Supplementary Information

'Naked' and Hydrated Conformers of the Conserved Core-Pentasaccharide of *N*-linked Glycoproteins and its Building Blocks

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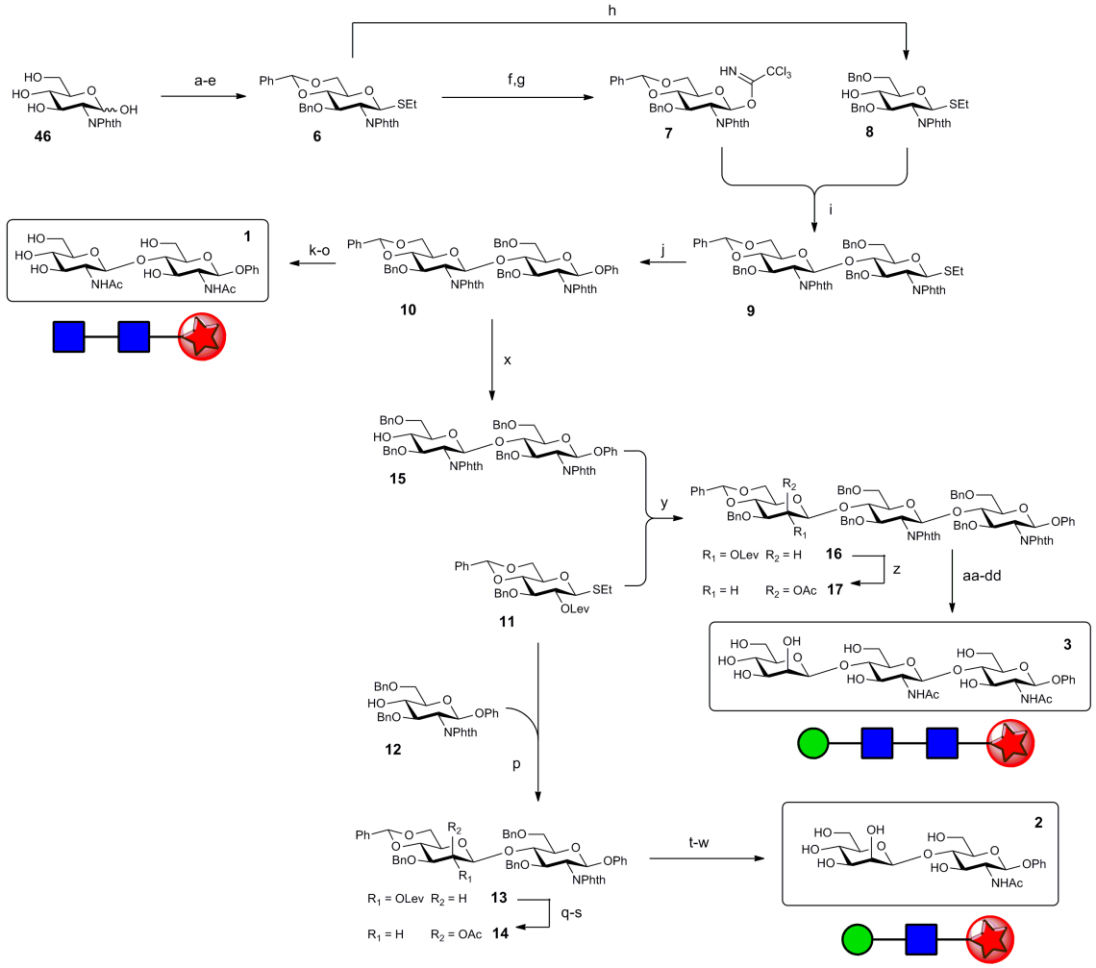
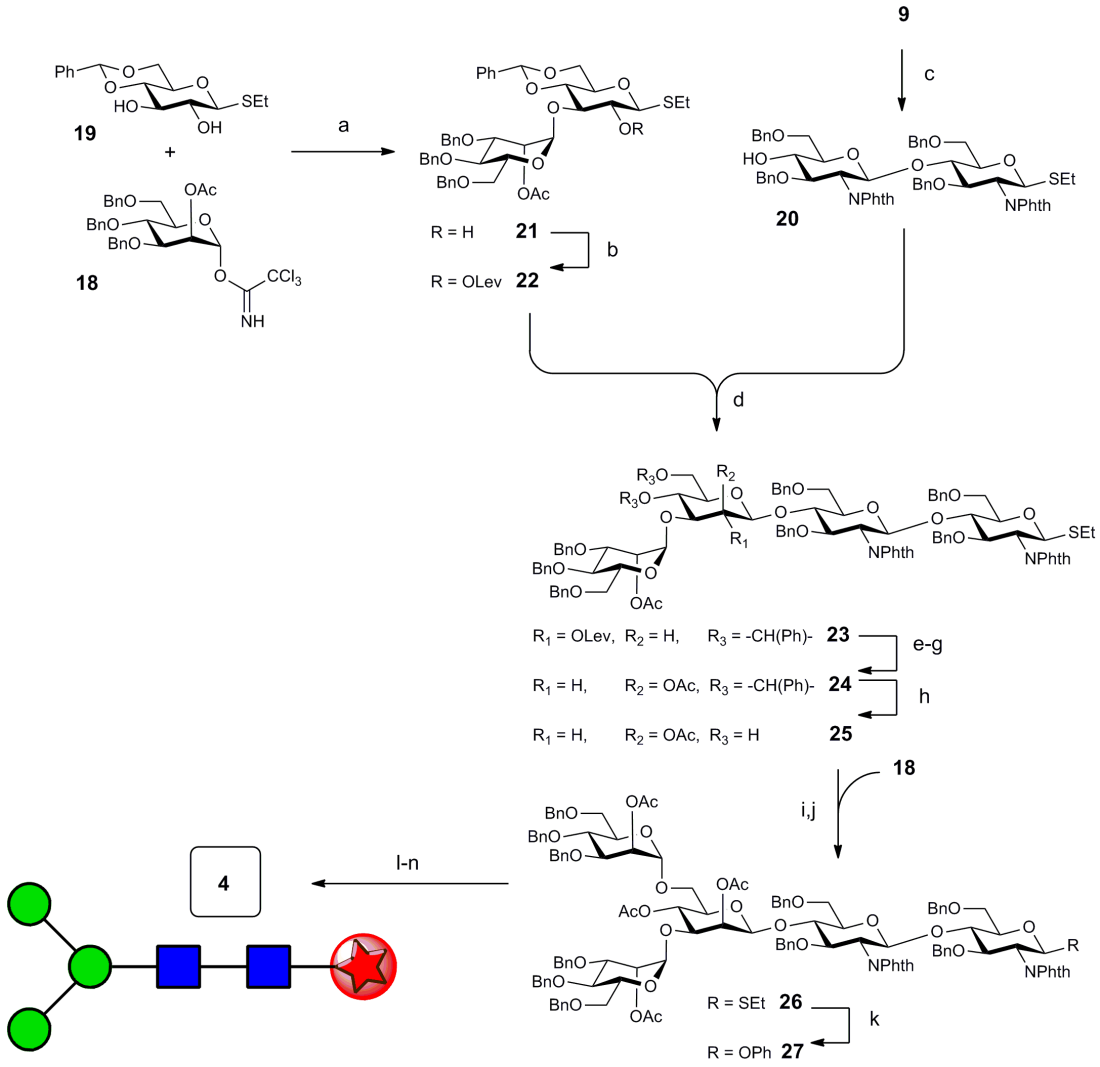
Synthetic Schemes

Full synthetic scheme detailing the synthesis of compounds **1**, **2** and **3**.



Supplementary Figure S1. *Reagents & conditions:* a) Ac_2O, pyridine, rt, 67%; b) EtSH, TMS-OTf, DCM, rt, 80%; c) NaOMe, MeOH, rt, 99%, d) benzaldehyde dimethylacetal, TsOH, MeCN, rt, 94%; e) i: NaH, DMF, rt, ii: BnBr, TBAI, DMF, 91%; f) NBS, acetone/H_2O, -10^{o}C; g) Cl_3CCN, DBU, DCM, rt, 84% over two steps; h) $NaBH_3CN$, HCl/dioxane, THF, 0^{o}C-rt, 82%; i) TMS-OTf, DCM, -78^{o}C, 95%; j) PhOH, NIS, TMS-OTf, DCM, 4Å MS, -10 ^{o}C, 37%; k) 1,2-ethylenediamine, BuOH, Δ; l) Ac_2O, pyridine, 66% over two steps; m) H_2, $Pd(OH)_2$, EtOH; n) Ac_2O, pyridine, 92% over two steps; o) NaOMe, MeOH, 94%; p) NIS, TMSOTf, 4 Å MS, 88%; q) H_2NNH_2.HOAc, MeOH, 55 ^{o}C, 95%; r) Tf_2O, DCM, pyridine; s) Bu_4N.OAc, toluene,))), 84% over two steps; t) H_2, $Pd(OH)_2$, EtOH; u) 1,2-ethylenediamine, BuOH, Δ; v) Ac_2O, pyridine, 74% over three steps; w) NaOMe, MeOH, 94%; x) $NaBH_3CN$, HCl/dioxane, THF, 0^{o}C-rt, 80%; y) MeOTf, DCM, 4 Å MS, 75%; z) i - H_2NNH_2.HOAc, MeOH, 55 ^{o}C; ii - Tf_2O, DCM, pyridine; iii - Bu_4N.OAc, toluene,))), 68% over three steps; aa) H_2, $Pd(OH)_2$, EtOH; bb)1,2-ethylenediamine, BuOH, Δ; cc) Ac_2O, pyridine, 94% over three steps; dd) NaOMe, MeOH, 86%.

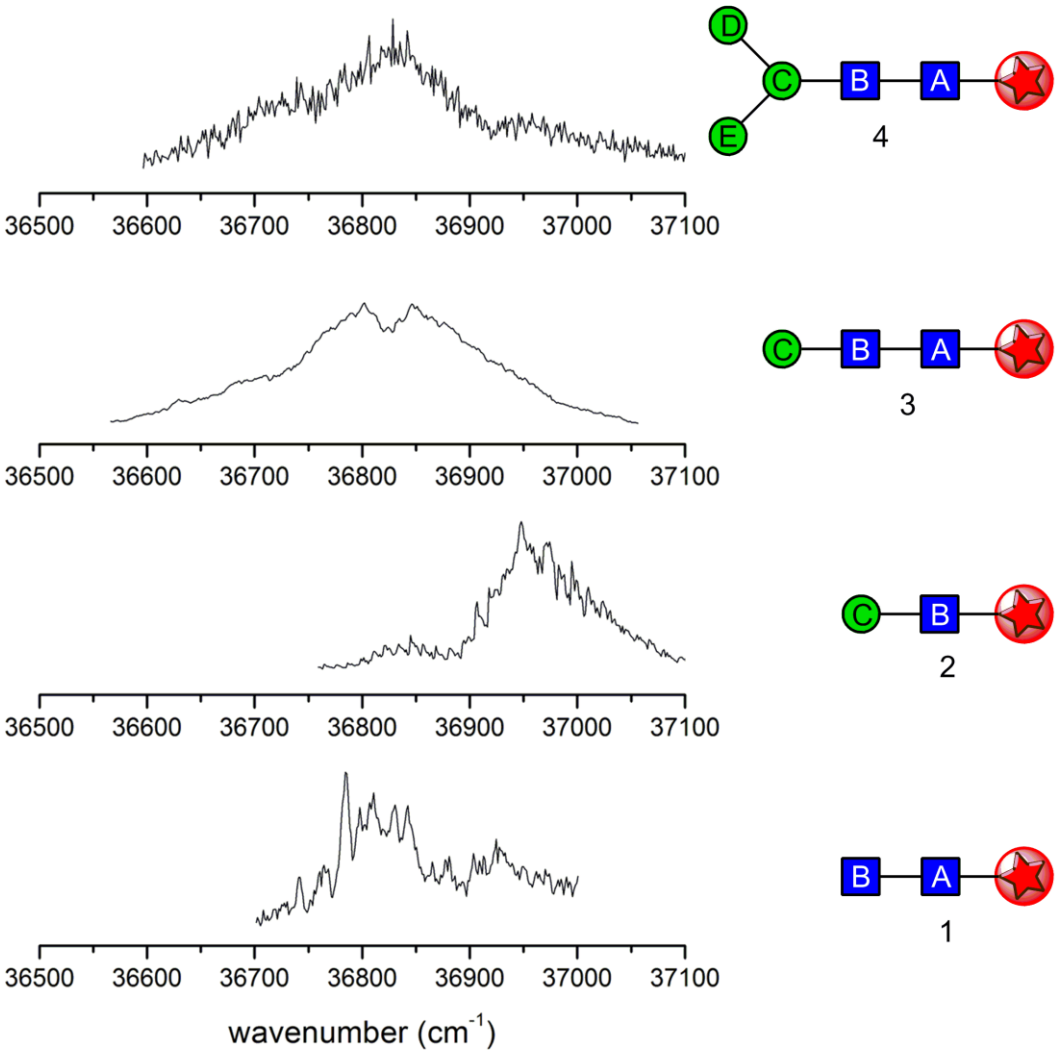
Full synthetic scheme detailing the completion of the synthesis of **4**.



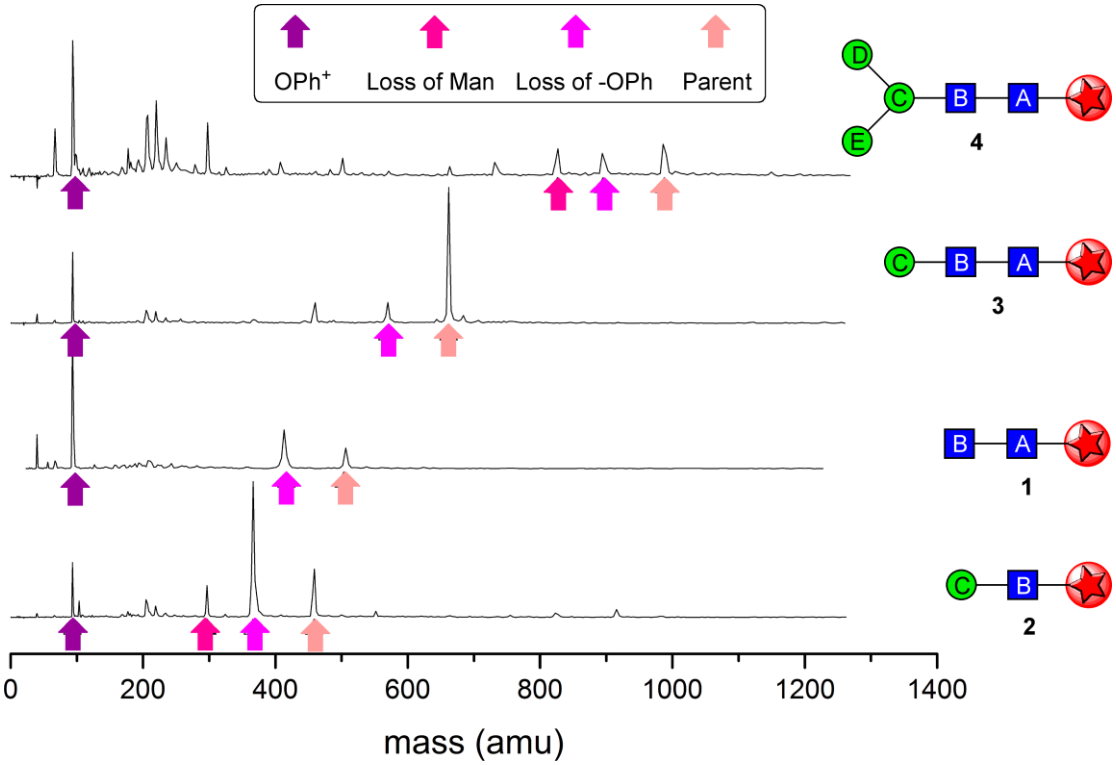
Supplementary Figure S2. *Reagents & conditions:* a) TMS-OTf, DCM, -78^{o}C, 76%; b) LevOH, DIC, DCM, 94%; c) $NaBH_3CN$, HCl/dioxane, THF, 0^{o}C-rt, 91%; d) Ph_2O, Tf_2O, DTBMP, DCM, -40 ^{o}C – rt, 64%; e) H_2NNH_2.HOAc, MeOH, 55 ^{o}C, 64%; f) Tf_2O, DCM, pyridine; g) Bu_4N.OAc, toluene,))), 88% over two steps; h)TsOH.H_2O, MeOH, 1,4-Dioxane, 85 ^{o}C, 92%; i) **18**, TMS-OTf, DCM, -40 ^{o}C, 85%; j) Ac_2O, pyridine; k) PhOH, NIS, TMS-OTf, DCM, 4Å MS, -10 ^{o}C, 48% over two steps; l) 1,2-ethylenediamine, MeOH, Δ, then Ac_2O, pyridine, 80% over two steps; m) H_2, $Pd(OH)_2$-C, MeOH, 97%; n) NaOMe, MeOH, 88%.

Photoionisation and time of flight mass spectra of 1-4.

Resonant 2-photon ionisation (R2PI) spectra of **2**, **3** and **4** were recorded in their parent ion channels. The two-colour photo-ionisation spectrum of **1** was recorded with ω1 fixed at 36,232 cm^{-1} while ω2 was scanned.



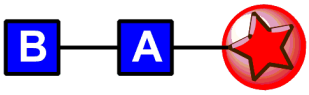
Supplementary Figure S3. Two-colour photo-ionisation spectrum of **1**, and R2PI spectra of **2**, **3** and **4**.



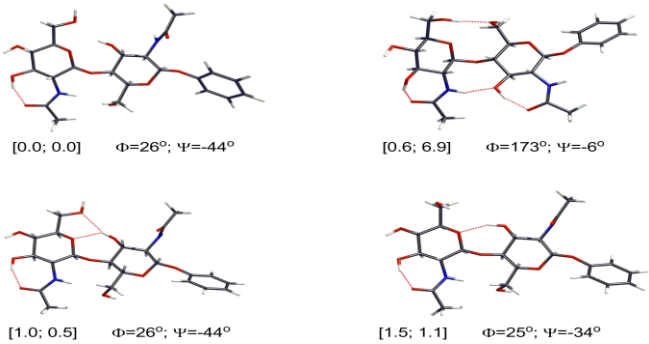
Supplementary Figure S4. Time of flight photoionisation mass spectra of **1**-**4**.

Lowest energy structures, relative- and free energies of 1 and 1·H_2O.

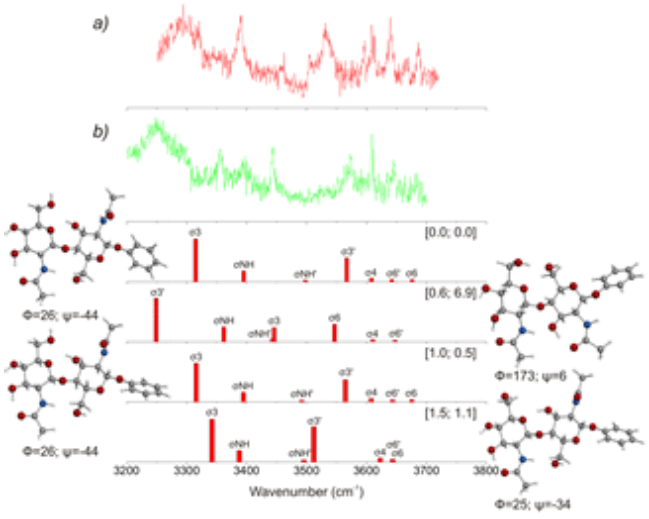
Calculated structures of **1 (**GlcNAc-β-1,4-GlcNAc-β-1-OPh) and it's mono-hydrate **1·H_2O**. Calculated optimised structures were calculated using DFT (B3LYP/6-311+G*). Relative energies (kJ mol^{-1}), calculated using single point B3LYP//MP2/6-311++G**, and corrected for zero point and free energy using the frequency calculations performed at the B3LYP level are shown in square brackets. Dihedral angles $H1_B$-$C1_B$-$O1_B$-$C4_A$ and $C1_B$-$O1_B$-$C4_A$-$H4_A$ are denoted by φ, ψ respectively.



1

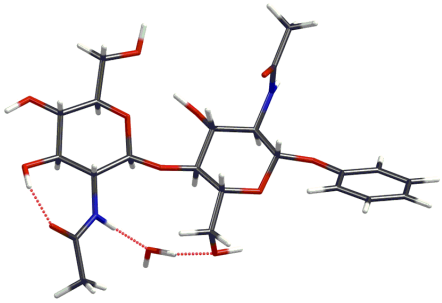


(i)

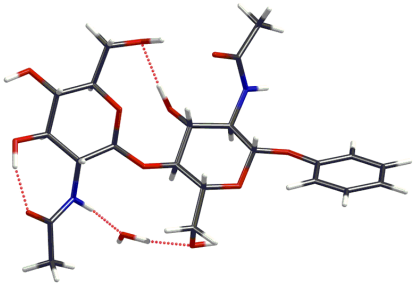


(ii)

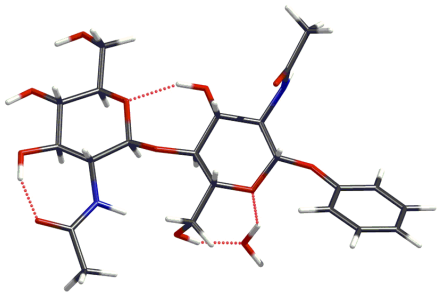
Supplementary Figure S5. (i) The computed lowest energy structures of **1**; relative- and free-energies (in brackets) are in kJ mol^{-1} and dihedral angles (φ and ψ) are in degrees. **(ii)** The experimental (IRID) and computed vibrational spectra of the four lowest energy conformers. Note: the first and third structures only differ in the orientation of the phenyl ring.



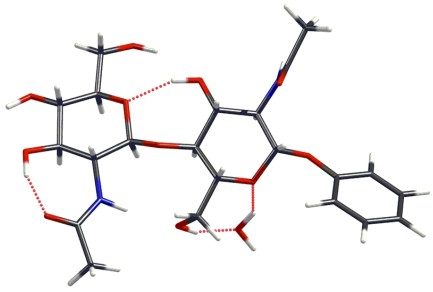
[0.0; 0.0] Φ=34°; Ψ=-50°



[0.6; 5.3] Φ=38°; Ψ=-68°

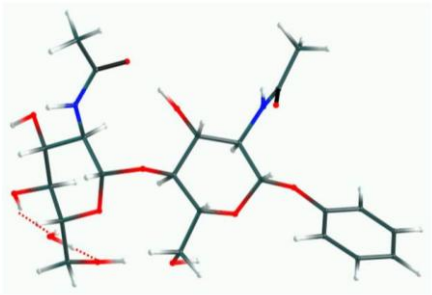


[0.7; 1.3] Φ=28°; Ψ=-27°



[1.5; 0.1] Φ=32°; Ψ=-19°

(i)



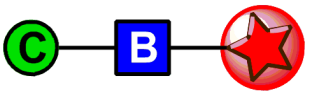
[4.5; 8.0] Φ=162°; Ψ=2°

(ii)

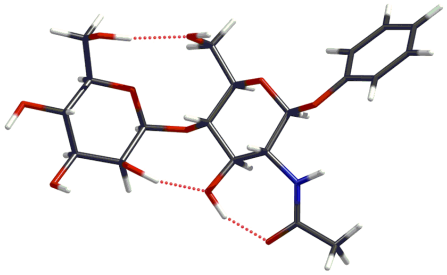
Supplementary Figure S6. The computed lowest energy structures of (i), *trans* **1·H$_2$O** and (ii) *cis* **1·H$_2$O.** Relative energies and free-energies (in brackets) are in kJ mol^{-1}; dihedral angles (φ and ψ) are in degrees.

Lowest energy structures, relative- and free energies of 2, 2·H_2O, 2-B and 2-B·H_2O.

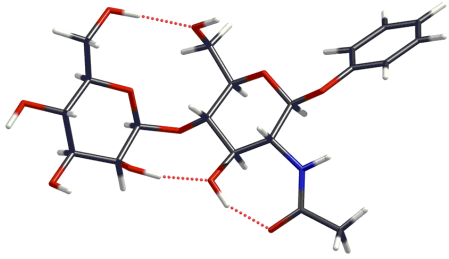
Calculated structures of **2** (Man-β-1,4-GlcNAc-β-1-OPh), its mono-hydrate **2·H_2O**, the blocked disaccharide **2-B** (Man(6-OMe)-β-1,4-GlcNAc-β-1-OPh) and its mono-hydrate **2-B·H_2O**. Optimised structures were calculated using DFT (B3LYP/6-311+G*). Relative and free energies (kJ mol^{-1} shown in square brackets) were calculated using single point B3LYP//MP2/6-311++G**. Dihedral angles $H1_C$-$C1_C$-$O1_C$-$C4_B$ and $C1_C$-$O1_C$-$C4_B$-$H4_B$ are denoted by φ, ψ respectively.



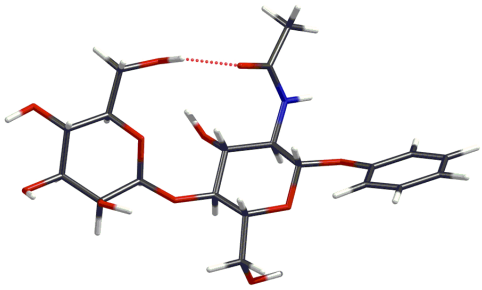
2



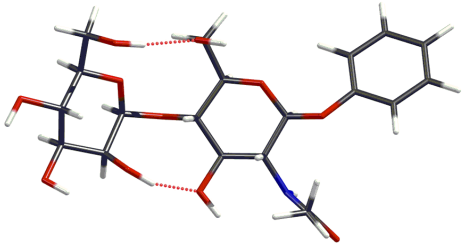
[0.0; 0.0] Φ=170°; Ψ=4°



[1.8; 0.4] Φ=150°; Ψ=5°

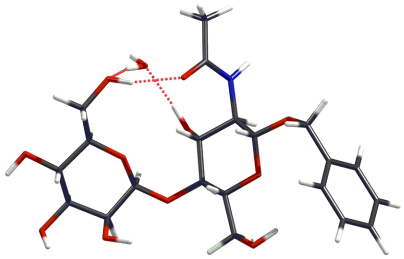


[9.9; 9.0] Φ=41°; Ψ=-72°

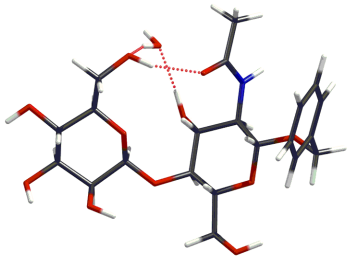


[12.1; 11.7] Φ=169°; Ψ=4°

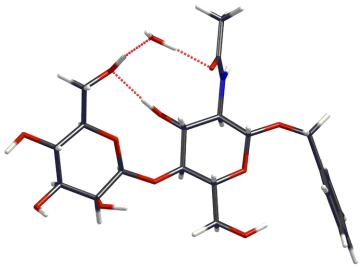
Supplementary Figure S7. The computed lowest energy structures of **2**; relative- and free-energies (in brackets) are in kJ mol^{-1}, dihedral angles (φ and ψ) are in degrees.



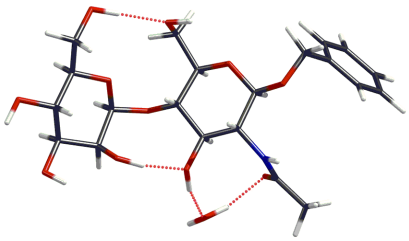
[0.0; 4.5] Φ=42°; Ψ=-93°



[0.9; 3.8] Φ=40°; Ψ=-90°

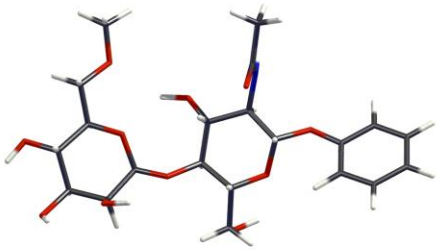


[1.7; 3.0] Φ=37°; Ψ=-66°

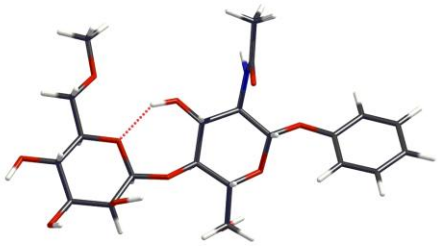


[2.9; 3.6] Φ=156°; Ψ=3°

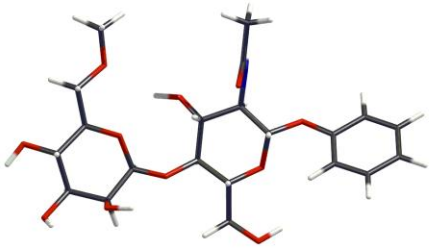
Supplementary Figure S8. The computed lowest energy structures of **2·H_2O** (relative- and free-energies (in brackets) are in kJ mol^{-1}, dihedral angles (φ and ψ) are in degrees). *Note*: Calculated for the –*O*-benzyl glycoside.



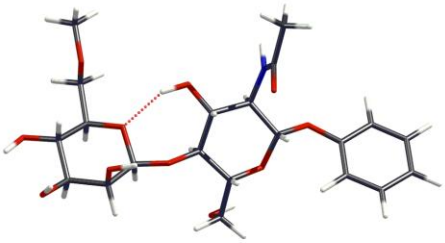
[0.0; 0.0] Φ=35°; Ψ=-40°



[0.9; 0.0] Φ=38°; Ψ=-33°

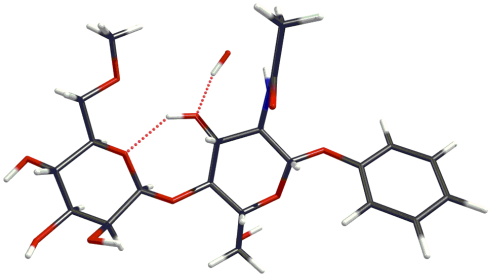


[1.8; 3.7] Φ=36°; Ψ=-44°

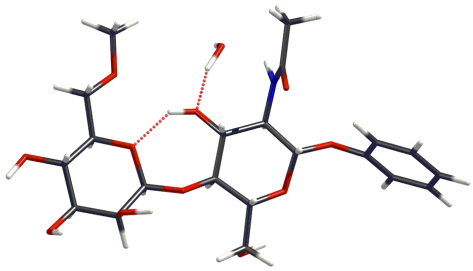


[2.0; 2.3] Φ=50°; Ψ=-12°

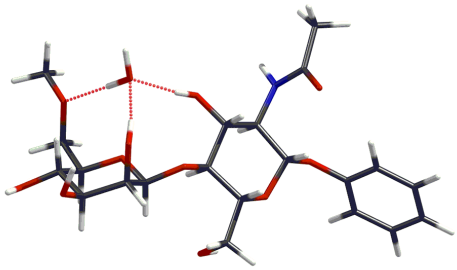
Supplementary Figure S9. The computed lowest energy structures of **2-B** (relative- and free-energies (in brackets) are in kJ mol^{-1}, dihedral angles (φ and ψ) are in degrees).



[0.0; 0.0] Φ=36°; Ψ=-38°



[1.0; 0.9] Φ=36°; Ψ=-37°

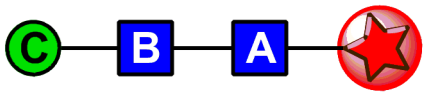


[2.9; 5.3] Φ=54°; Ψ=13°

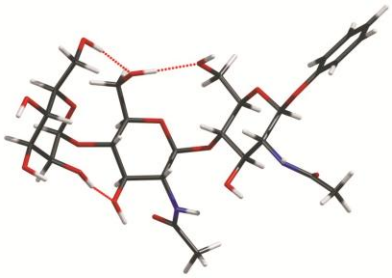
Supplementary Figure S10. The computed lowest energy structures of **2-B·H_2O** (relative- and free-energies (in brackets) are in kJ mol^{-1}, dihedral angles (φ and ψ) are in degrees).

Lowest energy structures, relative- and free energies of 3 and 3-B.

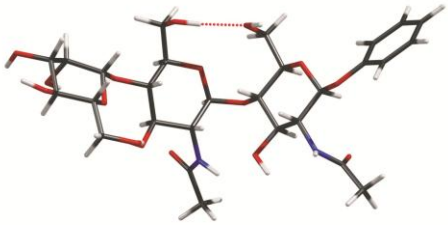
Calculated structures of **3** (Man-β-1,4-GlcNAc-β-1,4-GlcNAc-β-1-OPh) and it's blocked trisaccharide **3-B** (Man(6-OMe)-β-1,4-GlcNAc-β-1,4-GlcNAc-β-1-OPh). Calculated optimised structures and relative and free energies (kJ mol^{-1} shown in square brackets) were calculated using DFT (M06-2X/6-31+G*). Free energies were determined at 298 K. Dihedral angles $H1_C$-$C1_C$-$O1_C$-$C4_B$, $C1_C$-$O1_C$-$C4_B$-$H4_B$, $H1_B$-$C1_B$-$O1_B$-$C4_A$ and $C1_B$-$O1_B$-$C4_C$-$H4_C$ are denoted by φ_1, ψ_1, φ_2 and ψ_2 respectively.



3

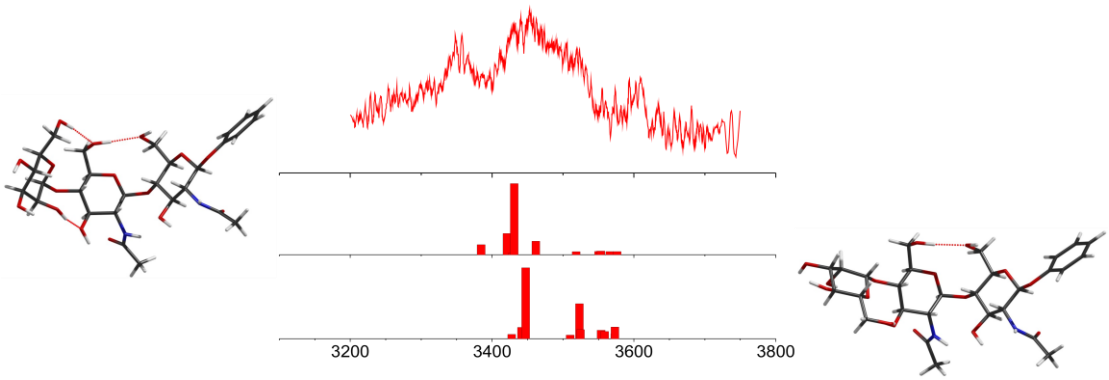


ϕ_1=157; ψ_1=6 and ϕ_2=170; ψ_2=3 [0.0; 0.0]



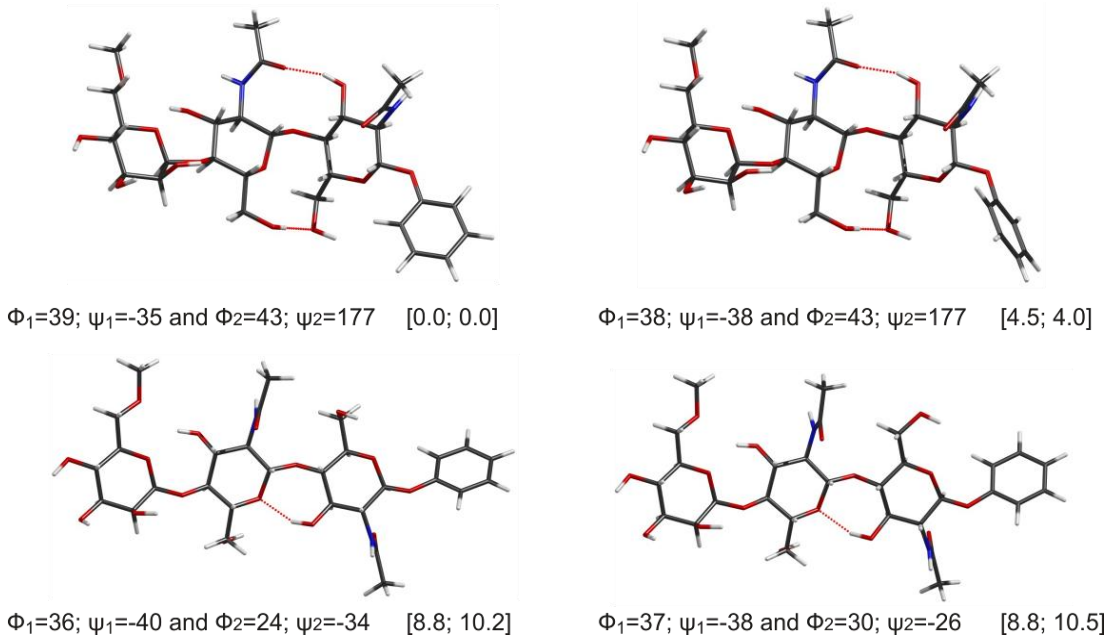
ϕ_1=51; ψ_1=−5 and ϕ_2=174; ψ_2=−1 [12.2; 7.8]

(a)



(b)

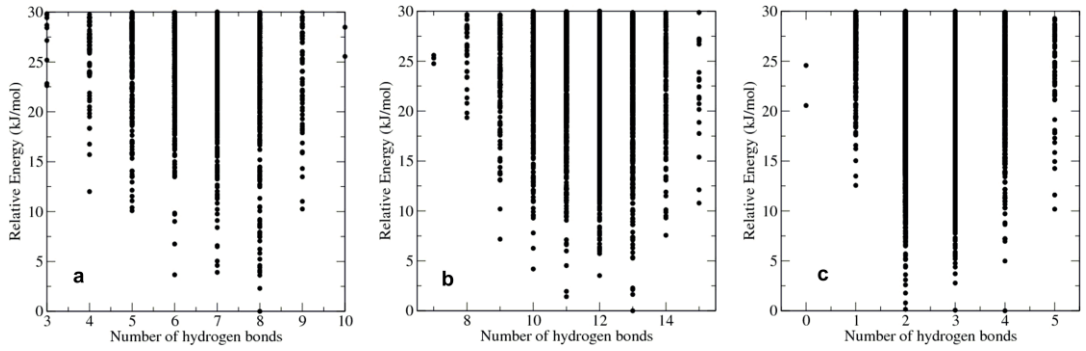
Supplementary Figure S11. (a) The computed lowest energy structures of **3** (relative- and free-energies (in brackets) are in kJ mol^{-1}, dihedral angles (φ and ψ) are in degrees). **(b)** The experimental (IRID) and computed vibrational spectra of the two lowest energy conformers.



Supplementary Figure S12. The computed lowest energy structures of **3-B** (relative- and free-energies (in brackets) are in kJ mol^{-1}, dihedral angles (φ and ψ) are in degrees).

Hydrogen bonding distributions of 4, obtained from MM/OPLS2005 calculations (see pp. S21-S22)

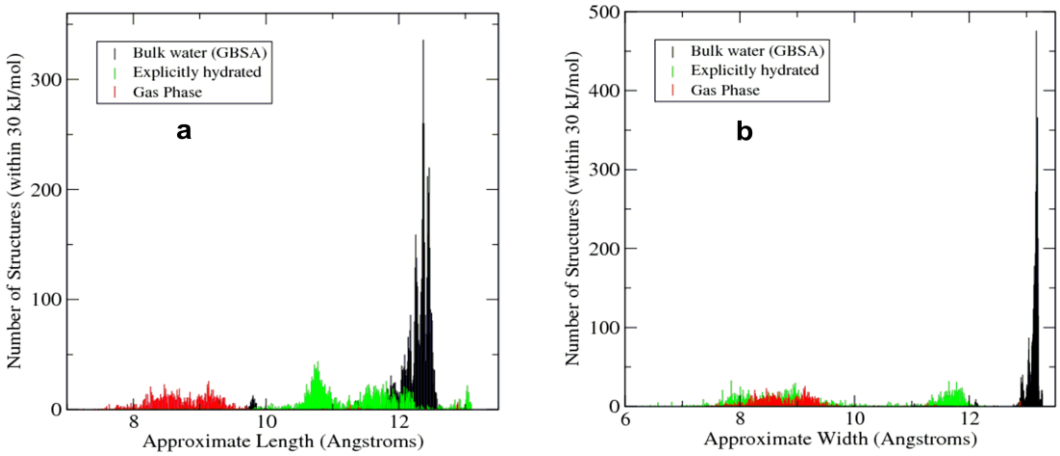
An analysis of the number of hydrogen bonds (r[OH··O] > 2.5Å, θ[OH··O] > 120º) present for each converged structure within 30 kJ/mol of the global minimum was conducted for **4** in the gas phase, explicitly hydrated with three water molecules, and in bulk water (Supplementary Figure S13). An optimum of 6-8 intra-molecular hydrogen bonds was found in the gas phase structures. The addition of three water molecules was seen to increase the importance of hydrogen bonding in the low energy structures, allowing for an optimal number of 10-13 hydrogen bonds (including bonds to the water molecules). In the bulk simulation intra-molecular hydrogen bonds are replaced with hydrogen bonds to the bulk solvent. The optimum number of intra-molecular hydrogen bonds was seen to decrease to just 2-4 in the low energy ensemble.



Supplementary Figure S13. Hydrogen bonding patterns for **4** in (a) gas phase, (b) explicitly hydrated, and (c) bulk water.

Molecular shape/size distributions of 4, obtained from MM/OPLS2005 calculations (see pp. S21-S22)

In addition to using the longest intramolecular distances as an indicator of the molecular conformations (main text), the molecular length and width of the core pentasaccharide (without the *O*-phenyl glycoside) were also measured by identifying an approximate length (the distance between $C1_A$ of GlcNAc and $C4_C$ of the bridging mannose) and an approximate width (the distance between $C4_D$ of the C3-linked mannose and $C3_E$ of the C6 linked mannose) (Supplementary Figure S14). In the gas phase the shortest molecular length distribution indicates compact structures which become increasingly extended in explicitly hydrated and bulk water simulations. The explicitly hydrated core-pentasaccharide **4** shows a bimodal distribution which reflects the potential for mannose-E to fold back to interact with the chitobiose stem, although there is no conserved water insertion structure associated with each distribution.



Supplementary Figure S14: (a) Approximate molecular length and (b) approximate molecular width of the core pentasaccharide **4** in bulk water (black), explicitly hydrated (green) and in the gas phase (red).

The molecular widths provide an approximate estimate of how widely separated the branching mannose groups are from each other, even if this separation is achieved by folding back along the chitobiose stem. The bulk water structures show decreased flexibility and the largest separation of the mannose head groups. The explicitly hydrated width varies with a bimodal distribution; the longer distance

relates to structures where the mannose-E head group folds back in interaction with the chitobiose stem creating a larger perceived width. The gas phase structures, and the majority of the explicitly hydrated structures, favour compact conformations in comparison to those adopted in bulk solution.

Supplementary Methods

General Experimental

Optical rotations were measured on a Perkin-Elmer 241 polarimeter with a path length of 1.0 dm and are reported with implied units of 10^{-1} deg cm^2 g^{-1}. Concentrations (c) are given in g/100 mL.

Melting points (m.p.) were recorded on a Leica Galen III hot stage microscope equipped with a Testo 720 thermocouple probe and are uncorrected.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker DPX400 (400 MHz), a Bruker AV400 (400 MHz) or a Bruker AVII500 (500 MHz) spectrometer, as indicated. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AV400 (100 MHz) spectrometer or on a Bruker AVII500 (125 MHz) spectrometer, as indicated. NMR Spectra were fully assigned using COSY, HSQC, HMBC and DEPT 135. All chemical shifts are quoted on the δ scale in ppm using residual solvent as the internal standard (^{1}H NMR: $CDCl_3$ = 7.26, CD_3OD = 4.87; DMSO-d_6 = 2.50 and ^{13}C NMR: $CDCl_3$ = 77.0; CD_3OD= 49.0; DMSO-d_6 = 39.5). Coupling constants (J) are reported in Hz with the following splitting abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, and a = apparent.

Infrared (IR) spectra were recorded on a Bruker Tensor 27 Fourier Transform spectrophotometer using thin films on NaCl plates for liquids and oils and KBr discs for solids and crystals. Absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}) and classified as strong (s) or broad (br).

Low resolution mass spectra (LRMS) were recorded on a Waters Micromass LCT Premier TOF spectrometer using electrospray ionization (ESI) and high resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF ESI mass spectrometer. Nominal and exact m/z values are reported in Daltons.

Thin layer chromatography (TLC) was carried out using Merck aluminium backed sheets coated with $60F_{254}$ silica gel. Visualization of the silica plates was achieved using a UV lamp (λmax = 254 nm), and/or acid dip (1:1 MeOH/H_2O, 10% H_2SO_4) and/or ammonium molybdate 5% in 2M H_2SO_4, and/or potassium permanganate (5% $KMnO_4$ in 1M NaOH with 5% potassium carbonate). Column chromatography was carried out using BDH PROLAB® 40-63 mm silica gel (VWR). Mobile phases are reported in ratio of solvents (e.g. 4:1 petrol/ ethyl acetate)

Anhydrous solvents were purchased from Fluka or Acros with the exception of dichloromethane and THF, which were dried over alumina cartiges. All other solvents were used as supplied (Analytical or HPLC grade), without prior purification. Distilled water was used for chemical reactions and Milli-Q™ purified water for protein manipulations. Reagents were purchased from Sigma Aldrich and used as supplied, unless otherwise indicated. 'Petrol' refers to the fraction of light petroleum ether boiling in the range 40–60 ºC. All reactions using anhydrous conditions were performed using flame-dried apparatus under an atmosphere of argon or nitrogen. 3Å and 4Å molecular sieves were activated by heating in a 400 °C furnace and were also employed for anhydrous reactions. Brine refers to a saturated solution of sodium chloride. Anhydrous magnesium sulfate ($MgSO_4$) or sodium sulfate (Na_2SO_4) were used as drying agents after reaction workup, as indicated. DOWEX 50WX8 (H^+ form) was conditioned as follows: 100 g of the commercial resin was placed in a 500 mL sintered filter funnel and allowed to swell with 200 mL of acetone for 5 minutes. The solvent was removed by suction and the resin was washed successively with 800 mL of acetone, 500 mL methanol, 500 mL 5M HCl, and then 1 L of water or until the pH of filtrate was ~ 7, as indicated by pH paper. The resin was partially dried on the filter and then stored and used as needed.

Molecular beam spectroscopy of carbohydrates was performed as follows. The carbohydrates were mixed with graphite powder or carbon black, and vaporized into a supersonic jet of argon using a home-built laser desorption system. The expanding jet passed through a 2 mm skimmer to create a collimated molecular beam which intersected tuneable UV and IR laser beams in the extraction region of a linear time-

of-flight mass spectrometer (Jordan). One, or two colour, mass-selected photoionisation spectra, recorded using a frequency-doubled pulsed Nd:YAG-pumped dye laser operating at 10 Hz, were followed by conformer-specific spectroscopy in the UV and IR using UV-UV and IR-UV ion dip (IRID) double resonance spectroscopy. The tuneable IR radiation was provided by a second dye laser using difference frequency generation in a $LiNbO_3$ crystal (Continuum Powerlite 8010/ND6000/IRP module) or directly, using an OPO/OPA laser system (LaserVision). The delay between the pump and the probe laser pulses was ~150 ns in both the IRID and UV-UV double resonance experiments.

Computational Strategies

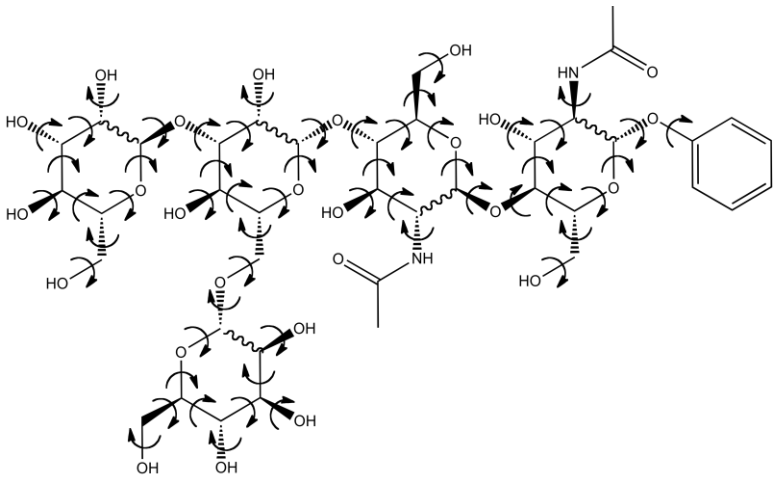
The structural conformational search followed an iterative approach. The spectroscopic calculations began with completely unrestricted and exhaustive surveys of the conformational landscapes of each of the carbohydrate 'building blocks', and their singly hydrated complexes, using a molecular mechanics method (MMFFs-force field)[1] until no additional new structures were obtained. Water molecules were free to find their most favoured binding sites. Their conformers were identified with the advanced hybrid[2] Large-Scale Low-Mode[3]/Monte Carlo algorithm[4] (LM/MC) (see p. S21) implemented in MacroModel, v.9.2, Schrödinger, LLC21.[5] These surveys, generated 2000-5000 structures depending on the system (<25 kJ mol^{-1}). The initial sets of structures were grouped into families. The ~50 lowest-lying energy conformers (<15 kJ mol^{-1}) and a representative member of each group that might have a significant population in the cooled adiabatic expansion (typically ~100 structures), were re-optimized through density functional theory calculations (B3LYP/6-311+G*) using the Gaussian 09 program package[6] to provide a new energy ranking of the lowest energy structures and their associated harmonic vibrational spectra. Zero-point corrected relative energies were computed through subsequent single point ab initio calculations (MP2/6-311++G**) and final optimizations were based upon comparisons with the experimental spectra themselves, to provide feedback and guide the 'fine-tuning' of the predicted structures. Calculations at the MP2 level were not feasible for the bare and 'blocked' trisaccharides, **3** and **3-B**, and dispersion was taken into account using the M06-2X functional, to obtain fully optimized structures, frequencies and relative energies. The quantum mechanical calculations used the Gaussian09 package running in two supercomputers employing a maximum of 96 processors per calculation.

Vibrational, structural and conformational assignments were based primarily on the level of correspondence between the experimental and computed OH vibrational spectra, scaled by the 'anharmonicity' factors, 0.9734 (OH) and 0.9600 (NH), to bring them into better accord with experiment. The best agreement between experiment and theory for the most strongly populated structures corresponded, in all cases, with the calculated minimum energy structures.

Conformational analysis of the core pentasaccharide, 4.

The gas phase conformational preferences of the core pentasaccharide 4, were investigated using (a) the OPLS2005 force field[7] of Macromodel version 9.5[5] selected after a series of evaluations of alternative fields[1] using the known conformational preferences of **1** as a reference (Figure 3a, main text), and (b) the GLYCAM06 force field[8], specifically parameterized for carbohydrates. (Note: a recent investigation[9] of a range of alternative force fields found OPLS2005 and GLYCAM (using the 2006 parameters) to be similar in terms of disaccharide characterisation).

The potential energy surface (PES) was exhaustively sampled, again using the 1:1 hybrid Low Mode Monte Carlo (LM/MC) conformational sampling technique. The MC step randomly varied between 2 to 56 of the torsions (Supplementary Figure S15). Each LM step explored the potential in the vicinity of a minimum by taking random steps between 3-6 Å along the 10 lowest eigenvectors. All chiral centres were preserved in the conformational search, and amide bonds were constrained to trans geometry. The ring-opening method of Still[10] was used to explore additional ring conformations.



Supplementary Figure S15: Conformational search strategy for the core-pentasaccharide, **4**. Torsions varied in the conformation search indicated by arrows, bond breaking indicated by wavy bonds.

New structures were evaluated *via* heavy atom and polar hydrogen superposition with previously found conformers. Structures were saved as unique

[1] The OPLS2005 force field possessed the fewest low quality stretch, bend and torsional parameters.

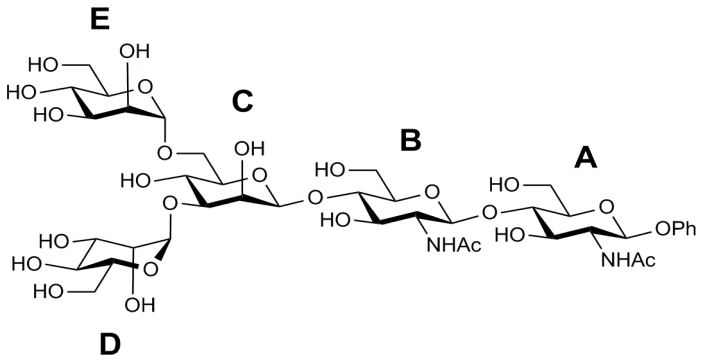
provided a minimum distance of 0.25 Å between atom pairs. Each structure was subjected to 500 steps of the Truncated Newton Conjugate Gradient[11] (TNCG) minimization method. LM/MC searching was performed in 5000 step blocks. Exhaustive PES sampling was achieved by monitoring the convergence of the global minimum energy and the number of converged structures found, as well as by an increase in the frequency of global minimum sampling. In each subsequent CS block, the least sampled structure was used as a starting point for additional LM/MC steps.

Conformational searches were similarly performed to determine solvent effects. Bulk water simulations were performed using the Generalized Born Surface Area[12] (GBSA) continuum solvation model in conjunction with the OPLS2005s or GLYCAM06 force field. Subsequent calculations, performed to determine the effect of hydration in the gas phase, included explicitly hydrated complexes incorporating three water molecules located at binding sites based upon the lowest energy preferences of singly hydrated trimannose[13], chitobiose **1**, and Man-β-1,4-GlcNAc-β-1-OPh **2** (Figure 4, main text). Water molecules were allowed translational freedom of 1Å. For the gas phase CS, 175,000 steps were used to achieve convergence and 1420 minimized structures were obtained within 30 kJ/mol of the global minimum. The bulk water and explicitly hydrated conformational searches required 75,000 steps for convergence and resulted in 6146 and 2740 structures within 30 kJ mol^{-1} of the global minimum, respectively.

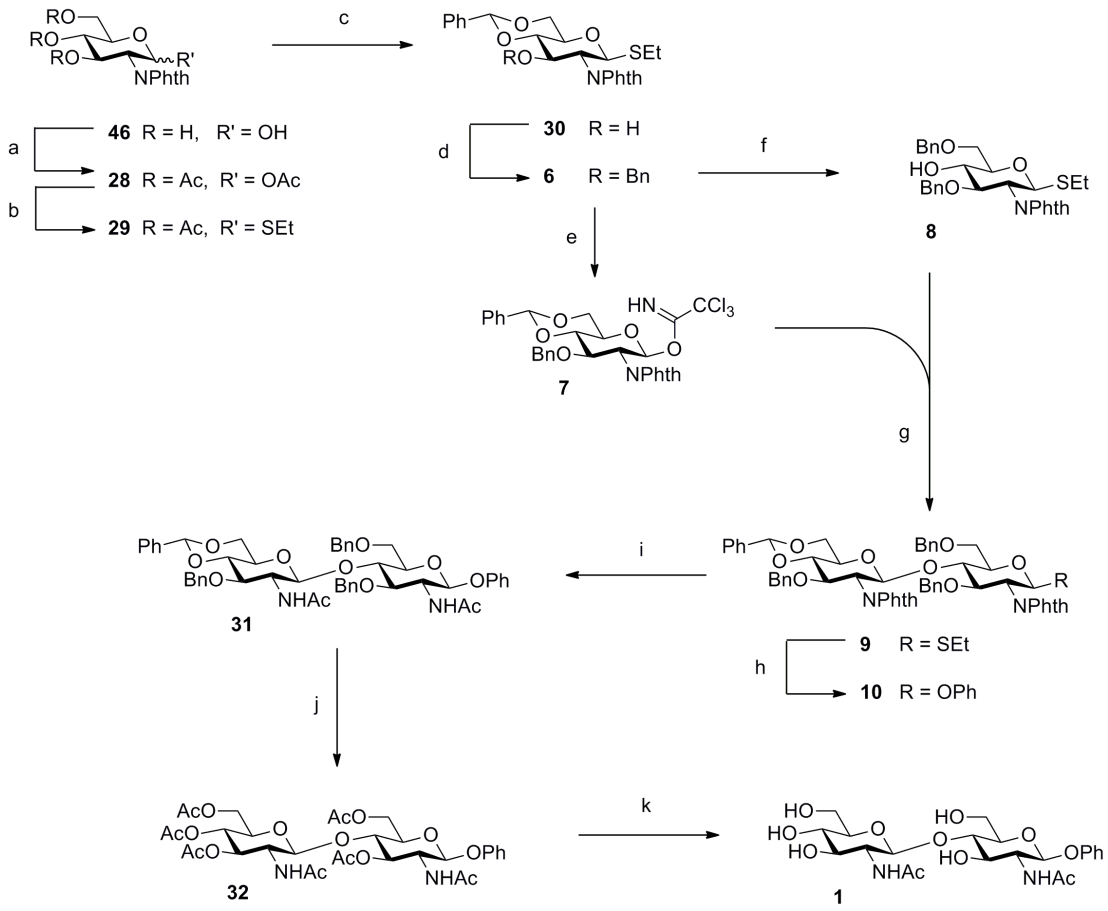
Supplementary chemistry schemes, synthesis and characterization

General Synthetic Considerations

The hexose rings of all compounds are defined A – E as detailed below. These definitions are used throughout to denote the hexose rings in the characterisation of compounds. Compounds **11**[14], **34**[15] and **46**[16] were synthesized as has been recorded previously and their characterization matched previously reported spectroscopic data.

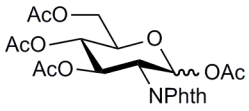


Synthesis of compound 1.



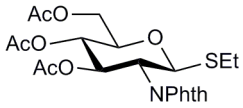
Reagents and conditions: a) Ac_2O, pyridine, rt, 67%; b) EtSH, TMS-OTf, DCM, rt, 74%; c) i- NaOMe, MeOH, rt, ii- benzaldehyde dimethylacetal, $TsOH.H_2O$, MeCN, rt, 87%; d) NaH, BnBr, TBAI, DMF, rt, 91%; e) i- NBS, acetone/water, -10 ^oC, ii- Cl_3CCN, DBU, DCM, rt, 84%; f) $NaCNBH_3$, THF, 0 ^oC, 82%; g) TMS-OTf, 4Å MS, DCM, -78 ^oC, 89%; h)) PhOH, NIS, TMS-OTf, 4Å MS, DCM, 0 ^oC, 37%; i) i- 1,2-ethylenediamine, MeOH, 80 ^oC, ii- Ac_2O, pyridine, rt, 66%; j) i- H_2, $Pd(OH)_2$, MeOH, rt, ii- Ac_2O, pyridine, rt, 92%; k) NaOMe, MeOH, rt, 94%.

Acetyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside[17]



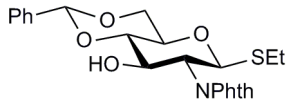
Acetic anhydride (147.4 ml, 1559.8 mmol) was added dropwise to a suspension of 2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside[16] **46** (88.0 g, 283.6 mmol) in dry pyridine (750 ml) at rt under an atmosphere of nitrogen. The mixture was stirred for 25h at rt then concentrated *in vacuo*. The resulting oil was dissolved in DCM (600 ml) and washed successively with water (300 ml), 1M hydrochloric acid (3x 300 ml), saturated aqueous sodium hydrogencarbonate (300 ml) and brine (2x 300 ml). The organic layer was dried ($MgSO_4$), filtered and concentrated *in vacuo* to give acetyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **28** (91.2 g, 67%) as a pale yellow oil (α/β ~2:1); δ_H (400 MHz, $CDCl_3$) **28-α**: 1.86 (3H, s), 2.05 (3H, s), 2.08 (3H, s), 2.11 (3H, s), 4.12 (1H, dd, *J* 12.3, 1.5, 6-*H*H), 4.30 (1H, ddd, *J* 9.9, 4.0, 1.5, 5-H), 4.35 (1H, dd, *J* 12.3, 4.0, 6-H*H*), 4.71 (1H, dd, *J* 11.6, 3.3, 2-H), 5.20 (1H, dd, *J* 9.9, 9.2, 4-H), 6.27 (1H, d, *J* 3.5, 1-H), 6.55 (1H, dd, *J* 11.4, 9.2, 3-H), 7.71-7.77 (2H, m), 7.81-7.88 (2H, m); δ_C (100 MHz, $CDCl_3$) 20.4 (-OAc), 20.6 (-OAc), 20.64 (2x -OAc), 20.7 (2x -OAc), 20.8 (-OAc), 52.8 (C-2α), 53.47 (C-2β), 61.5 (C-6α), 65.8 (C-6β), 67.0 (C-3α), 68.3 (C-4β), 69.4 (C-4α), 70.2 (C-5α), 70.5 (C-3β), 72.6 (C-5β), 89.7 (C-1α), 90.5 (C-1β), 123.7, 123.8, 131.2, 134.5, 168.6, 169.3, 169.46, 169.52, 169.8, 170.0, 170.7; *m/z* (ES^+) 495.17 ($[M.NH_4]^+$, 27%), 500.11 ($[M.Na]^+$ 77%), 977.18 ($[2M.Na]^+$ 100%); δ_H (400 MHz, $CDCl_3$) **28-β**: 1.85 (3H, s), 1.99 (3H, s), 2.03 (3H, s), 2.10 (3H, s), 4.02 (1H, ddd, *J* 10.2, 4.0, 1.8, 5-H), 4.13 (1H, dd, *J* 12.3, 1.8, 6-*H*H), 4.28-4.32 (1H, m, 6-H*H*), 4.46 (1H, dd, *J* 10.3, 8.9, 2-H), 5.15 (1H, dd, *J* 10.1, 9.1), 5.87 (1H, dd, *J* 10.1, 9.1), 6.50 (1H, d, *J* 8.9, 1-H), 7.71-7.77 (2H, m), 7.81-7.88 (2H, m); δ_C (100 MHz, $CDCl_3$) 20.4 (-OAc), 20.6 (-OAc), 20.64 (2x -OAc), 20.7 (2x -OAc), 20.8 (-OAc), 52.8 (C-2α), 53.47 (C-2β), 61.5 (C-6α), 65.8 (C-6β), 67.0 (C-3α), 68.3 (C-4β), 69.4 (C-4α), 70.2 (C-5α), 70.5 (C-3β), 72.6 (C-5β), 89.7 (C-1α), 90.5 (C-1β), 123.7, 123.8, 131.2, 134.5, 168.6, 169.3, 169.46, 169.52, 169.8, 170.0, 170.7; *m/z* (ES^+) 495.17 ($[M.NH_4]^+$, 27%), 500.11 ($[M.Na]^+$ 77%), 977.18 ($[2M.Na]^+$ 100%).

Ethyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside[18]



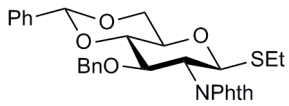
Trimethylsilyl-trifluoromethanesulfonate (3.33 ml, 18.4 mmol) was added slowly to a solution of acetyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **28** (8.00 g, 16.7 mmol) and ethanethiol (2.23 ml, 30.1 mmol) in dry DCM (80 ml) at rt under an atmosphere of nitrogen. The mixture was stirred at rt for 24h whereupon TLC analysis (50% EtOAc/Petrol) indicated complete consumption of starting material and formation of a product (R_f=0.55). Triethylamine (5 ml) was added and the mixture was stirred for 20 min. The mixture was added to saturated aqueous sodium hydrogen carbonate solution (200 ml) and DCM (100 ml). The layers were separated and the aqueous layer was extracted with DCM (2x 80 ml). The combined organic layers were washed with saturated aqueous sodium hydrogencarbonate solution (100 ml) and brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a pale yellow oil which was purified by flash column chromatography on silica gel eluting with 40% EtOAc/petrol to give ethyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **29** as a white solid (5.9g, 74%); m.p. 115-117 ^oC; $[\langle]_D^{25}$ +39.5 (c=1.0, $CHCl_3$) [lit. $[\langle]_D^{22}$ +44.0 (c=0.8, $CHCl_3$)][18]; δ_H (400 MHz, $CDCl_3$) 1.22 (3H, t, *J* 7.4, -CH_2CH_3), 1.86 (3H, s, -OAc), 2.03 (3H, s, -OAc), 2.10 (3H, s, -OAc), 2.66 (1H, dq, *J* 12.6, 7.4, -SC*H*H-), 2.72 (1H, dq, *J* 12.6, 7.4, -SCH*H*-), 3.90 (1H, ddd, *J* 10.1, 5.0, 1.9, 5-*H*), 4.17 (1H, dd, *J* 12.3, 1.9, 6-*H*H), 4.31 (1H, dd, *J* 12.3, 5.0, 6-H*H*), 4.39 (1H, app t, *J* 10.5, 2-*H*), 5.18 (1H, dd, *J* 10.1, 9.0, 4-*H*), 5.49 (1H, d, *J* 10.5, 1-*H*), 5.83 (1H, dd, *J* 10.5, 9.0, 3-*H*), 7.71-7.78 (4H, m, 4x Ar-*H*), 7.82-7.90 (4H, m, 4x Ar-*H*); δ_C (100 MHz, $CDCl_3$) 14.9 (-SCH_2CH_3), 20.5 (-OAc), 20.6 (-OAc), 20.8 (-OAc), 24.4 (-SCH_2CH_3), 53.7 (C-2), 62.3 (C-6), 68.9 (C-4), 71.5 (C-3), 75.9 (C-5), 81.2 (C-1), 123.7, 131.1, 131.6, 134.3, 134.4, 167.2, 167.8, 169.5, 170.1, 170.7; *m/z* (ES^-) 478.15 ($[M-H]^-$, 100%).

Ethyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside[19]



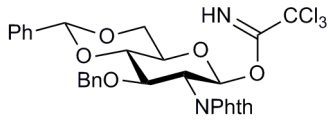
Sodium methoxide (138 mg, 2.4 mmol) was added to a solution of ethyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **29** (23.0 g, 48.0 mmol) in dry methanol (175 ml) at rt under an atmosphere of nitrogen. The mixture was stirred for 16h then activated Dowex-H^+ (~4g) was added. The mixture was stirred for 1h then filtered and concentrated *in vacuo* to give a white foam (16.82 g) which was dissolved in dry acetonitrile (300 ml) at rt under an atmosphere of nitrogen. *p*-Benzaldehyde dimethylacetal (13.93 ml, 98.2 mmol) and TsOH.H_2O (265 mg, 1.4 mmol) were added and the mixture was stirred for 65h whereupon TLC analysis (30% EtOAc/petrol) indicated complete consumption of the starting material and formation of a product (R_f=0.29). Triethylamine (3 ml) was added, the mixture was stirred for an additional 1h and then concentrated *in vacuo*. The resulting oil was partitioned between DCM (250 ml) and saturated aqueous sodium hydrogencarbonate solution (200 ml). The layers were separated and the aqueous layer was extracted with DCM (4x 75 ml). The combined organic layers were washed with brine (2x 150 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a brown oil which was purified by flash column chromatography on silica gel eluting with 2% MeOH/DCM to give a yellow solid which was further purified by recrystallisation from diethyl ether/petrol to give ethyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **30** as a white solid (17.8g, 87%); $[\langle]_D^{25}$ -5.3 (c=1.0, $CHCl_3$) [lit. $[\langle]_D^{25}$ -5.0 (c=1.2, $CHCl_3$)][19]; δ_H (400 MHz, $CDCl_3$) 1.20 (3H, t, *J* 7.5, -C*H*$_3$), 2.66 (1H, dq, *J* 12.5, 7.5, -SC*H*H-), 2.73 (1H, dq, *J* 12.5, 7.5, -SCH*H*-), 3.61 (1H, t, *J* 9.1, 4-H), 3.70 (1H, td, *J* 9.7, 4.8, 5-H), 3.81 (1H, t, *J* 10.2, 6-*H*H), 4.33 (1H, t, *J* 10.2, 2-H), 4.40 (1H, dd, *J* 10.2, 4.8, 6-H*H*), 4.66 (1H, dd, *J* 9.7, 9.1, 3-H), 5.41 (1H, d, *J* 10.6, 1-H), 5.58 (1H, s, Ph-C*H*-), 7.36-7.41 (3H, m), 7.47-7.53 (2H, m), 7.70-7.76 (2H, m), 7.82-7.91 (2H, m); δ_C (100 MHz, $CDCl_3$) 14.9, 24.2, 55.5 (C-2), 68.6 (C-6), 69.5 (C-3), 70.4 (C-5), 81.9 (C-1), 82.1 (C-4), 101.9, 126.3, 128.4, 129.0, 129.4, 129.8, 134.2, 134.5; *m/z* (ES^+) 464.12 ($[M.Na]^+$, 100%), 905.27 ($[2M.Na]^+$, 92%).

Ethyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside[17]



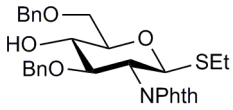
Sodium hydride (1.88 g of 60%w/w, 46.93 mmol) was added in portions to a solution of ethyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **30** (17.25 g, 39.11 mmol) in dry DMF (250 ml) at r.t. under an atmosphere of nitrogen. The mixture was stirred for 30 min then benzyl bromide (5.58 ml, 46.93 mmol) and tetra-*N*-butylammonium iodide (100 mg) were added. The reaction mixture was stirred for 3.5h whereupon TLC analysis (100% DCM) indicated the formation of a single product (Rf=0.09). Methanol (2.5 ml) was added slowly. The mixture was stirred at r.t. for 15 min then concentrated *in vacuo*. The resulting residue was partitioned between DCM (300 ml) and water (300 ml). The layers were separated and the aqueous layer was extracted with DCM (2x 150 ml). The combined organic layers were washed with water (150 ml) brine (2x 150 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a yellow oil which was purified by flash column chromatography on silica gel eluting with 0-1% MeOH/DCM to give ethyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **6** as a pale yellow solid (18.85g, 91%); m.p. 91-96 ^{o}C; $[\langle]_D^{25}$ +59.9 (c=1.0, $CHCl_3$) [lit. $[\langle]_D^{20}$ +53.5 (c=1.0, $CHCl_3$)][17]; δ_H (400 MHz, $CDCl_3$) 1.17 (3H, t, *J* 7.5, -C*H*$_3$), 2.63 (1H, dq, *J* 12.5, 7.5, -SC*H*H-), 2.70 (1H, dq, *J* 12.5, 7.5, -SCH*H*-), 3.72 (1H, td, *J* 9.7, 4.8, 5-H), 3.84 (1H, t, *J* 9.1, 4-H), 3.85 (1H, t, *J* 10.2, 6-*H*H), 4.31 (1H, t, *J* 10.3, 2-H), 4.43 (1H, dd, *J* 10.4, 4.8, 6-H*H*), 4.47 (1H, dd, *J* 9.7, 9.0, 3-H), 4.52 (1H, d, 12.3, Ph-C*H*H-), 4.80 (1H, d, 12.3, Ph-CH*H*-), 5.36 (1H, d, *J* 10.8, 1-H), 5.64 (1H, s, Ph-C*H*-), 6.86-6.96 (3H, m), 6.98-7.03 (2H, m), 7.36-7.45 (3H, m), 7.51-7.56 (2H, m), 7.62 (1H, d, *J* 6.5), 7.68-7.76 (2H, m), 7.86 (1H, d, *J* 6.5); δ_C (100 MHz, $CDCl_3$) 14.9 (-*C*H$_3$), 24.1 (-S*C*H$_2$-), 54.7 (C-2), 68.7 (C-6), 70.4 (C-5), 74.2 (-Bn), 75.4 (C-3), 81.8 (C-1), 83.0 (C-4), 101.3, 126.1, 127.4, 127.8, 128.1, 128.12, 128.3, 129.0, 129.8, 134.0, 134.5, 137.3, 137.8; *m/z* (ES^+) 532.19 ($[M.H]^+$, 5%), 549.22 ($[M.NH_4]^+$ 19%), 554.15 ($[M.Na]^+$ 100%).

3-*O*-Benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-1',1',1'-trichloroacetimidate[20]



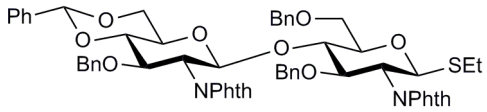
N-Bromosuccinimide (10.30 g, 57.85 mmol) was added to a solution of ethyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **6** (6.15 g, 11.57 mmol) in 10:1 acetone/water (75 ml) at -10 ^{o}C. The reaction mixture was stirred for 10 min whereupon TLC analysis (33% EtOAc/petrol) indicated complete consumption of the starting material (Rf=0.54) and the formation of a single product (Rf=0.13). The reaction mixture was diluted with DCM (300 ml) and washed with washed with saturated aqueous sodium hydrogencarbonate solution (100 ml), 10% aqueous sodium thiosulfate solution (2x 100 ml) and brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting white solid (6.21 g) was dissolved in dry DCM (75 ml) at r.t. under a nitrogen atmosphere and trichloroacetonitrile (11.60 ml, 115.70 mmol) and DBU (173 µl, 1.16 mmol) were added. The reaction mixture was stirred at r.t. for 75 min whereupon TLC analysis (2% EtOAc/DCM) indicated the formation of a single product (Rf=0.27). The mixture was concentrated *in vacuo* at 30 ^{o}C and purified immediately by flash column chromatography on silica gel eluting with an increasing proportion of EtOAc/DCM from 0-2% to give 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-1',1',1'-trichloroacetimidate **7** as a white solid (6.12 g, 84%): $[\langle]_D^{25}$ +87.1 (c=1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 3.83-3.98 (3H, m, 3-*H*, 5-*H*, 6-*H*H), 4.46-4.61 (4H, m, 2-*H*, 4-*H*, 6-H*H*, PhC*H*H-), 4.83 (1H, d, *J* 12.4, PhCH*H*-), 5.66 (1H, s, PhC*H*-), 6.50 (1H, d, *J* 8.3, 1-*H*), 6.86-6.97 (3H, m, 3x Ar-*H*), 7.00-7.05 (2H, m, 2x Ar-*H*), 7.37-7.45 (3H, m, 3x Ar-*H*), 7.51-7.57 (2H, m, 2x Ar-*H*), 7.66-7.81 (4H, m, 4x Ar-*H*), 8.59 (1H, s, N*H*); δ_C (400 MHz, $CDCl_3$) 54.7 (C-2), 66.9 (C-3), 68.5 (C-6), 74.2 (-*C*H_2Ph), 74.3 (C-4), 82.6 (C-5), 90.2 (-*C*Cl_3), 94.3 (C-1), 101.5 (-*C*HPh), 123.4, 126.1, 127.5, 128.1, 128.3, 129.1, 131.4, 134.0, 137.1, 137.8, 160.8; *m/z* (ES^+) 653.11 ($[M.Na]^+$, 81%), 654.11 ($[M.Na]^+$, 39%), 655.11 ($[M.Na]^+$, 100%), 656.11 ($[M.Na]^+$, 51%).

