Supporting Information

Synthesis of neamine-derived pseudodisaccharides by stereo- and regio-selective functional group transformations

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Contents

Experimental Section

General procedures

Unless otherwise noted, all reactions were carried out in oven-dried glassware under an atmosphere of argon or nitrogen. Tetrahydrofuran and toluene were dried and distilled from sodium metal. Acetonitrile and dichloromethane were distilled from calcium hydride. Methanol was dried by heating under reflux with magnesium and then distilled. *N*, *N*-Dimethylformamide was dried over P_2O_5 and distilled under vacuum. Reactions were monitored by analytical thin-layer chromatography (TLC) on Merck silica gel $60F_{254}$ plates (0.25 mm), visualized by ultraviolet light and/ or by staining with ceric ammonium molybdate or ninhydrin. Optical rotations were measured at ambient temperature (25 ^{o}C) using RUDOLPH AUTOPOL III. ^{1}H NMR spectra were obtained on Varian INOVA-500 or JEOL JNM-AL300 spectrometer at ambient temperature. Data were reported as follows: chemical shift on the δ scale (using either TMS or residual proton solvent as internal standard), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constant(s) in hertz. ^{13}C NMR spectra were obtained with proton decoupling on a Varian INOVA-500 (125 MHz) or JEOL JNM-AL-300 (75 MHz) spectrometer and were reported in ppm with residual solvent for internal standard (77.0 for $CDCl_3$). High resolution mass spectra were obtained on a PE SCLEX QSTAR spectrometer. Elemental analysis data were recorded on a PE-2400C elemental analyzer.

Methyl 2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-deoxy-α-D-xylo-hex-5-enopyranoside (17). To a solution of **15**[1] (5.12g, 10.6 mmol) in DMF (40 mL), *p*-methoxybenzyl chloride (4.3 mL, 4.95 g, 31.6 mmol) and sodium hydride (1.69 g, 60% in mineral oil, 42.3 mmol) were added at 0 ^{o}C. After stirring for 3 h at room temperature, TLC monitoring (petroleum ether/EtOAc 3: 1) indicated completion of the reaction. Excess of NaH was quenched by sat. $NaHCO_3$ aqueous solution (100 mL) at 0 ^{o}C, and the mixture was extracted with EtOAc (100 mL). The aqueous layer was extracted with EtOAc (2×50 mL). The organic layer and the combined extracts were dried over Na_2SO_4, filtered, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 15:1) to afford **17** (4.64 g, 92%) as a white solid: R_f = 0.37 (petroleum ether /EtOAc 4:1); $[\alpha]_D$ = -0.7 (*c* = 0.4, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.36-7.26 (m, 12H, Ar), 6.86-6.84 (m, 2H, Ar), 4.90-4.81 (m, 4H, $PhCH_2$), 4.70-4.65 (m, 4H, H-6a, H-6b, PMB), 4.61 (d, 1H, *J* = 3.5 Hz, H-1), 3.94 (t, 1H, *J* = 9.5 Hz, H-3), 3.88 (dt, 1H, *J* = 3.0 , 9.0 Hz, H-4), 3.80 (s, 3H, OCH_3), 3.59 (dd, 1H, *J* = 3.5, 9.0 Hz, H-2), 3.41 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.27 (PMB), 153.70 (C-6), 138.68, 138.04, 130.08, 129.55, 128.44, 128.35, 128.09, 128.00, 127.61, 131.78, 99.01 (C-1), 96.81, 81.16, 79.18, 75.74, 74.20, 73.60, 55.42 (OCH_3), 55.25 (OCH_3); MS (ESI) *m/e* calcd for $C_{29}H_{32}O_6$ ($M+Na^+$) 499, found 499; elemental analysis calcd (%) for $C_{29}H_{32}O_6$: C 73.09, H 6.77, found: C 72.94, H 6.83.

