

Supporting Information

3, 5-Di(trifluoromethyl)phenyl(cyano)iodonium Triflate as a  
Novel and Potential Activator for *p*-Tolyl Thioglycoside Donors

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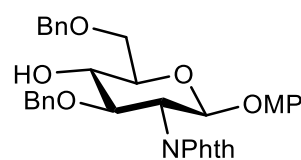
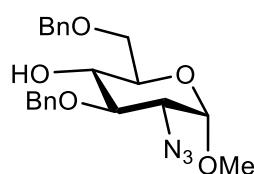
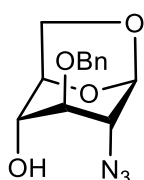
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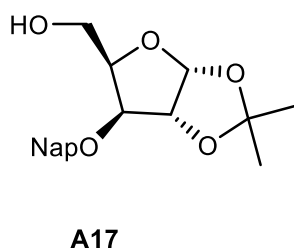
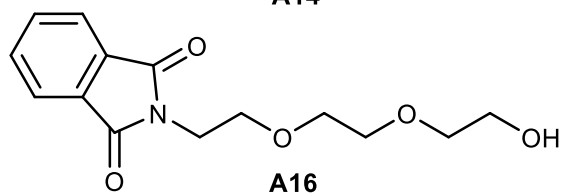
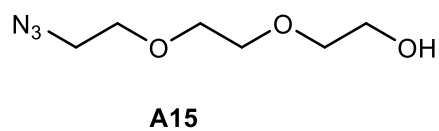
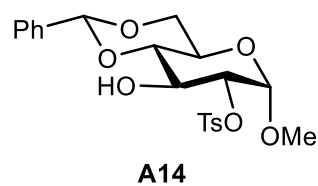
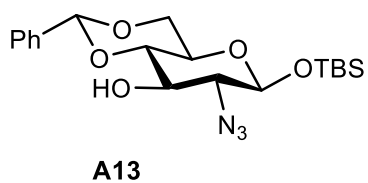
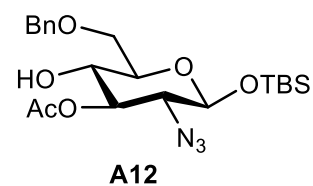
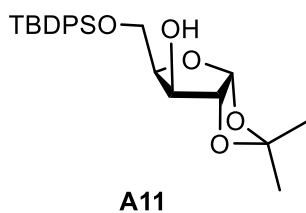
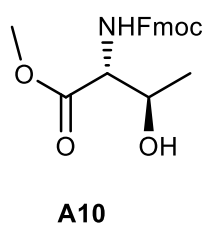
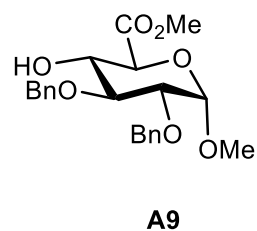
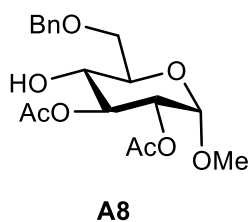
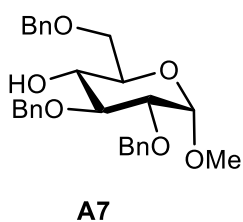
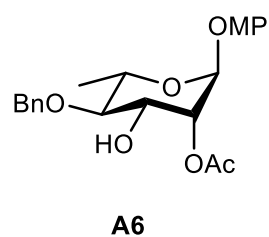
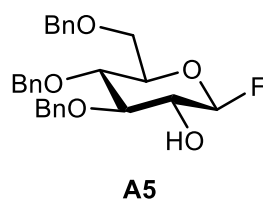
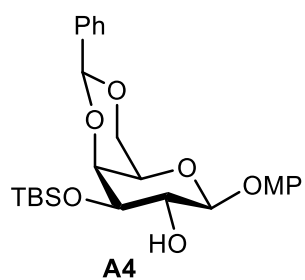
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## General information

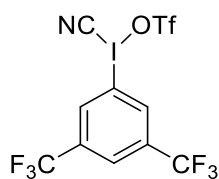
All reagents used were purchased from commercial sources and were used without further purification unless noted. All glassware was oven-dried before use.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker 400 spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm relative to the residual undeuterated chloroform in  $\text{CDCl}_3$  ( $\delta = 7.26$  for  $^1\text{H}$  and  $77.16$  for  $^{13}\text{C}$  NMR). The following abbreviations were used to express multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) methods on a Waters mass spectrometer. Column chromatography was carried out on silica gel (200-300 mesh). Analytical thin-layer chromatography was performed on glass plates coated with silica gel 60-F254. Visualization on the developed plates were achieved by UV irradiation or spraying with 10% ethanolic sulfuric acid solution followed by heating. Crude anomeric ratios were collected by integration of quantitative  $^1\text{H}$  NMR spectra of the reaction mixtures prior to purification. Stereochemistry of the newly formed glycosidic bonds was determined by the observation of the coupling constants  $^3J_{\text{H1},\text{H2}}$  through  $^1\text{HNMR}$  or  $^1J_{\text{C1},\text{H1}}$  through HSQC. Smaller coupling constants of  $^3J_{\text{H1},\text{H2}}$  (around 3 Hz) indicate  $\alpha$ -anomers while larger coupling constants  $^3J_{\text{H1},\text{H1}}$  (above 7.0 Hz) indicate  $\beta$ - linkages.  $^1J_{\text{C1},\text{H1}}$  around 170 Hz indicates  $\alpha$  linkages and 160 Hz suggests  $\beta$  linkages. The melting points were measured with

The following alcoholic acceptors including **A1**<sup>[1]</sup>, **A2**<sup>[2]</sup>, **A3**<sup>[3]</sup>, **A4**<sup>[4]</sup>, **A5**<sup>[5]</sup>, **A6**<sup>[6]</sup>, **A7**<sup>[7]</sup>, **A8**<sup>[8]</sup>, **A9**<sup>[9]</sup>, **A10**<sup>[10]</sup>, **A11**<sup>[11]</sup>, **A12**<sup>[12]</sup>, **A13**<sup>[13]</sup>, **A14**<sup>[14]</sup>, **A15**<sup>[15]</sup>, **A16**<sup>[16]</sup>, and **A17**<sup>[17]</sup> are known compounds.



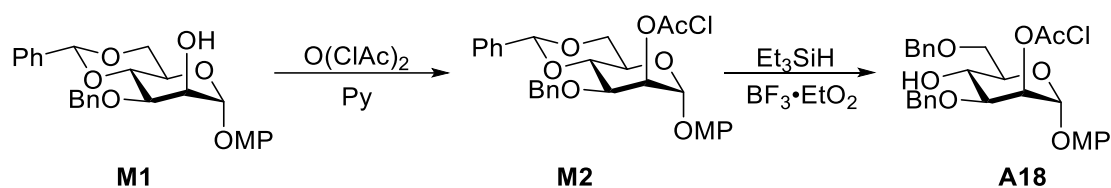


**Multigram-scale synthesis of 3, 5-di(trifluoromethyl)phenyl(cyano)iodonium triflates (DFCT)**



A 30 wt% aqueous solution of H<sub>2</sub>O<sub>2</sub> (16 mL) was added dropwise to a solution of trifluoroacetic anhydride (80 mL) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) with mechanical stirring and cooling (-50°C) in a nitrogen atmosphere within 0.5 h. Then, a solution of 1-iodo-3, 5-bis(trifluoromethyl)benzene (12.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added dropwise. The reaction mixture was gradually equilibrated to room temperature and then was concentrated in the reduced pressure to furnish a white solid which was directed used for the next step without further purification. Its solution in dried CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was reacted with trimethylsilyl cyanide (12 mmol) in the presence of TMSOTf (12 mmol) at room temperature. The resulting white precipitation was collected through the suction filtration and washed with petroleum ether to afford the title compound (5.4 g, 88%). White solid (from chloroform), mp 171°C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz): δ 8.98 (s, 2 H, ArH), 8.47 (s, 1 H, ArH). The spectroscopic data correspond with those previously reported. <sup>[18]</sup>

### Preparation and characterization of new alcoholic acceptors(A18-21) *p*-Methoxyphenyl 3, 6-di-*O*-benzyl- 2-*O*-chloroacetyl- $\alpha$ -D-mannopyranoside (A18)

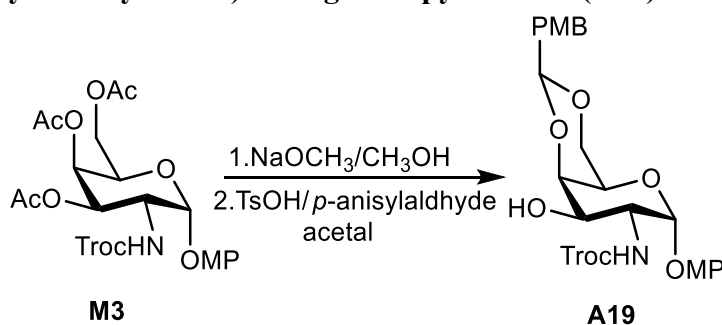


An ice-cooled solution of alcohol **M1**<sup>[19]</sup> (1.16 g, 2.5 mmol) in dry pyridine (25 mL) was treated with chloroacetic anhydride (0.51 g, 3.0 mmol) for 3 h. The reaction mixture was diluted with DCM, then washed with saturated aqueous CuSO<sub>4</sub> solution and brine. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the filtrate was concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel to give **M2** (1.25 g, 92.6%) as a colorless oil. *R*<sub>f</sub> 0.55 (PE/EA, 4:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 - 7.49 (m, 2H), 7.42 - 7.37 (m, 5H),

7.36 - 7.27 (m, 3H), 6.99 - 6.94 (m, 2H), 6.86 - 6.81 (m, 2H), 5.65 (s, 1H), 5.64 (dd,  $J = 3.6, 2.0$  Hz, 1H), 5.43 (d,  $J = 2.0$  Hz, 1H), 4.80 - 4.72 (m, 2H), 4.27 - 4.22 (m, 2H), 4.21 (s, 2H), 4.11 (t,  $J = 9.6$  Hz, 1H), 4.05 (td,  $J = 9.6, 4.4$  Hz, 1H), 3.84 (t,  $J = 9.6$  Hz, 1H), 3.78 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 155.6, 149.6, 137.9, 137.4, 129.1, 128.6, 128.3, 127.9, 127.9, 126.2, 118.1, 114.9, 101.8, 97.6, 78.3, 73.8, 72.7, 71.7, 68.6, 64.5, 55.8, 40.9; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{29}\text{H}_{29}\text{ClO}_8$  563.1449; Found: 563.1437.

Triethylsilane (0.5 mL, 3.2 mmol) and boron trifluoride etherate (0.4 mL, 3.2 mmol) sequentially added to an iced-cooled solution of compound **M2** (0.9 g, 1.6 mmol) in DCM (20 mL). The reaction mixture was allowed to warm up to room temperature with stirring for 1 h and then quenched with  $\text{Et}_3\text{N}$  (2 mL). The resulting mixture was washed with saturated brine. The organic phase was dried over  $\text{Na}_2\text{SO}_4$  and filtered. Removal of solvent on a rotary evaporator left a dark residue, which was subjected to flash chromatography (PE/EA, 3:1) over silica gel to afford **A18** as a colorless oil (0.78 g, 87%).  $R_f$  0.45 (PE/EA, 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 - 7.27 (m, 10H), 7.05 - 7.00 (m, 2H), 6.83 - 6.79 (m, 2H), 5.58 (dd,  $J = 3.6, 1.6$  Hz, 1H), 5.46 (d,  $J = 1.6$  Hz, 1H), 4.79 (dd,  $J = 11.2$  Hz, 1H), 4.61 (d,  $J = 12.0$  Hz, 1H), 4.57 (d,  $J = 11.2$  Hz, 1H), 4.52 (d,  $J = 12.0$  Hz, 1H), 4.14 (s, 2H), 4.07 - 3.94 (m, 3H), 3.81 - 3.72 (m, 5H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.97, 155.47, 149.97, 138.15, 137.51, 128.73, 128.43, 128.30, 128.27, 127.72, 127.64, 118.19, 114.76, 97.05, 77.34, 73.56, 72.20, 71.82, 69.92, 69.56, 67.22, 55.71, 40.86; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{29}\text{H}_{31}\text{ClO}_8$  565.1605; Found: 565.1585.

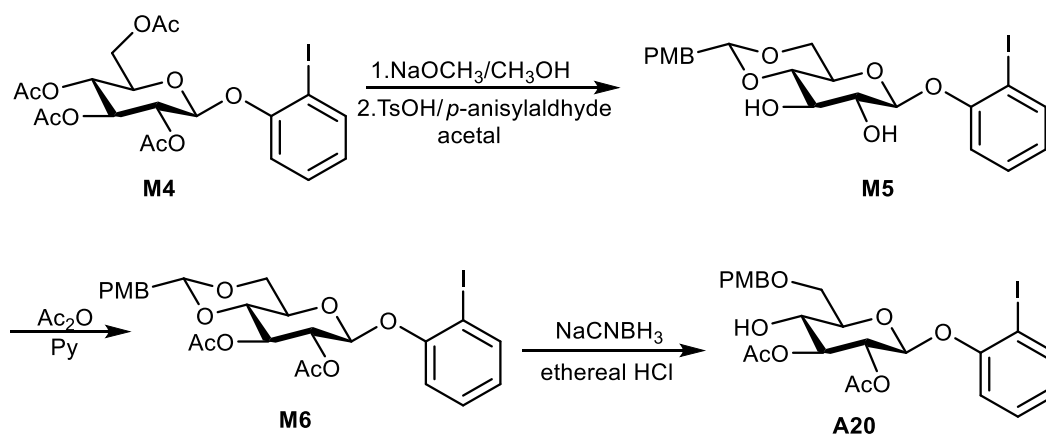
***p*-Methoxyphenyl 4, 6-*O*-*p*-methoxybenzylidene-2-deoxy-2-(2', 2', 2'-trichloroethoxycarbonylamino)- $\alpha$ -D-galactopyranoside (**A19**)**



To a methanolic solution (30 mL) of protected galactosamine **M3** <sup>[20]</sup> (3.5 g, 6.0 mmol),

methanolic NaOMe (0.2 mL, 5.4 mol/L) was added dropwise at 0°C until pH was 9. The mixture was stirred for 6 h at 0°C, when TLC (1:1 CH<sub>2</sub>Cl<sub>2</sub>-acetone) showed the deacetylation was finished. Strong acidic cationic exchange resin Amberlist-15 was added to neutralize, then the mixture was filtered, and the filtrate was concentrated. The resultant residue was dissolved in acetonitrile (30 mL), to which *p*-TsOH (207 mg, 1.2 mmol) followed by *p*-anisylaldehyde dimethyl acetal (1.8 mL, 12.0 mmol) was added. The mixture was stirred for 6 h under reflux at 80°C, monitoring by TLC (PE/EA, 1:1). When the reaction was complete, triethylamine (1 mL) was added to neutralize. The mixture was concentrated and the residue was purified on silica gel (PE/EA, 2:1) to afford a syrupy product **A19** (3.1 g, 88.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 - 7.42 (m, 2H), 7.05 - 6.99 (m, 2H), 6.94 - 6.88 (m, 2H), 6.86 - 6.81 (m, 2H), 5.66 (d, *J* = 3.2 Hz, 1H), 5.55 (s, 1H), 5.40 (d, *J* = 9.6 Hz, 1H), 4.79 - 4.71 (m, 2H), 4.37 - 4.27 (m, 2H), 4.24 (dd, *J* = 12.8, 2.0 Hz, 1H), 4.12 - 4.00 (m, 2H), 3.84 - 3.80 (m, 4H), 3.78 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.5, 155.4, 155.2, 150.3, 132.1, 130.0, 127.8, 117.5, 114.9, 113.8, 101.4, 97.6, 95.5, 75.3, 74.9, 69.3, 68.5, 63.6, 55.8, 55.5, 52.8; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>24</sub>H<sub>26</sub>Cl<sub>3</sub>NO<sub>9</sub> 600.0571; Found: 600.0568.

***o*-Iodophenyl 2, 3-di-*O*-acetyl-6-*O*-*p*-methoxyphenzyl- β-*D*-glucopyranoside (**A20**)**



To a methanolic solution (30 mL) of peracetylated iodophenyl glucoside **M4** <sup>[21]</sup> (3.3 g, 6.0 mmol), methanolic NaOMe (0.2 mL, 5.4 mol/L) was added dropwise at 0°C until pH was 9. The mixture was stirred for 6 h at 0°C, when TLC (CH<sub>2</sub>Cl<sub>2</sub>-acetone, 1:1) showed the deacetylation was finished. Strong acidic cationic exchange resin Amberlist-15 was added to neutralize, then the mixture was filtered, and the filtrate was

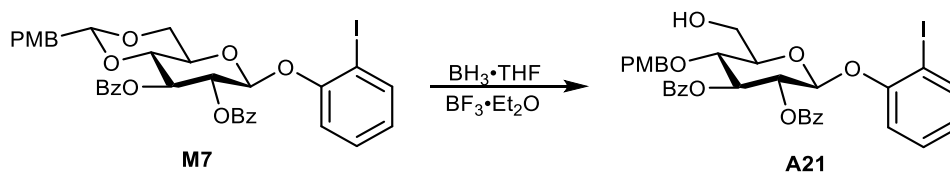
concentrated. The resultant residue was dissolved in acetonitrile (30 mL), to which *p*-TsOH (207 mg, 1.2 mmol) followed by *p*-anisylaldehyde dimethyl acetal (1.8 mL, 12.0 mmol) was added. The mixture was stirred for 5 h under reflux at 80°C and neutralized with triethylamine. The slurry was then concentrated and crystallized from hexane-ethyl acetate to give the white solid **M5** (2.8 g, about 92%); mp 205°C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.75 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.36 - 7.29 (m, 3H), 7.14 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.92 - 6.86 (m, 2H), 6.77 (td, *J* = 7.5, 1.3 Hz, 1H), 5.52 - 5.49 (m, 2H), 5.41 (d, *J* = 5.2 Hz, 1H), 5.21 (d, *J* = 7.2 Hz, 1H), 4.17- 4.11 (m, 1H), 3.72 (s, 3H), 3.68 - 3.50 (m, 3H), 3.48 - 3.38 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-*D*<sub>6</sub>) δ 159.6, 155.7, 139.1, 130.1, 129.6, 127.7, 123.9, 115.0, 113.3, 100.6, 100.4, 87.0, 80.1, 74.1, 73.1, 67.7, 65.9, 55.1; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>20</sub>H<sub>21</sub>IO<sub>7</sub> 523.0230; Found: 523.0247.

To a stirred solution **M5** (2.0 g, 3.9 mmol) in pyridine (10 mL), Ac<sub>2</sub>O (5 mL, 53 mmol) was added. After 1 hour, the reaction was concentrated under reduced pressure, diluted in CH<sub>2</sub>Cl<sub>2</sub>, washed with aqueous hydrogen chloride and brine, and dried with Na<sub>2</sub>SO<sub>4</sub>. The organic phase was concentrated to give an inseparable crude white solid **M6** (1.8 g, 80.8%) which was used to next step. *R<sub>f</sub>* 0.6 (PE: EA, 3:1).

Sodium cyanoborohydride (1.85 g, 30 mmol) was added to a solution of **M6** (1.2 g, 2.0 mmol) in THF (20mL) containing 3 Å molecular sieves at ambient temperature. Under vigorous stirring the mixture was treated with ethereal hydrogen chloride until the evolution of gas ceased. After the complete conversion indicated by TLC the reaction mixture was filtered through a pad of Celite and the filtrate was then partitioned between saturated aqueous NaHCO<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>. The water phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic fraction was washed with brine, dried, and concentrated. The residue was purified by silica gel column chromatography (PE/EA, 3:1) to give compound **A20** (0.87 g, 73%) as a colorless oil. *R<sub>f</sub>* 0.5 (PE/EA, 2:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.24 - 7.20 (m, 3H), 7.06 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.88 - 6.82 (m, 2H), 6.79 (td, *J* = 8.0, 1.6 Hz, 1H), 5.30 (dd, *J* = 9.6, 8.0 Hz, 1H), 5.10 (t, *J* = 9.6 Hz, 1H), 5.01 (d, *J* = 8.0 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H),

4.48 (d,  $J = 11.6$  Hz, 1H), 3.84 - 3.74 (m, 6H), 3.71 - 3.65 (m, 1H), 2.10 (s, 3H), 2.09 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.5, 169.6, 159.5, 156.2, 139.6, 129.7, 129.7, 129.5, 124.8, 115.9, 114.0, 99.8, 86.9, 75.7, 74.8, 73.6, 70.8, 70.5, 69.6, 55.4, 21.3, 21.0; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{27}\text{IO}_9$  609.0598; Found: 609.1120.

***o*-Iodophenyl 2, 3-di-*O*-benzoyl-4-*O*-*p*-methoxyphenzyl-  $\beta$ -D-glucopyranoside (A21)**



To a stirred solution (20 mL) of borane/tetrahydrofuran complex (1 mol/L) was added benzylidene **M7** (1.4 g, 2 mmol) in a nitrogen atmosphere at room temperature. Then boron trifluoride diethyl etherate (0.32 mL 2.5 mmol) was added dropwise under ice bath. The stirring was continued for another 1 h and subsequently neutralized with  $\text{Et}_3\text{N}$ . The solvent was evaporated in vacuo and further purified with chromatograph on silica gel (PE/EA, 2:1) to give **A21** (0.89 g, 62%) as a colorless oil.  $R_f$  0.35 (PE/EA, 2:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 - 7.91 (m, 4H), 7.72 - 7.68 (m, 1H), 7.55 - 7.50 (m, 1H), 7.50 - 7.44 (m, 1H), 7.41 - 7.36 (m, 2H), 7.35 - 7.27 (m, 3H), 7.13 - 7.05 (m, 3H), 6.81 - 6.75 (m, 1H), 6.72 - 6.67 (m, 2H), 5.83 - 5.72 (m, 2H), 5.32 (d,  $J = 7.2$  Hz, 1H), 4.61 - 4.53 (m, 2H), 4.06 (t,  $J = 9.2$  Hz, 1H), 4.00 (dd,  $J = 12.0, 3.2$  Hz, 1H), 3.86 (dd,  $J = 12.0, 4.0$  Hz, 1H), 3.79 - 3.74 (m, 1H), 3.71 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 165.3, 159.5, 156.0, 139.8, 133.4, 133.2, 130.1, 130.0, 129.9, 129.7, 129.6, 129.4, 129.3, 128.5, 128.4, 125.0, 115.8, 113.9, 99.9, 87.2, 76.0, 74.9, 74.9, 74.6, 71.5, 61.6, 55.2; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{34}\text{H}_{31}\text{IO}_9$  733.0911; Found: 733.0911.

**The general procedures for *tert*-butyldimethylsilylation of secondary carbohydrate alcohols**

A solution of secondary alcohol (1 mmol) in dried  $\text{CH}_2\text{Cl}_2$  (20 mL) was cooled down to  $-20^\circ\text{C}$ , then 2, 6-lutidine (1.2 mmol) and TBSOTf (1.2 mmol) were added



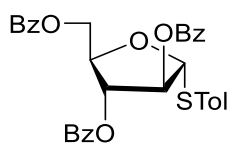
sequentially. The resulting solution was warmed up to room temperature with stirring. Upon complete consumption of alcohol as evidenced by TLC, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL) and washed with saturated aqueous CuSO<sub>4</sub> and brine. The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. The resulting syrup was chromatographed on silica gel using petroleum-ethyl acetate as an eluant to afford the goal silyl ether.

### The general procedures for 4, 6-*O*-di-*tert*-butylsilylenation of thioglycosides

To a stirred solution of diol (2.0 mmol) and 2, 6-lutidine (2.4 mmol) in dried CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was added <sup>t</sup>Bu<sub>2</sub>Si(OTf)<sub>2</sub> (2.4 mmol) at -20 °C under argon. Then at room temperature stirring was continued until TLC indicated the thorough consumption of diol. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with saturated aqueous CuSO<sub>4</sub> and brine. The combined organic fraction was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated. The subsequent purification of the resulting residue through chromatography over silica gel to give the goal products.

### Preparation and characterization of thioglycoside donors (D1-16)

#### *p*-Methylphenyl 2, 3, 5- tri-*O*-benzoyl- $\alpha$ -D-arabofuranoside (D1)

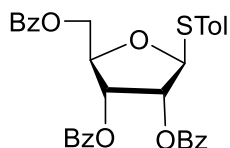


**D1**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 - 8.11 (m, 2H), 8.07 - 7.97 (m, 4H), 7.65 - 7.56 (m, 2H), 7.55 - 7.45 (m, 5H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.77 (s, 1H), 5.71 (t, *J* = 1.6 Hz, 1H), 5.58 (dt, *J* = 4.8, 1.2 Hz, 1H), 4.89 (t, *J* = 4.8 Hz, 1H), 4.81 (dd, *J* = 12.0, 3.6 Hz, 1H), 4.74 (dd, *J* = 12.0, 5.2 Hz, 1H), 2.33 (s, 3H).

<sup>1</sup>H NMR spectroscopic data for **D1** are consistent with those previously reported. [22]

#### *p*-Methylphenyl 2, 3, 5- tri-*O*-benzoyl- $\beta$ -D-ribofuranoside (D2)

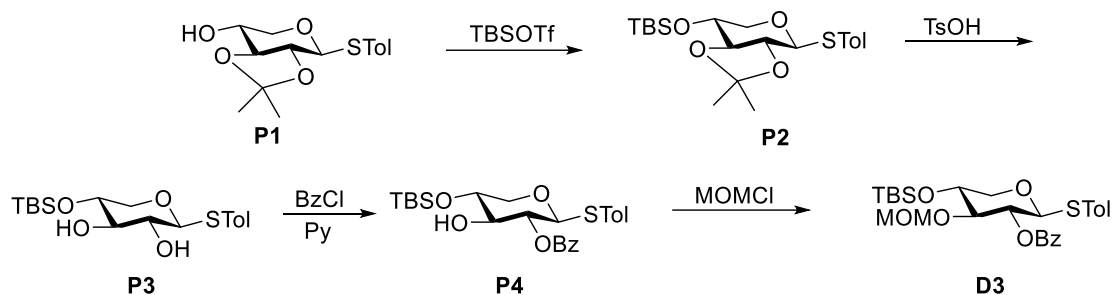


**D2**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 - 8.03 (m, 2H), 8.02 - 7.97 (m, 2H), 7.93 - 7.88 (m, 2H), 7.59 - 7.50 (m, 3H), 7.48 - 7.38 (m, 6H), 7.37 - 7.32 (m, 2H), 7.06 (d,  $J = 8.0$  Hz, 2H), 5.72 (t,  $J = 5.2$  Hz, 1H), 5.64 (t,  $J = 5.2$  Hz, 1H), 5.56 (d,  $J = 5.2$  Hz, 1H), 4.67 - 4.59 (m, 2H), 4.52 - 4.46 (m, 1H), 2.22 (s, 3H).

$^1\text{H}$  NMR spectroscopic data for **D2** were in agreement with those previously reported. [23]

***p*-Methylphenyl 2-*O*-benzoyl-4-*O*-*tert*-butyldimethylsilyl- 3-*O*-methoxymethoxyl-1-thio- $\beta$ -D- xylopyranoside(**D3**)**



According to the general procedures for *tert*-butyldimethylsilylation. The treatment of the known compound **P1** [24] (1.48 g, 5 mmol) with TBSOTf (1.38 mL, 6 mmol) afforded 4-*O*-silyl ether **P2** (1.96 g, 93%) as a pale yellow oil.  $R_f$  0.35 (PE/EA, 30:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 - 7.44 (m, 2H), 7.15 - 7.10 (m, 2H), 4.69 (d,  $J = 9.2$  Hz, 1H), 3.96 (dd,  $J = 11.6, 5.2$  Hz, 1H), 3.86 (td,  $J = 8.8, 5.2$  Hz, 1H), 3.45 (t,  $J = 8.8$  Hz, 1H), 3.20 - 3.12 (m, 2H), 2.34 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H), 0.87 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.4, 133.5, 129.7, 128.2, 110.6, 85.6, 83.2, 75.2, 70.9, 69.9, 26.9, 26.6, 25.8, 21.3, 18.3, 18.1, -4.5, -4.9; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{21}\text{H}_{34}\text{O}_4\text{SSi}$  433.1845; Found: 433.1843.

To a stirred solution of **P2** (1.5 g, 3.6 mmol) in a mixed solvent of MeOH (10 mL) and  $\text{CH}_2\text{Cl}_2$  (10 mL), TsOH (62 mg, 0.36 mmol) was added at room temperature and stirring was continued for 3 h before TLC indicated the disappearance of the starting material.

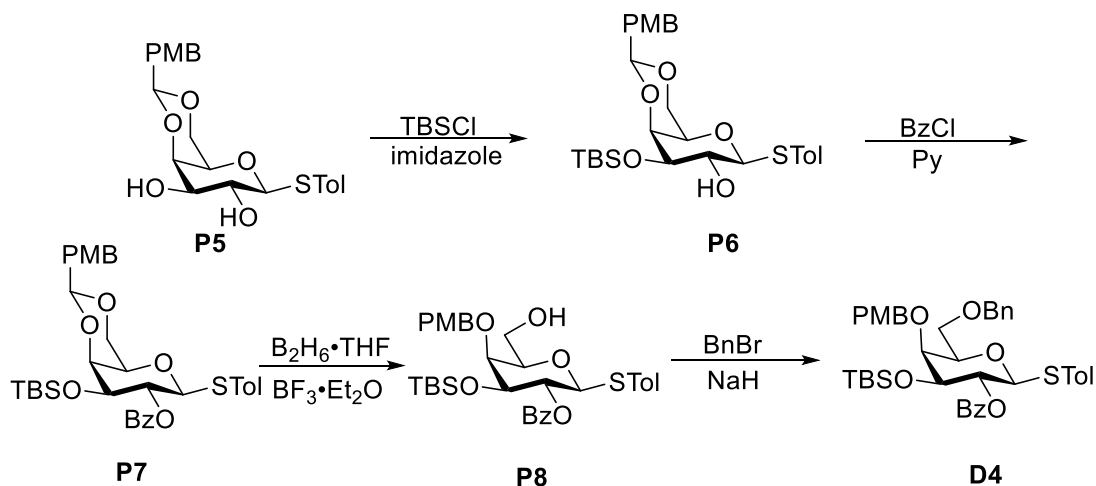
Et<sub>3</sub>N was added to the reaction mixture and subsequently the solvent was removed under reduced pressure to yield the crude product, which was further purified by silica gel column chromatography (PE/EA, 6:1) to afford diol **P3** (1.1 g, 85%). *R<sub>f</sub>* 0.53 (PE/EA, 4:1); White solid (from hot isopropanol), mp 121 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 -7.40 (m, 2H), 7.14 - 7.09 (m, 2H), 4.51 (d, *J* = 8.8 Hz, 1H), 3.96 (dd, *J* = 11.6, 4.8 Hz, 1H), 3.61 (ddd, *J* = 9.6, 8.4, 4.8 Hz, 1H), 3.51 (t, *J* = 8.4 Hz, 1H), 3.37 (t, *J* = 8.4 Hz, 1H), 3.23 (dd, *J* = 11.6, 9.6 Hz, 1H), 2.33 (s, 3H), 0.87 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.5, 133.3, 129.9, 128.3, 89.1, 77.6, 71.8, 70.7, 69.4, 25.8, 21.3, 18.1, -4.5, -4.6; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>18</sub>H<sub>30</sub>O<sub>4</sub>SSi 393.1532; Found: 393.1510.

BzCl (0.26 mL, 2.2 mmol) was added to a solution of **P3** (0.74 g, 2 mmol), Et<sub>3</sub>N (0.3 mL, 2.2 mmol), and DMAP (27 mg, 0.22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) at 0 °C. The resulting mixture was warmed to room temperature and stirred for 2h. The mixture was quenched by the addition of methanol, diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with saturated aqueous NaHCO<sub>3</sub> and brine. The organic layer was dried and the solvents were removed under reduced pressure. The resultant residue was purified by flash chromatography (PE/EA, 10:1) to afford **P4** (0.92 g, 97%). *R<sub>f</sub>* 0.65 (PE/EA, 5:1); white solid (from PE-CH<sub>2</sub>Cl<sub>2</sub>), mp 62 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 - 8.07 (m, 2H), 7.63 - 7.56 (m, 1H), 7.50 - 7.44 (m, 2H), 7.37 - 7.32 (m, 2H), 7.12 - 7.07 (m, 2H), 5.01 (dd, *J* = 10.0, 8.8 Hz, 1H), 4.72 (d, *J* = 8.8 Hz, 1H), 3.99 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.78 - 3.67 (m, 2H), 3.28 (dd, *J* = 11.2, 10.0 Hz, 1H), 2.33 (s, 3H), 0.87 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.2, 138.5, 133.5, 130.1, 129.9, 128.7, 128.6, 87.1, 77.6, 72.9, 71.5, 70.1, 25.8, 21.3, 18.1, -4.5, -4.5; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>25</sub>H<sub>34</sub>O<sub>5</sub>SSi 497.1794; Found: 497.1820.

To a solution of **P4** (0.8 g, 1.7 mmol) in dried CH<sub>2</sub>Cl<sub>2</sub> (15 mL) containing diisopropylethylamine (0.35 mg, 2 mmol) (3.0 ml) was added MOMCl (16 mg, 2 mmol). The mixture was stirred at room temperature for 10 h, at which time TLC show the completion of the reaction. Then the solution was poured into saturated aqueous NH<sub>4</sub>Cl and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic fraction was dried over anhydrous

Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The resultant residue was purified by silica gel chromatography (EtOAc/hexane, 1:15) to give xyloside donor **D3** (710 mg, 81%). *R<sub>f</sub>* 0.54 (PE/EA 10:1); white solid (from PE-CH<sub>2</sub>Cl<sub>2</sub>), mp 115°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 - 8.08 (m, 2H), 7.61 - 7.55 (m, 1H), 7.49 - 7.43 (m, 2H), 7.36 - 7.31 (m, 2H), 7.11 - 7.04 (m, 2H), 5.13 (t, *J* = 8.8 Hz, 1H), 4.86 (d, *J* = 6.8 Hz, 1H), 4.76 (d, *J* = 8.8 Hz, 1H), 4.58 (d, *J* = 6.8 Hz, 1H), 4.01 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.82 (ddd, *J* = 9.6, 8.4, 5.2 Hz, 1H), 3.74 (t, *J* = 8.4 Hz, 1H), 3.29 (dd, *J* = 11.6, 9.6 Hz, 1H), 3.02 (s, 3H), 2.31 (s, 3H), 0.86 (s, 9H), 0.08 (s, 3H), 0.08 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.6, 138.2, 133.3, 133.0, 130.2, 130.0, 129.8, 129.5, 128.5, 98.2, 87.8, 82.1, 71.5, 71.2, 69.8, 56.0, 25.8, 21.3, 18.0, -4.6, -4.7; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>27</sub>H<sub>38</sub>O<sub>6</sub>SSi 541.2056; Found: 541.2051.

***p*-Methylphenyl 2-*O*-benzoyl- 6-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-5-*O*-*p*-methoxybenzyl- 1-thio - β-*D*-galacopyranoside (**D4**)**



To a stirring solution of compound **P5** <sup>[25]</sup> (2.02 g, 5 mmol) and imidazole (0.4 g, 6 mmol) in absolute DMF (50 mL) was added *tert*-butyldimethylchlorosilane (0.9 g, 6 mmol) at 0°C. The mixture was stirred at room temperature overnight and then was partitioned between water and CH<sub>2</sub>Cl<sub>2</sub>. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were dried and concentrated. Then crystallization from PE-EA gave **P6** as an unpurified white crude solid (2.2 g, 85%), which was used for the next step without further purification.

To a stirring solution of compound **P6** (2.0 g, 3.76 mmol) in dried pyridine (40 mL) was added benzoyl chloride (0.52 mL, 5.31 mmol) at room temperature. The mixture

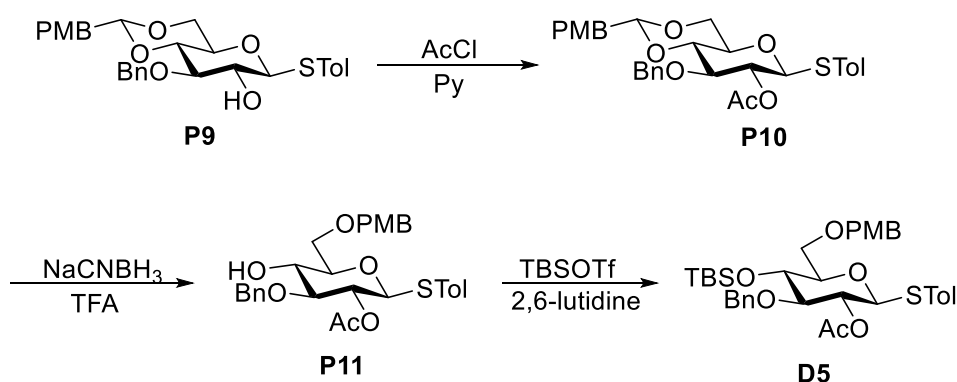
was warmed to room temperature and continuously stirred overnight. Most of pyridine was removed under reduced pressure and the residue was taken up in CH<sub>2</sub>Cl<sub>2</sub>. The resulting solution was washed with saturated aqueous CuSO<sub>4</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The resulting crude solid **P7** was used to the next step without further purification.

To an ice-cooled solution of **P7** (1.9 g, 3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) borane tetrahydrofuran (30 mL, 1 mol/L solution in THF) was added. Then boron trifluoride diethyl etherate was added dropwise. The reaction mixture was allowed to stirred in the ice bath for another 1 h and subsequently neutralized with Et<sub>3</sub>N. The solvent was evaporated *in vacuo* and further purified with chromatograph on silica gel (PE/EA, 3:1) to give **P8** (1.5 g, 82%) as a colorless oil. *R<sub>f</sub>* 0.50 (PE/EA, 2:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 - 7.95 (m, 2H), 7.54 - 7.47 (m, 1H), 7.38 (td, *J* = 8.0, 2.0 Hz, 2H), 7.25 - 7.18 (m, 4H), 6.97 - 6.92 (m, 2H), 6.85 - 6.79 (m, 2H), 5.55 (t, *J* = 9.6 Hz, 1H), 4.93 (d, *J* = 11.2 Hz, 1H), 4.65 (d, *J* = 9.6 Hz, 1H), 4.44 (d, *J* = 11.2 Hz, 1H), 3.92 - 3.85 (m, 1H), 3.81 - 3.73 (m, 4H), 3.68 (t, *J* = 2.0 Hz, 1H), 3.54 - 3.45 (m, 2H), 2.21 (s, 3H), 0.71 (s, 9H), 0.03 (s, 3H), -0.17 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.4, 159.4, 137.8, 133.1, 132.6, 130.7, 130.5, 130.0, 129.8, 129.7, 128.5, 113.9, 87.5, 79.0, 76.5, 76.0, 74.4, 71.4, 62.4, 55.4, 25.7, 21.2, 17.9, -3.9, -4.9; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>34</sub>H<sub>44</sub>O<sub>7</sub>SSi 647.2475 Found: 647.2473 .

NaH (60% dispersion in mineral oil, 160 mg, 4 mmol) were added to a solution of **P8** (1.22g, 2.0 mmol) in anhydrous DMF (20 mL) under argon atmosphere. Then to the resulting suspension benzyl bromide (2.50 mmol) were added dropwise at 0 °C. The reaction mixture was stirred at room temperature overnight and poured into saturated aqueous NH<sub>4</sub>Cl. After the extraction with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic fraction was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. The resultant residue underwent the purification through chromatography on silica gel (PE/EA, 10:1) to afford **D4** (1.1 g, 79%). *R<sub>f</sub>* 0.57 (PE/EA, 5:1); white solid (from PE-CH<sub>2</sub>Cl<sub>2</sub>), mp 104°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 - 8.02 (m, 2H), 7.59 - 7.53 (m, 1H), 7.47 - 7.41 (m, 2H), 7.37 - 7.24 (m, 9H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.89 - 6.83 (m, 2H), 5.61

(t,  $J = 9.6$  Hz, 1H), 4.99 (d,  $J = 10.6$  Hz, 1H), 4.70 (d,  $J = 9.6$  Hz, 1H), 4.52 - 4.41 (m, 3H), 3.99 - 3.91 (m, 1H), 3.83 - 3.79 (m, 4H), 3.74 - 3.69 (m, 1H), 3.68 - 3.59 (m, 2H), 2.27 (s, 3H), 0.77 (s, 9H), 0.09 (s, 3H), -0.11 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 159.2, 138.2, 137.6, 133.0, 132.5, 131.1, 130.6, 130.2, 129.9, 129.6, 129.5, 128.5, 128.4, 128.0, 127.9, 113.7, 87.6, 77.9, 77.4, 76.9, 75.9, 74.8, 73.7, 69.2, 55.4, 25.7, 21.2, 17.9, -3.9, -4.9; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{41}\text{H}_{50}\text{O}_7\text{SSi}$  737.2945; Found: 737.2943.

***p*-Methylphenyl 2-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl- 6-*O*-*p*-methoxybenzyl- 1-thio- $\beta$ -D-glucopyranoside (**D5**)**



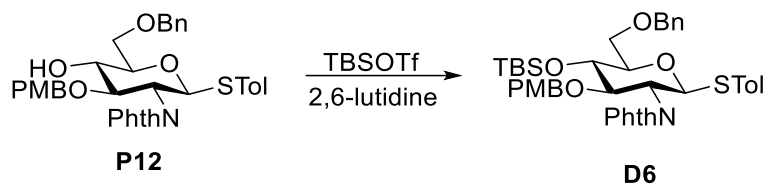
**P9**<sup>[26]</sup> (2.0 g, 4 mmol) was dissolved in a mixture of pyridine (20 mL) and  $\text{Ac}_2\text{O}$  (4 mL). After the reaction mixture was stirred for 1 h at room temperature, TLC showed complete conversion. Then the mixture was concentrated under reduced pressure. Crystallization of the resulting residue from PE-EA to give **P10** (2.12 g, 96%) as a colorless needle. mp 128 °C,  $R_f$  0.50 (PE/EA, 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 - 7.38 (m, 2H), 7.36 (d,  $J = 7.9$  Hz, 2H), 7.33 - 7.24 (m, 5H), 7.11 (d,  $J = 7.9$  Hz, 2H), 6.92 - 6.87 (m, 2H), 5.51 (s, 1H), 5.02 - 4.95 (m, 1H), 4.84 (d,  $J = 12.0$  Hz, 1H), 4.67 - 4.59 (m, 2H), 4.35 (dd,  $J = 10.8, 5.2$  Hz, 1H), 3.80 (s, 3H), 3.78 - 3.74 (m, 1H), 3.73 - 3.66 (m, 2H), 3.46 (td,  $J = 8.8, 4.8$  Hz, 1H), 2.33 (s, 3H), 2.03 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 160.2, 138.6, 138.2, 133.5, 129.8, 128.4, 128.0, 127.8, 127.4, 113.7, 101.3, 87.1, 81.4, 79.9, 74.4, 71.4, 70.6, 68.6, 55.4, 21.3, 21.1; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{30}\text{H}_{32}\text{O}_7\text{S}$  559.1767; Found: 559.1754.

Sodium cyanoborohydride (943 mg, 15 mmol) was added at room temperature to a solution of **P10** (1.65 g, 3 mmol) containing 3 Å molecular sieves in dried DMF (30

mL). Under vigorous stirring the mixture was treated with trifluoroacetic acid (30 mmol). After no starting material was detected as evidenced by TLC, the reaction mixture was filtered through a pad of Celite and the filtrate was then partitioned between saturated aqueous NaHCO<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>. The water phase was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic fraction was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The resultant residue was chromatographically purified over silica gel (PE/EA 5:1) to provide **P11** (1.2 g, 72.7%). *R*<sub>f</sub> 0.50 (PE/EA, 3:1); white solid (from PE-CH<sub>2</sub>Cl<sub>2</sub>), mp 72 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41 - 7.37 (m, 2H), 7.36 - 7.32 (m, 2H), 7.31 - 7.27 (m, 3H), 7.26 - 7.22 (m, 2H), 7.08 - 7.04 (m, 2H), 6.91 - 6.86 (m, 2H), 4.97 (dd, *J* = 10.0, 9.2 Hz, 1H), 4.77 - 4.69 (m, 2H), 4.57 (d, *J* = 10.0 Hz, 1H), 4.54 - 4.45 (m, 2H), 3.81 (s, 3H), 3.77 - 3.73 (m, 2H), 3.69 (t, *J* = 9.2 Hz, 1H), 3.53 (t, *J* = 9.2 Hz, 1H), 3.51 - 3.46 (m, 1H), 2.31 (s, 3H), 2.05 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.6, 159.4, 138.3, 138.2, 133.1, 130.0, 129.7, 129.5, 129.1, 128.6, 127.9, 113.9, 86.6, 83.9, 78.2, 74.7, 73.5, 72.1, 71.5, 70.2, 55.4, 21.2, 21.2; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>30</sub>H<sub>34</sub>O<sub>7</sub>S 561.1923; Found: 561.1910.

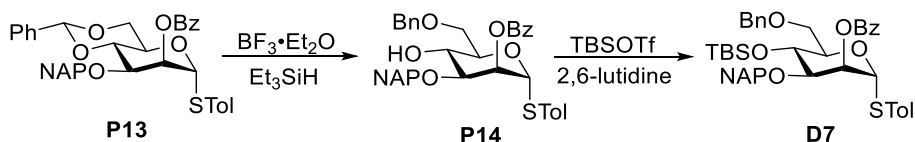
The treatment of alcohol **P11** (1 g, 1.9 mmol) with TBSOTf furnished the product **D5** (1.1 g, 89%) according to the general procedure for *tert*-butyldimethylsilylation. White powder (from PE-CH<sub>2</sub>Cl<sub>2</sub>), mp 100 °C, *R*<sub>f</sub> 0.50 (PE/EA 10:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 - 7.41 (m, 2H), 7.35 - 7.30 (m, 2H), 7.28 - 7.24 (m, 5H), 7.05 - 7.00 (m, 2H), 6.92 - 6.87 (m, 2H), 5.02 (dd, *J* = 10.0, 8.8 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 10.0 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 3.82 (s, 3H), 3.78 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.65 (dd, *J* = 9.6, 8.8 Hz, 1H), 3.59 (dd, *J* = 10.8, 6.4 Hz, 1H), 3.53 - 3.46 (m, 2H), 2.31 (s, 3H), 1.93 (s, 3H), 0.87 (s, 9H), 0.02 (s, 3H), -0.02 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.7, 159.2, 138.3, 137.8, 132.6, 130.6, 129.7, 129.6, 129.3, 128.4, 127.5, 127.4, 113.8, 86.4, 85.1, 80.9, 75.3, 73.2, 72.3, 71.1, 69.2, 55.4, 26.0, 21.2, 21.1, 18.1, -3.7, -4.7; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>36</sub>H<sub>48</sub>O<sub>7</sub>SSi 675.2788; Found: 675.2784.

***p*-Methylphenyl 6-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl- 2-deoxy- 3-*O*-*p*-methoxybenzyl-2-phthalimido- 1-thio-β-D-glucopyranoside (D6)**



According to the general procedures for *tert*-butyldimethylsilylation. The treatment of alcohol **P12**<sup>[27]</sup> (1.25 g, 2 mmol) with TBSOTf furnished the product **D6** (1.33 g, 90%). White solid (from PE-EA), mp 66 °C;  $R_f$  0.62 (PE/EA, 3:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 - 7.56 (m, 4H), 7.37 - 7.32 (m, 4H), 7.32 - 7.28 (m, 1H), 7.28 - 7.25 (m, 2H), 6.92 (d,  $J$  = 7.9 Hz, 2H), 6.89 - 6.85 (m, 2H), 6.38 - 6.34 (m, 2H), 5.53 - 5.45 (m, 1H), 4.68 (d,  $J$  = 12.2 Hz, 1H), 4.62 (d,  $J$  = 12.0 Hz, 1H), 4.51 (d,  $J$  = 12.0 Hz, 1H), 4.23 - 4.14 (m, 3H), 3.81 (d,  $J$  = 9.6 Hz, 1H), 3.71 - 3.60 (m, 3H), 3.56 (s, 3H), 2.23 (s, 3H), 0.88 (s, 9H), 0.10 (s, 3H), 0.05 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.3, 167.4, 158.6, 138.6, 137.8, 133.7, 132.9, 131.7, 131.7, 130.5, 129.6, 129.2, 128.6, 128.4, 127.7, 127.6, 123.4, 123.1, 113.4, 83.5, 81.9, 80.7, 75.4, 73.4, 72.8, 69.4, 55.1, 54.9, 26.0, 21.2, 18.1, -3.6, -4.3; HRMS (ESI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>42</sub>H<sub>49</sub>NO<sub>7</sub>SSi 762.2897; Found: 762.2890.

***p*-Methylphenyl 2-*O*-benzoyl-6-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-3-*O*-naphthylmethyl-1-thio- $\alpha$ -D-mannopyranoside(**D7**)**



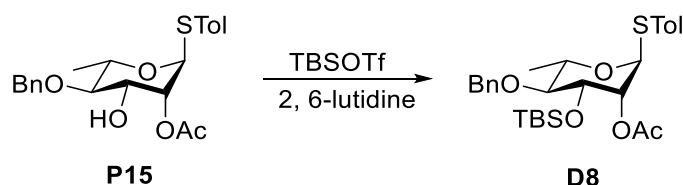
Triethylsilane (1.3 mL, 8 mmol) and borate trifluoride etherate (0.99 mL, 8.0 mmol) were sequentially added to an iced-cooled solution of compound **P13**<sup>[28]</sup> (2.5 g, 4.0 mmol) in DCM (50 mL). The reaction mixture was allowed to warm up to room temperature stirred for 1 h and then quenched with Et<sub>3</sub>N (1 mL). The resulting mixture was washed with saturated brine. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the filtrate was concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA 6:1) to give **P14** (1.93 g, 77%) as a colorless oil.  $R_f$  0.49 (PE/EA 4:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 - 8.06 (m, 2H), 7.84 - 7.74 (m, 4H), 7.60 - 7.55 (m, 1H), 7.49 - 7.31 (m, 12H), 7.08 (d,  $J$  = 8.0 Hz, 2H), 5.94 (dd,  $J$  =



2.8, 1.6 Hz, 1H), 5.64 (d,  $J = 1.6$  Hz, 1H), 4.99 (d,  $J = 11.6$  Hz, 1H), 4.74 (d,  $J = 11.6$  Hz, 1H), 4.69 (d,  $J = 12.0$  Hz, 1H), 4.59 (d,  $J = 12.0$  Hz, 1H), 4.46 (ddd,  $J = 10.0, 4.8, 2.8$  Hz, 1H), 4.28 (t,  $J = 9.6$  Hz, 1H), 4.00 - 3.92 (m, 2H), 3.89 (dd,  $J = 10.8, 2.8$  Hz, 1H), 2.32 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 138.1, 137.8, 134.6, 133.1, 133.0, 132.9, 132.4, 129.7, 129.7, 129.5, 128.2, 128.2, 128.1, 127.7, 127.5, 127.3, 126.9, 125.9, 125.8, 125.7, 86.6, 77.8, 73.3, 72.2, 71.4, 69.8, 69.6, 67.4, 20.9; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{38}\text{H}_{36}\text{O}_6\text{S}$  643.2131; Found: 643.2129.

According to the general procedures for *tert*-butyldimethylsilylation, the treatment of diol **P14** (1.24 g, 2.0 mmol) with TBSOTf (0.55 mL, 2.4 mmol) furnished the product **D7** (1.41 g, 96%) . White solid ( from  $\text{PE-CH}_2\text{Cl}_2$ ), mp  $73^\circ\text{C}$ ;  $R_f$  0.65 (PE/EA 6:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 - 8.02 (m, 2H), 7.81 - 7.76 (m, 1H), 7.73 - 7.68 (m, 2H), 7.65 - 7.61 (m, 1H), 7.61 - 7.55 (m, 1H), 7.45 - 7.30 (m, 12H), 7.07 (d,  $J = 8.0$  Hz, 2H), 5.91 (dd,  $J = 2.8, 1.6$  Hz, 1H), 5.60 (d,  $J = 1.6$  Hz, 1H), 4.95 (d,  $J = 11.6$  Hz, 1H), 4.70 - 4.64 (m, 2H), 4.60 (d,  $J = 12.0$  Hz, 1H), 4.48 (ddd,  $J = 10.0, 4.8, 2.8$  Hz, 1H), 4.30 (t,  $J = 9.2$  Hz, 1H), 3.94 (dd,  $J = 10.8, 4.8$  Hz, 1H), 3.90 (dd,  $J = 9.2, 2.8$  Hz, 1H), 3.85 (dd,  $J = 10.8, 2.8$  Hz, 1H), 2.32 (s, 3H), 0.87 (s, 9H), 0.05 (s, 3H), 0.00 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 138.8, 138.1, 135.2, 133.3, 133.0, 132.7, 130.0, 130.0, 130.0, 129.9, 128.6, 128.3, 128.0, 127.9, 127.7, 127.4, 127.4, 126.8, 126.0, 125.9, 125.8, 86.8, 78.9, 74.1, 73.3, 71.2, 70.3, 69.6, 68.3, 26.1, 21.2, 18.3, -3.7, -5.0; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{44}\text{H}_{50}\text{O}_6\text{SSi}$  757.2995; Found: 757.2984.

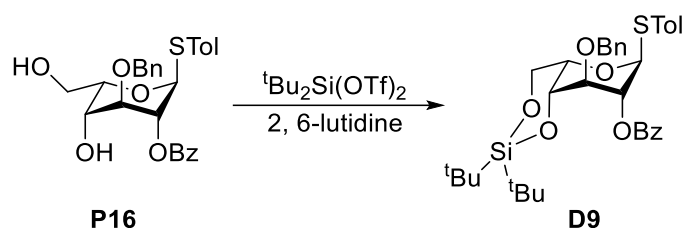
***p*-Methylphenyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*- *tert*-butyldimethylsilyl -1-thio- $\alpha$ -L-rhamnopyranoside (**D8**)**



According to the general procedures for *tert*-butyldimethylsilylation, the treatment of diol **P15** <sup>[29]</sup> (804 mg, 2 mmol) with DTB(OTf)<sub>2</sub> (0.55 mL, 2.4 mmol) furnished the product **D8** (902 mg, 87.4%) as a colorless oil.  $R_f$  0.73 (PE/EA, 6:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 - 7.33 (m, 6H), 7.33 - 7.28 (m, 1H), 7.13 - 7.09 (m, 2H), 5.32 -

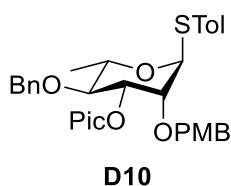
5.28 (m, 2H), 4.92 (d,  $J = 11.2$  Hz, 1H), 4.63 (d,  $J = 11.2$  Hz, 1H), 4.26 - 4.17 (m, 1H), 4.09 (dd,  $J = 9.2, 3.2$  Hz, 1H), 3.45 (t,  $J = 9.2$  Hz, 1H), 2.32 (s, 3H), 2.14 (s, 3H), 1.31 (d,  $J = 6.4$  Hz, 3H), 0.91 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 138.4, 137.9, 132.3, 130.4, 130.0, 128.5, 127.9, 127.8, 86.6, 81.6, 75.6, 74.6, 71.6, 69.2, 25.9, 21.2, 21.2, 17.9, 17.9, -4.6; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{28}\text{H}_{40}\text{O}_5\text{SSi}$  539.2264; Found: 539.2261.

***p*-Methylphenyl 2-*O*-benzoyl-3-*O*-benzyl-4, 6-*O*-di-*tert*-butylsilylene-1-thio- $\alpha$ -L-idopyranoside (**D9**)**



According to the general procedures for *tert*-butyldimethylsilylation, the treatment of diol **P16**<sup>[30]</sup> (960 mg, 2.0 mmol) with DTB(OTf)<sub>2</sub> (0.55 mL, 2.4 mmol) furnished the product **D9** (1.18 g, 95.2%). White solid (from PE-ethyl ether), mp 147 °C,  $R_f$  0.4 (PE:EA, 25:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 - 8.06 (m, 2H), 7.59 - 7.53 (m, 1H), 7.48 - 7.40 (m, 6H), 7.40 - 7.34 (m, 2H), 7.33 - 7.28 (m, 1H), 7.16 - 7.10 (m, 2H), 5.66 (s, 1H), 5.40 - 5.36 (m, 1H), 5.00 (d,  $J = 11.8$  Hz, 1H), 4.73 (d,  $J = 11.8$  Hz, 1H), 4.55 - 4.50 (m, 1H), 4.36 (dd,  $J = 12.8, 2.4$  Hz, 1H), 4.31 - 4.27 (m, 1H), 4.20 (dd,  $J = 12.4, 2.4$  Hz, 1H), 3.95 - 3.90 (m, 1H), 2.34 (s, 3H), 1.02 (s, 9H), 0.96 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.4, 137.9, 137.6, 133.4, 132.3, 132.2, 130.4, 129.9, 129.7, 128.6, 128.3, 128.0, 127.9, 87.4, 76.1, 72.6, 70.8, 70.0, 67.5, 65.4, 28.0, 27.1, 23.4, 21.3, 20.7; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{35}\text{H}_{44}\text{O}_6\text{SSi}$  643.2526; Found: 643.2502.

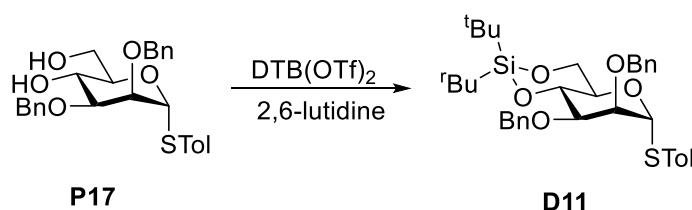
***p*-Methylphenyl 4-*O*-benzyl-2-*O*-*p*-methoxybenzyl- 3-*O*-picolinoyl -1-thio- $\alpha$ -L-rhamnopyranoside (**D10**)**



It was prepared as described in the literature. <sup>[31]</sup>  $^1\text{H}$  NMR spectroscopic data for **D10**

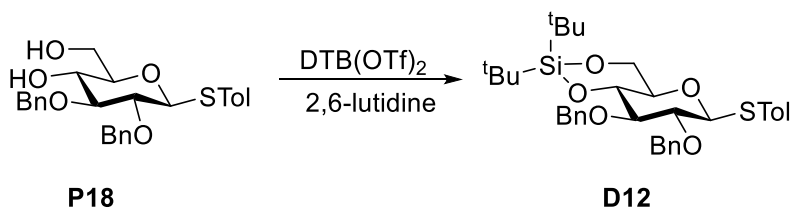
corresponded to those previously reported.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (d,  $J = 4.4$  Hz, 1H), 8.01 (d,  $J = 8.0$  Hz, 1H), 7.84 (td,  $J = 7.6, 1.6$  Hz, 1H), 7.55 - 7.49 (m, 1H), 7.36 (d,  $J = 8.0$  Hz, 2H), 7.26 - 7.17 (m, 5H), 7.16 - 7.10 (m, 4H), 6.63 - 6.56 (m, 2H), 5.47 (dd,  $J = 9.2, 3.2$  Hz, 1H), 5.41 (d,  $J = 1.6$  Hz, 1H), 4.88 (d,  $J = 11.0$  Hz, 1H), 4.70 (d,  $J = 11.0$  Hz, 1H), 4.61 (d,  $J = 12.0$  Hz, 1H), 4.42 (d,  $J = 12.0$  Hz, 1H), 4.33 - 4.25 (m, 1H), 4.24 - 4.21 (m, 1H), 3.91 (t,  $J = 9.6$  Hz, 1H), 3.70 (s, 3H), 2.34 (s, 3H), 1.39 (d,  $J = 6.1$  Hz, 3H).

***p*-Methylphenyl 2, 3-di-*O*-benzyl-4, 6-*O*-di-*tert*-butylsilylene-1-thio- $\alpha$ -D-mannopyranoside (D11)**



According to the general procedures for 4, 6-*O*-di-*tert*-butylsilylenation, the treatment of diol **P17** <sup>[32]</sup> (932 mg, 2 mmol) with  $\text{DTB(OTf)}_2$  (0.55 mL, 2.4 mmol) furnished the product **D11** (1.08 g, 89.0%) as a colorless oil.  $R_f$  0.55 (PE/EA, 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 - 7.27 (m, 10H), 7.25 - 7.20 (m, 2H), 7.11 - 7.07 (m, 2H), 5.35 (d,  $J = 1.6$  Hz, 1H), 4.90 (d,  $J = 12.4$  Hz, 1H), 4.77 - 4.67 (m, 3H), 4.44 (t,  $J = 9.6$  Hz, 1H), 4.19 (td,  $J = 9.6, 5.2$  Hz, 1H), 4.07 - 3.97 (m, 2H), 3.96 (dd,  $J = 3.2, 1.6$  Hz, 1H), 3.69 (dd,  $J = 9.6, 3.2$  Hz, 1H), 2.33 (s, 3H), 1.09 (s, 9H), 1.05 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.1, 138.1, 137.9, 132.1, 130.4, 130.0, 128.5, 128.5, 128.2, 127.8, 127.7, 127.6, 87.4, 79.0, 78.0, 75.6, 73.6, 72.9, 69.2, 66.6, 27.6, 27.3, 22.8, 21.2, 20.2; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{35}\text{H}_{46}\text{O}_5\text{SSi}$  629.2733; Found: 629.2724.

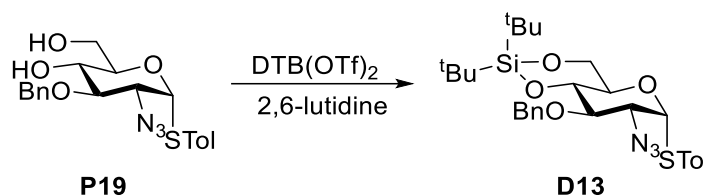
***p*-Methylphenyl 2, 3-di-*O*-benzyl 4, 6-*O*-di-*tert*-butylsilylene- 1-thio- $\beta$ -D-glucopyranoside (D12)**



According to the general procedures for 4, 6-*O*-di-*tert*-butylsilylenation, the treatment

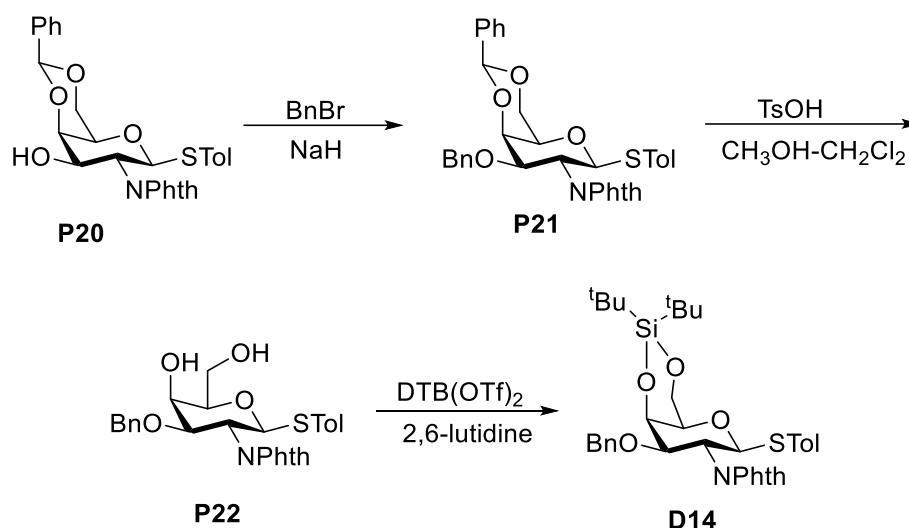
of diol **P18**<sup>[33]</sup> (932 mg, 2 mmol) with DTB(OTf)<sub>2</sub> (0.55 mL, 2.4 mmol) furnished the product **D12** (1.13 g, 93.4%) as a colorless oil. *R<sub>f</sub>* 0.60 (PE/EA, 20:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 - 7.41 (m, 4H), 7.41 - 7.34 (m, 5H), 7.34 - 7.27 (m, 3H), 7.14 - 7.10 (m, 2H), 5.03 (d, *J* = 10.8 Hz, 1H), 4.85 (d, *J* = 10.0 Hz, 1H), 4.83 - 4.78 (m, 2H), 4.65 (d, *J* = 10.0 Hz, 1H), 4.22 (dd, *J* = 10.0, 4.8 Hz, 1H), 3.99 - 3.91 (m, 2H), 3.63 (t, *J* = 8.8 Hz, 1H), 3.46 - 3.38 (m, 2H), 2.35 (s, 3H), 1.11 (s, 9H), 1.00 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.7, 138.4, 138.2, 133.2, 129.9, 129.4, 128.5, 128.4, 128.3, 127.9, 127.9, 88.6, 86.4, 80.0, 78.0, 75.9, 75.8, 74.5, 66.4, 27.6, 27.1, 22.8, 21.3, 20.1; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>35</sub>H<sub>46</sub>O<sub>5</sub>SSi 629.2733; Found: 629.2720.

***p*-Methylphenyl 2-azido-3-*O*-benzyl-4, 6-*O*-di-*tert*-butylsilylene-2-deoxy-1-thio- $\alpha$ -D-glucopyranoside (**D13**)**



According to the general procedures for 4, 6-*O*-di-*tert*-butylsilylenation, the treatment of diol **P19**<sup>[34]</sup> (802 mg, 2 mmol) with DTB(OTf)<sub>2</sub> furnished the product **D13** (981 mg, 90.7%) as a colorless oil. *R<sub>f</sub>* 0.48 (PE/EA, 2:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 - 7.42 (m, 2H), 7.39 - 7.29 (m, 5H), 7.16 - 7.11 (m, 2H), 5.40 (d, *J* = 5.6 Hz, 1H), 5.07 (d, *J* = 10.5 Hz, 1H), 4.84 (d, *J* = 10.5 Hz, 1H), 4.38 (td, *J* = 10.1, 5.6 Hz, 1H), 4.03 (dd, *J* = 10.1, 4.8 Hz, 1H), 3.98 (dd, *J* = 9.6, 8.4 Hz, 1H), 3.91 - 3.82 (m, 2H), 3.75 (dd, *J* = 10.0, 8.4 Hz, 1H), 2.33 (s, 3H), 1.09 (s, 9H), 1.08 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.3, 138.0, 132.9, 130.1, 129.4, 128.6, 128.6, 128.1, 87.9, 80.9, 79.0, 75.7, 67.6, 66.5, 63.0, 27.5, 27.2, 22.8, 21.3, 20.2; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>28</sub>H<sub>39</sub>N<sub>3</sub>O<sub>4</sub>SSi 564.2329; Found: 564.2303.

***p*-Methylphenyl 3-*O*-benzyl- 4, 6-*O*-di-*tert*-butylsilylene- 2-deoxy -2-phthalimido-1-thio- $\beta$ -D-galactopyranoside (**D14**)**



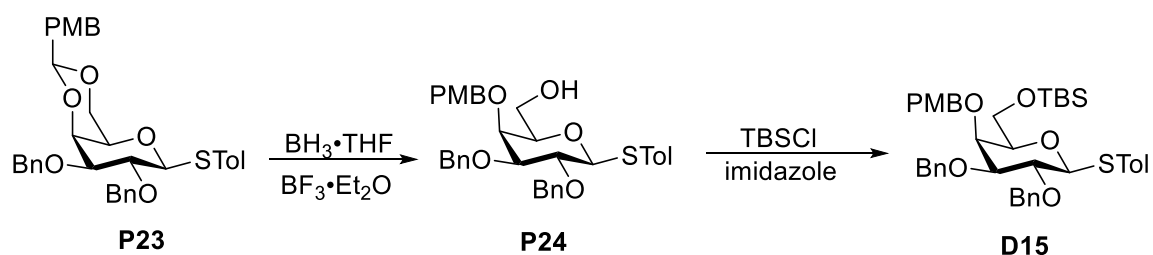
To a solution of **P20**<sup>[35]</sup> (2.52 g, 5.0 mmol) in DMF (100 mL) was added NaH (60% in mineral oil, 800 mg, 20 mmol) at 0 °C. The resulting slurry was stirred for 30 min, then benzyl bromide (0.72 mL, 6 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 2h. After saturated aqueous NH<sub>4</sub>Cl solution was added to quench reaction, the mixture was extracted with ethyl acetate. The combined organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and dried under reduced pressure. The residue is subjected to chromatographical purification over silica gel (ethyl acetate in petroleum ether, 4:1) to give **P21** (2.28 g, 76.8%). White solid (from PE-EA), mp: 229 °C; *R<sub>f</sub>* 0.51 (PE/EA, 3:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 - 7.85 (m, 1H), 7.76 - 7.70 (m, 3H), 7.52 - 7.47 (m, 2H), 7.43 - 7.37 (m, 5H), 7.09 - 7.00 (m, 7H), 5.54 (d, *J* = 10.4 Hz, 1H), 5.50 (s, 1H), 4.71 (t, *J* = 10.4 Hz, 1H), 4.59 (d, *J* = 12.8 Hz, 1H), 4.42 - 4.36 (m, 3H), 4.28 - 4.24 (m, 1H), 4.03 (dd, *J* = 12.4, 2.0 Hz, 1H), 3.60 - 3.56 (m, 1H), 2.31 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.6, 167.2, 138.2, 137.9, 137.8, 134.1, 134.1, 133.9, 131.9, 131.8, 129.6, 129.1, 128.3, 128.2, 127.8, 127.7, 127.6, 126.8, 123.7, 123.2, 101.4, 83.1, 74.8, 72.7, 71.0, 70.2, 69.6, 50.9, 21.3; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>35</sub>H<sub>31</sub>NO<sub>6</sub>S 616.1770; Found: 616.1769.

TsOH (52 mg, 0.3 mmol) and **P21** (1.78 g, 3 mmol) was added to in the mixed solvent of MeOH (8 mL) and CH<sub>2</sub>Cl<sub>2</sub> (52 mL). After stirring at room temperature for 2 h, the reaction mixture was quenched with Et<sub>3</sub>N and concentrated. The further purification through chromatography (petroleum ether: EtOAc, 2:1) over silica gel to give diol **P22** (1.41 g, 93%). White solid (from hot isopropyl alcohol), mp 201°C;. *R<sub>f</sub>* 0.2 (PE/EA,

1:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 - 7.81 (m, 1H), 7.75 - 7.62 (m, 3H), 7.26 - 7.23 (m, 2H), 7.03 - 6.97 (m, 5H), 6.97 - 6.92 (m, 2H), 5.46 (d,  $J = 10.4$  Hz, 1H), 4.60 (d,  $J = 12.4$  Hz, 1H), 4.53 (t,  $J = 10.4$  Hz, 1H), 4.30 (d,  $J = 12.4$  Hz), 4.26 (dd,  $J = 10.4$ , 2.8 Hz, 1H), 4.19 - 4.15 (m, 1H), 4.00 (dd,  $J = 11.6$ , 6.8 Hz, 1H), 3.84 (dd,  $J = 11.6$ , 4.4 Hz, 1H), 3.71 - 3.65 (m, 1H), 2.25 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 167.6, 138.1, 137.1, 134.2, 134.0, 132.9, 131.7, 129.7, 128.5, 128.4, 128.1, 128.0, 123.7, 123.3, 84.1, 78.4, 75.6, 71.4, 66.3, 62.8, 51.2, 21.2; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{28}\text{H}_{27}\text{NO}_6\text{S}$  528.1457; Found: 528.1463.

According to the general procedures for 4, 6-*O*-di-*tert*-butylsilylenation, the treatment of diol **P22** (1.01 g, 2 mmol) with DTB(OTf)<sub>2</sub> (0.55 mL, 2.4 mmol) furnished the donor **D14** (1.13 g, 87.6%). White solid (from PE- $\text{CH}_2\text{Cl}_2$ ), mp 160 °C;  $R_f$  0.49 (PE/EA, 5:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 - 7.85 (m, 1H), 7.76 - 7.69 (m, 3H), 7.26 - 7.23 (m, 2H), 7.16 - 7.08 (m, 5H), 7.00 - 6.95 (m, 2H), 5.47 (d,  $J = 10.4$  Hz, 1H), 4.86 (t,  $J = 10.4$  Hz, 1H), 4.64 (d,  $J = 12.4$  Hz, 1H), 4.61 - 4.58 (m, 1H), 4.45 (d,  $J = 12.4$  Hz, 1H), 4.30 - 4.21 (m, 3H), 3.51 - 3.44 (m, 1H), 2.24 (s, 3H), 1.20 (s, 9H), 1.08 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 167.6, 138.1, 137.1, 134.2, 134.0, 132.9, 131.7, 129.7, 128.5, 128.4, 128.1, 128.0, 123.7, 123.3, 84.1, 78.4, 75.6, 71.4, 66.3, 62.8, 51.2, 21.2; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{36}\text{H}_{43}\text{NO}_6\text{SSi}$  668.2478; Found: 668.2473.

***p*-Methoxyphenyl 2, 3-di-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-6-*O*-(*p*-methoxyphenyl)-1-thio- $\beta$ -D-galactopyranoside (D15)**

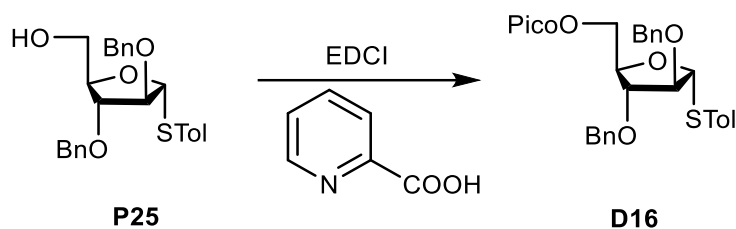


Compound **P23** <sup>[36]</sup> (1.5 g, 2.5 mmol) was dissolved in a solution of  $\text{BH}_3$  in THF (1 mol/L, 25 mL, 25 mmol), then treated with boron trifluoride diethyl etherate (0.3 mL, 2.5 mmol) at 0 °C. The reaction mixture was stirred at 0 °C until TLC analysis confirmed total consumption of the starting material.  $\text{Et}_3\text{N}$  was added to quench the reaction and then methanol was dropped until effervescence ceased. The solution was concentrated under

reduced pressure to provide the syrup, which was subjected to chromatographic purification (PE: EA, 2:1) to give **P24** (1.23 g, 82%). White solid (from PE-EA), mp 77°C;  $R_f$  = 0.5 (PE/EA, 2:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J$  = 8.0 Hz, 2H), 7.41 (d,  $J$  = 7.3 Hz, 2H), 7.38 - 7.29 (m, 8H), 7.26 - 7.23 (m, 2H), 7.03 (d,  $J$  = 8.0 Hz, 2H), 6.91 - 6.85 (m, 2H), 4.91 - 4.82 (m, 2H), 4.80 - 4.73 (m, 3H), 4.61 - 4.56 (m, 2H), 3.92 (dd,  $J$  = 10.0, 8.8 Hz, 1H), 3.84 - 3.76 (m, 5H), 3.59 (dd,  $J$  = 9.2, 2.4 Hz, 1H), 3.52 - 3.45 (m, 1H), 3.43 - 3.36 (m, 1H), 2.30 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 138.4, 138.3, 137.5, 132.3, 130.5, 130.3, 130.0, 129.7, 128.6, 128.5, 128.4, 127.9, 127.9, 127.8, 113.9, 88.3, 84.4, 78.8, 77.8, 75.8, 73.8, 73.2, 72.8, 62.4, 55.4, 21.2; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{35}\text{H}_{38}\text{O}_6\text{S}$  609.2287; Found: 609.2286.

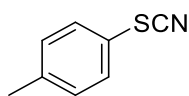
To a solution of **P24** (587 mg, 1 mmol) in dried  $\text{CH}_2\text{Cl}_2$  (20 mL) was added imidazole (82 mg, 1.2 mmol). After stirring at room temperature for 10 min, *t*-butyldimethylchlorosilane (181 mg, 1.2 mmol) was added, and the mixture was stirred at room temperature for another 3 h. The mixture was concentrated under vacuum, and the residue was purified by silica gel column chromatography (EtOAc/hexane 1:15) to give **D15** (616 mg, 88%) as a colorless oil.  $R_f$  0.5 (PE/EA, 15:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J$  = 8.0 Hz, 2H), 7.42 - 7.38 (m, 2H), 7.37 - 7.25 (m, 10H), 7.03 - 6.96 (m, 2H), 6.89 - 6.84 (m, 2H), 4.90 (d,  $J$  = 10.8 Hz, 1H), 4.80 (d,  $J$  = 10.0 Hz, 1H), 4.77 - 4.69 (m, 3H), 4.60 - 4.54 (m, 2H), 3.95 - 3.87 (m, 2H), 3.82 (s, 3H), 3.78 - 3.66 (m, 2H), 3.58 (dd,  $J$  = 9.2, 2.8 Hz, 1H), 3.41 (t,  $J$  = 6.8 Hz, 1H), 2.30 (s, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 138.7, 138.6, 137.1, 132.1, 131.3, 130.7, 129.7, 129.5, 128.5, 128.5, 128.4, 127.8, 127.7, 113.7, 88.2, 84.4, 79.1, 77.6, 75.7, 74.2, 73.2, 72.9, 61.8, 55.4, 26.1, 21.2, 18.3, -5.2, -5.3; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{41}\text{H}_{52}\text{O}_6\text{SSi}$  723.3152; Found: 723.3157.

***p*-Methylphenyl 2, 3-di-*O*-benzyl -6-*O*-picolinoyl -1-thio- $\alpha$ -D-arabinofuranoside (D16)**



2-Picolinic acid (246 mg, 2.0 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI, 403 mg, 2.1 mmol), and 4-dimethylaminopyridine (24 mg, 0.2 mmol) were added to a solution of **P25**<sup>[37]</sup> (872 mg, 2.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and the resulting mixture was stirred under nitrogen for 1 h at room temperature. The reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> and washed with brine. The organic phase was separated, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography (3:1, PE/EA) to afford compound as a brown oil (920 mg, 85%). *R<sub>f</sub>* 0.40 (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH, 20:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.75 (d, *J* = 4.0 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.69 (td, *J* = 7.6, 2.0 Hz, 1H), 7.44 (ddd, *J* = 8.0, 4.8, 1.2 Hz, 1H), 7.42 - 7.38 (m, 2H), 7.38 - 7.25 (m, 10H), 7.13 - 7.05 (m, 2H), 5.55 (d, *J* = 2.8 Hz, 1H), 4.66 - 4.54 (m, 6H), 4.51 (d, *J* = 11.6 Hz, 1H), 4.15 (t, *J* = 2.8 Hz, 1H), 4.09 - 4.03 (m, 1H), 2.31 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.7, 150.0, 147.7, 137.7, 137.5, 137.3, 137.1, 132.4, 130.7, 129.8, 128.6, 128.5, 128.1, 128.0, 128.0, 127.0, 125.5, 90.9, 88.4, 83.9, 79.2, 72.5, 72.3, 64.6, 21.2. HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>32</sub>H<sub>31</sub>NO<sub>5</sub>S 564.1821; found 564.1828.

#### Characterization of *p*-tolyl thiocyanate as a byproduct driving from glycosylation



The byproduct was isolated as a colorless oil from the reaction mixture through column chromatography (PE: EA, 70:1) over silica gel.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 - 7.40 (m, 2H), 7.25 - 7.22 (m, 2H), 2.37 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.4, 131.1, 130.9, 120.7, 111.3(SCN), 21.3. These spectroscopic data are identical with those previously reported. <sup>[38]</sup>

#### General procedures for glycosidation products

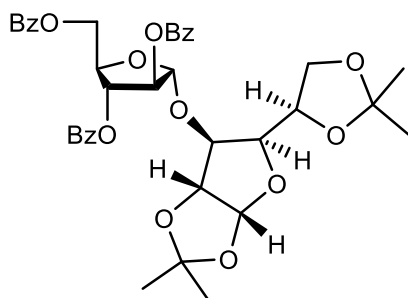
To a solution of alcohol (0.12 mmol) and thioglycoside (0.1 mmol) in anhydrous DCM



(2 mL) containing freshly activated 4 Å molecular sieves and 2, 4, 6-tri-*tert*-butylpyrimidine (TTBP, 0.1 mmol) DFCT(0.12 mmol for thiofuranosyl donors and 0.2 mmol for thiopyransoyl donors) was added and stirred at room temperature until TLC analysis shows the thorough consumption of thioglycoside. The reaction mixture was then filtered and concentrated under reduced pressure. The resultant residue was purified by flash chromatography to provide the goal glycoside. All the solid products were subjected to crystallization or recrystallization before their melting points were measured.

### Characterization of glycosylation products (G1-44)

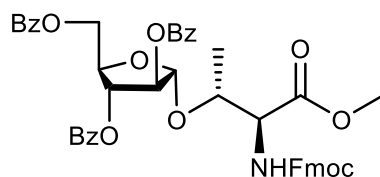
#### (2', 3', 5'-Tri-*O*-benzoyl- $\alpha$ -D-arabinofuranosyl)-(1 $\rightarrow$ 3)-1, 2, 5, 6-di-*O*-isopropylidene- $\alpha$ -D-glucofuranoside (G1)



Yield: 69 mg (98%); colorless oil.  $R_f$  = 0.38 (PE/EA 6:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 - 8.04 (m, 4H), 8.02 - 7.97 (m, 2H), 7.64 - 7.55 (m, 2H), 7.55 - 7.50 (m, 1H), 7.49 - 7.44 (m, 2H), 7.43 - 7.37 (m, 2H), 7.36 - 7.30 (m, 2H), 5.92 (d,  $J$  = 3.2 Hz, 1H), 5.62 - 5.58 (m, 2H), 5.57 (s, 1H), 4.83 (dd,  $J$  = 12.0, 3.6 Hz, 1H), 4.70 (dd,  $J$  = 12.0, 5.2 Hz, 1H), 4.66 - 4.61 (m, 2H), 4.44 - 4.37 (m, 2H), 4.15 (dd,  $J$  = 8.4, 6.0 Hz, 1H), 4.11 (dd,  $J$  = 8.8, 2.4 Hz, 1H), 4.01 (dd,  $J$  = 8.8, 5.2 Hz, 1H), 1.51 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H), 1.20 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 165.8, 165.3, 133.8, 133.7, 133.3, 130.0, 129.9, 129.7, 129.1, 129.0, 128.7, 128.7, 128.5, 112.3, 109.4, 106.5, 105.5, 84.3, 81.8, 81.7, 81.5, 79.7, 77.8, 72.3, 67.8, 63.9, 27.0, 26.9, 26.4, 25.1; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{38}\text{H}_{40}\text{O}_{13}$  727.2367; Found: 727.2364.

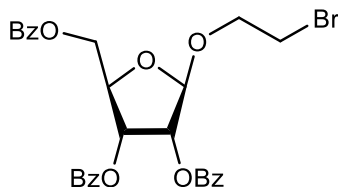
#### *O*-(2, 3, 5-tri-*O*-benzoyl- $\alpha$ -D-arabinofuranosyl)-*N*-9-fluorenylmethyloxycarbonyl-*L*-threonine methyl ester (G2)



Yield: 77 mg (96%); colorless oil.  $R_f = 0.55$  (PE/EA, 3:1)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 - 8.08 (m, 2H), 8.08 - 8.04 (m, 2H), 8.01 (dd,  $J = 8.0, 1.5$  Hz, 2H), 7.76 (d,  $J = 7.6$  Hz, 2H), 7.64 - 7.61 (m, 2H), 7.59 - 7.54 (m, 2H), 7.53 - 7.50 (m, 1H), 7.47 - 7.37 (m, 6H), 7.36 - 7.31 (m, 2H), 7.31 - 7.26 (m, 2H), 5.68 (d,  $J = 9.2$  Hz, 1H), 5.60 (dd,  $J = 5.2, 1.8$  Hz, 1H), 5.42 (d,  $J = 1.8$  Hz, 1H), 5.31 (s, 1H), 4.81 (dd,  $J = 11.6, 3.6$  Hz, 1H), 4.72 - 4.62 (m, 2H), 4.55 - 4.43 (m, 3H), 4.37 (dd,  $J = 10.4, 7.6$  Hz, 1H), 4.25 (t,  $J = 7.6$  Hz, 1H), 3.79 (s, 3H), 1.39 (d,  $J = 6.3$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 166.3, 165.8, 165.6, 156.8, 144.0, 143.8, 141.4, 133.8, 133.7, 133.3, 130.0, 130.0, 129.9, 129.7, 129.1, 129.0, 128.7, 128.7, 128.5, 127.8, 127.2, 125.3, 125.2, 120.1, 106.5, 82.5, 81.0, 77.6, 75.5, 67.4, 63.8, 58.9, 52.9, 47.2, 18.6; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{46}\text{H}_{41}\text{NO}_{12}$  822.2527; Found: 822.2515.

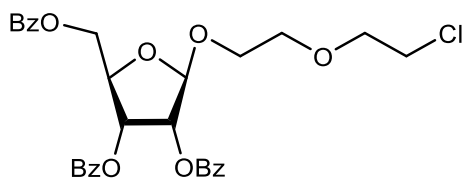
### 2-Bromoethyl 2, 3, 5-tri-*O*-benzoyl- $\beta$ -D-ribofuranoside (G3)



Yield: 51 mg (89%); colorless oil.  $R_f = 0.47$  (PE/EA, 4:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 - 8.05 (m, 2H), 8.05 - 8.00 (m, 2H), 7.92 - 7.87 (m, 2H), 7.61 - 7.49 (m, 3H), 7.46 - 7.37 (m, 4H), 7.32 (t,  $J = 7.6$  Hz, 2H), 5.89 (dd,  $J = 6.4, 4.8$  Hz, 1H), 5.74 (d,  $J = 4.8$  Hz, 1H), 5.32 (s, 1H), 4.79 - 4.72 (m, 2H), 4.62 - 4.53 (m, 1H), 4.07 (dt,  $J = 10.8, 6.4$  Hz, 1H), 3.82 (dt,  $J = 10.8, 6.4$  Hz, 1H), 3.43 - 3.38 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 165.5, 165.3, 133.6, 133.5, 133.3, 129.9, 129.8, 129.8, 129.3, 129.0, 128.6, 128.5, 105.7, 79.4, 75.6, 72.4, 68.4, 64.9, 29.8; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{28}\text{H}_{25}\text{BrO}_8$  591.0631; Found: 591.0636.

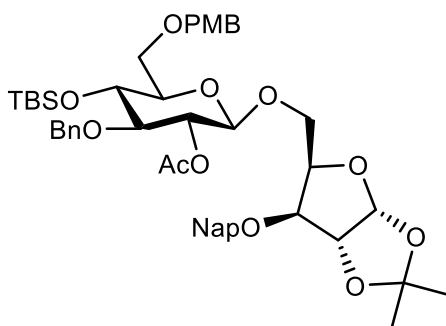
### 2-(2-Chloroethoxy)ethyl 2, 3, 5-tri-*O*-benzoyl- $\beta$ -D-ribofuranoside (G4)



Yield: 53 mg (94%); colorless oil.  $R_f = 0.40$  (PE/EA, 5:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 - 8.04 (m, 2H), 8.04 - 8.00 (m, 2H), 7.91 - 7.85 (m, 2H), 7.60 - 7.47 (m, 3H), 7.45 - 7.36 (m, 4H), 7.34 - 7.28 (m, 2H), 5.89 (dd,  $J = 6.4, 4.8$  Hz, 1H), 5.73 (d,  $J = 4.8$  Hz, 1H), 5.34 (s, 1H), 4.77 - 4.70 (m, 2H), 4.59 - 4.51 (m, 1H), 3.93 - 3.86 (m, 1H), 3.77 - 3.66 (m, 3H), 3.65 - 3.57 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 165.5, 165.3, 133.6, 133.5, 133.2, 129.9, 129.8, 129.3, 129.1, 128.6, 128.5, 128.4, 105.7, 79.2, 75.6, 72.7, 71.5, 70.3, 67.4, 65.1, 42.8; HRMS (ESI):  $m/z$  [ $\text{M} + \text{Na}$ ] $^+$  calcd for  $\text{C}_{30}\text{H}_{29}\text{ClO}_9$  591.1398; Found: 591.1397.

**(2'-*O*-acetyl-3'-*O*-benzyl- 4'-*O*-*tert*-butyldimethylsilyl- 6'-*O*-*p*-methoxybenzyl-  $\beta$ -D-glucopyranosyl)-(1 $\rightarrow$ 5)- 1, 2-*O*-isopropylidene-3-*O*-naphthylmethyl- $\alpha$ -D-xylofuranoside (G5)**

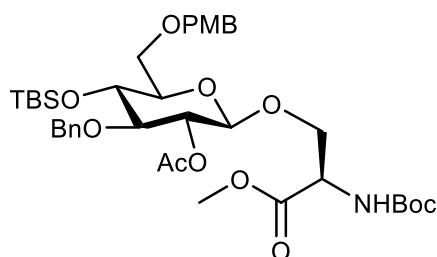


Yield: 66 mg (77%); colorless oil.  $R_f = 0.40$  (PE/EA, 3:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 - 7.77 (m, 3H), 7.74 (s, 1H), 7.49 - 7.44 (m, 2H), 7.42 (dd,  $J = 8.4, 1.7$  Hz, 1H), 7.32 - 7.27 (m, 2H), 7.26 - 7.23 (m, 3H), 7.21 (d,  $J = 8.4$  Hz, 2H), 6.82 - 6.77 (m, 2H), 5.93 (d,  $J = 3.6$  Hz, 1H), 4.99 (dd,  $J = 9.2, 8.0$  Hz, 1H), 4.75 (d,  $J = 12.4$  Hz, 1H), 4.72 - 4.66 (m, 2H), 4.63 (d,  $J = 11.6$  Hz, 1H), 4.58 (d,  $J = 4.0$  Hz, 1H), 4.55 - 4.49 (m, 2H), 4.38 (d,  $J = 11.6$  Hz, 1H), 4.30 (td,  $J = 6.4, 2.8$  Hz, 1H), 4.15 (dd,  $J = 11.2, 5.6$  Hz, 1H), 3.99 (d,  $J = 3.2$  Hz, 1H), 3.86 (dd,  $J = 11.2, 6.4$  Hz, 1H), 3.73 (s, 3H), 3.70 (dd,  $J = 10.7, 2.0$  Hz, 1H), 3.64 (t,  $J = 8.8$  Hz, 1H), 3.52 (dd,  $J = 10.7, 6.0$  Hz, 1H), 3.46 (t,  $J = 8.9$  Hz, 1H), 3.41 (ddd,  $J = 8.3, 6.0, 1.9$  Hz, 1H), 1.89 (s, 3H), 1.45 (s, 3H), 1.29 (s, 3H), 0.83 (s, 9H), -0.03 (s, 3H), -0.04 (s, 3H);  $^{13}\text{C}$  NMR

(101 MHz, CDCl<sub>3</sub>)  $\delta$  169.8, 159.2, 138.5, 135.2, 133.3, 133.2, 130.5, 129.3, 128.5, 128.4, 128.1, 127.8, 127.5, 127.4, 126.7, 126.3, 126.1, 125.8, 113.8, 111.8, 105.3, 101.6, 83.4, 82.7, 81.8, 79.9, 76.8, 74.9, 73.8, 73.2, 72.5, 71.1, 69.1, 67.3, 55.3, 27.0, 26.5, 26.0, 21.0, 18.1, -3.7, -4.7; HRMS (ESI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>48</sub>H<sub>62</sub>O<sub>12</sub>Si 881.3909; Found: 881.3910.

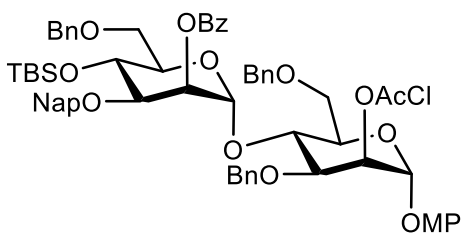
***O*-(2-*O*-acetyl-3-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-6-*O*-*p*-methoxybenzyl-  $\beta$ -D-glucopyranosyl)-*N*-(*tert*-butyloxycarbonyl)-*L*-serine methyl ester (G6)**



Yield: 63 mg (84%); colorless oil.  $R_f$  = 0.70 (PE/EA, 3:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 - 7.22 (m, 7H), 6.89 - 6.84 (m, 2H), 5.35 (d,  $J$  = 8.4 Hz, 1H), 4.94 (dd,  $J$  = 9.0, 8.8 Hz, 1H), 4.69 (d,  $J$  = 12.0 Hz, 1H), 4.61 (d,  $J$  = 12.0 Hz, 1H), 4.56 (d,  $J$  = 11.6 Hz, 1H), 4.46 - 4.35 (m, 3H), 4.21 (dd,  $J$  = 10.4, 3.6 Hz, 1H), 3.81 - 3.74 (m, 4H), 3.70 (s, 3H), 3.70 - 3.61 (m, 2H), 3.53 (dd,  $J$  = 10.7, 5.8 Hz, 1H), 3.47 - 3.38 (m, 2H), 1.90 (s, 3H), 1.43 (s, 9H), 0.82 (s, 9H), -0.03 (s, 3H), -0.05 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  170.7, 169.6, 159.3, 155.6, 138.4, 130.4, 129.4, 128.4, 127.5, 127.4, 113.9, 101.1, 83.3, 80.1, 74.8, 73.3, 73.2, 70.9, 69.0, 68.8, 55.4, 54.0, 52.7, 28.5, 26.0, 20.9, 18.1, -3.7, -4.7; HRMS (ESI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>38</sub>H<sub>57</sub>NO<sub>12</sub>Si 770.3548; Found: 770.3555.

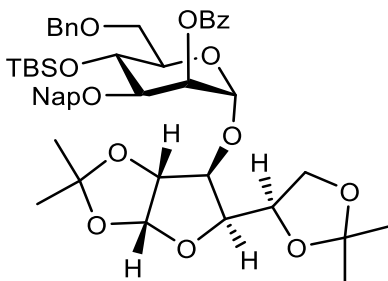
***p*-Methoxyphenyl (2'-*O*-benzoyl-6'-*O*-benzyl-4'-*O*-*tert*-butyldimethylsilyl-3'-*O*-naphthylmethyl - $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 4)-3, 6-di-*O*-benzyl-2-*O*-chloroacetyl- $\alpha$ -D-mannopyranoside (G7)**



Yield: 105 mg (91%); colorless oil.  $R_f = 0.46$  (Toluene/EA, 25:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 - 8.02 (m, 2H), 7.80 - 7.75 (m, 1H), 7.71 (d,  $J = 8.4$  Hz, 1H), 7.67 - 7.56 (m, 3H), 7.44 - 7.27 (m, 17H), 7.24 - 7.16 (m, 3H), 7.11 - 7.06 (m, 2H), 6.89 - 6.82 (m, 2H), 5.77 (t,  $J = 2.8$  Hz, 1H), 5.59 - 5.56 (m, 2H), 5.47 (d,  $J = 2.0$  Hz, 1H), 4.96 (d,  $J = 11.2$  Hz, 1H), 4.66 (d,  $J = 10.8$  Hz, 1H), 4.64 - 4.53 (m, 6H), 4.27 - 4.18 (m, 3H), 4.09 (s, 2H), 4.07 - 4.02 (m, 1H), 3.86 - 3.75 (m, 8H), 3.64 (dd,  $J = 10.8, 2.0$  Hz, 1H), 0.82 (s, 9H), -0.02 (s, 3H), -0.07 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 165.5, 155.5, 150.1, 138.8, 138.5, 137.0, 135.5, 133.3, 133.2, 133.0, 130.2, 130.0, 128.8, 128.6, 128.4, 128.1, 128.0, 127.8, 127.7, 127.4, 126.7, 126.1, 125.9, 125.7, 118.4, 114.8, 99.4, 96.7, 78.3, 77.7, 74.4, 73.4, 73.3, 72.3, 71.9, 71.7, 71.1, 69.9, 69.7, 69.4, 68.6, 67.6, 55.8, 40.8, 26.1, 18.3, -3.8, -5.1; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{66}\text{H}_{73}\text{ClO}_{14}\text{Si}$  1175.4356; Found: 1175.4353.

