Supplementary Information

Re-writing the Bacterial Glycocalyx via Suzuki-Miyaura Cross-Coupling

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General Considerations

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AV400 (400 MHz) spectrometer. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AV400 (100 MHz) or a Bruker AVII500 (125 MHz) spectrometer as indicated. NMR shifts were assigned using COSY, HSQC and HMBC spectra. 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; D_2O = 4.79; DMSO-d_6 = 2.50 and ^{13}C NMR: $CDCl_3$ = 77.16, DMSO-d_6

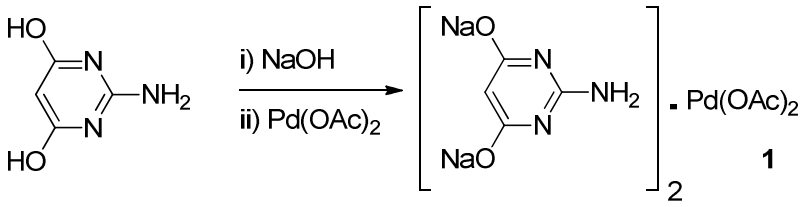
= 39.52). Coupling constants (*J*) are reported in Hz with the following splitting abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, app = apparent, m = multiplet. Melting points (m.p.) were recorded on a Leica Galen III hot stage microscope equipped with a Testo 720 thermocouple probe and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Tensor 27 Fourier Transform spectrophotometer with a diamond ATR module. Absorption maxima (υ_{max}) are reported in wavenumbers (cm^{-1}). 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. 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. Thin layer chromatography (TLC) was carried out using aluminium backed sheets coated with 60F254 silica gel (Merck). Visualization of the silica plates was achieved using a UV lamp (λ_{max} = 254 nm or 318 nm), and/or ammonium molybdate (5 % in 2M H_2SO_4), and/or potassium permanganate (5 % $KMnO_4$ in 1M NaOH with 5 % potassium carbonate). Flash column chromatography was carried out using Geduran Si 60 (40-63 μm) silica (Merck). Mobile phases are reported as % volume of more polar solvent in less polar solvent. Anhydrous solvents were purchased from Acros and used as supplied, with the exception of DCM and THF which were dried through an activated alumina column prior to use. All other solvents were used as supplied (Analytical or HPLC grade), without prior purification. Deionized water was used for chemical reactions and Milli-Q purified water for protein and cellular manipulations. Reagents were purchased from Aldrich and used as supplied, unless otherwise indicated. Bis(pinacolato) diborane was purchased from Frontier Scientific. ‘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 nitrogen. Brine refers to a saturated solution of sodium chloride. Anhydrous magnesium sulfate ($MgSO_4$) or sodium sulphate (Na_2SO_4) were used as the drying agent after reaction workup as specified.

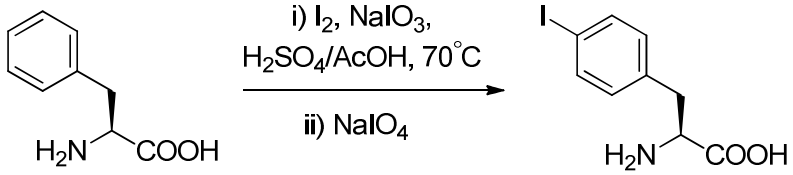
Plasmid pEVOL (*p*IPhe) was generously donated by the group of Prof. P. G. Schultz at The Scripps Institute. *E. coli* cell line JW2203-1, deficient for host OmpC production, was purchased from the Yale *E. coli* Genetic Stock Centre. Plasmid pOmpC was synthesised by Genscript. SDS-PAGE gels were run using pre-cast gels purchased from Invitrogen (NuPAGE 4-12 % Bis-Tris gel), and stained using Instant*Blue*™ (Expedeon). Chloramphenicol and kanamycin were both used at a concentration of 50 mg L^{-1} and ampicillin was used at a concentration of 100 mg L^{-1}. All biological manipulations were undertaken under sterile conditions in a HERAsafe KSP12 laminar flow hood (Thermo Scientific). Fluorescein labelled Lens Culinaris Agglutinin, Griffonia simplicifolia Lectin and Concanavalin A were purchased from Vector Labs

Microscopy experiments were performed on a Leica Microsystems SP5 Inverted Confocal Microscope. All experiments were performed with the pinhole set at 1 Airy diameter. All images were captured at 512 x 512 pixels at 400 Hz or 1400 Hz capture rates. All experiments were performed with the 62 x oil objective with further magnification being achieved with the optical zoom. Fluorescein was excited at 488 nm (Ar laser) and emission collected between 500-640 nm. Images were processed using the Leica LAS software. Gains were kept constant throughout measurements, at a point where saturation was not reached in the most fluorescent sample.

Chemical Syntheses

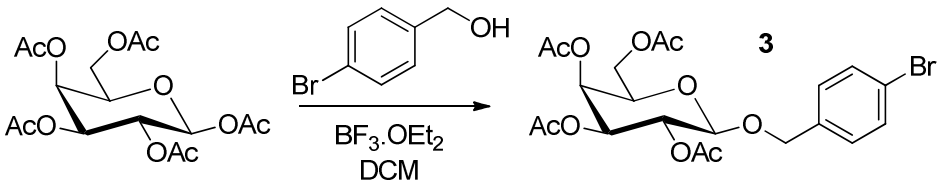


2-amino-4,6-dihydroxypyrimidine (13 mg, 0.1 mmol) was dissolved in NaOH (0.1 M, 2 mL) at 65 ºC. Palladium acetate (11 mg, 0.05 mmol) was then added and the solution stirred at 65 ºC for 30 min. The orange solution was then allowed to cool to rt and diluted to 5 mL with distilled water to give a stock 0.01 M catalyst solution, **1**.[2]



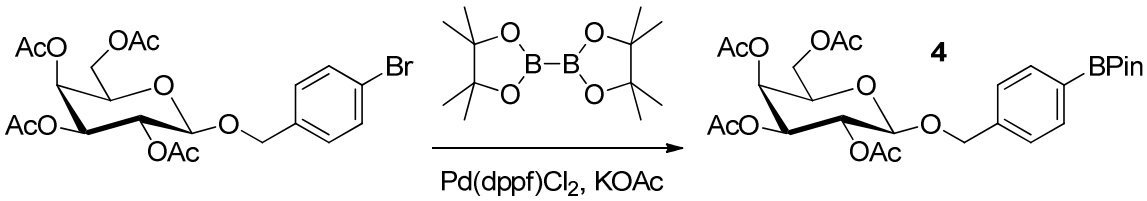
To a solution of L-phenylalanine (41.3 g, 250 mmol) in acetic acid (250 mL) and concentrated sulphuric acid (31 mL) was added Iodine (25.2 g, 100 mmol) and sodium iodate (9.9 g, 50 mmol). The mixture was heated to 70 ºC for 18 hrs. Two portions of sodium periodate (2 × 1.05 g) were then added and stirring continued at 70 ºC for ~30 min until the mixture turned orange. The acetic acid was then removed *in vacuo*, and the crude mixture was diluted with water (400 mL) then washed with ether (2 x 200 mL) and DCM (2 x 300 mL). To the aqueous layer was added 2 M NaOH until a white precipitate was formed. The solid was collected by filtration and re-crystallized from boiling water:ethanol (160 mL:100 mL). The resulting crystals were collected and dried *in vacuo*, to yield L-*p*-iodophenylalanine as white crystals. A yield of 33.01 g, 113 mmol (57 %) was obtained. Spectroscopic data was consistent with that previously reported.[1] ^{1}H NMR (400 MHz, NaOD/D_2O): δ= 7.60 (2H, d, *J* = 8.7 Hz, *ortho*-H), 6.93 (2H, d, *J* = 8.7 Hz, *meta*-H), 3.37 (1H, t, *J* = 6.1 Hz, H_α), 2.82 (1H,

dd, *J* = 14.5, 6.1 Hz, -C<u>H</u>$_2$Ar ABX system), 2.68 (1H, dd, *J* = 14.5, 6.1 Hz, -C<u>H</u>$_2$Ar ABX system); m.p: 260-263 ºC; $[\alpha]_D$ = + 20 (c = 1.0, 0.5 M HCl) (Lit[2]: + 20, c = 1.0, 0.5 M HCl);



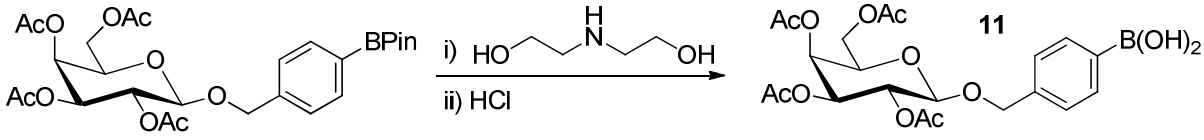
β-D-galactose penta-acetate (2.8 g, 7.2 mmol) was dissolved in dry DCM (30 mL) under nitrogen and cooled to 0 °C. Boron trifluoride diethyl etherate (1.35 mL, 10.8 mmol) was added drop-wise, followed by 4-bromobenzyl alcohol (2.01 g, 10.8 mmol). After warming to rt, the reaction was stirred for 18 hrs. Sat. $NaHCO_3$ (50 mL) was then added to quench the reaction and the mixture stirred for a further 30 min. The mixture was extracted with DCM (2 x 50 mL) and the organics dried with $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chomratography, eluting with 20-28 % EtOAc:Petrol. Pure fractions were concentrated to give the DP as a colourless oil. A yield of 2.2 g, 4.3 mmol (60 %) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (2H, d, *J* = 8.5 Hz, *o*-<u>H</u>), 7.16 (2H, d, *J* = 8.5 Hz, *m*-<u>H</u>), 5.38 (1H, dd, *J* = 3.4, 0.9 Hz, <u>H</u>4), 5.27 (1H, dd, *J* = 10.5, 8.0 Hz, <u>H</u>2), 4.99 (1H, dd, *J* = 10.5, 3.4 Hz, <u>H</u>3), 4.85 (1H, d, *J* = 12.5 Hz, -C<u>H</u>$_2$Ar), 4.57 (1H, d, *J* = 12.5 Hz, -C<u>H</u>$_2$Ar), 4.51 (1H, d, *J* = 8.0 Hz, <u>H</u>1), 4.06-4.10 (2H, m, <u>H</u>6), 3.89 (1H, td, *J* = 6.7, 1.0 Hz, <u>H</u>5), 2.15 (3H, s, -O<u>Ac</u>), 2.03 (3H, s, -O<u>Ac</u>), 2.02 (3H, s, -O<u>Ac</u>), 1.97 (3H, s, -O<u>Ac</u>) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.34 (-O<u>Ac</u>), 170.20 (-O<u>Ac</u>), 170.07 (-O<u>Ac</u>), 169.33 (-O<u>Ac</u>), 135.81 (*p*-<u>H</u>), 131.56 (*o*-<u>H</u>), 129.22 (*m*-<u>H</u>), 121.86 (*i*-<u>H</u>), 99.99 (<u>C</u>1), 70.83 (<u>C</u>5), 70.76 (<u>C</u>3), 69.95 (-<u>C</u>H$_2$Ar), 68.77 (<u>C</u>2), 66.99 (<u>C</u>4), 61.25 (<u>C</u>6), 20.71 (-O<u>Ac</u>), 20.65 (-O<u>Ac</u>), 20.63 (-O<u>Ac</u>), 20.53 (-O<u>Ac</u>) ppm; HRMS *m/z* (ESI+): Found: 539.0523/541.0504 (M+Na)

Calc.: 539.0516/541.0503; IR (ν_{max}, oil): 1743, 1367, 1214, 1045 cm^{-1}; $[\alpha]_D$ = -29 (c = 1.0, $CHCl_3$);



Benzyl bromide **3** (2 g, 3.9 mmol), bis(pinacolato) diborane (1.5 g, 5.8 mmol) and potassium acetate (1.53 g, 15.6 mmol) were charged under nitrogen and dissolved in dry dioxane (30 mL). $Pd(dppf)Cl_2$ (142 mg, 0.2 mmol) was then added and the mixture refluxed for 18 hrs. The mixture was cooled and concentrated *in vacuo*. The residue was re-dissolved in DCM (250 mL) and washed with H_2O (100 mL). The aqueous was extracted with DCM (100 mL) and the combined organics washed with brine (100 mL). The organics were then dried with $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography eluting with 20-25 % EtOAc:Petrol. Pure fractions were concentrated *in vacuo* to give the DP as a colourless oil. A yield of 1.37 g, 1.9 mmol (51 %) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (2H, d, *J* = 8.0 Hz, *o*-H), 7.28 (2H, d, *J* = 8.0 Hz, *m*-H), 5.37 (1H, d, *J* = 3.2 Hz, H4), 5.27 (1H, dd, *J* = 10.4, 8.0 Hz, H2), 4.94 (1H, dd, *J* = 10.4, 3.2 Hz, H3), 4.92 (1H, d, *J* = 12.8 Hz, -CH_2Ar), 4.64 (1H, d, *J* = 12.8 Hz, -CH_2Ar), 4.47 (1H, d, *J* = 8.0 Hz, H1), 4.19 (1H, dd, *J* = 11.3, 6.7 Hz, H6), 4.12 (1H, dd, *J* = 11.3, 7.3 Hz, H6), 3.86 (1H, dd, *J* = 7.3, 6.7 Hz, H5), 2.15 (3H, s, -OAc), 2.06 (3H, s, -OAc), 2.02 (3H, s, -OAc), 1.96 (3H, s, -OAc), 1.34 (12H, s, Pin) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.38 (-OAc), 170.27(-OAc), 170.10(-OAc), 169.40 (-OAc), 139.72 (*p*-C), 134.89 (*o*-C), 126.89 (*m*-C), 99.61 (C1), 83.84 (-BOCR$_3$), 70.88 (C3), 70.68 (C5), 70.42 (-CH_2Ar), 68.79 (C2), 67.05 (C4), 61.32 (C6), 24.83 (-BOC(CH_3)$_2$), 20.74 (-OAc), 20.68 (-OAc), 20.66 (-OAc), 20.55 (-

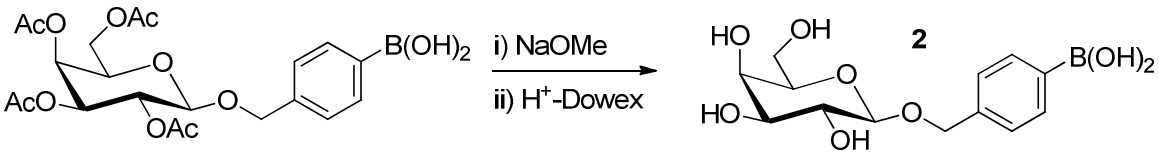
OAc) ppm; HRMS *m/z* (ESI+): Found: 587.2269 (M+Na) Calc.: 587.2275; IR (ν_{max}, oil): 2979, 1746, 1359, 1214, 1143, 1046 cm^{-1}; $[\alpha]_D$ = -23 (c = 0.5, $CHCl_3$);



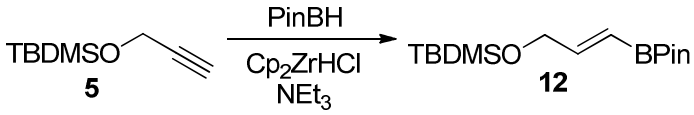
Pinacol ester **4** (700 mg, 1.2 mmol) was dissolved in diethyl ether (30 mL) and diethanolamine (195 mg, 1.9 mmol) was added. After stirring for 18 hrs the resultant white precipitate was collected by filtration and washed with diethyl ether (30 mL). NMR confirmed the presence of the intermediate DEA ester: ^{1}H NMR (400 MHz, DMSO): δ = 7.43 (2H, d, *J* = 7.9 Hz, *o*-H), 7.11 (2H, d, *J* = 7.9 Hz, *m*-H), 6.84-6.91 (1H, m, -NH),5.26 (1H, d, *J* = 3.6 Hz, H4), 5.16 (1H, dd, *J* = 10.4, 3.6 Hz, H3), 4.98 (1H, dd, *J* = 10.4, 7.9 Hz, H2), 4.75 (1H, d, *J* = 7.9 Hz, H1), 4.73 (1H, d, *J* = 12.0 Hz, -CH_2Ar), 4.51 (1H, d, *J* = 12.0 Hz, -CH_2Ar), 4.21 (1H, dd, *J* = 6.6, 6.3 Hz, H5), 4.11 (1H, dd, *J* = 11.3, 6.6 Hz, H6), 4.07 (1H, dd, *J* = 11.3, 6.3 Hz, H6), 3.83-3.91 (2H, m, -CH_2NH-), 3.75-3.81 (2H, m, -CH_2NH-), 3.03-3.14 (2H, m, -BOCH_2-), 2.81-2.88 (2H, m, -BOCH_2-), 2.13 (3H, s, -OAc), 2.04 (3H, s, -OAc), 2.00 (3H, s, -OAc), 1.92 (3H, s, -OAc) ppm;

The residue was re-suspended in diethyl ether (30 mL) and hydrochloric acid (0.1 M, 30 mL) was added. Afer stirring for 2 hrs, the aqueous was washed with diethyl ether (100 mL) and the combined organics dried with $MgSO_4$, filtered and concentrated *in vacuo*. The DP was obtained as white crystals. A yield of 350 mg, 0.72 mmol (61 %) was obtained. ^{1}H NMR (400 MHz, DMSO): δ = 8.03 (2H, s, -B(OH)$_2$), 7.78 (2H, d, *J* = 7.9 Hz, *o*-H), 7.25 (2H, d, *J* = 7.9 Hz, *m*-H), 5.27 (1H, dd, *J* = 3.5, 1.0 Hz, H4), 5.18 (1H, dd, *j* = 10.4, 3.5 Hz, H3), 5.00 (1H, dd, *J* = 10.4, 7.9 Hz, H2), 4.79-4.82 (2H, m, -CH_2Ar), 4.60 (1H, d, *J* = 12.6 Hz, H1), 4.22 (1H, td, *J* = 6.3, 1.0 Hz, H5), 4.05-4.12 (2H, m, H6), 2.13 (3H, s, -OAc), 2.03 (3H, s, -

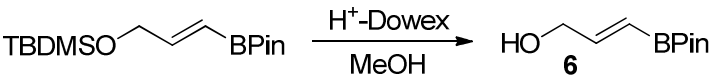
OAc), 2.00 (3H, s, -OAc), 1.92 (3H, s, -OAc) ppm; ^{13}C NMR (100 MHz, DMSO): δ = 169.97 (-OAc), 169.91 (-OAc),169.49 (-OAc), 169.15 (-OAc), 139.06 (*p*-C), 134.12 (*o*-C), 126.39 (*m*-C), 99.24 (C1), 70.16 (C3), 70.10 (-CH_2Ar), 69.90 (C5), 68.75 (C2), 67.32 (C4), 61.26 (C6), 20.52 (-OAc), 20.48 (-OAc), 20.40 (-OAc), 20.33 (-OAc)ppm; HRMS *m/z* (ESI+): Found: 505.1481 (M+Na) Calc.: 505.1492; IR (ν_{max}, solid): 1743, 1367, 1217, 1045, 819, 648 cm^{-1}; M.p: >300 °C;



