 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.66 – 7.57 (m, 3H), 7.49 – 7.27 (m, 14H), 7.24 – 7.15 (m, 6H), 5.77 (dd, *J* = 10.1, 8.0 Hz, 1H), 5.35 (t, *J* = 7.8 Hz, 1H), 5.05 (d, *J* = 11.5 Hz, 1H), 4.69 (t, *J* = 12.2 Hz, 2H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.41 (dd, *J* = 7.3, 1.7 Hz, 2H), 4.32 (dd, *J* = 11.1, 6.5 Hz, 1H), 4.27 – 4.20 (m, 2H), 4.11 – 3.99 (m, 2H), 3.97 (dd, *J* = 2.9, 1.3 Hz, 1H), 3.83 (td, *J* = 6.2, 1.3 Hz, 1H), 3.77 – 3.63 (m, 3H), 1.70 (s, 1H), 1.59 (dtd, *J* = 8.9, 6.9, 5.8 Hz, 2H), 1.42 – 1.20 (m, 5H), 1.06 – 0.95 (m, 2H), 0.87 (t, *J*= 7.4 Hz, 3H), 0.67 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 154.8, 143.34, 143.30, 141.4, 137.8, 137.1, 133.4, 130.0, 129.6, 128.6, 128.57, 128.55, 128.1, 127.9, 127.34, 127.32, 125.2, 120.2, 97.0, 96.9, 79.3, 74.7, 73.2, 72.3, 71.9, 71.4, 71.3, 70.1, 68.1, 68.05, 68.00, 67.9, 66.1, 46.7, 32.1, 32.0, 31.88, 31.80, 18.6, 18.3, 13.6, 13.4; ESI HR-MS: m/z $[M+Na]^+$ calcd. for $C_{50}H_{55}NaO_{12}P$: 901.3329; Found 901.3344.



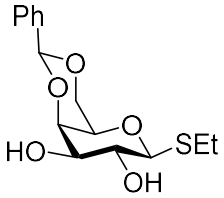
11

The building block **11** was purchased from GlycoUniverse. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.93 (m, 2H), 7.59 – 7.51 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.34 – 7.20 (m, 13H), 7.18 – 7.04 (m, 4H), 6.97 – 6.92 (m, 2H), 5.61 (t, *J* = 9.8 Hz, 1H), 4.94 (d, *J* = 11.6 Hz, 1H), 4.66 (d, *J* = 10.0 Hz, 1H), 4.57 (t, *J* = 11.8 Hz, 2H), 4.49 – 4.35 (m, 3H), 3.98 (d, *J* = 2.7 Hz, 1H), 3.63 (ddt, *J* = 8.0, 5.1, 2.1 Hz, 4H), 2.23 (s, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 138.6, 137.9, 137.7, 137.6, 133.1, 132.8, 130.2, 130.0, 129.8, 129.6, 128.5, 128.46, 128.43, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 87.3, 81.2, 77.7, 74.4, 73.7, 72.7, 71.8, 70.5, 68.9, 21.2; ESI HR-MS: m/z $[M+Na]^+$ calcd. for $C_{41}H_{40}NaO_6S$: 683.2443; Found 683.2458.



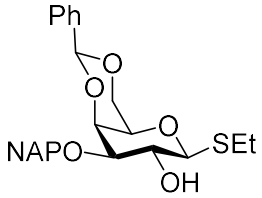
6

Anhydrous CH_2Cl_2 (45 mL) was added to a powdered, flame-dried 4 Å molecular sieves (4 g), followed by the addition of thioglycoside **11**(3.8 g, 5.7 mmol) and dibutyl phosphate (3.4 mL, 17.1 mmol). The reaction mixture was stirred for 30 min at roomtemperature and was then cooled to -15 °C. At this temperature, NIS (3.8 g, 17.2mmol) and TfOH (0.15 mL, 1.7 mmol) were added dropwise and continued the reaction to stir at -15^{o}C for 4 h. After completion of the reaction as indicted by TLC (ethyl acetate/*n*-hexanes: 2/8), the reaction was quenched with Et_3N, then filtered through pad of Celite® washed subsequently with sat. $Na_2S_2O_3$, water, brine,dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressureand crude compound subjected to flash column chromatography to yield titled compound**6** (3.4 g, 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.05 (m, 2H), 7.73 – 7.64 (m, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.50 – 7.36 (m, 12H), 7.32 – 7.22 (m, 4H), 5.83 (dd, *J* = 10.1, 8.0 Hz, 1H), 5.42 (t, *J* = 7.7 Hz, 1H), 5.11 (d, *J* = 11.5 Hz, 1H), 4.79 – 4.73 (m, 2H), 4.63 – 4.52 (m, 3H), 4.15 (d, *J* = 2.9 Hz, 1H), 4.09 (tdd, *J* = 10.0, 6.6, 3.3 Hz, 2H), 3.93 – 3.60 (m, 6H), 1.78 (s, 1H), 1.67 (dd, *J* = 8.3, 6.1 Hz, 2H), 1.48 – 1.31 (m, 5H), 1.16 – 1.04 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.76 (t, *J*= 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 138.4, 137.8, 137.4, 133.2, 130.0, 129.8, 128.6, 128.4, 128.4, 128.0, 127.9, 127.89, 127.82, 97.27, 97.22, 79.47, 79.45, 74.8, 74.4, 73.7, 72.4, 71.9, 71.7, 71.6, 68.08, 68.02, 67.96, 67.92, 67.8, 32.1, 32.0, 31.9, 31.8, 18.6, 18.3, 13.6, 13.4; ESI HR-MS: m/z $[M+Na]^+$ calcd. for $C_{42}H_{51}NaO_{10}P$: 769.3118; Found 769.3139.



12

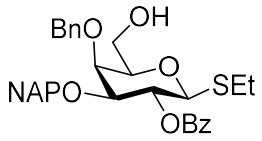
The building block **12** was purchased from GlycoUniverse. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.36 (dd, *J* = 5.1, 2.0 Hz, 3H), 5.51 (s, 1H), 4.35 – 4.28 (m, 2H), 4.20 (dd, *J* = 3.7, 1.2 Hz, 1H), 4.00 (dd, *J* = 12.5, 1.9 Hz, 1H), 3.79 (t, *J* = 9.3 Hz, 1H), 3.65 (dd, *J* = 9.3, 3.5 Hz, 1H), 3.46 (q, *J* = 1.5 Hz, 1H), 2.92 (d, *J* = 20.0 Hz, 2H), 2.86 – 2.67 (m, 2H), 1.33 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 129.3, 128.3, 126.5, 101.5, 85.3, 75.7, 73.9, 70.1, 69.7, 69.3, 23.5, 15.3; ESI HR-MS: m/z $[M+Na]^+$ calcd. for $C_{15}H_{20}NaO_5S$: 335.0929; Found 335.0954.



13

A solution of **12** (6.0 g, 91.2 mmol) and Bu_2SnO (5.1 g, 20.4 mmol) in MeOH (80 mL) was refluxed for 4.0 h. Then, the reaction mixture was concentrated to dryness, further co-evaporated with toluene to remove any traces of water and dried under high vacuum. To this,2-(Bromomethyl)-naphthalene (4.2 g, 18.9 mmol), CsF (7.3 g, 48.0 mmol) were added in anhydrous DMF (100 mL) and the mixture was refluxed for 16 h. After cooling to r.t., the mixture was filtered through a layer of Celite, concentrated and purified by silica gel column chromatography to afford corresponding(bromomethyl)-naphthalene derivative **13** (6.0 g, 69%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.74 (m, 4H), 7.56 – 7.44 (m, 5H), 7.41 – 7.32 (m, 3H), 5.43 (s, 1H), 4.94 (s, 2H), 4.35 (d, *J* = 9.6 Hz, 1H), 4.30 (dd, *J* = 12.4, 1.6 Hz, 1H), 4.19 (dd, *J* = 3.4, 1.1 Hz, 1H), 4.11 (td, *J* = 9.4, 1.4 Hz, 1H), 3.94 (dd, *J* = 12.5, 1.8 Hz, 1H), 3.55 (dd, *J* = 9.2,

3.4 Hz, 1H), 3.39 (q, *J* = 1.5 Hz, 1H), 2.92 – 2.69 (m, 2H), 2.59 (d, *J* = 1.7 Hz, 1H), 1.34 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 135.7, 133.3, 133.2, 129.1, 128.4, 128.3, 128.0, 127.8, 126.8, 126.5, 126.3, 126.1, 125.9, 101.4, 85.4, 80.3, 73.8, 71.8, 70.2, 69.5, 68.2, 23.1, 15.4; ESI HR-MS: m/z $[M+Na]^+$ calcd. for $C_{26}H_{28}NaO_5S$: 475.1555; Found 475.1560.

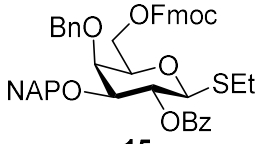


14

To a solution of **13**(6.0 g, 13.2 mmol) in pyridine (100 mL) was added PhCOCl (2.3 mL, 19.7 mmol) dropwise at 0°C.Subsequently 4-DMAP (0.5 g, 4.0 mmol) was added to maintain the basic *p*H. The reaction mixture was stirred overnight at room temperature, at the end of which time TLC (ethyl acetate/n-hexanes: 2/8) indicated it was finished. The reaction was quenched with MeOH, diluted with CH_2Cl_2, and the mixture was washed with 1M HCl, aq. $NaHCO_3$, brine and dried over $MgSO_4$. The combined organic layers were filtered, and concentrated. The residue was purified by silica gel column chromatography to afford corresponding 2-O-benzoylated derivative (6.2 g, 85%).

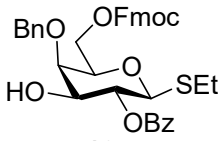
Anhydrous CH_2Cl_2 (100 mL) was added to a powdered, flame-dried 4 Å molecular sieves and 2-O-benzoylated derivative (6.0 g, 10.7 mmol) from the above step, cooled to 0°C. At this temperature, BH_3-THF (7.6 mL, 79.4 mmol), TMSOTf (1.2 mL, 6.6 mmol) were added and continued to stir the reaction for 4 h at 0°C. After completion of the reaction as indicated by TLC (ethyl acetate/*n*-hexanes: 3/7), MeOH was added and concentrated. The crude mixture was purified by silica gel column chromatography and afforded **14**(5.5 g, 75%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.02 – 7.98 (m, 2H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.64 (s, 1H), 7.59 (ddd, *J* = 12.9, 7.9, 5.7 Hz, 3H), 7.47 – 7.41 (m, 4H), 7.40 – 7.34 (m, 4H), 7.33 – 7.28 (m, 2H), 5.74 (t, *J* = 9.7 Hz, 1H), 5.05 (d, *J* = 12.0 Hz, 1H), 4.85 (d, *J* = 12.4 Hz, 1H), 4.71 (dd, *J* = 12.2, 9.0 Hz, 2H), 4.49 (d, *J* = 9.9 Hz, 1H), 3.98 (d, *J* = 2.6 Hz, 1H), 3.84 (dd, *J* = 11.3, 6.7 Hz, 1H), 3.74 (dd, *J* = 9.6, 2.7 Hz, 1H), 3.55 (dt, *J* = 10.6, 4.7 Hz, 1H), 3.51 (t, *J* = 6.1 Hz, 1H), 2.87 – 2.64 (m, 2H), 1.21 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (176

MHz, $CDCl_3$) δ 165.5, 138.2, 135.0, 133.2, 133.1, 133.0, 130.1, 130.0, 128.64, 128.60, 128.49, 128.45, 128.1, 127.9, 127.8, 126.8, 126.2, 126.1, 125.9, 83.9, 81.2, 79.1, 74.2, 72.2, 72.1, 70.2, 62.2, 23.9, 14.9; ESI HR-MS: m/z $[M+Na]^+$ calcd. for $C_{33}H_{34}NaO_6S$: 581.1974; Found 581.1978.



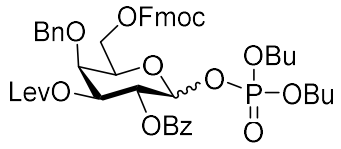
15

To a stirred solution of **14** (3.3 g, 5.9 mmol) in anhydrous CH_2Cl_2 at 0 °C, FmocCl(3.8 g, 14.7 mmol) and pyridine (2.3 mL, 28.5 mmol) were successively added and stirred at same temperature under ice bath for 4 h. After completion of the reaction as indicated by TLC (ethyl acetate/*n*-hexanes: 2/8), the reaction mixture was diluted with CH_2Cl_2 and washed with 1M HCl, aq. $NaHCO_3$, brine. The combined organic layers were dried over $MgSO_4$, concentrated and purified by column chromatography using silica gel to give **15** (4 g,88%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.00 – 7.98 (m, 2H), 7.78 (d, *J*= 7.5 Hz, 2H), 7.76 – 7.73 (m, 1H), 7.65 – 7.56 (m, 6H), 7.46 – 7.40 (m, 6H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.33 (qd, *J* = 7.5, 4.8 Hz, 4H), 7.28 (dd, *J* = 8.1, 1.9 Hz, 2H), 5.74 (t, *J* = 9.7 Hz, 1H), 5.08 (d, *J* = 11.7 Hz, 1H), 4.85 (d, *J* = 12.4 Hz, 1H), 4.71 (dd, *J* = 19.5, 12.0 Hz, 2H), 4.51 (d, *J* = 9.9 Hz, 1H), 4.44 – 4.35 (m, 3H), 4.25 (t, *J* = 7.3 Hz, 1H), 4.19 (dd, *J* = 11.1, 5.7 Hz, 1H), 4.05 – 3.99 (m, 1H), 3.79 – 3.69 (m, 2H), 2.82 – 2.62 (m, 2H), 1.21 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 165.5, 154.9, 143.4, 143.3, 141.4, 138.1, 135.0, 133.2, 133.1, 133.0, 130.09, 130.02, 128.5, 128.49, 128.47, 128.44, 128.0, 127.9, 127.8, 127.3, 126.7, 126.2, 126.1, 125.8, 125.2, 120.2, 83.9, 81.0, 76.1, 74.5, 72.4, 72.2, 70.1, 70.0, 66.7, 46.8, 24.0, 14.9; ESI HR-MS: m/z $[M+Na]^+$ calcd. for $C_{48}H_{44}NaO_8S$: 803.2655; Found 803.2671.



16

Compound **15**(3.57 g, 4.5 mmol) was treated with DDQ (1.34g, 5.9mmol), in three equal portions in half-hour intervals in mixed solvent (CH_2Cl_2/H_2O = 18/1, 95ml) at room temperature. After 6 hours of stirring, the reaction mixture was quenched with 10%aqueous $Na_2S_2O_4$ solution and filtered through a pad of Celite®. The filtrate was concentratedunder reduced pressure. The residue was purified by flash column chromatography (ethylacetate/hexanes = 1/3) on silica gel to provide the expected compound**16**(2.38 g, 81%). ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.08 – 8.05 (m, 2H), 7.78 (dd, *J* = 7.6, 3.1 Hz, 2H), 7.61 (dd, *J* = 7.6, 3.9 Hz, 2H), 7.60 – 7.57 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.42 (td, *J* = 7.3, 4.2 Hz, 2H), 7.39 – 7.36 (m, 4H), 7.33 (td, *J* = 7.5, 1.1 Hz, 3H), 5.33 (t, *J* = 9.7 Hz, 1H), 4.83 – 4.73 (m, 2H), 4.58 (d, *J* = 9.9 Hz, 1H), 4.48 – 4.41 (m, 3H), 4.26 (t, *J* = 7.2 Hz, 1H), 4.18 (dd, *J* = 11.1, 6.3 Hz, 1H), 3.91 (dd, *J* = 3.5, 1.1 Hz, 1H), 3.84 (td, *J* = 8.9, 3.4 Hz, 1H), 3.80 (td, *J* = 6.4, 1.2 Hz, 1H), 2.73 (ddq, *J* = 48.8, 12.5, 7.5 Hz, 2H), 2.53 (d, *J* = 9.0 Hz, 1H), 1.25 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 166.8, 154.9, 143.3, 141.4, 137.7, 133.5, 130.1, 129.7, 128.8, 128.5, 128.3, 128.1, 127.33, 127.30, 125.22, 125.20, 120.2, 83.5, 76.4, 76.0, 75.7, 74.4, 72.3, 70.0, 66.1, 46.8, 24.2, 15.1; ESI HR-MS: m/z $[M+Na]^+$ calcd. for $C_{37}H_{36}NaO_8S$: 663.2029; Found 663.2039.

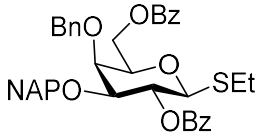


4

To a stirred solution compound **16** (2.4 g, 3.7 mmol) in anhydrous CH_2Cl_2 (30 mL), LevOH (1.0 mL, 9.8 mmol) was added and stirred at 0 °C. At this temperature, DCC (4.0 g, 19.2 mmol) and 4-DMAP (0.2 g, 1.63 mmol) were added successively and continued to stir for 3h. After the reaction as noted by TLC, the reaction was diluted with CH_2Cl_2,filtered through pad of Celite®andwashed $CH_2Cl_2$and brine. The combined organic layers were dried over $MgSO_4$and concentrated. The residue was purified by flash column chromatography to yield corresponding fully protected thioglycoside (1.7 g, 62%).

Anhydrous CH_2Cl_2 (20 mL) was added to a powdered, flame-dried 4 Å molecular sieves (2 g), followed by the addition of thioglycoside (1.7g, 2.3 mmol) from the above step and dibutyl phosphate (1.4 mL, 7.0 mmol). The reaction mixture was stirred for 30

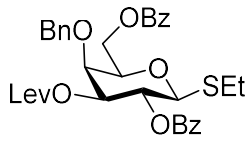
min at roomtemperature and was then cooled to -15 °C. At this temperature, NIS (1.5 g, 6.6mmol) and TfOH (60µL, 0.67 mmol) were added dropwise and continued the reaction to stir at -15°C for 4 h. After completion of the reaction as indicted by TLC (ethyl acetate/*n*-hexanes: 2/8), the reaction was quenched with Et_3N, then filtered through pad of Celite® washed subsequently with sat. $Na_2S_2O_3$, water, brine,dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressureand crude compound subjected to flash column chromatography to yield titled compound**4** (1.5 g, 79%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.78 (dt, *J* = 7.6, 0.9 Hz, 2H), 7.64 – 7.54 (m, 3H), 7.48 – 7.37 (m, 7H), 7.37 – 7.33 (m, 3H), 5.75 (dd, *J* = 10.5, 8.0 Hz, 1H), 5.44 (t, *J* = 7.8 Hz, 1H), 5.20 (dd, *J* = 10.5, 3.0 Hz, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.44 – 4.37 (m, 2H), 4.32 (dd, *J* = 11.0, 6.4 Hz, 1H), 4.24 (t, *J* = 7.3 Hz, 1H), 4.17 (dd, *J* = 11.0, 6.3 Hz, 1H), 4.09 – 3.93 (m, 4H), 3.81 – 3.63 (m, 2H), 2.67 (ddd, *J* = 20.5, 10.7, 5.4 Hz, 1H), 2.59 – 2.46 (m, 2H), 2.41 – 2.29 (m, 1H), 2.04 (s, 3H), 1.64 – 1.54 (m, 2H), 1.40 – 1.26 (m, 5H), 1.09 – 0.96 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.68 (t, *J* = 7.4 Hz, 3H);^{13}C NMR (101 MHz, $CDCl_3$) δ 206.1, 172.1, 165.3, 154.7, 143.3, 141.4, 137.5, 133.6, 130.0, 129.2, 128.67, 128.65, 128.4, 128.1, 128.0, 127.3, 125.3, 125.2, 120.2, 96.86, 96.82, 75.3, 73.56, 73.51, 73.0, 70.2, 70.0, 69.9, 68.1, 68.1, 68.0, 67.9, 65.4, 46.7, 37.7, 32.1, 32.0, 31.9, 31.8, 29.6, 27.9, 18.6, 18.3, 13.7, 13.5.



17

To a solution of **14** (2.0 g, 3.5 mmol) in pyridine (30 mL) was added PhCOCl (0.83 mL, 7.1 mmol) dropwise at 0°C.Subsequently 4-DMAP (0.2 g, 1.6 mmol) was added to maintain the basic *p*H. The reaction mixture was stirred overnight at room temperature, at the end of which time TLC (ethyl acetate/n-hexanes: 2/8) indicated it was finished. The reaction was quenched with MeOH, diluted with CH_2Cl_2, and the mixture was washed with 1M HCl, aq. $NaHCO_3$, brine and dried over $MgSO_4$. The combined organic layers were filtered, and concentrated. The residue was purified by silica gel column chromatography to afford **17**(2.0 g, 86%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.98 (m, 2H), 7.97 – 7.93 (m, 2H), 7.78 – 7.73 (m, 1H), 7.67 – 7.64 (m, 1H), 7.63 – 7.55 (m, 4H), 7.48 – 7.37 (m, 8H), 7.34 – 7.28 (m, 3H), 7.25 – 7.21 (m, 1H), 5.77 (t, *J* = 9.7 Hz, 1H), 5.10 (d, *J* = 11.7 Hz, 1H), 4.85 (d, *J* = 12.3 Hz, 1H), 4.75

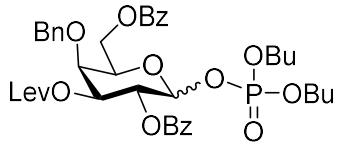
(dd, *J* = 18.0, 12.0 Hz, 2H), 4.54 (dd, *J* = 10.4, 5.2 Hz, 2H), 4.41 (dd, *J* = 11.2, 5.9 Hz, 1H), 4.06 (dd, *J* = 2.7, 1.1 Hz, 1H), 3.88 – 3.72 (m, 2H), 2.85 – 2.58 (m, 2H), 1.22 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 165.5, 138.1, 135.0, 133.3, 133.19, 133.17, 133.10, 130.1, 129.9, 129.8, 129.7, 128.5, 128.47, 128.41, 127.95, 127.92, 127.7, 126.7, 126.2, 126.1, 125.8, 84.0, 81.4, 76.4, 74.5, 72.7, 72.5, 70.3, 24.1, 15.0; ESI HR-MS: m/z $[M+Na]^+$ calcd. for $C_{40}H_{38}NaO_7S$: 685.2236; Found 685.2222.



18

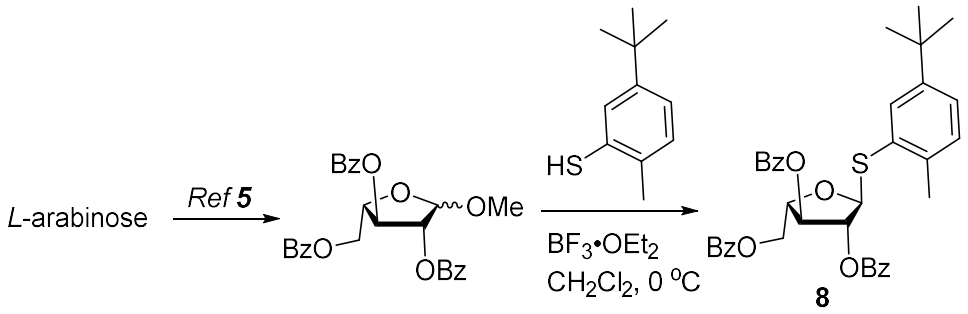
Compound **17**(2.0 g, 4.5 mmol) was treated with DDQ (1.0 g, 5.9 mmol), in three equal portions in half-hour intervals in mixed solvent (CH_2Cl_2/H_2O = 18/1, 95ml) at room temperature. After 5 hours of stirring, the reaction mixture was quenched with 10%aqueous $Na_2S_2O_4$ solution and filtered through a pad of Celite®. The filtrate was concentratedunder reduced pressure. The residue was purified by flash column chromatography (ethyl acetate/hexanes: 1/3) on silica gel to provide the corresponding compound(1 g).

To a stirred solution of compound (1.0 g, 1.9 mmol) from the above step in anhydrous CH_2Cl_2 (50 mL), LevOH (0.44 g, 3.78 mmol), EDC.HCl (0.73 g, 3.8 mmol) and 4-DMAP (0.1 g, 0.8 mmol) were successively added at room temperature and stirred for 4 h. After completion of the reaction as noted by TLC, the reaction mixture was washed with H_2O, brine and dried over anhydrous $MgSO_4$. The organic layers were concentrated and purified by silica gel column chromatography to yield compound **18** (1.0 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 2H), 7.99 – 7.94 (m, 2H), 7.61 – 7.54 (m, 2H), 7.48 – 7.38 (m, 6H), 7.32 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.25 – 7.21 (m, 1H), 5.71 (t, *J* = 9.9 Hz, 1H), 5.27 (dd, *J* = 10.0, 3.0 Hz, 1H), 4.89 (d, *J*= 11.7 Hz, 1H), 4.65 (dd, *J* = 10.8, 4.1 Hz, 1H), 4.53 (dd, *J* = 11.1, 6.3 Hz, 1H), 4.35 (dd, *J* = 11.2, 6.6 Hz, 1H), 4.10 (dd, *J* = 3.0, 1.1 Hz, 1H), 3.97 (td, *J* = 6.4, 1.1 Hz, 1H), 2.85 – 2.56 (m, 3H), 2.55 – 2.44 (m, 2H), 2.41 – 2.26 (m, 1H), 2.02 (s, 3H), 1.23 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0, 172.2, 166.1, 165.4, 137.7, 133.4, 133.3, 130.0, 129.8, 129.7, 129.6, 128.58, 128.55, 128.3, 128.0, 84.0, 76.2, 75.2, 75.1, 74.1, 68.7, 62.9, 37.8, 29.6, 28.1, 24.3, 15.0.

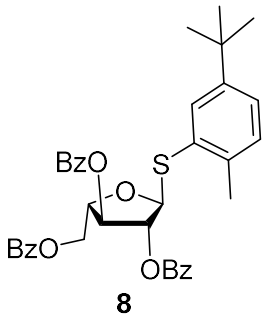


5

Anhydrous CH_2Cl_2 (20 mL) was added to a powdered, flame-dried 4 Å molecular sieves (2 g), followed by the addition of thioglycoside **18**(1.0 g, 1.6 mmol) and dibutyl phosphate (1.0 mL, 5.0 mmol). The reaction mixture was stirred for 30 min at roomtemperature and was then cooled to -15 °C. At this temperature, NIS (1.0 g, 4.4mmol) and TfOH (42µL, 0.47 mmol) were added dropwise and continued the reaction to stir at -15^{o}C for 4 h. After completion of the reaction as indicted by TLC (ethyl acetate/*n*-hexanes: 2/8), the reaction was quenched with Et_3N, then filtered through pad of Celite® washed subsequently with sat. $Na_2S_2O_3$, water, brine,dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressureand crude compound subjected to flash column chromatography to yield titled compound**5** (0.8 g, 72%).^{1}H NMR (700 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 2H), 7.98 – 7.95 (m, 2H), 7.61 – 7.55 (m, 2H), 7.44 (dt, *J* = 9.0, 7.7 Hz, 4H), 7.40 (d, *J* = 7.1 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (s, t, *J* = 7.4 Hz, 1H), 5.78 (dd, *J* = 10.5, 7.9 Hz, 1H), 5.47 (t, *J* = 7.7 Hz, 1H), 5.24 (dd, *J* = 10.5, 2.9 Hz, 1H), 4.90 (d, *J* = 11.5 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.52 (dd, *J* = 11.2, 6.5 Hz, 1H), 4.33 (dd, *J* = 11.2, 6.1 Hz, 1H), 4.12 – 4.07 (m, 2H), 3.99 (ddp, *J* = 13.8, 6.7, 3.3 Hz, 2H), 3.74 (dq, *J* = 9.9, 6.6 Hz, 1H), 3.68 (dq, *J* = 9.9, 6.7 Hz, 1H), 2.66 (dq, *J* = 16.7, 5.8 Hz, 1H), 2.56 – 2.49 (m, 2H), 2.41 – 2.33 (m, 1H), 2.04 (s, 3H), 1.55 – 1.49 (m, 2H), 1.28 (td, *J* = 8.4, 6.4 Hz, 5H), 1.01 (q, *J* = 7.5 Hz, 2H), 0.88 (td, *J* = 7.1, 2.4 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 3H), 0.67 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 206.1, 172.3, 166.6, 165.4, 137.5, 133.3, 133.4, 130.4, 129.5, 129.3, 129.7, 128.7, 128.58, 128.52, 128.2, 96.94, 96.91, 75.3, 73.7, 73.6, 73.4, 70.1, 70.0, 68.06, 68.03, 67.9, 62.7, 37.7, 32.1, 32.0, 31.9, 31.8, 29.8, 29.6, 28.0, 18.6, 18.3, 13.6, 13.5.

