Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Chiral Phosphoric Acid Directed Regioselective Acetalization of Carbohydrate-Derived 1,2-Diols**

*Enoch Mensah, Nicole Camasso, Will Kaplan, and Pavel Nagorny**

ange_201304298_sm_miscellaneous_information.pdf

I. General Methods

Method and Reagents. All reactions were carried out under an atmosphere of nitrogen in oven dried glassware with a magnetic stirrer, unless otherwise noted. Air–sensitive reactions were cooled via external cooling baths: ice water (0 °C), dry ice–acetonitrile (–50 °C), dry ice–acetone (–78 °C), Neslab CB 80 immersion cooler (10 to –60 °C) or Neslab cryocool immersion cooler CC-100II (–20 to –100 °C). Heating was achieved by use of a silicone bath with heating controlled by electronic contact thermometer. Deionized water was used in the preparation of all aqueous solutions and for all aqueous extractions. Solvents used for extraction and column chromatography were ACS or HPLC grade. Reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were filtered through a column of activated alumina under nitrogen atmosphere (Innovative Technologies). Analytical thin-layer chromatography (TLC) was routinely used to monitor the progress of the reactions and performed using precoated glass plates with 230-400 mesh silica gel impregnated with a fluorescent indicator (250 nm). Visualization was achieved using UV light or ceric ammonium molybdate. Purification of the reactions mixtures was performed by flash column chromatography using SiliCycle Silia Flash P60 (230-400 mesh) silica gel. 4 Å molecular sieves were also pre-activated before use.

Instrumentation.^{1}H NMR spectra were recorded on Varian vnmrs 500 (500 MHz), Varian INOVA 500 (500 MHz) or Varian MR400 (400 MHz) spectrometers and chemical shifts (δ) are reported in parts per million (ppm) with solvent resonance as the internal standard ($CDCl_3$ at δ 7.24, C_6D_6 at δ 7.15 and CD_3OD at δ 4.78 and 3.30). Data are reported as (br = broad, s = singlet, d = doublet, t = triplet, at = apparent triplet, q = quartet, qn = quintet, sext = sextet, m = multiplet; coupling constant(s) in Hz; integration). Proton-decoupled ^{13}C NMR spectra were recorded on Varian vnmrs 500 (500 MHz) or Varian INOVA 500 (500 MHz) spectrometers and chemical shifts (δ) are reported in ppm with solvent resonance as the internal standard ($CDCl_3$ at δ 77.0, C_6D_6 at

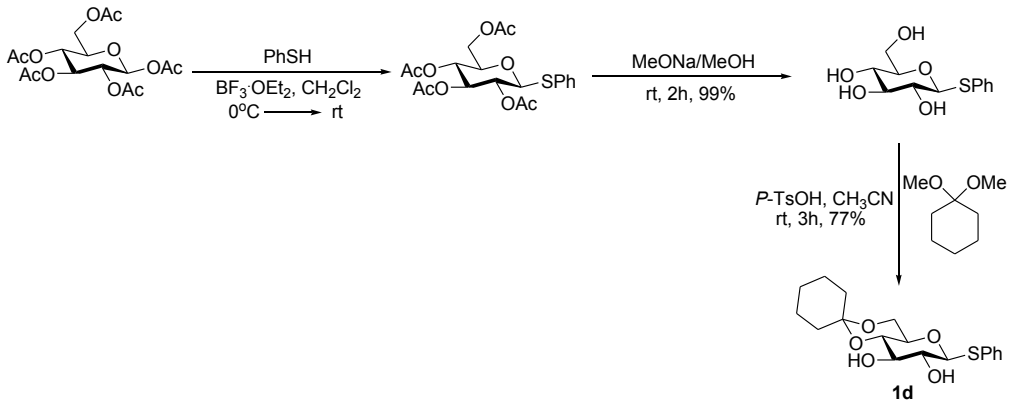
1 Perrin, D. D.; Armarego, W. L. *Purification of Laboratory Chemicals*; Third Addition; Pergamon Press: Oxford, 1988.

δ 127.7 CD_3OD at δ 49.0). High resolution mass spectra (HRMS) were recorded on Micromass AutoSpec Ultima or VG (Micromass) 70-250-S Magnetic sector mass spectrometers at the University of Michigan mass spectrometry laboratory. Infrared (IR) spectra were recorded as thin films on NaCl plates on a Perkin Elmer Spectrum BX FT-IR spectrometer. Transmittance (%) peaks were reported in wavenumbers (cm^{-1}). Optical rotations were measured in CH_2Cl_2 on JASCO P-2000 polarimeter at 589 nm (D-line) and reported as follows: $[\alpha]_{24}^{D}$ (*c* g/100 ml, CH_2Cl_2).

Catalysts. Catalysts (*R*)- and (*S*)-**2a**, **2b** and **2c** as well as diphenylphosphoric acid were purchased from Sigma Aldrich, dissolved in dichloromethane, washed with 4 N HCl, then dried with Na_2SO_4, concentrated and further dried under high vacuum for at least 48 h. Catalysts (*R*)- and (*S*)-**2d** where prepared according to the known procedure reported by Yamamoto and coworkers (Jiao, P.; Nakashima, D.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2008**, *47*, 2411). Racemic **2d** was obtained by mixing equimolar solutions of (*R*)- and (*S*)-**2d**.

II. Regioselective Tetrahydropyranylation.

Part I : Synthesis of Substrates 1d and 1e.



Synthesis of substrate **1d** began using β-D-glucose pentaacetate (10 g, 25.696 mmol,) as the starting material. This was converted to the corresponding thioglycoside in 86% yield, using the reported general protocol by Node *et al*.[2] To this thioglycoside (9.7 g, 22.098 mmol, 1 equiv.) in a 250 mL round bottom flask was added methanol (110 mL), followed

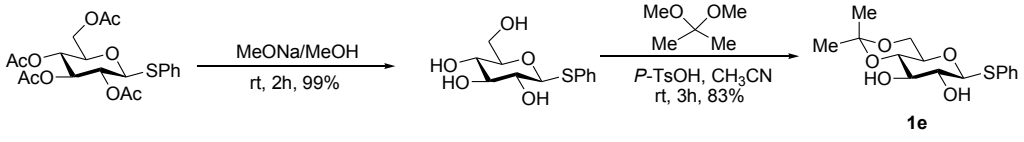
2. Node *et al*. *Carbohyd. Res*. **2005**, 340, 2360 – 2368.

by a small chip of sodium metal. The resulting pale yellow reaction mixture was stirred at room temperature for 2 hours. When the reaction was completed as monitored by TLC, the reaction was neutralized using few drops of ACS grade acetic acid, and concentrated *in vacuo* to form pale yellow oil as the crude tetraol. This was purified by flash column chromatography (10/1 Ethyl acetate / Methanol) to afford the pure tetraol as white solids (6 g, 99%). To this tetraol (0.5 g, 1.836 mmol, 1 equiv.) in an oven dried and nitrogen flushed 50 mL round bottom flask, anhydrous acetonitrile (15 mL) was added. To the resulting white suspension, 1,1-dimethoxycyclohexane (0.4 mL, 2.754 mmol, 1.5 equiv.) was added followed by *p*-TsOH (17.5 mg, 0.092 mmol, 5 mol%). The resulting reaction mixture was stirred at room temperature for 3 hours. When the reaction was completed as indicated by TLC, the reaction mixture was quenched with triethylamine and concentrated *in vacuo* to form a pale yellow solid as the crude product. The crude product was purified by flash column chromatography (1/1 Hexanes/Ethyl acetate) to afford pure **1d** as a pale yellow solid (0.5g, 77%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.35 – 7.30 (m, 3H), 4.58 (d, *J* = 9.7 Hz, 1H), 3.95 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.78 (at, *J* = 10.5 Hz, 1H), 3.70 (dd, *J* = 12.7, 4.9 Hz, 1H), 3.55 (at, *J* = 9.4 Hz, 1H), 3.44 – 3.39 (m, 1H), 3.35 (td, *J* = 9.9, 5.4 Hz, 1H), 2.81 (s, 1H), 2.72 (d, *J* = 1.8 Hz, 1H), 2.06 – 1.92 (m, 1H), 1.91 – 1.79 (m, 1H), 1.69 – 1.53 (m, 4H), 1.53 – 1.34 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 132.9, 131.4, 129.0, 128.4, 99.9, 88.6, 77.3, 77.0, 76.8, 75.1, 72.6, 72.0, 71.8, 61.2, 37.8, 27.7, 25.5, 22.8, 22.5

IR (film, cm^{-1}) 3429, 2936, 1649, 1261, 1077, 908. **HRMS(ESI)** Calc. for $C_{18}H_{24}O_5SNa$ (M + Na) : 375.1237; found : 375.1234.



1e

An oven dried 50 mL round bottom flask was charged with tetraacetate[3] (1 g, 2.27 mmol, 1 equiv.), methanol (17 mL) and a small chip of sodium metal. The resulting pale yellow reaction mixture was stirred at room temperature for 2 hours. When the reaction was

3. Magnusson *et al. Carbohydr. Res.* **2000**, *329*, 49-55.

completed as indicated by TLC, the reaction was neutralized using few drops of ACS grade acetic acid, and concentrated *in vacuo* to form a pale yellow oil as the crude tetraol. The crude tetraol was purified by flash column chromatography (10/1 Ethyl acetate / Methanol) to afford the pure tetraol as a white solid (0.52 g, 84%). To this tetraol (0.5 g, 1.836 mmol, 1 equiv.) in an oven dried and nitrogen flushed 50 mL round bottom flask, anhydrous acetonitrile (15 mL) was added. To the resulting white suspension, 1,1-dimethoxypropane (0.25 mL, 2.754 mmol, 1.2 equiv.) was added, followed by *p*-TsOH (17.5 mg, 0.092 mmol, 5 mol%). The resulting reaction mixture was stirred at room temperature for 3 hours. When the reaction was completed as indicated by TLC, the reaction mixture was quenched with triethylamine and concentrated *in vacuo* to form a yellow solid as the crude product, which was subsequently purified by flash column chromatography (1/2 Hexanes/Ethyl acetate) to afford pure **1e** as a pale yellow foamy solid (0.48g, 83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.47 (m, 2H), 7.36 – 7.29 (m, 3H), 4.59 (d, *J* = 9.7 Hz, 1H), 3.96 (dd, *J* = 10.8, 5.3 Hz, 1H), 3.78 (at, *J* = 10.6 Hz, 1H), 3.69 (at, *J* = 8.8 Hz, 1H), 3.54 (at, *J* = 9.4 Hz, 1H), 3.43 (at, *J* = 9.0 Hz, 1H), 3.34 (td, *J* = 9.9, 5.4 Hz, 1H), 2.96 (s, 1H), 2.80 (s, 1H), 1.51 (d, *J* = 10.7 Hz, 3H), 1.43 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 132.8, 131.5, 129.1, 128.4, 99.8, 88.7, 77.3, 77.0, 76.8, 75.0, 72.8, 72.8, 71.5, 62.0, 29.0, 19.1.
IR (film, cm^{-1}) 3420, 2884, 1581, 1373, 1264, 1198, 1079, 856. **HRMS(ESI)** Calc. for $C_{15}H_{20}O_5SNa$ (M + Na) : 335.0924; found : 335.0928.

Part II. General Procedure for Regioselective Tetrahydropyranylation

General Procedure I.

An oven dried and nitrogen flushed 10 mL round bottom flask was charged with diol **1** (1 equiv.), (which was previously dried by azeotropic removal of moisture with toluene), anhydrous dichloromethane resulting in 0.04M concentration, and activated 4Å molecular sieves. This mixture was submerged in an ice-bath and 3,4-dihydro-2H-pyran (1.2 equiv.) was added, followed by (*R*)-**2d** (2 mol%). The resulting white suspension was transferred into a Neslab CB 80 immersion cooler and stirred at 10 °C for 5hours. When the reaction was completed as monitored by TLC, the reaction mixture was

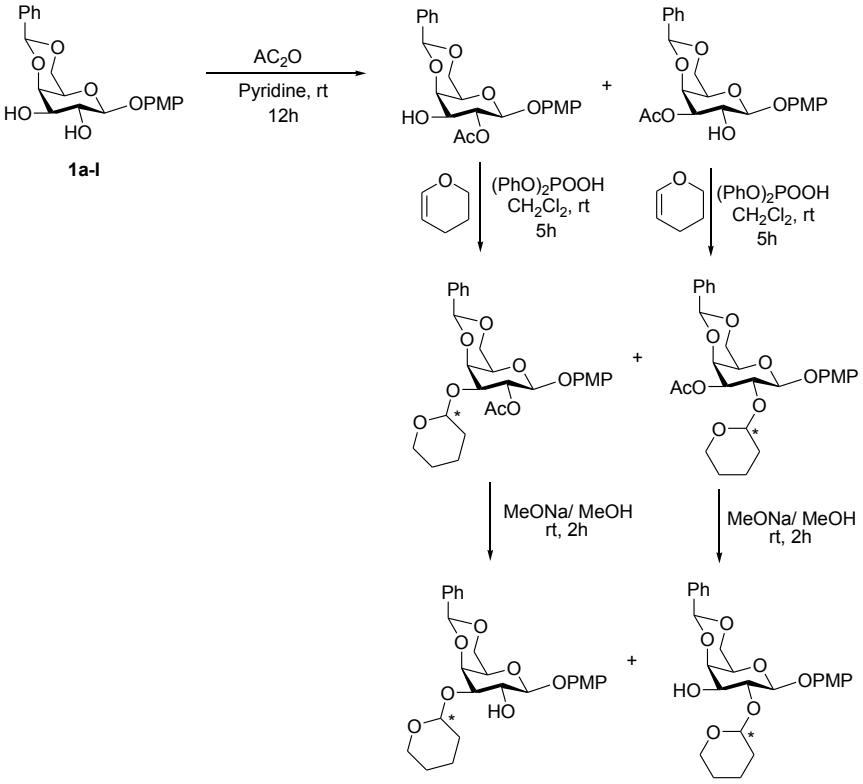
quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried with anhydrous $NaSO_4$, filtered and concentrated *in vacuo* to form pale yellow oil as the crude product. The crude product was purified by flash column chromatography to afford the mono functionalized products as pale yellow oils.

General Procedure 1I.

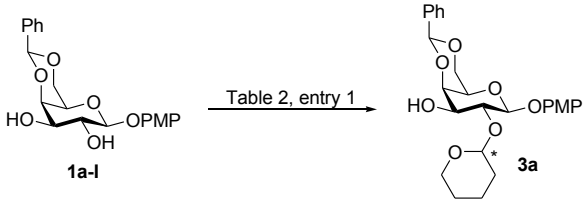
An oven dried and nitrogen flushed 10 mL round bottom flask was charged with thioglycoside diol **1** (1 equiv.), (which was previously dried by azeotropic removal of moisture with toluene)**,** anhydrous dichloromethane resulting in 0.04M concentration, and activated 4Å molecular sieves. This mixture was submerged in dry ice-acetonitrile bath and 3, 4-dihydro-2H-pyran (1.2 equiv.) was added, followed by (*R*)-**2d** (2 mol%). The resulting reaction mixture was transferred into a Neslab CB 80 immersion cooler and stirred at –20 °C. When the reaction was completed as monitored by TLC, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried with anhydrous $NaSO_4$, filtered, and concentrated *in vacuo* to form pale yellow oil as the crude product. The crude product was purified by flash column chromatography to afford the respective mono functionalized products as pale yellow oils.

The assessment of the regioselectivity was accomplished by analysis of the ^1H NMR spectra of the products obtained by the CPA-controlled tetrahydropyranylation. This analysis was based on comparison with the independently synthesized C2 and C3 regioisomers of **3a**. A typical procedure for the synthesis of C2 and C3 regioisomeric standards of **3a** began using galactose diol **1a-I** as starting material (see Scheme below). Mono acetylation of **1a-I** afforded the C2/C3 mixture of mono acetates, which were separated by a preparative TLC. The identity of the regioisomers was accessed by COSY NMR techniques (the protons next to the acetoxy group are typically shifted downfield). The pure C2 and C3 mono acetates were independently protected using 3,4-dihydro-2H-pyran (DHP) to afford the fully protected substrates, which were subsequently deacetylated using sodium methoxide in methanol, and each purified by flash column

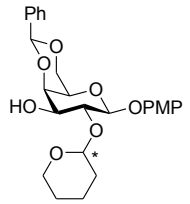
chromatography (1/1 Hexanes/Ethyl acetate) to afford the C2 and C3 standards as pale yellow oils. This protocol was followed in preparing C2 and C3 regio isomers of mono functionalized products **4a** – **4e** by using their respective starting materials **1a – 1e**.



Part III. Regioselective Tetrahydropyranylation Reactions (Table 2)



Galactose diol **1a-I** was prepared according to the known literature procedure by Magnusson *et al*.[3] Using substrate **1a-I** (20 mg, 0.053 mmol, 1 equiv.) as the starting material, synthesis of **3a** was accomplished by following general procedure I. This product was purified by flash column chromatography (2/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **3a** as a pale yellow oil (18.9 mg, 78 %), and as an 8:1 mixture of diastereoisomers.

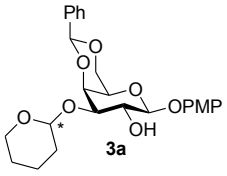


3a (C_2 Standard)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 4H), 7.43 – 7.30 (m, 5H), 7.09 – 7.01 (m, 4H), 6.86 – 6.78 (m, 4H), 5.58 (s, 1H), 5.56 (s, 1H), 4.85 (d, *J* = 10.0 Hz, 1H), 4.852 (d, *J* = 10.0 Hz, 1H), 5.23 (at, *J* = 3.4 Hz, 1H), 4.69 (d, *J* = 6.1 Hz, 1H), 4.35 (dd, *J* = 12.4, 1.3 Hz, 2H), 4.30 (d, *J* = 3.5 Hz, 1H), 4.22 (d, *J* = 3.8 Hz, 1H), 4.19 – 4.12 (m, 2H), 4.11 – 4.04 (m, 3H), 3.98 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.82 (td, *J* = 9.2, 3.9 Hz, 1H), 3.78 (s, 4H), 3.73 (dt, *J* = 9.6, 3.3 Hz, 1H), 3.59 – 3.47 (m, 4H), 2.85 (d, *J* = 9.1 Hz, 1H), 1.91 – 1.79 (m, 4H), 1.78 – 1.67 (m, 2H), 1.56 – 1.49 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 155.2, 151.8, 137.7, 137.4, 129.3, 129.1, 128.2, 128.2, 126.7, 126.6, 119.3, 118.8, 114.4, 102.5, 102.1, 101.7, 101.6, 101.5, 98.1, 79.4, 77.3, 77.0, 76.8, 75.5, 75.2, 74.0, 73.9, 71.1, 69.1, 69.0, 66.7, 66.5, 65.5, 62.1, 55.6, 31.3, 30.3, 25.4, 24.9, 21.3, 19.0.

IR (film, cm^{-1}) 3398, 2919, 2862,1634, 1507, 1452, 1369,1222, 1174 1167, 1077, 1053, 1027, 1005, 968, 913. **HRMS(ESI)** Calc. for $C_{25}H_{30}O_8$ Na(M + Na) : 481.1833; found : 481.1849; **[α]$^{26}_D$** = –72° (*c* 0.12, CH_2Cl_2).



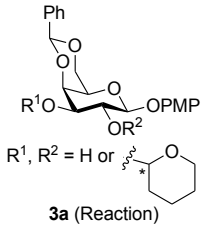
3a (C_3 Standard)

^{1}H NMR (500 MHz, $CDCl3_3$) δ 7.57 – 7.49 (m, 4H), 7.40 – 7.30 (m, 5H), 7.13 – 7.05 (m, 4H), 6.85 – 6.78 (m, 4H), 5.57 (s, 1H), 5.55 (s, 1H), 4.97 (at, *J* = 3.5 Hz, 1H), 4.84 (d, *J* = 7.7 Hz, 1H), 4.82 (d, *J* = 7.8 Hz, 1H), 4.75 (dd, *J* = 5.4, 2.8 Hz, 1H), 4.36 (dd, *J* = 5.2, 2.5 Hz, 2H), 4.34 (dd, *J* = 7.7, 1.4 Hz, 1H), 4.28 (d, *J* = 3.4 Hz, 1H), 4.19 (dd, *J* = 9.8, 8.0 Hz, 1H), 4.16 – 4.11 (m, 1H), 4.08 (dd, *J* = 12.4, 1.3 Hz, 2H), 4.05 – 3.97 (m,

2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.72 (dd, *J* = 9.9, 3.5 Hz, 2H), 3.62 – 3.42 (m, 5H), 2.64 (s, 1H), 1.91 – 1.66 (m, 7H), 1.57 – 1.48 (m, 5H).

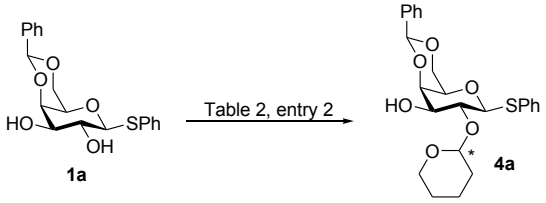
^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 155.35, 151.3, 151.2, 137.9, 137.7, 128.9, 128.8, 128.1, 126.4, 126.3, 119.4, 119.2, 114.4, 114.3, 102.9, 102.7, 101.2, 101.0, 100.9, 97.8, 79.4, 78.3, 77.3, 77.0, 76.6, 76.1, 73.2, 69.4, 69.2, 69.1, 68.6, 66.9, 66.7, 63.7, 62.5, 55.6, 55.6, 30.8, 30.6, 25.4, 25.0, 19.9, 19.4.

IR (film, cm^{-1}) 3398, 2919, 2862,1634, 1507, 1452, 1369,1222, 1174 1167, 1077, 1053, 1027, 1005, 968, 913. **HRMS(ESI)** Calc. for $C_{25}H_{30}O_8$ Na (M + Na) : 481.1833; found : 481.1849; **[α]$^{26}_D$** = –51.4° (*c* 0.12, CH_2Cl_2).



3a (Reaction)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 4H), 7.43 – 7.33 (m, 6H), 7.13 – 7.10 (m, 0.3H), 7.10 – 7.05 (m, 3H), 6.88 – 6.79 (m, 4H), 5.59 (s, 1H), 5.57 (s, 0.6H), 5.57 (s, 0.1H), 5.25 (at, *J* = 3.4 Hz, 0.6H), 4.98 (at, *J* = 3.6 Hz, 0.08H), 4.88 – 4.85 (m, 2H), 4.84 (d, *J* = 7.8 Hz, 0.1H), 4.77 (dd, *J* = 5.4, 2.7 Hz, 0.1H), 4.73 – 4.68 (m, 1H), 4.37 (d, *J* = 12.4 Hz, 2H), 4.32 (d, *J* = 3.2 Hz, 1H), 4.30 (d, *J* = 3.8 Hz, 0.1H), 4.24 (dd, *J* = 3.9, 0.8 Hz, 0.7H), 4.21 – 4.19 (m, 0.3H), 4.19 – 4.15 (m, 1H), 4.14 (s, 0.2H), 4.13 – 4.10 (m, 2H), 4.10 – 4.08 (m, 1H), 4.08 – 4.04 (m, 1H), 4.00 (dd, *J* = 9.6, 7.8 Hz, 1H), 3.84 (dd, *J* = 9.3, 3.9 Hz, 0.6H), 3.79 (s, 5H), 3.78 (d, *J* = 1.8 Hz, 1H), 3.75 (dd, *J* = 9.6, 3.7 Hz, 1H), 3.59 – 3.51 (m, 4H), 1.91 – 1.80 (m, 3H), 1.79 – 1.72 (m, 2H), 1.63 – 1.60 (m, 2H), 1.54 (s, 4H).



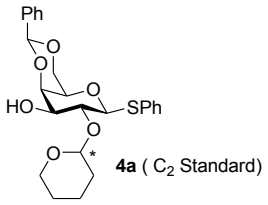
1a **4a**

Galactose diol **1a** was prepared according to the known literature procedure by Magnusson *et al*.[3] Using the galactose diol **1a** (20 mg, 0.056 mmol, 1 equiv.) as the starting material, synthesis of **4a** was accomplished by following general procedure II.

This product was purified by flash column chromatography (1/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **4a** as a pale yellow oil (18.5 mg, 74 %), and as an 8:1 mixture of diastereoisomers.

Scaled up Synthesis of 4a

An oven dried and nitrogen flushed 100 mL round bottom flask was charged with thioglycoside diol **1a** (400 mg, 1.11 mmol, 1 equiv.), (which was previously dried by azeotropic removal of moisture with toluene)**,** anhydrous dichloromethane (26 mL) and activated 4 Å molecular sieves. This mixture was submerged in dry ice-acetonitrile bath and 3, 4-dihydro-2H-pyran (0.12 mL, 1.33 mmol, 1.2 equiv.) was added, followed by (*R*)-**2d** (20.8 mg, 0.022 mmol, 2 mol %). The resulting reaction mixture was transferred into a Neslab CB 80 immersion cooler and stirred at –20 °C. When the reaction was completed as monitored by TLC, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with ethyl acetate (3 x 50 mL). The combined organic layer was dried with anhydrous $NaSO_4$, filtered, and concentrated *in vacuo* to form pale yellow oil as the crude product. The crude product was purified by flash column chromatography (1/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **4a** as a pale yellow oil (0.35 g, 72 %), and as an 8:1 mixture of diastereoisomers.



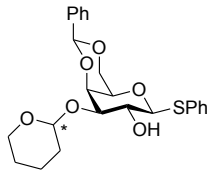
4a (C_2 Standard)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 4H), 7.52 – 7.48 (m, 2H), 7.48 – 7.42 (m, 2H), 7.42 – 7.32 (m, 6H), 7.29 – 7.26 (m, 4H), 7.25 – 7.24 (m, 1H), 5.54 (s, 1H), 5.52 (s, 1H), 5.12 (dd, *J* = 4.6, 3.2 Hz, 1H), 4.62 (d, *J* = 6.4 Hz, 1H), 4.60 (d, *J* = 6.1 Hz, 1H), 4.57 (d, *J* = 1.4 Hz, 1H), 4.40 – 4.33 (m, 2H), 4.30 (d, *J* = 2.8 Hz, 1H), 4.25 – 4.20 (m, 2H), 4.18 – 4.13 (m, 1H), 4.05 (dd, *J* = 12.4, 1.6 Hz, 1H), 4.02 (dd, *J* = 12.4, 1.7 Hz, 1H), 3.94 (at, *J* = 9.2 Hz, 2H), 3.80 – 3.74 (m, 2H), 3.69 (ddd, *J* = 9.1, 3.4, 1.4 Hz, 1H), 3.52 – 3.50 (m, 2H), 3.49 – 3.47 (m, 1H), 3.40 – 3.36 (m, 1H), 2.89 (d, *J* = 9.1 Hz, 1H), 1.95 –

1.92 (m, 1H), 1.88 – 1.83 (m, 2H), 1.76 – 1.71 (m, 2H), 1.67 – 1.64 (m, 1H), 1.54 – 1.49 (m, 5H), 1.30 – 1.26 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 137.5, 133.2, 132.8, 132.6, 132.6, 129.3, 129.1, 128.9, 128.6, 128.2, 128.1, 127.7, 127.3, 126.8, 126.6, 102.6, 101.8, 101.5, 98.8, 86.0, 85.7, 78.1, 77.3, 77.0, 76.7, 75.8, 75.3, 75.1, 73.1, 72.87, 70.1, 69.8, 69.4, 69.2, 66.0, 63.3, 31.2, 307, 29.7, 25.3, 24.8, 21.6, 19.6.

IR (film, cm^{-1}) 3410, 2927, 2848, 1583, 1454, 1436, 1357, 1266, 1161, 1097, 1071, 1025, 900. **HRMS(ESI)** Calc. for $C_{24}H_{28}O_6SNa$ (M + Na) : 467.1499; found : 467.1514; **[α]$^{26}_D$** = –35.9° (*c* 0.11, CH_2Cl_2).

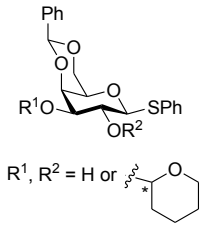


4a (C_3 Standard)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 3H), 7.47 – 7.38 (m, 4H), 7.38 – 7.31 (m, 5H), 7.29 – 7.26 (m, 3H), 7.25 – 7.17 (m, 4H), 5.53 (s, 1H), 5.50 (s, 1H), 4.91 (t, *J* = 5.0 Hz, 1H), 4.68 (dd, *J* = 6.0, 2.7 Hz, 1H), 4.55 (d, *J* = 9.5 Hz, 2H), 4.39 (dd, *J* = 6.5, 1.6 Hz, 1H), 4.37 (dd, *J* = 6.5, 1.5 Hz, 1H), 4.34 (d, *J* = 2.7 Hz, 1H), 4.26 (d, *J* = 2.6 Hz, 1H), 4.04 (d, *J* = 1.6 Hz, 1H), 4.02 (d, *J* = 1.6 Hz, 1H), 3.98 (dd, *J* = 11.3, 5.7 Hz, 1H), 3.96 – 3.91 (m, 2H), 3.88 (at, *J* = 9.4 Hz, 1H), 3.83 (s, 1H), 3.70 (td, *J* = 9.2, 3.3 Hz, 2H), 3.55 (d, *J* = 1.0 Hz, 1H), 3.54 – 3.46 (m, 3H), 2.50 (s, 1H), 1.87 – 1.65 (m, 7H), 1.53 – 1.45 (m, 5H).

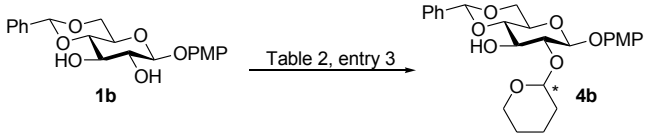
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.02, 137.85, 133.68, 133.44, 131.33, 130.90, 128.96, 128.89, 128.87, 128.72, 128, 76.99, 76.74, 76.30, 73.67, 70.24, 70.06, 69.39, 69.31, 66.88, 66.19, 64.10, 62.58, 30.82, 30.57, 25.33, 24.92, 20.24, 19.38.

IR (film, cm^{-1}) 3410, 2927, 2848, 1583, 1454, .05, 127.94, 127.78, 126.49, 126.42, 101.28, 101.01, 100.94, 98.40, 87.40, 87.05, 80.58, 80.10, 77.251436, 1357, 1266, 1161, 1097, 1071, 1025, 900. **HRMS(ESI)** Calc. for $C_{24}H_{28}O_6S$ Na(M + Na) : 467.1499; found : 467.1514; **[α]$^{26}_D$** = –9.0° (*c* 0.07, CH_2Cl_2).

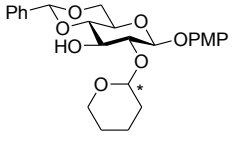


4a (Reaction)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 2H), 7.55 – 7.49 (m, 2H), 7.49 – 7.44 (m, 1H), 7.43 – 7.33 (m, 3H), 7.33 – 7.25 (m, 4H), 5.56 (s, 0.7H), 5.54 (s, 0.3H), 5.52 (s, 0.02H), 5.36 (at, *J* = 4.6 Hz, 0.04H), 5.13 (dd, *J* = 4.7, 3.1 Hz, 0.3H), 4.66 – 4.59 (m, 2H), 4.57 (d, *J* = 9.4 Hz, 0.05H), 4.40 (dd, *J* = 12.4, 1.6 Hz, 1H), 4.36 (d, *J* = 1.4 Hz, 0.2H), 4.32 (d, *J* = 2.8 Hz, 0.7H), 4.27 (d, *J* = 2.6 Hz, 0.02H), 4.26 – 4.21 (m, 1H), 4.17 (dt, *J* = 11.4, 5.9 Hz, 0.3H), 4.07 (dd, *J* = 12.4, 1.6 Hz, 0.7H), 4.03 (dd, *J* = 12.4, 1.6 Hz, 0.4H), 3.95 (t, *J* = 9.2 Hz, 1H), 3.89 (d, *J* = 8.8 Hz, 0.04H), 3.77 (at, *J* = 9.2 Hz, 1H), 3.71 (ddd, *J* = 9.1, 3.4, 1.3 Hz, 0.7H), 3.57 – 3.47 (m, 1H), 3.44 – 3.34 (m, 0.7H), 2.92 (d, *J* = 9.0 Hz, 0.3H), 1.97 – 1.94 (m, 1H), 1.91 – 1.79 (m, 1H), 1.79 – 1.72 (m, 0.3H), 1.71 – 1.60 (m, 0,6H), 1.59 – 1.42 (m, 4H), 1.27 – 1.24 (m, 1H).



Diol **1b** was prepared according to the known literature procedure by Bundle *et al*.[4] Using glucose diol **1b** (20 mg, 0.056 mmol, 1 equiv.) as the starting material, synthesis of **4b** was accomplished by following general procedure I. This product was then purified by flash column chromatography (2/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **4b** as a pale yellow oil (13.2 mg, 54 %), and as a 6:1 mixture of diastereoisomers.



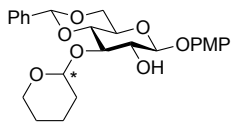
4b (C_2 Standard)

4. Bundle *et al*. *J. Org. Chem*. **2005**, *65*, 3064 – 3073.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 3H), 7.41 – 7.32 (m, 5H), 7.03 – 6.98 (m, 3H), 6.88 – 6.83 (m, 3H), 5.59 (s, 1H), 4.94 (d, *J* = 10.0Hz, 1H), 4.70 (d, *J* = 5.0 Hz, 1H), 4.58 (s, 1H), 4.38 (dd, *J* = 12.8, 6.4 Hz, 1H), 4.08 (at, *J* = 5.0 Hz, 1H), 4.05 (at, *J* = 5.0 Hz, 1H), 3.90 – 3.82 (m, 3H), 3.80 (s, 4H), 3.70 – 3.64 (m, 3H), 3.62 (td, *J* = 9.8, 5.1 Hz, 2H), 3.55 (td, *J* = 9.8, 5.1 Hz, 2H), 1.64 – 1.56 (m, 8H), 1.22 – 1.17 (m, 11H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 155.4, 151.5, 151.3, 137.0, 136.9, 129.2, 129.1, 128.4, 128.3, 128.2, 126.3, 126.32, 128.2, 126.3, 126.25, 118.9, 118.6, 118.4, 114.6, 114.57, 114.5, 102.4, 102.2, 101.8, 101.8, 101.79, 101.5, 98.6, 83.8, 80.5, 80.5, 80.3, 77.3, 77.0, 76.7, 74.1, 73.2, 72.1, 68.7, 68.7, 66.2, 66.0, 65.4, 63.3, 55.6, 31.1, 30.3, 29.7, 25.3, 24.9, 21.1, 19.6.

IR (film, cm^{-1}) 3407, 2932, 2857, 1652, 1507, 1456, 1386, 1220, 1073, 1022. **HRMS(ESI)** Calc. for $C_{25}H_{30}O_8$ Na (M + Na) : 481.1833; found : 481.1852; **$[\alpha]^{26}_D$** = – 0.8° (*c* 0.5, CH_2Cl_2).

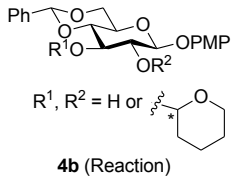


4b (C_3 Standard)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 3H), 7.42 – 7.31 (m, 5H), 7.08 – 6.97 (m, 3H), 6.88 – 6.78 (m, 4H), 5.58 (s, 1H), 5.56 (s, 1H), 5.11 (at, *J* = 3.8 Hz, 1H), 4.94 (d, *J* = 7.5 Hz, 1H), 4.89 (d, *J* = 7.8 Hz, 1H), 4.66 (s, 1H), 4.63 – 4.59 (m, 1H), 4.57 (s, 1H), 4.37 (dt, *J* = 10.3, 5.1 Hz, 2H), 4.09 – 4.05 (m, 1H), 4.05 – 3.99 (m, 2H), 3.84 – 3.82 (m, 1H), 3.81 – 3.79 (m, 1H), 3.78 (s, 2H), 3.77 (s, 3H), 3.73 (d, *J* = 7.6 Hz, 1H), 3.68 (td, *J* = 11.0, 10.0, 2.0 Hz, 2H), 3.56 – 3.47 (m, 4H), 1.92 – 1.80 (m, 5H), 1.77 – 1.65 (m, 5H), 1.59 – 1.51 (m, 8H).

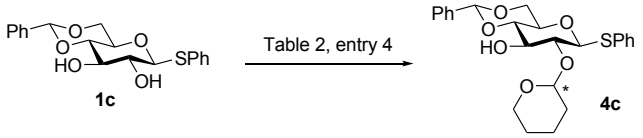
^{13}C NMR (125 MHz, $CDCl_3$) δ 155.6, 155.5 151.1, 151.0, 137.23, 137.2, 129.0, 128.9, 128.2, 128.1, 126.0, 125.99, 118.9, 118.8, 118.7, 114.6, 114.5, 103.0, 102.8, 102.2, 101.4, 101.3, 98.3, 82.9, 79.1,, 79.0, 77.3, 77.0, 76.7, 75.8, 74.9, 73.0, 68.7, 68.7, 68.66, 67.0, 66.6, 65.3, 62.9, 55.6, 55.60, 31.0, 30.2, 25.3, 24.9, 21.1, 19.5.

IR (film, cm^{-1}) 3407, 2932, 2857, 1652, 1507, 1456, 1386, 1220, 1073, 1022. **HRMS(ESI)** Calc. for $C_{25}H_{30}O_8$ Na (M + Na) : 481.1833; found : 481.1843; $[\alpha]^{26}_D$ = – 25.8° (*c* 0.11, CH_2Cl_2).

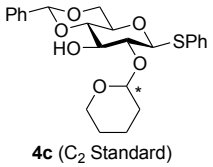


4b (Reaction)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 4H), 7.42 – 7.33 (m, 6H), 7.09 – 7.05 (m, 0.3H), 7.05 – 6.99 (m, 4H), 6.88 – 6.83 (m, 4H), 5.59 (s, 1H), 5.58 (s, 1H), 5.57 (s, 0.7H), 5.17 (at, *J* = 5.0 Hz, 0.7H), 5.13 (at, *J* = 3.9 Hz, 0.1H), 5.03 – 4.99 (m, 0.7H), 4.95 (d, *J* = 7.6 Hz, 1H), 4.91 (d, *J* = 7.8 Hz, 0.1H), 4.73 – 4.69 (m, 1H), 4.67 (s, 0.1H), 4.62 (dd, *J* = 10.0, 5.0 Hz, 0.1H), 4.59 (s, 1H), 4.38 (dd, *J* = 10.0, 5.0 Hz, 2H), 4.11 – 4.02 (m, 2H), 3.99 – 3.92 (m, 1H), 3.90 – 3.82 (m, 3H), 3.80 (s, 3H), 3.80 (s, 3H), 3.79 (s, 1H), 3.76 – 3.70 (m, 0.5H), 3.69 – 3.64 (m, 3H), 3.63 – 3.58 (m, 2H), 3.58 – 3.52 (m, 2H), 3.19 (d, *J* = 1.5 Hz, 1H), 3.08 (d, *J* = 2.3 Hz, 1H), 1.93 – 1.82 (m, 3H), 1.81 – 1.71 (m, 2H), 1.58 – 1.49 (m, 5H).



Compound **4c** was prepared according to general procedure II, using glucose diol **1c**[5] (20 mg, 0.056 mmol, 1 equiv.) as the starting material. Crude **4c** was purified by flash column chromatography (5/2 Hexanes/Ethyl acetate + 1% triethylamine) to afford pure **4c** as a pale yellow oil (21.5 mg, 86 %), and as an 11:1 diastereoisomeric mixture.



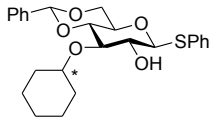
4c (C_2 Standard)

5. Soumik *et al*. *Carbohydr. Res*. **2008**, *343*, 2523 – 2529.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 5H), 7.37 – 7.29 (m, 6H), 5.56 (s, 1H), 5.53 (s, 1H), 5.10 (dd, *J* = 5.7, 2.8 Hz, 1H), 4.89 (s, 1H), 4.78 (d, *J* = 9.8 Hz, 1H), 4.73 (d, *J* = 9.8 Hz, 1H), 4.57 (s, 1H), 4.46 (d, *J* = 7.3 Hz, 1H), 4.40 – 4.32 (m, 2H), 4.19 – 4.10 (m, 2H), 3.96 – 3.92 (m, 2H), 3.81 – 3.79 (m, 1H), 3.75 (dd, *J* = 9.1, 7.7 Hz, 2H), 3.64 (s, 1H), 3.59 – 3.55 (m, 2H), 3.53 – 3.47 (m, 2H), 3.38 (at, *J* = 8.2 Hz, 2H), 3.33 (d, *J* = 1.9 Hz, 1H), 1.86 – 1.80 (m, 4H), 1.70 – 1.66 (m, 2H), 1.52 – 1.48 (m, 5H), 1.29 – 1.27 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.9, 133.2, 132.2, 132.2, 129.2, 129.0, 128.9, 128.3, 128.2, 128.0, 127.7, 126.3, 126.2, 102.7, 101.8, 101.8, 98.7, 87.4, 86.9, 83.3, 80.4, 80.3, 80.3, 77.0, 76.7, 76.5, 75.2, 73.4, 70.2, 70.1, 68.6, 65.5, 64.2, 31.9, 31.0, 30.6, 29.7, 25.2, 24.8, 21.1, 20.1, 14.1.

IR (film, cm^{-1}) 3376, 2927, 2848,1634, 1652, 1557, 1540, 1456, 1438, 1415, 1086, 1075, 1029. **HRMS(ESI)** Calc. for $C_{24}H_{28}O_6SNa$ (M + Na) : 467.1499; found : 467.1516; **[α]$^{26}_D$** = –3.3° (*c* 0.03, CH_2Cl_2).

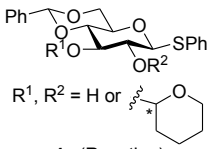


4c (C_3 Standard)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 4H), 7.50 – 7.43 (m, 4H), 7.40 – 7.27 (m, 12H), 5.55 (s, 1H), 5.53 (s, 1H), 5.08 (at, *J* = 4.0 Hz, 1H), 4.83 (s, 1H), 4.67 (d, *J* = 9.7 Hz, 1H), 4.63 (d, *J* = 9.8 Hz, 1H), 4.58 – 4.53 (m, 2H), 4.38 (dd, *J* = 10.5, 4.9 Hz, 2H), 4.08 – 4.01 (m, 2H), 3.97 (t, *J* = 8.9 Hz, 1H), 3.78 (td, *J* = 10.1, 2.8 Hz, 2H), 3.71 (at, *J* = 8.4 Hz, 1H), 3.60 – 3.56 (m, 2H), 3.53 – 3.47 (m, 6H), 3.14 (d, *J* = 1.7 Hz, 1H), 1.87 – 1.82 (m, 3H), 1.72 – 1.67 (m, 2H), 1.53 – 1.50 (m, 5H), 1.27 – 1.25 (m, 3H).

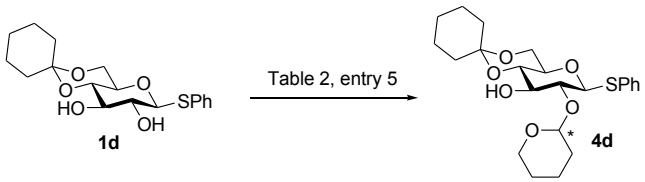
^{13}C NMR (125 MHz, $CDCl_3$) δ 137.24, 137.21, 133.1, 133.0, 132.1, 131.4, 129.0, 129.0, 128.96, 128.85, 128.3, 128.2, 128.1, 128.0, 126.0, 126.0, 125.97, 102.5, 101.3, 101.2, 98.3, 89.0, 88.3, 84.3, 79.1, 79.0, 77.3, 77.0, 76.7, 73.1, 71.4, 71.1, 70.8, 68.6, 68.6, 65.6, 62.9, 53.4, 31.0, 30.2, 29.7, 25.2, 24.8, 21.2, 19.5.

IR (film, cm^{-1}) 3398, 2931, 2853,, 1456, 1438, 1375, 1264, 1081, 1025, 908. **HRMS(ESI)** Calc. for $C_{24}H_{28}O_6SNa$ (M + Na) : 467.1499; found : 467.1518; **[α]$^{26}_D$** = –10.1° (*c* 0.08, CH_2Cl_2).

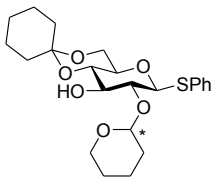


4c (Reaction)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.42 (m, 6H), 7.37 – 7.27 (m, 8H), 5.54 (s, 1H), 5.53 (s, 0.1H), 5.51 (s, 0.3H), 5.09 (dd, *J* = 5.7, 2.7 Hz, 0.2H), 5.06 (at, *J* = 3.9 Hz, 0.07H), 4.87 (s, 1H), 4.80 (s, 0.1H), 4.76 (d, *J* = 9.8 Hz, 0.2H), 4.71 (d, *J* = 9.8 Hz, 1H), 4.65 (d, *J* = 9.7 Hz, 0.2H), 4.61 (d, *J* = 9.8 Hz, 0.1H), 4.54 (d, *J* = 5.9 Hz, 0.2H), 4.48 – 4.42 (m, 1H), 4.36 (dd, *J* = 10.5, 4.9 Hz, 1H), 4.32 (d, *J* = 4.8 Hz, 0.2H), 4.17 – 4.09 (m, 0.2H), 4.03 – 3.96 (m, 1H), 3.95 – 3.89 (m, 0.2H), 3.83 – 3.73 (m, 3H), 3.72 – 3.68 (m, 0.2H), 3.59 – 3.42 (m, 5H), 3.38 (dd, *J* = 9.6, 8.3 Hz, 1H), 3.31 (s, 0.2H), 3.11 (s, 0.1H), 1.93 – 1.78 (m, 3H), 1.71 – 1.64 (m, 0.4H), 1.53 – 1.48 (m, 2H), 1.26 – 1.21 (m, 3H).



Compound **4d** was prepared using general procedure II with glucose diol **1d** (20 mg, 0.056 mmol, 1 equiv.) as starting material. Crude **4d** was purified by flash column chromatography (2/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford pure **4d** as a pale yellow oil (20.5 mg, 82%), and as a 6:1 diastereoisomeric mixture.



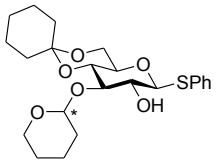
4d (C_2 Standard)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 3H), 7.35 – 7.26 (m, 5H), 5.10 (dd, *J* = 5.5, 2.7 Hz, 1H), 4.81 (s, 1H), 4.72 (d, *J* = 9.6 Hz, 1H), 4.66 (d, *J* = 9.8 Hz, 1H), 4.45 – 4.40 (m, 1H), 4.18 – 4.11 (m, 1H), 4.00 (d, *J* = 10.5 Hz, 1H), 3.96 – 3.89 (m, 2H), 3.81 – 3.75 (m, 2H), 3.69 (dd, *J* = 16.8, 8.4 Hz, 1H), 3.63 (dd, *J* = 10.4, 8.2 Hz, 1H), 3.60 – 3.48

(m, 3H), 3.36 – 3.27 (m, 3H), 3.22 (s, 1H), 2.06 – 1.99 (m, 1H), 1.97 – 1.77 (m, 7H), 1.70 – 1.56 (m, 10H), 1.48 – 1.40 (m, 6H), 1.27 – 1.23 (m, 6H), 0.90 – 0.84 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 133.4, 133.0, 132.1, 132.0, 129.0, 128.8, 127.83, 127.5, 102.7, 99.8, 99.7, 98.6, 87.3, 86.8, 83.4, 77.2, 77.0, 76.7, 76.4, 75.8, 73.9, 72.1, 72.0, 71.4, 71.2, 65.5, 64.1, 61.3, 61.3, 37.8, 37.8, 31.0, 30.6, 29.7, 29.6, 29.3, 27.7, 27.7, 25.6, 25.5, 25.2, 24.8, 22.9, 22.6, 22.5, 21.1, 20.0.

IR (film, cm^{-1}) 3424, 2932, 2853, 1439, 1364, 1270, 1101, 1075, 1025, 921, 906. **HRMS(ESI)** Calc. for $C_{23}H_{32}O_6SNa$ (M + Na) : 459.1812; found : 459.1821; $[\alpha]^{26}_D$ = – 22.2° (*c* 0.104, CH_2Cl_2).

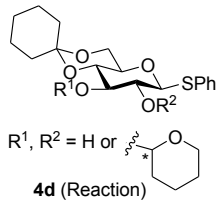


4d (C_3 Standard)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 3H), 7.34 – 7.26 (m, 4H), 5.13 (at, *J* = 3.6 Hz, 1H), 4.60 (d, *J* = 6.3 Hz, 1H), 4.56 (d, *J* = 9.8 Hz, 1H), 4.50 (s, 1H), 4.19 – 4.12 (m, 1H), 4.05 – 3.99 (m, 1H), 3.97 – 3.90 (m, 2H), 3.84 – 3.76 (m, 3H), 3.61 – 3.53 (m, 3H), 3.53 – 3.47 (m, 1H), 3.46 – 3.27 (m, 4H), 3.01 (d, *J* = 1.9 Hz, 1H), 2.25 – 2.10 (m, 2H), 1.91 – 1.75 (m, 3H), 1.72 – 1.45 (m, 22H), 1.40 – 1.25 (m, 4H).

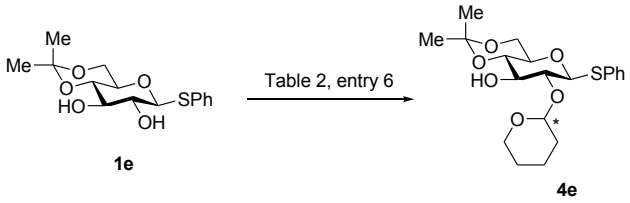
^{13}C NMR (125 MHz, $CDCl_3$) δ 133.0, 132.9, 132.2, 131.5, 129.0, 128.1, 128.2, 127.9, 102.2, 99.7, 99.6, 97.4, 88.9, 88.2, 84.3, 77.2, 77.0, 76.7, 73.4, 72.3, 72.0, 71.4, 71.3, 70.9, 65.3, 62.4, 61.6, 61.6, 37.9, 37.8, 31.1, 30.2, 29.7, 27.8, 27.7, 25.6, 25.6, 25.4, 24.9, 22.9, 22.7, 22.4, 22.4, 21.1, 19.2.

IR (film, cm^{-1}) 3407, 2936, 2862, 1584, 1481, 1439, 1362, 1264, 1172, 1156, 1106, 1075, 1025, 968. **HRMS(ESI)** Calc. for $C_{23}H_{32}O_6SNa$ (M + Na) : 459.1812; found : 459.1827; $[\alpha]^{26}_D$ = –22.2° (*c* 0.122, CH_2Cl_2).



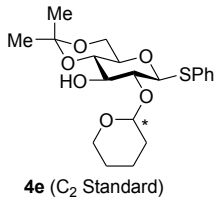
4d (Reaction)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.44 (m, 4H), 7.35 – 7.25 (m, 5H), 5.11 (at, *J* = 3.6 Hz, 0.1H), 5.08 (dd, *J* = 5.6, 2.8 Hz, 0.4H), 4.80 (s, 1H), 4.70 (d, *J* = 9.6 Hz, 0.4H), 4.64 (d, *J* = 9.8 Hz, 1H), 4.59 (d, *J* = 9.7 Hz, 0.3H), 4.54 (d, *J* = 9.8 Hz, 0.1H), 4.49 (s, 0.2H), 4.43 – 4.38 (m, 1H), 4.17 – 4.09 (m, 0.5H), 4.01 – 3.95 (m, 1H), 3.93 (dd, *J* = 10.8, 5.5 Hz, 1H), 3.90 – 3.86 (m, 0.4H), 3.83 – 3.71 (m, 2H), 3.71 – 3.65 (m, 0.4H), 3.65 – 3.58 (m, 2H), 3.58 – 3.45 (m, 3H), 3.44 – 3.35 (m, 0.4H), 3.35 – 3.25 (m, 3H), 3.22 (s, 0.3H), 2.99 (s, 0.1H), 2.04 – 1.97 (m, 1H), 1.94 – 1.73 (m, 5H), 1.71 – 1.59 (m, 5H), 1.54 – 1.48 (m, 7H), 1.45 – 1.38 (m, 4H), 1.27 – 1.23 (m, 3H).



1e **4e**

Compound **4e** was prepared according to general procedure II, using glucose diol **1e** (20 mg, 0.056 mmol, 1 equiv.) as the starting material. Crude product **4e** was purified by flash column chromatography (2/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford pure **4e** as a pale yellow oil (19.5 mg, 77 %), and as a 10:1 diastereoisomeric mixture.



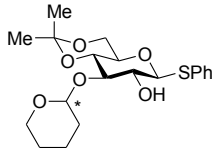
4e (C_2 Standard)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 3H), 7.35 – 7.26 (m, 4H), 7.26 (s, 1H), 5.06 (dd, *J* = 6.0, 2.6 Hz, 1H), 4.87 (s, 1H), 4.73 (d, *J* = 9.6 Hz, 1H), 4.67 (d, *J* = 9.8 Hz, 1H), 4.43 (d, *J* = 7.3 Hz, 1H), 4.13 (dd, *J* = 10.8, 5.1 Hz, 1H), 4.00 (d, *J* = 10.4 Hz, 1H), 3.94 (ddd, *J* = 16.2, 10.8, 5.4 Hz, 2H), 3.85 – 3.73 (m, 2H), 3.73 – 3.68 (m, 1H), 3.67 –

3.62 (m, 1H), 3.62 – 3.46 (m, 4H), 3.45 – 3.22 (m, 4H), 1.96 – 1.76 (m, 4H), 1.70 – 1.56 (m, 4H), 1.52 (s, 3H), 1.50 (s, 2H), 1.45 (s, 3H), 1.42 (s, 2H), 1.25 (s, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 133.4, 133.0, 132.1, 131.9, 129.0, 128.8, 127.9, 127.6, 102.8, 99.7, 99.6, 98.6, 87.35, 86.8, 83.4, 77.2, 77.0, 76.73, 76.5, 75.4, 73.8, 73.0, 72.95, 71.1, 71.0, 65.6, 64.5, 62.0, 31.2, 30.6, 29.7, 29.0, 25.2, 24.8, 21.1, 20.3, 19.1, 19.0.

IR (film, cm^{-1}) 3424, 2923, 2853, 1584, 1481, 1437, 1375, 1264, 1200, 1165, 1128, 1075, 1027, 858. **HRMS(ESI)** Calc. for $C_{20}H_{28}O_6SNa$ (M + Na) : 419.1499; found : 419.1509; **$[\alpha]^{26}_D$** = –16.4° (*c* 0.1, CH_2Cl_2).

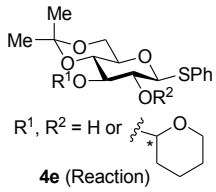


4e (C_3 Standard)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.47 (m, 3H), 7.36 – 7.27 (m, 4H), 5.02 (at, *J* = 3.8 Hz, 1H), 4.72 (s, 1H), 4.62 (at, *J* = 7.0 Hz, 1H), 4.57 (d, *J* = 9.8 Hz, 1H), 4.53 (d, *J* = 6.0 Hz, 1H), 4.11 – 4.05 (m, 1H), 4.02 (dd, *J* = 14.3, 3.1 Hz, 1H), 3.98 – 3.92 (m, 2H), 3.80 – 3.73 (m, 3H), 3.55 (ddd, *J* = 17.0, 15.2, 8.7 Hz, 3H), 3.50 – 3.44 (m, 2H), 3.43 – 3.37 (m, 1H), 3.37 – 3.31 (m, 1H), 3.28 (dt, *J* = 16.1, 7.8 Hz, 1H), 3.04 (s, 1H), 1.88 – 1.74 (m, 3H), 1.74 – 1.60 (m, 4H), 1.59 – 1.50 (m, 5H), 1.47 (d, *J* = 6.5 Hz, 3H), 1.46 (s, 2H), 1.39 (s, 3H), 1.38 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 132.9, 132.8, 132.3, 131.7, 129.0, 128.8, 128.2, 127.9, 102.3, 99.6, 99.5, 99.5, 98.1, 89.0, 88.3, 84.4, 77.7, 77.3, 77.0, 76.8, 76.6, 73.1, 72.1, 72.1, 71.8, 71.6, 71.5, 65.5, 62.6, 62.2, 62.2, 31.0, 30.7, 30.2, 29.1, 29.0, 25.4, 25.4, 24.9, 21.2, 19.5, 19.2, 19.1.

IR (film, cm^{-1}) 3407, 2993, 2941, 2884, 1584, 1481, 1441, 1375, 1264, 1202, 1171, 1119, 1079, 1024, 970 908. **HRMS(ESI)** Calc. for $C_{20}H_{28}O_6SNa$ (M + Na) : 419.1499; found : 419.1511; **$[\alpha]^{26}_D$** = –124.9° (*c* 0.12, CH_2Cl_2).



4e (Reaction)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 3H), 7.33 – 7.25 (m, 4H), 5.04 (dd, *J* = 6.0, 2.7 Hz, 0.2H), 5.01 (s, 1H), 4.85 (s, 0.7H), 4.71 (d, *J* = 9.6 Hz, 0.3H), 4.65 (d, *J* = 9.8 Hz, 1H), 4.55 (d, *J* = 9.8 Hz, 0.03H), 4.44 – 4.39 (m, 1H), 4.11 (dd, *J* = 9.8, 5.7 Hz, 0.3H), 4.01 – 3.96 (m, 1H), 3.94 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.92 – 3.88 (m, 0.2H), 3.81 – 3.72 (m, 2H), 3.71 – 3.66 (m, 0.2H), 3.65 – 3.56 (m, 2H), 3.56 – 3.47 (m, 2H), 3.45 – 3.40 (m, 0.07H), 3.36 – 3.24 (m, 2H), 1.94 – 1.81 (m, 2H), 1.78 (dd, *J* = 11.9, 8.7 Hz, 0.4H), 1.68 – 1.62 (m, 0.5H), 1.61 – 1.52 (m, 3H), 1.50 (s, 4H), 1.47 (d, *J* = 6.8 Hz, 1H), 1.43 (s, 3H), 1.40 (s, 1H), 1.27 – 1.20 (m, 2H).

III. Regioselective Acetalization (Table 3)

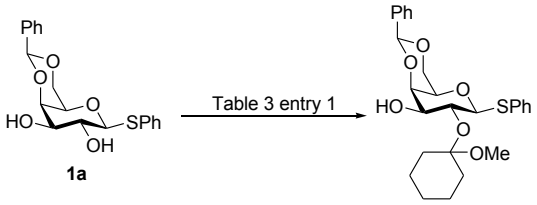
General Procedure A.

An oven dried and nitrogen flushed 10 mL round bottom flask was charged with thioglycoside diol **1** (1 equiv.), (which was previously dried by azeotropic removal of moisture with toluene)**,** anhydrous dichloromethane resulting in 0.04 M concentration, and activated 4Å molecular sieves. This mixture was submerged in a dry ice/acetone bath and 1-methoxycyclohexene (1.2 equiv.) was added, followed by (*R*)-**2d** (2 mol %). The resulting reaction mixture was transferred into a Neslab CB 80 immersion cooler and stirred at –50 °C overnight. When the reaction was completed as indicated by TLC, the reaction mixture was quenched with triethylamine, and concentrated *in vacuo* to form the crude product. This crude product was purified by flash column chromatography to afford pale yellow oil.

General Procedure B

An oven dried and nitrogen flushed 10 mL round bottom flask was charged with thioglycoside diol **1** (1 equiv.), (which was previously dried by azeotropic removal of moisture with toluene)**,** anhydrous dichloromethane resulting in 0.04 M concentration and activated 4Å molecular sieves. This mixture was submerged in a dry ice/acetone bath and 2-methoxypropene (1.2 equiv.) followed by (*R*)-**2d** (2 mol%) was added. The resulting

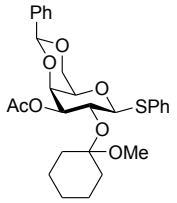
reaction mixture was transferred into a Neslab CB 80 immersion cooler and stirred at –78 °C overnight. When the reaction was completed as indicated by TLC, the reaction mixture was quenched with triethylamine, and concentrated *in vacuo* to form the crude product. This crude product was purified by flash column chromatography to afford pale yellow oil.



Using galactose diol **1a**[3] (20 mg, 0.056 mmol, 1 equiv.) as the starting material, synthesis of **5a-I** was accomplished by following general procedure A. This product was purified by flash column chromatography (1/1 Hexanes/Ethyl acetate + 2% triethylamine) to afford **5a-I** as a pale yellow oil (20.5 mg, 76 %, C2:C3 = 10:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.67 – 7.61 (m, 2H), 7.60 – 7.55 (m, 2H), 7.45 – 7.35 (m, 3H), 7.27 – 7.19 (m, 3H), 5.64 (s, 1H), 4.72 (d, *J* = 9.3 Hz, 1H), 4.34 (dd, *J* = 3.5, 0.7 Hz, 1H), 4.24 (dd, *J* = 12.4, 1.6 Hz, 1H), 4.17 – 4.08 (m, 2H), 3.73 (dd, *J* = 8.8, 3.5 Hz, 1H), 3.62 (d, *J* = 1.0 Hz, 1H), 3.34 (s, 3H), 1.94 – 1.81 (m, 1H), 1.75 – 1.63 (m, 3H), 1.49 – 1.43 (m, 1H), 1.40 – 1.34 (m, 3H), 1.26 – 1.23 (m, 1H), 0.93 – 0.86 (m, 1H).
^{13}C NMR (125 MHz, CD_3OD) δ 138.3, 134.0, 130.9, 128.5, 128.5, 127.7, 126.6, 126.2, 101.5, 100.9, 85.8, 75.4, 73.5, 69.97, 69.5, 68.8, 48.1, 47.9, 47.8, 47.6, 47.4, 47.2, 47.1, 47.0, 33.0, 32.7, 24.8, 22.3, 22.2.
IR (film, cm^{-1}) 3371, 2927, 2857, 1581 1456, 1367, 1263, 1158, 1101, 1042, 1027, 998.
HRMS(ESI) Calc. for $C_{26}H_{32}O_6SNa$ (M + Na) : 495.1812; found : 495.1814; $[\alpha]^{26}_D$ = – 36.6° (*c* 0.32, CH_2Cl_2).

Determination of the C2/C3 ratios was performed by acetylating the crude reaction mixture and analyzing the COSY NMR spectrum of the acetylated **5a-I** (acetylation result in significant shift of the proton next to the acetoxy group to 4.2-4.6 ppm region).



