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Supporting Information

69451 Weinheim, Germany

De Novo Asymmetric Synthesis of the Anthrax Tetrasaccharide via a Palladium Catalyzed Glycosylation Reaction

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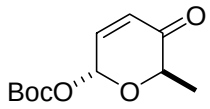
Section A: General Information:

General Methods and materials: ^{1}H and ^{13}C spectra were recorded on Jeol 270 and Varian 600 spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm) or CD_3OD (δ 4.89 ppm) for ^{1}H and $CDCl_3$ (δ 77.1 ppm) or CD_3OD (δ 49.15 ppm) for ^{13}C. Optical rotations were measured with digital polarimeter in the solvent specified. Infrared (IR) spectra were obtained on a prospect. High resolution mass spectra were obtained via electrospray ionization on a Thermo Electron LTQ-FT spectrometer. Flash column chromatography was performed on 60 (60-200 mesh) silica gel. Analytical thin-layer chromatography was performed with precoated glass-backed plates and visualized by quenching of fluorescence and by charring after treatment with *p*-anisaldehyde or phosphomolybdic acid or potassium permanganate stain. R_f values were obtained by elution in the stated solvent ratios (v/v). Ether, THF, methylene chloride and triethylamine were dried by passing through activated alumina (8 x 14 mesh) column with nitrogen gas pressure. Commercial reagents were used without purification unless otherwise noted. Air and/or moisture-sensitive reactions were carried out under an atmosphere of argon/nitrogen using oven/flamed-dried glassware and standard syringe/septa techniques.

Section B: Experimental Procedures:

(2*S*, 6*S*)-*tert*-butyl -5,6-dihydro-6-methyl-5-oxo-2*H*-pyran-2-yl carbonate (8)[1]:

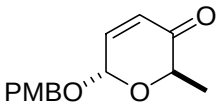


To a 1000 mL flask was added furan ketone **7** (40 g, 363.5 mmol), CH_2Cl_2 (240 mL), formic acid/triethylamine (5:4 (molar ratio), 480 mL) and Noyori asymmetric transfer hydrogenation catalyst (*R*)-Ru(η^6-mesitylene)-(*R, R*)-TsDPEN (222 mg, 0.1 mol%). The resulting solution was stirred at room temperature for 24 h. The reaction mixture was diluted with water (500 mL) and extracted with EtOAc (3 x 700 mL). The combined organic layers were washed with saturated $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude furan alcohol was dissolved in 603 mL of THF/H_2O (3:1) and cooled to 0 ^oC. Solid $NaHCO_3$ (60.9 g, 727.8 mmol), NaOAc•$3H_2O$ (49.6 g, 363.9 mmol), and NBS (64.3 g, 363.7 mmol) were added to the solution and the mixture was stirred for 1 h at 0 ^oC. The reaction was quenched with saturated $NaHCO_3$ (600 mL), extracted (3 x 800 mL) with Et_2O, dried (Na_2SO_4), concentrated under reduced pressure. The crude mixture was dissolved in CH_2Cl_2 (500 mL) and the solution was cooled to -78 ^oC. $(Boc)_2O$ (93 g, 400 mmol) and a catalytic amount of DMAP (1.5 g) was added to the reaction mixture. The reaction was stirred for 12 h at -78 to -30 ^oC, and quenched with saturated $NaHCO_3$, extracted with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 6% EtOAc/Hexane to give 46.1 g (201.9 mmol, 60%) of Boc-protected pyranone **8** : R_f (20% Et_2O/Hexane) = 0.58; $[\alpha]^{25}_D$ = - 98 (*c* = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2984, 2942, 1752, 1703, 1371, 1273, 1254,

[1] Pyranone **8** was prepared in three steps one chromatography.

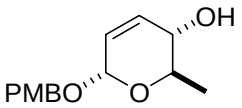
1153, 938, 838; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.78 (dd, *J* = 10.2, 3.6 Hz, 1H), 6.22 (d, *J* = 3.6 Hz, 1H), 6.09 (d, *J* = 10.2 Hz, 1H), 4.53 (q, *J* = 6.6 Hz, 1H), 1.40 (s, 9H), 1.28 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.5, 151.7, 140.9, 128.2, 89.1, 83.3, 72.0, 27.5, 15.1; ClHRMS: Calculated for [$C_{11}H_{16}O_5Na^+$]: 251.0890, Found: 251.0883.

(2R, 6S)-6-(4-methoxybenzyloxy)-2-methyl-2H-pyran-3(6H)-one (9):



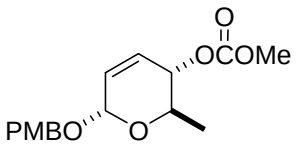
To a solution of Boc-protected pyranone **8** (13 g, 57.0 mmol) and *para*-methoxyl benzyl alcohol (157.3 g, 114.0 mmol) in dry CH_2Cl_2 (57 mL) was added $Pd_2(DBA)_3$•$CHCl_3$ (294 mg, 0.5 mol% Pd) and PPh_3 (297 mg, 2.0 mol%) at 0 ^{o}C under argon atmosphere. After stirring for 2 h, the solution was warmed to room temperature, the reaction mixture was quenched with 300 mL of saturated $NaHCO_3$, extracted (3 x 300 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 5% EtOAc/Hexane to give PMB-ether **9** (13.6 g, 54.7 mmol, 96%) as a colorless oil: R_f (20% EtOAc/Hexane) = 0.37; $[\alpha]^{25}_D$ = -51 (*c* = 1.92, CH_2Cl_2); IR (thin film, cm^{-1}) 2984, 2939, 2876, 1697, 1611, 1513, 1246, 1080, 1023, 808; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.78 (dd, *J* = 10.2, 3.6 Hz, 1H), 6.04 (d, *J* = 10.2 Hz, 1H), 5.22 (d, *J* = 3.6 Hz, 1H), 4.75 (d, *J* = 11.4 Hz, 1H), 4.60 (d, *J* = 11.4 Hz, 1H), 4.53 (q, *J* = 6.6 Hz, 1H), 3.78 (s, 3H), 1.36 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 159.5, 143.5, 129.8 (2 C), 129.2, 127.3, 113.9, 91.9, 70.3, 55.2, 15.1; ClHRMS: Calculated for [$C_{14}H_{16}O_4Na^+$]: 271.0946, Found: 271.0941.

(2R, 3S, 6S)-6-(4-methoxybenzyloxy)-3, 6-dihydro-2-methyl-2H-pyran-3-ol (10a):



A solution of pyranone **9** (13.5 g, 54.4 mmol) in dry CH_2Cl_2 (54.4 mL) and 0.4 M $CeCl_3$/MeOH (54.4 mL) was cooled to -78 °C. $NaBH_4$ (2.08 g, 55.5 mmol) was added and the reaction mixture was stirred for 4 h at -78 °C. The resulting solution was diluted with Et_2O (400 mL) and was quenched with 200 mL of saturated $NaHCO_3$, extracted (3 x 400 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel chromatography eluting with 40% EtOAc/Hexane to give 12.6 g (50.6 mmol, 93%) of allylic alcohol **10a** as a white solid, mp: 62.5-64.0 °C; R_f = 0.30 (40% EtOAc/Hexane); $[\alpha]^{25}_D$ = + 18 (c = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 3391, 2972, 2933, 2837, 1612, 1513, 1246, 1029, 999, 819; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 5.88 (d, J = 10.2 Hz, 1H), 5.72 (ddd, J = 10.2, 3.0, 1.8 Hz, 1H), 5.00 (d, J = 1.8 Hz, 1H), 4.71 (d, J = 11.4 Hz, 1H), 4.52 (d, J = 11.4 Hz, 1H), 3.79 (s, 3H), 3.79 (m, 1H), 3.74 (dq, J = 9.0, 6.6, 1H), 1.95 (d, J = 1.8 Hz, 1H, OH), 1.30 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 133.6, 130.1, 129.7, 126.7, 113.9, 93.2, 69.7, 69.6, 68.1, 55.3, 18.0; CIHRMS: Calculated for [$C_{14}H_{18}O_4Na^+$]: 273.1102, Found: 273.1100.

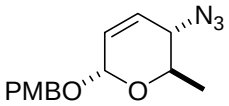
(2R, 3S, 6S)-6-(4-methoxybenzyloxy)-3, 6-dihydro-2-(methyl)-2H-pyran-3-yl methyls carbonate (10):



To a stirred solution of allylic alcohol **10a** (20 g, 80 mmol), pyridine (38.8 mL, 480

mmol) and DMAP (1.96 g) in dry CH_2Cl_2 (400 mL), was dropwise added methyl chloroformate (33.9 mL, 480 mmol) at 0 ^oC. After reacting 1 h at 0 ^oC, water (300 mL) was added and the reacted mixture was extracted with CH_2Cl_2 (3 x 400 mL), dried (Na_2SO_4), concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 10% EtOAc/Hexane to give 24.4 g (79.2 mmol, 99%) carbonate **10** as colorless oil**:** R_f (30% EtOAc/Hexane) = 0.56; $[\alpha]^{25}_D$ = + 79 (c = 2.02, CH_2Cl_2); IR (thin film, cm^{-1}) 2957, 2935, 2803, 1746, 1513, 1248, 1017, 1006, 819; ^1H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, J = 8.4 Hz, 2H), 6.88 d, J = 8.4 Hz, 2H), 5.92 (d, J = 10.2 Hz, 1H), 5.80 (ddd, J = 10.2, 3.0, 1.8 Hz, 1H), 5.03 (d, J = 1.8 Hz, 1H), 4.89 (ddd, J = 9.6, 3.0, 1.8 Hz, 1H), 4.71 (d, J = 11.4 Hz, 1H), 4.52 (d, J = 11.4 Hz, 1H), 4.02 (dq, J = 9.0, 6.6, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 1.25 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 155.4, 130.0, 129.6, 129.2, 128.3, 113.9, 93.3, 74.7, 69.8, 64.7, 55.3, 55.0, 17.9; CIHRMS: Calculated for [$C_{16}H_{20}O_6Na^+$]: 331.1157, Found: 331.1152.

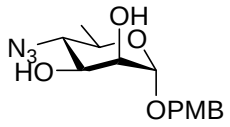
(2R, 3S, 6S)-6-(4-methoxybenzyloxy)-3-azido-3, 6-dihydro-2-methyl-2H-pyran (11):



To a stirred solution of carbonate **10** (30 g, 97.4 mmol), allylpalladium chloride dimer (378 mg, 1.0 mmol %) and 1, 4-bis(diphenylphosphino)butane (1.68 g, 4.0 mmol %) in dry THF (97.2 mL) was added $TMSN_3$ (15.5 mL, 116.9 mmol) under argon atmosphere. The reaction mixture was stirred at room temperature for 0.5 h, evaporated solvent under reduced pressure, purified using silica gel flash chromatography eluting with 7 % EtOAc/Hexane to give 24.9 g (90.6 mmol, 93%) allylic azide **11** as colorless oil: R_f(20% EtOAc/Hexane) = 0.46; $[\alpha]^{25}_D$ = + 130 (c = 1.02, CH_2Cl_2); IR (thin film, cm^{-1}) 2935,

2903, 2837, 2094, 1612, 1513, 1033, 1006, 818; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.95 (d, *J* = 10.2 Hz, 1H), 5.89 (ddd, *J* = 10.2, 3.0, 1.8 Hz, 1H), 5.03 (d, *J* = 1.2 Hz, 1H), 4.71 (d, *J* = 11.4 Hz, 1H), 4.52 (d, *J* = 11.4 Hz, 1H), 3.86 (dq, *J* = 9.6, 6.6, 1H), 3.81 (s, 3H), 3.55 (dd, *J* = 9.6, 1.8 Hz, 1H), 1.33 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.4, 130.0, 129.6, 128.9, 128.4, 113.9, 93.0, 69.7, 66.0, 60.3, 55.3, 18.4; CIHRMS: Calculated for [$C_{14}H_{17}N_3O_3Na^+$]: 298.1167, Found: 298.1162.

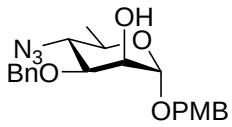
(2S, 3S, 4S, 5S, 6R)-2-(4-methoxybenzyloxy)-5-azido-tetrahydro-6-methyl-2H-pyran-3,4-diol (12a):



To a *t*-butanol, acetone (145.4 mL, 1:1 (v/v), 1 M) solution of allylic azide **11** (20 g, 72.7 mmol) at 0 ^{o}C, was added a solution of *N*-methyl morpholine *N*-oxide/water (50% w/v, 50 mL). Crystalline OsO_4 (185 mg, 1 mol %) was added and the reaction was allowed to stir for 24 h. The reaction mixture was quenched with 200 mL saturated $Na_2S_2O_3$ solution, extracted with EtOAc (3 x 500 mL), dried (Na_2SO_4), concentrated under reduced pressure, and then purified using silica gel flash chromatography eluting with 90% EtOAc/Hexane to give diol **12a** (22.0 g, 71.2 mmol, 98%); R_f = 0.63 (80% EtOAc/Hexane); $[\alpha]^{25}_D$ = + 99 (*c* = 0.96, CH_2Cl_2); IR (thin film, cm^{-1}) 3345, 2935, 2915, 2837, 2112, 1613, 1515, 1250, 1072, 1006, 823; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.84 (d, *J* = 1.2 Hz, 1H), 4.59 (d, *J* = 11.4 Hz, 1H), 4.42 (d, *J* = 11.4 Hz, 1H), 3.88 (dd, *J* = 3.6, 1.2 Hz, 1H), 3.86 (dd, *J* = 9.6, 3.6 Hz,

1H), 3.80 (s, 3H), 3.62 (dq, *J* = 9.6, 6.6, 1H), 3.29 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.85 (d, *J* = 6.6 Hz, 1H), 2.77 (d, *J* = 4.2 Hz, 1H), 1.33 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 129.8(2 C), 129.0, 114.0, 98.4, 70.5, 70.3, 66.9, 66.0, 55.4, 18.4; CIHRMS: Calculated for [$C_{14}H_{19}N_3O_5Na^+$]: 332.1222, Found: 332.1218.

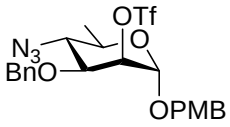
(2S, 3S, 4S, 5R, 6R)-2-(4-methoxybenzyloxy)-5-azido-4-(benzyloxy)-tetrahydro-6-methyl-2H-pyran-3-ol (12):



A stirred mixture of diol **12a** (1.5 g, 4.85 mmol) and *n*-Bu_2SnO (1.24 g, 4.97 mmol) in toluene (60 mL) was refluxed for 3 h. After cooling to room temperature, CsF (0.75 g), tetrabutylammonium iodide (1.83 g, 4.97 mmol) and BnBr (0.58 mL, 4.97 mmol) were added and refluxed for 2 h. The solution was cooled to room temperature. The reaction mixture was diluted in 200 mL saturated $NaHCO_3$ solution, and then extracted with ethyl ether (3 x 200), dried (Na_2SO_4). The extraction was concentrated under reduced pressure, and then purified using silica gel chromatography eluting with 15% EtOAc/Hexane to give Bn-ether **12** (1.9 g, 4.80 mmol, 99%) as white powder, mp: 83-84 °C; R_f = 0.68 (50% EtOAc/Hexane); $[\alpha]^{25}_D$ = + 125 (*c* = 1.21, CH_2Cl_2); IR (thin film, cm^{-1}) 3472, 2933, 2837, 2112, 1613, 1515, 1249, 1055, 993, 823; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.40 (m, 5H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.84 (d, *J* = 1.2 Hz, 1H), 4.70 (d, *J* = 11.4 Hz, 1H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 3.89 (dd, *J* = 3.6, 1.2 Hz, 1H), 3.82 (s, 3H), 3.78 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.60 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.43 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.43 (s, 1H), 1.33 (d, *J*

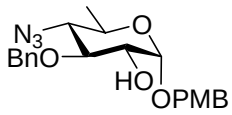
= 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 138.0, 129.8, 128.9, 128.4, 128.1, 127.8, 114.0, 97.4, 81.3, 75.2, 73.1，69.6, 67.5, 66.4, 55.2, 18.3; CIHRMS: Calculated for [$C_{21}H_{25}N_3O_5Na^+$]: 422.1692, Found: 422.1688.

(2S, 3S, 4S, 5R, 6R)-2-(4-methoxybenzyloxy)-5-azido-4-(benzyloxy)-tetrahydro-6-methyl-2H-pyran-3-yl trifluoromethanesulfonate (13a):



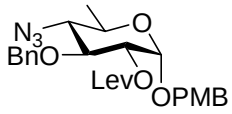
To a solution of alcohol **12** (2.0 g, 5.01 mmol) in CH_2Cl_2 (35.3 mL) and pyridine (2 mL), was added triflic anhydride (5.9 mmol, 0.94 mL) at 0 ^oC. The reaction was stirred for 0.5 h, then quenched with 2 mL water, and extracted with ethyl ether (3 x 50 mL). The organic mixture was washed with saturated $CuSO_4$ solution (3 x 20 mL), dried (Na_2SO_4), concentrated under reduced pressure, and then purified using silica gel flash chromatography eluting with 10% EtOAc/Hexane to give triflate **13a** (2.66 g, 5.01 mmol, 99%) as colorless oil: R_f = 0.53 (20% EtOAc/Hexane); $[\alpha]^{25}_D$ = + 71 (*c* = 0.99, CH_2Cl_2); IR (thin film, cm^{-1}) 2935, 2837, 2117, 1613, 1515, 1245, 1206, 1064, 1026, 916; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.44 (m, 5H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 5.08 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.02 (d, *J* = 1.2 Hz, 1H), 4.83 (d, *J* = 11.4 Hz, 1H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.48 (d, *J* = 11.4 Hz, 1H), 3.90 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.84 (s, 3H), 3.62 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.45 (dd, *J* = 9.6, 9.6 Hz, 1H), 1.37 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) 159.9, 136.6, 129.8, 128.5, 128.4, 128.2, 128.1, 119.5, 114.1, 95.7, 81.1, 75.2, 72.7, 69.7, 67.6, 63.7, 55.3, 18.3; CIHRMS: Calculated for [$C_{22}H_{24}N_3O_7SF_3Na^+$]: 554.1184, Found: 554.1179.

(2S, 3R, 4S, 5R, 6R)-2-(4-methoxybenzyloxy)-5-azido-4-(benzyloxy)-tetrahydro-6-methyl-2H-pyran-3-ol (13):



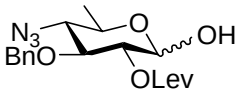
To a solution of triflate **13a** (2.66 g, 5.01 mmol) in DMF (16 mL), was added $NaNO_2$ (940 mg, 15.1 mmol). The mixture was stirred at 45 ^oC for 30 h, quench with 50 mL water, extracted with ethyl ether (3 x 100 mL), dried (Na_2SO_4), concentrated under reduced pressure, and then purified using silica gel flash chromatography eluting with 15% EtOAc/Hexane to give alcohol **13** (1.12 g, 2.8 mmol, 56%) as colorless oil: R_f = 0.62 (50% EtOAc/Hexane); $[\alpha]^{25}_D$ = + 151 (*c* = 1.03, CH_2Cl_2); IR (thin film, cm^{-1}) 3454, 2934, 2836, 2107, 1613, 1515, 1249, 1072, 1032, 823; ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.37 (m, 2H), 7.29 (m, 3H), 6.92 (d, *J* = 8.4 Hz, 2H), 4.95 (d, *J* = 11.4 Hz, 1H), 4.90 (d, *J* = 3.6 Hz, 1H), 4.83 (d, *J* = 11.4 Hz, 1H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.49 (d, *J* = 11.4 Hz, 1H), 3.82 (s, 3H), 3.70 (ddd, *J* = 9.6, 3.0, 3.0 Hz, 1H), 3.64 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.63 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.10 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.25 (d, *J* = 3.0 Hz, 1H, OH), 1.31 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.6, 138.1, 129.9, 128.9, 128.4, 128.2, 127.8, 114.0, 97.4, 81.4, 75.2, 73.2, 69.6, 67.5, 66.5, 55.3, 18.4; CIHRMS: Calculated for $[C_{21}H_{25}N_3O_5Na^+]$: 422.1692, Found: 422.1685.

(2S, 3R, 4S, 5R, 6R)-2-(4-methoxybenzyloxy)-5-azido-4-(benzyloxy)-tetrahydro-6-methyl-2H-pyran-3-yl 4-oxopentanoate (14a):



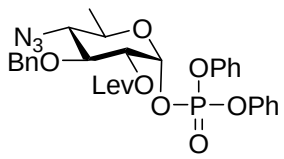
To a solution of levulinic acid (872 mg, 7.52 mmol) in CH_2Cl_2 (21 mL), was added DMAP (917 mg, 7.52 mmol) at 0 ^oC. After stirring for 10 minutes, DCC (1.55 g, 7.52 mmol) was added, and then insoluble white precipitate was formed. The supension was stirred for 10 minutes; alcohol **13** (1.5 g, 3.76 mmol) was added, kept stirring from 0 ^oC to room temperature for 4 h, filtered over a pad of celite, evaporated under reduced pressure, and then purified using silica gel flash chromatography eluting with 15% EtOAc/Hexane to give levulinoyl ester **14a** (1.76 g, 3.53 mmol, 94%) as colorless oil: R_f = 0.70 (50% EtOAc/Hexane); $[\alpha]^{25}_D$ = + 153 (*c* = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 2931, 2836, 2107, 1741, 1719, 1613, 1515, 1249, 1057, 1036, 823; ^1H NMR (600 MHz, $CDCl_3$) δ 7.33-7.36 (m, 4H), 7.25-7.31 (m, 3H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.01(d, *J* = 3.6 Hz, 1H), 4.82 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.81 (d, *J* = 11.4 Hz, 1H), 4.77 (d, *J* = 11.4 Hz, 1H), 4.62 (d, *J* = 11.4 Hz, 1H), 4.46 (d, *J* = 11.4 Hz, 1H), 3.92 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.82 (s, 3H), 3.66 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.17 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.59-2.69 (m, 2H), 2.54 (ddd, *J* = 18.0, 7.2, 6.6, Hz, 1H), 2.50 (ddd, *J* = 18.0, 7.2, 6.6 Hz, 1H), 2.15 (s, 3H), 1.29 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.0, 171.9, 159.5, 138.1, 129.7, 129.3, 128.5, 127.9, 127.8, 113.9, 95.2, 78.3, 75.3, 74.0, 69.7, 68.1, 66.3, 55.3, 37.8, 29.8, 27.9, 18.3.

(2R, 3S, 4S, 5R)-5-azido-4-(benzyloxy)-tetrahydro-2-hydroxy-6-methyl-2H-pyran-3-yl 4-oxopentanoate (14)：



To a solution of PMB-ether **14a** (300 mg**,** 0.56 mmol) in 7.4 mL CH_2Cl_2 /H_2O (10/1) at 0 ^oC, was added DDQ (134 mg, 0.67 mmol). This reaction mixture was a stirred from 0 ^oC to room temperature for 8 h, quenched with a saturated $NaHCO_3$ solution, extracted with ethyl ether (3 x 100 mL), dried (Na_2SO_4), concentrated under reduced pressure, and then purified using silica gel chromatography eluting with 45% EtOAc/Hexane to give anomer alcohol **14** (213 mg, 0.56 mmol, 95%) as white powder, mp: 98-103 °C; R_f = 0.45 (50% EtOAc/Hexane); $[\alpha]^{25}_D$ = + 135 (c = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 3461, 2970, 2941, 2108, 1739, 1366, 1228, 1071; ^1H NMR (600 MHz, $CDCl_3$, major) δ 7.27-7.36 (m, 5H), 5.32 (dd, J = 4.2, 3.6 Hz, 1H), 4.85 (d, J = 11.4 Hz, 1H), 4.81 (dd, J = 9.6, 3.6 Hz, 1H), 4.77 (d, J = 11.4 Hz, 1H), 3.92 (dd, J = 9.6, 9.6 Hz, 1H), 3.88 (dq, J = 9.6, 6.6 Hz, 1H), 3.56 (br, 1H, OH), 3.16 (dd, J = 9.6, 9.6 Hz, 1H), 2.70-2.81 (ddd, J = 18.6, 8.4, 5.4 Hz, 1H), 2.63-2.68 (ddd, J = 18.6, 7.2, 6.0 Hz, 1H), 2.54-2.61 (ddd, J = 18.6, 8.4, 5.4 Hz, 1H), 2.39-2.44 (ddd, J = 18.6, 7.2, 6.0 Hz, 1H), 2.17 (s, 3H), 1.30 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.2, 172.1, 138.1, 128.5, 128.0, 127.9, 90.1, 77.9, 75.3, 74.5, 68.1, 66.2, 38.1, 29.8, 28.0, 18.4; Calculated for $[C_{18}H_{23}N_3O_6Na^+]$: 400.1485, Found: 400.1481.

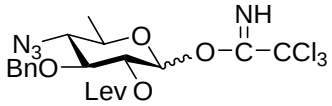
(2R, 3S, 4S, 5R)-5-azido-4-(benzyloxy)-tetrahydro-3-(4-oxopentanoxy)-6-methyl-2H-pyran-2-yl diphenyl phosphate (6):



To a solution of alcohol **14** (377 mg, 1 mmol) in CH_2Cl_2 (4 mL) was added DMAP (244 mg, 2 mmol), and diphenyl chlorophosphate (536 mg, 2 mmol) at 0 ^oC. The reaction

mixture was stirred for 3 h, quenched with crushed ice, extracted with Et_2O (3 x 100 mL) and dried (Na_2SO_4). The organic extract was concentrated under reduced pressure, and purified using silica gel flash chromatography eluting with 35% EtOAc/Hexane to give phosphate **6** (505 mg, 0.83 mmol, 83%) as white solid, mp: 67-68 °C; R_f = 0.56 (50% EtOAc/Hexane); $[\alpha]^{25}_D$ = + 117 (c = 1.03, CH_2Cl_2); IR (thin film, cm^{-1}) 2931, 2920, 2110, 1749, 1719, 1590, 1489, 1188, 1160, 957; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.38 (m, 10H), 7.20-7.25 (m, 5H), 5.96 (dd, J = 6.6, 3.0 Hz, 1H), 4.91(ddd, J = 10.2, 3.0, 3.0 Hz, 1H), 4.76 (d, J = 11.4 Hz, 1H), 4.74 (d, J = 11.4 Hz, 1H), 3.80 (dd, J = 9.6, 9.6 Hz, 1H), 3.66 (dq, J = 9.6, 6.6 Hz, 1H), 3.20 (dd, J = 9.6, 9.6 Hz, 1H), 2.70 (ddd, J = 18.6, 7.2, 7.2Hz, 1H), 2.62 (ddd, J =18.6, 7.2, 6.0 Hz, 1H), 2.52 (ddd, J = 18.6, 7.2, 7.2 Hz, 1H), 2.42 (ddd, J = 18.6, 7.2, 6.0 Hz, 1H), 2.10 (s, 3H), 1.21 (d, J = 6.6 Hz, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 206.0, 171.9, 150.4, 150.3, 137.5, 129.8, 128.5, 128.2, 128.1, 125.7, 120.3, 120.2, 120.1, 120.0, 95.6, 77.2, 75.4, 72.7, 68.8, 67.0, 37.7, 29.7, 27.6, 18.1; CIHRMS: Calculated for [$C_{30}H_{32}N_3O_9PNa^+$]: 632.1774, Found: 632.1770.