Ethyl-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside[21]



A solution of ethyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **6** (5.10g, 9.58 mmol) in dry THF (20 ml + 15 ml washings) was added *via* cannula to a suspension of sodium cyanoborohydride (6.02g, 95.80 mmol), methyl orange (~2mg) and freshly activated 3Å molecular sieves (3.0 g) in dry THF (85 ml) at 0^{o}C under a nitrogen atmosphere. HCl (4M solution in dioxane) was added slowly (Caution: effervescence) until the yellow colour of the solution changed to a persistent pink (~20ml). The resulting reaction mixture was stirred 17h slowly warming to r.t. whereupon TLC analysis (33% EtOAc/petrol) indicated the complete consumption of the starting material (Rf=0.53) and formation of a single product (Rf=0.32). The reaction was quenched by the addition of saturated aqueous sodium hydrogencarbonate solution (200 ml). The resulting yellow solution was filtered through celite and diluted with DCM (200 ml). The layers were separated and the aqueous layer was extracted with DCM (2x 150 ml). The combined organic layers were washed with saturated aqueous sodium hydrogencarbonate solution (150 ml) and brine (150 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* three times from MeOH to give white solid which was stirred with DCM (200 ml) and filtered through celite. The filtrate wasoncentrated *in vacuo* to give a pale yellow solid which was purified by flash column chromatography on silica gel eluting with an increasing proportion of EtOAc/DCM from 5-10% to give ethyl-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **8** as a white solid (4.18 g, 82%): $[\langle]_D^{25}$ +41.1 (c=1.0, $CHCl_3$) [lit. $[\langle]_D^{25}$ +42 (c=1.2, $CHCl_3$)][21]; δ_H (400 MHz, $CDCl_3$) 1.17 (3H, t, *J* 7.3, -SCH_2CH_3), 2.59 (1H, dq, *J* 12.5, 7,3, -SC*H*HCH_3), 2.67 (1H, dq, *J* 12.5, 7,3, -SC*H*HCH_3), 3.69 (1H, dt, *J* 9.5, 5.2, 5-*H*), 3.78 (1H, dd, *J* 10.1, 5.2, 6-*H*H), 3.81-3.88 (2H, m, 4-*H*, 6-H*H*), 4.20-4.31 (2H, m, 2-*H*, 3-*H*), 4.55 (1H, d, *J* 12.1, PhC*H*H-), 4.59 (1H, d, *J* 12.0, PhC*H*H-), 4.65 (1H, d, *J* 12.0, PhCH*H*-), 4.76 (1H, d, *J* 12.1, PhCH*H*-), 5.28 (1H, d, *J* 9.9, 1-*H*), 6.92-7.84 (14H, m, 14x Ar-*H*); δ_C (400 MHz, $CDCl_3$) 14.9 (-SCH_2CH_3), 24.0 (-SCH_2CH_3), 54.4 (C-2), 70.9 (C-6), 73.8 (PhCH_2-), 74.46 (PhCH_2-), 74.48 (C-4), 77.6 (C-5), 79.5 (C-3), 81.1 (C-1), 123.3, 123.5, 127.4, 127.8, 127.9, 128.2, 128.5, 131.6, 133.8, 133.9, 137.6, 138.1, 167.5, 168.0; *m/z* (ES^-) 532.21 ($[M-H]^-$, 100%).

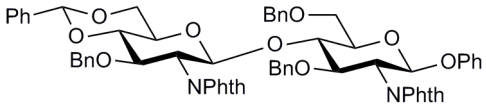
Ethyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside



A mixture of 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-1',1',1'-trichloroacetimidate **7** (5.51 g, 8.72 mmol) and ethyl-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **8** (4.23 g, 7.93 mmol) was concentrated from toluene (4x 50 ml) and dried under vacuum. The dried mixture was dissolved in dry DCM (25 ml + 25 ml washings) and added *via* cannula to a flask containing freshly activated 4Å molecular sieves (3.1 g) at r.t. under a nitrogen atmosphere. The resulting suspension was stirred at r.t. for 30 min then cooled to -78 ^{o}C. Trimethylsilyltrifluoromethanesulfonate (143 μl, 0.79 mmol) was added and the mixture was stirred at -78 ^{o}C for 5 min whereupon TLC analysis (10% EtOAc/toluene) indicated complete consumption of the donor **7** (Rf=0.42) and the acceptor **8** (Rf=12) and the formation of a major product (Rf=0.30). Triethylamine (2.5 ml) was added and the mixture was warmed to r.t. and filtered through celite. The filtrate was diluted with DCM (100 ml) and saturated aqueous sodium hydrogencarbonate solution (150 ml). The layers were separated and the aqueous layer was extracted with DCM (2x 100 ml). The combined organic layers were washed with saturated aqueous sodium hydrogencarbonate solution (100 ml), water (100 ml) and brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a pale yellow foam which was purified by flash column chromatography on silica gel eluting with an increasing proportion of EtOAc/toluene from 2-10% to give ethyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **9** (7.07 g, 89%) as a white solid: $[\langle]_D^{25}$ +29.8 (c=1.0, $CHCl_3$) [lit. $[\langle]_D^{25}$ (c=1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 1.12 (3H, t, *J* 7.3, -SCH_2CH_3), 2.52 (1H, dq, *J* 12.6, 7.3, -SC*H*HCH_3), 2.61 (1H, dq, *J* 12.6, 7.3, -SCH*H*CH_3), 3.34-3.45 (3H, m, 5-*H*, 5-*H*, 6-*H*H), 3.50-3.59, (2H, m, 6-*H*H, 6-H*H*), 3.73 (1H, app t, *J* 8.9, 4-*H*), 4.18-4.28 (5H, m, 2-*H*, 2-*H*, 3-*H*, 4-*H*, 6-H*H*), 4.43 (1H, d, *J* 11.9, PhC*H*H-), 4.46 (1H, dd, *J* 9.9, 8.9, 3-

H), 4.49 (1H, d, *J* 11.9, PhC*H*H-), 4.50 (1H, d, *J* 12.3, PhC*H*H-), 4.53 (1H, d, *J* 12.3, PhC*H*H-), 4.81 (1H, d, *J* 12.3, PhC*H*H-), 4.85 (1H, d, *J* 12.3, PhC*H*H-), 5.11 (1H, d, *J* 9.1, 1a-*H*), 5.42 (1H, d, *J* 8.5, 1b-*H*), 5.53 (1H, s, PhC*H*-), 6.88-7.95 (28H, m, 28x Ar-*H*); δ_C (400 MHz, $CDCl_3$) 14.9 (-SCH_2CH_3), 23.6 (-SCH_2CH_3), 54.7 (C-2a), 56.6 (C-2b), 65.8 (C-5), 68.2 (C-6), 68.7 (C-6), 72.7 (PhCH_2-), 74.1 (PhCH_2-), 74.49 (PhCH_2-), 74.51 (C-3), 76.1, 77.8, 78.8 (C-5), 80.8 (C-1a), 83.2 (-CCl_3), 97.7 (C-1b), 101.2 (PhCH-), 123.2, 123.5, 126.1, 127.1, 127.3, 127.4, 127.5, 127.8, 127.98, 128.04, 128.26, 128.27, 129.00, 129.04, 131.6, 133.7, 133.8, 133.99, 134.03, 137.4, 137.9, 138.3, 138.5, 167.5, 167.9; *m/z* (ES^+) 1025.41 ($[M.Na]^+$ 100%); ESI^+ [$C_{58}H_{54}N_2NaO_{12}S$] requires 1025.3290, found 1025.3279.

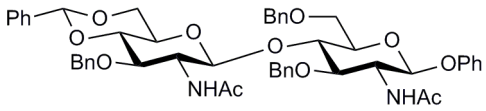
Phenyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside



Ethyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **9** (1.50 g, 1.50 mmol) was concentrated *in vacuo* from toluene (3x 25 ml) then dissolved in dry DCM (20 ml) and stirred over freshly activated 4Å molecular sieves (0.5 g) at r.t. under a nitrogen atmosphere for 1h. The mixture was cooled to 0 ^{o}C and NIS (422 mg, 1.88 mmol, dried by stirring over freshly activated 4Å molecular sieves) was added followed immediately by TMS-OTf (27 μL, 0.15 mmol). The mixture was stirred at 0 ^{o}C for 15 min then phenol (212 mg, 2.25 mmol, concentrated *in vacuo* from toluene (3x 10 ml) and stirred over freshly activated 4Å molecular sieves) in dry DCM (10 ml) was added. The reaction mixture was stirred for 4 h in the dark, slowly warming to rt ^{o}C then filtered through celite and diluted with DCM (100 ml) and 5% aqueous sodium thiosulfate solution (100 ml). The layers were separated and the aqueous phase was extracted with DCM (3x 80 ml). The combined organic extracts were washed with 5% aqueous sodium thiosulfate solution (100 ml) and brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a yellow oil which was purified by flash column chromatography (Biotage SNAP 100g) on silica gel eluting with an increasing proportion of EtOAc/petrol from 25-70% to give phenyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **10** (570 mg, 37%) as a white solid: $[\alpha]_D^{21}$ +27.7 (c, 0.65 in $CHCl_3$); ™$_H$ (500 MHz, $CDCl_3$) 3.38-3.53 (4H, m, H5a, H5b, H6a, H6'a), 3.57 (1H, at, *J* 10.1 Hz, H6b), 3.75 (1H, at, *J* 9.2 Hz, H4b), 4.21-4.31 (4H, m, H2b, H3a, H4a, H6'b), 4.37-4.47 (4H m, H2a, H3b, 2 x PhCH), 4.50, 4.80 (2H, ABq, *J* 12.3 Hz, $PhCH_2$), 4.54, 4.85 (2H, ABq, *J* 12.3 Hz, $PhCH_2$), 5.40 (1H, d, $J_{1,2}$ 8.2 Hz, H1b), 5.54 (1H, s, PhCH), 5.61 (1H, d, $J_{1,2}$ 8.5 Hz, H1a), 6.77-7.92 (33H, m, ArH); ™$_C$ (125 MHz, $CDCl_3$) 55.5 (d, C2a), 56.5 (d, C2b), 65.8 (d, C5), 67.8 (t, C6), 68.7 (t, C6a), 72.7 (t, $PhCH_2$), 74.1 (t, $PhCH_2$), 74.4 (d, C5), 74.5 (t,

$PhCH_2$), 74.6 (d, C3b), 76.7, 77.0 (2 x d, C3a, C4a), 83.1 (d, C4b), 96.2 (d, C1a), 97.8 (d, C1b), 101.2 (d, PhCH), 116.9, 122.6, 123.3, 126.1, 127.1, 127.3, 127.4, 127.5, 127.8, 128.0, 128.2, 128.3, 129.0, 129.2 (14 x d, 33 x ArH), 139.3, 137.8, 137.9, 138.1, 138.4, 156.7 (6 x s, 9 x ArC). *m/z* (ES^+) 1093 (100%, $M+NH_4$/MeCN).

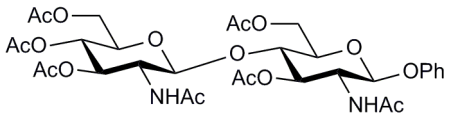
Phenyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside



Phenyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **10** (1.0 g, 0.97 mmol) was dissolved in methanol (50 mL), and 1,2-ethylenediamine (10 mL) was added and the reaction was heated to 80 ^{o}C. After 16 h, t.l.c. (ethyl acetate) showed the formation of a product (R_f 0) with complete consumption of the starting material (R_f 0.7). The reaction was co-evaporated with toluene (3 x 50 mL). The resulting residue was taken up in acetic anhydride (30 mL) and pyridine (50 mL). After 16 h, t.l.c. (ethyl acetate) showed the formation of a product (R_f 0.5) with complete consumption of the starting material (R_f 0). The reaction was partitioned between ethyl acetate (50 mL) and water (100 mL) and the phases separated. The aqueous phase was re-extracted with ethyl acetate (2 x 50 mL). The combined organic layers were washed with dilute hydrochloric acid (300 mL, 1M aqueous solution), sodium hydrogen carbonate (50 mL of a saturated aqueous solution), brine (50 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting residue was precipitated from acetone/petrol to afford phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside **31** (550 mg, 66%) as a white amorphous solid; $[\alpha]_D^{19}$ -9.2 (c, 0.5 in 1:1 MeOH/$CHCl_3$); J_{max} (KBr) 3275 (bs, NH), 1655, 1549 (s, C=O) cm^{1}; ™$_H$ (500 MHz, $CDCl_3$) 1.77, 1.90 (6H, 2 x s, 2 x NHAc), 3.20 (1H, dat, $J_{5,6}$ 4.7 Hz, *J* 9.4 Hz, H5b), 3.49-3.74 (7H, m, H3a, H3b, H4b, H5a, H6a, H6b, H6'b), 3.82 (1H, at, *J* 9.2 Hz, H2b), 3.88 (1H, at, *J* 5.2 Hz, H4a), 4.13 (1H, dd, $J_{5,6'}$ 4.9 Hz, $J_{6,6'}$ 10.6 Hz, H6a), 4.24-4.27 (2H, m, H2a, PhCH), 4.344.39 (2H, m, H1b, PhCH), 4.56, 4.77 (2H, ABq, *J* 12.0 Hz, $PhCH_2$), 4.62, 4.68 (2H, ABq, *J* 11.6 Hz, $PhCH_2$), 5.10 (1H, d, $J_{1,2}$ 5.4 Hz, H1a), 5.46 (1H, s, PhCH), 6.87-7.41 (25H, m, ArH); ™$_C$ (125 MHz, $CDCl_3$) 23.9, 24.2 (2 x q, 2 x NHAc), 52.1 (d, C-2a), 56.4 (d, C2b), 67.1 (d, C5b), 69.7 (t, C6a), 70.7 (t, C6b), 73.9, 74.9, 75.3 (3 x t, 3 x $PhCH_2$), 75.5 (d, C4a), 75.8, 78.8 (2 x d, C3a, C3b), 78.7, 83.3 (2 x d, C4b, C5a), 99.4 (d, C1a), 101.8

(d, C1b), 102.4 (d, PhCH), 117.6, 123.5, 127.2, 128.8, 129.0, 129.2, 129.3, 129.5, 129.6, 129.7, 130.3, 130.6 (12 x d, 25 x ArC), 138.3, 138.8, 139.4, 139.6, 158.3 (5 x s, 5 x ArC), 172.6, 173.1 (2 x s, 2 x CO). *m/z* (ES^+) 917 (100%, $M+NH_4$/MeCN). HRMS found 881.3627. calcd 881.3620 for $C_{50}H_{54}N_2NaO_{11}$.

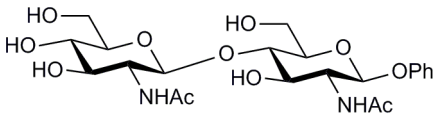
Phenyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside



Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside **31** (500 mg, 100 mmol) and Pearlman's catalyst ($Pd(OH)_2$, moist, 400 mg) were suspended in absolute methanol (20 mL). The resulting solution was degassed and purged with hydrogen gas, then left to stir under an atmosphere of hydrogen. After a 24 h period, t.l.c. (ethyl acetate) indicated the formation of a major product (R_f 0.0) with complete consumption of the starting material (R_f 0.9). The solution was filtered through celite® and concentrated *in vacuo*. The resulting residue resuspended in acetic anhydride (10 mL) and pyridine (15 mL) and stirred at RT. After 18 h t.l.c. (petrol:ethyl acetate, 2:3) indicated the formation of a product (R_f 0.4) with complete consumption of the starting material (R_f 0). The reaction was diluted with water (20 mL) and partitioned with ethyl acetate (20 mL) and the phases separated. The aqueous layer was reextracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with dilute hydrochloric acid (500 mL, 1M), sodium hydrogen carbonate (50 mL of a saturated aqueous solution), brine (30 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside **32** (380 mg, 92%) as a white amorphous foam; $[\alpha]_D^{21}$ -31.3 (c, 0.45 in $CHCl_3$); ν_{max} (KBr) 3272 (bs, NH), 1748, 1660, 1560 (s, C=O) cm^{-1}; δ_H (500 MHz, $CDCl_3$) 1.93, 1.99, 2.01, 2.09 (21H, 4 x s, 7 x OAc), 3.75 (1H, at, *J* 9.5 Hz, H2b), 3.78-3.80 (1H, m, H5b), 3.83-3.89 (2H, m, H4a, H5a), 4.05 (1H, bd, $J_{6,6'}$ 12.3 Hz, H6b), 4.12-4.17 (2H, m, H2a, H6a), 4.44 (1H, dd, $J_{5,5'}$ 4.0 Hz, $J_{6,6'}$ 12.4 Hz, H6'b), 4.50 (1H, d, $J_{6,6'}$ 11.7 Hz, H6'a), 4.76 (1H, d, $J_{1,2}$ 8.5 Hz, H1b), 5.00 (1H, at, *J* 9.6 Hz, H4b), 5.14 (1H, d, $J_{1,2}$ 8.2 Hz, H1a), 5.23 (1H, at, *J* 9.0 Hz, H3a), 5.30 (1H, at, *J* 10.0 Hz, H3b), 6.98 (2H, d, *J* 8.2 Hz, ArH), 7.03 (1H, t, *J* 7.4 Hz, ArH), 7.27 (2H, t, *J* 7.4 Hz, ArH); δ_C (125 MHz, $CDCl_3$) 21.1, 21.2, 21.3, 21.4, 23.2, 23.3 (6 x q, 7 x OAc), 55.4 (d, C2a), 56.2 (d, C2b), 63.1 (t,

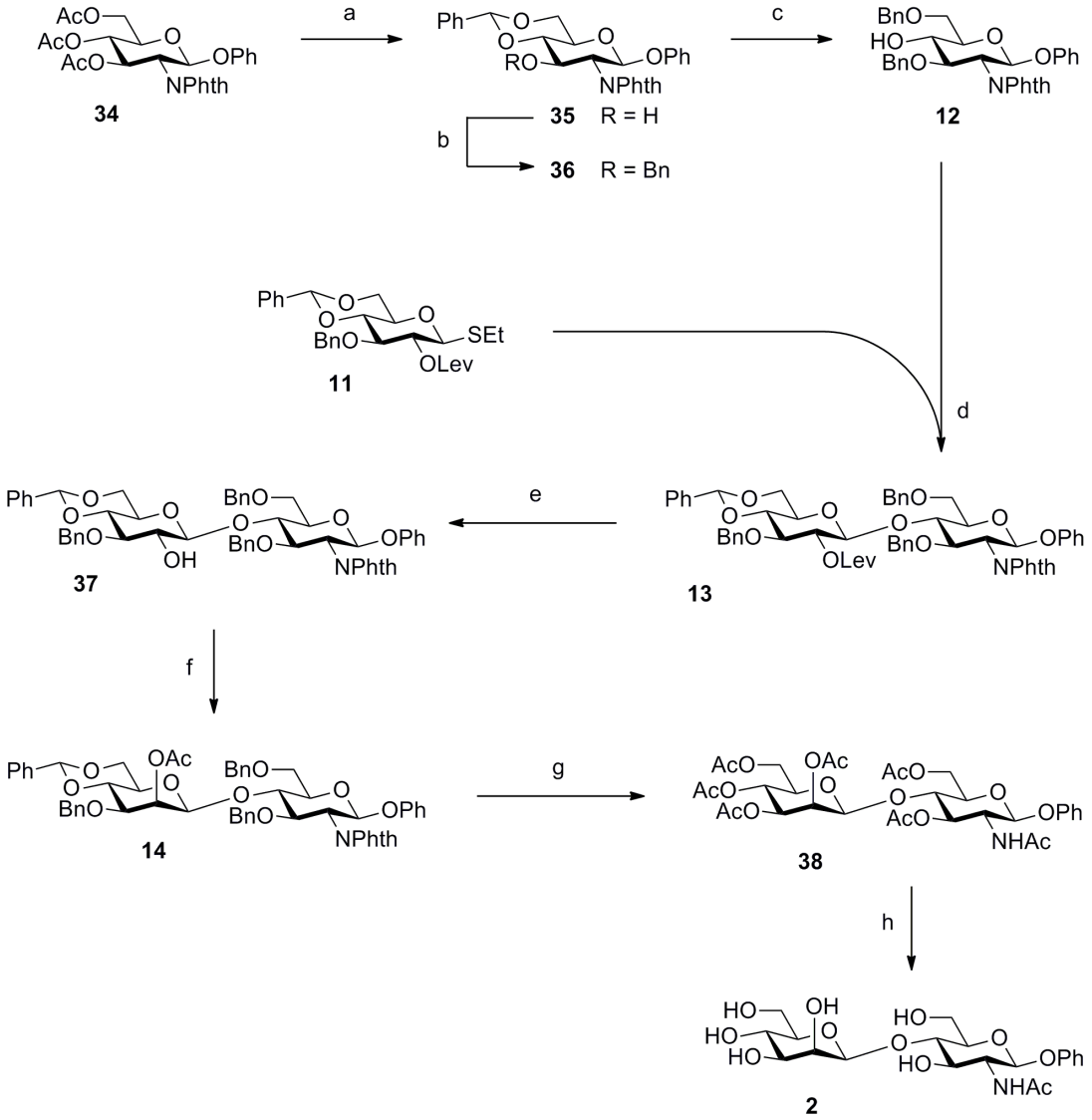
C6b), 63.9 (t, C6a), 69.8 (d, C4b), 72.9 (d, C5b), 73.7 (d, C3b), 74.1 (d, C5a), 74.6 (d, C3a), 77.7 (d, C4a), 100.0 (d, C1a), 102.1 (d, C1b), 117.9, 124.1, 130.6 (3 x d, 5 x ArC), 158.6 (s, ArC), 171.4, 172.0, 172.4, 172.5, 173.6 (5 x s, 7 x CO). *m/z* (ES^+) 733 (100%, M+Na). HRMS found 733.2432. calcd 733.2436 for $C_{32}H_{42}N_2NaO_{16}$.

Phenyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside



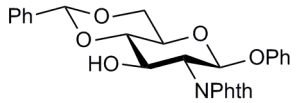
Phenyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside **32** (380 mg, 0.53 mmol) and sodium methoxide (3 mg, 0.53 mmol) were added to a stirred solution of methanol (20 mL). After 1 h, t.l.c. (ethyl acetate/petrol, 1:1) indicated the formation of a product (R_f 0) with complete consumption of the starting material (R_f 0.5). The reaction was neutralised by the addition of Dowex-50 ion exchange resin® after which point the reaction was filtered and concentrated *in vacuo* to afford phenyl 2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside **1** (250 mg, 94%) as a white amorphous solid; $[\alpha]_D^{21}$ -6.0 (c, 0.25 in H_2O); J_{max} (KBr) 3384 (bs, NH, OH), 1746, 1657, 1558 (s, C=O) cm^{-1}; ™$_H$ (500 MHz, $CDCl_3$) 1.99, 1.99 (6H, 2 x s, 2 x NHAc), 3.26-3.43 (3H, m, H3b, H4b, H5a), 3.57-3.74 (6H, m, H2a, H2b, H3a, H4a, H6a, H6b), 3.79 (1H, d, *J* 10.7 Hz, H6'a), 384 (1H, d, *J* 12.3 Hz, H6'b), 3.93 (1H, dd, $J_{1,2}$ 8.9 z, $J_{2,3}$ 9.9 Hz, H2a), 4.53 (1H, d, $J_{1,2}$ 8.2 Hz, H1b), 5.07 (1H, d, $J_{1,2}$ 8.5 Hz, H1a), 6.96 (2H, d, *J* 8.5 Hz, ArH), 7.06 (1H, t, *J* 7.4 Hz, ArH), 7.30 (2H, t, *J* 8.1 Hz, ArH); ™$_C$ (125 MHz, $CDCl_3$) 21.9, 22.0 (2 x q, 2 x NHAc), 54.9 (d, C2a), 55.5 (d, C2b), 59.9 (t, C6a), 60.5 (t, C6b), 69.7, 73.4 (2 x d, C3b, C4b), 72.2, 74.6, 79.1 (3 x d, C2a, C3a, C4a), 75.9 (d, C5b), 99.3 (d, C1a), 101.4 (d, C1b), 116.5, 123.3, 129.8 (3 x d, 5 x ArC), 156.6 (s, ArC), 174.4, 174.5 (2 x s, 2 x CO). *m/z* (ES^-) 499 (100%, MH^+). HRMS found 499.1932. calcd 499.1933 for $C_{22}H_{31}N_2O_{11}$.

Synthesis of compound 2.



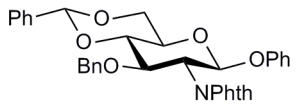
Reagents and conditions: a) i- NaOMe, MeOH, rt, ii- benzaldehyde dimethylacetal, $TsOH.H_2O$, MeCN, rt, 87%; b) NaH, BnBr, TBAI, DMF, rt, 75%; c) $NaCNBH_3$, THF, 0 ^oC, 81%; d) NIS, TMS-OTf, 4Å MS, DCM, 0 ^oC, 88%; e) $H_2NNH_2.AcOH$, MeOH, rt, 95%; f) i- Tf_2O, DCM, pyridine, ii- $Bu_4N.OAc$, toluene,))), 84%; g) i- H_2, $Pd(OH)_2$, EtOH, ii- 1,2-ethylenediamine, BuOH, Δ, iii- Ac_2O, pyridine, 74%; h) NaOMe, MeOH, 94%.

Phenyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside



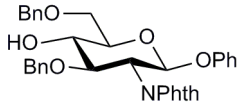
Phenyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside[15] (15.8 g, 31.1 mmol) and sodium methoxide (170 mg, 3.1 mmol) were added to a stirred solution of methanol (100 mL). After 30 min, t.l.c. (ethyl acetate) indicated the formation of a product (R_f 0) with complete consumption of the starting material (R_f 0.7). The reaction was concentrated *in vacuo*. The resulting residue was dissolved in anhydrous dimethylformamide (100 mL) and benzaldehyde dimethyl acetal (8.9 mL, 5.92 mmol) and camphor sulfonic acid (1.49 g, 5.92 mmol) were added. The resulting solution was heated to 60 ^oC at a reduced pressure of 240 mbar. After 4 h, t.l.c. (petrol:ethyl acetate, 1:1) showed the formation of a product (R_f 0.5) with complete consumption of the starting material (R_f 0). The reaction was cooled to RT and quenched by the addition of sodium hydrogen carbonate (400 mL of a saturated aqueous solution). The solution was partitioned between DCM (200 mL) and the phases separated. The aqueous phase was re-extracted with DCM (2 x 100 mL). The combined organic layers were washed with brine (2 x 200 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo.* The resulting residue was purified by flash column chromatography (ethyl acetate/petrol) to afford phenyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **35** (10.0 g, 68%) as a white amorphous foam; $[\langle]_D^{22}$ +11.5 (c, 0.65 in $CHCl_3$); J_{max} (KBr) 3476 (s, OH), 1777, 1714 (s, NCO) cm^{-1}; ™$_H$ (360 MHz, $CDCl_3$) 2.64 (1H, d, *J* 3.6 Hz, OH3), 3.55 (1H, at, *J* 9.0 Hz, H4), 3.60 (1H, dat, $J_{5,6'}$ 4.9 Hz, *J* 9.0 Hz, H5), 3.71 (1H, at, *J* 9.8 Hz, H6), 4.26 (1H, dd, $J_{5,6'}$ 4.4 Hz, $J_{6,6'}$ 10.3 Hz, H6'), 4.39 (1H, dd, $J_{1,2}$ 8.4 Hz, $J_{2,3}$ 10.4 Hz, H2), 4.57 (1H, ddd, $J_{2,3}$ 10.4 Hz, $J_{3,4}$ 8.6 Hz, *J* 3.6 Hz, H3), 5.45 (1H, s, PhCH), 5.77 (1H, d, $J_{1,2}$ 8.4 Hz, H1), 6.76-7.70 (14H, m, ArH); ™$_C$ (90 MHz, $CDCl_3$) 56.8 (d, C2), 66.7 (d, C5), 68.9, 69.0 (d, t, C3, C6), 82.4 (d, C4), 97.3 (d, C1), 102.4 (d, PhCH), 117.3, 125.5, 126.8, 128.8, 129.8, 129.9, 131.9 (7 x d, 14 x ArC), 134.6, 137.3, 156.9 (3 x s, 4 x ArC), 168.6, 171.6 (2 x s, 2 x CO); *m/z* (ES^+) 964 ($M_2NH_4^+$, 100%). HRMS (ES^+) Calcd. for $C_{27}H_{23}NO_7Na$ (MNa^+) 496.1367. Found 496.1377.

Phenyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside



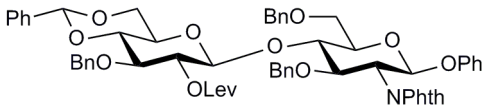
Phenyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **35** (8.3 g, 16.0 mmol) was suspended in anhydrous dimethylformamide (150 mL) to which benzyl bromide (2.9 mL, 24 mmol) was added. The mixture was cooled to 0 ^{o}C and sodium hydride (60% in mineral oil, 950 mg, 2.4 mmol) was added portionwise. After 18 h, t.l.c. (petrol:ethyl acetate, 1:1) showed the formation of a major product (R_f 0.8). The reaction was quenched by the careful addition of methanol (*ca* 50 mL). The mixture was partitioned between diethyl ether (100 mL) and water (100 mL) and the phases separated. The aqueous phase was re-extracted with diethyl ether (2 x 50 mL). The combined organic layers were washed with brine (2 x 250 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 7:3) and recrystallised from ethylacetate/petrol to afford phenyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **36** (6.8 g, 75%) as a white foam; m.p. 129130 ˚C; $[\langle]_D^{22}$ +153.8 (c, 0.65 in $CHCl_3$); J_{max} (KBr) 1777, 1715 (s, NCO) cm^{-1}; ™$_H$ (360 MHz, $CDCl_3$) 3.85 (1H, dat, $J_{5,6'}$ 4.5 Hz, *J* 9.7 Hz, H5), 3.92-4.01 (2H, m, H4, H6), 4.49 (1H, dd, $J_{5,6'}$ 4.9 Hz, $J_{6,6'}$ 10.3 Hz, H6'), 4.58-4.63 (3H, m, H2, H3, PhCHH), 4.90 (1H, d, *J* 12.5 Hz, PhCHH), 5.72 (1H, s, PhCH), 5.93-5.95 (1H, m, H1), 6.93-7.75 (19H, m, ArH); ™$_C$ (90 MHz, $CDCl_3$) 56.1 (d, C2), 66.7 (d, C5), 69.2 (t, C6), 74.6 (t, $PhCH_2$), 83.3 (d, C4), 97.3 (d, C1), 101.8 (d, PhCH), 117.3, 123.5, 123.9, 126.5, 127.4, 127.9, 128.1, 128.5, 128.8, 129.0, 131.9 (13 x d, 19 x ArC), 134.4, 137.7, 138.2, 156.9 (4 x s, 5 x ArC), 168.1, 171.6 (2 x s, 2 x CO); *m/z* (ES^+) 581 (MNH_4^+, 100%). HRMS (ES^+) Calcd. for $C_{34}H_{29}NO_7Na$ (MNa^+) 586.1836. Found 586.1821.

Phenyl-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside



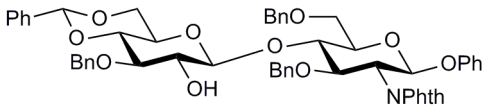
Phenyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-®-D-glucopyranoside **36** (17.2 g, 29.6 mmol) was dissolved in anhydrous THF (400 mL) and the resulting solution was cooled to 0 ^{o}C, to which methyl orange (speck) and sodium cyanoborohydride (37 g, 593 mmol) was added. The resulting solution was acidified by the slow addition of hydrochloric acid in dioxane (4M, ~200 mL to keep the indicator intensely pink). The resulting mixture was stirred under argon at RT. After a 12 h period, t.l.c. (petrol:ethyl acetate, 2:1) indicated the formation of a product (R_f 0.3) with complete consumption of the starting material (R_f 0.4). The reaction was diluted with ice water (1L) and filtered through celite. The filtrate was extracted with DCM (3 x 300 mL) and the combined organics were stirred in aqueous hydrochloric acid (2M, 400 mL) overnight. The organic layer was then washed with sodium hydrogen carbonate (600 mL, of a saturated aqueous solution), dried ($MgSO_4$) and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 2:1) to afford phenyl-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-®-D-glucopyranoside **12** (13.5 g, 81%) as a white amorphous solid; $[\langle]_D^{22}$ +115.1 (c, 1.4 in $CHCl_3$); J_{max} (KBr) 3474 (bs, OH), 1776, 1713 (s, NCO) cm^{-1}; ™$_H$ (360 MHz, $CDCl_3$) 3.10 (1H, bs, OH), 3.81-3.89 (3H, m, H5, H6, H6'), 3.96 (1H, at, *J* 8.8 Hz, H4), 4.39 (1H, dd, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 8.3 Hz, H3), 4.50 (1H, dd, $J_{1,2}$ 8.4 Hz, $J_{2,3}$ 10.5 Hz, H2), 4.60-4.70 (3H, m, 3 x PhCH), 4.83 (1H, d, *J* 12.3 Hz, PhCH), 5.84 (1H, d, $J_{1,2}$ 8.2 Hz, H1), 6.91-7.72 (19H, m, ArH); ™$_C$ (90 MHz, $CDCl_3$) 55.6 (d, C2), 67.5 (t, C6), 74.2, 74.3 (2 x t, 2 x $PhCH_2$), 74.6, 74.9 (2 x d, C4, C5), 79.0 (d, C3), 96.8 (d, C1), 117.0, 117.4, 123.2, 123.9, 127.9, 128.3, 128.4, 128.6, 128.9, 129.8, 129.9, 131.9 (12 x d, 19 x ArC), 138.0, 138.4, 157.1 (3 x s, 5 x ArC); *m/z* (ES^+) 583 (MNH_4^+, 70%), 1148 ($M_2NH_4^+$, 100%). HRMS (ES^+) Calcd. for $C_{34}H_{31}NO_7Na$ (MNa^+) 588.1993. Found 588.1993.

Phenyl-3-*O*-benzyl-4-*O*-benzylidene-2-*O*-levulinoyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside



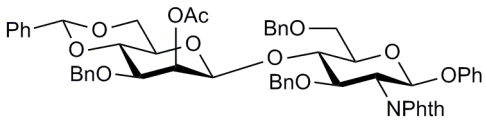
Phenyl-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-®-D-glucopyranoside **12** (100 mg, 0.17 mmol), ethyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-levulinoyl-1-thio-®-glucopyranoside[14] **11** (93 mg, 0.19 mmol) and *N*-iodosuccinimide (76 mg, 0.34 mmol) were dissolved in anhydrous DCM (20 mL) and stirred over 4Å MS for 1 h. The reaction was cooled to 0°C and trimethylsilyl trifluoromethanesulfonate (3 µL, 0.017) was added. After a 2.5 h period, t.l.c. (petrol:ethyl acetate, 2:1) indicated the formation of a product (R_f 0.3) with complete consumption of the starting material (R_f 0.4). The reaction was filtered through celite and washed with aqueous sodium thiosulfate (30 mL, 10% w/v), brine (30 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 1:1) to afford phenyl 3-*O*-benzyl-4-*O*-benzylidene-2-*O*-levulinoyl-®-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-®-D-glucopyranoside **13** (225 mg, 88%) as a white amorphous solid; $[\langle]_D^{21}$ +28.0 (c, 1.25 in $CHCl_3$); J_{max} (KBr) 1776, 1777, 1751, 1716, 1591 (s, CO) cm^{-1}; ™$_H$ (500 MHz, $CDCl_3$) 2.11 (3H, s, CH_3), 2.27-2.45 (2H, m, CH_2Lev), 2.54-2.76 (2H, m, CH_2Lev), 3.13 (1H, dat, $J_{5,6'}$ 4.9 Hz, J 9.8 Hz, H5b), 3.38 (1H, at, J 10.2 Hz, H6b), 3.47 (1H, at, J 9.3 Hz, H3b), 3.55 (1H, at, J 9.2 Hz, H4b), 3.63-3.66 (1H, m, H5a), 3.70-3.73 (1H, m, H6a), 3.80 (1H, dd, $J_{5,6'}$ 3.2 Hz, $J_{6,6'}$ 11.7 Hz, H6'a), 4.04-4.08 (1H, m, H4a), 4.18 (1H, dd, $J_{5,6'}$ 4.9 Hz, $J_{6,6'}$ 10.5 Hz, H6'b), 4.23 (1H, dd, $J_{2,3}$ 8.6 Hz, dd, $J_{3,4}$ 9.9 Hz, H3a), 4.31-4.37 (3H, m, H2a, 2 x PhCH), 4.49 (1H, d, $J_{1,2}$ 7.9 Hz, H1b), 4.57, 4.76 (2H, ABq, J 12.2 Hz, $PhCH_2$), 4.68 (1H, d, J 12.0 Hz, PhCH), 4.70 (1H, d, J 12.2 Hz, PhCH), 4.89 (1H, at, J 8.5 Hz, H2b), 5.38 (1H, s, PhCH), 5.65 (1H, d, $J_{1,2}$ 8.4 Hz, H1a), 6.78-7.55 (29H, m, ArH); ™$_C$ (125 MHz, $CDCl_3$) 28.2 (t, CH_2), 30.4 (q, CH_3), 38.7 (t, CH_2), 55.9 (d, C2a), 66.3 (d, C5b), 67.9 (t, C6a), 69.0 (t, C6b), 70.0 (t, $PhCH_2$), 74.5 (d, C2b), 75.1, 75.4 (2 x t, 2 x $PhCH_2$), 77.0 (d, C5a), 77.1 (d, C3a), 78.2 (d, C4a), 78.9 (d, C3b), 82.1 (d, C4b), 96.7 (d, C1a), 101.1 (d, PhCH), 117.4, 123.1, 123.8, 126.5, 127.5, 128.1, 128.2, 128.3, 128.4, 128.6, 128.9, 129.5, 129.7, 131.9, 134.2 (15 x d, 29 x ArC), 137.6, 138.3, 138.7, 138.9, 157.2 (5 x s, 7 x ArC), 171.7 (s, CO), 206.7 (s, CO); *m/z* (ES^+) 1026 (MNa^+, 100%).

Phenyl-3-*O*-benzyl-4-*O*-benzylidene-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside



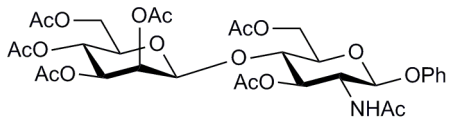
Phenyl 3-*O*-benzyl-4-*O*-benzylidene-2-*O*-levulinoyl-®-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-®-D-glucopyranoside **13** (1.2 g, 1.19 mmol) and hydrazine acetate (490 mg, 5.38 mmol) were dissolved in methanol (100 mL). After 16 h the reaction was partitioned between water (100 mL) and DCM (100 mL) and the phases separated. The aqueous phase was re-extracted with DCM (2 x 100 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 1:1) to afford phenyl-3-*O*-benzyl-4-*O*-benzylidene-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **37** (1.8 g, 95%) as a white foam; $[\langle]_D^{21}$ +28.0 (c, 1.25 in $CHCl_3$); J_{max} (KBr) 1776, 1777, 1751, 1716, 1591 (s, CO) cm^{-1}; ™$_H$ (360 MHz, $CDCl_3$) 2.94 (1H, d, *J* 1.8 Hz, OH), 3.15 (1H, dat, $J_{5,6}$ 5.0 Hz, *J* 10.7 Hz, H5b), 3.43-3.56 (4H, m, H2b, H3b, H4b, H6a), 3.68-3.72 (1H, m, H5a), 3.78 (1H, dd, $J_{5,6}$ 1.8 Hz, $J_{6,6'}$ 11.4 Hz, H6a), 3.96 (1H, dd, $J_{5,6'}$ 3.6 Hz, $J_{6,6'}$ 11.4 Hz, H6'a), 4.09-4.15 (2H, m, H4a, H6'b), 4.36-4.39 (3H, m, H2a, H3a, PhCH), 4.56, 4.63 (2H, ABq, *J* 12.0 Hz, $PhCH_2$), 4.57 (1H, m, H1b), 4.70-4.83 (2H, ABq, *J* 11.8 Hz, $PhCH_2$), 7.73 (1H, d, *J* 12.5 Hz, $PhCH_2$), 5.41 (1H, s, PhCH), 5.65 (1H, m, H1a), 6.78-7.57 (29H, m, ArH); ™$_C$ (90 MHz, $CDCl_3$) 56.1 (d, C2a), 66.7 (d, C5b), 68.4 (t, C6a), 69.1 (t, C6b), 73.9, 75.0, 75.2 (3 x t, $PhCH_2$), 75.4 (d, C5a), 75.4, 80.8, 81.8 (3 x d, C2b, C3b, C4b), 78.2 (d, C4a), 79.2 (d, C3a), 96.9 (d, C1a), 101.6 (d, PhCH), 103.8 (d, C1b), 123.3, 123.8, 126.4, 127.6, 127.9, 128.3, 128.4, 128.5, 128.6, 128.8, 128.9, 129.4, 129.8, 134.3 (14 x d, 29 x ArC), 137.7, 138.2, 138.8, 157.2 (4 x s, 7 x ArC), 168.2 (s, CO); *m/z* (ES^+) 1026 (MNa^+, 100%).

Phenyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside



Phenyl-3-*O*-benzyl-4-*O*-benzylidene-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **37** (106 mg, 0.14 mmol) and anhydrous pyridine (325 µL, 1.71 mmol) were dissolved in anhydrous DCM (4 mL). The reaction was cooled to 0 ^{o}C and trifluoromethanesulfonic anhydride (285 µL, 1.71 mmol) was added. The reaction was allowed to warm to RT over a 2 h period, at which point the reaction was partitoned between DCM (10 mL) and sodium hydrogen carbonate (20 mL) and the phases separated. The organic phase was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting orange residue was dried under vacuum for 2 h, at which point it was taken up into anhydrous toluene (10 mL) and tetrabutylammonium acetate (250 mg, 0.84 mmol) was added. The reaction was placed under sonication for 16 h then concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 2:1) to afford phenyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **14** (94 mg, 84%) as a white foam; $[\langle]_D^{21}$ +28.0 (c, 1.25 in $CHCl_3$); J_{max} (KBr) 1776, 1777, 1751, 1716, 1591 (s, CO) cm^{-1}; ™$_H$ (360 MHz, $CDCl_3$) 2.02 (3H, s, OAc), 3.00 (1H, dat, *J* 9.6 Hz, $J_{5,6'}$ 5.0 Hz, H5b), 3.31 (1H, dd, $J_{2,3}$ 3.5 Hz, $J_{3,4}$ 9.9 Hz, H3b), 3.43 (1H, at, *J* 9.5 Hz, H6b), 3.55-3.58 (1H, m, H5a), 3.62 (1H, dd, $J_{5,6}$ 1.7 Hz, $J_{6,6'}$ 11.2 Hz, H6a), 3.69 (H, dd, $J_{5,6'}$ 3.1 Hz, $J_{6,6'}$ 11.2 Hz, H6'a), 3.72 (1H, at, *J* 9.5 Hz, H4b), 4.02-4.08 (2H, m, H4a, H6b), 4.19 (1H, dd, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 8.4 Hz, H3a), 4.26-4.31 (3H, m, H2a, 2 x PhCH), 4.40 (1H, d, *J* 12.5 Hz, PhCH), 4.49-4.53 (2H, m, H1b, PhCH), 4.59 (1H, d, *J* 12.0 Hz, PhCH), 4.71 (1H, d, *J* 12.3 Hz, PhCH), 5.31 (1H, bd, *J* 2.7 Hz, H2b), 5.36 (1H, s, PhCH), 5.58 (1H, d, *J* 8.4 Hz, H1a), 6.69-7.51 (29H, m, ArH); ™$_C$ (90 MHz, $CDCl_3$) 21.5 (q, OAc), 55.9 (d, C2a), 67.4 (d, C5b), 68.6 (t, C6a), 69.6 (d, C2b), 72.1, 73.9 (2 x t, 2 x $PhCH_2$), 75.0 (d, C5a), 75.1 (t, $PhCH_2$), 76.2 (d, C3b), 77.3 (d, C3a), 78.3 (d, C4b), 79.3 (d, C4a), 96.9 (d, C1a), 99.9 (d, C1b), 101.9 (d, PhCH), 117.4, 123.2, 123.8, 126.5, 127.7, 128.0, 128.2, 128.4, 128.6, 128.8, 129.0, 129.4, 129.8, 134.2 (14 x d, 29 x ArC), 137.8, 138.1, 138.2, 138.9, 157.2 (5 x s, 7 x ArC), 170.7 (s, CO); *m/z* (ES^+) 1026 (MNa^+, 100%).

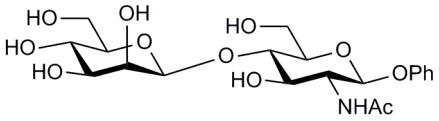
Phenyl-2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetamido-β-D-glucopyranoside



Phenyl-2-*O*-acetyl-3-*O*-benzyl-4-*O*-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **14** (950 mg, 1.18 mmol) and Pearlman's catalyst ($Pd(OH)_2$, moist, 800 mg) were suspended in absolute ethanol (10 mL). The resulting solution was degassed and purged with hydrogen gas, then left to stir under an atmosphere of hydrogen. After a 48 h period, the solution was filtered through celite® and concentrated *in vacuo*. The resulting residue was dissolved in 1-butanol (5 mL) and 1,2-ethylenediamine (4 mL) and the reaction was heated to 80 ^oC. After 16 h the reaction was co-evaporated with toluene (3 x 50 mL). The resulting residue was taken up in acetic anhydride (10 mL) and pyridine (15 mL). After 16 h, t.l.c. the reaction was quenched by the addition of water (50 mL). The reaction was partitioned with ethyl acetate (30 mL) and the phases separated. The aqueous phase was re-extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with dilute hydrochloric acid (300 mL of a 1M aqueous solution), sodium hydrogen carbonate (50 mL of a saturated aqueous solution), brine (50 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (ethyl acetate) to afford phenyl-2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetamido-β-D-glucopyranoside **38** (623 mg, 74%) as a white amorphous solid; $[\langle]_D^{21}$ +28.0 (c, 1.25 in $CHCl_3$); J_{max} (KBr) 1776, 1777, 1751, 1716, 1591 (s, CO) cm^{-1}; $™_H$ (500 MHz, $CDCl_3$) 1.92, 1.96, 2.02, 2.05, 2.07, 2.10, 2.13 (21H, 7 x s, 7 x $COCH_3$), 3.63-3.66 (1H, m, H5b), 3.76-3.79 (1H, m, H5a), 3.90 (1H, at, *J* 8.9 Hz, H4a), 4.07-4.10 (1H, m, H6b), 4.19-4.25 (2H, m, H2a, H6a), 4.30-4.37 (2H, m, H6'a, H6'b), 4.72 (1H, s, H1b), 5.03 (1H, dd, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 9.8 Hz, H3b), 5.08 (1H, d, $J_{1,2}$ 7.9 Hz, H1a), 5.16-5.24 (2H, m, H3a, H4a), 5.40 (1H, d, $J_{2,3}$ 3.2 Hz, H2b), 5.94 (1H, d, *J* 9.2 Hz, NHa), 6.94-7.27 (5H, m, ArH); $™_C$ (125 MHz, $CDCl_3$) 20.6, 20.7, 20.8, 20.9, 23.2 (5 x q, 7 x $CO\underline{C}H_3$), 53.7 (d, C2a), 62.3 (t, C6a), 62.7 (t, C6b), 65.8 (d, C3a), 68.5 (d, C2b), 76.7 (d, C3b), 71.8 (d, C4b), 72.5, 72.6 (2 x d, C5a, C5b), 74.7 (d, C4a), 97.6 (d,

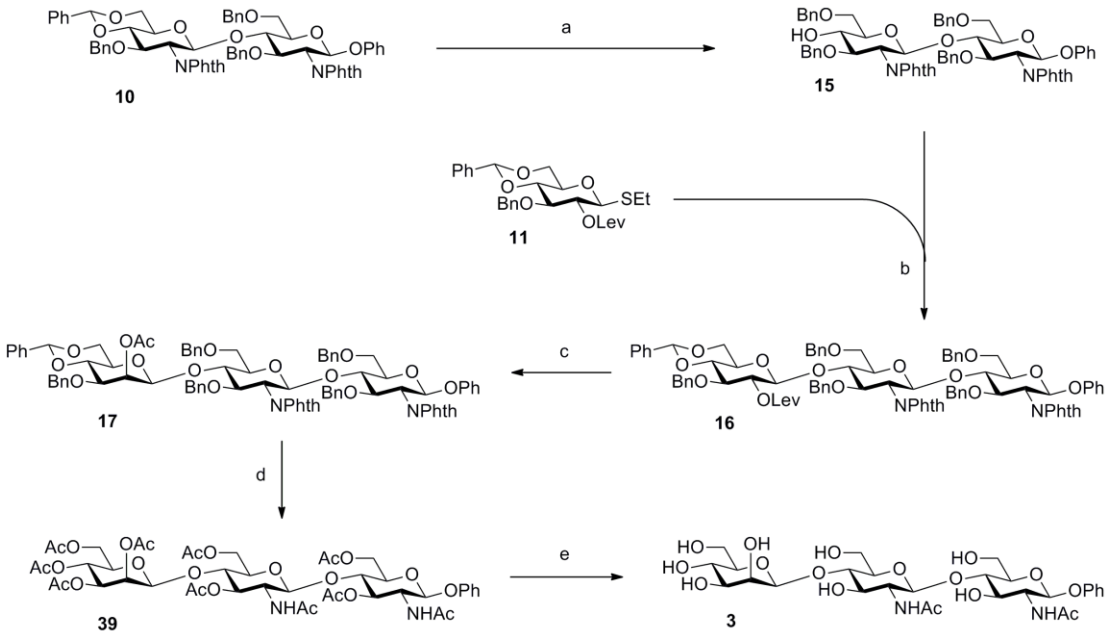
C1b), 99.1 (d, C1a), 116.0, 123.1, 129.6 (3 x d, 5 x ArC), 157.1 (s, ArC), 169.6, 170.0, 170.4, 170.5, 170.6, 170.8 (6 x s, CO); *m/z* (ES^+) 770 (MNH_4MeCN^+, 100%). HRMS (ES^+) Calcd. for $C_{32}H_{41}NO_{17}Na$ (MNa^+) 734.2272 Found 734.2272.

Phenyl-β-D-mannopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside



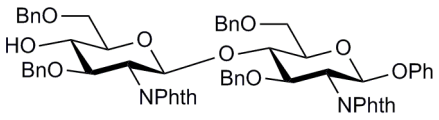
Phenyl-2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetamido-β-D-glucopyranoside **38** (420 mg, 0.59 mmol) and sodium methoxide (4 mg, 0.07 mmol) were added to a stirred solution of methanol (10 mL). After 1 h, t.l.c. (ethyl acetate, 1:1) indicated the formation of a product (R_f 0). The reaction was neutralised by the addition of Dowex-50 ion exchange resin® after which point the reaction was filtered and concentrated *in vacuo* to afford phenyl-β-D-mannopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside **2** (268 mg, 99%) as a white amorphous solid; $[\alpha]_D^{21}$ -6.0 (c, 0.25 in H_2O); J_{max} (KBr) 3289 (bs, NH, OH), 1656, 1551 (s, C=O) cm^{-1}; ™$_H$ (500 MHz, D_2O) 1.94 (3H, s, NHAc), 3.35 (1H, ddd, $J_{4,5}$ 9.1 Hz, $J_{5,6}$ 2.3 Hz, $J_{6,6'}$ 6.7 Hz, H5b), 3.50 (1H, at, *J* 9.8 Hz, H4b), 3.57 (1H, dd, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 9.8 Hz, H3b), 3.64-3.67 (2H, m, H6b, H2/3/4a), 3.70 (1H, dd, $J_{5,6}$ 4.6 Hz, $J_{6,6'}$ 12.6 Hz, H6a), 3.75-3.79 (2H, m, H2/3/4a), 3.84 (1H, dd, $J_{5,6'}$ 1.8 Hz, $J_{6,6'}$ 12.7 Hz, H6'a), 3.86 (1H, dd, $J_{5,6'}$ 2.2 Hz, $J_{6,6'}$ 12.2 Hz, H6'b), 3.94 (1H, at, *J* 9.3 Hz, H2a), 4.00 (1H, d, $J_{2,3}$ 3.1 Hz, H2b), 4.72 (1H, bs, H1b), 5.09 (1H, d, $J_{1,2}$ 8.5 Hz, H1a), 7.00 (2H, d, *J* 7.8 Hz, ArH), 7.06 (1H, dd, *J* 7.3 Hz, ArH), 7.30 (2H, t, *J* 7.8 Hz, ArH); ™$_C$ (125 MHz, D_2O) 22.1 (q, $COCH_3$), 54.9 (d, C2), 60.0 (t, C6b), 60.9 (t, C6a), 66.6 (d, C4b), 70.5 (d, C2b), 72.0, 74.7, 78.6 (3 x d, C3a, C4a, C5a), 72.7 (d, C3b), 76.4 (d, C5b), 99.5 (d, C1b), 100.1 (d, C1a), 116.6, 123.5, 129.9 (3 x d, 5 x ArC), 156.7 (s, ArC), 174.8 (s, CO). *m/z* (ES^-) 458 (100%, MH^+). HRMS found 458.1668. calcd 458.1662 for $C_{20}H_{28}NO_{11}$.

Synthesis of compound 3.



Reagents and conditions: a) $NaBH_3CN$, HCl/dioxane, THF, 0^oC-rt, 80%; b) MeOTf, DCM, 4 Å MS, 75%; c) i - H_2NNH_2.HOAc, MeOH, 55 ^oC; ii - Tf_2O, DCM, pyridine; iii - Bu_4N.OAc, toluene,))), 68%; d) i- H_2, $Pd(OH)_2$, EtOH, ii- 1,2-ethylenediamine, BuOH, Δ, iii- Ac_2O, pyridine, 94%; e) NaOMe, MeOH, 86%.

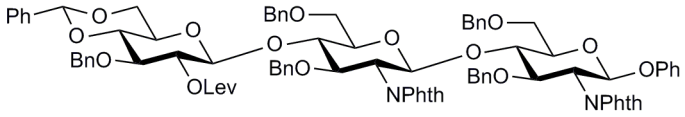
Phenyl-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside



Phenyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **10** (3.6 g, 4.85 mmol) was dissolved in anhydrous THF (100 mL) and the resulting solution was cooled to 0 ^{o}C, to which methyl orange (speck) and sodium cyanoborohydride (4.4 g, 69.6 mmol) was added. The resulting solution was acidified by the slow addition of hydrochloric acid in dioxane (4M, ~100 mL to keep the indicator intensely pink). The resulting mixture was stirred under argon at RT. After a 12 h period, t.l.c. (petrol:ethyl acetate, 1:1) indicated the formation of a product (R_f 0.4) with complete consumption of the starting material (R_f 0.6). The reaction was diluted with ice water (1L) and filtered through celite. The filtrate was extracted with DCM (3 x 200 mL) and the combined organics were stirred in aqueous hydrochloric acid (2M, 500 mL) overnight. The organic layer was then washed with sodium hydrogen carbonate (600 mL, of a saturated aqueous solution), dried ($MgSO_4$) and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 1:1) to afford phenyl 3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **15** (2.88 g, 80%) as a white amorphous foam; m.p. 113-115 ˚C; $[\alpha]_D^{22}$ +25.3 (c, 2.2 in $CHCl_3$); ™$_H$ (500 MHz, $CDCl_3$) 3.19 (1H, bs, OH), 3.42-3.50 (3H, m, H5a, H5b, H6b), 3.573.62 (2H, m, H6a, H6'b), 3.74 (1H, dd, $J_{5,6'}$ 4.3 Hz, $J_{6,6'}$ 9.8 Hz, H6'a), 3.85 (1H, at, *J* 8.8 Hz, H4b), 4.19 (1H, dd, $J_{1,2}$ 8.2 Hz, $J_{2,3}$ 10.7 Hz, H2b), 4.23-4.30 (3H, m, H3a, H3b, H4a), 4.40 (1H, dd, $J_{1,2}$ 8.7 Hz, $J_{2,3}$ 10.6 Hz, H2a), 4.44 (1H, d, *J* 11.6 Hz, PhCH), 4.50-4.56 (5H, m, 5 x PhCH), 4.80-4.85 (2H, m, 2 x PhCH), 5.34 (1H, d, $J_{1,2}$ 8.2 Hz, H1b), 5.60 (1H, d, $J_{1,2}$ 8.5 Hz, H1a), 6.78-7.91 (33H, m, ArH); ™$_C$ (125 MHz, $CDCl_3$) 55.5 (d, C2a), 56.1 (d, C2b), 67.1 (t, C6b), 68.1 (t, C6a), 70.8, 72.7 (2 x t, 2 x $PhCH_2$), 73.0 (d, C5b), 73.7 (t, $PhCH_2$), 74.4 (t, $PhCH_2$), 74.7 (d, C5a), 75.2 (d, C4b), 75.7, 76.5, 78.3 (3 x d, C3a, C3b, C4a), 96.2

(d, C1a), 97.1 (d, C1b), 116.9, 122.6, 123.2, 123.3, 123.7, 127.0, 127.3, 127.4, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.5, 128.6, 129.2, 131.5, 131.8, 133.7, 133.9, 134.1 (22 x d, 33 x ArC), 137.5, 138.2, 138.3, 138.4 (4 x s, 8 x ArC), 156.7 (s, ArC), 167.6, 168.4 (2 x s, 4 x CO). *m/z* (ES^+) 1059 (100%, $M+Na^+$).

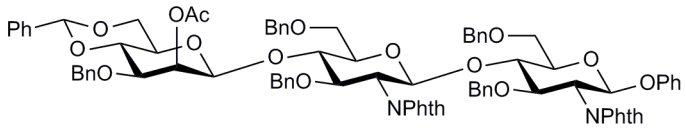
Phenyl-2-*O*-levulinoyl-3-*O*-benzyl-4,6-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside



Ethyl 3-*O*-benyzl-4,6-*O*-benzylidene-2-*O*-levulinyl-1-thio-®-D-glucopyranoside[14] **11** (370 mg, 0.96 mmol) in anhydrous DCM (20 mL) and phenyl 3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **15** (713 mg, 0.96 mmol) in DCM (20 mL) were added to a dried flask containing activated 4Å molecular sieves (*ca* 500 mg) *via* cannula. The resulting solution was stirred for 1 h, after which point methyl trifluromethanesulfonate (215 µL, 1.89 mmol) was added. After a 20 h period, t.l.c. (toluene:ethyl acetate, 3:1) indicated the formation of a major product (R_f 0.6) with complete consumption of the starting material (R_f 0.5). The reaction was quenched with sodium hydrogen carbonate (30 mL of a saturated aqueous solution) and the solution was concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (toluene:ethyl acetate, 3:1) to afford phenyl-2-*O*-levulinoyl-3-*O*-benzyl-4,6-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **16** (769 mg, 75%) as a white amorphous foam; $[\alpha]_D^{20}$ +24.0 (c, 0.65 in $CHCl_3$); J_{max} (KBr) 1778, 1747, 1712 (s, C=O) cm^{-1}; ™$_H$ (500 MHz, $CDCl_3$) 2.18, 2.38 (2 x 3H, 2 x s, 2 x $COCH_3$), 2.44-2.49 (2H, m, CH_2Lev), 2.72-2.75 (2H, m, CH_2Lev), 3.22 (1H, dat, $J_{5,6}$ 5.0 Hz, *J* 9.8 Hz, H5c), 3.42-3.46 (2H, m, H6b, H6c), 3.47-3.51 (2H, m, H5a, H5b), 3.55-3.57 (1H, m, H6'b), 3.60 (1H, at, *J* 8.9 Hz, H3c), 3.65 (1H, at, *J* 9.2 Hz, H4c), 3.75-3.81 (2H, m, H6a, H6'a), 4.15 (1H, dd, $J_{3,4}$ 8.5 Hz, $J_{4,5}$ 9.8 Hz, H4a/b), 4.22-4.34 (5H, m, H2b, H3a, H3b, H4a/b, H6'c), 4.39-4.45 (3H, m, H2a, 2 x PhCH), 4.48 (1H, d, *J* 11.9 Hz, PhCH), 4.52 (1H, d, *J* 12.0 Hz, PhCH), 4.56 (1H, d, *J* 12.9 Hz, PhCH), 4.64 (1H, d, $J_{1,2}$ 7.9 Hz, H1c), 4.67 (1H, d, *J* 12.0 Hz, PhCH), 4.70, 4.87 (2H, ABq, *J* 12.0 Hz, $PhCH_2$), 4.81 (1H, d, *J* 12.3 Hz, PhCH), 4.94 (1H, d, *J* 12.5 Hz, PhCH), 5.01 (1H, at, *J* 8.5 Hz, H2c), 5.32 (1H, d, $J_{1,2}$ 8.5 Hz, H1b), 5.47 (1H, s, PhCH), 5.59 (1H, d, $J_{1,2}$ 8.5 Hz, H1a), 6.77-7.69 (43H, m, ArH); ™$_C$

(125 MHz, $CDCl_3$) 21.5 (q, $COCH_3$), 27.8 (t, CH_2), 29.8 (q, $COCH_3$), 37.8 (t, CH_2), 55.5 (d, C2a), 56.5 (d, C2b), 65.9 (d, C5c), 67.2 (t, C6a), 68.0 (t, C6b), 68.6 (t, C6c), 72.7, 73.8 (2 x t, 2 x $PhCH_2$), 73.3 (d, C2a), 73.6, 74.1 (2 x t, 3 x $PhCH_2$), 74.7 (2 x d, C5a, C5b), 76.1, 76.7, 76.9, 77.9 (4 x d, C3a, C3c, C4a, C4b), 78.6 (d, C3c), 81.7 (d, C4c), 96.3 (d, C1a), 97.2 (d, C1b), 100.7 (d, C1c), 101.2 (d, PhCH), 116.7, 126.0, 126.9, 127.0, 127.2, 127.3, 127.6, 127.8, 127.9, 128.1, 128.2, 128.6, 129.0, 129.2 (14 x d, 43 x ArC), 138.0, 138.2, 138.6, 138.7, 156.8 (5 x s, 11 x ArC), 167.6, 168.4, 171.3 (3 x s, 5 x CO), 205.9 (s, CO). *m/z* (ES^+) 1533 (100%, $M+NH_4/MeCN^+$).

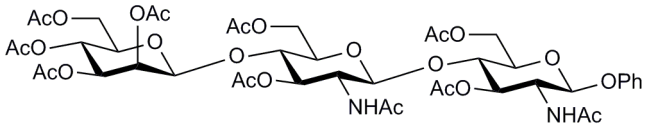
Phenyl-2-*O*-acetyl-3-*O*-benzyl-4,6-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside



Phenyl-2-*O*-levulinoyl-3-*O*-benzyl-4,6-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **16** (700 mg, 0.66 mmol) and hydrazine acetate (180 mg, 1.93 mmol) were dissolved in methanol (50 mL) and heated to 55 ^{o}C. After 16 h the reaction was partitioned between water (100 mL) and DCM (100 mL) and the phases separated. The aqueous phase was re-extracted with DCM (2 x 100 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 1:1). The purified intermediate and anhydrous pyridine (1.0 mL, 12.2 mmol) were dissolved in anhydrous DCM (15 mL). The reaction was cooled to 0 ^{o}C and trifluoromethanesulfonic anhydride (860 µL, 5.17 mmol) was added. The reaction was allowed to warm to RT over a 2 h period, at which point the reaction was partitoned between DCM (20 mL) and sodium hydrogen carbonate (20 mL) and the phases separated. The organic phase was dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting orange residue was dried under vacuum for 2 h, at which point it was taken up into anhydrous toluene (20 mL) and tetrabutylammonium acetate (800 mg, 2.16 mmol) was added. The reaction was placed under sonication for 16 h then concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 1:1) to afford phenyl-2-*O*-acetyl-3-*O*-benzyl-4,6-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **17** (506 mg, 68%) as a white amorphous foam; $[\alpha]_D^{22}$ +17.3 (c, 0.45 in $CHCl_3$); J_{max} (KBr) 1778, 1747, 1714 (s, C=O) cm^{-1}; ™$_H$ (500 MHz, $CDCl_3$) 2.34 (3H, s, OAc), 3.18 (1H, dat, *J* 5.1 Hz, *J*

9.8 Hz, H5c), 3.32 (1H, bd, *J* 9.8 Hz, H5b), 3.48-3.54 (3H, m, H3c, H5a, H6a), 3.57-3.63 (2H, m, H6c, H6'a), 3.69 (1H, dd, $J_{5,6}$ 2.2 Hz, $J_{6,6'}$ 11.3 Hz, H6b), 3.74 (1H, bd, *J* 11.3 Hz, H6'b), 3.92 (1H, at, *J* 9.8 Hz, H4c), 4.18-4.23 (2H, m, H4b, H6'c), 4.25-4.36 (4H, m, H2b, H3a, H3b, H4b), 4.44-4.73 (9H, m, H2a, 9 x PhCH), 4.75 (1H, bd, H1c), 4.92 (1H, d, *J* 11.9 Hz, PhCH), 4.94 (1H, d, *J* 12.7 Hz, PhCH), 5.33 (1H, d, $J_{1,2}$ 8.2 Hz, H1b), 5.53 (1H, d, $J_{2,3}$ 3.1 Hz, H2c), 5.55 (1H, s, PhCH), 5.63 (1H, d, $J_{1,2}$ 8.5 Hz, H1a), 6.81-7.76 (43H, m, ArH); ™$_C$ (125 MHz, $CDCl_3$) 21.1 (q, OAc), 55.6 (d, C2a), 56.6 (d, C2b), 66.9 (d, C5c), 67.8 (t, C6b), 68.1 (t, C6c), 68.5 (t, C6a), 69.1 (d, C2c), 71.6, 72.9, 73.2 (3 x t, 3 x $PhCH_2$), 74.3 (d, C5b), 74.5, 74.6 (2 x t, 2 x $PhCH_2$), 74.7 (d, C5a), 75.8 (d, C3c), 75.9 (d, C3a), 76.6 (d, C4a), 76.9 (d, C3b), 77.8 (d, C4c), 78.9 (d, C4b), 96.3 (d, C1a), 97.1 (d, C1b), 99.4 (d, C1c), 101.4 (d, PhCH), 116.9-129.2 (20 x d, 43 x ArC), 137.4, 137.8, 137.9, 138.2, 138.5, 138.6 (6 x s, 18 x ArC), 156.8 (s, ArC), 170.2 (s, CO). *m/z* (ES^+) 1477 (100%, $M+NH_4/MeCN^+$).

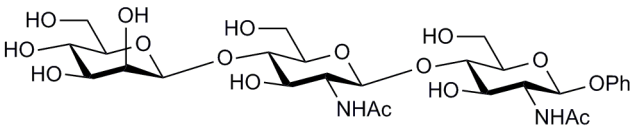
Phenyl-2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetamido-β-D-glucopyranoside



Phenyl-2-*O*-acetyl-3-*O*-benzyl-4,6-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **17** (450 mg, 0.40 mmol) and Pearlman's catalyst ($Pd(OH)_2$, moist, 300 mg) were suspended in absolute methanol (20 mL). The resulting solution was degassed and purged with hydrogen gas, then left to stir under an atmosphere of hydrogen. After a 24 h period, t.l.c. (ethyl acetate) indicated the formation of a major product (R_f 0.0) with complete consumption of the starting material (R_f 0.9). The solution was filtered through celite® and concentrated *in vacuo*. The resulting residue was resuspended in methanol (20 mL), and 1,2-ethylenediamine (5 mL) was added and the reaction was heated to 80 ^oC. After 16 h the reaction was co-evaporated with toluene (3 x 50 mL). The resulting residue was taken up in acetic anhydride (10 mL) and pyridine (20 mL). After 16 h, t.l.c. (ethyl acetate/methanol, 9:1) showed the formation of a product (R_f 0.5) with complete consumption of the starting material (R_f 0). The reaction was partitioned between chloroform (50 mL) and water (100 mL) and the phases separated. The aqueous phase was re-extracted with chloroform (2 x 50 mL). The combined organic layers were washed with dilute hydrochloric acid (300 mL, 1M aqueous solution), sodium hydrogen carbonate (50 mL of a saturated aqueous solution), brine (50 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography to afford phenyl-2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetamido-β-D-glucopyranoside **39** (376 mg, 94%) as a white amorphous foam; $[\alpha]_D^{22}$ +17.3 (c, 0.45 in $CHCl_3$); J_{max} (KBr) 1778, 1747, 1714 (s, C=O) cm^{-1}; ™$_H$ (500 MHz, $CDCl_3$) 1.90, 1.94, 2.00, 2.01, 2.02, 2.03, 2.06, 2.07, 2.11 (30H, 9 x s, 10 x $COCH_3$), 3.58-3.62 (2H, m, H5b, H5c), 3.79-3.83 (3H, m, H4a, H4b, H5a), 3.88 (1H, q, *J* 9.3 Hz, H2b), 4.05-4.11 (2H, m, 2 x H6),

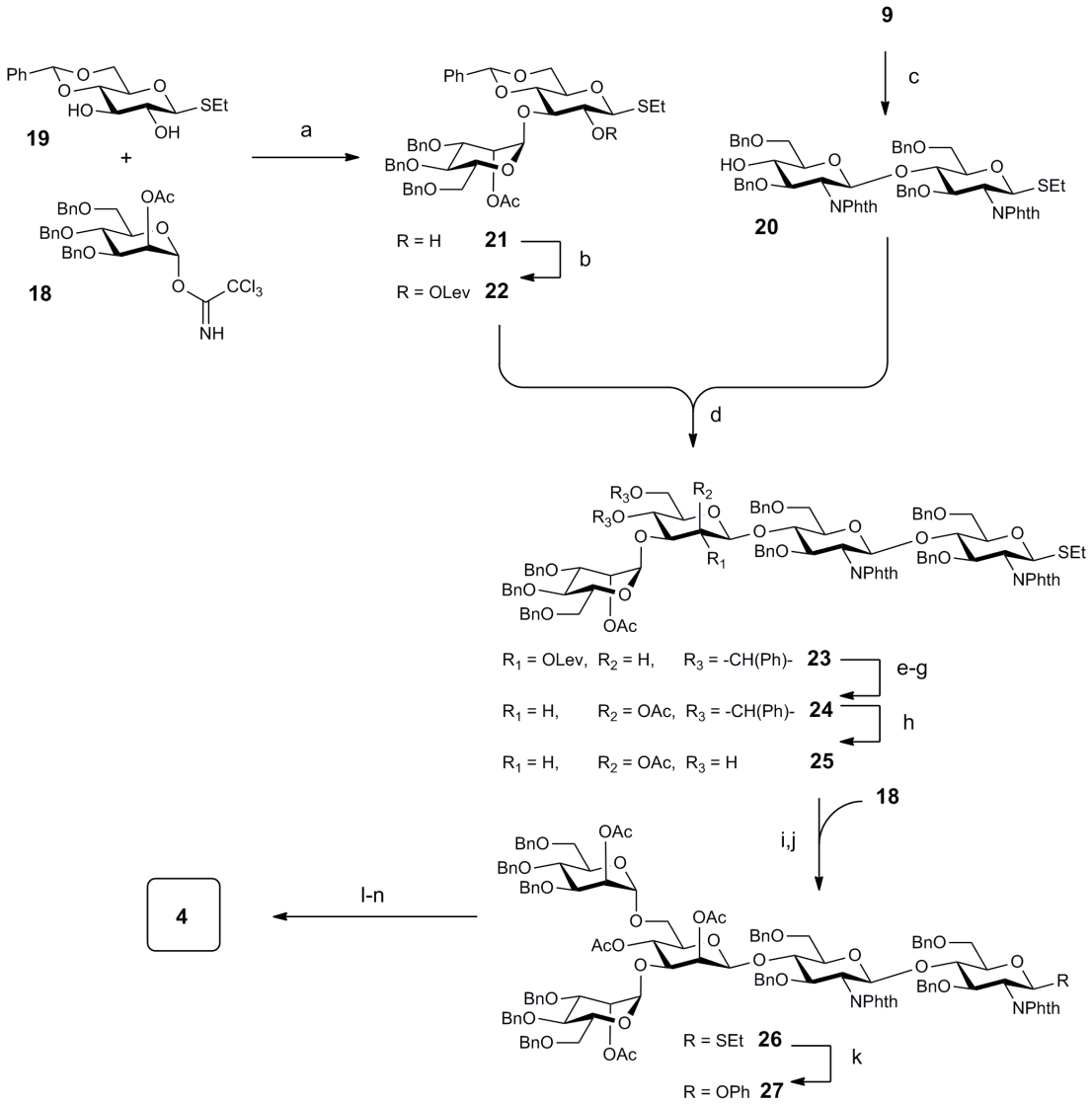
4.21-4.35 (5H, m, H2a, 4 x H6), 4.53 (1H, d, $J_{1,2}$ 8.2 Hz, H1b), 4.68 (1H, s, H1c), 4.99 (1H, dd, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 9.9 Hz, H3c), 5.07-5.11 (2H, m, H1a, H3b), 5.17 (1H, at, *J* 10.0 Hz, H4c), 5.22 (1H, at, *J* 8.1 Hz, H3a), 5.36 (1H, d, $J_{2,3}$ 3.1 Hz, H2c), 6.42-6.46 (2H, m, 2 x NH), 6.93 (2H, d, *J* 7.8 Hz, 2 x ArH), 6.97 (1H, t, *J* 7.8 Hz, ArH), 7.20 (2H, t, *J* 7.9 Hz, ArH); ™$_C$ (125 MHz, $CDCl_3$) 20.5, 20.6, 20.7, 20.8 (4 x q, 8 x CO<u>C</u>H_3), 23.1 (q, 2 x NHCOCH_3), 53.1 (d, C2a), 54.2 (d, C2b), 62.2, 62.6, 62.7 (3 x t, C6a, C6b, C6c), 65.7 (d, C4c), 68.4 (d, C2c), 70.7 (d, C3c), 72.3 (2 x d, C5b, C5c), 72.5 (2 x d, C3a, C3b), 72.7, 74.5, 75.8 (3 x d, 5 x ArC), 156.9 (s, ArC), 169.5, 169.8, 170.3, 170.4, 170.5, 170.6, 170.7, 170.9, 171.1 (9 x s, 10 x CO). *m/z* (ES^+) 1057 (100%, M+NH_4/$MeCN^+$). HRMS found 999.3444. calcd 999.3452 for $C_{44}H_{59}O_{24}N_2$.