**(2'-*O*-benzoyl- 6'-*O*-benzyl-4'-*O*-*tert*-butyldimethylsilyl-3'-*O*-naphthylmethyl-  $\alpha$ -D-mannopyranosyl)- (1  $\rightarrow$  3)-1, 2:5, 6-di-*O*-isopropylidene- $\alpha$ -D-glucofuranoside (G8)**

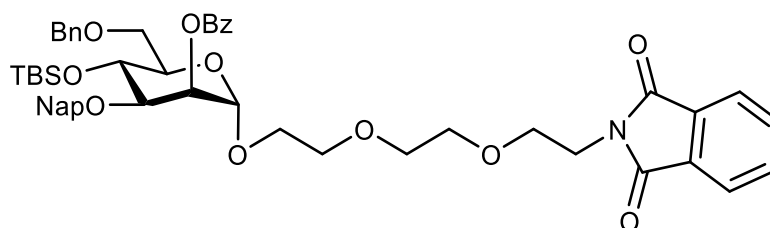


Yield: 75 mg (86%); colorless oil.  $R_f = 0.29$  (PE/EA, 10:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 - 8.00 (m, 2H), 7.77 - 7.72 (m, 1H), 7.67 (d,  $J = 8.4$  Hz, 1H), 7.63 - 7.55 (m, 3H), 7.42 - 7.28 (m, 10H), 5.93 (d,  $J = 3.6$  Hz, 1H), 5.68 - 5.64 (m, 1H), 5.28 - 5.23 (m, 1H), 4.90 (d,  $J = 11.2$  Hz, 1H), 4.81 (d,  $J = 3.6$  Hz, 1H), 4.64 (s, 2H), 4.60 (d,  $J = 11.2$  Hz, 1H), 4.34 - 4.31 (m, 1H), 4.26 - 4.21 (m, 1H), 4.18 (t,  $J = 9.2$  Hz, 1H), 4.13 - 4.08 (m, 2H), 3.98 (dd,  $J = 8.4, 5.6$  Hz, 1H), 3.89 - 3.80 (m, 4H), 1.50 (s, 3H), 1.38 (s, 3H), 1.31 - 1.28 (m, 3H), 1.26 (s, 3H), 0.81 (s, 9H), -0.01 (s, 3H), -0.06 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 138.6, 135.3, 133.3, 133.3, 133.0, 130.1, 130.0, 128.6, 128.5, 128.0, 127.9, 127.7, 127.6, 127.5, 126.7, 126.0, 126.0, 125.8, 112.1, 109.5, 105.5, 99.2, 83.6, 81.5, 78.2, 77.4, 74.1, 73.5, 72.5, 71.2, 69.8, 68.3, 68.1,

67.8, 27.0, 26.9, 26.3, 26.1, 25.2, 18.4, -3.7, -5.0; HRMS (ESI):  $m/z$   $[M + Na]^+$  calcd for  $C_{49}H_{62}O_{12}Si$  893.3909; Found: 893.3906.

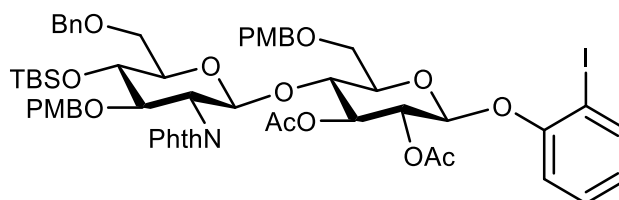
**2-(2-(2-Phthalimidoethoxy)ethoxy)ethoxy 2-O-benzoyl-6-O-benzyl-4-O-tert-butyltrimethylsilyl-3-O-naphthylmethyl- $\alpha$ -D-mannopyranoside (G9)**



Yield: 78 mg (88%); colorless oil.  $R_f$  = 0.60 (PE/EA, 3:1).

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.05 - 8.00 (m, 2H), 7.85 - 7.80 (m, 2H), 7.76 - 7.71 (m, 1H), 7.69 - 7.61 (m, 4H), 7.59 - 7.53 (m, 2H), 7.40 - 7.27 (m, 10H), 5.68 - 5.65 (m, 1H), 5.01 - 4.97 (m, 1H), 4.92 (d,  $J$  = 11.2 Hz, 1H), 4.69 - 4.57 (m, 3H), 4.20 (t,  $J$  = 8.4 Hz, 1H), 3.93 - 3.88 (m, 3H), 3.87 - 3.72 (m, 6H), 3.65 - 3.57 (m, 7H), 0.80 (s, 9H), -0.02 (s, 3H), -0.08 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  168.4, 165.8, 138.8, 135.7, 134.0, 133.3, 133.2, 132.9, 132.3, 130.2, 130.0, 128.6, 128.4, 127.9, 127.8, 127.7, 127.4, 127.4, 126.5, 125.9, 125.8, 125.7, 123.3, 98.0, 78.4, 77.4, 73.4, 73.1, 70.9, 70.7, 70.3, 69.6, 68.6, 68.1, 68.0, 67.1, 37.4, 26.1, 18.3, -3.7, -5.1; HRMS (ESI):  $m/z$   $[M + Na]^+$  calcd for  $C_{51}H_{59}NO_{11}Si$  912.3755; Found: 912.3761.

***O*-idophenyl (6'-*O*-benzyl-4'-*O*-tert-butyltrimethylsilyl-2'-deoxy-3'-*O*-*p*-methoxybenzyl-2-phthalimido- $\beta$ -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3-di-*O*-acetyl-6-*O*-*p*-methoxybenzyl- $\beta$ -D-glucopyranoside (G10)**

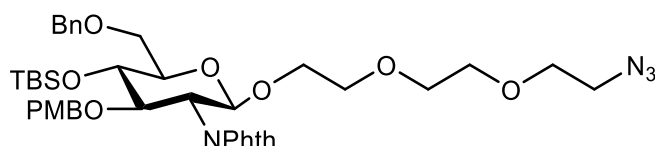


Yield: 108 mg (90%); colorless oil.  $R_f$  = 0.25 (PE/EA, 3:1).

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.71 (dd,  $J$  = 7.9, 1.6 Hz, 1H), 7.69 - 7.59 (m, 4H), 7.38 - 7.30 (m, 4H), 7.22 (tt,  $J$  = 7.2, 2.0 Hz, 1H), 7.14 - 7.08 (m, 3H), 6.92 (dd,  $J$  = 8.3, 1.4 Hz, 1H), 6.90 - 6.85 (m, 2H), 6.82 - 6.77 (m, 2H), 6.73 (td,  $J$  = 7.6, 1.4 Hz, 1H), 6.41 - 6.36 (m, 2H), 5.26 - 5.19 (m, 3H), 4.85 - 4.77 (m, 1H), 4.69 (d,  $J$  = 12.2 Hz, 1H), 4.61

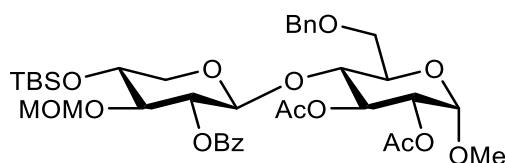
(d,  $J = 12.2$  Hz, 1H), 4.53 (d,  $J = 12.2$  Hz, 1H), 4.29 (d,  $J = 11.2$  Hz, 1H), 4.24 - 4.16 (m, 2H), 4.13 (dd,  $J = 10.8, 8.0$  Hz, 1H), 4.04 (dd,  $J = 10.8, 8.0$  Hz, 1H), 3.98 (ddd,  $J = 9.6, 6.4, 3.2$  Hz, 1H), 3.78 (s, 3H), 3.74 - 3.68 (m, 2H), 3.58 (s, 3H), 3.58 - 3.46 (m, 4H), 3.35 (dd,  $J = 11.0, 5.3$  Hz, 1H), 2.06 (s, 3H), 2.00 (s, 3H), 0.88 (s, 9H), 0.10 (s, 3H), 0.05 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.3, 169.6, 159.2, 158.6, 156.3, 139.5, 138.3, 133.8, 131.7, 130.6, 130.3, 129.6, 129.2, 129.0, 128.5, 127.6, 127.4, 124.6, 123.2, 116.1, 113.8, 113.4, 99.7, 96.9, 87.0, 80.9, 76.1, 75.2, 75.1, 73.6, 73.1, 72.7, 72.5, 71.5, 69.1, 67.9, 56.4, 55.4, 54.9, 26.1, 21.3, 21.0, 18.1, -3.6, -4.3; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{59}\text{H}_{68}\text{INO}_{16}\text{Si}$  1224.3250; Found: 1224.3229.

**2-[2-(2-Azidoethoxy)ethoxy]ethyl 6-*O*-benzyl-4-*O*-*tert*-butyldimethylsilyl-2-deoxy-3-*O*-*p*-methoxybenzyl-2-phthalimido- $\beta$ -D-glucopyranoside (G11)**



Yield: 65 mg (82%); white solid (from PE-EA), mp 51 °C.  $R_f = 0.30$  (PE/EA, 2:1).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 - 7.60 (m, 4H), 7.38 - 7.31 (m, 4H), 7.30 - 7.26 (m, 11H), 6.92 - 6.87 (m, 2H), 6.40 - 6.34 (m, 2H), 5.17 (d,  $J = 8.2$  Hz, 1H), 4.73 - 4.66 (m, 2H), 4.54 (d,  $J = 12.4$  Hz, 1H), 4.21 (d,  $J = 12.4$  Hz, 1H), 4.18 - 4.08 (m, 2H), 3.90 - 3.83 (m, 1H), 3.80 - 3.76 (m, 1H), 3.70 - 3.57 (m, 4H), 3.56 (s, 3H), 3.50 - 3.43 (m, 4H), 3.36 - 3.23 (m, 6H), 0.87 (s, 9H), 0.11 (s, 3H), 0.04 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.6, 138.5, 133.6, 131.8, 130.7, 129.1, 128.5, 127.7, 127.7, 123.1, 113.3, 98.2, 80.8, 76.3, 75.2, 73.4, 73.1, 70.6, 70.5, 70.1, 70.0, 69.4, 68.8, 56.1, 54.9, 50.7, 26.0, 18.1, -3.6, -4.4; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{41}\text{H}_{54}\text{N}_4\text{O}_{10}\text{Si}$  813.3507; Found: 813.3498.

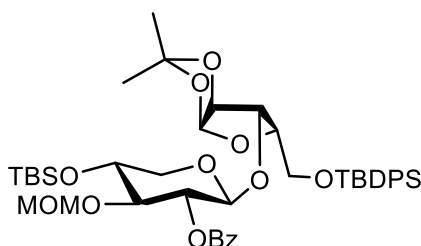
**Methyl (2'-*O*-benzoyl-4'-*O*-*tert*-butyldimethylsilyl-3'-*O*-methoxymethyl- $\beta$ -D-xylopyranosyl)-(1 $\rightarrow$ 4)- 2, 3-di-*O*-acetyl- 6-*O*-benzyl-  $\alpha$ -D-glucopyranoside (G12)**



Yield: 74 mg (97%); colorless oil.  $R_f = 0.30$  (PE/EA, 4:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 - 8.01 (m, 2H), 7.59 - 7.53 (m, 1H), 7.46 - 7.37 (m, 4H), 7.35 - 7.28 (m, 3H), 5.40 (t,  $J = 9.2$  Hz, 1H), 5.02 (dd,  $J = 9.6, 7.6$  Hz, 1H), 4.85 - 4.79 (m, 3H), 4.55 - 4.50 (m, 2H), 4.42 (d,  $J = 7.6$  Hz, 1H), 4.28 (d,  $J = 12.0$  Hz, 1H), 3.86 (t,  $J = 9.2$  Hz, 1H), 3.80 - 3.70 (m, 2H), 3.63 - 3.57 (m, 2H), 3.53 (dd,  $J = 9.6, 8.0$  Hz, 1H), 3.39 - 3.33 (m, 1H), 3.28 (s, 3H), 3.19 - 3.07 (m, 1H), 2.95 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 0.89 (s, 9H), 0.08 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 169.9, 165.0, 138.2, 133.2, 130.2, 130.0, 128.6, 128.5, 128.0, 127.9, 101.9, 98.2, 96.9, 81.4, 76.2, 73.5, 72.8, 71.5, 71.3, 70.5, 69.6, 67.6, 66.2, 56.0, 55.3, 25.8, 21.1, 20.9, 18.0, -4.6, -4.7; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{38}\text{H}_{54}\text{O}_{14}\text{Si}$  785.3181; Found: 785.3080.

**(2'-*O*-benzoyl-4'-*O*-*tert*-butyldimethylsilyl-3'-*O*-methoxymethyl- $\beta$ -D-xylopyranosyl)-(1 $\rightarrow$ 3)-5-*O*-*tert*-butyldiphenylsilyl-1, 2-*O*-isopropylidene- $\alpha$ -xylofuranoside (G13)**



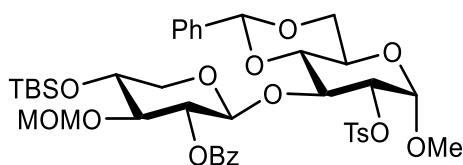
Yield: 78 mg (95%); White solid (from PE-ethyl ether), mp 79°C;  $R_f = 0.35$  (PE/EA, 8:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 - 8.06 (m, 2H), 7.74 - 7.66 (m, 4H), 7.59 - 7.54 (m, 1H), 7.46 - 7.35 (m, 8H), 5.34 (d,  $J = 4.0$  Hz, 1H), 5.03 (dd,  $J = 8.4, 7.2$  Hz, 1H), 4.84 (d,  $J = 6.8$  Hz, 1H), 4.65 - 4.55 (m, 2H), 4.32 - 4.21 (m, 3H), 3.97 (dd,  $J = 10.0, 6.8$  Hz, 1H), 3.85 - 3.68 (m, 4H), 3.23 - 3.15 (m, 1H), 3.06 (s, 3H), 1.41 (s, 3H), 1.11 (s, 3H), 1.04 (s, 9H), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 135.8, 133.9, 133.7, 133.4, 130.1, 129.7, 129.7, 128.6, 127.8, 127.7, 111.9, 104.9, 100.4, 97.9, 82.9, 80.6, 80.4, 80.3, 72.5, 71.3, 66.0, 61.0, 55.9, 26.9, 26.1, 25.8, 19.4, 18.1, -4.6, -4.7; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{44}\text{H}_{62}\text{O}_{11}\text{Si}_2$  845.3729; Found: 845.3730.

**Methyl (2'-*O*-benzoyl-4'-*O*-*tert*-butyldimethylsilyl-3'-*O*-methoxymethyl-  $\beta$ -D-**



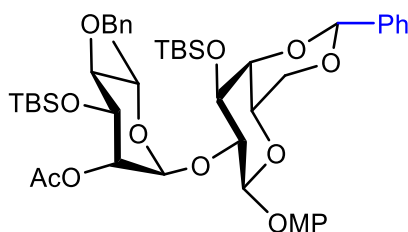
**xylopyranosyl)-(1→3)-4, 6-*O*-benzylidene-2-*O*-*p*-toluenesulphonyl- $\alpha$ -D-glucopyranoside (G14)**



Yield: 69 mg (83%); White solid (from PE-CH<sub>2</sub>Cl<sub>2</sub>), mp 61 °C. *R*<sub>f</sub> = 0.50 (PE/EA, 4:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.13 - 8.08 (m, 2H), 7.77 - 7.72 (m, 2H), 7.58 - 7.52 (m, 1H), 7.50 - 7.46 (m, 2H), 7.45 - 7.40 (m, 2H), 7.37 - 7.32 (m, 3H), 7.29 - 7.26 (m, 2H), 5.49 (s, 1H), 4.90 (dd, *J* = 8.0, 6.4 Hz, 1H), 4.83 - 4.75 (m, 3H), 4.59 (d, *J* = 6.8 Hz, 1H), 4.35 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.29 - 4.21 (m, 2H), 3.87 - 3.76 (m, 2H), 3.72 - 3.65 (m, 2H), 3.62 (t, *J* = 7.6 Hz, 1H), 3.55 (t, *J* = 9.2 Hz, 1H), 3.23 (s, 3H), 3.04 (s, 3H), 3.03 - 2.96 (m, 1H), 2.40 (s, 3H), 0.81 (s, 9H), 0.07 (d, *J* = 0.98 Hz, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  165.7, 145.1, 137.3, 133.5, 133.0, 130.6, 130.3, 130.3, 129.9, 129.2, 129.2, 128.3, 128.3, 128.2, 128.0, 126.3, 101.8, 100.3, 98.1, 97.8, 80.3, 79.5, 78.8, 73.3, 72.2, 70.8, 69.0, 65.2, 62.3, 55.9, 55.7, 25.8, 25.8, 21.8, 18.0, -4.7, -4.7; HRMS (ESI): *m/z* [M + Na]<sup>+</sup> calcd for C<sub>41</sub>H<sub>54</sub>O<sub>14</sub>SSi 853.2902; Found: 853.2893.

***p*-Methoxyphenyl (2'-*O*-acetyl -4'-*O*-benzyl-3'-*O*-*tert*-butyldimethylsilyl- $\alpha$ -L-rhamnopyranosyl)-(1→2)-4, 6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl- $\beta$ -D-galactopyranoside (G15)**

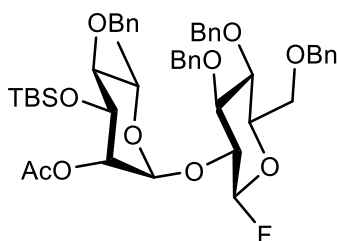


Yield: 81 mg (92%); White solid (from PE-ethyl ether), mp 101°C. *R*<sub>f</sub> = 0.60 (PE/EA, 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56 - 7.51 (m, 2H), 7.39 - 7.26 (m, 8H), 7.09 - 7.04 (m, 2H), 6.80 - 6.74 (m, 2H), 5.51 (s, 1H), 5.24 (dd, *J* = 3.6, 2.0 Hz, 1H), 5.18 (d, *J* = 2.0 Hz, 1H), 4.87 - 4.82 (m, 2H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.42 - 4.33 (m, 2H), 4.24 (dd, *J* = 9.2, 8.0 Hz, 1H), 4.12 - 4.06 (m, 2H), 4.02 (dd, *J* = 9.2, 3.2 Hz, 1H), 3.95 - 3.91 (m,

1H), 3.76 (d,  $J = 1.1$  Hz, 3H), 3.50 (s, 1H), 3.32 (t,  $J = 9.2$  Hz, 1H), 2.10 (d,  $J = 0.8$  Hz, 3H), 1.28 (d,  $J = 6.2$  Hz, 3H), 0.91 -0.87 (m, 9H), 0.85 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H), 0.07 (s, 3H), -0.03 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 155.3, 152.0, 139.1, 137.8, 128.9, 128.2, 128.2, 127.3, 127.1, 126.3, 118.7, 114.5, 101.3, 100.8, 98.4, 81.5, 76.6, 75.3, 74.8, 73.3, 72.4, 71.1, 69.3, 67.9, 66.7, 55.7, 25.9, 25.8, 21.1, 18.2, 18.0, 17.9, -4.0, -4.6, -4.7, -4.8; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{47}\text{H}_{68}\text{O}_{12}\text{Si}_2$  903.4147; Found: 903.4122.

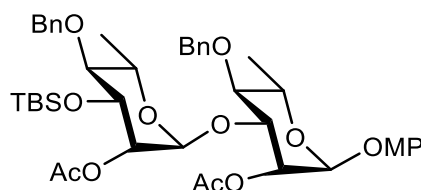
**(2'-*O*-acetyl- 4'-*O*-benzyl-3'-*O*-*tert*-butyldimethylsilyl-  $\alpha$ -L-rhamnopyranosyl)-(1  $\rightarrow$ 2)-3, 4, 6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl fluoride (G16)**



Yield: 74 mg (88%); White powder (from PE-ethyl ether), mp 86°C.  $R_f = 0.50$  (PE/EA, 5:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 - 7.27 (m, 18H), 7.17 - 7.13 (m, 2H), 5.30 - 5.14 (m, 2H), 5.04 - 5.02 (m, 1H), 4.89 (d,  $J = 11.2$  Hz, 1H), 4.86 - 4.75 (m, 3H), 4.66 - 4.59 (m, 2H), 4.58 - 4.52 (m, 2H), 4.06 (dd,  $J = 8.8, 3.6$  Hz, 1H), 3.95 - 3.86 (m, 1H), 3.83 - 3.66 (m, 5H), 3.63 (dd,  $J = 9.6, 3.2$  Hz, 1H), 3.38 (t,  $J = 9.6$  Hz, 1H), 2.11 (s, 3H), 1.28 (d,  $J = 6.3$  Hz, 3H), 0.91 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 138.4, 137.9, 137.8, 137.8, 128.5, 128.5, 128.5, 128.1, 128.0, 128.0, 127.9, 127.8, 108.9, 106.8, 98.9, 83.9, 83.8, 81.2, 78.2, 78.0, 75.6, 75.3, 75.0, 74.9, 73.7, 72.7, 70.9, 68.4, 68.4, 25.9, 21.1, 17.9, 17.7, -4.6, -4.7; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{48}\text{H}_{61}\text{FO}_{10}\text{Si}$  867.3916; Found: 867.3906.

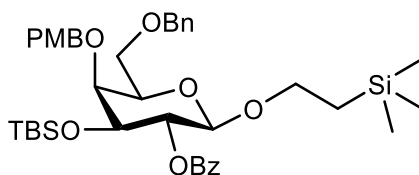
***p*-Methoxyphenyl (2'-*O*-acetyl- 4'-*O*-benzyl-3'-*O*-*tert*-butyldimethylsilyl-  $\alpha$ -L-rhamnopyranosyl)-(1  $\rightarrow$ 3)- 2-*O*-acetyl-4-*O*-benzyl- $\alpha$ -D-rhmnopyranoside (G17)**



Yield: 76 mg (96%); colorless oil.  $R_f = 0.45$  (PE/EA, 8:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 - 7.32 (m, 8H), 7.32 - 7.27 (m, 2H), 6.97 - 6.91 (m, 2H), 6.83 - 6.78 (m, 2H), 5.35 (d,  $J = 2.0$  Hz, 1H), 5.31 (dd,  $J = 3.6, 2.0$  Hz, 1H), 5.22 (dd,  $J = 3.6, 2.0$  Hz, 1H), 5.05 (d,  $J = 2.0$  Hz, 1H), 4.94 - 4.87 (m, 2H), 4.62 (d,  $J = 11.2$  Hz, 2H), 4.32 (dd,  $J = 9.6, 3.6$  Hz, 1H), 4.10 (dd,  $J = 9.2, 3.6$  Hz, 1H), 3.95 - 3.84 (m, 1H), 3.81 - 3.72 (m, 4H), 3.55 (t,  $J = 9.6$  Hz, 1H), 3.37 (t,  $J = 9.2$  Hz, 1H), 2.19 (s, 3H), 2.12 (s, 3H), 1.28 (d,  $J = 6.4$  Hz, 3H), 1.26 (d,  $J = 6.4$  Hz, 3H), 0.88 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 170.3, 155.2, 150.2, 138.7, 138.0, 128.6, 128.4, 128.2, 128.0, 127.8, 127.7, 117.8, 114.7, 99.9, 96.2, 81.2, 80.3, 77.4, 75.6, 75.3, 73.1, 72.4, 70.9, 69.0, 68.5, 55.8, 25.9, 21.2, 21.1, 18.1, 18.0, -4.7; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{43}\text{H}_{58}\text{O}_{12}\text{Si}$  817.3596; Found: 817.3594.

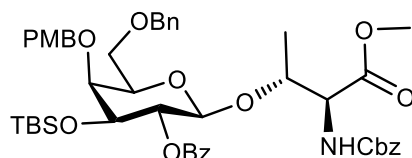
**2'-Trimethylsilylethyl 2-O-benzoyl-6-O-benzyl -3-O-tert-butyldimethylsilyl- 4-O-p-methoxybenzyl- $\beta$ -D-galactopyranoside (G18)**



Yield: 64 mg (90%); White solid (PE-ethyl ether), mp  $57^\circ\text{C}$ .  $R_f = 0.50$  (PE/EA, 10:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 - 8.02 (m, 2H), 7.58 - 7.51 (m, 1H), 7.48 - 7.39 (m, 2H), 7.37 - 7.26 (m, 7H), 6.88 - 6.82 (m, 2H), 5.56 (dd,  $J = 10.0, 8.0$  Hz, 1H), 5.00 (d,  $J = 10.8$  Hz, 1H), 4.52 - 4.40 (m, 4H), 3.98 - 3.89 (m, 2H), 3.81 - 3.76 (m, 4H), 3.71 - 3.59 (m, 3H), 3.52 - 3.43 (m, 1H), 0.90 - 0.75 (m, 11H), 0.11 (s, 3H), -0.08 (s, 3H), -0.13 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 159.2, 138.1, 132.9, 131.1, 130.7, 129.9, 129.8, 128.6, 128.3, 128.0, 127.9, 113.7, 101.1, 76.7, 74.8, 74.7, 73.8, 73.7, 73.0, 69.1, 67.0, 55.4, 25.7, 18.0, 17.9, -1.4, -3.9, -4.9; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{39}\text{H}_{56}\text{O}_8\text{Si}_2$  731.3412; Found: 731.3413.

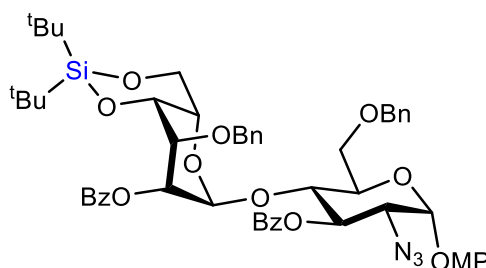
**O-(2-O-benzoyl- 6-O-benzyl-3-O-tert-butyldimethylsilyl-4-O-p-methoxybenzyl-  $\beta$ -D-galactopyranosyl)-N-benzyloxycarbonyl-L-threonine methyl ester (G19)**



Yield: 74 mg (86%); colorless oil.  $R_f = 0.55$  (PE/EA, 3:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 - 8.00 (m, 2H), 7.57 - 7.51 (m, 1H), 7.40 (t,  $J = 7.7$  Hz, 2H), 7.35 - 7.31 (m, 5H), 7.31 - 7.28 (m, 2H), 7.28 - 7.25 (m, 4H), 7.19 - 7.15 (m, 1H), 6.86 (d,  $J = 8.7$  Hz, 2H), 5.71 (d,  $J = 8.8$  Hz, 1H), 5.45 (dd,  $J = 10.0, 8.0$  Hz, 1H), 5.10 - 5.02 (m, 2H), 4.98 (d,  $J = 11.2$  Hz, 1H), 4.47 - 4.42 (m, 2H), 4.37 (s, 2H), 4.34 - 4.26 (m, 1H), 4.21 - 4.16 (m, 1H), 3.93 - 3.87 (m, 1H), 3.79 (s, 3H), 3.76 (d,  $J = 2.7$  Hz, 1H), 3.59 (s, 3H), 3.59 - 3.54 (m, 2H), 3.51 - 3.45 (m, 1H), 1.00 (d,  $J = 6.4$  Hz, 3H), 0.78 (s, 9H), 0.10 (s, 3H), -0.08 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.0, 165.3, 159.2, 156.9, 138.0, 136.5, 133.0, 130.9, 130.3, 129.7, 129.1, 128.6, 128.5, 128.5, 128.3, 128.0, 128.0, 128.0, 127.9, 125.4, 113.7, 100.8, 76.6, 75.5, 75.0, 74.3, 73.6, 73.6, 72.9, 68.4, 66.9, 58.7, 55.4, 52.5, 25.6, 21.6, 17.9, 17.8, -4.0, -4.9; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{47}\text{H}_{59}\text{NO}_{12}\text{Si}$  880.3705; Found: 880.3706.

***p*-Methoxyphenyl (2'-*O*-benzoyl- 3'-*O*-benzyl-4', 6'-*O*-di-*tert*-butylsilylene- $\alpha$ -D-idopyranosyl)- (1  $\rightarrow$  4)-3-*O*-benzoyl-6-*O*-benzyl-2-azido-2-deoxy- $\alpha$ -D-glucopyranoside (G20)**

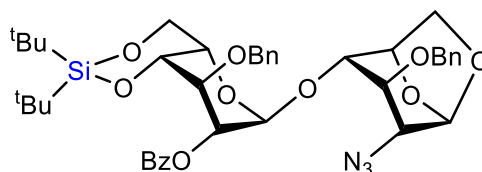


Yield: 93 mg (93%); White solid (from PE-ethyl ether), mp 63°C.  $R_f = 0.55$  (PE/EA, 5:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 - 8.06 (m, 2H), 7.99 - 7.93 (m, 2H), 7.62 - 7.51 (m, 2H), 7.47 (t,  $J = 7.6$  Hz, 2H), 7.36 (t,  $J = 7.6$  Hz, 2H), 7.29 (d,  $J = 4.4$  Hz, 4H), 7.24 - 7.18 (m, 6H), 7.12 - 7.07 (m, 2H), 6.85 - 6.80 (m, 2H), 5.98 (dd,  $J = 10.4, 8.8$  Hz, 1H), 5.54 (d,  $J = 3.6$  Hz, 1H), 5.16 - 5.10 (m, 2H), 4.78 (d,  $J = 12.0$  Hz, 1H), 4.66 (d,  $J = 12.0$  Hz, 1H), 4.46 (d,  $J = 11.6$  Hz, 1H), 4.39 (d,  $J = 11.6$  Hz, 1H), 4.30 (t,  $J = 9.6$  Hz,

1H), 4.09 - 4.03 (m, 2H), 3.85 (d,  $J = 2.4$  Hz, 1H), 3.82 - 3.75 (m, 5H), 3.70 (t,  $J = 4.0$  Hz, 1H), 3.62 (dd,  $J = 11.2, 2.0$  Hz, 1H), 3.55 (dd,  $J = 12.4, 2.4$  Hz, 1H), 3.38 (dd,  $J = 10.4, 3.6$  Hz, 1H), 0.91 (s, 9H), 0.83 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.0, 165.7, 155.6, 150.5, 138.2, 137.7, 133.4, 130.2, 130.0, 129.9, 129.5, 128.6, 128.4, 128.4, 128.3, 127.8, 127.7, 127.7, 127.6, 118.1, 114.8, 99.9, 98.1, 77.3, 74.3, 73.5, 72.0, 71.6, 71.4, 71.0, 69.6, 68.3, 66.4, 65.6, 61.7, 55.8, 27.8, 27.0, 23.1, 20.5; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{55}\text{H}_{63}\text{N}_3\text{O}_{13}\text{Si}$  1024.4028; Found: 1024.4036.

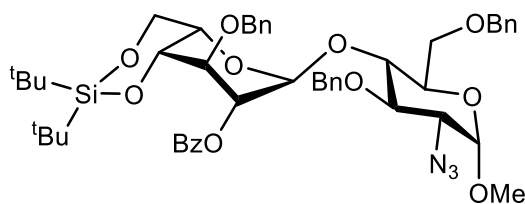
**(2'-*O*-benzoyl- 3'-*O*-benzyl- 4', 6'-*O*-di-*tert*-butylsilylene- $\alpha$ -D-idopyranosyl)-(1 $\rightarrow$ 4)- 1, 6-anhydro-2-azido- 3-*O*-benzyl-2-deoxy-  $\beta$ -D-glucopyranoside (G21)**



Yield: 67 mg (87%); colorless oil.  $R_f = 0.32$  (PE/EA, 8:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 - 8.05 (m, 2H), 7.60 - 7.54 (m, 1H), 7.46 - 7.40 (m, 2H), 7.39 - 7.34 (m, 2H), 7.34 - 7.26 (m, 6H), 7.24 - 7.21 (m, 2H), 5.49 (s, 1H), 5.25 - 5.19 (m, 2H), 4.93 (d,  $J = 11.6$  Hz, 1H), 4.73 - 4.67 (m, 2H), 4.59 (d,  $J = 11.6$  Hz, 1H), 4.52 (d,  $J = 11.6$  Hz, 1H), 4.24 - 4.21 (m, 1H), 4.10 - 3.99 (m, 3H), 3.95 - 3.92 (m, 1H), 3.87 - 3.82 (m, 1H), 3.76 (dd,  $J = 7.2, 6.0$  Hz, 1H), 3.74 - 3.71 (m, 1H), 3.69 - 3.65 (m, 1H), 3.21 (d,  $J = 2.0$  Hz, 1H), 1.02 (s, 9H), 1.00 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 138.1, 137.5, 133.4, 130.3, 129.7, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.9, 101.2, 97.4, 78.2, 76.7, 74.2, 73.4, 73.2, 72.1, 71.1, 68.4, 67.0, 65.9, 65.1, 61.2, 27.9, 27.2, 23.4, 20.7; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{41}\text{H}_{51}\text{N}_3\text{O}_{10}\text{Si}$  796.3242; Found: 796.3238.

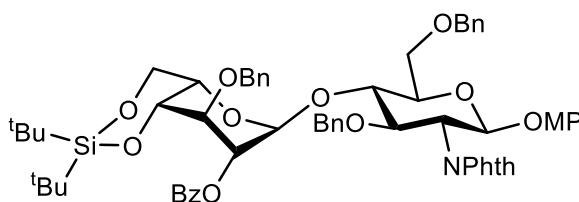
**Methyl (2'-*O*-benzoyl- 3'-*O*-benzyl- 4', 6'-*O*-di-*tert*-butylsilylene-  $\alpha$ -D-idopyranosyl)-(1 $\rightarrow$ 4)- 2-azido- 3, 6-di-*O*-benzyl-2-deoxy-  $\alpha$ -D-glucopyranoside (G22)**



Yield: 84 mg (94%); White powder (from PE-ethyl ether), mp 108°C.  $R_f = 0.70$  (Toluene/EA, 15:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 - 7.95 (m, 2H), 7.55 (td,  $J = 7.6, 1.4$  Hz, 1H), 7.41 - 7.36 (m, 4H), 7.36 - 7.26 (m, 5H), 7.24 - 7.13 (m, 8H), 5.18 - 5.11 (m, 2H), 4.87 - 4.77 (m, 3H), 4.70 (d,  $J = 11.6$  Hz, 1H), 4.59 (d,  $J = 10.8$  Hz, 1H), 4.52 (d,  $J = 11.6$  Hz, 1H), 4.41 (d,  $J = 11.6$  Hz, 1H), 4.12 - 4.02 (m, 2H), 3.93 (s, 1H), 3.84 - 3.74 (m, 4H), 3.69 - 3.62 (m, 2H), 3.51 - 3.45 (m, 1H), 3.42 (s, 3H), 3.05 (d,  $J = 12.4$  Hz, 1H), 0.95 (s, 18H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.17, 138.12, 137.99, 137.69, 133.36, 130.18, 129.60, 128.56, 128.46, 128.37, 128.34, 128.29, 128.23, 127.99, 127.89, 127.71, 127.65, 98.74, 98.17, 79.47, 77.76, 77.32, 75.41, 73.58, 72.56, 72.26, 71.38, 70.96, 69.13, 68.47, 66.28, 64.77, 64.40, 55.33, 27.85, 27.09, 23.14, 20.54; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{49}\text{H}_{61}\text{N}_3\text{O}_{11}\text{Si}$  918.3973; Found: 918.3976.

***p*-Methoxyphenyl (2'-*O*-benzoyl-3'-*O*-benzyl- 4', 6'-*O*-di-*tert*-butylsilylene-  $\alpha$ -D-idopyranosyl)-(1  $\rightarrow$  4)-3, 6-di-*O*-benzyl-2-deoxy-2-phthalimido- $\beta$ -D-glucopyranoside (G23)**

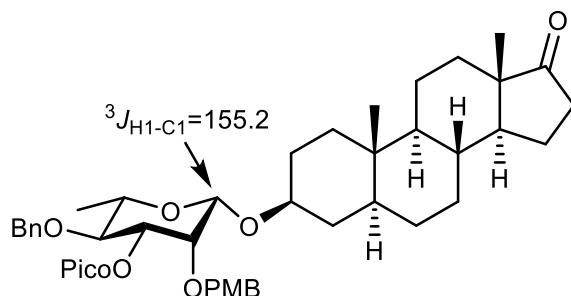


Yield: 98 mg (90%); White solid (from PE-ethyl ether), mp 74°C.  $R_f = 0.31$  (PE/EA, 5:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 - 7.99 (m, 2H), 7.80 - 7.69 (m, 2H), 7.68 - 7.62 (m, 2H), 7.60 - 7.54 (m, 1H), 7.44 - 7.38 (m, 2H), 7.38 - 7.29 (m, 4H), 7.28 - 7.26 (m, 1H), 7.24 - 7.18 (m, 5H), 7.01 - 6.90 (m, 5H), 6.84 - 6.78 (m, 2H), 6.70 - 6.64 (m, 2H), 5.62 (dd,  $J = 8.4, 1.2$  Hz, 1H), 5.26 - 5.21 (m, 2H), 4.84 (d,  $J = 12.0$  Hz, 1H), 4.72 (d,  $J = 12.0$  Hz, 1H), 4.57 (dd,  $J = 11.6, 5.2$  Hz, 2H), 4.51 - 4.43 (m, 2H), 4.38 - 4.32 (m, 1H),

4.28 (d,  $J = 11.6$  Hz, 1H), 4.20 (t,  $J = 9.2$  Hz, 1H), 4.15 - 4.12 (m, 1H), 4.02 (s, 1H), 3.90 (d,  $J = 12.8$  Hz, 1H), 3.85 - 3.72 (m, 3H), 3.71 - 3.66 (m, 4H), 3.45 (d,  $J = 12.0$  Hz, 1H), 0.98 (s, 9H), 0.96 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 155.5, 151.1, 138.2, 138.1, 138.1, 134.1, 133.4, 131.7, 130.3, 129.7, 128.5, 128.4, 128.4, 128.2, 128.2, 127.9, 127.7, 127.6, 127.4, 123.5, 118.9, 114.5, 98.6, 97.9, 78.7, 78.1, 75.7, 75.3, 74.4, 73.5, 72.3, 72.1, 69.5, 68.6, 66.4, 65.4, 56.3, 55.7, 27.9, 27.2, 23.2, 20.7; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{63}\text{H}_{69}\text{NO}_{14}\text{Si}$  1114.4385; Found: 1114.4376.

**Epiandrosteronyl 4-*O*-benzyl-2-*O*-*p*-methoxybenzyl-3-*O*-picolinoyl- $\beta$ -L-rhamnopyranoside (G24)**

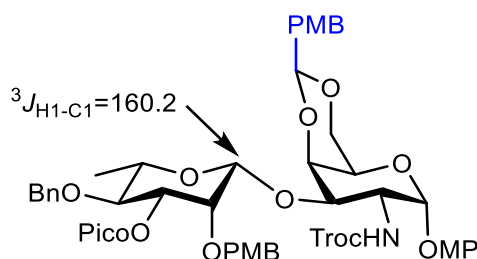


Yield: 61 mg (81%); colorless oil.  $R_f = 0.50$  (toluene/EA, 4:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78 (d,  $J = 4.4$  Hz, 1H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.78 (td,  $J = 7.6, 1.6$  Hz, 1H), 7.48 (dd,  $J = 8.0, 4.8$  Hz, 1H), 7.22 - 7.15 (m, 7H), 6.53 - 6.47 (m, 2H), 5.05 (dd,  $J = 9.6, 3.2$  Hz, 1H), 4.87 - 4.79 (m, 2H), 4.72 - 4.64 (m, 2H), 4.61 (d,  $J = 12.4$  Hz, 1H), 4.05 (d,  $J = 3.2$  Hz, 1H), 3.83 (t,  $J = 9.6$  Hz, 1H), 3.72 - 3.61 (m, 4H), 3.48 - 3.40 (m, 1H), 2.43 (dd,  $J = 19.2, 8.8$  Hz, 1H), 2.12 - 1.99 (m, 1H), 1.98 - 1.85 (m, 2H), 1.84 - 1.72 (m, 4H), 1.70 - 1.62 (m, 1H), 1.60 - 1.48 (m, 2H), 1.48 - 1.42 (m, 2H), 1.41 (d,  $J = 6.0$  Hz, 3H), 1.40 - 1.19 (m, 5H), 1.18 - 1.09 (m, 1H), 1.04 - 0.92 (m, 2H), 0.86 (s, 6H), 0.75 - 0.65 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  221.2, 164.1, 158.9, 149.9, 147.8, 138.2, 136.8, 130.6, 130.2, 128.3, 127.9, 127.6, 126.8, 125.2, 113.3, 98.9, 78.5, 77.9, 75.2, 74.1, 71.7, 55.0, 54.5, 51.5, 47.8, 44.9, 36.9, 36.0, 35.9, 35.8, 35.1, 31.6, 30.9, 28.5, 27.9, 21.8, 20.5, 18.1, 13.9, 12.3; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{46}\text{H}_{57}\text{NO}_8$  774.3982; Found: 774.3988.

***p*-Methoxyphenyl (4'-*O*-benzyl-2'-*O*-*p*-methoxybenzyl-3'-*O*-picolinoyl- $\beta$ -L-rhamnopyranosyl)- (1  $\rightarrow$  3)-4, 6-*O*-*p*-methoxybenzylidene-2-deoxy-(2, 2, 2-**

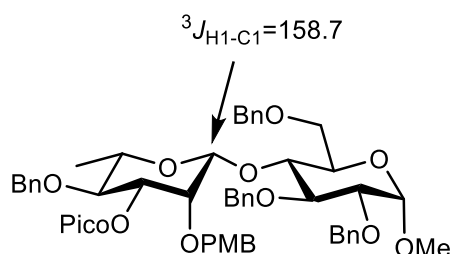
**trichloroethoxycarbamoyl)- $\alpha$ -D-galactopyranoside (G25)**



Yield: 90 mg (87%); White solid (from isopropanol), mp 151°C.  $R_f$  = 0.50 (toluene/EA, 2:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J$  = 4.4 Hz, 1H), 7.99 - 7.91 (m, 1H), 7.80 (t,  $J$  = 7.6 Hz, 1H), 7.753 - 7.47 (m, 3H), 7.24 - 7.18 (m, 5H), 7.07 - 7.02 (m, 4H), 6.91 - 6.86 (m, 2H), 6.85 - 6.80 (m, 2H), 6.34 - 6.30 (m, 2H), 6.25 - 6.20 (m, 1H), 5.96 (d,  $J$  = 3.2 Hz, 1H), 5.61 (s, 1H), 5.10 - 5.02 (m, 1H), 4.85 (d,  $J$  = 11.2 Hz, 1H), 4.81 (s, 1H), 4.78 - 4.72 (m, 2H), 4.69 (d,  $J$  = 10.8 Hz, 1H), 4.64 - 4.58 (m, 2H), 4.48 (ddd,  $J$  = 10.8, 6.0, 3.2 Hz, 1H), 4.40 - 4.31 (m, 2H), 4.27 (d,  $J$  = 12.4 Hz, 1H), 4.13 - 4.06 (m, 2H), 3.90 (t,  $J$  = 9.4 Hz, 1H), 3.85 (s, 1H), 3.75 (s, 6H), 3.60 (s, 3H), 3.58 - 3.52 (m, 1H), 1.52 (d,  $J$  = 6.0 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0, 160.1, 158.9, 155.2, 154.7, 150.8, 149.9, 147.6, 138.0, 136.8, 130.3, 130.2, 129.9, 128.3, 127.9, 127.7, 127.6, 127.0, 125.2, 117.9, 114.7, 113.6, 113.2, 100.9, 99.0, 97.6, 95.7, 78.1, 76.7, 75.3, 74.4, 73.5, 73.2, 73.1, 73.1, 72.2, 69.3, 63.4, 55.6, 55.2, 55.0, 50.5, 18.0; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{51}\text{H}_{53}\text{Cl}_3\text{N}_2\text{O}_{15}$  1061.2410; Found: 1061.2401.

**Methyl (4'-O-benzyl-2'-O-p-methoxybenzyl 3'-O-picolinoyl- $\beta$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 4)- 2, 3, 6-tri-O-benzyl- $\alpha$ -D-glucopyranoside (G26)**



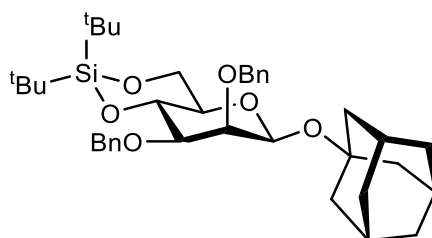
Yield: 71 mg (77%); colorless oil.  $R_f$  = 0.46 (PE/EA, 2:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.80 (d,  $J$  = 4.2 Hz, 1H), 7.95 (dd,  $J$  = 7.6, 1.2 Hz, 1H), 7.78 (t,  $J$  = 8.0 Hz, 1H), 7.48 - 7.37 (m, 5H), 7.36 - 7.17 (m, 18H), 6.61 - 6.55 (m, 2H),



5.01 - 4.94 (m, 2H), 4.90 (s, 1H), 4.82 - 4.52 (m, 10H), 4.02 (d,  $J = 3.2$  Hz, 1H), 3.98 - 3.90 (m, 2H), 3.81 - 3.66 (m, 4H), 3.64 (s, 3H), 3.56 (dd,  $J = 10.0, 3.2$  Hz, 1H), 3.43 (s, 3H), 3.34 - 3.25 (m, 1H), 1.28 (d,  $J = 6.0$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.1, 159.2, 150.2, 148.1, 138.9, 138.3, 138.2, 136.9, 130.7, 130.0, 129.1, 128.8, 128.7, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 127.0, 125.3, 113.6, 101.3, 98.0, 81.9, 80.4, 78.8, 77.5, 77.2, 76.4, 75.6, 75.4, 74.5, 73.5, 73.4, 71.7, 70.1, 69.6, 55.5, 55.2, 18.0; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{55}\text{H}_{59}\text{NO}_{12}$  948.3935; Found: 948.3946.

**Adamantanyl 2, 3-di-*O*-benzyl-4, 6-*O*-di-*tert*-butylsilylene- $\beta$ -D-mannopyranoside (G27)** <sup>[39]</sup>

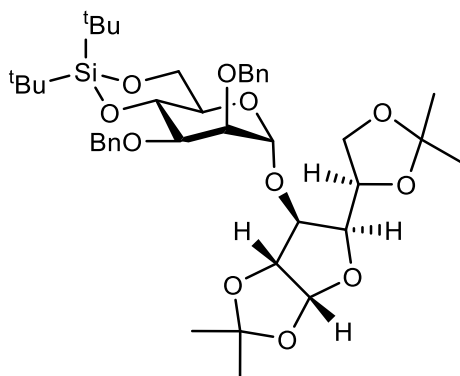


Yield: 58 mg (92%); colorless oil.  $R_f = 0.30$  (toluene).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 - 7.47 (m, 2H), 7.34 - 7.26 (m, 8H), 5.01 - 4.92 (m, 2H), 4.77 (d,  $J = 12.6$  Hz, 1H), 4.71 - 4.64 (m, 2H), 4.37 (t,  $J = 9.4$  Hz, 1H), 4.07 (d,  $J = 7.2$  Hz, 2H), 3.70 - 3.65 (m, 1H), 3.34 - 3.29 (m, 1H), 3.27 - 3.18 (m, 1H), 2.17 - 2.11 (m, 3H), 1.86 - 1.79 (m, 3H), 1.75 - 1.69 (m, 3H), 1.66 - 1.56 (m, 6H), 1.09 (s, 9H), 1.01 (s, 9H).

**(2', 3'-Di-*O*-benzyl-4',6'-*O*-di-*tert*-butylsilylene-  $\alpha$ -D-mannopyranosyl)- (1 $\rightarrow$ 3)-1,**

**2: 5, 6-di-*O*-isopropylidene- $\alpha$ -D-glucofuranoside (G28- $\alpha$ )** <sup>[39]</sup>

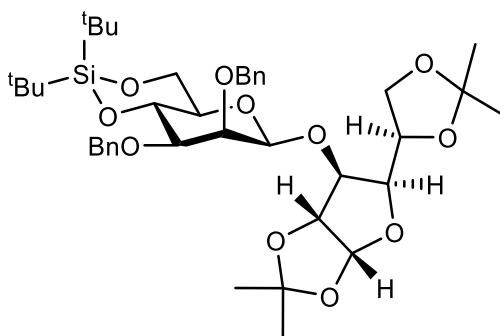


Yield: 10 mg (13%); colorless oil.  $R_f = 0.48$  (PE/EA, 8:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 - 7.27 (m, 10H), 5.81 (d,  $J = 3.6$  Hz, 1H), 5.09 (d,  $J = 1.6$  Hz, 1H), 4.89 (d,  $J = 12.4$  Hz, 1H), 4.74 (s, 2H), 4.66 (d,  $J = 12.4$  Hz, 1H), 4.44 (d,  $J = 3.6$  Hz, 1H), 4.39 (t,  $J = 9.2$  Hz, 1H), 4.22 (d,  $J = 2.4$  Hz, 1H), 4.12 (dd,  $J = 10.4$ , 4.8 Hz, 1H), 4.08 - 3.96 (m, 5H), 3.75 (dd,  $J = 3.2$ , 1.6 Hz, 1H), 3.71 (td,  $J = 10.0$ , 4.8 Hz, 1H), 3.62 (dd,  $J = 9.6$ , 3.2 Hz, 1H), 1.49 (s, 3H), 1.39 (s, 3H), 1.30 (d,  $J = 2.0$  Hz, 6H), 1.09 (s, 9H), 1.02 (s, 9H).

**(2', 3'-Di-*O*-benzyl-4',6'-*O*-di-*tert*-butylsilylene- $\beta$ -D-mannopyranosyl)- (1 $\rightarrow$ 3)-1,**

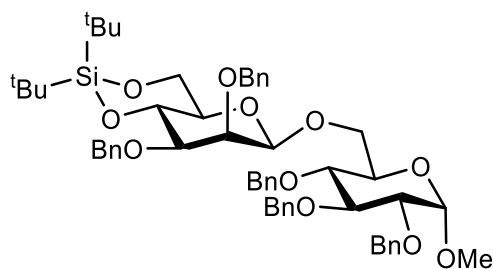
**2: 5, 6-di-*O*-isopropylidene- $\alpha$ -D-glucofuranoside (G28- $\beta$ )** <sup>[39]</sup>



Yield: 57 mg (77%); colorless oil.  $R_f = 0.40$  (PE/EA 8:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 - 7.39 (m, 2H), 7.33 (d,  $J = 4.4$  Hz, 4H), 7.32 - 7.26 (m, 4H), 5.86 (d,  $J = 3.6$  Hz, 1H), 4.87 - 4.81 (m, 3H), 4.70 (d,  $J = 12.4$  Hz, 1H), 4.48 (s, 1H), 4.41 - 4.31 (m, 3H), 4.28 (dd,  $J = 5.2$ , 3.2 Hz, 1H), 4.22 (d,  $J = 3.2$  Hz, 1H), 4.15 - 4.00 (m, 4H), 3.77 (d,  $J = 2.7$  Hz, 1H), 3.34 (dd,  $J = 9.3$ , 3.2 Hz, 1H), 3.27 (td,  $J = 9.6$ , 5.2 Hz, 1H), 1.48 (s, 3H), 1.42 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 1.09 (s, 9H), 1.00 (s, 9H).

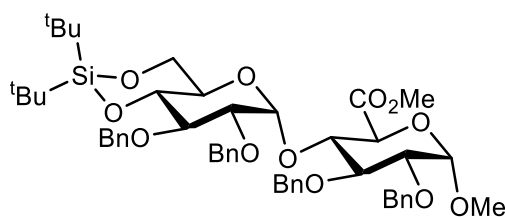
**Methyl (2', 3'-di-*O*-benzyl-4',6'-*O*-di-*tert*-butylsilylene- $\beta$ -D-mannopyranosyl)- (1 $\rightarrow$ 6)-2, 3, 4-tri-*O*-benzyl- $\alpha$ -glucopyranoside (G29)** <sup>[39]</sup>



Yield: 90 mg (95%); White solid (from PE-CH<sub>2</sub>Cl<sub>2</sub>), mp 107°C .  $R_f$  = 0.33 (PE/EA, 6:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42 - 7.27 (m, 19H), 7.25 - 7.14 (m, 6H), 5.02 (d,  $J$  = 11.8 Hz, 1H), 4.90 (d,  $J$  = 12.4 Hz, 1H), 4.85 - 4.75 (m, 5H), 4.72 - 4.64 (m, 2H), 4.58 (d,  $J$  = 3.6 Hz, 1H), 4.46 (d,  $J$  = 11.6 Hz, 1H), 4.35 (t,  $J$  = 9.6 Hz, 1H), 4.13 - 3.97 (m, 5H), 3.77 - 3.71 (m, 1H), 3.66 - 3.63 (m, 1H), 3.50 (dd,  $J$  = 9.6, 3.2 Hz, 1H), 3.46 - 3.39 (m, 2H), 3.31 (s, 3H), 3.26 - 3.14 (m, 2H), 1.08 (s, 9H), 1.01 (s, 9H).

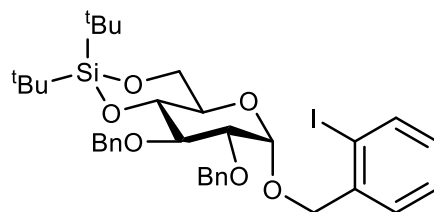
**Methyl (2', 3'-di-*O*-benzyl-4', 6'-*O*-di-*tert*-butylsilylene- $\alpha$ -D- glucopyranosyl)-(1→4)-2, 3-di-*O*-benzyl- $\alpha$ -D-glucuronide methyl ester (G30)**



Yield: 79 mg (89%); colorless oil.  $R_f$  = 0.25 (PE/EA, 10:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 - 7.32 (m, 2H), 7.28 - 7.26 (m, 5H), 7.25 - 7.20 (m, 11H), 7.17 (dd,  $J$  = 7.3, 2.3 Hz, 2H), 5.34 (d,  $J$  = 4.0 Hz, 1H), 4.98 (d,  $J$  = 10.8 Hz, 1H), 4.90 (d,  $J$  = 11.2 Hz, 1H), 4.83 - 4.76 (m, 2H), 4.75 - 4.70 (m, 2H), 4.57 - 4.53 (m, 2H), 4.49 (d,  $J$  = 12.0 Hz, 1H), 4.17 (d,  $J$  = 9.6 Hz, 1H), 4.15 - 4.07 (m, 2H), 4.01 (dd,  $J$  = 9.6, 8.0 Hz, 1H), 3.83 - 3.76 (m, 3H), 3.75 (s, 3H), 3.68 (td,  $J$  = 9.6, 4.4 Hz, 1H), 3.55 (dd,  $J$  = 9.6, 3.6 Hz, 1H), 3.43 - 3.37 (m, 4H), 1.07 (s, 9H), 1.03 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.4, 139.1, 139.0, 138.4, 137.9, 128.6, 128.4, 128.3, 128.3, 128.2, 127.7, 127.7, 127.6, 127.3, 127.2, 98.6, 98.4, 81.4, 80.7, 79.1, 78.5, 78.4, 77.4, 75.7, 75.1, 73.9, 73.8, 70.5, 67.1, 66.5, 55.8, 52.8, 27.7, 27.2, 22.9, 20.0; HRMS (ESI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>50</sub>H<sub>64</sub>O<sub>12</sub>Si 907.4065; Found: 907.4069.

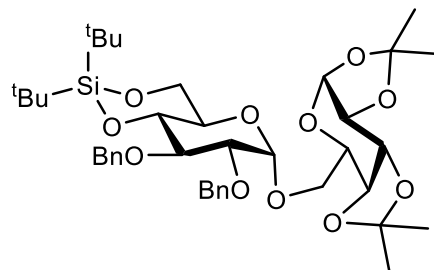
***o*-Iodobenzyl 2, 3-di-*O*-benzyl-4, 6-*O*-di-*tert*-butylsilylene- $\alpha$ -D-glucopyranoside (G31)**



Yield: 57 mg (79%); colorless oil.  $R_f = 0.23$  (PE/EA, 20:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (dt,  $J = 7.9, 0.9$  Hz, 1H), 7.57 (dd,  $J = 7.7, 1.7$  Hz, 1H), 7.48 - 7.43 (m, 2H), 7.39 - 7.28 (m, 9H), 7.01 (td,  $J = 7.6, 1.7$  Hz, 1H), 5.04 (d,  $J = 10.8$  Hz, 1H), 4.89 (d,  $J = 5.2$  Hz, 1H), 4.87 - 4.84 (m, 2H), 4.72 - 4.65 (m, 2H), 4.62 (d,  $J = 13.6$  Hz, 1H), 4.00 - 3.96 (m, 1H), 3.95 - 3.79 (m, 4H), 3.53 (dd,  $J = 8.8, 3.6$  Hz, 1H), 1.09 (s, 9H), 1.02 (s, 9H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 139.3, 139.2, 138.5, 129.5, 129.4, 128.5, 128.4, 128.2, 128.1, 127.9, 127.7, 98.0, 97.8, 81.9, 78.9, 78.5, 75.9, 74.0, 73.8, 66.8, 27.6, 27.2, 22.8, 20.1; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{35}\text{H}_{45}\text{IO}_6\text{Si}$  739.1928; Found: 739.1927.

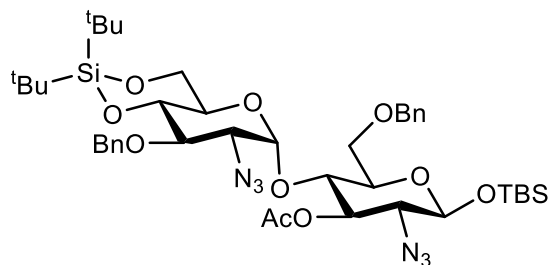
**(2', 3'-Di-*O*-benzyl- 4', 6'-*O*-di-*tert*-butylsilylene - $\alpha$ -D-glucopyranosyl)-(1  $\rightarrow$  6)-1, 2:3, 4-di-*O*-isopropylidene- $\alpha$ -D-galactopyranoside (G32)**



Yield: 70 mg (94%); White solid (from PE- $\text{CH}_2\text{Cl}_2$ ), mp 98°C.  $R_f = 0.32$  (PE/EA, 10:1).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 - 7.41 (m, 2H), 7.39 - 7.35 (m, 2H), 7.35 - 7.27 (m, 6H), 5.53 (d,  $J = 5.0$  Hz, 1H), 4.99 (d,  $J = 11.1$  Hz, 1H), 4.87 - 4.81 (m, 2H), 4.78 (d,  $J = 12.0$  Hz, 1H), 4.71 (d,  $J = 12.0$  Hz, 1H), 4.60 (dd,  $J = 7.6, 2.0$  Hz, 1H), 4.36 (dd,  $J = 7.6, 1.9$  Hz, 1H), 4.32 (dd,  $J = 4.8, 2.4$  Hz, 1H), 4.12 - 4.03 (m, 2H), 3.89 - 3.81 (m, 4H), 3.79 - 3.72 (m, 2H), 3.48 (dd,  $J = 8.8, 4.0$  Hz, 1H), 1.53 (s, 3H), 1.46 (s, 3H), 1.32 (s, 6H), 1.08 (s, 9H), 1.01 (s, 9H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.3, 138.6, 128.5, 128.4, 128.2, 127.9, 127.8, 127.6, 109.3, 108.7, 98.0, 96.4, 81.9, 78.8, 78.5, 77.4, 75.8, 73.1, 70.9, 70.8, 70.7, 66.9, 66.7, 66.3, 65.8, 27.6, 27.2, 26.2, 26.2, 25.0, 24.7, 22.8, 20.1; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{40}\text{H}_{58}\text{O}_{11}\text{Si}$  765.3646; Found: 765.3648.

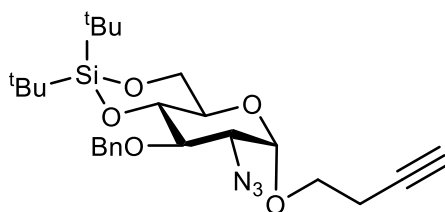
***Tert*-butyldimethylsilyl (2'-azido-3'-*O*-benzyl- 4', 6'-*O*-di-*tert*-butylsilylene-2-deoxy- $\alpha$ -D- glucopyranosyl)-(1 $\rightarrow$ 4)-6-*O*-benzyl-3-*O*-acetyl-2-azido-2-deoxy- $\beta$ -D- glucopyranoside (G33)**



Yield: 78 mg (90%); colorless oil.  $R_f = 0.53$  (PE/EA, 10:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 - 7.39 (m, 2H), 7.38 - 7.33 (m, 6H), 7.32 - 7.27 (m, 2H), 5.12 - 5.02 (m, 3H), 4.77 (d,  $J = 10.5$  Hz, 1H), 4.65 (d,  $J = 7.7$  Hz, 1H), 4.62 (s, 2H), 4.09 - 4.01 (m, 1H), 3.96 - 3.88 (m, 2H), 3.86 - 3.68 (m, 5H), 3.56 - 3.51 (m, 1H), 3.33 - 3.24 (m, 2H), 2.16 (s, 3H), 1.09 (s, 9H), 1.05 (s, 9H), 0.95 (s, 9H), 0.18 (s, 3H), 0.17 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.8, 138.1, 138.0, 128.6, 128.5, 128.5, 128.1, 127.8, 127.6, 99.5, 97.1, 78.9, 78.7, 75.7, 75.1, 74.8, 73.8, 73.7, 68.6, 67.8, 66.7, 66.5, 62.5, 27.6, 27.2, 25.7, 22.8, 21.2, 20.1, 18.1, -4.3, -5.1; HRMS (ESI):  $m/z$  [ $\text{M} + \text{Na}$ ] $^+$  calcd for  $\text{C}_{42}\text{H}_{64}\text{N}_6\text{O}_{10}\text{Si}$  891.4120; Found: 891.4109.

**1'-Butynyl 2-azido- 3-*O*-benzyl-4, 6-*O*-di-*tert*-butylsilylene- 2-deoxy-  $\alpha$ -D- glucopyranoside (G34)**

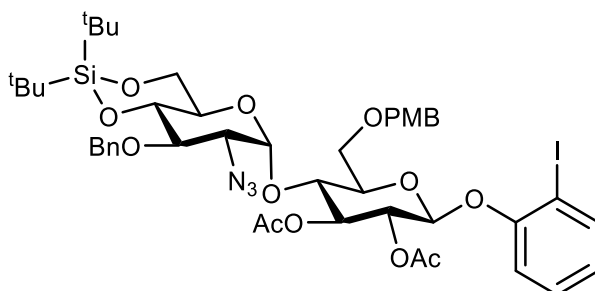


Yield: 43 mg (88%); colorless oil.  $R_f = 0.55$  (PE/EA, 10:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 - 7.41 (m, 2H), 7.38 - 7.33 (m, 2H), 7.32 - 7.27 (m, 1H), 5.06 (d,  $J = 10.8$  Hz, 1H), 4.86 - 4.80 (m, 2H), 4.12 (dd,  $J = 9.6, 3.6$  Hz, 1H), 3.98 - 3.91 (m, 2H), 3.91 - 3.84 (m, 2H), 3.80 (dt,  $J = 9.7, 6.8$  Hz, 1H), 3.66 (dt,  $J = 9.6, 6.4$  Hz, 1H), 3.30 (dd,  $J = 9.8, 3.6$  Hz, 1H), 2.55 (td,  $J = 6.4, 2.4$  Hz, 2H), 1.99 (t,  $J = 2.6$  Hz, 1H), 1.09 (s, 9H), 1.04 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.2, 128.6, 128.5,

128.0, 98.3, 80.9, 79.2, 79.1, 75.6, 69.8, 66.9, 66.8, 66.7, 62.4, 27.6, 27.2, 22.8, 20.1, 20.0; HRMS (ESI):  $m/z$   $[M + Na]^+$  calcd for  $C_{25}H_{37}N_3O_5Si$  510.2400; Found: 510.2411.

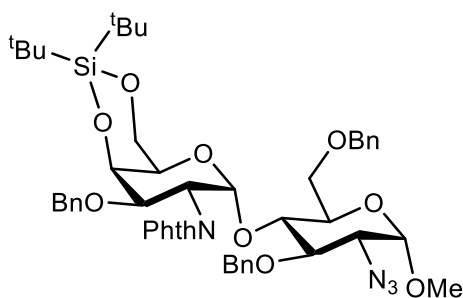
***o*-Idophenyl (2'-azido- 3'-*O*-benzyl -4', 6'-*O*-di-*tert*-butylsilylene- 2'-deoxy- $\alpha$ -D-glucopyranosyl)-(1  $\rightarrow$  4)-2, 3-di-*O*-acetyl-6-*O*-*p*-methoxybenzyl- $\beta$ -D-glucopyranoside (G35)**



Yield: 92 mg (92%); White solid (from PE- $CH_2Cl_2$ ), mp 49°C.  $R_f$  = 0.50 (PE/EA, 5:1).

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.77 (dd,  $J$  = 7.9, 1.5 Hz, 1H), 7.42 - 7.38 (m, 2H), 7.37 - 7.32 (m, 2H), 7.32 - 7.27 (m, 1H), 7.25 - 7.21 (m, 3H), 7.11 (dd,  $J$  = 8.4, 1.4 Hz, 1H), 6.87 - 6.84 (m, 2H), 6.83 - 6.78 (m, 1H), 5.37 (t,  $J$  = 9.2 Hz, 1H), 5.24 (dd,  $J$  = 9.6, 7.6 Hz, 1H), 5.08 (d,  $J$  = 4.0 Hz, 1H), 5.07 - 5.03 (m, 2H), 4.78 (d,  $J$  = 10.8 Hz, 1H), 4.53 (s, 2H), 4.04 (d,  $J$  = 5.6 Hz, 1H), 4.00 (d,  $J$  = 8.8 Hz, 1H), 3.97 - 3.92 (m, 1H), 3.83 (d,  $J$  = 7.2 Hz, 2H), 3.81 - 3.74 (m, 7H), 3.30 (dd,  $J$  = 10.4, 4.0 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 1.09 (s, 9H), 1.06 (s, 9H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  170.1, 169.9, 159.4, 156.3, 139.6, 138.0, 130.1, 129.8, 129.3, 128.6, 128.5, 128.1, 124.9, 116.3, 113.9, 99.7, 99.6, 87.1, 78.8, 75.6, 75.2, 75.0, 73.5, 71.7, 68.5, 67.8, 66.5, 62.4, 55.4, 27.5, 27.2, 22.8, 21.3, 21.0, 20.2, 1.2; HRMS (ESI):  $m/z$   $[M + Na]^+$  calcd for  $C_{45}H_{58}IN_3O_{13}Si$  1026.2682; Found: 1026.2684.

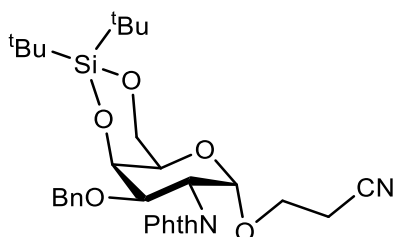
**Methyl (3'-*O*-benzyl 4',6'-*O*-di-*tert*-butylsilylene- 2'-deoxy-2'-phthalimido- $\alpha$ -D-galactopyranosyl)-(1 $\rightarrow$ 4)- 2-azido-6-*O*-benzyl-2-deoxy- $\alpha$ -D-glucopyranoside (G36)**



Yield: 79 mg (86%); colorless oil.  $R_f = 0.39$  (toluene/EA, 25:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 7.2$  Hz, 1H), 7.76 - 7.64 (m, 3H), 7.36 - 7.26 (m, 12H), 7.26 - 7.22 (m, 3H), 5.74 (d,  $J = 3.6$  Hz, 1H), 4.97 (dd,  $J = 11.6, 3.6$  Hz, 1H), 4.86 (dd,  $J = 11.6, 2.4$  Hz, 1H), 4.80 (d,  $J = 3.6$  Hz, 1H), 4.65 - 4.59 (m, 2H), 4.59 - 4.53 (m, 2H), 4.46 (d,  $J = 12.0$  Hz, 1H), 4.40 (d,  $J = 2.8$  Hz, 1H), 4.22 (d,  $J = 10.0$  Hz, 1H), 4.01 (dd,  $J = 10.0, 8.8$  Hz, 1H), 3.96 - 3.87 (m, 2H), 3.77 - 3.60 (m, 5H), 3.42 (s, 3H), 3.39 (dd,  $J = 10.4, 3.6$  Hz, 1H), 1.10 (s, 9H), 1.03 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.0, 168.3, 138.6, 138.0, 136.8, 134.1, 133.9, 132.6, 131.3, 128.6, 128.4, 128.3, 128.0, 127.9, 127.9, 127.7, 123.3, 123.2, 98.8, 96.9, 80.6, 73.8, 73.0, 72.1, 70.5, 70.3, 69.9, 69.7, 69.1, 68.4, 67.0, 63.2, 55.6, 50.8, 27.7, 27.5, 23.5, 20.9; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{50}\text{H}_{60}\text{N}_4\text{O}_{11}\text{Si}$  943.3926; Found: 943.3911.

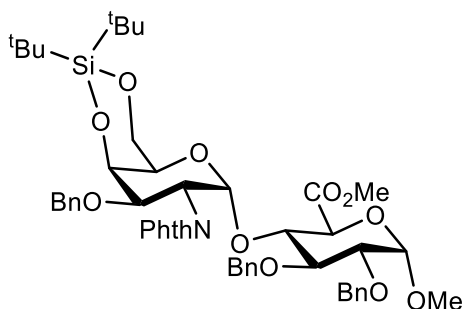
**2'-Cyanoethyl 3-O-benzyl-4,6-O-di-*tert*-butylsilylene- 2-deoxy-2-phthalimido- $\alpha$ -D-galactopyranoside (G37)**



Yield: 48 mg (81%); White solid (from PE- $\text{CH}_2\text{Cl}_2$ ), mp  $91^\circ\text{C}$ .  $R_f = 0.50$  (PE/EA, 20:1).

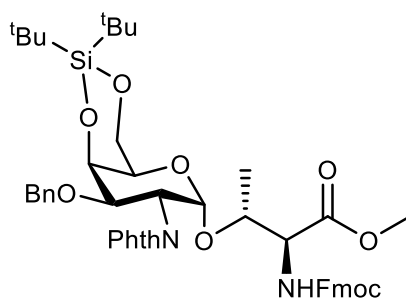
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (dd,  $J = 18.4, 6.8$  Hz, 2H), 7.74 - 7.66 (m, 2H), 7.34 - 7.29 (m, 2H), 7.26 - 7.17 (m, 3H), 5.10 (dd,  $J = 11.6, 2.8$  Hz, 1H), 5.03 (d,  $J = 3.2$  Hz, 1H), 4.95 (dd,  $J = 11.6, 3.6$  Hz, 1H), 4.69 - 4.63 (m, 2H), 4.59 (d,  $J = 11.6$  Hz, 1H), 4.29 (dd,  $J = 12.8, 2.0$  Hz, 1H), 4.20 (dd,  $J = 12.8, 2.0$  Hz, 1H), 3.92 - 3.83 (m, 2H), 3.62 - 3.55 (m, 1H), 2.58 - 2.51 (m, 2H), 1.14 (s, 9H), 1.06 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.3, 168.0, 138.5, 134.2, 133.9, 132.7, 131.4, 128.4, 128.1, 127.7, 123.3, 123.2, 117.5, 98.8, 72.1, 70.7, 69.9, 68.5, 67.4, 63.1, 50.8, 27.7, 27.5, 23.6, 20.9, 19.0; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{32}\text{H}_{40}\text{N}_2\text{O}_7\text{Si}$  615.2503; Found: 615.2502.

**Methyl (3'-O-benzyl- 4',6'-O-di-*tert*-butylsilylene -2'-deoxy-2'-phthalimido- $\alpha$ -D-galactopyranosyl)-(1 $\rightarrow$ 4)-2, 3-di-O-benzyl- $\alpha$ -D-glucuronide methyl ester (G38)**



Yield: 83 mg (90%); White needle (from PE-EA), mp 172°C.  $R_f = 0.60$  (PE/EA, 3:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 - 7.72 (m, 1H), 7.65 - 7.60 (m, 1H), 7.60 - 7.56 (m, 2H), 7.30 - 7.26 (m, 2H), 7.24 - 7.16 (m, 11H), 7.06 - 7.02 (m, 2H), 5.65 (d,  $J = 3.6$  Hz, 1H), 4.96 (dd,  $J = 11.6, 3.2$  Hz, 1H), 4.91 (dd,  $J = 11.6, 2.4$  Hz, 1H), 4.67 (d,  $J = 11.2$  Hz, 1H), 4.62 (d,  $J = 11.6$  Hz, 1H), 4.58 - 4.54 (m, 2H), 4.52 (d,  $J = 1.6$  Hz, 1H), 4.49 (d,  $J = 3.6$  Hz, 1H), 4.40 (d,  $J = 12.0$  Hz, 1H), 4.19 - 4.13 (m, 4H), 4.05 (dd,  $J = 10.0, 8.4$  Hz, 1H), 3.72 (s, 4H), 3.59 (s, 1H), 3.49 (dd,  $J = 9.6, 3.6$  Hz, 1H), 3.34 (s, 3H), 1.13 (s, 9H), 1.04 (s, 9H);  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 168.9, 167.9, 138.6, 138.1, 137.7, 134.0, 133.7, 132.4, 131.2, 128.6, 128.4, 128.3, 128.2, 128.0, 127.6, 127.4, 127.1, 123.2, 123.1, 98.3, 98.2, 80.7, 80.0, 74.3, 74.2, 73.5, 72.0, 70.6, 70.5, 70.2, 68.4, 67.4, 56.0, 52.5, 50.7, 27.7, 27.5, 23.6, 21.0; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{51}\text{H}_{61}\text{NO}_{13}\text{Si}$  946.3810; Found: 946.3804.

***O*-(3-*O*-benzyl-4, 6-*O*-di-*tert*-butylsilylene- 2-deoxy-2-phthalimido- $\alpha$ -D-galactopyranosyl)-*N*- 9-fluorenylmethyloxycarbonyl -*L*-threonine methyl ester (G39)**

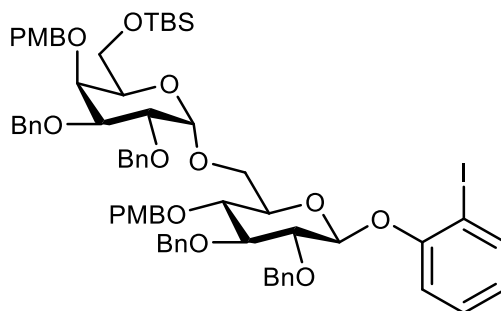


Yield: 73 mg (83%); White solid (from hot ethanol), mp 92°C.  $R_f = 0.40$  (PE/EA, 3:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 - 7.79 (m, 6H), 7.68 (dd,  $J = 5.5, 3.0$  Hz, 2H), 7.47 - 7.41 (m, 2H), 7.39 (dd,  $J = 7.4, 1.3$  Hz, 1H), 7.37 - 7.33 (m, 1H), 7.33 - 7.29 (m, 2H), 7.24 - 7.16 (m, 3H), 5.86 (d,  $J = 10.4$  Hz, 1H), 5.05 (dd,  $J = 11.6, 2.8$  Hz, 1H), 4.99 (d,



$J = 3.2$  Hz, 1H), 4.92 (dd,  $J = 11.6, 3.6$  Hz, 1H), 4.68 (d,  $J = 11.6$  Hz, 1H), 4.65 (d,  $J = 2.8$  Hz, 1H), 4.60 (d,  $J = 11.6$  Hz, 1H), 4.47 - 4.28 (m, 5H), 4.24 - 4.16 (m, 2H), 3.88 (s, 1H), 3.13 (s, 3H), 1.32 (d,  $J = 6.4$  Hz, 3H), 1.15 (s, 9H), 1.07 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.0, 169.5, 169.1, 157.1, 144.2, 144.1, 141.5, 141.5, 138.6, 134.3, 133.9, 133.3, 131.4, 128.4, 127.9, 127.7, 127.3, 125.8, 125.7, 123.3, 123.1, 120.2, 120.1, 100.4, 77.3, 75.9, 72.2, 70.7, 70.2, 68.4, 67.4, 58.8, 52.0, 50.9, 47.4, 27.8, 27.5, 23.6, 20.9, 19.6; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{49}\text{H}_{56}\text{N}_2\text{O}_{11}\text{Si}$  899.3551; Found: 899.3548.

**Iodophenyl (2', 3'-di-*O*-benzyl- 6'-*O*-*tert*-butyldimethylsilyl-4'-*O*-*p*-methoxybenzyl-  $\alpha$ -D-galactopyranosyl)-(1 $\rightarrow$ 6)- 2, 3-di-*O*-benzyl-4-*O*-*p*-methoxybenzyl- $\beta$ -D-glucopyranoside (G40)**

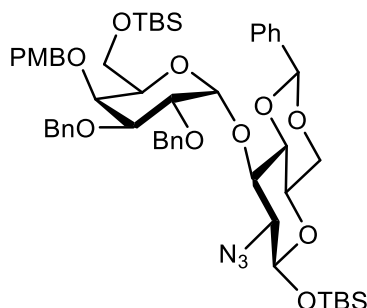


Yield: 107 mg (85%); White solid (from PE-EA), mp 81°C.  $R_f = 0.45$  (PE/EA, 6:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (dd,  $J = 7.6, 1.6$  Hz, 1H), 7.45 - 7.41 (m, 2H), 7.40 - 7.37 (m, 2H), 7.37 - 7.31 (m, 8H), 7.31 - 7.25 (m, 7H), 7.24 - 7.20 (m, 3H), 7.20 - 7.16 (m, 2H), 7.13 - 7.06 (m, 1H), 7.02 (dd,  $J = 8.4, 1.6$  Hz, 1H), 6.86 - 6.79 (m, 4H), 6.69 (td,  $J = 7.2, 1.2$  Hz, 1H), 5.26 (d,  $J = 10.4$  Hz, 1H), 5.01 (d,  $J = 7.2$  Hz, 1H), 4.97 - 4.92 (m, 2H), 4.87 - 4.70 (m, 8H), 4.55 (d,  $J = 10.8$  Hz, 1H), 4.51 (d,  $J = 10.8$  Hz, 1H), 4.02 (dd,  $J = 10.0, 3.6$  Hz, 1H), 3.87 (dd,  $J = 10.0, 2.8$  Hz, 1H), 3.81 - 3.74 (m, 9H), 3.73 - 3.61 (m, 5H), 3.55 (dd,  $J = 10.0, 6.4$  Hz, 1H), 3.47 (dd,  $J = 10.0, 6.4$  Hz, 1H), 0.85 (s, 9H), -0.01 (s, 3H), -0.04 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 159.3, 156.4, 139.8, 139.2, 139.0, 138.8, 138.5, 131.2, 130.4, 129.9, 129.8, 129.5, 129.0, 128.5, 128.5, 127.9, 127.8, 127.7, 127.6, 127.5, 124.0, 115.3, 114.0, 113.7, 100.9, 98.0, 86.3, 84.9, 82.0, 78.7, 77.7, 77.0, 75.8, 75.7, 75.3, 74.9, 74.8, 74.5, 73.2, 72.9, 71.3, 66.2, 62.1, 55.4, 55.4, 26.1, 18.3, -5.2, -5.3; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for

C<sub>68</sub>H<sub>79</sub>IO<sub>13</sub>Si 1281.4233; Found: 1281.4235.

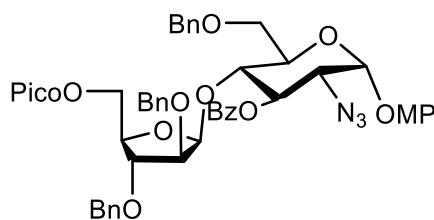
***Tert*-butyldimethylsilyl (2', 3'-di-*O*-benzyl-6'-*O*-*tert*-butyldimethylsilyl-4'-*O*-*p*-methoxybenzyl-  $\alpha$ -D-galactopyranosyl)- (1 $\rightarrow$ 3)- 2-azido-4, 6-*O*-benzylidene-2-deoxy - $\beta$ -D-glucopyranoside (G41)**



Yield: 77 mg (78%); White solid (from PE-ethyl ether).  $R_f$  = 0.15 (PE/EA, 20:1). mp 63 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 - 7.37 (m, 2H), 7.36 - 7.30 (m, 7H), 7.30 - 7.27 (m, 1H), 7.24 - 7.19 (m, 2H), 7.18 - 7.09 (m, 3H), 7.08 - 7.03 (m, 2H), 6.82 - 6.77 (m, 2H), 5.58 (d,  $J$  = 2.4 Hz, 1H), 5.40 (s, 1H), 4.88 (d,  $J$  = 11.6 Hz, 1H), 4.83 (d,  $J$  = 10.8 Hz, 1H), 4.72 (d,  $J$  = 11.6 Hz, 1H), 4.66 (d,  $J$  = 7.6 Hz, 1H), 4.59 - 4.50 (m, 2H), 4.47 (d,  $J$  = 12.0 Hz, 1H), 4.25 (dd,  $J$  = 10.8, 5.2 Hz, 1H), 4.13 (t,  $J$  = 6.8 Hz, 1H), 4.01 - 3.95 (m, 3H), 3.86 (t,  $J$  = 9.6 Hz, 1H), 3.80 (d,  $J$  = 9.2 Hz, 1H), 3.78 (s, 3H), 3.75 (d,  $J$  = 10.4 Hz, 1H), 3.70 - 3.59 (m, 2H), 3.48 - 3.38 (m, 2H), 0.95 (s, 9H), 0.91 (s, 9H), 0.17 (s, 3H), 0.16 (s, 3H), 0.07 (s, 3H), 0.07 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.3, 139.2, 138.5, 137.0, 131.2, 130.0, 129.5, 128.5, 128.4, 128.2, 127.6, 127.5, 127.5, 127.4, 126.3, 113.7, 101.9, 98.0, 96.9, 82.4, 78.6, 75.9, 74.7, 74.7, 73.4, 73.2, 72.0, 71.3, 68.9, 67.8, 66.3, 61.6, 55.4, 26.0, 25.7, 18.4, 18.1, -4.2, -5.0, -5.3, -5.4; HRMS (ESI):  $m/z$  [M + Na]<sup>+</sup> calcd for C<sub>53</sub>H<sub>73</sub>N<sub>3</sub>O<sub>11</sub>Si<sub>2</sub> 1006.4682; Found: 1006.4685.

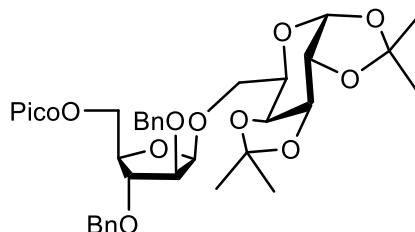
***p*-Methoxyphenyl (2, 3-di-*O*-benzyl-5-*O*-picolinoyl- $\beta$ -D-arabinofuranosyl)- (1 $\rightarrow$ 4)- 2-azido-3-*O*-benzoyl- 6-*O*-benzyl-2-deoxy- $\alpha$ -D-glucopyranoside (G42)**



Yield: 74 mg (80%); colorless oil.  $R_f = 0.23$  (toluene/EA, 5:1)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.71 (d,  $J = 4.0$  Hz, 1H), 8.10 - 8.02 (m, 3H), 7.71 (td,  $J = 7.6, 2.0$  Hz, 1H), 7.51 - 7.45 (m, 1H), 7.41 - 7.25 (m, 12H), 7.24 - 7.15 (m, 6H), 7.13 - 7.08 (m, 2H), 6.86 - 6.80 (m, 2H), 5.90 (dd,  $J = 10.4, 8.4$  Hz, 1H), 5.49 (d,  $J = 3.6$  Hz, 1H), 5.08 (d,  $J = 4.4$  Hz, 1H), 4.57 (s, 4H), 4.41 (d,  $J = 12.0$  Hz, 1H), 4.33 - 4.26 (m, 3H), 4.19 (dd,  $J = 7.2, 6.0$  Hz, 1H), 4.17 - 4.12 (m, 1H), 4.06 (dd,  $J = 10.4, 8.8$  Hz, 1H), 3.97 - 3.90 (m, 3H), 3.78 (s, 3H), 3.70 (dd,  $J = 10.8, 1.6$  Hz, 1H), 3.25 (dd,  $J = 10.8, 3.6$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 164.6, 155.7, 150.7, 149.9, 148.0, 138.3, 137.9, 137.8, 137.0, 133.0, 130.3, 129.9, 128.5, 128.5, 128.4, 128.4, 127.9, 127.8, 127.8, 127.7, 127.7, 126.8, 125.5, 118.6, 114.8, 103.3, 98.6, 83.4, 82.2, 78.6, 77.8, 73.4, 72.7, 72.6, 71.8, 70.8, 68.3, 66.0, 61.5, 55.8; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{52}\text{H}_{50}\text{N}_4\text{O}_{12}$  945.3323; Found: 945.3323.

**(2, 3-Di-*O*-benzyl-5-*O*-picolinoyl- $\beta$ -D-arabinofuranosyl)-(1 $\rightarrow$ 6)-1, 2:3, 4-di-*O*-isopropylidene- $\alpha$ -D-galactopyranoside (G43)**

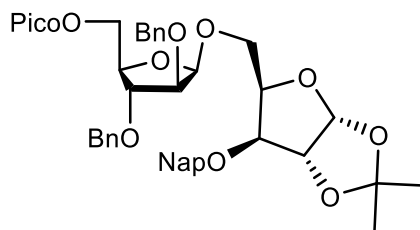


Yield: 60 mg (88%); colorless oil.  $R_f = 0.27$  (toluene/EA, 2:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.76 (d,  $J = 4.0$  Hz, 1H), 8.09 (d,  $J = 7.6$  Hz, 1H), 7.79 (td,  $J = 7.6, 2.0$  Hz, 1H), 7.48 - 7.44 (m, 1H), 7.43 - 7.40 (m, 2H), 7.37 - 7.31 (m, 3H), 7.30 - 7.24 (m, 5H), 5.54 (d,  $J = 4.8$  Hz, 1H), 5.20 (d,  $J = 4.4$  Hz, 1H), 4.79 - 4.73 (m, 2H), 4.65 (d,  $J = 11.6$  Hz, 1H), 4.62 - 4.50 (m, 4H), 4.33 - 4.25 (m, 3H), 4.22 (dd,  $J = 8.0, 2.0$  Hz, 1H), 4.10 (dd,  $J = 6.8, 4.4$  Hz, 1H), 4.07 - 4.02 (m, 1H), 3.88 (dd,  $J = 11.2, 4.4$  Hz, 1H), 3.71 (dd,  $J = 11.6, 7.6$  Hz, 1H), 1.45 (s, 3H), 1.41 (s, 3H), 1.31 (s, 3H), 1.31 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 150.1, 147.9, 138.1, 138.0, 137.1, 128.5, 128.1, 127.9, 127.8, 127.8, 127.0, 125.4, 109.4, 108.6, 101.3, 96.4, 83.9, 83.1, 78.9, 72.5, 72.1, 71.1, 70.7, 70.6, 68.1, 67.6, 66.3, 26.1, 26.0, 25.0, 24.4; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{37}\text{H}_{43}\text{NO}_{11}$  700.2734; Found: 700.2731.

**(2, 3-Di-*O*-benzyl-5-*O*-picolinoyl- $\beta$ -D-arabinofuranosyl)-(1 $\rightarrow$ 5)-1, 2 -*O*-**

### isopropylidene-3-*O*-naphthylmethyl- $\alpha$ -D-xylofuranoside (G44)



Yield: 56 mg (75%); colorless oil.  $R_f = 0.28$  ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ , 200:1).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.71 (d,  $J = 4.4$  Hz, 1H), 7.98 (d,  $J = 7.6$  Hz, 1H), 7.82 - 7.75 (m, 3H), 7.72 (s, 1H), 7.65 (t,  $J = 8.0$  Hz, 1H), 7.47 - 7.43 (m, 2H), 7.42 - 7.37 (m, 4H), 7.35 - 7.25 (m, 8H), 5.98 (d,  $J = 4.0$  Hz, 1H), 5.17 (d,  $J = 4.0$  Hz, 1H), 4.81 - 4.74 (m, 2H), 4.72 (d,  $J = 11.6$  Hz, 1H), 4.68 - 4.61 (m, 3H), 4.57 (d,  $J = 11.6$  Hz, 1H), 4.52 (dd,  $J = 11.2, 6.4$  Hz, 1H), 4.48 - 4.41 (m, 2H), 4.32 - 4.24 (m, 2H), 4.10 (dd,  $J = 6.4, 4.0$  Hz, 1H), 4.03 - 3.97 (m, 2H), 3.88 (dd,  $J = 11.6, 7.2$  Hz, 1H), 1.45 (s, 3H), 1.30 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 149.9, 147.7, 138.1, 137.8, 137.1, 135.0, 133.3, 133.2, 128.5, 128.5, 128.4, 128.0, 128.0, 127.8, 127.8, 127.0, 126.6, 126.3, 126.1, 125.6, 125.4, 111.8, 105.4, 101.7, 84.0, 82.6, 82.3, 82.2, 80.2, 78.9, 72.6, 72.3, 72.1, 67.2, 66.6, 26.9, 26.4; HRMS (ESI):  $m/z$   $[\text{M} + \text{Na}]^+$  calcd for  $\text{C}_{44}\text{H}_{45}\text{NO}_{10}$  770.2941; Found: 770.2933.