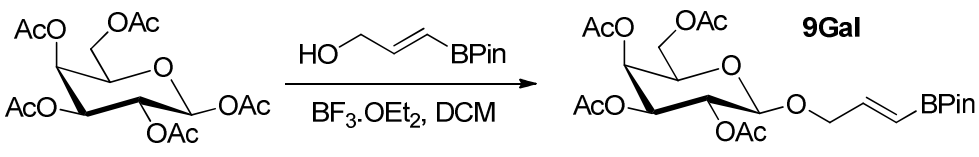
Boronic acid **11** (400 mg, 0.83 mmol) was dissolved in methanol (10 mL) and sodium methoxide was added (179 mg, 3.32 mmol). After stirring for 2 hrs, a white precipitate had formed. The reaction was neutralised with pre-activated Dowex-50WX8 and the mixture stirred for 20 min. The residue was collected by filtration and washed with methanol (2 x20 mL). Water (2 x 20 mL) was then added and the suspension stirred for 1 hr. The water was then collected by filtration and concentrated *in vacuo* to afford the DP as white crystals. A yield of 94 mg, 0.3 mmol (36 %) was obtained. ^{1}H NMR (400 MHz, NaOD/D_2O): δ = 6.97 (2H, d, *J* = 7.9 Hz, *o*-H), 6.76 (2H, d, *J* = 7.9 Hz, *p*-H), 4.28 (1H, d, *J* = 11.3 Hz, -CH_2Ar), 4.07 (1H, d, *J* = 11.3 Hz, -CH_2Ar), 3.76 (1H, d, *J* = 7.2 Hz, H1), 3.26 (1H, d, *J* = 2.8 Hz, H4), 3.07-3.12 (2H, m, H2 and H3), 2.90 (1H, dd, $J_1 = J_2$ = 6.0 Hz, H5), 2.77-2.87 (2H, m, H6) ppm; ^{13}C NMR (125 MHz, NaOD/D_2O): δ = 133.52 (*p*-C), 131.03 (*o*-C), 127.45 (*m*-C), 102.96 (C1), 76.49 (C5), 74.52 (C6), 71.14 (C7), 69.43 (C4), 60.96 (C3), 60.96 (C2) ppm; HRMS *m/z* (ESI-): Found: 341.1400 (M-H) Calc.: 341.1416; IR (ν_{max}, solid): 1611, 1311, 1261, 1174, 1076, 1041 cm^{-1}; M.p: >300 °C; $[\alpha]_D$ = -29 (c = 0.7, 2 M NaOH);



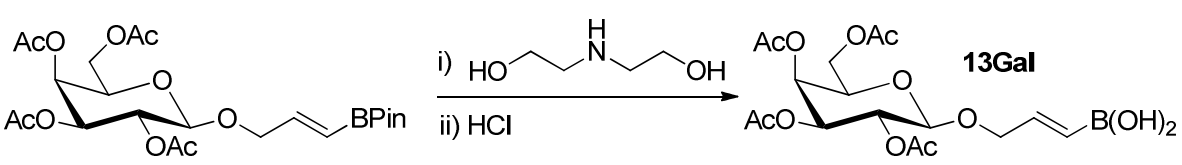
Tert-butyl-dimethyl(2-propynyloxy) silane (12.16 mL, 60 mmol) was charged under nitrogen and pinacolborane (9.5 mL, 66 mmol) was added, followed by Schwartz's reagent (1.59 g, 6 mmol) and triethylamine (842 µL, 6 mmol). After heating to 60 °C for 18 hrs, petrol (40 mL) was added and the mixture filtered through silica. Petrol and remaining starting material were removed *in vacuo* to give the DP, **12**, as a colourless oil. A yield of 15.8 g, 53 mmol (88 %) was obtained. Spectroscopic data was consistent with that previously reported.[3] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.68 (1H, dt, *J* = 17.9, 3.4 Hz, -C<u>H</u>CHBPin), 5.76 (1H, dt, *J* = 17.9, 2.0 Hz, -C<u>H</u>BPin), 4.25 (2H, dd, *J* = 3.4, 2.0 Hz, -C<u>H</u>$_2$OR), 1.27 (12H, s, Pin), 0.91 (9H, s, *t*-Bu), 0.06 (6H, s, Me) ppm;



Silane **12** (15.8 g, 53 mmol) was dissolved in methanol (60 mL) and activated Dowex-50WX8 (~5 g) was added. After stirring for 72 hrs, the methanol was removed *in vacuo* and the residue purified by flash column chromatography, eluting with 30 % EtOAc: Petrol. Pure fractions were concentrated *in vacuo* to give the DP as a colourless oil. A yield of 9.7 g, 53 mmol (100 %) was obtained. Spectroscopic data matched that previously obtained.[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.73 (1H, dt, *J* = 18.2, 4.2 Hz, -C<u>H</u>CHBPin), 5.68 (1H, dt, *J* = 18.2, 1.9 Hz, -C<u>H</u>CHBPin), 4.21 (2H, app s, -C<u>H</u>$_2$OH), 1.25 (12H, s, Pin) ppm;



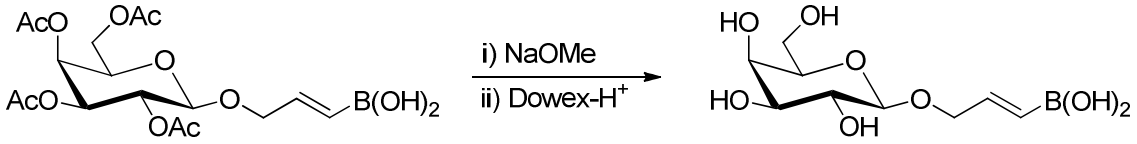
β-D-Galactose pentaacetate (3.90 g, 10 mmol) was dissolved in dry DCM (50 mL) under nitrogen in a flame dried flask and cooled to 0 °C. Boron trifluoride diethyl etherate (1.88 mL, 15 mmol) was added followed by vinyl alcohol **6** (2.20 g, 12 mmol). The reaction was allowed to warm to rt and stirred for 18 hrs, The reaction was then quenched with water (50 mL) and the aqueous extracted with DCM (50 mL). The combined organics were dried with $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography eluting with 30 % EtOAc:Petrol. Pure fractions were concentrated *in vacuo* to give a light yellow oil. A yield of 2.1 g, 3.9 mmol (39 %) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.56 (1H, dt, *J* = 18.3, 4.8 Hz, -CHCHBPin), 5.68 (1H, dt, *J* = 18.3, 1.7 Hz, -CHBPin), 5.38 (1H, dd, *J* = 3.4, 0.85 Hz, H4), 5.25 (1H, dd, *J* = 10.6, 8.0 Hz, H2), 5.02 (1H, dd, *J* = 10.6, 3.4 Hz, H3), 4.51 (1H, d, *J* = 8.0 Hz, H1), 4.42 (1H, ddd, *J* = 14.7, 4.3, 0.85 Hz, H5), 4.39 (1H, d, *J* = 4.8 Hz, -CH_2CHCHBPin), 4.11-4.22 (2H, m, H6), 3.89 (1H, dd, *J* = 6.7, 1.0 Hz, -CH_2CHCHBPin), 2.16 (3H, s, -OAc), 2.09 (3H, s, -OAc), 2.06 (3H, s, -OAc), 1.99 (3H, s, -OAc), 1.27 (12H, s, Pin) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.30 (-OAc), 170.21 (-OAc), 170.06 (-OAc), 169.37 (-OAc), 147.24 (-CHCHBPin), 119.96 (-CHBPin), 100.15 (C1), 83.23 (-BOCR_3), 70.85 (C3), 70.55 (C5), 70.35 –CH_2CHCHBPin), 68.75 (C2), 67.00 (C4), 61.22 (C6), 24.71 (-BOC(CH_3)$_2$), 20.68 (-OAc), 20.55 (-OAc), 20.46 (-OAc) ppm; HRMS *m/z* (ESI+): Found: 537.2118 (M+Na) Calc: 537.2099; IR (ν_{max}, oil): 2979, 1746, 1645, 1368, 1219, 1143, 1062 cm^{-1}; $[\alpha]_D$ = +6.2 (c = 0.5, $CHCl_3$);



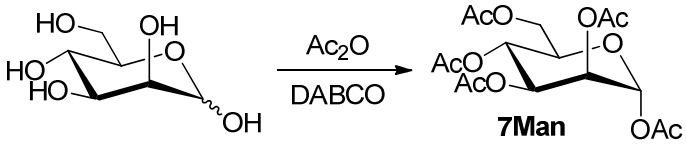
Vinyl galactose **9Gal** (2 g, 3.9 mmol) was dissolved in diethyl ether (80 mL) and diethanolamine (613 mg, 5.8 mmol) was added. After stirring for 18 hrs the resultant white

precipitate was collected by filtration, washed with diethyl ether (50 mL) and dried *in vacuo*. The presence of the corresponding DEA ester was confirmed by ^{1}H NMR (400 MHz, DMSO): δ = 6.75 (1H, br s, -NH), 5.72 (1H, dt, *J* = 17.6, 5.3 Hz, -CHCHBOR$_2$), 5.56 (1H, d, *J* = 17.6, -CHBOR$_2$), 5.26 (1H, dd, *J* = 3.4, 0.5 Hz, H4), 5.15 (1H, dd, *J* = 10.4, 3.4 Hz, H3), 4.94 (1H, dd, *J* = 10.4, 8.0 Hz, H2), 4.68 (1H, d, *J* = 8.0 Hz, H1), 4.16 (2H, dd, *J* = 12.6, 5.3 Hz, -CH$_2$CHCHBOR$_2$), 4.02-47.07 (2H, m, H6), 3.98 (1H, ddd, *J* = 13.0, 5.6, 0.5 Hz, H5), 3.69-3.75 (2H, m, -OCH$_2$CH$_2$NH-), 3.58-3.64 (2H, m, -OCH$_2$CH$_2$NH-), 2.93-3.03 (2H, m, -CH$_2$NH-), 2.69-2.76 (2H, m, -CH$_2$NH-), 2.12 (3H, s, -OAc), 2.03 (3H, s, -OAc), 2.01 (3H, s, -OAc), 1.92 (3H, s, -OAc) ppm;

The white solid was resuspended in ether (30 mL) and stirred with hydrochloric acid (0.1 M, 30 mL) for 2 hrs. The aqueous was washed with ether (100 mL) and the combined organics dried with MgSO$_4$, filtered and dried *in vacuo* to give the DP as white crystals. A yield of 520 mg, 1.2 mmol (31 %) was obtained. ^{1}H NMR (400 MHz, DMSO): δ = 7.71 (2H, br s, -B(OH)$_2$), 6.41 (1H, dt, *J* = 18.0, 4.5 Hz, -CHCHB(OH)$_2$), 5.45 (1H, d, *J* = 18.0 Hz, -CHB(OH)$_2$), 5.27 (1H, d, *J* = 3.4 Hz, H4), 5.20 (1H, dd, *J* = 10.2, 3.4 Hz, H3), 4.98 (1H, dd, *J* = 10.2, 7.9 Hz, H2), 4.73 (1H, d, *J* = 7.9 Hz, H1), 4.05-4.34 (4H, m, H5, H6 and –CH$_2$CHCHB(OH)$_2$), 2.14 (3H, s, -OAc), 2.06 (3H, s, -OAc), 2.03 (3H, s, -OAc), 1.94 (3H, s, -OAc) ppm; ^{13}C NMR (125 MHz, DMSO): δ = 169.95 (-OAc), 169.90 (-OAc), 169.50 (-OAc), 169.19 (-OAc), 144.31 (-CHCHBPin), 125.56 (-CHBPin), 99.25 (C1), 70.23 (-CH$_2$CHCHBPin), 70.19 (C3), 69.83 (C5), 68.89 (C2), 67.33 (C4), 61.24 (C6), 20.52 (-OAc), 20.49 (-OAc), 20.39 (-OAc), 20.33 (-OAc) ppm; M.p: >300 °C; IR (ν_{max}, solid): 2916, 2849, 1742, 1645, 1368, 1220, 1045 cm^{-1};

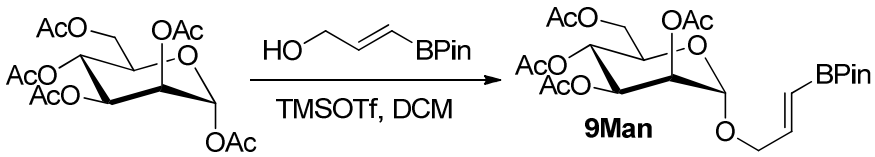


Protected galactose boronic acid **13Gal** (432 mg, 1 mmol) was dissolved in methanol (10 mL) and sodium methoxide (216 mg, 4 mmol) was added. After stirring for 90 min, pre-activated Dowex-50WX8 was added until the pH was neutral, and the mixture stirred for a further 90 min. The reaction was then filtered and the solvent removed *in vacuo* to give 230 mg of DP as a white solid. A further 120 mg was obtained by washing the Dowex with water, and concentrating in vacuo. ^{1}H NMR (400 MHz, D_2O): δ = 6.42 (1H, dt, *J* =18.3, 5.1 Hz, -CHCHB(OH)2), 5.64 (1H, d, *J* = 18.3 Hz, -CHB(OH)$_2$), 4.35 (1H, ddd, *J* = 14.2, 4.8, 1.7 Hz, -CH$_2$CH=CH), 4.30 (1H, d, *J* = 7.9 Hz, H1), 4.20 (1H, ddd, *J* = 14.2, 5.3, 1.4 Hz, -CH$_2$CH=CH), 3.79 (1H, d, *J* = 3.4 Hz, H4), 3.55-3.69 (3H, m, H5 and H6), 3.52 (1H, dd, *J* = 9.9, 3.4 Hz, H3), 3.42 (1H, dd, *J* = 9.9, 7.8 Hz, H2) ppm; ^{13}C NMR (125 MHz, D_2O): δ = 145.47 (-CHCHB(OH)$_2$), 124.11 (-CHB(OH)$_2$), 102.01 (C1), 75.14 (C5), 72.74 (C3), 71.05 (-CH$_2$CH=CH), 70.75 (C2), 68.61 (C4), 60.93 (C6) ppm; HRMS *m/z* (ESI+): Found: 287.0909 (M+Na) Calc: 287.0910; M.p: >300 °C; IR (ν_{max}, solid):3364, 1641, 1419, 1362, 1323, 1266, 1204, 1034 cm^{-1}; $[\alpha]_D$ = -12 (c = 1.0, H_2O);



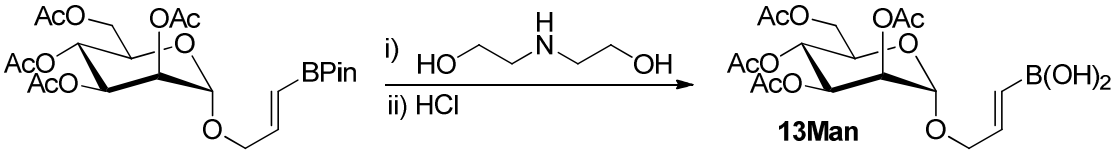
The synthesis was adapted from Ch *et* al.[4] D-Mannose (1.8 g, 10 mmol) was suspended in acetic anhydride (5.7 mL, 60 mmol) and DABCO (1.12 g, 10 mmol) was added, causing a large exotherm. After stirring for 18 hrs, the resultant light brown solution was poured into ice/water (100 mL). The product was extracted with DCM (2 x 100 mL) and the combined organics washed with sat. $NaHCO_3$ (50 mL), dried with Na_2SO_4, filtered and concentrated *in*

vacuo. The DP was obtained as a colourless oil. A yield of 3.62 g, 9.3 mmol (93 %) was obtained. Spectroscopic data matched that previously obtained.[5] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.08 (1H, d, *J* = 1.9 Hz, H1), 5.33-5.37 (2H, m, H3 and H4), 5.26 (1H, t, *J* = 2.2 Hz, H2), 4.28 (1H, dd, *J* = 12.3, 5.0 Hz, H6), 4.10 (1H, dd, *J* = 12.5, 2.4 Hz, H6), 4.03-4.06 (1H, m, H5), 2.22 (3H, s, -OAc), 2.18 (3H, s, -OAc), 2.17 (3H, s, -OAc), 2.10 (3H, s, -OAc), 2.05 (3H, s, -OAc), 2.01 (3H, s, -OAc) ppm;

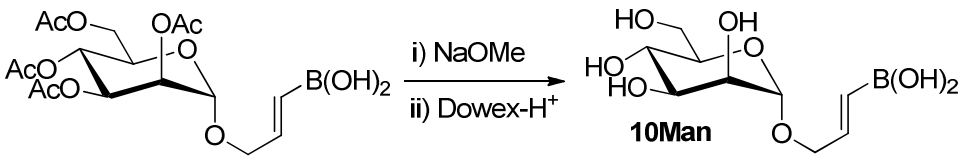


D-Mannose pentaacetate (3.2 g, 8.2 mmol) and vinyl alcohol **6** (2.02 g, 11 mmol) were dissolved in dry DCM (50 mL) under nitrogen and cooled to 0 °C. Trimethylsilyl trifluoromethanesulfonate (1.99 mL, 11 mmol) was then added drop-wise and the reaction allowed to warm to rt. After stirring for 18 hrs the reaction was washed with water (20 mL) and the organics dried with $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography eluting with 25 % EtOAc:Petrol. Pure fractions were concentrated to give the DP as a light yellow oil. A yield of 1.1 g, 2.1 mmol (26 %) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.60 (1H, dt, *J* = 18.0, 4.7 Hz, -CHCHBPin), 5.73 (1H, dt, *J* = 18.0, 1.6 Hz, -CHBPin), 5.37 (1H, dd, *J* = 10.1, 3.5 Hz, H3), 5.26-5.30 (H2 and H4), 4.85 (1H, d, *J* = 1.6 Hz, H1), 4.25-4.30 (2H, m, H6 and –CH_2CHCHBPin), 4.07-4.14 (2H, m, H6 and –CH_2CHCHBPin), 3.97-4.02 (1H, m, H5), 2.15 (3H, s, -OAc), 2.10 (3H, s, -OAc), 2.04 (3H, s, -OAc), 1.99 (3H, s, -OAc), 1.28 (12H, s, -BPin) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.63 (-OAc) 169.97 (-OAc), 169.74 (-OAc), 146.72 (-CHCHBPin), 120.69 (-CHBPin), 96.92 (C1), 83.44 (-BOCR_3), 69.47 (C2), 69.18 (-CH_2CHCHBPin), 69.05 (C3), 68.55 (C5), 66.09 (C4), 62.38 (C6), 24.75 (-BOCR(CH_3)$_2$), 20.87 (-OAc), 20.72 (-

OAc), 20.68 (-OAc), 20.65 (-OAc) ppm; HRMS *m/z* (ESI+): Found: 537.2111 (M+Na) Calc.: 537.2118; IR (ν_{max}, solid): 1743, 1367, 1359, 1217, 1045 cm^{-1}; $[\alpha]_D$ = +26 (c = 1.0, $CHCl_3$);

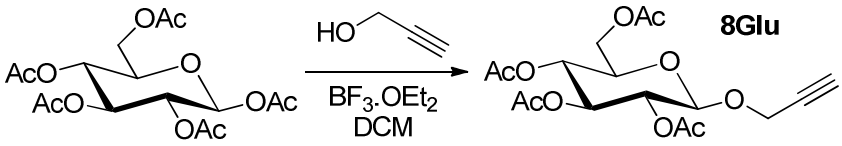


Pinacol ester **9Man** (900 mg, 1.75 mmol) was dissolved in ether (30 mL) and diethanolamine (273 mg, 2.6 mmol) was added. After stirring for 7 hrs, the intermediate DEA ester was collected by filtration and dried under suction. NMR confirmed the presence of the intermediate DEA ester. ^{1}H NMR (400 MHz, DMSO): δ =6.59 (1H, br s, -NH), 5.79 (1H, dt, *J* = 17.6. 5.8 Hz, -CHCHBR$_3$), 5.64 (1H, d, *J* = 17.6 Hz, -CHBR$_3$), 5.07-5.15 (2H, m, H3 and H4), 4.88 (1H, d, *J* = 1.2 Hz, H1), 4.02-4.20 (3H, m, H5 and H6), 3.89-3.97 (2H, m, -CH$_2$CHCHBR$_3$), 3.69-3.77 (2H, m, -BOCH$_2$-), 3.58-3.65 (2H, m, -BOCH$_2$-), 2.95-3.05 (2H, m, -NHCH$_2$-), 2.69-2.77 (2H, m, -NHCH$_2$-), 2.11 (3H, s, -OAc), 2.04 (3H, s, -OAc), 2.03 (3H, s, -OAc), 1.95 (3H, s, -OAc) ppm; The DEA ester was suspended in ether and hydrochloric acid (10 %, 50 mL) was added. After stirring for 1 hr the aqueous was washed with ether (100 mL) and the combined organics dried with $MgSO_4$, filtered and concentrated *in vacuo* to give the DP as white crystals. A yield of 329 mg, 0.76 mmol (44 %) was obtained. The product was used in the subsequent de-protection step without further analysis.