Phenyl-β-D-mannopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside



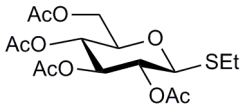
Phenyl-2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-acetyl-2-deoxy-2-*N*-acetamido-β-D-glucopyranoside **39** (210 mg, 0.21 mmol) and sodiummethoxide (3 mg, 0.04 mmol) were added to a stirred solution of methanol (10 mL).After 3 days the reaction was neutralised by the addition of Dowex-50 ion exchangeresin® after which point the reaction was filtered and concentrated *in vacuo* to afford phenyl-β-D-mannopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside **3** (120 mg, 86%) as a white amorphous solid; $[\alpha]_D^{20}$ -12.0 (c, 0.85 in CHCl3); ν_{max} (KBr) 1753, 1713 (s, C=O) cm-1; δ_H (500 MHz, D_2O) 1.94, 1.99 (6H, 2 x s, 2 x NHAc), 3.32-3.36 (1H, m, H-5c), 3.47-3.75 (12H, m,H-2b, H-3a, H-3b, H-3c, H-4a, H-4b, H-4c, H-5a, H-5b, H-6a, H-6b, H-6c), 3.78-3.86(3H, m, H-6'a, H-6'b, H-6'c), 3.93 (1H, dd, $J_{1,2}$ 8.8 Hz, $J_{2,3}$ 10.2 Hz, H-2a), 3.98 (1H,bd, $J_{2,3}$ 3.1 Hz, H-2c), 4.54 (1H, d, $J_{1,2}$ 8.0 Hz, H-1b), 4.68 (1H, s, H-1c), 5.06 (1H, d, $J_{1,2}$ 8.6 Hz, H-1a), 6.97 (2H, d, *J* 7.8 Hz, ArH), 7.06 (1H, t, *J* 7.2 Hz, ArH), 7.30 (2H,m, 7.9 Hz, ArH); δ_C (125 MHz, D_2O) 22.0, 22.1 (2 x q, 2 x OAc), 54.9 (d, C-2a, 55.0(d, C-2b), 59.9, 60.0, 60.9 (3 x t, C-6a, C-6b, C-6c), 66.6 (d, C-2c), 70.5, 71.9, 72.1,72.7, 74.6, 74.7, 78.6, 78.9 (8 x d, C-3a, C-3b, C-3c, C-4a, C-4b, C-4c, C-5a, C-5b),76.4 (d, C-5c), 99.4 (d, C-1a), 100.1 (d, C-1c), 101.4 (d, C-1b), 116.6, 123.4, 129.9 (3x d, 5 x ArC), 174.6, 174.8 (2 x s, 2 x C=O). *m/z* (ES-) 661 (100%, M-H+); ESI^+ $[C_{28}H_{42}N_2NaO_{16}]$ requires 685.2427, found 685.2417.

Synthesis of compound 4.



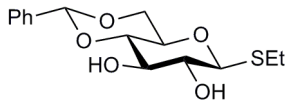
Reagents & conditions: a) TMS-OTf, DCM, -78^{o}C, 76%; b) LevOH, DIC, DCM, 94%; c) $NaBH_3CN$, HCl/dioxane, THF, 0^{o}C-rt, 91%; d) Ph_2O, Tf_2O, DTBMP, DCM, -40 ^{o}C – rt, 64%; e) H_2NNH_2.HOAc, MeOH, 55 ^{o}C, 64%; f) Tf_2O, DCM, pyridine; g) u_4N.OAc, toluene,))), 88% over two steps; h)TsOH.H_2O, MeOH, 1,4-Dioxane, 85 ^{o}C, 92%; i) **18**, TMS-OTf, DCM, -40 ^{o}C, 85%; j) Ac_2O, pyridine; k) PhOH, NIS, TMS-OTf, DCM, 4Å MS, -10 ^{o}C, 48% over two steps; l) 1,2-ethylenediamine, MeOH, Δ, then Ac_2O, pyridine, 80% over two steps; m) H_2, $Pd(OH)_2$-C, MeOH, 97%; n) NaOMe, MeOH, 88%.

Ethyl-2,3,4,6-tetra-*O*-acetly-1-thio-β-D-glucopyranoside[22]



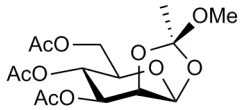
Tin (IV) chloride (1.12 ml, 9.61 mmol) was added dropwise to a solution of penta-acetyl-D-glucose (25.00g, 64.05 mmol) and ethanethiol (5.69 ml, 76.86 mmol) in dry dichloromethane (250 ml) at rt under an atmosphere of nitrogen. The reaction mixture was stirred at rt for 19h by which time TLC analysis (2:1 petrol/EtOAc) indicated that all starting material was consumed and one major (Rf=0.32) and one minor (Rf=0.40) product had formed. The reaction mixture was diluted with dichloromethane (150 ml) and washed with saturated aqueous sodium hydrogencarbonate solution (3x 200ml) and brine (200 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a pale yellow oil. The oil was dissolved in boiling hexane/ethanol (3:1) and upon cooling ethyl-2,3,4,6-tetra-*O*-acetly-1-thio-β-D-glucopyranoside **33** precipitated as a white solid (24.73g, 98%); m.p. 79-83 ^{o}C; $[\alpha]_D^{25}$ -29.3 (c=1.0, $CHCl_3$) [lit. $[\alpha]_D^{25}$ -28 (c=1.0, $CHCl_3$)][23]; δ_H (400 MHz, $CDCl_3$) 1.26 (3H, t, *J* 7.5, -CH_2CH_3), 2.00 (3H, s, -OAc), 2.02 (3H, s, -OAc), 2.05 (3H, s, -OAc), 2.07 (3H, s, -OAc), 2.67 (1H, dq, *J* 12.4, 7.5, -SC*H*H-), 2.73 (1H, dq, *J* 12.4, 7.5, -SCH*H*-), 3.70 (1H, ddd, *J* 9.9, 5.0, 1.9, 5-*H*), 4.13 (1H, dd, *J* 12.2, 1.9, 6-*H*H), 4.24 (1H, dd, *J* 12.2, 5.0, 6-H*H*), 4.49 (1H, d, *J* 10.0, 1-*H*), 5.03 (1H, dd, *J* 10.0, 9.4, 2-*H*), 5.07 (1H, dd, *J* 9.9, 9.4, 4-*H*), 5.21 (1H, app t, *J* 9.4, 3-*H*); δ_C (100 MHz, $CDCl_3$) 14.8 (-SCH_2CH_3), 20.57 (-OAc), 20.60 (-OAc), 20.7 (2x -OAc), 24.2 (-SCH_2CH_3), 62.1 (C-6), 68.3 (C-4), 69.8 (C-2), 73.9 (C-3), 75.8 (C-5), 83.5 (C-1), 169.37, 169.39, 170.2, 170.6; *m/z* (ES^+) 415.08 ($[M.Na]^+$, 100%).

Ethyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[24]



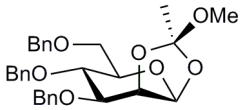
Sodium methoxide (4.37M solution in MeOH, 1.86 ml, 8.15 mmol) was added to a solution of ethyl-2,3,4,6-tetra-*O*-acetly-1-thio-β-D-glucopyranoside **33** (16.00 g, 40.77 mmol) in dry MeOH (150 ml) at rt under an atmosphere of nitrogen. The reaction mixture was stirred at rt for 18h. Activated Dowex-H^+ resin (4g) was added and the mixture stirred at rt for 1h then filtered and concentrated *in vacuo* to give a colourless oil. The oil was dissolved in dry MeCN (250 ml) at rt under an atmosphere of nitrogen. Benzaldehyde dimethylacetal (7.29 ml, 48.6 mmol) followed by *p*-toluenesulfonic acid monohydrate (200 mg, 1.1 mmol) were added. The reaction mixture was stirred at rt for 14h then triethylamine (1.5 ml, 10.1 mmol) was added, the mixture was stirred for 15 min then concentrated *in vacuo* to give a yellow oil which was purified using a Biotage by column chromatography on silica gel eluting with an increasing proportion of MeOH/DCM from 2-8% to afford ethyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside **19** (10.86g, 86%) as a white solid; $[\alpha]_D^{25}$ -54.6 (c=1.0, $CHCl_3$) [lit. $[\alpha]_D^{25}$ -61 (c=1.0, $CHCl_3$)][19]; 1.33 (3H, t, *J* 7.4, -CH_2CH_3), 2.72-2.79 (2H, m, -SCH_2-), 3.45-3.53 (2H, m, 2-*H*, 5-*H*), 3.56 (1H, app t, *J* 8.8, 3-*H*), 3.75 (1H, app t, *J* 10.5, 6-*H*H), 3.81 (1H, app t, *J* 8.8, 4-*H*), 4.34 (1H, dd, *J* 10.5, 4.7, 6-H*H*), 4.45 (1H, d, *J* 9.9, 1-*H*), 5.53 (1H, s, PhC*H*-), 7.35-7.41 (3H, m, 3x Ar-*H*), 7.47-7.52 (2H, m, 2 Ar-*H*); δ_C (100 MHz, $CDCl_3$) 15.2 (-SCH_2CH_3), 24.7 (-SCH_2CH_3), 68.6 (C-6), 70.5 (C-5), 73.2 (C-2), 74.5 (C-4), 80.3 (C-3), 86.5 (C-1), 101.5 (Ph*C*H-), 126.3, 128.4, 129.3, 136.9; *m/z* (ES^+) 335.10 ($[M.Na]^+$, 26%), 647.17 ($[2M.Na]^+$, 100%).

3,4,6-Tri-*O*-acetyl-1,2-*O*-(1-*R*-methoxyethylidene)-β-D-mannopyranose[25]



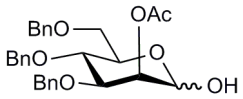
Hydrobromic acid (33% in acetic acid, 173.0 ml, 986 mmol) was added slowly over 1h to a solution of penta-*O*-acetyl-mannose (110.0g, 282 mmol) in dry dichloromethane (300 ml) at rt under a nitrogen atmosphere. After 3h TLC analysis (30% EtOAc/petrol)indicated the formation of a single product (Rf = 0.32) and complete consumption of the starting material (Rf = 0.23). Dichloromethane (200 ml) and ice-water (200 ml) were added. The layers were separated and the organic phase was extracted with dichloromethane (3x 150 ml). The combined organic layers were washed with water until the pH was neutral then washed with brine (200 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting pale yellow oil was dissolved in dry tetrahydrofuran (500 ml) and dry methanol (11.3 ml, 280 mmol) at room temperature under a nitrogen atmosphere. 2,6-Lutidine (130 ml, 1120 mmol) was added and t he mixture was heated at 80 ^oC for 5h then cooled to room temperature and concentrated *in vacuo*. The residue was diluted with ethyl acetate (250 ml) and water (250 ml). The layers were separated and the aqueous phase was extracted with ethyl acetate (3x 150 ml). The combined organic extracts were washed with saturated aqueous sodium hydrogencarbonate solution (150 ml) and brine (150 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a pale yellow solid which was purified by recrystalisation from 30% methanol/water to give 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-*R*-methoxyethylidene)-β-D-mannopyranose **40** as a white solid (77.1 g, 76%); m.p. 99-102 ^oC [lit. 114-115 ^oC][26]; $[\alpha]_D^{18}$ -22.3 (c=1.0, $CHCl_3$), [lit. $[\alpha]_D^{18}$ -21.4 (c=1.8, $CHCl_3$)][26]; δ_H (400 MHz, $CDCl_3$) 1.74 (3H, s, -Me), 2.05 (3H, s, -OAc), 2.07 (3H, s, -OAc), 2.12 (3H, s, -OAc), 3.28 (3H, s, -OMe), 3.68 (1H, ddd, *J* 9.7, 5.0, 2.6, 5-H), 4.14 (1H, dd, *J* 12.1, 2.6, 6-*H*H), 4.24 (1H, dd, *J* 12.1, 5.0, 6-H*H*), 4.61 (1H, dd, *J* 3.9, 2.5, 2-H), 5.14 (1H, dd, *J* 9.7, 3.9, 3-H), 5.30 (1H, app t, *J* 9.7, 4-H), 5.49 (1H, d, *J* 2.5, 1-H); δ_C (100 MHz, $CDCl_3$) 20.65 (-OAc), 20.69 (-OAc), 20.73 (-OAc), 24.4 (-*C*H_3), 49.9 (-O*C*H_3), 62.3 (C-6), 65.5 (C-4), 70.6 (C-3), 71.3 (C-5), 76.6 (C-2), 97.3 (C-1), 124.5 (C-7), 169.4 (-OAc), 170.4 (-OAc), 170.6 (-OAc); *m/z* (ES^+) 385.1 ($[MNa]^+$, 19%), 421.2 ($[M(MeCN)NH_4]^+$, 100%).

3,4,6-Tri-*O*-benzyl-1,2-*O*-(1-*R*-methoxyethylidene)-β-D-mannopyranose[27]



A mixture of 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-*R*-methoxyethylidene)-β-D-mannopyranose **40** (25.0 g, 69.0 mmol) and benzyl chloride (140 ml, 1173 mmol) in dry tetrahydrofuran (40 ml) was heated to reflux under nitrogen. The heat source was removed and freshly crushed potassium hydroxide (50.0 g, 897 mmol) was added portion-wise (*Care:* exotherm!). The mixture was stirred for 36h then water (200 ml) and dichloromethane (150 ml) were added. The layers were separated and the aqueous phase was extracted with dichloromethane (150 ml). The combined organic extracts were washed with saturated aqueous sodium hydrogencarbonate solution (2x 150 ml) and brine (150 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a yellow oil which solidified on standing. The yellow solid was recrystalised from diethyl ether/hexane to give 3,4,6-tri-*O*-benzyl-1,2-*O*-(1-*R*-methoxyethylidene)-β-D-mannopyranose **41** as white needles (26.3 g, 75%); m.p. 73-76 ^{o}C [lit. 87-88 ^{o}C][28]; $[\alpha]_D^{18}$ +33.7 (c=1.0, $CHCl_3$), [lit. $[\alpha]_D^{18}$ +37.0 (c=1.0, $CHCl_3$)][xxviii=23]; (400 MHz, $CDCl_3$) 1.76 (3H, s, -Me), 3.30 (3H, s, -OMe), 3.44 (1H, ddd, *J* 9.4, 4.2, 2.4, 5-H), 3.70-3.80 (3H, m, 3-H, 6-H_2), 3.94 (1H, dd, *J* 9.4, 8.9, 4-H), 4.41 (1H, dd, *J* 4.1, 2.6, 2-H), 4.57 (1H, d, *J* 11.8, PhC*H*H-), 4.60 (1H, d, *J* 11.4, PhC*H*H-), 4.63 (1H, d, *J* 11.8, PhCH*H*-), 4.78 (1H, d, *J* 12.1, PhC*H*H-), 4.82 (1H, d, *J* 12.1, PhCH*H*-), 4.92 (1H, d, *J* 11.4, PhCH*H*-), 5.37 (1H, d, *J* 2.6, 1-H); δ_C (100 MHz, $CDCl_3$) 24.4 (-*C*H_3), 49.8 (-O*C*H_3), 69.0 (C-6), 72.4 (Ph*C*H_2-), 73.4 (Ph*C*H_2-), 74.15 (C-5), 74.20 (C-4), 75.3 (Ph*C*H_2-), 77.1 (C-2), 97.6 (C-1), 124.0 (C-7), 127.5, 127.8, 128.0, 128.1, 128.3, 128.4, 128.5, 137.8, 138.2; %); *m/z* (ES^+) 529.2 ($[M.Na]^+$, 8%), 545.2 (34%), 565.3 ($[M.NH_4.MeCN]^+$, 100%).

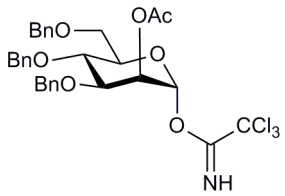
2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-D-mannopyranose[29]



A solution of 3,4,6-tri-*O*-benzyl-1,2-*O*-(1-*R*-methoxyethylidene)-β-D-mannopyranose **41** (38.0 g, 75.0 mmol) in acetic acid (300 ml) and water (200 ml) was stirred at r.t. for 4h whereupon TLC analysis (50% EtOAc/petrol) indicated the complete consumption of the starting material (Rf=0.62) and formation of a three products (Rf=0.24, 0.36, 0.51). The mixture was concentrated *in vacuo* and partitioned between water (400 ml) and ethyl acetate (400 ml). The layers were separated and the aqueous phase was extracted with ethyl acetate (2x 175 ml). The combined organic extracts were washed with saturated aqueous sodium hydrogencarbonate solution (2x 200 ml) and brine (200 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a yellow oil which was dissolved in dry pyridine (250 ml) under an atmosphere of nitrogen. The resulting solution was cooled to 0 ^oC and acetic anhydride (100 ml) was added dropwise over 30 min. The mixture was stirred for 16 h, slowly warming to r.t. whereupon TLC analysis (50% EtOAc/petrol) indicated the complete consumption of the starting materials (Rf=0.24, 0.36, 0.51) and formation of a single product (Rf=0.88). The mixture was concentrated *in vacuo* to give a pale yellow oil (39.0 g) which was dissolved in dry THF (400 ml) at r.t. under an atmosphere of nitrogen. Benzylamine (12.0 ml, 109.5 mmol) was added slowly and the resulting solution was stirred at r.t. for 22 h whereupon TLC analysis (50% EtOAc/petrol) indicated the complete consumption of the starting material (Rf=0.88) and formation of a major product (Rf=0.66). The mixture was concentrated *in vacuo* and dissolved in ethyl acetate (500 ml). The organic phase was washed with cold aqueous 1M HCl (2x 175 ml), saturated aqueous sodium hydrogencarbonate solution (200 ml) and brine (200 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a pale yellow oil (45.6 g) which was purified by flash column chromatography on silica gel (Biotage SNAP 340g) eluting with an increasing proportion of ethyl acetate/petrol from 8-66% to give 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-mannopyranose **42** (34.34 g, 98%) as a pale yellow oil (predominantly α-anomer): Data for **42-α**: $[\alpha]_D^{25}$ +17.8 (c=1.0, $CHCl_3$), [lit. $[\alpha]_D^{25}$ +16.7 (c=0.8, $CHCl_3$)][30]; δ_H (400 MHz, $CDCl_3$) 2.18 (3H, s, -OAc), 3.68-3.74 (2H,

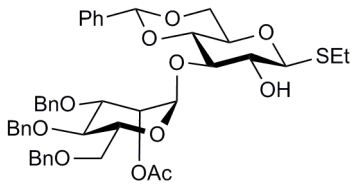
m, 6-*H*$_2$), 3.75 (1H, t, *J* 9.5, 4-*H*), 4.07 (1H, dd, *J* 9.5, 3.1, 3-*H*), 4.08-4.14 (2H, m, 5-*H* and –O*H*), 4.49 (1H, d, *J* 10.9, -C*H*HPh), 4.53 (1H, d, *J* 12.1, -C*H*HPh), 4.55 (1H, d, *J* 11.1, -C*H*HPh), 4.63 (1H, d, *J* 12.1, -CH*H*Ph), 4.73 (1H, d, *J* 11.1, -CH*H*Ph), 4.89 (1H, d, *J* 10.9, -CH*H*Ph), 5.22 (1H, br s, 1-*H*), 5.39 (1H, m, 2-*H*), 7.28-7.38 (15H, m, 15x Ar-*H*); δ_C (100 MHz, $CDCl_3$) 21.2 (-OC(O)*C*H$_3$), 69.2 (C-2), 69.3 (C-6), 71.0 (C-5), 71.8 (-*C*H$_2$Ph), 73.4 (-*C*H$_2$Ph), 74.7 (C-4), 75.1 (-*C*H$_2$Ph), 77.7 (C-3), 92.4 (C-1), 127.7, 127.8, 127.9, 128.10, 128.12, 128.35, 128.41, 128.42, 137.8, 137.9, 138.3, 170.6 (-O*C*(O)CH$_3$).

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-1',1',1'-trichloroacetimidate[31]



DBU (897 µl, 6.0 mmol) was added to a solution of 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-mannopyranose **42** (28.7 g, 60.0 mmol) and trichloroacetonitrile (30.1 ml, 300.0 mmol) in dry DCM (500 ml) at 0 ^{o}C under a nitrogen atmosphere. The reaction mixture was stirred at 0 ^{o}C for 1 h whereupon TLC analysis (33% EtOAc/petrol) indicated complete consumption of the starting material (Rf=0.18) and formation of a single product (Rf=0.45). The mixture was concentrated *in vacuo* and purified immediately by flash column chromatography on silica gel eluting with an increasing proportion of EtOAc/petrol from 17.5-25% to give 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-1',1',1'-trichloroacetimidate **18** as a pale yellow oil (35.44 g, 94%): $[\alpha]_D^{25}$ +38.1 (c=1.0, $CHCl_3$ [lit. $[\alpha]_D^{25}$ +36.3 (c=0.9, $CHCl_3$)][31]; δ_H (400 MHz, $CDCl_3$) 2.21 (3H, s, -OAc), 3.73 (1H, dd, *J* 11.3, 1.1, 6-*H*H), 3.86 (1H, dd, *J* 11.3, 3.5, 6-H*H*), 3.97-4.12 (3H, m, 3-H, 4-H, 5-H), 4.52 (1H, d, *J* 10.9, PhC*H*H-), 4.54 (1H, d, *J* 12.1, PhC*H*H-), 4.60 (1H, d, *J* 11.3, PhC*H*H-), 4.70 (1H, d, *J* 12.1, PhCH*H*-), 4.75 (1H, d, *J* 11.3, PhCH*H*-), 4.89 (1H, d, *J* 10.9, PhCH*H*-), 5.52 (1H, dd, *J* 2.4, 1.5, H-2), 6.32 (1H, d, *J* 1.5, 1-H), 7.26-7.40 (15H, m, 15x Ar-*H*), 8.70 (1H, s, N*H*); δ_C (400 MHz, $CDCl_3$) 21.0 (-OAc), 67.3 (C-2), 68.4 (C-6), 72.1(Ph*C*H_2-), 73.4 (Ph*C*H_2-), 73.7, 74.4, 75.5 (Ph*C*H_2-), 77.4, 90.8 (-*C*Cl_3), 95.4 (C-1), 127.6, 127.8, 127.9,128.1, 128.30, 128.33, 128.4, 128.5, 137.5, 138.1, 138.2, 160.0, 170.1 (-OAc); *m/z* (ES^+) 636.37 ($[M.Na]^+$, 10%), 557.21 (74%), 529.19 (100%).

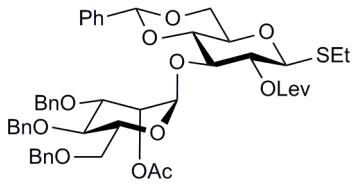
Ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside-(1-3)-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[14]



A mixture of 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-1',1',1'-trichloroacetimidate **18** (600 mg, 0.94 mmol) and ethyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside **19** (245 mg, 0.79 mmol) were concentrated *in vacuo* from toluene (2x 30 ml), dried under vacuum, dissolved in dry DCM (20 ml) and added *via* cannula to a flask containing freshly activated 4Å molecular sieves (0.5 g) at r.t. under a nitrogen atmosphere. The resulting suspension was stirred at r.t. for 1 h then cooled to -78 ^{o}C and trimethylsilyltrifluoromethanesulfonate (14 µl, 0.08 mmol) was added. The reaction mixture was stirred for 19 h slowly warming to 10 ^{o}C, whereupon TLC analysis (33% EtOAc/petrol) indicated complete consumption of **18** (Rf=0.60) and **19** (Rf=0.11) and the formation of a major product (Rf=0.48). Triethylamine (50 µl) was added and the mixture was filtered through celite and diluted with DCM (40 ml) and saturated aqueous sodium hydrogencarbonate solution (30 ml). The layers were separated and the aqueous layer was extracted with DCM (3x 20 ml). The combined organic layers were washed with saturated aqueous sodium hydrogencarbonate solution (30 ml) water (30 ml) and brine (30 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a residue which was recrystallised form EtOAc/petrol to give ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside-(1-3)-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside **21** as a white solid (**CB322-2**, 341 mg, 55 %): m.p. 130-135 ^{o}C; $[\alpha]_D^{25}$ -24.1 (c=1.0, $CHCl_3$) [lit. $[\alpha]_D^{25}$ -24 (c=0.6, $CHCl_3$)][14]; δ_H (500 MHz, $CDCl_3$) 1.32 (3H, t, *J* 7.5, -SCH_2CH_3), 2.12 (3H, s, -OAc), 2.74 (1H, dq, *J* 12.6, 7.5, -SC*H*HCH_3), 2.75 (1H, dq, *J* 12.6, 7.5, -SC*H*HCH_3), 3.01 (1H, d, *J* 3.2, -O*H*), 3.44 - 3.54 (2H, m, 2c-*H*, 5c-*H*), 3.66 (1H, t, *J* 9.1, 4c-*H*), 3.73 (1H, dd, *J* 10.4, 1.9, 6d-*H*H), 3.77 (1H, t, *J* 10.4, 6c-*H*H), 3.79 (1H, dd, *J* 10.4, 4.7, 6d-H*H*), 3.89 (1H, t, *J* 9.5, 4d-*H*), 3.89 (1H, t, *J* 9.1, 3c-*H*), 4.03 (1H, dd, *J* 9.5, 3.5, 3d-*H*), 4.25 (1H, ddd, *J* 9.5, 4.4, 1.9, 5d-*H*), 4.37 (1H, dd, *J* 10.4, 5.0, 6c-H*H*), 4.42 (1H, d, *J* 9.8, 1c-*H*), 4.49 (1H, d, *J* 10.7, -C*H*HPh), 4.51 (1H, d, *J* 12.0, -C*H*HPh), 4.53 (1H, d, *J*

11.0, -C*H*HPh), 4.70 (1H, d, *J* 12.0, -CH*H*Ph), 4.71 (1H, d, *J* 11.0, -CH*H*Ph), 4.86 (1H, d, *J* 10.7, -CH*H*Ph), 5.28 (1H, d, *J* 1.6, 1d-*H*), 5.55 (1H, dd, *J* 3.5, 1.6, 2d-*H*), 5.58 (1H, s, -C*H*Ph), 7.16 - 7.19 (2H, m, 2x Ar-*H*), 7.25 – 7.39 (16H, m, 16x Ar-*H*), 7.45 – 7.49 (2H, m, 2x Ar-*H*); δ_C (125 MHz, $CDCl_3$) 15.2 (-SCH_2CH_3), 21.0 (-OAc), 24.7 (-SCH_2CH_3), 68.5 (2C, C-6c, C-6d), 68.8 (C-2d), 70.4 (C-5c), 71.6 (C-5d), 71.8 (-CH_2Ph), 72.1 (C-2c), 73.4 (-CH_2Ph), 74.3 (C-4d), 75.1 (-CH_2Ph), 78.1 (C-3d), 79.9 (C-3c), 80.6 (C-4c), 87.0 (C-1c), 98.7 (C-1d), 101.0 (C-7d), 125.9 (2x C-Ar), 127.60 (C-Ar), 127.62 (C-Ar), 127.7 (C-Ar), 127.89 (2x C-Ar), 127.93 (2x C-Ar), 128.0 (2x C-Ar), 128.2 (2x C-Ar), 128.29 (2x C-Ar), 128.32 (2x C-Ar), 128.4 (2x C-Ar), 128.9 (C-Ar), 136.9 (C-Ar), 138.0 (C-Ar), 138.1 (C-Ar), 138.4 (C-Ar), 170.1 (-OAc); *m/z* (ES^+) 809.28 ($[M.Na]^+$, 100%); ESI^+ [$C_{44}H_{50}NaO_{11}S$] requires 809.2966, found 809.2976.

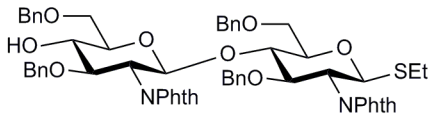
Ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-4,6-*O*-benzylidene-2-levulinoyl-1-thio-β-D-glucopyranoside[14]



N,N-DIC (6.45 ml, 41.4 mmol) was added to a solution of ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside-(1-3)-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside **21** (16.3 g, 20.7 mmol), levulinic acid (5.30 ml, 51.8 mmol) and DMAP (114 mg, 2.0 mmol) in dry DCM (400 ml) at r.t. under a nitrogen atmosphere. The resulting solution was stirred at r.t. for 26 h whereupon TLC analysis (33% EtOAc/petrol) indicated the complete consumption of the starting material (Rf=0.44) and formation of a major product (Rf=0.40). The mixture was diluted with DCM (300 ml) and water (300 ml). The layers were separated and the aqueous layer was extracted with DCM (3x 150 ml). The combined organic layers were washed with saturated aqueous sodium hydrogencarbonate solution (2x 200 ml) and brine (2x 200 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a brown oil which was purified by flash column chromatography on silica gel (Biotage SNAP 340g) eluting with an increasing proportion of diethyl ether/petrol from 20-100% to give ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-4,6-*O*-benzylidene-2-levulinoyl-1-thio-β-D-glucopyranoside **22** as a colourless oil (17.21 g, 94%): $[\alpha]_D^{25}$ -11.1 (c=1.0, $CHCl_3$) [lit. $[\alpha]_D^{25}$ -35.0 (c=1.0, $CHCl_3$)][14]; δ_H (400 MHz, $CDCl_3$) 1.28 (3H, t, *J* 7.4, -SCH_2CH_3), 1.90 (3H, s, -C(O)C*H*$_3$), 2.10 (3H, s, -OAc), 2.32-2.78 (6H, m, -S*CH*$_2$CH$_3$, 1'-*H*$_2$ and 2'-*H*$_2$), 3.51 (1H, td, *J* 9.6, 5.1, 5c-*H*), 3.71-3.90 (7H, m, 4c-*H*, 6c-*H*H, 3d-*H*, 4d-*H*, 5d-*H* and 6d-*H*$_2$), 4.10 (1H, t, *J* 9.6, 3c-*H*), 4.39 (1H, dd, *J* 10.6, 5.1, 6c-H*H*), 4.50 (1H, d, *J* 11.1, -C*H*HPh), 4.54 (1H, d, *J* 12.3, -C*H*HPh), 4.68 (1H, d, *J* 11.1, -C*H*HPh), 4.69 (1H, d, *J* 12.3, -C*H*HPh), 4.83 (1H, d, *J* 11.1, -C*H*HPh), 5.06 (1H, t, *J* 9.6, 2c-*H*), 5.42 (1H, d, *J* 1.3, 1d-*H*), 5.48 (1H, dd, *J* 2.0, 1.3, 2d-*H*), 5.59 (1H, s, 7-*H*), 7.07-7.13 (2H, m, 2x Ar-*H*), 7.23-7.39 (16H, m, 16x Ar-*H*), 7.43-7.47 (2H, m, 2x Ar-*H*); δ_C (100 MHz, $CDCl_3$) 14.9 (-SCH_2CH_3), 21.1 (-OC(O)*C*H$_3$), 24.2 (-*C*H$_2$CH$_2$-), 27.9 (-CH$_2$*C*H$_2$-), 29.6 (-C(O)*C*H$_3$), 37.5 (-S*C*H$_2$CH$_3$), 68.1 (C-2d), 68.5 (C-6c), 68.8 (C-6d), 70.3 (C-2c), 70.4 (C-5c), 71.7 (-*C*H$_2$Ph), 71.8

(C-5d), 73.4 (-*C*H_2Ph), 73.9 (C-4d), 74.8 (C-3c), 75.0 (-*C*H_2Ph), 77.9 (C-3d), 81.6 (C-4c), 84.3 (C-1c), 97.4 (C-1d), 101.2 (-C*H*Ph), 126.1, 127.5, 127.6, 127.7, 127.8, 128.18, 128.22, 128.28, 128.34, 128.4, 129.0, 136.7, 137.9, 138.2, 138.6, 170.2, 171.5, 206.0; ESI^+ [$C_{49}H_{56}NaO_{13}S$] requires 907.3334, found 907.3333.

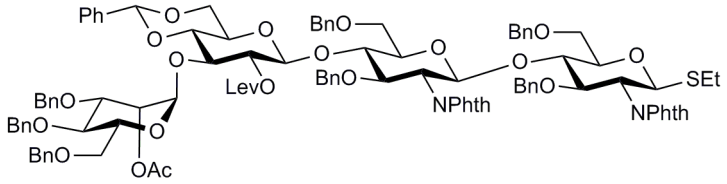
Ethyl-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside



A solution of ethyl-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **9** (14.20g, 14.16 mmol) in dry THF (60 ml + 60 ml washings) was added *via* cannula to a suspension of sodium cyanoborohydride (8.90 g, 141.16 mmol), methyl orange (~2mg) and freshly activated 3Å molecular sieves (3.0 g) in dry THF (280 ml) at 0^{o}C under a nitrogen atmosphere. HCl (4M solution in dioxane) was added slowly (Caution: effervescence) until the yellow colour of the solution changed to a persistent pink. The resulting reaction mixture was stirred 21h slowly warming to r.t. whereupon TLC analysis (40% EtOAc/petrol) indicated the complete consumption of the starting material (Rf=0.49) and formation of a single product (Rf=0.35). The reaction was quenched by addition to saturated aqueous sodium hydrogencarbonate solution (500 ml). The resulting yellow solution was filtered through celite and the layers were separated. The aqueous layer was extracted with DCM (3x 200 ml). The combined organic layers were washed with saturated aqueous sodium hydrogencarbonate solution (2x 200 ml) and brine (200 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a pale yellow oil which was dissolved in methanol (1000 ml) and heated at 55 ^{o}C for 6h then concentrated *in vacuo* to give a yellow foam which was purified by flash column chromatography on silica gel eluting with 6% Et_2O/DCM to give ethyl-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **20** as a white solid (12.91 g, 91%): $[\alpha]_D^{18}$ +18.8 (c=0.5, $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 1.11 (3H, t, *J* 7.6, -SCH_2CH_3), 2.51 (1H, dq, *J* 12.6, 7.6, -SC*H*HCH_3), 2.59 (1H, dq, *J* 12.6, 7.6, -SCH*H*CH_3), 3.13 (1H, d, *J* 1.9, -O*H*), 3.33-3.41 (2H, m, 5a-*H*, 5b-*H*), 3.43 (1H, dd, *J* 11.2, 3.9, 6a-*H*H), 3.53-3.59 (2H, m, 6a-H*H*, 6b-*H*H), 3.71 (1H, dd, *J* 9.9, 4.3, 6b-H*H*), 3.82 (1H, td, *J* 8.6, 1.9, 4b-*H*), 4.15-4.22 (4H, m, 2a-*H*, 2b-*H*, 3a-*H*, 4a-*H*), 4.26 (1H, dd, *J* 10.7, 8.6, 3b-*H*), 4.46-4.55 (6H, m, 6x -C*H*Ph-), 4.80 (1H, d, *J* 12.3, -C*H*HPh), 4.81(1H, d, *J* 12.3, -C*H*HPh),

5.08 (1H, d, *J* 9.2, 1a-*H*), 5.32 (1H, d, *J* 8.2, 1b-*H*), 6.83-6.87 (3H, m, 3x Ar-*H*), 6.93-6.97 (3H, m, 3x Ar-*H*), 6.98-7.01 (2H, m, 2x Ar-*H*), 7.03-7.06 (2H, m, 2x Ar-*H*), 7.25-7.39 (1H, m, Ar-*H*), 7.57-7.80 (6H, m, 6x Ar-*H*), 7.86-7.91 (1H, m, Ar-*H*); δ_C (125 MHz, $CDCl_3$) 14.9 (-SCH_2*C*H_3), 23.6 (-S*C*H_2CH_3), 54.7 (C-2a), 56.1 (C-2b), 68.3 (C-6a), 70.9 (C-6b), 72.6 (-*C*H_2Ph), 72.8 (C-5b), 73.7 (-*C*H_2Ph), 74.3 (-*C*H_2Ph), 75.4 (C-4b), 75.5 (C-3a), 77.6 (C-4a), 78.3 (C-3b), 78.8 (C-5a), 80.7 (C-1a), 96.9 (C-1b), 123.2, 123.4, 123.6, 126.9, 127.3, 127.4, 127.7, 127.75, 127.84, 127.9, 128.1, 128.2, 128.5, 131.6, 133.6, 133.7, 133.9, 134.0, 137.5, 138.3, 138.4, 138.5, 167.5, 167.7, 167.8, 168.4; ESI^+ [$C_{58}H_{56}N_2NaO_{12}S$] requires 1027.3446, found 1027.3463.

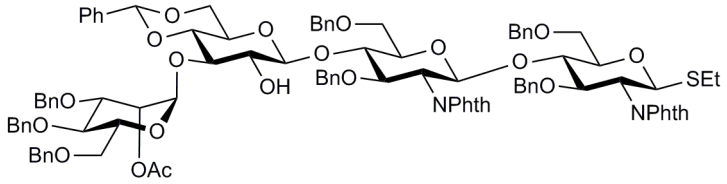
Ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-4,6-*O*-benzylidene-2-levulinoyl-β-D-glucopyranosyl-(1-4) -3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside



A mixture of ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-4,6-*O*-benzylidene-2-levulinoyl-1-thio-β-D-glucopyranoside **22** (89 mg, 0.10 mmol), 2,6-di-*tert*-butyl-4-methylpyridine (51 mg, 0.25 mmol) and diphenylsulfoxide (40 mg, 0.20 mmol) were concentrated from toluene (3x 20 ml), dissolved in dry DCM (10 ml) under a nitrogen atmosphere and added *via* cannula to a flask containing freshly activated 4Å molecular sieves (150 mg) at r.t. under a nitrogen atmosphere. The suspension was stirred at r.t. for 30 min then cooled to -40 ^{o}C. Triflic anhydride (17 µl, 0.10 mmol) was added and the mixture was stirred for 40 min. A solution of ethyl-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **20** (100 mg, 0.10 mmol) in dry DCM (5 ml) was added dropwise *via* cannula. The resulting solution was stirred at -40 ^{o}C for 45 min then warmed to 0 ^{o}C and stirred for 22 h slowly warming to r.t. whereupon TLC analysis (20% EtOAc/toluene) indicated the complete consumption of the starting material **20** (Rf=0.40) and formation of a major product (Rf=0.53). Saturated aqueous sodium hydrogencarbonate solution (20 ml) was added and the layers were separated. The aqueous layer was extracted with DCM (2x 15 ml). The combined organic layers were washed with saturated aqueous sodium hydrogencarbonate solution (20 ml) and brine (20 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a pale yellow oil which was purified by flash column chromatography on silica gel (Biotage SNAP 25g) eluting with an increasing proportion of ethyl acetate/toluene from 3-25% to give ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-4,6-*O*-benzylidene-2-levulinoyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-

glucopyranoside **23** as a colourless oil (117 mg, 64%): $[\alpha]_D^{18}$ +7.7 (c=0.7, $CHCl_3$), Lit. $[\alpha]_D^{18}$ (c=1.0, $CHCl_3$);δ_H (500 MHz, $CDCl_3$): 1.10 (3H, t, *J* 7.6, -SCH_2CH_3), 1.88 (3H, s, -CH_3), 2.07 (3H, s, -C(O)CH_3), 2.30 (1H, dt, *J* 18.3, 6.0, 9c-*H*H), 2.46-2.51 (2H, m, 8c-H_2), 2.50 (1H, dq, *J* 12.6, 7.6, -SC*H*HCH_3), 2.58 (1H, dq, *J* 12.6, 7.6, -SCH*H*CH_3), 3.10 (1H, td, *J* 9.5, 4.9, 5c-*H*), 3.32-3.40 (3H, m, 5a-*H*, 6b-*H*H, 6c-*H*H), 3.47-3.54 (2H, m, 4a-*H*, 6b-H*H*), 3.62 (1H, t, *J* 9.3, 4c-*H*), 3.69-3.74 (1H, m, 5d-*H*), 3.72 (1H, br d, *J* 9.8, 6d-*H*H), 3.77 (1H, dd, *J* 9.8, 3.8, 6d-H*H*), 3.78-3.86 (4H, m, 3d-*H*, 4d-*H*, 6a-H_2), 3.91 (1H, t, *J* 9.3, 3c-*H*), 4.13 (1H, t, *J* 9.2, 4b-*H*), 4.15-4.24 (5H, m, 2a-*H*, 2b-*H*, 3a-*H*, 5b-*H*, 6c-H*H*), 4.29 (1H, dd, *J* 10.5, 9.2, 3b-*H*), 4.39 (1H, d, *J* 12.7, -C*H*HPh), 4.40 (1H, d, *J* 11.3, -C*H*HPh), 4.41 (1H, d, *J* 12.3, -C*H*HPh), 4.43 (1H, d, *J* 12.0, -C*H*HPh), 4.46 (1H, d, *J* 11.3, -C*H*HPh), 4.51 (1H, d, *J* 11.3, -C*H*HPh), 4.52 (1H, d, *J* 11.3, -C*H*HPh), 4.53 (1H, d, *J* 11.4, -C*H*HPh), 4.62 (1H, d, *J* 12.0, -C*H*HPh), 4.63 (1H, d, *J* 8.5, 1c-*H*), 4.65 (1H, d, *J* 11.4, -C*H*HPh), 4.68 (1H, d, *J* 12.3, -C*H*HPh), 4.79 (1H, d, *J* 12.3, -C*H*HPh), 4.81 (1H, d, *J* 12.3, -C*H*HPh), 4.91 (1H, d, *J* 12.7, -C*H*HPh), 4.96 (1H, dd, *J* 9.3, 8.5, 2c-*H*), 5.08 (1H, d, *J* 9.1, 1a-*H*), 5.31 (1H, d, *J* 8.2, 1b-*H*), 5.37 (1H, br s, 1d-*H*), 5.42 (1H, s, 7c-*H*), 5.44 (1H, br s, 2d-*H*), 6.74-6.78 (3H, m, 3x Ar*H*), 6.87-7.03 (7H, m, 7x Ar*H*), 7.06-7.11 (2H, m, 2x Ar*H*), 7.20-7.41 (23H, m, 23x Ar*H*), 7.43-7.49 (4H, m, 4x Ar*H*), 7.52-7.56 (1H, m, Ar*H*), 7.61-7.78 (8H, m, 8x Ar*H*), 7.83-7.88 (1H, m, Ar*H*); δ_C (125 MHz, $CDCl_3$): 14.9 (-SCH_2CH_3), 21.0 (-OC(O)CH_3), 23.7 (-SCH_2CH_3), 27.7 (C-8c), 29.5 (-C(O)CH_3), 37.4 (C-9c), 54.8 (C-2a), 56.6 (C-2b), 65.4 (C-5c), 67.3 (C-6a), 68.0 (C-2d), 68.2 (C-6b), 68.4 (C-6c), 68.8 (C-6d), 71.7 (-CH_2Ph), 71.8 (C-5d), 72.4 (C-2c), 72.6 (-CH_2Ph), 73.2 (-CH_2Ph), 73.5 (-CH_2Ph), 73.8 (C-4d), 74.0 (C-3c), 74.6 (C-4a and 2x -CH_2Ph), 75.0 (-CH_2Ph), 75.9 (C-5b), 76.6 (C-3b), 77.9 (C-3a, 3d and 4b), 78.8 (C-5a), 80.7 (C-1a), 81.7 (C-4c), 97.0 (C-1b), 97.3 (C-1d), 100.4 (C-1c), 101.1 (C-7c), 123.1, 123.3, 123.6, 124.8, 126.1, 126.8, 127.0, 127.2, 127.3, 127.5, 127.6, 127.65, 127.69, 127.72, 127.76, 127.80, 127.86, 127.89, 127.93, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.9, 129.3, 131.0, 131.4, 131.7, 131.8, 133.5, 133.7, 133.9, 136.8, 137.9, 138.0, 138.1, 138.4, 138.6, 138.7, 145.6, 167.5, 167.6, 167.7, 168.3, 170.1 (-O*C*(O)CH_3), 171.3 (-O*C*(O)CH_2-), 205.7 (-*C*(O)-); ESI^+ [$C_{105}H_{106}N_2NaO_{25}S$] requires 1849.6698, found 1849.6718.

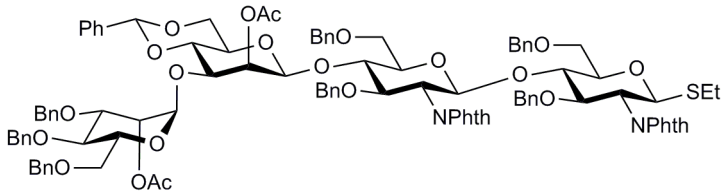
Ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside



Hydrazine acetate (148 mg, 1.64 mmol) was added to a suspension of ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-4,6-*O*-benzylidene-2-levulinoyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **23** (1.00 g, 0.55 mmol) in methanol (40 ml). The mixture was heated to 55 ^{o}C under reflux for 20 h whereupo n TLC analysis (40% EtOAc/petrol) indicated the complete consumption of the starting material (Rf=0.31) and formation of a major product (Rf=0.35). The mixture was diluted with water (150 ml) and DCM (150 ml). The layers were separated and the aqueous layer was extracted with DCM (3x 100ml). The combined organic layers were washed with water (100 ml) and brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a pale yellow foam which was purified by flash column chromatography on silica gel (Biotage SNAP 100g) eluting with an increasing proportion of ethyl acetate/petrol from 8-50% to give ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **3**as a white powder (641 mg, 68%): $[\alpha]_D^{18}$ (c=1.0, $CHCl_3$), Lit. $[\alpha]_D^{18}$ (c=1.0, $CHCl_3$); δ_H (500 MHz, $CDCl_3$): 1.11 (3H, t, *J* 7.3, -SCH_2CH_3), 2.52 (1H, dq, *J* 12.6, 7.3, -SC*H*HCH_3), 2.60 (1H, dq, *J* 12.6, 7.3, -SCH*H*CH_3), 3.13 (1H, td, *J* 9.5, 5.0, 5c-*H*), 3.31-3.35 (2H, m, 5a-*H*, 5b-*H*), 3.39-3.56 (4H, m, 2c-*H*, 4c-*H*, 6a-*H*H, 6c-*H*H), 3.58 (1H, br d, *J* 11.0, 6a-H*H*), 3.68 (1H, br d, *J* 10.8, 6b-*H*H), 3.70 (1H, br d, *J* 11.7, 6d-*H*H), 3.75 (1H, t, *J* 9.1, 3c-*H*), 3.79 (1H, dd, *J* 10.8, 4.4, 6d-H*H*), 3.86 (1H, br d, *J* 11.3, 6b-H*H*), 3.91 (1H, t, *J* 9.3, 4d-*H*), 4.02 (1H, dd, *J* 9.3, 3.0, 3d-*H*), 4.11 (1H, dd, *J* 10.2, 5.0, 6c-H*H*), 4.13 (1H, app t, *J* 9.2, 4b-*H*), 4.16 (1H, app t, *J*

9.2, 3a-*H*), 4.20-4.24 (3H, m, 2a-*H*, 2b-*H*, 5d-*H*), 4.25 (1H, dd, *J* 10.5, 9.2, 4a-*H*), 4.40 (1H, dd, *J* 10.5, 9.2, 3b-*H*), 4.41 (1H, d, *J* 12.6, -C*H*HPh), 4.48-4.53 (5H, m, 5x -C*H*HPh), 4.53 (1H, d, *J* 11.7, -C*H*HPh), 4.54 (1H, d, *J* 12.6, -C*H*HPh), 4.57 (1H, d, *J* 12.0, -C*H*HPh), 4.62 (1H, d, *J* 7.6, 1c-*H*), 4.70 (1H, d, *J* 12.0, -C*H*HPh), 4.71 (1H, d, *J* 11.0, -C*H*HPh), 4.81 (1H, d, *J* 12.3, -C*H*HPh), 4.86 (1H, d, *J* 12.3, -C*H*HPh), 4.87 (1H, d, *J* 11.0, -C*H*HPh), 5.08 (1H, d, *J* 10.1, 1a-*H*), 5.24 (1H, br s, 1d-*H*), 5.28 (1H, d, *J* 8.5, 1b-*H*), 5.45 (1H, s, 7c-*H*), 5.53 (1H, dd, *J* 3.0, 0.7, 2d-*H*), 6.73-6.81 (3H, m, 3x Ar*H*), 6.87-7.06 (8H, m, 8x Ar*H*), 7.15-7.44 (28H, m, 28x Ar*H*), 7.52-7.57 (1H, m, Ar*H*), 7.62-7.89 (8H, m, 8x Ar*H*); δ_C (125 MHz, $CDCl_3$): 14.9 (-SCH_2CH_3), 21.0 (-$OC(O)CH_3$), 23.6 (-SCH_2CH_3), 54.7 (C-2a), 56.6 (C-2b), 65.9 (C-5c), 67.6 (C-6b), 68.3 (C-6a), 68.47 (C-6c), 68.53 (C-2d), 68.8 (C-6d), 71.5 (C-5d), 71.8 (-CH_2Ph), 72.6 (-CH_2Ph), 73.3 (-CH_2Ph), 73.4 (-CH_2Ph), 74.1 (C-2c), 74.3 (C-4d), 74.51 (C-5d or -CH_2Ph), 74.53 (C-5d or -CH_2Ph), 74.7 (-CH_2Ph), 75.1 (-CH_2Ph), 75.4 (C-4a), 77.5 (C-3a), 78.08 (C-3b), 78.12 (C-3d), 78.75 (C-4b), 78.78 (C-5a), 78.9 (C-3c), 80.7 (C-4c), 80.8 (C-1a), 96.9 (C-1b), 98.6 (C-1d), 100.9 (C-7c), 103.8 (C-1c), 123.2, 123.3, 123.7, 125.9, 126.9, 127.1, 127.23, 127.25, 127.4, 127.6, 127.65, 127.66, 127.76, 127.82, 127.9, 127.99, 128.01, 128.08, 128.10, 128.2, 128.29, 128.34, 128.5, 128.8, 131.4, 131.66, 131.74, 133.6, 133.7, 133.9, 134.0, 137.0, 137.6, 138.0, 138.1, 138.4, 138.45, 138.49, 167.5, 167.7, 168.5, 170.1 (-O*C*(O)CH_3); ESI^+ [$C_{100}H_{100}N_2NaO_{23}S$] requires 1751.6330, found 1751.6310.

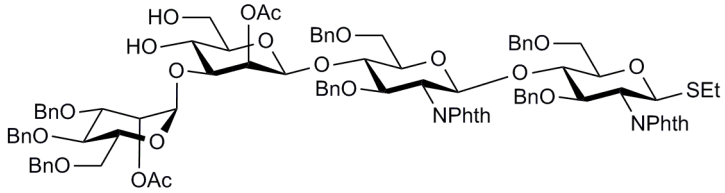
Ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside



Triflic anhydride (838 µl, 4.980 mmol) was added dropwise to a solution of ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **44** (575 mg, 0.332 mmol) in dry DCM (40 ml) at -5 ^{o}C under a nitrogen atmosphere. The resulting mixture was stirred for 3 h slowly warming to r.t. whereupon TLC analysis (15% EtOAc/petrol) indicated the complete consumption of the starting material (Rf=0.36) and formation of a single product (Rf=0.53). The reaction mixture was diluted with DCM (50 ml) and washed with saturated aqueous sodium hydrogencarbonate solution (2x 40 ml) and brine (40 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give an orange oil which was purified by flash column chromatography on silica gel eluting with 35% ethyl acetate/petrol to give the intermediate triflate as a white solid (543 mg, 88%). The triflate (543 mg) and tetra-*n*-butylammonium acetate (751 mg, 2.49 mmol) were dissolved in dry toluene under a nitrogen atmosphere and sonicated at r.t. for 4h. The mixture was diluted with water (500 ml) and DCM (200 ml). The layers were separated and the aqueous layer was extracted with DCM (3x 150 ml). The combined organic extracts were washed with brine (150 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a yellow oil which was purified by flash column chromatography on silica gel (Biotage SNAP 25g) eluting with an increasing proportion of ethyl acetate/toluene from 10-80% to give ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **24** (516 mg, 88%) as a pale yellow oil: $[\alpha]_D^{18}$ +7.6 (c=1.0,

$CHCl_3$), Lit. $[\alpha]_D^{18}$ (c=1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$): 1.13 (3H, t, *J* 7.6, -SCH_2CH_3), 2.11 (3H, s, -OAc), 2.12 (3H, s, -OAc), 2.54 (1H, dq, *J* 12.5, 7.6, -SC*H*HCH_3), 2.62 (1H, dq, *J* 12.5, 7.6, -SCH*H*CH_3), 3.12 (1H, td, *J* 9.0, 4.6, 5c-*H*), 3.25 (1H, br d, *J* 9.6, 5b-*H*), 3.37 (1H, dd, *J* 9.6, 2.3, 5a-*H*), 3.45 (1H, dd, *J* 11.0, 3.5,6a-*H*H), 3.54 (1H, d, *J* 10.4, 6c-*H*H), 3.60 (1H, d, *J* 11.0, 6a-H*H*), 3.61 (1H, d, *J* 11.1, 6b-*H*H), 3.68 (1H, d, *J* 11.1, 6b-H*H*), 3.73 (1H, d, *J* 10.6, 6d-*H*H), 3.83 (1H, dd, *J* 10.6, 3.6, 6d-H*H*), 3.86-3.98 (5H, m, 3c-*H*, 4c-*H*, 3d-*H*, 4d-*H* and 5d-*H*), 4.16-4.34 (7H, m, 2a-*H*, 3a-*H*, 4a-*H*, 2b-*H*, 3b-*H*, 4b-*H* and 6c-H*H*), 4.42-4.61 (9H, m, 9x –C*H*HPh), 4.69 (1H, d, *J* 12.1, -C*H*HPh), 4.71 (1H, d, *J* 12.1, -C*H*HPh), 4.76 (1H, br s, 1c-*H*), 4.89-4.92 (3H, m, 3x –C*H*HPh), 5.11 (1H, d, *J* 10.4, 1a-*H*), 5.27 (1H, br s, 1d-*H*), 5.30 (1H, d, *J* 8.1, 1b-*H*), 5.44 (1H, d, *J* 2.5, 2c-*H*), 5.51 (1H, br s, 2d-*H*), 5.53 (1H, s, 7c-*H*), 6.78-6.82 (3H, m, 3x Ar-*H*), 6.94-7.07 (7H, m, 7x Ar-*H*), 7.24-7.40 (28H, m, 28x Ar-*H*), 7.43-7.47 (2H, m, 2x Ar-*H*), 7.55-7.90 (8H, m, 8x Ar-*H*); δ_C (100 MHz, $CDCl_3$): 14.9 (-SCH_2CH_3), 20.9 (-OC(O)CH_3), 21.0 (-OC(O)CH_3), 23.7 (-SCH_2CH_3), 54.8 (C-2a), 56.6 (C-2b), 66.5 (C-5c), 67.6 (C-6b), 68.3 (C-6a and C-6c), 68.6 (C-2d), 68.9 (C-6d), 70.8 (C-2c), 71.7 (-CH_2Ph), 72.8 (-CH_2Ph), 73.1 (C-5d and -CH_2Ph), 73.4 (2x -CH_2Ph), 74.2 (-CH_2Ph), 74.4, 74.5, 74.6 (-CH_2Ph),74.8 (-CH_2Ph), 75.5 (C-4a), 76.9 (C-3b), 77.6 (C-3a), 77.7, 78.6 (C-4b), 78.8, 78.9 (C-5a), 80.8 (C-1a), 97.0 (C-1b), 98.6 (C-1d), 99.2 (C-1c), 101.2 (C-7c), 123.2, 123.3, 123.7, 126.9, 127.2, 127.5, 127.55, 127.58, 127.66, 127.72, 127.80, 127.84, 127.95, 128.0, 128.1, 128.26, 128.30, 128.4, 128.6, 128.9, 131.7, 133.6, 133.7, 133.9, 134.1, 137.1, 137.97, 138.02, 138.2, 138.3, 138.6, 138.7, 167.5, 167.7, 169.6 (-O*C*(O)CH_3), 170.1 (-O*C*(O)CH_3); ESI^+ $[C_{102}H_{102}N_2NaO_{24}S]$ requires 1793.6435, found 1705.6353.

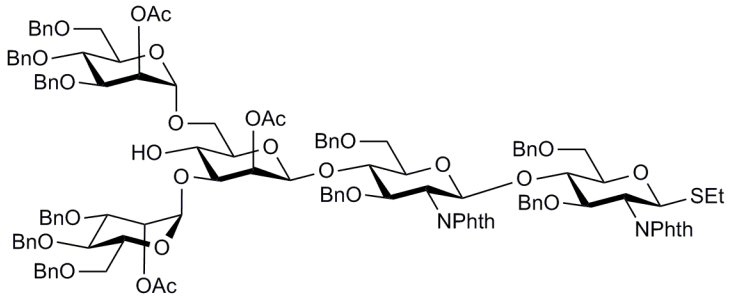
Ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-2-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside



p-Toluenesulfonic acid monohydrate (68 mg, 0.36 mmol) was added to a solution of ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-2-*O*-acetyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **24** (6.35 g, 3.58 mmol) in dry methanol (128 ml) and dey 1,4-dioxane (72 ml) at r.t under a nitrogen atmosphere. The resulting solution was heated to 85 ^{o}C for 3.5 h whereupon TLC analysis (50% EtOAc/petrol) indicated the complete consumption of the starting material (Rf=0.68) and formation of a single product (Rf=0.21). The reaction mixture was diluted with DCM (400 ml) and saturated aqueous sodium hydrogencarbonate solution (300 ml). The layers were separated and the aqueous layer was extracted with DCM (3x 150 ml). The combined organic extracts were washed with saturated aqueous sodium hydrogencarbonate solution (150 ml) and brine (150 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a white solid which was purified by flash column chromatography on silica gel eluting with an increasing proportion of ethyl acetate/petrol from 50-80% to give ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-2-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **25** (5.56 g, 92%) as a white solid: $[\alpha]_D^{25}$ +19.6 (c=1.0, $CHCl_3$); δ_H (500 MHz, $CDCl_3$): 1.11 (3H, t, *J* 7.6, -SCH_2CH_3), 2.06 (3H, s, -OAc), 2.15 (3H, s, -OAc), 2.52 (1H, dq, *J* 12.6, 7.6, -SC*H*HCH_3), 2.60 (1H, dq, *J* 12.6, 7.6, -SC*H*HCH_3), 3.03 (1H, ddd, *J* 9.5, 4.7, 3.2, 5c-*H*), 3.23 (1H, br d, *J* 9.6, 5b-*H*), 3.34 (1H, dd, *J* 9.6, 3.8, 5a-*H*), 3.41 (1H, dd, *J* 11.4, 3.8, 6a-*H*H), 3.27-3.59 (4H, m, 3d-*H*, 6a-H*H*, 6b-*H*H, 6c-*H*H), 3.63 (1H, br d, *J* 11.0, 6b-H*H*), 3.68 (1H, dd, *J* 11.7, 3.2, 6c-H*H*), 3.72-

3.75 (2H, m, 6d-*H*$_2$), 3.80-3.86 (2H, m, 4c-*H*, 4d-*H*), 3.88 (1H, dd, *J* 9.3, 3.0, 3c-*H*), 3.97 (1H, dt, *J* 9.5, 3.5, 5d-*H*), 4.10 (1H, dd, *J* 9.6, 8.5, 4b-*H*), 4.16 (1H, dd, *J* 9.8, 8.2, 3a-*H*), 4.17-4.23 (3H, m, 2a-*H*, 2b-*H*, 4a-*H*), 4.25 (1H, dd, *J* 10.5, 8.5, 3b-*H*), 4.39 (1H, d, *J* 12.0, (-C*H*HPh), 4.43 (1H, d, *J* 12.0, -C*H*HPh), 4.47-4.58 (7H, m, 7x -C*H*HPh), 4.65 (1H, d, *J* 11.7, -C*H*HPh), 4.65 (1H, br s, 1c-*H*), 4.67 (1H, d, *J* 11.7, -C*H*HPh), 4.86 (1H, d, *J* 11.3, -C*H*HPh), 4.87 (1H, d, *J* 12.7, -C*H*HPh), 4.88 (1H, d, *J* 11.3, -C*H*HPh), 5.07 (1H, d, *J* 10.1, 1a-*H*), 5.25 (1H, d, *J* 1.5, 1d-*H*), 5.26 (1H, d, *J* 8.2, 1b-*H*), 5.27 (1H, dd, *J* 2.3, 1.5, 2d-*H*), 5.34 (1H, d, *J* 3.5, 2c-*H*), 6.74-6.78 (3H, m, 3x Ar*H*), 6.93-7.02 (7H, m, 7x Ar*H*), 7.19-7.23 (2H, m, 2x Ar*H*), 7.24-7.37 (23H, m, 23x Ar*H*), 7.52-7.56 (1H, m, Ar*H*), 7.60-7.79 (6H, m, 6x Ar*H*), 7.84-7.91 (1H, m, Ar*H*); δ_C (125 MHz, $CDCl_3$): 14.9 (-SCH_2CH_3), 21.0 (-C(O)CH_3), 21.1 (-C(O)CH_3), 23.6 (-SCH_2CH_3), 54.7 (C-2a), 56.5 (C-2b), 62.1 (C-6c), 67.0 (C-4c), 67.4 (C-6b), 68.3 (C-6a), 69.0 (C-6d), 69.3 (C-2d), 71.0 (C-2c), 71.76 (C-5d), 71.82 (-CH_2Ph), 72.7 (-CH_2Ph), 73.1 (-CH_2Ph), 73.4 (-CH_2Ph), 74.2 (C-4d), 74.37 (C-5b), 74.42 (-CH_2Ph), 74.6 (-CH_2Ph), 74.8 (-CH_2Ph), 75.4 (C-5c), 75.6 (C-4a), 76.8 (C-3b), 77.4 (C-3c), 77.7 (C-3a), 78.0 (C-4b), 78.6 (C-3d), 78.8 (C-5a), 80.7 (C-1a), 97.0 (C-1b), 98.15 (C-1c or 1d), 98.21 (C-1c or 1d), 123.2, 123.3, 123.7, 126.9, 127.28, 127.34, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.11, 128.14, 128.3, 128.35, 128.39, 128.6, 131.4, 131.65, 131.69, 133.5, 133.6, 133.9, 134.1, 137.8, 137.9, 138.3, 138.4, 138.5, 167.5, 167.6, 167.7, 168.4, 169.7 (-C(O)CH_3), 170.6 (-C(O)CH_3); ESI^+ [$C_{95}H_{98}N_2NaO_{24}S$] requires 1705.6122, found 1705.6059.

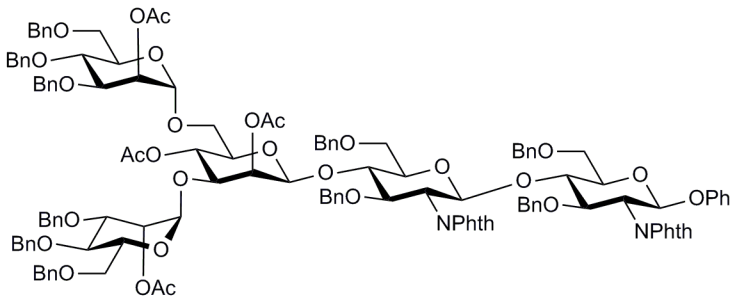
Ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)]-2-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside



A mixture of ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)-2-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **25** (25 mg, 15 μmol) and 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-1',1',1'-trichloroacetimidate **18** (10 mg, 16 μmol) was concentrated from toluene (3x 2 ml) and dried under vacuum. The dried mixture was dissolved in dry DCM (1 ml) and added *via* cannula to a flask containing freshly activated 4Å molecular sieves (100 mg) at r.t. under a nitrogen atmosphere. The resulting suspension was stirred at r.t. for 30 min then cooled to -40 ^{o}C. Trimethylsilyltrifluoromethanesulfonate (0.2 μl, 1.5 mmol) was added and the mixture was stirred at -40 ^{o}C for 20 min whereupon TLC analysis (33% EtOAc/toluene) indicated complete consumption of the acceptor **25** (Rf=0.07) and donor **18** (Rf=0.67), and the formation of a product (Rf=0.38). Triethylamine (100 μl) was added and the mixture was warmed to r.t. and filtered through celite. The filtrate was concentrated *in vacuo* to give a colourless oil which was purified by flash column chromatography (Biotage SNAP 10g) on silica gel eluting with an increasing proportion of EtOAc/petrol from 10-75% to give ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)]-2-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **44** (27 mg, 85%) as a white solid: $[\alpha]_D^{18}$ +42.6 (c=0.5, $CHCl_3$), Lit. $[\alpha]_D^{18}$ (c=1.0, $CHCl_3$); δ_H (700 MHz, $CDCl_3$): 1.11 (3H, t, *J* 7.4, -

SCH_2CH_3), 1.95 (3H, s, -OAc), 2.08 (3H, s, -OAc), 2.14 (3H, s, -OAc), 2.51 (1H, dq, *J* 12.4, 7.4, -SC*H*HCH_3), 2.59 (1H, dq, *J* 12.4, 7.4, -SCH*H*CH_3), 3.06 (1H, dt, *J* 9.5, 2.9, 5c-*H*), 3.23 (1H, br d, *J* 9.9, 5b-*H*), 3.32 (1H, dd, *J* 9.9, 3.4, 5a-*H*), 3.37 (1H, dd, *J* 11.0, 3.4, 6a-*H*H), 3.53 (1H, br d, *J* 11.0, 6a-H*H*), 3.55 (1H, dd, *J* 11.2, 2.6, 6b-*H*H), 3.59 (1H, dd, *J* 9.6, 3.3, 3c-*H*), 3.62-3.65 (2H, m, 6b-H*H* and 6c-*H*H), 3.67-3.69 (2H, m, 6e-H_2), 3.72-3.76 (2H, m, 5e-*H* and 6d-*H*H), 3.79-3.82 (3H, m, 3e-*H*, 4d-*H* and 6d-H*H*), 3.89-3.93 (3H, m, 3d-*H*, 4e-*H* and 6c-H*H*), 3.95 (1H, t, *J* 9.5, 4c-*H*), 3.98-4.01 (1H, m, 5d-*H*), 4.10-4.24 (7H, m, 2a-*H*, 3a-*H*, 4a-*H*, 2b-*H*, 3b-*H*, 4b-*H* and –C*H*HPh), 4.40-4.58 (12H, m, 12x –C*H*HPh), 4.65-4.68 (4H, m, 1c-*H* and 3x –C*H*HPh), 4.77 (1H, d, *J* 10.7, –C*H*HPh), 4.81 (1H, br s, 1e-*H*), 4.85-4.89 (3H, m, 3x –C*H*HPh), 5.06 (1H, d, *J* 10.4, 1a-*H*), 5.23 (1H, s, 1d-*H*), 5.24 (1H, d, *J* 8.3, 1b-*H*), 5.30 (1H, br s, 2e-*H*), 5.37 (1H, d, *J* 3.2, 2c-*H*), 5.43 (1H, br s, 2d-*H*), 6.74-6.81 (6H, m, 6x Ar-*H*), 6.95-6.99 (4H, m, 4x Ar-*H*), 7.09-7.12 (2H, m, 2x Ar-*H*), 7.14-7.17 (2H, m, 2x Ar-*H*), 7.22-7.36 (36H, m, 36x Ar-*H*), 7.54-7.82 (8H, m, 8x Ar-*H*); δ_C (175 MHz, $CDCl_3$): 14.9 (-SCH_2CH_3), 20.9 (-C(O)CH_3), 21.0 (-C(O)CH_3), 21.1 (-C(O)CH_3), 23.7 (-SCH_2CH_3), 54.7 (C-2a), 56.6 (C-2b), 66.1 (C-6c), 67.0 (C-4c), 67.6 (C-6b), 68.3 (C-6a), 68.5 (C-2e), 68.7 (C-6e), 68.87 (C-6d), 68.93 (C-2d), 71.1 (-CH_2Ph), 71.5 (-CH_2Ph), 71.82 (C-4d), 71.85 (-CH_2Ph), 71.9 (C-5d), 72.7 (-CH_2Ph), 73.0 (-CH_2Ph), 73.37 (-CH_2Ph), 73.44 (-CH_2Ph), 74.1 (C-4e), 74.3 (C-5e), 74.4 (C-5b), 74.50 (C-5c), 74.54 (2x -CH_2Ph), 74.7 (-CH_2Ph), 75.4 (-CH_2Ph), 75.5 (C-3a), 76.9 (C-3b), 77.7 (C-4a), 77.8 (C-3d), 78.0 (C-3c), 78.2 (C-3e), 78.8 (C-4b and C-5a), 80.7 (C-1a), 96.9 (C-1b), 97.9 (C-1e), 99.1 (C-1c), 99.4 (C-1d), 123.1, 123.2, 123.3, 123.5, 126.8, 127.1, 127.4, 127.5, 127.60, 127.62, 127.65, 127.7, 127.76, 127.8, 127.9, 127.98, 128.02, 128.11, 128.14, 128.2, 128.3, 128.35, 128.4, 128.5, 131.4, 131.7, 131.8, 133.5, 133.58, 133.62, 133.8, 137.8, 137.9, 138.0, 138.1, 138.2, 138.3, 138.6, 138.65, 138.7, 167.5, 167.7, 168.2, 169.9 (-*C*(O)CH_3), 170.0 (-*C*(O)CH_3), 170.4 (-*C*(O)CH_3); ESI^+ [$C_{124}H_{128}N_2NaO_{30}S$] requires 2180.8198, found 2180.8187.

Phenyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)]-2,4-di-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside

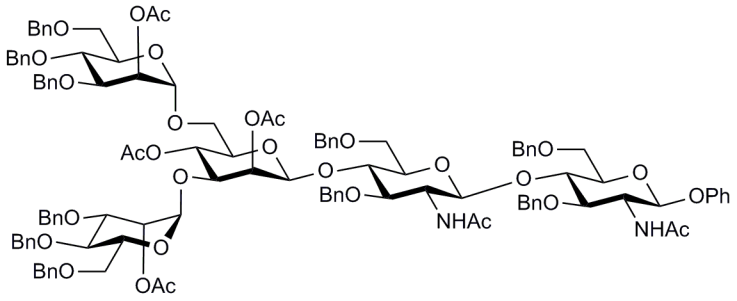


Acetic anhydride (30.0 ml, 317.4 mmol) was added dropwise to a solution of ethyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)]-2-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-1-thio-β-D-glucopyranoside **44** (2.53 g, 1.35 mmol) in dry pyridine (45 ml) at rt under an atmosphere of nitrogen. The mixture was stirred for 7h at rt whereupon TLC analysis (50% EtOAc/petrol) indicated the complete consumption of the starting material (Rf=0.36) and formation of a single product (Rf=0.41). The reaction mixture was concentrated *in vacuo*. The resulting oil was again concentrated *in vacuo* from methanol (2x 100 ml) then partitioned between DCM (150 ml) and saturated aqueous sodium hydrogencarbonate solution (100 ml). The layers were separated and the organic phase was washed with brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a white solid which was purified by flash column chromatography (Biotage SNAP 100g) on silica gel eluting with an increasing proportion of EtOAc/petrol from 11-75% to give a white solid (2.48 g) which was concentrated *in vacuo* from toluene (3x 75 ml) then dissolved in dry DCM (20 ml) and stirred over freshly activated 4Å molecular sieves (1.0 g) at r.t. under a nitrogen atmosphere for 1h. The mixture was cooled to -10 ^{o}C and NIS (511 mg, 2.27 mmol, dried by stirring over freshly activated 4Å molecular sieves) was added followed immediately by TMS-OTf (21 μL, 0.11 mmol). The mixture was stirred at -10 ^{o}C for 15 min then phenol (252 mg, 2.68 mmol, concentrated *in vacuo*

from toluene (3x 10 ml) and stirred over freshly activated 4Å molecular sieves) in dry DCM (10 ml) was added. The reaction mixture was stirred for 2 h slowly warming to -5 ^{o}C then filtered through celite and diluted with DCM (150 ml) and 5% aqueous sodium thiosulfate solution (100 ml). The layers were separated and the aqueous phase was extracted with DCM (3x 80 ml). The combined organic extracts were washed with 5% aqueous sodium thiosulfate solution (100 ml) and brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a yellow oil which was purified by flash column chromatography (Biotage SNAP 100g) on silica gel eluting with an increasing proportion of EtOAc/petrol from 25-70% to give phenyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)]-2,4-di-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **27** (1.21 g, 48%) as a white solid; $[\alpha]_D^{18}$ +31.7 (c=0.6, $CHCl_3$), Lit. $[\alpha]_D^{18}$ (c=1.0, $CHCl_3$); δ_H (500 MHz, $CDCl_3$): 1.92 (3H, s, -OAc), 2.11 (3H, s, -OAc), 2.13 (3H, s, -OAc), 2.16 (3H, s, -OAc), 3.22-3.28 (2H, m, 5b-*H*, 5c-*H*), 3.39 (1H, dd, *J* 10.7, 4.4, 6c-*H*H), 3.44 (1H, app dd, *J* 8.6, 4.3, 5a-*H*), 3.51-3.59 (3H, m, 6c-H*H*, 6-*H*, 6-*H*), 3.62-3.68 (4H, m, 3c-*H*, 6-*H*, 6-*H*, 6-*H*), 3.70-3.74 (2H, m, 5e-*H*, 6-*H*), 3.76 (1H, dd, *J* 10.7, 4.1, 6-*H*), 3.81-3.87 (3H, m, 3d-*H*, 4e-*H*, 6-*H*), 3.91 (1H, dd, *J* 9.3, 3.0, 3e-*H*), 3.93-3.99 (2H, m, 4d-*H*, 5d-*H*), 4.12-4.25 (5H, m, 2b-*H*, 3a-*H*, 3b-*H*, 4a-*H*, 4b-*H*), 4.37-4.74 (16H, m, 16x PhC*H*-), 4.39-4.42 (1H, m, 2a-*H*), 4.79-4.88 (4H, m, 4x PhC*H*-), 4.82 (1H, d, *J* 2.8, 1e-*H*), 4.94 (1H, d, *J* 1.9, 1d-*H*), 5.13 (1H, dd, *J* 3.2, 1.9, 2d-*H*), 5.22 (1H, app t, *J* 9.5, 4c-*H*), 5.23 (1H, d, *J* 7.6, 1b-*H*), 5.31 (1H, dd, *J* 3.0, 1.9, 2e-*H*), 5.40 (1H, d, *J* 3.2, 2c-*H*), 5.57 (1H, d, *J* 8.5, 1a-*H*), 6.72-6.82 (7H, m, 7x Ar*H*), 6.87-6.99 (5H, m, 5x Ar*H*), 7.05-7.40 (44H, m, 44x Ar*H*), 7.56-7.82 (7H, m, 7x Ar*H*); δ_C (125 MHz, $CDCl_3$): 20.78 (-*C*H_3), 20.83 (-*C*H_3), 21.0 (-*C*H_3), 21.1 (-*C*H_3), 55.5 (C-2a), 56.5 (C-2b), 66.7 (C-6), 67.5 (C-6), 68.0 (C-6c), 68.4 (C-2e), 68.66 (C-4c), 68.68 (C-6), 68.8 (C-6), 69.2 (C-2d), 70.8 (C-2c) 71.70 (C-5a), 71.74 (-*C*H_2Ph), 71.78 (-*C*H_2Ph), 72.1 (C-5d), 72.68 (C-5c), 72.73 (-*C*H_2Ph), 73.0 (-*C*H_2Ph), 73.4 (2x -*C*H_2Ph), 73.9 (C-4d), 74.1 (C-4e), 74.42 (C-5b), 74.43 (-*C*H_2Ph), 74.5 (-*C*H_2Ph), 74.6 (-*C*H_2Ph), 74.7 (C-5a), 75.0 (-*C*H_2Ph), 75.8 (C-3a, 3b or 4a), 76.3 (C-3a, 3b or 4a), 76.6 (C-3a, 3b or 4a), 77.4 (C-3c), 78.2 (C-3e),

79.0 (C-4b), 96.2 (C-1a), 97.1 (C-1b), 97.9 (C-1e), 98.8 (C-1c), 100.0 (C-1d), 116.9, 122.6, 123.1, 123.2, 123.5, 126.9, 127.2, 127.37, 127.40, 127.45, 127.49, 127.54, 127.62, 127.67, 127.73, 127.79, 128.0, 128.15, 128.18, 128.20, 128.23, 128.26, 128.35, 128.36, 128.6, 129.2, 131.4, 131.6, 131.8, 133.6, 133.8, 137.9, 138.00, 138.03, 138.1, 138, 2, 138.3, 138.4, 138.5, 138.6, 156.8, 167.4, 168.1, 169.7, 170.0, 170.1, 170.5; ESI^+ [$C_{130}H_{130}N_2Na_2O_{32}$] requires 1138.4196, found 1138.4222.

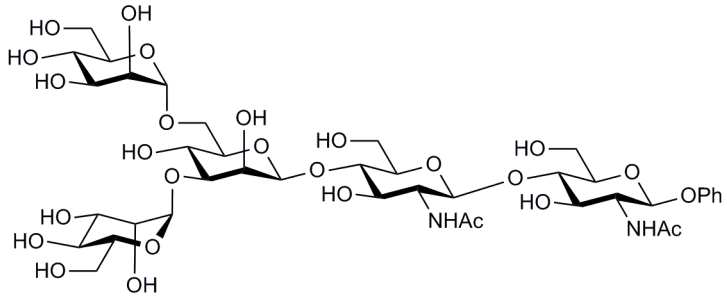
Phenyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)]-2,4-di-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*- acetyl-β-D-glucopyranoside



Methanol (25 ml) was added to a solution of phenyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)]-2,4-di-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-phthalamido-β-D-glucopyranoside **27** (1.14 g, 0.51 mmol) in 1,2-ethylenediamine (5.11 ml, 76.50 mmol) at r.t under a nitrogen atmosphere. The mixture was heated to reflux and stirred for 6 h then concentrated *in vacuo* from toluene (3x 40 ml). The resulting yellow oil was dissolved in dry pyridine (24 ml) and acetic anhydride (16 ml) at r.t under a nitrogen atmosphere. The mixture was stirred for 16 h whereupon TLC analysis (75% EtOAc/petrol) indicated the formation of a single product (Rf=0.57). The reaction mixture was concentrated *in vacuo*. The resulting oil was again concentrated *in vacuo* from methanol (2x 150 ml) then partitioned between EtOAc (100 ml) and water (100 ml). The layers were separated and the aqueous layer was extracted with EtOAc (4x 75 ml). The combined organic extracts were washed with brine (150 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a pale yellow solid which was purified by flash column chromatography on silica gel eluting with 60% ethyl acetate/petrol to give phenyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)]-2,4-di-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*- acetyl-β-D-glucopyranoside **45** (838 mg, 80%) as a colourless oil: $[\alpha]_D^{18}$ +26.5 (c=0.5, $CHCl_3$), Lit. $[\alpha]_D^{18}$ (c=1.0, $CHCl_3$); δ_H (500 MHz, $CDCl_3$): 1.58 (3H, s, -C*H*$_3$), 1.91 (3H, s, -C*H*$_3$), 2.03 (3H, s, -

C*H*$_3$),2.05 (3H, s, -C*H*$_3$), 2.13 (3H, s, -C*H*$_3$), 2.15 (3H, s, -C*H*$_3$), 3.20-3.27 (2H, m, 5b-*H*, 5c-*H*), 3.44-3.53 (3H, m, 3b-*H*, 6c-*H*H, 6-*H*), 3.53-3.71 (8H, m, 2b-*H*, 3c-*H*, 6a-*H*H, 6b-*H*$_2$, 6c-H*H*, 2x 6-*H*), 3.73-3.95 (10H, m, 3a-*H*, 3d-*H*, 3e-*H* 4d-*H*, 4e-*H*, 5a-*H*, 5d-*H*, 5e-*H*, 6a-H*H*, 6-*H*), 3.96-3.99 (1H, m, 4a-*H*), 4.04 (1H, app t, *J* 8.8, 4b-*H*), 4.30 (1H, d, *J* 8.2, 1b-*H*), 4.33 (2H, s, PhC*H*$_2$-), 4.37 (1H, d, *J* 11.0, PhC*H*H-), 4.38 (1H, d, *J* 12.0, PhC*H*H-), 4.41-4.45 (1H, m, 2a-*H*), 4.43 (1H, d, *J* 12.0, PhC*H*H-), 4.45-4.63 (9H, m, 9x PhC*H*H-), 4.59 (1H, br s, 1c-*H*), 4.63 (1H, d, *J* 12.3, PhC*H*H-), 4.66 (1H, d, *J* 12.3, PhC*H*H-), 4.67 (1H, d, *J* 8.2, -N*H*Ac), 4.78 (1H, d, *J* 12.0, PhC*H*H-), 4.81 (1H, d, *J* 12.0, PhC*H*H-), 4.82 (1H, d, *J* 11.0, PhC*H*H-), 4.85 (1H, d, *J* 11.4, PhC*H*H-), 4.86 (1H, br s, 1e-*H*), 4.92 (1H, d, *J* 1.7, 1d-*H*), 5.11 (1H, dd, *J* 2.8, 1.7, 2d-*H*), 5.17 (1H, app t, *J* 9.9, 4c-*H*), 5.23 (1H, d, *J* 4.1, 1a-*H*), 5.33 (1H, d, *J* 3.1, 2c-*H*), 5.34 (1H, dd, *J* 2.8, 1.9, 2e-*H*), 6.75 (1H, d, *J* 9.5, -N*H*Ac), 6.94-7.00 (3H, m, 3x Ar*H*), 7.14-7.20 (6H, m, 6x Ar*H*), 7.21-7.37 (46H, m, 46x Ar*H*); δ_C (125 MHz, $CDCl_3$): 20.8 (-OC(O)*C*H$_3$), 20.9 (-OC(O)*C*H$_3$), 21.0 (-OC(O)*C*H$_3$), 21.1 (-OC(O)*C*H$_3$), 23.0 (-NHC(O)*C*H$_3$), 23.4 (-NHC(O)*C*H$_3$), 49.1 (C-2a), 55.0 (C-2b), 66.4 (C-6c), 68.3 (C-6b), 68.4 (C-4c), 68.6 (C-2e, 6e or 6d), 68.69 (C-2e, 6e or 6d), 68.71 (C-2e, 6e or 6d), 69.0 (C-2d), 70.1 (C-6a), 71.6 (C-5e), 71.7 (-*C*H$_2$Ph), 71.86 (-*C*H$_2$Ph), 71.90 (-*C*H$_2$Ph), 72.1 (C-5d), 72.8 (C-5c), 73.0 (C-4a), 73.32 (2x -*C*H$_2$Ph), 73.35 (-*C*H$_2$Ph), 73.36 (-*C*H$_2$Ph), 73.7 (-*C*H$_2$Ph), 73.8 (C-4e), 74.3 (C-4d), 74.4 (C-5b), 74.6 (-*C*H$_2$Ph), 74.8 (C-5a), 75.2 (-*C*H$_2$Ph), 76.4 (C-3a), 76.8 (C-4b), 77.3 (C-3c and 3d), 77.7 (C-3b), 78.4 (C-3e), 97.75 (C-1a and 1e), 98.0 (C-1c), 99.9 (C-1d), 100.0 (C-1b), 116.4, 122.0, 127.4, 127.5, 127.57, 127.59, 127.65, 127.68, 127.71, 127.80, 127.86, 127.91, 127.92, 128.00, 128.04, 128.08, 128.19, 128.26, 128.27, 128.32, 128.37, 128.59, 128.64, 128.9, 129.3, 137.76, 137.78, 137.9, 138.1, 138.2, 138.3, 138.4, 138.55, 138.63, 157.1, 169.8 (-*C*(O)CH$_3$), 170.0 (-*C*(O)CH$_3$), 170.33 (-*C*(O)CH$_3$), 170.35(-*C*(O)CH$_3$), 170.5(-*C*(O)CH$_3$), 170.7 (-*C*(O)CH$_3$); ESI^+ [$C_{118}H_{130}N_2NaO_{30}$] requires 2077.8601, found 2077.8651.

Phenyl-α-D-mannopyranosyl-(1-6)-[α-D-mannopyranosyl-(1-3)]-β-D-mannopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside



A mixture of $Pd(OH)_2$ on carbon (20% w/w, 400 mg, 0.376 mmol) and phenyl-2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-6)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1-3)]-2,4-di-*O*-acetyl-β-D-mannopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-3,6-di-*O*-benzyl-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside **46** (650 mg, 0.316 mmol) was suspended in dry methanol (50 ml) at r.t under a nitrogen atmosphere. The flask was evacuated and purged with hydrogen twice. A balloon of hydrogen was attached and the mixture was stirred at r.t for 64 h whereupon MS analysis indicated complete conversion. The reaction vessel was purged with nitrogen and the reaction mixture was filtered through a short celite pad under a constant stream of nitrogen. The resulting solution was concentrated *in vacuo* to give a white solid which was purified by column chromatography on silica gel eluting with 25% methanol/DCM to give a white solid (331 mg) which was dissolved in dry MeOH (50 ml) at rt under an atmosphere of nitrogen. Sodium methoxide (4.37 M solution in MeOH, 17 μL, 0.074 mmol) was added and the reaction mixture was stirred at rt for 8h whereupon MS analysis indicated complete reaction. Activated Dowex-H^+ resin (2.0 g) was added and the mixture stirred at rt for 30 min then filtered and concentrated *in vacuo* to give phenyl-α-D-mannopyranosyl-(1-6)-[α-D-mannopyranosyl-(1-3)]-β-D-mannopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranosyl-(1-4)-2-deoxy-2-*N*-acetyl-β-D-glucopyranoside **4** (258 mg, 88%) as a white solid: $[\alpha]_D^{18}$ -12.9 (c=0.1, H_2O); δ_H (700 MHz, D_2O): 1.94 (3H, s, -

NHC(O)CH_3), 2.01 (3H, s, -NHC(O)CH_3), 3.54-3.62 (7H, m, 3d-*H*, 3e-*H*, 5a-*H*, 5b-*H*, 5c-*H*, 5d-*H*, 6a-*H*H), 3.62-3.70 (8H, m, 3a-*H*, 3c-*H*, 4a-*H*, 4b-*H*, 4c-*H*, 6a-H*H*, 2x 6-*H*), 3.70-3.75 (4H, m, 2b-*H*, 3b-*H*, 5d-*H*, 6c-*H*H), 3.78-3.86 (7H, m, 4d-*H*, 4e-*H*, 6c-H*H*, 6-H_2, 2x 6-*H*), 3.89 (1H, dd, *J* 3.4, 1.4, 2e-*H*), 3.93 (1H, dd, *J* 10.5, 8.5, 2a-*H*), 3.99 (1H, dd, *J* 3.2, 1.5, 2d-*H*), 4.18 (1H, d, *J* 2.0, 2c-*H*), 4.55 (1H, d, *J* 8.2, 1b-*H*), 4.70 (1H, br s, 1c-*H*), 4.84 (1H, d, *J* 1.4, 1e-*H*), 5.02 (1H, d, *J* 1.5, 1d-*H*), 5.07 (1H, d, *J* 8.5, 1a-*H*), 6.98 (2H, d, *J* 8.2, 2x Ar-H_{ortho}), 7.07 (1H, t, *J* 7.2, Ar-H_{para}), 7.30 (2H, dd, *J* 8.2, 7.2, 2x Ar-H_{meta}); δ_C (175 MHz, D_2O): 22.1 (-NHC(O)*C*H_3), 22.2 (-NHC(O)*C*H_3), 54.87 (C-2b), 54.92 (C-2a), 59.9 (C-6), 60.0 (C-6a), 60.9 (C-6), 61.1 (C-6), 65.8 (C-4c and 6c), 66.8 (C-3e or 3d), 66.9 (C-3e or 3d), 69.9 (C-2e), 70.0 (C-2d), 70.1 (C-2c), 70.3 (C-4d or 4e), 70.4 (C-4d or 4e), 71.9 (C-3a), 72.1 (C-3b), 72.7 (C-5e), 73.4 (C-5d), 74.2 (C-5c), 74.4 (C-5b), 74.7 (C-5a), 79.0 (C-4a), 79.6 (C-4b), 80.5 (C-3c), 99.4 (C-1a), 99.6 (C-1e), 100.4 (C-1c), 101.4 (C-1b), 102.5 (C-1d), 116.6 (C-*ortho*), 123.5 (C-*para*), 130.0 (C-*meta*), 156.6 (C-*ipso*), 174.7 (-*C*(O)CH_3), 174.9 (-*C*(O)CH_3); ESI^+ [$C_{40}H_{62}N_2NaO_{26}$] requires 1009.3483, found 1009.3456.

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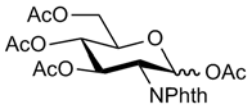
NMR Spectra



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NMR@CHEM.OX

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FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	90.5
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DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec

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PL1	0.00 dB
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SSB	0
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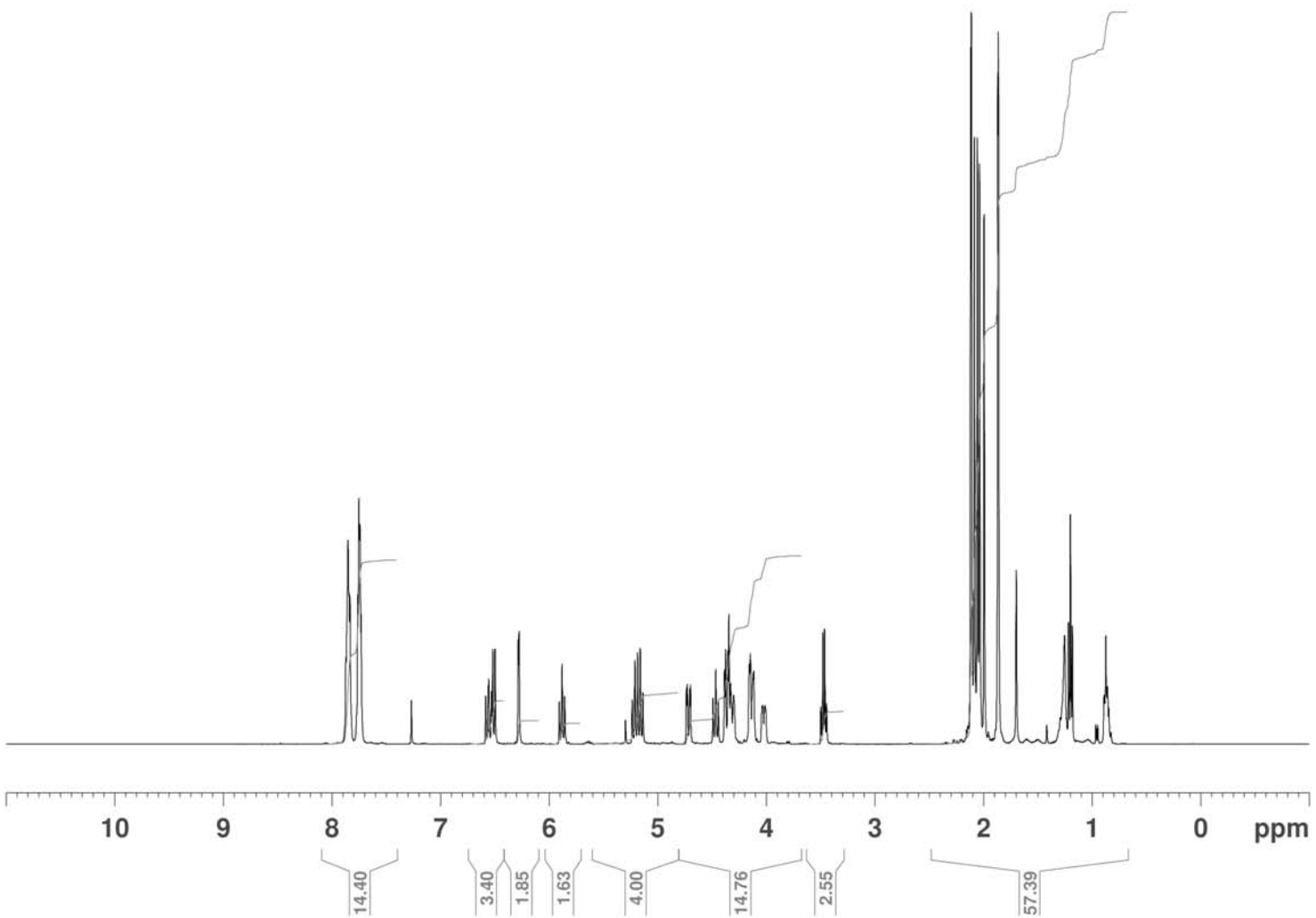
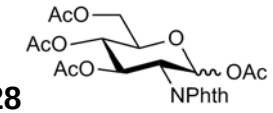
GB	0
PC	1.00





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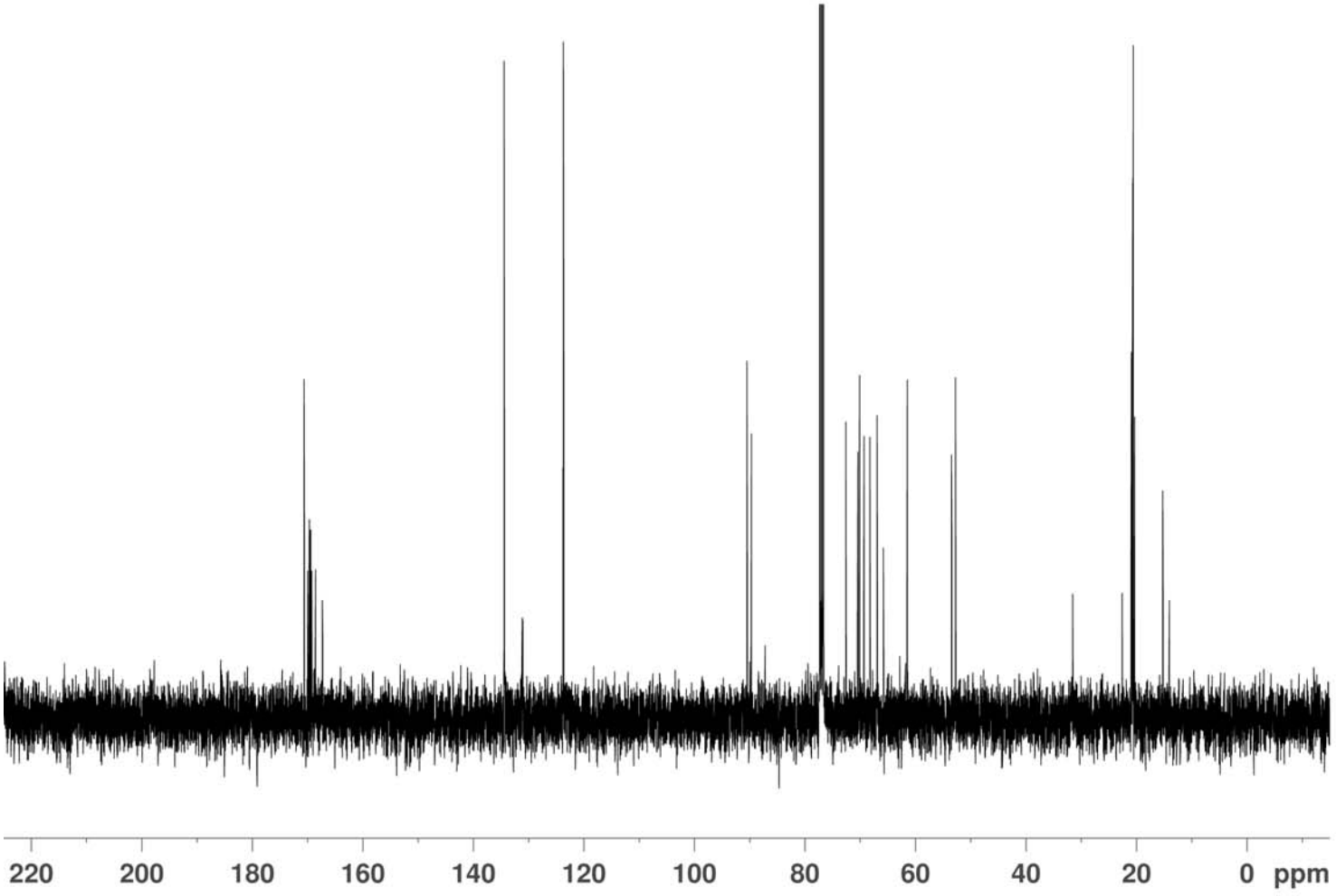

NMR@CHEM.OX

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FIDRES	0.798889 Hz
AQ	0.6259188 sec
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DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
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NUC1	13C
P1	9.50 usec
PL1	0.00 dB
SFO1	100.6403931 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	25.00 dB
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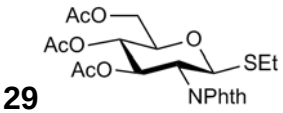
GB	0
PC	1.40



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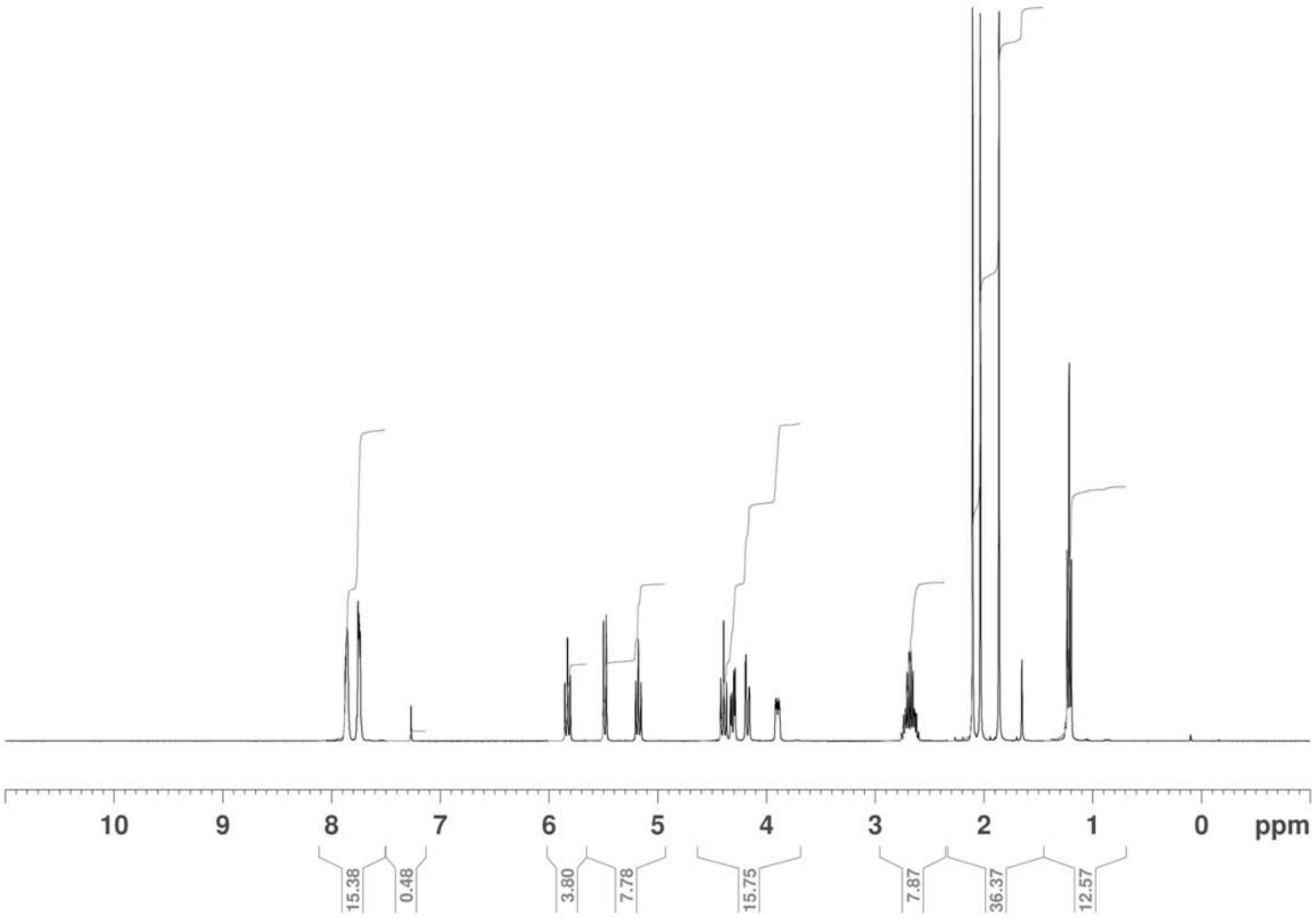

NMR@CHEM.OX

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RG	128	
DW	60.400	usec
DE	7.50	usec
TE	300.0	K
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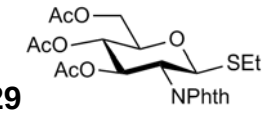

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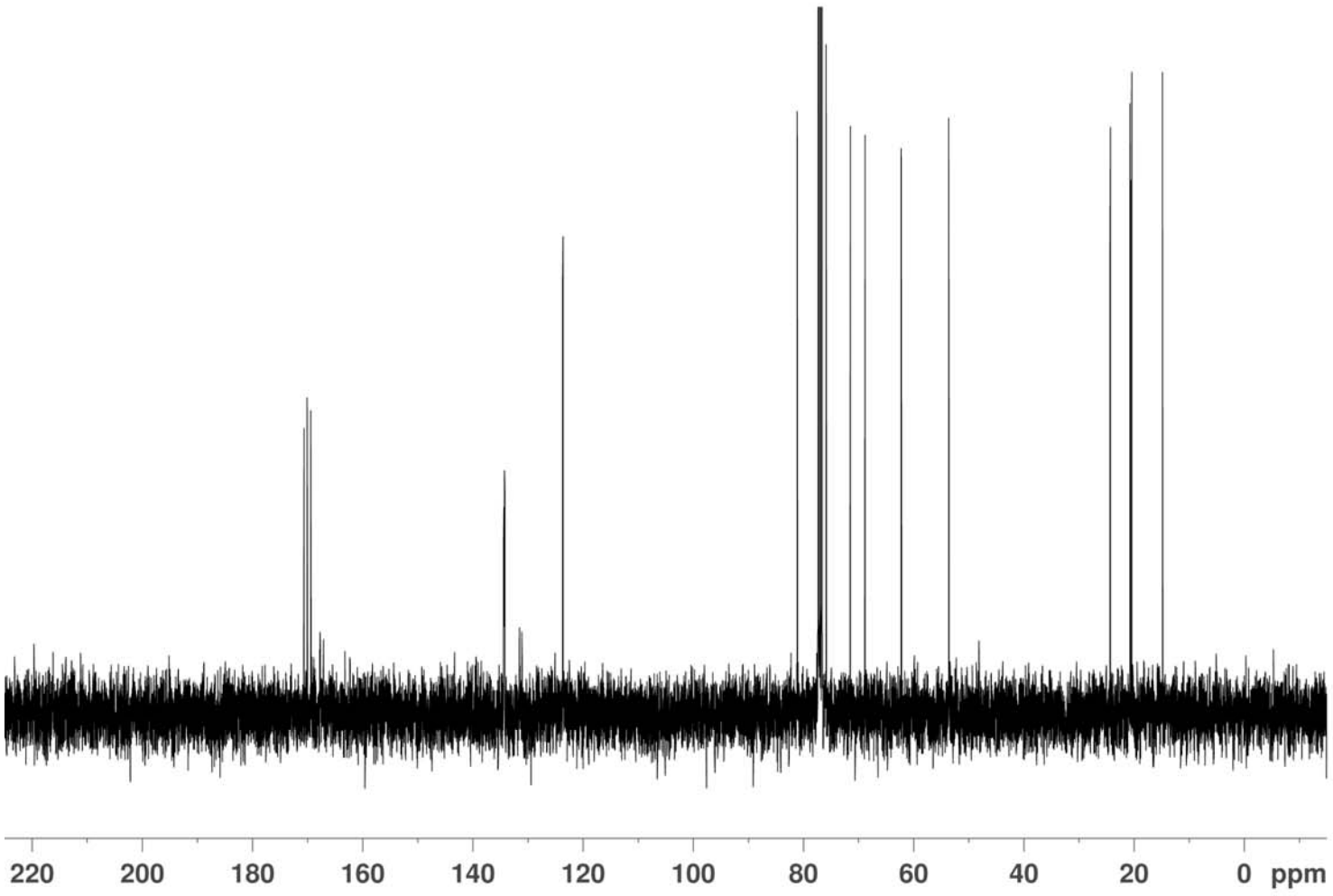

NMR@CHEM.OX

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DS	4	
SWH	26178.010	Hz
FIDRES	0.798889	Hz
AQ	0.6259188	sec
RG	32768	
DW	19.100	usec
DE	7.50	usec
TE	300.0	K
D1	1.00000000	sec
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TD0	1	
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P1	9.50	usec
PL1	0.00	dB
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PL12	19.00	dB
PL13	25.00	dB
SFO2	400.2016008	MHz
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SF	100.6303718	MHz
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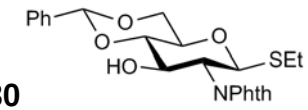

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NMR@CHEM.OX

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PROCNO                1

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TD                32768
SOLVENT           CDCl3
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DS                    2
SWH            5592.841 Hz
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AQ             2.9295092 sec
RG                   64
DW               89.400 usec
DE               17.00 usec
TE                300.0 K
D1           1.00000000 sec

======== CHANNEL f1 ========
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PL1               0.00 dB
SFO1        400.1320007 MHz

F2 - Processing parameters
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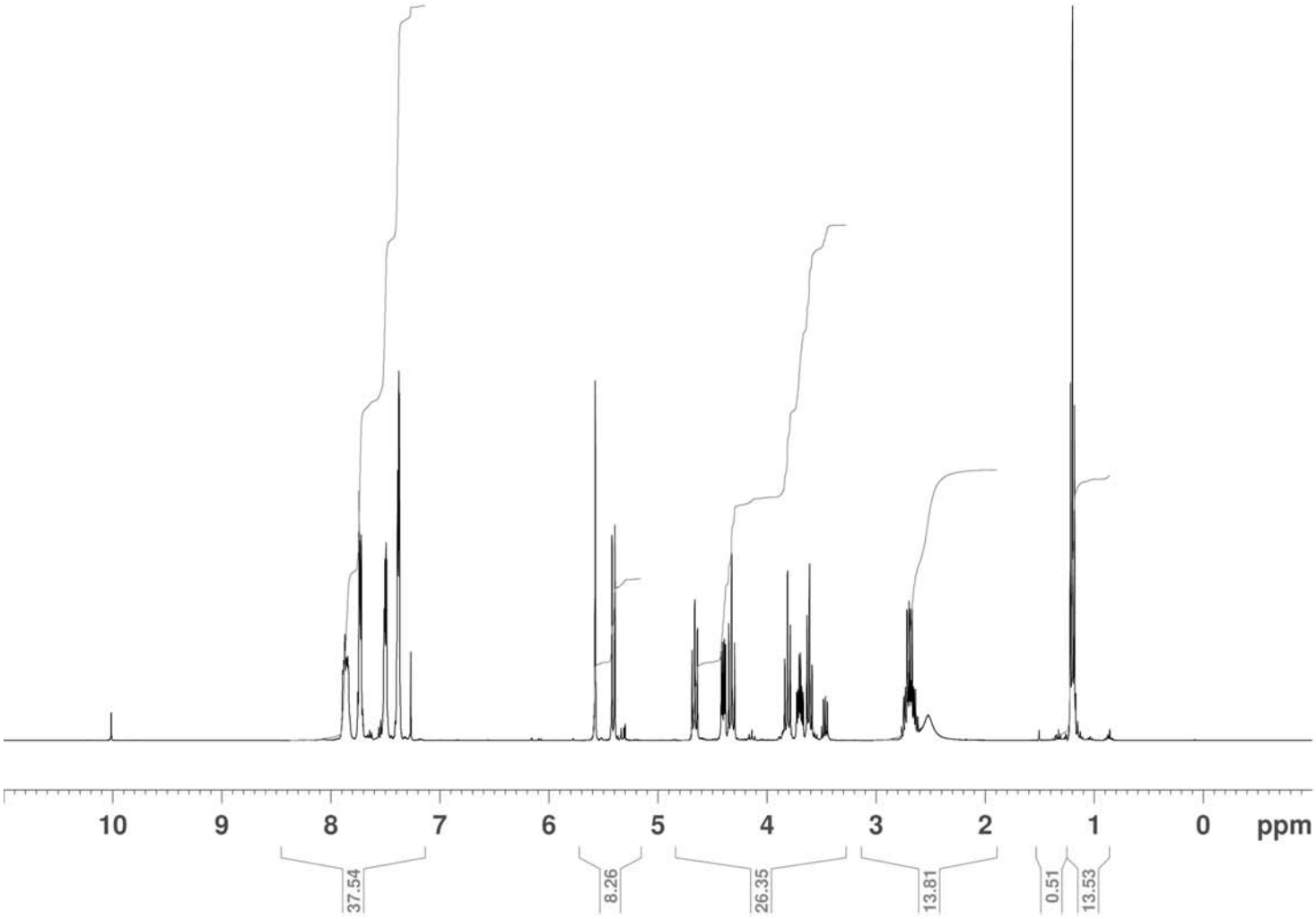

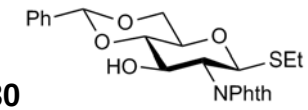

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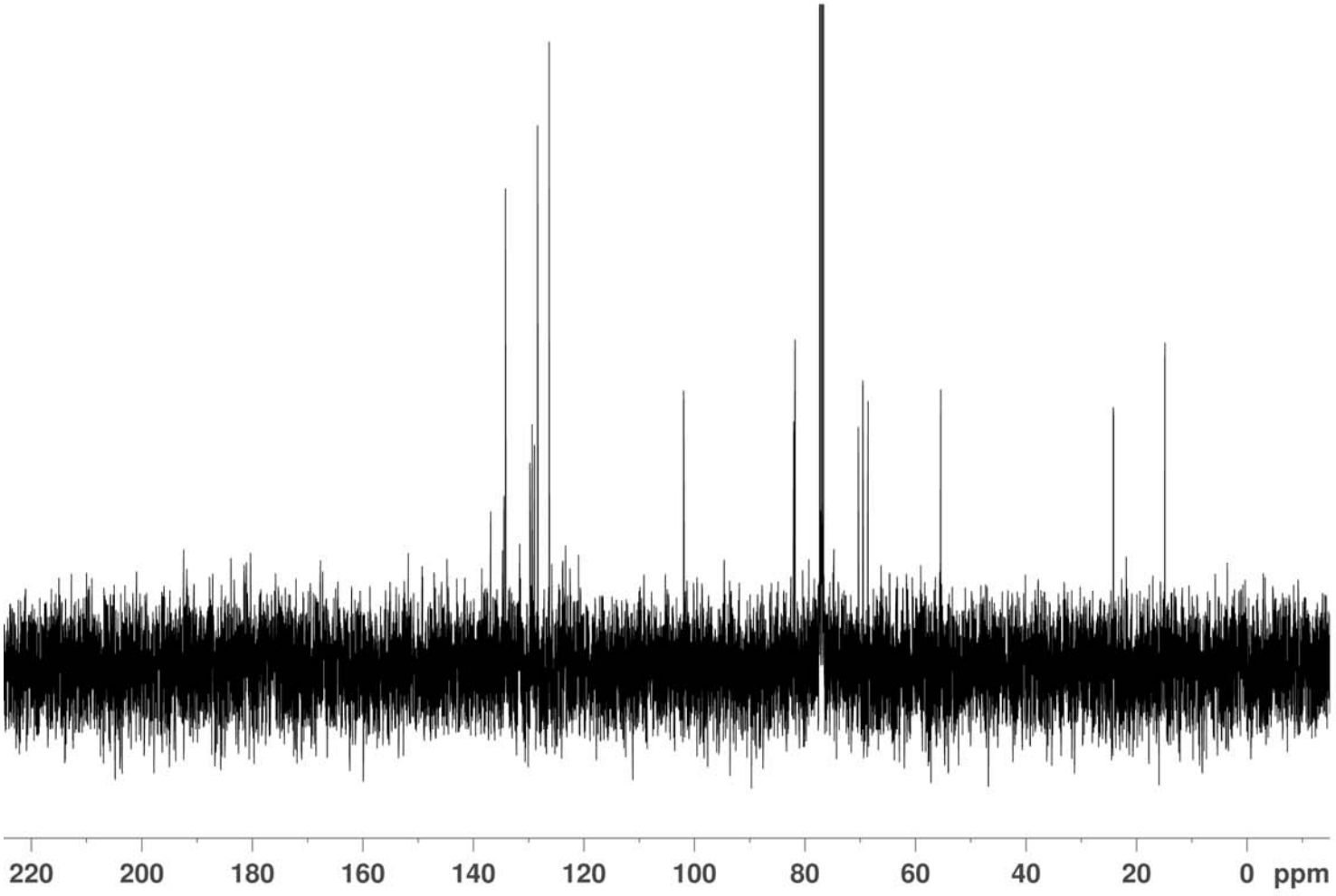

NMR@CHEM.OX

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SOLVENT	CDC13	
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SWH	26178.010	Hz
FIDRES	0.798889	Hz
AQ	0.6259188	sec
RG	32768	
DW	19.100	usec
DE	7.50	usec
TE	300.0	K
D1	1.00000000	sec
D11	0.03000000	sec
TD0	1	
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P1	9.50	usec
PL1	0.00	dB
SFO1	100.6403931	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	19.00	dB
PL13	25.00	dB
SFO2	400.2016008	MHz
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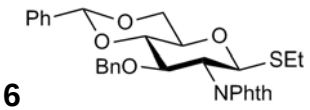

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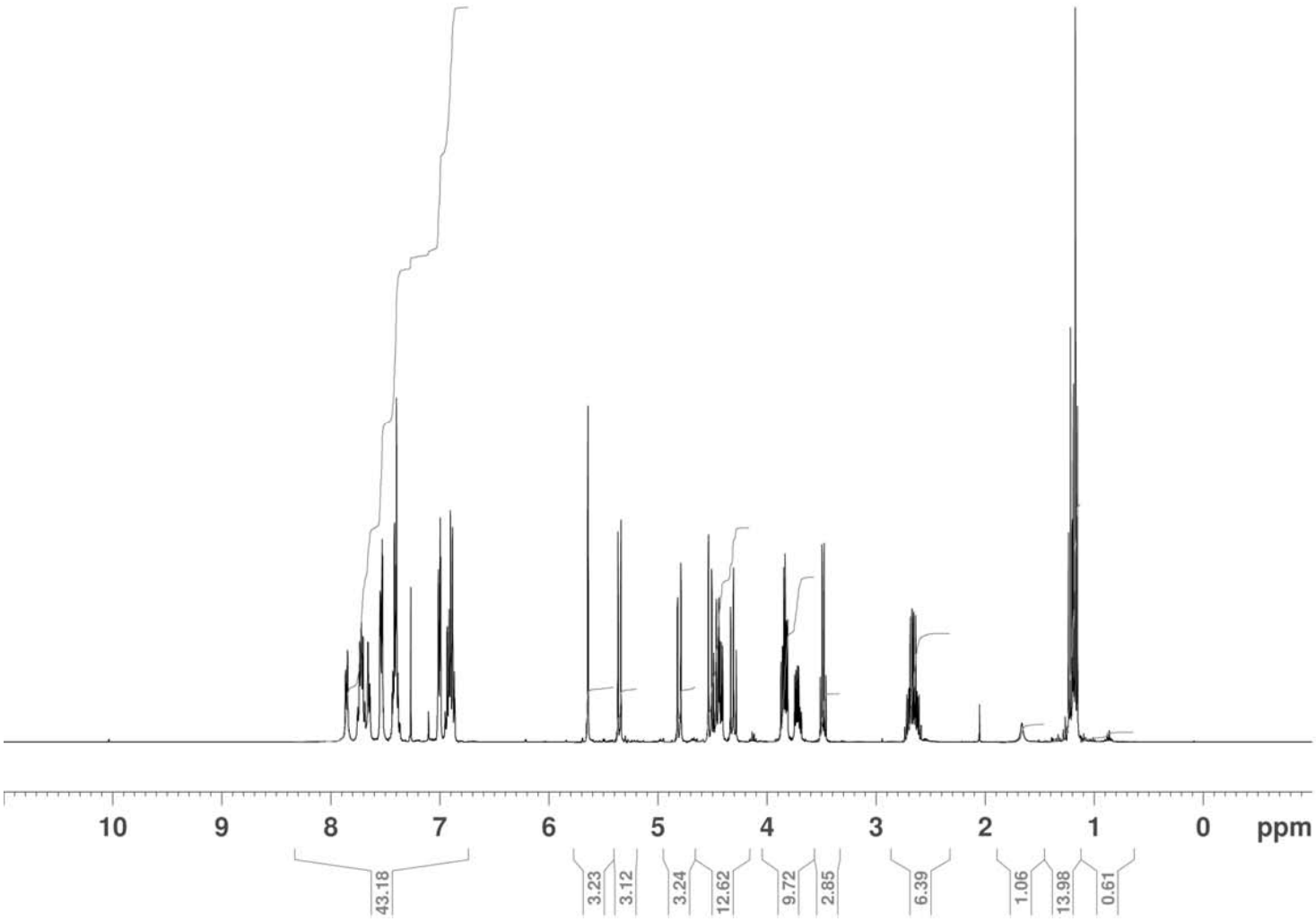

NMR@CHEM.OX

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TD                 32768
SOLVENT            CDCl3
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DS                     2
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RG                  45.3
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DE                17.00 usec
TE                300.0 K
D1           1.00000000 sec

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PL1                 0.00 dB
SFO1        400.1320007 MHz

F2 - Processing parameters
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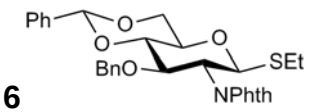

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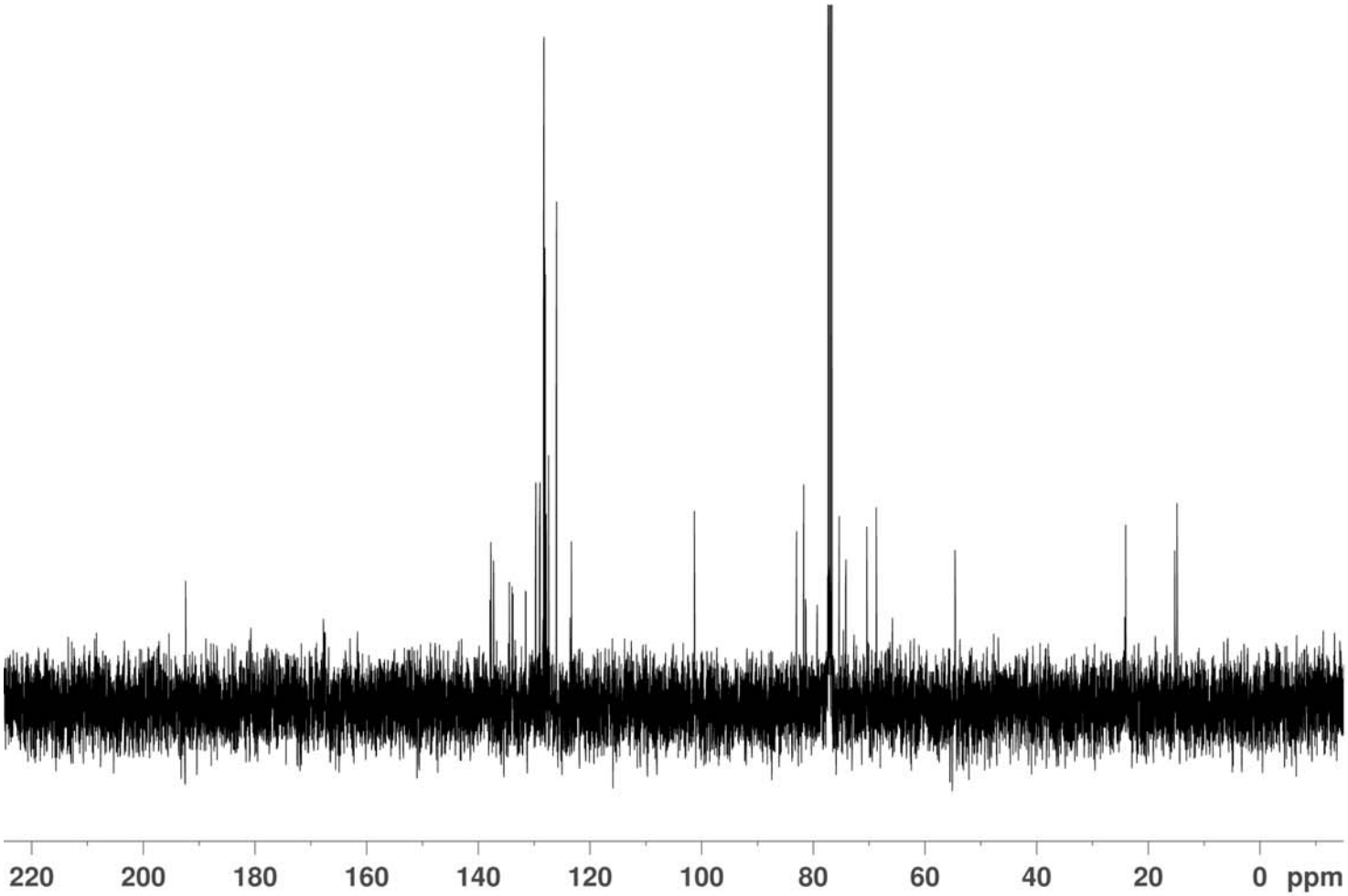
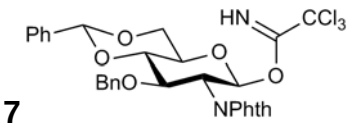


NMR@CHEM.OX

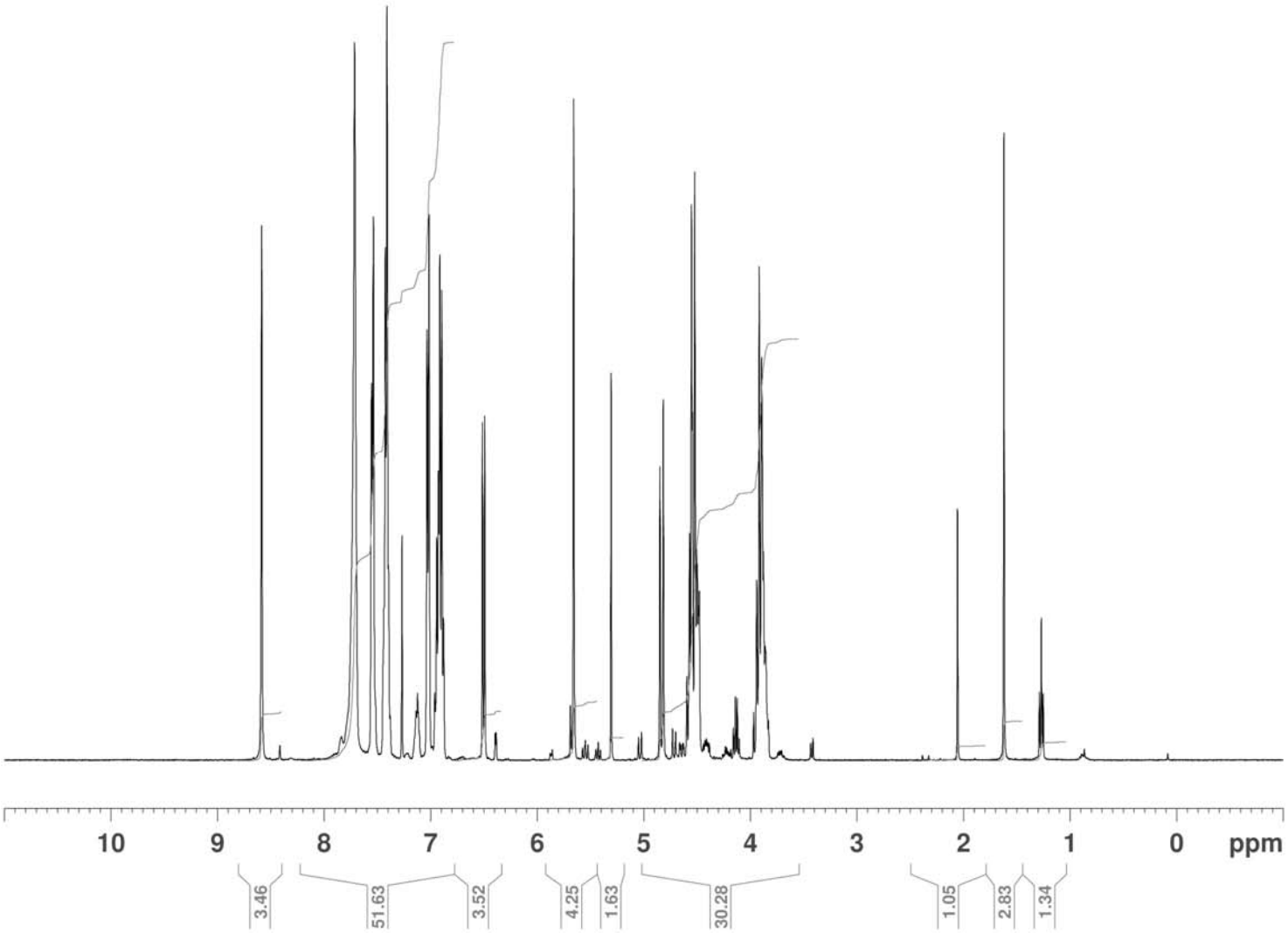
NAME	Sep28-2009-15
EXPNO	3
PROCNO	1
Date_	20090928
Time	14.17
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDC13
NS	256
DS	4
SWH	26178.010 Hz
FIDRES	0.798889 Hz
AQ	0.6259188 sec
RG	32768
DW	19.100 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	0.00 dB
SFO1	100.6403931 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	25.00 dB
SFO2	400.2016008 MHz
SI	32768
SF	100.6303718 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

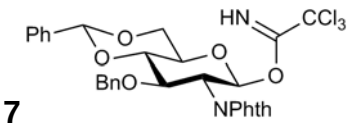


7

NMR@CHEM.OX

NAME	Jan26-2010-1
EXPNO	1
PROCNO	1
Date_	20100126
Time	8.42
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zg60
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	181
DW	60.400 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	400.2024714 MHz
SI	32768
SF	400.2000028 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00





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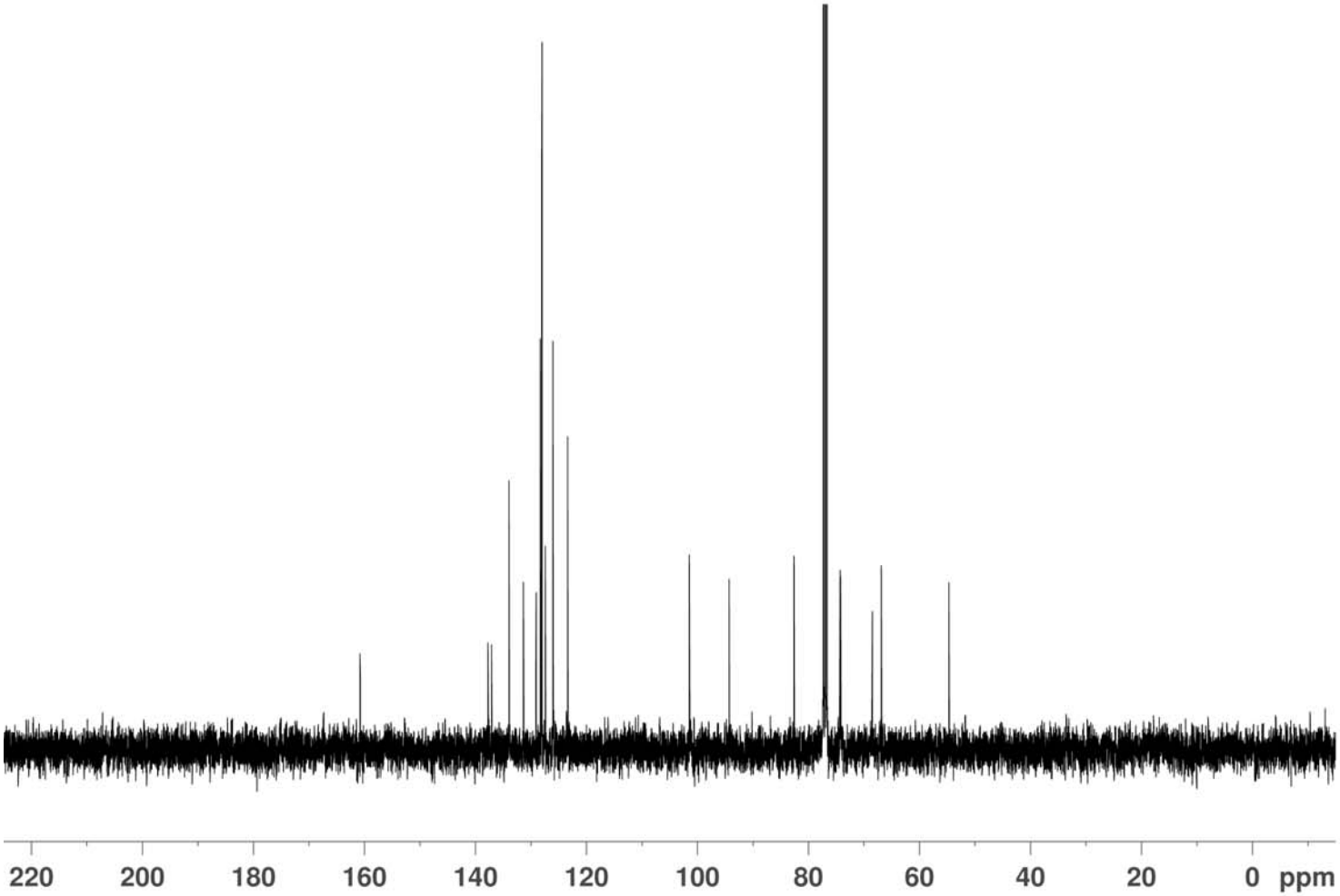
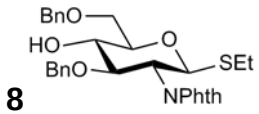


NMR@CHEM.OX

NAME	Jan26-2010-1
EXPNO	2
PROCNO	1
Date_	20100126
Time	8.50
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDC13
NS	256
DS	4
SWH	26178.010 Hz
FIDRES	0.798889 Hz
AQ	0.6259188 sec
RG	32768
DW	19.100 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	0.00 dB
SFO1	100.6403931 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	25.00 dB
SFO2	400.2016008 MHz
SI	32768
SF	100.6303718 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



8

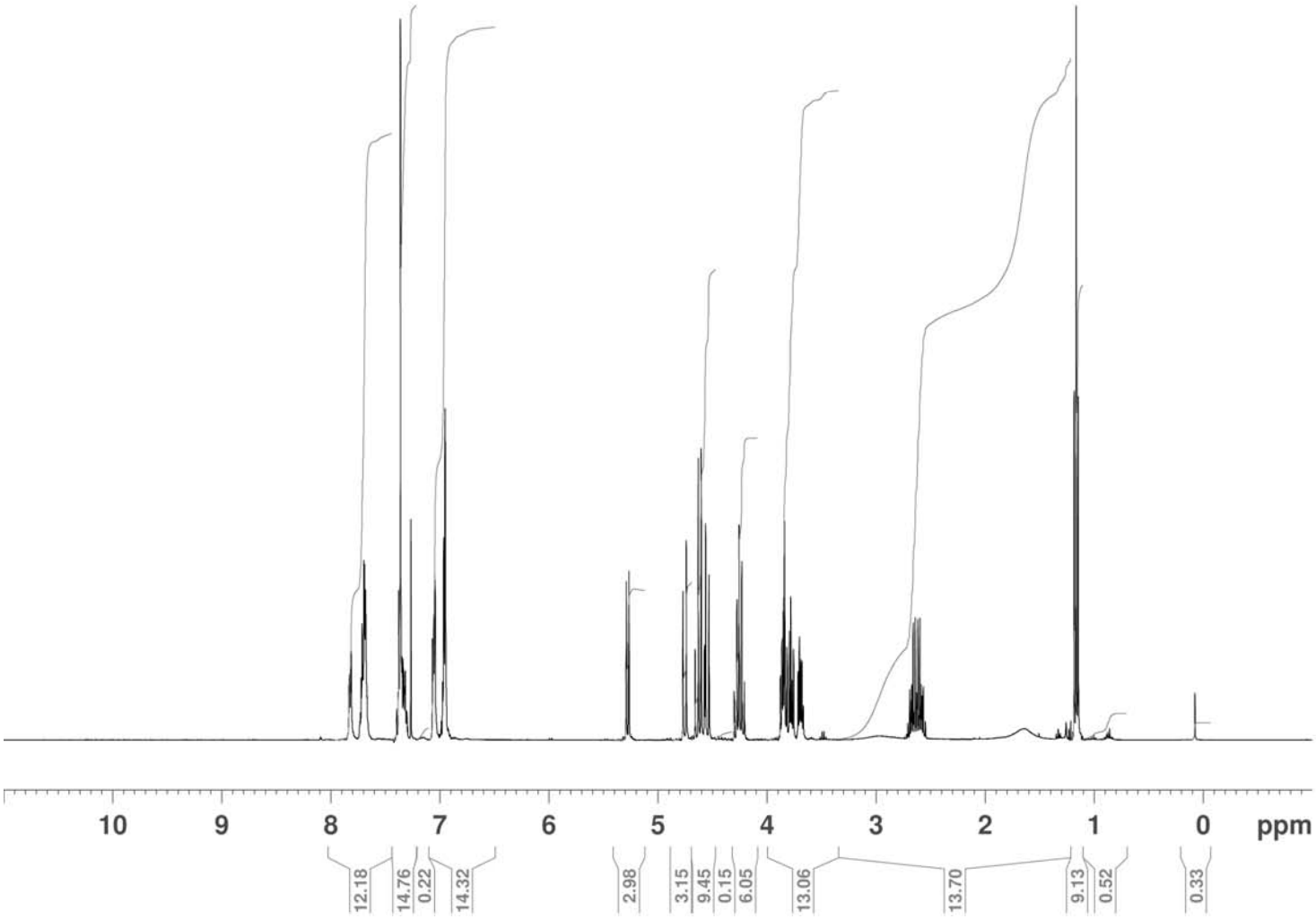
NMR@CHEM.OX

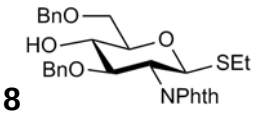
```
Current Data Parameters
NAME       Feb15-2010-33
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100215
Time               17.14
INSTRUM          dpx400
PROBHD   5 mm Dual 1H/1
PULPROG             zg60
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5592.841 Hz
FIDRES          0.170680 Hz
AQ              2.9295092 sec
RG                   128
DW                89.400 usec
DE                17.00 usec
TE                300.0 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.30 usec
PL1                0.00 dB
SFO1        400.1320007 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300182 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 0.60
```





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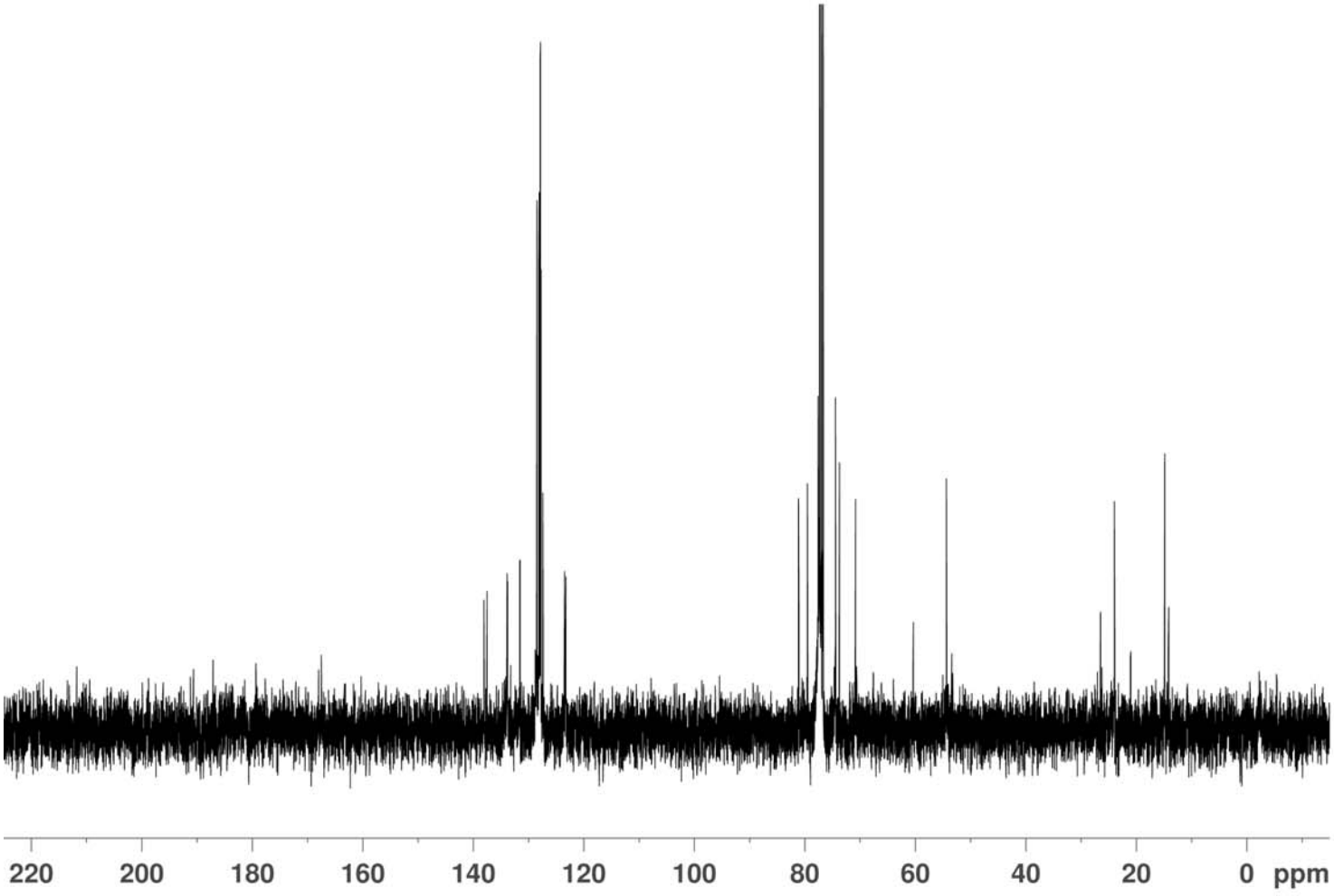
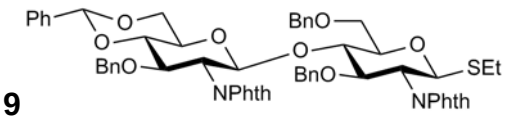


NMR@CHEM.OX

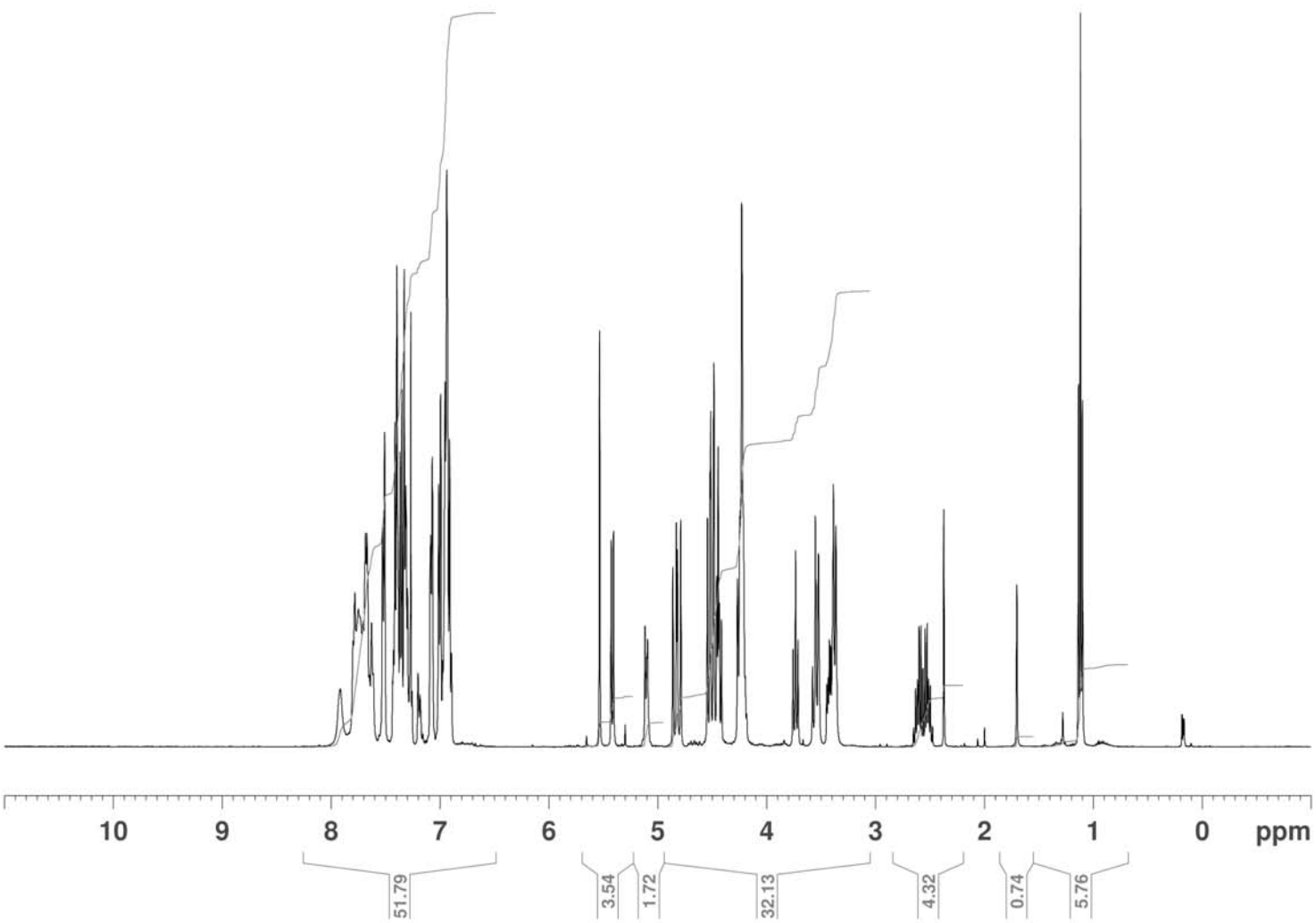
NAME	Jan25-2010-4
EXPNO	7
PROCNO	1
Date_	20100126
Time	1.54
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDC13
NS	256
DS	4
SWH	26178.010 Hz
FIDRES	0.798889 Hz
AQ	0.6259188 sec
RG	32768
DW	19.100 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	0.00 dB
SFO1	100.6403931 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	25.00 dB
SFO2	400.2016008 MHz
SI	32768
SF	100.6303718 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

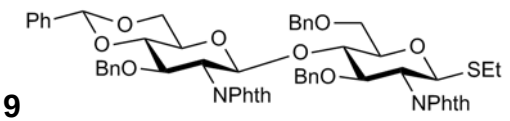


9

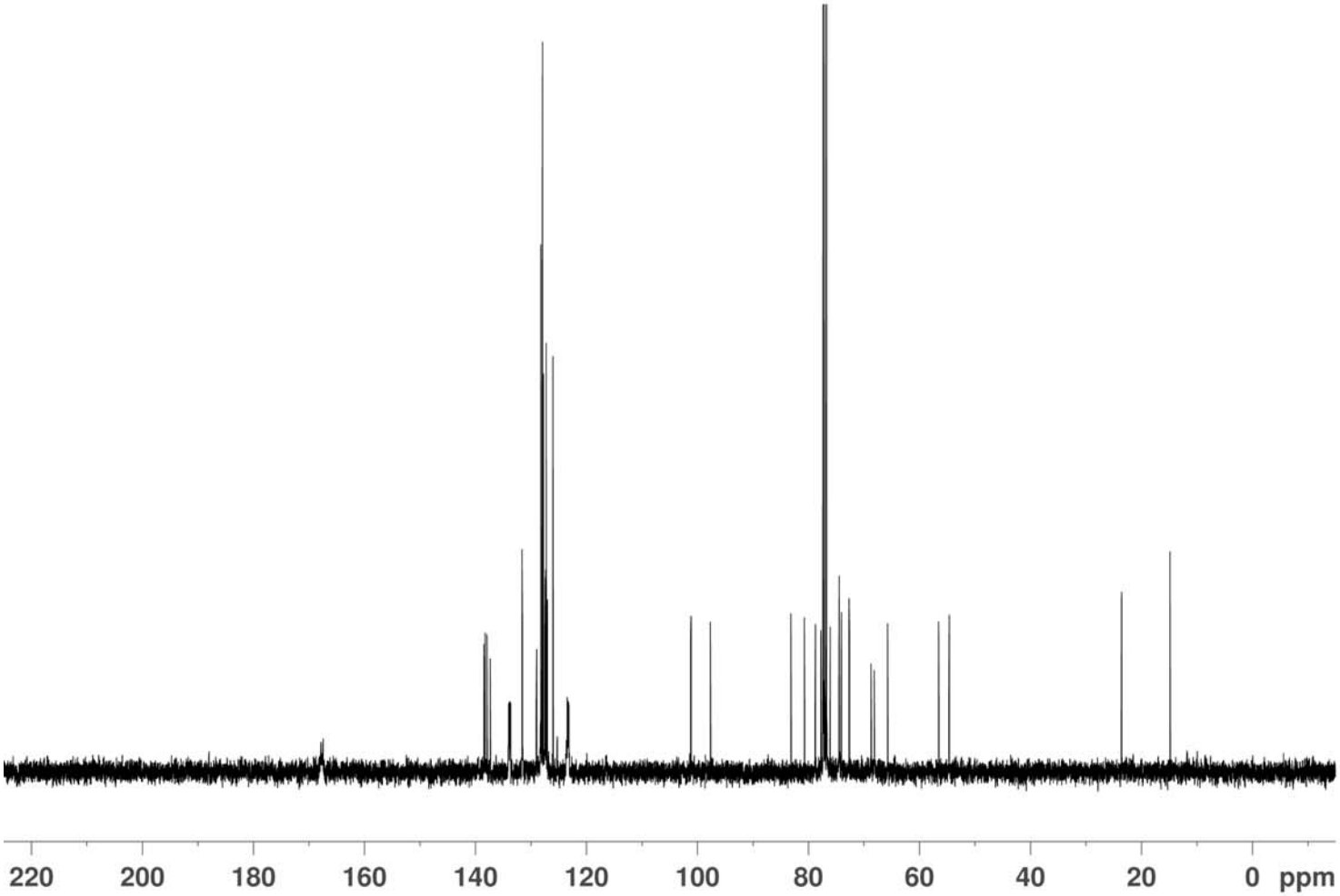
NMR@CHEM.OX

NAME	Jan27-2010-1
EXPNO	1
PROCNO	1
Date_	20100127
Time	19.38
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zg60
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	40.3
DW	60.400 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	400.2024714 MHz
SI	32768
SF	400.2000028 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00