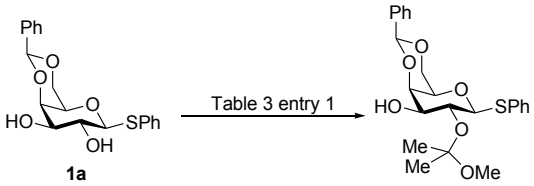
5a-I-Ac

R_f = 0.3 (Hexane/Ethyl acetate, 2/1 + 1% Triethylamine)

^{1}H NMR (500 MHz, CD_3OD) δ 7.69 – 7.64 (m, 2H), 7.62 – 7.57 (m, 1H), 7.56 – 7.50 (m, 2H), 7.49 – 7.35 (m, 6H), 7.31 – 7.17 (m, 5H), 5.59 (s, 1H), 5.59 (s, 0.4H), 5.19 (at, *J* = 9.8 Hz, 0.4H), 5.00 (dd, *J* = 9.1, 3.7 Hz, 1H), 4.85 (d, *J* = 9.3 Hz, 0.4H), 4.76 (d, *J* = 9.3 Hz, 1H), 4.39 (d, *J* = 3.0 Hz, 0.4H), 4.37 (dd, *J* = 3.7, 0.8 Hz, 1H), 4.30 (t, *J* = 9.8 Hz, 1H), 4.27 – 4.21 (m, 2H), 4.16 – 4.08 (m, 2H), 3.70 (d, *J* = 1.0 Hz, 1H), 3.68 (d, *J* = 1.0 Hz, 0.4H), 3.25 (s, 0.3H), 3.22 (s, 1H), 3.12 (s, 3H), 2.08 (s, 1H), 2.07 (s, 3H), 1.89 – 1.83 (m, 1H), 1.78 – 1.74 (m, 1H), 1.63 – 1.58 (m, 2H), 1.54 – 1.47 (m, 2H), 1.44 – 1.37 (m, 4H), 1.31 – 1.29 (m, 3H), 1.17 – 1.11 (m, 2H), 0.92 – 0.86 (m, 2H).

^{13}C NMR (125 MHz, CD_3OD) δ 170.7, 169.9, 138.2, 133.8, 132.4, 131.1, 128.6, 128.5, 128.4, 128.4, 127.7, 127.62, 127.2, 126.6, 126.2, 126.1, 117.7, 101.8, 101.4, 101.0, 100.7, 86.5, 85.1, 75.8, 75.5, 74.7, 74.2, 71.0, 69.7, 69.5, 68.9, 68.7, 68.0, 66.4, 33.5, 33.3, 33.2, 33.0, 25.0, 22.7, 22.6, 22.4, 22.2, 19.8, 19.8.

IR (film, cm^{-1}) 2927, 2857, 1748, 1452, 1371, 1239, 1167, 1095, 1055. **HRMS(ESI)** Calc. for $C_{28}H_{34}O_7SNa$ (M + Na) : 537.1917; found : 537.1923; **$[\alpha]^{26}_D$** = 9.6° (*c* 0.18, CH_2Cl_2).



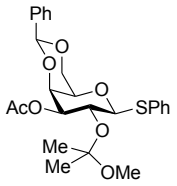
1a **5a-II**

Using galactose diol **1a**[3] (20 mg, 0.056 mmol, 1 equiv.) as the starting material, preparation of **5a-II** was accomplished by following general procedure B. This product

was purified by flash column chromatography (1/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **5a-II** as a pale yellow oil (22.2 mg, 93%, C2:C3 = 20:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 2H), 7.54 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.42 – 7.33 (m, 3H), 7.25 – 7.18 (m, 3H), 5.58 (s, 1H), 5.16 (s, 1H), 4.60 (d, *J* = 9.3 Hz, 1H), 4.37 (dd, *J* = 12.3, 1.1 Hz, 1H), 4.31 (d, *J* = 3.2 Hz, 1H), 4.17 – 4.02 (m, 2H), 3.65 (dd, *J* = 8.6, 3.0 Hz, 1H), 3.50 (s, 1H), 3.31 (s, 3H), 1.43 (s, 3H), 1.14 (d, *J* = 18.0 Hz, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 133.4, 131.7, 129.0, 128.8, 128.1, 127.1, 126.6, 101.9, 101.4, 86.0, 77.3, 77.0, 76.8, 75.4, 73.8, 70.9, 70.1, 69.3, 49.7, 25.0, 23.6.
IR (film, cm^{-1}) 3382, 2989, 2923, 2857, 1471, 1456, 1439, 1375, 1156, 1099, 1044.
HRMS(ESI) Calc. for $C_{23}H_{28}O_6SNa$ (M + Na) : 455.1499; found : 455.1509; $[\alpha]^{26}_D$ = – 5.4° (*c* 0.02, CH_2Cl_2).

Determination of the C2/C3 ratios was performed by acetylating the crude reaction mixture and analyzing the COSY NMR spectrum of the acetylated **5a-II.**



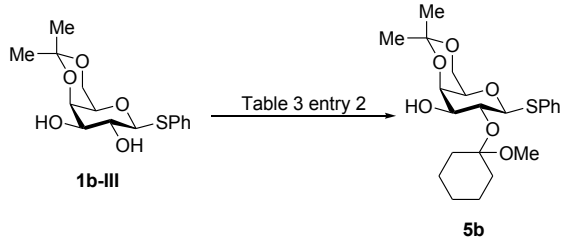
5a-II-Ac

R_f = 0.3 (Hexane/Ethyl acetate, 5/2 + 1% Triethylamine)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.63 (m, 2H), 7.56 – 7.49 (m, 2H), 7.46 – 7.37 (m, 3H), 7.25 – 7.18 (m, 3H), 5.51 (s, 1H), 4.92 (dd, *J* = 9.2, 3.6 Hz, 1H), 4.65 (d, *J* = 9.3 Hz, 1H), 4.38 (dd, *J* = 12.4, 1.5 Hz, 1H), 4.33 (d, *J* = 3.0 Hz, 1H), 4.26 (at, *J* = 9.3 Hz, 1H), 4.03 (dd, *J* = 12.4, 1.6 Hz, 1H), 3.57 (d, *J* = 0.8 Hz, 1H), 3.21 (s, 3H), 2.11 (s, 3H), 1.34 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8, 137.9, 133.3, 131.9, 129.0, 128.7, 128.1, 127.2, 126.4, 101.8, 100.9, 87.1, 77.3, 77.0, 76.7, 75.0, 74.0, 69.6, 69.1, 67.6, 49.1, 29.7, 25.4, 24.9, 21.2.

IR (film, cm^{-1}) 2984, 2923 2857, 1745, 1456, 1371, 1237, 1097, 1055. **HRMS(ESI)** Calc. for $C_{25}H_{30}O_7SNa$ (M + Na) : 497.1604; found : 497.1619; **$[\alpha]^{26}_D$** = –5.4° (*c* 0.25, CH_2Cl_2).



Using galactose diol **1b-III**[6] (20 mg, 0.064 mmol, 1 equiv.) as the starting material, synthesis of **5b** was accomplished by following general procedure A. This product was purified by flash column chromatography (2/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **5b** as a pale yellow oil (13.8 mg, 51%, C2:C3 = 25:1).

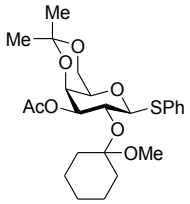
^{1}H NMR (500 MHz, C_6D_6) δ 7.83 – 7.74 (m, 2H), 7.09 – 7.01 (m, 2H), 6.97 – 6.90 (m, 1H), 5.09 (s, 1H), 4.51 (d, *J* = 9.2 Hz, 1H), 4.39 (at, *J* = 9.0 Hz, 1H), 3.93 (d, *J* = 3.4 Hz, 1H), 3.75 (dd, *J* = 12.6, 1.7 Hz, 1H), 3.45 (dd, *J* = 12.6, 2.1 Hz, 1H), 3.37 (ddd, *J* = 8.7, 3.4, 1.4 Hz, 1H), 3.03 (s, 3H), 2.51 (s, 1H), 1.77 – 1.66 (m, 2H), 1.64 – 1.57 (m, 1H), 1.53 (s, 4H), 1.31 (at, *J* = 16.9 Hz, 3H), 1.20 (s, 4H), 1.15 – 1.08 (m, 1H), 1.09 – 1.00 (m, 1H).

^{13}C NMR (125 MHz, C_6D_6) δ 134.8, 131.8, 128.6, 127.9, 127.8, 127.7, 127.5, 126.7, 101.5, 98.7, 86.3, 74.1, 70.2, 70.1, 68.3, 62.6, 47.2, 33.3, 33.2, 29.4, 25.1, 22.7, 22.4, 18.3.

IR (film, cm^{-1}) 3385, 2932, 2857, 1441, 1378, 1285, 1154, 1097, 1057, 1042. **HRMS(ESI)** Calc. for $C_{22}H_{32}O_6SNa$ (M + Na) : 447.1812; found : 447.1828; **$[\alpha]^{26}_D$** = 1.3° (*c* 0.08, CH_2Cl_2).

6. Pedretti *et al*. *Tetrahedron.* **1990**, *46*, 77 – 88.

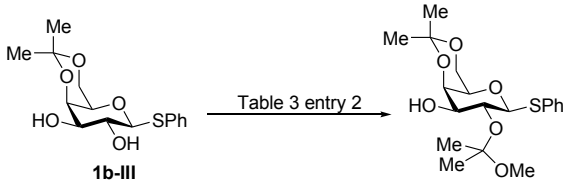
Determination of the C2/C3 ratios was performed by acetylating the crude reaction mixture and analyzing the COSY NMR spectrum of the acetylated **5b.**



5b-Ac

$\mathbf{R_f}$ = 0.3 (Hexane/Ethyl acetate, 2/1 + 1% Triethylamine)

^{1}H NMR (500 MHz, c_6d_6) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.10 – 7.04 (m, 3H), 6.99 – 6.92 (m, 1H), 4.94 (dd, *J* = 8.6, 3.6 Hz, 1H), 4.59 – 4.46 (m, 2H), 4.00 (d, *J* = 3.7 Hz, 1H), 3.67 (d, *J* = 12.6 Hz, 1H), 3.33 (d, *J* = 12.6 Hz, 1H), 3.14 (s, 3H), 2.47 (s, 1H), 2.00 – 1.91 (m, 1H), 1.88 (s, 3H), 1.87 – 1.80 (m, 1H), 1.65 – 1.59 (m, 1H), 1.47 (s, 3H), 1.40 – 1.36 (m, 2H), 1.34 – 1.24 (m, 5H), 1.23 – 1.18 (m, 1H), 1.09 (s, 3H), 1.06 – 0.99 (m, 1H).
^{13}C NMR (125 MHz, C_6D_6) δ 169.8, 134.5, 132.0, 128.6, 127.9, 127.8, 127.6, 127.5, 127.4, 126.8, 101.5, 98.4, 87.2, 74.8, 69.3, 67.2, 67.0, 62.3, 47.4, 33.8, 33.7, 29.8, 29.2, 25.4, 23.0, 20.7, 18.4.
IR (film, cm^{-1}) 2927, 2871, 1748, 1450, 1373, 1242, 1180, 1147, 1095, 1057, 974, 917.
HRMS(ESI) Calc. for $C_{24}H_{34}O_7SNa$ (M + Na) : 489.1917; found : 489.1930; $[\alpha]^{26}_D$ = 14.2° (*c* 0.127, CH_2Cl_2).

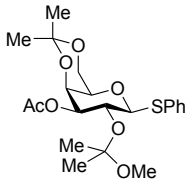


1b-III **5b-II**

Using galactose diol **1b-III**[6] (20 mg, 0.064 mmol, 1 equiv.) as the starting material, synthesis of **5b-II** was accomplished by following general procedure B. This product was purified by flash column chromatography (2/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **5b-II** as a pale yellow oil (20.6 mg, 84%, C2:C3 = 20:1).

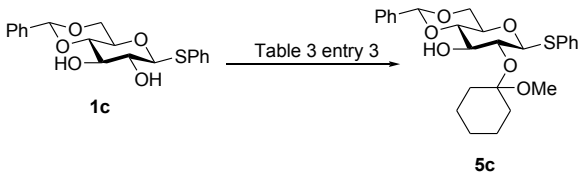
^{1}H NMR (500 MHz, C_6D_6) δ 7.84 – 7.77 (m, 2H), 7.11 – 7.04 (m, 2H), 6.99 – 6.92 (m, 1H), 4.98 (d, *J* = 1.3 Hz, 1H), 4.50 (d, *J* = 9.3 Hz, 1H), 4.35 (at, *J* = 9.0 Hz, 1H), 3.91 (d, *J* = 2.8 Hz, 1H), 3.75 (dd, *J* = 12.6, 1.7 Hz, 1H), 3.48 – 3.40 (m, 2H), 2.90 (s, 3H), 2.49 (d, *J* = 0.9 Hz, 1H), 1.54 (s, 3H), 1.22 (s, 3H), 1.20 (s, 3H), 1.09 (s, 3H).
^{13}C NMR (125 MHz, C_6D_6) δ 134.7, 131.6, 128.6, 127.8, 127.6, 127.4, 126.7, 101.7, 98.4, 86.2, 74.0, 71.4, 69.9, 68.2, 62.6, 49.1, 29.8, 29.4, 24.8, 23.3, 18.3.
IR (film, cm^{-1}) 3398, 2989, 2923, 1486, 1380, 1277, 1200, 1141, 1096, 1055, 1042.
HRMS(ESI) Calc. for $C_{19}H_{28}O_8SNa$ (M + Na) : 407.1499; found : 407.1512; **$[\alpha]^{26}_D$** = – 0.42° (*c* 0.24, CH_2Cl_2).

Determination of the C2/C3 ratios was performed by acetylating the crude reaction mixture and analyzing the COSY NMR spectrum of the acetylated **5b-II.**



5b-II-Ac

^{1}H NMR (500 MHz, C_6D_6) δ 7.85 – 7.75 (m, 2H), 7.11 – 7.04 (m, 2H), 6.99 – 6.93 (m, 1H), 4.94 (dd, *J* = 9.0, 3.7 Hz, 1H), 4.51 (d, *J* = 9.3 Hz, 1H), 4.44 (at, *J* = 9.1 Hz, 1H), 3.98 (dd, *J* = 3.5, 0.5 Hz, 1H), 3.66 (dd, *J* = 12.5, 2.0 Hz, 1H), 3.32 (dd, *J* = 12.5, 2.0 Hz, 1H), 3.18 (s, 3H), 2.45 (d, *J* = 0.9 Hz, 1H), 1.86 (s, 3H), 1.45 (s, 3H), 1.34 (s, 3H), 1.19 (s, 3H), 1.07 (s, 3H).
^{13}C NMR (125 MHz, C_6D_6) δ 169.7, 134.4, 132.0, 128.6, 127.9, 127.8, 127.6, 127.4, 126.9, 101.6, 98.4, 87.1, 74.8, 69.3, 68.3, 67.2, 62.3, 52.9, 48.6, 29.8, 29.2, 25.3, 24.8, 20.6, 18.4.
IR (film, cm^{-1}) 2993, 2927 1745, 1441, 1380, 1244, 1202, 1180, 1147, 1093, 1058. .
HRMS(ESI) Calc. for $C_{21}H_{30}O_7SNa$ (M + Na) : 449.1604; found : 449.1610; **$[\alpha]^{26}_D$** = 10.7° (*c* 0.23, CH_2Cl_2).



Using diol **1c**[5] (20 mg, 0.056 mmol, 1 equiv.) as the starting material, preparation of **5c** was accomplished by following general procedure A. This product was purified by flash column chromatography (7/1 Hexanes/Ethyl acetate + 2% triethylamine) to afford **5c** as a pale yellow oil (18.6 mg, 69%, C2:C3 = 25:1).

Scaled up Synthesis of 5c

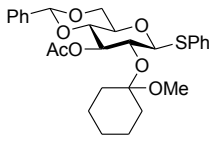
An oven dried and nitrogen flushed 250 mL round bottom flask was charged with thioglycoside diol **1c**[5] (1 g, 2.78 mmol, 1 equiv.), (which was previously dried by azeotropic removal of moisture with toluene)**,** anhydrous dichloromethane (65 mL) and activated 4Å molecular sieves. This mixture was submerged in dry ice/acetone bath and 1-methoxycylohexene (0.42 mL, 3.34 mmol, 1.2 equiv.) was added, followed by (*R*)-**2d** (52 mg, 0.056 mmol, 2 mol%). The resulting reaction mixture was transferred into a Neslab CB 80 immersion cooler and stirred at –50 °C. When the reaction was completed as monitored by TLC, the reaction mixture was quenched with triethylamine, filtered through celite, and concentrated *in vacuo* to form the crude product. The crude product was purified by flash column chromatography (7/1 Hexanes/Ethyl acetate + 2% triethylamine) to afford **5c** as a pale yellow foam (1.24 g, 95 %, C2:C3 = >25:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.76 (s, 0.02H), 7.56 – 7.52 (m, 0.1H), 7.51 – 7.43 (m, 5H), 7.41 – 7.30 (m, 6H), 7.29 – 7.23 (m, 1H), 5.59 (s, 1H), 5.54 (s, 0.02H), 4.85 (d, *J* = 8.5 Hz, 1H), 4.26 (dd, *J* = 10.0, 5.0 Hz, 1H), 3.83 – 3.71 (m, 3H), 3.59 (at, *J* = 9.2 Hz, 1H), 3.56 – 3.48 (m, 1H), 3.34 (s, 3H), 3.18 (s, 0.1H), 2.88 – 2.80 (m, 0.2H), 1.98 – 1.79 (m, 2H), 1.74 – 1.70 (m, 1H), 1.67 – 1.60 (m, 2H), 1.55 – 1.45 (m, 2H), 1.43 – 1.35 (m, 2H), 1.29 – 1.25 (m, 1H), 1.14 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (125 MHz, CD_3OD) δ 147.3, 146.5, 137.6, 134.0, 132.2, 131.3, 130.9, 128.6, 128.5, 127.6, 127.6, 127.0, 126.1, 125.9, 101.6, 101.6, 101.5, 101.4, 87.9, 87.0, 79.7, 79.6, 74.9, 74.3, 72.5, 70.2, 69.7, 68.2, 48.1, 47.9, 47.7, 47.6, 47.4, 47.2, 47.1, 45.9, 43.2, 36.6, 36.1, 33.8, 33.0, 32.9, 31.0, 30.8, 29.2, 25.0, 24.9, 22.3, 22.2.

IR (film, cm^{-1}) 3380, 2931, 2857, 1581, 1557, 1541, 1463, 1367, 1272, 1250, 1149, 1090, 1014, 917. **HRMS(ESI)** Calc. for $C_{26}H_{32}O_6SNa$ (M + Na) : 495.1812; found : 495.1826; $[\alpha]^{26}_D$ = –27.5° (*c* 0.35, CH_2Cl_2).

Determination of the C2/C3 ratios was performed by acetylating the crude reaction mixture and analyzing the COSY NMR spectrum of the acetylated **5c.**



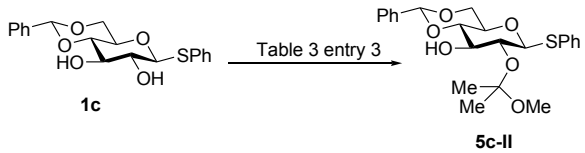
5c-Ac

R$_f$ = 0.4 (Hexane/Ethyl acetate, 5/1 + 1% Triethylamine)

^{1}H NMR (500 MHz, CD$_3$OD) δ 7.52 – 7.45 (m, 2H), 7.43 – 7.37 (m, 2H), 7.36 – 7.25 (m, 6H), 5.56 (s, 0.1H), 5.53 (s, 1H), 5.18 (d, *J* = 10.0 Hz, 1H), 4.88 (d, *J* = 11.6 Hz, 1H), 4.28 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.24 – 4.19 (m, 0.2H), 4.02 (at, *J* = 8.5 Hz, 1H), 3.76 (at, *J* = 10.1 Hz, 1H), 3.67 (at, *J* = 9.5 Hz, 1H), 3.63 – 3.58 (m, 1H), 3.12 (s, 3H), 3.03 (s, 0.4H), 2.12 – 2.11 (m, 0.4H), 2.06 (s, 3H), 1.96 – 1.86 (m, 2H), 1.68 – 1.45 (m, 6H), 1.37 – 1.31 (m, 1H), 1.28 (s, 1H), 1.26 – 1.22 (m, 1H).

^{13}C NMR (125 MHz, CD$_3$OD) δ 170.5, 169.96, 137.4, 133.8, 131.8, 131.1, 128.6, 128.6, 128.5, 128.5, 127.6, 127.5, 127.1, 126.0, 125.9, 101.6, 101.5, 101.1, 87.8, 86.5, 80.2, 78.6, 75.1, 72.4, 72.2, 71.2, 70.3, 69.4, 68.1, 68.1, 48.1, 47.9, 47.9, 47.7, 47.6, 47.5, 47.4, 47.2, 47.1, 47.1, 34.2, 33.5, 33.4, 29.3, 25.1, 22.8, 22.7, 22.7, 22.6, 20.0, 19.9.

IR (film, cm^{-1}) 2932, 2857, 1747, 1452, 1459, 1367, 1231, 1092, 1044, 1027. **HRMS(ESI)** Calc. for $C_{28}H_{34}O_7SNa$ (M + Na) : 537.1917; found : 537.1930; $[\alpha]^{26}_D$ = –27.8° (*c* 0.35, CH_2Cl_2).



1c **5c-II**

Using diol **1c**[5] (20 mg, 0.056 mmol, 1 equiv.) as the starting material, synthesis of **5c-II** was accomplished by following general procedure B. This product was purified by flash

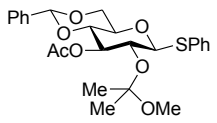
column chromatography (7/1 Hexanes/Ethyl acetate + 2% triethylamine) to afford **5c-II** as a pale yellow oil (17.3 mg, 72%, C2:C3 = 25:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.58 – 7.41 (m, 4H), 7.41 – 7.20 (m, 6H), 5.60 (s, 1H), 5.52 (s, 0.06H), 4.83 – 4.77 (m, 1H), 4.73 (d, *J* = 9.1 Hz, 0.07H), 4.27 (dd, *J* = 10.0, 5.0 Hz, 1H), 3.91 (d, *J* = 9.0 Hz, 0.1H), 3.82 – 3.68 (m, 3H), 3.63 – 3.55 (m, 1H), 3.51 (td, *J* = 9.7, 4.9 Hz, 1H), 3.35 (s, 3H), 3.18 (s, 0.2H), 1.45 (s, 3H), 1.41 (s, 3H), 1.38 (s, 0.2H), 1.28 (s, 0.2H).

^{13}C NMR (125 MHz, CD_3OD) δ 137.6, 133.8, 131.1, 128.6, 128.5, 127.6, 127.1, 126.1, 101.8, 101.5, 88.3, 87.0, 78.0, 79.8, 75.5, 74.3, 72.3, 70.3, 69.6, 68.2, 49.2, 48.7, 48.1, 47.9, 47.8, 47.6, 47.4, 47.2, 47.1, 24.5, 24.03, 23.9, 23.4.

IR (film, cm^{-1}) 3374, 2963,2927, 2870, 1579, 1461, 1380, 1275, 1204, 1141, 1123, 1077, 1044, 1022. **HRMS(ESI)** Calc. for $C_{23}H_{28}O_6SNa$ (M + Na) : 455.1499; found : 455.1511; $[\alpha]^{26}_D$ = –25.9° (*c* 0.34, CH_2Cl_2).

Determination of the C2/C3 ratios was performed by acetylating the crude reaction mixture and analyzing the COSY NMR spectrum of the acetylated **5c-II.**



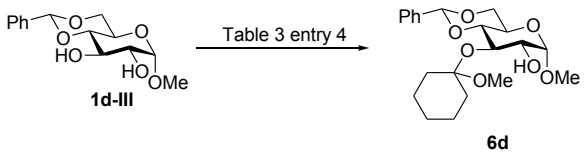
5c-II-Ac

R_f = 0.3 (Hexane/Ethyl acetate, 7/1 + 1% Triethylamine)

^{1}H NMR (500 MHz, CD_3OD) δ 7.54 – 7.45 (m, 2H), 7.44 – 7.37 (m, 2H), 7.36 – 7.22 (m, 6H), 5.55 (s, 1H), 5.19 (at, *J* = 10.0 Hz, 1H), 4.29 (dd, *J* = 10.3, 4.9 Hz, 1H), 3.96 (t, *J* = 8.6 Hz, 1H), 3.77 (at, *J* = 10.1 Hz, 1H), 3.68 (at, *J* = 9.5 Hz, 1H), 3.65 – 3.55 (m, 1H), 3.17 (s, 3H), 3.04 (s, 0.3H), 2.12 (s, 0.4H), 2.06 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ 170.6, 137.4, 133.7, 131.2, 128.6, 128.5, 127.6, 127.1, 125.9, 101.8, 101.1, 87.9, 78.5, 75.1, 72.7, 69.5, 68.1, 48.4, 48.1, 47.9, 47.7, 47.6, 47.4, 47.2, 47.1, 24.5, 24.0, 19.9.

IR (film, cm^{-1}) 2989, 2914, 2848, 1748, 1456, 1369, 1233, 1088, 1058, 1029, 1001. **HRMS(ESI)** Calc. for $C_{25}H_{30}O_7SNa$ (M + Na) : 497.1604; found : 497.1612; $[\alpha]^{26}_D$ = –10.0° (*c* 0.30, CH_2Cl_2).



1d-III **6d**

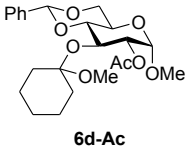
Using diol **1d-III** (20 mg, 0.071 mmol, 1 equiv.) as the starting material, synthesis of **6d** was accomplished by following general procedure A. This product was purified by flash column chromatography (3/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **6d** as a pale yellow oil (22.1 mg, 79%, C2:C3 = 1:8.8).

^{1}H NMR (500 MHz, CD_3OD) δ 7.89 (d, *J* = 8.1 Hz, 0.1H), 7.77 (s, 0.1H), 7.51 – 7.44 (m, 2H), 7.39 (d, *J* = 7.9 Hz, 0.2H), 7.37 – 7.31 (m, 3H), 7.25 (d, *J* = 1.9 Hz, 0.1H), 7.22 – 7.18 (m, 0.2H), 7.15 (d, *J* = 1.9 Hz, 0.1H), 7.10 (d, *J* = 8.5 Hz, 0.2H), 5.57 (s, 0.1H), 5.54 (s, 1H), 4.78 (d, *J* = 3.6 Hz, 0.1H), 4.74 (d, *J* = 3.8 Hz, 1H), 4.26 – 4.17 (m, 1H), 4.07 (at, *J* = 9.1 Hz, 1H), 3.83 (d, *J* = 8.1 Hz, 0.1H), 3.79 – 3.69 (m, 3H), 3.52 (dd, *J* = 9.1, 3.8 Hz, 1H), 3.48 (td, *J* = 9.2, 3.0 Hz, 1H), 3.43 (s, 3H), 3.40 (s, 0.3H), 3.26 (s, 0.3H), 3.17 (s, 3H), 3.05 (dd, *J* = 14.6, 7.6 Hz, 0.3H), 2.14 – 2.05 (m, 0.5H), 1.99 (at, *J* = 8.4 Hz, 1H), 1.85 – 1.77 (m, 2H), 1.73 – 1.66 (m, 2H), 1.62 – 1.55 (m, 2H), 1.48 – 1.39 (m, 2H), 1.36 – 1.31 (m, 1H), 1.27 – 1.23 (m, 1H), 1.20 – 1.15 (m, 1H).

^{13}C NMR (125 MHz, CD_3OD) δ 137.8, 128.5, 127.6, 126.1, 126.0, 101.7, 101.6, 101.5, 100.6, 100.3, 81.5, 80.6, 71.9, 70.9, 69.0, 68.7, 68.6, 62.7, 62.1, 54.3, 53.9, 48.0, 47.9, 47.7, 47.6, 47.6, 47.4, 47.2, 47.1, 43.2, 36.6, 34.0, 33.3, 33.1, 25.1, 25.0, 22.8, 22.6, 22.4, 22.2.

IR (film, cm^{-1}) 3376, 2927, 2853, 1452, 1371, 1275, 1255, 1121, 1078, 1055, 1040, 1022, 996. **HRMS(ESI)** Calc. for $C_{21}H_{30}O_7SNa$ (M + Na) : 417.1899; found : 417.1899; $[\alpha]^{26}_{D}$ = +25.7° (*c* 0.41, CH_2Cl_2).

Determination of the C2/C3 ratios was performed by acetylating the crude reaction mixture and analyzing the COSY NMR spectrum of the acetylated **6d.**



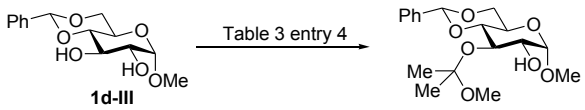
6d-Ac

R_f = 0.5 (Hexane/Ethyl acetate 4/1 + 1% Triethylamine)

^{1}H NMR (500 MHz, CD_3OD) δ 7.52 – 7.45 (m, 2H), 7.41 (dd, *J* = 6.8, 2.9 Hz, 0.16H), 7.39 – 7.30 (m, 3H), 5.57 (s, 1H), 5.54 (s, 0,06H), 4.86 (d, *J* = 3.0 Hz, 1H), 4.73 (dd, *J* = 9.6, 3.7 Hz, 1H), 4.29 (at, *J* = 9.4 Hz, 1H), 4.25 – 4.18 (m, 1H), 3.82 – 3.73 (m, 2H), 3.57 (at, *J* = 10.0 Hz, 1H), 3.43 (s, 0.3H), 3.39 (s, 3H), 3.26 – 3.23 (m, 0.2H), 3.05 (s, 3H), 2.09 (s, 3H), 2.04 (s, 0.2H), 1.87 – 1.75 (m, 2H), 1.60 – 1.47 (m, 5H), 1.43 – 1.25 (m, 3H), 1.23 – 1.12 (m, 1H).

^{13}C NMR (125 MHz, CD_3OD) δ 170.4, 137.7, 128.6, 127.6, 127.6, 126.1, 126.0, 101.8, 101.7, 101., 101.4, 100.1, 97.8, 81.1, 79.3, 72.9, 70.1, 69.8, 68.5, 67.7, 62.7, 62.2, 54.2, 53.9, 48.1, 48.0, 47.9, 47.9, 47.7, 47.6, 47.5, 47.4, 47.3, 47.2, 47.1, 34.2, 33.7, 33.5, 33.1, 25.1, 25.0, 22.8, 22.7, 22.5, 22.3, 19.7, 19.6.

IR (film, cm^{-1}) 2932, 2853, 1741, 1454, 1369, 1237, 1191, 1154, 1125, 1097, 1049, 998, 924. **HRMS(ESI)** Calc. for $C_{23}H_{32}O_8SNa$ (M + Na) : 459.1989; found : 459.2000; **$[\alpha]^{26}_D$** = +17.7° (*c* 0.42, CH_2Cl_2).



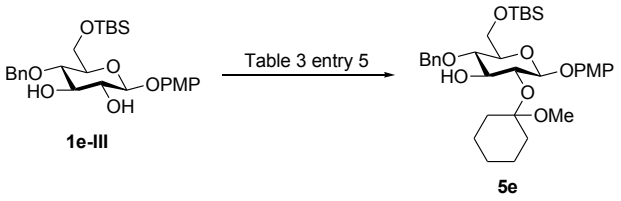
1d-III **6d-II**

Using diol **1d-III** (20 mg, 0.071 mmol, 1 equiv.) as the starting material, synthesis of **6d-II** was accomplished by following general procedure B. This product was purified by flash column chromatography (2/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **6d-II** as a pale yellow oil (17.3 mg, 69%, C2:C3 = 1:6.3).

^{1}H NMR (500 MHz, CD_3OD) δ 7.54 – 7.42 (m, 3H), 7.40 – 7.28 (m, 4H), 5.57 (s, 0.2H), 5.52 (s, 1H), 4.77 (d, *J* = 3.6 Hz, 0.2H), 4.73 (d, *J* = 3.6 Hz, 1H), 4.25 – 4.16 (m, 1H), 4.01 (at, *J* = 9.2 Hz, 1H), 3.86 – 3.79 (m, 0.4H), 3.79 – 3.65 (m, 3H), 3.51 (dd, *J* = 9.2, 3.5 Hz, 1H), 3.49 – 3.45 (m, 1H), 3.43 (s, 3H), 3.41 (s, 0.7H), 3.27 (s, 0.5H), 3.15 (s, 3H), 1.41 (s, 0.7H), 1.40 (s, 0.7H), 1.38 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (12 MHz, CD_3OD) δ 137.8, 137.7, 128.5, 128.5, 127.6, 127.6, 126.3, 126.1, 101.8, 101.6, 101.5, 100.8, 100.2, 81.5, 81.4, 80.8, 73.0, 72.1, 71.7, 70.6, 70.6, 69.0, 68.7, 68.6, 62.8, 62.1, 54.4, 54.3, 54.0, 49.0, 48.3, 48.1, 47.9, 47.8, 47.6, 47.4, 47.2, 47.1, 43.2, 36.6, 29.2, 24.6, 24.0, 24.0.

IR (film, cm^{-1}) 3429, 2993, 2932, 2914, 2857, 1456, 1384, 1373, 1207, 1147, 1072, 1075, 992. . **HRMS(ESI)** Calc. for $C_{18}H_{26}O_7SNa$ (M + Na) : 377.1571; found : 377.1583; $[\alpha]^{26}_D$ = +68.6° (*c* 0.37, CH_2Cl_2).



1e-III **5e**

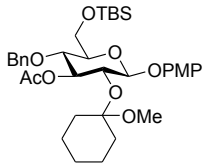
Using diol **1e-III** (20 mg, 0.04 mmol, 1 equiv.) as the starting material, synthesis of **5e** was accomplished by following general procedure A. This product was purified by flash column chromatography (5/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **5e** as a pale yellow oil (19 mg, 79%, C2:C3 = 5:1).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 5H), 7.08 (d, 0.4H), 7.00 (d, 2H), 6.80 (d, 2H), 5.32 – 5.28 (m, 0.3H), 5.05 (s, 1H), 5.02 (d, *J* = 11.2 Hz, 1H), 4.85 (d, *J* = 11.0 Hz, 0.2H), 4.77 (d, *J* = 7.5 Hz, 1H), 4.68 (d, *J* = 11.2 Hz, 1H), 4.65 (d, *J* = 11.0 Hz, 0.2H), 3.98 (at, *J* = 8.5 Hz, 0.2H), 3.94 – 3.88 (m, 1H), 3.86 – 3.79 (m, 1H), 3.77 (s, 3H), 3.75 – 3.67 (m, 2H), 3.58 – 3.41 (m, 2H), 3.39 (s, 0.4H), 3.36 (s, 3H), 2.05 – 1.98 (m, 1H), 1.86 – 1.70 (m, 3H), 1.68 – 1.48 (m, 6H), 1.45 – 1.29 (m, 2H), 1.26 (s, 2H), 0.89 (s, 9H), 0.06 (s, 0.4H), 0.05 (s, 3H), 0.02 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 155.2, 155.0, 152.0, 151.6, 138.6, 138.3, 128.4, 128.3, 128.1, 127.8, 127.6, 119.1, 118.2, 114.4, 114.3, 102.3, 101.6, 101.5, 101.2, 78.9, 77.6, 77.4, 77.2, 77.0, 76.7, 76.1, 76.1, 75.9, 75.4, 75.1, 74.8, 73.3, 62.7, 62.4, 55.6, 55.6, 48.2, 48.1, 33.8, 33.6, 33.5, 32.9, 29.7, 25.9, 25.3, 25.3, 22.8, 22.8, 21.9, 18.3, -5.2, -5.3, -5.35, -5.41.

IR (film, cm^{-1}) 3380, 2927, 2852, 1507, 1463, 1250, 1226, 1154, 1093, 1038, 919. **HRMS(ESI)** Calc. for $C_{33}H_{50}O_8SiNa$ (M + Na) : 625.3167; found : 625.3182; $[\alpha]^{26}_D$ = – 5.9° (*c* 0.24, CH_2Cl_2).

Determination of the C2/C3 ratios was performed by acetylating the crude reaction mixture and analyzing the COSY NMR spectrum of the acetylated **5e.**



5e-Ac

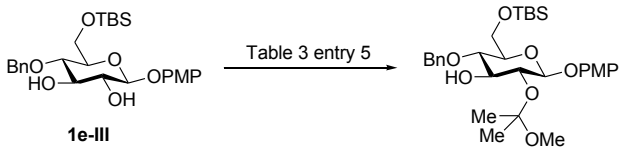
$\mathbf{R_f}$ = 0.4 (Hexane/Ethyl acetate 5/1 + 1% Triethylamine)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 3H), 7.31 – 7.27 (m, 3H), 7.02 – 6.97 (m, 2H), 6.94 (d, *J* = 10.0 Hz, 0.4H), 6.84 – 6.76 (m, 3H), 5.21 (t, *J* = 8.5 Hz, 1H), 5.05 (at, *J* = 7.5 Hz, 0.4H), 4.87 (d, *J* = 6.9 Hz, 1H), 4.83 (dd, *J* = 9.2, 6.4 Hz, 0.6H), 4.66 – 4.58 (m, 2H), 4.15 (at, *J* = 7.8 Hz, 0.4H), 4.00 (dd, *J* = 8.0, 7.1 Hz, 1H), 3.88 – 3.85 (m, 0.3H), 3.83 (dd, *J* = 11.4, 2.3 Hz, 1H), 3.78 (d, *J* = 4.5 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 0.8H), 3.66 (at, *J* = 10.5 Hz, 1H), 3.62 (d, *J* = 8.0 Hz, 0.3H), 3.51 (ddd, *J* = 9.2, 4.4, 2.4 Hz, 1H), 3.16 (s, 0.6H), 3.13 (s, 3H), 2.10 (s, 0.6H), 2.01 (s, 3H), 1.92 – 1.84 (m, 2H), 1.58 – 1.55 (m, 2H), 1.54 – 1.50 (m, 2H), 1.46 – 1.40 (m, 2H), 1.27 – 1.23 (m, 5H), 0.89 (s, 9H), 0.88 (s, 2H), 0.04 (s, 0.7H), 0.03 (s, 3H), 0.02 (s, 0.7H), 0.01 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 169.7, 155.2, 155.0, 151.6, 151.4, 138.2, 137.9, 128.4, 128.0, 127.8, 127.8, 118.5, 118.3, 114.4, 101.8, 101.6, 101.5, 100.6, 77.2, 77.2, 77.0, 76.7, 76.7, 76.5, 76.2, 76.0, 75.7, 74.5, 74.2, 73.9, 73.5, 71.7, 62.4, 62.2, 55.6, 48.4, 48.2, 34.4, 34.1, 34.0, 33.9, 31.9, 29.7, 29.4, 25.9, 25.4, 23.1, 23.0, 22.7, 21.4, 21.3, 18.3, 14.1, -5.17, -5.2, -5.4, -5.5

IR (film, cm^{-1}) 2927, 2853, 1750, 1507, 1463, 1364, 1222, 1154, 1088, 1060, 924, 836.

HRMS(ESI) Calc. for $C_{35}H_{52}O_8SiNa$ (M + Na) : 667.3273; found : 667.3283; $[\alpha]^{26}_D$ = – 13.9° (*c* 0.32, CH_2Cl_2).



1e-III **5e-II**

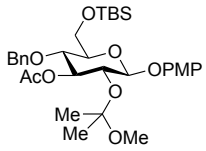
Using diol **1e-III** (20 mg, 0.04 mmol, 1 equiv.) as the starting material, synthesis of **5e-II** was accomplished by following general procedure B. This product was purified by flash column chromatography (5/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **5e-II** as pale yellow oil (20.2 mg, 88%, C2:C3 = 7:1).

^{1}H NMR (500 MHz, CD_3OD) δ 7.37 (d, *J* = 1.5 Hz, 1H), 7.36 – 7.35 (m, 2H), 7.34 – 7.32 (m, 2H), 7.31 – 7.31 (m, 0.5H), 7.30 – 7.25 (m, 1H), 7.05 – 7.01 (m, 1H), 6.99 – 6.95 (m, 2H), 6.82 – 6.81 (m, 1H), 6.80 – 6.79 (m, 1H), 4.95 (d, *J* = 11.2 Hz, 1H), 4.82 – 4.78 (m, 1H), 4.72 (d, *J* = 7.8 Hz, 0.3H), 4.69 – 4.64 (m, 1H), 3.94 (at, *J* = 8.6 Hz, 0.2H), 3.87 – 3.84 (m, 1H), 3.78 – 3.74 (m, 1H), 3.74 – 3.72 (m, 6H), 3.72 – 3.69 (m, 1H), 3.69 – 3.64 (m, 1H), 3.62 (d, *J* = 9.1 Hz, 0.4H), 3.50 – 3.46 (m, 1H), 3.45 – 3.43 (m, 0.4H), 3.43 – 3.39 (m, 1H), 3.36 (s, 0.5H), 3.32 (s, 3H), 1.51 (s, 3H), 1.47 (s, 1H), 1.46 (s, 3H), 0.89 (s, 3H), 0.88 (d, *J* = 2.8 Hz, 9H), 0.04 (s, 0.5H), 0.04 (s, 0.5H), 0.03 (s, 3H), -0.01 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ 155.2, 155.1, 151.7, 151.6, 138.6, 138.3, 128.0, 127.9, 127.7, 127.7, 127.5, 127.3, 118.0, 117.9, 117.5, 114.0, 113.9, 101.9, 101.8, 100.7, 78.7, 77.7, 77.6, 76.9, 76.8, 76.3, 75.8, 75.8, 75.6, 75.3, 74.6, 74.4, 74.4, 73.9, 73.1, 62.3, 54.6, 49.1, 48.1, 47.9, 47.8, 47.6, 47.4, 47.2, 47.1, 25.0, 24.5, 23.8, 17.8, -6.4, -6.6.

IR (film, cm^{-1}) 3407, 2931, 2853, 1509, 1463, 1384, 1370, 1228, 1066, 834. **HRMS(ESI)** Calc. for $C_{30}H_{46}O_8SiNa$ (M + Na) : 585.2854; found : 585.2850; $[\alpha]^{26}_D$ = – 13.7° (*c* 0.09, CH_2Cl_2).

Determination of the C2/C3 ratios was performed by acetylating the crude reaction mixture and analyzing the COSY NMR spectrum of the acetylated **5e-II.**



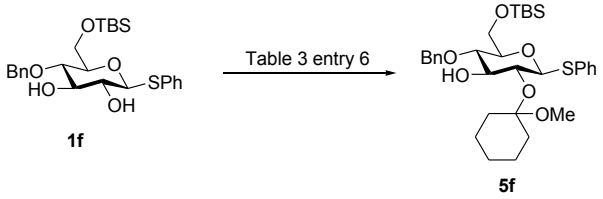
5e-II-Ac

R_f = 0.3 (Hexane/Ethyl acetate, 4.5/1 + 2% Triethylamine)

^{1}H NMR (500 MHz, CD_3OD) δ 7.36 – 7.31 (m, 2H), 7.31 – 7.25 (m, 3H), 7.04 – 7.01 (m, 0.2H), 7.00 – 6.96 (m, 2H), 6.94 – 6.91 (m, 0.3H), 6.85 – 6.78 (m, 2H), 5.16 (at, *J* = 10.0 Hz, 1H), 4.95 – 4.89 (m, 1H), 4.70 – 4.57 (m, 2H), 3.90 – 3.85 (m, 2H), 3.81 (dd, *J* = 11.7, 4.3 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 1H), 3.69 (at, *J* = 9.4 Hz, 1H), 3.58 (d, *J* = 9.4 Hz, 0.2H), 3.52 (ddd, *J* = 9.6, 4.2, 2.0 Hz, 1H), 3.19 (s, 1H), 3.17 (s, 3H), 2.09 (s, 0.3H), 2.00 (s, 3H), 1.43 (s, 44H), 1.40 (s, 3H), 1.38 (s, 3H), 1.28 (s, 0.4H), 0.91 (s, 1H), 0.90 (s, 9H), 0.06 (s, 0.4H), 0.05 (s, 3H), 0.02 (s, 0.4H), 0.01 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ 170.6, 155.2, 151.2, 138.1, 128.0, 127.7, 127.5, 127.4, 118.1, 117.8, 117.4, 114.1, 101.7, 100.8, 100.2, 77.0, 76.2, 75.9, 75.4, 75.4, 74.0, 73.8, 73.0, 62.1, 61.9, 54.6, 48.7, 48.1, 48.0, 47.9, 47.9, 47.7, 47.6, 47.4, 47.2, 47.1, 25.0, 24.9, 24.7, 24.2, 24.1, 20.1, 19.9, 17.8, -6.4, -6.7.

IR (film, cm^{-1}) 2923, 1748, 1505, 1459, 1367, 1218, 1057. **HRMS(ESI)** Calc. for $C_{32}H_{48}O_9SiNa$ (M + Na) : 627.2960; found : 627.2950; **[α]$^{26}_D$** = –5.3° (*c* 0.39, CH_2Cl_2).



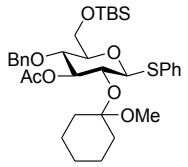
Using diol **1f** (20 mg, 0.04 mmol, 1 equiv.) as the starting material, preparation of **5f** was accomplished by following general procedure A. This product was purified by flash column chromatography (9/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **5f** as a pale yellow oil (16.2 mg, 78%, C2:C3 = 7:1).

^{1}H NMR (500 MHz, C_6D_6) δ 7.77 (d, *J* = 5.0 Hz, 0.5H), 7.61 (dd, *J* = 12.7, 5.4 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 0.5H), 7.19 – 7.13 (m, 2H), 7.08 – 7.02 (m, 4H), 7.01 – 6.91 (m, 2H), 5.38 (s, 1H), 5.33 (d, *J* = 10.0 Hz, 1H), 4.87 (d, *J* = 11.4 Hz, 1H), 4.74 – 4.66 (m, 1H), 3.94 – 3.86 (m, 2H), 3.86 – 3.78 (m, 3H), 3.78 – 3.70 (m, 2H), 3.62 (d, *J* = 9.4 Hz, 0.3H), 3.54 (at, *J* = 8.4 Hz, 0.3H), 3.27 (ddd, *J* = 9.7, 4.7, 1.6 Hz, 1H), 3.06 (d, *J* = 9.8 Hz, 0.3H), 2.93 (s, 3H), 2.86 (s, 0.5H), 1.74 – 1.55 (m, 5H), 1.43 (d, *J* = 5.1 Hz, 1H), 1.36 – 1.28 (m, 4H), 1.18 (d, *J* = 8.9 Hz, 2H), 0.96 (s, 9H), 0.89 – 0.83 (m, 1H), 0.39 (s, 0.7H), 0.14 (s, 0.5H), 0.11 (s, 3H), 0.07 (s, 0.5H), 0.06 (s, 3H).

^{13}C NMR (126 MHz, C_6D_6) δ 139.3, 139.1, 135.4, 134.6, 132.8, 131.0, 128.7, 128.5, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.5, 127.3, 127.1, 127.0, 126.6, 101.3, 101.2, 87.6, 86.6, 80.6, 79.9, 79.2, 77.0, 75.9, 74.9, 74.7, 74.6, 72.58, 62.8, 62.4, 47.3, 33.4, 33.3, 33.1, 29.8, 25.9, 25.8, 25.1, 25.0, 22.6, 22.5, 22.4, 22.2, 18.3, -5.1, -5.3, -5.5, -5.5.

IR (film, cm^{-1}) 3380, 2928, 2855, 1462, 1361, 1253, 1153, 1091, 1042, 1025, 919, 906. **HRMS(ESI)** Calc. for $C_{32}H_{48}O_6SSiNa$ (M + Na) : 611.2833; found : 611.2840; **[α]$^{26}_D$** = –2.73° (*c* 0.07, CH_2Cl_2).

Determination of the C2/C3 ratios was performed by acetylating the crude reaction mixture and analyzing the COSY NMR spectrum of the acetylated **5f.**



5f-Ac

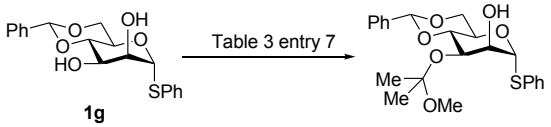
R_f = 0.3 (Hexane/Ethyl acetate, 9/1 + 2% Triethylamine)

^{1}H NMR (500 MHz, C_6D_6) δ 7.60 (dd, *J* = 8.1, 7.0 Hz, 2H), 7.37 (d, *J* = 7.1 Hz, 2H), 7.16 – 7.13 (m, 3H), 7.08 – 7.03 (m, 3H), 6.97 – 6.93 (m, 1H), 5.42 (at, *J* = 8.2 Hz, 1H), 4.69 (d, *J* = 8.7 Hz, 1H), 4.65 (s, 2H), 4.06 (at, *J* = 8.3 Hz, 1H), 3.76 (at, *J* = 9.1 Hz, 1H), 3.71 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.64 (dd, *J* = 11.5, 1.8 Hz, 1H), 3.16 (s, 3H), 3.10 (dt, *J* = 5.1, 4.5 Hz, 1H), 3.07 (s, 0.2H), 1.99 – 1.93 (m, 1H), 1.91 (s, 0.3H), 1.80 (s, 3H), 1.63 – 1.56 (m, 1H), 1.51 – 1.38 (m, 4H), 1.34 – 1.24 (m, 4H), 1.09 – 1.03 (m, 1H), 0.95 (s, 9H), 0.38 (s, 2H), 0.11 (s, 3H), 0.09 – 0.07 (m, 1H), 0.06 – -0.01 (m, 3H).

^{13}C NMR (125 MHz, C_6D_6) δ 169.1, 138.6, 135.2, 131.5, 131.3, 128.7, 128.3, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 126.8, 101.6, 87.67, 79.1, 77.0, 75.9, 73.8, 71.4, 62.1, 47.9, 34.0, 33.8, 29.8, 25.8, 25.4, 23.2, 23.0, 20.9, 18.2, -5.2, -5.6.

IR (film, cm^{-1}) 2927, 2852, 1750, 1471, 1459, 1362, 1231, 1088, 1048, 921, 908, 836. .

HRMS(ESI) Calc. for $C_{34}H_{50}O_7SSiNa$ (M + Na) : 653.2939; found : 653.2948; **[α]$^{26}_D$** = –3.32° (*c* 0.15, CH_2Cl_2).



1g **6g**

Using diol **1g** (20 mg, 0.04 mmol, 1 equiv.) as the starting material, synthesis of **6g** was accomplished by following general procedure B. This product was purified by flash column chromatography (3/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford **6g** as a pale yellow oil (16.2 mg, 78%, C2:C3 = 1:12.6).

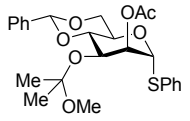
^{1}H NMR (500 MHz, CD_3OD) δ 7.54 – 7.43 (m, 4H), 7.39 – 7.25 (m, 6H), 5.58 (s, 1H), 5.48 (s, 1H), 4.29 (td, *J* = 9.8, 4.8 Hz, 1H), 4.22 (d, *J* = 3.0 Hz, 1H), 4.19 (dd, *J* = 10.0, 3.1 Hz, 1H), 4.11 (dd, *J* = 10.2, 4.8 Hz, 1H), 4.05 (at, *J* = 9.7 Hz, 1H), 3.82 (at, *J* = 10.3 Hz, 1H), 3.21 (s, 3H), 1.40 (d, *J* = 12.0 Hz, 3H), 1.37 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ 137.9, 133.7, 131.6, 128.8, 128.5, 127.6, 127.3, 126.0, 102.0, 101.5, 89.5, 77.3, 72.5, 68.1, 65.7, 48.6, 48.1, 47.1, 24.5, 24.2.

IR (film, cm^{-1}) 3433, 2985, 2923, 2853, 1456, 1373, 1211, 1169, 1095, 1031, 970. .

HRMS(ESI) Calc. for $C_{23}H_{28}O_6SNa$ (M + Na) : 455.1499; found : 455.1513; **[α]$^{26}_D$** = +48.9° (*c* 0.51, CH_2Cl_2).

Determination of the C2/C3 ratios was performed by acetylating the crude reaction mixture and analyzing the COSY NMR spectrum of the acetylated **6g.**



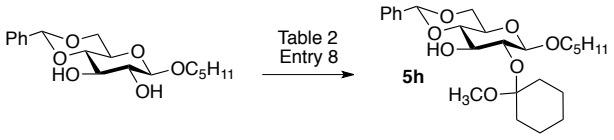
6g-Ac

R_f = 0.35 (Hexane/Ethyl acetate, 4/1 + 1% Triethylamine)

^{1}H NMR (500 MHz, CD_3OD) δ 7.54 – 7.50 (m, 2H), 7.50 – 7.45 (m, 2H), 7.39 – 7.28 (m, 6H), 5.62 (s, 1H), 5.50 – 5.46 (m, 2H), 4.37 – 4.28 (m, 2H), 4.14 (dd, *J* = 10.3, 4.9 Hz, 1H), 4.03 (at, *J* = 9.8 Hz, 1H), 3.84 (at, *J* = 10.3 Hz, 1H), 3.13 (s, 3H), 2.13 (s, 3H), 1.37 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD) δ 170.3, 137.7, 132.9, 131.89, 128.9, 128.6, 127.7, 127.65, 126.0, 102.1, 101.6, 87.0, 77.6, 73.6, 67.9, 66.7, 65.7, 48.7, 48.1, 47.9, 47.7, 47.6, 47.4, 47.2, 47.1, 24.1, 23.9, 19.4.

IR (film, cm^{-1}) 2998, 2919, 1744, 1458, 1373, 1233, 1099, 1033. **[α]$^{26}_D$** = + 92.1° (*c* 0.51, CH_2Cl_2).

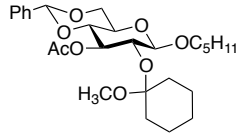


5h

Using the above diol (20 mg, 0.059 mmol, 1 equiv.) as the starting material, synthesis of the acetal was accomplished by following general procedure A. This product was purified by flash column chromatography (9/1 Hexanes/Ethyl acetate + 2% triethylamine) to afford the acetal as a pale yellow oil (21.3 mg, 80%, C2:C3 = > 22.1).

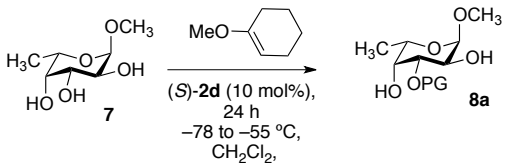
^{1}H NMR (500 MHz, C_6D_6) δ 7.67 (d, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 1H), 7.09 – 7.04 (m, 1H), 5.37 (s, 1H), 5.03 (s, 1H), 4.30 (d, *J* = 5.0 Hz, 1H), 4.26 – 4.18 (m, 1H), 3.90 – 3.77 (m, 3H), 3.63 (at, *J* = 9.1 Hz, 1H), 3.55 (at, *J* = 10.2 Hz, 1H), 3.37 – 3.27 (m, 2H), 2.98 (s, 3H), 1.98 (d, *J* = 9.3 Hz, 1H), 1.74 – 1.62 (m, 3H), 1.59 – 1.46 (m, 3H), 1.45 – 1.05 (m, 9H), 0.94 – 0.87 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (125 MHz, C_6D_6) δ 138.2, 128.5, 127.9, 127.8, 127.6, 127.5, 126.5, 102.4, 101.3, 101.3, 80.7, 76.7, 73.6, 69.6, 68.7, 66.0, 47.4, 33.7, 32.9, 29.6, 28.3, 25.4, 22.7, 22.4, 21.7, 13.9.
IR (film, cm^{-1}) 3382, 2936, 2867, 1456, 1368, 1093, 1018.
HRMS(ESI) Calc. for $C_{25}H_{38}O_7Na$ (M + Na) : 473.2510; found : 473.2506; **$[\alpha]^{26}_D$** = – 27.8° (*c* 0.56, CH_2Cl_2).

Determination of C2/C3 ratios was done using COSY experiments of acetylated product.



^{1}H NMR (400 MHz, C_6D_6) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.07 – 6.97 (m, 2H), 5.50 (dd, *J* = 9.3, 7.7 Hz, 1H), 5.24 (s, 1H), 4.31 (d, *J* = 6.5 Hz, 1H), 4.13 (dd, *J* = 10.0, 4.6 Hz, 1H), 4.03 (t, *J* = 7.0 Hz, 1H), 3.77 – 3.68 (m, 1H), 3.58 (t, *J* = 9.4 Hz, 1H), 3.44 (t, *J* = 10.0 Hz, 1H), 3.40 – 3.32 (m, 1H), 3.31 – 3.23 (m, 1H), 3.16 (s, 3H), 1.92 – 1.81 (m, 2H), 1.79 (s, 3H), 1.75 – 1.64 (m, 1H), 1.64 – 1.42 (m, 6H), 1.40 – 1.32 (m, 2H), 1.31 – 1.13 (m, 5H), 0.89 (t, *J* = 7.2 Hz, 1H), 0.81 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, C_6D_6) δ 169.0, 137.8, 128.6, 127.9, 127.8, 127.6, 127.5, 127.4, 126.3, 102.9, 101.5, 101.3, 79.2, 73.9, 72.5, 69.4, 68.9, 65.3, 47.9, 34.2, 34.0, 29.5, 28.3, 25.5, 23.1, 23.0, 22.4, 20.6, 13.8.
IR (film, cm^{-1}) 2931, 2861, 1753, 1365, 1231, 1093.

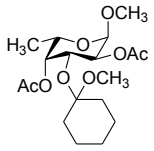
HRMS(ESI) Calc. for $C_{27}H_{40}O_8Na$ (M + Na) : 515.2615; found : 515.2611; $[\alpha]^{26}_D$ = – 28.0° (*c* 0.1, CH_2Cl_2).



Using the above fucose Triol (20 mg, 0.1123mmol, 1 equiv.) as the starting material, synthesis of the acetal was accomplished by following general procedure A. This product was purified by flash column chromatography (2/3 Hexanes/Ethyl acetate + 1% triethylamine) to afford the acetal as white solid (16.8 mg, 51.5%, C3:C3:C4 = C3 only).

^{1}H NMR (400 MHz, CD_3OD) δ 4.62 (d, *J* = 3.8 Hz, 1H), 3.97 (dd, *J* = 10.2, 3.2 Hz, 1H), 3.88 (q, *J* = 6.6 Hz, 1H), 3.76 (dd, *J* = 10.1, 3.8 Hz, 1H), 3.68 (d, *J* = 2.8 Hz, 1H), 3.36 (s, 3H), 3.26 (s, 3H), 1.89 (d, *J* = 12.7 Hz, 2H), 1.70 – 1.47 (m, 6H), 1.46 – 1.34 (m, 2H), 1.31 – 1.22 (m, 2H), 1.18 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (100 MHz, CD_3OD) δ 101.6, 100.4, 72.2, 69.6, 67.0, 65.7, 54.1, 48.2, 48.0, 47.8, 47.6, 47.3, 47.1, 46.9, 33.7, 33.5, 25.1, 22.7, 22.6, 15.3.
IR (film, cm^{-1}) 3473, 2932, 1362, 1161, 1095, 1045, 950, 928. **HRMS(ESI)** Calc. for $C_{14}H_{26}O_6Na$(M + Na) : 313.1622; found : 313.1621; $[\alpha]^{26}_D$ = – 109.8° (*c* 0.3, CH_2Cl_2).

Determination of C2/C3/C4 ratios was done using COSY experiments of acetylated product.

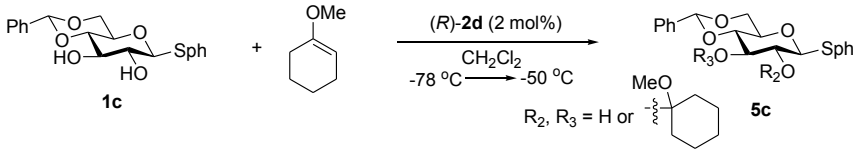


^{1}H NMR (400 MHz, CD_3OD) δ 5.21 (d, *J* = 3.2 Hz, 1H), 4.91 (dd, *J* = 10.6, 3.6 Hz, 1H), 4.81 (d, *J* = 3.5 Hz, 1H), 4.38 (dd, *J* = 10.6, 3.3 Hz, 1H), 4.06 (q, *J* = 6.5 Hz, 1H), 3.34 (s, 3H), 3.20 (s, 3H), 2.12 (s, 3H), 2.04 (s, 3H), 1.90 – 1.76 (m, 2H), 1.63 – 1.50 (m, 4H), 1.43 – 1.26 (m, 4H), 1.06 (d, *J* = 6.5 Hz, 3H).
^{13}C NMR (100 MHz, CD_3OD) δ 171.1, 170.7, 101.8, 97.4, 74.5, 69.9, 64.7, 64.6, 54.2, 48.2, 48.0, 47.8, 47.6, 47.3, 47.1, 46.9, 33.8, 33.2, 24.9, 22.7, 22.7, 19.6, 19.3, 15.1.

IR (film, cm^{-1}) 2932, 1741, 1369, 1233, 1053, 928. **HRMS(ESI)** Calc. for $C_{18}H_{30}O_8Na$(M + Na) : 397.1833; found : 397.1832; $[\alpha]^{26}_D = -34.1°$ (*c* 0.3, CH_2Cl_2).

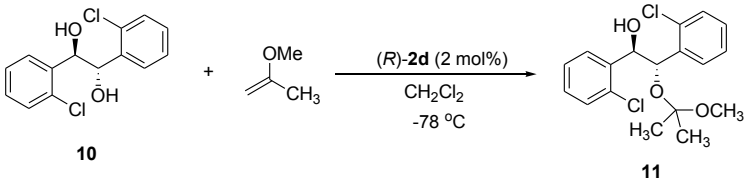
Acetalization Reactions: Time Dependent study

An oven dried and nitrogen flushed 25 mL round bottom flask was charged with thioglycoside diol **1c**[5] (60 mg, 0.17 mmol, 1 equiv.), (which was previously dried by azeotropic removal of moisture with toluene)**,** anhydrous dichloromethane (4 mL) and activated 4Å molecular sieves. This mixture was submerged in dry ice/acetone bath and 1-methoxycylohexene (25.2 µL, 0.20 mmol, 1.2 equiv.), followed by (*R*)-**2d** (3.1 mg, 0.003 mmol, 2 mol%) was added. The formation of **5c** and its respective C2/C3 ratio was monitored every hour by quenching about 0.2 mL of the reaction mixture with triethylamine, then concentrating it *in vacuo* and analyzing it by ^{1}HNMR. This routine was repeated every hour for the next 6 hours. The remaining reaction mixture was transferred into a Neslab CB 80 immersion cooler and stirred at –50 °C overnight. The formation of **5c** as well as its C2/C3 ratio as the reaction progresses is displayed below.



Time (hr)	% conversion	$C_2 : C_3$
1	49	25 : 1
2	57	25 : 1
3	68	25 : 1
4	76	25 : 1
5	81	25 : 1
6	81	25 : 1
Overnight	> 90	25 : 1

IV. Meso Diol Desymmetrization Studies



An oven dried and nitrogen flushed 10 mL round bottom flask was charged with meso-1,2-bis(2-chlorophenyl)-1,2-ethane diol **10** (15.9 mg, 0.056 mmol, 1 equiv.), (which was previously dried by azeotropic removal of moisture with toluene)**,** anhydrous dichloromethane (1.3 mL) and activated 4Å molecular sieves. This mixture was submerged in dry ice/acetone bath and 2-methoxypropene (6.4 µL, 0.067 mmol, 1.2 equiv.), followed by (*R*)-**2d** (1.1 mg, 0.001 mmol, 2 mol%) was added. The resulting reaction mixture was transferred into a Neslab CB 80 immersion cooler and stirred at –78 °C. When the reaction was completed as monitored by TLC, the reaction mixture was quenched with triethylamine, and concentrated *in vacuo* to form pale yellow oil as the crude product. The crude product **11** was subsequently analysed by HPLC (99/1 Hexanes/Isopropanol with CHIRALPAK AD-H Column, R_{f1}=18.4 min, R_{f2}=21.9) to determine its enantiomeric ratio. The crude product was then purified by silica gel flash column chromatography (5/1 Hexanes/Ethyl acetate + 1% triethylamine) to afford pure **11** as a pale yellow oil (16.8 mg, 85%, e.r. = 86:14).