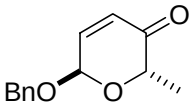
(3S, 4S, 5R)-2-(2, 2, 2-trichloroacetoyloxy)-5-azido-4-(benzyloxy)-tetrahydro-6-methyl-2H-pyran-3-yl-4-oxopentanoate (15):



To a CH_2Cl_2 (7 mL) solution of alcohol **14** (530 mg, 1.41 mmol) and trichloroacetonitrile (8 mL) was added catalytic amount NaH (10 mg) at 0 ^oC. The reaction mixture was stirred for 1.5 h at 0 ^oC, The solvent was removed under reduced pressure, and purified using silica gel flash chromatography eluting with 50% EtOAc/Hexane to give imidate **15**

(610 mg, 1.17 mmol, 83%) as colorless oil: R_f = 0.70 (50% EtOAc/Hexane); $[\alpha]^{25}_D$ = + 86 (c = 1.07, CH_2Cl_2); IR (thin film, cm^{-1}) 3343, 2931, 2918, 2109, 1748, 1718, 1675, 1359, 1276, 1152, 1059, 736; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64 (s, 1H, α), 8.60 (s, 1H, β), 7.28-7.38 (m, 5H), 6.40 (d, J = 3.0 Hz, 1H, α), 5.72 (d, J = 8.4 Hz, 1H, β), 5.25 (dd, J = 9.6, 9.6 Hz, 1H, α), 5.03 (dd, J = 9.6, 3.6 Hz, 1H, β), 4.84 (d, J = 11.4 Hz, 1H, α), 4.79 (d, J = 11.4 Hz, 1H, β), 4.78 (d, J = 11.4 Hz, 1H, α), 4.72 (d, J = 11.4 Hz, 1H, β), 3.96 (dd, J = 9.6, 9.6 Hz, 1H, α), 3.81 (m, 1H, α), 3.63 (dd, J = 9.6, 9.6 Hz, 1H, β), 3.47 (m, 1H, β), 3.30 (dd, J = 9.6, 9.6 Hz, 1H, α), 3.27 (dd, J = 9.6, 9.6 Hz, 1H, β), 2.59-2.69 (m, 2H), 2.43-2.51 (m, 2H), 2.15 (s, 3H, α), 2.14 (s, 3H, β), 1.41 (d, J = 6.6 Hz, 3H, β), 1.35 (d, J = 6.6 Hz, 3H, α); ^{13}C NMR (150 MHz, $CDCl_3$, α /β mixture) δ 205.96, 205.92, 171.9, 171.1, 161.3, 160.9, 137.6, 137.5, 128.5, 128.3, 128.1, 95.7, 93.6, 81.1, 77.5, 75.3, 75.0, 72.8, 72.5, 72.0, 69.3, 67.4, 67.3, 37.7, 37.6, 29.9, 29.8, 27.8, 27.7, 18.5, 18.4; CIHRMS: Calculated for [$C_{20}H_{23}N_4O_6Na^+$]: 543.0581, Found: 543.0580.

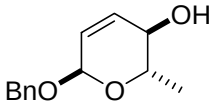
(2S, 6R)-6-(benzyloxy)-2-methyl-2H-pyran-3 (6H)-one (16a):



To a solution of Boc-protected pyranone **(*ent*)-8** (22.8 g, 100 mmol) and benzyl alcohol (21.6 g, 200.0 mmol) in dry CH_2Cl_2 (100 mL) was added $Pd_2(DBA)_3$•$CHCl_3$ (257 mg, 0.25 mol% Pd) and PPh_3 (262 mg, 1.0 mol%) at 0 ^oC under argon atmosphere. After stirring for 2 h from 0 ^oC to room temperature, the reaction mixture was quenched with 300 mL of saturated $NaHCO_3$, extracted (3 x 300 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 4% EtOAc/Hexane to give Bn-ether **16a** (19.6 g, 90

mmol, 90%) as a colorless oil, R_f (30% EtOAc/Hexane) = 0.71; $[\alpha]^{25}_D$ = + 46 (*c* = 1.11, CH_2Cl_2); IR (thin film, cm^{-1}) 2985, 2939, 2873, 1697, 1231, 1022, 953; ^1H NMR (270 MHz, $CDCl_3$) δ 7.32-7.38 (m, 5H), 6.85 (dd, *J* = 10.2, 3.6 Hz, 1H), 6.11 (d, *J* = 10.2 Hz, 1H), 5.28 (d, *J* = 3.6 Hz, 1H), 4.86 (d, *J* = 11.4 Hz, 1H), 4.70 (d, *J* = 11.4 Hz, 1H), 4.57 (q, *J* = 6.7 Hz, 1H), 1.36 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 197.0, 143.5, 137.2, 126.6, 128.2, 128.1, 127.5, 92.4, 70.8, 70.5, 15.3; CIHRMS: $[C_{13}H_{14}O_3Na^+]$: 241.0835, Found: 241.0843.

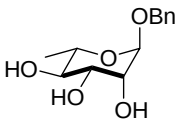
(2S, 3R, 6R)-6-(benzyloxy)-3, 6-dihydro-2-methyl-2H-pyran-3-ol (16b):



A solution of pyranone **16a** (19.6 g, 90 mmol) in dry CH_2Cl_2 (90 mL) and 0.4 M $CeCl_3$/MeOH (90 mL) was cooled to -78 °C. $NaBH_4$ (3.74 g, 99 mmol) was added and the reaction mixture was stirred for 4 h at -78 °C. The resulting solution was diluted with ether (400 mL) and was quenched with 200 mL of saturated $NaHCO_3$, extracted (3 x 400 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel chromatography eluting with 35% EtOAc/Hexane to give 17.6 g (80.1 mmol, 89%) of allylic alcohol **16b** as a colorless oil; R_f = 0.58 (50% EtOAc/Hexane); $[\alpha]^{25}_D$ = - 32 (*c* = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 3394, 2974, 2933, 2892, 1377, 1039, 1004; ^1H NMR (270 MHz, $CDCl_3$) δ 7.25-7.36 (m, 5H), 5.95 (d, *J* = 10.2 Hz, 1H), 5.77 (ddd, *J* = 10.2, 3.0, 1.8 Hz, 1H), 5.03 (d, *J* = 1.6 Hz, 1H), 4.80 (d, *J* = 11.4 Hz, 1H), 4.61 (d, *J* = 11.4 Hz, 1H), 3.84 (m, 1H), 3.74 (dq, *J* = 9.6, 6.6 Hz, 1H), 1.30 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 137.9, 133.6, 128.5, 128.1,

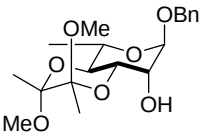
127.8, 126.7, 93.6, 70.1, 69.7, 68.2, 18.0; CIHRMS: [$C_{13}H_{16}O_3Na^+$]: 243.0992, Found: 243.0990.

(3S, 4S, 5R)-2-(benzyloxy)-tetrahydro-6-methyl-2H-pyran-3, 4, 5-triol (16):



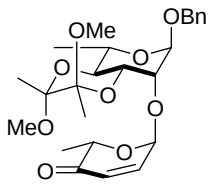
To a *t*-butanol, acetone (57.3 mL, 1:1 (v/v), 1 M) solution of allylic alcohol **16b** (12.5 g, 57.3 mmol) at 0 °C was added a solution of *N*-methyl morpholine *N*-oxide/water (50% w/v, 28.7 mL). Crystalline OsO_4 (116 mg, 0.8 mol %) was added and the reaction was stirred for 24 h. Solid $Na_2S_2O_3$ (5 g) was added to the reaction mixture and kept stirring for 0.5 h. The reaction mixture was then quenched with saturated sodium bicarbonate solution (300 mL), removed acetone in vacuo, extracted with EtOAc (5 x 500 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel chromatography eluting with pure EtOAc to give 13.6 g (53.9 mmol, 94%) of triol **25**: R_f (10% MeOH/ EtOAc) = 0.52; $[\alpha]^{25}_D$ = - 84 (*c* = 1.19, MeOH); IR (thin film, cm^{-1}) 3375, 2974, 2911, 1454, 1384, 1046, 979; ^{1}HNMR (600 MHz, CD_3OD) δ 7.27-7.33 (m, 5H), 4.78 (d, *J* = 1.2 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 3.86 (dd, *J* = 3.6, 1.2 Hz, 1H), 3.72 (dd, *J* = 9.0, 3.6 Hz, 1H), 3.64 (dq, *J* = 9.0, 6.0 Hz, 1H), 3.43 (dd, *J* = 9.0, 9.0 Hz, 1H), 1.28 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 139.1, 129.5, 129.1, 128.8, 100.9, 74.0, 72.5, 72.3, 70.1 (2 C), 18.1; CIHRMS: [$C_{13}H_{18}O_5Na^+$]: 277.1046, Found: 277.1043.

(4aS, 8S, 8aR)-7-(benzyloxy)-hexahydro-2, 3-dimethoxy-2, 3, 5-trimethyl-2H-pyrano [3, 4-b] [1, 4] dioxin-8-ol (17):



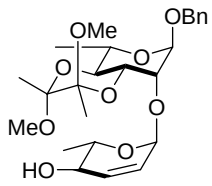
TsOH (2.48 g, 14.4 mmol) was added to a solution of trimethylorthoacetate (98.0 mL, 768.0 mmol) and 2, 3-butanedione (16.8 mL, 192.0 mmol) in dry methanol 300 mL. The reaction was refluxed at 70 ^{o}C for 12 h. Triol **16** (12.2 g, 48.0 mmol) was added to the stirred reaction mixture and kept refluxed for 5 h. After cooling to room temperature, triethylamine was added to reaction mixture to neutralize the acid. The solvent was concentrated under reduced pressure and then purified by silica gel chromatography column eluting with 40% EtOAc/Hexane to give Ley-protected rhamnose **17** (15.5 g, 42.2 mmol, 88%); R_f = 0.52 (50% EtOAc/Hexane); $[\alpha]^{25}_{D}$ = - 207 (c = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 3472, 2932, 2833, 1455, 1376, 1111, 1035, 730; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27-7.33 (m, 5H), 4.85 (d, J = 1.2 Hz, 1H), 4.68 (d, J = 12.0 Hz, 1H), 4.48 (d, J = 12.0 Hz, 1H), 3.99 (dd, J = 9.0, 3.6 Hz, 1H), 3.94 (dd, J = 3.6, 1.2 Hz, 1H), 3.86 (dq, J = 9.0, 6.0 Hz, 1H), 3.73 (dd, J = 9.0, 9.0 Hz, 1H), 3.24 (s, 3H), 3.22 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 1.26 (d, J = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.3, 128.4, 128.1, 127.8, 100.1, 99.8, 99.2, 68.5, 69.2, 68.3 (2 C), 66.8, 48.1, 47.6, 17.8, 17.6, 16.5; CIHRMS: [$C_{19}H_{28}O_7Na^{+}$]: 391.1727, Found: 391.1734.

6-((4aS, 8S, 8aS)-7-(benzyloxy)-hexahydro-2, 3-dimethoxy-2, 3, 5-trimethyl-2H-pyrano [3, 4-b] [1, 4] dioxin-8-yloxy)-2-methyl-2H-pyran-3 (6H)-one (18):



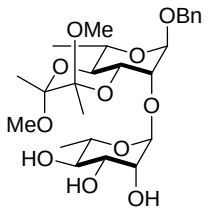
To a solution of Boc-pyranone ***(ent)*-8** (2.74 g, 21.44 mmol) and Ley-spiroketal rhamnose **17** (680 mg, 2.68 mmol) in dry CH_2Cl_2 (3 mL), was added $Pd_2(DBA)_3$•$CHCl_3$ (69.2 mg, 2.5 mol% Pd) and PPh_3 (70.2 mg, 10 mol%) at 0 ^oC under argon atmosphere. After stirring for 2 h from 0 ^oC to room temperature, the reaction mixture was quenched with 50 mL of saturated $NaHCO_3$, extracted (3 x 100 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 15% EtOAc/Hexane to give benzyl-ether **18** (1.1 g, 2.30 mmol, 86%) as a yellow oil: R_f (30% EtOAc/Hexane) = 0.59; $[\alpha]^{25}_D$ = - 160 (*c* = 1.45, CH_2Cl_2); IR (thin film, cm^{-1}) 2990, 2935, 2833, 1700, 1375, 1113, 1019, 930; ^1H NMR (600 MHz, $CDCl_3$) δ 7.21-7.29 (m, 5H), 6.89 (dd, *J* = 10.2, 3.0 Hz, 1H), 5.98 (d, *J* = 10.2, 1H), 5.54 (d, *J* = 3.0 Hz, 1H), 4.80 (d, *J* = 1.2 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.43 (q, *J* = 6.6 Hz, 1H), 4.05 (m, 1H), 4.03 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.80 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.67 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.19 (s, 3H), 3.18 (s, 3H), 1.24 (d, *J* = 6.6 Hz, 3H), 1.23 (s, 3H), 1.22 (s, 3H), 1.21 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.6, 143.6, 137.0, 128.2, 127.8, 127.6, 126.6, 99.5, 99.4, 98.5, 93.8, 75.1, 70.1, 68.9, 68.7, 68.4, 67.0, 47.8, 47.4, 17.6, 17.5, 16.4, 15.0; CIHRMS: [$C_{25}H_{34}O_9Na^+$]: 501.2101, Found: 501.2095.

(3R)-6-((4aS, 8S, 8aS)-7-(benzyloxy)-hexahydro-2, 3-dimethoxy-2, 3, 5-trimethyl-2H-pyrano [3, 4-b] [1, 4] dioxin-8-yloxy)-3, 6-dihydro-2-methyl-2H-pyran-3-ol (19a):



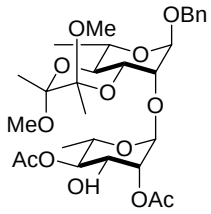
A solution of disaccharide pyranone **18** (5.5 g, 11.5 mmol) in dry CH_2Cl_2 (11.5 mL) and 0.4 M $CeCl_3$/MeOH (11.5 mL) was cooled to -78 °C. $NaBH_4$ (458.8 mg, 12.01 mmol) was added and the reaction mixture was stirred for 4 h at the temperature of -78 °C. The resulting solution was diluted with ether (200 mL) and was quenched with 100 mL of saturated $NaHCO_3$, extracted (3 x 200 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 25% EtOAc/Hexane to give 5.0 g (10.4 mmol, 90%) of allylic alcohol **19a** as white powder, mp: 56-59 °C; R_f (30% EtOAc/Hexane) = 0.25; $[\alpha]^{25}_D$ = - 191 (*c* = 1.22, CH_2Cl_2); IR (thin film, cm^{-1}) 3451, 2933, 2901, 1454, 1376, 1025, 1001, 729; ^{1}H NMR (600 MHz, CD_3Cl) δ 7.27-7.36 (m, 5H), 5.88 (m, 2H), 5.31(s, 1H), 4.78 (d, *J* = 1.2 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.03 (dd, *J* = 3.0, 1.2 Hz, 1H), 4.01 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.84 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.79 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.73 (dd, *J* = 9.6, 9.6Hz, 1H), 3.66 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.24 (s, 3H), 3.23 (s, 3H), 1.27 (s, 3H), 1.26 (d, *J* = 6.6 Hz, 3H), 1.24 (s, 3H), 1.20 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CD_3Cl) δ 137.5, 132.7, 128.5, 128.0, 127.8, 127.3, 99.7, 99.6, 99.4, 95.2, 74.9, 69.9, 69.0, 68.9, 68.8, 68.0, 67.2, 48.0, 47.7, 18.0, 17.9, 17.8, 16.7; CIHRMS: Calculated for [$C_{25}H_{36}O_9Na^+$]: 503.2257, Found: 503.2254.

(3S, 4S, 5R)-2-((4aS, 8S, 8aS)-7-(benzyloxy)-hexahydro-2, 3-dimethoxy-2, 3, 5-trimethyl- 2H-pyrano [3, 4-b][1, 4] dioxin-8-yloxy)-tetrahydro-6-methyl-2H-pyran-3, 4, 5-triol (19):



To a *t*-butanol, acetone (18 mL, 1:1 (v/v), 0.5 M) solution of allylic alcohol **19a** (4.3 g, 9.0 mmol) at 0 °C was added a solution of *N*-methyl morpholine *N*-oxide/water (50% w/v, 9 mL). Crystalline OsO_4 (23 mg, 1 mol %) was added and the reaction was stirred for 12 h. The reaction mixture was quenched with 30 mL saturated $Na_2S_2O_3$ solution, extracted with EtOAc (5 x 200 mL), dried (Na_2SO_4), concentrated under reduced pressure, and then purified using silica gel flash chromatography eluting with 70% EtOAc/Hexane to give triol **19** (4.26 g, 8.3 mmol, 92%) as white foam, mp: 81-84 °C; R_f = 0.19 (80% EtOAc/Hexane); $[\alpha]^{25}_D$ = - 192 (*c* = 1.0, CH_2Cl_2); IR (thin film, cm^{-1}) 3401, 2934, 2833, 1455, 1377, 1028, 982; ^{1}H NMR (600 MHz, CD_3Cl) δ 7.27-7.35 (m, 5H), 5.13 (d, *J* = 1.8 Hz, 1H), 4.79 (d, *J* = 1.2 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.09 (dd, *J* = 3.0, 1.2 Hz, 1H), 4.01 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.96 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.83 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.80 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.65 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.62 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.45 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.23 (s, 3H), 3.22 (s, 3H), 3.21 (br, 1H, OH), 3.18 (br, 1H, OH), 2.03 (br, 1H, OH), 1.26 (s, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.25 (s, 3H), 1.22 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CD_3Cl) δ 137.3, 128.5, 128.0, 127.9, 100.8, 99.8, 99.7, 98.9, 74.7, 73.4, 71.6, 70.8, 69.2, 68.7, 68.5, 67.2, 48.1, 47.7, 17.9, 17.8, 17.6, 16.7; CIHRMS: Calculated for $[C_{25}H_{38}O_{11}Na^+]$: 537.2311, Found: 537.2304.

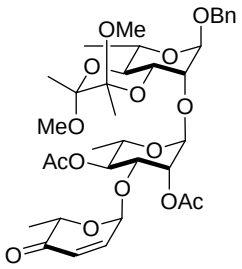
(3R, 4R, 5S)-6-((4aS, 8S, 8aS)-7-(benzyloxy)-hexahydro-2, 3-dimethoxy-2, 3, 5-trimethyl-2H-pyrano [3, 4-b][1, 4] dioxin-8-yloxy)-tetrahydro-4-dihydroxy-2-methyl-2H-pyran-3, 5-yl-diacetate (20):



To a solution of triol **19** (4 g, 7.8 mmol) and trimethyl orthoacetate (2.94 mL, 23.4 mmol) in CH_2CN (23.4 mL) was added *p*-toluenesulfonic acid monohydrate (74.1 mg, 0.39 mmol). After stirring for 0.5 h, Py (2 mL) was added to neutralize the acid and then the solvent was evaporated. The resulting residue was dissolved in pyridine (10 mL) and 4.5 mL Ac_2O, and 50 mg DMAP was added, stirring for 6 h. Water was added to destroy the excess Ac_2O. The mixture was diluted in ether, washed with saturated $CuSO_4$ solution and the solvent was evaporated. The residue was treated with 80% AcOH for 0.5 h, followed quenched with sodium bicarbonate solution (100 mL), extracted with Et_2O (3 x 200 mL), dried (Na_2SO_4), concentrated under reduced pressure and purified by silica gel flash chromatography eluting with 20% EtOAc/Hexane to give 4.52 g (7.6 mmol, 97%) 2,4-diacetate **20** as white foam, mp: 138-139 °C; R_f (60% EtOAc/Hexane) = 0.58; $[\alpha]^{25}_D$ = - 161 (*c* = 1.1, CH_2Cl_2); IR (thin film, cm^{-1}) 3478, 2980, 2936, 2834, 1743, 1373, 1227, 1034, 908; ^1H NMR (600 MHz, $CDCl_3$) δ 7.27-7.35 (m, 5H), 5.29 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.15 (d, *J* = 1.2 Hz, 1H), 4.82 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.78 (d, *J* = 1.2 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.12 (ddd, *J* = 9.6, 7.2, 3.6 Hz, 1H), 4.01 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.91 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.83 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.79 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.80 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.25 (s, 3H), 3.22 (s,

3H), 2.27 (d, J = 7.2 Hz, 1H, OH), 2.12 (s, 3H), 2.10 (s, 3H), 1.26 (s, 3H), 1.25 (s, 3H), 1.25 (d, J = 6.6 Hz, 3H), 1.12 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CD_3Cl) δ 171.4, 170.3, 137.2, 128.5, 128.0, 127.9, 99.9, 99.7, 98.7, 98.3, 75.4, 74.8, 72.6, 69.2, 68.6, 68.5, 68.4, 67.4, 66.4, 48.1, 47.7, 21.1, 21.0, 17.8, 17.6, 17.5, 16.7; CIHRMS: Calculated for $[C_{29}H_{42}O_{13}Na^+]$: 621.2523, Found: 621.2515.

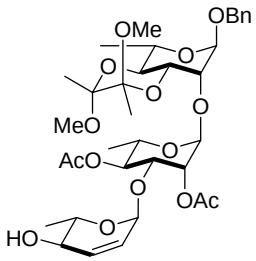
(3S, 4S, 5S)-6-((4aS, 8S, 8aS)-7-(benzyloxy)-hexahydro-2, 3-dimethoxy-2, 3, 5-trimethyl-2H-pyrano [3, 4-b][1, 4] dioxin-8-yloxy)-4-(5, 6-dihydro-6-methyl-5-oxo-2H-pyran-2-yloxy)-tetrahydro-2-methyl-2H-pyran-3, 5-yl-diacetate (21):



To a solution of Boc-pyranone **(*ent*)-8** (5.14 g, 40.2 mmol) and disaccharide rhamnose **20** (4 g, 6.7 mmol) in dry CH_2Cl_2 (6.7 mL), was added $Pd_2(DBA)_3$•$CHCl_3$ (69.2 mg, 1.0 mol% Pd) and PPh_3 (70.2 mg, 4 mol%) at 0 ^oC under argon atmosphere. After stirring for 2 h from 0 ^oC to room temperature, the reaction mixture was quenched with 100 mL of saturated $NaHCO_3$, extracted (3 x 200 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel chromatography eluting with 25% EtOAc/Hexane to give pyranone **21** (4.74 g, 6.3 mmol, 94%) as white foam mp: 143- 146 ^oC, R_f (40% EtOAc/Hexane) = 0.52; $[\alpha]^{25}_D$ = - 130 (c = 1.02, CH_2Cl_2); IR (thin film, cm^{-1}) 2986, 2936, 2834, 1746, 1374, 1223, 1032, 911; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.37 (m, 5H), 6.62 (dd, J = 10.2, 3.6 Hz, 1H), 6.05 (d, J = 10.2, 1H), 5.42 (dd, J = 3.6, 1.8 Hz, 1H), 5.28 (d, J = 3.6 Hz, 1H), 5.12 (d, J = 1.8 Hz,

1H), 5.03 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.78 (d, *J* = 1.2 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.68 (dd, *J* = 13.2, 6.6 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.21 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.01 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.91 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.86 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.79 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.75 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.25 (s, 3H), 3.23 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 1.39 (d, *J* = 6.6 Hz, 3H), 1.29 (d, *J* = 6.6 Hz, 3H), 1.27 (s, 3H), 1.26 (s, 3H), 1.12 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CD_3Cl) δ 196.2, 169.3, 169.2, 141.8, 136.9, 128.2, 127.7, 127.6, 127.3, 99.6, 99.4, 98.7, 98.3, 94.9, 75.1, 75.0, 72.8, 71.0, 70.2, 68.8, 68.3, 68.0, 67.0, 66.6, 47.7, 47.2, 20.6, 20.5, 17.5, 17.23, 17.22, 16.4, 14.4; CIHRMS: Calculated for [$C_{35}H_{48}O_{15}Na^+$]: 731.2891, Found: 731.2881.

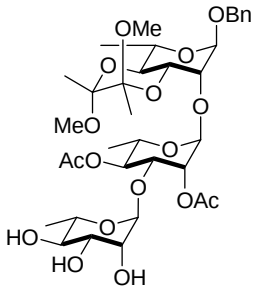
(3S, 4S, 5S)-6-((4aS, 8S, 8aS)-7-(benzyloxy)-hexahydro-2, 3-dimethoxy-2, 3, 5-trimethyl-2H-pyrano [3, 4-b][1, 4] dioxin-8-yloxy)-4-((5R)-5, 6-dihydro-5-hydroxy-6-methyl-2H-pyran-2-yloxy)-tetrahydro-2-methyl-2H-pyran-3, 5-yl diacetate (22a):



To a solution of trisaccharide pyranone **21** (4.1 g, 5.79 mmol) in dry CH_2Cl_2 (5.79 mL) and 0.4 M $CeCl_3$/MeOH (5.79 mL) at the temperature of -78 °C, was added $NaBH_4$ (224 mg, 5.90 mmol). The reaction mixture was stirred at -78 °C for 4 h, diluted with ether (50 mL), quenched with 50 mL of saturated $NaHCO_3$, extracted (3 x 200 mL) with Et_2O, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified using silica gel flash chromatography eluting with 50% EtOAc/Hexane to give 3.66 g

(5.15 mmol, 89%) of allylic alcohol **22a** as white powder, mp: 96-99 °C: R_f (60% EtOAc/Hexane) = 0.50; $[\alpha]^{25}_D$ = - 140 (*c* = 1.06, CH_2Cl_2); IR (thin film, cm^{-1}) 3465, 2988, 2935, 2834, 1746, 1376, 1226, 1034, 908; ^1H NMR (600 MHz, $CDCl_3$) δ 7.27-7.36 (m, 5H), 5.90 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.60 (ddd, *J* = 10.2, 4.8, 2.4 Hz, 1H), 5.35 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.10 (d, *J* = 1.8 Hz, 1H), 5.01 (d, *J* = 1.8 Hz, 1H), 4.99 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.77 (d, *J* = 1.2 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.15 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.01 (dd, *J* = 10.2, 3.0 Hz, 1H), 3.93 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.86 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.71-3.81 (m, 2H), 3.75 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.66 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.25 (s, 3H), 3.23 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H), 1.52 (d, *J* = 2.4 Hz, 1H), 1.34 (d, *J* = 6.6 Hz, 3H), 1.28 (d, *J* = 6.6 Hz, 3H), 1.27 (s, 3H), 1.26 (s, 3H), 1.11 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CD_3Cl) δ 169.9(2 C), 137.3, 133.9, 128.5, 128.0, 127.9, 126.2, 99.9, 99.7, 98.8, 98.7, 96.2, 75.1, 74.3, 73.3, 72.0, 69.8, 69.2, 68.6, 68.4, 68.3, 67.4, 66.9, 48.1, 47.6, 21.2, 20.9, 17.8(2 C), 17.7, 17.6, 16.7; CIHRMS: Calculated for $[C_{35}H_{50}O_{15}Na^+]$: 731.3047, Found: 733.3040.

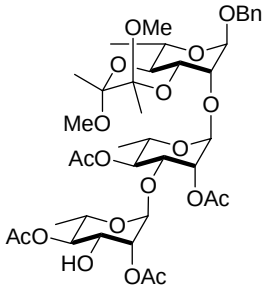
(3S, 4S, 5S)-4-((3S, 4S, 5R)-tetrahydro-3, 4, 5-trihydroxy-6-methyl-2H-pyran-2-yloxy)-6-((4aS, 8S, 8aS)-7-(benzyloxy)-hexahydro-2, 3-dimethoxy-2, 3, 5-trimethyl-2H-pyrano[3, 4-b][1, 4]dioxin-8-yloxy)-tetrahydro-2-methyl-2H-pyran-3, 5-yl diacetate (22):



To a *t*-butanol, acetone (7.0 mL, 1:1 (v/v), 0.5 M) solution of allylic alcohol **22a** (2.5 g, 3.52 mmol) at 0 °C was added a solution of *N*-methyl morpholine *N*-oxide/water (50% w/v, 3.5 mL) and crystalline OsO_4 (9 mg, 1 mol %), stirring for 12 h from 0 °C to room temperature. The reaction mixture was quenched with 30 mL saturated NaS_2O_3 solution, extracted with EtOAc (3 x 200 mL), dried (Na_2SO_4), concentrated under reduced pressure, and then purified using silica gel flash chromatography eluting with pure EtOAc to give triol **22** (2.32 g, 3.31 mmol, 94%) as white foam, mp: 181-184 °C; R_f = 0.50 (5% Methanol/EtOAc); $[\alpha]^{25}_D$ = - 137 (*c* = 1.07, MeOH); IR (thin film, cm^{-1}) 3416, 2980, 2933, 1749, 1376, 1225, 1036, 983; ^{1}H NMR (600 MHz, CD_3OD) δ 7.36-7.44 (m, 5H), 5.38 (d, *J* = 3.6, 1.8 Hz, 1H), 5.12 (d, *J* = 1.8 Hz, 1H), 5.03 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.88 (d, *J* = 1.8 Hz, 1H), 4.87 (d, *J* = 1.8 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.17 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.05 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.93 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.94 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.84 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.79 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.76 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.69 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.43 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.39 (m, 1H), 3.34 (s, 3H), 3.30 (s, 3H), 2.18 (s, 3H), 2.16 (s, 3H), 1.36 (s, 3H), 1.34 (d, *J* = 6.6 Hz, 3H), 1.32 (s, 3H), 1.31 (d, *J* = 6.6 Hz, 3H), 1.11 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 171.8, 171.3, 138.7, 129.6, 129.3, 129.1, 103.8, 101.3, 101.0, 99.8, 99.5, 76.9, 75.5, 74.4, 73.7, 72.9, 72.4, 72.2, 70.6, 70.2, 70.0, 69.5, 68.5, 68.2, 48.4, 48.1, 21.1, 20.9, 18.2, 18.1, 18.0, 17.9, 17.3; CIHRMS: Calculated for [$C_{35}H_{52}O_{17}Na^+$]: 767.3102, Found: 767.3101.