9



NMR@CHEM.OX

NAME	Jan27-2010-1
EXPNO	2
PROCNO	1
Date_	20100127
Time	19.46
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDC13
NS	256
DS	4
SWH	26178.010 Hz
FIDRES	0.798889 Hz
AQ	0.6259188 sec
RG	32768
DW	19.100 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	0.00 dB
SFO1	100.6403931 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	25.00 dB
SFO2	400.2016008 MHz
SI	32768
SF	100.6303718 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

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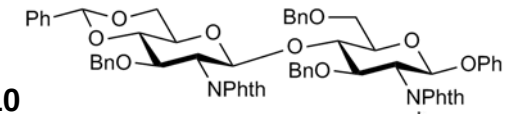
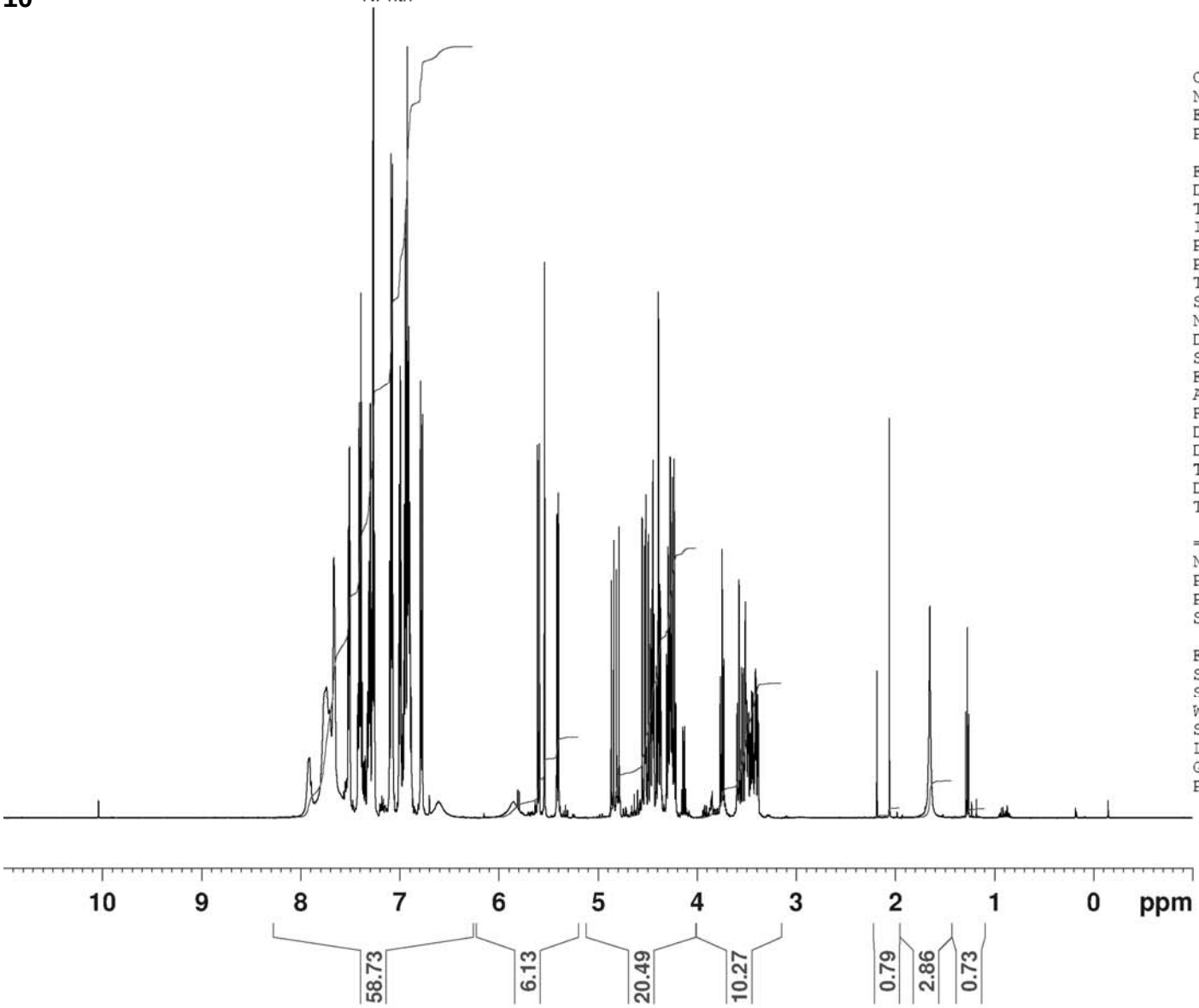
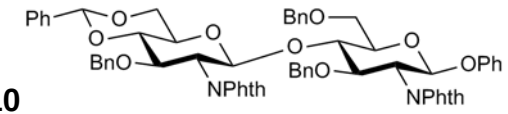
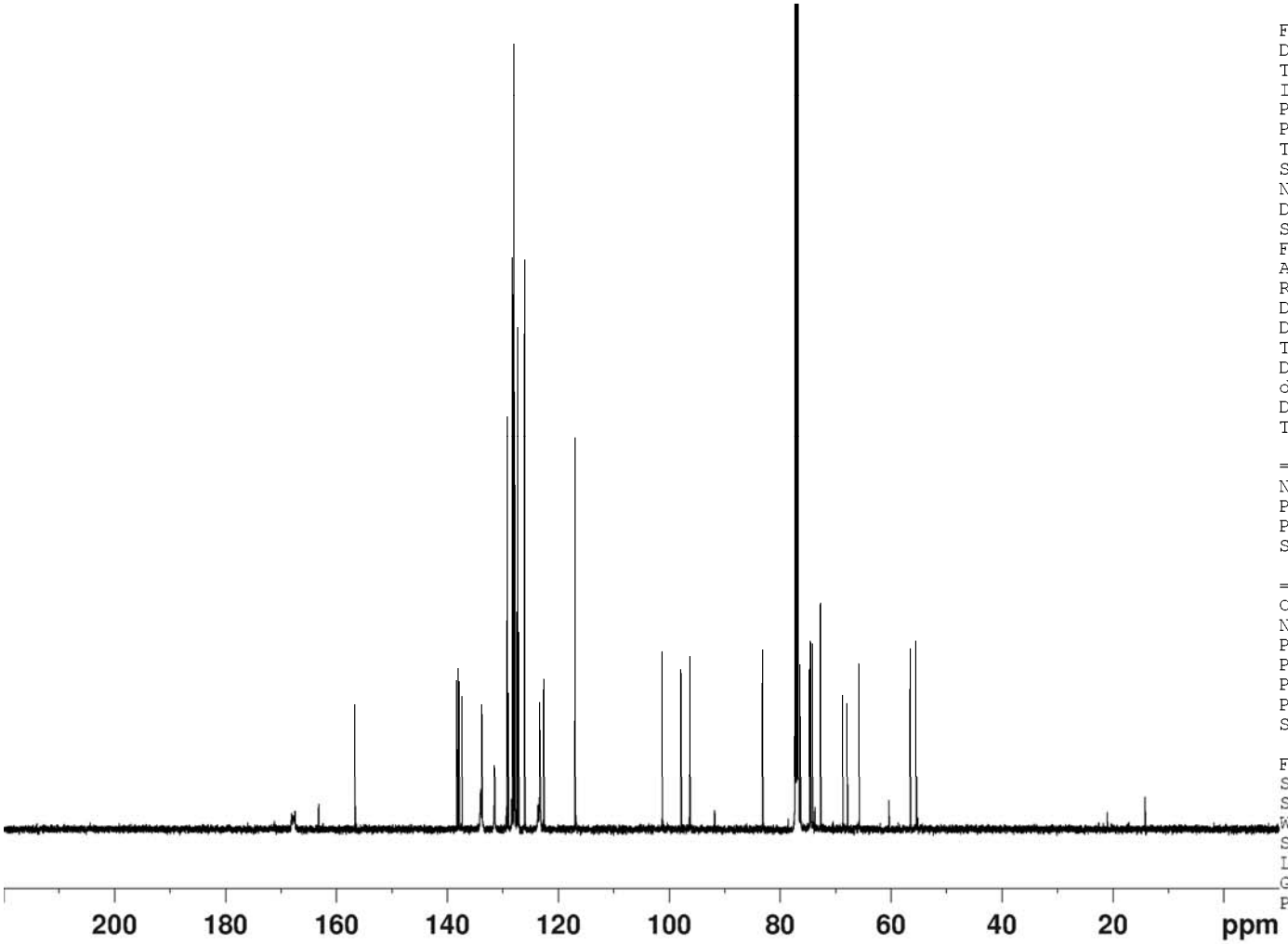




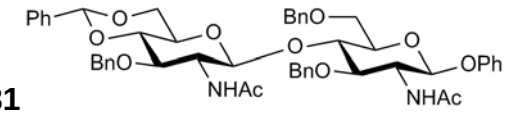

```
Current Data Parameters
NAME          dg32180311
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051104
Time                4.37
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                      4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                   1H
P1                  9.60 usec
PL1                -6.00 dB
SFO1        500.3030896 MHz

F2 - Processing parameters
SI                 32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



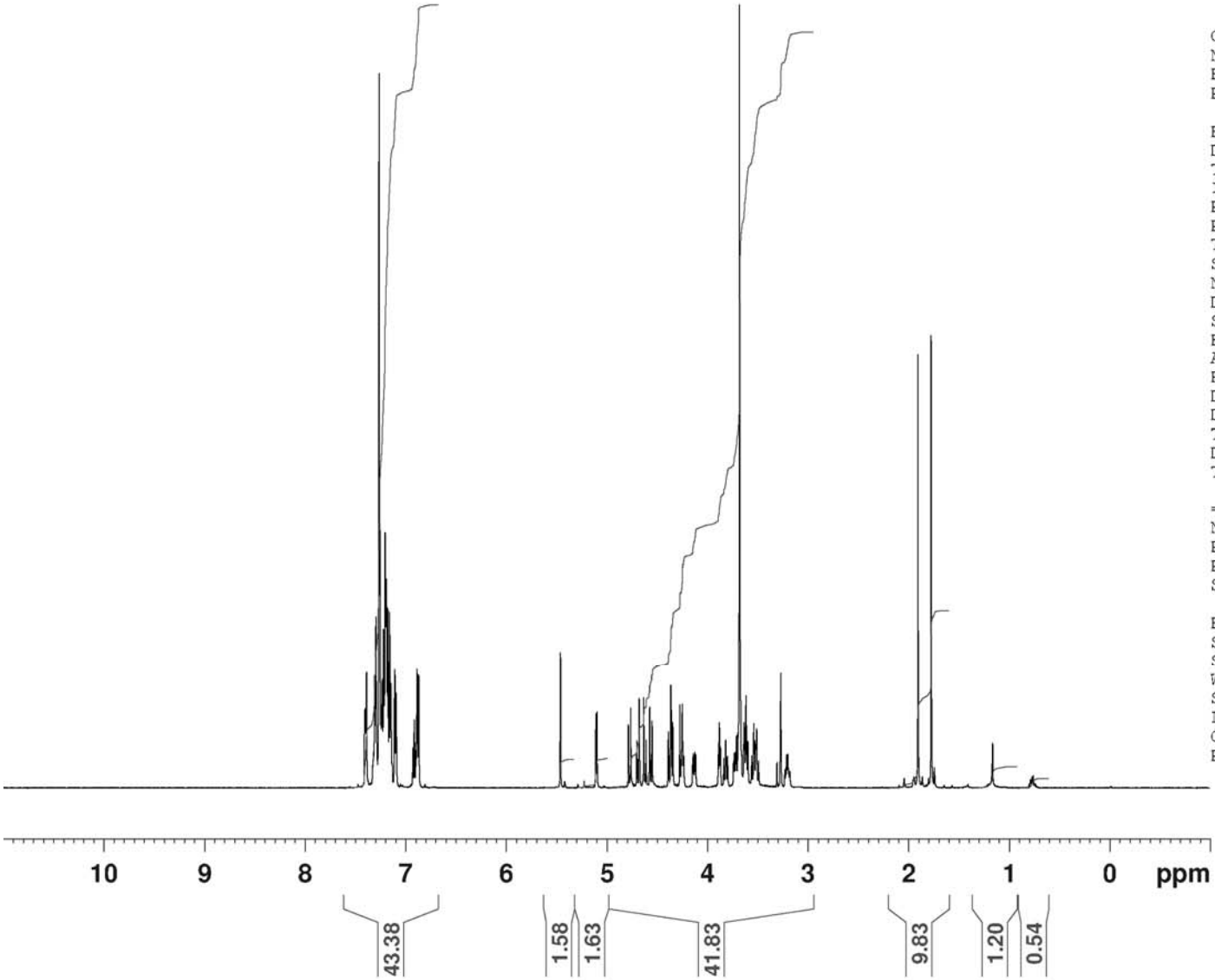
10



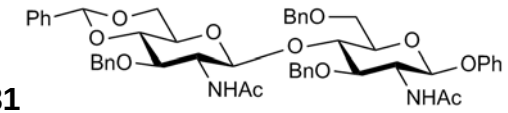

```
Current Data Parameters
NAME          dg32180311
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051104
Time                5.09
INSTRUM           avc500
PROBHD   5 mm CPDUL 13C
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0486259 sec
RG                 1620
DW               16.000 usec
DE               20.00 usec
TE               298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.00 usec
PL1               -4.40 dB
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.40 dB
PL13              17.00 dB
SFO2        500.3020012 MHz

F2 - Processing parameters
SI                 32768
SF          125.8005438 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```



31




```
Current Data Parameters
NAME          dg33532311
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051124
Time               18.40
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.60 usec
PL1                -6.00 dB
SFO1        500.3030896 MHz

F2 - Processing parameters
SI                 32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



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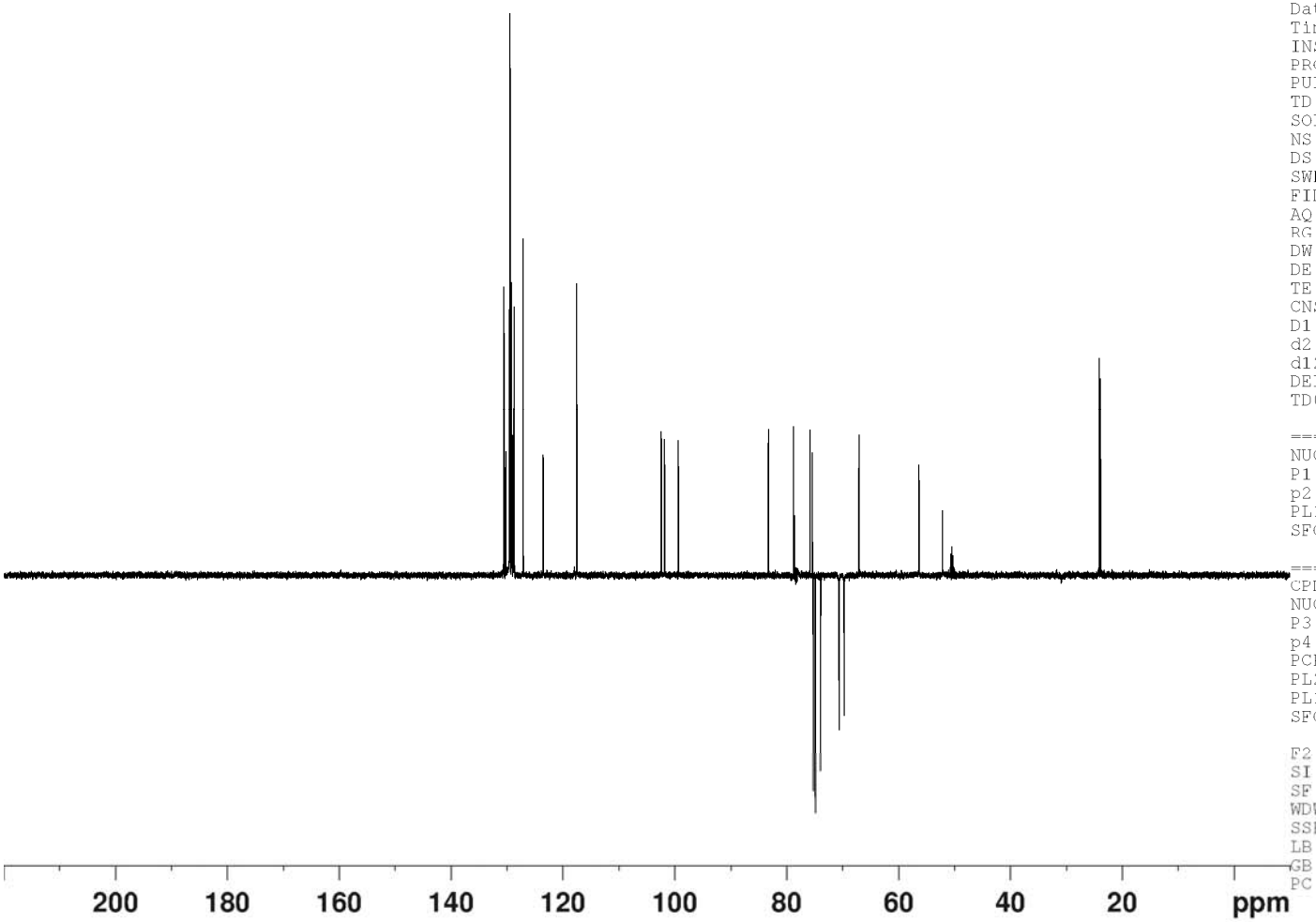


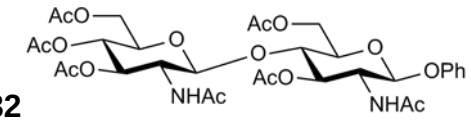

```
Current Data Parameters
NAME          dg33532311
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051123
Time               12.58
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          dept135
TD                 65536
SOLVENT             MeOD
NS                   256
DS                     2
SWH            31250.000 Hz
FIDRES         0.476837 Hz
AQ             1.0486259 sec
RG                  1620
DW                16.000 usec
DE                20.00 usec
TE                297.7 K
CNST2        145.0000000
D1            2.00000000 sec
d2            0.00344828 sec
d12           0.00002000 sec
DELTA         0.00001019 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  8.00 usec
p2                 16.00 usec
PL1                -4.40 dB
SFO1         125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
P3                 10.60 usec
p4                 21.20 usec
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.40 dB
SFO2         500.3020012 MHz

F2   Processing parameters
SI                 32768
SF          125.8003564 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



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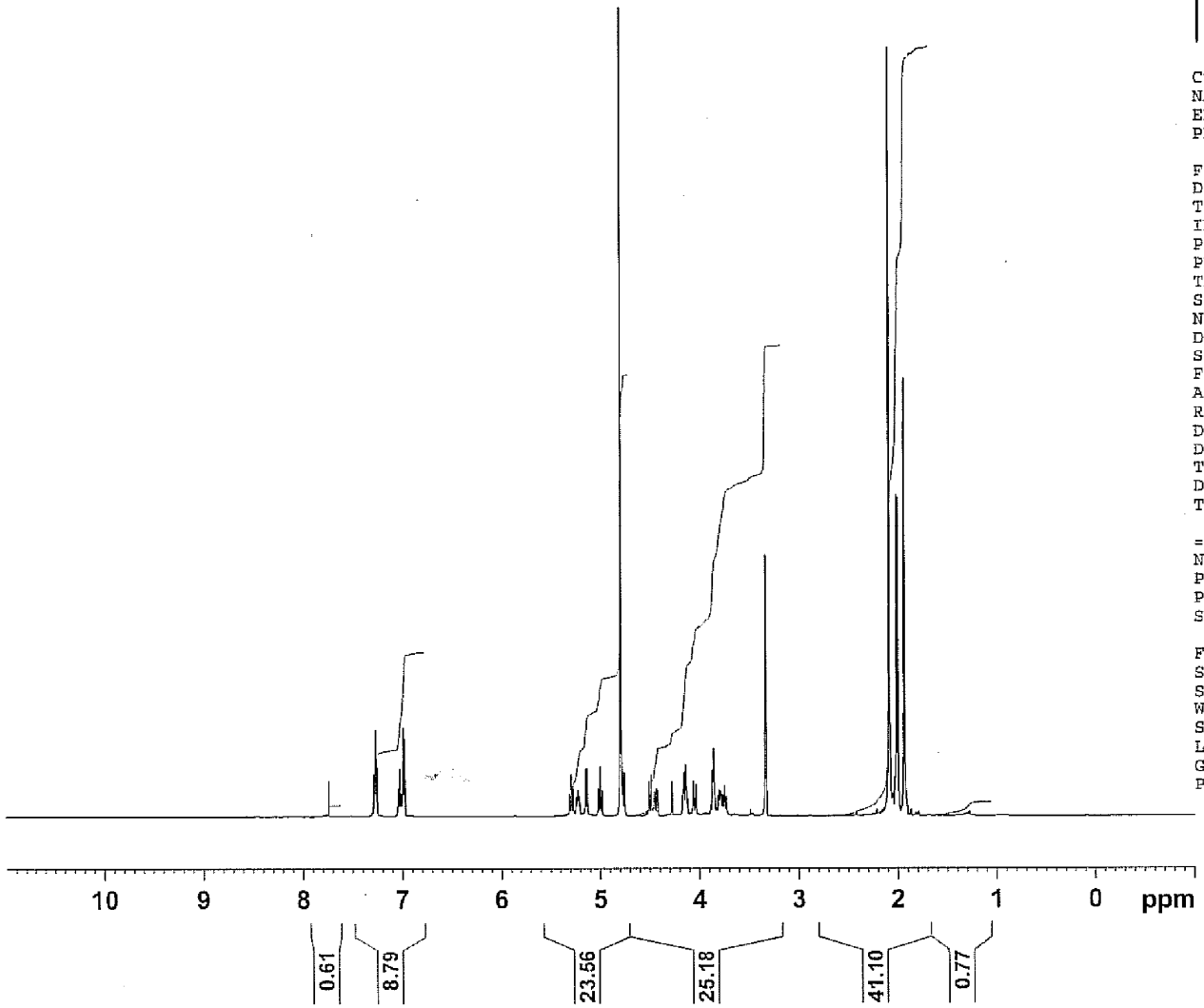


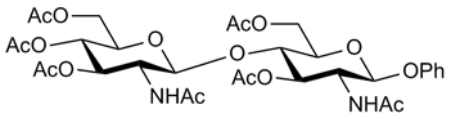
NMR@CHEM.OX

```
Current Data Parameters
NAME          dg28852608
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050826
Time               12.17
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT             MeOD
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
SFO1        500.3030896 MHz

F2 - Processing parameters
SI                 32768
SF          500.3000000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



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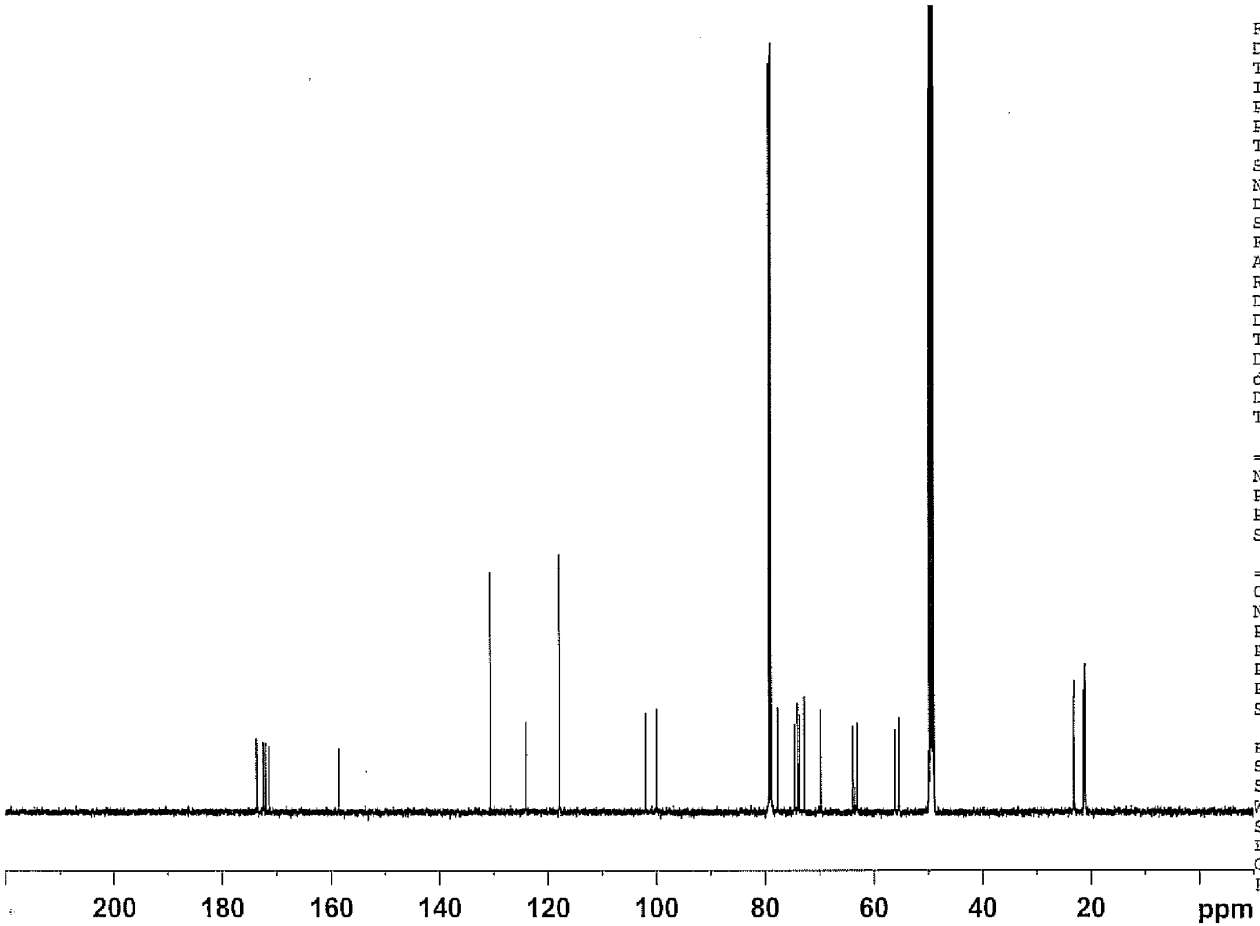
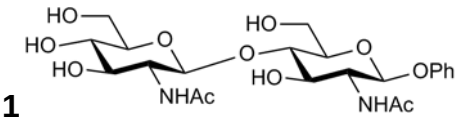
NMR@CHEM.OX

```
Current Data Parameters
NAME          dg28852608
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050826
Time               12.36
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT             MeOD
NS                   256
DS                     2
SWH          31250.000 Hz
FIDRES        0.476837 Hz
AQ            1.0486259 sec
RG                  1620
DW               16.000 usec
DE               20.00 usec
TE                298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.00 usec
PL1               -4.40 dB
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.40 dB
PL13              17.00 dB
SFO2        500.3020012 MHz

F2 - Processing parameters
SI                 32768
SF          125.8003564 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```





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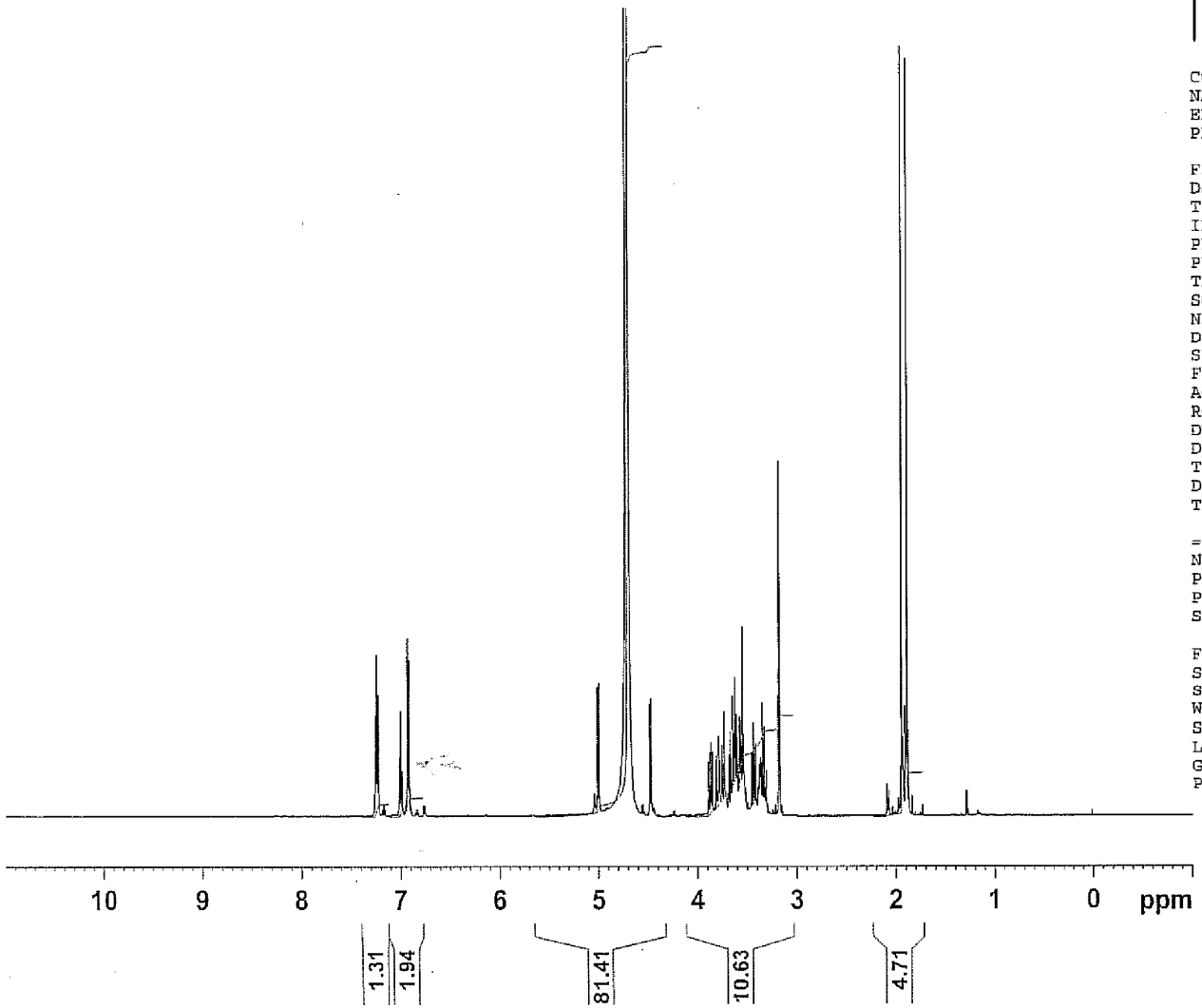


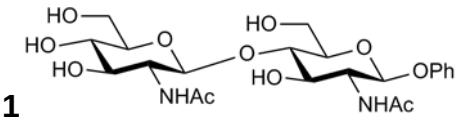
NMR@CHEM.OX

```
Current Data Parameters
NAME          dg33722511
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051125
Time              10.34
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT              D2O
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                     4
DW               48.400 usec
DE                6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
SFO1        500.3030896 MHz

F2 - Processing parameters
SI                 32768
SF          500.3000000 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```



1

NMR@CHEM.OX

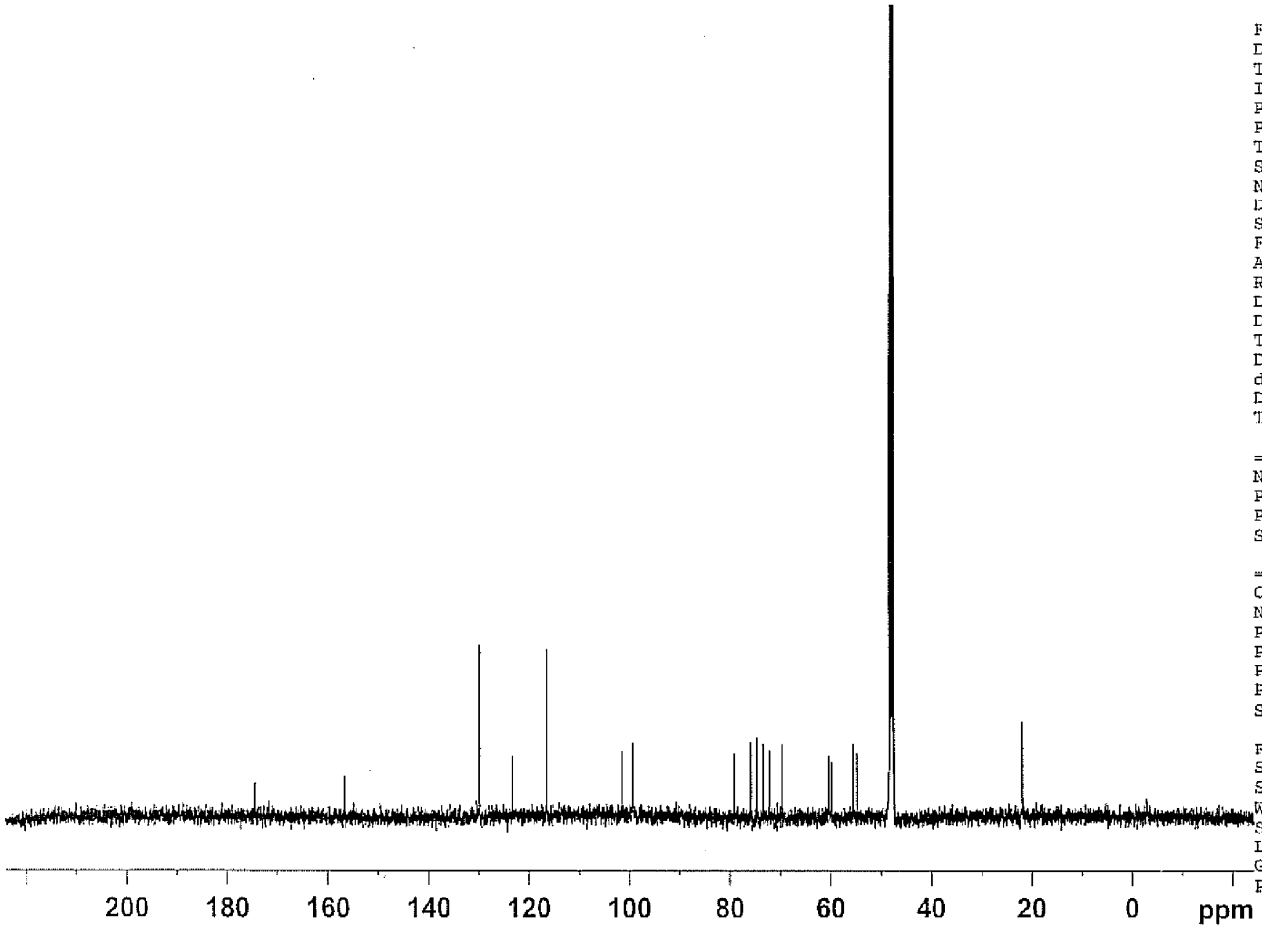
```
Current Data Parameters
NAME          dg33722511
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051125
Time               10.42
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT             D2O
NS                  256
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ             1.0486259 sec
RG                  812
DW               16.000 usec
DE               20.00 usec
TE               298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 8.00 usec
PL1               -4.40 dB
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.40 dB
PL13              17.00 dB
SFO2        500.3020012 MHz

F2 - Processing parameters
SI                  32768
SF          125.8005350 MHz
WDW                    EM
SSB                    0
LB                 2.00 Hz
GB                     0
PC                 1.40
```



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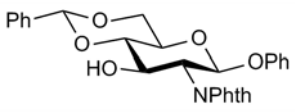

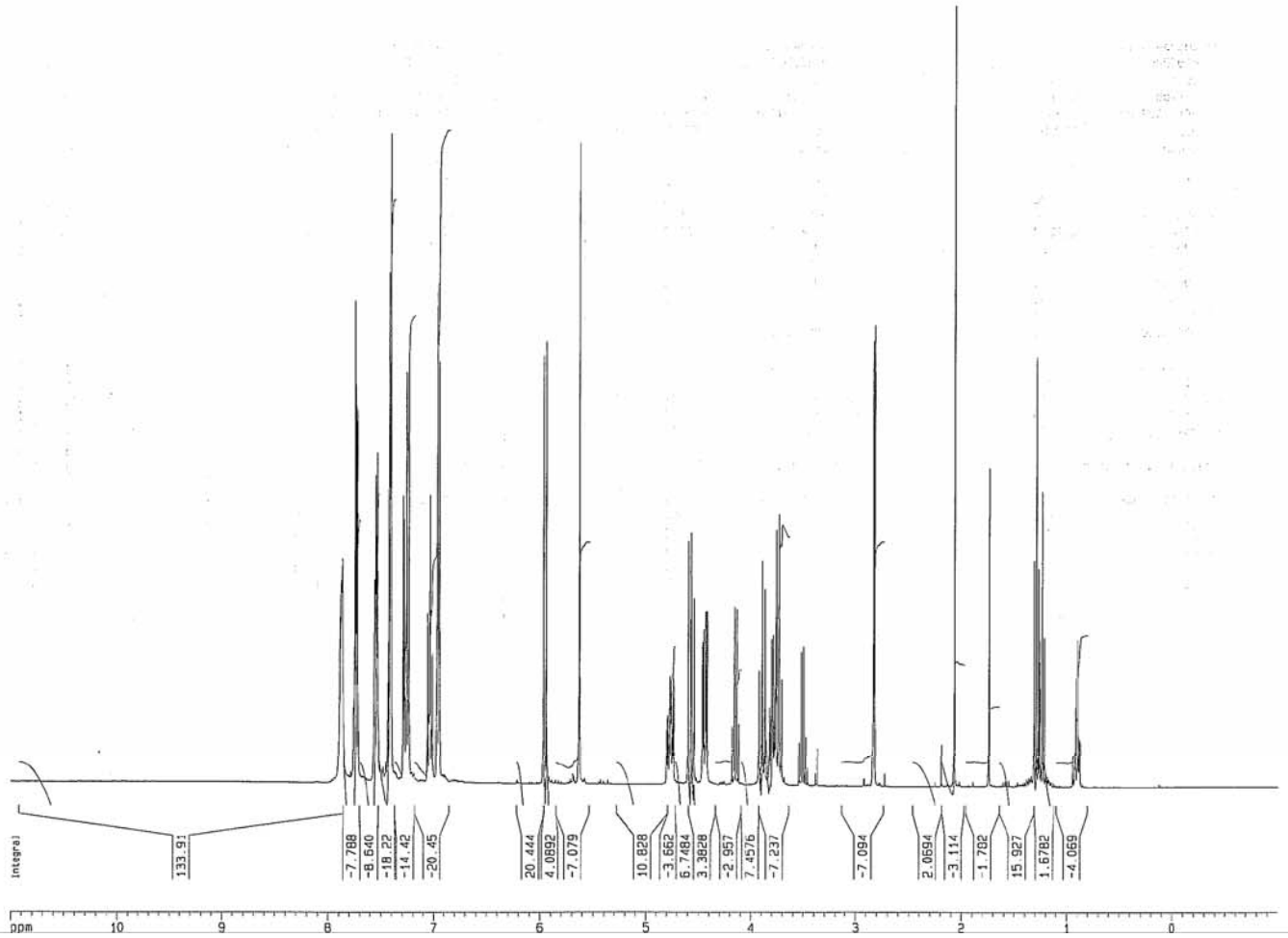


```
Current Data Parameters
NAME          Jun14-2005
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050615
Time                4.29
INSTRUM          dpx360
PROBHD     5mm DUAL 13C
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            7440.476 Hz
FIDRES        0.113533 Hz
AQ            4.4040694 sec
RG                161.3
DW               67.200 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec

============ CHANNEL f1 =============
NUC1                  1H
P1                 9.80 usec
PL1                -3.50 dB
SFO1         360.1322240 MHz

F2 - Processing parameters
SI                 32768
SF           360.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 30.00 cm
F1P               11.000 ppm
F1                3361.43 Hz
F2P               -1.000 ppm
F2                -360.13 Hz
PPMCM          0.40000 ppm/cm
HZCM          144.05200 Hz/cm
```

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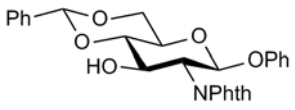
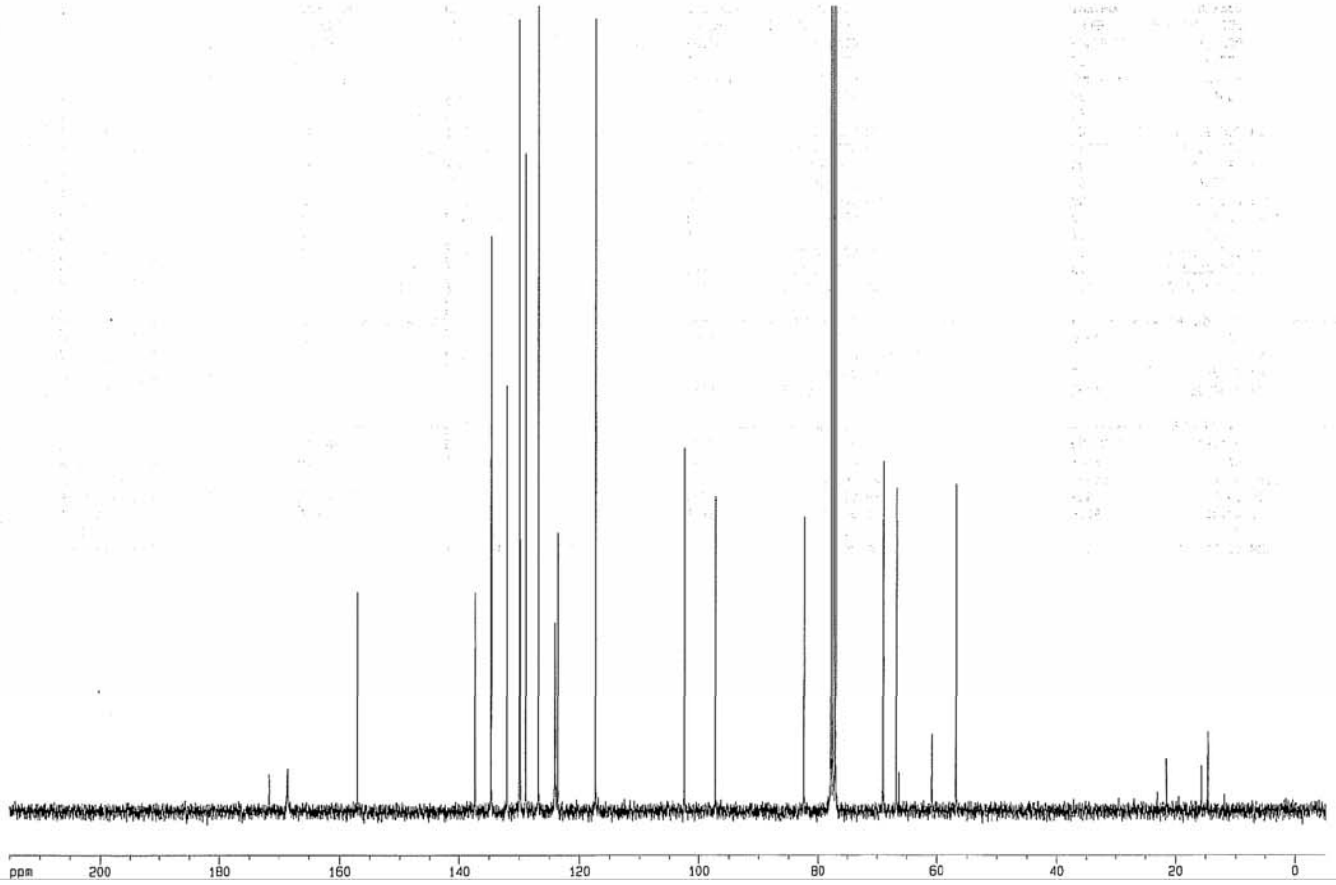
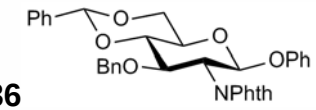





```
Current Data Parameters
NAME          Jun14-2005
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_          20050615
Time               5.52
INSTRUM           dpx360
PROBHD     5mm DUAL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           22522.523 Hz
FIDRES        0.343666 Hz
AQ            1.4549491 sec
RG              11585.2
DW               22.200 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 =============
NUC1               13C
P1                6.40 usec
PL1              -6.00 dB
SFO1         90.5646855 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              18.00 dB
PL13              21.00 dB
SFO2         360.1314405 MHz

F2 - Processing parameters
SI                 32768
SF           90.5547250 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                30.00 cm
F1P              215.000 ppm
F1             19469.27 Hz
F2P               -5.000 ppm
F2              -452.77 Hz
PPMCM            7.33333 ppm/cm
HZCM           664.06799 Hz/cm
```



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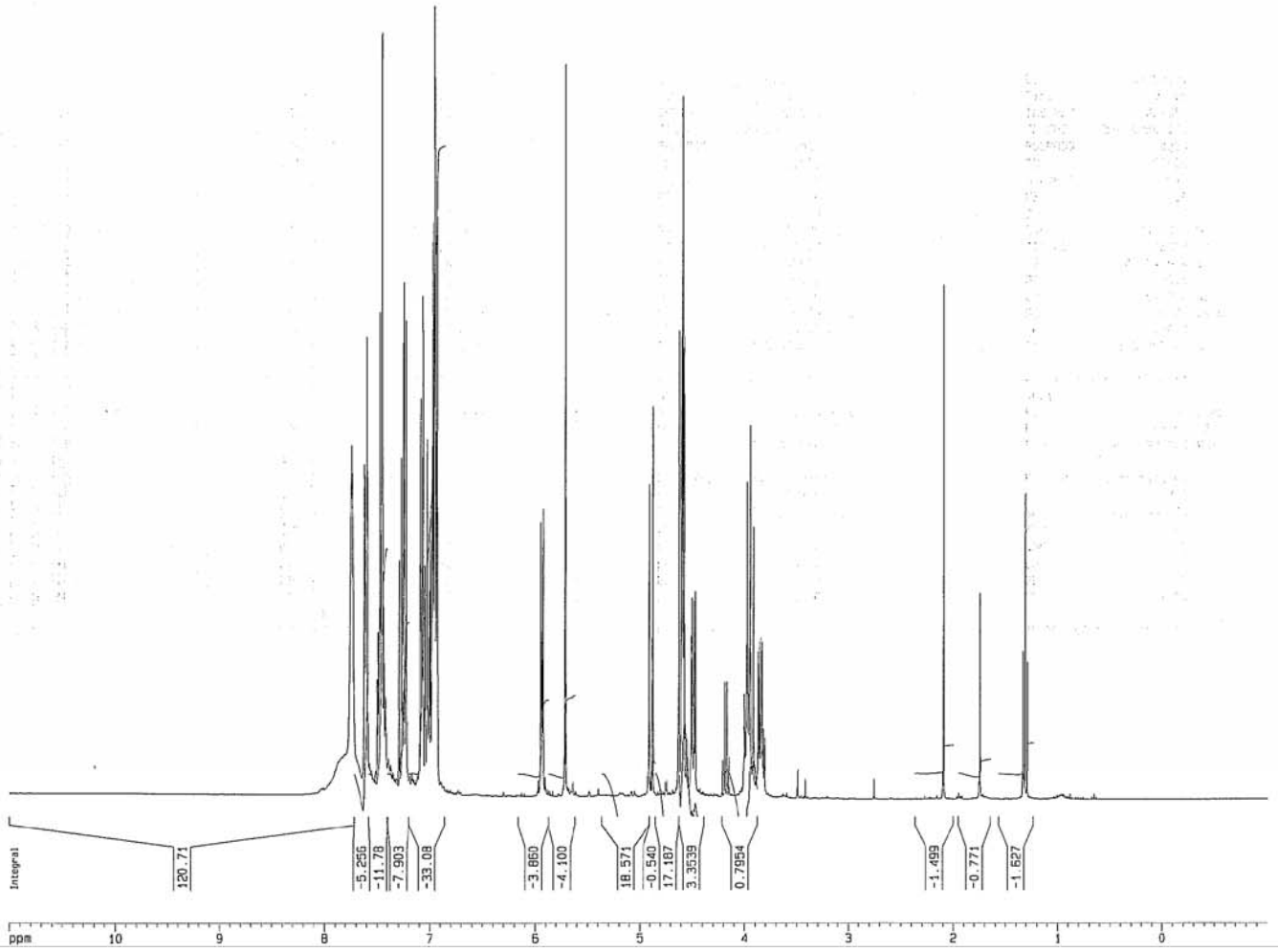
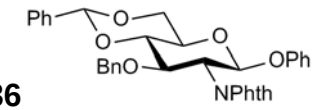
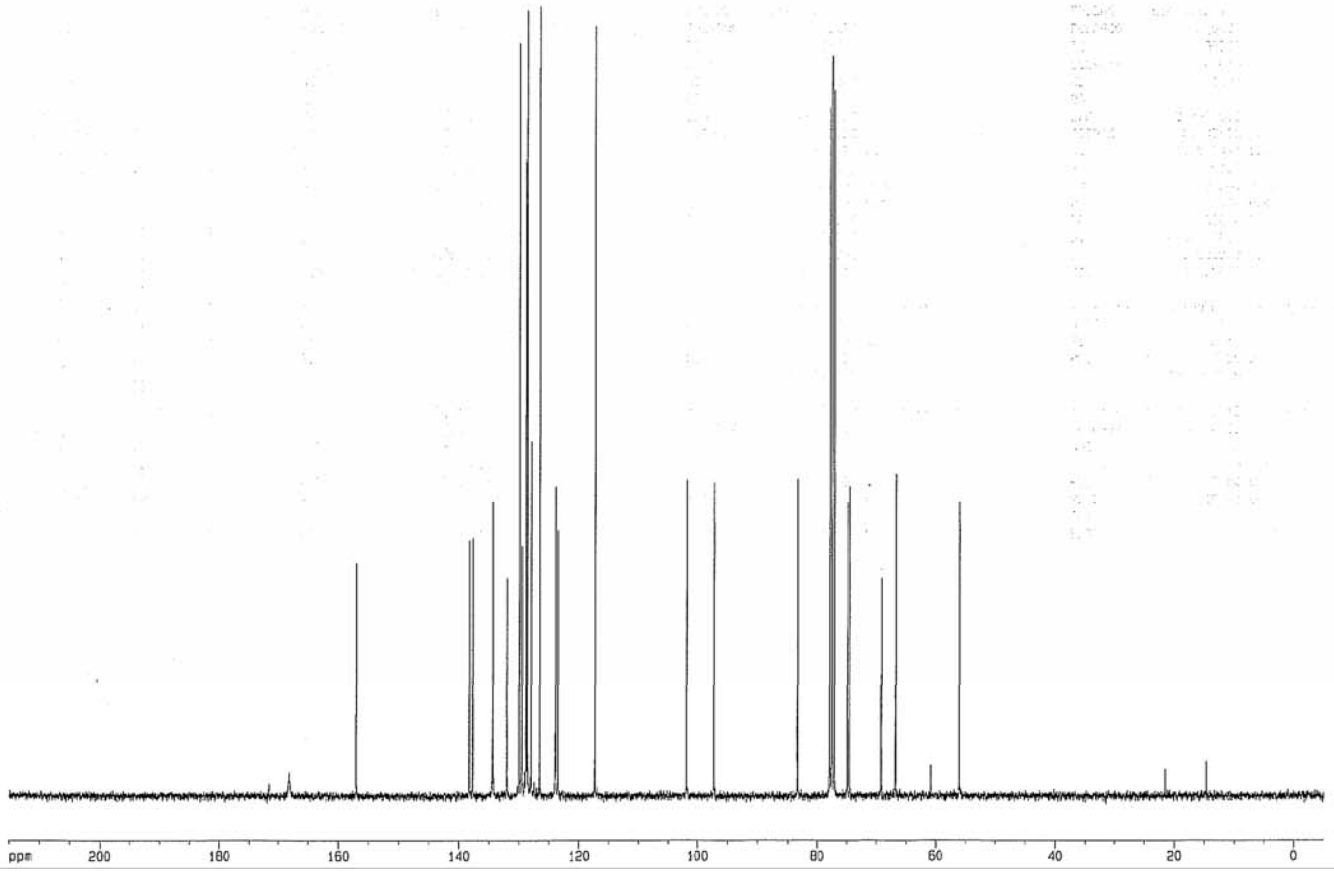


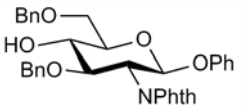

```
Current Data Parameters
NAME          Jun21-2005
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050621
Time               20.05
INSTRUM           dpx360
PROBHD     5mm DUAL 13C
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              7440.476 Hz
FIDRES           0.113533 Hz
AQ               4.4040694 sec
RG                   90.5
DW                 67.200 usec
DE                  6.00 usec
TE                 300.0 K
D1              1.00000000 sec

============ CHANNEL f1 =============
NUC1                   1H
P1                  9.80 usec
PL1                -3.50 dB
SFO1         360.1322240 MHz

F2 - Processing parameters
SI                  32768
SF           360.1300000 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                  30.00 cm
F1P                11.000 ppm
F1                3961.43 Hz
F2P                -1.000 ppm
F2               -360.13 Hz
PPMCM             0.40000 ppm/cm
HZCM            144.05200 Hz/cm
```



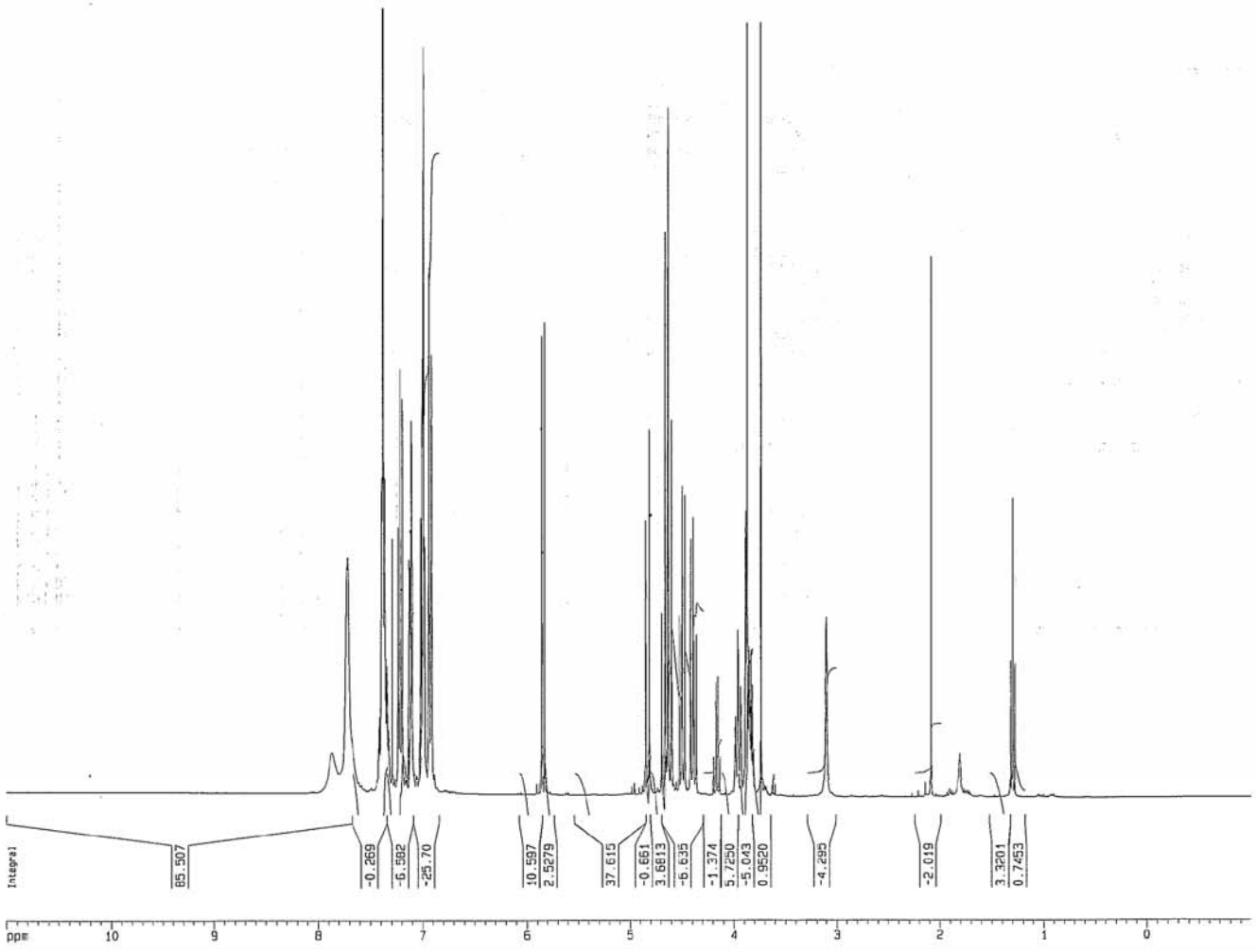
36



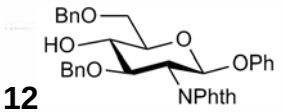

```
Current Data Parameters
NAME          Jun21-2005
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050621
Time              21.35
INSTRUM           dpx360
PROBHD     5mm DUAL 13C
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           22522.523 Hz
FIDRES         0.343666 Hz
AQ             1.454491 sec
RG                 8192
DW               22.200 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1                 6.40 usec
PL1               -6.00 dB
SFO1          90.5646855 MHz

============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              18.00 dB
PL13              21.00 dB
SFO2          360.1314405 MHz

F2 - Processing parameters
SI                 32768
SF            90.5547250 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 30.00 cm
F1P               215.000 ppm
F1              19469.27 Hz
F2P               -5.000 ppm
F2               -452.77 Hz
PPMCM             7.33333 ppm/cm
HZCM            664.06799 Hz/cm
```



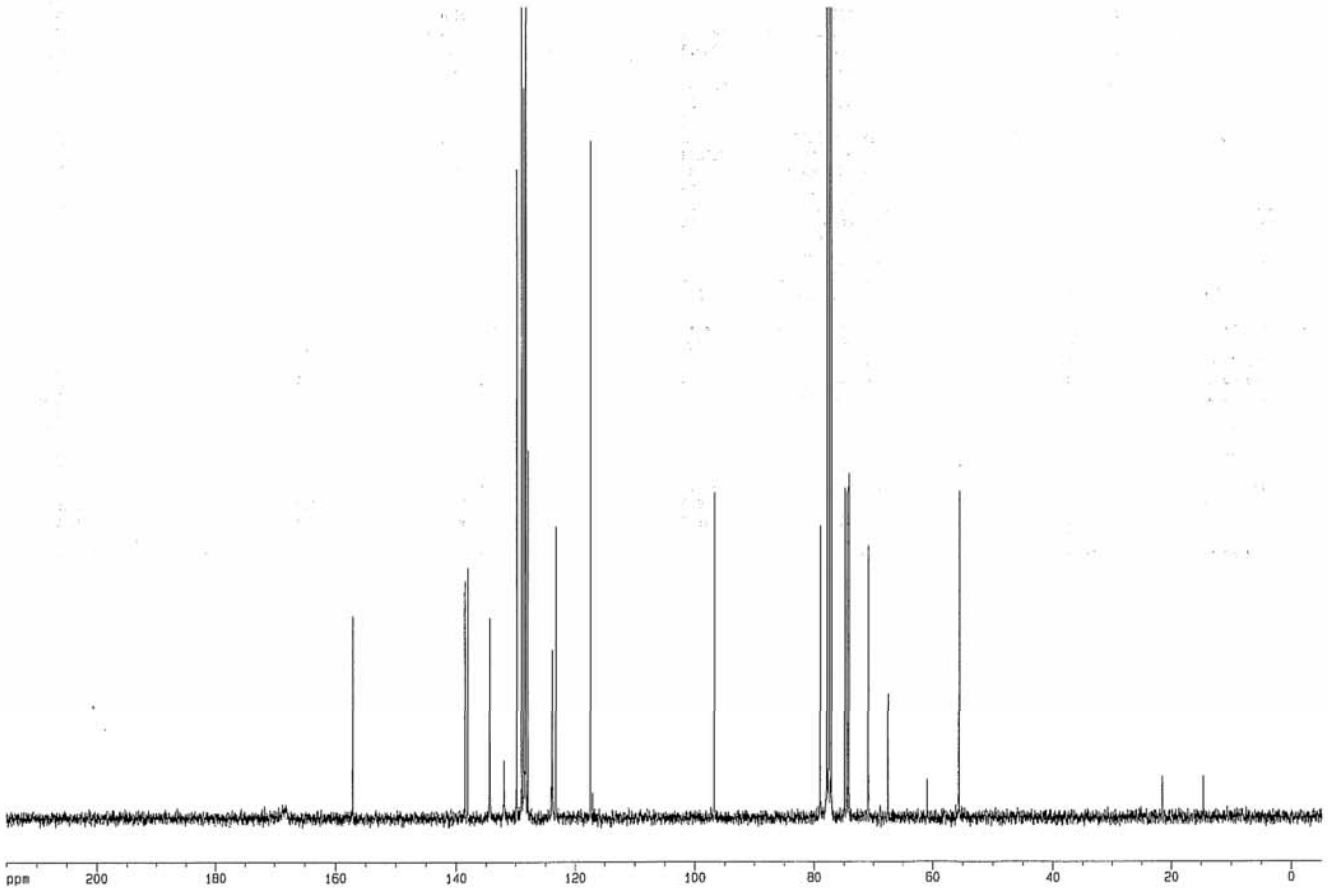
12




```
Current Data Parameters
NAME          Jun30-2005
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050701
Time                2.50
INSTRUM           dpx360
PROBHD     5mm DUAL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             7440.476 Hz
FIDRES          0.113533 Hz
AQ              4.4040594 sec
RG                   114
DW                67.200 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 =============
NUC1                  1H
P1                 9.80 usec
PL1               -3.50 dB
SFO1         360.1322240 MHz

F2 - Processing parameters
SI                 32768
SF          360.1300000 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00

1D NMR plot parameters
CX                30.00 cm
F1P               11.000 ppm
F1              3961.43 Hz
F2P               -1.000 ppm
F2              -360.13 Hz
PPMCM           0.40000 ppm/cm
HZCM          144.05200 Hz/cm
```



12




```
Current Data Parameters
NAME          Jun30-2005
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_          20050701
Time               4.12
INSTRUM          dpx360
PROBHD     5mm DUAL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           22522.523 Hz
FIDRES        0.343666 Hz
AQ            1.4549491 sec
RG              11585.2
DW               22.200 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                 6.40 usec
PL1               -6.00 dB
SFO1          90.5646855 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2             100.00 usec
PL2                -3.00 dB
PL12               18.00 dB
PL13               21.00 dB
SFO2          360.1314405 MHz

F2 - Processing parameters
SI                 32768
SF            90.5547250 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 30.00 cm
F1P               215.000 ppm
F1              19469.27 Hz
F2P               -5.000 ppm
F2               -452.77 Hz
PPMCM             7.33333 ppm/cm
HZCM            664.06799 Hz/cm
```

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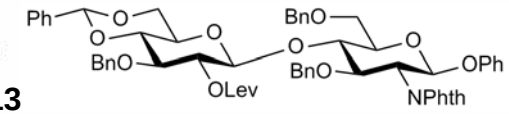
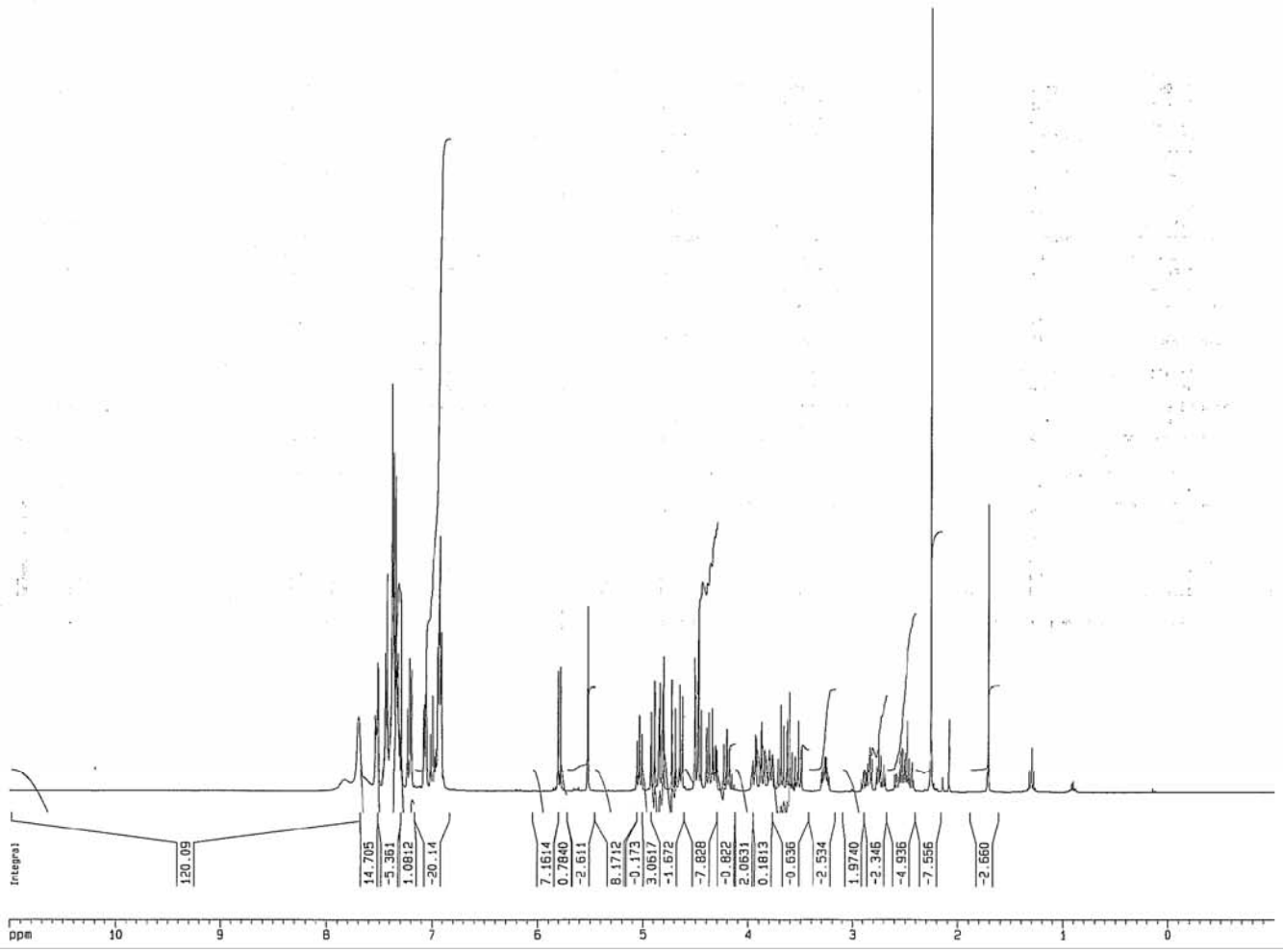




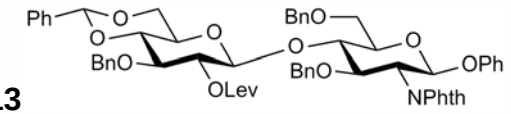

```
Current Data Parameters
NAME          Aug31-2005
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050831
Time               20.05
INSTRUM           dpx360
PROBHD     5mm DUAL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             7440.476 Hz
FIDRES          0.113533 Hz
AQ              4.4040694 sec
RG                 143.7
DW                67.200 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 ============
NUC1                  1H
P1                 9.80 usec
PL1               -3.50 dB
SFO1         360.1322240 MHz

F2 - Processing parameters
SI                 32768
SF           360.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                30.00 cm
F1P               11.000 ppm
F1              3961.43 Hz
F2P               -1.000 ppm
F2              -360.13 Hz
PPMCM           0.40000 ppm/cm
HZCM          144.05200 Hz/cm
```



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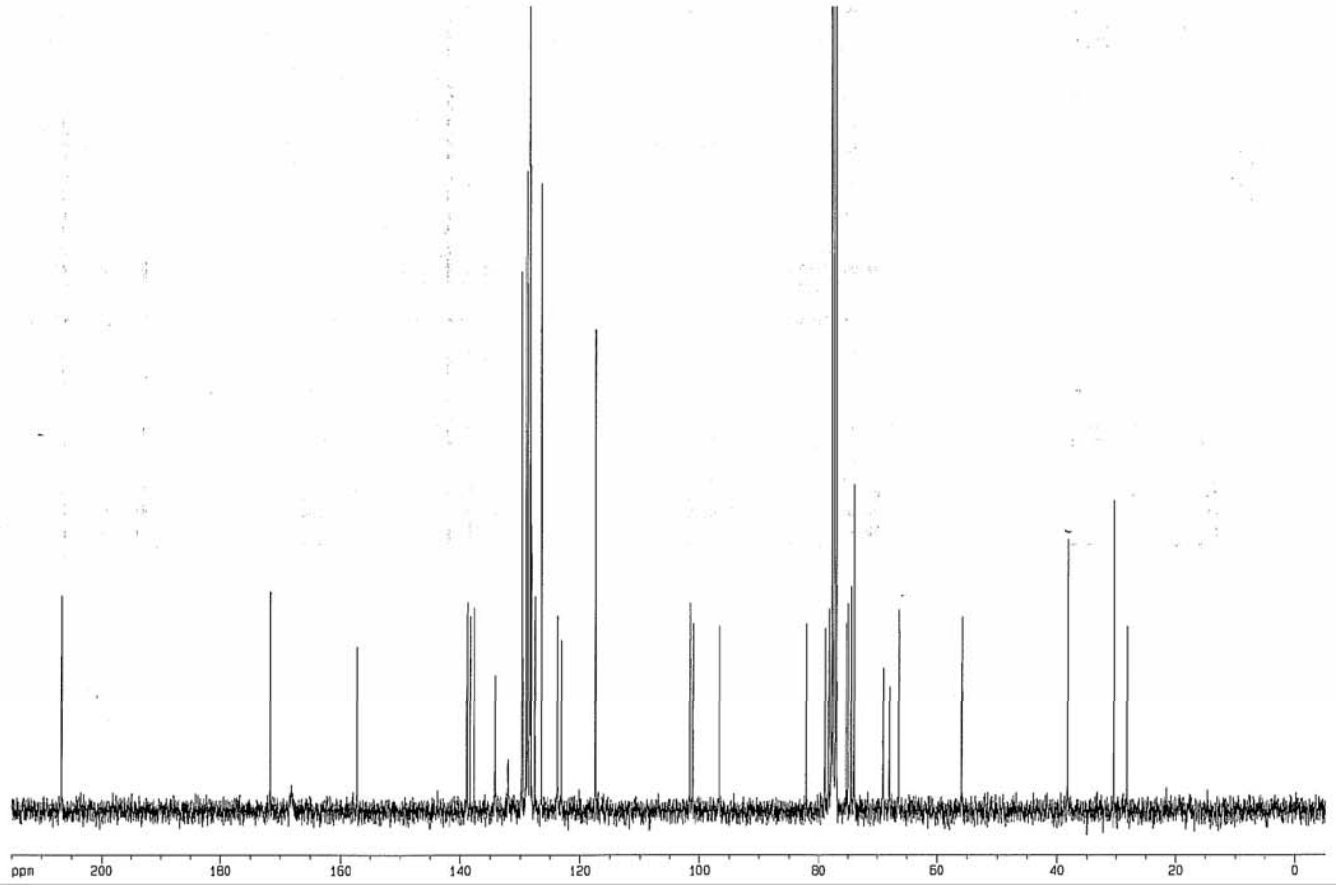


```
Current Data Parameters
NAME          Aug31-2005
EXPNO                 13
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050831
Time              21.41
INSTRUM           dpx360
PROBHD     5mm DUAL 13C
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           22522.523 Hz
FIDRES        0.343666 Hz
AQ            1.4549491 sec
RG                16384
DW               22.200 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 ============
NUC1                 13C
P1                6.40 usec
PL1               -6.00 dB
SFO1         90.5646855 MHz

============ CHANNEL f2 ============
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              18.00 dB
PL13              21.00 dB
SFO2        360.1314405 MHz