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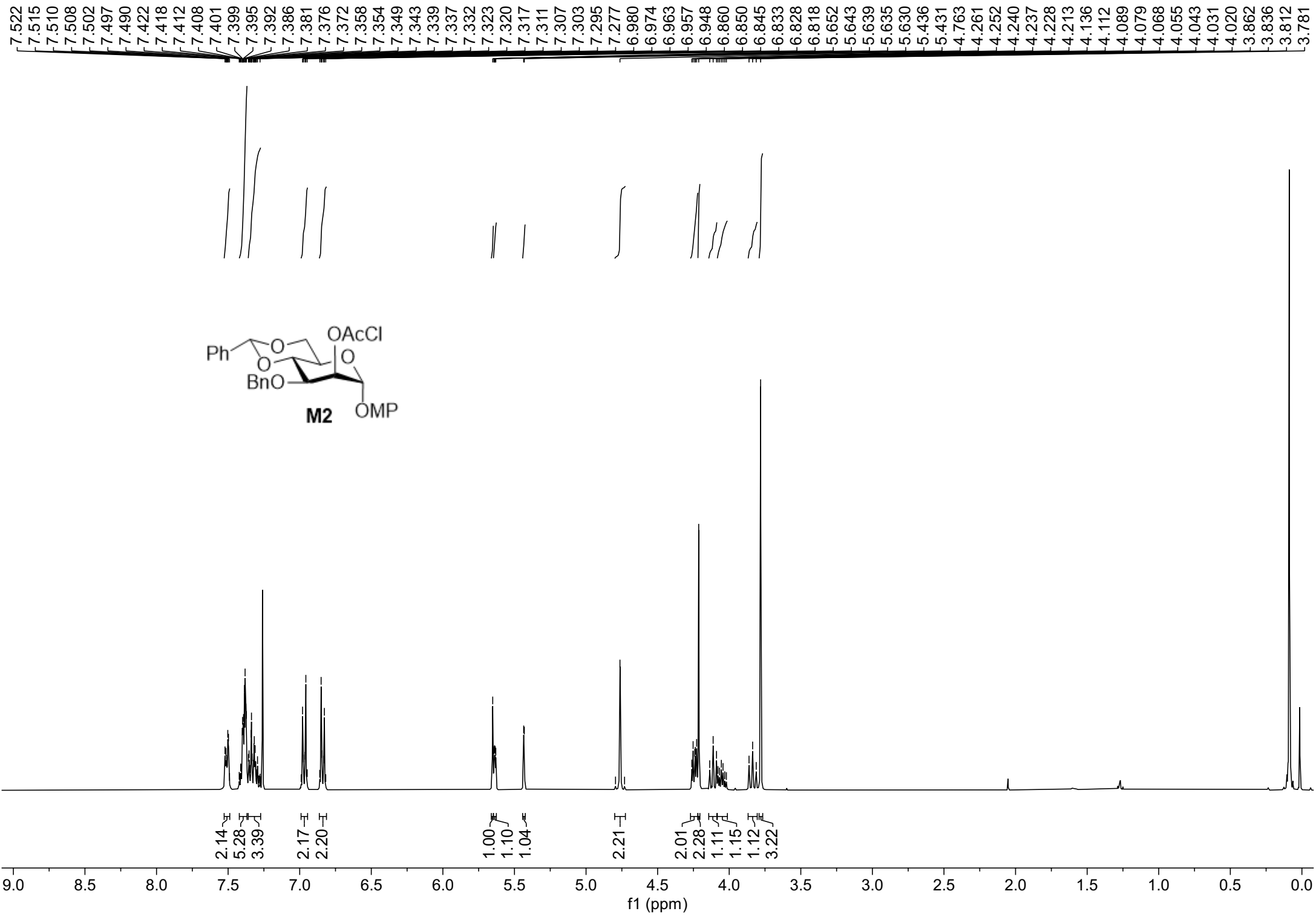
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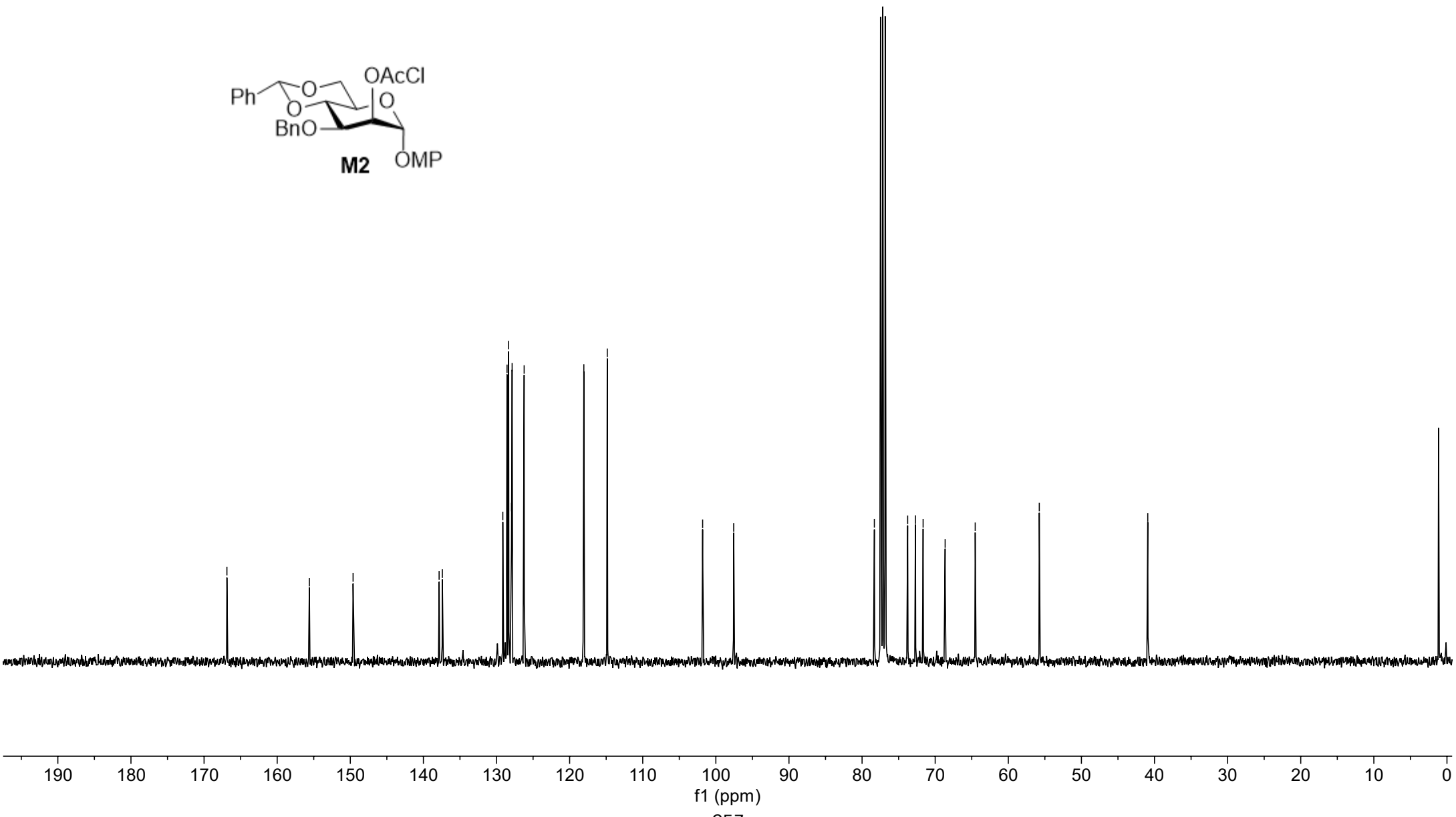
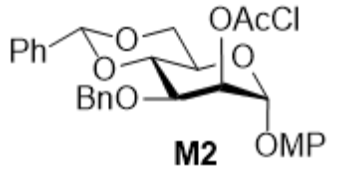
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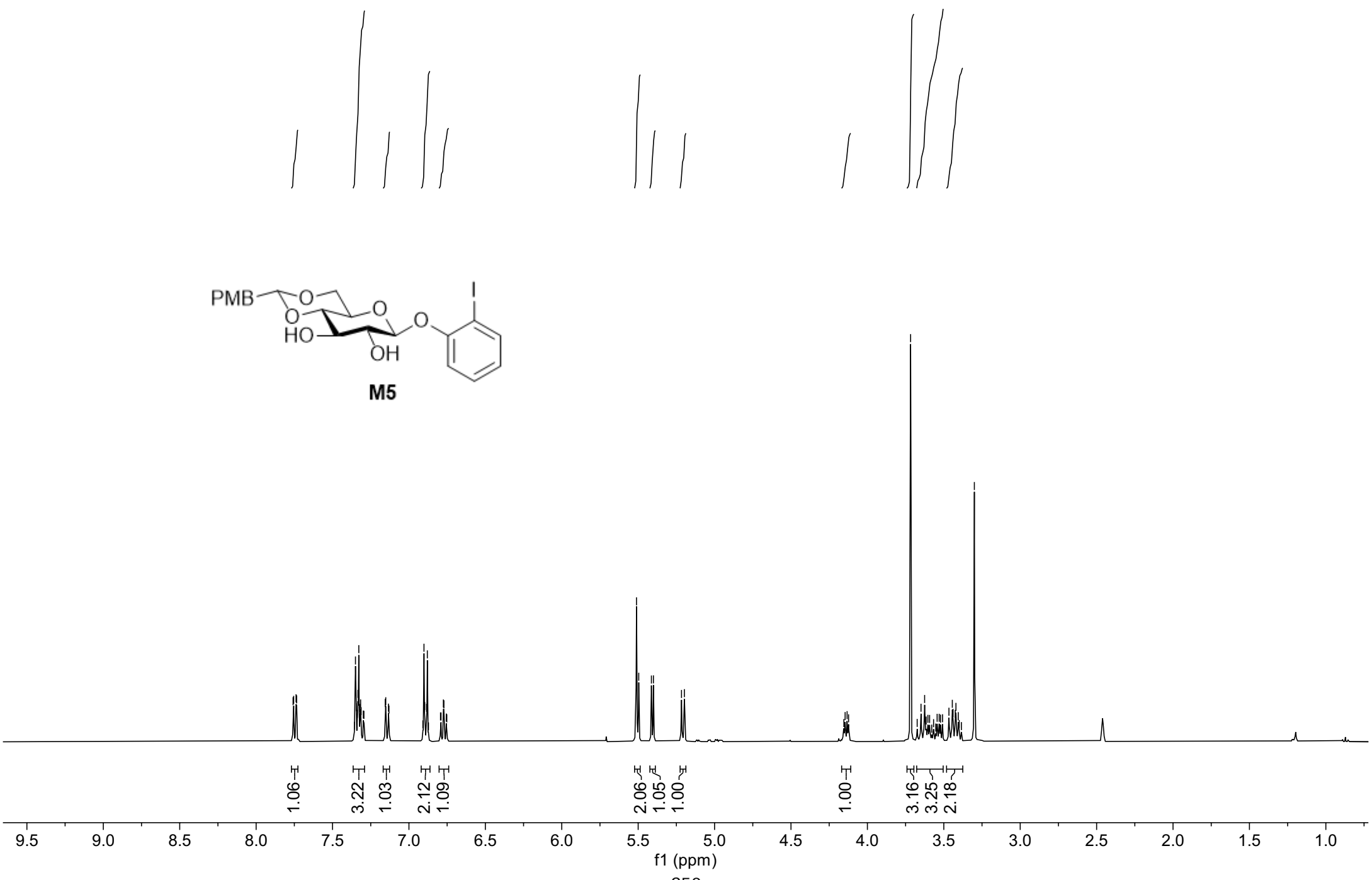
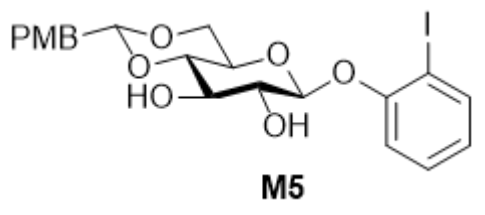


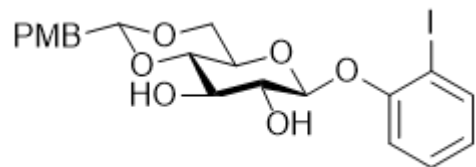
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7.758  
7.754  
7.739  
7.735  
7.357  
7.350  
7.345  
7.338  
7.334  
7.328  
7.320  
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7.155  
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5.400  
5.216  
5.198

4.154  
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4.123  
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3.674  
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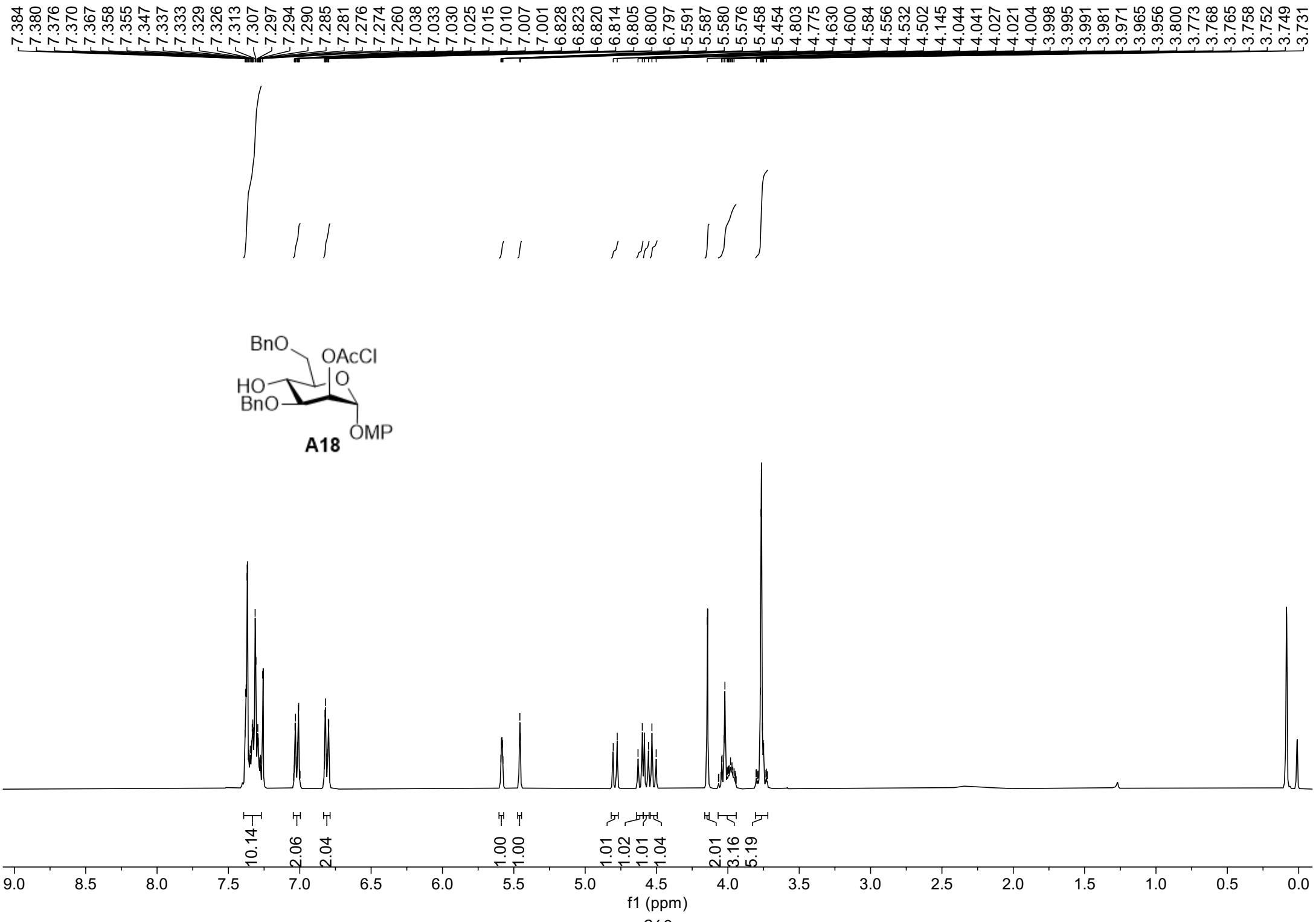
**M5**

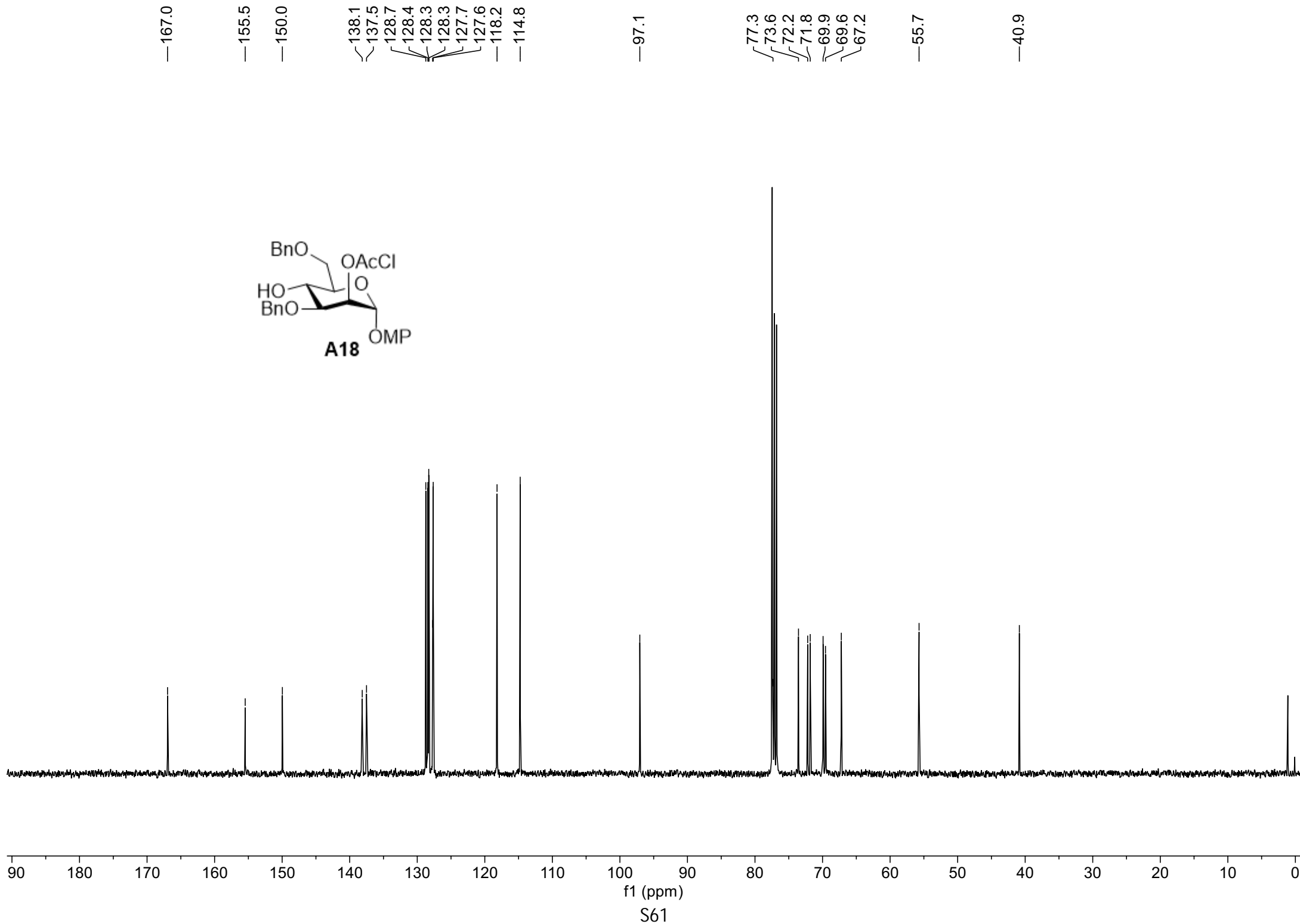
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—127.7  
—123.9  
  
—115.0  
—113.3  
  
—100.6  
—100.4  
  
—87.0  
—80.1  
—74.1  
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—67.7  
—65.9  
  
—55.1

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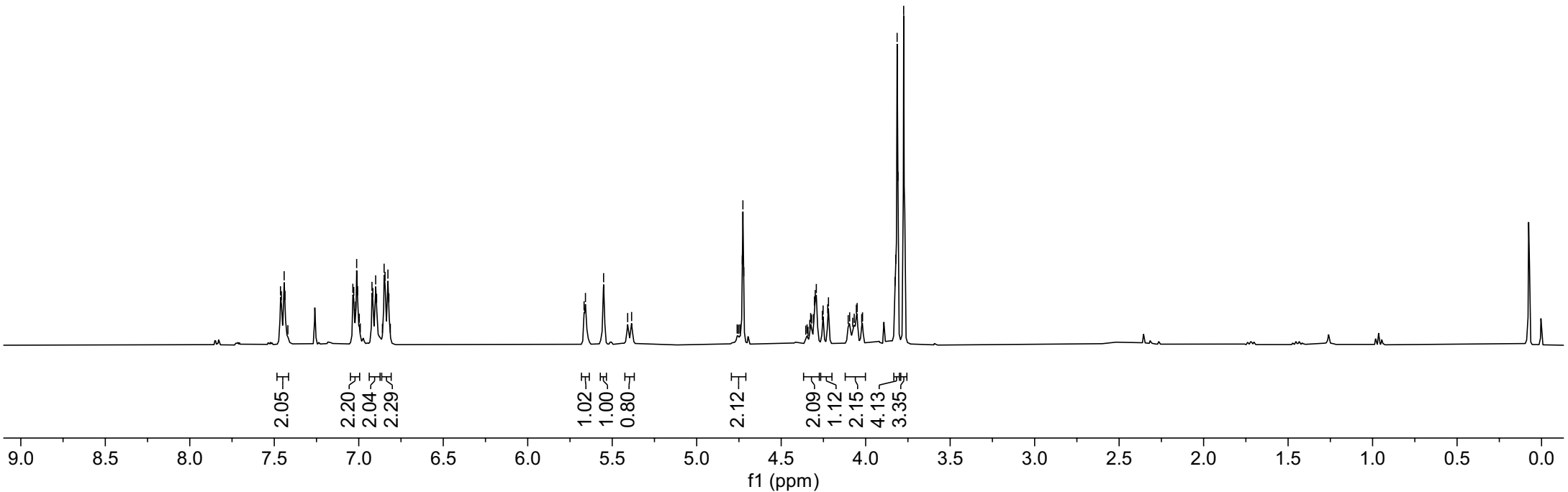
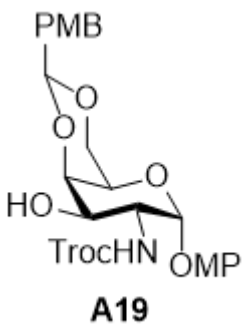
f1 (ppm)

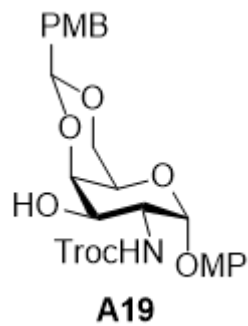
S59





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7.458  
7.441  
7.436  
7.419  
7.035  
7.030  
7.024  
7.019  
7.012  
7.007  
6.997  
6.991  
6.922  
6.917  
6.900  
6.894  
6.860  
6.850  
6.844  
6.837  
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6.822  
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5.658  
5.551  
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5.385  
4.761  
4.754  
4.745  
4.730  
4.727  
4.721  
4.354  
4.347  
4.341  
4.331  
4.326  
4.320  
4.309  
4.303  
4.298  
4.292  
4.256  
4.252  
4.225  
4.220  
4.103  
4.095  
4.077  
4.068  
4.055  
4.050  
4.023  
4.019  
3.826  
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3.814  
3.809  
3.775





~160.5  
 ~155.4  
 ~155.2  
 ~150.3

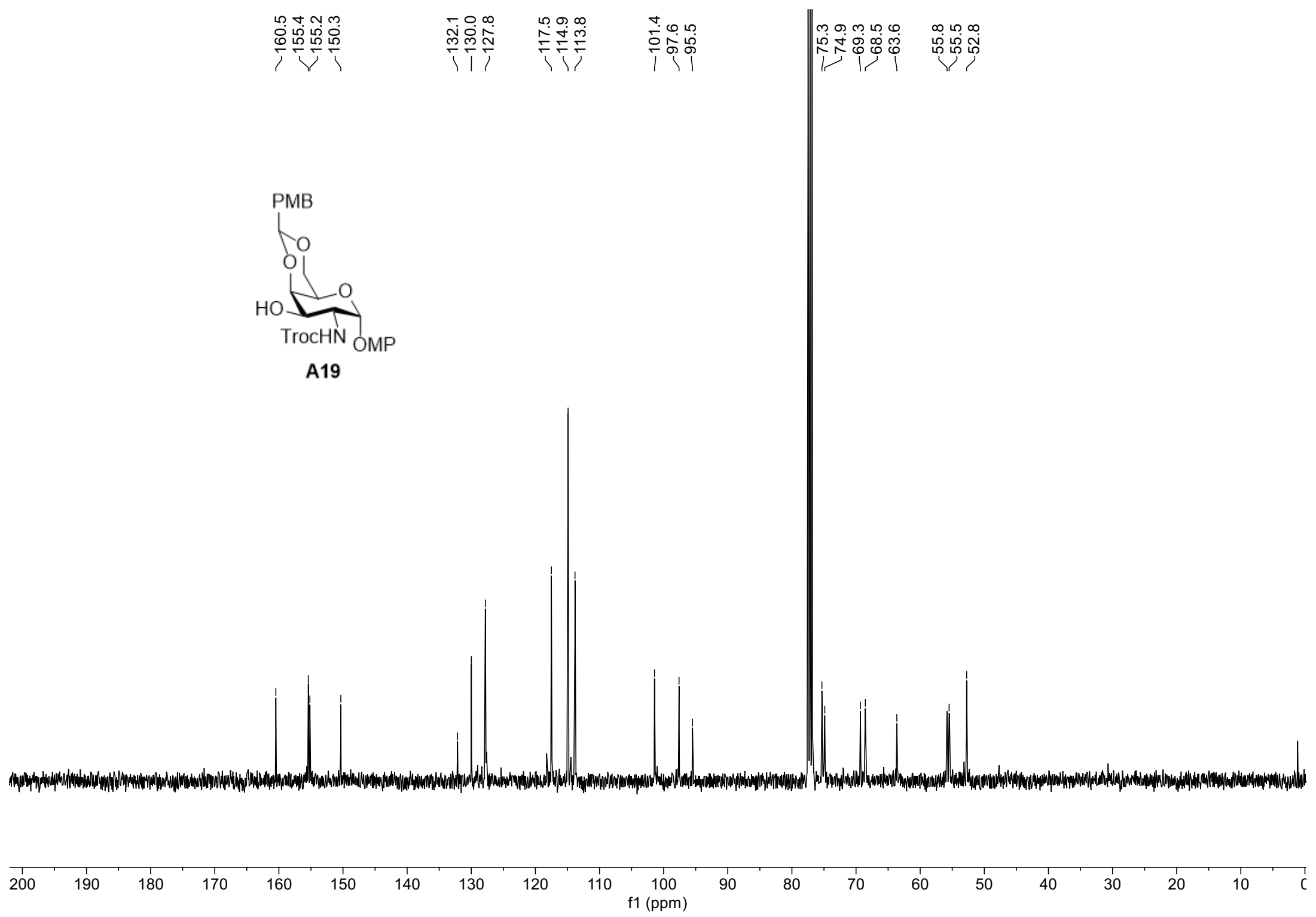
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 ~130.0  
 ~127.8

~117.5  
 ~114.9  
 ~113.8

~101.4  
 ~97.6  
 ~95.5

~75.3  
 ~74.9  
 ~69.3  
 ~68.5  
 ~63.6

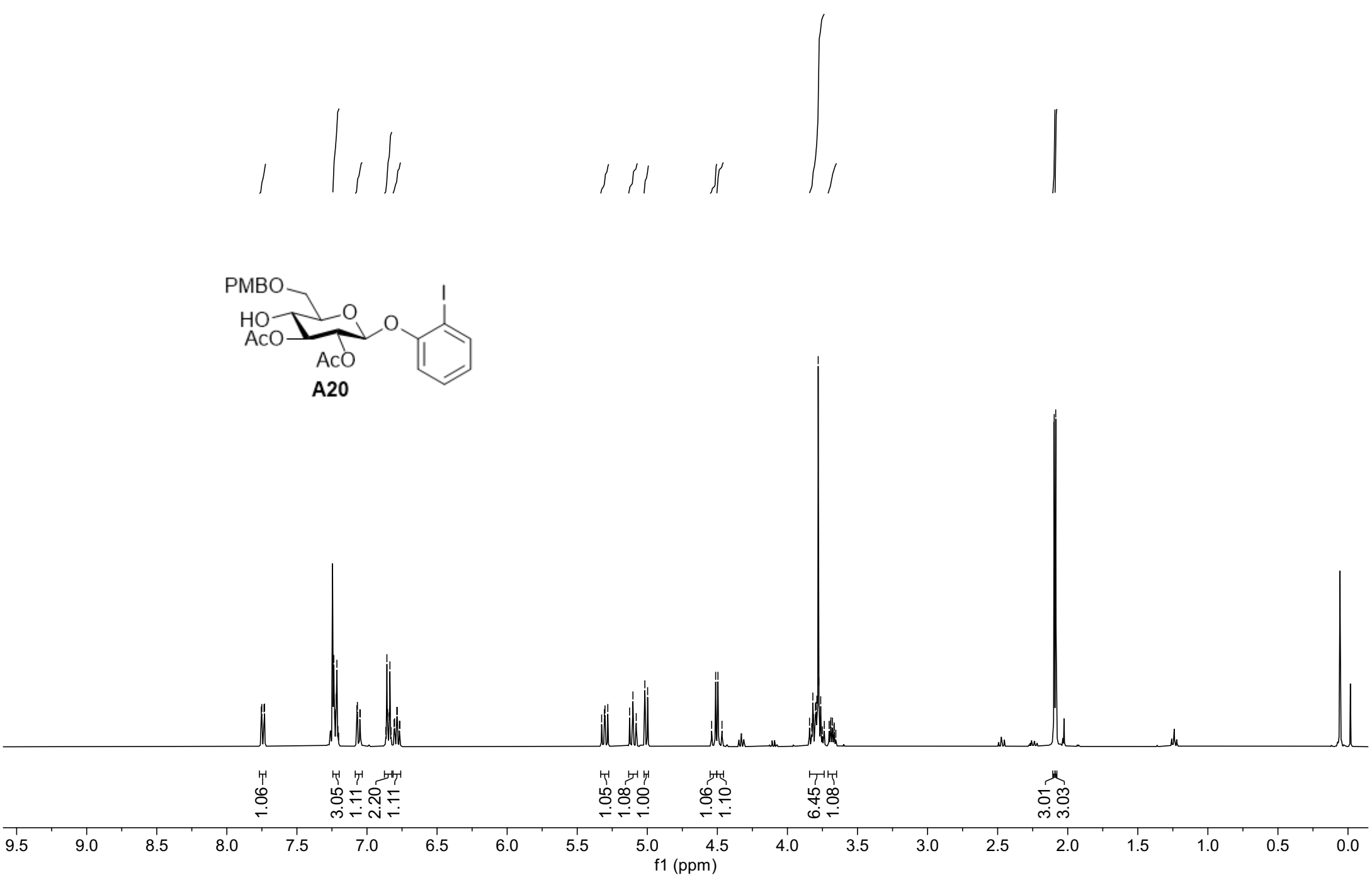
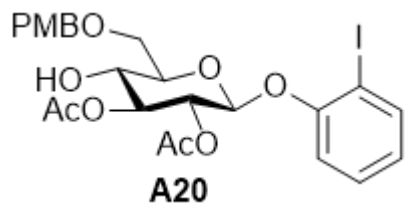
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 ~55.5  
 ~52.8



S63



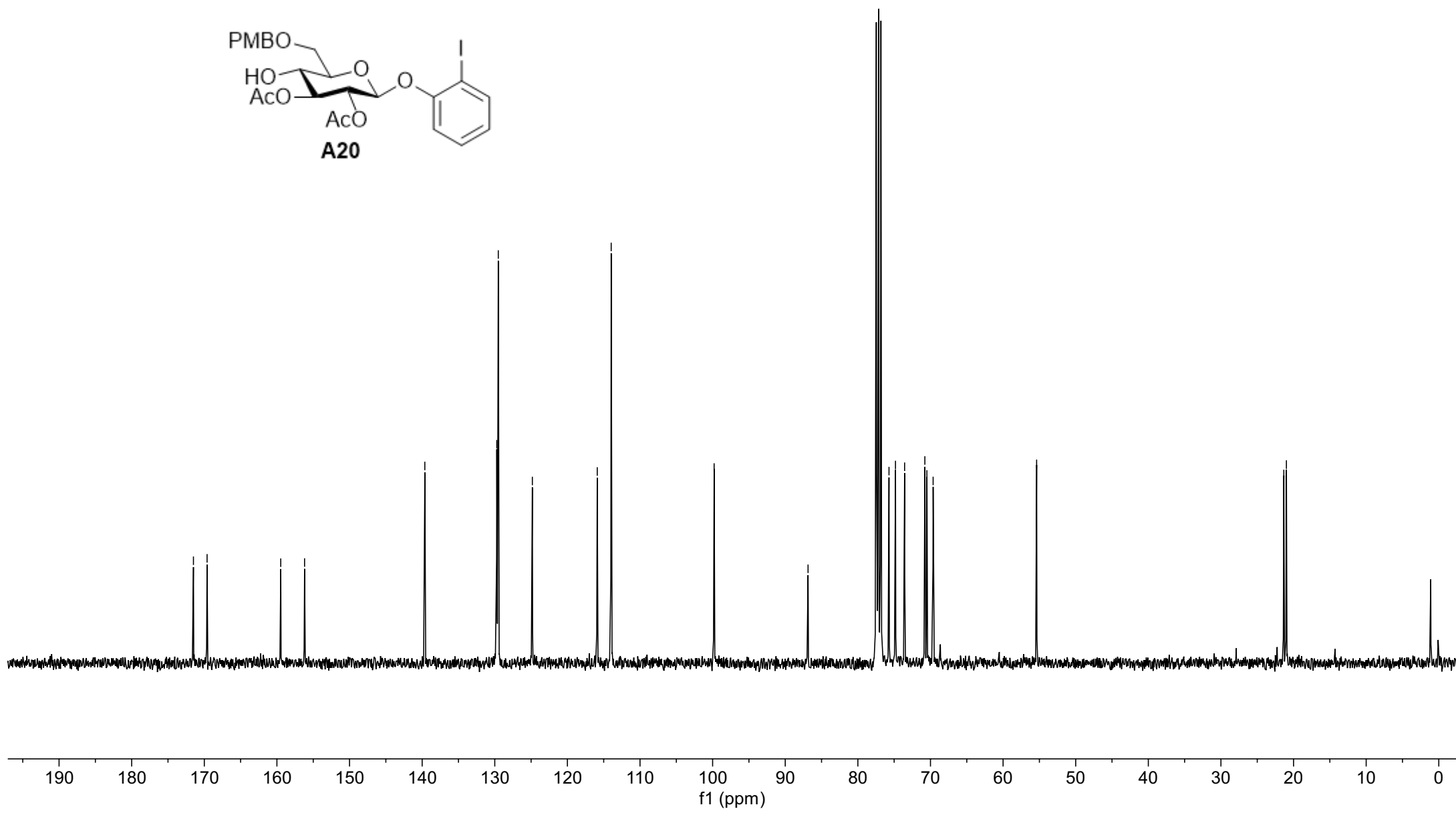
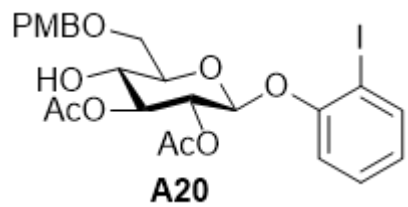
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6.865  
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6.836  
6.829  
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6.803  
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0.000



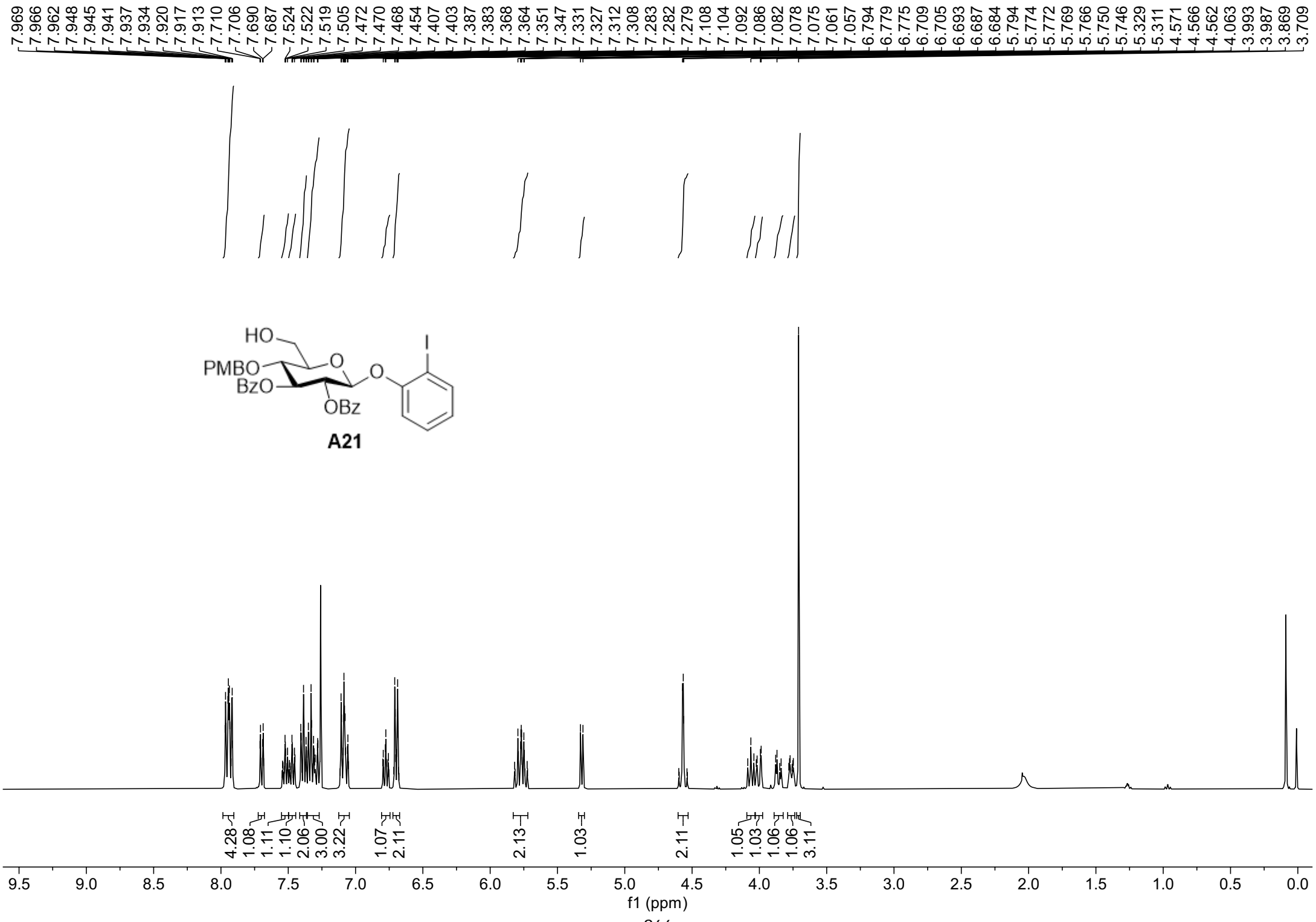
f1 (ppm)

S64

171.5  
169.6  
159.5  
156.2  
139.6  
129.7  
129.7  
129.5  
124.8  
115.9  
114.0  
99.8  
86.9  
75.7  
74.8  
73.6  
70.8  
70.5  
69.6  
55.4  
21.3  
21.0



S65



165.8  
165.3  
— 159.5  
— 156.0  
139.8  
133.4  
133.2  
130.1  
130.0  
129.9  
129.7  
129.6  
129.4  
129.3  
128.5  
128.4  
125.0  
— 115.8  
— 113.9

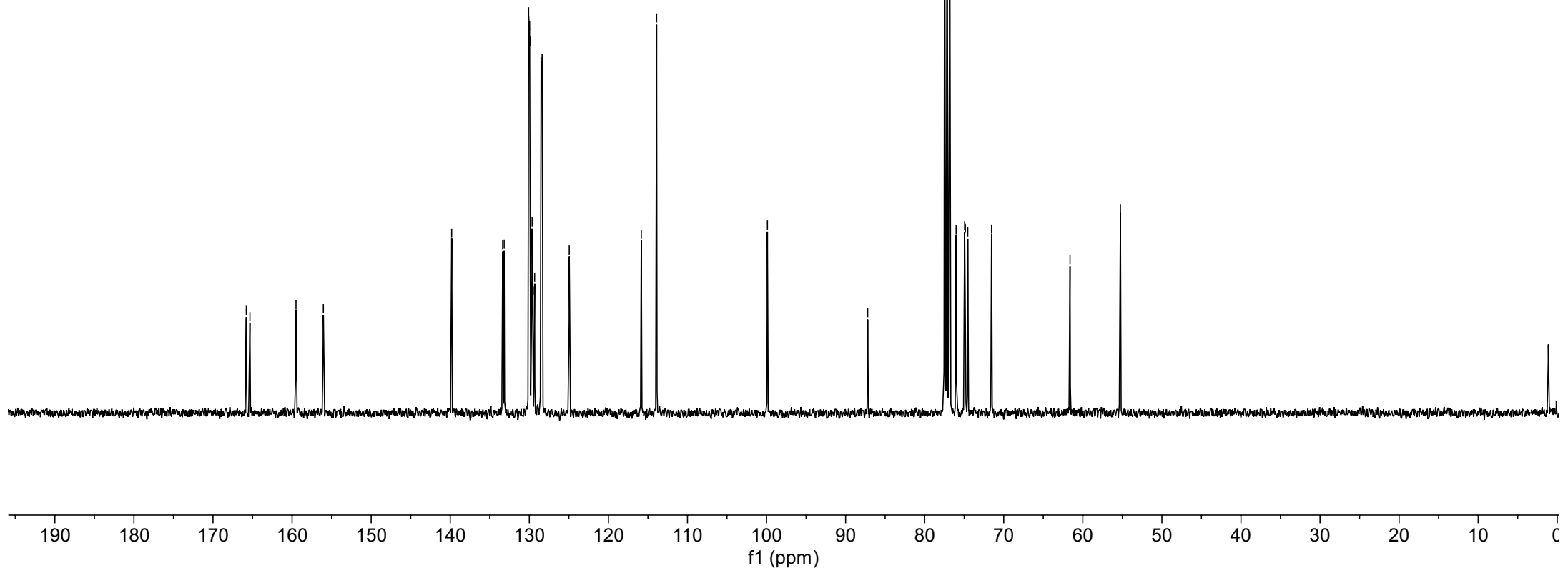
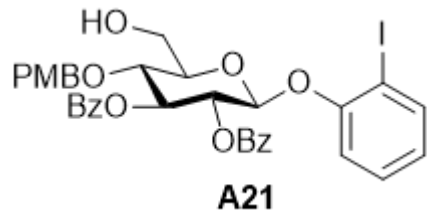
— 99.9

— 87.2

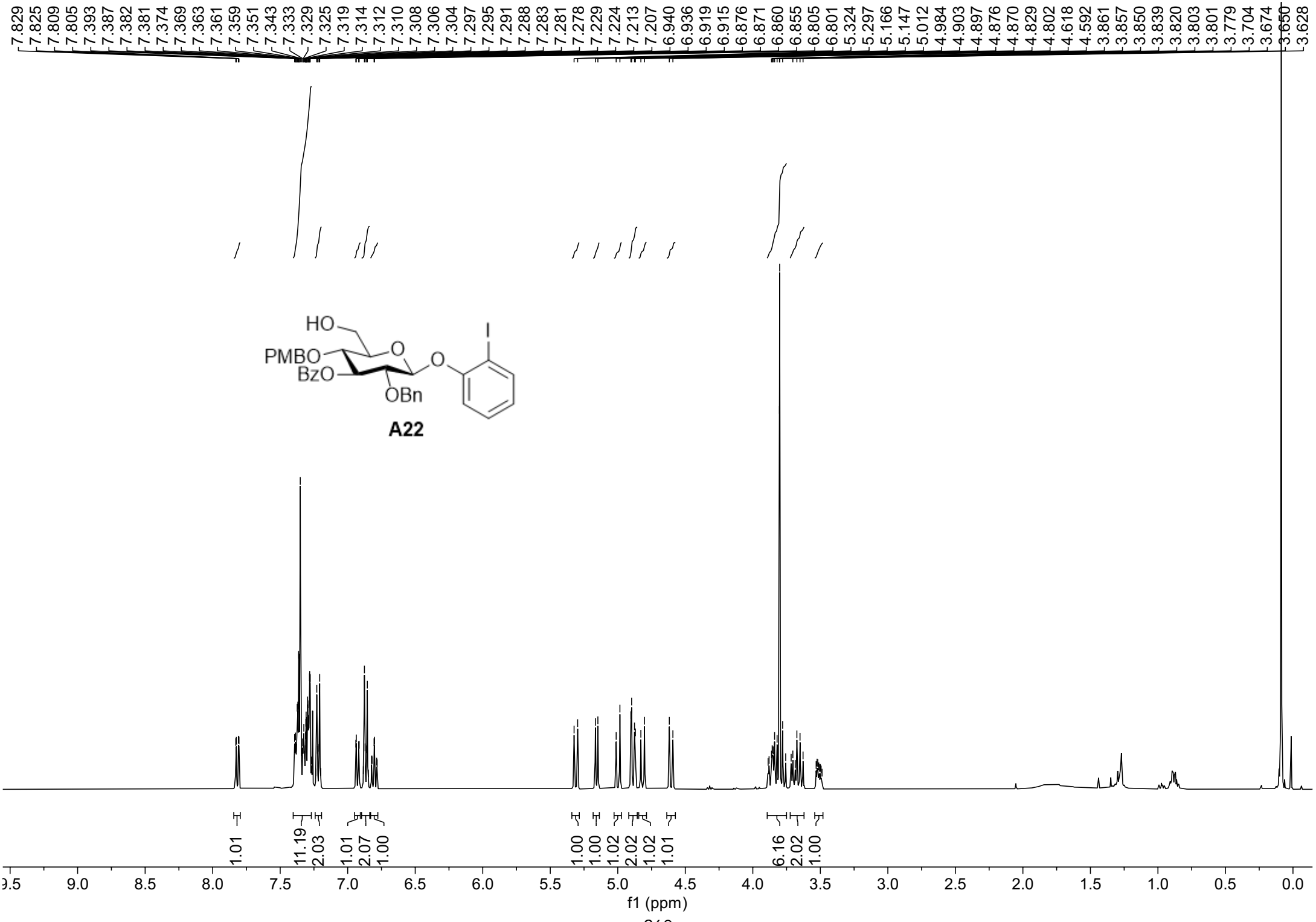
76.0  
74.9  
74.9  
74.6  
71.5

— 61.6

— 55.2



S67



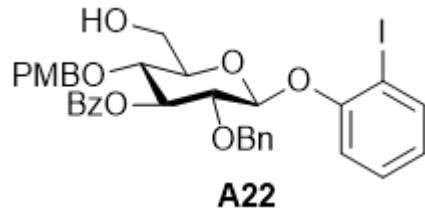
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— 155.9  
140.0  
138.6  
138.3  
130.1  
129.9  
129.6  
128.5  
128.5  
128.4  
127.9  
127.8  
127.8  
124.2  
114.4  
114.0

— 100.5

~ 86.4  
~ 84.6  
~ 81.9  
75.8  
75.6  
74.9

— 62.1

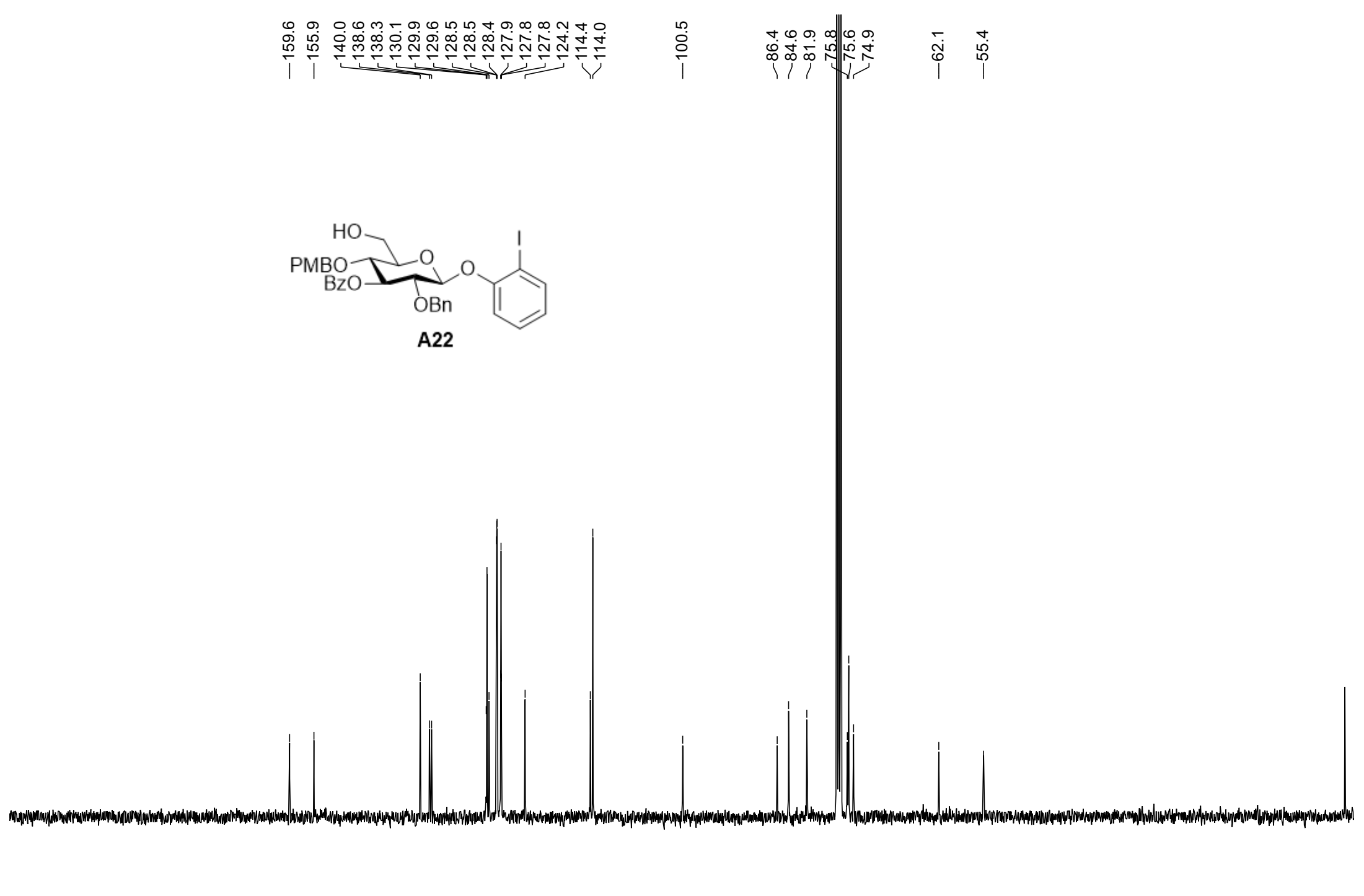
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200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

S69



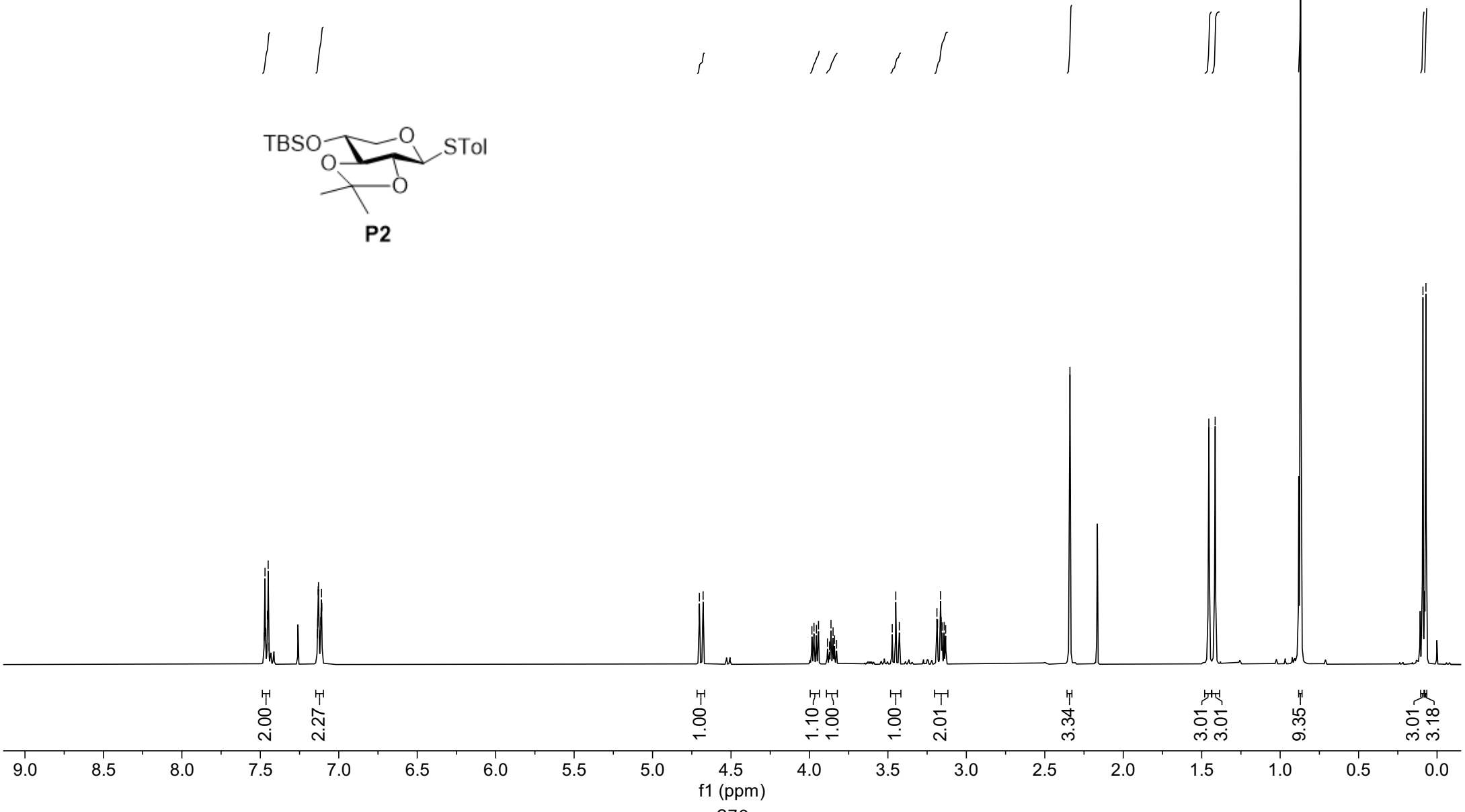
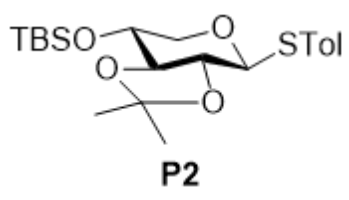
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7.129  
7.125  
7.115  
7.113  
7.110  
7.108

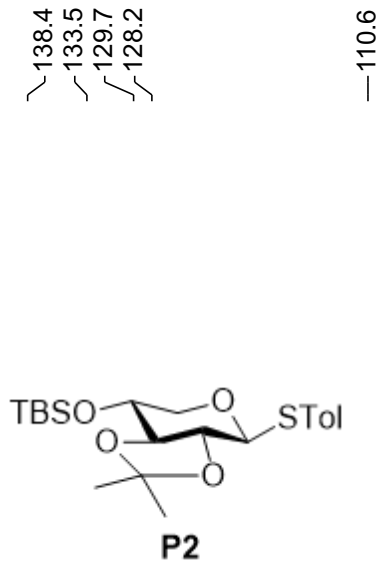
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3.840  
3.827  
3.472  
3.450  
3.427  
3.188  
3.184  
3.164  
3.161  
3.155  
3.141  
3.132  
2.340

1.455  
1.414

0.869

0.090  
0.071





138.4  
133.5  
129.7  
128.2

110.6

85.6  
83.2

75.2  
70.9  
69.9

26.9  
26.6  
25.8  
21.3  
18.3  
18.1

4.5  
4.9

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

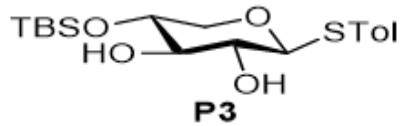
S71



7.435  
7.429  
7.424  
7.413  
7.408  
7.403  
7.131  
7.126  
7.124  
7.120  
7.109  
7.104

4.523  
4.501  
3.985  
3.973  
3.956  
3.944  
3.640  
3.628  
3.620  
3.617  
3.607  
3.604  
3.596  
3.584  
3.534  
3.514  
3.493  
3.392  
3.370  
3.349  
3.259  
3.236  
3.231  
3.207  
2.331

0.101  
0.074



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2.02

2.02

1.00

1.00

1.00

1.01

1.02

1.06

3.04

9.08

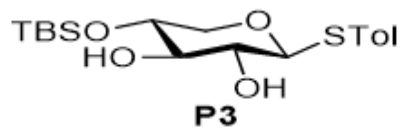
3.00

3.28

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f1 (ppm)

S72



—138.5  
—133.3  
—129.9  
—128.3

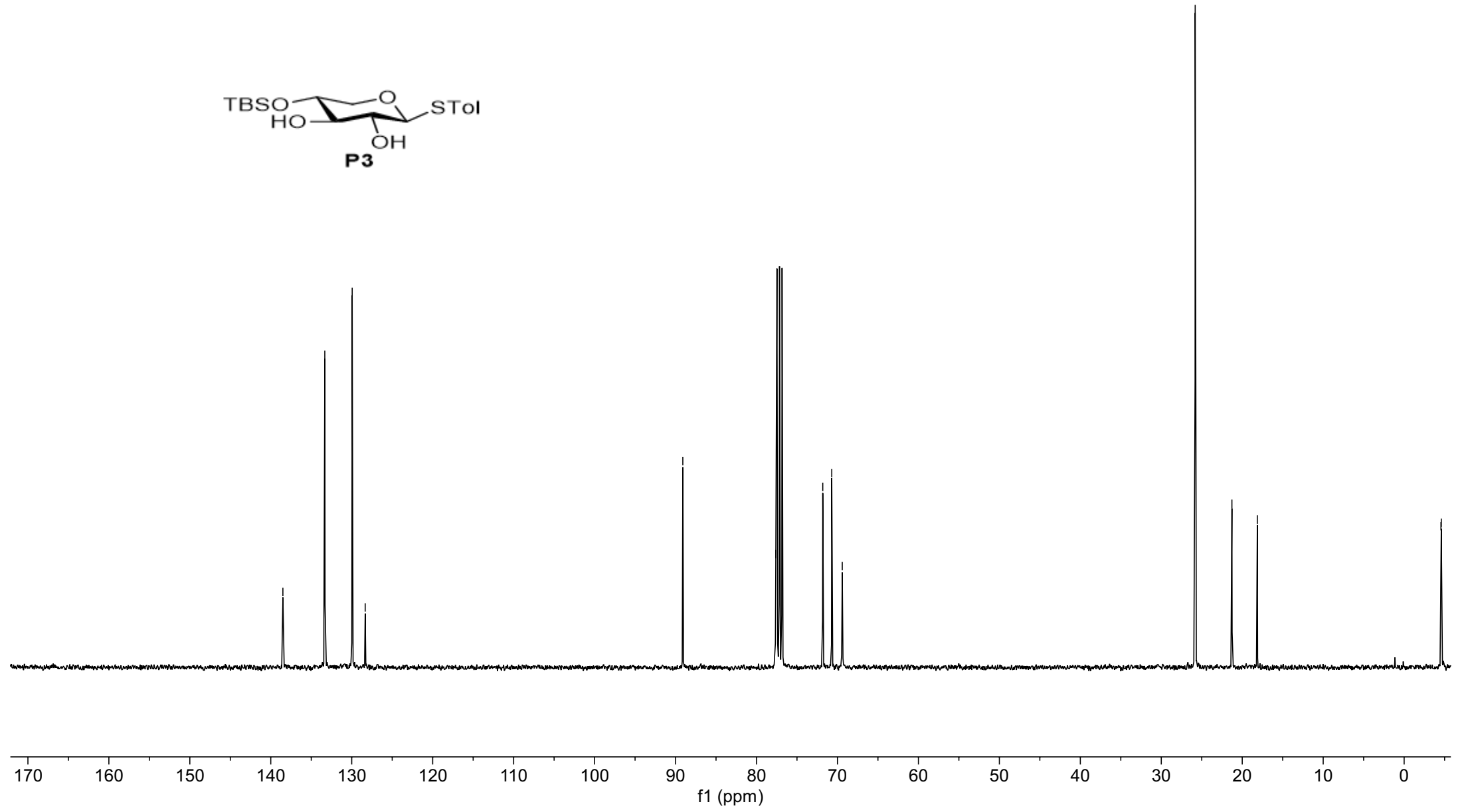
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—77.6

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—69.4

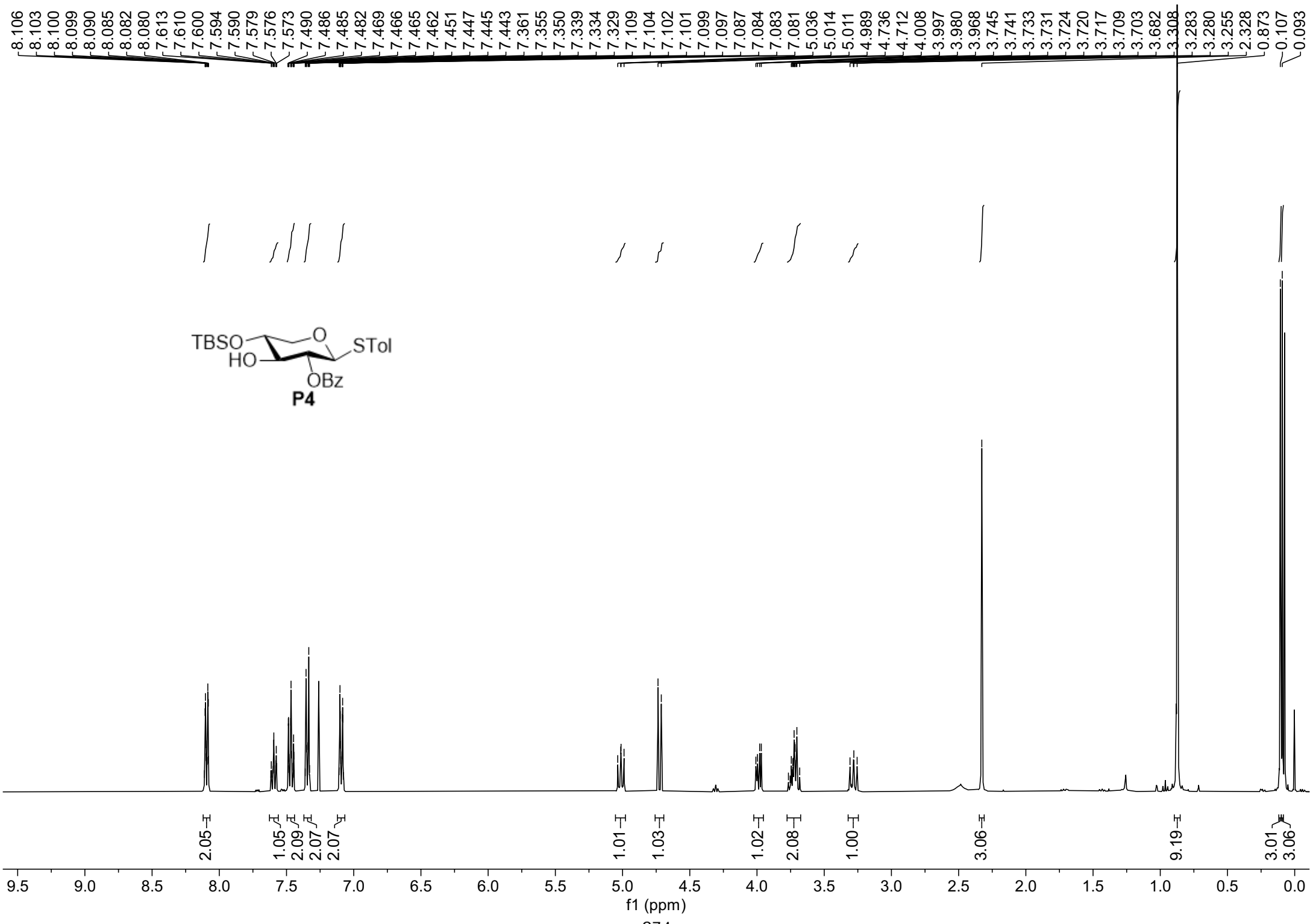
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—21.3  
—18.1

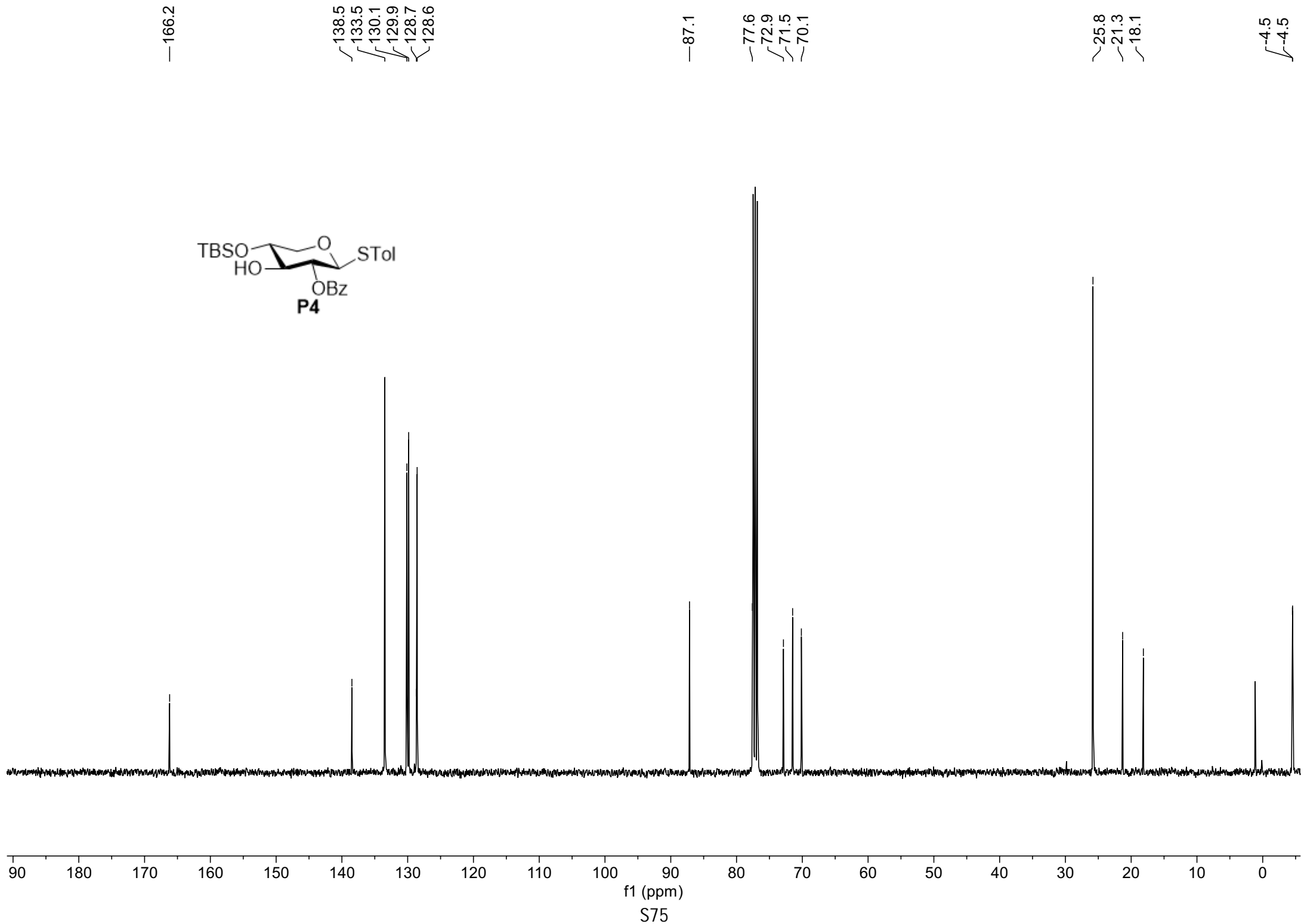
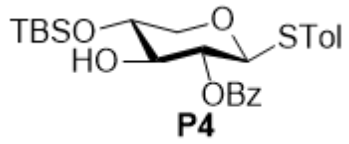
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—4.6

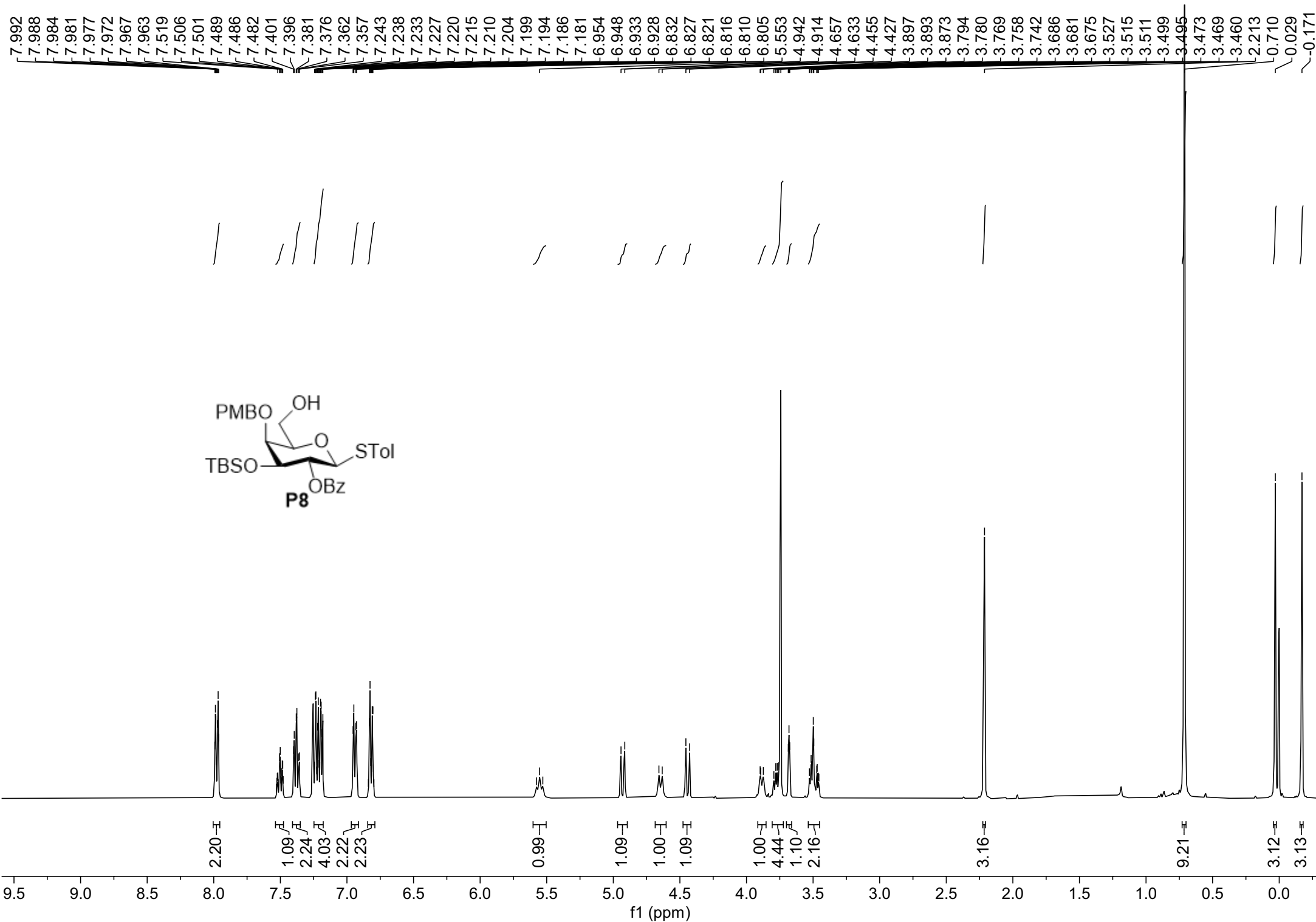


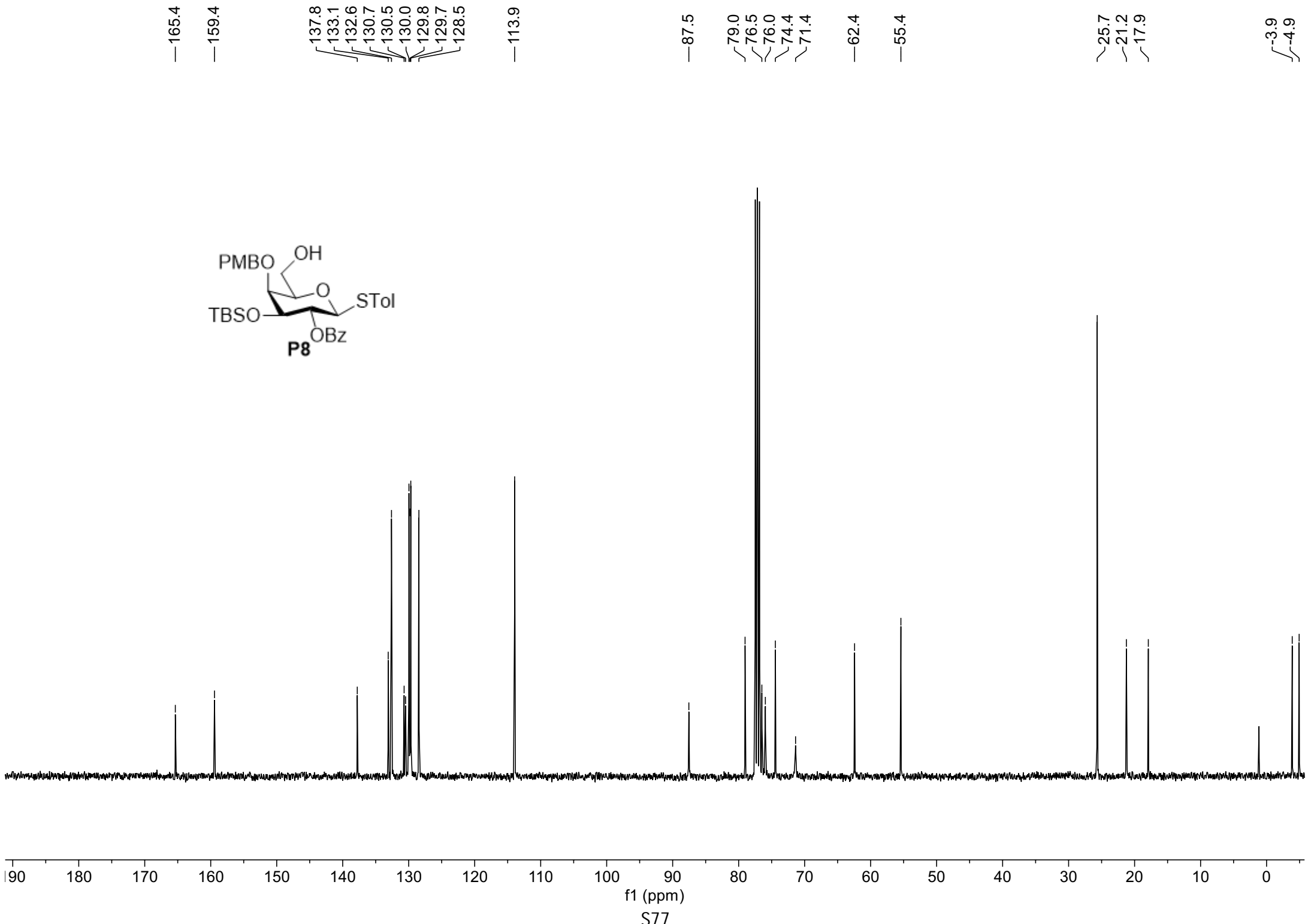
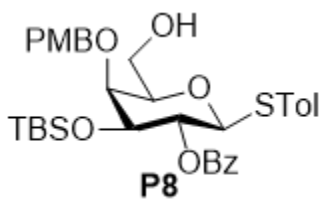
f1 (ppm)

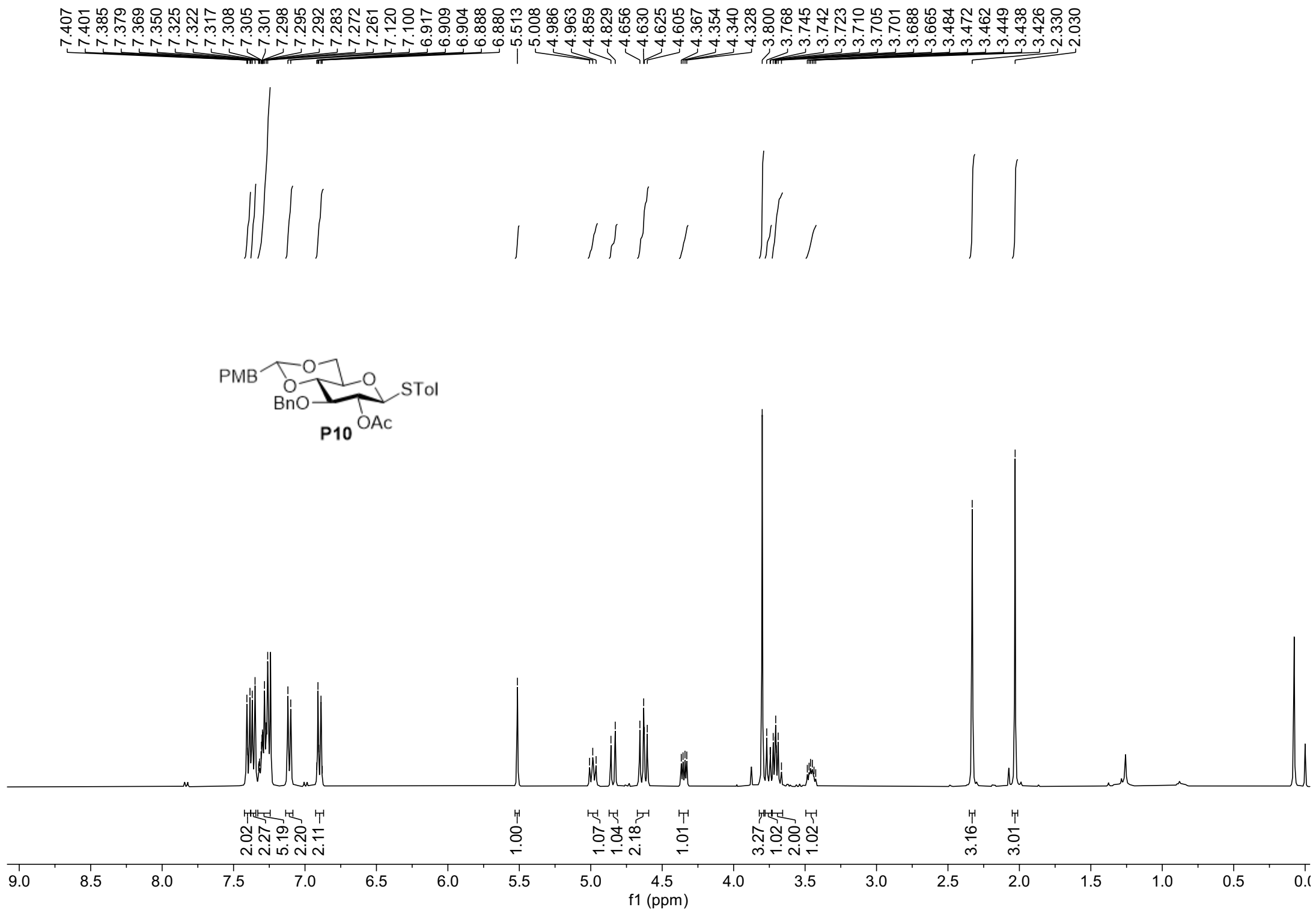
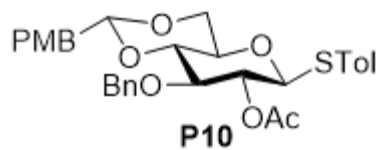
S73











—169.4

—160.2

138.6

138.2

133.5

129.8

128.4

128.0

127.8

127.4

—113.7

—101.3

—87.1

81.4

79.9

74.4

71.4

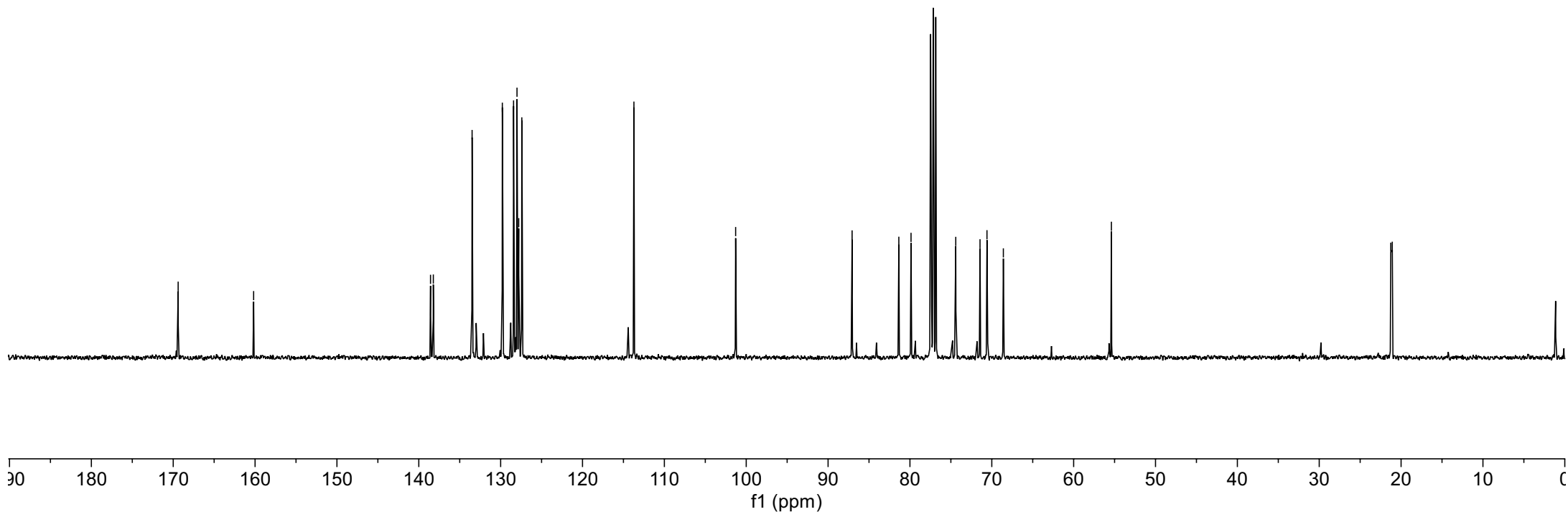
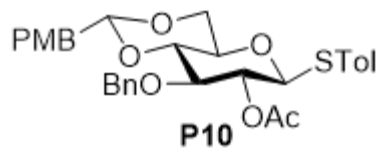
70.6

68.6

—55.4

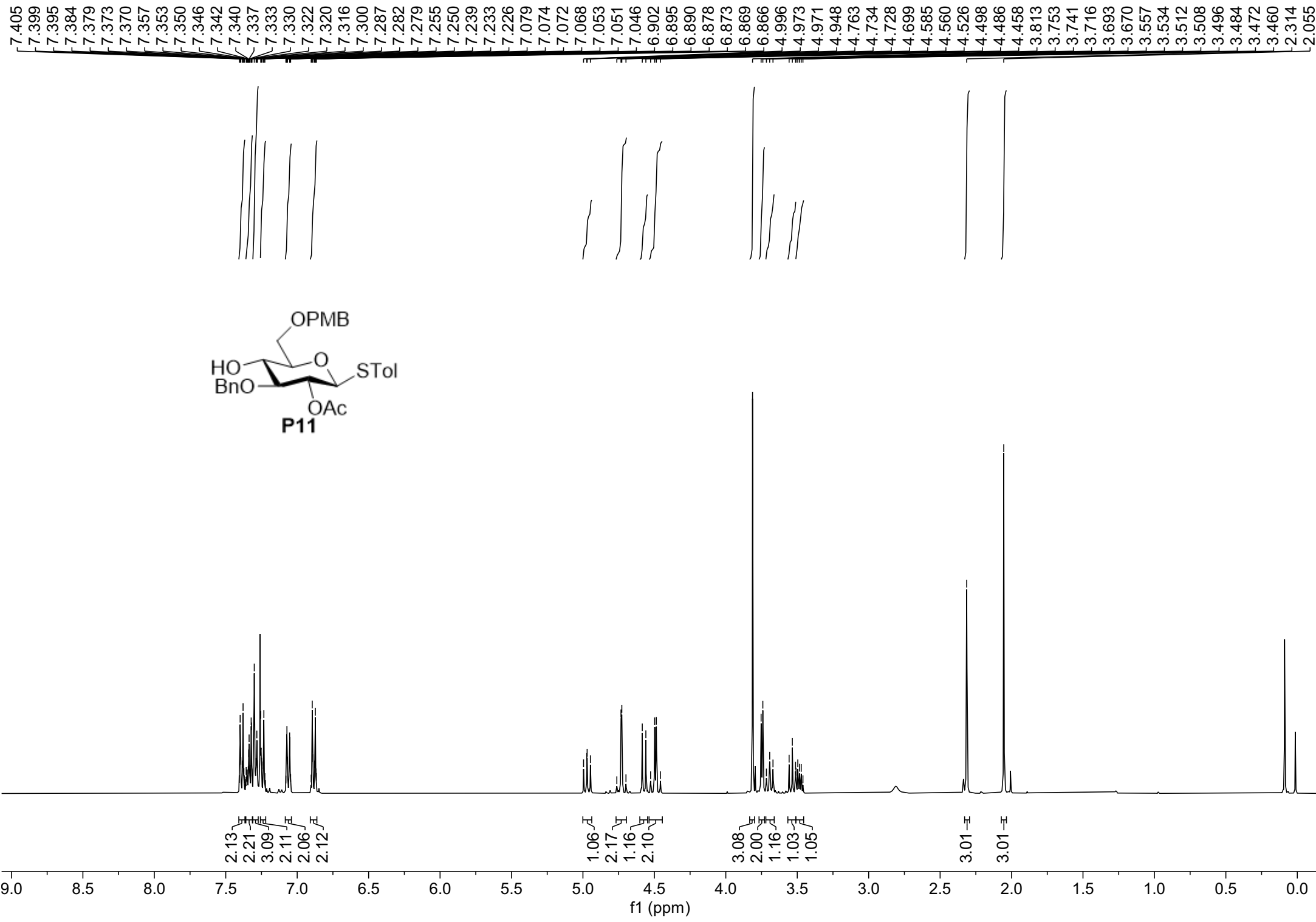
21.3

21.1



S79

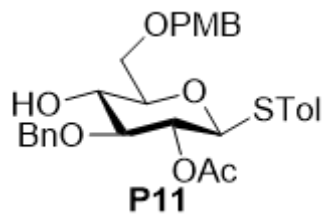




9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

S80



—169.6

—159.4

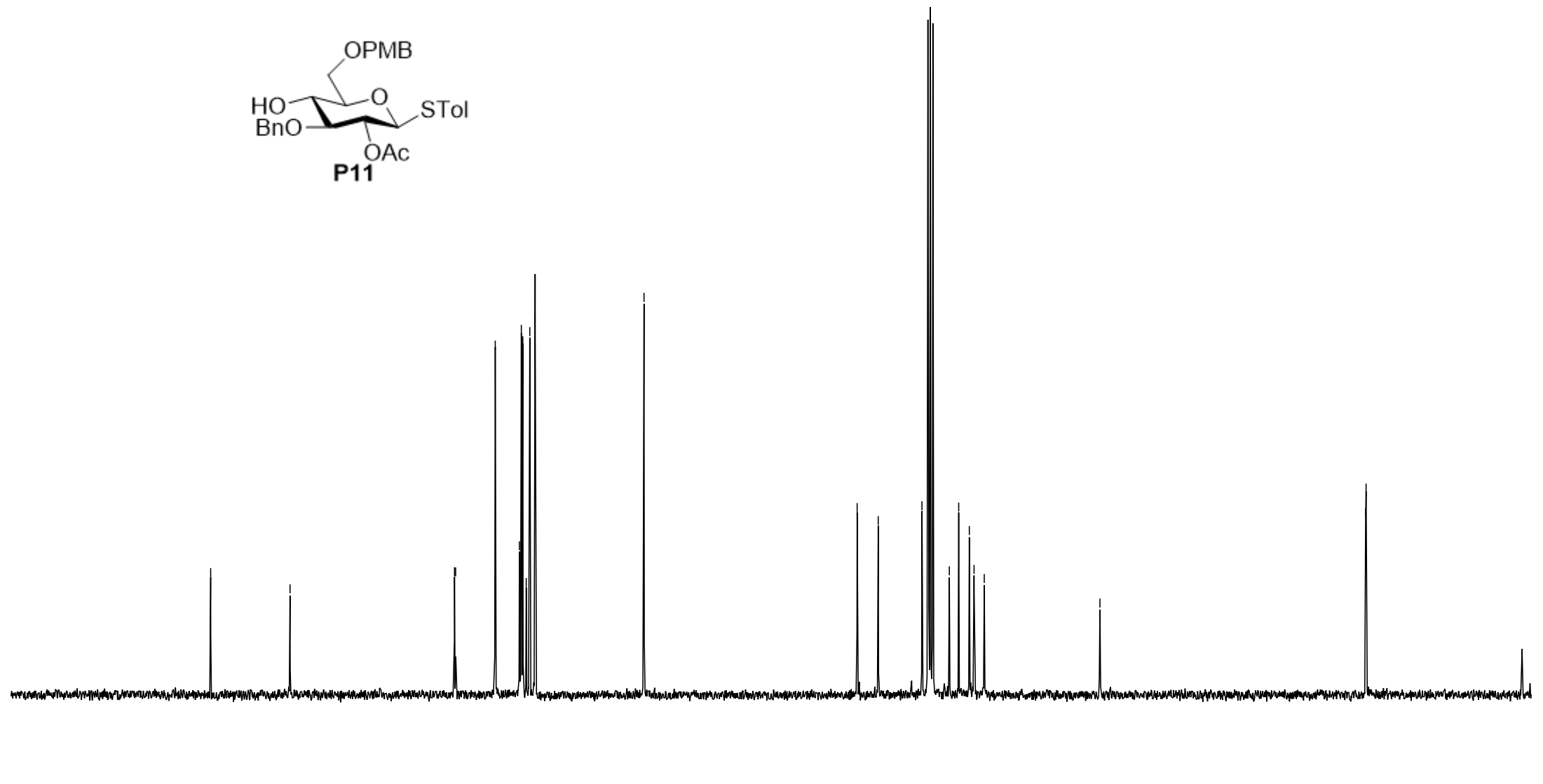
138.3  
138.2  
133.1  
130.0  
129.7  
129.5  
129.1  
128.6  
127.9

—113.9

—86.6  
—83.9  
78.2  
74.7  
73.5  
72.1  
71.5  
70.2

—55.4

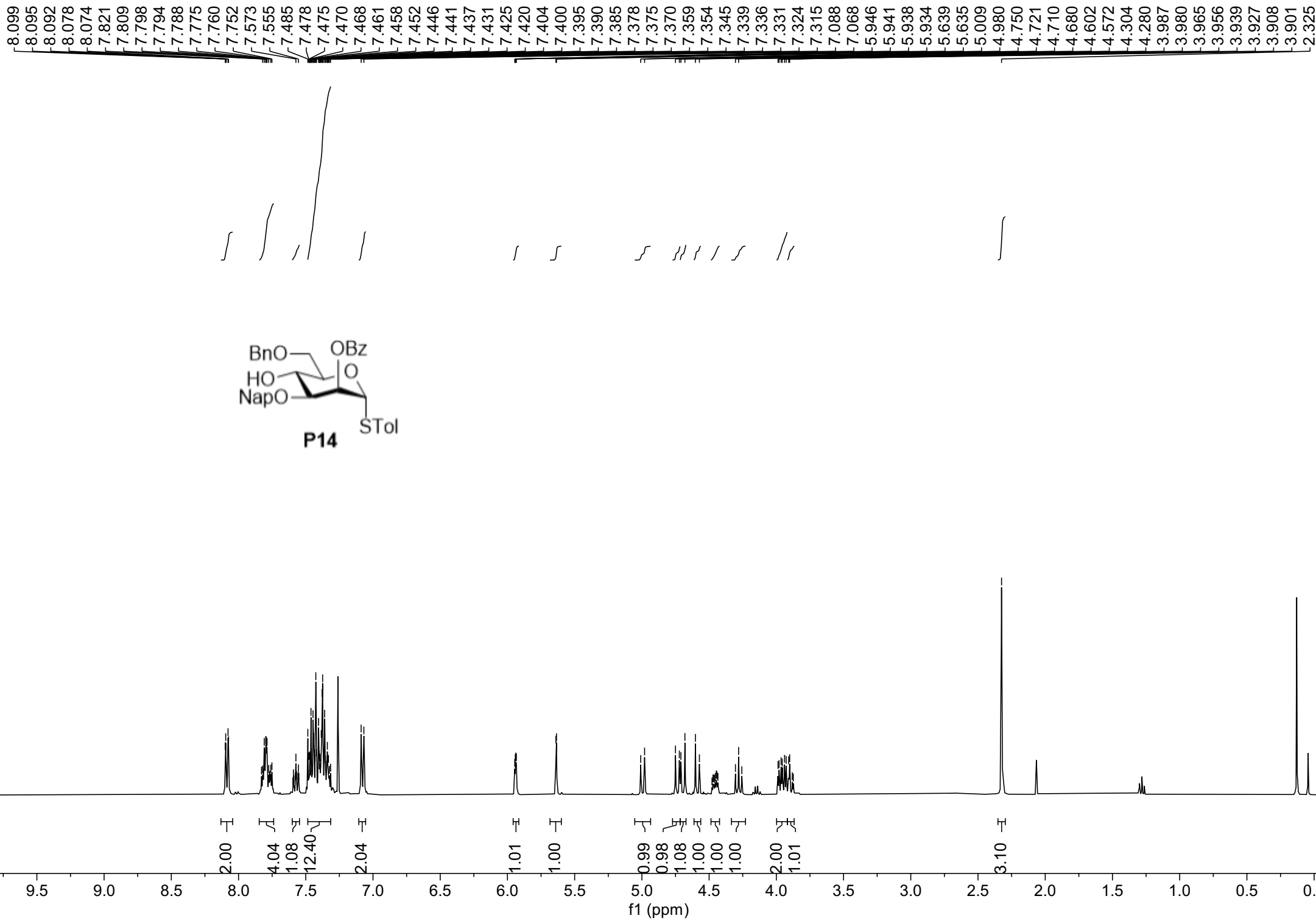
21.2  
21.2



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

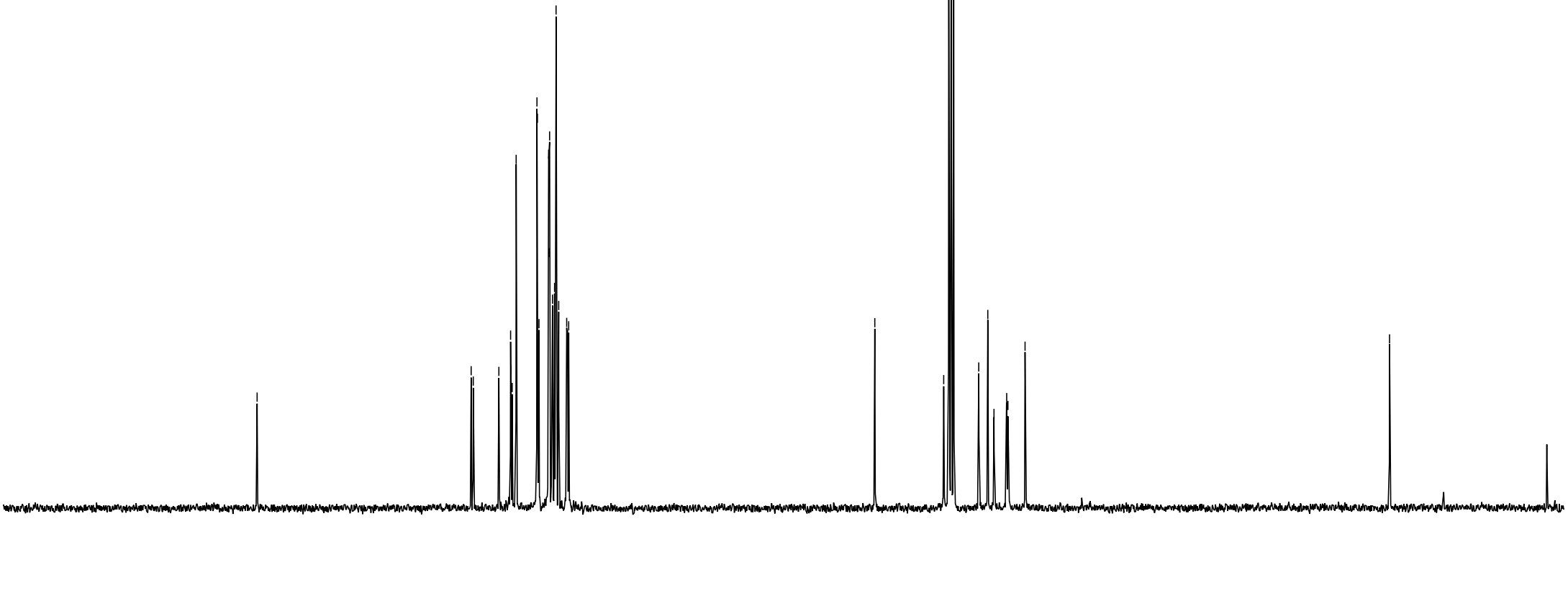
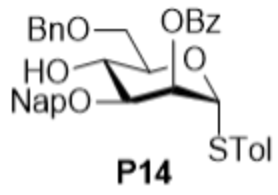
S81



165.4  
138.1  
137.8  
134.6  
133.1  
133.0  
132.9  
132.4  
129.7  
129.7  
129.5  
128.2  
128.2  
128.1  
127.7  
127.5  
127.3  
126.9  
125.9  
125.8  
125.7

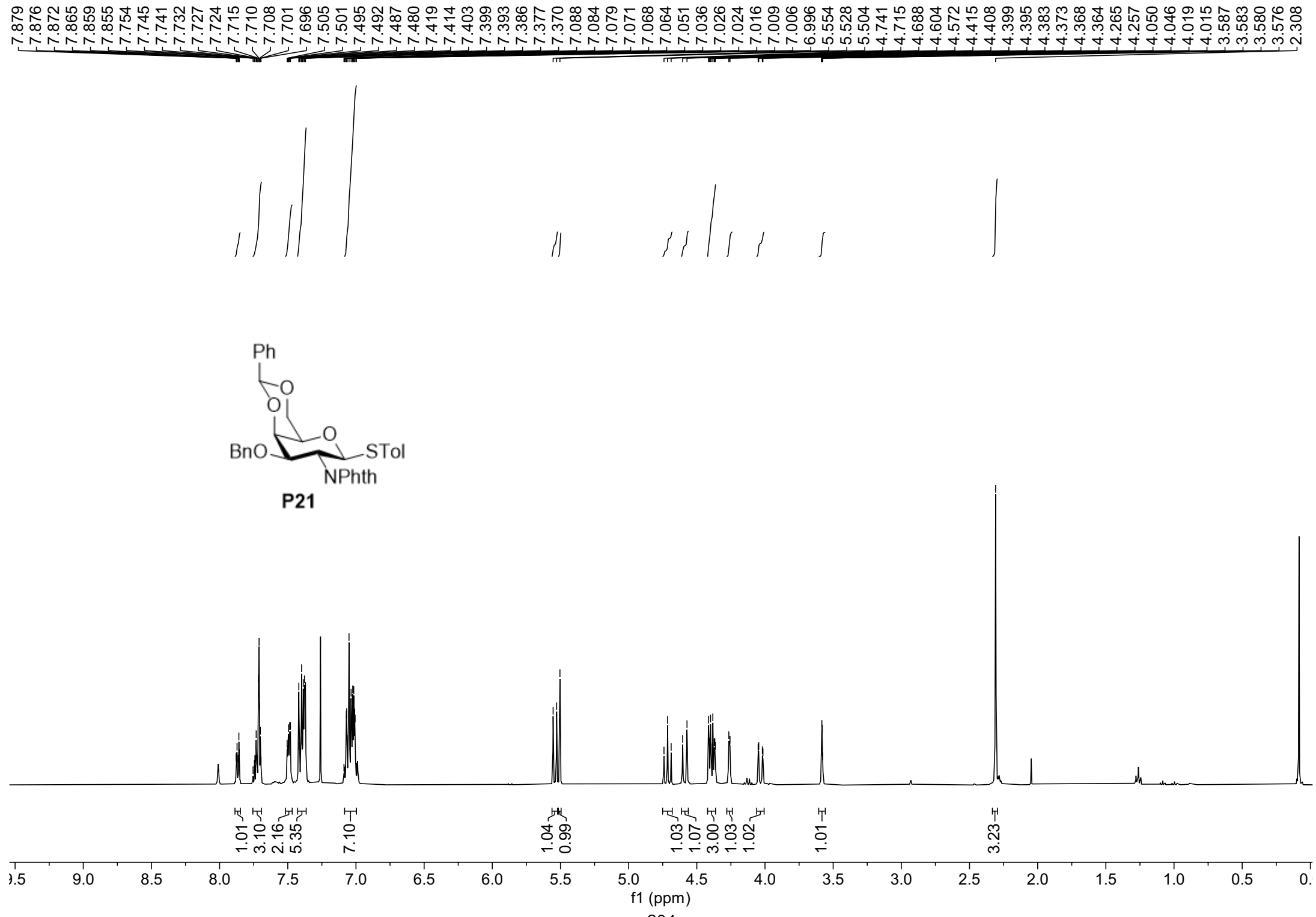
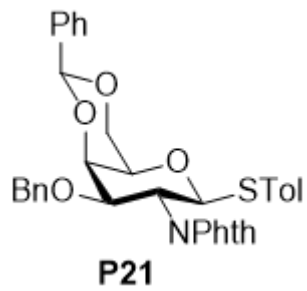
86.6  
77.8  
73.3  
72.2  
71.4  
69.8  
69.6  
67.4

20.9



f1 (ppm)

S83



168.6  
167.2

138.2  
137.9  
137.8  
134.1  
134.1  
133.9  
131.9  
131.8  
129.6  
129.1  
128.3  
128.2  
127.8  
127.7  
127.6  
126.8  
123.7  
123.2