(3S, 4S, 5R)-2-((3S, 4S, 5S)-2-((4aS, 8S, 8aS)-7-(benzyloxy)-hexahydro-2, 3-dimethoxy-2, 3, 5-trimethyl-2H-pyrano [3, 4-b][1, 4] dioxin-8-yloxy)-tetrahydro-3, 5-

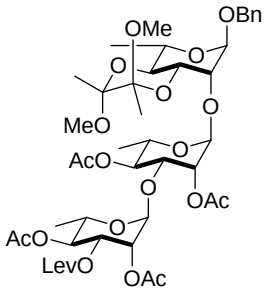
diacetoxy-6-methyl-2H-pyran-4-yloxy)-tetrahydro-4-hydroxy-6-methyl-2H-pyran-3, 5-yl diacetate (23):



To a solution of triol **22** (2 g, 2.68 mmol) and trimethyl orthoacetate (1.02 mL, 8.1 mmol) mixture in CH_3CN (8.1 mL) was added *p*-toluenesulfonic acid monohydrate (25.5 mg, 0.13 mmol), stirring for 0.5 h. A few drops pyridine was added to neutralize acid and then the solvent was evaporated. The resulting residue was dissolved in pyridine (3 mL), Ac_2O (1.5 mL) and DMAP (17 mg) was added. After stirring for 6 h, water was added to decompose excess Ac_2O. The mixture was diluted in ether, washed with saturated $CuSO_4$ solution and the solvent was evaporated. The residue was treated with 2 mL 80 % AcOH for 0.5 h, quenched with sodium bicarbonate solution (50 mL), extracted with Et_2O (3 x 100 mL), dried (Na_2SO_4), concentrated under reduced pressure and purified by silica gel flash chromatography eluting with 55% EtOAc/Hexane to give 2.11 g (2.55 mmol, 95%) diacetate **23** as white foam, mp: 100-103 °C; R_f = 0.25 (50% EtOAc/Hexane); $[\alpha]^{25}_D$ = -126 (c = 1.13, CH_2Cl_2); IR (thin film, cm^{-1}) 3484, 2985, 2938, 2834, 1741, 1372, 1224, 1034, 909; ^1H NMR (600 MHz, $CDCl_3$) δ 7.27-7.34 (m, 5H), 5.27 (dd, J = 3.6, 1.8 Hz, 1H), 5.06 (d, J = 1.8 Hz, 1H), 5.02 (dd, J = 9.6, 9.6 Hz, 1H), 4.91 (m, 1H), 4.86 (d, J = 1.8 Hz, 1H), 4.81 (dd, J = 9.6, 9.6 Hz, 1H), 4.75 (d, J = 1.2 Hz, 1H), 4.68 (d, J = 12.0 Hz, 1H), 4.48 (d, J = 12.0 Hz, 1H), 4.12 (m, 2H), 3.99 (dd, J = 10.2, 3.6 Hz, 1H), 3.81-3.88 (m, 4H), 3.73 (dq, J = 9.0, 6.6 Hz, 1H), 3.68 (dd, J = 9.6, 9.6 Hz, 1H), 3.22 (s, 3H), 3.21

(s, 3H), 2.12 (s, 9H), 2.10 (s, 3H), 1.23 (d, J = 6.6 Hz, 3H), 1.25 (s, 3H), 1.23 (s, 3H), 1.20 (d, J = 6.6 Hz, 3H), 1.07 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.7, 170.4, 170.3, 169.8, 137.2, 128.5, 128.0, 127.9, 99.9, 99.7, 98.9, 98.7, 98.6, 75.5, 74.5, 74.4, 73.0, 72.7, 71.3, 69.2, 68.6, 68.3, 68.2, 67.2, 67.0, 66.6, 48.0, 47.5, 21.1, 21.0, 20.9, 20.8, 17.8, 17.5, 17.4, 17.0, 16.6; CIHRMS: Calculated for [$C_{39}H_{56}O_{19}Na^+$]: 851.3308, Found: 851.3313.

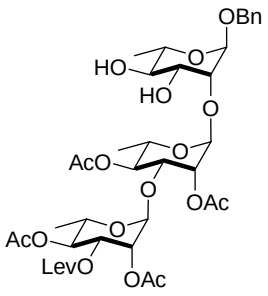
(3S, 4S, 5S)-2-((3S, 4S, 5S)-2-((4aS, 8S, 8aS)-7-(benzyloxy)-hexahydro-2, 3-dimethoxy-2, 3, 5-trimethyl-2H-pyrano [3, 4-b][1, 4] dioxin-8-yloxy)-tetrahydro-3, 5-diacetoxy-6-methyl-2H-pyran-4-yloxy)-tetrahydro-3, 5-diacetoxy-6-methyl-2H-pyran-4-yl 4-oxopentanoate (24a):



To a solution of levulinic acid (336 mg, 2.9 mmol) in CH_2Cl_2 (9 mL), was added DMAP (354 mg, 2.9 mmol) at 0 ^oC. After stirring for 10 min., DCC (586 mg, 2.9 mmol) was added, and an insoluble white precipitate appeared. The solution was stirred for 10 min.. Alcohol **23** (1.2 g, 1.45 mmol) was added to the mixture. The suspension was stirred from 0 ^oC to room temperature for 4 h. The suspension was filtered over a pad of celite, evaporated under reduced pressure, and purified using silica gel flash chromatography eluting with 50% EtOAc/Hexane to give levulinoyl ester **24a** (1.29 g, 1.39 mmol, 96%) as white foam, mp: 87-89 °C; R_f = 0.58 (70% EtOAc/Hexane); $[\alpha]^{25}_D$ = - 113 (c = 1.01,

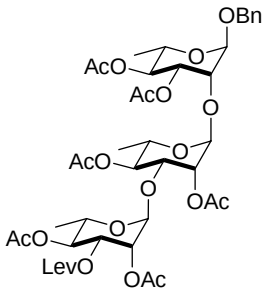
CH_2Cl_2); IR (thin film, cm^{-1}) 2986, 2935, 1748, 1371, 1223, 1037, 916; ^1H NMR (600 MHz, $CDCl_3$) δ 7.27-7.35 (m, 5H), 5.31 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.16 (dd, *J* = 9.6, 3.6 Hz, 1H), 5.08 (d, *J* = 1.2 Hz, 1H), 5.05 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.04 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.01 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.85 (d, *J* = 1.8 Hz, 1H), 4.75 (d, *J* = 1.2 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.11 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.00 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.95 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.89 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.83 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.74 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.68 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.23 (s, 3H), 3.22 (s, 3H), 2.73 (ddd, *J* = 18.6, 8.4, 5.4 Hz, 1H), 2.61 (ddd, *J* = 18.6, 6.6, 5.4 Hz, 1H), 2.52 (ddd, *J* = 18.6, 8.4, 5.4 Hz, 1H), 2.43 (ddd, *J* = 18.6, 6.6, 5.4 Hz, 1H), 2.16 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 1.26 (d, *J* = 6.6 Hz, 3H), 1.26 (s, 3H), 1.24 (s, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 171.4, 170.4, 170.2, 170.1, 170.0, 137.2, 128.5, 128.1, 127.9, 99.9, 99.7, 98.8, 98.7, 98.6, 75.6, 74.5, 72.9, 71.0, 70.8, 70.3, 69.2, 68.8, 68.6, 68.3, 67.3, 67.1, 67.0, 48.1, 47.6, 37.7, 29.8, 27.9, 21.1, 21.0, 20.9, 20.8, 17.8, 17.6, 17.5, 17.1, 16.7; CIHRMS: Calculated for $[C_{44}H_{62}O_{21}Na^+]$: 949.3681, Found: 949.3688.

(3R, 4S, 5S)-5-((3S, 4S, 5S)-4-((3S, 4S, 5S)-4-(4-oxopentanoxy)-tetrahydro-3, 5-diacetoxy-6-methyl-2H-pyran-2-yloxy)-tetrahydro-3, 5-diacetoxy-6-methyl-2H-pyran-2-yloxy)-6-(benzyloxy)-tetrahydro-2-methyl-2H-pyran-3, 4-diol (24):



To a solution of Lev-protected trisacchride **24a** (1.34 g, 1.45 mmol) in CH_2Cl_2 (15 mL), was added the 2.93 mL of 10:1 TFA-H_2O. The reaction was stirred at room temperature for 40 min, quenched with saturated $NaHCO_3$ solution (50 mL), extracted with Et_2O (3 x 200 mL), dried (Na_2SO_4), concentrated under reduced pressure and purified by passing a pad of silica gel eluting with pure EtOAc to give 1.17 g (1.44 mmol, 99%) diol **24** as white foam, mp: 94-97 °C; R_f = 0.36 (70% EtOAc/Hexane); $[\alpha]^{25}_D$ = - 126 (*c* = 0.43, CH_2Cl_2); IR (thin film, cm^{-1}) 3453, 2982, 29385, 1747, 1372, 1225, 1047, 983; ^{1}H NMR (600 MHz, $CDCl_3$,) δ 7.27-7.36 (m, 5H), 5.23 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.14 (dd, *J* = 9.6, 3.6 Hz, 1H), 5.05 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.04 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.03 (dd, *J* = 3.6, 1.8Hz, 1H), 4.92 (d, *J* = 1.8 Hz, 1H), 4.90 (d, *J* = 1.8 Hz, 1H), 4.84 (d, *J* = 1.8 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.11 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.04 (dd, *J* = 9.6, 3.6Hz, 1H), 3.89 (dd, *J* = 3.6, 1.8 Hz, 1H), 3.88 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.87 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.79 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.68 (dq, *J* = 9.6, 6.6 Hz, 1H), 2.71 (ddd, *J* = 18.6, 8.4, 5.4 Hz, 1H), 2.62 (ddd, *J* = 18.6, 6.6, 5.4 Hz, 1H), 2.52 (ddd, *J* = 18.6, 8.4, 5.4 Hz, 1H), 2.42 (ddd, *J* = 18.6, 6.6, 5.4 Hz, 1H), 2.16 (s, 3H), 2.15 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 1.74 (s, 1H), 1.43 (s, 1H), 1.33 (d, *J* = 6.6 Hz, 3H), 1.17 (d, *J* = 6.6 Hz, 3H), 1.03 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 171.3, 170.6, 170.3, 170.2, 170.1, 137.1, 128.6, 128.1, 128.0, 99.5, 98.7, 97.5, 79.1, 74.9, 73.8, 72.2, 71.5, 71.1, 70.6, 70.1, 69.1, 68.8, 68.3, 67.4, 67.3, 37.7, 29.8, 27.9, 21.1, 21.0, 20.9, 20.8, 17.7, 17.4, 17.3; CIHRMS: Calculated for $[C_{38}H_{52}O_{19}K^+]$: 851.2734, Found: 851.2734.

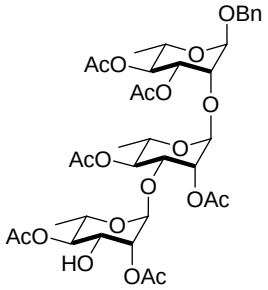
(3S, 4S, 5S)-2-((3S, 4S, 5S)-2-((3S, 4S, 5S)-2-(benzyloxy)-tetrahydro-4, 5-diacetoxy-6-methyl-2H-pyran-3-yloxy)-tetrahydro-3, 5-diacetoxy-6-methyl-2H-pyran-4-yloxy)-3, 5-diacetoxy-tetrahydro-6-methyl-2H-pyran-4-yl 4-oxopentanoate (5a):



To a solution of diol **24** (812 mg, 1 mmol) in pyridine (1 mL), was added Ac_2O (0.5 mL) and DMAP (17.5 mg). The reaction mixture was stirred for 12 h. Water was added to destroy the excess acetic anhydride, extracted (3 x 50 mL) with Et_2O washed with 20 mL of saturated $CuSO_4$ solution for three times, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was passed over a silica gel pad with pure ether to give 897 mg (1.0 mmol, 99 %) of acetate **5a** as white foam, mp: 78-80 °C; R_f (50% EtOAc/Hexanes) = 0.20; $[\alpha]^{25}_D$ = - 48 (*c* = 1.18, CH_2Cl_2); IR (thin film, cm^{-1}) 2940, 2984, 1741, 1370, 1219, 1039, 914; ^1H NMR (600 MHz, $CDCl_3$) δ 7.27-7.35 (m, 5H), 5.24 (dd, *J* = 9.6, 3.6 Hz, 1H), 5.18 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.14 (dd, *J* = 9.6, 3.0 Hz, 1H), 5.05 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.04 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.04 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.02 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.91 (d, *J* = 1.8 Hz, 1H), 4.74 (d, *J* = 1.8 Hz, 1H), 4.73 (d, *J* = 1.8 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.09 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.99 (dd, *J* =3.6, 1.8 Hz, 1H), 3.86 (dq, *J* = 9.0, 6.6 Hz, 2H), 3.72 (dq, *J* = 9.6, 6.6 Hz, 1H), 2.74 (ddd, *J* = 18.6, 8.4, 5.4 Hz, 1H), 2.60 (ddd, *J* = 18.6, 6.6, 5.4 Hz, 1H), 2.51 (ddd, *J* = 18.6, 8.4, 5.4 Hz, 1H), 2.43 (ddd, *J* = 18.6, 6.6, 5.4 Hz, 1H), 2.15 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.20

(d, J = 6.6 Hz, 3H), 1.18 (d, J = 6.6 Hz, 3H), 1.00 (d, J = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.1, 171.3, 170.5, 170.3 (2 C), 170.1 (2 C), 169.8, 136.7, 128.6, 128.1, 128.0, 99.4, 98.7, 97.3, 77.1, 74.3, 72.1, 71.4, 71.2, 70.7, 70.6, 70.1, 69.2, 68.9, 67.4, 67.3, 66.5, 37.7, 29.7, 27.9, 21.0, 20.93, 20.9, 20.8, 20.7 (2 C), 17.5, 17.1 (2 C); CIHRMS: Calculated for [$C_{42}H_{56}O_{21}Na^+$]: 919.3212, Found: 919.3219.

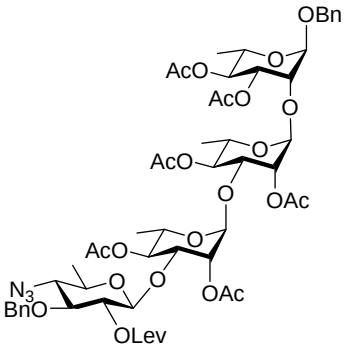
(3S, 4S, 5R)-2-((3S, 4S, 5S)-2-((3S, 4S, 5S)-2-(benzyloxy)-tetrahydro-4, 5-diacetoxy-6-methyl-2H-pyran-3-yloxy)-tetrahydro-3, 5-diacetoxy-6-methyl-2H-pyran-4-yloxy)-tetrahydro-4-hydroxy-6-methyl-2H-pyran-3, 5-yl diacetate (5)



To a solution of levulinoyl ester **5a** (1.4 g, 1.56 mmol) in CH_2Cl_2 (31.2 mL) was added a solution of hydrazinium acetate (1.5 M, 1.1 mL) in methanol. The reaction was stirred for 2 h, quenched with saturated $NaHCO_3$ solution (100 mL), extracted with Et_2O (3 x 200 mL), dried (Na_2SO_4), concentrated under reduced pressure and purified by passing a pad of silica gel eluting with 80% EtOAc/Hexane to give 1.18 g (1.48 mmol, 95%) alcohol **5** as white foam, mp: 94-97 °C; R_f = 0.58 (80% EtOAc/Hexane); $[\alpha]^{25}_D$ = - 55 (c = 0.92, CH_2Cl_2); IR (thin film, cm^{-1}) 3494, 2983, 2939, 1741, 1374, 1223, 1039, 916; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.36 (m, 5H), 5.23 (dd, J = 9.6, 3.6 Hz, 1H), 5.14 (dd, J = 3.6, 1.8 Hz, 1H), 5.04 (dd, J = 9.6, 9.6 Hz, 1H), 5.03 (dd, J = 9.6, 9.6 Hz, 1H), 4.96 (d, J = 1.8 Hz, 1H), 4.88 (dd, J = 3.6, 1.8 Hz, 1H), 4.82 (dd, J = 9.6, 9.6 Hz, 1H), 4.75 (d, J = 1.8 Hz,

1H), 4.73 (d, *J* = 1.8 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.09 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.00 (dd, *J* =3.6, 1.8 Hz, 1H), 3.86 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.85 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.80 (dq, *J* = 9.0, 6.6 Hz, 1H), 3.73 (dq, *J* = 9.0, 6.6 Hz, 1H), 2.13 (s, 9H), 2.11 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.73 (s, 1H, OH), 1.20 (d, *J* = 6.6 Hz, 3H), 1.19 (d, *J* = 6.6 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.7, 170.4, 170.38, 170.35, 170.2, 169.8, 136.7, 128.6, 128.1, 128.0, 99.5, 98.7, 97.4, 77.1, 74.5, 74.1, 72.9, 72.2, 71.5, 71.4, 70.7, 69.2, 68.3, 67.4, 66.8, 66.6, 21.1, 20.0, 20.9, 20.8(2 C), 20.7, 17.5, 17.1, 17.0; CIHRMS: Calculated for [$C_{37}H_{50}O_{19}Na^+$]: 821.2844, Found: 821.2846.

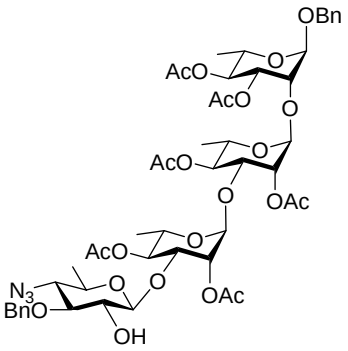
(2S, 3S, 4S, 5R)-2-((2S, 4S, 5S)-2-((2S, 4S, 5S)-2-((2R, 4S, 5S)-2-(benzyloxy)-tetrahydro-4, 5-diacetoxy-6-methyl-2H-pyran-3-yloxy)-tetrahydro-3, 5-diacetoxy-6-methyl-2H-pyran-4-yloxy)-tetrahydro-3, 5-diacetoxy-6-methyl-2H-pyran-4-yloxy)-5-azido-4- (benzyloxy)-tetrahydro-6-methyl-2H-pyran-3-yl 4-oxopentanoate (4):



To a solution of trisaccharide **5** (89.5 mg, 0.112 mmol) and phosphate **6** (100 mg, 0.168 mmol) in 0.2 mL CH_2Cl_2 with molecular sieve at 0 ^oC was added to TMSOTf (37 mg, 0.168 mmol). The reaction was stirred at 0 ^oC for 0.5 h, quenched with saturated $NaHCO_3$ solution (10 mL), extracted with Et_2O (3 x 50 mL), dried (Na_2SO_4),

concentrated under reduced pressure and purified by passing a pad of silica gel eluting with 60% EtOAc/Hexane to give 109 mg (0.10 mmol, 90%) tetrasaccharide **5** as white foam, white foam, mp: 87-90 °C; R_f = 0.40 (50% EtOAc/Hexane); $[\alpha]^{25}_{D}$ = -20 (*c* = 0.98, CH_2Cl_2); IR (thin film, cm^{-1}) 2986, 2939, 2111, 1743, 1371, 1223, 1041, 916; ^1H NMR (600 MHz, $CDCl_3$) δ 7.26-7.36 (m, 10H), 5.23 (dd, *J* = 9.6, 3.6 Hz, 1H), 5.15 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.02 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.01 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.97 (dd, *J* = 9.6, 9.6 Hz, 1H), 4.96(dd, *J* = 3.6, 1.8 Hz, 1H), 4.88 (dd, *J* = 9.6, 7.8 Hz, 1H), 4.87 (d, *J* = 1.8 Hz, 1H), 4.75 (d, *J* = 1.8 Hz, 1H), 4.74 (d, *J* = 1.8 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 7.8 Hz, 1H), 4.09 (dd, *J* = 9.6, 3.0 Hz, 1H), 4.00 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.87 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.86 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.72 (dq, *J* = 9.6, 6.6 Hz, 2H), 3.44 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.23 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.16 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.76 (ddd, *J* = 18.0, 7.2, 7.2 Hz, 1H), 2.64 (ddd, *J* = 18.0, 6.6, 6.6 Hz, 1H), 2.50 (dd, *J* = 18.0, 7.2, 6.6 Hz, 2H), 2.14 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.35 (d, *J* = 6.6 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 1.14 (d, *J* = 6.6 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.3, 171.3, 170.4, 170.36, 170.34, 170.1, 169.8, 169.7, 137.6, 136.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 100.8. 99.4, 99.3, 97.3, 81.1, 76.9, 74.8, 74.7, 73.7, 73.4, 72.6, 72.1, 71.8, 71.6, 71.4, 71.0, 70.7, 69.2, 67.6, 67.3, 67.2, 66.6, 37.9, 29.8, 27.7, 21.1, 21.0, 20.9, 20.84, 20.8, 20.7, 18.2, 17.5, 17.2, 17.1; CIHRMS: Calculated for $[C_{55}H_{71}N_3Na^+]$: 1180.4325, Found: 1180.4334.

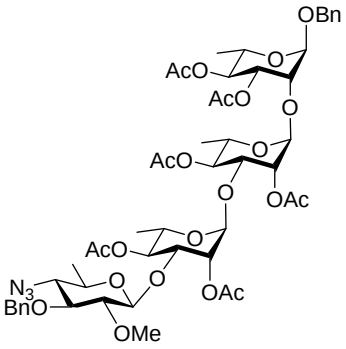
(2S, 3S, 4S, 5R)-2-((2S, 4S, 5S)-2-((2S, 4S, 5S)-2-((2R, 4S, 5S)-2-(benzyloxy)-tetrahydro-4, 5-diacetoxy-6-methyl-2H-pyran-3-yloxy)-tetrahydro-3, 5-diacetoxy-6-methyl-2H-pyran-4-yloxy)-tetrahydro-3, 5-diacetoxy-6-methyl-2H-pyran-4-yloxy)-5-azido-4- (benzyloxy)-tetrahydro-6-methyl-2H-pyran-3-ol (25a):



To a solution of levulinoyl ester **4** (0.8 g, 0.69 mmol) in CH_2Cl_2 (13.8 mL) was added a solution of hydrazinium acetate (1.5 M, 0.48 mL) in methanol. The reaction was stirred for 2 h, quenched with saturated $NaHCO_3$ solution (50 mL), extracted with Et_2O (3 x 150 mL), dried (Na_2SO_4), concentrated under reduced pressure and purified using silica gel flash chromatography eluting with 60% EtOAc/Hexane to give 702 mg (0.66 mmol, 96%) alcohol **25a** as white foam, mp: 100-102 °C; R_f = 0.54 (50% EtOAc/Hexane); $[\alpha]^{25}_D$ = - 22 (c = 0.85, CH_2Cl_2); IR (thin film, cm^{-1}) 3475, 2984, 2941, 2110, 1743, 1373, 1223, 1039, 912; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27-7.40 (m, 10H), 5.24 (dd, J = 9.6, 3.6 Hz, 1H), 5.17 (dd, J = 3.6, 1.8 Hz, 1H), 5.03 (dd, J = 9.6, 9.6 Hz, 1H), 5.027 (dd, J = 9.6, 9.6 Hz, 1H), 5.02 (dd, J = 9.6, 9.6 Hz, 1H), 4.96 (dd, J = 3.6, 1.8 Hz, 1H), 4.93 (d, J = 12.0, Hz, 1H), 4.91 (d, J = 1.8 Hz, 1H), 4.80 (d, J = 12.0 Hz, 1H), 4.76 (d, J = 1.8 Hz, 1H), 4.75 (d, J = 1.8 Hz, 1H), 4.71 (d, J = 12.0 Hz, 1H), 4.52 (d, J = 12.0 Hz, 1H), 4.21(d, J = 7.8 Hz, 1H), 4.06 (dd, J = 9.6, 3.0 Hz, 1H), 4.00 (dd, J = 3.0, 1.8 Hz, 1H), 3.82 (dd, J = 9.6, 3.6 Hz, 1H), 3.87 (dq, J = 9.6, 6.6 Hz, 1H), 3.77 (dq, J = 9.6, 6.6 Hz, 1H), 3.73 (dq,

J = 9.6, 6.6 Hz, 1H), 3.45 (ddd, *J* = 9.6, 7.8, 2.4 Hz, 1H), 3.36 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.20 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.07 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.44 (d, *J* = 2.4 Hz, 1H), 2.14 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.32 (d, *J* = 6.6 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 1.18 (d, *J* = 6.6 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 170.5, 170.36, 170.33, 170.2, 169.8, 138.1, 136.7, 128.6, 128.4, 128.3, 128.1, 128.0, 127.9, 103.9. 99.4, 99.2, 97.3, 82.2, 77.0, 75.3, 75.1, 74.9, 74.7, 72.6, 72.4, 72.1, 71.6, 71.4, 70.9, 70.7, 69.2, 67.3, 67.2, 67.1, 66.6, 21.2, 21.1, 21.0, 20.9, 20.8, 20.7, 18.4, 17.5, 17.2, 17.1; CIHRMS: Calculated for [$C_{50}H_{65}N_3O_{22}Na^+$]: 1082.3958, Found: 1082.3961.

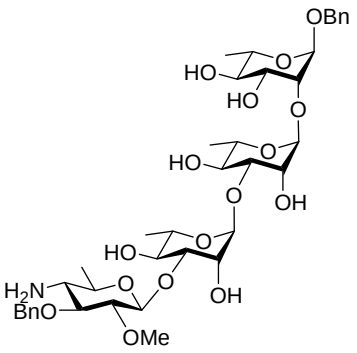
(2S, 4S, 5S)-4-((2S, 3S, 4S, 5R)-5-azido-4- (benzyloxy)-tetrahydro-3-methoxy-6-methyl-2H-pyran-2-yloxy)-2-((2S, 4S, 5S)-2-((2R, 4S, 5S)-2-benzyloxy-4, 5-diacetoxy-tetrahydro-6-methyl-2H-pyran-3-yloxy)-3, 5-diacetoxy-tetrahydro-6-methyl-2H-pyran-4-yloxy) tetrahydro-6-methyl-2H-pyran-3, 5-yl diacetate (25):



To a mixture of alcohol **25a** (424 mg, 0.40 mmol) and silver (I) oxide (1.84 g, 8 mmol), was added 2 mL CH_3I. The reaction suspension was stirred at 55 ^oC for 3 days. The reaction mixture was then passed through a celite pad with 150 mL Et_2O, concentrated under reduced pressure and purified using silica gel flash chromatography eluting with

50% EtOAc/Hexane to give 400 mg (0.372 mmol, 94%) alcohol **25** as white foam, mp: 91-93 °C; R_f = 0.67 (50% EtOAc/Hexane); $[\alpha]^{25}_{D}$ = - 23 (*c* = 1.31, CH_2Cl_2); IR (thin film, cm^{-1}) 2938, 2984, 2110, 1744, 1371, 1224, 1041, 916; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.39 (m, 10H), 5.23 (dd, *J* = 9.6, 3.6 Hz, 1H), 5.16 (dd, *J* = 3.6, 1.8 Hz, 1H), 5.10 (dd, *J* = 9.6, 9.6 Hz, 1H), 5.03 (dd, *J* = 9.6, 9.6 Hz, 2H), 5.00 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.91 (d, *J* = 1.2, Hz, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.76 (d, *J* = 1.8 Hz, 1H), 4.75 (d, *J* = 1.8 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.29(d, *J* = 7.8 Hz, 1H), 4.07 (dd, *J* = 9.6, 3.0 Hz, 1H), 4.00 (dd, *J* =3.0, 1.8 Hz, 1H), 3.88 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.86 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.74 (dq, *J* = 9.6, 6.6 Hz, 2H), 3.46 (s, 3H), 3.30 (dd, *J* =9.6, 9.6 Hz, 1H), 3.16 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.03 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.01 (dd, *J* = 9.6, 7.8 Hz, 1H), 2.16 (s, 3H), 2.14 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.29 (d, *J* = 6.6 Hz, 3H), 1.21 (d, *J* = 6.6 Hz, 3H), 1.19 (d, *J* = 6.6 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 170.4, 170.3, 170.2, 170.1, 169.7, 138.0, 136.7, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 104.2. 99.4, 99.2, 97.3, 84.0, 82.8, 77.0, 75.4, 75.1, 74.7, 72.4, 72.3, 72.1, 71.7, 71.4, 70.7, 70.5, 69.2, 67.5, 67.4, 67.3, 66.6, 60.7, 21.2, 21.1, 21.0 (2 C), 20.7 (2 C), 18.3, 17.6, 17.2 (2 C); CIHRMS: Calculated for $[C_{51}H_{67}N_3O_{22}Na^+]$: 1096.4114, Found: 1096.4114.