2L-(2,4,5/3)-2-*O*-Allyl-3,4-di-*O*-benzyl-2,3,4,5-tetrahydroxycyclohexanone (18). To a stirred solution of **16**[2] (5.20 g, 13.1 mmol) in acetone-water (2:1, 50 mL) was added $Hg(OCOCF_3)_2$ (0.56 g, 1.31 mmol) at room temperature. After stirring for 3 h, sat. $NaHCO_3$ aqueous solution was added to neutralize the mixture to pH 6~7. The mixture was partially evaporated to remove acetone, and the suspension was extracted with EtOAc (50 mL×2), the organic layer was collected and sequentially washed with water and brine (50 mL), dried over Na_2SO_4, filtered, concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 4:1) to give **18** (3.71 g, 74%) as colorless solids: R_f = 0.36 (petroleum ether/EtOAc 1:1); $[\alpha]_D$ = -20.0 (*c* = 2.2, EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40-7.26 (m, 10H, Ar), 5.94 (ddt, 1H, *J* = 6.0, 10.5, 17.5 Hz, =CH-), 5.25 (dq, 1H, *J* = 1.5, 17.5 Hz, $=CH_2$), 5.18 (dq, 1H, *J* = 1.5, 12.5 Hz, $=CH_2$), 4.93 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.85-4.71 (m, 3H, $PhCH_2$), 4.40 (ddt, 1H, *J* = 1.5, 5.0, 12,5 Hz, C=C-CH_2), 4.25-4.24 (m, 1H, H-2), 4.07 (ddt, 1H, *J* = 1.5, 5.0, 12.5 Hz, C=C-CH_2), 4.00-3.95 (m, 2H, H-3&H-4), 3.78 (dt, 1H, *J* = 2.7, 6.3 Hz, H-5), 2.62 (dd, 1H, *J* = 3.6, 14.7 Hz, H-6eq), 2.47-2.41 (m, 2H, -OH, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 203.94 (C=O), 138.27, 137.58, 134.24 (=CH-), 128.37, 128.21, 128.02, 127.86, 127.74, 127.58, 117.49, 85.03, 81.64, 81.30, 75.83, 72.93, 72.51, 66.30, 42.53 (C-6); HRMS (ESI) *m/e* calcd for $C_{24}H_{28}O_4$ ($M+Na^+$) 405.1672, found: 405.1672.

2L-(2,4,5/3)-2-*O*-(4-Methoxybenzyl)-3,4-di-*O*-benzyl-2,3,4,5-tetrahydroxycyclohexanone (19) and

2L-(2,4/5,3)-2-*O*-(4-methoxybenzyl)-3,4-di-*O*-benzyl-2,3,4,5-tetrahydroxycyclohexanone (20). To a stirred solution of **17** (4.64 g, 9.7 mmol) in acetone-water (2:1, 90 mL) was added $Hg(OCOCF_3)_2$ (0.42 g, 0.98 mmol) at room temperature. After stirring for 3 h, sat. $NaHCO_3$ was added to neutralize the mixture to pH 6~7. The mixture was partially evaporated, the suspension was extracted with EtOAc (50 mL×2), the organic layer was collected and sequentially washed with water and brine (50 mL), dried over Na_2SO_4, filtered, concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 3:1) to give **20** (696 mg, 15%) as a white solid: R_f = 0.42 (petroleum ether/EtOAc 1:1); $[\alpha]_D$ = -9.3 (*c* = 0.4, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$, 40 ^{o}C) δ = 7.36-7.24 (m, 12H, Ar), 6.86-6.83 (m, 2H, Ar), 4.99 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.92 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.83 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.73 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.69 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.47 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.13 (d, 1H, *J* = 8.0 Hz, H-2), 3.79 (s, 3H, OCH_3), 3.73-3.62 (m, 3H, H-3, H-4, H-5), 2.74 (dd, 1H, *J* = 4.5, 13.5 Hz, H-6eq), 2.48 (t, 1H, *J* =13.5 Hz, H-6ax), 2.43 (s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 203.20 (C=O), 159.43(PMB), 138.01, 129.90, 129.47, 128.72, 128.44, 128.07, 127.98, 127.84, 113.83, 85.68, 84.65, 81.90, 75.60, 75.44, 73.30, 67.99, 55.26 (OCH_3), 44.08 (C-6); HRMS(ESI) *m/e* calcd for $C_{28}H_{30}O_6$ ($M+Na^+$) 485.1935, found: 485.1931. Further elution gave isomer **19** (3.33 g, 75%) as a white solid: R_f = 0.35 (petroleum ether/EtOAc 1:1); $[\alpha]_D$ = -22.4 (*c* = 0.7, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33-7.26 (m, 12H, Ar), 6.83 (d, 2H, *J* = 8.5 Hz, Ar), 4.93-4.69 (m, 5H, $PhCH_2$), 4.50 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.23-4.22 (m, 1H, H-2), 4.02-4.01 (m, 2H,

H-1, H-3), 3.80-3.76 (m, 4H, H-4, OCH_3), 2.66 (dd, 1H, *J* = 4.0, 15.0 Hz, H-6eq), 2.48 (dd, 1H, *J* = 4.0, 15.0 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 203.97 (C=O), 159.28, 138.36, 137.58, 129.81, 129.71, 128.56, 128.34, 128.06, 127.88, 127.69, 113.73, 84.87, 81.67, 81.45, 75.92, 73.20, 73.09, 66.47, 55.23 (OCH_3), 42.50 (C-6); HRMS (ESI) *m/e* calcd for $C_{28}H_{30}O_6$ ($M+Na^+$) 485.1935, found: 485.1937.