F2 - Processing parameters
SI                32768
SF           90.5547250 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                30.00 cm
F1P              215.000 ppm
F1               19469.27 Hz
F2P               -5.000 ppm
F2                -452.77 Hz
PPMCM             7.33333 ppm/cm
HZCM           664.06799 Hz/cm
```

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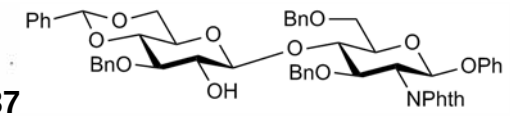

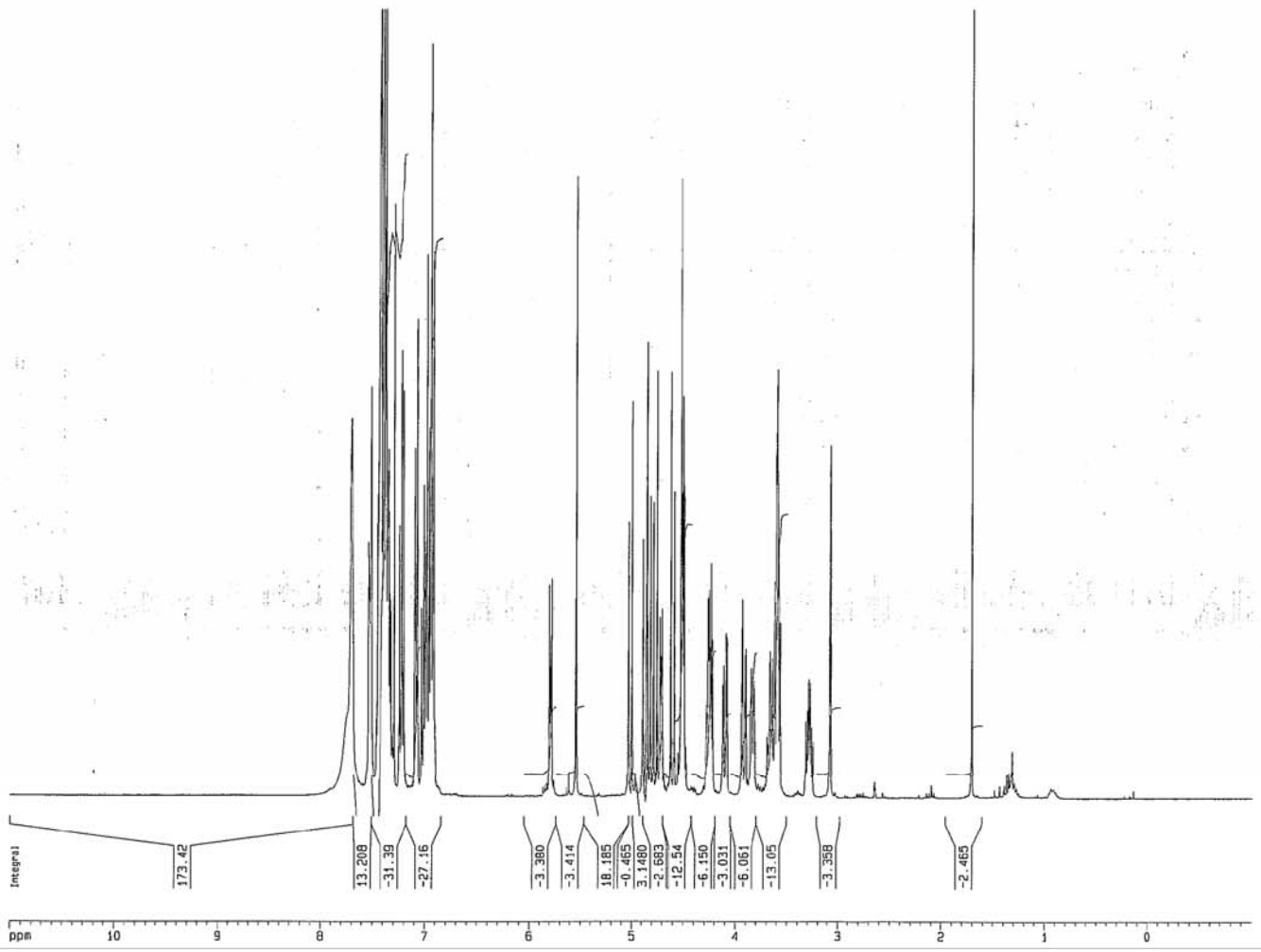


```
Current Data Parameters
NAME          Sep07-2005
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050907
Time               21.18
INSTRUM          dpx360
PROBHD     5mm DUAL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            7440.476 Hz
FIDRES         0.113533 Hz
AQ             4.4040694 sec
RG                   114
DW                67.200 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec

============ CHANNEL f1 =============
NUC1                  1H
P1                 9.80 usec
PL1               -3.50 dB
SFO1        360.1322240 MHz

F2 - Processing parameters
SI                 32768
SF          360.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                30.00 cm
F1P               11.000 ppm
F1              3961.43 Hz
F2P               -1.000 ppm
F2              -360.13 Hz
PPMCM          0.40000 ppm/cm
HZCM         144.05200 Hz/cm
```

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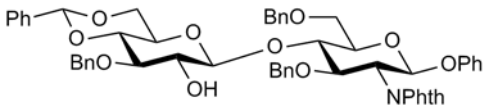

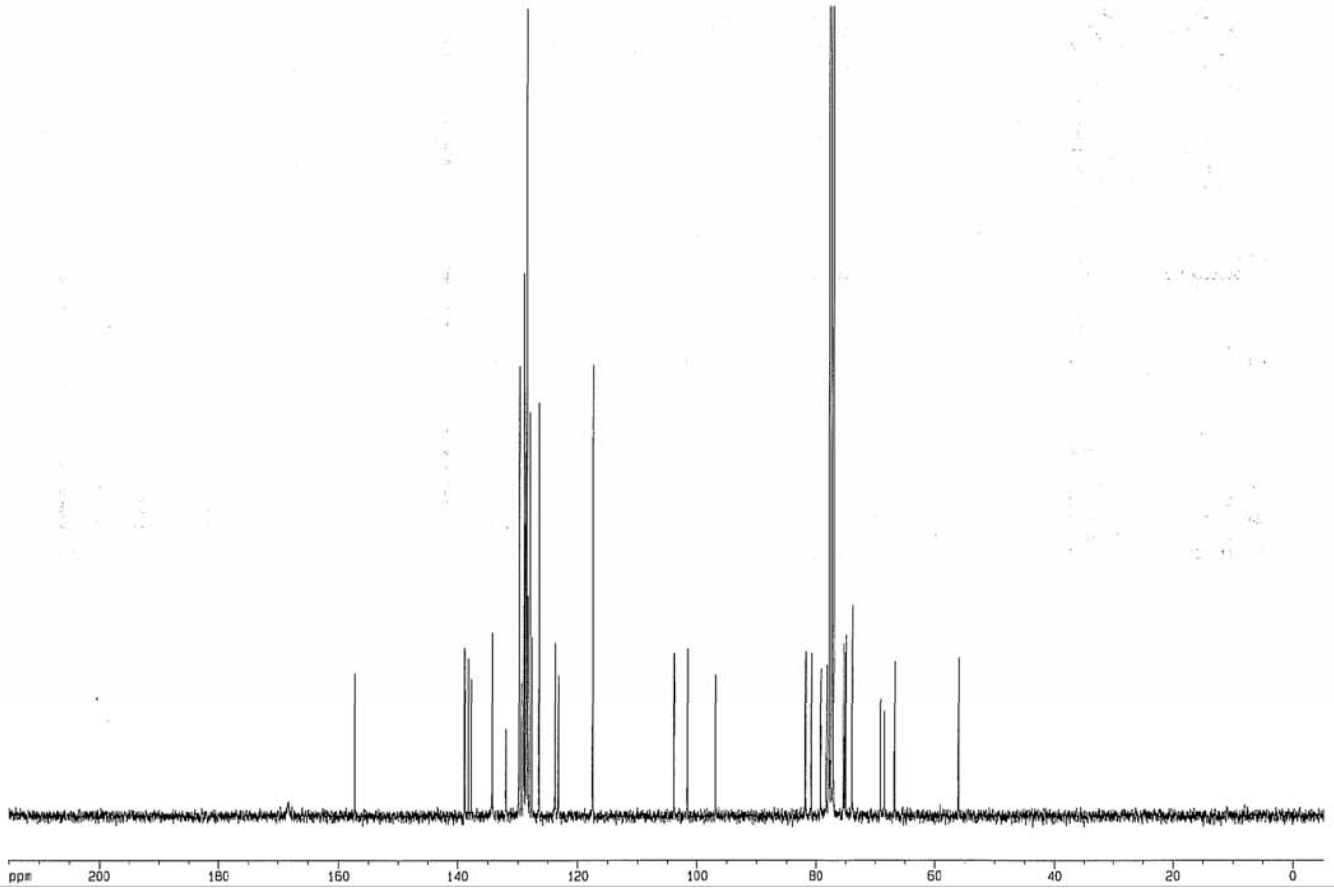


```
Current Data Parameters
NAME          Sep07-2005
EXPNO                 24
PROCNO                 1

F2 - Acquisition Parameters
Date_          20050907
Time              23.04
INSTRUM           dpx360
PROBHD     5mm DUAL 13C
PULPROG           zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           22522.523 Hz
FIDRES         0.343666 Hz
AQ             1.4549491 sec
RG               11585.2
DW                22.200 usec
DE                 6.00 usec
TE                300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
d12            0.00002000 sec

============ CHANNEL f1 ============
NUC1                13C
P1                 6.40 usec
PL1               -6.00 dB
SFO1          90.5646855 MHz

============ CHANNEL f2 ============
CPDPRG2         waltz16
NUC2                1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              18.00 dB
PL13              21.00 dB
SFO2          360.1314405 MHz

F2 - Processing parameters
SI                 32768
SF            90.5547250 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 30.00 cm
F1P               215.000 ppm
F1              19469.27 Hz
F2P                -5.000 ppm
F2               -452.77 Hz
PPMCM              7.33333 ppm/cm
HZCM             664.06799 Hz/cm
```

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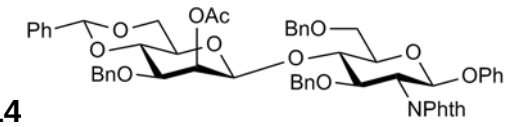

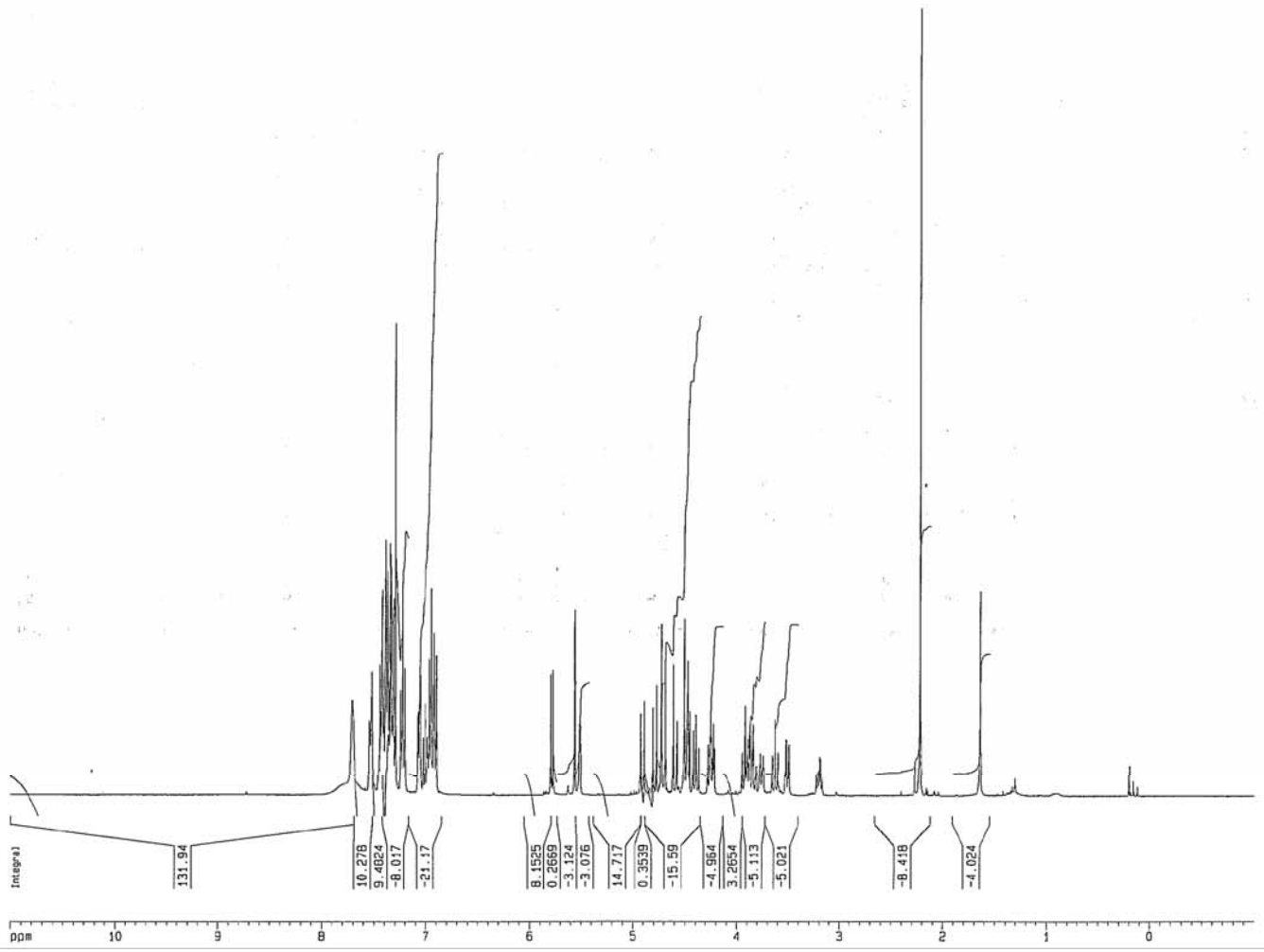


```
Current Data Parameters
NAME          Sep07-2005
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20050907
Time               23.25
INSTRUN          dpx360
PROBHD     5mm DUAL 13C
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            7440.476 Hz
FIDRES        0.113533 Hz
AQ            4.4040694 sec
RG                203.2
DW               67.200 usec
DE                6.00 usec
TE               300.0 K
D1            1.00000000 sec

============ CHANNEL f1 ============
NUC1                  1H
P1                 9.80 usec
PL1               -3.50 dB
SFO1       360.1322240 MHz

F2 - Processing parameters
SI                 32768
SF         360.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 30.00 cm
F1P               11.000 ppm
F1               3961.43 Hz
F2P               -1.000 ppm
F2               -360.13 Hz
PPMCM            0.40000 ppm/cm
HZCM           144.05200 Hz/cm
```

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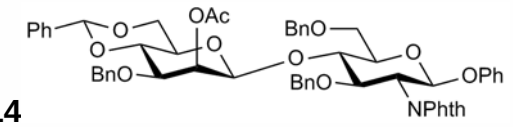
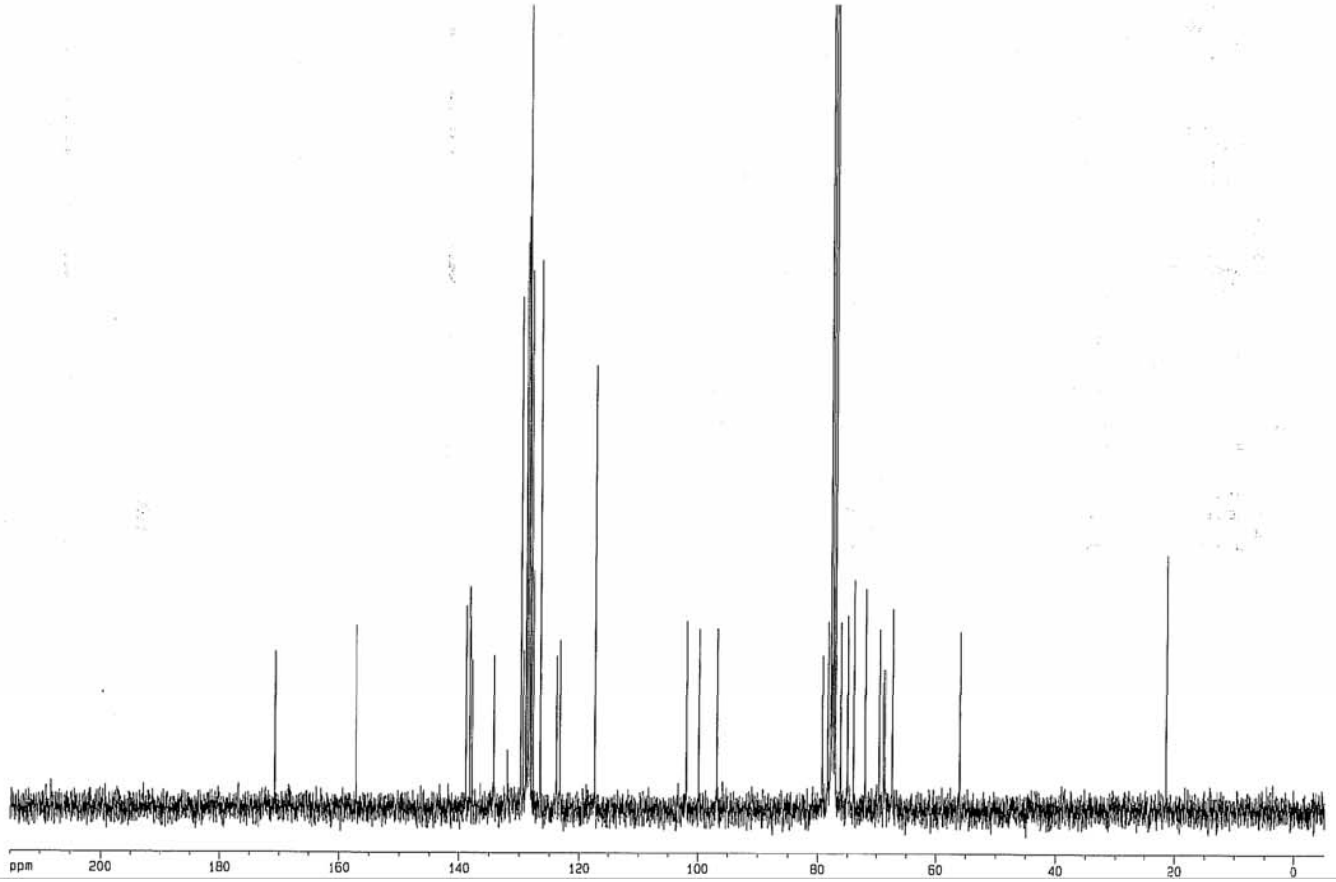
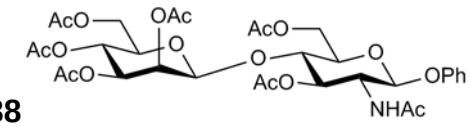





```
Current Data Parameters
NAME          Sep07-2005
EXPNO                 34
PROCNO                 1

F2 - Acquisition Parameters
Date_          20050908
Time               1.24
INSTRUM          dpx360
PROBHD     5mm DUAL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           22522.523 Hz
FIDRES        0.343666 Hz
AQ            1.454491 sec
RG              11585.2
DW               22.200 usec
DE                6.00 usec
TE               300.0 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

============ CHANNEL f1 =============
NUC1                13C
P1                 6.40 usec
PL1               -6.00 dB
SFO1         90.5646855 MHz

============ CHANNEL f2 =============
CPDPRG2         waltz16
NUC2                1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              18.00 dB
PL13              21.00 dB
SFO2         360.1314405 MHz

F2 - Processing parameters
SI                 32768
SF           90.5547250 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                30.00 cm
F1P              215.000 ppm
F1             19469.27 Hz
F2P              -5.000 ppm
F2              -452.77 Hz
PPMCM            7.33333 ppm/cm
HZCM          664.06799 Hz/cm
```



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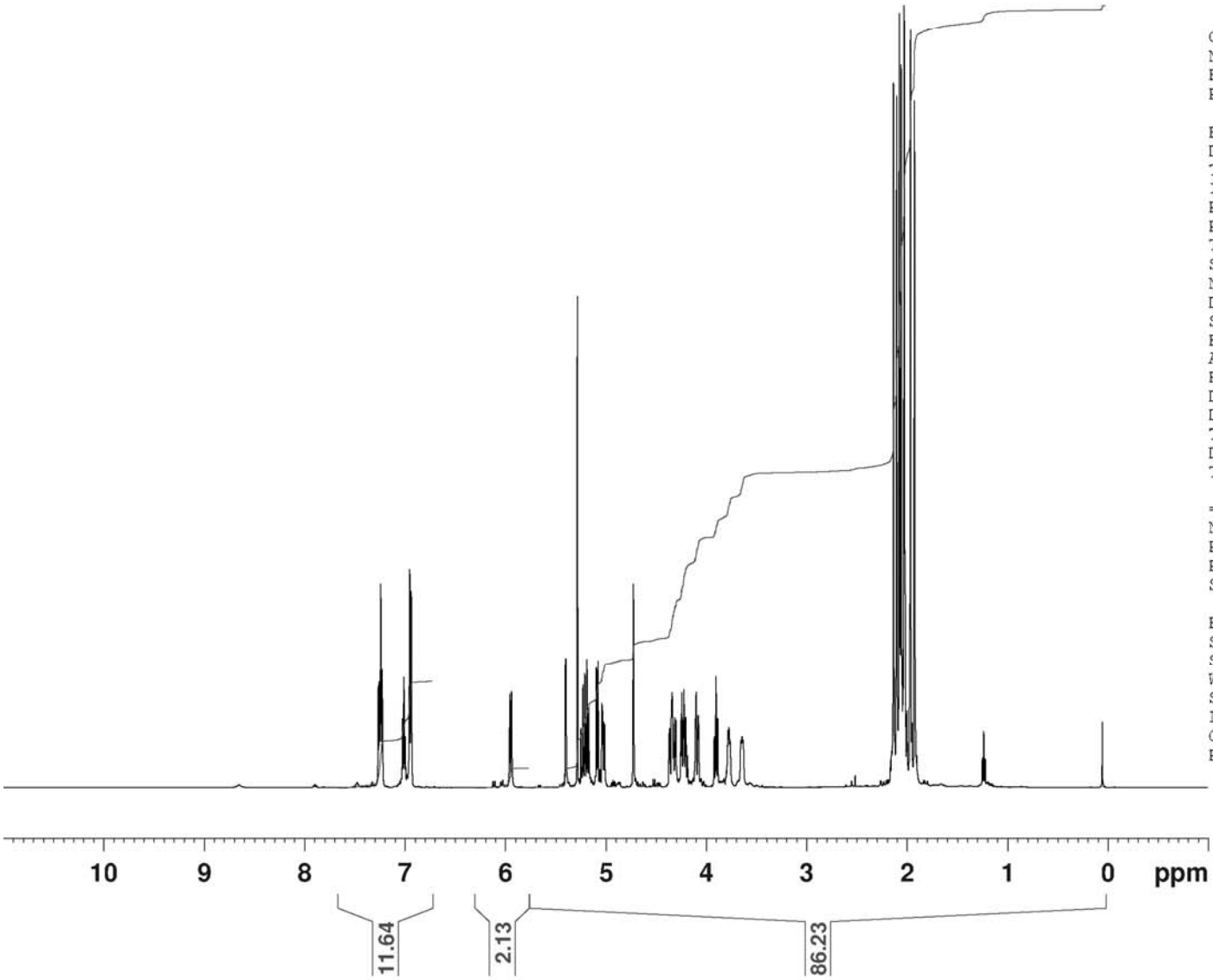
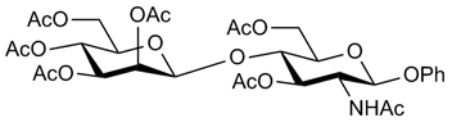
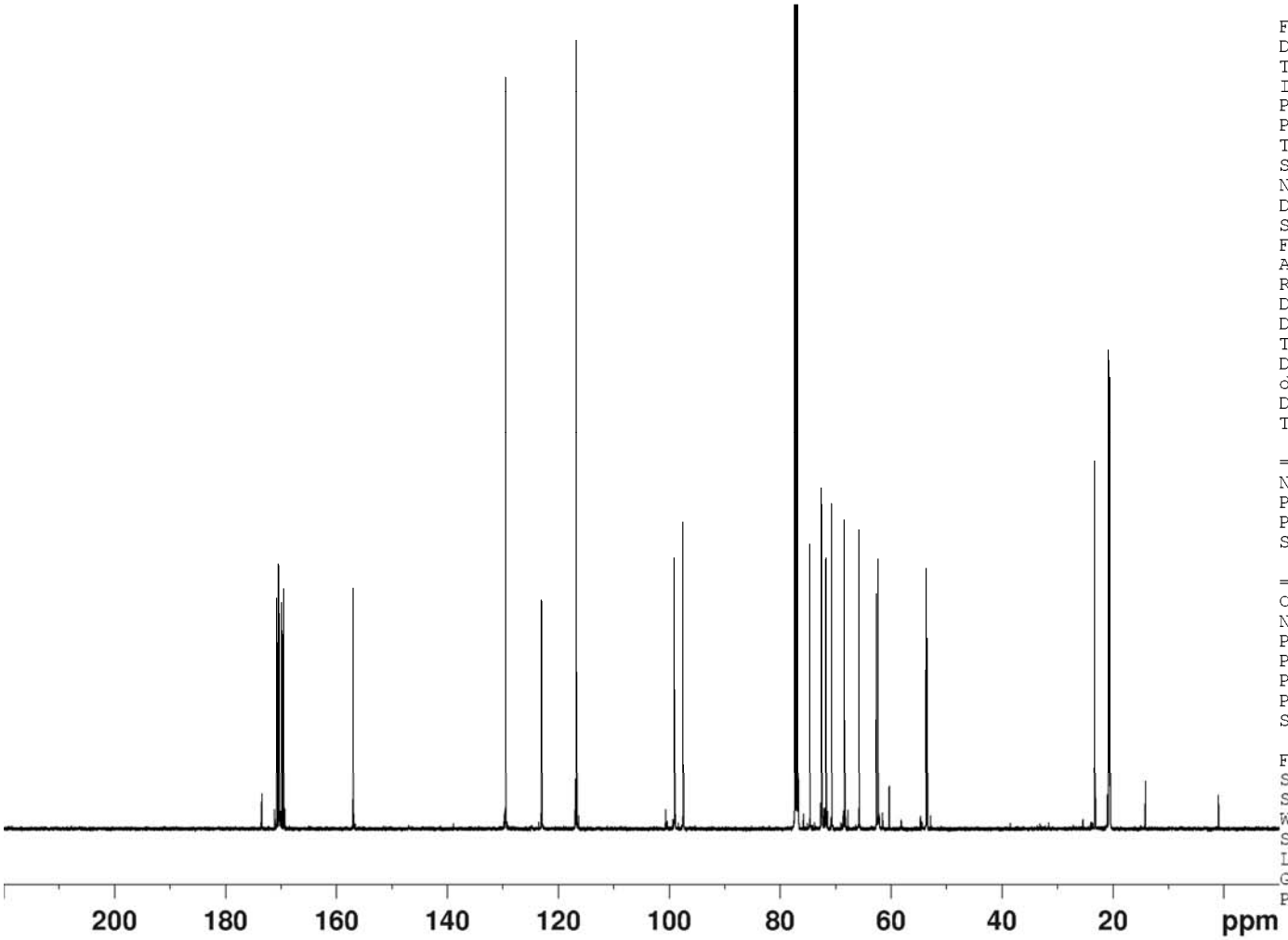



```
Current Data Parameters
NAME          dg30500410
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051004
Time               12.34
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.60 usec
PL1                -6.00 dB
SFO1        500.3030896 MHz

F2 - Processing parameters
SI                 32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

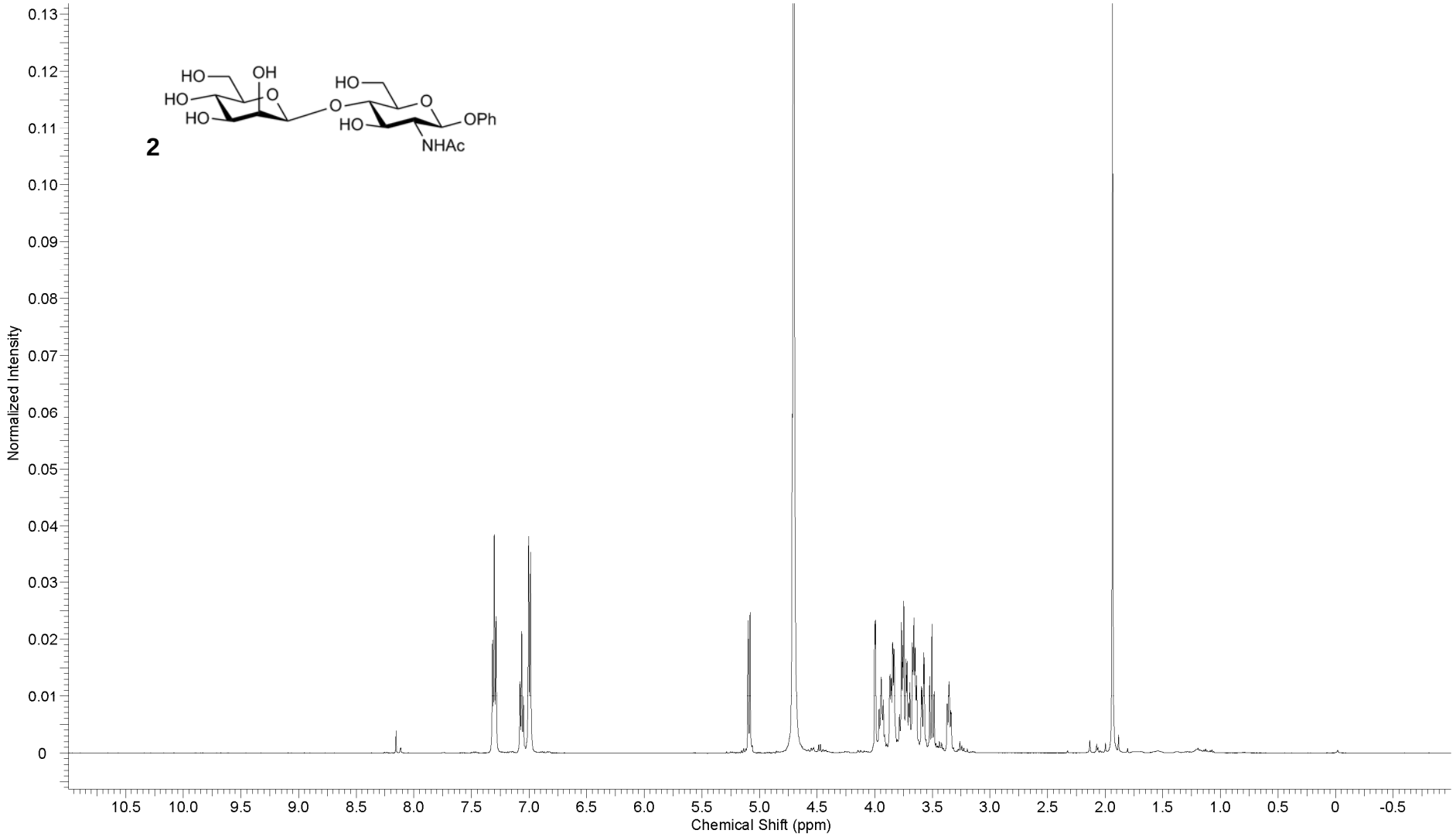


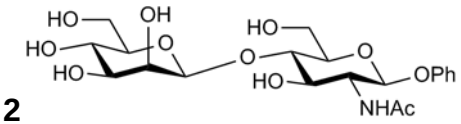
38



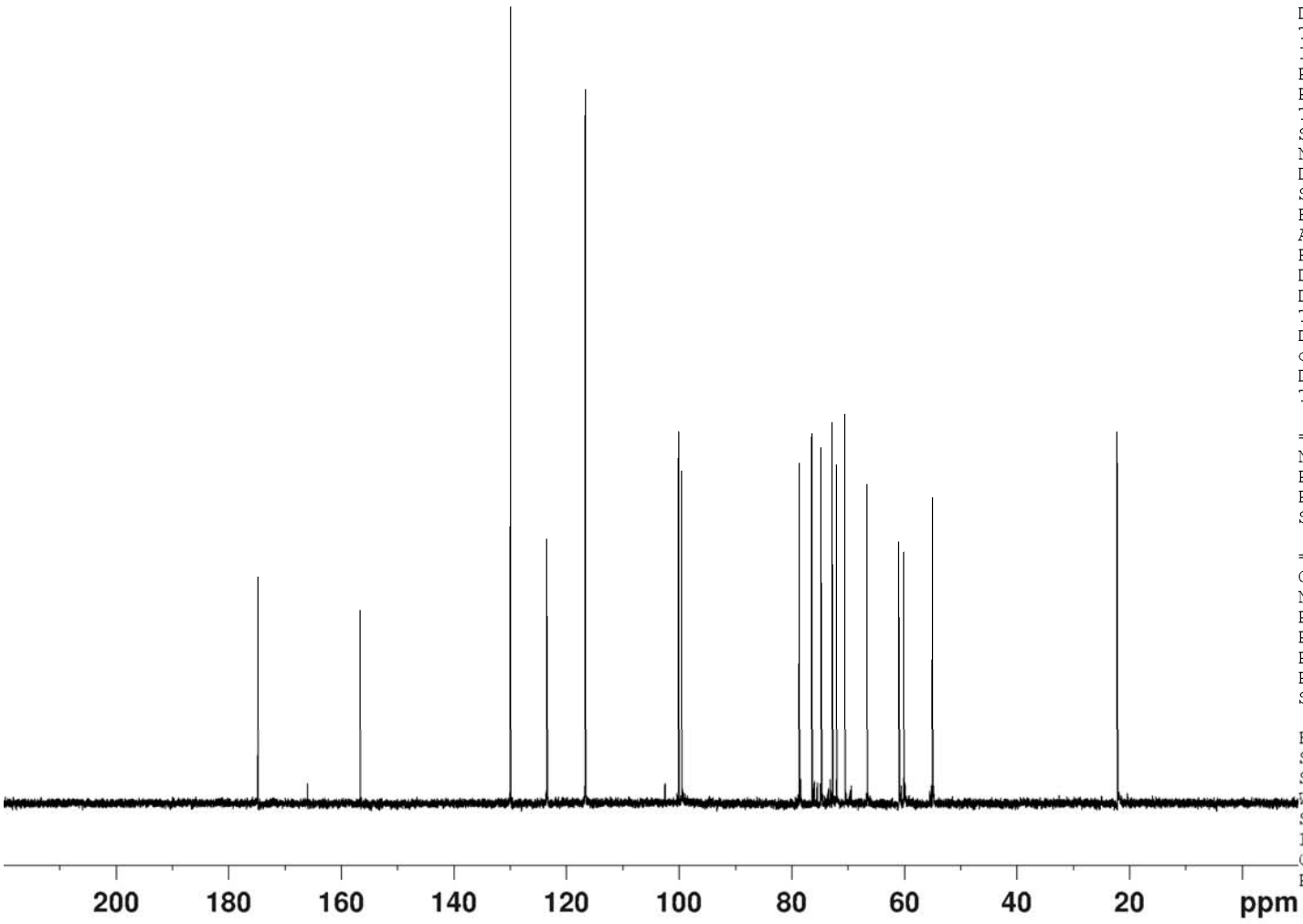

```
Current Data Parameters
NAME          dg30500410
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051004
Time               12.53
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0486259 sec
RG                 1620
DW               16.000 usec
DE               20.00 usec
TE               298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.00 usec
PL1               -4.40 dB
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.40 dB
PL13              17.00 dB
SFO2        500.3020012 MHz

F2 - Processing parameters
SI                 32768
SF          125.8005438 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

Acquisition Time (sec)	3.1719	***Comment***	Instrument AVC500 D P GAMBLIN 3409 30/11/05			***Date***	01 Dec 2005 12:37:20
Date Stamp	01 Dec 2005 12:37:20			***File Name***	\\CHEM-DS4\VICTORIA\LAB10\CONOR\AA_DAVE_NMR\2_DG34093011\15\PDATA\1\1R		
Frequency (MHz)	500.30	***Nucleus***	1H	***Number of Transients***	9	***Origin***	avc500
Original Points Count	32768	***Owner***	dp-nmrgroup	***Points Count***	32768	***Pulse Sequence***	zg30
Receiver Gain	5.00	***SW(cyclical) (Hz)***	10330.58	***Solvent***	DEUTERIUM OXIDE		
Spectrum Offset (Hz)	3089.5557	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	10330.26	***Temperature (degree C)***	24.970



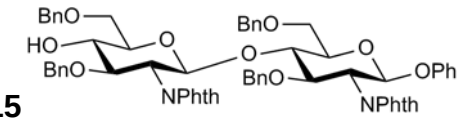


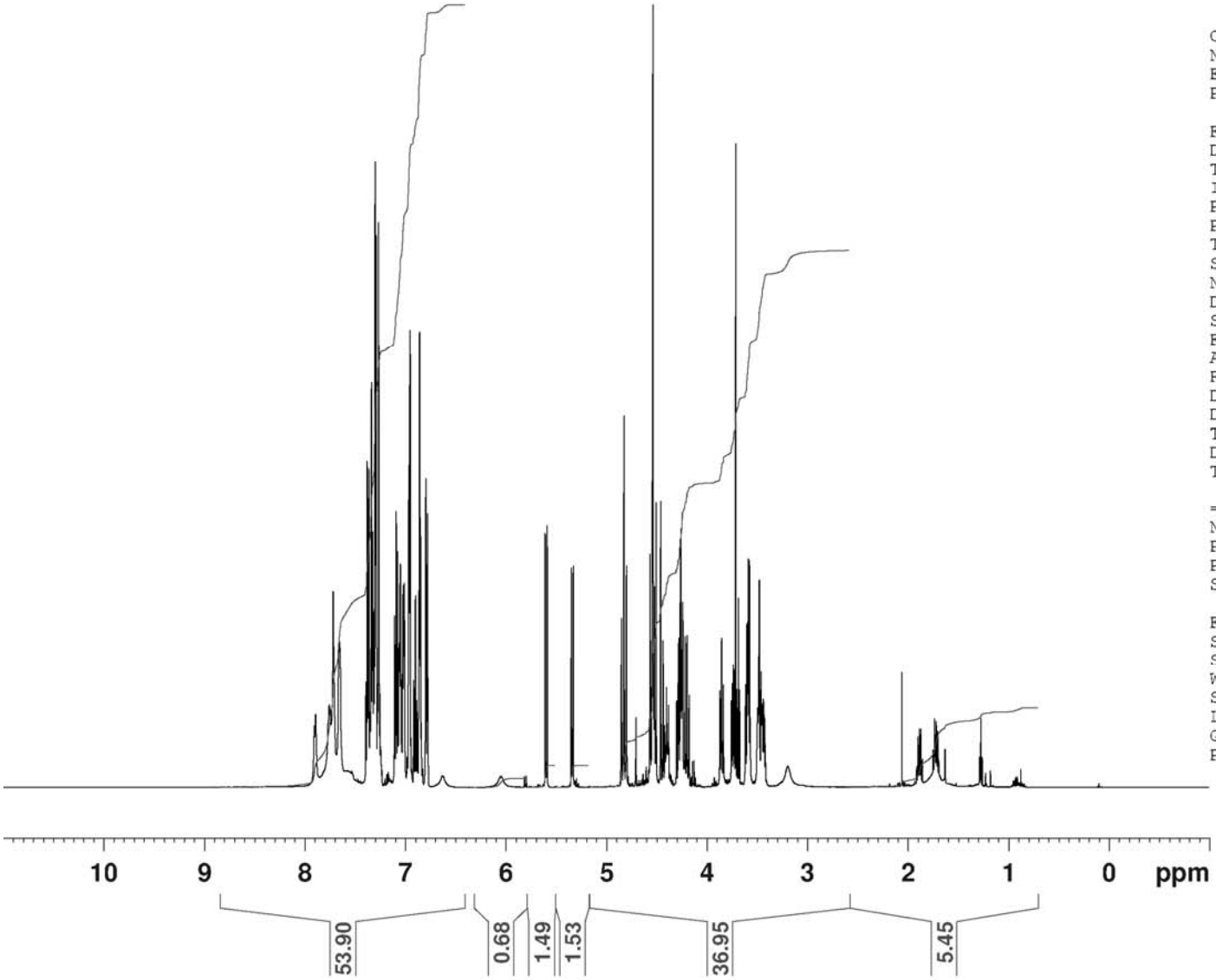
2




```
Current Data Parameters
NAME          dg34093011
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051130
Time               18.24
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT             D2O
NS                  256
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0486259 sec
RG                  912
DW               16.000 usec
DE               20.00 usec
TE               298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                8.00 usec
PL1               -4.40 dB
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            80.00 usec
PL2               -6.00 dB
PL12              12.40 dB
PL13              17.00 dB
SFO2        500.3020012 MHz

F2 - Processing parameters
SI                32768
SF          125.8005350 MHz
WDW                  EM
SSB                   0
LB                1.00 Hz
GB                    0
PC                1.40
```

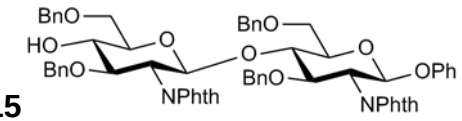
15

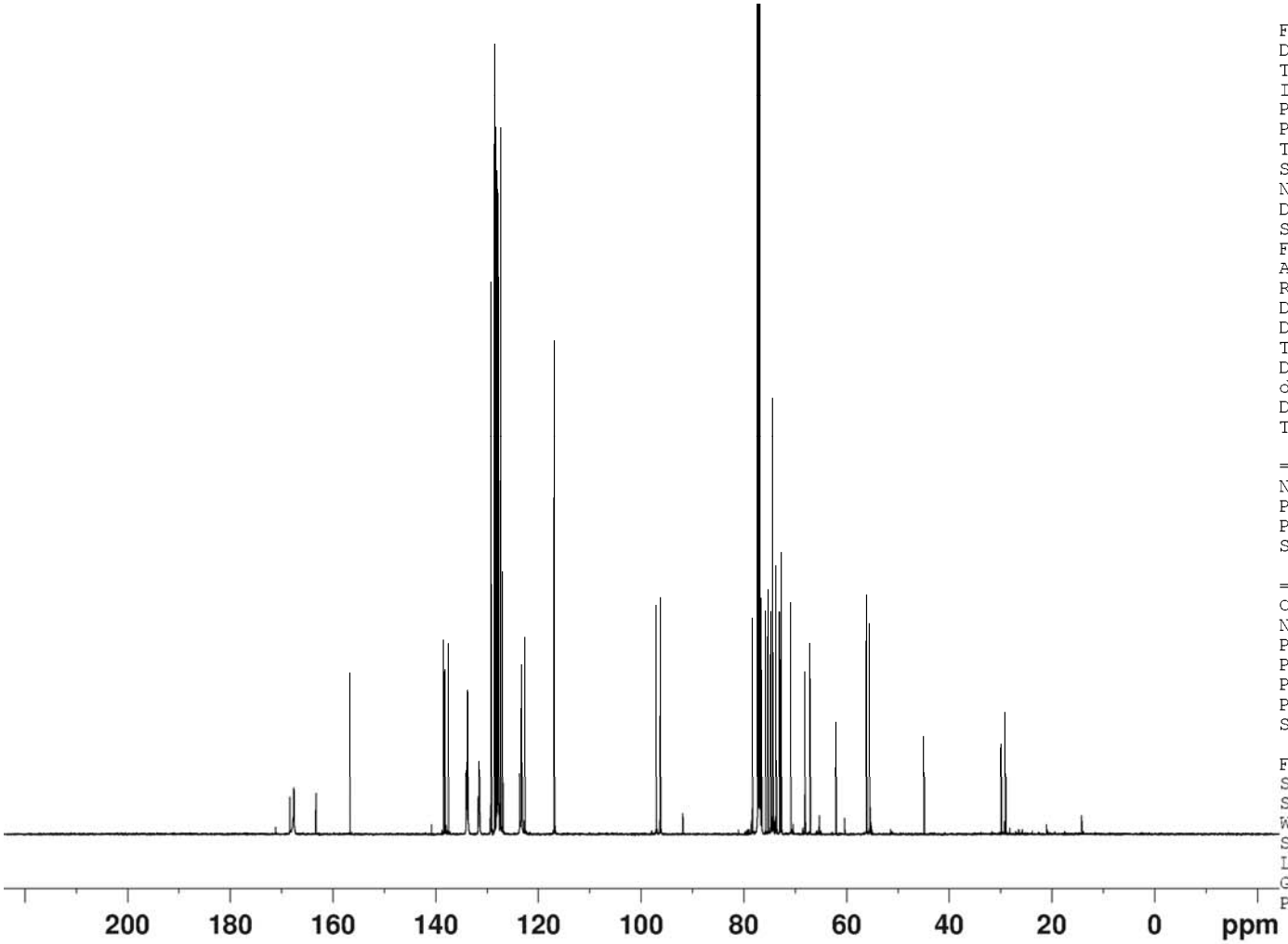





```
Current Data Parameters
NAME          dg32901511
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051115
Time               15.32
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.60 usec
PL1                -6.00 dB
SFO1        500.3030896 MHz

F2 - Processing parameters
SI                 32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

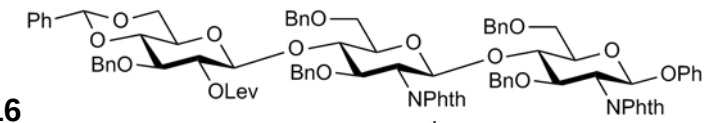
15

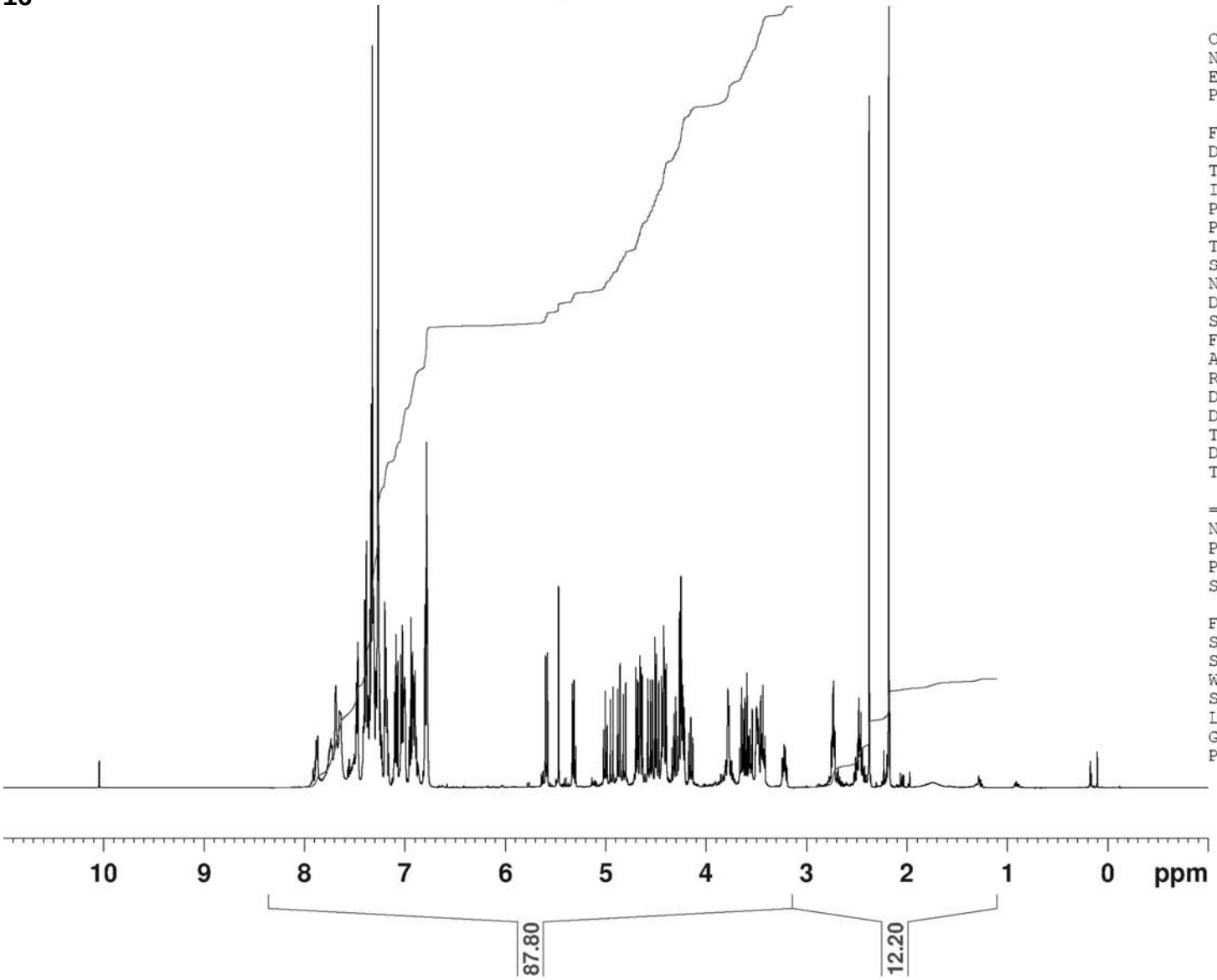





```
Current Data Parameters
NAME          dg32901511
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051115
Time               17.24
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 2048
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ            1.0486259 sec
RG                 1820
DW               16.000 usec
DE               20.00 usec
TE               298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.00 usec
PL1               -4.40 dB
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.40 dB
PL13              17.00 dB
SFO2        500.3020012 MHz

F2 - Processing parameters
SI                 32768
SF          125.8005438 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.40
```

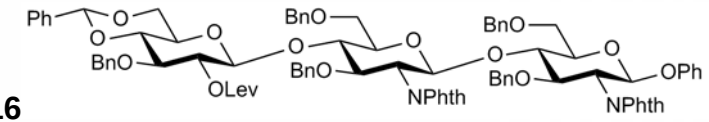
16

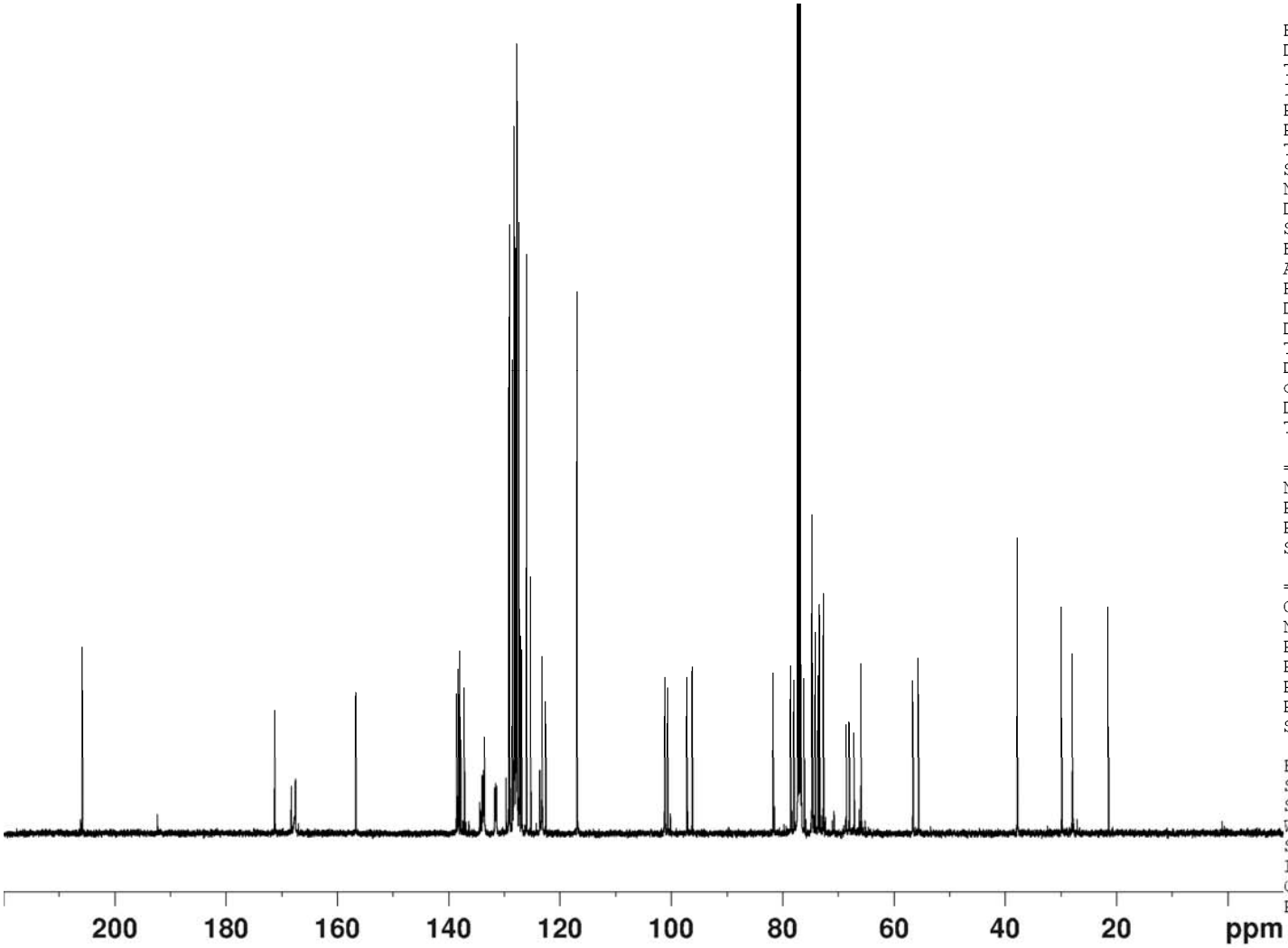





```
Current Data Parameters
NAME          dg34560712
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051208
Time               19.40
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                     4
DW               48.400 usec
DE                6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
SFO1        500.3030896 MHz

F2 - Processing parameters
SI                 32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

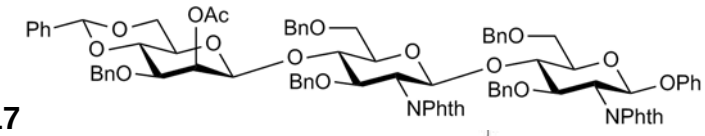
16

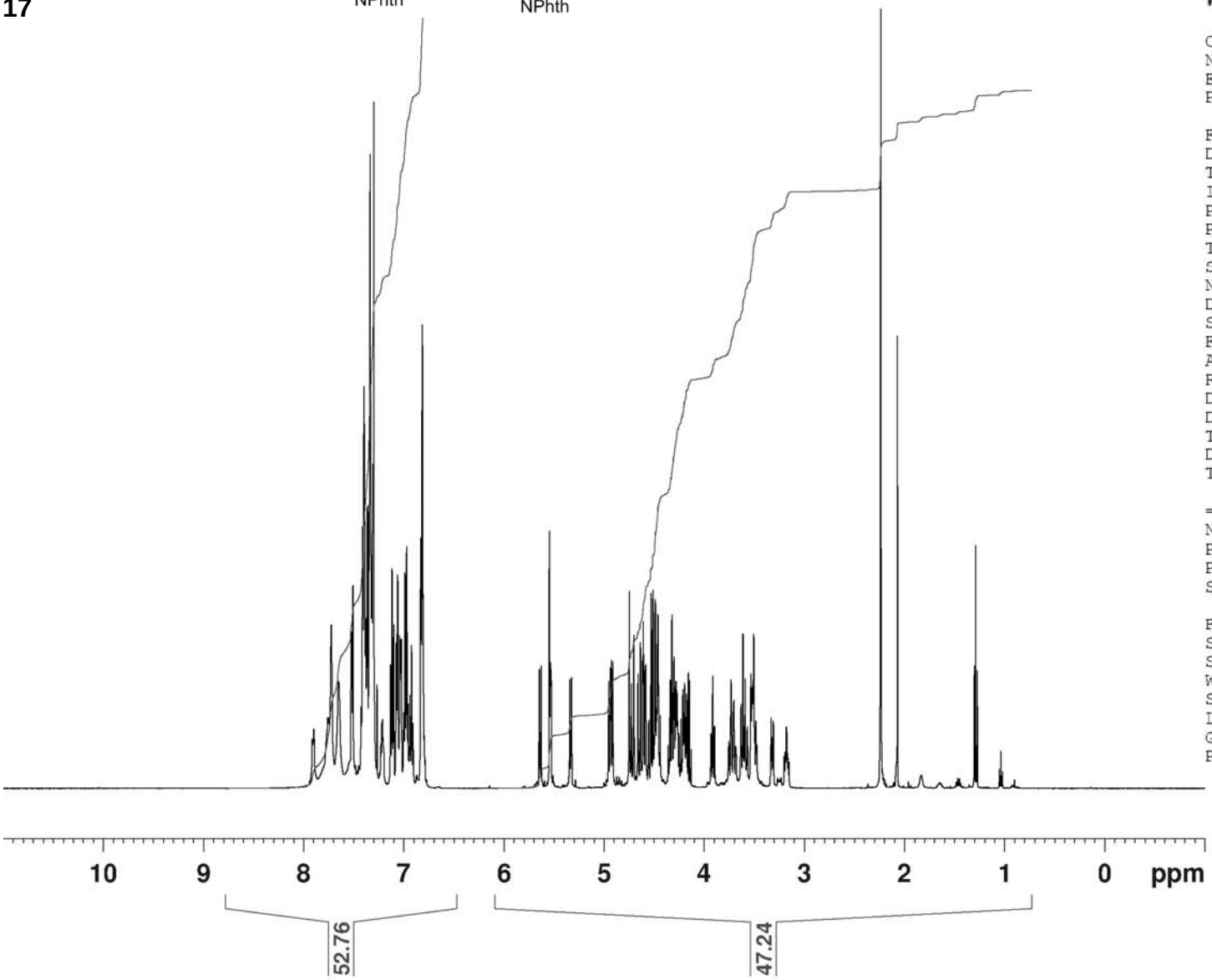





```
Current Data Parameters
NAME          dg34560712
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameters
Date_           20051208
Time               20.32
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ             1.0486259 sec
RG                 1620
DW               16.000 usec
DE               20.00 usec
TE               298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.00 usec
PL1               -4.40 dB
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.40 dB
PL13              17.00 dB
SFO2        500.3020012 MHz

F2 - Processing parameters
SI                 32768
SF          125.8005438 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

17

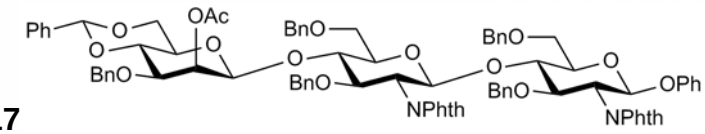


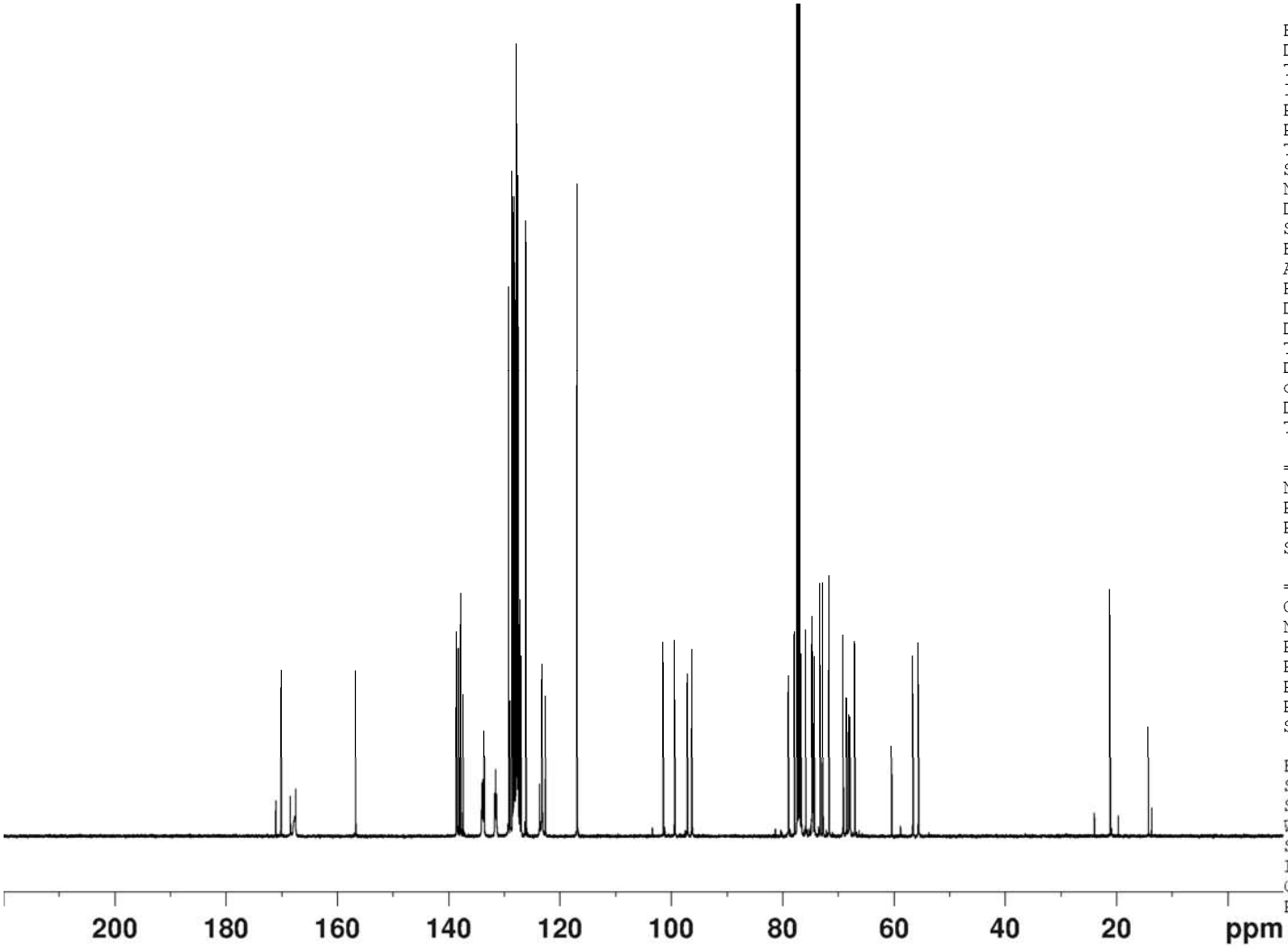


NMR@CHEM.OX

```
Current Data Parameters
NAME          dg38191502
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060215
Time                8.11
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                     4
DW               48.400 usec
DE                6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
SFO1        500.3030896 MHz

F2 - Processing parameters
SI                 32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```

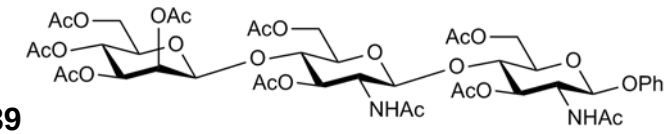
17





NMR@CHEM.OX

```
Current Data Parameters
NAME          dg38191502
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060215
Time                8.26
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ             1.0486259 sec
RG                 1150
DW               16.000 usec
DE               20.00 usec
TE               298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.00 usec
PL1               -4.40 dB
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.40 dB
PL13              17.00 dB
SFO2        500.3020012 MHz

F2 - Processing parameters
SI                 32768
SF          125.8005438 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```



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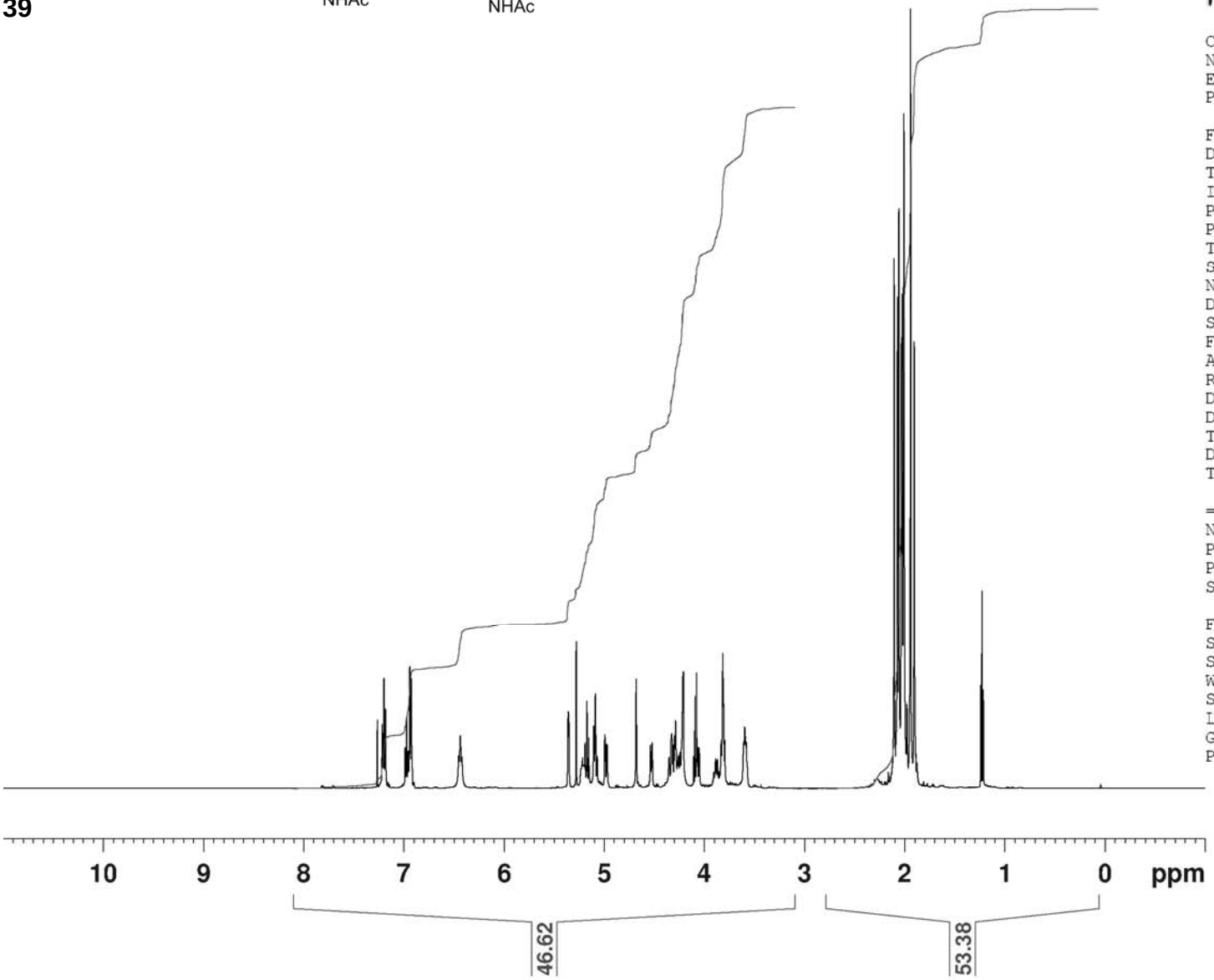
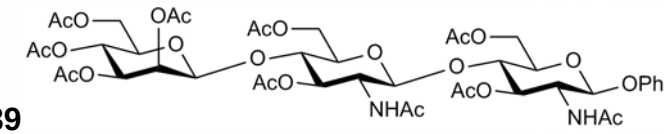
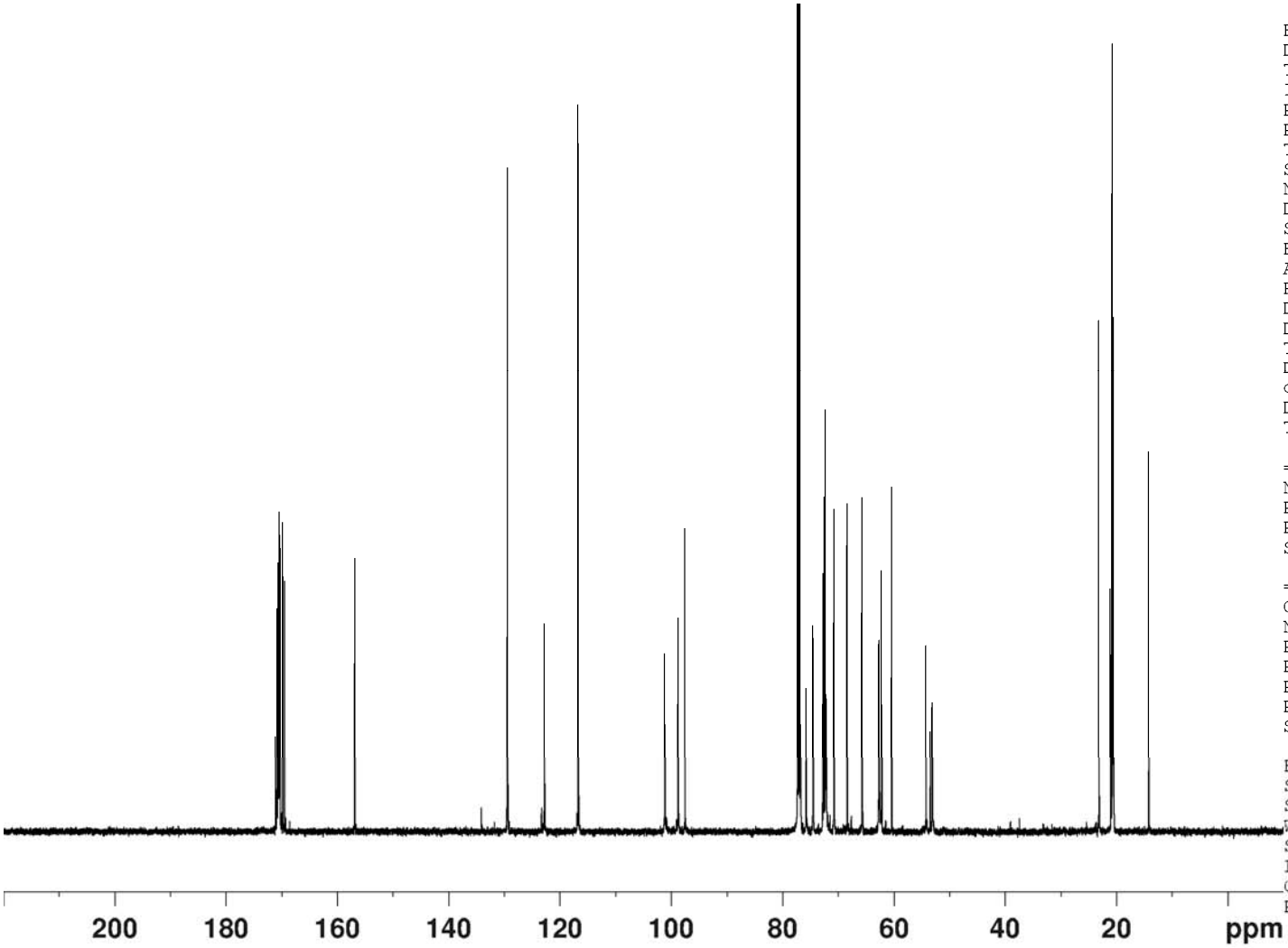
NMR@CHEM.OX

```
Current Data Parameters
NAME          dg40762703
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060327
Time               11.15
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                     4
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
SFO1        500.3030896 MHz

F2 - Processing parameters
SI                 32768
SF          500.3000240 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



39

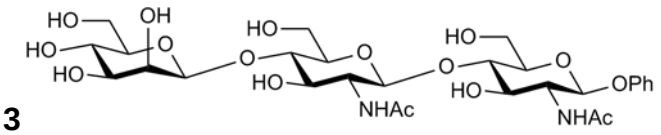




NMR@CHEM.OX

```
Current Data Parameters
NAME          dg40762703
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060327
Time               11.45
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  256
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ             1.0486259 sec
RG                 1620
DW               16.000 usec
DE               20.00 usec
TE               298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.00 usec
PL1               -4.40 dB
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.40 dB
PL13              17.00 dB
SFO2        500.3020012 MHz

F2 - Processing parameters
SI                 32768
SF          125.8005438 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