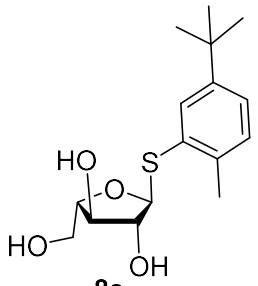


Methyl 2,3,5-tri-O-benzoyl-α-L-arabinofuranoside was synthesized from commercially available L-arabinosein 3 steps following the Literature.[5]



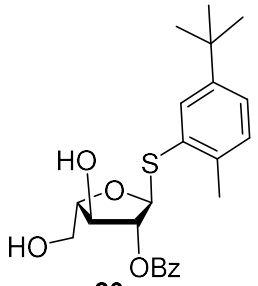
To a solution of methyl 2,3,5-tri-O-benzoyl-α-L-arabinofuranoside(20.0 g, 42.0 mmol) and ethanethiol (3.6mL, 50.0 mmol) in anhydrous DCM (400 mL) at 0 °C was added BF_3•OEt_2 (16.0 mL, 125.0 mmol) dropwise over 30 min. The reaction mixture was stirred for 5 h at 0 °C, diluted with DCM (200 mL), washed with saturated $NaHCO_3$ solution, and brine dried with $MgSO_4$ and concentrated. The crude product was purified by chromatography (Hexanes–EtOAc: 8:1) to give corresponding **8**(15 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.17 (m, 2H), 8.11 – 8.05 (m, 4H), 7.71 (d, *J*= 2.1 Hz, 1H), 7.68 – 7.59 (m, 2H), 7.58 – 7.50 (m, 3H), 7.48 – 7.42 (m, 2H), 7.38 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 5.83 – 5.79 (m, 2H), 5.69 (ddd, *J* = 4.8, 1.5, 0.8 Hz, 1H), 4.93 (td, *J* = 5.1, 3.5 Hz, 1H), 4.86 (dd, *J* = 11.9, 3.5 Hz, 1H), 4.78 (dd, *J* = 11.9, 5.6 Hz, 1H), 2.51 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.7, 165.4, 149.8, 137.4, 133.79, 133.71, 133.2, 132.1, 130.8, 130.1, 130.0, 129.8,

129.7, 129.07, 129.02, 128.69, 128.66, 128.4, 125.4, 91.4, 82.7, 81.3, 78.2, 63.8, 34.5, 31.3, 20.6; ESI HR-MS: m/z [M+Na]$^+$ calcd. for $C_{37}H_{36}NaO_7S$: 647.2079; Found 647.2086.



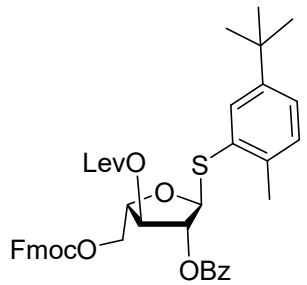
8a

To a stirred solution of compound **8** (10 g, 16.0 mmol) in DCM–MeOH (1:2, 100 mL) and solid NaOMe (1.0 g,18.5 mmol) was added. After stirring for 5h at room temperature, the reaction mixture was neutralized with Amberlite IR-120 H$^+$ resin, filtered, and concentrated and purified by silica gel chromatography (10:1 DCM–MeOH) to afford corresponding unprotected thiofuranoside **8a** (4.4 g, 89%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.21 (dd, *J* = 8.0, 2.1 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 5.33 (d, *J* = 3.8 Hz, 1H), 4.97 (d, *J* = 5.6 Hz, 1H), 4.56 (d, *J* = 4.9 Hz, 1H), 4.16 (q, *J* = 4.5 Hz, 2H), 4.11 – 4.02 (m, 1H), 3.77 (q, *J* = 14.1 Hz, 3H), 2.37 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 137.2, 132.1, 130.5, 130.1, 125.3, 91.6, 83.0, 82.3, 76.7, 60.9, 34.5, 31.4, 20.5; ESI HR-MS: m/z [M+Na]$^+$ calcd. for $C_{16}H_{24}NaO_4S$: 335.1293; Found 335.1311.



20

To a stirred solution of thiofuranoside**8a** (2.0 g, 6.4 mmol) in anhydrous pyridine (40 mL) was added 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (2.2 mL, 7.0 mmol) at room temperature. After stirring for 48 h at the same temperature, the reaction was cool to0 °C. At this temperature, benzoyl chloride (1.1 mL, 9.5 mmol), 4-DMAP (0.23g, 1.8 mmol) were added successively and continued to stir overnight.After completion of the reaction, the reaction mixture was diluted with water and extracted twice with DCM. The combined organic layers were washed with water, 1M HCl, saturated $NaHCO_3$, and brine, dried over $MgSO_4$ and concentrated. The crude residue was dissolvedin anhydrous THF/Py., at 0 ^oC, 30% HF·Py.,(2.66 mL, 29.55 mmol)was added and stirred for 3.5 h. After completion of the reaction as indicated by TLC (ethyl acetate/*n*-hexanes: 6/4), the reaction was diluted with ethyl acetate, aq. $NaHCO_3$was added to quench the excess of acid and the two layers were separated. The organic portion was washed with 1M HCl, aq. $NaHCO_3$, brine. quenched by the addition of sat. $NaHCO_3$, extracted with $CHCl_3$. The combined organic layers were washed with brine, dried over $MgSO_4$andpurified to afford **20**(2.1 g, 81%).^{1}H NMR (700 MHz, $CDCl_3$) δ 8.05 – 8.02 (m, 2H), 7.64 – 7.59 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 5.69 (d, *J* = 3.2 Hz, 1H), 5.17 (t, *J* = 3.5 Hz, 1H), 4.37 (dt, *J* = 7.1, 3.4 Hz, 1H), 4.29 (dd, *J* = 7.2, 3.6 Hz, 1H), 3.95 (dd, *J* = 12.3, 2.7 Hz, 1H), 3.82 (d, *J* = 11.8 Hz, 1H), 3.56 (s, 1H), 2.43 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 167.5, 149.8, 137.4, 133.9, 132.0, 130.7, 130.2, 130.0, 128.9, 128.7, 125.6, 89.1, 87.8, 82.8, 76.4, 61.4, 34.6, 31.4, 20.5.



9

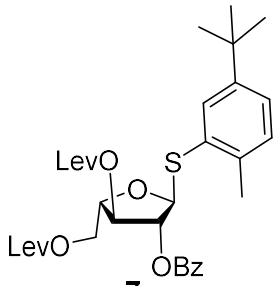
To a stirred solution compound **20** (3.3 g, 7.9 mmol) in anhydrous pyridine (50 mL), trityl chloride (6.6 g, 23.67 mmol) was added in portion wise and stirred the reaction at room temperature for 48 h. After completion of the reaction as indicated by TLC, the reaction

was subjected to evaporation under reduced pressure and residue was dissolved in CH_2Cl_2, washed with water, brine. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated.

The crude trityl protected L-arabinothiofuranoside (2.3 g, 3.5 mmol) from the above step was dissolved in CH_2Cl_2, LevOH (0.7 mL, 6.8 mmol), EDC.HCl (1.3 g, 6.9 mmol) and 4-DMAP (0.12 g, 0.99 mmol) were successively added at room temperature and stirred for 4 h. After completion of the reaction as noted by TLC, the reaction mixture was washed with H_2O, brine and dried over anhydrous $MgSO_4$. The organic layers were concentrated and taken forward for the next step.

The fully protected L-arabinothiofuranoside (2.5 g, 3.3 mmol) in MeOH/CH_2Cl_2(3/1), CSA was added and stirred 5 h at room temperature. After which, the reaction was evaporated and the crude residue was dissolved in dissolved in CH_2Cl_2, washed with water, brine. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated. This compound (1.0 g, 1.9 mmol), was dissolved in anhydrous CH_2Cl_2 (30 mL) and cooled to 0 ^oC. At this temperature, Fmoc chloride (1.25 g, 4.8 mmol), pyridine (0.78 mL, 9.6 mmol)were added successively and the reaction mixture was allowed to warm to room temperature and monitored by TLC (Hexane:EtOAc, 8:2). After completion of the reaction (2.5 h), the reaction mixture was evaporated to dryness.The residue was dissolved in $CH_2Cl_2$and washed with 1M HCl, sat. $NaHCO_3$ and brine and dried over $MgSO_4$. The combined organic layers were concentrated and purified through column chromatography to obtain compound **9** (1.1 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dt, *J* = 7.0, 1.6 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.63 (t, *J* = 6.8 Hz, 2H), 7.55 (t, *J*= 7.4 Hz, 1H), 7.46 – 7.37 (m, 4H), 7.33 – 7.25 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 1H), 5.70 (d, *J* = 2.5 Hz, 1H), 5.64 (dq, *J* = 2.8, 1.6 Hz, 1H), 5.37 (dt, *J* = 4.7, 2.1 Hz, 1H), 4.71 – 4.61 (m, 2H), 4.60 – 4.53 (m, 1H), 4.45 – 4.37 (m, 2H), 4.26 (t, *J* = 7.6 Hz, 1H), 2.86 (t, *J* = 6.9 Hz, 2H), 2.74 (td, *J* = 6.4, 3.9 Hz, 2H), 2.49 (s, 3H), 2.23 (s, 3H), 1.34 (d, *J* = 1.4 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.3, 172.0, 165.4, 155.1, 149.8, 143.4, 141.3, 137.5, 133.7, 132.0, 131.0, 130.1, 130.0, 129.0, 128.6, 127.9, 127.3, 125.5, 125.3, 120.1, 91.3, 82.2, 80.7, 77.7,

70.3, 66.6, 46.7, 38.0, 34.5, 31.4, 31.3, 29.8, 28.0, 20.5; ESI HR-MS: m/z [M+Na]$^+$ calcd. for $C_{43}H_{44}NaO_9S$: 759.2604; Found 759.2612.

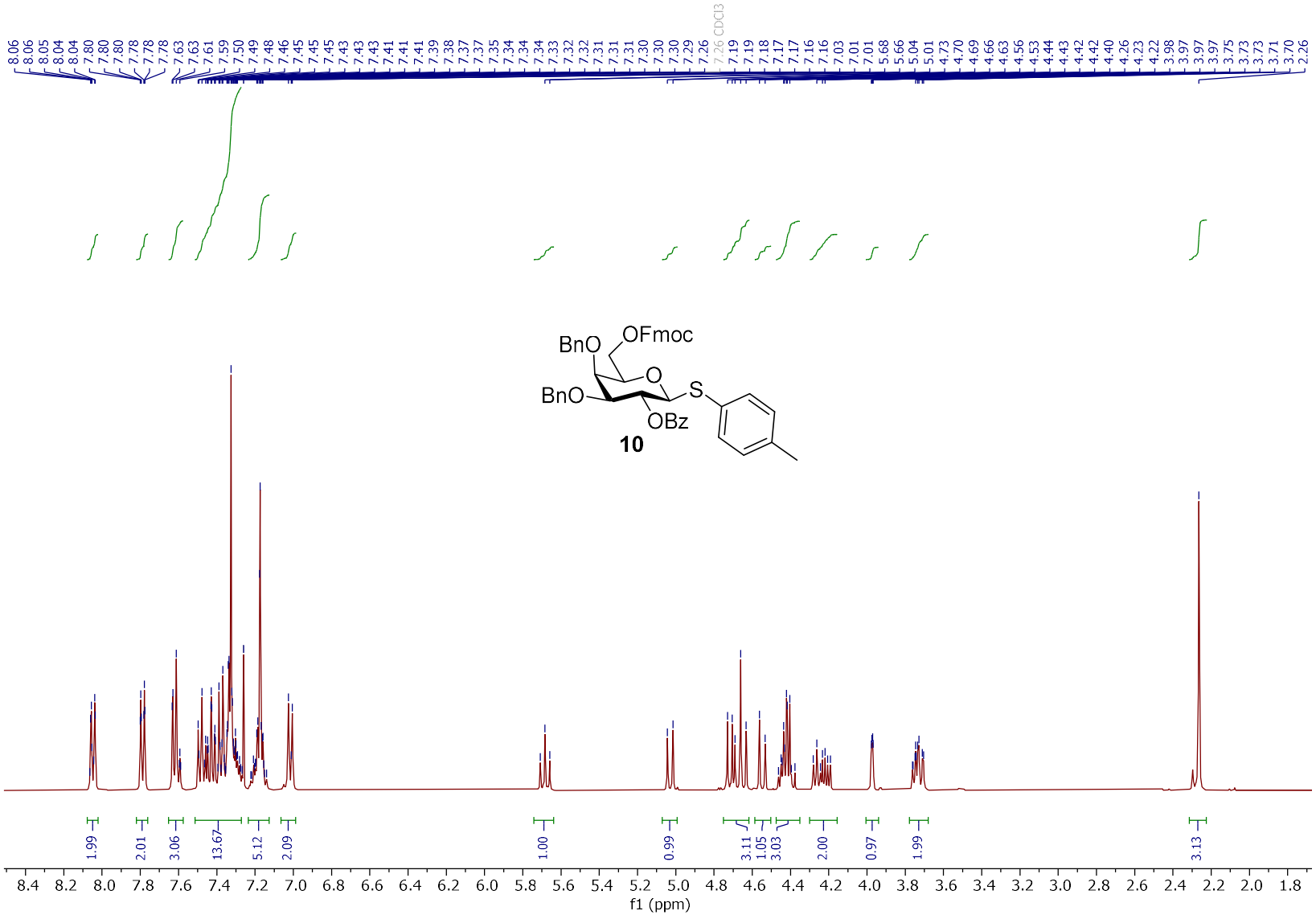


7

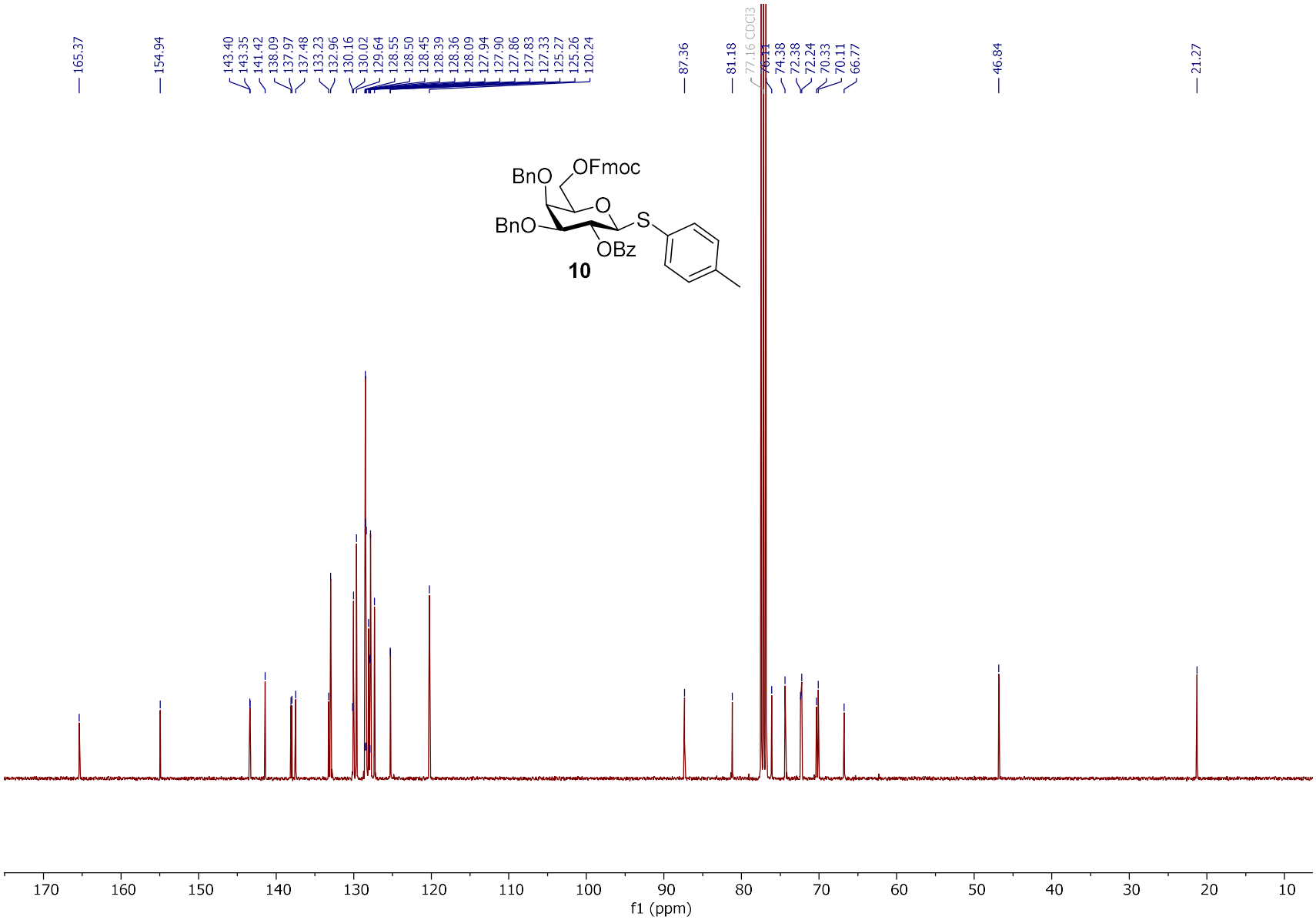
To a stirred solution compound **20** (3.3 g, 7.9 mmol) in anhydrous CH_2Cl_2 (30 mL), LevOH (2.0 mL, 19.6 mmol) was added and stirred at 0 ^oC. At this temperature, DCC (8.0 g, 38.7 mmol) and 4-DMAP (0.3 g, 2.45 mmol) were added successively and continued to stir for 3h. After the reaction as noted by TLC, the reaction was diluted with CH_2Cl_2,filtered through pad of Celite®and washed $CH_2Cl_2$and brine. The combined organic layers were dried over $MgSO_4$and concentrated. The residue was purified by flash column chromatography to yield corresponding fully protected thioglycoside **7** (3.8 g, 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.98 (m, 2H), 7.65 – 7.55 (m, 2H), 7.53 – 7.43 (m, 2H), 7.22 (ddd, *J* = 8.7, 5.5, 2.0 Hz, 1H), 7.17 – 7.10 (m, 1H), 5.61 (dd, *J* = 1.7, 0.8 Hz, 1H), 5.54 (t, *J* = 1.7 Hz, 1H), 5.23 (ddd, *J* = 5.1, 1.9, 0.8 Hz, 1H), 4.57 (td, *J* = 5.3, 3.7 Hz, 1H), 4.46 (dt, *J* = 11.9, 4.2 Hz, 1H), 4.35 (dd, *J* = 11.9, 5.6 Hz, 1H), 2.82 (td, *J* = 6.5, 2.8 Hz, 2H), 2.75 – 2.67 (m, 4H), 2.59 (ddd, *J* = 7.9, 3.9, 2.8 Hz, 2H), 2.43 (s, 3H), 2.20 (s, 3H), 2.15 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.5, 206.3, 172.5, 171.9, 165.3, 149.8, 137.5, 133.7, 132.0, 130.9, 130.1, 129.9, 129.0, 128.6, 125.5, 91.2, 82.3, 80.5, 77.6, 63.4, 38.0, 37.9, 34.5, 31.4, 31.3, 29.96, 29.93, 28.0, 27.8, 20.5; ESI HR-MS: m/z [M+Na]$^+$ calcd. for $C_{33}H_{40}NaO_9S$: 635.2291; Found 635.2285.

Heptadecasaccharide Repeating Unit of Arabinogalactan Polysaccharide HH1-1 (**1**):Sodium methoxide in methanol (0.5 M, *p*H = 13) was added to a solution of protected oligosaccharide (20 mg) **21** in methanol:CH_2Cl_2 (1:1), and stirred at room temperature for 8 h, neutralized with Amberlite ion exchange (H^+) resin, filtered and concentrated in vacuo and carried forward directly into hydrogenolysis without purification. The Zemplén methanolysis product was dissolved in EtOAc:*t*-BuOH:H_2O (2:1:1) and transferred to cylindrical vials. $Pd(OH)_2/C$ (20%), (100 wt %) was added and the reaction mixture was stirred in hydrogen reactor with 5 bar pressure for 48 h. The reaction mixture was filtered through a pad of Celite and washed with methanol and water. The filtrates were concentrated in vacuo and purified on size exclusion chromatography (Method B) Hypercarb column and lyophilized to give a pure compound **1** in 13% yield over 2 steps. ^{1}H NMR (700 MHz, D_2O) δ 5.23 (d, J = 7.0 Hz, 2H), 5.14 (s, 1H), 5.04 (s, 2H), 4.67 – 4.61 (m, 2H), 4.58 (d, J = 7.9 Hz, 1H), 4.53 – 4.47 (m, 3H), 4.44 (t, J = 8.0 Hz, 2H), 4.39 (dd, J = 15.0, 7.9 Hz, 2H), 4.34 (d, J = 18.4 Hz, 1H), 4.21 – 4.18 (m, 3H), 4.17 (dd, J = 8.9, 2.4 Hz, 2H), 4.09 – 4.03 (m, 7H), 4.00 (dd, J = 6.8, 2.7 Hz, 7H), 3.94 – 3.86 (m, 27H), 3.84 – 3.77 (m, 10H), 3.75 – 3.70 (m, 15H), 3.67 (tq, J = 8.2, 4.0 Hz, 24H), 3.61 (m, 4H), 3.50 – 3.46 (m, 4H), 2.95 (t, J = 7.7 Hz, 2H), 1.63 (p, J = 7.1 Hz, 4H), 1.42 (p, J = 7.9 Hz, 2H); ^{13}C NMR (176 MHz, D_2O) δ 109.2, 107.2, 104.1, 103.3, 102.6, 83.8, 82.0, 81.0, 80.8, 79.5, 76.3, 75.0, 74.9, 74.8, 74.5, 72.4, 70.9, 70.6, 70.1, 69.1, 68.5, 68.4, 61.0, 60.8, 39.3, 28.1, 22.0, 19.9;MALDI-TOF-MS: $[M+Na]^+$ calcd for $C_{102}H_{173}NO_{81}Na$, 2732.4218, found 2732.7070.

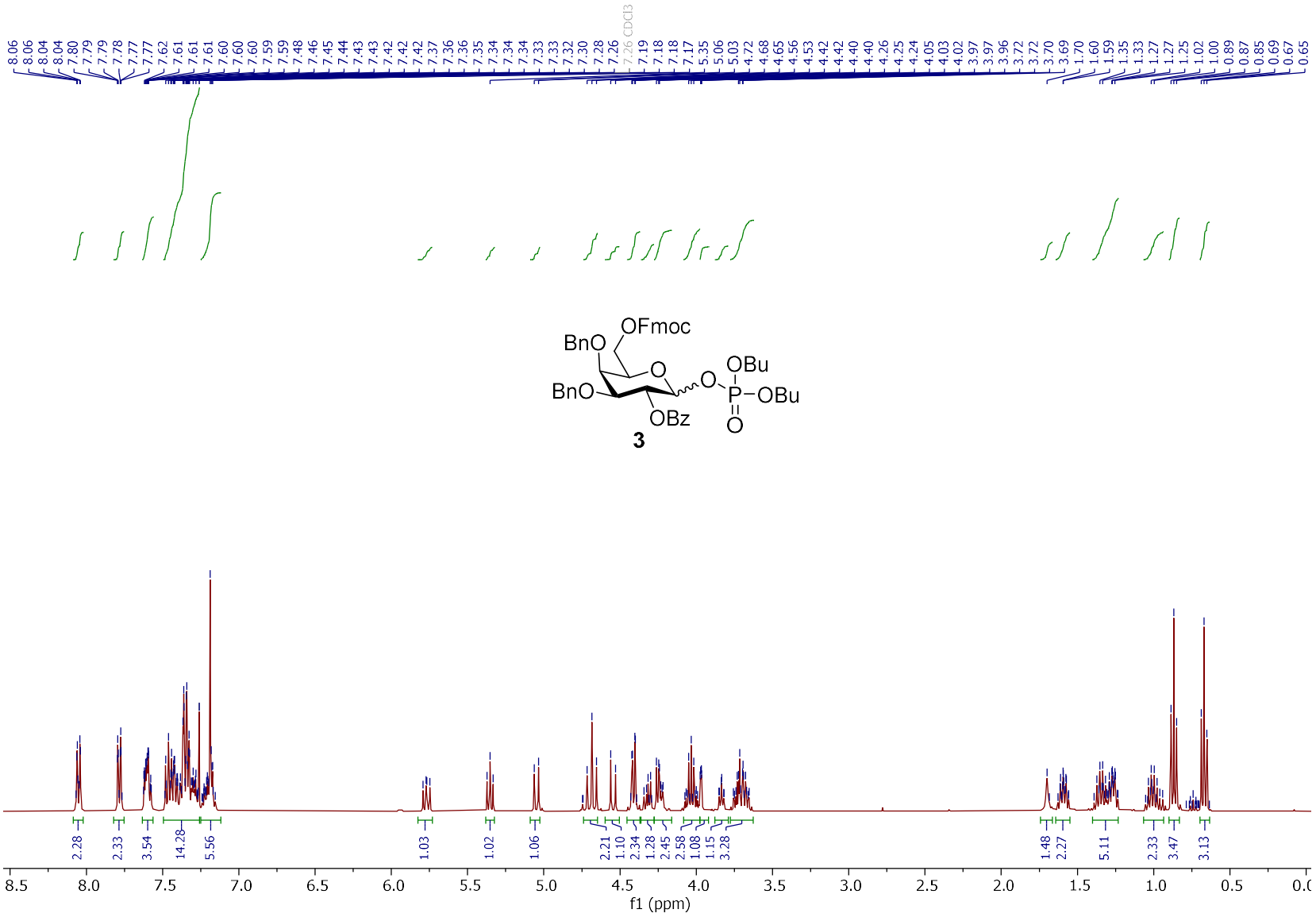
7. NMR spectra



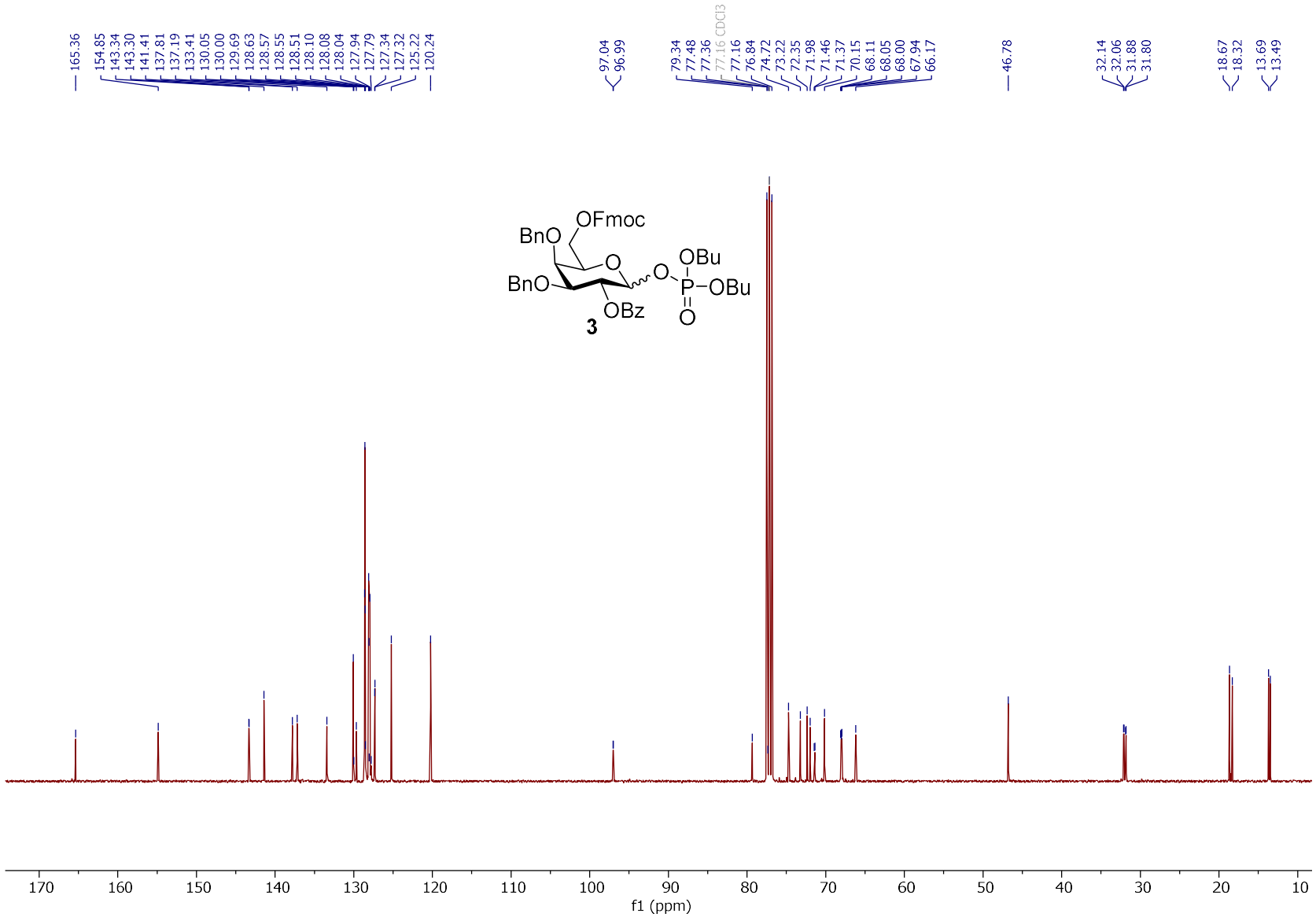
The ^{1}H Spectrum of Compound **10** (400 MHz, $CDCl_3$)