^{1}H NMR (500 MHz, C_6D_6) δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.08 (dd, *J* = 9.6, 3.6 Hz, 1H), 6.96 – 6.85 (m, 2H), 6.76 – 6.62 (m, 3H), 5.86 (d, *J* = 3.6 Hz, 1H), 5.58 (d, *J* = 3.7 Hz, 1H), 2.96 (s, 3H), 2.40 (s, 1H), 1.23 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (125 MHz, C_6D_6) δ 137.5, 137.3, 133.6, 133.1, 130.5, 129.0, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 126.0, 125.7, 101.4, 73.0, 70.1, 48.8, 25.4, 24.5.

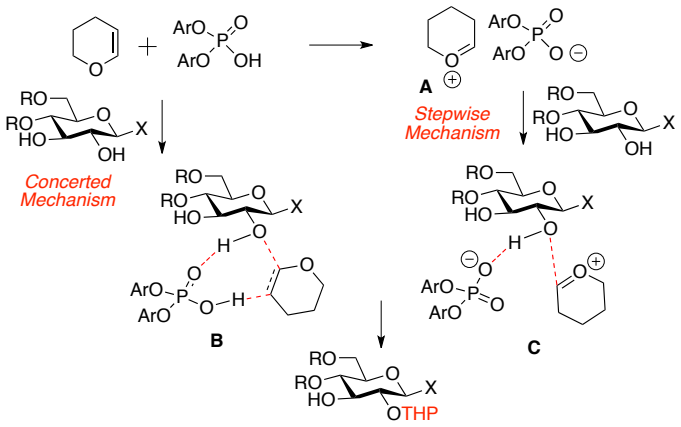
IR (film, cm^{-1}) 3464, 2989, 2940, 1597, 1573, 1471, 1441, 1382, 1209, 1147, 1075, 1053, 1029, 880.

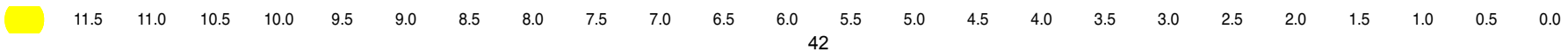
$[\alpha]^{26}_D$ = –7.84° (*c* 0.5, CH_2Cl_2).

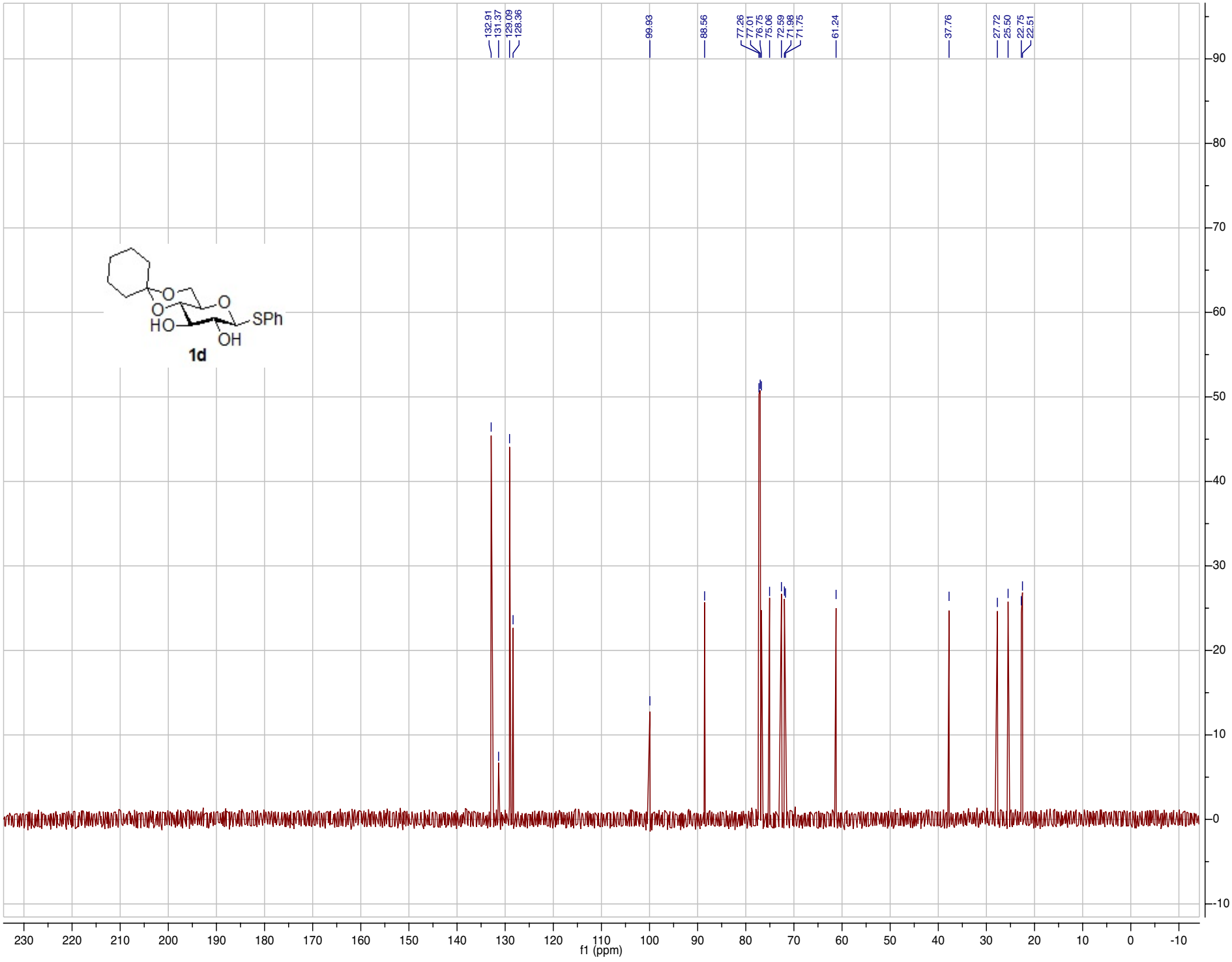
V. Proposed Mechanism

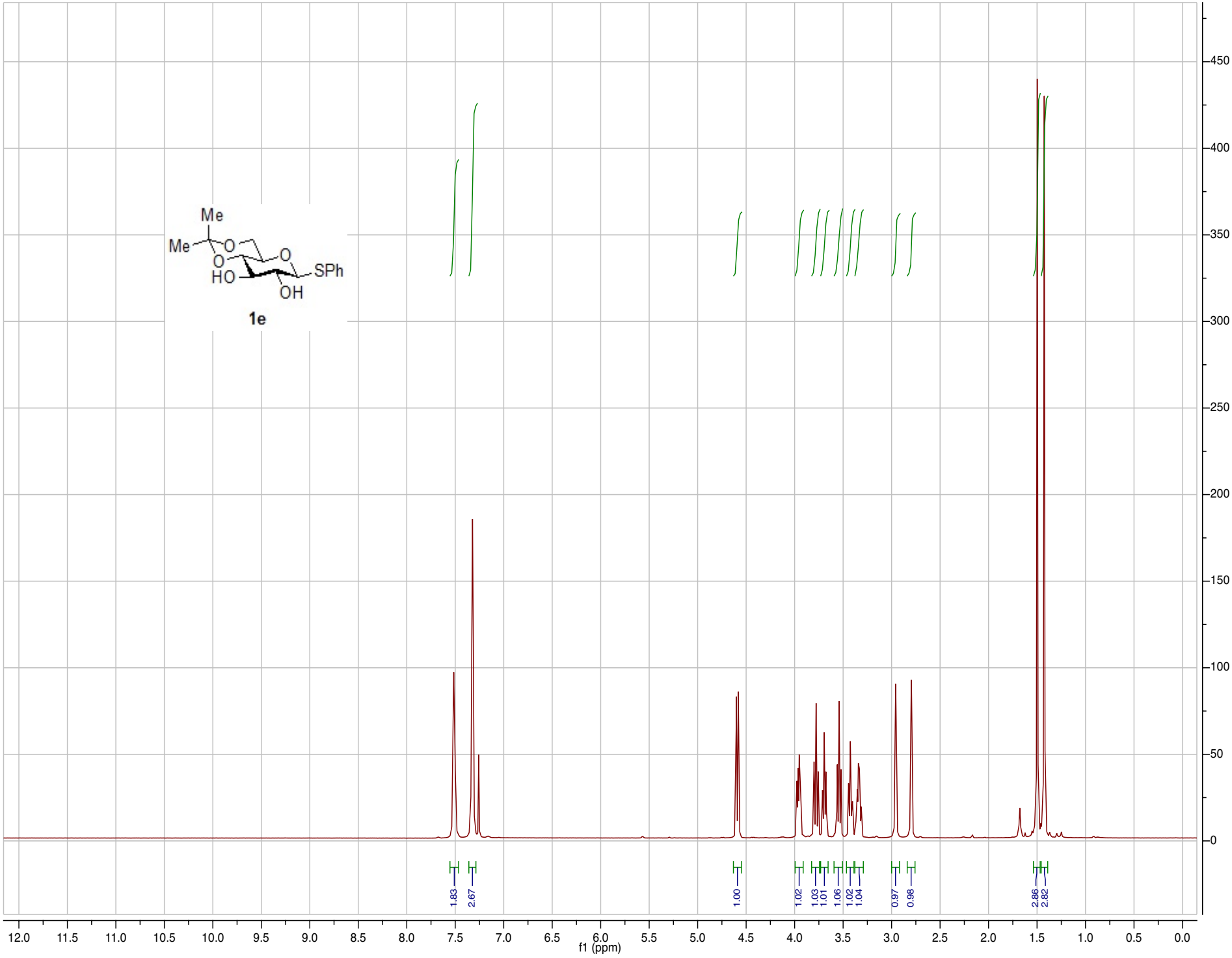
The tentative mechanism for the regioselective chiral phosphoric acid-catalyzed acetalizations is provided in Scheme 1SI. While the precise nature of the reaction intermediates has yet to be investigated, our preliminary results suggest that the acetalization reactions take place under kinetic control. Although the THP ethers are not prone to acid-promoted migration, the products **5** and **6** (Table 3, Manuscript) could in theory equilibrate or further react under the reaction conditions. However, no isomerization of the products (or formation of side-products from **5** and **6**) was observed under the reaction conditions. To rationalize the observations, both a concerted mechanism proceeding through **B** or a more traditional stepwise mechanism proceeding through **A** and bmight be proposed (Scheme 1SI). Thus, either phosphoric acid (**B**) or phosphate anion (**C**) are involved in the formation of a hydrogen bond with the diol, and the observed regioselectivities likely result from a more favored coordination of the catalyst to the substrate.

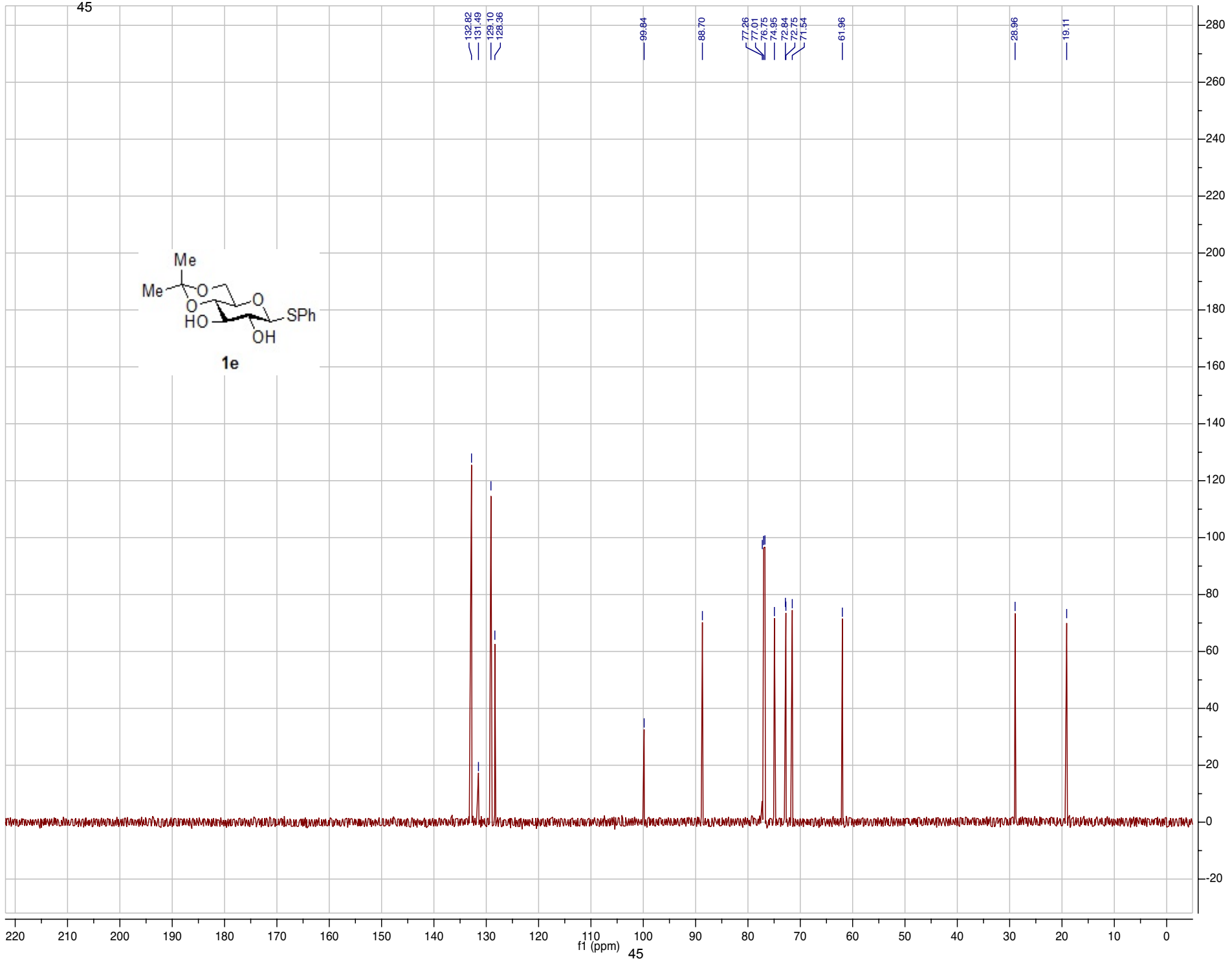
Scheme 1SI

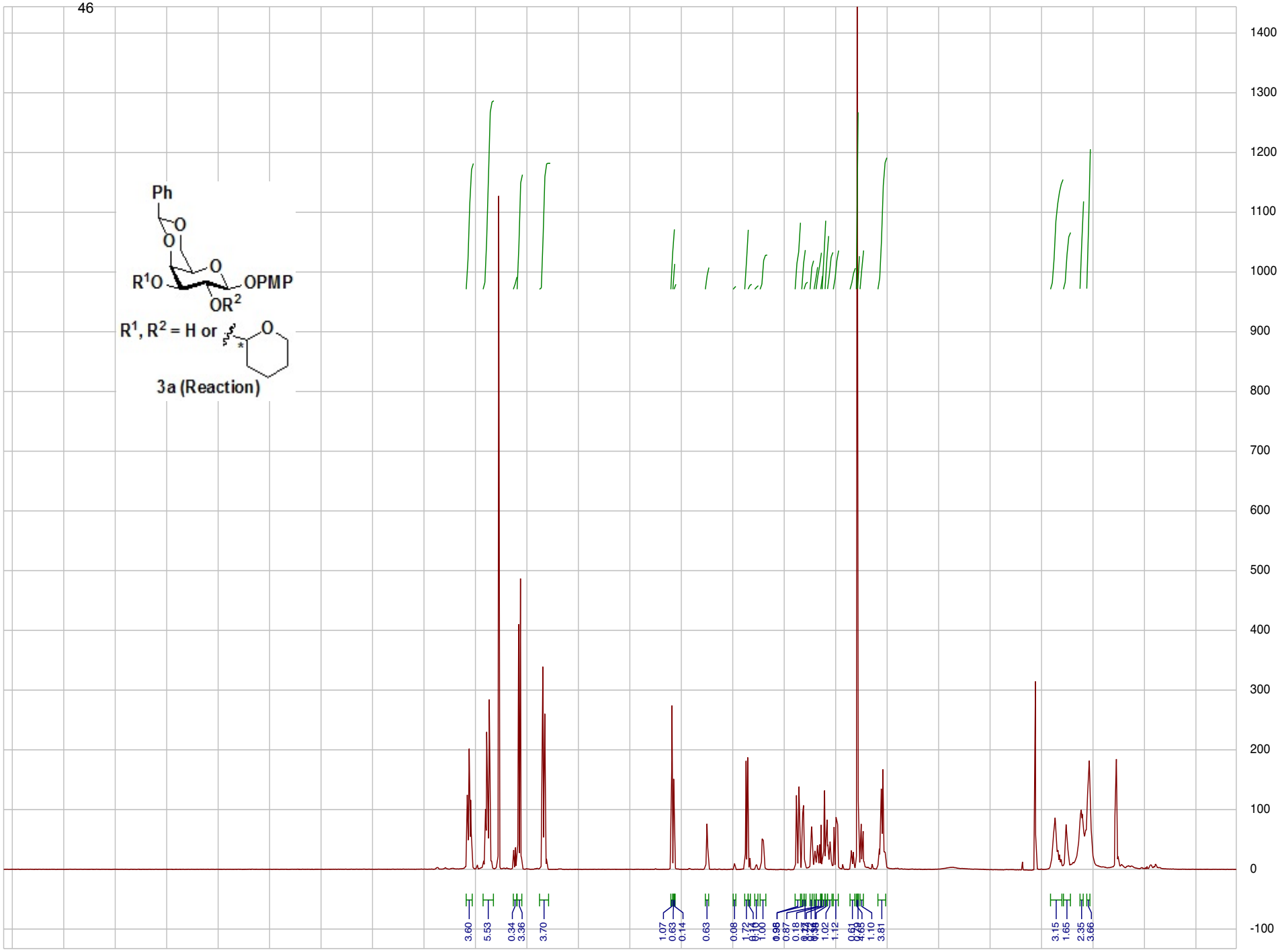


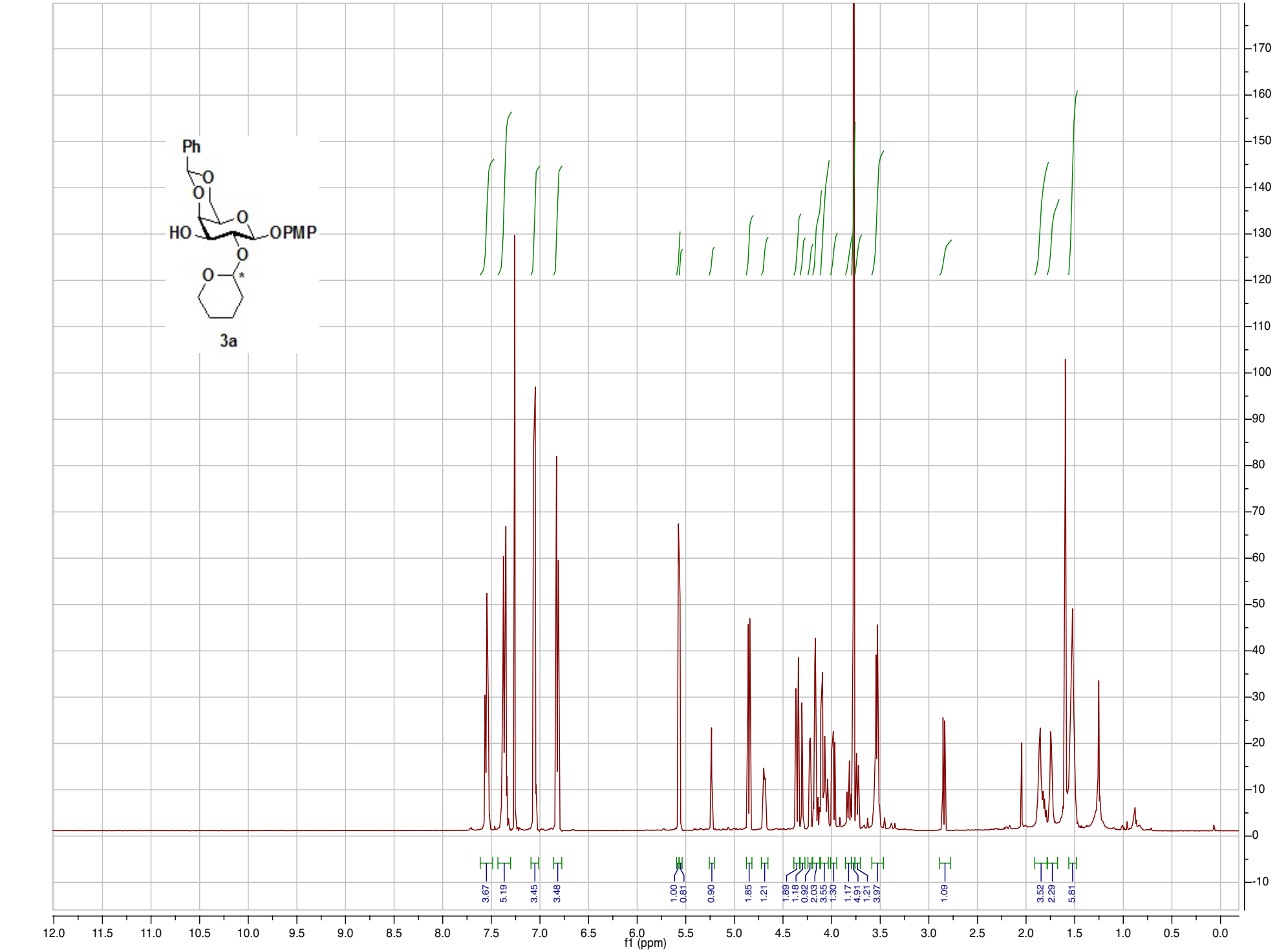

11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

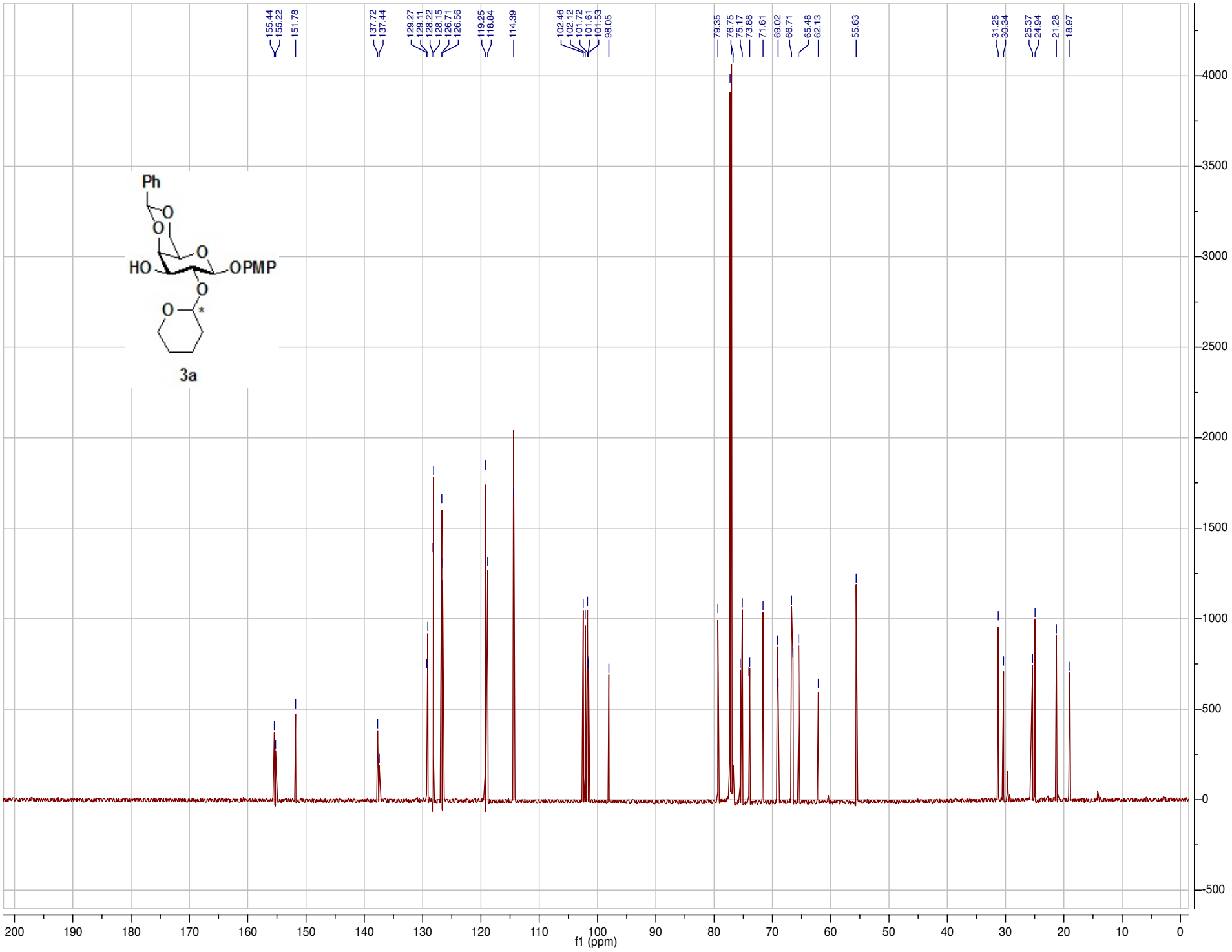

132.91
131.37
129.09
128.36
99.93
88.56
77.26
77.01
76.75
75.06
72.59
71.98
71.75
61.24
37.76
27.72
25.50
22.75
22.51
O
O
O
HO
OH
SPh
1d
f1 (ppm)

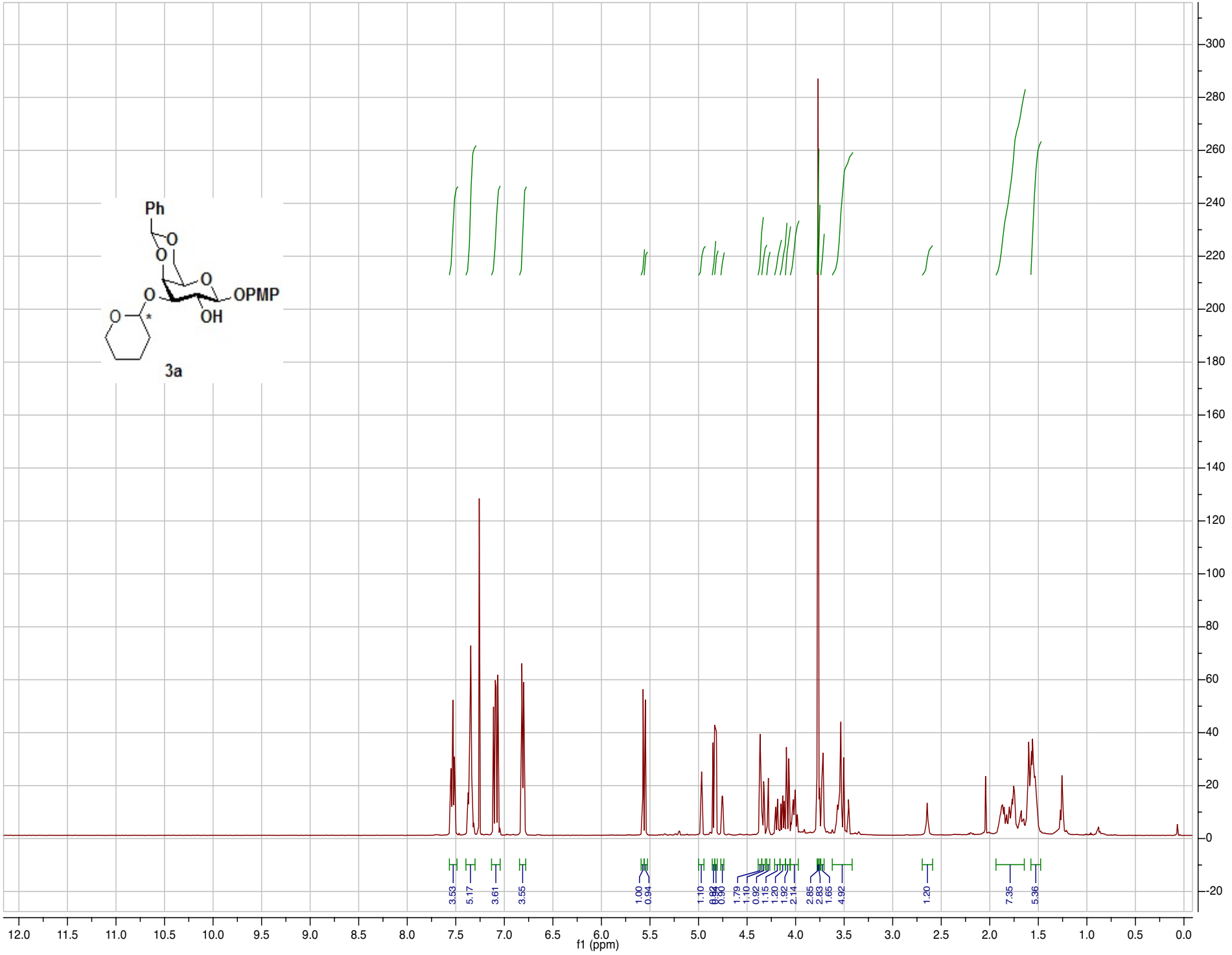

Me
Me
O
O
O
HO
SPh
OH
1e
450
400
350
300
250
200
150
100
50
0
1.83
2.67
1.00
1.02
1.03
1.01
1.06
1.02
1.04
0.97
0.98
2.86
2.82
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

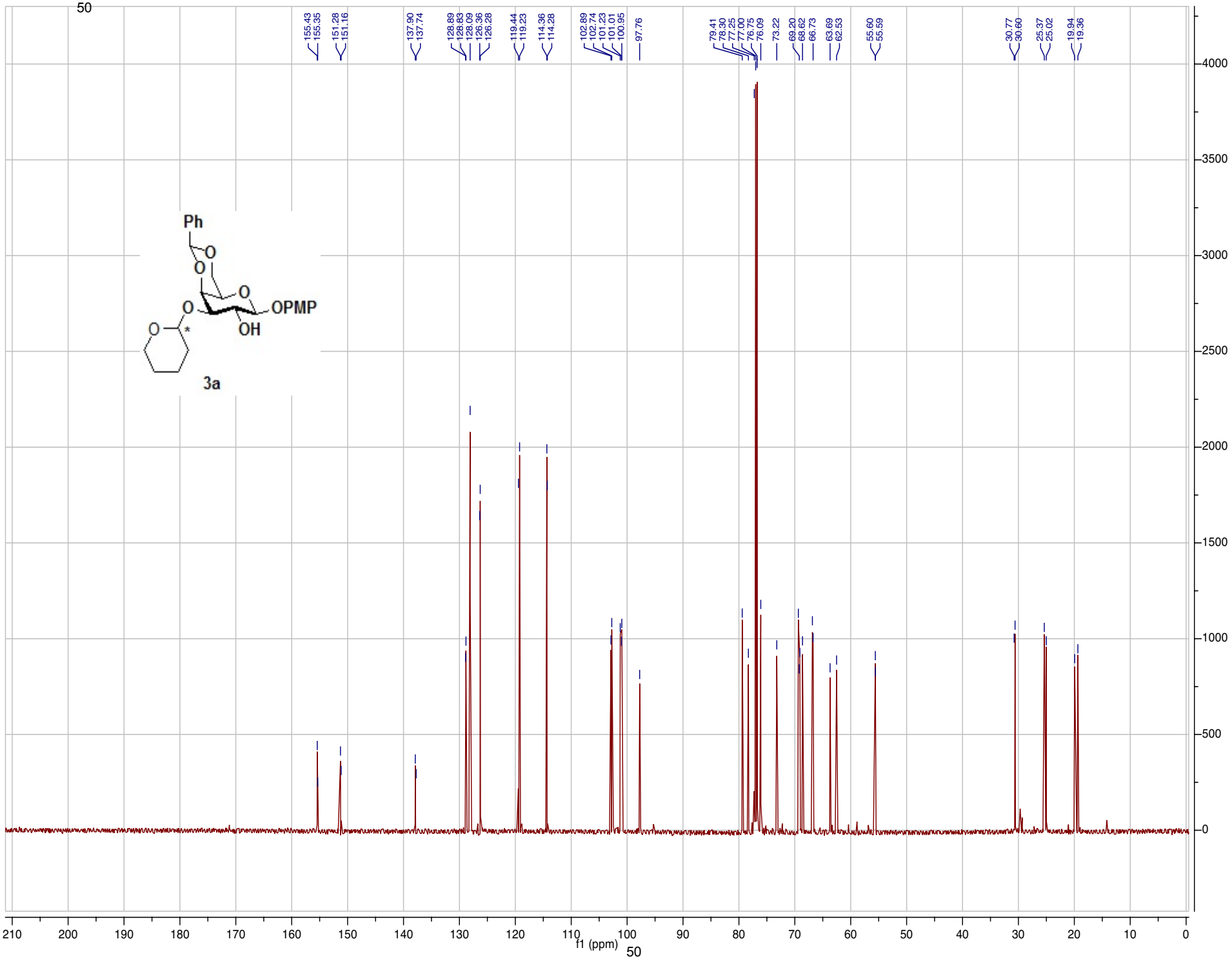

132.82
131.49
129.10
128.36
99.84
88.70
77.26
77.01
76.75
74.95
72.84
72.75
71.54
61.96
28.96
19.11
Me
Me
O
O
O
HO
OH
SPh
1e
f1 (ppm)

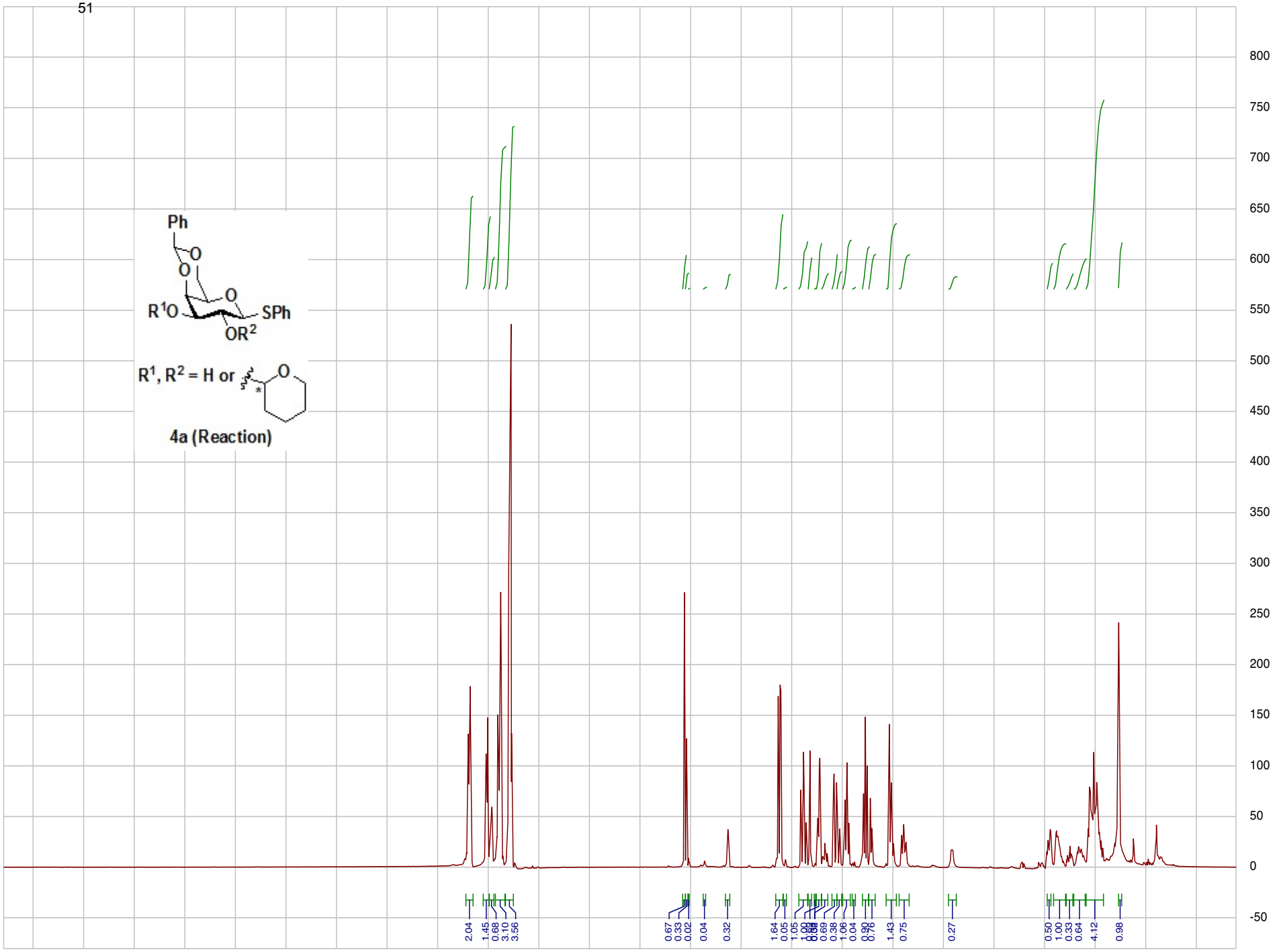

Ph
O
O
O
R1O
OPMP
OR2
R1, R2 = H or
O
3a (Reaction)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
3.60
5.53
0.34
3.36
3.70
1.07
0.63
0.14
0.63
0.08
1.72
1.00
1.02
1.12
0.61
1.10
3.81
3.15
1.65
2.35
3.66

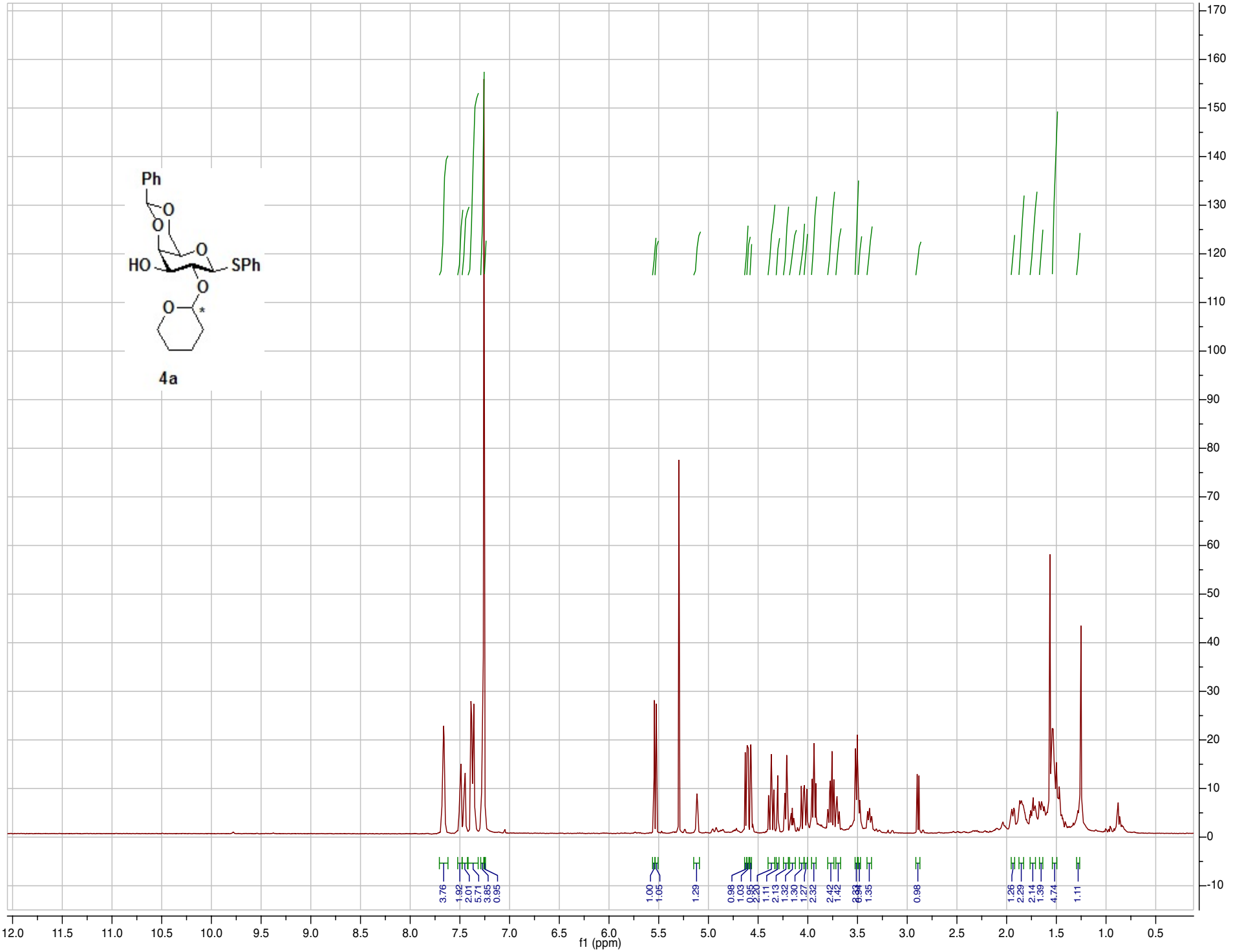

Ph
O
O
O
HO
OPMP
O
O
*
3a
3.67
5.19
3.45
3.48
1.00
0.81
0.90
1.85
1.21
1.89
1.18
0.92
2.03
3.55
1.30
1.17
4.91
1.21
3.97
1.09
3.52
2.29
5.81
f1 (ppm)

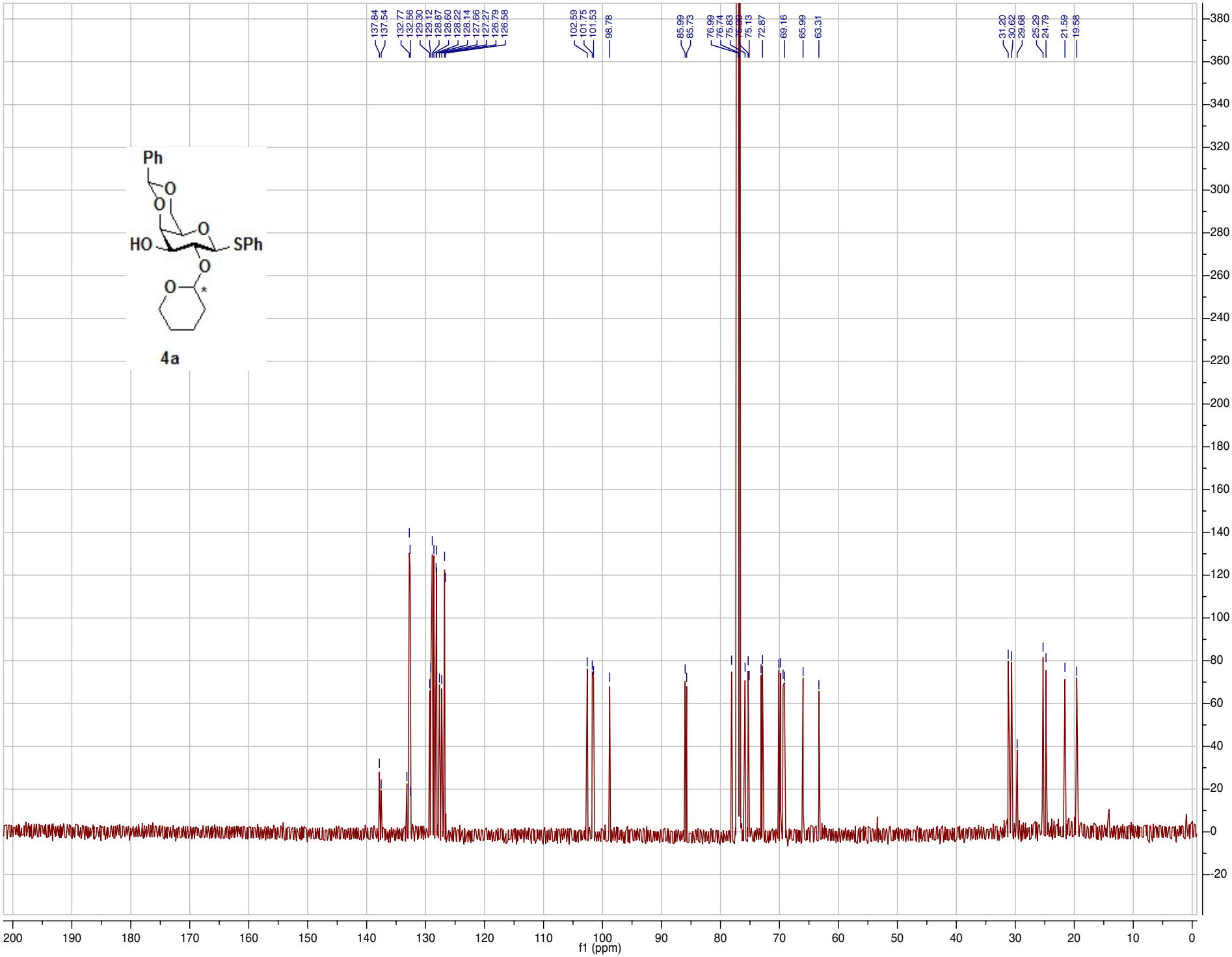

155.44
155.22
151.78
137.72
137.44
129.27
129.11
128.22
128.15
126.71
126.56
119.25
118.84
114.39
102.46
102.12
101.72
101.61
101.53
98.05
79.35
76.75
75.17
73.88
71.61
69.02
66.71
65.48
62.13
55.63
31.25
30.34
25.37
24.94
21.28
18.97
Ph
HO
OPMP
3a
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

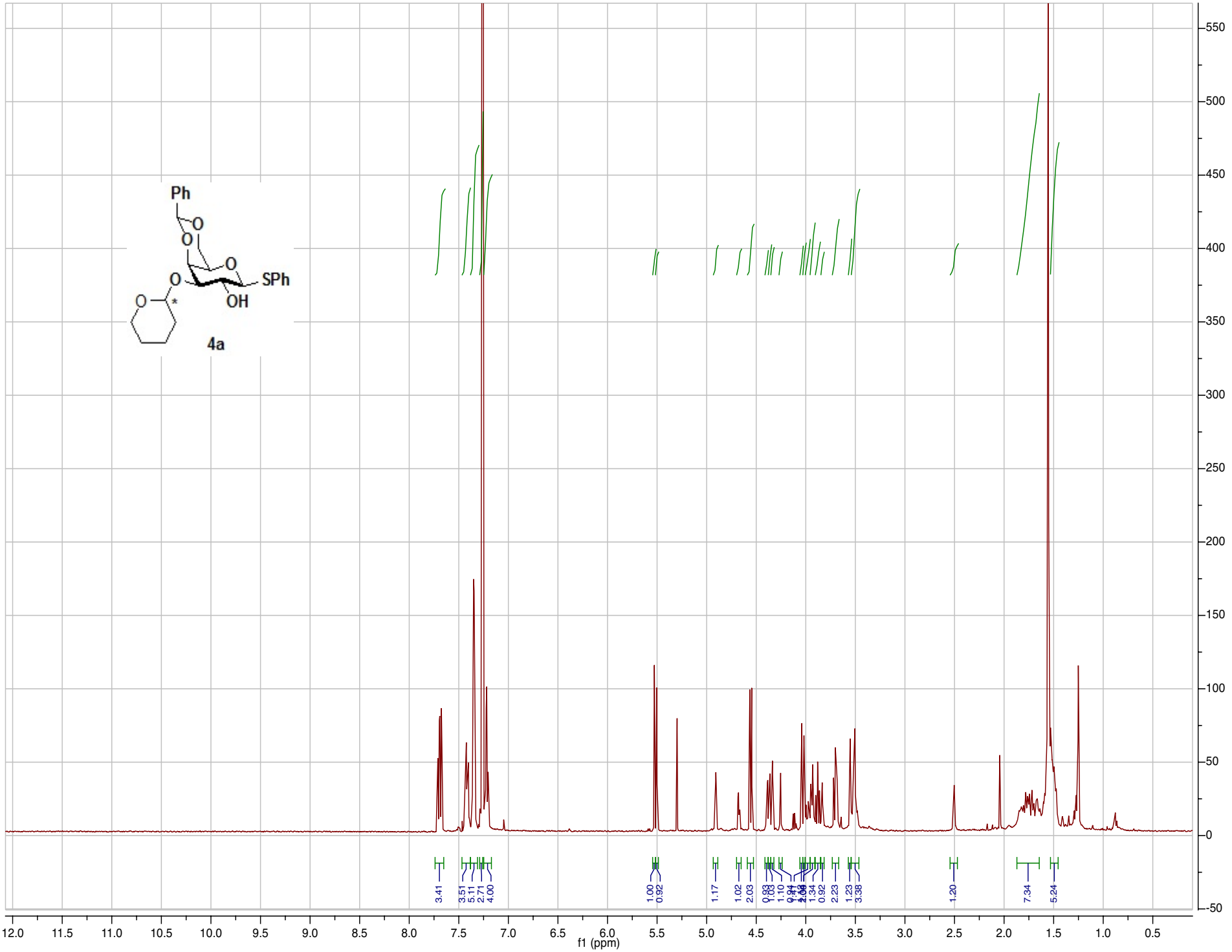

Ph
O
O
O
O
OPMP
O
*
OH
3a
f1 (ppm)

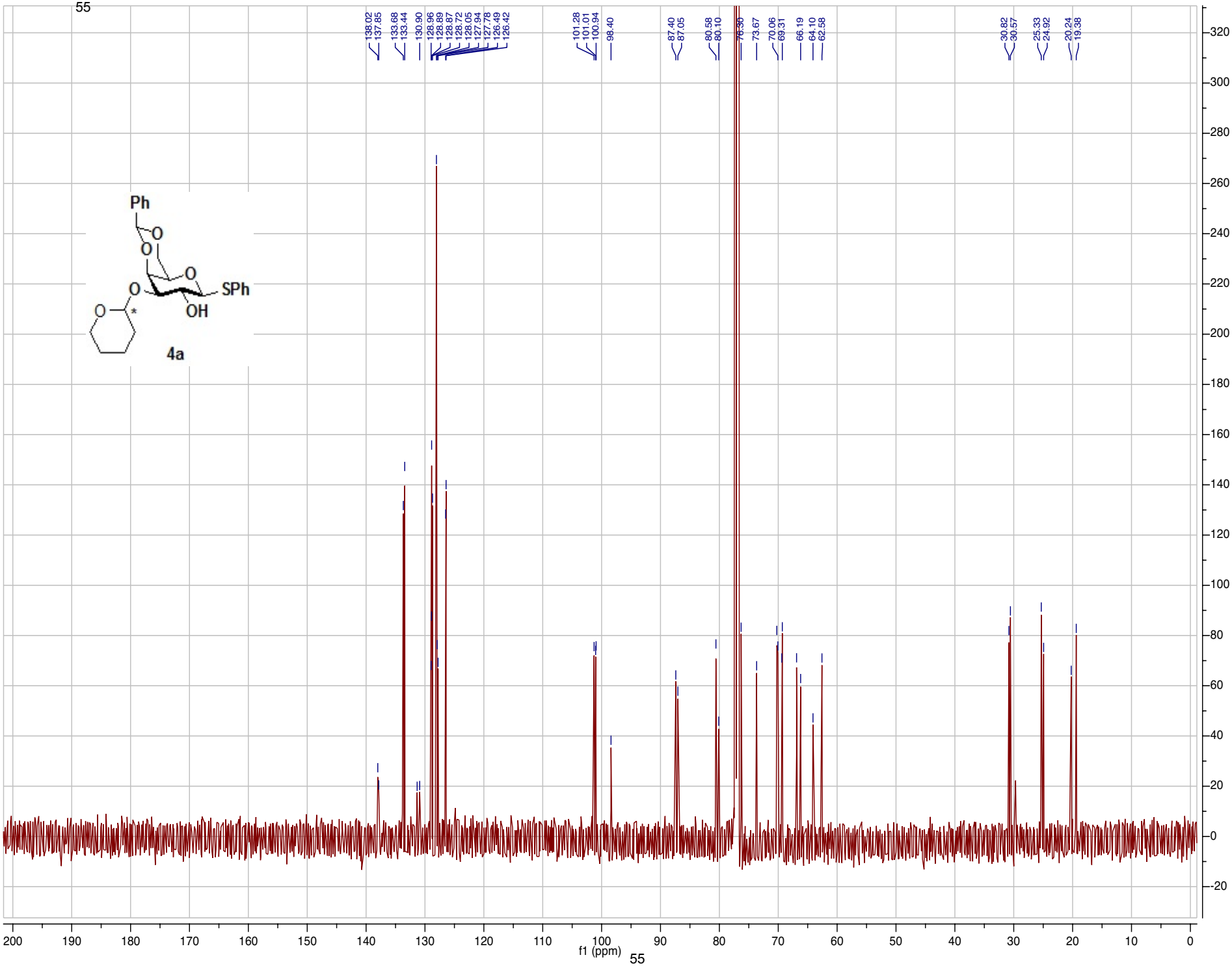

155.43
155.35
151.28
151.16
137.90
137.74
128.89
128.83
128.09
126.36
126.28
119.44
119.23
114.36
114.28
102.89
102.74
101.23
101.01
100.95
97.76
79.41
78.30
77.25
77.00
76.75
76.09
73.22
69.20
68.62
66.73
63.69
62.53
55.60
55.59
30.77
30.60
25.37
25.02
19.94
19.36
Ph
OPMP
OH
3a
f1 (ppm)

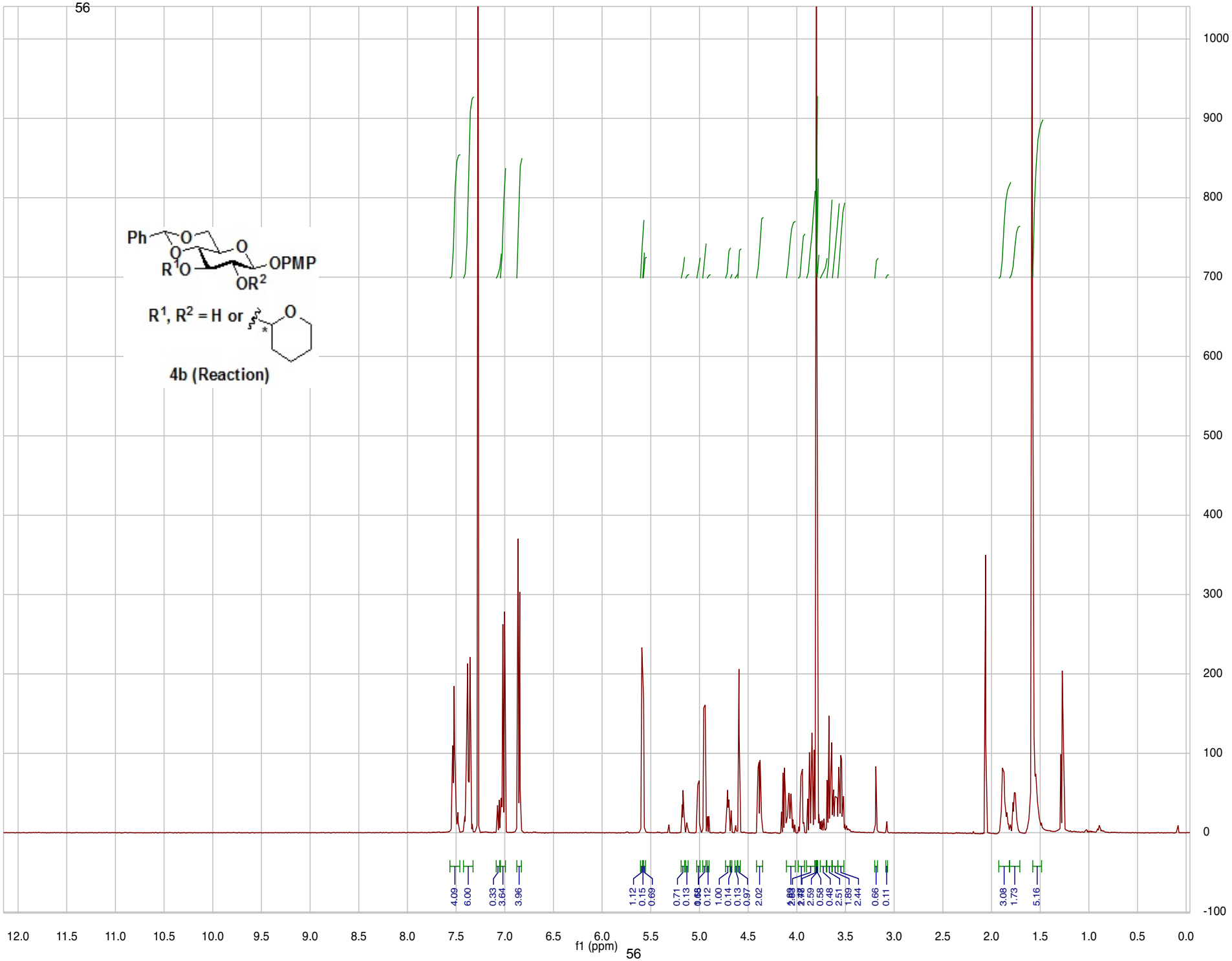

Ph
O
O
O
R1O
SPh
OR2
R1, R2 = H or
O
4a (Reaction)
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
2.04
1.45
0.68
3.10
3.56
0.67
0.33
0.02
0.04
0.32
1.64
0.05
1.05
0.69
0.38
1.06
0.04
1.43
0.75
0.27
0.50
1.00
0.33
0.64
4.12
0.98
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

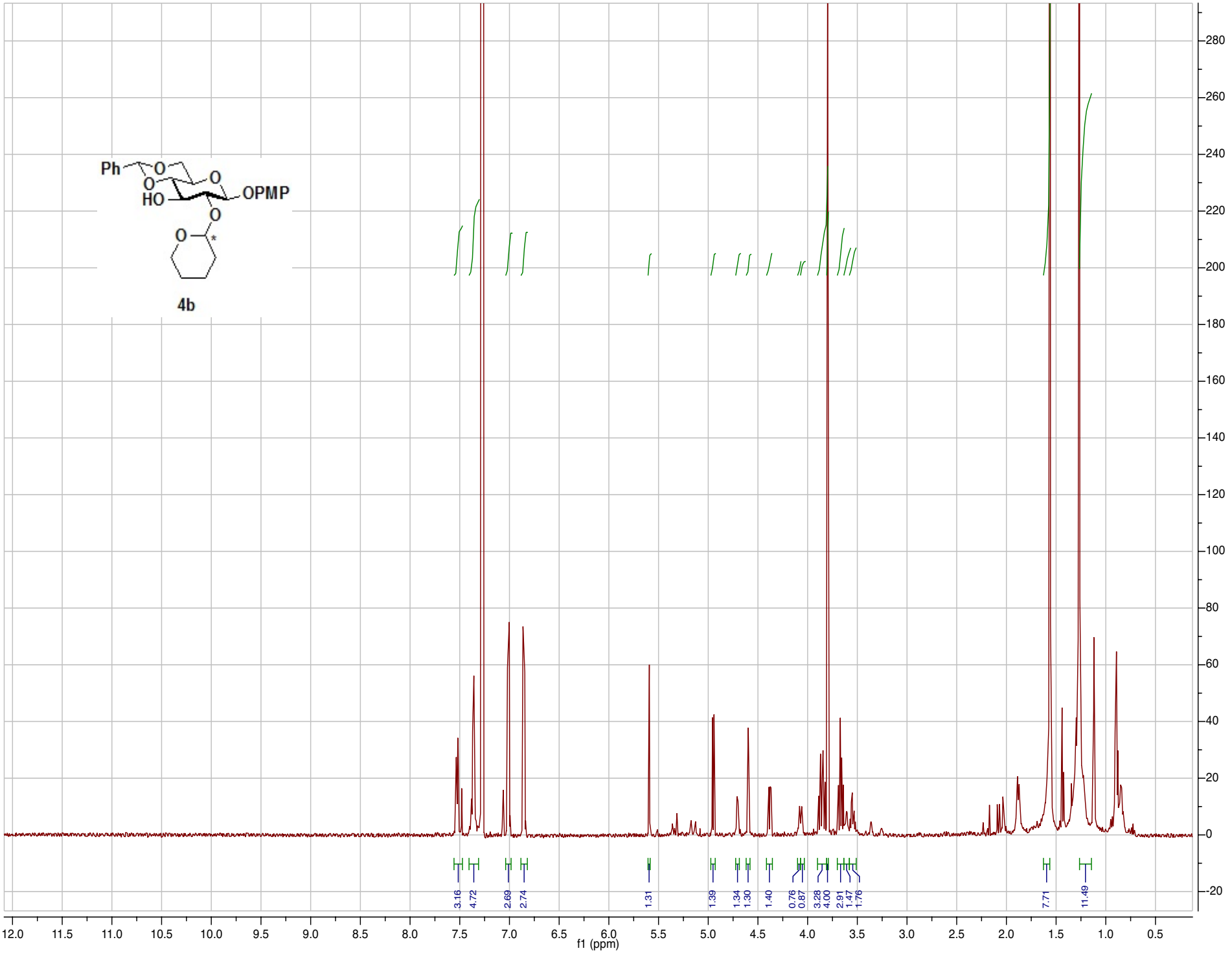

Ph
O
O
O
HO
SPh
O
O
*
4a
f1 (ppm)

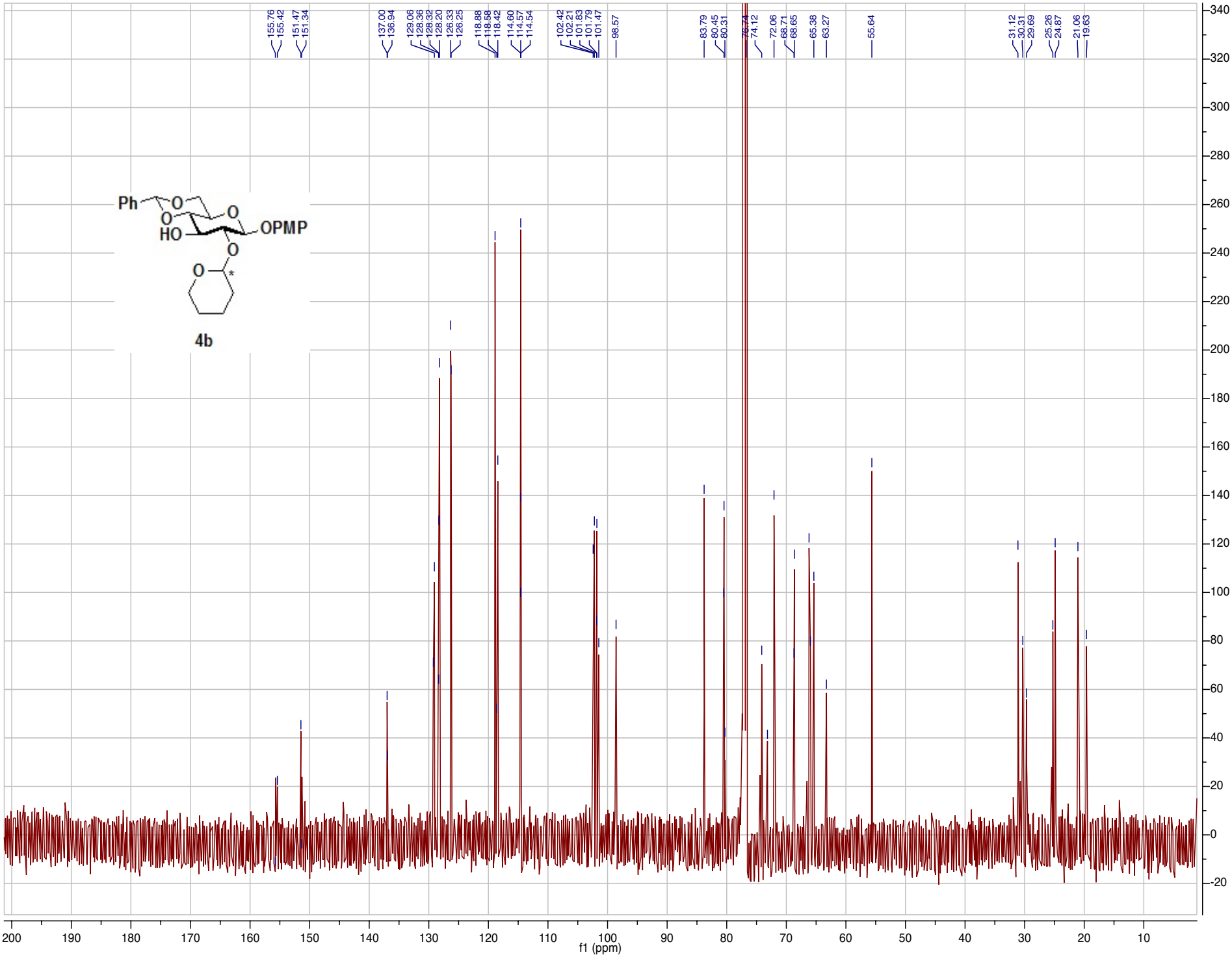

137.84
137.54
132.77
132.56
129.30
129.12
128.87
128.60
128.22
128.14
127.66
127.27
126.79
126.58
102.59
101.75
101.53
98.78
85.99
85.73
76.99
76.74
75.83
75.13
72.87
69.16
65.99
63.31
31.20
30.62
29.68
25.29
24.79
21.59
19.58
Ph
O
O
O
HO
SPh
O
O
*
4a
f1 (ppm)

