Non-stoichiometric O-acetylation of polysaccharide antigens: convergent synthesis and antibody recognition of acetylated *Shigella flexneri* 2a decasaccharides

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SUPPORTING INFORMATION

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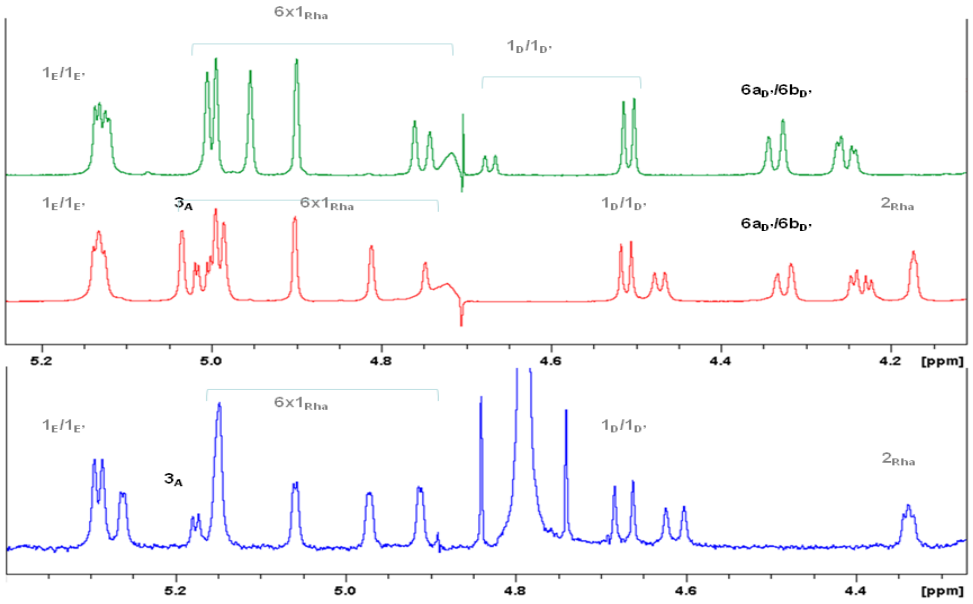
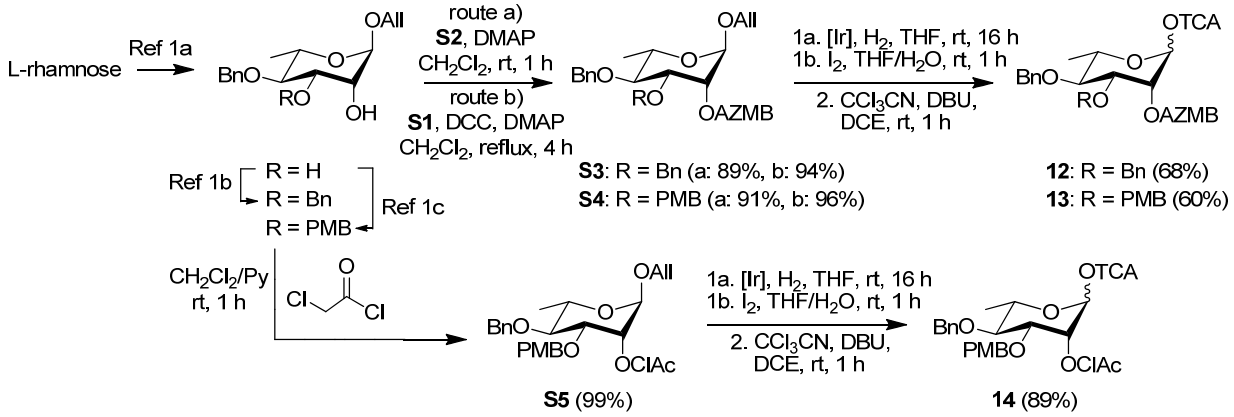
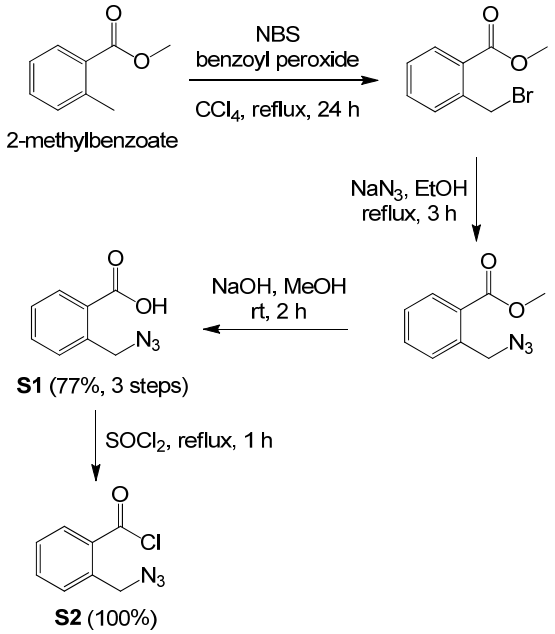


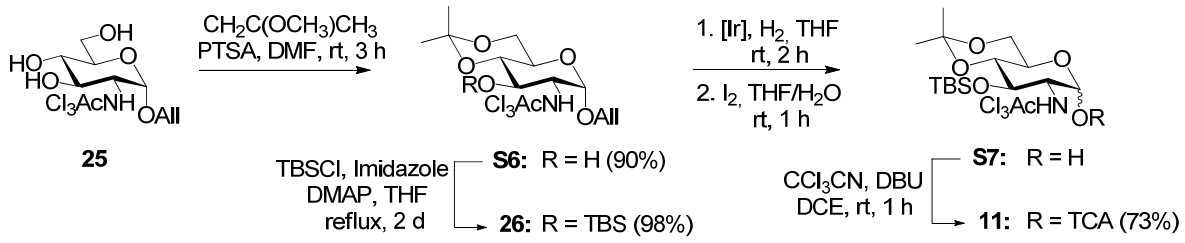
Figure S1. Anomeric region of the ^{1}H NMR spectra (Bruker AVII700 spectrometer equipped with a 5 mm $^{1}H(^{13}C/^{15}N)$ inverse TCI cryoprobe optimized for ^{1}H observation, 700 MHz, D_2O, 303 K, water suppression) of decasaccharides **2** (red) and **3** (green) to that (Bruker Avance spectrometer equipped with a 5 mm BBO probe, 400 MHz, D_2O, 303 K) of decasaccharide **1 (**Blue). The protons geminal to the acetylated hydroxyls are indicated.



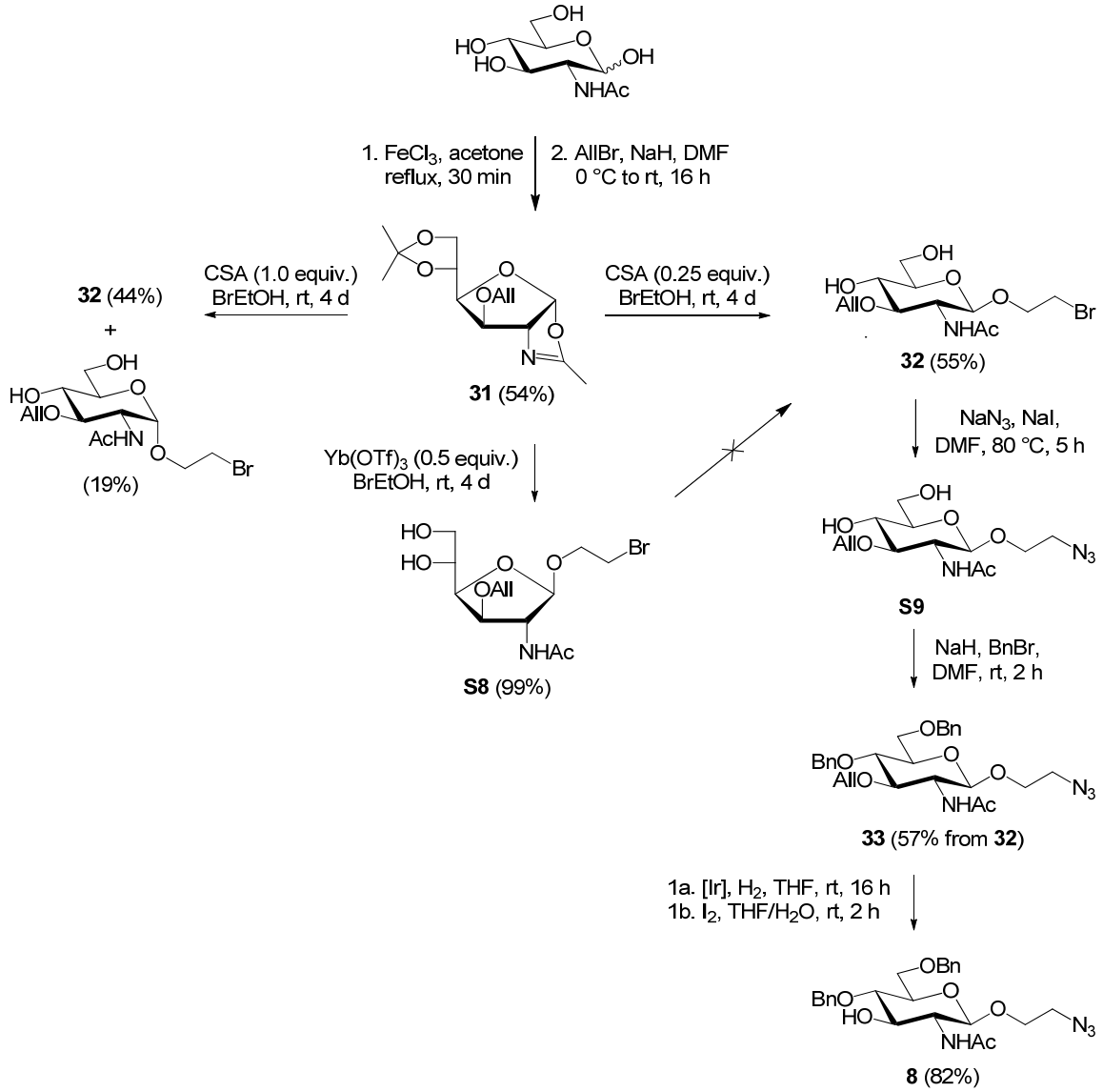
Scheme S1. Synthesis of L-rhamnosyl trichloroacetimidate donors (**12**-**14**).[1-3]
[Ir]: $Ir(COD)\{PCH_3(C_6H_5)_2\}_2^+.PF_6^-$



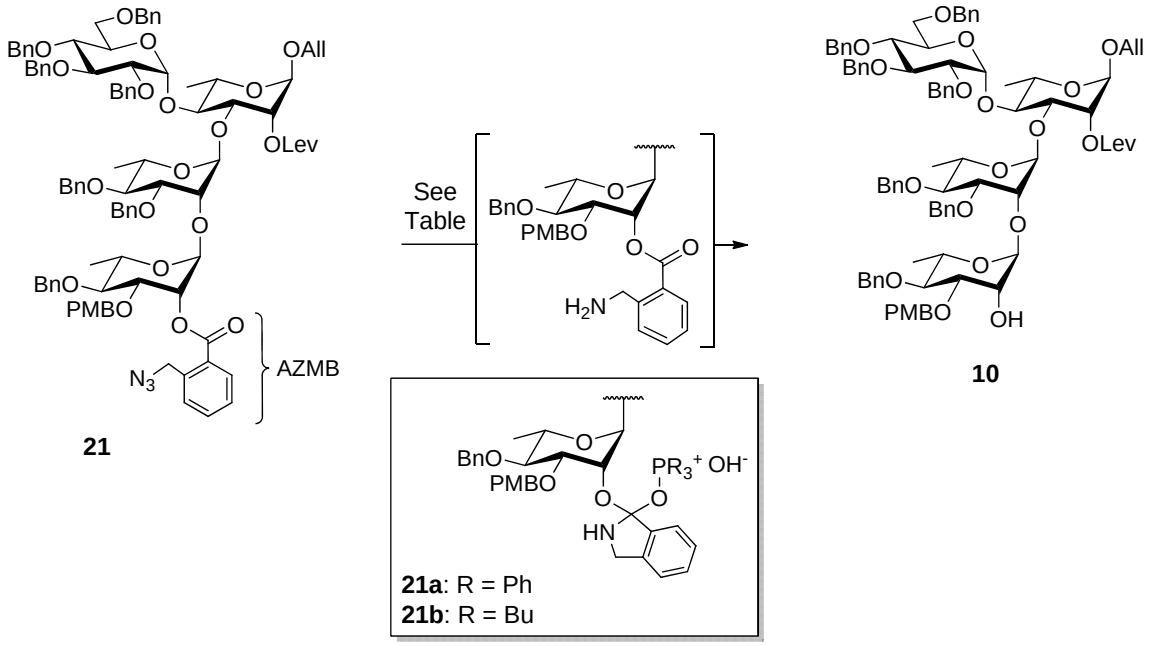
Scheme S2. Synthesis of AZMBOH (**S1**) and AZMBCl (**S2**) reagents inspired from a combination of known protocols.[4, 5]



Scheme S3. Synthesis of the D-glucosaminyl donor **11** showing all isolated intermediates.



Scheme S4. Synthesis of *N*-acetyl-D-glucosamine acceptor **8** *via* acid-catalyzed oxazoline-opening. [Ir]: $Ir(COD)\{PCH_3(C_6H_5)_2\}_2^+.PF_6^-$



Scheme S5. Side products observed during attempted AZMB removal in compound **21** using Staudinger conditions.

Table S1. Attempts to remove the AZMB group on tetrasaccharide **21**.

Entry	Reagents (equiv.)	Solvent	Temp. *Time*	**10** Yield (%)[a]
1[5]	PBu_3 (3.0) H_2O (5.0)	THF	rt 4 h	47% 53%[b]
2[6]	PBu_3 (3.0) then H_2O (5.0)	THF	rt 2 h	trace[c]
3[7]	PPh_3 (10.) SiO_2	THF/H_2O 9:1	rt 2 d	61% 66%[b]
4	PPh_3 (10) SiO_2	THF/H_2O 9:1	reflux 6 h	trace[c]
5[8]	H_2S	Py/H_2O 4:1	reflux 24 h	trace[d]
6	H_2S	Py/H_2O 4:1	140 °C (μW)[e] 4 h	44%[d]
7[9]	$HS(CH_2)_3SH$ (50) Et_3N (10)	CH_2Cl_2/MeOH 1:1	reflux 2 d	degradation
8[7]	$NaBH_4$ (3.0) $NiCl_2.6H_2O$ (0.1)	CH_2Cl_2/EtOH 1:1	rt 1 h	27%

[a] Isolated yield. [b] Based on recovery starting material. [c] The phosphonium derivative (**21a** or **21b**) was the major product. These polar side-products were unambiguously identified from ^1H, ^{13}C and ^{31}P NMR analysis as well as by HR-ESI-TOF-MS (**21a**: δ (^{31}P NMR, $CDCl_3$) 40.1 ppm (s, $OPPh_3$), *m/z* 1900.8340 $[M]^+$, calcd for $C_{115}H_{123}NO_{22}P$, 1900.8274; **21b**: *m/z* 1840.9080 $[M]^+$, calcd for $C_{109}H_{135}NO_{22}P$, 1840.9208). [d] H_2S was bubbled for 1 h through the solution before heating. [e] μW: microwave.

Materials and Methods

Antigenicity analysis

Panel of protective anti-SF2a mIgGs: The protective mIgGs specific for the SF2a O-Ag used in this study – A2-1, D15-7, C1-7, E4-1, F22-4 – were described previously.[10]

Panel of synthetic decasaccharides: Decasaccharide **4** was described previously.[11] For each one of the four decasaccharides (**1**-**4**), the concentration of the mother solution was measured by a method adapted from amino acid analysis. The method allows hexosamine quantification[12] and was found appropriate to overcome the inherent difficulties associated in accurately measuring small amounts of low molecular weight antigens.[13] Briefly, the amino sugar compositions of the decasaccharide mother solutions ready for antigenicity analysis were determined with a L-8800 Hitachi automatic amino acid analyzer (classical post column derivatization with ninhydrin after ion-exchange chromatography separation), after hydrolysis in 1% phenol 6N HCl in glass tubes at 95 °C for 16 h, and evaporation of the volatiles.

Inhibition ELISA for IC_{50} measurement: The binding of the available mIgGs to decasaccharides **1**-**4** was measured according to a known protocol.[14] The mIgG concentration to be used was defined in the first step. To do so, a standard curve was established for each mAb. The mIgGs were incubated at different concentrations, overnight at 4 °C, on microtiter plates coated with purified SF2a LPS at a concentration of 2.5 µg/mL in a carbonate buffer (pH 9.6), then with PBS-BSA 1% for 30 min at 4°C. After washing with PBS-Tween 20 (0.05%), alkaline phosphatase-conjugated anti-mouse IgG was added at a dilution of 1/5,000 (Sigma-Aldrich) for 1 h at 37 °C. After washing with PBS-Tween 20 (0.05%), the substrate was added (12 mg of *p*-nitrophenylphosphate in 1.2 mL of 1 M Tris-HCl buffer (pH 8.8) and 10.8 mL of 5 M NaCl). Once the color developed, the plate was read at 405 nm Dynatech MR400 microplate reader). A standard curve OD = f([Ab]) was fitted to the quadratic equation $Y= aX^2 + bX + c$, where Y is the OD and X is the Ab concentration. A correlation factor (r^2) of 0.99 was routinely obtained.

The IC_{50}, defined as the concentration of oligosaccharides required to inhibit 50% of mIgG binding to LPS, were measured in a second step. Each mIgG at a given concentration (chosen as the minimal concentration of mAb which gives the maximal OD on the standard curve mentioned above) was incubated overnight at 4 °C with each of decasaccharides **1**-**4** at various concentrations in PBS-BSA 1%. The maximum concentration tested was 0.5 mM for all decasaccharides. Measurement of unbound mIgG was performed as described above using microtiter plates coated with purified SF2a LPS. The mAb concentration was deduced from the standard curve.

NMR analysis (Fig. 2)

The ^{1}H NMR spectra of decasaccharide **4** and pentadecasaccharide [AB(E)CD]$_3$ shown in Fig. 2 were run on a Varian Unity Inova 600 MHz spectrometer equipped with a cryogenically-cooled triple resonance ^{1}H{^{13}C/^{15}N} PFG probe (D_2O, 308 K).

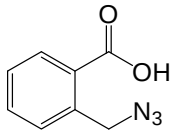
Synthesis: General methods.

Chemical reagents were used as received. Air and water sensitive reactions were performed in dried glassware under Ar atmosphere. Moisture sensitive reagents were introduced via a dry syringe. Anhydr. toluene (Tol), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), 1,2-dichloroethane (DCE), tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), acetonitrile (CH_3CN), ethanol (EtOH), methanol (MeOH) and pyridine (Py) were supplied on MS and were used as received. Additional solvents commonly cited in the text are abbreviated as Chex (cyclohexane), DMSO (dimethyl sulfoxide) and CCl_4 (carbon tetrachloride). Powered 4Å MS (MS) and powered 4Å acid-washed molecular sieves (AW-MS) were activated before use by heating at ≥250 °C under vacuum. Analytical thin-layer chromatography was performed with silica gel 60 F_{254}, 0.25 mm pre-coated TLC plates. Compounds were visualized using UV_{254} and/or orcinol (1 mg·mL^{-1}) in 10% aq. H_2SO_4 with charring. Flash column chromatography was carried out using silica gel (particle size 0.040–0.063 mm). Nuclear magnetic resonance (NMR) spectra of all intermediates were recorded at 303 K on a Bruker Avance spectrometer equipped with a BBO probe at 400 MHz (^{1}H) and 100 MHz (^{13}C). NMR spectra of decasaccharides **2**-**3** were recorded at 303 K on a Bruker AVII700 equipped with a 5 mm ^{1}H(^{13}C/^{15}N) inverse TCI cryoprobe optimised for ^{1}H observation and with a cold ^{13}C channel at 700 MHz (^{1}H) and 175 MHz (^{13}C). Elucidations of chemical structures were based on ^{1}H, COSY, DEPT-135, HSQC, ^{13}C, ^{13}C gated decoupling and HMBC experiments. Signals are reported as m (multiplet), s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dq (doublet of quadruplet), ddd (doublet of doublet of doublet), ddt (doublet of doublet of triplet), br s (broad singlet), br d (broad doublet) and coupling constants are reported in hertz (Hz). The chemical shifts are reported in ppm (δ) relative to residual solvent peak. Of the two magnetically non-equivalent geminal protons at C-6, the one resonating at lower field is denoted H-6a, and the one at higher field is denoted H-6b. Interchangeable assignments are marked with an asterisk in the listing of signal assignments. Sugar residues are serially lettered according to the lettering of the repeating unit of the *S. flexneri* 2a O-Ag and identified by a subscript in the listing of signal assignments. The values of the $^{1}J_{C,H}$ constants of the anomeric carbons/protons were measured from the HSQC for $^{1}J_{C,H}$ spectrum of decasaccharide **2**, only. This ascertained that target **2** had the required structure. Since all novel decasaccharides described in the manuscript are issued from decasaccharide **5**, this result ensured that all residues pertaining to all synthesized new oligosaccharides have the correct anomery. High resolution electrospray ionisation/time-of-flight mass spectra (HR-ESI-TOF-MS) were recorded in the positive-ion mode with 1:1 CH_3CN/H_2O containing 0.1% formic acid as the ESI-TOF spectrometer solution. High resolution matrix-assisted laser desorption-ionisation/time-of-flight mass spectra (HR-MALDI-TOF-MS) were recorded in the positive-ion mode. The former were measured at the UMR CNRS 3523, Institut Pasteur, Paris, France and the

later were obtained at the Institut de Chimie des Substances Naturelles, Gif sur Yvettes, France. Optical rotations were obtained using sodium D line at rt (22 °C) on a Bellingham + Stanley Ltd. ADP220 polarimeter. $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.

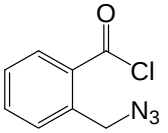
Synthesis: Experimental procedures

2-(Azidomethyl)benzoic acid[4] (S1).



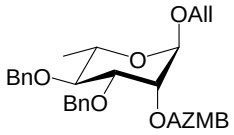
NBS (102 g, 572 mmol, 1.01 equiv.) and benzoyl peroxide (1.37 g, 6.66 mmol, 0.01 equiv) were added to methyl 2-methylbenzoate (85.0 g, 566 mmol) in anhydr. CCl_4 (1.0 L). CAUTION! This reaction is very exothermic, care must be taken in order to minimize the risks of runaway reaction. The mixture was stirred for 24 h at reflux under Ar. After cooling to 0 ºC, the precipitate was removed by filtration. The organic phase was evaporated to dryness. NaN_3 (37.2 g, 572 mmol, 1.01 equiv.) was added to the residue in anhydr. EtOH (1.6 L) and the mixture was stirred for 3 h at reflux under Ar. Brine (250 mL) was added and the mixture was concentrated (to 1/3 volume) under reduced pressure. The aq. phase was extracted with CH_2Cl_2 (3×500 mL), the organic layer was dried over anhydr. Na_2SO_4, filtered, and concentrated to dryness. NaOH (51.0 g) was added to the residue in MeOH/H_2O (1.2 L, 5:2 *v/v*) and. The mixture was stirred for 2 h at rt, and concentrated (to 1/3 volume) under reduced pressure. The aq. phase was extracted with CH_2Cl_2 (3×500 mL) and acidified with 6 N aq. HCl. The precipitated acid was then extracted with CH_2Cl_2 (3×250 mL), the organic phases were pooled and concentrated to dryness to give a yellow solid residue. The crude material was recrystallized from Chex to give **S1** (77.3 g, 77%, 3 steps) as a white powder. Physical and analytical data were in agreement with those published.[4]

2-(Azidomethyl)benzoyl chloride[5] (S2).



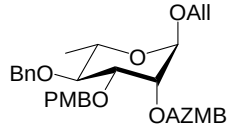
Compound **S1** (7.00 g, 41.2 mmol) was dissolved in $SOCl_2$ (6.0 mL, 82 mmol, 2.0 equiv.) and the mixture was stirred at reflux for 1 h under Ar. Volatiles were evaporated under reduced pressure and co-evaporated with toluene to dryness to give crude acyl chloride **S2** as a yellow oil, which was used for the next step without purification. Physical and analytical data were in agreement with those published.[5]

Allyl 2-*O*-(2-(azidomethyl)benzoyl)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (S3).



Route a. DMAP (3.18 g, 26.0 mmol, 2.0 equiv.) and acyl chloride **S2** (3.02 g, 26.0 mmol, 2.0 equiv.) were added to allyl 3,4-di-*O*-benzyl-α-L-rhamnopyranoside[2] (5.00 g, 13.0 mmol) in anhydr. CH_2Cl_2 (130 mL). The mixture was stirred for 1 h at rt under Ar. The organic phase was washed with satd aq. $NaHCO_3$ (2×50 mL) and brine (1×50 mL). The solution was dried over anhydr. Na_2SO_4, filtered and solvents were evaporated. The residue was purified by FC (Chex/EtOAc 95:5 to 9:1) to give allyl glycoside **S3** (6.78 g, 94%) as a colorless oil.
Route b. DMAP (10.9 g, 88.8 mmol, 1.0 equiv), DCC (36.7 g, 178 mmol, 2.0 equiv.) and benzoic acid **S1** (23.6 g, 133 mmol, 1.5 quiv) were added to allyl 3,4-di-*O*-benzyl-α-L-rhamnopyranoside[2] (34.2 g, 88.9 mmol) in anhydr. CH_2Cl_2 (910 mL). The mixture was stirred for 4 h at reflux under Ar, and cooled to rt. The mixture was filtered over a pad of Celite®, and the solvents were removed under reduced pressure. The residue was purified by FC (Chex/EtOAc 95:5 to 7:3) to give allyl glycoside **S3** (43.1 g, 89%) as a light yellow oil. R_f 0.84 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ +16° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.14-8.11 (m, 1H, C*H*$_{Ph}$), 7.64-7.29 (m, 13H, C*H*$_{Ph}$), 5.98 (m, 1H, H-2$_{All}$), 5.71 (dd, $J_{2,3}$ = 3.2 Hz, $J_{1,2}$ = 1.8 Hz, 1H, H-2) 5.38 (ddd, J = 17.2, 3.1, 1.5 Hz, 1H, H-3a$_{All}$), 5.29 (ddd, J = 10.4, 2.5, 1.3 Hz, 1H, H-3b$_{All}$), 5.02 (d, J = 10.9 Hz, 1H, C*H*$_2$Ph), 5.02 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1), 4.89-4.82 (m, 3H, C*H*$_2$Ph, C*H*$_2$N$_3$), 4.74 (d, J = 10.9 Hz, 1H, C*H*$_2$Ph), 4.69 (d, J = 11.3 Hz, 1H, C*H*$_2$Ph), 4.26 (ddt, J = 12.9, 5.3, 1.4 Hz, 1H, H-1a$_{All}$), 4.18 (dd, $J_{3,4}$ = 9.4 Hz, $J_{2,3}$ = 3.3 Hz, 1H, H-3), 4.09 (ddt, J = 12.9, 6.0, 1.3 Hz, 1H, H-1b$_{All}$), 3.94 (dq, 1H, H-5), 3.64 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, 1H, H-4), 1.45 (d, $J_{5,6}$ = 6.1 Hz, 3H, H-6). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.0 (*C*=O), 138.5 (C$_{Ph}$), 138.1 (C$_{Ph}$), 137.3 (C$_{Ph}$) 133.6 (C-2$_{All}$), 132.8-127.7 (*C*H$_{Ph}$), 117.7 (C-3$_{All}$), 96.8 (C-1), 80.2 (C-4), 78.2 (C-3), 75.5 (*C*H$_2$Ph), 71.8 (*C*H$_2$Ph), 70.0 (C-2), 68.2 (C-1$_{All}$), 67.9 (C-5), 53.0 (*C*H$_2$N$_3$), 18.2 (C-6). HR-ESI-TOF-MS *m/z* 566.2254 $[M + Na]^+$ (calcd for $C_{31}H_{33}N_3O_6Na$, 566.2267).

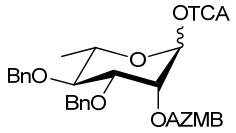
Allyl 2-*O*-(2-(azidomethyl)benzoyl)-4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranoside (S4).



Route a. DMAP (2.95 g, 24.1 mmol, 2.0 equiv.) and acyl chloride **S2** (2.80 g, 24.1 mmol, 2.0 equiv) were added to allyl 4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranoside[3] (5.00 g, 12.1 mmol) in anhydr. CH_2Cl_2 (121 mL). The mixture was stirred for 1 h at rt under Ar. The organic phase was washed with satd aq. $NaHCO_3$ (2×50 mL) and brine (1×50 mL). The solution was dried over anhydr. Na_2SO_4, filtered, and solvents were evaporated. The residue was purified by FC (Chex/EtOAc 95:5 to 8:2) to give allyl glycoside **S4** (6.26 g, 91%) as a colorless oil.

Route b. DMAP (4.13 g, 33.8 mmol, 1.0 equiv), DCC (13.9 g, 67.6 mmol, 2.0 equiv.) and the benzoic acid **S1** (8.98 g, 50.7 mmol, 1.5 equiv) were added to allyl 4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranoside[15] (14.0 g, 33.8 mmol) in anhydr. CH_2Cl_2 (338 mL). The mixture was stirred for 4 h at reflux under Ar, and cooled to rt. The mixture was filtered over a pad of Celite®, washed with several portions of CH_2Cl_2, and solvents were evaporated. The residue was purified by FC (Chex/EtOAc 95:5 to 7:3) to give allyl glycoside **S4** (18.6 g, 96%) as a light yellow oil. R_f 0.79 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ +32° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.05-8.02 (m, 1H, C*H*$_{Ph}$), 7.60-7.56 (m, 1H, C*H*$_{Ph}$), 7.53-7.50 (m, 1H, C*H*$_{Ph}$), 7.45-7.40 (m, 1H, C*H*$_{Ph}$), 7.36-7.22 (m, 7H, C*H*$_{Ph}$), 6.83-6.78 (m, 2H, C*H*$_{Ph}$), 5.91 (m, 1H, H-2$_{All}$), 5.60 (dd, 1H, H-2), 5.30 (ddd, *J* = 17.2, 3.2, 1.6 Hz, 1H, H-3a$_{All}$), 5.22 (ddd, *J* = 10.4, 2.8, 1.3 Hz, 1H, H-3b$_{All}$), 4.92 (d, *J* = 10.9 Hz, 1H, C*H*$_2$Ph), 4.92 (d, $J_{1,2}$ = 1.7 Hz, 1H, H-1), 4.78 (br s, 2H, C*H*$_2$N$_3$), 4.71 (d, *J* = 10.9 Hz, 1H, C*H*$_2$Ph), 4.64 (d, *J* = 11.0 Hz, 1H, C*H*$_2$Ph), 4.54 (d, 1H, C*H*$_2$Ph), 4.19 (ddt, *J* = 12.8, 5.1, 1.5 Hz, 1H, H-1a$_{All}$), 4.07 (dd, $J_{3,4}$ = 9.3 Hz, $J_{2,3}$ = 3.4 Hz, 1H, H-3), 4.01 (ddt, *J* = 12.8, 6.1, 1.3 Hz, 1H, H-1b$_{All}$), 3.84 (dq, 1H, H-5), 3.77 (s, 3H, OC*H*$_3$), 3.52 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, 1H, H-4), 1.35 (d, $J_{5,6}$ = 6.3 Hz, 3H, H-6). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.1 (*C*=O), 159.4 (C$_{Ph}$), 138.6 (C$_{Ph}$), 137.4 (C$_{Ph}$), 133.7 (C-2$_{All}$), 132.9-127.8 (*C*H$_{Ph}$), 117.8 (C-3$_{All}$), 113.9 (*C*H$_{Ph}$), 96.9 (C-1), 80.3 (C-4), 78.0 (C-3), 75.5 (*C*H$_2$Ph), 71.6 (*C*H$_2$Ph), 70.1 (C-2), 68.3 (C-1$_{All}$), 67.9 (C-5), 55.4 (O*C*H$_3$), 53.1 (*C*H$_2$N$_3$), 18.2 (C-6). HR-ESI-TOF-MS *m/z* 596.2415 $[M + Na]^+$ (calcd for $C_{32}H_{35}N_3O_7Na$, 596.2372).

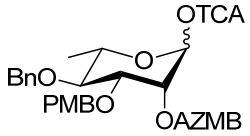
2-*O*-(2-(Azidomethyl)benzoyl)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl trichloroacetimidate (12).



[Ir] (467 mg, 0.55 mmol, 0.05 equiv.) was dissolved in anhydr. THF (81 mL) and the resulting red solution was degassed under Ar. Hydrogen was bubbled through the solution for 5 min, and the resulting yellow solution was degassed under Ar. Allyl glycoside **S3** (6.00 g, 11.0 mmol) in anhydr. THF (110 mL) was added, and the mixture was stirred for 2 h at rt under Ar. Iodine (5.60 g, 22.1 mmol, 2.0 equiv.) in THF/H_2O (72 mL, 4:1 *v/v*) was added to the mixture, which was stirred for 1 h at rt. Freshly prepared 10% aq. sodium bisulfite (75 mL) was added. The mixture was concentrated (to 1/3 volume) under reduced pressure and the aq. phase was extracted with CH_2Cl_2 (3×150 mL). The organic layer was washed with H_2O (2×100 mL), brine (100 mL), dried over anhydr. Na_2SO_4, filtered and evaporated. CCl_3CN (5.5 mL, 55 mmol, 5.0 equiv.) and DBU (0.46 mL, 3.1 mmol, 0.28 equiv.) were added to the residue in anhydr. DCE (99 mL). The mixture was stirred for 1 h at rt under Ar, and solvents were evaporated. The residue was purified by FC (Chex/EtOAc 95:5 to 8:2 + 0.5% Et_3N) to give trichloroacetimidate **12** (4.84 g, 68%) as a yellow oil. R_f 0.81 (Chex/EtOAc 7:3); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.70 (s, 1H, N*H*), 8.09-8.06 (m, 1H, C*H*$_{Ph}$), 7.64-7.59 (m, 1H, C*H*$_{Ph}$), 7.56-7.53 (m, 1H, C*H*$_{Ph}$), 7.49-7.44 (m, 1H, C*H*$_{Ph}$),

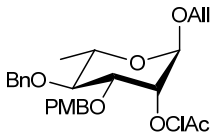
7.37-7.25 (m, 10H, CH_{Ph}), 6.33 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1), 5.71 (dd, 1H, H-2), 4.95 (d, J = 10.9 Hz, 1H, CH_2Ph), 4.80 (d, J = 11.4 Hz, 1H, CH_2Ph), 4.78 (br s, 2H, CH_2N_3), 4.68 (d, 1H, CH_2Ph), 4.66 (d, 1H, CH_2Ph), 4.12 (dd, $J_{3,4}$ = 9.4 Hz, $J_{2,3}$ = 3.2 Hz, 1H, H-3), 4.02 (m, 1H, H-5), 3.64 (pt, $J_{4,5}$ = 9.6 Hz, 1H, H-4), 1.38 (d, $J_{5,6}$ = 5.7 Hz, 3H, H-6). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 165.7 (*C*=O), 160.3 (*C*=NH), 138.2 (C_{Ph}), 137.7 (2×C_{Ph}), 133.3-128.1 (*C*H$_{Ph}$), 95.3 (C-1), 91.0 (*C*Cl_3), 79.6 (C-4), 77.4 (C-3), 75.8 (*C*H_2Ph), 72.2 (*C*H_2Ph), 70.9 (C-5), 68.7 (C-2), 53.1 (*C*H_2N_3), 18.3 (C-6).

2-*O*-(2-(Azidomethyl)benzoyl)-4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranosyl trichloroacetimidate (13).



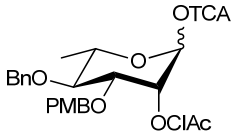
[Ir] (663 mg, 0.784 mmol, 0.03 equiv.) was dissolved in anhydr. THF (131 mL) and the resulting red solution was degassed under Ar. Hydrogen was bubbled through the solution for 5 min, and the resulting yellow solution was degassed under Ar. Allyl glycoside **S4** (15.0 g, 26.2 mmol) in anhydr. THF (131 mL) was added and the mixture was stirred for 2 h at rt under Ar. Iodine (13.3 g, 52.3 mmol, 2.0 equiv.) in THF/H_2O (157 mL, 4:1 *v/v*) was added to the mixture, which was stirred for 3 h at rt. Freshly prepared 10% aq. sodium bisulfite (100 mL) was added. The mixture was concentrated (to 1/3 volume) under reduced pressure and the aq. phase was extracted with CH_2Cl_2 (3×250 mL). The organic layer was washed with H_2O (100 mL), brine (250 mL), dried over anhydr. Na_2SO_4, filtered and evaporated. CCl_3CN (13.1 mL, 131 mmol, 5.0 equiv.) and DBU (1.1 mL, 7.3 mmol, 0.28 equiv.) were added to the residue in anhydr. DCE (114 mL). The mixture was stirred for 1 h at rt under Ar, and the solvents were evaporated. The crude material was purified by FC (CH_2Cl_2 + 0.5% Et_3N) to give **13** (10.7 g, 60%) as a yellow oil. R_f 0.76 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ –3° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.71 (s, 1H, N*H*), 8.09-8.06 (m, 1H, CH_{Ph}), 7.65-7.61 (m, 1H, CH_{Ph}), 7.58-7.55 (m, 1H, CH_{Ph}), 7.50-7.45 (m, 1H, CH_{Ph}), 7.39-7.25 (m, 7H, CH_{Ph}), 6.85-6.81 (m, 2H, CH_{Ph}), 6.33 (d, $J_{1,2}$ = 1.9 Hz, 1H, H-1), 5.70 (dd, 1H, H-2), 4.95 (d, J = 10.8 Hz, 1H, CH_2Ph), 4.81 (br s, 2H, CH_2N_3), 4.74 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.68 (d, 1H, CH_2Ph), 4.61 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.11 (dd, $J_{3,4}$ = 9.5 Hz, $J_{2,3}$ = 3.3 Hz, 1H, H-3), 4.01 (dq, 1H, H-5), 3.80 (s, 3H, OCH_3), 3.63 (t, $J_{4,5}$ = 9.6 Hz, 1H, H-4), 1.39 (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 165.7 (*C*=O), 160.3 (*C*=NH), 159.6 (C_{Ph}), 138.3 (C_{Ph}), 137.7 (C_{Ph}), 133.2-128.0 (*C*H$_{Ph}$), 114.0 (C_{Ph}), 95.3 (C-1), 91.0 (*C*Cl_3), 79.5 (C-4), 77.0 (C-3), 75.8 (*C*H_2Ph), 71.8 (*C*H_2Ph), 70.9 (C-5), 68.7 (C-2), 55.4 (O*C*H_3), 53.2 (*C*H_2N_3), 18.3 (C-6).

Allyl 4-*O*-benzyl-2-*O*-chloroacetyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranoside (S5).



Chloroacetyl chloride (192 µL, 2.41 mmol, 4.0 equiv.) was carefully added to allyl 4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranoside[15] (250 mg, 0.603 mmol) in cold (0 °C) anhydr. CH_2Cl_2/Py (5.4 mL, 8:1 *v*/*v*). The mixture was stirred for 3 h at rt under Ar, then diluted with CH_2Cl_2 (100 mL). The organic phase was washed with 10% aq HCl (50 mL), satd $NaHCO_3$ (50 mL) and brine (50 mL), then dried over anhydr. Na_2SO_4. Volatiles were evaporated and the residue was purified on a short pad of silica gel (CH_2Cl_2, then Chex/EtOAc 7:3) to give the fully protected **S5** (296 mg, 100%) as a yellow oil. R_f 0.75 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ –22° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.37-7.23 (m, 7H, C*H*$_{Ph}$), 6.87-6.83 (m, 2H, C*H*$_{Ph}$), 5.88 (m, 1H, H-2$_{All}$), 5.44 (dd, $J_{2,3}$ = 3.3 Hz, 1H, H-2), 5.28 (ddd, *J* = 17.2, 3.2, 1.5 Hz, 1H, H-3a$_{All}$), 5.21 (ddd, *J* = 10.3, 2.6, 1.3 Hz, 1H, H-3a$_{All}$), 4.89 (d, *J* = 10.8 Hz, 1H, C*H*$_2$Ph), 4.80 (d, $J_{1,2}$ = 1.7 Hz, 1H, H-1), 4.64 (d, *J* = 10.8 Hz, 1H, C*H*$_2$Ph), 4.60 (d, 1H, C*H*$_2$Ph), 4.47 (d, 1H, C*H*$_2$Ph), 4.16 (ddt, *J* = 12.7, 5.3, 1.5 Hz, 1H, H-1a$_{All}$), 4.16 (s, 2H, C*H*$_2$Cl), 4.01-3.95 (m, 2H, H-1b$_{All}$, H-3), 3.82-3.75 (dq, 1H, H-5), 3.80 (s, 3H, OC*H*$_3$), 3.39 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1H, H-4), 1.32 (d, $J_{5,6}$ = 6.1 Hz, 3H, H-6). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.0 (*C*=O), 159.5 (C$_{Ph}$), 138.5 (C$_{Ph}$), 133.5 (C-2$_{All}$), 129.9-127.8 (*C*H$_{Ph}$), 117.9 (C-3$_{All}$), 114.0 (*C*H$_{Ph}$), 96.5 (C-1), 80.0 (C-4), 77.8 (C-3), 75.5 (*C*H$_2$Ph), 71.8 (*C*H$_2$Ph), 71.1 (C-2), 68.2 (C-1$_{All}$), 67.9 (C-5), 55.4 (O*C*H$_3$), 41.1 (*C*H$_2$Cl), 18.0 (C-6). HR-ESI-TOF-MS *m/z* 513.1653 $[M + Na]^+$ (calcd for $C_{26}H_{31}ClO_7Na$, 513.1656).

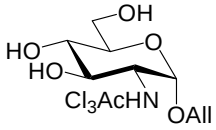
4-*O*-Benzyl-2-*O*-chloroacetyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranosyl trichloroacetimidate (14).



[Ir] (122 mg, 0.14 mmol, 0.05 equiv.) was dissolved in anhydr. THF (14 mL) and the resulting red solution was degassed under Ar. Hydrogen was bubbled through the solution for 15 min, and the resulting yellow solution was degassed under Ar. The allyl glycoside **S5** (1.42 g, 2.89 mmol) in anhydr. THF (14 mL) was then added. The mixture was stirred overnight at rt under Ar. Iodine (1.47 g, 5.78 mmol, 2.0 equiv.) in THF/H_2O (6.0 mL, 4:1 *v*/*v*) was added to the mixture, which was stirred for 1 h at rt. Freshly prepared 10% aq sodium bisulfite was added. The mixture was concentrated (to 1/3 volume) under reduced pressure and the aq phase was extracted three times with CH_2Cl_2. The organic layer was washed twice with H_2O, once with brine, dried over anhydr. Na_2SO_4, filtered and evaporated. CCl_3CN (1.5 mL, 14 mmol, 5.0 equiv.) and DBU (130 µL, 0.87 mmol, 0.30 equiv.) were added to the residue in anhydr. DCE (5.8 mL). The mixture was stirred for 1 h at rt under Ar, and directly purified by FC (Chex/EtOAc 9:1 to 8:2 + 1% Et_3N) to give **14** (1.53 g, 89%) as a yellow oil. R_f 0.73 (Chex/EtOAc 7:3); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (α): 8.68

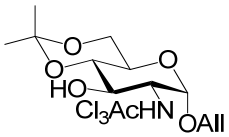
(s, 1H, N*H*), 7.38-7.22 (m, 7H, CH_{Ph}), 6.87-6.82 (m, 2H, CH_{Ph}), 6.20 (br s, 1H, H-1), 5.51 (br s, 1H, H-2), 4.91 (d, J = 10.8 Hz, 1H, CH_2Ph), 4.66 (d, J = 11.9 Hz, 1H, CH_2Ph), 4.63 (d, 1H, CH_2Ph), 4.52 (d, 1H, CH_2Ph), 4.19 (s, 2H, CH_2Cl), 4.02-3.91 (m, 2H, H-3, H-5), 3.80 (s, 3H, OCH_3), 3.48 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1H, H-4), 1.34 (d, $J_{5,6}$ = 6.1 Hz, 3H, H-6). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (α): 166.7 (*C*=O), 160.1 (*C*=NH), 159.6 (C_{Ph}), 138.1 (C_{Ph}), 130.2-128.1 (*C*H$_{Ph}$), 114.0 (*C*H$_{Ph}$), 94.8 (C-1), 90.9 (*C*Cl_3), 79.1 (C-4), 76.7 (C-3), 75.8 (*C*H_2Ph), 72.0 (*C*H_2Ph), 70.9 (C-5), 69.6 (C-2), 55.4 (O*C*H_3), 40.9 (*C*H_2Cl), 18.0 (C-6).

Allyl 2-deoxy-2-trichloroacetamido-α-D-glucopyranoside (25).



D-Glucosamine hydrochloride (10.0 g, 46.4 mmol) was dissolved in anhydr. MeOH (199 mL) and the mixture was stirred for 1 h at rt under Ar. After 15 min, trichloroacetic anhydride (12.7 mL, 69.6 mmol, 1.5 equiv.) was added dropwise at 0 °C and the mixture was stirred for 2 h at this temperature. The reaction was neutralized with Dowex resin (H^+ form), filtered and solvents were evaporated. Acetyl chloride (0.37 mL, 5.2 mmol, 3.4 equiv.) was slowly added to the residue in allylic alcohol (3.1 mL) at 0 °C. The mixture was stirred for 3 h at 70 °C, and diluted with MeOH. Solid $NaHCO_3$ was added until neutrality was reached. After filtration, solvents were evaporated and the residue was purified by FC (CH_2Cl_2/MeOH 95:5 to 9:1) to give triol **25** (7.53 g, 45%, 2 steps) as an amorphous brownish solid. R_f 0.16 (CH_2Cl_2/MeOH 95:5); $[\alpha]^{25}_D$ +113° (*c* 1.0, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.14 (d, $J_{NH,2}$ = 8.8 Hz, 1H, N*H*), 5.85 (m, 1H, H-2$_{All}$), 5.29 (ddd, 1H, J = 17.1, 3.0, 1.5 Hz, 1H, H-3a$_{All}$), 5.21 (ddd, 1H, J = 10.4, 2.5, 1.1 Hz, 1H, H-3b$_{All}$), 4.95 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 4.19 (ddt, J = 13.0, 5.2, 1.4 Hz, 1H, H-1a$_{All}$), 4.08 (ddd, $J_{2,3}$ = 9.5 Hz, 1H, H-2), 4.00 (ddt, J = 13.0, 6.3, 1.2 Hz, 1H, H-1b$_{All}$), 3.94 (dd, $J_{6a,6b}$ = 12.5 Hz, $J_{5,6a}$ = 2.3 Hz, 1H, H-6a), 3.88-3.81 (m, 2H, H-6b, H-3), 3.77 (pt, $J_{3,4}$ = 9.3 Hz, 1H, H-4), 3.64 (dt, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 2.5 Hz, 1H, H-5). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 162.9 (*C*=O), 133.3 (C-2$_{All}$), 118.5 (C-3$_{All}$), 96.1 (C-1), 92.6 (*C*Cl_3), 72.8 (C-3), 72.0 (C-5), 70.1 (C-4), 68.7 (C-1$_{All}$), 61.3 (C-6), 55.5 (C-2). HR-ESI-TOF-MS *m/z* 364.0120 $[M + H]^+$ (calcd for $C_{12}H_{17}Cl_3NO_6$, 364.0121).

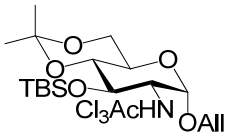
Allyl 2-deoxy-4,6-*O*-isopropylidene-2-trichloroacetamido-α-D-glucopyranoside (S6).



2-Methoxypropene (4.2 mL, 44.4 mmol, 2.0 equiv.) and *p*TSA (422 mg, 2.22 mmol, 0.1 equiv.) were added to triol **25** (8.07 g, 22.1 mmol) in anhydr. DMF (75 mL). The mixture was stirred for

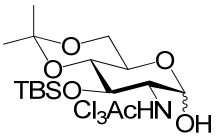
1 h at rt under Ar. Et_3N (3.0 mL) was added and solvents were evaporated. The residue was purified by FC (Chex/EtOAc 8:2 to 7:3) to give alcohol **S6** (8.09 g, 90%) as a white amorphous powder. R_f 0.36 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ +95° (*c* 1.0, $CHCl_3$); ^{1}H NMR (Py-d_5, 400 MHz) δ: 10.35 (d, $J_{NH,2}$ = 8.1 Hz, 1H, N*H*), 7.69 (d, $J_{OH,3}$ = 5.3 Hz, 1H, O*H*), 6.01 (m, 1H, H-2$_{All}$), 5.36 (ddd, *J* = 17.2, 3.2, 1.6 Hz, 1H, H-3a$_{All}$), 5.36 (d, $J_{1,2}$ = 3.8 Hz, 1H, H-1), 5.18 (ddd, *J* = 10.3, 2.8, 1.3 Hz, 1H, H-3b$_{All}$), 4.72 (ddd, $J_{2,3}$ = 10.2 Hz, 1H, H-2), 4.50 (m, 1H, H-3), 4.28 (ddt, *J* = 13.0, 5.3, 1.4 Hz, 1H, H-1a$_{All}$), 4.09 (ddt, *J* = 13.0, 6.2, 1.3 Hz, 1H, H-1b$_{All}$), 4.04-3.90 (m, 4H, H-4, H-5, H-6a, H-6b), 1.49 (s, 3H, C(*C*H$_3$)$_2$), 1.44 (s, 3H, C(*C*H$_3$)$_2$). ^{13}C NMR (Py-d_5, 100 MHz) δ: 163.6 (*C*=O), 134.9 (C-2$_{All}$), 118.2 (C-3$_{All}$), 100.2 (*C*(CH$_3$)$_2$), 97.8 (C-1), 94.5 (*C*Cl$_3$), 76.6 (C-4), 69.3 (C-1$_{All}$), 68.8 (C-3), 65.0 (C-5), 63.0 (C-6), 58.1 (C-2), 29.7 (C(*C*H$_3$)$_2$), 19.6 (C(*C*H$_3$)$_2$). HR-ESI-TOF-MS *m/z* 404.0441 $[M + H]^+$ (calcd for $C_{15}H_{21}Cl_3NO$, 404.0435).

Allyl 3-*O*-*tert*-butyldimethylsilyl-2-deoxy-4,6-*O*-isopropylidene-2-trichloroacetamido-α-D-glucopyranoside (26).



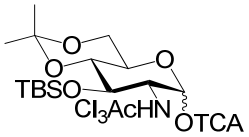
DMAP (241 mg, 2.0 mmol, 0.1 equiv.), imidazole (3.36 g, 49.3 mmol, 2.5 equiv.) and TBSCl (8.92 g, 59.2 mmol, 3.0 equiv.) were added to alcohol **S6** (7.98 g, 19.7 mmol) in anhydr. THF (59 mL). The mixture was stirred for 2 d at reflux under Ar. After cooling to rt, the reaction was filtered and the filtrate was evaporated. The residue was purified by FC (Chex to Chex/EtOAc 9:1) to give **26** (10.0 g, 98%) as a white amorphous powder. R_f 0.82 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ +73° (*c* 1.0, $CHCl_3$); ^{1}H NMR (Py-d_5, 400 MHz) δ: 8.91 (d, $J_{NH,2}$ = 9.1 Hz, 1H, N*H*), 5.90 (m, 1H, H-2$_{All}$), 5.27 (br dd, *J* = 17.2, 2.9 Hz, 1H, H-3a$_{All}$), 5.16-5.11 (m, 2H, H-1, H-3b$_{All}$), 4.54 (pdt, $J_{2,3}$ = 9.5 Hz, $J_{1,2}$ = 3.8 Hz, 1H, H-2), 4.26 (pt, $J_{3,4}$ = 9.3 Hz, 1H, H-3), 4.22 (ddt, *J* = 13.0, 5.5, 1.3 Hz, 1H, H-1a$_{All}$), 4.06-3.99 (m, 2H, H-1b$_{All}$, H-6a), 3.97-3.85 (m, 2H, H-5, H-6b), 3.71 (pt, $J_{4,5}$ = 8.9 Hz, 1H, H-4), 1.52 (s, 3H, C(C*H*$_3$)$_2$), 1.49 (s, 3H, C(C*H*$_3$)$_2$), 1.00 (s, 9H, C(C*H*$_3$)$_3$), 0.16 (s, 3H, Si(C*H*$_3$)$_2$), 0.14 (s, 3H, Si(C*H*$_3$)$_2$). ^{13}C NMR (Py-d_5, 100 MHz) δ: 163.1 (*C*=O), 134.5 (C-2$_{All}$), 118.8 (C-3$_{All}$), 100.1 (*C*(CH$_3$)$_2$), 97.5 (C-1), 94.0 (*C*Cl$_3$), 75.8 (C-4), 71.4 (C-3), 69.3 (C-1$_{All}$), 64.5 (C-5), 62.8 (C-6), 57.9 (C-2), 29.7 (C(*C*H$_3$)$_2$), 26.6 (C(*C*H$_3$)$_3$, 3C), 19.5 (C(*C*H$_3$)$_2$), 18.9 (*C*(CH$_3$)$_3$), -3.2 (Si(*C*H$_3$)$_2$), -4.3 (Si(*C*H$_3$)$_2$). HR-ESI-TOF-MS *m/z* 518.1277 $[M + H]^+$ (calcd for $C_{20}H_{35}Cl_3NO_6Si$, 518.1299).

3-*O*-*tert*-Butyldimethylsilyl-2-deoxy-4,6-*O*-isopropylidene-2-trichloroacetamido-α/β-D-glucopyranose (S7).



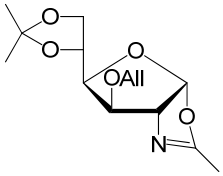
[Ir] (815 mg, 0.96 mmol, 0.05 equiv.) was dissolved in anhydr. THF (96 mL) and the resulting red solution was degassed under Ar. Hydrogen was bubbled through the solution for 5 min, and the resulting yellow solution was degassed under Ar. Allyl glycoside **26** (10.0 g, 19.3 mmol) in anhydr. THF (96 mL) was added and the mixture was stirred overnight at rt under Ar. Iodine (9.78 g, 38.5 mmol, 2.0 equiv.) in THF/H_2O (115 mL, 4:1 *v/v*) was added to the mixture, which was stirred for 1 h at rt. Freshly prepared 10% aq sodium bisulfite (75 mL) was added. The mixture was concentrated (to 1/3 volume) under reduced pressure and the aq phase was extracted three times with CH_2Cl_2 (3×250 mL). The organic layer was washed with H_2O (2×250 mL), brine (250 mL), dried over anhydr. Na_2SO_4, filtered and evaporated. The residue was purified by FC (Chex/EtOAc 9:1 to 6:4) to give hemiacetal **S7** (7.99 g, 87%, ratio α/β ≈ 7:1) as a yellow amorphous powder. R_f 0.46 (Chex/EtOAc 7:3); ^{1}H NMR (Py-d_5, 400 MHz) δ (α): 9.31 (br s, 1H, O*H*), 8.37 (br d, 1H, N*H*), 5.65 (pt, $J_{1,OH}$ = 3.4 Hz, 1H, H-1), 4.55 (td, $J_{2,3}$ = $J_{2,NH}$ = 9.5 Hz, $J_{1,2}$ = 3.7 Hz, 1H, H-2), 4.39 (pt, $J_{3,4}$ = 9.0 Hz, 1H, H-3), 4.34 (dt, $J_{5,6a}$ = $J_{5,6b}$ = 5.1 Hz, 1H, H-5), 4.02 (dd, $J_{6a,6b}$ = 10.7 Hz, $J_{5,6a}$ = 5.4 Hz, 1H, H-6a), 3.92 (pt, $J_{5,6a}$ = 10.6 Hz, 1H, H-6b), 3.79 (pt, $J_{4,5}$ = 9.2 Hz, 1H, H-4), 1.55 (s, 3H, C(CH_3)$_2$), 1.53 (s, 3H, C(CH_3)$_2$), 1.06 (s, 9H, C(CH_3)$_3$), 0.25 (s, 6H, Si(CH_3)$_2$). ^{13}C NMR (Py-d_5, 100 MHz) δ (α): 163.0 (*C*=O), 100.1 (*C*(CH$_3$)$_2$), 94.2 (*C*Cl$_3$), 92.7 (C-1), 76.2 (C-4), 71.6 (C-3), 64.1 (C-5), 63.3 (C-6), 58.7 (C-2), 29.7 (C(*C*H$_3$)$_2$), 26.6 (C(*C*H$_3$)$_3$), 19.5 (C(*C*H$_3$)$_2$), 19.0 (*C*(CH$_3$)$_3$), -3.2 (Si(*C*H$_3$)$_2$), -4.2 (Si(*C*H$_3$)$_2$). HR-ESI-TOF-MS *m/z* 478.0997 $[M + H]^+$ (calcd for $C_{17}H_{31}Cl_3NO_6Si$, 478.0968).

3-*O*-*tert*-Butyldimethylsilyl-2-deoxy-4,6-*O*-isopropylidene-2-trichloroacetamido-α/β-D-glucopyranosyl trichloroacetimidate (11).



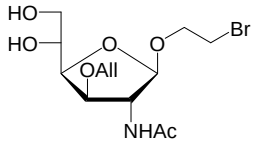
CCl_3CN (8.3 mL, 82 mmol, 5.0 equiv.) and DBU (0.74 mL, 4.9 mmol, 0.3 equiv.) were added to hemiacetal **S7** (7.88 g, 16.5 mmol) in anhydr. DCE (33 mL). The mixture was stirred for 1 h at rt under Ar, and directly purified by FC (Chex/EtOAc 9:1 + 1% Et_3N) to give trichloroacetimidate **11** (8.62 g, 84%, α/β 7:1) as a white foam. R_f 0.74 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ +63° (*c* 1.0, $CHCl_3$); ^{1}H NMR (Py-d_5, 400 MHz) δ (α): 10.48 (s, 1H, C=N*H*), 8.26 (d, $J_{NH,2}$ = 8.7 Hz, 1H, N*H*), 6.97 (d, $J_{1,2}$ = 3.9 Hz, 1H, H-1), 4.78 (td, $J_{2,3}$ = 9.4 Hz, 1H, H-2), 4.48 (t, $J_{3,4}$ = 9.3 Hz, 1H, H-3), 4.22 (dq, 1H, H-5), 4.06 (dd, $J_{6a,6b}$ = 10.7 Hz, $J_{5,6a}$ = 5.1 Hz, 1H, H-6a), 3.95-3.87 (m, 2H, H-6b, H-4), 1.55 (s, 3H, C(CH_3)$_2$), 1.51 (s, 3H, C(CH_3)$_2$), 1.00 (s, 9H, C(CH_3)$_3$), 0.21 (s, 3H, Si(CH_3)$_2$), 0.18 (s, 3H, Si(CH_3)$_2$). ^{13}C NMR (Py-d_5, 100 MHz) δ (α): 163.0 (*C*=O), 160.1 (*C*=NH), 100.5 (*C*(CH$_3$)$_2$), 95.6 (C-1), 93.5 (*C*Cl$_3$), 91.7 (*C*Cl$_3$), 74.9 (C-4), 71.6 (C-3), 67.1 (C-5), 62.5 (C-6), 57.2 (C-2), 29.5 (C(*C*H$_3$)$_2$), 26.5 (C(*C*H$_3$)$_3$, 3C), 19.5 (C(*C*H$_3$)$_2$), 18.9 (*C*(CH$_3$)$_3$), -3.2 (Si(*C*H$_3$)$_2$), -4.3 (Si(*C*H$_3$)$_2$).

(2-Methyl-(3-*O*-allyl-1,2-dideoxy-5,6-*O*-isopropylidene-α-D-glucofurano)-[2,1-d]-2-oxazoline (31).



NaH (60% oil dispersion, 414 mg, 12.3 mmol, 3.0 equiv.) was added to the crude oxazoline **30**[16] (1.00 g, 4.11 mmol) in anhydr. DMF (12.3 mL) at 0 °C. After 1 h at this temperature, allyl bromide (1.07 mL, 12.3 mmol, 3.0 equiv.) was added dropwise and the mixture was stirred overnight at rt under Ar. After cooling to 0 °C, MeOH was carefully added. H_2O (50 mL) was added and the aq. phase was extracted with CH_2Cl_2 (3×100 mL). The organic layer was dried over anhydr. Na_2SO_4, filtered and evaporated to dryness. The residue was purified by FC (Chex/EtOAc 7:3 to 2:8) to give oxazoline **31** (892 mg, 77% from *N*-acetyl-D-glucosamine) as a yellow oil. R_f 0.28 (CH_2Cl_2/MeOH 95:5); $[\alpha]^{25}_D$ –46° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.10 (d, $J_{1,2}$ = 5.1 Hz, 1H, H-1), 5.90 (m, 1H, H-2$_{All}$), 5.31 (ddd, *J* = 17.3, 3.3, 1.5 Hz, 1H, H-3a$_{All}$), 5.20 (ddd, *J* = 10.5, 2.9, 1.4 Hz, 1H, H-3b$_{All}$), 4.48 (m, 1H, H-2), 4.32 (dt, $J_{5,6a}$ = $J_{5,6b}$ = 6.0 Hz, 1H, H-5), 4.18 (ddt, *J* = 12.9, 5.3, 1.4 Hz, 1H, H-1a$_{All}$), 4.14-4.04 (m, 4H, H-1b$_{All}$, H-6a, H-3, H-6b), 3.81 (dd, $J_{4,5}$ = 7.1 Hz, $J_{3,4}$ = 3.1 Hz, 1H, H-4), 2.01 (d, $J_{2,Me}$ = 1.5 Hz, 3H, C*H*$_3$), 1.40 (s, 3H, C(C*H*$_3$)$_2$), 1.34 (s, 3H, C(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.0 (*C*=N), 134.3 (C-2$_{All}$), 117.5 (C-3$_{All}$), 109.1 (*C*(CH$_3$)$_2$), 107.1 (C-1), 81.6 (C-4), 81.5 (C-3), 75.8 (C-2), 72.7 (C-5), 71.2 (C-1$_{All}$), 67.0 (C-6), 26.9 (C(*C*H$_3$)$_2$), 25.5 (C(*C*H$_3$)$_2$), 14.3 (*C*H$_3$). HR-ESI-TOF-MS *m/z* 284.1468 $[M + H]^+$ (calcd for $C_{14}H_{22}NO_5$, 284.1498).

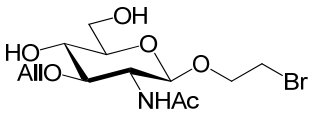
2-Bromoethyl 2-acetamido-3-*O*-allyl-2-deoxy-β-D-glucofuranoside (S8).



$Yb(OTf)_3$ (5.47 g, 8.82 mmol, 0.5 equiv.) was added to oxaxoline **31** (5.00 g, 17.6 mmol) in anhydr. 2-bromoethanol (29 mL). The mixture was stirred overnight at rt under Ar. Solvents were evaporated and the residue was purified by FC (CH_2Cl_2/MeOH 95:5 to 85:15) to give **S8** (6.47 g, 99%) as a brownish foam. R_f 0.12 (CH_2Cl_2/MeOH 95:5); $[\alpha]^{25}_D$ –71° (*c* 1.0, MeOH); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 6.43 (d, $J_{NH,2}$ = 7.7 Hz, 1H, N*H*), 5.89 (m, 1H, H-2$_{All}$), 5.32 (br d, *J* = 17.3 Hz, 1H, H-3a$_{All}$), 5.19 (br d, *J* = 10.5 Hz, 1H, H-3b$_{All}$), 4.95 (s, 1H, H-1), 4.41 (d, 1H, H-2), 4.32 (br dd, *J* = 13.0, 4.9 Hz, 1H, H-1a$_{All}$), 4.26 (dd, $J_{4,5}$ = 8.7 Hz, $J_{3,4}$ = 6.1 Hz, 1H, H-4), 4.09-4.02 (m, 3H, H-1b$_{All}$, H-5, H-3), 3.93 (dt, $J_{a,b}$ = 11.1, J_{vic} = 6.0 Hz, 1H, OC*H*$_2$a), 3.82 (m, J_{vic} = 3.1 Hz, 1H, H-6a), 3.76-3.67 (m, 2H, H-6b, OC*H*$_2$b), 3.44 (m, *J* = 6.1 Hz, 2H, C*H*$_2$Br), 2.98 (br s, 2H, O*H*), 1.98 (s, 3H, C(O)C*H*$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.2 (*C*=O), 133.8 (C-2$_{All}$), 118.1

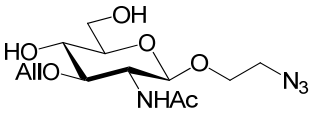
(C-3_{All}), 107.0 (C-1), 83.0 (C-3), 80.1 (C-4), 70.9 (C-1_{All}), 70.8 (C-5), 68.2 (O*C*H_2), 64.0 (C-6), 59.7 (C-2), 30.2 (*C*H_2Br), 23.2 (C(O)*C*H_3). HR-ESI-TOF-MS *m/z* 390.0522 $[M + Na]^+$ (calcd for $C_{13}H_{22}BrNO_6Na$, 390.0528).

2-Bromoethyl 2-acetamido-3-*O*-allyl-2-deoxy-β-D-glucopyranoside (32).



CSA (20 mg, 86 μmol, 0.25 equiv.) was added to oxazoline **31** (100 mg, 353 μmol) in anhydr. 2-bromoethanol (0.71 mL). The mixture was stirred for 4 d at rt under Ar, and neutralized by adding solid $NaHCO_3$, then filtered. Solvents were evaporated and the residue was purified by FC (CH_2Cl_2/MeOH 95:5 to 9:1) to give diol **32** (70 mg, 55%) as a white amorphous powder. R_f 0.13 (CH_2Cl_2/MeOH 95:5); $[\alpha]^{25}_D$ –19° (*c* 1.0, MeOH); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 7.78 (d, $J_{NH,2}$ = 9.1 Hz, 1H, N*H*), 5.84 (m, 1H, H-2_{All}), 5.18 (ddd, *J* = 17.2, 3.8, 1.8 Hz, 1H, H-$3a_{All}$), 5.04 (ddd, *J* = 10.4, 3.5, 1.5 Hz, 1H, H-$3b_{All}$), 4.41 (d, $J_{1,2}$ = 8.5 Hz, 1H, H-1), 4.21 (ddt, *J* = 13.1, 5.3, 1.5 Hz, 1H, H-$1a_{All}$), 4.05 (ddt, *J* = 13.1, 5.3, 1.5 Hz, 1H, H-$1b_{All}$), 3.95 (dt, *J* = 11.6, 5.8 Hz, 1H, O*C*H_2a), 3.76 (dt, *J* = 11.7, 6.0 Hz, 1H, O*C*H_2b), 3.68 (br d, $J_{6a,6b}$ = 10.7 Hz, 1H, H-6a), 3.60-3.43 (m, 4H, *C*H_2Br, H-6b, H-2), 3.32 (br s_o, 2H, O*H*), 3.29 (pt$_o$, 1H, H-3), 3.20 (pdt, $J_{4,5}$ = 9.5 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 5.9 Hz, 1H, H-5), 3.13 (ddd, $J_{3,4}$ = 9.4 Hz, $J_{4,OH}$ = 2.0 Hz, 1H, H-4), 1.80 (s, 3H, C(O)C*H*$_3$). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 168.9 (*C*=O), 136.0 (C-2_{All}), 115.4 (C-3_{All}), 100.7 (C-1), 82.3 (C-3), 77.0 (C-4), 72.3 (C-1_{All}), 69.9 (C-5), 68.3 (O*C*H_2), 60.8 (C-6), 54.0 (C-2), 31.9 (*C*H_2Br), 23.0 (C(O)*C*H_3). HR-ESI-TOF-MS *m/z* 390.0540 $[M + Na]^+$ (calcd for $C_{13}H_{22}BrNO_6Na$, 390.0528).

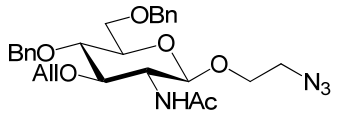
2-Azidoethyl 2-acetamido-3-*O*-allyl-2-deoxy-β-D-glucopyranoside (S9).



To a solution of diol **32** (3.19 g, 8.67 mmol) in anhydr. DMF (43.4 mL) were sequentially added NaI (6.50 g, 43.4 mmol, 5.0 equiv.) and NaN_3 (2.82 g, 43.4 mmol, 5.0 equiv). The mixture was stirred overnight at 80 °C, and the solvents were removed under reduced pressure. The residue was adsorbed on silica gel (22 g) and purified by FC (CH_2Cl_2/MeOH 95:5 to 9:1) to give the azidoethyl glycoside **S9** contaminated with sodium salts (6.78 g). Available analytical data for diol **S9**: R_f 0.11 (CH_2Cl_2/MeOH 95:5); $[\alpha]^{25}_D$ –19° (*c* 1.0, MeOH); ^{1}H NMR (Py-d_5, 400 MHz) δ: 10.56 (bd, 1H, N*H*), 7.15 (m, 1H, H-2_{All}), 6.42 ($J_{1,2}$ = 8.7), 6.38 (m, 1H, H-3_{All}), 6.10 (br d, *J* = 10.4 Hz, *J* = 1.4 Hz, 1H, H-$3b_{All}$), 5.78 (m, 2H, H-$1a_{All}$, H-$1b_{All}$), 5.60 (p, $J_{1,2}$ = 9.9 Hz, $J_{2,3}$ = 9.2 Hz, 9.0 1H, H-2), 5.50-5.40 (m, 2H, H-3, H-6a), 5.35 (dd, $J_{6a,6b}$ = 11.8 Hz, $J_{5,6b}$ = 4.5 Hz, 1H, H-6b), 4.19-4.10 (m, 3H, CH_2N_3a, H-4, OH), 5.04-4.90 (m, 2H, CH_2N_3b, H-5), 4.64 (m, 1H,

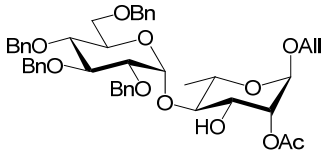
OCH_2a), 4.50 (m, 1H, OCH_2b), 3.31 (s, 3H, C(O)CH_3). ^{13}C NMR (Py-d_5, 100 MHz) δ: 172.5 (*C*=O), 136.4 (C-2_{All}), 116.6 (C-3_{All}), 102.0 (C-1), 83.7 (C-3), 78.0 (C-5), 74.5 (C-1_{All}), 71.9 (C-4), 68.8 (*C*H_2N_3), 62.2 (C-6), 56.1 (C-2), 51.3 (O*C*H_2), 23.9 (C(O)*C*H_3). HR-ESI-TOF-MS *m/z* 353.1406 $[M + Na]^+$ (calcd for $C_{13}H_{22}N_4O_6Na$, 353.1437).

2-Azidoethyl 2-acetamido-3-*O*-allyl-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (33).



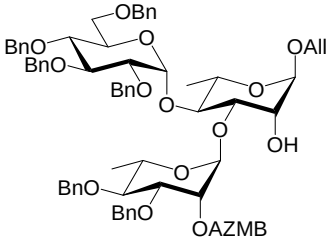
NaI (6.50 g, 43.4 mmol, 5.0 equiv.) and NaN_3 (2.82 g, 43.4 mmol, 5.0 equiv.) were sequentially added to diol **32** (3.19 g, 8.67 mmol) in anhydr. DMF (43.4 mL). The mixture was stirred overnight at 80 °C, and solvents were removed under reduced pressure. The residue was adsorbed on silica gel (22 g) and purified by FC (CH_2Cl_2/MeOH 95:5 to 9:1) to give the azidoethyl glycoside (6.78 g) contaminated with sodium salts. BnBr (3.91 mL, 32.9 mmol, 4.0 equiv.) was slowly added to the above crude material (2.72 g) in anhydr. DMF (165 mL) stirred at 0 °C. NaH (858 mg, 25.5 mmol, 3.0 equiv.) was added portionwise and stirring went on for 2 h at 0 °C. MeOH was added and the mixture was diluted with EtOAc (250 mL). H_2O was added carefully (250 mL) and the aq. phase was extracted with EtOAc (3×250 mL). The organic layer was washed with H_2O (1×250 mL), dried (anhydr. Na_2SO_4), filtered and solvents were removed under reduced pressure. The residue was purified by FC (Chex/EtOAc 6:4 to 0:10) to give fully protected **33** (2.39 g, 57%, 2 steps from **32**) as a white amorphous powder. R_f 0.06 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ +1° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.35-7.21 (m, 10H, CH_{Ph}), 5.89 (m, 1H, H-2_{All}), 5.73 (d, $J_{NH,2}$ = 7.3 Hz, 1H, N*H*), 5.24 (ddd, *J* = 17.3, 3.2, 1.6 Hz, 1H, H-$3a_{All}$), 5.15 (br d, *J* = 10.4 Hz, 1H, H-$3b_{All}$), 4.96 (d, $J_{1,2}$ = 7.8 Hz, 1H, H-1), 4.78 (d, *J* = 11.1 Hz, 1H, CH_2Ph), 4.60 (d, *J* = 12.2 Hz, 1H, CH_2Ph), 4.57 (d, 1H, CH_2Ph), 4.54 (d, 1H, CH_2Ph), 4.27 (br dd, *J* = 12.6, 5.5 Hz, 1H, H-$1a_{All}$), 4.15 (br dd, *J* = 12.6, 5.8 Hz, 1H, H-$1b_{All}$), 4.11-4.00 (m, 2H, H-3, OCH_2a), 3.76-3.66 (m, 3H, OCH_2b, H-6a, H-6b), 3.60-3.52 (m, 2H, H-4, H-5), 3.48 (ddd, *J* = 13.2, 8.0, 3.4 Hz, 1H, CH_2N_3a), 3.32-3.22 (m, 2H, H-2, CH_2N_3b), 1.98 (s, 3H, C(O)CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.8 (*C*=O), 138.1 (2C, C_{Ph}), 134.9 (C-2_{All}), 128.4-127.7 (*C*H_{Ph}), 117.0 (C-3_{All}), 99.7 (C-1), 80.3 (C-3), 78.4 (C-4) 74.8 (C-5), 74.7 (*C*H_2Ph), 73.8 (C-1_{All}), 73.5 (*C*H_2Ph), 68.9 (C-6), 68.3 (O*C*H_2), 57.4 (C-2), 50.7 (*C*H_2N_3), 23.7 (C(O)*C*H_3). HR-ESI-TOF-MS *m/z* 511.2566 $[M + H]^+$ (calcd for $C_{27}H_{35}N_4O_6$, 511.2556).

Allyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2-*O*-acetyl-α-L-rhamnopyranoside (16).



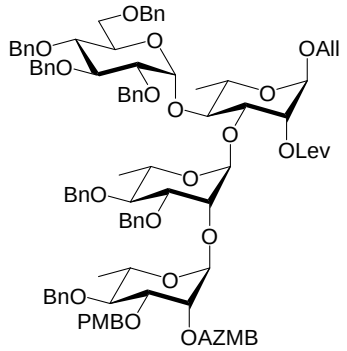
$MeC(OMe)_3$ (1.04 mL, 8.25 mmol, 2.0 equiv.) and *p*TSA (14 mg, 0.081 mmol, 0.02 equiv.) were added to diol **9**[17] (2.96 g, 4.07 mmol) in anhydr. CH_3CN (8.3 mL). The mixture was stirred for 1 h at rt, then 80% aq. HOAc (8.3 mL) was added at 0 °C. The mixture was stirred for another 1 h at rt, then cold H_2O (50 mL) was added dropwise. The aq. phase was extracted with CH_2Cl_2 (3×100 mL), and the organic layer was washed with brine (50 mL), dried over anhydr. Na_2SO_4 and evaporated to dryness. Crude acetate **16** was obtained as a colorless oil and used without further purification. Available analytical data for acceptor **16**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.38-7.12 (m, 20H, C*H*$_{Ph}$), 5.90 (m, 1H, H-2$_{All}$), 5.30 (ddd, *J* = 17.2, 3.2, 1.6 Hz, 1H, H-3a$_{All}$), 5.21 (ddd, *J* = 10.4, 2.8, 1.3 Hz, 1H, H-3b$_{All}$), 5.14 (dd, $J_{2,3}$ = 3.7 Hz, 1H, H-2$_C$), 4.97 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1$_E$), 4.95 (d, 1H, *J* = 11.0 Hz, C*H*$_2$Ph), 4.82 (d, *J* = 10.9 Hz, 1H, C*H*$_2$Ph), 4.81 (d, *J* = 10.9 Hz, 1H, C*H*$_2$Ph), 4.77 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1$_C$), 4.71 (d, 1H, *J* = 11.7 Hz, C*H*$_2$Ph), 4.68 (d, 1H, *J* = 11.7 Hz, C*H*$_2$Ph), 4.56 (d, 1H, *J* = 12.2 Hz, C*H*$_2$Ph), 4.47 (d, 1H, *J* = 12.2 Hz, C*H*$_2$Ph), 4.46 (d, *J* = 10.9 Hz, 1H, C*H*$_2$Ph), 4.15 (ddt, *J* = 12.6, 5.1, 1.5 Hz, 1H, H-1a$_{All}$), 4.08 (ddd, $J_{4,5}$ = 10.1 Hz, $J_{5,6b}$ = 4.9 Hz, 1H, H-5$_E$), 4.01-3.93 (m, 3H, H-1b$_{All}$, H-3$_C$, H-3$_E$), 3.78 (dq, 1H, $J_{4,5}$ = 9.5 Hz, H-5$_C$), 3.64 (dd, $J_{5,6a}$ = 2.4 Hz, $J_{6a,6b}$ = 10.2 Hz, 1H, H-6a$_E$), 3.63-3.56 (m, 2H, H-6b$_E$, H-2$_E$), 3.54 (dd, $J_{3,4}$ = 9.0 Hz, 1H, H-4$_E$), 3.37 (pt, $J_{3,4}$ = 9.2 Hz, 1H, H-4$_C$), 2.11 (s, 3H, C(O)C*H*$_3$), 1.39 (d, $J_{5,6}$ = 6.4 Hz, 3H, H-6$_C$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.6 (*C*=O), 138.8 (C$_{Ph}$), 138.2 (C$_{Ph}$), 138.1 (C$_{Ph}$), 137.8 (C$_{Ph}$), 133.8 (C-2$_{All}$), 129.2-127.8 (*C*H$_{Ph}$), 117.7 (C-3$_{All}$), 98.8 (C-1$_E$), 96.7 (C-1$_C$), 85.4 (C-4$_C$), 81.9 (C-3$_C$), 80.2 (C-2$_E$), 78.1 (C-4$_E$), 75.8, 75.3 (2C, *C*H$_2$Ph), 73.8 (2C, *C*H$_2$Ph), 72.4 (C-2$_C$), 71.4 (C-5$_E$), 68.9 (C-6$_E$), 68.4 (C-1$_{All}$), 68.4 (C-3$_E$), 66.8 (C-5$_C$), 21.2 (C(O)*C*H$_3$), 17.9 (C-6$_C$). HR-ESI-TOF-MS *m/z* 769.3573 $[M + H]^+$ (calcd for $C_{45}H_{53}O_{11}$, 769.3588), *m/z* 791.3387 $[M + Na]^+$ (calcd for $C_{45}H_{52}O_{11}Na$, 791.3408.

Allyl (2-*O*-(2-(azidomethyl)benzoyl)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-α-L-rhamnopyranoside (18).



Route b. Bu_2SnO (24 mg, 0.096 mmol, 2.0 equiv) was added to trisaccharide **17** (60 mg, 0.048 mmol) in anhydr. MeOH (4.0 mL). The mixture was refluxed overnight under Ar. Solvents were evaporated under reduced pressure and the residue was purified by FC (Tol/EtOAc 9:1 to 8:2) to give alcohol **18** (36 mg, 62%) as a colorless oil. See manuscript for *route a* and analytical data.

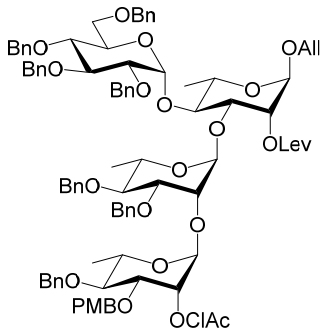
Allyl (2-*O*-(2-(azidomethyl)benzoyl)-4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-levulinoyl-α-L-rhamnopyranoside (21).



Acceptor **20** (5.36 g, 4.66 mmol) and donor **13** (4.74 g, 6.99 mmol, 1.5 equiv.) in anhydr. Et_2O (70 mL) containing 4 Å AW-MS (7.0 g) were stirred for 30 min at -10 °C under Ar. TMSOTf (84 μL, 0.47 mmol, 0.1 equiv.) was added keeping rigorously anhydr. conditions. After stirring for 1 h at -10 °C to rt, Et_3N (300 μL) was added. The suspension was filtered and solvents were evaporated. The residue was purified by FC (Tol/EtOAc 95:5 to 9:1) to give tetrasaccharide **21** as a white sticky solid slightly contaminated with trichloroacetamide (6.18 g), along with unreacted **20** (1.35 g, 20%). Available analytical data for tetrasaccharide **21**: R_f 0.45 (Chex/EtOAc 7:3); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.94-7.91 (m, 1H, C*H*$_{Ph}$), 7.55-7.47 (m, 2H, C*H*$_{Ph}$), 7.36-7.02 (m, 38H, C*H*$_{Ph}$), 6.80-6.76 (m, 2H, C*H*$_{Ph}$), 5.88 (m, 1H, H-2$_{All}$), 5.74 (dd, $J_{2,3}$ = 3.2 Hz, 1H, H-2$_A$), 5.27 (ddd, J = 17.3, 3.2, 1.5 Hz, 1H, H-3a$_{All}$), 5.19 (ddd, J = 10.4, 2.6, 1.2 Hz, 1H, H-3b$_{All}$), 5.19 (d, $J_{1,2}$ = 1.7 Hz, 1H, H-1$_A$), 5.11 (dd, $J_{2,3}$ = 3.5 Hz, $J_{1,2}$ = 1.9 Hz, 1H, H-2$_C$), 4.98 (d, $J_{1,2}$ = 3.2 Hz, 1H, H-1$_E$), 4.96 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1$_B$), 4.93-4.89 (m, 3H, C*H*$_2$Ph), 4.81 (d, J = 10.9 Hz, 1H, C*H*$_2$Ph), 4.76-4.69 (m, 5H, C*H*$_2$N$_3$a, H-1$_C$, C*H*$_2$Ph (3H)), 4.67-4.44 (m, 8H, C*H*$_2$Ph, C*H*$_2$N$_3$b), 4.44 (m, 1H, H-2$_B$), 4.38 (d, J = 10.8 Hz, 1H, C*H*$_2$Ph), 4.28 (d, J = 12.1 Hz, 1H, C*H*$_2$Ph), 4.11 (m, J = 13.0, 5.3, 1.5 Hz, 1H, H-1a$_{All}$), 4.05 (dd, $J_{3,4}$ = 9.4 Hz, $J_{2,3}$ = 3.1 Hz, 1H, H-3$_A$), 4.01-3.90 (m, 5H, H-1b$_{All}$, H-5$_A$, H-2$_E$, H-3$_C$, H-5$_E$), 3.79-3.67 (m, 7H, OC*H*$_3$, H-5$_C$, H-6a$_E$, H-6b$_E$, H-3$_B$), 3.64 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, 1H, H-4$_E$), 3.60-3.49 (m, 3H, H-4$_A$, H-5$_B$, H-4$_C$), 3.47-3.38 (m, 2H, H-3$_E$, H-4$_B$), 2.74-2.54 (m, 4H, C*H*$_{2Lev}$), 2.08 (s, 3H, C(O)C*H*$_3$), 1.36 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6$_A$), 1.30 (d, $J_{5,6}$ = 6.3 Hz, 3H, H-6$_C$), 1.20 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6$_B$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 206.3 (*C*(O)CH$_{2Lev}$), 172.3 (*C*=O), 165.5 (*C*=O), 159.3 (C$_{Ph}$), 138.8 (C$_{Ph}$), 138.8 (C$_{Ph}$), 138.7 (C$_{Ph}$), 138.6 (C$_{Ph}$), 138.3 (C$_{Ph}$), 138.3 (C$_{Ph}$), 138.1 (C$_{Ph}$), 137.7 (C$_{Ph}$), 133.7 (C-2$_{All}$), 132.9 (*C*H$_{Ph}$), 131.4 (*C*H$_{Ph}$), 130.2 (*C*H$_{Ph}$), 129.8 (*C*H$_{Ph}$), 129.5 (*C*H$_{Ph}$), 128.7-127.4 (*C*H$_{Ph}$), 117.7 (C-3$_{All}$), 113.8 (*C*H$_{Ph}$), 101.4 (C-1$_B$), 99.3 (C-1$_A$), 97.8 (C-1$_E$), 95.9 (C-1$_C$), 81.8 (C-5$_E$), 81.3 (C-3$_E$), 80.3 (C-4$_C$), 80.1 (C-4$_B$), 79.9 (C-3$_C$), 79.1 (C-3$_B$), 77.7 (C-4$_A$), 77.4 (C-3$_A$, C-4$_E$), 75.7, 75.4, 75.1 (4C, *C*H$_2$Ph), 74.8 (C-2$_B$), 73.9, 73.0 (2C, *C*H$_2$Ph), 72.5 (C-2$_C$), 71.4 (*C*H$_2$Ph), 71.4 (C-5$_A$), 71.0 (*C*H$_2$Ph), 70.1 (C-2$_A$), 68.9 (C-5$_B$), 68.5 (C-1$_{All}$), 68.4 (C-2$_E$), 68.3 (C-6$_E$), 67.6

(C-5_C), 55.3 (O*C*H_3), 53.1 (*C*H_2N_3), 38.1 (*C*H_{2Lev}), 31.0 (C(O)*C*H_3), 28.3 (*C*H_{2Lev}), 18.7 (C-6_C), 18.6 (C-6_A), 18.2 (C-6_B). HR-ESI-TOF-MS *m/z* 1688.7185 $[M + Na]^+$ (calcd for $C_{97}H_{107}N_3O_{22}Na$, 1688.7244).

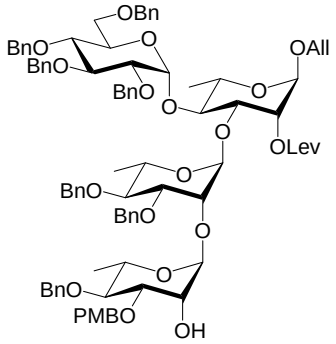
Allyl (4-*O*-benzyl-2-*O*-chloroacetyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-levulinoyl-α-L-rhamnopyranoside (22).



Acceptor **20** (769 mg, 668 μmol) and donor **14** (791 mg, 1.34 mmol, 2.0 equiv.) in anhydr. Et_2O (10 mL) containing 4 Å AW-MS were stirred for 30 min at -10 °C under Ar. TMSOTf (12 μL, 67 μmol, 0.1 equiv.) was added keeping rigorously anhydr. conditions. After stirring for 1 h at -10 °C to rt, Et_3N (100 μL) was added. The suspension was filtered and solvents were evaporated. The residue was purified by FC (Tol/EtOAc 95:5 to 8:2) to give tetrasaccharide **22** (1.03 g) as a white sticky solid slightly contaminated with trichloroacetamide. R_f 0.46 (Chex/EtOAc 7:3); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.38-7.09 (m, 37H, C*H*$_{Ph}$), 6.84-6.80 (m, 2H, C*H*$_{Ph}$), 5.89 (m, 1H, H-2_{All}), 5.57 (dd, $J_{2,3}$ = 2.9 Hz, $J_{1,2}$ = 1.8 Hz, 1H, H-2_A), 5.29 (ddd, *J* = 17.3, 3.1, 1.5 Hz, 1H, H-$3a_{All}$), 5.20 (ddd, *J* = 10.4, 2.6, 1.3 Hz, 1H, H-$3b_{All}$), 5.11 (dd, $J_{2,3}$ = 3.0 Hz, $J_{1,2}$ = 2.1 Hz, 1H, H-2_C), 5.06 (d, $J_{1,2}$ = 1.3 Hz, 1H, H-1_A), 5.01 (d, $J_{1,2}$ = 3.1 Hz, 1H, H-1_E), 4.95 (br s, 1H, H-1_B), 4.94 (d, *J* = 11.1 Hz, 1H, C*H*$_2$Ph), 4.89 (d, *J* = 11.0 Hz, 1H, C*H*$_2$Ph), 4.88 (d, *J* = 10.9 Hz, C*H*$_2$Ph), 4.85-4.74 (m, 4H, C*H*$_2$Ph, H-1_C), 4.67-4.52 (m, 7H, C*H*$_2$Ph), 4.47 (d, *J* = 11.0 Hz, 1H, C*H*$_2$Ph), 4.45 (d, *J* = 11.0 Hz, 1H, C*H*$_2$Ph), 4.40 (bdd, $J_{2,3}$ = $J_{1,2}$ = 2.0 Hz, 1H, H-2_B), 4.36 (d, *J* = 12.0 Hz, 1H, C*H*$_2$Ph), 4.13 (m, *J* = 12.8, 5.3, 1.6 Hz, 1H, H-$1a_{All}$), 4.04-3.90 (m, 7H, C*H*$_2$Cla, H-5_A, H-$1b_{All}$, H-5_E, H-3_C, H-3_A, H-3_E), 3.84 (d, *J* = 15.0 Hz, 1H, C*H*$_2$Clb), 3.81-3.66 (m, 8H, H-$6a_E$, H-$6b_E$, H-4_E, H-3_B, H-5_C, OC*H*$_3$), 3.62-3.53 (m, 2H, H-4_A, H-5_B), 3.49 (dd, $J_{3,4}$ = 9.7 Hz, $J_{3,4}$ = 3.3 Hz, 1H, H-2_E), 3.37 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 2H, H-4_B, H-4_C), 2.77-2.53 (m, 4H, C*H*$_{2Lev}$), 2.08 (s, 3H, C(O)C*H*$_3$), 1.33 (d, $J_{5,6}$ = 6.1 Hz, 6H, H-6_A, H-6_C), 1.20 (d, $J_{5,6}$ = 6.1 Hz, 3H, H-6_B). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 206.2 (*C*(O)CH_{2Lev}), 172.3 (*C*=O$_{Lev}$), 166.5 (*C*=O$_{AcCl}$), 159.3 (C$_{Ph}$), 138.8-137.9 (C$_{Ph}$), 133.7 (C-2_{All}), 130.1-125.4 (*C*H$_{Ph}$), 117.8 (C-3_{All}), 113.9 (*C*H$_{Ph}$), 101.4 (C-1_B), 99.0 (C-1_A), 97.7 (C-1_E), 95.9 (C-1_C), 81.8 (C-3_E), 81.1 (C-2_E), 80.0 (C-4_B*), 79.9 (C-4_C*), 79.7 (C-3_C), 79.0 (C-3_B), 77.6 (C-4_A), 77.4 (C-4_E), 77.2 (C-3_A), 75.7, 75.4, 75.3, 75.1 (4C, *C*H_2Ph), 74.8 (C-2_B), 73.9, 72.9 (2C, *C*H_2Ph), 72.5 (C-2_C), 71.7 (*C*H_2Ph), 71.3 (C-5_A), 71.1 (C-2_A), 70.9 (*C*H_2Ph), 68.8 (C-5_B), 68.5 (C-1_{All}), 68.4 (C-5_E), 68.2 (C-6_E), 67.5 (C-5_C), 55.3 (O*C*H_3), 41.0

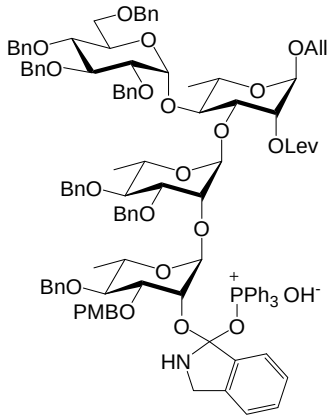
(CH_2Cl), 38.0 (CH_{2Lev}), 29.9 (C(O)CH_3), 28.2 (CH_{2Lev}), 18.7 (C-6_A*), 18.4 (C-6_C*), 18.1 (C-6_B). HR-ESI-TOF-MS *m/z* 1583.6742 $[M + H]^+$ (calcd for $C_{91}H_{104}ClO_{22}$, 1583.6708), *m/z* 1605.6541 $[M + Na]^+$ (calcd for $C_{91}H_{103}ClO_{22}Na$, 1605.6527).

Allyl (4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-levulinoyl-α-L-rhamnopyranoside (10).



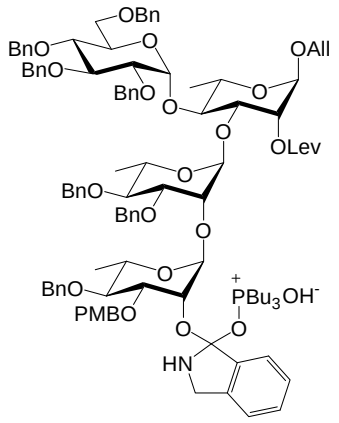
Route b. PPh_3 (4.84 g, 18.4 mmol, 5.0 equiv.) and SiO_2 (1.54 g) were added to tetrasaccharide **21** (6.15 g) in THF/H_2O (36.9 mL, 9:1 *v/v*). The mixture was stirred for 24 h at rt, then additional portions of PPh_3 (4.84 g, 18.4 mmol, 5.0 equiv.) and SiO_2 (1.54 g) were added. The mixture was stirred overnight at rt, filtered, washed with several portions of CH_2Cl_2 and solvents were evaporated. The residue was purified by FC (Tol/EtOAc 95:5 to 8:2) to give acceptor **10** (3.39 g, 60% from **20**) as a white foam along with unreacted **21** (476 mg, 8%). See manuscript for *route a* and analytical data.

Allyl (4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-2-*O*-(1-*O*-(triphenylphosphonium)isoindol-1-yl)-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-levulinoyl-α-L-rhamnopyranoside (21a).



Eluting the chromatographic column of the precedent reaction (*route a*, see manuscript) using CH_2Cl_2/MeOH 95:5 to 100% MeOH gave **21a** (632 mg, 9%) as a white foam. R_f 0.16 (CH_2Cl_2/MeOH 95:5); $[\alpha]^{25}_D$ +15° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.51 (m, *J* = 7.4 Hz, 1H, N*H*), 8.16-8.12 (m, 1H, CH_{Ph}), 7.82-7.03 (m, 55H, CH_{Ph}), 6.79-6.75 (m, 2H, CH_{Ph}), 5.89 (m, 1H, H-2_{All}), 5.54 (dd, $J_{2,3}$ = 3.3 Hz, $J_{1,2}$ = 2.0 Hz, 1H, H-2_A), 5.29 (m, *J* = 17.2, 3.0, 1.5 Hz, 1H, H-$3a_{All}$), 5.20 (m, *J* = 10.4, 2.6, 1.3 Hz, 1H, H-$3b_{All}$), 5.13-5.10 (m, 2H, H-2_C, H-1_A), 5.01-4.72 (m, 11H, CH_2NH, H-1_E, H-1_B, H-1_C, CH_2Ph), 4.66-4.37 (m, 10H, CH_2Ph (9H), H-2_B), 4.29 (d, *J* = 11.8 Hz, 1H, CH_2Ph), 4.13 (m, *J* = 12.9, 5.3, 1.4 Hz, 1H, H-$1a_{All}$), 4.02-3.91 (m, 6H, H-5_A, H-$1b_{All}$, H-3_A, H-3_C, H-5_E, H-2_E), 3.81-3.69 (m, 7H, OCH_3, H-5_C, H-$6a_E$, H-$6b_E$, H-3_B), 3.68-3.52 (m, 3H, H-4_E, H-4_A, H-5_B), 3.50-3.42 (m, 2H, H-4_C, H-3_E), 3.67 (pt, $J_{3,4} = J_{4,5}$ = 9.3 Hz, 1H, H-4_B), 2.76-2.54 (m, 4H, CH_{2Lev}), 2.08 (s, 3H, CH_3), 1.35 (d, $J_{5,6}$ = 6.2 Hz, 3H, C-6_A), 1.33 (d, $J_{5,6}$ = 6.2 Hz, 3H, C-6_C), 1.20 (d, $J_{5,6}$ = 6.2 Hz, 3H, C-6_B). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 205.9 (*C*(O)CH_{2Lev}), 172.2 (*C*(O)CH_{2Lev}), 165.5 (*C*OPPh_3^+), 159.3 (C_{Ph}), 141.4 (C_{Ph}), 141.3 (C_{Ph}), 138.8 (C_{Ph}), 138.8 (C_{Ph}), 138.6 (C_{Ph}), 138.6 (C_{Ph}), 138.4 (C_{Ph}), 138.3 (C_{Ph}), 138.0 (C_{Ph}), 134.6 (C-2_{All}), 133.7-126.9 (*C*H$_{Ph}$), 117.6 (C-3_{All}), 113.9 (*C*H$_{Ph}$), 101.3 (C-1_B), 99.1 (C-1_A), 97.8 (C-1_E), 96.0 (C-1_C), 81.8 (C-5_E), 81.3 (C-3_E), 80.3 (C-4_C), 80.1 (C-4_B), 79.8 (C-3_C), 79.1 (C-3_B), 78.0 (C-4_A), 77.8 (C-4_E), 77.0 (C-3_A), 75.7, 75.2, 75.1 (4C, *C*H_2Ph), 74.4 (C-2_B), 73.9, 73.0 (2C, *C*H_2Ph), 72.5 (C-2_C), 71.4 (C-5_A), 71.2, 70.9 (2C, *C*H_2Ph), 69.9 (C-2_A), 68.9 (C-5_B), 68.5 (C-1_{All}), 68.5 (C-2_E), 68.3 (C-6_E), 67.6 (C-5_C), 55.4 (O*C*H_3), 43.2 (*C*H_2NH), 38.1 (*C*H_{2Lev}), 29.8 (C(O)*C*H_3), 28.3 (*C*H_{2Lev}), 18.7 (C-6_A), 18.6 (C-6_C), 18.1 (C-6_B). ^{31}P NMR ($CDCl_3$, 100 MHz) δ: 40.1 ppm (s, PPh_3). HR-ESI-TOF-MS *m/z* 1900.8340 $[M]^+$ (calcd for $C_{115}H_{123}NO_{22}P$, 1900.8274).

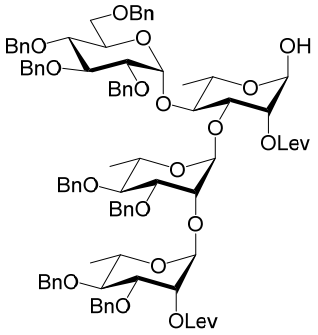
Allyl (4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-2-*O*-(1-*O*-(tributylphosphonium)isoindol-1-yl)-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-levulinoyl-α-L-rhamnopyranoside (21b).



PBu_3 (225 μL, 0.90 mmol, 3.0 equiv.) was added to tetrasaccharide **21** (500 mg) in anhydr. THF (10 mL). The mixture was stirred for 2 h at rt, then H_2O (27 μL, 1.5 mmol, 5.0 equiv.) was added. The mixture was stirred overnight at rt and solvents were evaporated. The residue was purified by

FC (CH_2Cl_2/MeOH 95:5 to 9:1) to give **21b** (245 mg, 49% from **21**) as a white foam. R_f 0.15 (CH_2Cl_2/MeOH 95:5); $[\alpha]^{25}_D$ +13° (*c* 1.0, $CHCl_3$); ^{1}H NMR (Py-d_5, 400 MHz) δ: 9.41 (m, $J_{2,NH}$ = 7.6 Hz, 1H, N*H*), 8.34-8.30 (m, 1H, CH_{Ph}), 7.63-7.20 (m, 40H, CH_{Ph}), 7.04-6.99 (m, 2H, CH_{Ph}), 6.28 (br s, 1H, H-2_A), 5.85 (m, 1H, H-2_{All}), 5.81 (br s, 1H, H-1_A), 5.71 (br s, 1H, H-2_C), 5.64 (br s, 1H, H-1_B), 5.49 (d, 1H, H-1_E), 5.28-4.63 (m, 22H, CH_2Ph, H-$3a_{All}$, H-1_C, H-$3b_{All}$, H-2_B, CH_2NHa, CH_2NHb), 4.57 (dd, $J_{3,4}$ = 8.9 Hz, $J_{2,3}$ = 2.4 Hz, 1H, H-3_C), 4.49 (dd, $J_{3,4}$ = 9.3 Hz, $J_{2,3}$ = 2.9 Hz, 1H, H-3_A), 4.46-4.38 (m, 2H, H-5_A, H-5_C), 4.36-4.27 (m, 2H, H-3_E, H-3_B), 4.22-4.04 (m, 6H, H-$1a_{All}$, H-$6a_E$, H-4_C, H-5_B, H-5_E, H-$6b_E$), 4.03-3.90 (m, 4H, H-$1b_{All}$, H-4_E, H-4_A, H-4_B), 3.82 (dd, $J_{2,3}$ = 9.8 Hz, $J_{1,2}$ = 3.0 Hz, 1H, H-2_E), 3.66 (s, 3H, OCH_3), 2.82-2.69 (m, 4H, CH_{2Lev}), 2.47-2.37 (m, 6H, CH_{2Bu}), 2.03 (s, 3H, CH_{3Lev}), 1.64 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6_B), 1.63-55 (m, 6H, CH_{2Bu}), 1.52 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_C), 1.50 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6_A), 1.38-1.26 (m, 6H, CH_{2Bu}), 0.82-0.77 (m, 9H, CH_{3Bu}). ^{13}C NMR (Py-d_5, 100 MHz) δ: 206.1 (*C*(O)CH_{2Lev}), 173.1 (*C*(O)CH_{2Lev}), 167.1 (*C*OPBu_3^+), 160.2 (C_{Ph}), 143.0-139.4 (C_{Ph}), 134.7 (C-2_{All}), 133.9-128.2 (*C*H$_{Ph}$), 117.7 (C-3_{All}), 114.8 (*C*H$_{Ph}$), 102.4 (C-1_B), 100.1 (C-1_A), 98.6 (C-1_E), 96.8 (C-1_C), 82.6 (C-3_E), 82.3 (C-2_E), 81.2 (C-4_A), 80.9 (C-4_B), 80.7 (C-3_C), 80.2 (C-3_B), 79.0 (C-4_C), 78.8 (C-4_E), 78.3 (C-3_A), 76.1, 75.8, 75.6, 75.5 (4C, *C*H_2Ph), 75.5 (C-2_B), 74.3, 73.7 (2C, *C*H_2Ph), 73.4 (C-2_C), 72.4 (C-5_A), 72.0, 71.8 (2C, *C*H_2Ph), 71.1 (C-2_A), 69.8 (C-5_B), 69.7 (C-6_E), 69.4 (C-5_C), 68.8 (C-1_{All}), 68.6 (C-5_E), 55.7 (O*C*H$_3$), 42.4 (*C*H_2NH), 38.5 (*C*H_{2Lev}), 29.9 (C(O)*C*H$_3$), 29.1 (*C*H_{2Lev}), 24.5 (*C*H_{2Bu}), 24.4 (*C*H_{2Bu}), 23.8 (*C*H_{2Bu}), 22.6 (*C*H_{2Bu}), 22.0 (*C*H_{2Bu}), 19.7, 19.0, 19.0 (3C, C-6_A, C-6_B, C-6_C), 13.9 (*C*H_{3Bu}). HR-ESI-TOF-MS *m/z* 1840.9080 $[M]^+$ (calcd for $C_{109}H_{135}NO_{22}P$, 1841.9247).

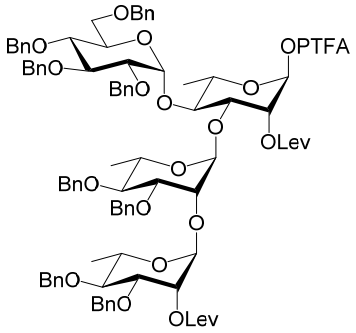
(3,4-Di-*O*-benzyl-2-*O*-levulinyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-levulinyl-α-L-rhamnopyranose (24).