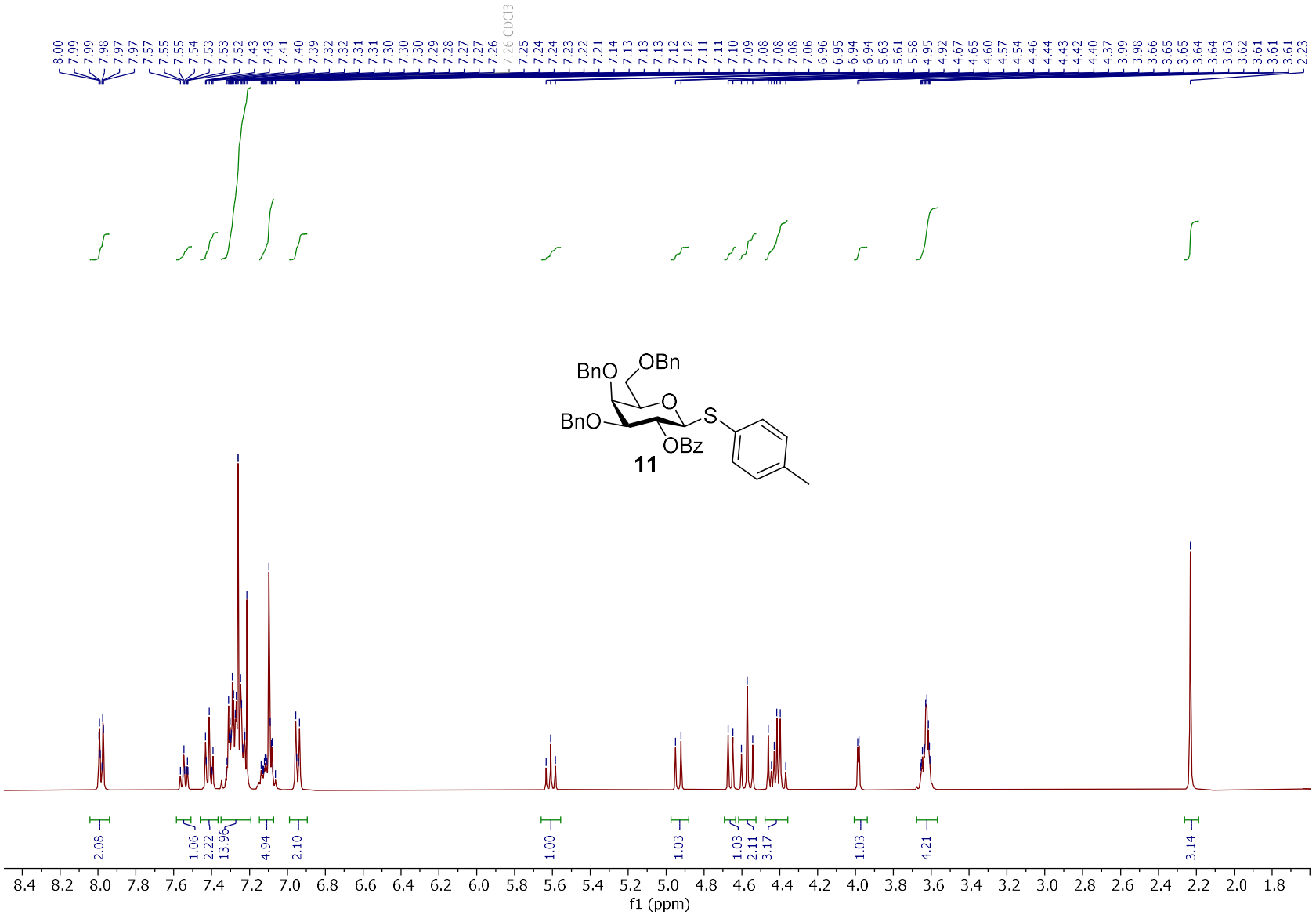
The $^{13}C\{^{1}H\}$ Spectrum of Compound **10** (100 MHz, $CDCl_3$)



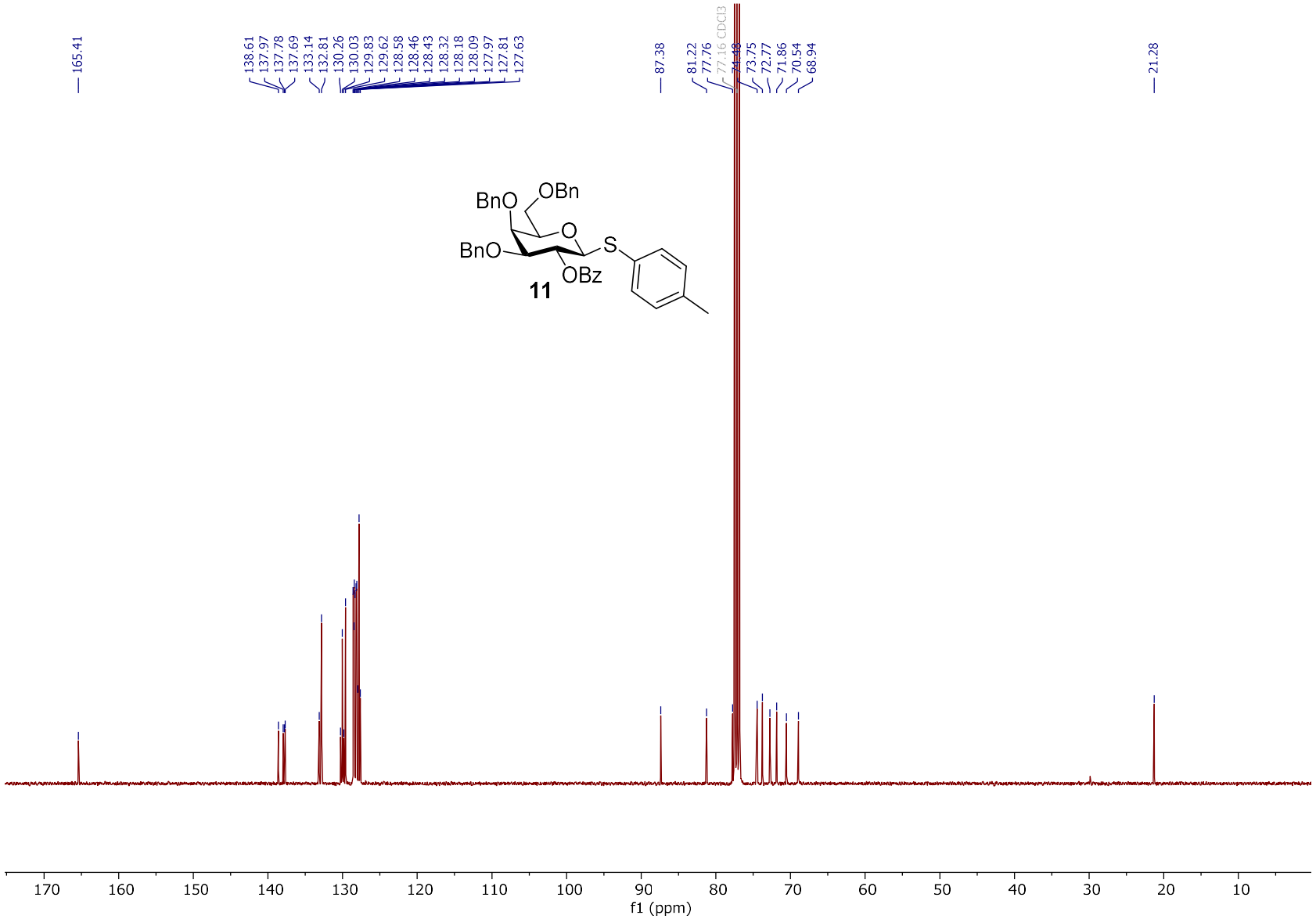
The ^{1}H Spectrum of Compound **3** (400 MHz, $CDCl_3$)



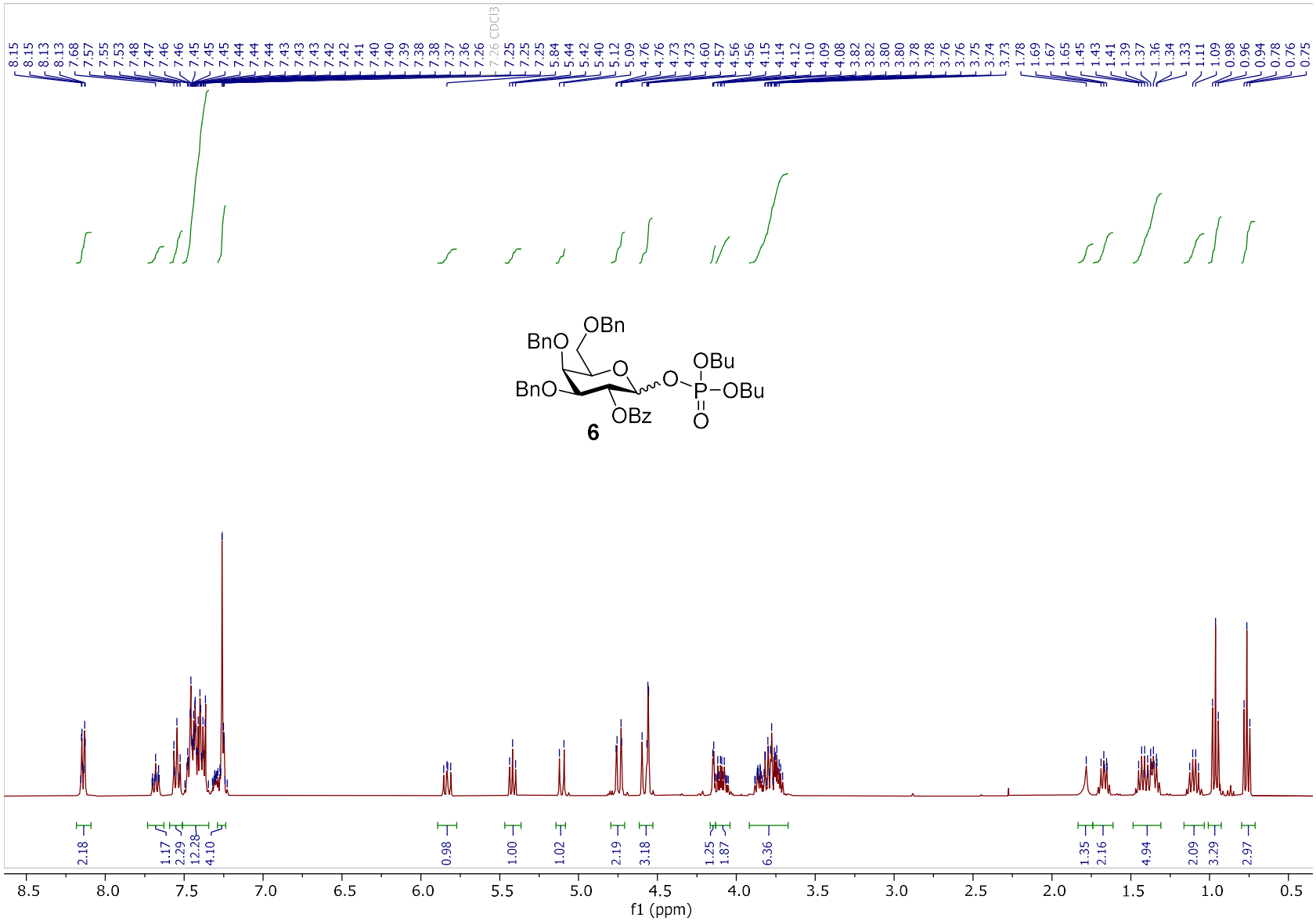
The $^{13}C\{^{1}H\}$ Spectrum of Compound **3** (100 MHz, $CDCl_3$)



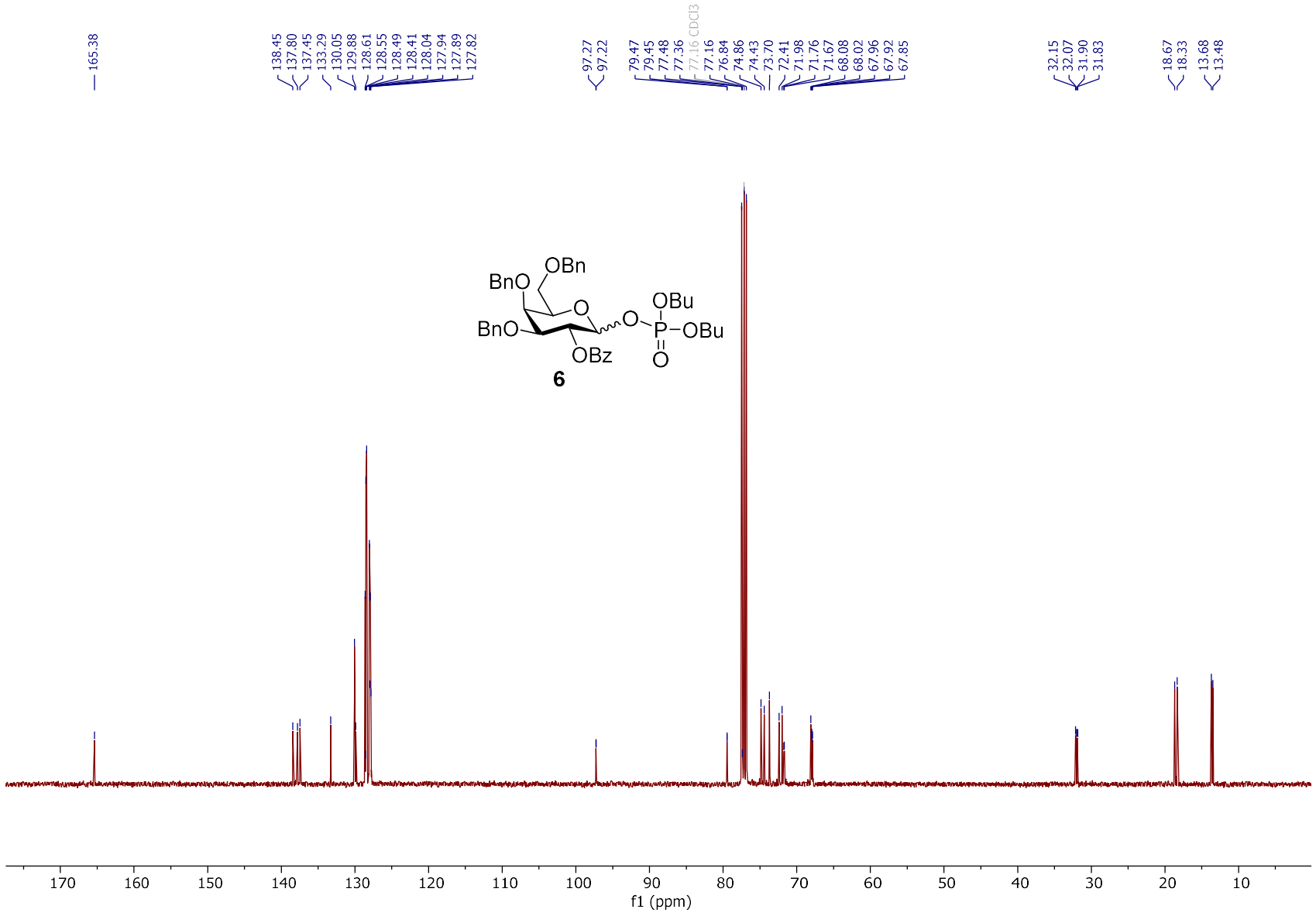
The ^{1}H Spectrum of Compound **11** (400 MHz, $CDCl_3$)



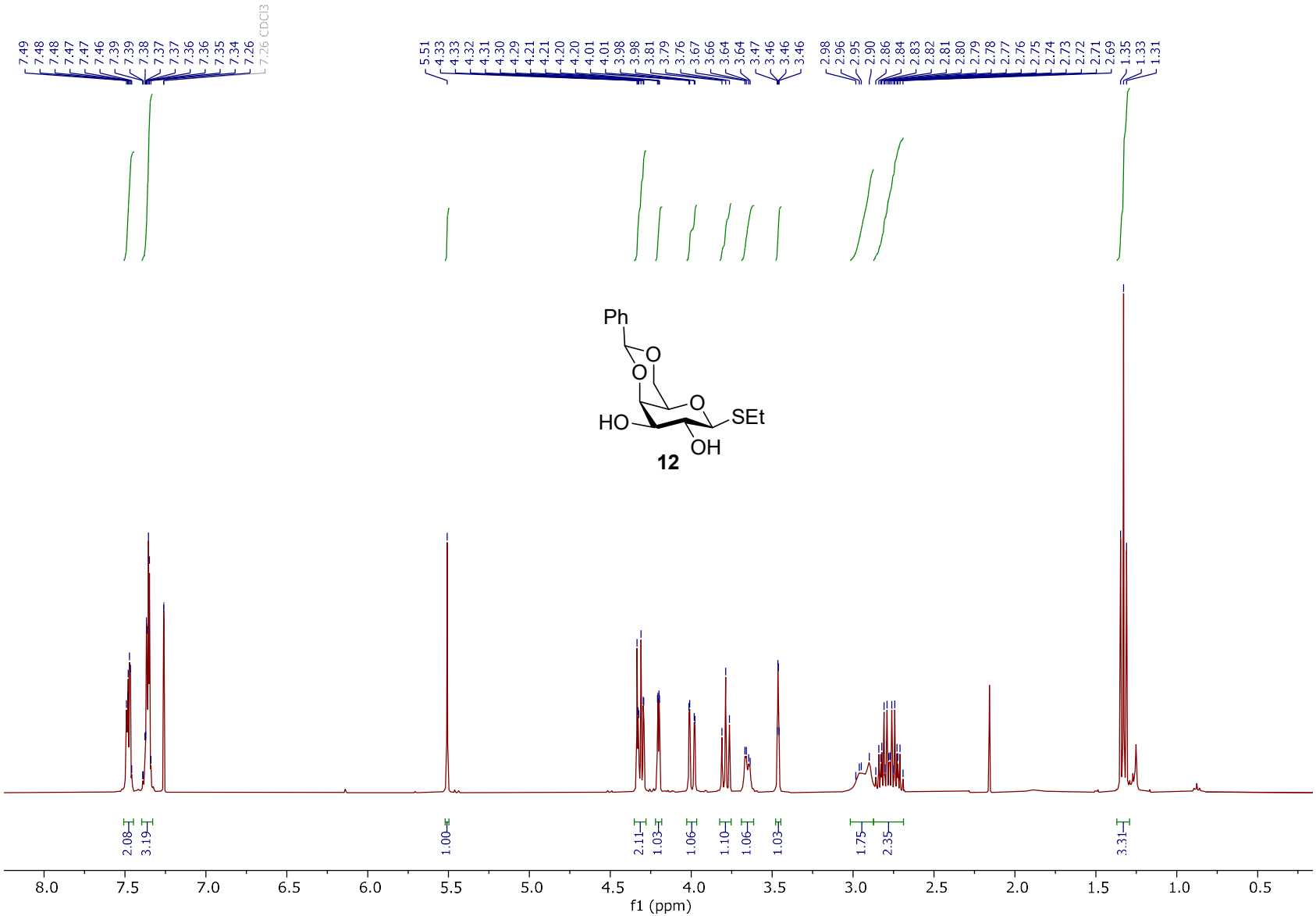
The $^{13}C\{^{1}H\}$ Spectrum of Compound **11** (100 MHz, $CDCl_3$)



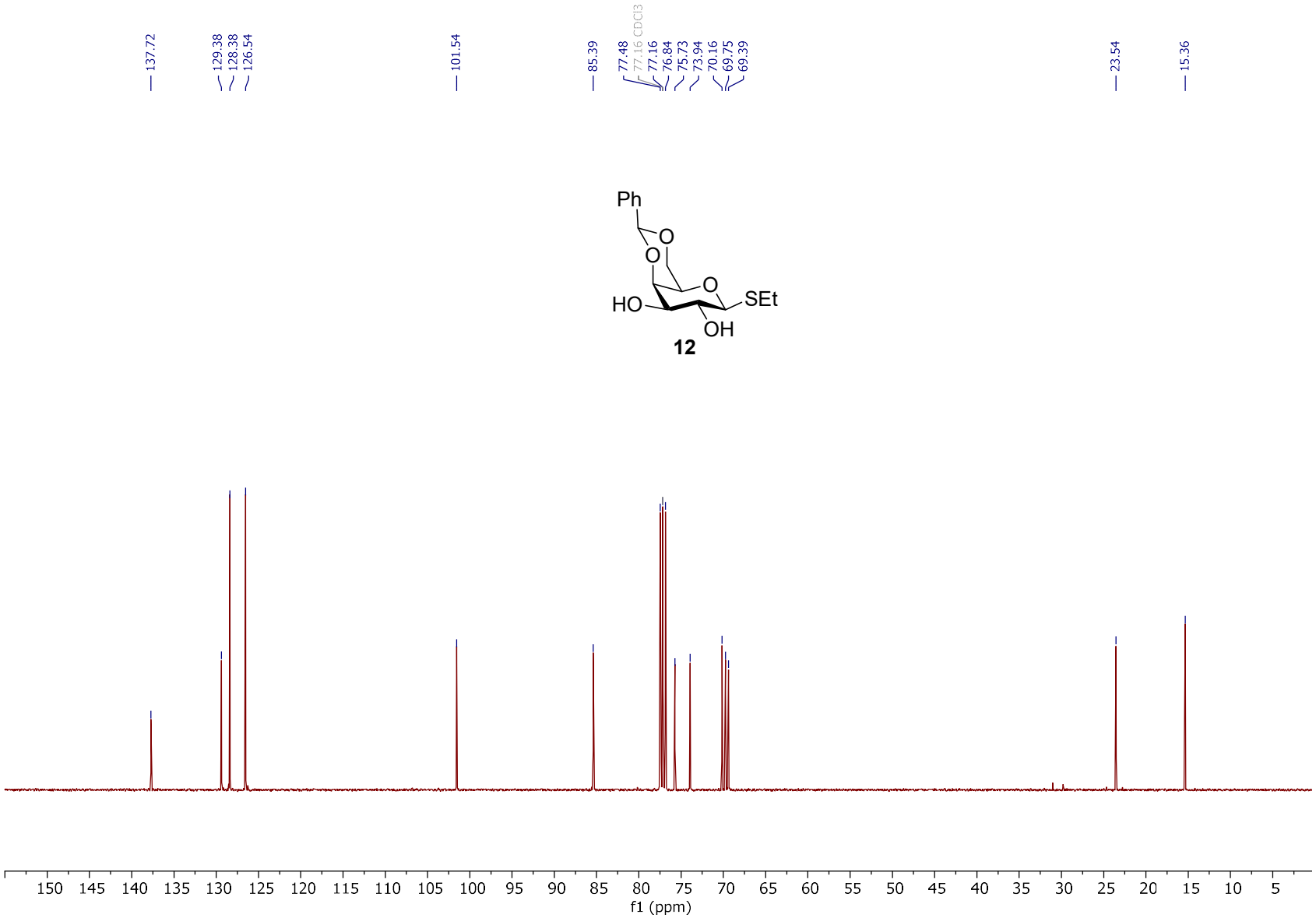
The ^{1}H Spectrum of Compound **6** (400 MHz, $CDCl_3$)



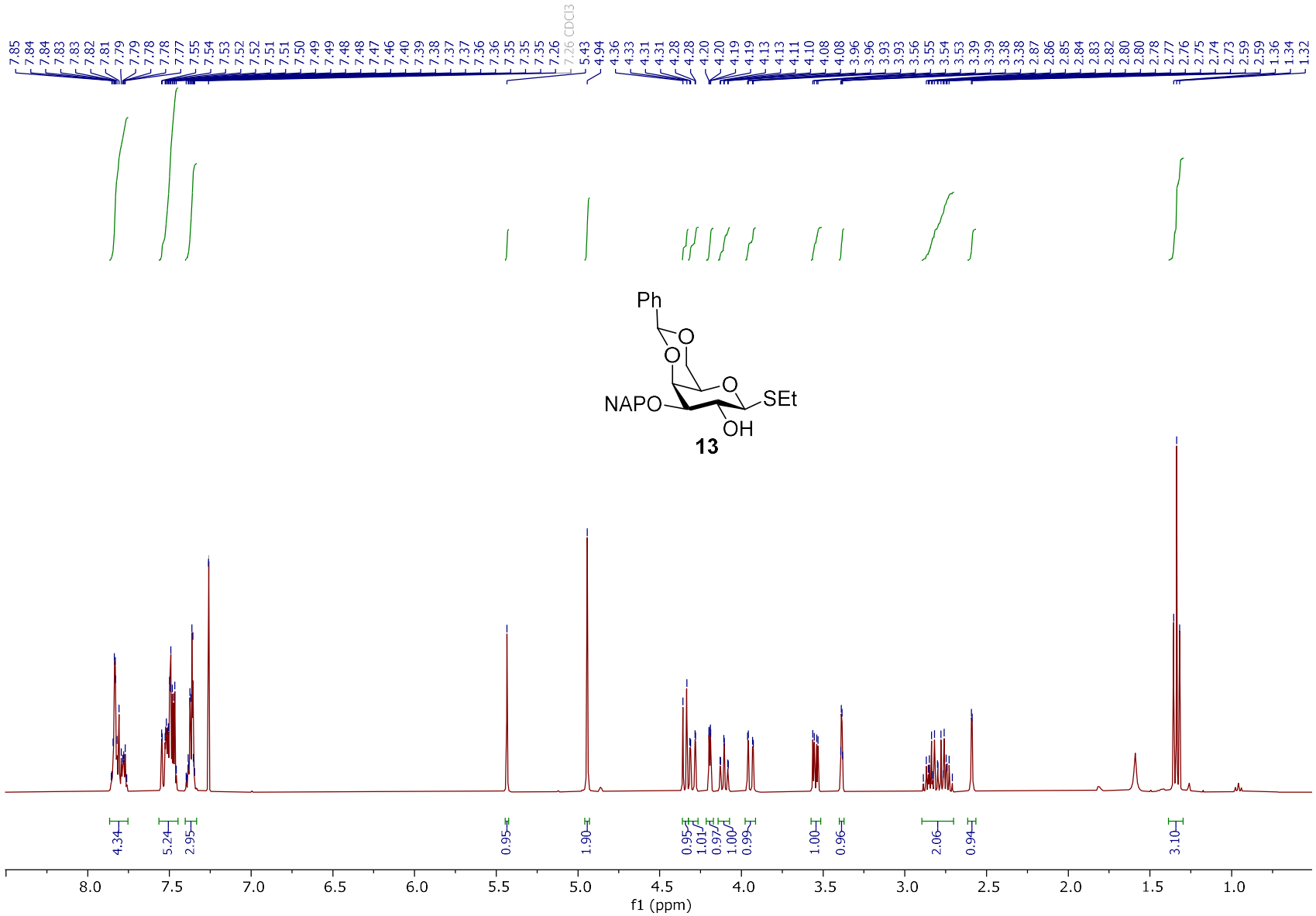
The $^{13}C\{^{1}H\}$ Spectrum of Compound **6** (100 MHz, $CDCl_3$)