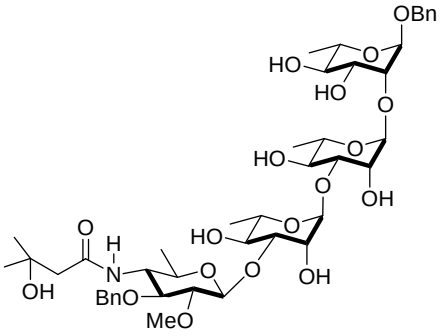
(3R, 4S, 6R)-5-((2S, 4S, 5S)-4-((2S, 4R, 5S)-4-((2S, 3S, 4S, 5R)-5-amino-4-(benzyloxy)-tetrahydro-3-methoxy-6-methyl-2H-pyran-2-yloxy)-tetrahydro-3, 5-dihydroxy-6-methyl-2H-pyran-2-yloxy)-tetrahydro-3, 5-dihydroxy-6-methyl-2H-pyran-2-yloxy)-6-(benzyloxy)-tetrahydro-2-methyl-2H-pyran-3, 4-diol (26a):



To a stirred solution of acetate **25** (332 mg, 0.31 mmol) in 4.2 mL MeOH/THF/H_2O (10/10/1), was added PEt_3 (110 mg, 0.93 mmol) for 10 min., and then added LiOH (90 mg, 3.72 mmol). This reaction was stirred for 2 h, evaporated solvent under reduced pressure, and purified using silica gel flash chromatography eluting with 20% MeOH/CH_2Cl_2. The resulted product was applied to ion-exchange chromatography (Dowex 1x 8, 200 mesh, H^+ form) eluting with water. Removal of water in vacuo to give 231 mg (0.29 mmol, 95%) alcohol **26a** as white powder, mp: 118.0-121 °C; R_f = 0.41 (20% Methanol/EtOAc); $[\alpha]^{25}_D$ = - 97 (*c* = 2.06, MeOH); IR (thin film, cm^{-1}) 3355, 2974, 2934, 2542, 1565, 1225, 1062, 987; ^{1}H NMR (600 MHz, CD_3OD) δ 7.26-7.39 (m, 10H), 5.05 (d, *J* = 1.2 Hz, 1H), 4.95 (d, *J* = 11.4 Hz, 1H), 4.88 (d, *J* = 1.2 Hz, 1H), 4.83 (d, *J* = 1.2 Hz, 1H), 4.75 (d, *J* = 11.4 Hz, 1H), 4.68 (d, *J* = 7.8 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.17 (dd, *J* = 3.0, 1.8 Hz, 1H), 4.05 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.92 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.83 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.82 (m, 1H), 3.81(dd, *J* = 9.6, 3.0 Hz, 1H), 3.76 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.62 (s, 3H), 3.60-3.64 (m, 2H), 3.56 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.48 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.43 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.38 (dd, *J* = 9.6, 9.6 Hz, 2H), 3.30 (ddd, *J* = 3.0, 1.8, 1.8 Hz, 1H), 3.19 (dd, *J* = 9.6, 7.8 Hz, 1H), 1.29 (d, *J* = 6.6 Hz, 6H), 1.27 (d, *J* = 6.6 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 140.0, 138.9, 129.6, 129.5, 129.3, 129.2, 129.0, 128.9, 105.7,

104.0, 103.5, 99.1, 86.0, 82.8, 81.8, 80.1, 79.2, 75.8, 74.4, 73.3, 73.1, 72.3 (2 C), 71.9, 71.8, 70.6, 70.4, 70.2, 69.9, 61.0, 58.5, 18.5, 18.3, 18.1, 17.9; CIHRMS: Calculated for $[C_{39}H_{57}NO_{16}H^{+}]$: 796.3756, Found: 796.3750.

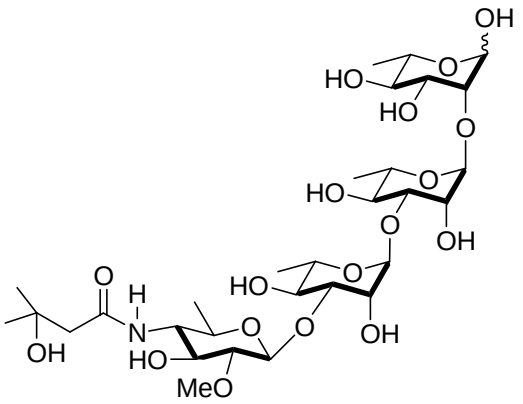
N-((3R, 5S, 6S)-6-((2S, 3S, 4S, 5S)-2-((2S, 3S, 4S, 5S)-2-((2R, 3S, 4S, 5S)-2-(benzyloxy)-4, 5-dihydroxy-tetrahydro-6-methyl-2H-pyran-3-yloxy)-3, 5-dihydroxy-tetrahydro-6-methyl-2H-pyran-4-yloxy)-3, 5-dihydroxy-tetrahydro-6-methyl-2H-pyran-4-yloxy)-4-(benzyloxy)-tetrahydro-5-methoxy-2-methyl-2H-pyran-3-yl)-3-hydroxy-3-methylbutanamide (26):



To a solution of amine **26a** (34 mg, 0.042 mmol) in 0.1 mL THF and Et_3N (12.6 µl, 0.08 mmol), was added HBTU (20 mg, 0.05 mmol) and 3-hydroxy-3-methylbutanoic acid (7.5 mg, 0.063 mmol). The reaction was stirred for 10 h, evaporated solvent under reduced pressure, and purified using silica gel flash chromatography eluting with 15% MeOH/CH_2Cl_2 to give 35 mg (38 µmol, 90 %) amide **26** as white powder, mp: 128-130 °C; R_f = 0.55 (20% Methanol/EtOAc); $[\alpha]^{25}_D$ = - 77 (*c* = 1.65, MeOH); IR (thin film, cm^{-1}) 3415, 2977, 2934, 2523, 1649, 1455, 1122, 1040, 843; ^{1}H NMR (600 MHz, CD_3OD) δ 7.30-7.41 (m, 10H), 5.12 (d, *J* = 1.8 Hz, 1H), 4.95 (d, *J* = 1.2 Hz, 1H), 4.92 (d, *J* = 1.8 Hz, 1H), 4.90 (d, *J* = 12.0 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 12.0

Hz, 1H), 4.70(d, *J* = 7.8 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.25 (dd, *J* = 3.0, 1.8 Hz, 1H), 4.12 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.99 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.92 (dq, *J* = 9.6, 6.6 Hz, 1H), 3.89-3.86 (m, 2H), 3.84 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.78 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.70-3.66 (m, 2H), 3.65 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.55 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.53 (dq, *J* = 9.6, 6.0 Hz, 1H), 3.51 (dq, *J* = 9.6, 6.0 Hz, 1H), 3.45 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.26 (dd, *J* = 9.6, 7.8 Hz, 1H), 2.36 (s, 2H), 1.37 (d, *J* = 6.6 Hz, 3H), 1.34 (d, *J* = 6.6 Hz, 3H), 1.30 (s, 3H), 1.29 (s, 3H), 1.28 (d, *J* = 6.6 Hz, 3H), 1.17 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 174.5, 140.3, 138.9, 129.6, 129.4, 129.3, 129.0, 128.8, 128.6, 105.6, 104.1, 103.6, 99.1, 85.9, 83.0, 81.9, 80.2, 79.2, 75.7, 74.5, 73.4, 73.2, 72.3, 72.2, 71.9, 71.8, 70.7, 70.6, 70.3, 70.2, 69.9, 61.2, 57.1, 49.6, 29.8, 29.6, 18.5, 18.3, 18.1, 17.9; CIHRMS: Calculated for [$C_{44}H_{65}NO_{18}Na^+$]: 918.4099, Found: 918.4096.

Anthrax Tetrasaccharide (1):

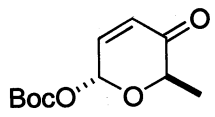


To a solution of Bn-ether **26** 35 mg (0.038 mmol) in 2 mL MeOH was added 10 % Pd/C (20 mg). The reaction suspension was stirred with hydrogen balloon for 30 h, filtered by passing celite pad, concentrated under reduced pressure and vacuo to give 27 mg anthrax tetrasaccharide **1** (0.036 mmol, 96 %) as white powder, mp: 168-174 °C; R_f = 0.55 (20% Methanol/EtOAc); $[\alpha]^{25}_D$ = - 46 (*c* = 1.08, MeOH); IR (thin film, cm^{-1}) 3410, 2975, 2936,

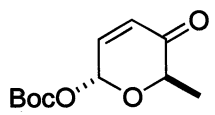
1644, 1450, 1121, 1067; ^{1}H NMR (600 MHz, CD_3OD)[2] δ 5.19 (d, *J* = 1.8 Hz, 1H), 5.13 (d, *J* = 1.2 Hz, 1H), 4.99 (d, *J* = 1.8 Hz, 1H), 4.70 (d, *J* = 7.8 Hz, 1H), 4.25 (dd, *J* = 3.0, 1.8 Hz, 1H), 4.13 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.98 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.91 (dq, *J* = 9.6, 6.0 Hz, 1H), 3.90 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.87 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.86 (dd, *J* = 3.0, 1.8 Hz, 1H), 3.85 (dq, *J* = 9.6, 6.0 Hz, 1H), 3.81 (dq, *J* = 9.6, 6.0 Hz, 1H), 3.72 (s, 3H), 3.67 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.64 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.58 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.50 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.49 (dq, *J* = 9.6, 6.0 Hz, 1H), 3.42 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.09 (dd, *J* = 9.6, 7.8 Hz, 1H), 2.45 (pquart., 2H), 1.36 (d, *J* = 6.0 Hz, 3H), 1.35 (s, 3H), 1.34 (s, 3H), 1.314 (d, *J* = 6.6 Hz, 3H), 1.313 (d, *J* = 6.6 Hz, 3H), 1.28 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.8, 105.5, 103.9, 103.6, 94.7, 85.7, 82.0, 80.9, 79.3, 75.2, 74.7, 73.5, 73.2, 72.3, 72.0 (2 C), 71.9, 70.8, 70.6, 70.3, 69.5, 61.3, 58.2, 49.7, 29.8, 29.7, 18.6, 18.4, 18.1, 18.0; CIHRMS: Calculated for [$C_{30}H_{53}NO_{18}Na^{+}$]: 738.3160, Found: 738.3160.

Section C: ^{1}H NMR and ^{13}C NMR Spectra

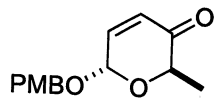
[2] We found ^{1}H NMR data of Anthrax Tetrasacchride **1** with DMSO as solvent (2 mg dissolved in DMSO) matched what reported for the isolated natural product. See: Daubenspeck, J. M; Zeng, H.; Chen, P.; Dong, S.; Steichen, C. T; Krishna, N. R.; Pritchard, D. G.; Turnbough, C. L. Jr. *J. Biol. Chem.* **2004**, *279*, 30945–30953.



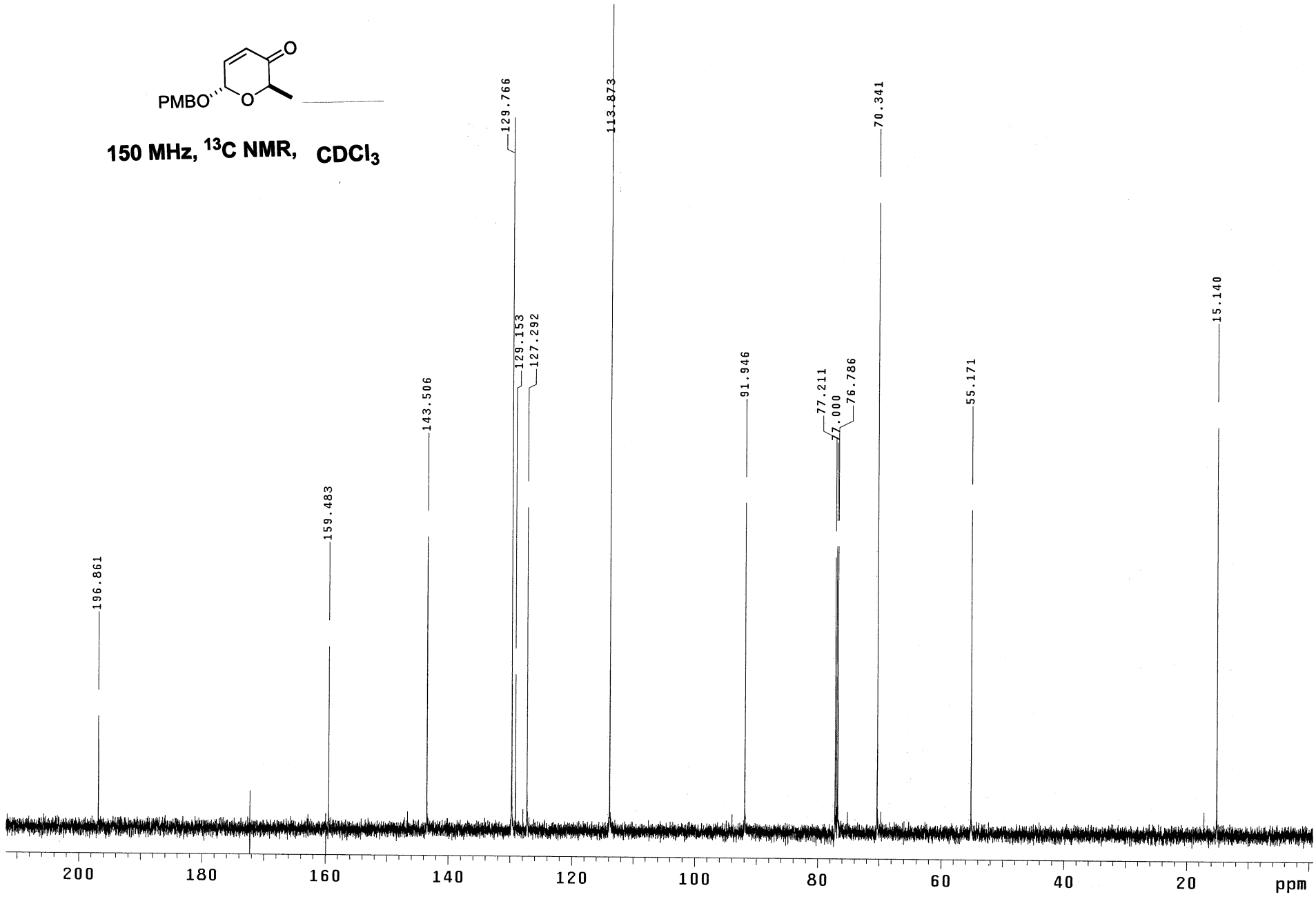
600 MHz, ^{1}H NMR, $CDCl_3$

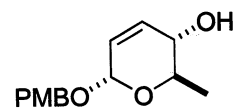


150 MHz, ^{13}C NMR, $CDCl_3$

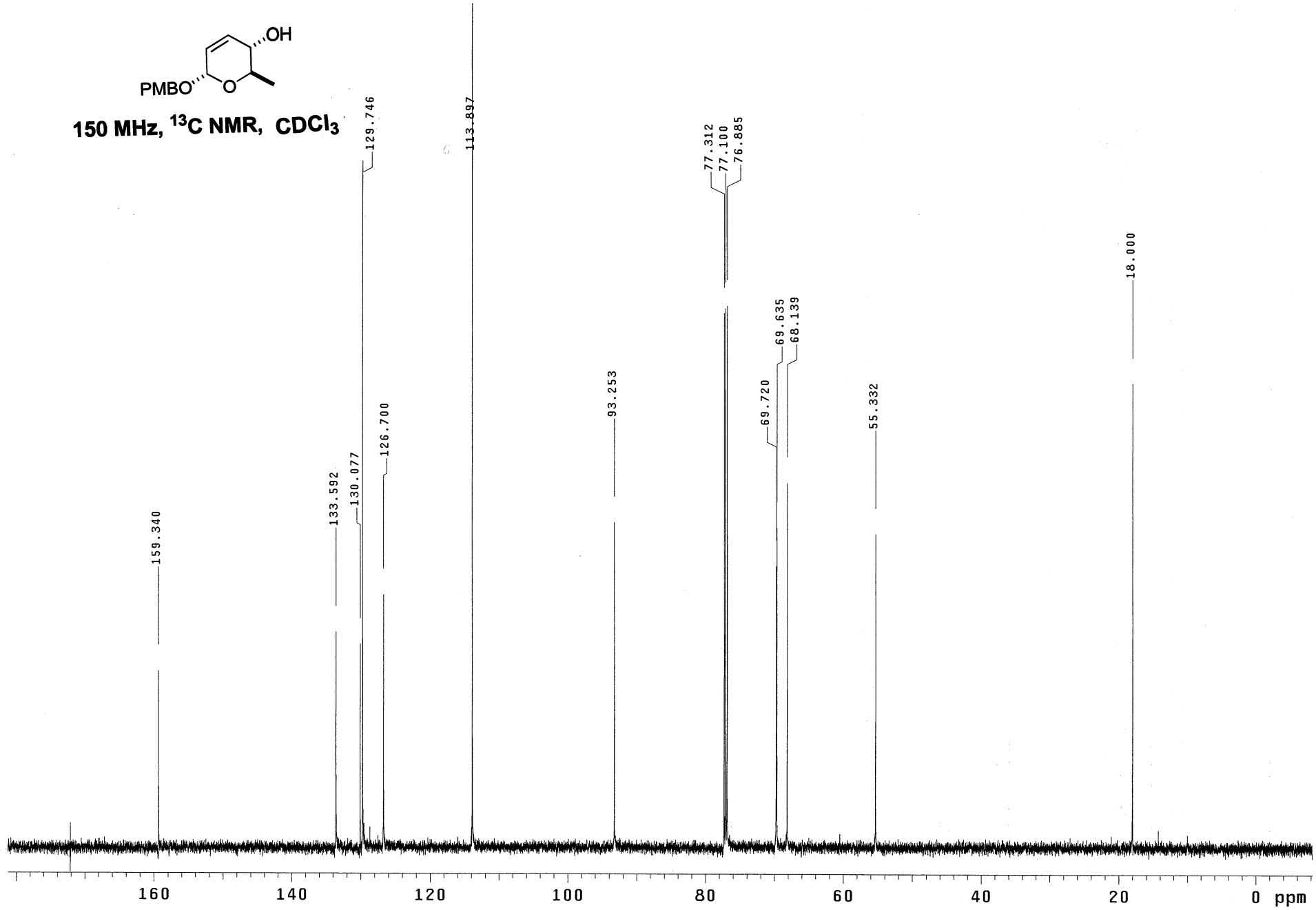


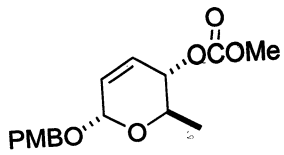
600 MHz, ^{1}H NMR, $CDCl_3$


PMBO
O
O
150 MHz, ^{13}C NMR, $CDCl_3$
196.861
159.483
143.506
129.766
129.153
127.292
113.873
91.946
77.211
77.000
76.786
70.341
55.171
15.140
200
180
160
140
120
100
80
60
40
20
ppm

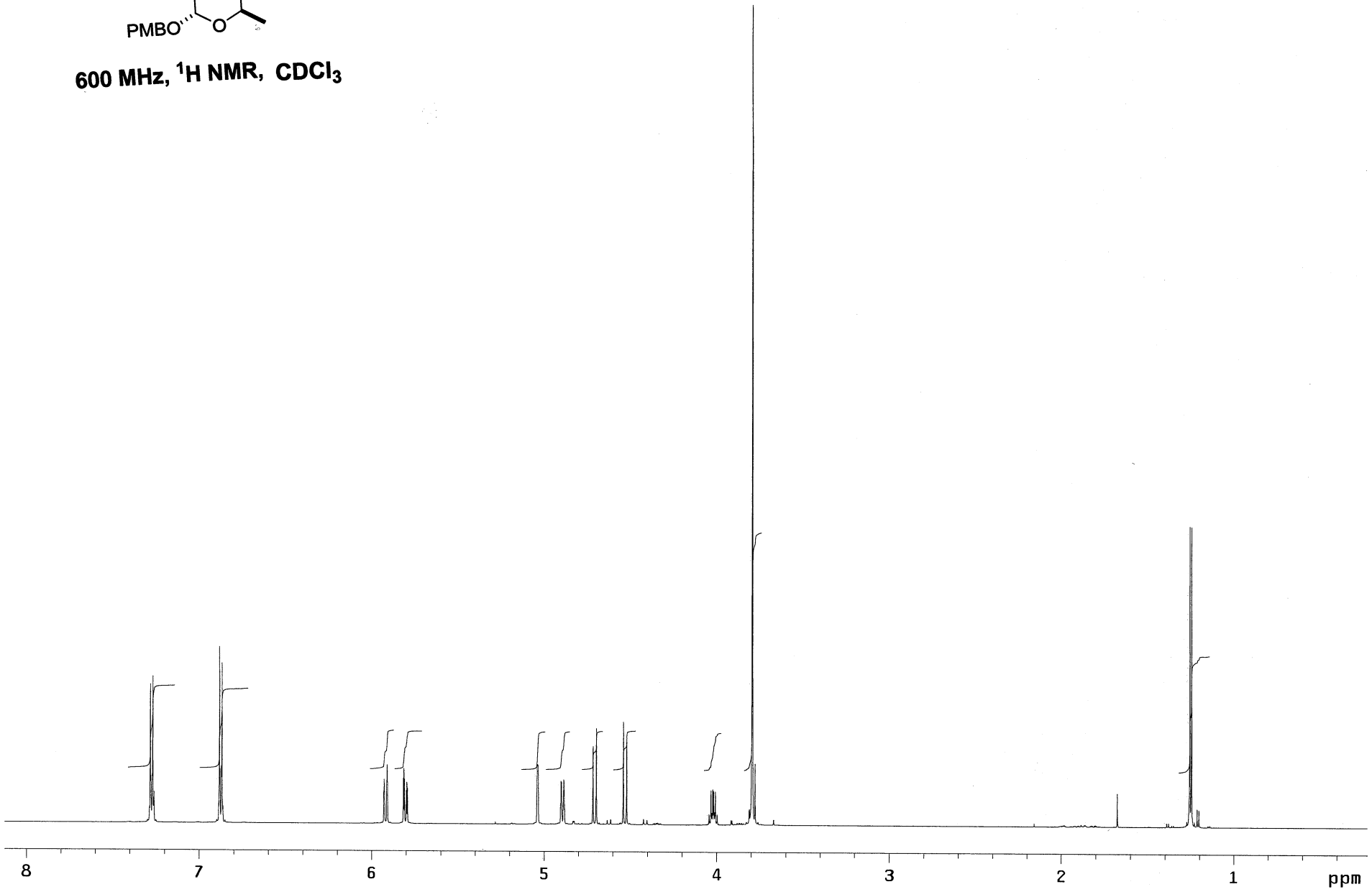


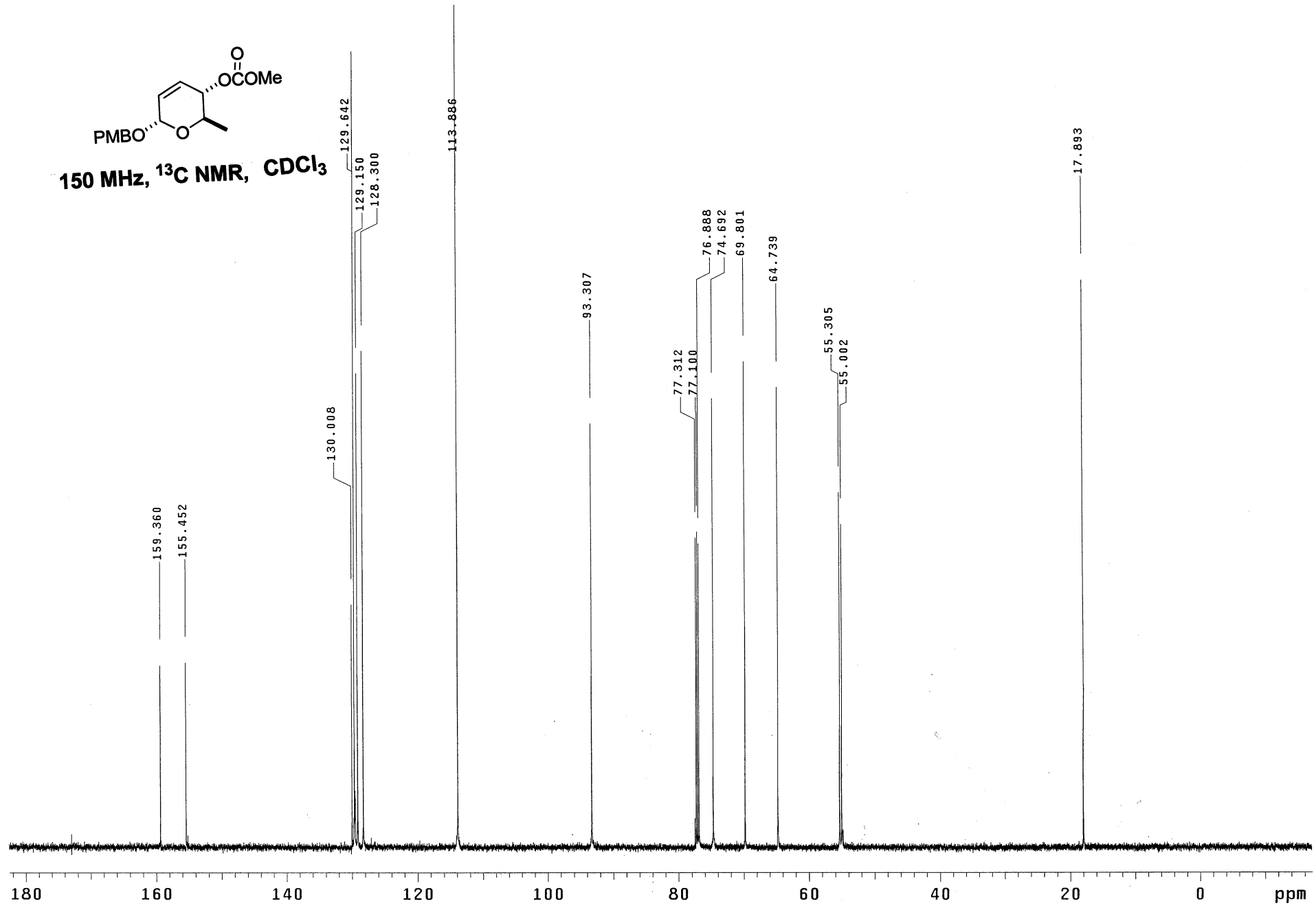
600 MHz, ^{1}H NMR, $CDCl_3$

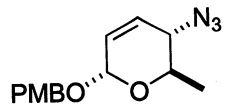

OH
PMBO
O
150 MHz, 13C NMR, CDCl3
159.340
133.592
130.077
129.746
126.700
113.897
93.253
77.312
77.100
76.885
69.720
69.635
68.139
55.332
18.000
160
140
120
100
80
60
40
20
0 ppm