[Ir] (91 mg, 0.11 mmol, 0.1 equiv.) was dissolved in anhydr. THF (5.4 mL) and the red solution was degassed. Hydrogen was bubbled through the solution for 15 min, and the resulting yellow solution was once again degassed. Tetrasaccharide **23** (1.69 g, 1.07 mmol) in anhydr. THF (5.4 mL) was added and the mixture was stirred for 20 h at rt under Ar. Iodine (544 mg, 2.14 mmol, 2.0 equiv.) in THF/H_2O (6.4 mL, 4:1 v/v) was added and the mixture was stirred for 1 h at rt. Freshly prepared 10% aq. $NaHSO_3$ was added and the mixture was diluted with CH_2Cl_2 (250 mL)

and water (100 mL). The aq. phase was extracted with CH_2Cl_2 (3×250 mL) and the organic layer was dried over anhydr. Na_2SO_4, filtered and evaporated to dryness. The residue was purified by FC (Tol/EtOAc 8:2 to 7:3) to give hemiacetal **24** (1.52 g, 92%, ratio α/β > 20:1) as a light yellow foam. R_f 0.19 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ +22° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (α): 7.37-7.11 (m, 40H, C*H*$_{Ph}$), 5.56 (dd, $J_{2,3}$ = 3.3 Hz, $J_{1,2}$ = 1.8 Hz, 1H, H-2$_A$), 5.12 (br d, 1H, H-2$_C$), 5.10-5.06 (m, 2H, H-1$_C$, H-1$_A$), 5.00-4.90 (m, 5H, H-1$_E$, H-1$_B$, C*H*$_2$Ph), 4.85 (d, *J* = 11.0 Hz, 1H, C*H*$_2$Ph), 4.81 (d, *J* = 11.0 Hz, 1H, *C*H$_2$Ph), 4.75 (d, *J* = 11.7 Hz, 1H, C*H*$_2$Ph), 4.72 (d, *J* = 11.4 Hz, 1H, C*H*$_2$Ph), 4.67-4.51 (m, 7H, C*H*$_2$Ph), 4.48 (d, *J* = 10.8 Hz, 1H, C*H*$_2$Ph), 4.41-4.36 (m, 2H, H-2$_B$, C*H*$_2$Ph), 4.05-3.91 (m, 6H, H-3$_C$, H-5$_A$, H-5$_E$, H-3$_A$, H-3$_E$, H-5$_C$), 3.82-3.68 (m, 4H, H-6a$_E$, H-6b$_E$, H-3$_B$, H-4$_E$), 3.62-3.53 (m, 2H, H-5$_B$, H-4$_A$), 3.48 (dd, $J_{2,3}$ = 9.7 Hz, $J_{1,2}$ = 3.1 Hz, 1H, H-2$_E$), 3.43 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, 1H, H-4$_C$), 3.40 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, 1H, H-4$_B$), 3.06 (d, $J_{OH,1}$ = 4.2 Hz, 1H, O*H*-1$_C$), 2.76-2.47 (m, 8H, C*H*$_{2Lev}$), 2.08 (s, 6H, CH$_{3Lev}$), 1.35 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6$_A$), 1.32 (d, $J_{5,6}$ = 6.3 Hz, 3H, H-6$_C$), 1.21 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6$_B$). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (α): 206.0 (2C, *C*(O)CH$_{2Lev}$), 172.2 (*C*=O), 171.8 (*C*=O), 138.9-138.3 (C$_{Ph}$), 128.7-127.4 (*C*H$_{Ph}$), 101.1 (C-1$_B$), 99.4 (C-1$_A$), 97.8 (C-1$_E$), 91.3 (C-1$_C$), 81.9 (C-3$_E$), 81.4 (C-2$_E$), 80.2 (C-4$_C$), 80.1 (C-4$_B$), 79.0 (C-3$_C$, C-3$_B$), 78.2 (C-4$_A$), 77.8 (2C, C-3$_A$, C-4$_E$), 75.7, 75.4, 75.4, 75.2 (4C, *C*H$_2$Ph), 74.9 (C-2$_B$), 73.9, 73.1 (4C, *C*H$_2$Ph), 72.8 (C-2$_C$), 71.7 (*C*H$_2$Ph), 71.5 (C-5$_A$), 70.9 (*C*H$_2$Ph), 69.5 (C-2$_A$), 68.9 (C-5$_B$), 68.5 (C-6$_E$), 68.4 (C-5$_E$), 67.6 (C-5$_C$), 38.2 (*C*H$_{2Lev}$), 38.1 (*C*H$_{2Lev}$), 29.8 (C(O)*C*H$_3$), 29.8 (C(O)*C*H$_3$), 28.3 (*C*H$_{2Lev}$), 28.2 (*C*H$_{2Lev}$), 18.9 (C-6$_A$), 18.5 (C-6$_C$), 18.1 (C-6$_B$). HR-ESI-TOF-MS *m/z* 1535.6907 $[M + H]^+$ (calcd for $C_{90}H_{103}O_{22}$, 1535.6941), *m/z* 1557.6749 $[M + Na]^+$ (calcd for $C_{90}H_{102}O_{22}Na$, 1557.6760).

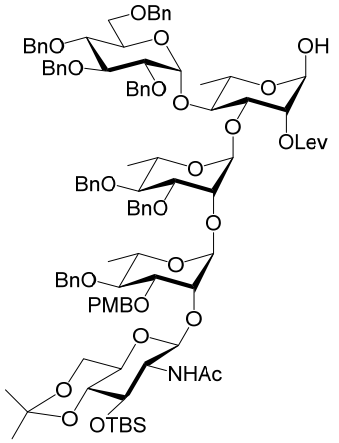
(3,4-Di-*O*-benzyl-2-*O*-levulinyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-levulinyl-α-L-rhamnopyranosyl *N*-(phenyl)trifluoroacetimidate (6).



PTFACl[18] (254 mg, 1.22 mmol, 2.0 equiv.) and Cs_2CO_3 (219 mg, 673 µmol, 1.1 equiv.) were added to hemiacetal **24** (940 mg, 612 µmol) in acetone (6.1 mL). The mixture was stirred for 3 h at rt, filtered and evaporated to dryness. The residue was purified by FC (Tol/EtOAc 95:5 to 9:1 + 1% Et_3N) to furnish PTFA **6** (971 mg, 93%) as a white foam. R_f 0.47 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ +11° (*c* 1.0, $CHCl_3$); ^{1}H NMR (Py-d$_5$, 400 MHz) δ: 7.67-7.10 (m, 45H, C*H*$_{Ph}$), 7.00 (bs, 1H, H-1$_C$), 6.09 (br s, 1H, H-2$_A$), 5.89 (br s, 1H, H-2$_C$), 5.72-5.68 (m, 2H, H-1$_A$, H-1$_B$), 5.50 (bd, $J_{1,2}$ =

3.0 Hz, 1H, H-1_E), 5.25-5.07 (m, 5H, CH_2Ph), 5.02-4.77 (m, 11H, CH_2Ph, H-2_B), 4.73 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.70-4.65 (m, 1H, H-3_C), 4.61 (d, J = 11.2 Hz, 1H, CH_2Ph), 4.45-4.08 (m, 10H, H-5_E, H-5_A, H-3_A, H-3_E, H-3_B, H-4_C, H-5_C, H-5_B, H-$6a_E$, H-$6b_E$), 4.01 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, 1H, H-4_E), 3.95 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, 1H, H-4_B), 3.90-3.83 (m, 2H, H-4_A, H-2_E), 2.90-2.70 (m, 8H, CH_{2Lev}), 2.03 (s, 3H, CH_{3Lev}), 2.02 (s, 3H, CH_{3Lev}), 1.64 (d, $J_{5,6}$ = 5.5 Hz, 3H, H-6_C), 1.53 (d, $J_{5,6}$ = 6.1 Hz, 3H, H-6_B), 1.52 (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6_A). ^{13}C NMR (Py-d_5, 100 MHz) δ: 206.3 (C(O)CH_{2Lev}), 206.0 (C(O)CH_{2Lev}), 172.9 (C=O), 172.8 (C=O), 144.3 (C=NPh), 140.2-139.2 (C_{Ph}), 129.7-128.2 (CH_{Ph}), 120.4 (CH_{Ph}), 102.4 (C-1_B), 100.5 (C-1_A), 99.0 (C-1_E), 82.5 (C-3_E), 82.1 (C-2_E), 81.0 (C-4_A), 80.6 (C-4_B), 79.9 (C-3_C), 79.8 (C-3_B), 78.8 (C-3_A), 78.5 (C-4_E), 77.9 (C-4_C), 76.0, 75.9 (2C, CH$_2$Ph), 75.8 (C-2_B), 75.6, 75.5, 74.3, 73.8 (4C, CH$_2$Ph), 72.5 (C-5_E), 72.0 (CH$_2$Ph), 71.6 (C-2_C), 71.6 (CH$_2$Ph), 71.4 (C-5_C), 70.1 (C-2_A), 70.0 (C-5_B), 69.5 (C-6_E), 69.3 (C-5_A), 38.4 (CH$_{2Lev}$), 38.3 (CH$_{2Lev}$), 29.9 (CH_{3Lev}), 29.8 (CH_{3Lev}), 28.9 (CH$_{2Lev}$), 28.8 (CH$_{2Lev}$), 19.6 (C-6_C), 18.9 (C-6_B*), 18.7 (C-6_A*).

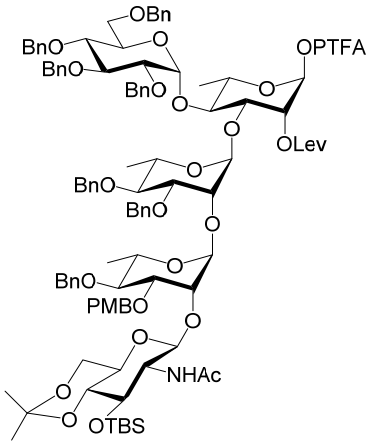
(2-Acetamido-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-(1→2)-(4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-levulinyl-α-L-rhamnopyranose (29).



Bu_3SnH (2.05 mL, 7.62 mmol, 10.0 equiv.) and AIBN (125 mg, 0.762 mmol, 1.0 equiv.) were added to allyl glycoside **27** (1.50 g, 0.762 mmol) in anhydr. toluene (30.5 mL). After stirring for 2 h at reflux under Ar, solvents were evaporated. The residue was purified by FC (Tol/EtOAc 95:5 to 9:1 + 1% Et_3N) to give acetamide **28** contaminated with tin salts (1.42 g) as a white foam. [Ir] (64 mg, 76 μmol, 0.10 equiv.) was dissolved in anhydr. THF (3.8 mL) and the red solution was degassed. Hydrogen was bubbled through the solution for 15 min and the resulting the yellow solution was once again degassed. The crude **28** in anhydr. THF (3.8 mL) was added. After stirring for 16 h at rt under Ar, iodine (387 mg, 1.52 mmol, 2.0 equiv.) in THF/H_2O (4.6 mL, 4:1 v/v) was added. After an additional 1 h at rt, freshly prepared 10% aq. $NaHSO_3$ was added. The mixture was partitioned between CH_2Cl_2 (100 mL) and water (50 mL) and the aq.

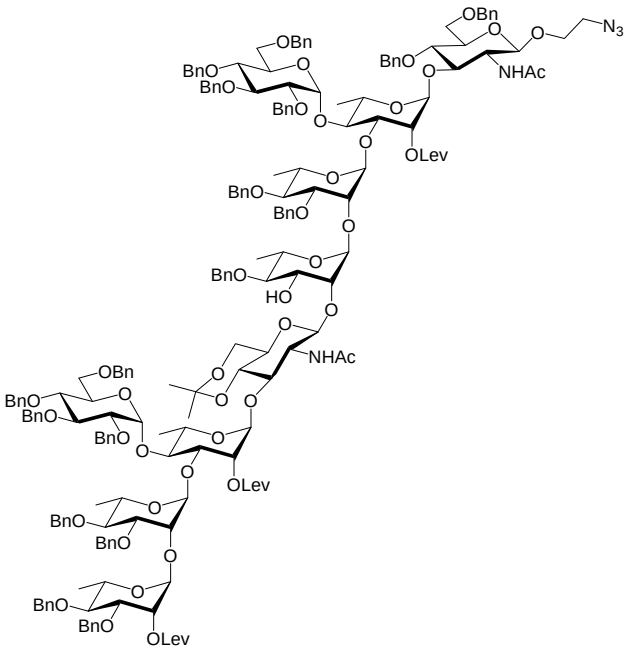
phase was extracted with CH_2Cl_2 (3×100 mL). The organic layer was dried over anhydr. Na_2SO_4, filtered and evaporated to dryness. The residue was purified by FC (Tol/EtOAc 9:1 to 6:4 + 1% Et_3N) to give hemiacetal **29** (810 mg, 58% from **27**) as a white foam. R_f 0.15 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ +12° (*c* 0.5, $CHCl_3$); ^{1}H NMR (Py-d_5, 400 MHz) δ: 9.27 (br s, 1H, N*H*), 7.68-7.26 (m, 37H, C*H*$_{Ph}$), 7.01-6.96 (m, 2H, C*H*$_{Ph}$), 5.85 (br s, 1H, H-2$_C$), 5.76-5.72 (m, 2H, H-1$_A$, H-1$_C$), 5.65 (d, $J_{1,2}$ = 7.2 Hz, 1H, H-1$_{D'}$), 5.58 (br s, 1H, H-1$_B$), 5.48 (d, $J_{1,2}$ = 2.7 Hz, 1H, H-1$_E$), 5.29-4.97 (m, 8H, C*H*$_2$Ph, H-2$_B$), 4.96-4.62 (m, 12H, C*H*$_2$Ph, H-3$_C$, H-2$_A$, H-3$_{D'}$), 4.55 (dq, 1H, H-5$_C$), 4.43 (br d, *J* = 9.9 Hz, 1H, H-5$_E$), 4.39-4.02 (m, 9H, H-3$_E$, H-3$_A$, H-3$_B$, H-5$_A$, H-6a$_E$, H-4$_C$, H-5$_B$, H-6b$_E$, H-4$_E$), 3.98 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, 1H, H-4$_A$), 3.88 (pt, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, 1H, H-4$_B$), 3.85-3.73 (m, 3H, H-2$_E$, H-2$_{D'}$, H-6a$_{D'}$), 3.58 (s, 3H, OC*H*$_3$), 3.56-3.42 (m, 3H, H-6b$_{D'}$, H-5$_{D'}$, H-4$_{D'}$), 2.83-2.65 (m, 4H, C*H*$_{2Lev}$), 2.28 (s, 3H, C(O)C*H*$_{3Ac}$), 1.99 (s, 3H, C(O)C*H*$_{3Lev}$), 1.68 (d, $J_{5,6}$ = 6.1 Hz, 3H, H-6$_C$), 1.52 (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6$_B$), 1.46 (s, 3H, C*H*$_{3Iso}$), 1.39 (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6$_A$), 1.29 (s, 3H, C*H*$_{3Iso}$), 1.02 (s, 9H, C(C*H*$_3$)$_3$), 0.24 (s, 3H, Si(C*H*$_3$)$_2$), 0.21 (s, 3H, Si(C*H*$_3$)$_2$). ^{13}C NMR (Py-d_5, 100 MHz) δ: 206.0 (*C*(O)CH$_{2Lev}$), 173.2 (*C*=O), 170.7 (*C*(O)CH$_{3Ac}$), 160.3 (C$_{Ph}$), 140.3-139.7 (C$_{Ph}$), 131.6-128.2 (*C*H$_{Ph}$), 114.7 (*C*H$_{Ph}$), 102.9 (C-1$_B$), 102.8 (C-1$_{D'}$), 102.5 (C-1$_A$), 99.8 (*C*(CH$_3$)$_2$), 98.6 (C-1$_E$), 92.1 (C-1$_C$), 82.6 (C-3$_E$), 82.6 (C-2$_E$), 81.7 (C-4$_A$), 81.3 (C-3$_C$, C-4$_B$), 80.2 (C-3$_A$), 79.7 (C-4$_C$), 79.6 (C-3$_B$), 78.4 (C-4$_E$), 76.7 (C-2$_A$), 76.1 (2C, *C*H$_2$Ph), 75.8 (C-4$_{D'}$), 75.8 (*C*H$_2$Ph), 75.5 (C-2$_B$), 75.3 (*C*H$_2$Ph), 75.0 (C-2$_C$), 74.2, 74.0, 72.8 (3C, *C*H$_2$Ph), 72.7 (C-3$_{D'}$), 72.5 (C-5$_E$), 71.8 (*C*H$_2$Ph), 69.8 (C-5$_B$), 69.7 (C-5$_A$), 69.6 (C-6$_E$), 67.9 (C-5$_C$), 67.5 (C-5$_{D'}$), 62.9 (C-6$_{D'}$), 60.4 (C-2$_{D'}$), 55.5 (O*C*H$_3$), 38.6 (*C*H$_{2Lev}$), 29.9 (C(O)*C*H$_{3Lev}$), 29.7 (*C*H$_{3Iso}$), 29.2 (*C*H$_{2Lev}$), 26.5 (C(*C*H$_3$)$_3$), 24.5 (C(O)*C*H$_{3Ac}$), 20.1 (C-6$_C$), 19.6 (*C*H$_{3Iso}$), 19.0 (C-6$_B$), 18.9 (*C*(CH$_3$)$_3$), 18.8 (C-6$_A$), -3.4 (Si(*C*H$_3$)$_2$), -4.2 (Si(*C*H$_3$)$_2$). HR-ESI-TOF-MS *m/z* 1824.8639 [M + H]$^+$ (calcd for $C_{103}H_{130}NO_{26}Si$, 1824.8650), *m/z* 1846.8492 [M + Na]$^+$ (calcd for $C_{103}H_{129}NO_{26}SiNa$, 1846.8469).

(2-Acetamido-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-(1→2)-(4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-2-*O*-levulinyl-α-L-rhamnopyranosyl *N*-(phenyl)trifluoroacetimidate (7).



N-(Phenyl)trifluoroacetimidoyl chloride[18] (177 mg, 0.851 mmol, 2.0 equiv.) and Cs_2CO_3 (153 mg, 468 μmol, 1.1 equiv.) were added to a solution of hemiacetal **29** (777 mg, 0.426 mmol) in acetone (2.1 mL). The mixture was stirred for 2 h at rt, filtered and evaporated to dryness. The residue was purified by flash chromatography (Tol/EtOAc 95:5 to 9:1 + 1% Et_3N) to furnish donor **7** (753 mg, 89%) as a white foam. R_f 0.48 (Chex/EtOAc 7:3); $[\alpha]^{25}_D$ +4° (*c* 0.5, $CHCl_3$); ^{1}H NMR (Py-d_5, 400 MHz) δ: 7.67-7.09 (m, 42H, CH_{Ph}), 7.03-6.97 (m, 4H, CH_{Ph}, NH, H-1_C), 5.86 (br s, 1H, H-2_C), 5.73 (br s, 1H, H-1_A), 5.65-5.59 (m, 2H, H-$1_{D'}$, H-1_B), 5.46 (d, 1H, $J_{1,2}$ = 2.7 Hz, H-1_E), 5.23-4.57 (m, 18H, CH_2Ph, H-2_B, H-2_A), 4.67-4.53 (m, 2H, H-$3_{D'}$,H-3_C), 4.38 (br d, *J* = 10.0 Hz, 1H, H-5_E), 4.35-4.13 (m, 7H, H-3_A, H-5_A, H-3_E, H-5_C, H-3_B, H-$6a_E$, H-4_C), 4.13-3.95 (m, 4H, H-5_B, H-$6b_E$, H-4_E, H-4_B), 3.88 (pt, $J_{3,4} = J_{4,5}$ = 9.1 Hz, 1H, H-4_A), 3.85-3.77 (m, 3H, H-2_E, H-$2_{D'}$, H-$6a_{D'}$), 3.63 (s, 3H, OCH_3), 3.61-3.44 (m, 3H, H-$6b_{D'}$, H-$5_{D'}$, H-$4_{D'}$), 2.75 (br s, 4H, CH_{2Lev}), 2.26 (s, 3H, C(O)CH_{3Ac}), 2.00 (s, 3H, C(O)CH_{3Lev}), 1.63 (d, $J_{5,6}$ = 5.6 Hz, 3H, H-6_C), 1.53 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6_B), 1.49 (d, $J_{5,6}$ = 6.1 Hz, 3H, H-6_A), 1.48 (s, 3H, CH_{3Iso}), 1.34 (s, 3H, CH_{3Iso}), 1.04 (s, 9H, C(CH_3)$_3$), 0.25 (s, 3H, Si(CH_3)$_2$), 0.23 (s, 3H, Si(CH_3)$_2$). ^{13}C NMR (Py-d_5, 100 MHz) δ: 205.9 (*C*(O)CH_{2Lev}), 172.9 (*C*=O), 170.7 (*C*(O)CH_{3Ac}), 160.3 (C_{Ph}), 144.3 (*C*=NPh), 140.2-138.4 (C_{Ph}), 131.6-126.2 (*C*H$_{Ph}$), 102.9 (2C, C-1_D, C-1_B), 102.7 (C-1_A), 99.8 (*C*(CH$_3$)$_2$), 99.3 (C-1_E), 82.6 (C-3_E), 82.4 (C-2_E), 81.7 (C-4_B), 81.2 (C-4_A), 80.3 (C-3_C), 80.2 (C-3_A), 79.6 (C-3_B), 79.0 (C-4_C), 78.5 (C-4_E), 76.7 (C-2_A), 76.2, 76.1 (2C, *C*H$_2$Ph), 75.9 (C-$4_{D'}$), 75.9 (*C*H$_2$Ph), 75.8 (C-2_B), 75.5, 74.5, 74.1 (3C, *C*H$_2$Ph), 72.8 (3C, *C*H$_2$Ph, C-$3_{D'}$, C-5_E), 71.8 (C-2_C), 71.4 (C-5_C), 71.3 (*C*H$_2$Ph), 70.1 (C-5_B), 69.8 (C-5_A), 69.5 (C-6_E), 67.6 (C-$5_{D'}$), 63.0 (C-$6_{D'}$), 60.4 (C-$2_{D'}$), 55.6 (O*C*H$_3$), 38.4 (*C*H$_{2Lev}$), 29.8 (C(O)*C*H$_{3Lev}$), 29.7 (*C*H$_{3Iso}$), 28.8 (*C*H$_{2Lev}$), 26.5 (C(*C*H$_3$)$_3$), 24.5 (C(O)*C*H$_{3Ac}$), 19.6 (C-6_C), 19.5 (*C*H$_{3Iso}$), 19.0 (C-6_B), 18.9 (*C*(CH$_3$)$_3$), 18.7 (C-6_A), -3.4 (Si(*C*H$_3$)$_2$), -4.2 (Si(*C*H$_3$)$_2$).

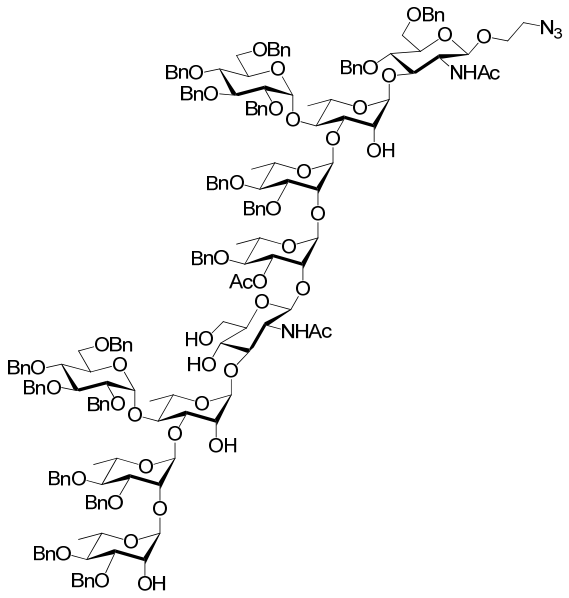
2-Azidoethyl (3,4-di-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-(2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranosyl)-(1→2)-(4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-(2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→3)-2-acetamido-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (36).



H_2O (425 μL) and DDQ (39 mg, 170 μmol, 2.0 equiv.) were added to decasaccharide **5** (313 mg, 85.0 μmol) in anhydr. CH_2Cl_2 (4.3 mL). The mixture was stirred for 1.5 h at rt under Ar. Satd aq $NaHCO_3$ (25 mL) was added and the aq phase was extracted with CH_2Cl_2 (3×25 mL) and dried over anhydr. Na_2SO_4. Solvents were evaporated and the residue was purified by FC (CH_2Cl_2/MeOH 99:1 to 98:2 + 0.5% Et_3N) to give alcohol **36** (211 mg, 70%) as a white foam along with unreacted **5** (40 mg, 13%). R_f 0.61 (CH_2Cl_2/MeOH 95:5); $[\alpha]^{25}_D$ –22° (*c* 0.32, $CHCl_3$); ^{1}H NMR (Py-d_5, 400 MHz) δ: 9.44 (d, J = 7.6 Hz, 1H, N*H*), 9.35 (br s, 1H, N*H*), 7.70-7.25 (m, 85H, CH_{Ph}), 6.63 (br s, 1H, O*H*), 6.09 (dd, $J_{2,3}$ = 2.7 Hz, $J_{1,2}$ = 1.8 Hz, 1H, H-$2_{A'}$), 5.78-5.40 (11H, H-1_A, H-$1_{A'}$, H-1_B, H-$1_{B'}$, H-1_C, H-$1_{C'}$, H-$1_{D'}$, H-1_E, H-$1_{E'}$, H-2_C, H-$2_{C'}$), 5.36-3.63 (m, 79H, H-2_A, H-3_A, H-$3_{A'}$, H-4_A, H-$4_{A'}$, H-5_A, H-$5_{A'}$, H-2_B, H-$2_{B'}$, H-3_B, H-$3_{B'}$, H-4_B, H-$4_{B'}$, H-5_B, H-$5_{B'}$, H-3_C, H-$3_{C'}$, H-4_C, H-$4_{C'}$, H-5_C, H-$5_{C'}$, H-1_D, H-2_D, H-$2_{D'}$, H-3_D, H-$3_{D'}$, H-4_D, H-5_D, H-$6a_D$, H-$6b_D$, H-$6a_{D'}$, H-2_E, H-$2_{E'}$, H-3_E, H-$3_{E'}$, H-4_E, H-$4_{E'}$, H-5_E, H-$5_{E'}$, H-$6a_E$, H-$6b_E$, H-$6a_{E'}$, H-$6b_{E'}$, OCH_2a, OCH_2b, CH_2Ph), 3.54-3.32 (m, 5H, H-$4_{D'}$, H-$5_{D'}$, H-$6b_{D'}$, CH_2N_3a, CH_2N_3b), 2.87-2.62 (m, 12H, 6×CH_{2Lev}), 2.50 (s, 3H, C(O)CH_{3Ac}), 2.36 (s, 3H, C(O)CH_{3Ac}), 2.02 (s, 3H, C(O)CH_{3Lev}), 2.02 (s, 3H, C(O)CH_{3Lev}), 2.00 (s, 3H, C(O)CH_{3Lev}), 1.68 (d, $J_{5,6}$ = 6.1 Hz, 3H, CH_{3Rha}), 1.53 (d, $J_{5,6}$ = 6.2 Hz, 3H, CH_{3Rha}), 1.51-1.43 (m, 12H, 3×CH_{3Rha}, CH_{3Iso}), 1.41 (d, $J_{5,6}$ = 6.1 Hz, 3H, CH_{3Rha}), 1.26 (s, 3H, CH_{3Iso}). ^{13}C NMR (Py-d_5, 100 MHz) δ (partial): 206.3, 206.1, 206.0 (3×*C*(O)CH_{2Lev}), 173.1, 173.0, 172.7 (3C, *C*=O_{Lev}), 171.9 (2C, *C*(O)CH_{3Ac}), 140.2-139.3 (C_{Ph}), 129.3-128.0 (*C*H$_{Ph}$), 103.4, 102.5 (2C), 102.4, 101.0, 100.3, 99.2, 98.4, 98.1, 97.8 (C-1_A, C-$1_{A'}$, C-1_B, C-$1_{B'}$, C-1_C, C-$1_{C'}$, C-1_D, C-$1_{D'}$, C-1_E, C-$1_{E'}$), 83.2, 82.7, 82.6, 82.5, 82.2, 81.4, 81.0, 80.7, 80.4, 80.2, 79.9, 79.6, 78.7, 78.6, 78.5, 78.4, 77.0, 76.1, 75.9, 75.8, 75.7, 75.5, 75.4, 75.0, 74.2, 74.0, 73.9, 73.7, 73.6, 72.8, 72.4, 72.2, 71.9, 71.6, 70.7, 70.0, 69.7, 69.4, 69.2, 68.6, 68.5, 68.1, 67.8 (C-2_A, C-$2_{A'}$, C-3_A, C-$3_{A'}$, C-4_A, C-$4_{A'}$, C-5_A, C-$5_{A'}$, C-2_B, C-$2_{B'}$, C-3_B, C-$3_{B'}$, C-4_B, C-$4_{B'}$, C-5_B, C-$5_{B'}$, C-2_C, C-$2_{C'}$, C-3_C, C-$3_{C'}$, C-4_C, C-$4_{C'}$, C-5_C, C-$5_{C'}$, C-3_D, C-$3_{D'}$, C-4_D, C-$4_{D'}$, C-

5_D, C-$5_{D'}$, C-6_D, C-2_E, C-$2_{E'}$, C-3_E, C-$3_{E'}$, C-4_E, C-$4_{E'}$, C-5_E, C-$5_{E'}$, C-6_E, C-$6_{E'}$, 17×*C*HPh$_2$), 62.9 (C-$6_{D'}$), 58.9 (C-$2_{D'}$), 58.2 (C-2_D), 51.5 (*C*H$_2$N$_3$), 38.4, 38.4, 38.3 (3C, *C*H$_{2Lev}$), 29.9, 29.8, 29.8 (3C, C(O)*C*H$_{3Lev}$), 29.0, 28.9, 28.9 (3C, *C*H$_{2Lev}$), 24.4, 24.2 (2C, C(O)*C*H$_{3Ac}$), 19.8, 19.6, 19.5, 19.0, 18.9 (3C), 18.8 (8C, 6 *C*H$_{3Rha}$, 2 *C*H$_{3Iso}$). HR-ESI-TOF-MS *m/z* 1780.38 $[M + 2H]^{2+}$ (calcd for $C_{203}H_{237}N_5O_{51}$, 1780.31).

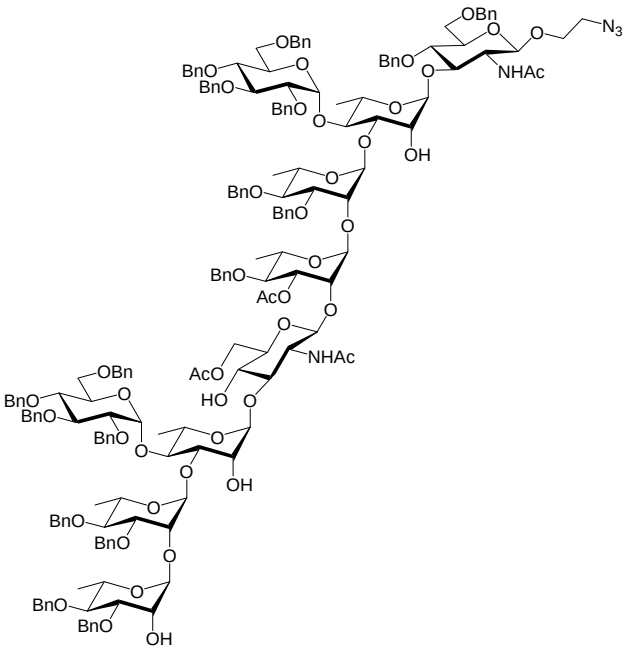
2-Azidoethyl (3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-(α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(3-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-(α-L-rhamnopyranosyl)-(1→3)-2--acetamido-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (38).



Ac_2O (531 μL, 5.62 mmol, 100 equiv.) and DMAP (7.0 mg, 56 μmol, 1.0 equiv) were added to alcohol **36** (200 mg, 56.2 μmol) in anhydr. Py (5.6 mL). The mixture was stirred for 1 h at rt under Ar. Solvents were evaporated and co-evaporated with toluene (3×). Aq TFA (50% *v/v*, 1.8 mL) was added dropwise to the residue (202 mg, 56.2 μmol) in CH_2Cl_2 (8.4 mL) at 0 °C. The mixture was stirred for 2 h from 0 °C to rt. The solution was diluted with CH_2Cl_2 (10 mL) and excess TFA was neutralized with satd aq $NaHCO_3$ (25 mL). The aq phase was extracted with CH_2Cl_2 (3×25 mL). The pooled organic layers were washed with brine (25 mL), dried over anhydr. Na_2SO_4, filtered, and solvents were evaporated. Hydrazine hydrate (35 μL, 1.12 mmol, 20 equiv.) was added to the residue (200 mg, 56.2 μmol) in anhydr. Py/AcOH (8.5 mL, 3:2 *v/v*). The mixture was stirred for 2 h at rt under Ar. The solution was diluted with CH_2Cl_2 (25 mL). The organic layer was washed with H_2O (25 mL) and the aq phase was extracted with CH_2Cl_2

(3×25 mL). Solvents were evaporated and co-evaporated with toluene (3×). The residue was purified by FC (CH_2Cl_2/MeOH 99:1 to 98:2) to give acetate **38** (145 mg, 79% over 3 steps) as a white powder. R_f 0.54 (CH_2Cl_2/MeOH 95:5); $[\alpha]^{25}_D$ –55° (*c* 0.20, $CHCl_3$); ^{1}H NMR (Py-d_5, 400 MHz) δ: 9.53 (d, $J_{NH,2}$ = 7.2 Hz, 1H, N*H*), 9.40 (d, $J_{NH,2}$ = 8.5 Hz, 1H, N*H*), 7.70-7.14 (m, 85H, C*H*$_{Ph}$), 6.01 (dd, $J_{3,4}$ = 9.8 Hz, $J_{2,3}$ = 2.4 Hz, 1H, H-3$_A$), 5.95-5.40 (9H, H-1$_A$, H-1$_{A'}$, H-1$_B$, H-1$_{B'}$, H-1$_C$, H-1$_{C'}$, H-1$_{D'}$, H-1$_E$, H-1$_{E'}$), 5.34-3.62 (m, 84H, H-2$_A$, H-2$_{A'}$, H-3$_{A'}$, H-4$_A$, H-4$_{A'}$, H-5$_A$, H-5$_{A'}$, H-2$_B$, H-2$_{B'}$, H-3$_B$, H-3$_{B'}$, H-4$_B$, H-4$_{B'}$, H-5$_B$, H-5$_{B'}$, H-2$_C$, H-2$_{C'}$, H-3$_C$, H-3$_{C'}$, H-4$_C$, H-4$_{C'}$, H-5$_C$, H-5$_{C'}$, H-1$_D$, H-2$_D$, H-2$_{D'}$, H-3$_D$, H-3$_{D'}$, H-4$_D$, H-4$_{D'}$, H-5$_D$, H-5$_{D'}$, H-6a$_D$, H-6a$_{D'}$, H-6b$_D$, H-6b$_{D'}$, H-2$_E$, H-2$_{E'}$, H-3$_E$, H-3$_{E'}$, H-4$_E$, H-4$_{E'}$, H-5$_E$, H-5$_{E'}$, H-6a$_E$, H-6a$_{E'}$, H-6b$_E$, H-6b$_{E'}$, OC*H*$_2$a, OC*H*$_2$b, C*H*$_2$Ph), 3.49-3.41 (m, 1H, C*H*$_2$N$_3$a), 3.34-3.27 (m, 1H, C*H*$_2$N$_3$b), 2.21 (s, 3H, C(O)C*H*$_{3Ac}$), 2.15, 2.09 (2s, 6H, C(O)C*H*$_{3NHAc}$), 1.68 (d, $J_{5,6}$ = 6.1 Hz, 3H, C*H*$_{3Rha}$), 1.54-1.42 (m, 15H, C*H*$_{3Rha}$). ^{13}C NMR (Py-d_5, 100 MHz) δ (partial): 171.1, 171.0, 170.9 (3×*C*(O)CH$_3$), 140.3-139.2 (C$_{Ph}$), 129.4-127.9 (*C*H$_{Ph}$), 103.9, 103.1, 102.8, 102.5, 102.3 (2C), 102.2, 101.5, 98.9, 98.4 (C-1$_A$, C-1$_{A'}$, C-1$_B$, C-1$_{B'}$, C-1$_C$, C-1$_{C'}$, C-1$_D$, C-1$_{D'}$, C-1$_E$, C-1$_{E'}$), 83.6, 83.2, 82.6, 82.5, 82.3, 82.2, 81.5, 81.4, 81.3, 81.1, 80.5, 80.3, 79.8, 78.9, 78.7, 78.5, 78.0, 77.8, 76.9, 76.0, 75.8, 75.8, 75.7, 75.5, 75.4, 75.3, 73.9, 73.8, 73.8, 73.7, 73.5, 72.7, 72.3, 72.1, 71.8, 71.7, 71.5, 71.0, 70.9, 69.9, 69.6, 69.5, 69.4, 69.2, 69.1, 68.9, 68.2 (C-2$_A$, C-3$_A$, C-4$_A$, C-5$_A$, C-2$_B$, C-3$_B$, C-4$_B$, C-5$_B$, C-2$_C$, C-3$_C$, C-4$_C$, C-5$_C$, C-3$_D$, C-4$_D$, C-5$_D$, C-6$_D$, C-2$_E$, C-3$_E$, C-4$_E$, C-5$_E$, C-6$_E$, C-2$_{A'}$, C-3$_{A'}$, C-4$_{A'}$, C-5$_{A'}$, C-2$_{B'}$, C-3$_{B'}$, C-4$_{B'}$, C-5$_{B'}$, C-2$_{C'}$, C-3$_{C'}$, C-4$_{C'}$, C-5$_{C'}$, C-3$_{D'}$, C-4$_{D'}$, C-5$_{D'}$, C-2$_{E'}$, C-3$_{E'}$, C-4$_{E'}$, C-5$_{E'}$, C-6$_{E'}$, O*C*H$_2$, 17×*C*H$_2$Ph), 63.1 (C-6$_{D'}$), 59.2 (C-2$_{D'}$), 57.5 (C-2$_D$), 51.4 (*C*H$_2$N$_3$), 24.0 (C(O)*C*H$_{3NHAc}$), 23.8 (C(O)*C*H$_{3NHAc}$), 21.4 (C(O)*C*H$_{3Ac}$), 19.7, 19.6, 19.1, 18.9, 18.8, 18.7 (6×*C*H$_{3Rha}$). HR-ESI-TOF-MS *m/z* 1634.33 $[M + 2H]^{2+}$ (calcd for $C_{187}H_{217}N_5O_{46}$, 1634.24).

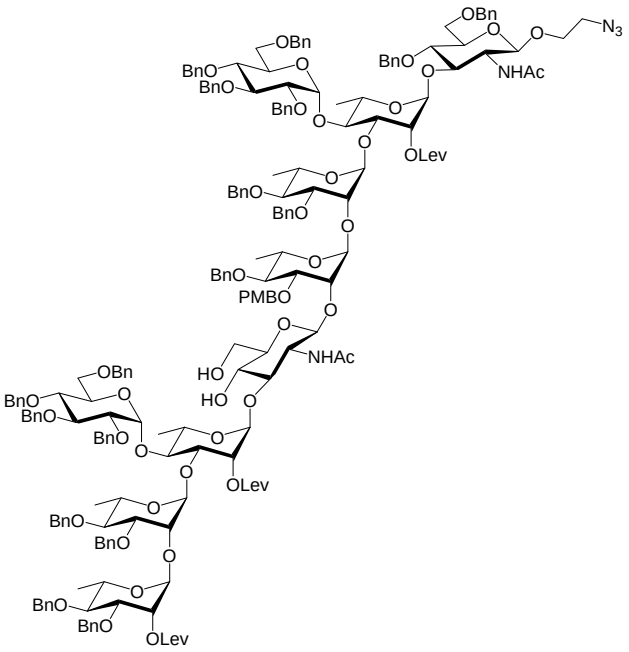
2-Azidoethyl (3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-(α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→2)-(3-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-(α-L-rhamnopyranosyl)-(1→3)-2-acetamido-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (39).



Ac_2O (536 µL, 5.67 mmol, 100 equiv.) and DMAP (7.0 mg, 56 µmol, 1.0 equiv) were added to alcohol **36** (202 mg, 56.7 µmol) in anhydr. Py (2.8 mL). The mixture was stirred for 1 h at rt under Ar, and solvents were evaporated and co-evaporated with toluene (3×). Aq TFA (50% *v/v*, 1.8 mL) was added dropwise to the residue (204 mg, 56.7 µmol) in CH_2Cl_2 (8.5 mL) at 0 °C. The mixture was stirred for 2 h from 0 °C to rt. The solution was diluted with CH_2Cl_2 (10 mL) and excess TFA was neutralized with satd aq $NaHCO_3$ (25 mL). The aq phase was extracted with CH_2Cl_2 (3×25 mL). The pooled organic layers were washed with brine (25 mL), dried over anhydr. Na_2SO_4, filtered, and solvents were evaporated. Acetyl chloride (113 µmol, 100 µL, 2.0 equiv.) was added from a fresh stock solution (80 µL of acetyl chloride in 1.0 mL anhydr. CH_2Cl_2) to the residue (202 mg, 56.7 µmol) in *sym*-collidine (2.2 mL) at -45 °C (CH_3CN/ice CO_2 bath) under Ar. Additional acetyl chloride (57 µmol, 50 µL of stock solution, 1.0 equiv.) was added after 60, 120, 180 and 240 min. During this time, the temperature was gradually raised from -45 °C to rt. After reaction completion (6 h), excess acetyl chloride was quenched with MeOH, CH_2Cl_2 was added and the organic phase was washed with 5% aq HCl, satd $NaHCO_3$ and brine, and dired over anhydr. Na_2SO_4. Solvents were evaporated and co-evaporated with toluene (3×). Hydrazine hydrate (35 µL, 1.12 mmol, 20 equiv.) was added to the residue (204 mg, 56.7 µmol) in anhydr. Py/AcOH (8.5 mL, 3:2 *v/v*). The mixture was stirred for 2 h at rt under Ar. The solution was diluted with CH_2Cl_2 (25 mL). The organic layer was washed with H_2O (25 mL) and the aq phase was extracted with CH_2Cl_2 (3×25 mL). Solvents were evaporated and co-evaporated with toluene (3×). The residue was purified by FC (CH_2Cl_2/MeOH 99:1 to 98:2) to give diacetate **39** (138 mg, 74%, 4 steps) as a white powder. R_f 0.63 (CH_2Cl_2/MeOH 95:5); $[\alpha]^{25}_D$ +15° (*c* 0.40, $CHCl_3$); ^{1}H NMR (Py-d_5, 400 MHz) δ: 9.59 (d, $J_{NH,2}$ = 7.3 Hz, 1H, N*H*), 9.25 (d, $J_{NH,2}$ = 8.5 Hz, 1H, N*H*), 7.69-7.17 (m, 85H, C*H*$_{Ph}$), 5.98 (dd, $J_{3,4}$ = 9.9 Hz, $J_{2,3}$ = 2.7 Hz, 1H, H-3$_A$), 5.86-5.47 (m, 9H, H-1$_A$, H-1$_{A'}$, H-1$_B$, H-1$_{B'}$, H-1$_C$, H-1$_{C'}$, H-1$_{D'}$, H-1$_E$, H-1$_{E'}$), 5.30-3.56 (m, 83H, H-2$_A$, H-

$2_{A'}$, H-$3_{A'}$, H-4_A, H-$4_{A'}$, H-5_A, H-$5_{A'}$, H-2_B, H-$2_{B'}$, H-3_B, H-$3_{B'}$, H-4_B, H-$4_{B'}$, H-5_B, H-$5_{B'}$, H-2_C, H-$2_{C'}$, H-3_C, H-$3_{C'}$, H-4_C, H-$4_{C'}$, H-5_C, H-$5_{C'}$, H-1_D, H-2_D, H-3_D, H-$3_{D'}$, H-4_D, H-$4_{D'}$, H-5_D, H-$5_{D'}$, H-6a$_D$, H-6a$_{D'}$, H-6b$_D$, H-6b$_{D'}$, H-2_E, H-$2_{E'}$, H-3_E, H-$3_{E'}$, H-4_E, H-$4_{E'}$, H-5_E, H-$5_{E'}$, H-6a$_E$, H-6a$_{E'}$, H-6b$_E$, H-6b$_{E'}$, OCH_2a, OCH_2b, CH_2Ph), 3.60 (m, $J_{1,2}$ = 8.3 Hz, 1H, H-$2_{D'}$), 3.48-3.41 (m, 1H, CH_2N_3a), 3.32 (ddd, J = 13.2, 5.3, 3.5 Hz, 1H, CH_2N_3b), 2.26 (s, 3H, C(O)CH_{3Ac}), 2.18, 2.09 (2s, 6H, C(O)CH_{3NHAc}), 1.73 (s, 3H, C(O)CH_{3Ac}), 1.65 (d, $J_{5,6}$ = 6.1 Hz, 3H, CH_{3Rha}), 1.54-1.40 (m, 15H, CH_{3Rha}). ^{13}C NMR (Py-d_5, 100 MHz) δ (partial): 171.2 (C(O)CH_{3Ac}), 171.0 (3×C(O)CH_{3Ac}), 140.4-139.3 (C$_{Ph}$), 129.4-127.9 (CH$_{Ph}$), 104.0, 103.2, 102.9, 102.6, 102.3, 102.2, 101.6 (2C), 99.0, 98.6 (C-1_A, C-$1_{A'}$, C-1_B, C-$1_{B'}$, C-1_C, C-$1_{C'}$, C-1_D, C-$1_{D'}$, C-1_E, C-$1_{E'}$), 83.4, 82.6, 82.6, 82.3, 81.9, 81.6, 81.6, 81.2, 80.7, 80.5, 80.3, 79.6, 78.9, 78.8, 78.6, 77.2, 77.0, 76.8, 76.1, 76.1, 76.1, 76.0, 75.8, 75.8, 75.7, 75.6, 75.5, 75.1, 74.9, 74.5, 74.4, 74.0, 73.9, 73.9, 73.8, 73.7, 72.9, 72.4, 72.2, 71.9, 71.8, 71.6, 71.0, 70.4, 70.0, 69.6, 69.5, 69.4, 69.3, 69.2, 69.1, 68.3 (C-2_A, C-$2_{A'}$, C-3_A, C-$3_{A'}$, C-4_A, C-$4_{A'}$, C-5_A, C-$5_{A'}$, C-2_B, C-$2_{B'}$, C-3_B, C-$3_{B'}$, C-4_B, C-$4_{B'}$, C-5_B, C-$5_{B'}$, C-2_C, C-$2_{C'}$, C-3_C, C-$3_{C'}$, C-4_C, C-$4_{C'}$, C-5_C, C-$5_{C'}$, C-3_D, C-$3_{D'}$, C-4_D, C-$4_{D'}$, C-5_D, C-$5_{D'}$, C-6_D, C-2_E, C-$2_{E'}$, C-3_E, C-$3_{E'}$, C-4_E, C-$4_{E'}$, C-5_E, C-$5_{E'}$, C-6_E, C-$6_{E'}$, OCH_2), 59.7 (C-$2_{D'}$), 57.5 (C-2_D), 51.5 (CH$_2$N$_3$), 24.1, 23.9 (2C, C(O)CH$_{3NHAc}$), 21.5, 21.0 (2C, C(O)CH$_{3Ac}$), 19.7, 19.7, 19.2, 18.9 (2C), 18.8 (6C, CH$_{3Rha}$). HR-MALDI-TOF-MS *m/z* 3331.47489 [M + Na]$^+$ (calcd for $C_{187}H_{217}N_5O_{47}Na$, 3331.46361).

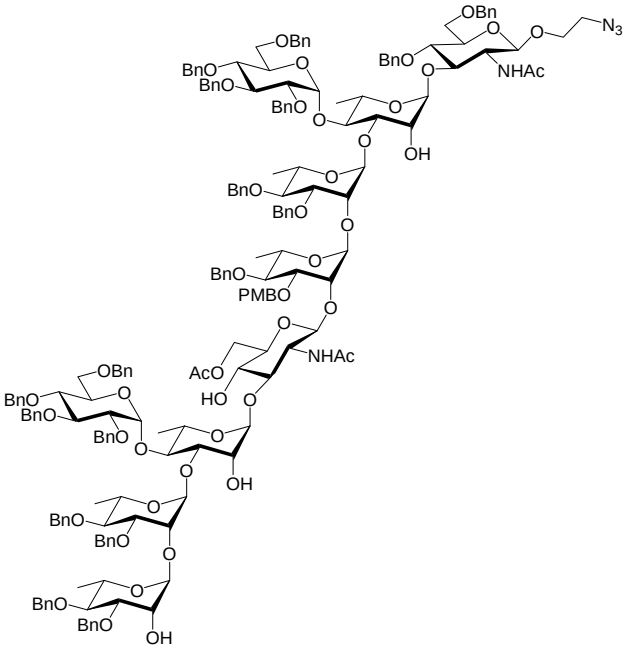
2-Azidoethyl (3,4-di-*O*-benzyl-2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-(2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-(2-*O*-levulinoyl-α-L-rhamnopyranosyl)-(1→3)-2-acetamido-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (40).



Aq TFA (50% *v/v*, 1.8 mL) was added to decasaccharide **5** (210 mg, 57.0 μmol) in CH_2Cl_2 (8.6 mL) at 0 °C. The mixture was stirred for 2 h from 0 °C to rt, then diluted with CH_2Cl_2 (10 mL) and washed with satd $NaHCO_3$ (25 mL). The aq phase was extracted with CH_2Cl_2 (3×25 mL), the pooled organic layers were washed with brine (25 mL), dried over anhydr. Na_2SO_4, filtered and solvents were evaporated. The residue was purified by FC (CH_2Cl_2/MeOH 99:1 to 98:2) to give diol **40** (187 mg, 90%) as a white powder. $[\alpha]^{25}_D$ –36° (*c* 0.22, $CHCl_3$); ^{1}H NMR (Py-d_5, 400 MHz) δ: 9.54 (br s, 1H, N*H*), 7.77-7.09 (m, 87H, C*H*$_{Ph}$), 6.98-6.94 (m, 2H, C*H*$_{Ph}$), 6.12 (br s, 1H, H-2$_{A'}$), 5.86-5.25 (m, 12H, H-2$_C$, H-2$_{C'}$, H-1$_A$, H-1$_{A'}$, H-1$_B$, H-1$_{B'}$, H-1$_C$, H-1$_{C'}$, H-1$_D$, H-1$_{D'}$, H-1$_E$, H-1$_{E'}$), 5.24-3.53 (m, 86H, H-2$_A$, H-3$_A$, H-3$_{A'}$, H-4$_A$, H-4$_{A'}$, H-5$_A$, H-5$_{A'}$, H-2$_B$, H-2$_{B'}$, H-3$_B$, H-3$_{B'}$, H-4$_B$, H-4$_{B'}$, H-5$_B$, H-5$_{B'}$, H-3$_C$, H-3$_{C'}$, H-4$_C$, H-4$_{C'}$, H-5$_C$, H-5$_{C'}$, H-2$_D$, H-2$_{D'}$, H-3$_D$, H-3$_{D'}$, H-4$_D$, H-4$_{D'}$, H-5$_D$, H-5$_{D'}$, H-6a$_D$, H-6a$_{D'}$, H-6b$_D$, H-6b$_{D'}$, H-2$_E$, H-2$_{E'}$, H-3$_E$, H-3$_{E'}$, H-4$_E$, H-4$_{E'}$, H-5$_E$, H-5$_{E'}$, H-6a$_E$, H-6a$_{E'}$, H-6b$_E$, H-6b$_{E'}$, OC*H*$_3$, OC*H*$_2$a, OC*H*$_2$b, C*H*$_2$Ph), 3.53-3.44 (m, 1H, C*H*$_2$N$_3$a), 3.41-3.33 (m, 1H, C*H*$_2$N$_3$b), 2.87-2.58 (m, 12H, C*H*$_{2Lev}$), 2.46, 2.40 (2s, 6H, C(O)C*H*$_{3NHAc}$), 2.04, 2.01, 1.99 (3s, 9H, C(O)C*H*$_{3Lev}$), 1.71 (d, $J_{5,6}$ = 5.9 Hz, 3H, C*H*$_{3Rha}$), 1.57 (d, $J_{5,6}$ = 6.3 Hz, 3H, C*H*$_{3Rha}$), 1.51 (d, $J_{5,6}$ = 6.0 Hz, 3H, C*H*$_{3Rha}$), 1.43-1.36 (m, 6H, C*H*$_{3Rha}$), 1.30 (d, $J_{5,6}$ = 5.8 Hz, 3H, C*H*$_{3Rha}$). ^{13}C NMR (Py-d_5, 100 MHz) δ (partial): 206.2 (*C*(O)CH$_{2Lev}$), 206.0 (2C, *C*(O)CH$_{2Lev}$), 173.0 (2C, *C*(O)CH$_{3Lev}$), 172.7 (*C*(O)CH$_{3Lev}$), 172.1, 172.0 (2C, *C*(O)CH$_{3NHAc}$), 160.2 (C$_{Ph}$), 140.3-139.2 (C$_{Ph}$), 130.9 (C*H*$_{Ph}$), 129.4-127.8 (C*H*$_{Ph}$), 114.6 (C*H*$_{Ph}$), 102.2 (5C), 101.1, 100.6, 99.2, 98.8, 98.5 (C-1$_A$, C-1$_{A'}$, C-1$_B$, C-1$_{B'}$, C-1$_C$, C-1$_{C'}$, C-1$_D$, C-1$_{D'}$, C-1$_E$, C-1$_{E'}$), 82.8, 82.6, 82.5, 81.6, 81.1, 80.9, 80.0, 79.8, 79.6, 79.4, 79.3, 78.7, 78.6, 78.6, 78.5, 78.1, 77.1, 76.4, 76.1, 76.0, 75.9, 75.8, 75.6, 75.0, 74.4, 74.2, 74.0, 73.8, 72.8, 72.5, 72.3, 72.0, 71.5, 71.3, 70.2, 70.0, 69.7, 69.5, 69.5, 69.2, 68.5, 68.4 (C-2$_A$, C-2$_{A'}$, C-3$_A$, C-3$_{A'}$, C-4$_A$, C-4$_{A'}$, C-5$_A$, C-5$_{A'}$, C-2$_B$, C-2$_{B'}$, C-3$_B$, C-3$_{B'}$, C-4$_B$, C-4$_{B'}$, C-5$_B$, C-5$_{B'}$, C-2$_C$, C-2$_{C'}$, C-3$_C$, C-3$_{C'}$, C-4$_C$, C-4$_{C'}$, C-5$_C$, C-5$_{C'}$, C-3$_D$, C-3$_{D'}$, C-4$_D$, C-4$_{D'}$, C-5$_D$, C-5$_{D'}$, C-6$_D$, C-2$_E$, C-2$_{E'}$, C-3$_E$, C-3$_{E'}$, C-4$_E$, C-

$4_{E'}$, C-5_E, C-$5_{E'}$, C-6_E, C-$6_{E'}$, O*C*H_2, *C*H_2Ph), 63.6 (C-$6_{D'}$), 59.6 (C-$2_{D'}$), 58.2 (C-2_D), 55.5 (O*C*H_3), 51.6 (*C*H_2N_3), 38.5, 38.5, 38.4 (3C, *C*H_{2Lev}), 29.9, 29.9, 29.8 (3C, C(O)*C*H_{3Lev}), 29.1, 29.1, 29.0 (6C, *C*H_{2Lev}), 24.5, 24.2 (2C, C(O)*C*H_{3NHAc}), 19.5-18.8 (6C, C-6_A, C-$6_{A'}$, C-6_B, C-$6_{B'}$, C-6_C, C-$6_{C'}$). HR-MALDI-TOF-MS *m/z* 3661.61385 $[M + Na]^+$ (calcd for $C_{208}H_{239}N_5O_{52}Na$, 3661.61034).

2-Azidoethyl (3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-(α-L-rhamnopyranosyl)-(1→3)-(2-acetamido-6-*O*-acetyl-2-deoxy-β-D-glucopyranosyl)-(1→2)-(4-*O*-benzyl-3-*O*-*para*-methoxybenzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)]-(α-L-rhamnopyranosyl)-(1→3)-2-acetamido-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (41).



Acetyl chloride (75.8 µmol, 100 µL, 2.0 equiv.) from a fresh stock solution (108 µL of acetyl chloride in 2.0 mL anhydr. CH_2Cl_2) was added to diol **40** (138 mg, 37.9 µmol) in *sym*-collidine (1.5 mL) at -45 °C (CH_3CN/ice CO_2 bath) under Ar. Additional acetyl chloride (190 µmol, 250 µL of stock solution, 5.0 equiv.) was added after 60, 120, 180, 240, 300 and 360 min. During this time, the temperature was gradually raised from -45 °C to rt. After reaction completion (8 h), excess acetyl chloride was quenched with MeOH, CH_2Cl_2 was added and the organic phase was washed with 10% aq HCl. The aq layer was extracted with CH_2Cl_2 (3×) and the pooled organic phases were washed with satd $NaHCO_3$ and brine, then dried over anhydr. Na_2SO_4. Solvents were evaporated and co-evaporated with toluene (3×). Hydrazine hydrate (24 µL, 0.76 mmol, 20 equiv.) was added to the residue (140 mg, 37.9 µmol) in anhydr. Py/AcOH (5.7 mL, 3:2 *v/v*). The mixture was stirred for 2 h at rt under Ar. The solution was diluted with CH_2Cl_2 (25 mL), the

organic layer was washed with H_2O (25 mL) and the aq phase was extracted with CH_2Cl_2 (3×25 mL). Solvents were evaporated and co-evaporated with toluene (3×). The residue was purified by FC (CH_2Cl_2/MeOH 99:1 to 98.5:1.5) to give acetate **41** (94 mg, 81%, 2 steps) as a white amorphous solid. $[\alpha]^{25}_D$ –4° (*c* 0.50, $CHCl_3$); ^{1}H NMR (Py-d_5, 400 MHz) δ: 9.20 (d, $J_{NH,2}$ = 8.6 Hz, 1H, N*H*), 9.05 (d, $J_{NH,2}$ = 7.7 Hz, 1H, N*H*), 7.72-7.20 (m, 87H, C*H*$_{Ph}$), 7.01-6.97 (m, 2H, C*H*$_{Ph}$), 5.87-5.48 (m, 9H, H-1$_A$, H-1$_{A'}$, H-1$_B$, H-1$_{B'}$, H-1$_C$, H-1$_{C'}$, H-1$_{D'}$, H-1$_E$, H-1$_{E'}$), 5.27-3.70 (m, 87 H, H-2$_A$, H-2$_{A'}$, H-3$_A$, H-3$_{A'}$, H-4$_A$, H-4$_{A'}$, H-5$_A$, H-5$_{A'}$, H-2$_B$, H-2$_{B'}$, H-3$_B$, H-3$_{B'}$, H-4$_B$, H-4$_{B'}$, H-5$_B$, H-5$_{B'}$, H-2$_C$, H-2$_{C'}$, H-3$_C$, H-3$_{C'}$, H-4$_C$, H-4$_{C'}$, H-5$_C$, H-5$_{C'}$, H-1$_D$, H-2$_D$, H-2$_{D'}$, H-3$_D$, H-3$_{D'}$, H-4$_D$, H-4$_{D'}$, H-5$_D$, H-5$_{D'}$, H-6a$_D$, H-6a$_{D'}$, H-6b$_D$, H-6b$_{D'}$, H-2$_E$, H-2$_{E'}$, H-3$_E$, H-3$_{E'}$, H-4$_E$, H-4$_{E'}$, H-5$_E$, H-5$_{E'}$, H-6a$_E$, H-6a$_{E'}$, H-6b$_E$, H-6b$_{E'}$, OC*H*$_2$a, OC*H*$_2$b, C*H*$_2$Ph), 3.65 (s, 3H, OC*H*$_3$), 3.49-3.41 (m, 1H, C*H*$_2$N$_3$a), 3.33 (ddd, *J* = 13.1, 5.1, 3.7 Hz, 1H, C*H*$_2$N$_3$b), 2.10, 2.09 (2s, 6H, C(O)C*H*$_{3NHAc}$), 1.79 (s, 3H, C(O)C*H*$_{3Ac}$), 1.66 (d, $J_{5,6}$ = 6.1 Hz, 3H, C*H*$_{3Rha}$), 1.54-1.39 (m, 15H, C*H*$_{3Rha}$). ^{13}C NMR (Py-d_5, 100 MHz) δ (partial): 171.1, 171.0, 170.9 (3C, *C*(O)CH$_{3Ac}$), 160.2 (C$_{Ph}$), 140.4-139.2 (C$_{Ph}$), 130.9 (*C*H$_{Ph}$), 129.5-127.8 (*C*H$_{Ph}$), 114.7 (*C*H$_{Ph}$), 104.0, 103.2, 102.8, 102.7, 102.5, 102.2, 102.0, 101.7, 99.0, 98.5 (C-1$_A$, C-1$_{A'}$, C-1$_B$, C-1$_{B'}$, C-1$_C$, C-1$_{C'}$, C-1$_D$, C-1$_{D'}$, C-1$_E$, C-1$_{E'}$), 84.0, 83.2, 82.6, 82.3, 81.9, 81.7, 81.6, 81.3, 80.6, 80.2, 79.5, 78.8, 78.7, 78.6, 77.0, 76.3, 76.1, 76.0, 75.9, 75.8, 75.6, 75.3, 73.9, 73.9, 73.8, 73.7, 72.9, 72.6, 72.3, 72.2, 71.9, 71.7, 70.9, 70.4, 70.1, 69.7, 69.5, 69.5, 69.3, 69.2, 68.3 (C-2$_A$, C-2$_{A'}$, C-3$_A$, C-3$_{A'}$, C-4$_A$, C-4$_{A'}$, C-5$_A$, C-5$_{A'}$, C-2$_B$, C-2$_{B'}$, C-3$_B$, C-3$_{B'}$, C-4$_B$, C-4$_{B'}$, C-5$_B$, C-5$_{B'}$, C-2$_C$, C-2$_{C'}$, C-3$_C$, C-3$_{C'}$, C-4$_C$, C-4$_{C'}$, C-5$_C$, C-5$_{C'}$, C-3$_D$, C-3$_{D'}$, C-4$_D$, C-4$_{D'}$, C-5$_D$, C-5$_{D'}$, C-6$_D$, C-2$_E$, C-2$_{E'}$, C-3$_E$, C-3$_{E'}$, C-4$_E$, C-4$_{E'}$, C-5$_E$, C-5$_{E'}$, C-6$_E$, C-6$_{E'}$, O*C*H$_2$, *C*H$_2$Ph), 64.7 (C-6$_{D'}$), 59.0 (C-2$_{D'}$), 57.4 (C-2$_D$), 55.6 (O*C*H$_3$), 51.5 (*C*H$_2$N$_3$), 24.1, 23.9 (2C, C(O)*C*H$_{3NHAc}$), 21.0 (C(O)*C*H$_{3Ac}$), 19.9, 19.7, 19.3, 19.0, 18.9 (6C, C-6$_A$, C-6$_{A'}$, C-6$_B$, C-6$_{B'}$, C-6$_C$, C-6$_{C'}$). HR-MALDI-TOF-MS *m/z* 3409.50588 $[M + Na]^+$ (calcd for $C_{195}H_{223}N_5O_{47}Na$, 3409.51056).

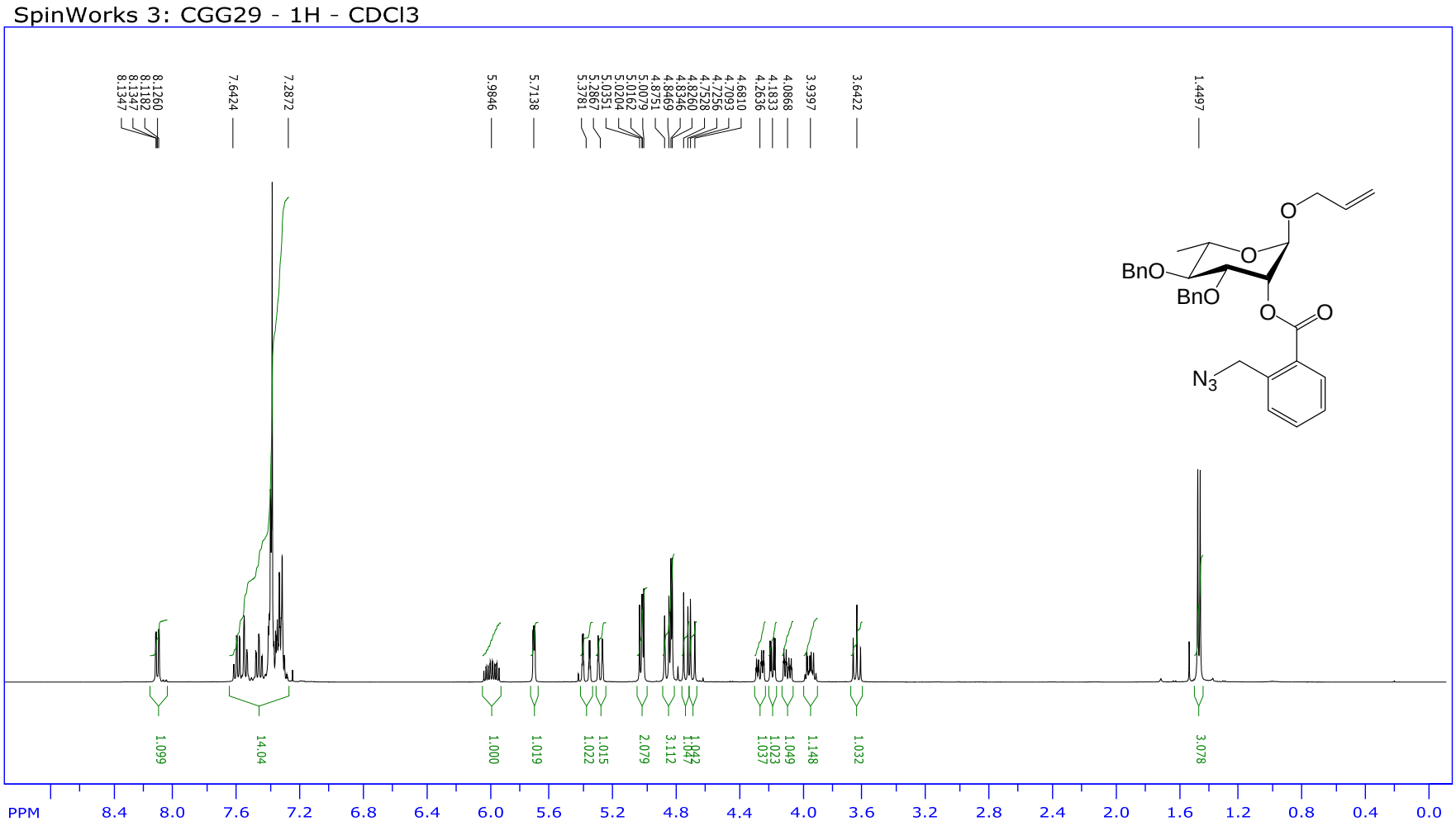
References

1. J. Boutet, C. Guerreiro and L. A. Mulard, *Tetrahedron*, 2008, **64**, 10558-10572.
2. J. Boutet and L. A. Mulard, *Eur. J. Org. Chem.*, 2008, 5526-5542.
3. P. Chassagne, L. Raibaut, C. Guerreiro and L. A. Mulard, *Tetrahedron*, 2013, **69**, 10337-10350.
4. H. Matsuda, N. Hashimoto and T. Okuno, *Synthetic Commun.*, 2002, **32**, 3347-3355.
5. K. R. Love, R. B. Andrade and P. H. Seeberger, *J. Org. Chem.*, 2001, **66**, 8165-8176.
6. J. F. Chen, Y. Zhou, C. Chen, W. C. Xu and B. Yu, *Carbohydr. Res.*, 2008, **343**, 2853-2862.
7. M. Alpe and S. Oscarson, *Carbohydr. Res.*, 2002, **337**, 1715-1722.
8. A. Popelova, K. Kefurt, M. Hlavackova and J. Moravcova, *Carbohydr. Res.*, 2005, **340**, 161-166.
9. Z. Wang, L. Y. Zhou, K. El-Boubbou, X. S. Ye and X. F. Huang, *J. Org. Chem.*, 2007, **72**, 6409-6420.

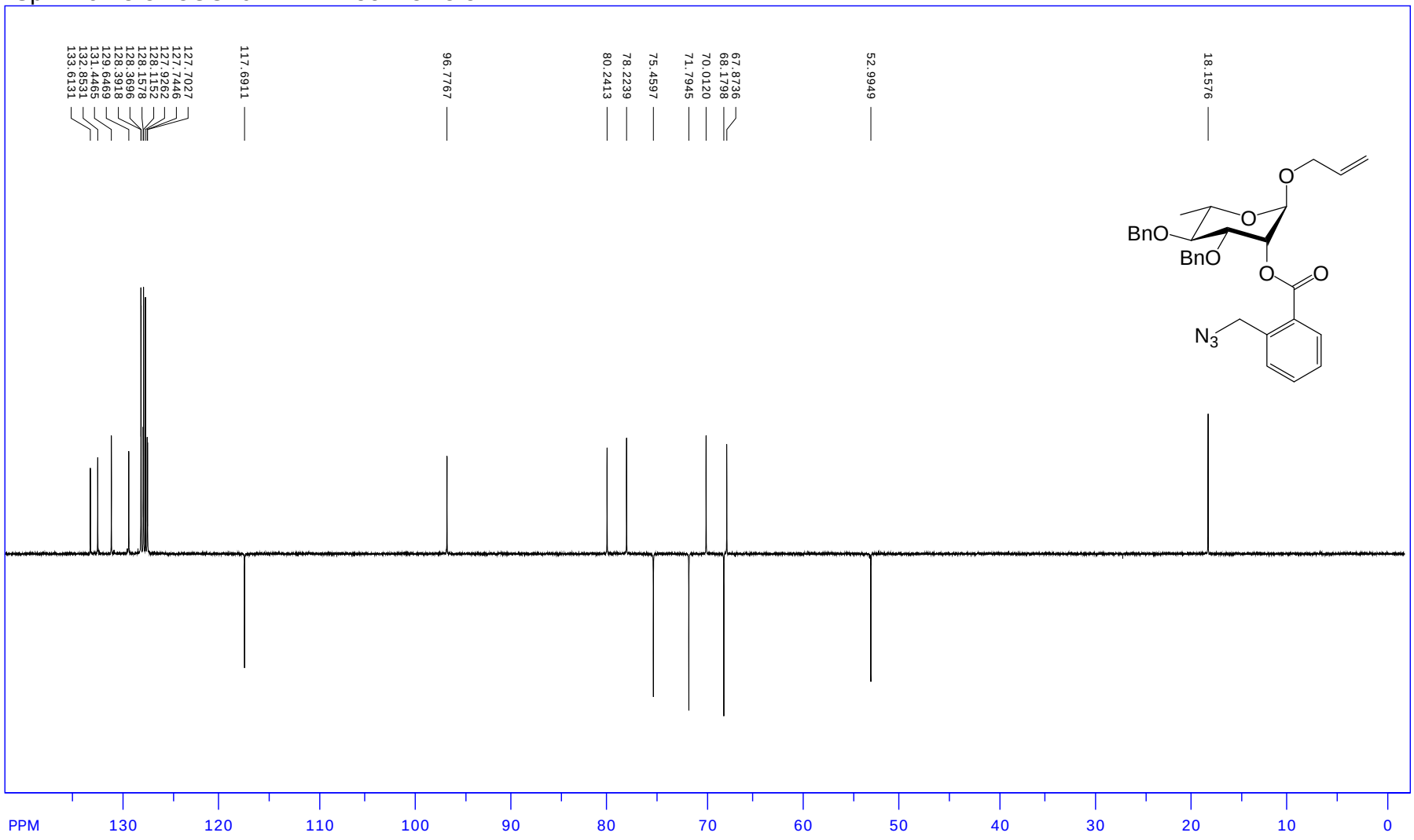
10. A. Phalipon, C. Costachel, C. Grandjean, A. Thuizat, C. Guerreiro, M. Tanguy, F. Nato, B. Vulliez-Le Normand, F. Belot, K. Wright, V. Marcel-Peyre, P. J. Sansonetti and L. A. Mulard, *J. Immunol.*, 2006, **176**, 1686-1694.
11. F. Belot, C. Guerreiro, F. Baleux and L. A. Mulard, *Chem. Eur. J.*, 2005, **11**, 1625-1635.
12. D. Mengin-Lecreulx and J. van Heijenoort, *J. Bacteriol.*, 1985, **163**, 208-212.
13. C. L. Brooks, S. Muller-Loennies, S. N. Borisova, L. Brade, P. Kosma, T. Hirama, C. R. Mackenzie, H. Brade and S. V. Evans, *Biochemistry*, 2010, **49**, 570-581.
14. B. Friguet, A. F. Chaffotte, L. Djavadiohaniance and M. E. Goldberg, *J. Immunol. Methods*, 1985, **77**, 305-319.
15. P. Chassagne, C. Fontana, C. Guerreiro, C. Gauthier, A. Phalipon, G. Widmalm and L. A. Mulard, *Eur. J. Org. Chem.*, 2013, 4085-4106.
16. Y. Cai, C. C. Ling and D. R. Bundle, *Org. Lett.*, 2005, **7**, 4021-4024.
17. L. A. Mulard, C. Costachel and P. J. Sansonetti, *J. Carbohydr. Chem.*, 2000, **19**, 849-877.
18. K. Tamura, H. Mizukami, K. Maeda, H. Watanabe and K. Uneyama, *J. Org. Chem.*, 1993, **58**, 32-35.

Relevant NMR spectra (^{1}H, DEPT, HSQC, ^{13}C, including HSQC for $^{1}J_{C,H}$ for compound 2 only) for new compounds listed below by order of appearance
S3, **S4**, **S6-S9**, **5-8**, **10-14**, **16-24**, **25-27**, **29**, **31-36**, **38-41**, **1-3**.

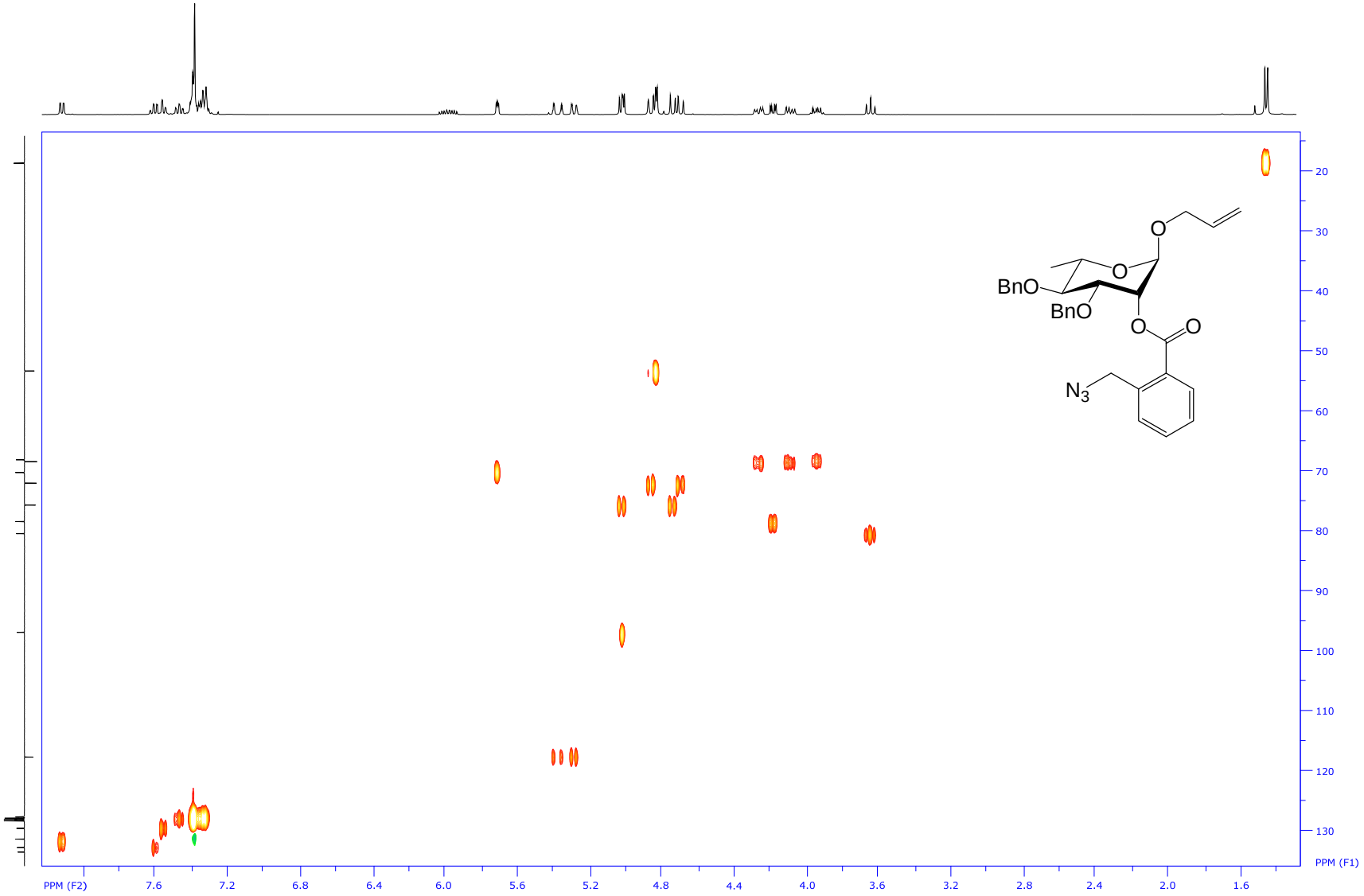
Compound **S3**


SpinWorks 3: CGG29 - 1H - CDCl3
8.1260
8.1182
8.1347
8.1347
7.6424
7.2872
5.9846
5.7138
5.3867
5.3781
5.0351
5.0204
5.0162
5.0079
4.8751
4.8469
4.8346
4.8260
4.7528
4.7256
4.7093
4.6610
4.2636
4.1833
4.0868
3.9397
3.6422
1.4497
BnO
BnO
O
O
O
O
N3
1.099
14.04
1.000
1.019
1.022
1.015
2.079
3.112
1.037
1.023
1.049
1.148
1.032
3.078
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

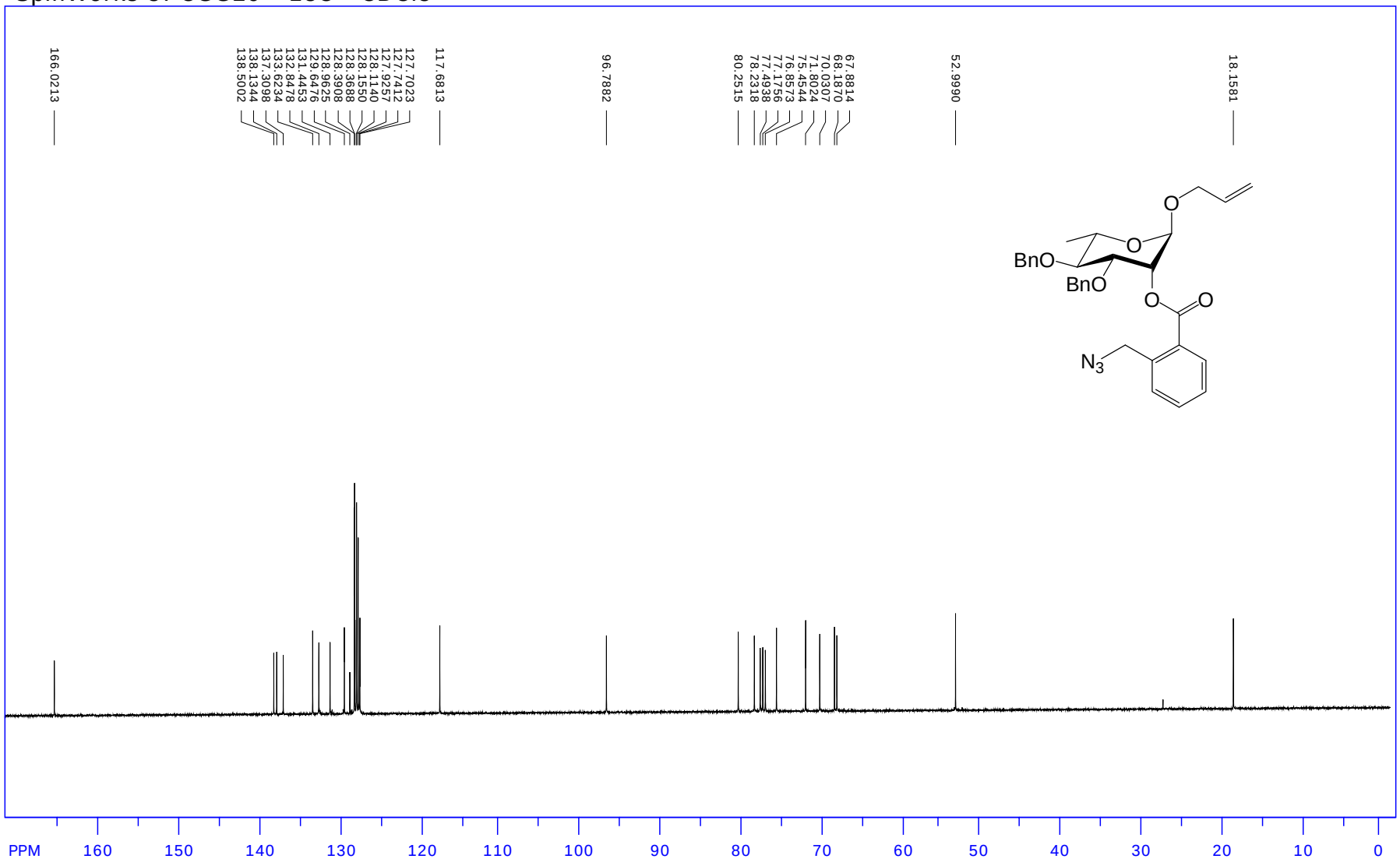
SpinWorks 3: CGG29 - DEPT135 - CDCl3



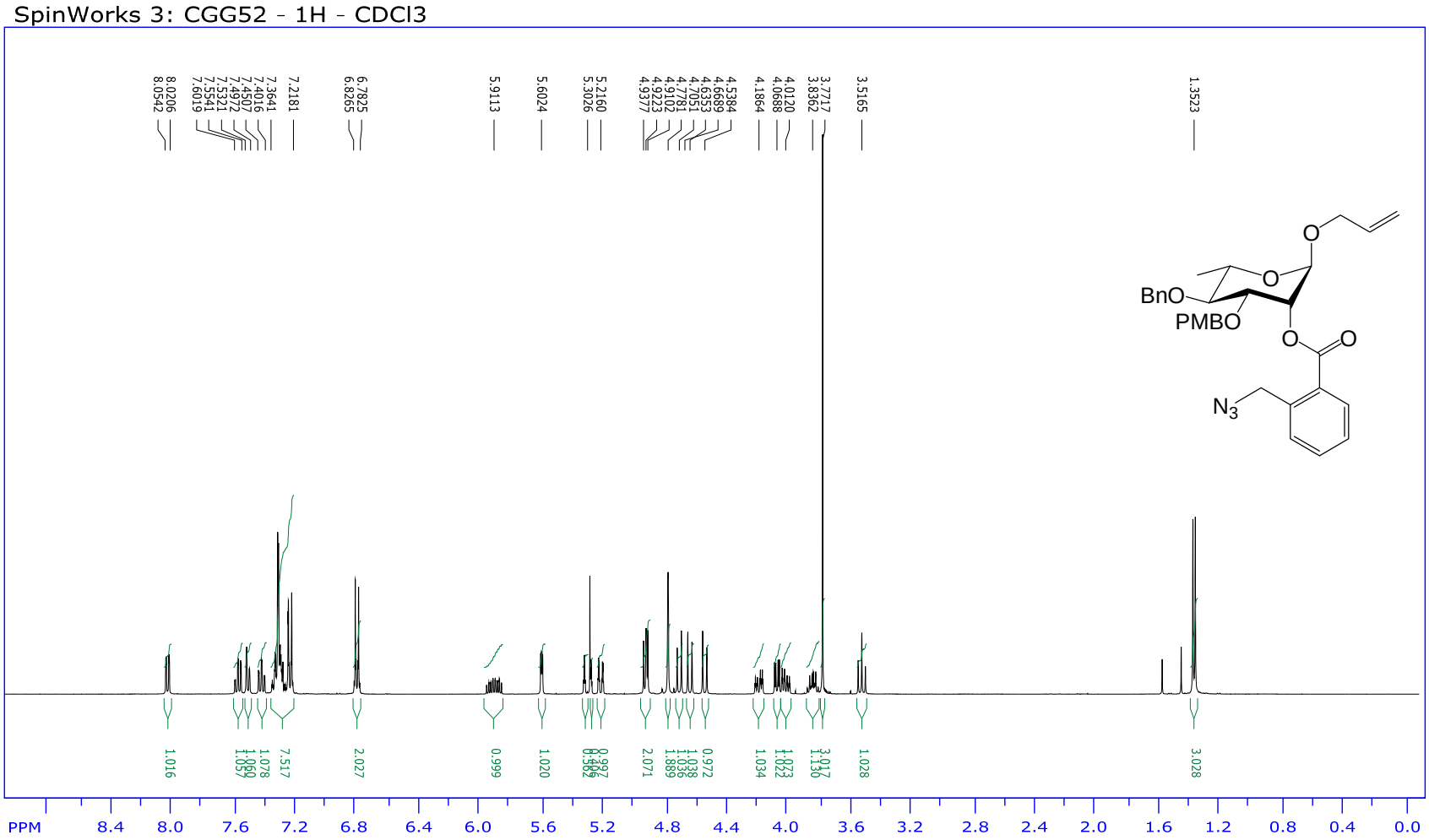
SpinWorks 3: CGG29 - COSY - CDCl3



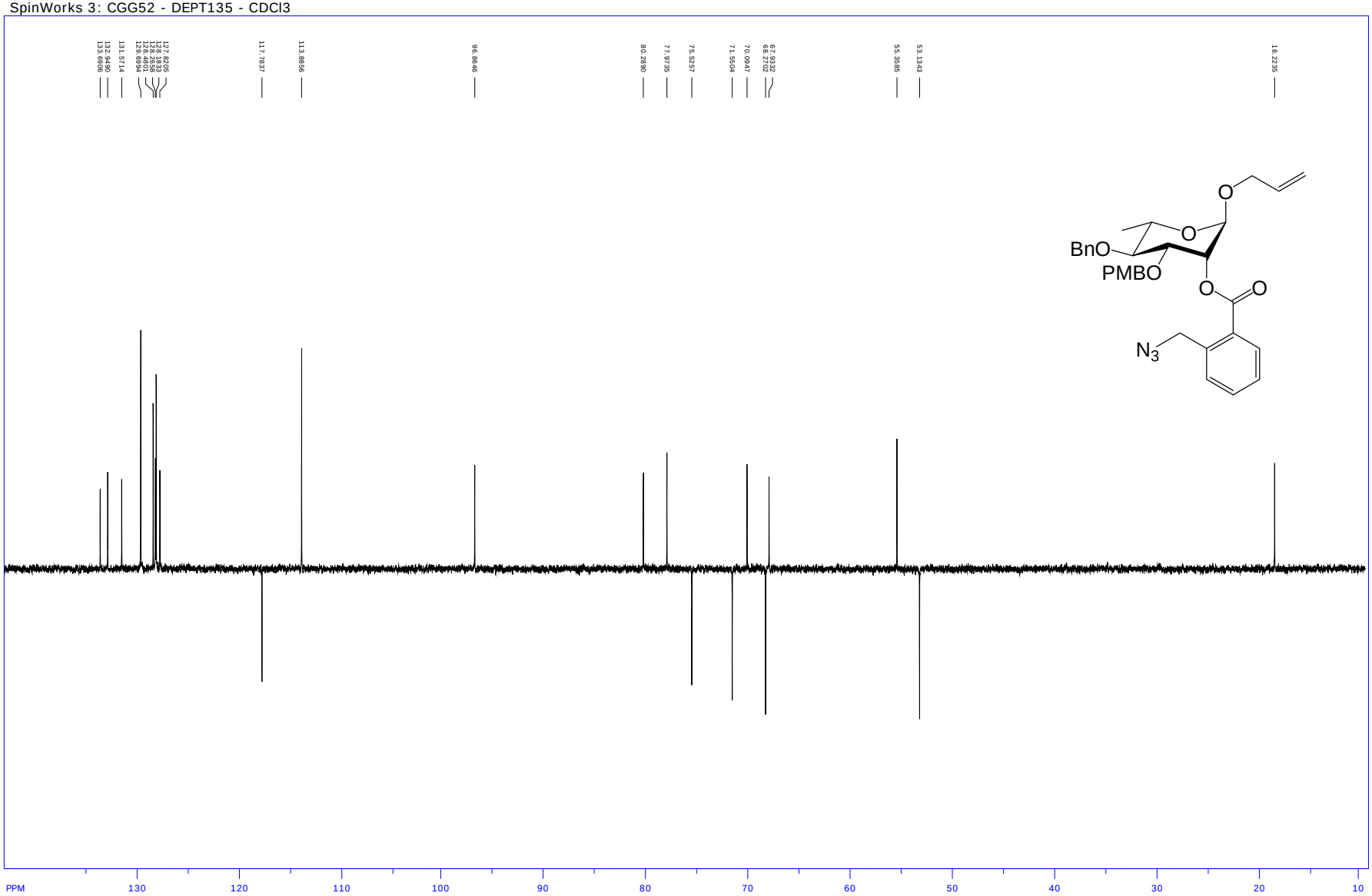
SpinWorks 3: CGG29 - 13C - CDCl3

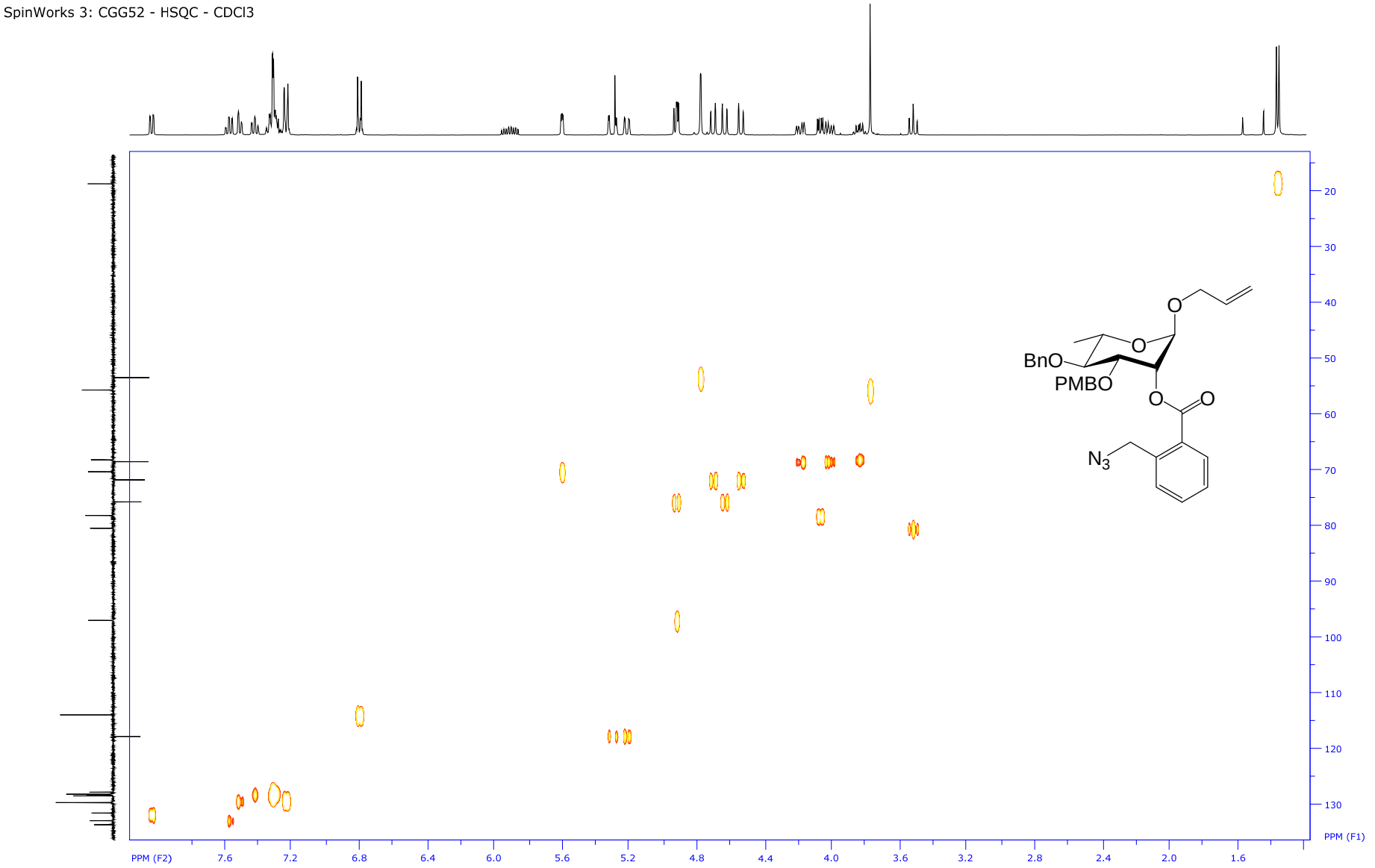


Compound **S4**

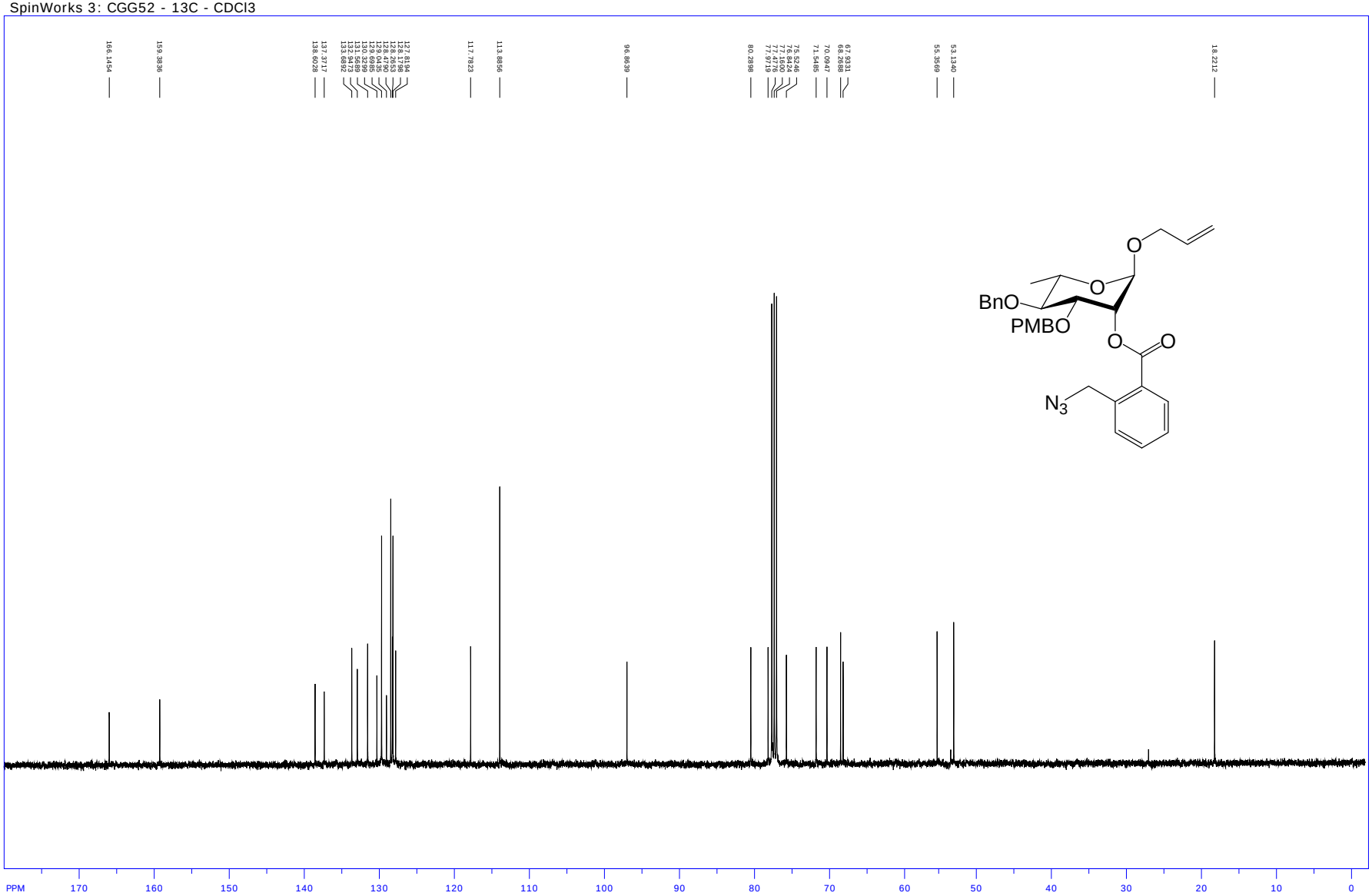

SpinWorks 3: CGG52 - 1H - CDCl3
8.0206
8.0542
7.6019
7.5541
7.5321
7.4972
7.4507
7.4016
7.3641
7.2181
6.7825
6.8265
5.9113
5.6024
5.3026
5.2160
4.9377
4.9223
4.9102
4.7781
4.7051
4.6353
4.6689
4.5384
4.1864
4.0688
4.0120
3.8362
3.7717
3.5165
1.3523
1.016
7.517
2.027
0.999
1.020
2.071
1.889
1.038
1.036
0.972
1.034
1.073
1.022
3.130
3.017
1.028
3.028
BnO
PMBO
O
O
O
O
O
N3
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

SpinWorks 3: CGG52 - DEPT135 - CDCl3

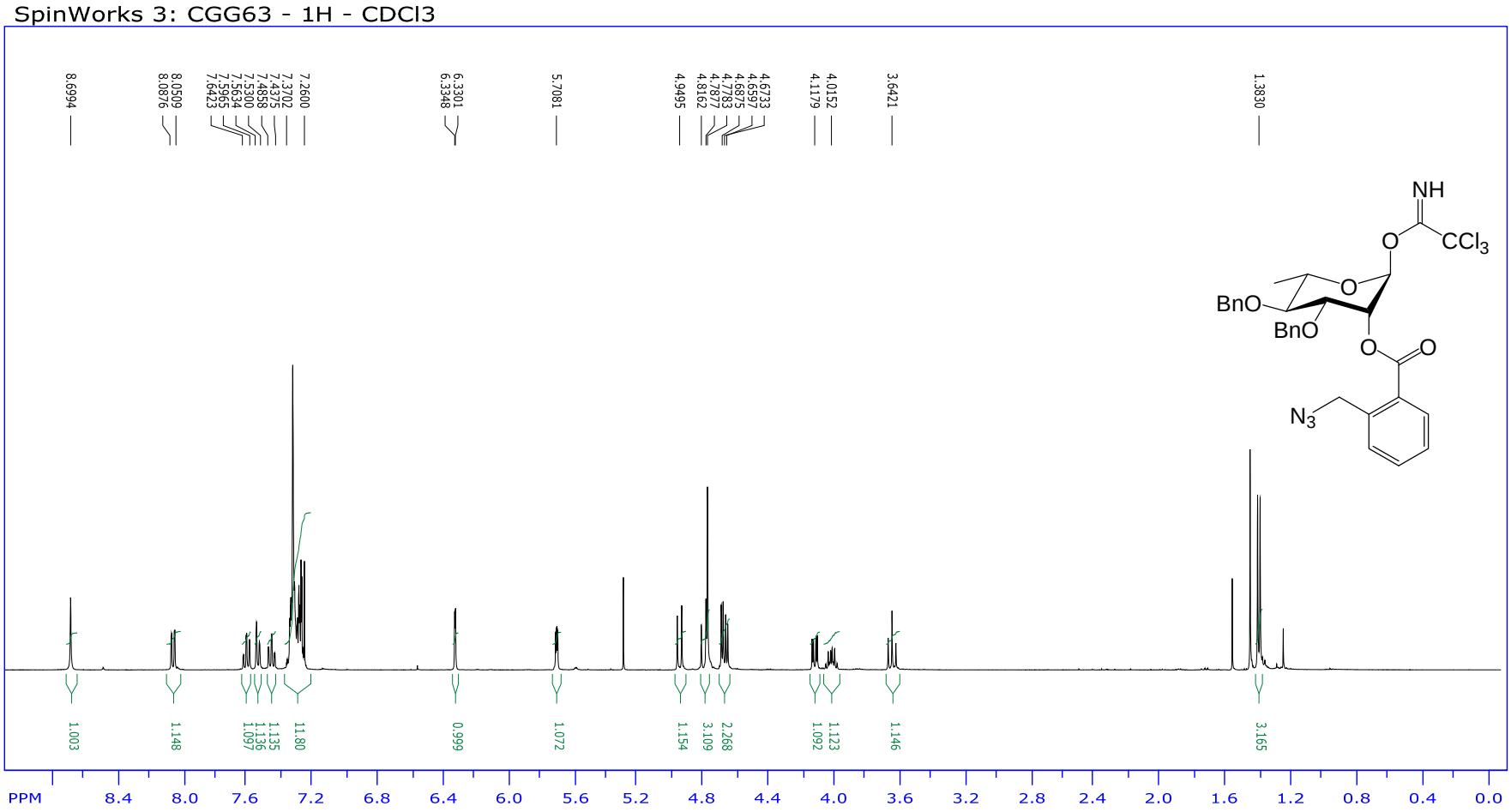



SpinWorks 3: CGG52 - HSQC - CDCl3
BnO
PMBO
O
O
O
O
N_3
PPM (F2)
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130