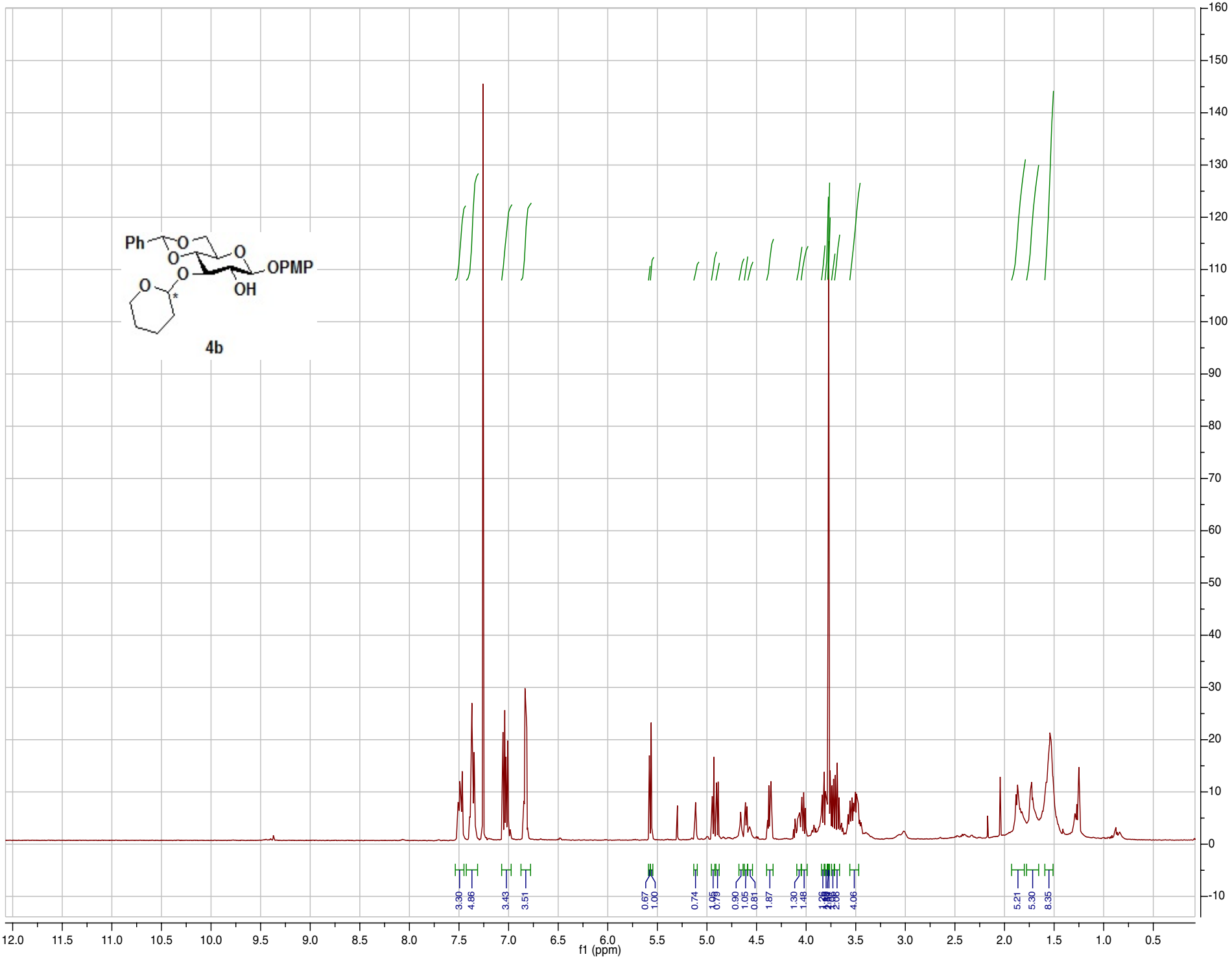

Ph
O
O
O
O
SPh
O
*
OH
4a
f1 (ppm)

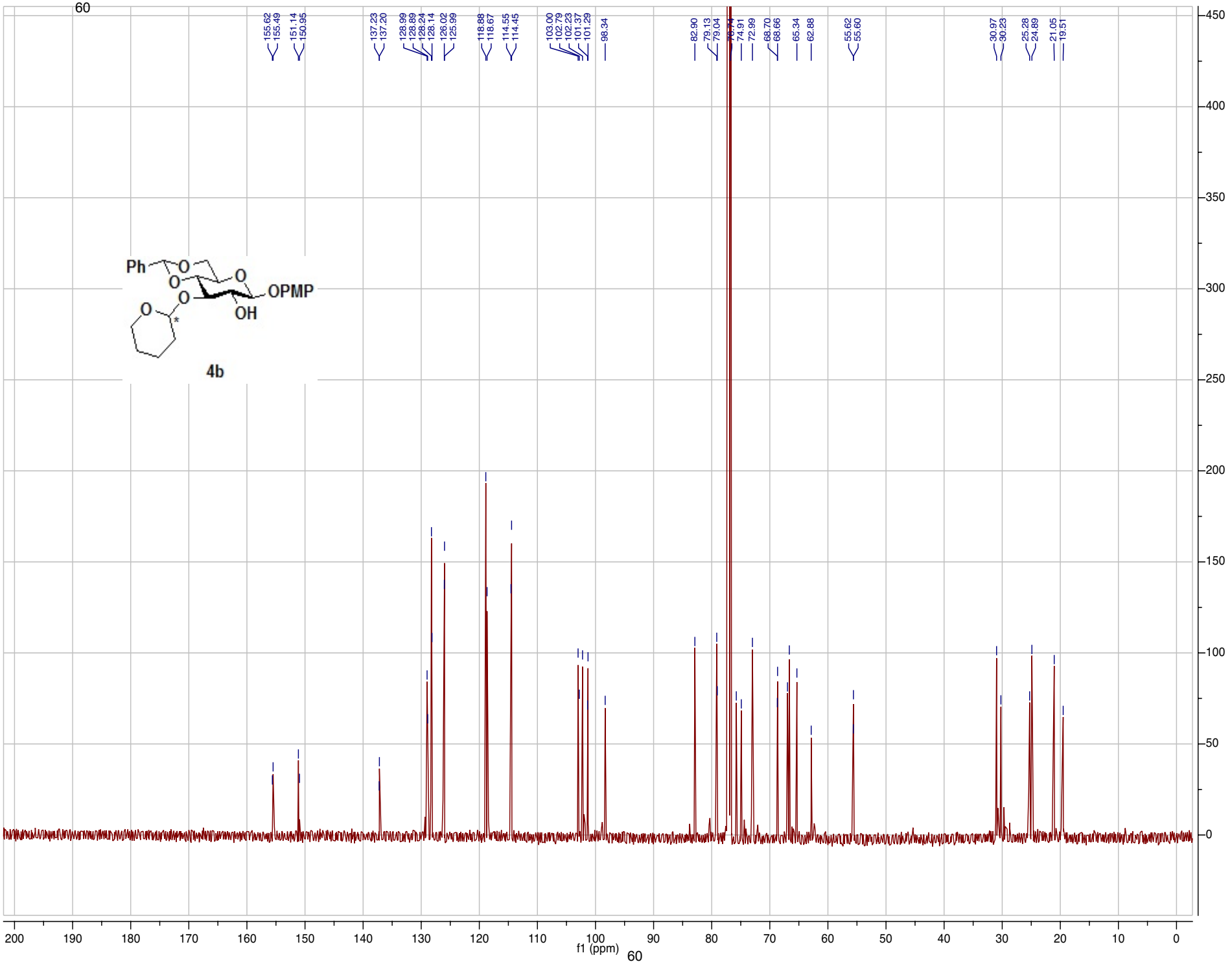

138.02
137.85
133.68
133.44
130.90
128.96
128.89
128.87
128.72
128.05
127.94
127.78
126.49
126.42
101.28
101.01
100.94
98.40
87.40
87.05
80.58
80.10
78.30
73.67
70.06
69.31
66.19
64.10
62.58
30.82
30.57
25.33
24.92
20.24
19.38
Ph
O
O
O
O
SPh
O
*
OH
4a
f1 (ppm)

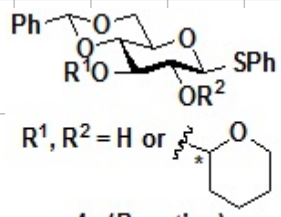

Ph
O
O
O
R1O
OPMP
OR2
R1, R2 = H or
O
4b (Reaction)
1000
900
800
700
600
500
400
300
200
100
0
-100
4.09
6.00
0.33
3.64
3.96
1.12
0.15
0.69
0.71
0.13
1.00
0.14
0.13
0.97
2.02
0.66
0.11
3.08
1.73
5.16
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Ph
O
O
HO
O
OPMP
O
O
*
4b
3.16
4.72
2.69
2.74
1.31
1.39
1.34
1.30
1.40
0.76
0.87
3.28
4.00
2.91
1.47
1.76
7.71
11.49
f1 (ppm)


155.76
155.42
151.47
151.34
137.00
136.94
129.06
128.36
128.32
128.20
126.33
126.25
118.88
118.58
118.42
114.60
114.57
114.54
102.42
102.21
101.83
101.79
101.47
98.57
83.79
80.45
80.31
74.12
72.06
68.71
68.65
65.38
63.27
55.64
31.12
30.31
29.69
25.26
24.87
21.06
19.63
Ph
O
O
O
HO
OPMP
O
O
*
4b
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

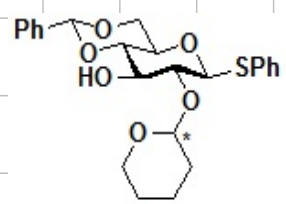

Ph
O
O
O
O
OPMP
OH
O
*
4b
f1 (ppm)


60
155.62
155.49
151.14
150.95
137.23
137.20
128.99
128.89
128.24
128.14
126.02
125.99
118.88
118.67
114.55
114.45
103.00
102.79
102.23
101.37
101.29
98.34
82.90
79.13
79.04
74.91
72.99
68.70
68.66
65.34
62.88
55.62
55.60
30.97
30.23
25.28
24.89
21.05
19.51
Ph
O
O
O
O
OPMP
OH
*
4b
f1 (ppm)
60


Ph
O
O
O
R1O
SPh
OR2
R1, R2 = H or
O
*

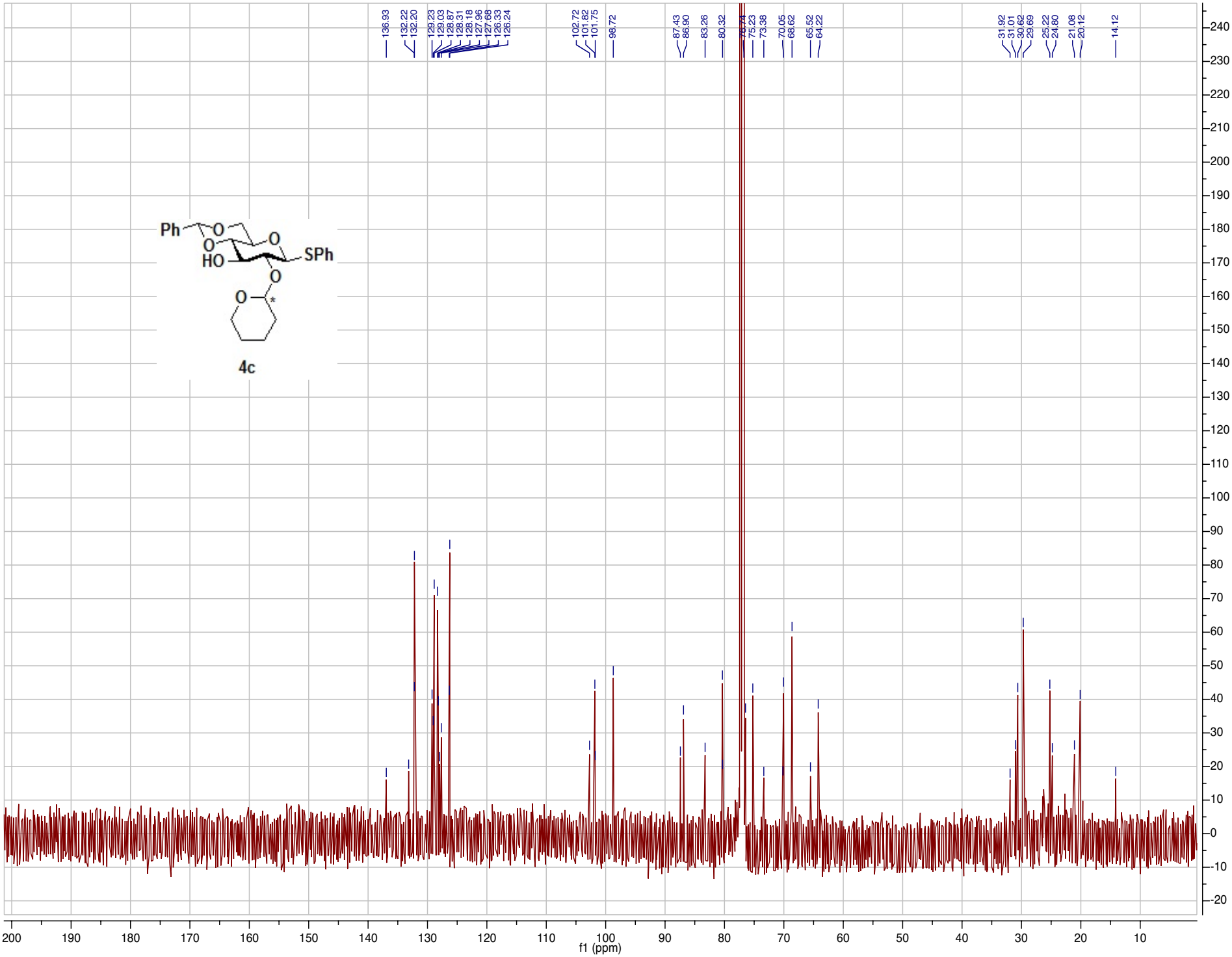
4c (Reaction)

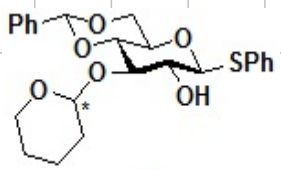
550
500
450
400
350
300
250
200
150
100
50
0
-50
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
5.87
8.42
0.96
0.13
0.30
0.16
0.07
0.98
0.16
0.15
0.11
0.15
1.00
1.27
0.16
0.18
1.28
0.20
2.62
0.16
4.70
1.16
0.17
0.10
2.64
0.39
2.31
2.88


Ph
O
O
O
HO
SPh
O
O
*

4c

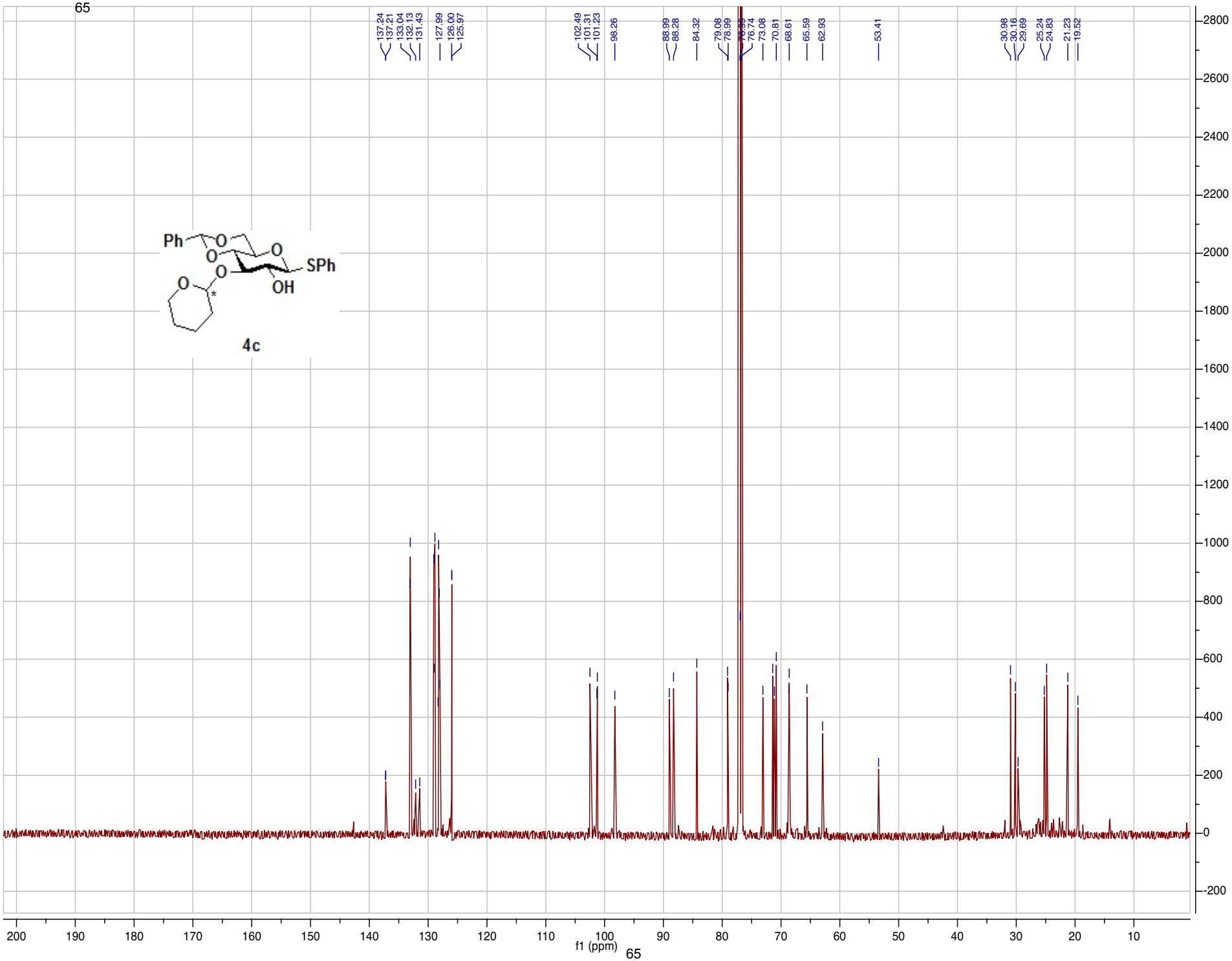
f1 (ppm)
4.73
6.44
0.54
1.00
1.18
0.70
0.71
0.78
1.83
2.00
2.08
1.27
4.10
5.29
3.28

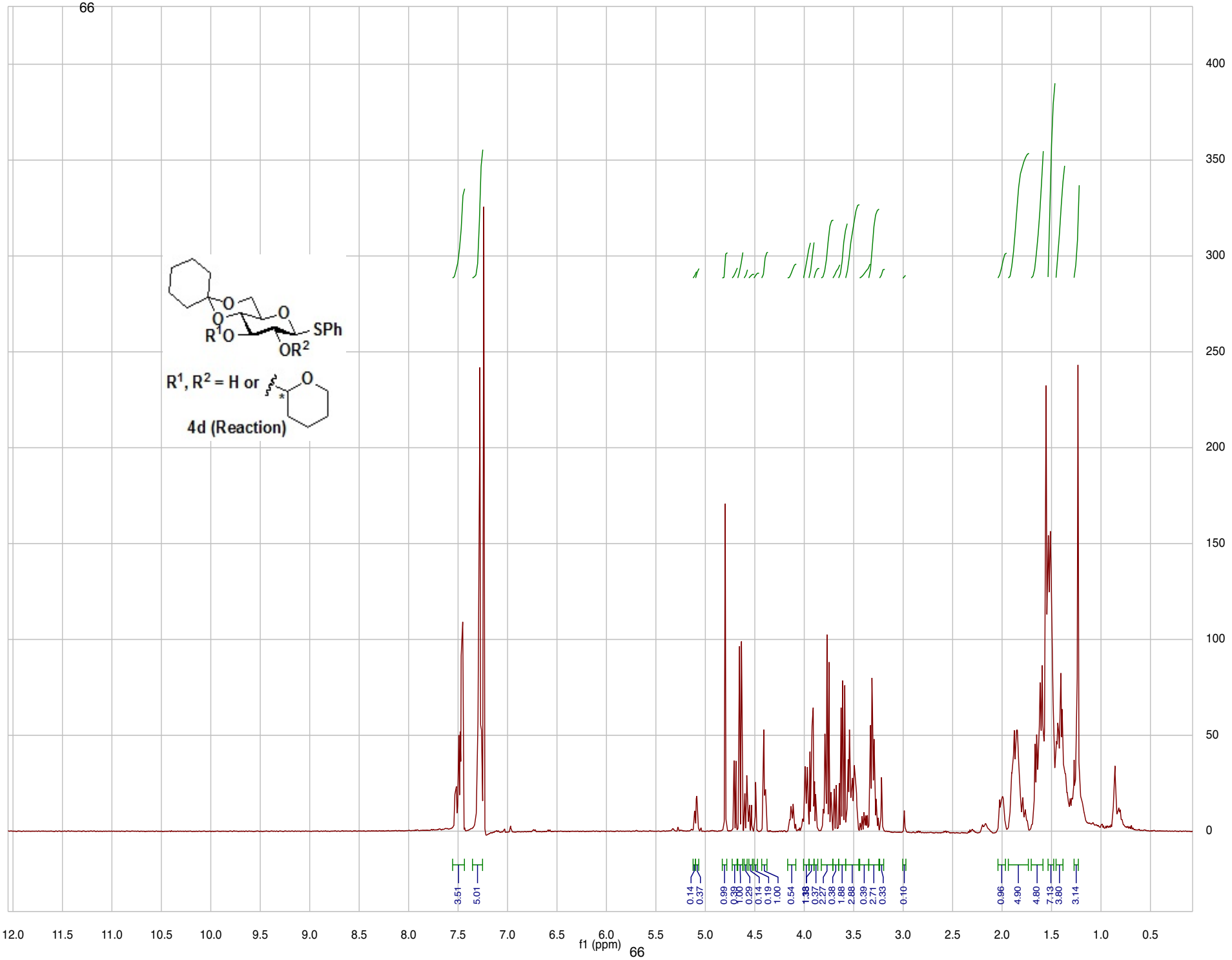

136.93
132.22
132.20
129.23
129.03
128.87
128.31
128.18
127.96
127.68
126.33
126.24
102.72
101.82
101.75
98.72
87.43
86.90
83.26
80.32
75.23
73.38
70.05
68.62
65.52
64.22
31.92
31.01
30.62
29.69
25.22
24.80
21.08
20.12
14.12
Ph
O
O
O
HO
SPh
O
O
*
4c
f1 (ppm)

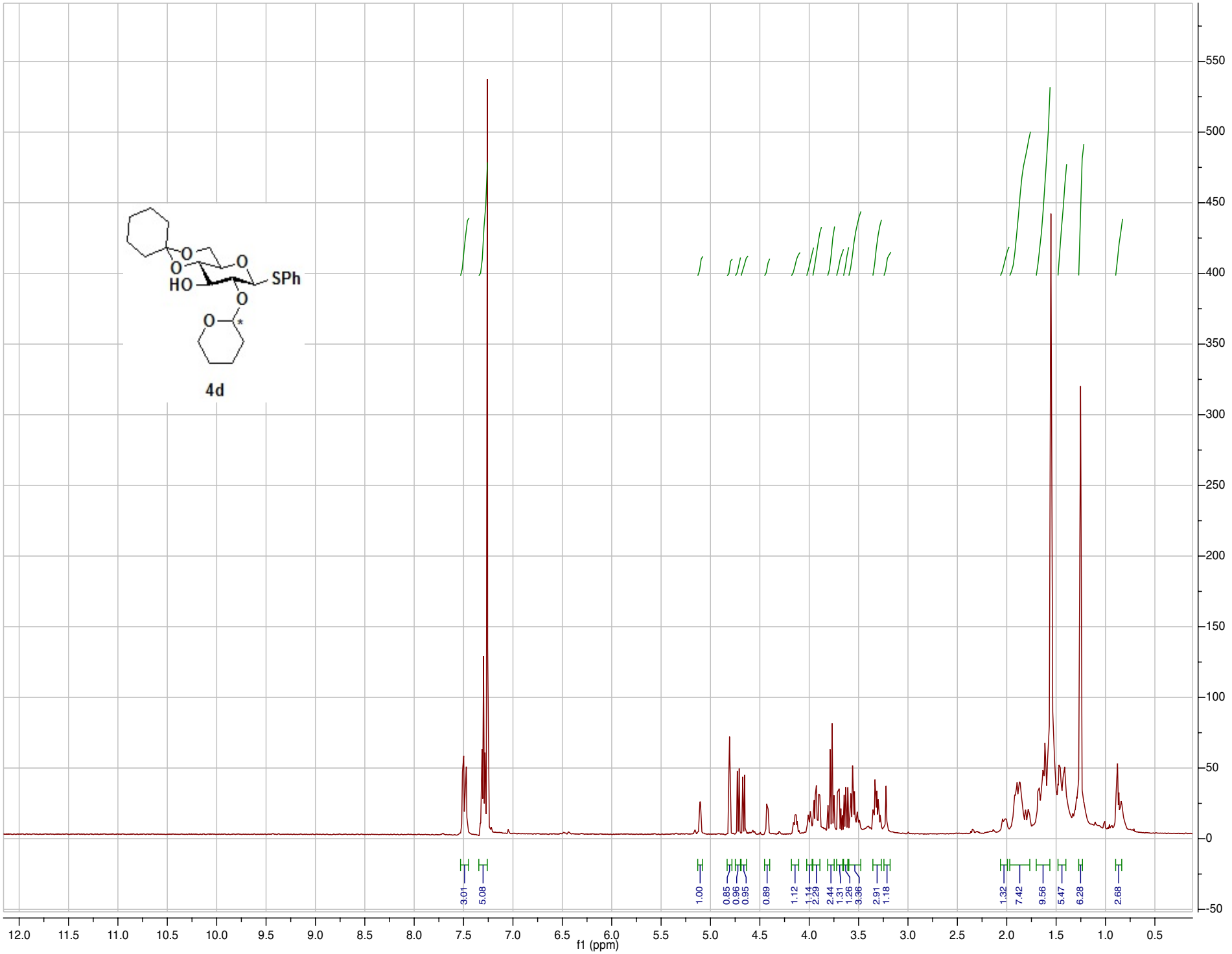

Ph
O
O
O
O
O
SPh
OH
*

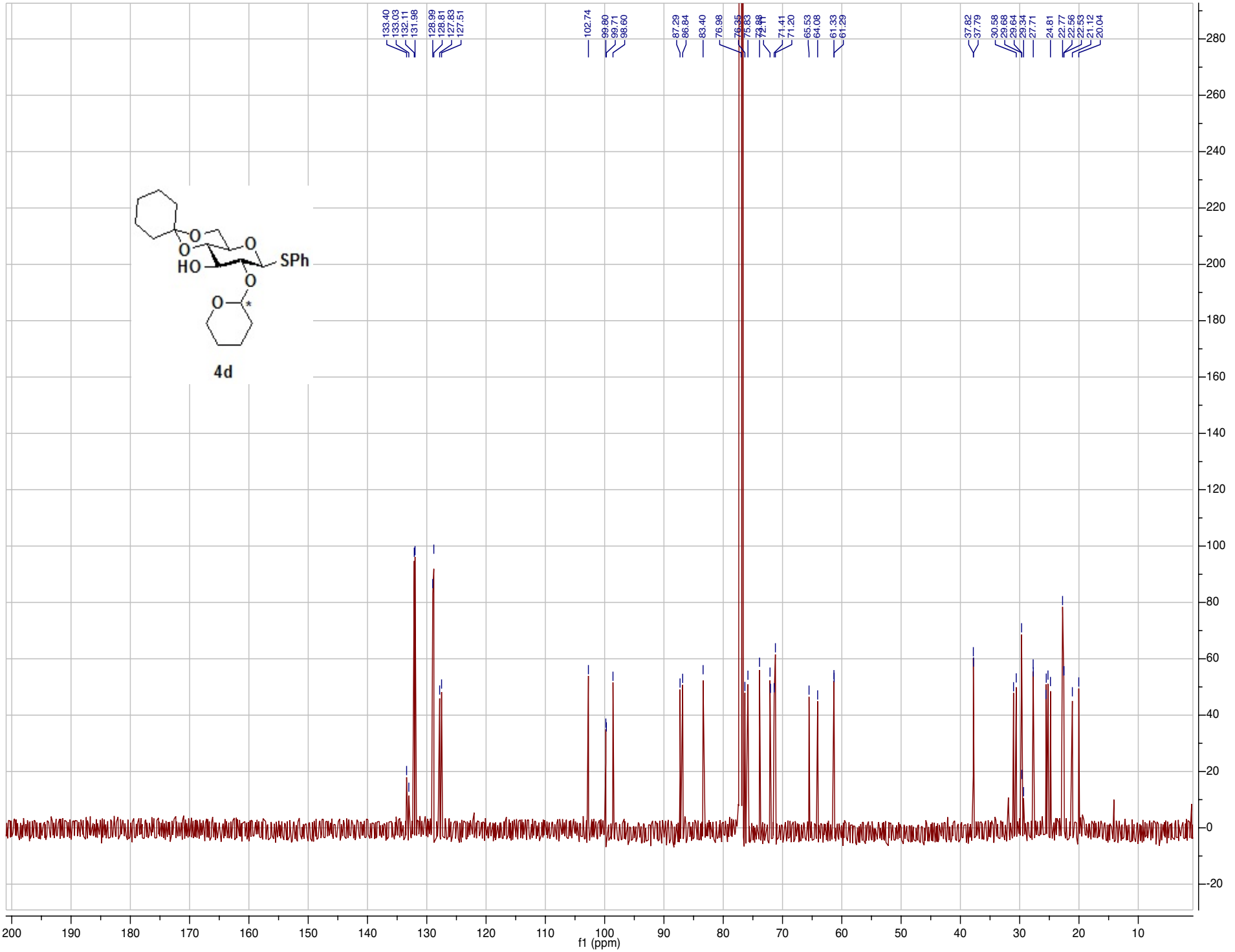
4c

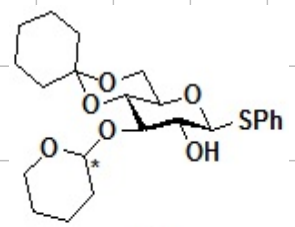
3.75
4.00
11.63
1.00
1.26
1.30
1.22
1.23
1.14
1.79
2.38
2.34
1.40
1.99
1.42
2.21
6.25
1.01
2.96
1.99
5.35
3.02
f1 (ppm)


137.24
137.21
133.04
132.13
131.43
127.99
126.00
125.97
102.49
101.31
101.23
98.26
88.99
88.28
84.32
79.08
78.99
76.74
73.08
70.81
68.61
65.59
62.93
53.41
30.98
30.16
29.69
25.24
24.83
21.23
19.52
Ph
O
O
O
O
SPh
OH
*
4c
f1 (ppm)


R1O
OR2
SPh
R1, R2 = H or
4d (Reaction)
400
350
300
250
200
150
100
50
0
12.0
11.5
11.0
10.5
10.0
9.5
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
f1 (ppm)
3.51
5.01
0.14
0.37
0.99
0.29
0.14
0.19
1.00
0.54
0.39
2.71
0.33
0.10
0.96
4.90
4.80
7.13
3.80
3.14

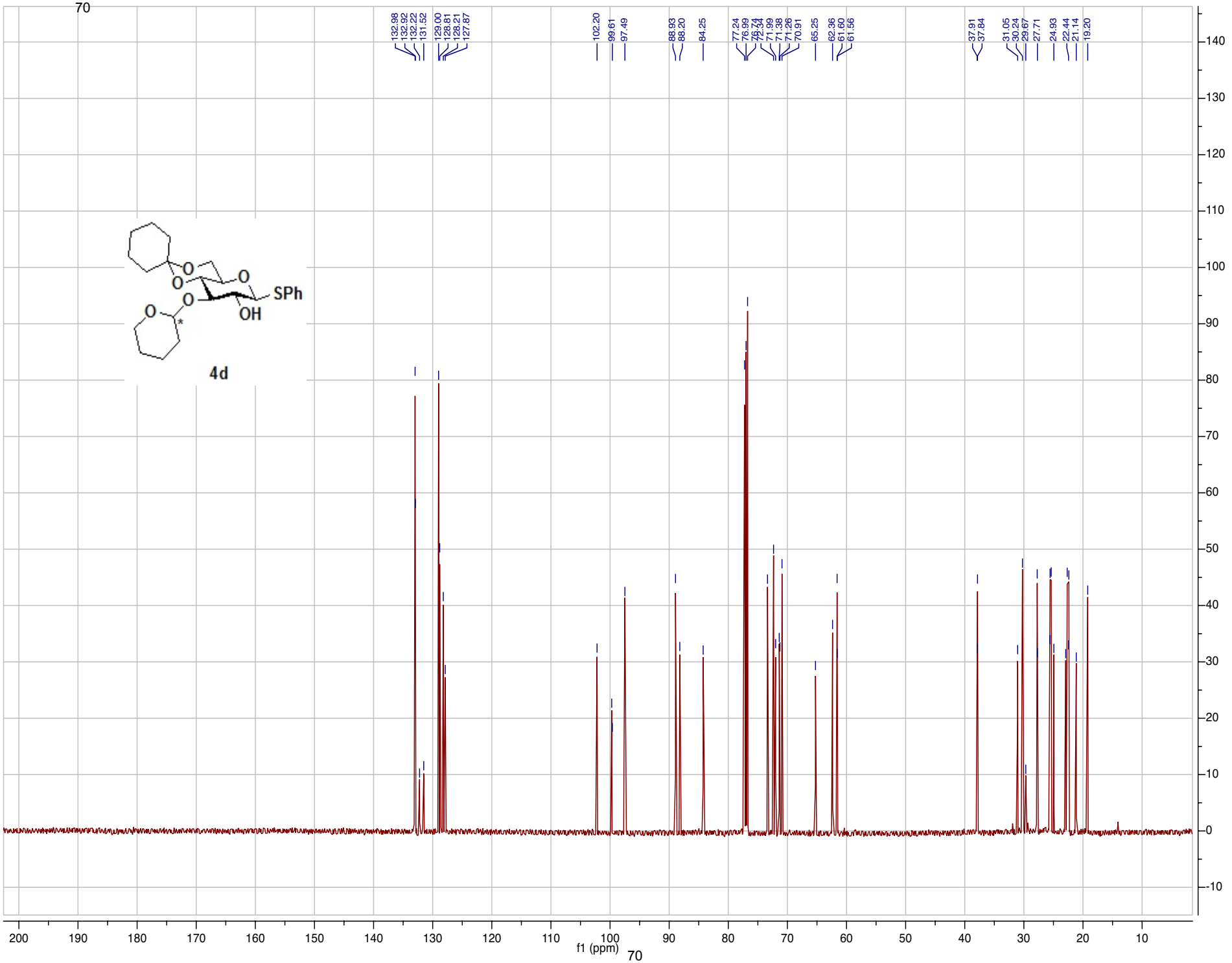

SPh
HO
4d
f1 (ppm)

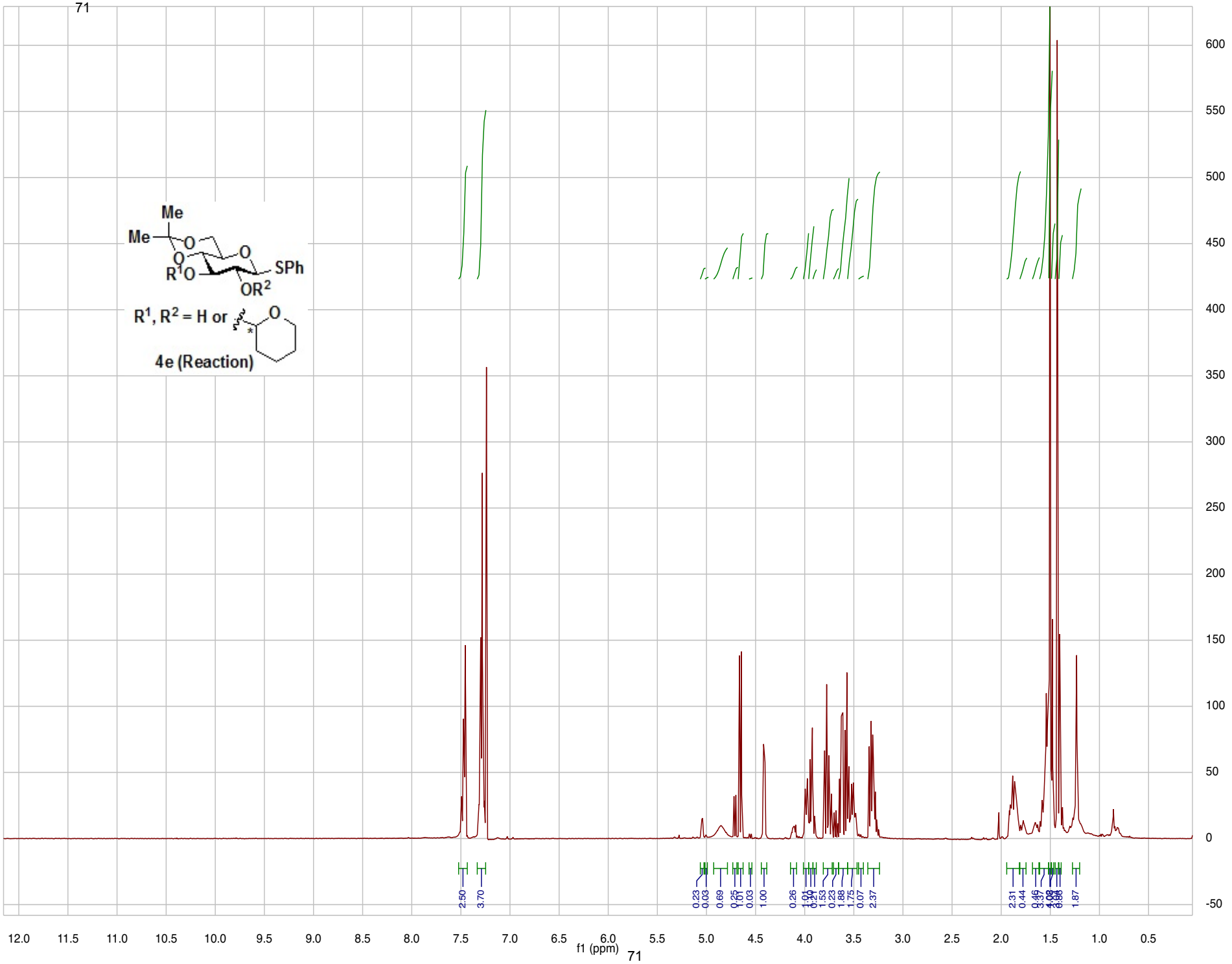

133.40
133.03
132.11
131.98
128.99
128.81
127.83
127.51
102.74
99.80
99.71
98.60
87.29
86.84
83.40
76.98
76.35
75.83
73.88
71.41
71.20
65.53
64.08
61.33
61.29
37.82
37.79
30.58
29.88
29.64
29.34
27.71
24.81
22.77
22.56
22.53
21.12
20.04
HO
SPh
4d
f1 (ppm)

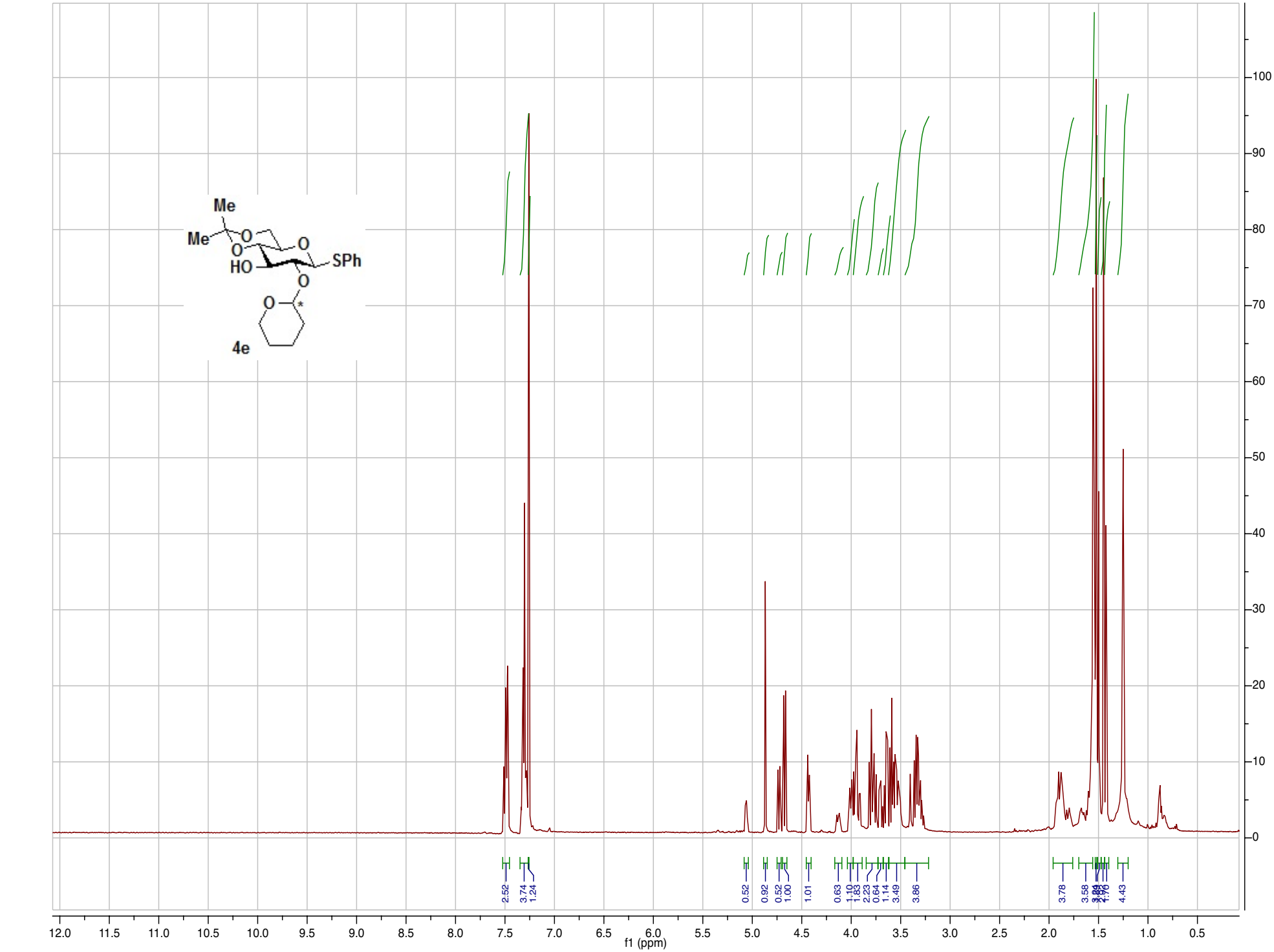

O
O
O
O
O
SPh
OH
*

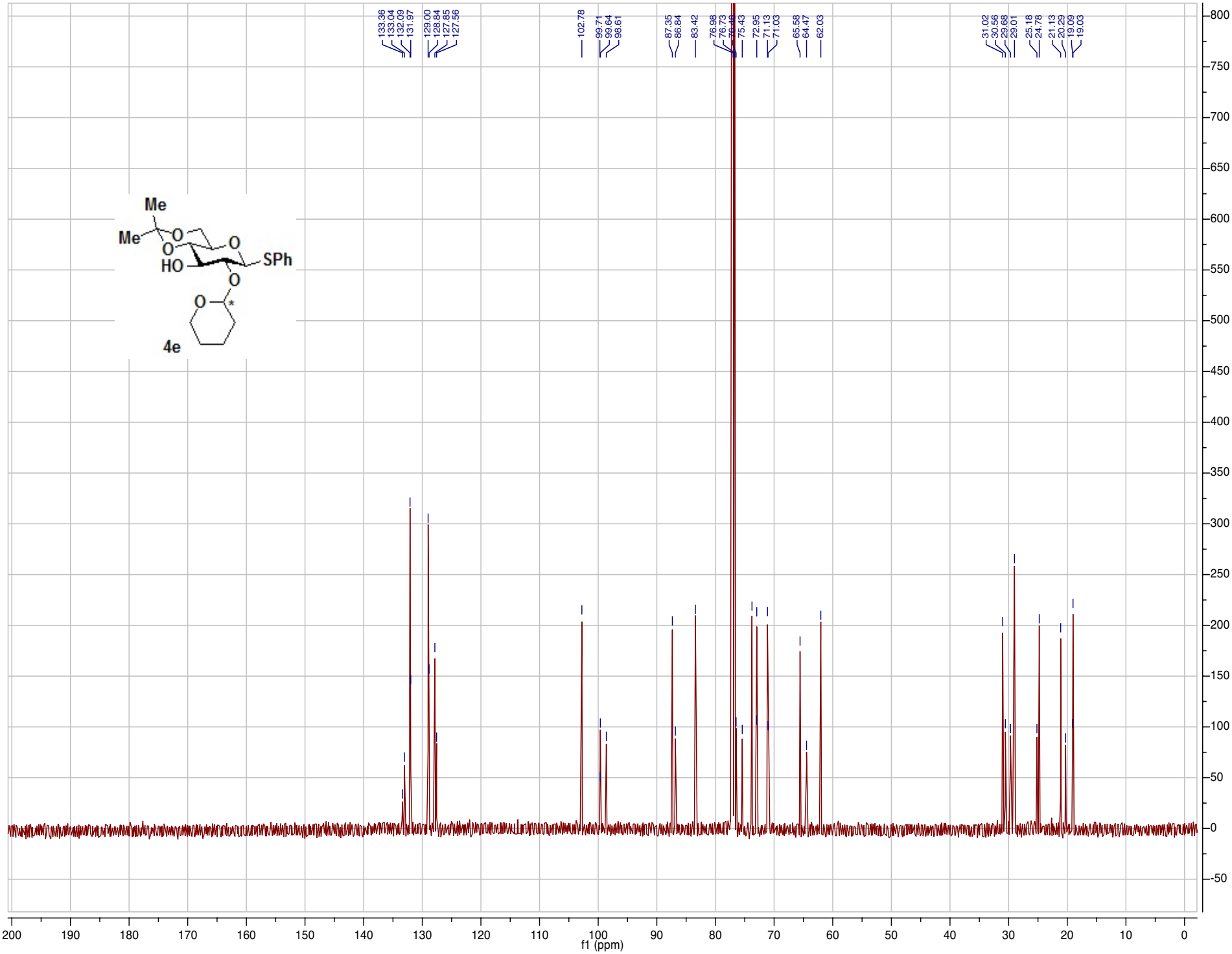
4d

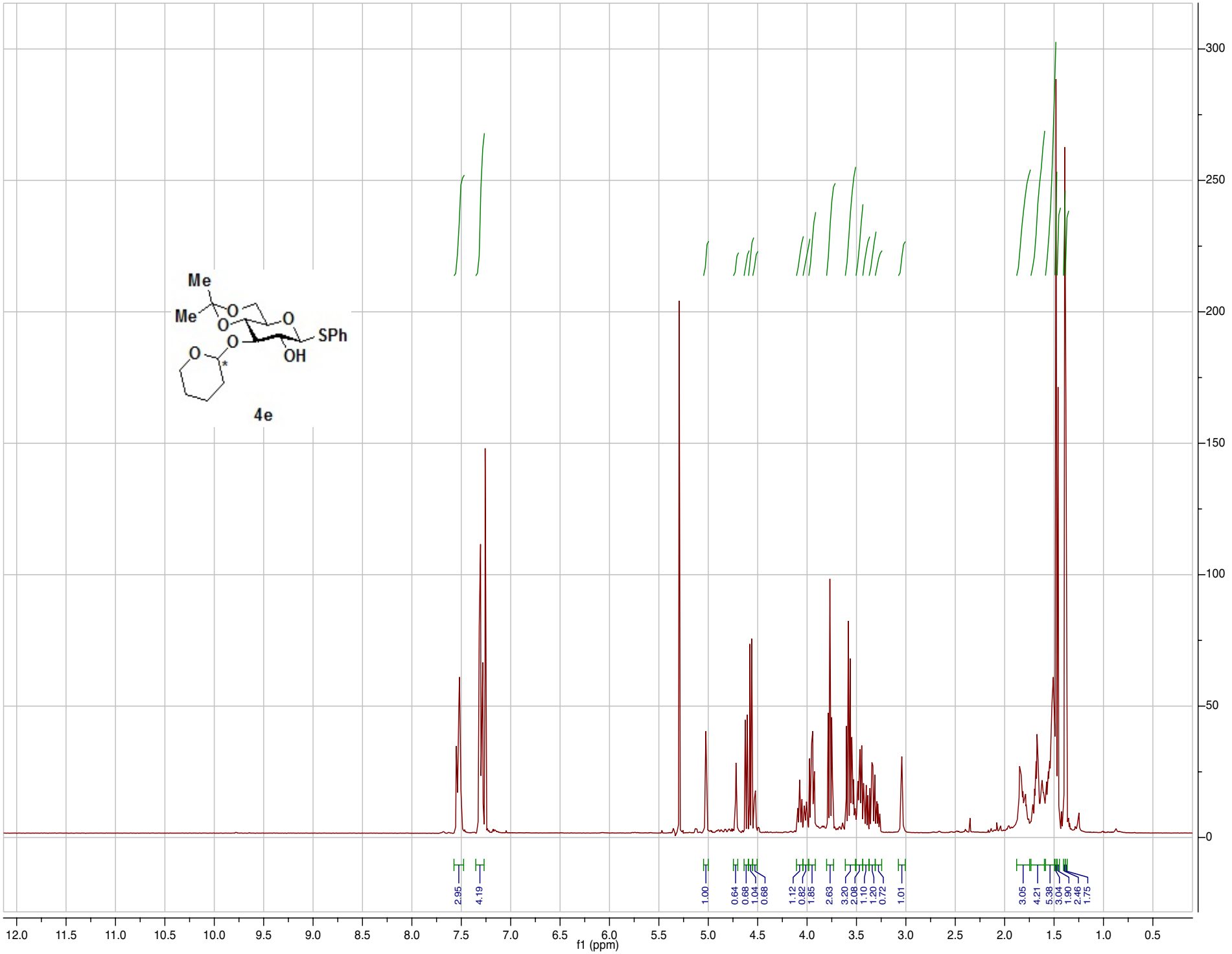
3.10
4.50
1.00
1.36
1.04
0.77
1.15
0.90
1.93
2.71
2.94
1.34
3.99
1.04
2.07
3.22
21.63
4.39
f1 (ppm)

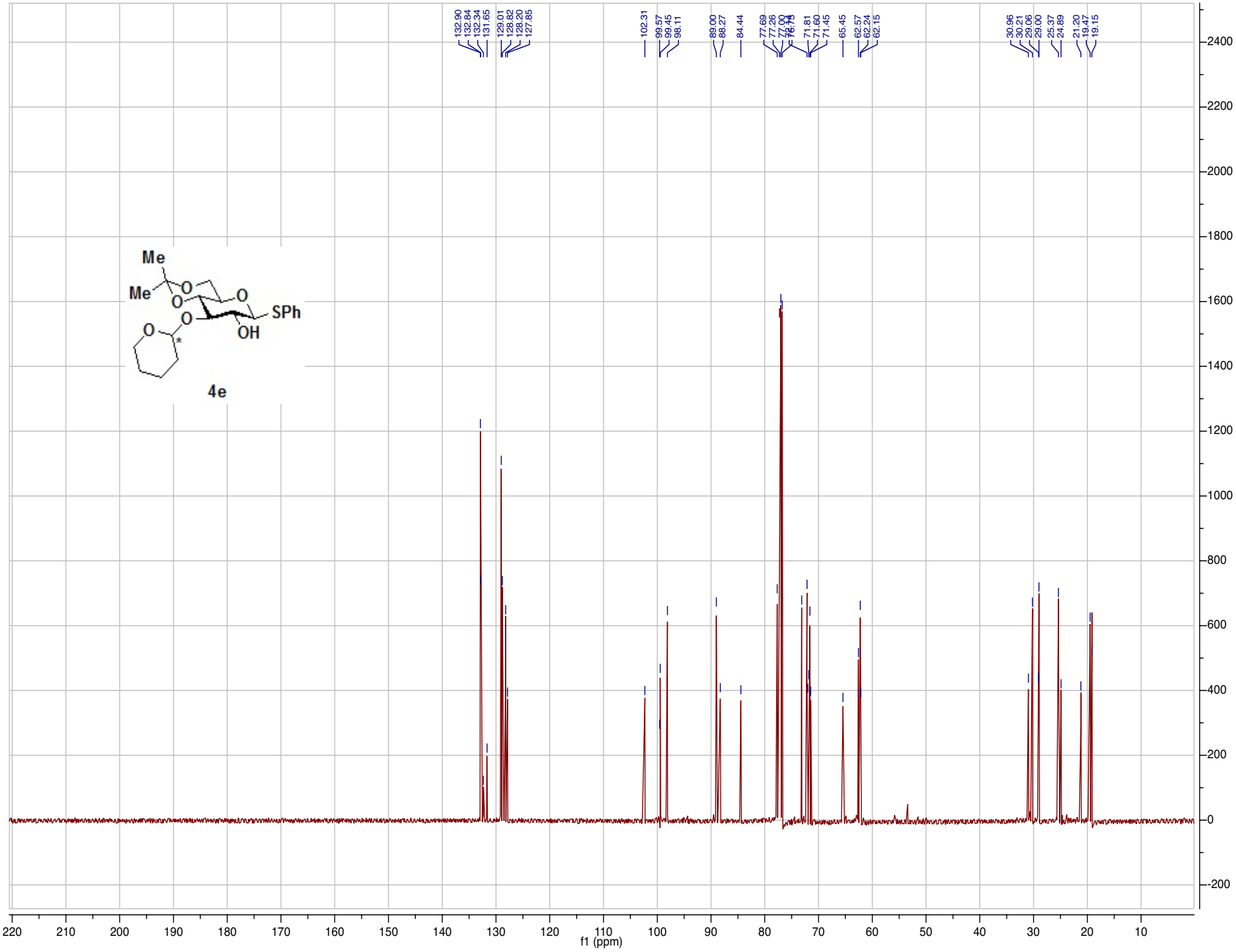

132.98
132.92
132.22
131.52
129.00
128.81
128.21
127.87
102.20
99.61
97.49
88.93
88.20
84.25
77.24
76.99
76.74
72.34
71.99
71.38
71.26
70.91
65.25
62.36
61.60
61.56
37.91
37.84
31.05
30.24
29.67
27.71
24.93
22.44
21.14
19.20
SPh
OH
4d
f1 (ppm)

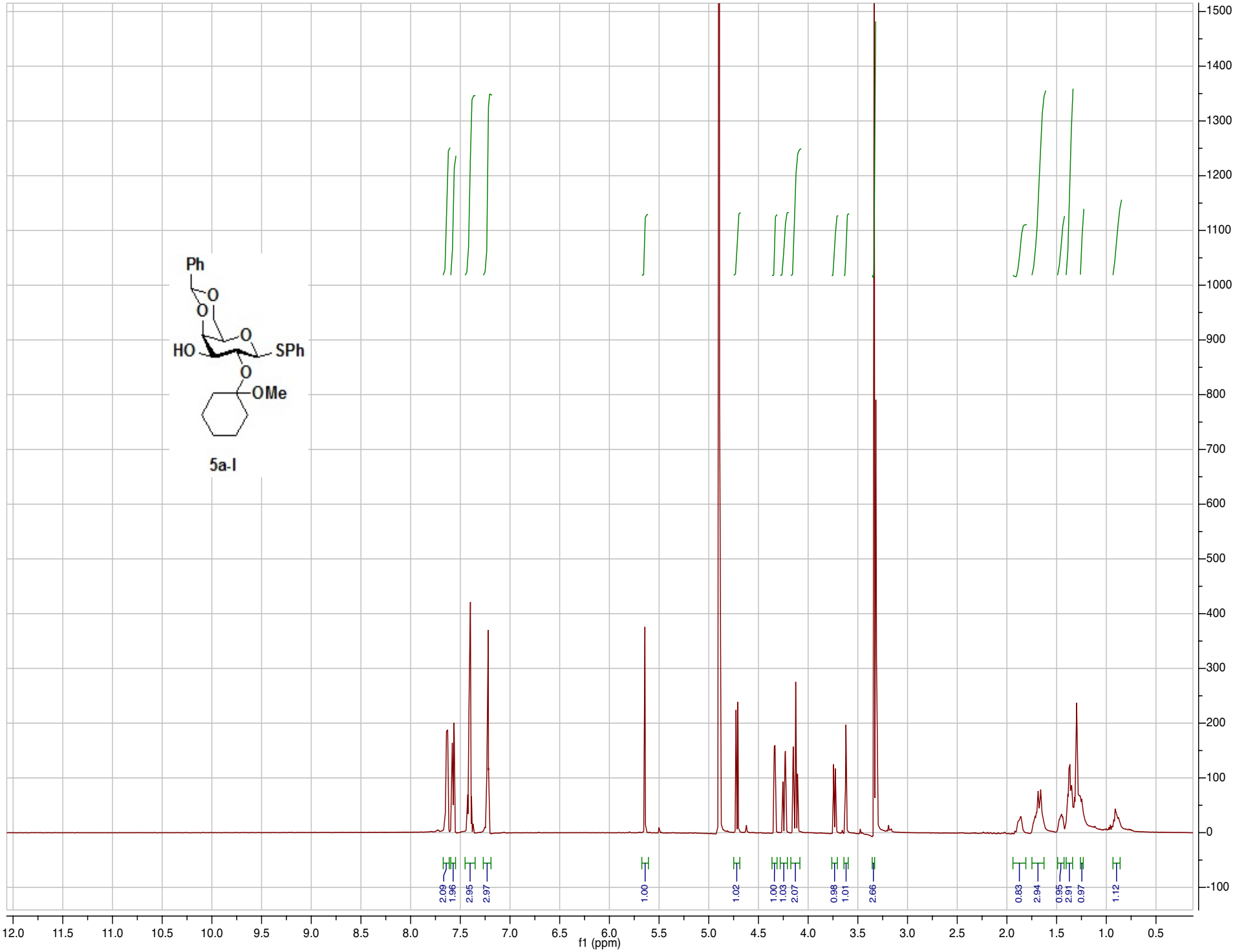

Me
Me
O
O
O
R1O
SPh
OR2
R1, R2 = H or
O
*
4e (Reaction)
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
2.50
3.70
0.23
0.03
0.69
0.25
0.01
0.03
1.00
0.26
1.53
0.23
1.88
1.75
0.07
2.37
2.31
0.44
1.87
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

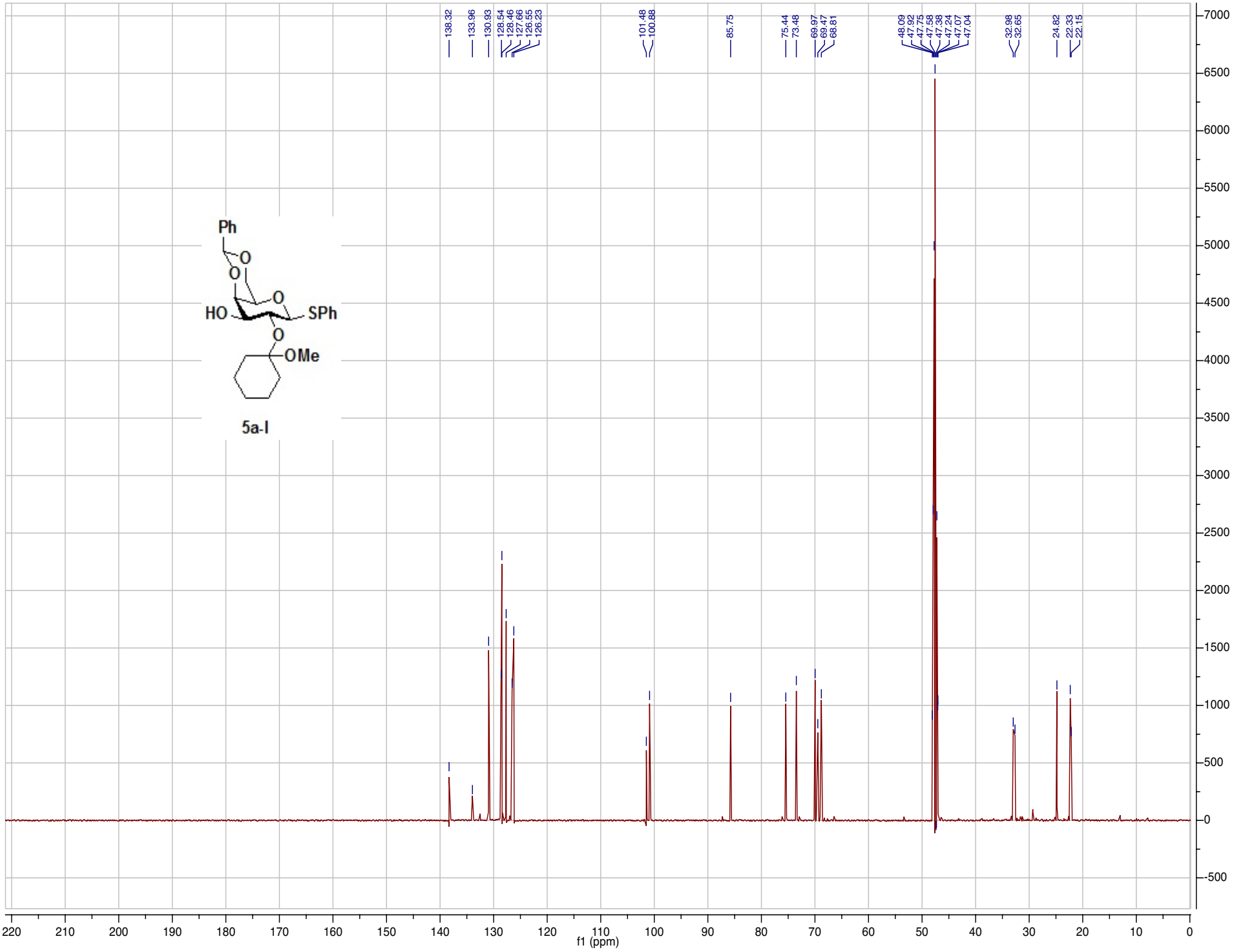

Me
Me
O
O
O
HO
SPh
O
O
*
4e
100
90
80
70
60
50
40
30
20
10
0
2.52
3.74
1.24
0.52
0.92
0.52
1.00
1.01
0.63
1.10
1.83
2.23
0.64
1.14
3.49
3.86
3.78
3.58
4.43
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