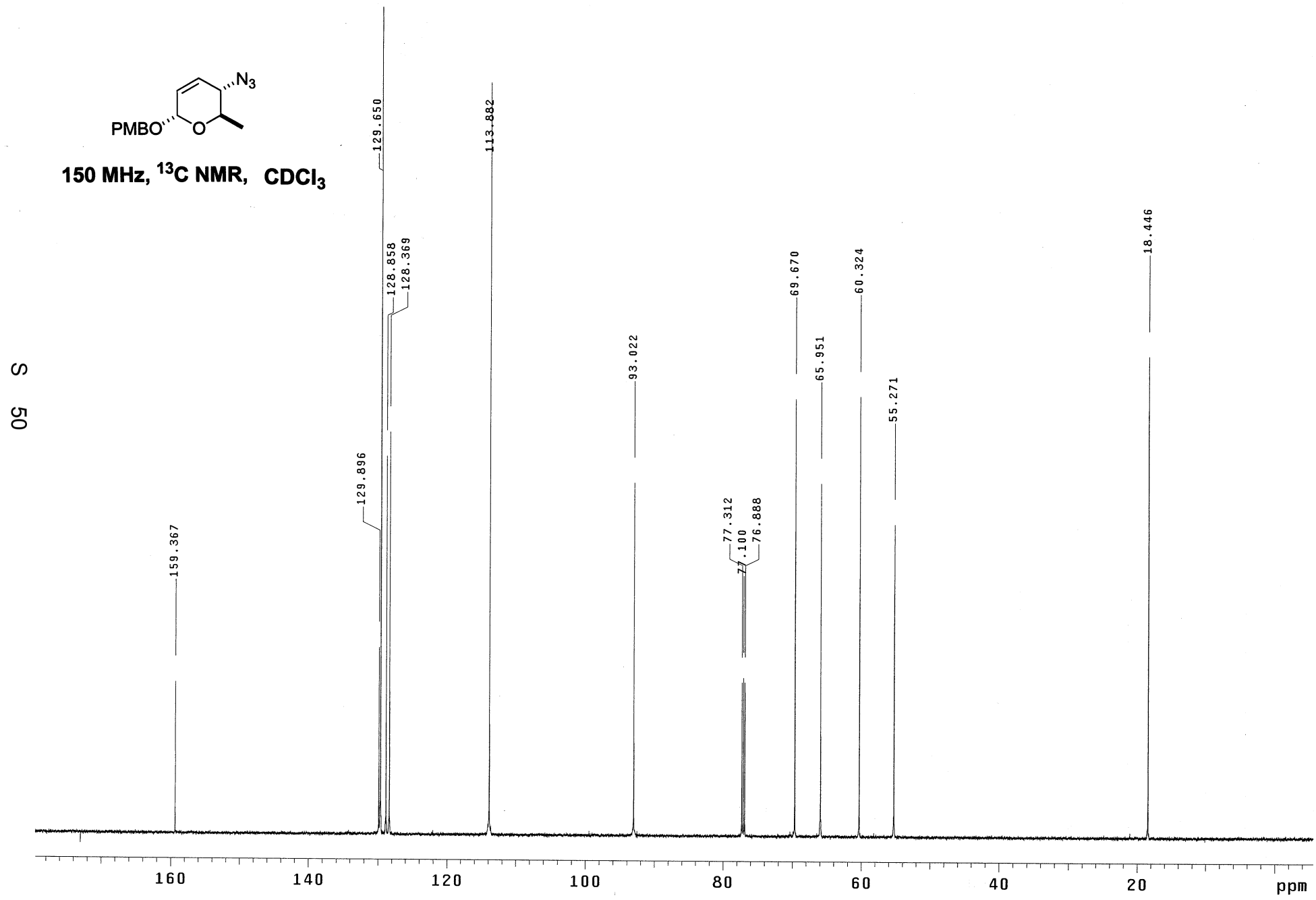
600 MHz, ^{1}H NMR, $CDCl_3$

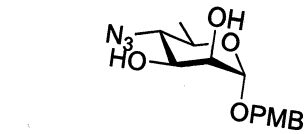



PMBO
OCOMe
O
150 MHz, ^{13}C NMR, $CDCl_3$
159.360
155.452
130.008
129.642
129.150
128.300
113.886
93.307
77.312
77.100
76.888
74.692
69.801
64.739
55.305
55.002
17.893
180
160
140
120
100
80
60
40
20
0
ppm

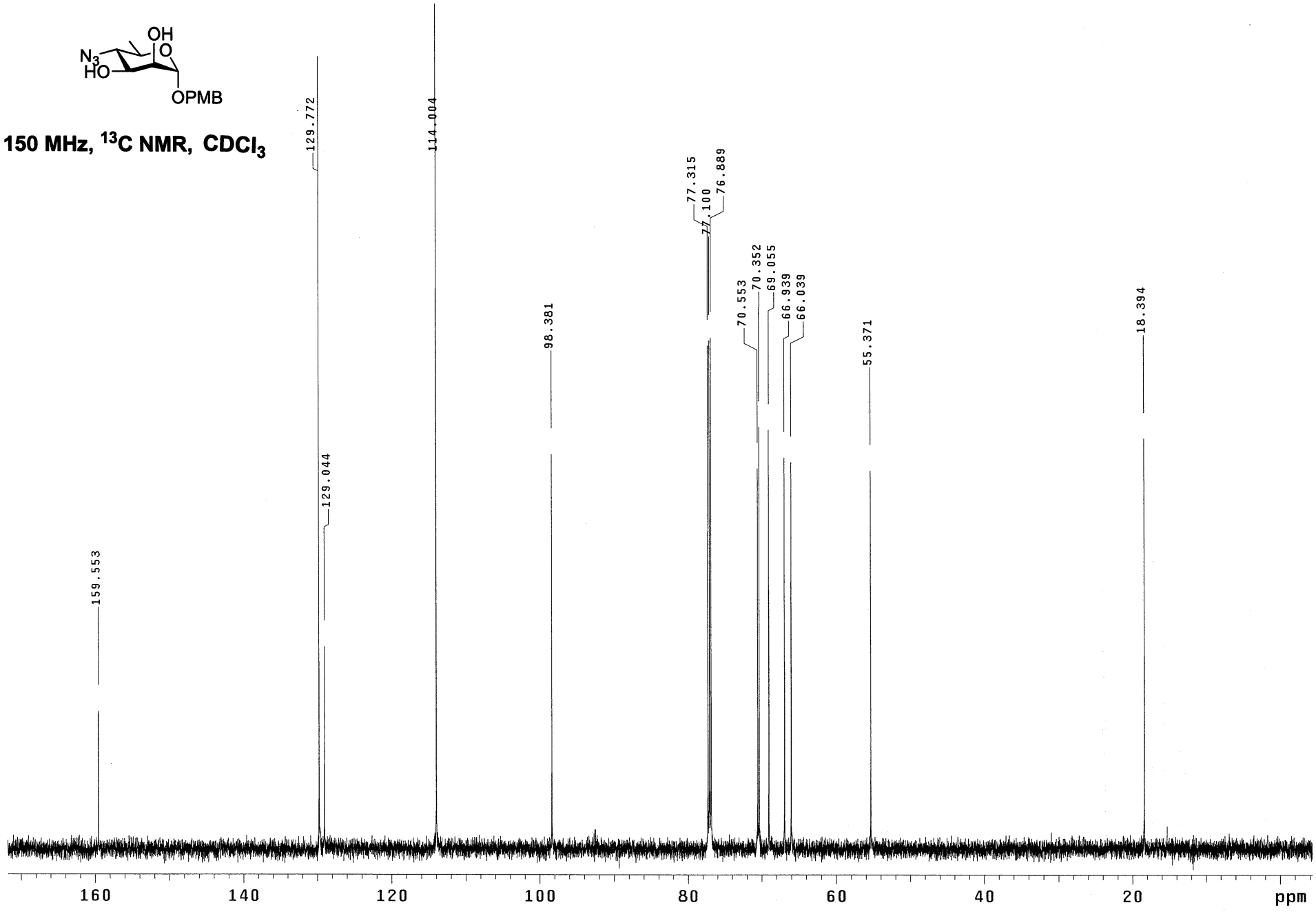


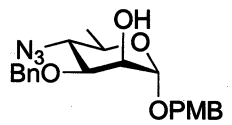
600 MHz, ^{1}H NMR, $CDCl_3$


PMBO
N3
150 MHz, 13C NMR, CDCl3
159.367
129.896
129.650
128.858
128.369
113.882
93.022
77.312
77.100
76.888
69.670
65.951
60.324
55.271
18.446
160
140
120
100
80
60
40
20
ppm

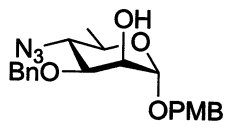


600 MHz, ^{1}H NMR, $CDCl_3$

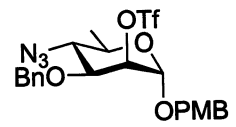

OH
O
N3
HO
OPMB
150 MHz, 13C NMR, CDCl3
159.553
129.772
129.044
114.004
98.381
77.315
77.100
76.889
70.553
70.352
69.055
66.939
66.039
55.371
18.394
160
140
120
100
80
60
40
20
ppm



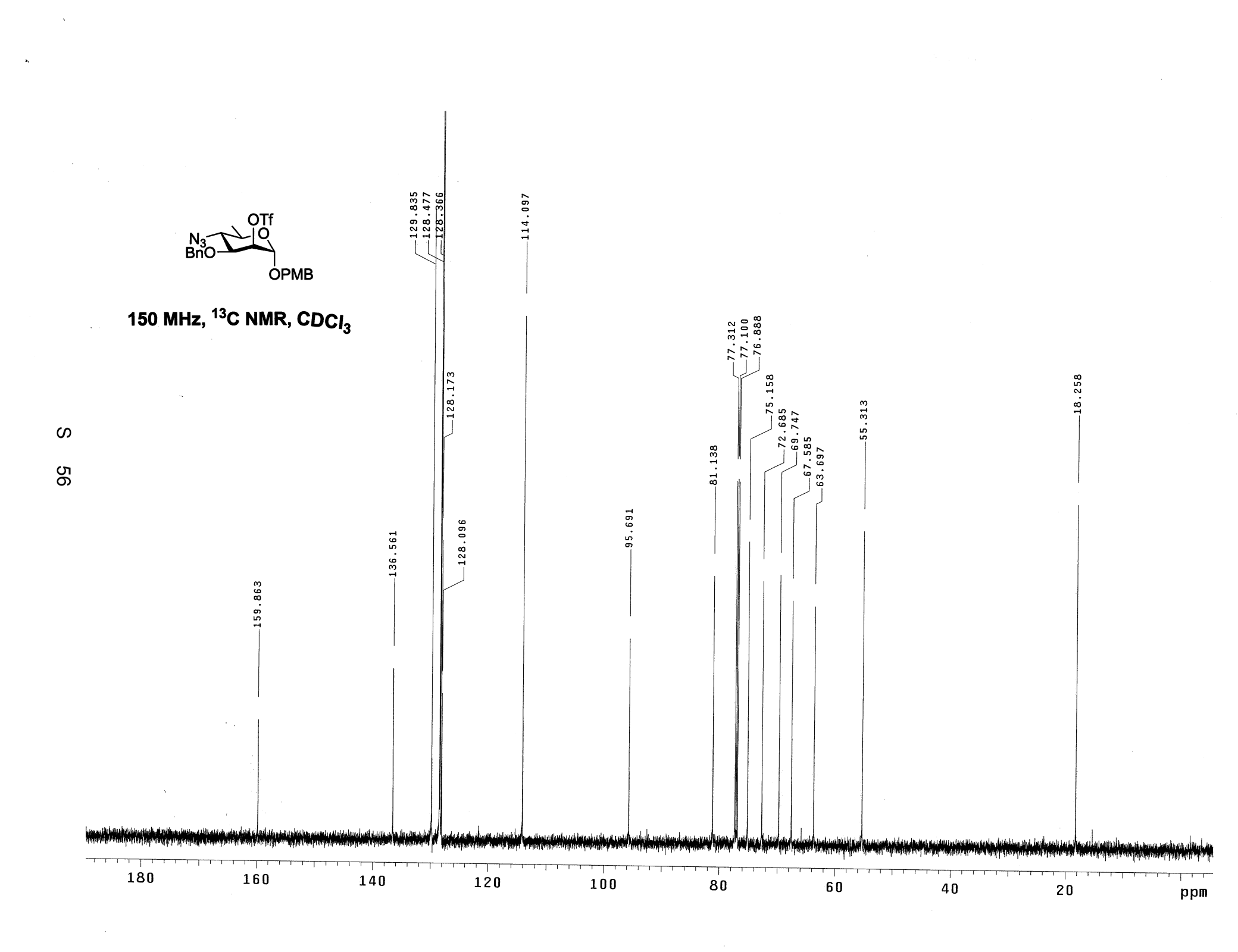
600 MHz, ^{1}H NMR, $CDCl_3$

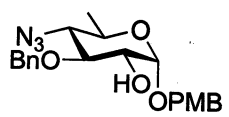


150 MHz, ^{13}C NMR, $CDCl_3$

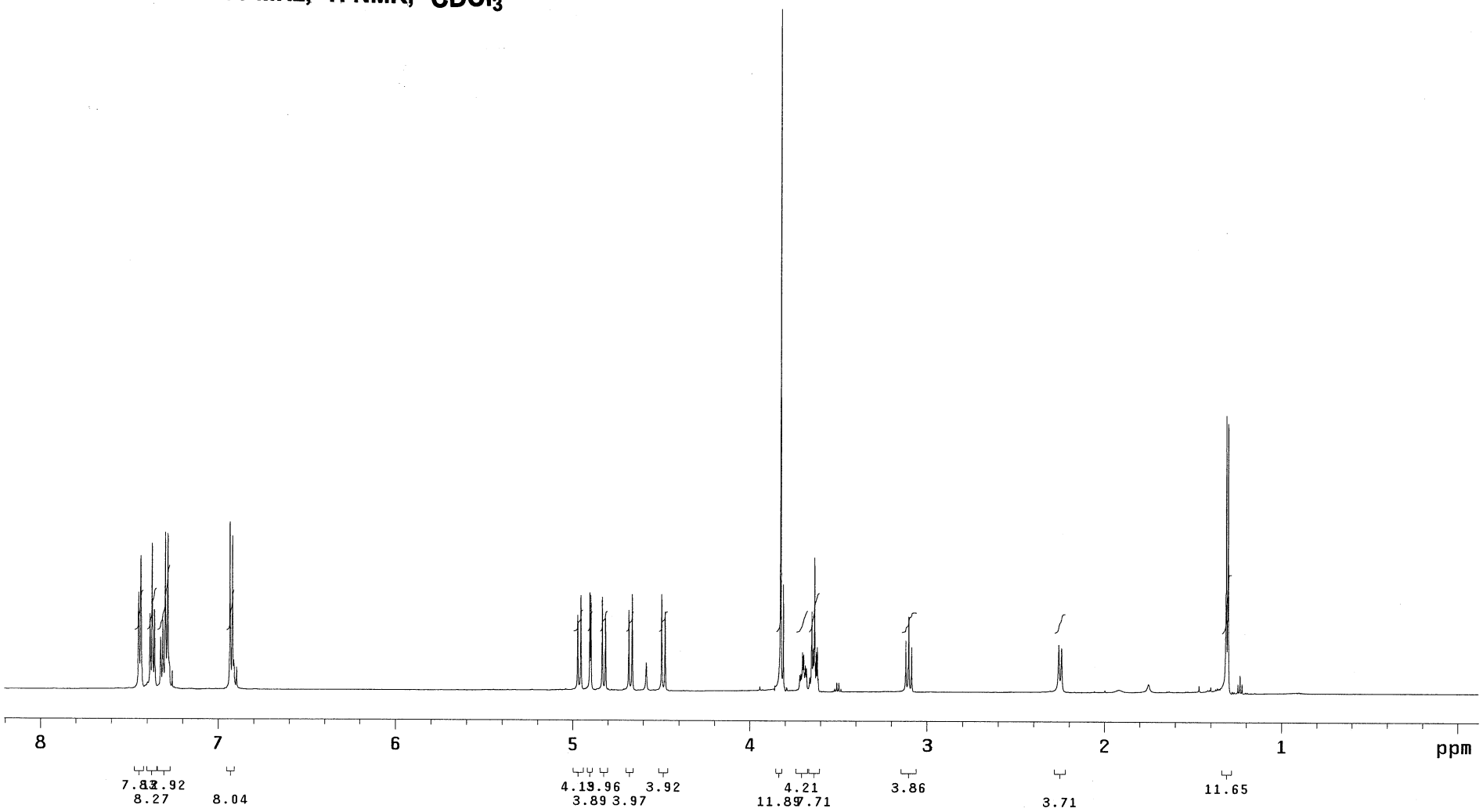


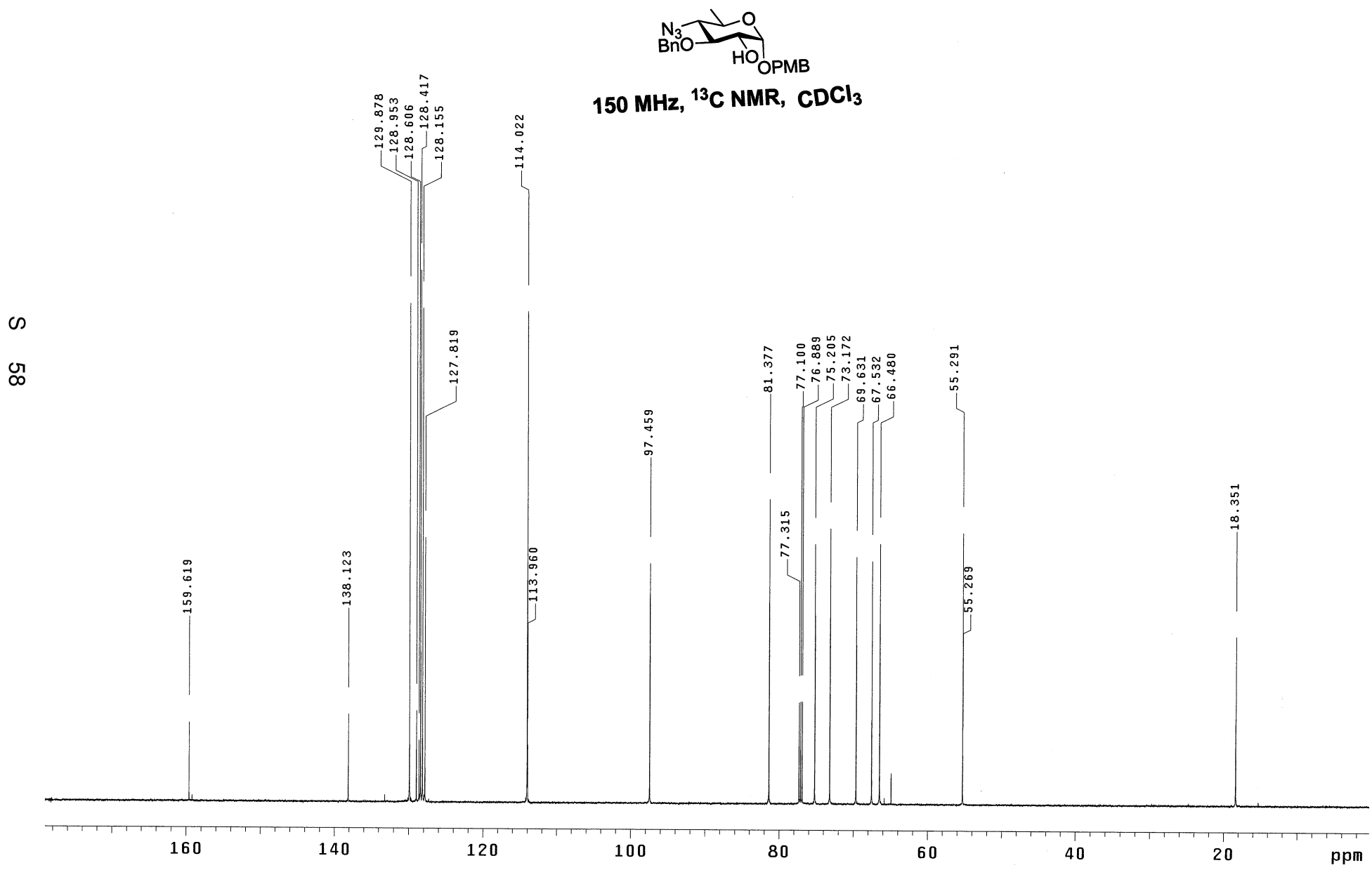
600 MHz, ^{1}H NMR, $CDCl_3$

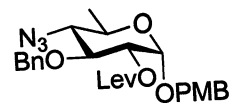

OTf
O
N3
BnO
OPMB
150 MHz, 13C NMR, CDCl3
129.835
128.477
128.366
114.097
128.173
128.096
159.863
136.561
95.691
81.138
77.312
77.100
76.888
75.158
72.685
69.747
67.585
63.697
55.313
18.258
180
160
140
120
100
80
60
40
20
ppm



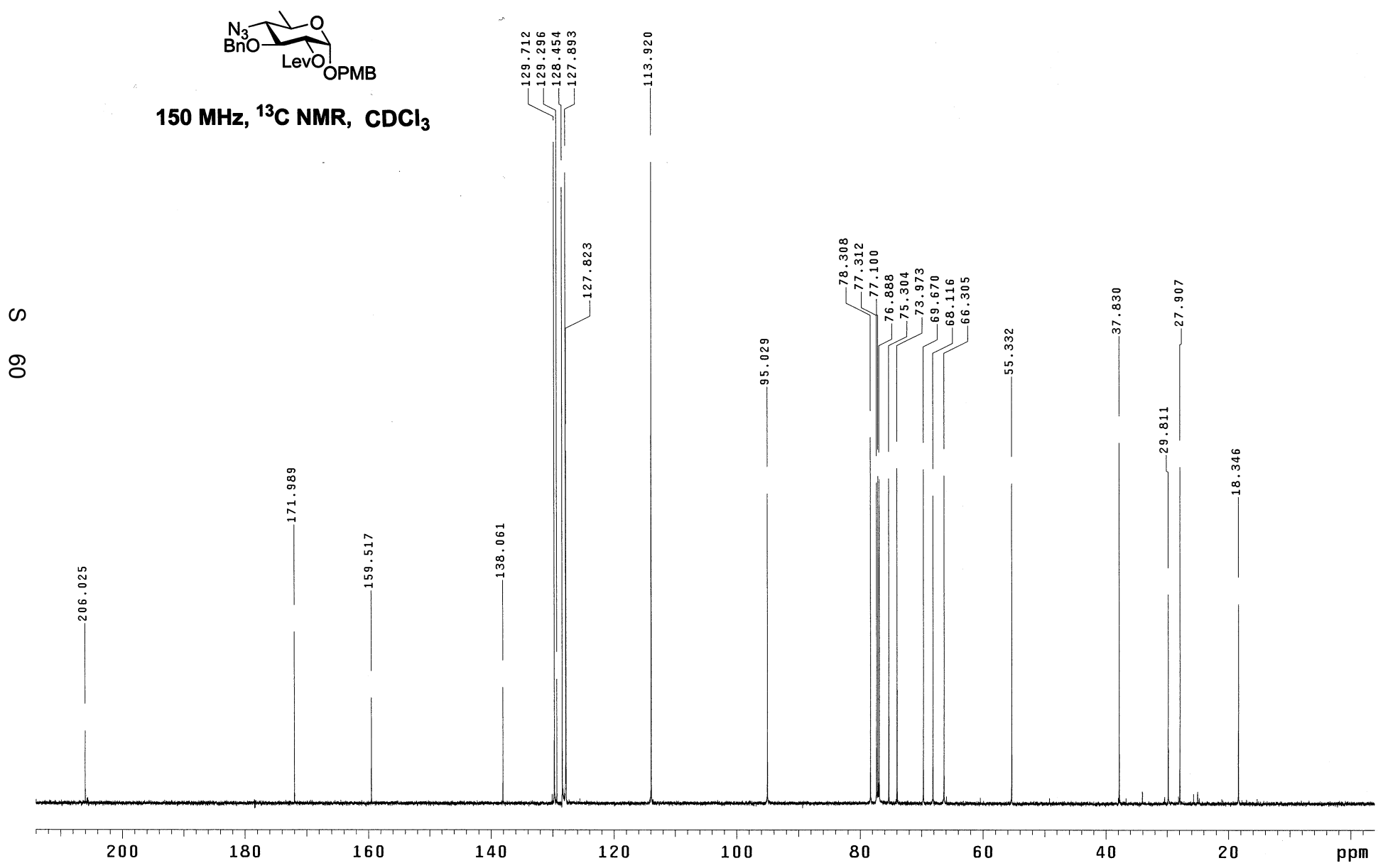
600 MHz, ^{1}H NMR, $CDCl_3$




N3
BnO
O
HO
OPMB
150 MHz, 13C NMR, CDCl3
129.878
128.953
128.606
128.417
128.155
127.819
114.022
113.960
159.619
138.123
97.459
81.377
77.315
77.100
76.889
75.205
73.172
69.631
67.532
66.480
55.291
55.269
18.351
160
140
120
100
80
60
40
20
ppm

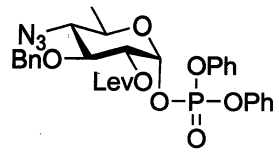


600 MHz, ^{1}H NMR, $CDCl_3$

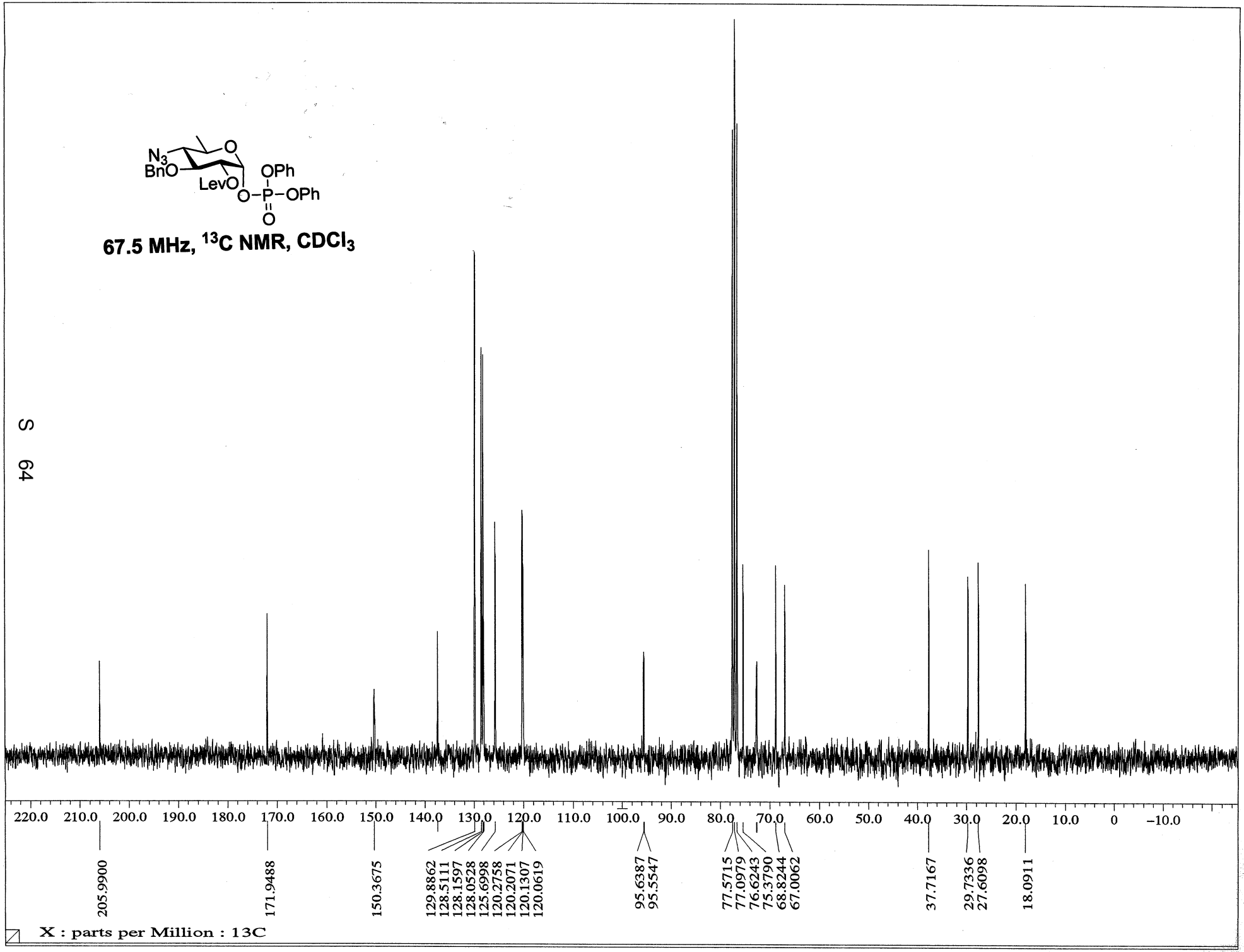

N3
BnO
O
LevO
OPMB
150 MHz, 13C NMR, CDCl3
S 60
206.025
171.989
159.517
138.061
129.712
129.296
128.454
127.893
127.823
113.920
95.029
78.308
77.312
77.100
76.888
75.304
73.973
69.670
68.116
66.305
55.332
37.830
29.811
27.907
18.346
200
180
160
140
120
100
80
60
40
20
ppm