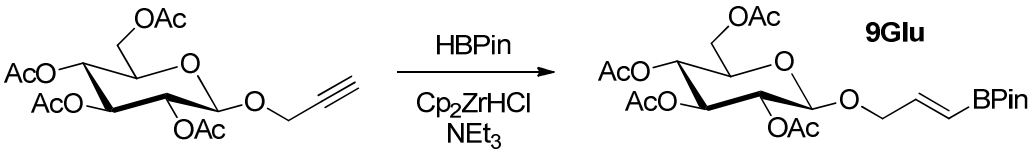
Boronic acid **13Man** (300 mg, 0.69 mmol) was dissolved in methanol (10 mL) and sodium methoxide (150 mg, 2.76 mmol) was added. After stirring for 1 hr, pre-activated Dowex-

50WX8 was added in small portions until the pH was neutral. Stirring was continued for 30 min and the reaction mixture was then filtered and concentrated *in vacuo*. The resultant brown oil was azeotroped with DCM (4 x 20 mL) to give the DP as a light pink solid. A yield of 132 mg, 0.5 mmol (72 %) was obtained. ^{1}H NMR (400 MHz, D_2O): δ = 6.42 (1H, dt, *J* = 18.3, 4.8 Hz, -CHCHB(OH)$_2$), 5.59 (1H, dt, *J* = 18.3, 1.5 Hz, -CHB(OH)$_2$), 4.78 (1H, d, *J* = 1.7 Hz, H1), 4.19 (1H, ddd, *J* = 14.3, 4.6, 1.7 Hz, -CH$_2$CHCHB(OH)$_2$) 4.04 (1H, ddd, *J* = 14.3, 5.1, 1.5 Hz, -CH$_2$CHCHB(OH)$_2$), 3.89 (1H, dd, *J* = 3.5, 1.6 Hz, H2) 3.79 (1H, dd, *J* = 12.3, 1.3 Hz, H2) 3.73-3.76 (1H, m, H3), 3.64-3.69 (1H, m, H6) 3.55-3.60 (2H, m, H4 and H5) ppm; ^{13}C NMR (125 MHz, D_2O): δ = 148.38 (-CHCHB(OH)$_2$), 123.68 (-CHB(OH)$_2$), 99.11 (C1), 72.83 (C3), 70.54 (C5), 69.95 (C2), 68.48 (-CH$_2$CHCHB(OH)$_2$), 66.70 (C4), 60.85 (C6) ppm; HRMS *m/z* (ESI+): Found: 287.0908 (M+Na) Calc: 287.0910; M.p: >300 °C; IR (ν_{max}, solid): 3334, 2917, 1643, 1328, 1029 cm^{-1}; $[\alpha]_D$ = +20 (c = 0.5, H_2O);

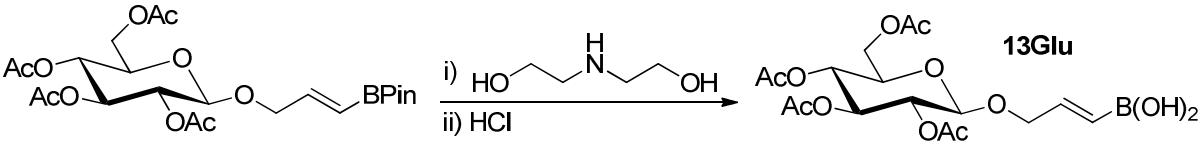


D-Glucose penta-acetate (5 g, 12.8 mmol) was dissolved in dry DCM (100 mL) under nitrogen and cooled to 0 °C. Propargyl alcohol (897 μL, 15.4 mmol) was added, followed by drop-wise addition of boron trifluoride diethyl etherate (2.41 mL, 19.2 mmol). After warming to rt, the reaction was stirred for 18 hrs. Potassium carbonate (2 g) was added to quench the reaction and stirred for 30 min. After filtering, the reaction was washed with water (2 x 50 mL) and the aqueous extracted with DCM (100 mL). The combined organics were dried with Na_2SO_4, filtered and concentrated *in vacuo*. The residue was re-crystallised from 10 mL petrol: 10 mL DCM. The DP was obtained as white crystals. A yield of 2.4 g, 6.2 mmol (49

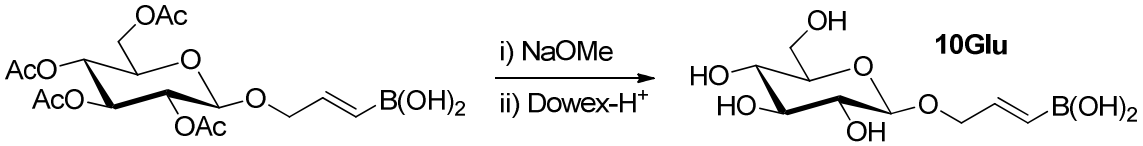
%) was obtained. Spectroscopic data matched that previously reported.[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.25 (1H, dd, *J* = 9.6, 9.4 Hz, H3), 5.11 (1H, dd, *J* = 9.7, 9.6 Hz, H4), 5.02 (1H, dd, *J* = 9.4, 8.0 Hz, H2), 4.78 (1H, d, *J* = 8.0 Hz, H1), 4.37 (2H, d, *J* = 2.4 Hz, -CH_2CCH), 4.28 (1H, dd, *J* = 12.3, 4.6 Hz, H6), 4.15 (1H, dd, *J* = 12.3, 2.4 Hz, H6), 3.74 (1H, ddd, *J* = 9.7, 4.6, 2.4 Hz, H5), 2.48 (1H, t, *J* = 2.4 Hz, -CCH), 2.09 (3H, s, -OAc), 2.06 (3H, s, -OAc), 2.03 (3H, s, -OAc), 2.01 (3H, s, -OAc) ppm;



Pinacolborane (838 μL, 5.83 mmol) was added to glucose derivative **8Glu** (1.5 g, 3.89 mmol) and Schwartz's reagent (100 mg, 0.39 mmol) under nitrogen. Triethylamine (55 μL, 0.39 mmol) was then added and the reaction heated to 65 °C for 18 hrs. After cooling to rt, the reaction was diluted with DCM (10 mL), filtered and purified by flash column chromatography eluting with 30-50 % EtOAc:Petrol. Pure fractions were concentrated *in vacuo* to give the DP as a colourless oil. A yield of 520 mg, 1.0 mmol (26 %) was obtained. Spectroscopic date matched that previously reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.58 (1H, dt, *J* = 18.1, 4.8 Hz, -CHCHBPin), 5.66 (1H, dt, *J* = 18.1, 1.7 Hz, -CHBPin), 5.25 (1H, dd, J_1 = J_2 = 9.7 Hz,), 4.98-5.06 (2H, m,), 4.57 (1H, d, *J* = 8.0 Hz, H1), 4.38 (1H, ddd, *J* = 14.5, 4.6, 1.9 Hz, -CH_2CHCHBPin), 4.22 (1H, ddd *J* = 14.5, 5.0, 1.5 Hz, -CH_2CHCHBPin), 3.72 (1H, dd, *J* = 12.5, 2.4 Hz, H6), 3.60 (1H, dd, *J* = 12.5, 5.0 Hz, H6), 3.50 (1H, ddd, *J* = 9.9, 5.0, 2.4 Hz, H5), 2.07 (3H, s, -OAc), 2.05 (3H, s, -OAc), 2.01 (3H, s, -OAc), 1.27 (12H, s, Pin) ppm;

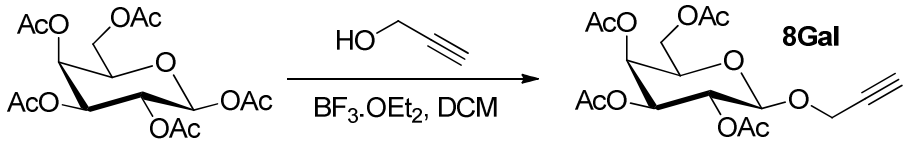


Pinacol ester **9Glu** (500 mg, 0.97 mmol) was dissolved in diethyl ether (20 mL) and diethanolamine (153 mg, 1.45 mmol) was added. After stirring for 18 hrs the resultant precipitate was collected by filtration and dried *in vacuo*,. The residue was then resuspended in ether (20 mL) and hydrochloric acid (10 %, 10 mL) was added. After stirring for 1 hr the aqueous was extracted with ether (20 mL) and the combined organics dried with $MgSO_4$, filtered and concentrated *in vacuo*. The resultant white solid was used in the subsequent deprotection without further purification or analysis.

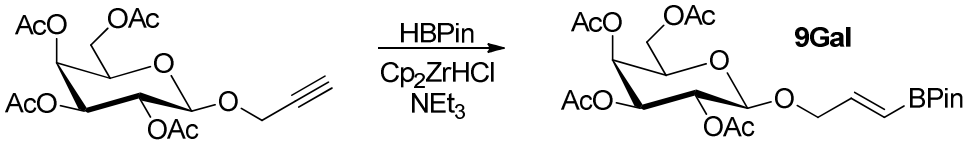


Boronic acid **13Glu** (240 mg, 0.55 mmol) was dissolved in methanol (10 mL) and sodium methoxide (120 mg, 2.22 mmol) was added. After stirring for 2 hrs the reaction was quenched through the addition of pre-activated Dowex-50WX8 until the pH was approximately neutral. After stirring for a further 30 min, the solid was removed by filtration and washed with methanol (20 mL). The filtrate was concentrated *in vacuo* to give the DP as an off white solid. A yield of 125 mg, 0.46 mmol (84 %) was obtained. ^{1}H NMR (400 MHz, D_2O): δ = 6.43 (1H, dt, *J* = 18.2, 5.1 Hz, -C<u>H</u>CHB(OH)$_2$), 5.64 (1H, d, *J* = 18.2 Hz, -C<u>H</u>B(OH)$_2$), 4.38 (1H, d, *J* = 8.1 Hz, <u>H</u>1), 4.36 (1H, dd, *J* = 14.2, 4.3 Hz, -C<u>H</u>$_2$CHCHB(OH)$_2$), 4.21 (1H, dd, *J* = 14.1, 5.3 Hz, -C<u>H</u>$_2$CHCHB(OH)$_2$), 3.80 (1H, app d, *J* = 11.6 Hz, <u>H</u>6), 3.60 (1H, dd, *J* = 11.6, 5.8 Hz, <u>H</u>6), 3.23-3.41 (3H, m, <u>H</u>3, <u>H</u>4 and <u>H</u>5), 3.19 (1H, dd, *J* = 8.8, 8.1 Hz, <u>H</u>2) ppm; ^{13}C NMR (125 MHz, D_2O): δ = 145.35 (-<u>C</u>HCHB(OH)$_2$),

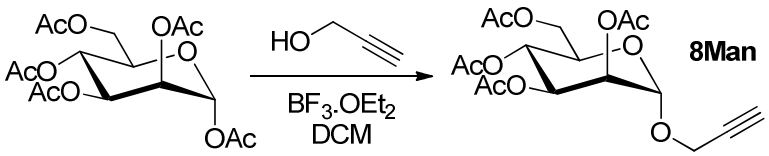
124.26 (Weak, -CHB(OH)$_2$), 101.41 (C1), 75.89 (C5), 75.72 (C3), 73.10 (C2), 71.08 (-CH$_2$CHCHB(OH)$_2$), 69.62 (C4), 60.71 (C6) ppm; HRMS *m/z* (ESI+): Found: 287.0912 (M+Na) Calc: 287.0910; M.p: >300 °C; IR (ν_{max}, solid): 3351, 2910, 1643, 1319, 1262, 1070, 1000 cm^{-1}; $[\alpha]_D$ = -18 (c = 1.0, H$_2$O);



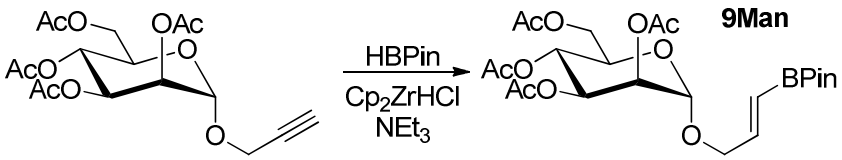
D-Galactose pentaacetate (3.91 g, 10 mmol) was dissolved in dry DCM (50 mL) under nitrogen and cooled to 0 °C. Propargyl alcohol (700 µL, 12 mmol) was added, followed by drop-wise addition of boron trifluoride diethyl etherate (1.88 mL, 15 mmol). After warming to rt, the reaction was stirred for 18 hrs. To quench the reaction, potassium carbonate (2 g) was added and stirred for 30 min. After filtration, the mixture was washed with water (2 x 75 mL) and the aqueous extracted with DCM (75 mL). The combined organics were dried with MgSO$_4$, filtered and concentrated *in vacuo* to give the DP as a light yellow oil. A yield of 3.9 g, 10 mmol (100 %) was obtained. Spectroscopic data matched that previously reported.[6] ^{1}H NMR (400 MHz, CDCl$_3$): δ = 5.40 (1H, dd, *J* = 3.4, 1.0 Hz, H4), 5.22 (1H, dd, *J* = 10.6, 8.0 Hz, H2), 5.06 (1H, dd, *J* = 10.6, 3.4 Hz, H3), 4.74 (1H, d, *J* = 8.0 Hz, H1), 4.39 (2H, d, *J* = 2.4 Hz, -CH$_2$CCH), 4.14-4.22 (2H, m, H6), 3.94 (1H, td, *J* = 6.8, 1.0 Hz, H5), 2.47 (1H, t, *J* = 2.4 Hz, -CCH), 2.16 (3H, s, -OAc), 2.08 (3H, s, -OAc), 2.06 (3H, s, -OAc), 1.99 (3H, s, -OAc) ppm;



β-Propargylgalactose tetra-acetate, **8Gal**, (0.5 g, 1.3 mmol) and Schwartz's reagent (84 mg, 0.33 mmol) were charged under nitrogen and pinacolborane (745 μL, 5.2 mmol) was added. Triethylamine (46 μL, 0.33 mmol) was then added and the mixture heated to 65 °C for 18 hrs. The mixture was then cooled to rt, diluted with ethyl acetate (10 mL) and filtered through a short plug of silica. The flow-through was concentrated *in vacuo* and purified by flash column chromatography, eluting with 25-30 % EtOAc:Petrol. Pure fractions were concentrated *in vacuo* to give the DP as a colourless oil. A yield of 270 mg, 0.53 mmol (40 %) was obtained. Spectroscopic data matched that previously obtained.



D-Mannose pentaacetate (1.5 g, 3.84 mmol) was dissolved in dry DCM (20 mL) under nitrogen and cooled to 0 °C. Propargyl alcohol (1.12 mL, 19.21 mmol) was added, followed by boron trifluoride diethyl etherate (4.86 mmol, 38.4 mmol) dropwise. After warming to rt, the reaction was stirred for 18 hrs. DCM (50 mL) was then added and the mixture washed sequentially with water (30 mL), sat. $NaHCO_3$ (3 x 30 mL) then water (50 mL). The organics were dried with Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography eluting with 30 % EtOAc:Petrol. Pure fractions were concentrated *in vacuo* to give the DP as an off white solid. A yield of 1.2 g, 3.11 mmol (81 %) was obtained. Spectroscopic data matched that previously reported.[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.27-5.37 (3H, m, H2, H3 and H4), 5.04 (1H, d, *J* = 1.5 Hz, H1), 4.27-4.33 (3H, m, H6 and –CH_2CCH), 4.12 (1H, dd, *J* = 12.3 Hz, 2.4 Hz, H6), 4.03 (1H, ddd, *J* = 9.0, 5.1, 2.4 Hz, H5), 2.48 (1H, t, *J* = 2.4 Hz, -CCH), 2.17 (3H, s, -OAc), 2.11 (3H, s, -OAc), 2.05 (3H, s, -OAc), 2.00 (3H, s, -OAc) ppm;



α-Propargylmannose tetra-acetate, **8Man**, (1 g, 2.6 mmol) and Schwartz's reagent (134 mg, 0.52 mmol) were charged under nitrogen and pinacolborane (518 μL, 3.9 mmol) was added. Triethylamine (73 μL, 0.52 mmol) was then added, and the reaction heated to 65 °C for 18 hrs. After cooling to rt, the mixture was diluted with DCM (30 mL) and washed with water (10 mL). The organics were dried with Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography eluting with 25-50 % EtOAc:Petrol. Pure fractions were concentrated *in vacuo* to give the DP as a yellow oil. A yield of 190 mg, 0.37 mmol (14 %) was obtained. Spectroscopic data was identical to that previously obtained.