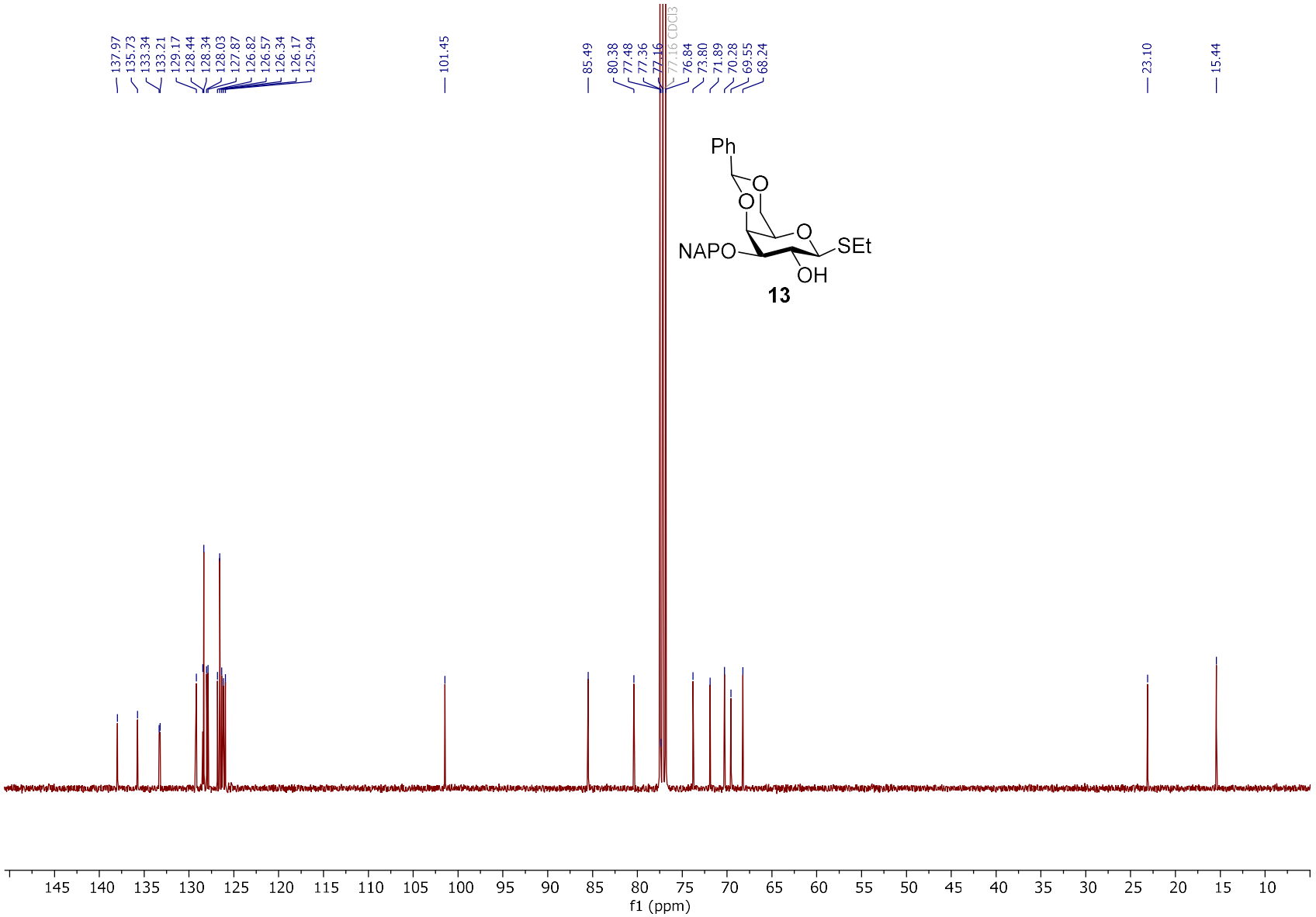
The ^{1}H Spectrum of Compound **12** (400 MHz, $CDCl_3$)



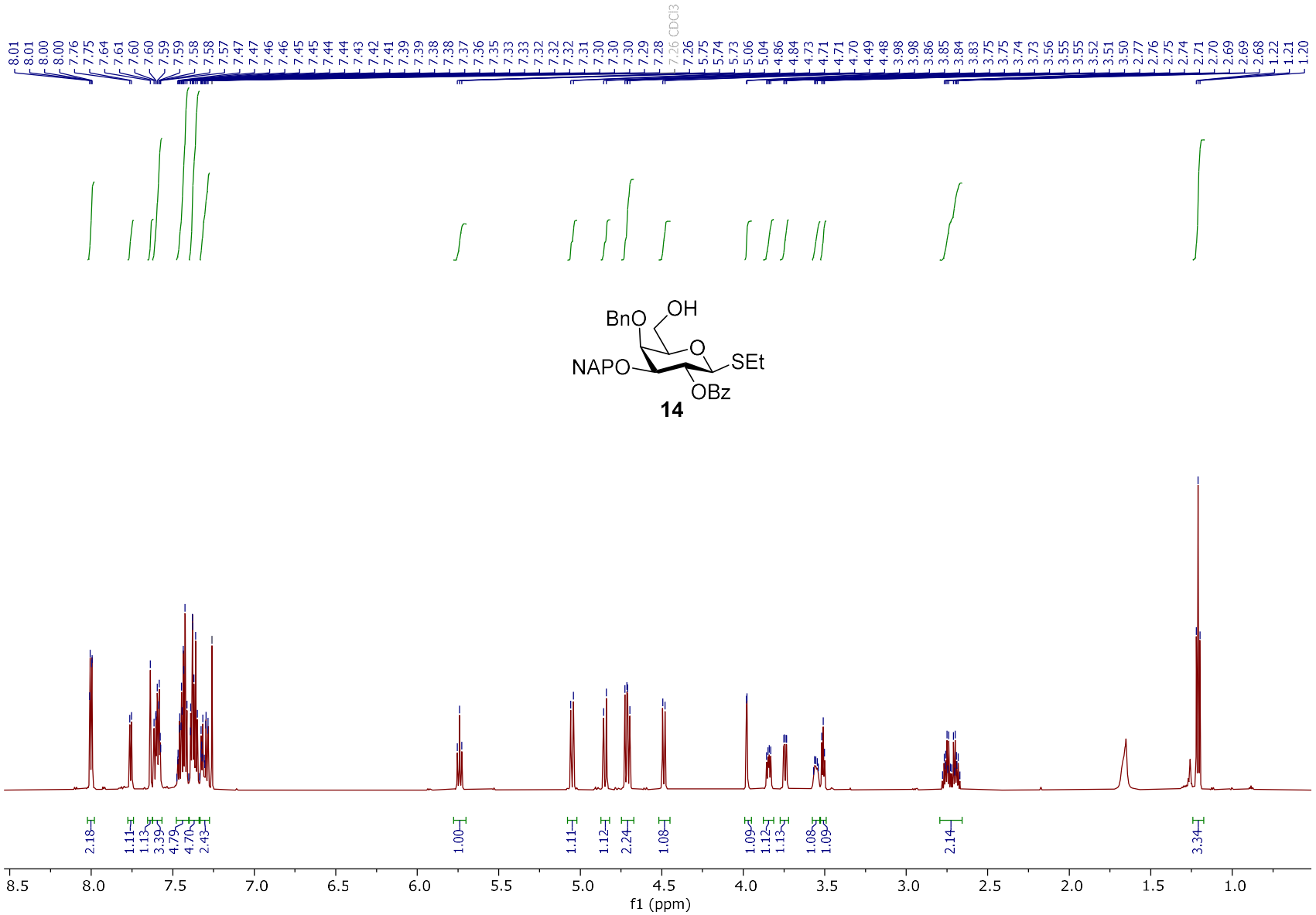
The $^{13}C\{^{1}H\}$ Spectrum of Compound **12** (100 MHz, $CDCl_3$)



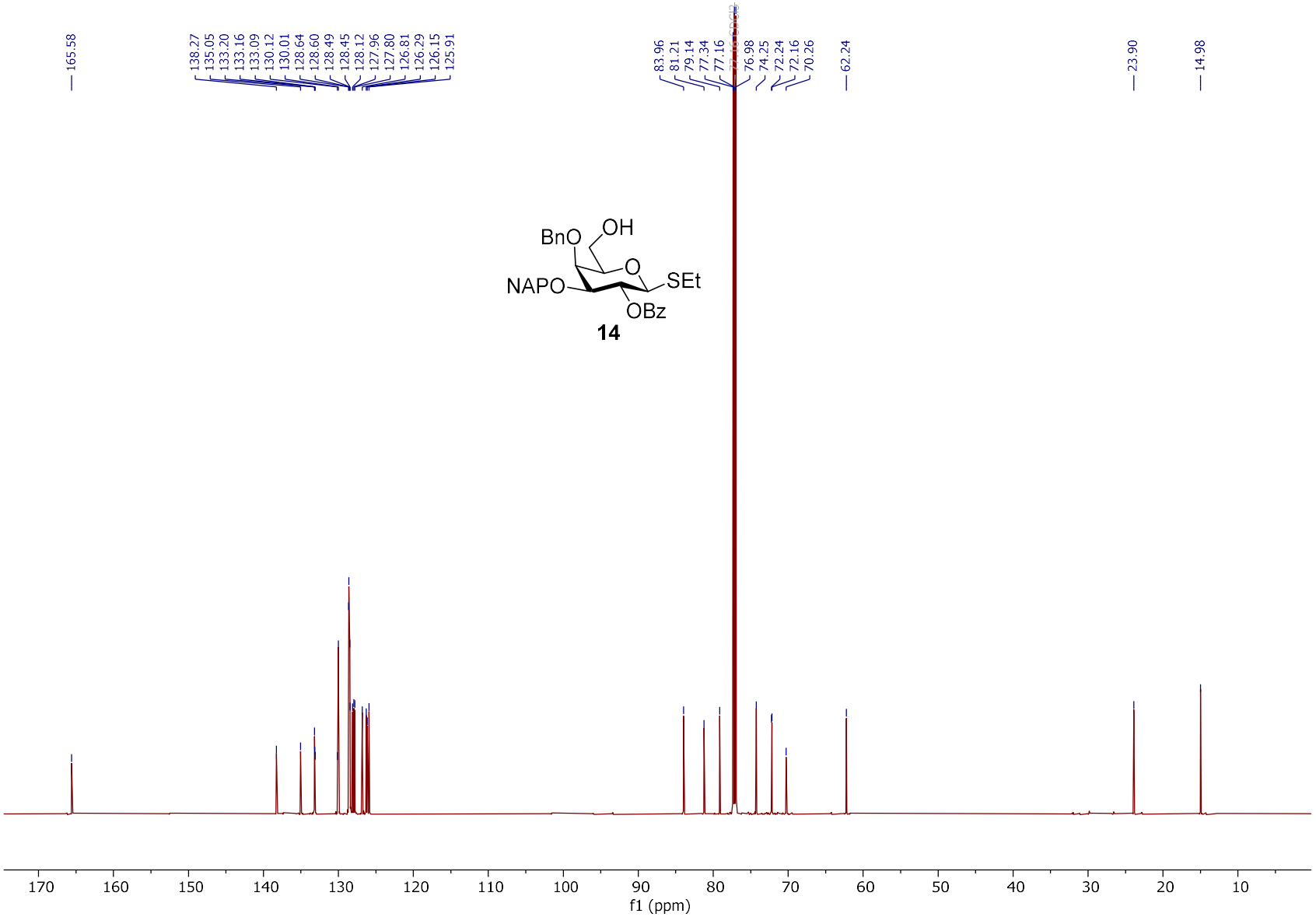
The ^{1}H Spectrum of Compound **13** (400 MHz, $CDCl_3$)



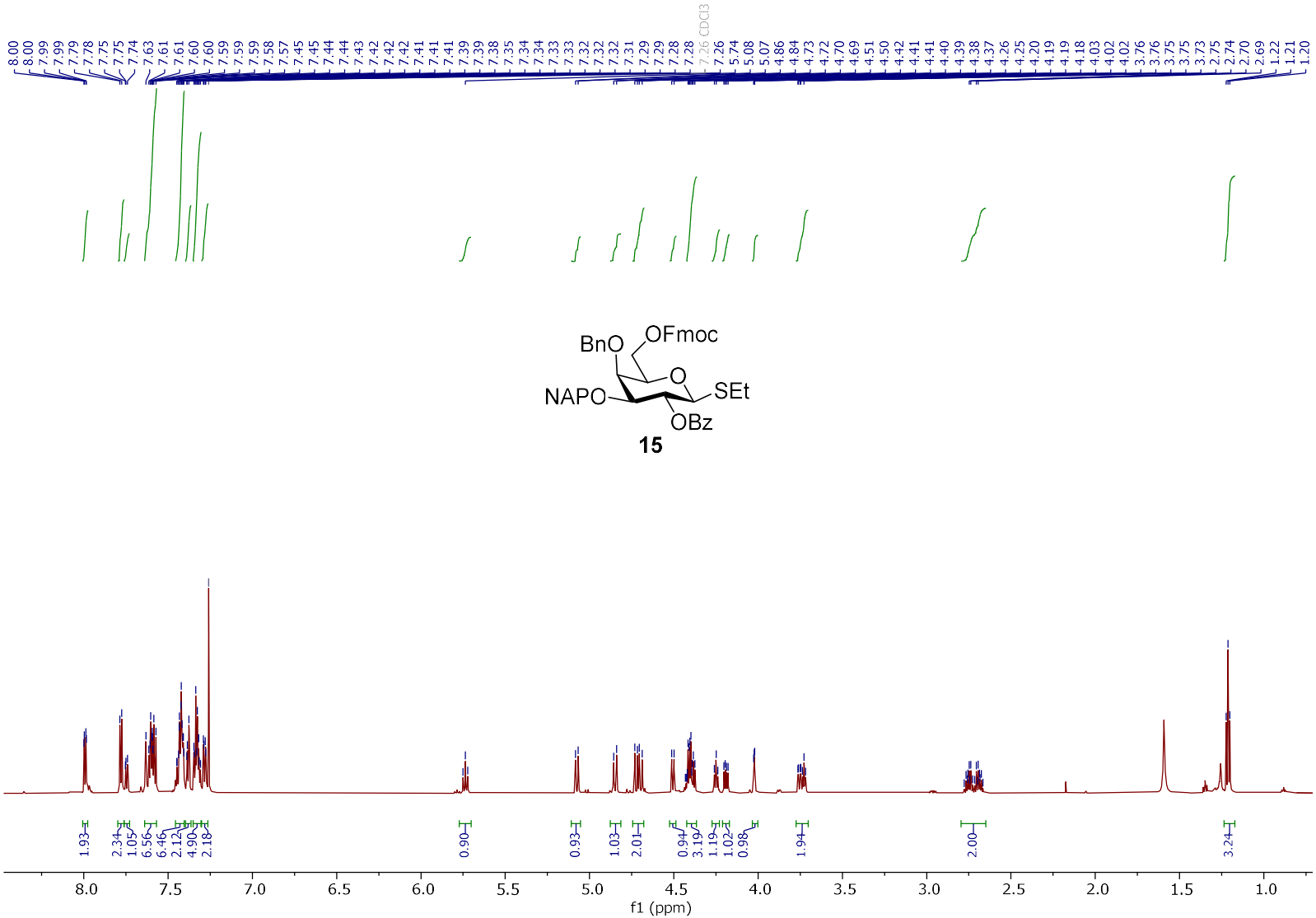
The $^{13}C\{^{1}H\}$ Spectrum of Compound **13** (100 MHz, $CDCl_3$)



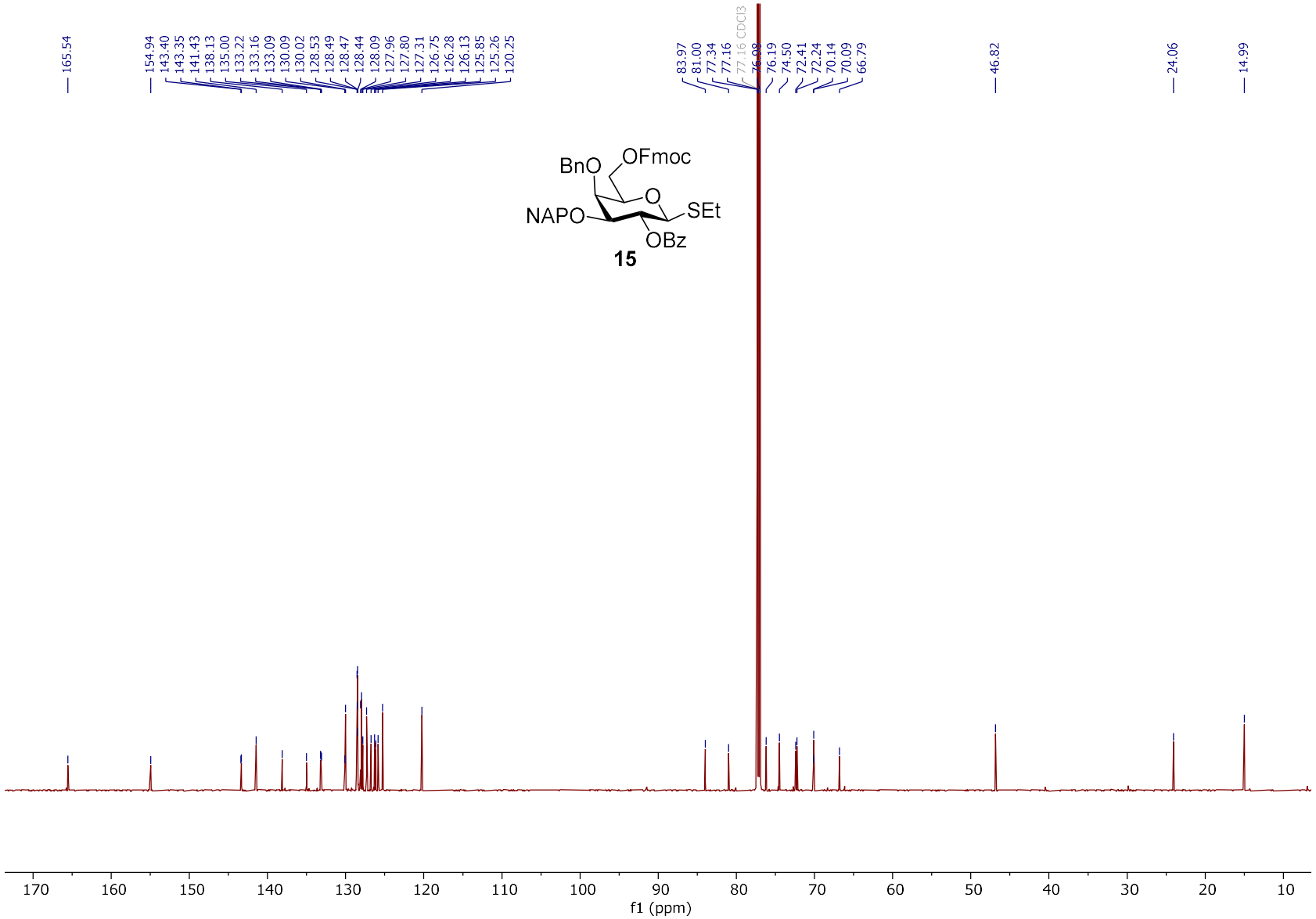
The ^{1}H Spectrum of Compound **14** (700 MHz, $CDCl_3$)



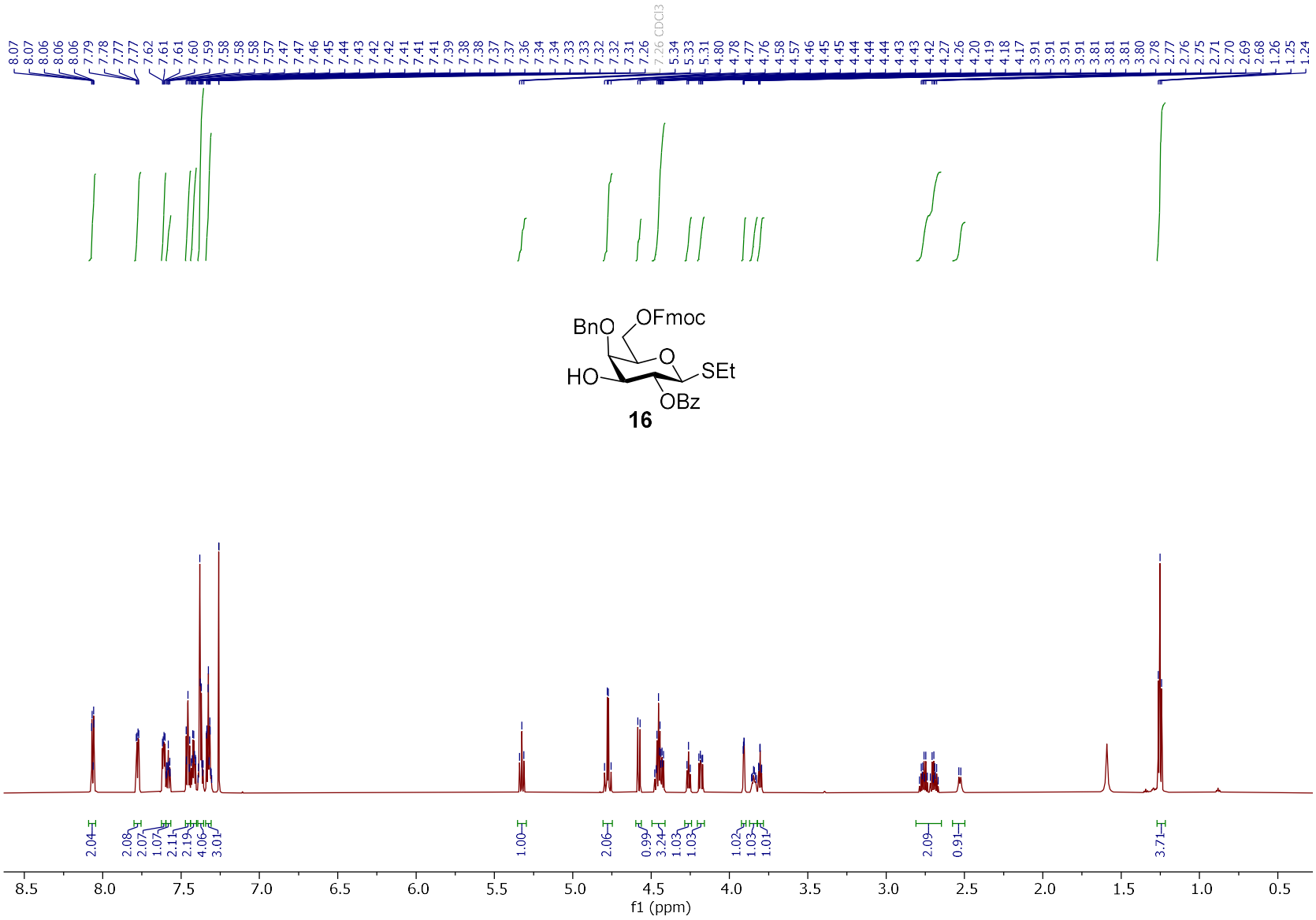
The $^{13}C\{^{1}H\}$ Spectrum of Compound **14** (175 MHz, $CDCl_3$)



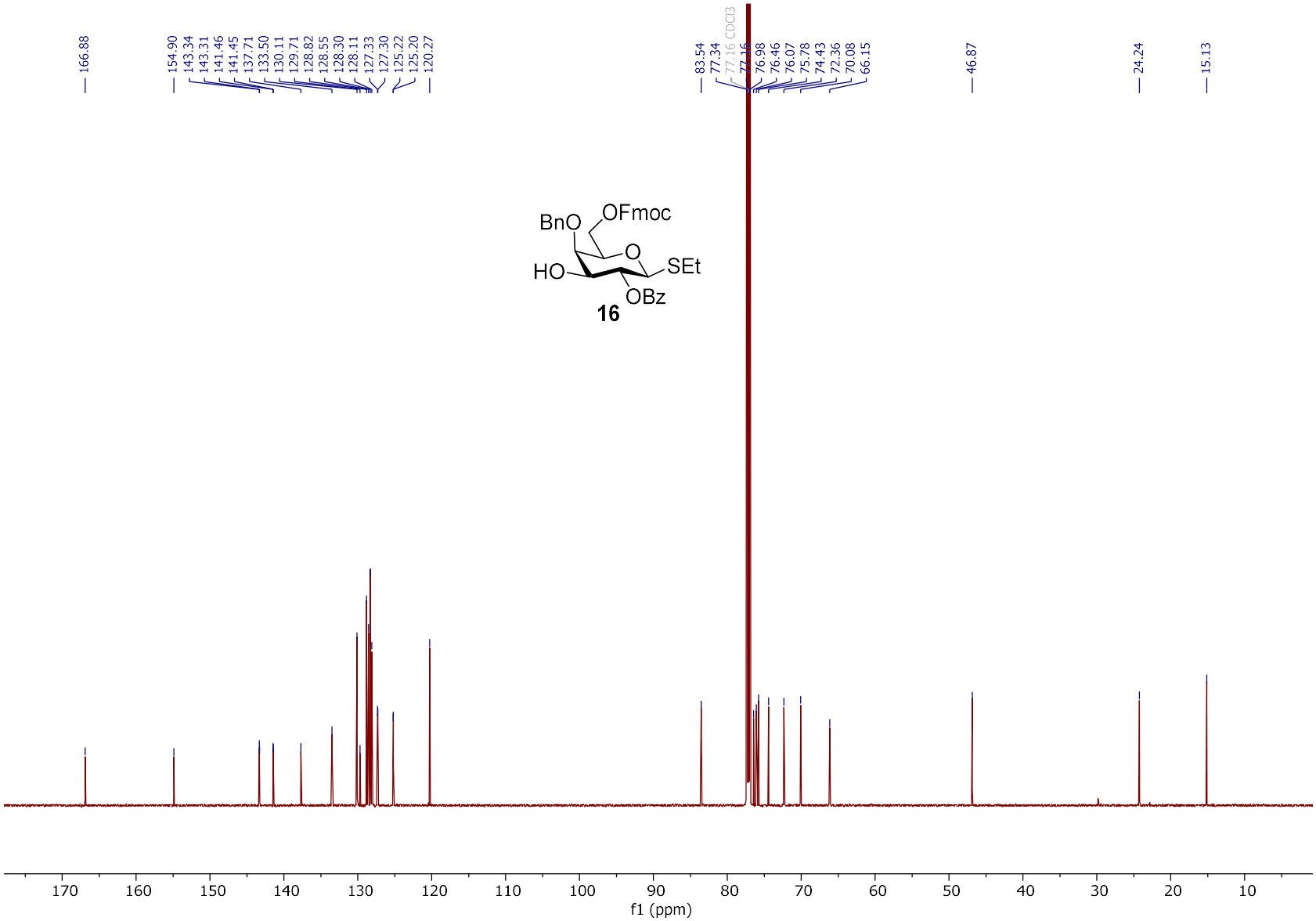
The ^{1}H Spectrum of Compound **15** (700 MHz, $CDCl_3$)