1D-(1,2,4/3,5)-4-*O*-Allyl-2,3-di-*O*-benzyl-1-*O*-methyl-5-hydroxylcyclohexanepentol (21) and 1D-(1,2,4,5/3)-4-*O*-allyl-2,3-di-*O*-benzyl-1-*O*-methyl-5-hydroxylcyclohexanepentol (22). To a solution of **16**[2] (1.73 g, 4.37 mmol) in toluene (10 mL), was added TIBAL (1M in toluene, 43.7 mL) dropwise under argon at room temperature. When the addition of TIABL was finished, the mixture was heated by oil bath at 50 ^oC. After stirring for 3.5 h, NaOH (2M aqueous solution, 100 mL) was added to quench the reaction, the mixture was diluted with EtOAc (50 mL) and washed with water (50 mL) and brine (50 mL). The organic layer was collected and dried over Na_2SO_4, concentrated and purified by column chromatography on silica gel (petroleum ether/EtOAc 4:1) to give **21** (402 mg, 24%) as a white solid: R_f = 0.48 (petroleum ether/EtOAc 1:2); $[\alpha]_D$ = +31.3 (*c* = 2.3, EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ = 7.38-7.28 (m, 10H, Ar), 5.95 (ddt, 1H, *J* = 5.7, 10.2, 17.4 Hz, =CH-), 5.27 (dq, 1H, *J* = 1.5, 17.4 Hz, $=CH_2$), 5.17 (dq, 1H, *J* = 1.5, 10.2 Hz, $=CH_2$), 4.94 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.75 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.71 (2d, 2H, *J* = 12.0 Hz, $PhCH_2$), 4.47 (ddt, 1H, *J* = 1.5, 5.7, 12.3 Hz, C=C-CH_2-), 4.19 (ddt, 1H, *J* = 1.5, 5.7, 12.3 Hz,

C=C-CH_2-), 3.87-3.76 (m, 2H, H-3, H-5), 3.63-3.62 (m, 1H, H-1), 3.44-3.40 (m, 4H, H-2, OCH_3), 3.14 (t, 1H, *J* = 9.3 Hz, H-4), 2.41 (br, 1H, OH), 2.30 (dt, 1H, *J* = 4.5, 14.1 Hz, H-6eq), 1.20 (ddd, 1H, *J* = 2.1, 12.0, 14.1 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.72, 138.30, 135.05, 128.33, 128.05, 127.83, 127.65, 127.55, 117.02, 85.98, 82.84, 81.68, 75.67, 75.06, 74.11, 72.66, 67.82, 57.34 (OCH_3), 30.76 (C-6); HRMS (ESI) *m/e* calcd for $C_{24}H_{30}O_{54}$ (M+Na^+) 421.1985, found: 421.1945. Further elution gave isomer **22** (1.27 g, 73%) as a colorless oil: R_f = 0.37 (petroleum ether/EtOAc 1:2); $[\alpha]_D$ = +7.5 (*c* = 2.1, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.41-7.26 (m, 10H, Ar), 5.97 (ddt, 1H, *J* = 6.0, 10.5, 17.5 Hz, =CH-), 5.30 (dq, 1H, *J* = 1.5, 17.5 Hz, =CH_2), 5.17 (dq, 1H, *J* = 1.5, 10.5 Hz, =CH_2), 4.92-4.67 (4×d, 4H, *J* = 12.0 Hz, PhCH_2), 4.23-4.20 (m, 2H, C=C-CH_2), 4.11-4.04 (m, 2H, H-3, H-5), 3.71-3.70 (m, 1H, H-1), 3.60 (d, 1H, *J* = 9.9 Hz, OH), 3.52 (s, 3H, OCH_3), 3.39 (dd, 1H, *J* = 3.0, 9.3 Hz, H-2), 3.27 (dd, 1H, *J* = 3.3, 9.3 Hz, H-4), 2.28 (dt, 1H, *J* = 3.3, 15.0 Hz, H-6eq), 1.33 (dt, 1H, *J* = 2.7, 15.0 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.90, 138.45, 135.18, 128.35, 128.28, 128.21, 127.75, 127.65, 127.53, 117.09, 82.47, 82.20, 78.95, 78.82, 75.97, 73.19, 71.64, 68.32, 59.01 (OCH_3), 29.54 (C-6); HRMS (ESI) *m/e* calcd for $C_{24}H_{30}O_5$ (M+Na^+) 421.1985, found: 421.1945.