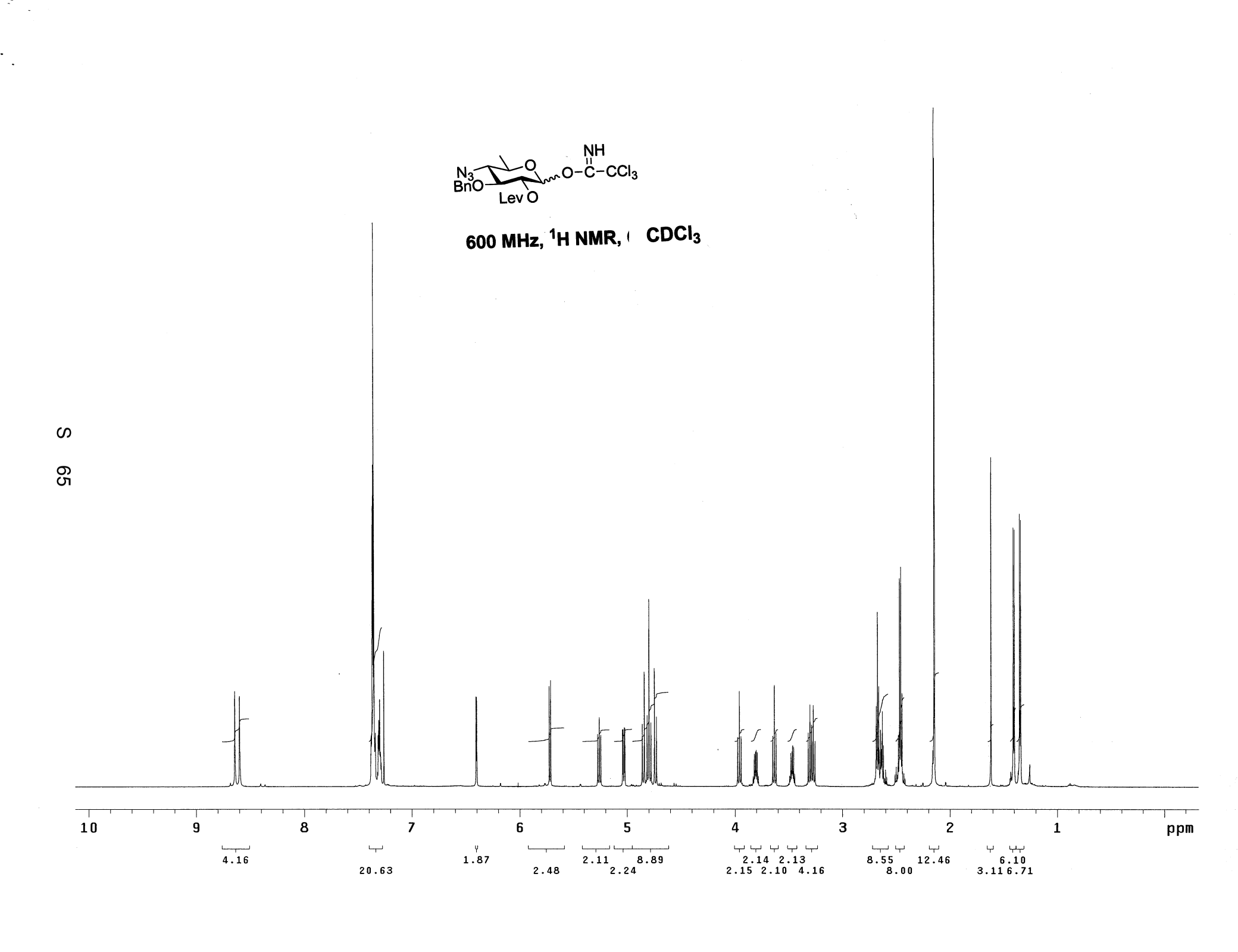
600 MHz, ^{1}H NMR, $CDCl_3$

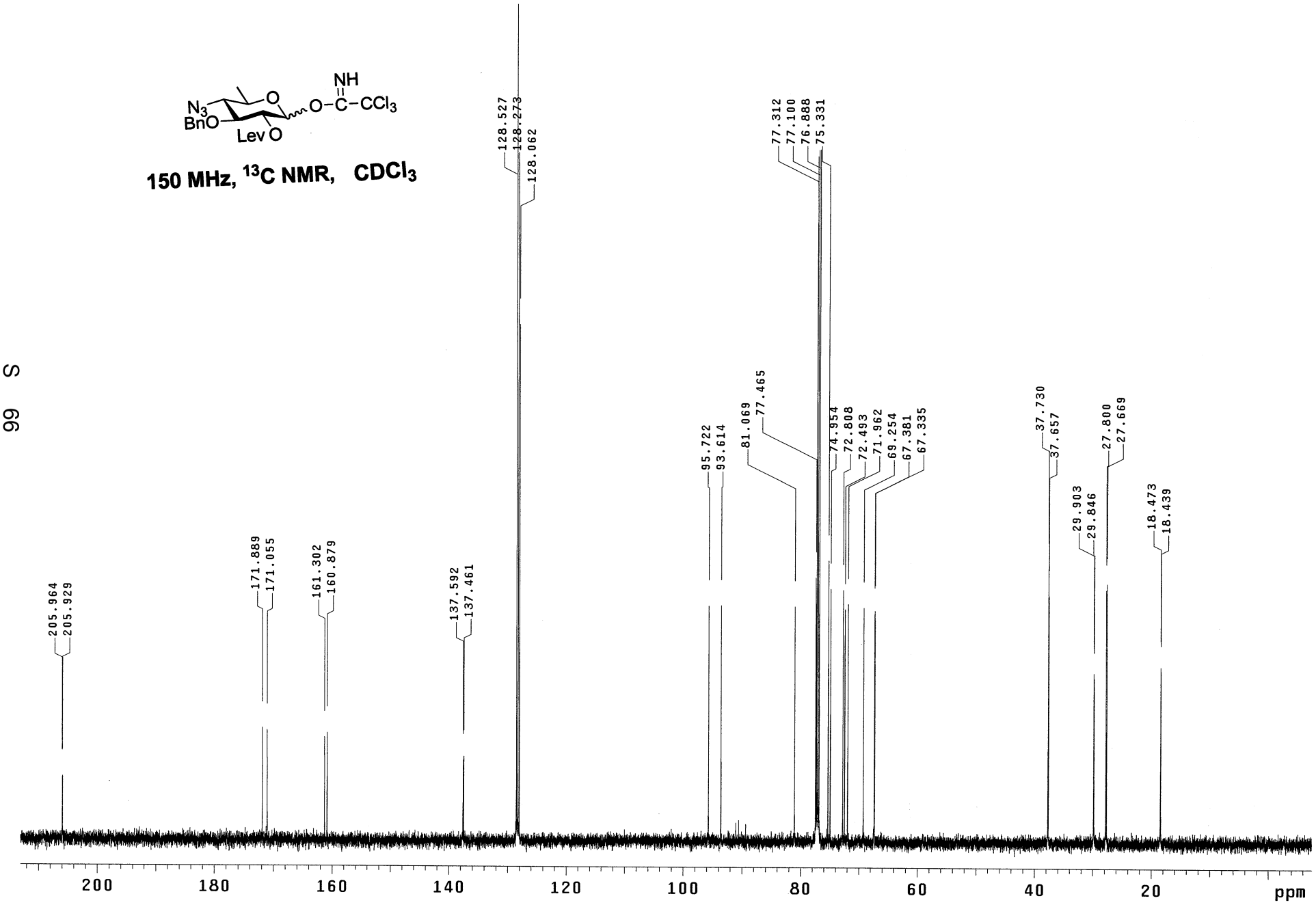
150 MHz, 13C NMR, CDCl3
OH
OLev
N3
BnO
207.156
172.128
138.061
128.550
128.500
128.162
128.054
127.962
127.893
95.514
90.091
80.854
77.865
77.315
77.100
76.888
76.423
75.354
75.177
74.458
71.143
68.066
67.801
66.220
38.095
37.910
29.850
28.034
18.443
ppm



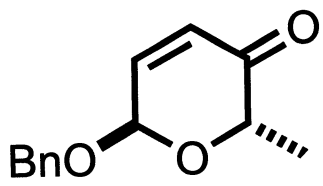
600 MHz, ^{1}H NMR, $CDCl_3$


67.5 MHz, 13C NMR, CDCl3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0
205.9900
171.9488
150.3675
129.8862
128.5111
128.1597
128.0528
125.6998
120.2758
120.2071
120.1307
120.0619
95.6387
95.5547
77.5715
77.0979
76.6243
75.3790
68.8244
67.0062
37.7167
29.7336
27.6098
18.0911
X : parts per Million : 13C


NH
N3
O
O–C–CCl3
BnO
Lev O
600 MHz, 1H NMR, (CDCl3
10
9
8
7
6
5
4
3
2
1
ppm
4.16
20.63
1.87
2.48
2.11
8.89
2.24
2.14
2.13
2.15
2.10
4.16
8.55
12.46
8.00
6.10
3.11
6.71

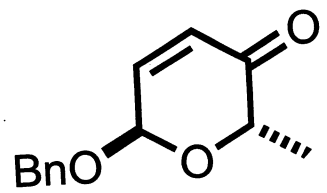

NH
N3
BnO
O
O–C–CCl3
Lev O
150 MHz, 13C NMR, CDCl3
205.964
205.929
171.889
171.055
161.302
160.879
137.592
137.461
128.527
128.273
128.062
95.722
93.614
81.069
77.465
77.312
77.100
76.888
75.331
74.954
72.808
72.493
71.962
69.254
67.381
67.335
37.730
37.657
29.903
29.846
27.800
27.669
18.473
18.439
200
180
160
140
120
100
80
60
40
20
ppm

99 S



270 MHz, ^{1}H NMR, $CDCl_3$

S 67



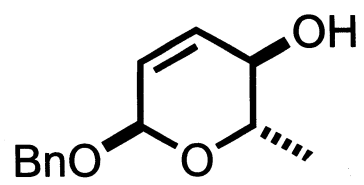
67.5 MHz, ^{13}C NMR, $CDCl_3$

89 S

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0

197.0386
143.4634
137.1686
128.6124
128.1923
128.1464
127.5047
92.3711
77.5735
77.0999
76.6263
70.8432
70.4842
15.2512

X : parts per Million : 13C



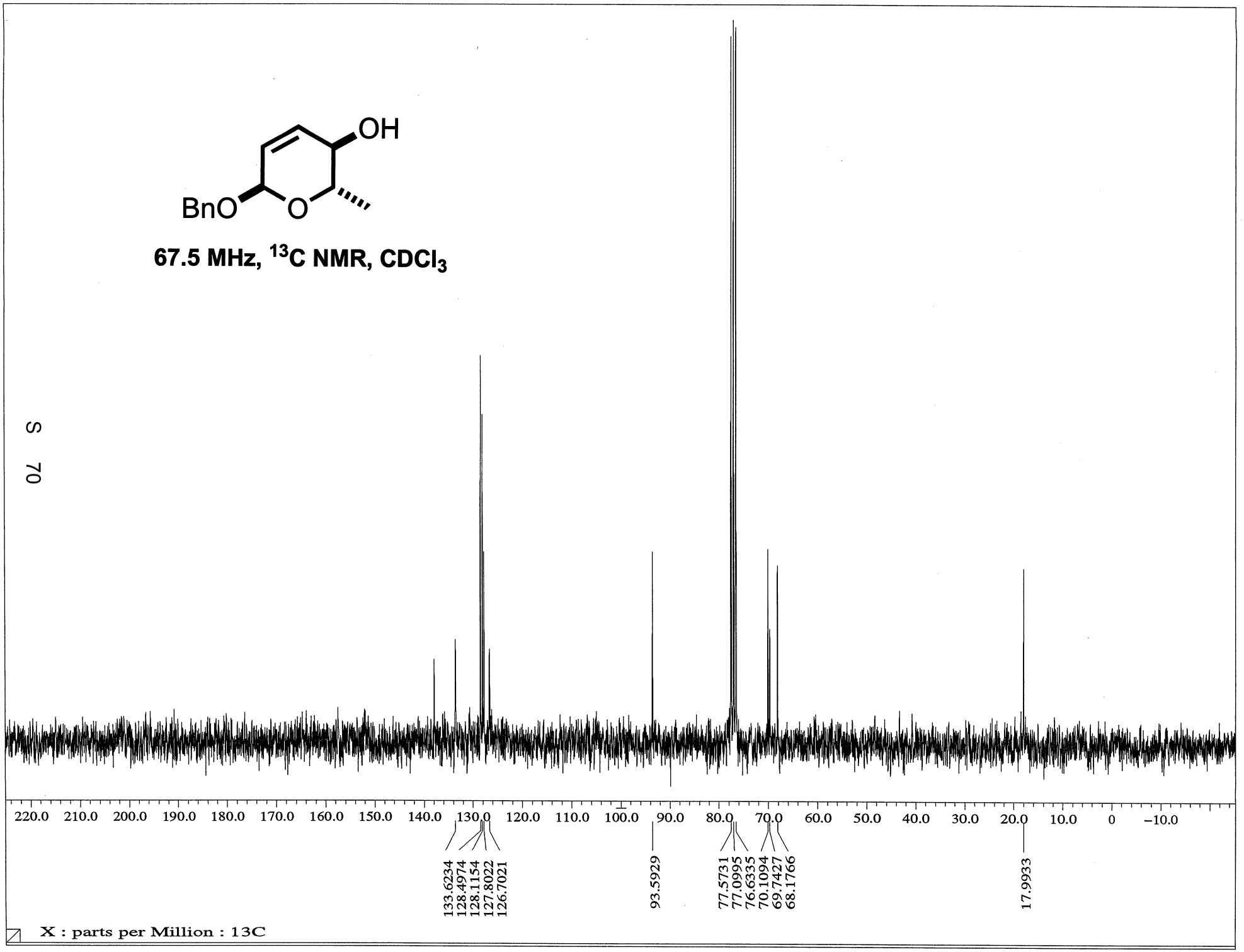
270 MHz, ^{1}H NMR, $CDCl_3$

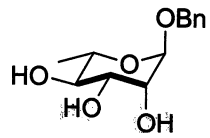
69 S

12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 −1.0 −2.0

7.3653 7.3497 7.3204 5.9507 5.9131 5.7849 5.7757 5.0373 4.8037 4.7597 4.6113 4.5673 3.8444 3.7757 3.7528 1.8306 1.7903 1.7592 1.7015 1.3038 1.2819

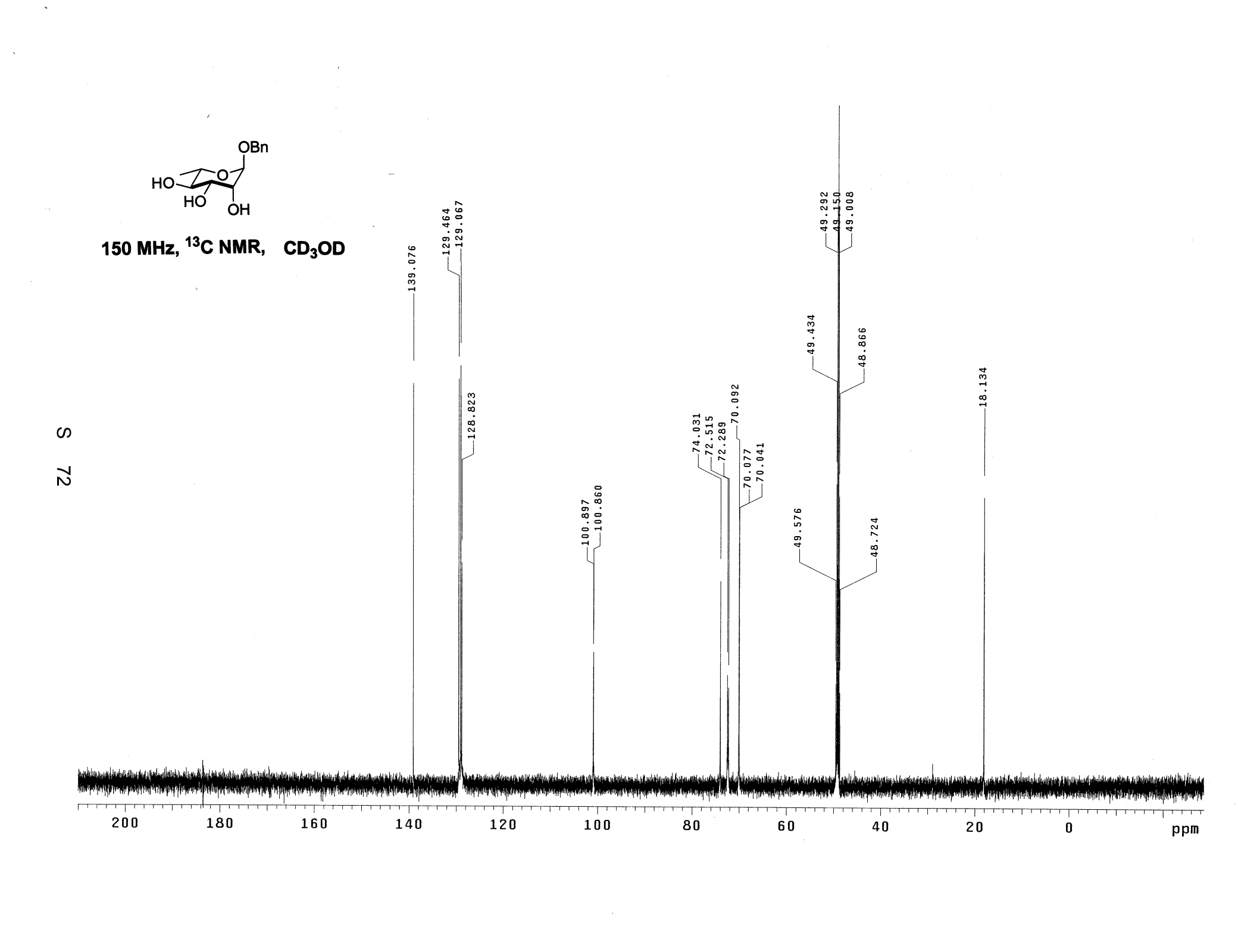
X : parts per Million : 1H

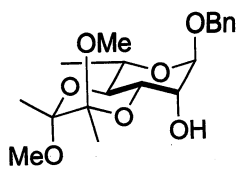

OH
BnO
O
67.5 MHz, 13C NMR, CDCl3
S 70
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0
133.6234
128.4974
128.1154
127.8022
126.7021
93.5929
77.5731
77.0995
76.6335
70.1094
69.7427
68.1766
17.9933
X : parts per Million : 13C



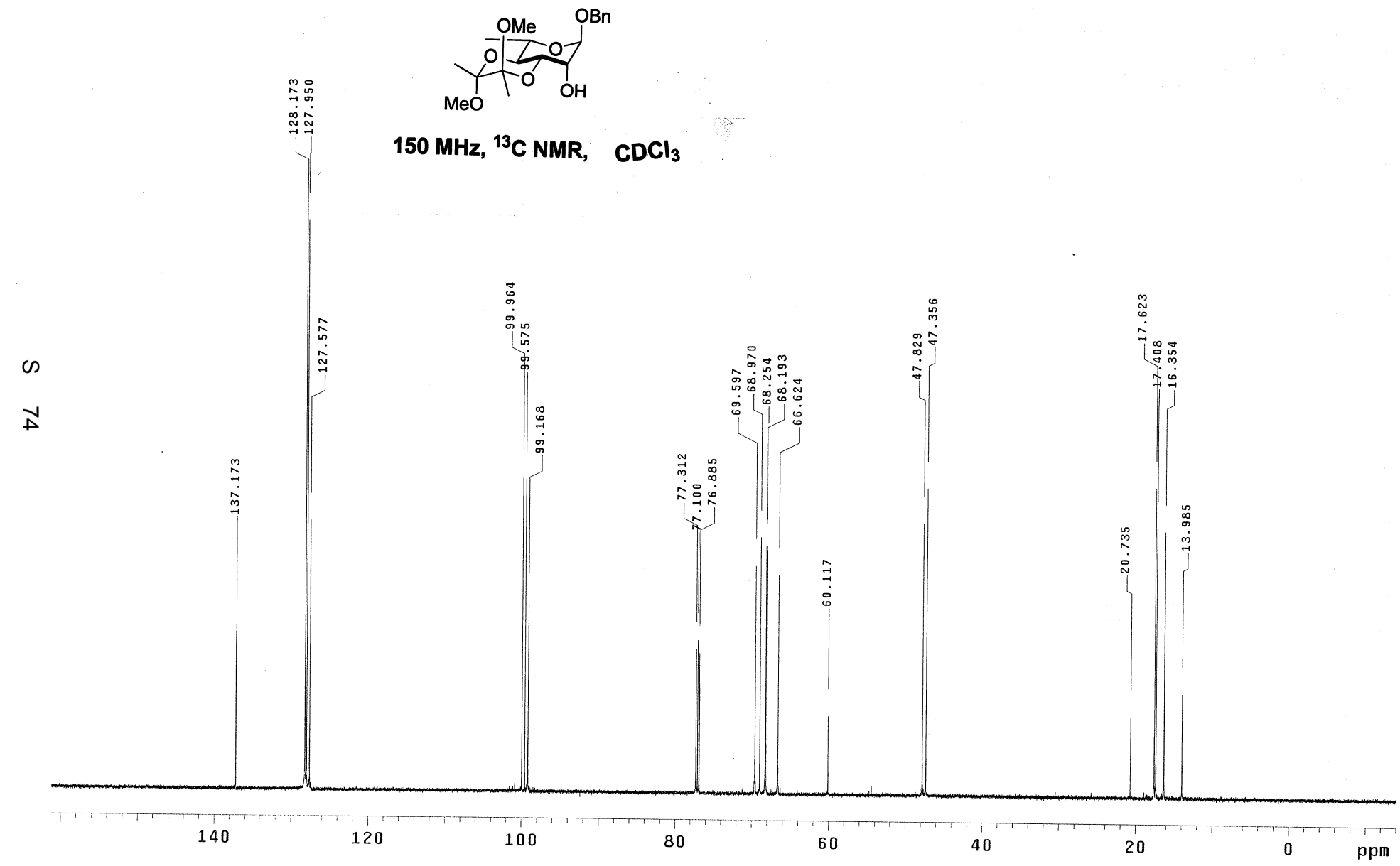
600 MHz, ^{1}H NMR, CD_3OD

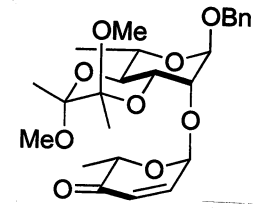
S 71


OBn
HO
HO
O
OH
150 MHz, 13C NMR, CD3OD
139.076
129.464
129.067
128.823
100.897
100.860
74.031
72.515
72.289
70.092
70.077
70.041
49.576
49.434
49.292
49.150
49.008
48.866
48.724
18.134
200
180
160
140
120
100
80
60
40
20
0
ppm



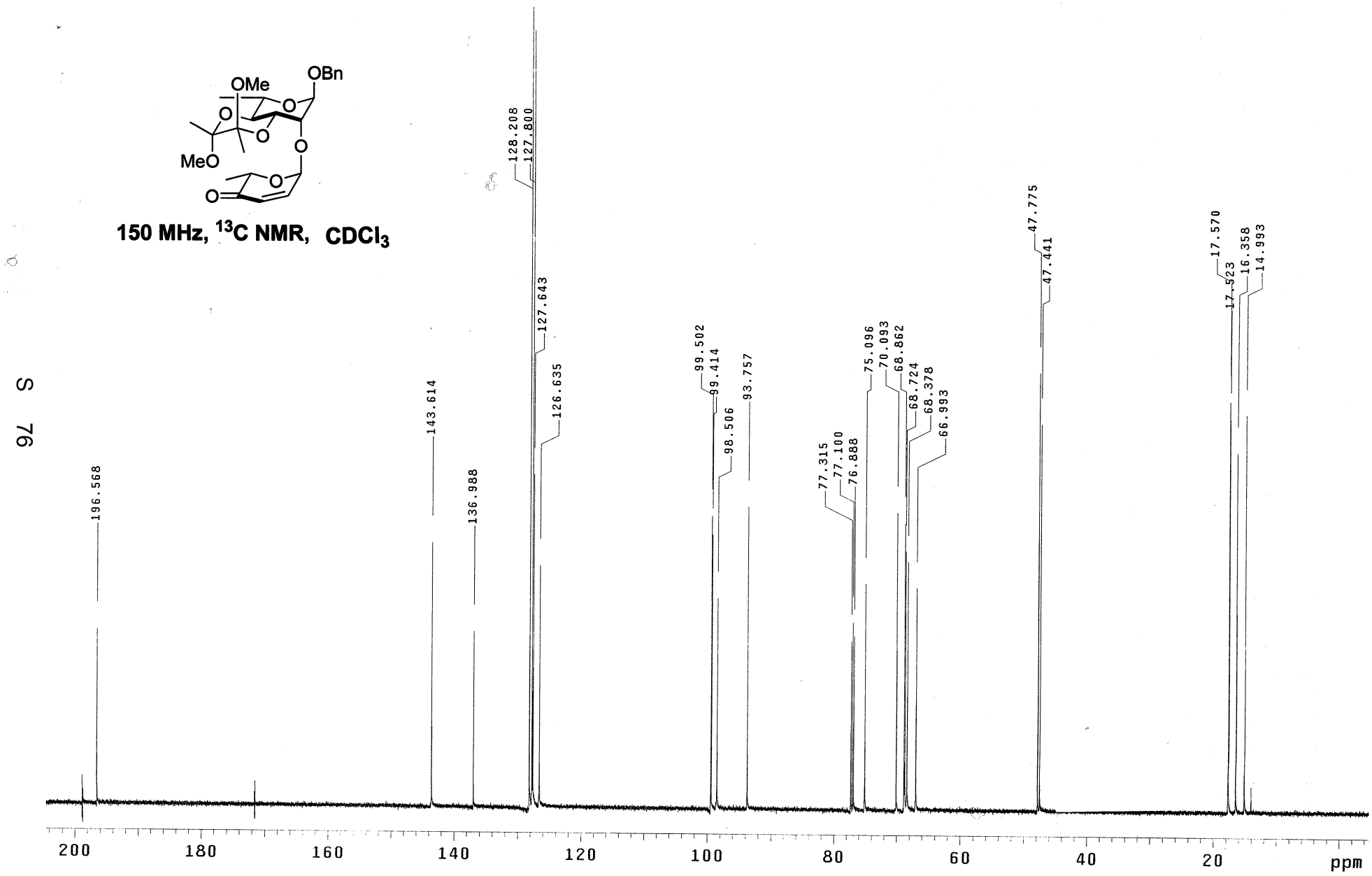
600 MHz, ^{1}H NMR, $CDCl_3$

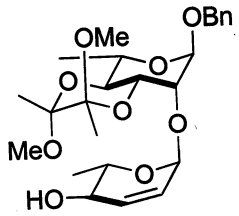

OMe
OBn
O
O
O
OH
MeO
150 MHz, 13C NMR, CDCl3
128.173
127.950
127.577
137.173
99.964
99.575
99.168
77.312
77.100
76.885
69.597
68.970
68.254
68.193
66.624
60.117
47.829
47.356
20.735
17.623
17.408
16.354
13.985
140
120
100
80
60
40
20
0
ppm