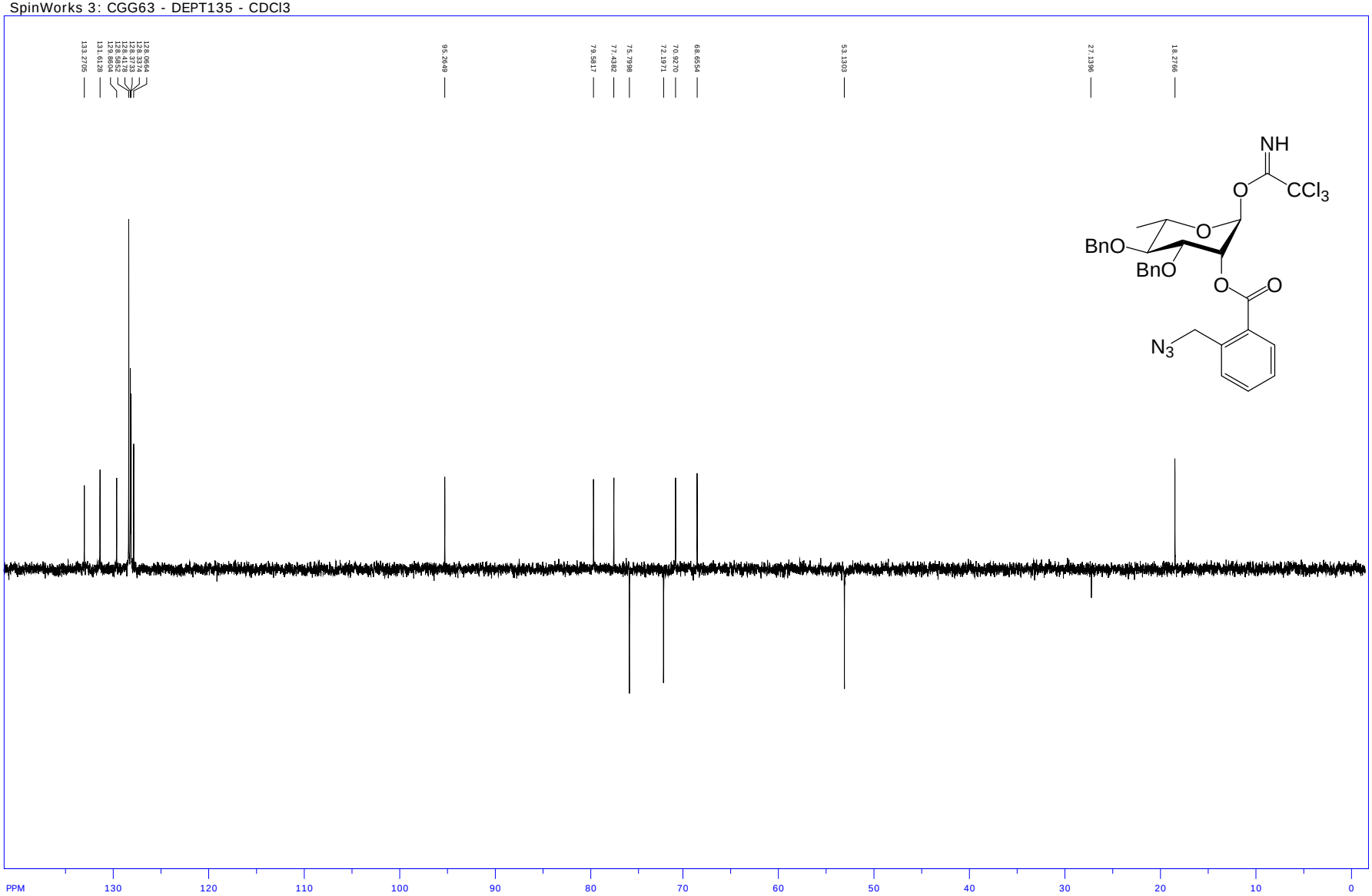
SpinWorks 3: CGG52 - 13C - CDCl3

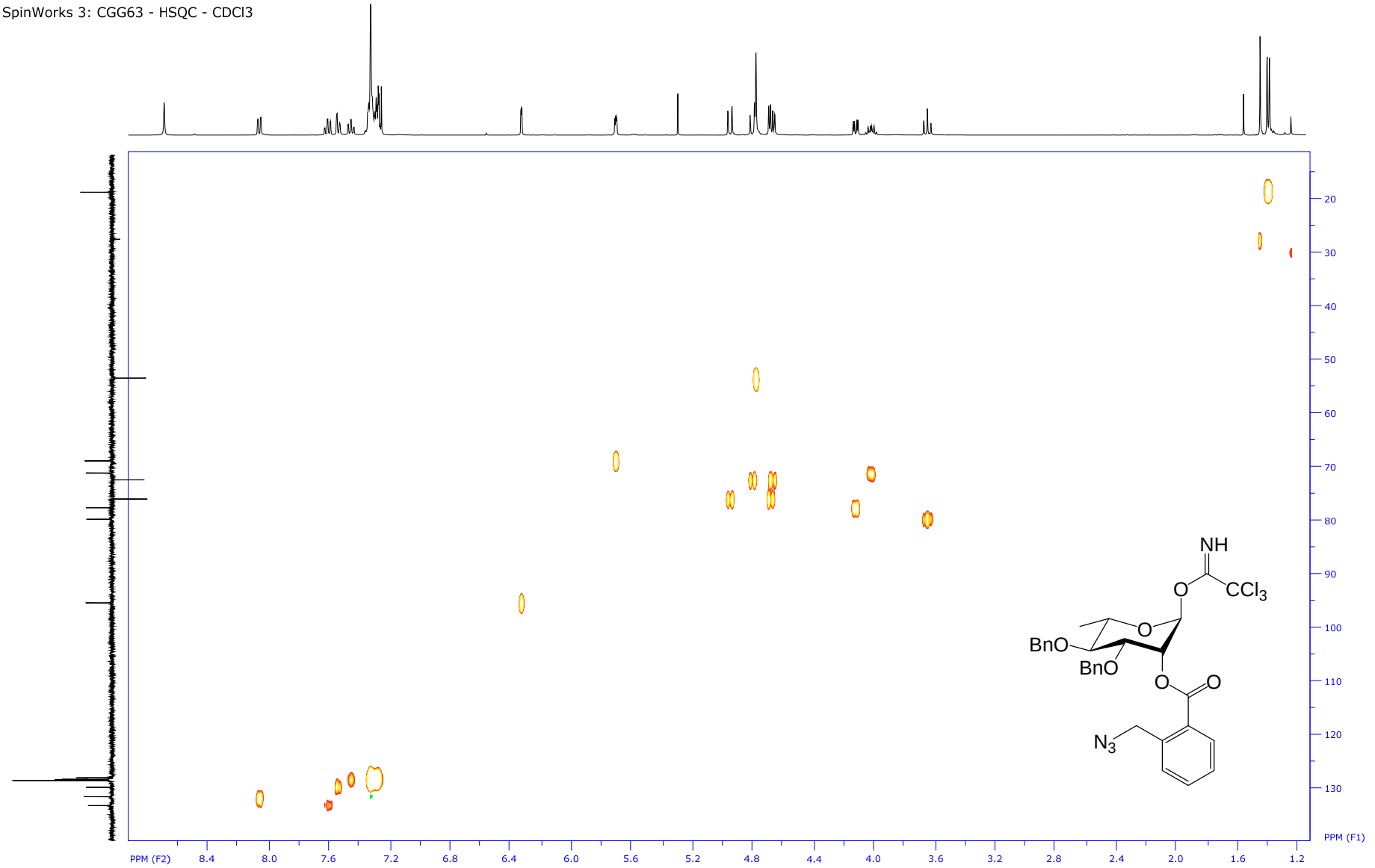


Compound **12**

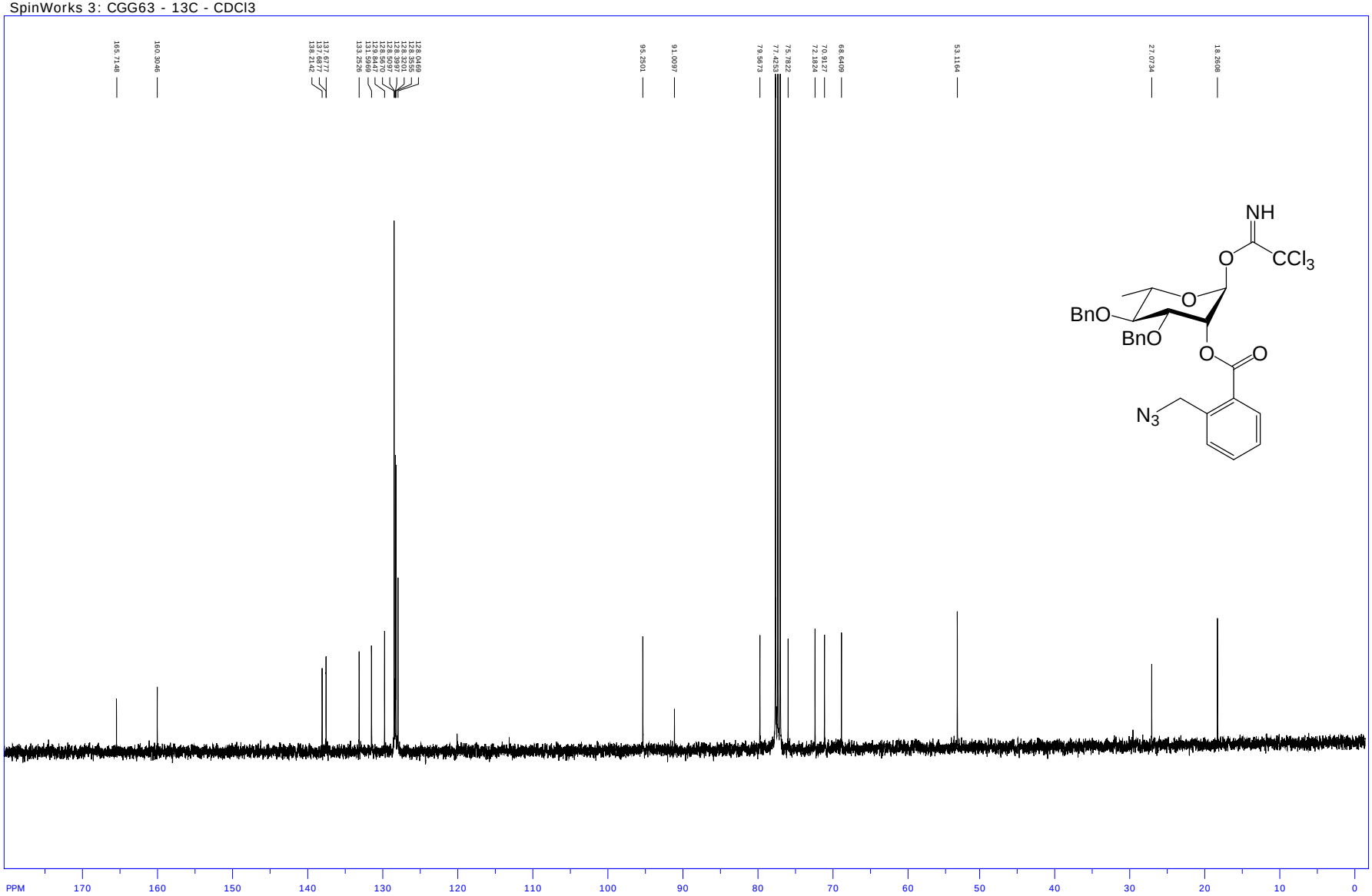

SpinWorks 3: CGG63 - 1H - CDCl3
8.6994
8.0509
8.0876
7.6423
7.5965
7.5634
7.5300
7.4858
7.4375
7.3702
7.2600
6.3301
6.3348
5.7081
4.9495
4.8162
4.7877
4.7783
4.6875
4.6597
4.6733
4.1179
4.0152
3.6421
1.3830
1.003
1.148
1.097
1.136
1.135
11.80
0.999
1.072
1.154
3.109
2.268
1.092
1.123
1.146
3.165
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
NH
O
CCl3
O
BnO
BnO
O
O
N3

SpinWorks 3: CGG63 - DEPT135 - CDCl3

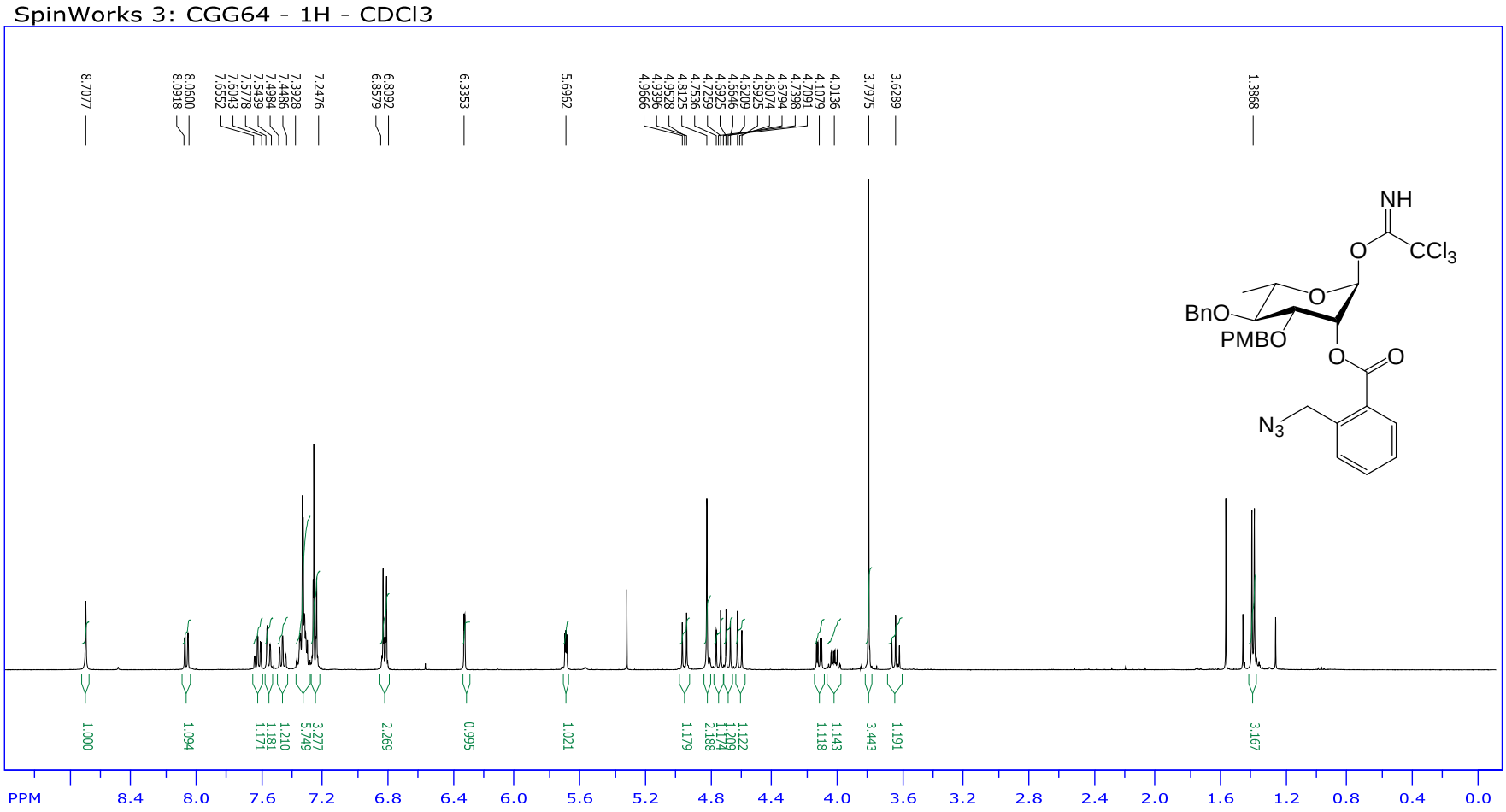



SpinWorks 3: CGG63 - HSQC - CDCl3
PPM (F2)
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
NH
O
CCl3
O
BnO
BnO
O
O
N3

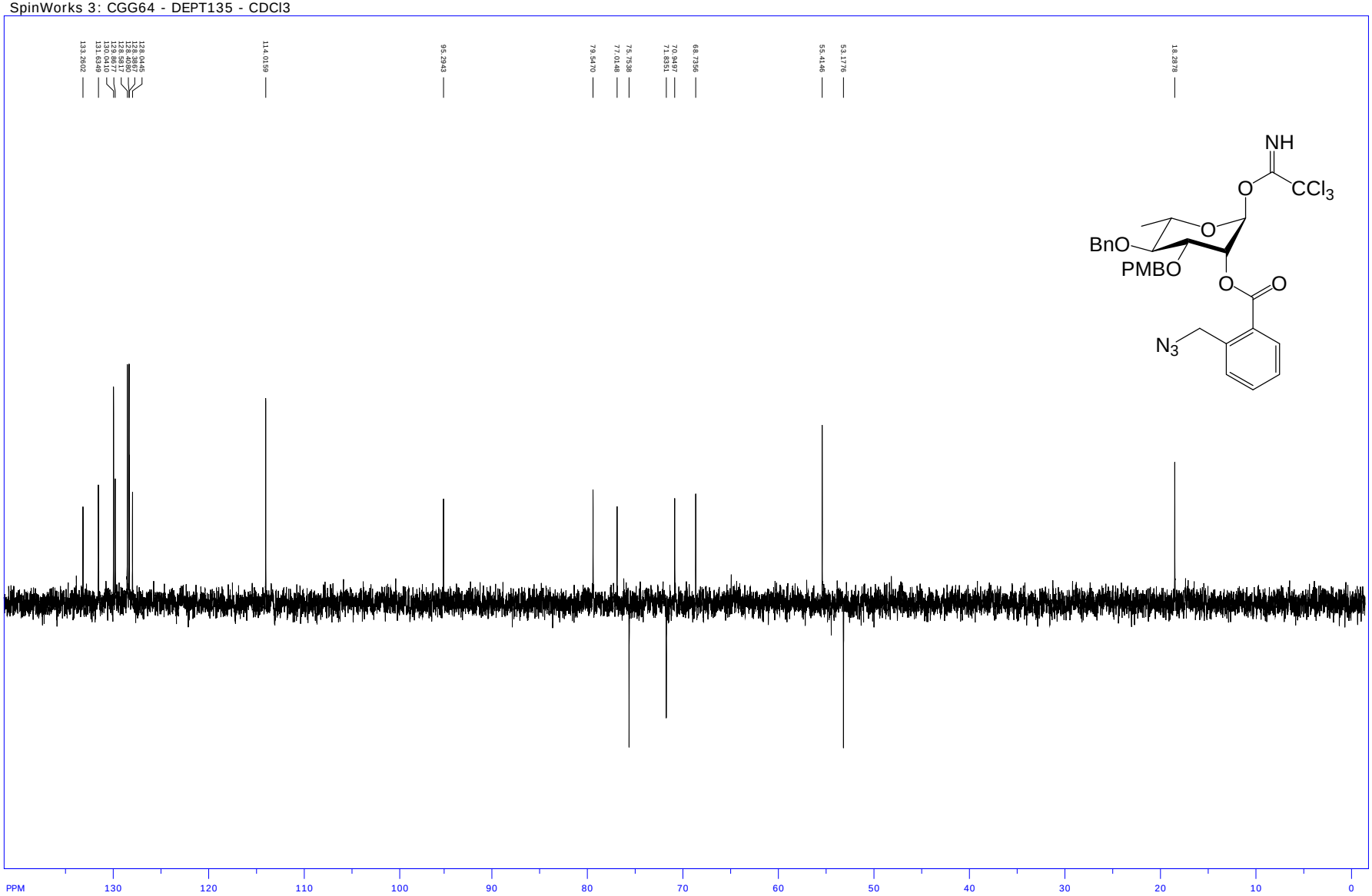
SpinWorks 3: CGG63 - 13C - CDCl3

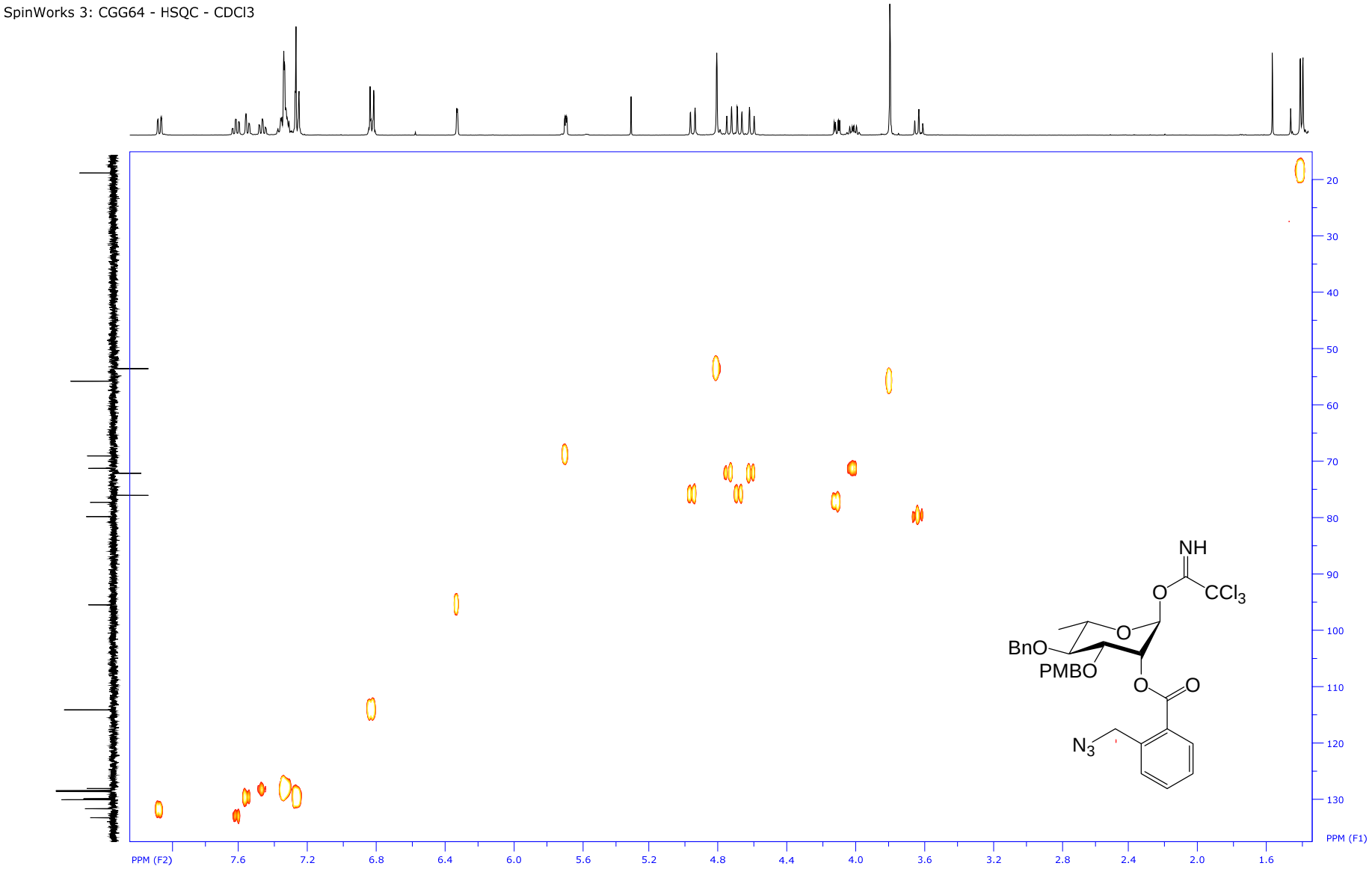


Compound **13**

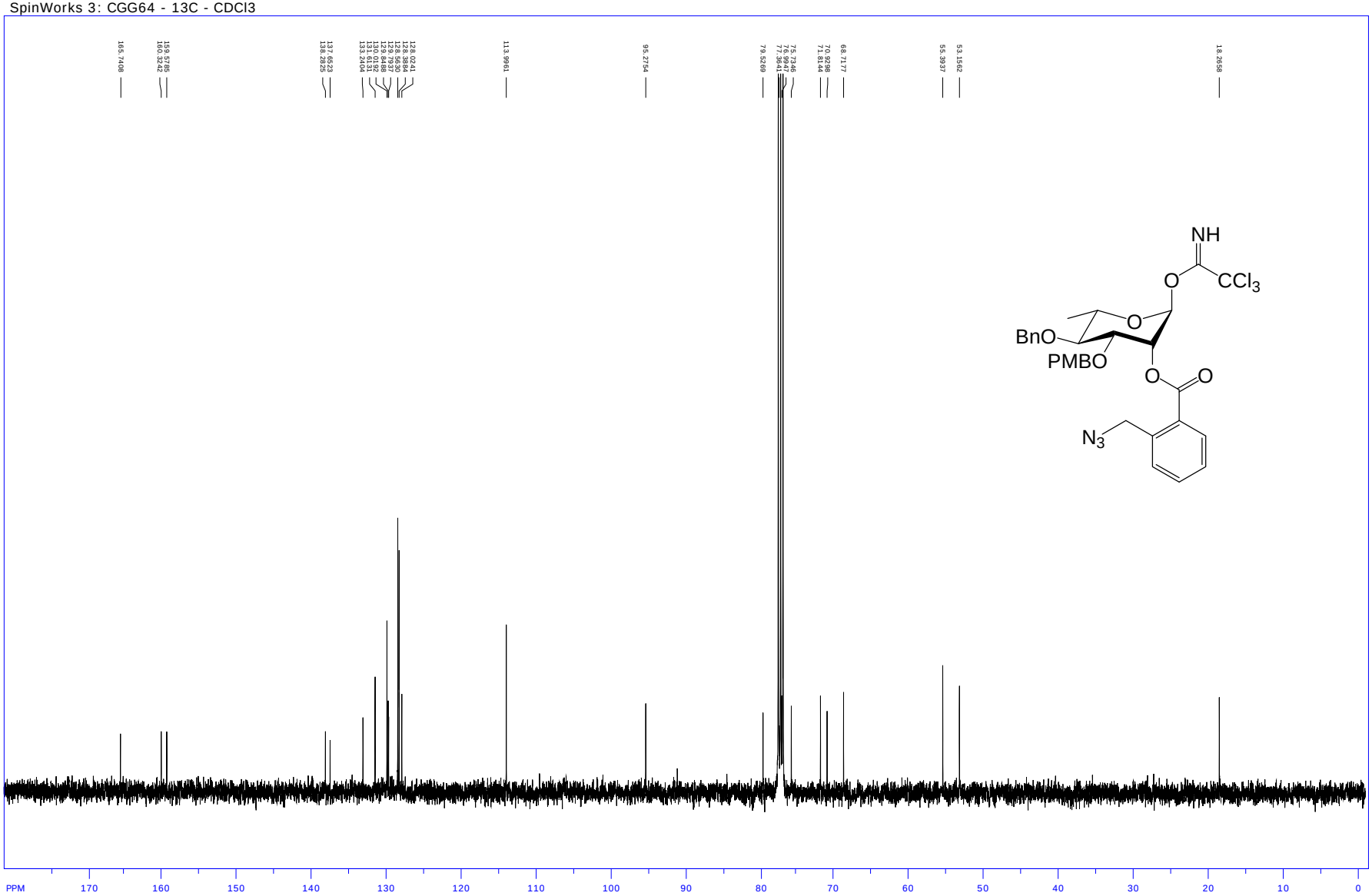

SpinWorks 3: CGG64 - 1H - CDCl3
8.7077
8.0918
8.0600
7.6552
7.6043
7.5778
7.5439
7.4984
7.4486
7.3928
7.2476
6.8579
6.8092
6.3353
5.6962
4.9666
4.9396
4.9528
4.8125
4.7536
4.7259
4.6925
4.6646
4.6209
4.5903
4.5921
4.6074
4.6794
4.7398
4.7091
4.1079
4.0136
3.7975
3.6289
1.3868
1.000
1.094
1.171
1.181
1.210
5.749
3.277
2.269
0.995
1.021
1.179
2.188
1.122
1.118
1.143
3.443
1.191
3.167
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
NH
O
CCl3
O
BnO
PMBO
O
O
N3

SpinWorks 3: CGG64 - DEPT135 - CDCl3

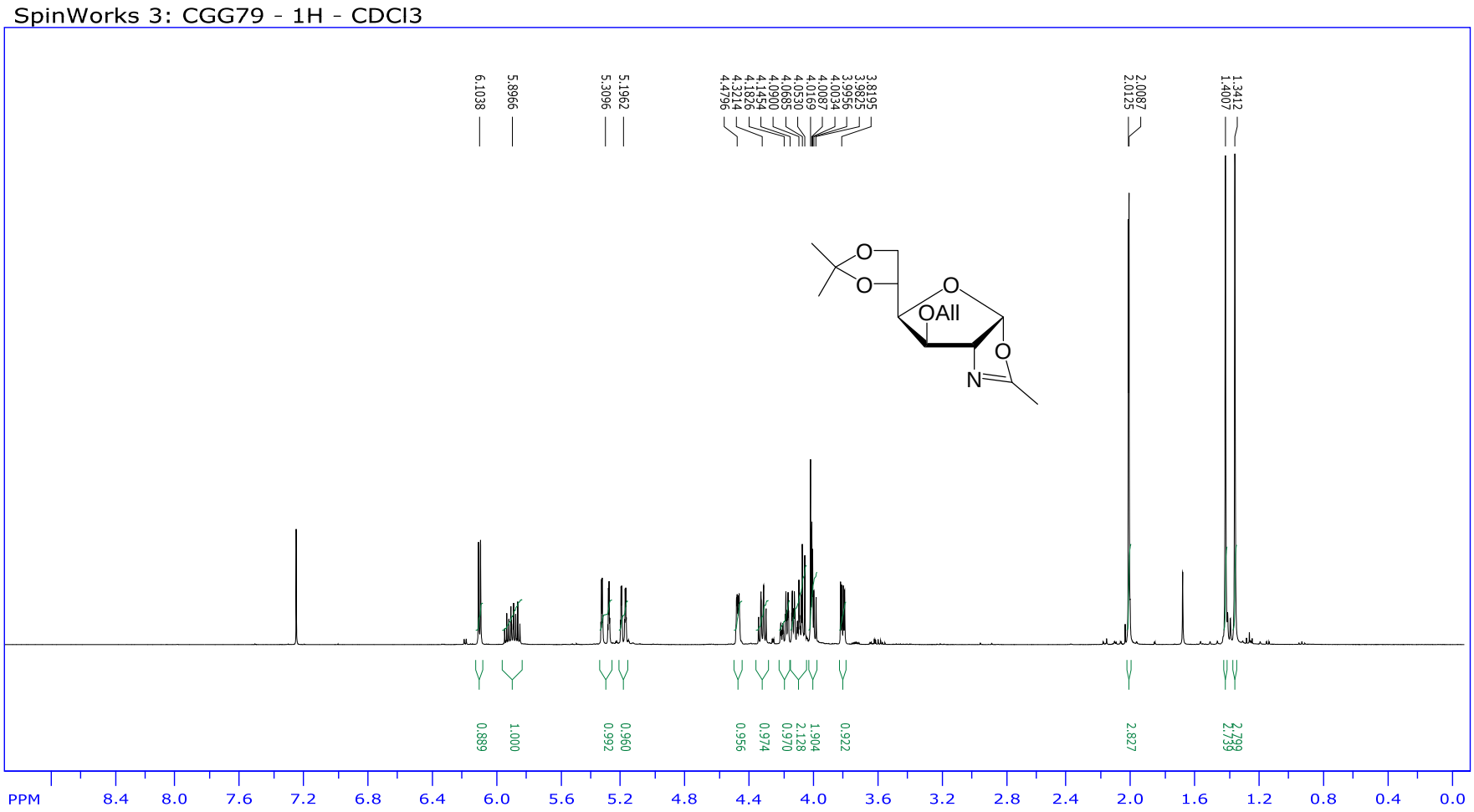


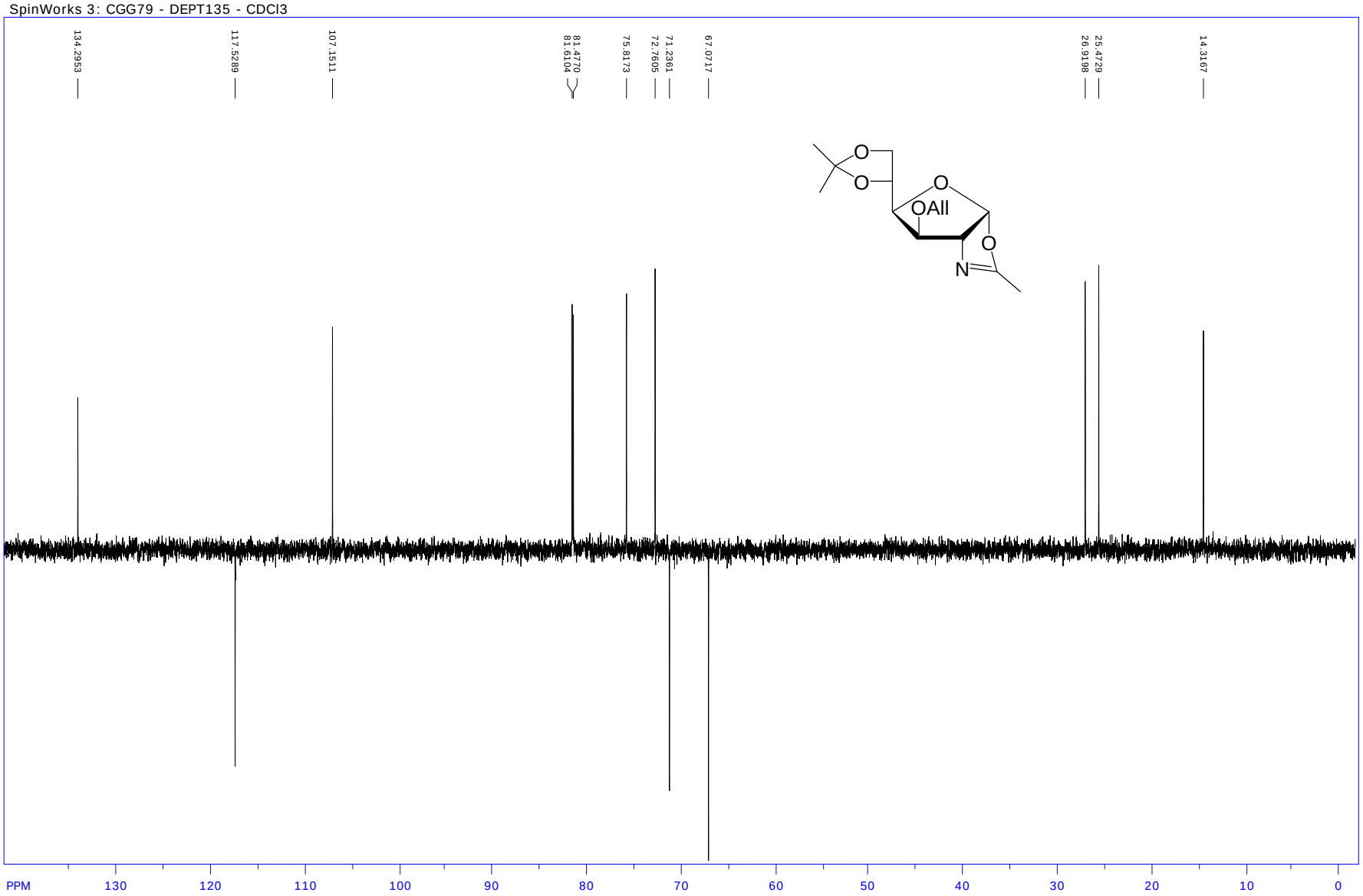

SpinWorks 3: CGG64 - HSQC - CDCl3
PPM (F2)
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
NH
O
CCl3
O
BnO
PMBO
O
O
N3

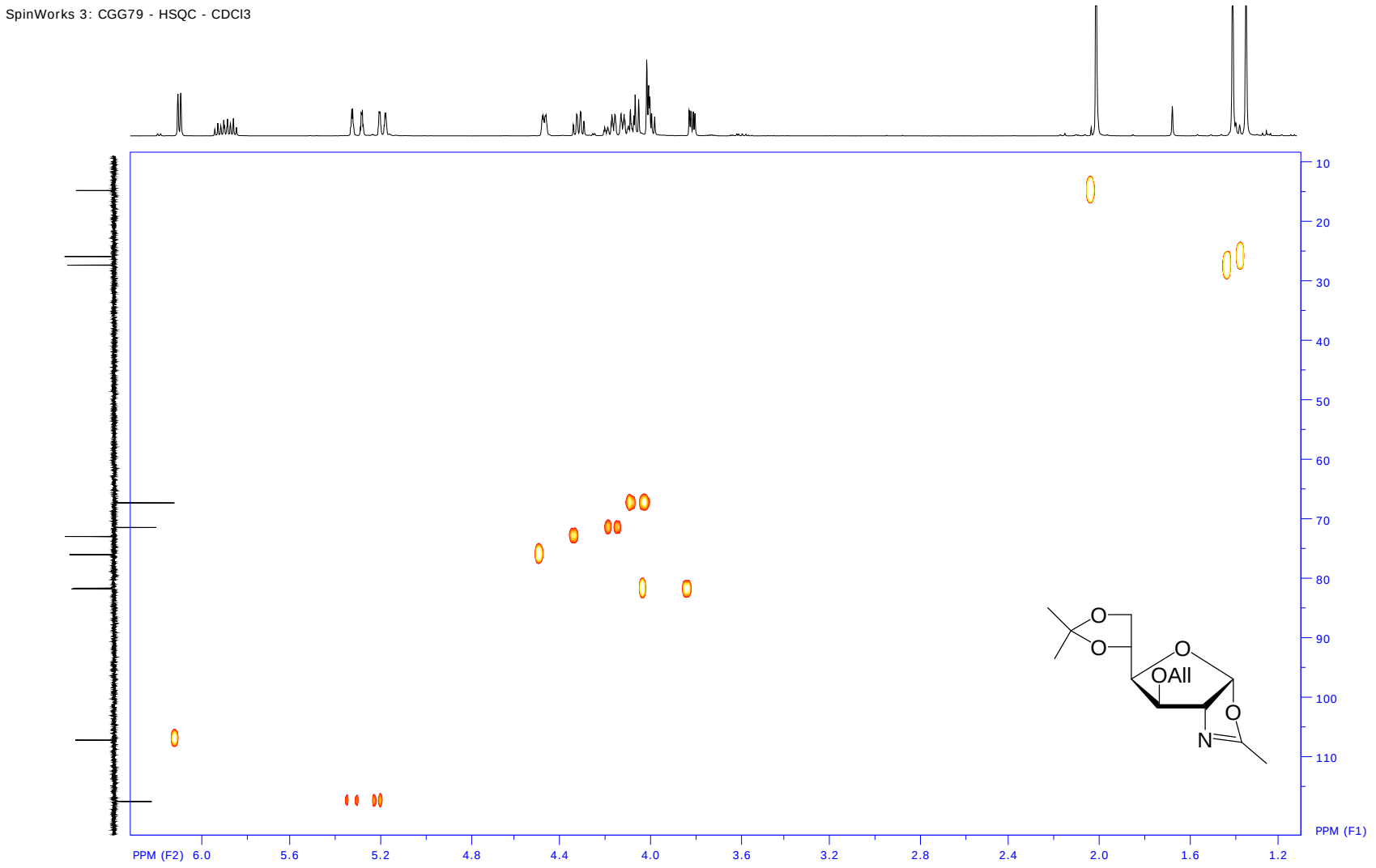
SpinWorks 3: CGG64 - 13C - CDCl3



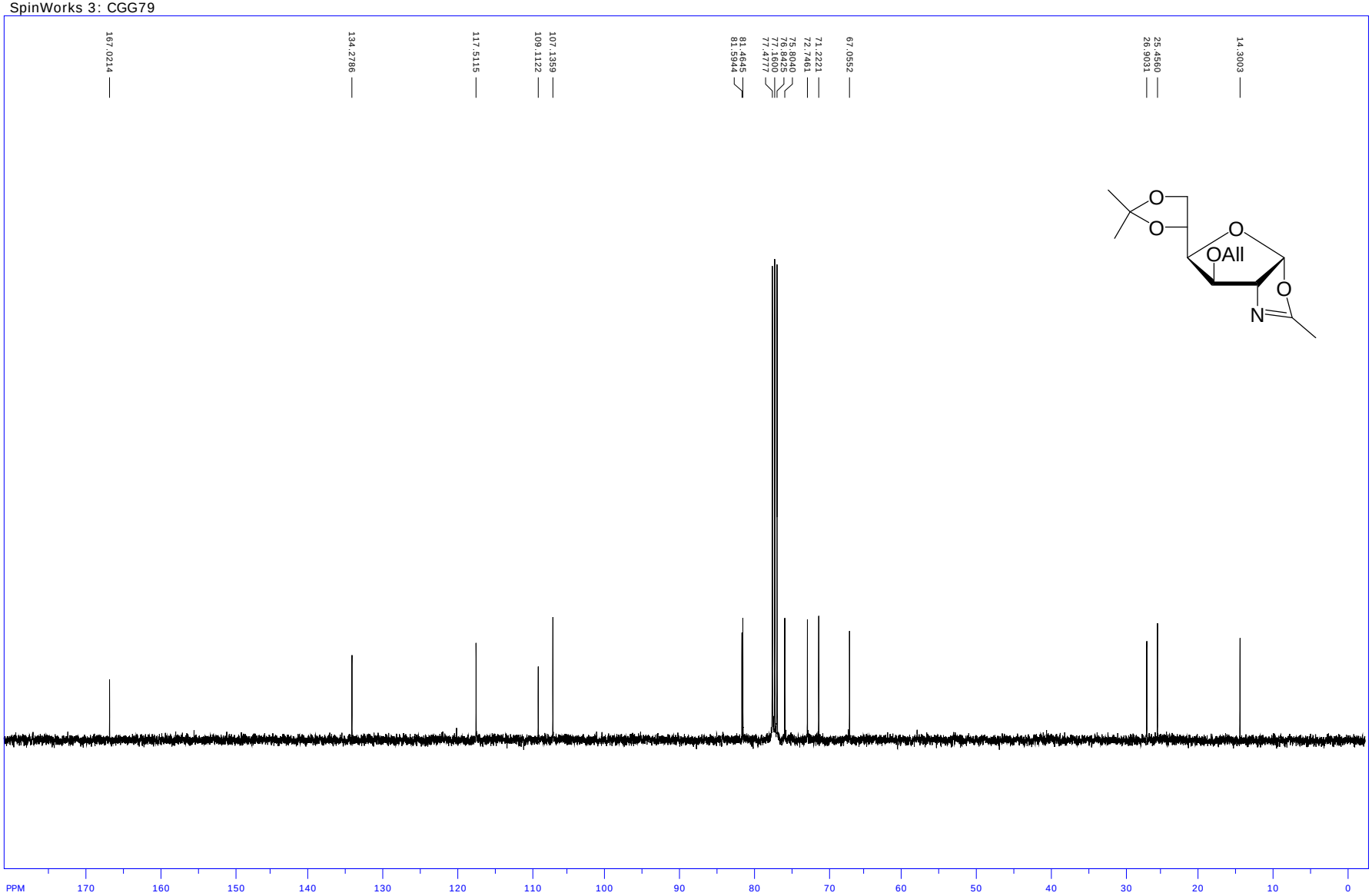
Compound **31**


SpinWorks 3: CGG79 - 1H - CDCl3
6.1038
5.8966
5.3096
5.1962
4.4796
4.3214
4.1826
4.1454
4.0900
4.0685
4.0530
4.0169
4.0087
4.0034
3.9956
3.9825
3.8195
2.0125
2.0087
1.4007
1.3412
OAll
0.889
1.000
0.992
0.960
0.956
0.974
0.970
2.128
1.904
0.922
2.827
2.739
2.799
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

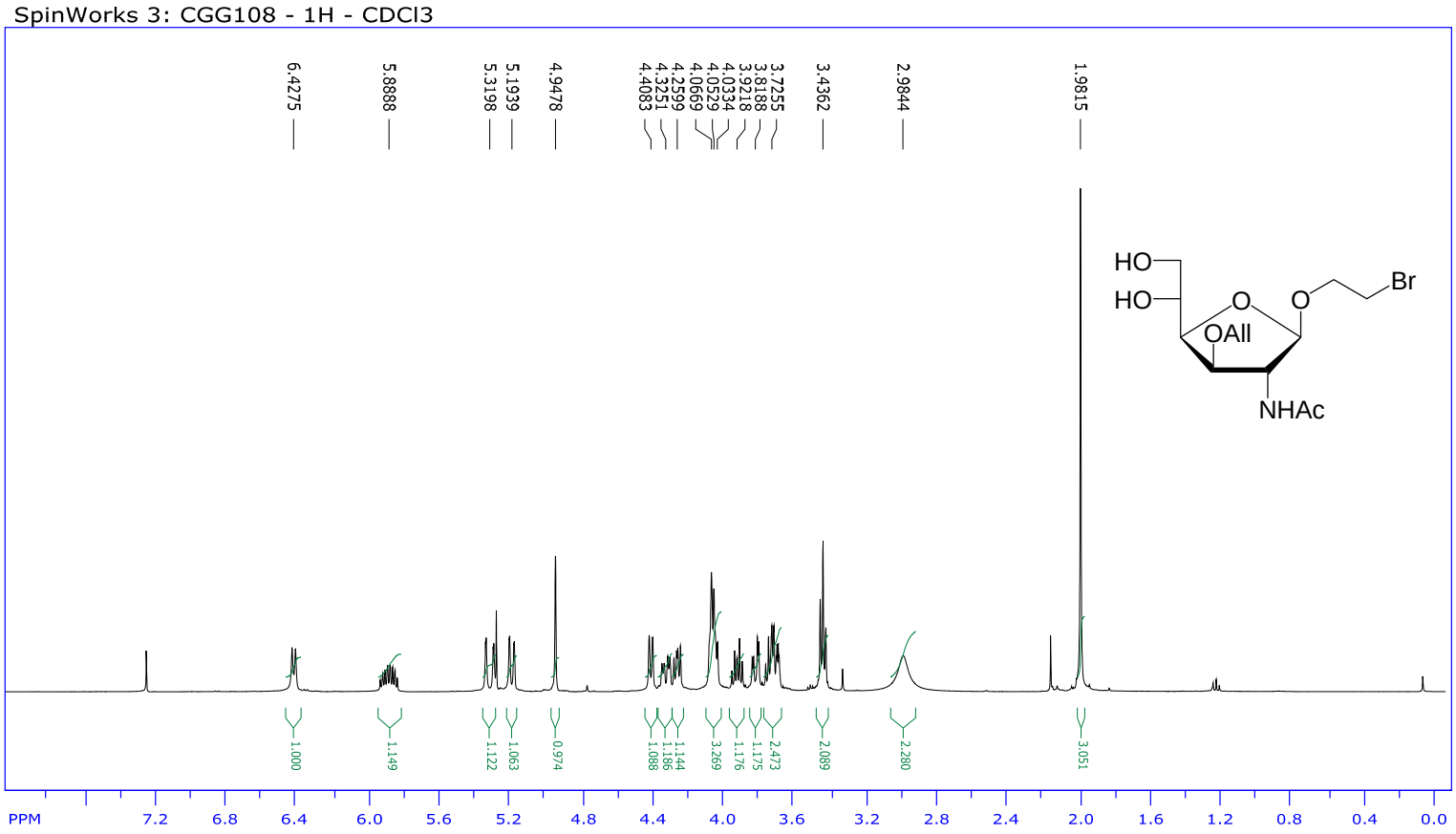

SpinWorks 3: CGG79 - DEPT135 - CDCl3
134.2953
117.5289
107.1511
81.4770
81.6104
75.8173
72.7605
71.2361
67.0717
26.9198
25.4729
14.3167
O
O
O
OAll
O
N
PPM
130
120
110
100
90
80
70
60
50
40
30
20
10
0


SpinWorks 3: CGG79 - HSQC - CDCl3
PPM (F2) 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2
PPM (F1) 10 20 30 40 50 60 70 80 90 100 110
O
O
O
OAll
O
N
file: ...s\Charles\Pasteur\RMN\CGG79\92\ser
expt: <hsqcetgp>
transmitter freq: 400.131629 MHz
time domain size: 2048 by 128 points
width (F2): 3019.32 Hz = 7.5458 ppm = 1.4743 Hz/pt
number of scans: 1
F2: freq. of 0 ppm: 400.1300000 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 57.930 ppm/cm: 0.14478
F1: freq. of 0 ppm: 100.6127690 MHz
processed size: 1024 complex points
window function: Sine Squared
shift: 90.0 degrees
Hz/cm: 549.976 ppm/cm: 5.46586

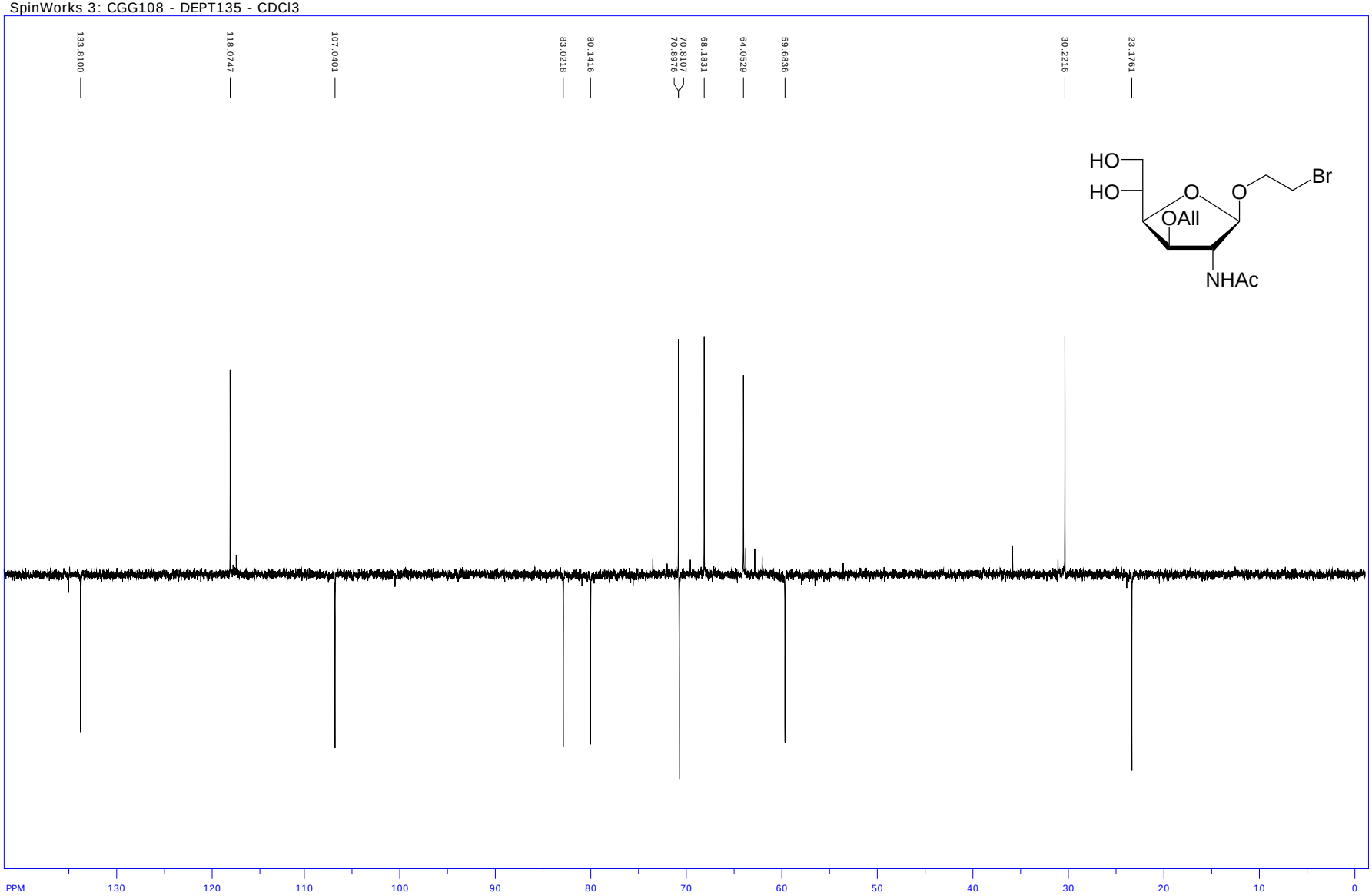
SpinWorks 3: CGG79

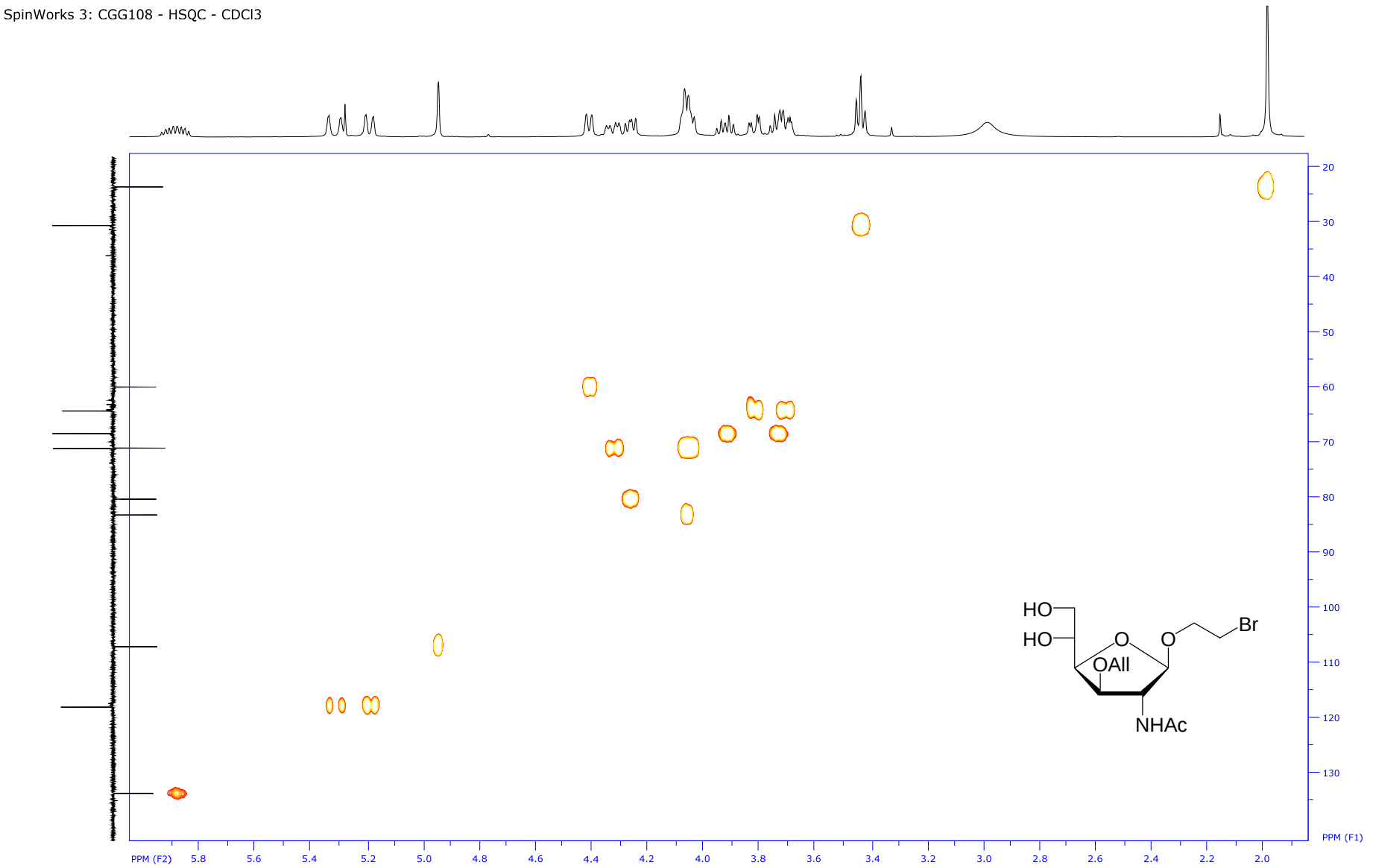


Compound **S8**

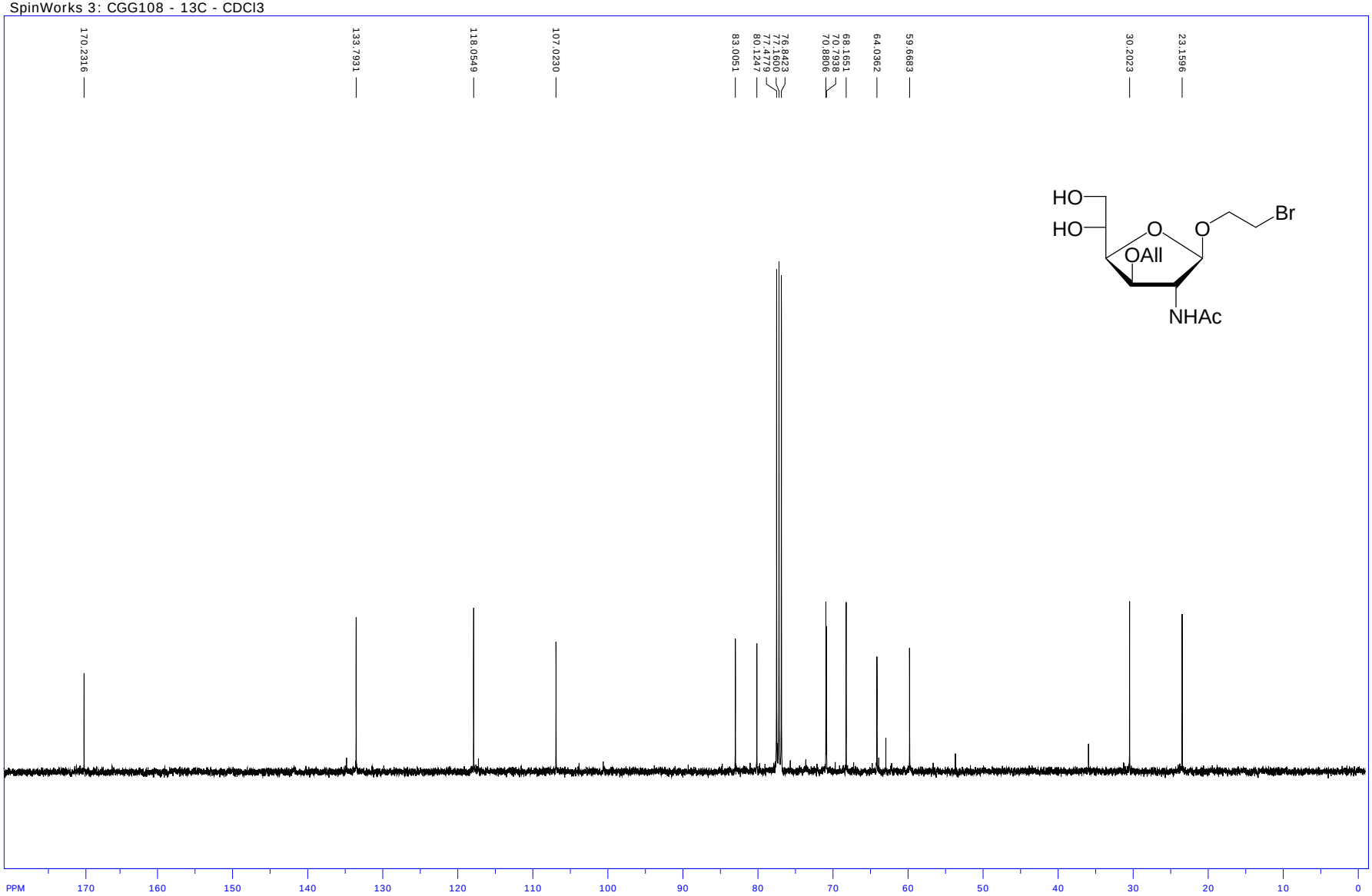

SpinWorks 3: CGG108 - 1H - CDCl3
6.4275
5.8888
5.3198
5.1939
4.9478
4.4083
4.3251
4.2599
4.0669
4.0529
4.0334
3.9218
3.8188
3.7255
3.4362
2.9844
1.9815
HO
HO
O
O
Br
OAll
NHAc
1.000
1.149
1.122
1.063
0.974
1.088
1.186
1.144
3.269
1.176
1.175
2.473
2.089
2.280
3.051
PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

SpinWorks 3: CGG108 - DEPT135 - CDCl3

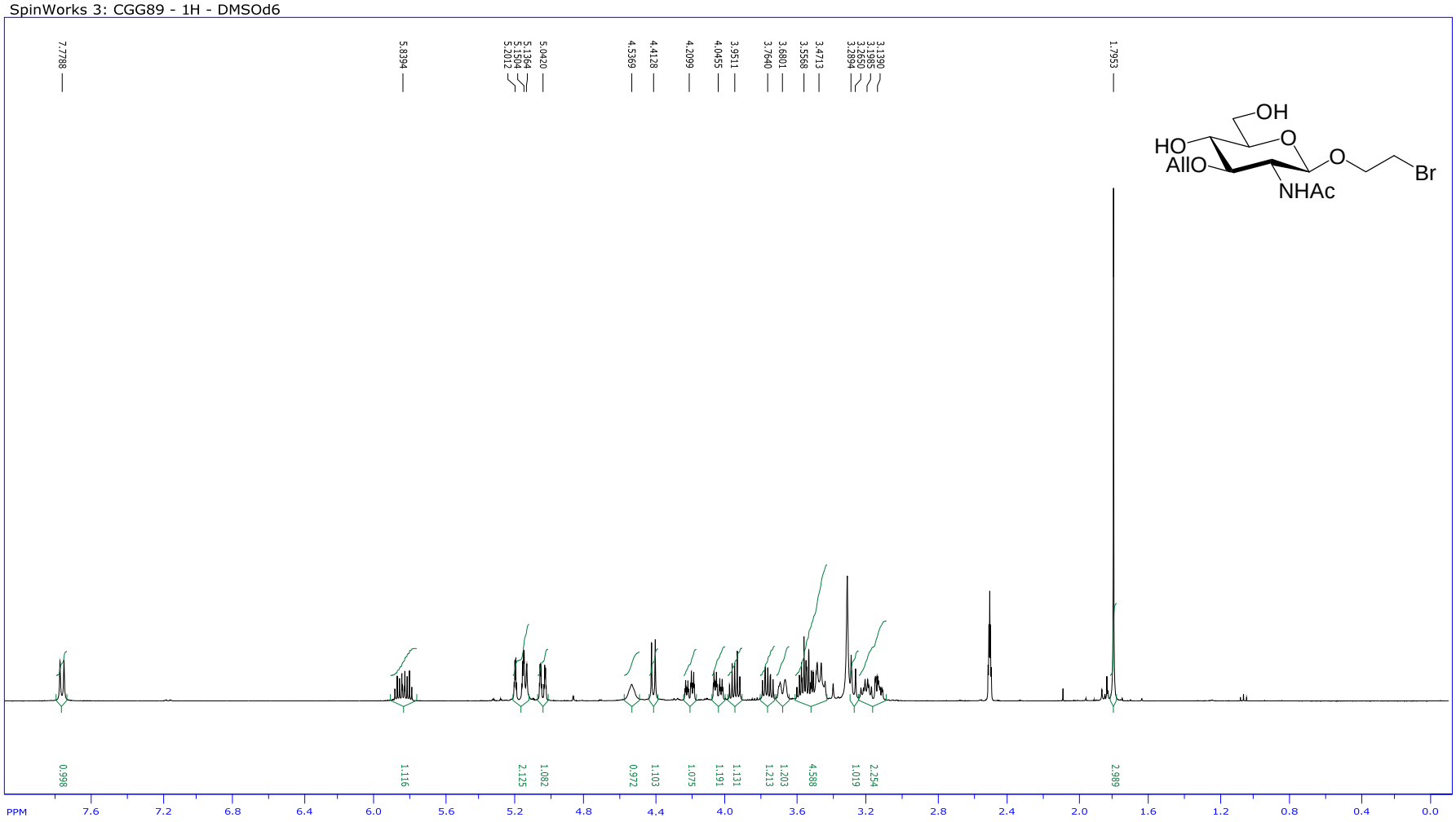



SpinWorks 3: CGG108 - HSQC - CDCl3
HO
HO
O
O
Br
OAll
NHAc
PPM (F2)
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130

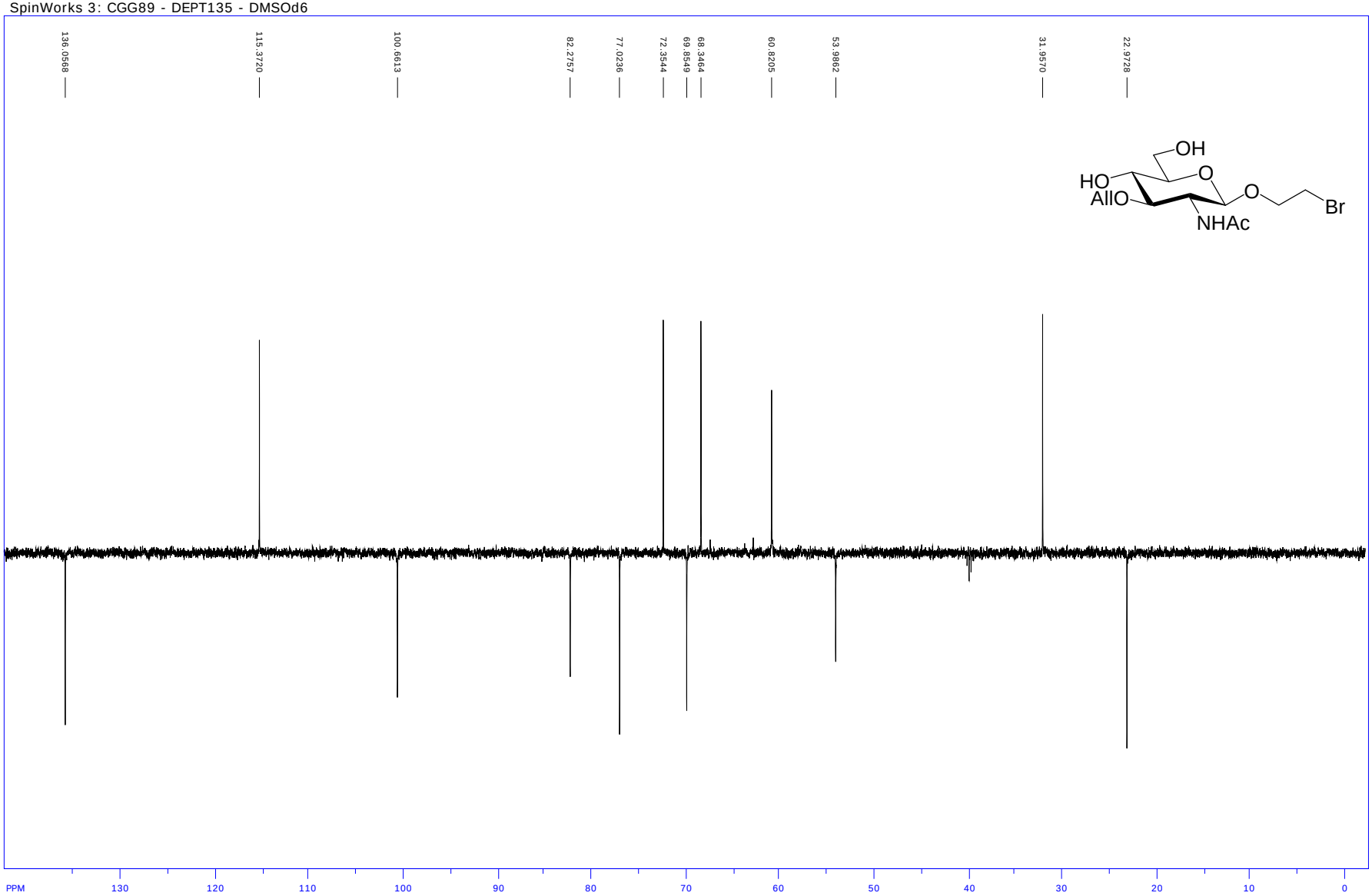
SpinWorks 3: CGG108 - 13C - CDCl3

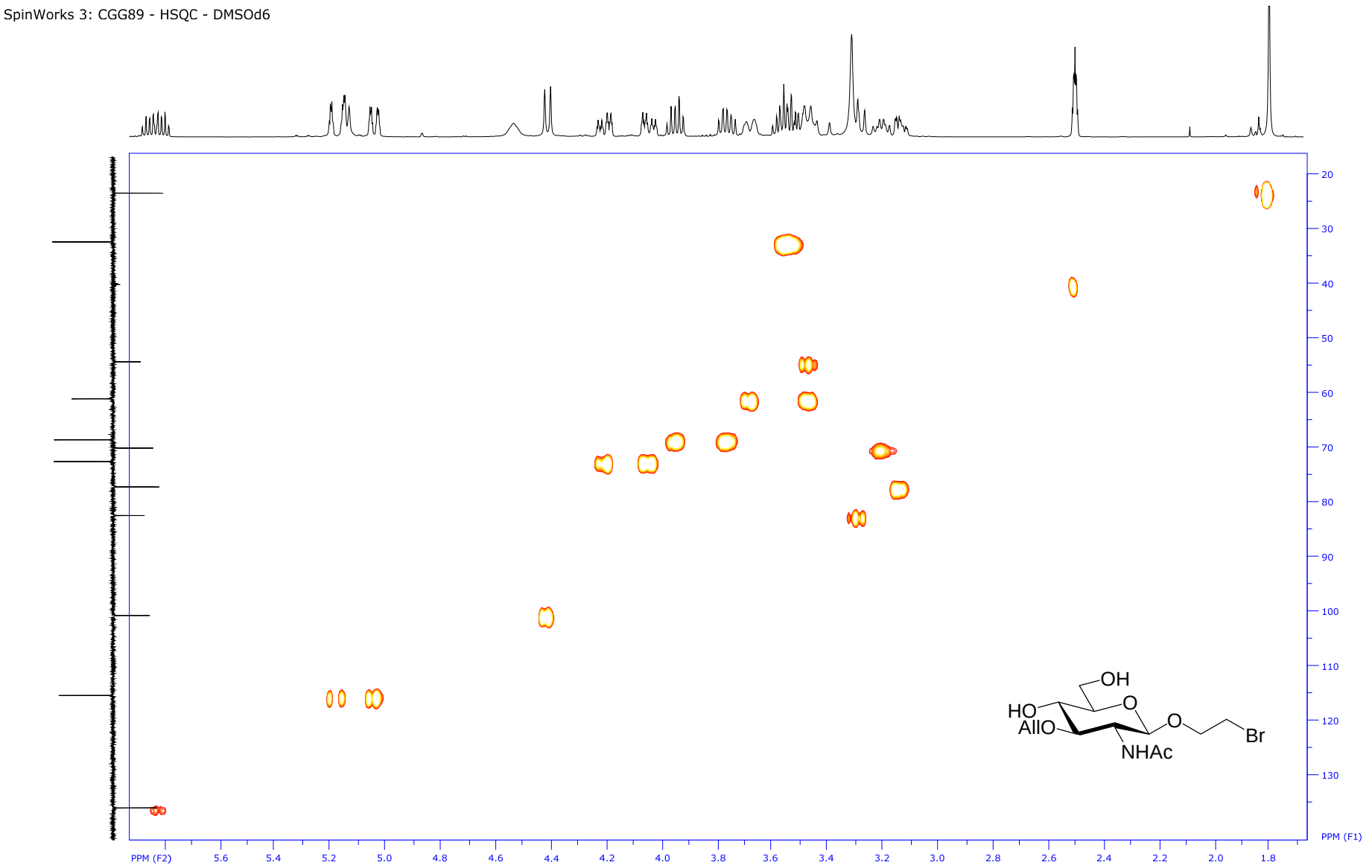


Compound **32**

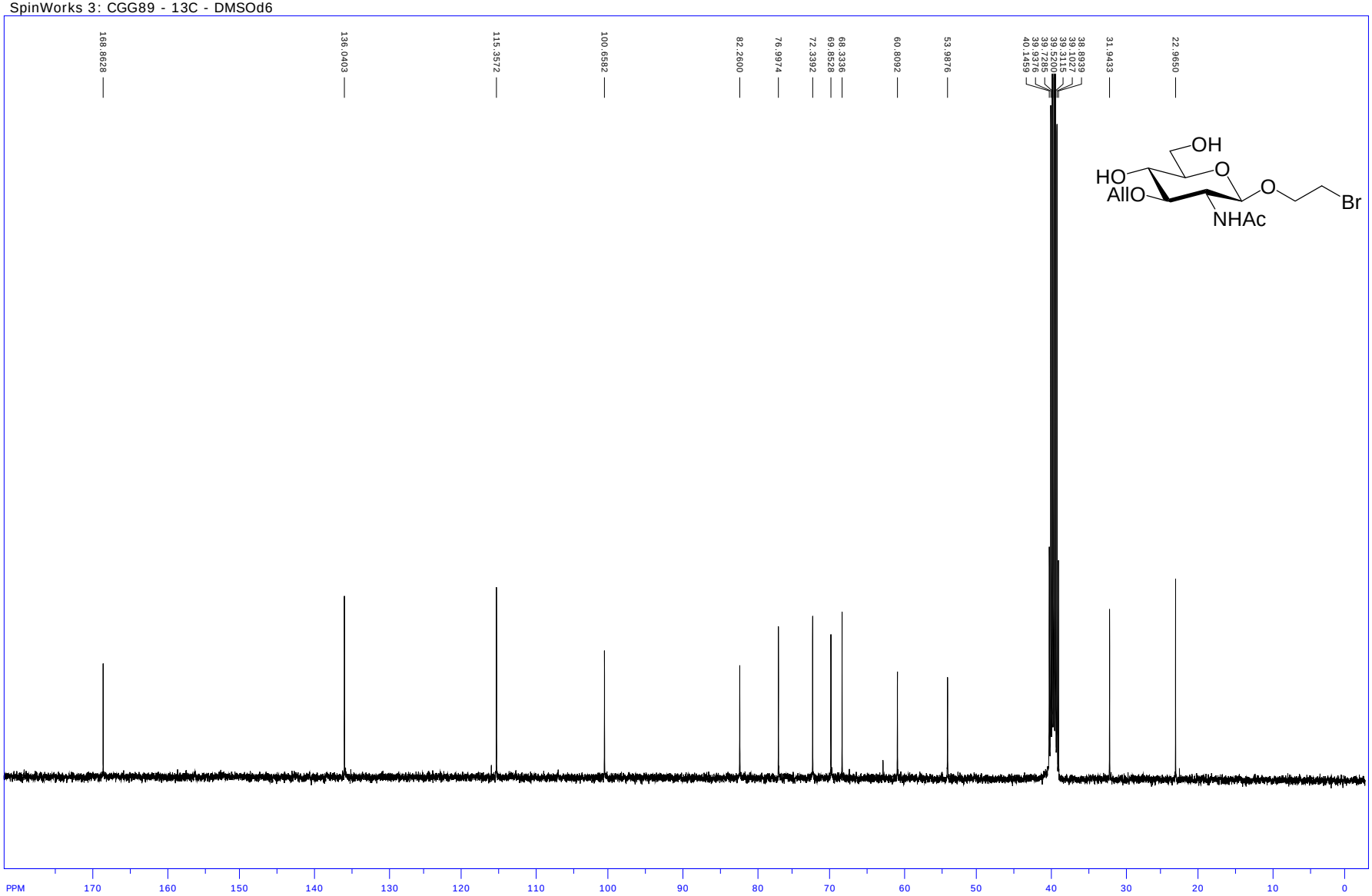

SpinWorks 3: CGG89 - 1H - DMSOd6
7.7788
5.8394
5.2012
5.1504
5.1364
5.0420
4.5369
4.4128
4.2099
4.0455
3.9511
3.7640
3.6801
3.5568
3.4713
3.2894
3.2650
3.1985
3.1390
1.7953
OH
HO
O
AllO
O
Br
NHAc
0.998
1.116
2.125
1.082
0.972
1.103
1.075
1.191
1.131
1.213
1.203
4.588
1.019
2.254
2.989
PPM
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

SpinWorks 3: CGG89 - DEPT135 - DMSOd6

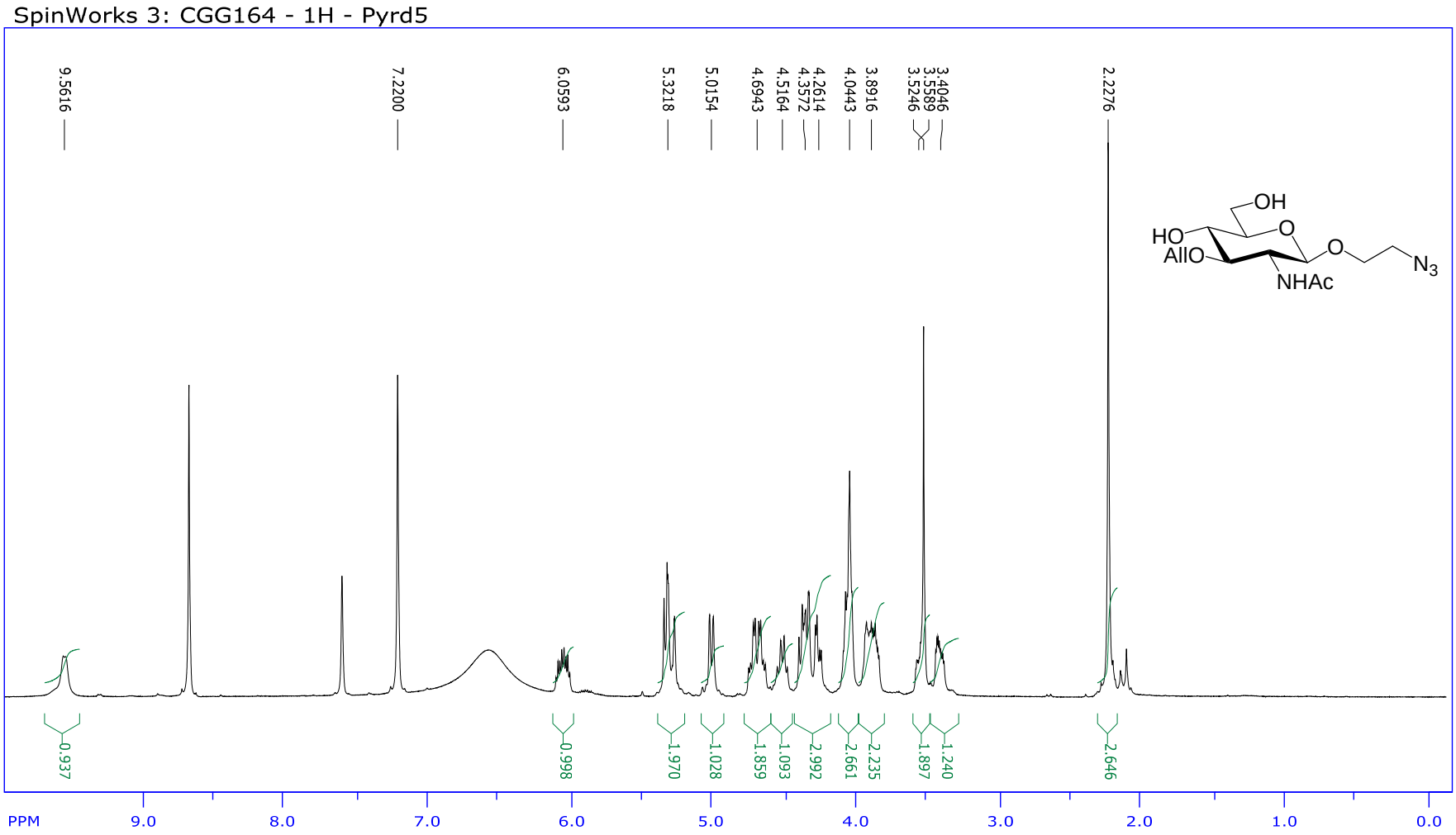



SpinWorks 3: CGG89 - HSQC - DMSOd6
PPM (F2)
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OH
HO
AllO
O
O
Br
NHAc

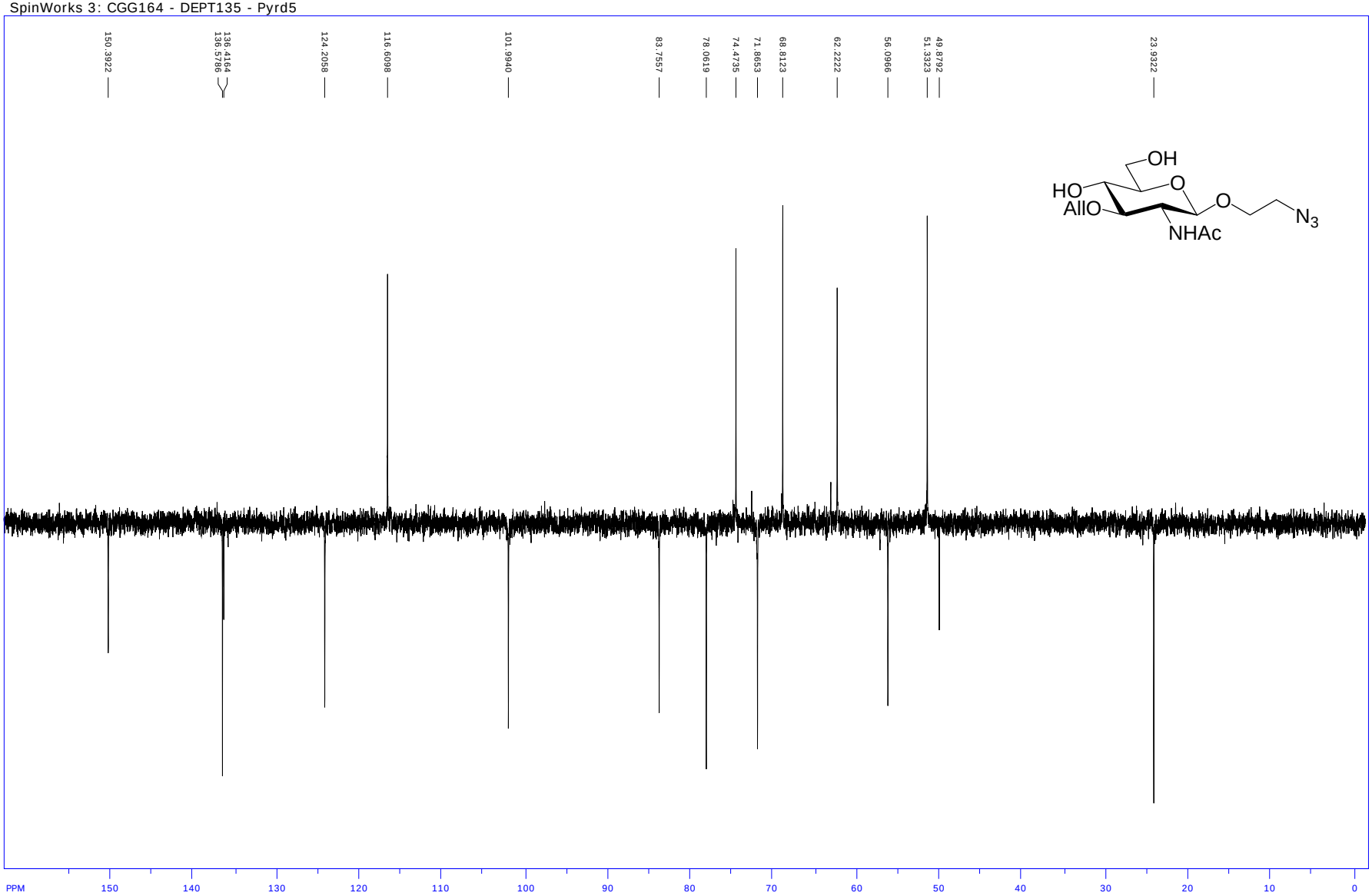
SpinWorks 3: CGG89 - 13C - DMSOd6

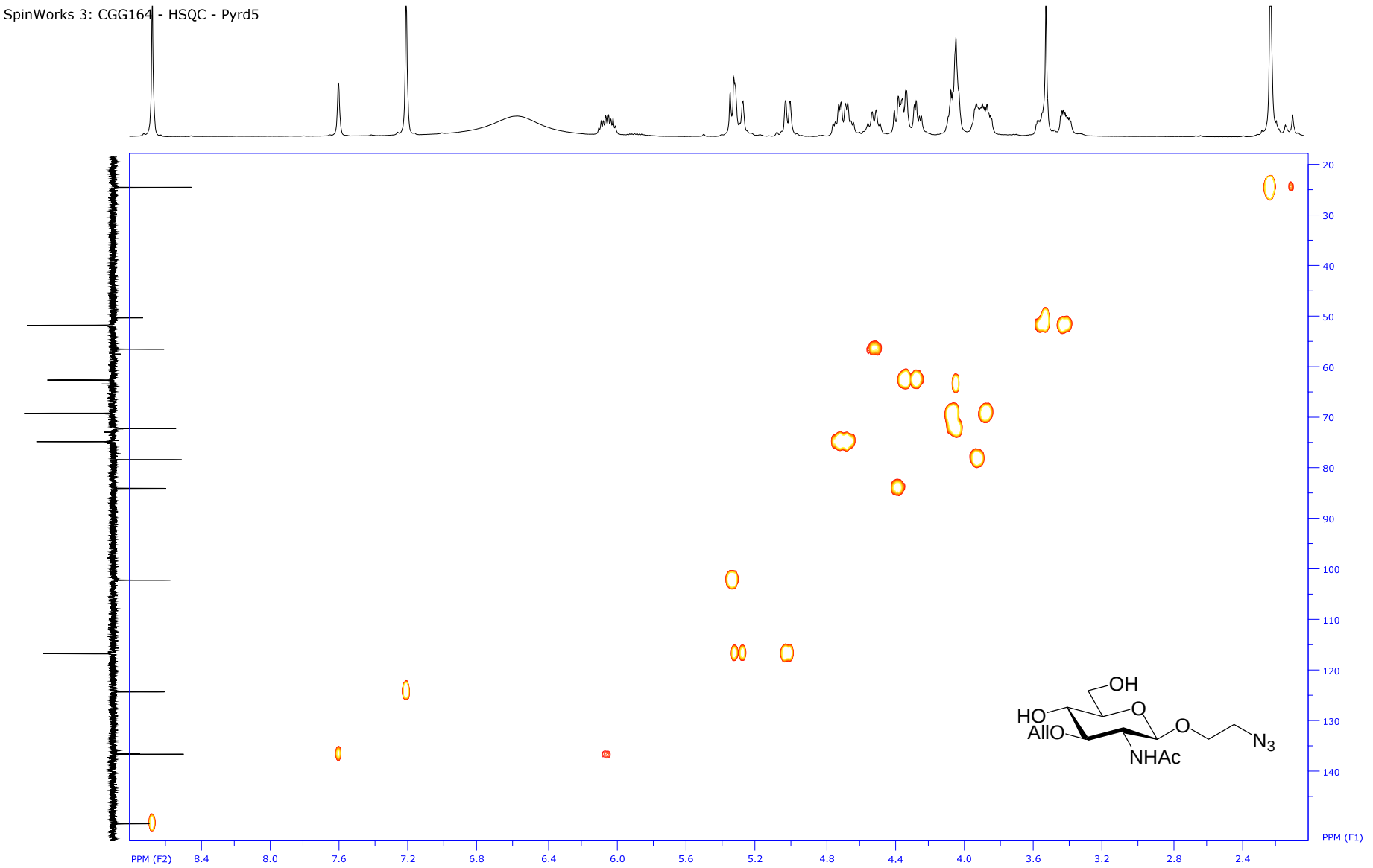


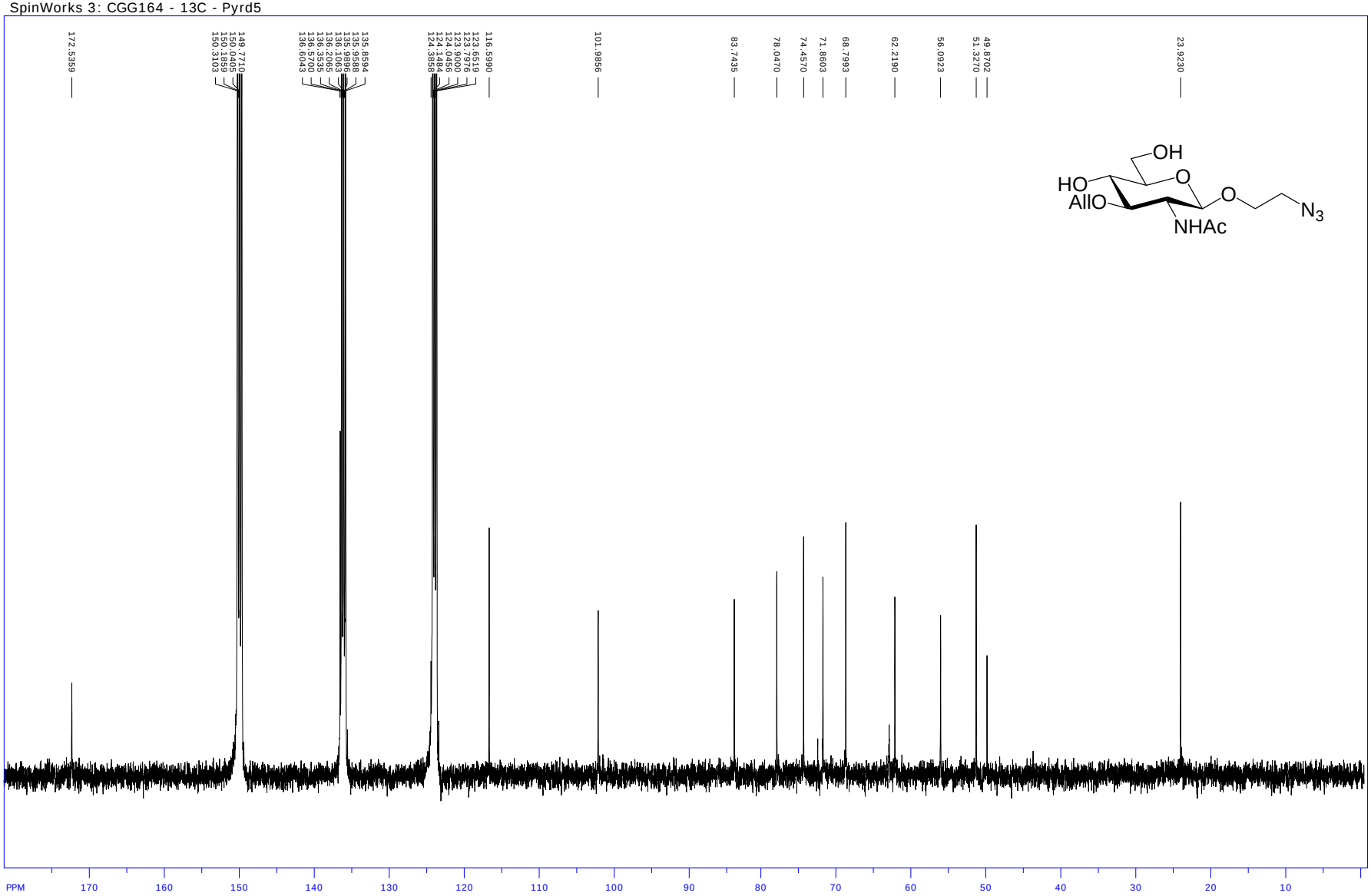
Compound **S9**


SpinWorks 3: CGG164 - 1H - Pyrd5
9.5616
7.2200
6.0593
5.3218
5.0154
4.6943
4.5164
4.3572
4.2614
4.0443
3.8916
3.5246
3.5589
3.4046
2.2276
OH
HO
AllO
O
O
N3
NHAc
0.937
0.998
1.970
1.028
1.859
1.093
2.992
2.661
2.235
1.897
1.240
2.646
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

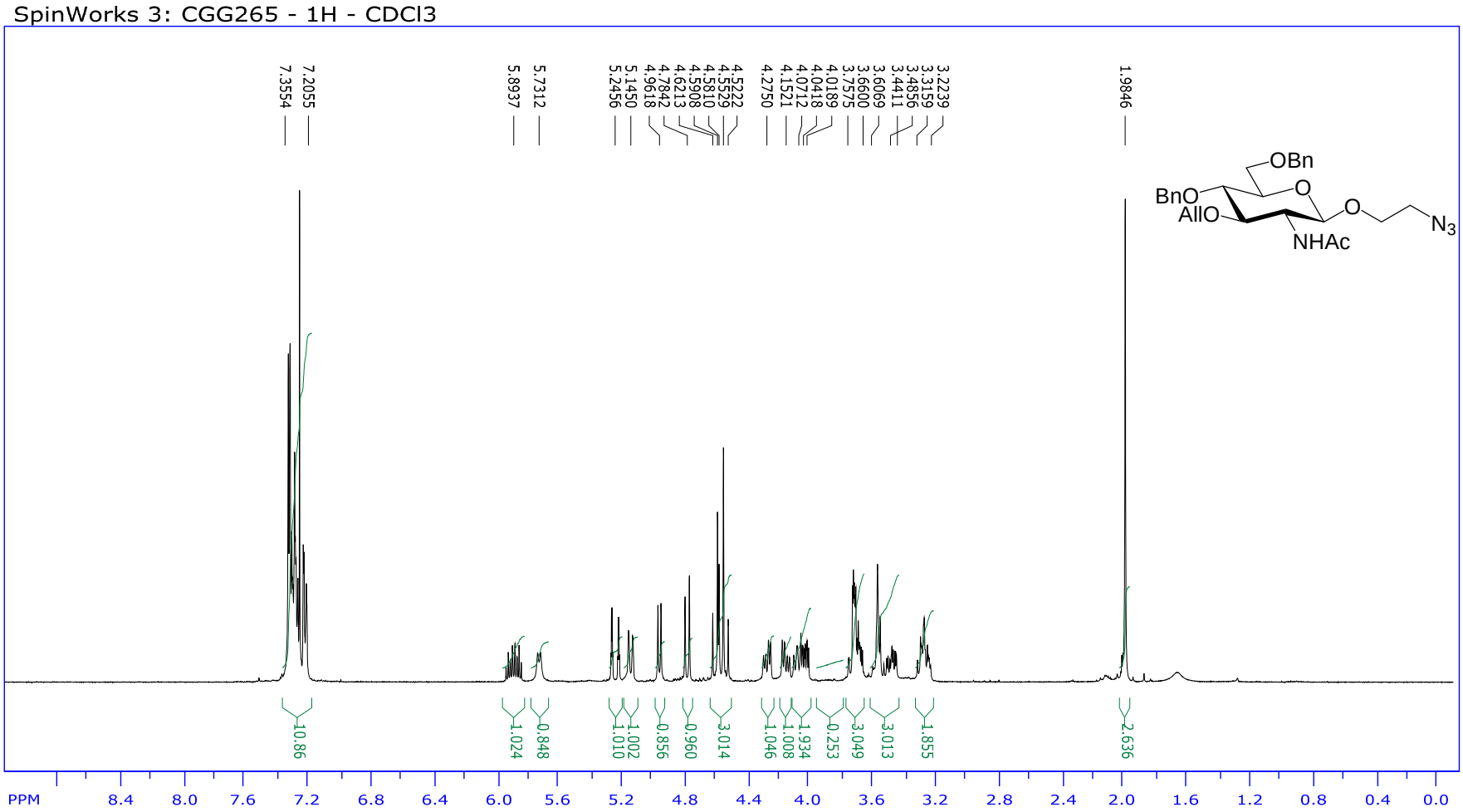
SpinWorks 3: CGG164 - DEPT135 - Pyrd5

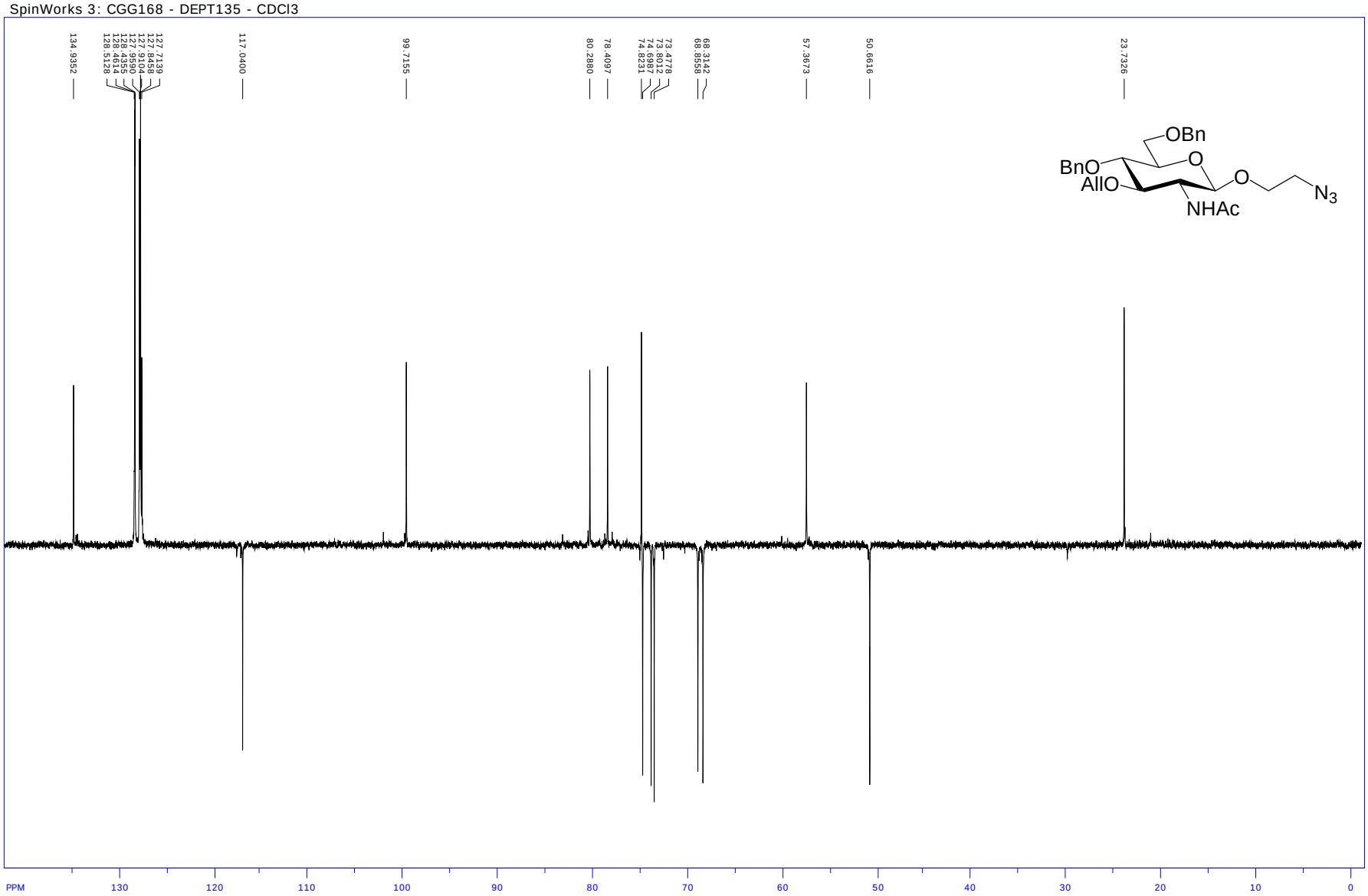


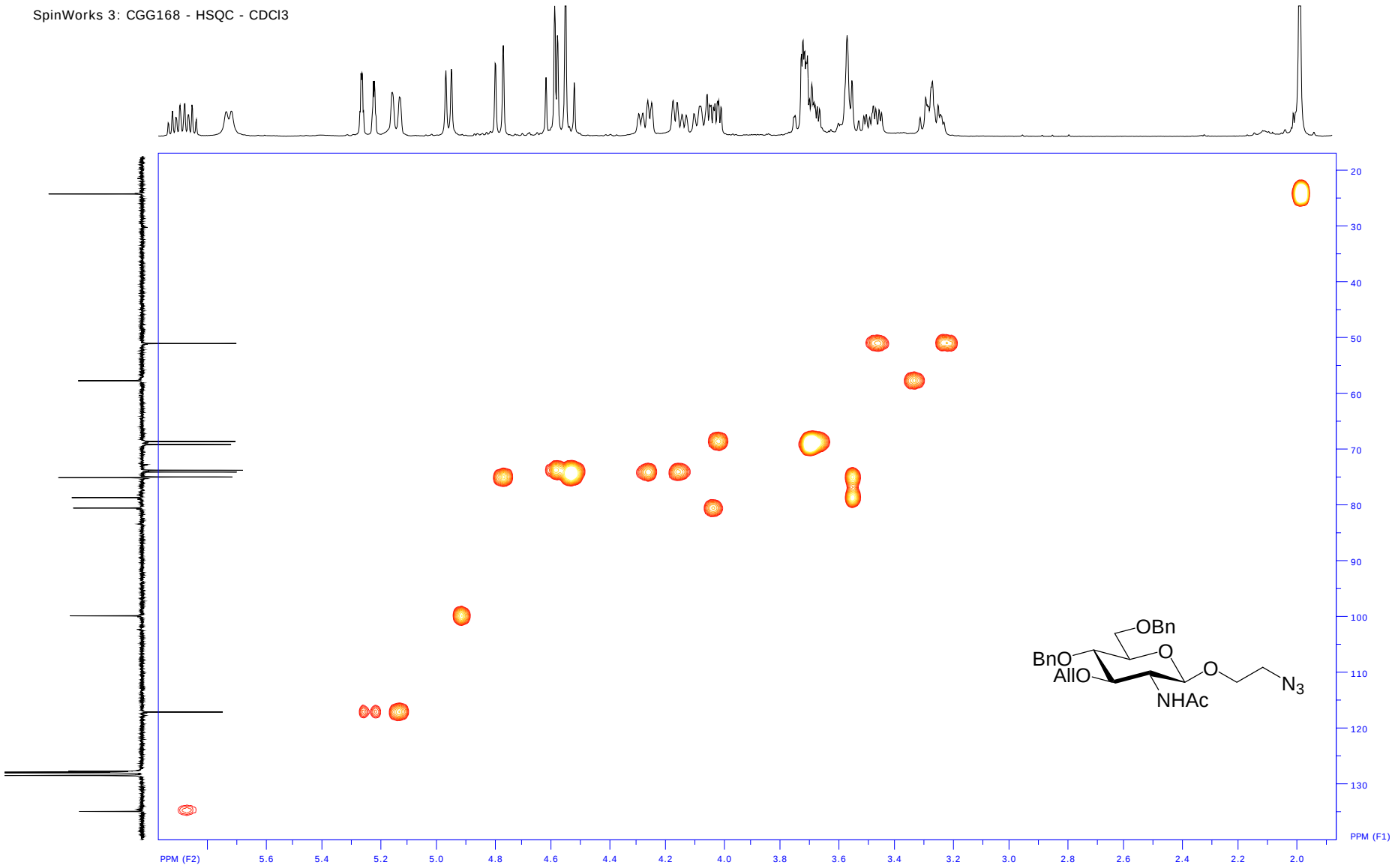

SpinWorks 3: CGG164 - HSQC - Pyrd5
PPM (F2)
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
140
OH
HO
AllO
O
O
NHAc
N3

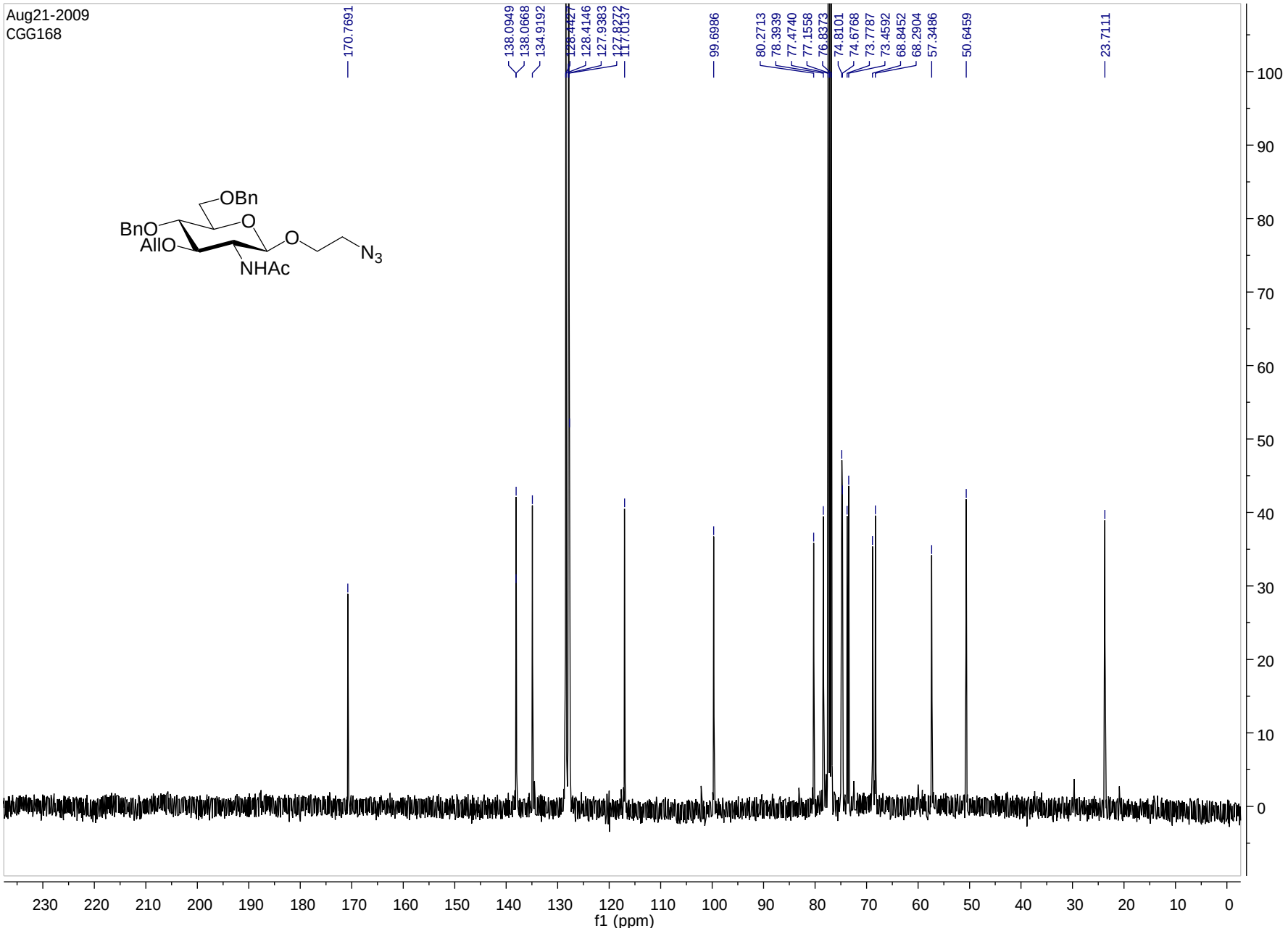

SpinWorks 3: CGG164 - 13C - Pyrd5
172.5359
150.3103
150.1859
150.0459
149.7710
136.6043
136.5700
136.3595
136.2063
136.1063
135.9896
135.9588
135.8594
124.3858
124.1484
123.6519
123.7976
123.0056
123.0001
116.5990
101.9856
83.7435
78.0470
74.4570
71.8603
68.7993
62.2190
56.0923
51.3270
49.8702
23.9230
OH
HO
AllO
O
O
N3
NHAc
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

Compound **33**

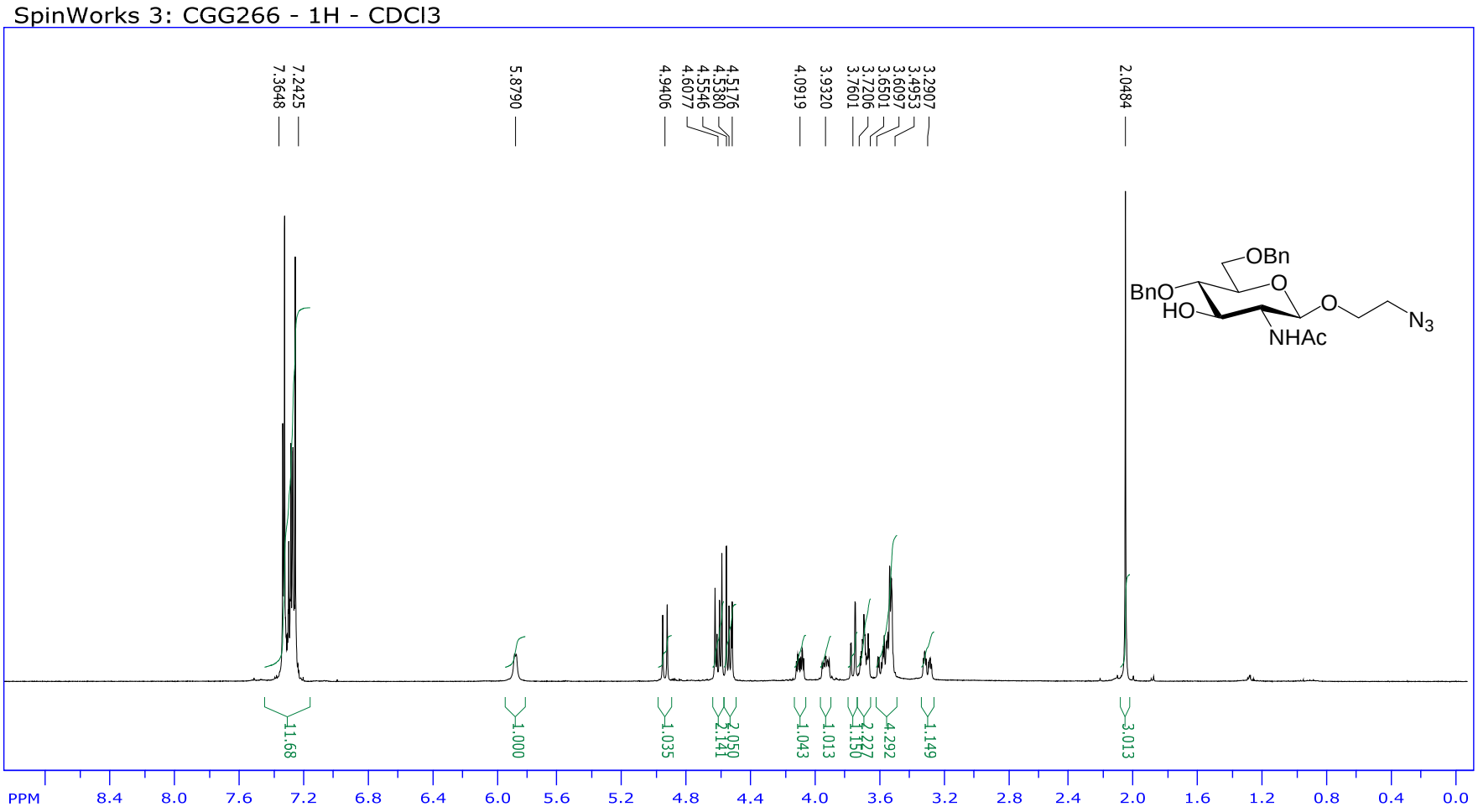

SpinWorks 3: CGG265 - 1H - CDCl3
7.3554
7.2055
5.8937
5.7312
5.2456
5.1450
4.9618
4.7842
4.6213
4.5908
4.5810
4.5529
4.5222
4.2750
4.1521
4.0712
4.0418
4.0189
3.7575
3.6600
3.6069
3.4411
3.4856
3.3159
3.2239
1.9846
OBn
O
BnO
AllO
O
N3
NHAc
10.86
1.024
0.848
1.010
1.002
0.856
0.960
3.014
1.046
1.008
1.934
0.253
3.049
3.013
1.855
2.636
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