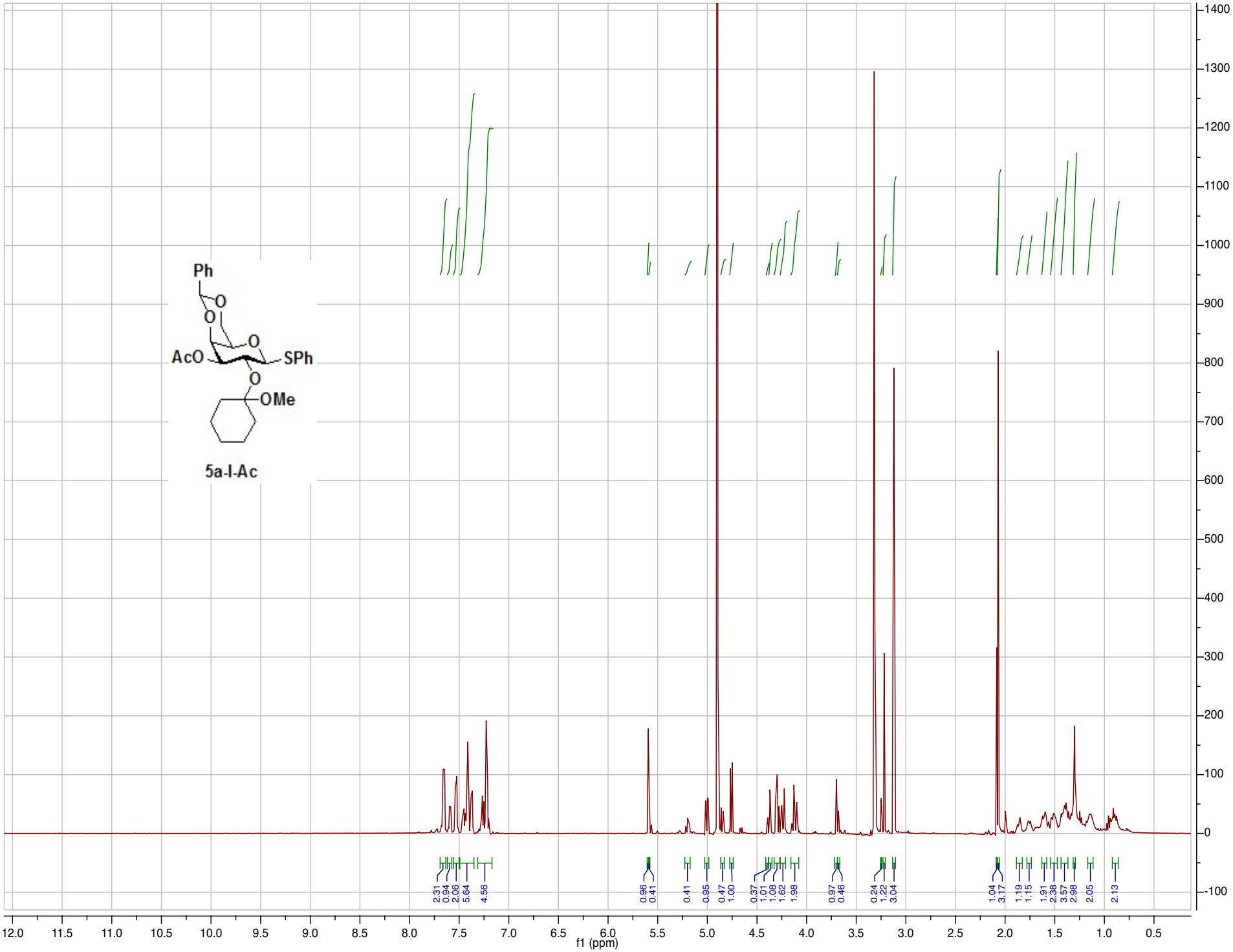

133.36
133.04
132.09
131.97
129.00
128.84
127.85
127.56
102.78
99.71
99.64
98.61
87.35
86.84
83.42
76.98
76.73
75.43
72.95
71.13
71.03
65.58
64.47
62.03
31.02
30.56
29.68
29.01
25.18
24.78
21.13
20.29
19.09
19.03
Me
Me
O
O
O
HO
SPh
O
O
*
4e
f1 (ppm)

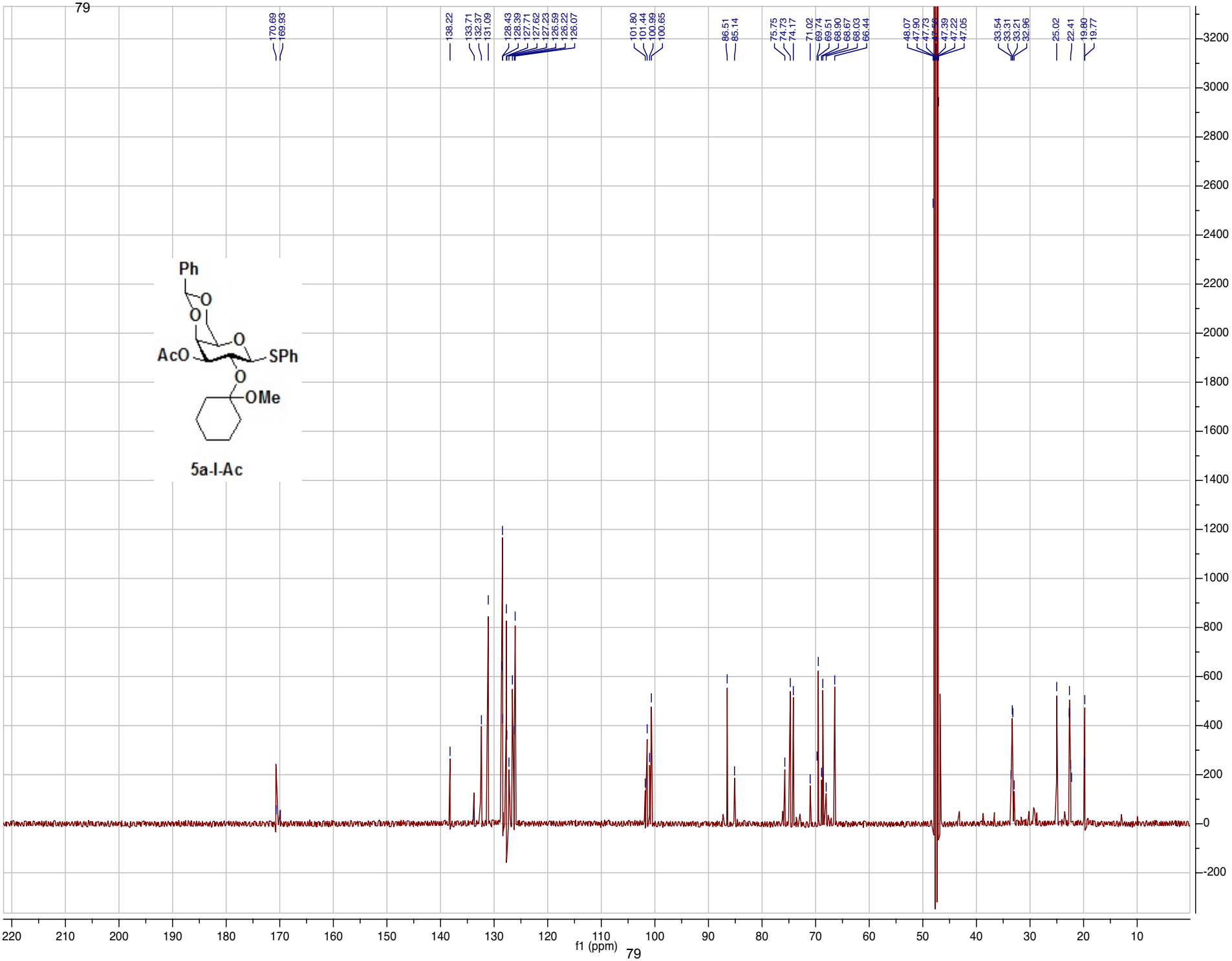

Me
Me
O
O
O
O
O
SPh
OH
*
4e
2.95
4.19
1.00
0.64
0.68
1.04
0.68
1.12
0.82
1.85
2.63
3.20
2.08
1.10
1.20
0.72
1.01
3.05
4.21
5.38
3.04
1.90
2.46
1.75
f1 (ppm)

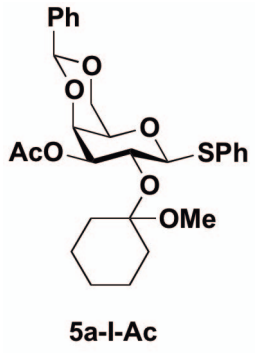

132.90
132.84
132.34
131.65
129.01
128.82
128.20
127.85
102.31
99.57
99.45
98.11
89.00
88.27
84.44
77.69
77.26
77.00
76.74
71.81
71.60
71.45
65.45
62.57
62.24
62.15
30.96
30.21
29.06
29.00
25.37
24.89
21.20
19.47
19.15
Me
Me
O
O
O
O
SPh
OH
O
*
4e
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Ph
O
O
O
HO
SPh
O
OMe
5a-I
2.09
1.96
2.95
2.97
1.00
1.02
1.00
1.03
2.07
0.98
1.01
2.66
0.83
2.94
0.95
2.91
0.97
1.12
f1 (ppm)

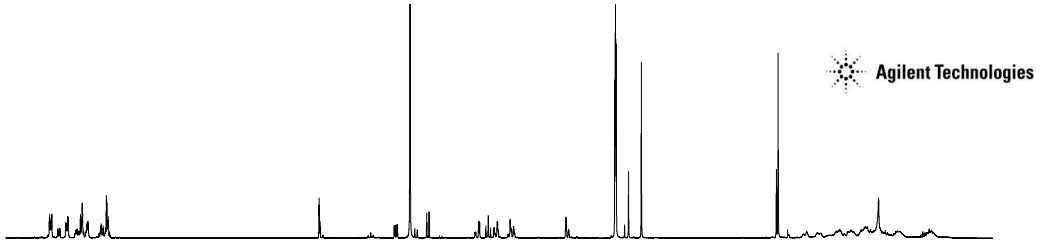

138.32
133.96
130.93
128.54
128.46
127.66
126.55
126.23
101.48
100.88
85.75
75.44
73.48
69.97
69.47
68.81
48.09
47.92
47.75
47.58
47.38
47.24
47.07
47.04
32.98
32.65
24.82
22.33
22.15
Ph
O
O
O
HO
SPh
O
OMe
5a-I
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

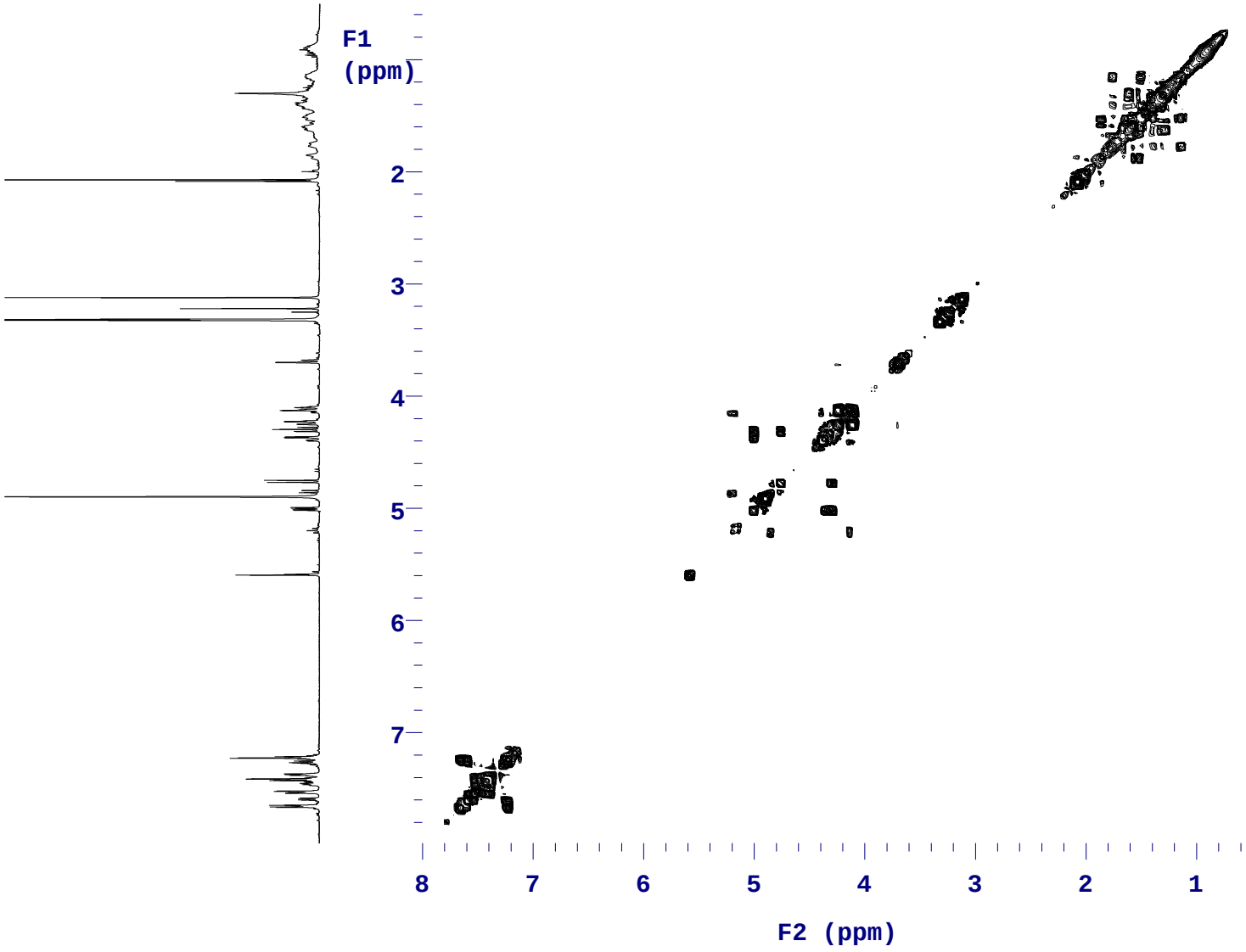

Ph
O
O
O
AcO
SPh
O
OMe
5a-I-Ac
f1 (ppm)

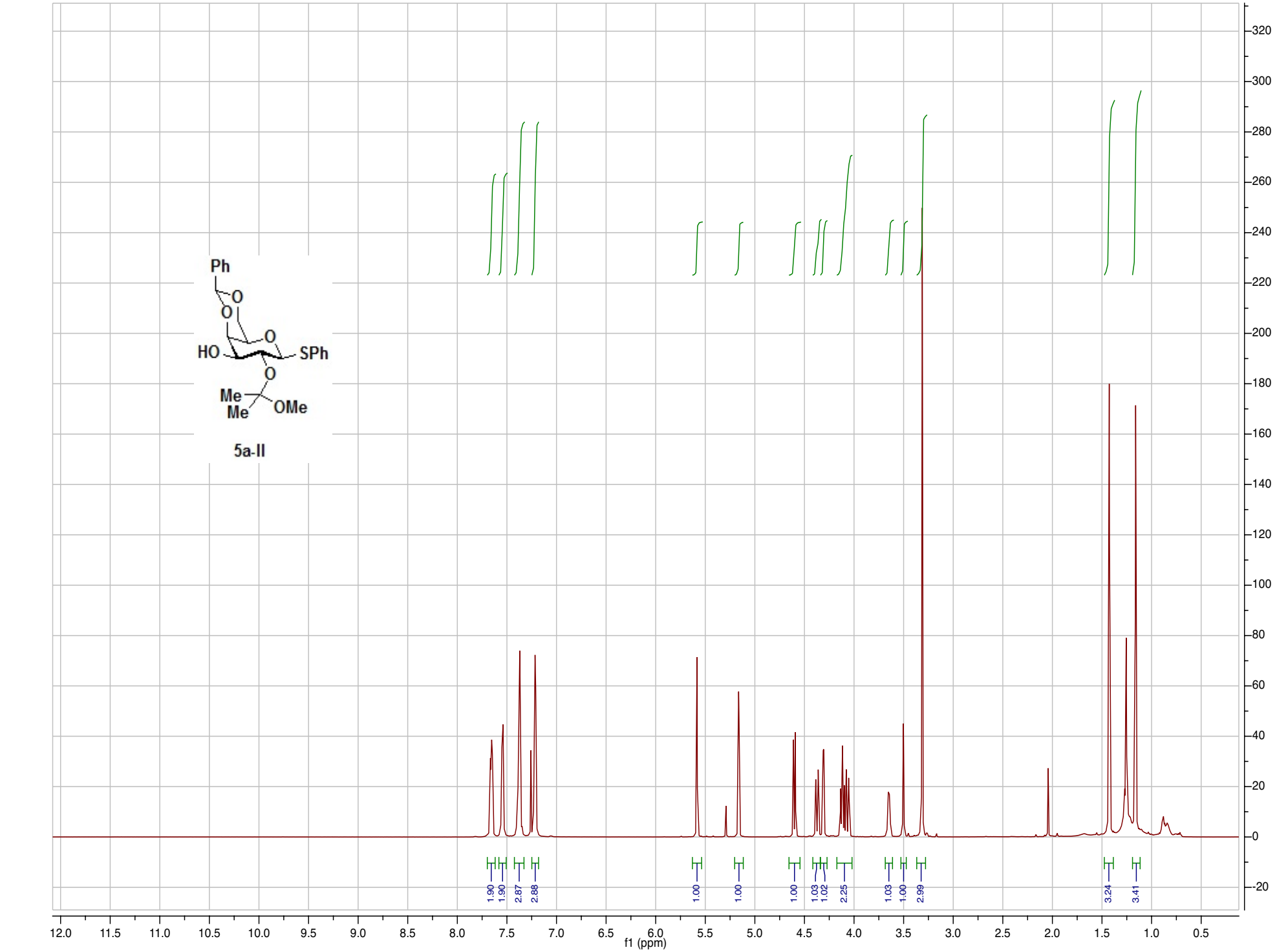

170.69
169.93
138.22
133.71
132.37
131.09
128.43
128.39
127.71
127.62
127.23
126.59
126.22
126.07
101.80
101.44
100.99
100.65
86.51
85.14
75.75
74.73
74.17
71.02
69.74
69.51
68.90
68.67
68.03
66.44
48.07
47.90
47.73
47.56
47.39
47.22
47.05
33.54
33.31
33.21
32.96
25.02
22.41
19.80
19.77
Ph
O
O
O
AcO
SPh
O
OMe
5a-I-Ac
f1 (ppm)

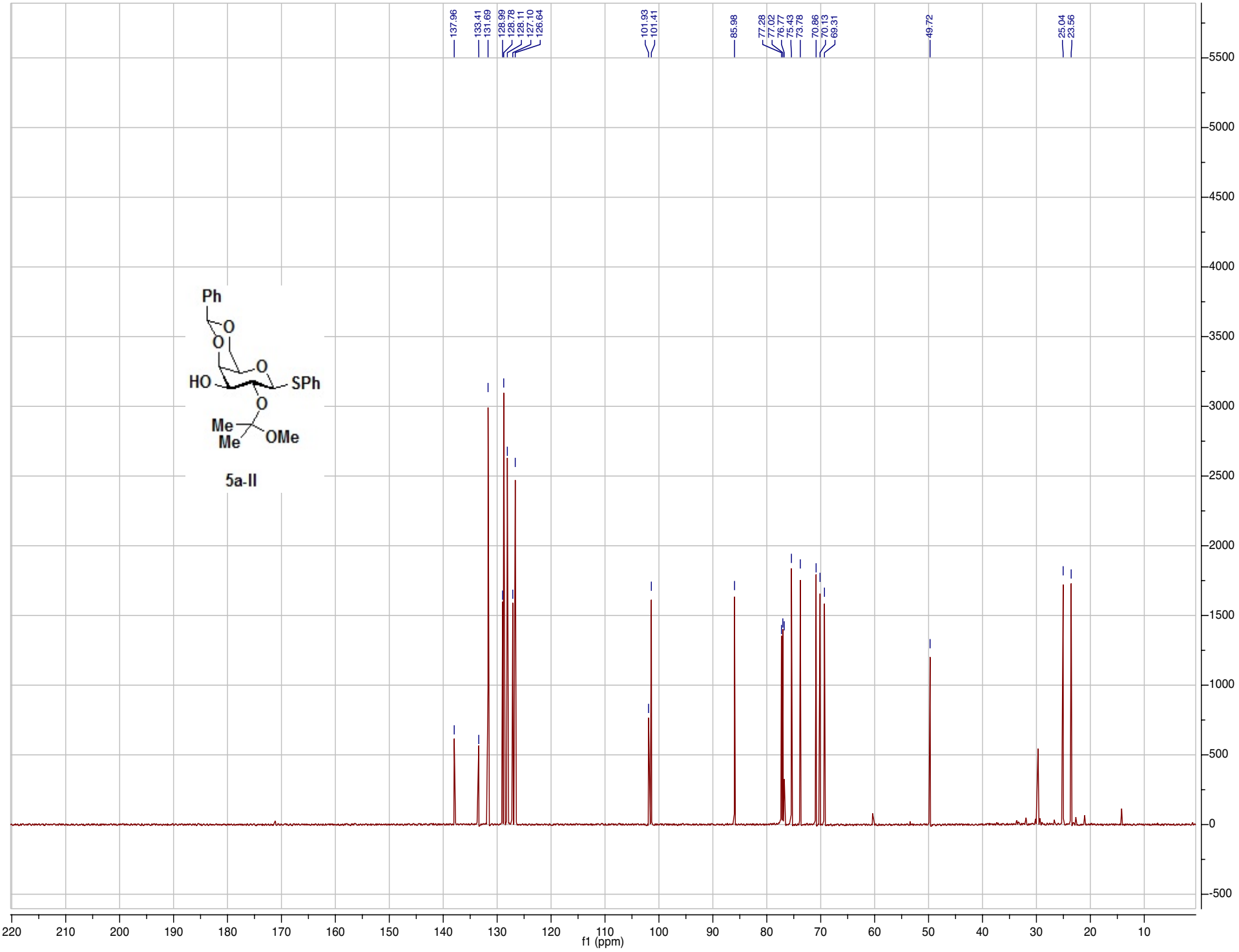

Ph
O
O
O
AcO
SPh
O
OMe

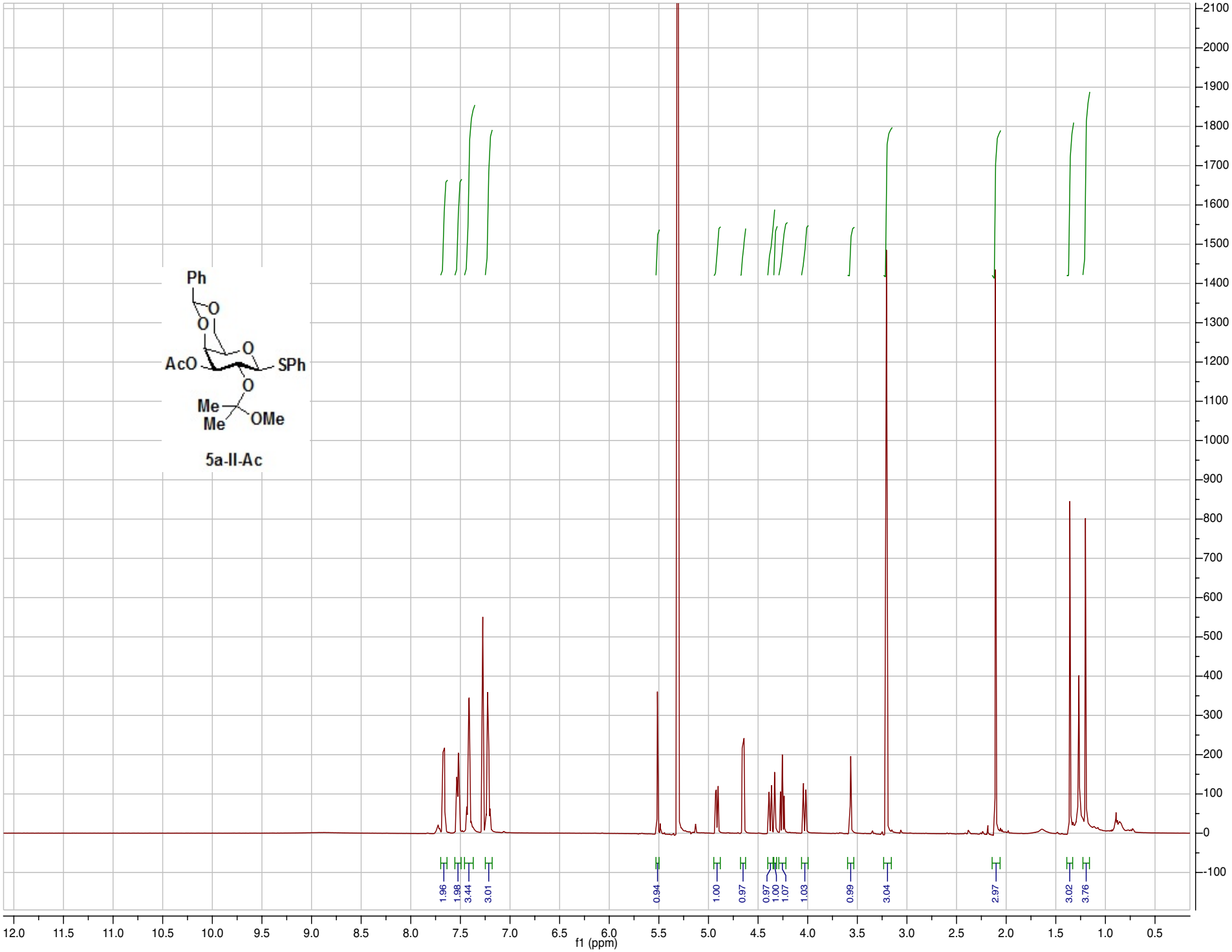
5a-l-Ac

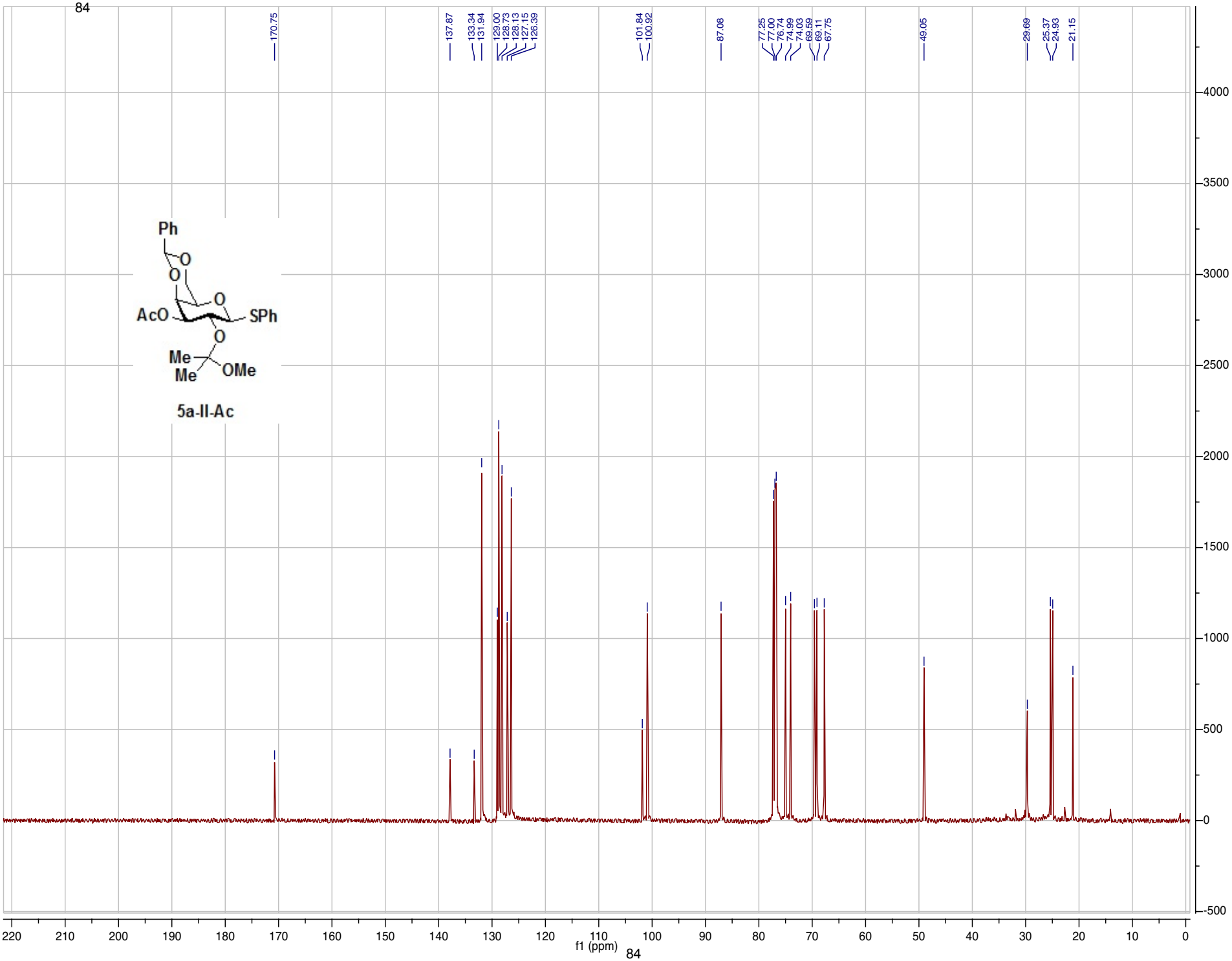

Agilent Technologies

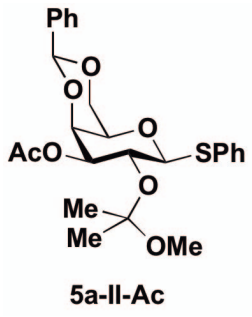

F1
(ppm)
2
3
4
5
6
7
8
7
6
5
4
3
2
1
F2 (ppm)


Ph
O
O
O
HO
SPh
O
Me
Me
OMe
5a-II
1.90
1.90
2.87
2.88
1.00
1.00
1.00
1.03
1.02
2.25
1.03
1.00
2.99
3.24
3.41
f1 (ppm)


137.96
133.41
131.69
128.99
128.78
128.11
127.10
126.64
101.93
101.41
85.98
77.28
77.02
76.77
75.43
73.78
70.86
70.13
69.31
49.72
25.04
23.56
Ph
O
O
O
HO
SPh
O
Me
Me
OMe
5a-II
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

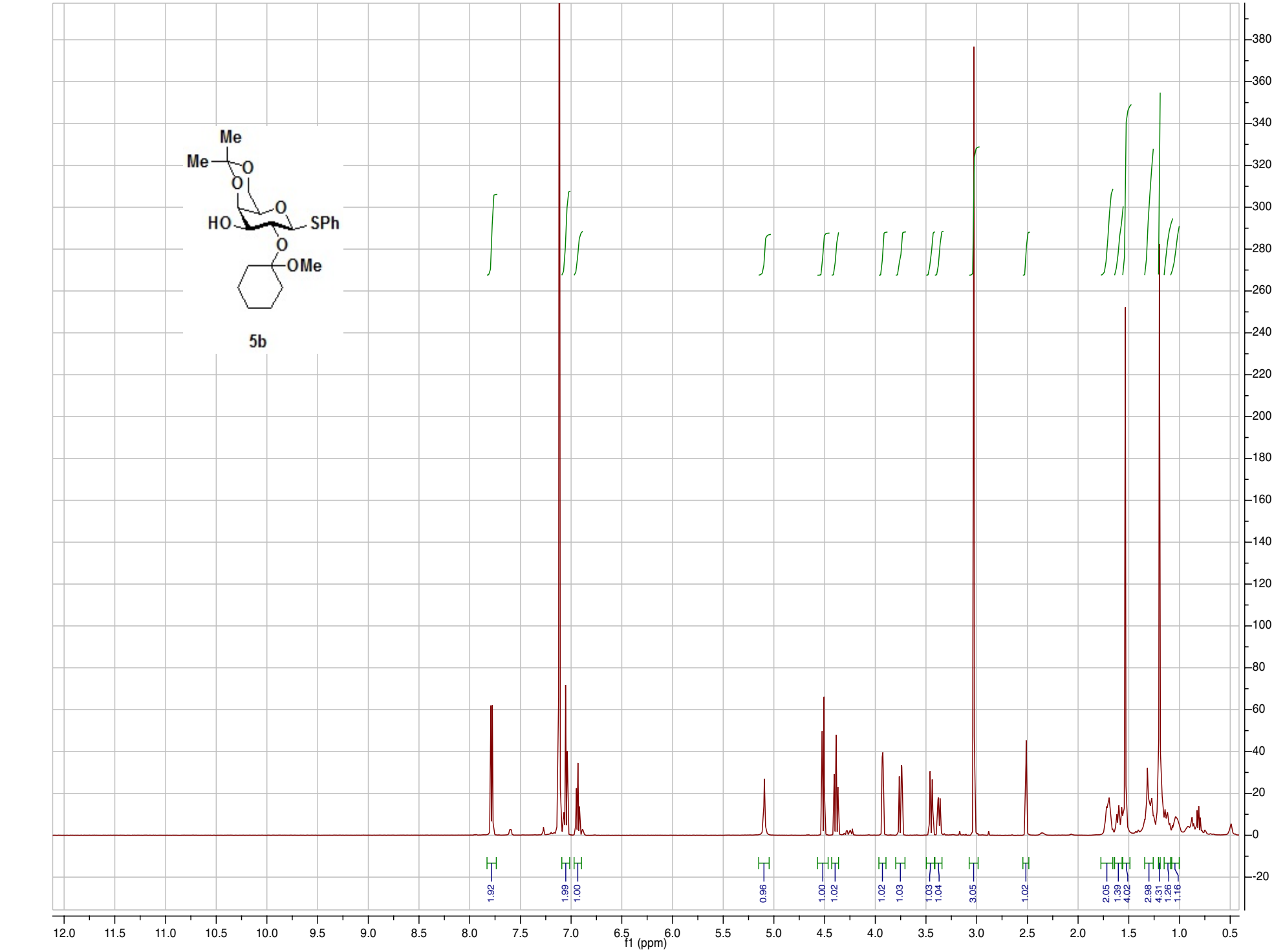

Ph
O
O
O
AcO
SPh
O
Me
Me
OMe
5a-II-Ac
1.96
1.98
3.44
3.01
0.94
1.00
0.97
0.97
1.00
1.07
1.03
0.99
3.04
2.97
3.02
3.76
f1 (ppm)

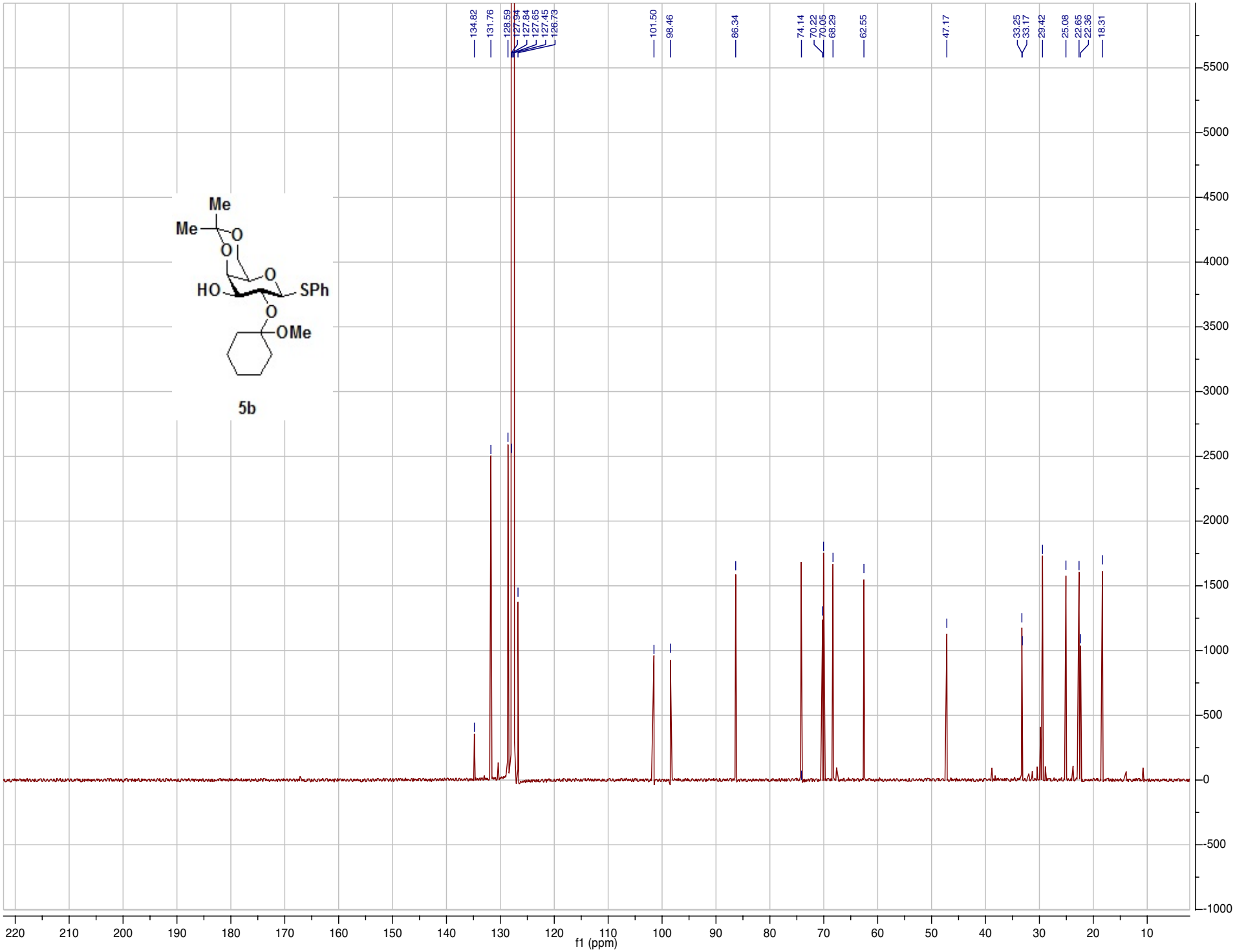

170.75
137.87
133.34
131.94
129.00
128.73
128.13
127.15
126.39
101.84
100.92
87.08
77.25
77.00
76.74
74.99
74.03
69.59
69.11
67.75
49.05
29.69
25.37
24.93
21.15
Ph
O
O
O
AcO
SPh
O
Me
Me
OMe
5a-II-Ac
4000
3500
3000
2500
2000
1500
1000
500
0
-500
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

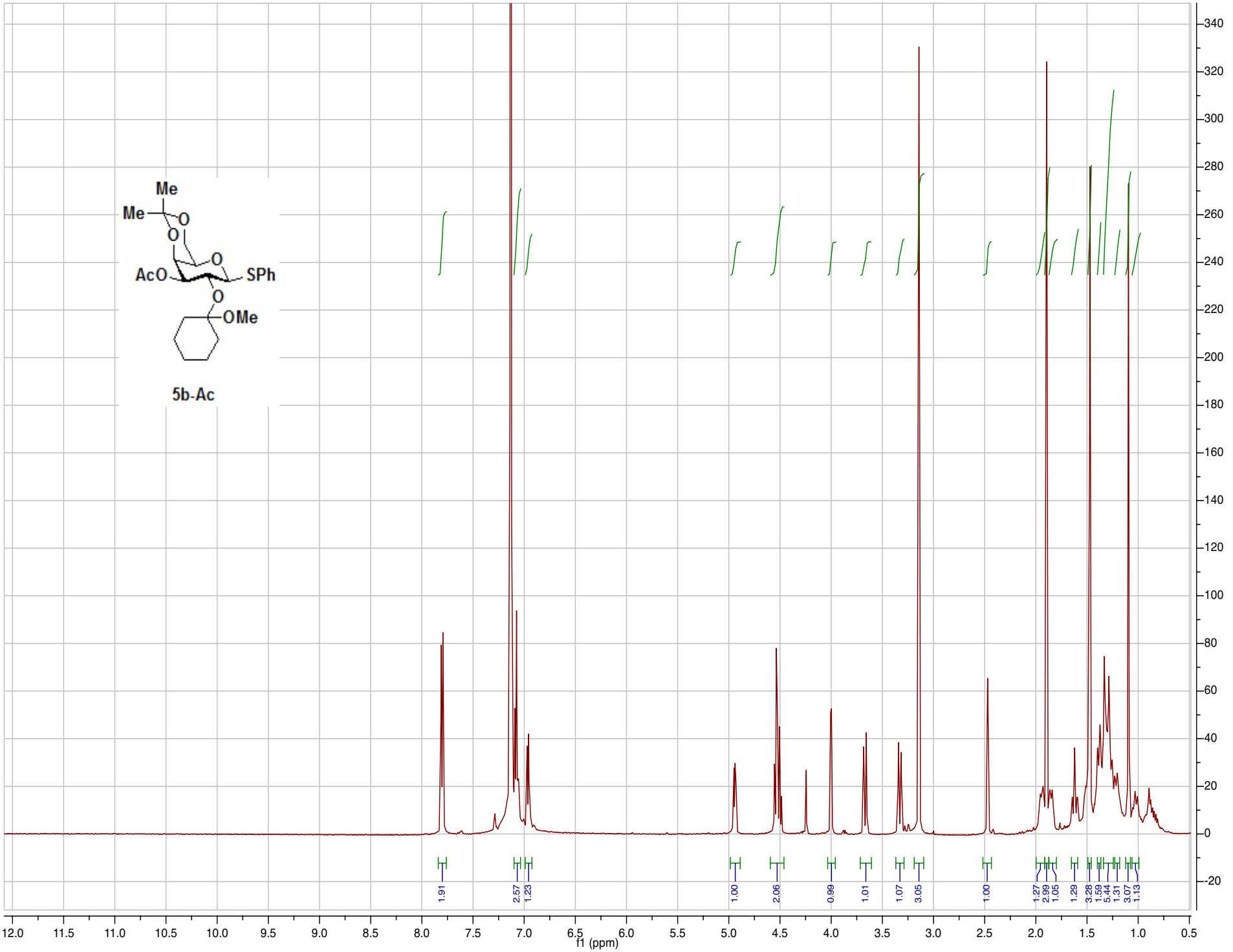

Ph
O
O
O
AcO
SPh
O
Me
Me
OMe

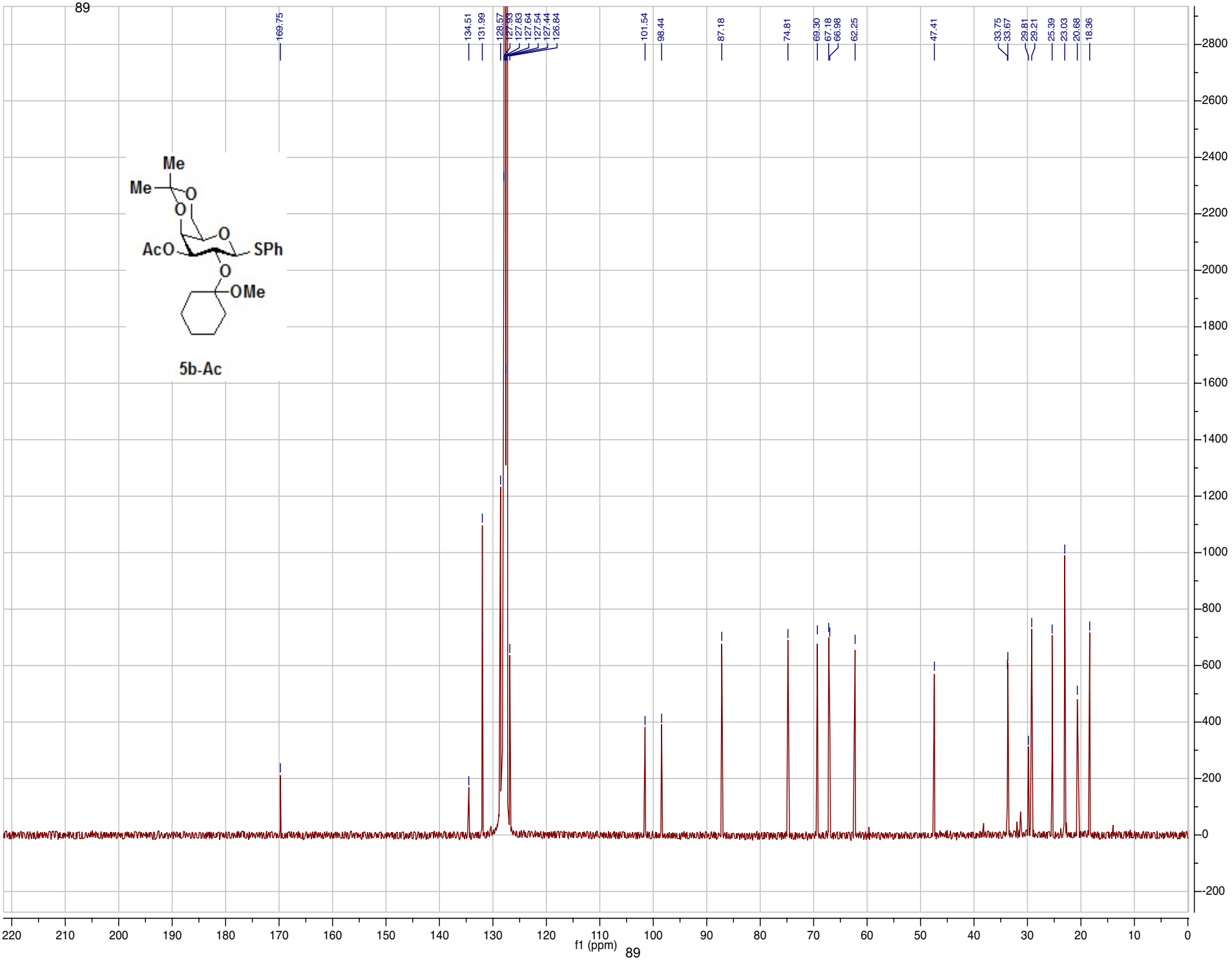
5a-II-Ac

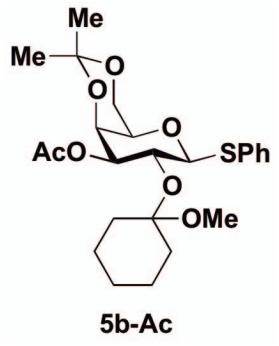
Agilent Technologies
F1 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
F2 (ppm)


Me
Me
O
O
O
HO
SPh
O
OMe
5b
f1 (ppm)
1.92
1.99
1.00
0.96
1.00
1.02
1.02
1.03
1.03
1.04
3.05
1.02
2.05
1.39
4.02
2.98
4.31
1.26
1.16

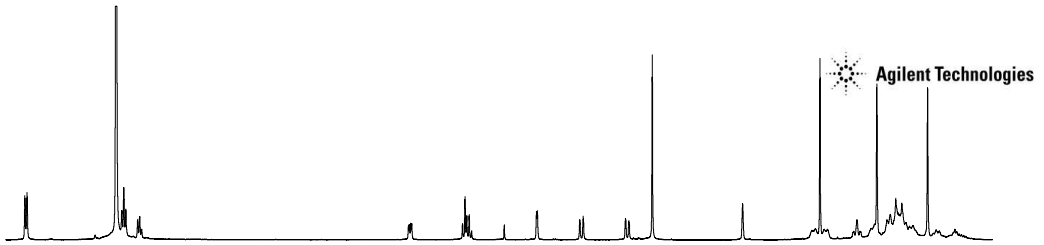

134.82
131.76
128.59
127.94
127.84
127.65
127.45
126.73
101.50
98.46
86.34
74.14
70.22
70.05
68.29
62.55
47.17
33.25
33.17
29.42
25.08
22.65
22.36
18.31
Me
Me
O
O
O
HO
SPh
O
OMe
5b
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

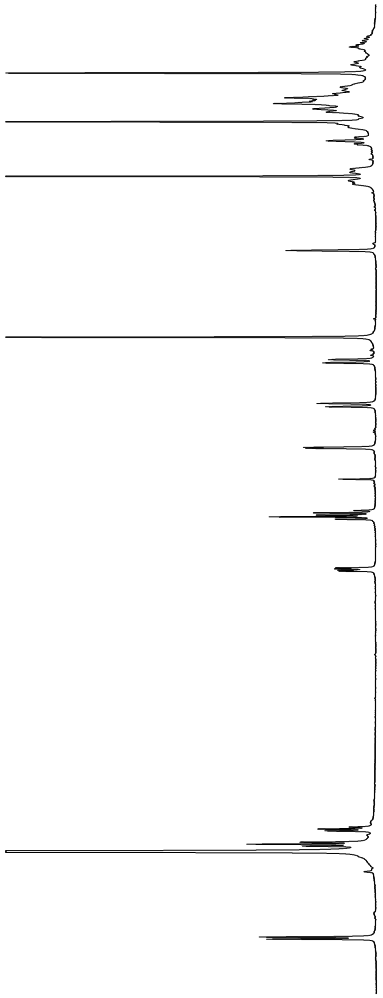

Me
Me
O
O
O
AcO
SPh
O
OMe
5b-Ac
f1 (ppm)

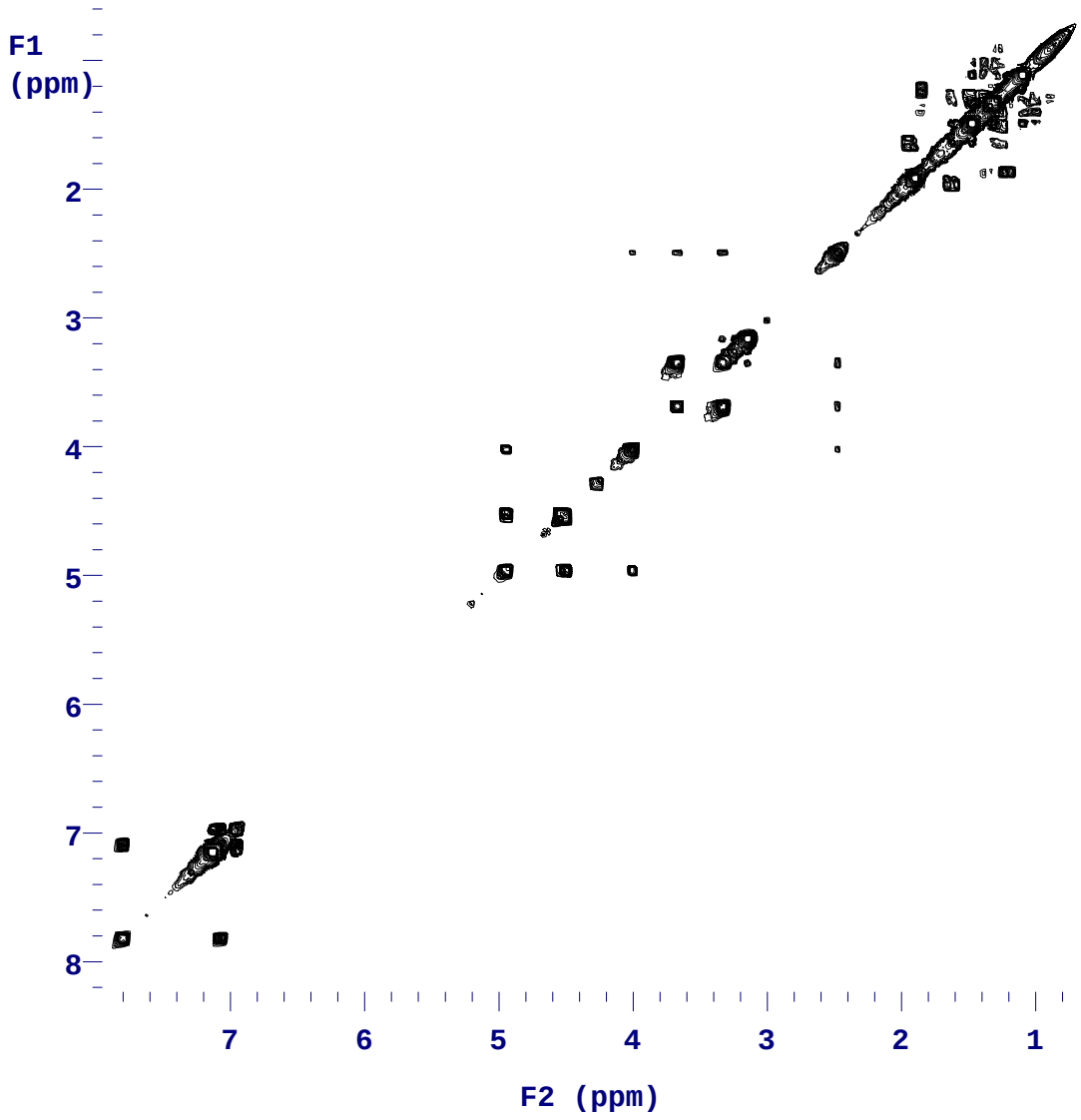

169.75
134.51
131.99
128.57
127.95
127.83
127.64
127.54
127.44
126.84
101.54
98.44
87.18
74.81
69.30
67.18
66.98
62.25
47.41
33.75
33.67
29.81
29.21
25.39
23.03
20.68
18.36
Me
Me
O
O
O
AcO
SPh
O
OMe
5b-Ac
f1 (ppm)

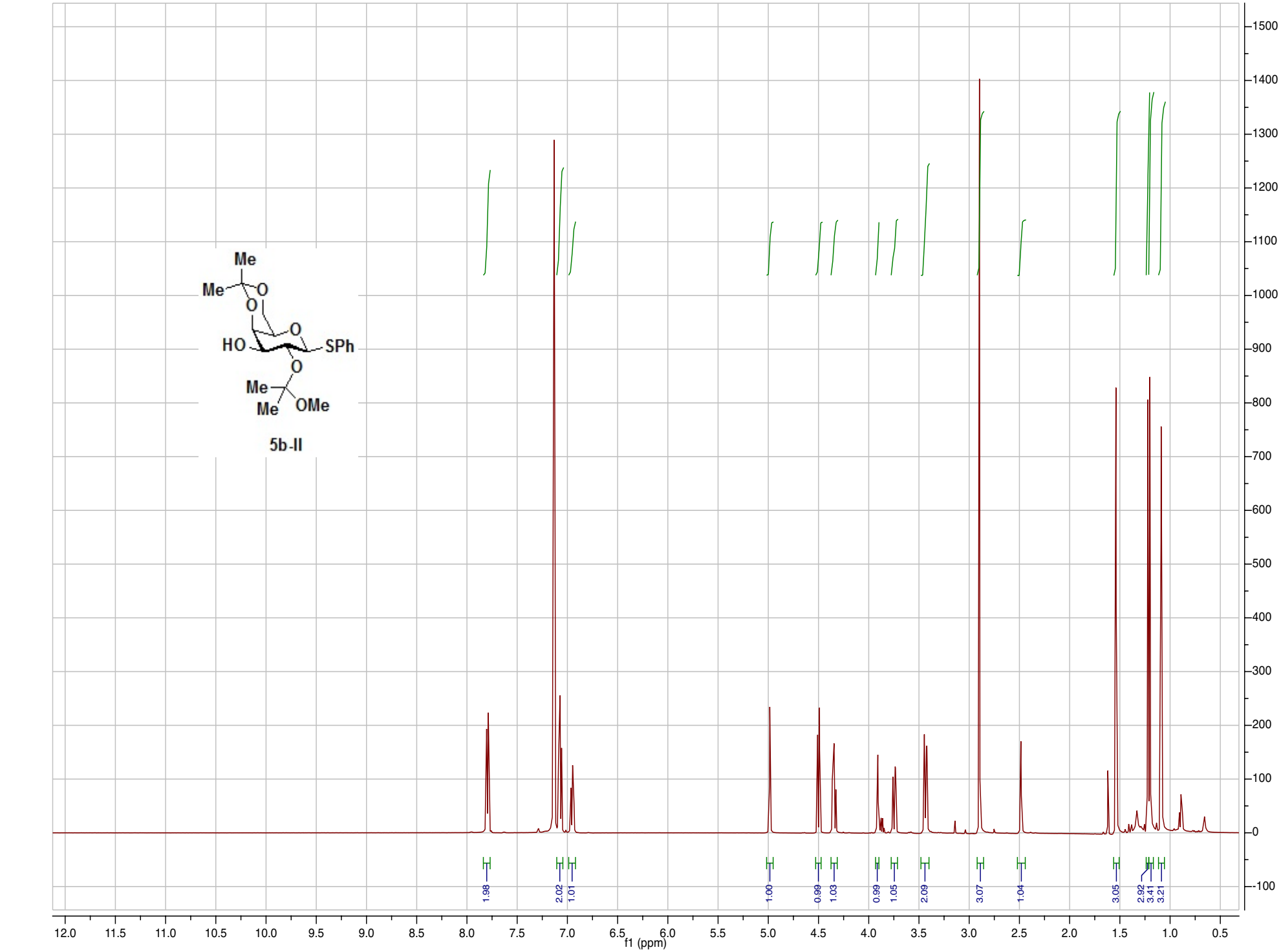

Me
Me
O
O
O
AcO
SPh
O
OMe

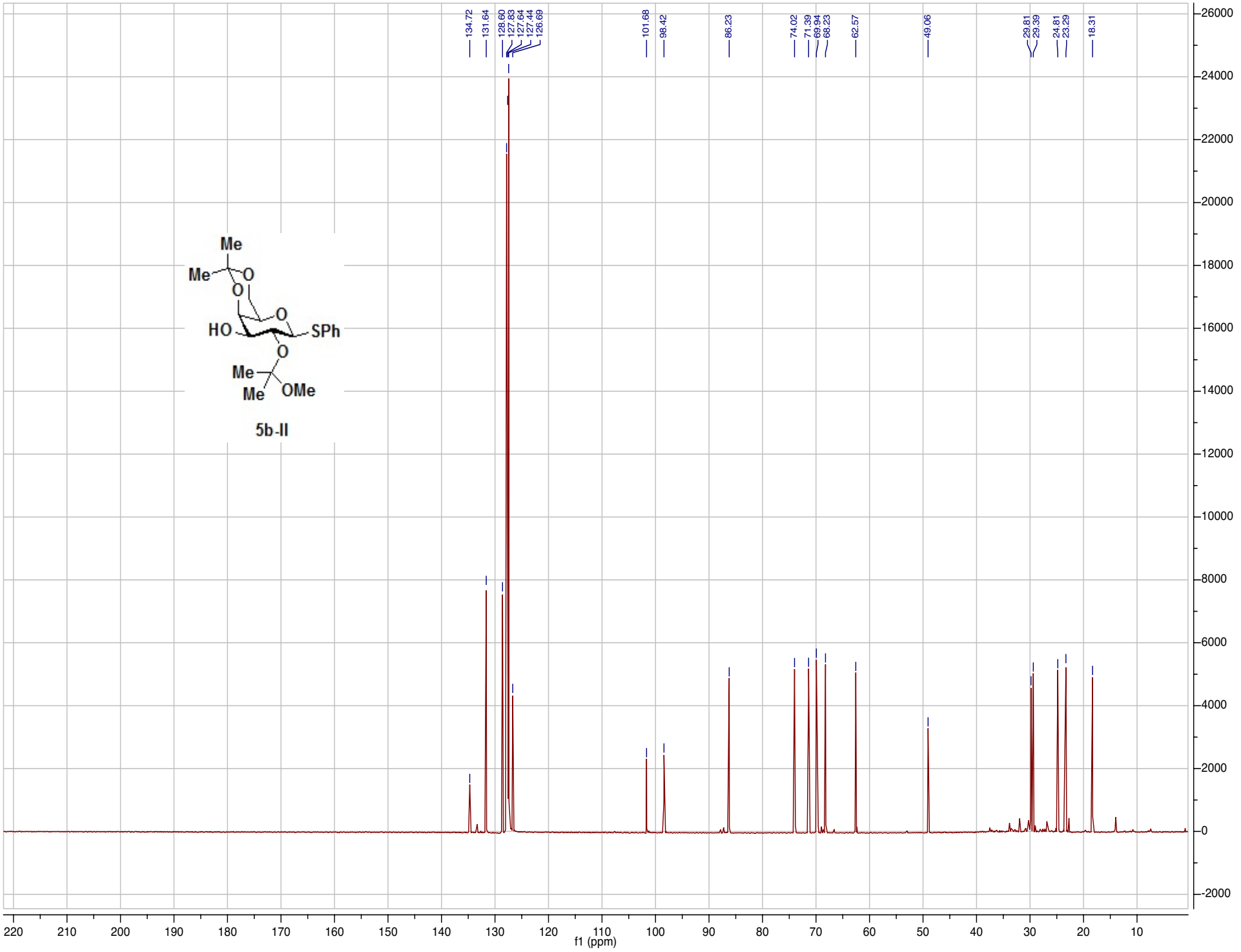
5b-Ac

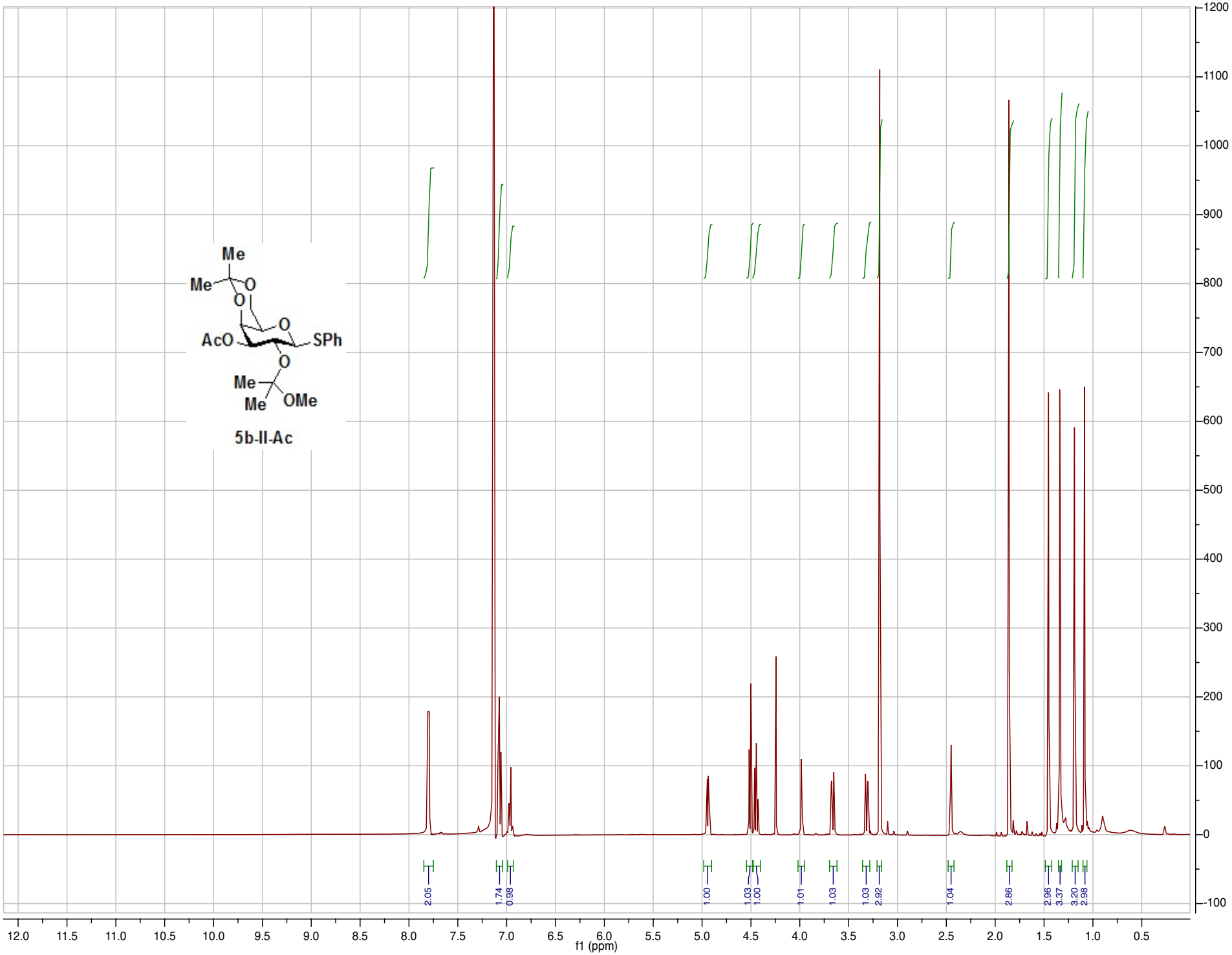

Agilent Technologies

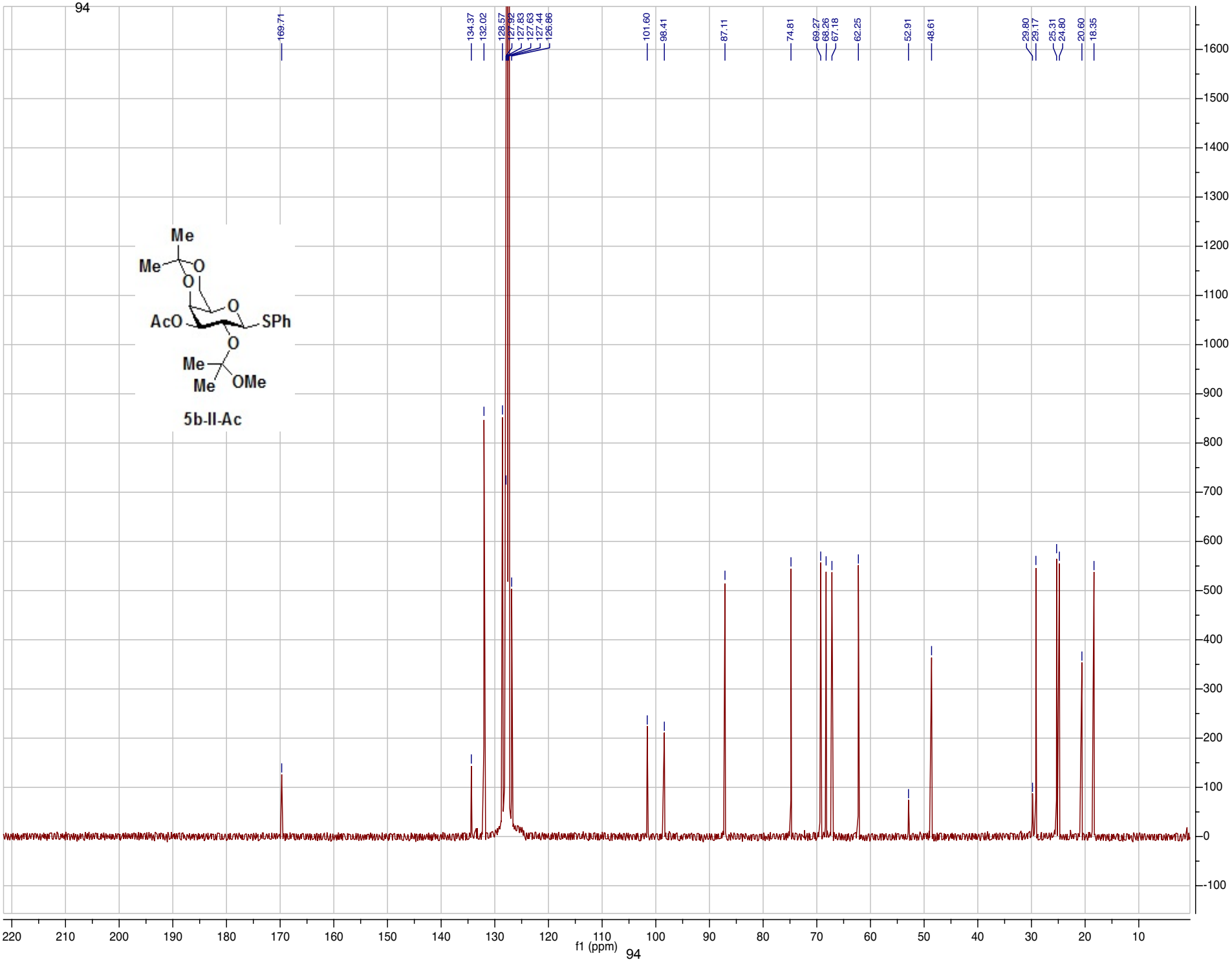


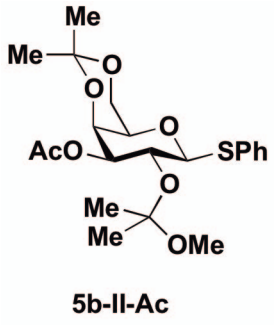

F1
(ppm)
2
3
4
5
6
7
8
7
6
5
4
3
2
1
F2 (ppm)