600 MHz, ^{1}H NMR, $CDCl_3$

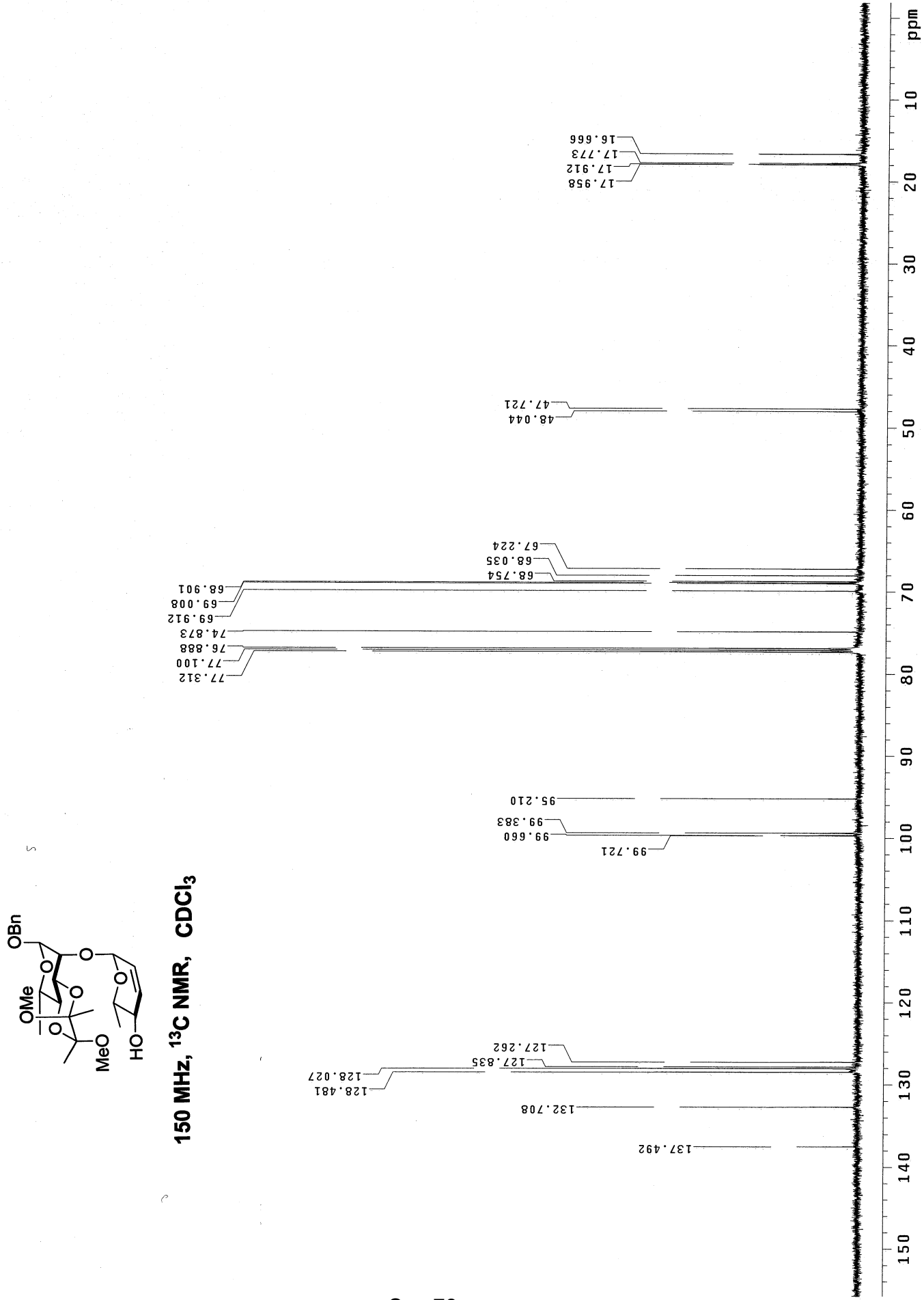
S 75

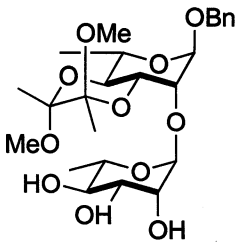

OMe
OBn
MeO
O
150 MHz, ^{13}C NMR, $CDCl_3$
196.568
143.614
136.988
128.208
127.800
127.643
126.635
99.502
99.414
98.506
93.757
77.315
77.100
76.888
75.096
70.093
68.862
68.724
68.378
66.993
47.775
47.441
17.570
17.523
16.358
14.993
200
180
160
140
120
100
80
60
40
20
ppm



600 MHz, ^{1}H NMR, $CDCl_3$

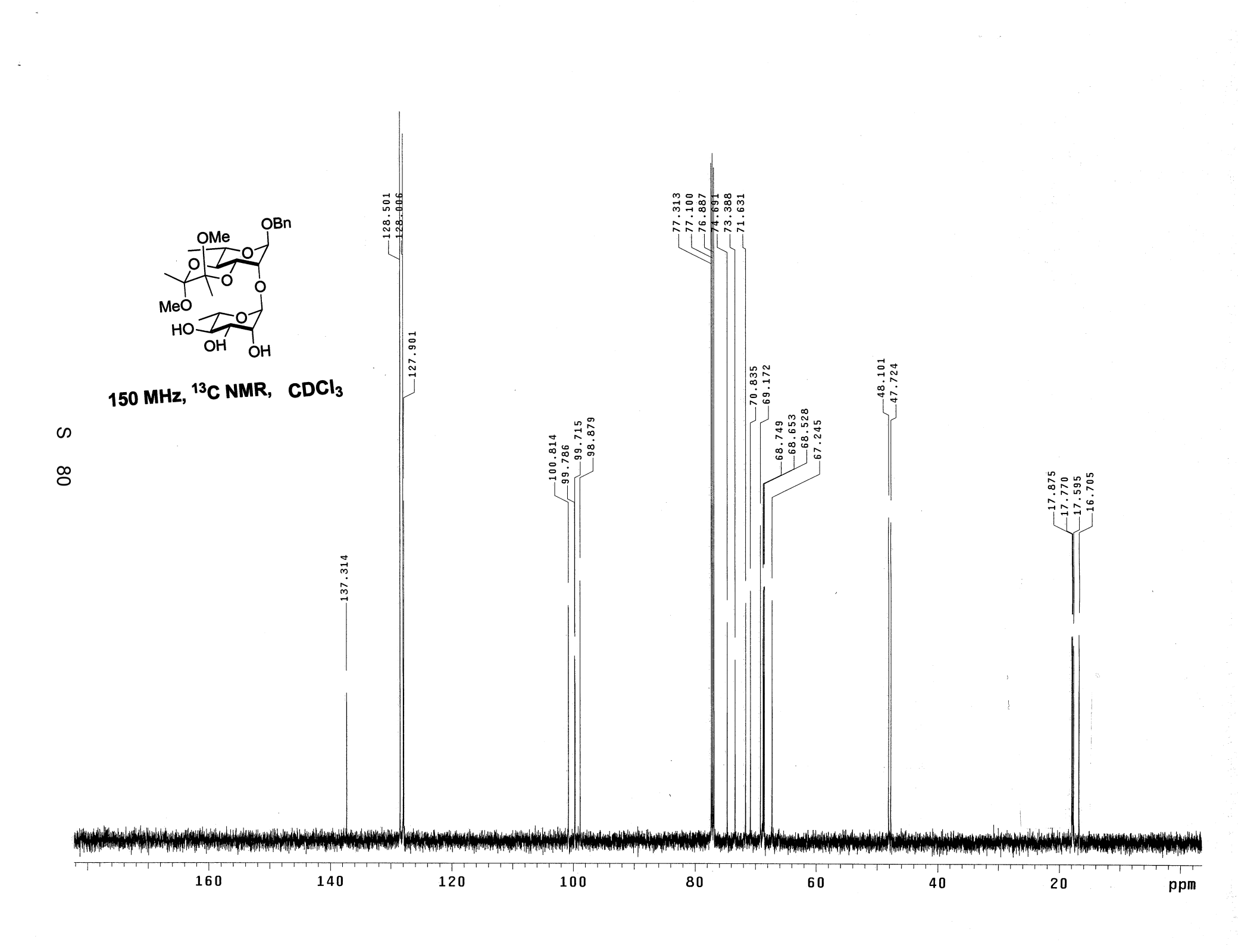
S 77

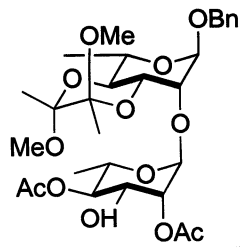

OBn
OMe
MeO
HO
150 MHz, 13C NMR, CDCl3
17.958
17.912
17.773
16.666
48.044
47.721
67.224
68.035
68.754
68.901
69.008
69.912
74.873
76.888
77.100
77.312
95.210
99.383
99.660
99.721
127.262
127.835
128.027
128.481
132.708
137.492
ppm



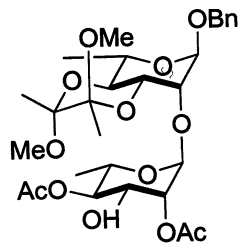
600 MHz, ^{1}H NMR, $CDCl_3$

S 79

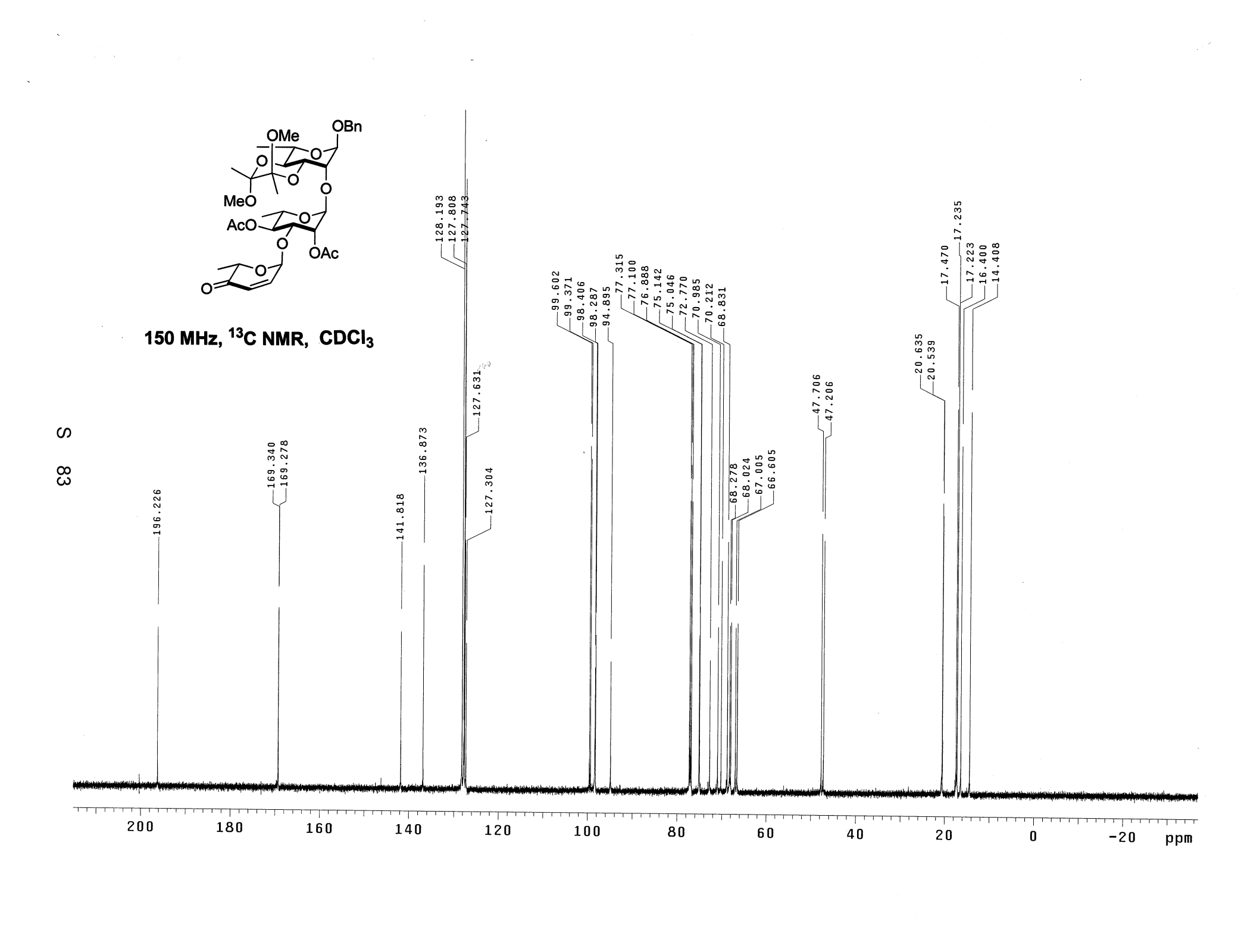

OBn
OMe
O
O
O
O
MeO
O
HO
OH
OH
150 MHz, 13C NMR, CDCl3
S 80
128.501
128.006
127.901
137.314
100.814
99.786
99.715
98.879
77.313
77.100
76.887
74.691
73.388
71.631
70.835
69.172
68.749
68.653
68.528
67.245
48.101
47.724
17.875
17.770
17.595
16.705
160
140
120
100
80
60
40
20
ppm

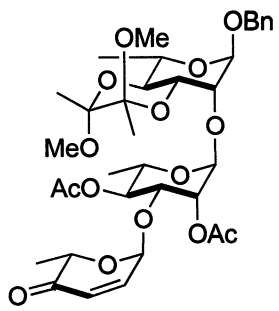


600 MHz, ^{1}H NMR, $CDCl_3$

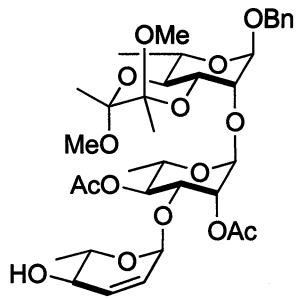


150 MHz, ^{13}C NMR, $CDCl_3$

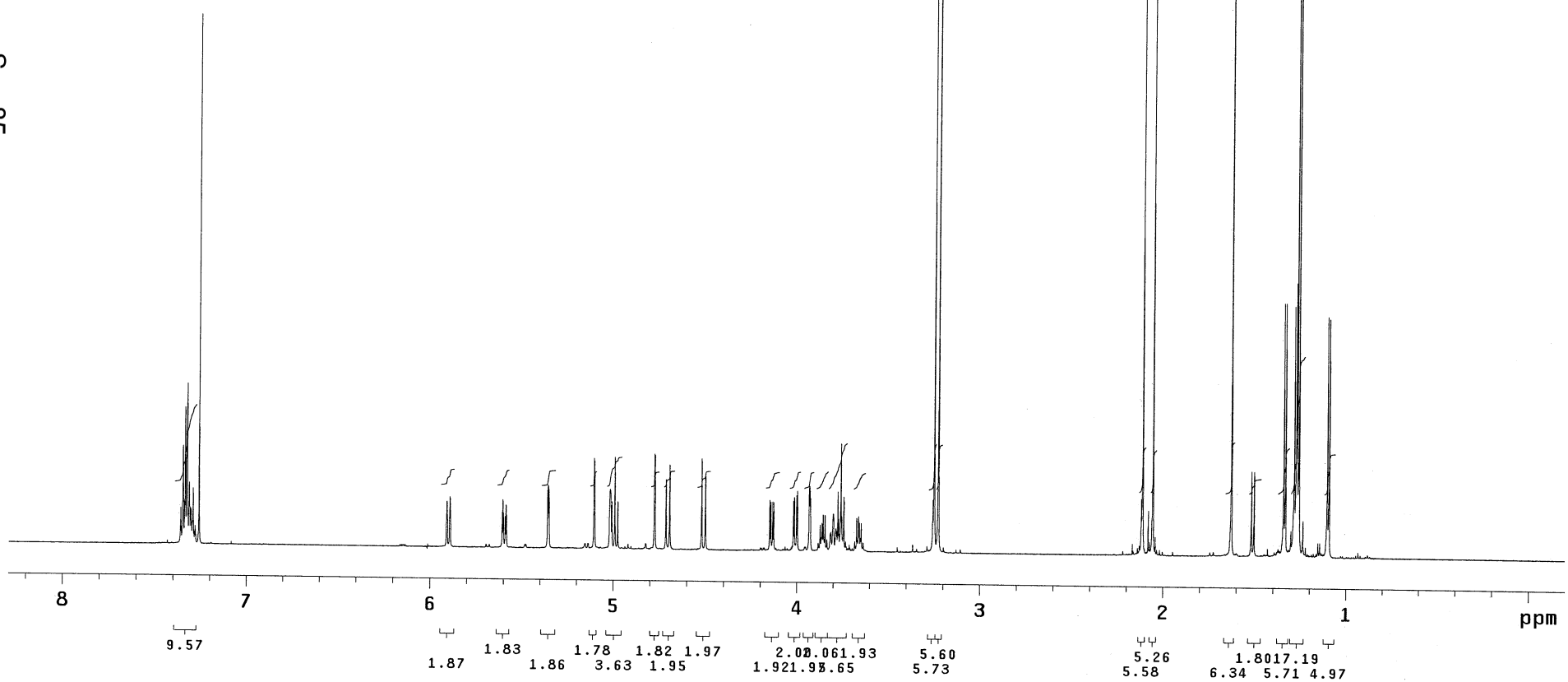

OMe
OBn
MeO
AcO
OAc
O
150 MHz, 13C NMR, CDCl3
196.226
169.340
169.278
141.818
136.873
128.193
127.808
127.743
127.631
127.304
99.602
99.371
98.406
98.287
94.895
77.315
77.100
76.888
75.142
75.046
72.770
70.985
70.212
68.831
68.278
68.024
67.005
66.605
47.706
47.206
20.635
20.539
17.470
17.235
17.223
16.400
14.408
200
180
160
140
120
100
80
60
40
20
0
-20
ppm

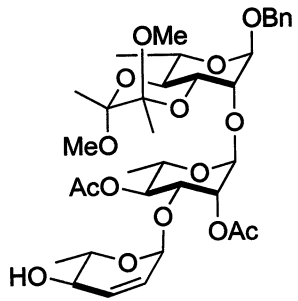


600 MHz, ^{1}H NMR, $CDCl_3$

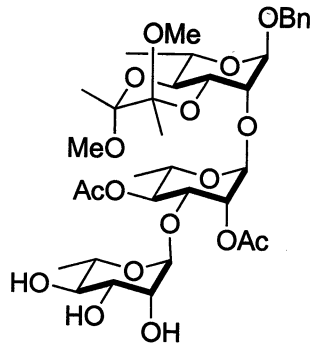


600 MHz, ^{1}H NMR, $CDCl_3$





150 MHz, ^{13}C NMR, $CDCl_3$

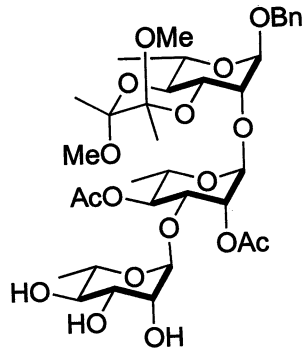


600 MHz, ^{1}H NMR, CD_3OD

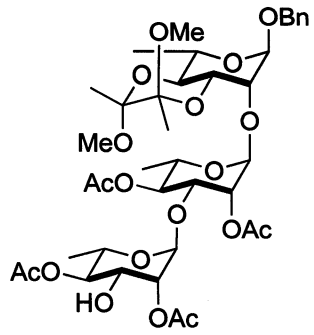
S 87

1.225

8 7 6 5 4 3 2 1 ppm

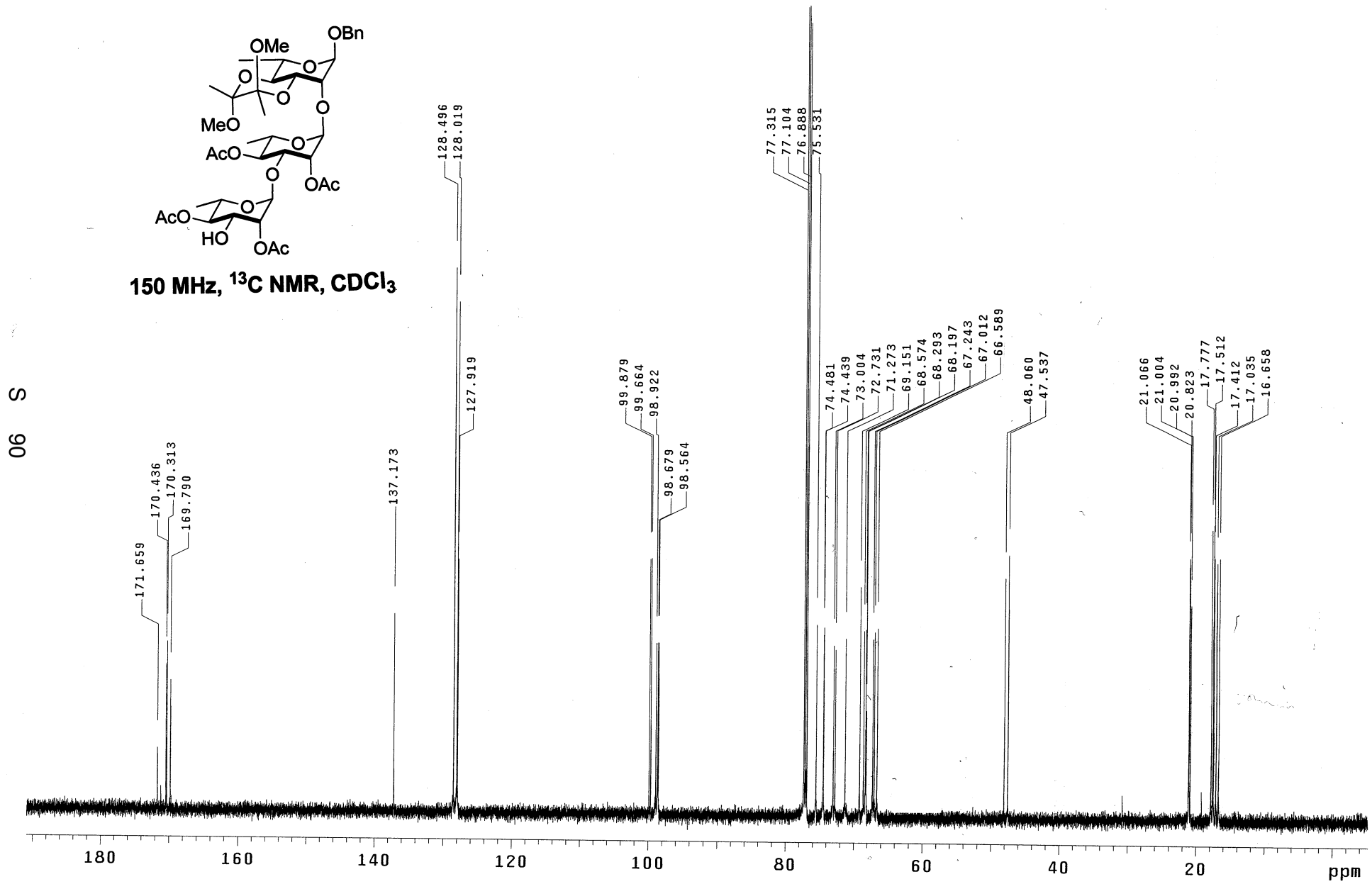


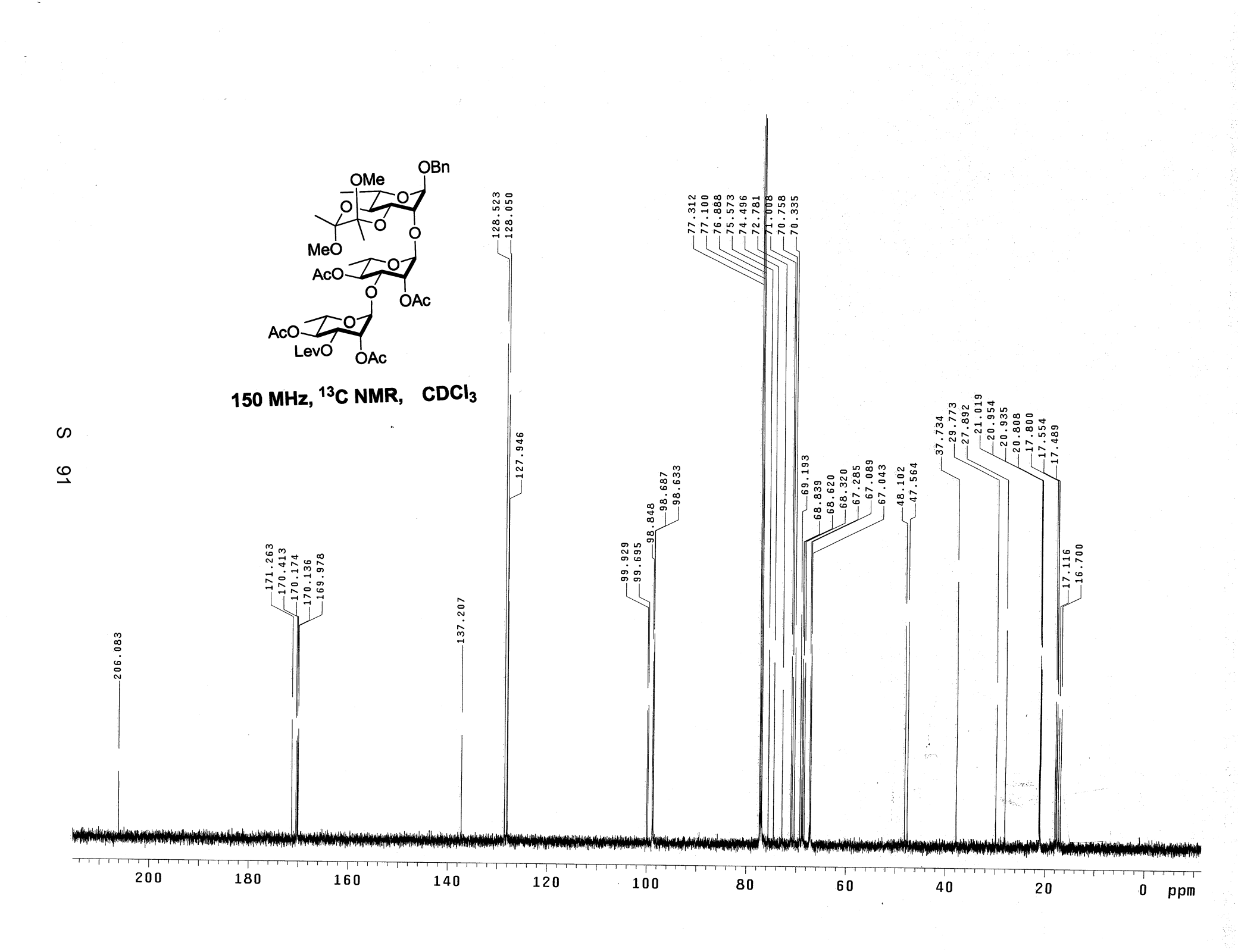
150 MHz, ^{13}C NMR, CD_3OD

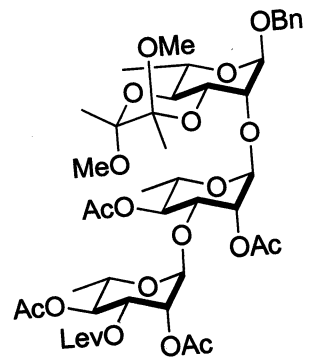


600 MHz, ^{1}H NMR, $CDCl_3$

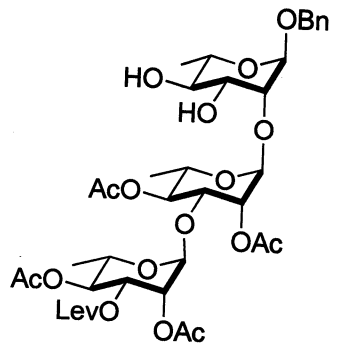
S 89


OBn
OMe
MeO
AcO
OAc
AcO
HO
OAc
150 MHz, 13C NMR, CDCl3
S 90
171.659
170.436
170.313
169.790
137.173
128.496
128.019
127.919
99.879
99.664
98.922
98.679
98.564
77.315
77.104
76.888
75.531
74.481
74.439
73.004
72.731
71.273
69.151
68.574
68.293
68.197
67.243
67.012
66.589
48.060
47.537
21.066
21.004
20.992
20.823
17.777
17.512
17.412
17.035
16.658
180
160
140
120
100
80
60
40
20
ppm