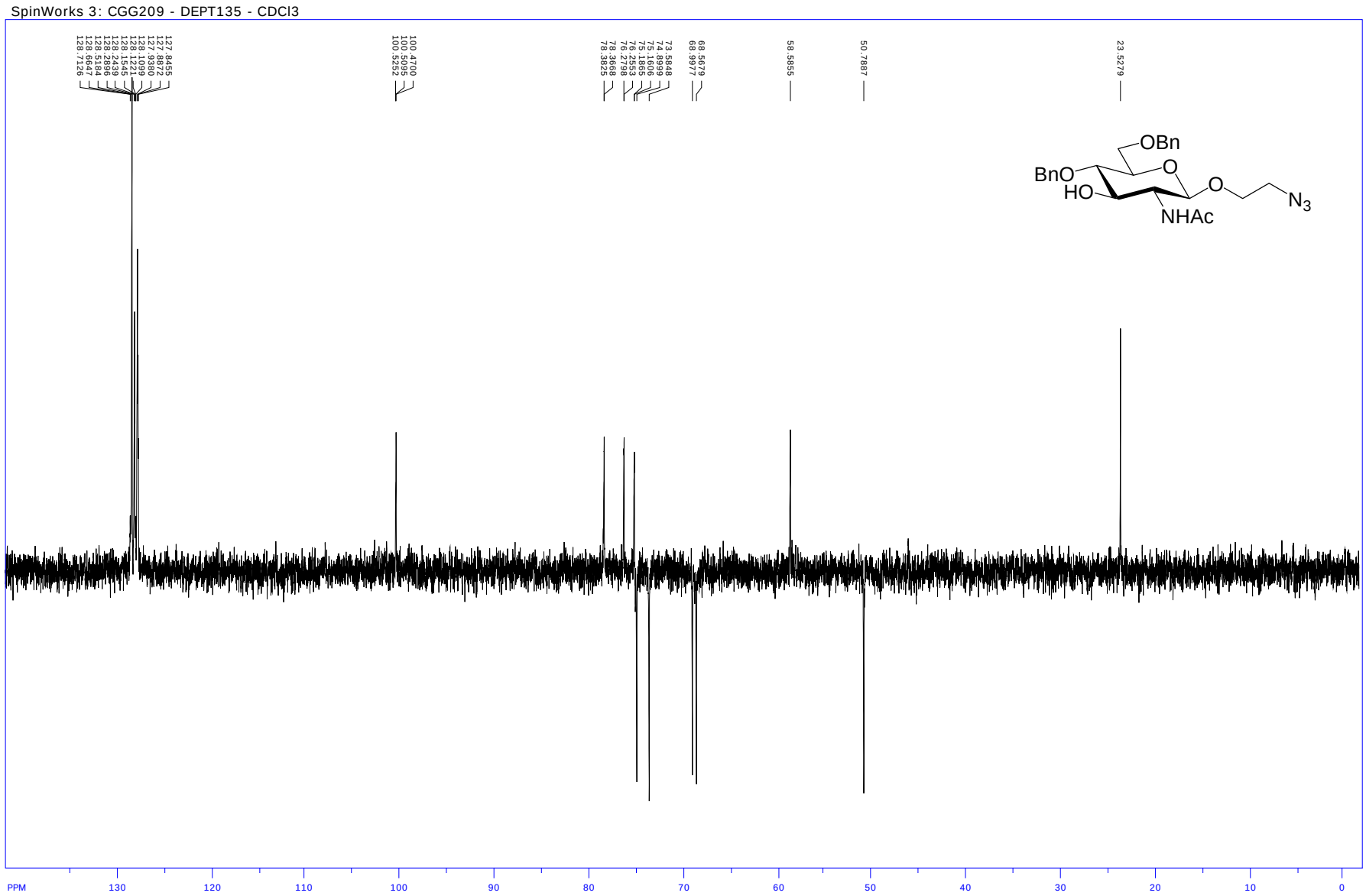

SpinWorks 3: CGG168 - DEPT135 - CDCl3
134.9352
128.5128
128.4814
128.4551
127.9590
127.9104
127.8458
127.7139
117.0400
99.7155
80.2880
78.4097
74.8291
73.8012
73.4778
68.8558
68.3142
57.3673
50.6616
23.7326
OBn
O
BnO
AllO
O
N3
NHAc
PPM
130
120
110
100
90
80
70
60
50
40
30
20
10
0

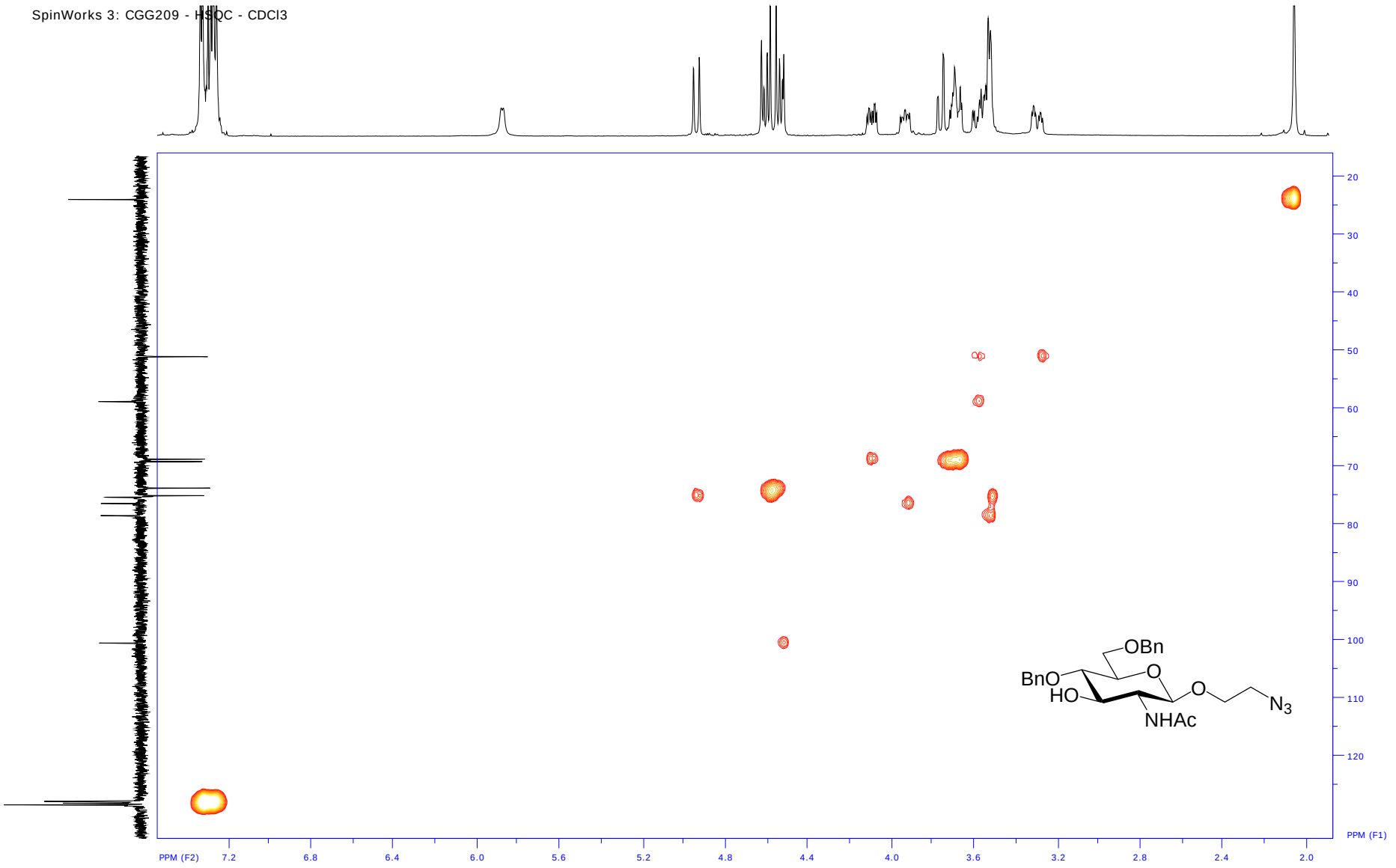

SpinWorks 3: CGG168 - HSQC - CDCl3
PPM (F2)
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
O
BnO
AllO
O
N3
NHAc

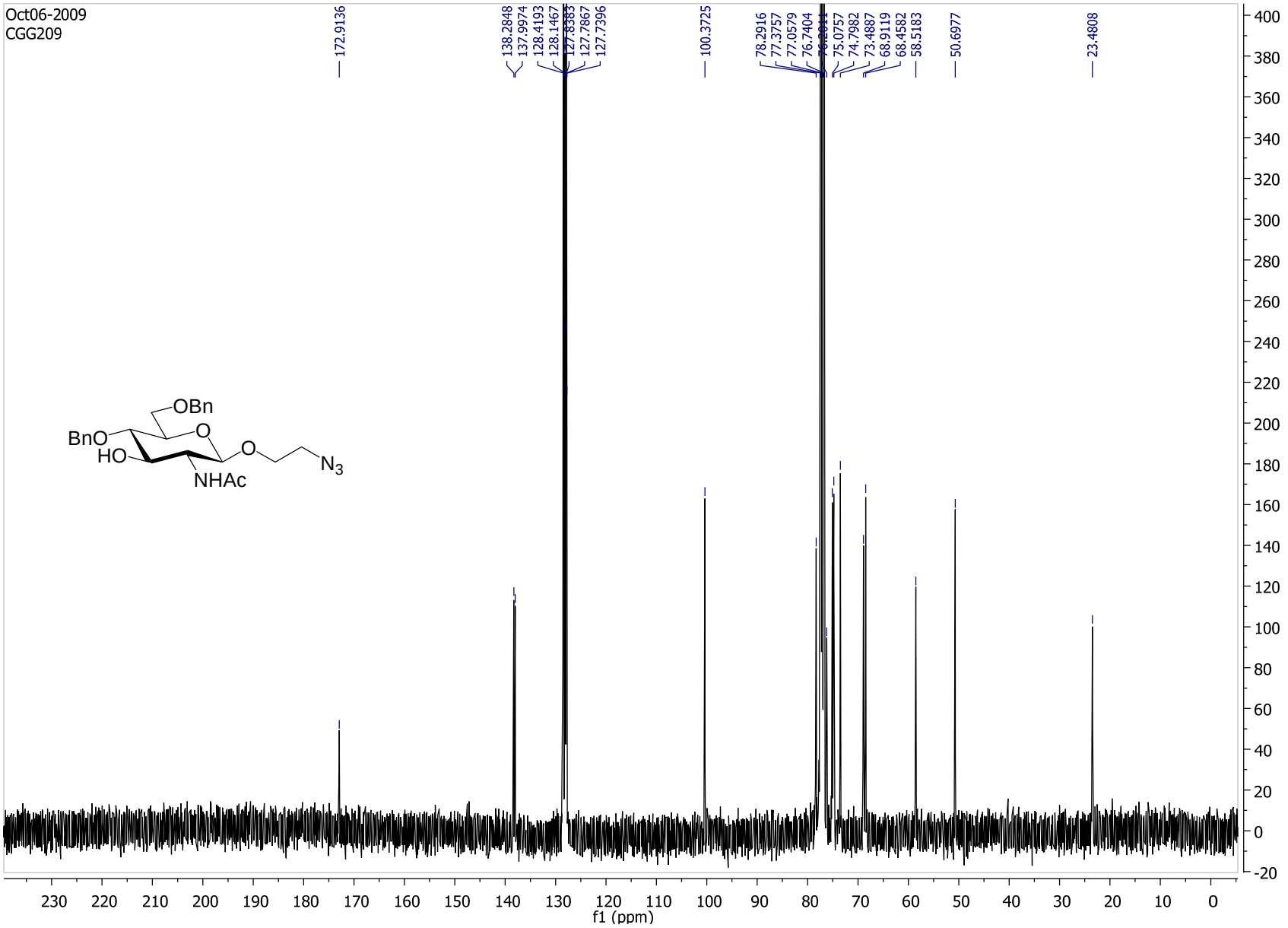

Aug21-2009
CGG168
170.7691
138.0949
138.0668
134.9192
128.4427
128.4146
127.9383
117.0137
99.6986
80.2713
78.3939
77.4740
77.1558
76.8373
74.8101
74.6768
73.7787
73.4592
68.8452
68.2904
57.3486
50.6459
23.7111
OBn
BnO
AllO
O
O
NHAc
N3
f1 (ppm)

Compound **8**

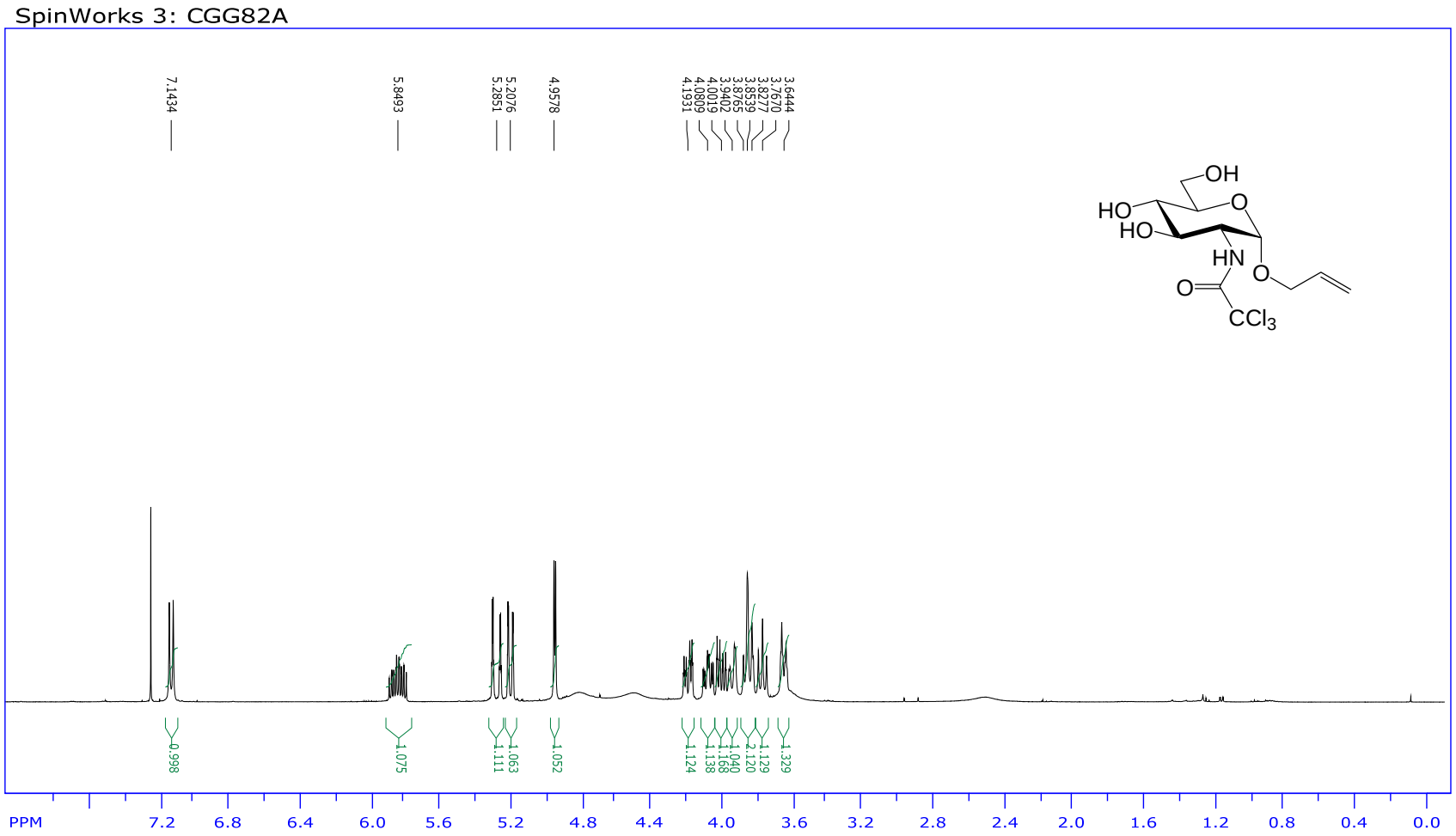

SpinWorks 3: CGG266 - 1H - CDCl3
7.3648
7.2425
5.8790
4.9406
4.6077
4.5546
4.5380
4.5176
4.0919
3.9320
3.7601
3.7206
3.6501
3.6097
3.4953
3.2907
2.0484
OBn
BnO
O
HO
O
N3
NHAc
11.68
1.000
1.035
2.050
2.141
1.043
1.013
1.150
1.327
4.292
1.149
3.013
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

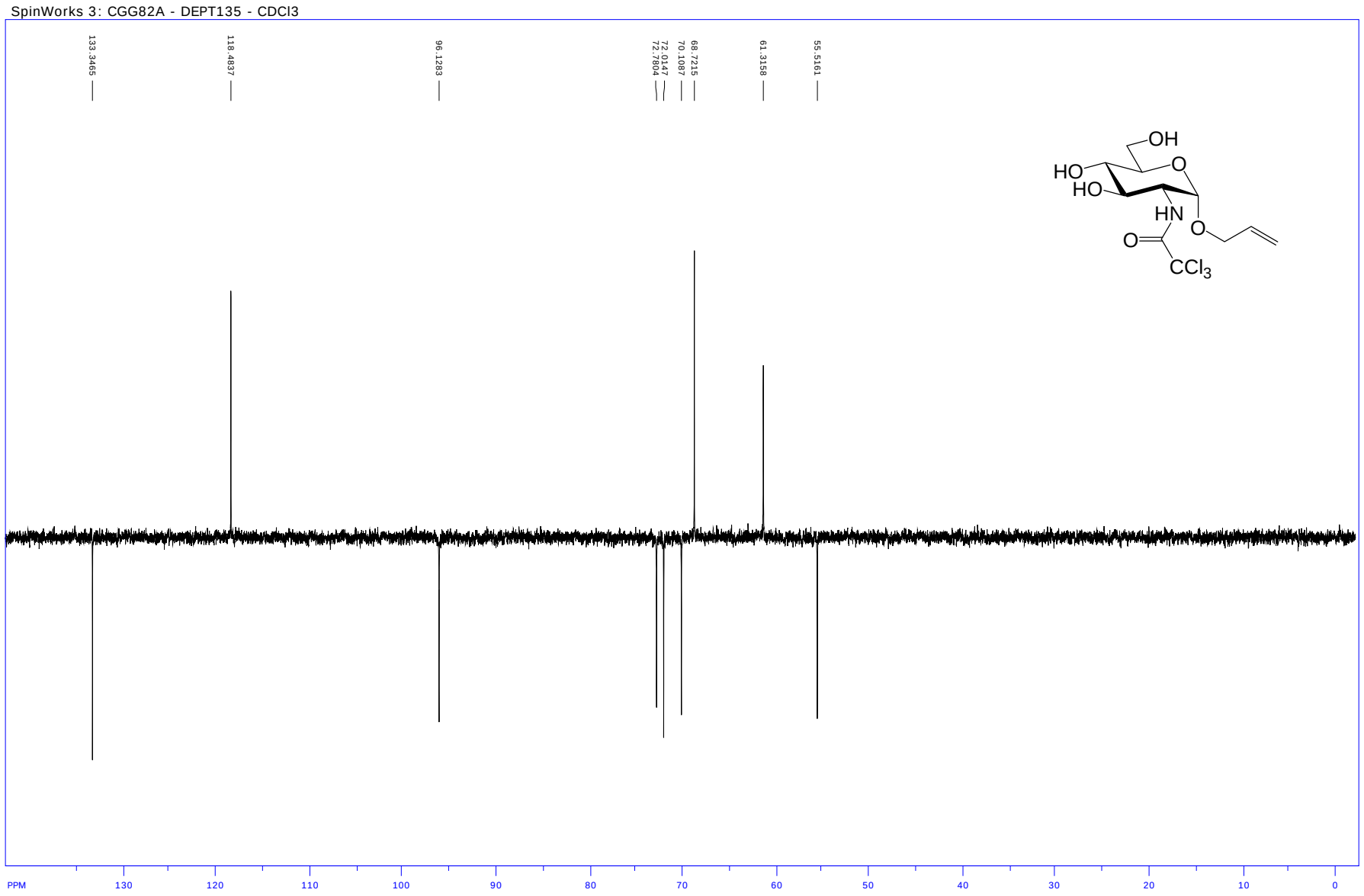

SpinWorks 3: CGG209 - DEPT135 - CDCl3
128.7126
128.6647
128.5184
128.2896
128.2439
128.1545
128.1221
128.1089
127.9907
127.8872
127.8455
100.4700
100.5095
100.5252
78.3825
78.3668
76.2758
75.1865
75.1606
74.8999
73.5848
68.9977
68.5679
58.5855
50.7887
23.5279
OBn
BnO
HO
O
O
NHAc
N3
PPM
130
120
110
100
90
80
70
60
50
40
30
20
10
0


SpinWorks 3: CGG209 - HSQC - CDCl3
PPM (F2)
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
OBn
BnO
O
HO
O
N3
NHAc

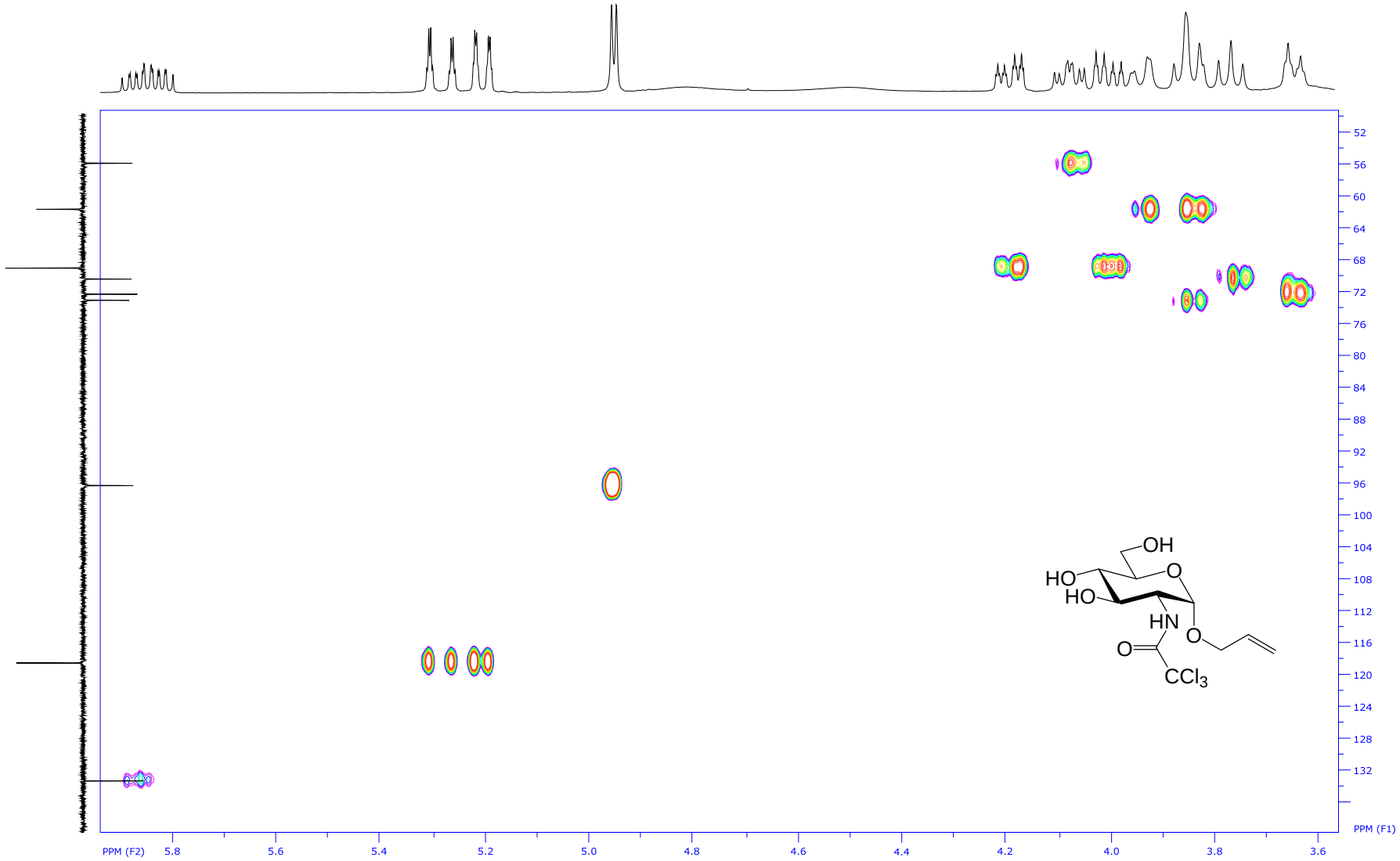

Oct06-2009
CGG209
172.9136
138.2848
137.9974
128.4193
128.1467
127.8383
127.7867
127.7396
100.3725
78.2916
77.3757
77.0579
76.7404
75.0757
74.7982
73.4887
68.9119
68.4582
58.5183
50.6977
23.4808
OBn
BnO
O
HO
O
N3
NHAc
f1 (ppm)

Compound **25**

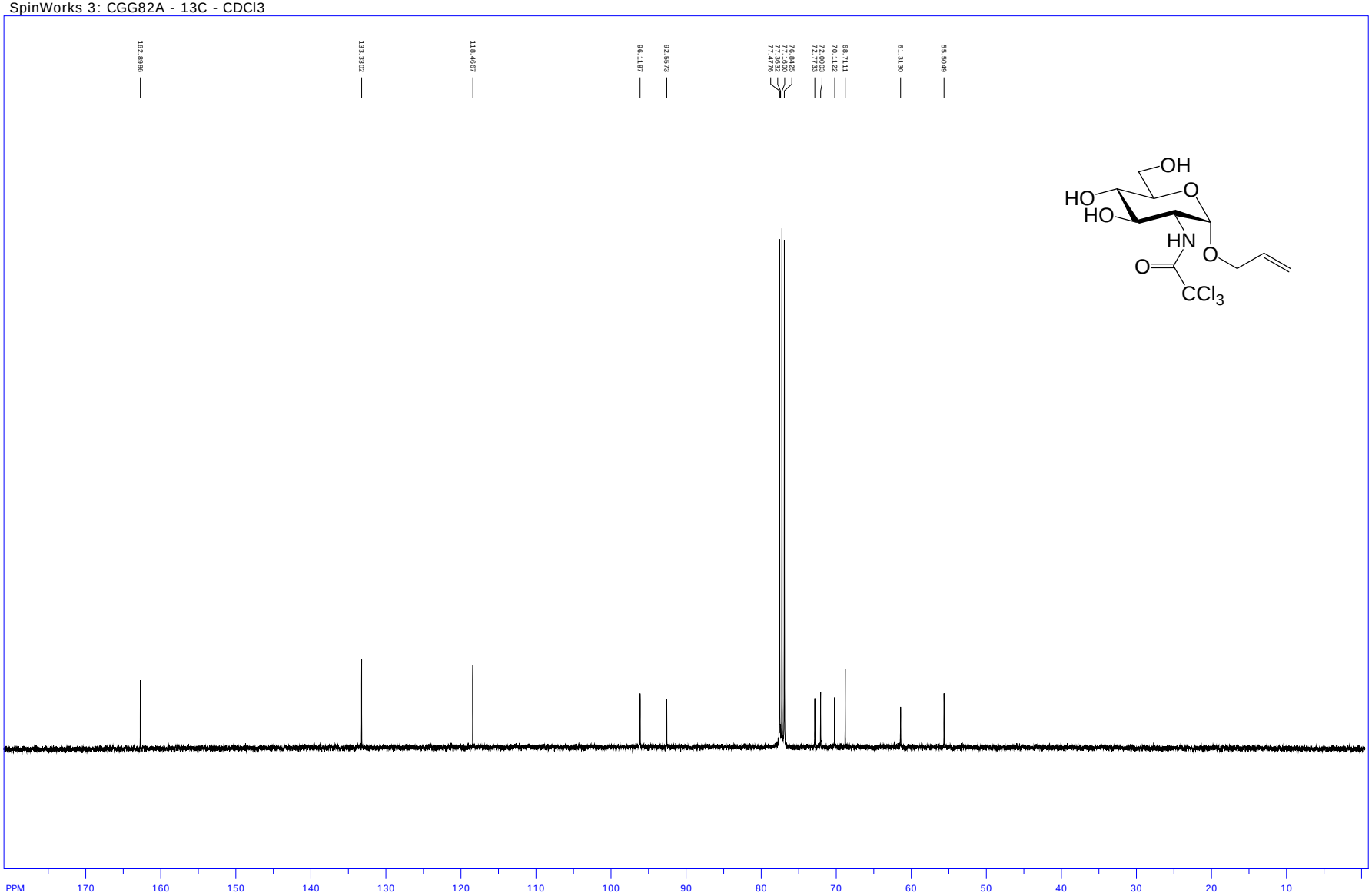

SpinWorks 3: CGG82A
7.1434
5.8493
5.2076
5.2851
4.9578
4.1931
4.0809
4.0019
3.9402
3.8765
3.8539
3.8277
3.7670
3.6444
OH
O
HO
HO
HN
O
O
CCl3
0.998
1.075
1.111
1.063
1.052
1.124
1.138
1.168
1.040
2.120
1.129
1.329
PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0


SpinWorks 3: CGG82A - DEPT135 - CDCl3
133.3465
118.4837
96.1283
72.7804
72.0147
70.1087
68.7215
61.3158
55.5161
OH
HO
HO
O
HN
O
O
CCl3
PPM
130
120
110
100
90
80
70
60
50
40
30
20
10
0

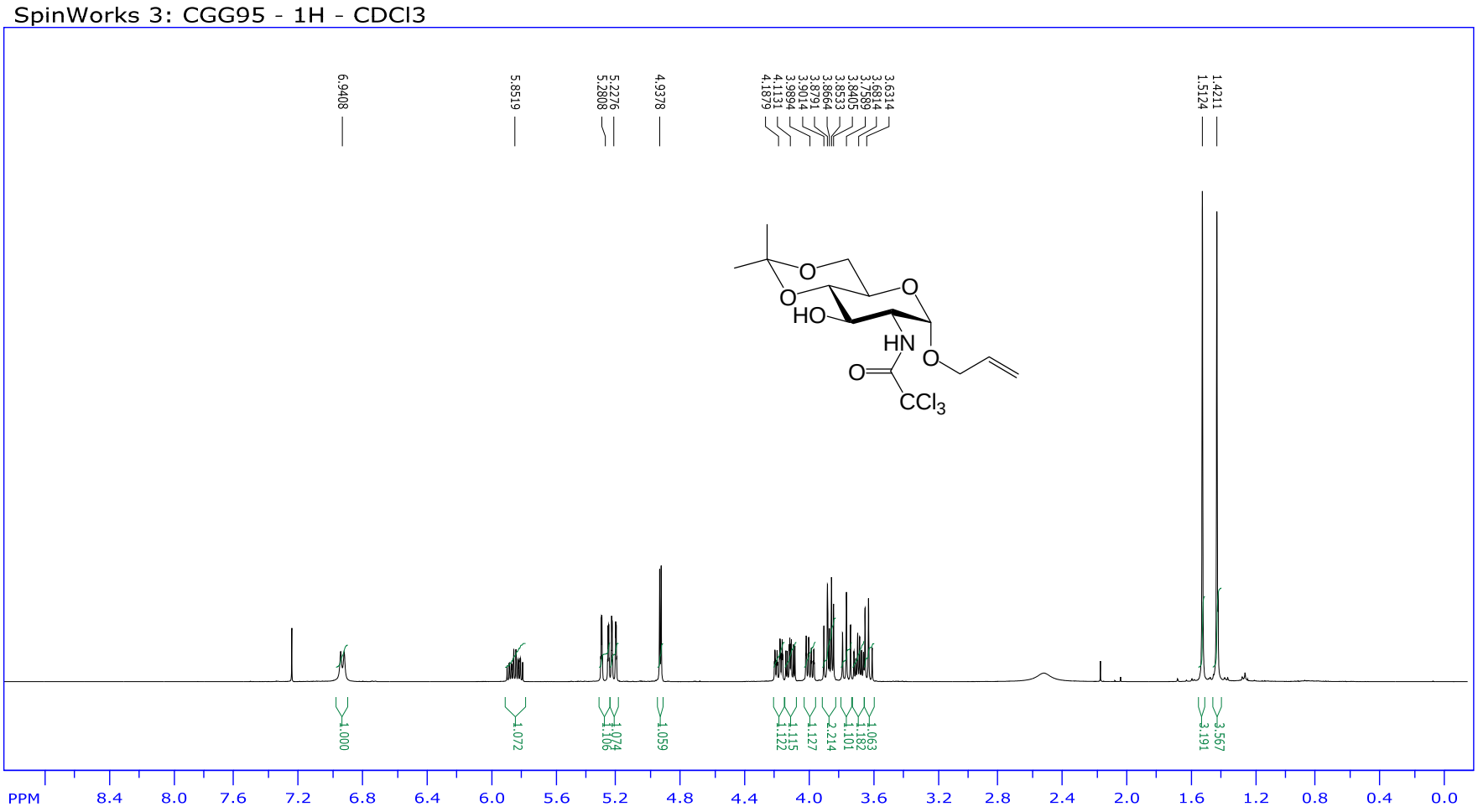
SpinWorks 3: CGG82A - HSQC - CDCl3



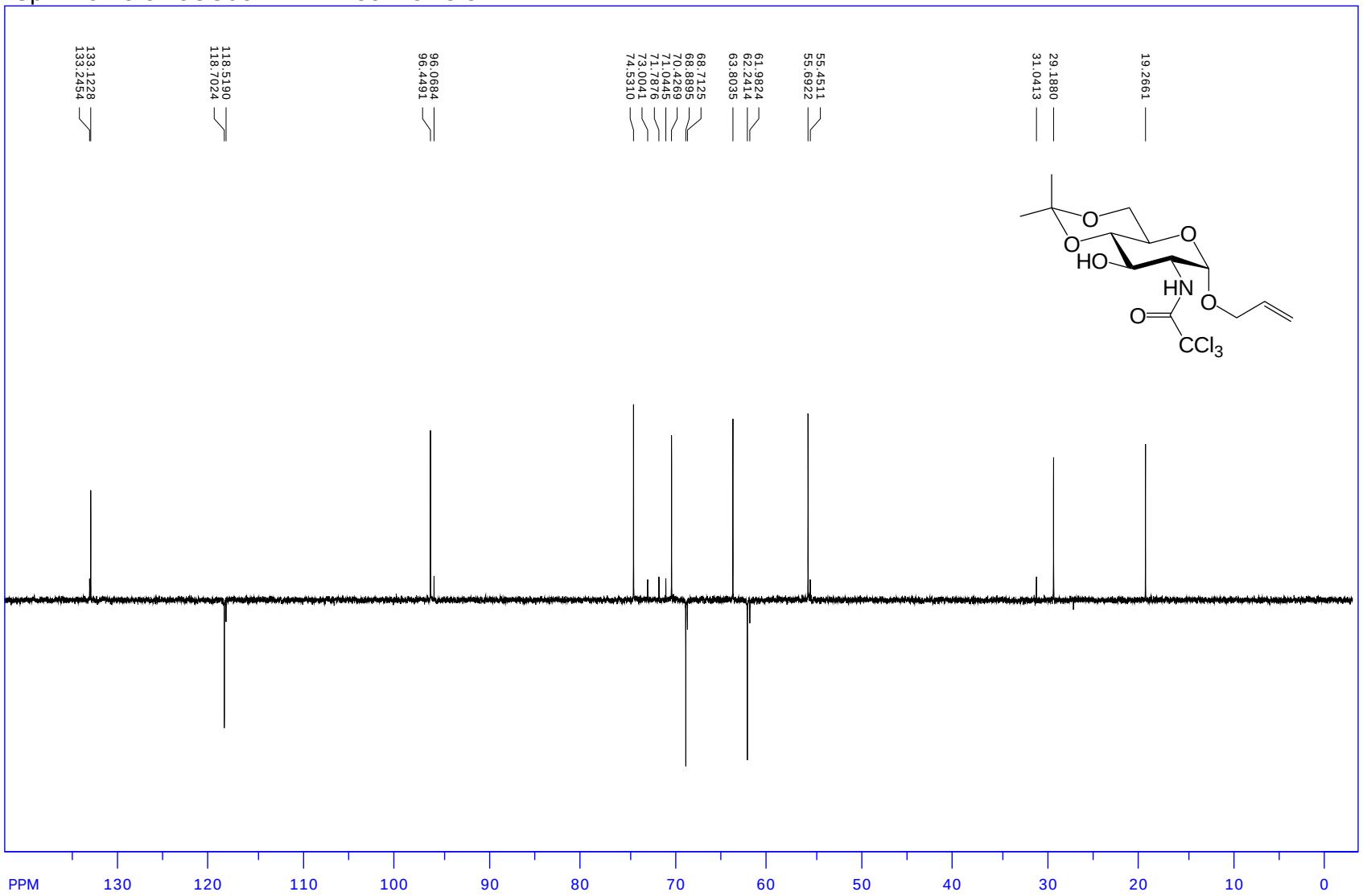
SpinWorks 3: CGG82A - 13C - CDCl3

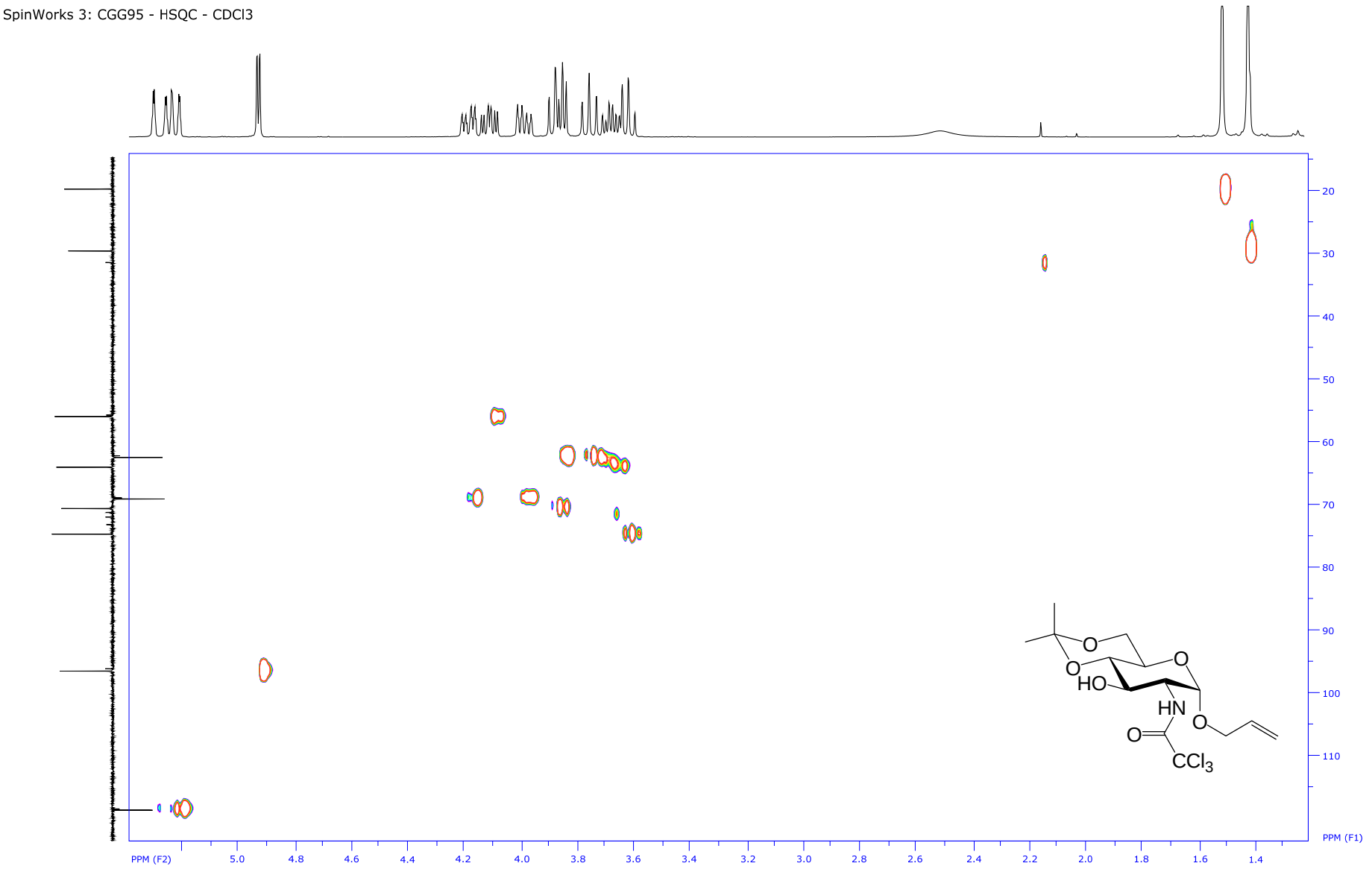


Compound **S6**

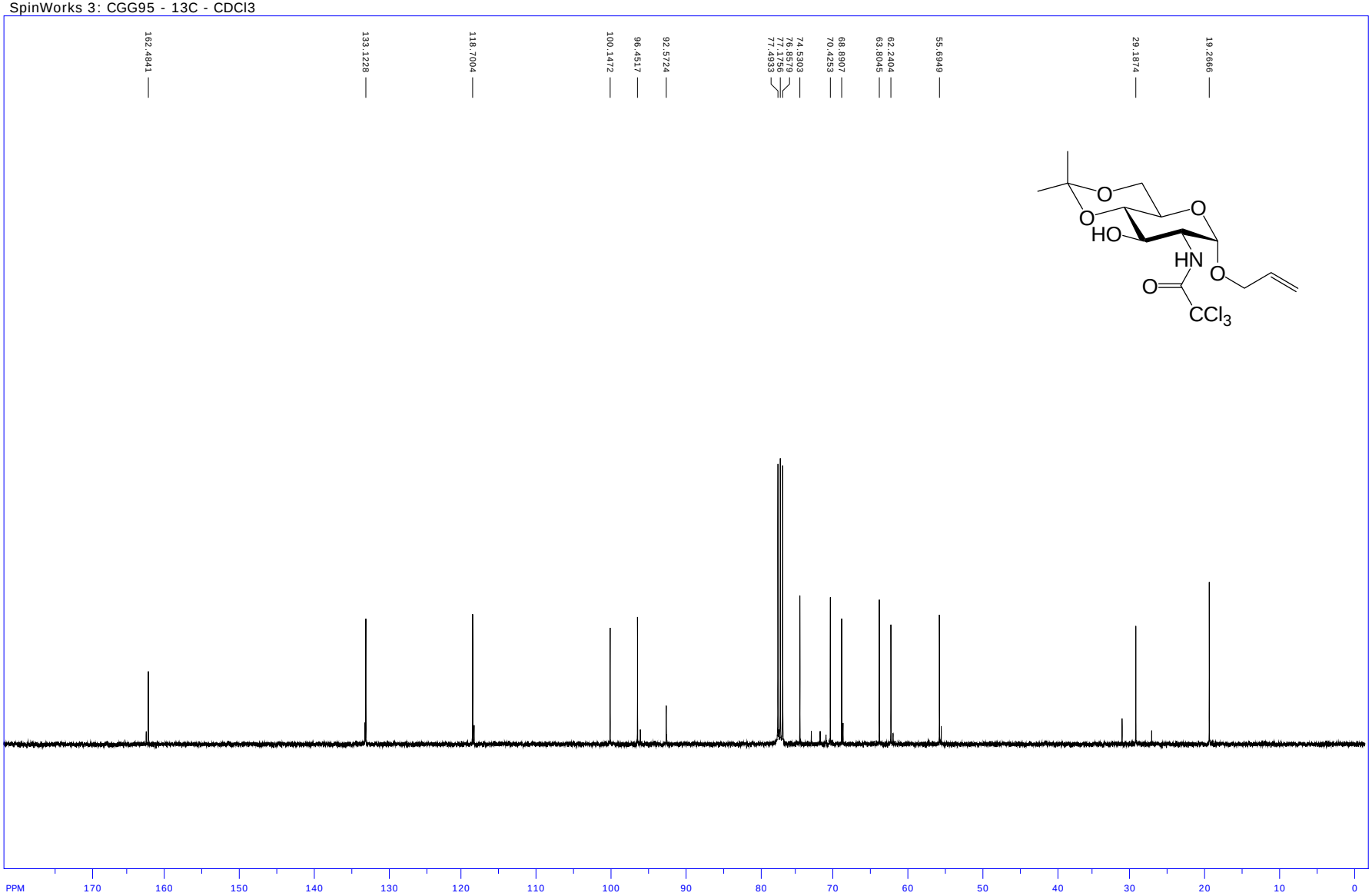

SpinWorks 3: CGG95 - 1H - CDCl3
6.9408
5.8519
5.2276
5.2808
4.9378
4.1879
4.1131
3.9894
3.9014
3.8791
3.8664
3.8533
3.8405
3.7589
3.6814
3.6314
1.5124
1.4211
HO
HN
O
CCl3
1.000
1.072
1.074
1.106
1.059
1.122
1.115
1.127
2.214
1.101
1.182
1.063
3.191
3.567
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

SpinWorks 3: CGG95 - DEPT135 - CDCl3

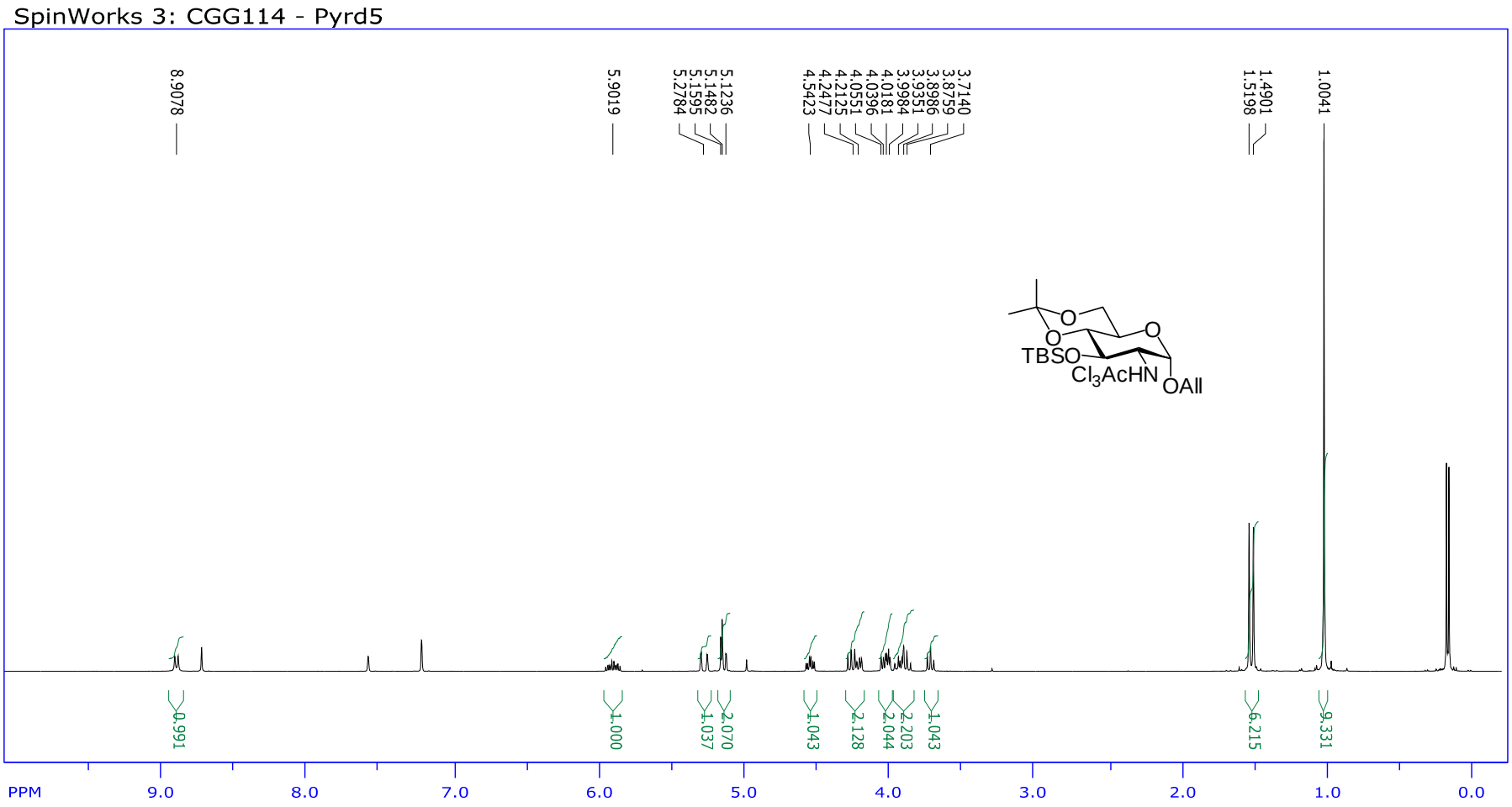



SpinWorks 3: CGG95 - HSQC - CDCl3
PPM (F2)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
PPM (F1)
20
30
40
50
60
70
80
90
100
110
O
O
O
HO
HN
O
O
CCl3

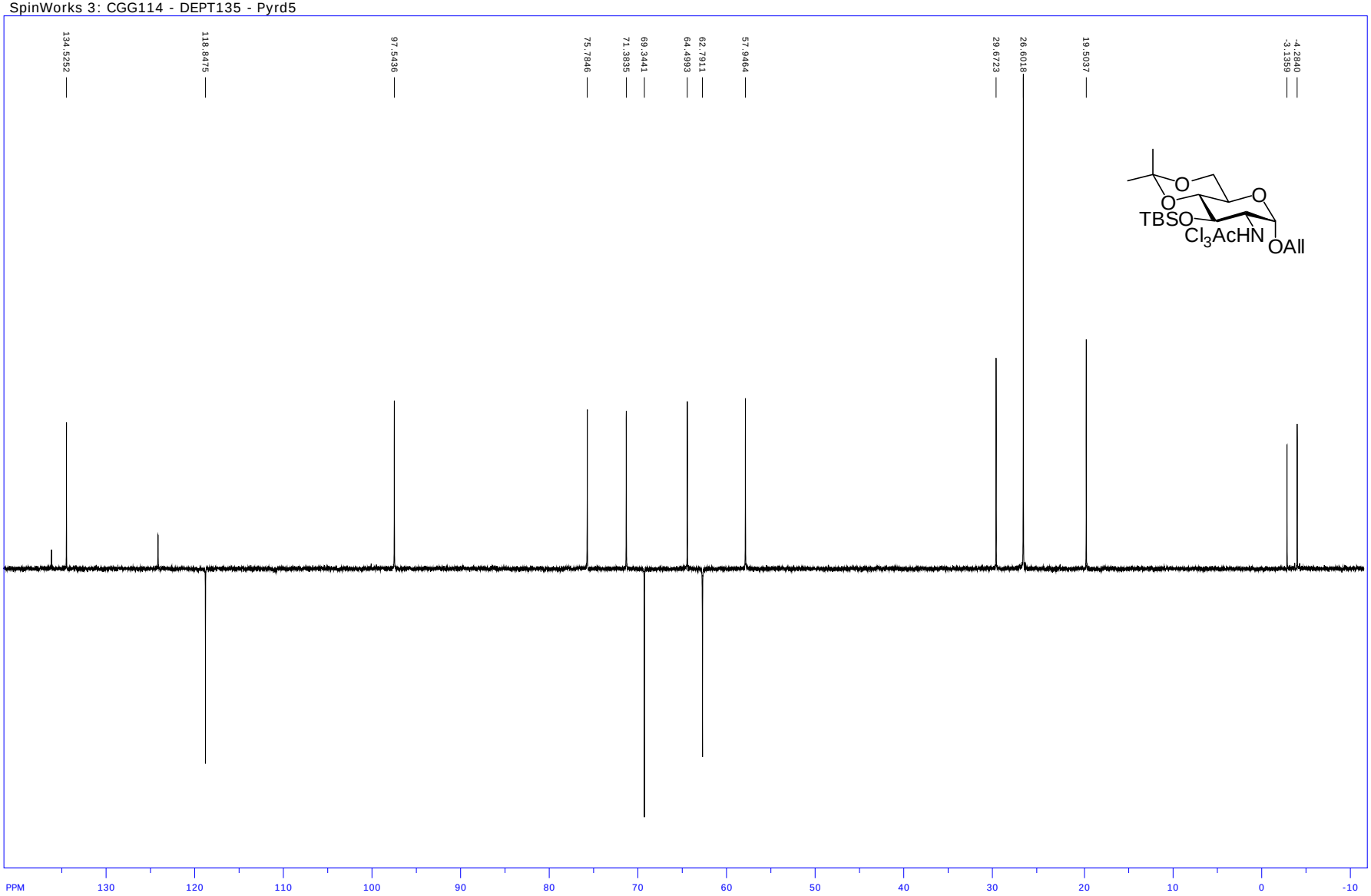
SpinWorks 3: CGG95 - 13C - CDCl3

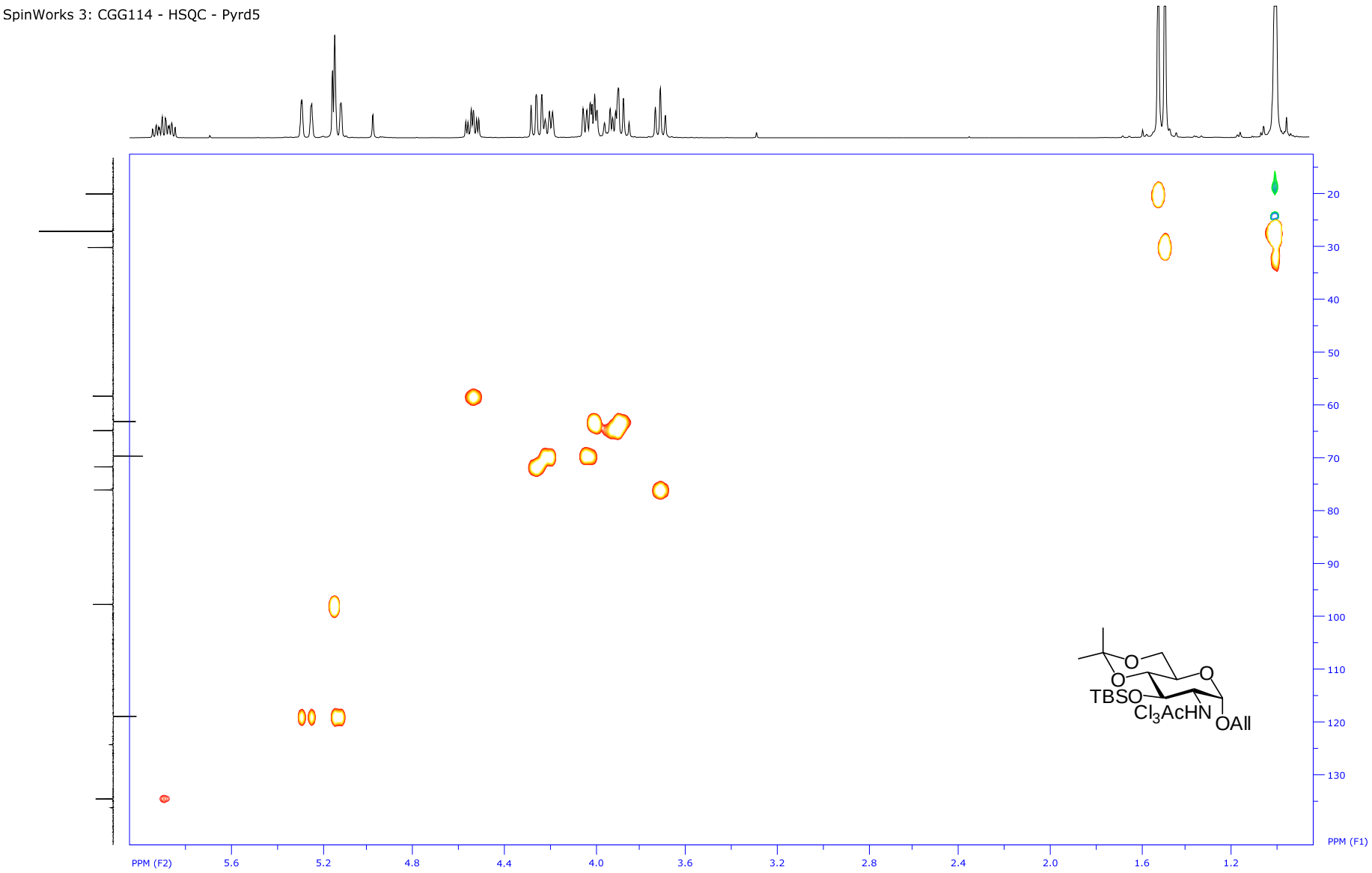


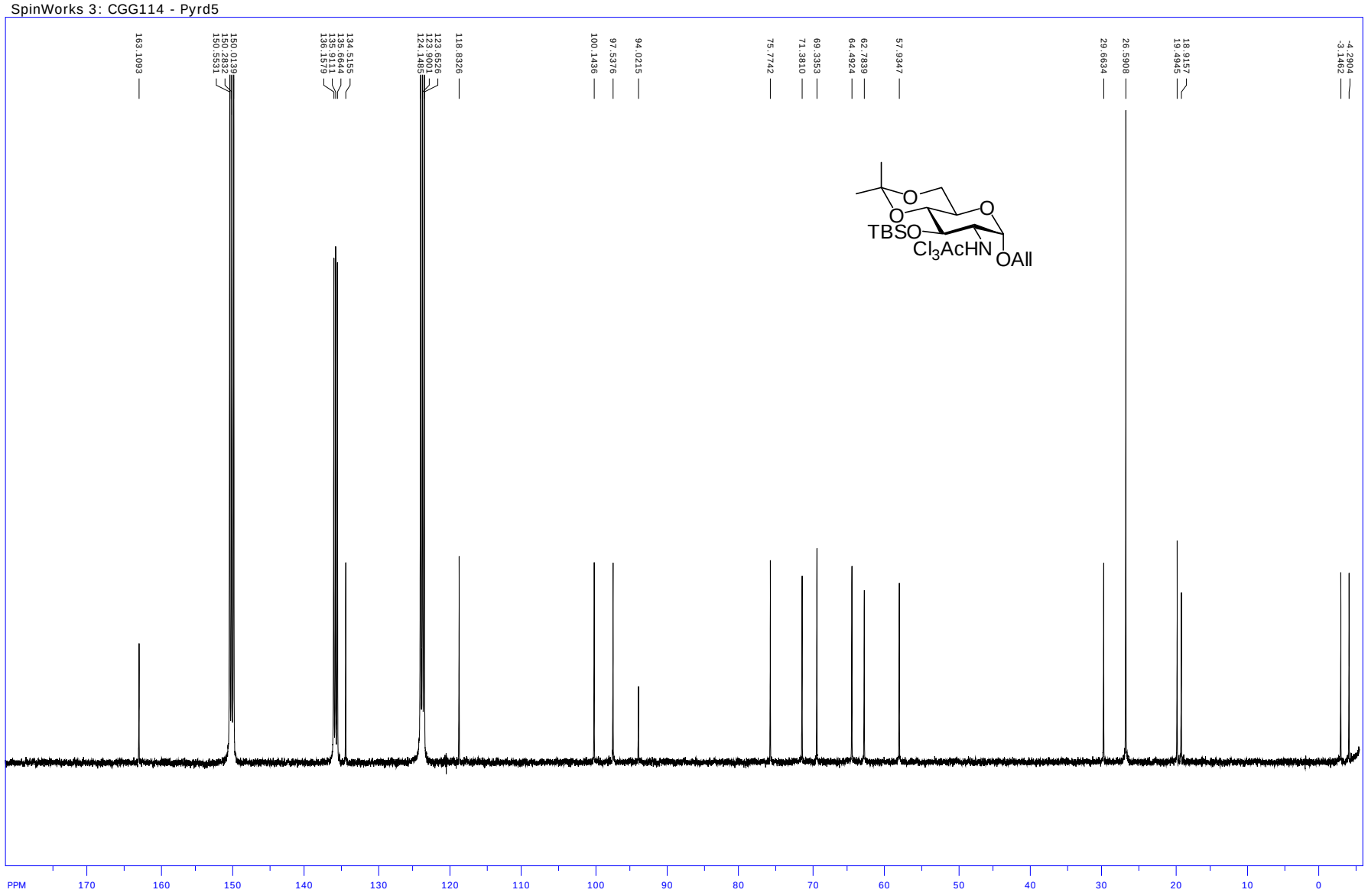
Compound **26**


SpinWorks 3: CGG114 - Pyrd5
8.9078
5.9019
5.2784
5.1595
5.1482
5.1236
4.5423
4.2477
4.2125
4.0551
4.0396
4.0181
3.9984
3.9351
3.8986
3.8759
3.7140
1.5198
1.4901
1.0041
TBSO
Cl3AcHN
OAll
0.991
1.000
1.037
2.070
1.043
2.128
2.044
2.203
1.043
6.215
9.331
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

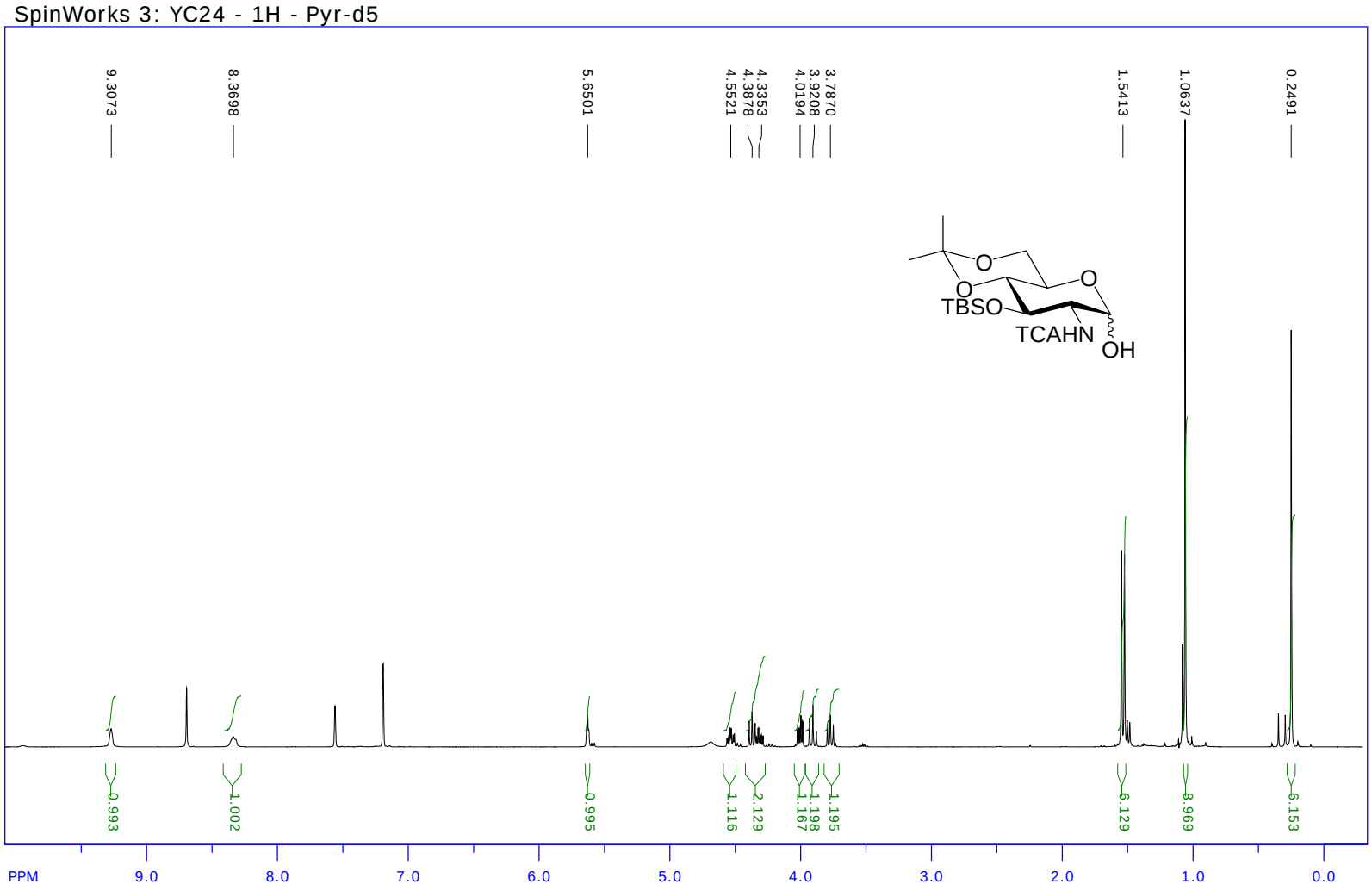
SpinWorks 3: CGG114 - DEPT135 - Pyrd5



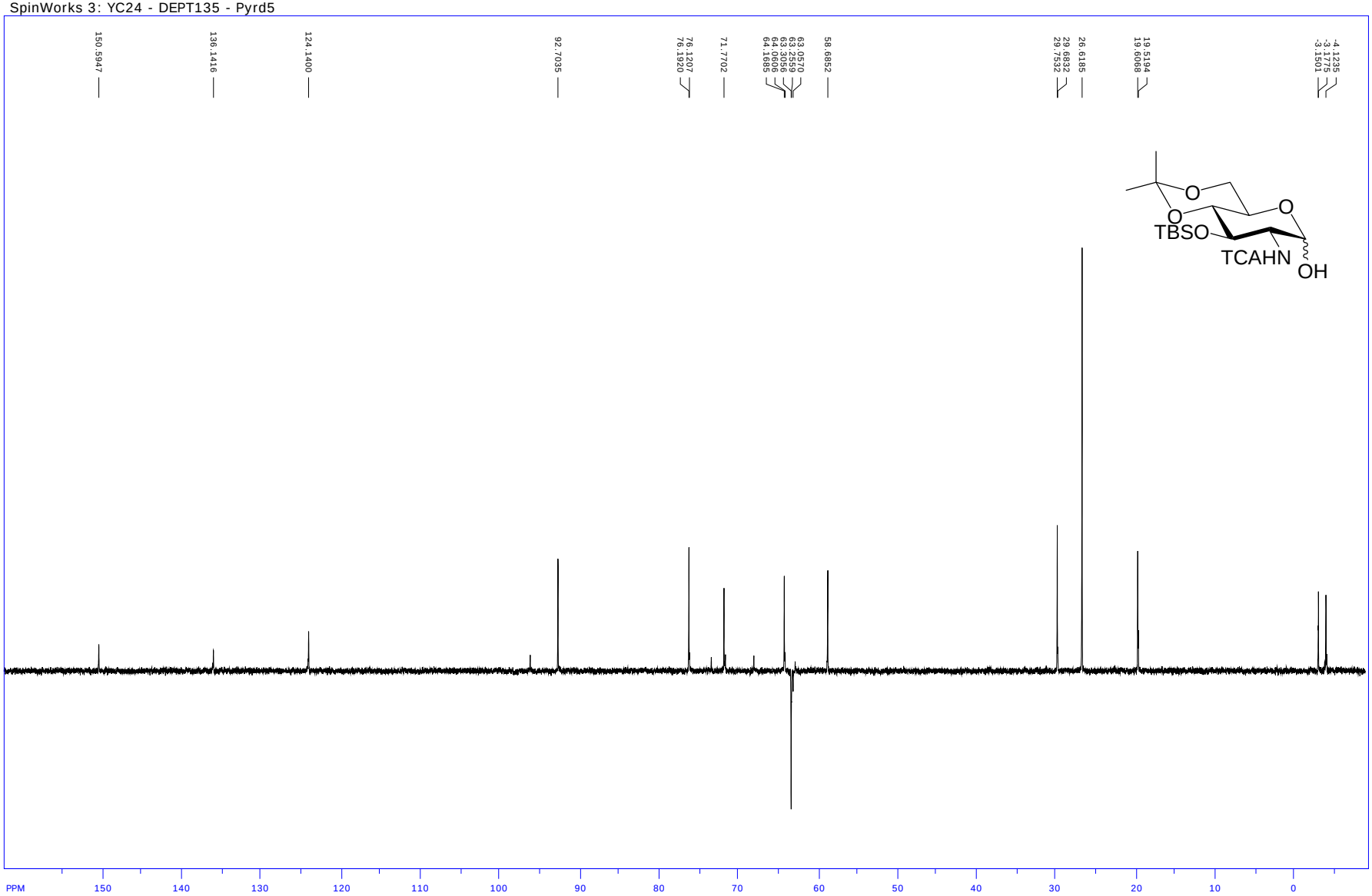

SpinWorks 3: CGG114 - HSQC - Pyrd5
PPM (F2)
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
TBSO
Cl3AcHN
OAll

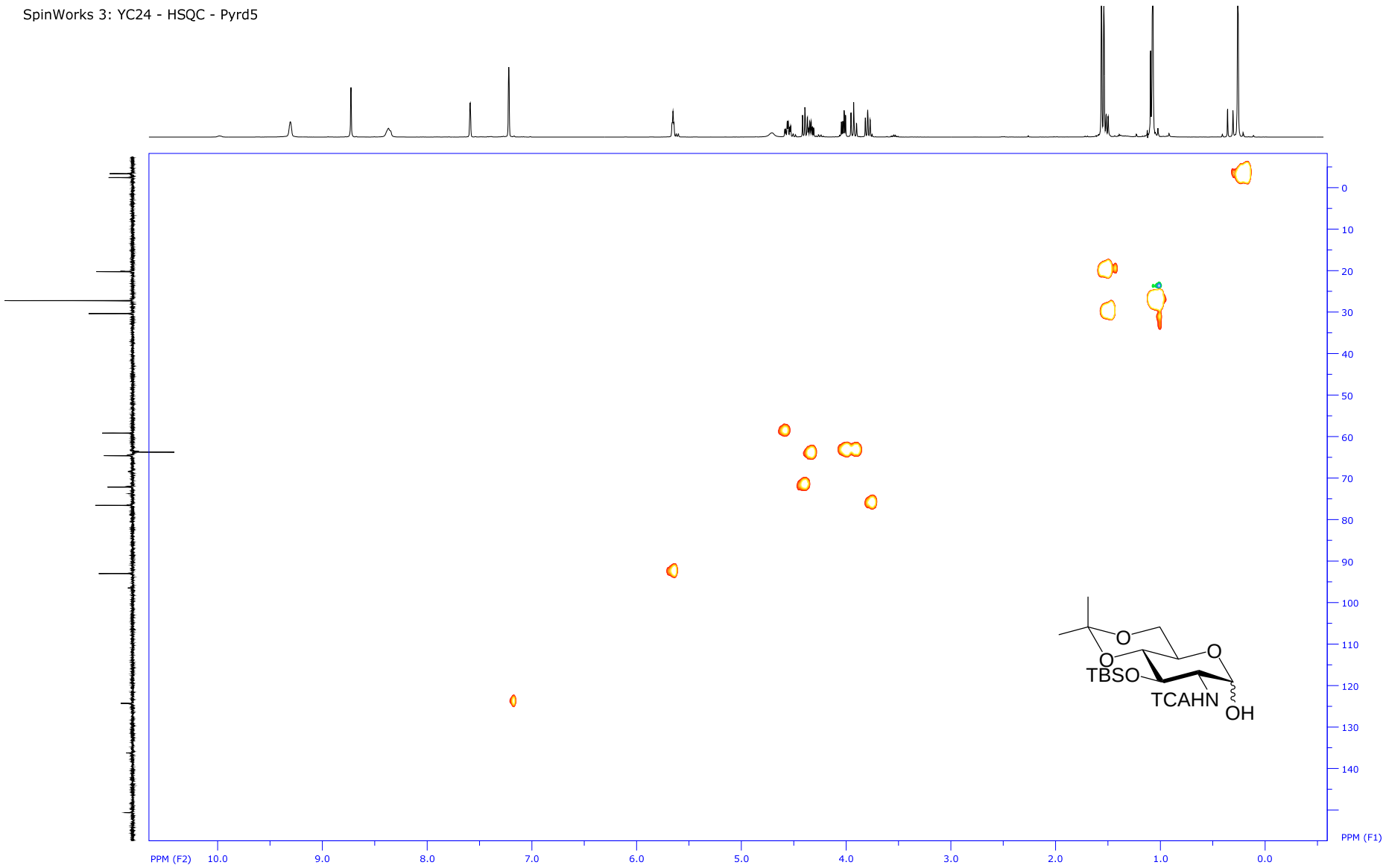

SpinWorks 3: CGG114 - Pyrd5
163.1093
150.0139
150.2832
150.5531
136.1579
135.9111
135.6644
134.5155
124.1485
123.9001
123.6526
118.8326
100.1436
97.5376
94.0215
75.7742
71.3810
69.3353
64.4924
62.7839
57.9347
29.6634
26.5908
19.4945
18.9157
-4.2904
-3.1462
O
O
O
TBSO
Cl3AcHN
OAll
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Compound **S7**

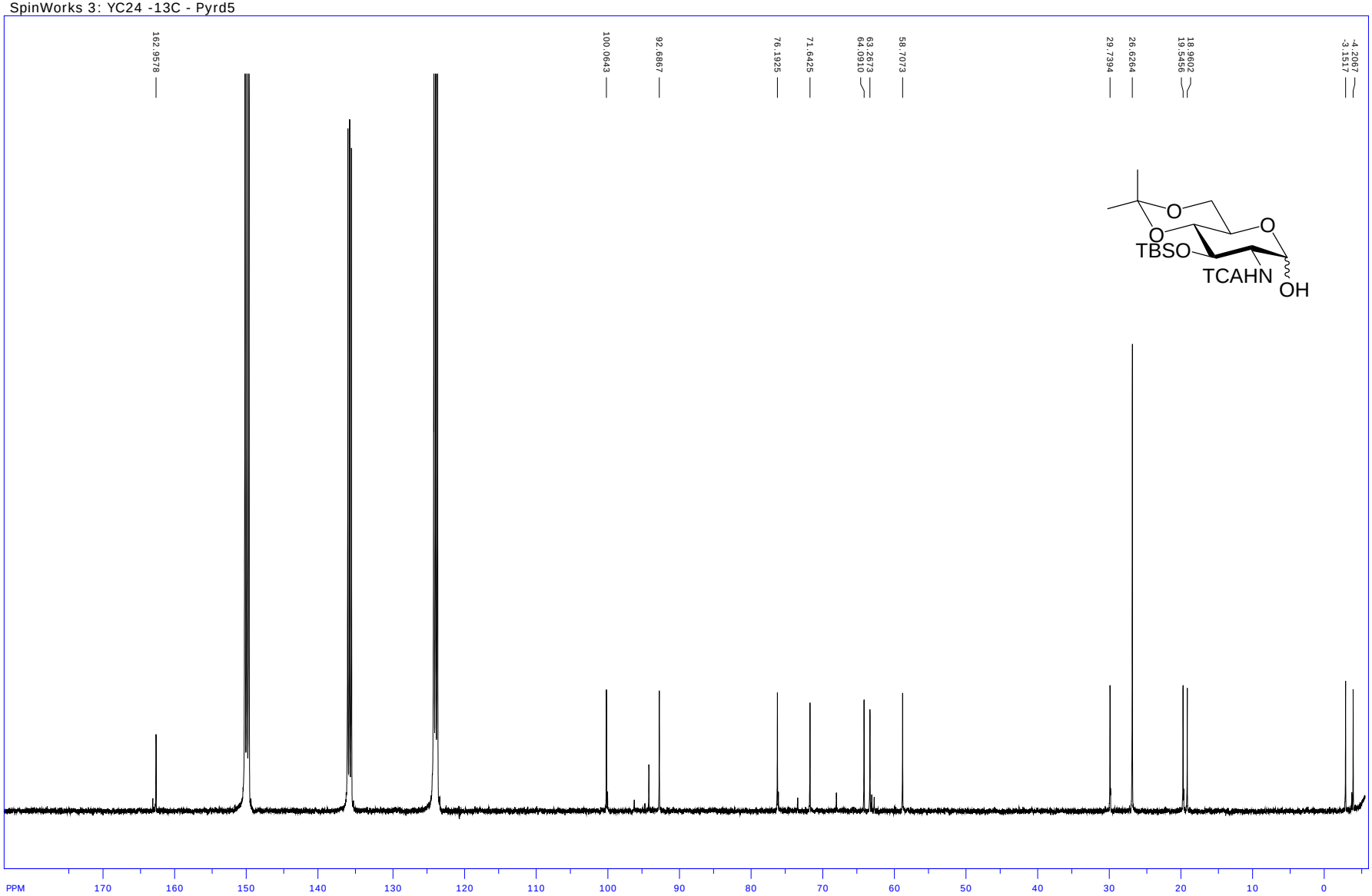

SpinWorks 3: YC24 - 1H - Pyr-d5
9.3073
8.3698
5.6501
4.5521
4.3878
4.3353
4.0194
3.9208
3.7870
1.5413
1.0637
0.2491
O
O
O
TBSO
TCAHN
OH
0.993
1.002
0.995
1.116
2.129
1.167
1.198
1.195
6.129
8.969
6.153
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

SpinWorks 3: YC24 - DEPT135 - Pyrd5

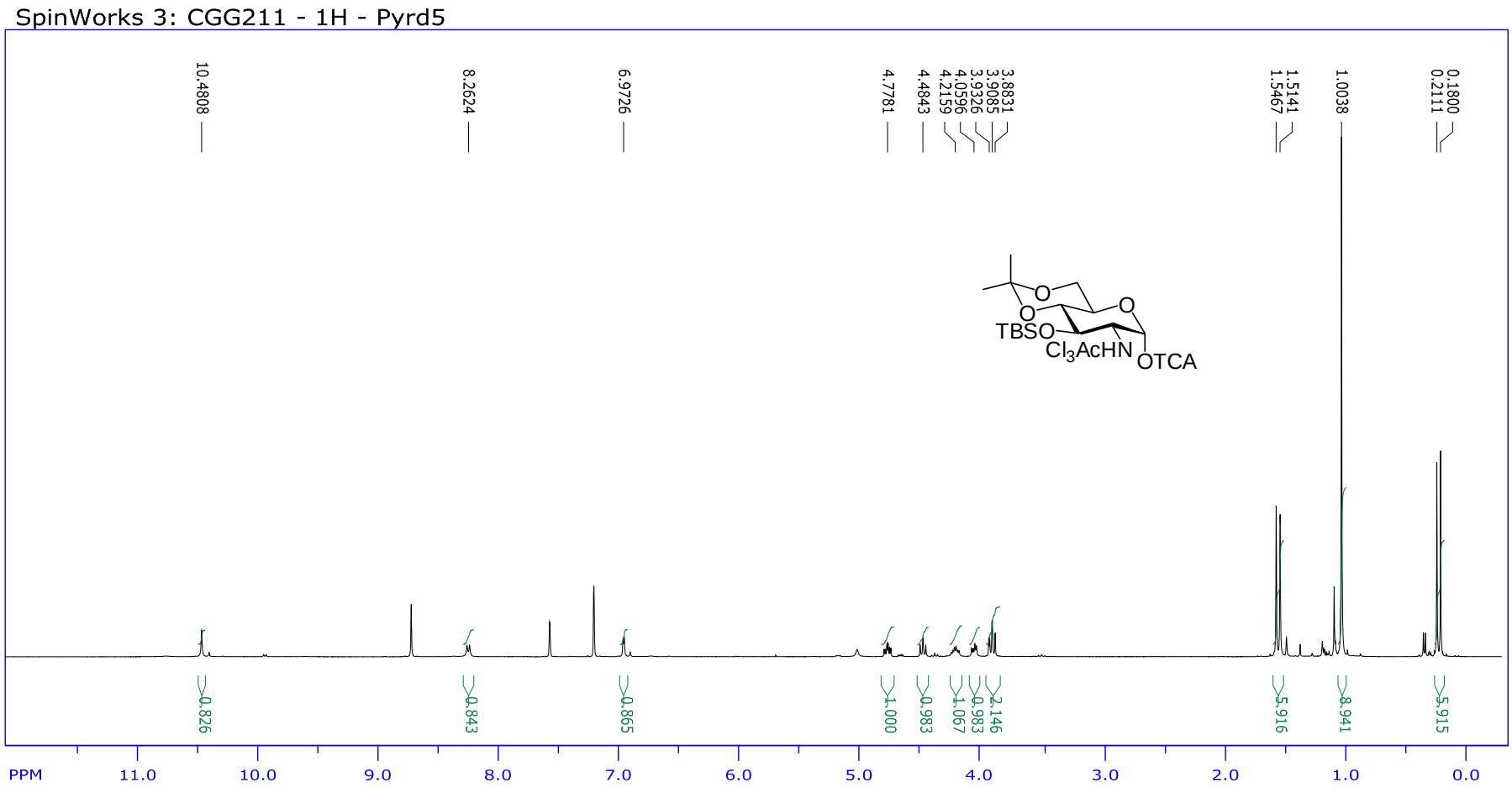



SpinWorks 3: YC24 - HSQC - Pyrd5
PPM (F2)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM (F1)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
O
O
O
TBSO
TCAHN
OH

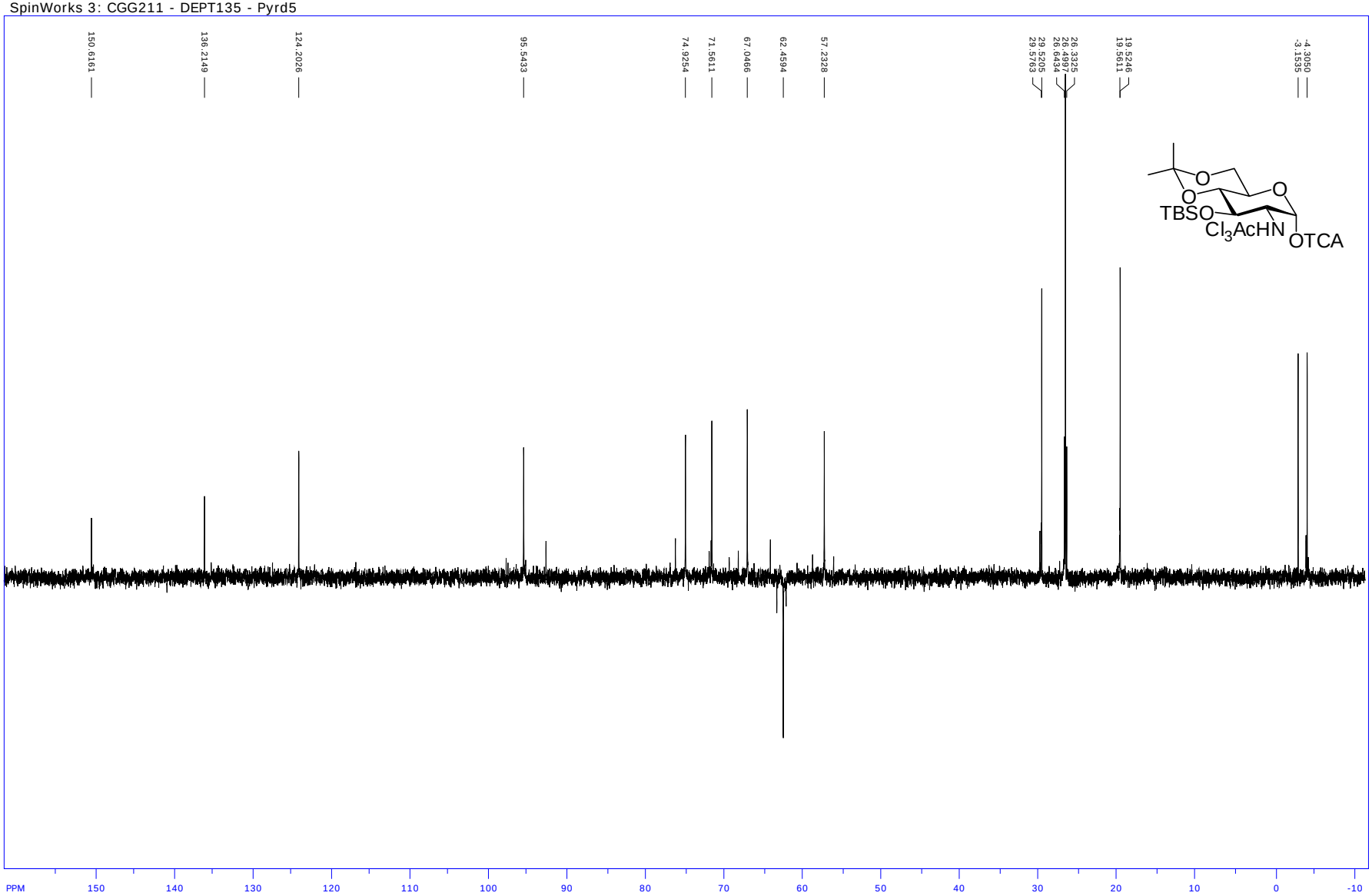
SpinWorks 3: YC24 -13C - Pyrd5

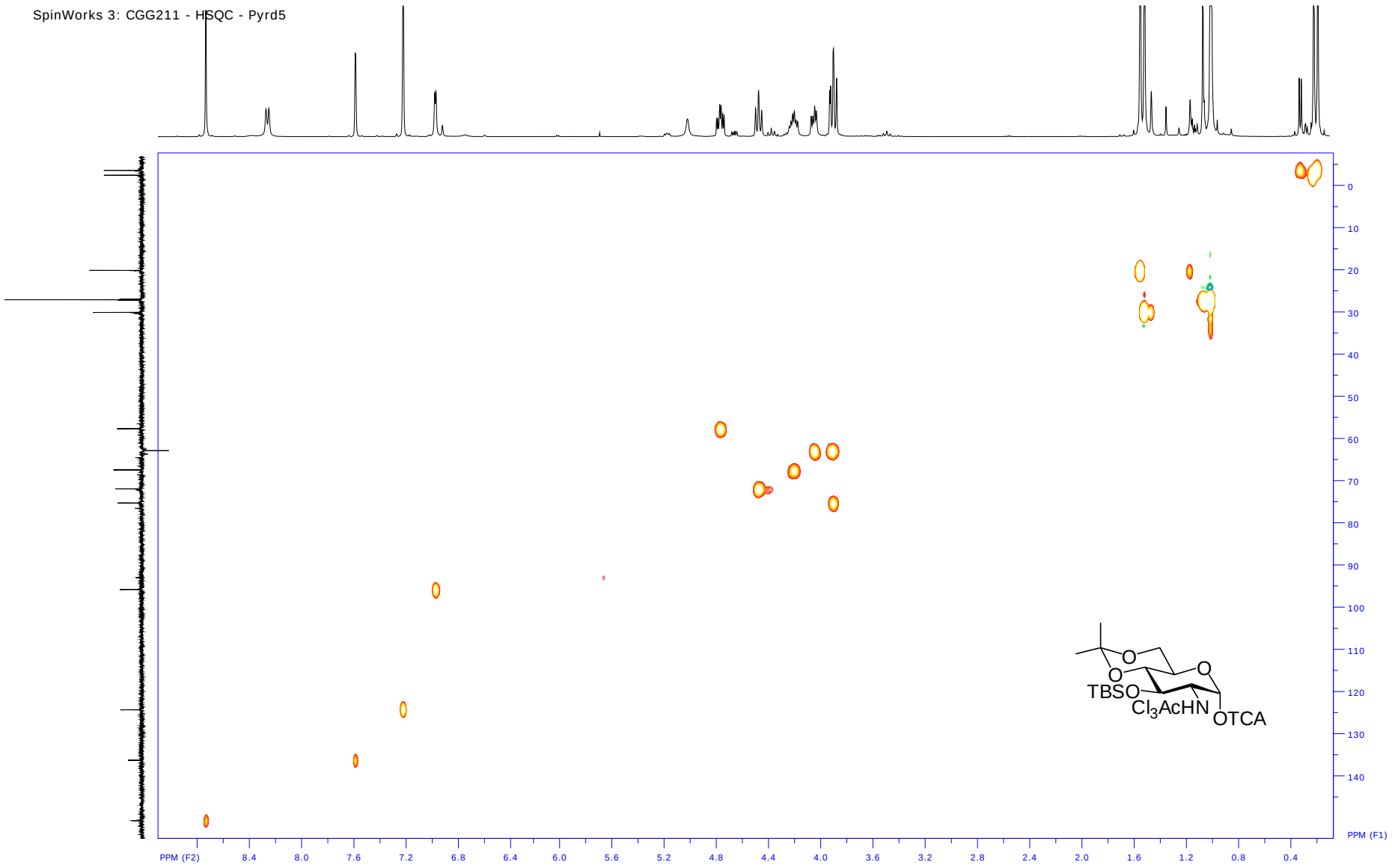


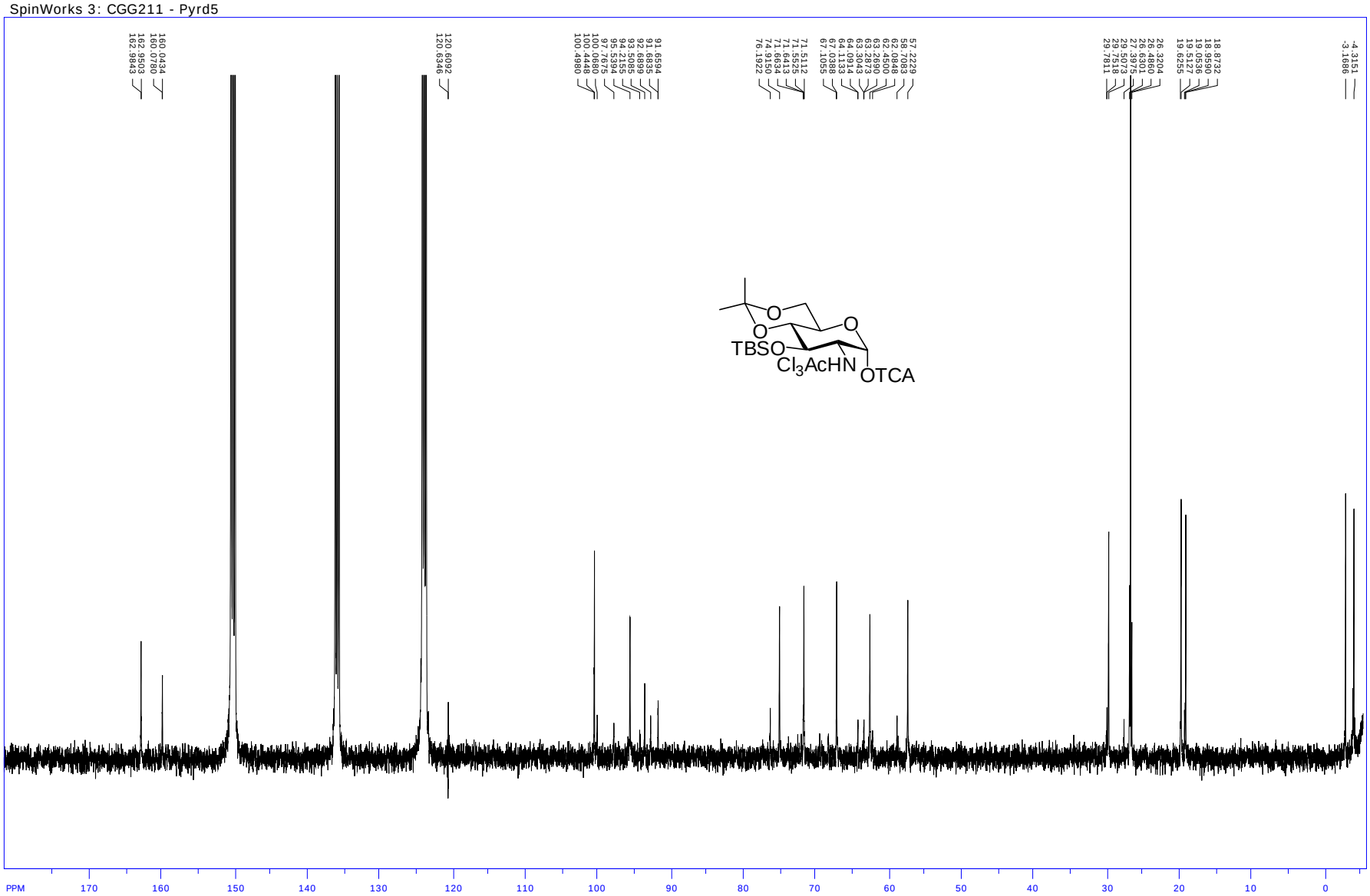
Compound **11**


SpinWorks 3: CGG211 - 1H - Pyrd5
10.4808
8.2624
6.9726
4.7781
4.4843
4.2159
4.0596
3.9326
3.9085
3.8831
1.5467
1.5141
1.0038
0.2111
0.1800
TBSO
Cl3AcHN
OTCA
0.826
0.843
0.865
1.000
0.983
1.067
0.983
2.146
5.916
8.941
5.915
PPM
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

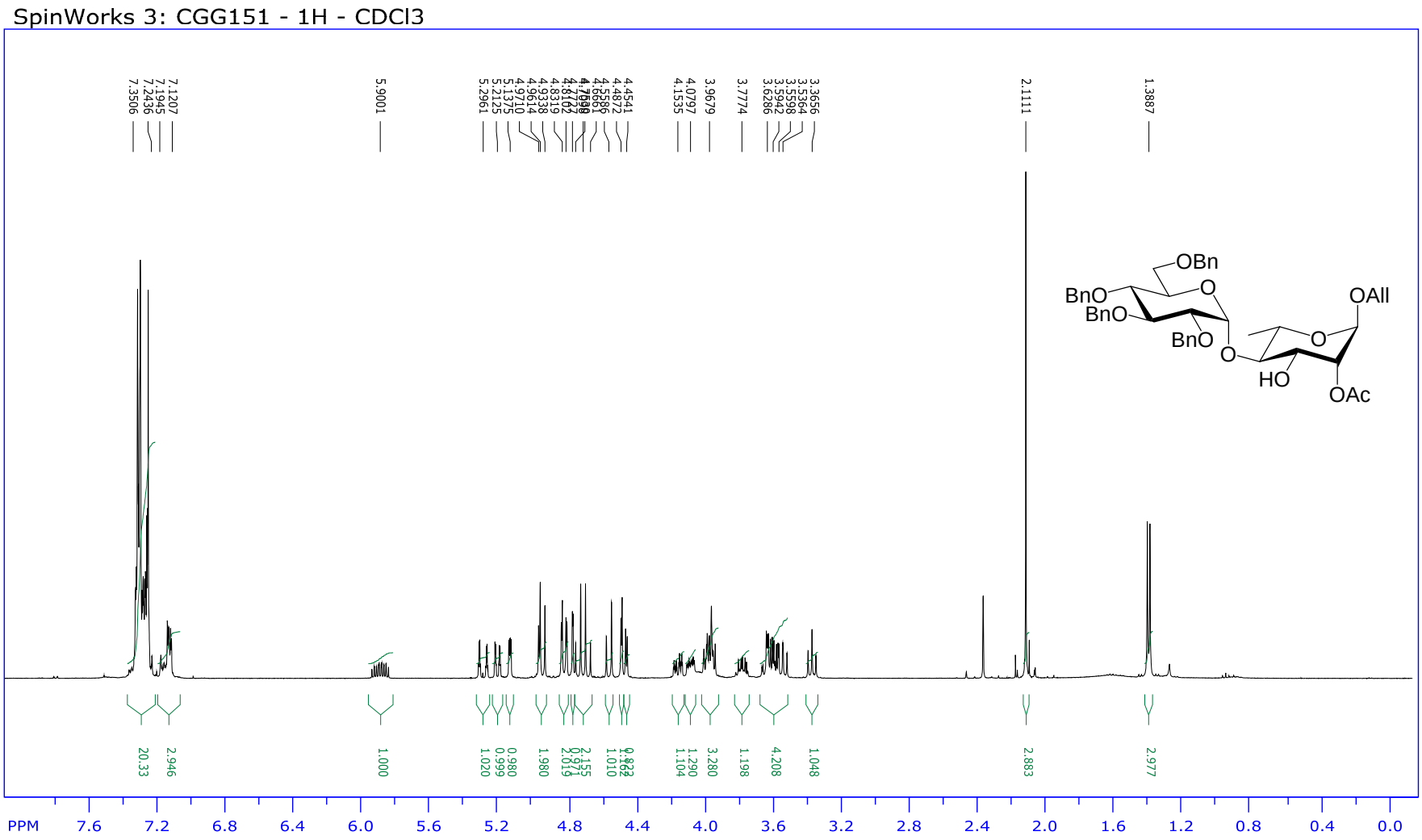
SpinWorks 3: CGG211 - DEPT135 - Pyrd5

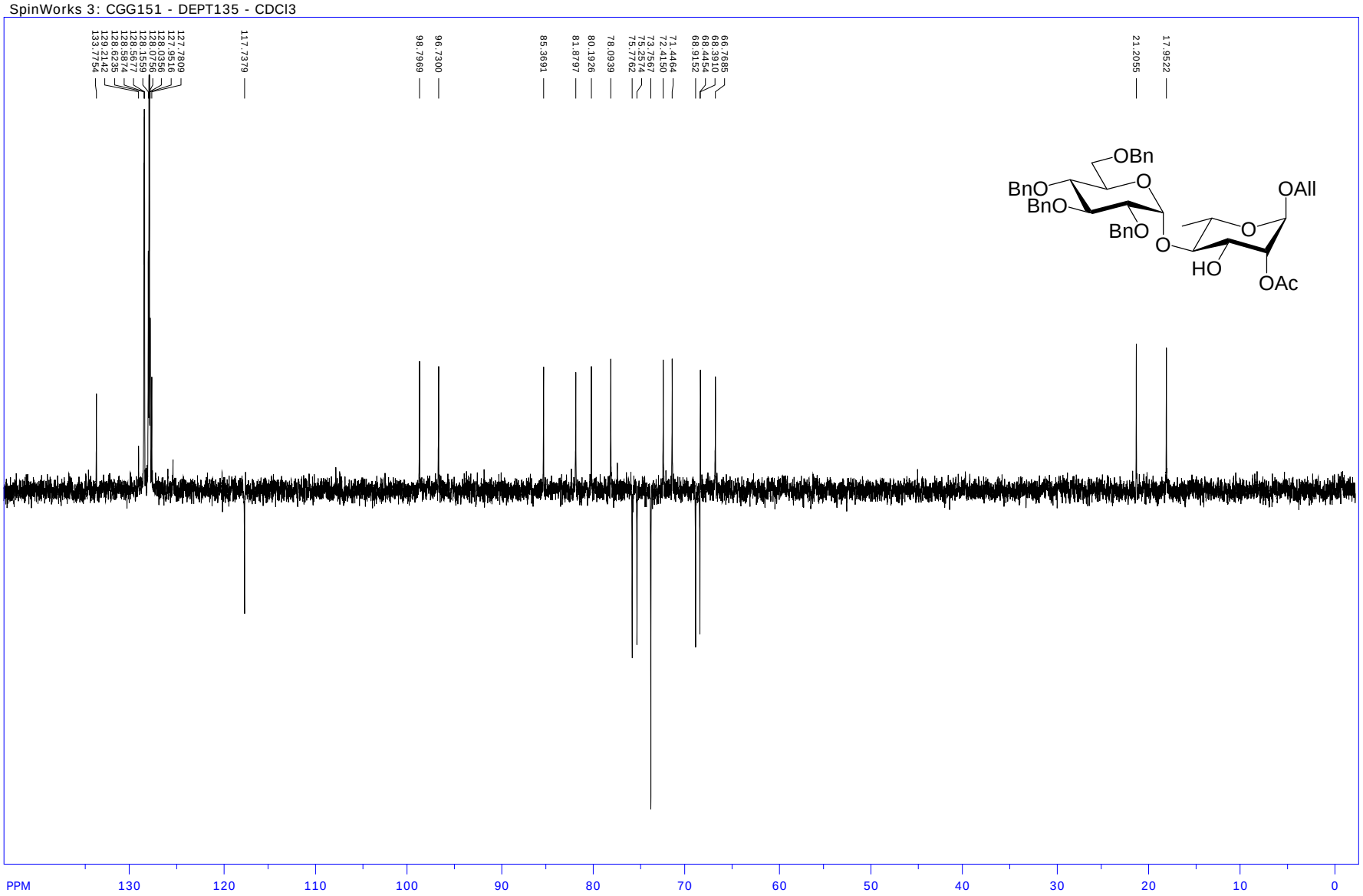


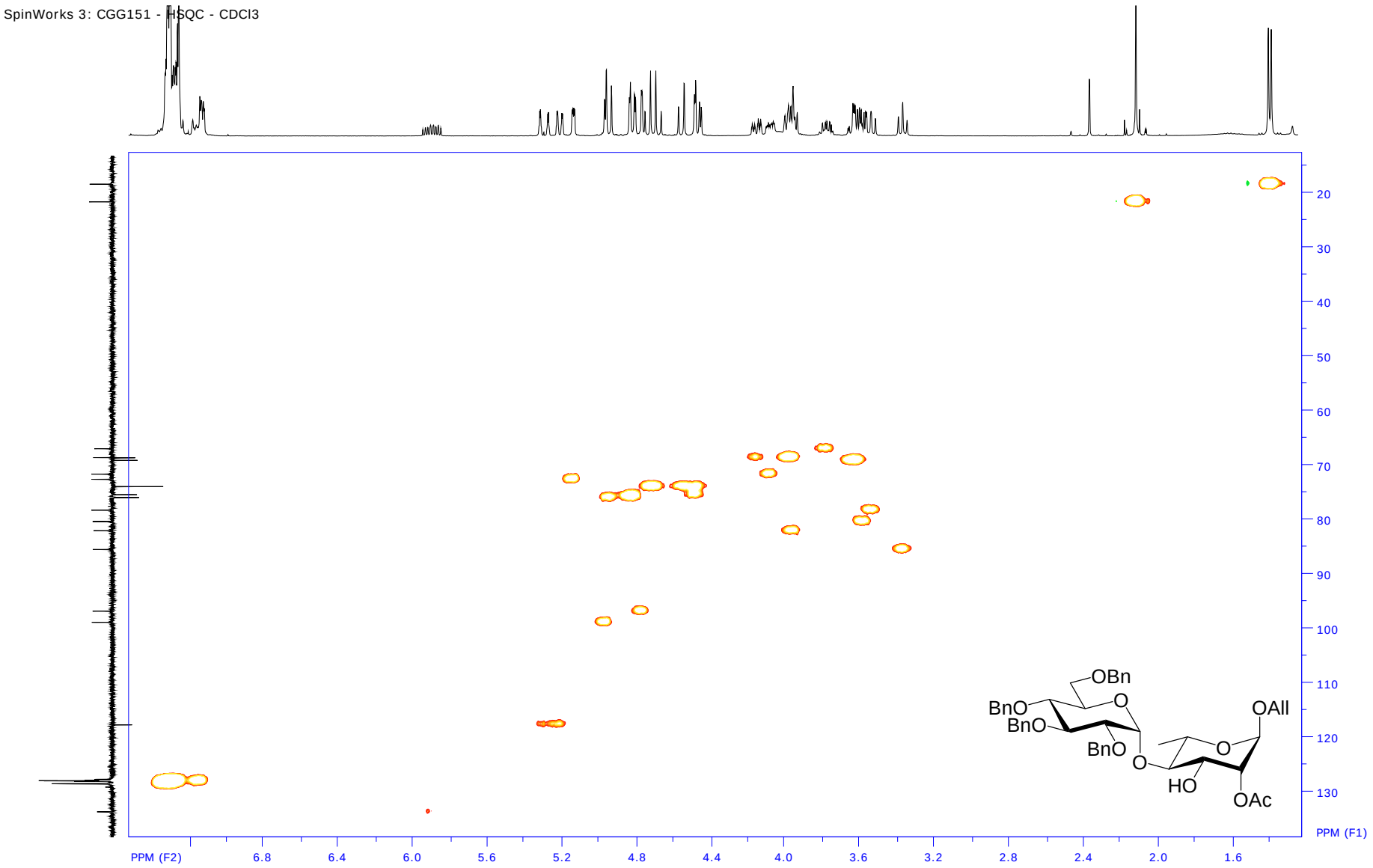

SpinWorks 3: CGG211 - HSQC - Pyrd5
PPM (F2)
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
PPM (F1)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
O
O
O
TBSO
Cl3AcHN
OTCA