Me
Me
O
O
HO
O
SPh
O
Me
Me
OMe
5b-II
1.98
2.02
1.01
1.00
0.99
1.03
0.99
1.05
2.09
3.07
1.04
3.05
2.92
3.41
3.21
f1 (ppm)

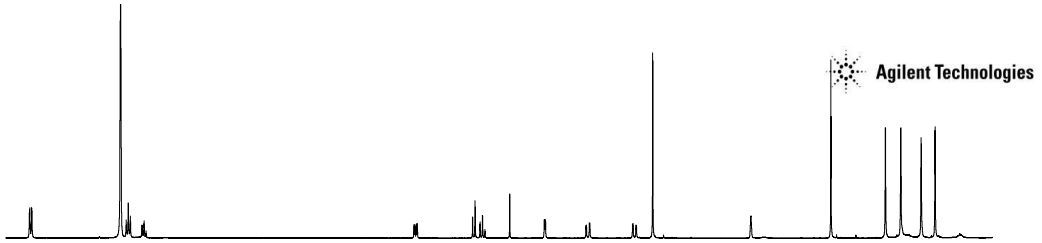

134.72
131.64
128.60
127.83
127.64
127.44
126.69
101.68
98.42
86.23
74.02
71.39
69.94
68.23
62.57
49.06
29.81
29.39
24.81
23.29
18.31
Me
Me
O
O
O
HO
SPh
O
Me
Me
OMe
5b-II
f1 (ppm)

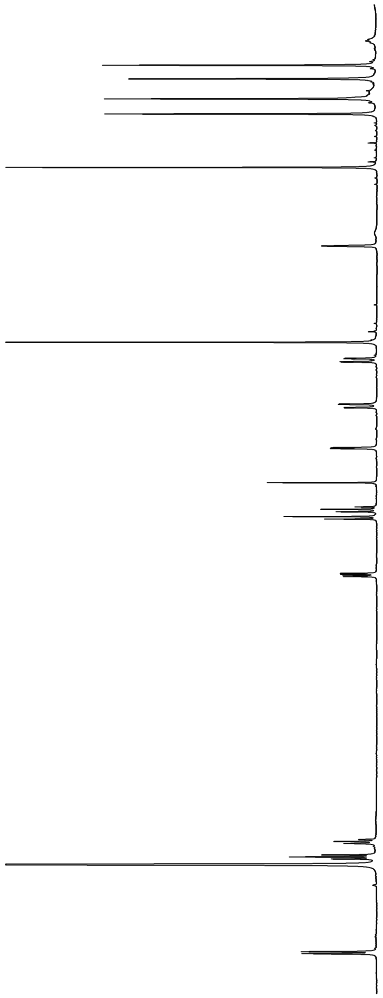

Me
Me
O
O
O
AcO
SPh
O
Me
Me
OMe
5b-II-Ac
2.05
1.74
0.98
1.00
1.03
1.00
1.01
1.03
1.03
2.92
1.04
2.86
2.96
3.37
3.20
2.98
f1 (ppm)

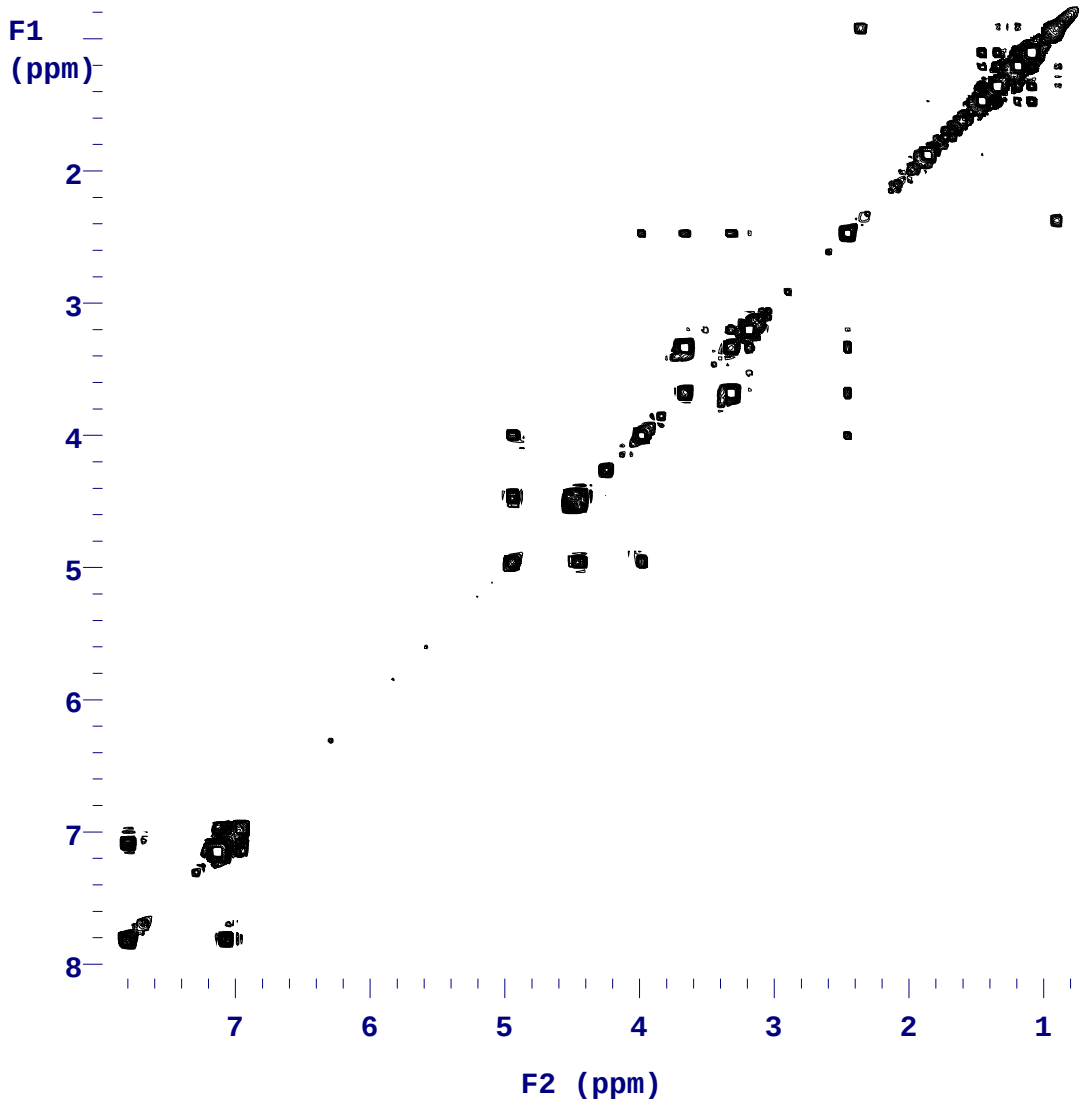

169.71
134.37
132.02
128.57
127.92
127.83
127.63
127.44
126.86
101.60
98.41
87.11
74.81
69.27
68.26
67.18
62.25
52.91
48.61
29.80
29.17
25.31
24.80
20.60
18.35
Me
Me
O
O
O
AcO
SPh
O
Me
Me
OMe
5b-II-Ac
f1 (ppm)

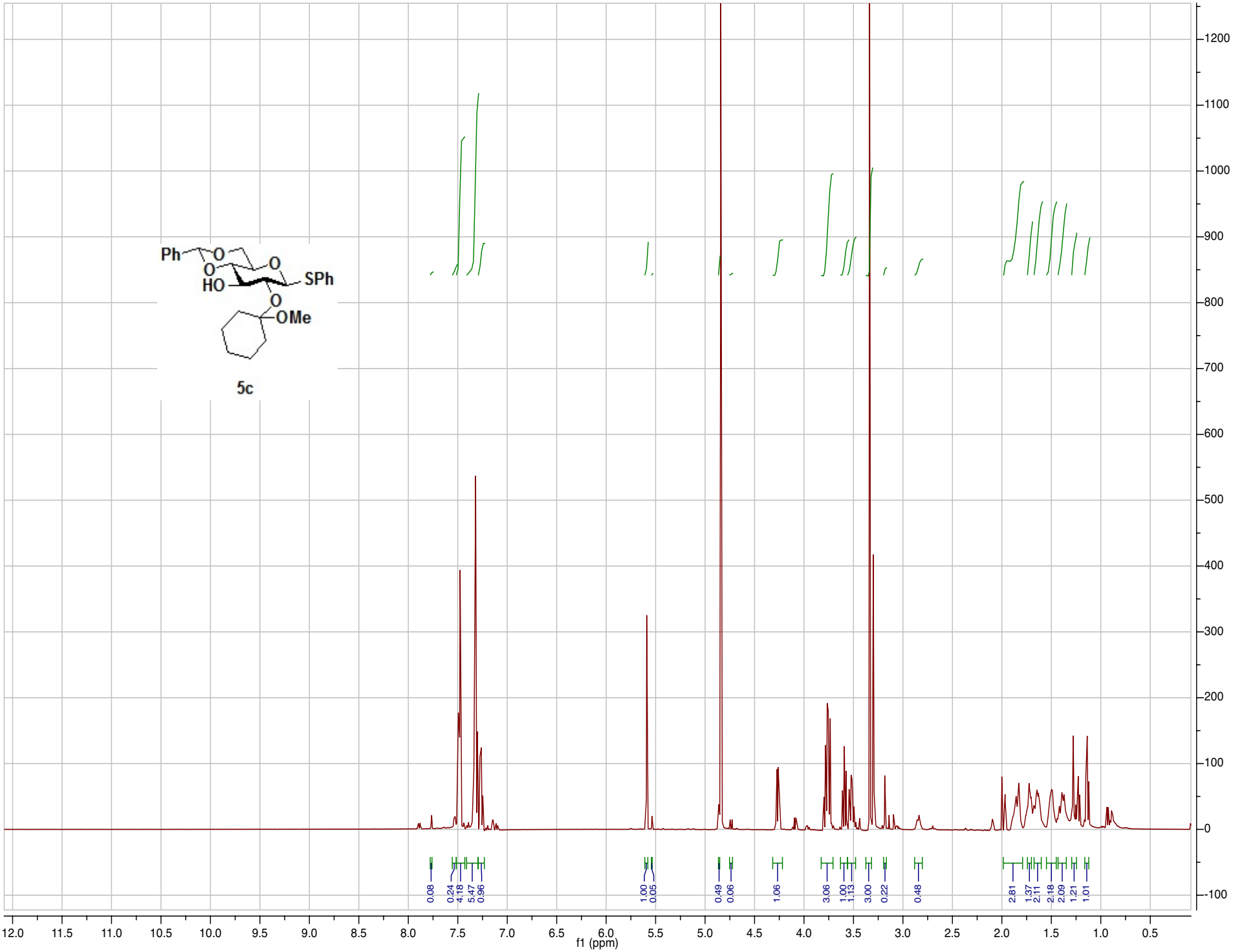

Me
Me
O
O
O
AcO
SPh
O
Me
Me
OMe

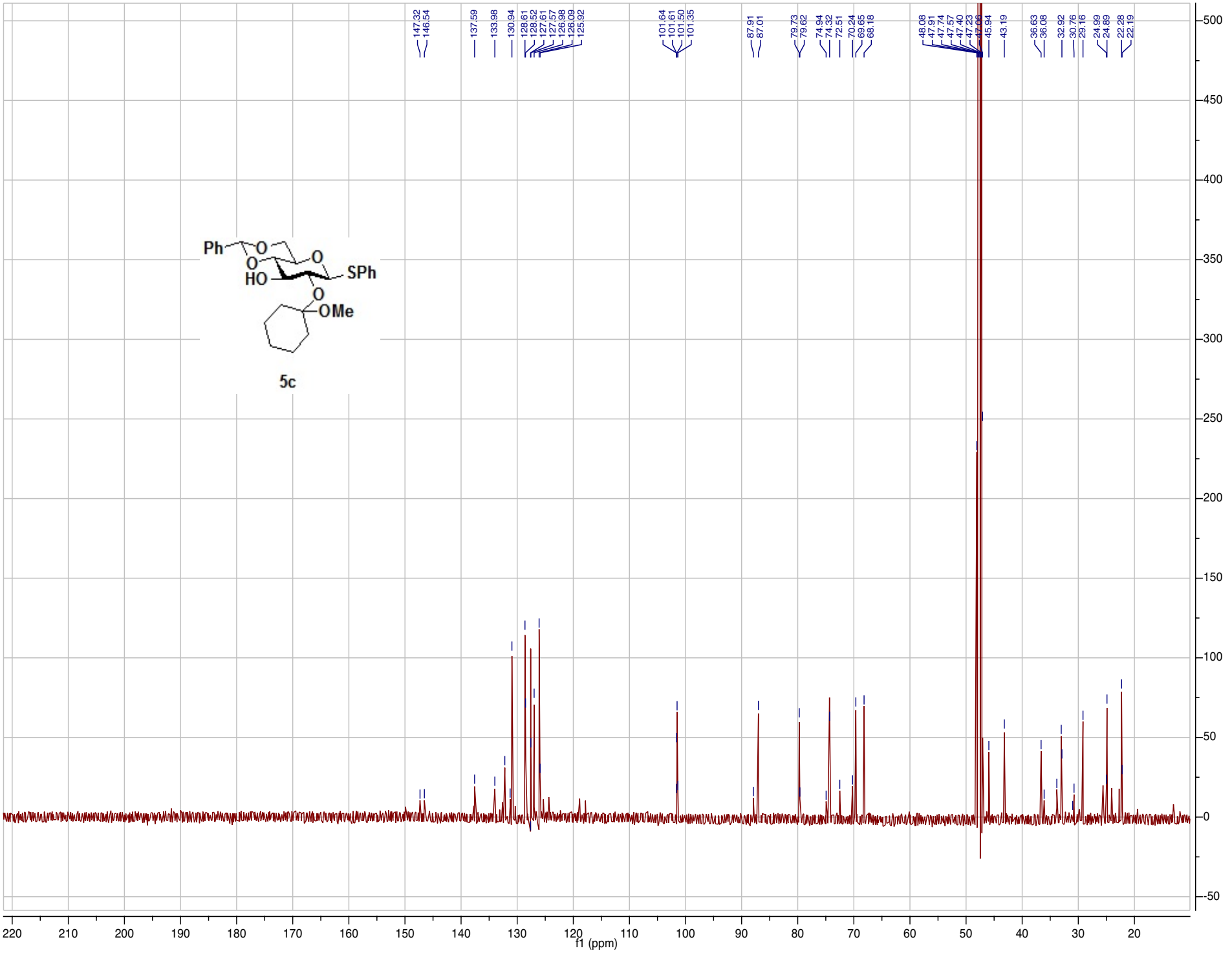
5b-II-Ac

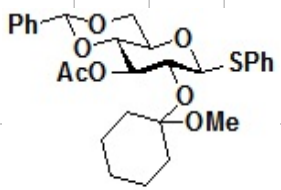

Agilent Technologies




F1
(ppm)
2
3
4
5
6
7
8
7
6
5
4
3
2
1
F2 (ppm)

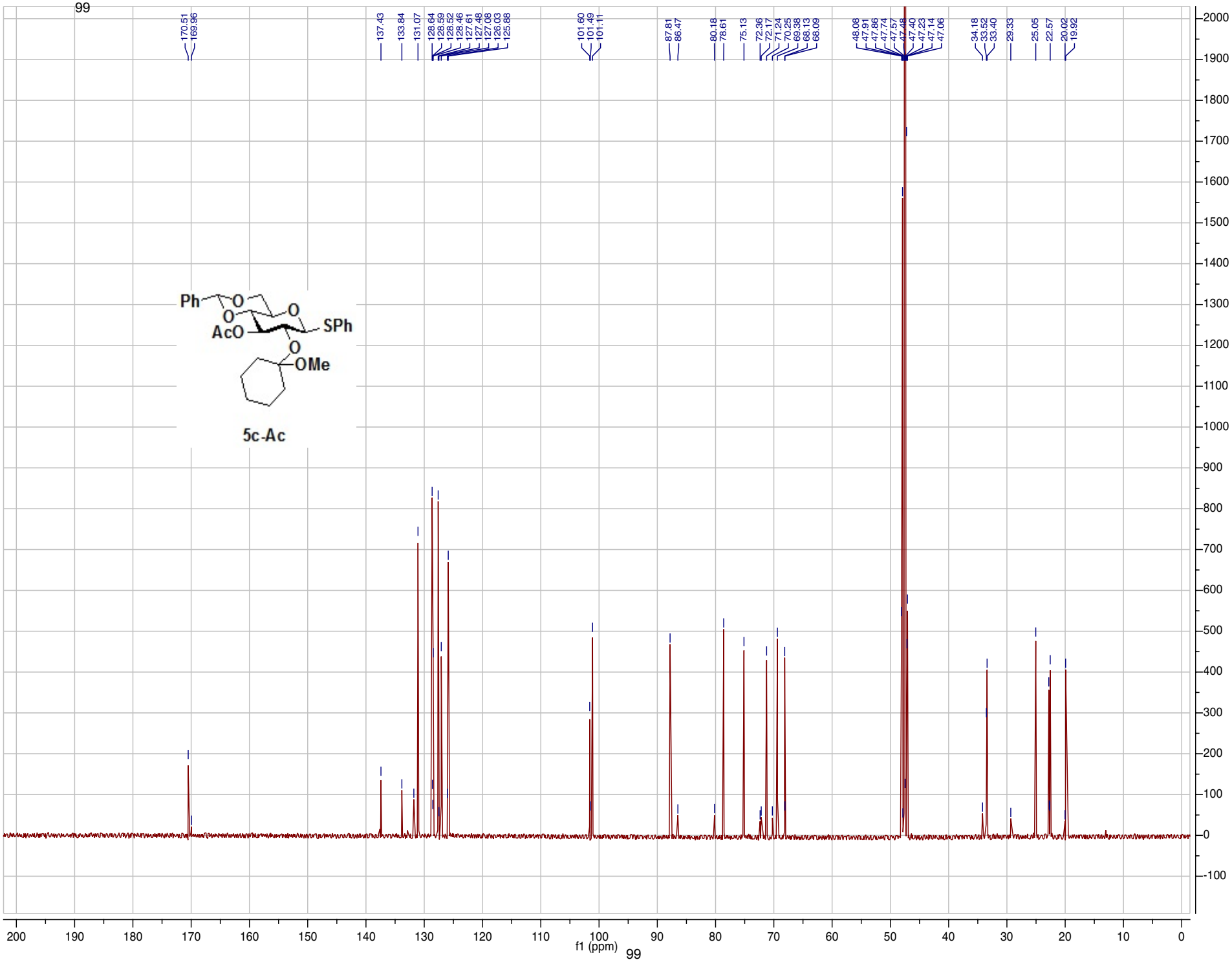

Ph
O
O
O
HO
SPh
O
OMe
5c
f1 (ppm)

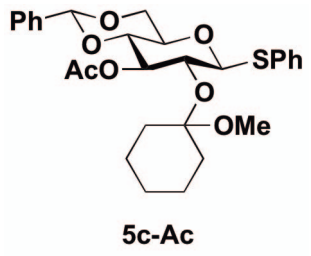

147.32
146.54
137.59
133.98
130.94
128.61
128.52
127.61
127.57
126.98
126.09
125.92
101.64
101.61
101.50
101.35
87.91
87.01
79.73
79.62
74.94
74.32
72.51
70.24
69.65
68.18
48.08
47.91
47.74
47.57
47.40
47.23
45.94
43.19
36.63
36.08
32.92
30.76
29.16
24.99
24.89
22.28
22.19
Ph
O
O
O
HO
SPh
O
OMe
5c
500
450
400
350
300
250
200
150
100
50
0
-50
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


Ph
O
O
O
AcO
SPh
O
OMe

5c-Ac

2.36
1.91
6.08
0.13
1.00
1.11
10.03
1.24
0.24
1.16
1.33
1.12
1.15
3.01
0.37
0.35
2.81
2.07
6.94
1.41
1.21
0.64
f1 (ppm)


170.51
169.96
137.43
133.84
131.07
128.64
128.59
128.52
128.46
127.61
127.48
127.08
126.03
125.88
101.60
101.49
101.11
87.81
86.47
80.18
78.61
75.13
72.36
72.17
71.24
70.25
69.38
68.13
68.09
48.08
47.91
47.86
47.74
47.57
47.48
47.40
47.23
47.14
47.06
34.18
33.52
33.40
29.33
25.05
22.57
20.02
19.92
Ph
O
O
O
AcO
SPh
O
OMe
5c-Ac
f1 (ppm)



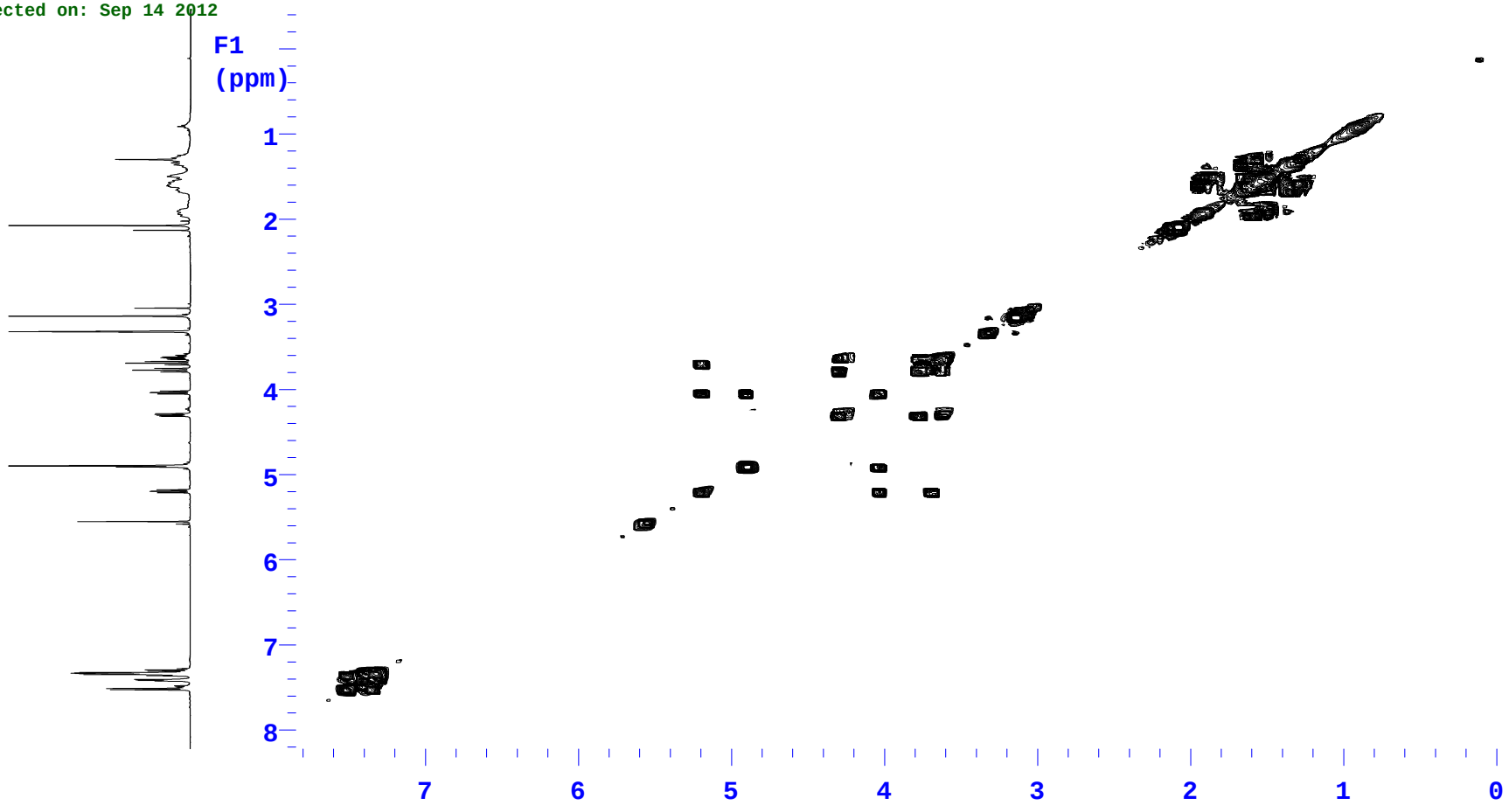
5c-Ac

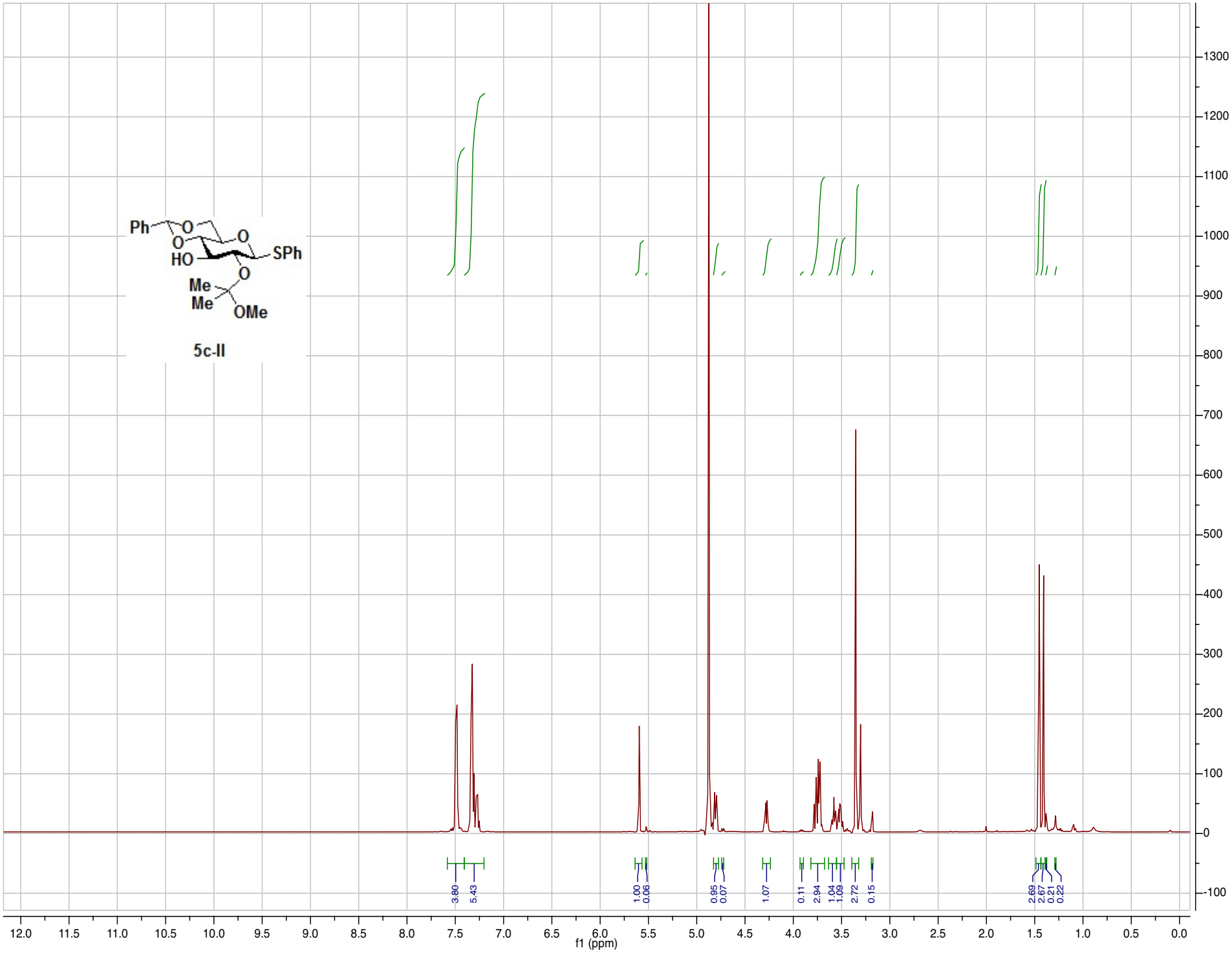
Sample Name:
EM-04-112PURECOSY-METHANOL-D4
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

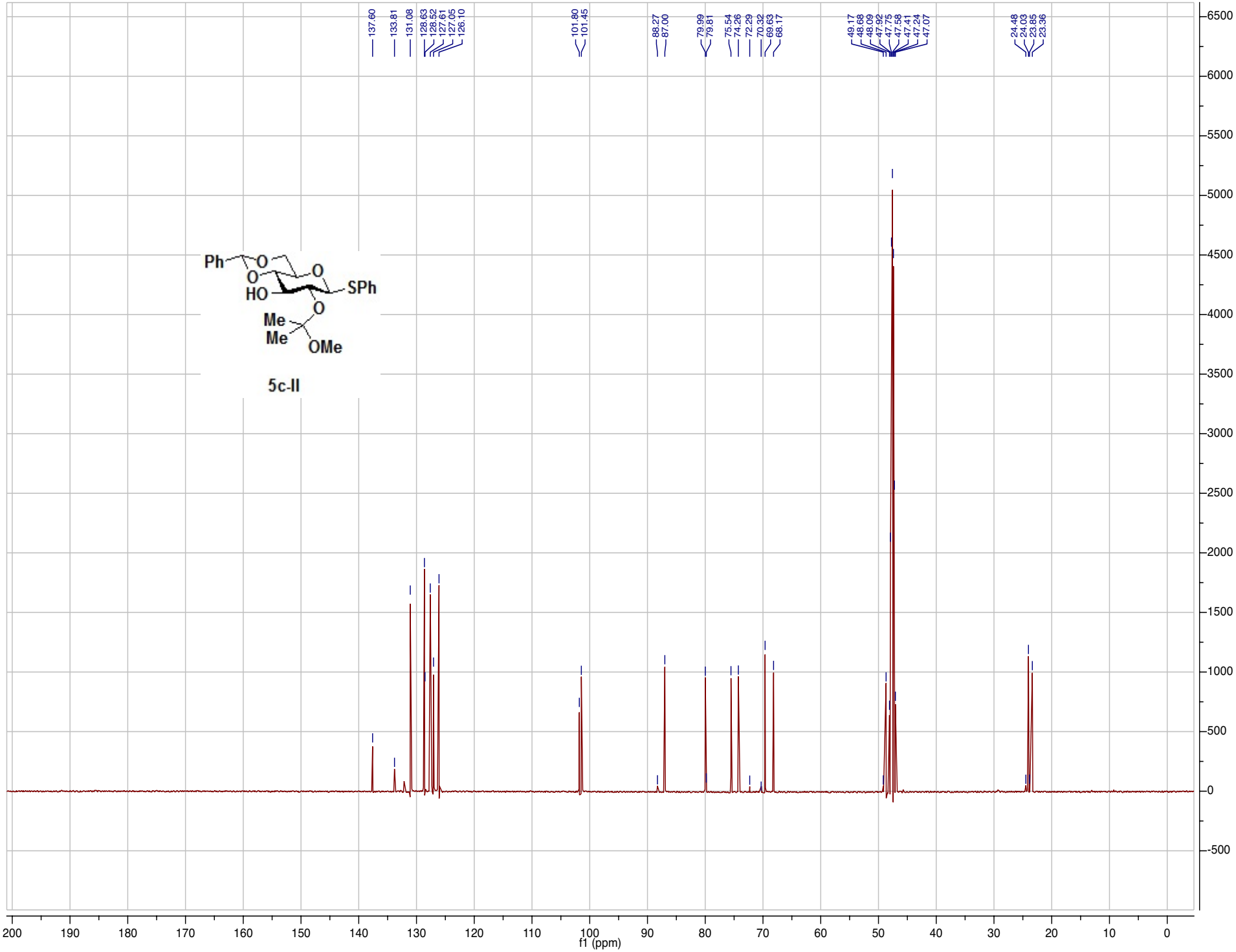
Sample directory:

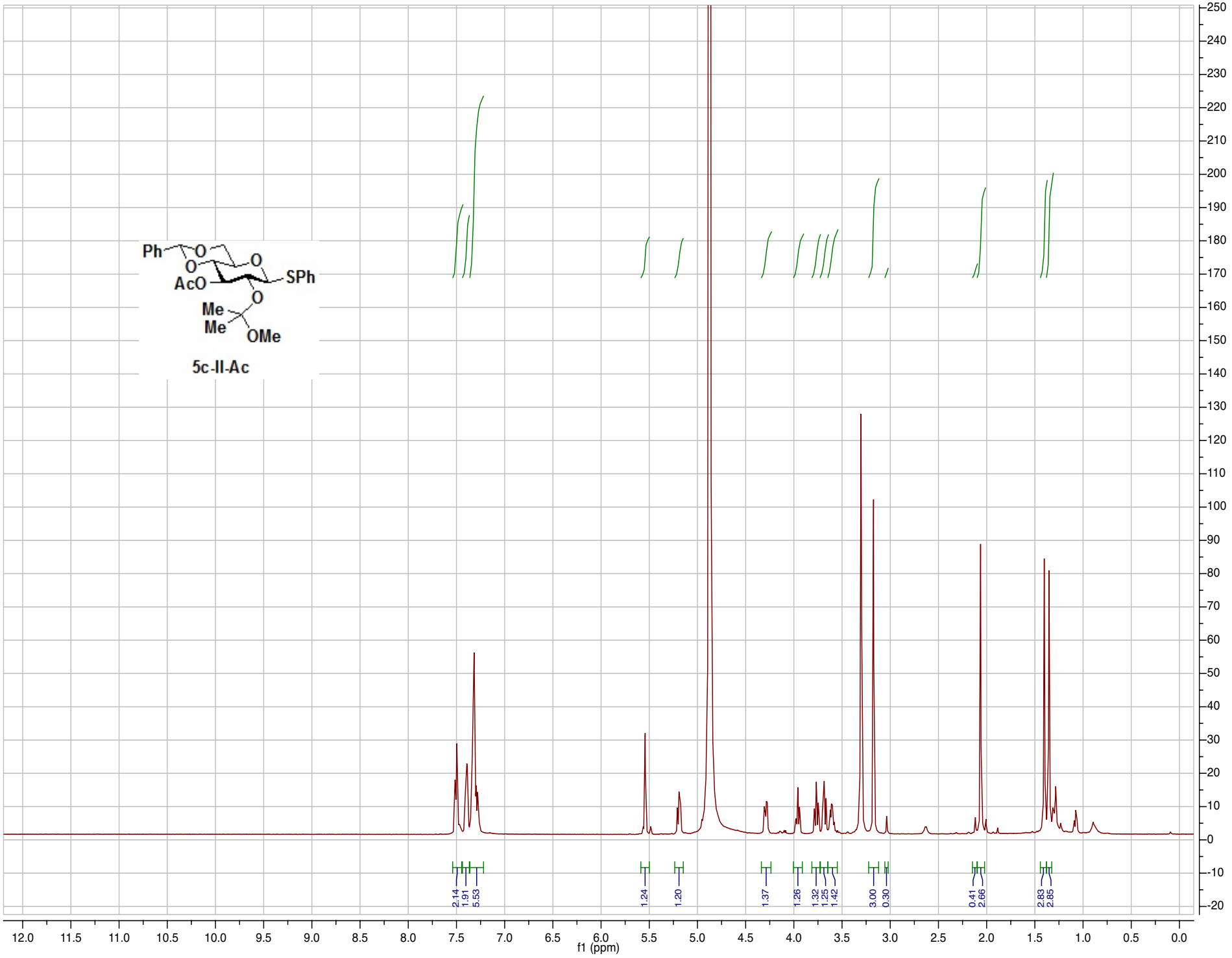
FidFile: EM-04-112PURECOSY-METHANOL-D4

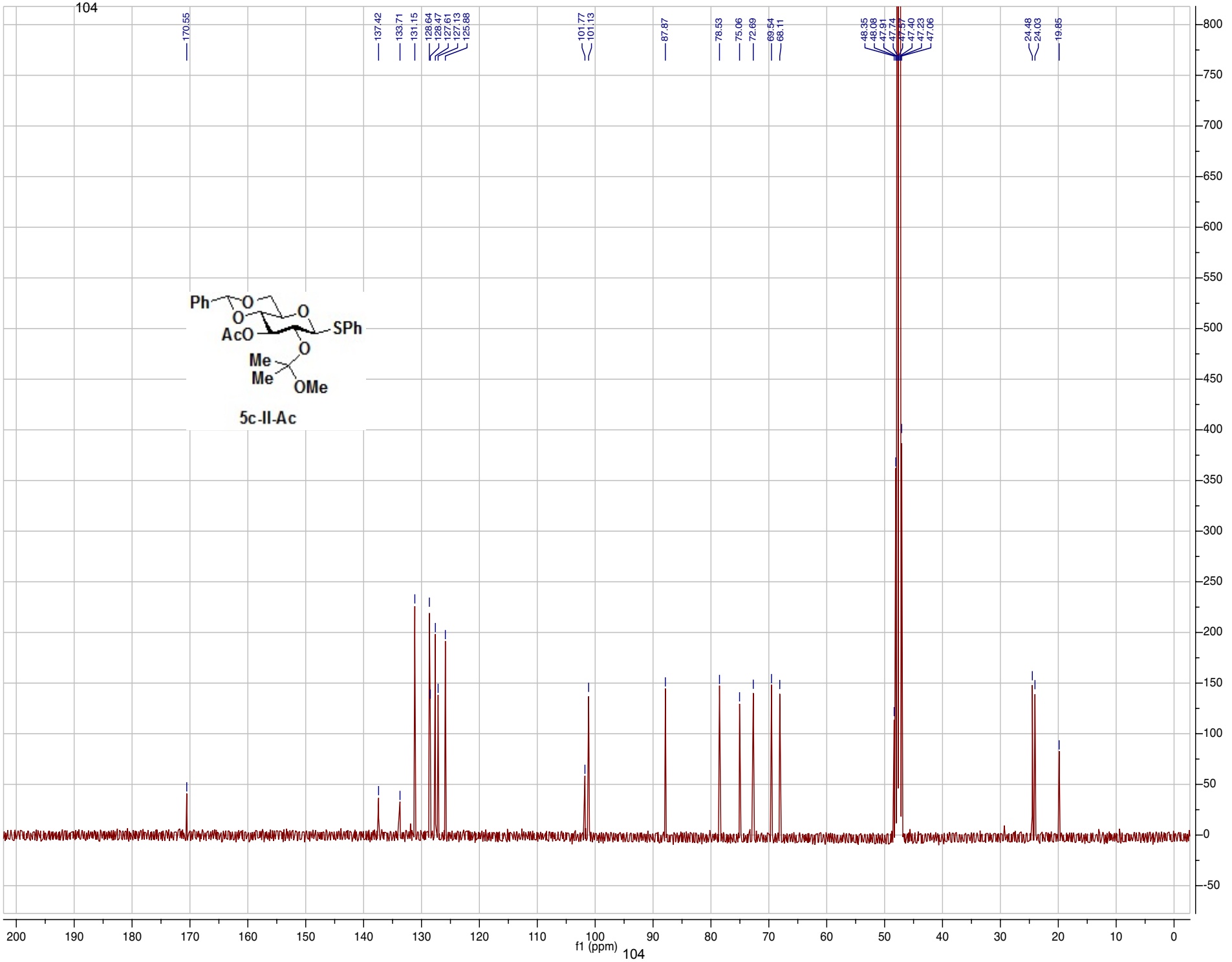
Pulse Sequence: gCOSY
Solvent: cd3od
Data collected on: Sep 14 2012

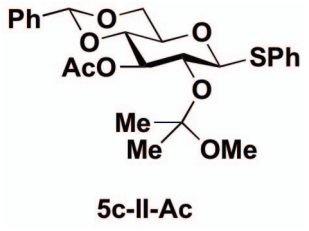



Ph
O
O
O
HO
SPh
O
Me
Me
OMe
5c-II
3.80
5.43
1.00
0.06
0.95
0.07
1.07
0.11
2.94
1.04
1.09
2.72
0.15
2.69
2.67
0.21
0.22
f1 (ppm)


137.60
133.81
131.08
128.63
128.52
127.61
127.05
126.10
101.80
101.45
88.27
87.00
79.99
79.81
75.54
74.26
72.29
70.32
69.63
68.17
49.17
48.88
48.09
47.92
47.75
47.58
47.41
47.24
47.07
24.48
24.03
23.85
23.36
Ph
O
O
O
HO
SPh
O
Me
Me
OMe
5c-II
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
O
O
O
AcO
SPh
O
Me
Me
OMe
5c-II-Ac
2.14
1.91
5.53
1.24
1.20
1.37
1.26
1.32
1.25
1.42
3.00
0.30
0.41
2.66
2.83
2.85
f1 (ppm)


170.55
137.42
133.71
131.15
128.64
128.47
127.61
127.13
125.88
101.77
101.13
87.87
78.53
75.06
72.69
69.54
68.11
48.35
48.08
47.91
47.74
47.57
47.40
47.23
47.06
24.48
24.03
19.85
Ph
O
O
O
AcO
SPh
O
Me
Me
OMe
5c-II-Ac
f1 (ppm)



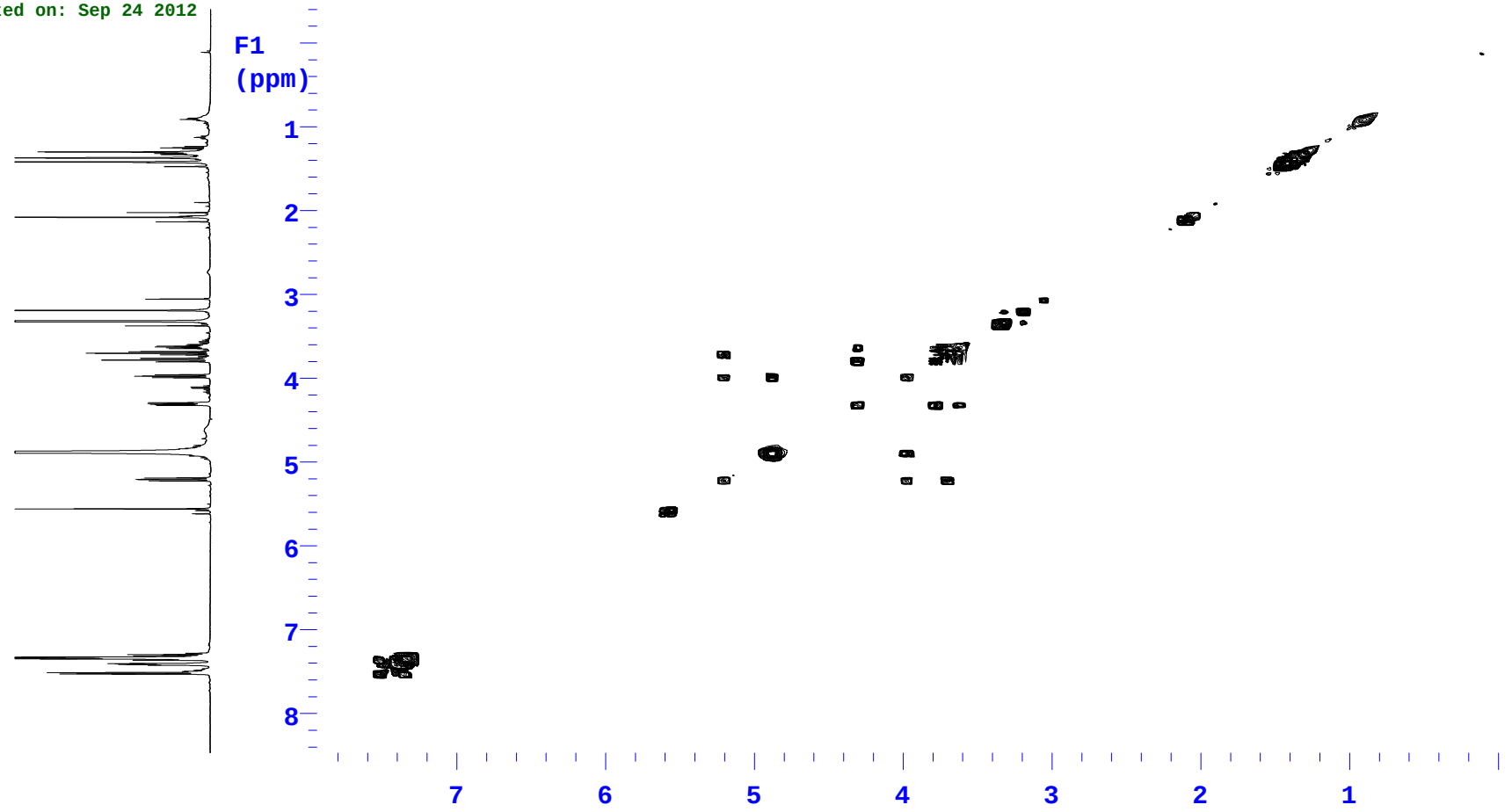
5c-II-Ac

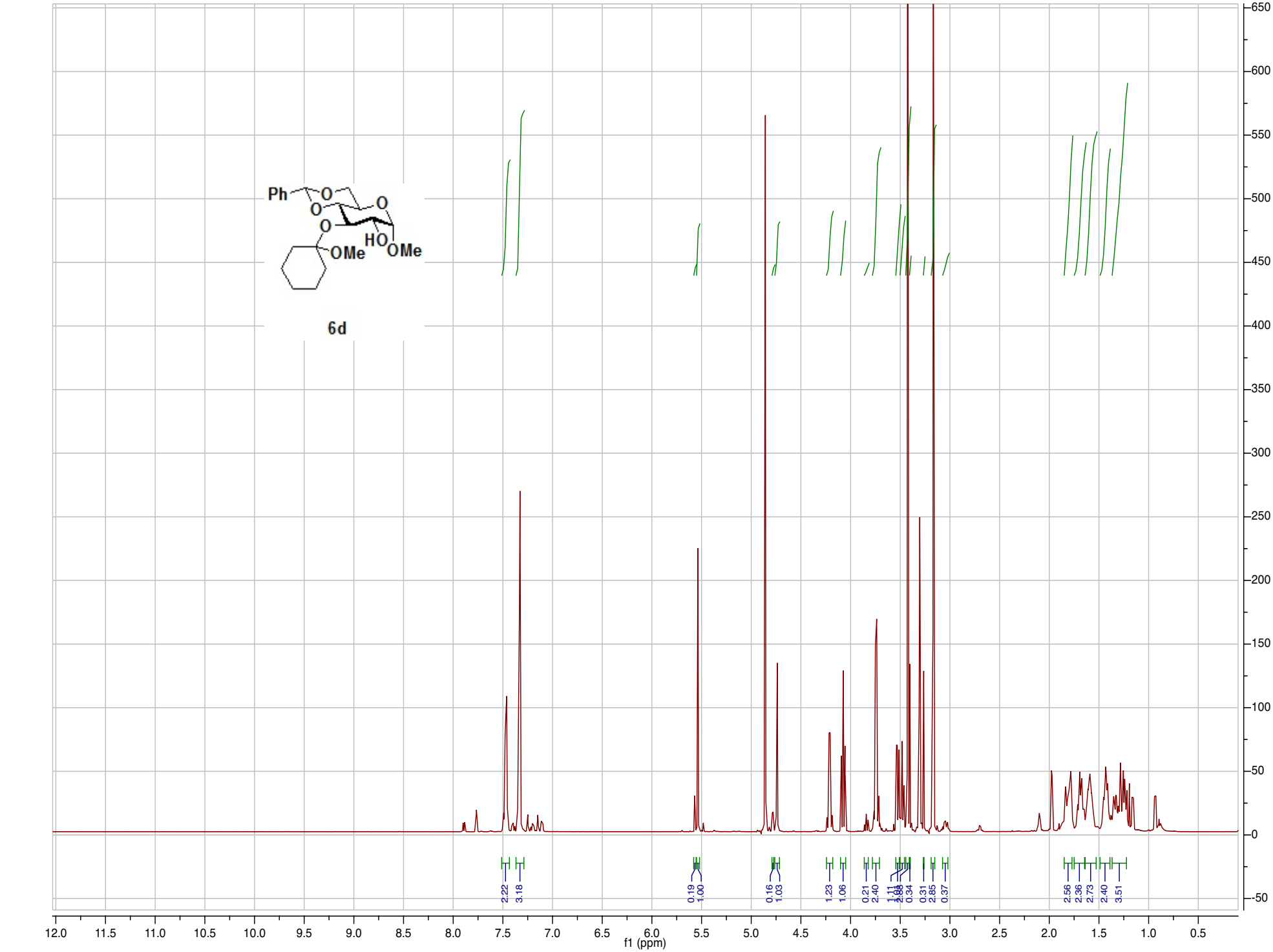
Sample Name:
EM-04-132PURECOSY-METHANOL-D4
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

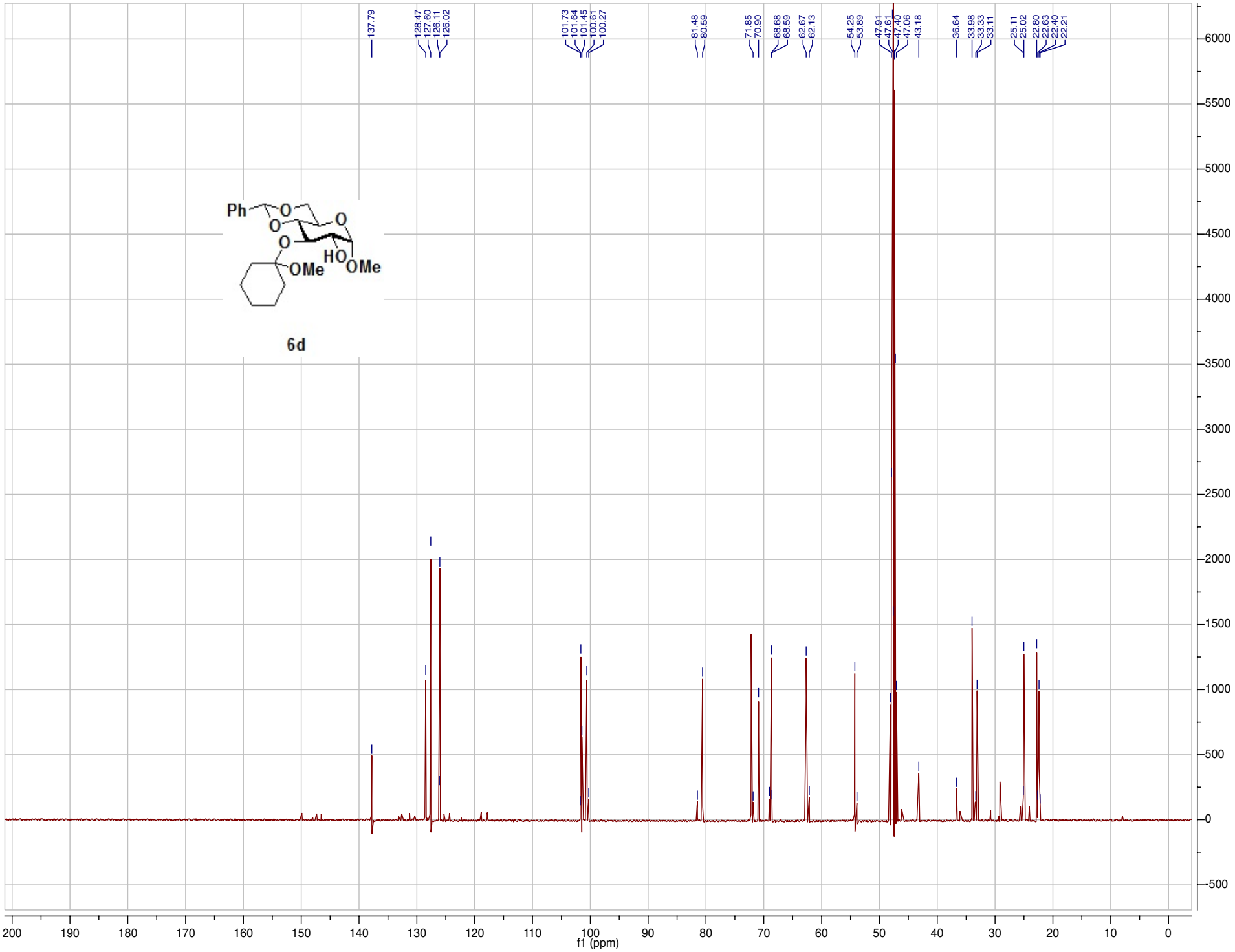
Sample directory:

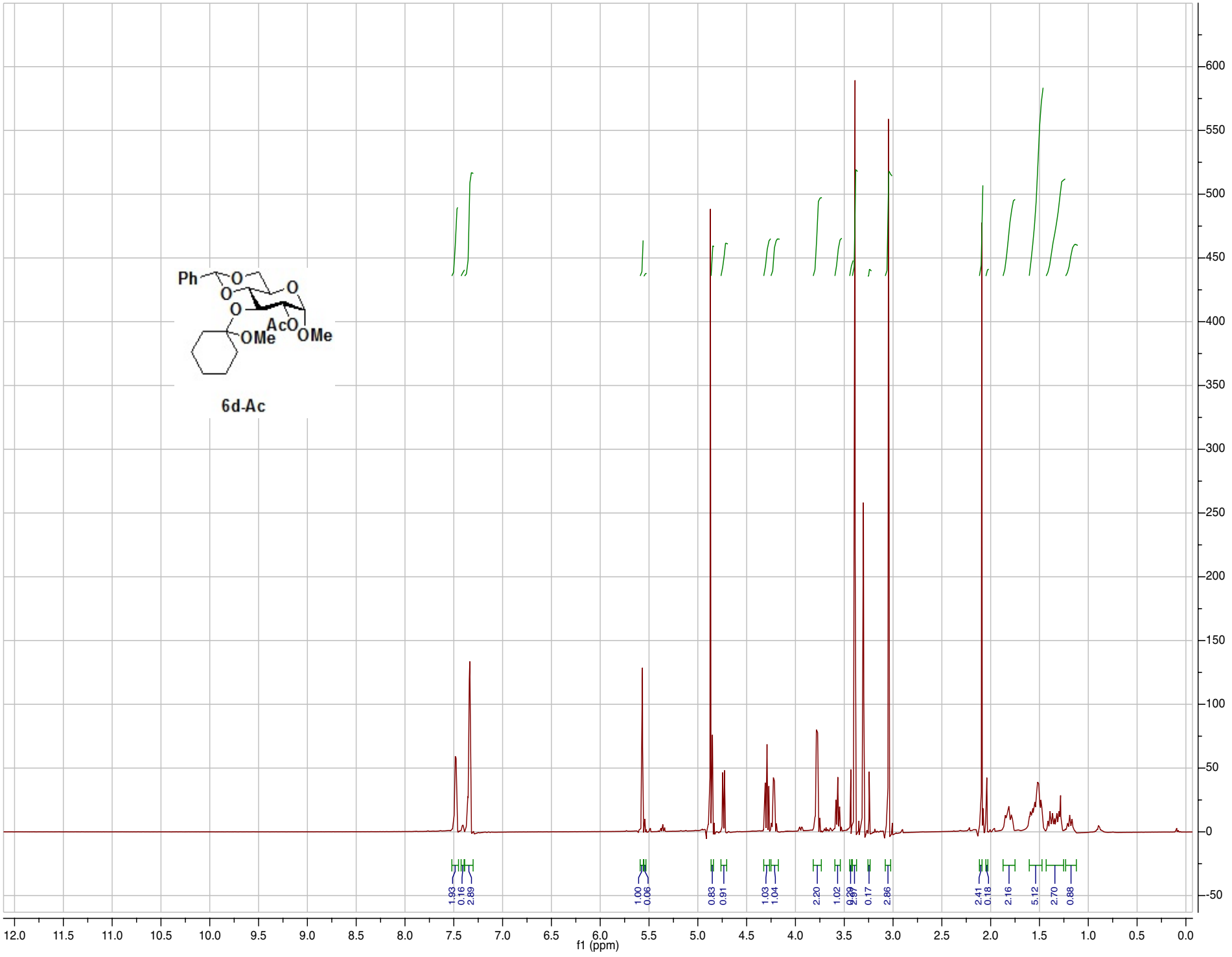
FidFile: EM-04-132PURECOSY-METHANOL-D4

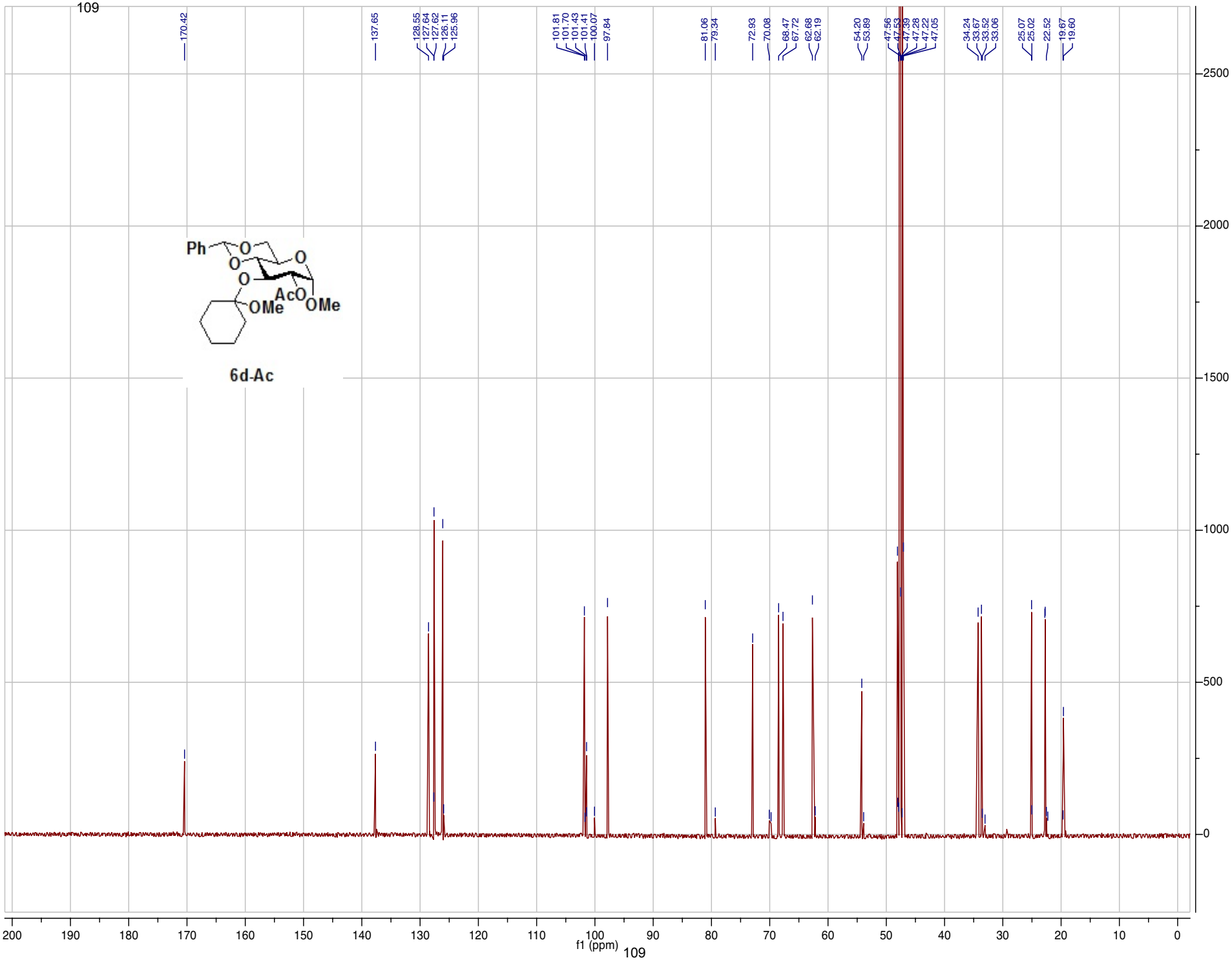
Pulse Sequence: gCOSY
Solvent: cd3od
Data collected on: Sep 24 2012