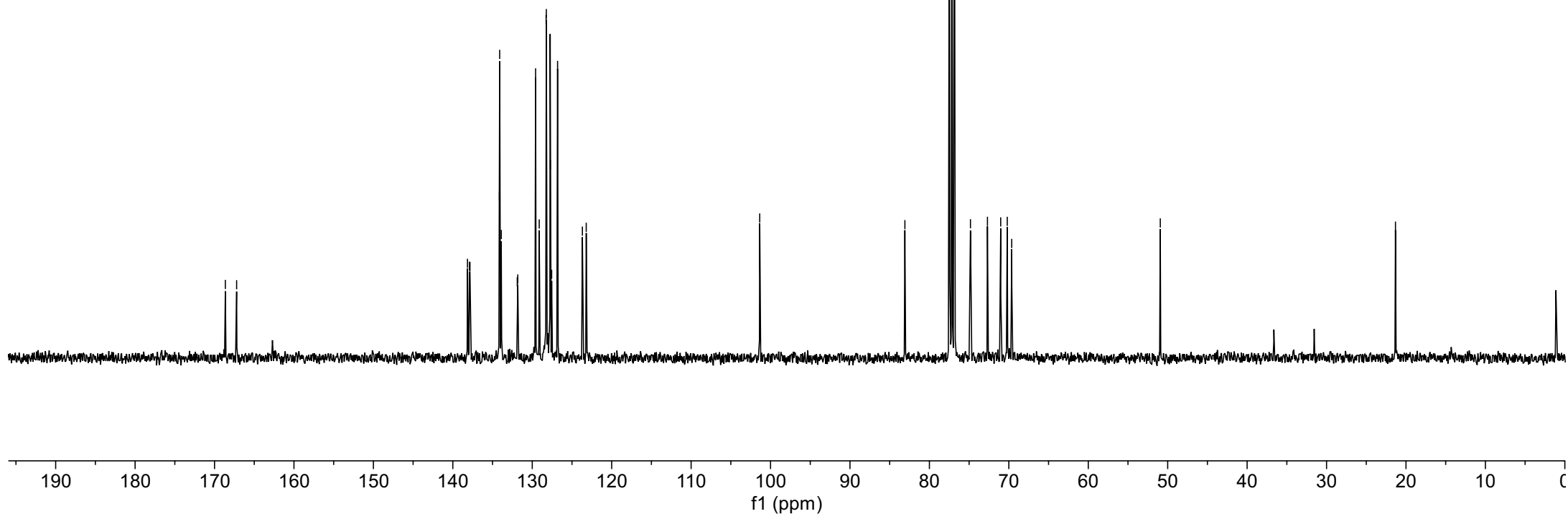
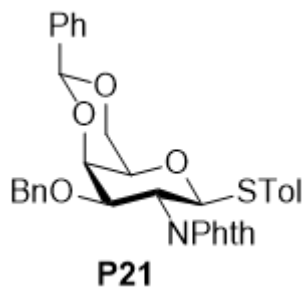
101.4

83.1

74.8  
72.7  
71.0  
70.2  
69.6

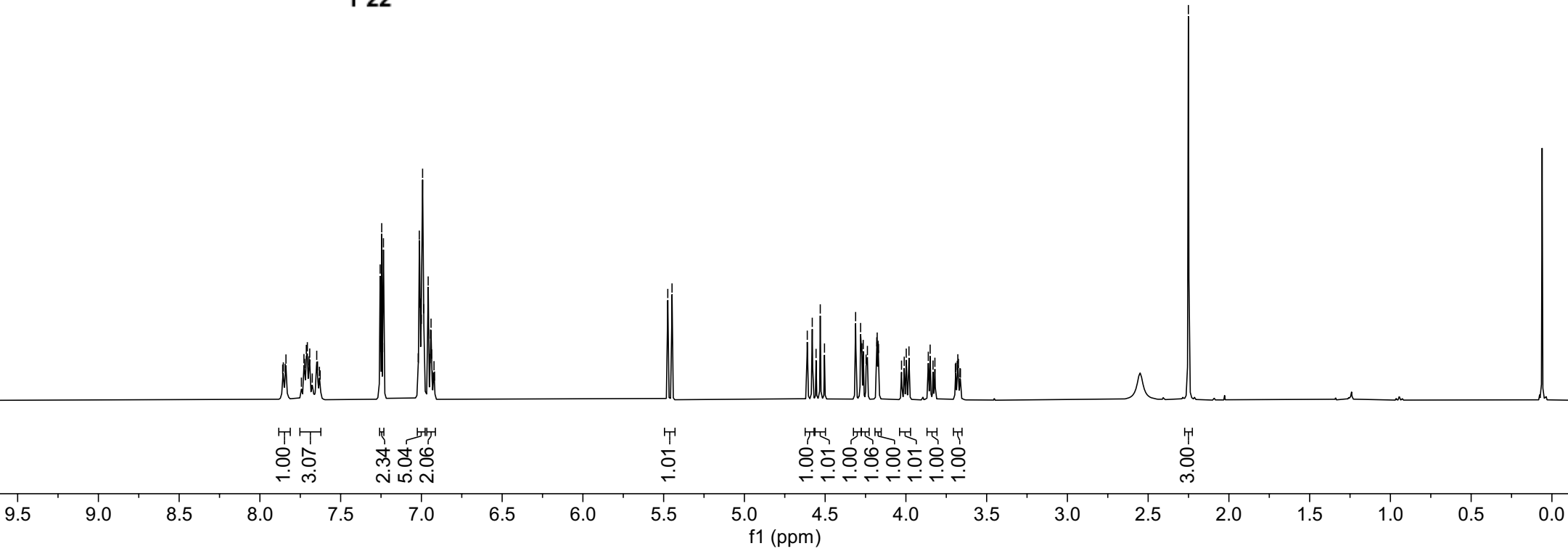
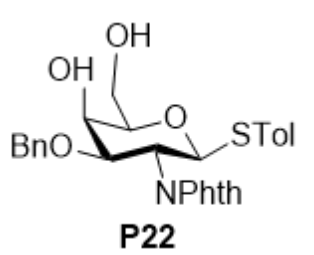
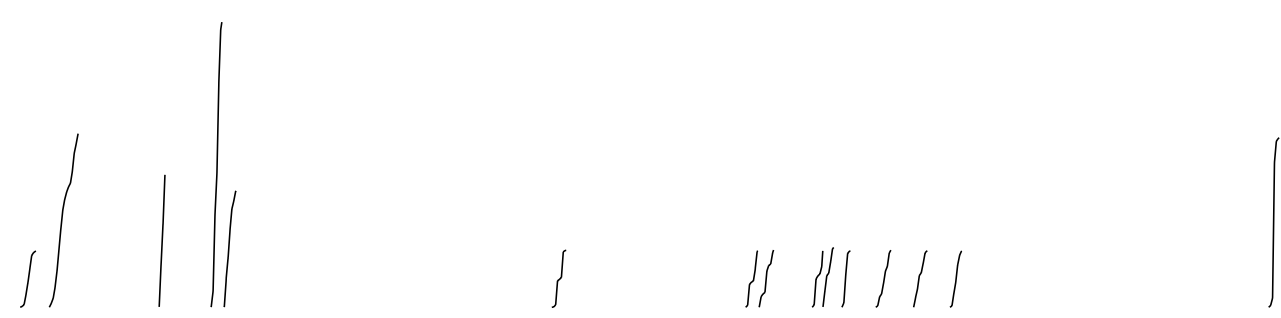
50.9

21.3



S85

7.859  
7.855  
7.843  
7.839  
7.743  
7.727  
7.723  
7.713  
7.706  
7.696  
7.692  
7.676  
7.648  
7.643  
7.631  
7.627  
7.255  
7.251  
7.246  
7.240  
7.235  
7.020  
7.013  
7.008  
7.000  
6.993  
6.985  
6.958  
6.946  
6.943  
6.940  
6.937  
6.933  
6.927  
6.922  
6.919  
5.474  
5.448  
4.611  
4.580  
4.556  
4.530  
4.504  
4.311  
4.281  
4.272  
4.264  
4.246  
4.238  
4.181  
4.178  
4.172  
4.169  
4.027  
4.010  
3.998  
3.981  
3.861  
3.850  
3.832  
3.820  
3.694  
3.691  
3.682  
3.678  
3.675  
3.665  
3.662  
2.251



168.3  
167.6

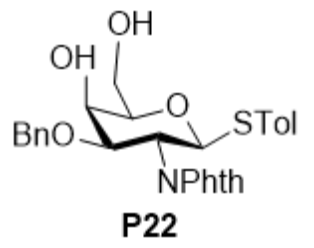
138.1  
137.1  
134.2  
134.0  
132.9  
131.7  
129.7  
128.5  
128.4  
128.1  
128.0  
123.7  
123.3

84.1

78.4  
75.6  
71.4  
66.3  
62.8

51.2

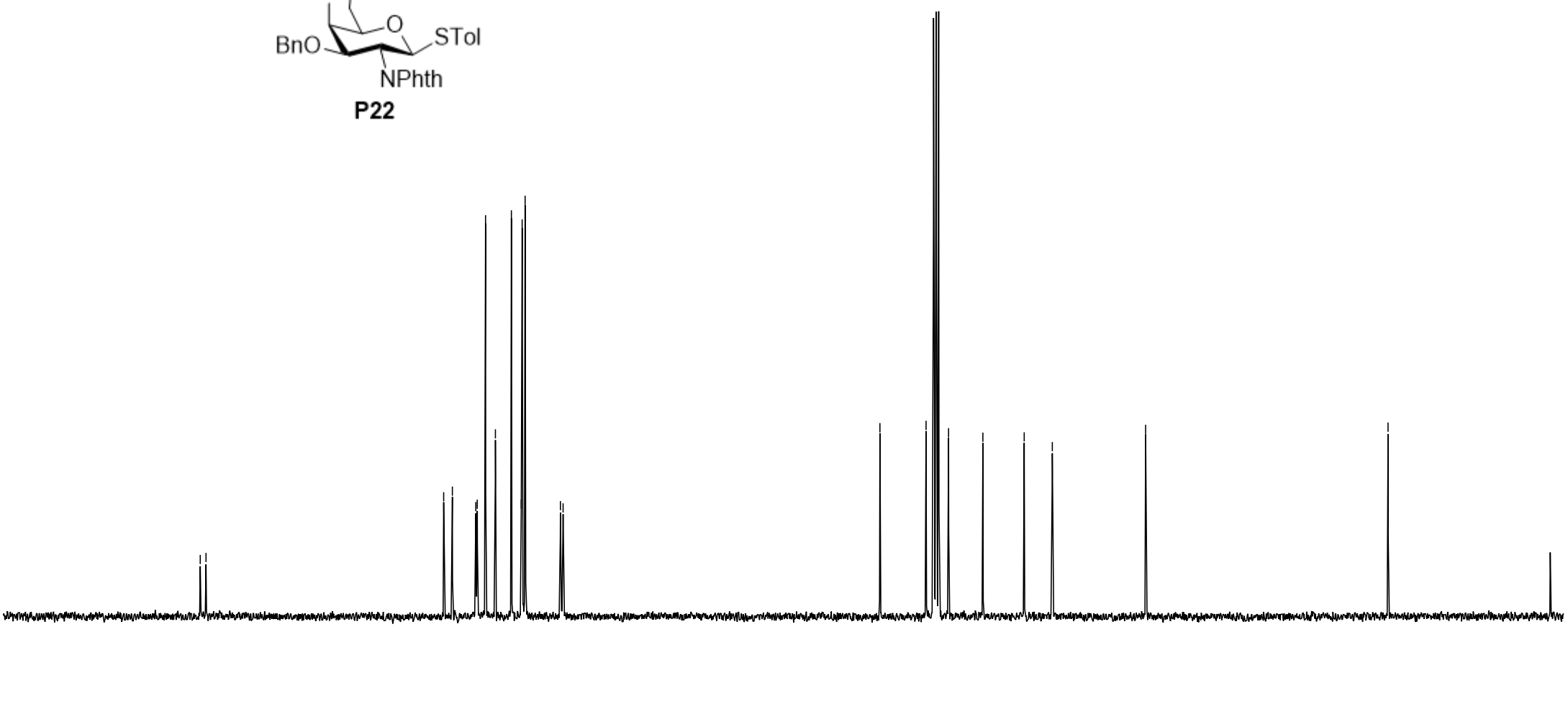
21.2



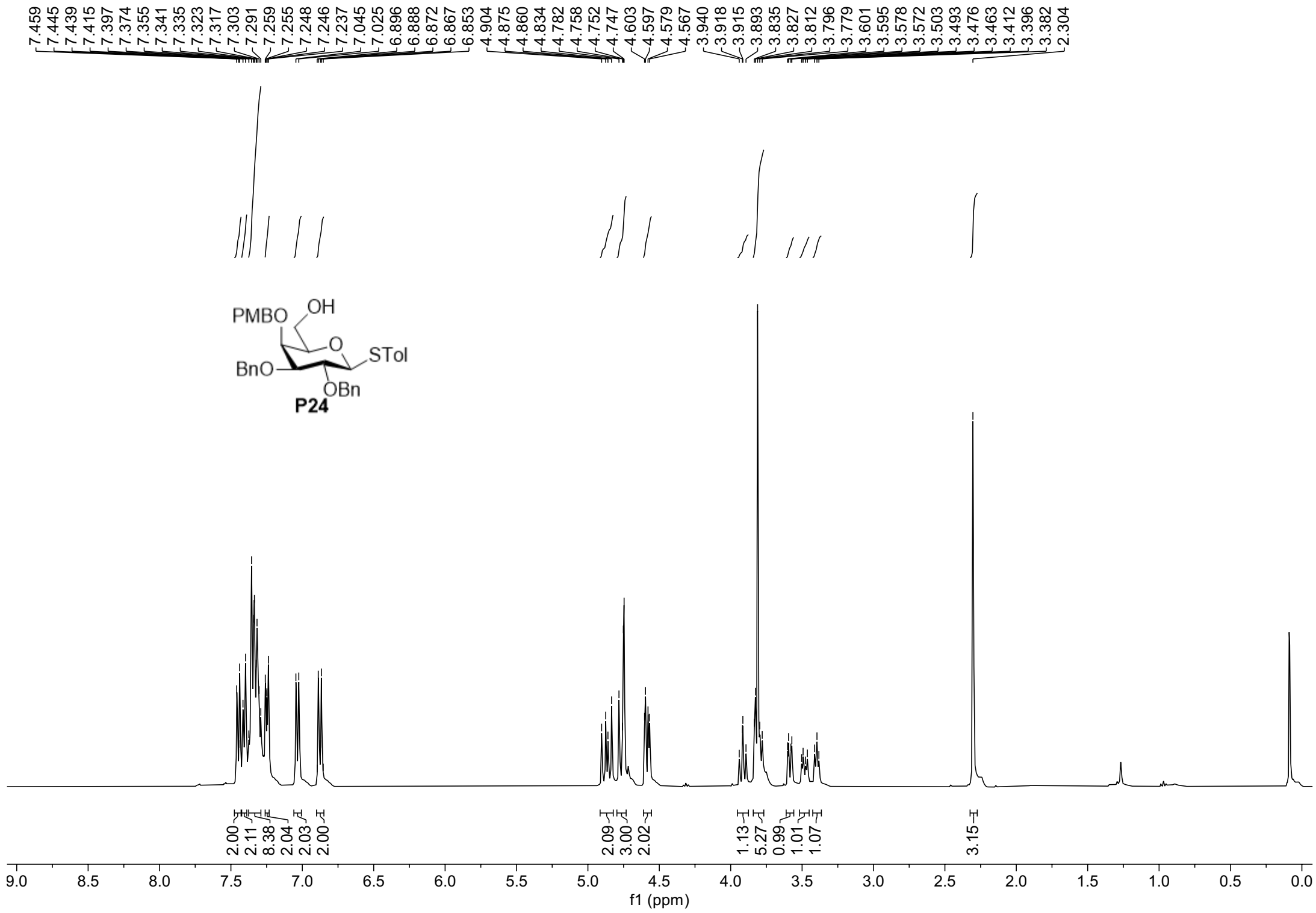
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

S87







—159.5

138.4  
138.3  
137.5  
132.3  
130.5  
130.3  
130.0  
129.7  
128.6  
128.5  
128.4  
127.9  
127.9  
127.8  
113.9

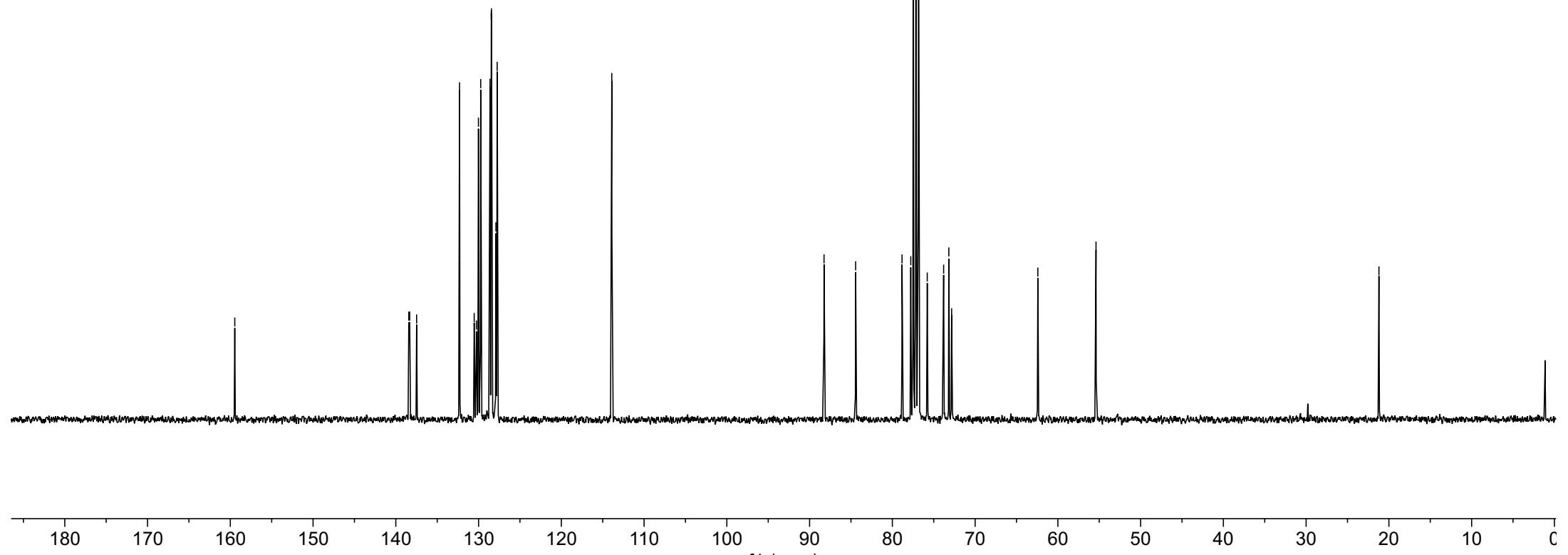
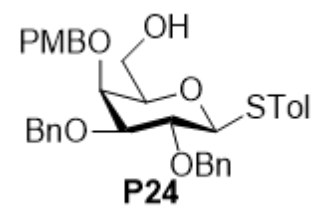
—88.3

—84.4  
78.8  
77.8  
75.8  
73.8  
73.2  
72.8

—62.4

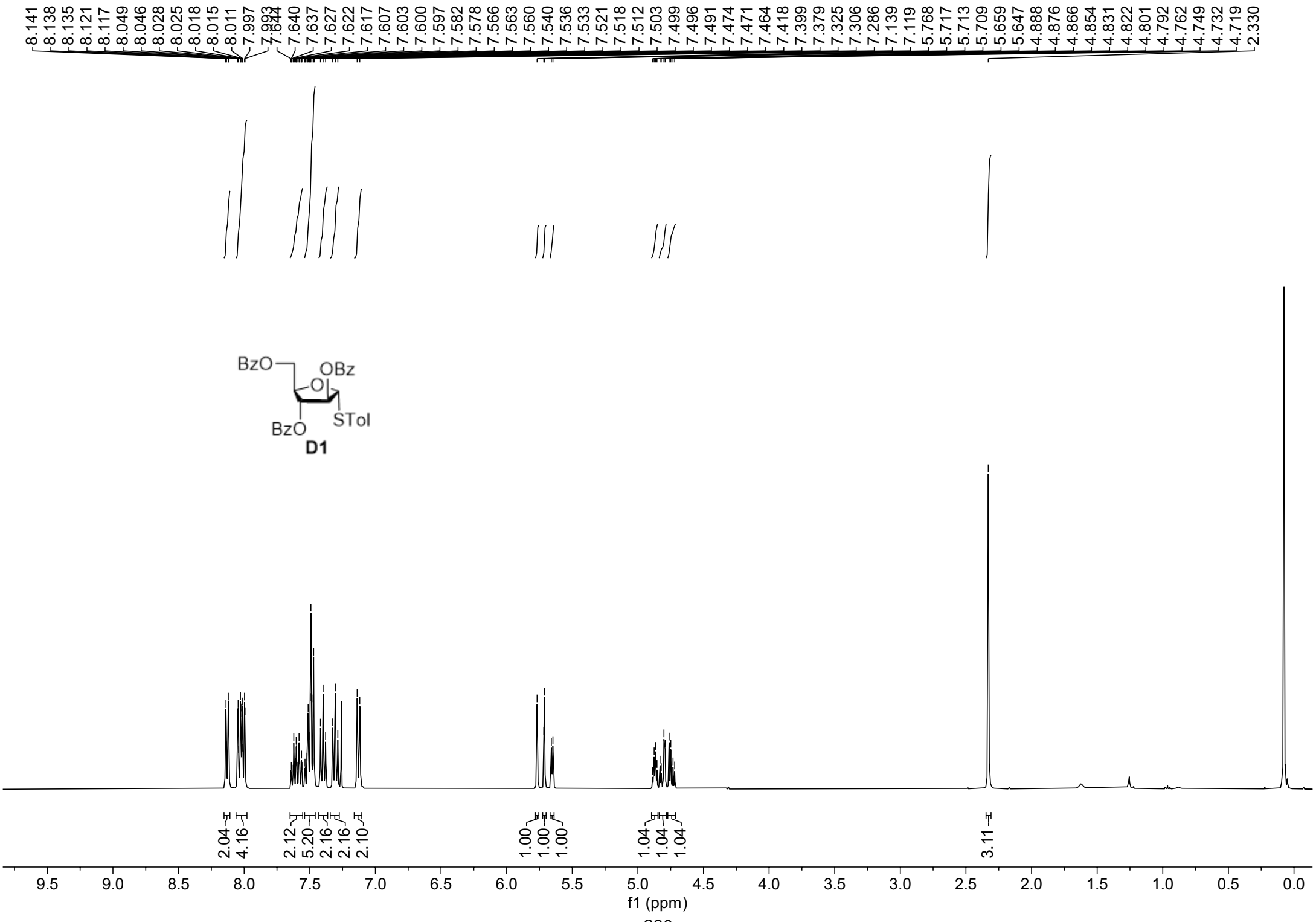
—55.4

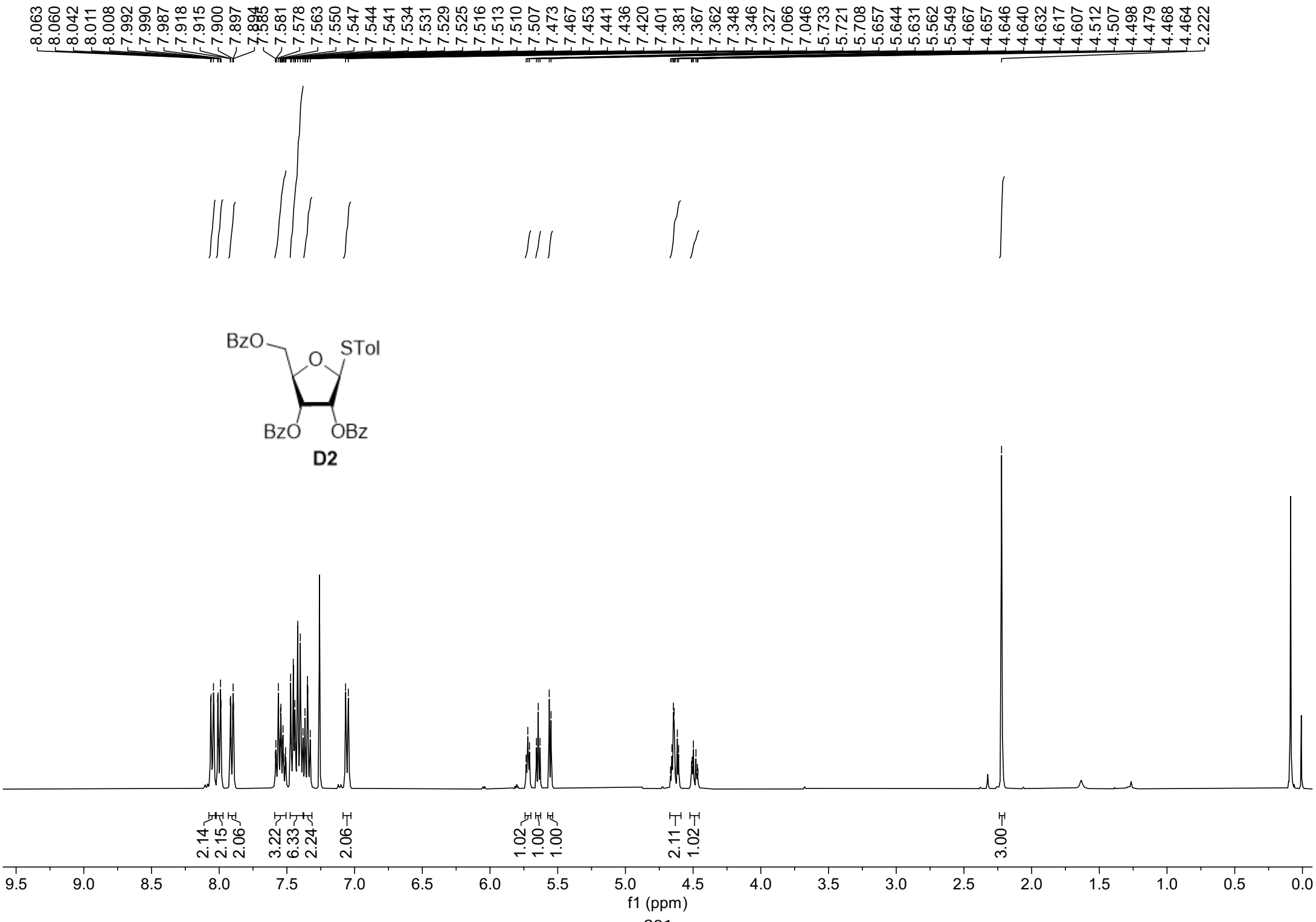
—21.2

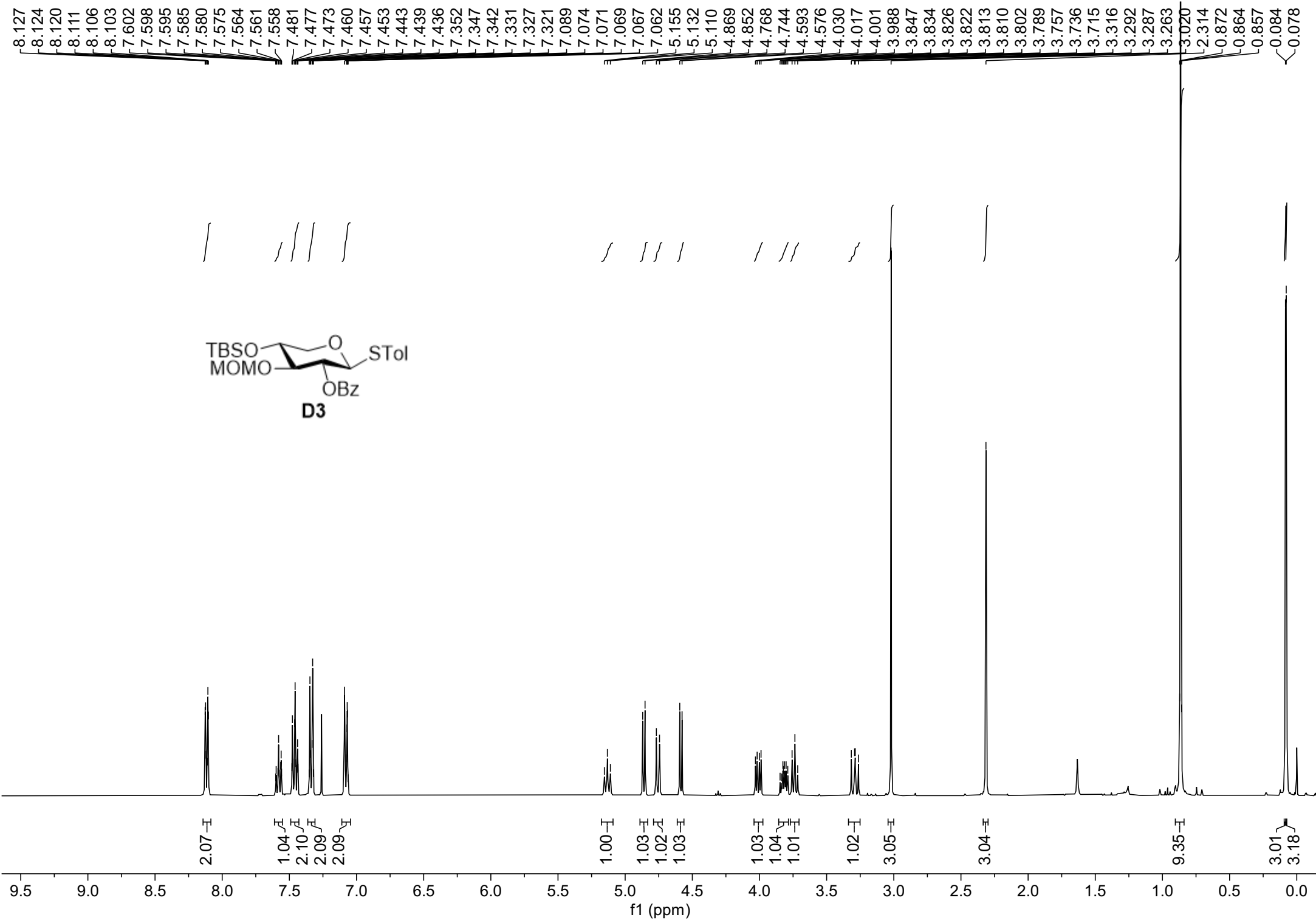


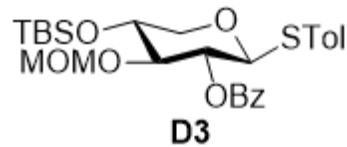
f1 (ppm)

S89









—165.6

138.2  
133.3  
133.0  
130.2  
130.0  
129.8  
129.5  
128.5

—98.2

—87.8

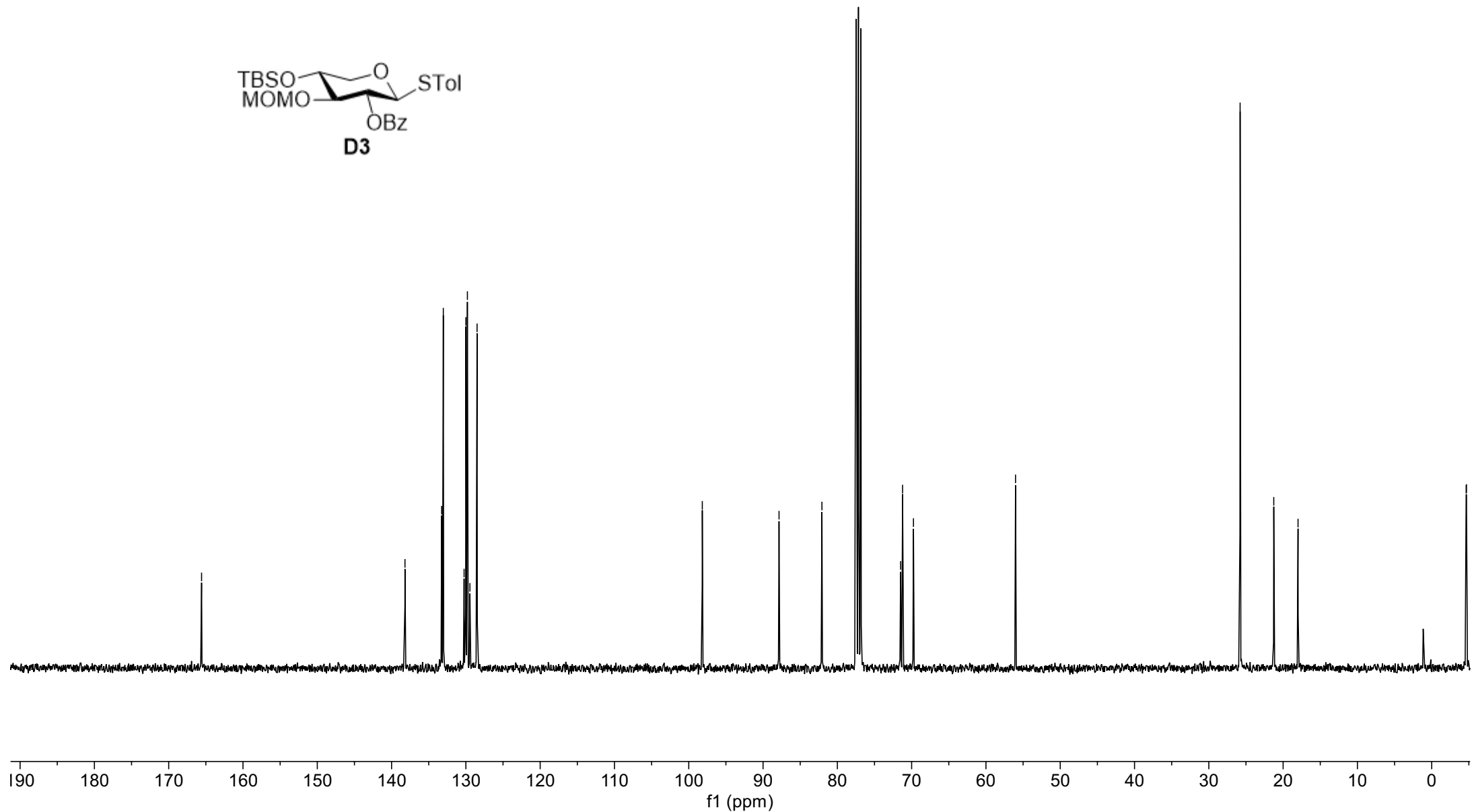
—82.1

71.5  
71.2  
69.8

—56.0

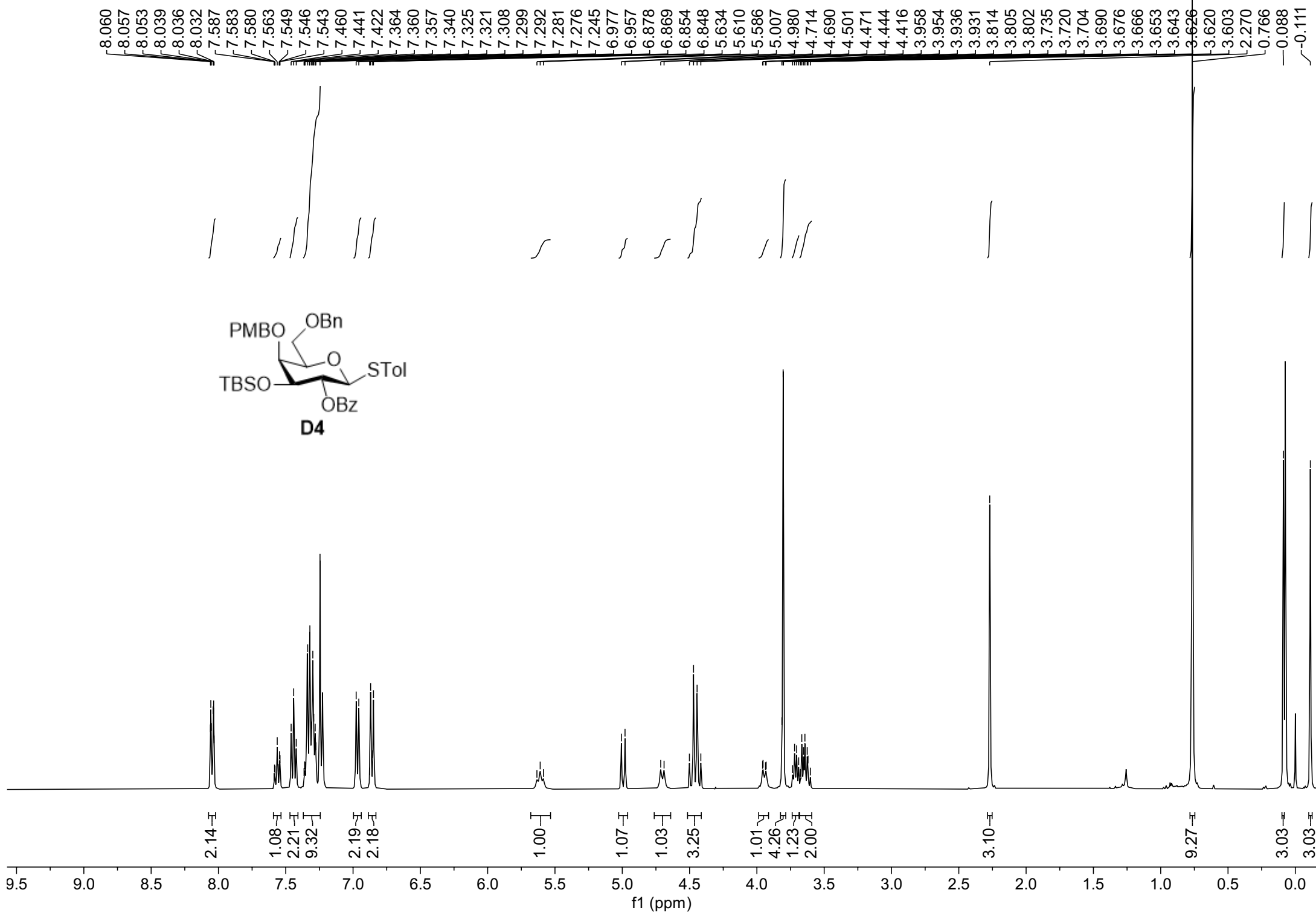
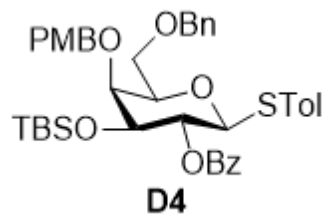
25.8  
21.3  
18.0

4.6  
4.7



f1 (ppm)

S93



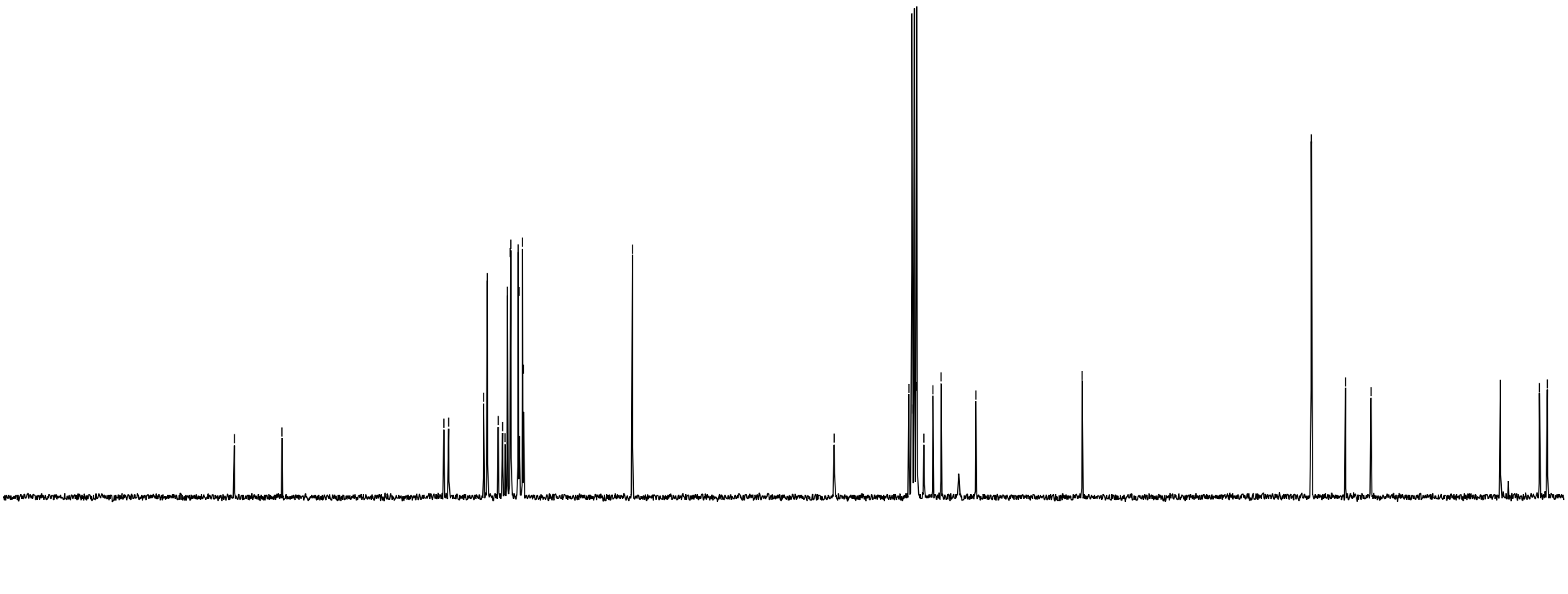
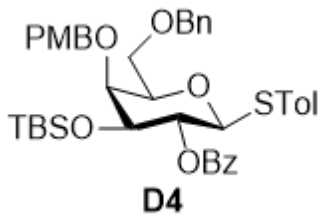
—165.4  
—159.2  
138.2  
137.6  
133.0  
132.5  
131.1  
130.6  
130.2  
129.9  
129.6  
129.5  
128.5  
128.4  
128.0  
127.9  
—113.7

—87.6  
77.9  
77.4  
76.9  
75.9  
74.8  
73.7  
69.2

—55.4

25.7  
21.2  
17.9

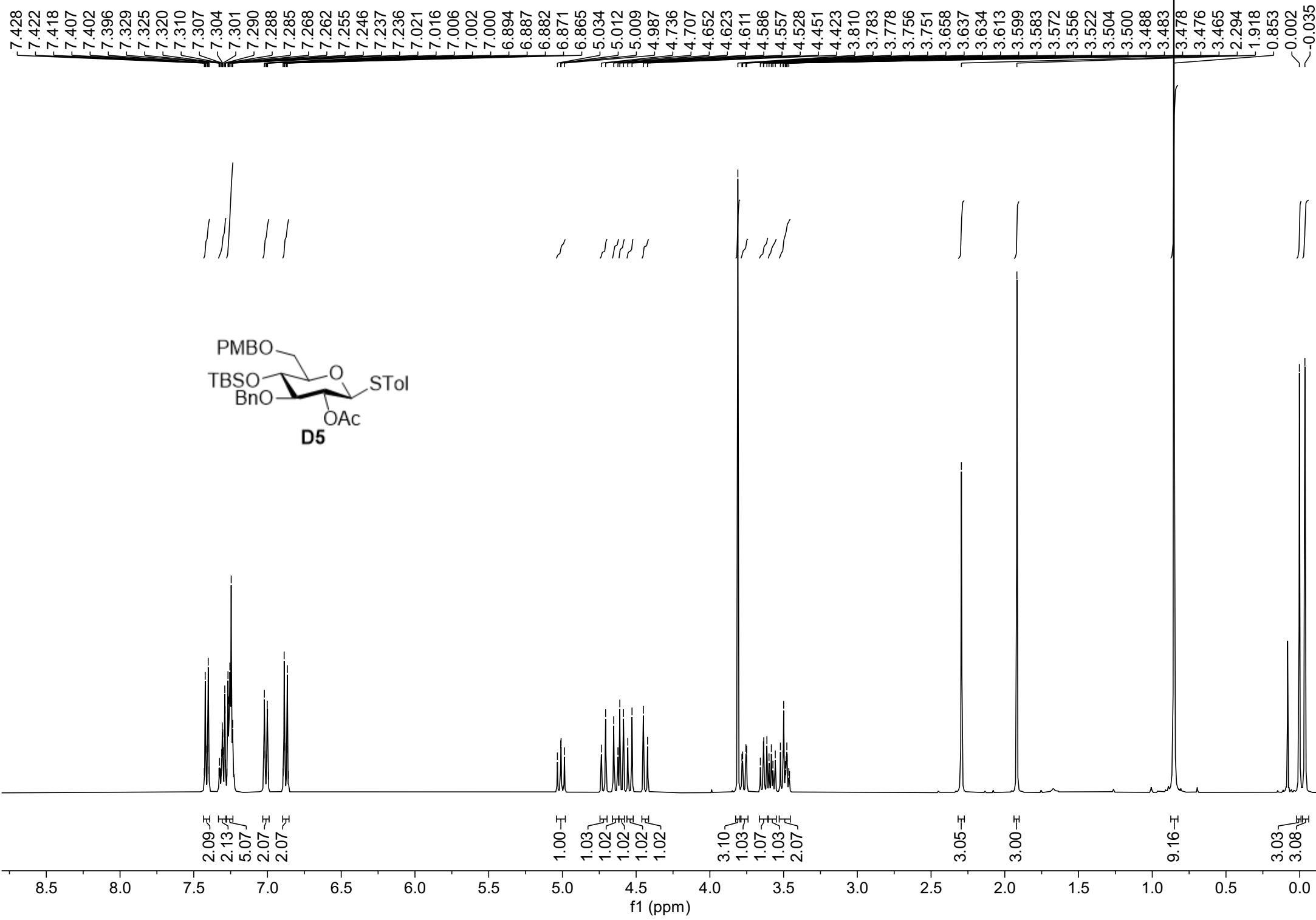
-3.9  
-4.9



f1 (ppm)

S95





—169.7

—159.2

138.3

137.8

132.6

130.6

129.7

129.6

129.3

128.4

127.5

127.4

—113.8

—86.4

—85.1

—80.9

75.3

73.2

72.3

71.1

69.2

—55.4

—26.0

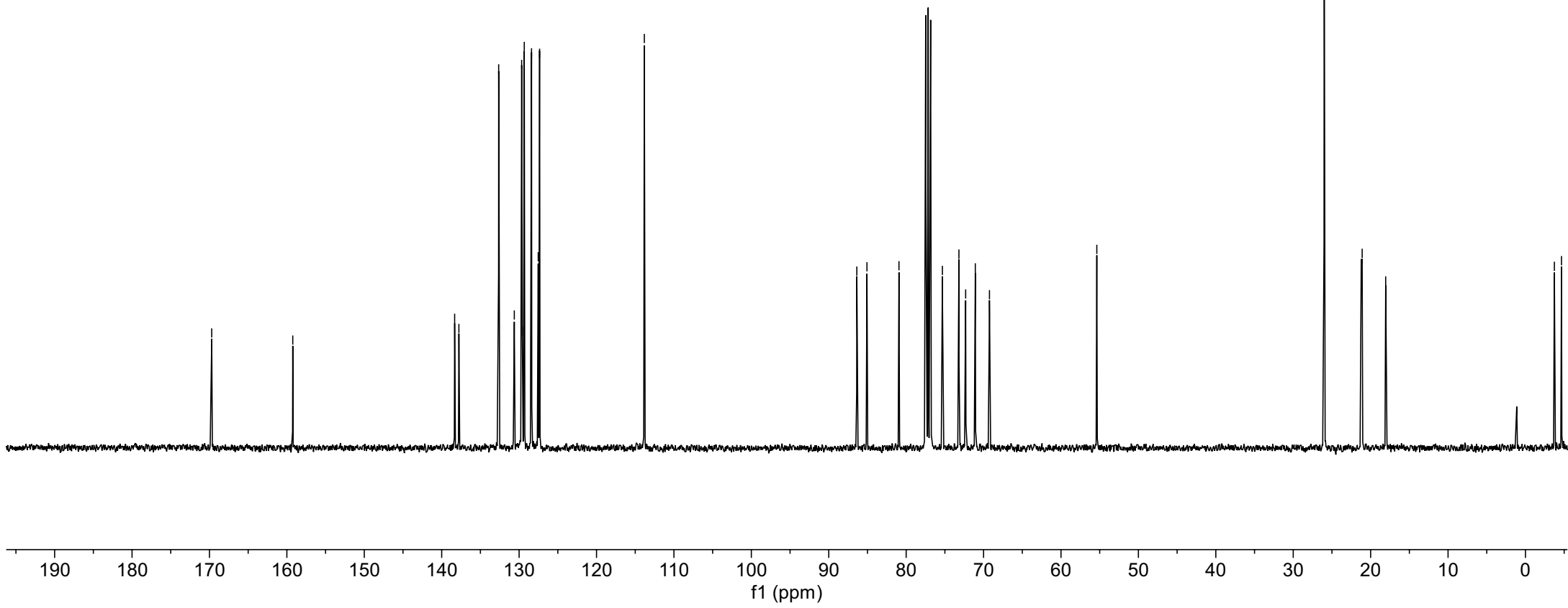
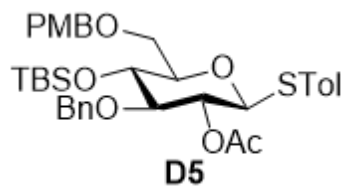
21.2

21.1

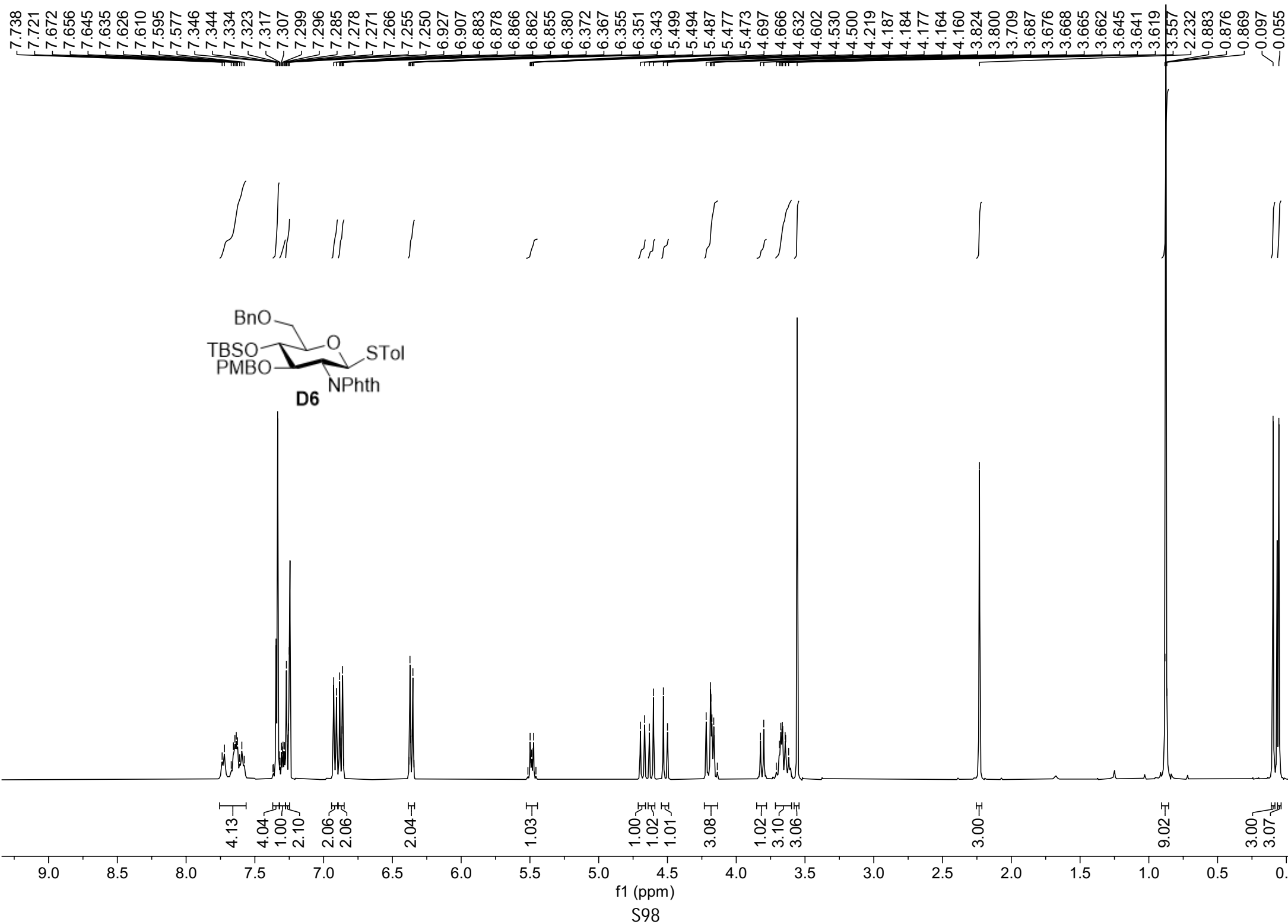
—18.1

—3.7

—4.7



S97



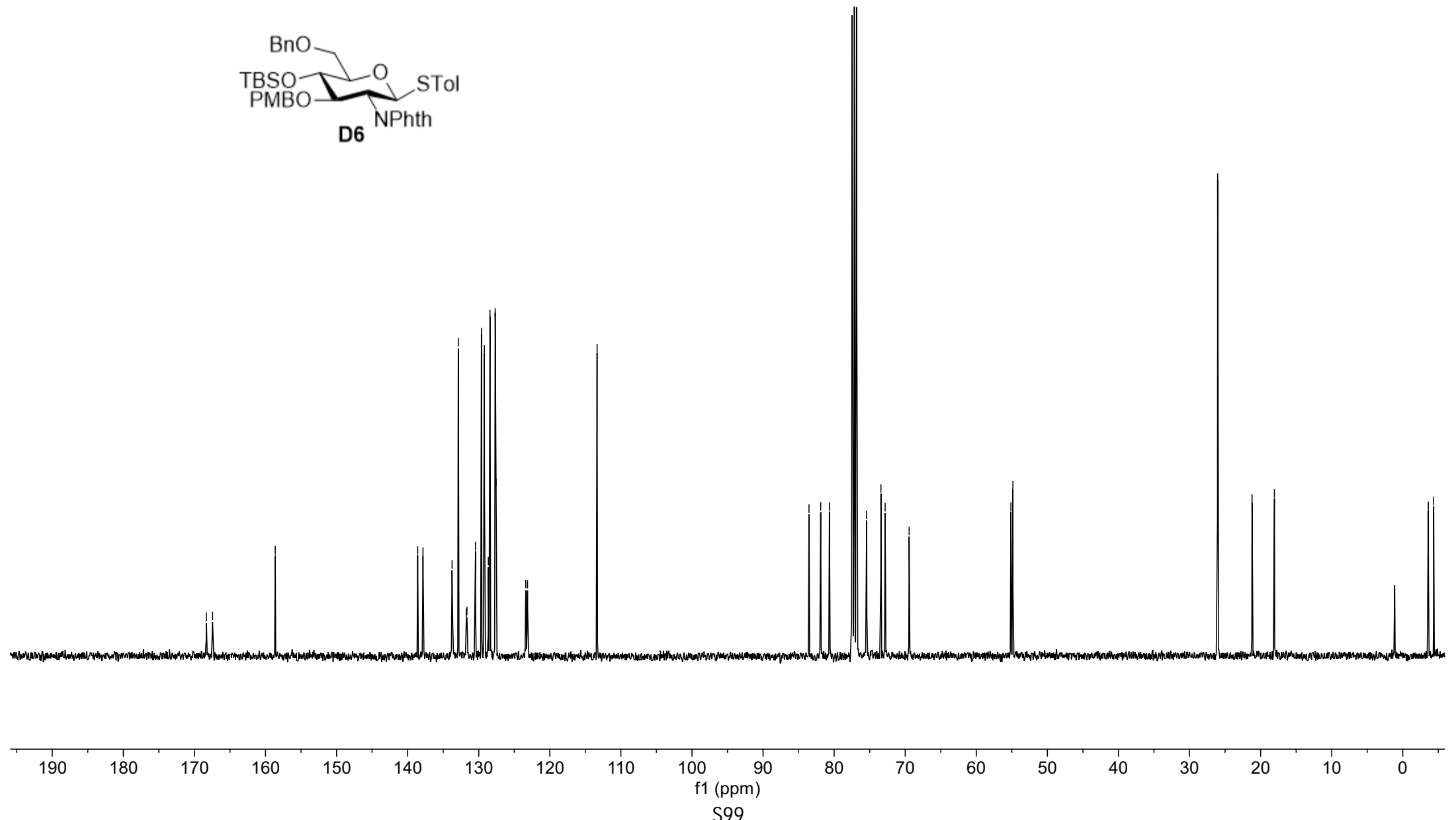
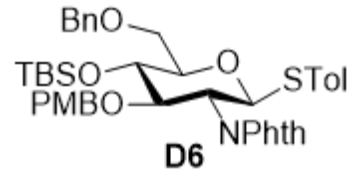
168.3  
167.4  
158.6  
138.6  
137.8  
133.7  
132.9  
131.7  
131.7  
130.5  
129.6  
129.2  
128.6  
128.4  
127.7  
127.6  
123.4  
123.1  
113.4

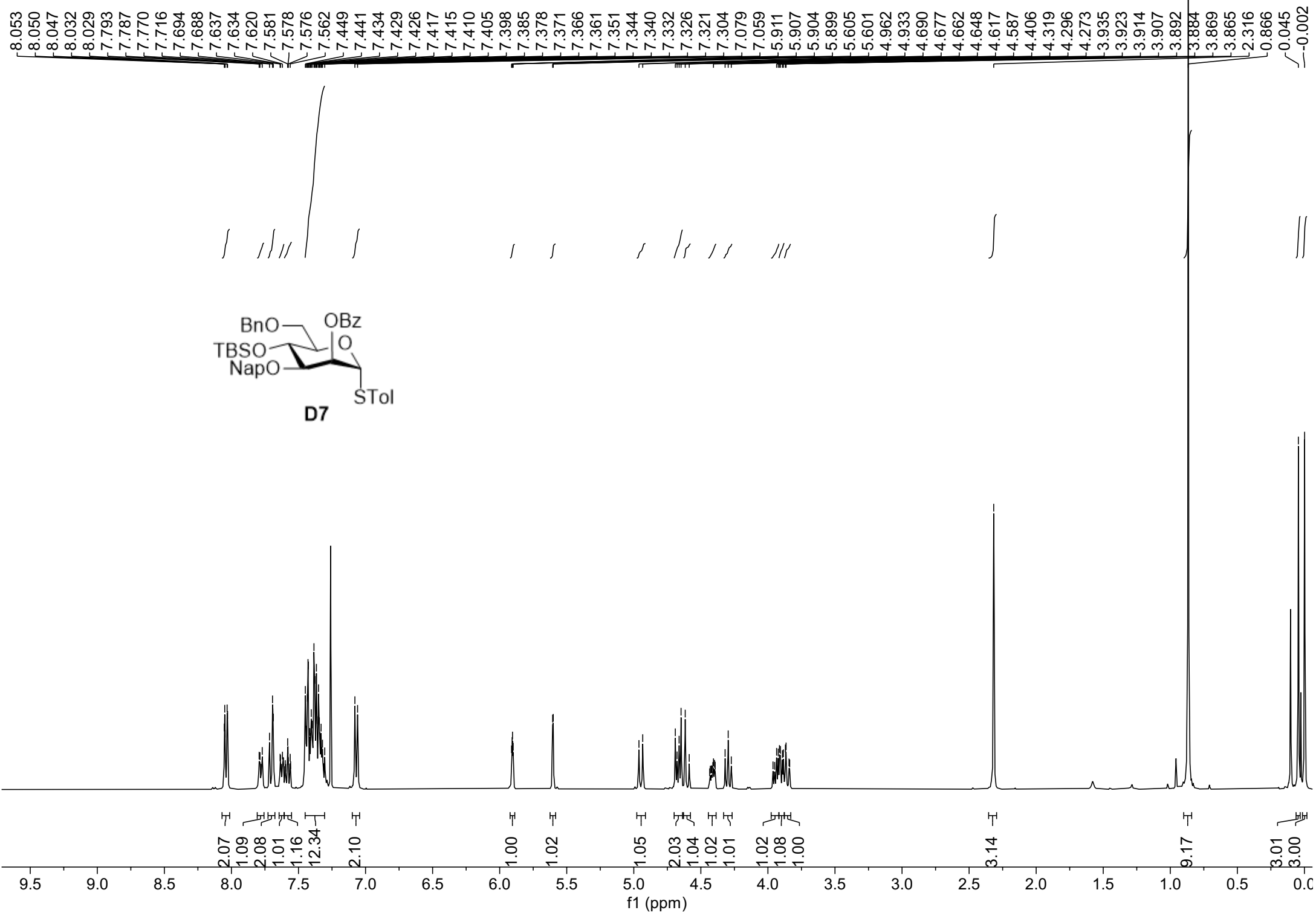
83.5  
81.9  
80.7  
75.4  
73.4  
72.8  
69.4

55.1  
54.9

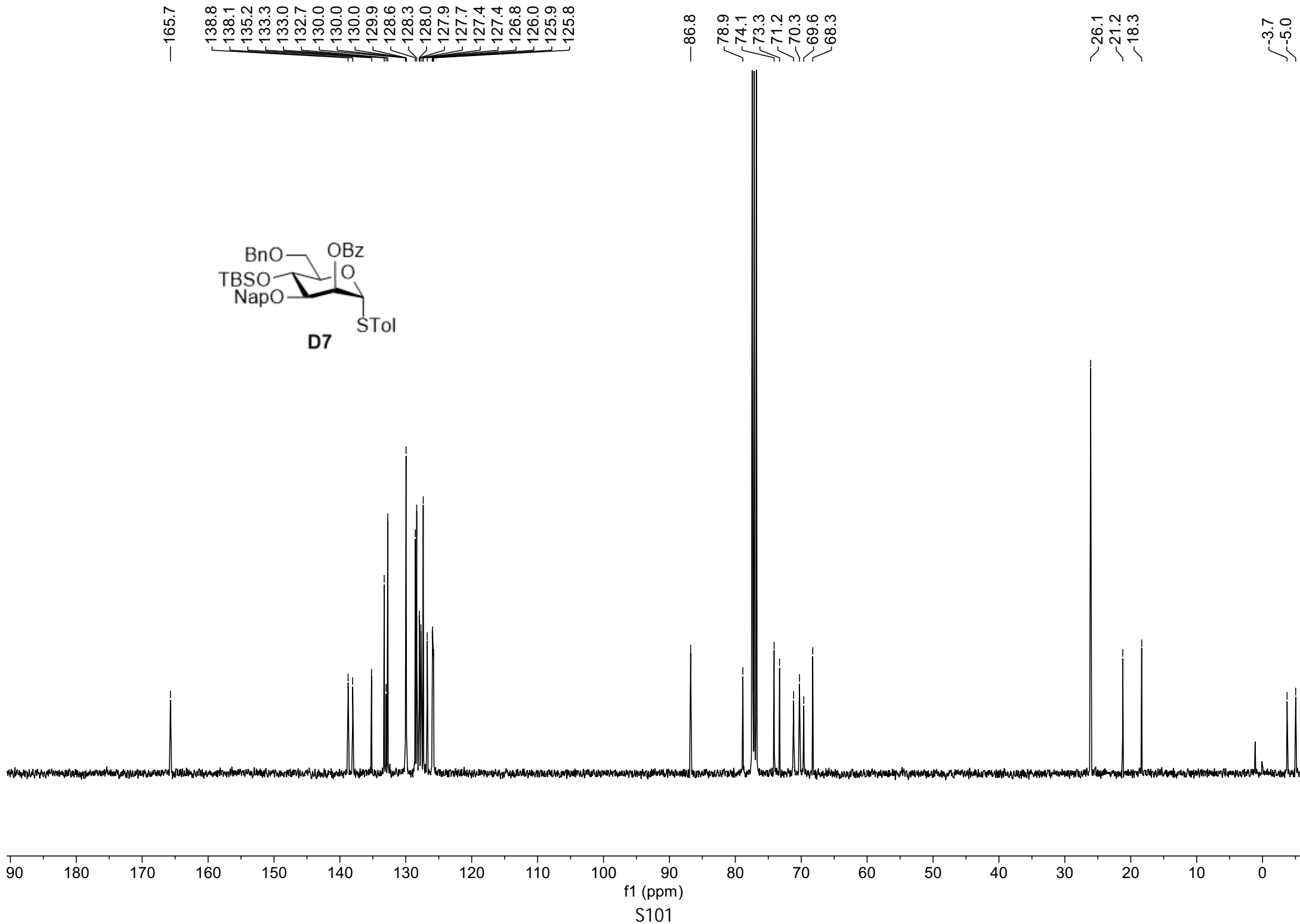
26.0  
21.2  
18.1

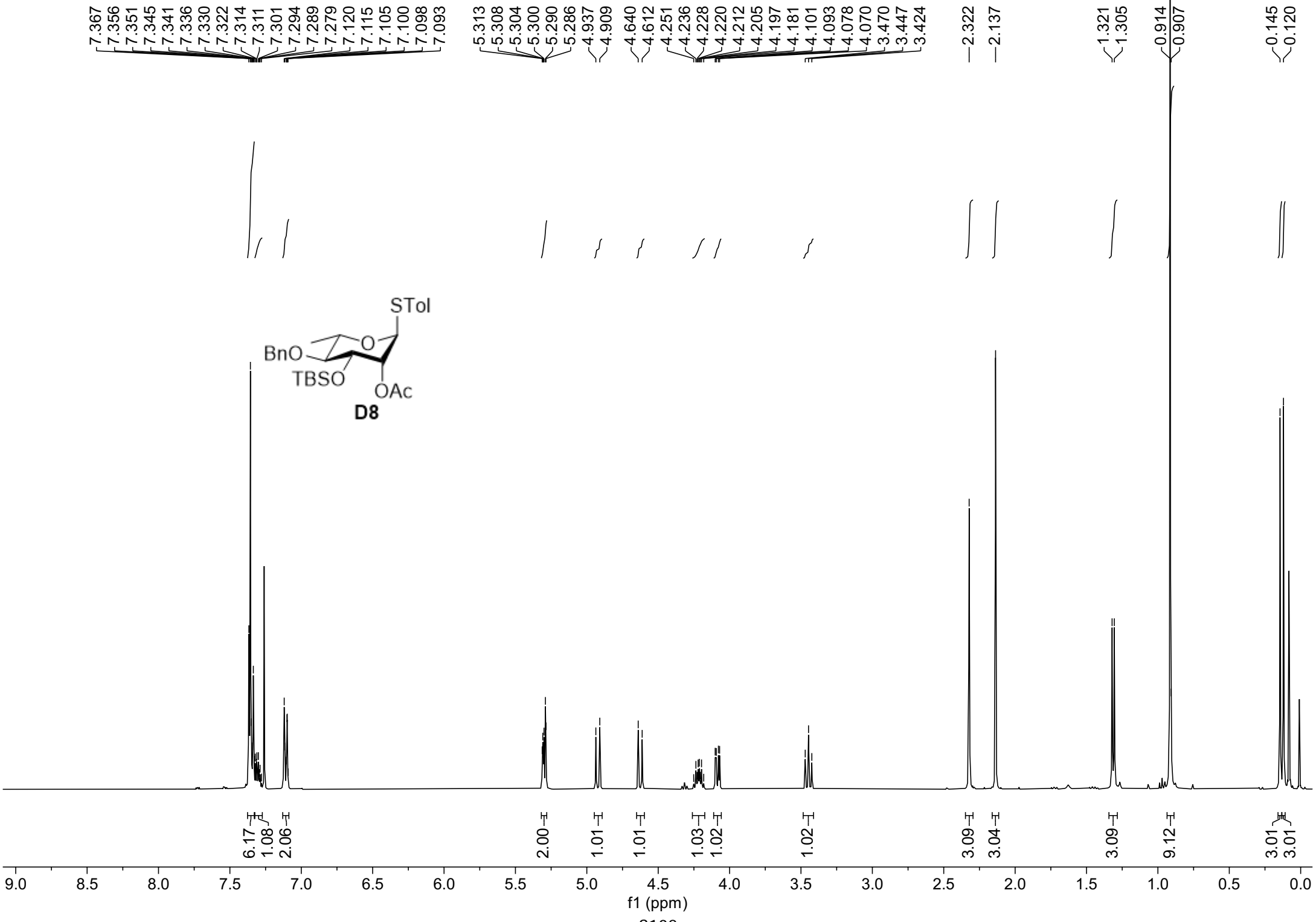
-3.6  
-4.3

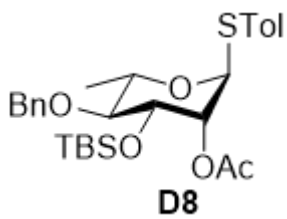




S100







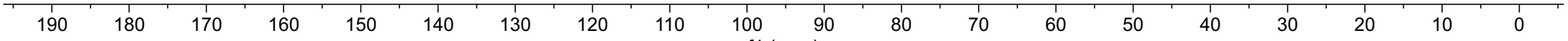
—170.4

138.4  
137.9  
132.3  
130.4  
130.0  
128.5  
127.9  
127.8

—86.6  
—81.6  
75.6  
74.6  
71.6  
69.2

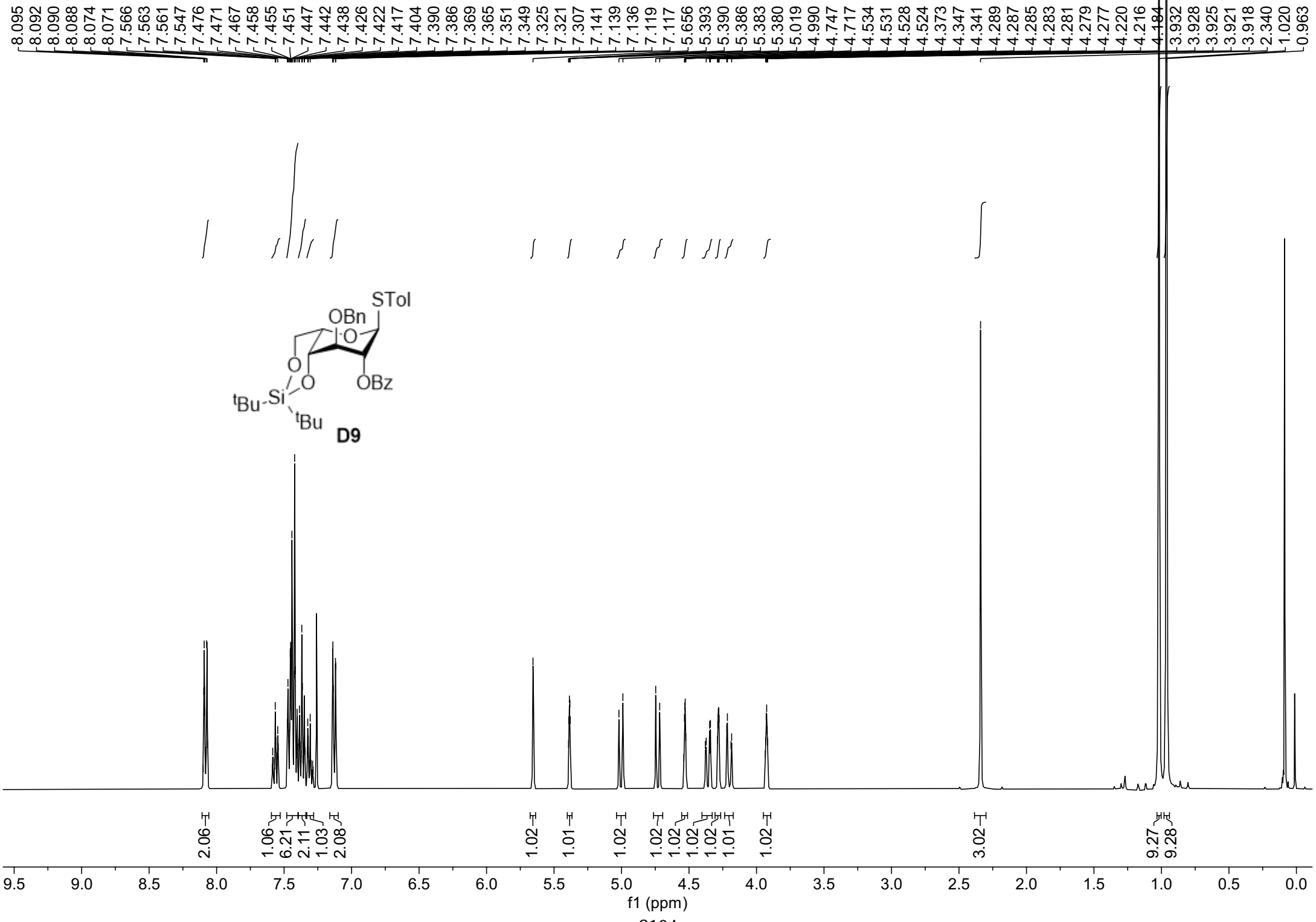
25.9  
21.2  
21.2  
17.9  
17.9

—4.6



S103





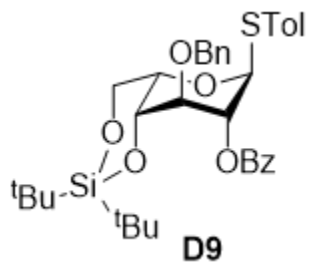
f1 (ppm)

S104

—166.4  
137.9  
137.6  
133.4  
132.3  
132.2  
130.4  
129.9  
129.7  
128.6  
128.3  
128.0  
127.9

—87.4  
76.1  
72.6  
70.8  
70.0  
67.5  
65.4

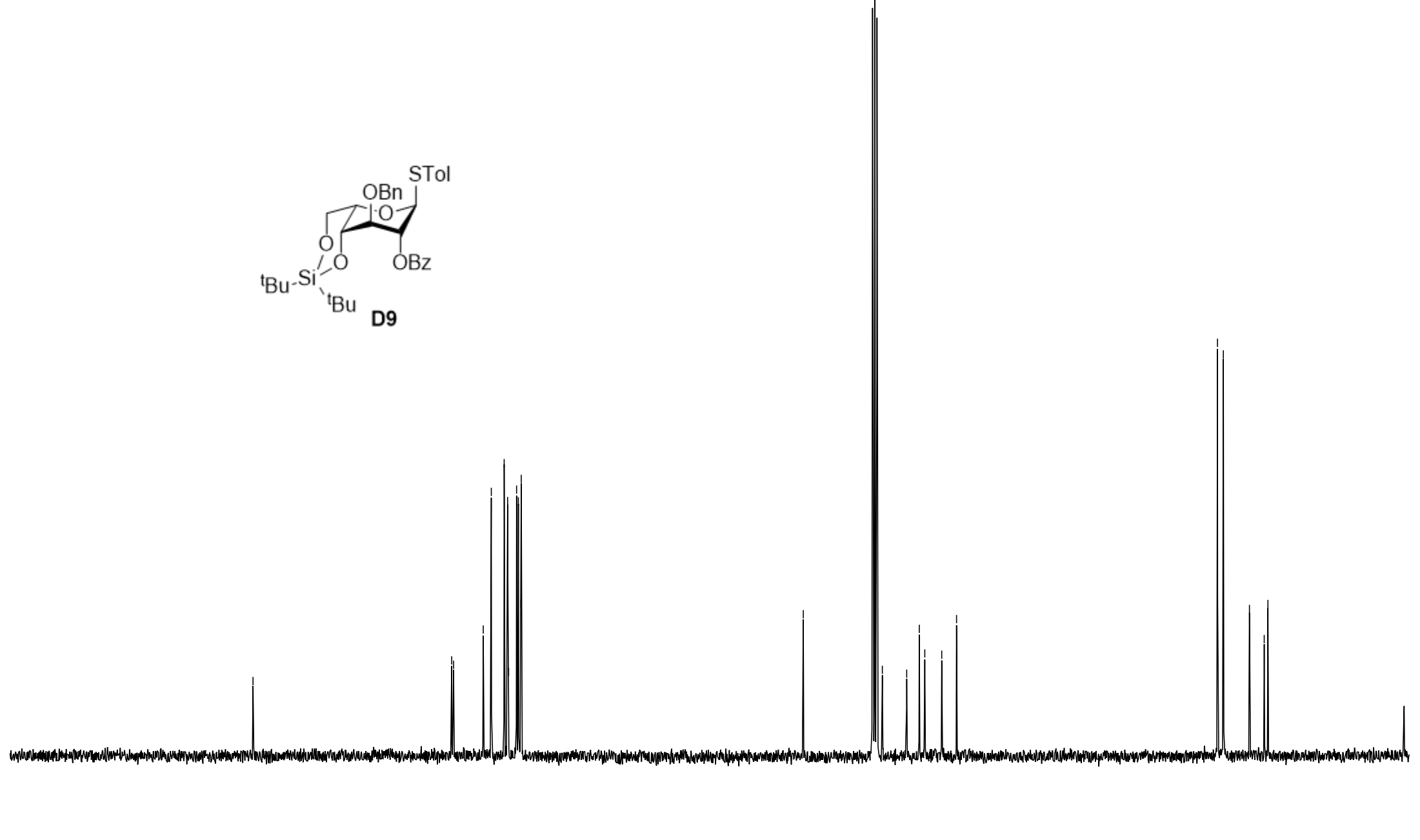
28.0  
27.1  
23.4  
21.3  
20.7

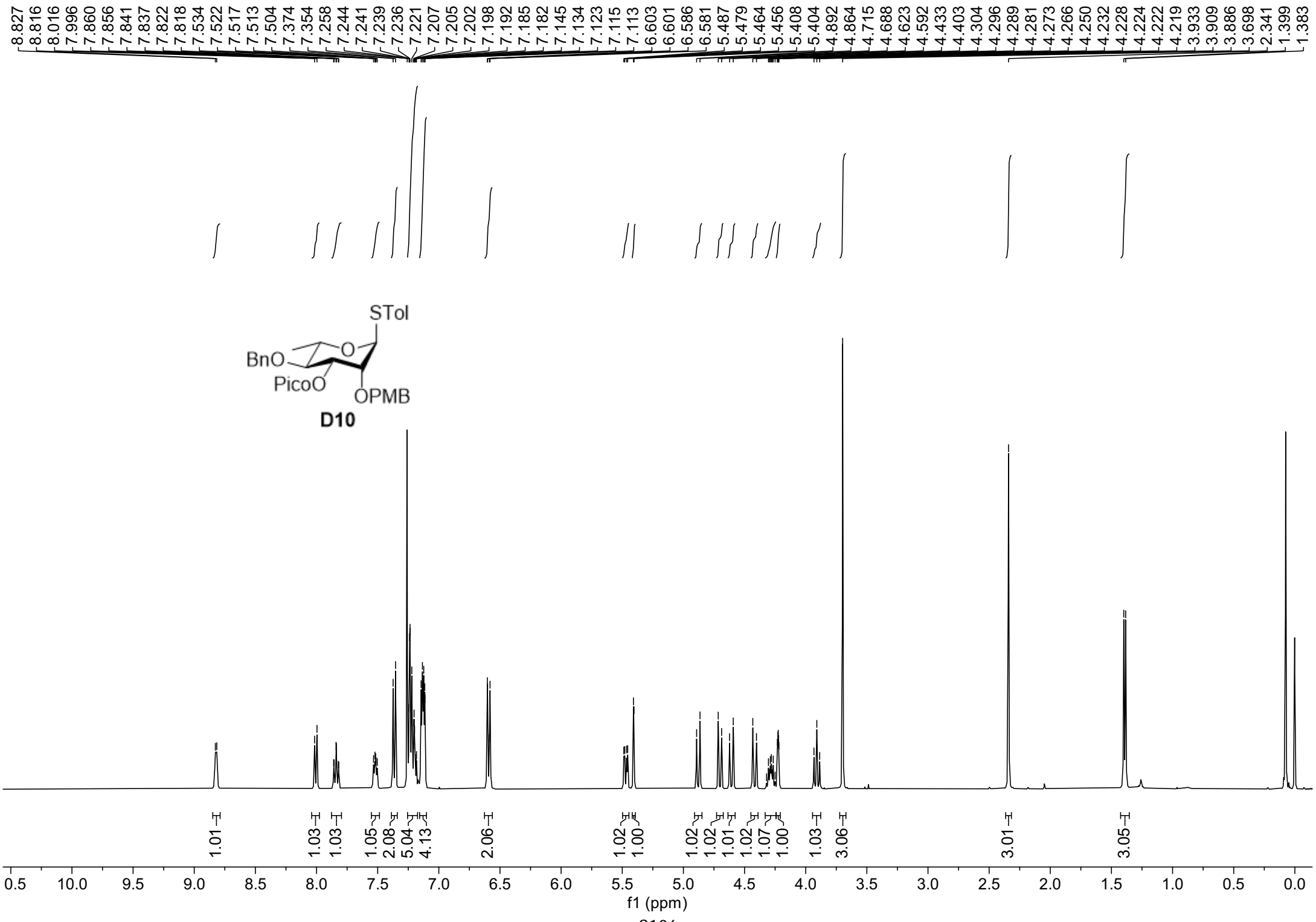


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

f1 (ppm)

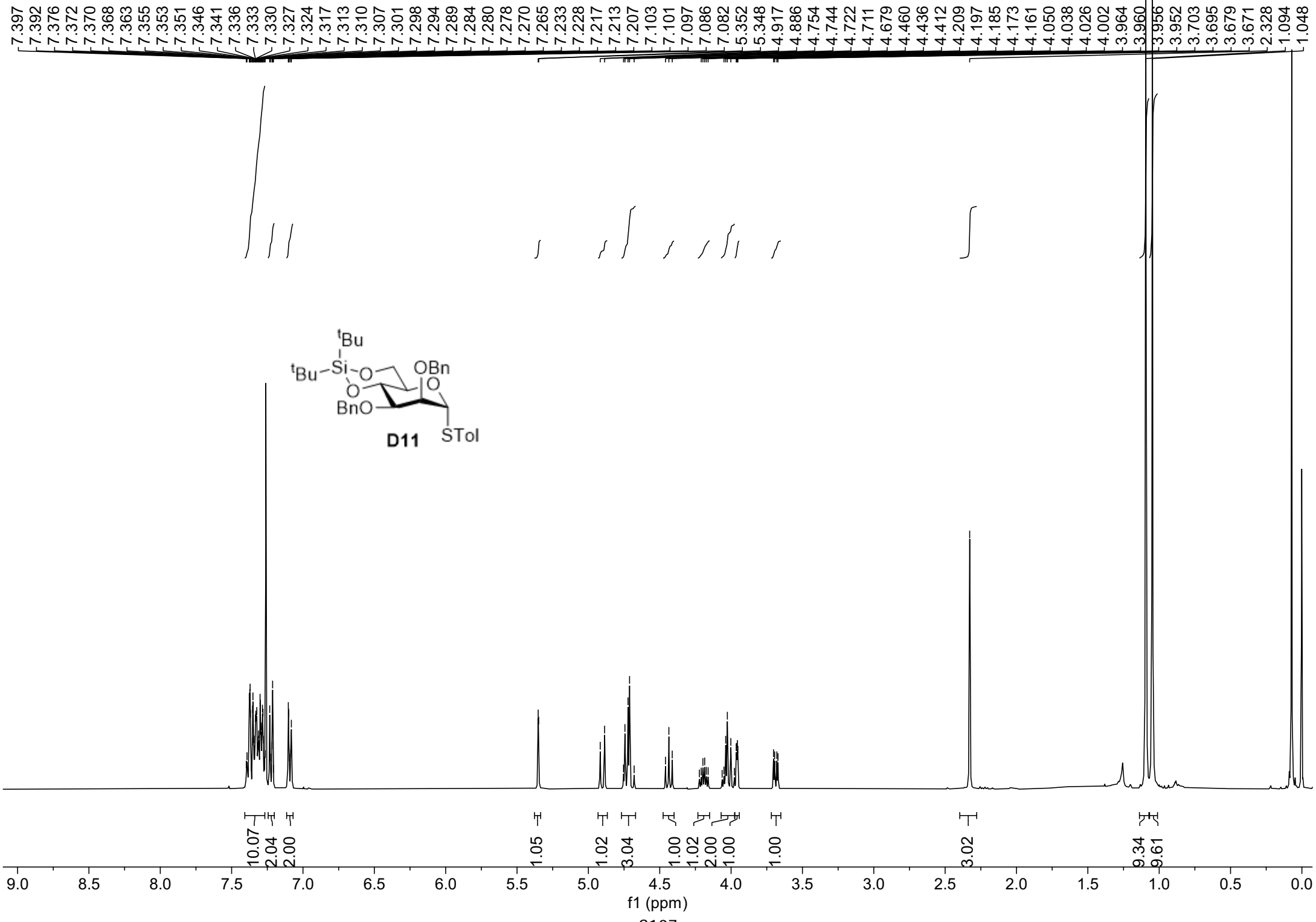
S105





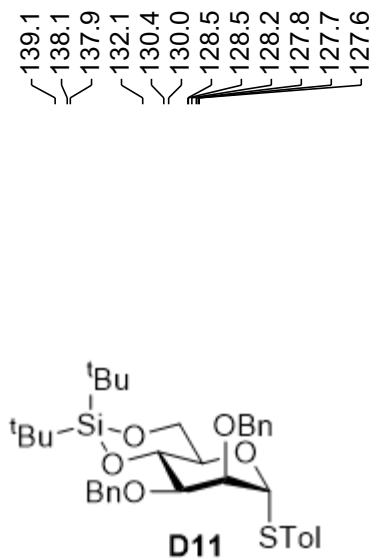
f1 (ppm)

S106



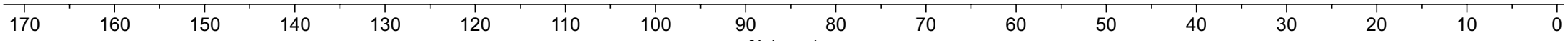
f1 (ppm)

S107



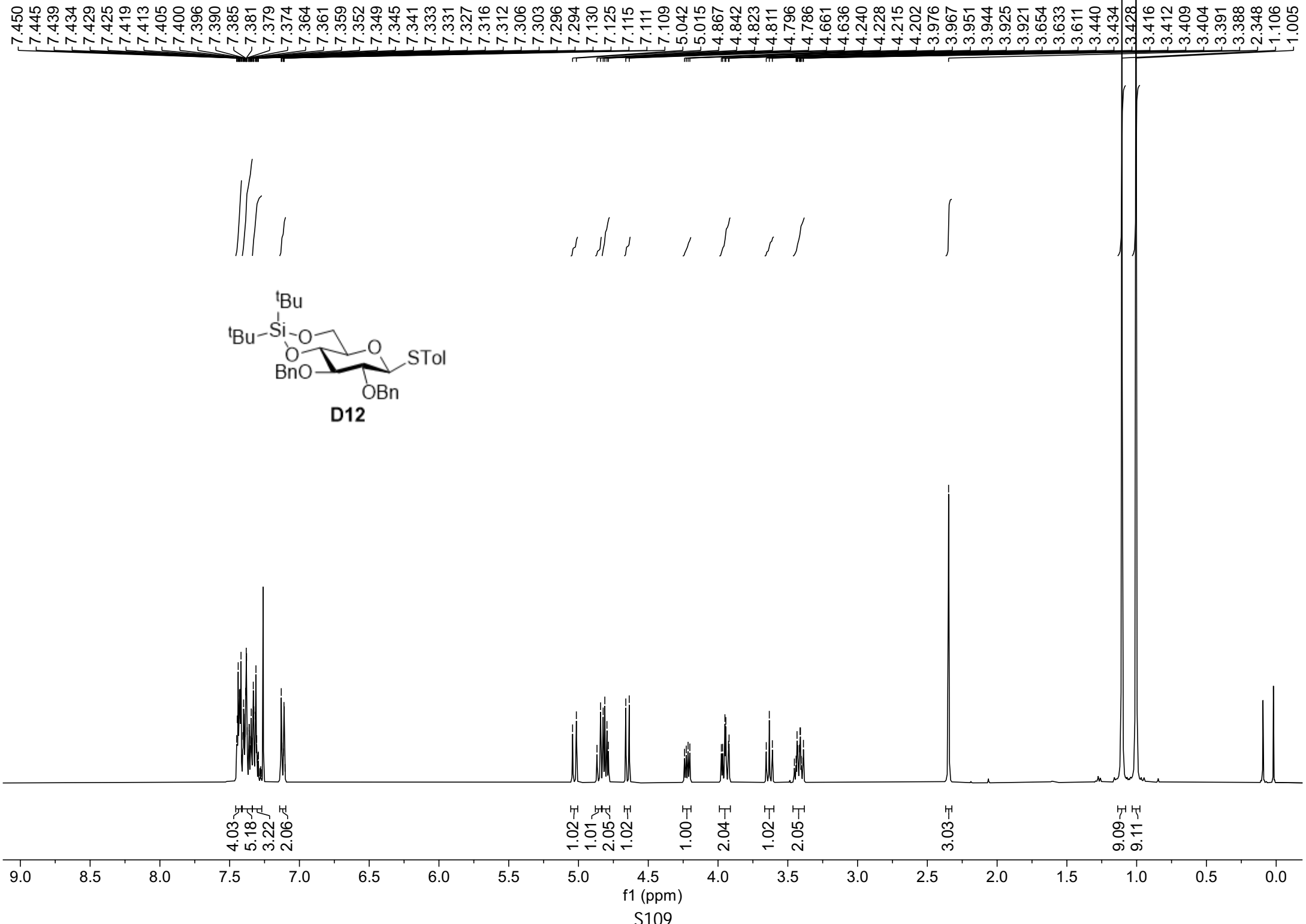
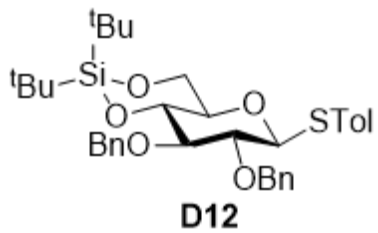
—87.4  
 79.0, 78.0, 75.6, 73.6, 72.9, 69.2, 66.6

27.6, 27.3, 22.8, 21.2, 20.2



f1 (ppm)

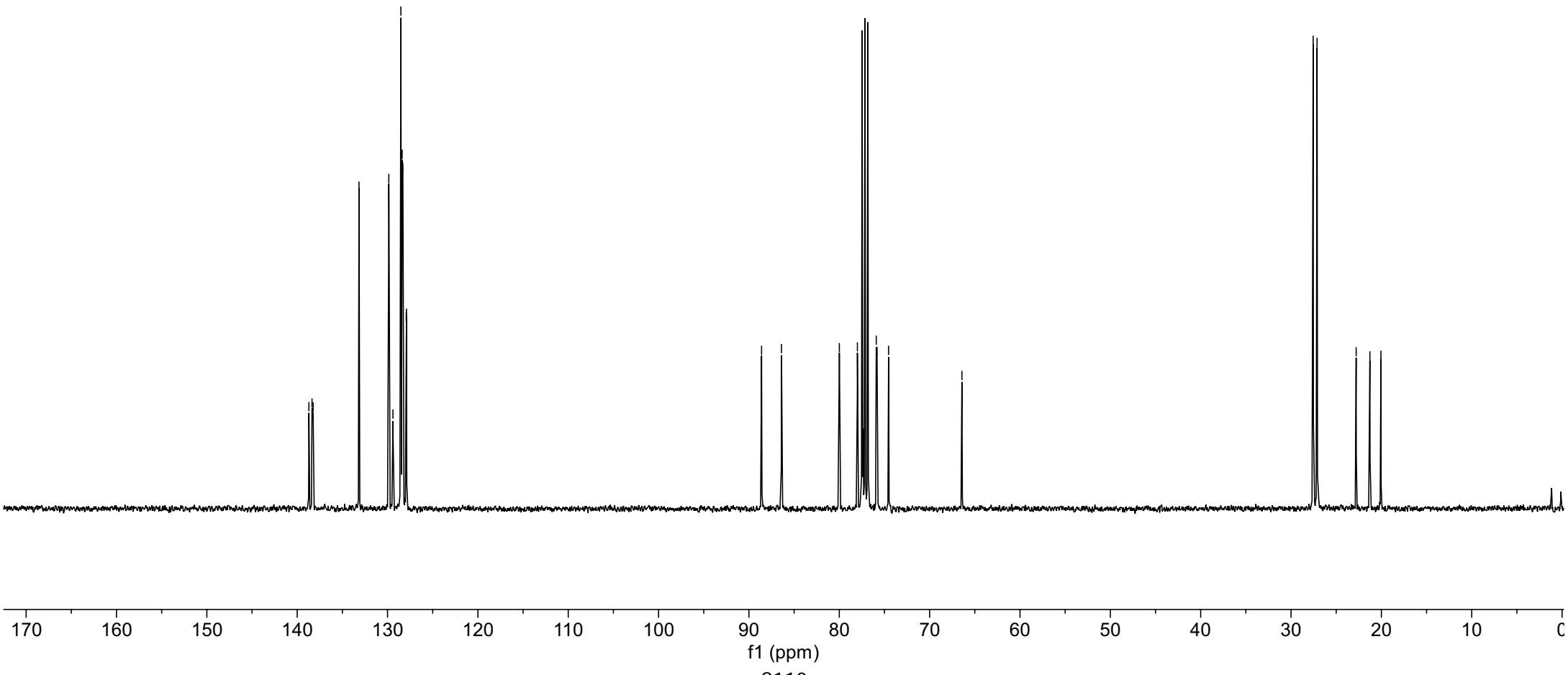
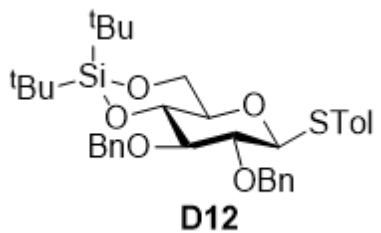
S108

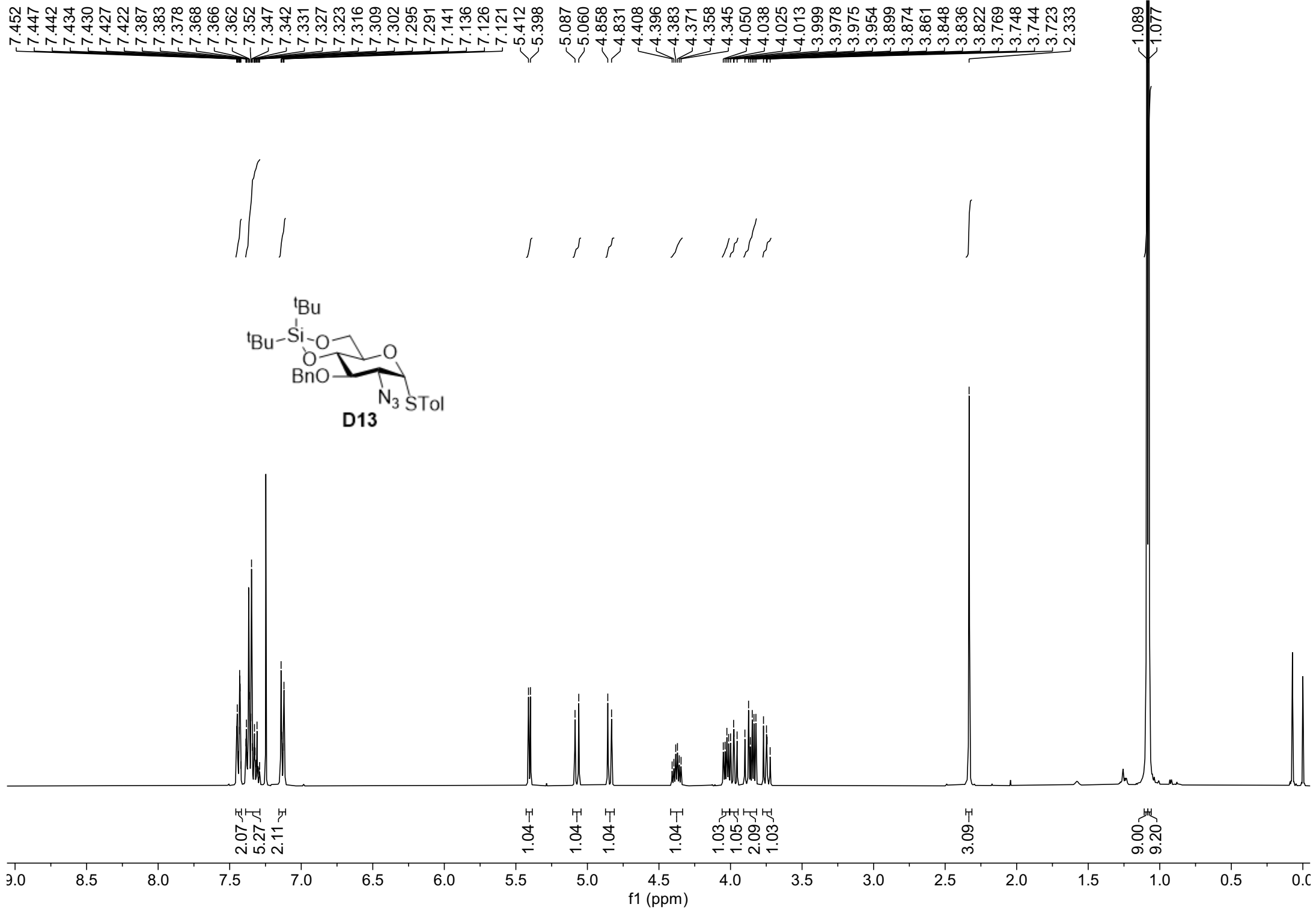


138.7  
138.4  
138.2  
133.2  
129.9  
129.4  
128.5  
128.4  
128.3  
127.9  
127.9