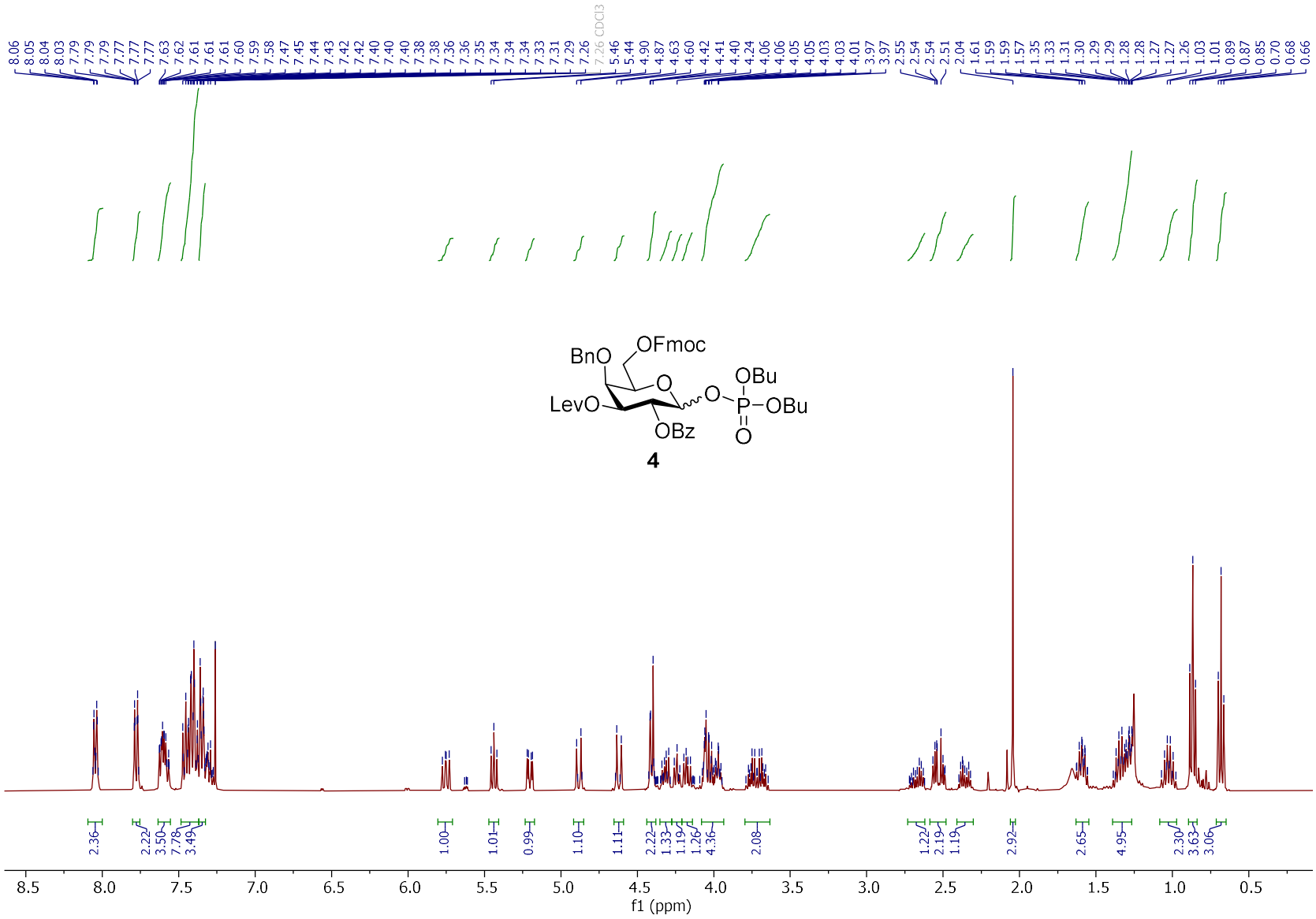
The $^{13}C\{^{1}H\}$ Spectrum of Compound **15** (175 MHz, $CDCl_3$)



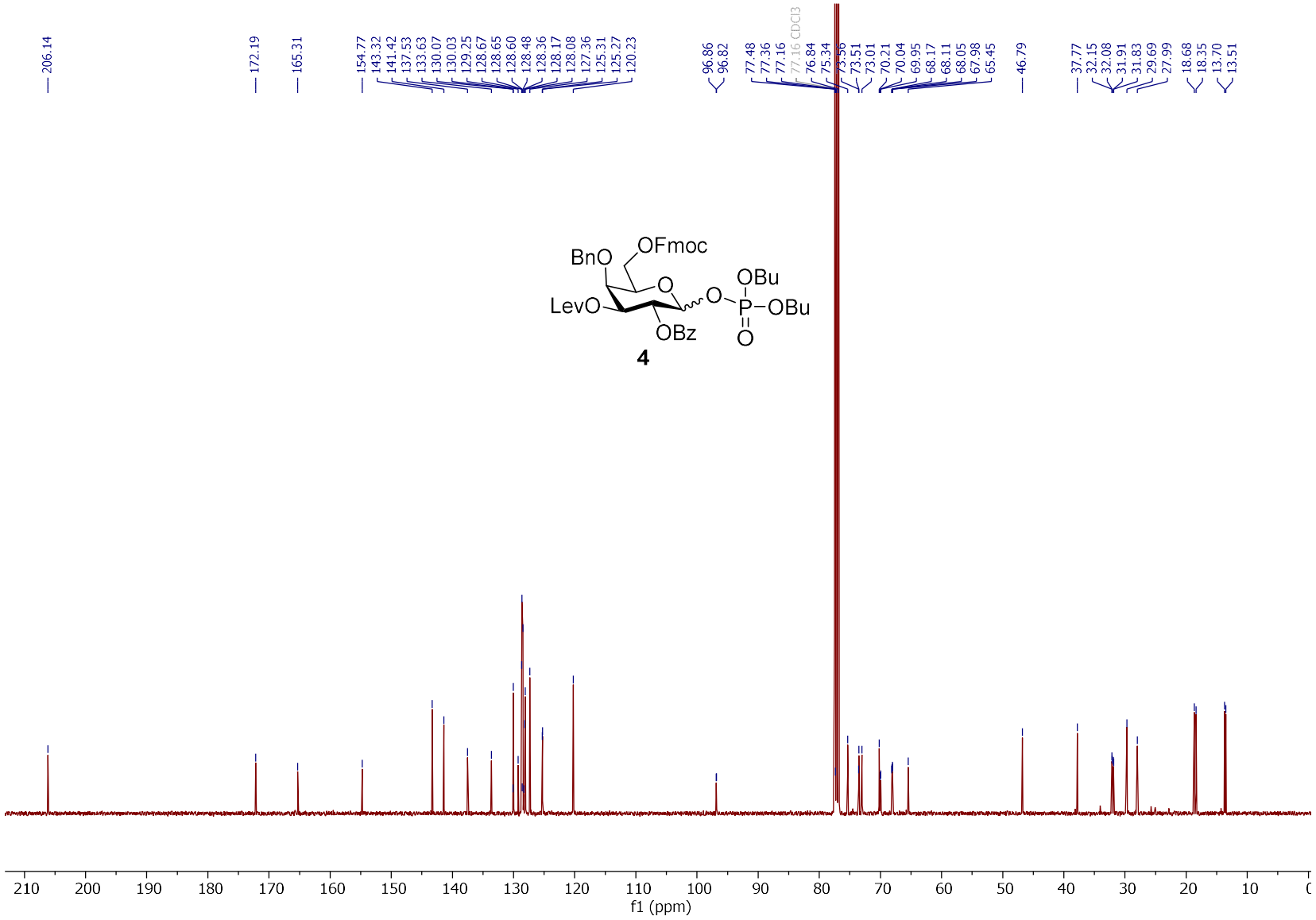
The ^{1}H Spectrum of Compound **16** (700 MHz, $CDCl_3$)



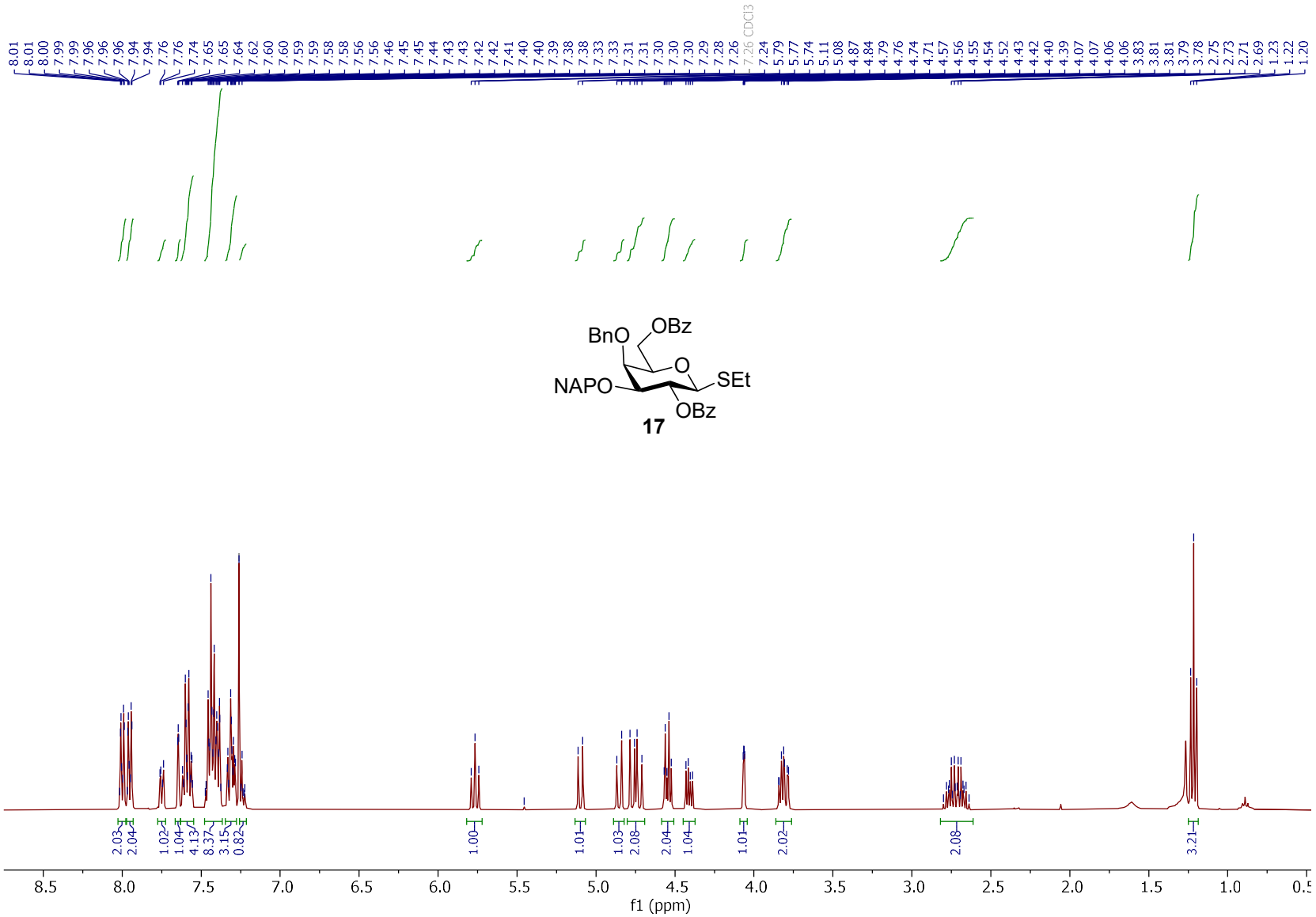
The $^{13}C\{^{1}H\}$ Spectrum of Compound **16** (175 MHz, $CDCl_3$)



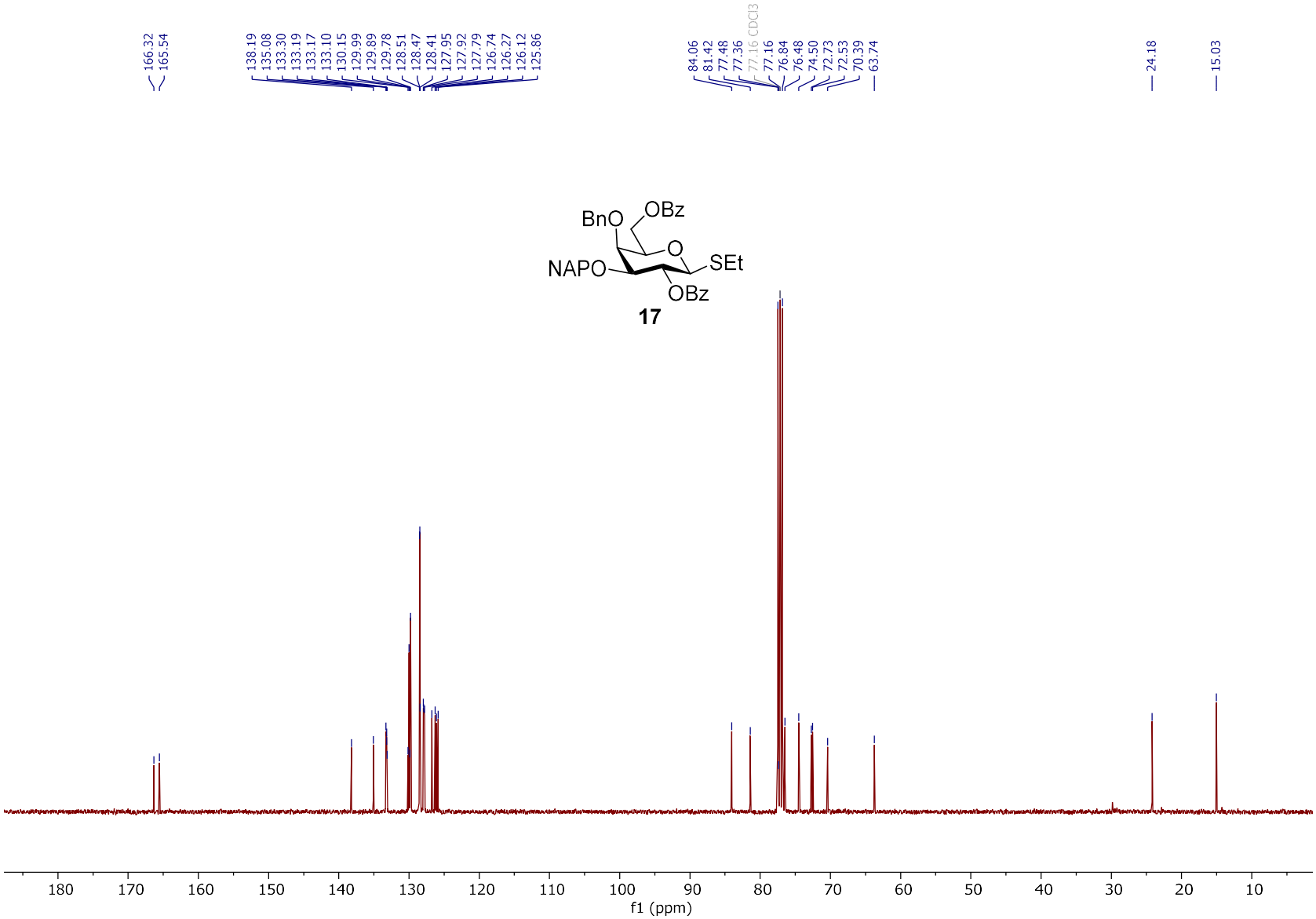
The ^{1}H Spectrum of Compound **4** (400 MHz, $CDCl_3$)



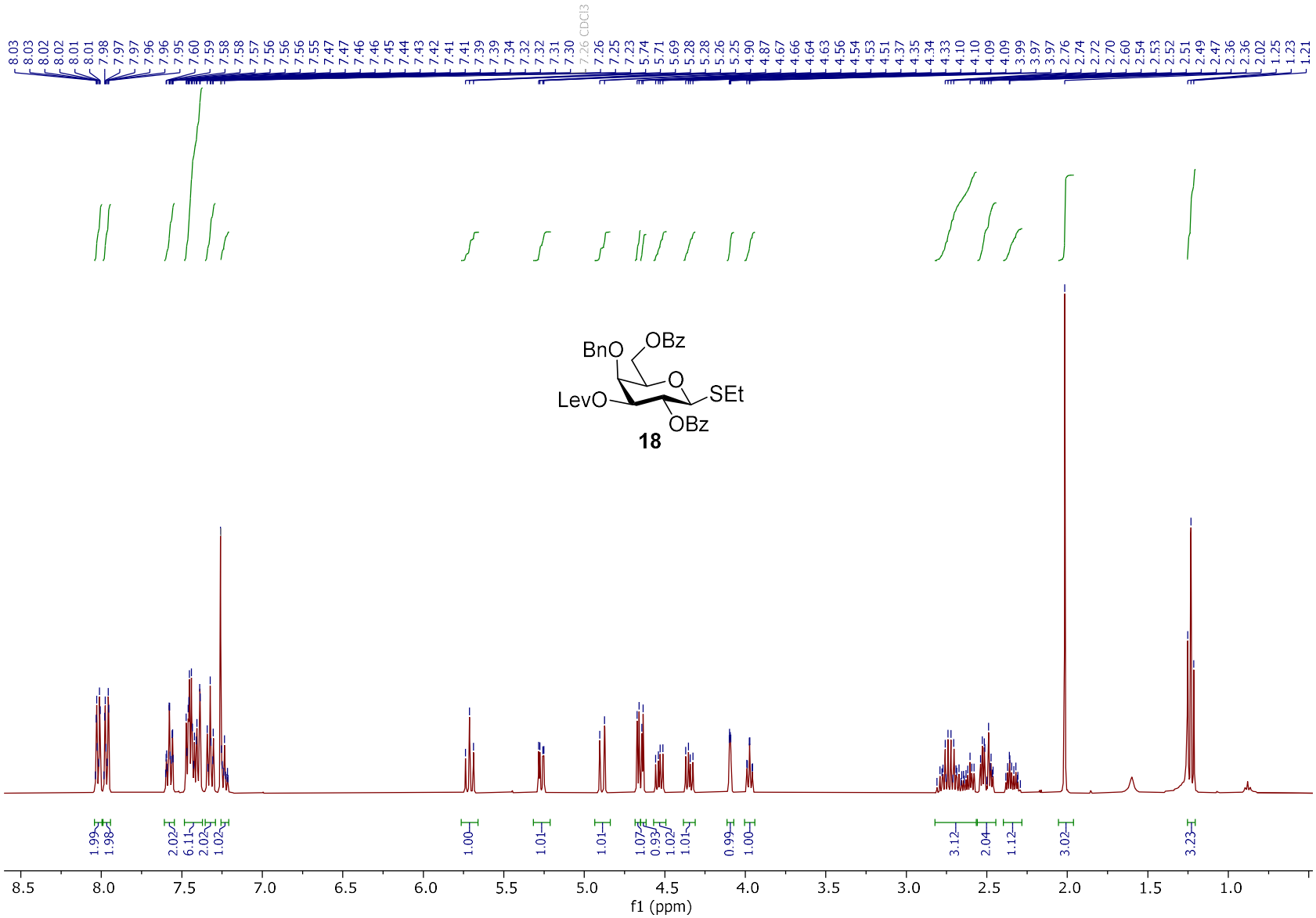
The $^{13}C\{^{1}H\}$ Spectrum of Compound **4** (100 MHz, $CDCl_3$)



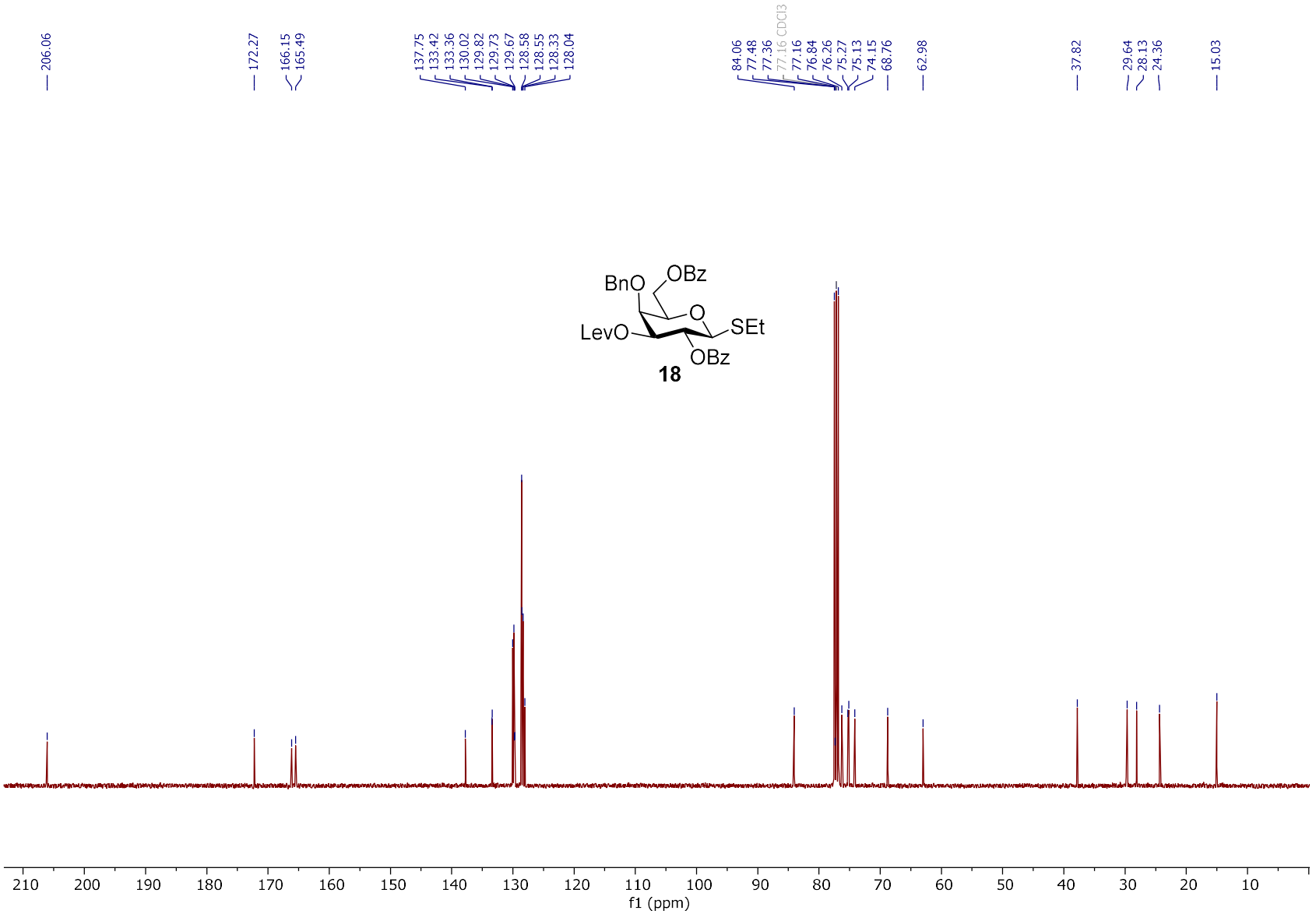
The ^{1}H Spectrum of Compound **17** (400 MHz, $CDCl_3$)



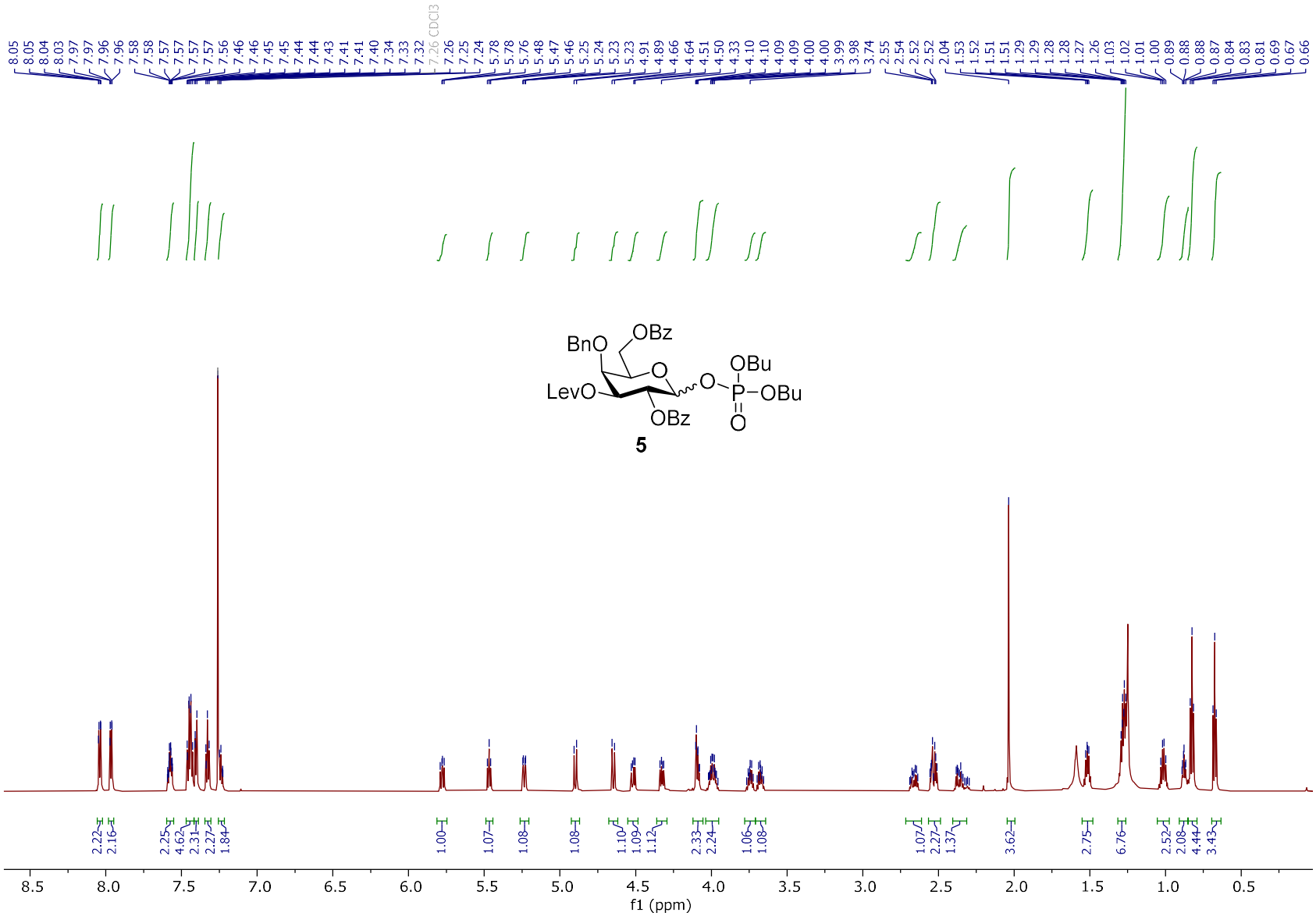
The $^{13}C\{^{1}H\}$ Spectrum of Compound **17** (100 MHz, $CDCl_3$)



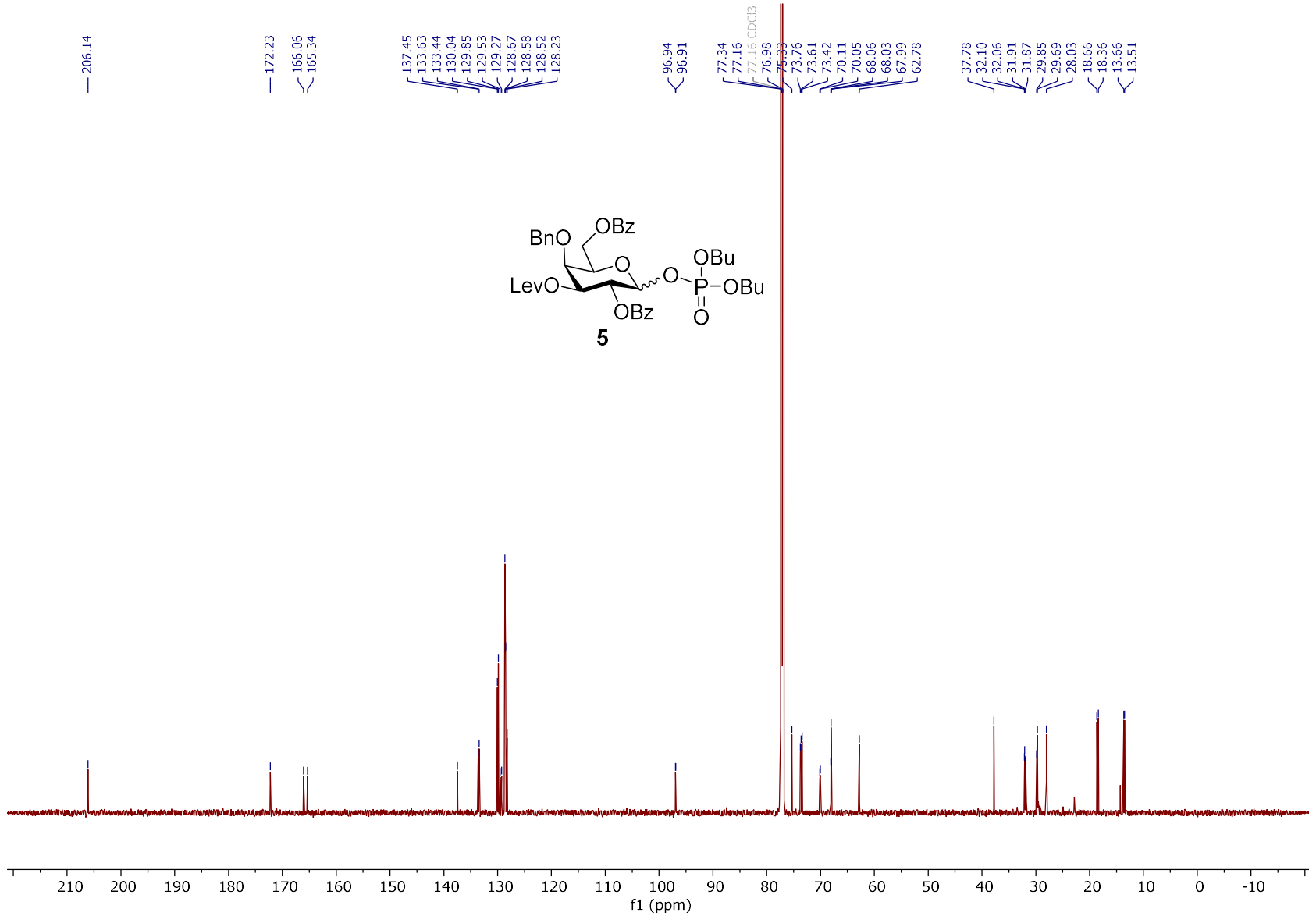
The ^{1}H Spectrum of Compound **18** (400 MHz, $CDCl_3$)