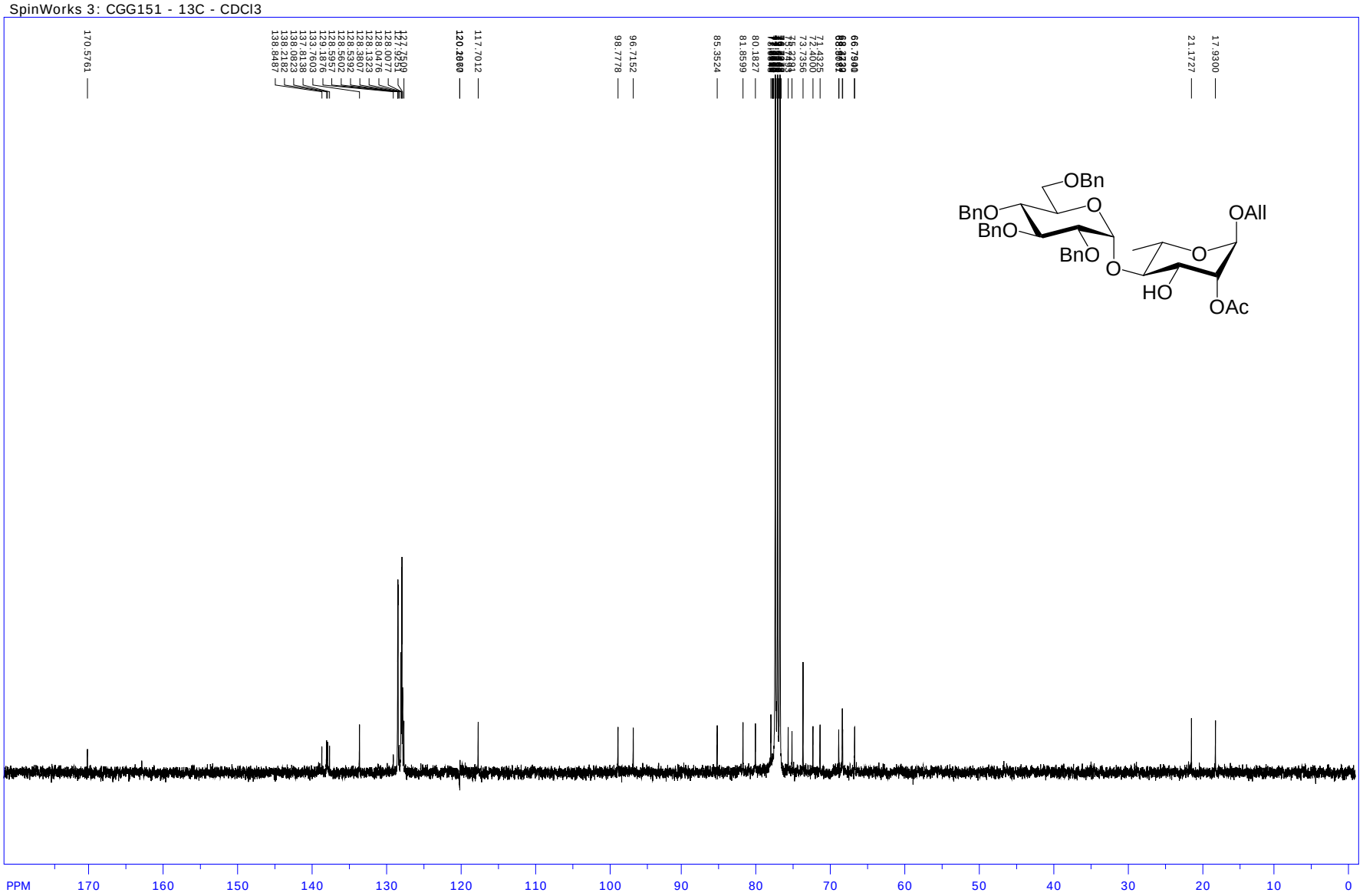

SpinWorks 3: CGG211 - Pyrd5
162.9843
162.9503
160.0780
160.0434
120.6346
120.6092
100.4980
100.0680
97.7675
95.5394
94.2155
93.5085
91.6835
91.6594
76.1922
74.9150
71.6634
71.6413
71.5525
71.5112
67.1055
67.0388
64.1133
64.0914
63.3043
63.2873
62.4500
62.0848
58.7083
57.2229
29.7811
29.7518
27.3975
27.3733
26.6301
26.4860
26.3204
19.6255
19.5127
18.9590
18.8732
-3.1686
-4.3151
TBSO
Cl3AcHN
OTCA
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Compound **16**

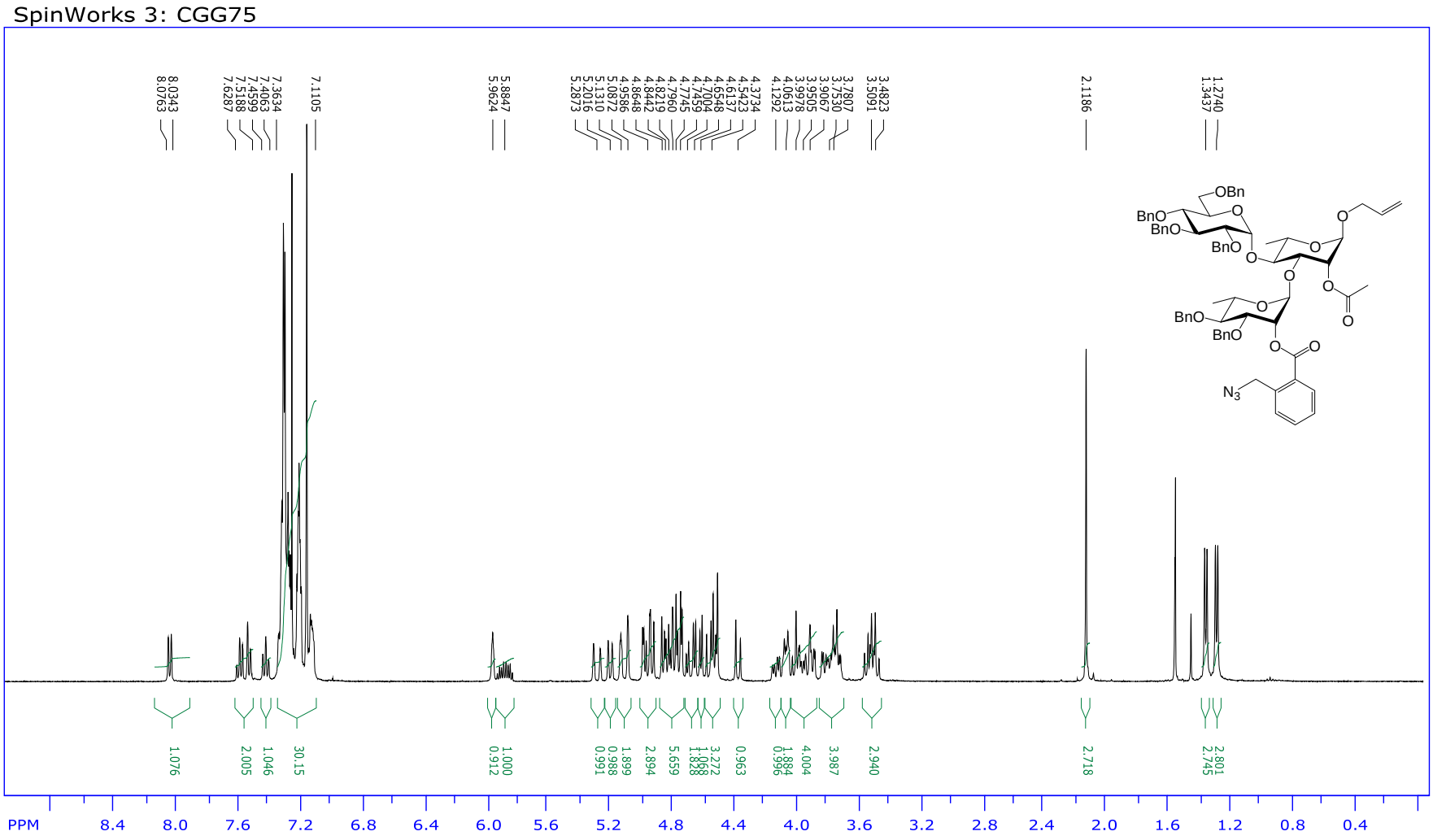

SpinWorks 3: CGG151 - 1H - CDCl3
7.3506
7.2436
7.1945
7.1207
5.9001
5.2961
5.2125
5.1375
4.9710
4.9614
4.9338
4.8319
4.8162
4.6681
4.6586
4.4872
4.4541
4.1535
4.0797
3.9679
3.7774
3.6286
3.5942
3.5598
3.5364
3.3656
2.1111
1.3887
OBn
BnO
BnO
O
BnO
O
O
HO
OAll
OAc
20.33
2.946
1.000
1.020
0.999
0.980
1.980
2.019
2.155
1.010
1.104
1.290
3.280
1.198
4.208
1.048
2.883
2.977
PPM
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

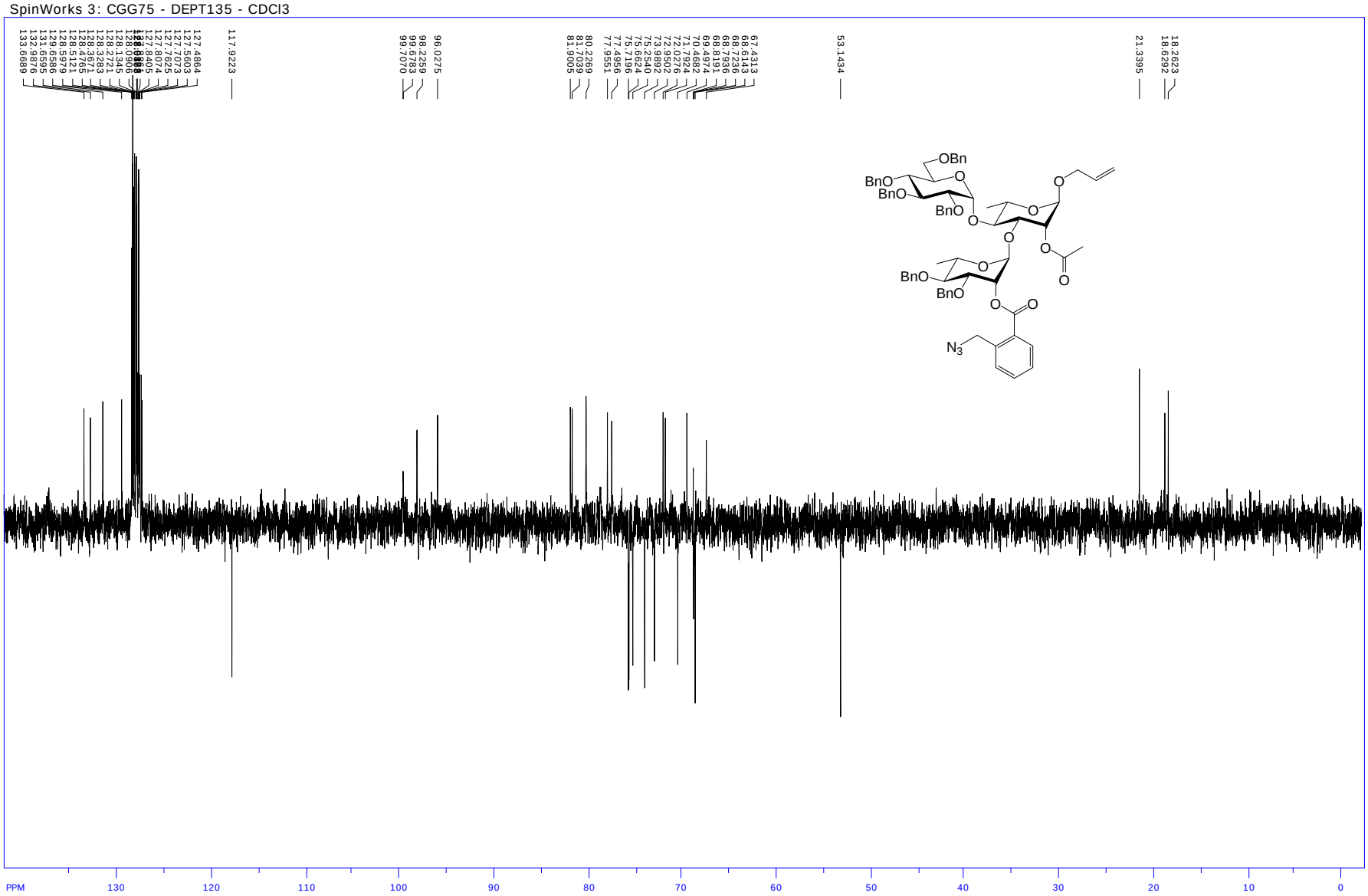

SpinWorks 3: CGG151 - DEPT135 - CDCl3
133.7754
129.2142
128.6325
128.5747
128.5677
128.1559
128.0756
128.0356
127.9516
127.7809
117.7379
98.7969
96.7300
85.3691
81.8797
80.1926
78.0939
75.7762
75.2574
73.7567
72.4150
71.4464
68.9152
68.4454
68.0510
66.7685
21.2055
17.9522
OBn
BnO
BnO
BnO
O
O
O
HO
OAll
OAc
PPM
130
120
110
100
90
80
70
60
50
40
30
20
10
0

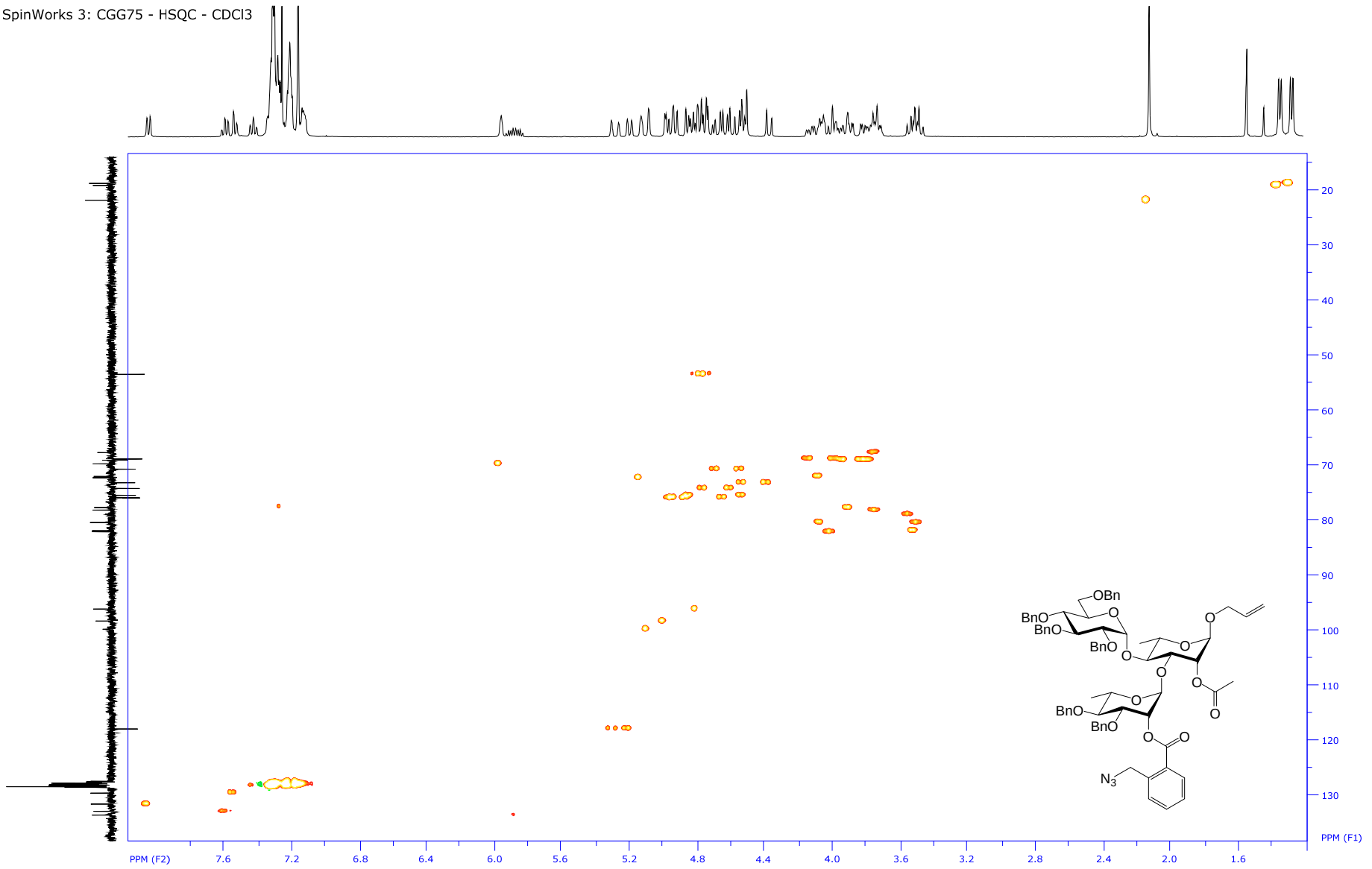

SpinWorks 3: CGG151 - HSQC - CDCl3
PPM (F2)
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
O
HO
OAll
OAc


SpinWorks 3: CGG151 - 13C - CDCl3
170.5761
138.8487
138.2182
138.0823
137.8138
133.7603
129.1876
128.5957
128.5602
128.5307
128.1323
128.0476
128.0077
127.9551
127.7509
120.2080
117.7012
98.7778
96.7152
85.3524
81.8599
80.1827
74.4325
73.7356
66.7900
21.1727
17.9300
OBn
BnO
BnO
BnO
O
O
O
HO
OAll
OAc
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

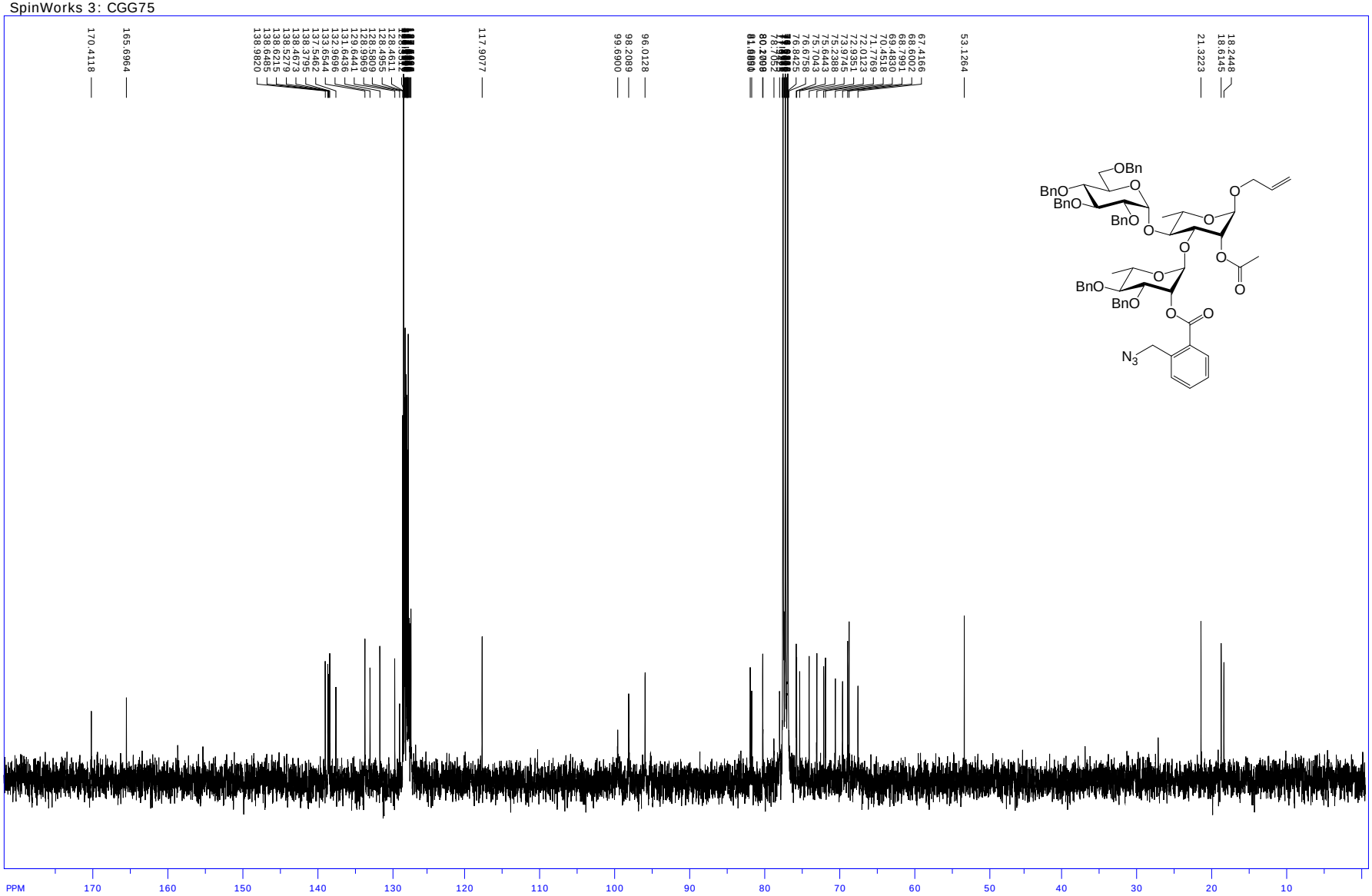
Compound **17**


SpinWorks 3: CGG75
8.0343
8.0763
7.6287
7.5188
7.4599
7.4063
7.3634
7.1105
5.8847
5.8624
5.2873
5.2016
5.1310
5.0872
4.9586
4.8648
4.8442
4.8219
4.7960
4.7745
4.7459
4.7004
4.6548
4.6137
4.5423
4.3734
4.1292
4.0613
3.9978
3.9505
3.9067
3.7807
3.7530
3.5091
3.4823
2.1186
1.3437
1.2740
1.076
2.005
1.046
30.15
1.000
0.912
0.991
0.988
1.899
2.894
5.659
1.068
1.028
3.272
0.963
0.996
1.884
4.004
3.987
2.940
2.718
2.745
2.801
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4

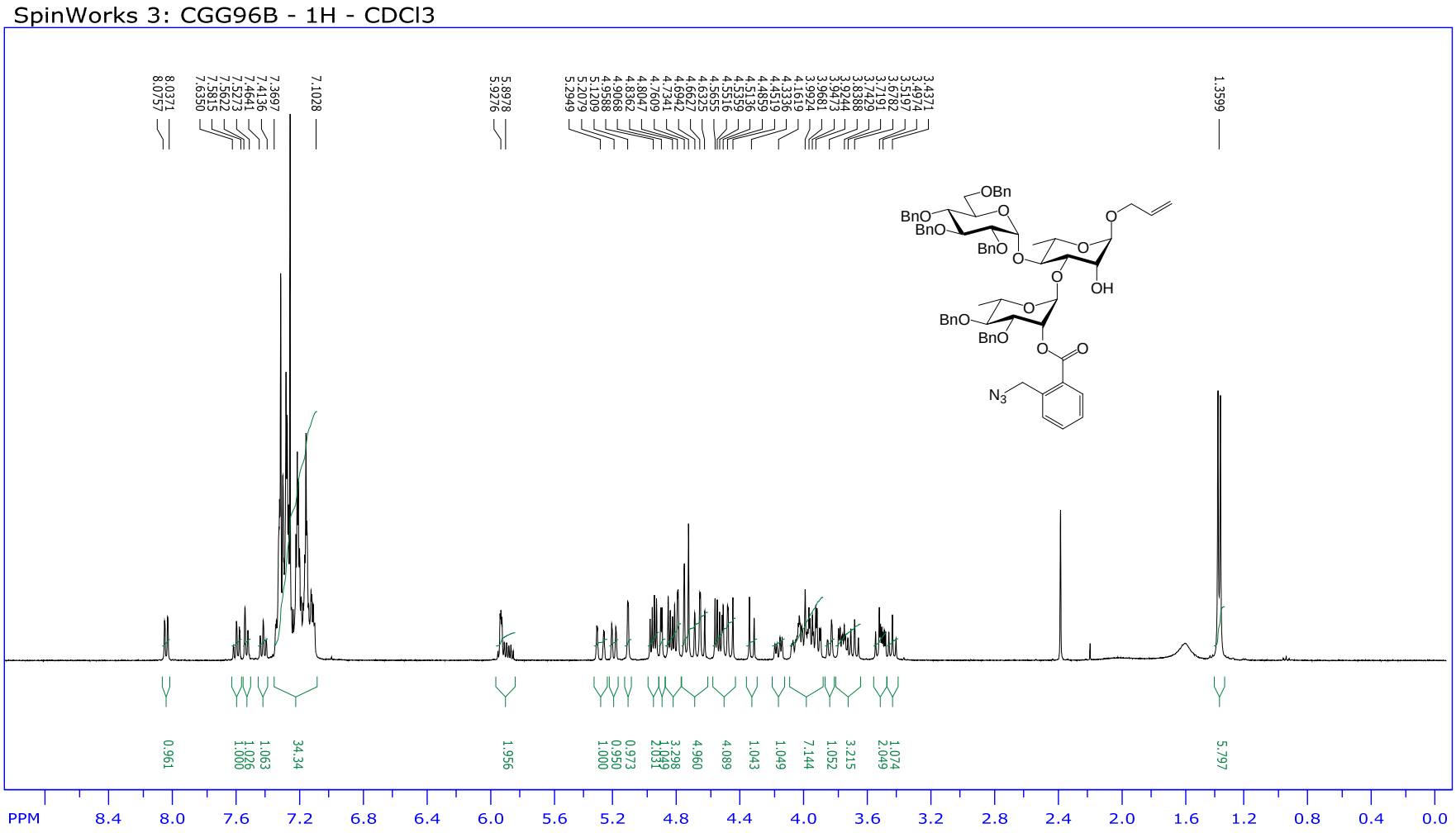

SpinWorks 3: CGG75 - DEPT135 - CDCl3
133.6689
132.9876
131.6595
129.6586
128.5979
128.5121
128.3675
128.3283
128.2721
128.1345
127.8405
127.8074
127.7625
127.7035
127.5603
127.4864
117.9223
99.7070
98.2259
96.0275
81.9005
81.7039
80.2269
77.4956
75.7196
75.6624
75.2540
73.9892
72.9502
72.0276
71.7924
70.4682
69.4974
68.8191
68.7936
68.6143
67.4313
53.1434
21.3395
18.6292
18.2623
OBn
BnO
BnO
BnO
O
O
O
O
O
O
O
BnO
BnO
O
O
N3
PPM
130
120
110
100
90
80
70
60
50
40
30
20
10
0


SpinWorks 3: CGG75 - HSQC - CDCl3
PPM (F2)
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
O
O
O
O
BnO
BnO
O
O
O
N3

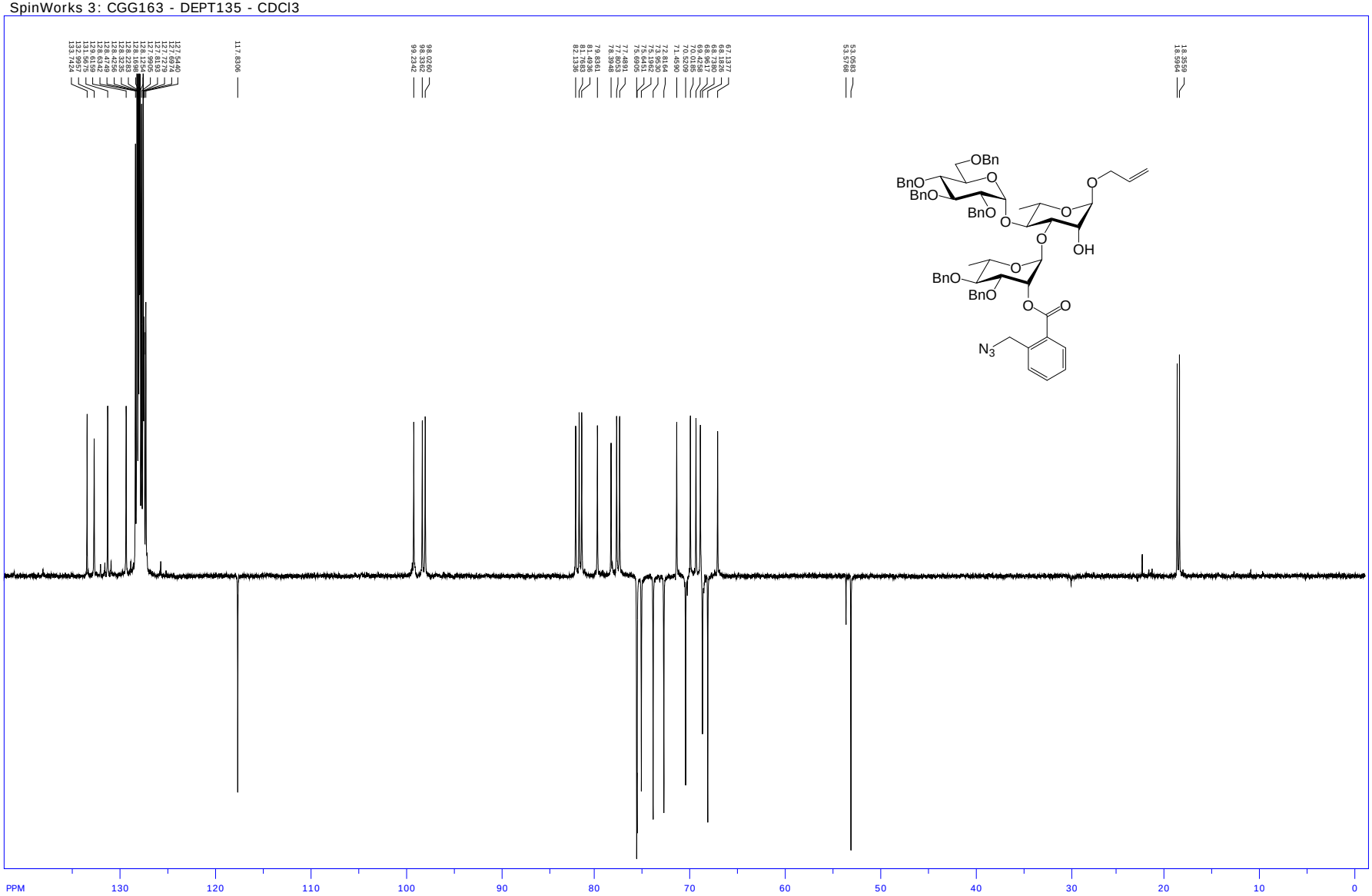
SpinWorks 3: CGG75

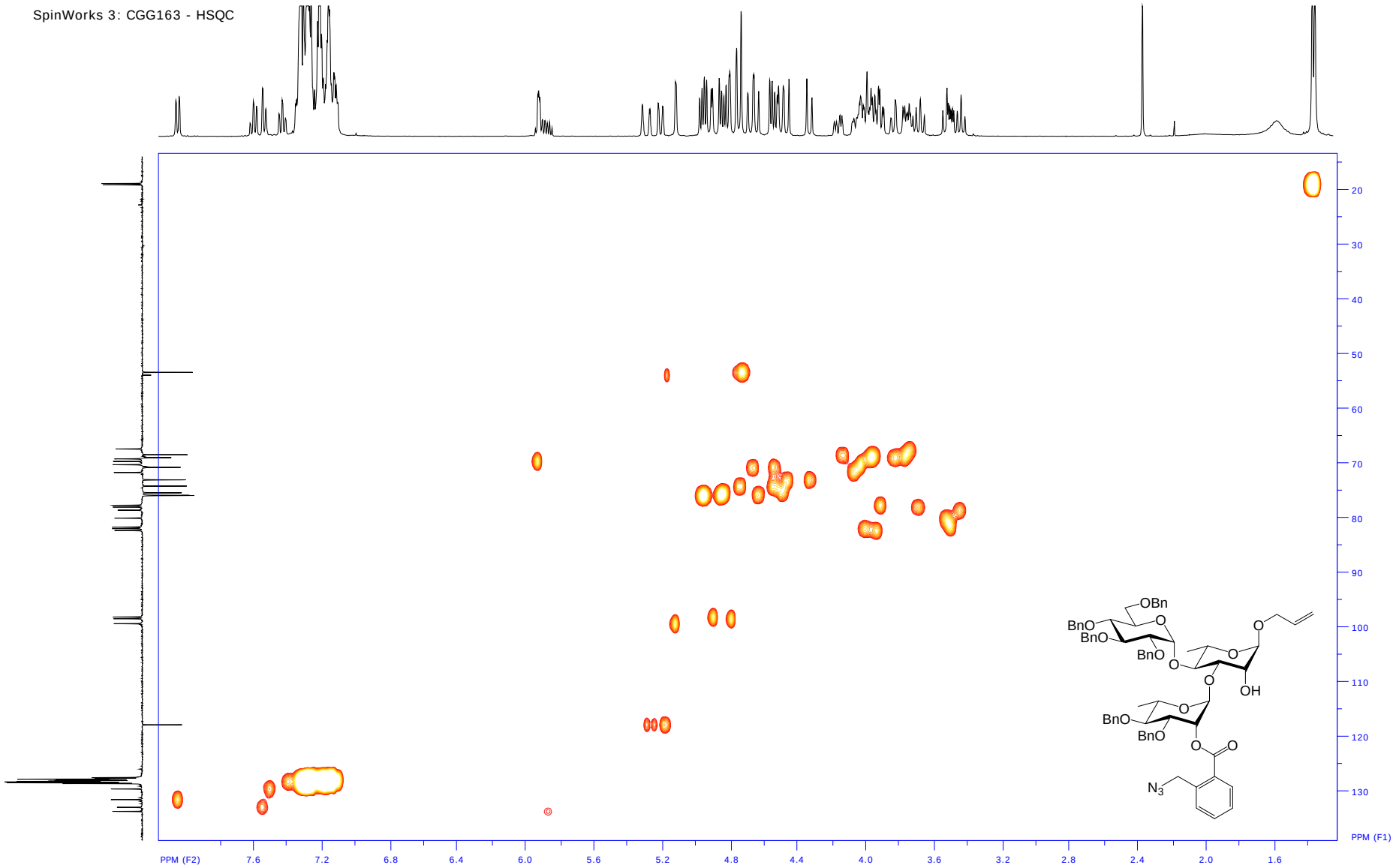


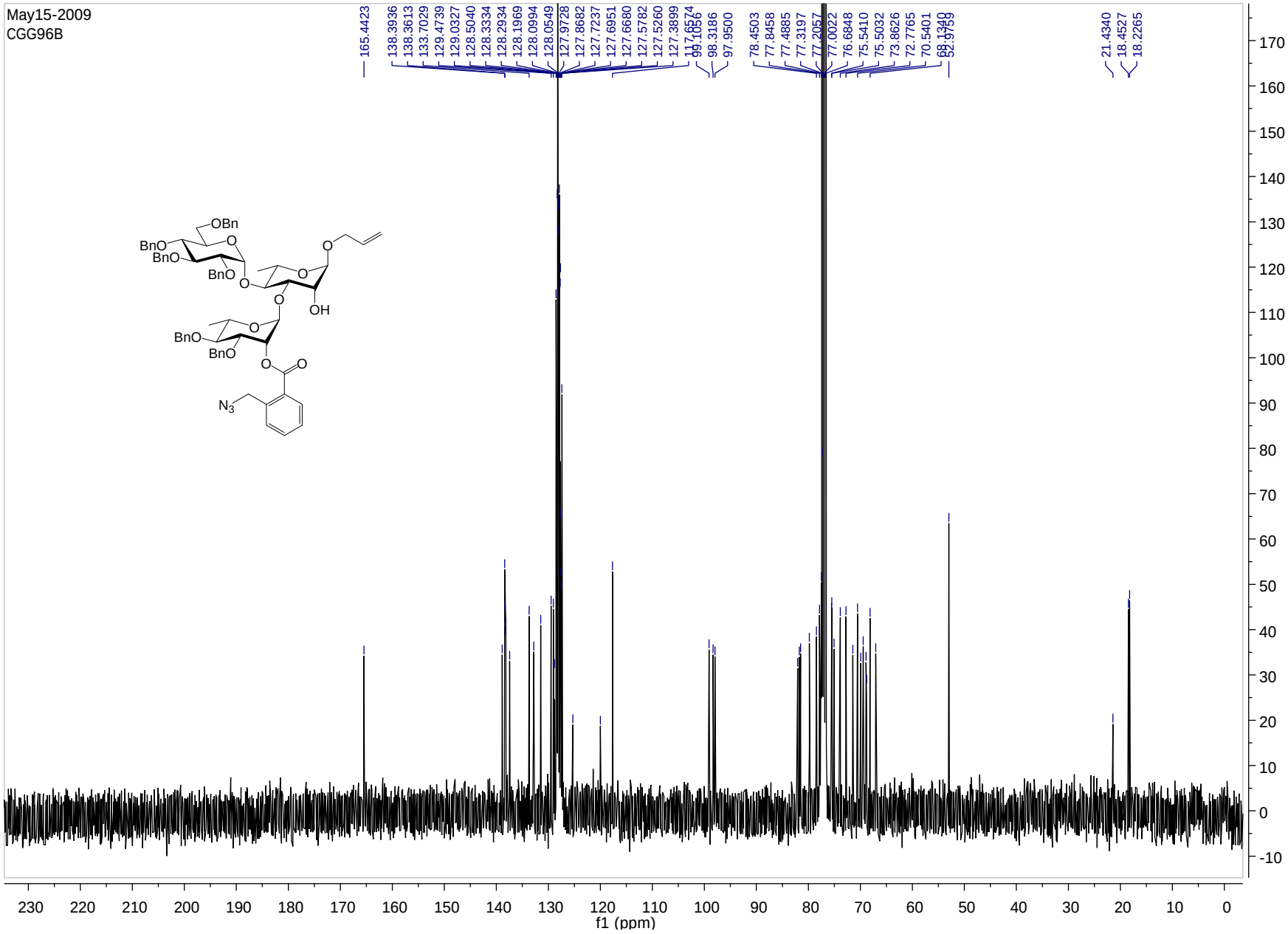
Compound **18**


SpinWorks 3: CGG96B - 1H - CDCl3
8.0371
8.0757
7.5350
7.5815
7.5622
7.5273
7.4641
7.4136
7.3697
7.1028
5.8978
5.9276
5.2949
5.2079
5.1209
4.9588
4.9066
4.8362
4.8047
4.7609
4.7341
4.6942
4.6627
4.6325
4.5655
4.5516
4.5359
4.5136
4.4859
4.4519
4.3336
4.1619
3.9924
3.9681
3.9473
3.9244
3.8388
3.7429
3.7191
3.6782
3.5197
3.4974
3.4271
1.3599
OBn
BnO
BnO
BnO
O
OH
N3
0.961
1.026
1.000
1.063
34.34
1.956
1.000
0.950
0.973
2.031
3.298
4.960
4.089
1.043
1.049
7.144
1.052
3.215
2.049
1.074
5.797
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

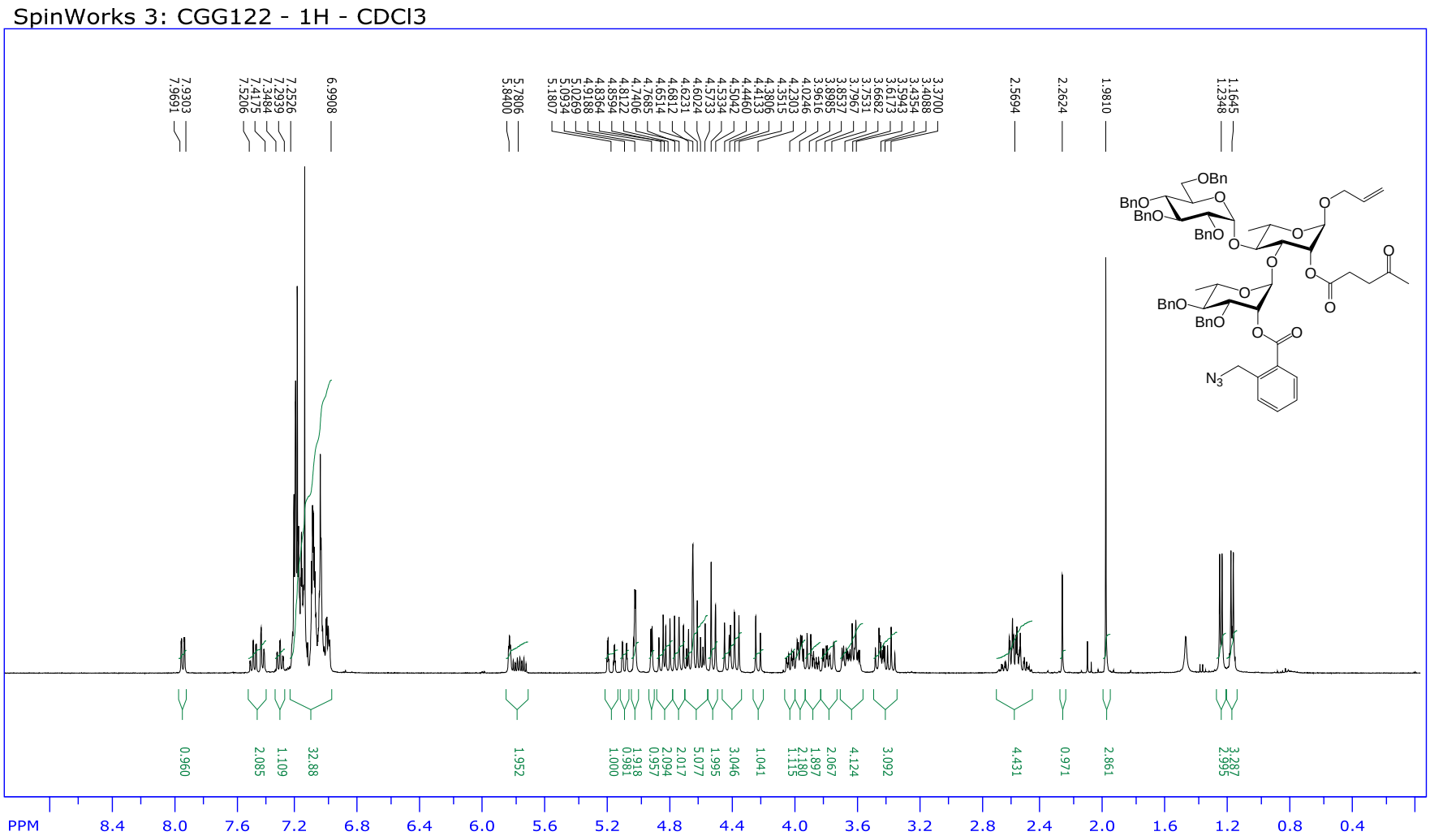
SpinWorks 3: CGG163 - DEPT135 - CDCl3



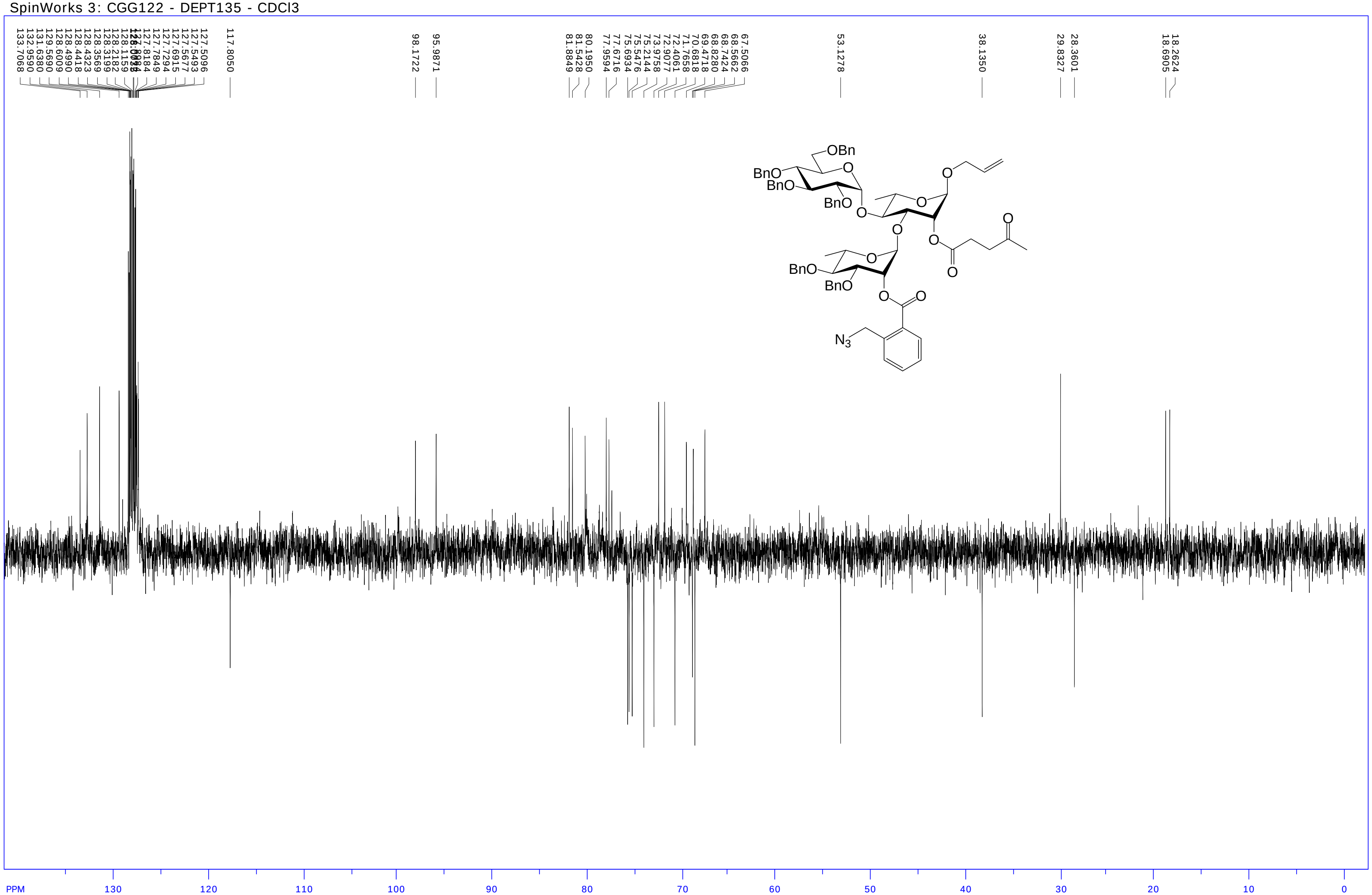

SpinWorks 3: CGG163 - HSQC
PPM (F2)
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
O
O
OH
BnO
BnO
O
O
O
N3

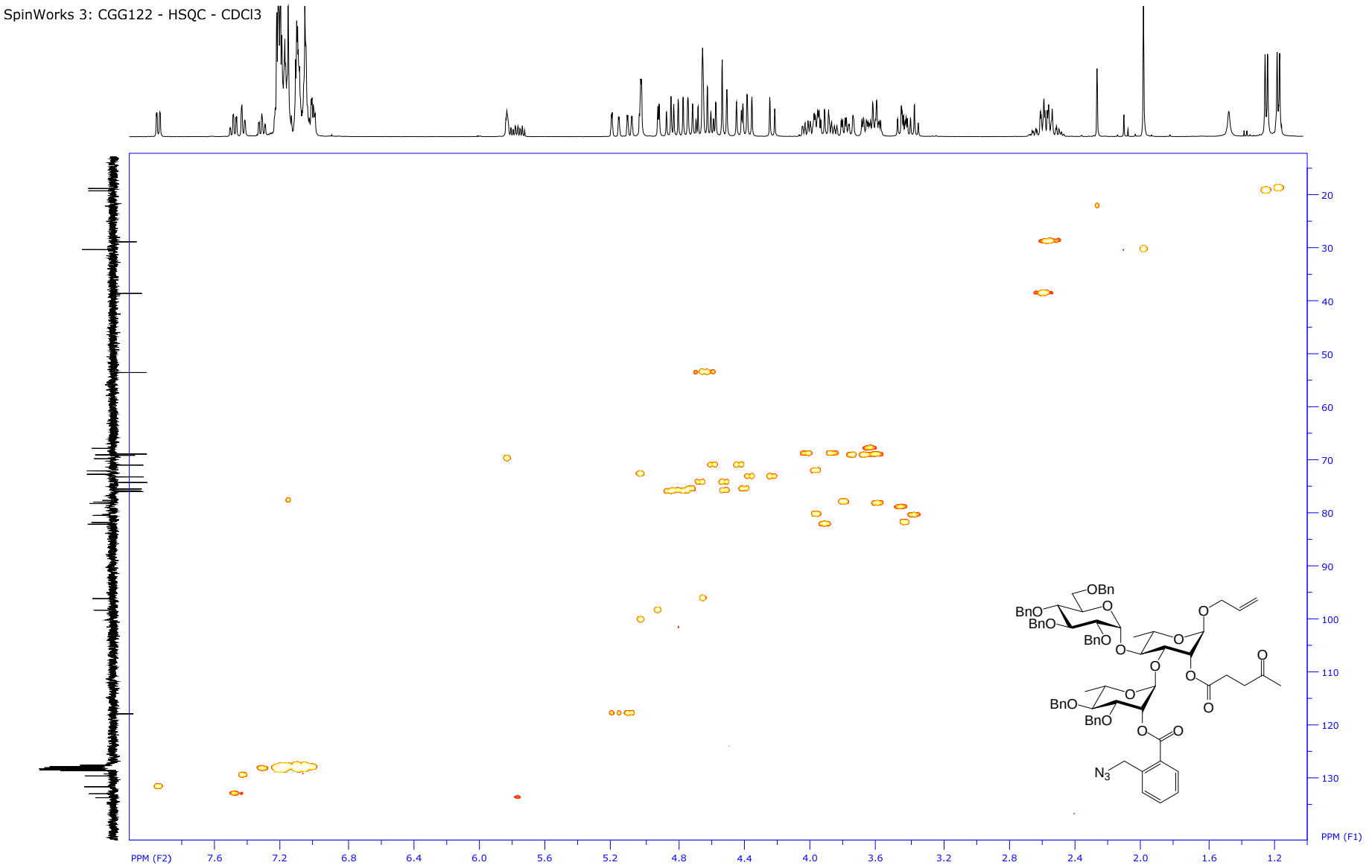

May15-2009
CGG96B
165.4423
138.3936
138.3613
133.7029
129.4739
129.0327
128.5040
128.3334
128.2934
128.1969
128.0994
128.0549
127.9728
127.8682
127.7237
127.6951
127.6680
127.5782
127.5260
127.3899
117.6574
99.1056
98.3186
97.9500
78.4503
77.8458
77.4885
77.3197
77.2057
77.0022
76.6848
75.5410
75.5032
73.8626
72.7765
70.5401
68.1340
52.9759
21.4340
18.4527
18.2265
OBn
BnO
BnO
BnO
O
O
O
O
O
OH
BnO
BnO
O
O
O
N3
f1 (ppm)

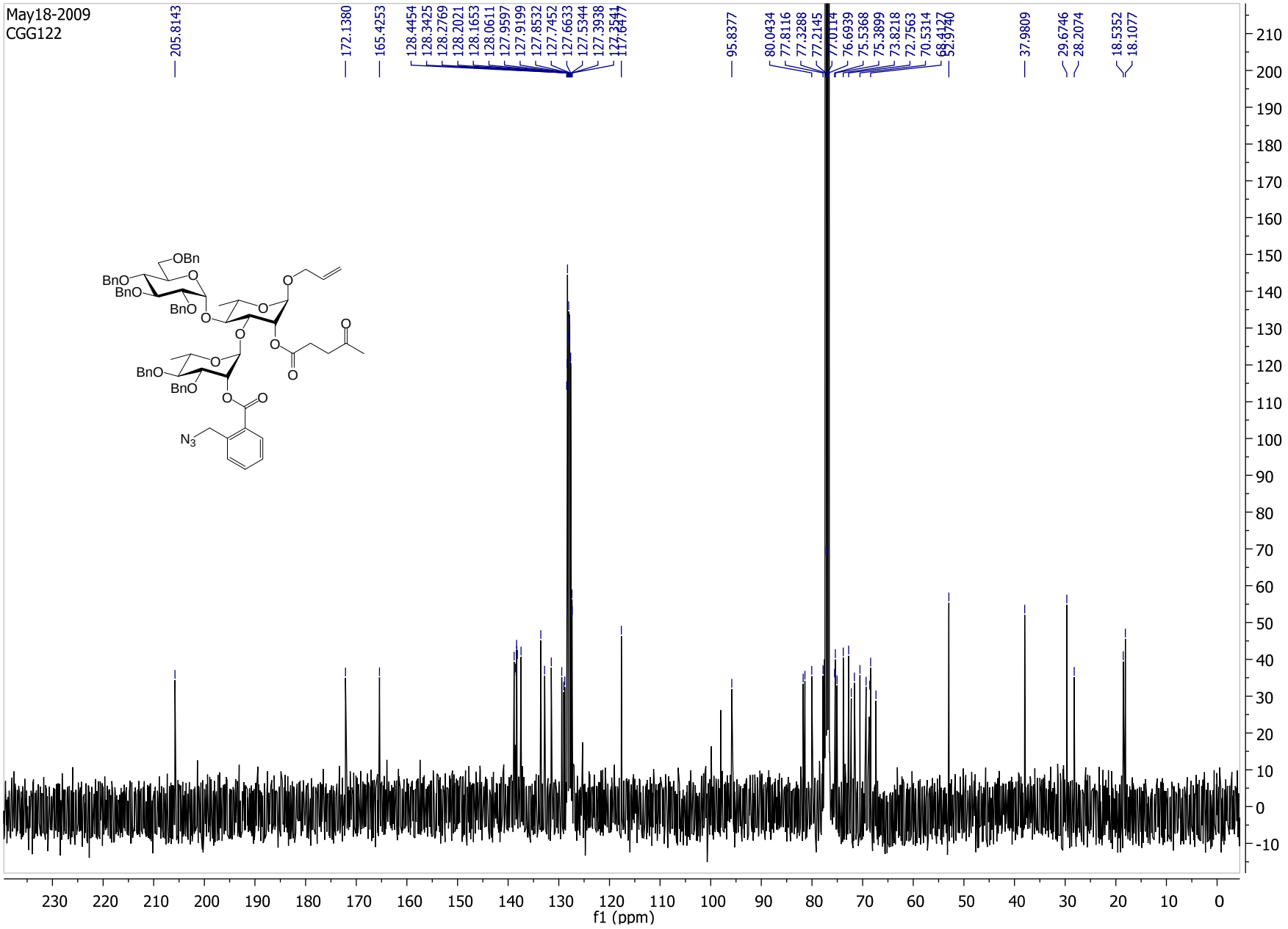
Compound **19**


SpinWorks 3: CGG122 - 1H - CDCl3
7.9303
7.9691
7.5206
7.4175
7.3484
7.2939
7.2526
6.9908
5.7806
5.8400
5.1807
5.0934
5.0269
4.9188
4.8364
4.8594
4.8122
4.7406
4.7685
4.6514
4.6812
4.6231
4.6024
4.5733
4.5334
4.5042
4.4460
4.4133
4.3806
4.3515
4.2303
4.0246
3.9616
3.8985
3.8537
3.7967
3.7531
3.6682
3.6173
3.5943
3.4354
3.4088
3.3700
2.5694
2.2624
1.9810
1.2348
1.1645
0.960
2.085
1.109
32.88
1.952
1.000
0.981
1.918
0.957
2.094
2.017
5.077
1.995
3.046
1.041
1.115
2.180
1.897
2.067
4.124
3.092
4.431
0.971
2.861
2.995
3.287
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4

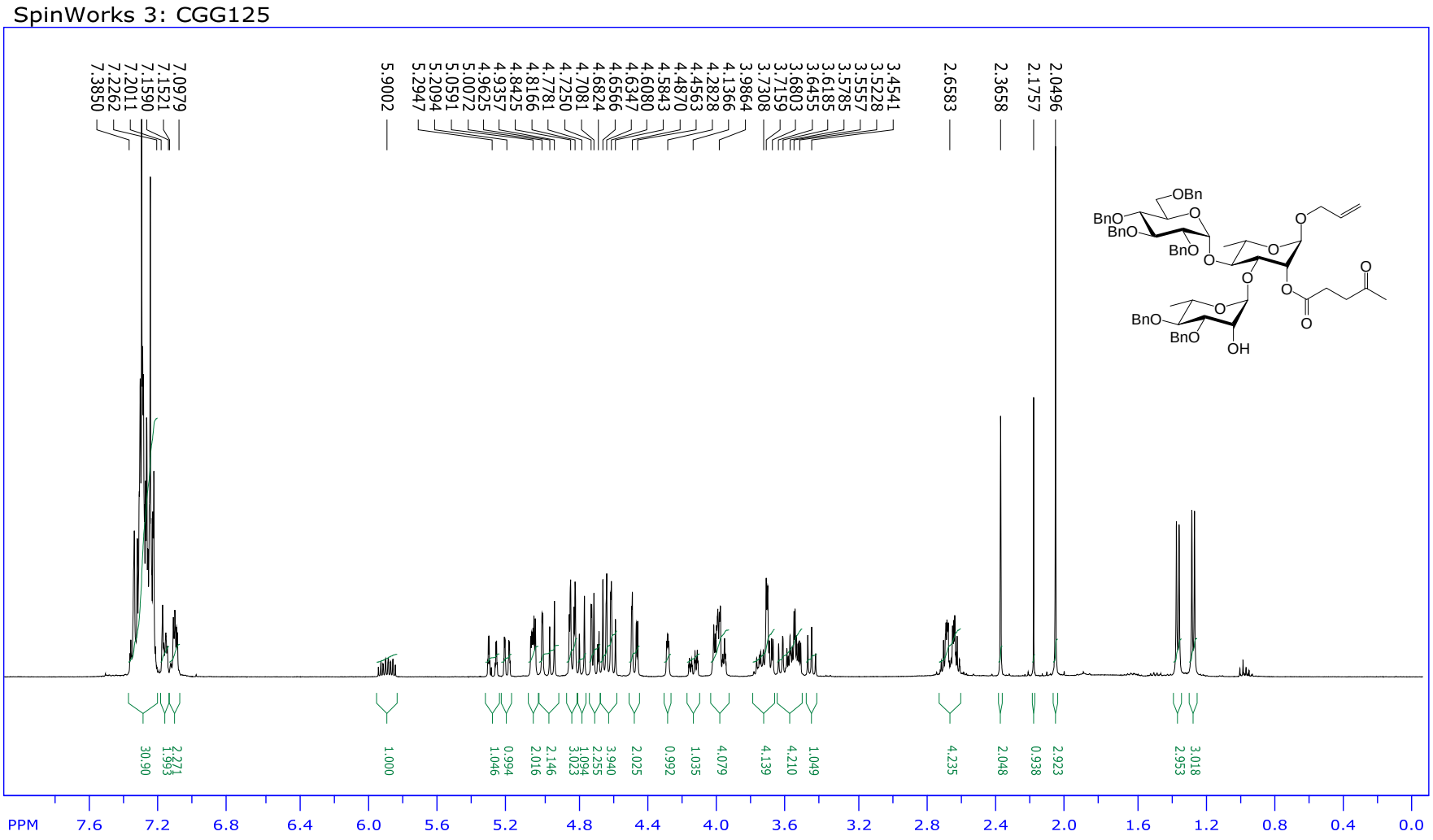
SpinWorks 3: CGG122 - DEPT135 - CDCl3



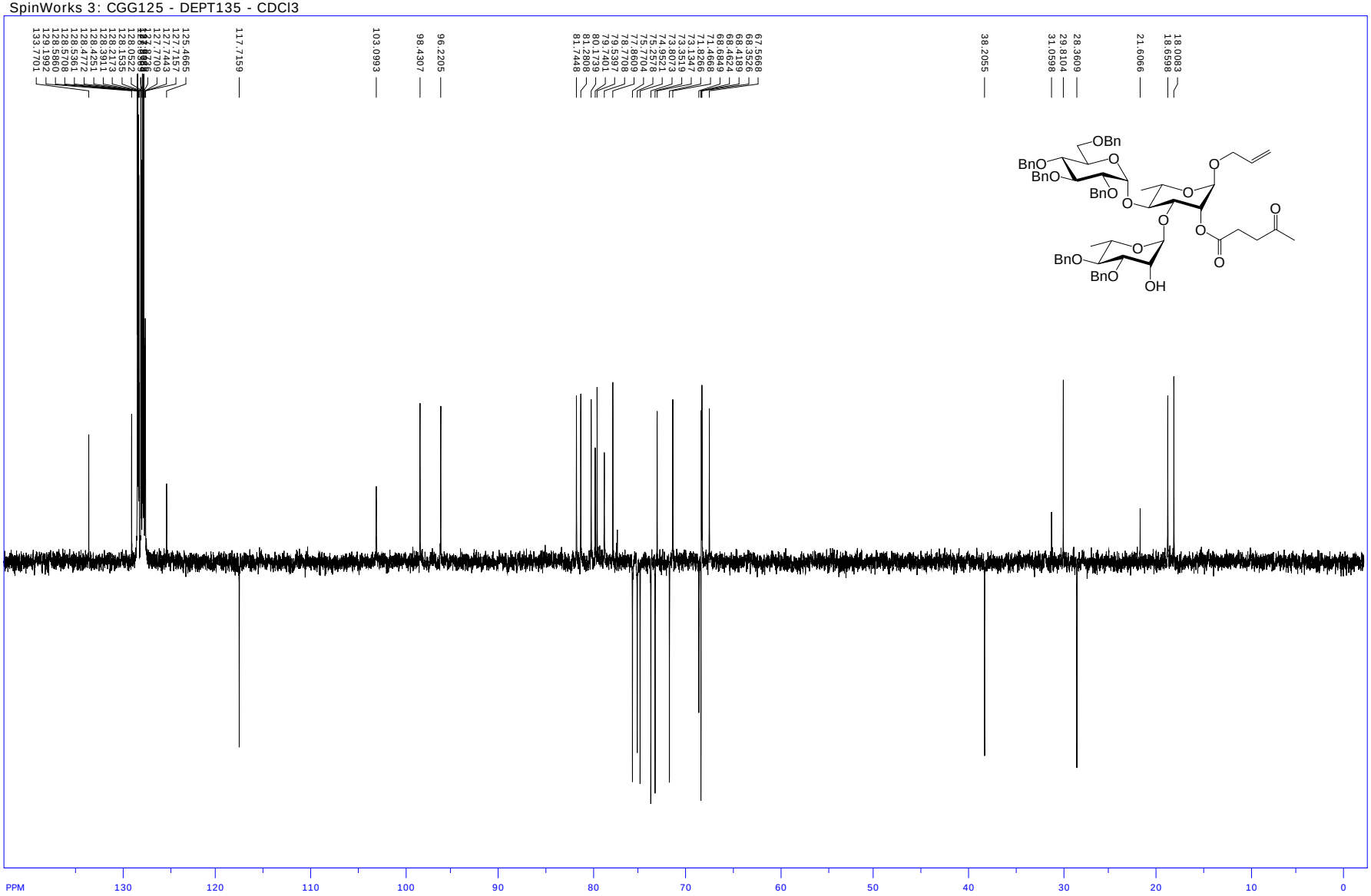

SpinWorks 3: CGG122 - HSQC - CDCl3
PPM (F2)
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
O
O
O
O
O
O
BnO
BnO
O
O
N3

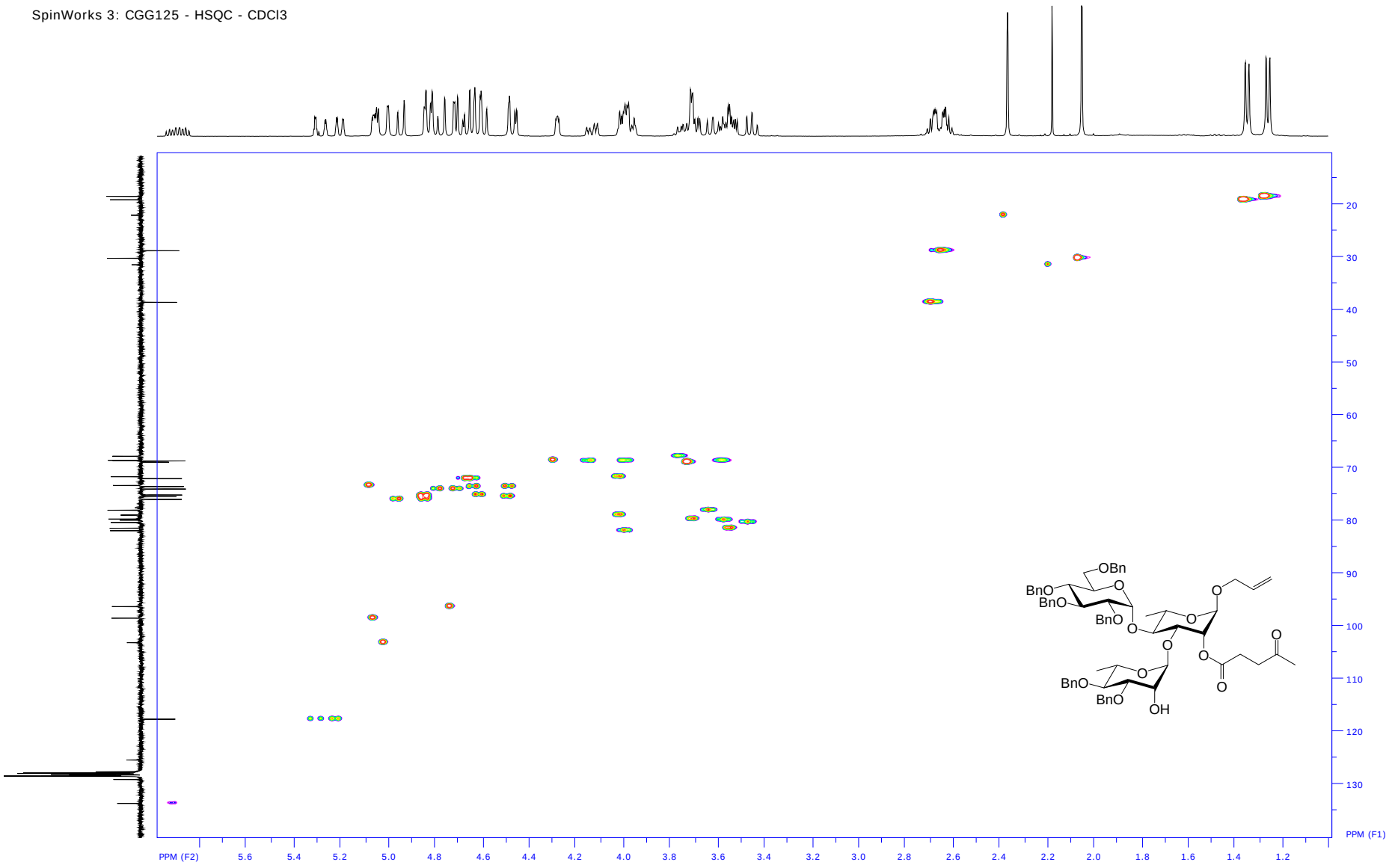

May18-2009
CGG122
205.8143
172.1380
165.4253
128.4454
128.3425
128.2769
128.2021
128.1653
128.0611
127.9597
127.9199
127.8532
127.7452
127.6633
127.5344
127.3938
117.6477
95.8377
80.0434
77.8116
77.3288
77.2145
77.0114
76.6939
75.5368
75.3899
73.8218
72.7563
70.5314
37.9809
29.6746
28.2074
18.5352
18.1077
OBn
BnO
BnO
BnO
BnO
BnO
N3
f1 (ppm)

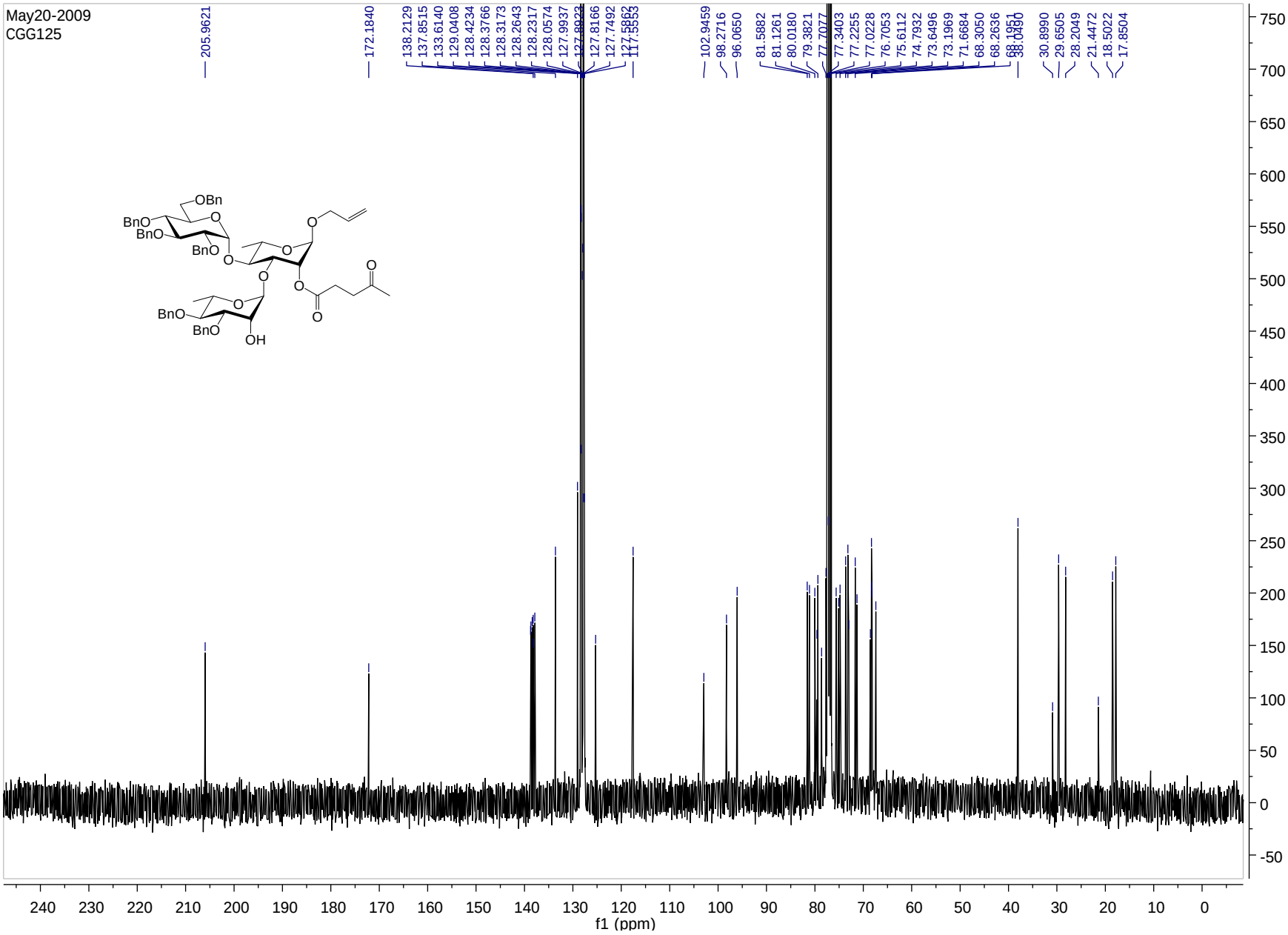
Compound **20**


SpinWorks 3: CGG125
7.3850
7.2262
7.2011
7.1590
7.1521
7.0979
5.9002
5.2947
5.2094
5.0591
5.0072
4.9625
4.9357
4.8425
4.8166
4.7781
4.7250
4.7081
4.6824
4.6566
4.6347
4.6080
4.5843
4.4870
4.4563
4.2828
4.1366
3.9864
3.7308
3.7159
3.6803
3.6455
3.6185
3.5785
3.5557
3.5228
3.4541
2.6583
2.3658
2.1757
2.0496
30.90
1.993
2.271
1.000
1.046
0.994
2.016
2.146
3.023
1.094
2.255
3.940
2.025
0.992
1.035
4.079
4.139
4.210
1.049
4.235
2.048
0.938
2.923
2.953
3.018
PPM
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
OBn
BnO
BnO
BnO
BnO
BnO
OH
O

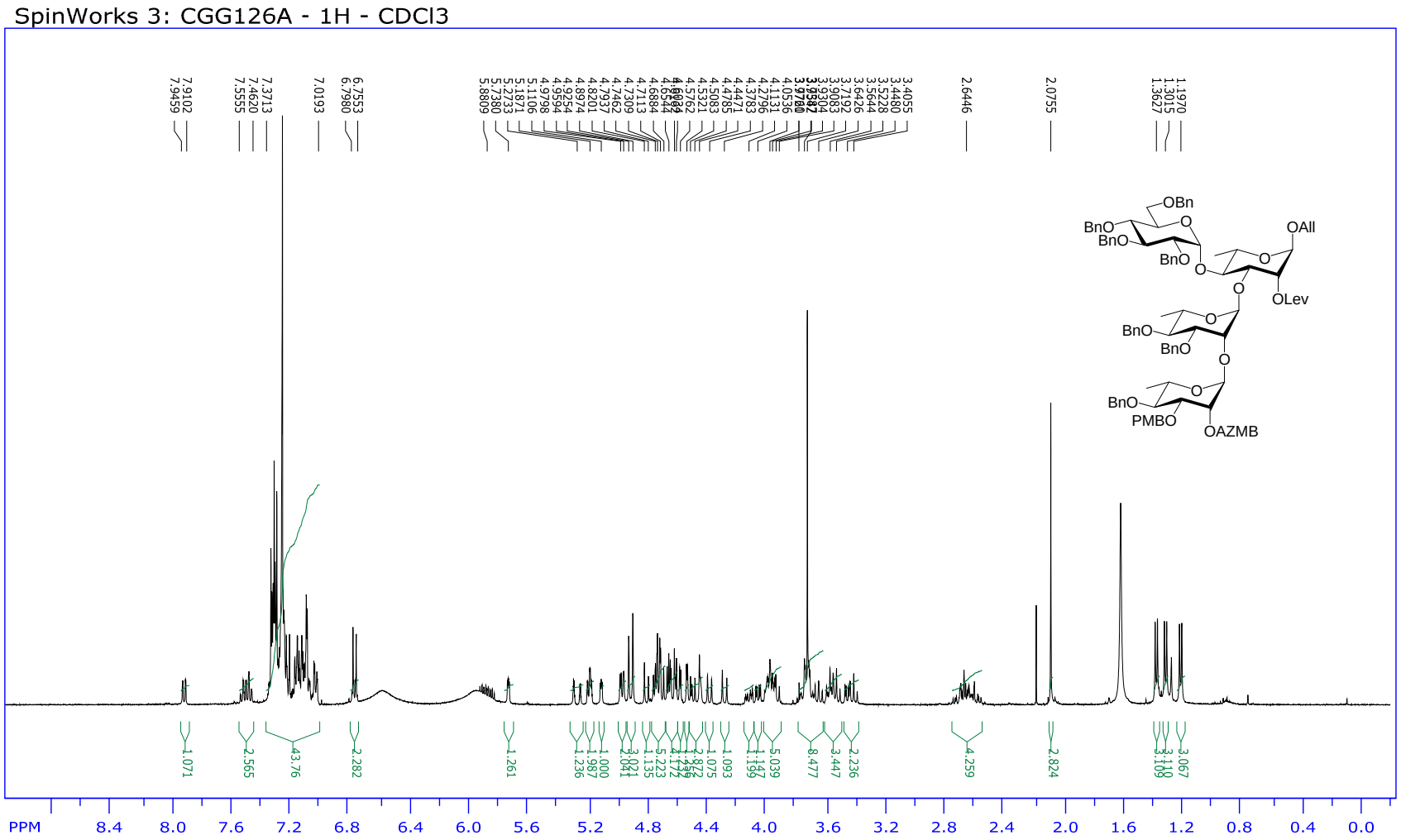
SpinWorks 3: CGG125 - DEPT135 - CDCl3

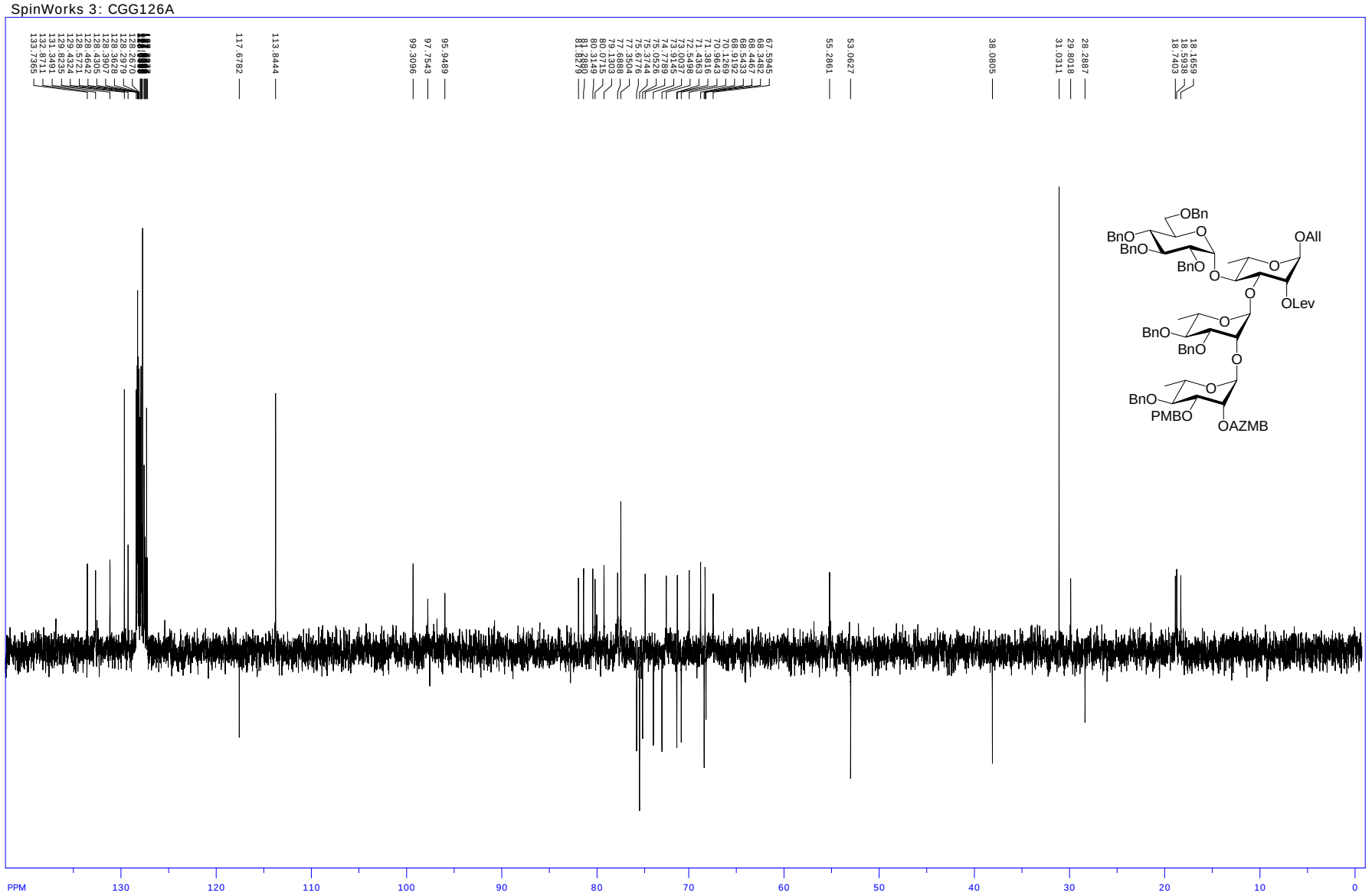


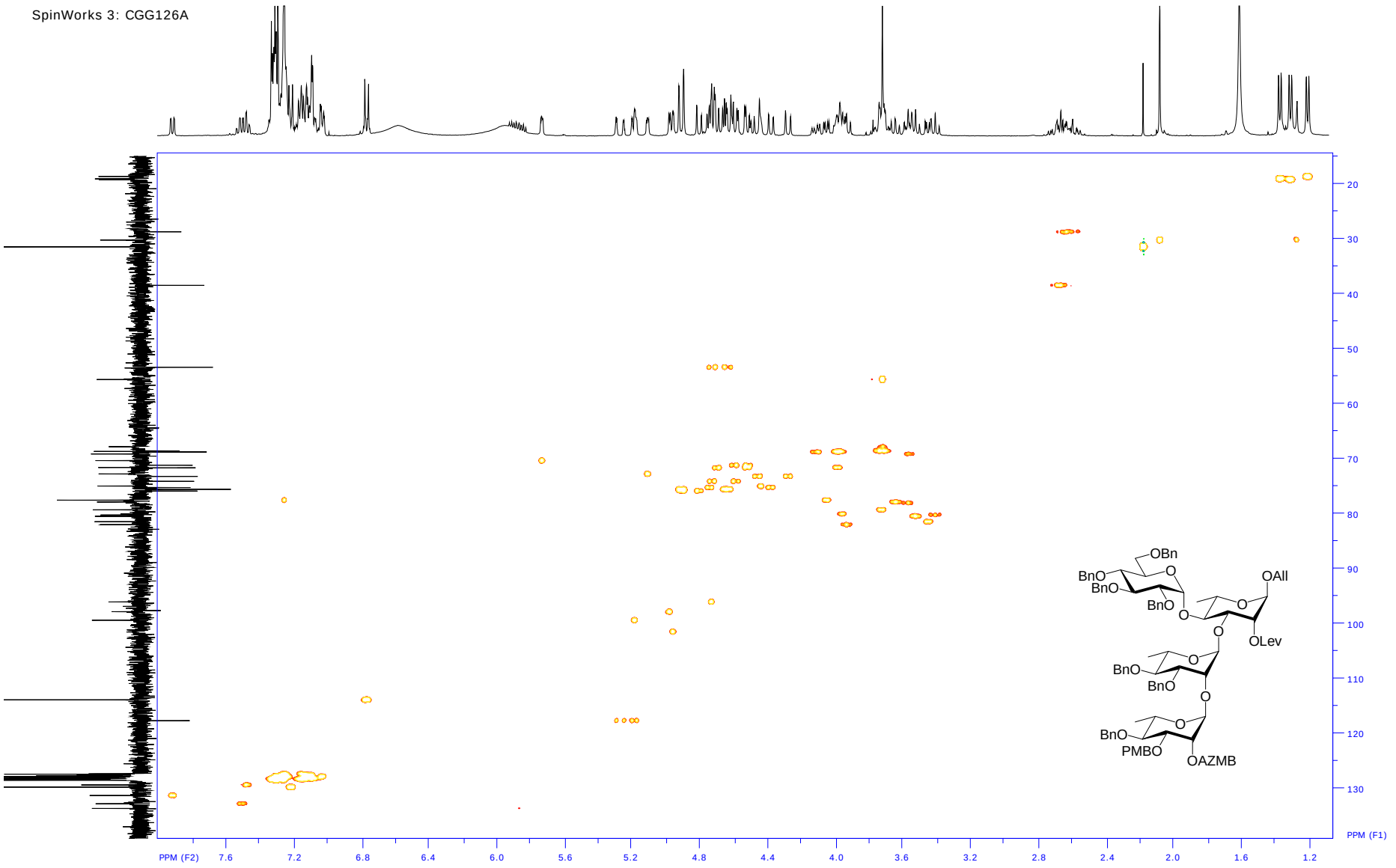

SpinWorks 3: CGG125 - HSQC - CDCl3
PPM (F2)
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
O
O
O
O
O
BnO
BnO
O
OH

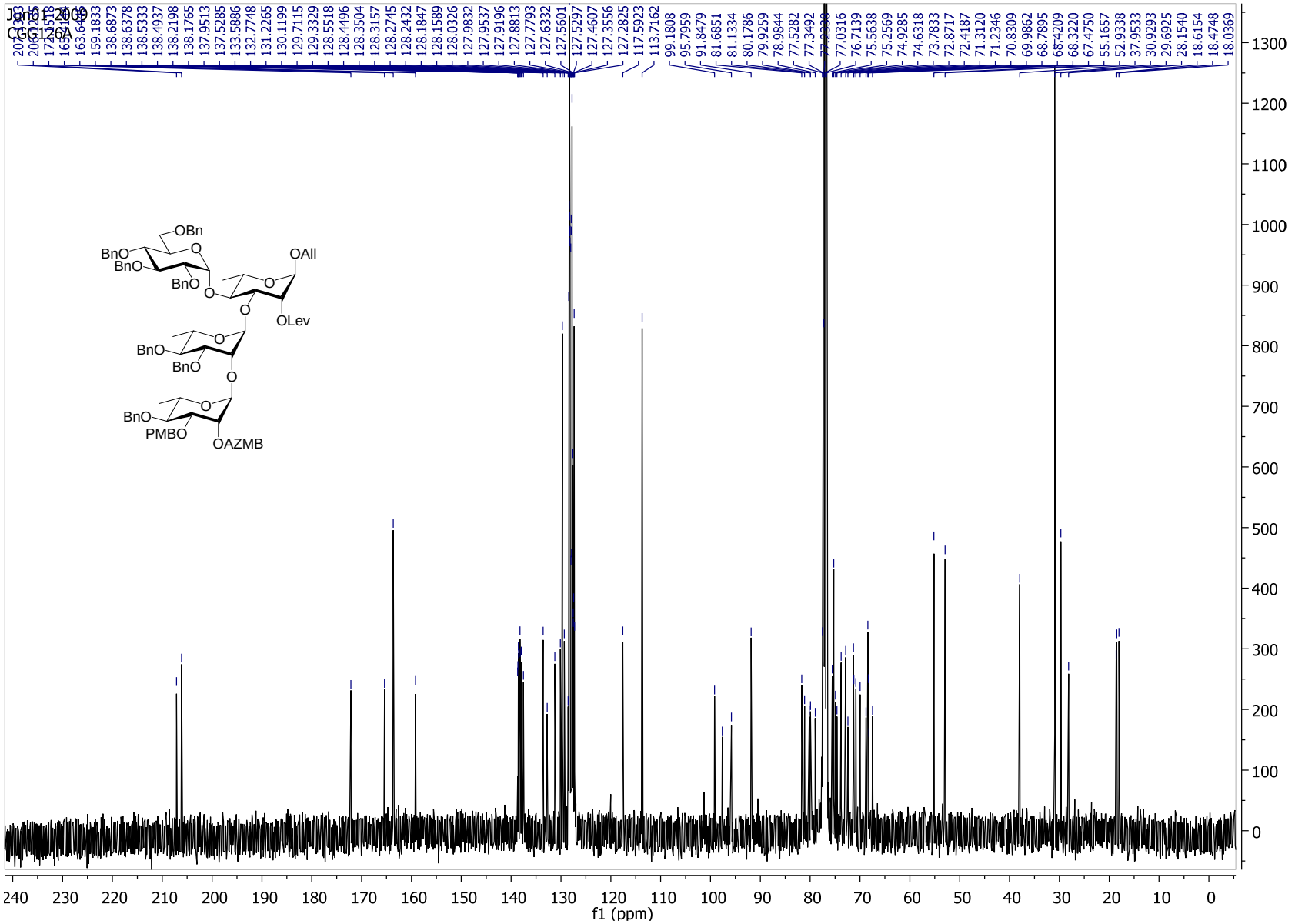

May20-2009
CGG125
205.9621
172.1840
138.2129
137.8515
133.6140
129.0408
128.4234
128.3766
128.3173
128.2643
128.2317
128.0574
127.9937
127.8166
127.7492
102.9459
98.2716
96.0650
81.5882
81.1261
80.0180
79.3821
77.7077
77.3403
77.2255
77.0228
76.7053
75.6112
74.7932
73.6496
73.1969
71.6684
68.3050
68.2636
30.8990
29.6505
28.2049
21.4472
18.5022
17.8504
OBn
BnO
BnO
BnO
O
O
O
O
O
O
O
O
BnO
BnO
OH
f1 (ppm)

Compound **21**

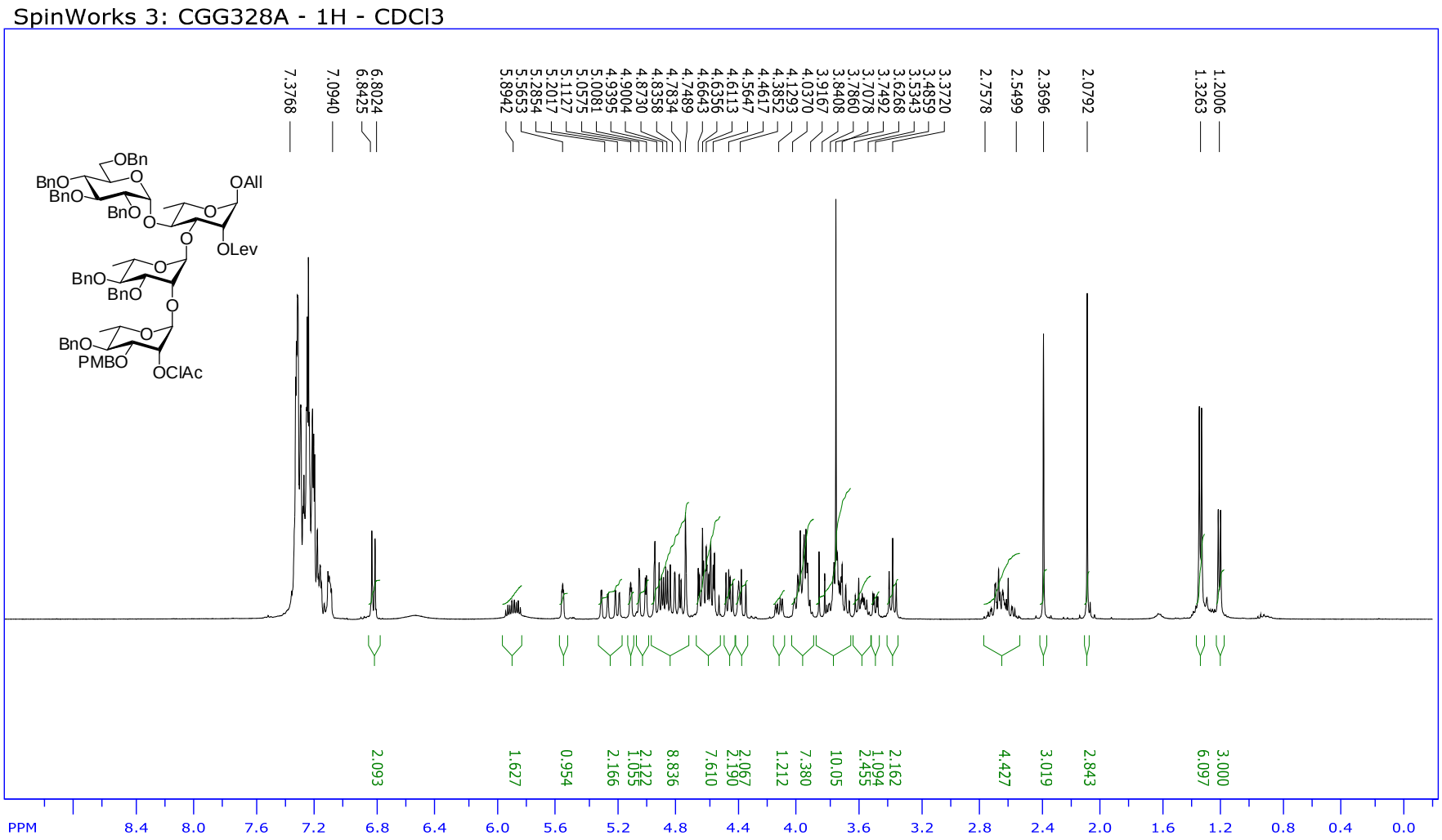

SpinWorks 3: CGG126A - 1H - CDCl3
OBn
BnO
BnO
O
BnO
O
OAll
O
O
OLev
BnO
BnO
O
O
BnO
PMBO
O
OAZMB
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

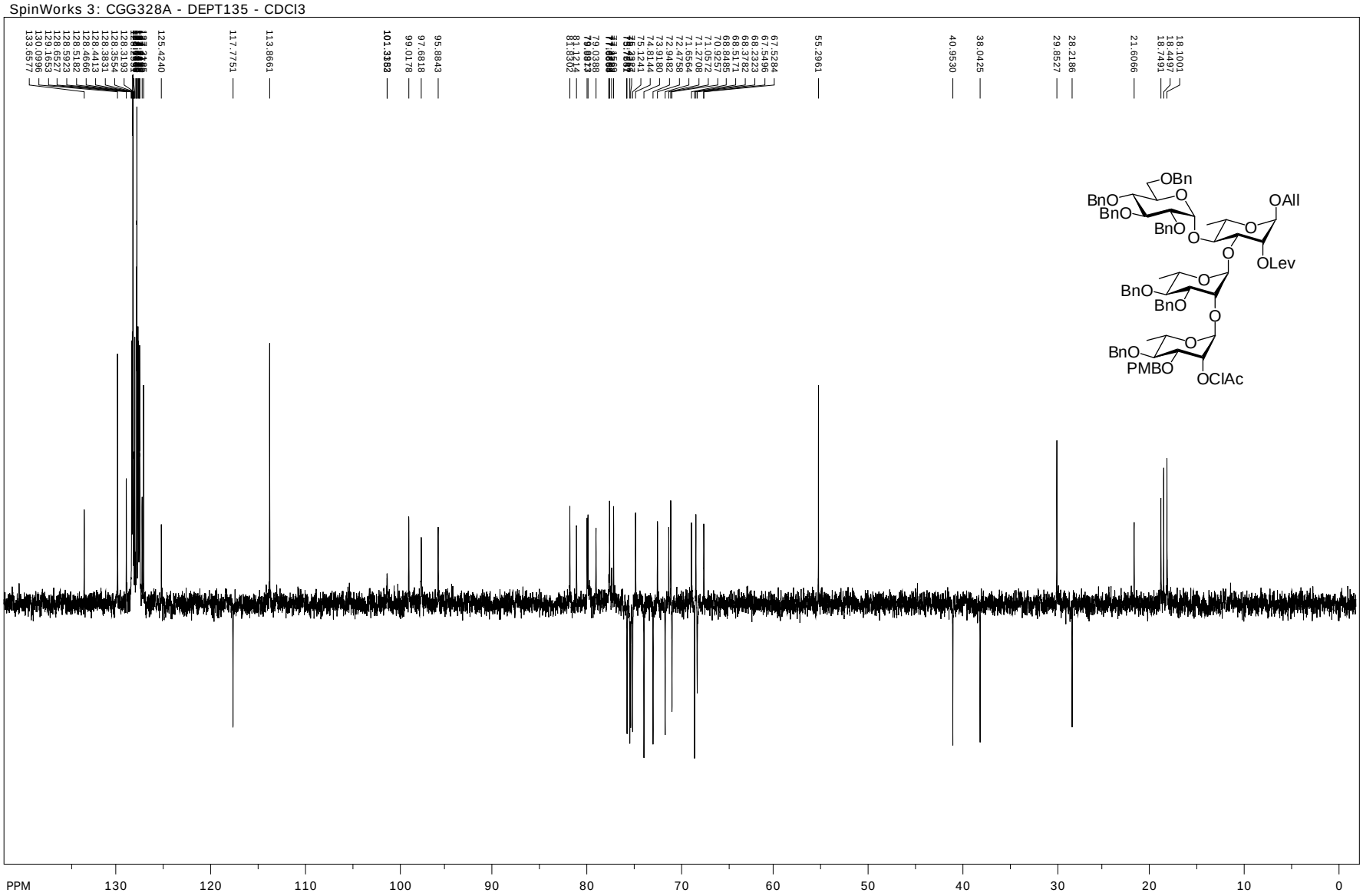

SpinWorks 3: CGG126A
133.7365
132.8711
131.3491
129.8235
129.4324
128.5721
128.4625
128.3907
128.3628
128.2979
128.2670
117.6782
113.8444
99.3096
97.7543
95.9489
81.8279
81.2880
80.3149
79.1303
77.6888
77.3504
75.6776
75.3744
74.7789
73.9145
73.0037
72.5498
71.3815
71.3533
70.9643
70.1269
68.9192
68.5453
68.3482
67.5945
55.2861
53.0627
38.0805
31.0311
29.8018
28.2887
18.7403
18.5938
18.1659
OBn
BnO
BnO
BnO
O
O
OAll
O
OLev
BnO
BnO
O
BnO
PMBO
O
OAZMB
PPM
130
120
110
100
90
80
70
60
50
40
30
20
10
0

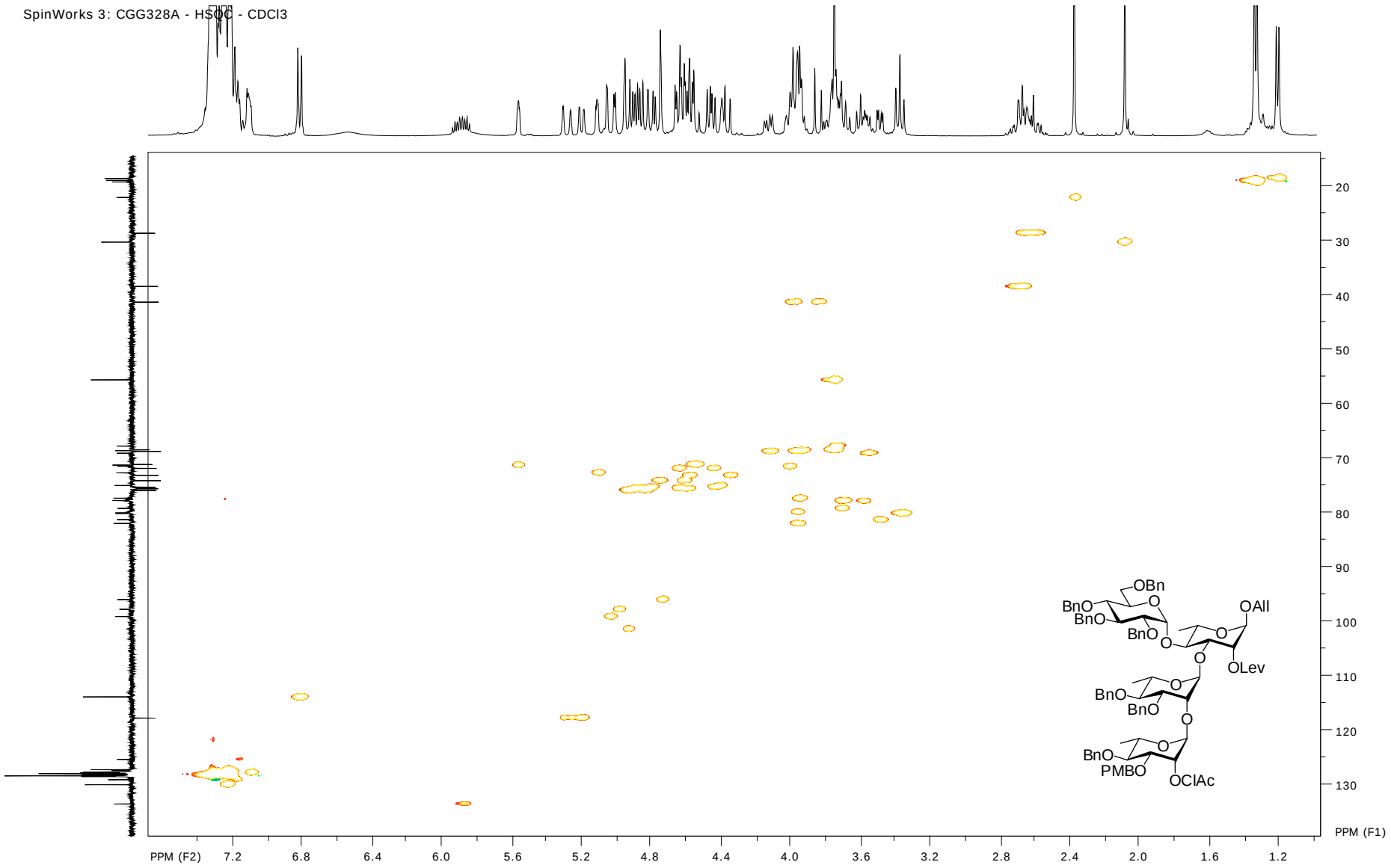

SpinWorks 3: CGG126A
PPM (F2)
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
OAll
O
OLev
BnO
BnO
O
O
BnO
PMBO
O
OAZMB

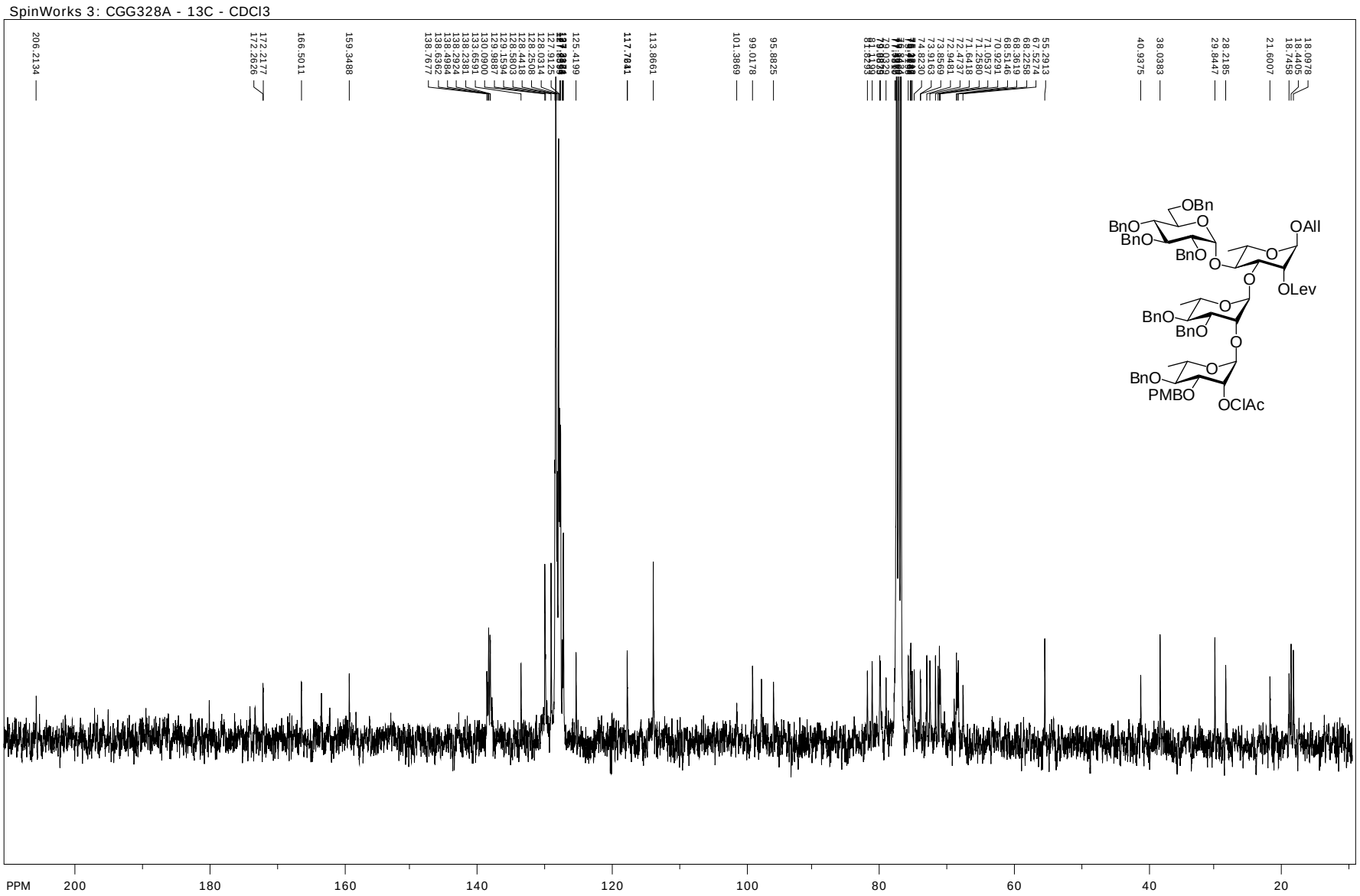

Jun01-2009
CGG126A
OBn
BnO
BnO
BnO
O
OAll
OLev
BnO
BnO
BnO
PMBO
OAZMB
f1 (ppm)