1D-(1,2,4/3,5)-4-*O*-Allyl-1,5-di-*O*-benzoyl-2,3-di-*O*-benzyl-cyclohexanepentol (23). To one portion of powdered Me_4NBH_4 (1.16 g, 0.013 mol) in dry round-bottomed flask under argon, freshly distilled AcOH (2.6 ml, 0.045 mol) was added dropwise at room temperature and stirred for 30 min. THF (8 mL) was then

added, the mixture was stirred at the same temperature for additional 3 h to ensure complete conversion of Me_4NBH_4 to $Me_4NBH(OAc)_3$. To the above mixture, a solution of **18** (1.108 g, 2.78 mmol) in CH_3CN (10 mL) was added dropwise. After stirring for 13 h at room temperature, sat. NH_4Cl aqueous solution was added to quench the reaction. The mixture was extracted with EtOAc (50 mL), washed with sat. $KHCO_3$ (50 mL), then dried over Na_2SO_4, concentrated to produce a colorless oil (899 mg). To a mixture of the colorless oil and DMAP (14 mg, 0.12 mmol) in pyridine (20 mL), BzCl (1.63 mL, 14.03 mmol) was added slowly at 0 ^oC. The mixture was allowed to stir for 6 h from 0 ^oC to room temperaure. The mixture was concentrated, diluted with EtOAc (50 mL), washed successively with sat. $NaHCO_3$ (50 mL) and water (50 mL). The organic layer was collected and dried over Na_2SO_4, concentrated, and purified by column chromatography on silica gel (petroleum ether/EtOAc 16:1) to give **23** (1.36 g, 80% over two steps) as colorless solids: R_f = 0.36 (EtOAc/ petroleum ehter 1:4); $[\alpha]_D$ = +42 (*c* = 2.0, EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ = 8.12-8.02 (m, 4H, Ar), 7.60-7.42 (m, 7H, Ar), 7.33-7.16 (m, 9H, Ar), 5.89-5.76 (m, 2H, H-1, H-5), 5.58-5.49 (m, 1H, =CH-), 5.16 (dd, 1H, *J* = 1.5, 17.1 Hz, $=CH_2$), 5.06 (d, 1H, *J* = 10.2 Hz, $=CH_2$), 4.92-4.81 (m, 3H, $PhCH_2$), 4.60 (d, 1H, *J* = 11.7 Hz, $PhCH_2$), 4.37 (dd, 1H, *J* = 5.7, 12.0 Hz, C=C-CH_2), 4.24 (dd, 1H, *J* = 6.3, 12.0 Hz, C=C-CH_2), 4.00 (t, 1H, *J* = 9.3 Hz, H-4), 3.67-3.60 (m, 2H, H-2, H-3), 2.49 (dt, 1H, *J* = 4.5, 14.1 Hz, H-6eq), 1.71 (ddd, 1H, *J* = 2.1, 12.0, 14.1 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.65 (PhCO), 165.56 (PhCO), 138.53, 137.82, 134.85, 133.18, 133.08, 130.02, 129.92, 129.57, 128.46, 128.40, 128.30, 128.14, 128.00,

127.65, 117.32, 82.91, 81.52, 80.69, 76.09, 74.68, 72.15, 71.57, 66.95, 31.07 (C-6); MS (FAB) *m/e* calcd for $C_{37}H_{36}O_7$: 592, found: 592 (M^+); elemental analysis calcd (%) for $C_{37}H_{36}O_7$: C 74.98, H 6.12; found: C 74.70, H 6.40.

1L-(1,2,4/3,5)-1,5-Di-*O*-acetyl-2-*O*-allyl-3,4-di-*O*-benzyl-cyclohexanepentol (24). To a solution of **23** (150 mg, 0.25 mmol) in MeOH (5 mL), 30% NaOMe (0.1 mL) was added at room temperature. After stirring for 1 h, the mixture was neutralized to pH = 6-7 with ion-exchange resin (Dowex 50, strong acid form) at room temperature. The mixture was filtered and concentrated to give colorless oil. To the crude oil, CH_2Cl_2 (2 mL) and pyridine (204 μL, 2.5 mmol) were added, followed by addition of Tf_2O (174 μL, 1.0 mmol) at 0 ^oC. After stirring for 10 min, sat. $NaHCO_3$ (20 mL) was added to neutralize the mixture. The mixyure was diluted with CH_2Cl_2 (20 mL) and washed with water (20 mL). The organic layer was collected, dried over Na_2SO_4, concentrated in vacuo and co-evaporated with toluene (3 mL) for three times to afford yellow oil. The crude product was dissolved in DMF (2 mL), n-Bu_4NOAc (226 mg, 0.75 mmol) was added to the mixture at 0 ^oC under argon, and stirred for 5 h at r.t. The mixture was concentrated, the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 9:1) to give **24** (42 mg, 35% over three steps) as a white solid: R_f = 0.32 (petroleum ether/EtOAc 3:1); $[\alpha]_D$ = -2.4 (*c* = 2.5, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34-7.26 (m, 10H, Ar), 5.95 (ddt, 1H, *J* = 5.7, 10.8, 17.4 Hz, =CH-), 5.43-5.42 (m, 1H, H-1), 5.29 (ddt, 1H, *J* = 1.2, 1.2, 17.4 Hz, =CH_2), 5.23-5.14 (m, 2H, =CH_2, H-5), 4.92-4.67 (m, 4H, PhCH_2), 4.18 (dd, 1H, *J* = 5.7, 12.6