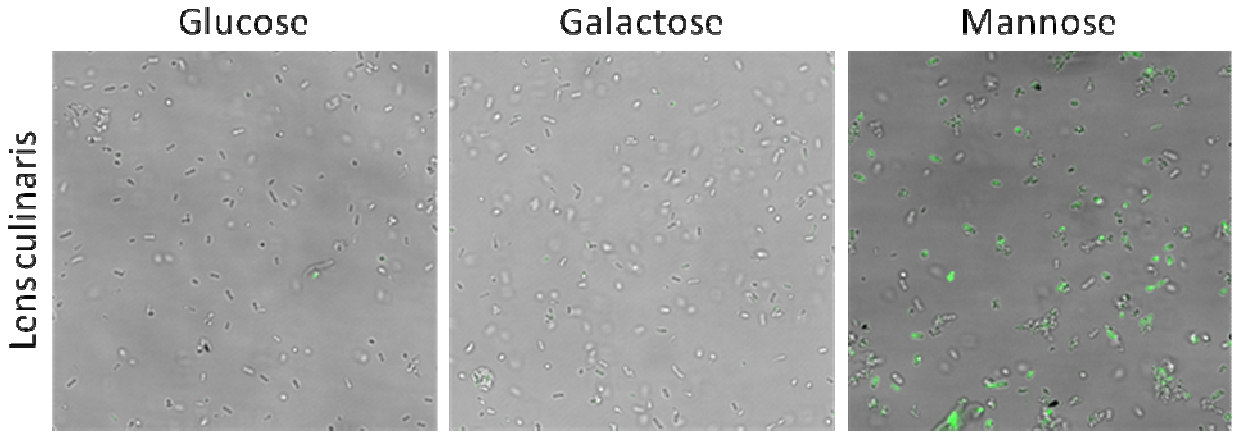
Induction of Protein Expression

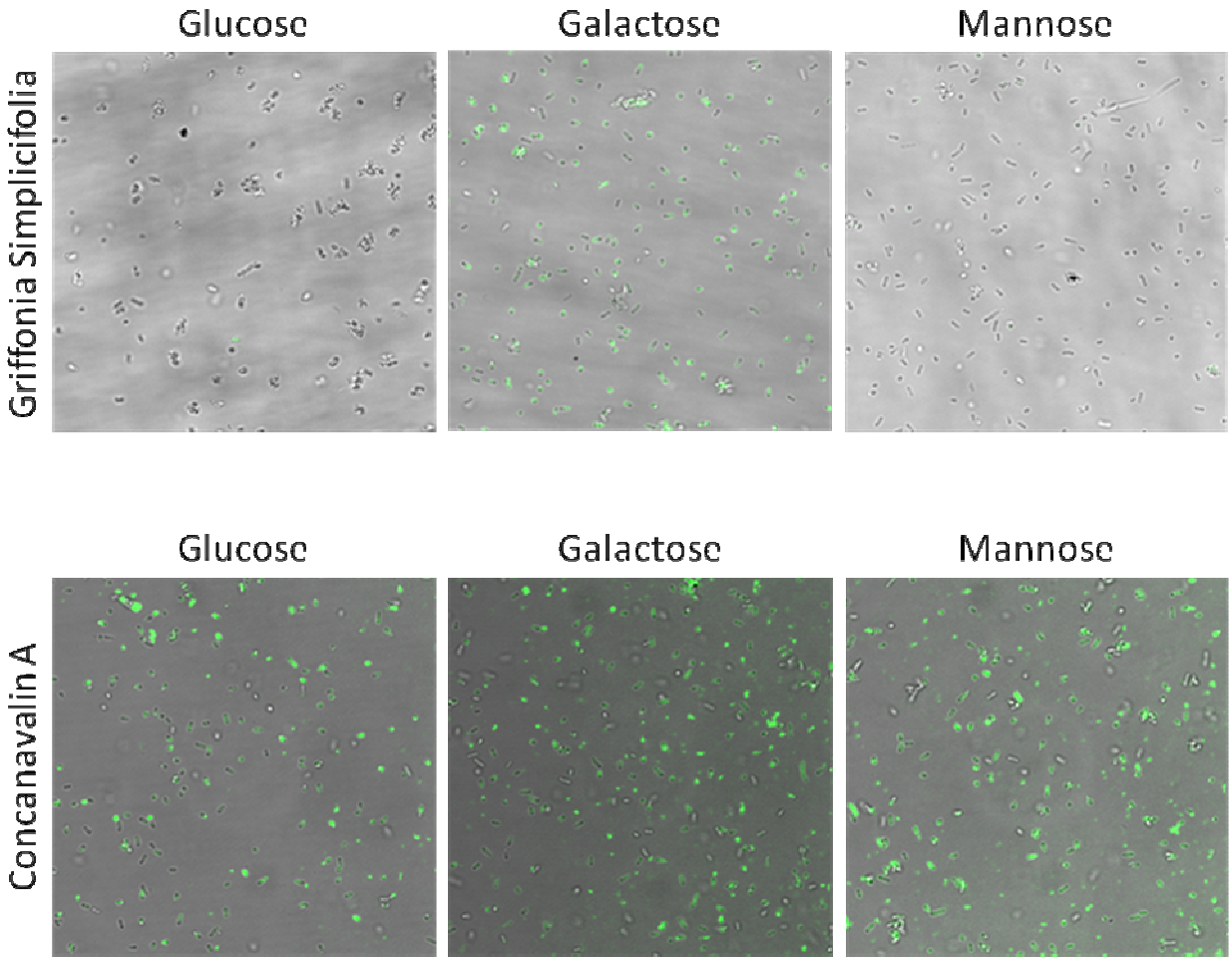
Cell line JW2203-1-pEvol(*p*IPhe)-OmpC(Y232·) was generated as a glycerol stock in a previous report.[8] The cell line codes for the expression of OmpC with an amber stop codon at position 232, with a pEVOL plasmid for *p*IPhe incorporation in response to the amber codon. The plasmids are carried by an OmpC-knockout cell line.

Overnight cultures were grown from the above glycerol stock in LB media containing ampicillin and chloramophenicol. 0.2 mL of this culture was then diluted in fresh media (30 mL) and grown to an $O.D_{600}$ ~ 0.6 at 37 °C. Protein production was then induced through the addition of 1 mM IPTG, 0.02 % *L*-arabinose, and 2 mM L-*p*-iodophenylalanine. Cells were then incubated at 30 °C for 14 hrs.

General Procedure for Cell Labelling

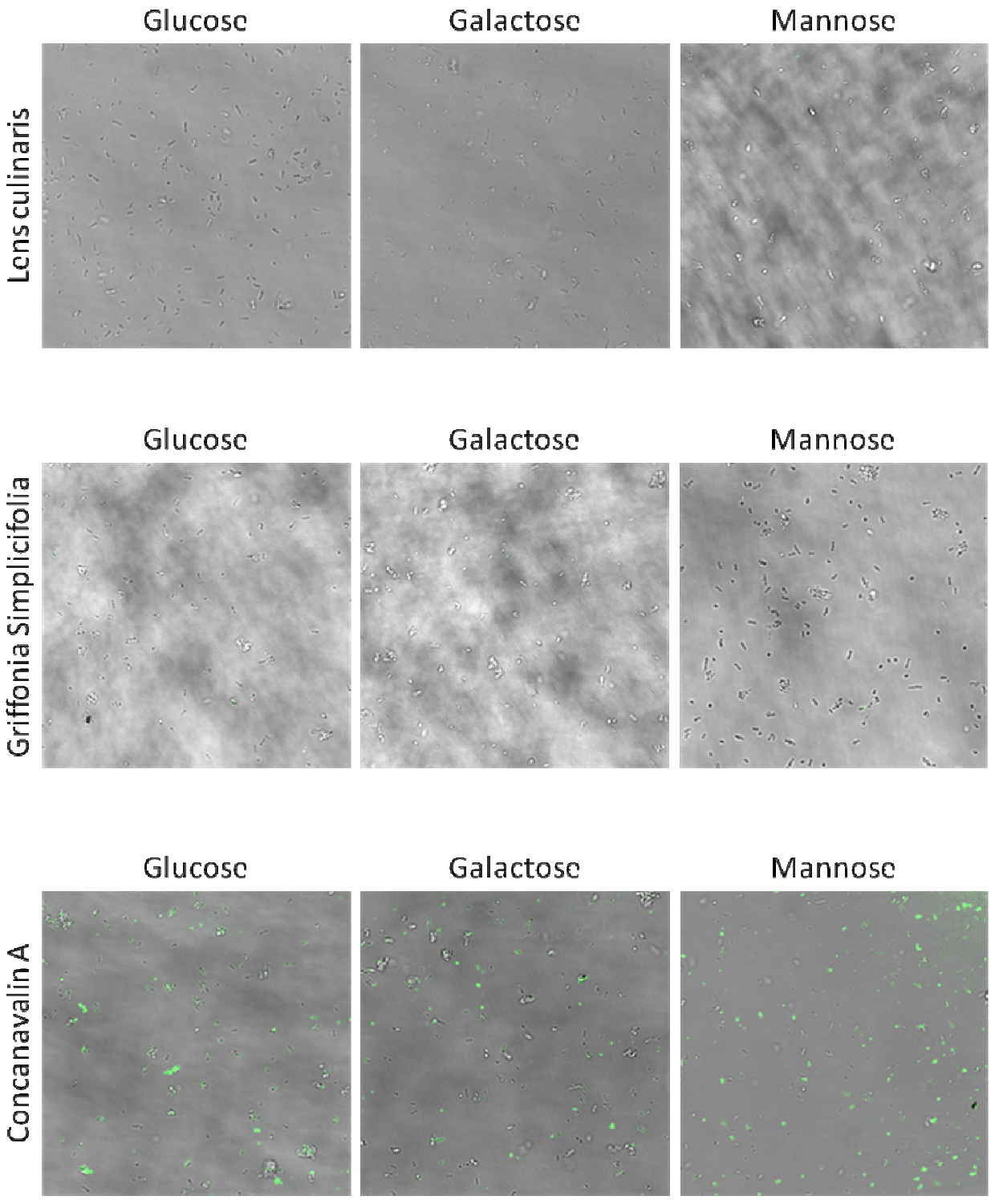
Induced cells were collected by centrifugation (rt, 10 min, 3000 rpm) and re-suspended in phosphate buffer (20 mL, 50 mM NaCl, 20 mM NaH_2PO_4, pH 8.0). This process was repeated twice in order to remove residual LB media and any residual unincorporated unnatural amino acid. The $O.D_{600}$ was then measured, and the culture diluted with phosphate buffer to give an $O.D_{600}$ = 0.2. In a standard experiment, a 200 µL aliquot was then added to a 1.5 mL Eppendorf tube. A stock solution of sugar boronic acid was prepared by dissolving 5 mg of the boronic acid with 5 mg of Na_2HPO_4 in 300 µL of water at 37 °C (18.9 µmol boronic acid, 35.2 µmol Na_2HPO_4). A 12 µL aliquot was added to the cells (0.76 µmol), followed by a 10 µL aliquot of stock palladium catalyst **1** (0.1 µmol). After the cells were incubated with shaking at 37 °C for 1 hr they were collected by centrifugation (rt, 5 min, 10,000 rpm) and re-suspended in a 0.85 % saline solution (400 µL). This process was repeated 5 times, to ensure complete removal of un-reacted boronic acid and palladium. Finally, the cells were re-suspended in 200 µL saline solution and fluorescein-labelled lectins were added to a final concentration of 25 µg/mL. Cells were then visualised by fluorescence microscopy.





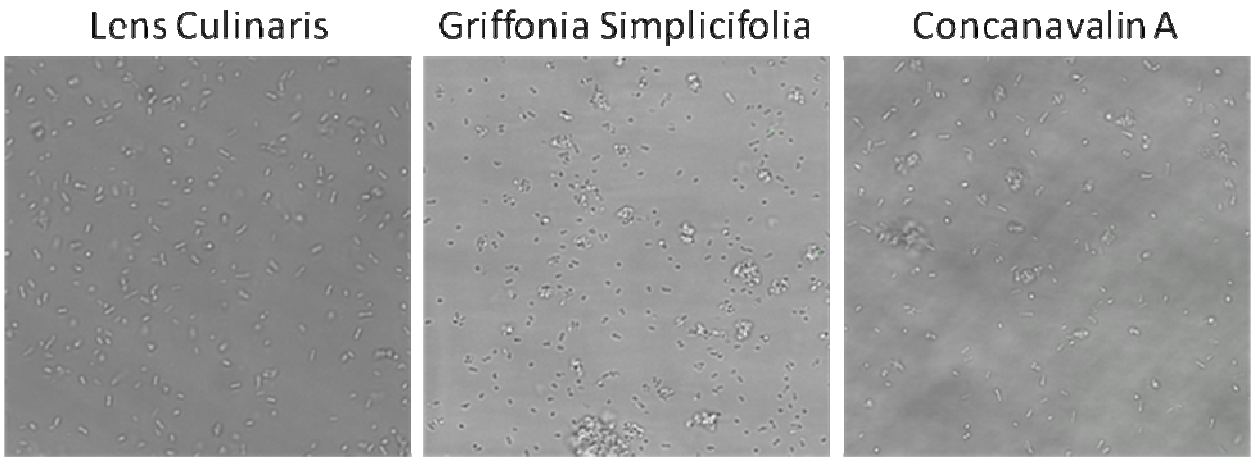
Labelling in the Absence of Palladium

Experiments were run as described above, replacing palladium with the addition of phosphate buffer. Cells were then visualised by fluorescence microscopy.



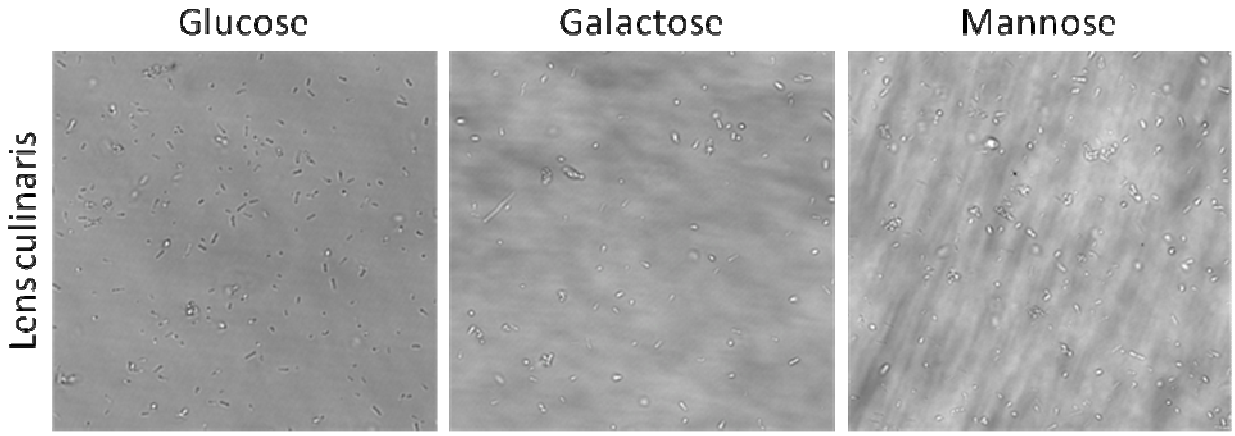
Labelling in the Absence of Boronic Acid

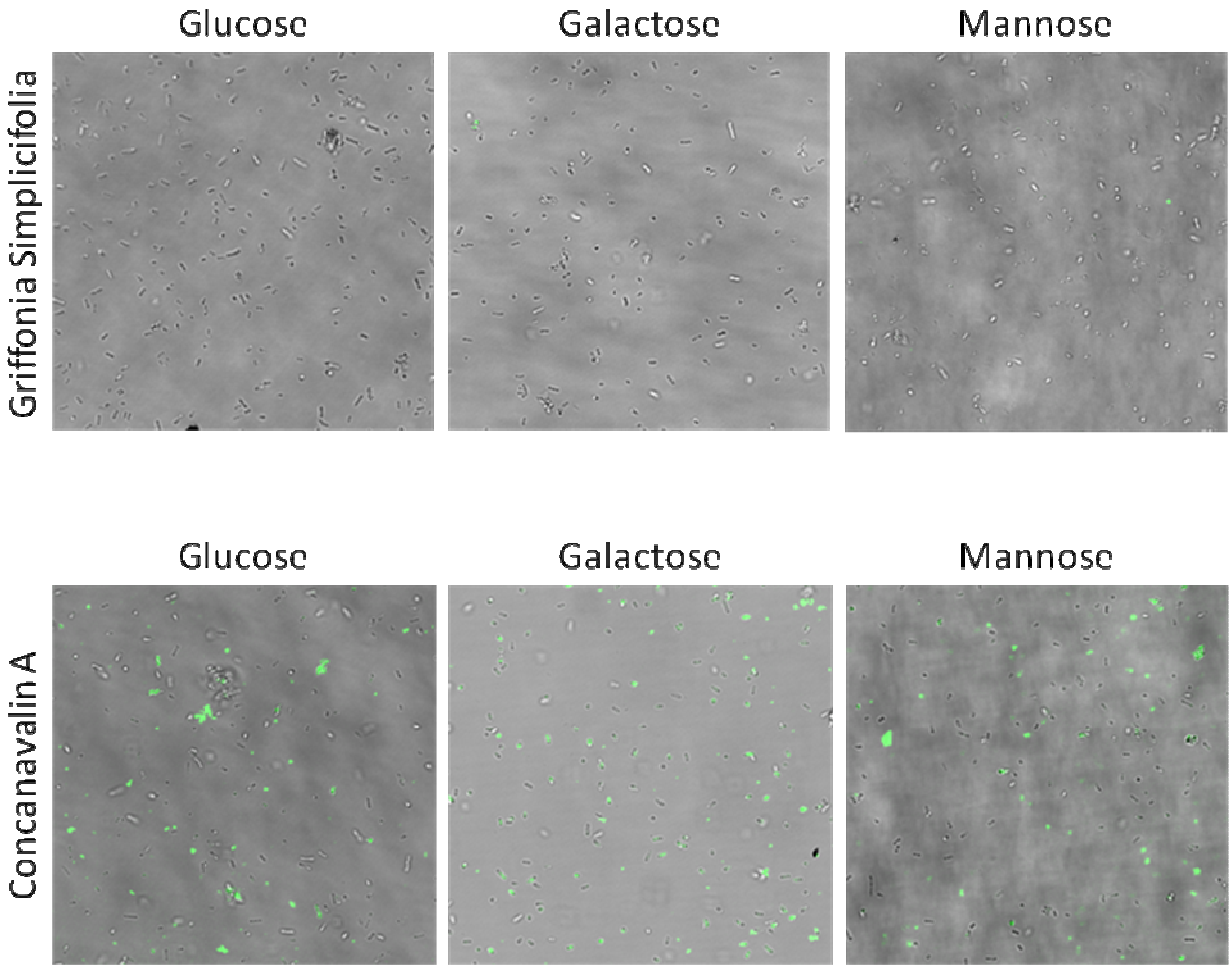
Experiments were run as described above, replacing the sugar boronic acid with the addition of phosphate buffer. Cells were then visualised by fluorescence microscopy.