88.6  
86.4  
80.0  
78.0  
75.9  
75.8  
74.5  
66.4

27.6  
27.1  
22.8  
21.3  
20.1





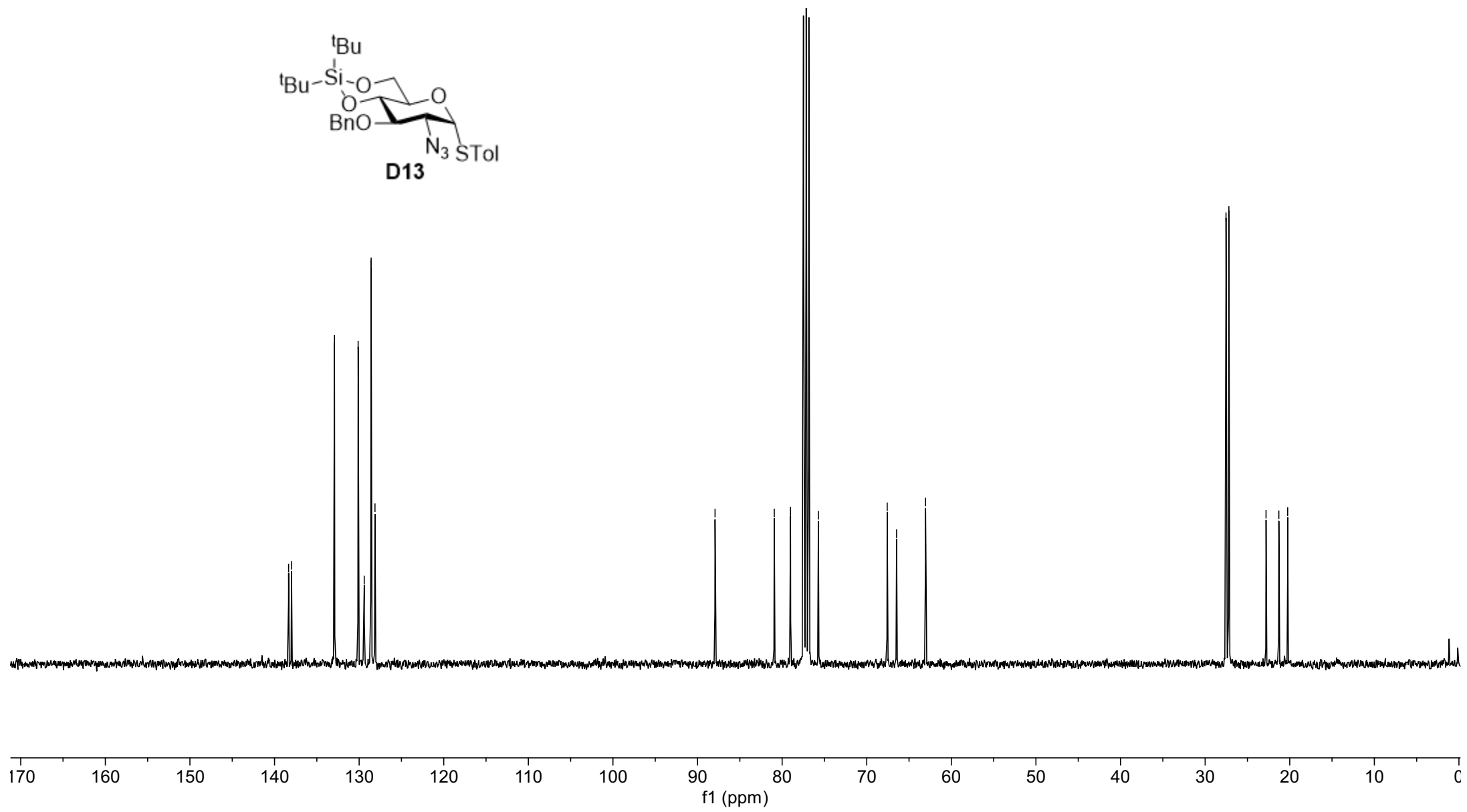
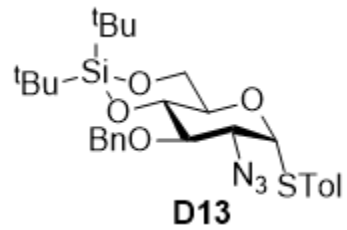


138.3  
138.0  
132.9  
130.1  
129.4  
128.6  
128.6  
128.1

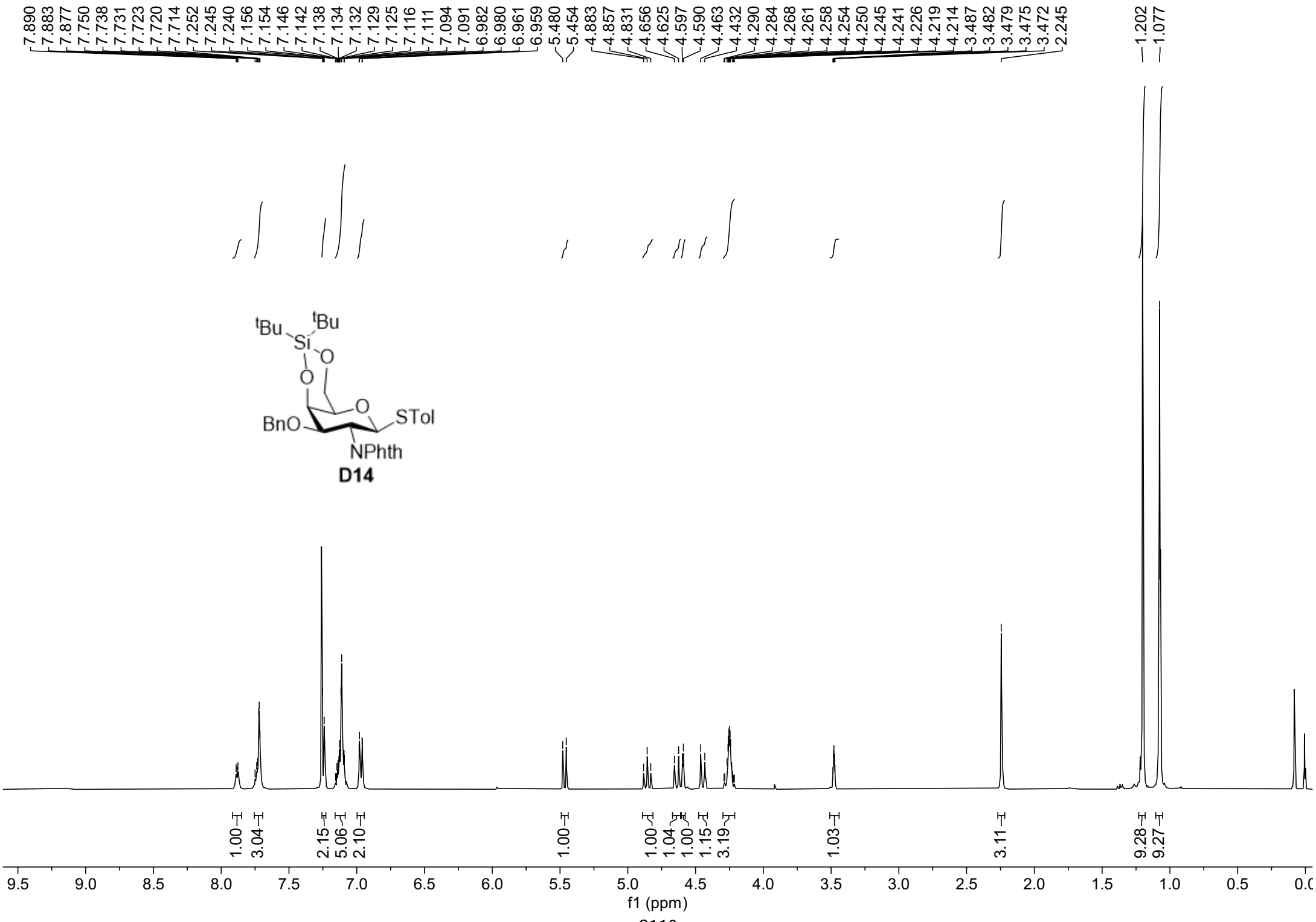
87.9  
80.9  
79.0  
75.7

67.6  
66.5  
63.0

27.5  
27.2  
22.8  
21.3  
20.2



S112



168.5  
167.8

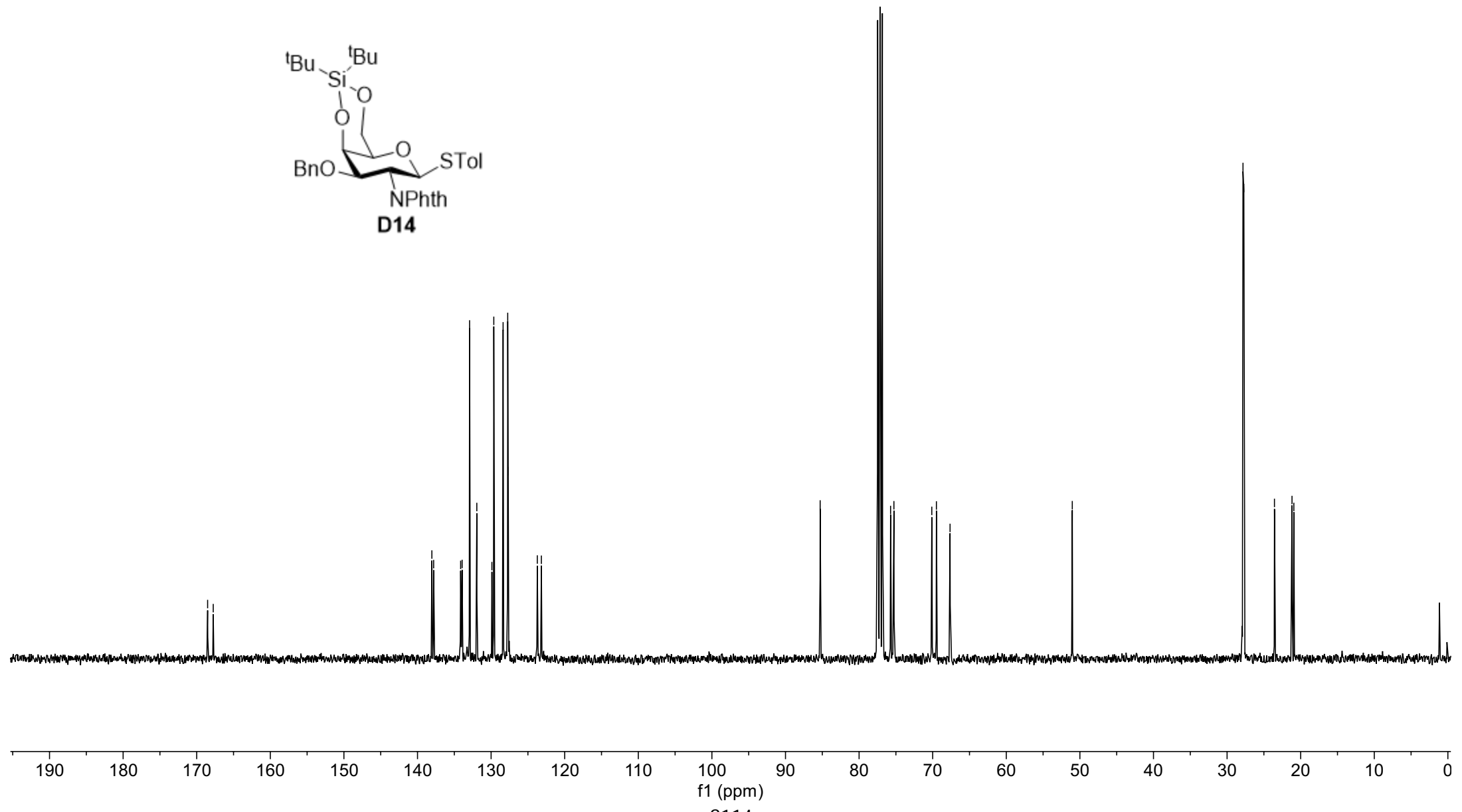
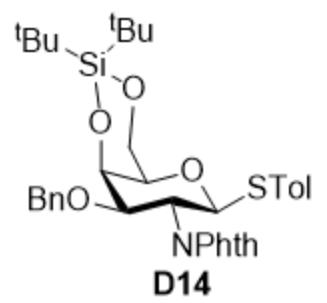
138.0  
137.8  
134.1  
133.9  
132.9  
131.9  
129.9  
129.6  
128.4  
127.7  
127.7  
123.7  
123.2

85.3

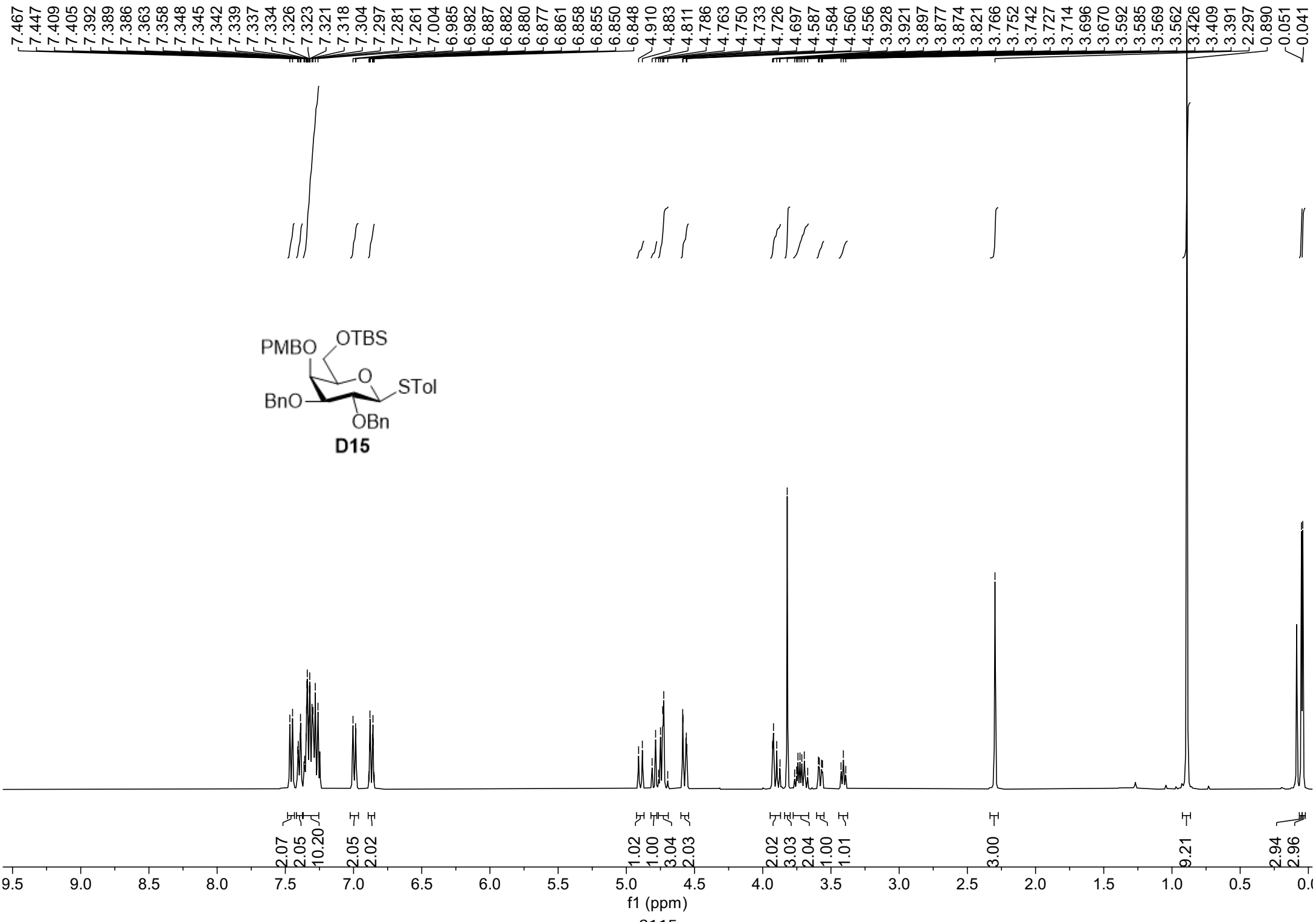
75.7  
75.3  
70.1  
69.5  
67.6

51.0

27.8  
27.7  
23.6  
21.2  
20.9



S114

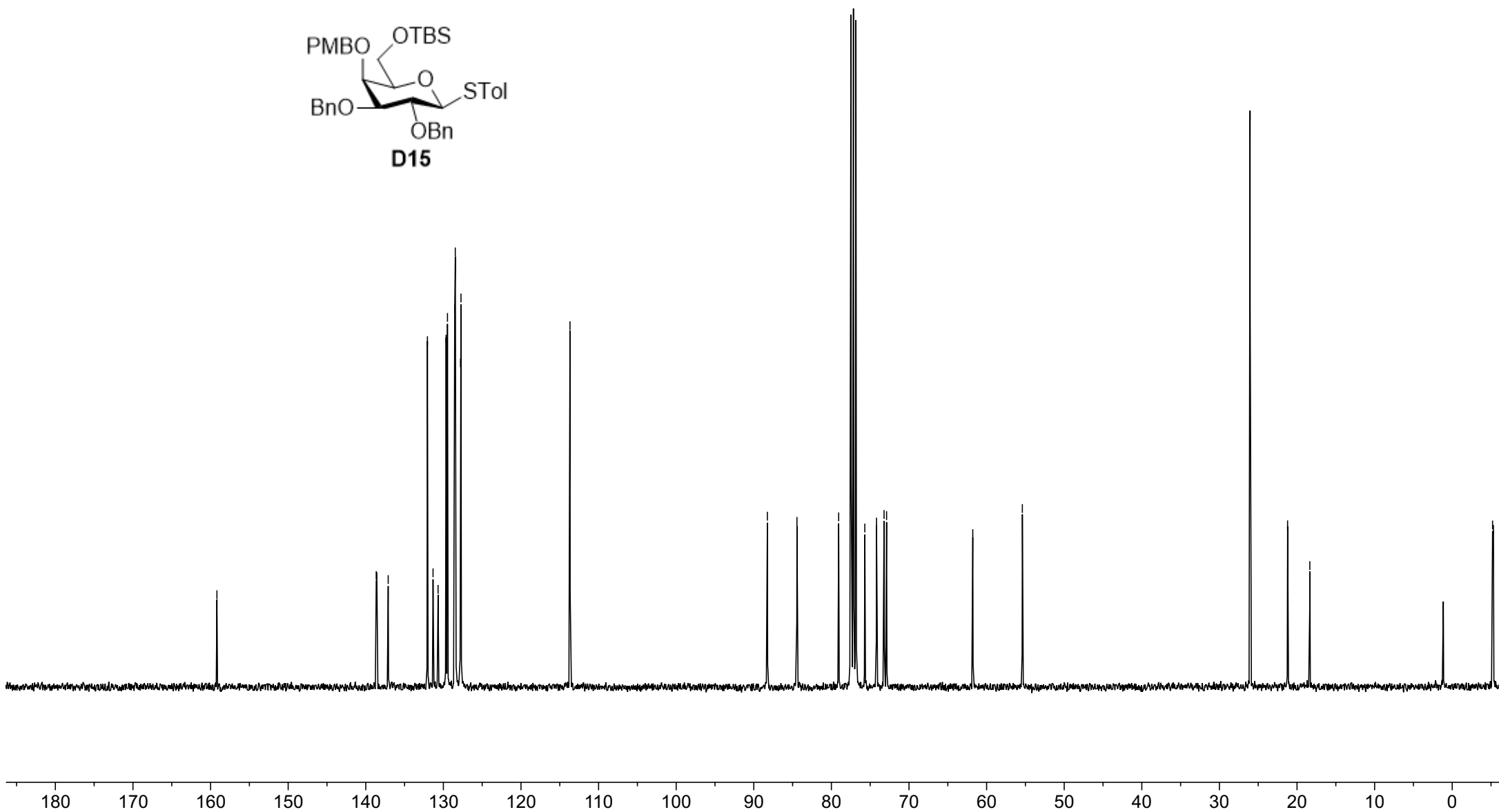
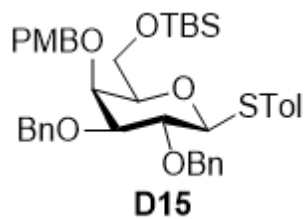


—159.2  
138.7  
138.6  
137.1  
132.1  
131.3  
130.7  
129.7  
129.5  
128.5  
128.5  
128.4  
127.8  
127.7  
—113.7

—88.2  
—84.4  
79.1  
77.6  
75.7  
74.2  
73.2  
72.9  
—61.8  
—55.4

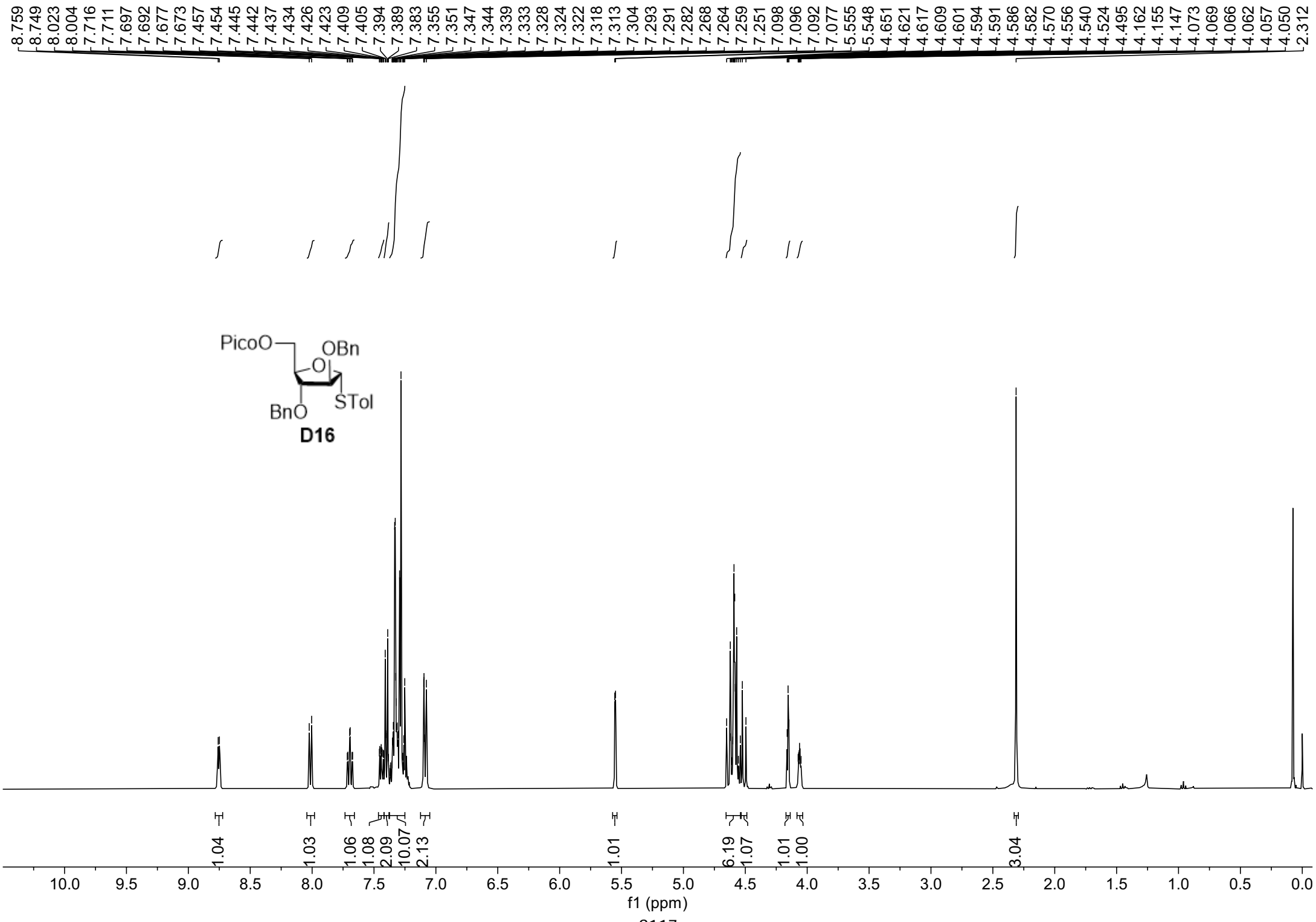
26.1  
21.2  
18.3

5.2  
5.3



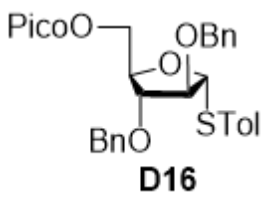
f1 (ppm)

S116



f1 (ppm)

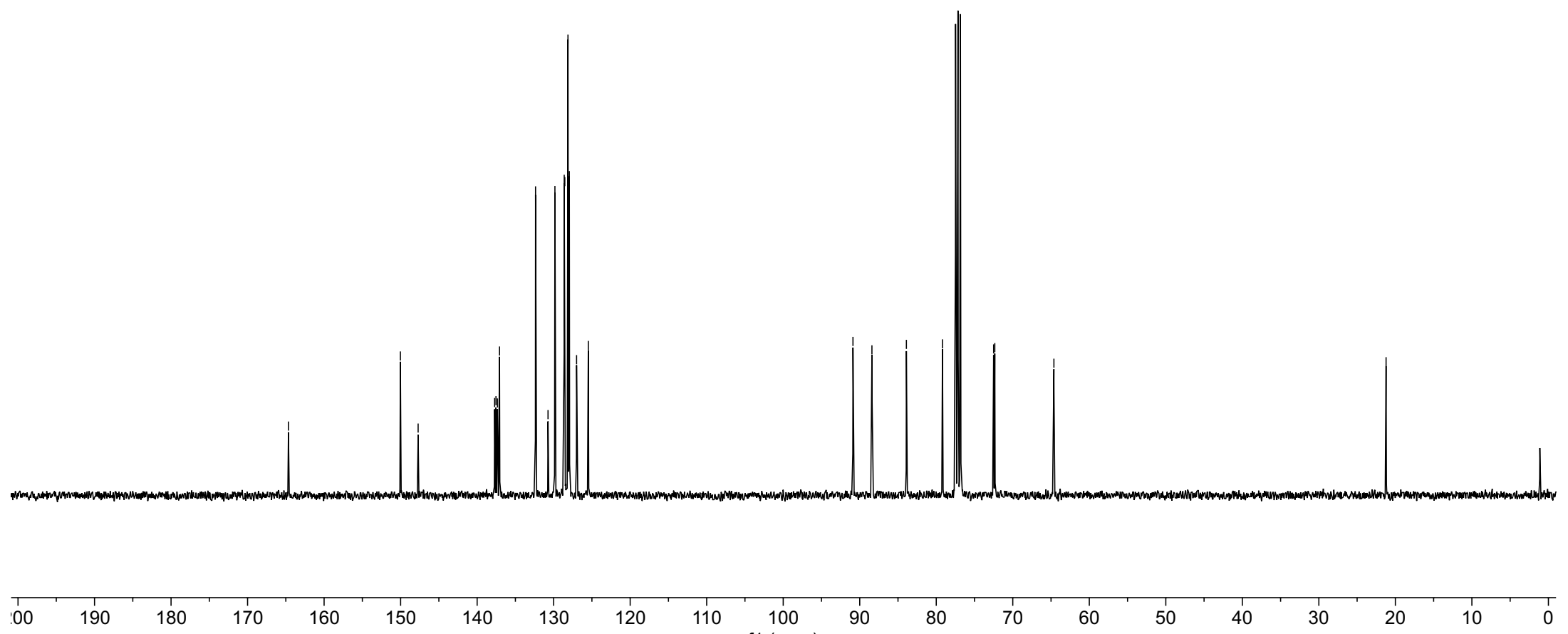
S117



164.7  
150.0  
147.7  
137.7  
137.5  
137.3  
137.1  
132.4  
130.7  
129.8  
128.6  
128.5  
128.1  
128.0  
128.0  
127.0  
125.5

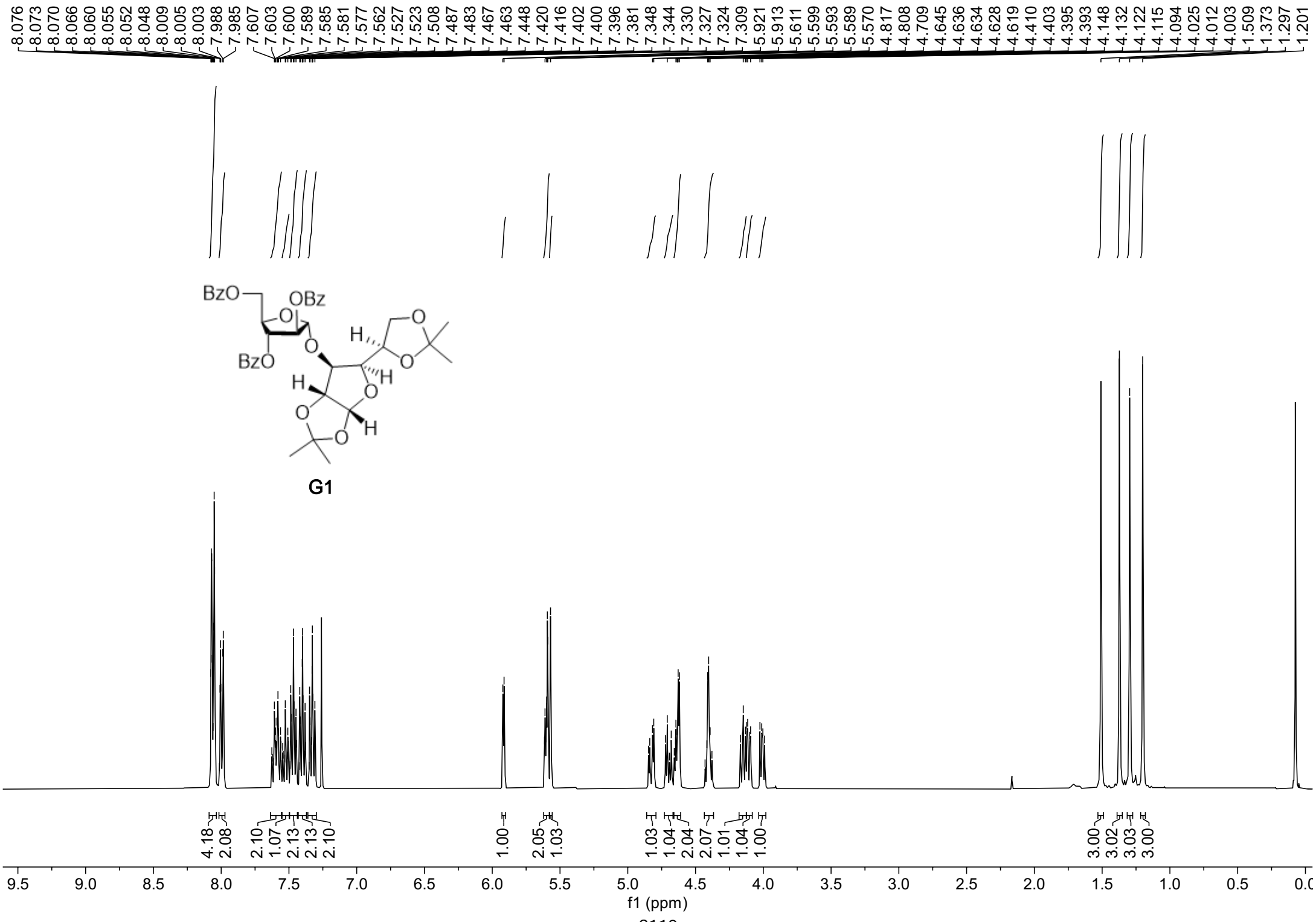
90.9  
88.4  
83.9  
79.2  
72.5  
72.3  
64.6

21.2



f1 (ppm)

S118





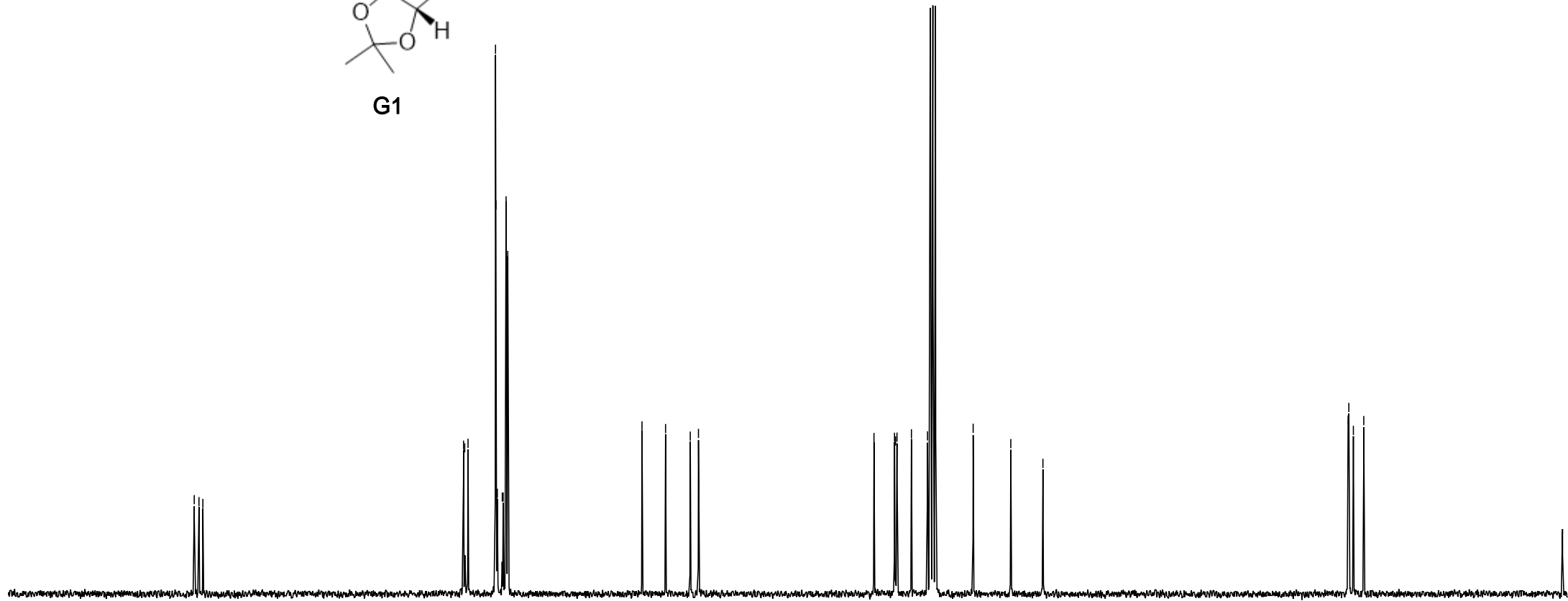
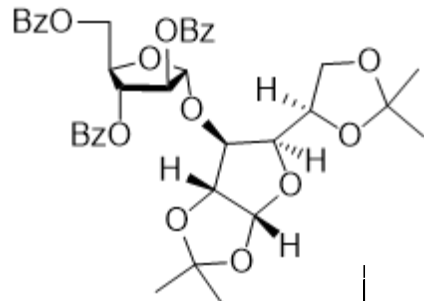
166.3  
165.8  
165.3

133.8  
133.7  
133.3  
130.0  
129.9  
129.7  
129.1  
129.0  
128.7  
128.7  
128.5

112.3  
109.4  
106.5  
105.5

84.3  
81.8  
81.7  
81.5  
79.7  
77.8  
72.3  
67.8  
63.9

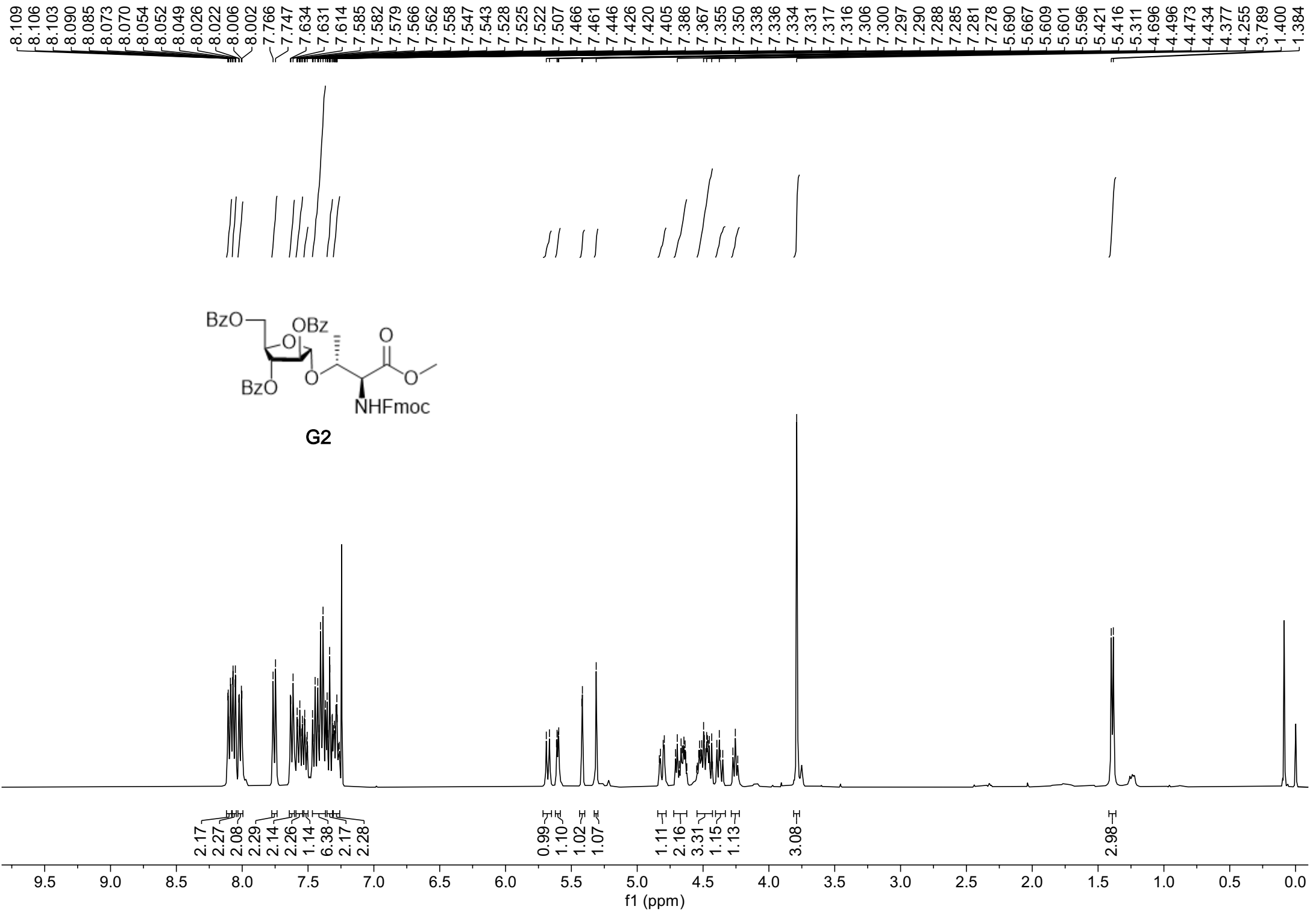
27.0  
26.9  
26.4  
25.1



180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

f1 (ppm)

S120



170.9  
166.3  
165.8  
165.6

156.8

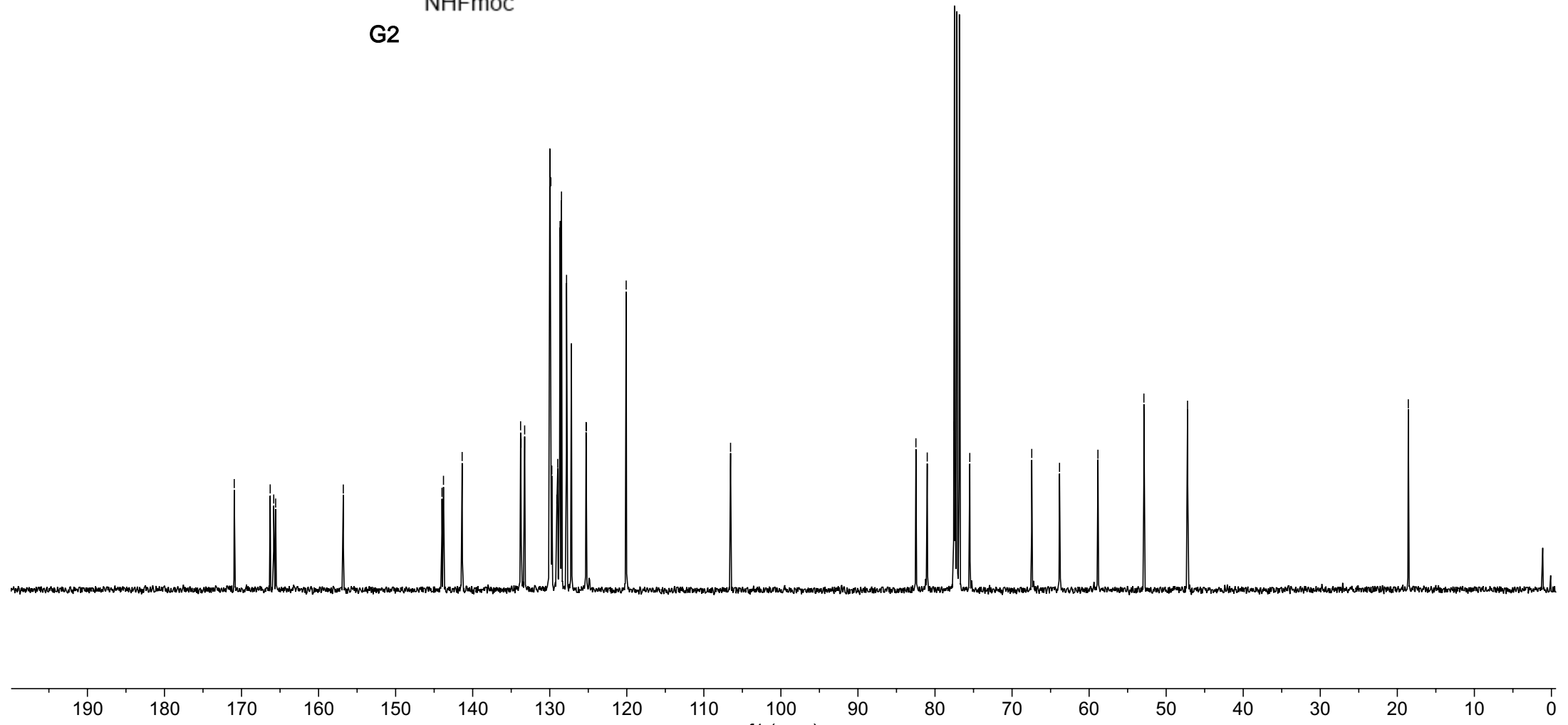
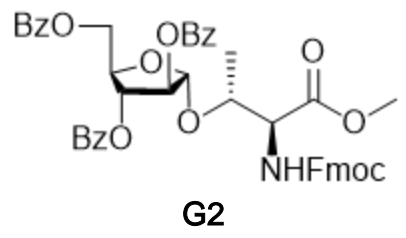
144.0  
143.8  
141.4  
133.8  
133.7  
133.3  
130.0  
130.0  
129.9  
129.7  
129.1  
129.0  
128.7  
128.7  
128.5  
127.8  
127.2  
125.3  
125.2  
120.1  
106.5

82.5  
81.0  
77.6  
75.5

67.4  
63.8  
58.9

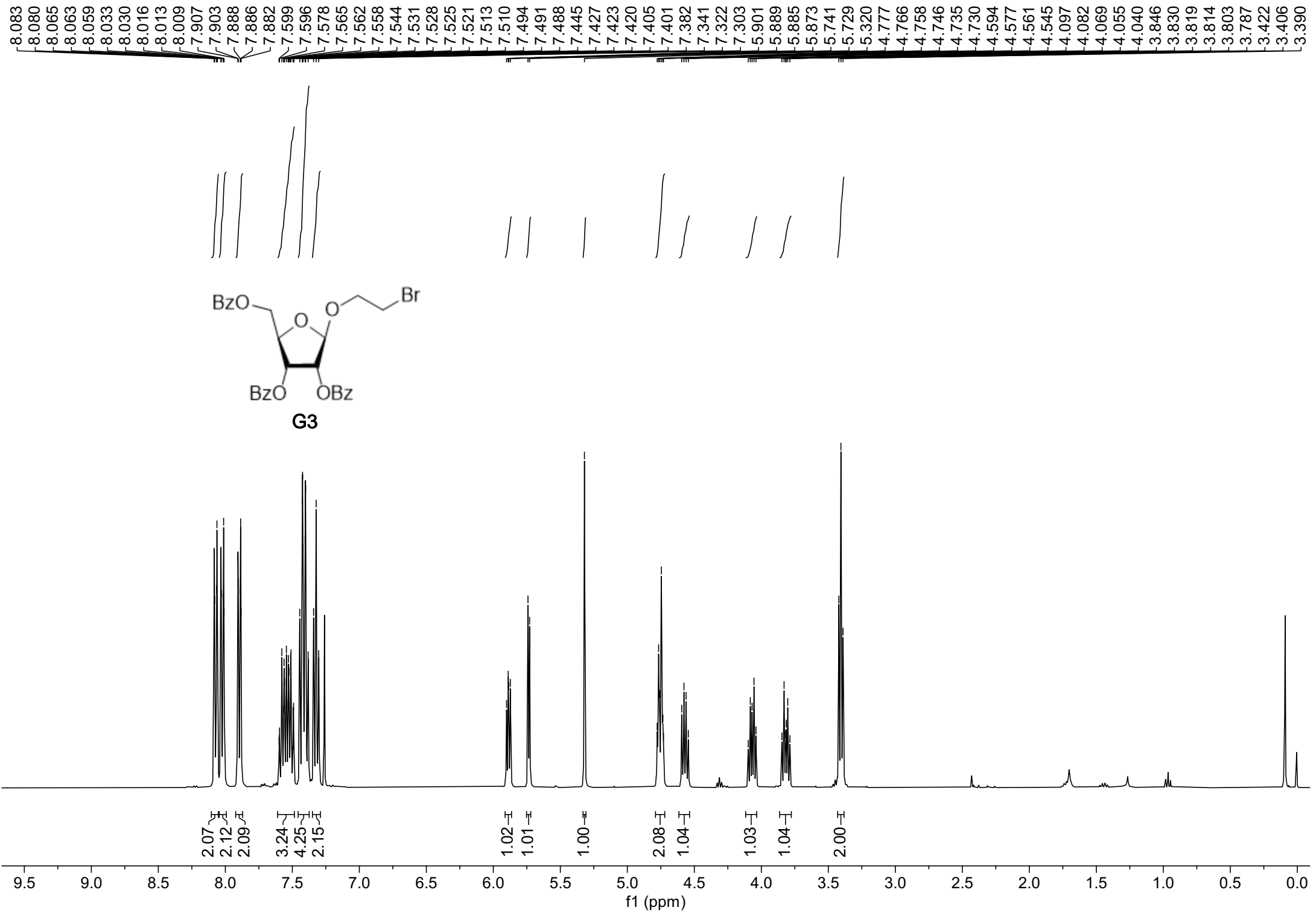
52.9  
47.2

18.6



f1 (ppm)

S122



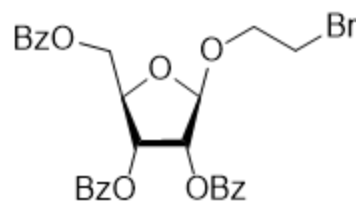
166.2  
165.5  
165.3

133.6  
133.5  
133.3  
129.9  
129.8  
129.8  
129.3  
129.0  
128.6  
128.5

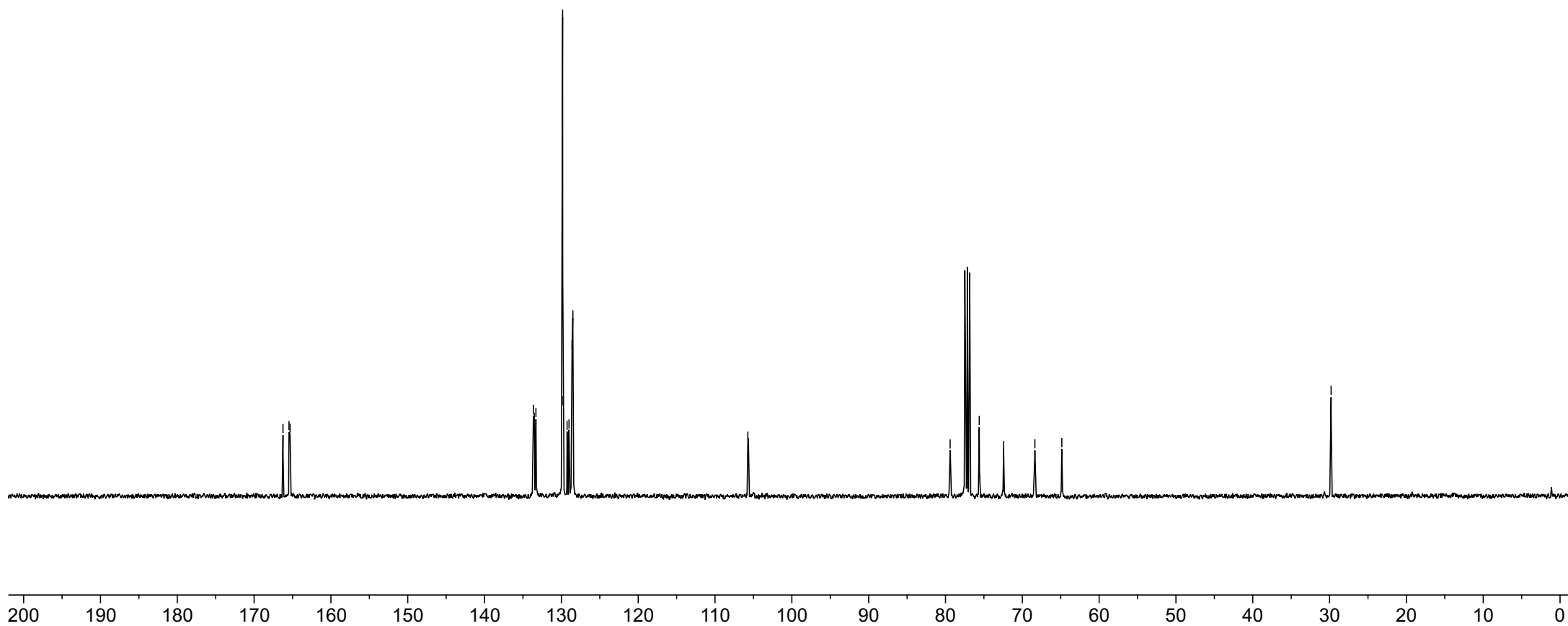
105.7

79.4  
75.6  
72.4  
68.4  
64.9

29.8

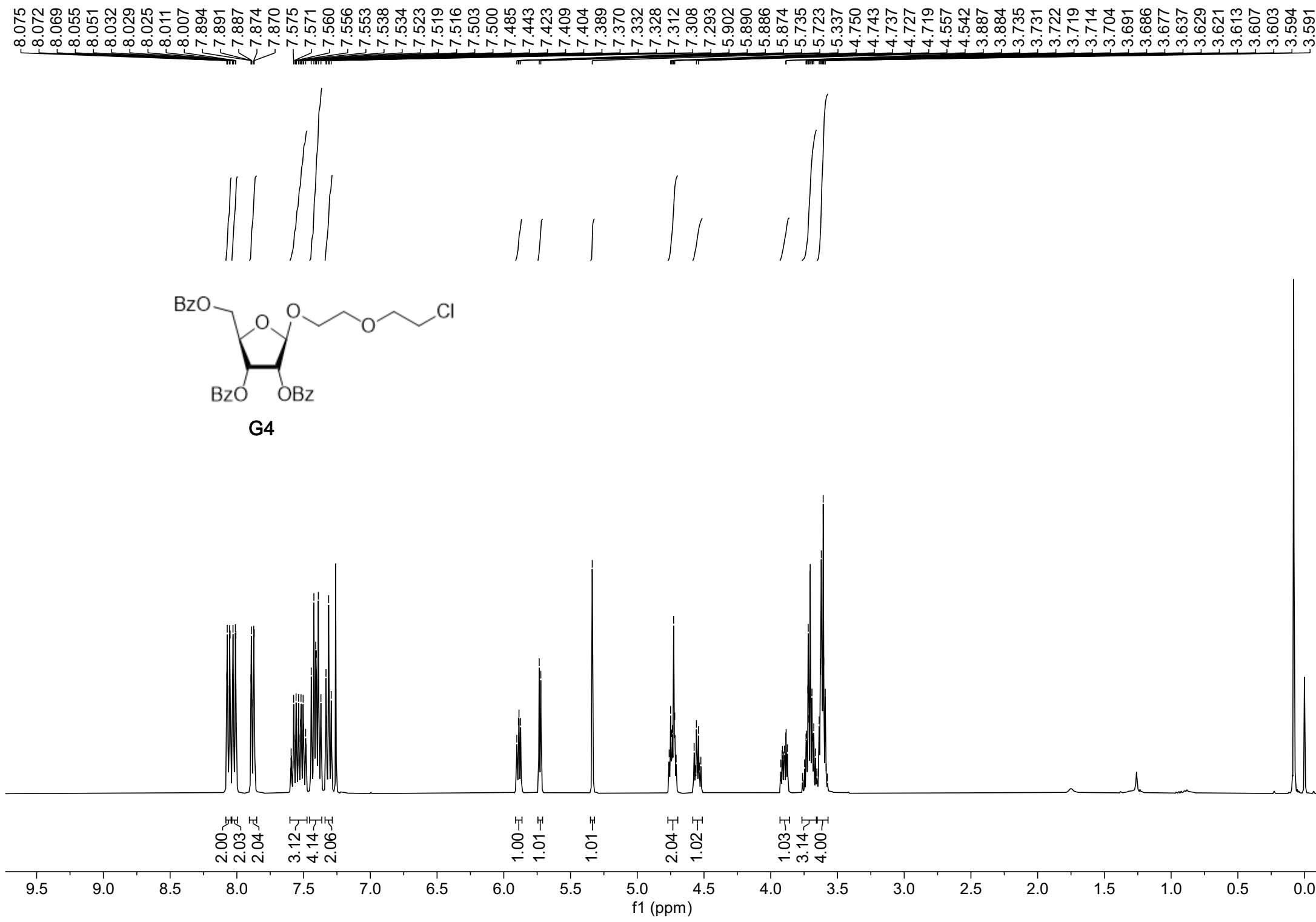


**G3**



f1 (ppm)

S124



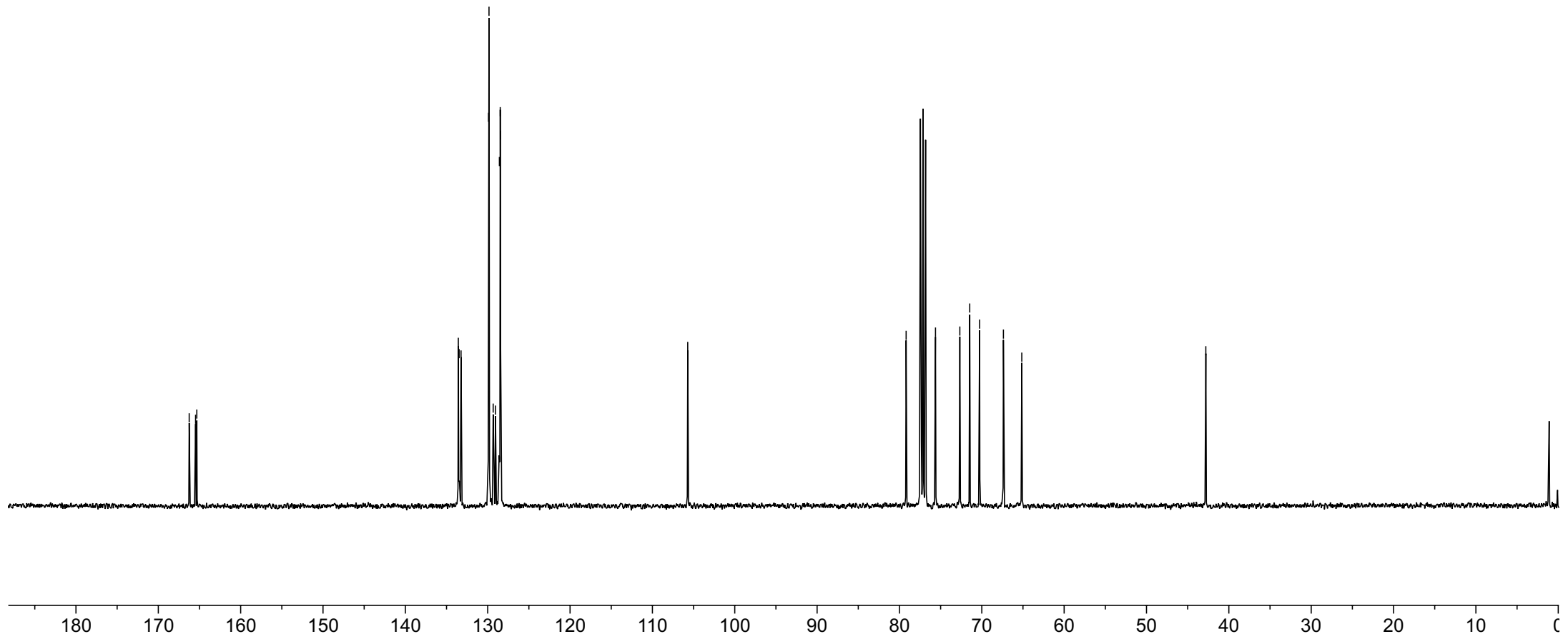
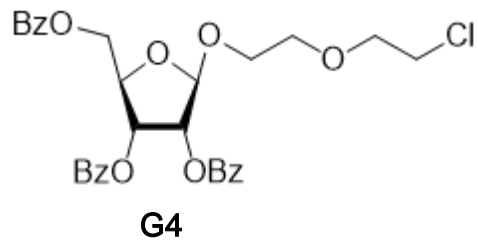
166.2  
165.5  
165.3

133.6  
133.5  
133.2  
129.9  
129.8  
129.3  
129.1  
128.6  
128.5  
128.4

105.7

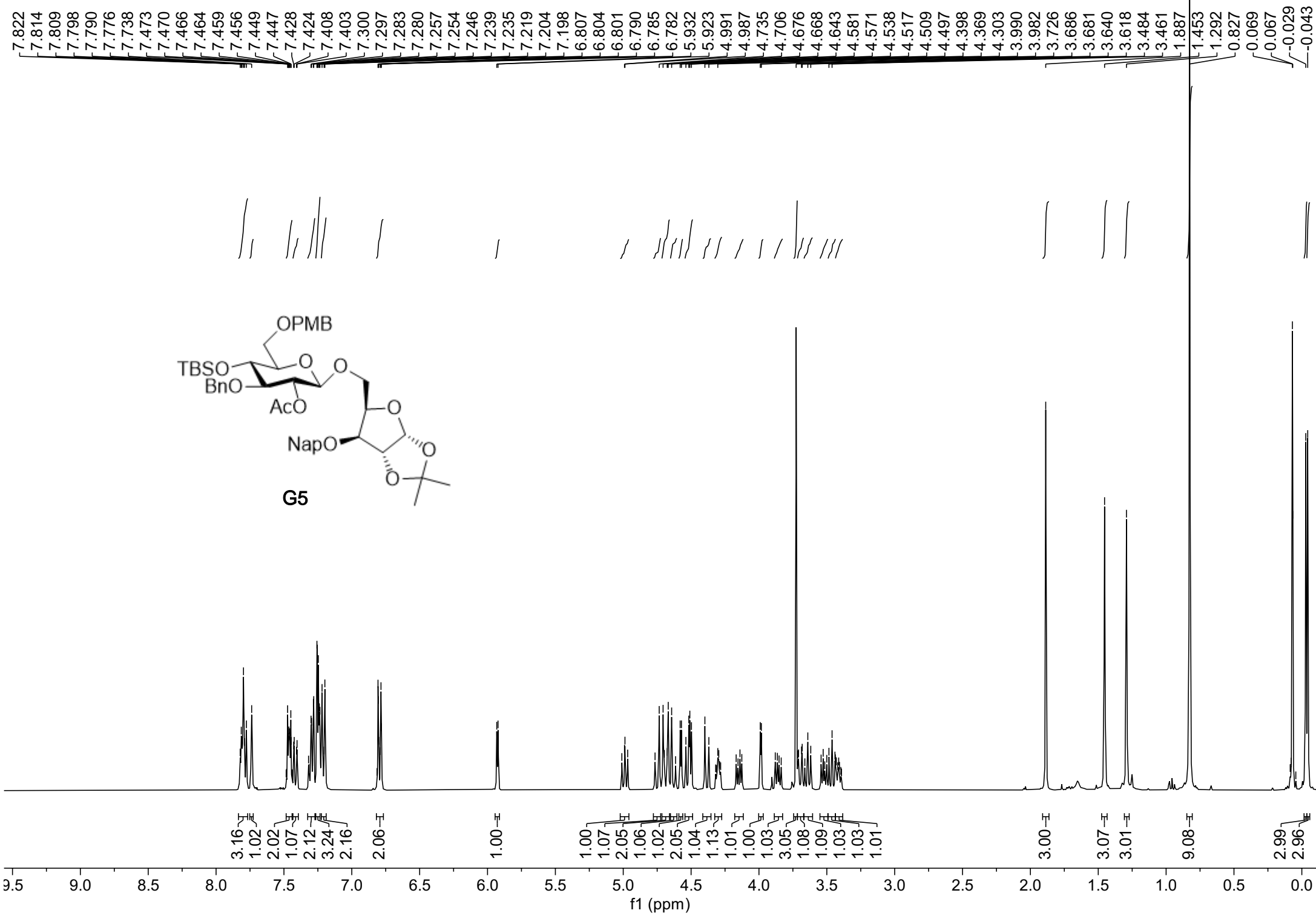
79.2  
75.6  
72.7  
71.5  
70.3  
67.4  
65.1

42.8

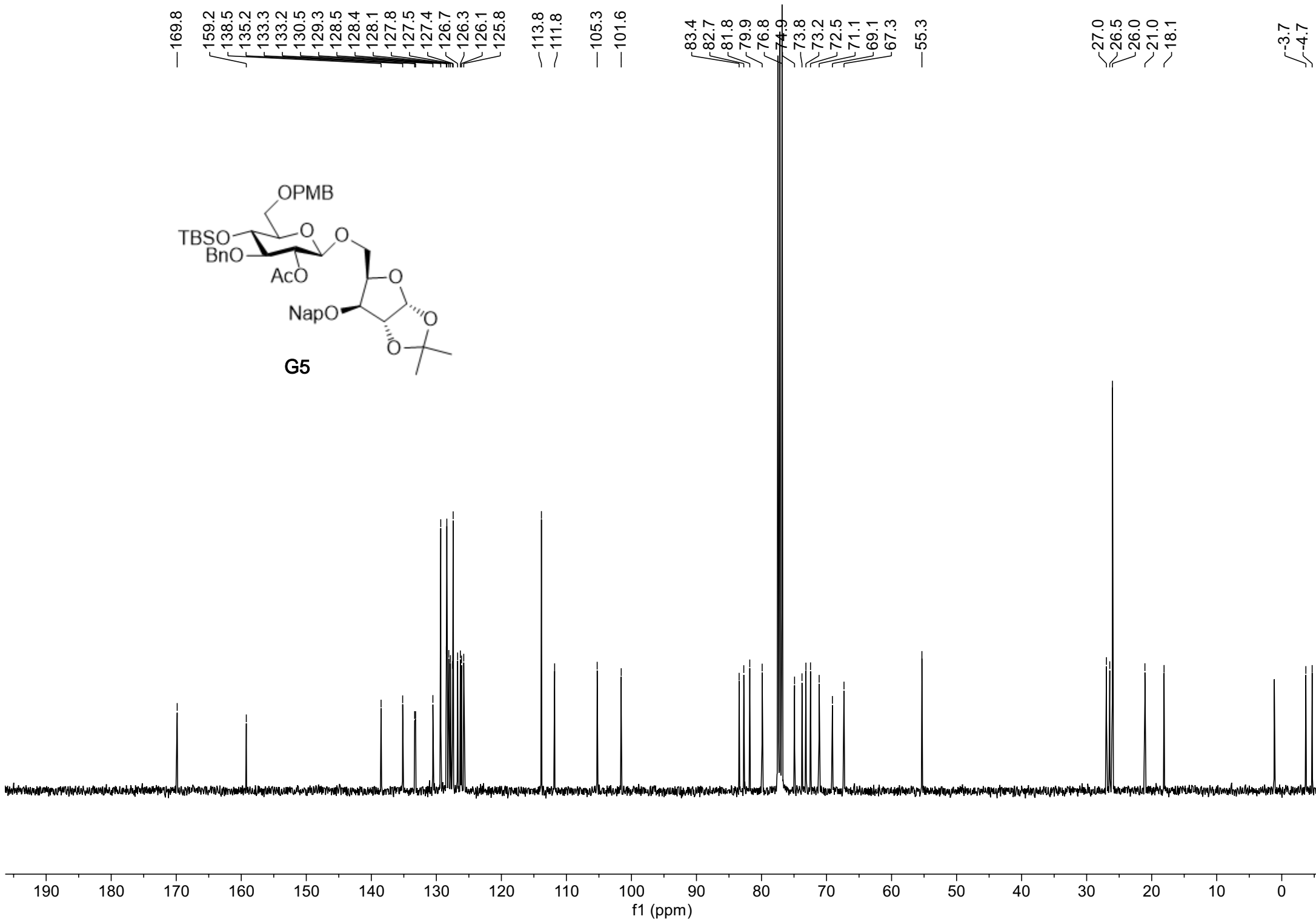


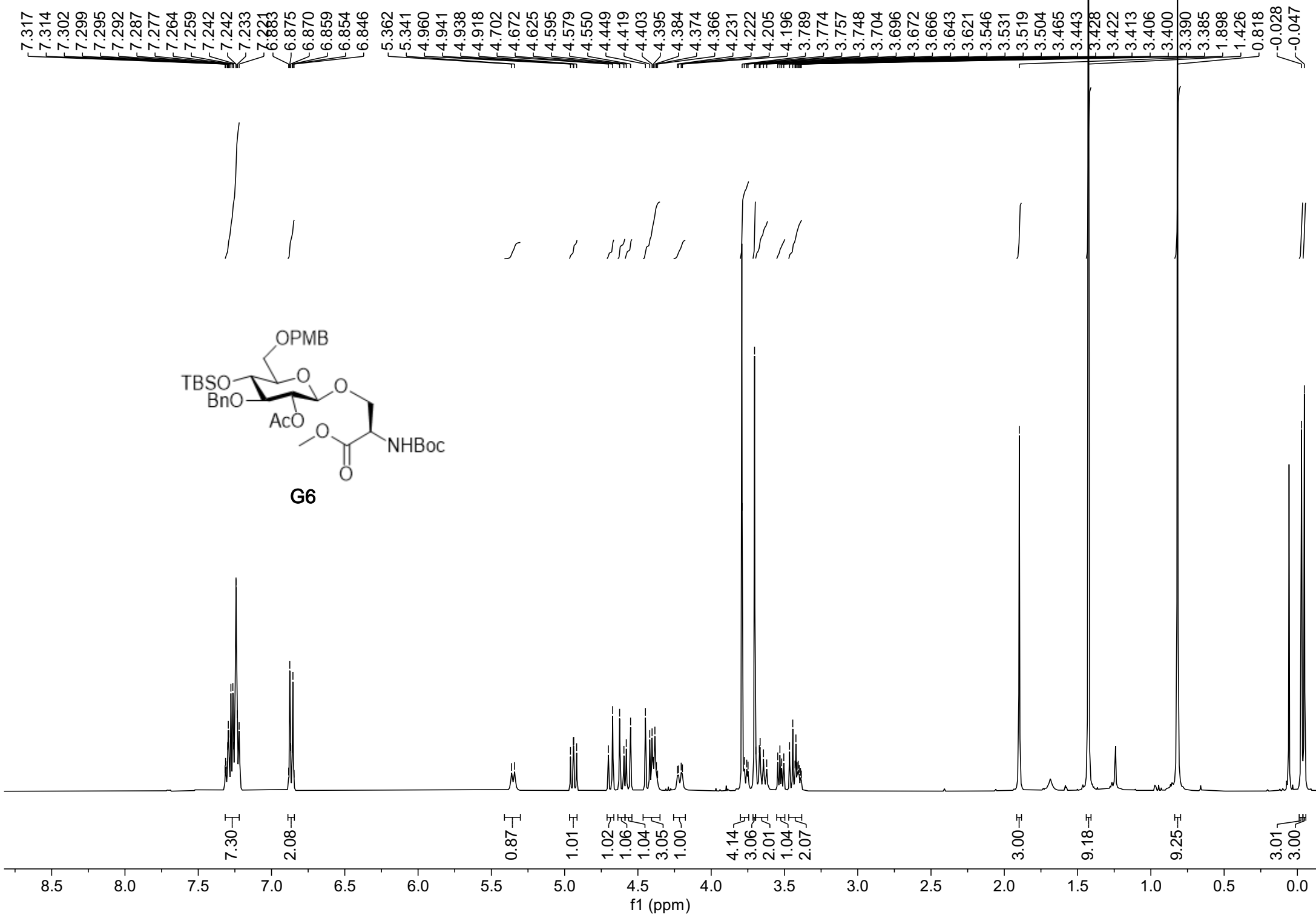
f1 (ppm)

S126









170.7  
169.6

159.3  
155.6

138.4  
130.4  
129.4  
128.4  
127.5  
127.4

113.9

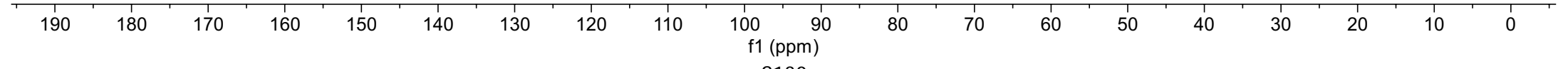
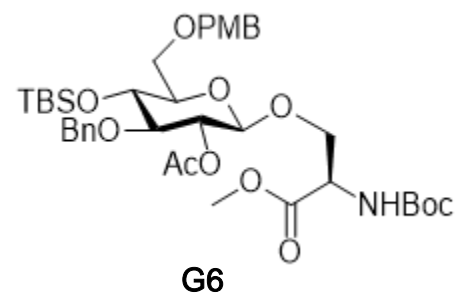
101.1

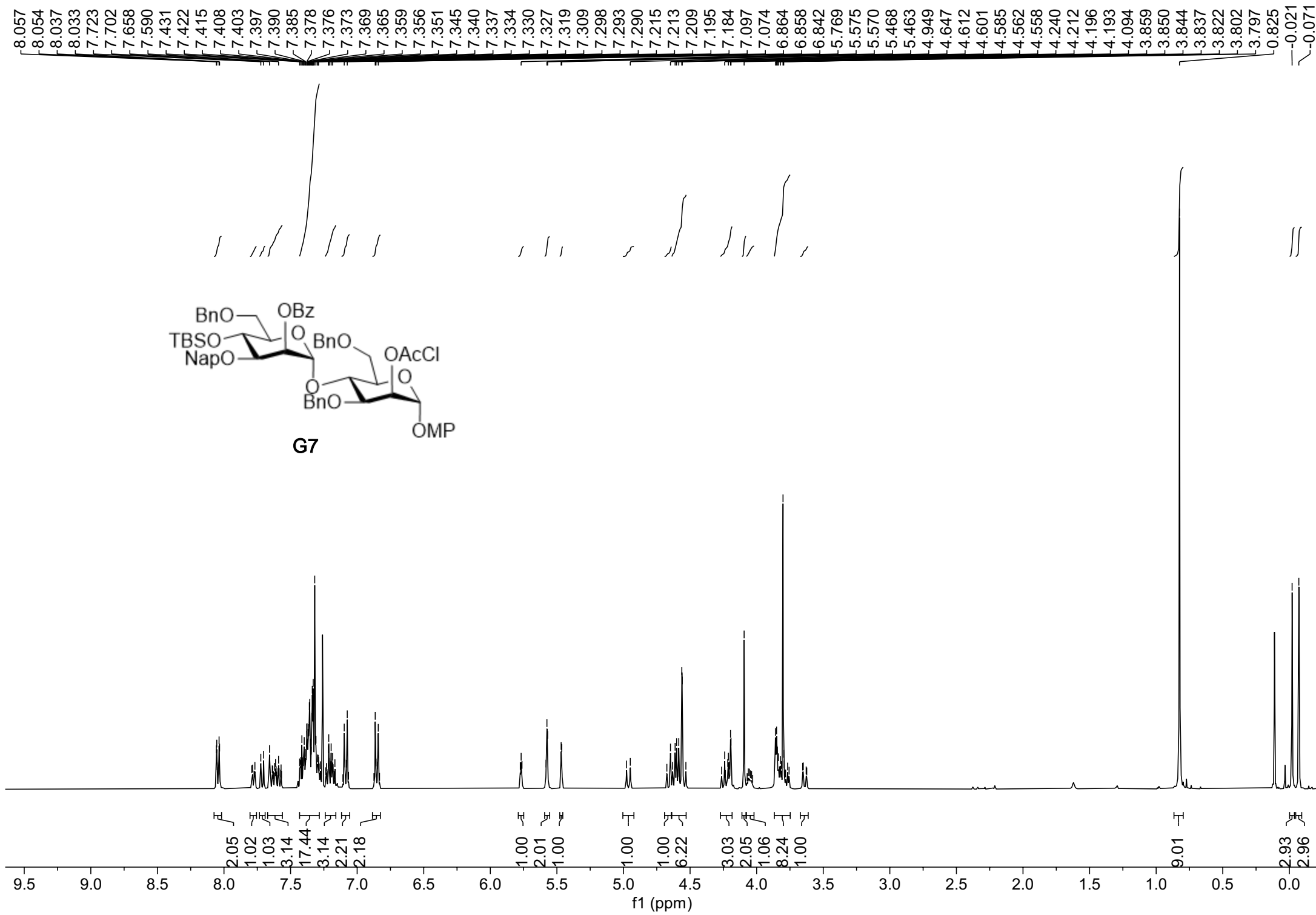
83.3  
80.1  
74.8  
73.3  
73.2  
70.9  
69.0  
68.8

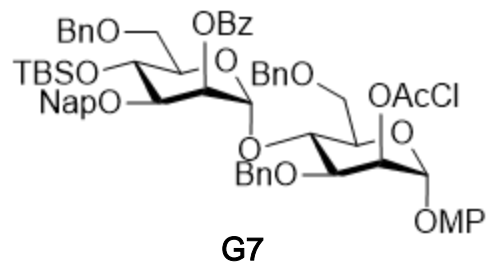
55.4  
54.0  
52.7

28.5  
26.0  
20.9  
18.1

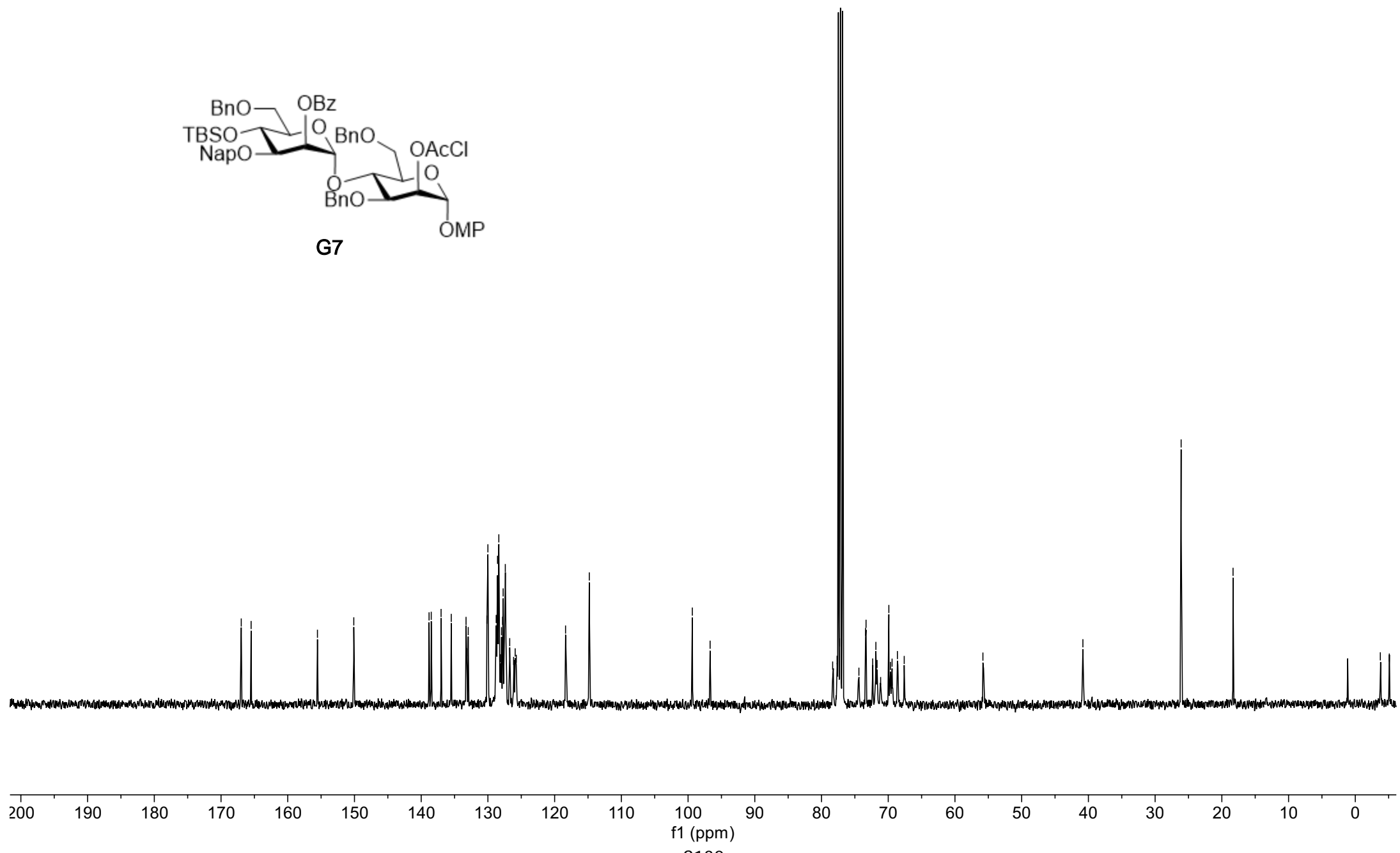
3.7  
4.7

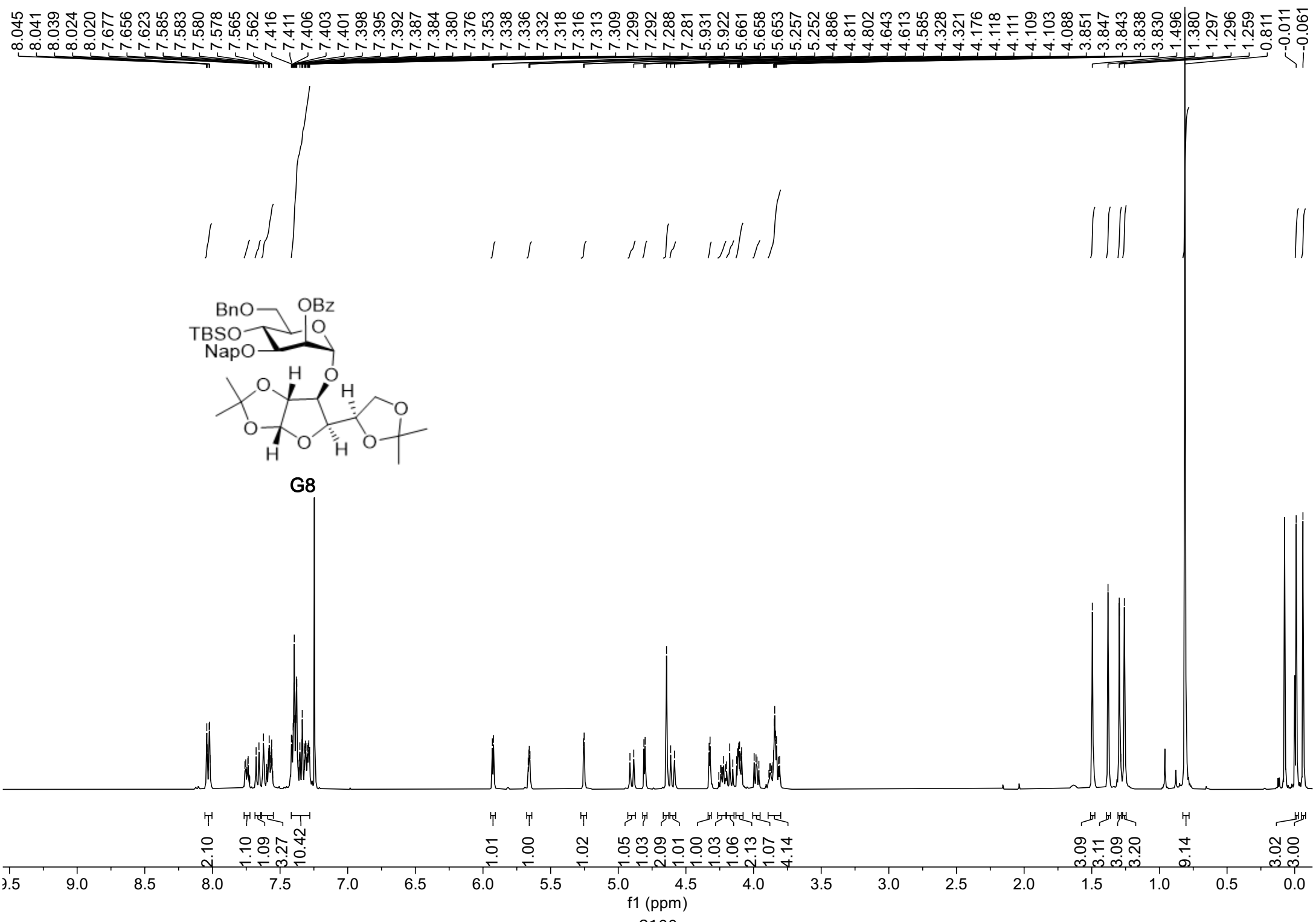


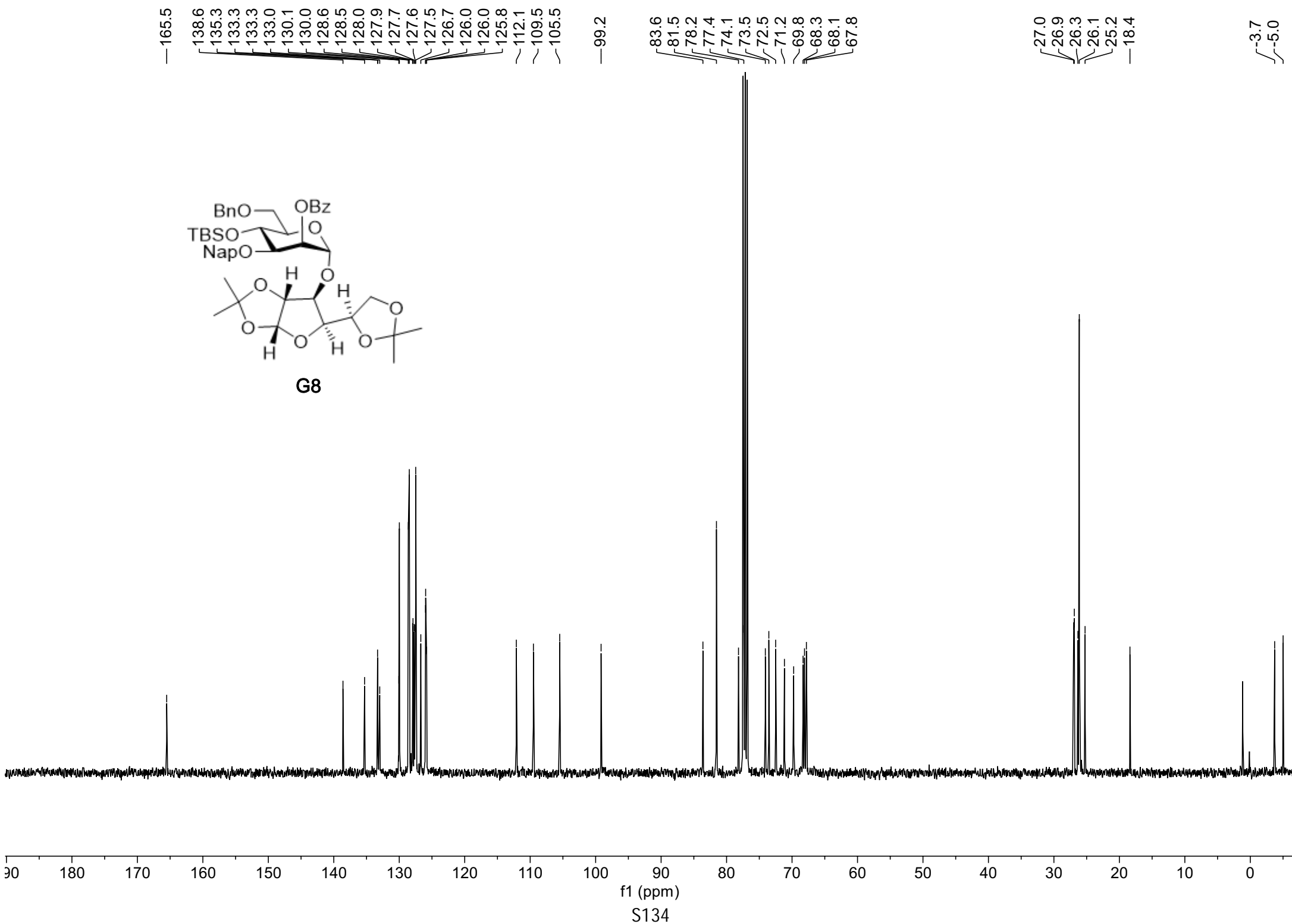


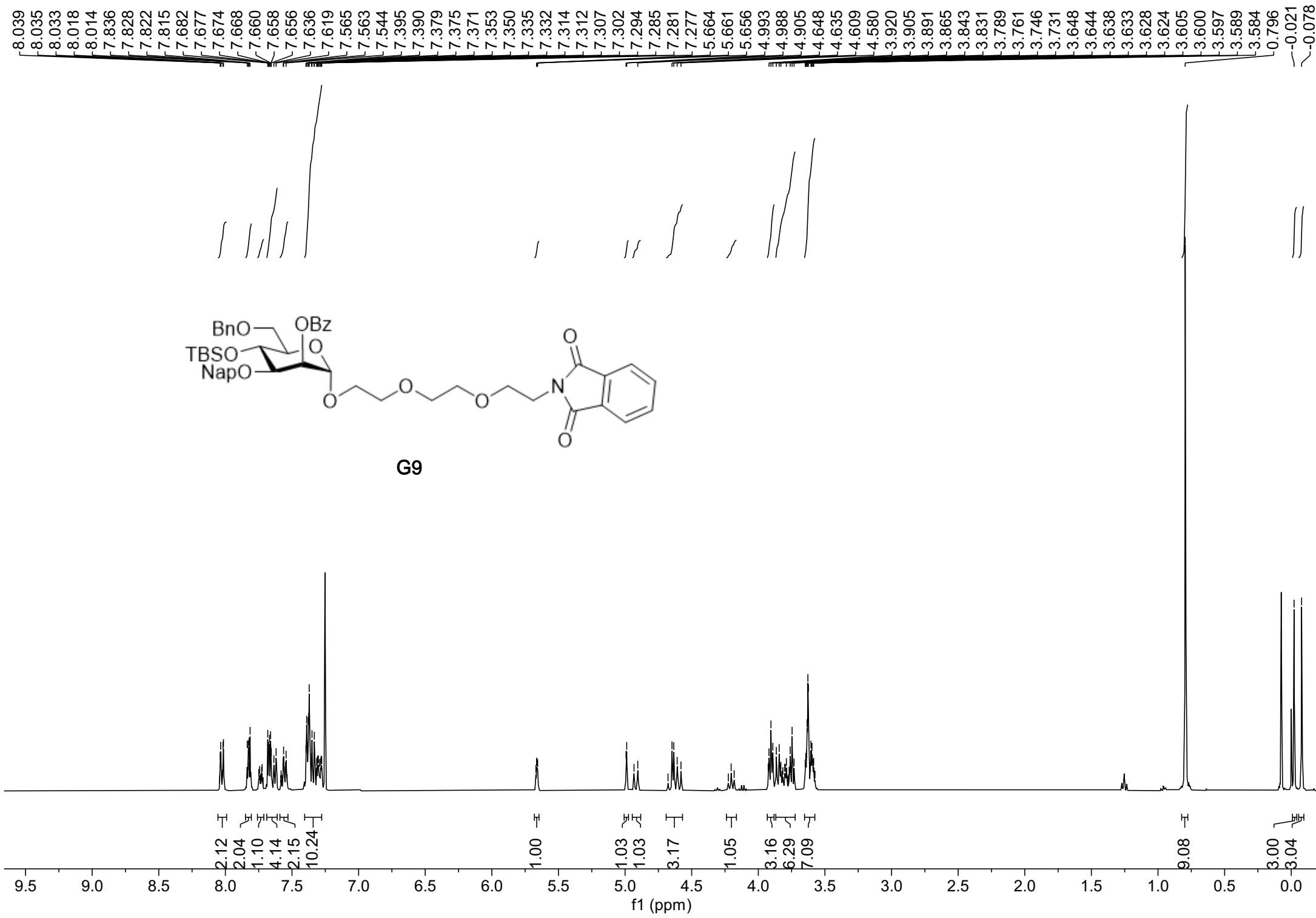


167.0  
 165.5  
 155.5  
 150.1  
 138.8  
 138.5  
 137.0  
 135.5  
 133.3  
 133.2  
 133.0  
 130.2  
 130.0  
 128.8  
 128.6  
 128.4  
 128.1  
 128.0  
 127.8  
 127.7  
 127.4  
 126.7  
 126.1  
 125.9  
 125.7  
 118.4  
 114.8  
 99.4  
 96.7  
 78.3  
 77.7  
 77.3  
 74.4  
 73.4  
 73.3  
 72.3  
 71.9  
 71.7  
 71.1  
 69.9  
 69.7  
 69.4  
 68.6  
 67.6  
 55.8  
 40.8  
 26.1  
 18.3  
 3.8  
 5.1

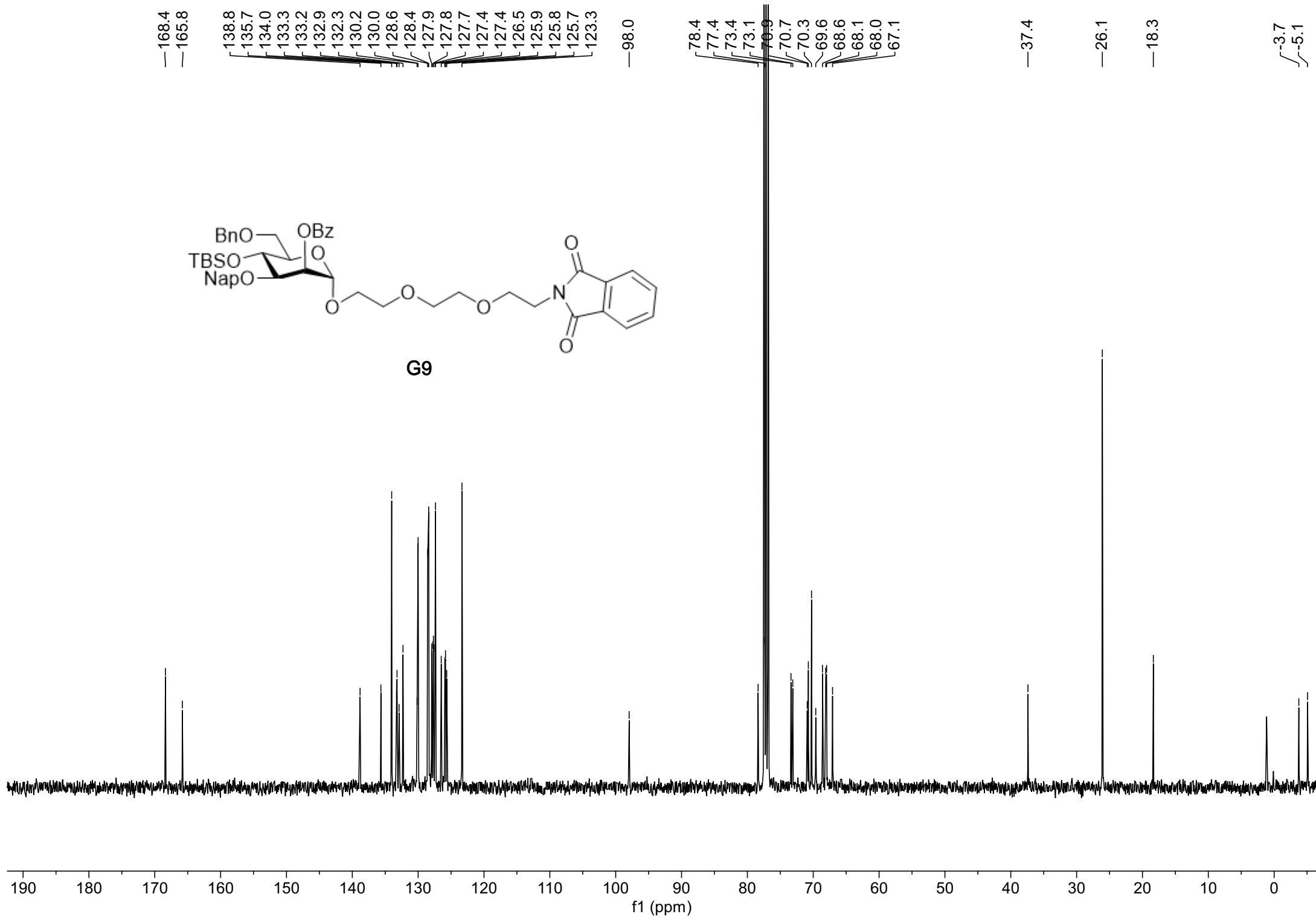






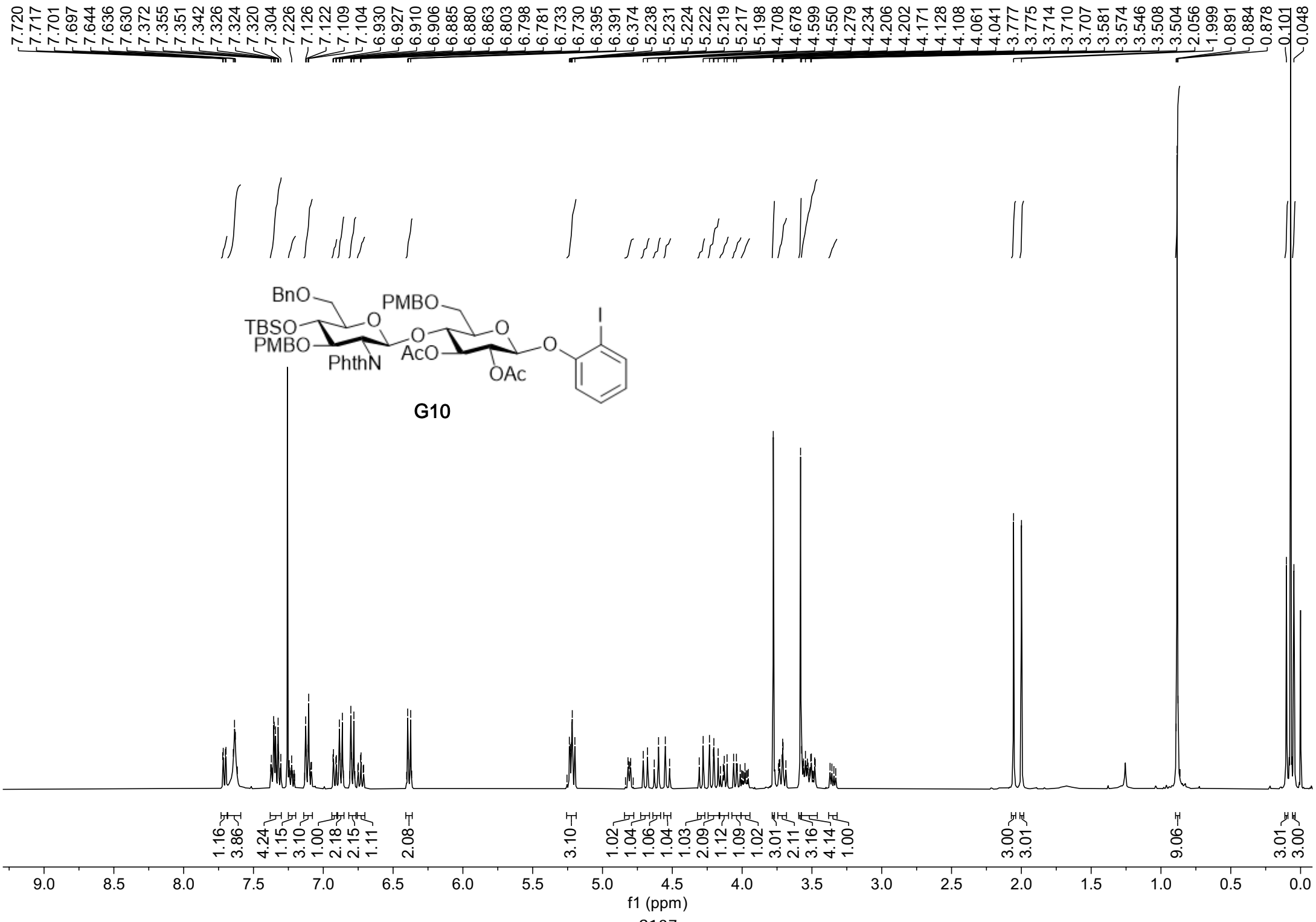






f1 (ppm)