Hz, C=C-CH_2), 4.06 (dd, 1H, *J* = 6.0, 12.6 Hz, C=C-CH_2), 3.85 (t, 1H, *J* = 9.3 Hz, H-4), 3.51 (t, 1H, *J* = 9.6 Hz, H-3), 3.42 (dd, 1H, *J* = 3.0, 9.6 Hz, H-2), 2.20 (dt, 1H, *J* = 4.5, 14.1 Hz, H-6eq), 2.13 (s, 3H, $COCH_3$), 1.95 (s, 3H, $COCH_3$), 1.47 (ddd, 1H, *J* = 2.7, 12.3, 14.1 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.19 ($COCH_3$), 170.09 ($COCH_3$), 138.57, 138.50, 134.55, 128.37, 128.15, 127.74, 127.69, 127.64, 117.45, 83.31, 81.57, 80.36, 76.09, 75.62, 71.36, 70.69, 66.66, 30.80 (C-6), 21.14 ($COCH_3$), 21.06 ($COCH_3$); HRMS (ESI) *m/e* calcd for $C_{27}H_{32}O_7$ ($M+Na^+$) 491.2040, found: 491.2039.

1D-(1,2,4,5/3)-4-*O*-Allyl-2,3-di-*O*-benzyl-1,5-dihydroxylcyclohexanepentol (25). To a solution of **18** (571 mg, 1.49 mmol) in methanol (15 mL) at 0 ^{o}C was added portion-wise $NaBH_4$ (225 mg, 5.96 mmol). After stirring for 10 min, sat. NH_4Cl aqueous solution was added to quench the reaction. The mixture was concentrated and extracted with EtOAc (30 mL) and water (30 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/acetone 4:1) to give **25** (467 mg, 82%) as a colorless oil: R_f = 0.28 (petroleum ether/acetone 2:1); $[\alpha]_D$ = +15.4 (*c* = 2.6, EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$, D_2O exchange) δ = 7.41-7.26 (m, 10H, Ar), 5.94 (ddt, 1H, *J* = 5.4, 10.5, 17.1 Hz, =CH-), 5.29 (dd, 1H, *J*= 1.8, 17.1 Hz, =CH_2), 5.18 (dd, 1H, *J* =1.8, 10.2 Hz, =CH_2), 5.16-4.73 (m, 4H, PhCH_2), 4.22-4.14 (m, 4H, H-1, H-5, =C-CH_2-), 4.05 (t, 1H, *J* = 9.3 Hz, H-3), 3.40-3.62 (m, 2H, H-2 or H-4, OH), 3.30 (dd, 1H, *J* = 3.3, 9.3 Hz, H-2 or H-4), 2.33 (dt, 1H, *J*= 3.6, 15.0 Hz, H-6eq), 1.46

(dt, 1H, J = 2.7, 15.0 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.80, 138.10, 134,82, 128.39, 128.30, 128.12, 127.84, 127.75, 127.56, 117.31, 82.26, 78.66, 76.06, 72.62, 71.70, 68.53, 31.23 (C-6); HRMS (ESI) *m/e* calcd for $C_{23}H_{28}O_5$ ($M+Na^+$) 407.1829, found: 407.1831.