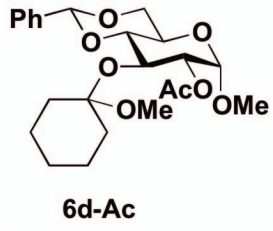



Ph
O
O
O
O
HO
OMe
OMe
6d
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
2.22
3.18
0.19
1.00
0.16
1.03
1.23
1.06
0.21
2.40
1.11
2.88
0.34
0.31
2.85
0.37
2.56
2.36
2.73
2.40
3.51


137.79
128.47
127.60
126.11
126.02
101.73
101.64
101.45
100.61
100.27
81.48
80.59
71.85
70.90
68.68
68.59
62.67
62.13
54.25
53.89
47.91
47.61
47.40
47.06
43.18
36.64
33.98
33.33
33.11
25.11
25.02
22.80
22.63
22.40
22.21
Ph
O
O
O
O
HO
OMe
OMe
6d
f1 (ppm)


Ph
O
O
O
O
AcO
OMe
OMe
6d-Ac
1.93
0.16
2.89
1.00
0.06
0.83
0.91
1.03
1.04
2.20
1.02
0.17
2.86
2.41
0.18
2.16
5.12
2.70
0.88
f1 (ppm)


170.42
137.65
128.55
127.64
127.62
126.11
125.96
101.81
101.70
101.43
101.41
100.07
97.84
81.06
79.34
72.93
70.08
68.47
67.72
62.68
62.19
54.20
53.89
47.56
47.53
47.39
47.28
47.22
47.05
34.24
33.67
33.52
33.06
25.07
25.02
22.52
19.67
19.60
Ph
O
O
O
O
AcO
OMe
OMe
6d-Ac
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



6d-Ac

STANDARD PROTON PARAMETERS

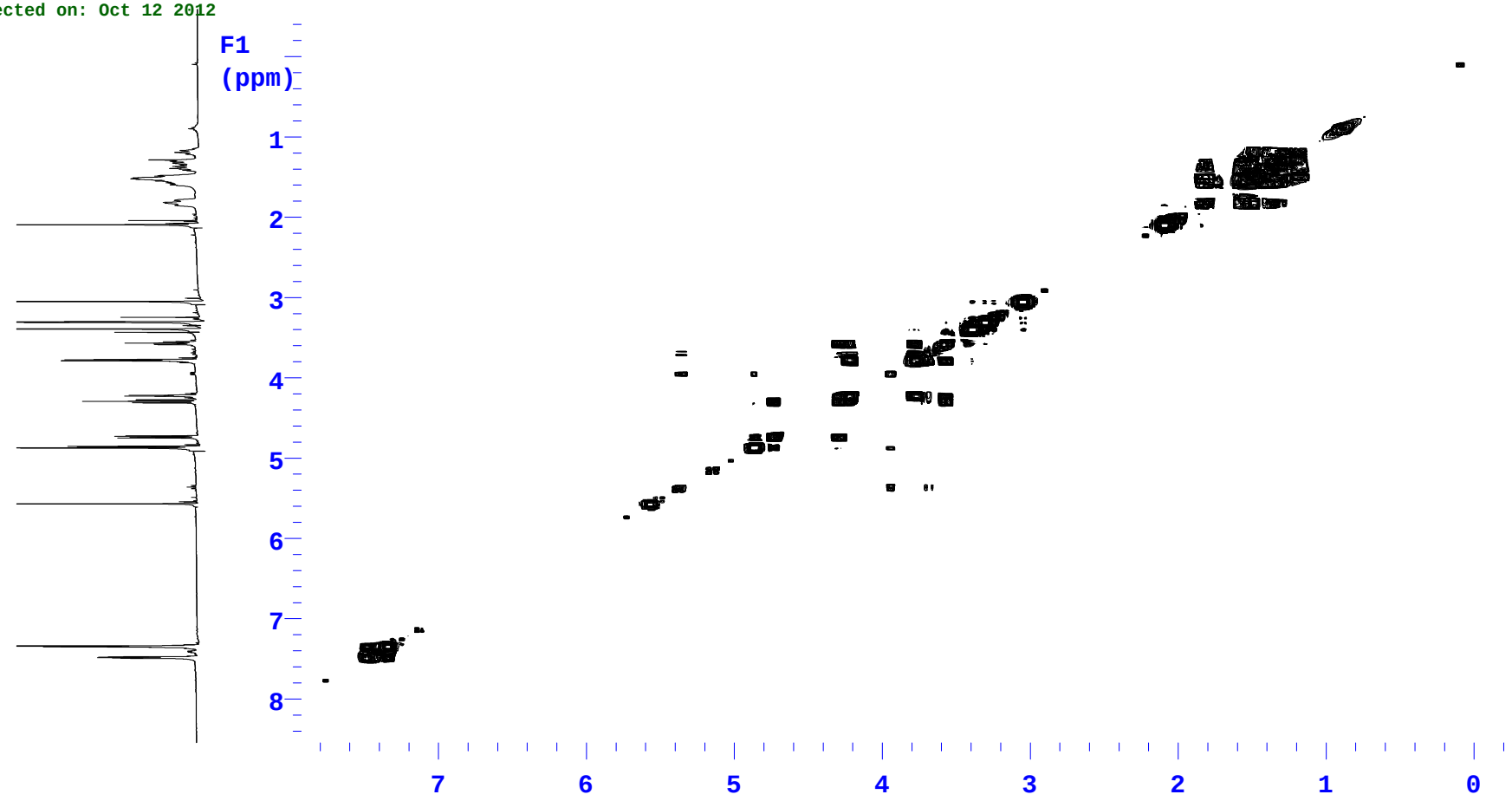
Sample Name:
EM-04-172PURECOSY-METHANOL-D4
Data Collected on:
Te-vnmrs500
Archive directory:

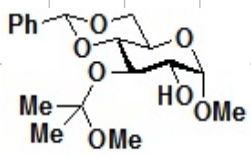
Sample directory:

FidFile: EM-04-172PURECOSY-METHANOL-D4

Pulse Sequence: gCOSY
Solvent: cd3od
Data collected on: Oct 12 2012

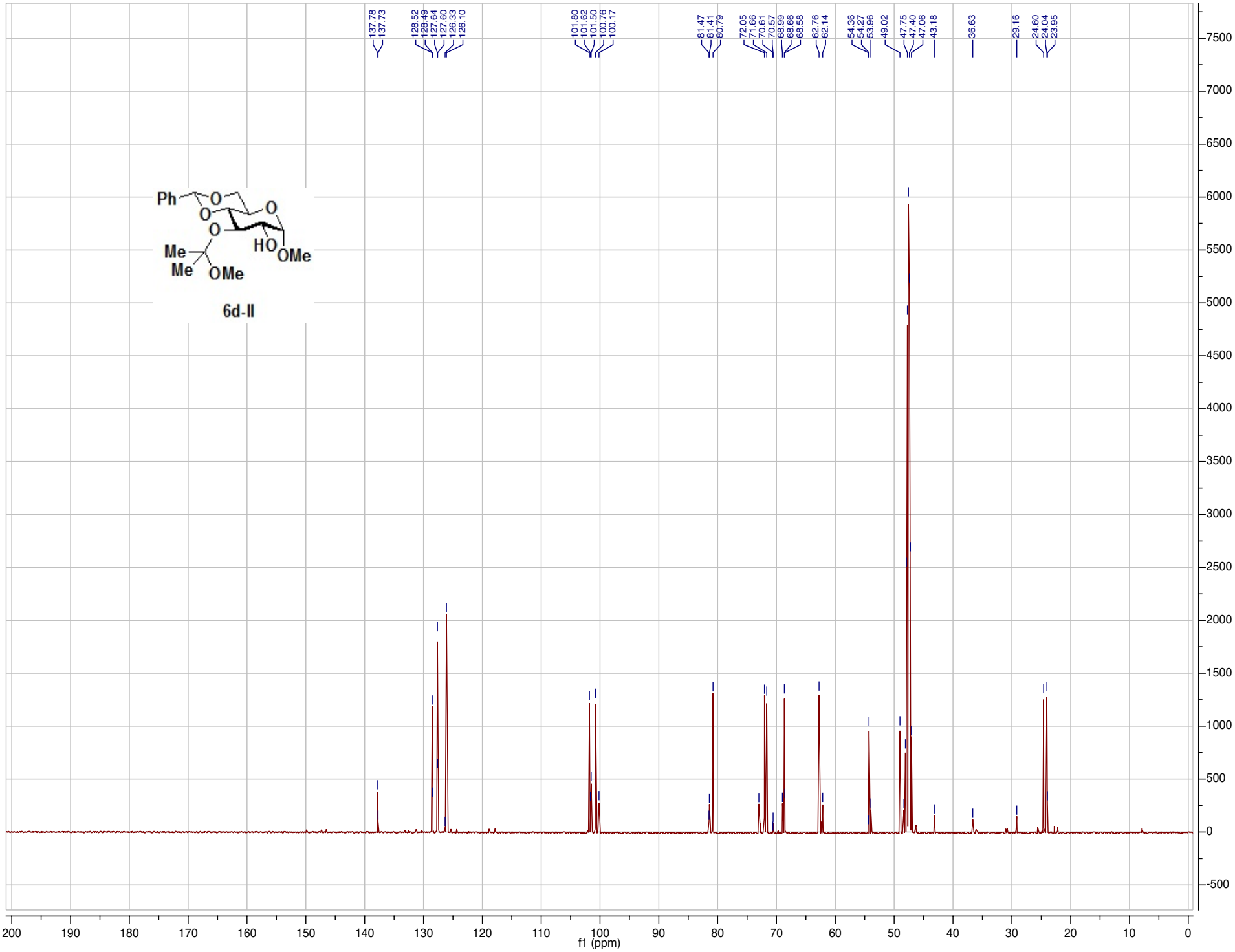
Agilent Technologies

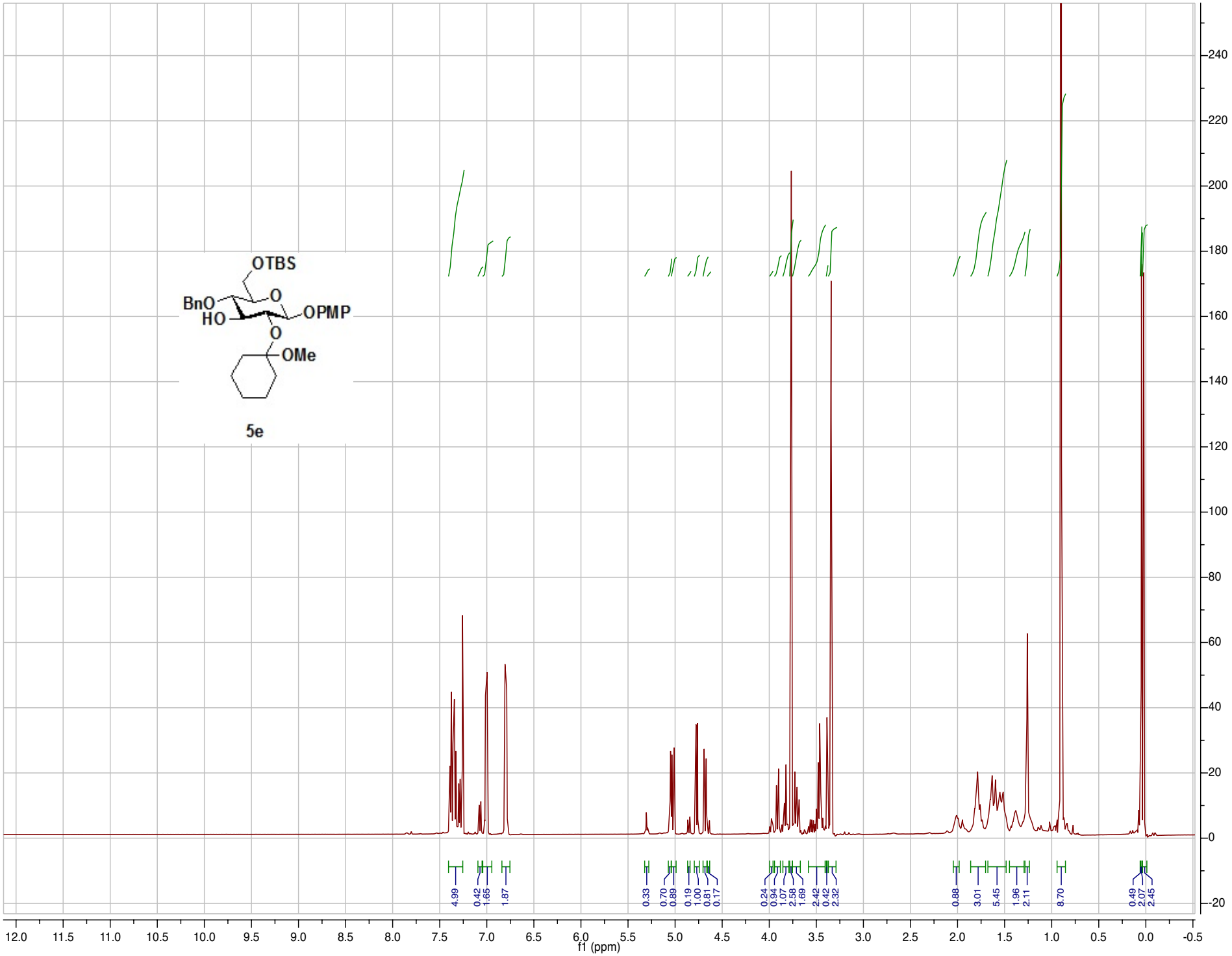


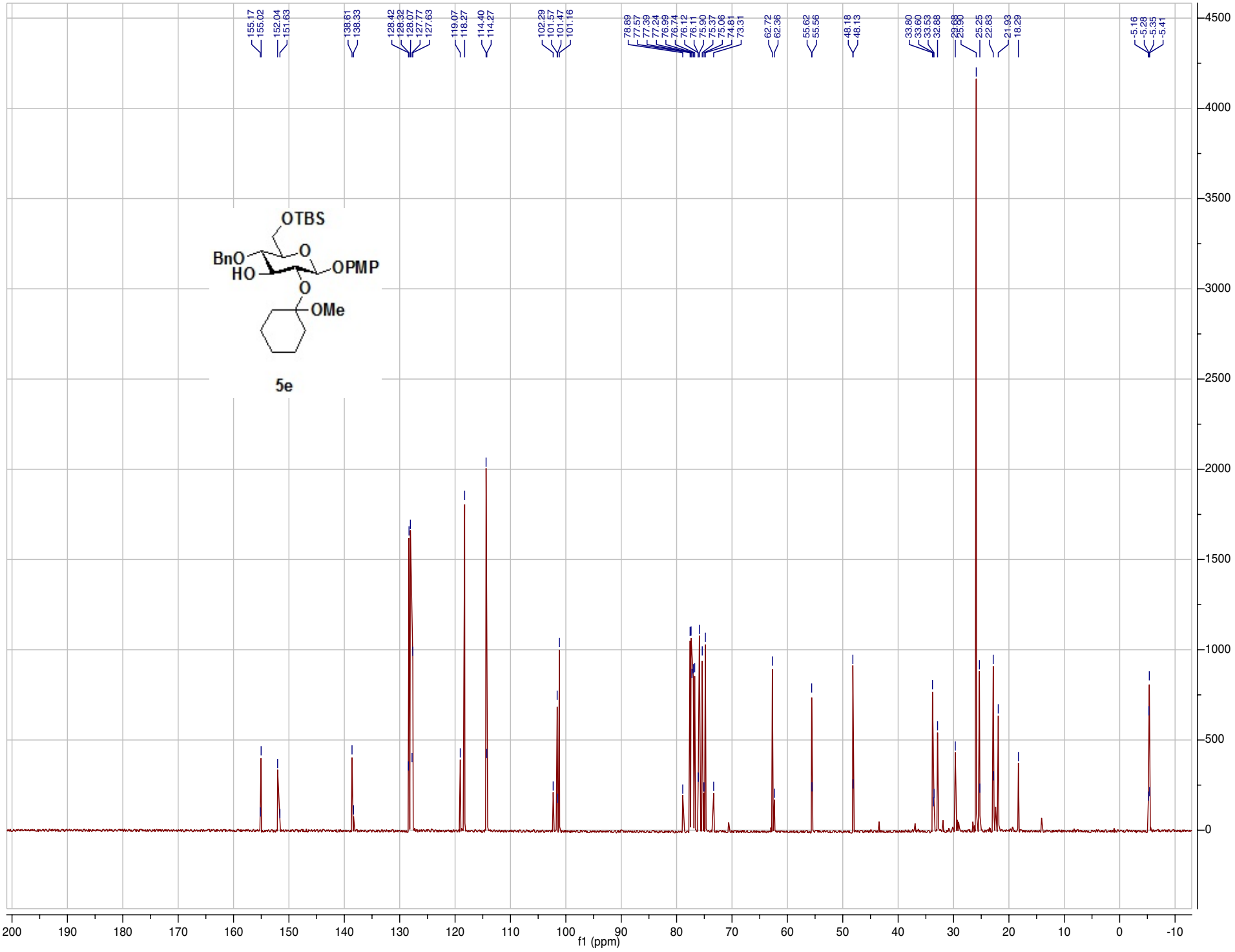

Ph
O
O
O
O
HO
OMe
Me
Me
OMe

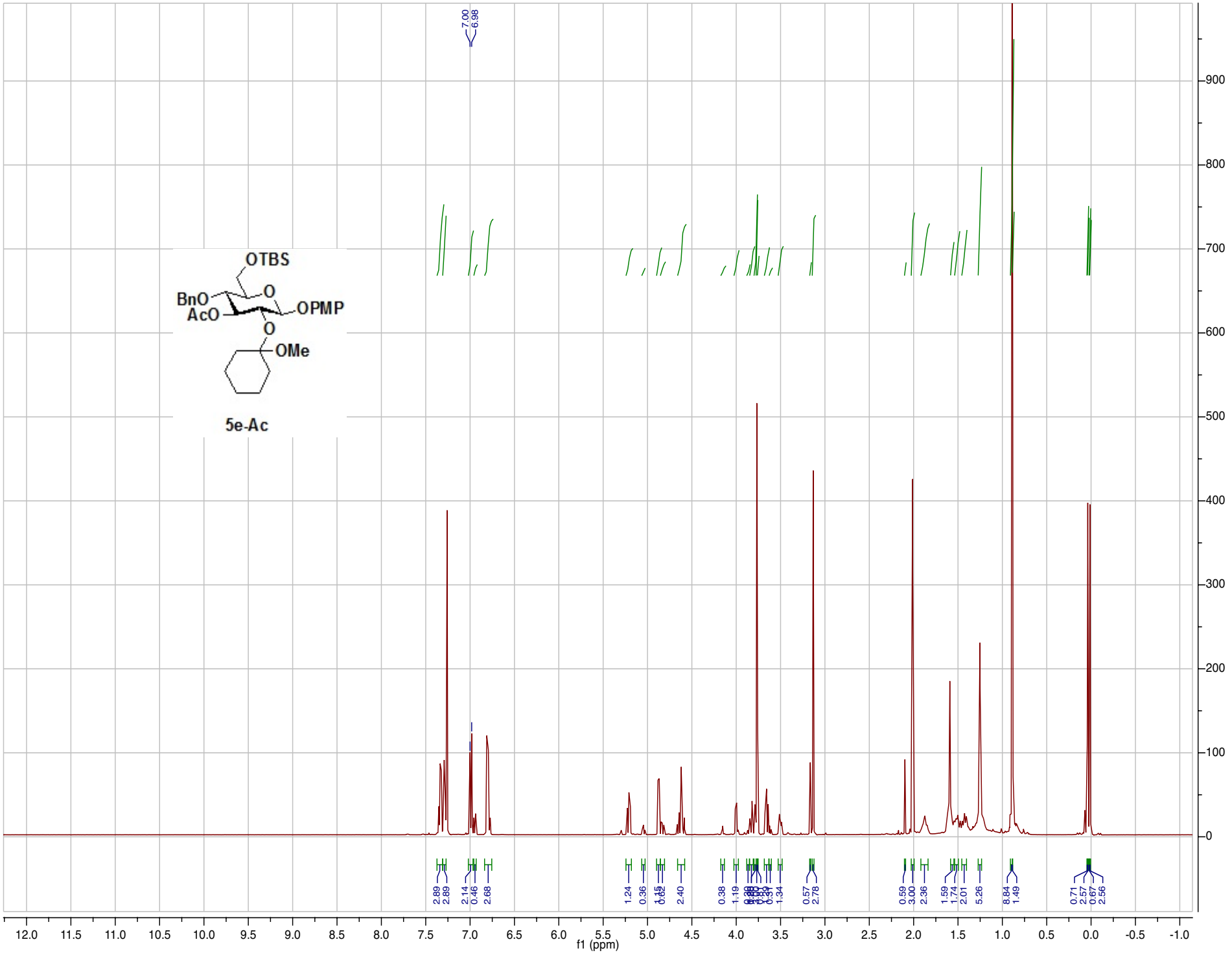
6d-II

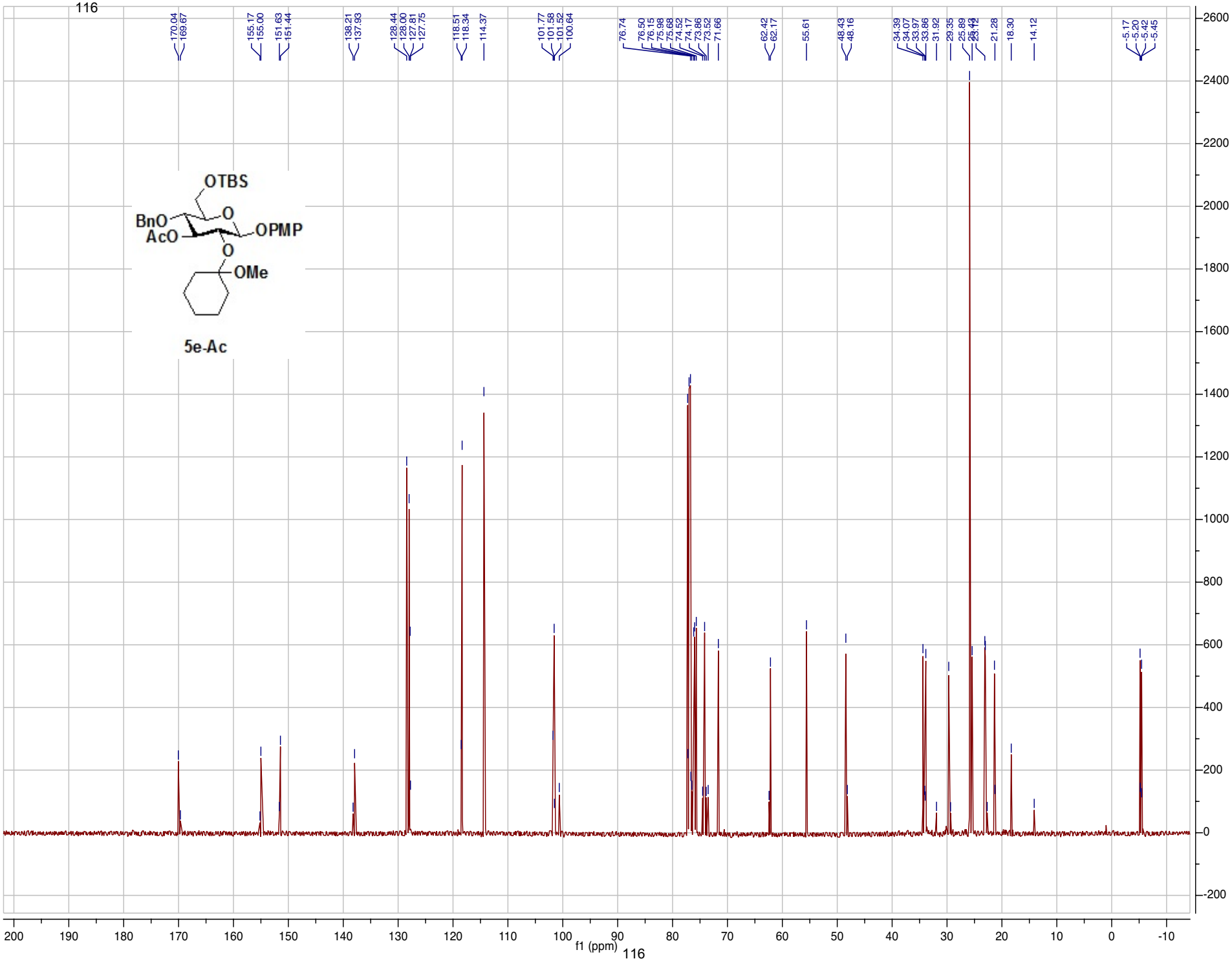
550
500
450
400
350
300
250
200
150
100
50
0
2.46
3.53
0.20
1.00
0.22
1.02
1.39
1.18
0.40
0.90
2.97
0.79
0.58
2.93
0.70
0.74
2.72
3.12
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

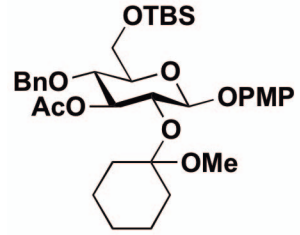

137.78
137.73
128.52
128.49
127.64
127.60
126.33
126.10
101.80
101.62
101.50
100.76
100.17
81.47
81.41
80.79
72.05
71.66
70.61
70.57
68.99
68.66
68.58
62.76
62.14
54.36
54.27
53.96
49.02
47.75
47.40
47.06
43.18
36.63
29.16
24.60
24.04
23.95
Ph
O
O
O
O
HO
OMe
Me
Me
OMe
6d-II
f1 (ppm)


OTBS
BnO
HO
O
OPMP
O
OMe
5e
f1 (ppm)
4.99
0.42
1.65
1.87
0.33
0.70
0.89
0.19
1.00
0.81
0.17
0.24
0.94
1.07
2.58
1.69
2.42
0.42
2.32
0.88
3.01
5.45
1.96
2.11
8.70
0.49
2.07
2.45


155.17
155.02
152.04
151.63
138.61
138.33
128.42
128.32
128.07
127.77
127.63
119.07
118.27
114.40
114.27
102.29
101.57
101.47
101.16
78.89
77.57
77.39
77.24
76.99
76.74
76.12
76.11
75.90
75.37
75.06
74.81
73.31
62.72
62.36
55.62
55.56
48.18
48.13
33.80
33.60
33.53
32.88
25.25
22.83
21.93
18.29
-5.16
-5.28
-5.35
-5.41
OTBS
BnO
HO
O
OPMP
O
OMe
5e
f1 (ppm)


OTBS
BnO
AcO
O
OPMP
O
OMe
5e-Ac
7.00
6.98
f1 (ppm)


170.04
169.67
155.17
155.00
151.63
151.44
138.21
137.93
128.44
128.00
127.81
127.75
118.51
118.34
114.37
101.77
101.58
101.52
100.64
76.74
76.50
76.15
75.98
75.68
74.52
74.17
73.86
73.52
71.66
62.42
62.17
55.61
48.43
48.16
34.39
34.07
33.97
33.86
31.92
29.35
25.89
25.49
25.12
21.28
18.30
14.12
-5.17
-5.20
-5.42
-5.45
OTBS
BnO
AcO
O
OPMP
O
OMe
5e-Ac
f1 (ppm)



5e-Ac

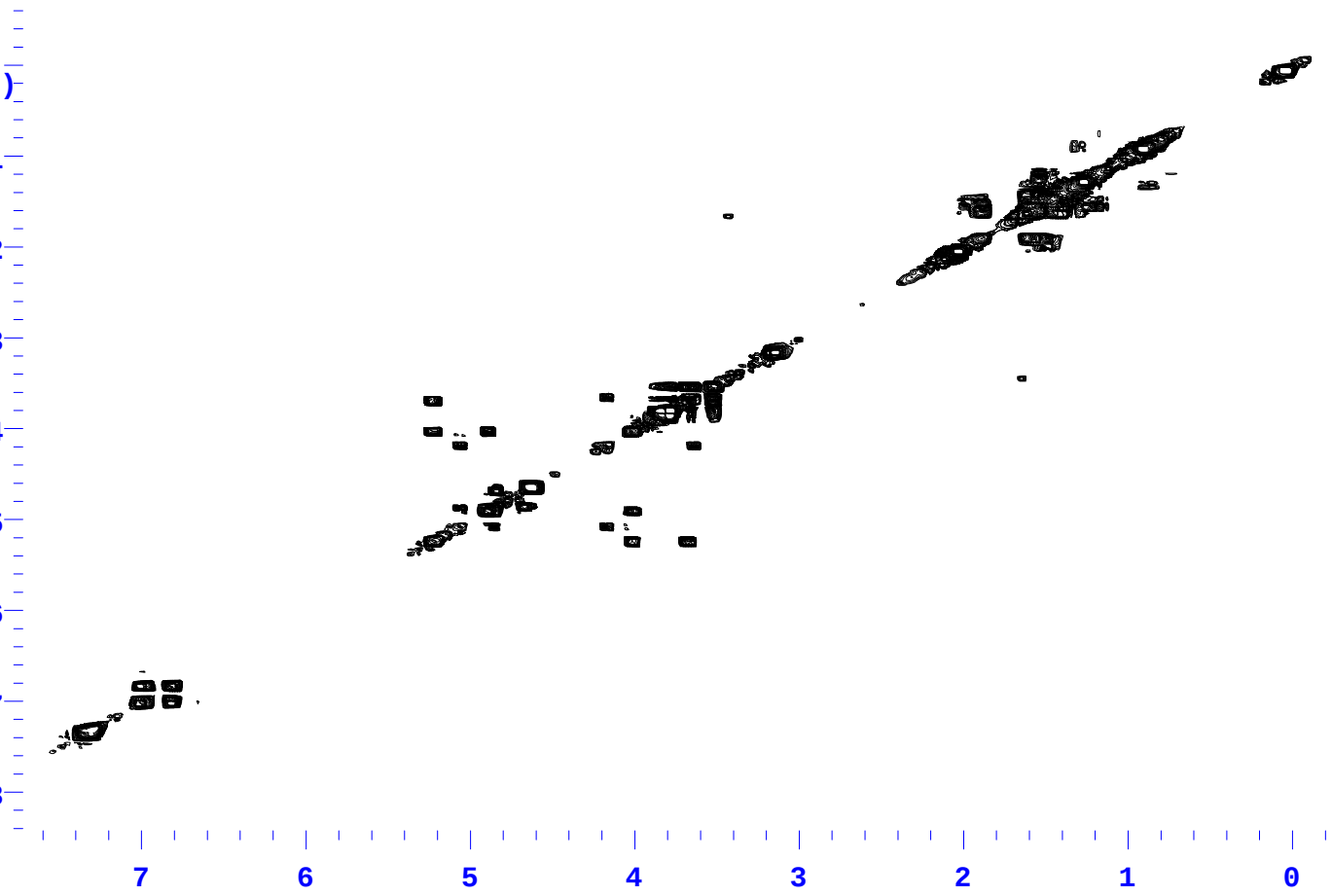
Agilent Technologies

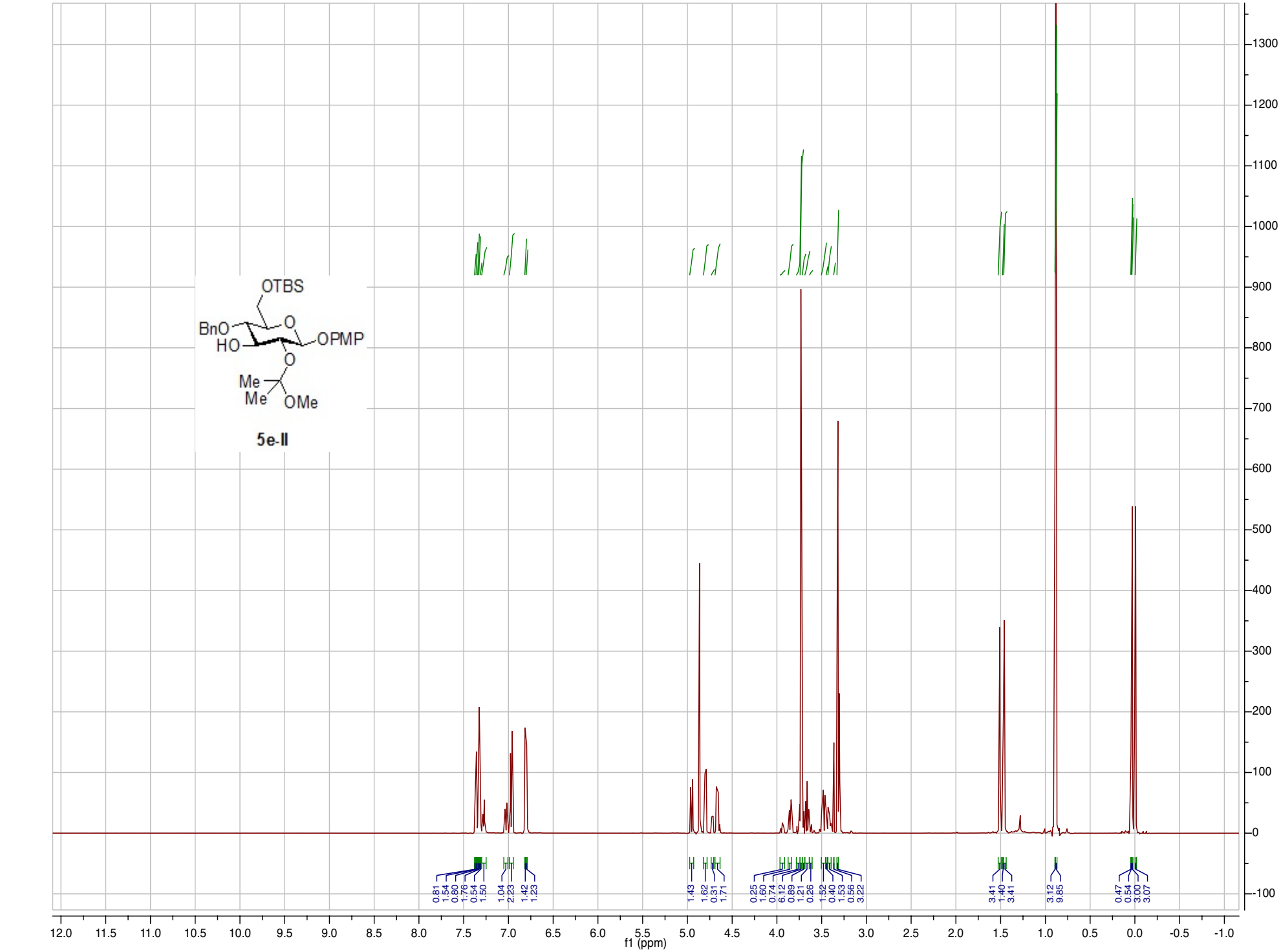
Sample Name:
EM-04-184PURECOSY-CDCL3
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

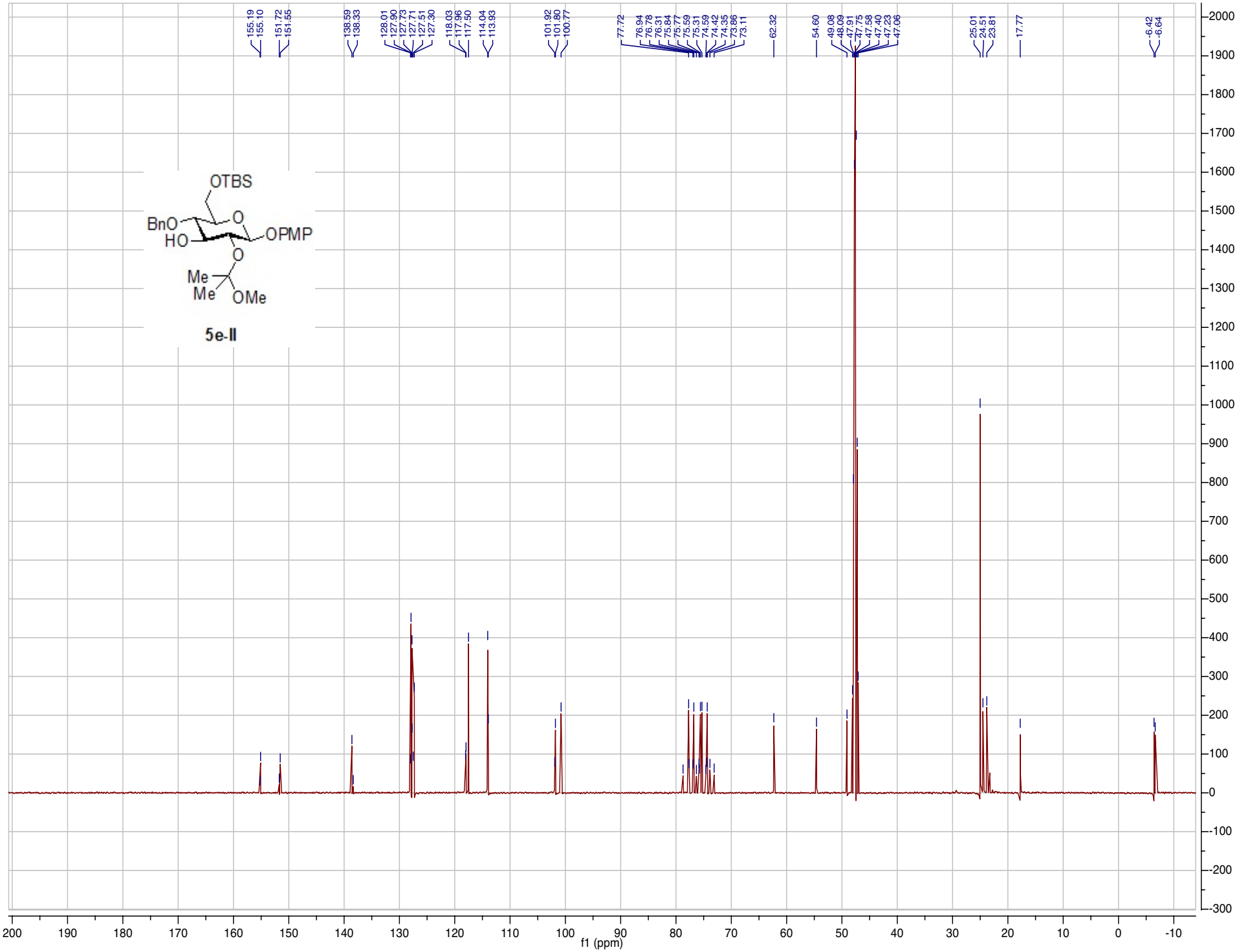
Sample directory:

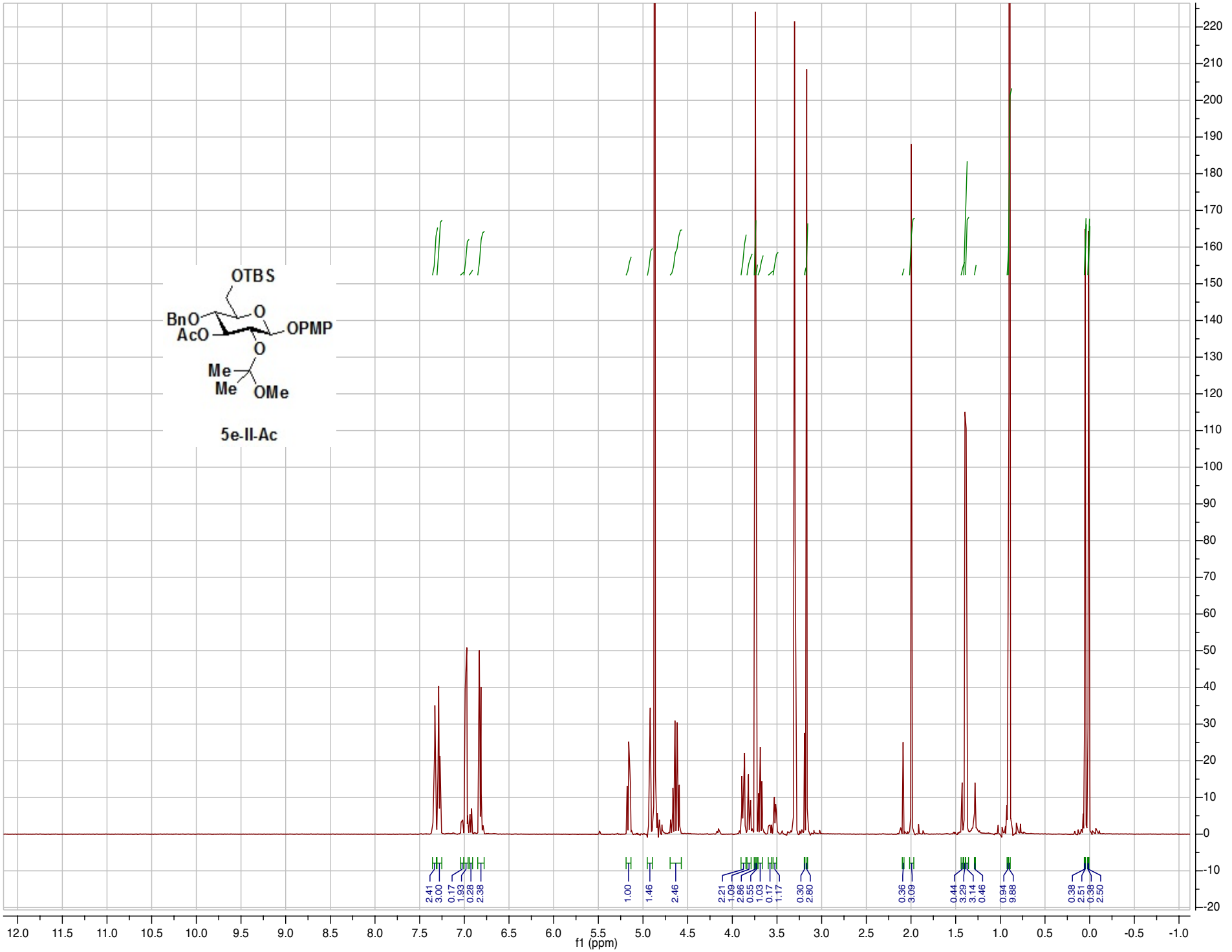
FidFile: EM-04-184PURECOSY-CDCL3

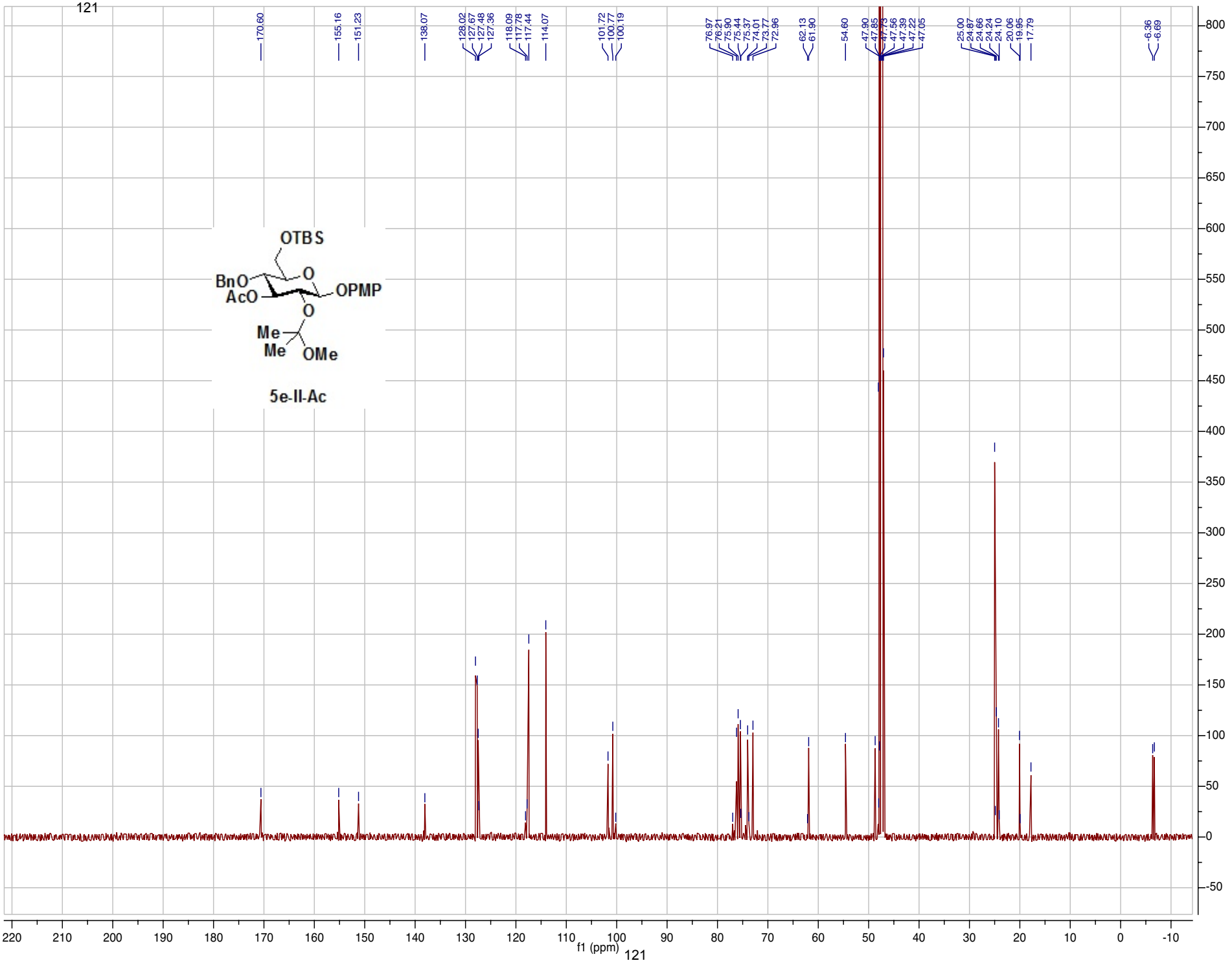
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Oct 23 2012

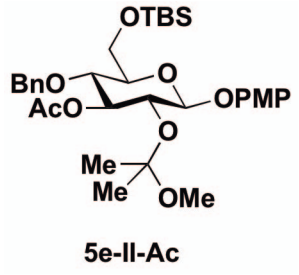



OTBS
BnO
HO
O
OPMP
O
Me
Me
OMe
5e-II
0.81
1.54
0.80
1.76
0.54
1.50
1.04
2.23
1.42
1.23
1.43
1.62
0.31
1.71
0.25
1.60
0.74
6.12
0.89
1.21
0.26
1.52
0.40
1.53
0.56
3.22
3.41
1.40
3.41
3.12
9.85
0.47
0.54
3.00
3.07
f1 (ppm)


155.19
155.10
151.72
151.55
138.59
138.33
128.01
127.90
127.73
127.71
127.51
127.30
118.03
117.96
117.50
114.04
113.93
101.92
101.80
100.77
77.72
76.94
76.78
76.31
75.84
75.77
75.59
75.31
74.59
74.42
74.35
73.86
73.11
62.32
54.60
49.08
48.09
47.91
47.75
47.58
47.40
47.23
47.06
25.01
24.51
23.81
17.77
-6.42
-6.64
OTBS
BnO
HO
O
OPMP
O
Me
Me
OMe
5e-II
f1 (ppm)


OTBS
BnO
AcO
O
OPMP
O
Me
Me
OMe
5e-II-Ac
2.41
3.00
0.17
1.93
0.28
2.38
1.00
1.46
2.46
2.21
1.09
2.86
0.55
1.03
0.17
1.17
0.30
2.80
0.36
3.09
0.44
3.29
3.14
0.46
0.94
9.88
0.38
2.51
0.38
2.50
f1 (ppm)


170.60
155.16
151.23
138.07
128.02
127.67
127.48
127.36
118.09
117.78
117.44
114.07
101.72
100.77
100.19
76.97
76.21
75.90
75.44
75.37
74.01
73.77
72.96
62.13
61.90
54.60
47.90
47.85
47.73
47.56
47.39
47.22
47.05
25.00
24.87
24.66
24.24
24.10
20.06
19.95
17.79
-6.36
-6.69
OTBS
BnO
AcO
O
OPMP
O
Me
Me
OMe
5e-II-Ac
f1 (ppm)



5e-II-Ac

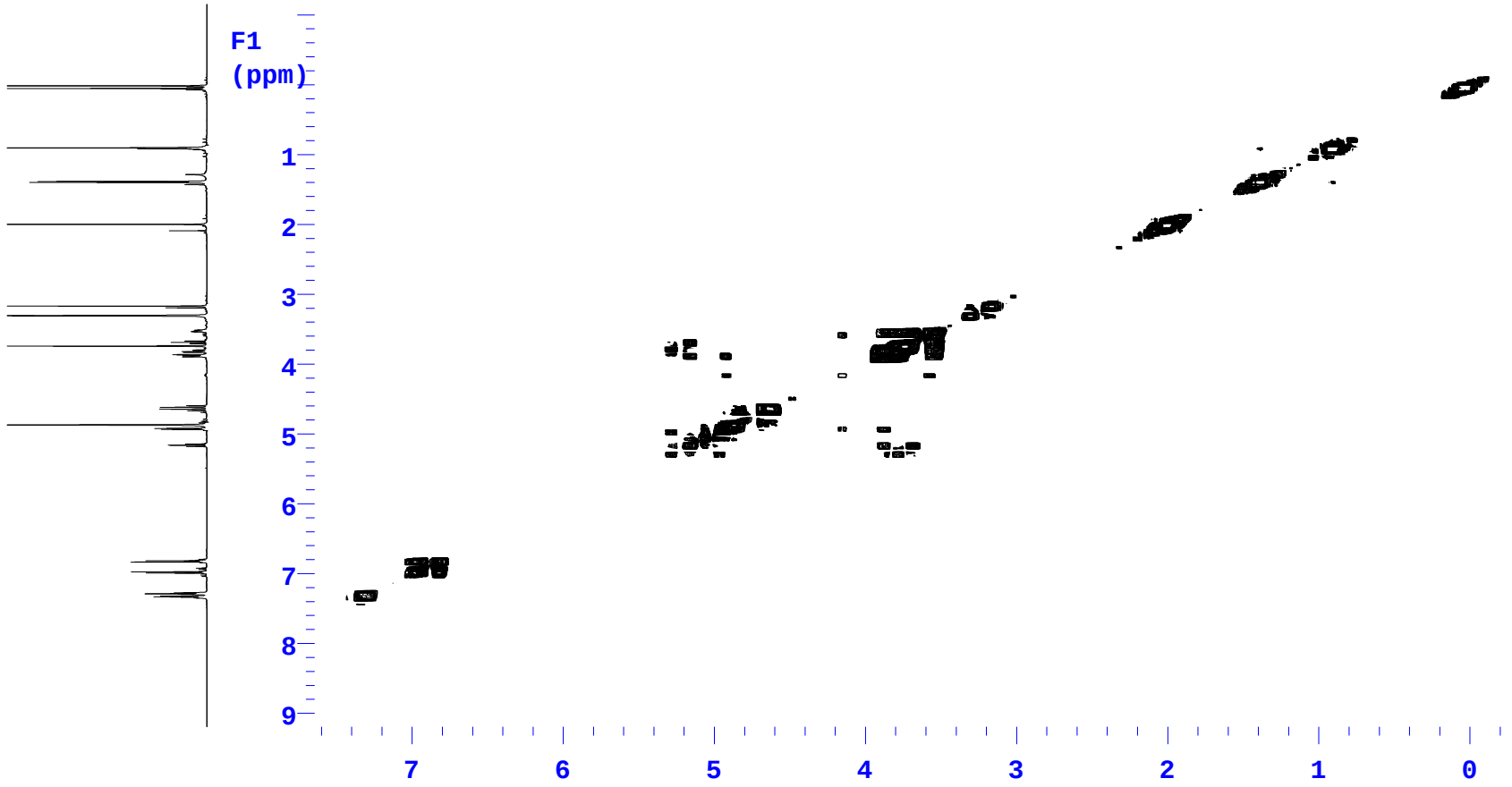
Automated Probe tuning parameter

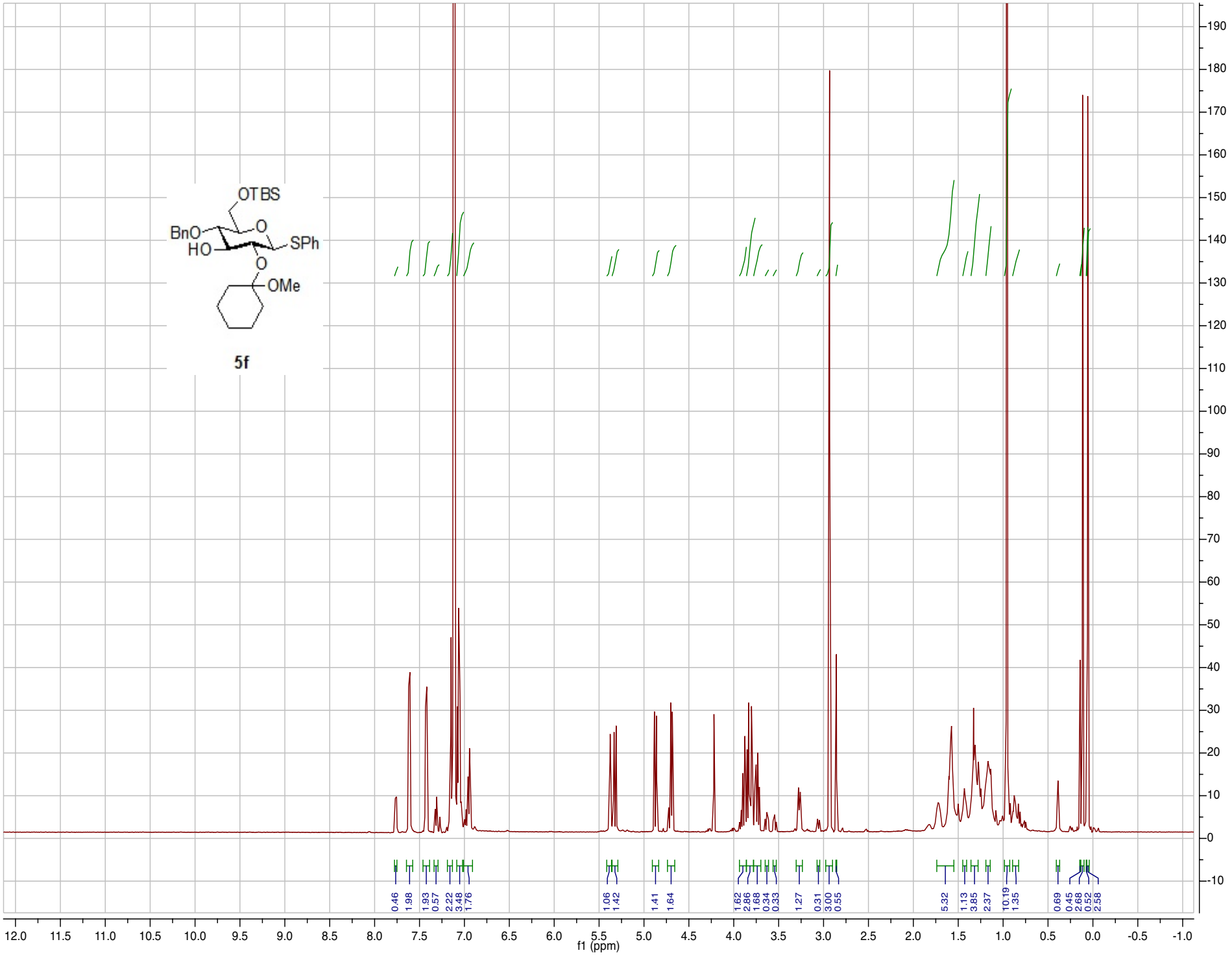
Sample Name:
EM-05-78PURECOSY-METHANOL-D4
Data Collected on:
Te-vnmrs500
Archive directory:

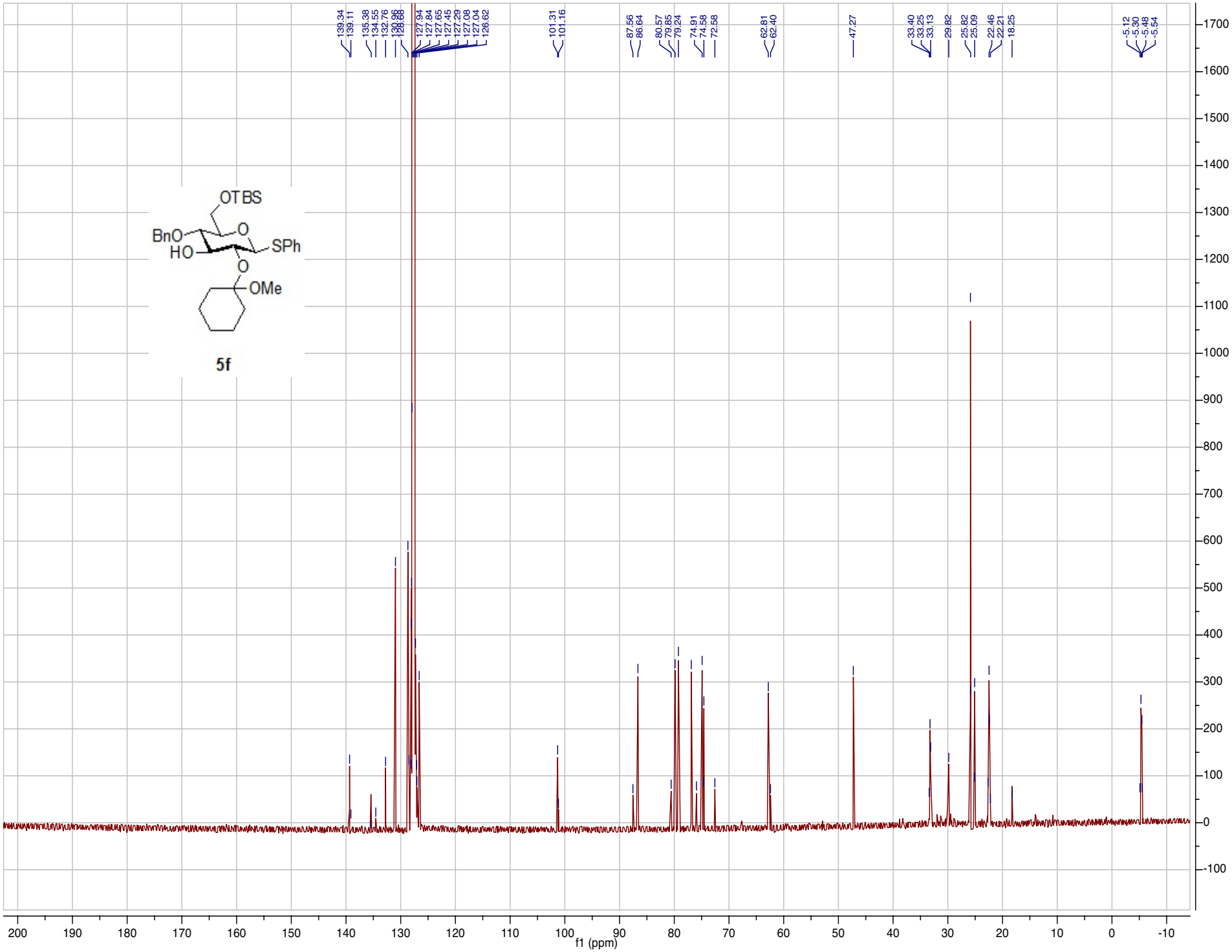
Sample directory:

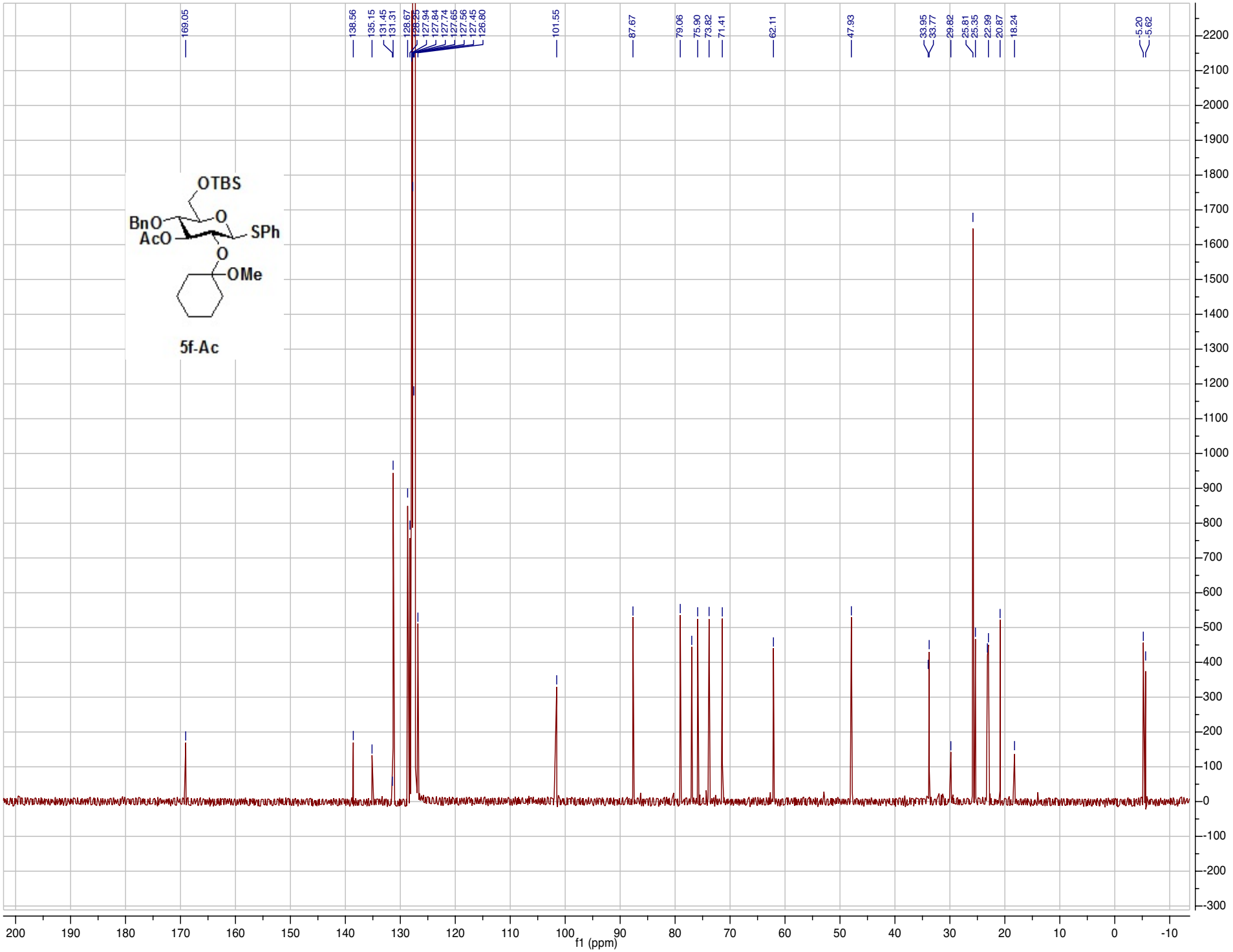
FidFile: EM-05-78PURECOSY-METHANOL-D4

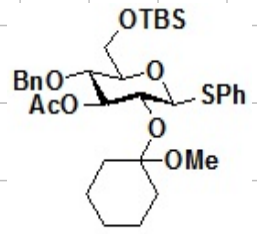
Pulse Sequence: gCOSY
Solvent: cd3od
Data collected on: Jan 18 2013