S136

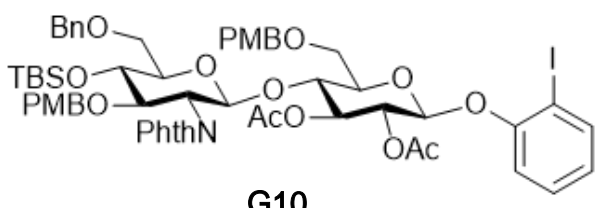


170.3  
169.6  
159.2  
158.6  
156.3  
139.5  
138.3  
133.8  
131.7  
130.6  
130.3  
129.6  
129.2  
129.0  
128.5  
127.6  
127.4  
124.6  
123.2  
116.1  
113.8  
113.4

99.7  
96.9  
87.0  
80.9  
76.1  
75.2  
75.1  
73.6  
73.1  
72.7  
72.5  
71.5  
69.1  
67.9  
56.4  
55.4  
54.9

26.1  
21.3  
21.0  
18.1

3.6  
4.3

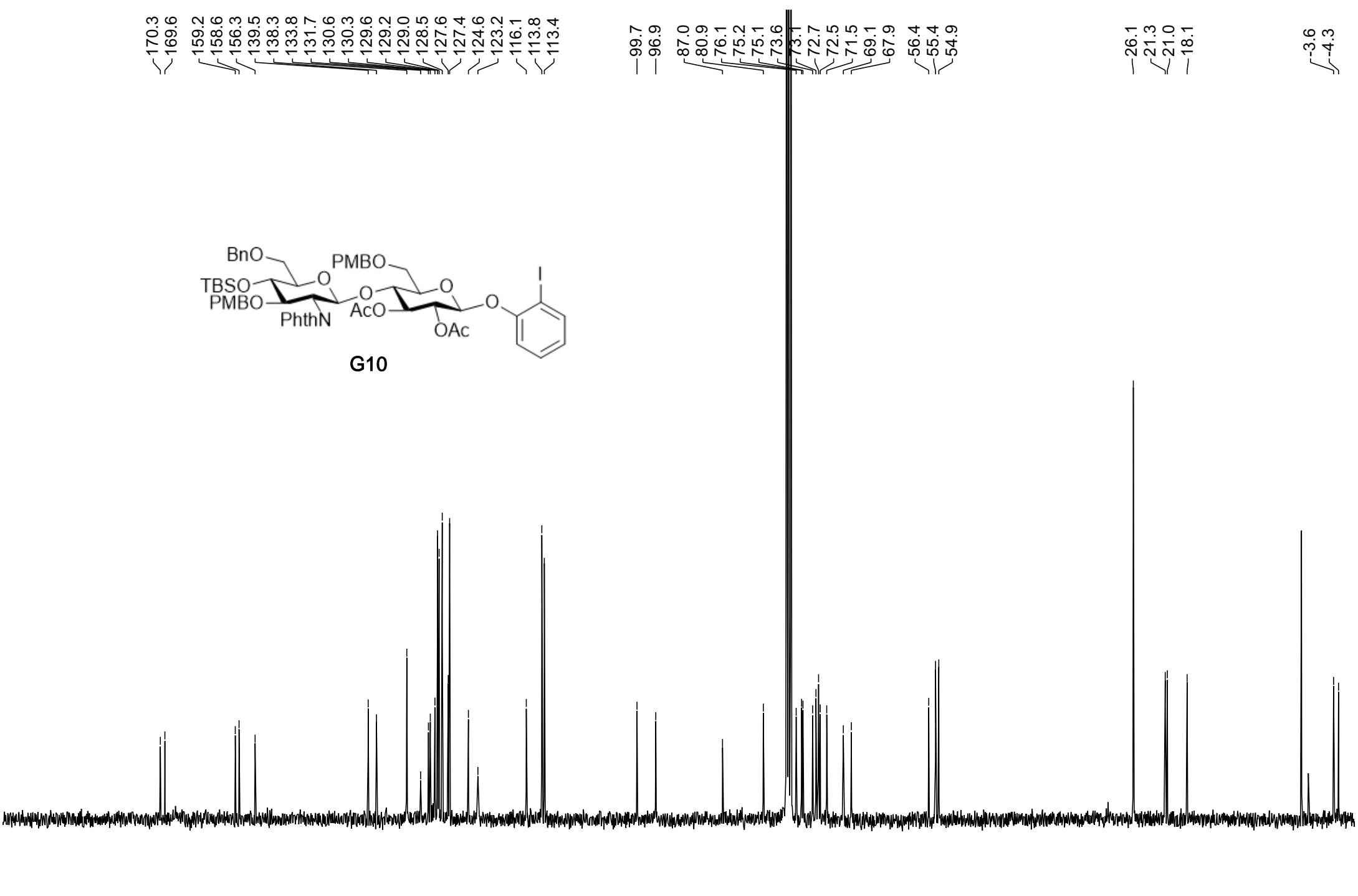


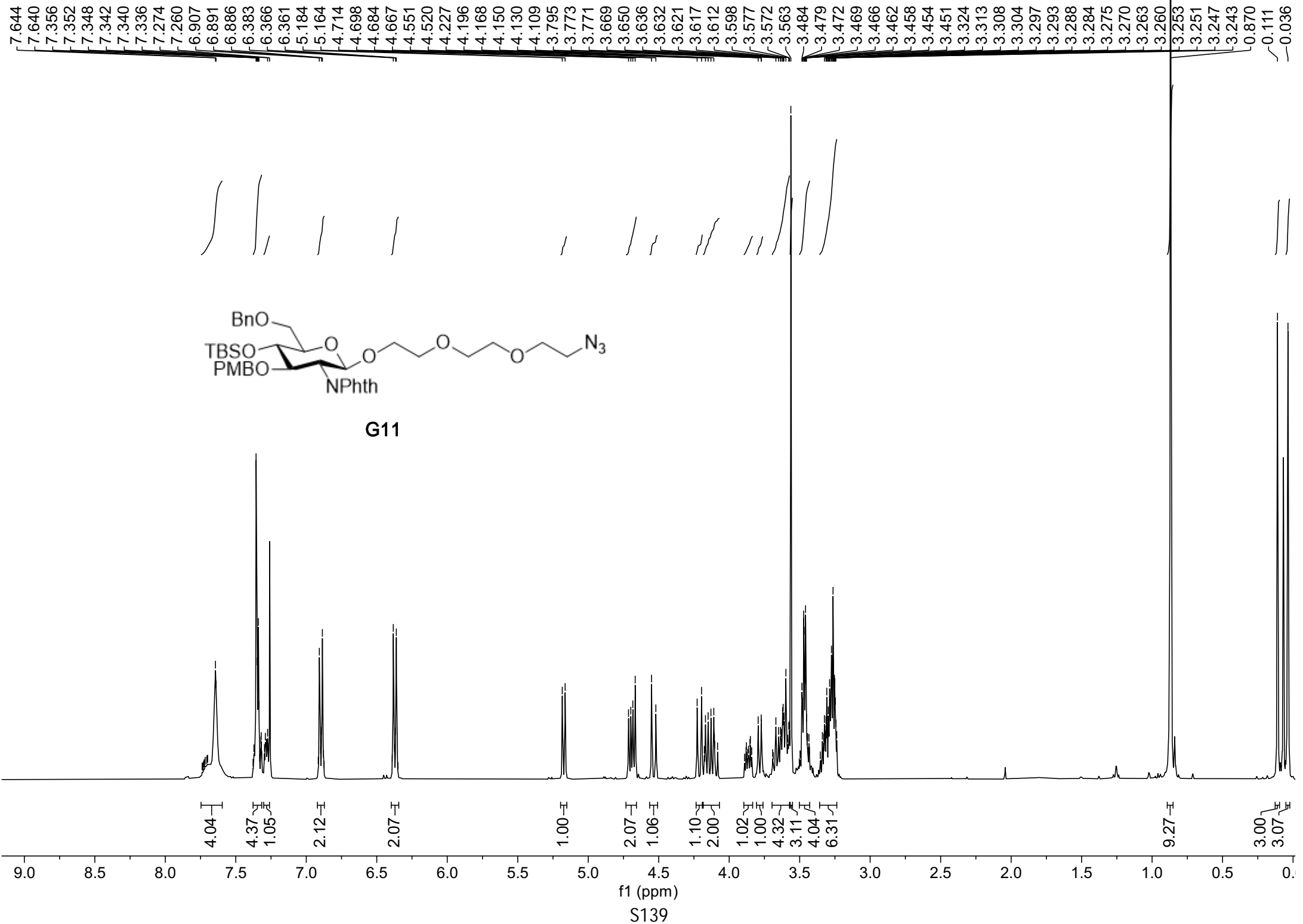
G10

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

S138





—158.6

138.5  
133.6  
131.8  
130.7  
129.1  
128.5  
127.7  
127.7  
123.1

—113.3

—98.2

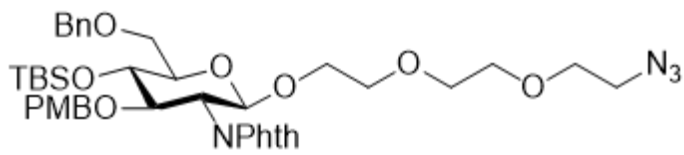
80.8  
76.3  
75.2  
73.4  
73.1  
70.6  
70.5  
70.1  
70.0  
69.4  
68.8

—56.1  
—54.9  
—50.7

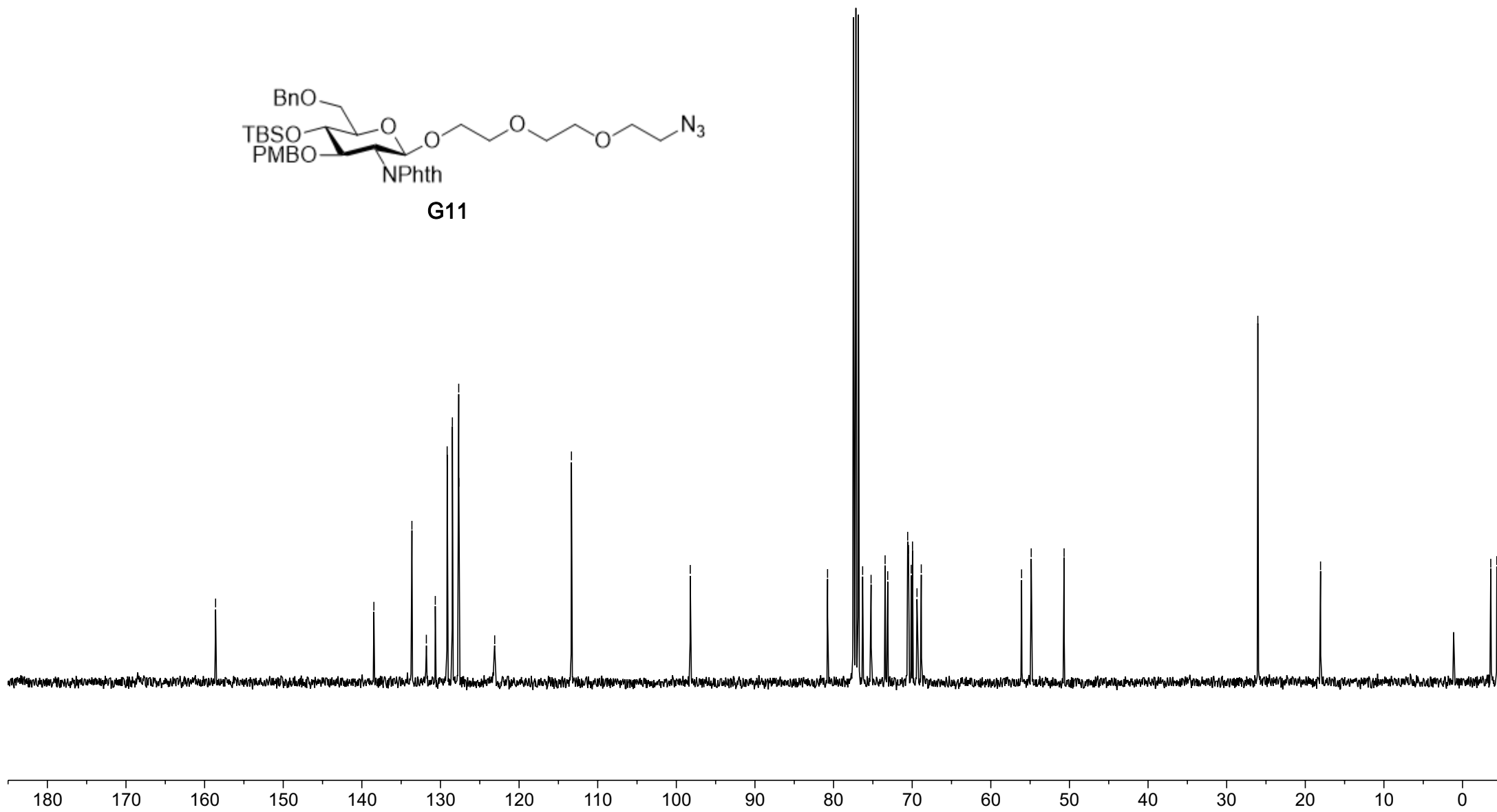
—26.0

—18.1

—3.6  
—4.4

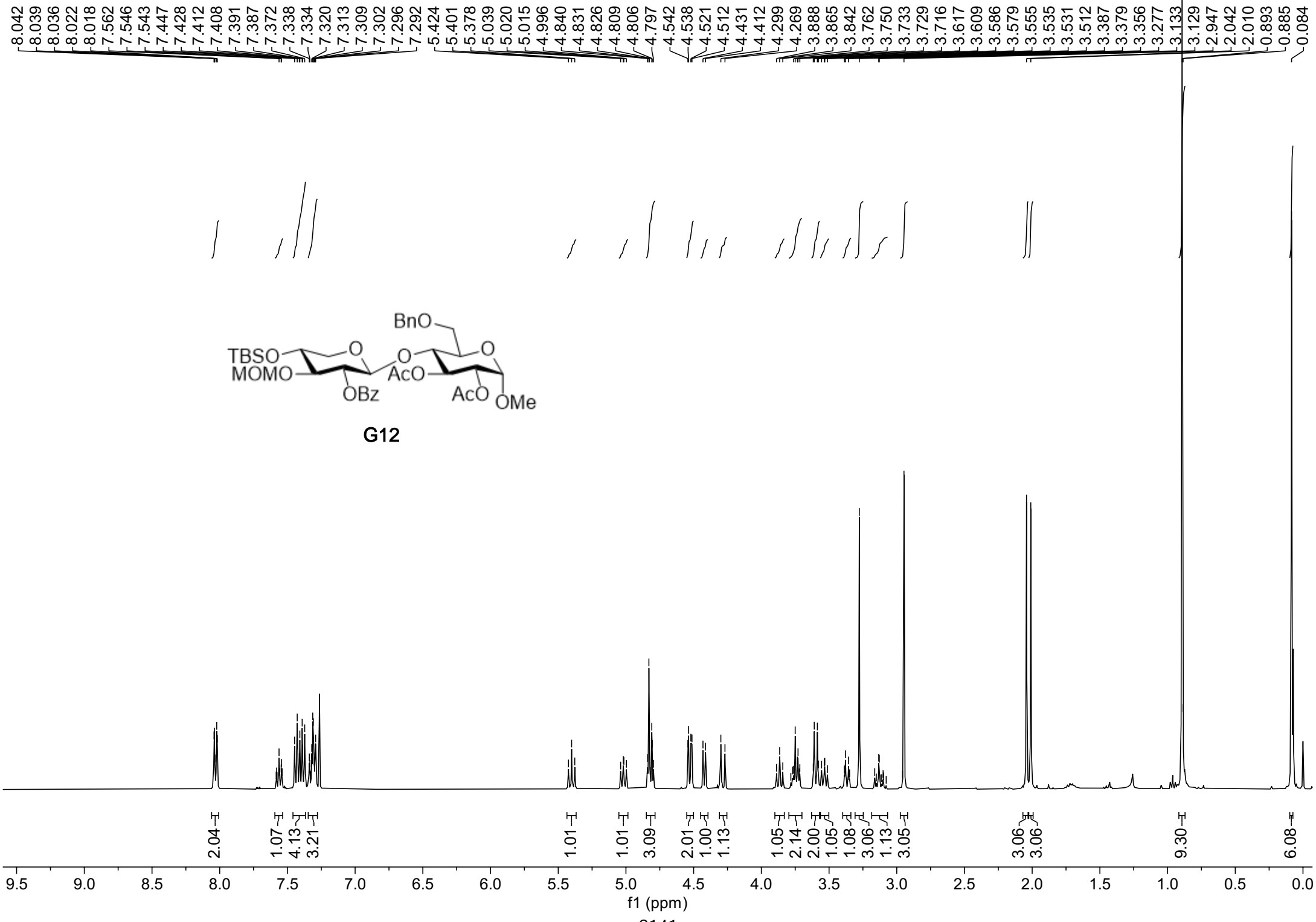


**G11**



f1 (ppm)

S140



170.5  
169.9  
165.0

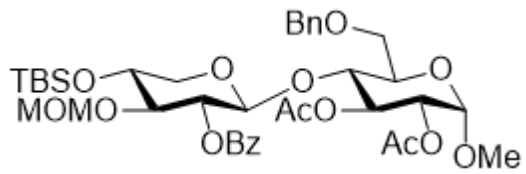
138.2  
133.2  
130.2  
130.0  
128.6  
128.5  
128.0  
127.9

101.9  
98.2  
96.9

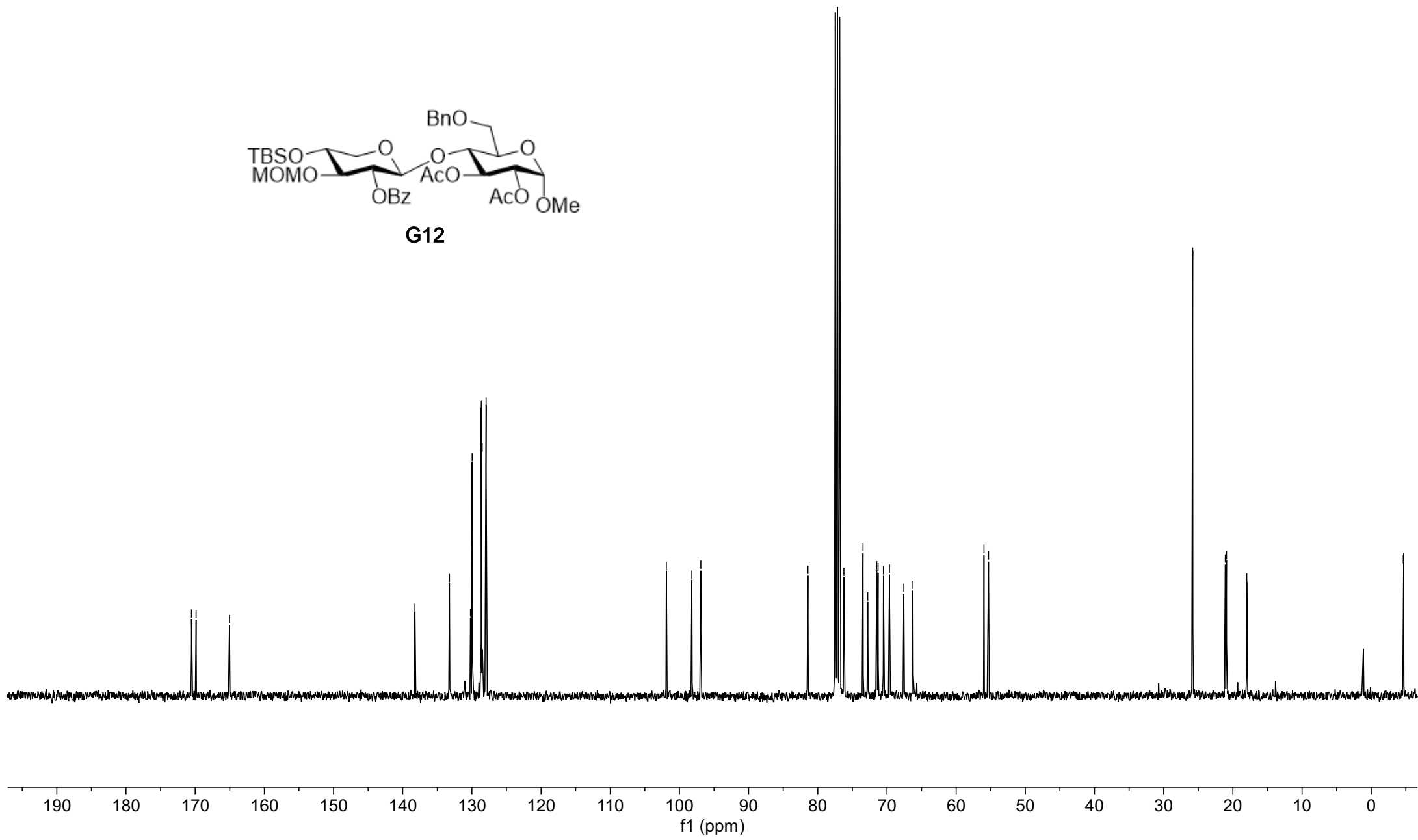
81.4  
76.2  
73.5  
72.8  
71.5  
71.3  
70.5  
69.6  
67.6  
66.2  
56.0  
55.3

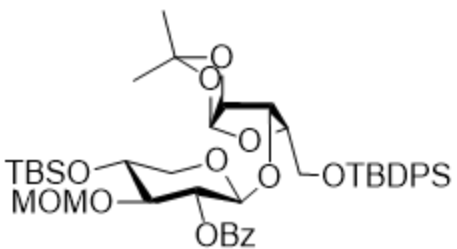
25.8  
21.1  
20.9  
18.0

-4.6  
-4.7

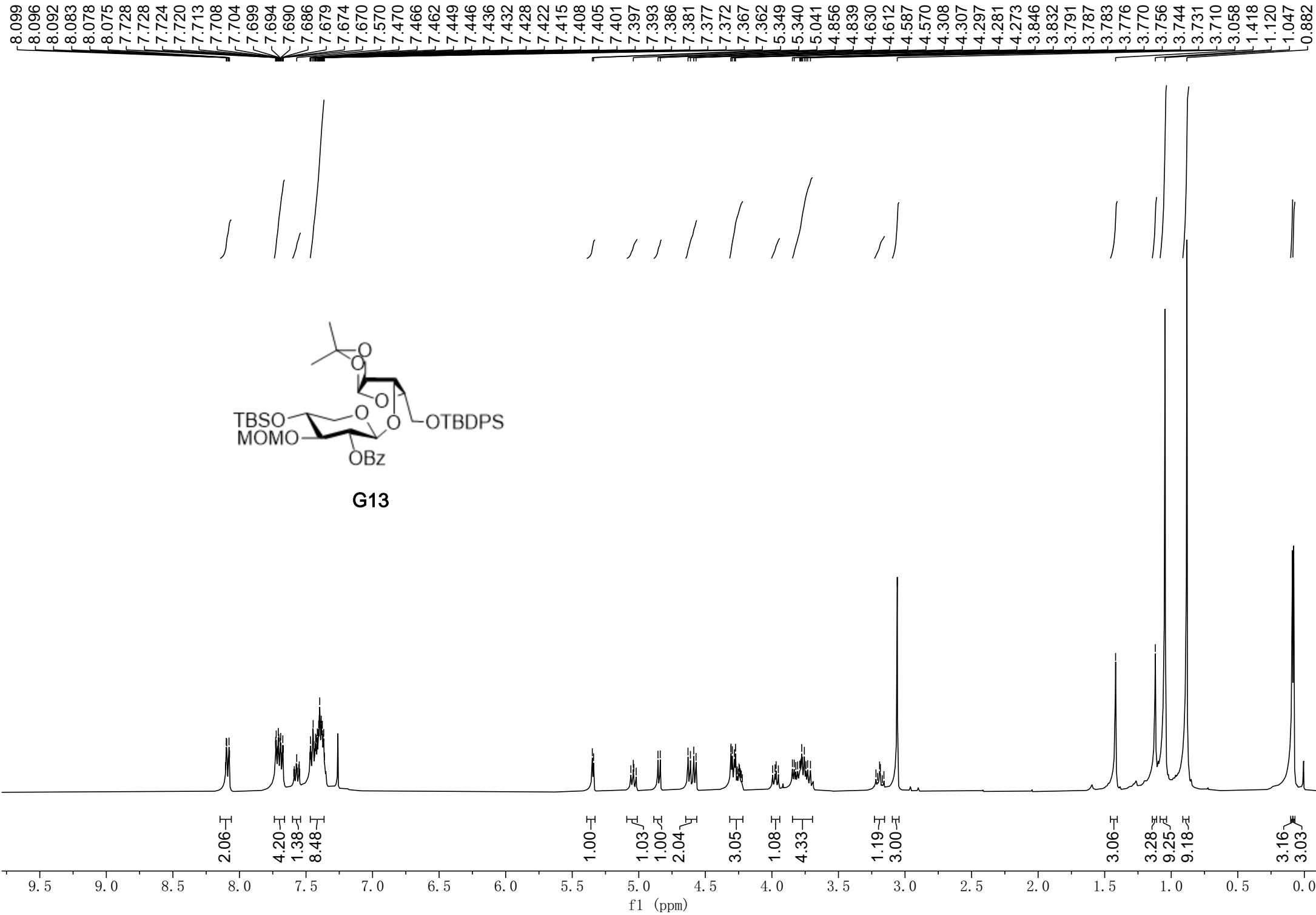


G12

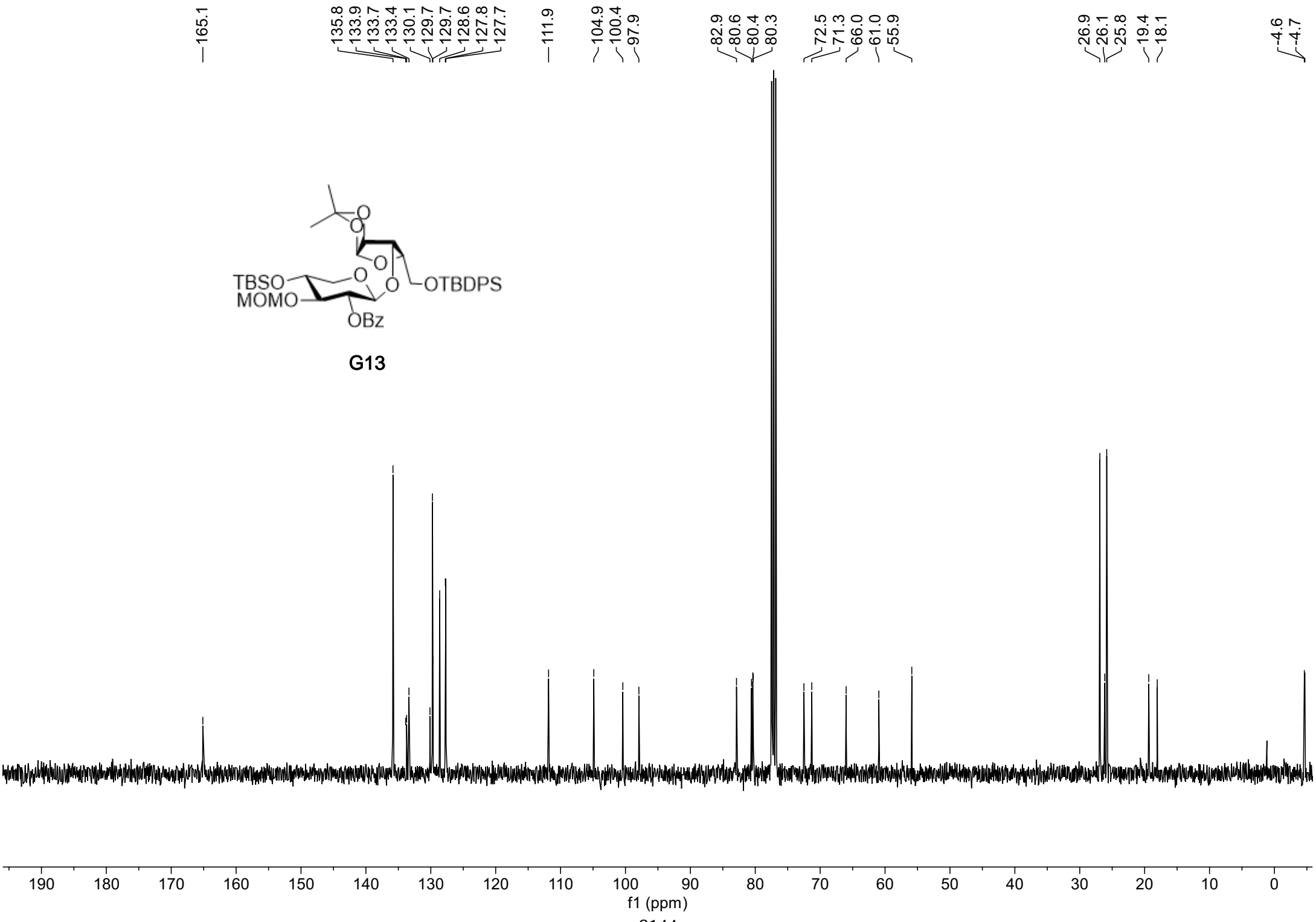




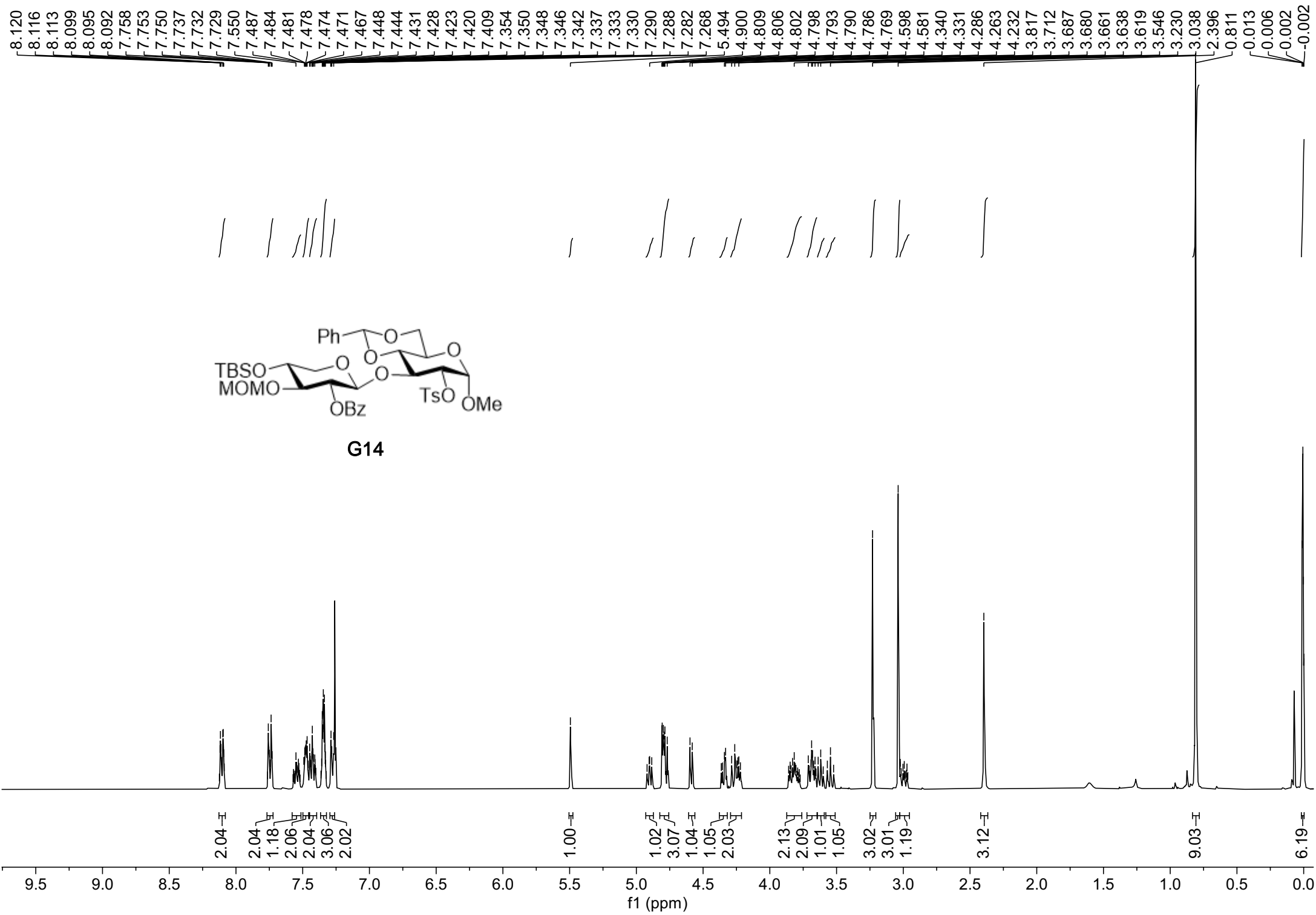
G13





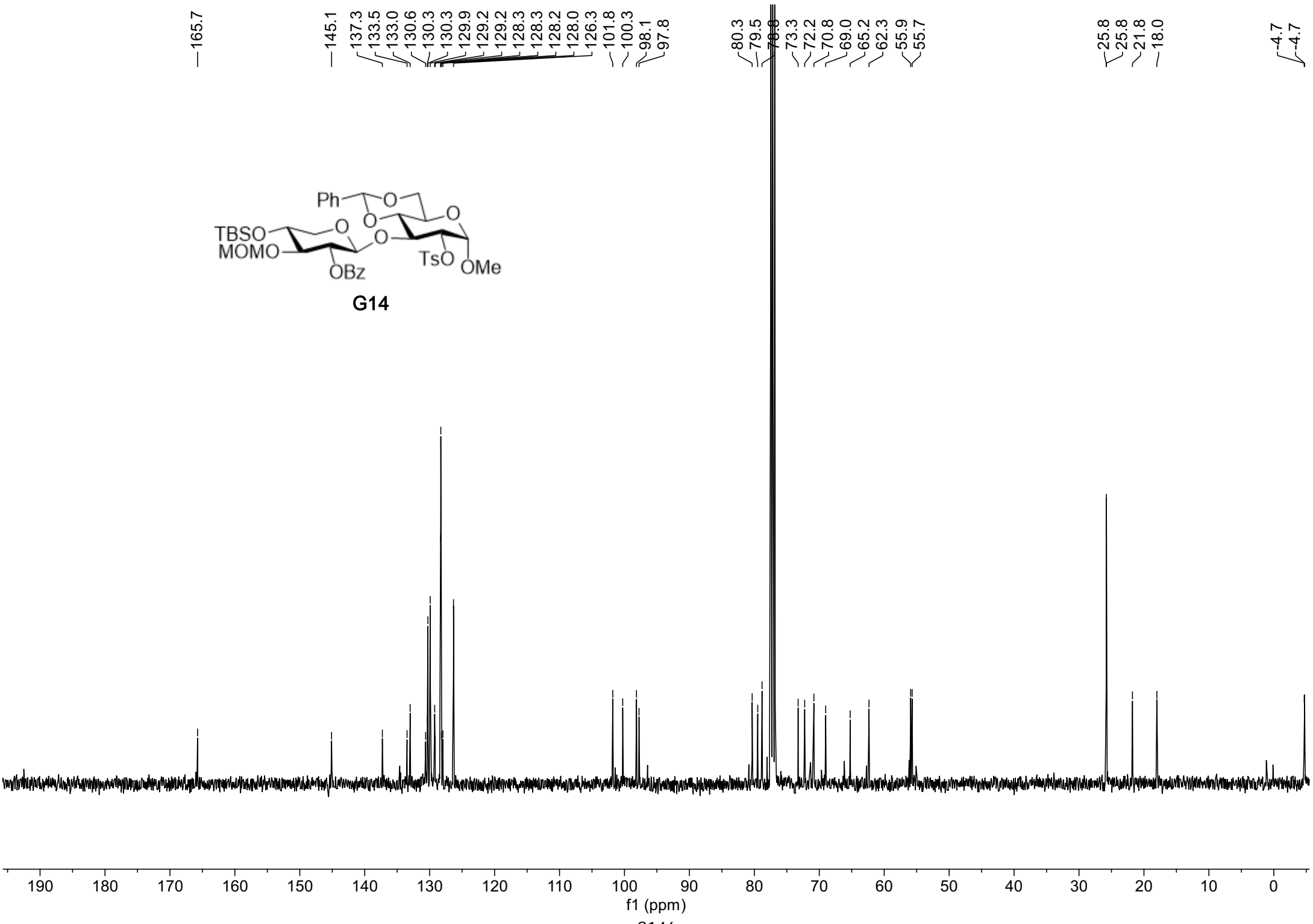


S144

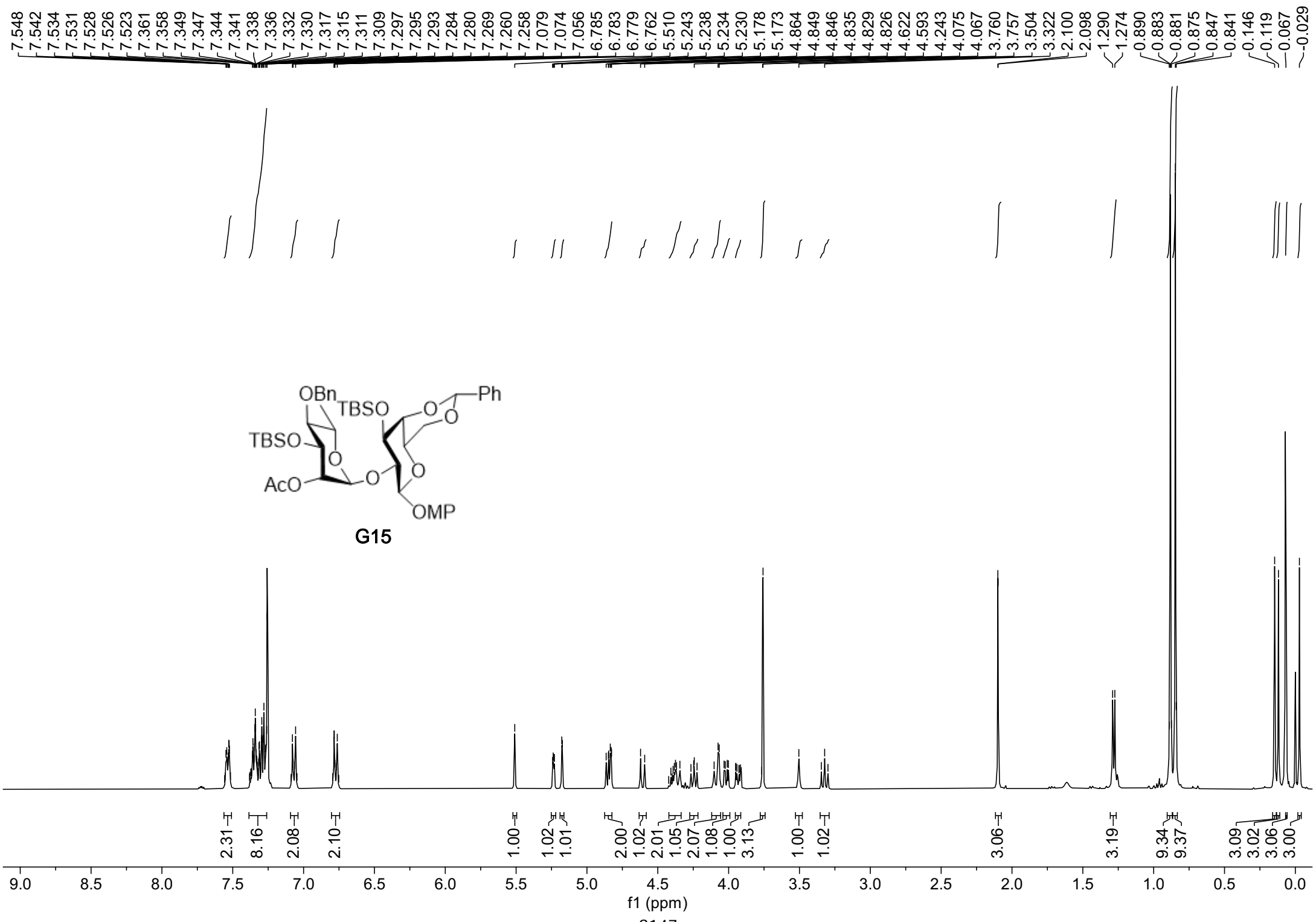


G14

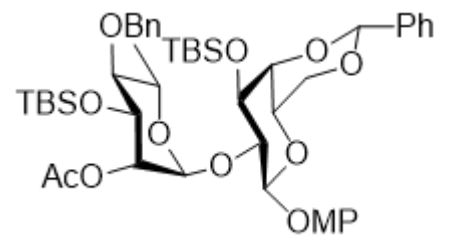
S145



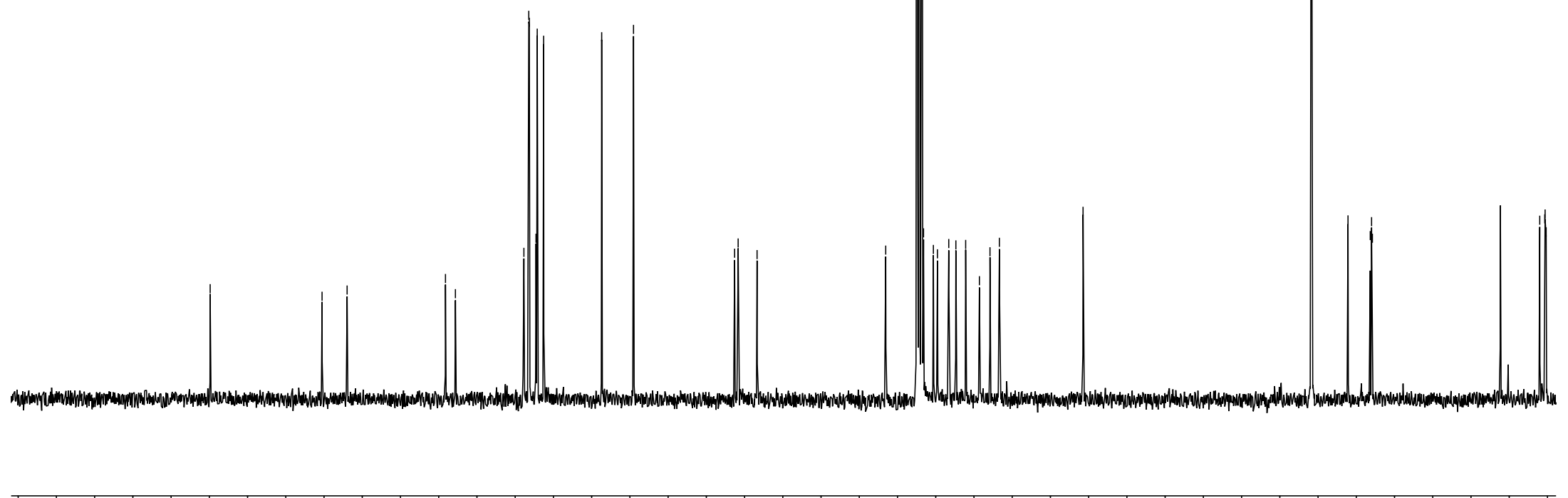
S146



—169.9  
 —155.3  
 —152.0  
 139.1  
 137.8  
 128.9  
 128.2  
 128.2  
 127.3  
 127.1  
 126.3  
 —118.7  
 —114.5  
 101.3  
 100.8  
 98.4  
 81.5  
 76.6  
 75.3  
 74.8  
 73.3  
 72.4  
 71.1  
 69.3  
 67.9  
 66.7  
 —55.7  
 25.9  
 25.8  
 21.1  
 18.2  
 18.0  
 17.9  
 4.0  
 4.6  
 4.7  
 4.8

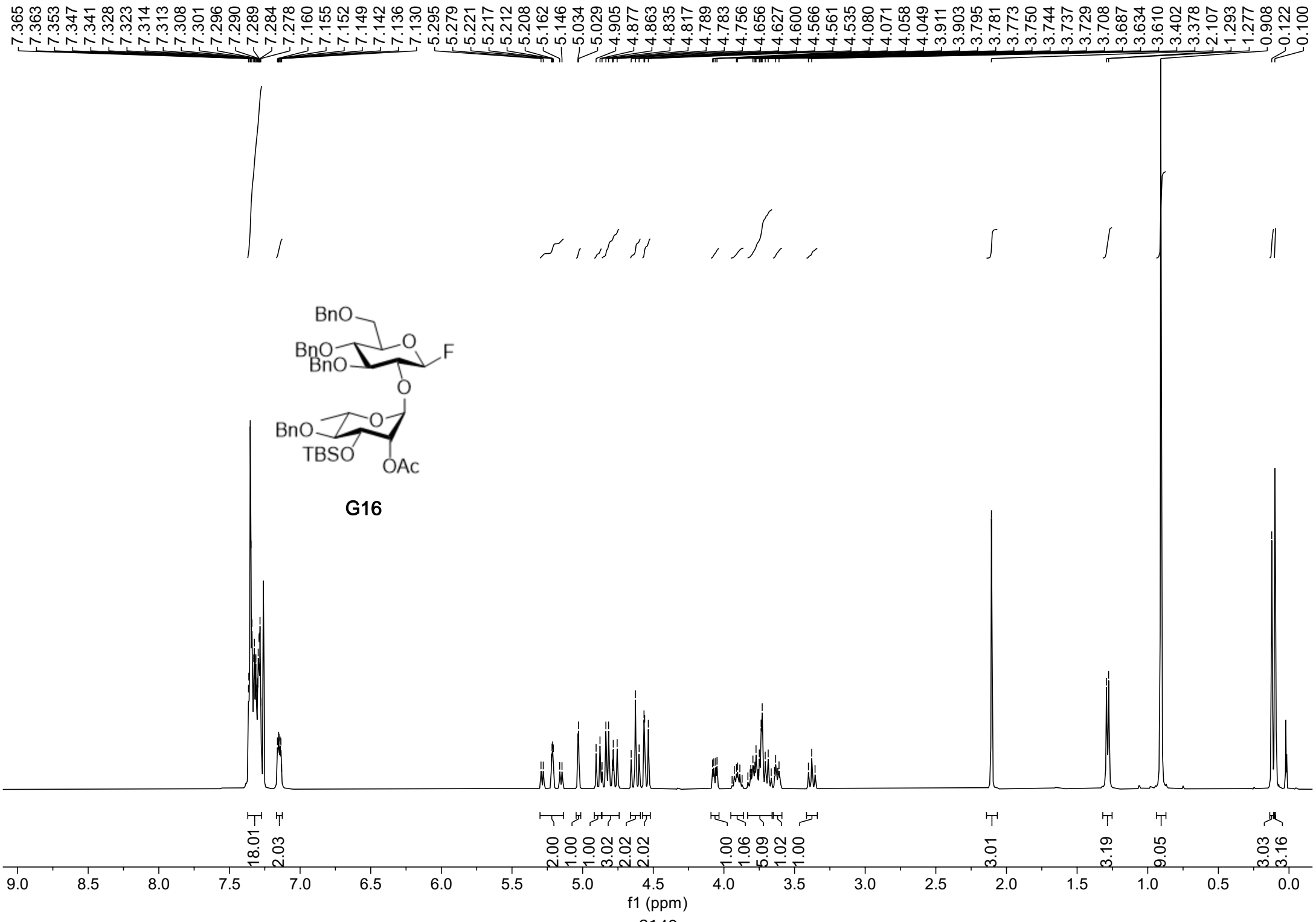


**G15**



f1 (ppm)

S148



—170.1

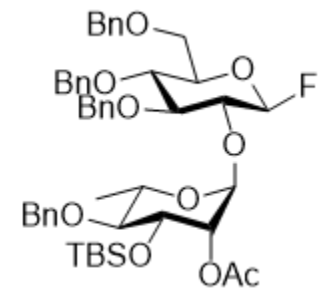
138.4  
137.9  
137.8  
137.8  
128.5  
128.5  
128.5  
128.1  
128.0  
128.0  
127.9  
127.8  
—108.9  
—106.8

—98.9

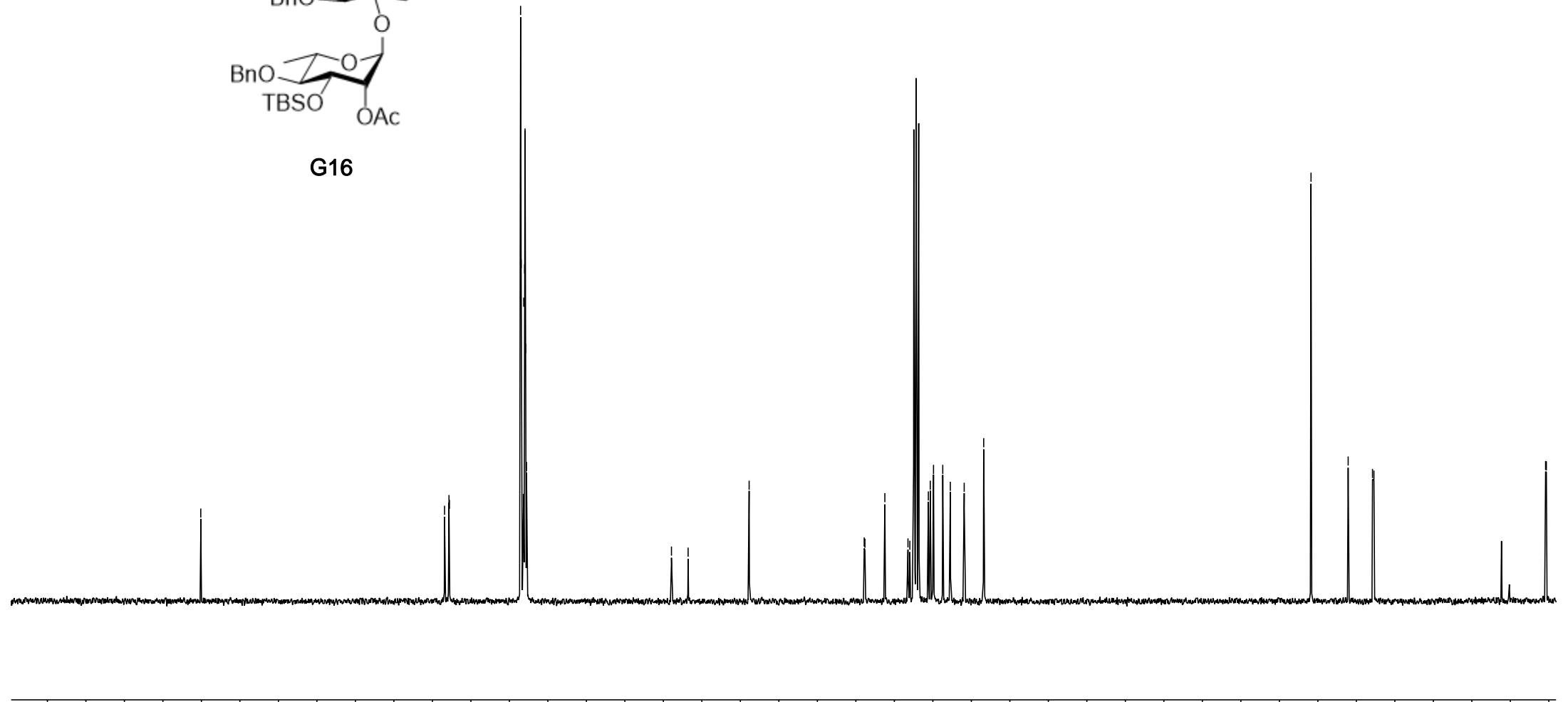
83.9  
83.8  
81.2  
78.2  
78.0  
75.6  
75.3  
75.0  
74.9  
73.7  
72.7  
70.9  
68.4  
68.4

—25.9  
21.1  
17.9  
17.7

—4.6  
—4.7



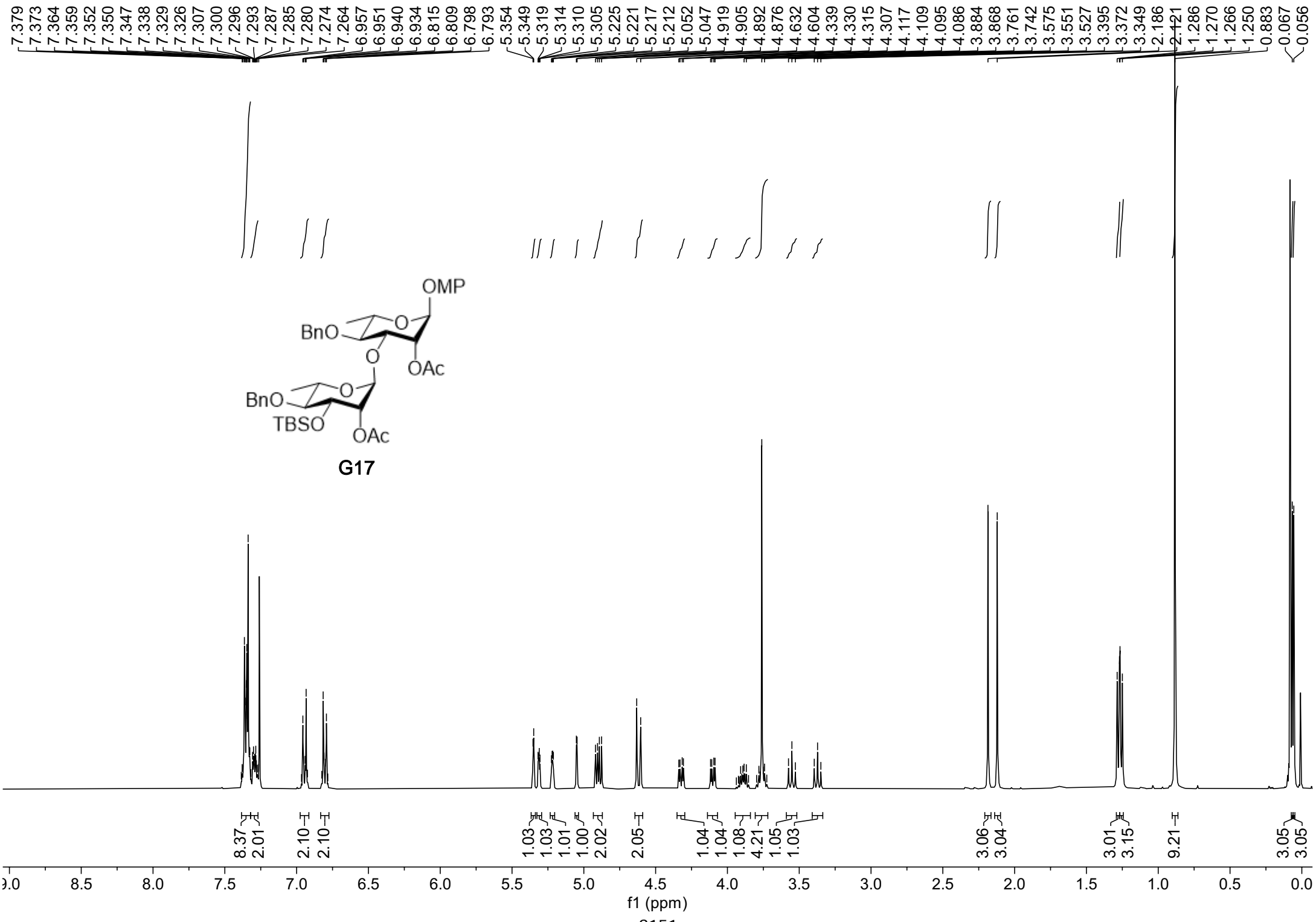
**G16**



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

S150





170.4  
170.3

155.2  
150.2

138.7  
138.0

128.6  
128.4  
128.2  
128.0  
127.8  
127.7  
117.8  
114.7

99.9  
96.2

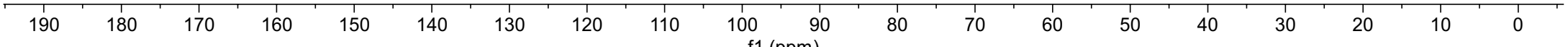
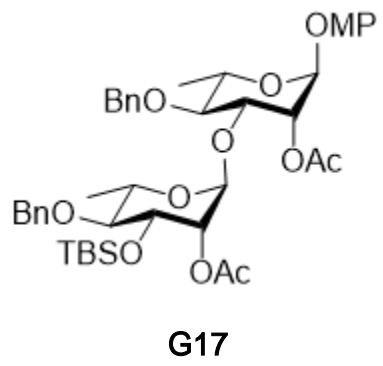
81.2  
80.3  
77.4  
75.6

75.3  
73.1  
72.4  
70.9  
69.0  
68.5

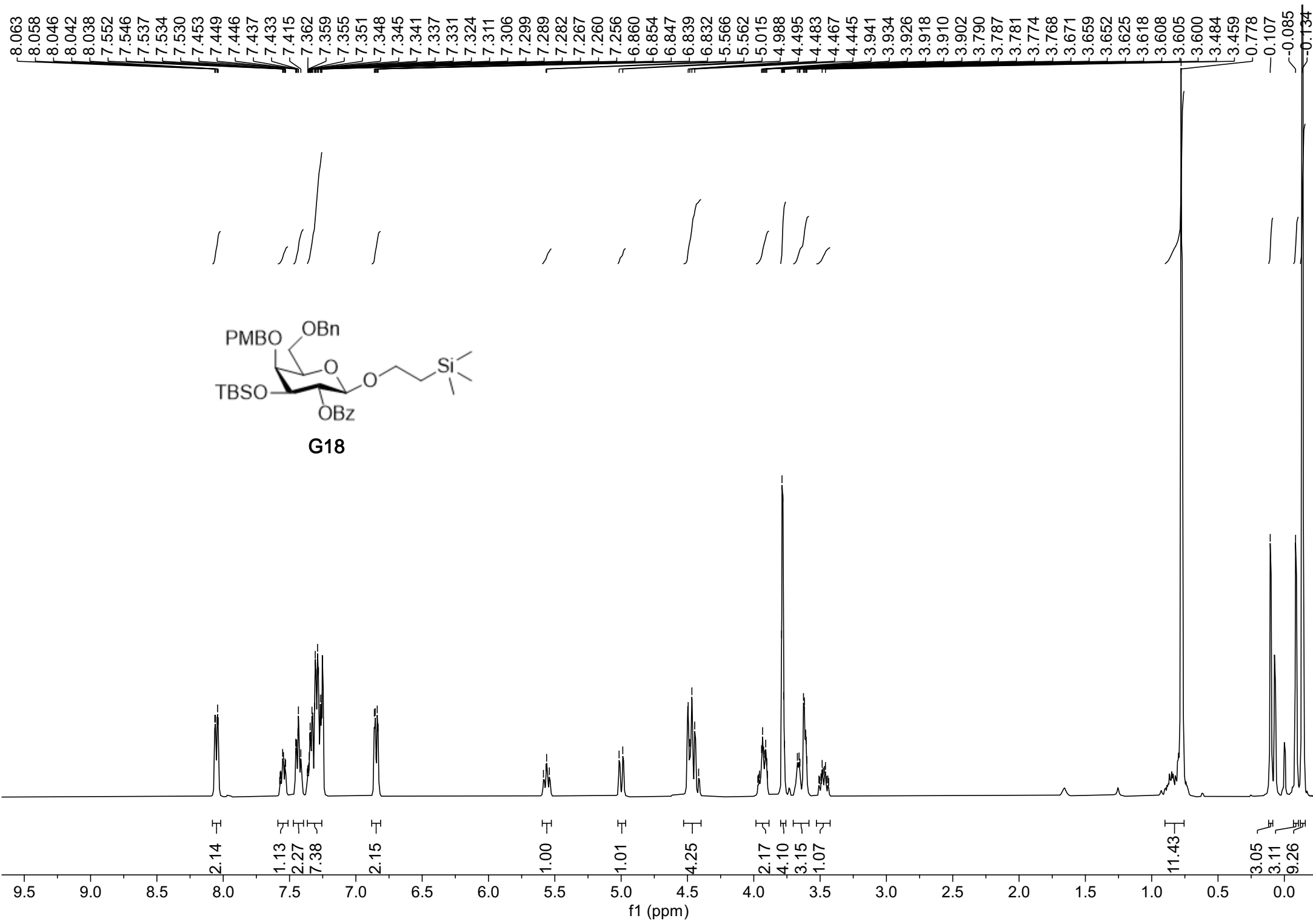
55.8

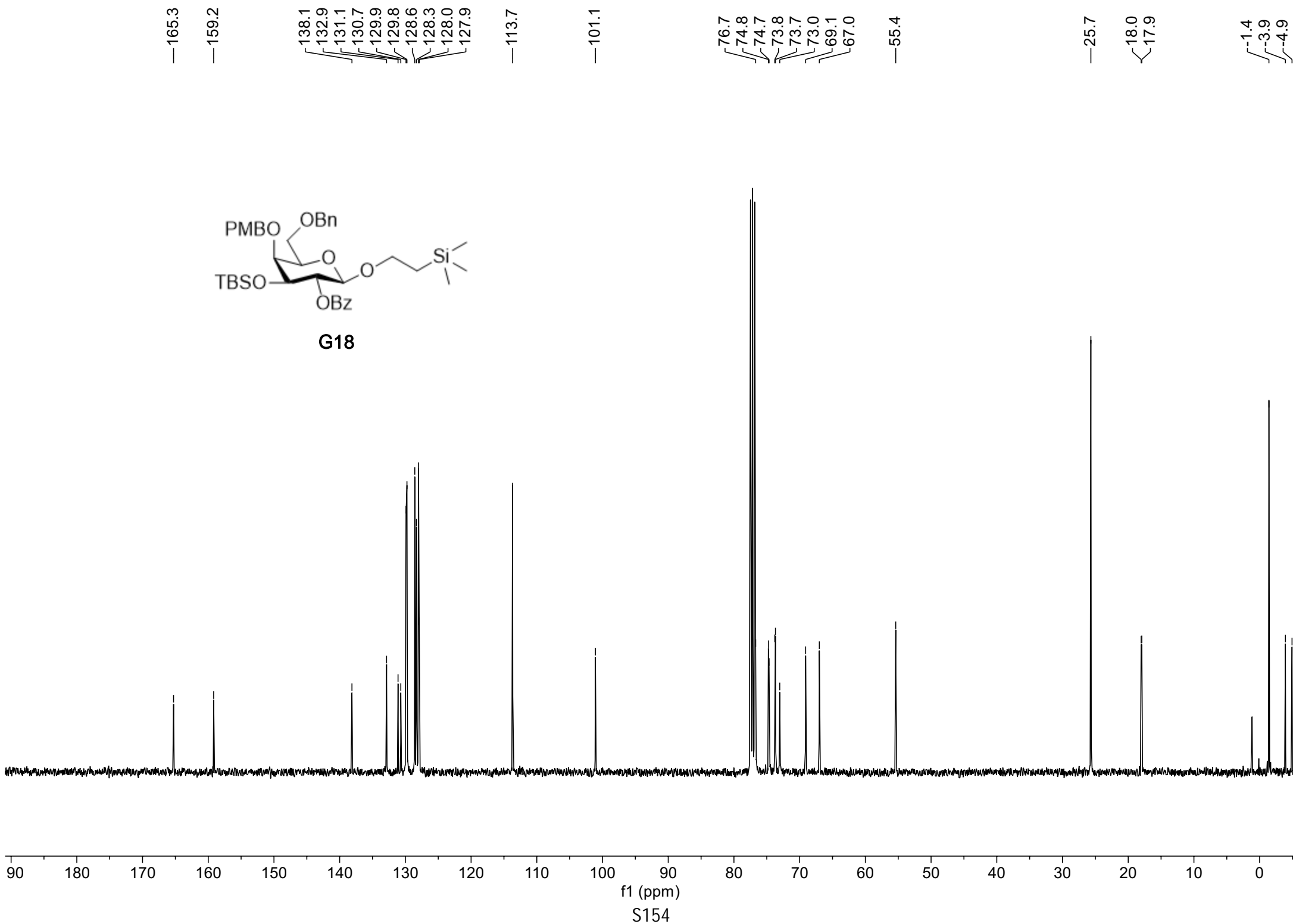
25.9  
21.2  
21.1  
18.1  
18.0

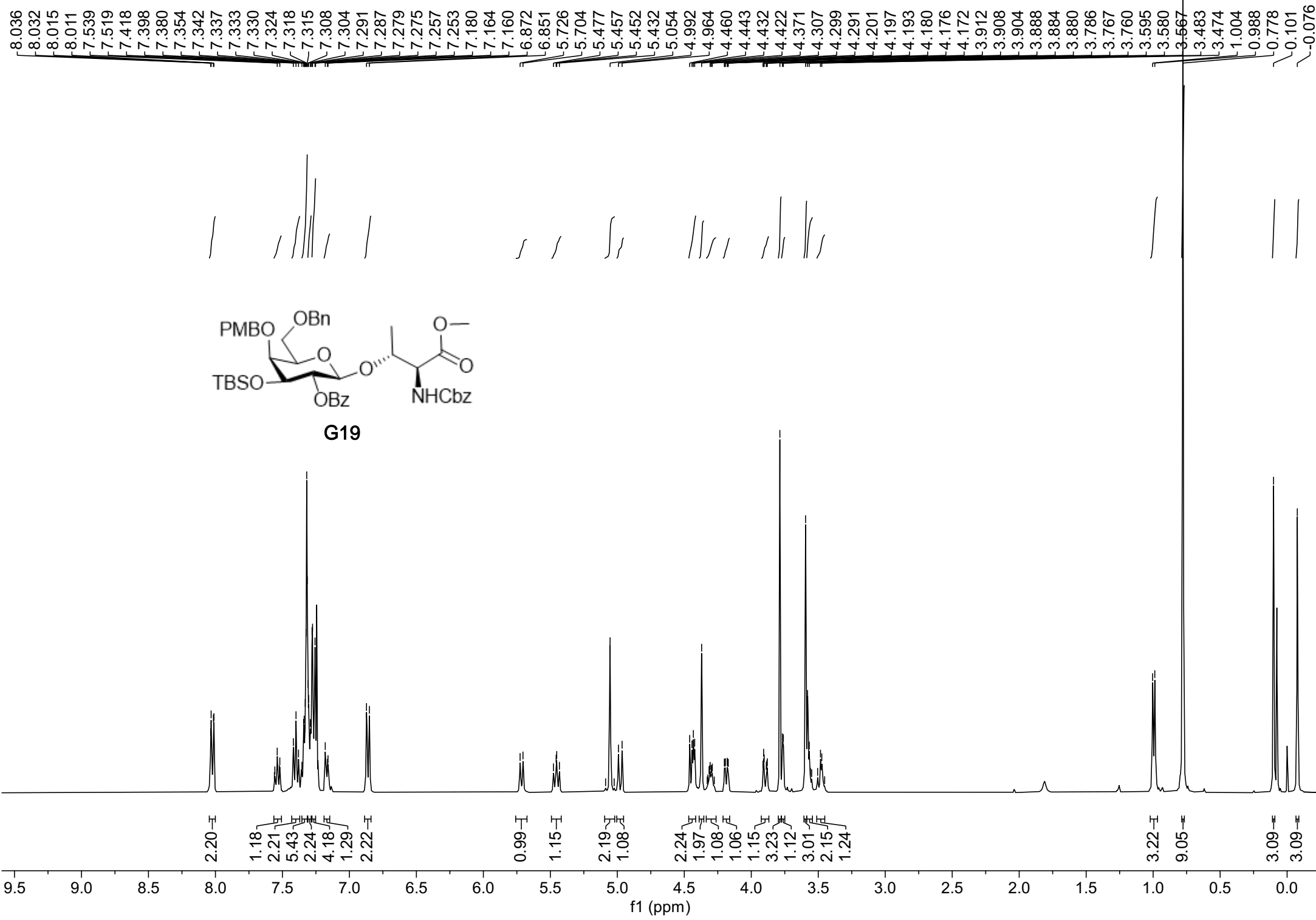
-4.7



S152







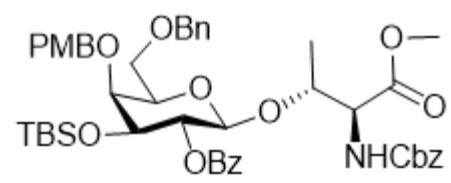
—171.0  
—165.3  
159.2  
156.9  
138.0  
136.5  
133.0  
130.9  
130.3  
129.7  
129.1  
128.6  
128.5  
128.5  
128.3  
128.0  
128.0  
128.0  
127.9  
125.4  
113.7

—100.8

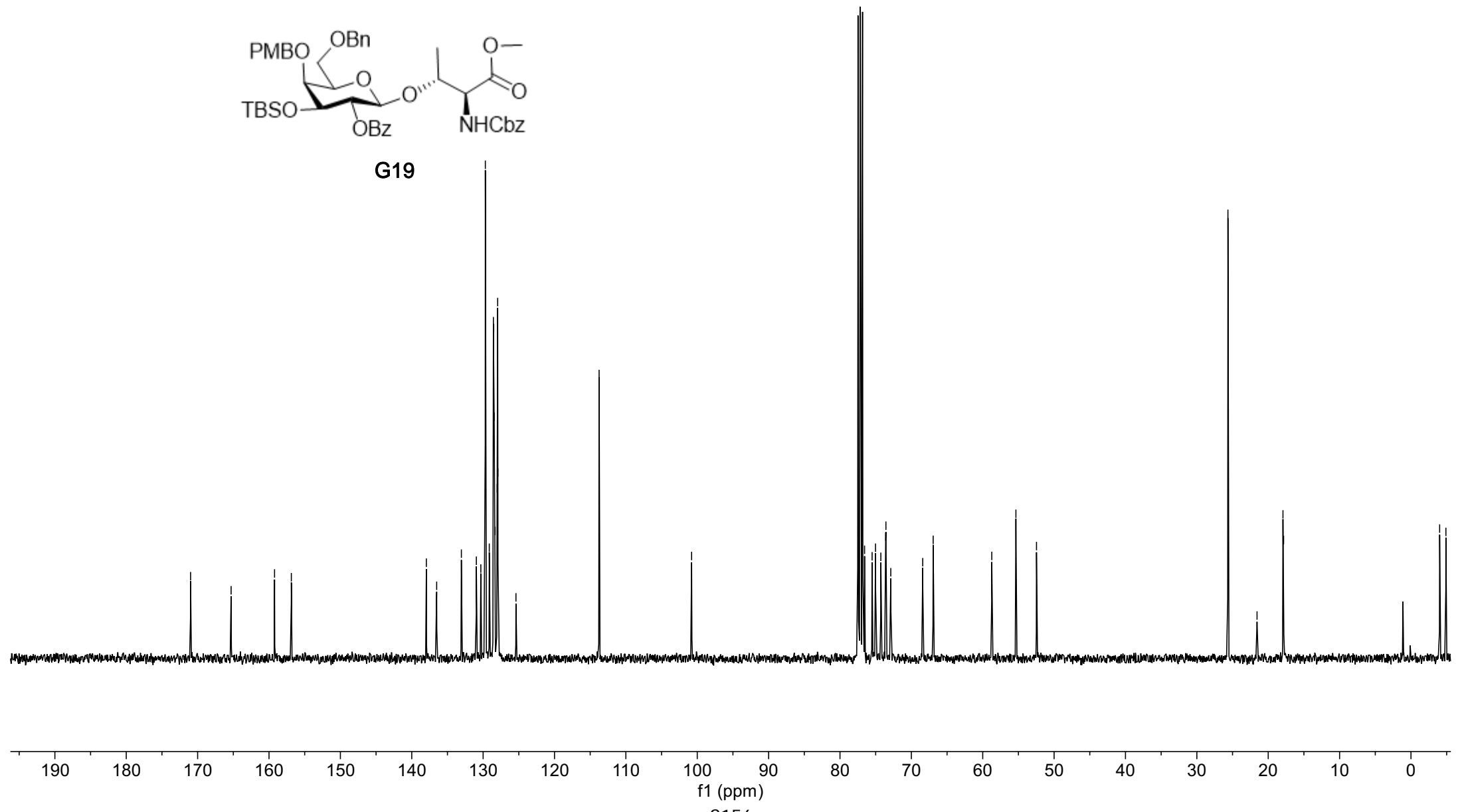
76.6  
75.5  
75.0  
74.3  
73.6  
73.6  
72.9  
68.4  
66.9  
58.7  
55.4  
52.5

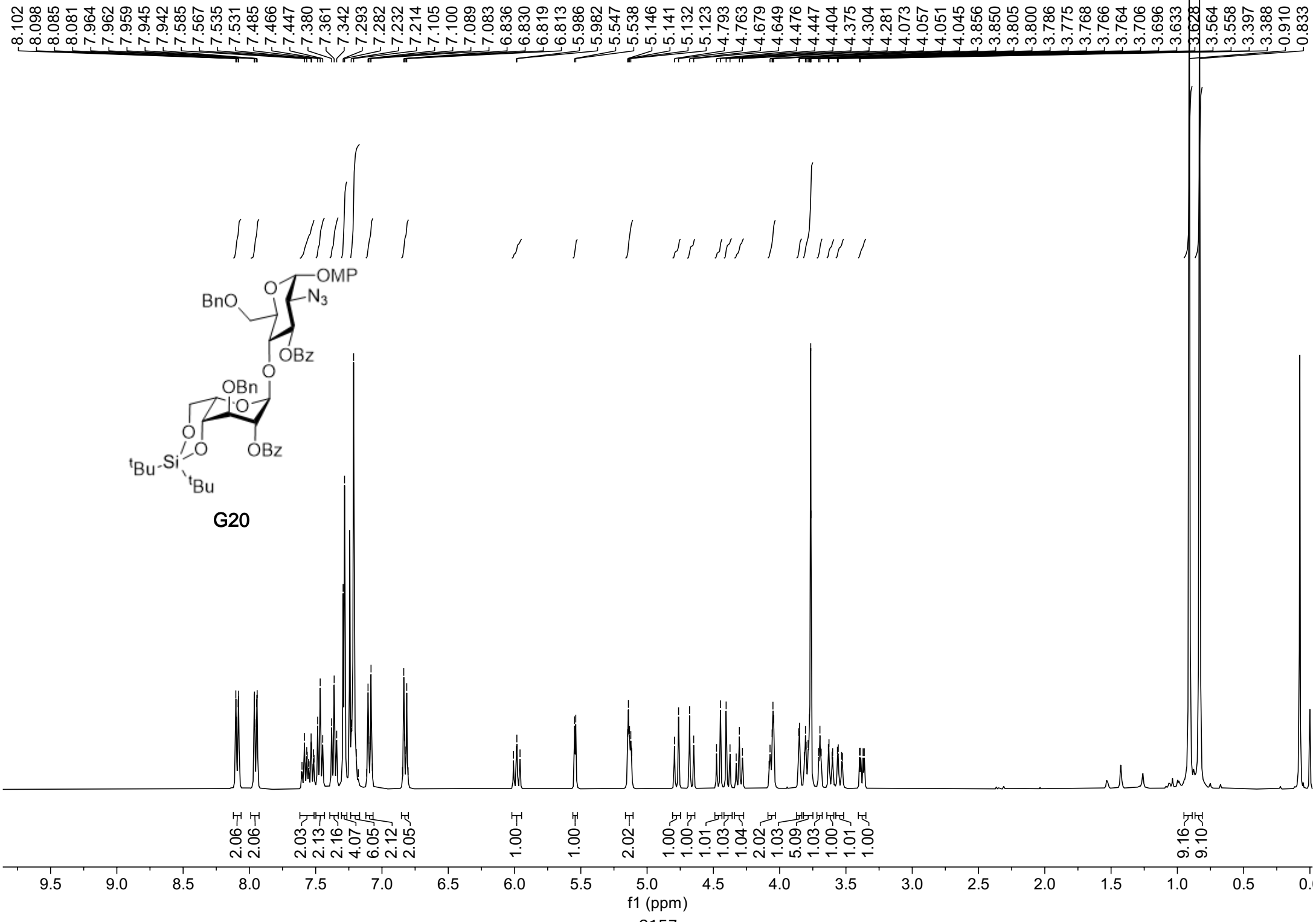
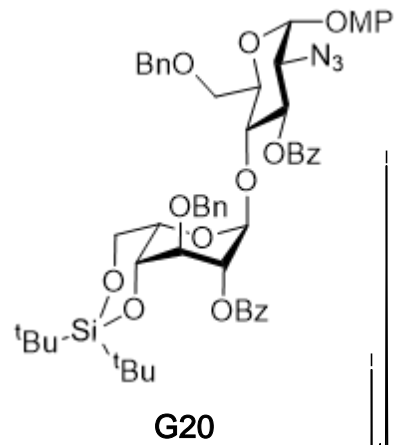
25.6  
21.6  
17.9  
17.8

4.0  
4.9



**G19**





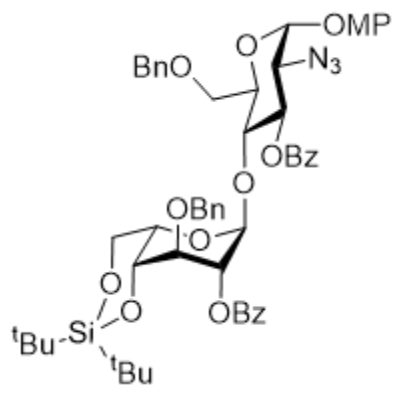
166.0  
165.7

155.6  
150.5  
138.2  
137.7  
133.4  
130.2  
130.0  
129.9  
129.5  
128.6  
128.4  
128.4  
128.3  
127.8  
127.7  
127.7  
127.6  
118.1  
114.8

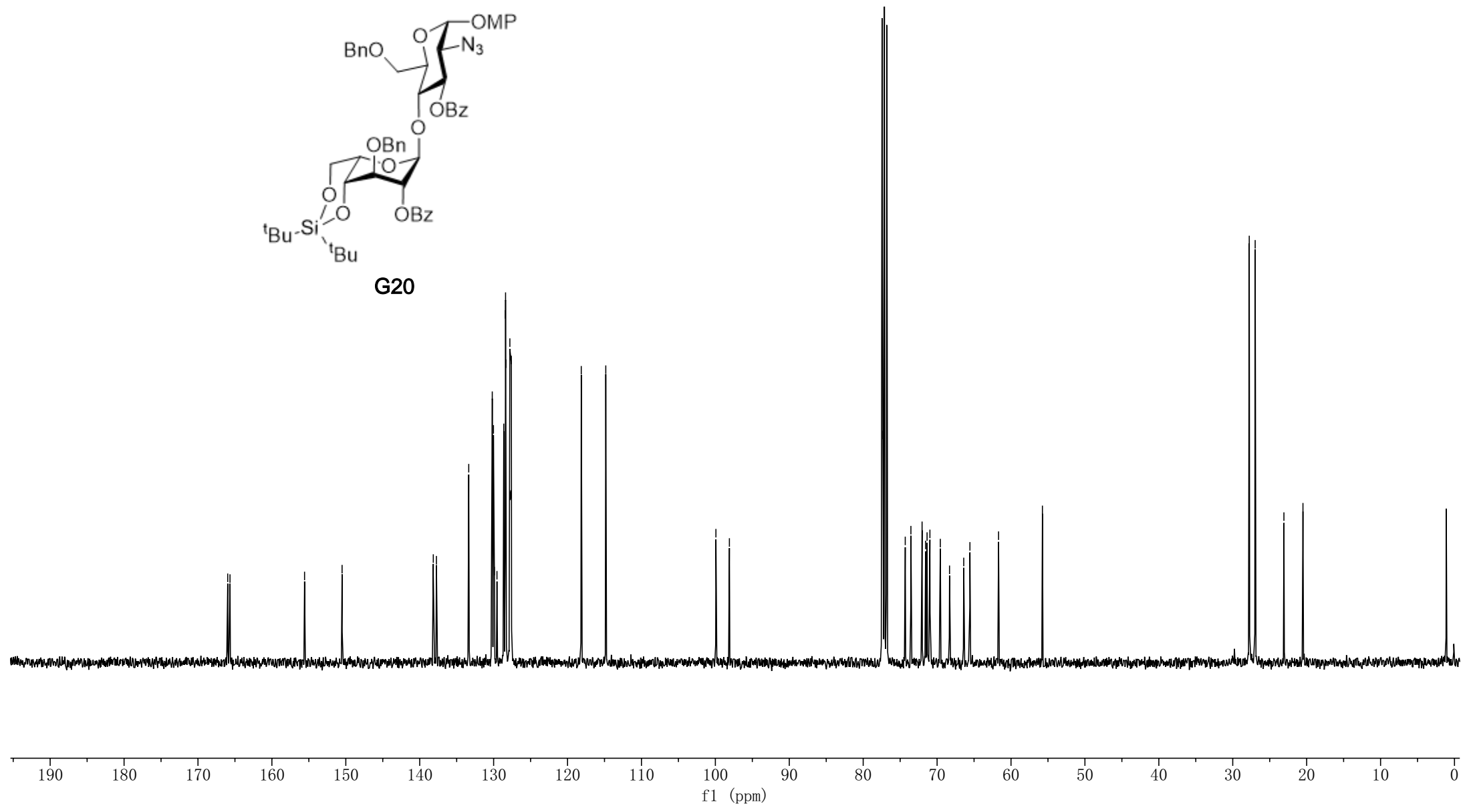
99.9  
98.1

77.3  
74.3  
73.5  
72.0  
71.6  
71.4  
71.0  
69.6  
68.3  
66.4  
65.6  
61.7  
55.8

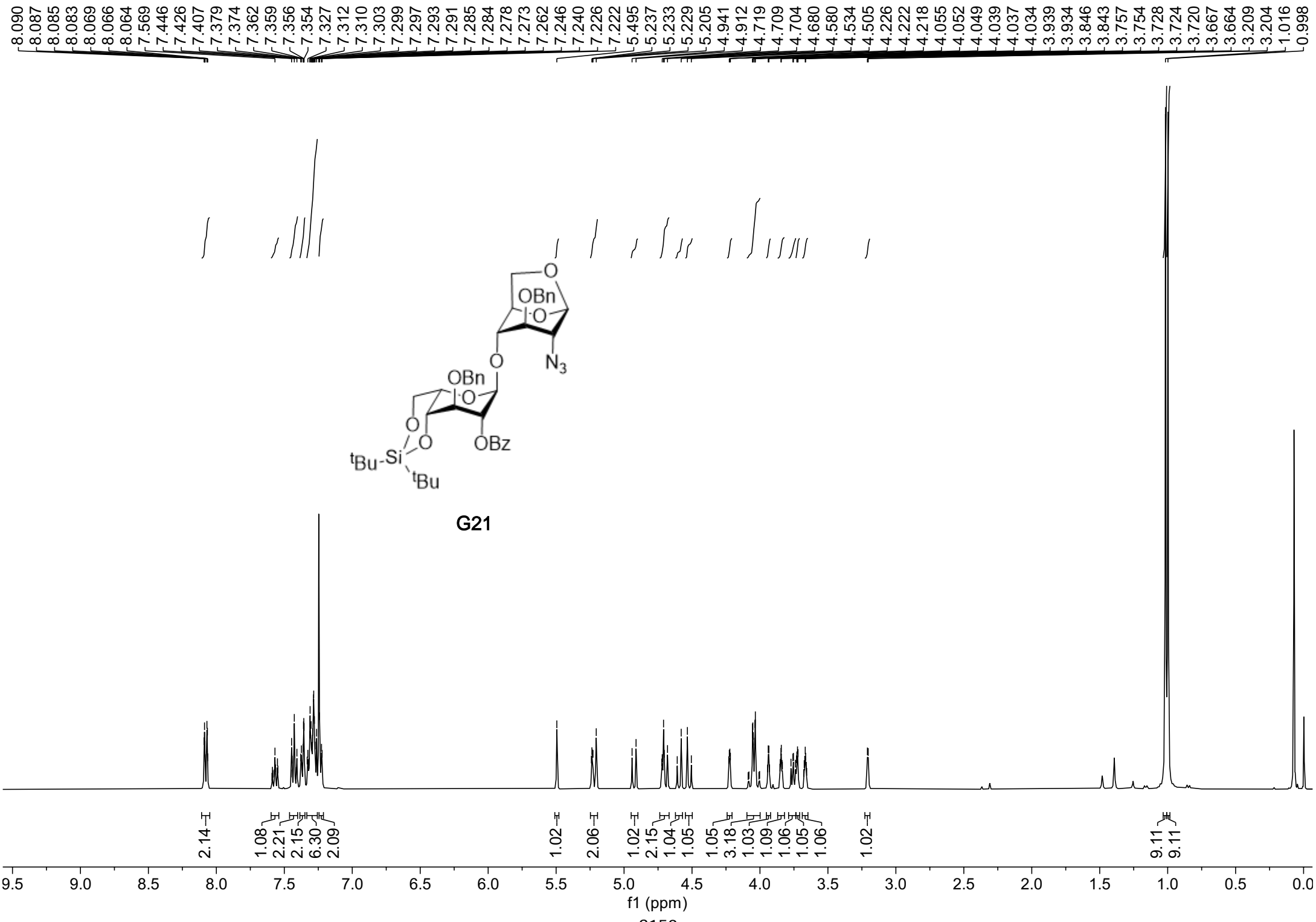
27.8  
27.0  
23.1  
20.5



G20



S158





—166.1

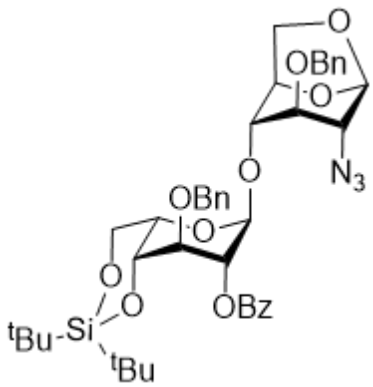
138.1  
137.5  
133.4  
130.2  
129.6  
128.6  
128.4  
128.3  
128.0  
127.9  
127.8  
127.8

—101.2

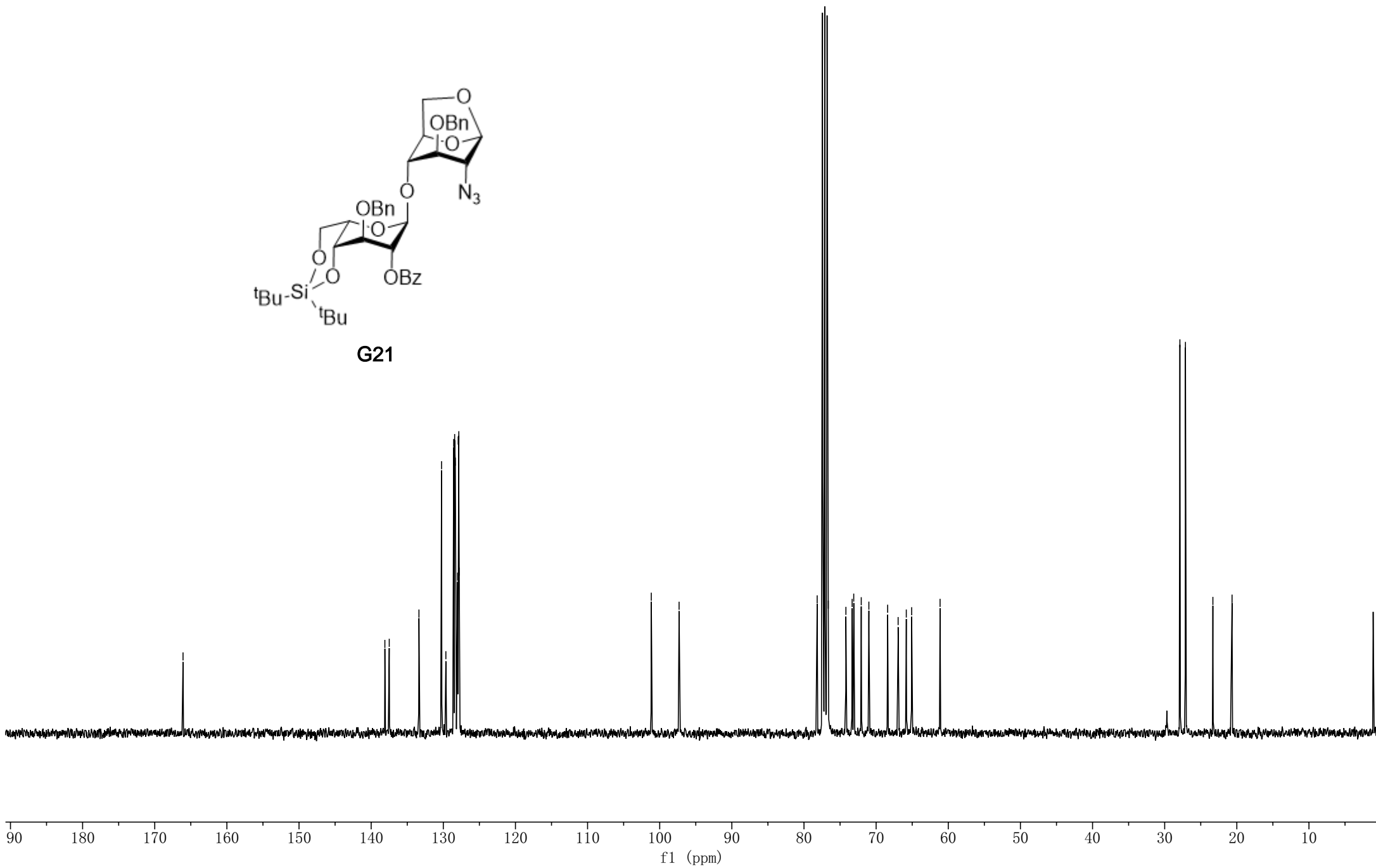
—97.3

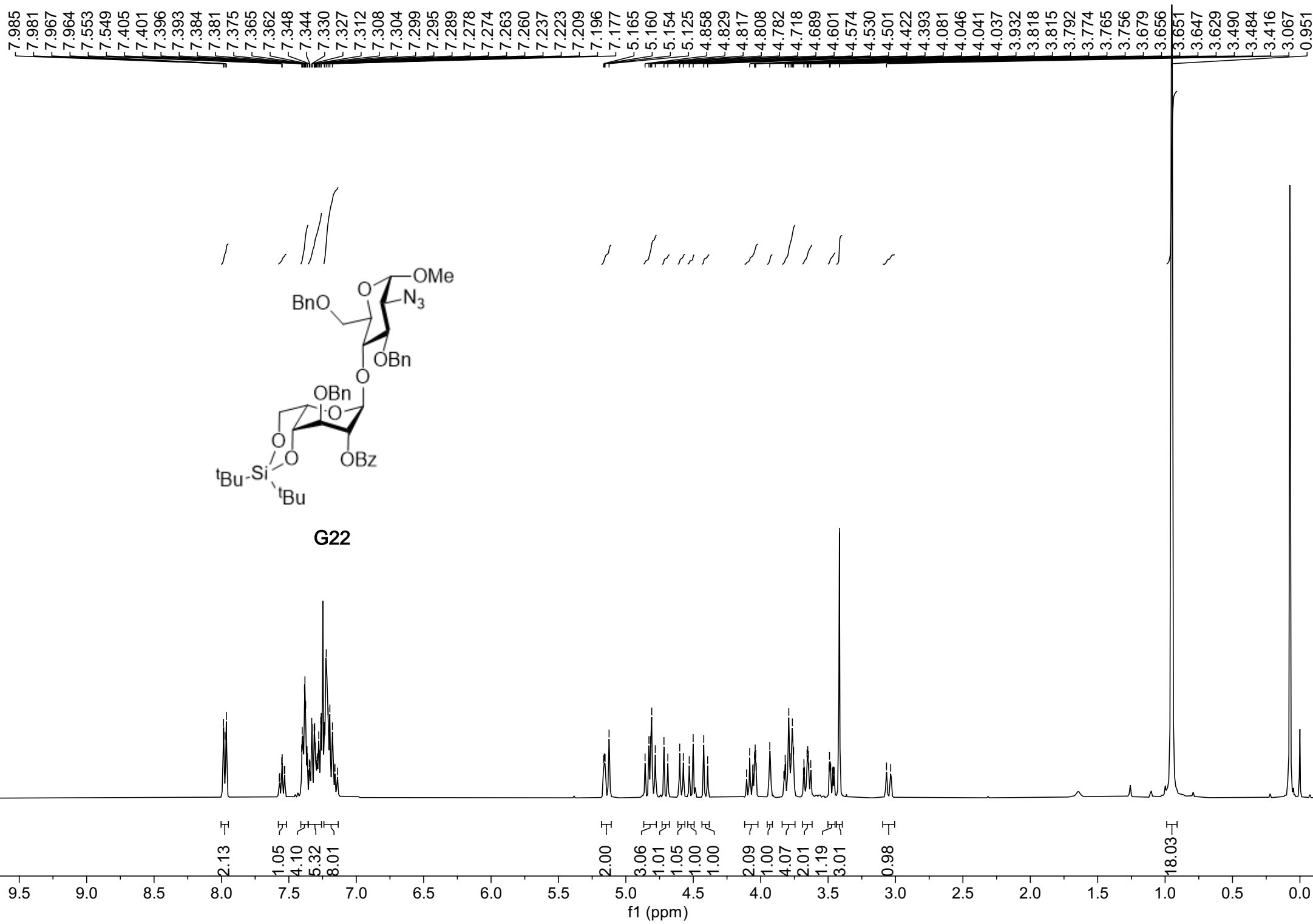
78.2  
76.6  
74.2  
73.3  
73.1  
72.1  
71.0  
68.4  
67.0  
65.8  
65.1  
61.1