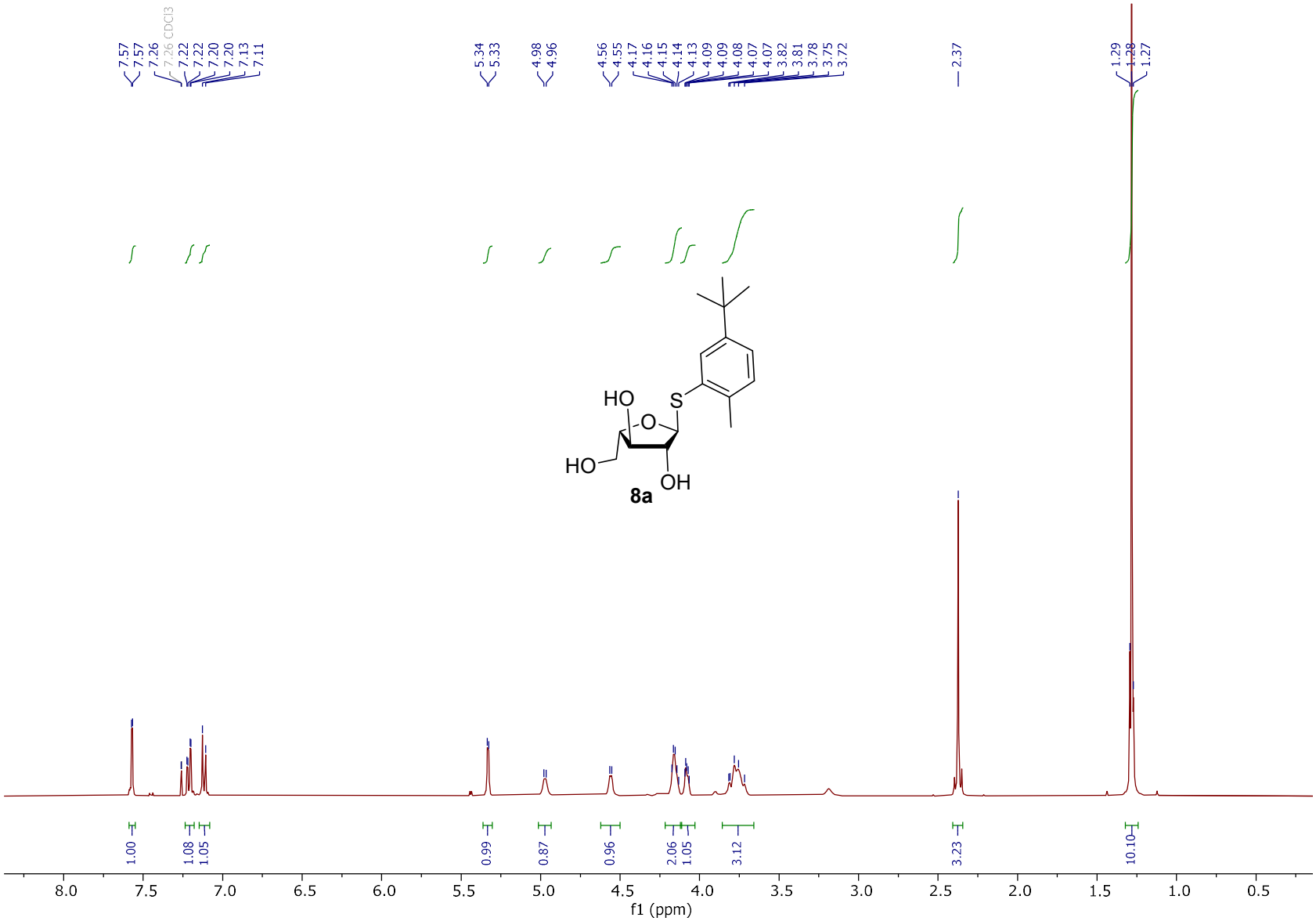
The $^{13}C\{^{1}H\}$ Spectrum of Compound **18** (100 MHz, $CDCl_3$)



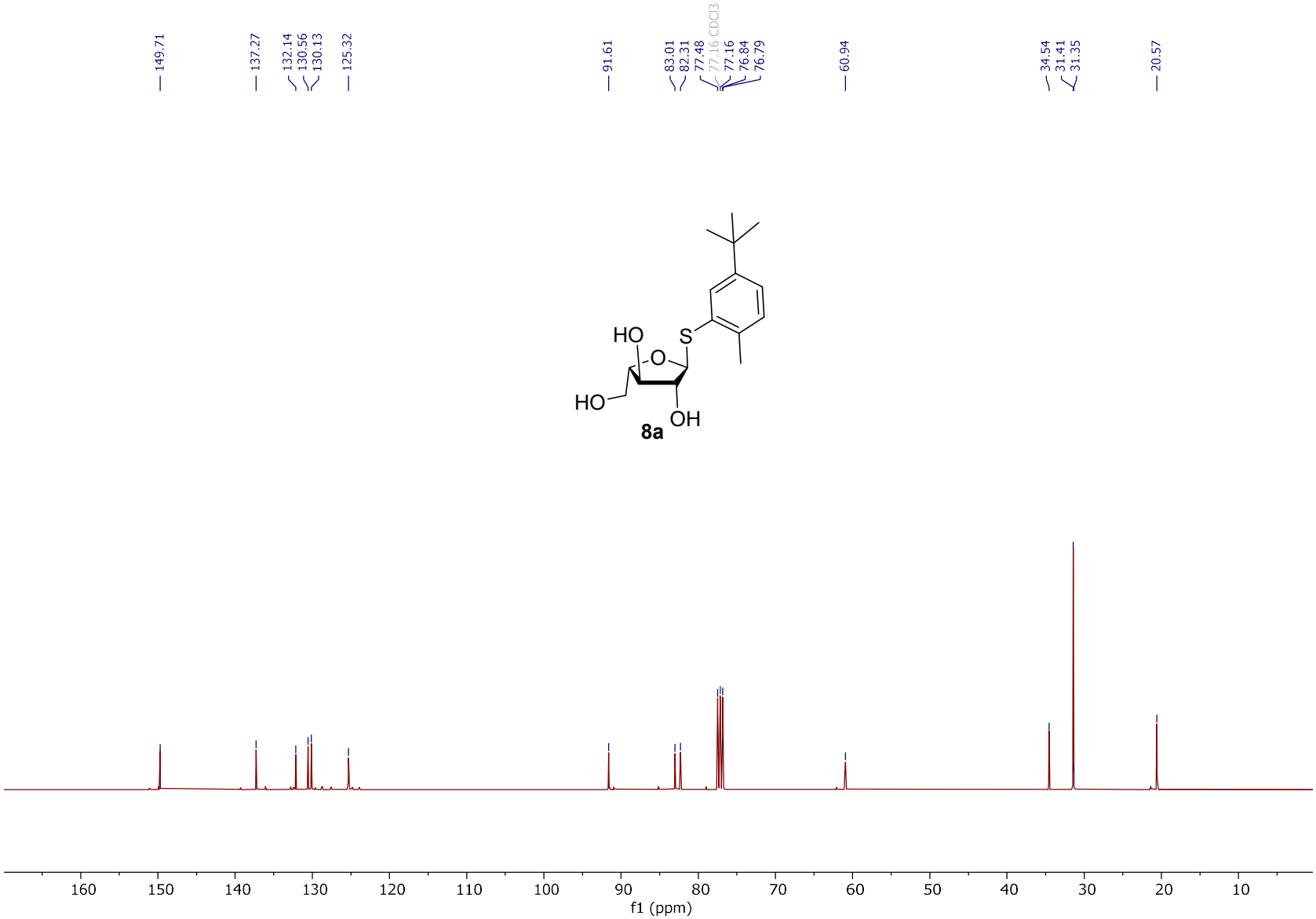
The ^{1}H Spectrum of Compound **5** (700 MHz, $CDCl_3$)



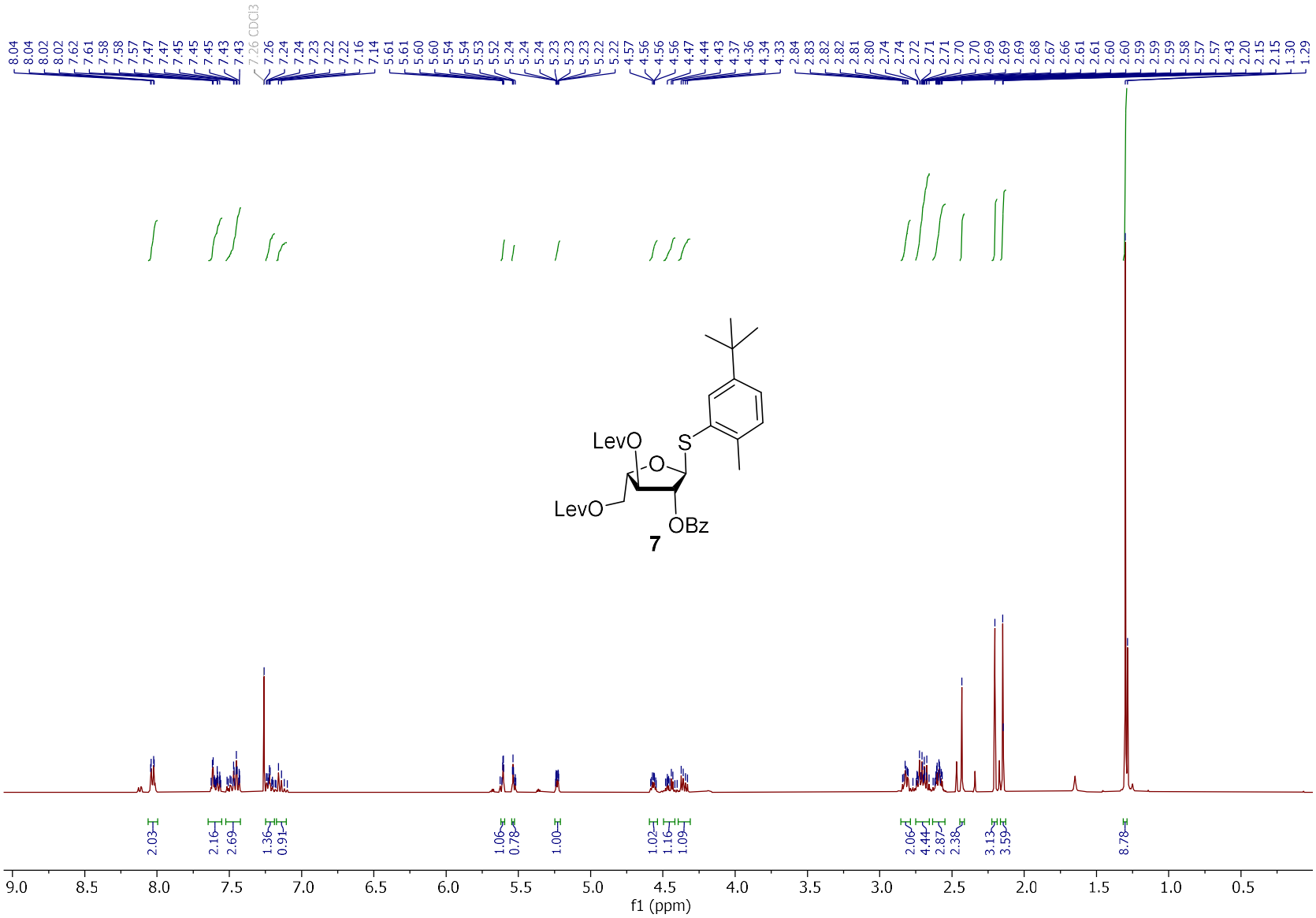
The $^{13}C\{^{1}H\}$ Spectrum of Compound **5** (175 MHz, $CDCl_3$)



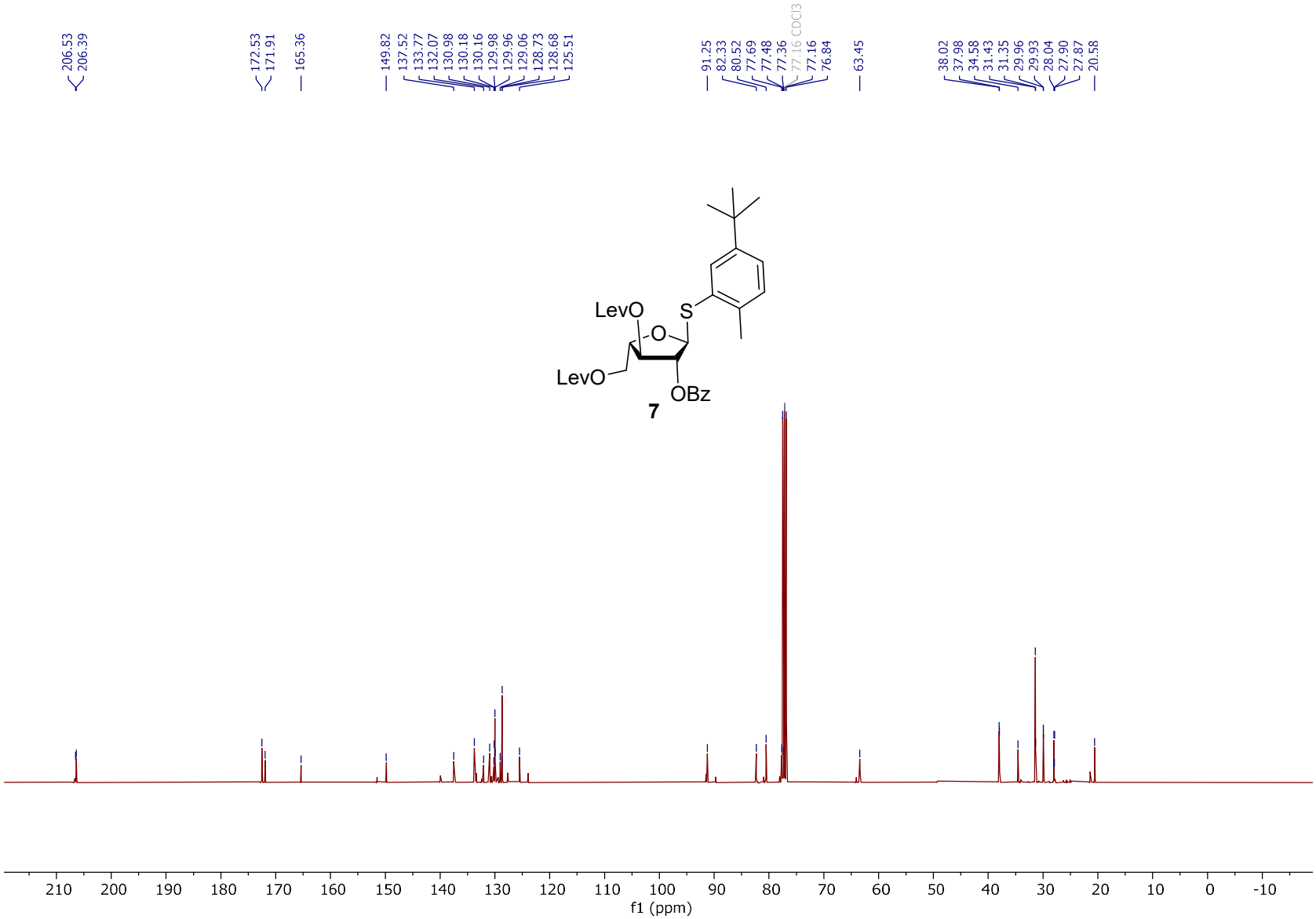
The ^{1}H Spectrum of Compound **8a** (400 MHz, $CDCl_3$)



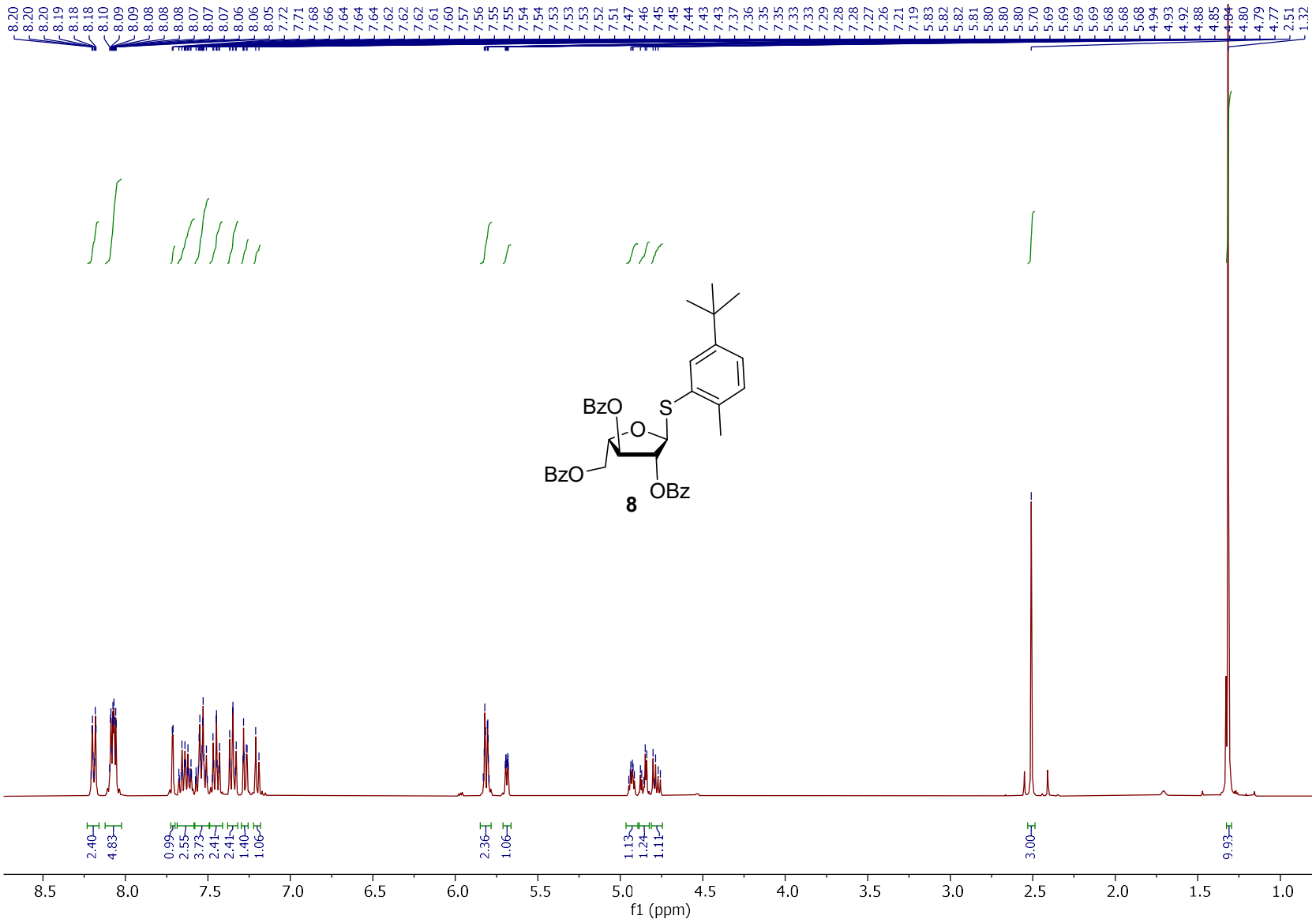
The $^{13}C\{^{1}H\}$ Spectrum of Compound **8a** (100 MHz, $CDCl_3$)



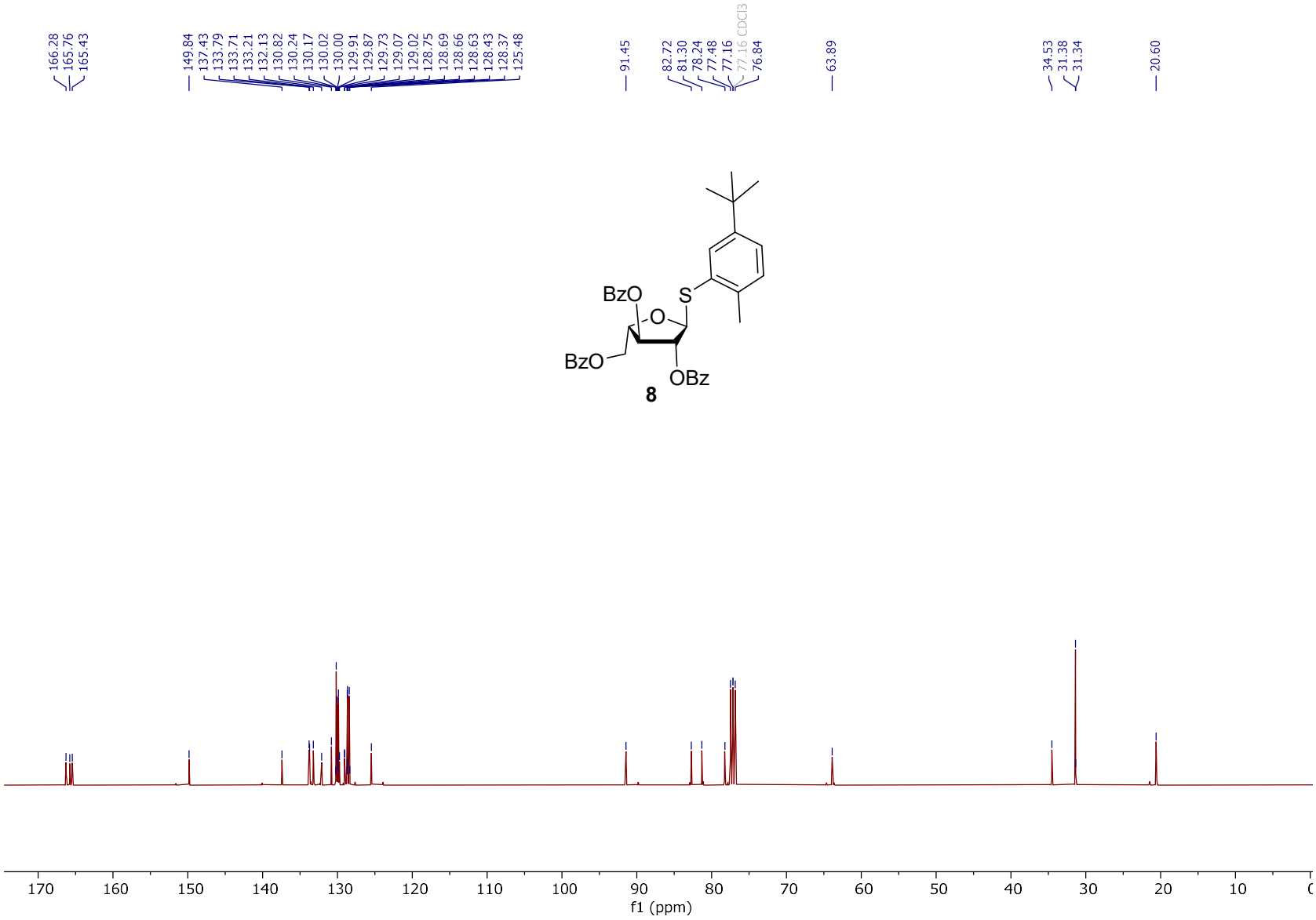
The ^{1}H Spectrum of Compound **7** (400 MHz, $CDCl_3$)



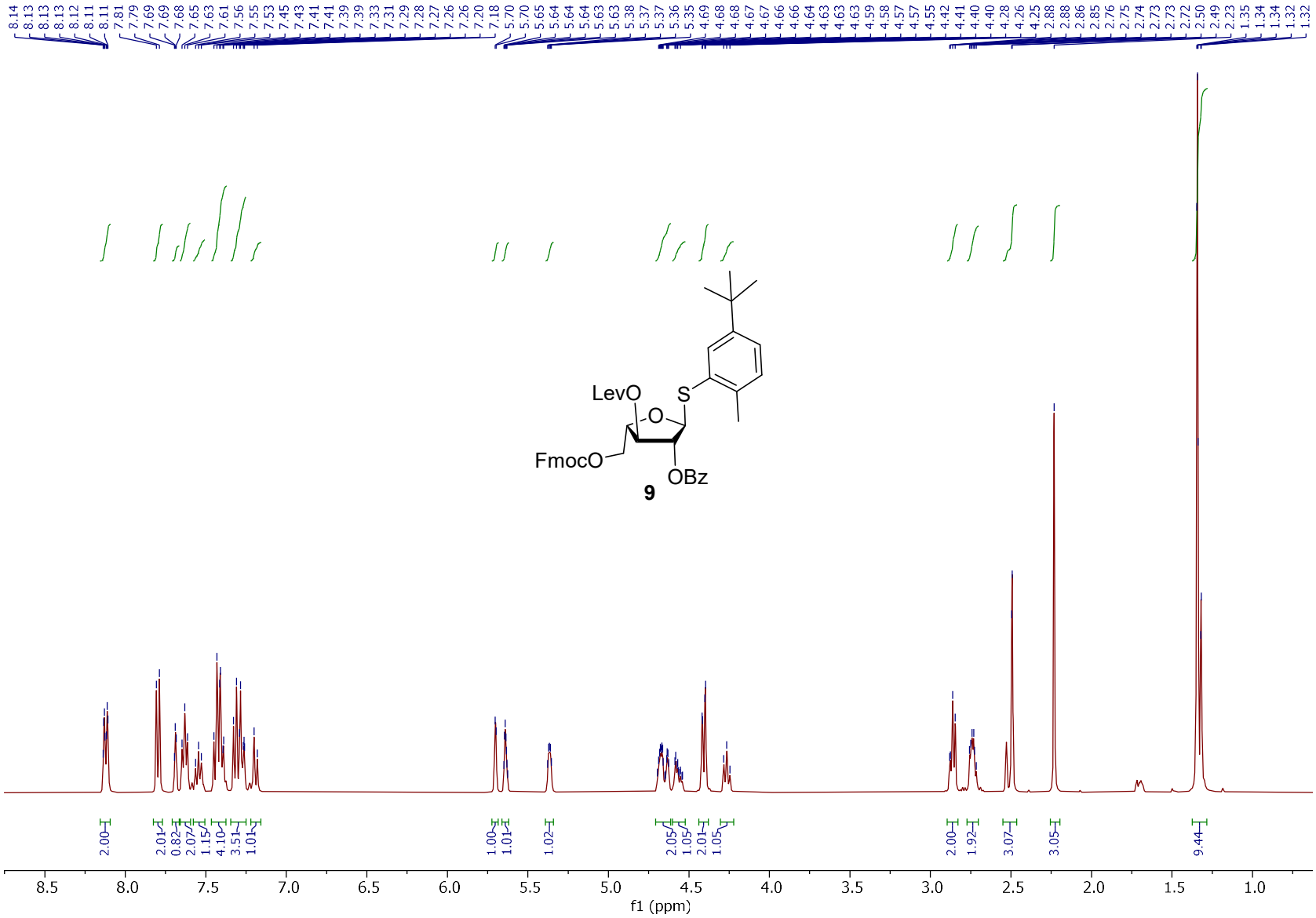
The $^{13}C\{^{1}H\}$ Spectrum of Compound **7** (100 MHz, $CDCl_3$)