Compound **22**

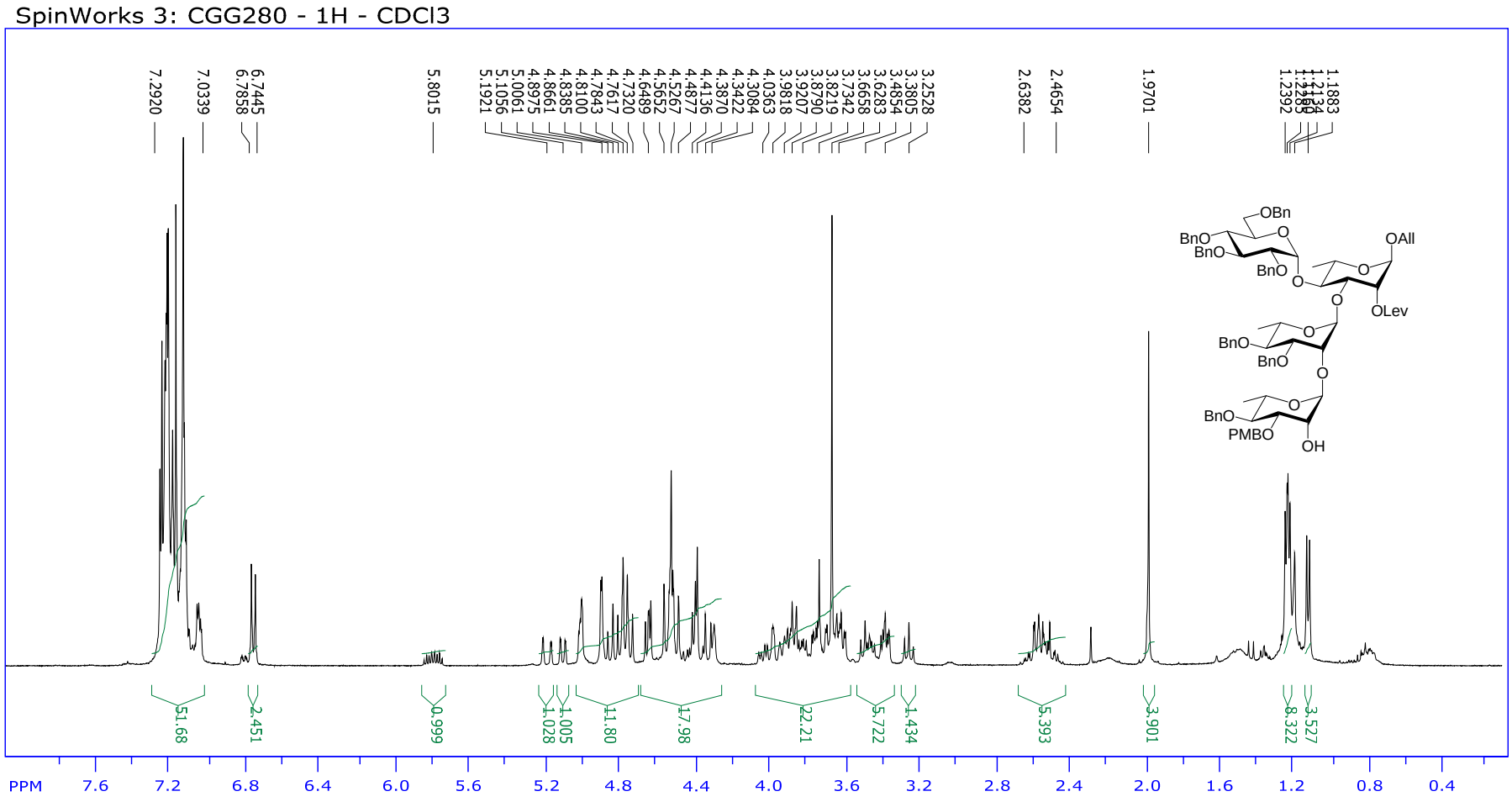

SpinWorks 3: CGG328A - 1H - CDCl3
OBn
BnO
BnO
BnO
OAll
OLev
BnO
BnO
BnO
PMBO
OClAc
7.3768
7.0940
6.8425
6.8024
5.8942
5.5653
5.2854
5.2017
5.1127
5.0575
5.0081
4.9395
4.9004
4.8730
4.8358
4.7834
4.7489
4.6643
4.6356
4.6113
4.5647
4.4617
4.3852
4.1293
4.0370
3.9167
3.8408
3.7860
3.7078
3.7492
3.6268
3.5343
3.4859
3.3720
2.7578
2.5499
2.3696
2.0792
1.3263
1.2006
2.093
1.627
0.954
2.166
1.055
2.122
8.836
7.610
2.190
2.067
1.212
7.380
10.05
2.455
1.094
2.162
4.427
3.019
2.843
6.097
3.000
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0


SpinWorks 3: CGG328A - DEPT135 - CDCl3
OBn
BnO
BnO
BnO
O
OAll
O
O
OLev
BnO
BnO
O
BnO
PMBO
OClAc
PPM
130
120
110
100
90
80
70
60
50
40
30
20
10
0

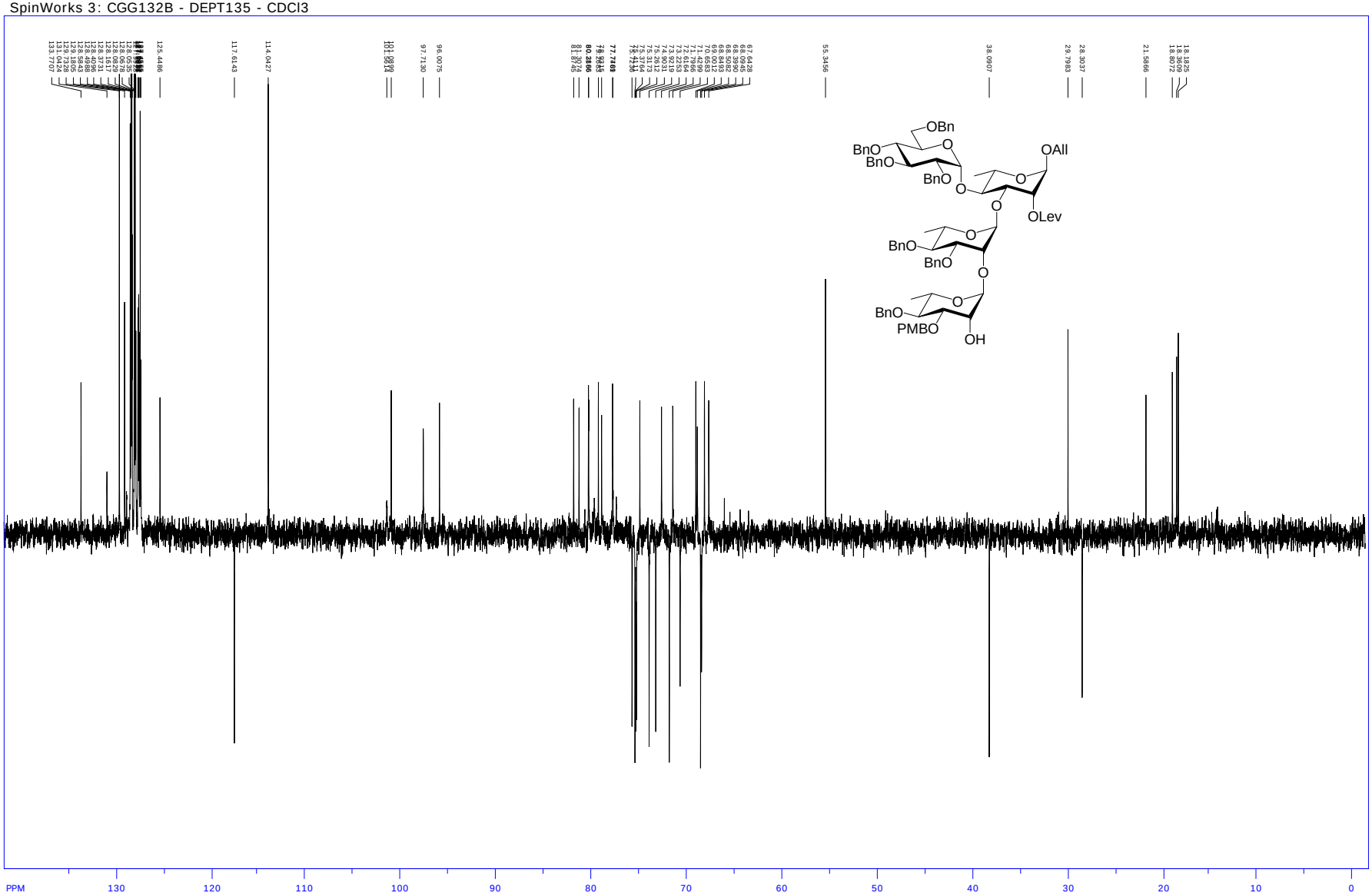

SpinWorks 3: CGG328A - HSQC - CDCl3
PPM (F2)
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
OAll
O
OLev
BnO
BnO
O
O
BnO
PMBO
OClAc

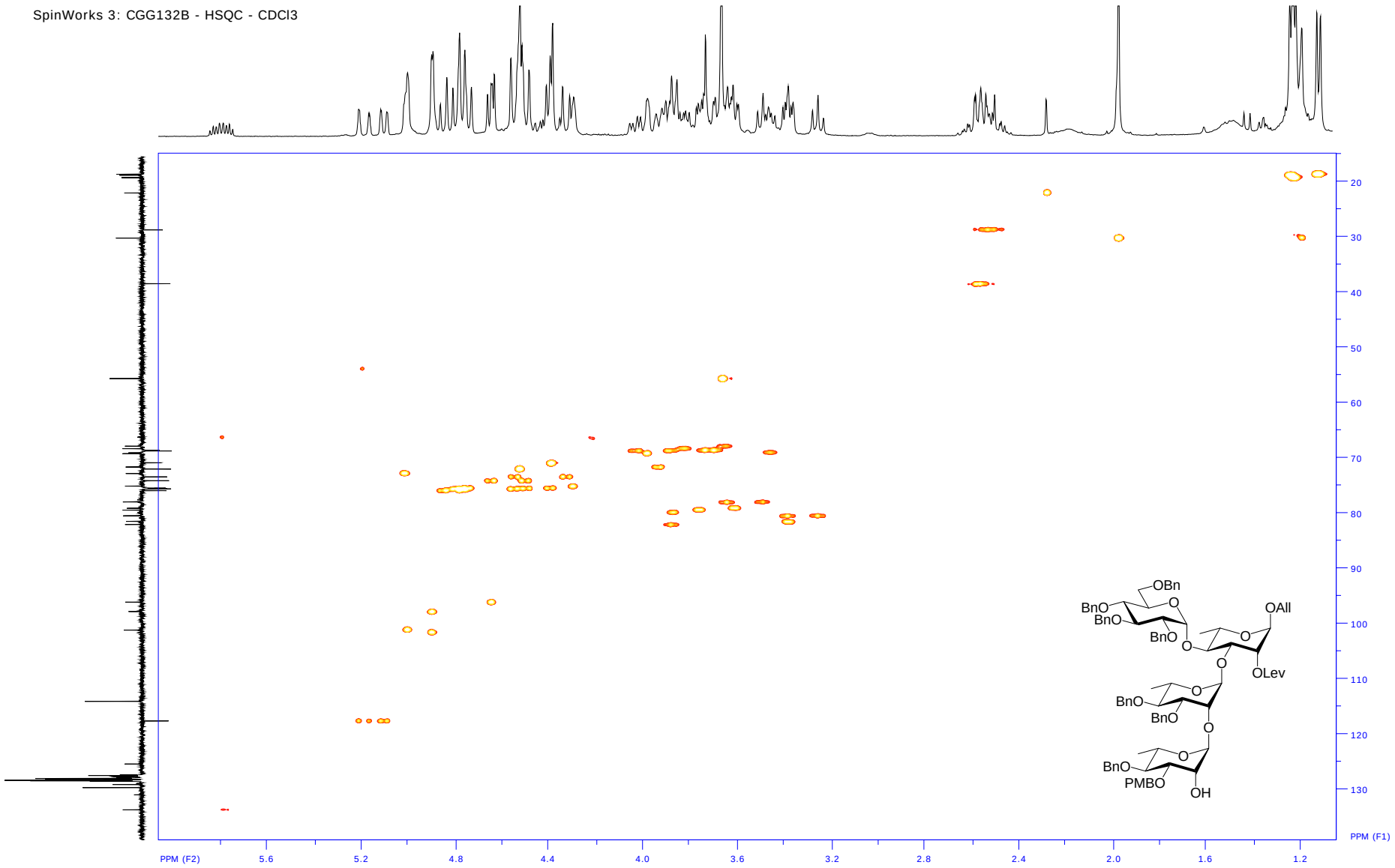

SpinWorks 3: CGG328A - 13C - CDCl3
206.2134
172.2177
172.2626
166.5011
159.3488
138.7677
138.6362
138.4984
138.4744
138.2381
133.6591
130.0900
129.9887
129.1594
128.5803
128.4418
128.0314
127.9125
125.4199
117.7841
113.8661
101.3869
99.0178
95.8825
81.8199
74.8230
73.9163
73.8569
72.9481
72.4777
71.6418
71.2580
71.0537
70.9291
68.5146
68.3619
68.2258
67.5274
55.2913
40.9375
38.0383
29.8447
28.2185
21.6007
18.7458
18.4405
18.0978
OBn
BnO
BnO
BnO
O
O
OAll
O
OLev
BnO
BnO
O
BnO
PMBO
OClAc
PPM
200
180
160
140
120
100
80
60
40
20

Compound **10**

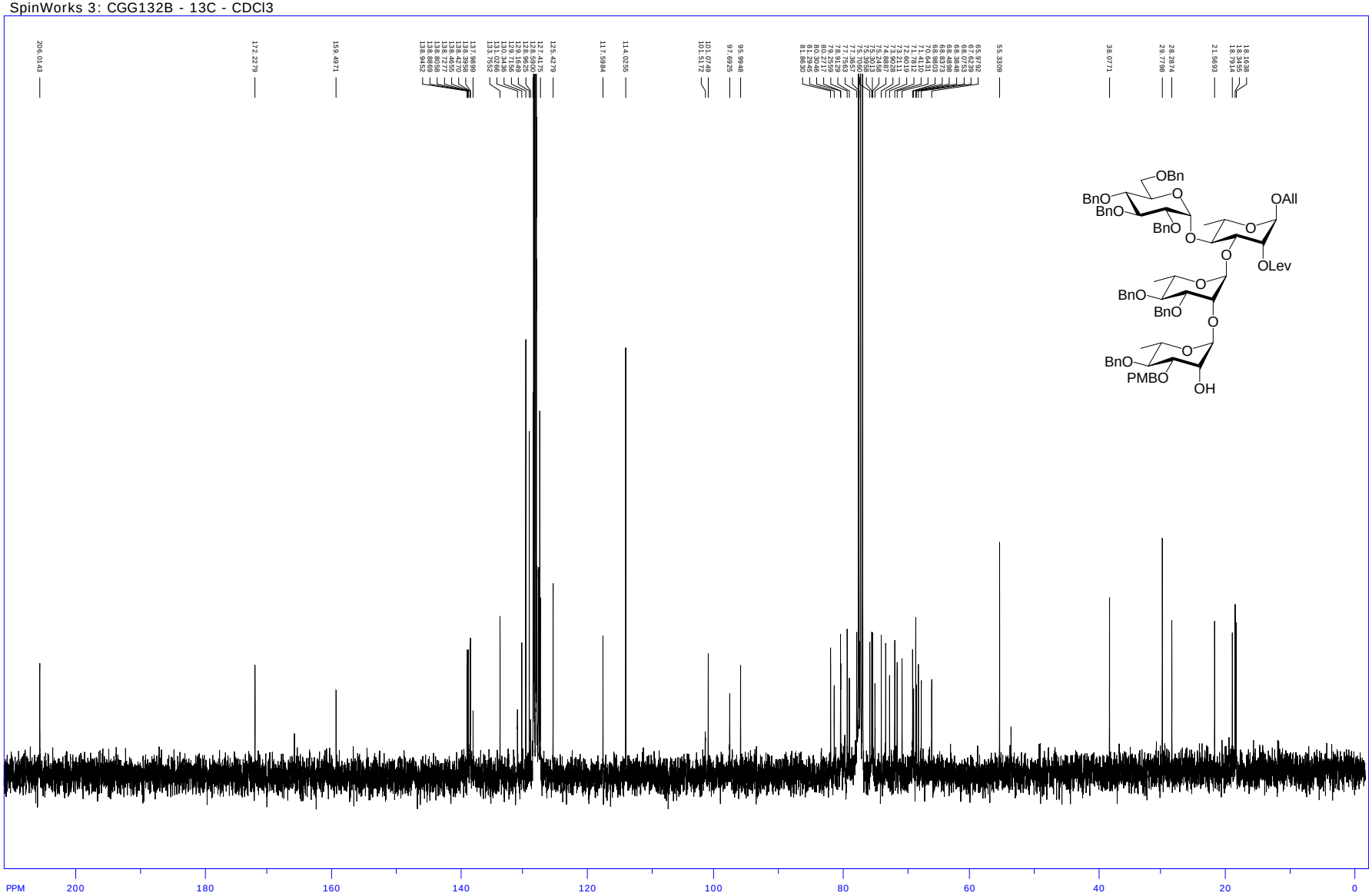

SpinWorks 3: CGG280 - 1H - CDCl3
7.2920
7.0339
6.7445
6.7858
5.8015
5.1921
5.1056
5.0061
4.8975
4.8661
4.8385
4.8100
4.7843
4.7617
4.7320
4.6489
4.5652
4.5267
4.4877
4.4136
4.3870
4.3422
4.3084
4.0363
3.9818
3.9207
3.8790
3.8219
3.7342
3.6658
3.6283
3.4854
3.3805
3.2528
2.6382
2.4654
1.9701
1.2392
1.1883
OBn
BnO
BnO
O
BnO
O
OAll
O
OLev
BnO
BnO
O
BnO
PMBO
O
OH
1.68
2.451
0.999
1.028
1.005
1.80
7.98
22.21
5.722
1.434
5.393
3.901
8.322
3.527
PPM
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4

SpinWorks 3: CGG132B - DEPT135 - CDCl3

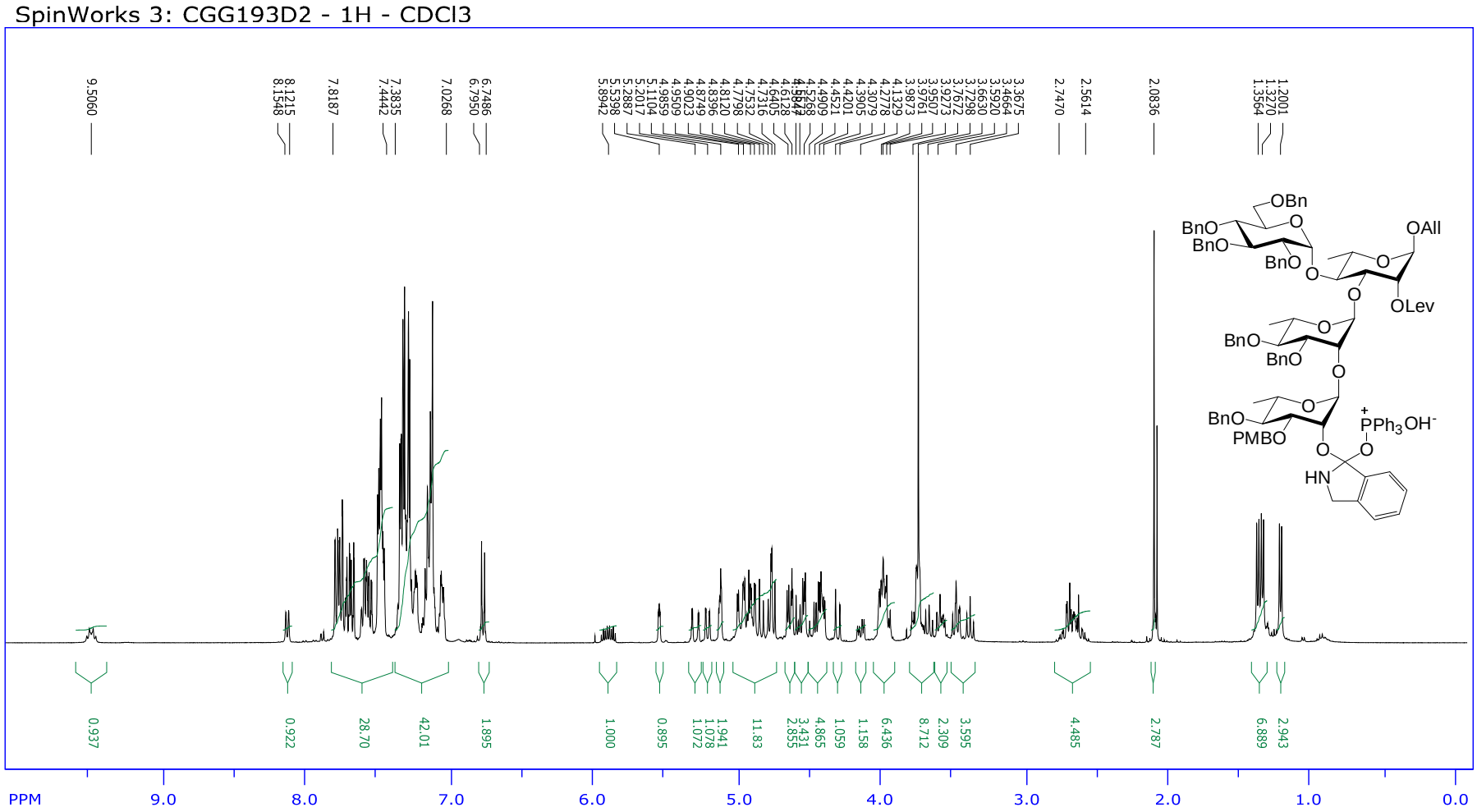



SpinWorks 3: CGG132B - HSQC - CDCl3
PPM (F2)
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
OAll
O
OLev
BnO
BnO
O
O
BnO
PMBO
O
OH

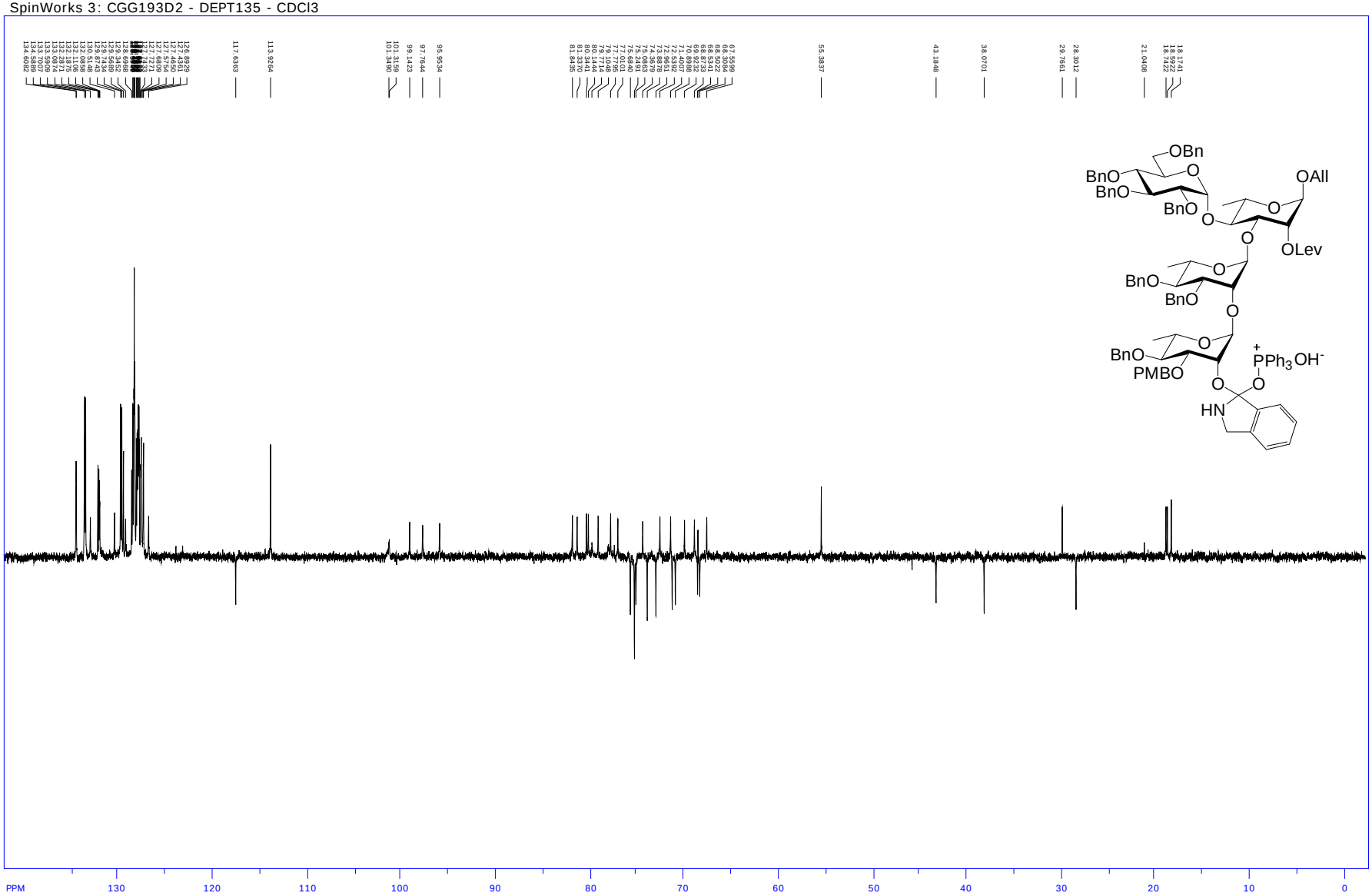
SpinWorks 3: CGG132B - 13C - CDCl3

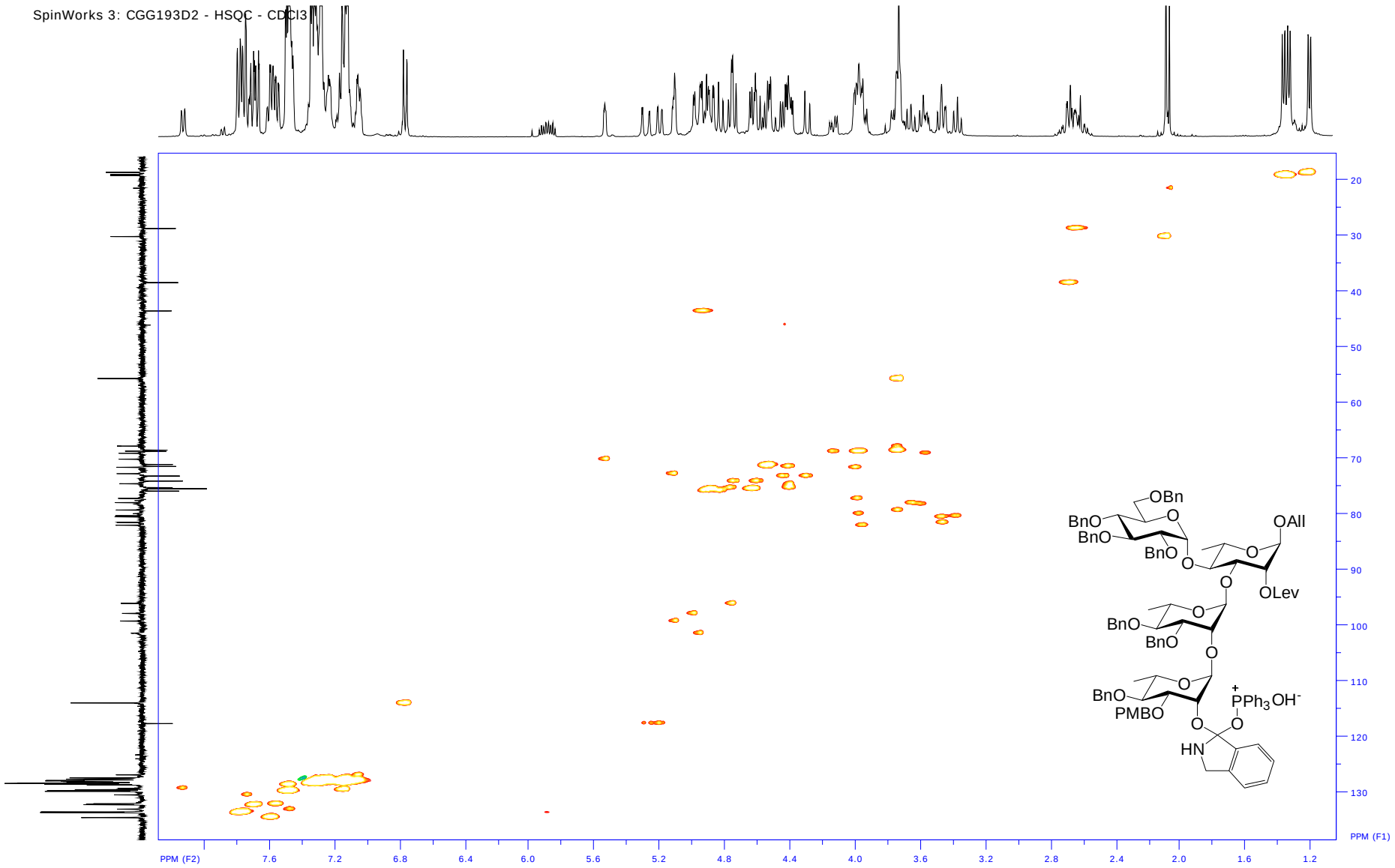


Compound **21a**

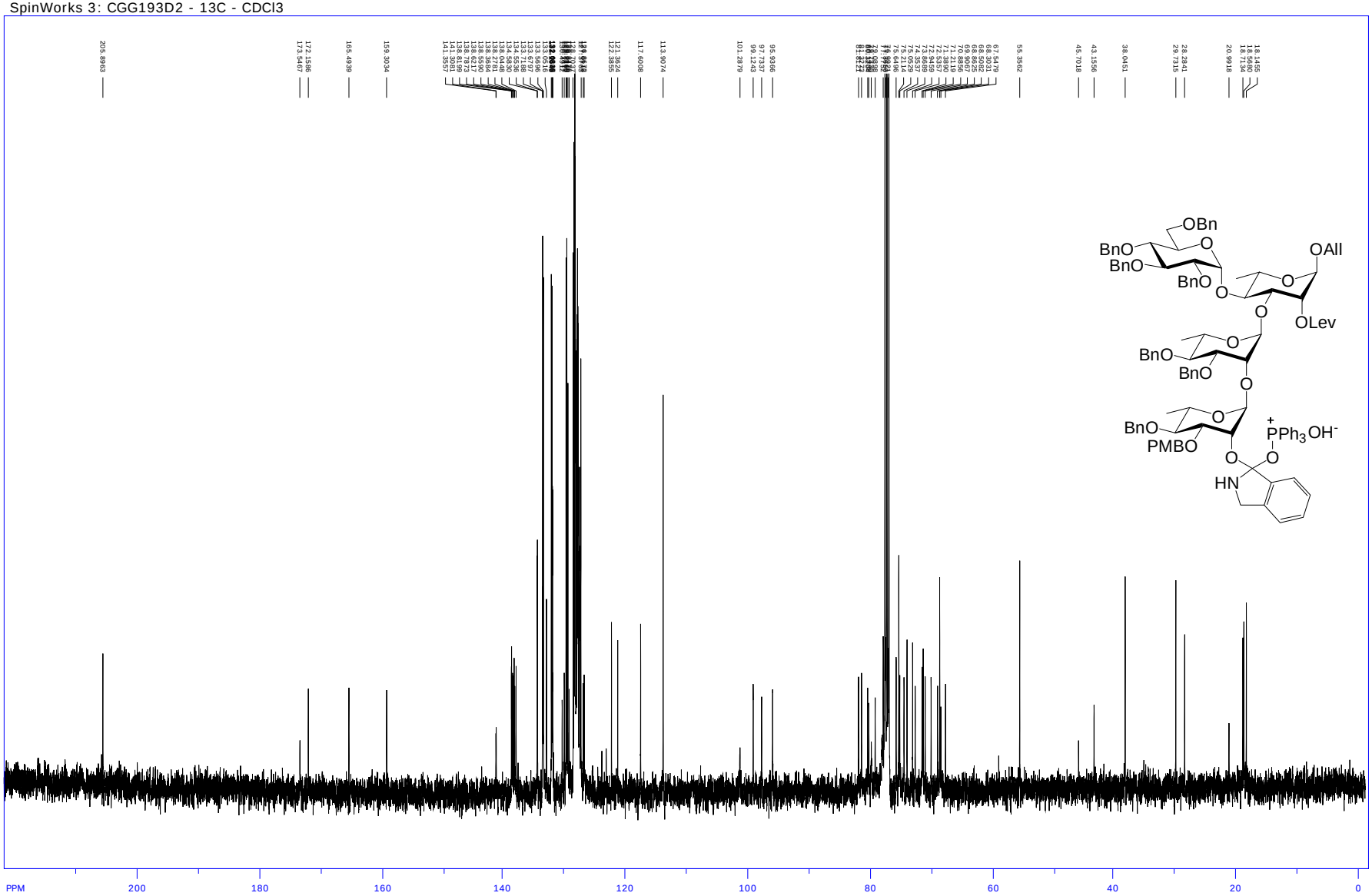


SpinWorks 3: CGG193D2 - DEPT135 - CDCl3

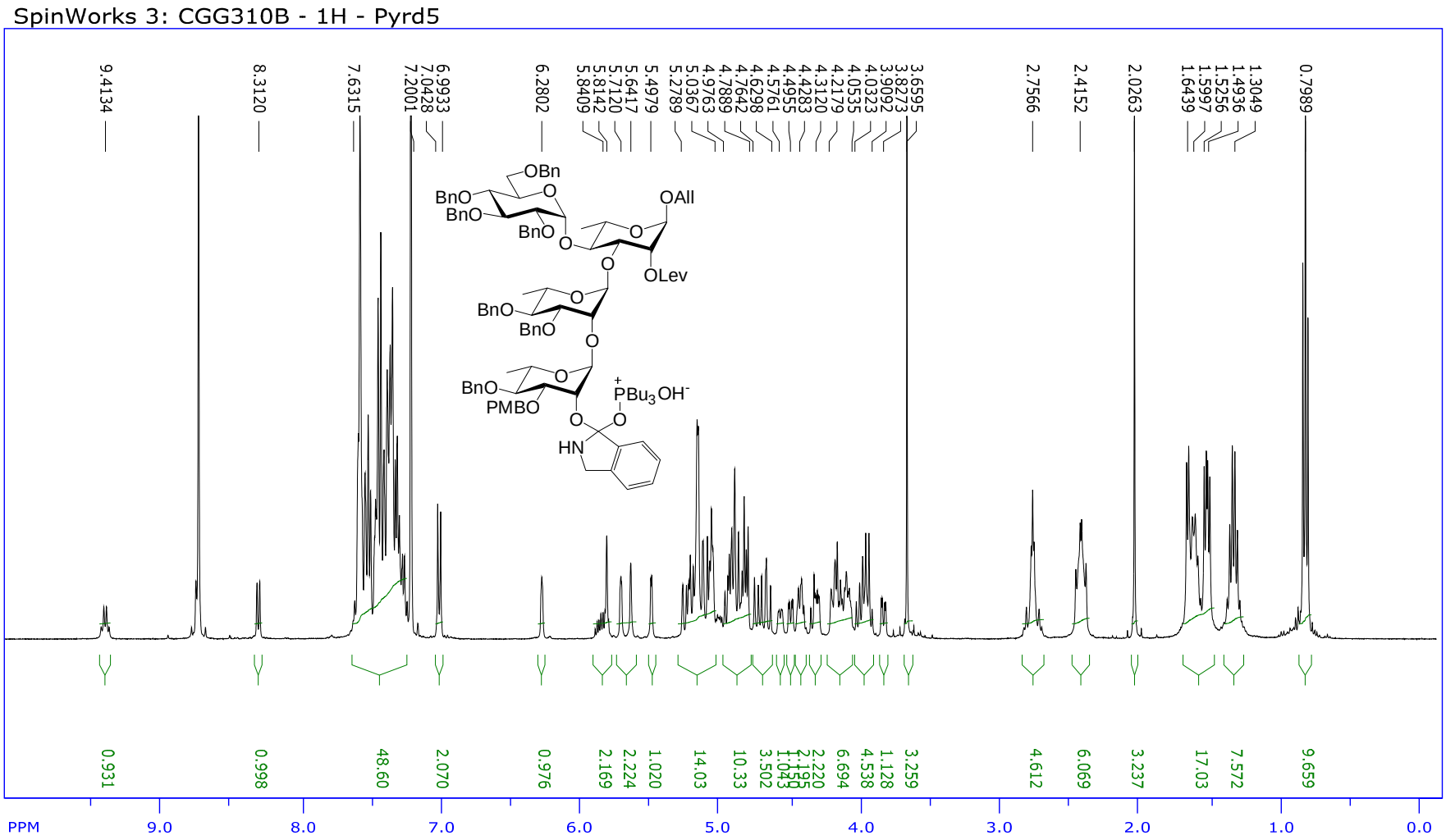


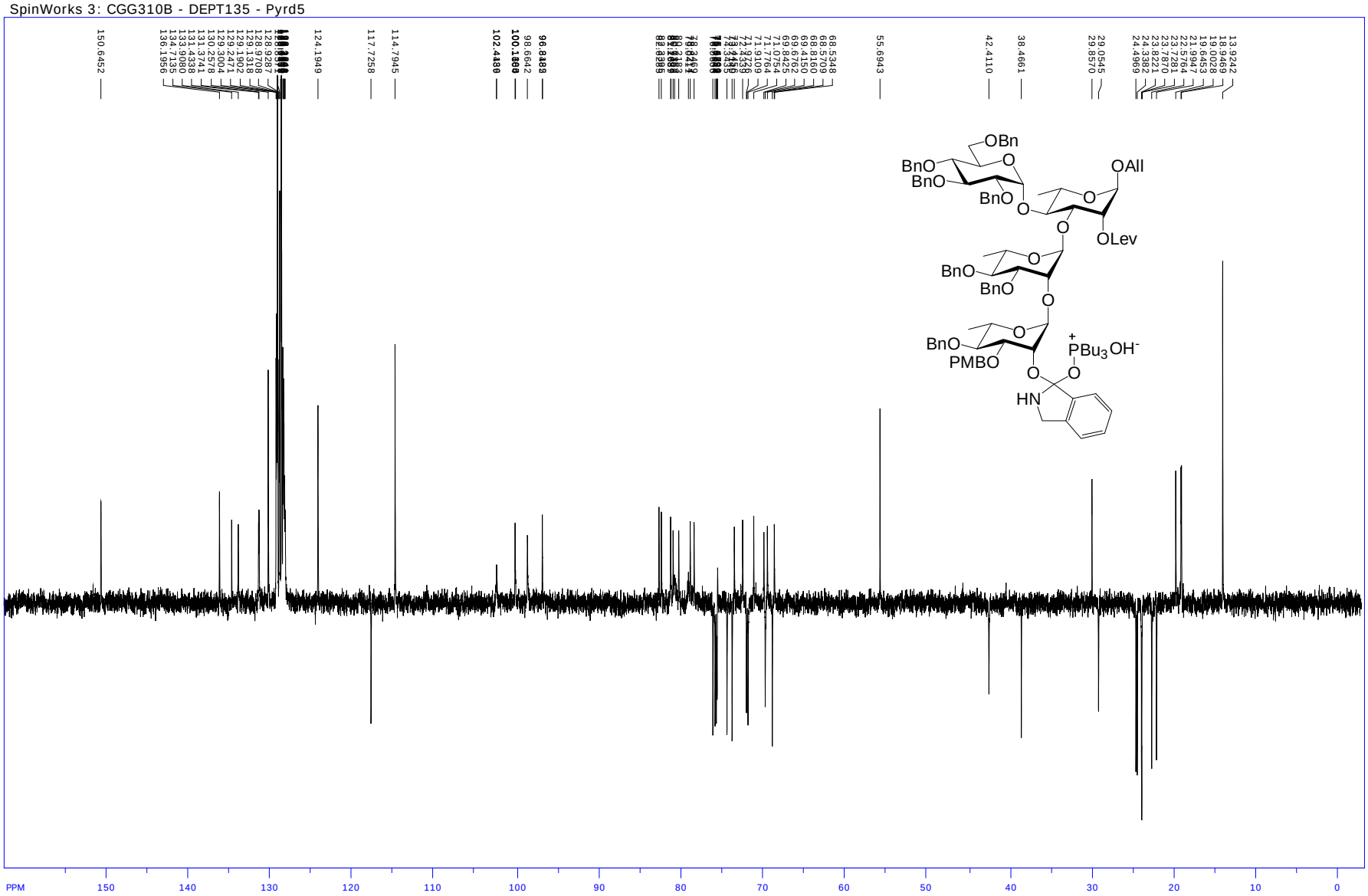

SpinWorks 3: CGG193D2 - HSQC - CDCl3
PPM (F2)
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
OAll
OLev
BnO
BnO
O
BnO
PMBO
O
O
PPh3OH-
HN

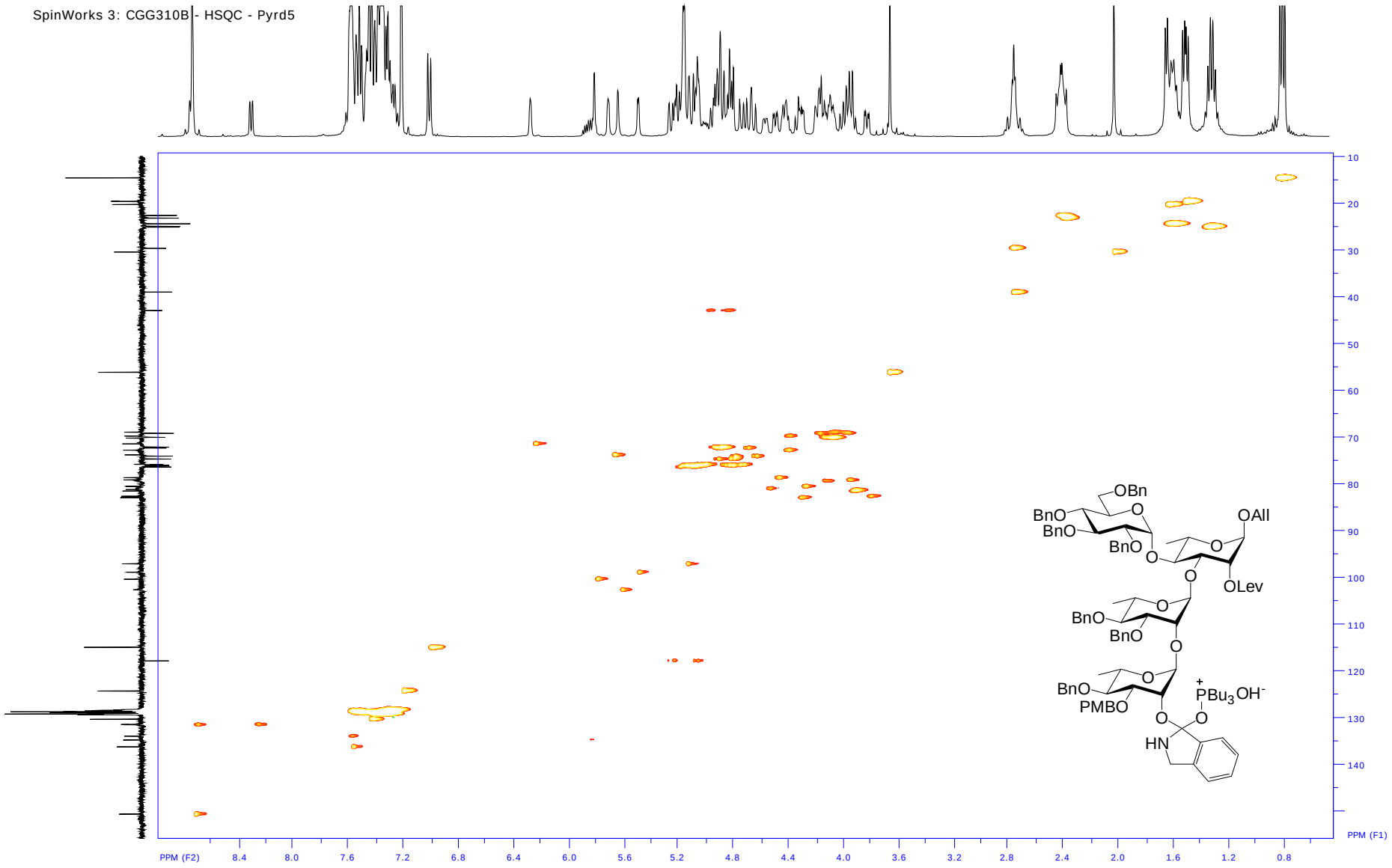
SpinWorks 3: CGG193D2 - 13C - CDCl3

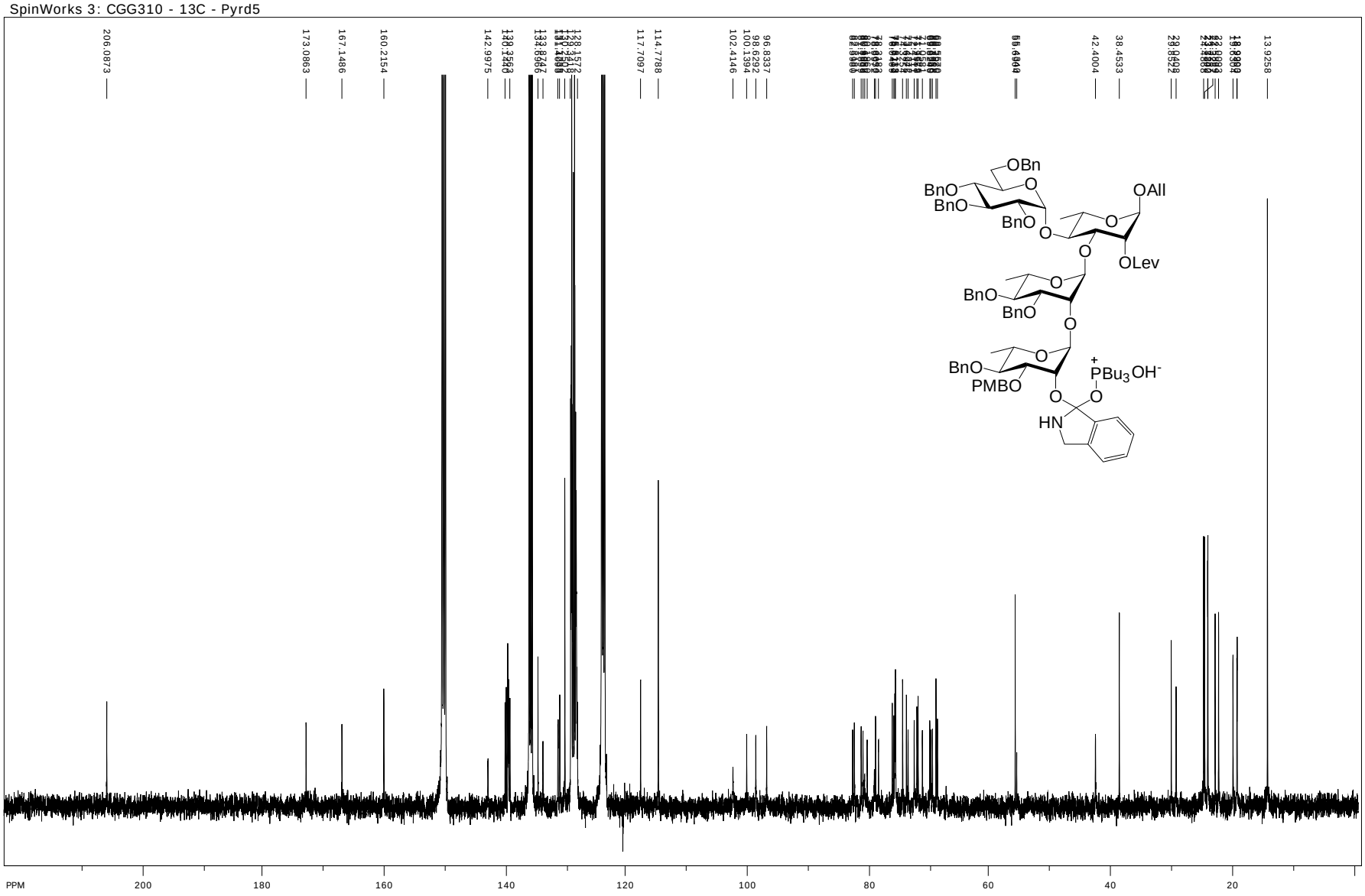


Compound **21b**

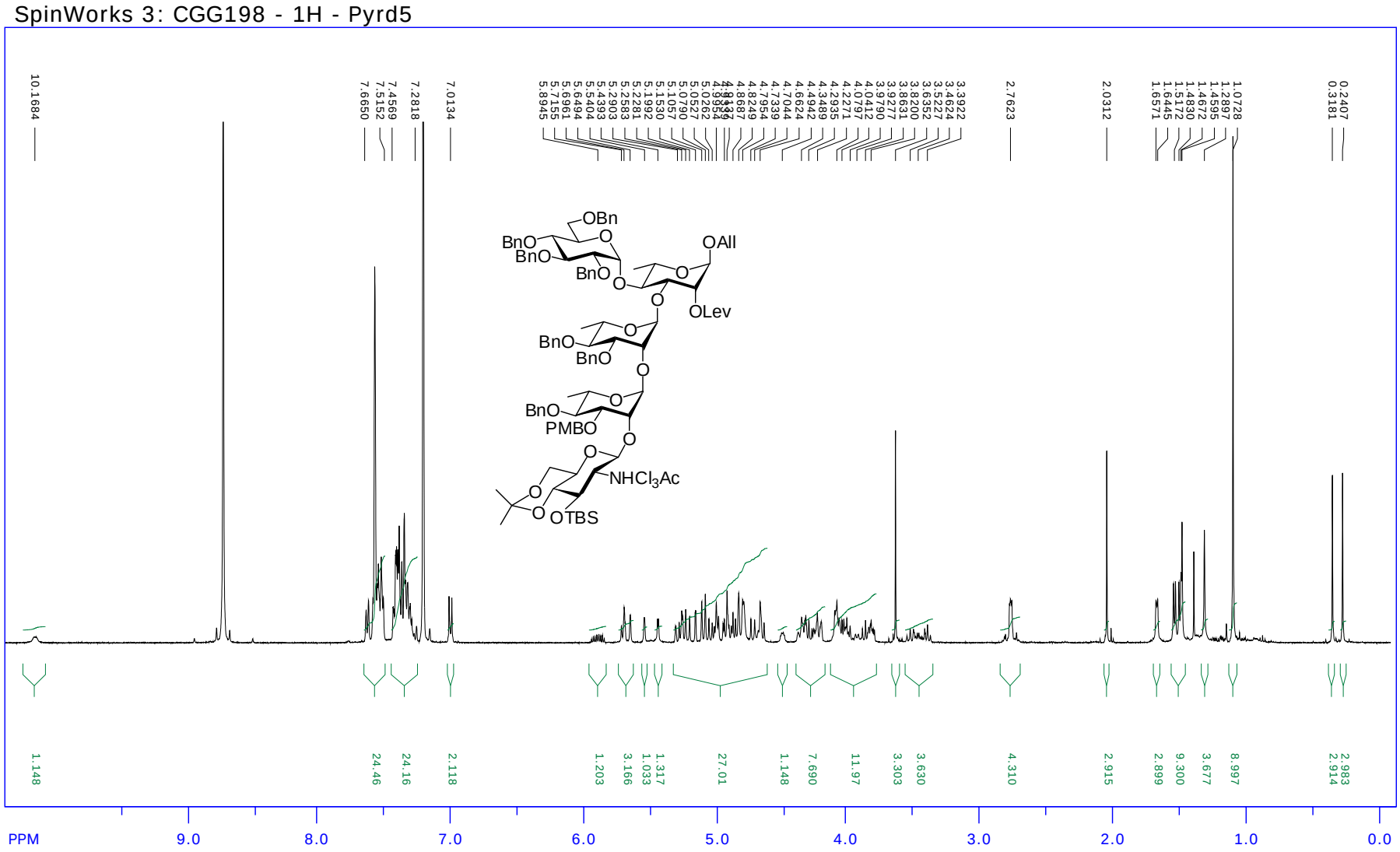



SpinWorks 3: CGG310B - DEPT135 - Pyrd5
150.6452
136.1956
134.7135
133.9080
131.4338
131.3741
130.2578
129.2471
129.1902
129.1318
128.9708
128.9287
124.1949
117.7258
114.7945
102.4480
100.1808
98.6642
96.8483
68.5348
68.5709
68.8160
69.4150
69.6762
69.8425
71.0754
71.1764
71.1009
71.9226
72.4359
55.6943
42.4110
38.4661
29.0545
28.8570
24.4969
24.3382
23.8221
23.7281
22.5764
21.9947
19.6453
19.0028
18.9469
13.9242
OBn
BnO
BnO
BnO
O
O
OAll
O
OLev
BnO
BnO
O
BnO
PMBO
O
O
HN
+
PBu3 OH-
PPM
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

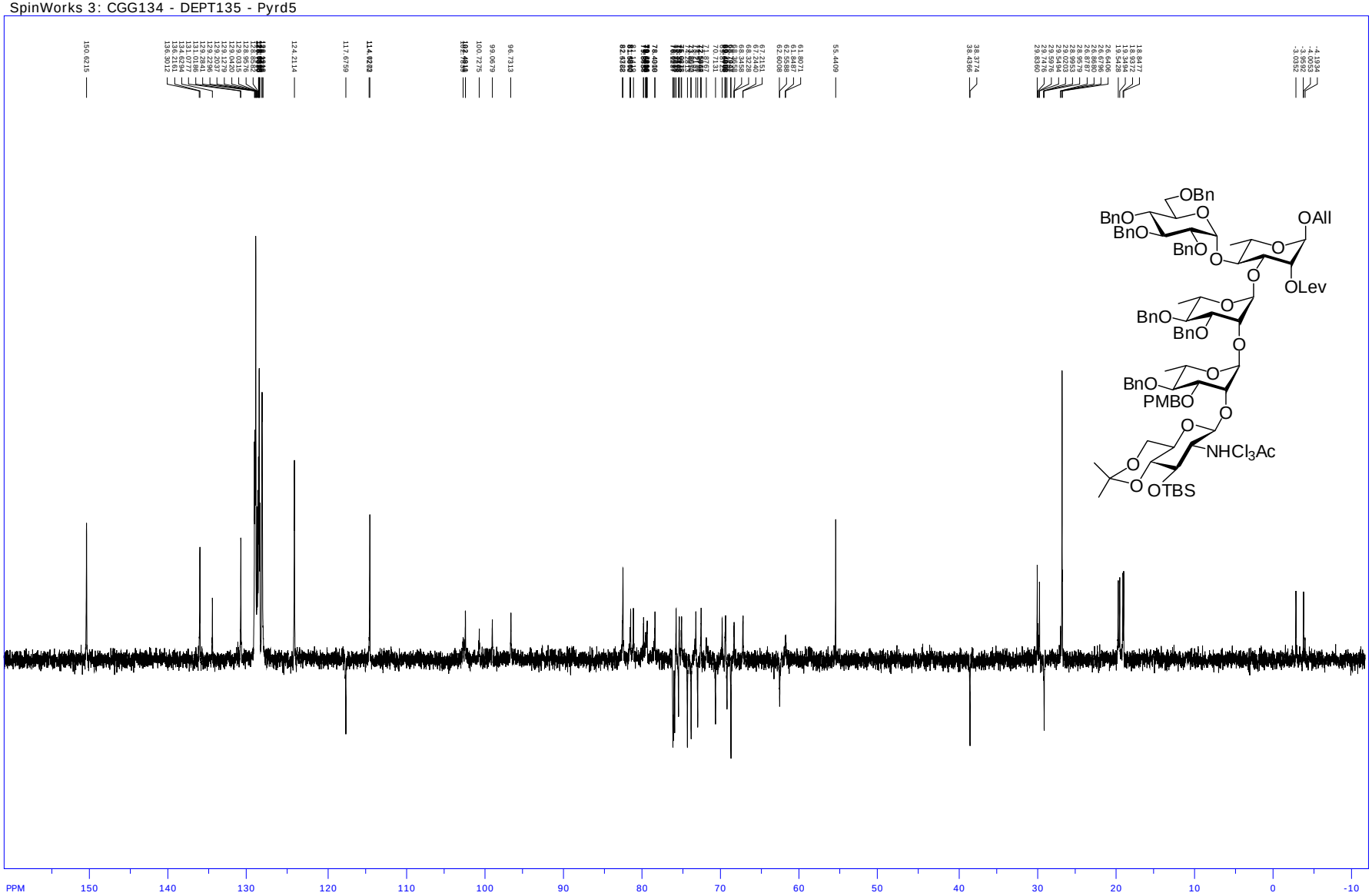

SpinWorks 3: CGG310B - HSQC - Pyrd5
PPM (F2)
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
PPM (F1)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
OBn
BnO
BnO
BnO
O
O
OAll
O
OLev
BnO
BnO
O
BnO
PMBO
O
O
+
PBu3 OH-
HN

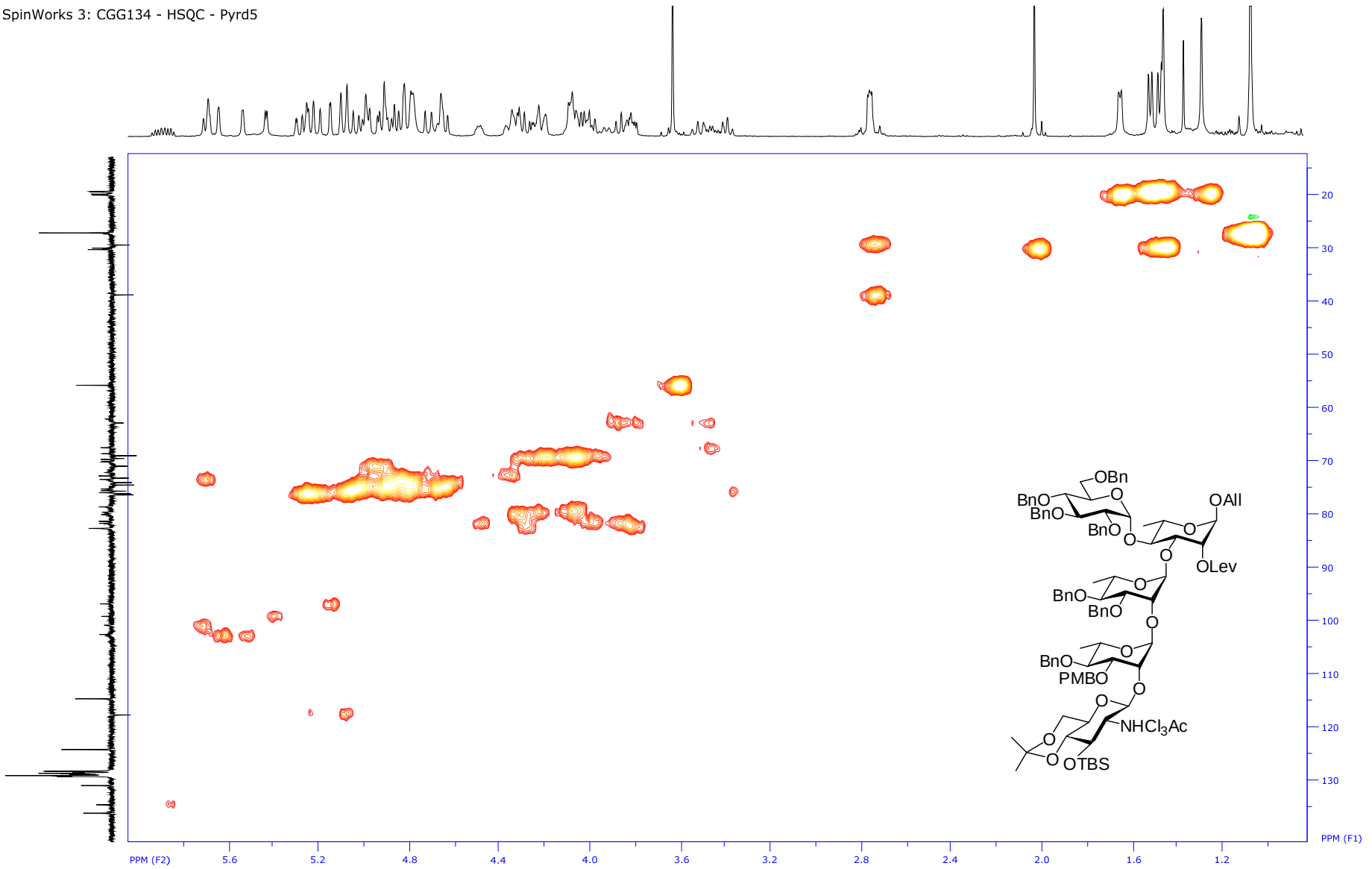

SpinWorks 3: CGG310 - 13C - Pyrd5
206.0873
173.0863
167.1486
160.2154
142.9975
114.7788
117.7097
102.4146
96.8337
55.4904
42.4004
38.4533
29.8928
13.9258
OBn
BnO
BnO
BnO
O
OAll
OLev
PMBO
PBu_3OH^-
HN
PPM
200
180
160
140
120
100
80
60
40
20

Compound **27**

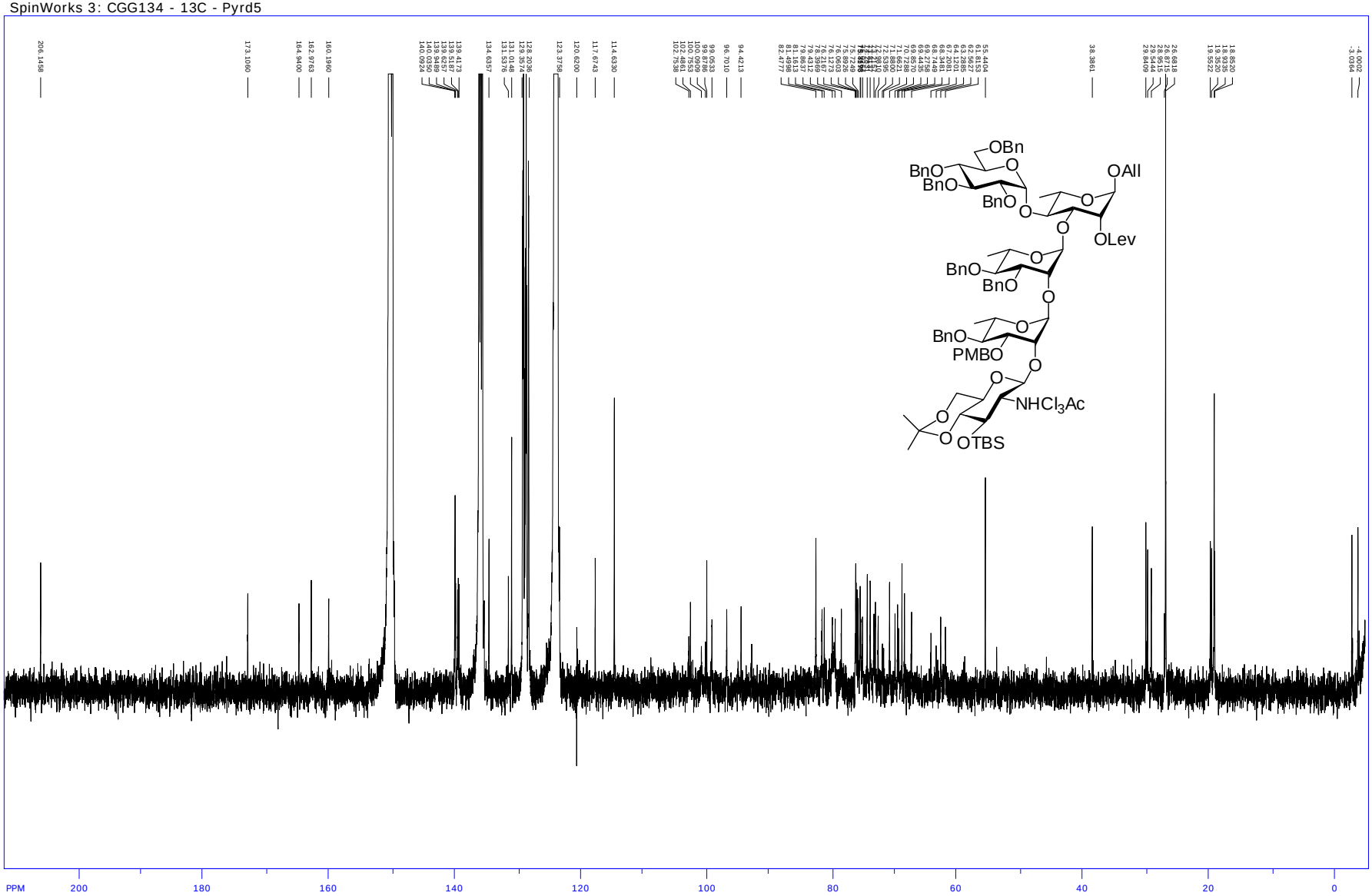

SpinWorks 3: CGG198 - 1H - Pyrd5
OBn
BnO
BnO
BnO
OAll
OLev
BnO
BnO
BnO
PMBO
NHCl3Ac
OTBS
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

SpinWorks 3: CGG134 - DEPT135 - Pyrd5

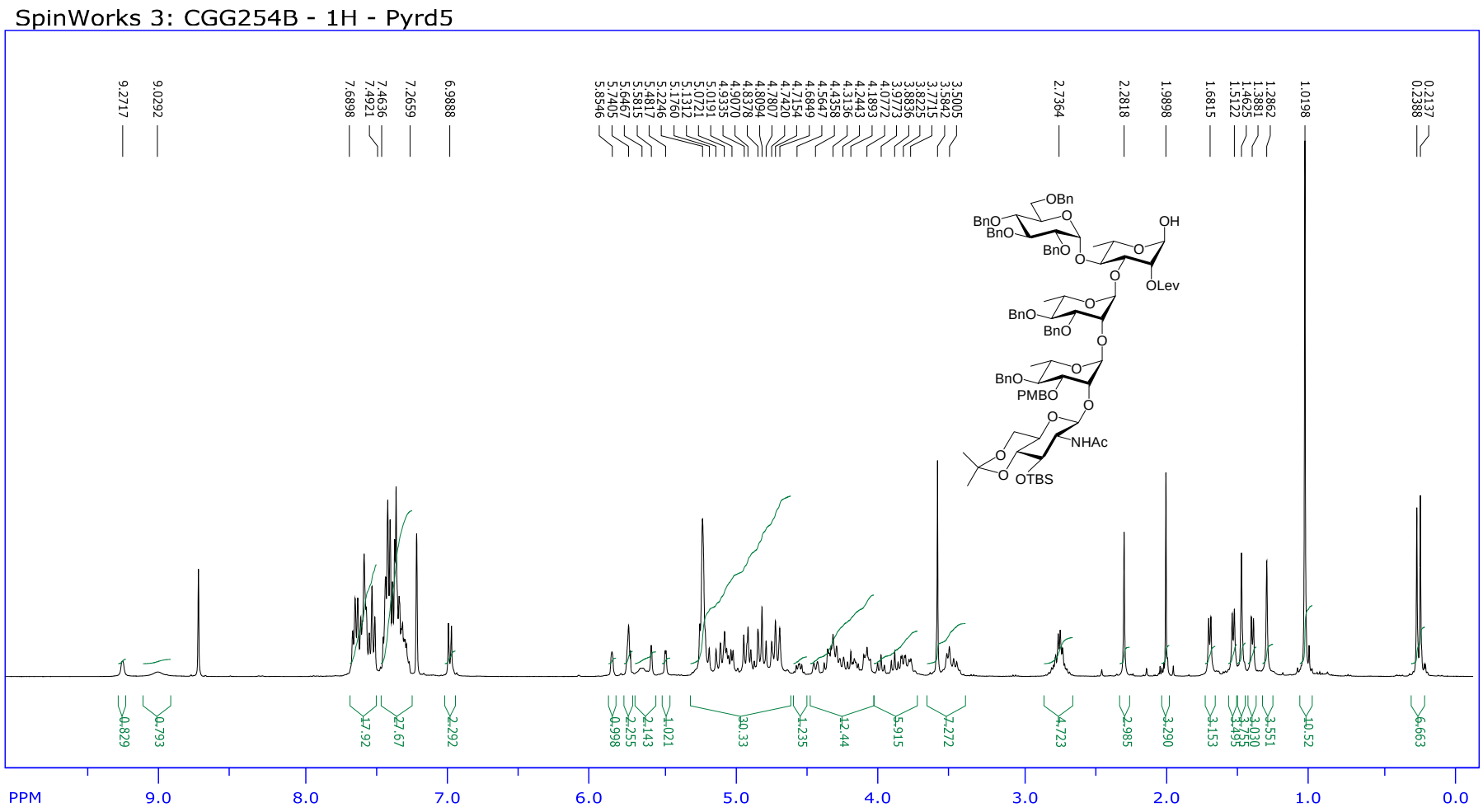



SpinWorks 3: CGG134 - HSQC - Pyrd5
PPM (F2)
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
OAll
O
OLev
BnO
BnO
O
BnO
PMBO
O
O
NHCl3Ac
O
O
OTBS

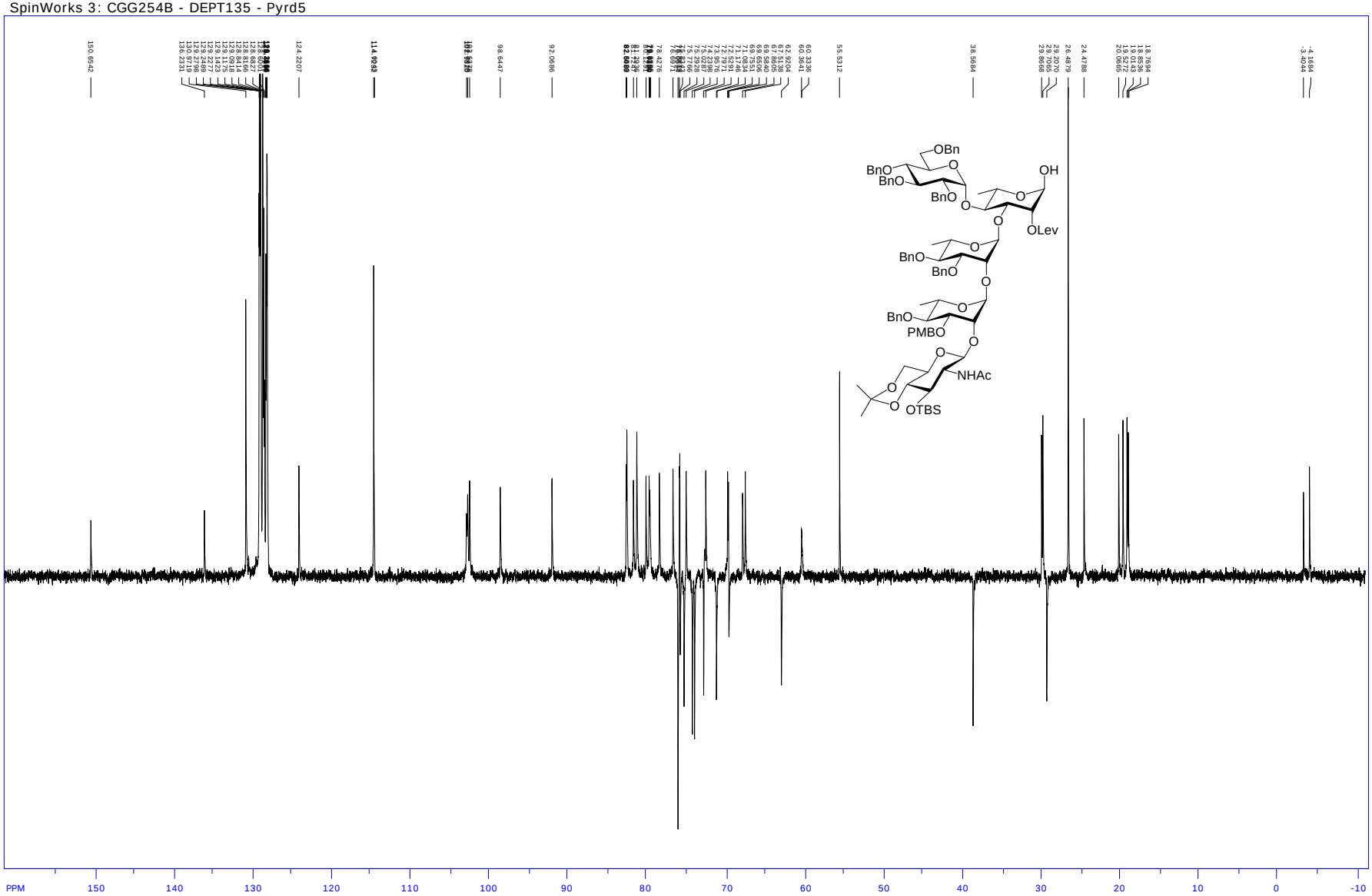
SpinWorks 3: CGG134 - 13C - Pyrd5

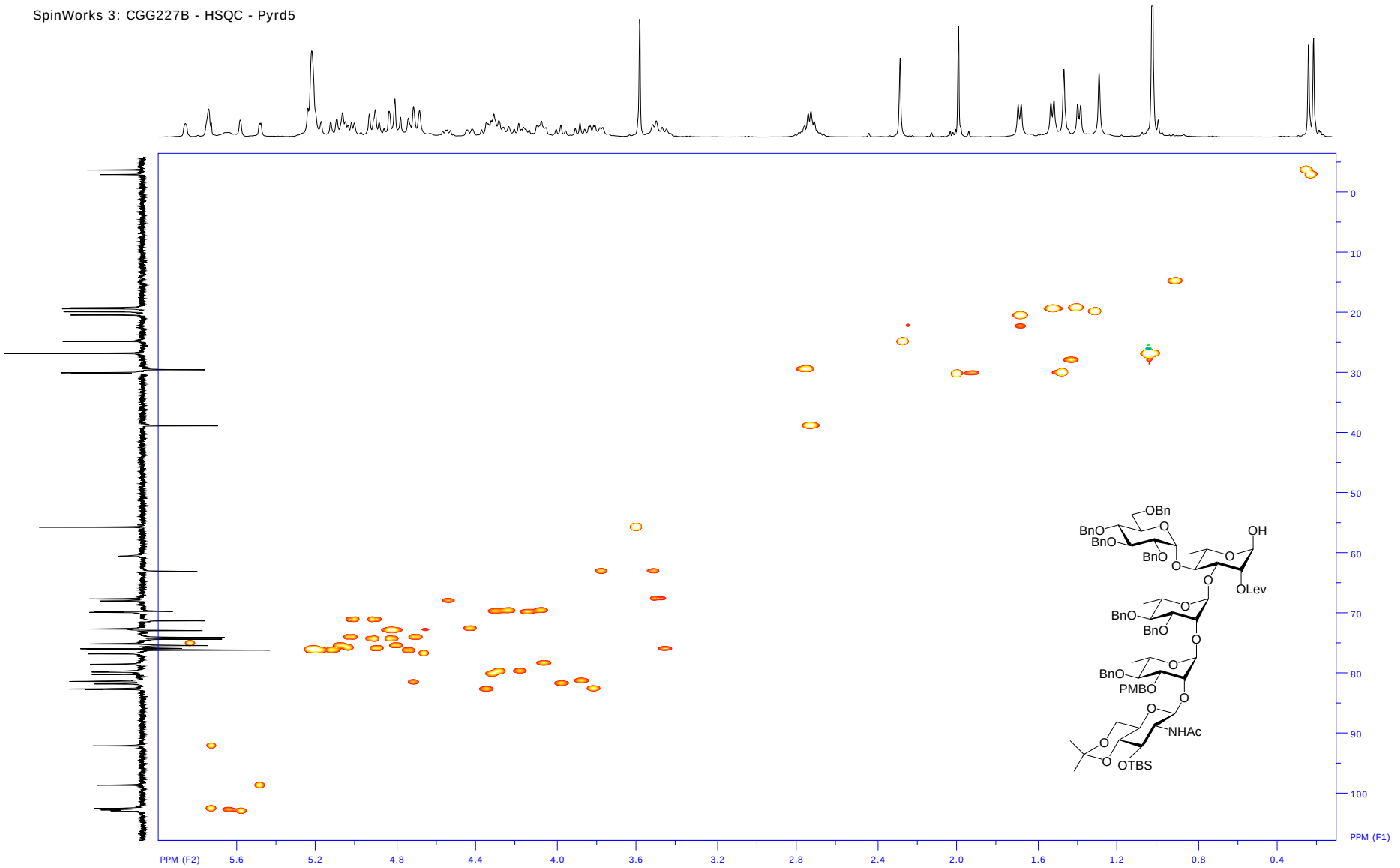


Compound **29**

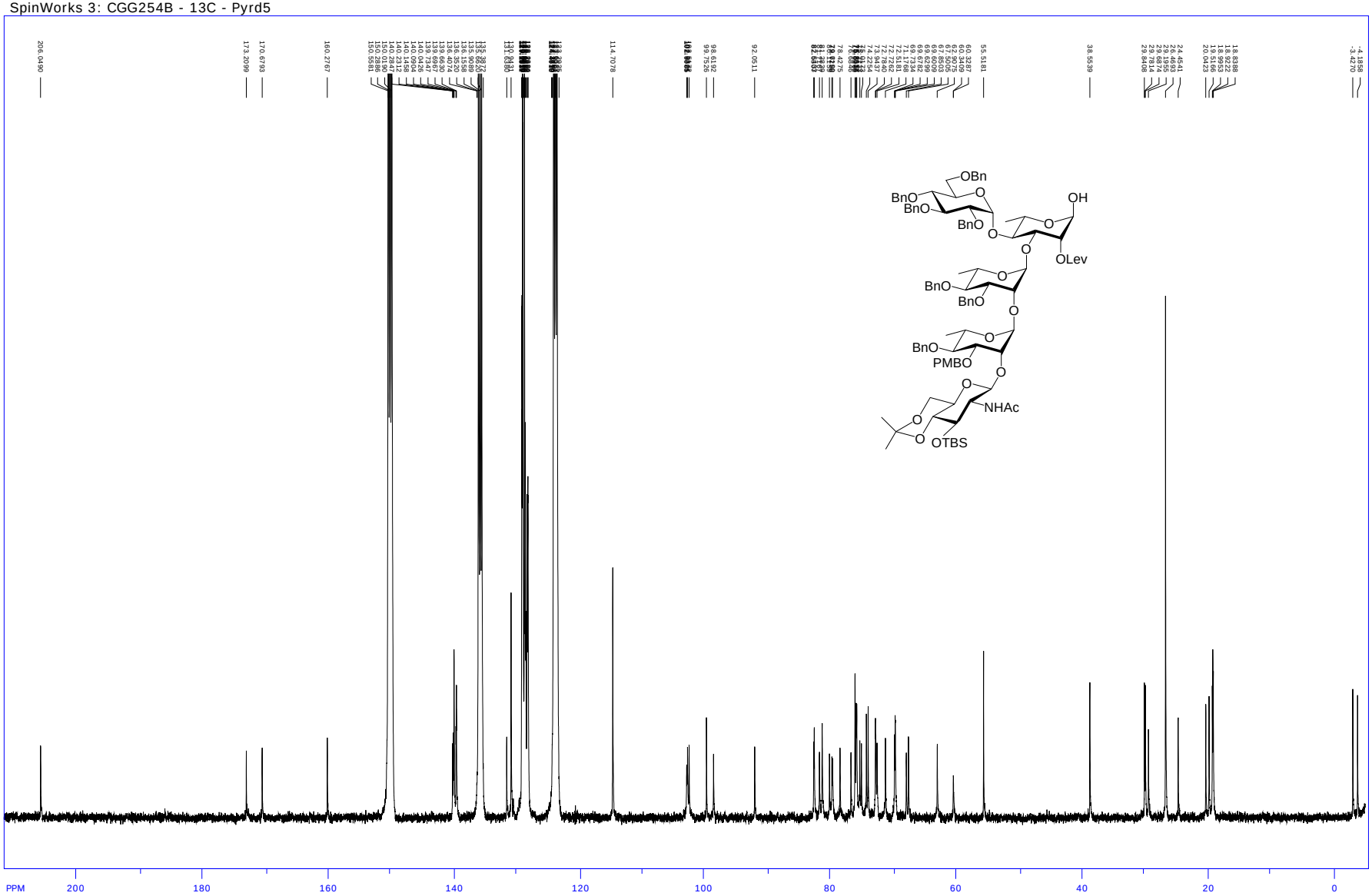

SpinWorks 3: CGG254B - 1H - Pyrd5
9.2717
9.0292
7.6898
7.4636
7.4921
7.2659
6.9888
5.8546
5.7405
5.6467
5.5815
5.4817
5.2246
5.1760
5.1312
5.0721
5.0191
4.9335
4.9070
4.8378
4.8094
4.7807
4.7420
4.7154
4.6849
4.5647
4.4358
4.3136
4.2443
4.1893
4.0772
3.9773
3.8836
3.8225
3.7715
3.5842
3.5005
2.7364
2.2818
1.9898
1.6815
1.5122
1.4625
1.3881
1.2862
1.0198
0.2388
0.2137
OBn
BnO
BnO
BnO
OH
OLev
PMBO
NHAc
OTBS
0.829
0.793
17.92
27.67
2.292
0.998
2.255
2.143
1.021
30.33
1.235
12.44
5.915
7.272
4.723
2.985
3.290
3.153
3.495
3.030
3.551
10.52
6.663
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

SpinWorks 3: CGG254B - DEPT135 - Pyrd5

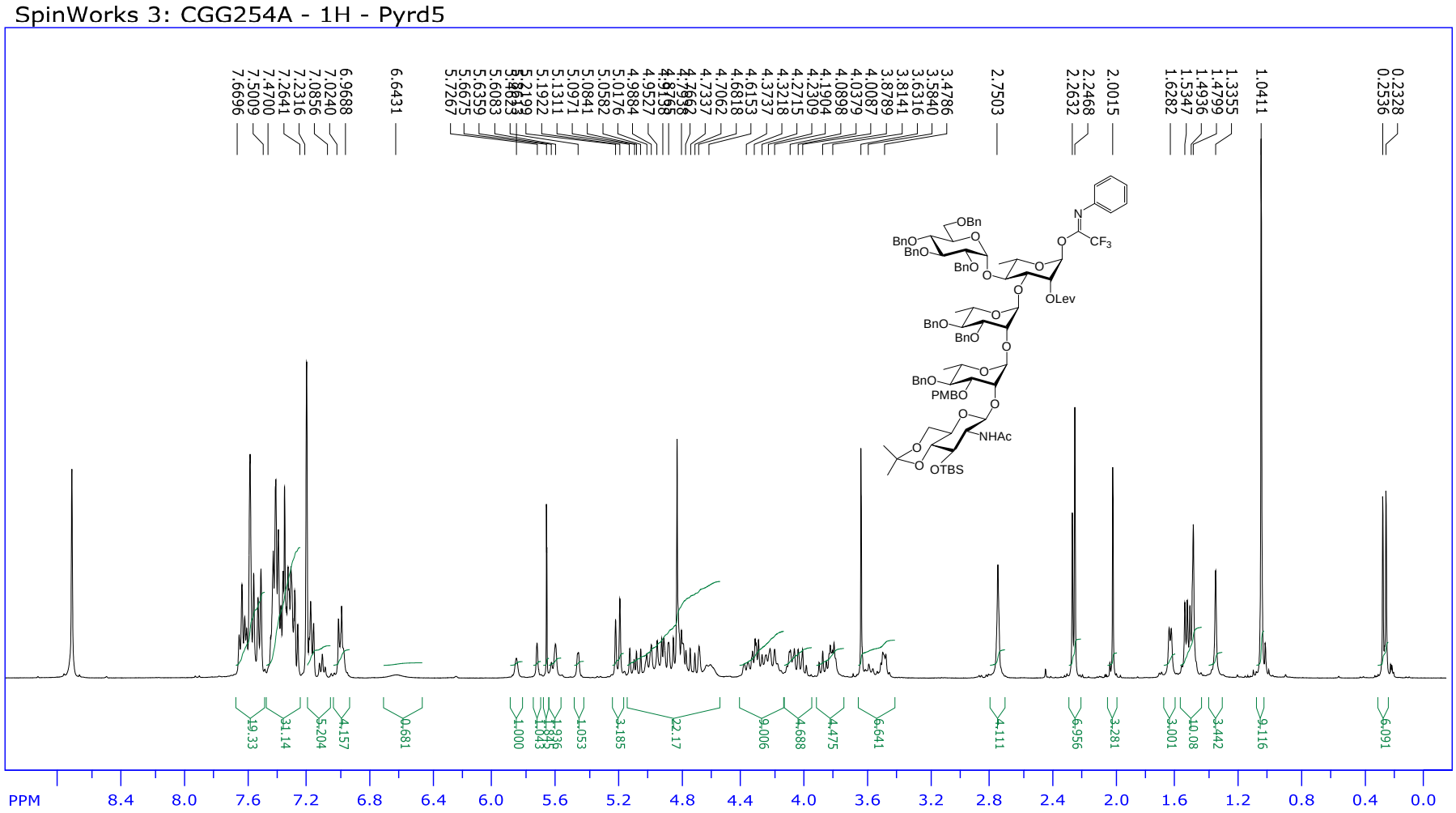



SpinWorks 3: CGG227B - HSQC - Pyrd5
PPM (F2)
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
PPM (F1)
0
10
20
30
40
50
60
70
80
90
100
OBn
BnO
BnO
BnO
O
O
OH
O
OLev
BnO
BnO
O
BnO
PMBO
O
O
NHAc
O
O
OTBS

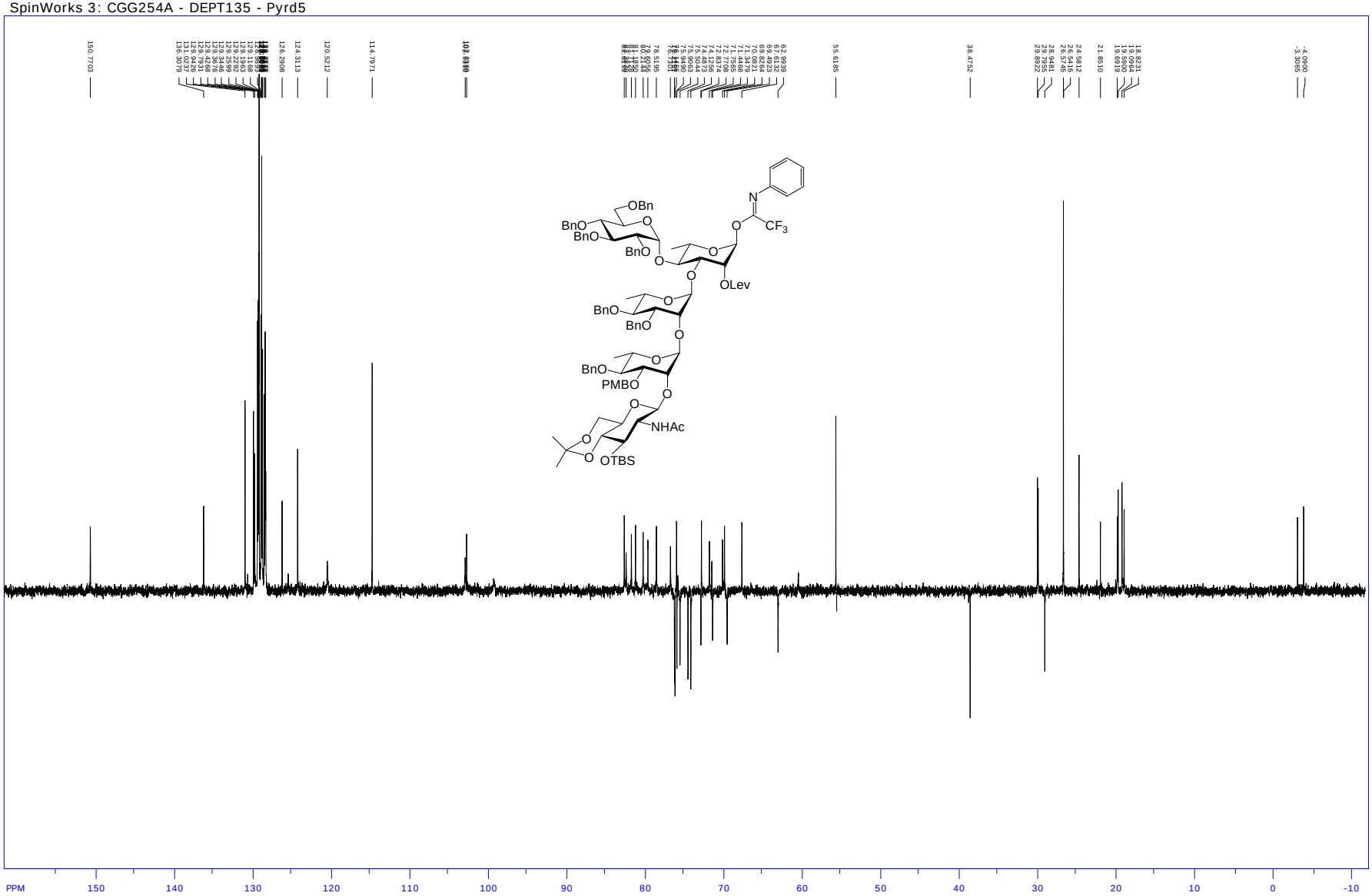
SpinWorks 3: CGG254B - 13C - Pyrd5

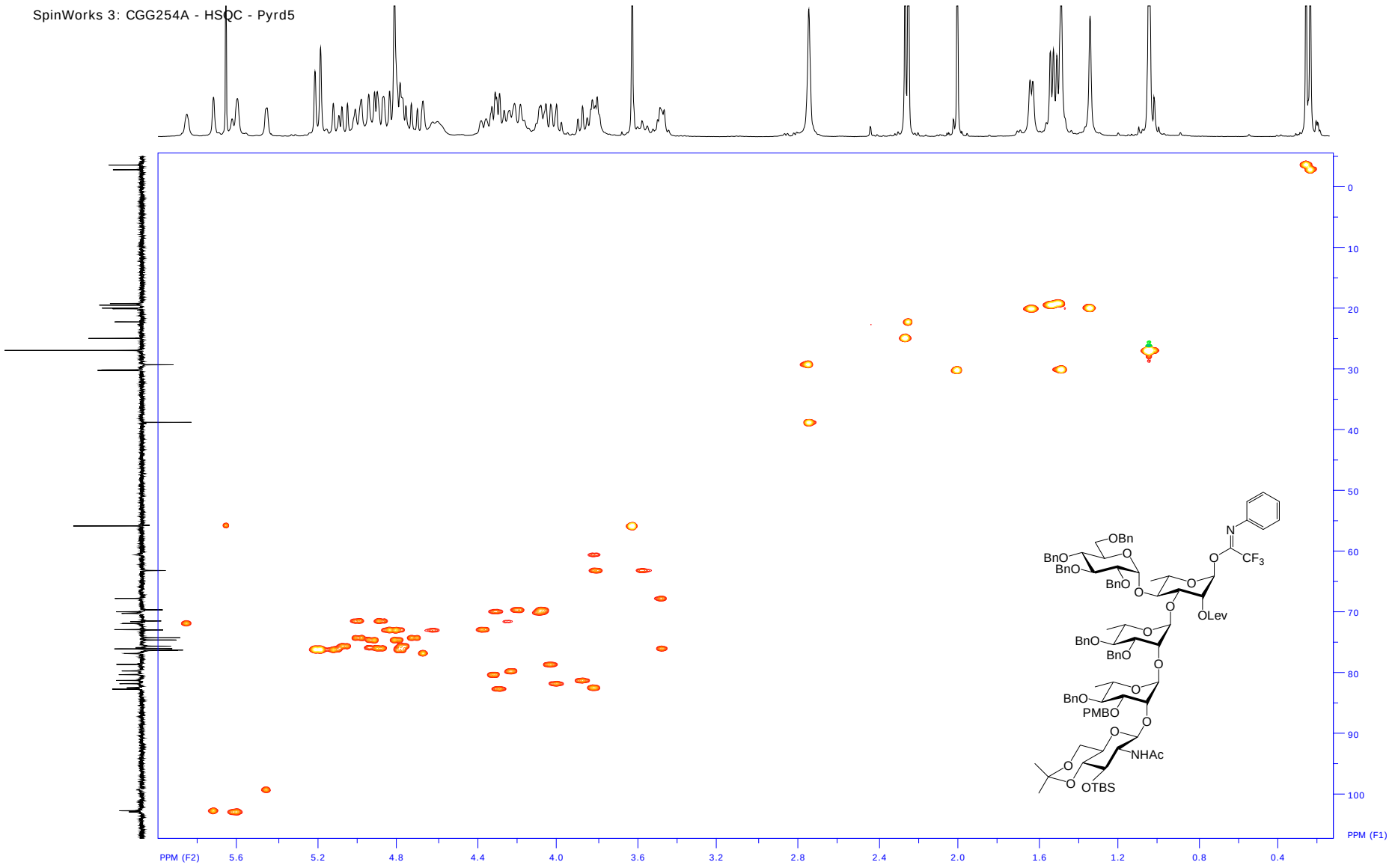


Compound **7**

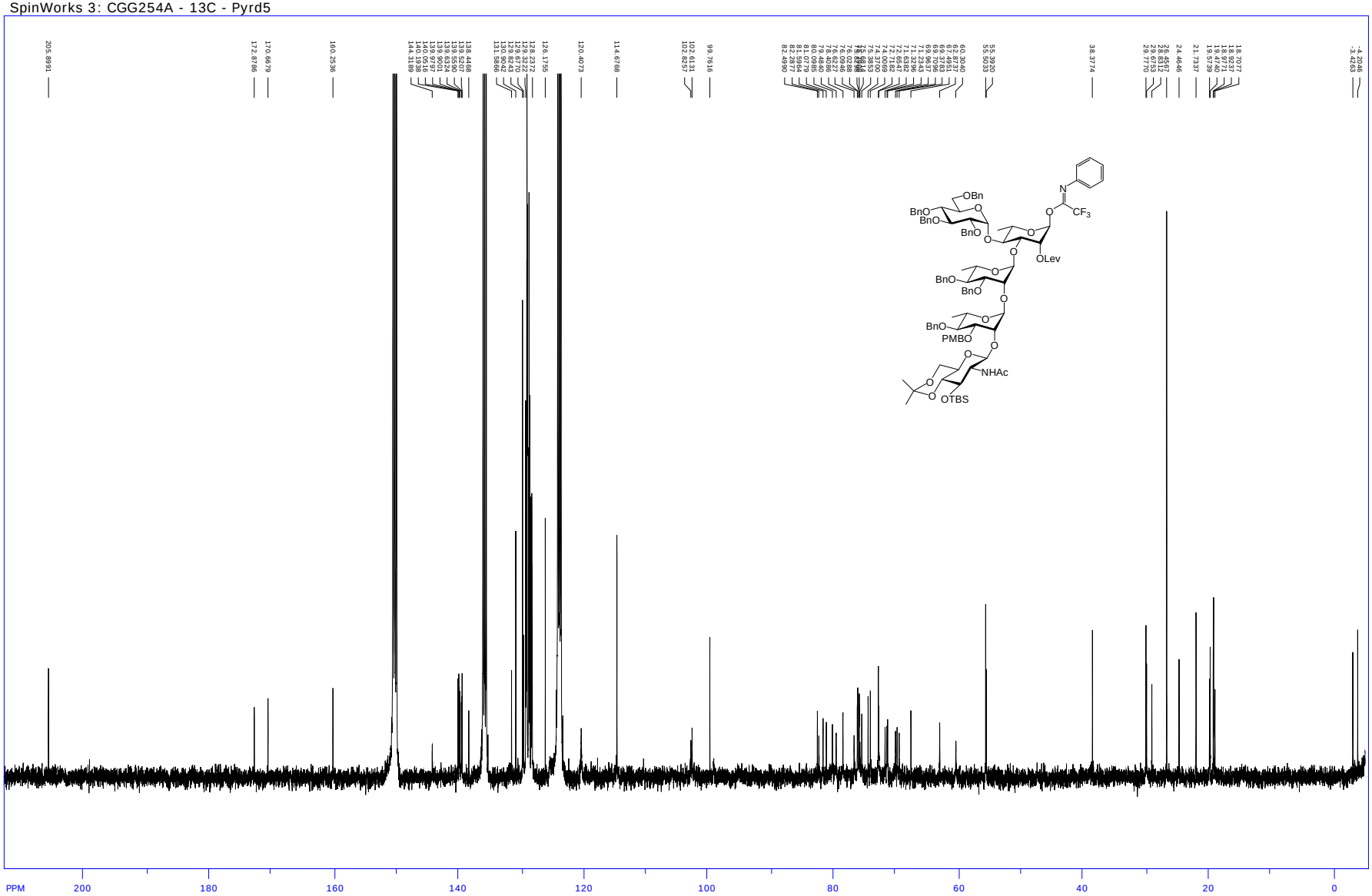

SpinWorks 3: CGG254A - 1H - Pyrd5
7.6696
7.5009
7.4700
7.2641
7.2316
7.0856
7.0240
6.9688
6.6431
5.7267
5.6675
5.6359
5.6083
5.1922
5.1311
5.0971
5.0841
5.0582
5.0176
4.9884
4.9527
4.7337
4.7062
4.6818
4.6153
4.3737
4.3218
4.2715
4.2309
4.1904
4.0898
4.0379
4.0087
3.8789
3.8141
3.6316
3.5840
3.4786
2.7503
2.2632
2.2468
2.0015
1.6282
1.5347
1.4936
1.4799
1.3355
1.0411
0.2536
0.2328
OBn
BnO
BnO
BnO
O
N
CF3
OLev
BnO
BnO
BnO
PMBO
NHAc
OTBS
19.33
31.14
5.204
4.157
0.681
1.000
1.053
3.185
22.17
9.006
4.688
4.475
6.641
4.111
6.956
3.281
3.001
10.08
3.442
9.116
6.091
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

SpinWorks 3: CGG254A - DEPT135 - Pyrd5

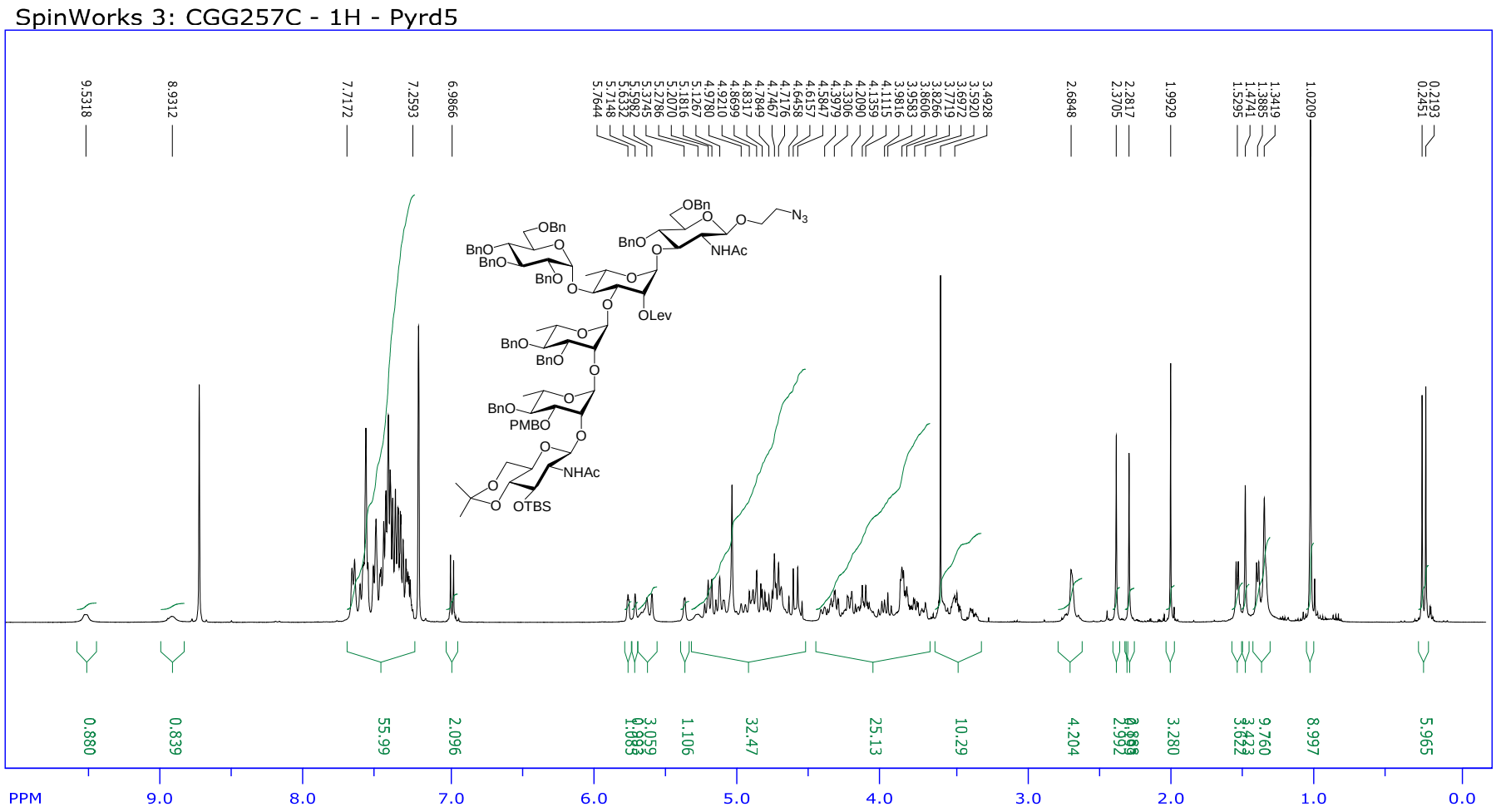



SpinWorks 3: CGG254A - HSQC - Pyrd5
PPM (F2)
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
PPM (F1)
0
10
20
30
40
50
60
70
80
90
100
OBn
BnO
BnO
BnO
O
O
O
N
CF3
OLev
BnO
BnO
BnO
PMBO
NHAc
OTBS