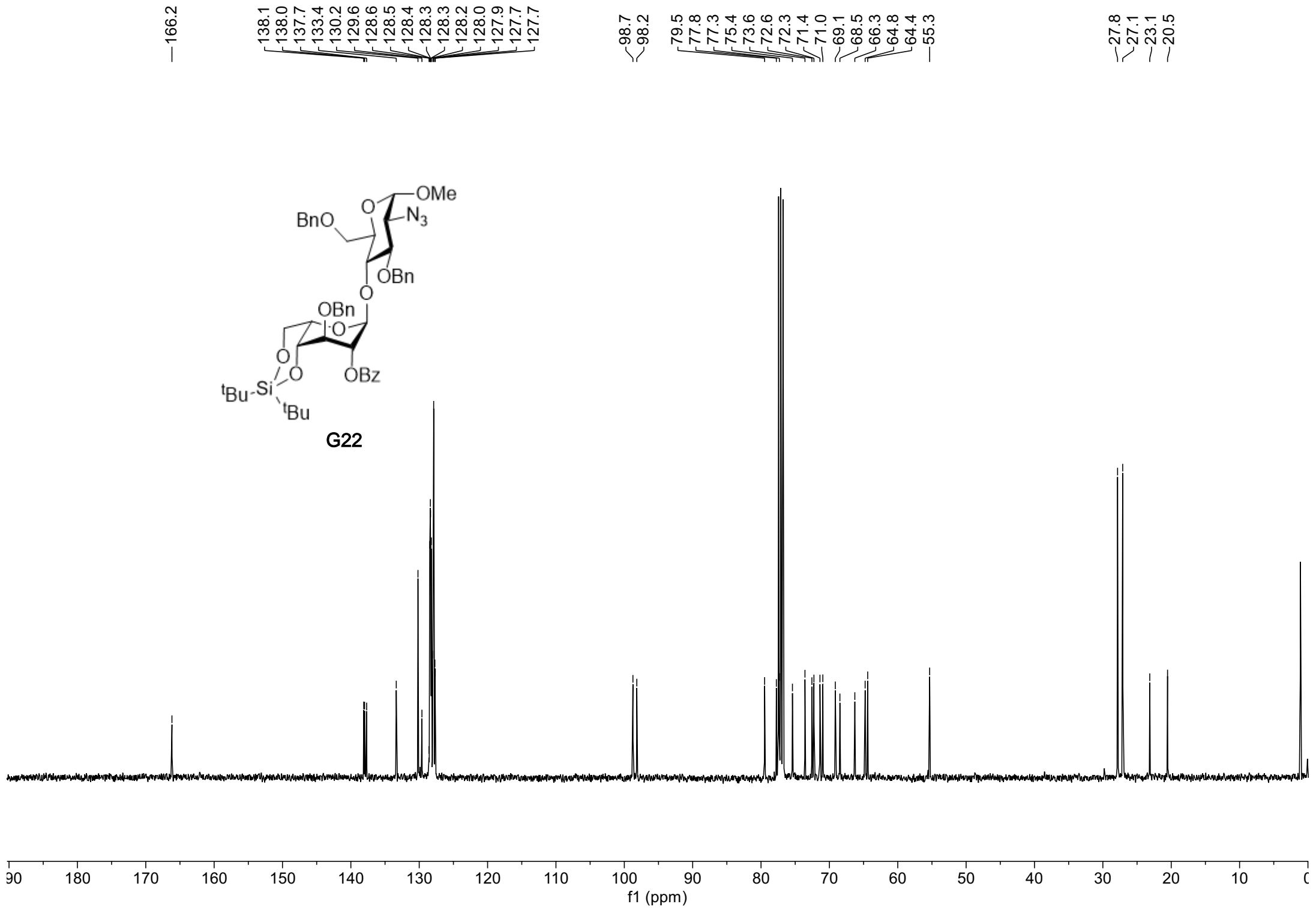
—27.9  
—27.1  
—23.3  
—20.7



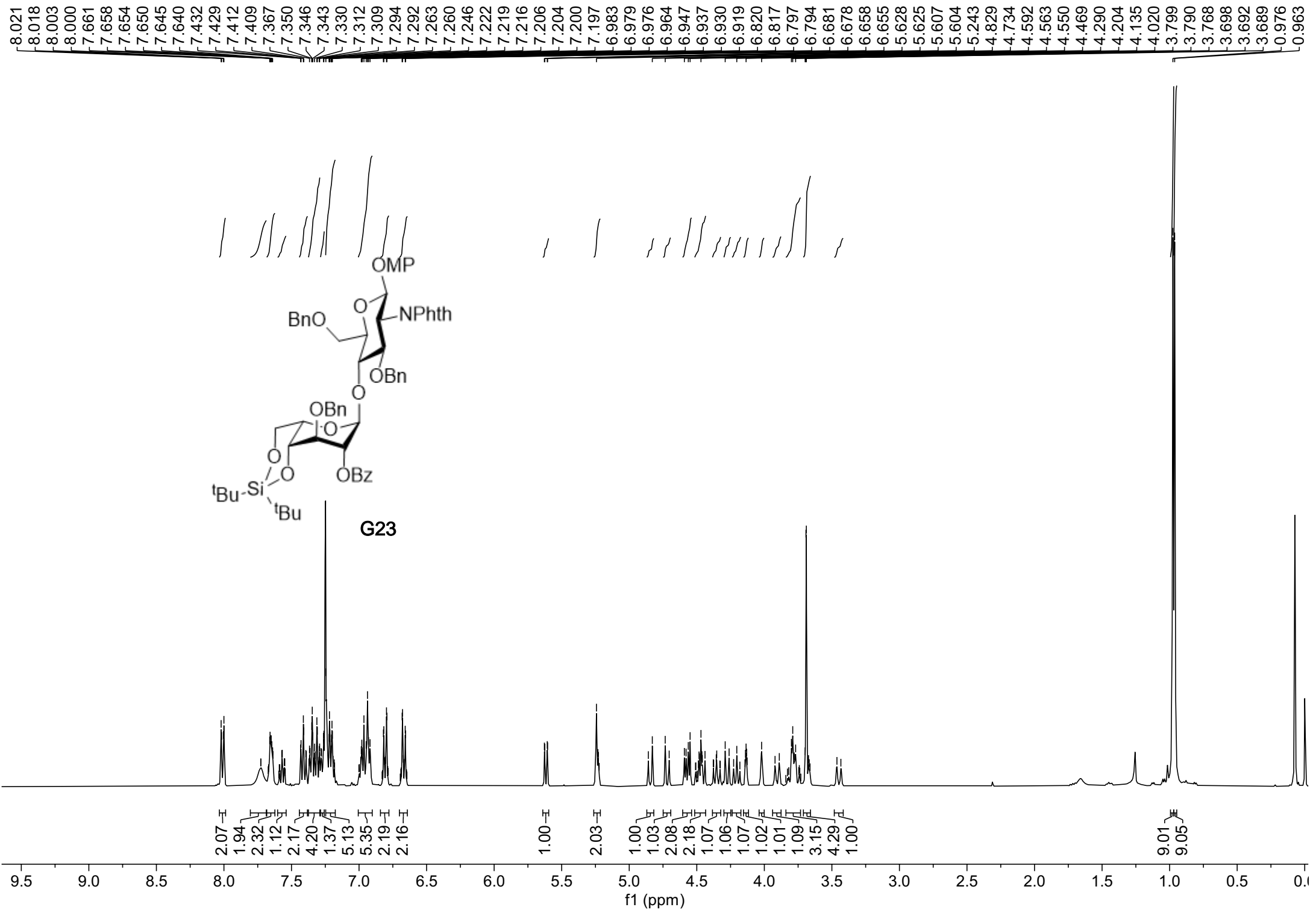
G21

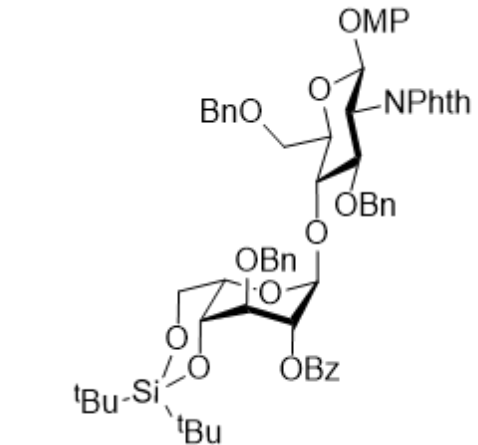






S162





**G23**

166.1  
155.5  
151.1  
138.2  
138.1  
138.1  
134.1  
133.4  
131.7  
130.3  
129.7  
128.5  
128.4  
128.4  
128.2  
128.2  
127.9  
127.7  
127.6  
127.4  
123.5  
118.9  
114.5

98.6  
97.9

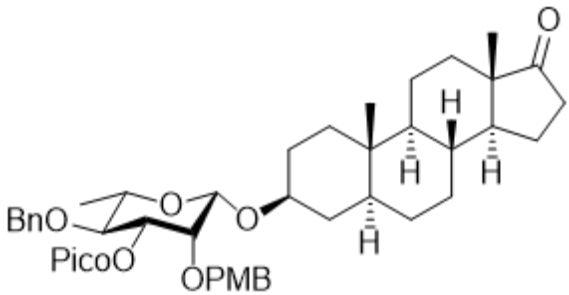
78.7  
78.1  
75.7  
75.3  
74.4  
73.5  
72.3  
72.1  
69.5  
68.6  
66.4  
65.4  
56.3  
55.7

27.9  
27.2  
23.2  
20.7

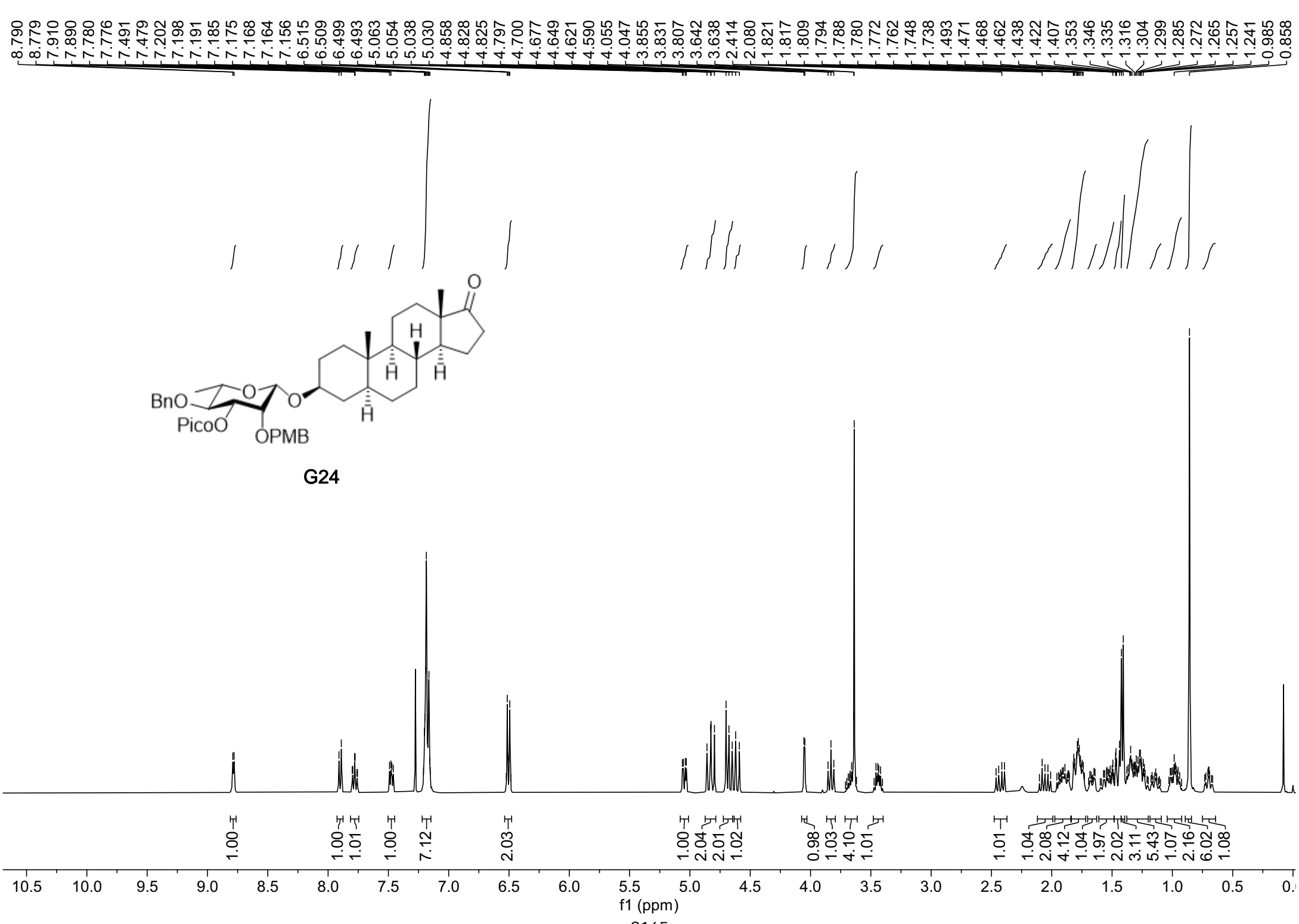
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

S164



G24



—221.4

—164.2

—159.1

~150.1

~147.9

138.3

136.9

130.7

130.3

128.4

128.1

127.8

127.0

125.4

—113.4

—99.0

78.7

78.1

77.5

75.3

74.3

71.8

55.1

54.7

51.6

48.0

45.1

37.0

36.1

36.0

36.0

35.2

31.8

28.6

28.1

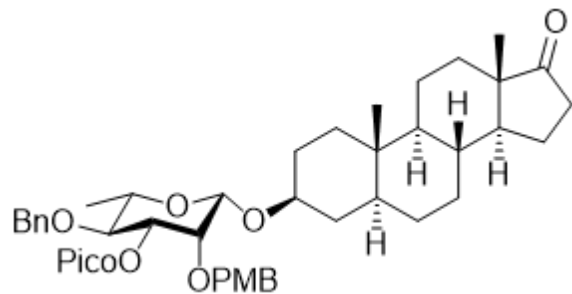
21.9

20.7

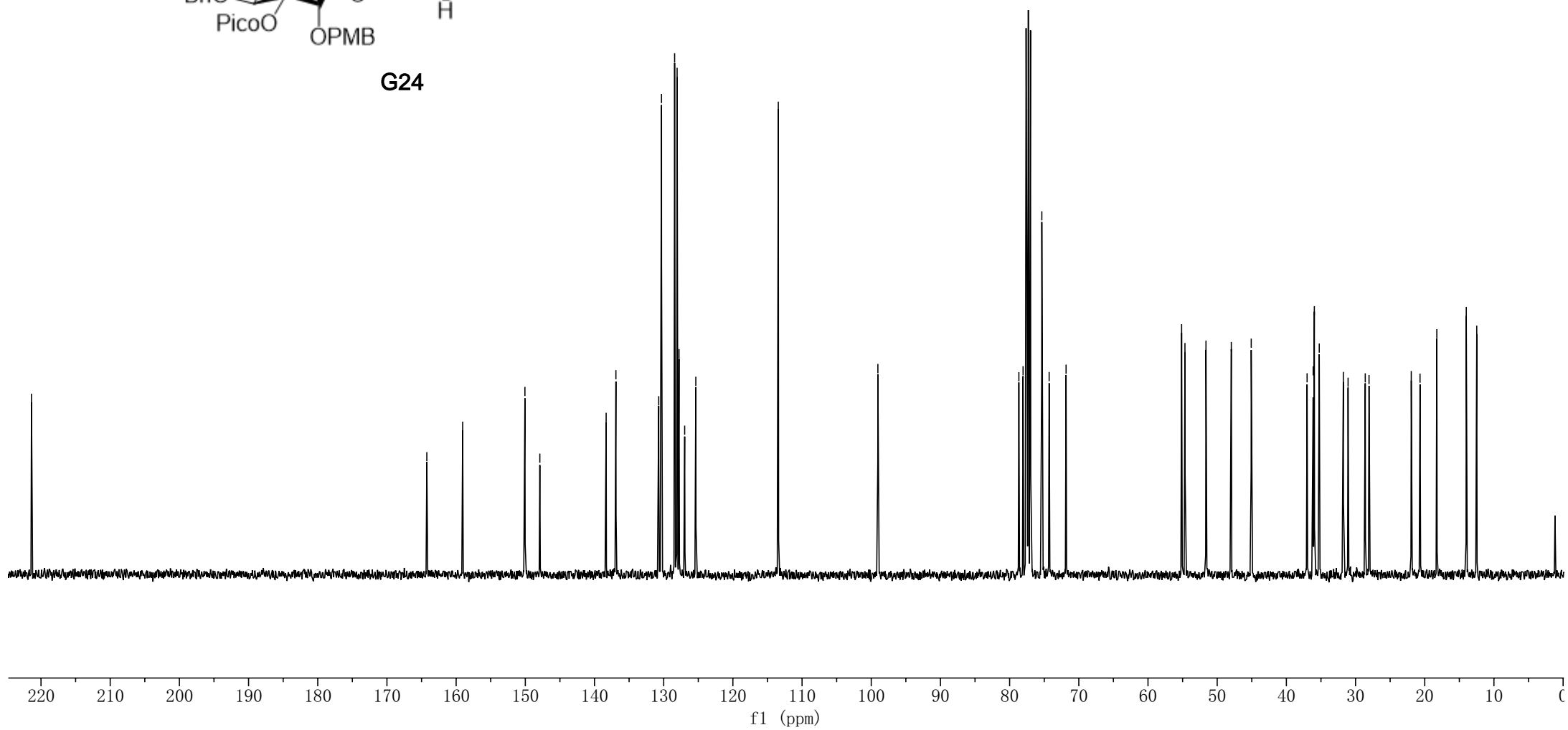
18.3

14.0

12.5

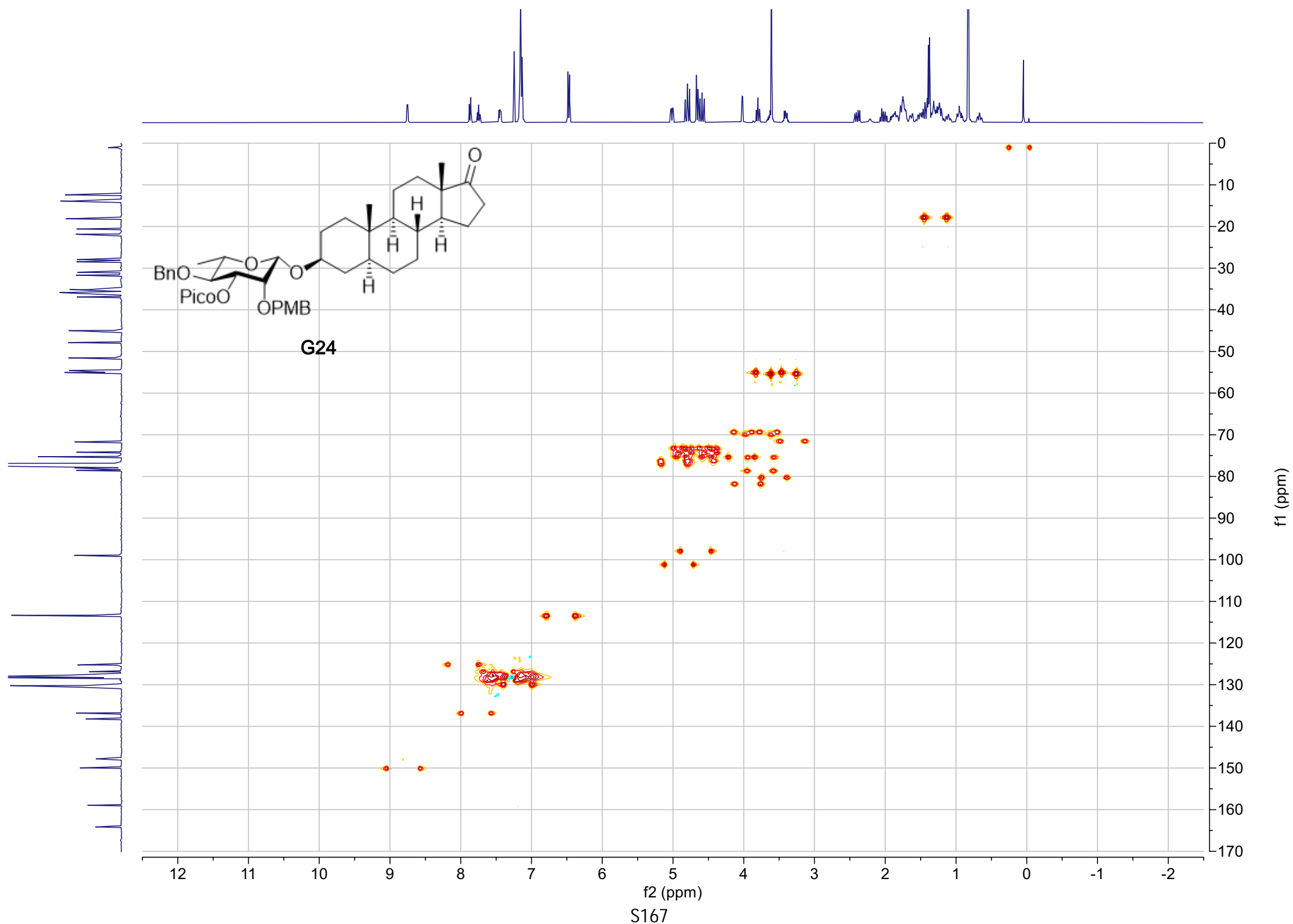


G24

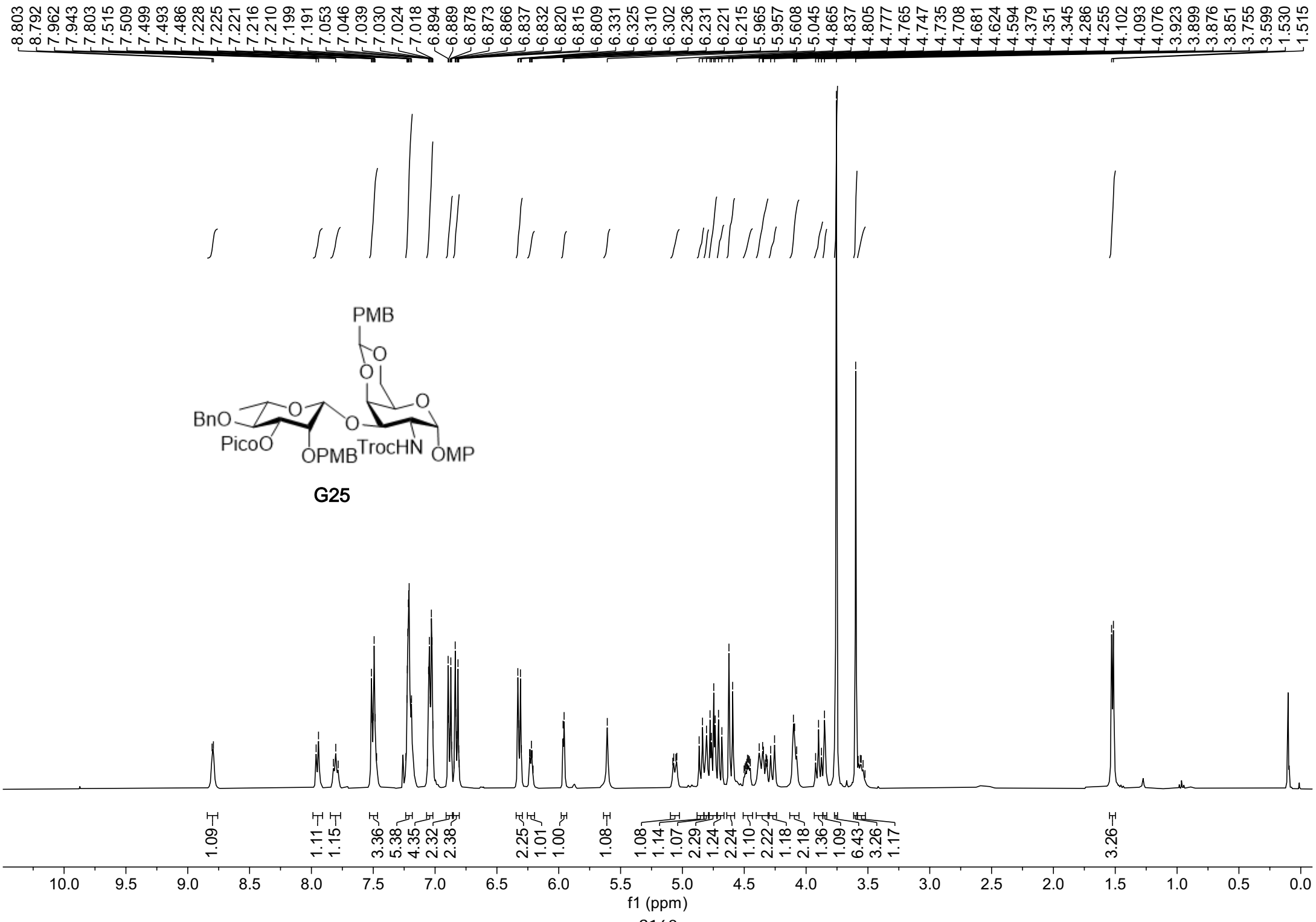


f1 (ppm)

S166





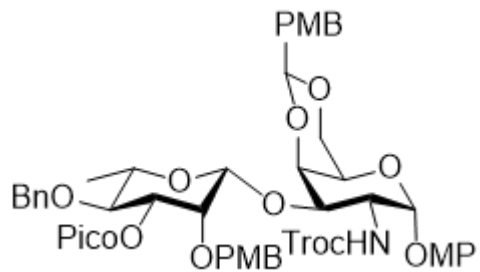


164.1  
160.3  
159.0  
155.3  
154.8  
150.9  
150.1  
147.7

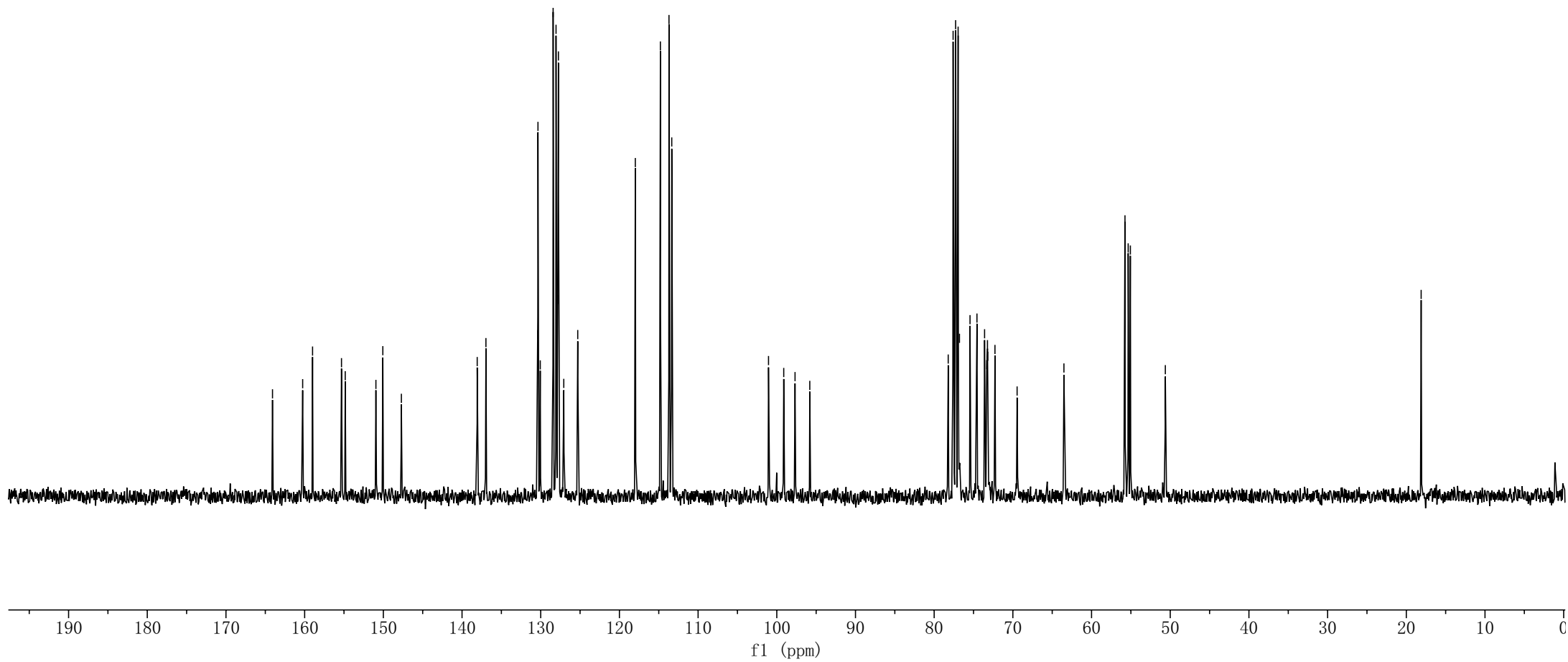
138.1  
137.0  
130.4  
130.3  
130.1  
128.4  
128.1  
127.9  
127.8  
127.1  
125.3  
118.0  
114.8  
113.7  
113.3  
101.1  
99.1  
97.7  
95.8

78.2  
77.6  
77.3  
77.0  
76.8  
75.4  
74.6  
73.6  
73.3  
73.2  
73.2  
72.3  
69.5  
63.5  
55.8  
55.3  
55.1  
50.6

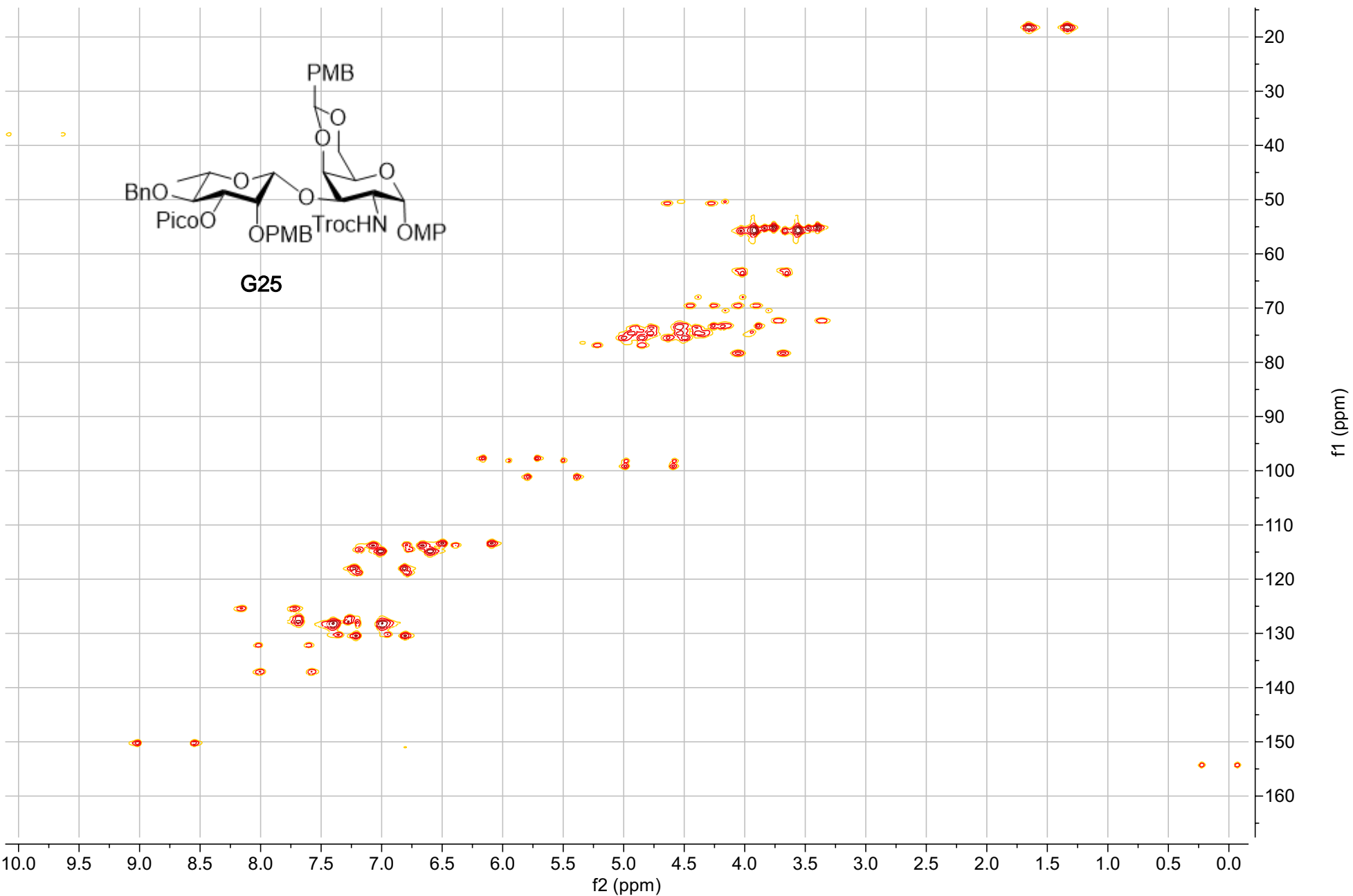
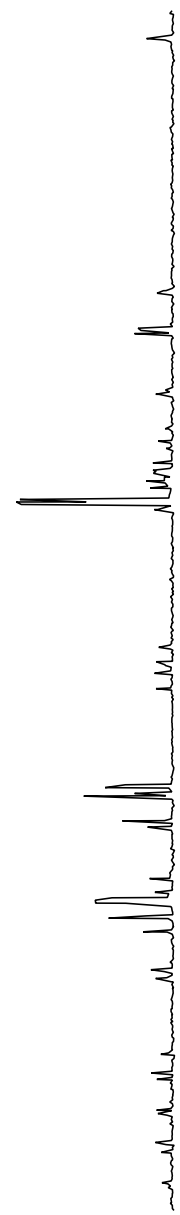
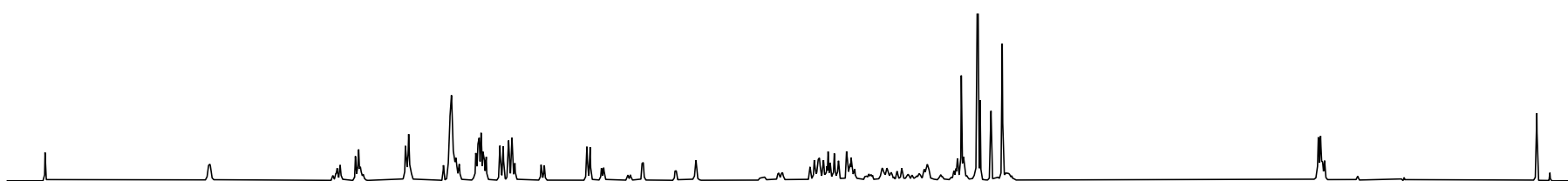
—18.1



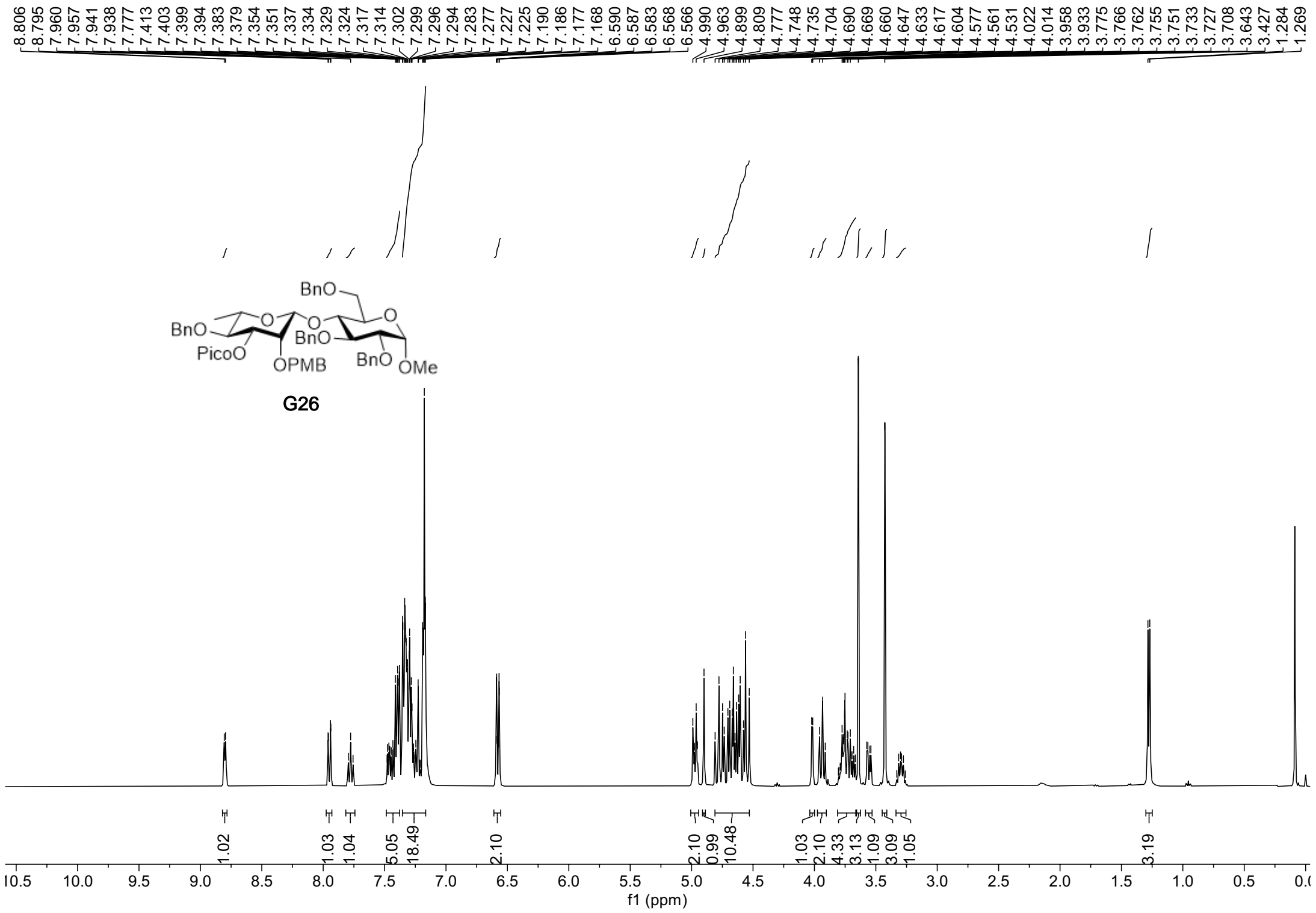
G25



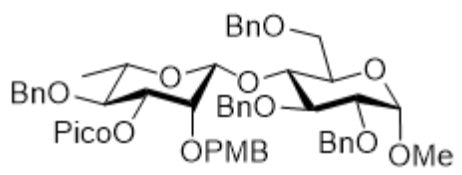
S169



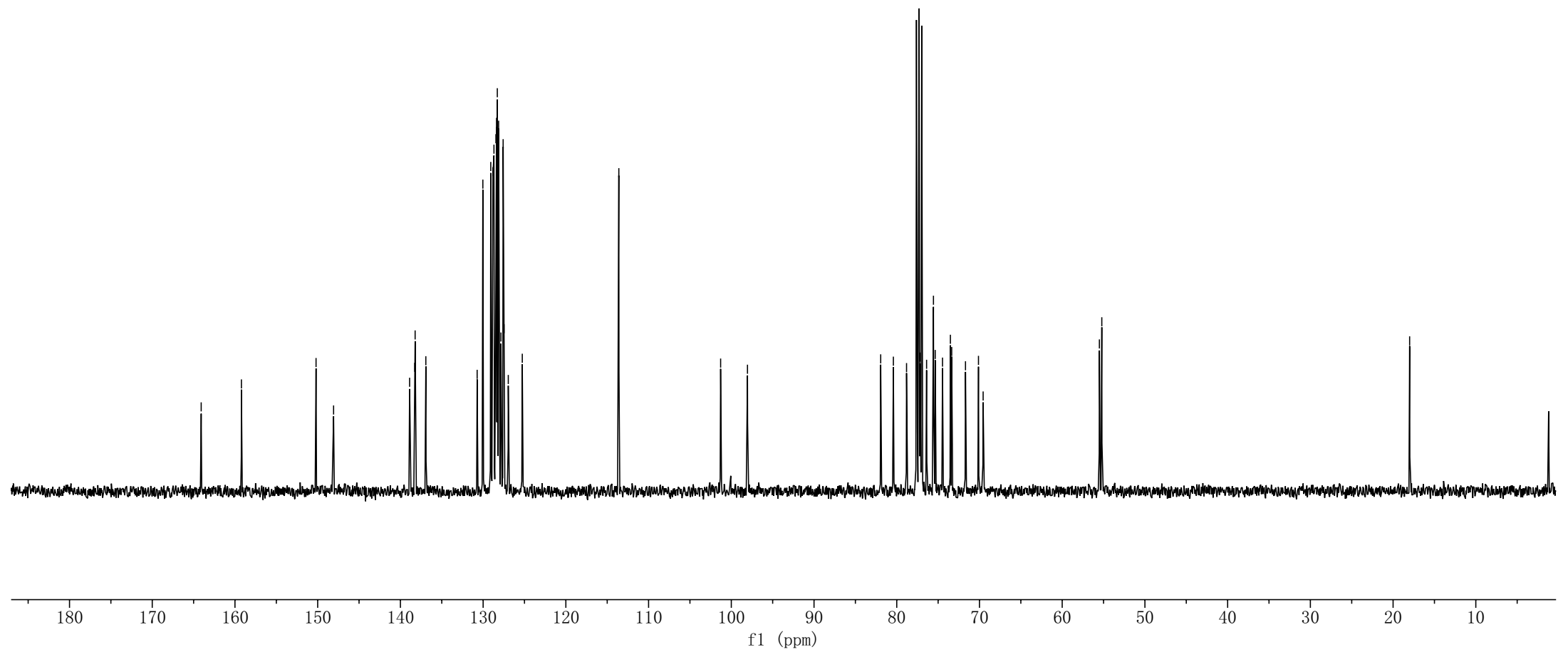
S170

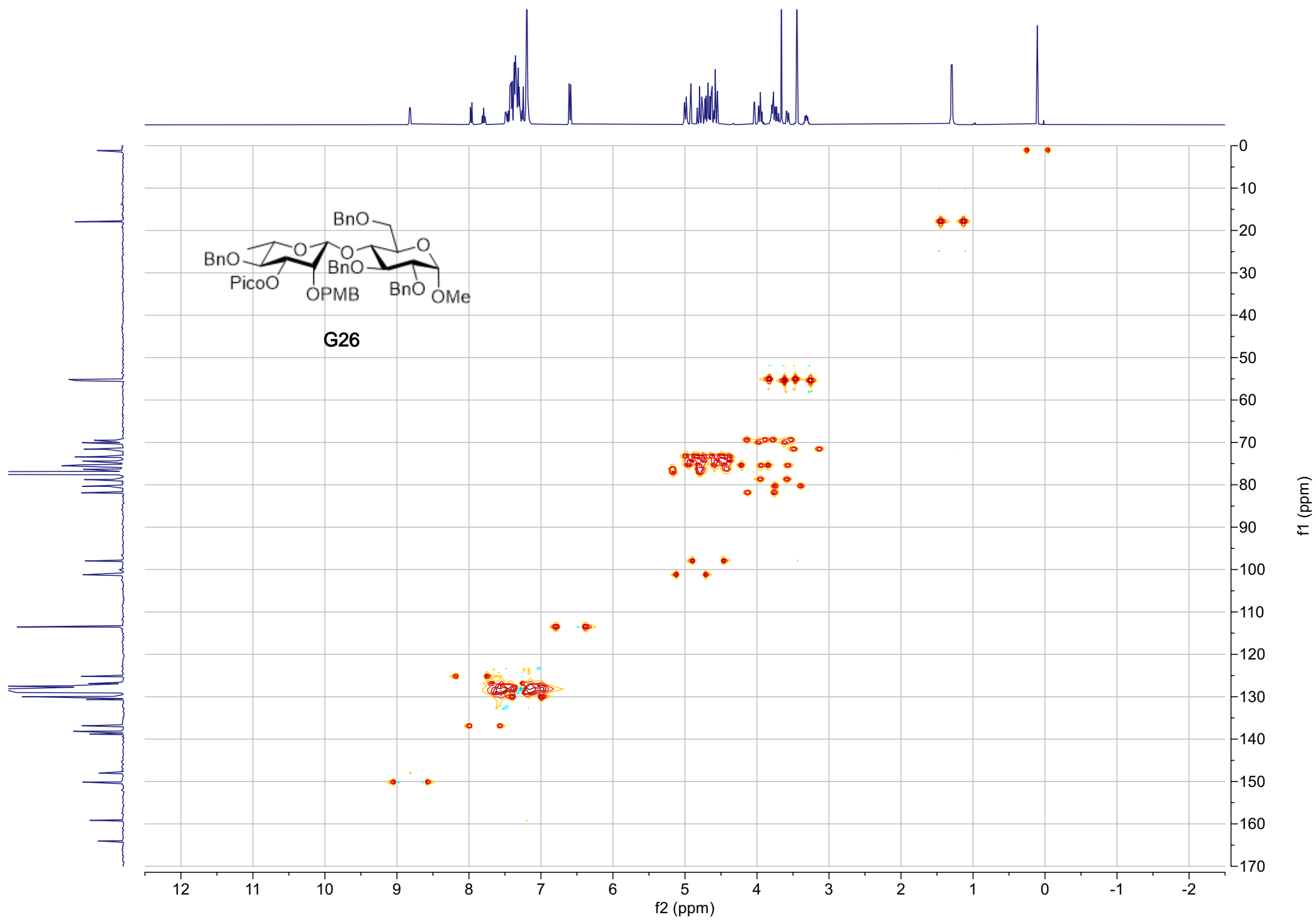


— 164.1  
 — 159.2  
 — 150.2  
 — 148.1  
 — 138.9  
 — 138.3  
 — 138.2  
 — 136.9  
 — 130.7  
 — 130.0  
 — 129.1  
 — 128.8  
 — 128.7  
 — 128.5  
 — 128.4  
 — 128.3  
 — 128.3  
 — 128.2  
 — 128.1  
 — 127.8  
 — 127.6  
 — 127.5  
 — 127.0  
 — 125.3  
 — 113.6  
 — 101.3  
 — 98.0  
 — 81.9  
 — 80.4  
 — 78.8  
 — 77.5  
 — 77.2  
 — 76.4  
 — 75.6  
 — 75.4  
 — 74.5  
 — 73.5  
 — 73.4  
 — 71.7  
 — 70.1  
 — 69.6  
 — 55.5  
 — 55.2  
 — 18.0

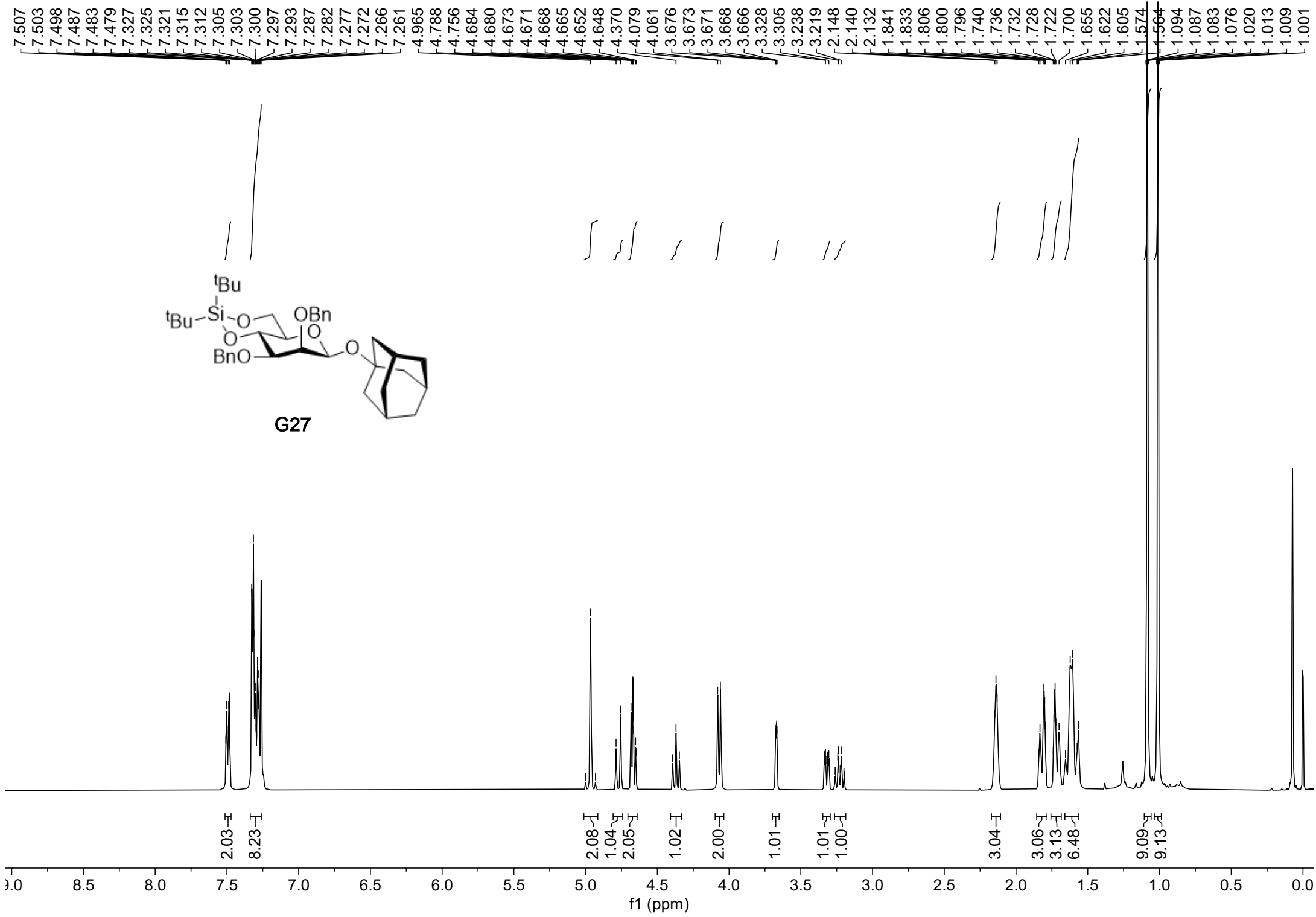


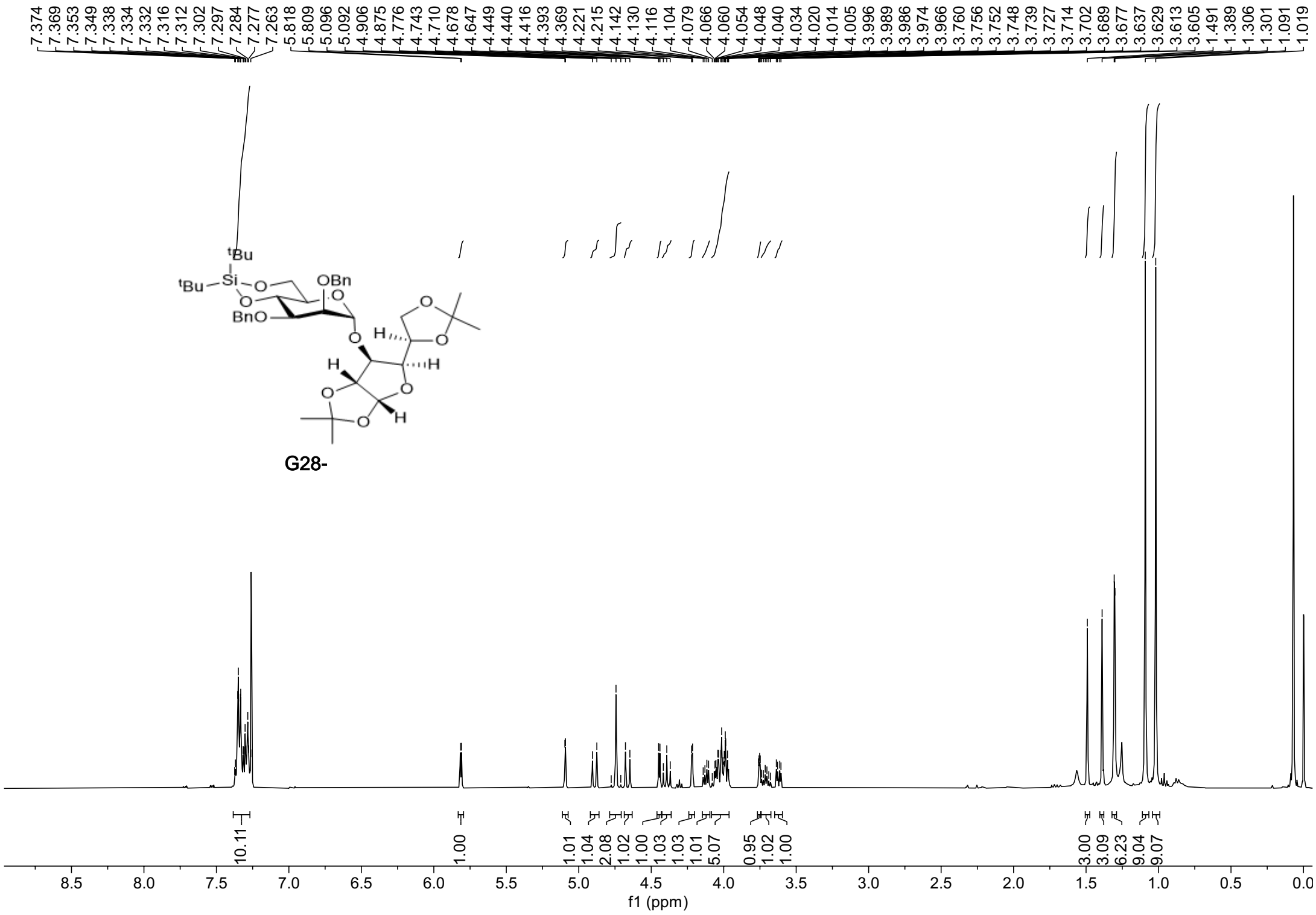
**G26**



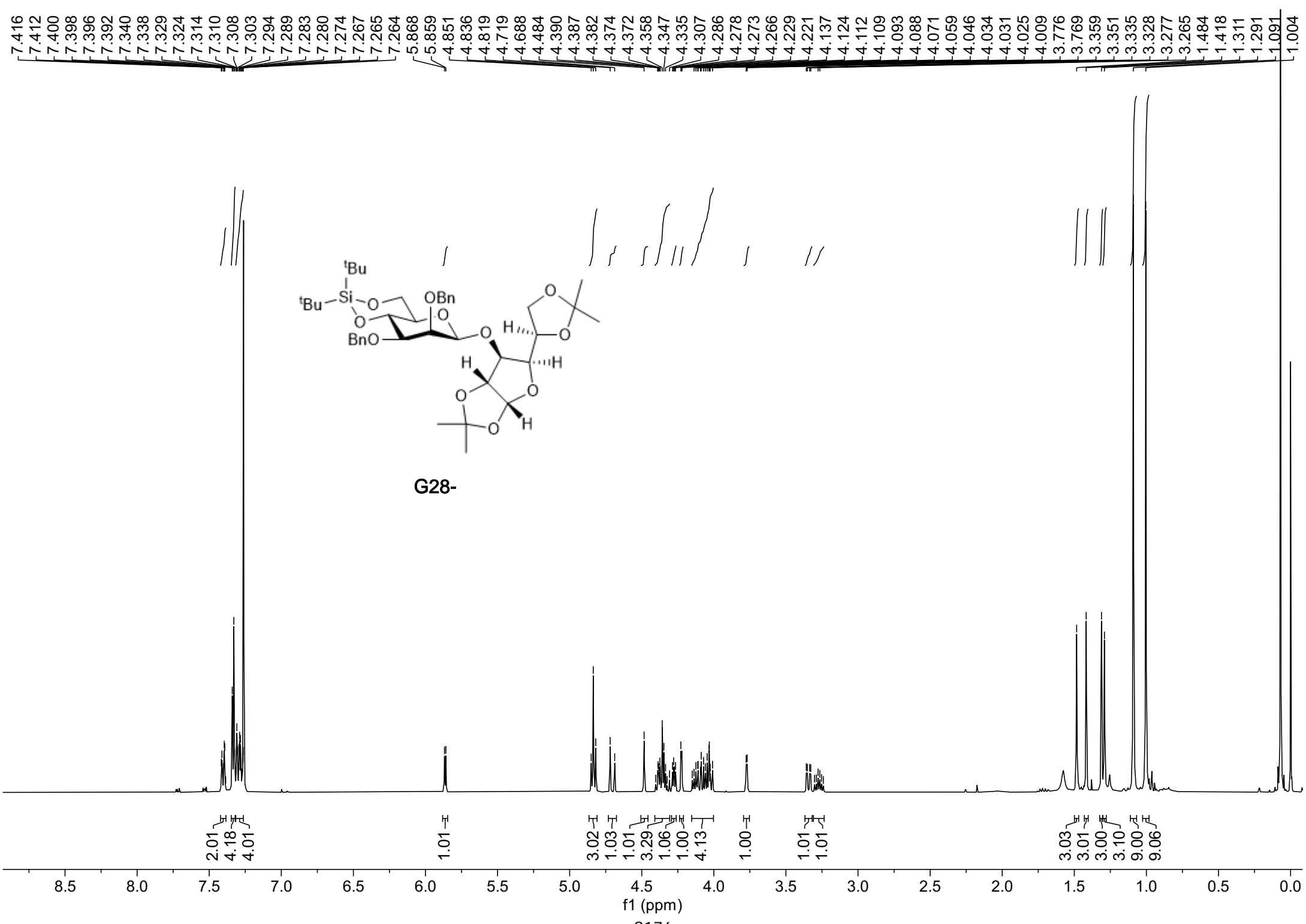


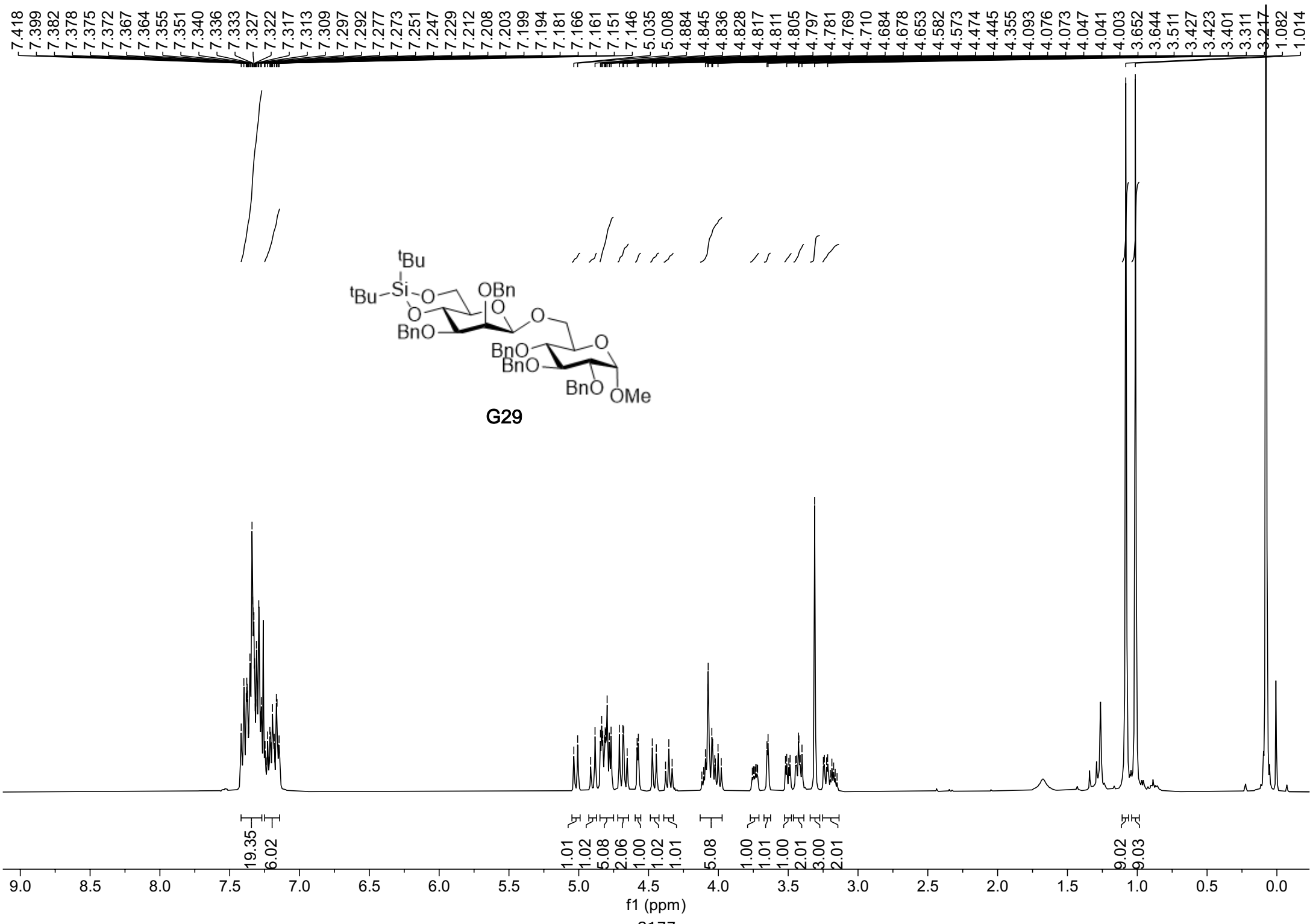
S173

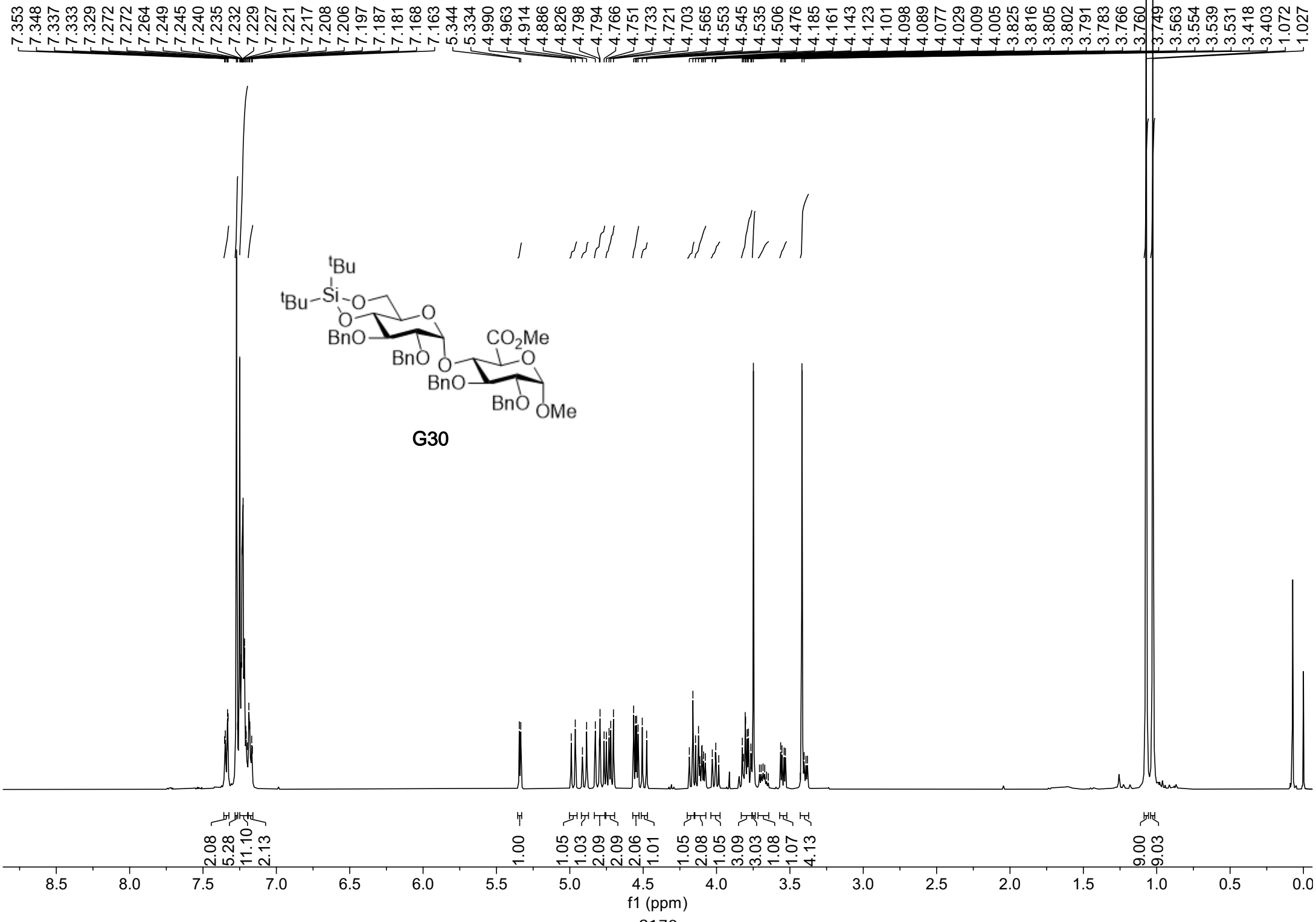












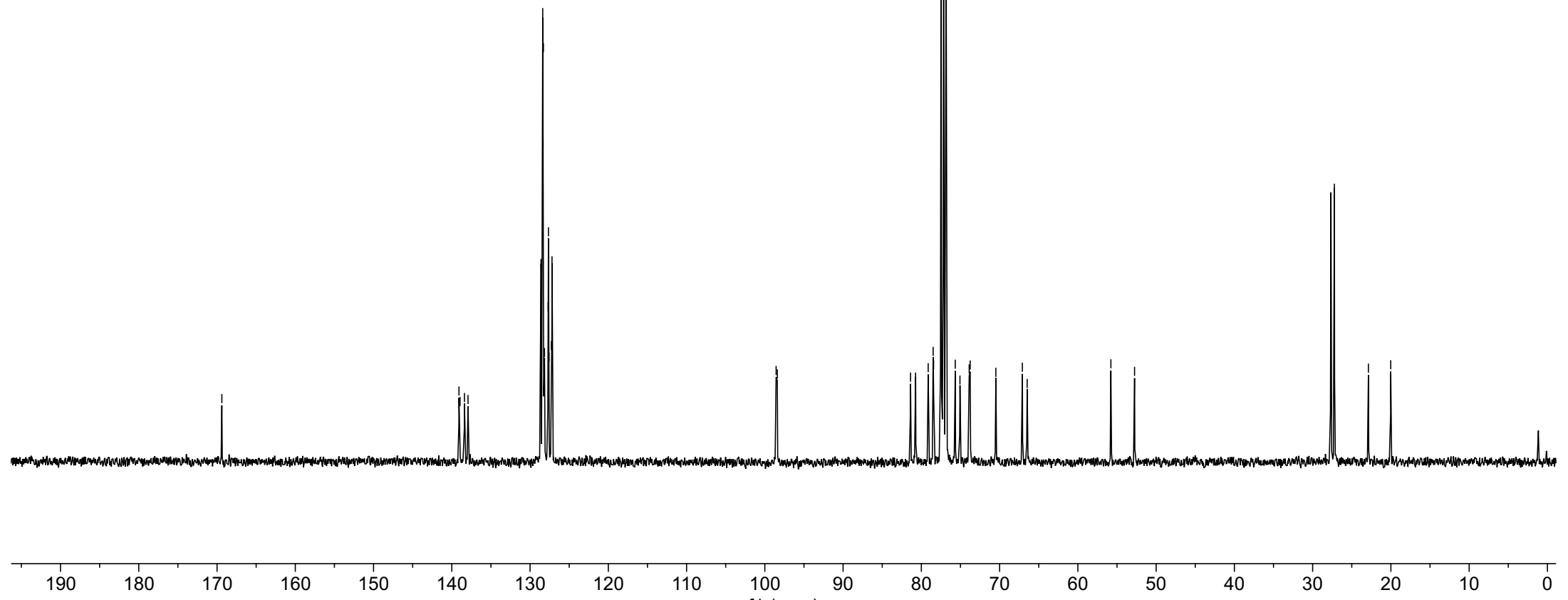
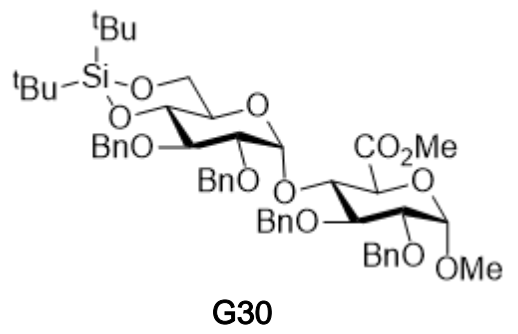
—169.4

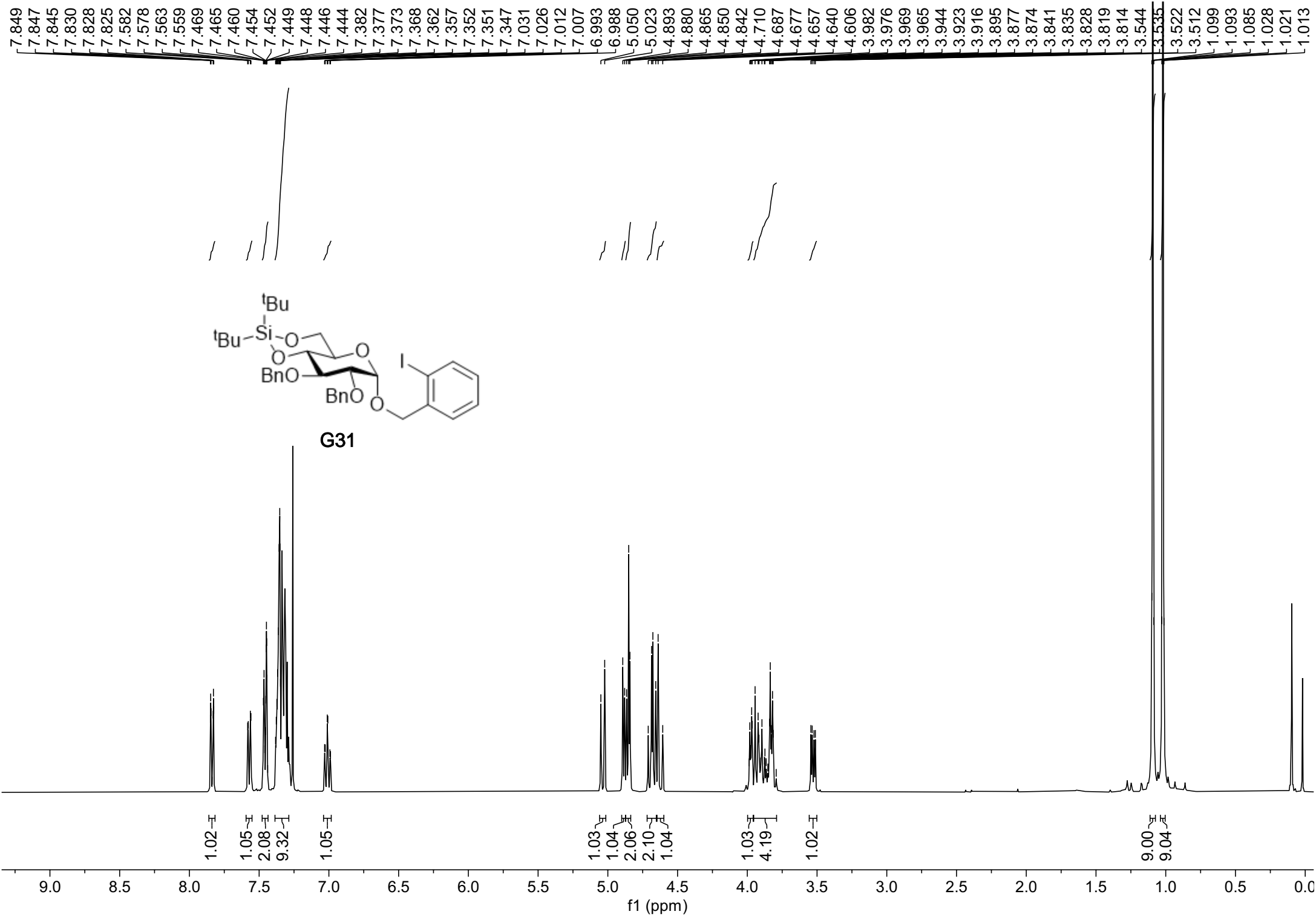
139.1  
139.0  
138.4  
137.9  
128.6  
128.4  
128.3  
128.3  
128.2  
127.7  
127.7  
127.6  
127.3  
127.2

98.6  
98.4

81.4  
80.7  
79.1  
78.5  
78.4  
77.4  
75.7  
75.1  
73.9  
73.8  
70.5  
67.1  
66.5  
55.8  
52.8

27.7  
27.2  
22.9  
20.0





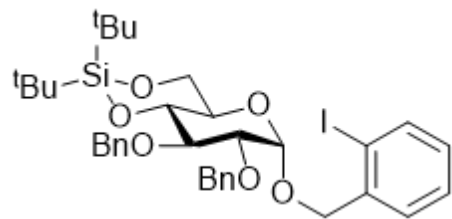
140.0  
139.3  
139.2  
138.5  
129.5  
129.4  
128.5  
128.4  
128.2  
128.1  
127.9  
127.7

98.0  
97.8

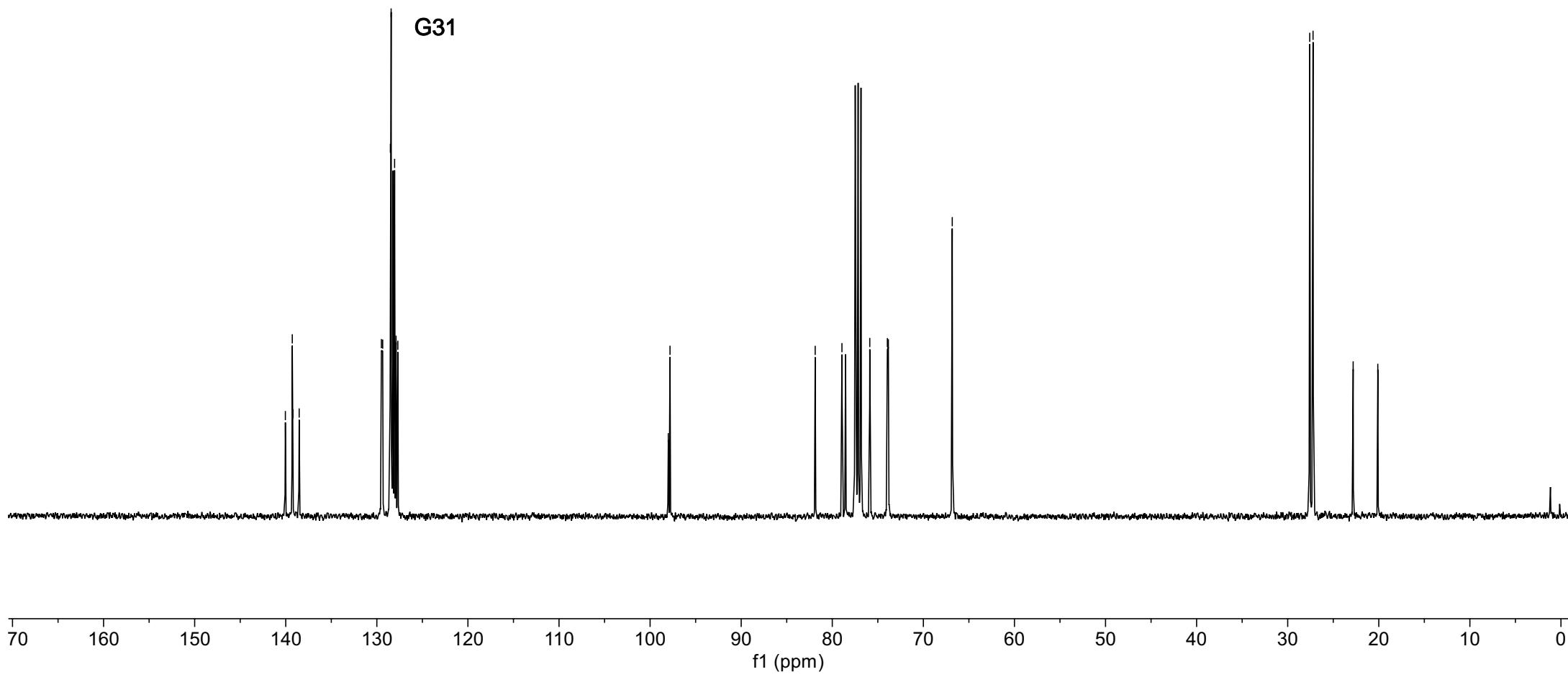
81.9  
78.9  
78.5  
75.9  
74.0  
73.8

66.8

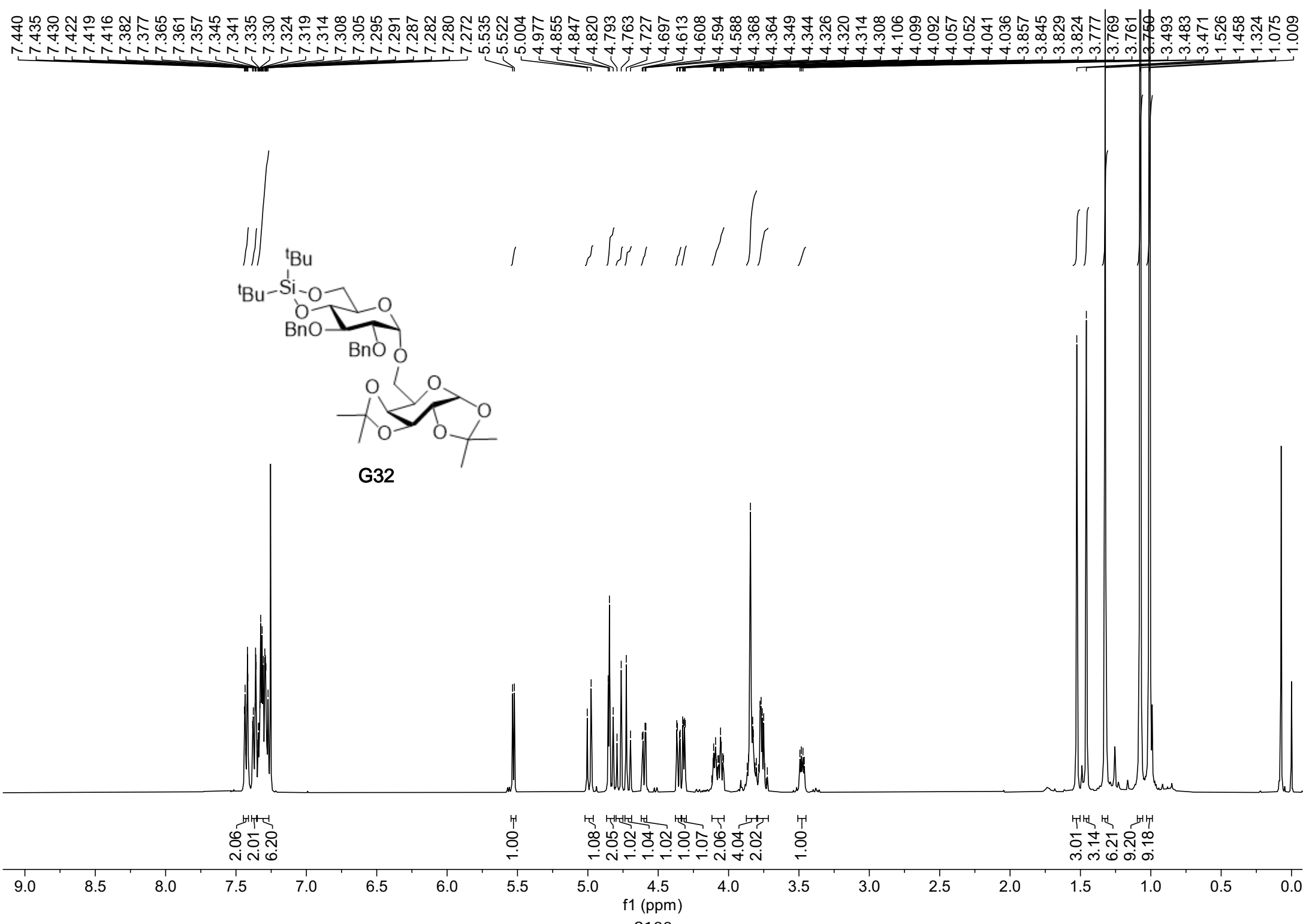
27.6  
27.2  
22.8  
20.1

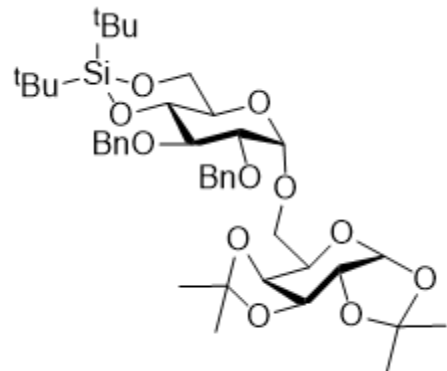


G31



S181





G32

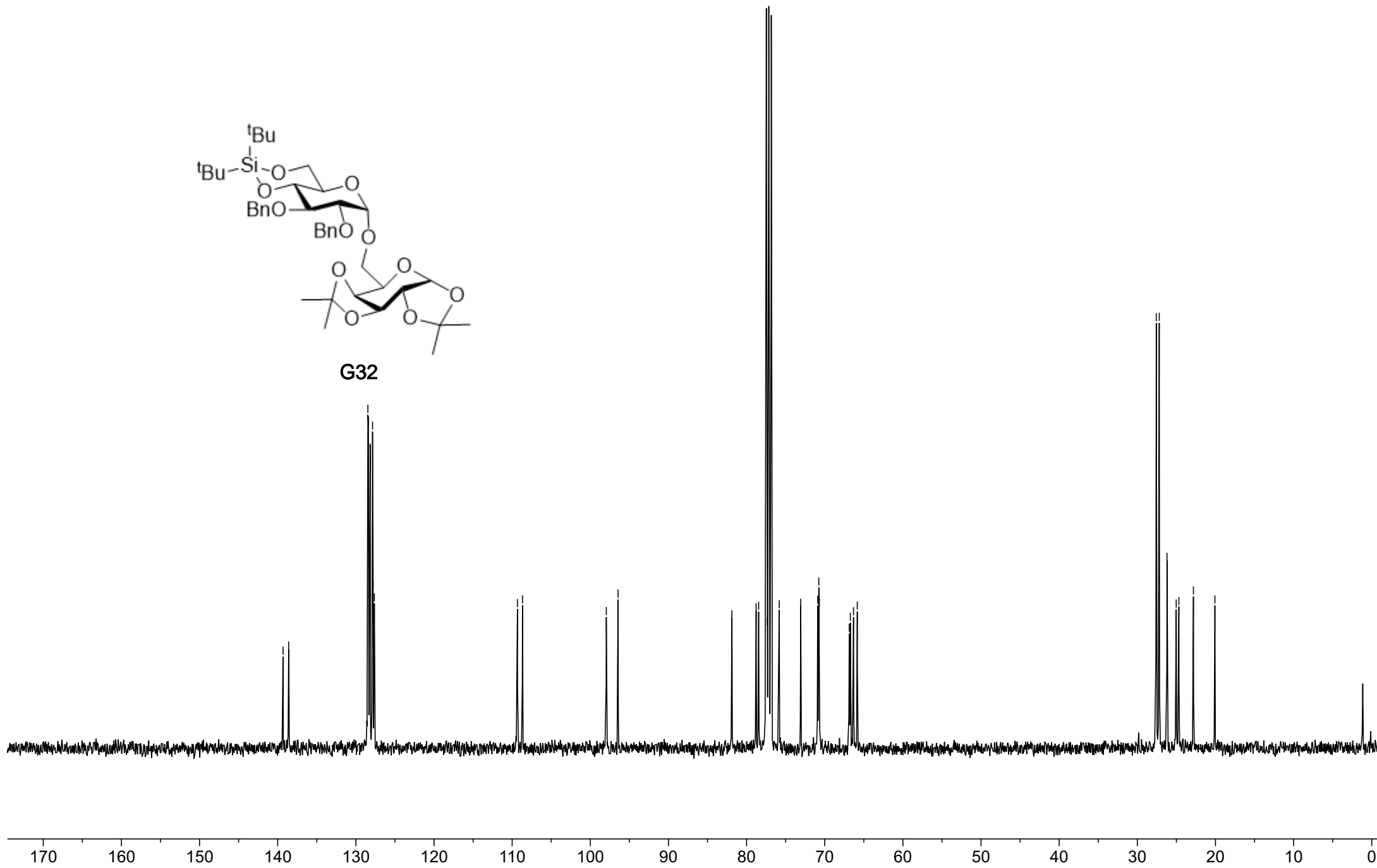
139.3  
138.6  
128.5  
128.4  
128.2  
127.9  
127.8  
127.6

109.3  
108.7

98.0  
96.4

81.9  
78.8  
78.5  
77.4  
75.8  
73.1  
70.9  
70.8  
70.7  
66.9  
66.7  
66.3  
65.8

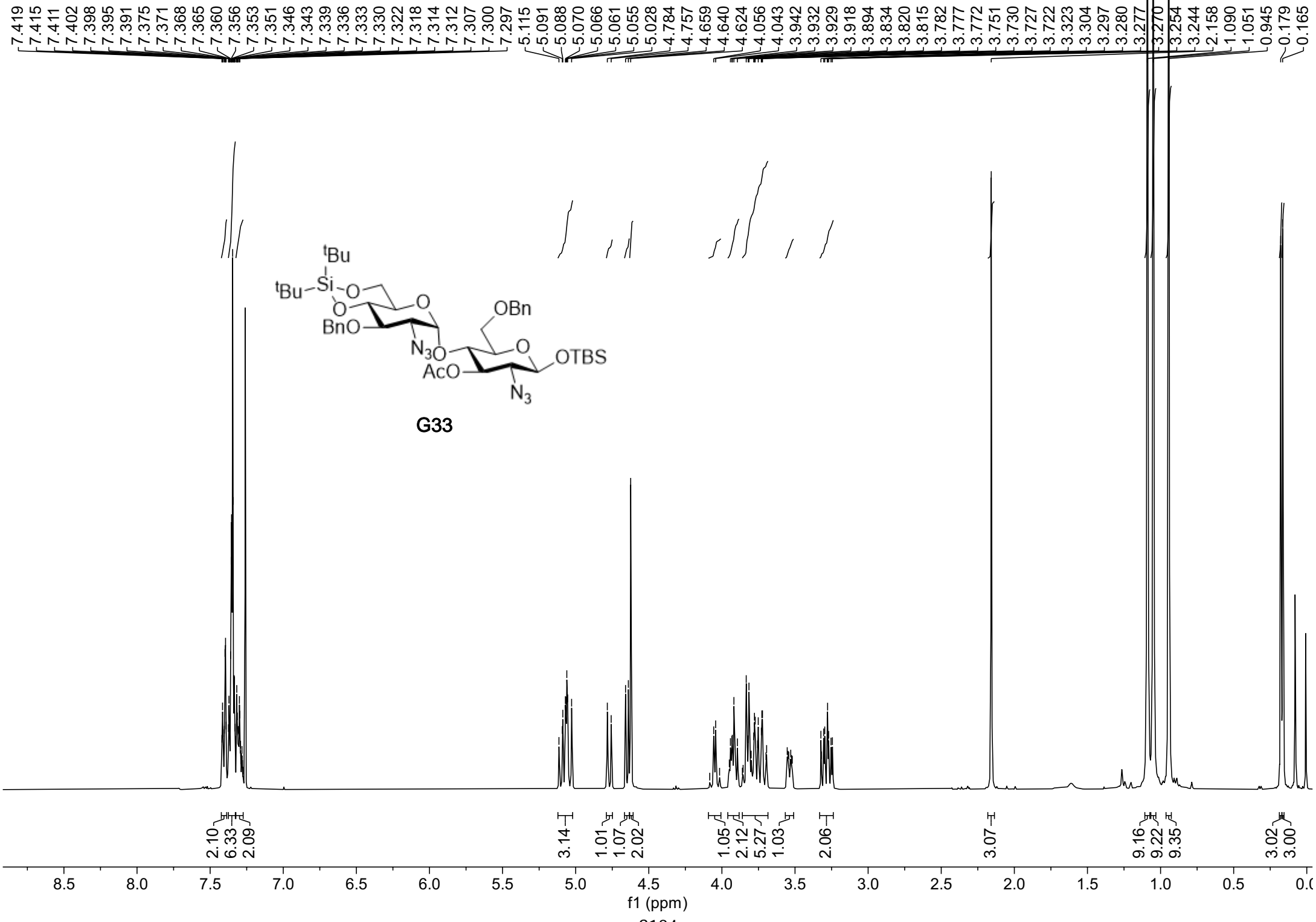
27.6  
27.2  
26.2  
26.2  
25.0  
24.7  
22.8  
20.1



f1 (ppm)

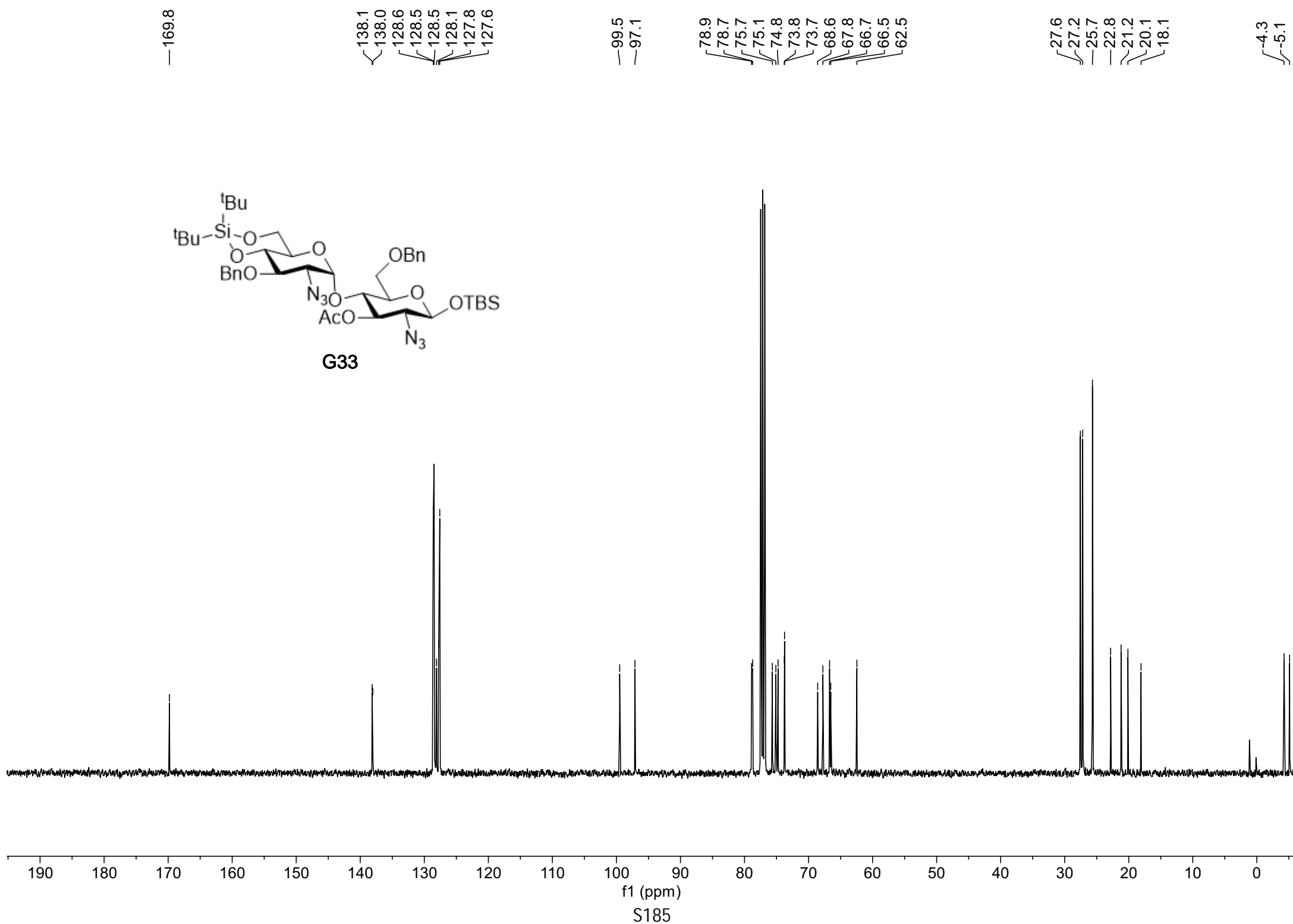
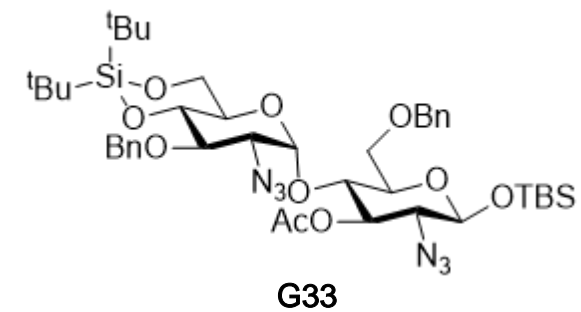
S183

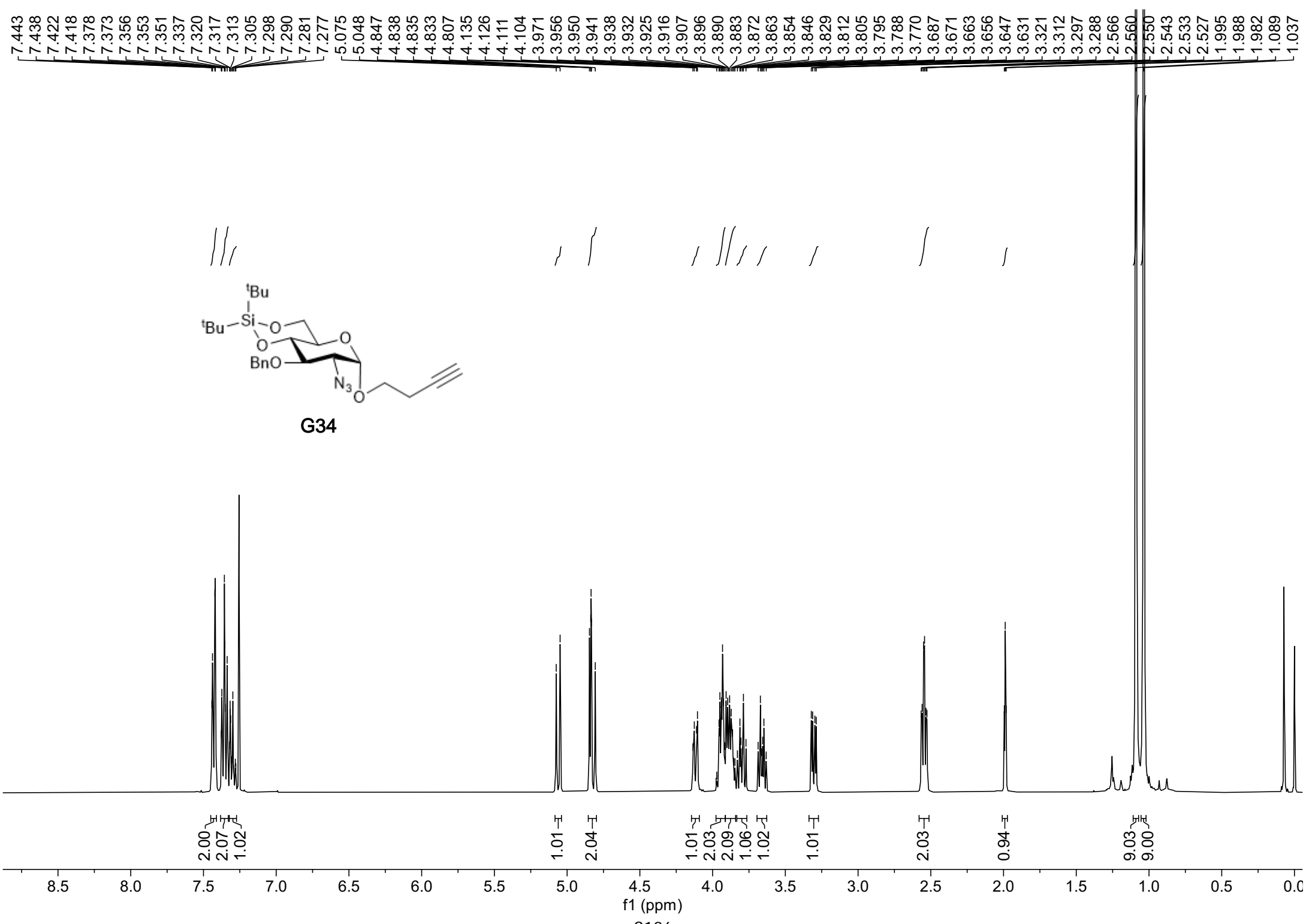


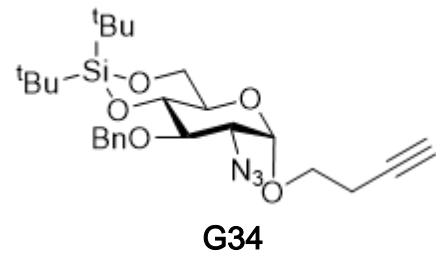


f1 (ppm)