2L-(2,4/3)-2-*O*-Allyl-3,4-di-*O*-benzyl-2,3,4-trihydroxy-5-cyclohexen-1-one (27). To a solution of **18** (260 mg, 0.6mmol) in CH_2Cl_2 (5 mL), MsCl (156 mg, 1.4mmol) was added dropwise at 0 ^oC, followed by addition of triethylamine (0.5 mL, 3.6 mmol). The mixture was stirred at 0 ^oC for 2 h, diluted with CH_2Cl_2 (50 mL), washed successively with 0.5 M H_2SO_4, sat. $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc 12:1) to give **27** (148 mg, 60%) as a colorless oil: R_f = 0.28 (petroleum ether/EtOAc 3:1); $[\alpha]_D$ = +21.0 (c = 0.6, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.40-7.30 (m, 10H, Ar), 6.80 (dd, 1H, J = 2.0, 10.5 Hz, H-6), 6.02 (dd, 1H, J =2 .0, 10.0 Hz, H-5), 6.04-5.95 (m, 1H, =CH-), 5.35 (dd, 1H, J= 1.5, 17.0 Hz, $=CH_2$), 5.21 (dd, 1H, J = 1.5, 10.5 Hz, $=CH_2$), 4.97 (d, 1H, J = 11.0 Hz, $PhCH_2$), 4.83(d, 1H, J = 11.5 Hz, $PhCH_2$), 4.81 (d, 1H, J = 10.5 Hz, $PhCH_2$), 4.74 (d, 1H, 12.0 Hz, $PhCH_2$), 4.51 (ddt, 1H, J = 1.5, 5.5, 12.5 Hz, $=C-CH_2-$), 4.35 (dt, 1H, J = 2.0 ,7.5 Hz, H-4), 4.25 (ddt, 1H, J = 1.5, 5.5, 12.5 Hz, $=C-CH_2-$), 3.97-3.91 (m, 2H, H-2, H-3); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 197.34 (C=O), 148.06, 138.17, 137.62, 134.39, 128.54, 128.40, 128.19, 128.03, 127.89, 127.82, 117.80, 84.72, 83.60, 78.89,

75.76, 73.66, 29.69; HRMS (ESI) *m/e* calcd for $C_{23}H_{24}O_4$ ($M+H^+$) 365.1770, found: 365.1770.

1L-(1,5/4,6)-6-*O*-Allyl-4,5-di-*O*-benzyl-cyclohex-2-en-1-ol (28). To a mixture of **27** (86 mg, 0.24 mmol) and $CeCl_3 \cdot 7H_2O$ (132 mg, 0.35 mmol) in methanol (5 mL) was added $NaBH_4$ (13 mg, 0.34 mmol) at 0 ^oC. After stirring for 15 min, the reaction was quenched with water and extracted with EtOAc (50 mL), washed with brine, dried over Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (petroleum ether/EtOAc 4:1) to give **28** (78 mg, 90%) as a light yellow oil: R_f = 0.22 (petroleum ether/acetone 2:1); $[\alpha]_D$ = +90.3 (*c* = 3.9, MeOH); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.38-7.27 (m, 10H, Ar), 5.95 (ddt, 1H, *J* = 6.0, 10.5, 17.5 Hz, =CH-), 5.72-5.67 (m, 2H, H-2, H-3), 5.28 (ddt, 1H, *J* = 1.5, 17.5 Hz, $=CH_2$), 5.19 (ddt, 1H, *J* = 1.5, 10.0 Hz, $=CH_2$), 4.89-4.65 (m, 4H, $PhCH_2$), 4.46 (ddt, 1H, *J* = 1.5, 5.0, 12.5Hz, $=C-CH_2$), 4.30 (d, 1H, *J* = 7.0 Hz, H-1), 4.23 (dd, 1H, *J* = 5.0, 12.5 Hz, $=C-CH_2$), 4.22-4.19 (m, 1H, H-4), 3.71 (dd, 1H, *J* = 7.5, 10.5 Hz, H-5), 3.41 (dd, 1H, *J* = 7.5, 10.0 Hz, H-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 138.54, 138.24, 134.97 (=CH-), 129.36 (C-2), 128.42, 128.36, 127.94, 127.80, 127.72, 127.45, 127.05 (C-3), 117.32 ($=CH_2$), 84.08 (C-6), 83.27 (C-5), 80.48 (C-4), 75.24 ($PhCH_2$), 74.12 ($=C-CH_2$), 72.28 ($PhCH_2$), 71.93 (C-1); MS (ESI) *m/e* calcd. for $C_{23}H_{26}O_4$: 389 ($M+Na^+$), found: 389; elemental analysis calcd (%) for $C_{23}H_{26}O_4$: C 75.38, H 7.15; found: C 75.29, H 7.23.