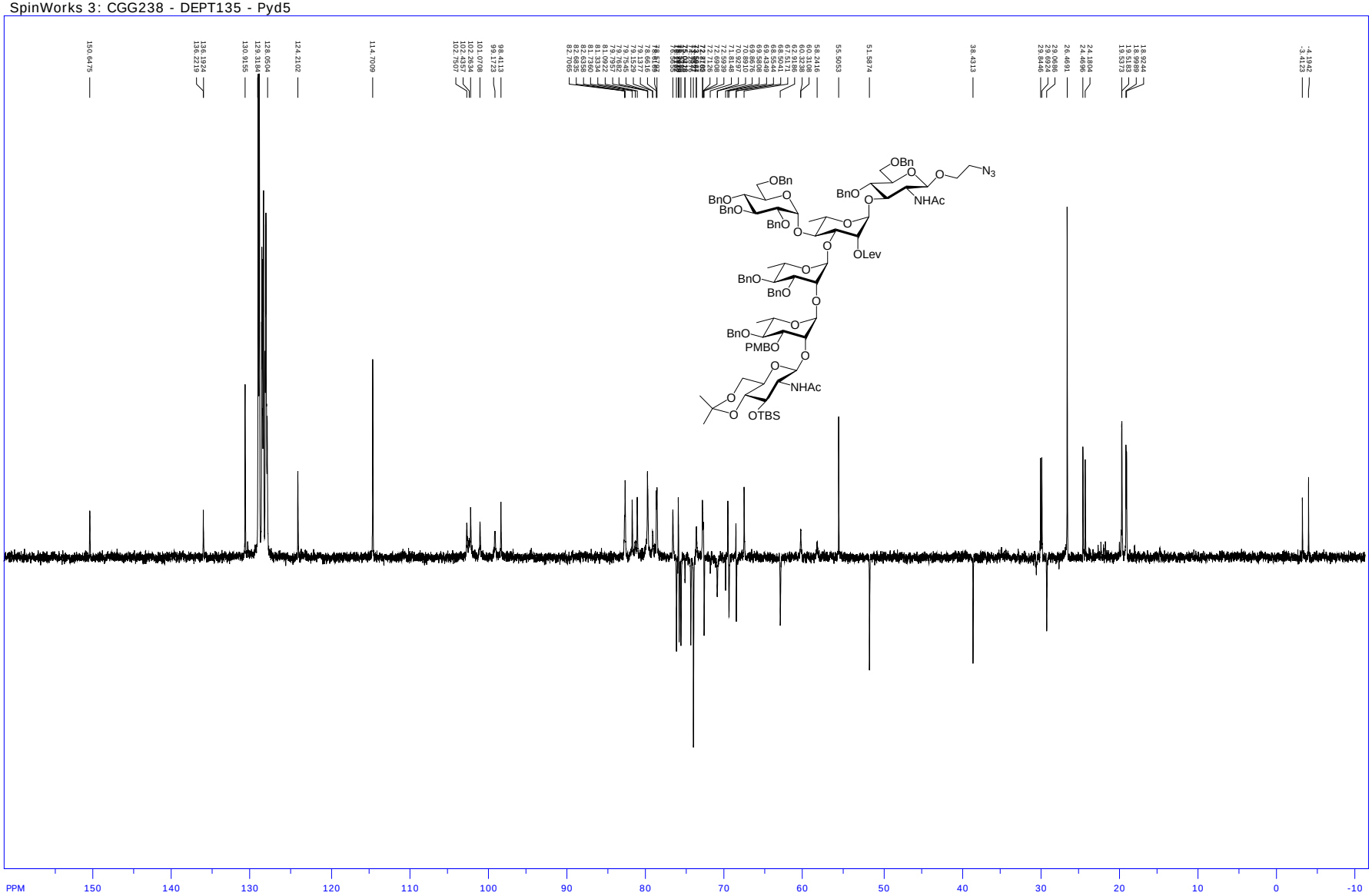
SpinWorks 3: CGG254A - 13C - Pyrd5

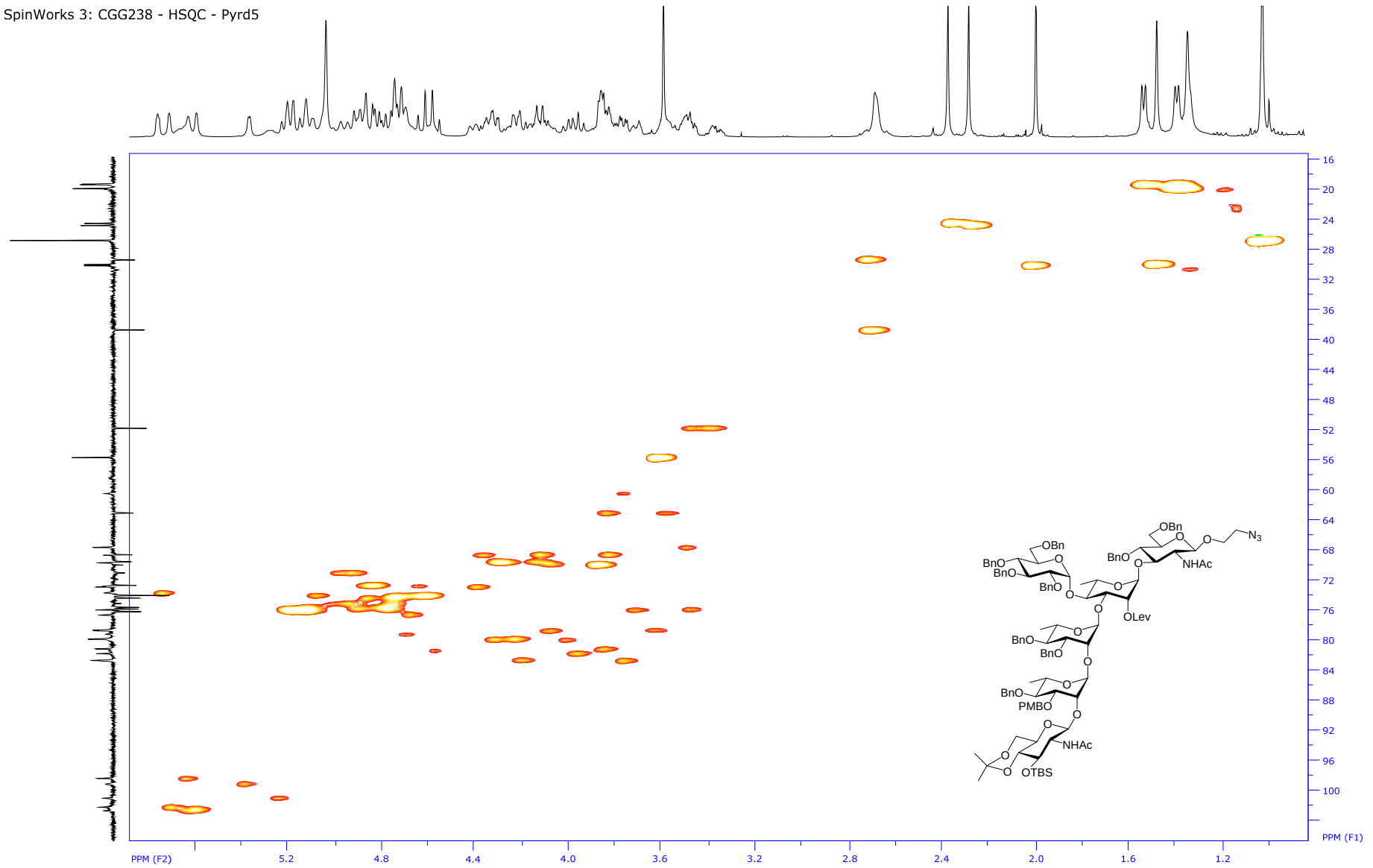


Compound **34**

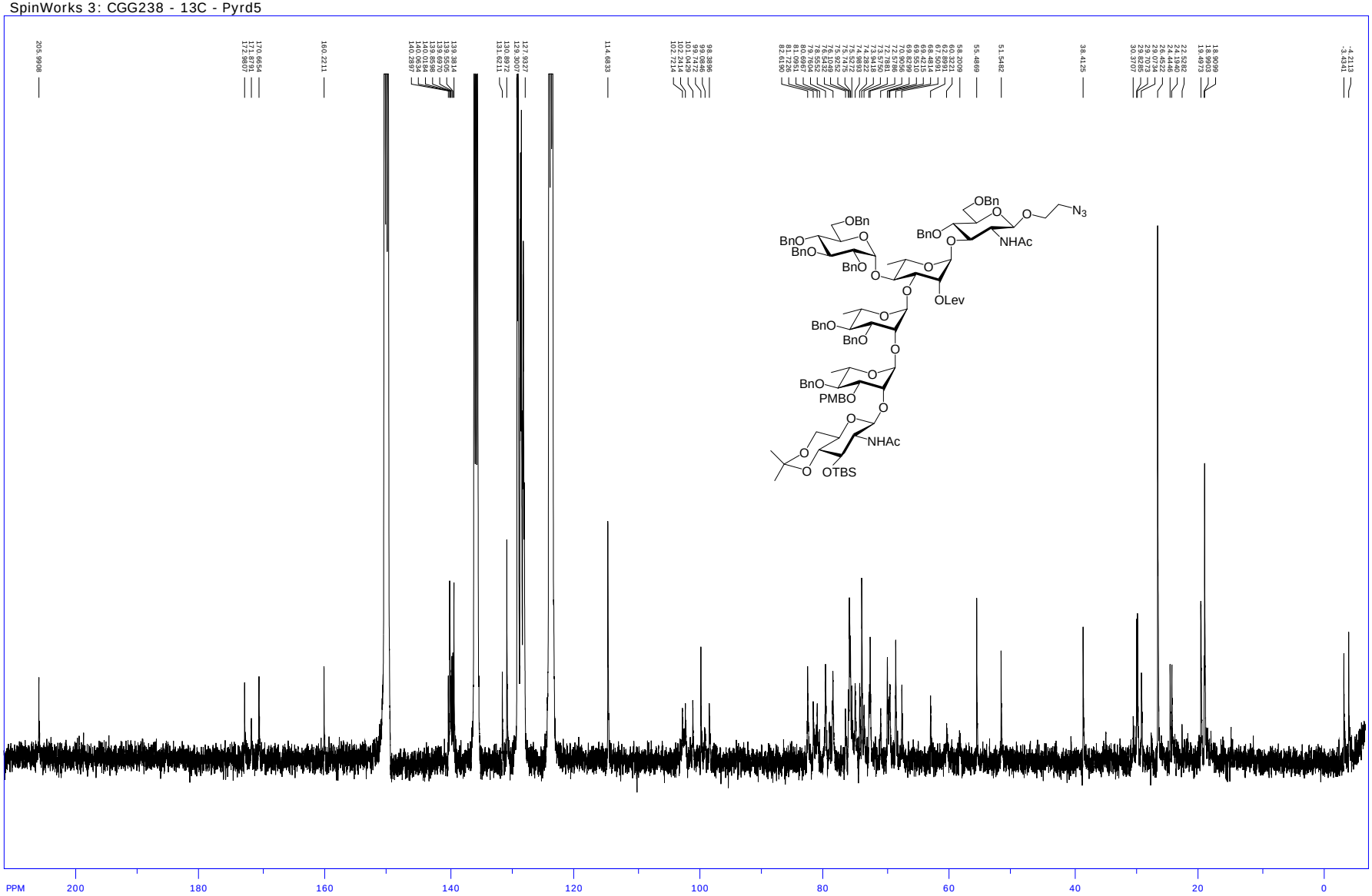

SpinWorks 3: CGG257C - 1H - Pyrd5
9.5318
8.9312
7.7172
7.2593
6.9866
5.7644
5.7148
5.6332
5.5982
5.3745
5.2786
5.2070
5.1816
5.1267
4.9780
4.9210
4.8699
4.8317
4.7849
4.7467
4.7176
4.6458
4.6157
4.5847
4.3979
4.3306
4.2090
4.1359
4.1115
3.9816
3.9583
3.8606
3.8266
3.7719
3.6972
3.5920
3.4928
2.6848
2.3705
2.2817
1.9929
1.5295
1.4741
1.3885
1.3419
1.0209
0.2451
0.2193
OBn
BnO
BnO
BnO
O
O
OLev
BnO
BnO
O
BnO
PMBO
O
O
NHAc
O
O
OTBS
BnO
O
NHAc
O
N3
0.880
0.839
55.99
2.096
3.059
1.083
1.106
32.47
25.13
10.29
4.204
2.992
3.280
3.622
9.760
8.997
5.965
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

SpinWorks 3: CGG238 - DEPT135 - Pyd5

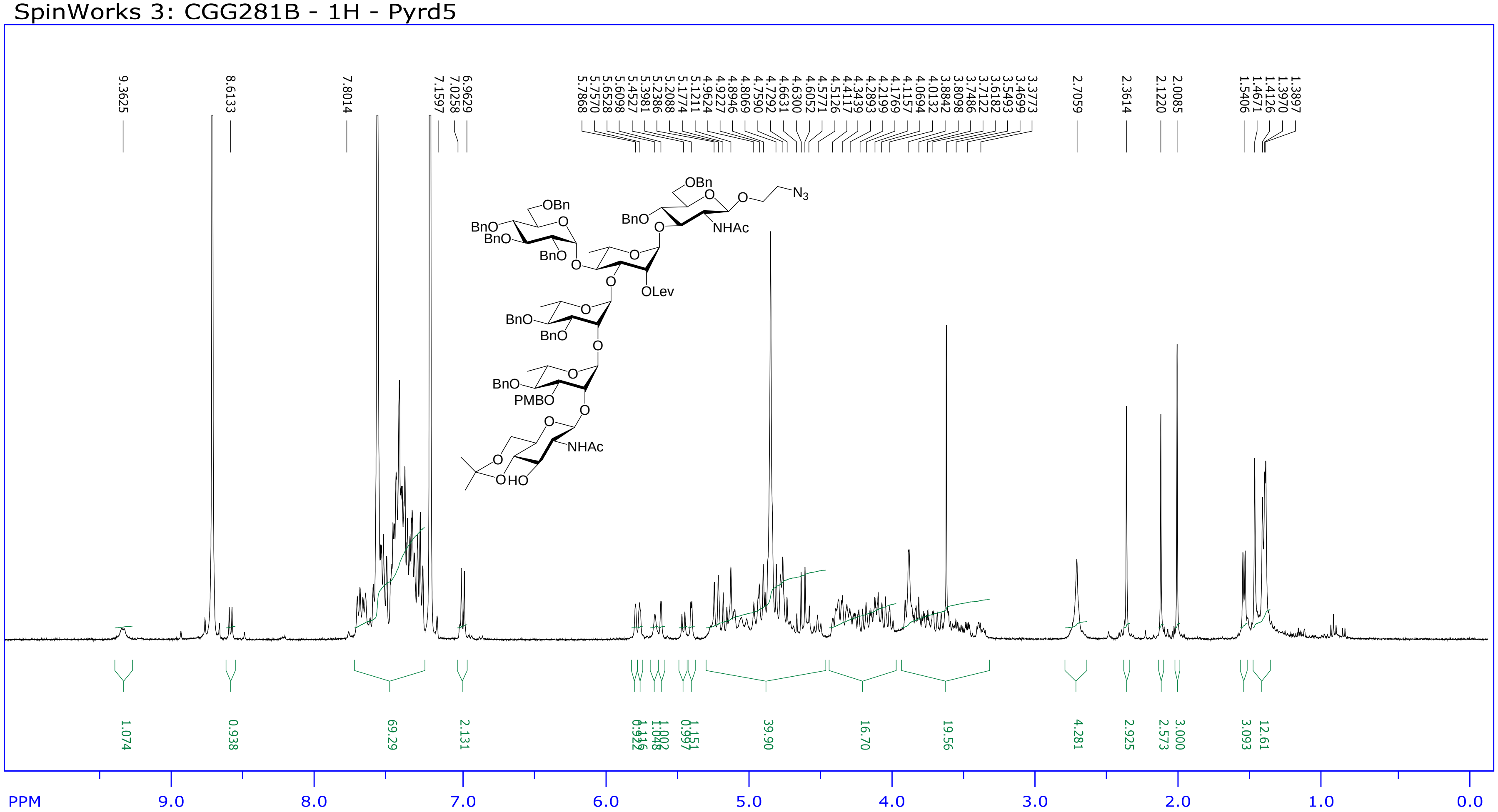



SpinWorks 3: CGG238 - HSQC - Pyrd5
PPM (F2)
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
80
84
88
92
96
100
OBn
BnO
BnO
BnO
O
O
O
O
OBn
O
O
N3
BnO
O
NHAc
OLev
BnO
BnO
O
O
BnO
PMBO
O
O
NHAc
O
O
O
OTBS

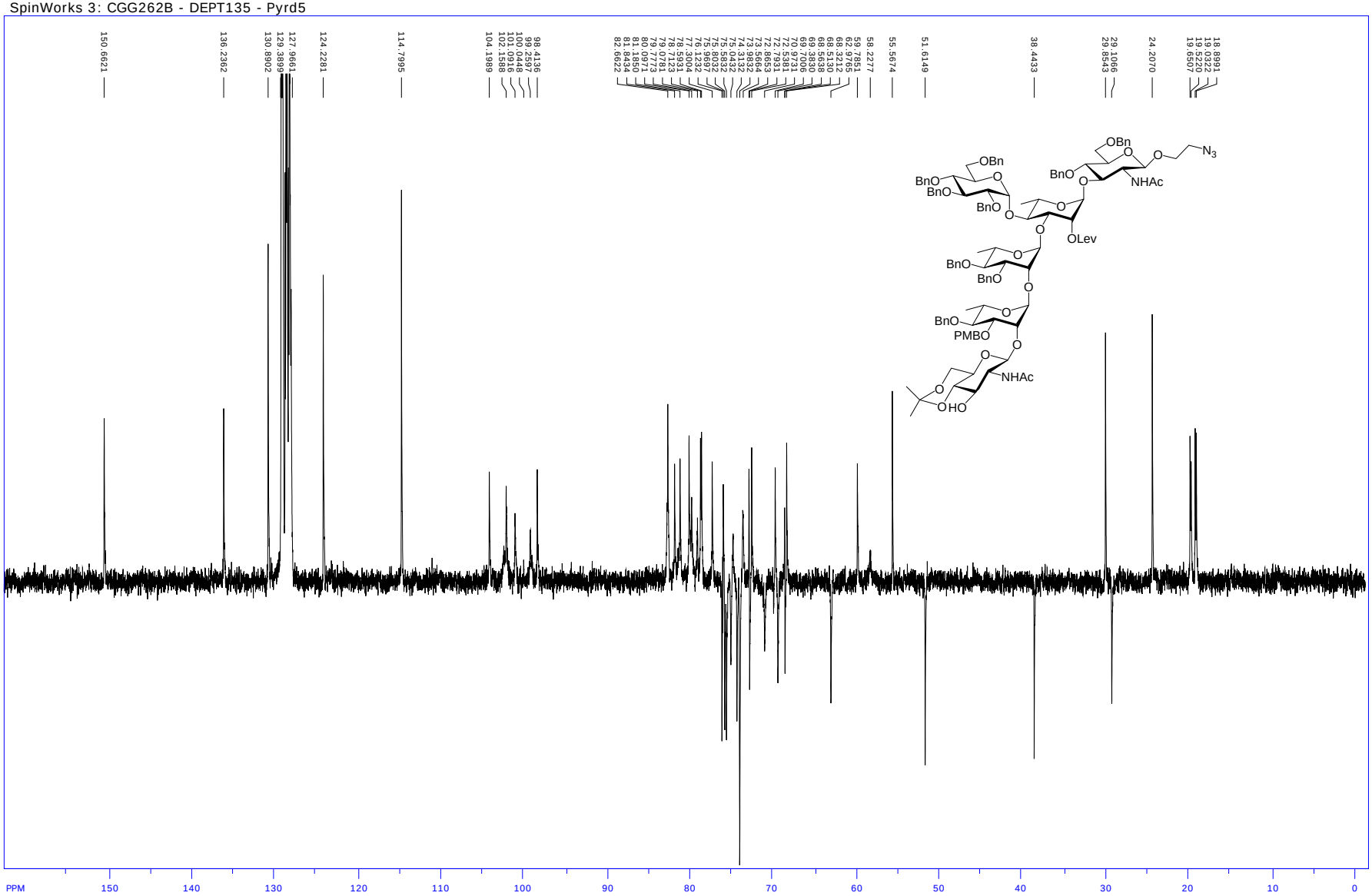
SpinWorks 3: CGG238 - 13C - Pyrd5

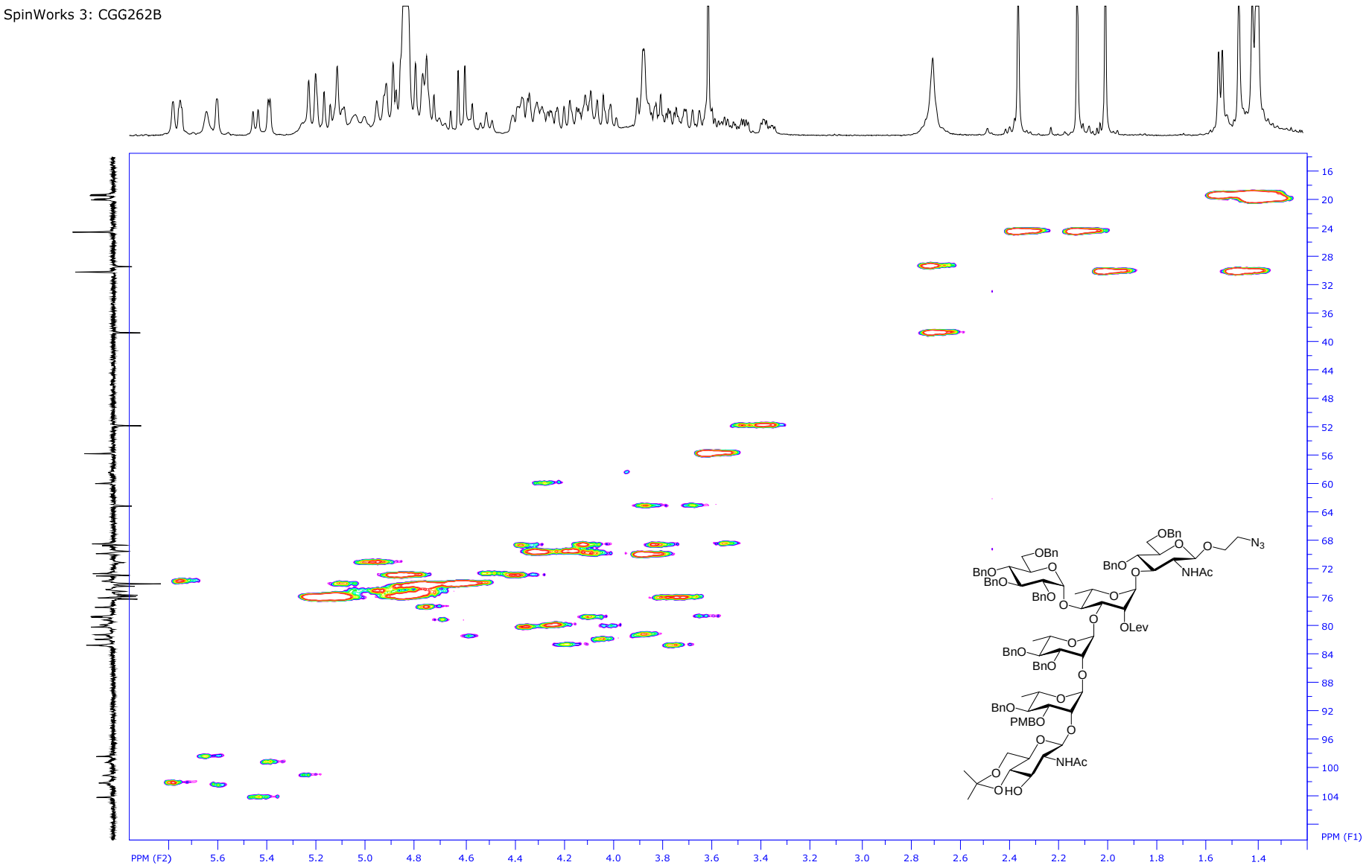


Compound **35**

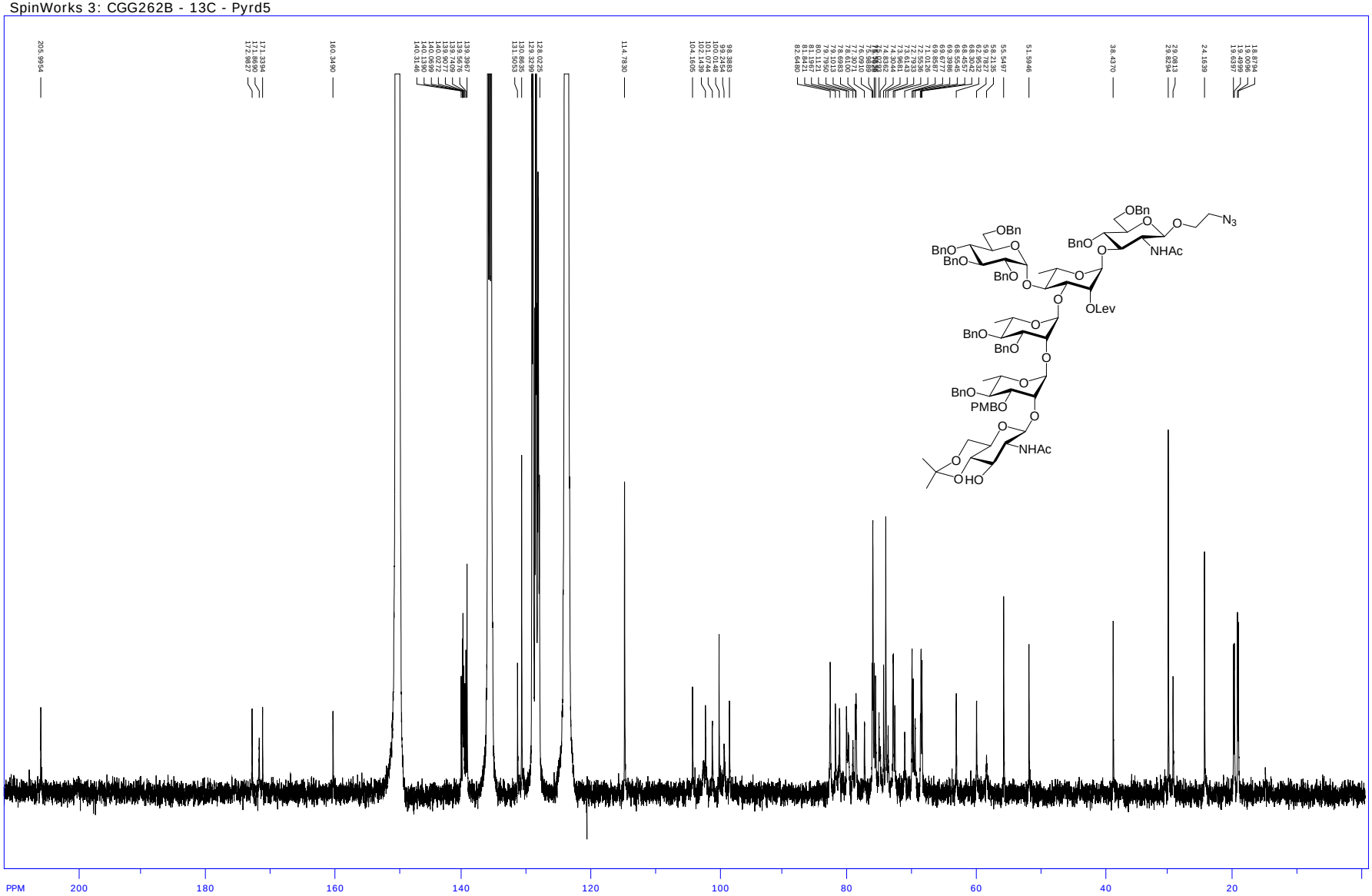

SpinWorks 3: CGG281B - 1H - Pyrd5
OBn
O
O
N3
BnO
O
NHAc
OBn
BnO
BnO
O
BnO
O
O
O
OLev
O
BnO
O
BnO
O
O
BnO
PMBO
O
O
NHAc
O
O
HO
PPM
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

SpinWorks 3: CGG262B - DEPT135 - Pyrd5

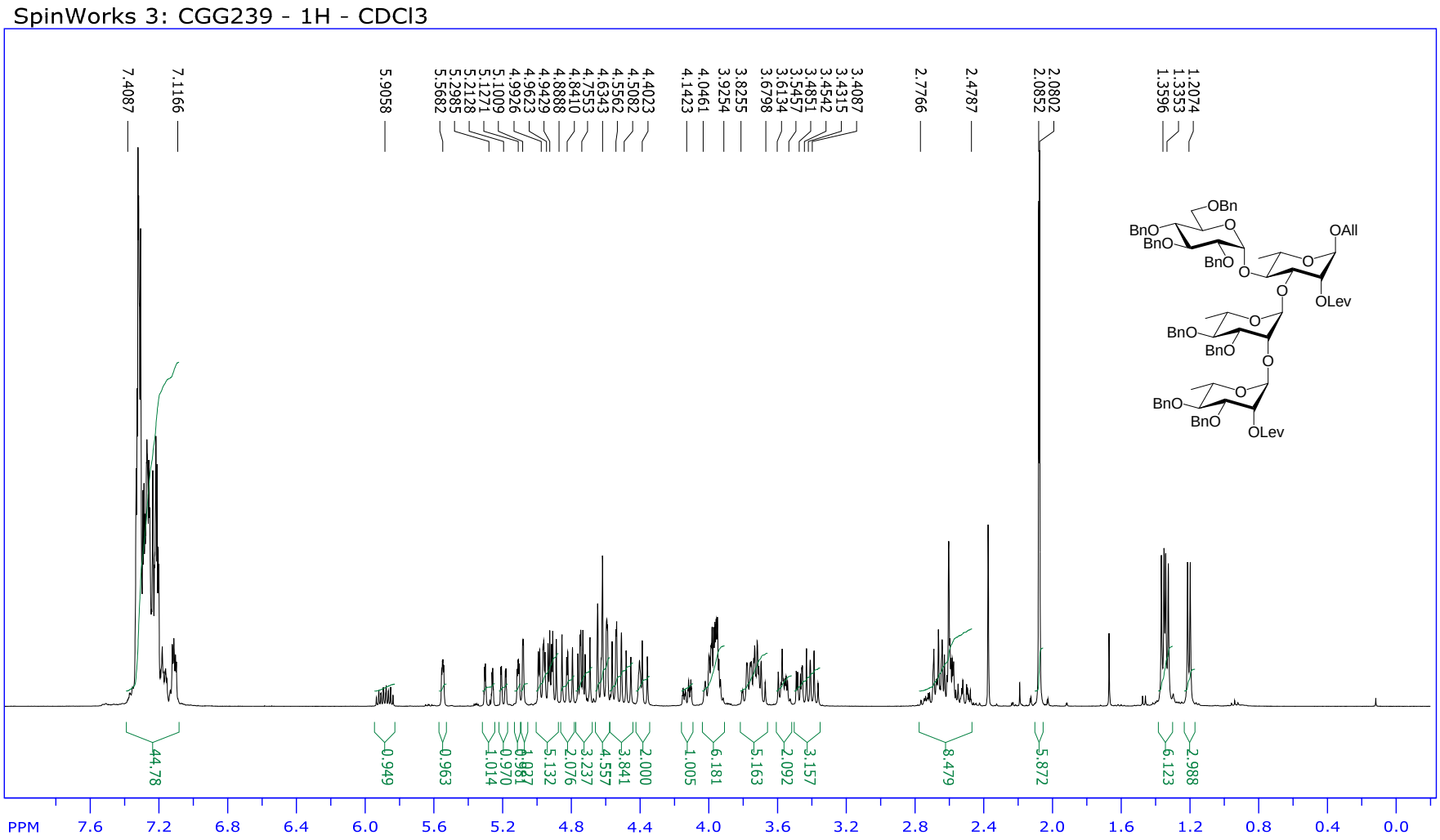


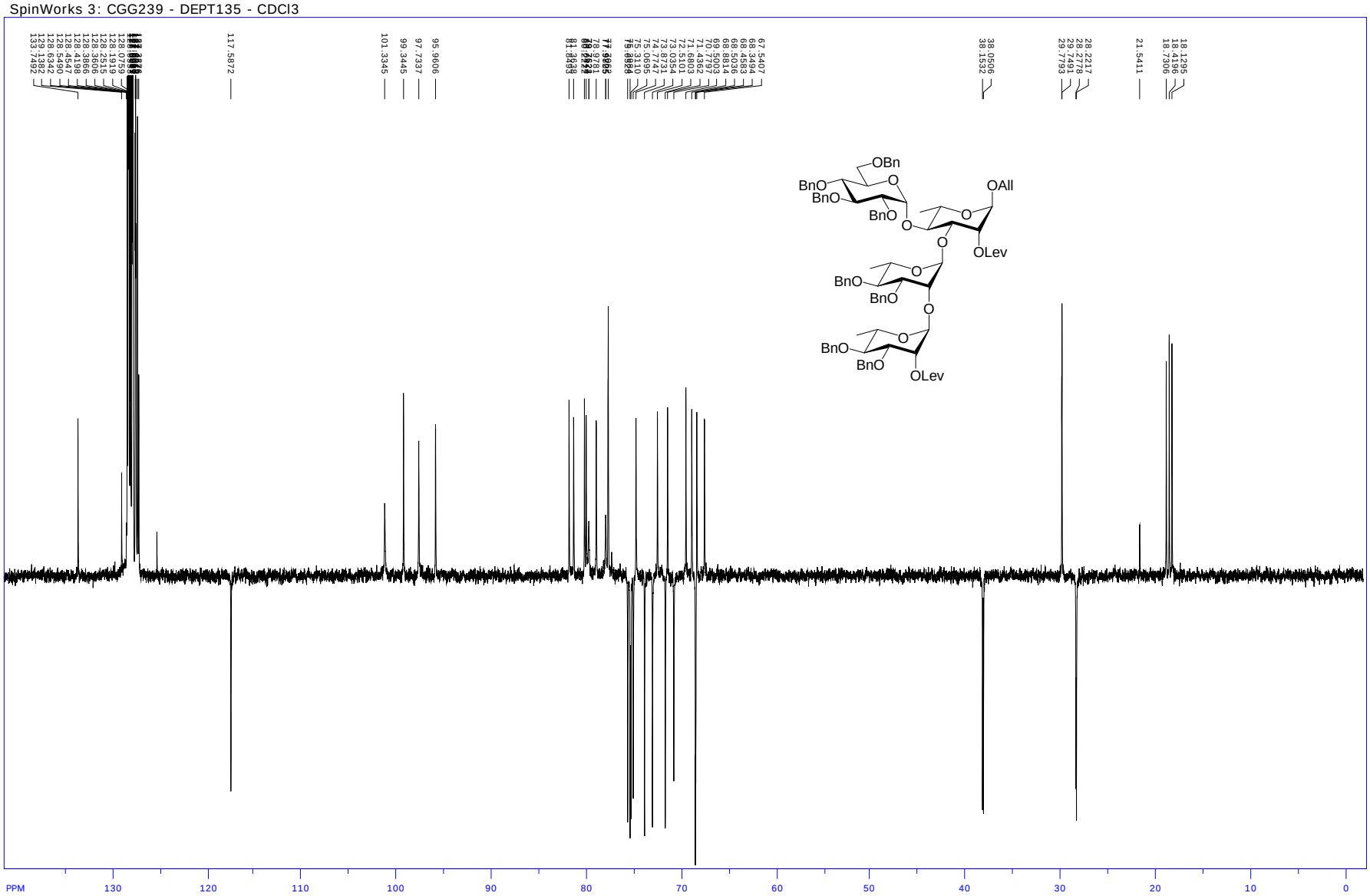

SpinWorks 3: CGG262B
PPM (F2)
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
PPM (F1)
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
80
84
88
92
96
100
104
OBn
BnO
BnO
BnO
O
O
O
OLev
BnO
BnO
O
BnO
PMBO
O
O
NHAc
O
O
HO
OBn
O
N3
BnO
O
NHAc

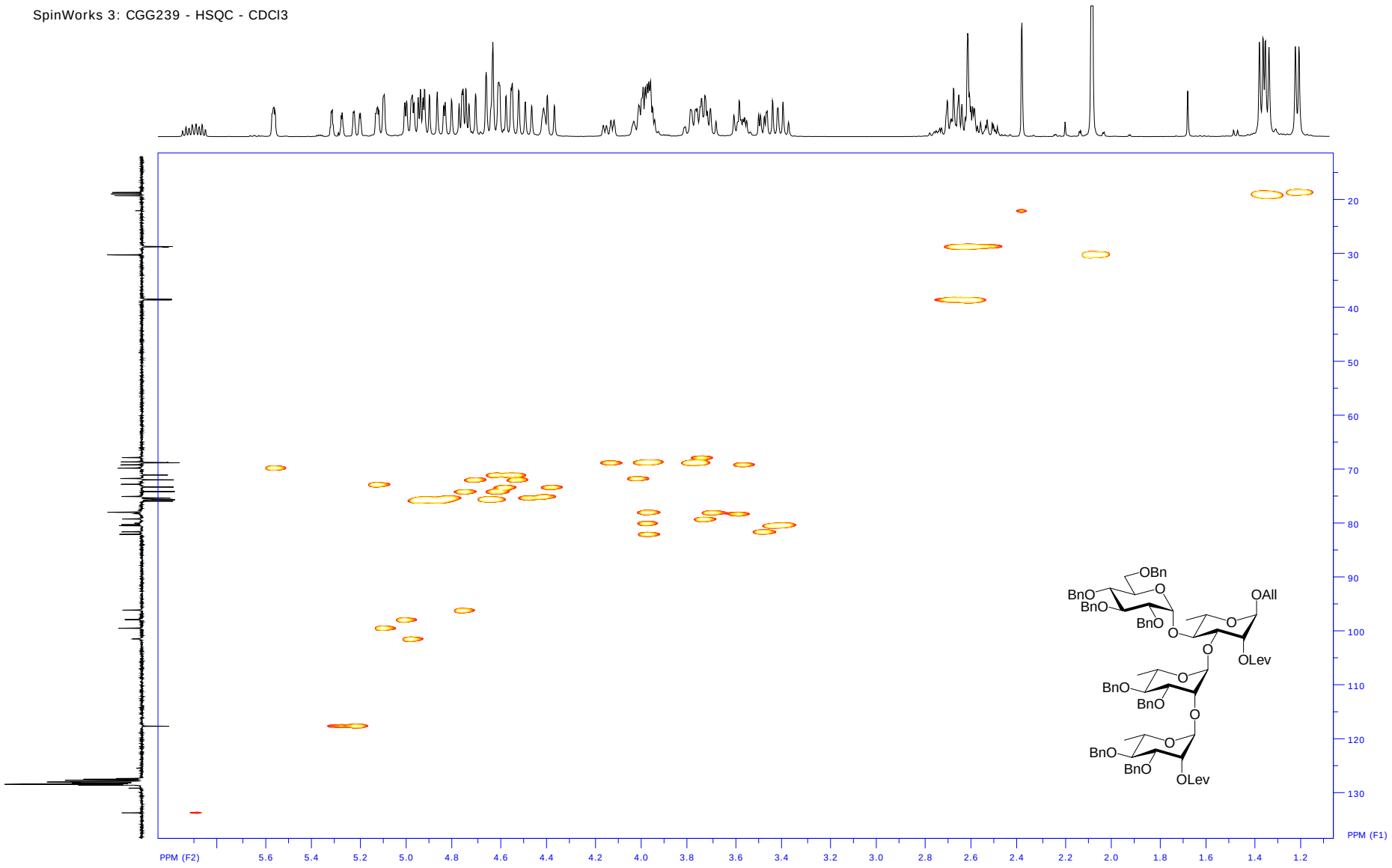
SpinWorks 3: CGG262B - 13C - Pyrd5



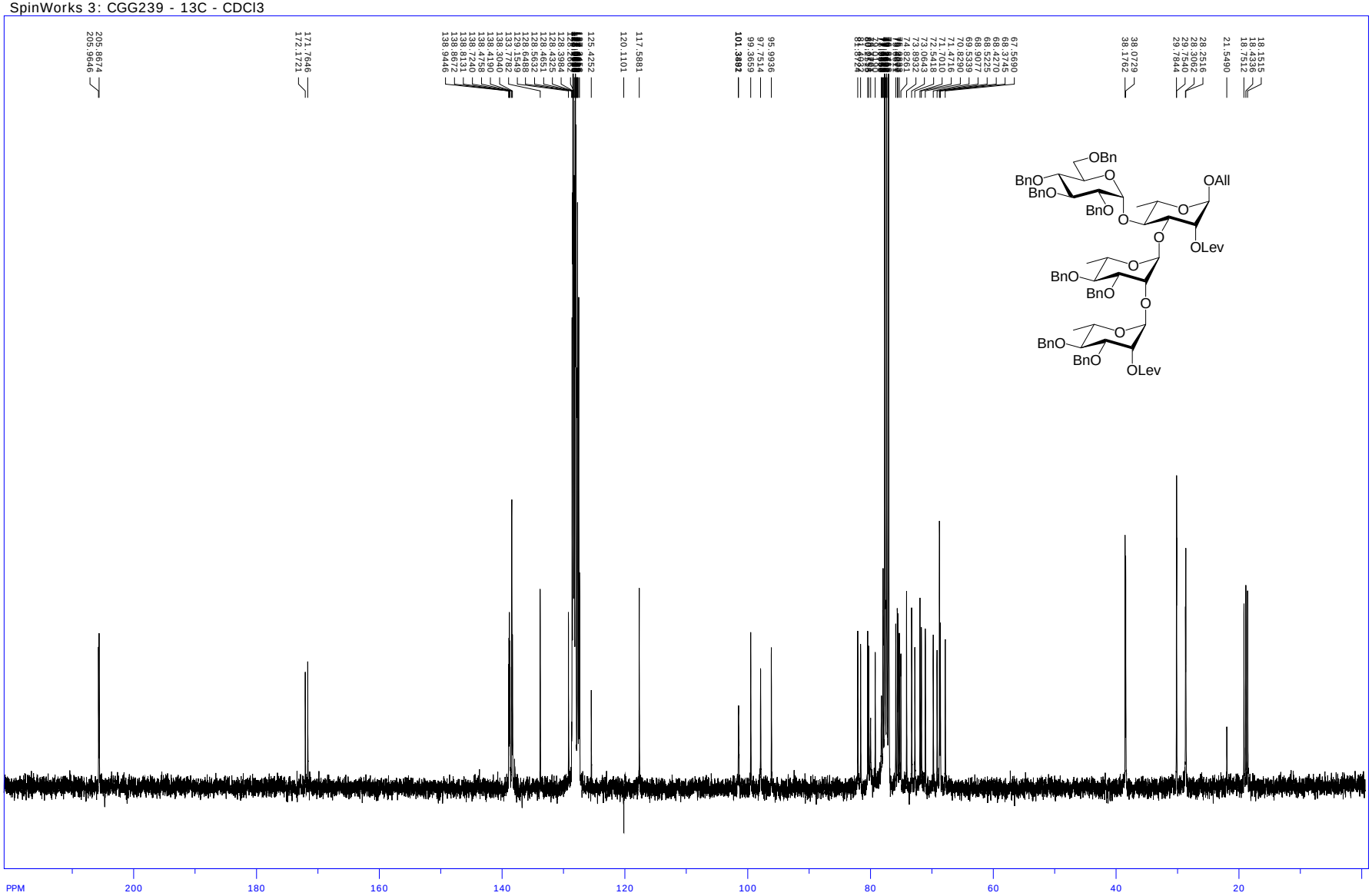
Compound **23**


SpinWorks 3: CGG239 - 1H - CDCl3
7.4087
7.1166
5.9058
5.5682
5.2985
5.2128
5.1271
5.1009
4.9926
4.9623
4.9429
4.8888
4.8410
4.7553
4.6343
4.5562
4.5082
4.4023
4.1423
4.0461
3.9254
3.8255
3.6798
3.6134
3.5457
3.4851
3.4542
3.4315
3.4087
2.7766
2.4787
2.0852
2.0802
1.3596
1.3353
1.2074
OBn
BnO
BnO
BnO
O
OAll
OLev
44.78
0.949
0.963
1.014
0.970
5.132
2.076
3.237
4.557
3.841
2.000
1.005
6.181
5.163
2.092
3.157
8.479
5.872
6.123
2.988
PPM
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

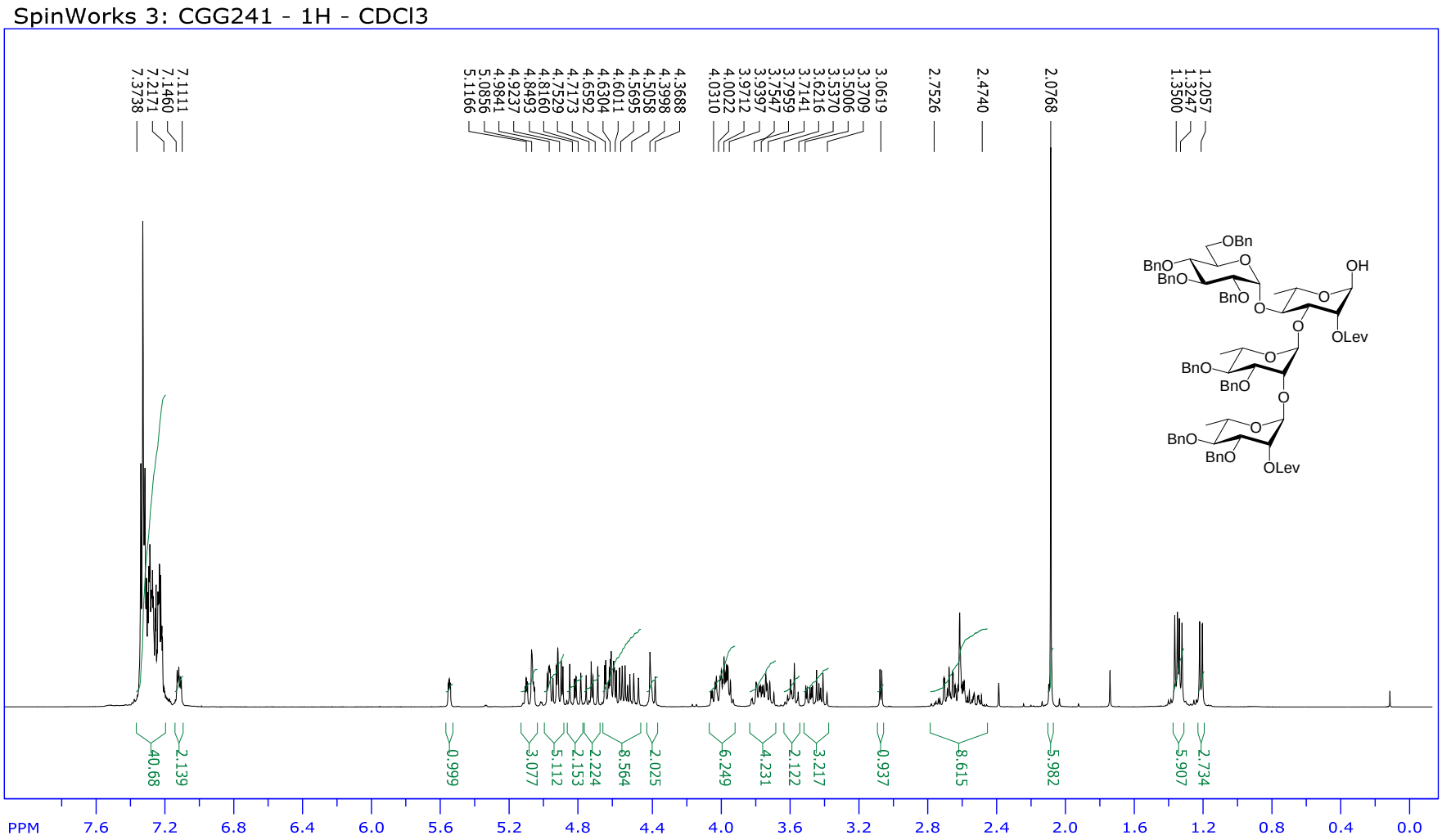

SpinWorks 3: CGG239 - DEPT135 - CDCl3
OBn
BnO
BnO
BnO
O
OAll
O
OLev
BnO
BnO
O
BnO
BnO
OLev
PPM
130
120
110
100
90
80
70
60
50
40
30
20
10
0

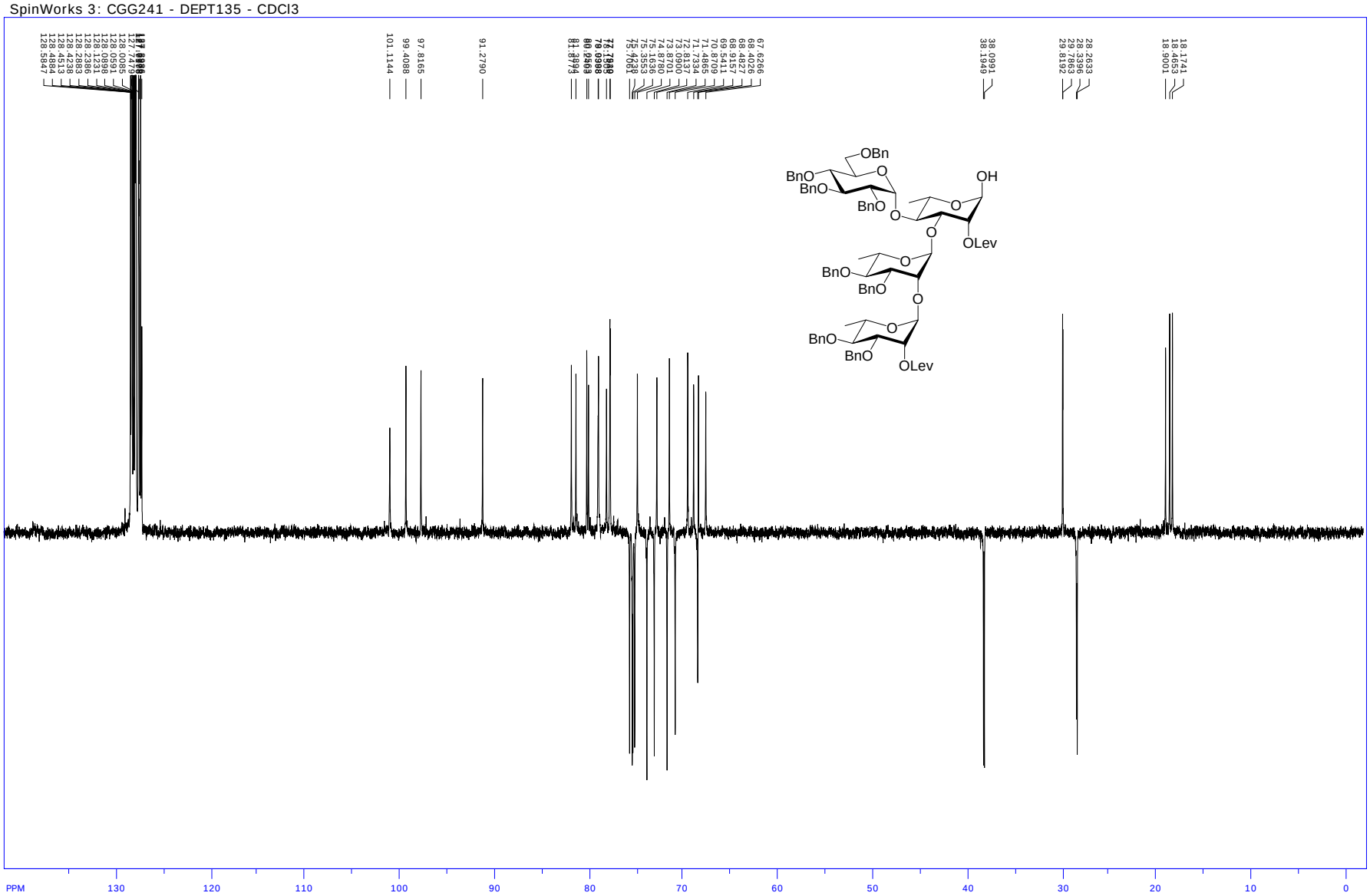

SpinWorks 3: CGG239 - HSQC - CDCl3
PPM (F2)
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
OAll
O
OLev
BnO
BnO
O
O
BnO
BnO
OLev

SpinWorks 3: CGG239 - 13C - CDCl3

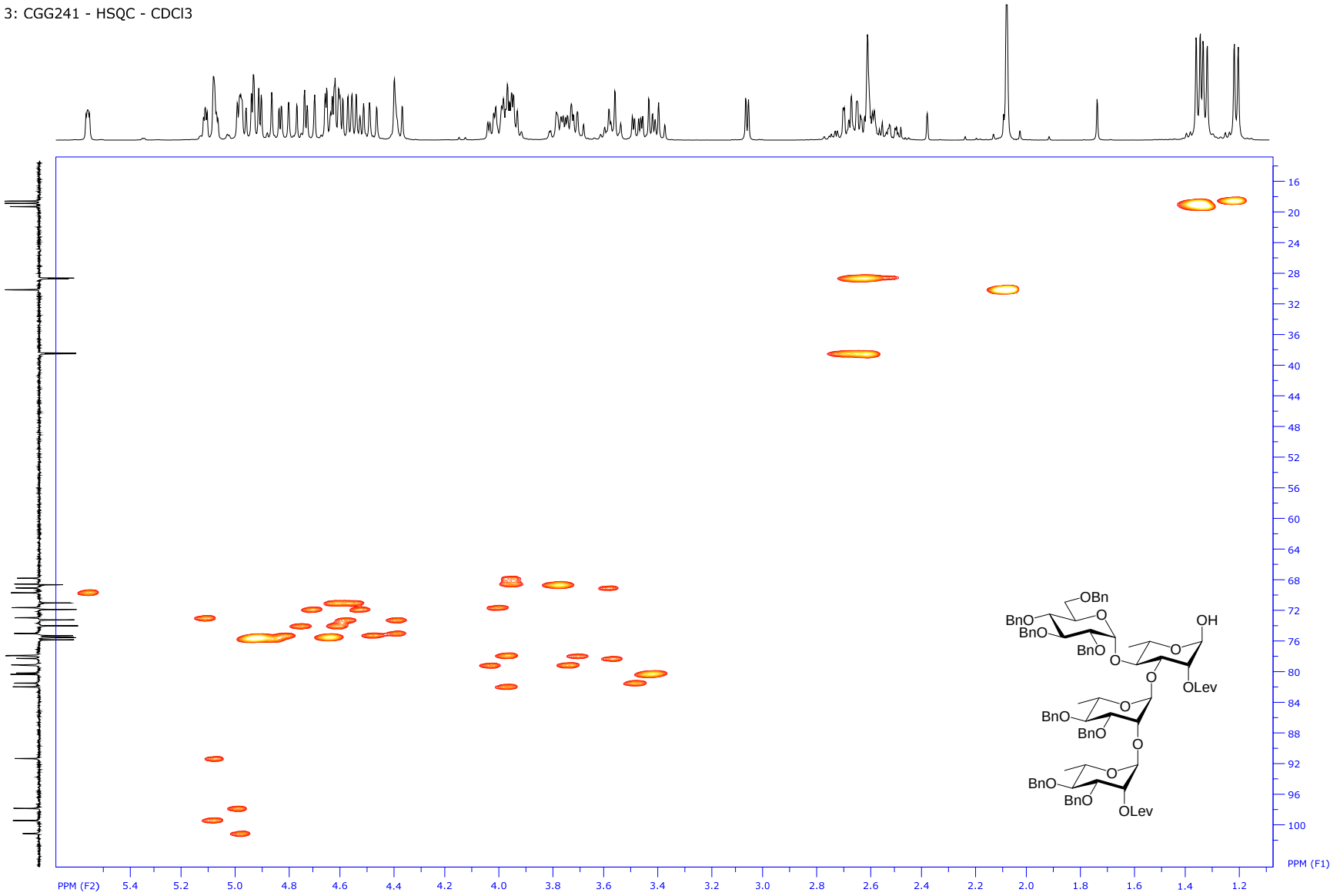


Compound **24**

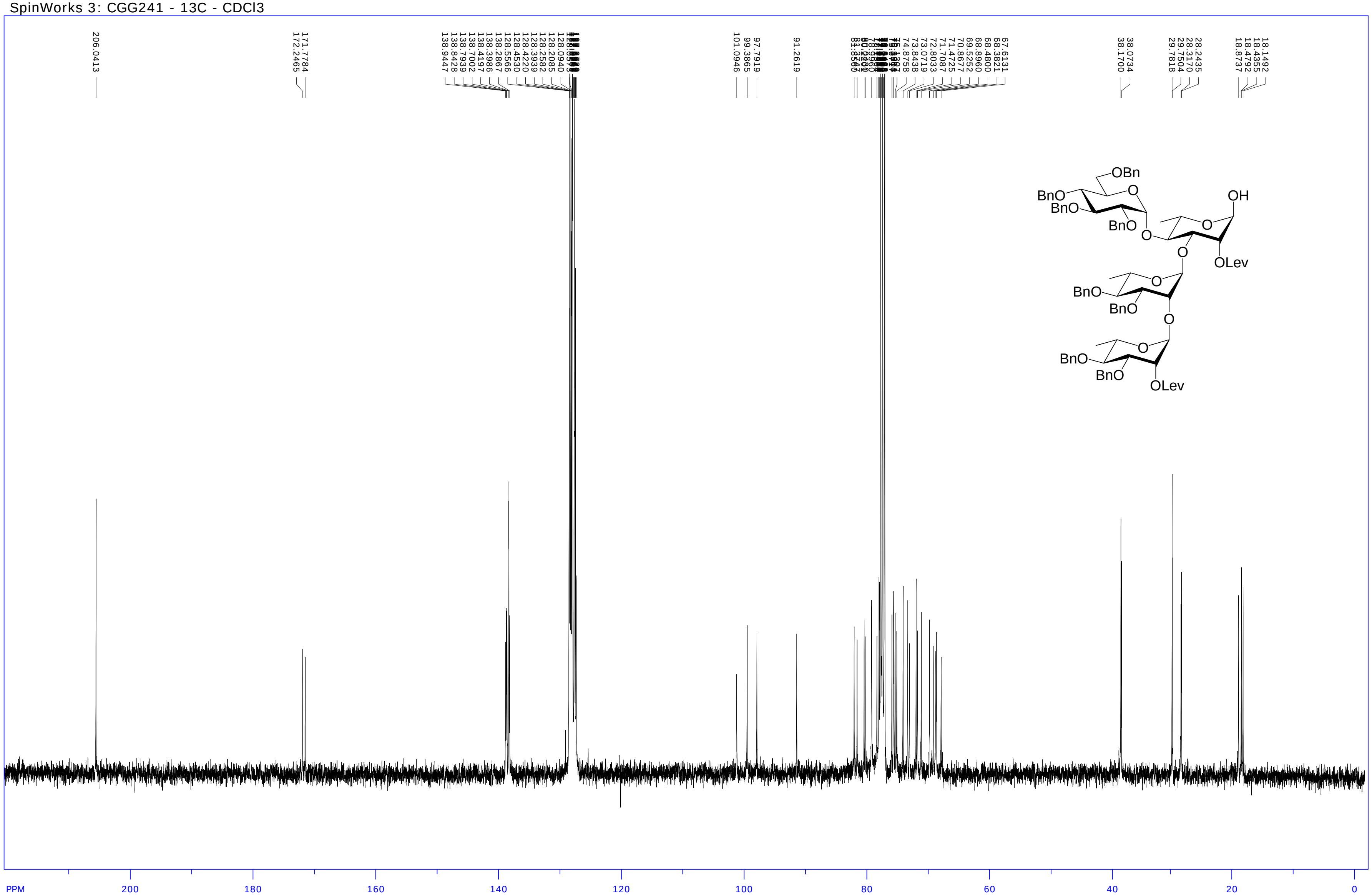

SpinWorks 3: CGG241 - 1H - CDCl3
7.3738
7.2171
7.1460
7.1111
5.1166
5.0856
4.9841
4.9237
4.8493
4.8160
4.7529
4.7173
4.6592
4.6304
4.6011
4.5695
4.5058
4.3998
4.3688
4.0310
4.0022
3.9712
3.9397
3.7959
3.7547
3.7141
3.6216
3.5370
3.5006
3.3709
3.0619
2.7526
2.4740
2.0768
1.3500
1.3247
1.2057
40.68
2.139
0.999
3.077
5.112
2.153
2.224
8.564
2.025
6.249
4.231
2.122
3.217
0.937
8.615
5.982
5.907
2.734
PPM
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
OBn
BnO
BnO
BnO
O
O
OH
O
OLev
BnO
BnO
O
BnO
BnO
OLev


SpinWorks 3: CGG241 - DEPT135 - CDCl3
OBn
BnO
BnO
BnO
O
O
OH
O
OLev
BnO
BnO
O
BnO
BnO
OLev
PPM
130
120
110
100
90
80
70
60
50
40
30
20
10
0

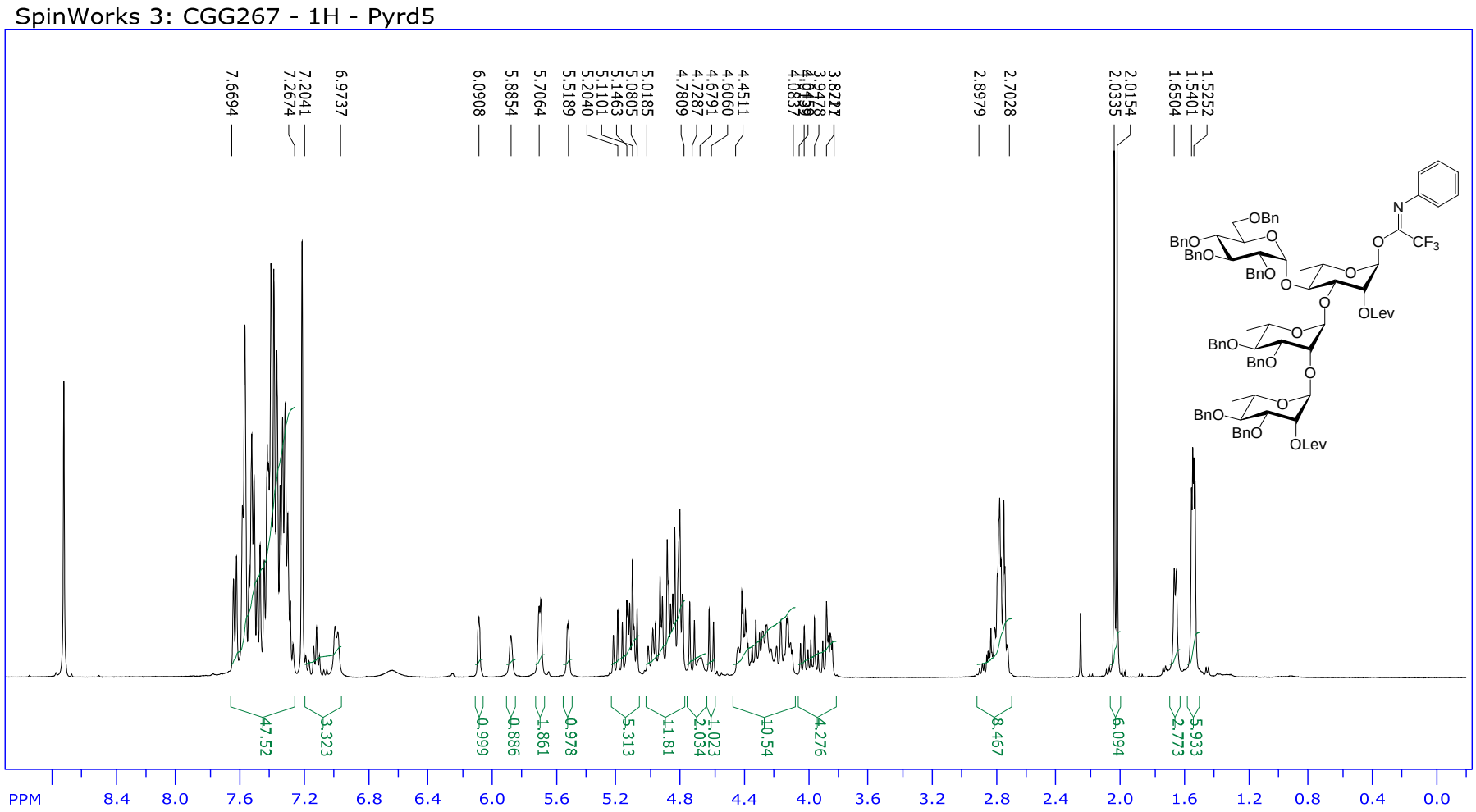
SpinWorks 3: CGG241 - HSQC - CDCl3

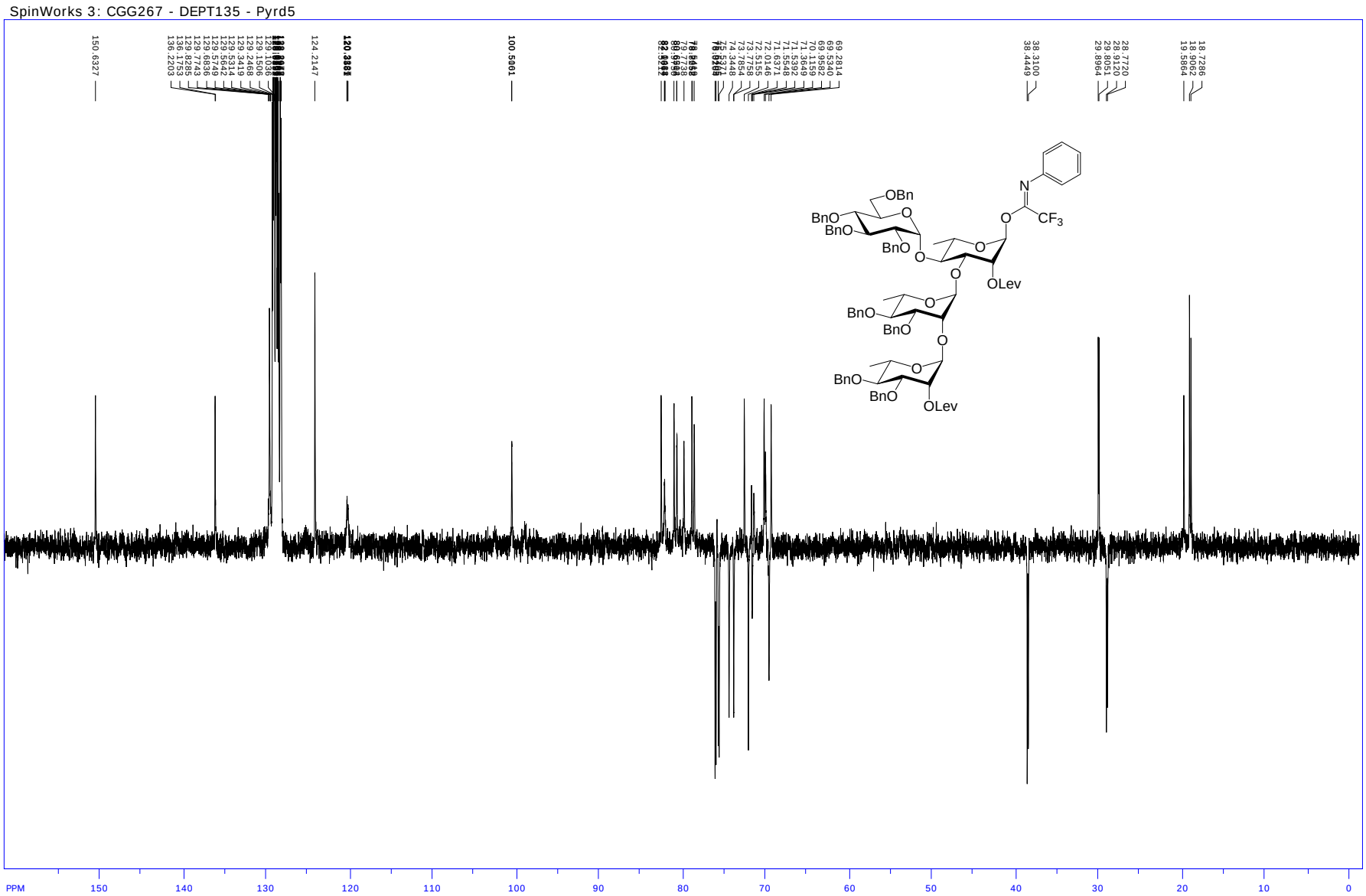


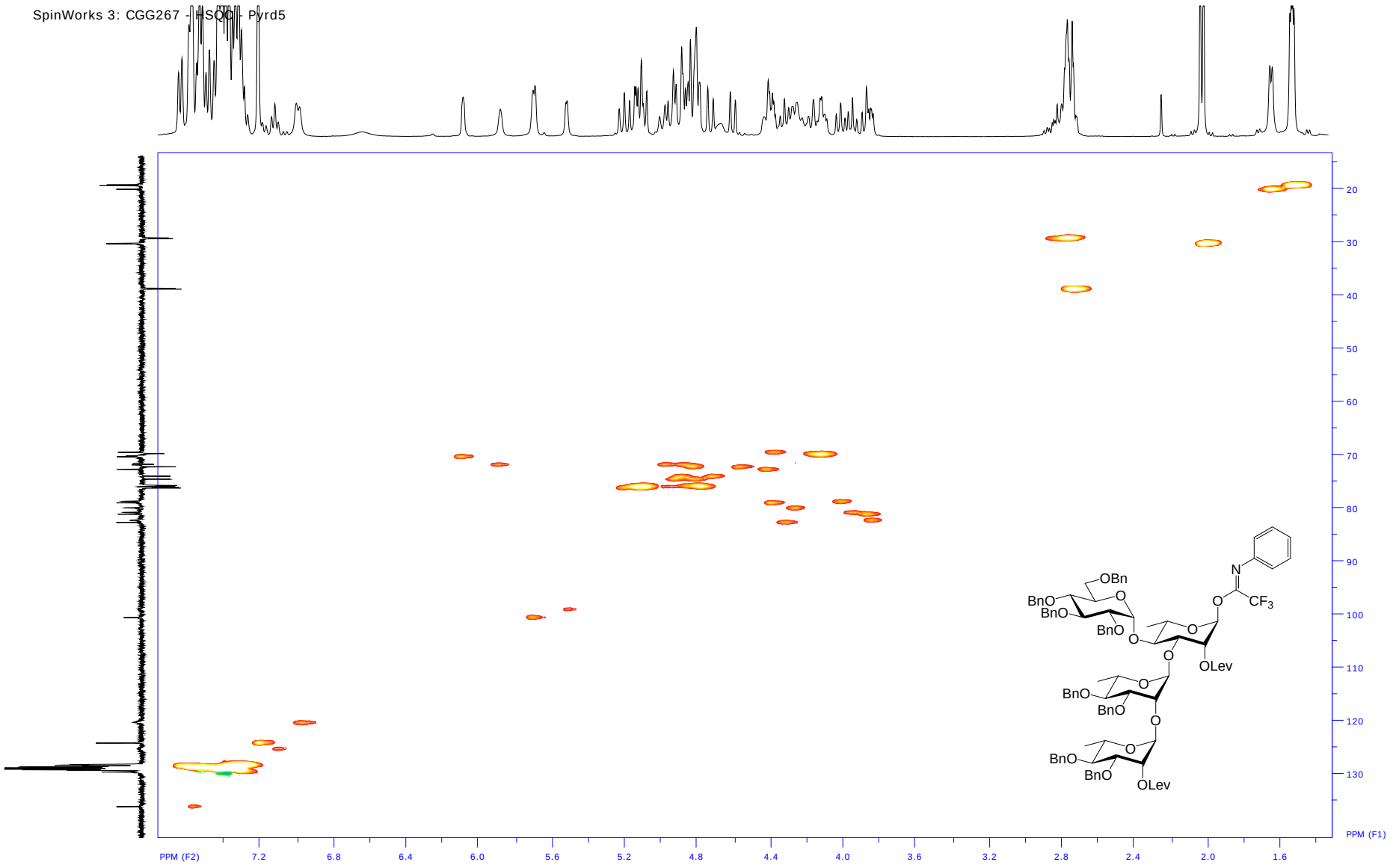
SpinWorks 3: CGG241 - 13C - CDCl3



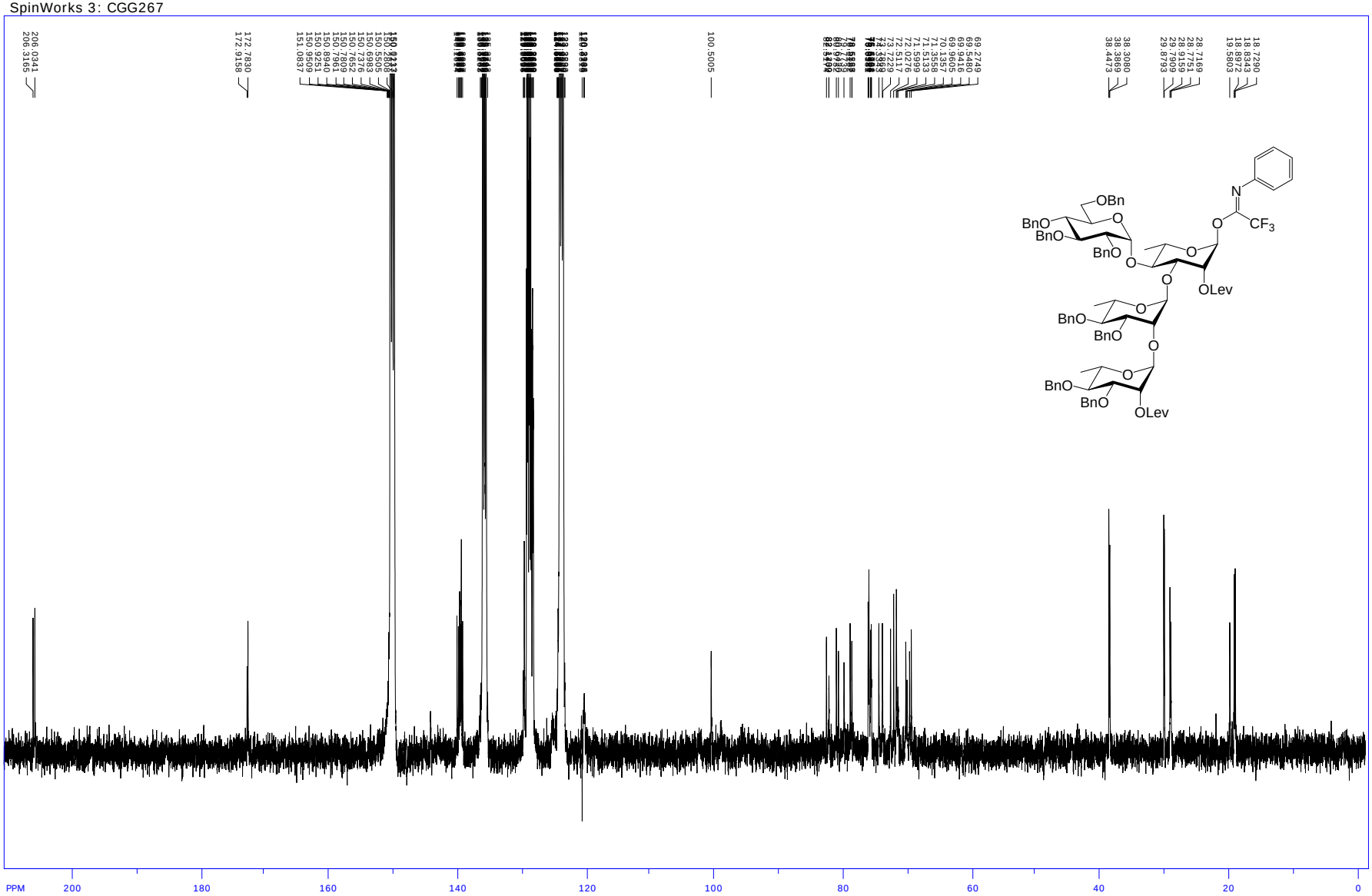
Compound **6**


SpinWorks 3: CGG267 - 1H - Pyrd5
7.6694
7.2674
7.2041
6.9737
6.0908
5.8854
5.7064
5.5189
5.2040
5.1101
5.1463
5.0805
5.0185
4.7809
4.7287
4.6791
4.6060
4.4511
4.0837
3.8727
2.8979
2.7028
2.0335
2.0154
1.6504
1.5401
1.5252
47.52
3.323
0.999
0.886
1.861
0.978
5.313
11.81
2.034
1.023
10.54
4.276
8.467
6.094
2.773
5.933
PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
OBn
BnO
BnO
BnO
O
O
O
O
O
OLev
N
CF3
BnO
BnO
BnO
BnO
OLev

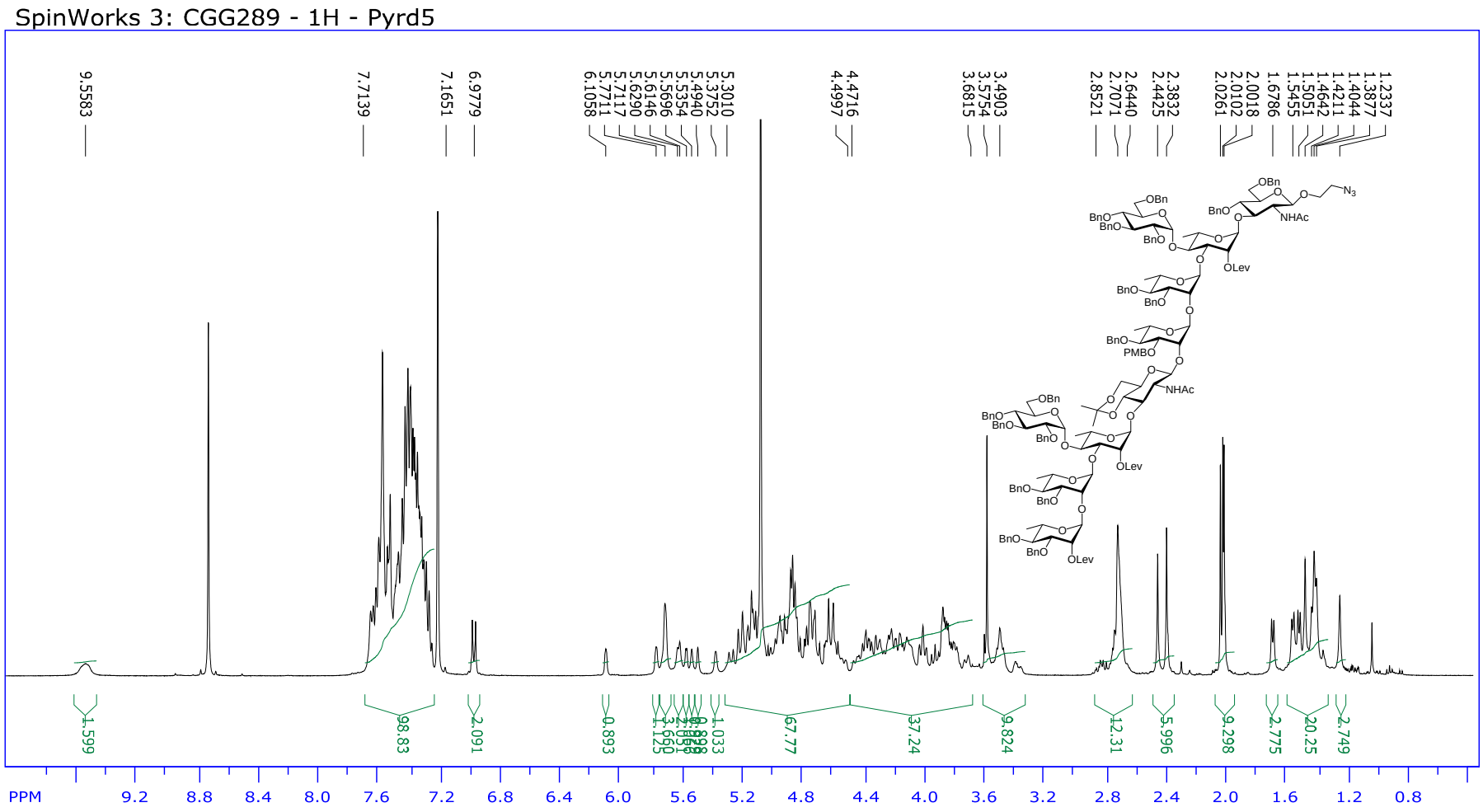

SpinWorks 3: CGG267 - DEPT135 - Pyrd5
150.6327
136.2203
124.2147
100.5001
69.2814
38.4449
29.8964
19.5864
PPM
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


SpinWorks 3: CGG267 - HSQC - Pyrd5
PPM (F2)
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
BnO
BnO
O
O
O
O
O
O
N
CF3
OLev
BnO
BnO
O
O
BnO
BnO
O
O
OLev

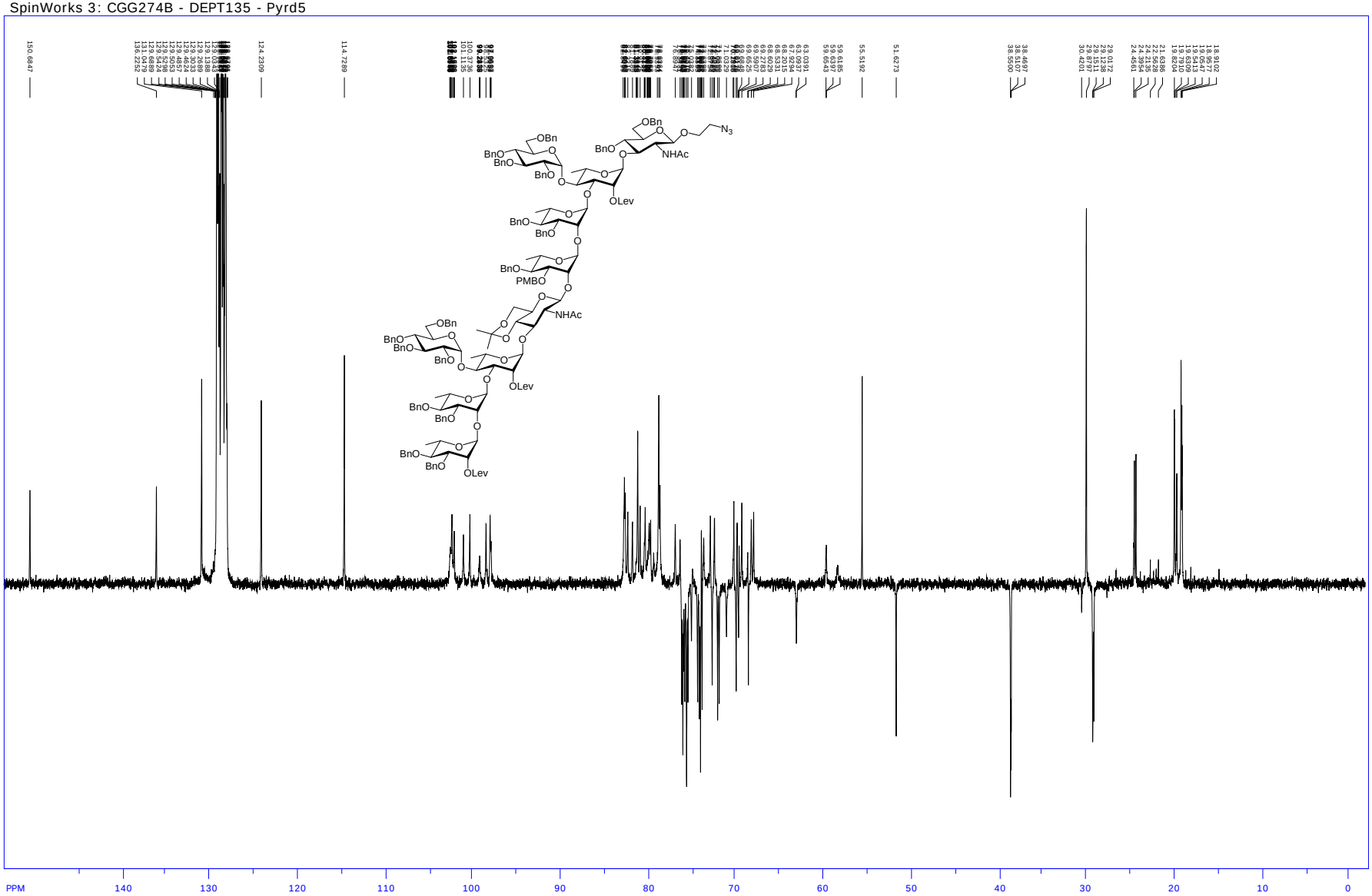
SpinWorks 3: CGG267

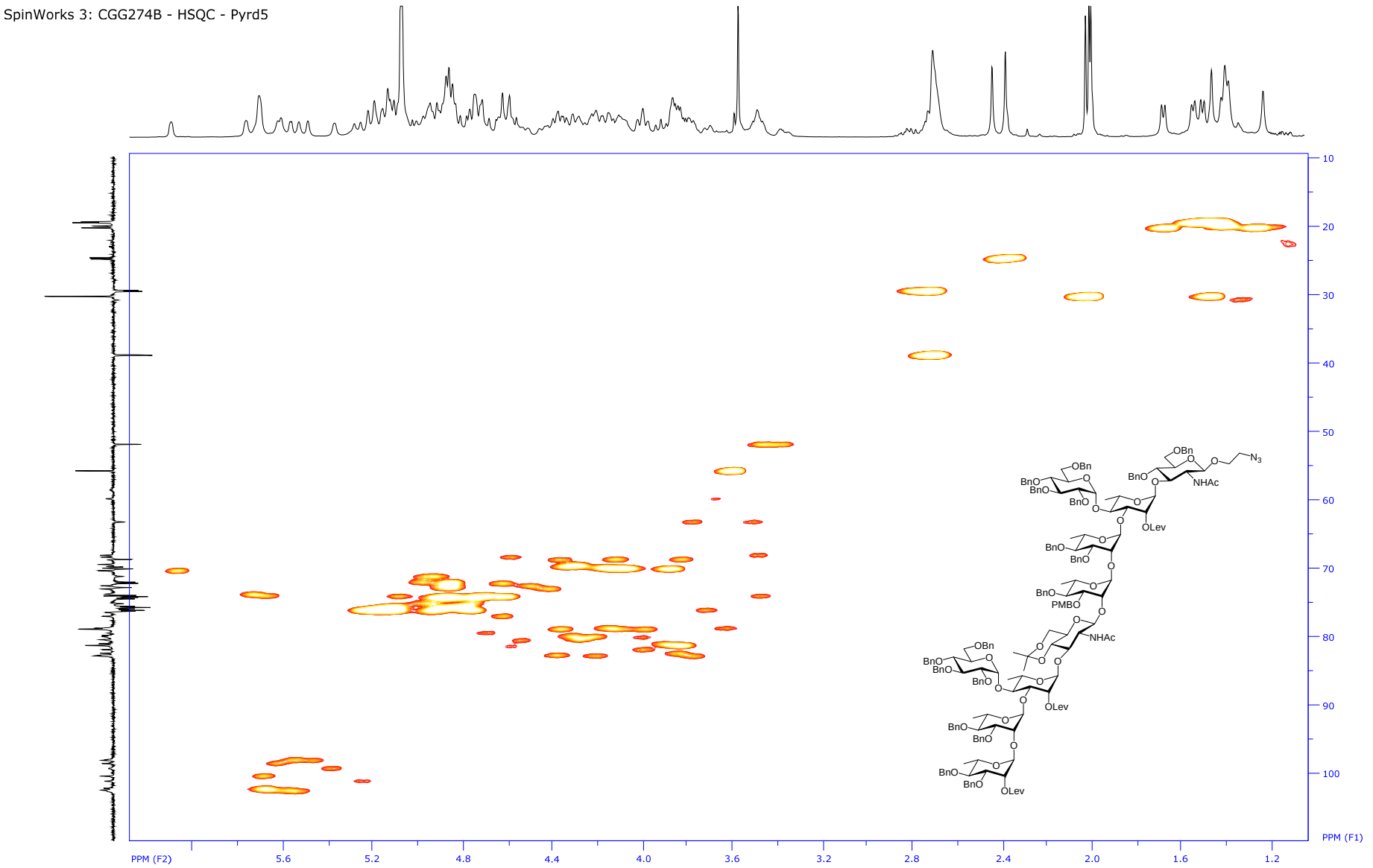


Compound **5**

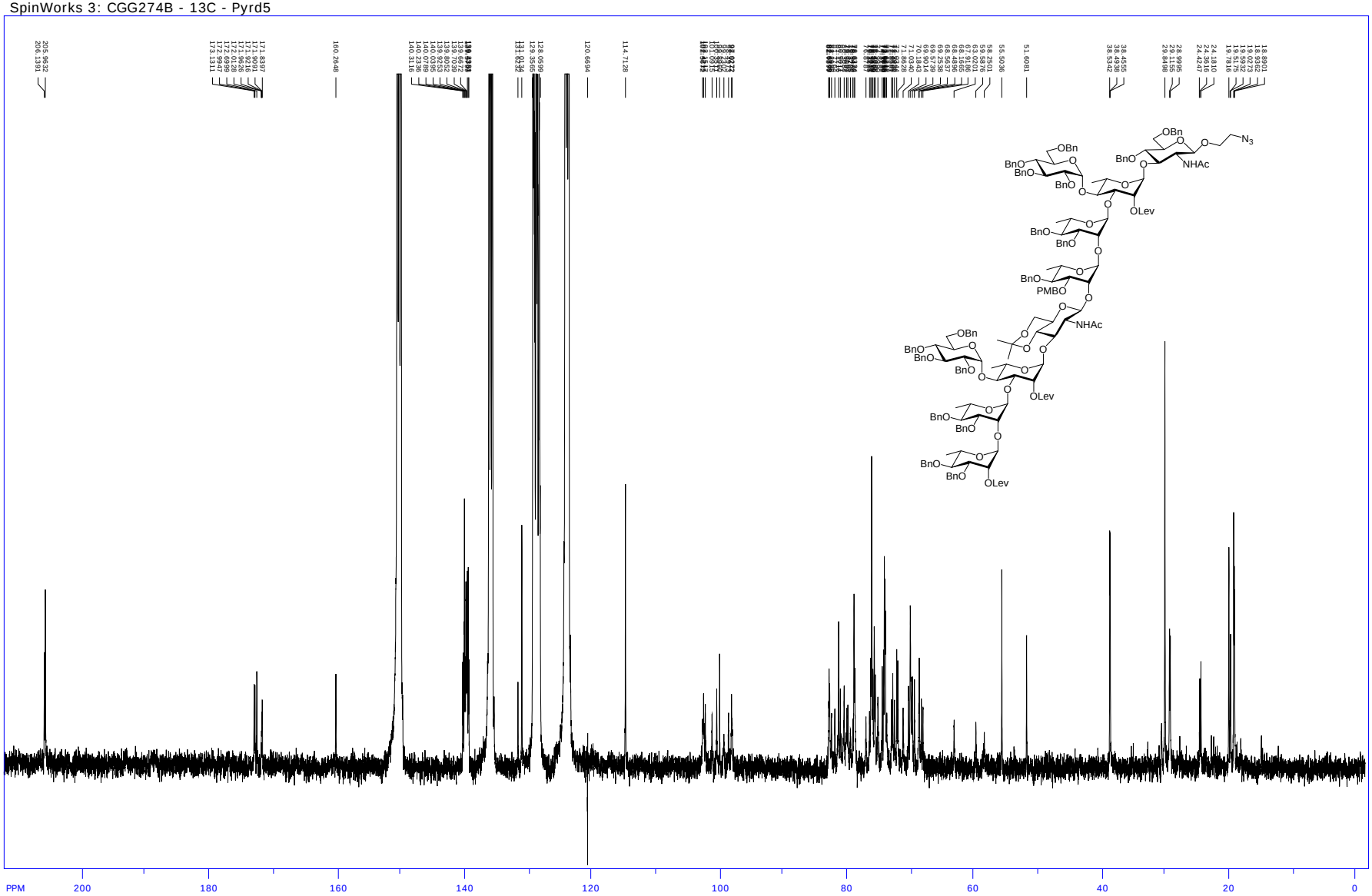

SpinWorks 3: CGG289 - 1H - Pyrd5
9.5583
7.7139
7.1651
6.9779
6.1058
5.7711
5.7117
5.6290
5.6146
5.5696
5.5354
5.4940
5.3752
5.3010
4.4997
4.4716
3.6815
3.5754
3.4903
2.8521
2.7071
2.6440
2.4425
2.3832
2.0261
2.0102
2.0018
1.6786
1.5455
1.5051
1.4642
1.4211
1.4044
1.3877
1.2337
1.599
98.83
2.091
0.893
1.125
1.033
67.77
37.24
9.824
12.31
5.996
9.298
2.775
20.25
2.749
PPM
9.2
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8

SpinWorks 3: CGG274B - DEPT135 - Pyrd5

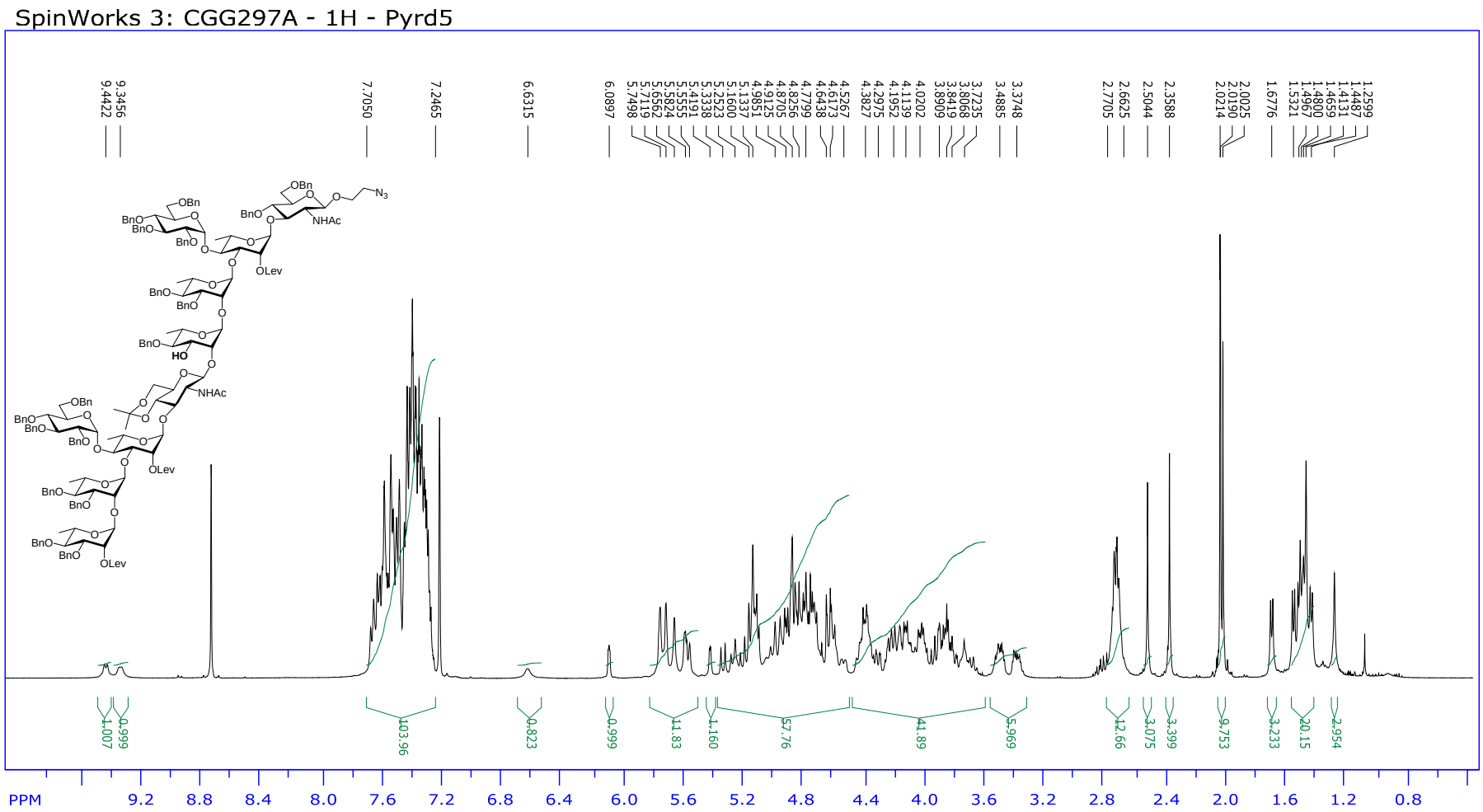



SpinWorks 3: CGG274B - HSQC - Pyrd5
PPM (F2)
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
10
20
30
40
50
60
70
80
90
100
OBn
BnO
NHAc
OLev
PMBO
N3

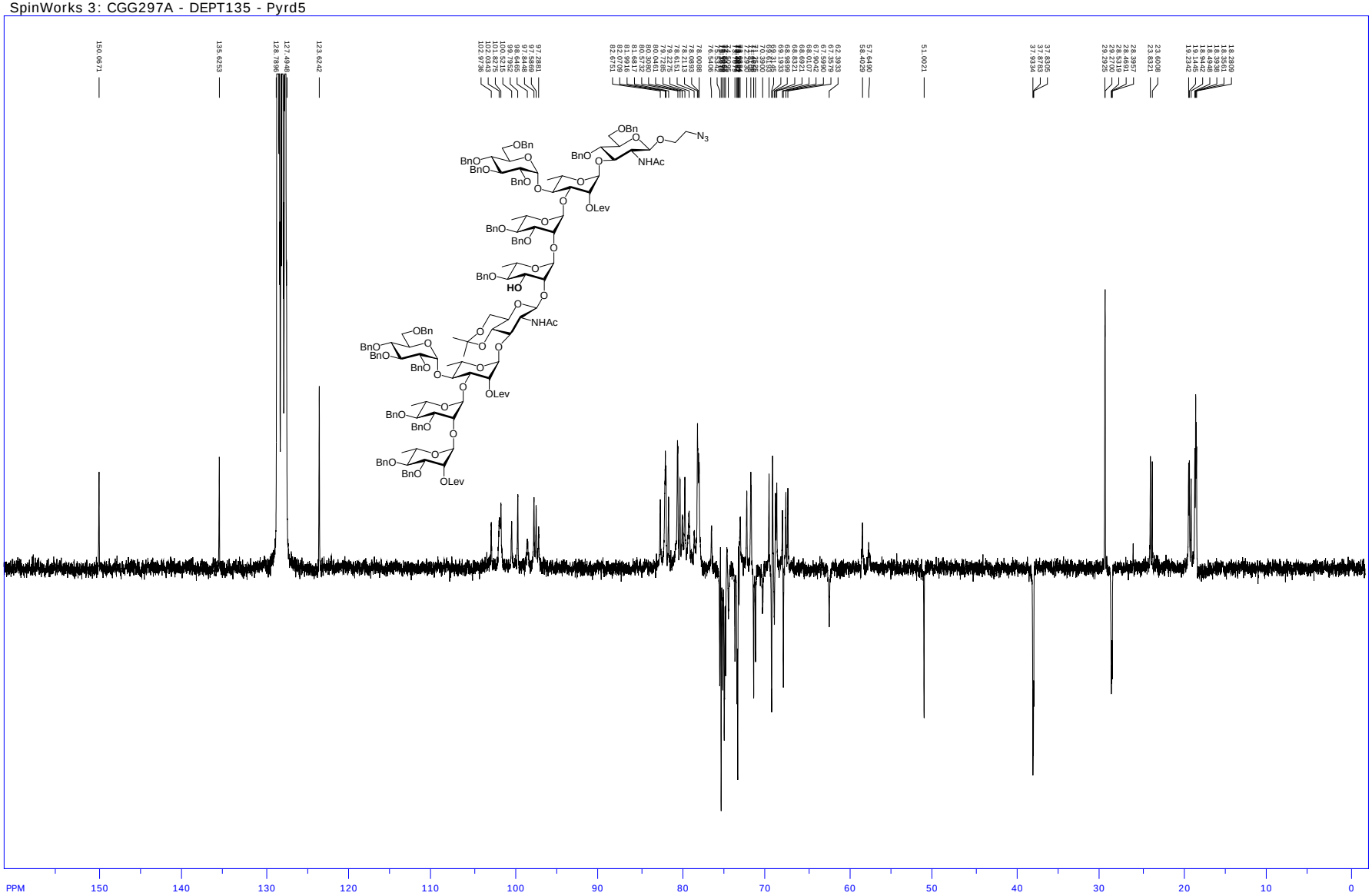
SpinWorks 3: CGG274B - 13C - Pyrd5

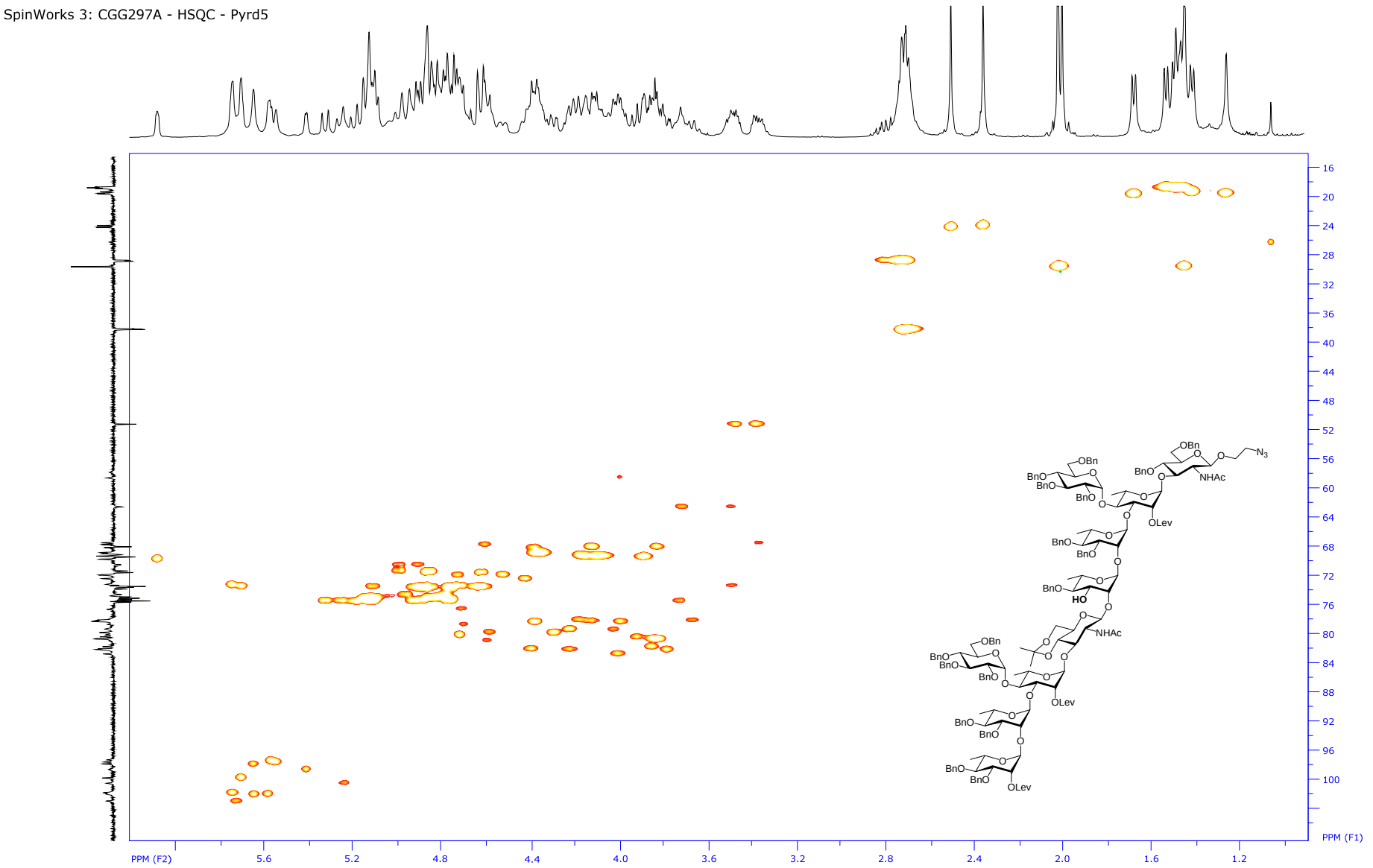


Compound **36**

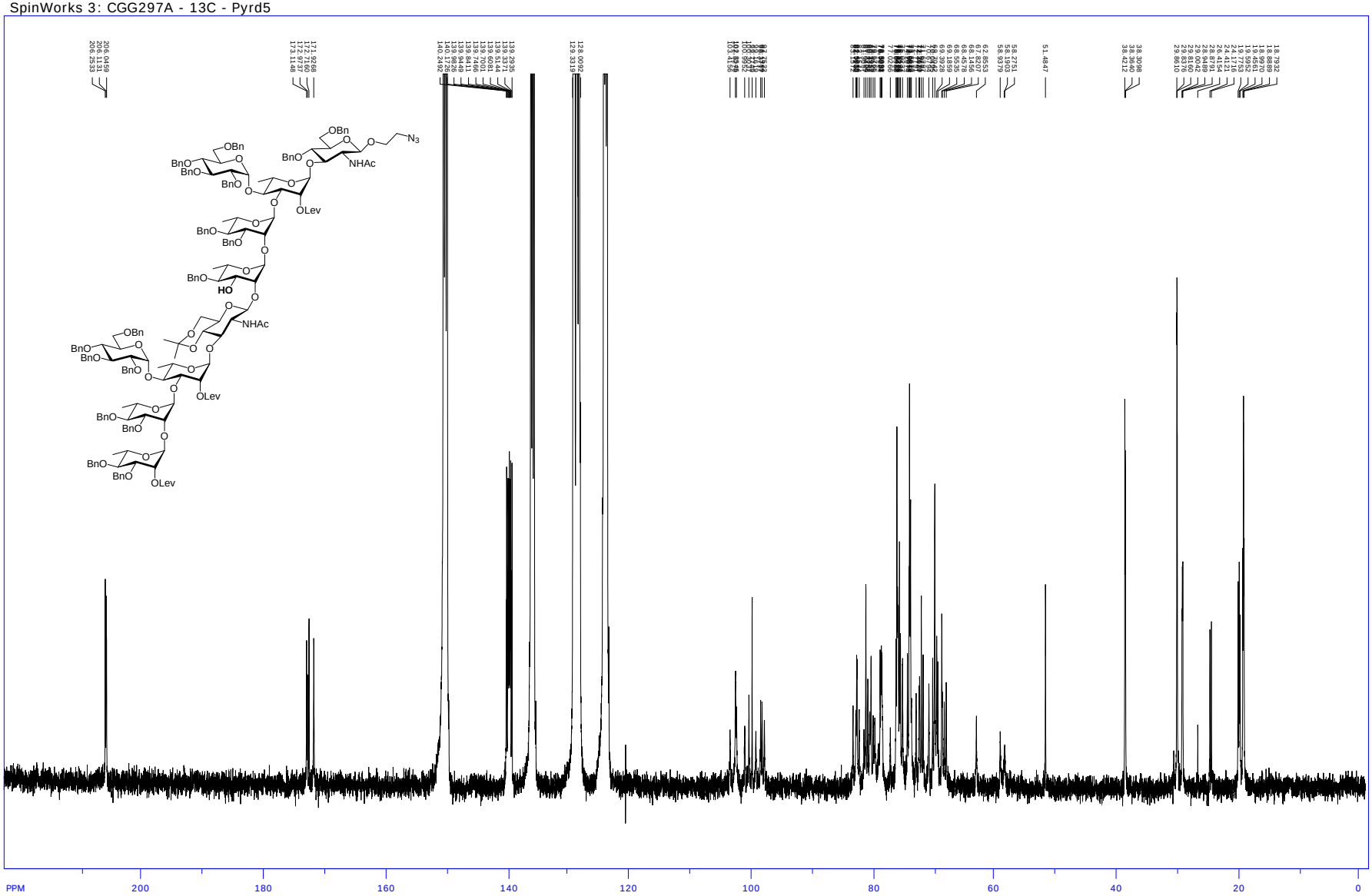

SpinWorks 3: CGG297A - 1H - Pyrd5
9.3456
9.4422
7.7050
7.2465
6.6315
6.0897
5.7498
5.7119
5.6562
5.5824
5.5555
5.4191
5.3338
5.2523
5.1600
5.1337
4.9851
4.9125
4.8705
4.8256
4.7799
4.6438
4.6173
4.5267
4.3827
4.2975
4.1952
4.1139
4.0202
3.8909
3.8419
3.8068
3.7235
3.4885
3.3748
2.7705
2.6625
2.5044
2.3588
2.0214
2.0190
2.0025
1.6776
1.5321
1.4967
1.4800
1.4659
1.4131
1.4487
1.2599
1.007
0.999
103.96
0.823
0.999
1.83
1.160
57.76
41.89
5.969
12.66
3.075
3.399
9.753
3.233
20.15
2.954
PPM
9.2
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8