OTBS
BnO
HO
O
SPh
O
OMe
5f
0.46
1.98
1.93
0.57
2.22
3.48
1.76
1.06
1.42
1.41
1.64
1.62
2.86
1.68
0.34
0.33
1.27
0.31
3.00
0.55
5.32
1.13
3.85
2.37
10.19
1.35
0.69
0.45
2.68
0.52
2.58
f1 (ppm)


OTBS
BnO
HO
O
SPh
O
OMe
5f
139.34
139.11
135.38
134.55
132.76
127.94
127.84
127.65
127.45
127.29
127.08
127.04
126.62
101.31
101.16
87.56
86.64
80.57
79.85
79.24
74.91
74.58
72.58
62.81
62.40
47.27
33.40
33.25
33.13
29.82
25.82
25.09
22.46
22.21
18.25
-5.12
-5.30
-5.48
-5.54
f1 (ppm)


169.05
138.56
135.15
131.45
131.31
128.67
128.25
127.94
127.84
127.74
127.65
127.56
127.45
126.80
101.55
87.67
79.06
75.90
73.82
71.41
62.11
47.93
33.95
33.77
29.82
25.81
25.35
22.99
20.87
18.24
-5.20
-5.62
OTBS
BnO
AcO
O
SPh
O
OMe
5f-Ac
f1 (ppm)



5f-Ac

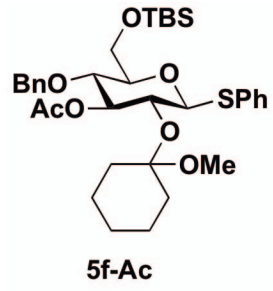
STANDARD PROTON PARAMETERS

Sample Name:
EM-04-268PURECOSY-BENZENE-D6
Data Collected on:
Te-vnmrs500
Archive directory:

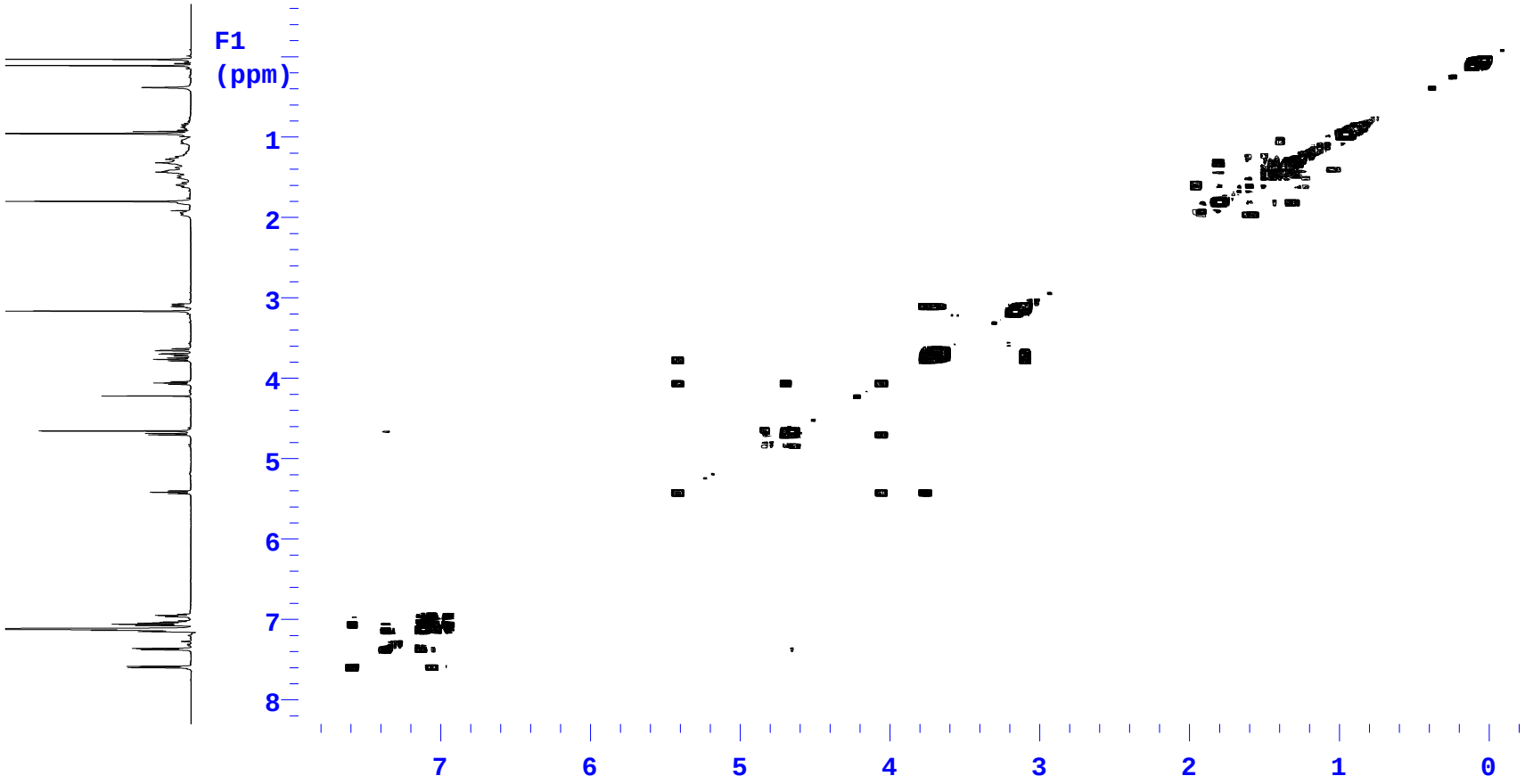
Sample directory:

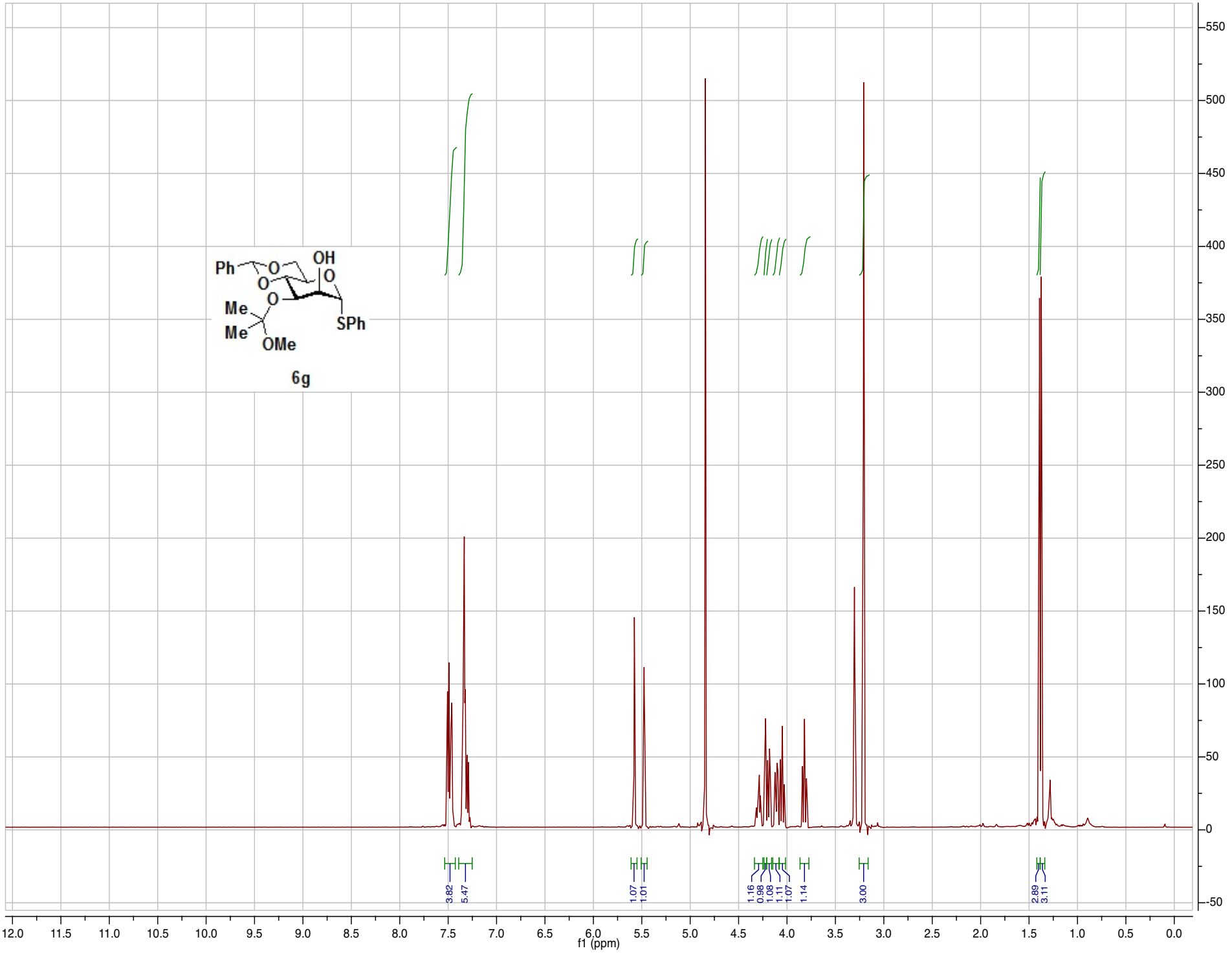
FidFile: EM-04-268COSY-BENZENE-D6

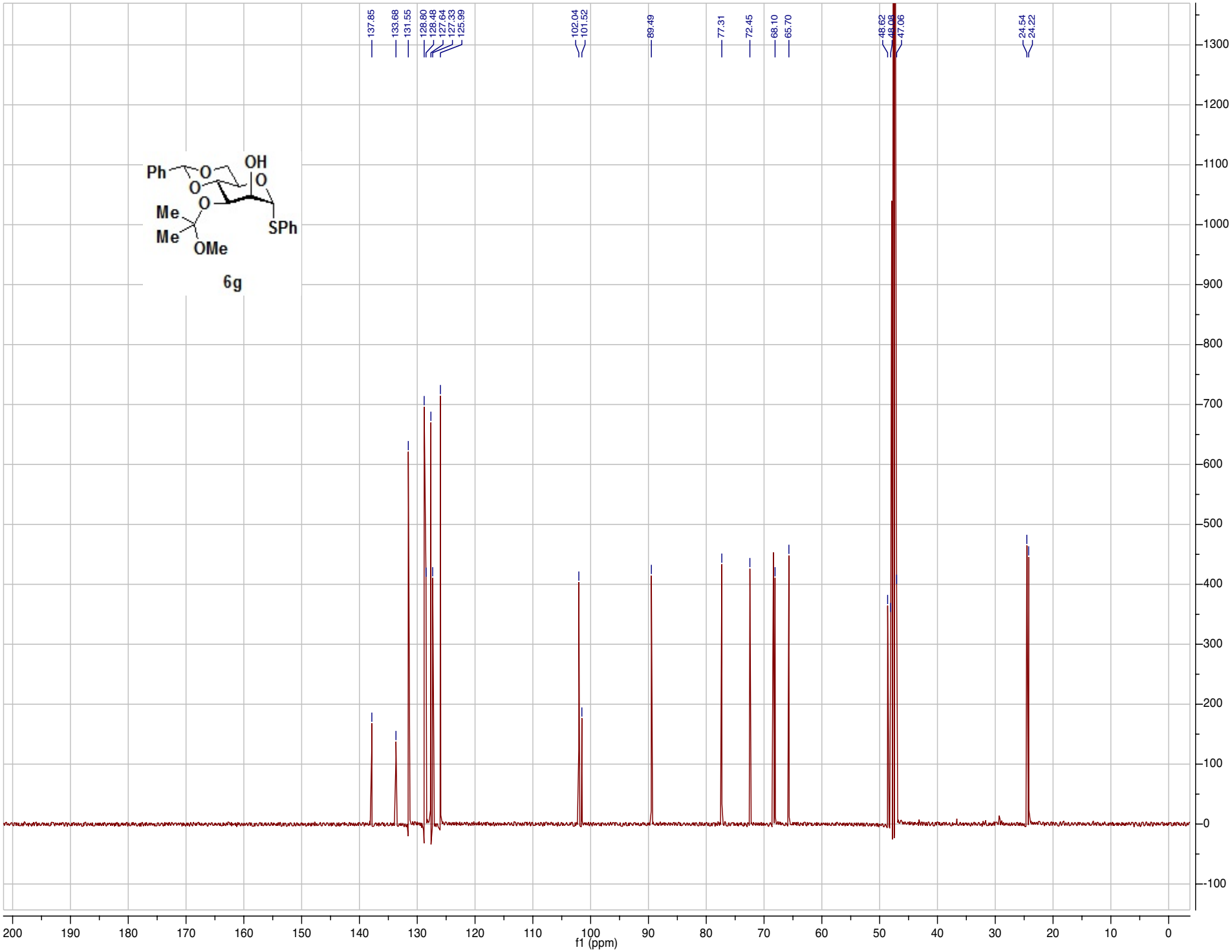
Pulse Sequence: gCOSY
Solvent: c6d6
Data collected on: Nov 16 2012

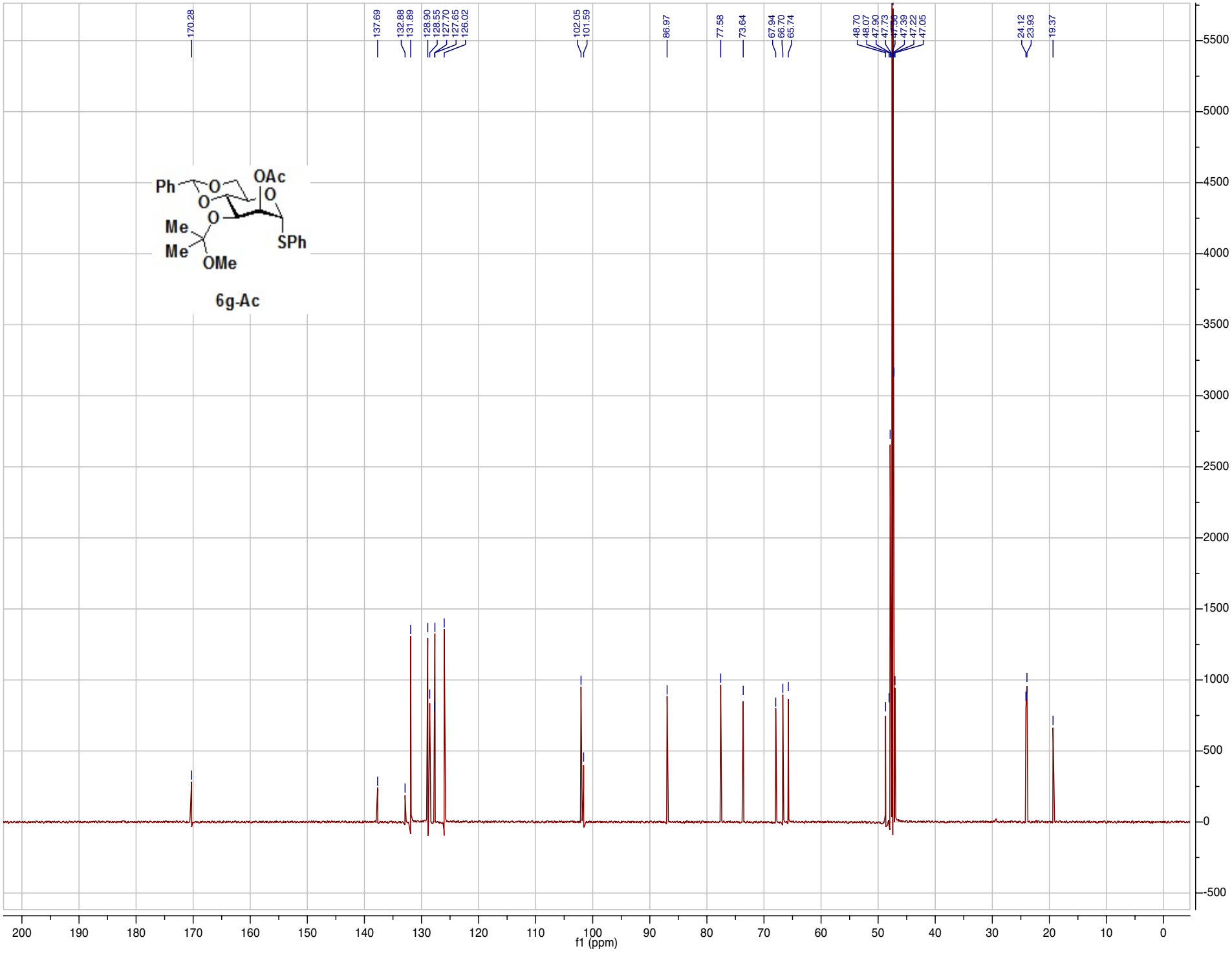


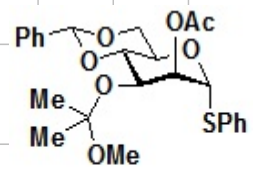
5f-Ac



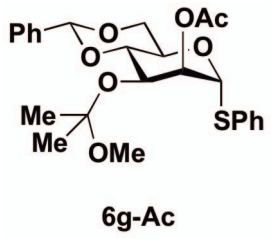

Ph
O
O
O
OH
O
Me
Me
OMe
SPh
6g
3.82
5.47
1.07
1.01
1.16
0.98
1.08
1.11
1.07
1.14
3.00
2.89
3.11
f1 (ppm)


137.85
133.68
131.55
128.80
128.48
127.64
127.33
125.99
102.04
101.52
89.49
77.31
72.45
68.10
65.70
48.62
48.08
47.06
24.54
24.22
Ph
O
OH
O
O
Me
Me
OMe
SPh
6g
f1 (ppm)


170.28
137.69
132.88
131.89
128.90
128.55
127.70
127.65
126.02
102.05
101.59
86.97
77.58
73.64
67.94
66.70
65.74
48.70
48.07
47.90
47.73
47.56
47.39
47.22
47.05
24.12
23.93
19.37
Ph
O
OAc
O
O
Me
Me
OMe
SPh
6g-Ac
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



6g-Ac



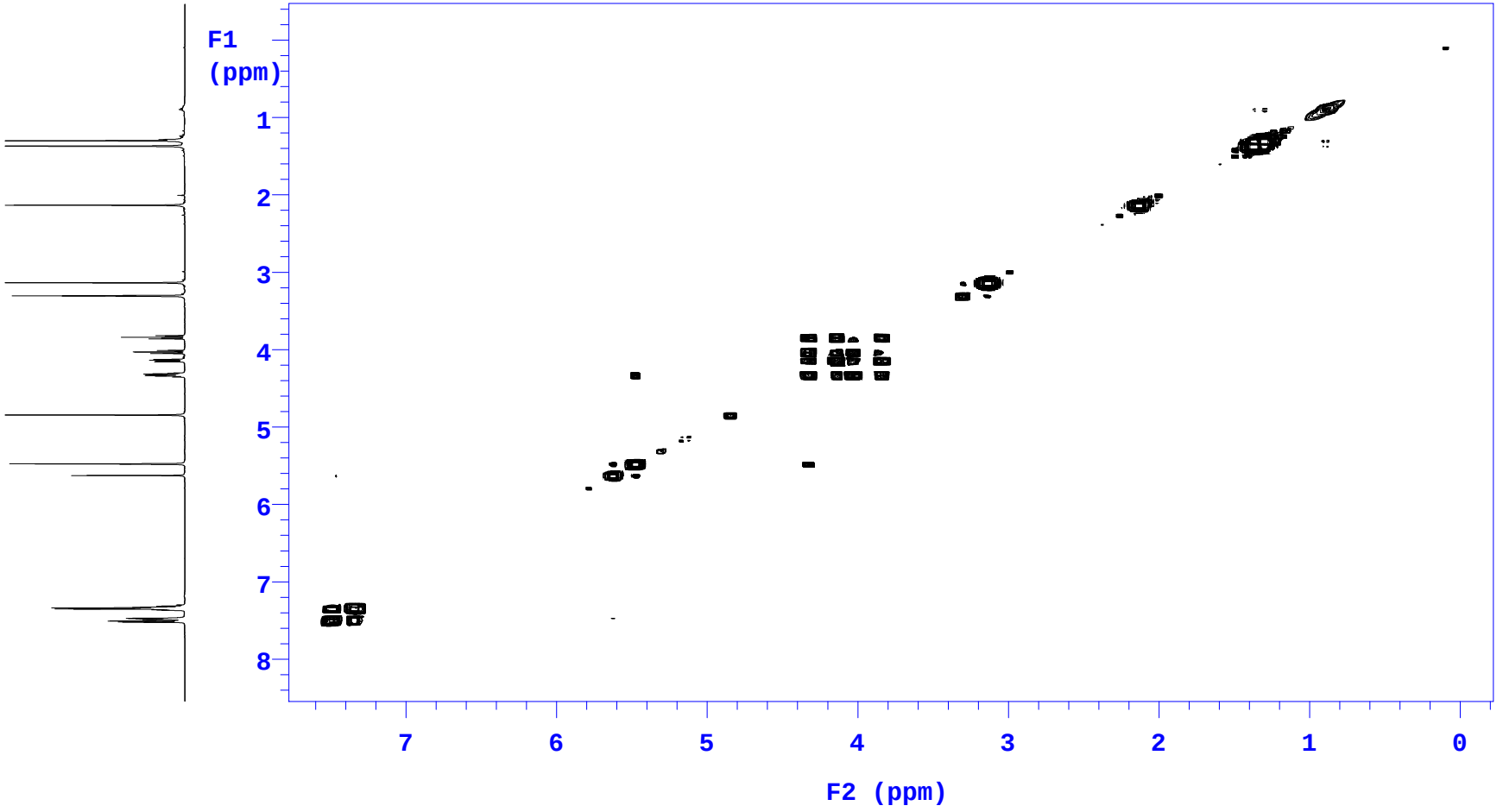
Automated Probe tuning parameter

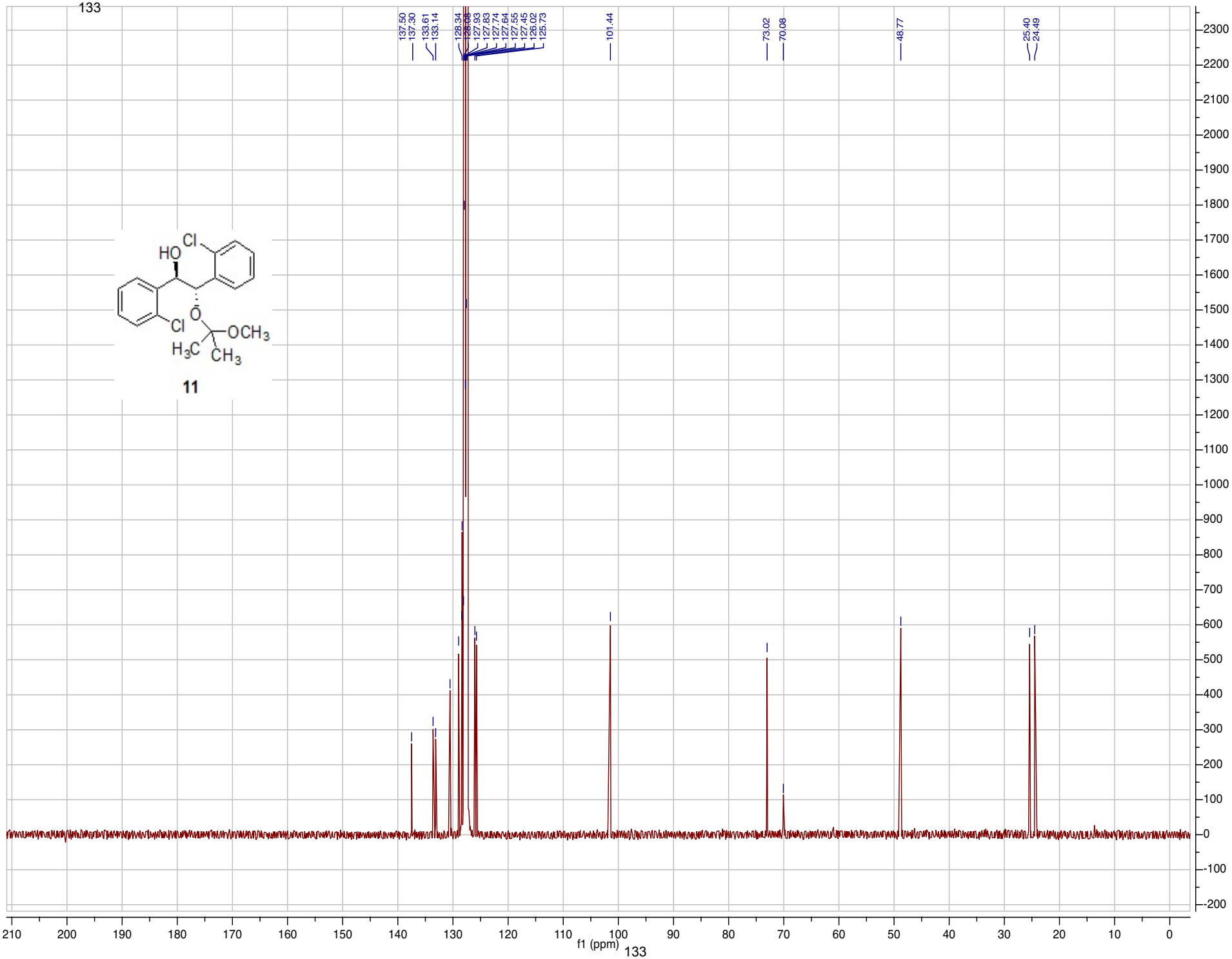
Sample Name:
EM-05-52PURECOSY-METHANOL-D4
Data Collected on:
Te-vnmrs500
Archive directory:

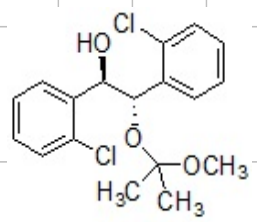
Sample directory:

FidFile: EM-05-52PURECOSY-METHANOL-D4

Pulse Sequence: gCOSY
Solvent: cd3od
Data collected on: Dec 18 2012



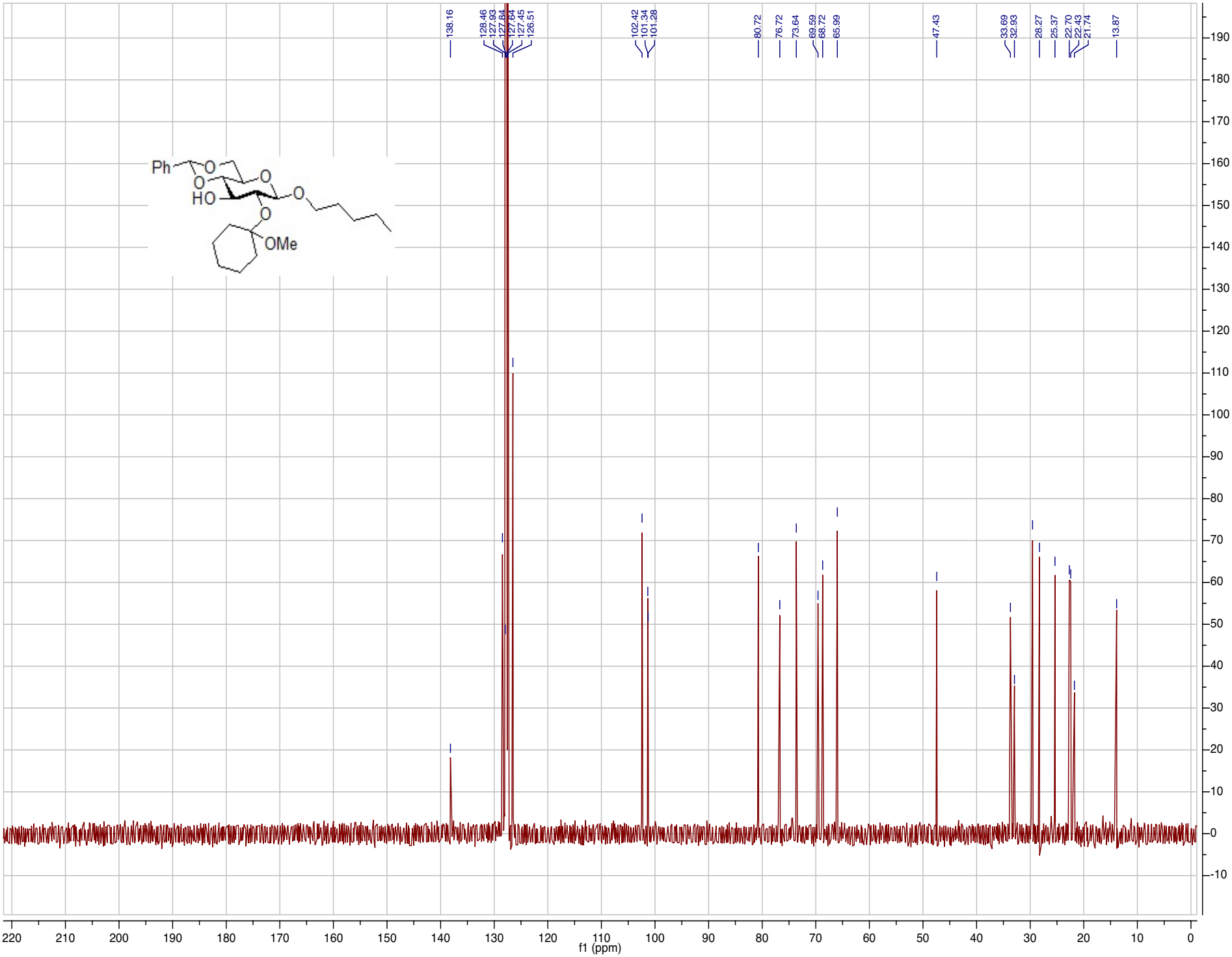

137.50
137.30
133.61
133.14
128.34
128.08
127.93
127.83
127.74
127.64
127.55
127.45
126.02
125.73
101.44
73.02
70.08
48.77
25.40
24.49
HO
Cl
Cl
O
OCH3
H3C
CH3
11
f1 (ppm)

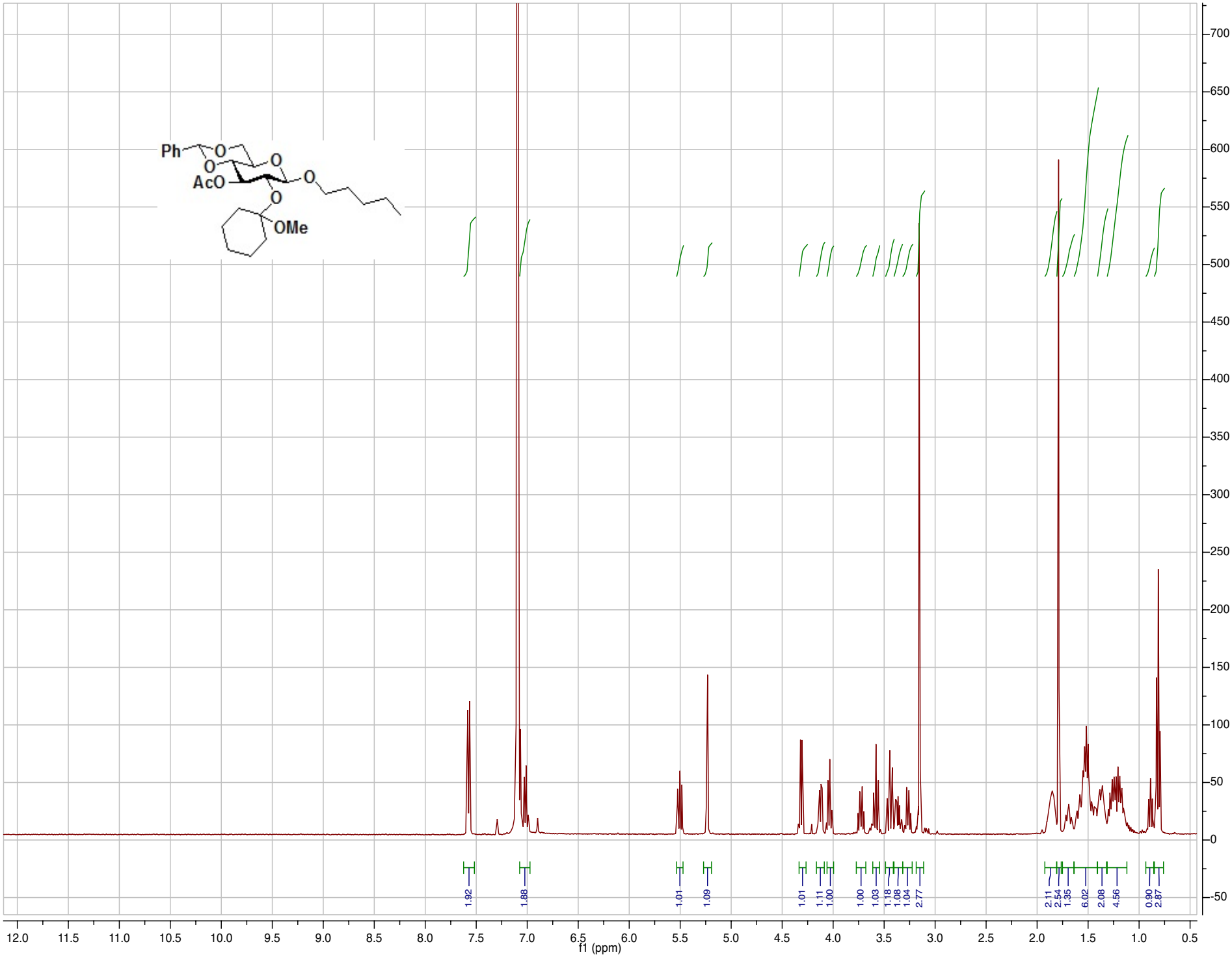

HO
Cl
Cl
O
OCH3
H3C
CH3

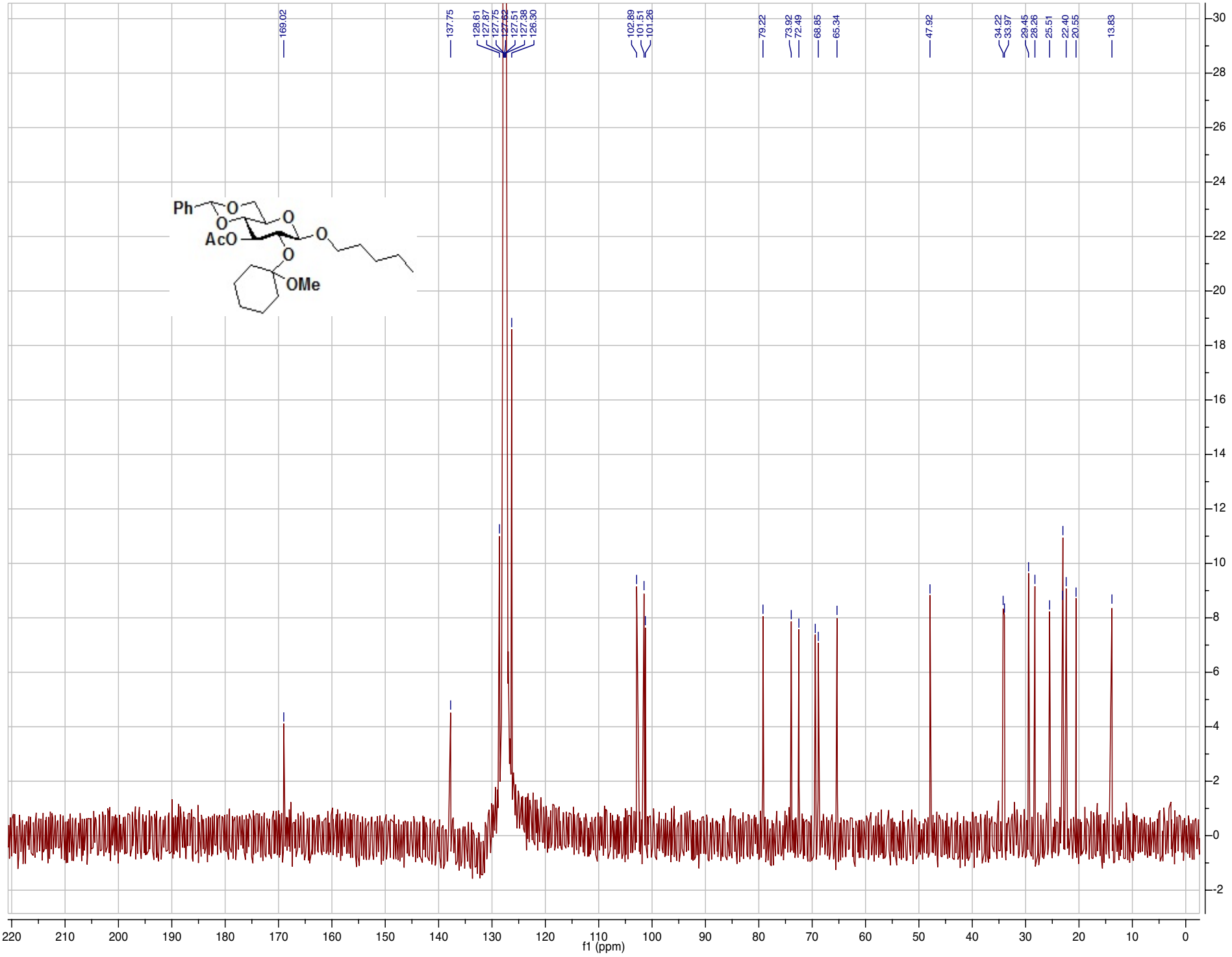
11

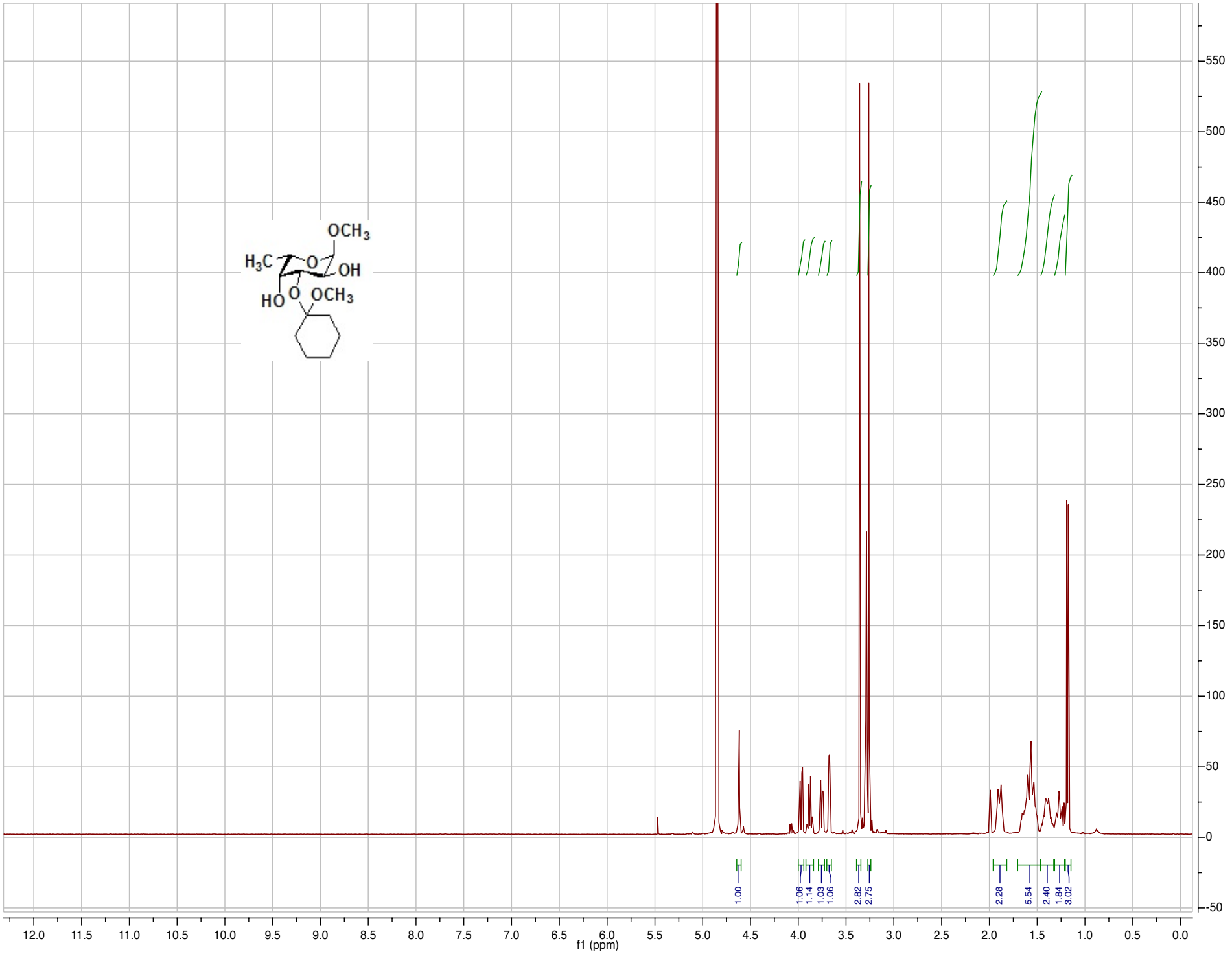
450
400
350
300
250
200
150
100
50
0
0.83
0.86
0.96
1.85
2.81
1.00
1.02
2.93
1.11
3.28
3.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

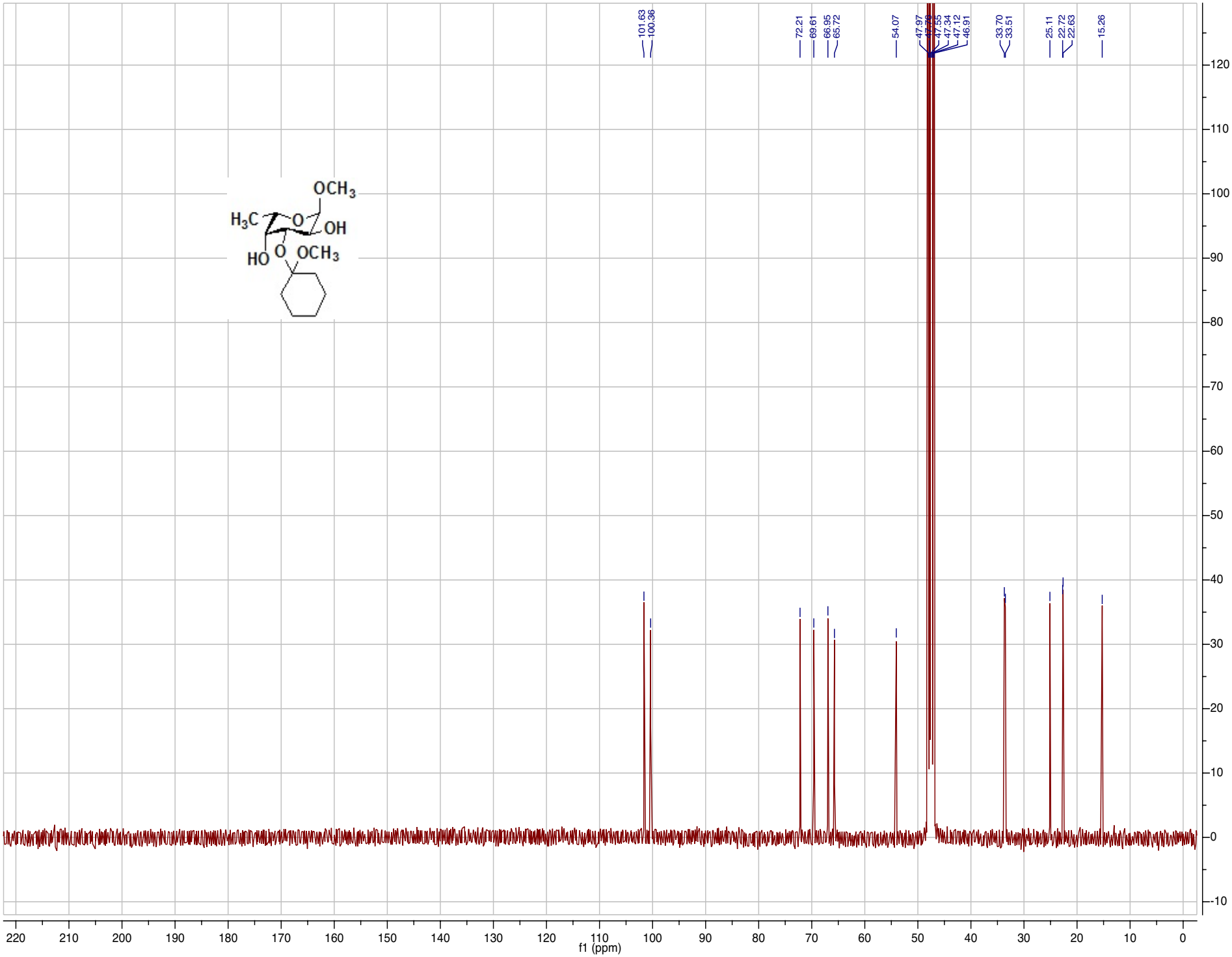

Ph
O
O
O
HO
O
O
OMe
1.78
1.39
0.78
1.00
0.80
0.85
1.03
2.79
0.98
0.97
1.80
2.81
1.06
2.86
2.83
8.85
0.87
2.65
f1 (ppm)

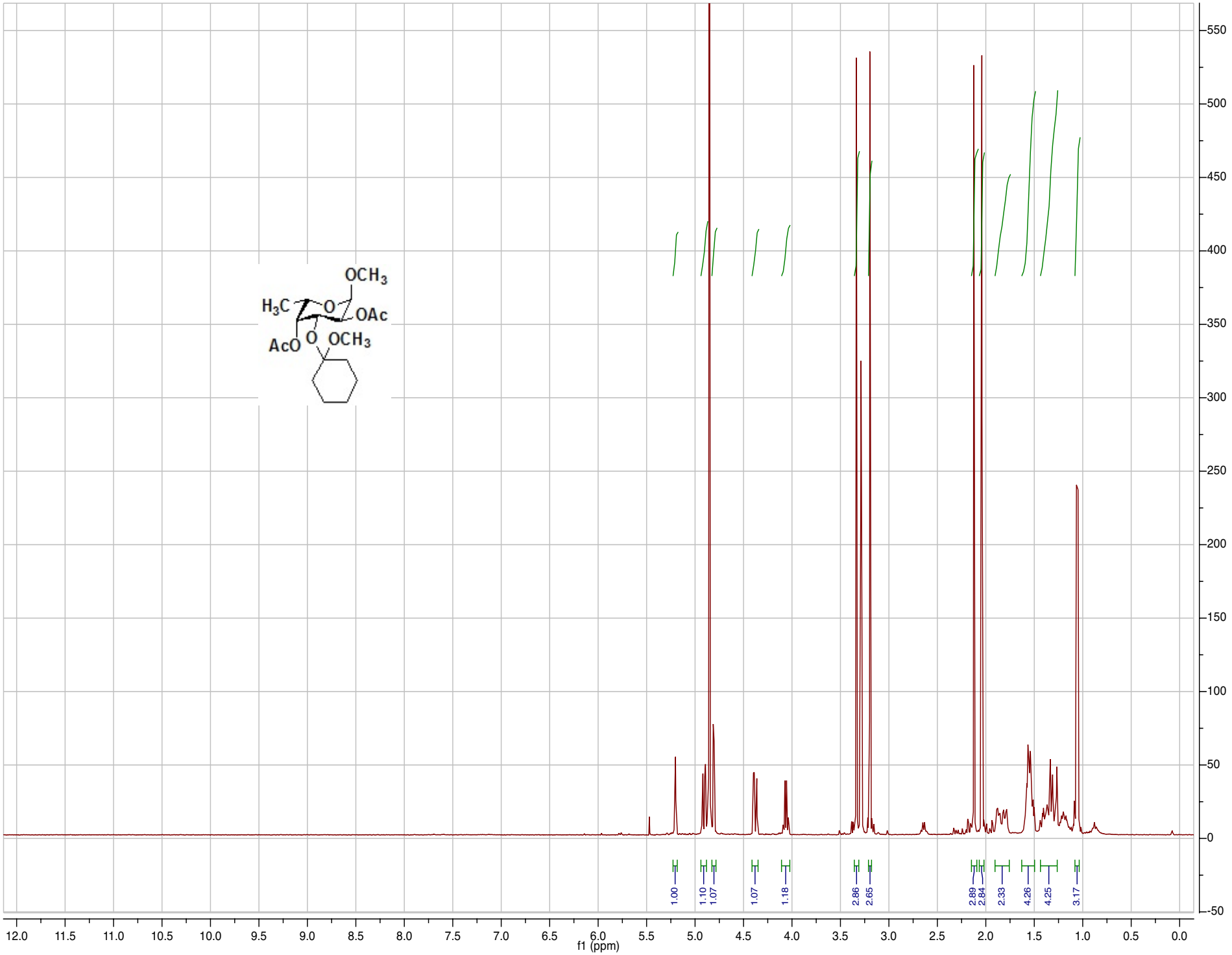

138.16
128.46
127.93
127.84
127.64
127.45
126.51
102.42
101.34
101.28
80.72
76.72
73.64
69.59
68.72
65.99
47.43
33.69
32.93
28.27
25.37
22.70
22.43
21.74
13.87
Ph
O
O
HO
O
O
O
OMe
f1 (ppm)


Ph
O
O
O
AcO
O
O
OMe
f1 (ppm)
1.92
1.88
1.01
1.09
1.01
1.11
1.00
1.00
1.03
1.18
1.08
1.04
2.77
2.11
2.54
1.35
6.02
2.08
4.56
0.90
2.87

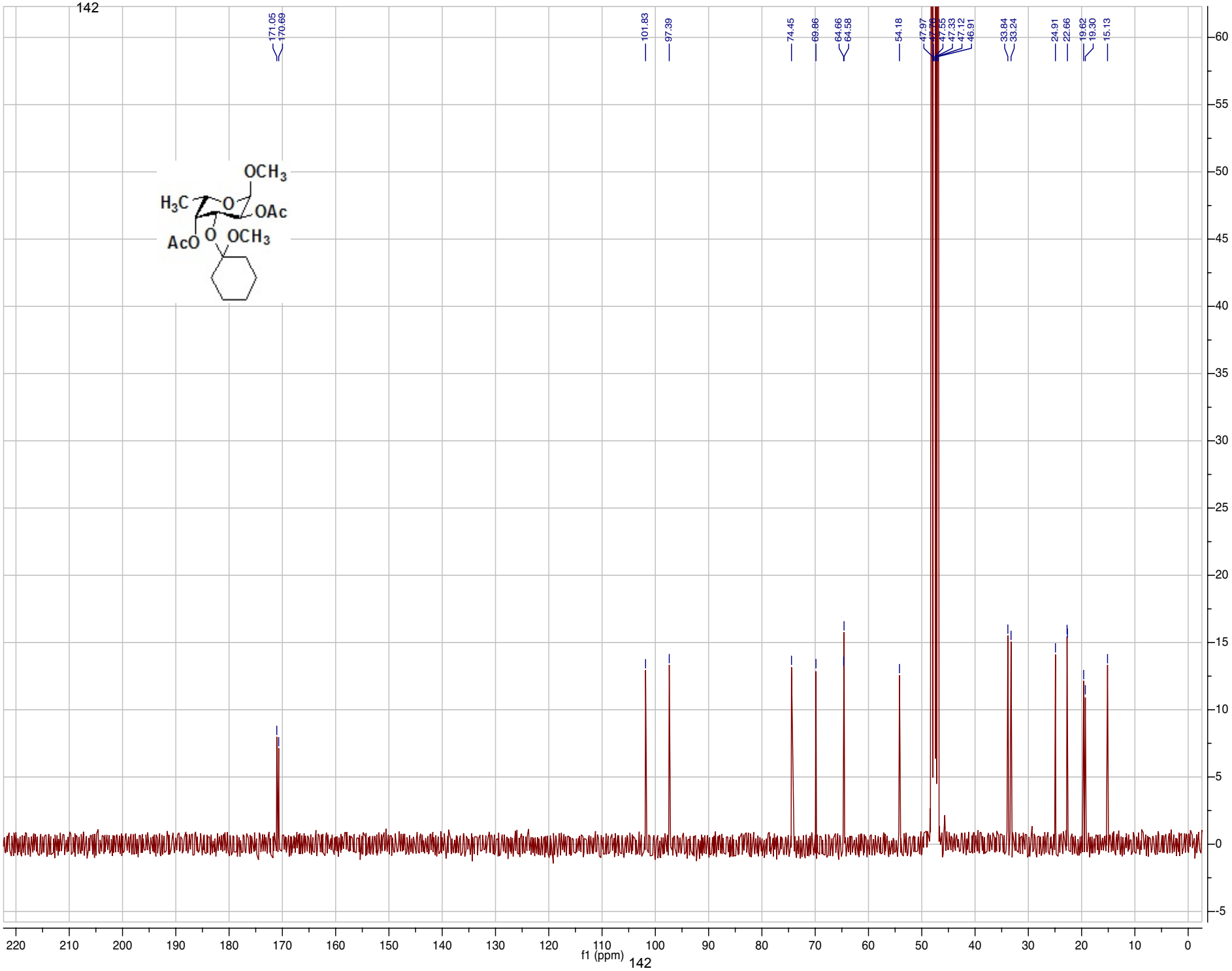

169.02
137.75
128.61
127.87
127.75
127.62
127.51
127.38
126.30
102.89
101.51
101.26
79.22
73.92
72.49
68.85
65.34
47.92
34.22
33.97
29.45
28.26
25.51
22.40
20.55
13.83
Ph
O
O
O
AcO
O
O
OMe
f1 (ppm)


OCH3
H3C
O
OH
HO
O
OCH3
1.00
1.06
1.14
1.03
1.06
2.82
2.75
2.28
5.54
2.40
1.84
3.02
f1 (ppm)


101.63
100.36
72.21
69.61
66.95
65.72
54.07
47.97
47.55
47.34
47.12
46.91
33.70
33.51
25.11
22.72
22.63
15.26
OCH3
H3C
O
OH
HO
O
OCH3
f1 (ppm)


OCH3
H3C
O
OAc
AcO
O
OCH3
1.00
1.10
1.07
1.07
1.18
2.86
2.65
2.89
2.84
2.33
4.26
4.25
3.17
f1 (ppm)

142

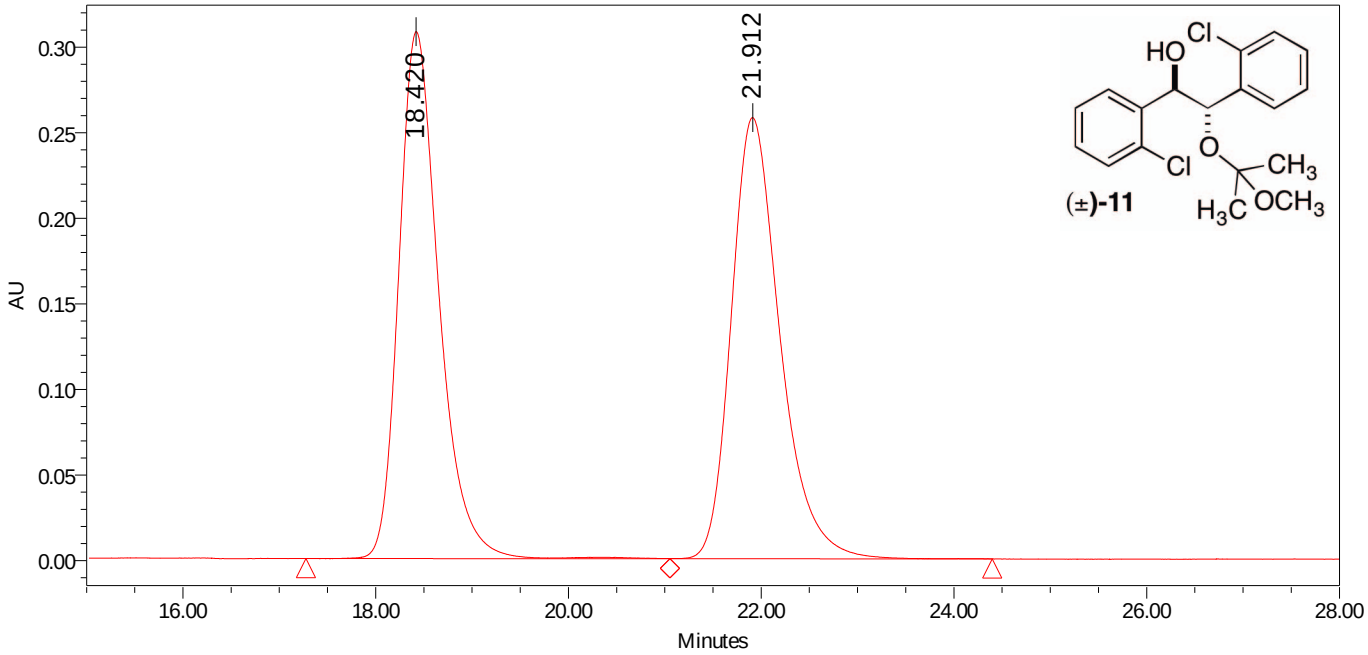

171.05
170.69
101.83
97.39
74.45
69.86
64.66
64.58
54.18
47.97
47.55
47.33
47.12
46.91
33.84
33.24
24.91
22.66
19.62
19.30
15.13
OCH3
H3C
O
OAc
AcO
O
OCH3
f1 (ppm)

142

SAMPLE INFORMATION

Sample Name:	EM-05-284CRUDE_99_1_Col	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	EM05284_99_1_Col 2_40min
Vial:	18	Acq. Method Set:	99_1_Col 2_40min
Injection #:	1	Processing Method	pn_Standard
Injection Volume:	10.00 ul	Channel Name:	210.2nm@5
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	PDA 210.2 nm
Date Acquired:	5/14/2013 8:11:18 PM EDT		
Date Processed:	5/17/2013 11:47:25 AM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height
1		18.420	8884279	307862
2		21.912	9036257	257709

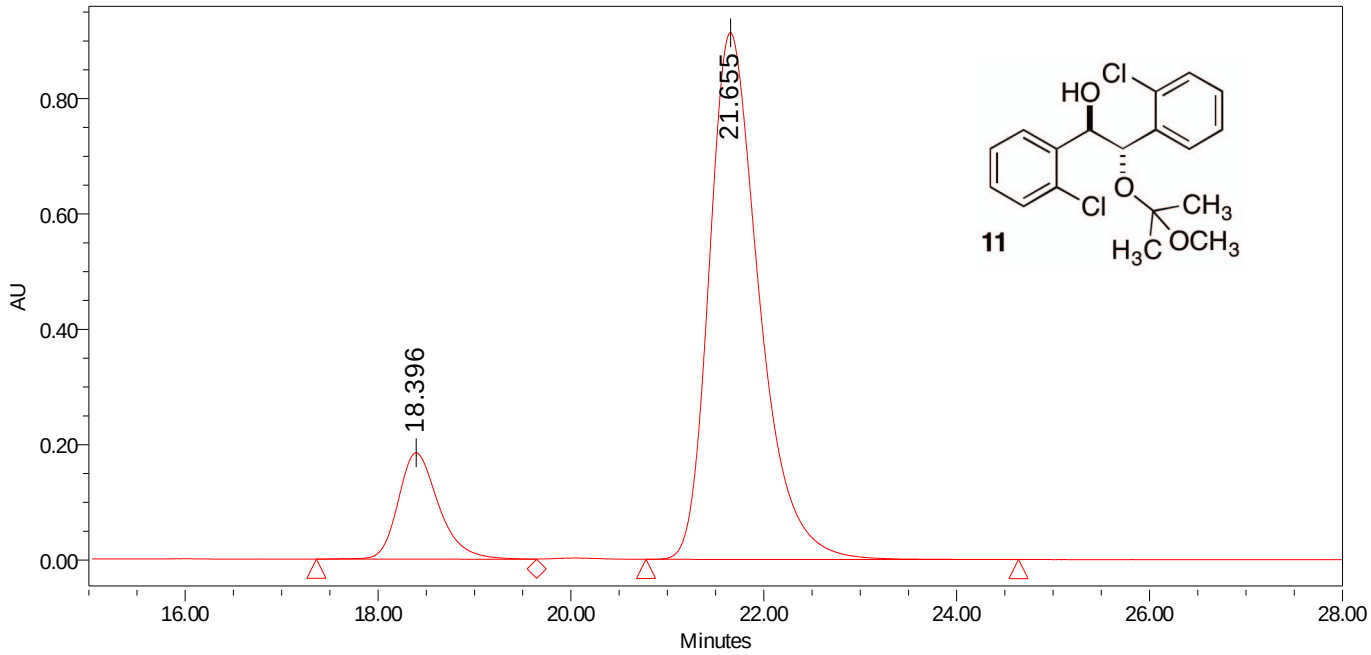
PDA Result Table

	Name	RT	Purity1 Angle	Purity1 Threshold
1		18.420	0.386	
2		21.912	0.402	

SAMPLE INFORMATION

Sample Name:	EM-05-286CRUDE_99_1_Col	Acquired By:	HPLCuser
Sample Type:	Unknown	Sample Set Name	EM05286_99_1_Col 2_40min
Vial:	23	Acq. Method Set:	99_1_Col 2_40min
Injection #:	1	Processing Method	pn_Standard
Injection Volume:	10.00 ul	Channel Name:	210.2nm@5
Run Time:	40.0 Minutes	Proc. Chnl. Descr.:	PDA 210.2 nm
Date Acquired:	5/15/2013 12:59:33 PM EDT		
Date Processed:	5/17/2013 11:42:44 AM EDT		

Auto-Scaled Chromatogram



Peak Results

	Name	RT	Area	Height
1		18.396	5389910	184313
2		21.655	32834196	913054

PDA Result Table

	Name	RT	Purity1 Angle	Purity1 Threshold
1		18.396	0.295	0.292
2		21.655	0.639	0.276