1D-(1,3,5/2,4)-1,6-Di-*O*-benzoyl-2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-cyclohexanepentol (30) and 1L-(1,2,4/3,5)-3,4-di-*O*-benzyl-2-*O*-(4-methoxybenzyl)-1,5-dihydroxylcyclohexane pentol (31). To a solution of **20** (150 mg, 0.32 mmol) in dry dioxane (6 mL), was added $NaBH_4$ (65 mg, 1.72 mmol) under argon. After stirring for 4h, water was added to quench the reaction at 0 ^oC, continued to stir until no bubble spreading out. Then the mixture was concentrated in vacuo, the residue was dissolved with EtOAc (20 mL), washed with water and brine, dried over Na_2SO_4, concentrated, purified by column chromatography on silica gel (CH_2Cl_2/MeOH 100:1) to give **31** (34 mg, 22%): R_f = 0.52 (CH_2Cl_2/ MeOH 20:1); $[\alpha]_D$ = -2.2 (*c* = 0.5, EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.36-7.24 (m, 12H, Ar), 6.86 (d, *J* = 8.5 Hz, Ar), 5.00 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.90 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.82 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.76 (2br, 2H, OH), 4.69-4.60 (m, 3H, $PhCH_2$), 4.08 (q, 1H, *J* = 3.0 Hz, H-1), 4.95 (ddd, 1H, *J* = 5.0, 9.5, 12.0 Hz, H-5), 3.83-3.80 (m, 4H, H-3, OCH_3), 3.48 (dd, 1H, *J* = 3.0, 9.0 Hz, H-2), 3.26 (t, 1H, *J* = 9.5 Hz, H-4), 2.24 (dt, 1H, *J* = 4.5, 14.0 Hz, H-6eq), 1.37 (ddd, 1H, *J* = 2.5, 12.0, 14.0 Hz, H-6ax); ^{13}C NMR(75 MHz, $CDCl_3$) δ = 159.42 (PMB), 138.61, 129.91, 129.52, 128.60, 128.41, 127.92, 127.83, 127.65, 113.92, 86.12, 82.93, 81.50, 75.68, 75.40, 72.45, 67.67, 65.78, 55.27 (OCH_3), 33.42 (C-6); HRMS (ESI) *m/e* calcd. for $C_{28}H_{32}O_6$ ($M+Na^+$) 487.2091, found: 487.2094. Another component **29** (116 mg) was collected as a colorless oil: R_f = 0.45 (CH_2Cl_2/ MeOH 20:1), but its purity was not satisfied in ^1H NMR spectrum. To the above crude oil (116 mg, 0.25 mmol) in pyridine (5 mL), was added BzCl (209 mg, 1.4 mmol) at 0 ^oC.

After stirring for 5 h, pyridine was evaporated under vacuum. The residue was diluted with EtOAc, washed with sat. $NaHCO_3$ and water. The organic layer was collected, dried over Na_2SO_4, concentrated, purified by column chromatography on silica gel (petroleum ether /EtOAc 12 : 1) to give **30** (150 mg, 89%) as a white solid: R_f = 0.30 (petroleum ether /EtOAc 3:1); $[\alpha]_D$ = +3.2 (*c* = 1.3, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.14-6.66 (m, 24H, Ar), 5.30 (ddd, 2H, *J* = 4.5, 9.0, 11.5 Hz, H-1, H-5), 4.89 (d, 2H, *J* = 11.5 Hz, $PhCH_2$), 4.86-4.69 (m, 4H, $PhCH_2$), 3.82 (t, 1H, *J* = 9.0 Hz, H-2), 3.79 (t, 1H, *J* = 9.0 Hz, H-4), 3.73 (t, 1H, *J* = 9.0 Hz, H-3), 3.71 (s, 3H, OCH_3), 2.58 (dt, 1H, *J* = 5.0, 12.5 Hz, H-6eq), 1.77 (q, 1H, *J* = 12.0 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.39 (PhCO), 159.11 (PMB), 138.35, 137.94, 133.08, 130.14, 129.87, 129.62, 128.37, 128.26, 127.94, 127.70, 127.63, 113.64, 83.07, 82.71, 76.10, 75.52, 75,13, 70.85, 70.79, 55.13 (OCH_3), 32.16 (C-6). HRMS (ESI) *m/e* calcd. for $C_{42}H_{40}O_8$ ($M+Na^+$) 695.2615, found: 695.2615.

1D-(1,2,4/3,5)-5-Azido-2,3-di-*O*-benzyl-1-*O*-methyl-1,2,3,4-cyclohexanetetrol (32). To a solution of **22** (34 mg, 0.085 mmol) in CH_2Cl_2 (1 mL), pyridine (28 μL, 0.34 mmol) was added and followed by the addition of Tf_2O (29 μL, 0.17 mmol) at 0 ^{o}C. After stirring for 10 min, sat. $NaHCO_3$ was added to quench the reaction, diluted with EtOAc, washed with water and brine. The extract was dried over Na_2SO_4, concentrated; the residue was co-evaporated with toluene for three times before dissolved in DMF (1 mL). To the mixture, NaN_3 (1.5 mg, 0.34 mmol) was added at 0 ^{o}C. After 5 h, the mixture was evaporated in vacuo, diluted with EtOAc, concentrated