S184







—138.2

128.6

128.5

128.0

—98.3

80.9

79.2

79.1

75.6

69.8

66.9

66.8

66.7

62.4

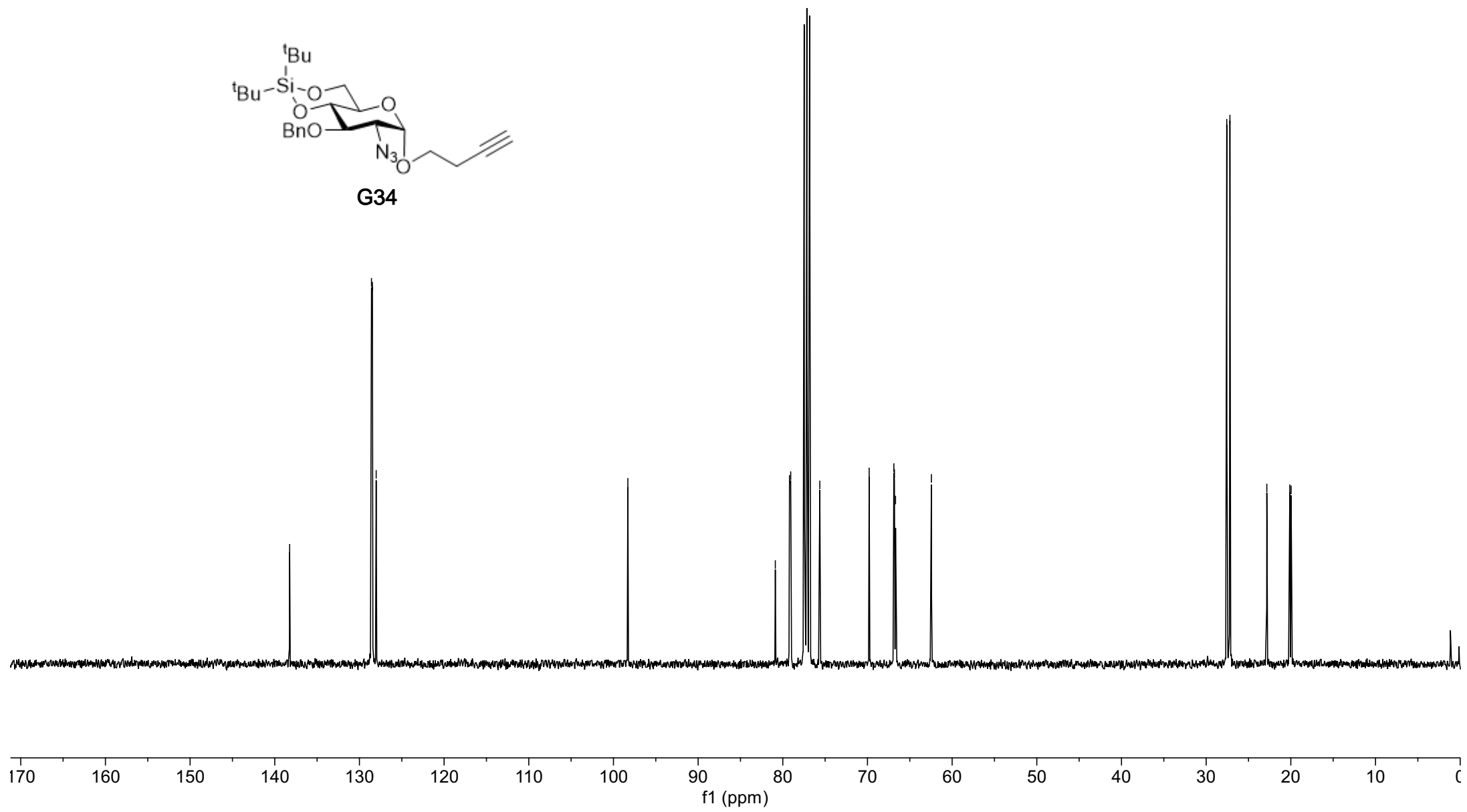
27.6

27.2

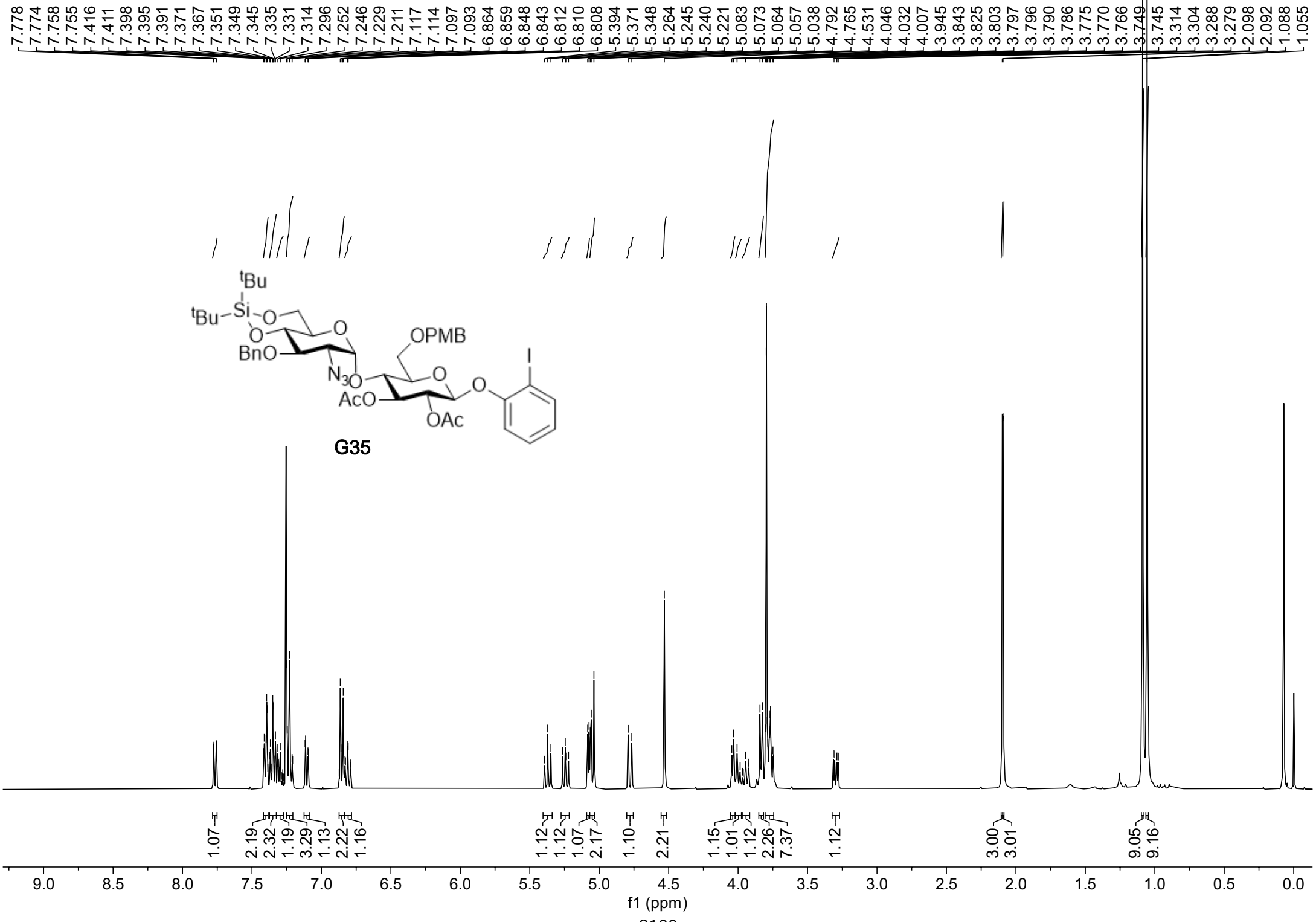
22.8

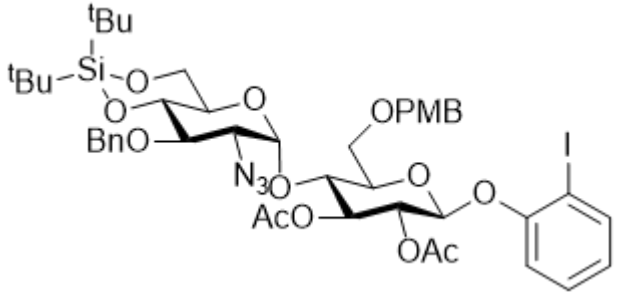
20.1

20.0

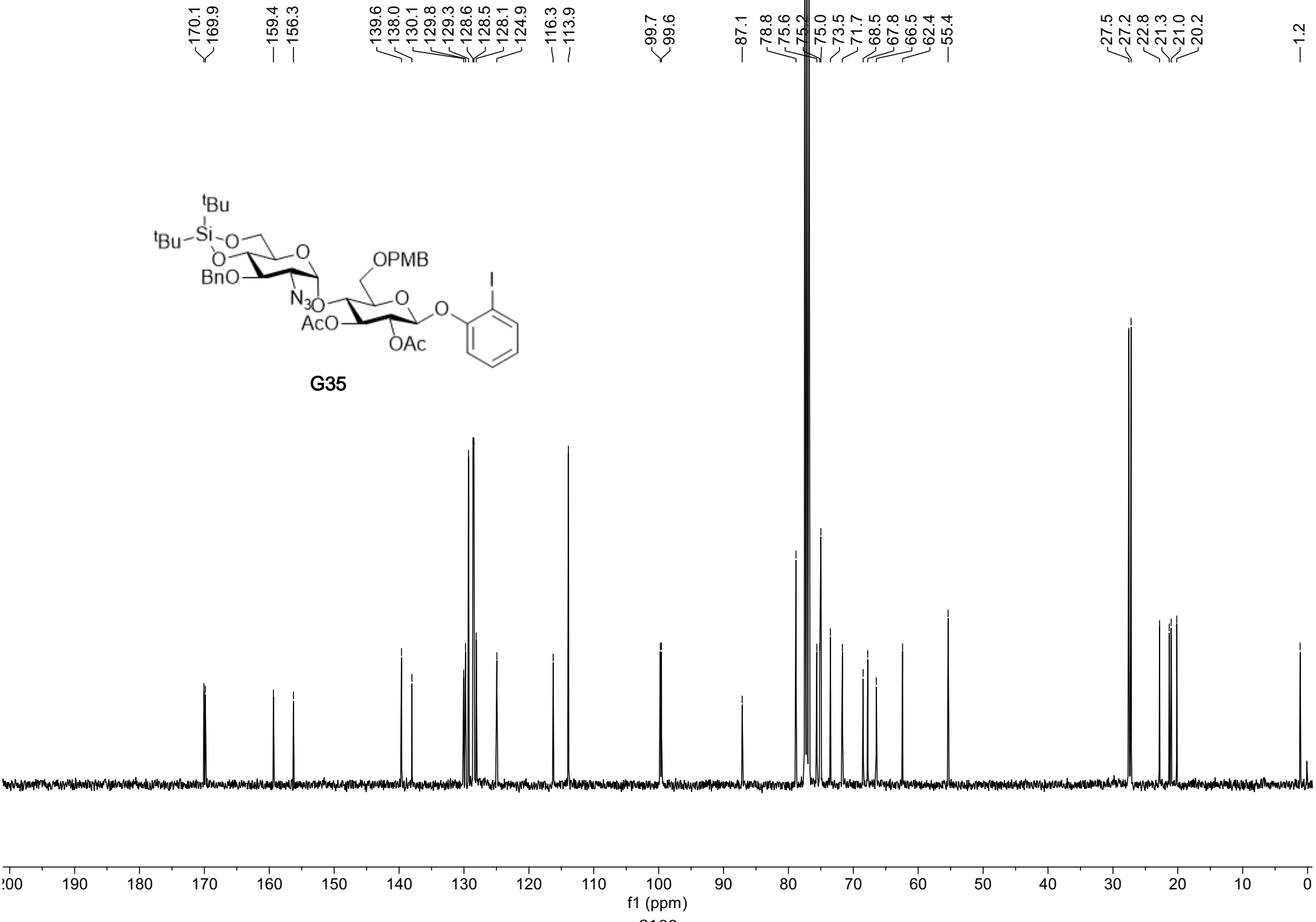


S187



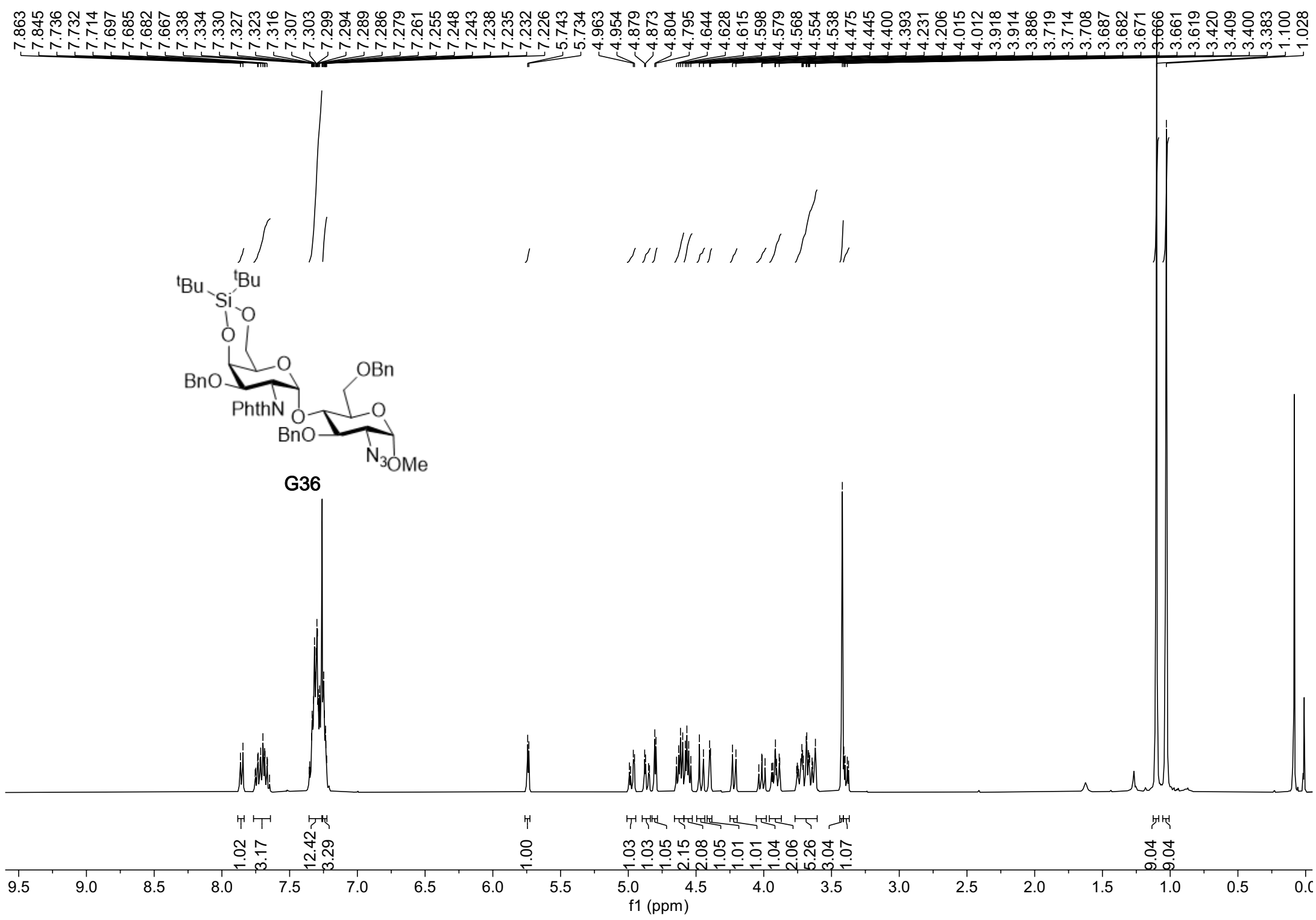


G35



f1 (ppm)

S189



169.0  
168.3

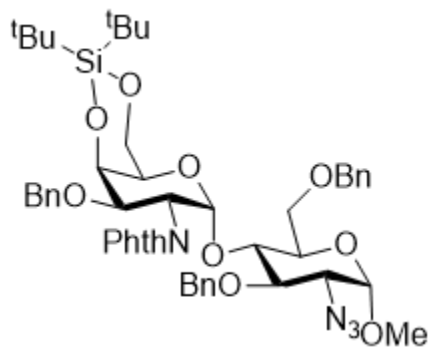
138.6  
138.0  
136.8  
134.1  
133.9  
132.6  
131.3  
128.6  
128.4  
128.3  
128.0  
127.9  
127.9  
127.7  
123.3  
123.2

98.8  
96.9

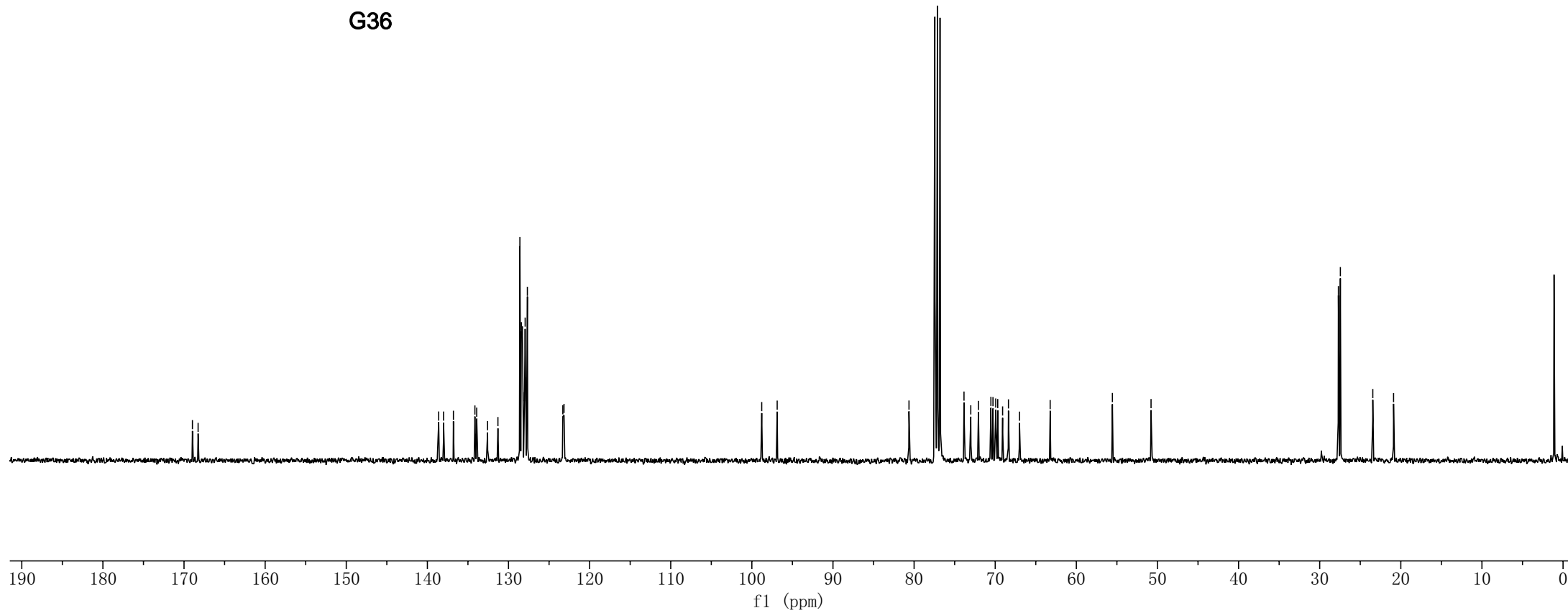
80.6  
73.8  
73.0  
72.1  
70.5  
70.3  
69.9  
69.7  
69.1  
68.4  
67.0  
63.2  
55.6

50.8

27.7  
27.5  
23.5  
20.9

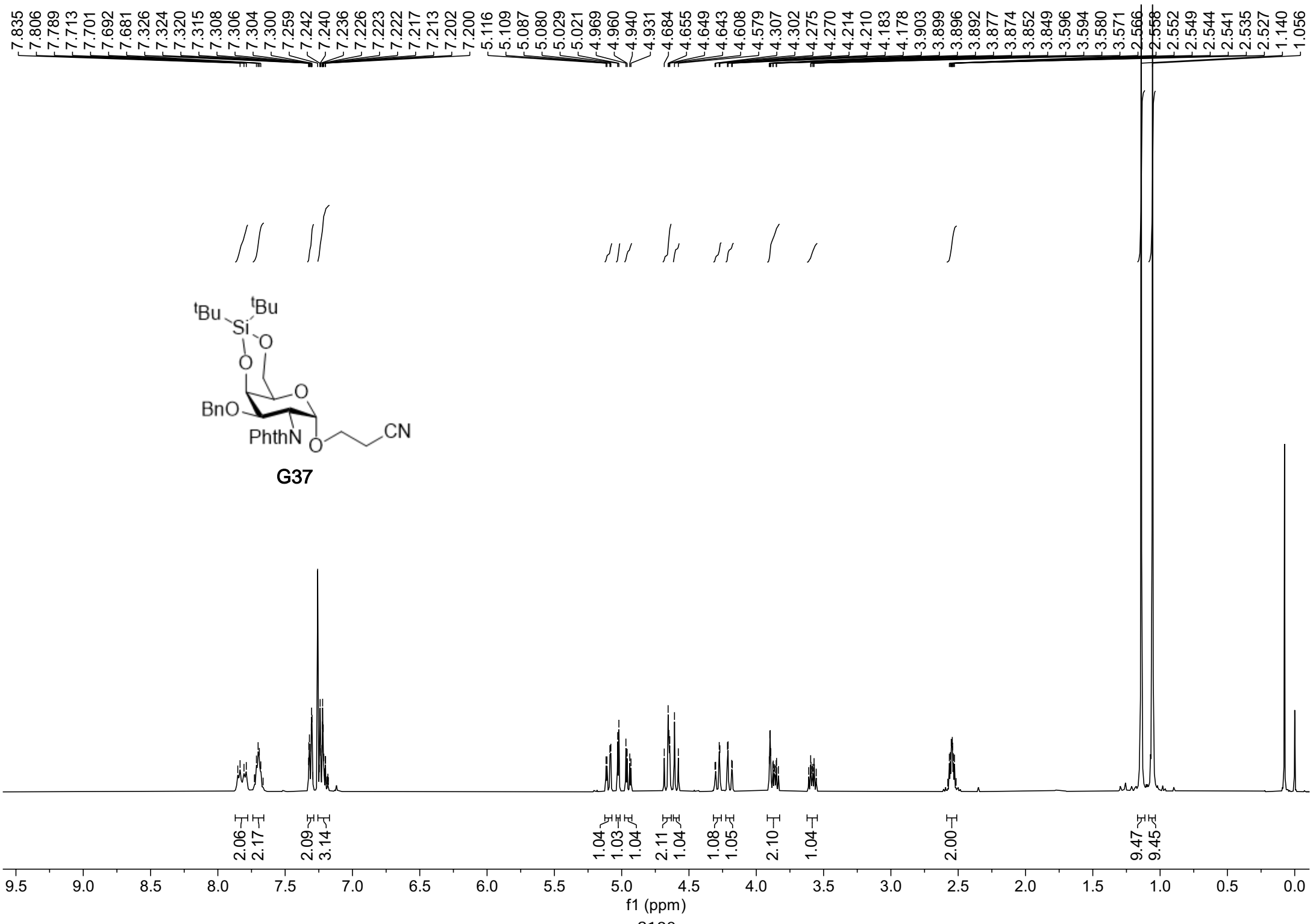


G36



S191





169.3  
168.0

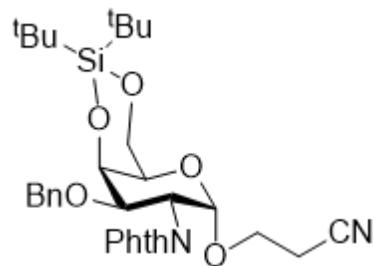
138.5  
134.2  
133.9  
132.7  
131.4  
128.4  
128.1  
127.7  
123.3  
123.2  
117.5

98.8

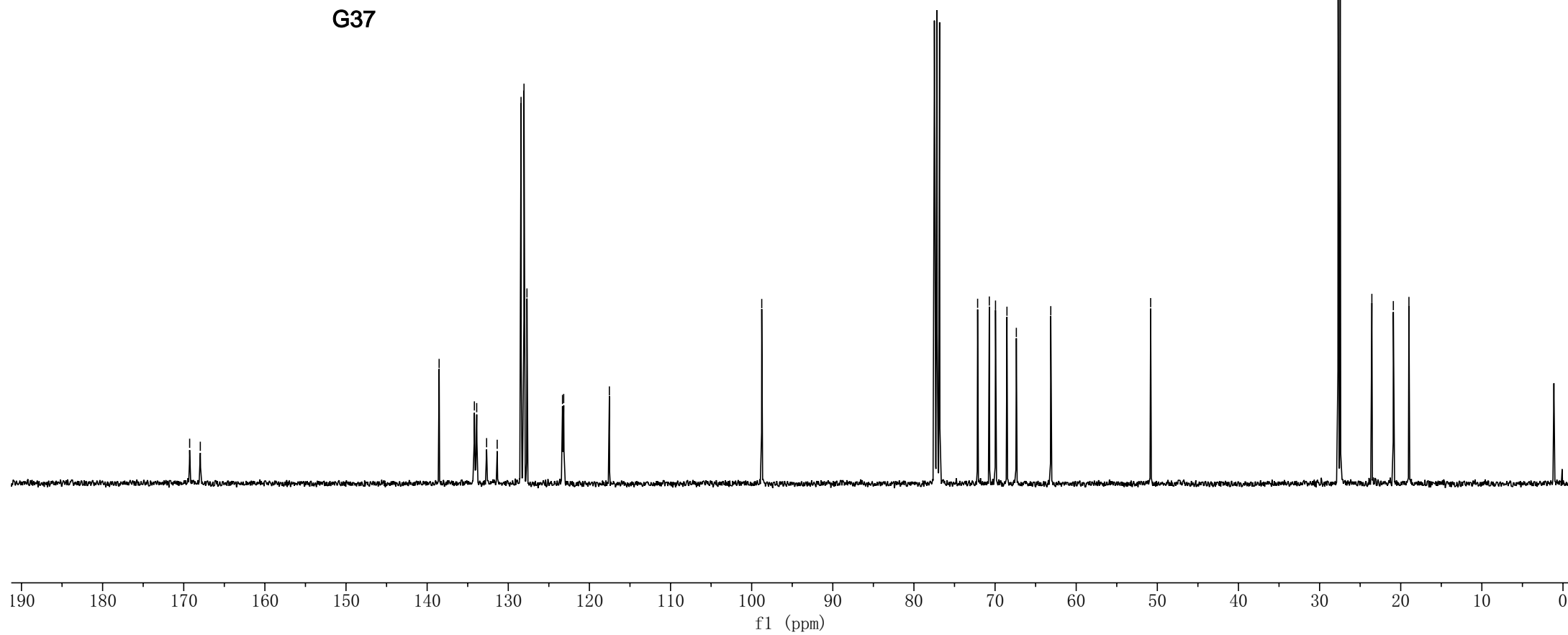
72.1  
70.7  
69.9  
68.5  
67.4  
63.1

50.8

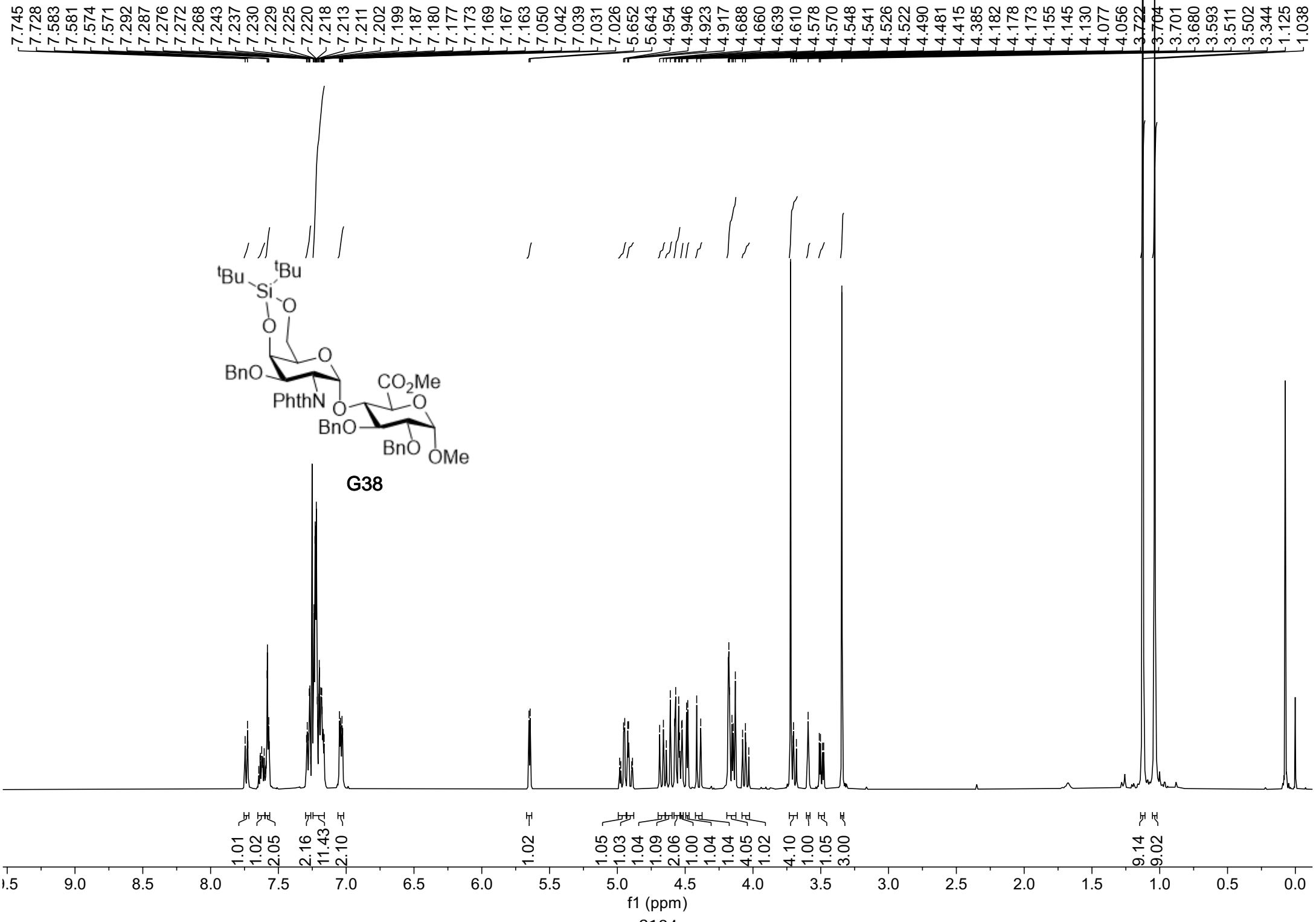
27.7  
27.5  
23.6  
20.9  
19.0



G37



S193



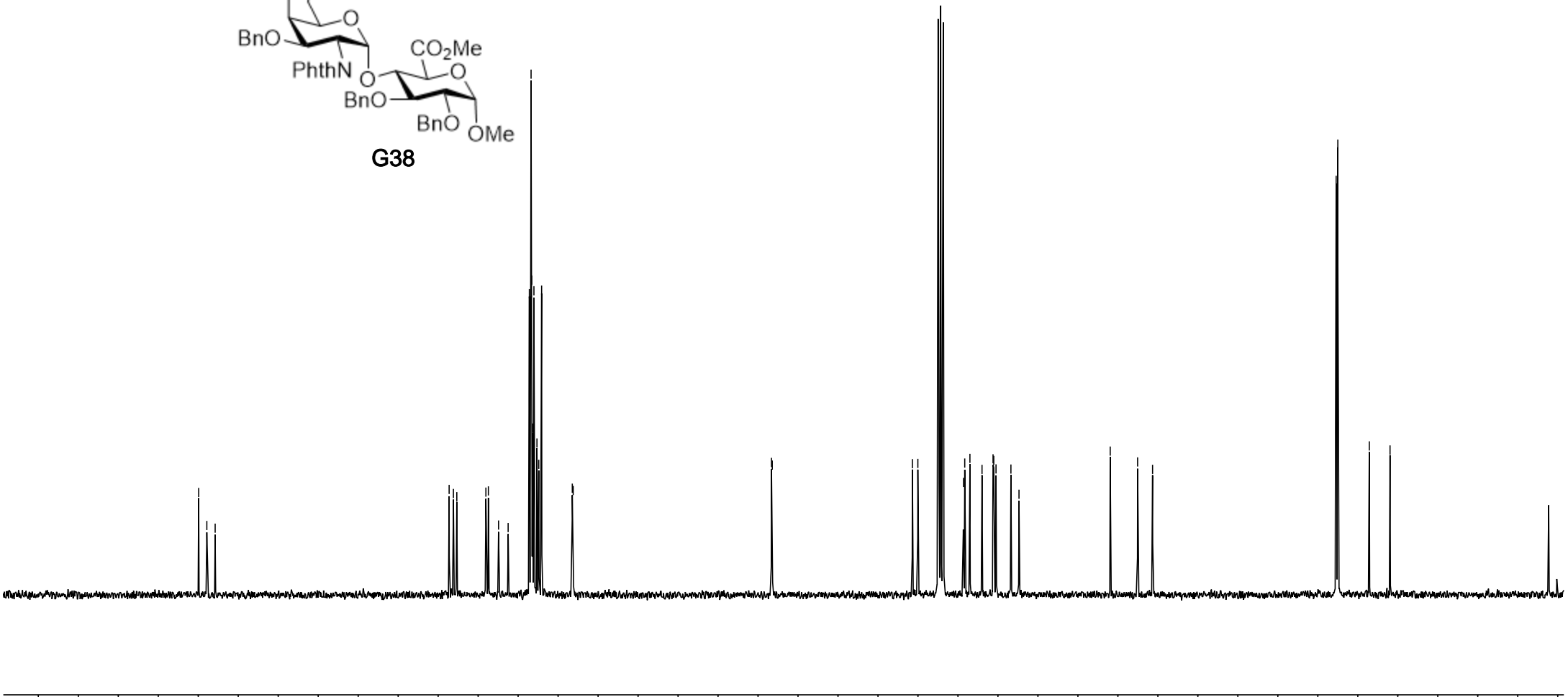
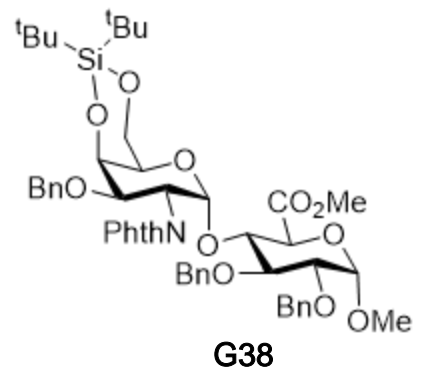
169.9  
168.9  
167.9

138.6  
138.1  
137.7  
134.0  
133.7  
132.4  
131.2  
128.6  
128.4  
128.3  
128.2  
128.0  
127.6  
127.4  
127.1  
123.2  
123.1

98.3  
98.2

80.7  
80.0  
74.3  
74.2  
73.5  
72.0  
70.6  
70.5  
70.2  
68.4  
67.4  
56.0  
52.5  
50.7

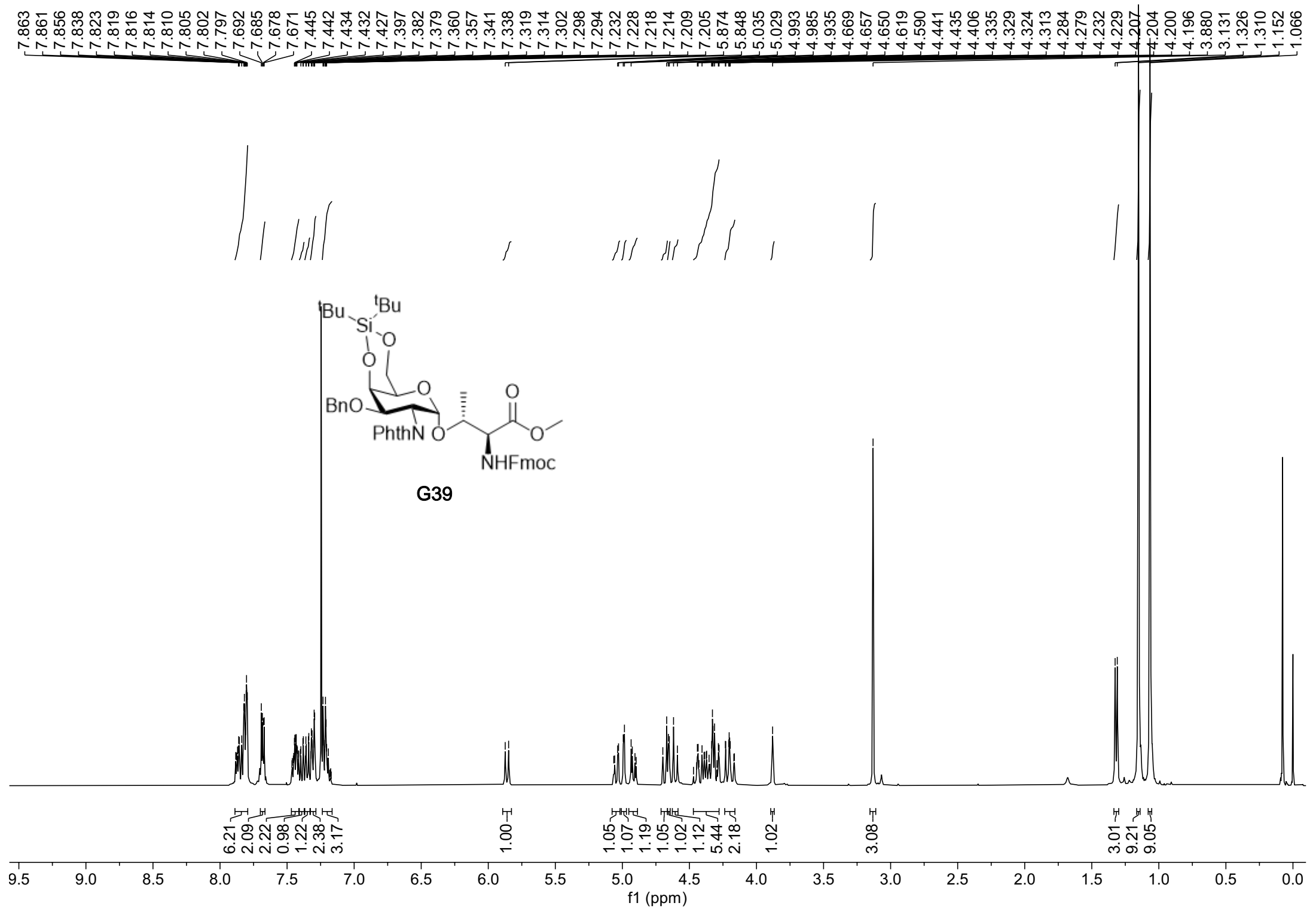
27.7  
27.5  
23.6  
21.0



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

S195

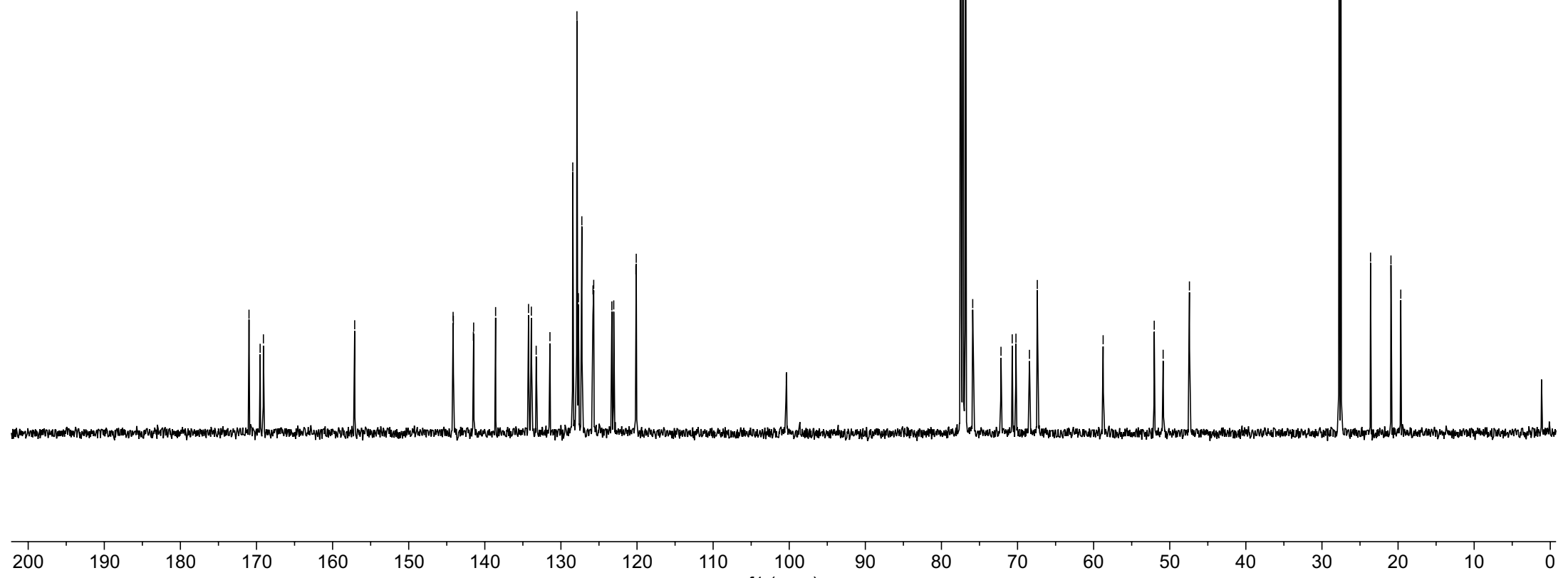
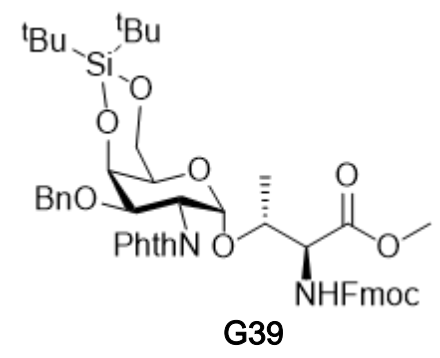


171.0  
169.5  
169.1

157.1  
144.2  
144.1  
141.5  
141.5  
138.6  
134.3  
133.9  
133.3  
131.4  
128.4  
127.9  
127.7  
127.3  
125.8  
125.7  
123.3  
123.1  
120.2  
120.1  
100.4

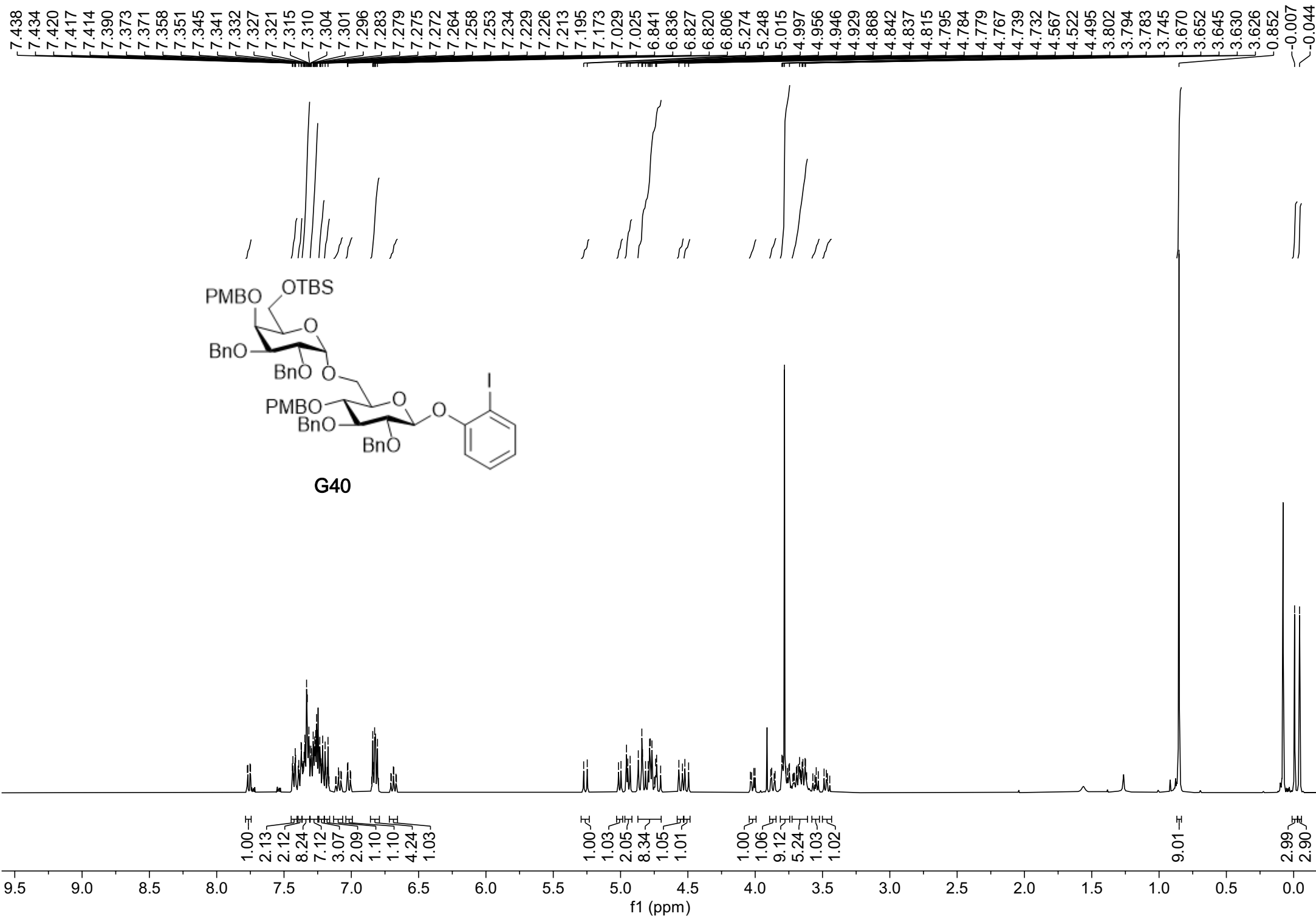
77.3  
75.9  
72.2  
70.7  
70.2  
68.4  
67.4  
58.8  
52.0  
50.9  
47.4

27.8  
27.5  
23.6  
20.9  
19.6



f1 (ppm)

S197



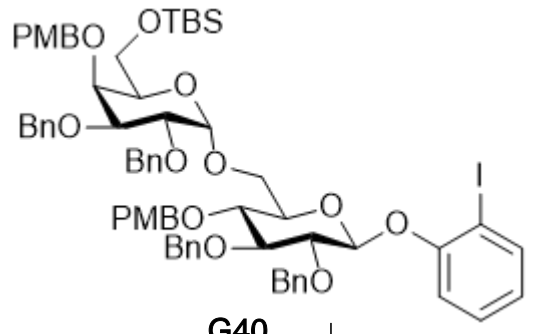
159.5  
159.3  
156.4

139.8  
139.2  
139.0  
138.8  
138.5  
131.2  
130.4  
129.9  
129.8  
129.5  
129.0  
128.5  
128.5  
127.9  
127.8  
127.7  
127.6  
127.5  
124.0  
115.3  
114.0  
113.7  
100.9  
98.0  
86.3  
84.9  
82.0  
78.7  
77.7  
77.0  
75.8  
75.7  
75.3  
74.9  
74.8  
74.5  
73.2  
72.9  
71.3  
66.2  
62.1  
55.4  
55.4

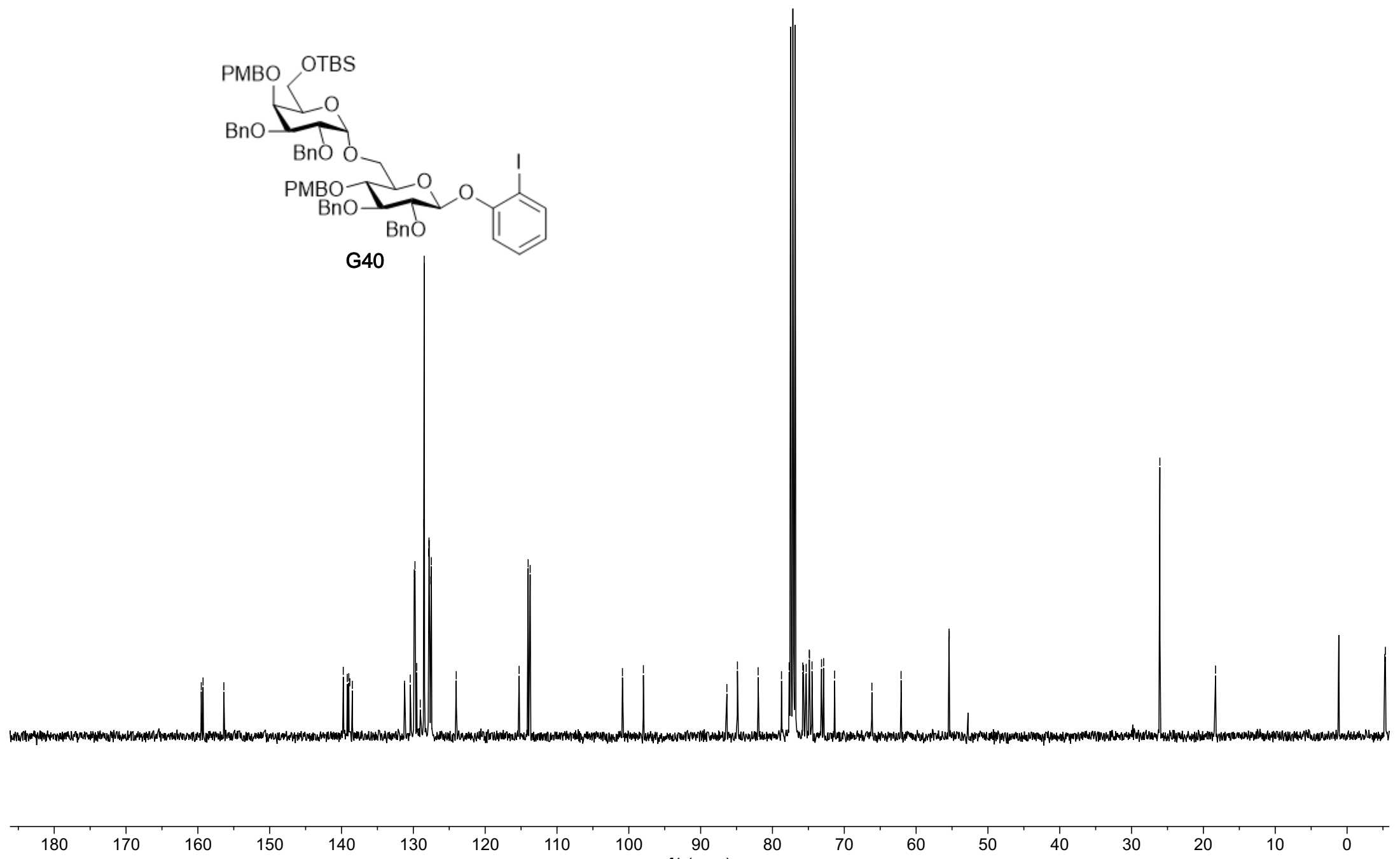
—26.1

—18.3

—5.2  
—5.3



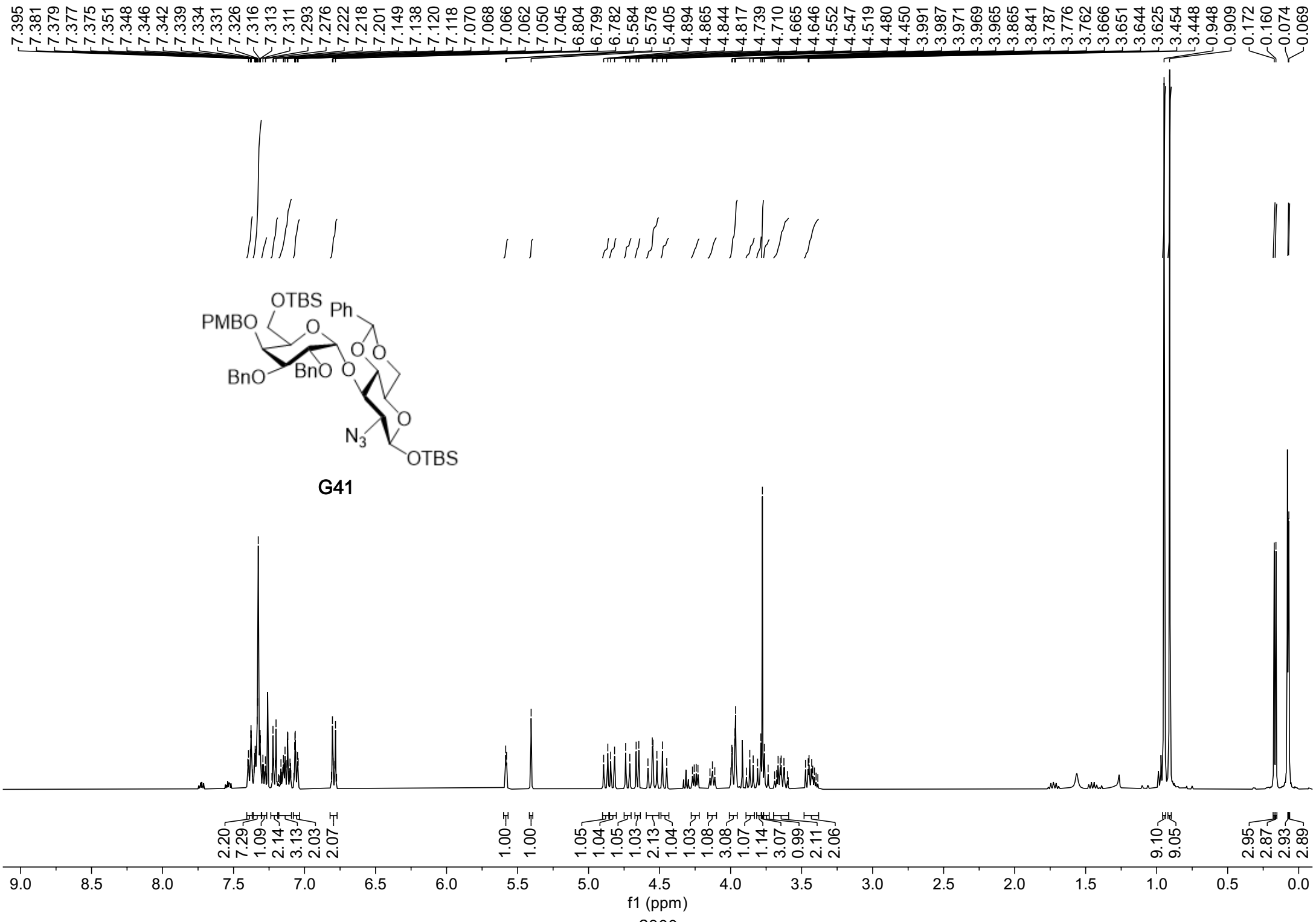
G40

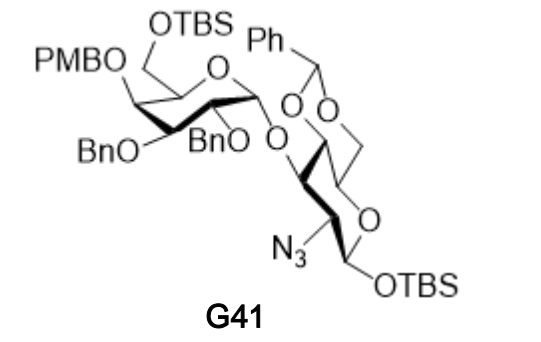


f1 (ppm)

S199







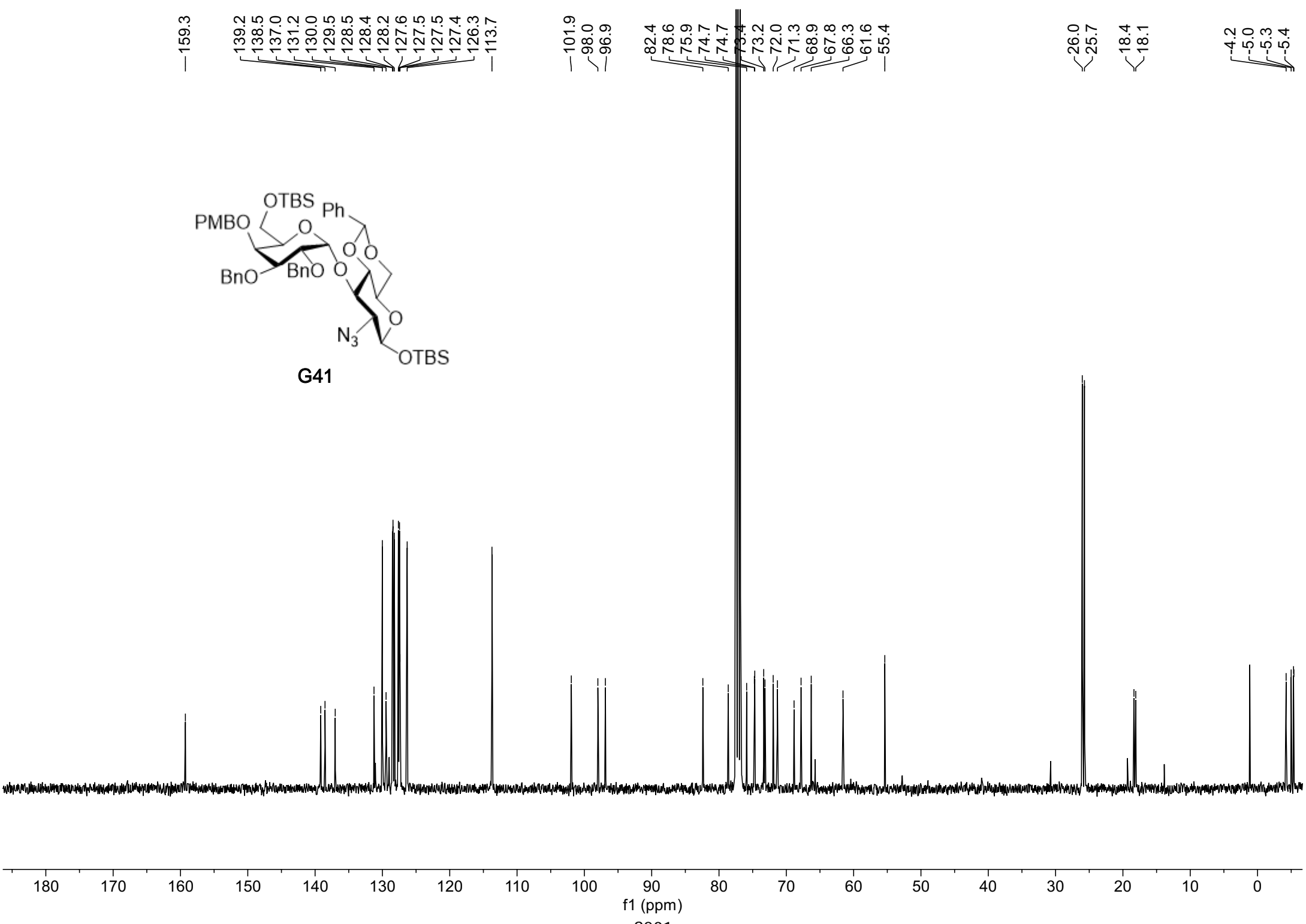
159.3  
 139.2  
 138.5  
 137.0  
 131.2  
 130.0  
 129.5  
 128.5  
 128.4  
 128.2  
 127.6  
 127.5  
 127.5  
 127.4  
 126.3  
 113.7

101.9  
 98.0  
 96.9

82.4  
 78.6  
 75.9  
 74.7  
 74.7  
 73.4  
 73.2  
 72.0  
 71.3  
 68.9  
 67.8  
 66.3  
 61.6  
 55.4

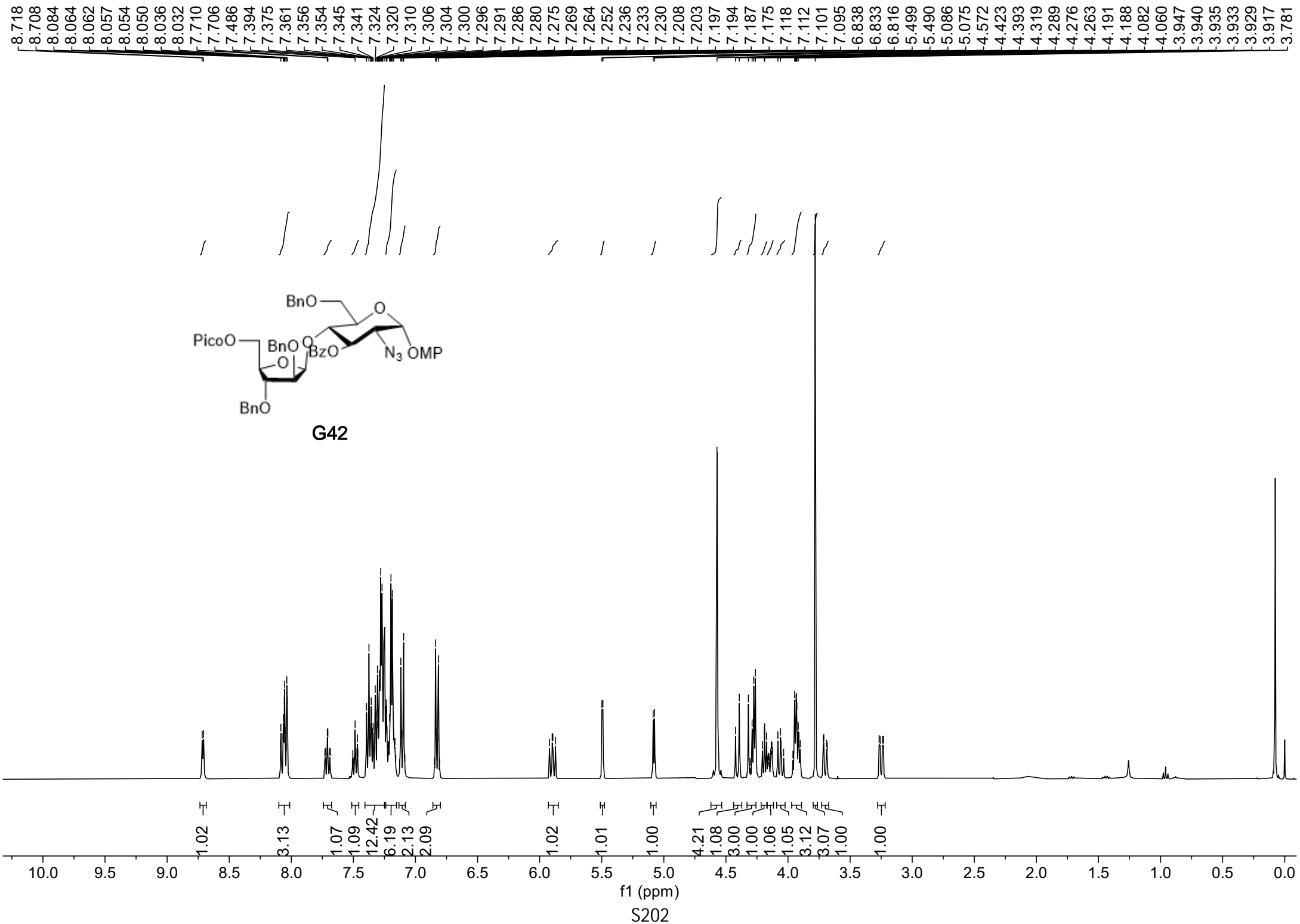
26.0  
 25.7  
 18.4  
 18.1

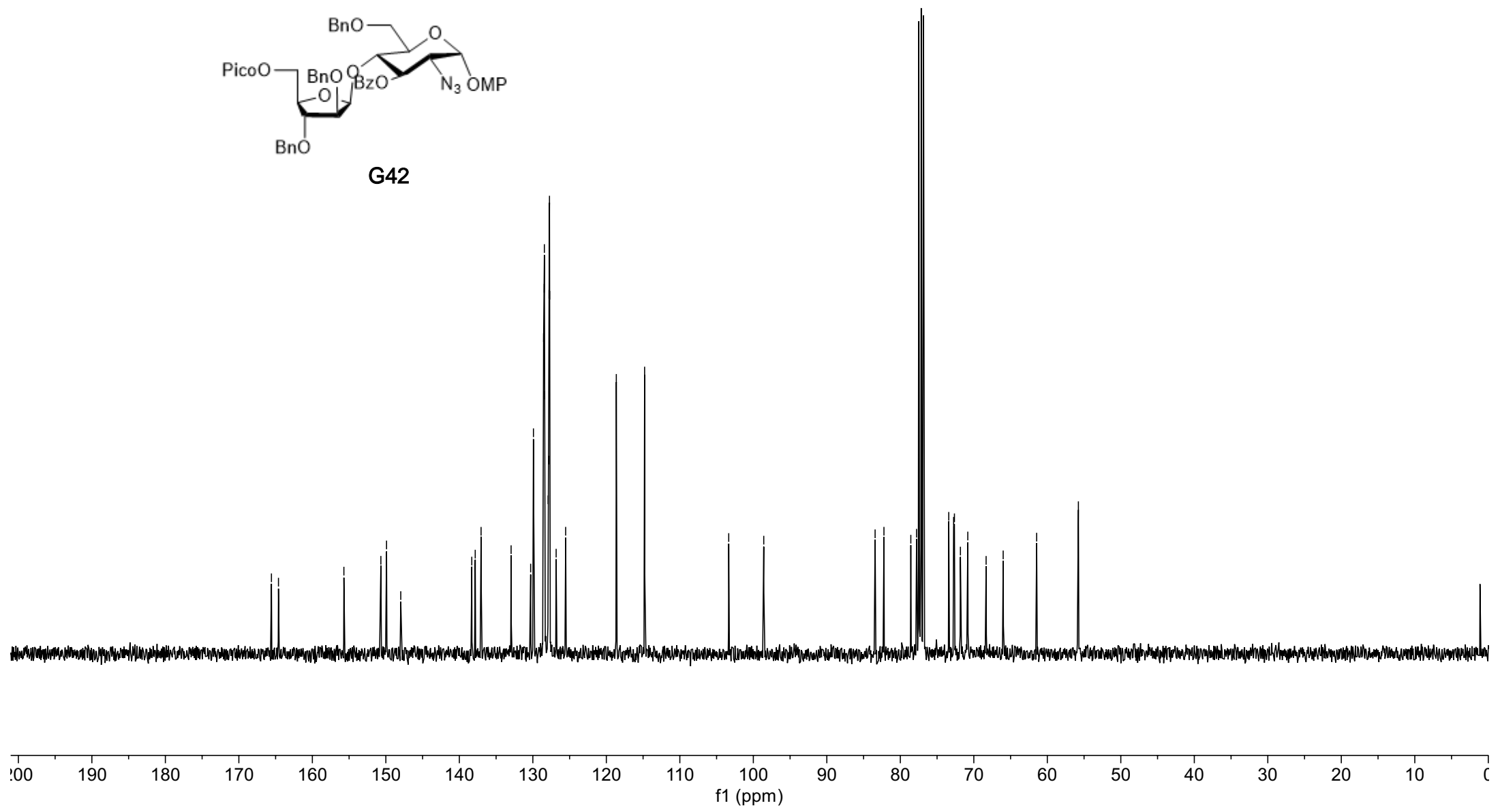
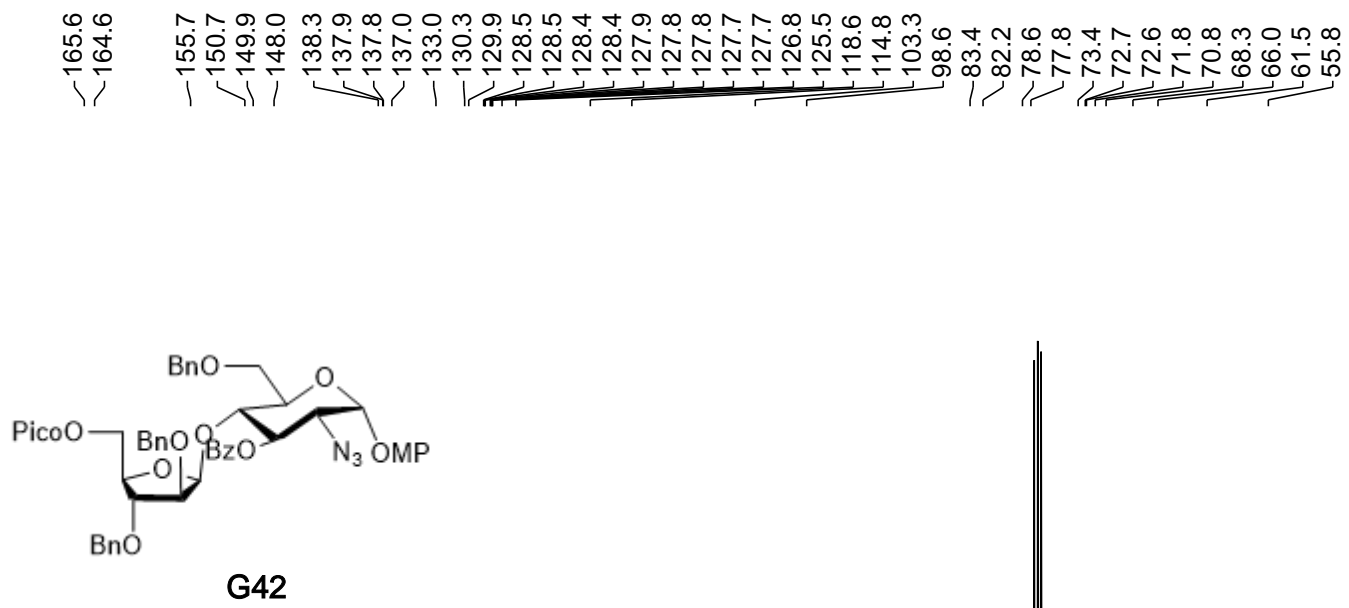
4.2  
 5.0  
 5.3  
 5.4



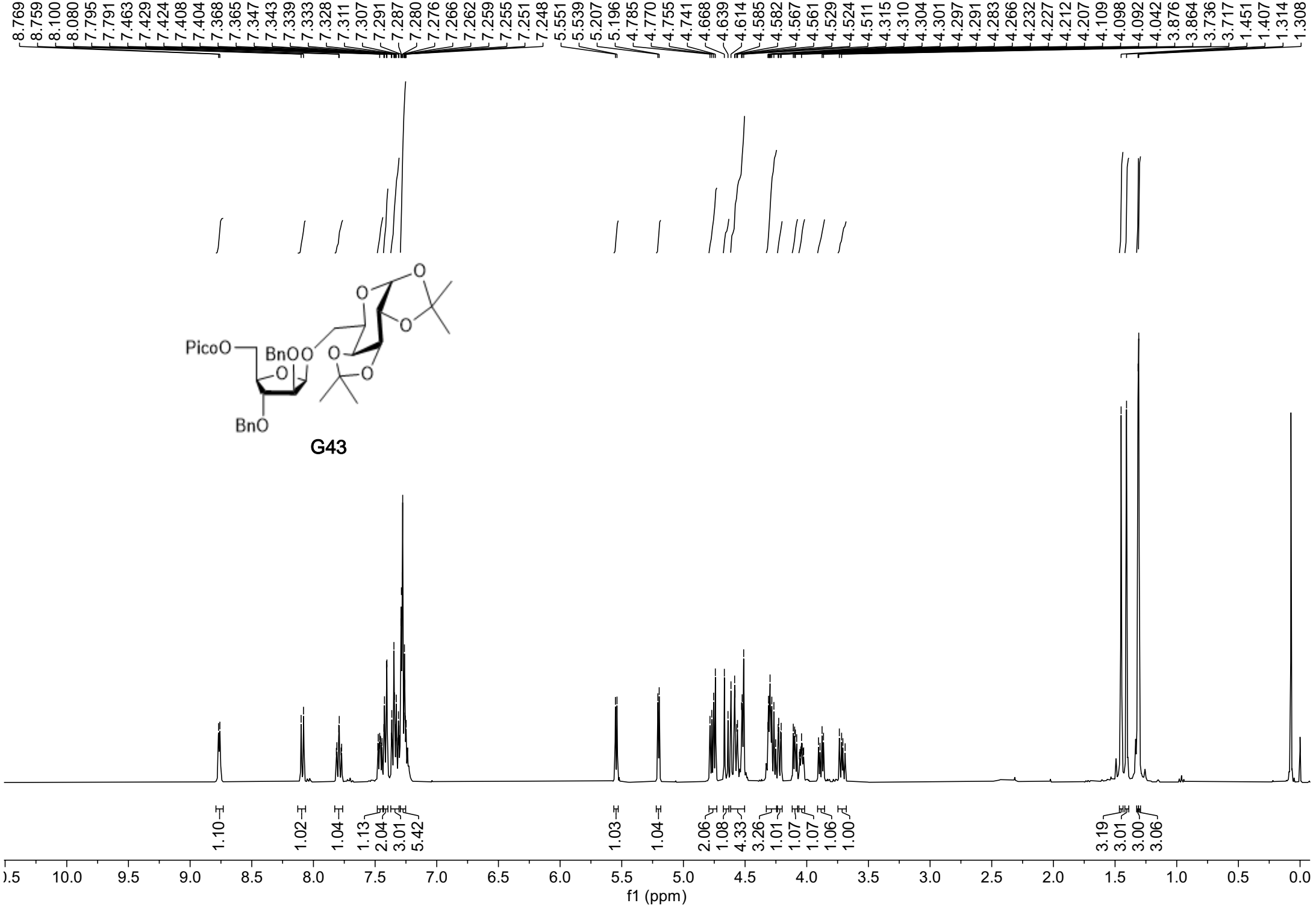
f1 (ppm)

S201

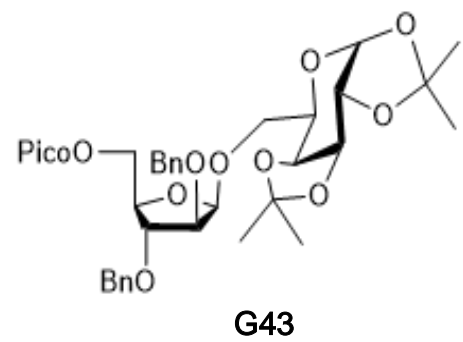




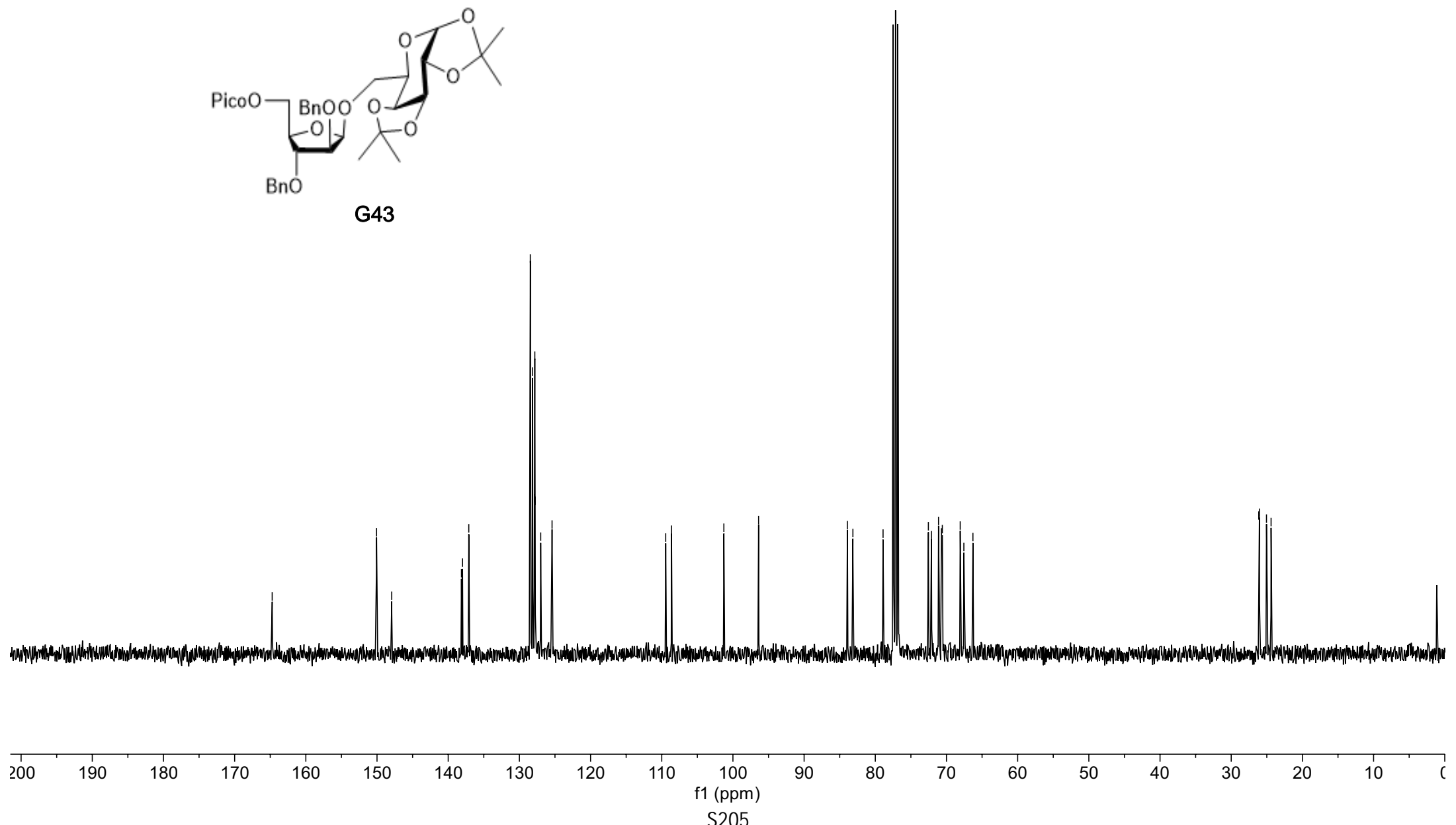
S203

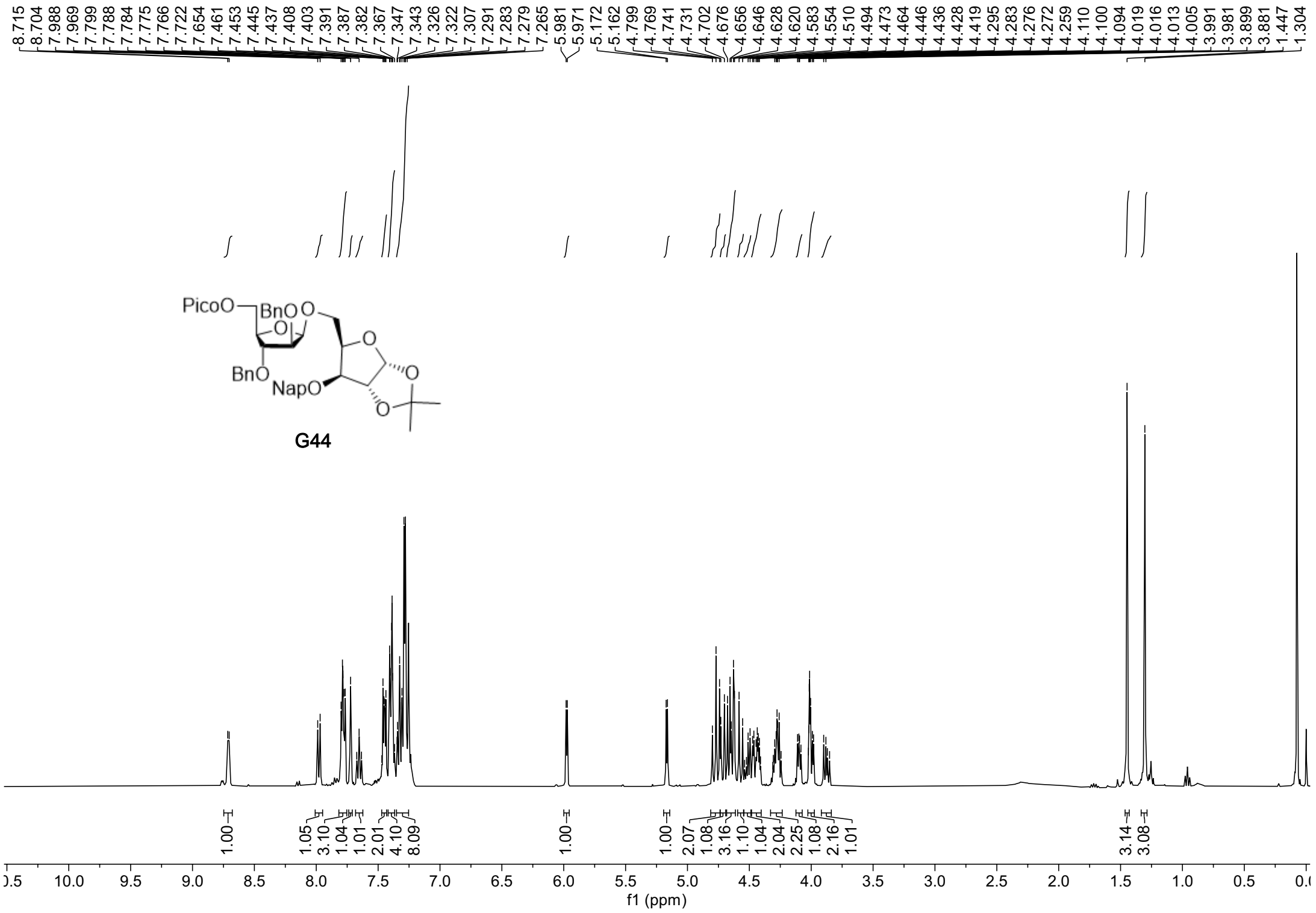


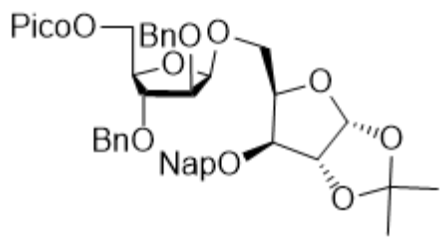
S204



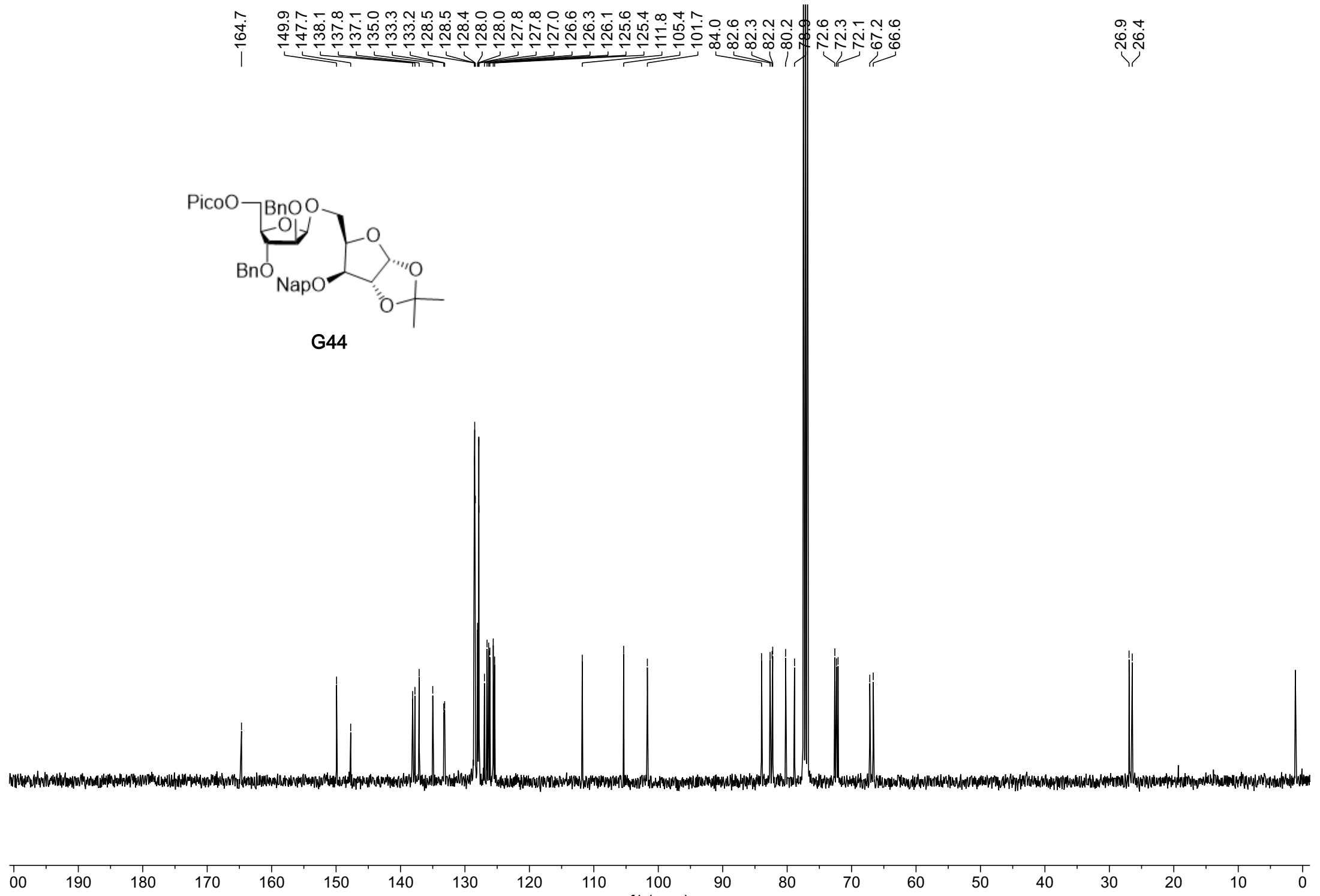
- 164.7
- 150.1
- 147.9
- 138.1
- 138.0
- 137.1
- 128.5
- 128.1
- 127.9
- 127.8
- 127.8
- 127.0
- 125.4
- 109.4
- 108.6
- 101.3
- 96.4
- 83.9
- 83.1
- 78.9
- 72.5
- 72.1
- 71.1
- 70.7
- 70.6
- 68.1
- 67.6
- 66.3
- 26.1
- 26.0
- 25.0
- 24.4







G44



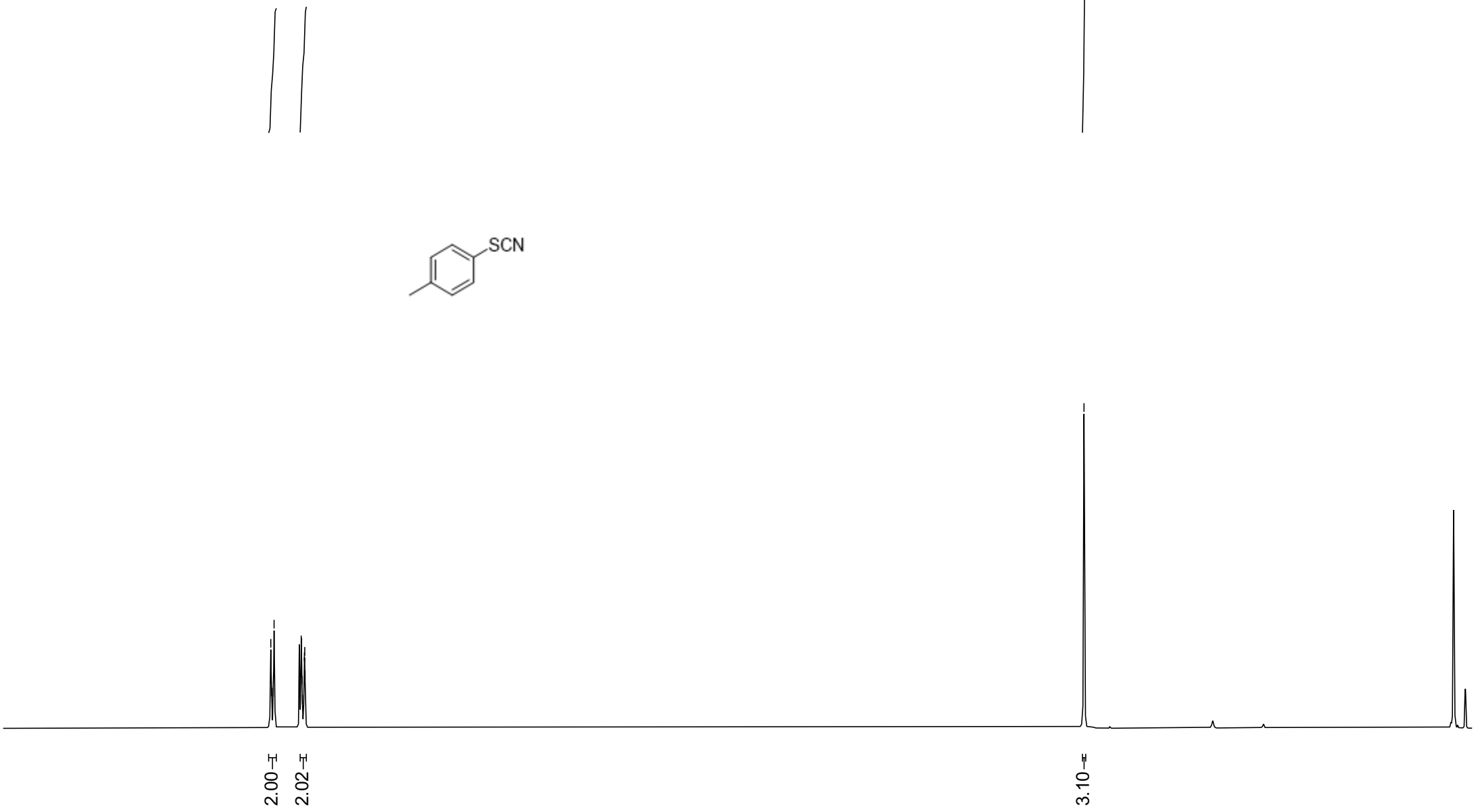
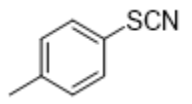
f1 (ppm)

S207



7.434  
7.428  
7.419  
7.413  
7.244  
7.242  
7.239  
7.237  
7.224  
7.222  
7.220

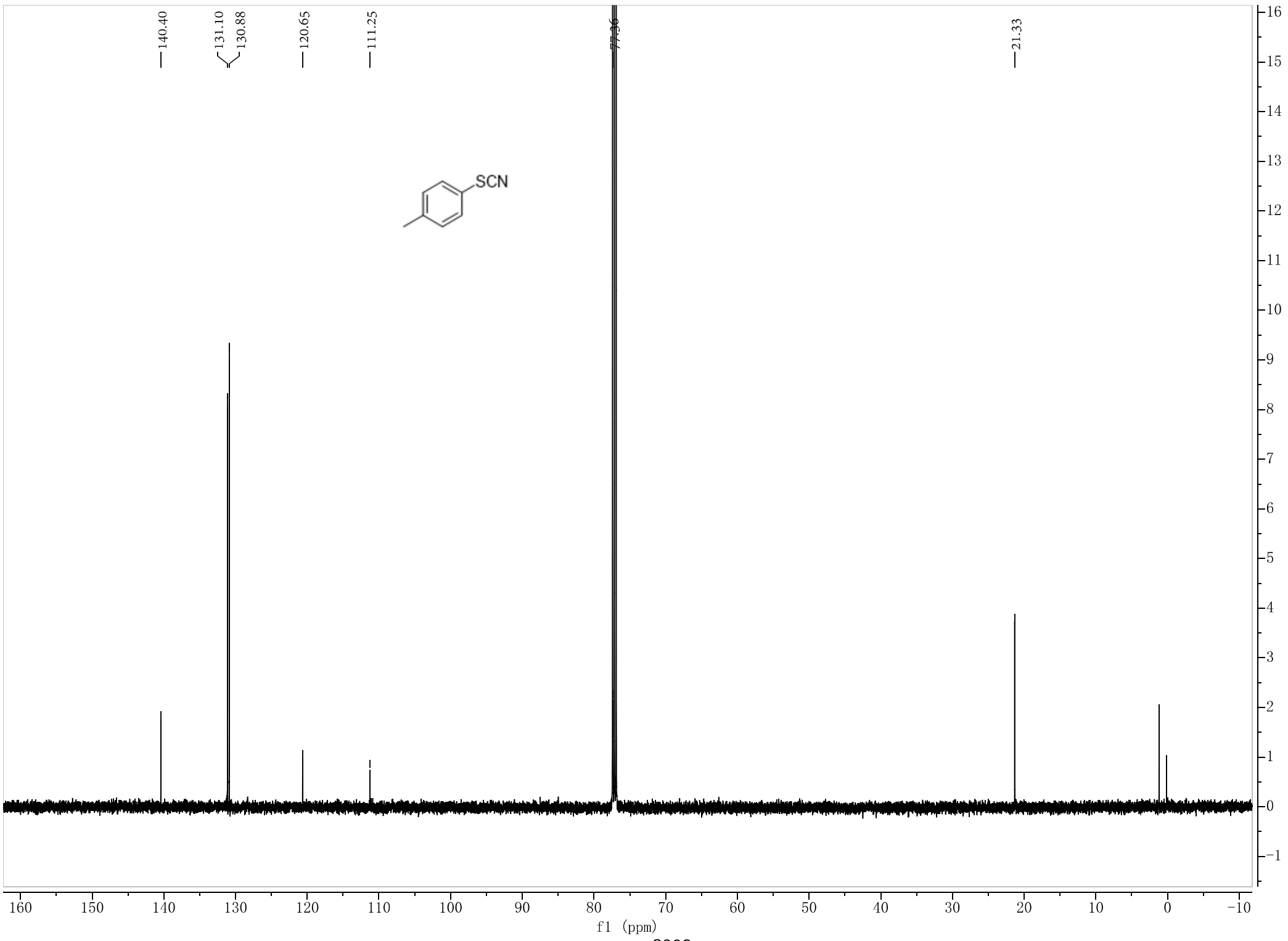
2.372



9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

S208



S209