Labelling in the Absence of Amino Acid

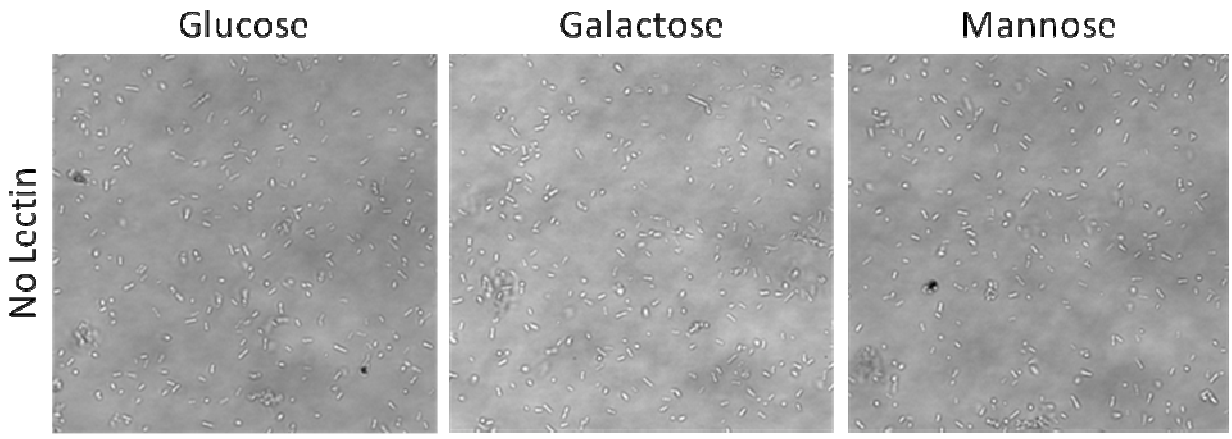
Cells were grown as described above, omitting the addition of *p*-iodophenylalanine during the induction step, to generate cells deficient in aryl halide display on the cell surface. Coupling reactions were then run as described above and the cells visualised by fluorescence microscopy.





Cells in the Absence of Fluorescein-Labelled Lectins

Experiments were run as described above, with phosphate buffer being added in place of fluorescent lectin conjugate. The cells were then visualised by fluorescence microscopy.



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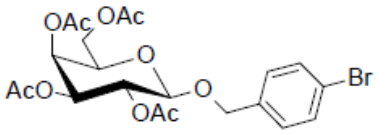
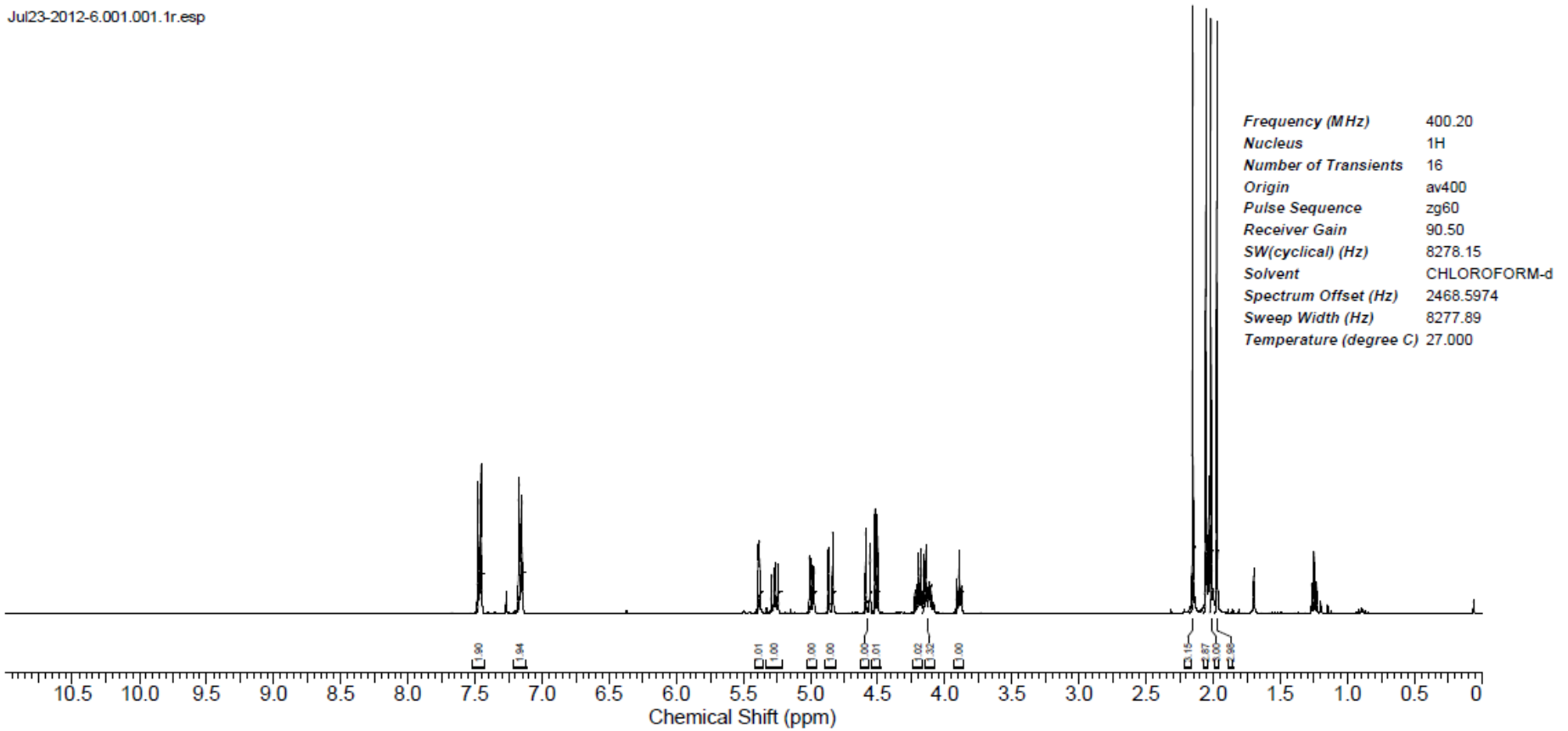
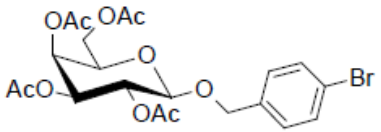
(8) Spicer, C. D.; Triemer, T.; Davis. B. G. *J. Am. Chem. Soc.*, **2012**, *134*, 800-803.



^{1}H NMR (400 MHz, $CDCl_3$)





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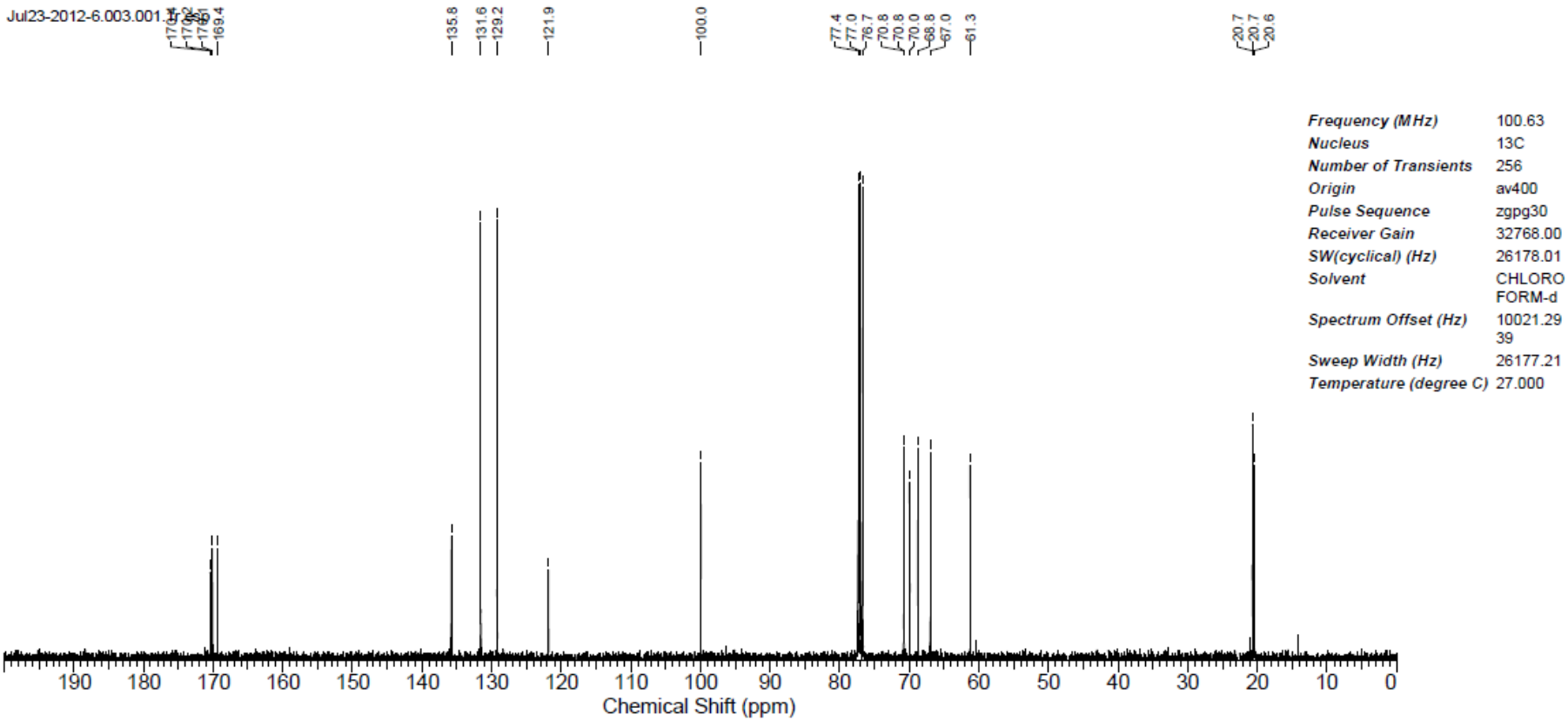

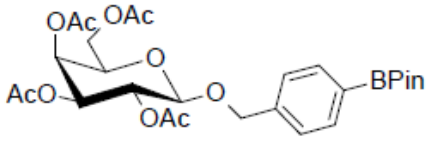

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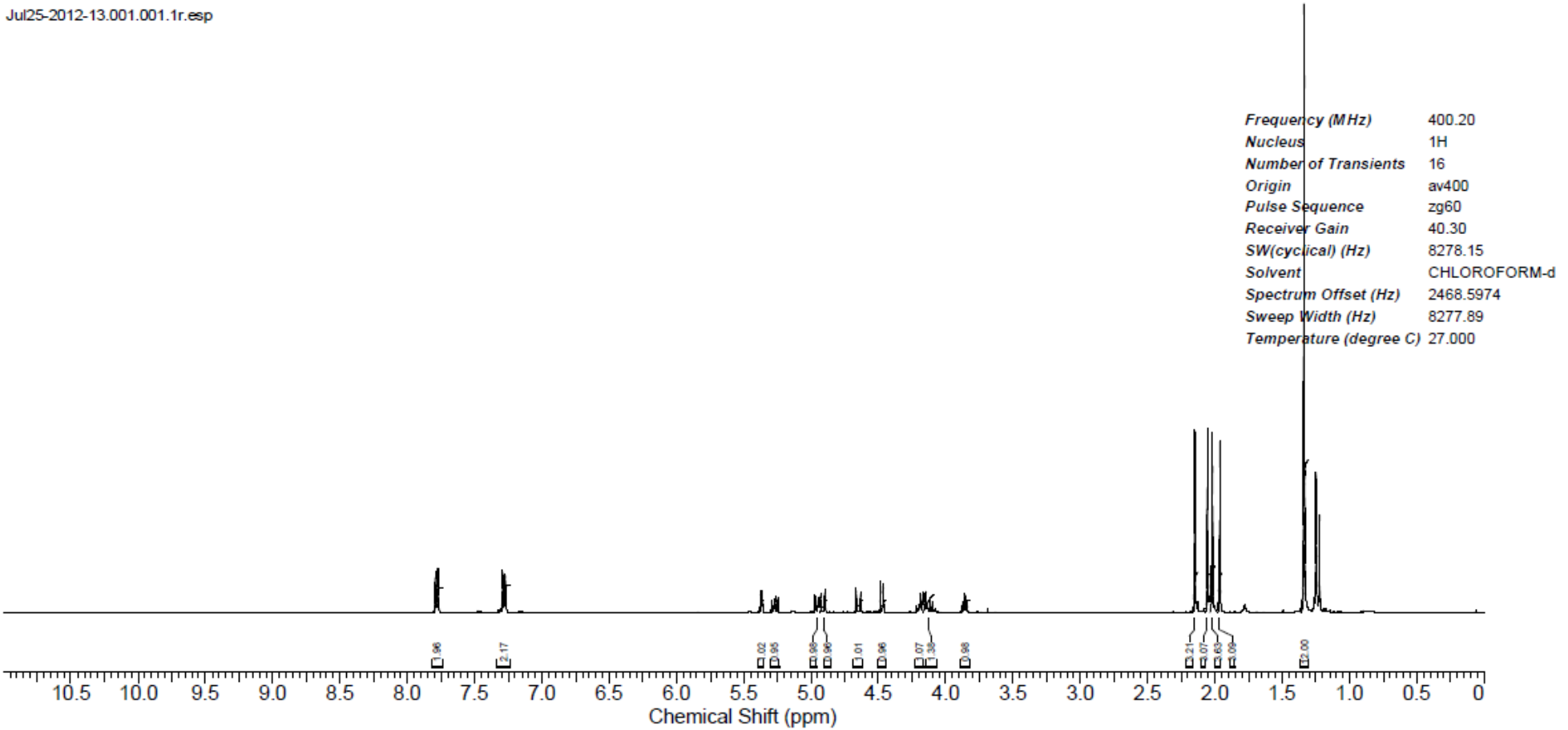

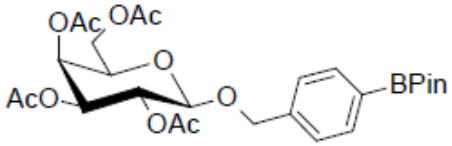

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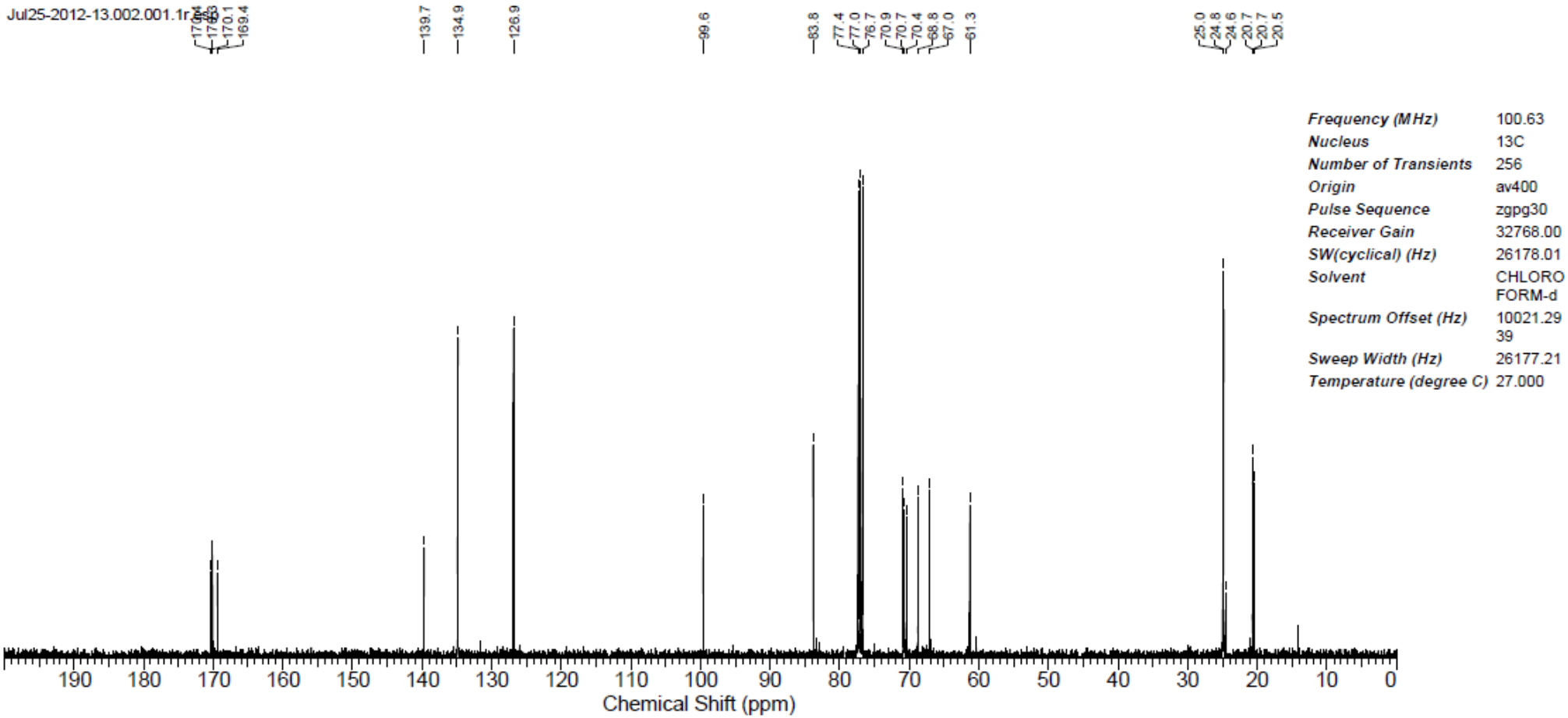