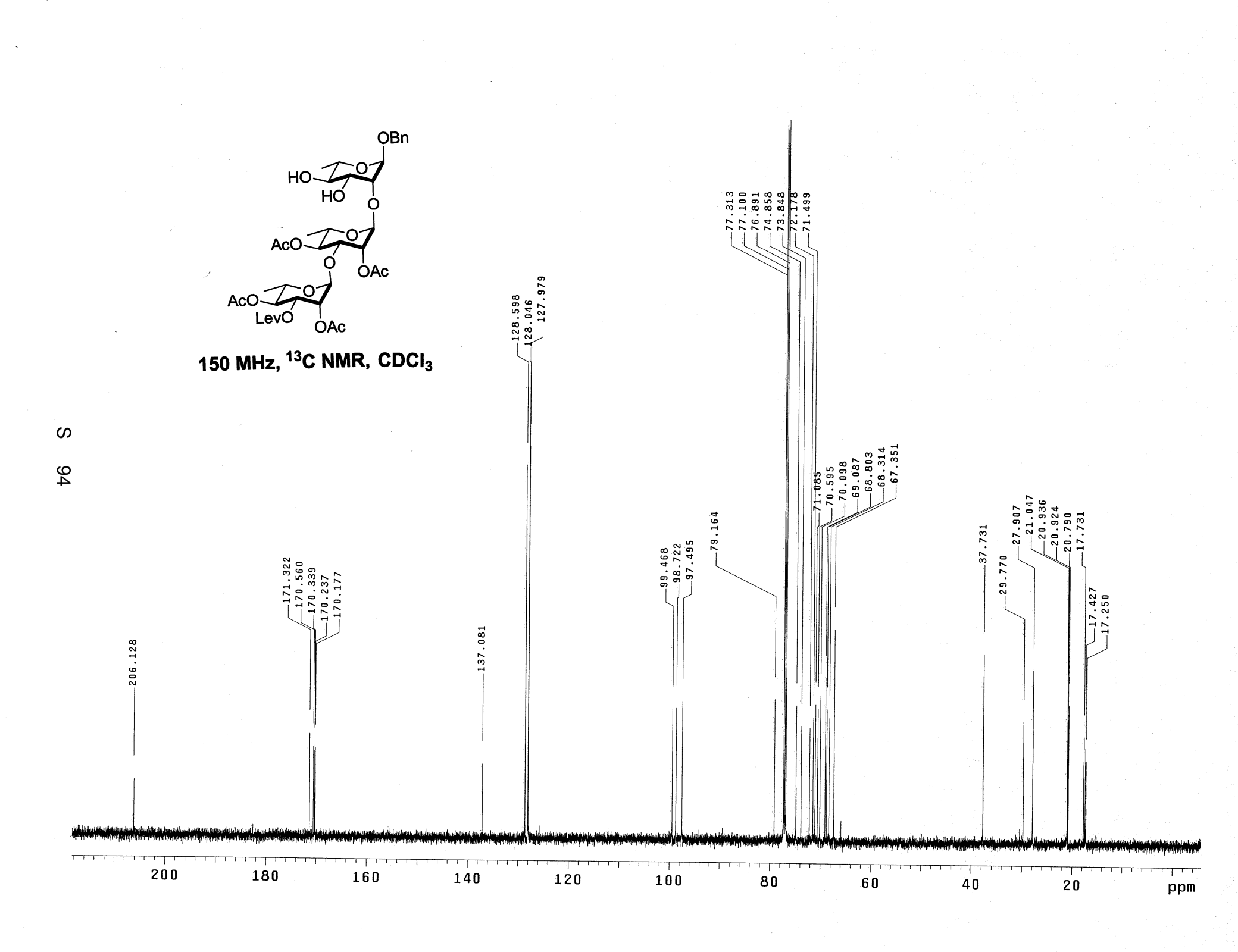

OBn
OMe
MeO
AcO
OAc
AcO
LevO
OAc
150 MHz, 13C NMR, CDCl3
206.083
171.263
170.413
170.174
170.136
169.978
137.207
128.523
128.050
127.946
99.929
99.695
98.848
98.687
98.633
77.312
77.100
76.888
75.573
74.496
72.781
71.008
70.758
70.335
69.193
68.839
68.620
68.320
67.285
67.089
67.043
48.102
47.564
37.734
29.773
27.892
21.019
20.954
20.935
20.808
17.800
17.554
17.489
17.116
16.700
200
180
160
140
120
100
80
60
40
20
0
ppm

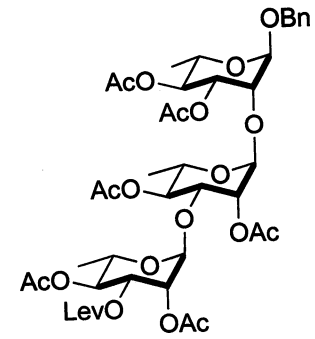


600 MHz, ^{1}H NMR, $CDCl_3$



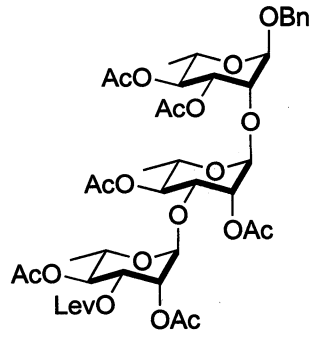
600 MHz, ^{1}H NMR, $CDCl_3$


OBn
HO
HO
O
AcO
O
OAc
AcO
LevO
OAc
150 MHz, 13C NMR, CDCl3
206.128
171.322
170.560
170.339
170.237
170.177
137.081
128.598
128.046
127.979
99.468
98.722
97.495
79.164
77.313
77.100
76.891
74.858
73.848
72.178
71.499
71.085
70.595
70.098
69.087
68.803
68.314
67.351
37.731
29.770
27.907
21.047
20.936
20.924
20.790
17.731
17.427
17.250
200
180
160
140
120
100
80
60
40
20
ppm



600 MHz, ^{1}H NMR, $CDCl_3$

S 95

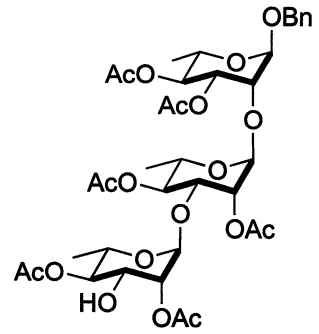


150 MHz, ^{13}C NMR, $CDCl_3$

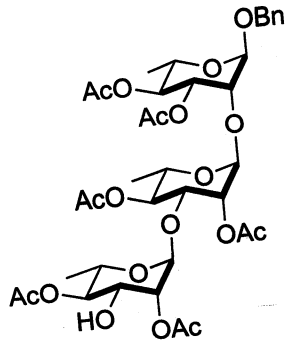
S 96

206.077
171.291
170.462
170.292
170.134
169.755
136.710
128.586
128.097
128.010
99.437
98.679
97.345
77.313
77.100
77.080
76.891
74.317
72.119
71.396
71.203
70.658
70.082
69.170
68.878
67.366
67.299
66.553
37.708
29.734
27.891
21.003
20.932
20.901
20.826
20.743
17.522
17.151

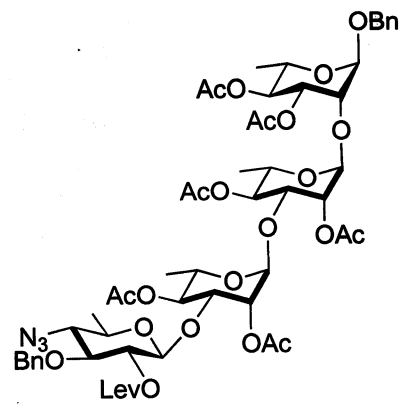
200 180 160 140 120 100 80 60 40 20 ppm



600 MHz, ^{1}H NMR, $CDCl_3$

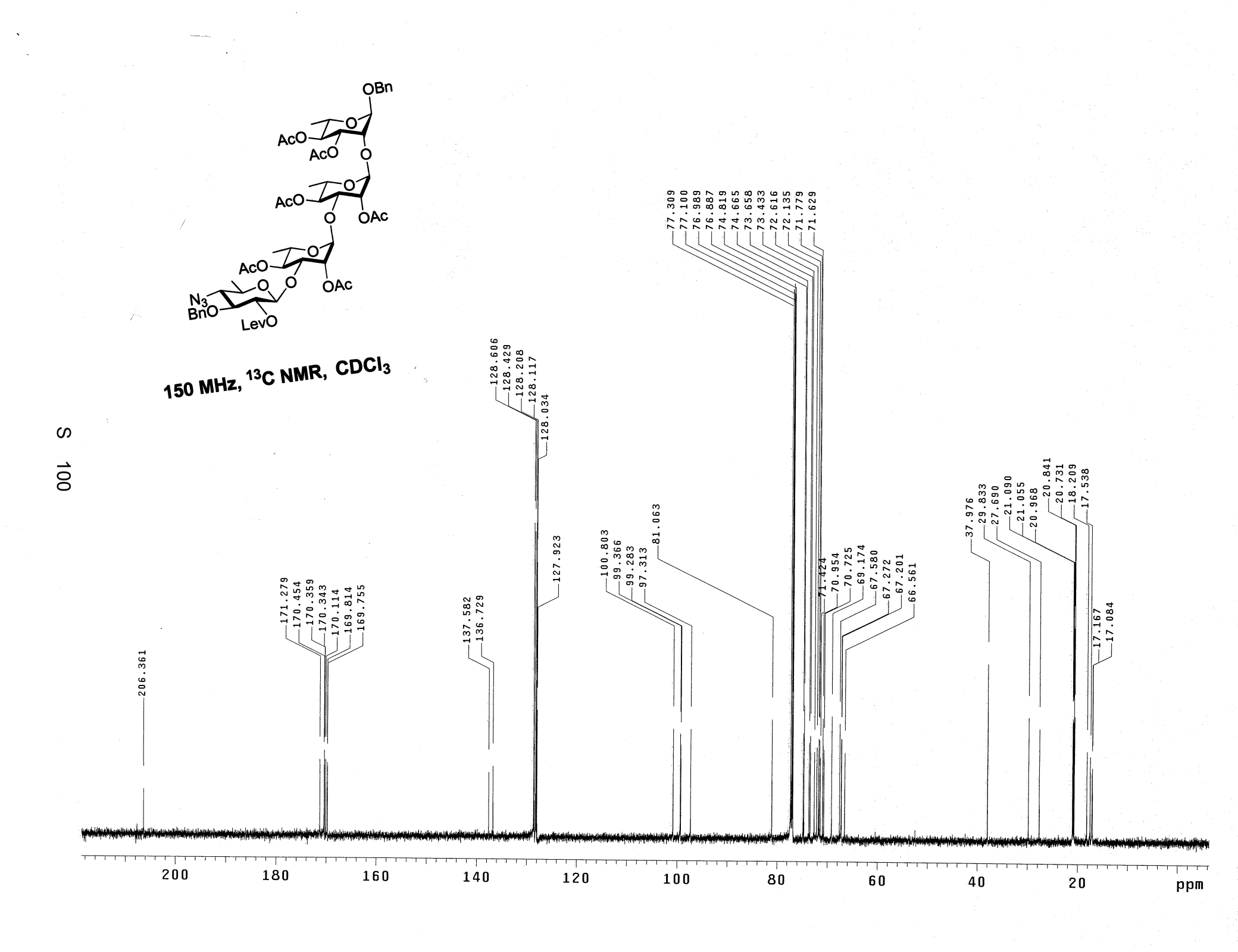


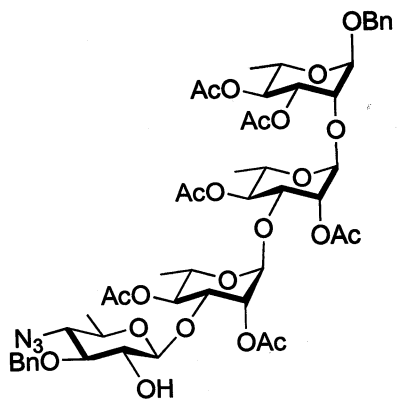
150 MHz, ^{13}C NMR, $CDCl_3$



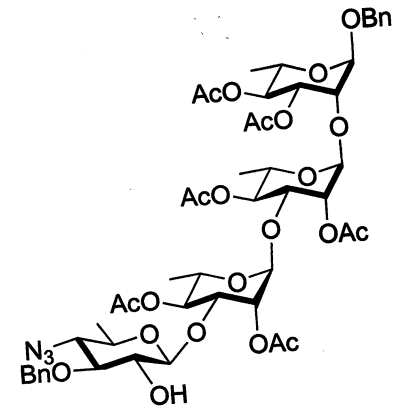
600 MHz, ^{1}H NMR, $CDCl_3$

S 99

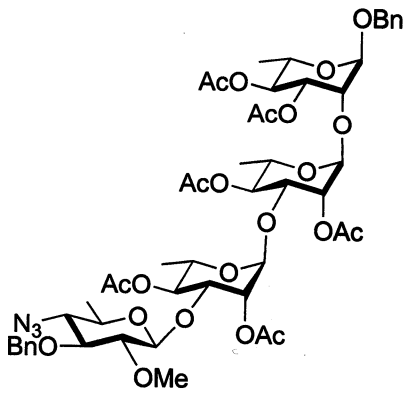

OBn
AcO
AcO
O
AcO
O
OAc
AcO
O
OAc
N3
BnO
LevO
150 MHz, 13C NMR, CDCl3
S 100
206.361
171.279
170.454
170.359
170.343
170.114
169.814
169.755
137.582
136.729
128.606
128.429
128.208
128.117
128.034
127.923
100.803
99.366
99.283
97.313
81.063
77.309
77.100
76.989
76.887
74.819
74.665
73.658
73.433
72.616
72.135
71.779
71.629
71.424
70.954
70.725
69.174
67.580
67.272
67.201
66.561
37.976
29.833
27.690
21.090
21.055
20.968
20.841
20.731
18.209
17.538
17.167
17.084
200
180
160
140
120
100
80
60
40
20
ppm



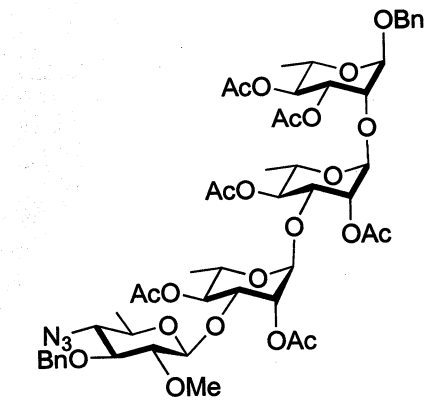
600 MHz, ^{1}H NMR, $CDCl_3$



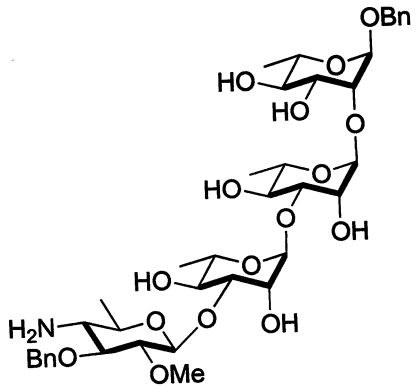
150 MHz, ^{13}C NMR, $CDCl_3$



600 MHz, ^{1}H NMR, $CDCl_3$

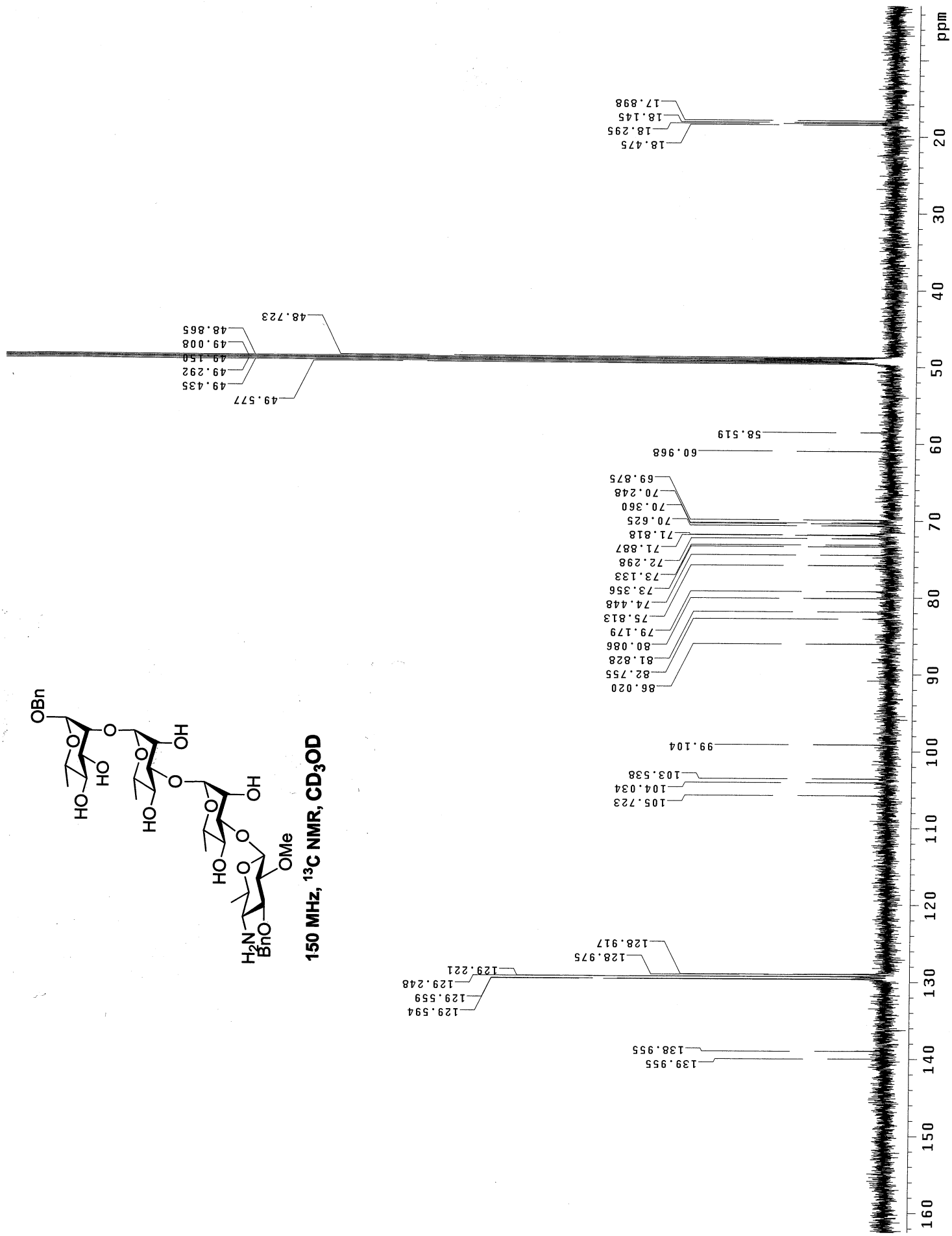


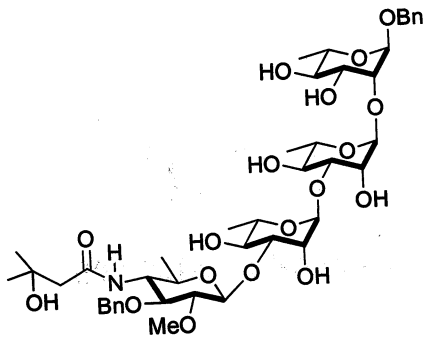
150 MHz, ^{13}C NMR, $CDCl_3$



600 MHz, ^{1}H NMR, CD_3OD

8 7 6 5 4 3 2 1 ppm


150 MHz, ^{13}C NMR, CD_3OD
ppm
17.898
18.145
18.295
18.475
48.723
48.865
49.008
49.150
49.292
49.435
49.577
58.519
60.968
69.875
70.248
70.360
70.625
71.818
71.887
72.298
73.133
73.356
74.448
75.813
79.179
80.086
81.828
82.755
86.020
99.104
103.538
104.034
105.723
128.917
128.975
129.221
129.248
129.559
129.594
138.955
139.955



600 MHz, ^{1}H NMR, CD_3OD

8 7 6 5 4 3 2 1 ppm

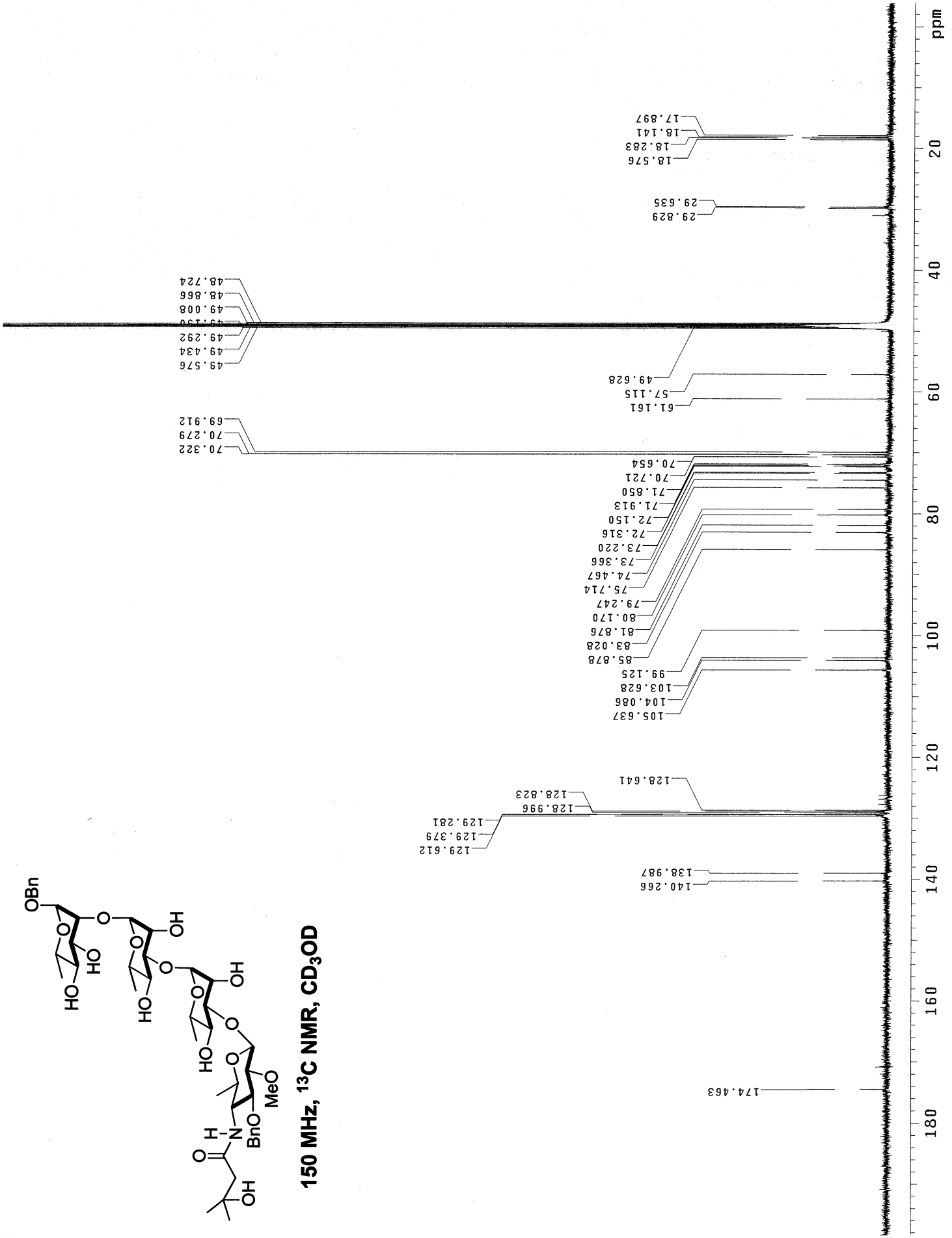
17.76

1.55 2.05 1.61 5.77 1.98

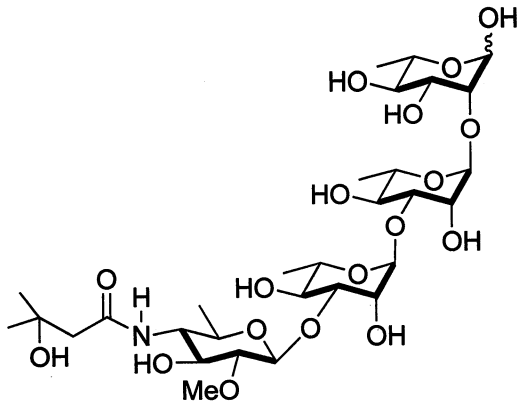
1.69 1.64 9.05 1.68 10.44 5.32 1.79 1.84

3.21

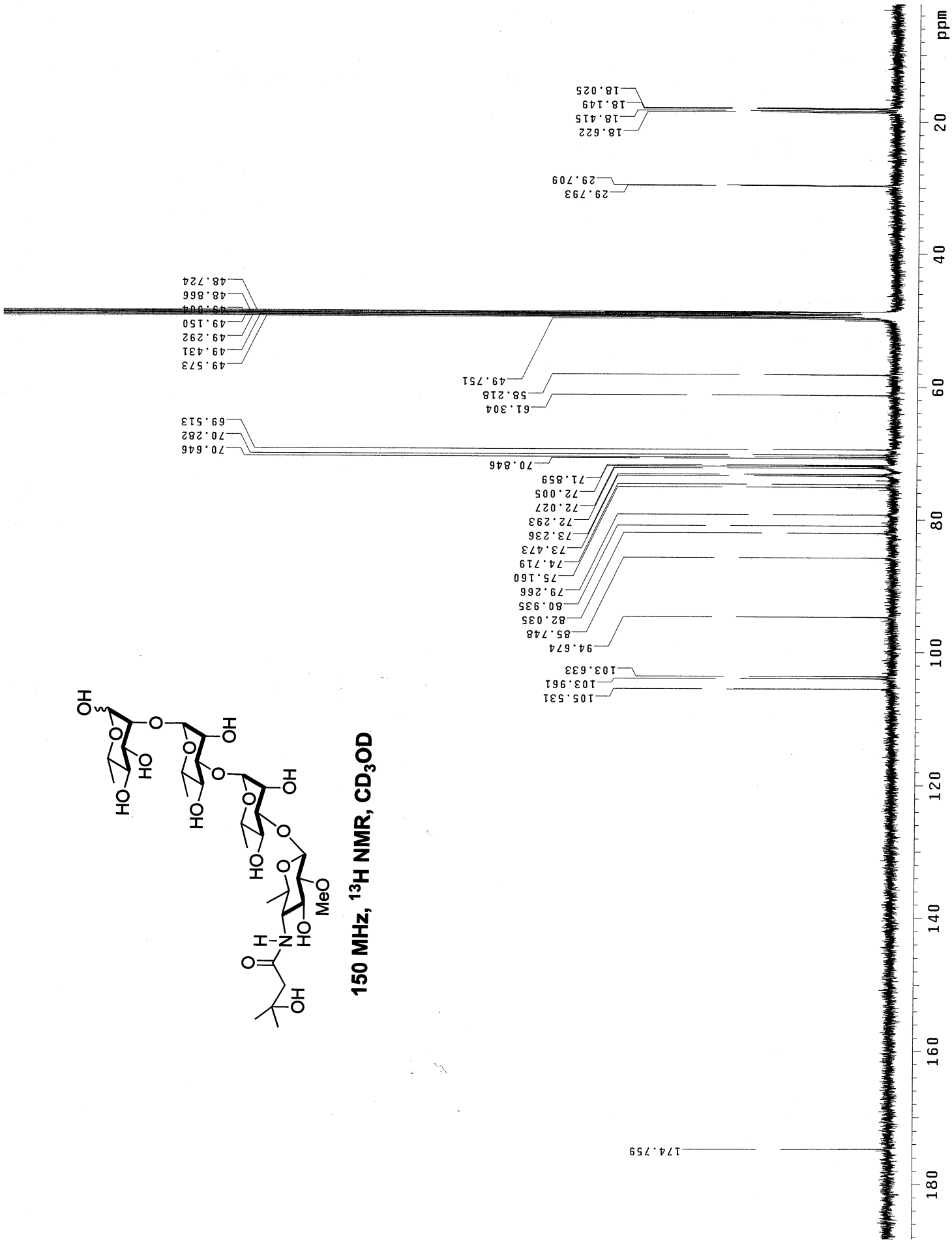
11.98 5.37 15.27

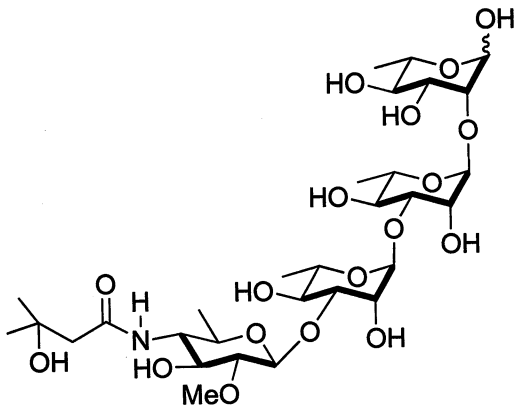


150 MHz, ^{13}C NMR, CD_3OD



600 MHz, ^{1}H NMR, CD_3OD


18.025
18.149
18.415
18.622
29.709
29.793
48.724
48.866
49.004
49.150
49.292
49.431
49.573
49.751
58.218
61.304
69.513
70.282
70.646
70.846
71.859
72.005
72.027
72.293
73.236
73.473
74.719
75.160
79.266
80.935
82.035
85.748
94.674
103.633
103.961
105.531
174.759
ppm
20
40
60
80
100
120
140
160
180
OH
O
HO
MeO
H-N
150 MHz, 13H NMR, CD3OD



600 MHz, ^{1}H NMR, 2 mg in DMSO

*** – DMSO # – H_2O**