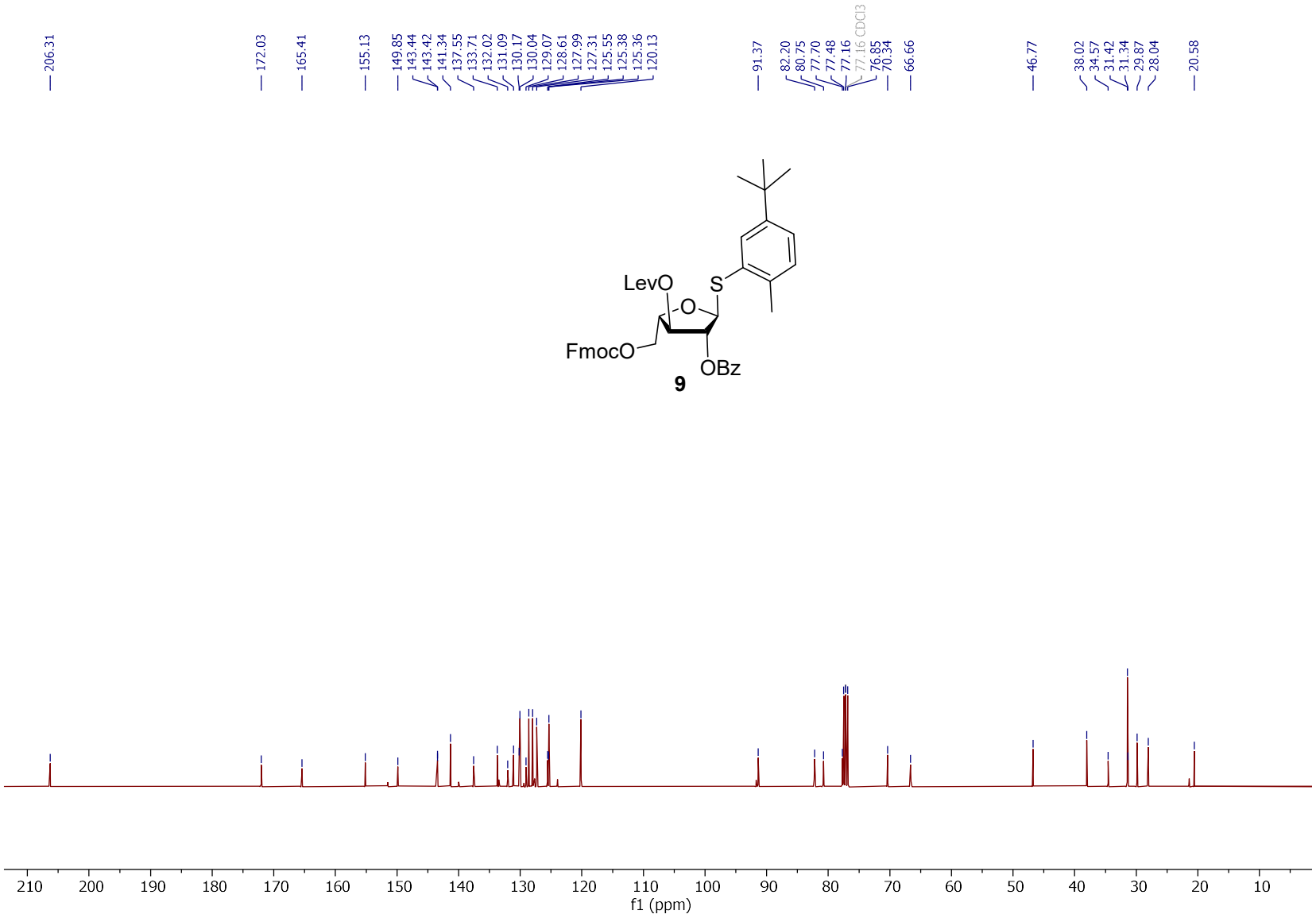
The ^{1}H Spectrum of Compound **8** (400 MHz, $CDCl_3$)



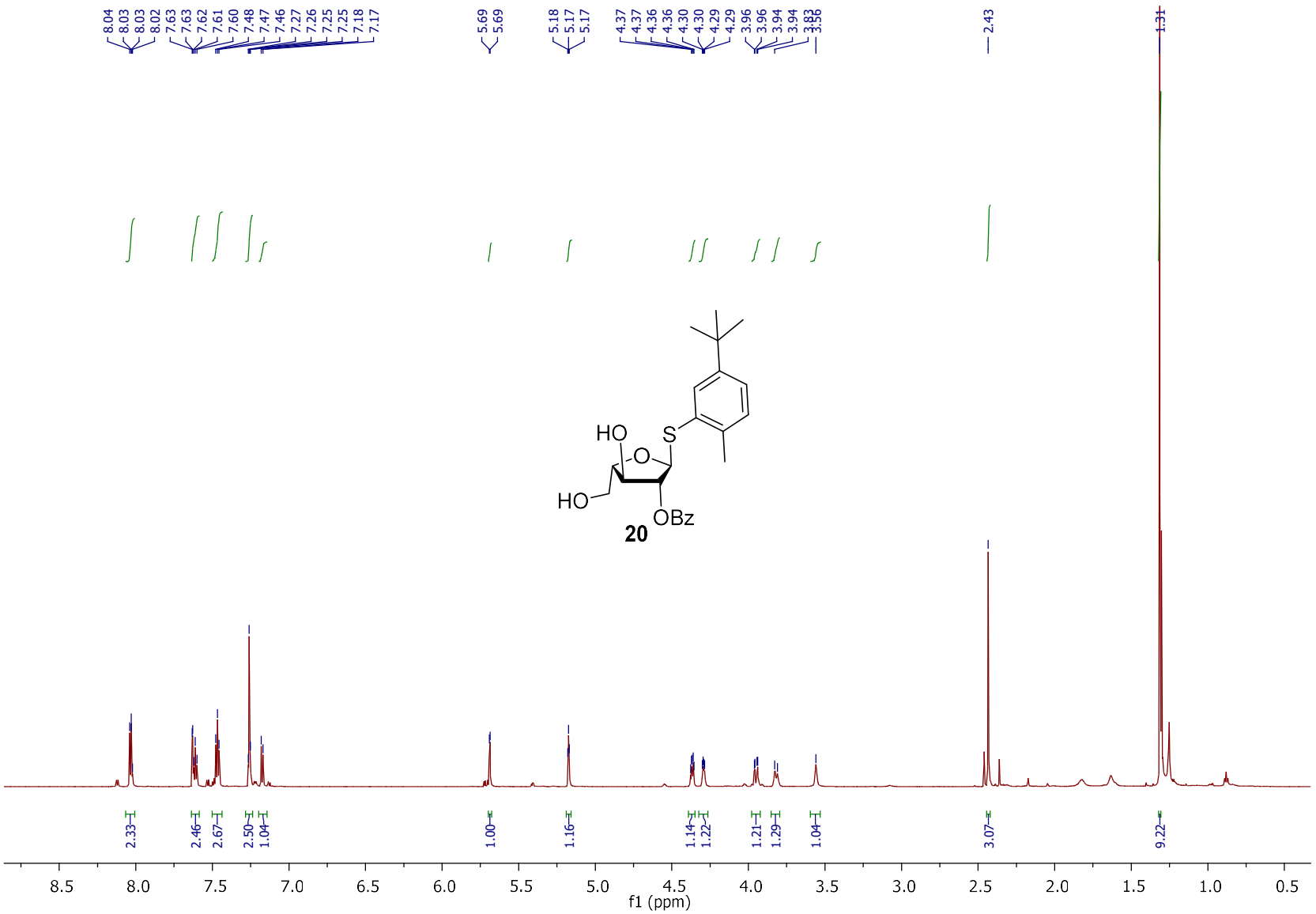
The $^{13}C\{^{1}H\}$ Spectrum of Compound **8** (100 MHz, $CDCl_3$)



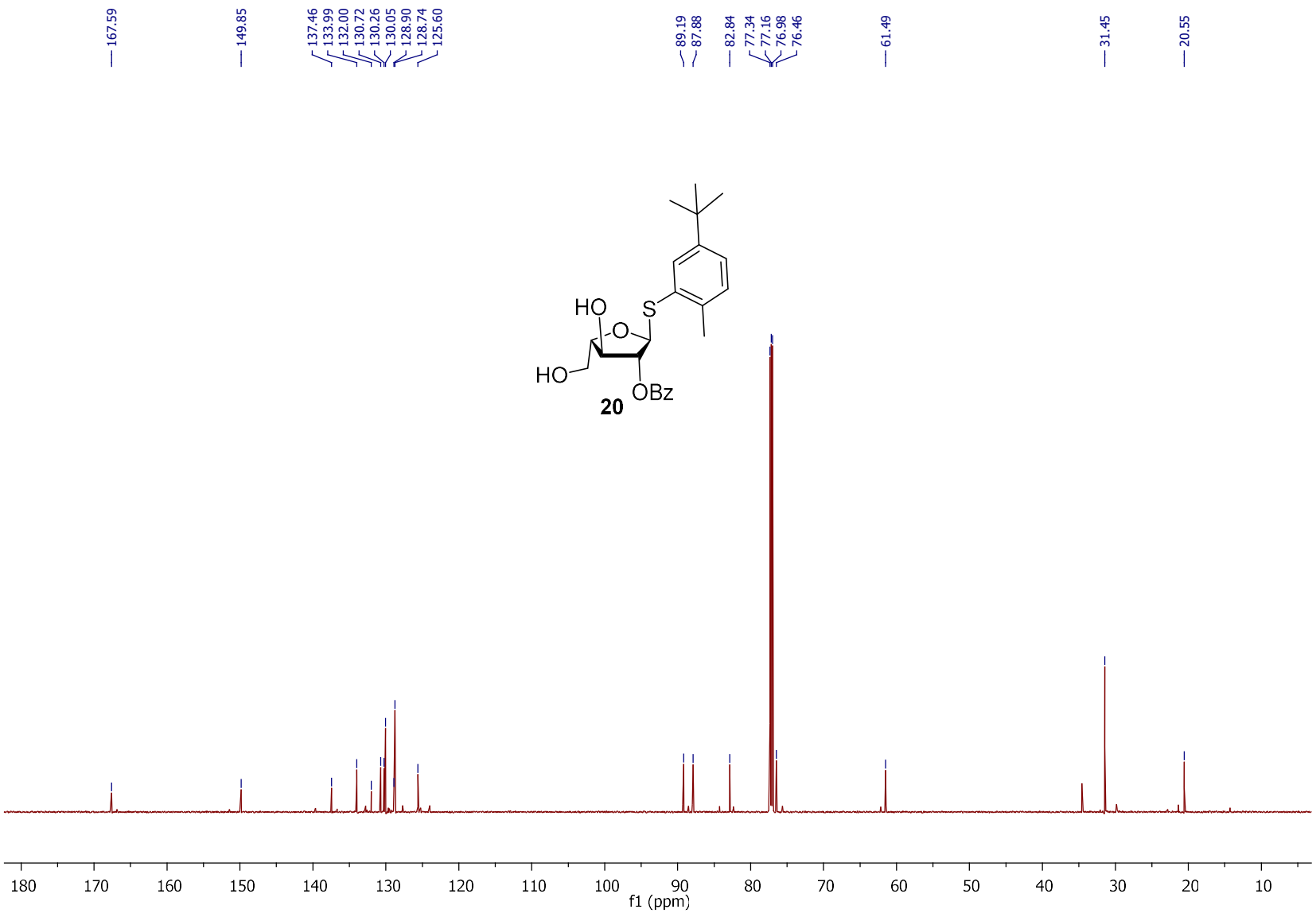
The ^{1}H Spectrum of Compound **9** (400 MHz, $CDCl_3$)



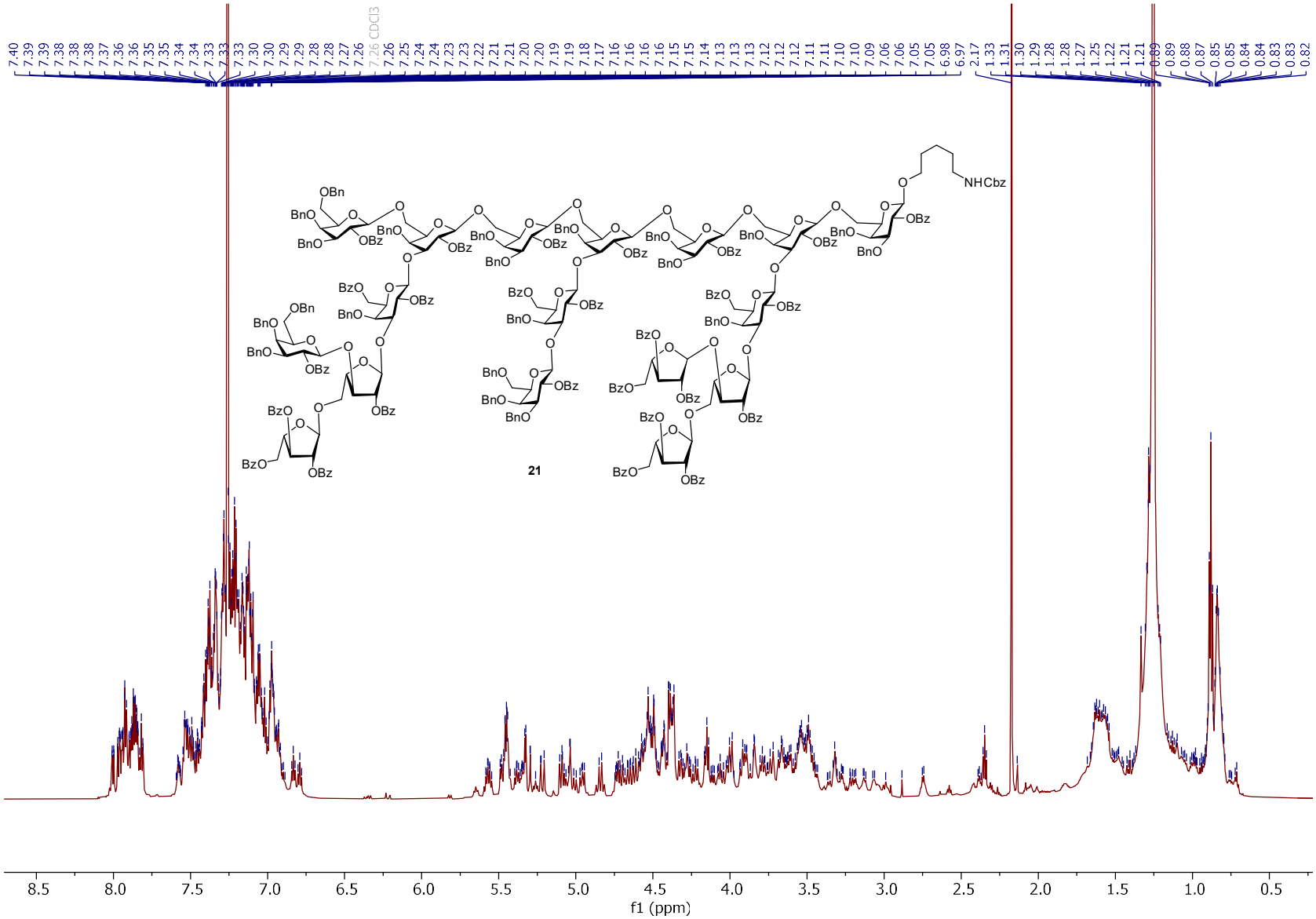
The $^{13}C\{^{1}H\}$ Spectrum of Compound **9** (100 MHz, $CDCl_3$)



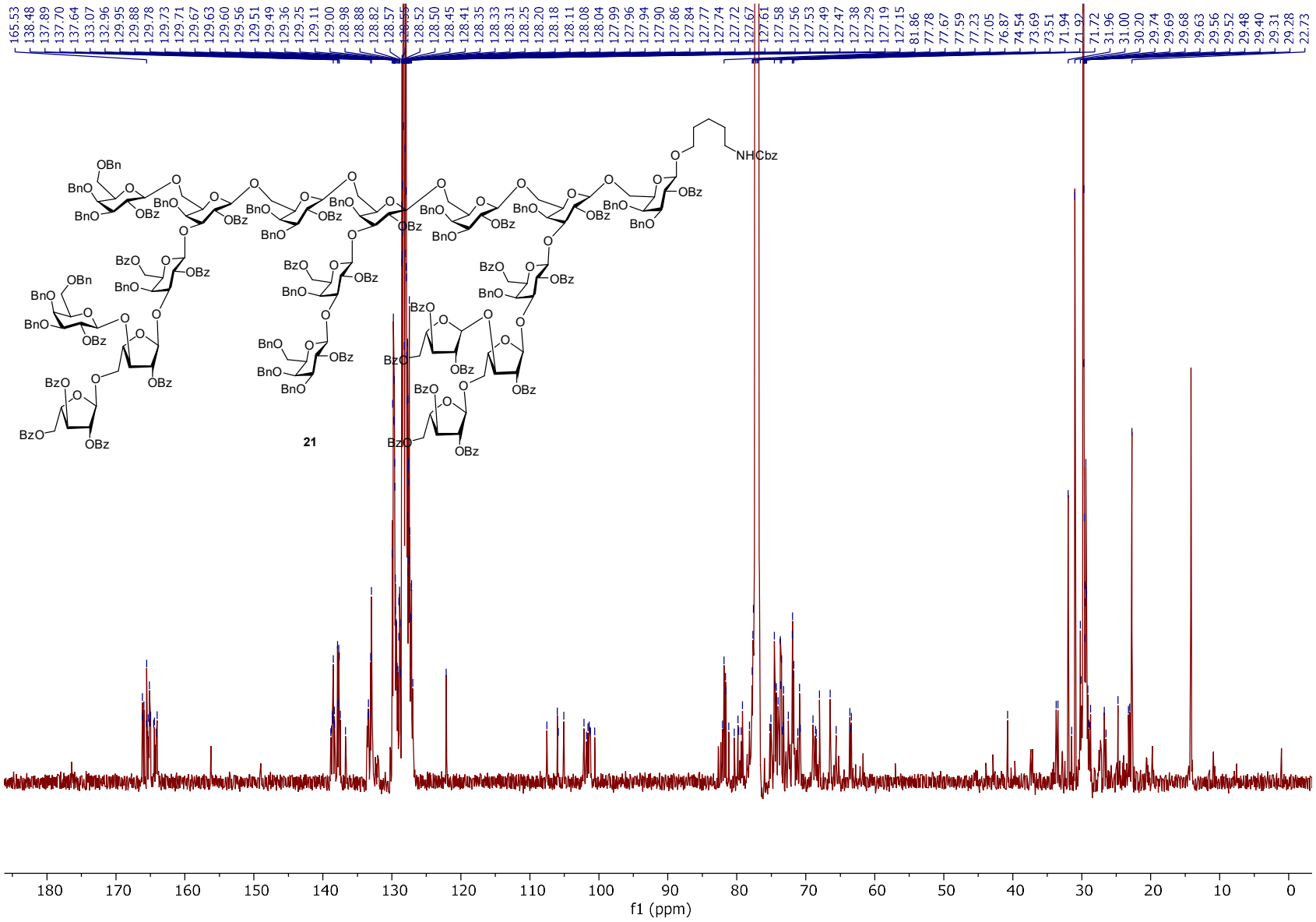
The ^{1}H Spectrum of Compound **20** (700 MHz, $CDCl_3$)



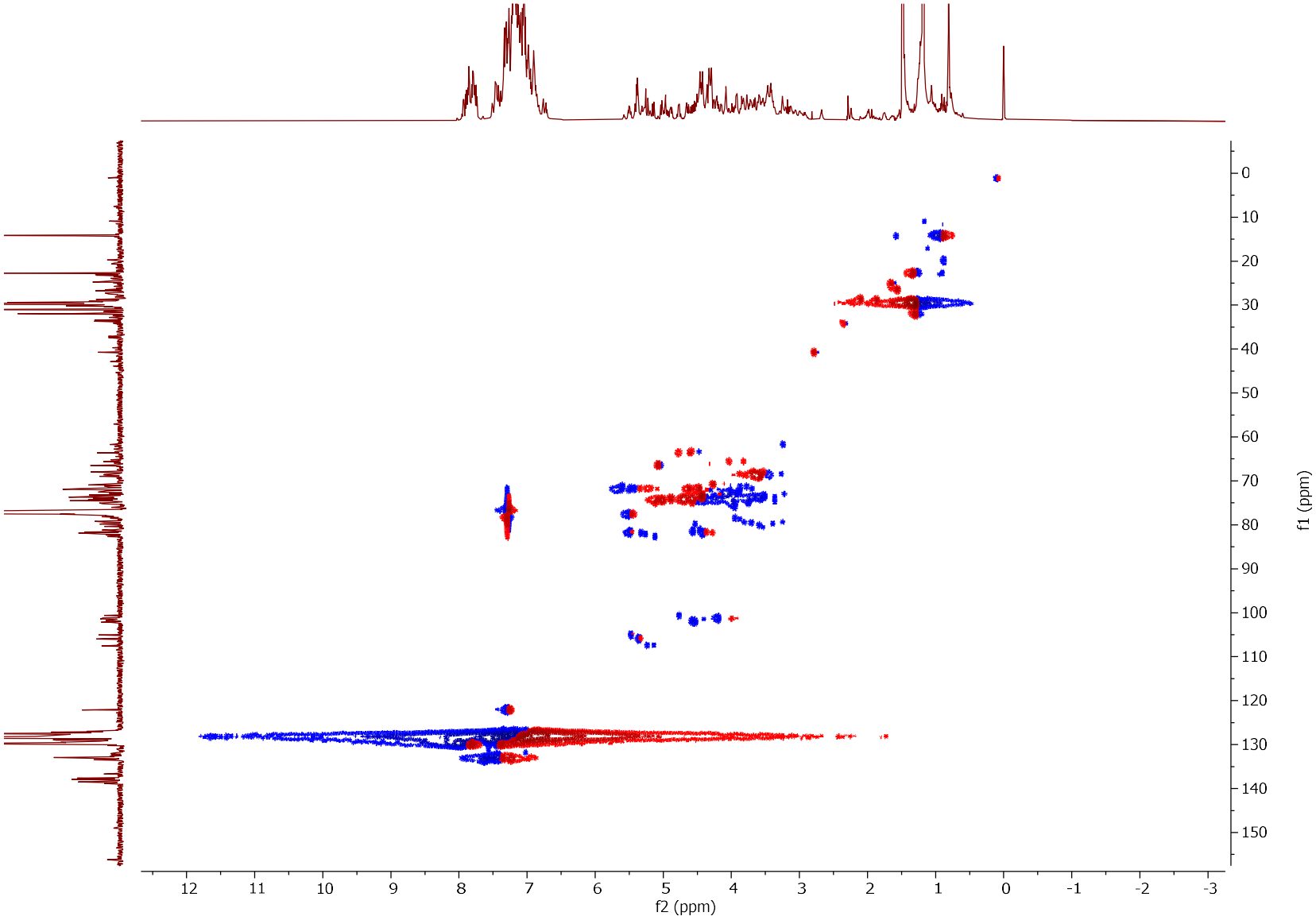
The $^{13}C\{^{1}H\}$ Spectrum of Compound **20** (175 MHz, $CDCl_3$)



The ^{1}H Spectrum of Compound **21** (700 MHz, $CDCl_3$)



The $^{13}C\{^{1}H\}$ Spectrum of Compound **21** (175 MHz, $CDCl_3$)



HSQCSpectrum of Compound **21** (700 MHz, $CDCl_3$)