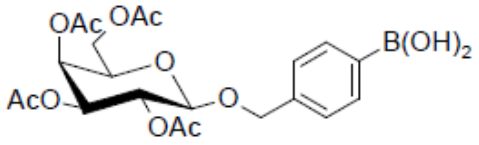

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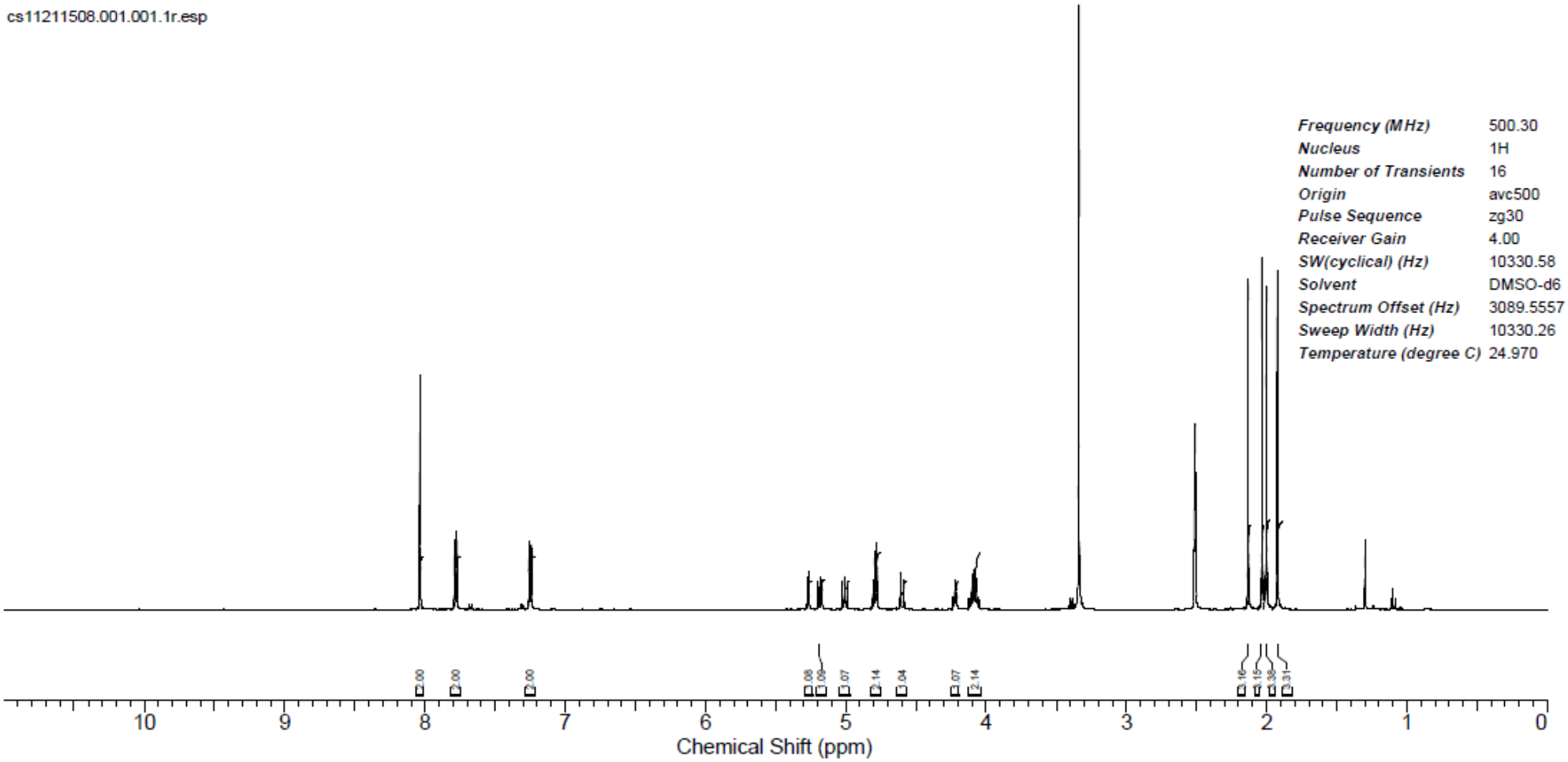

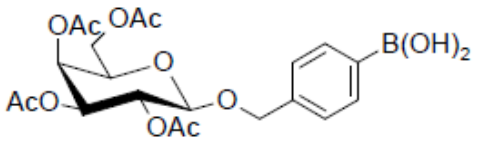

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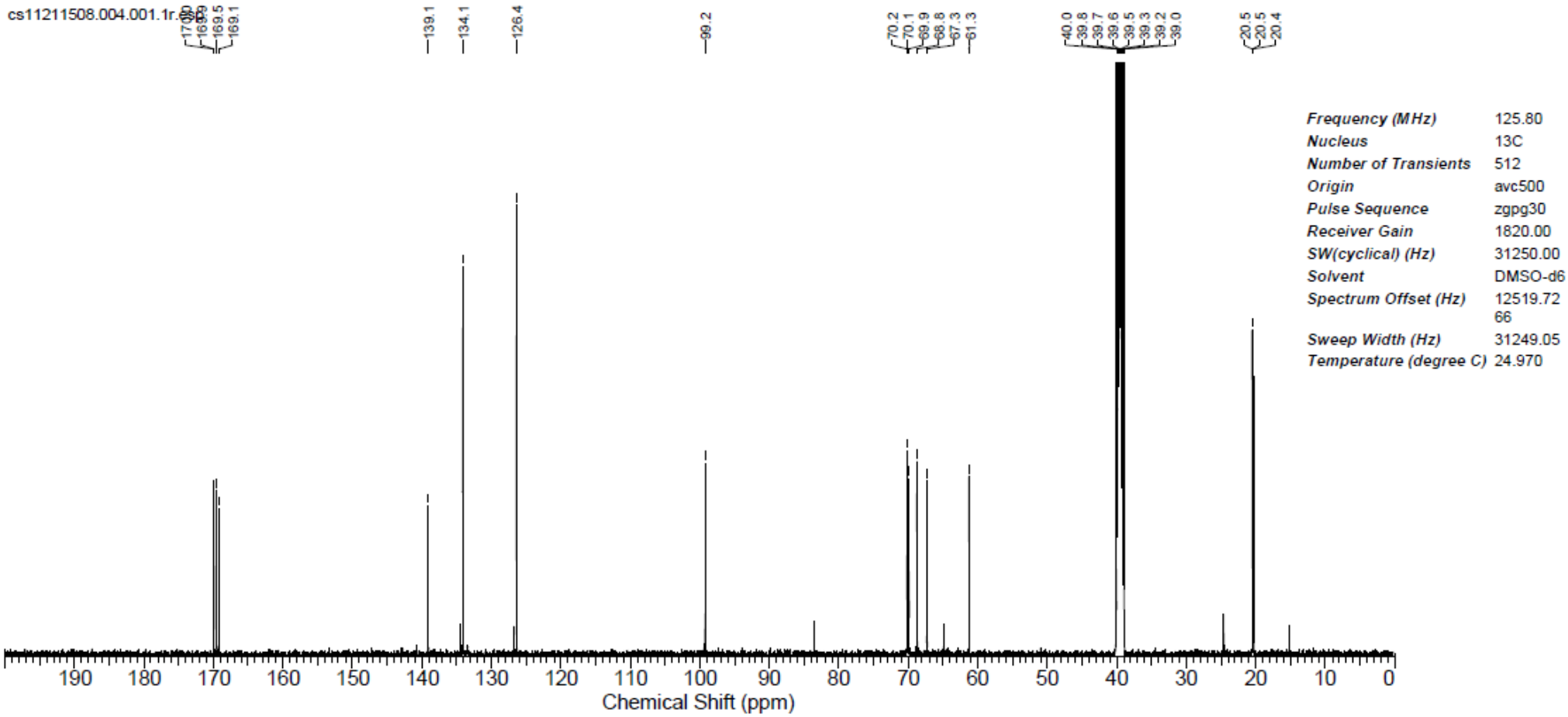

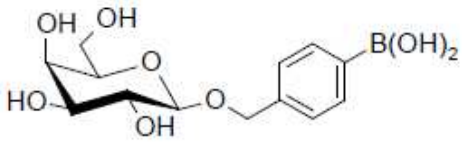

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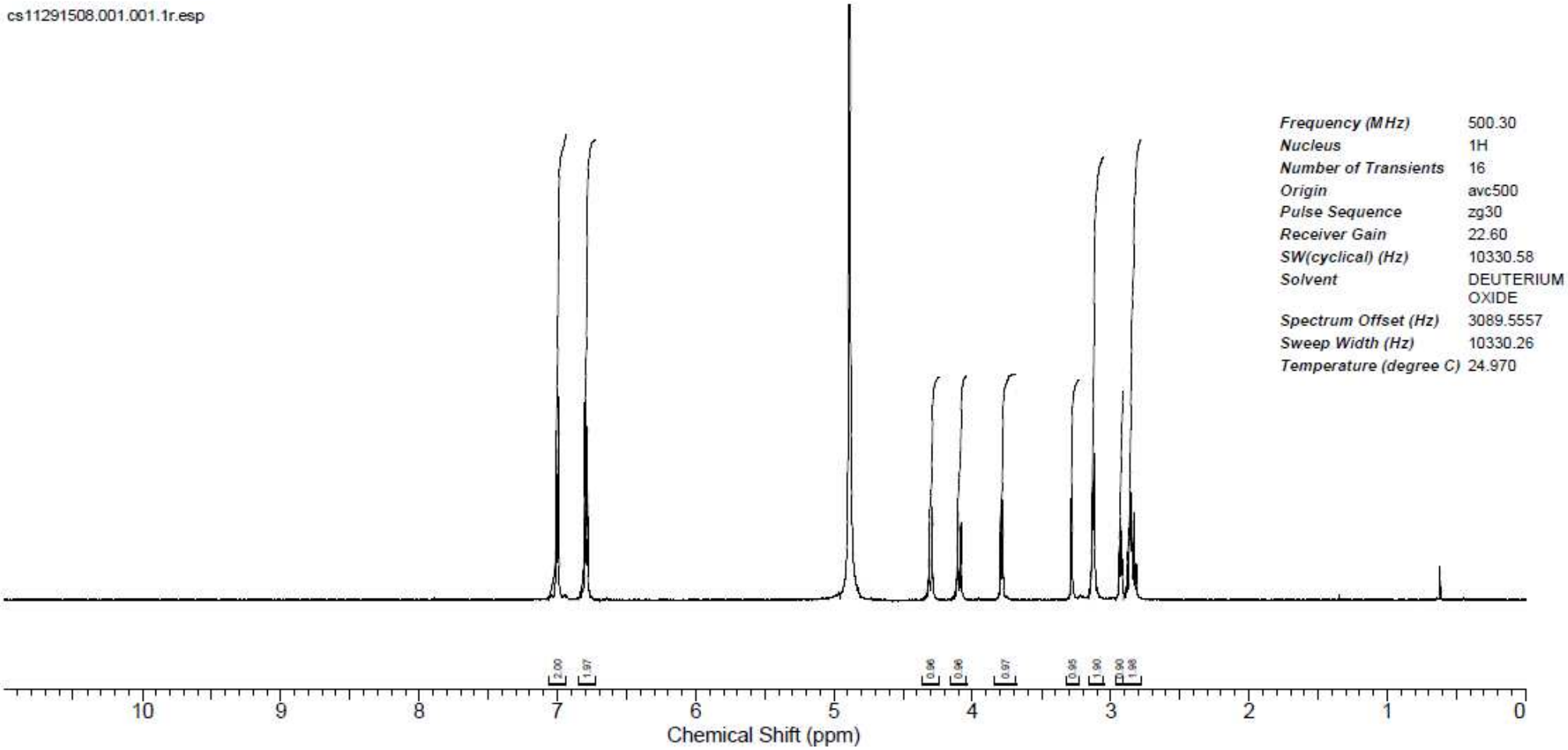

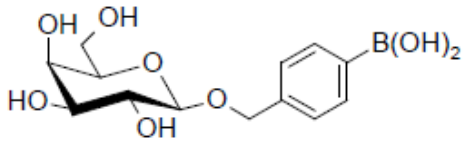

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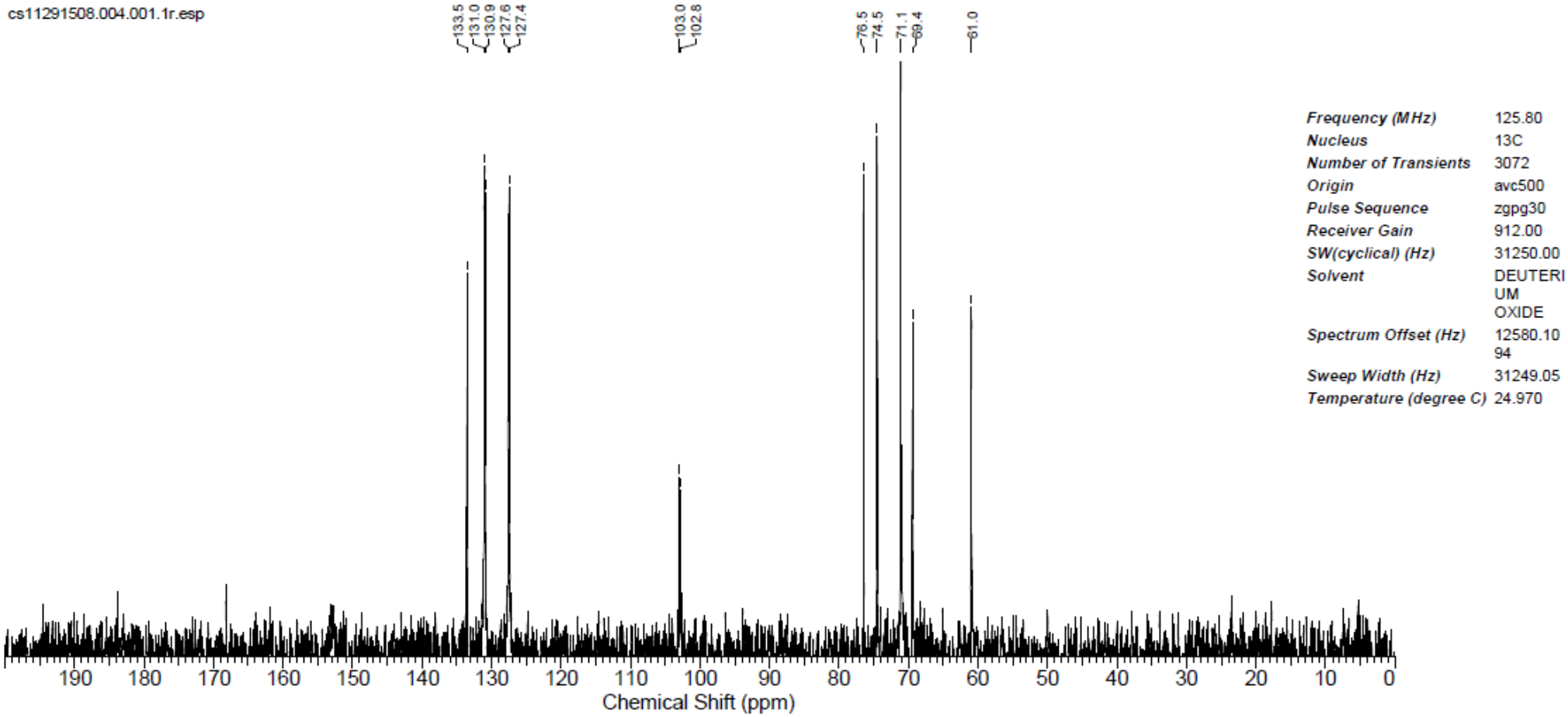

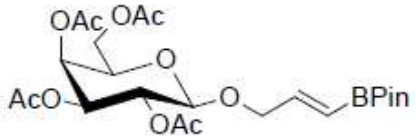

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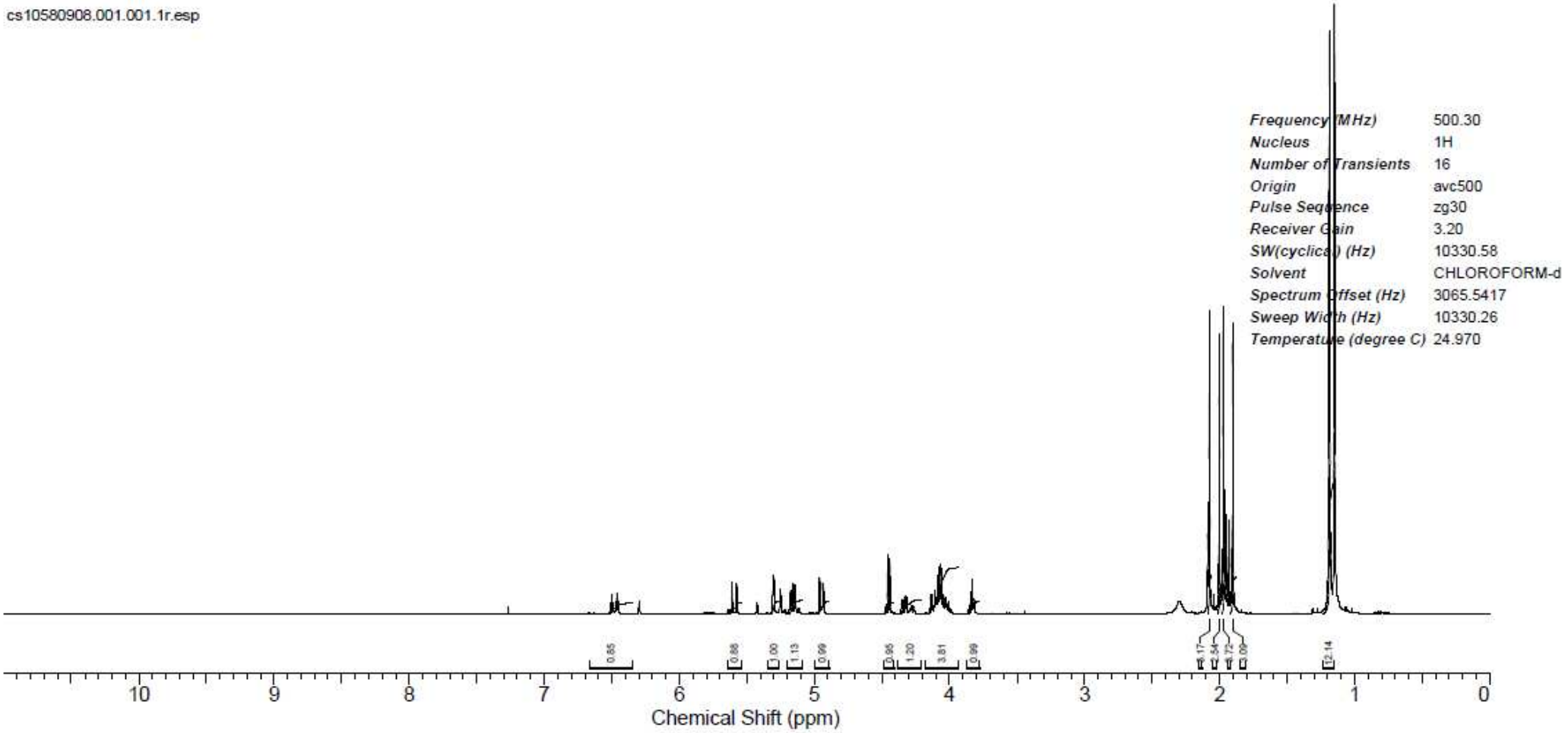