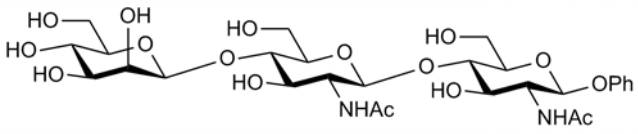
3

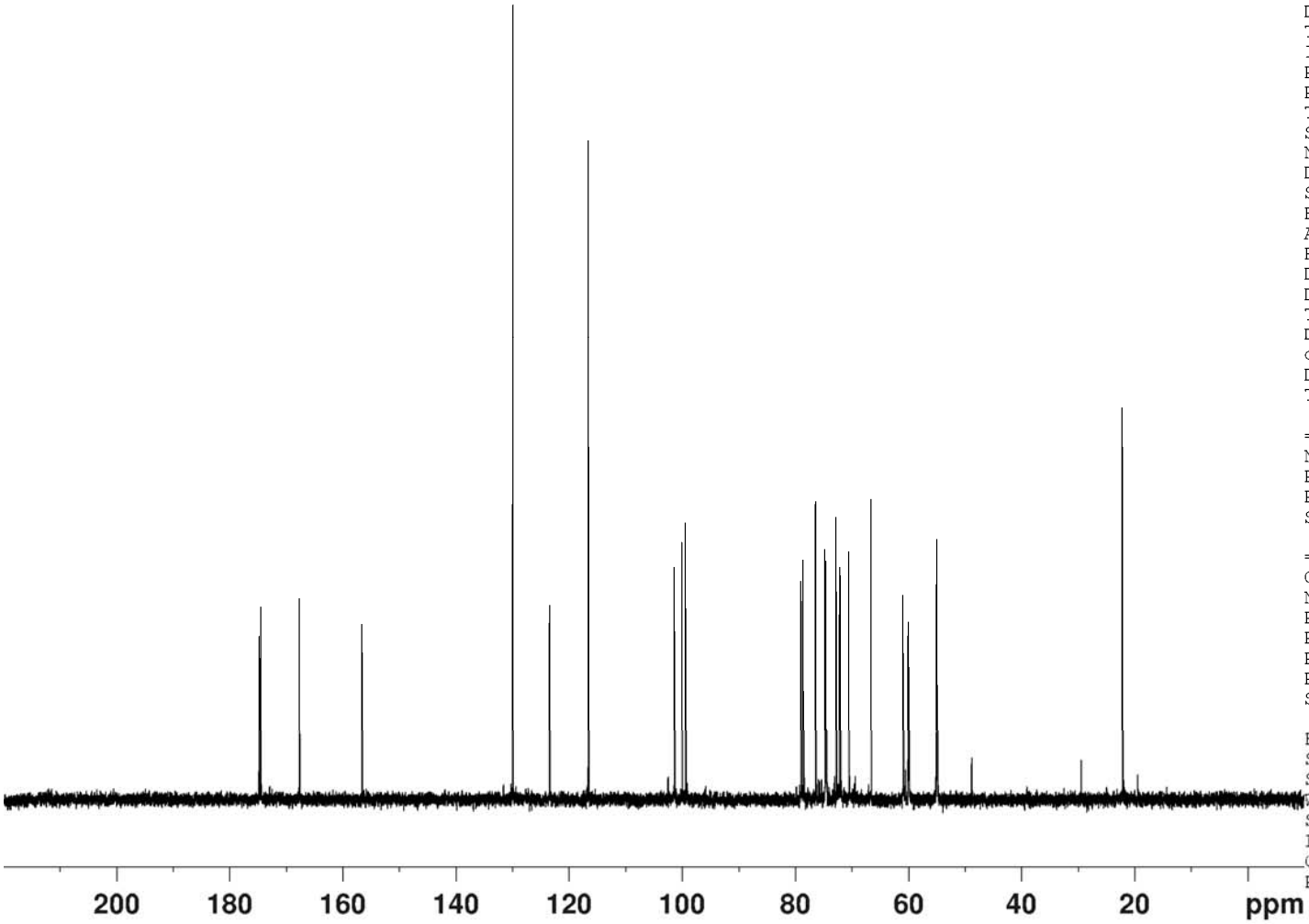


NMR@CHEM.OX

```
Current Data Parameters
NAME          dg41620604
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060406
Time               17.42
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG             zg30
TD                 65536
SOLVENT              D2O
NS                    16
DS                     2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                 12.7
DW                48.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.60 usec
PL1               -6.00 dB
SFO1        500.3030896 MHz

F2 - Processing parameters
SI                 32768
SF          500.3000000 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```

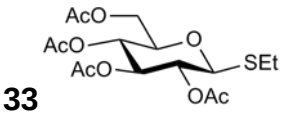
3



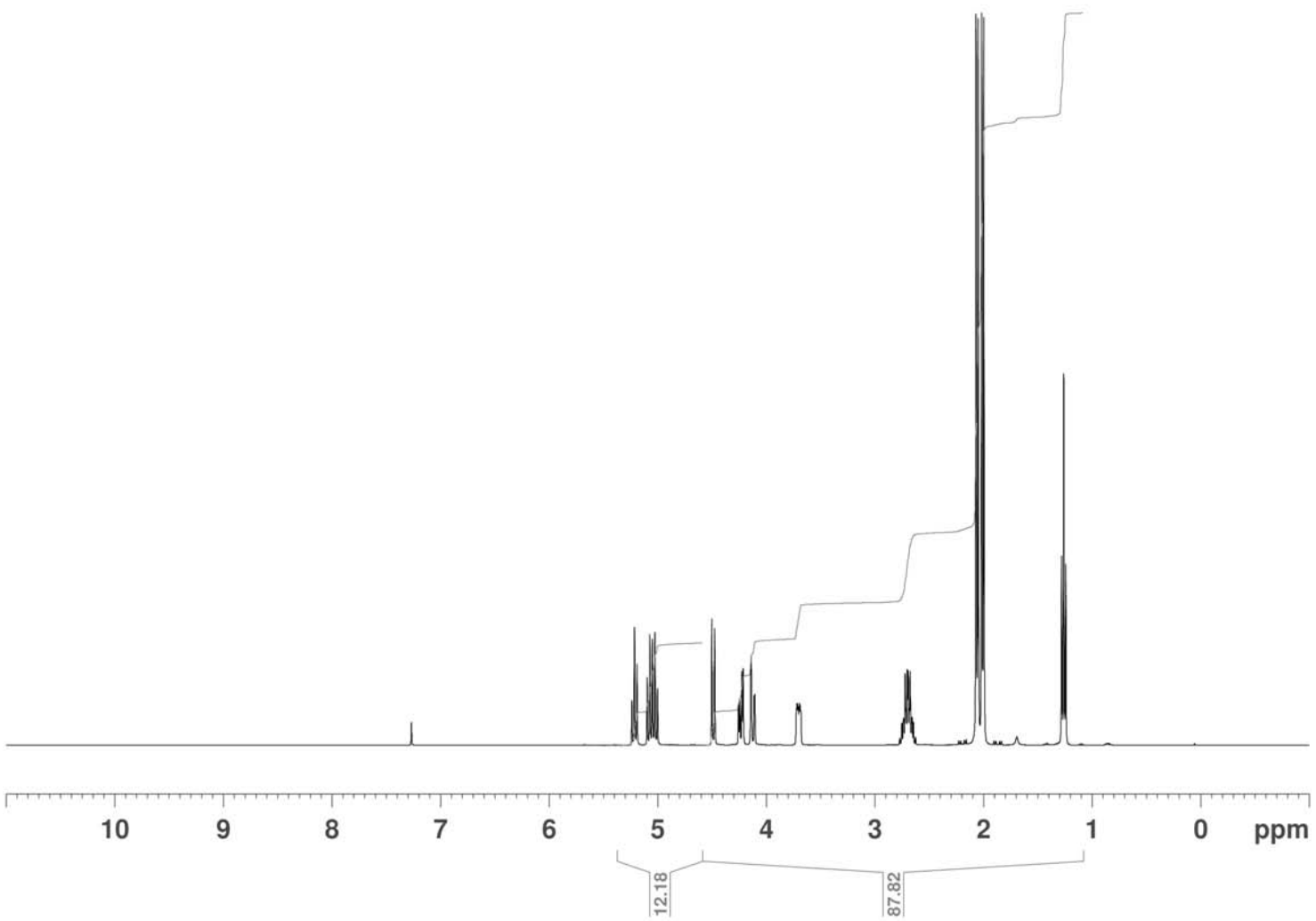


NMR@CHEM.OX

```
Current Data Parameters
NAME          dg41620604
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060406
Time               17.27
INSTRUM          avc500
PROBHD   5 mm CPDUL 13C
PULPROG          zgpg30
TD                65536
SOLVENT             D2O
NS                  256
DS                    2
SWH           31250.000 Hz
FIDRES         0.476837 Hz
AQ             1.0486259 sec
RG                 1620
DW               16.000 usec
DE               20.00 usec
TE               298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.00 usec
PL1               -4.40 dB
SFO1        125.8131151 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.40 dB
PL13              17.00 dB
SFO2        500.3020012 MHz

F2 - Processing parameters
SI                 32768
SF          125.8005350 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                 1.40
```

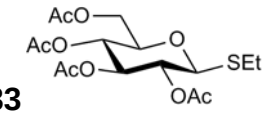


33



NMR@CHEM.OX

NAME	Jan08-2010-21	
EXPNO	1	
PROCNO	1	
Date_	20100109	
Time	5.28	
INSTRUM	av400	
PROBHD	5 mm QNP 1H/13	
PULPROG	zg60	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	8278.146	Hz
FIDRES	0.126314	Hz
AQ	3.9584243	sec
RG	90.5	
DW	60.400	usec
DE	7.50	usec
TE	300.0	K
D1	1.00000000	sec
======== CHANNEL f1 ========		
NUC1	1H	
P1	9.00	usec
PL1	0.00	dB
SFO1	400.2024714	MHz
SI	32768	
SF	400.2000028	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	



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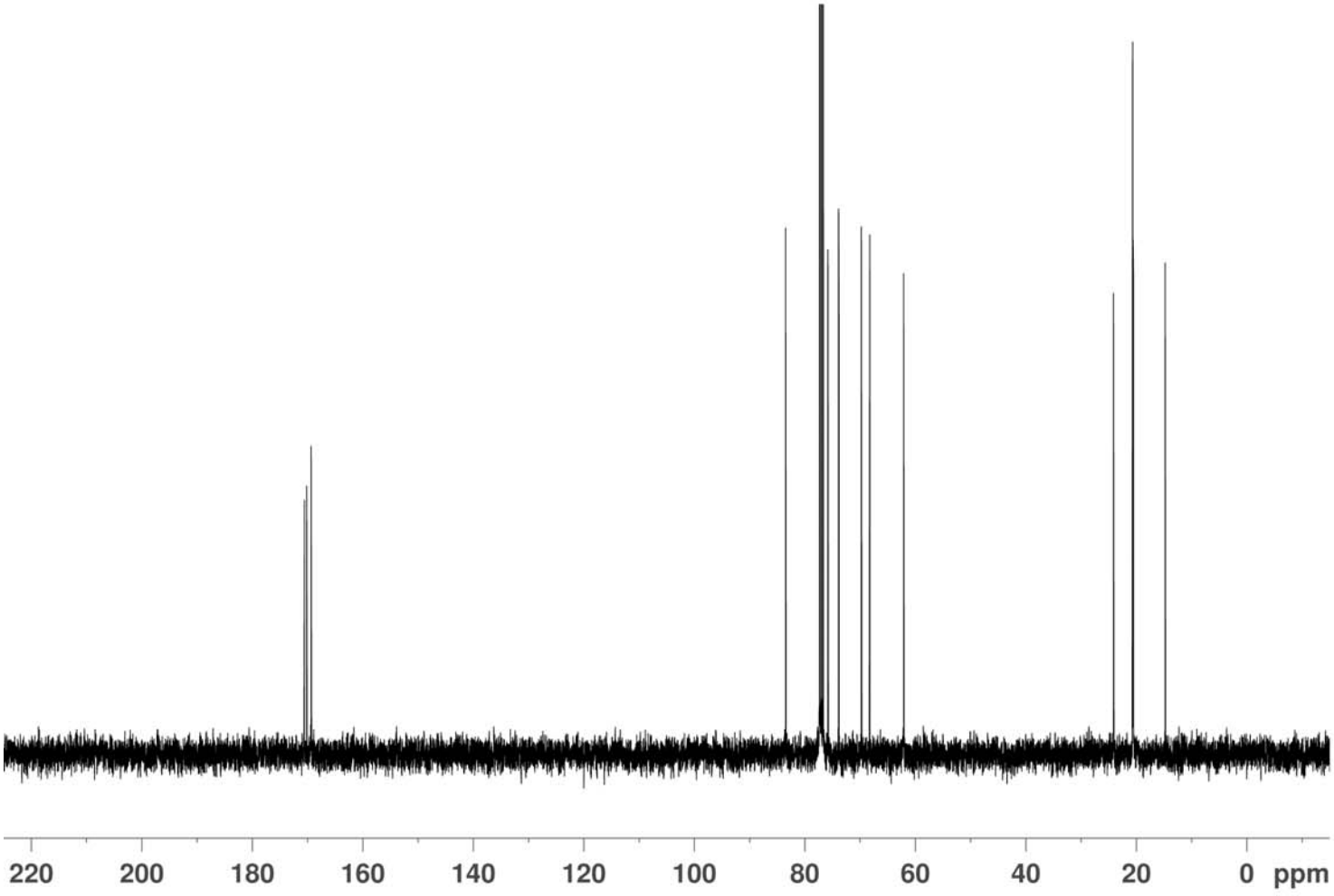
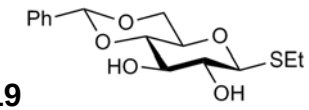


NMR@CHEM.OX

NAME	Jan08-2010-21
EXPNO	2
PROCNO	1
Date_	20100109
Time	5.35
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDC13
NS	256
DS	4
SWH	26178.010 Hz
FIDRES	0.798889 Hz
AQ	0.6259188 sec
RG	32768
DW	19.100 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	0.00 dB
SFO1	100.6403931 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	25.00 dB
SFO2	400.2016008 MHz
SI	32768
SF	100.6303718 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



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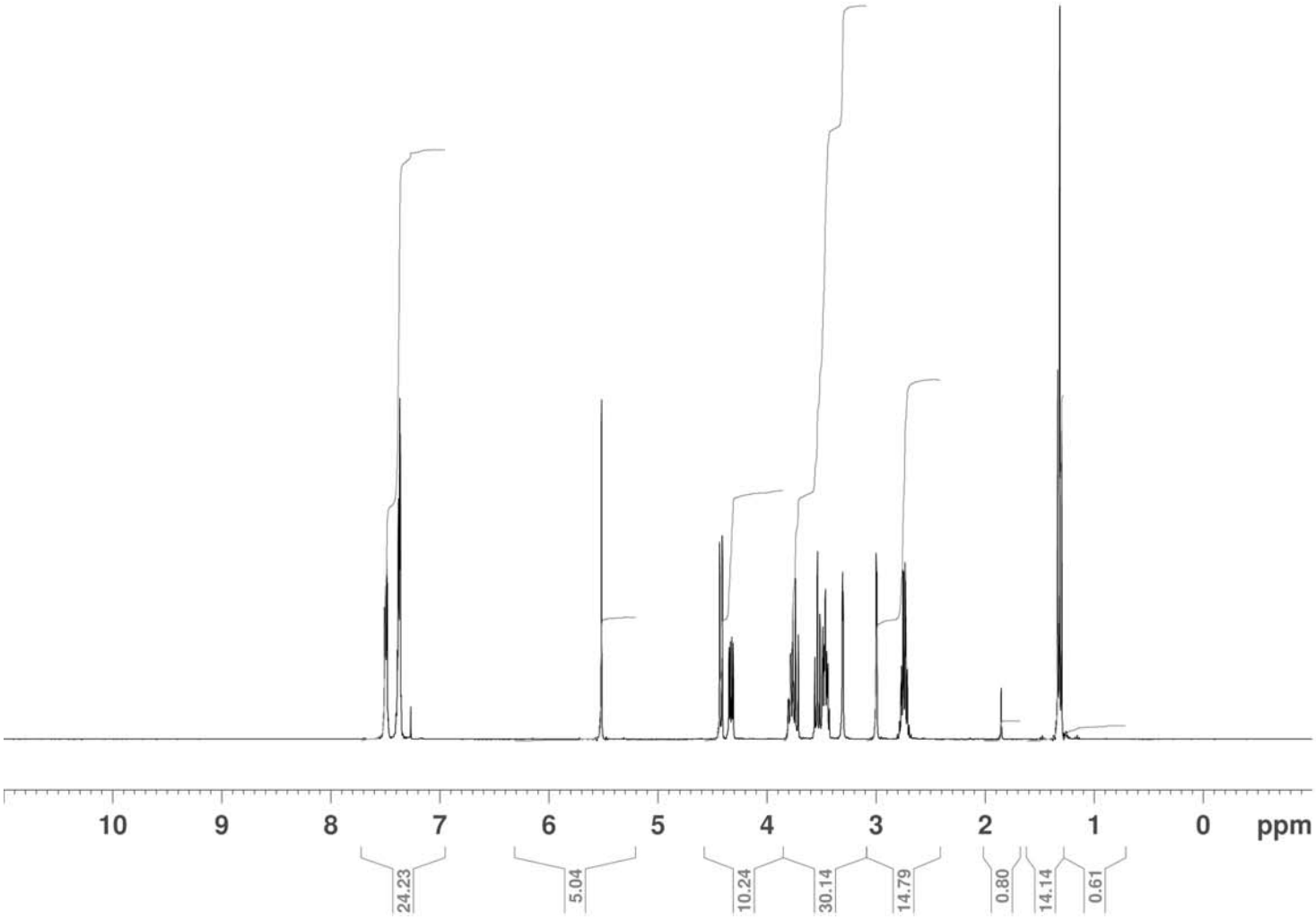
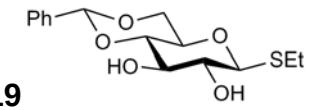
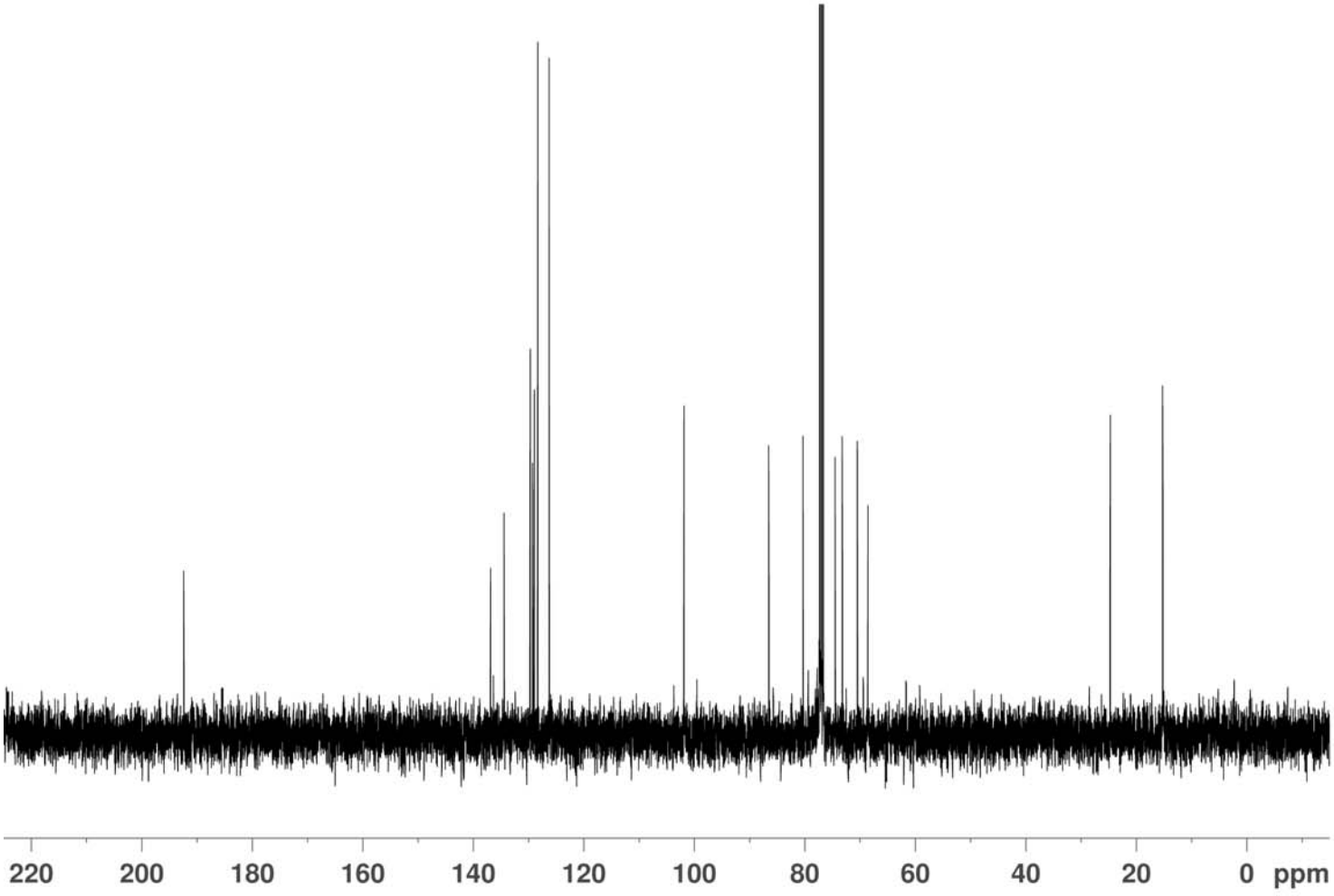
NMR@CHEM.OX

```
Current Data Parameters
NAME        May17-2010-9
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100517
Time                9.12
INSTRUM          dpx400
PROBHD   5 mm Dual 1H/1
PULPROG             zg60
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5592.841 Hz
FIDRES          0.170680 Hz
AQ              2.9295092 sec
RG                  45.3
DW                89.400 usec
DE                17.00 usec
TE                300.0 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  7.30 usec
PL1                 0.00 dB
SFO1         400.1320007 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300182 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  0.60
```



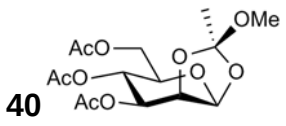


19

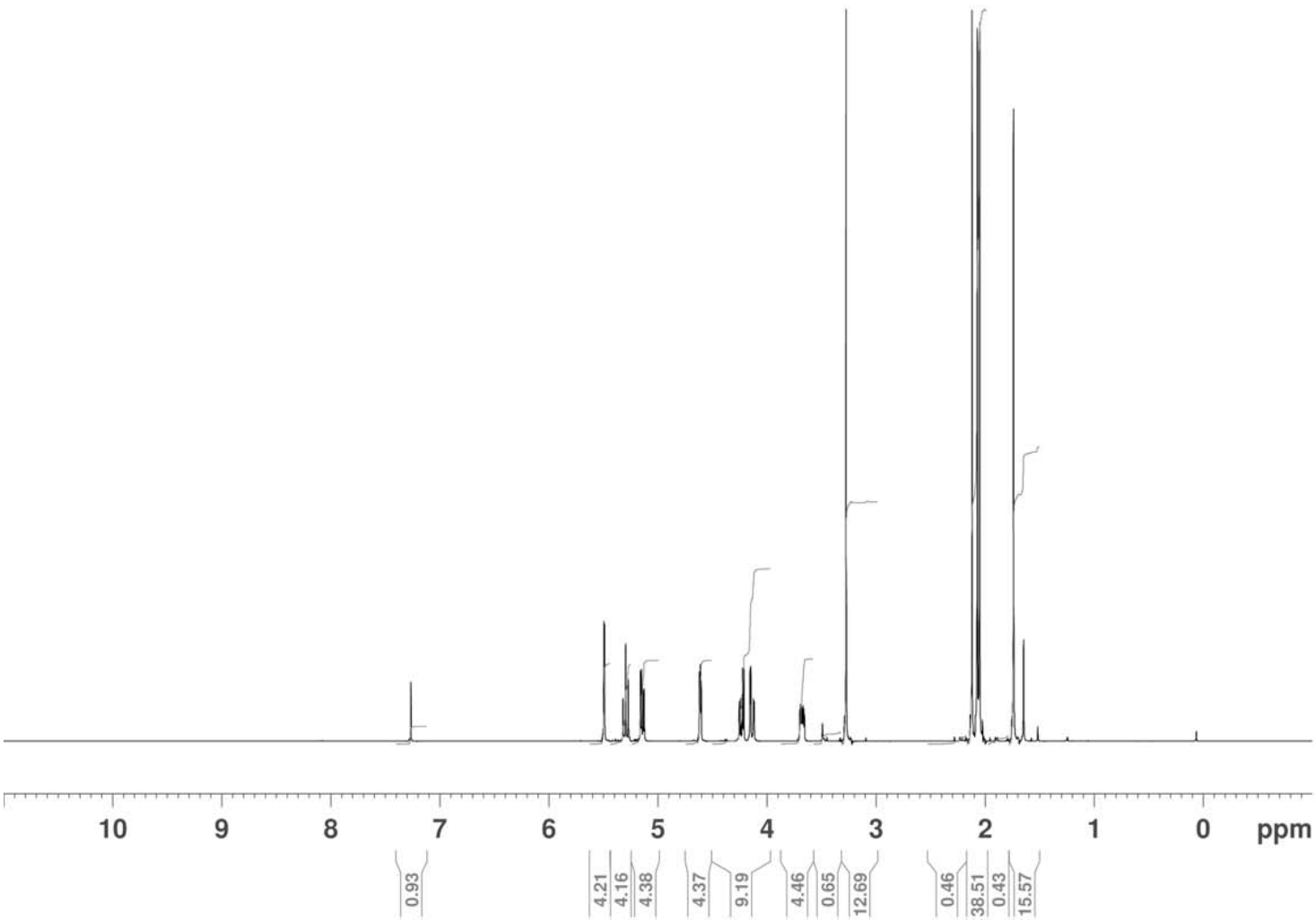


NMR@CHEM.OX

NAME	Feb10-2010-36
EXPNO	2
PROCNO	1
Date_	20100210
Time	20.34
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDC13
NS	256
DS	4
SWH	26178.010 Hz
FIDRES	0.798889 Hz
AQ	0.6259188 sec
RG	32768
DW	19.100 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	0.00 dB
SFO1	100.6403931 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	25.00 dB
SFO2	400.2016008 MHz
SI	32768
SF	100.6303718 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

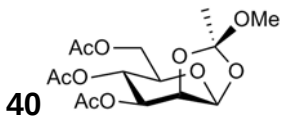


40



NMR@CHEM.OX

```
Current Data Parameters
NAME       Feb25-2009-20
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20090225
Time              12.20
INSTRUM         dpx400
PROBHD   5 mm Dual 1H/1
PULPROG             zg60
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5592.841 Hz
FIDRES          0.170680 Hz
AQ              2.9295092 sec
RG                 80.6
DW                89.400 usec
DE                17.00 usec
TE                300.0 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.30 usec
PL1                0.00 dB
SFO1        400.1320007 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300182 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 0.60
```



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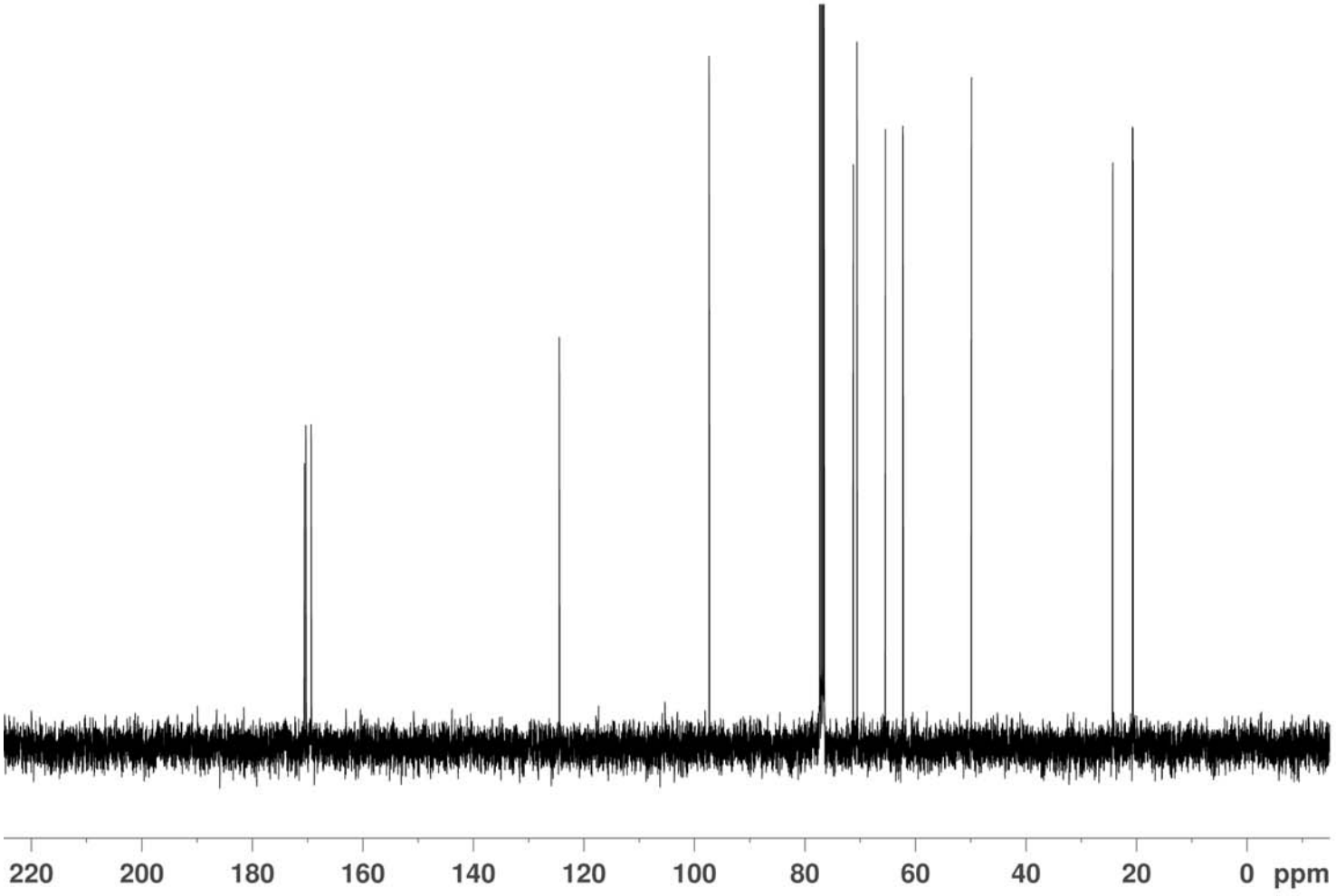
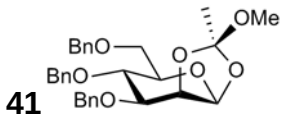


NMR@CHEM.OX

NAME	Mar30-2010-23
EXPNO	2
PROCNO	1
Date_	20100330
Time	10.37
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	256
DS	4
SWH	26178.010 Hz
FIDRES	0.798889 Hz
AQ	0.6259188 sec
RG	32768
DW	19.100 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	0.00 dB
SFO1	100.6403931 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	25.00 dB
SFO2	400.2016008 MHz
SI	32768
SF	100.6303718 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



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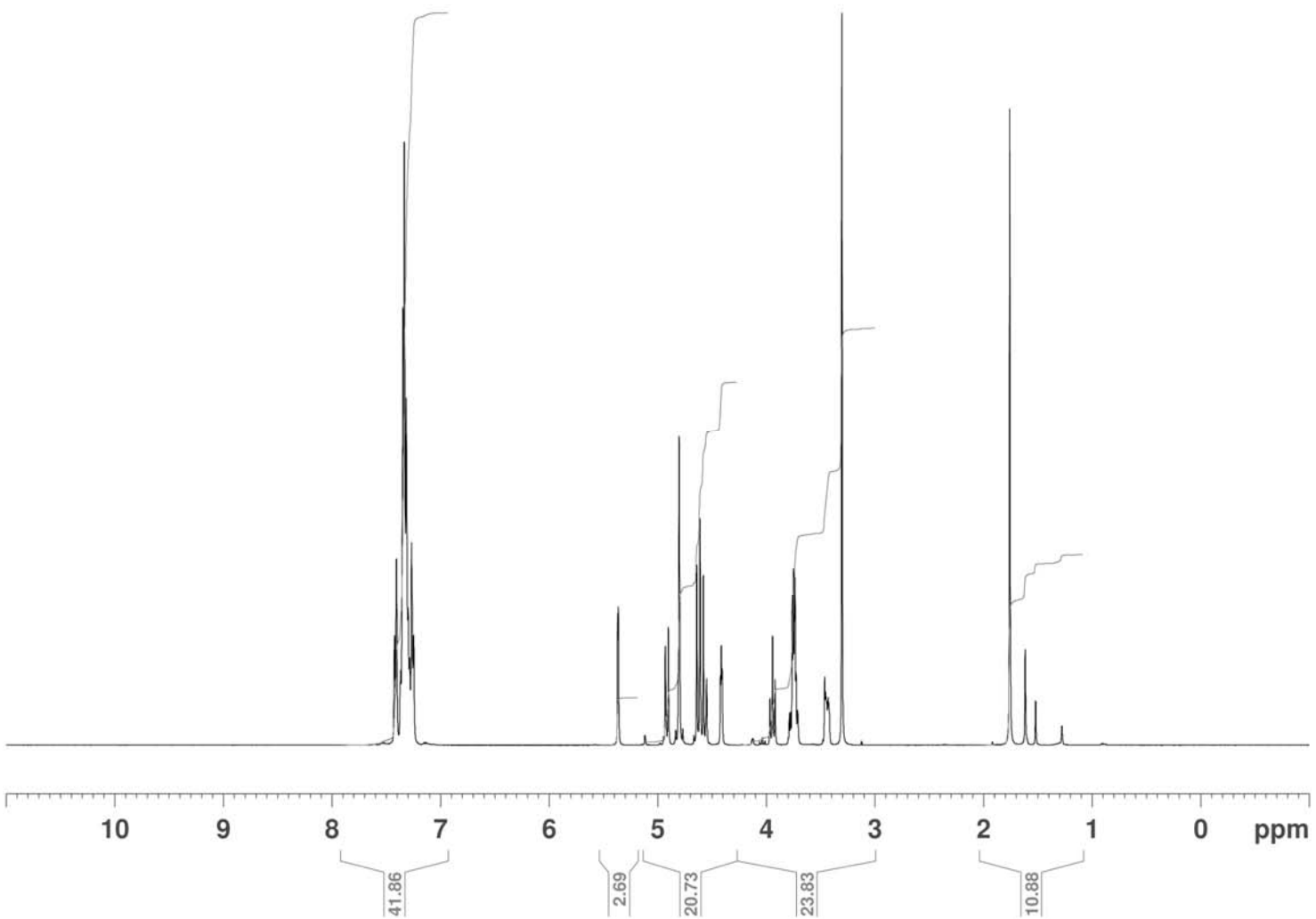
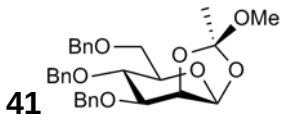
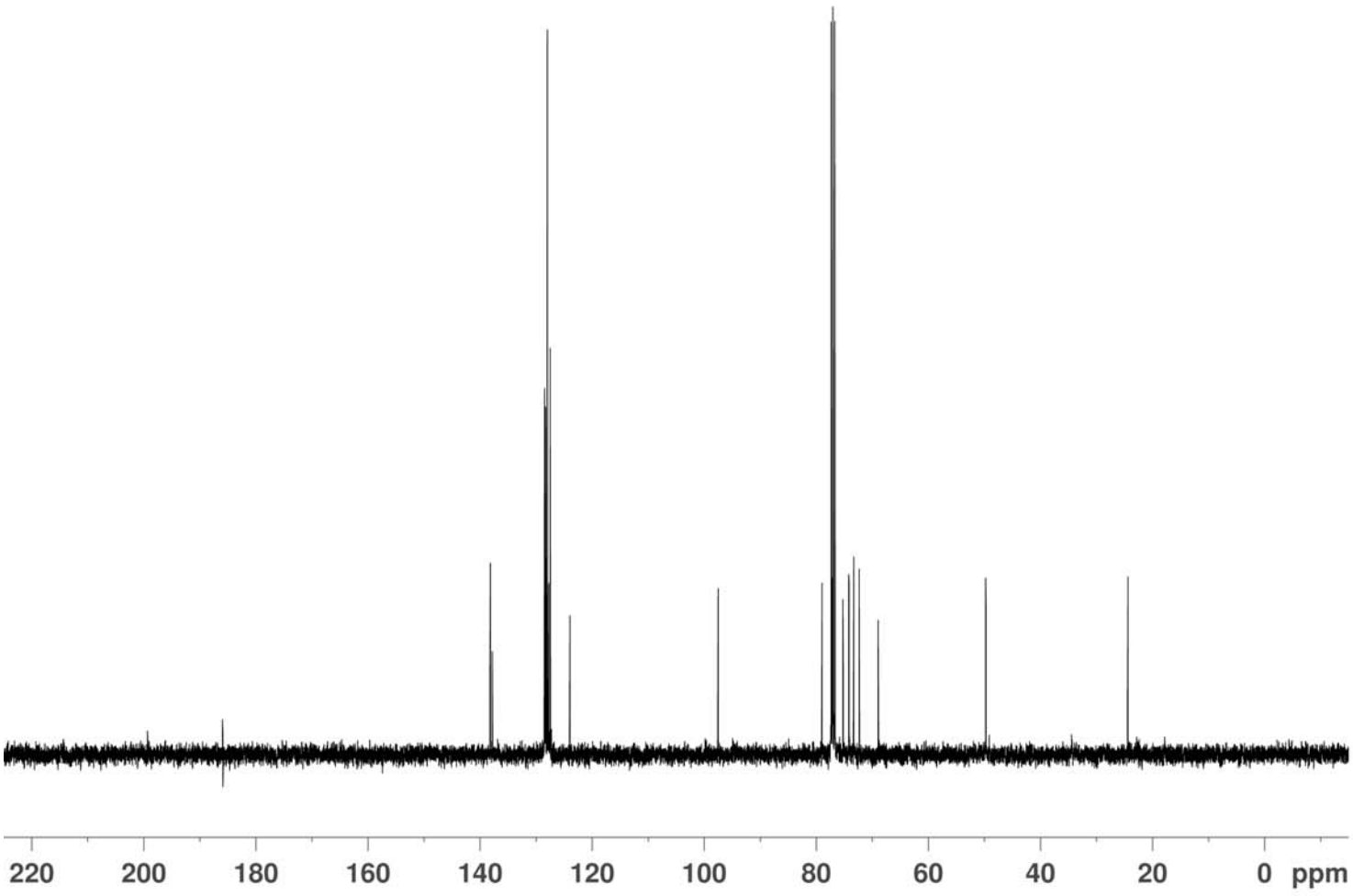
NMR@CHEM.OX

NAME	Mar30-2010-22	
EXPNO	1	
PROCNO	1	
Date_	20100330	
Time	10.04	
INSTRUM	av400	
PROBHD	5 mm QNP 1H/13	
PULPROG	zg60	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	8278.146	Hz
FIDRES	0.126314	Hz
AQ	3.9584243	sec
RG	90.5	
DW	60.400	usec
DE	7.50	usec
TE	300.0	K
D1	1.00000000	sec
======== CHANNEL f1 ========		
NUC1	1H	
P1	9.00	usec
PL1	0.00	dB
SFO1	400.2024714	MHz
SI	32768	
SF	400.2000028	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	



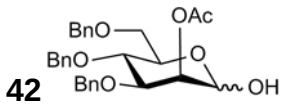


41



NMR@CHEM.OX

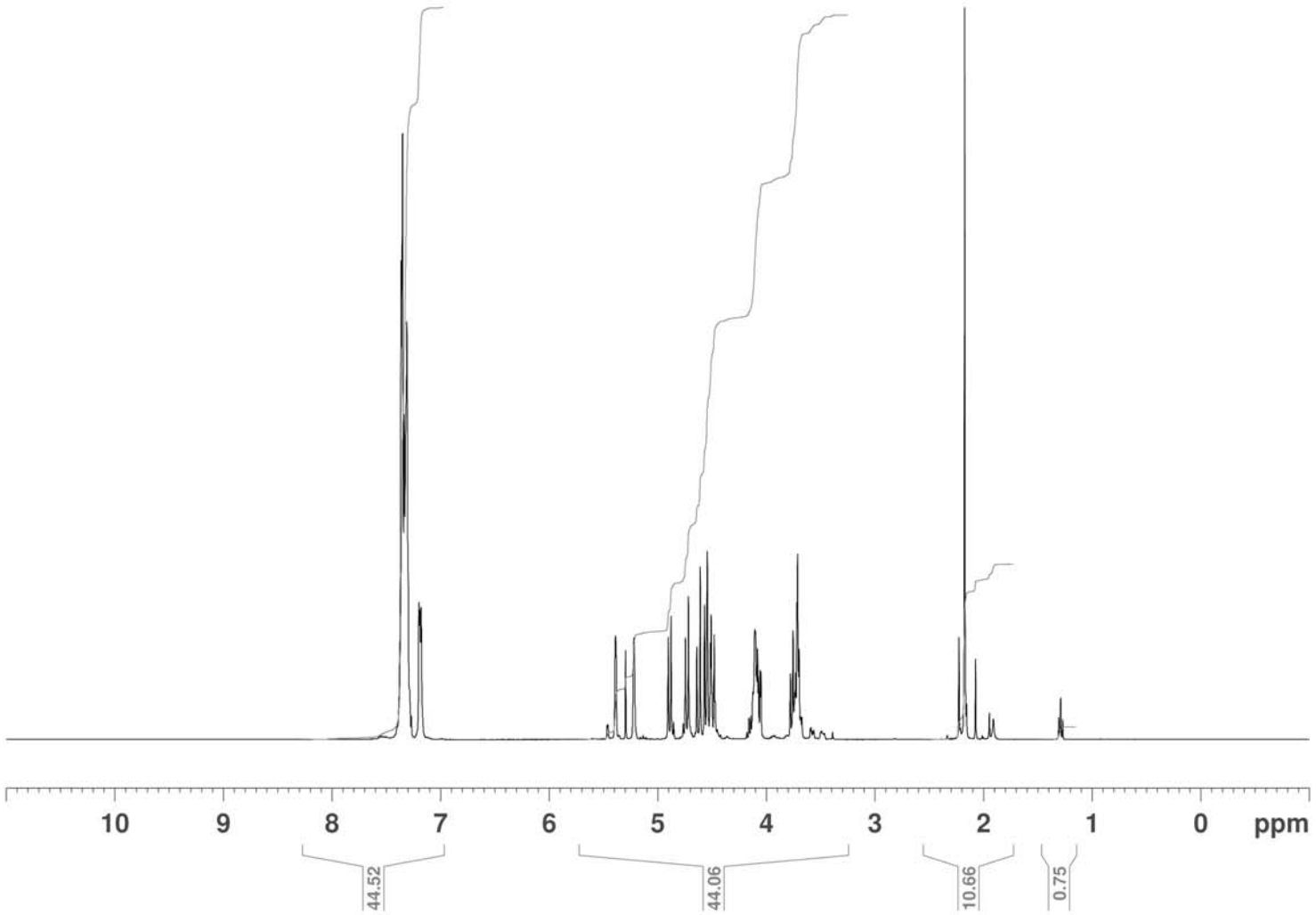
NAME	Mar30-2010-22
EXPNO	2
PROCNO	1
Date_	20100330
Time	10.12
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDC13
NS	256
DS	4
SWH	26178.010 Hz
FIDRES	0.798889 Hz
AQ	0.6259188 sec
RG	32768
DW	19.100 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	0.00 dB
SFO1	100.6403931 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	25.00 dB
SFO2	400.2016008 MHz
SI	32768
SF	100.6303718 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

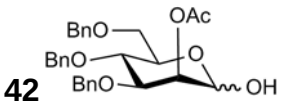


42

NMR@CHEM.OX

NAME	Apr21-2010-60
EXPNO	1
PROCNO	1
Date_	20100421
Time	20.44
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zg60
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	35.9
DW	60.400 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	400.2024714 MHz
SI	32768
SF	400.2000028 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00





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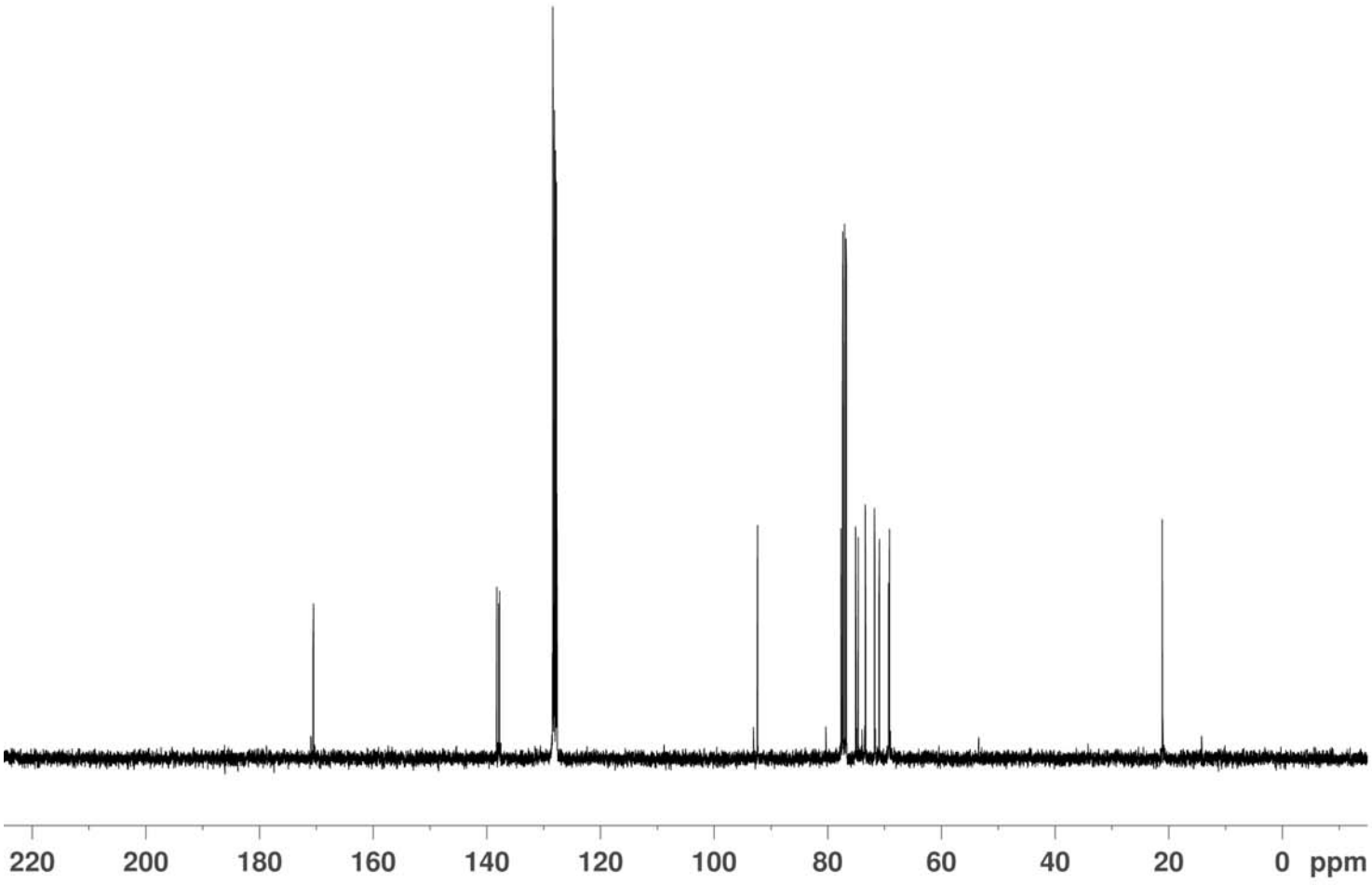
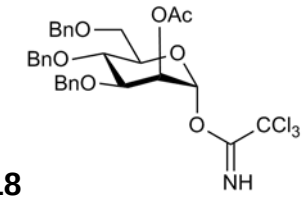


NMR@CHEM.OX

NAME	Apr21-2010-60
EXPNO	2
PROCNO	1
Date_	20100421
Time	20.51
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDC13
NS	256
DS	4
SWH	26178.010 Hz
FIDRES	0.798889 Hz
AQ	0.6259188 sec
RG	32768
DW	19.100 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	0.00 dB
SFO1	100.6403931 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	25.00 dB
SFO2	400.2016008 MHz
SI	32768
SF	100.6303718 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



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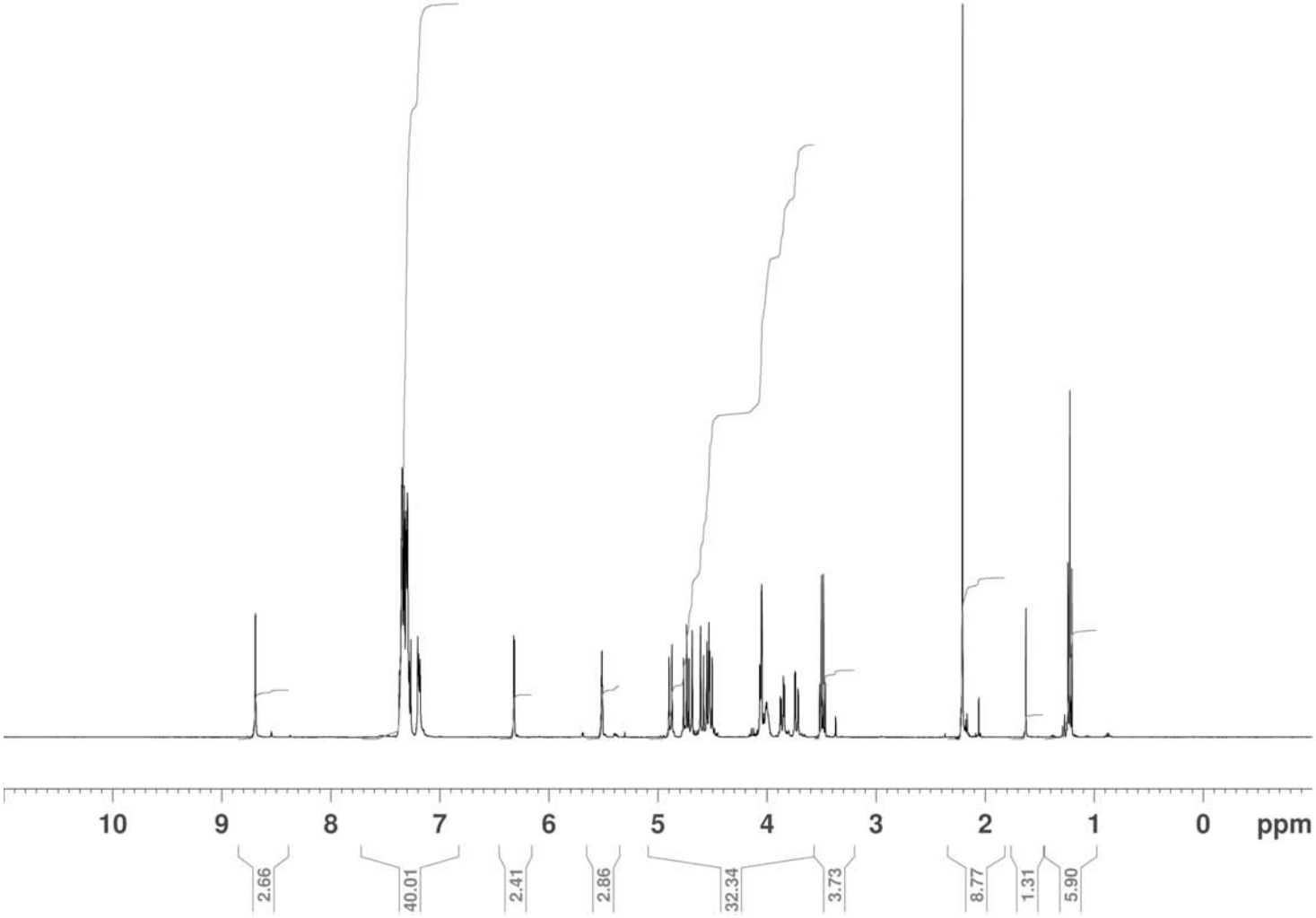
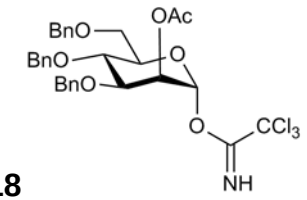
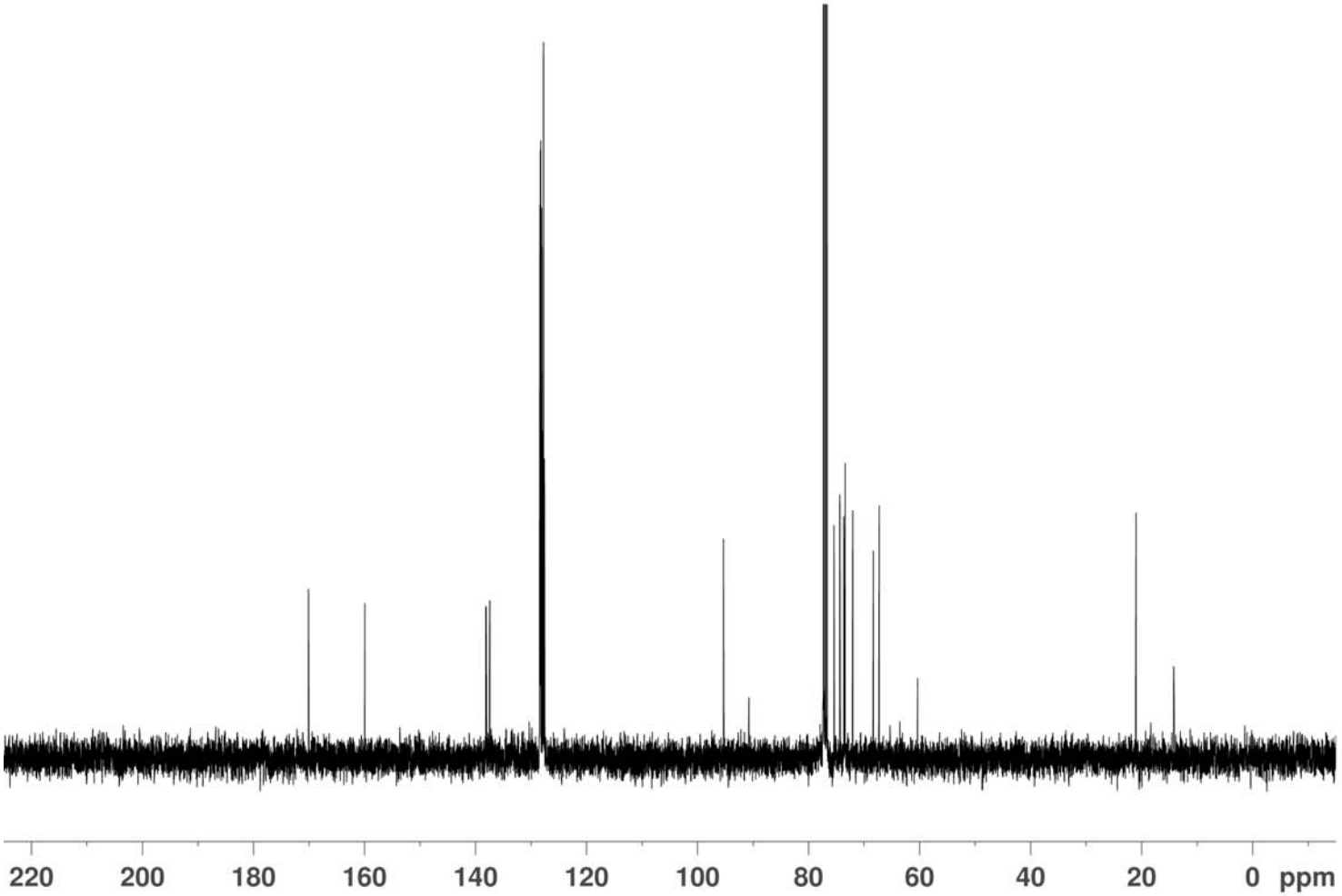


NMR@CHEM.OX

```
Current Data Parameters
NAME       Sep17-2009-20
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20090917
Time               19.38
INSTRUM          dpx400
PROBHD   5 mm Dual 1H/1
PULPROG             zg60
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             5592.841 Hz
FIDRES          0.170680 Hz
AQ              2.9295092 sec
RG                  45.3
DW                89.400 usec
DE                17.00 usec
TE                300.0 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 7.30 usec
PL1                0.00 dB
SFO1        400.1320007 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300182 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                 0.60
```



18



NMR@CHEM.OX

```
NAME          Feb10-2010-35
EXPNO                    2
PROCNO                   1
Date_             20100210
Time                 20.09
INSTRUM              av400
PROBHD    5 mm QNP 1H/13
PULPROG             zgpg30
TD                   32768
SOLVENT              CDC13
NS                     256
DS                       4
SWH              26178.010 Hz
FIDRES               0.798889 Hz
AQ                   0.6259188 sec
RG                   32768
DW                   19.100 usec
DE                    7.50 usec
TE                   300.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.50 usec
PL1                   0.00 dB
SFO1          100.6403931 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                   0.00 dB
PL12                 19.00 dB
PL13                 25.00 dB
SFO2          400.2016008 MHz
SI                   32768
SF            100.6303718 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

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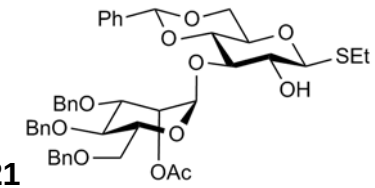
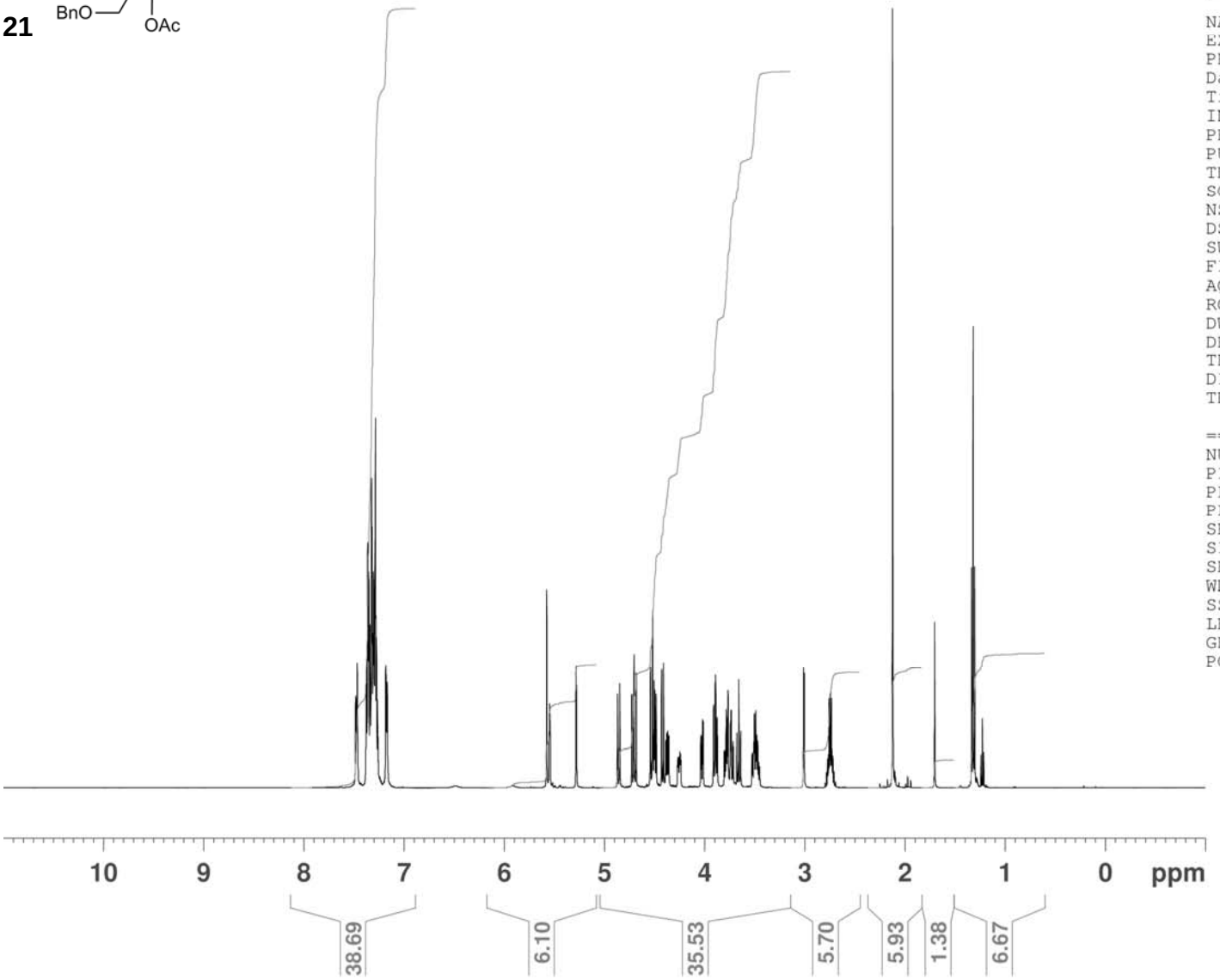
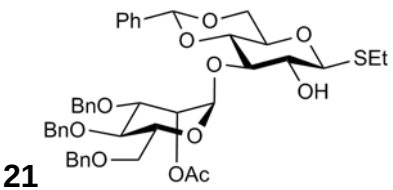


NMR@CHEM.OX

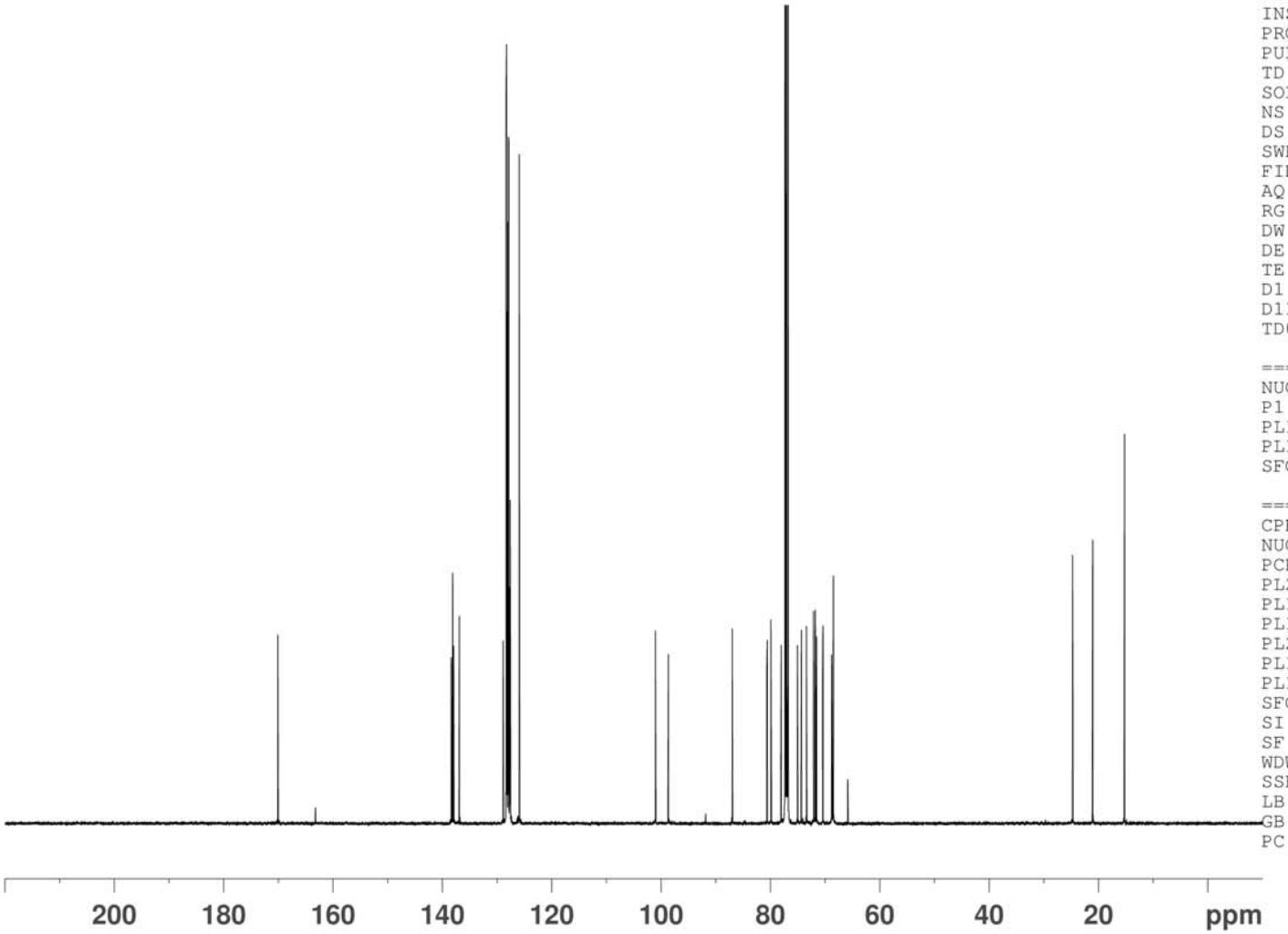
NAME	cb97160807
EXPNO	1
PROCNO	1
Date_	20100708
Time	19.07
INSTRUM	avc500
PROBHD	5 mm CPDUL 13C
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	4
DW	48.400 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========	
NUC1	1H
P1	9.60 usec
PL1	-6.00 dB
PL1W	15.19999981 W
SFO1	500.3030896 MHz
SI	32768
SF	500.3000240 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



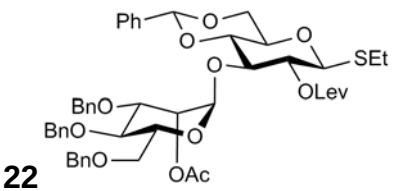


21



NMR@CHEM.OX

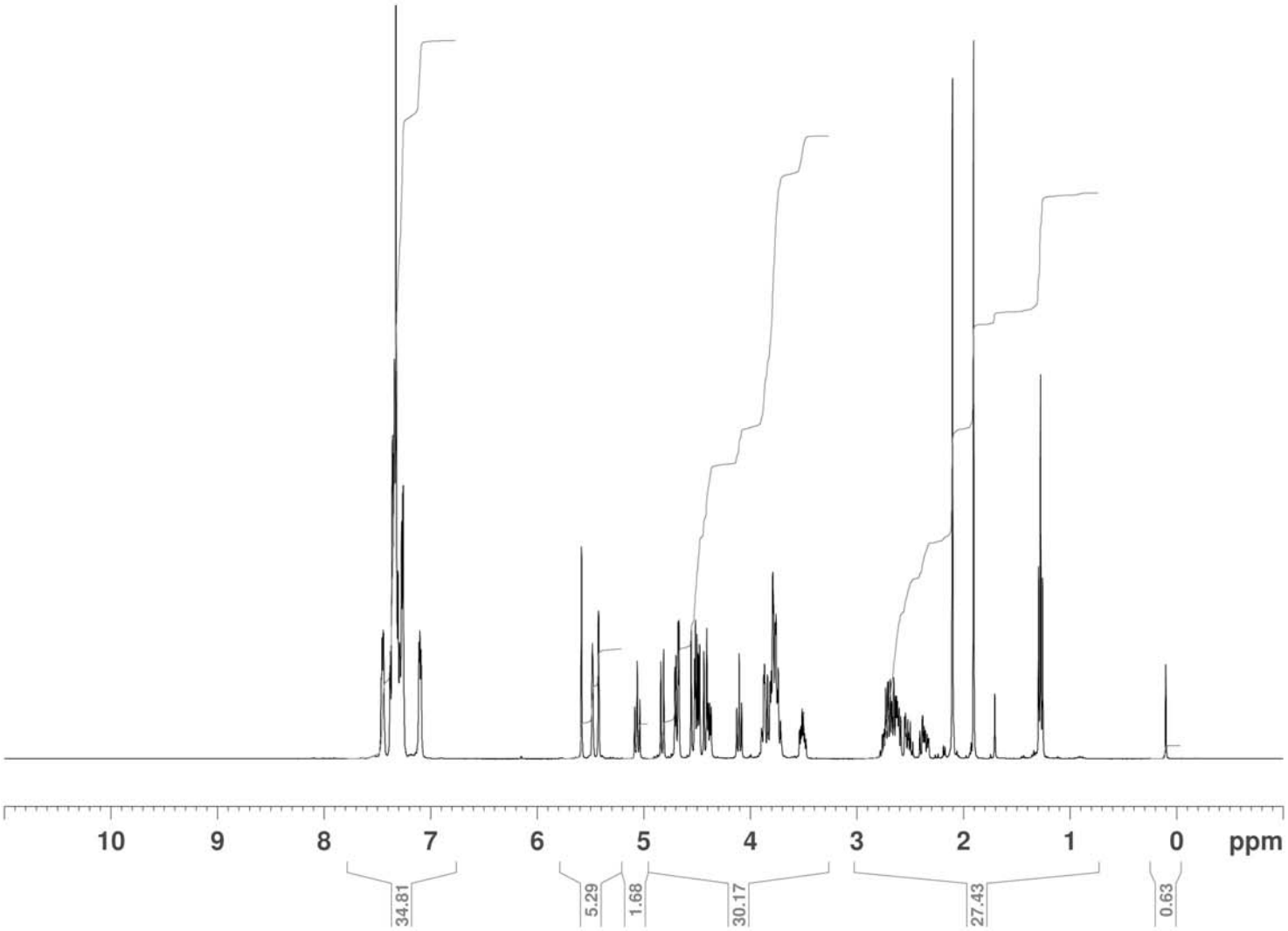
NAME	cb97160807
EXPNO	4
PROCNO	1
Date_	20100708
Time	20.16
INSTRUM	avc500
PROBHD	5 mm CPDUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	1024
DS	2
SWH	31250.000 Hz
FIDRES	0.476837 Hz
AQ	1.0486259 sec
RG	1820
DW	16.000 usec
DE	20.00 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-4.40 dB
PL1W	28.15752029 W
SFO1	125.8131151 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-6.00 dB
PL12	12.42 dB
PL13	120.00 dB
PL2W	15.19999981 W
PL12W	0.21869738 W
PL13W	0.00000000 W
SFO2	500.3020012 MHz
SI	32768
SF	125.8005438 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

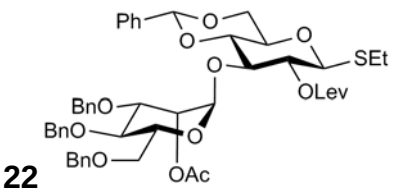


22

NMR@CHEM.OX

NAME	Apr21-2010-59
EXPNO	1
PROCNO	1
Date_	20100421
Time	20.18
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zg60
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	35.9
DW	60.400 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	400.2024714 MHz
SI	32768
SF	400.2000028 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00





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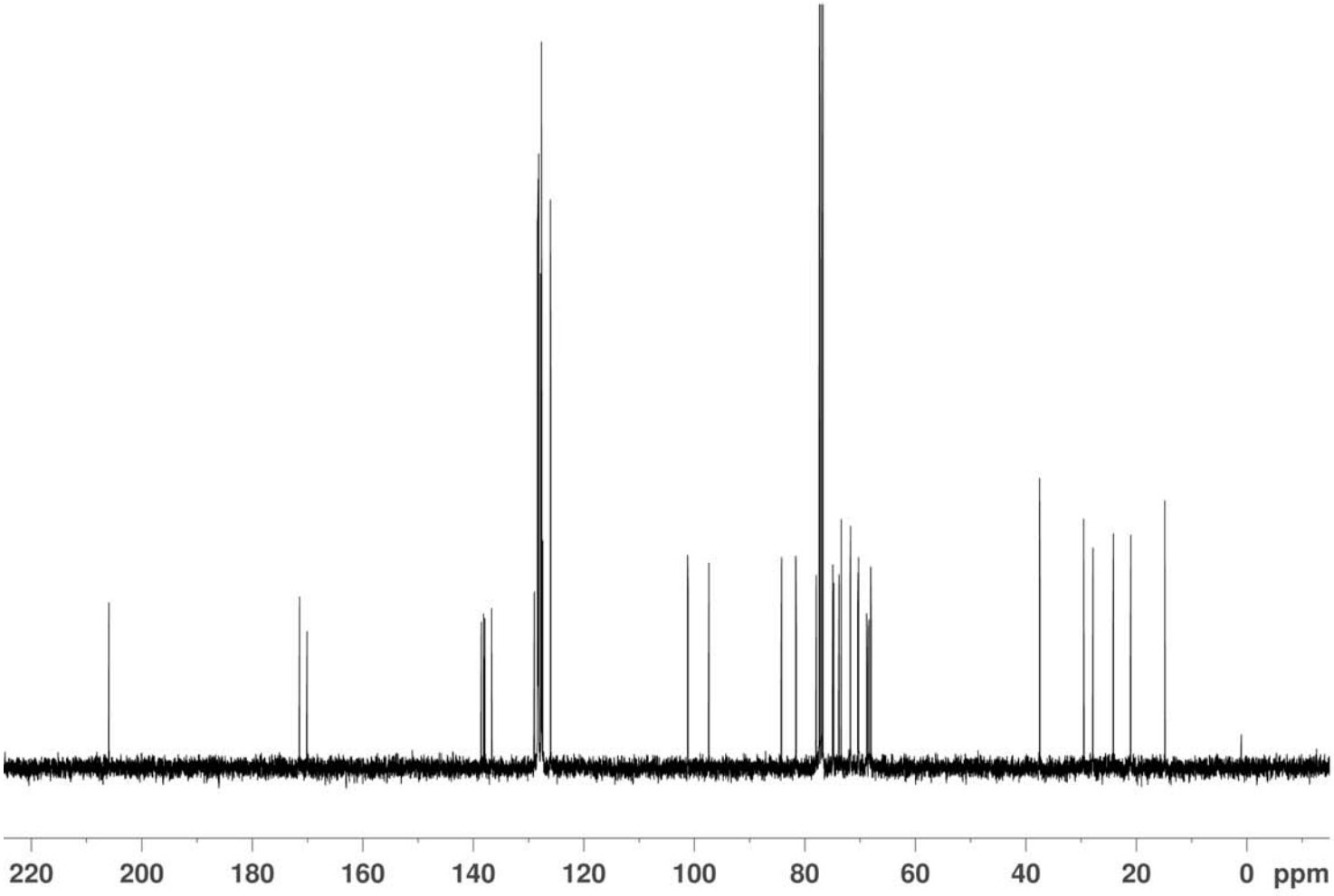

NMR@CHEM.OX

NAME	Apr21-2010-59
EXPNO	2
PROCNO	1
Date_	20100421
Time	20.26
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	32768
SOLVENT	CDC13
NS	256
DS	4
SWH	26178.010 Hz
FIDRES	0.798889 Hz
AQ	0.6259188 sec
RG	32768
DW	19.100 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	0.00 dB
SFO1	100.6403931 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	19.00 dB
PL13	25.00 dB
SFO2	400.2016008 MHz
SI	32768
SF	100.6303718 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

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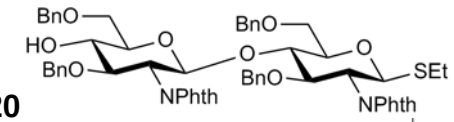