SpinWorks 3: CGG297A - DEPT135 - Pyrd5

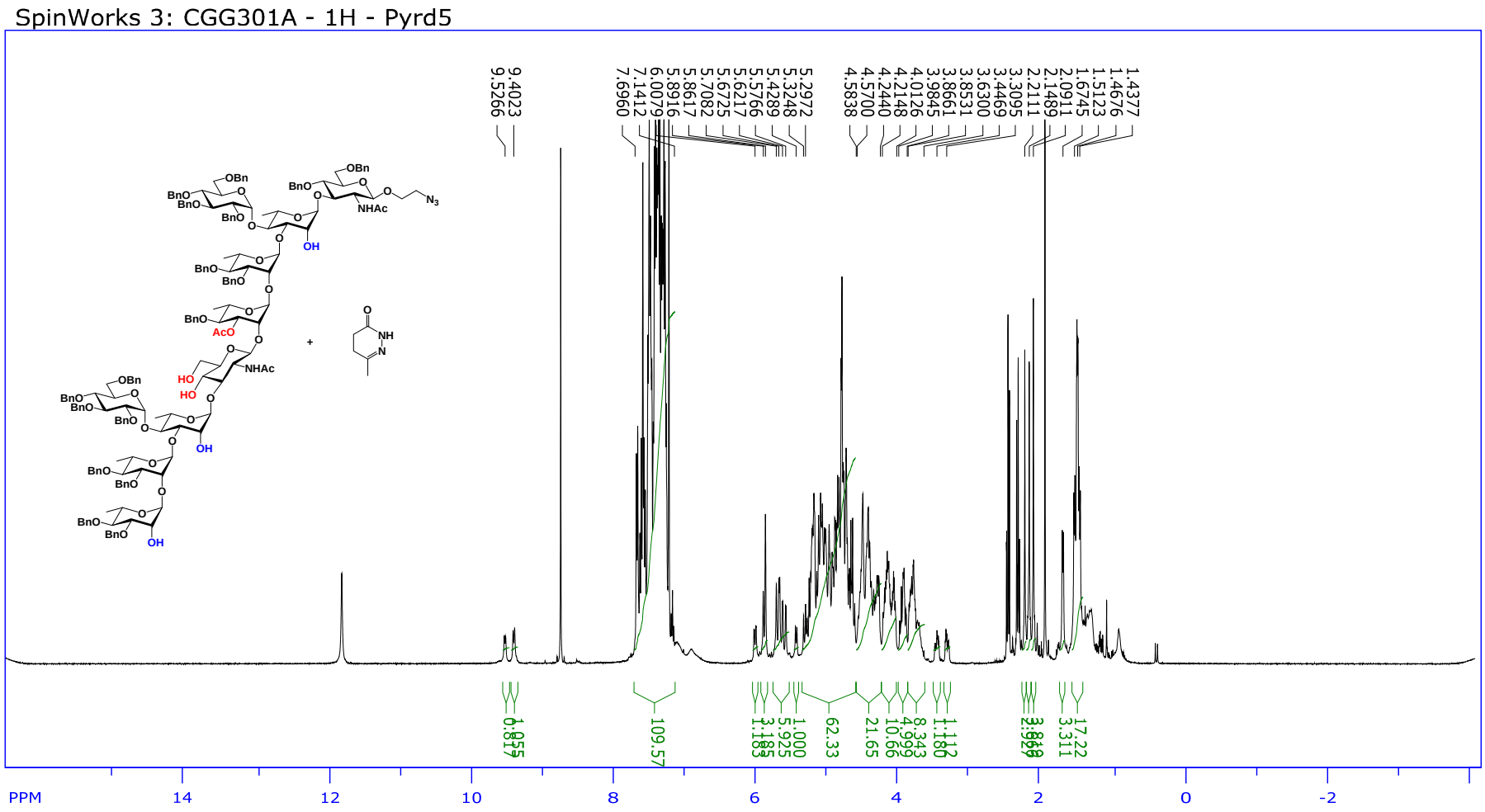



SpinWorks 3: CGG297A - HSQC - Pyrd5
PPM (F2)
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
80
84
88
92
96
100
OBn
BnO
NHAc
OLev
HO
N3

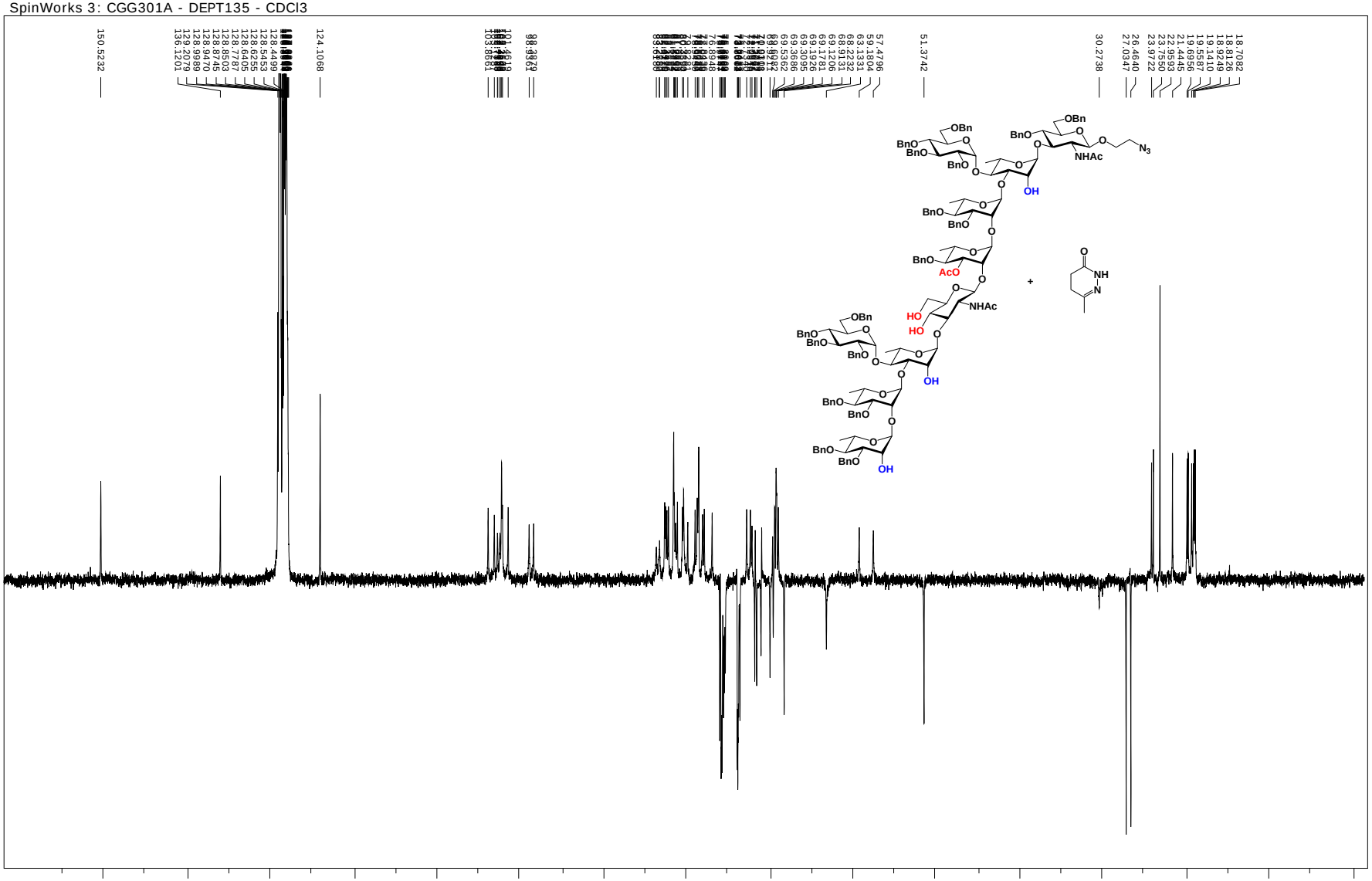
SpinWorks 3: CGG297A - 13C - Pyrd5

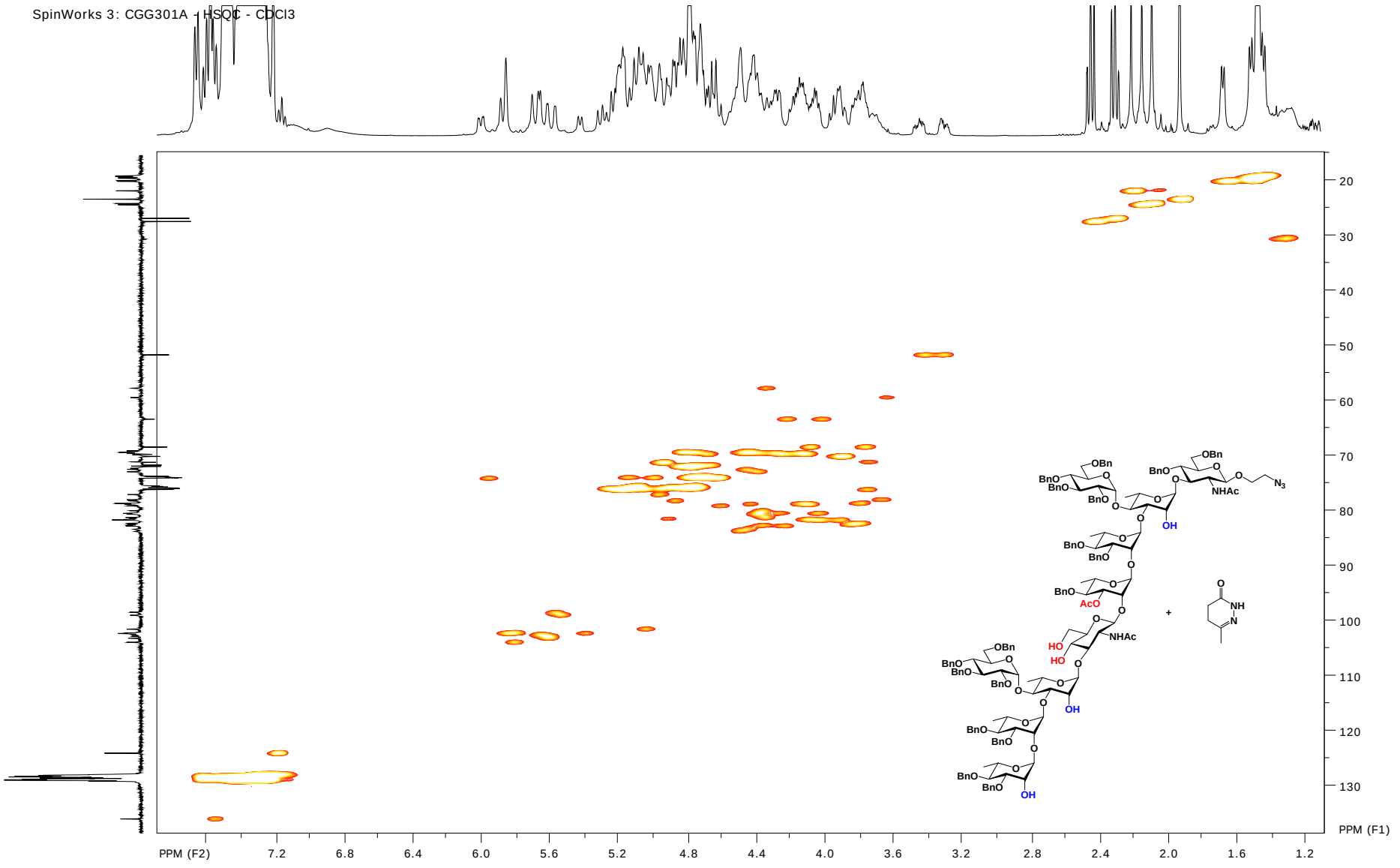


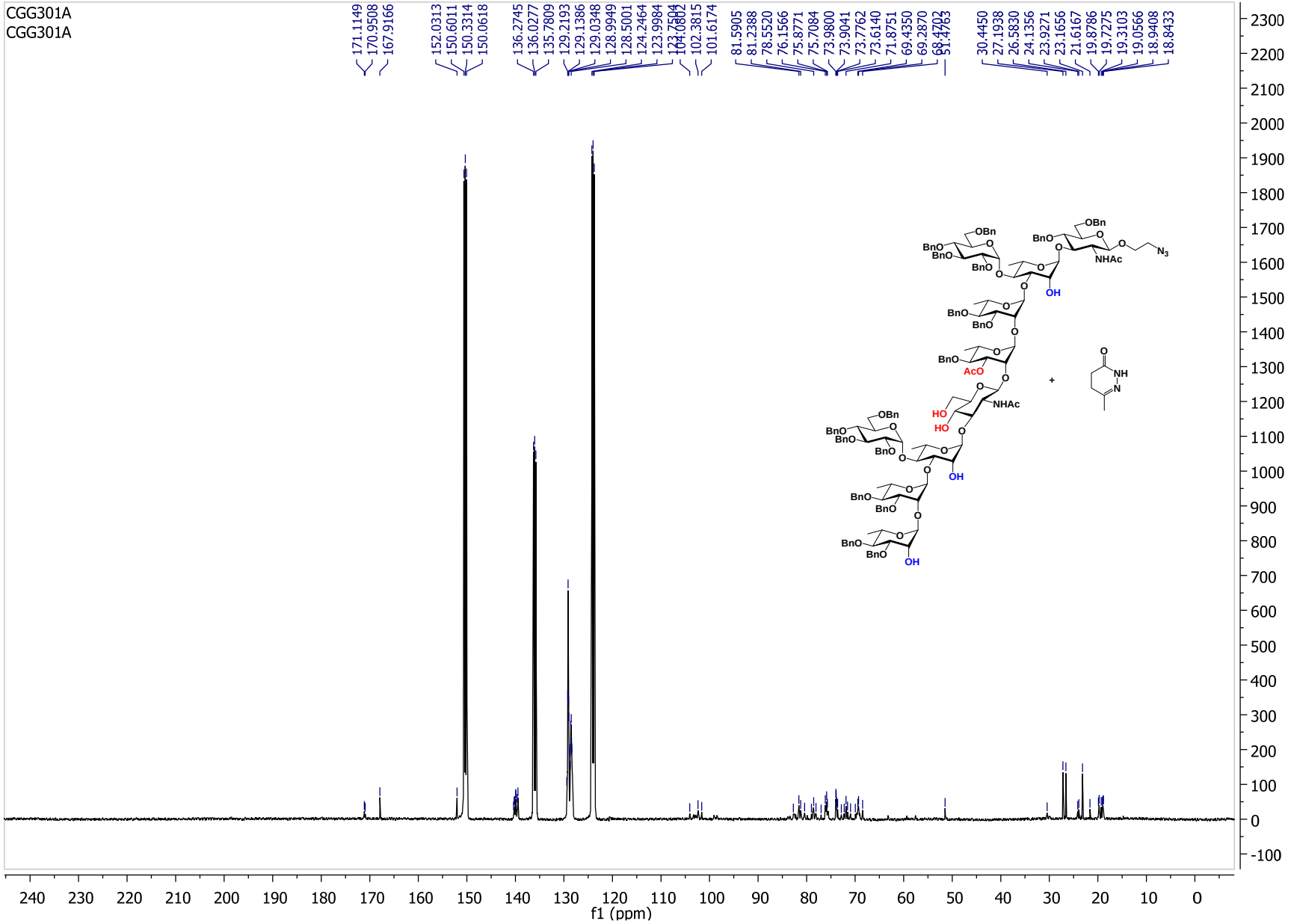
Compound **38**


SpinWorks 3: CGG301A - 1H - Pyrd5
9.4023
9.5266
7.6960
7.1412
6.0079
5.8916
5.8617
5.7082
5.6725
5.5766
5.4289
5.3248
5.2972
4.5838
4.5700
4.2440
4.2148
4.0126
3.9845
3.8661
3.8531
3.6300
3.4469
3.3095
2.2111
2.1489
2.0911
1.6745
1.5123
1.4676
1.4377
0.817
109.57
1.185
5.925
1.000
62.33
21.65
10.66
8.343
1.180
17.22
3.311
PPM
14
12
10
8
6
4
2
0
-2

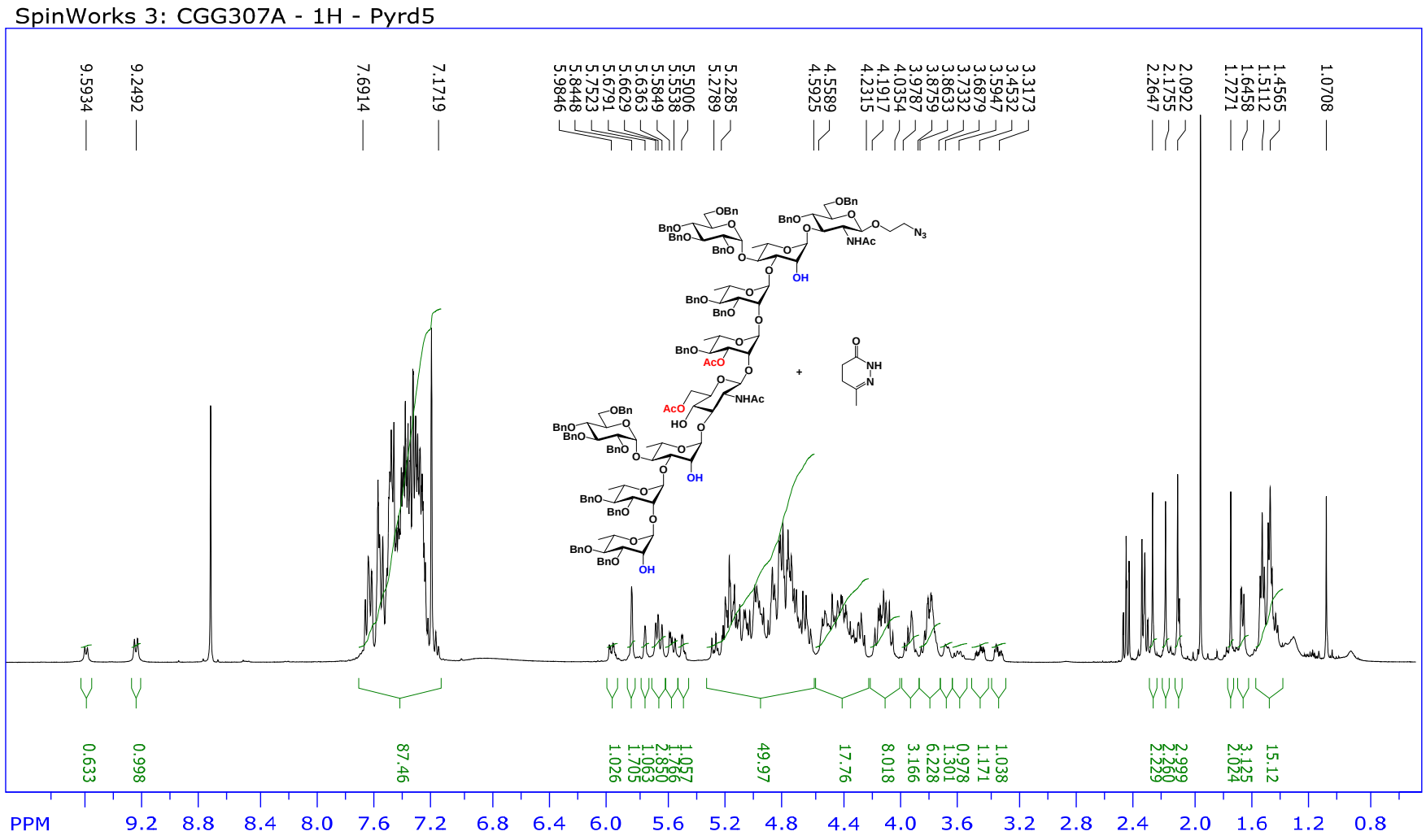
SpinWorks 3: CGG301A - DEPT135 - CDCl3

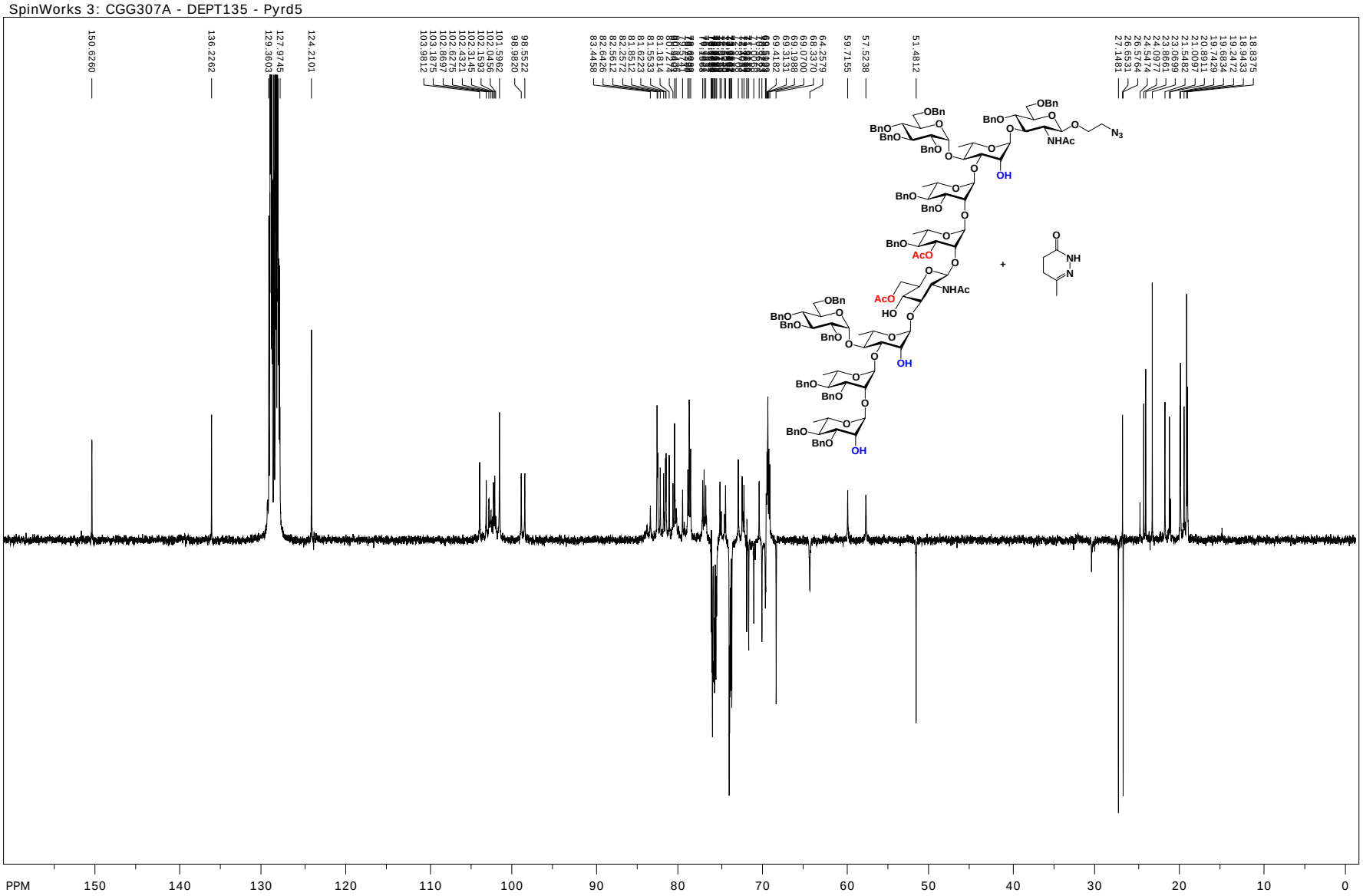


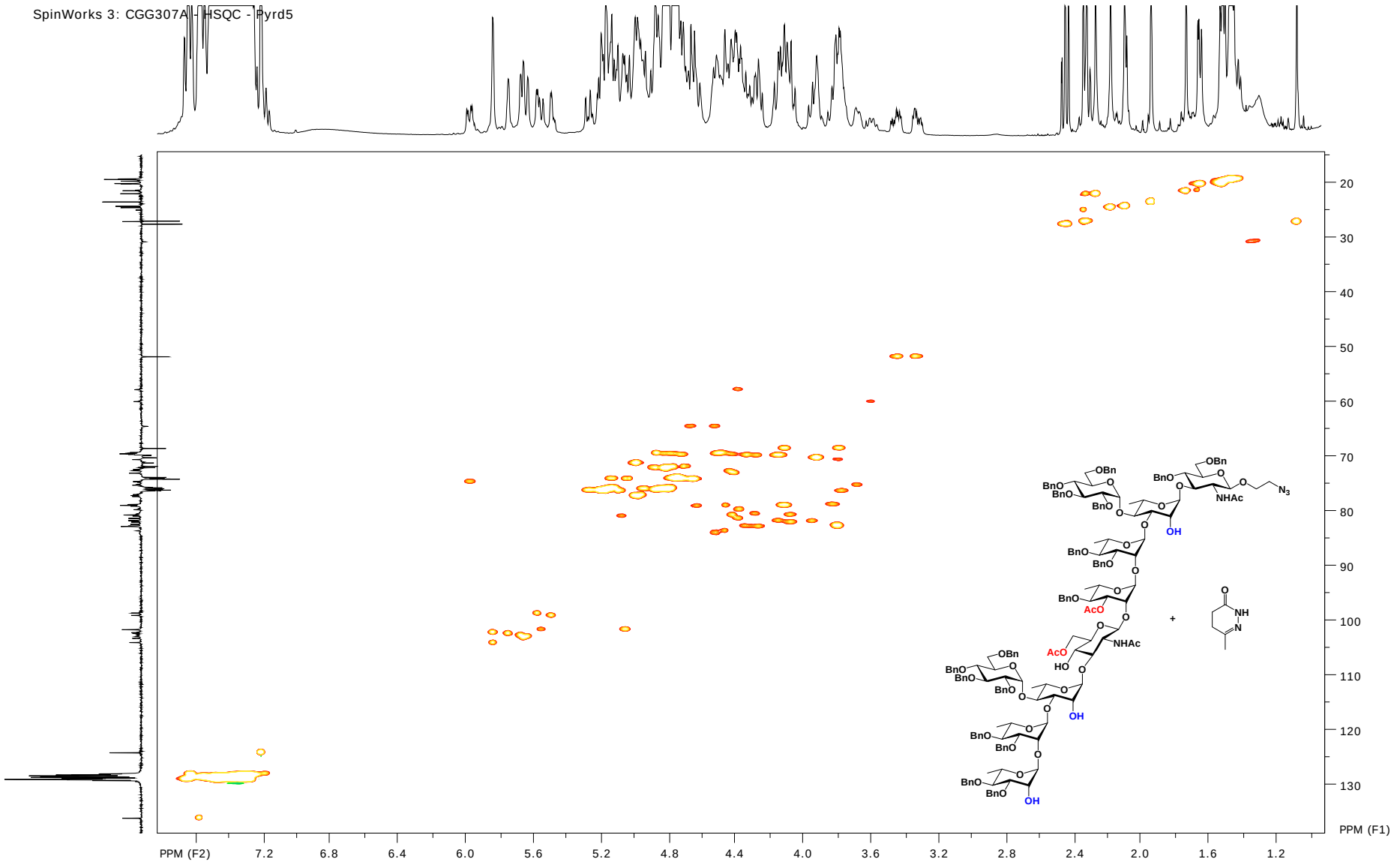

SpinWorks 3: CGG301A - HSQC - CDCl3
PPM (F2)
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
NHAc
N3
OH
AcO
HO
NH
N
+

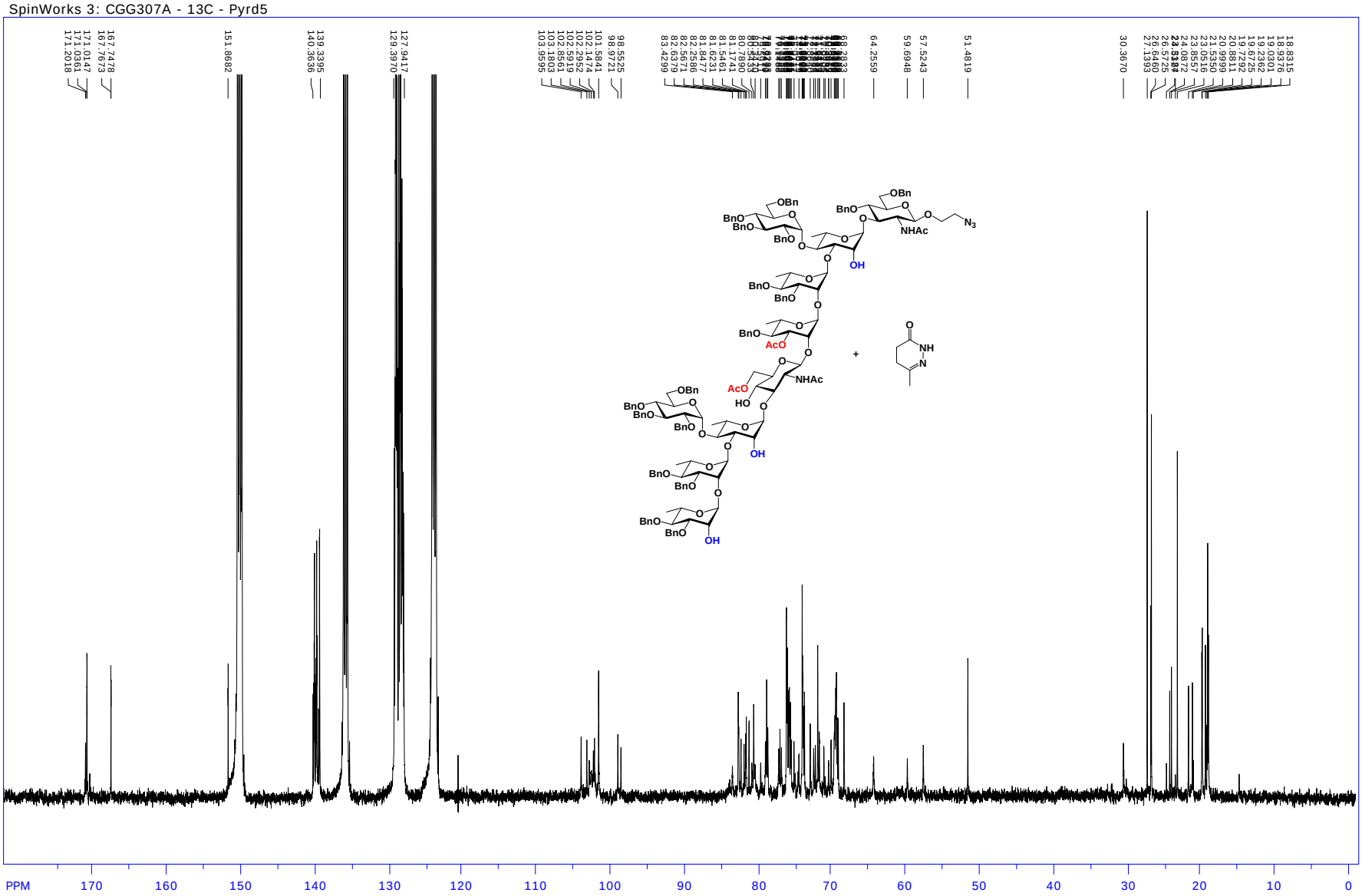

CGG301A
CGG301A
171.1149
170.9508
167.9166
152.0313
150.6011
150.3314
150.0618
136.2745
136.0277
135.7809
129.2193
129.1386
129.0348
128.9949
128.5001
124.2464
123.9984
104.0802
102.3815
101.6174
81.5905
81.2388
78.5520
76.1566
75.8771
75.7084
73.9800
73.9041
73.7762
73.6140
71.8751
69.4350
69.2870
68.4702
51.4763
30.4450
27.1938
26.5830
24.1356
23.9271
23.1656
21.6167
19.8786
19.7275
19.3103
19.0566
18.9408
18.8433
f1 (ppm)

Compound **39**

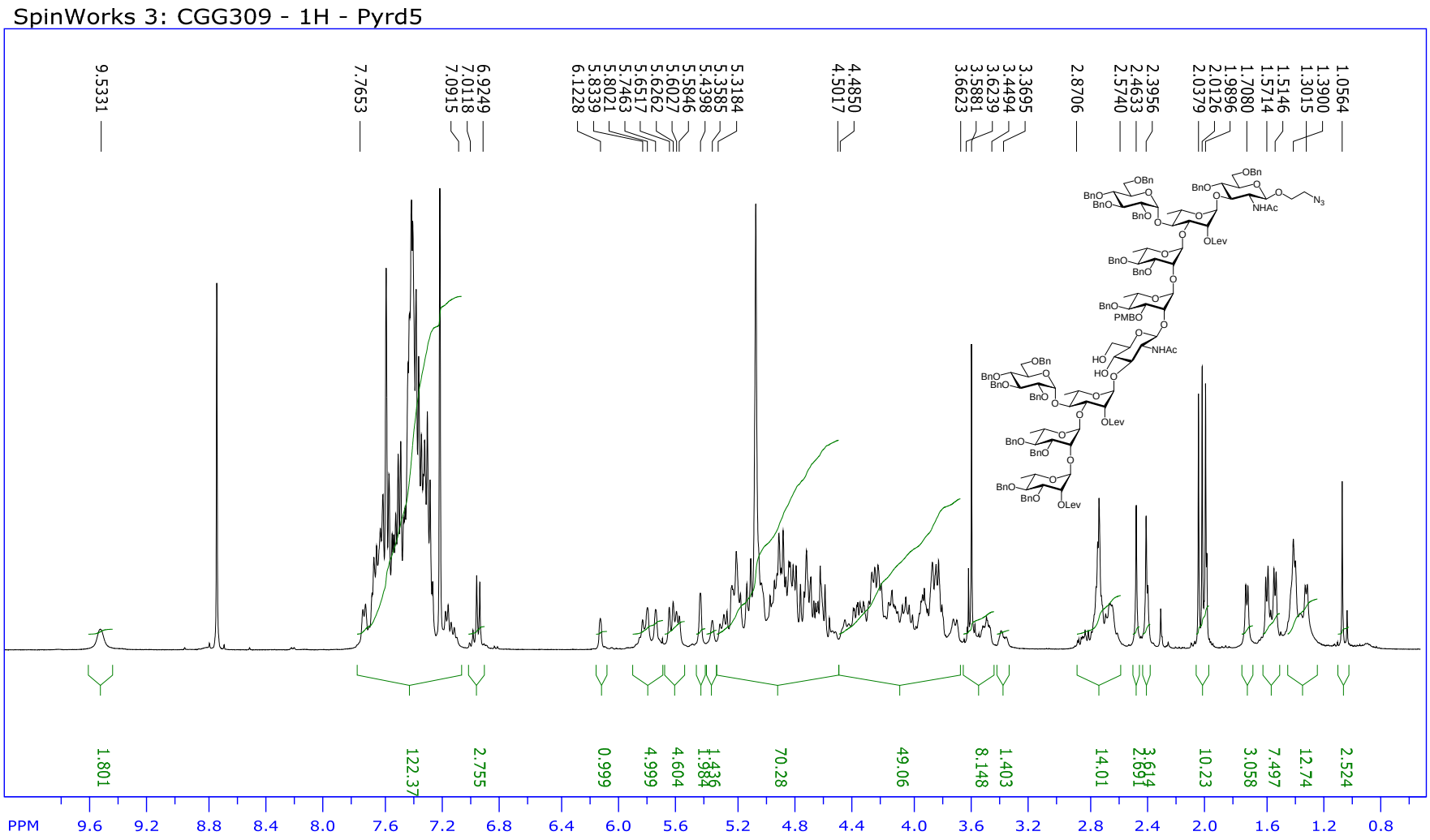

SpinWorks 3: CGG307A - 1H - Pyrd5
9.5934
9.2492
7.6914
7.1719
5.9846
5.8448
5.7523
5.6791
5.6629
5.6363
5.5849
5.5538
5.5006
5.2789
5.2285
4.5925
4.5589
4.2315
4.1917
4.0354
3.9787
3.8759
3.8633
3.7332
3.6879
3.5947
3.4532
3.3173
2.2647
2.1755
2.0922
1.7271
1.6458
1.5112
1.4565
1.0708
0.633
0.998
87.46
1.026
1.705
1.063
2.850
2.766
1.957
49.97
17.76
8.018
3.166
6.228
1.301
0.978
1.171
1.038
2.229
2.260
2.999
2.024
3.125
15.12
PPM
9.2
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8


SpinWorks 3: CGG307A - DEPT135 - Pyrd5
150.6280
136.2262
129.3603
127.9745
124.2101
103.9812
103.1875
102.8697
102.6275
102.4321
102.3145
102.1553
101.5962
98.9820
98.5522
83.4458
82.6426
82.5612
82.2572
81.8512
81.6622
81.5533
81.1814
59.7155
57.5238
51.4812
27.1481
26.6531
26.5764
24.5974
23.8651
23.0699
21.5482
21.0097
20.8911
19.7429
19.6834
19.2472
18.9433
18.8375
PPM
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

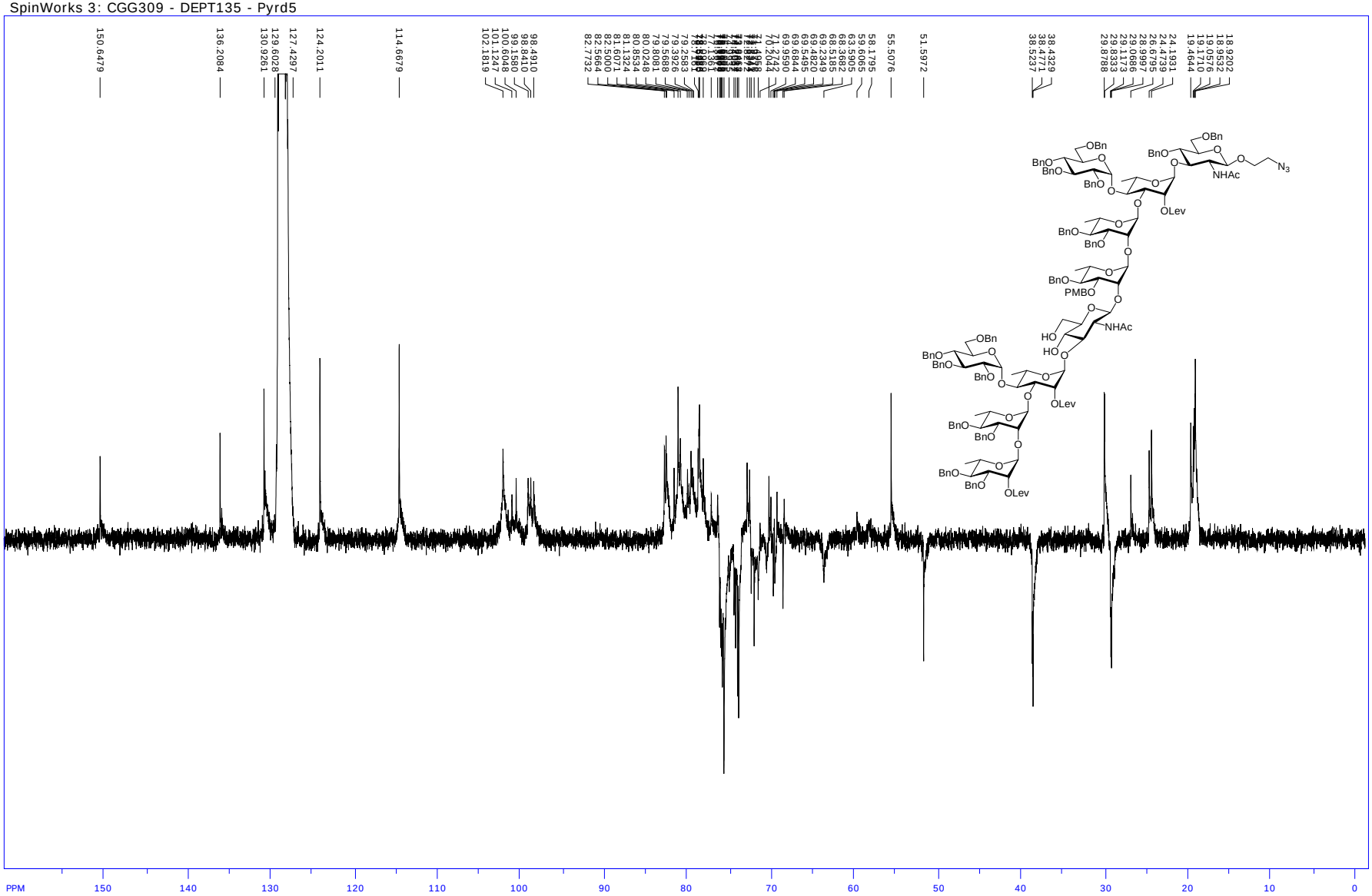

SpinWorks 3: CGG307A - HSQC - Pyrd5
PPM (F2)
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
PPM (F1)
20
30
40
50
60
70
80
90
100
110
120
130
OBn
BnO
NHAc
N3
OH
AcO
HO
NH
N
O

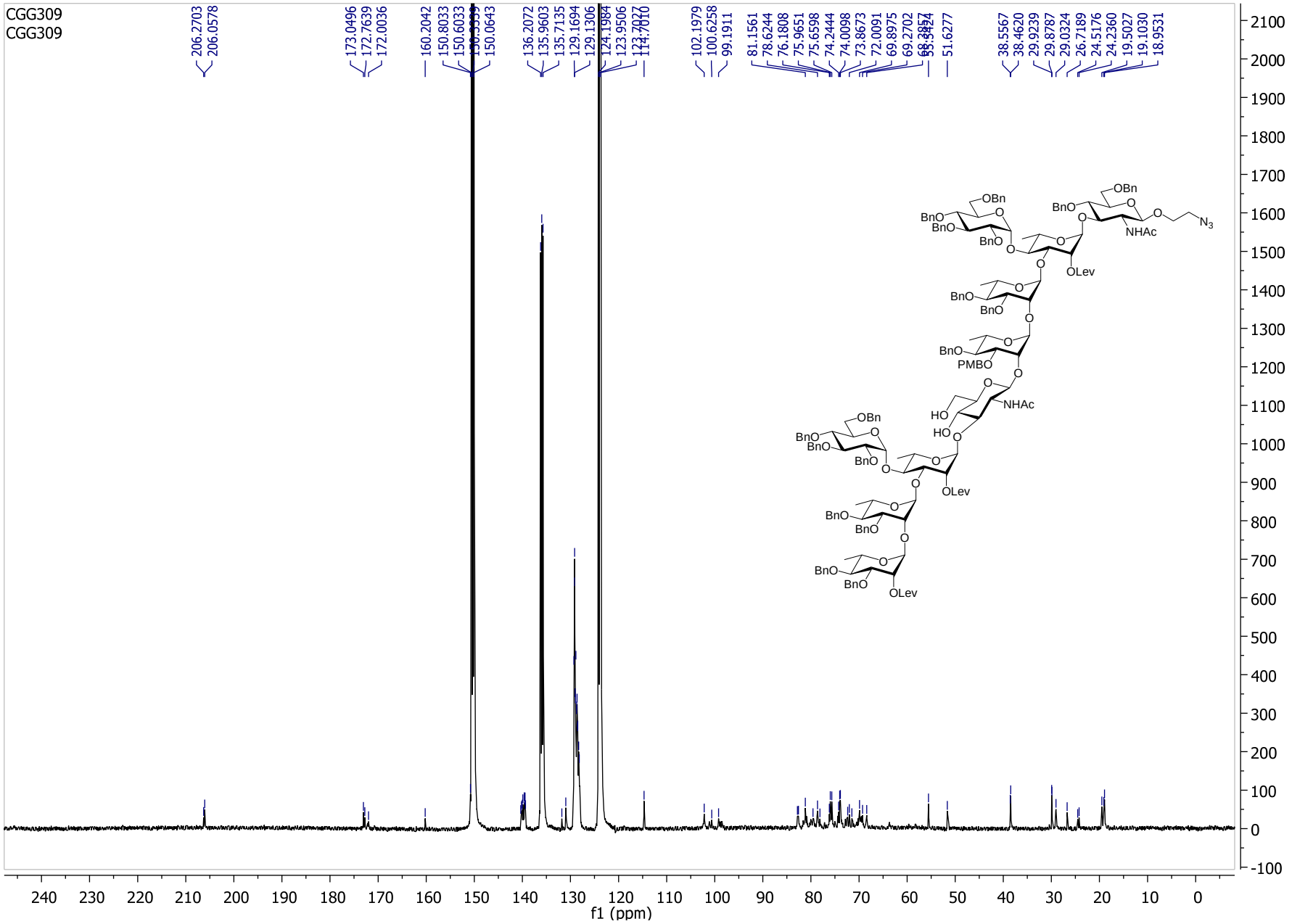

SpinWorks 3: CGG307A - 13C - Pyrd5
171.2018
171.0361
171.0147
167.7673
167.7478
151.8682
140.3636
139.3395
129.3970
127.9417
103.1803
102.8561
102.5919
102.2952
102.1474
101.5841
98.9721
98.5525
83.4299
82.6379
82.2596
81.8477
81.6231
81.5461
81.1741
80.7890
64.2559
59.6948
57.5243
51.4819
30.3670
25.1393
18.8315
18.9376
19.0301
19.2362
19.6725
20.9989
21.5350
23.0516
23.8557
24.0872
OBn
BnO
NHAc
N3
OH
AcO
HO
NH
N
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Compound **40**

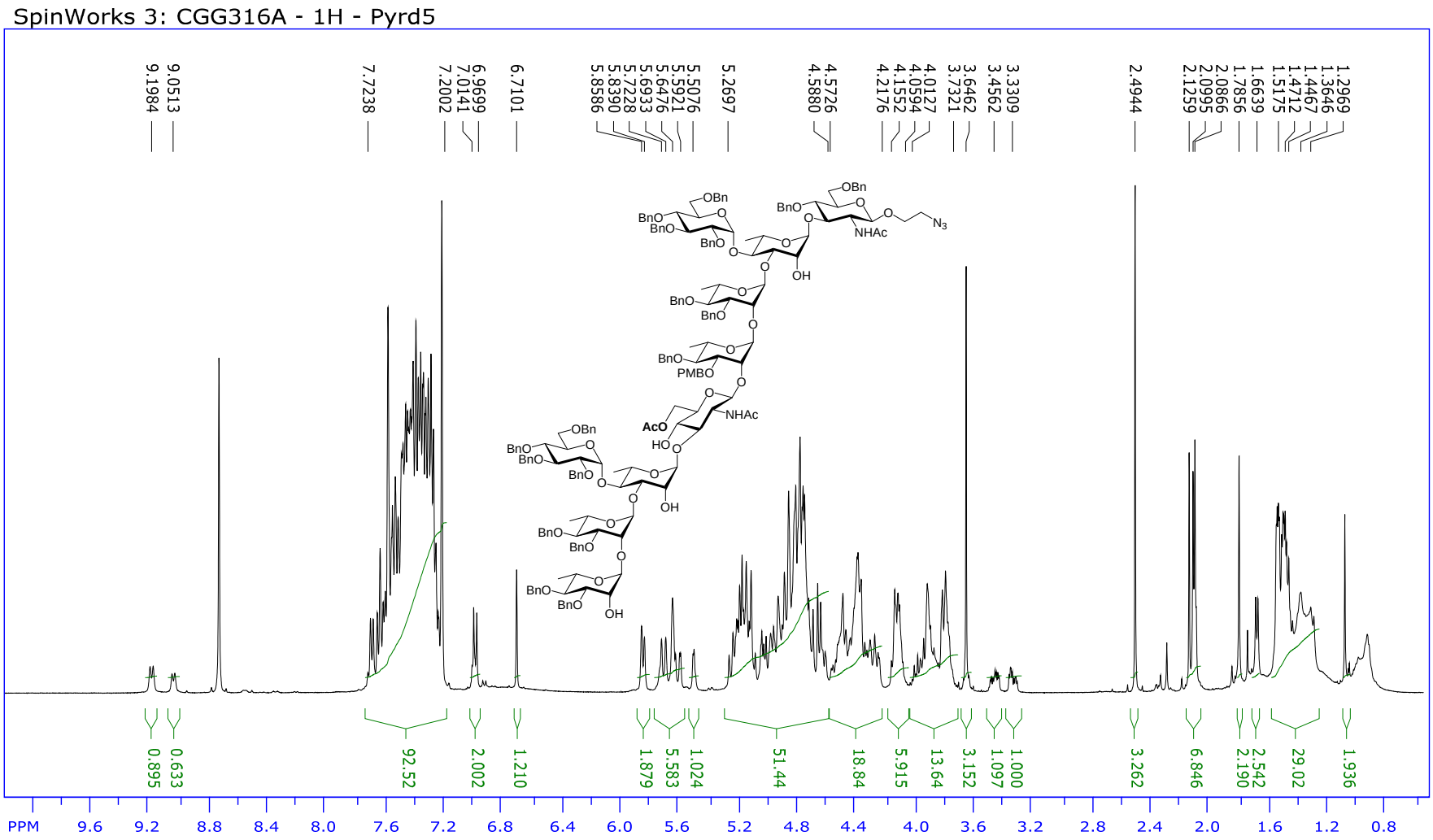

SpinWorks 3: CGG309 - 1H - Pyrd5
9.5331
7.7653
7.0915
7.0118
6.9249
6.1228
5.8339
5.8021
5.7463
5.6517
5.6262
5.6027
5.5846
5.4398
5.3585
5.3184
4.5017
4.4850
3.6623
3.5881
3.6239
3.4494
3.3695
2.8706
2.5740
2.4633
2.3956
2.0379
2.0126
1.9896
1.7080
1.5714
1.5146
1.3015
1.3900
1.0564
1.801
122.37
2.755
0.999
4.999
4.604
1.436
1.984
70.28
49.06
8.148
1.403
14.01
3.614
2.891
10.23
3.058
7.497
12.74
2.524
PPM
9.6
9.2
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8

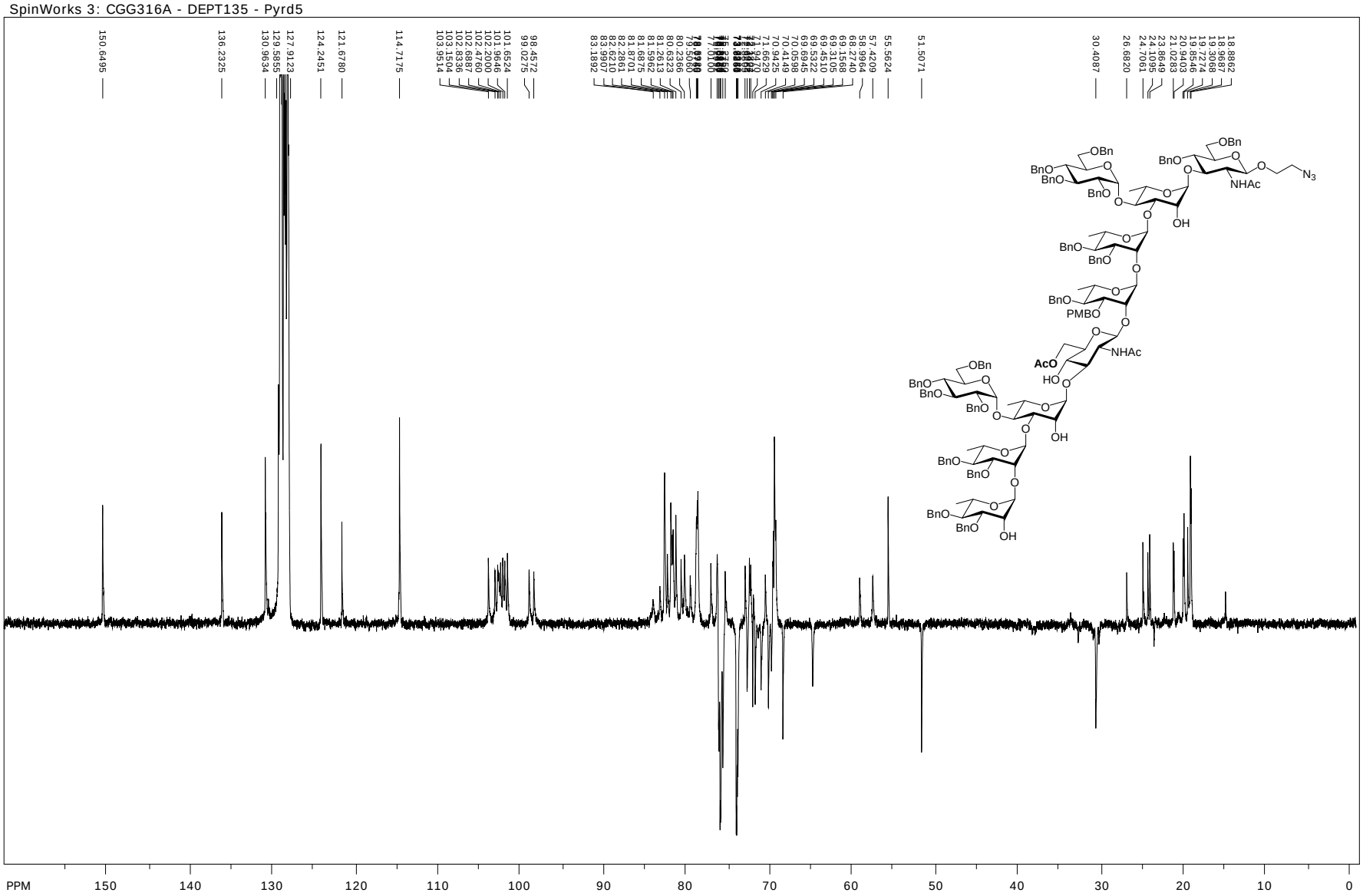
SpinWorks 3: CGG309 - DEPT135 - Pyrd5

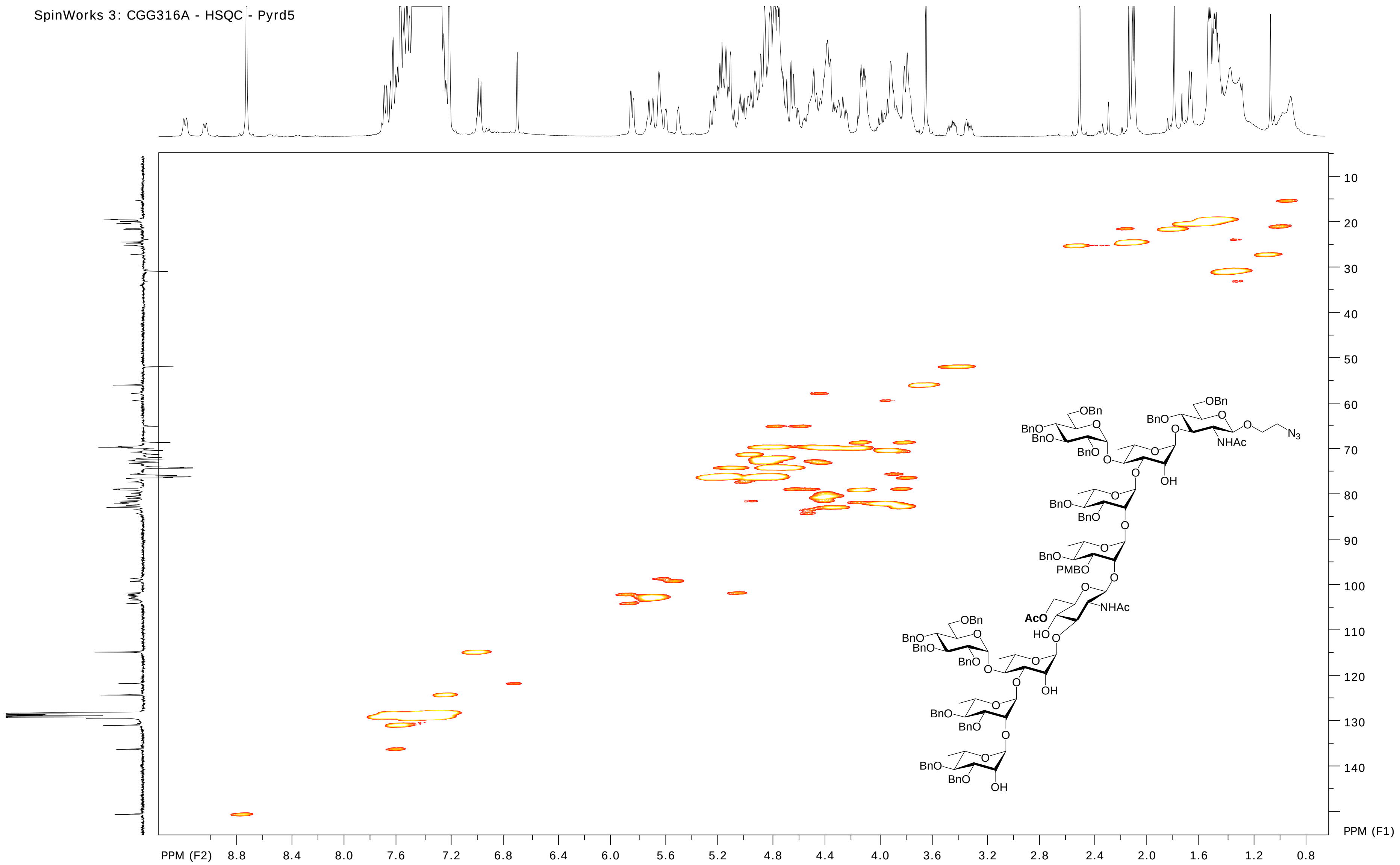



CGG309
CGG309
206.2703
206.0578
173.0496
172.7639
172.0036
160.2042
150.8033
150.6033
150.0643
136.2072
135.9603
135.7135
129.1694
129.1306
124.1984
123.9506
102.1979
100.6258
99.1911
81.1561
78.6244
76.1808
75.9651
75.6598
74.2444
74.0098
73.8673
72.0091
69.8975
69.2702
51.6277
38.5567
38.4620
29.9239
29.8787
29.0324
26.7189
24.5176
24.2360
19.5027
19.1030
18.9531
f1 (ppm)

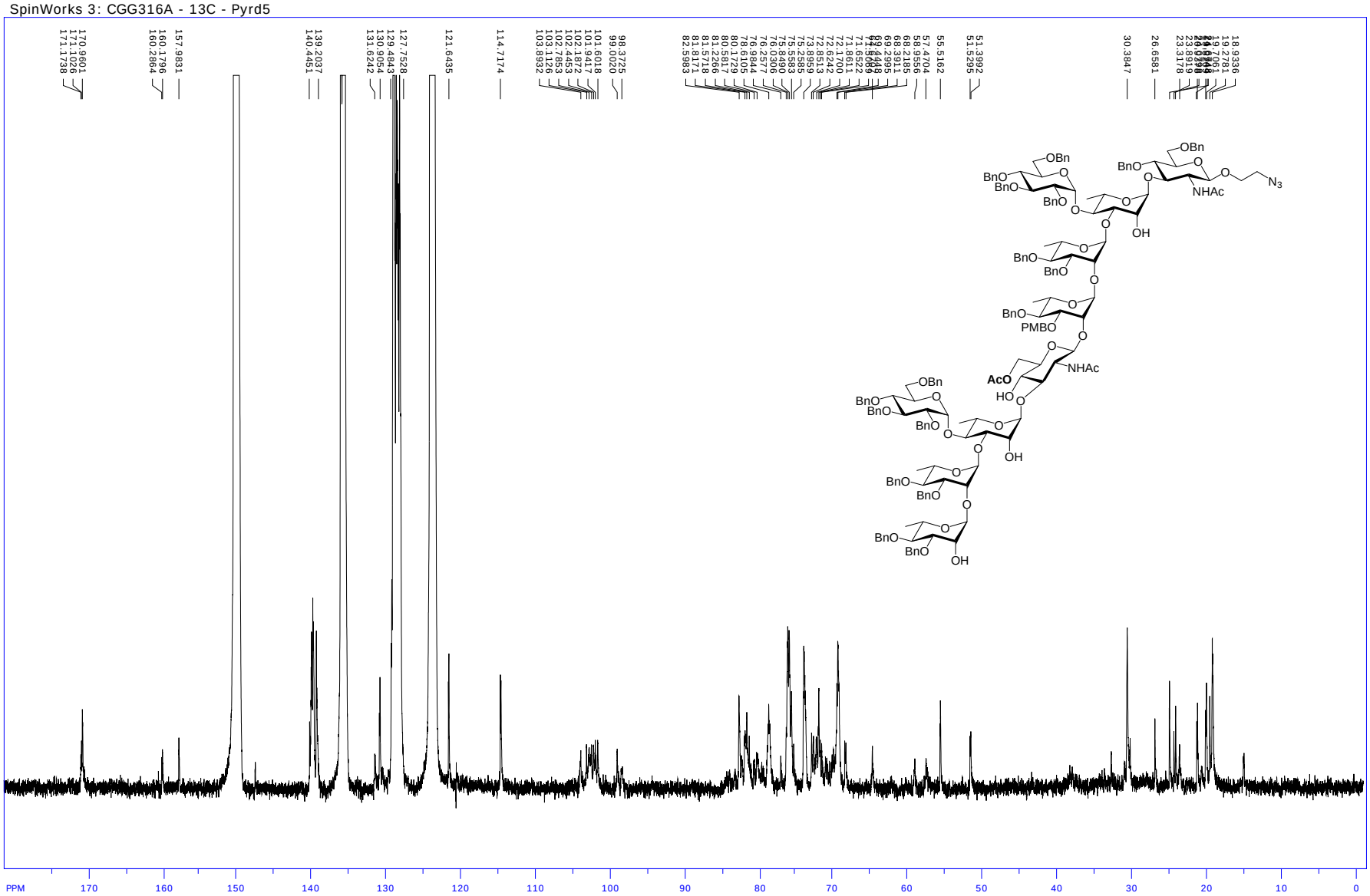
Compound **41**


SpinWorks 3: CGG316A - 1H - Pyrd5
9.1984
9.0513
7.7238
7.2002
7.0141
6.9699
6.7101
5.8586
5.8390
5.7228
5.6933
5.6476
5.5921
5.5076
5.2697
4.5880
4.5726
4.2176
4.1552
4.0594
4.0127
3.7321
3.6462
3.4562
3.3309
2.4944
2.1259
2.0995
2.0866
1.7856
1.6639
1.5175
1.4712
1.4467
1.3646
1.2969
0.895
0.633
92.52
2.002
1.210
1.879
5.583
1.024
51.44
18.84
5.915
13.64
3.152
1.097
1.000
3.262
6.846
2.190
2.542
29.02
1.936
PPM
9.6
9.2
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8

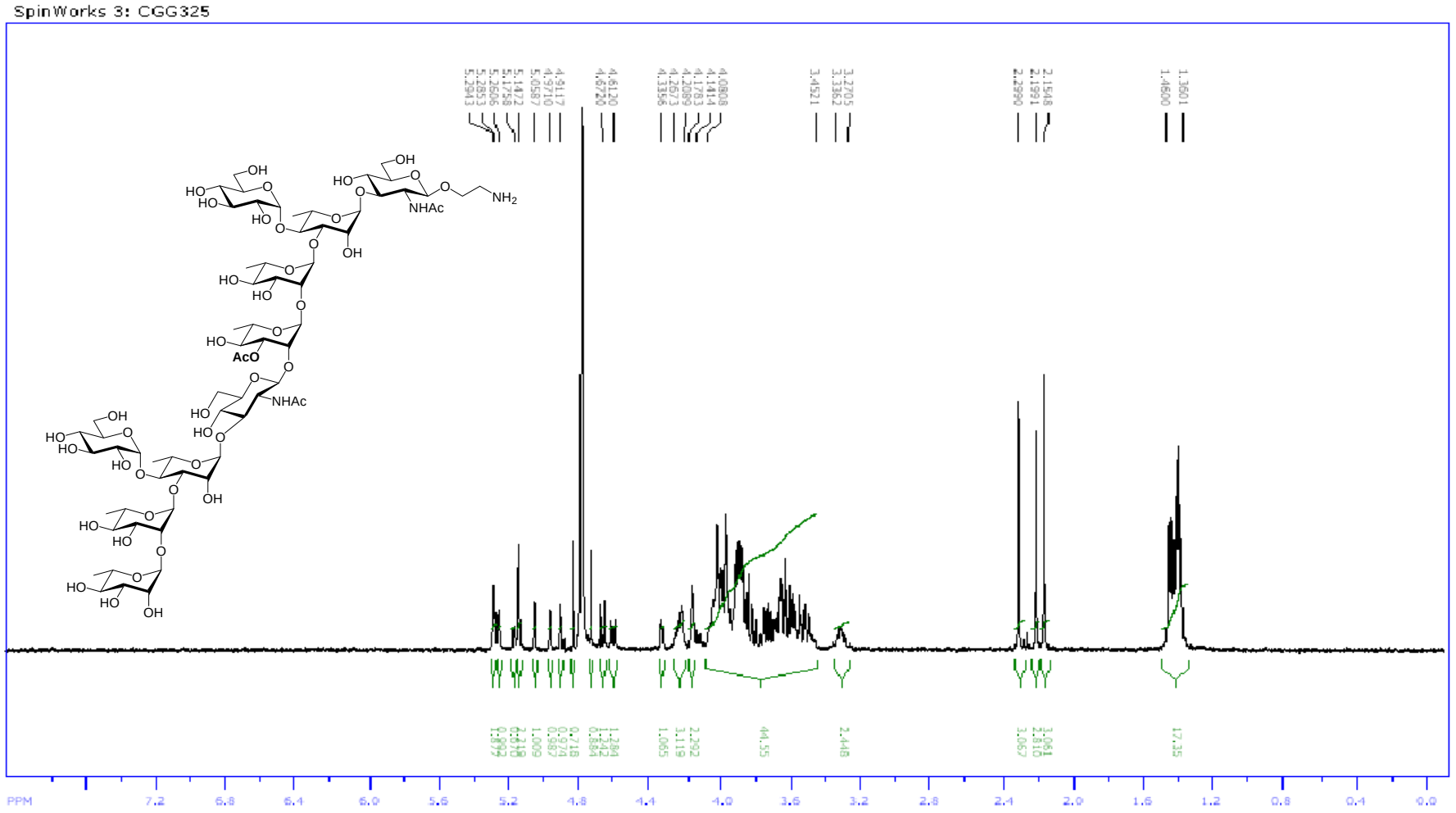

SpinWorks 3: CGG316A - DEPT135 - Pyrd5
PPM
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

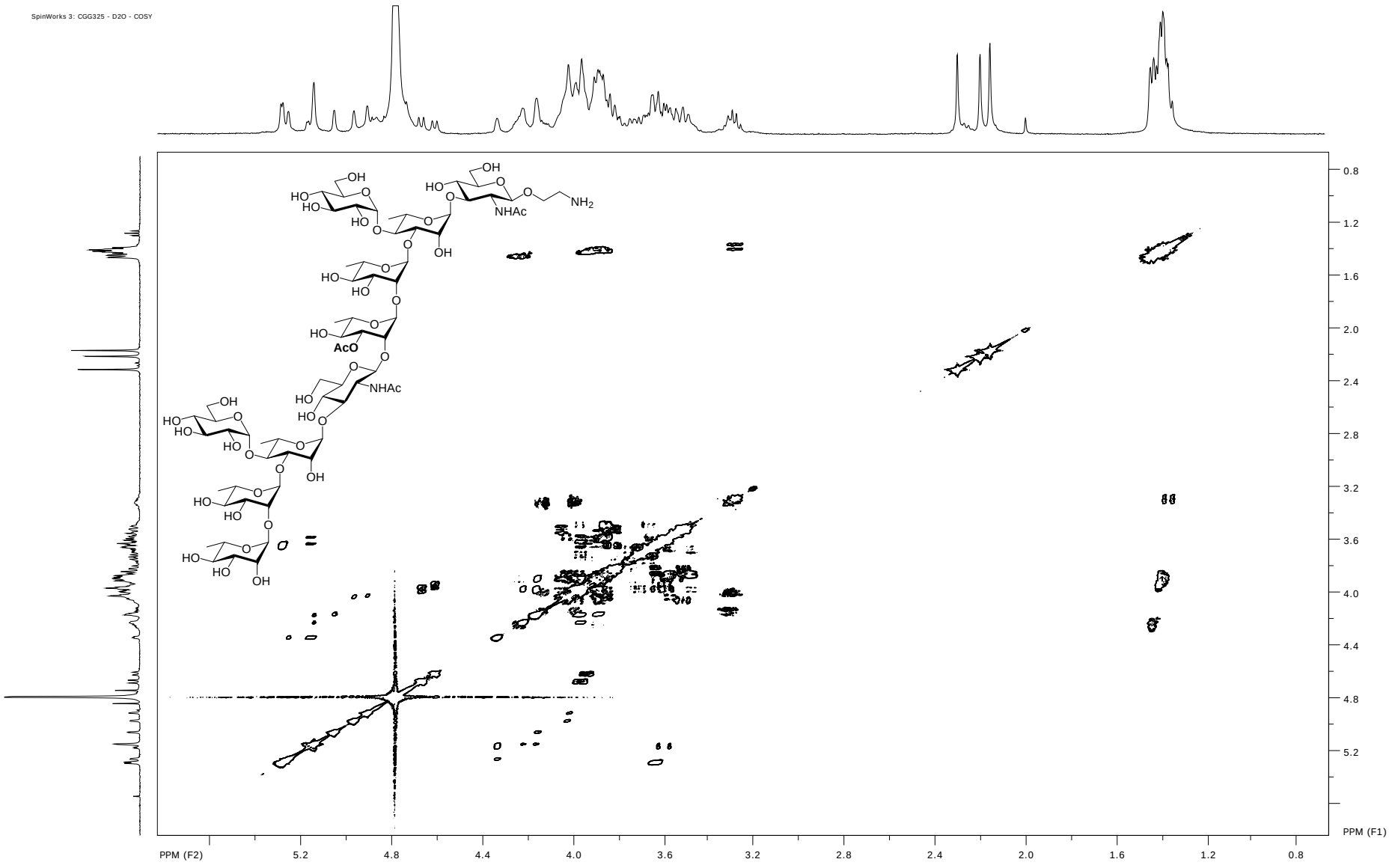


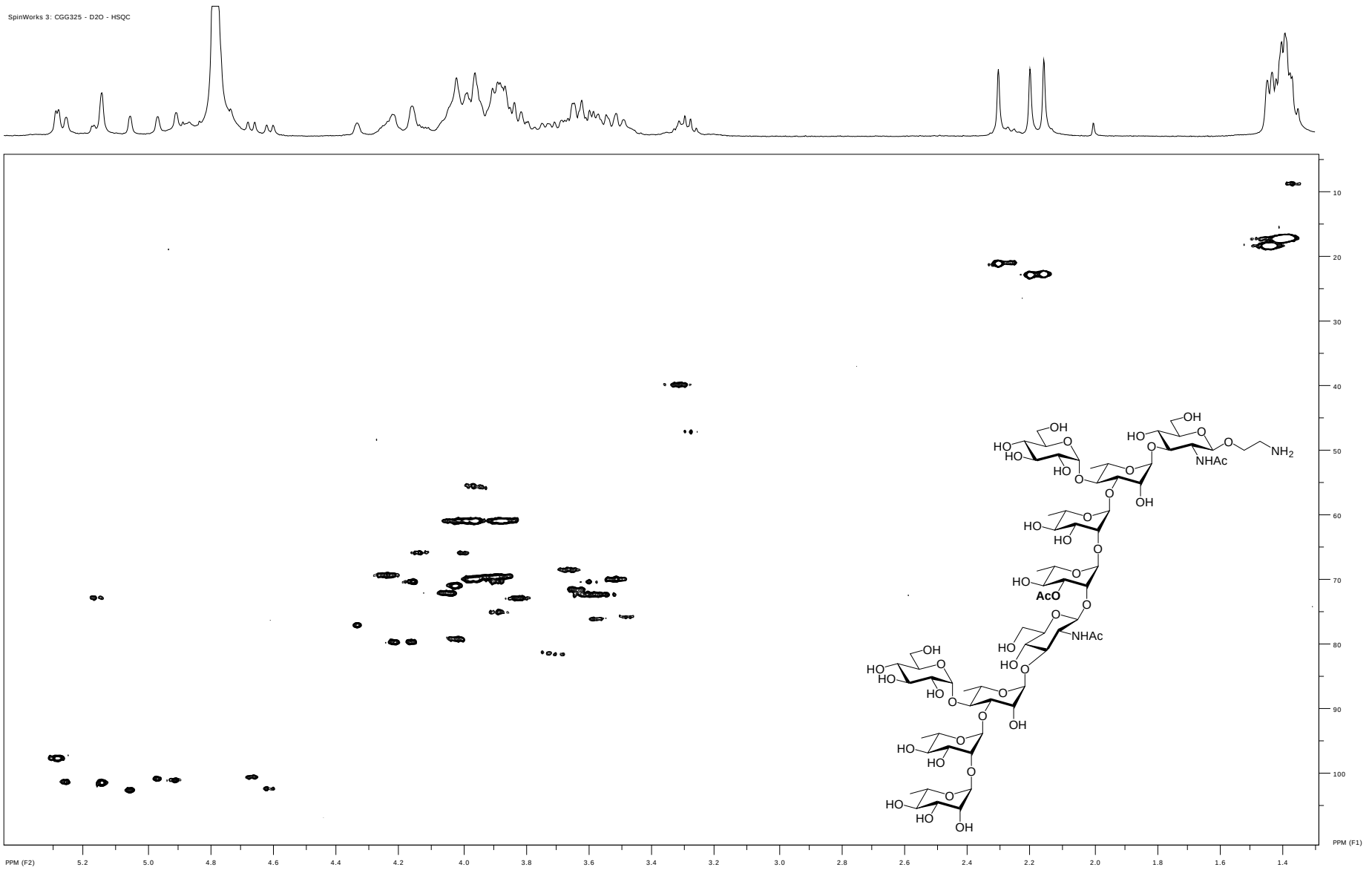
SpinWorks 3: CGG316A - HSQC - Pyrd5
PPM (F2)
PPM (F1)


SpinWorks 3: CGG316A - 13C - Pyrd5
170.9601
171.1026
171.1738
160.1796
160.2864
157.9831
139.2037
140.4451
130.9054
131.6242
129.4843
127.7528
121.6435
114.7174
103.8932
103.1126
102.7853
102.4453
102.1872
101.9417
101.6018
99.0020
98.3725
82.5983
81.8171
81.5718
80.5817
80.1729
78.6105
76.9844
76.2577
76.0306
75.8490
75.5583
73.8959
72.8513
72.6242
72.1700
71.8611
71.6522
58.9556
57.4704
55.5162
51.5295
51.3992
30.3847
26.6581
23.3178
19.2781
18.9336
OBn
BnO
BnO
BnO
O
O
O
O
OH
BnO
BnO
O
BnO
PMBO
O
O
NHAc
AcO
HO
O
OBn
BnO
BnO
BnO
O
O
O
OH
BnO
BnO
O
BnO
BnO
O
OH
OBn
BnO
O
O
NHAc
N3
PPM
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

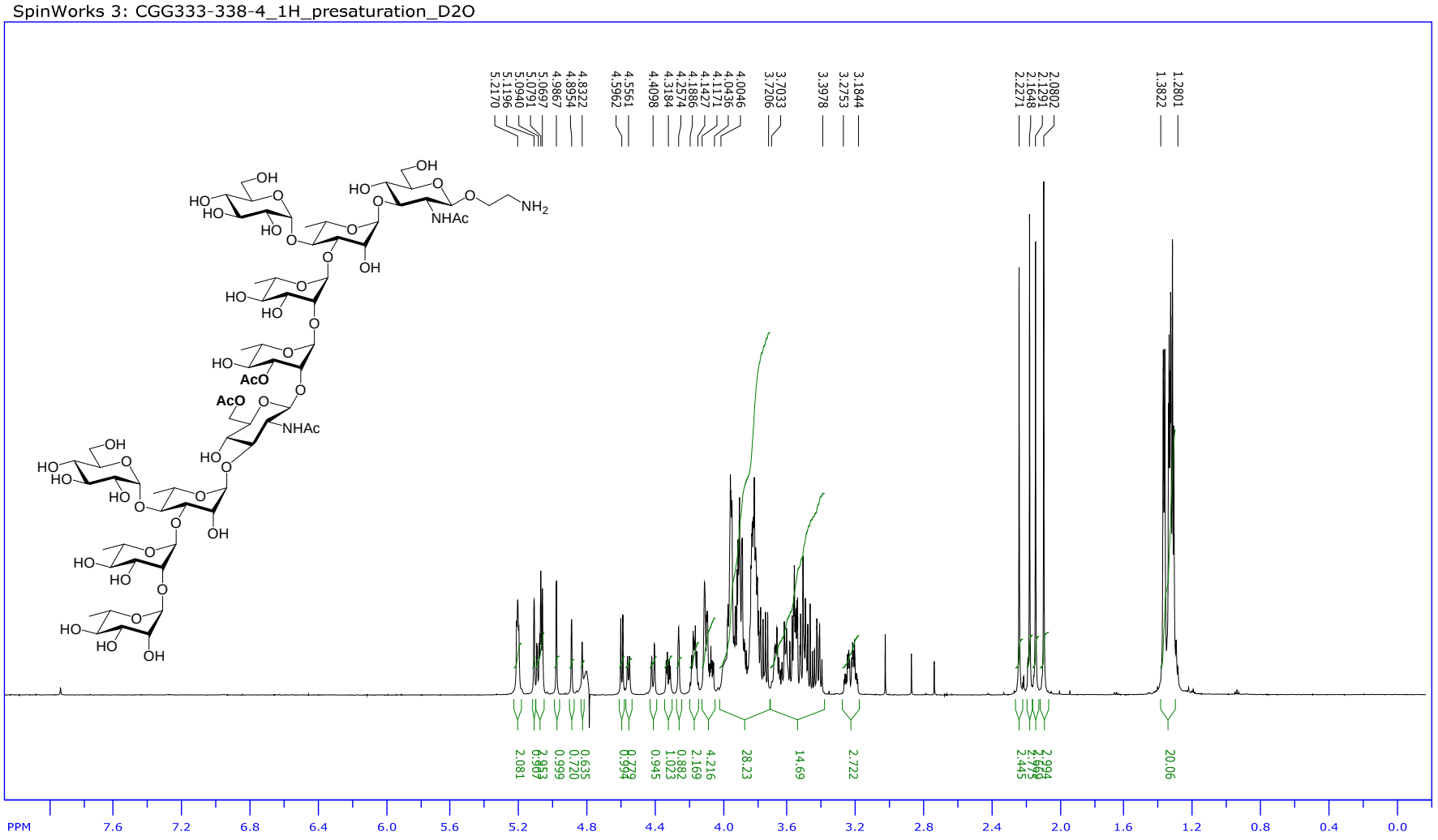
Compound **1**

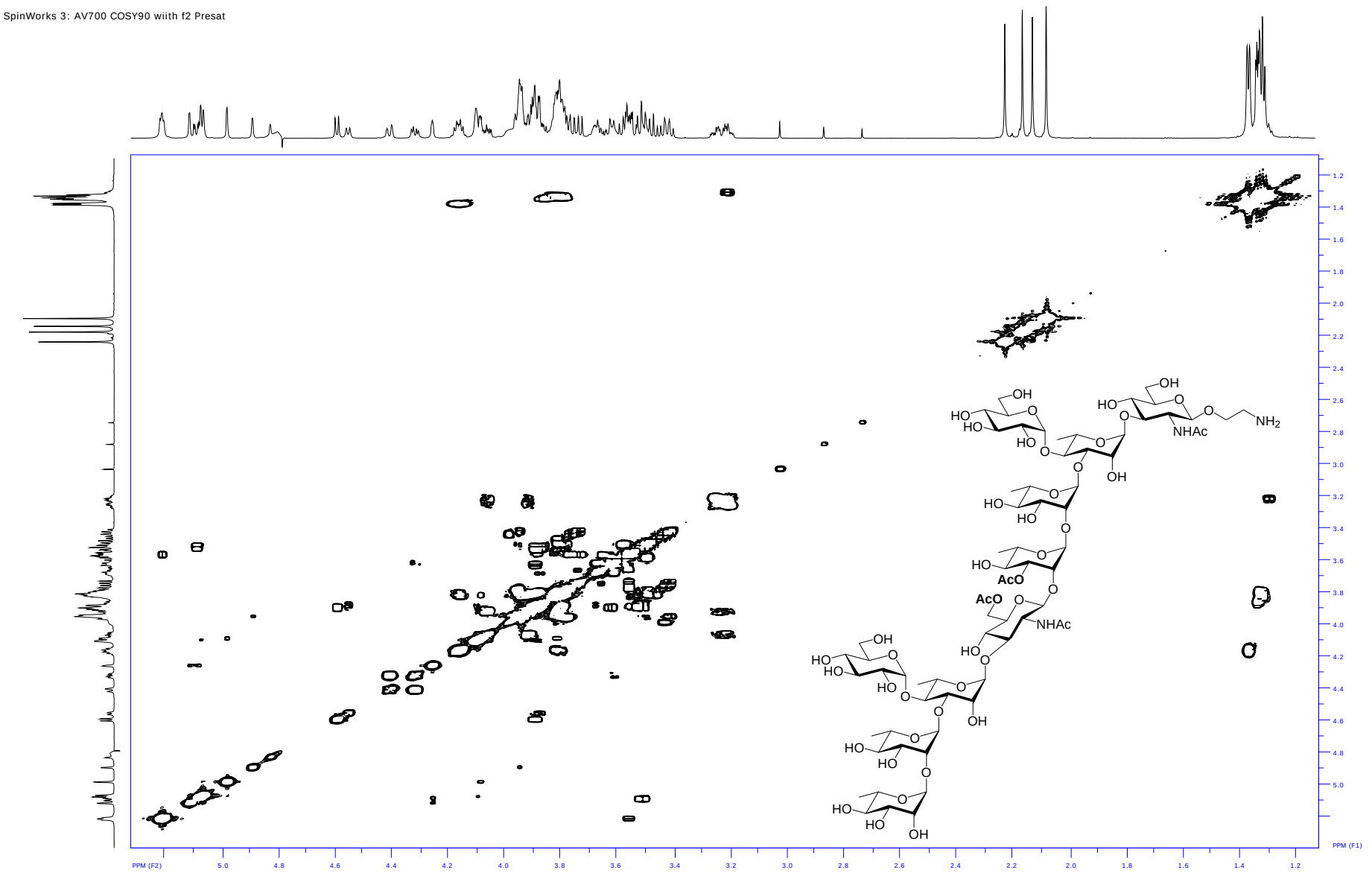

SpinWorks 3: CGG325
PPM
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0

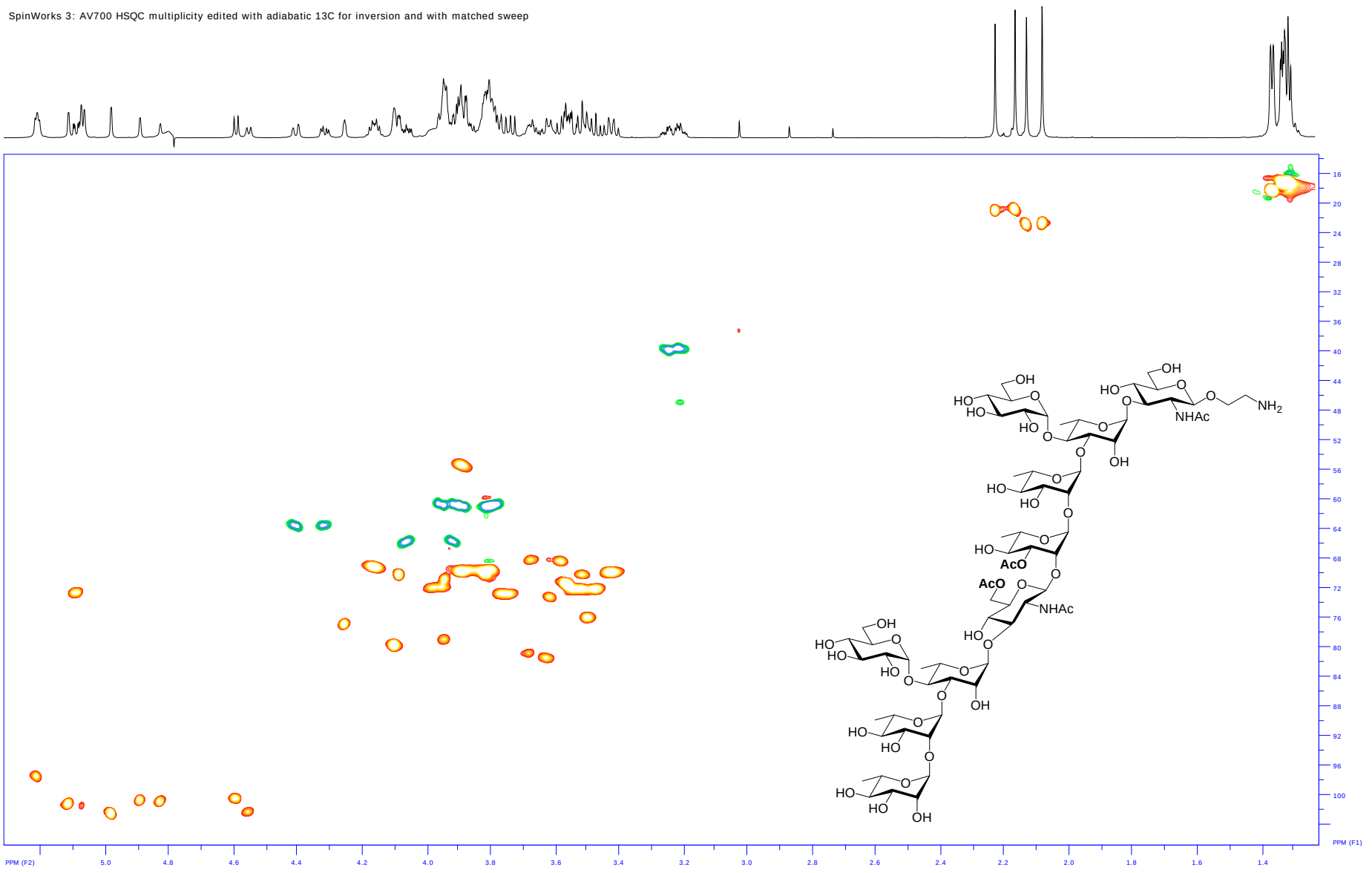

SpinWorks 3: CGG325 - D2O - COSY
AcO
NHAc
NHAc
NH2
PPM (F2)
PPM (F1)
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8

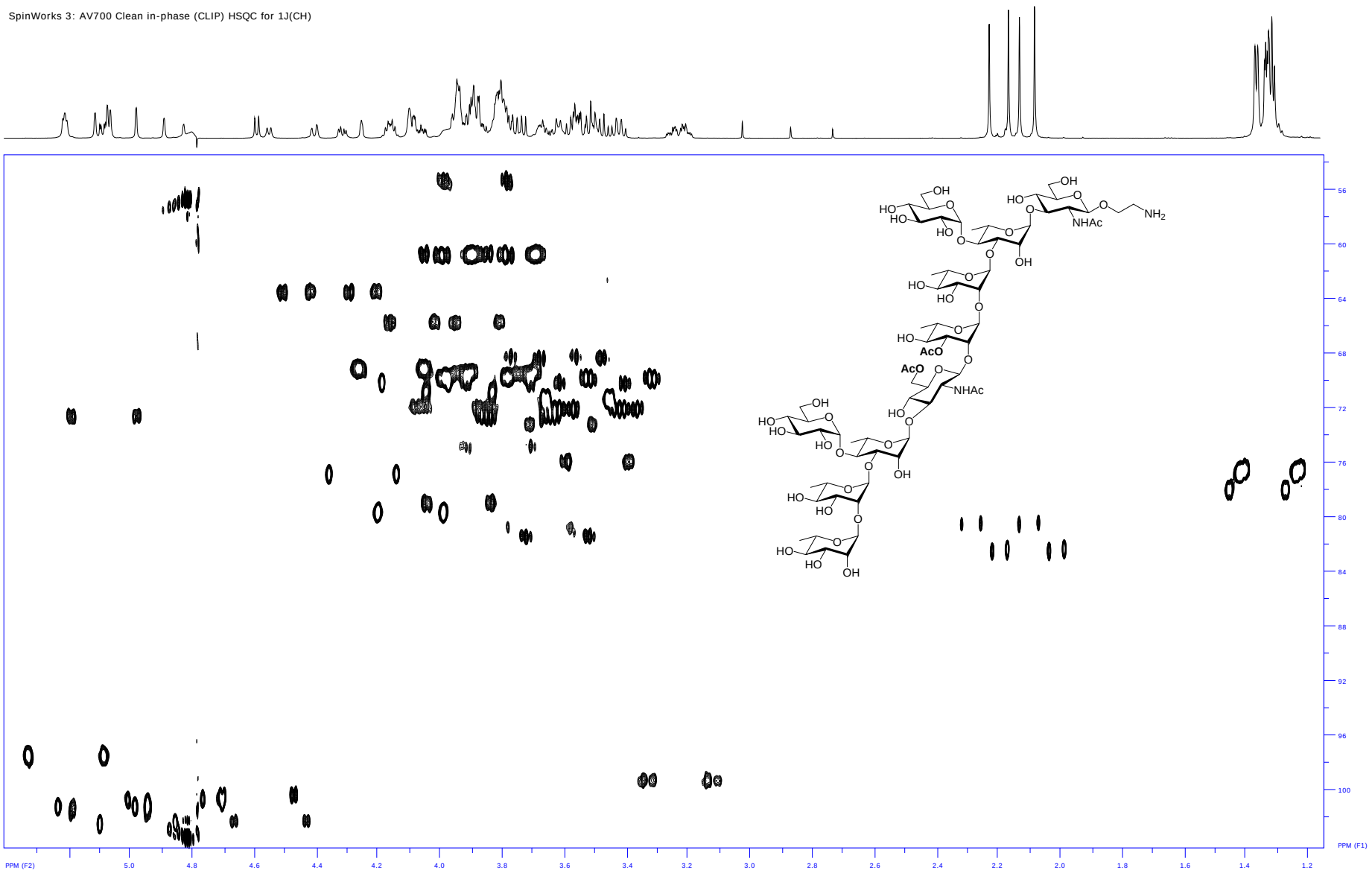

SpinWorks 3: CGG325 - D2O - HSQC
PPM (F2)
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
PPM (F1)
10
20
30
40
50
60
70
80
90
100
OH
HO
O
NHAc
NH2
AcO

Compound **2**

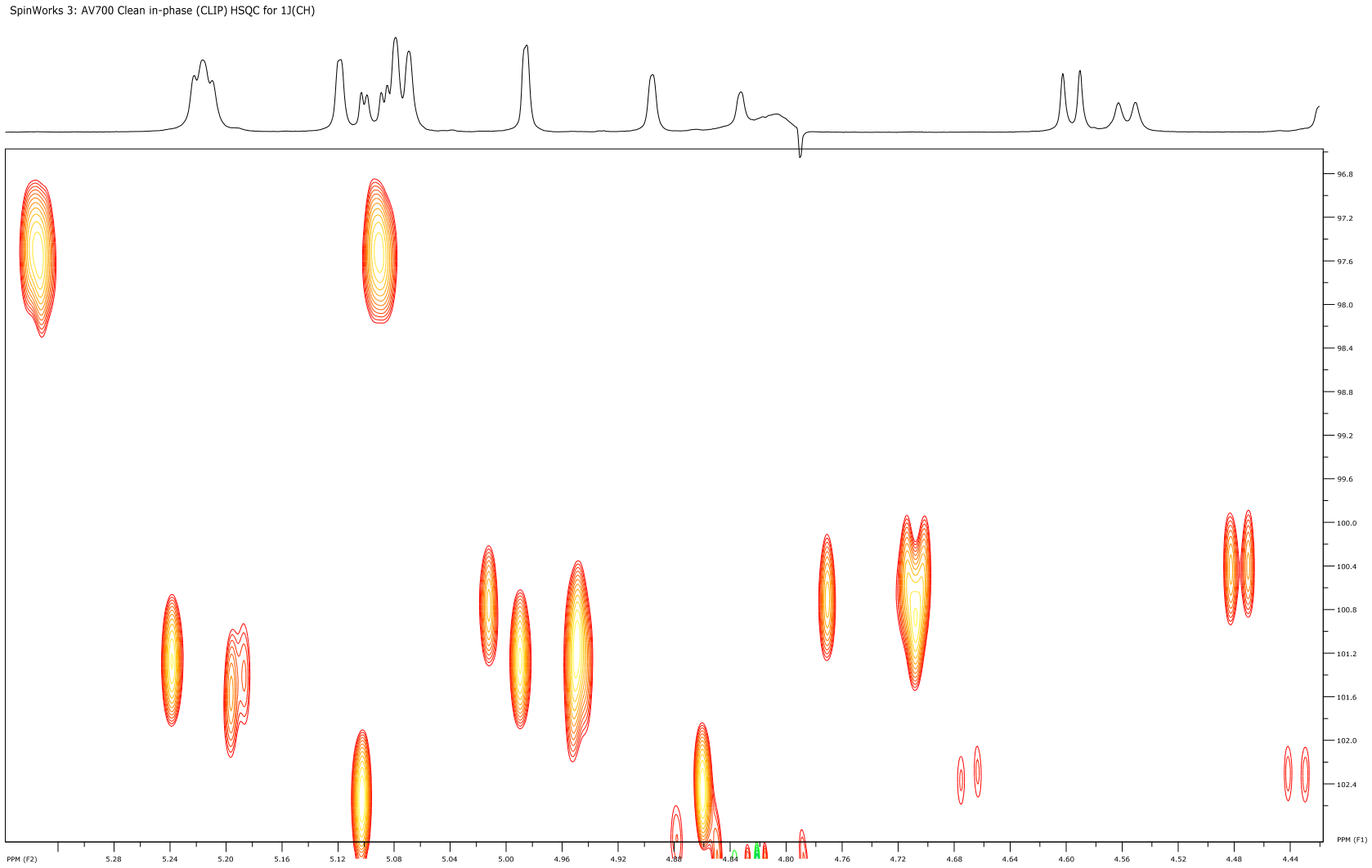

SpinWorks 3: CGG333-338-4_1H_presaturation_D2O
5.2170
5.1196
5.0940
5.0791
5.0697
4.9867
4.8954
4.8322
4.5962
4.5561
4.4098
4.3184
4.2574
4.1886
4.1427
4.1171
4.0436
4.0046
3.7206
3.7033
3.3978
3.2753
3.1844
2.2271
2.1648
2.1291
2.0802
1.3822
1.2801
2.081
0.907
0.999
0.720
0.635
0.994
0.779
1.023
0.945
0.882
2.169
4.216
28.23
14.69
2.722
2.445
20.06
PPM
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0


SpinWorks 3: AV700 COSY90 wiith f2 Presat
PPM (F2)
PPM (F1)
OH
HO
O
NHAc
NH2
AcO

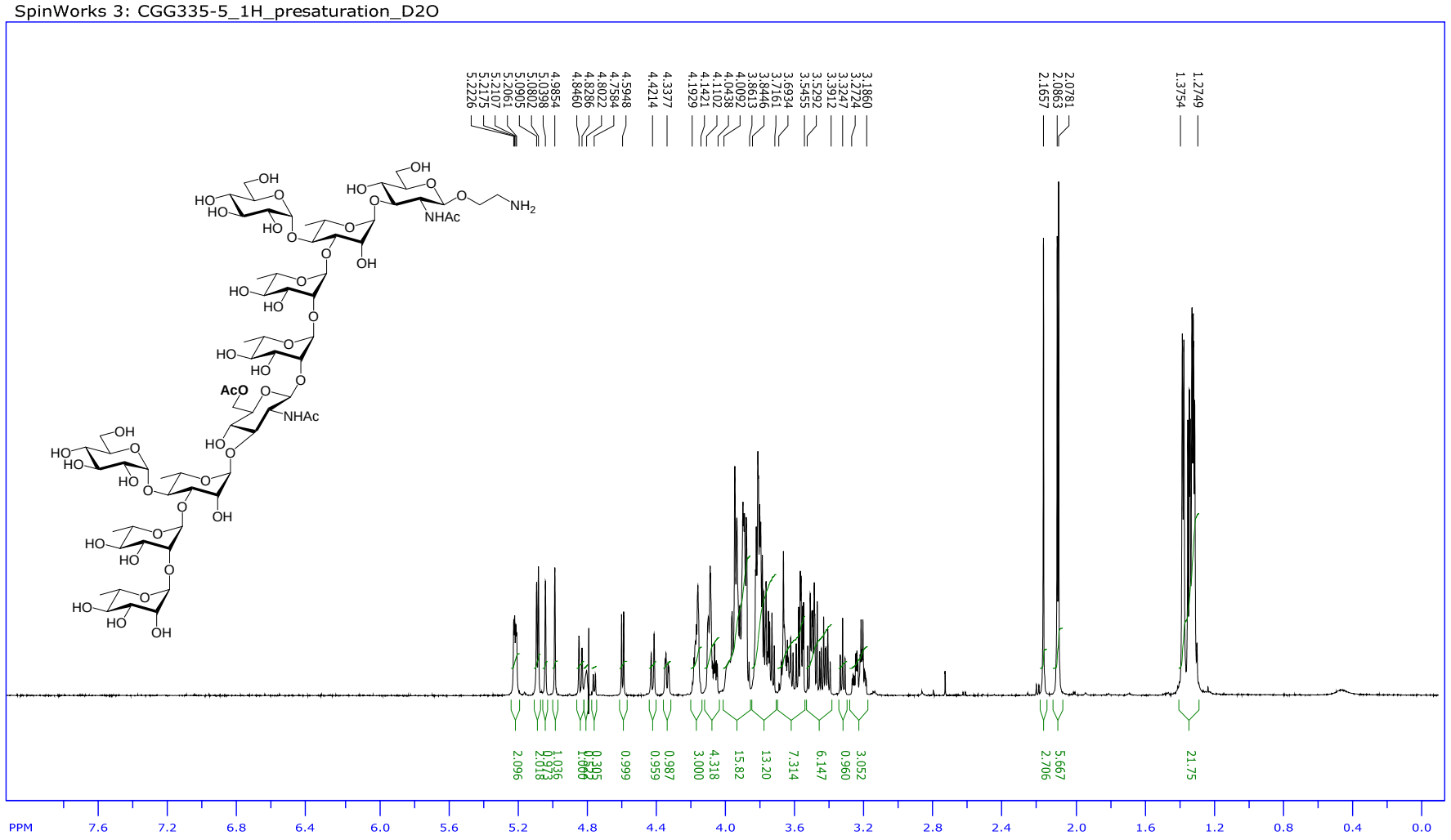

SpinWorks 3: AV700 HSQC multiplicity edited with adiabatic 13C for inversion and with matched sweep
PPM (F2)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
PPM (F1)
16
20
24
28
32
36
40
44
48
52
56
60
64
68
72
76
80
84
88
92
96
100
HO
OH
O
NHAc
NH2
AcO

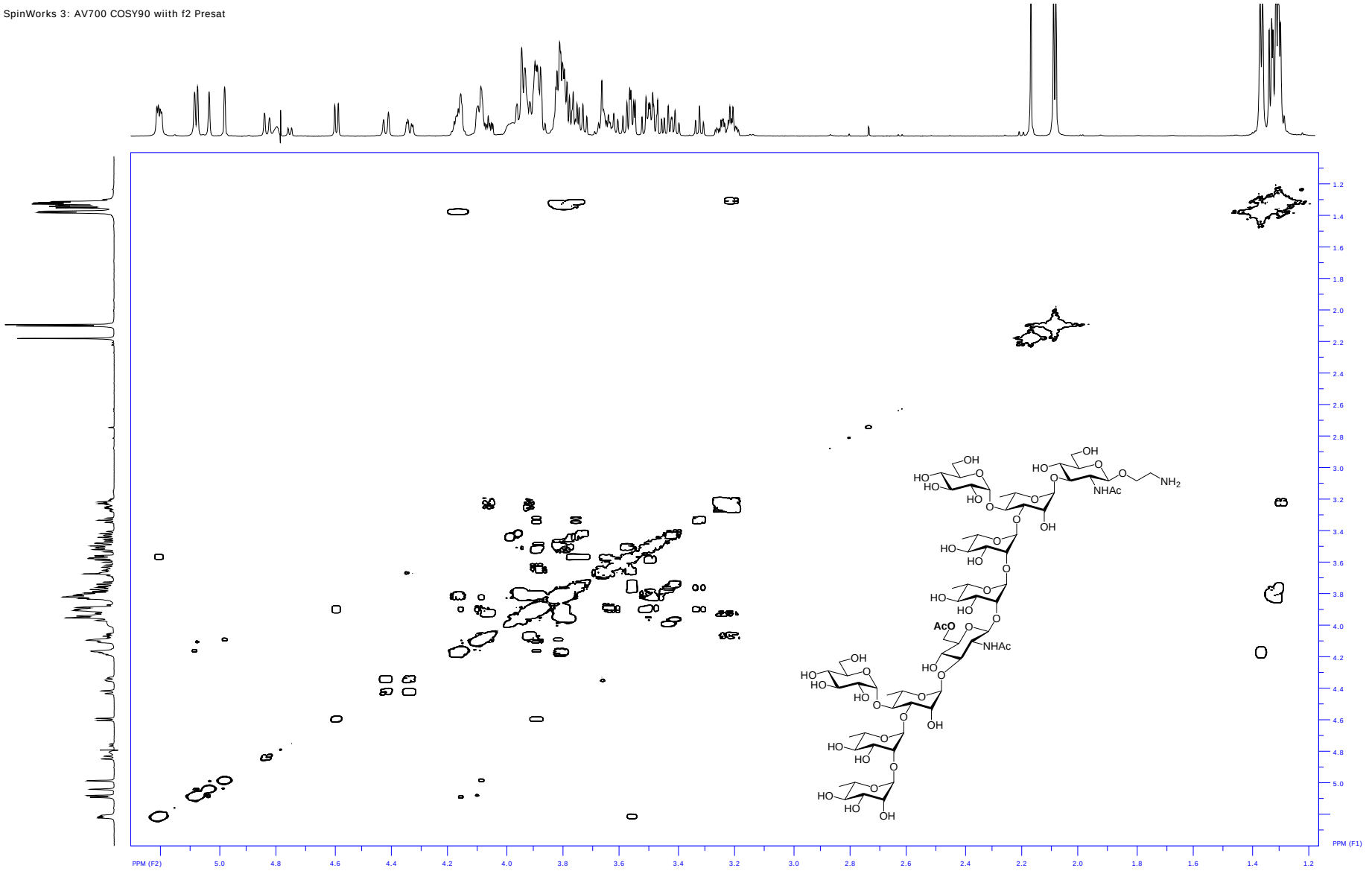

SpinWorks 3: AV700 Clean in-phase (CLIP) HSQC for 1J(CH)
PPM (F2)
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
PPM (F1)
56
60
64
68
72
76
80
84
88
92
96
100
OH
HO
O
NHAc
NH2
AcO
AcO

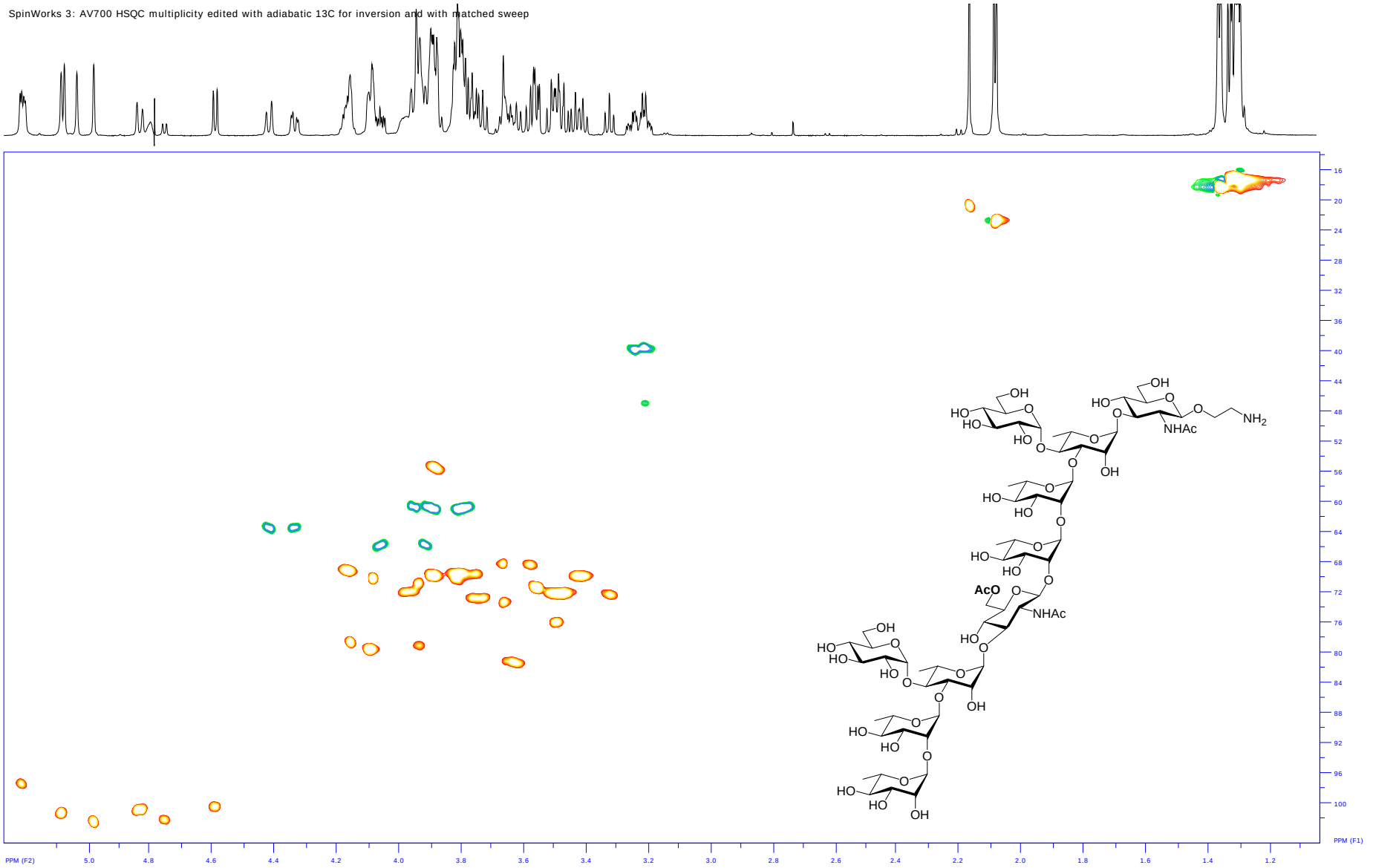
Enlargement of the above spectrum (HSQC for $^{1}J_{C,H}$) showing the anomeric region



Compound **3**


SpinWorks 3: CGG335-5_1H_presaturation_D2O
5.2226
5.2175
5.2107
5.2061
5.1905
5.1082
5.0398
4.9854
4.8460
4.8286
4.8022
4.7584
4.5948
4.4214
4.3377
4.1929
4.1421
4.1102
4.0438
4.0092
3.8613
3.8446
3.7161
3.6934
3.5455
3.5292
3.3912
3.3247
3.2724
3.1860
2.1657
2.0863
2.0781
1.3754
1.2749
2.096
2.018
1.973
1.036
0.999
0.959
0.987
3.000
4.318
15.82
13.20
7.314
6.147
0.960
3.052
2.706
5.667
21.75
PPM
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0


SpinWorks 3: AV700 COSY90 wiith f2 Presat
PPM (F2)
PPM (F1)
AcO
NHAc
NHAc
NH2


SpinWorks 3: AV700 HSQC multiplicity edited with adiabatic 13C for inversion and with matched sweep
PPM (F2)
PPM (F1)
AcO
NHAc
NHAc
NH2