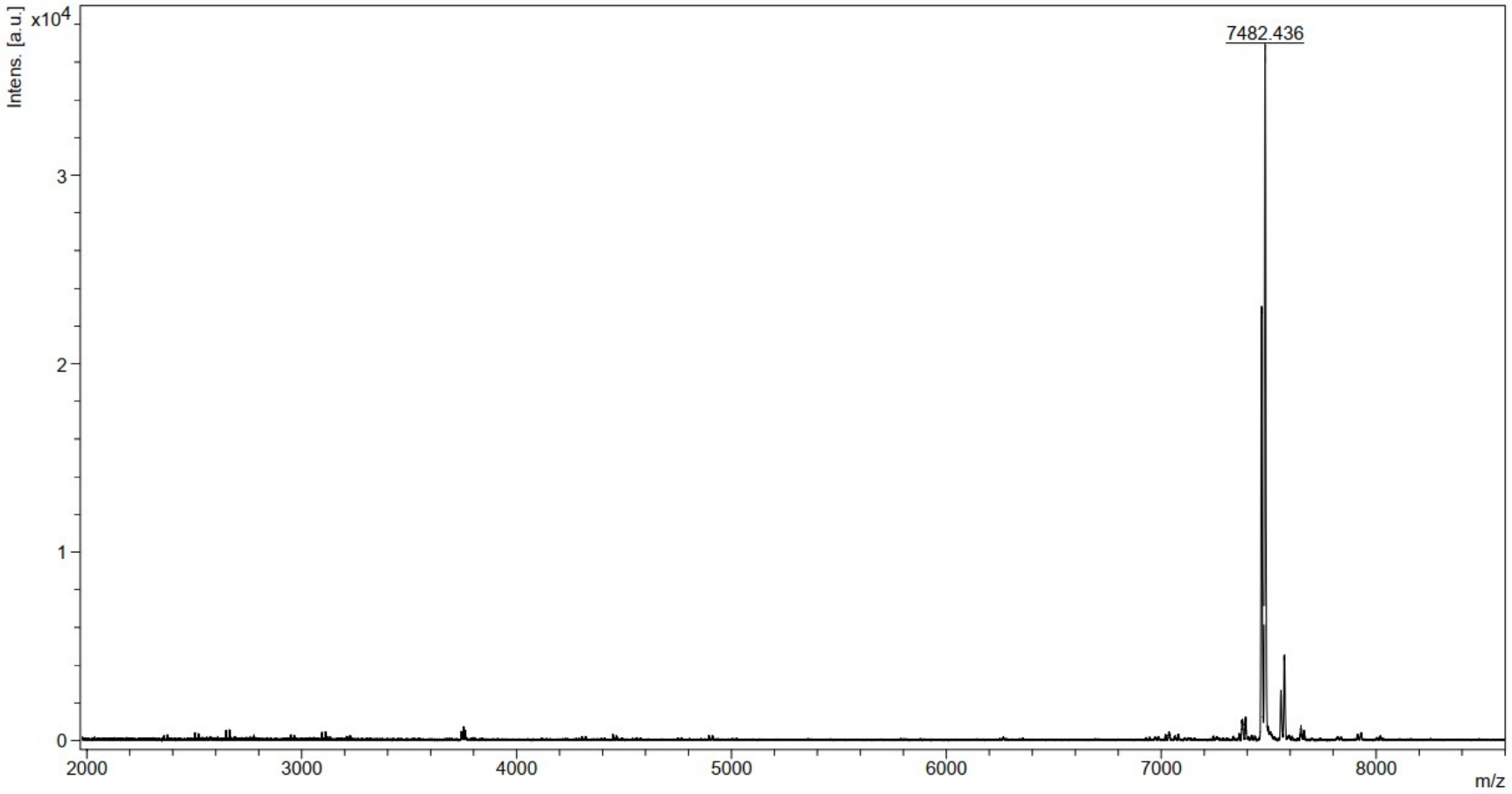
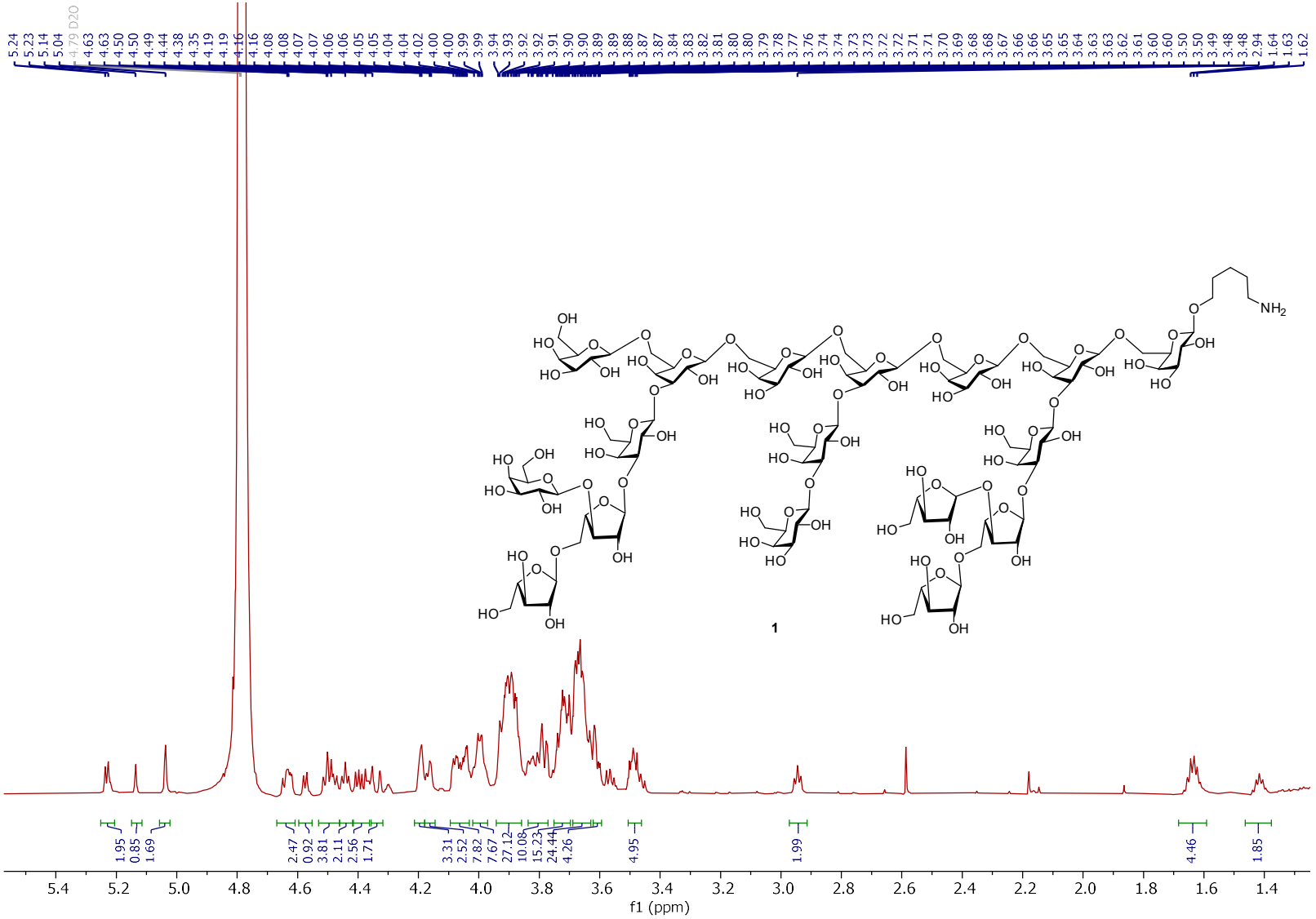
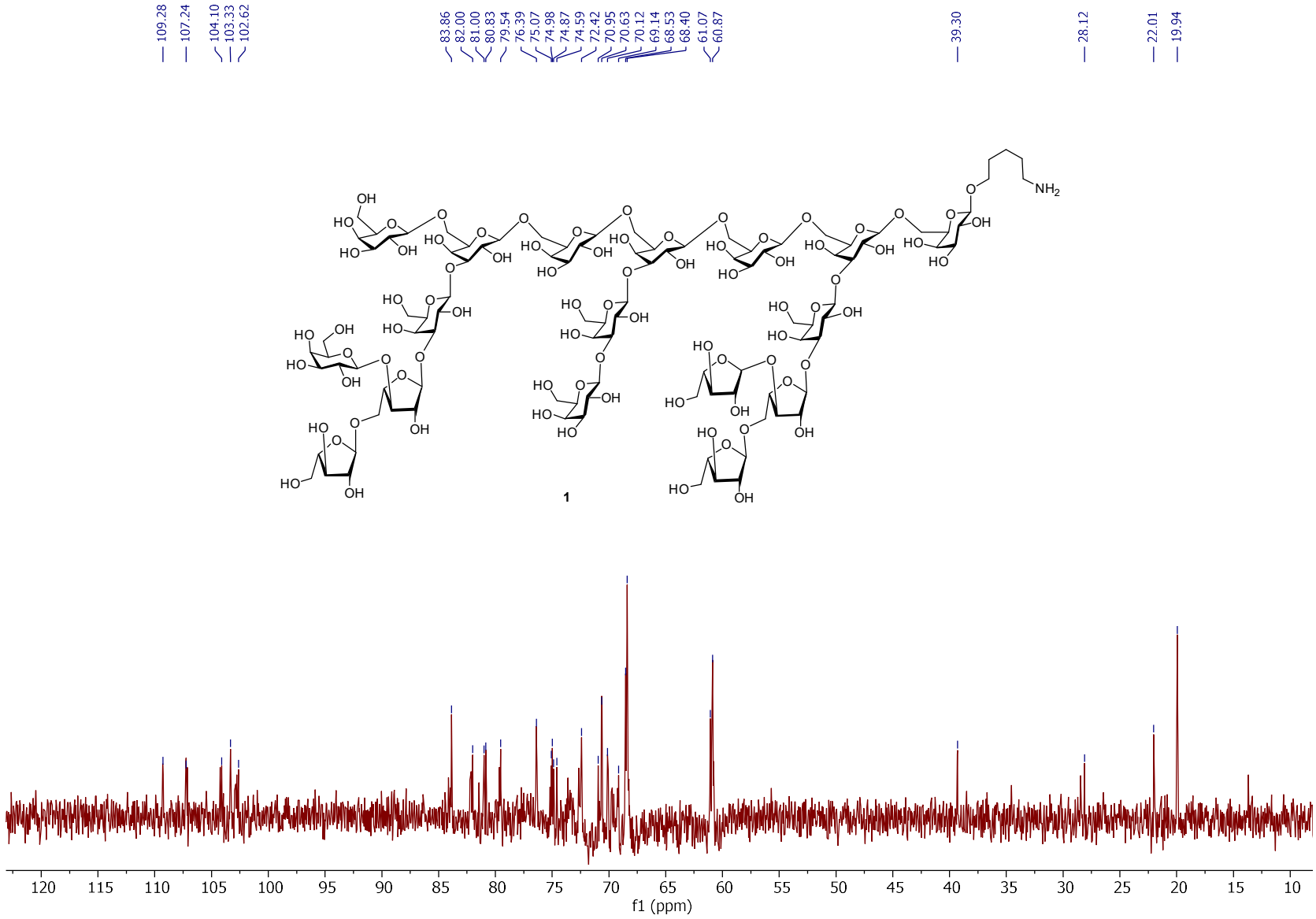


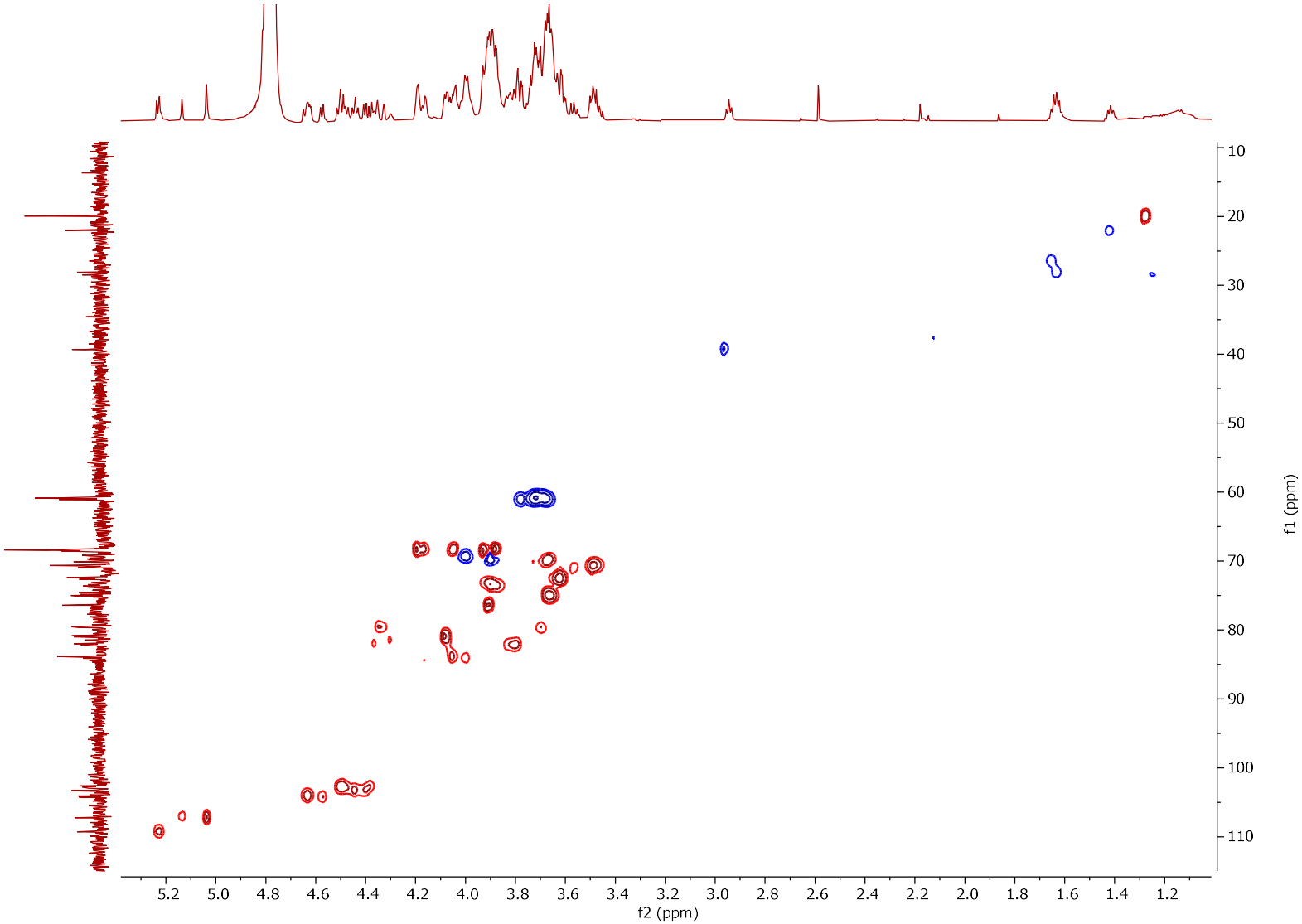
Figure S5. MALDI-TOF of protected Heptadecasaccharide Repeating Unit of Arabinogalactan Polysaccharide HH1-1 (**21**)



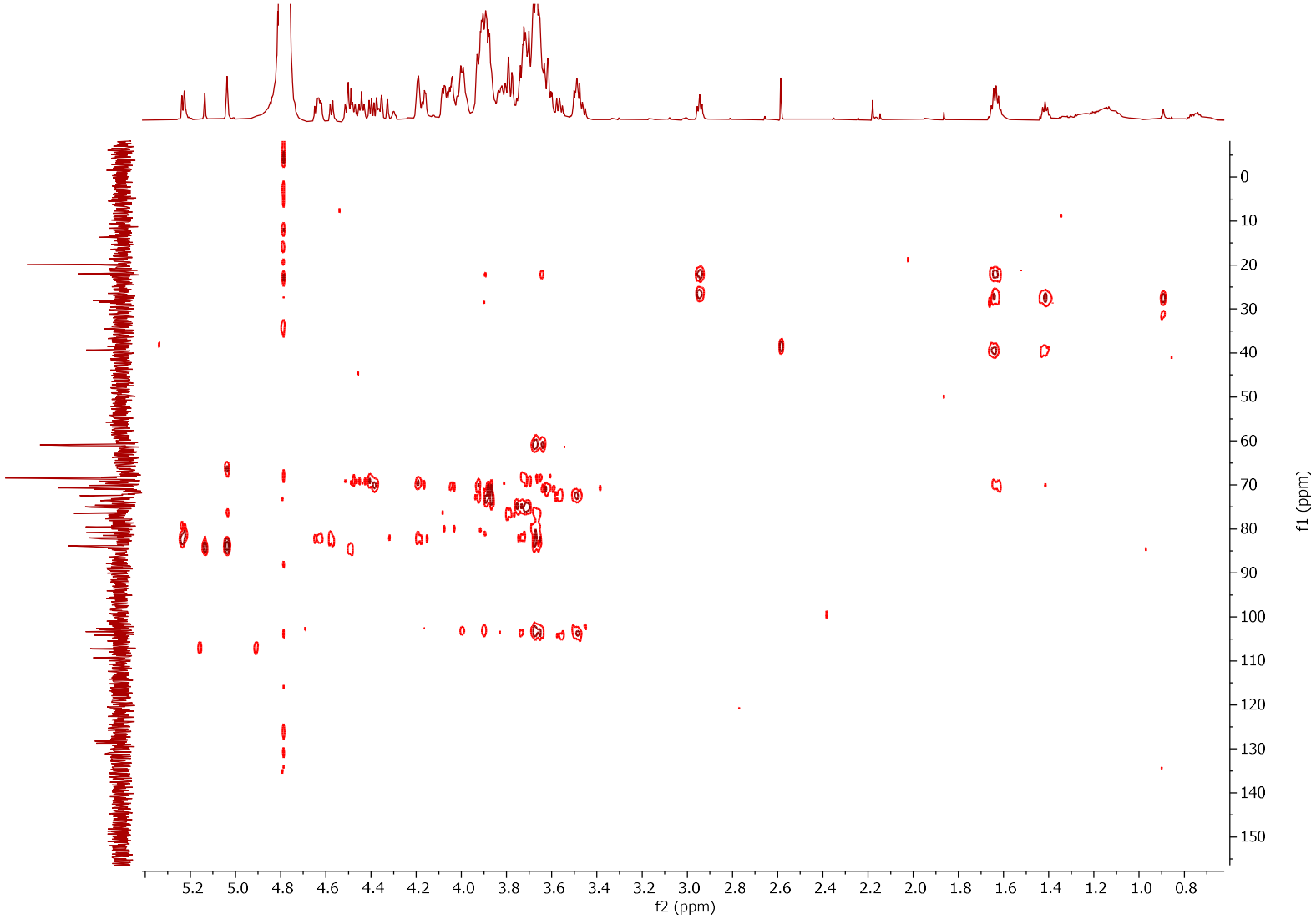
The ^{1}H Spectrum of Compound **1** (700 MHz, D_2O)



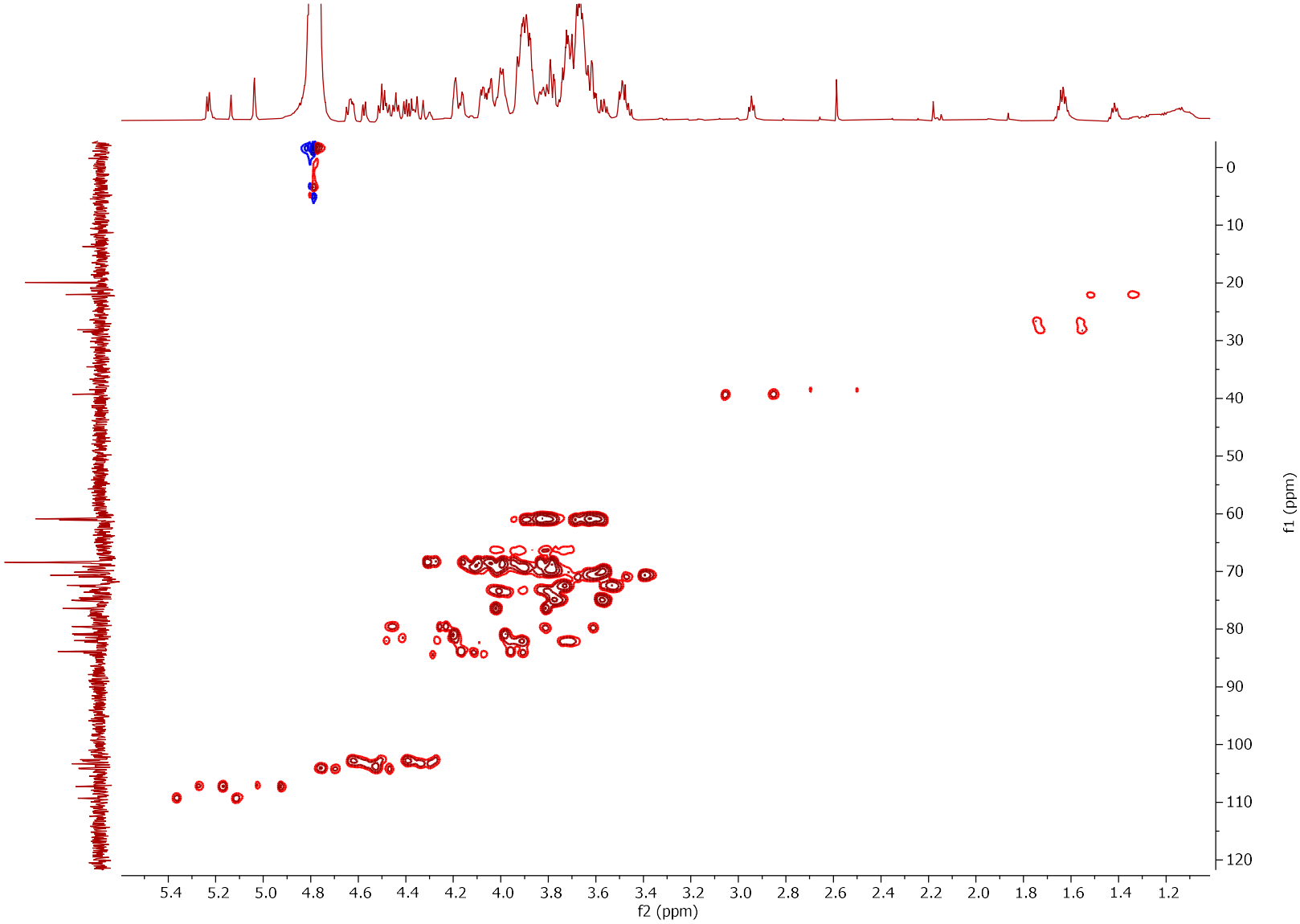
The $^{13}C\{^{1}H\}$ Spectrum of Compound **1** (175 MHz, D_2O)



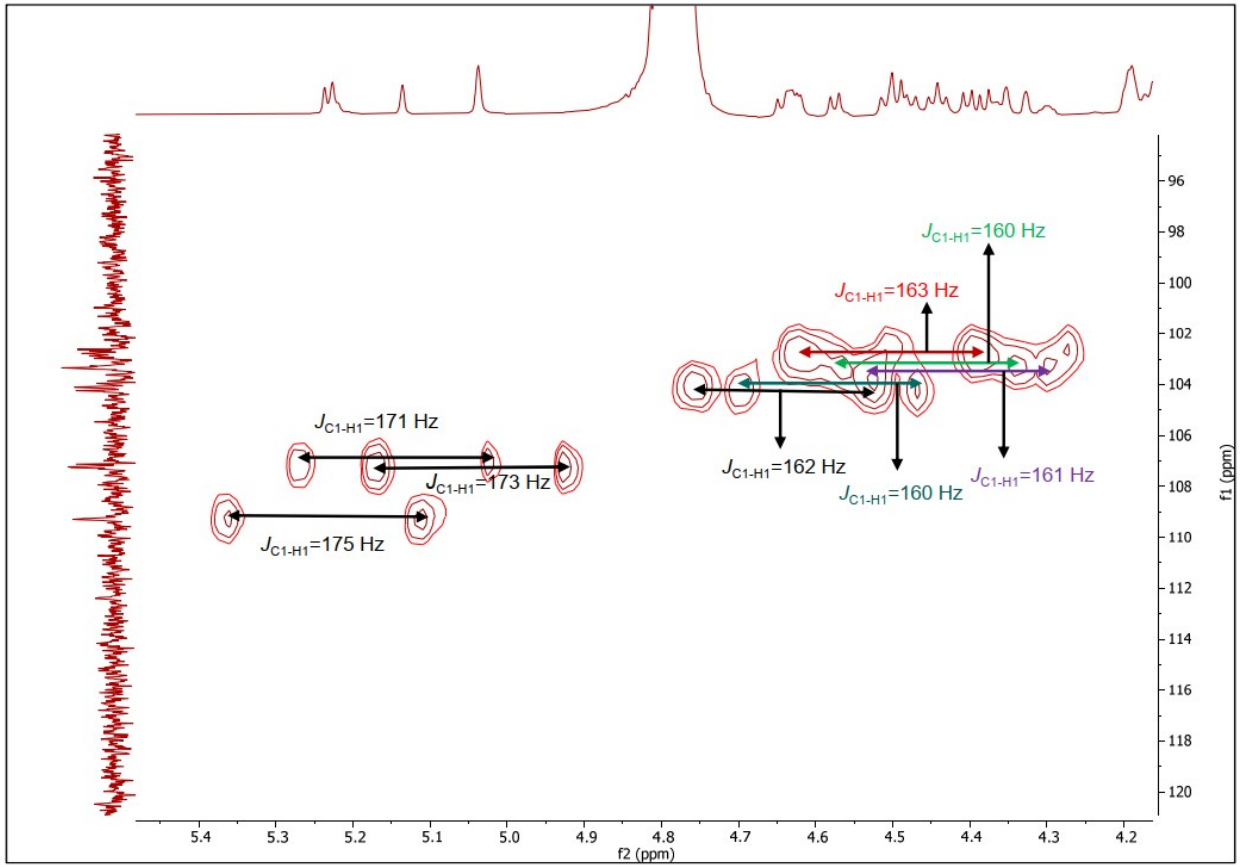
HSQCSpectrum of Compound **1** (700 MHz, D_2O)



HMBC Spectrum of Compound **1** (700 MHz, D_2O)



Non-decoupled HSQC Spectrum of Compound **1** (700 MHz, D_2O)



Expansion of Non-decoupled HSQC Spectrum of Compound **1** (700 MHz, D_2O) and β-glycosidic linkages were confirmed by measuring coupling constant between the anomeric carbon and proton (J_{C1-H1}) .

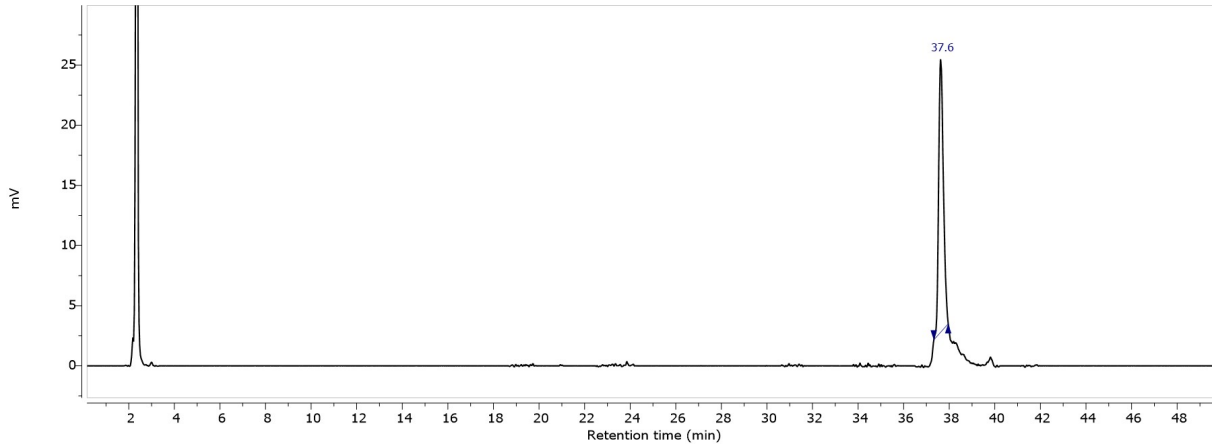


Figure S6. Analytical HPLC (Method C, ELSD trace) of Heptadecasaccharide Repeating Unit of Arabinogalactan Polysaccharide HH1-1 (**1**)

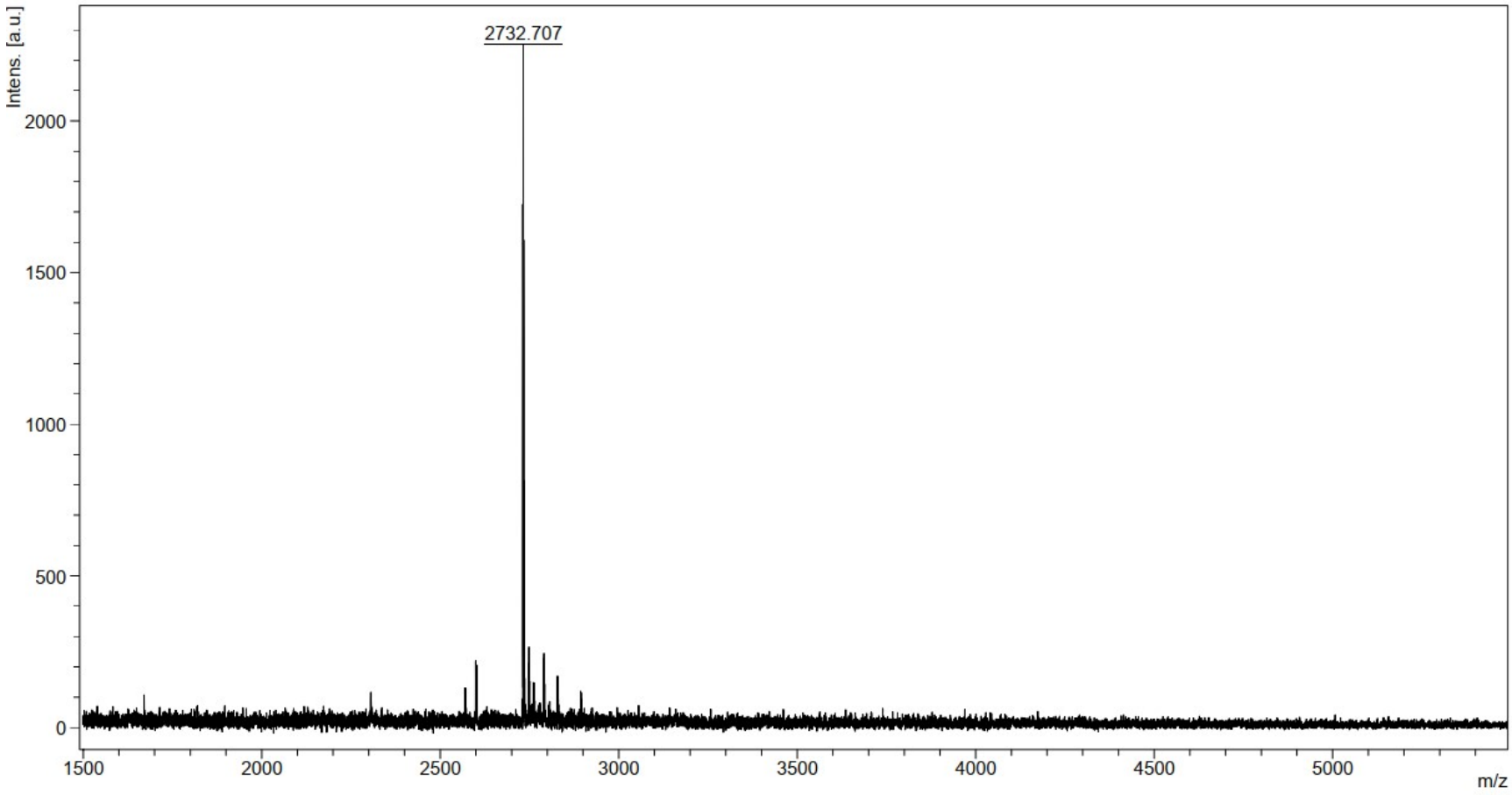


Figure S7.MALDI-TOF of Heptadecasaccharide Repeating Unit of Arabinogalactan Polysaccharide HH1-1 (**1**)

8. References

1. Hoang, K. L. M.; Pardo-Vargas, A.; Zhu, Y.; Yu, Y.; Loria, M.; Delbianco, M.; Seeberger, P. H. *J. Am. Chem. Soc.***2019**, *141*, 9079-9086.
2. Yu, Y.; Kononov, A.; Delbianco, M.; Seeberger, P. H. *Chem. Eur. J.***2018**, *24*, 6075-6078.
3. Naresh, K.; Schumacher, F.; Hahm, H. S.; Seeberger, P. H. *Chem. Commun.***2017**, *53*, 9085-9088.
4. (a) Hahm, H. S.; Liang, C.-F.; Lai, C.-H.; Fair, R. J.; Schuhmacher, F.; Seeberger, P. H. *J. Org. Chem.***2016**, *81*, 5866-5877; (b) Eller, S.; Collot, M.; Yin, J.; Hahm, H. S.; Seeberger, P. H. *Angew. Chem., Int. Ed.***2013**, *52*, 5858-5861.
5. Xie, N.; Taylor, C. M. *Org. Lett.,* **2010,** *12*,4968-4971.