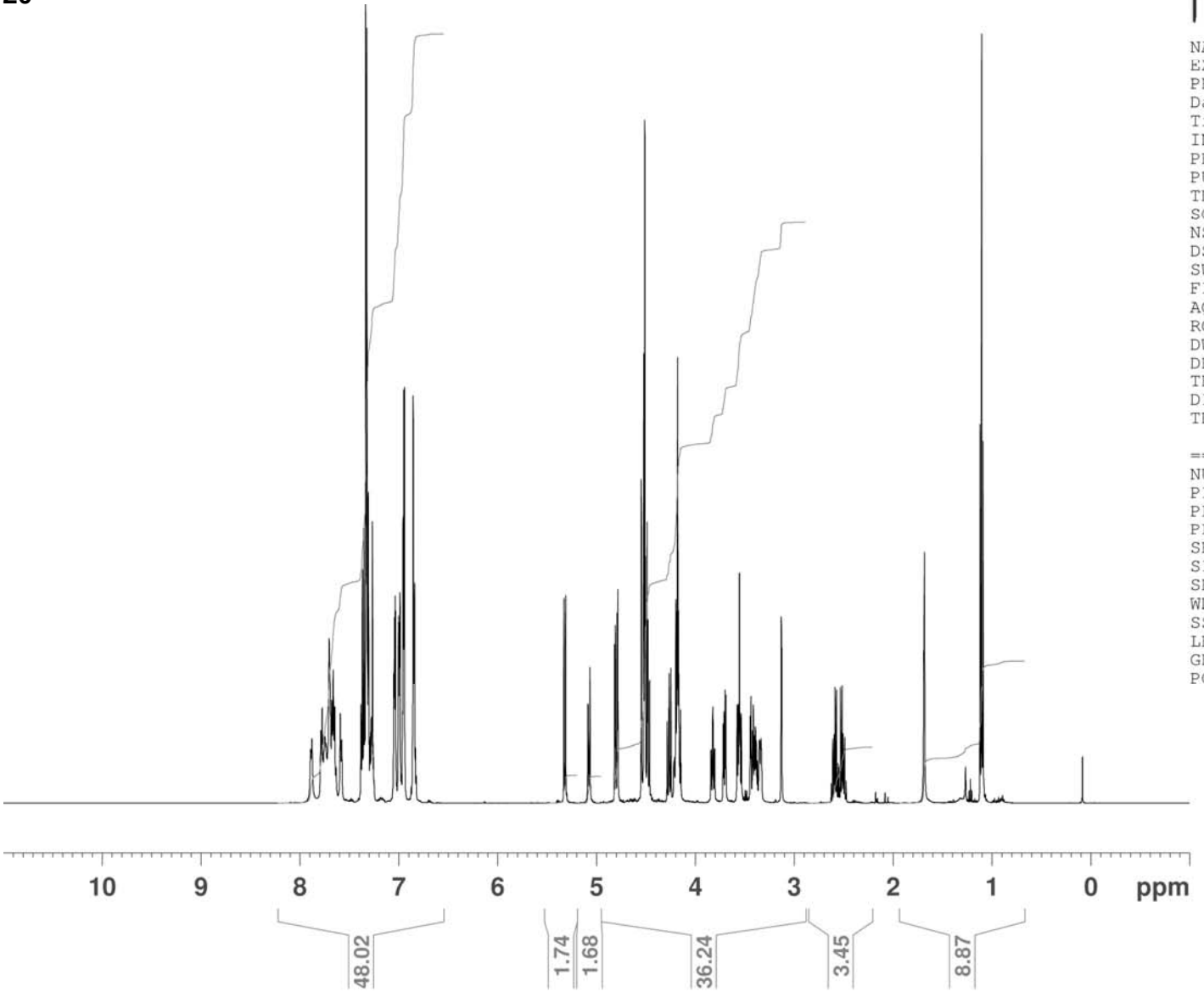

NMR@CHEM.OX

NAME	cb97150807
EXPNO	1
PROCNO	1
Date_	20100708
Time	16.50
INSTRUM	avc500
PROBHD	5 mm CPDUL 13C
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	4
DW	48.400 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.60 usec
PL1	-6.00 dB
PL1W	15.19999981 W
SFO1	500.3030896 MHz
SI	32768
SF	500.3000240 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

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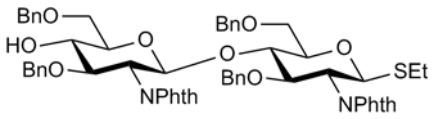

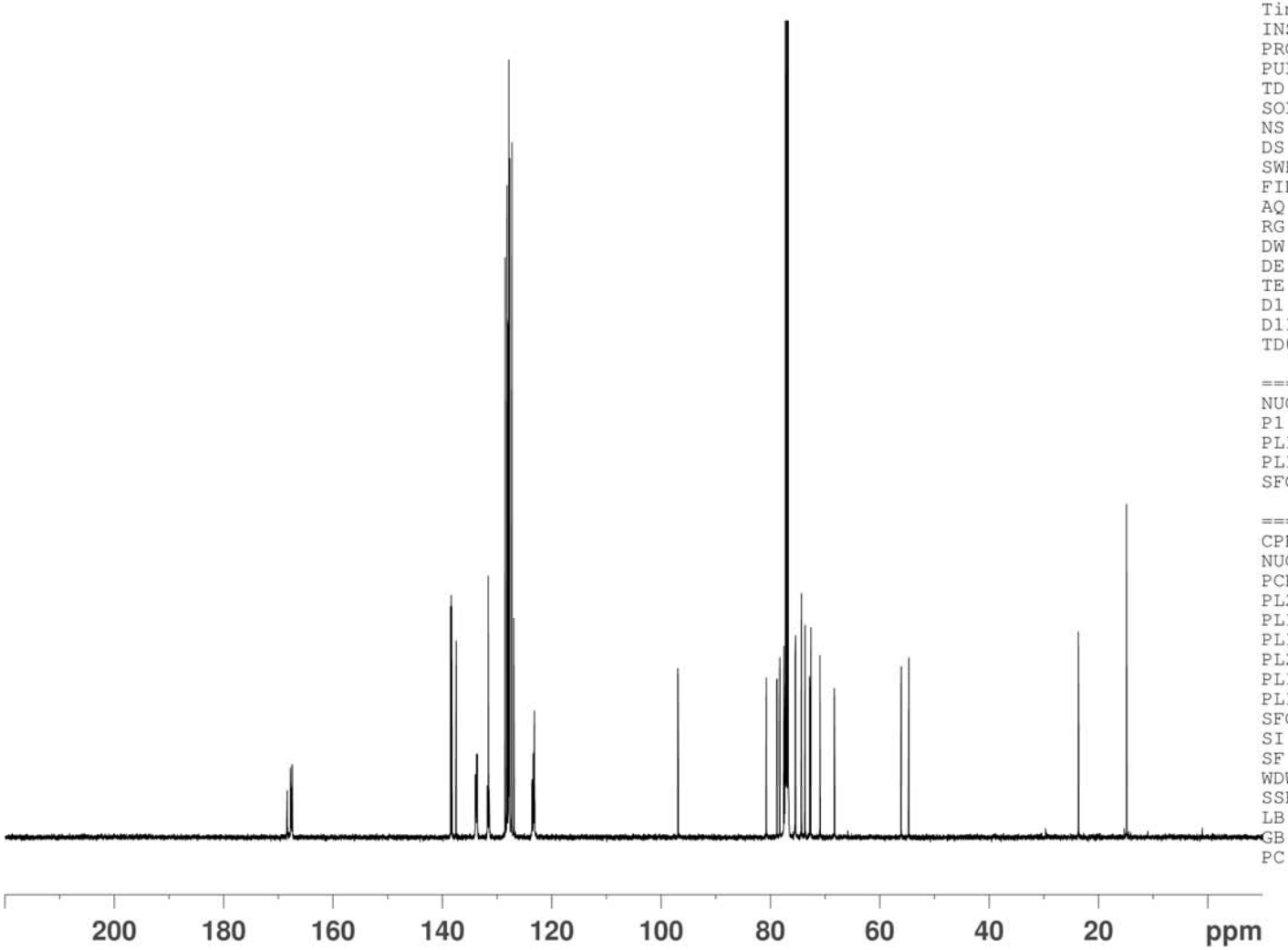

NMR@CHEM.OX

NAME	cb97150807
EXPNO	4
PROCNO	1
Date_	20100708
Time	18.00
INSTRUM	avc500
PROBHD	5 mm CPDUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	1024
DS	2
SWH	31250.000 Hz
FIDRES	0.476837 Hz
AQ	1.0486259 sec
RG	1820
DW	16.000 usec
DE	20.00 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-4.40 dB
PL1W	28.15752029 W
SFO1	125.8131151 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-6.00 dB
PL12	12.42 dB
PL13	120.00 dB
PL2W	15.19999981 W
PL12W	0.21869738 W
PL13W	0.00000000 W
SFO2	500.3020012 MHz
SI	32768
SF	125.8005438 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

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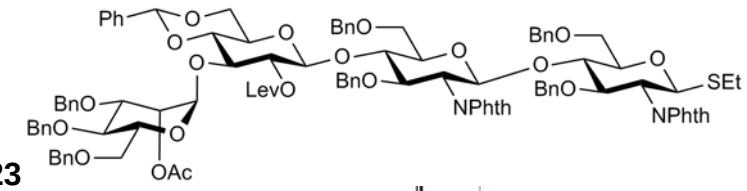
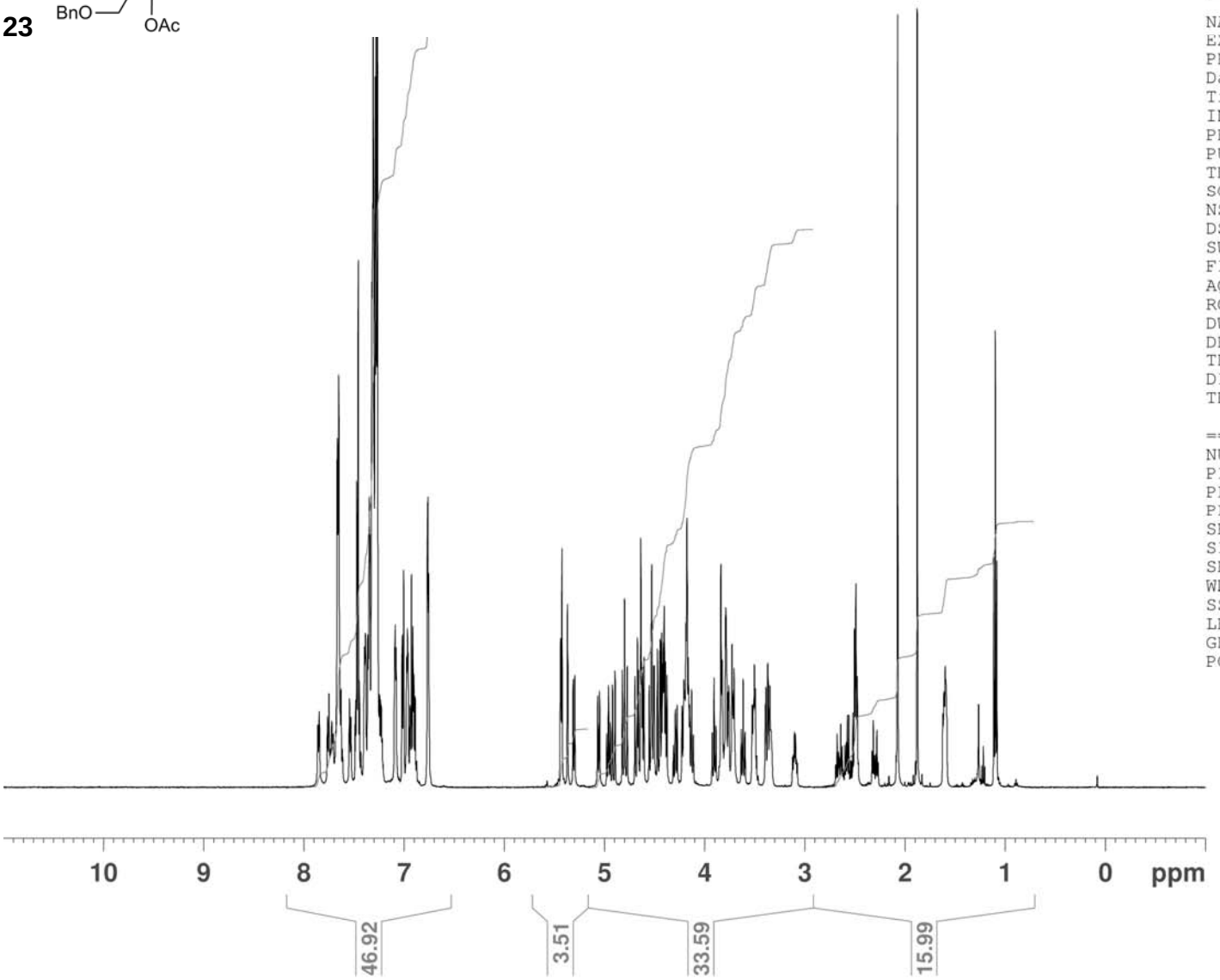


NMR@CHEM.OX

NAME	cb97170807
EXPNO	1
PROCNO	1
Date_	20100708
Time	21.23
INSTRUM	avc500
PROBHD	5 mm CPDUL 13C
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	4
DW	48.400 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.60 usec
PL1	-6.00 dB
PL1W	15.19999981 W
SFO1	500.3030896 MHz
SI	32768
SF	500.3000240 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



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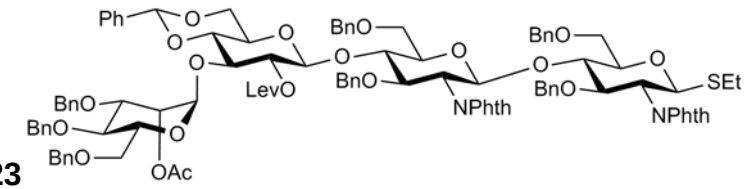

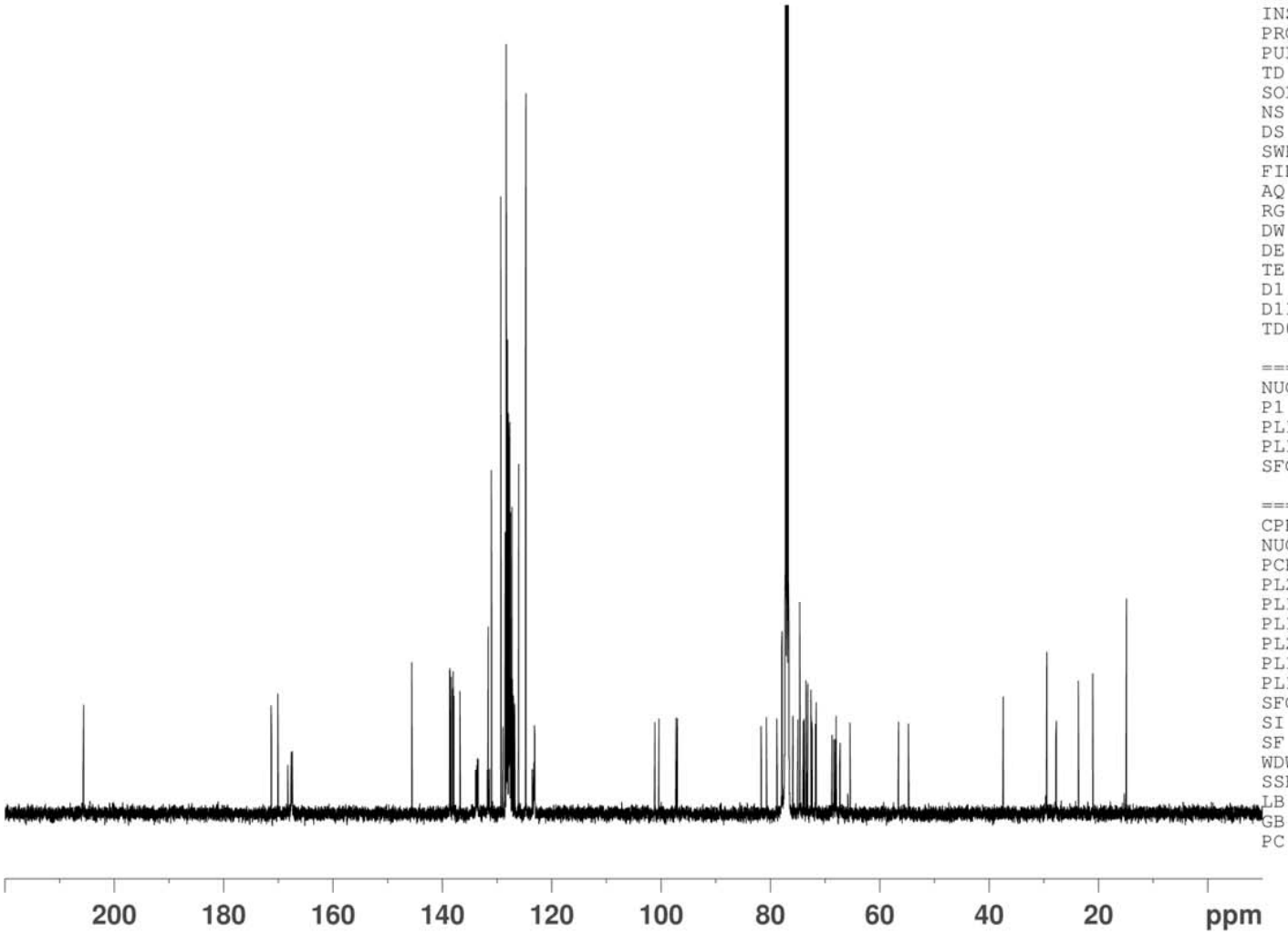

NMR@CHEM.OX

NAME	cb97170807
EXPNO	4
PROCNO	1
Date_	20100708
Time	22.33
INSTRUM	avc500
PROBHD	5 mm CPDUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	1024
DS	2
SWH	31250.000 Hz
FIDRES	0.476837 Hz
AQ	1.0486259 sec
RG	1820
DW	16.000 usec
DE	20.00 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-4.40 dB
PL1W	28.15752029 W
SFO1	125.8131151 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-6.00 dB
PL12	12.42 dB
PL13	120.00 dB
PL2W	15.19999981 W
PL12W	0.21869738 W
PL13W	0.00000000 W
SFO2	500.3020012 MHz
SI	32768
SF	125.8005438 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

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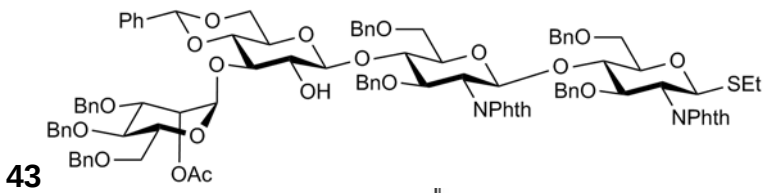
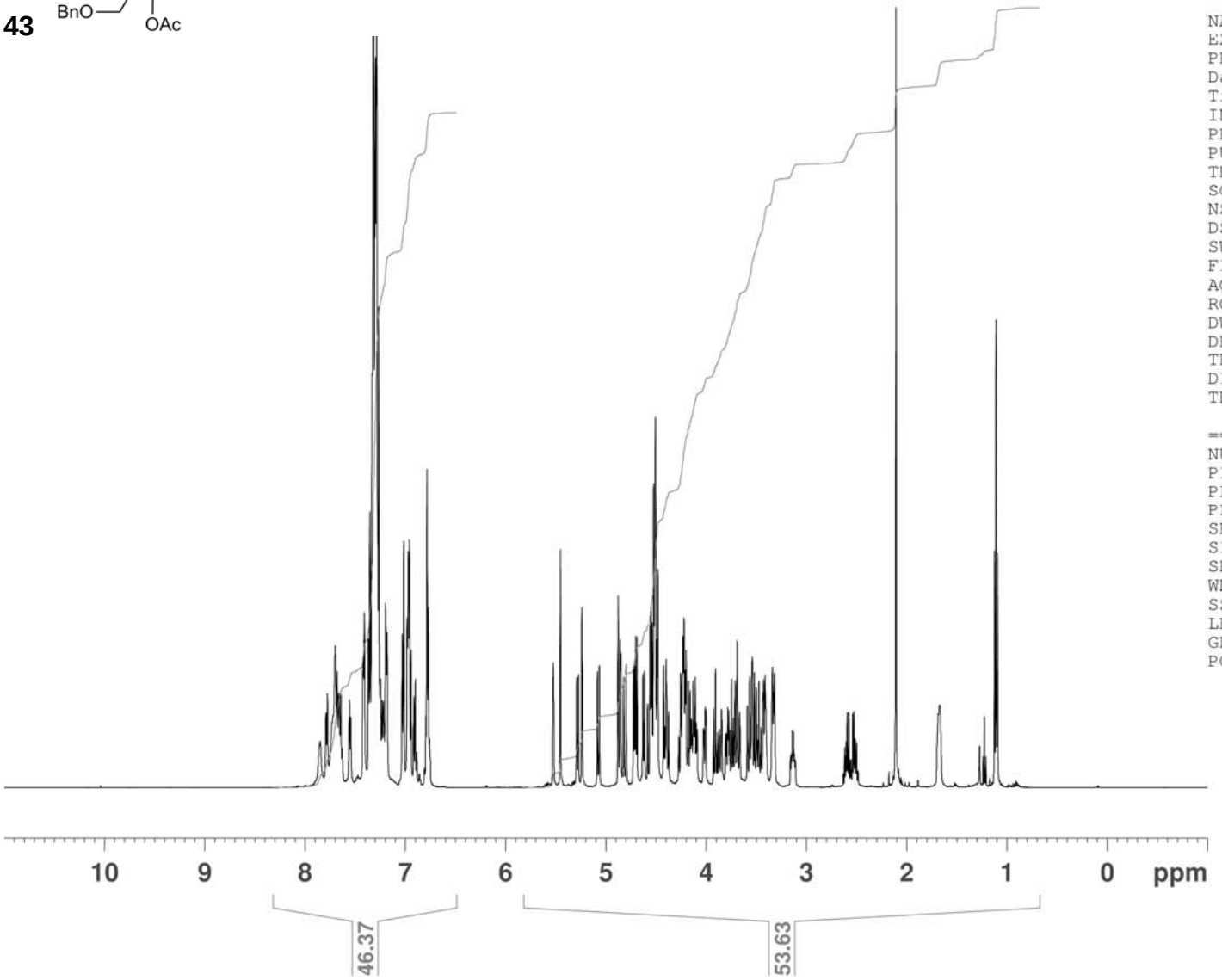
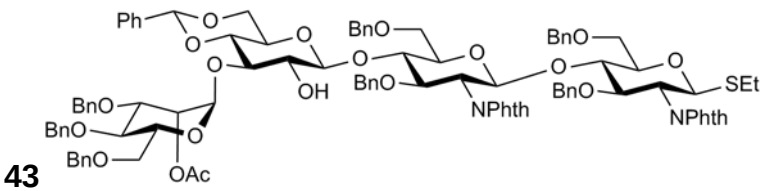




NMR@CHEM.OX

NAME	cb97180807
EXPNO	1
PROCNO	1
Date_	20100708
Time	23.40
INSTRUM	avc500
PROBHD	5 mm CPDUL 13C
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	4
DW	48.400 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.60 usec
PL1	-6.00 dB
PL1W	15.19999981 W
SFO1	500.3030896 MHz
SI	32768
SF	500.3000240 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



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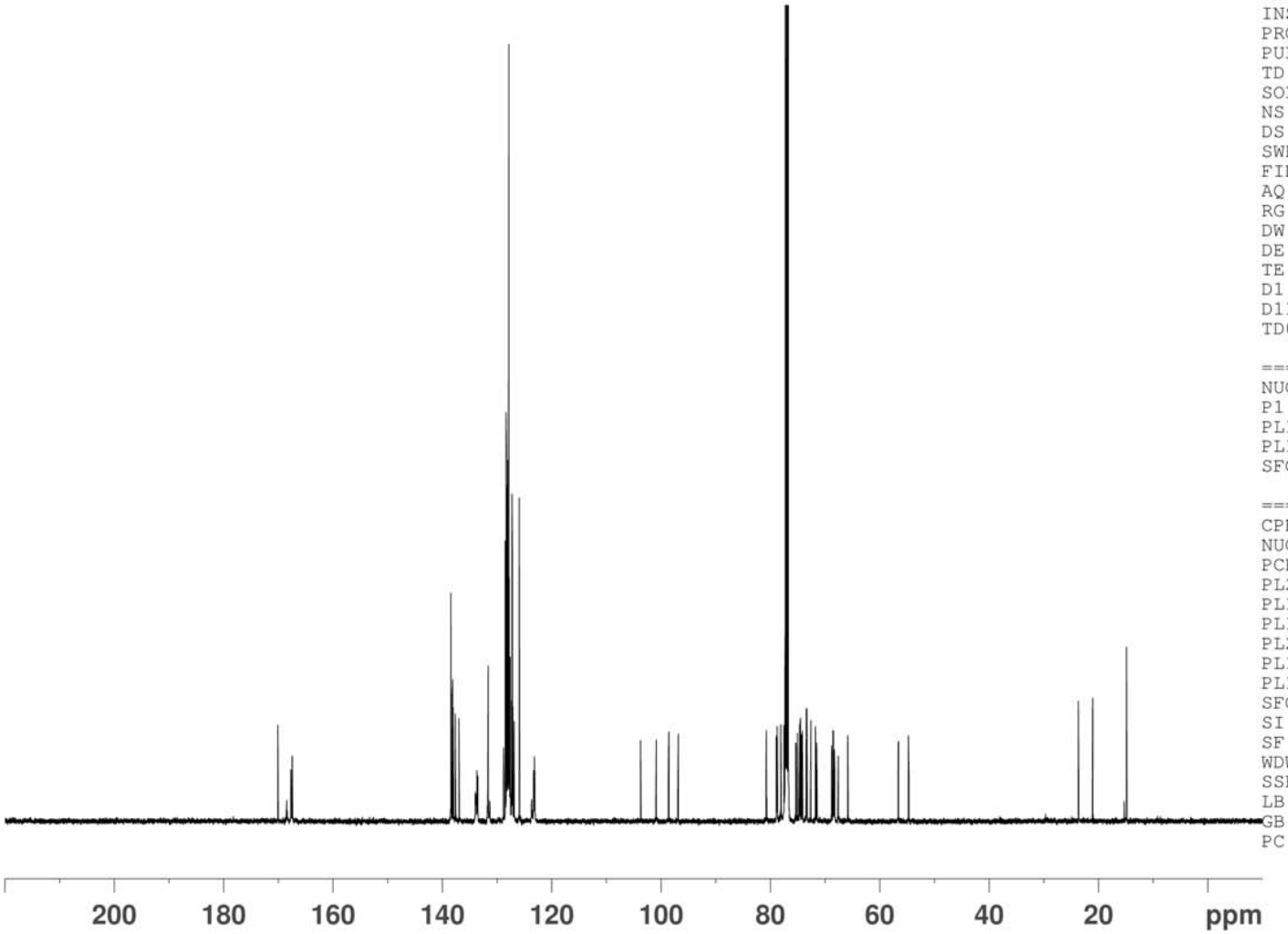
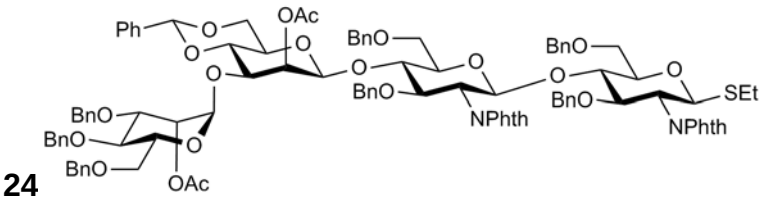


NMR@CHEM.OX

NAME	cb97180807
EXPNO	4
PROCNO	1
Date_	20100709
Time	0.50
INSTRUM	avc500
PROBHD	5 mm CPDUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	1024
DS	2
SWH	31250.000 Hz
FIDRES	0.476837 Hz
AQ	1.0486259 sec
RG	1820
DW	16.000 usec
DE	20.00 usec
TE	298.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-4.40 dB
PL1W	28.15752029 W
SFO1	125.8131151 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-6.00 dB
PL12	12.42 dB
PL13	120.00 dB
PL2W	15.19999981 W
PL12W	0.21869738 W
PL13W	0.00000000 W
SFO2	500.3020012 MHz
SI	32768
SF	125.8005438 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



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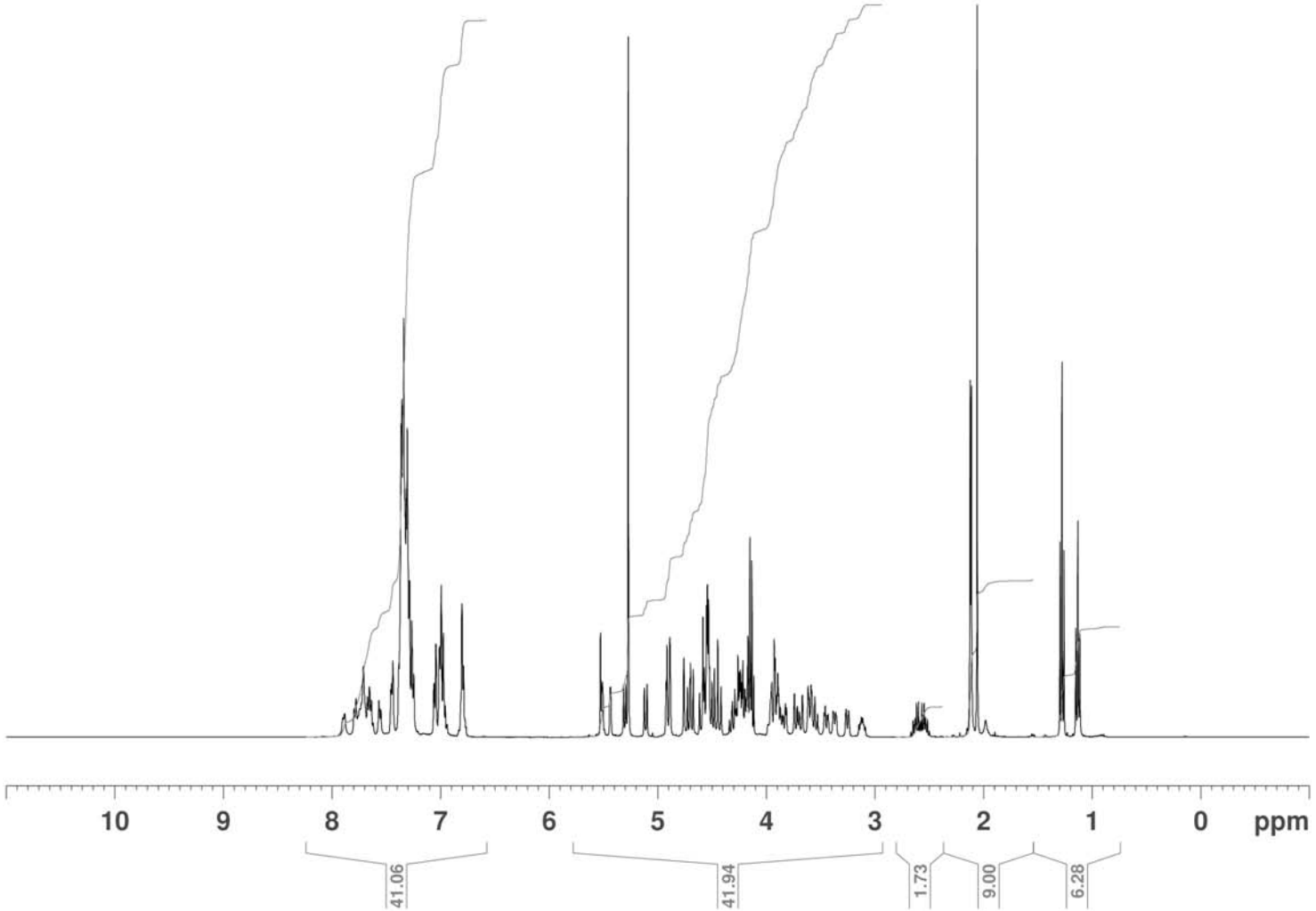
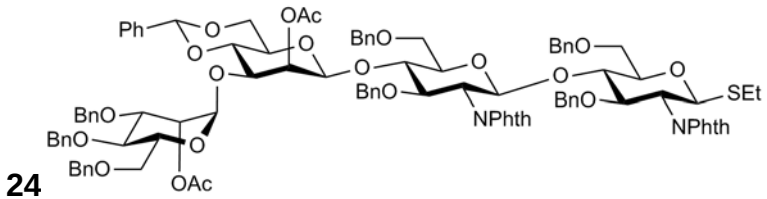
NMR@CHEM.OX

NAME	Jun26-2010-48
EXPNO	1
PROCNO	1
Date_	20100626
Time	12.30
INSTRUM	av400
PROBHD	5 mm QNP 1H/13
PULPROG	zg60
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	20.2
DW	60.400 usec
DE	7.50 usec
TE	300.0 K
D1	1.00000000 sec
======== CHANNEL f1 ========	
NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	400.2024714 MHz
SI	32768
SF	400.2000028 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00





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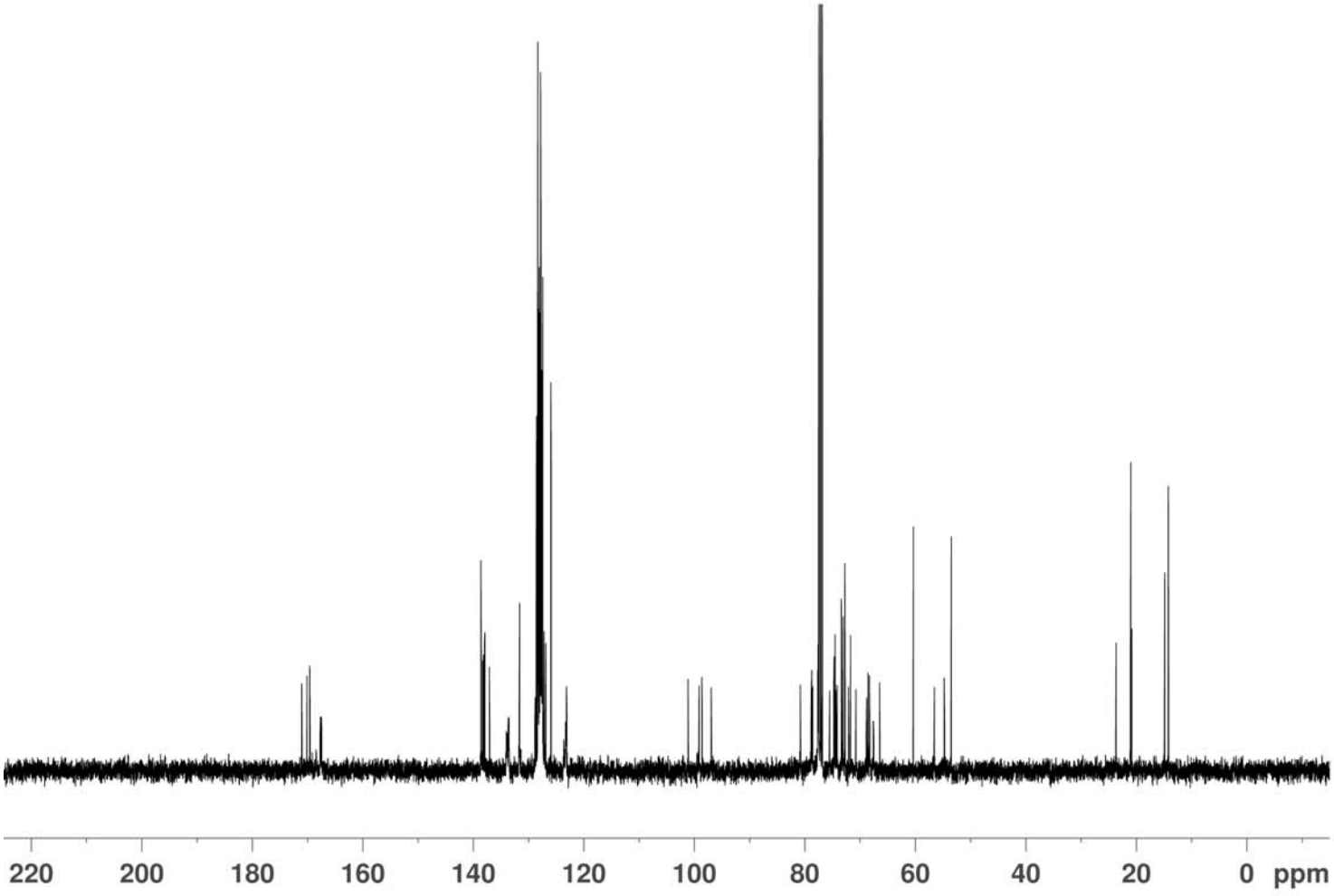

NMR@CHEM.OX

NAME	Jun26-2010-48	
EXPNO	2	
PROCNO	1	
Date_	20100626	
Time	12.38	
INSTRUM	av400	
PROBHD	5 mm QNP 1H/13	
PULPROG	zgpg30	
TD	32768	
SOLVENT	CDC13	
NS	256	
DS	4	
SWH	26178.010	Hz
FIDRES	0.798889	Hz
AQ	0.6259188	sec
RG	32768	
DW	19.100	usec
DE	7.50	usec
TE	300.0	K
D1	1.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	0.00	dB
SFO1	100.6403931	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	0.00	dB
PL12	19.00	dB
PL13	25.00	dB
SFO2	400.2016008	MHz
SI	32768	
SF	100.6303718	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

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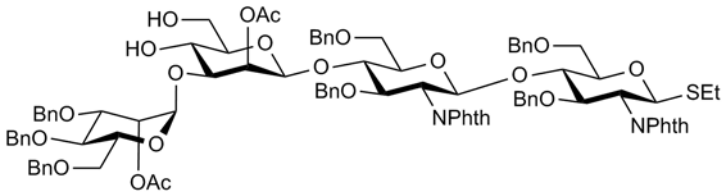
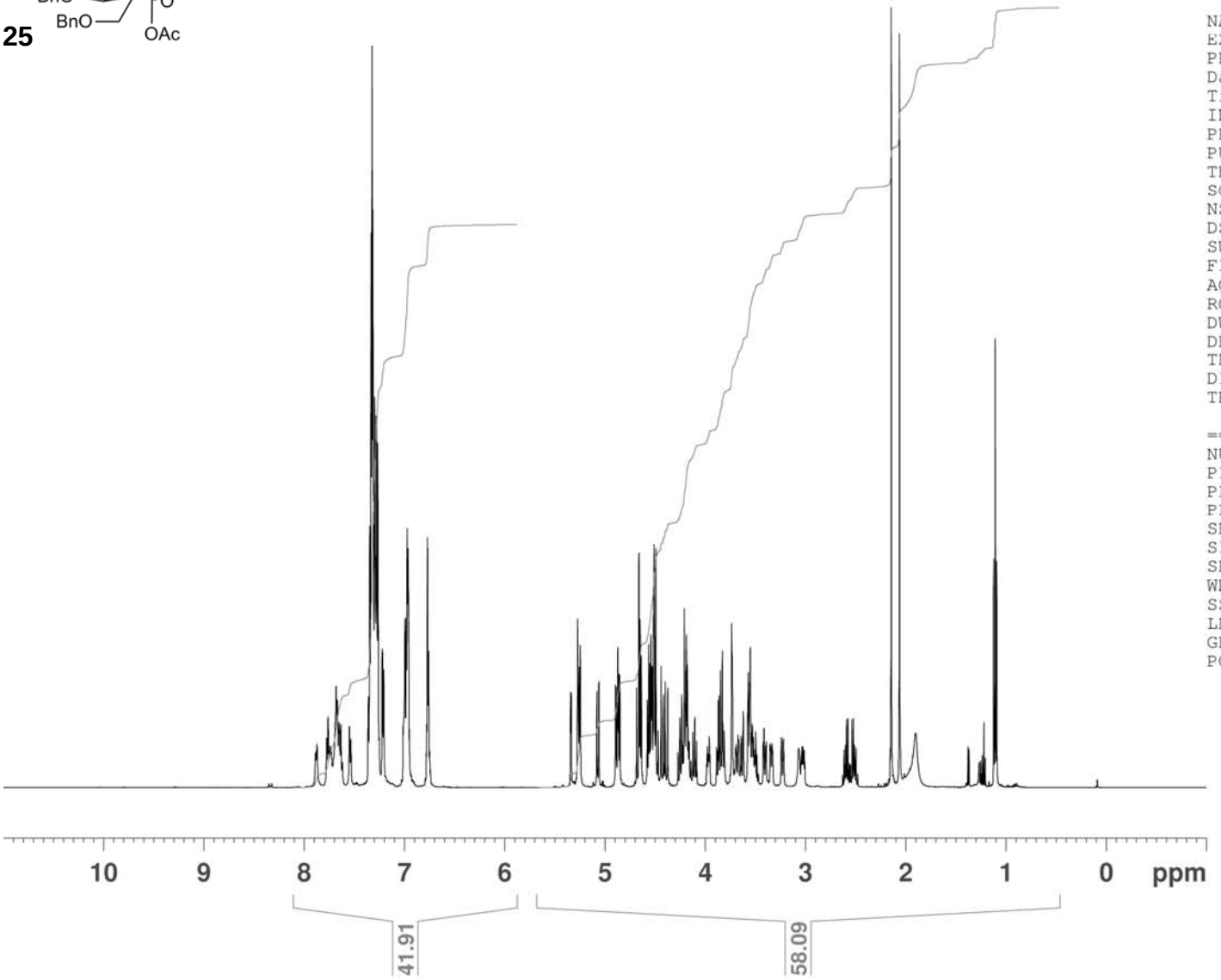
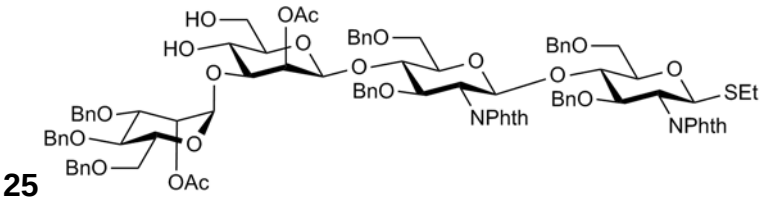




NMR@CHEM.OX

NAME	cb97190807
EXPNO	1
PROCNO	1
Date_	20100709
Time	1.58
INSTRUM	avc500
PROBHD	5 mm CPDUL 13C
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	4
DW	48.400 usec
DE	6.00 usec
TE	298.0 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	9.60 usec
PL1	-6.00 dB
PL1W	15.19999981 W
SFO1	500.3030896 MHz
SI	32768
SF	500.3000240 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



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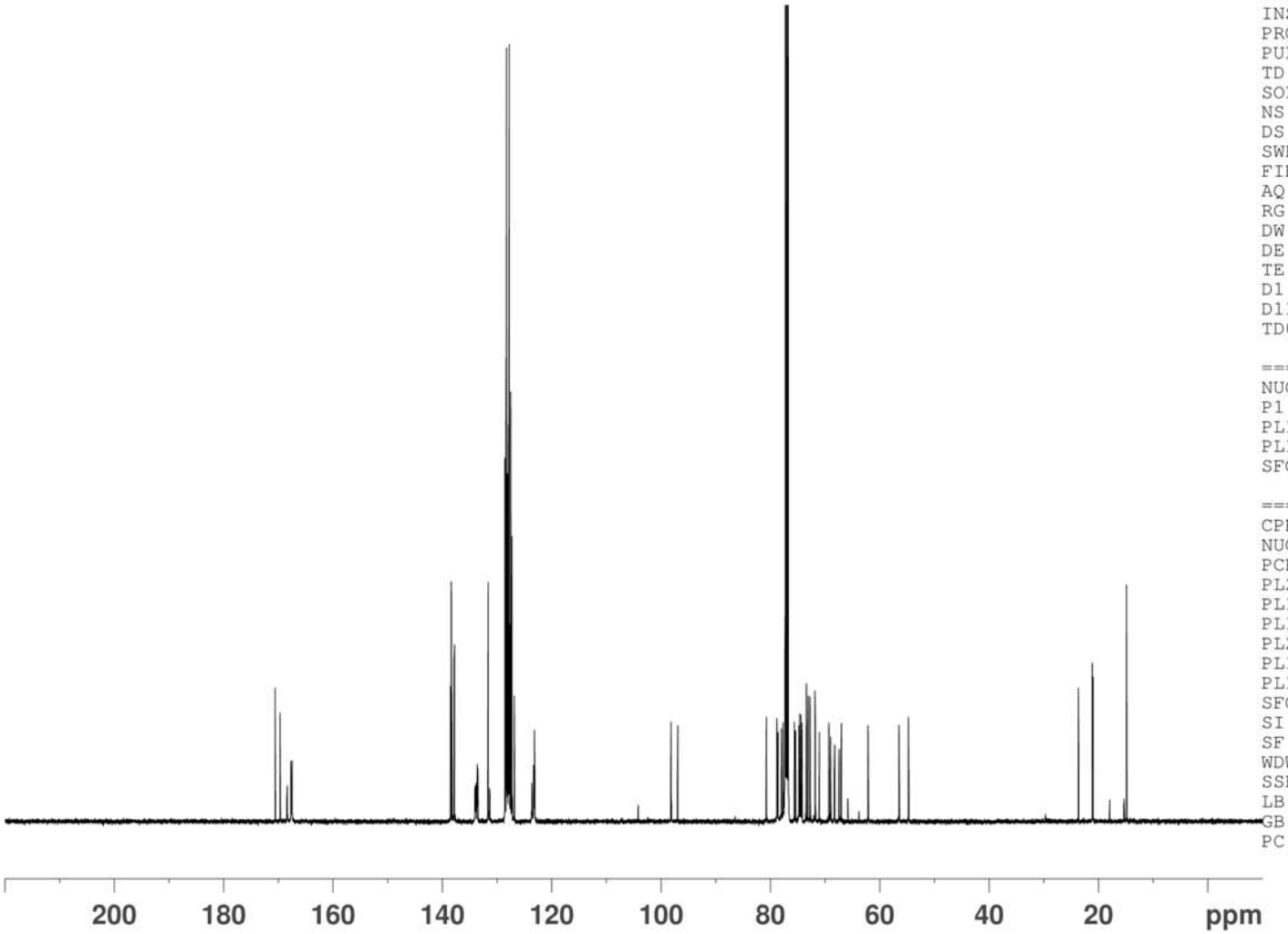
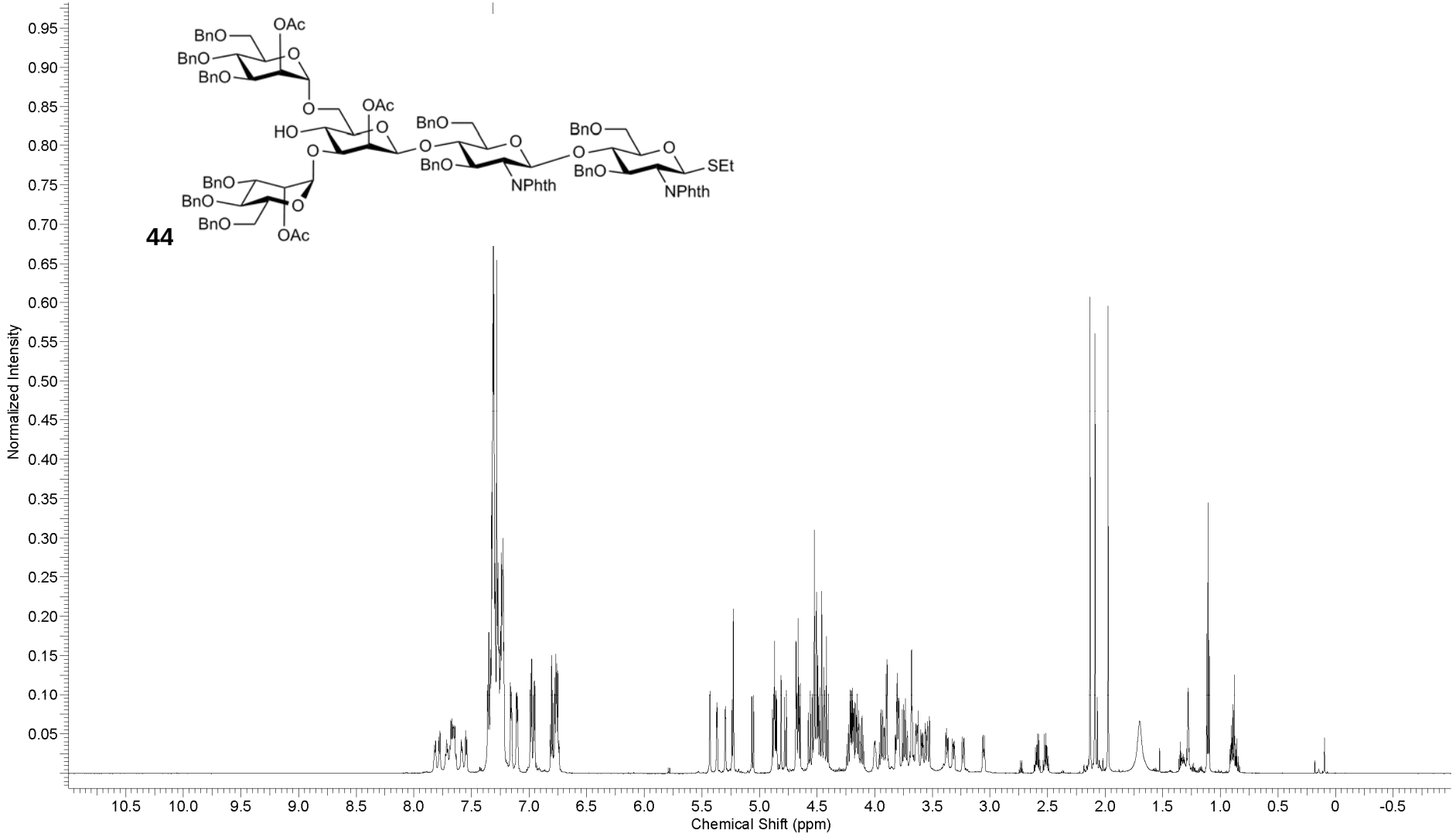


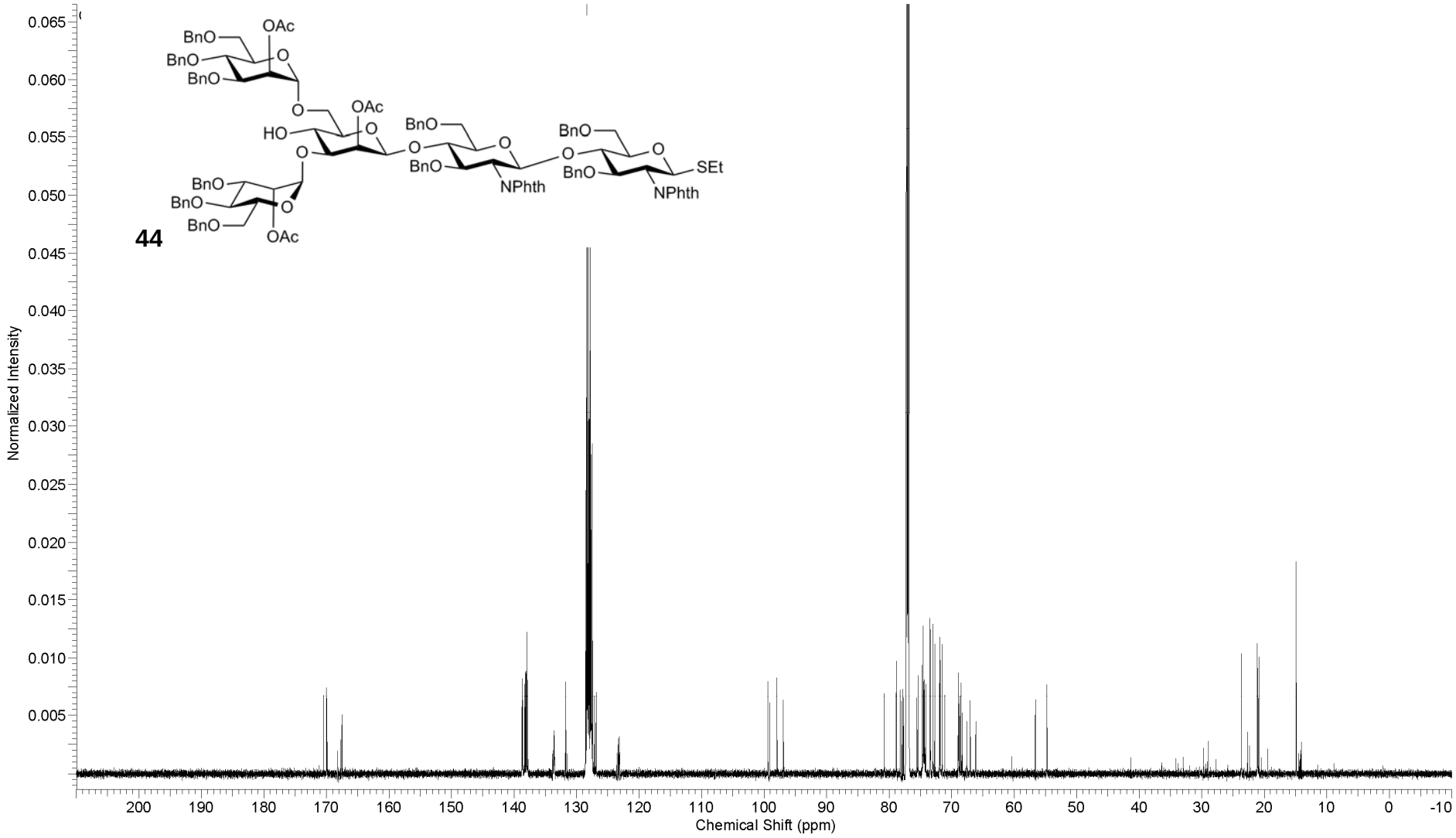
NMR@CHEM.OX

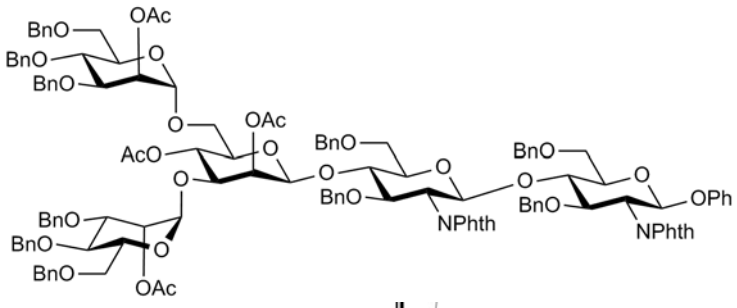
NAME	cb97190807
EXPNO	4
PROCNO	1
Date_	20100709
Time	3.07
INSTRUM	avc500
PROBHD	5 mm CPDUL 13C
PULPROG	zgpg30
TD	65536
SOLVENT	CDC13
NS	1024
DS	2
SWH	31250.000 Hz
FIDRES	0.476837 Hz
AQ	1.0486259 sec
RG	1820
DW	16.000 usec
DE	20.00 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-4.40 dB
PL1W	28.15752029 W
SFO1	125.8131151 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	-6.00 dB
PL12	12.42 dB
PL13	120.00 dB
PL2W	15.19999981 W
PL12W	0.21869738 W
PL13W	0.00000000 W
SFO2	500.3020012 MHz
SI	32768
SF	125.8005438 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Acquisition Time (sec)	2.9360	***Comment***	AV700 1H CONNOR BARRY 2751 25/2/11			***Date***	25 Feb 2011 10:01:36
Date Stamp	25 Feb 2011 10:01:36			***File Name***	C:\WORK DRIVE\DATA\NMR\FIDS\CB414-4_AVC700_CB27512502\1\PDATA\1\1R		
Frequency (MHz)	699.99	***Nucleus***	1H	***Number of Transients***	16	***Origin***	av700
Original Points Count	32768	***Owner***	dp-nmrgroup	***Points Count***	65536	***Pulse Sequence***	zg60
Receiver Gain	4.00	***SW(cyclical) (Hz)***	11160.71	***Solvent***	CHLOROFORM-d		
Spectrum Offset (Hz)	3499.9480	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	11160.54	***Temperature (degree C)***	25.020



Acquisition Time (sec)	0.7864	***Comment***	AV700 13C CONNOR BARRY 2751 25/2/11			***Date***	25 Feb 2011 14:38:56
Date Stamp	25 Feb 2011 14:38:56			***File Name***	C:\WORK DRIVE\DATA\NMR\FIDS\CB414-4_AVC700_CB27512502\7\PDATA\1\1R		
Frequency (MHz)	176.01	***Nucleus***	13C	***Number of Transients***	2902	***Origin***	av700
Original Points Count	32768	***Owner***	dp-nmrgroup	***Points Count***	65536	***Pulse Sequence***	zgpg30
Receiver Gain	2050.00	***SW(cyclical) (Hz)***	41666.67	***Solvent***	CHLOROFORM-d	***Spectrum Offset (Hz)***	17600.7637
Spectrum Type	STANDARD	***Sweep Width (Hz)***	41666.03	***Temperature (degree C)***	25.020		





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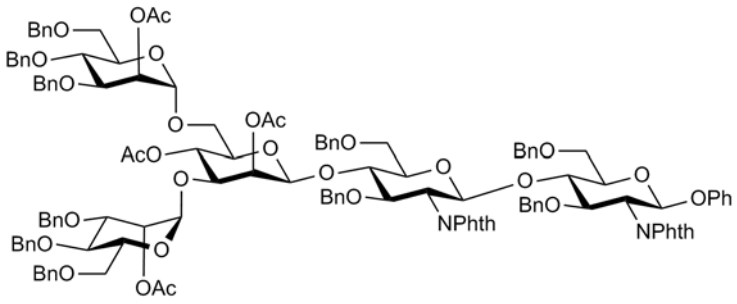
NMR@CHEM.OX

NAME	cb04880109	
EXPNO	1	
PROCNO	1	
Date_	20100901	
Time	17.54	
INSTRUM	avc500	
PROBHD	5 mm CPDUL 13C	
PULPROG	zg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	10330.578	Hz
FIDRES	0.157632	Hz
AQ	3.1719923	sec
RG	4	
DW	48.400	usec
DE	6.00	usec
TE	302.5	K
D1	1.00000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	1H	
P1	9.60	usec
PL1	-6.00	dB
PL1W	15.19999981	W
SFO1	500.3030896	MHz
SI	32768	
SF	500.3000240	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	



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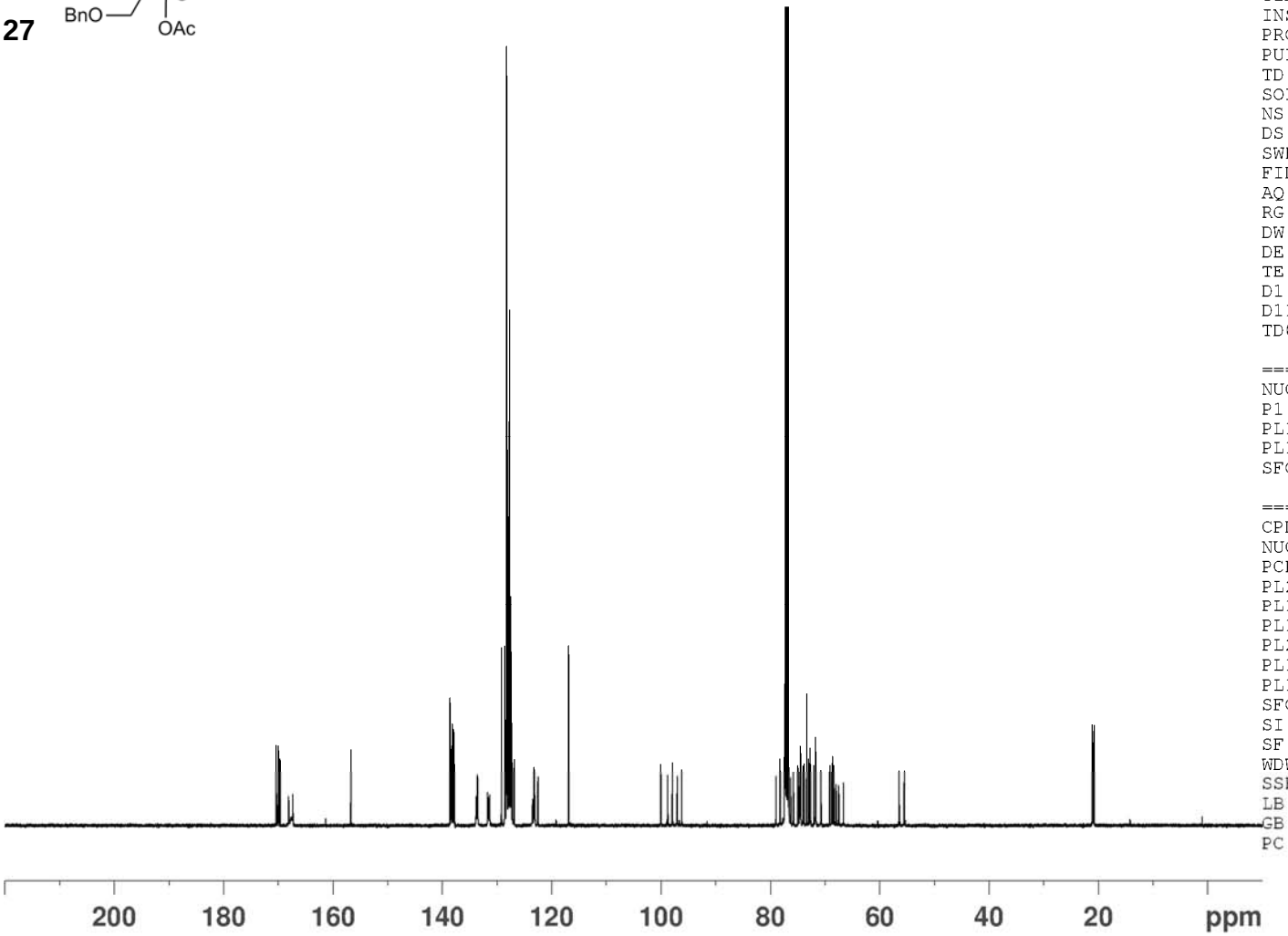
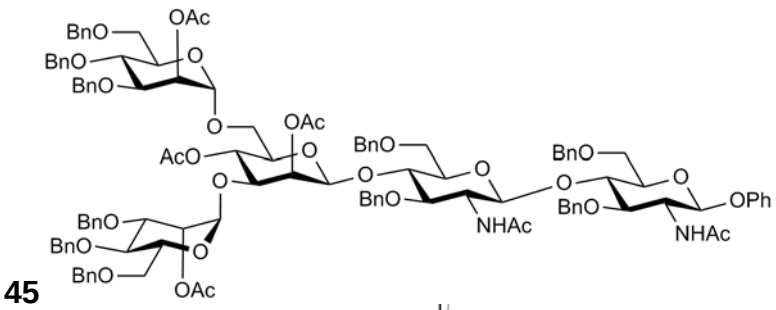


NMR@CHEM.OX

NAME	cb04880109	
EXPNO	4	
PROCNO	1	
Date_	20100901	
Time	19.03	
INSTRUM	avc500	
PROBHD	5 mm CPDUL 13C	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	1024	
DS	2	
SWH	31250.000	Hz
FIDRES	0.476837	Hz
AQ	1.0486259	sec
RG	1820	
DW	16.000	usec
DE	20.00	usec
TE	302.5	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-4.40	dB
PL1W	28.15752029	W
SFO1	125.8131151	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	-6.00	dB
PL12	12.42	dB
PL13	120.00	dB
PL2W	15.19999981	W
PL12W	0.21869738	W
PL13W	0.00000000	W
SFO2	500.3020012	MHz
SI	32768	
SF	125.8005438	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	



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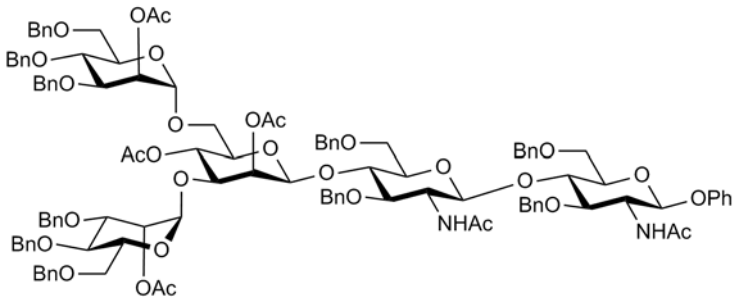
NMR@CHEM.OX

NAME	cb04950109	
EXPNO	1	
PROCNO	1	
Date_	20100902	
Time	4.48	
INSTRUM	avc500	
PROBHD	5 mm CPDUL 13C	
PULPROG	zg30	
TD	65536	
SOLVENT	CDCl3	
NS	16	
DS	2	
SWH	10330.578	Hz
FIDRES	0.157632	Hz
AQ	3.1719923	sec
RG	4	
DW	48.400	usec
DE	6.00	usec
TE	302.5	K
D1	1.00000000	sec
TD0	1	
========	CHANNEL f1	========
NUC1	1H	
P1	9.60	usec
PL1	-6.00	dB
PL1W	15.19999981	W
SFO1	500.3030896	MHz
SI	32768	
SF	500.3000240	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	



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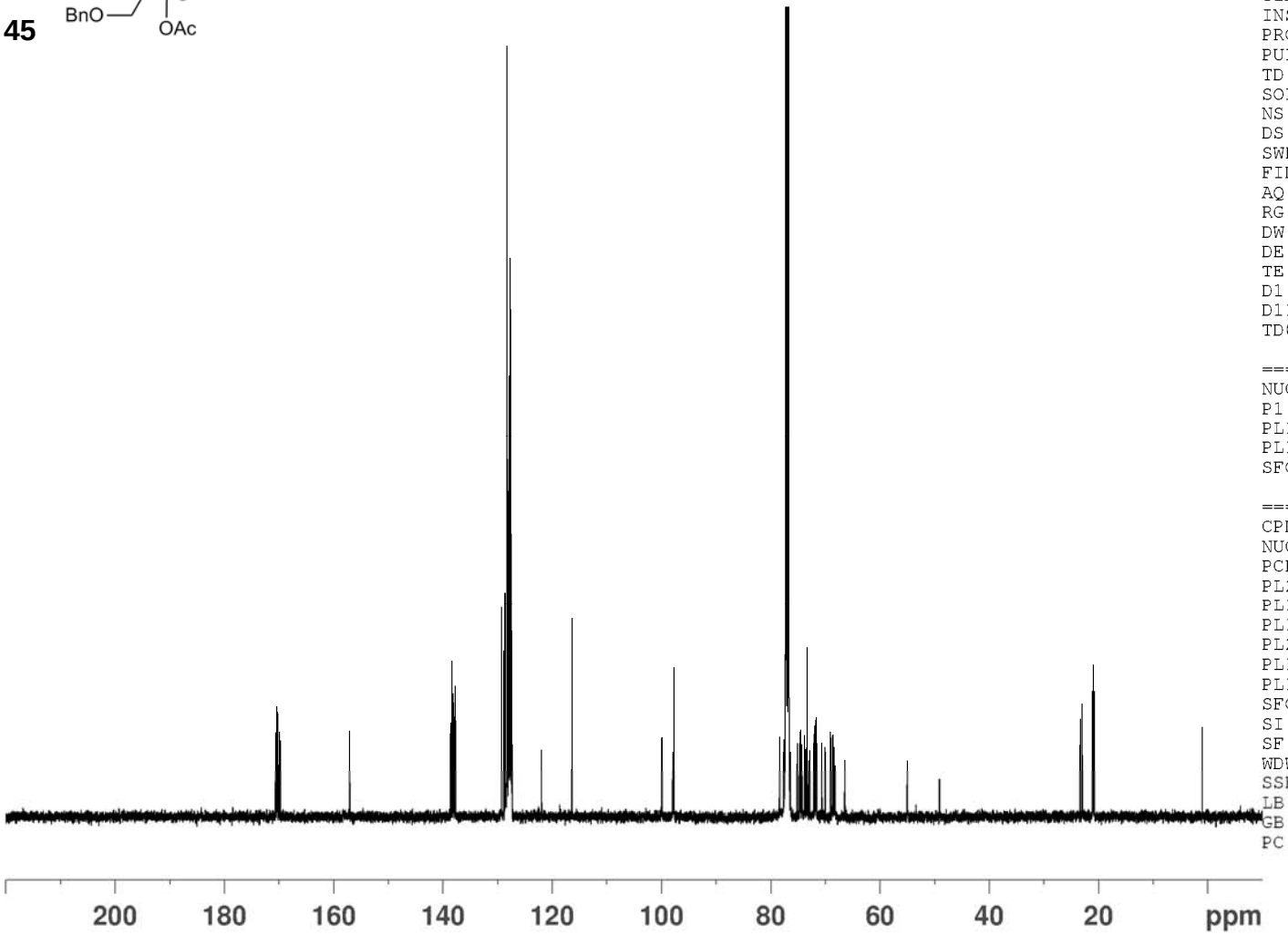
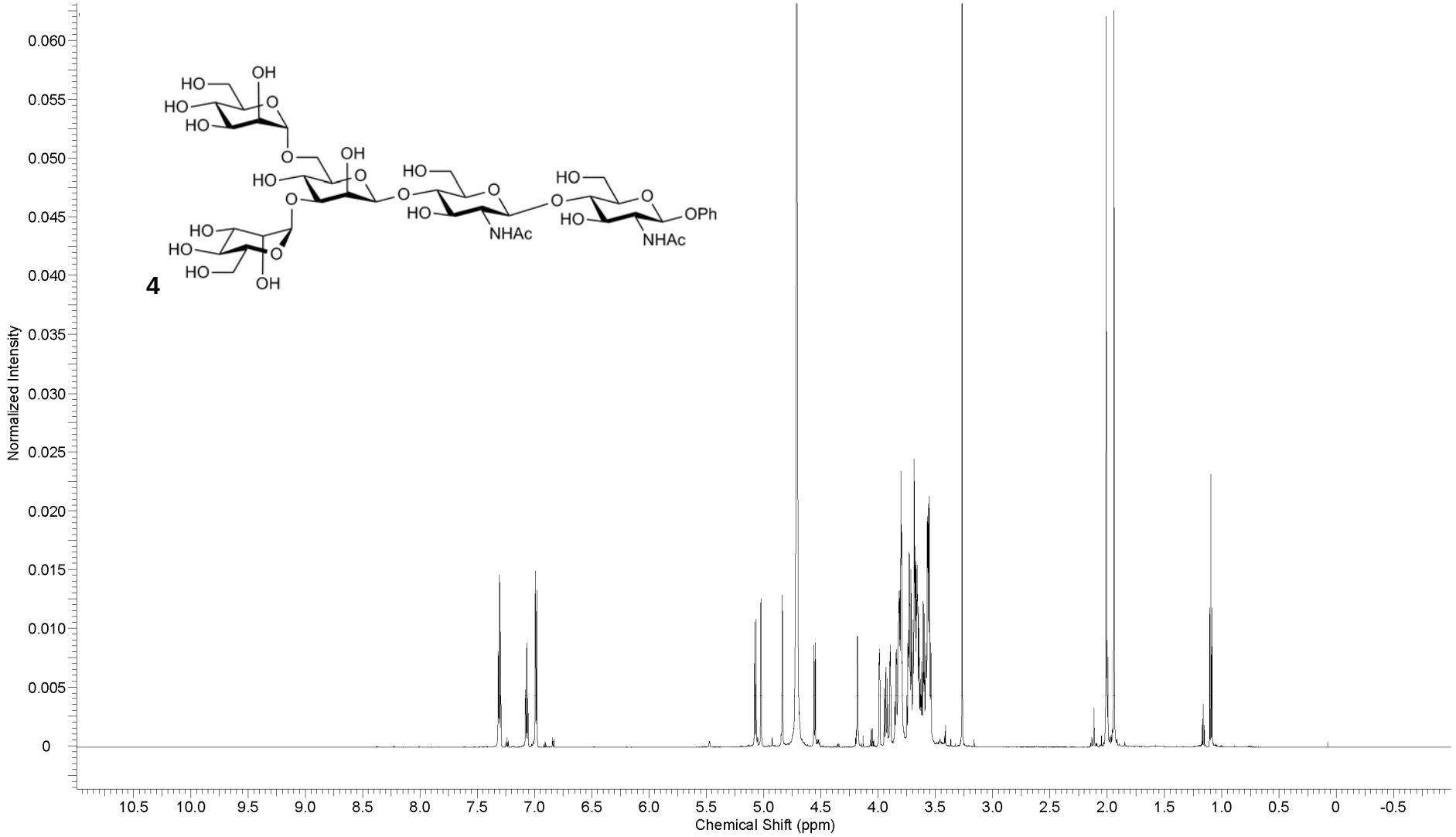


NMR@CHEM.OX

NAME	cb04950109	
EXPNO	4	
PROCNO	1	
Date_	20100902	
Time	5.58	
INSTRUM	avc500	
PROBHD	5 mm CPDUL 13C	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	1024	
DS	2	
SWH	31250.000	Hz
FIDRES	0.476837	Hz
AQ	1.0486259	sec
RG	1820	
DW	16.000	usec
DE	20.00	usec
TE	302.5	K
D1	2.00000000	sec
D11	0.03000000	sec
TD0	1	
======== CHANNEL f1 ========		
NUC1	13C	
P1	9.50	usec
PL1	-4.40	dB
PL1W	28.15752029	W
SFO1	125.8131151	MHz
======== CHANNEL f2 ========		
CPDPRG2	waltz16	
NUC2	1H	
PCPD2	80.00	usec
PL2	-6.00	dB
PL12	12.42	dB
PL13	120.00	dB
PL2W	15.19999981	W
PL12W	0.21869738	W
PL13W	0.00000000	W
SFO2	500.3020012	MHz
SI	32768	
SF	125.8005438	MHz
WDW	EM	
SSB	0	
LB	1.00	Hz
GB	0	
PC	1.40	

Acquisition Time (sec)	2.9360	***Comment***	AV700 1H Conor Barry 20547 17/9./10			***Date***	17 Sep 2010 11:10:08
Date Stamp	17 Sep 2010 11:10:08			***File Name***	C:\WORK DRIVE\DATA\NMR\FIDS\CB404-1_AV700\1\PDATA\1\1R		
Frequency (MHz)	699.99	***Nucleus***	1H	***Number of Transients***	16	***Origin***	av700
Original Points Count	32768	***Owner***	dp-nmrgroup	***Points Count***	65536	***Pulse Sequence***	zg60
Receiver Gain	6.35	***SW(cyclical) (Hz)***	11160.71	***Solvent***	DEUTERIUM OXIDE		
Spectrum Offset (Hz)	3499.9480	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	11160.54	***Temperature (degree C)***	25.020



Acquisition Time (sec)	0.7864	***Comment***	AV700 13C CONNOR BARRY 0547 17/9/10			***Date***	17 Sep 2010 15:36:48
Date Stamp	17 Sep 2010 15:36:48			***File Name***	C:\WORK DRIVE\DATA\NMR\FIDS\CB404-1_AV700\7\PDATA\1\1R		
Frequency (MHz)	176.01	***Nucleus***	13C	***Number of Transients***	1525	***Origin***	av700
Original Points Count	32768	***Owner***	dp-nmrgroup	***Points Count***	65536	***Pulse Sequence***	zgpg30
Receiver Gain	2050.00	***SW(cyclical) (Hz)***	41666.67	***Solvent***	DEUTERIUM OXIDE		
Spectrum Offset (Hz)	17600.7637	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	41666.03	***Temperature (degree C)***	25.020