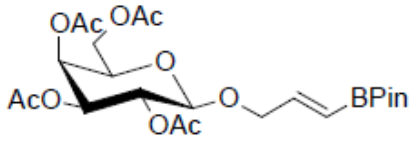

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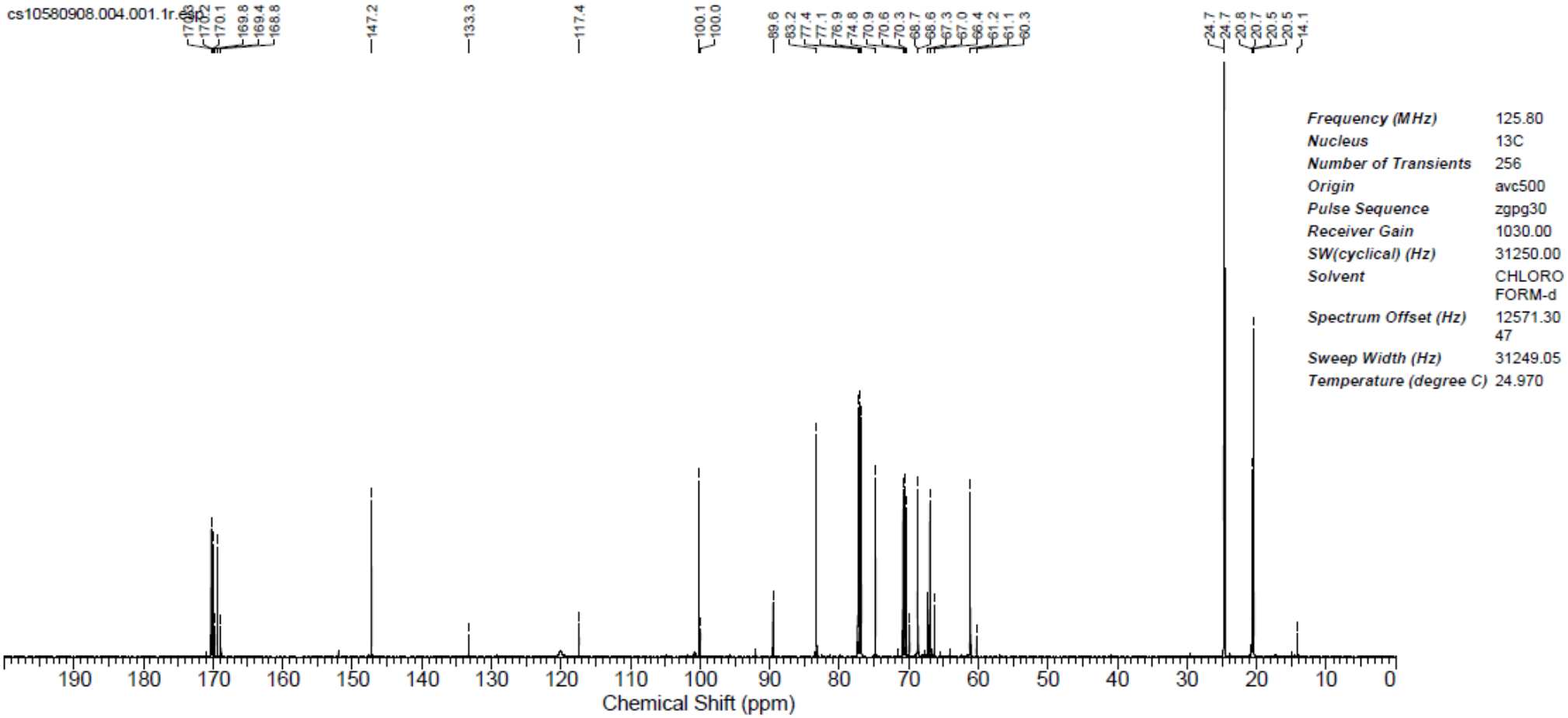

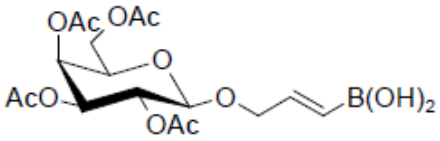

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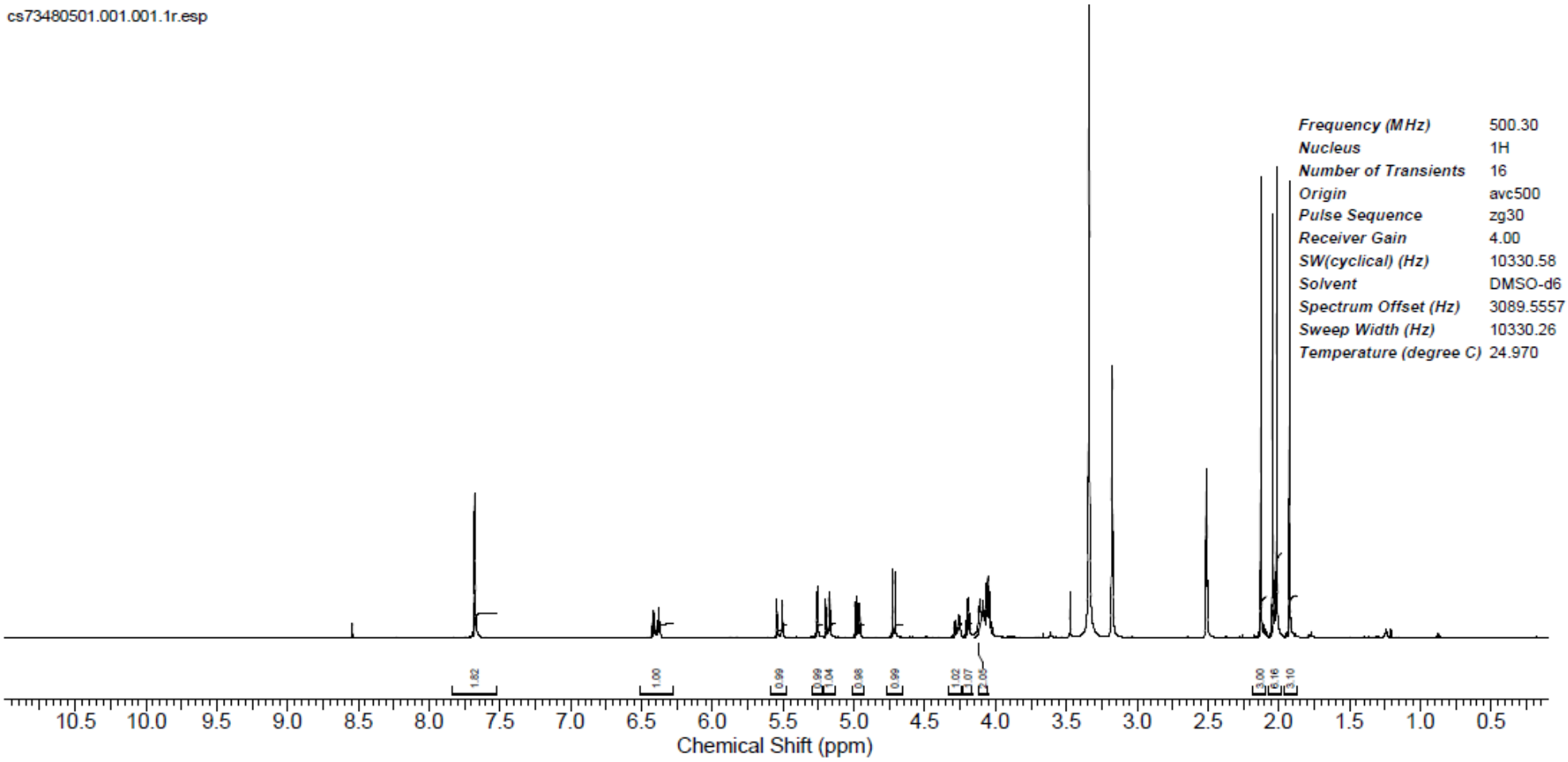

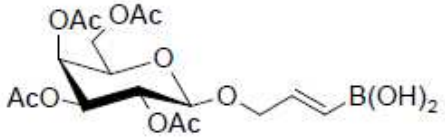

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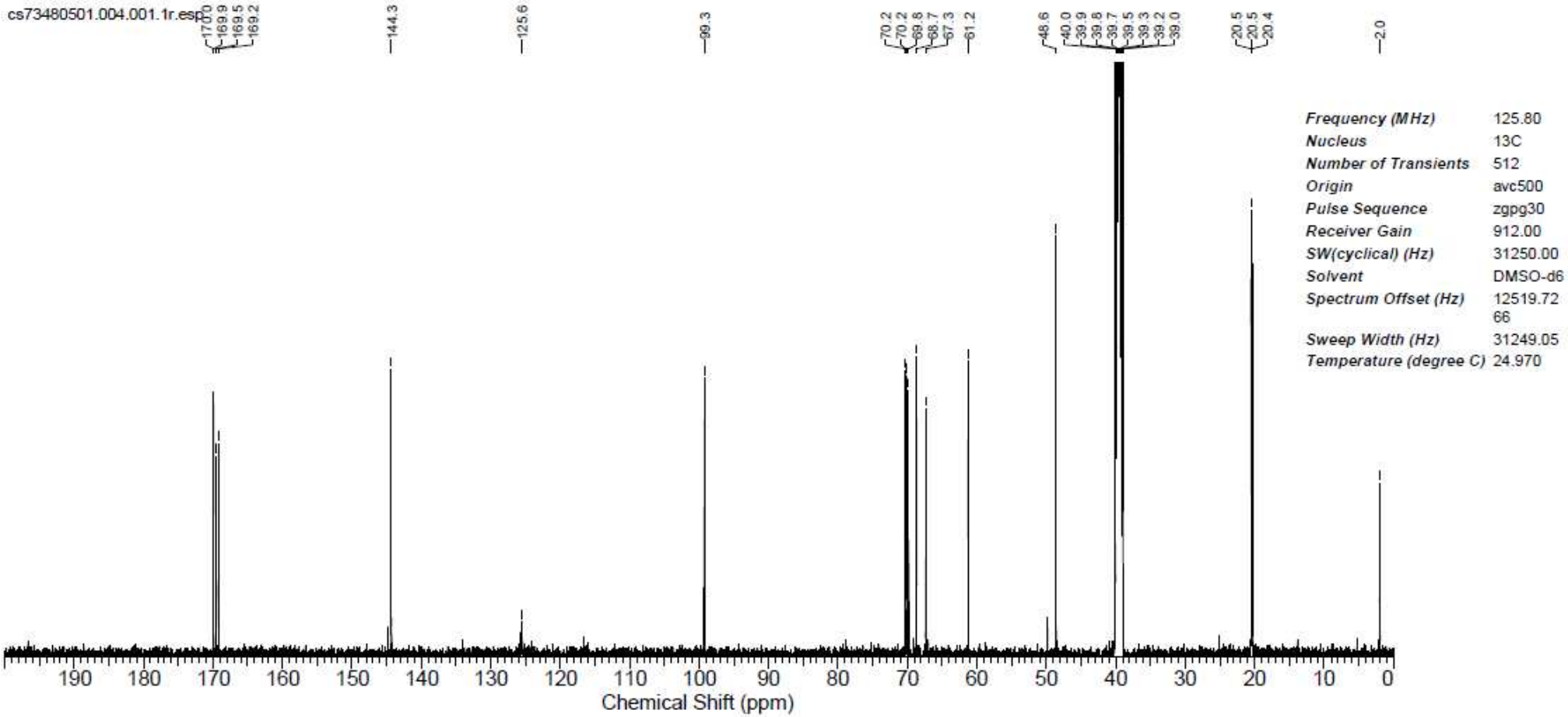

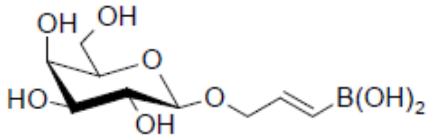

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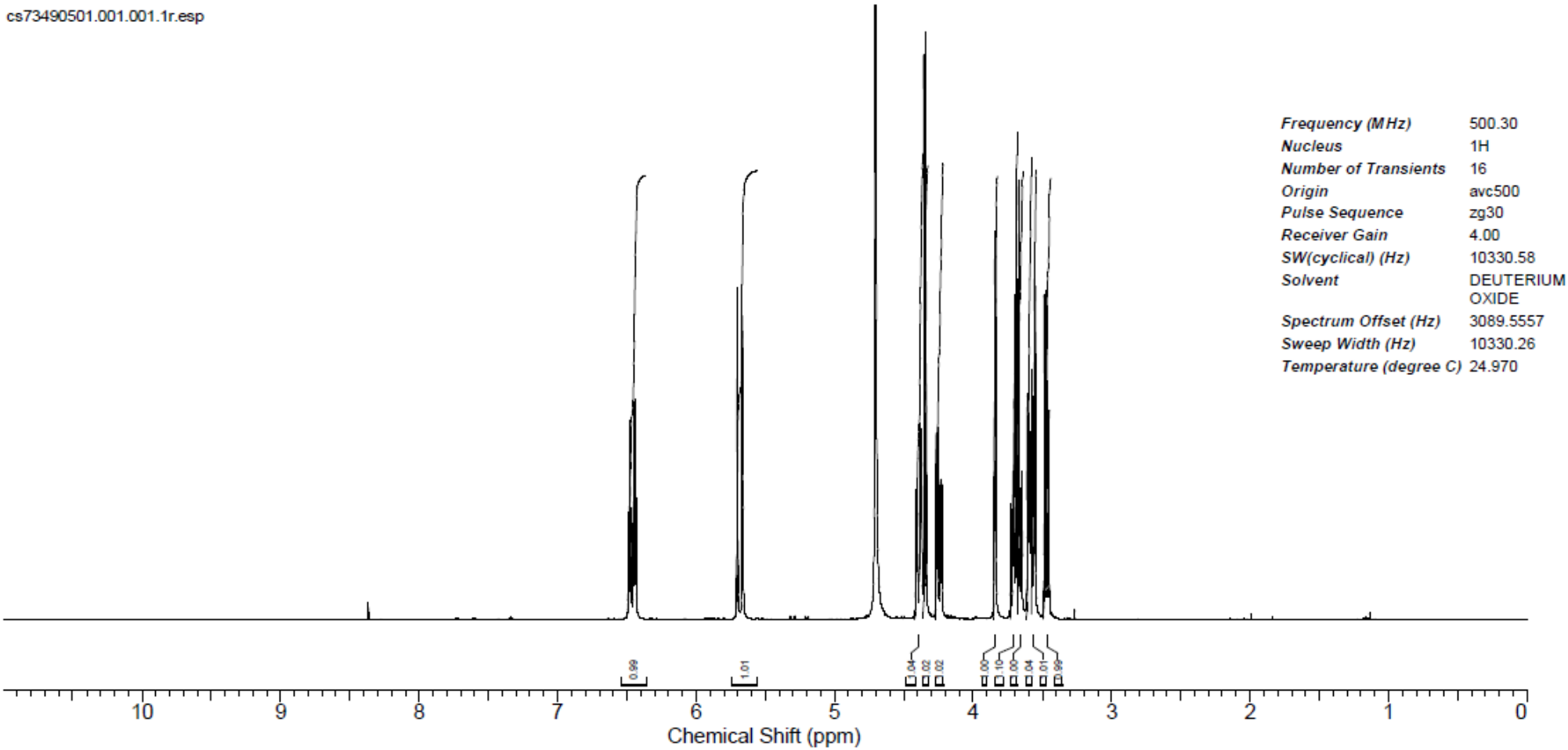

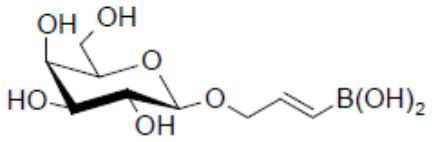

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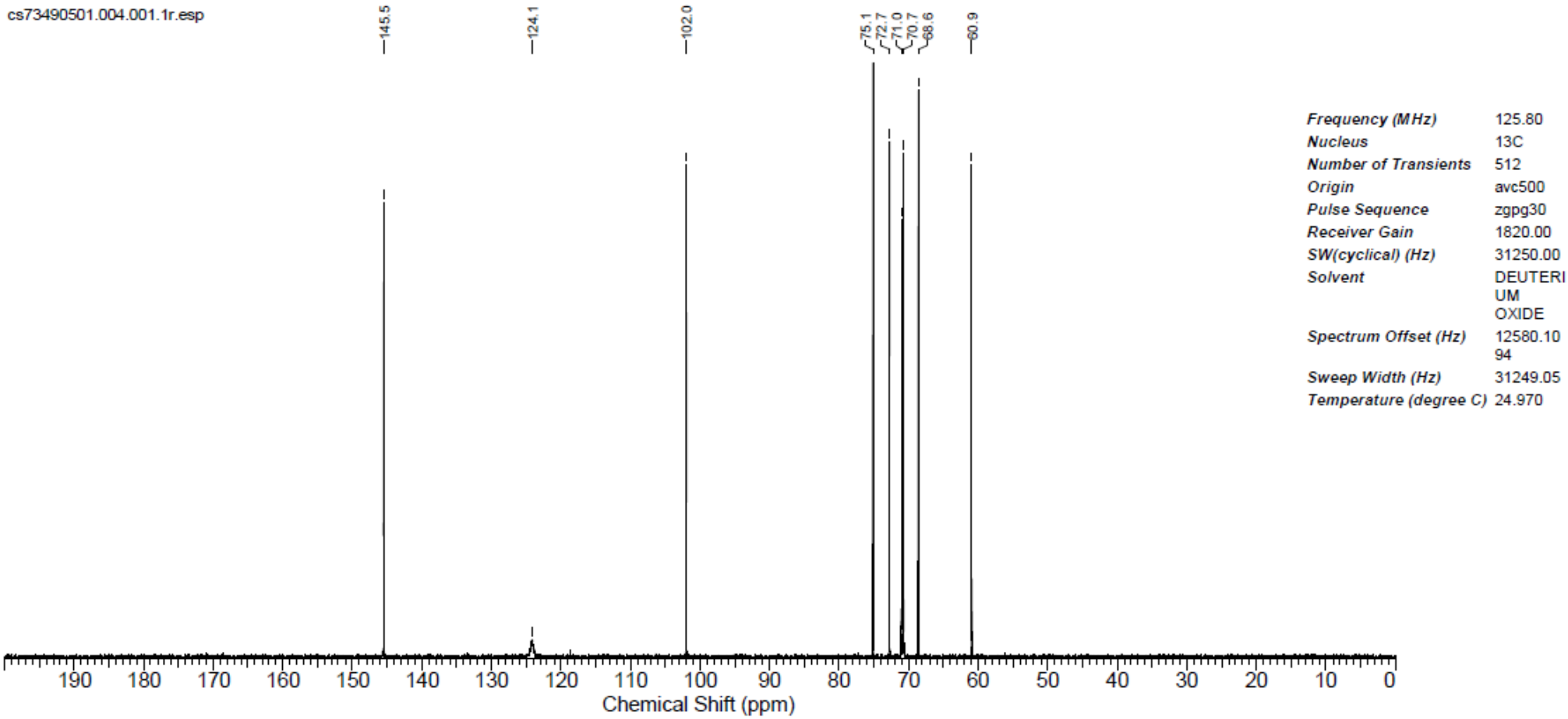

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Nucleus	13C
Number of Transients	512
Origin	avc500
Pulse Sequence	zgpg30
Receiver Gain	1820.00
SW(cyclical) (Hz)	31250.00
Solvent	DEUTERIUM OXIDE
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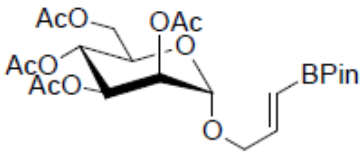
Sweep Width (Hz)	31249.05
Temperature (degree C)	24.970



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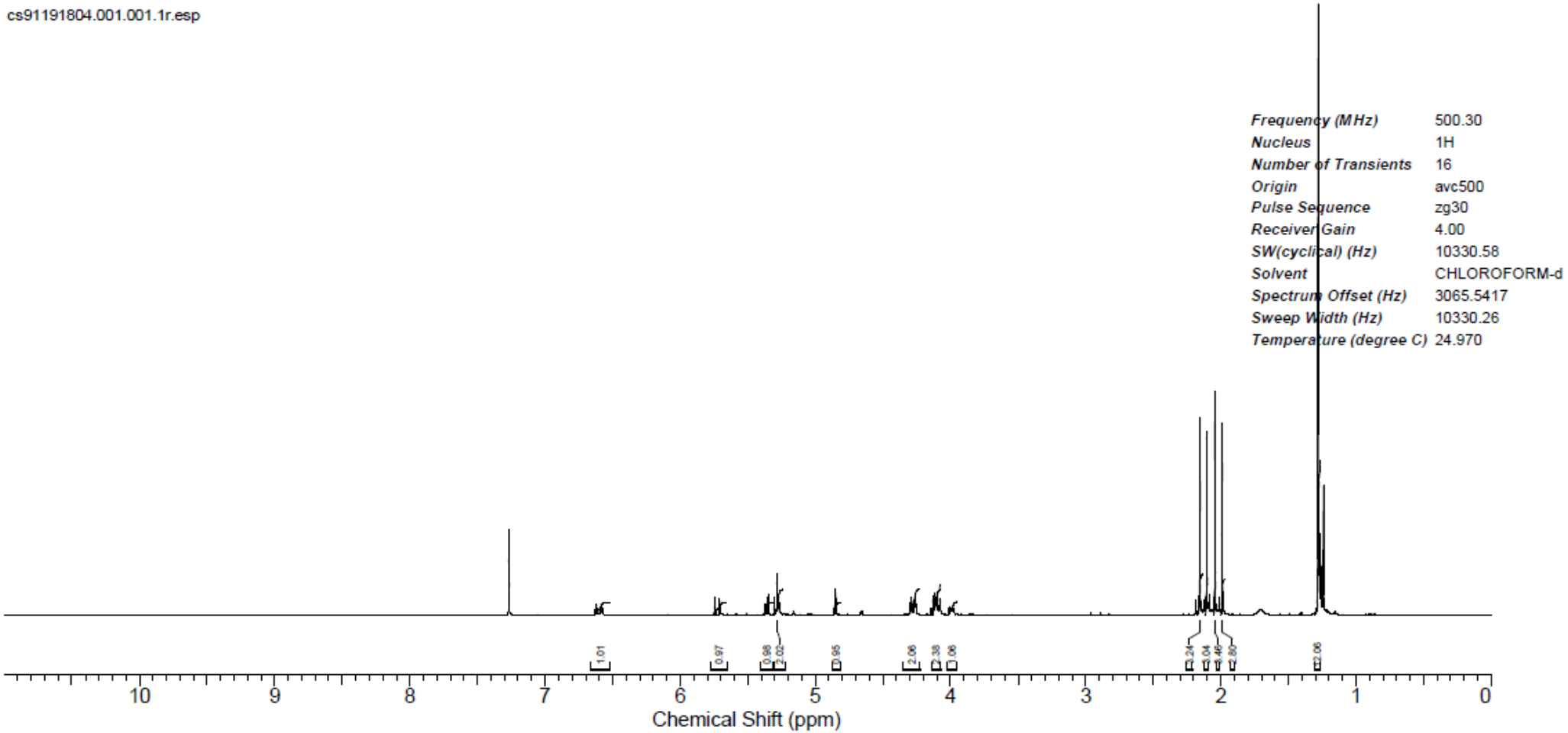

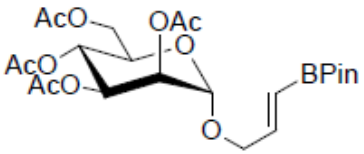

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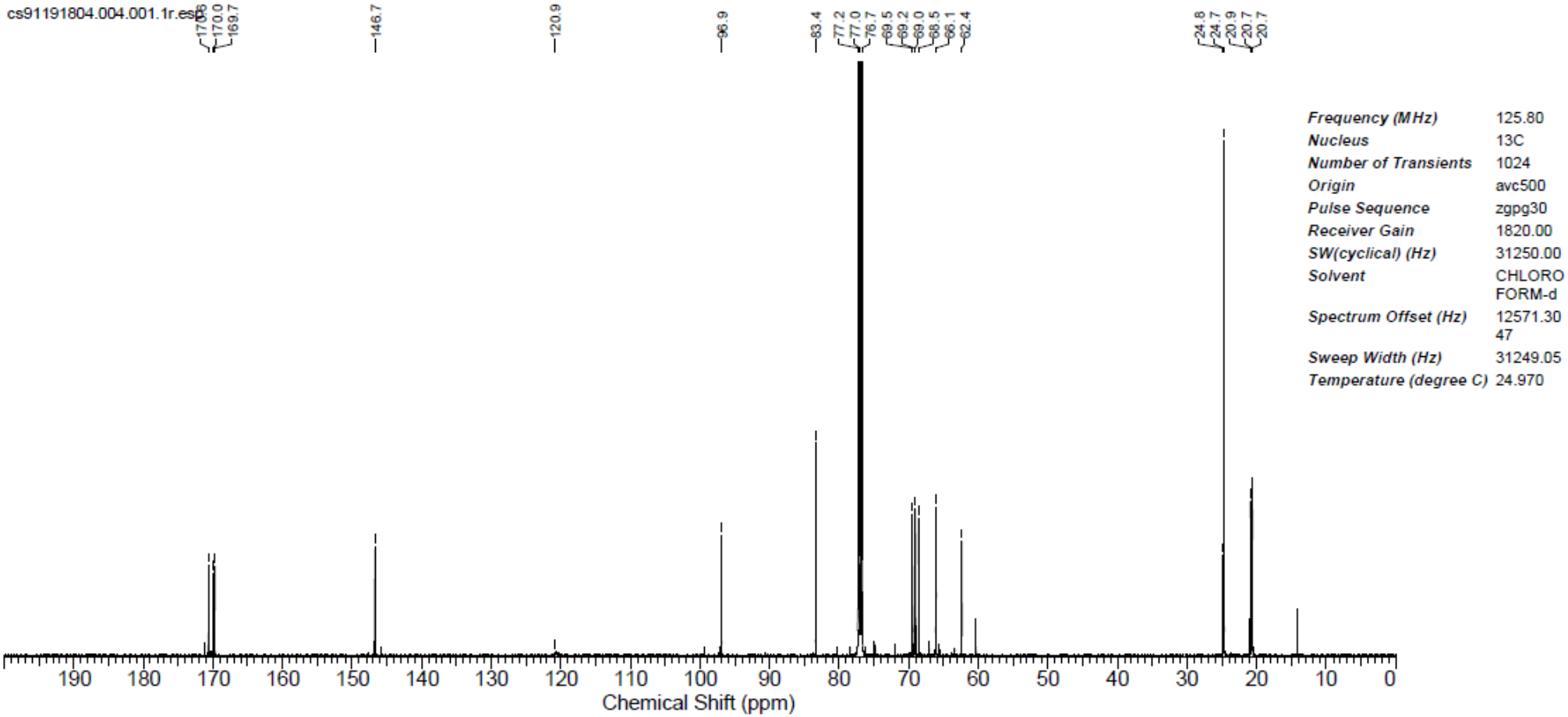
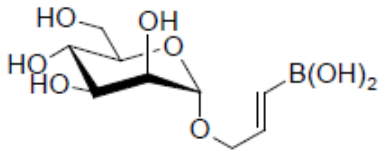
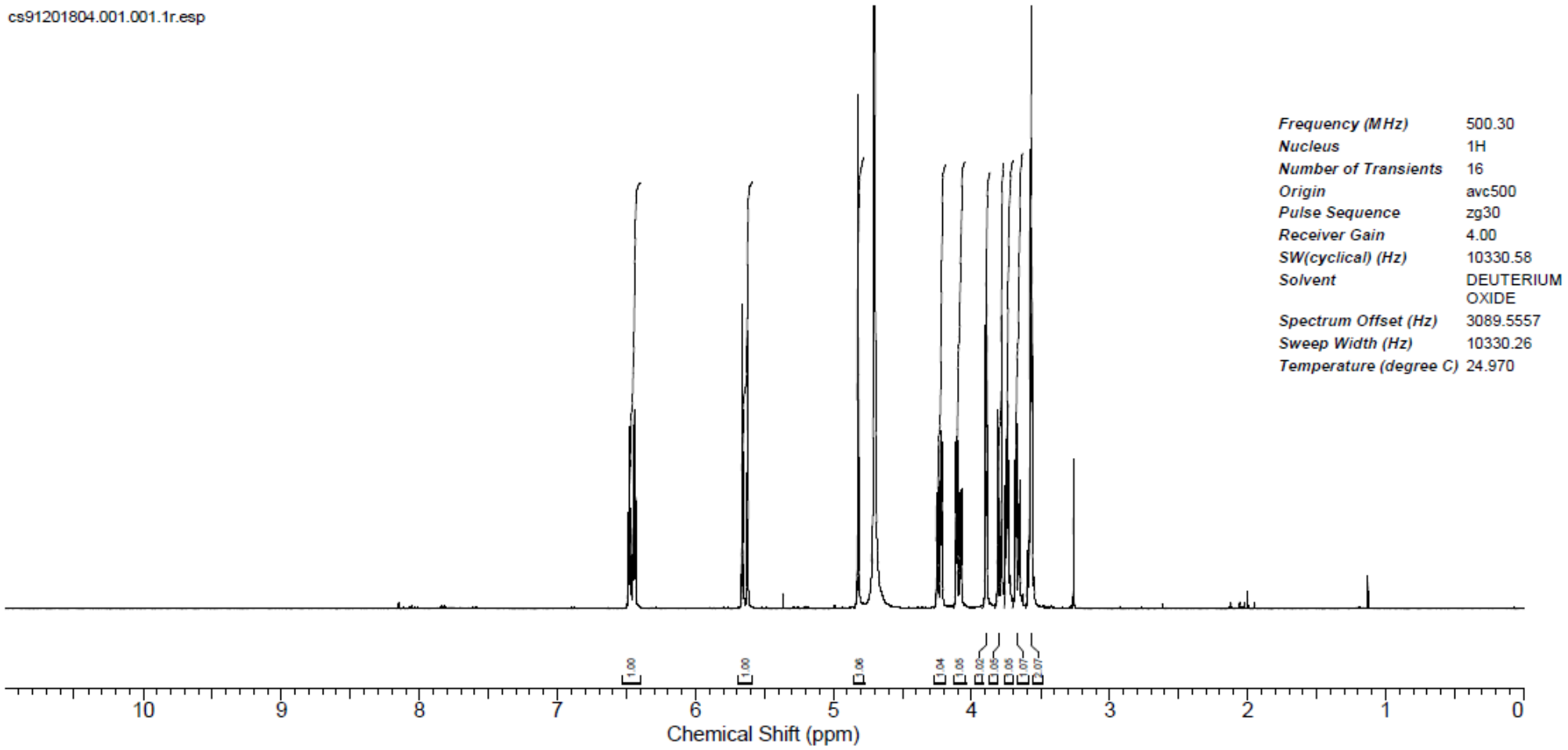
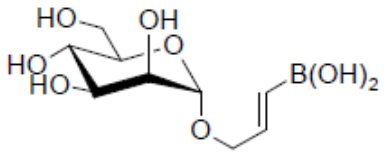


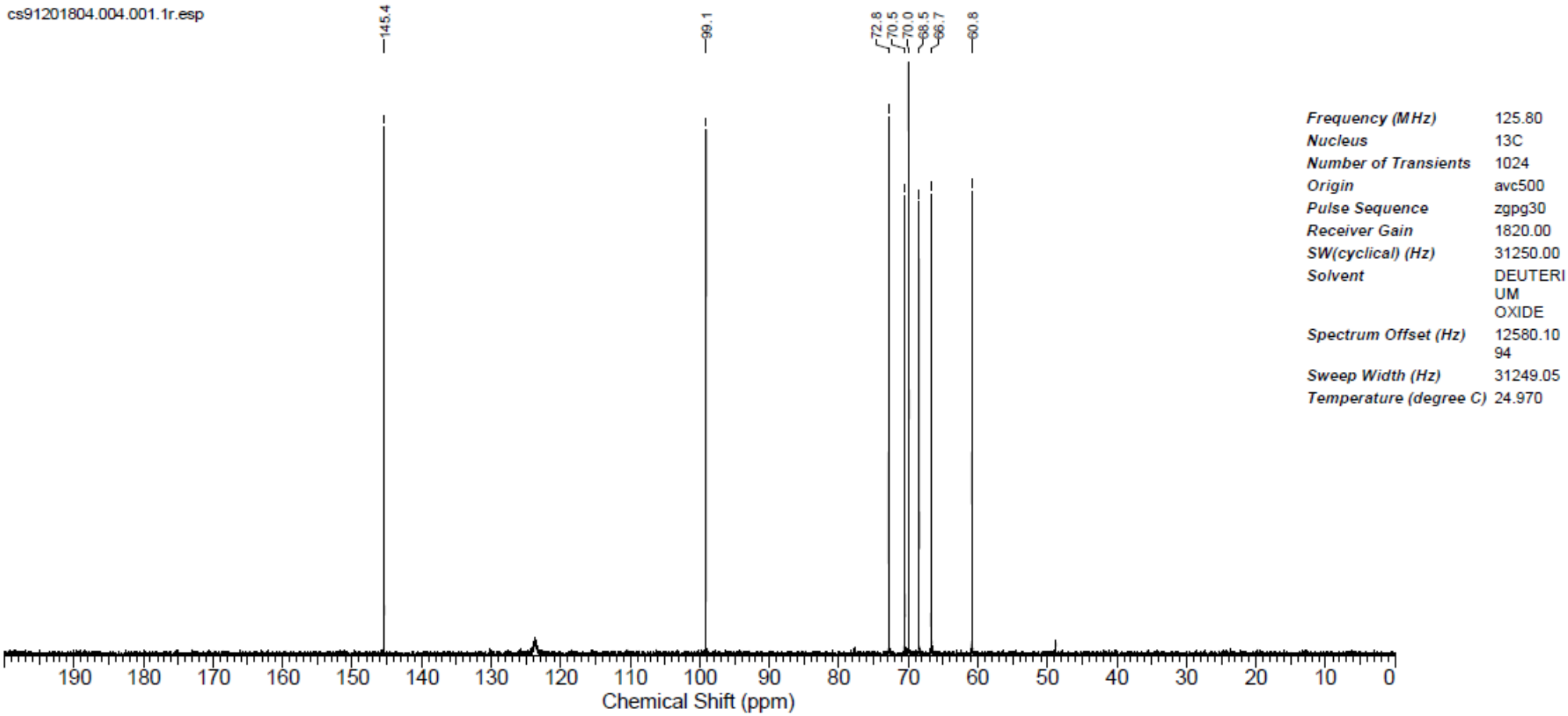


^{1}H NMR (400 MHz, $CDCl_3$)



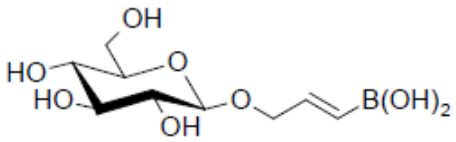


^{13}C NMR (100 MHz, $CDCl_3$)

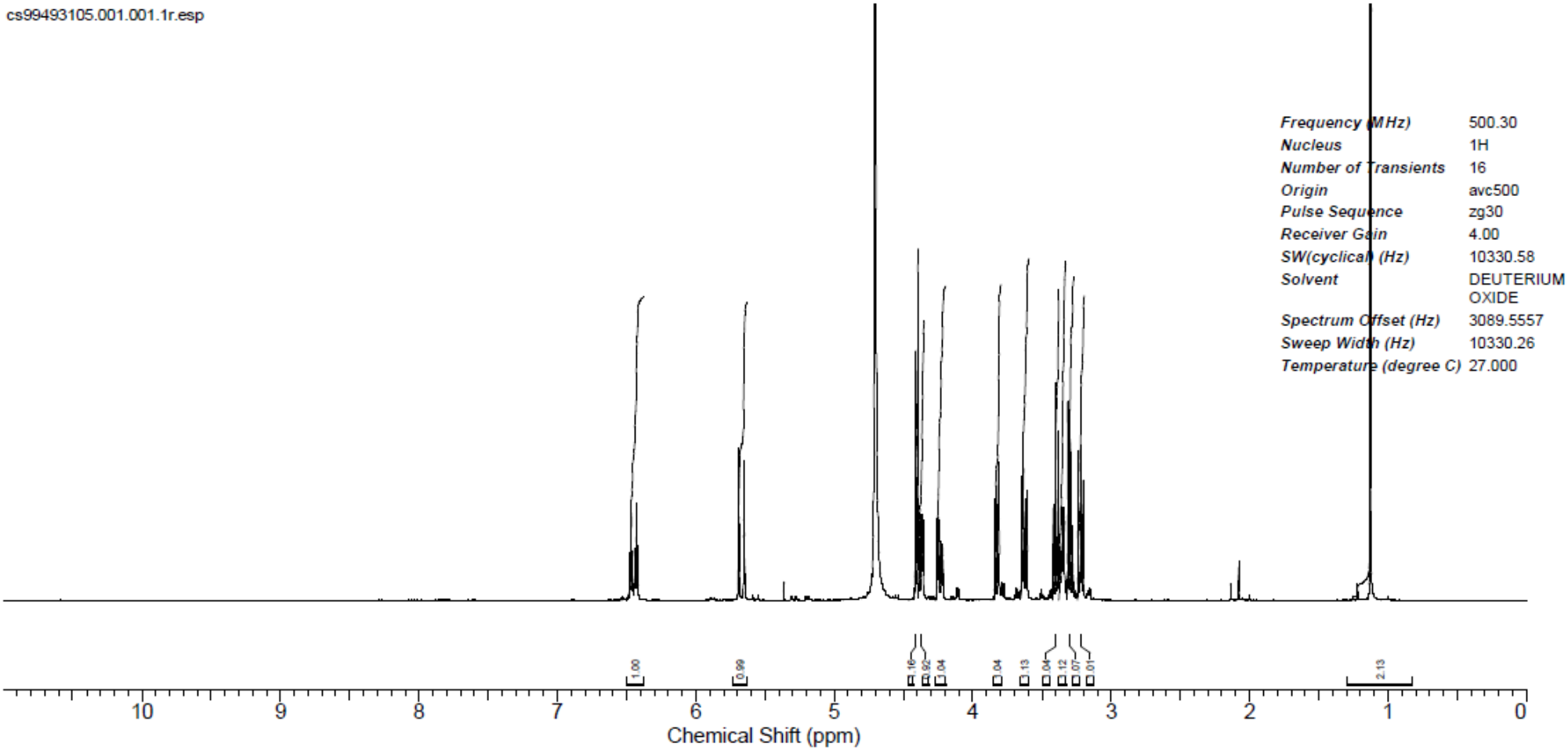


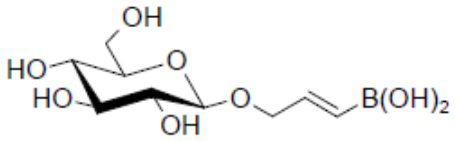
Frequency (MHz)	125.80
Nucleus	13C
Number of Transients	1024
Origin	avc500
Pulse Sequence	zgpg30
Receiver Gain	1820.00
SW(cyclical) (Hz)	31250.00
Solvent	DEUTERIUM OXIDE
Spectrum Offset (Hz)	12580.1094
Sweep Width (Hz)	31249.05
Temperature (degree C)	24.970

S45



^{1}H NMR (400 MHz, $CDCl_3$)





^{13}C NMR (100 MHz, $CDCl_3$)