to give a yellow oil. Mixed the oil with MeOH (1 mL), $PdCl_2$ (3 mg, 0.022 mmol) was added at r.t. After stirring for 12 h, the mixture was diluted with CH_2Cl_2, filtered, concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 4:1) to give **32** (9 mg, 35% for 3 steps) as a colorless oil: R_f = 0.34; $[\alpha]_D$ = -9.3 (*c* = 0.4, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.37-7.29 (m, 10H, Ar), 5.02 (d, 1H, *J* = 11.1 Hz, $PhCH_2$), 4.71 (s, 2H, $PhCH_2$), 4.69(d, 1H, *J* = 11.1 Hz, $PhCH_2$), 3.76 (t, 1H, *J* = 9.0 Hz, H-3), 3.66-3.61 (m, 2H, H-4, H-5), 3.45-3.41 (m, 4H, H-1,OCH_3), 3.39 (dd, 1H, *J* = 3.0, 9.0 Hz, H-2), 2.58 (d, 1H, *J* = 2.5 Hz, OH), 2.21 (dt, 1H, *J* = 4.0, 14.5 Hz, H-6eq), 1.19 (ddd, 1H, *J* = 2.5, 12.0, 14.5 Hz , H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.51, 137.98, 128.62, 128.46, 127.99, 127.93, 127.86, 82.05, 81.40, 76.49, 75.71, 74.86, 72.46, 58.93, 57.76 (OCH_3), 29.69 (C-6); IR υ = 2103.6 cm^{-1} (-N_3); HRMS (ESI) *m/e* calcd. for $C_{21}H_{25}N_3O_4$ ($M+NH_4^+$) 401.2183, found: 401.2189.

1,3-Di-azido-5,6-di-*O*-benzyl-2-deoxystreptamine (33). The initial synthesis of **33** was almost the same as that of **32**, yield: 35% for 3 steps. The other method is: after debenzoylation of **35** (447 mg, 0.64 mmol, in 2mL MeOH) with 30% NaOMe (in MeOH, 0.1 mL), the reaction mixture was neutralized with ion-exchange resin (Dowex 50, strong acid form), filtered, and concentrated to give crude diol. The crude diol was dissolved in CH_2Cl_2 (5 mL), pyridine (0.6 mL, 7 mmol) was added dropwise, followed by the addition of Tf_2O (0.5 mL, 2.8 mmol) at 0 ^{o}C. After stirring for 10 min, sat. $NaHCO_3$ was added to quench the reaction. The mixture was extracted with

EtOAc (20 mL), washed with water (20 mL), dried over Na_2SO_4, concentrated, and co-evaporated with toluene for three times. The crude product was dissolved in DMF (2 mL), NaN_3 (194 mg, 2.8 mmol) was added at 0 ^oC. After stirring for 5 h, the mixture was concentrated, diluted with EtOAc, washed with water, and concentrated again. The residue was dissolved in CH_2Cl_2/H_2O (18:1, 5 mL), DDQ (250 mg, 0.94 mmol) was added. And the mixture was stirred for 12 h at r.t., then quenched with sat. $NaHCO_3$, diluted with CH_2Cl_2 (20 mL), washed with water and brine. The extract was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 9:1) to give **33** (162 mg, 61% over four steps) as a colorless oil: R_f =0.38 (petroleum ether/acetone 3:1); $[\alpha]_D$ = +39.4 (*c* = 0.5, EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.38-7.25 (m, 10H, Ar), 4.94 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.89-4.84 (m, 2H, $PhCH_2$), 4.72 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 3.49-3.33 (m, 5H, H-1, H-3, H-4, H-5, H-6), 2.52 (s, 1H, OH), 2.17 (dt, 1H, *J* = 4.5, 13.0 Hz, H-2eq), 1.34 (q, 1H, *J* = 12.5 Hz, H-2ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.34, 137.84, 129.15, 128.92, 128.68, 128.56, 128.47, 128.26, 84.43, 84.09, 76.56, 76.20, 61.00, 60.25, 32.73 (C-2); HRMS (ESI) *m/e* calcd. for $C_{20}H_{22}N_6O_3$ ($M+NH_4^+$) 412.2092, found: 412.2091.

1D-(1,2,4,5/3)-1,5-Di-*O*-benzoyl-2,3-di-*O*-benzyl-1,2,3,4,5-cyclohexanepentol (34). To a solution of **25** (289 mg, 0.75 mmol) in pyridine (5 mL), BzCl (420 mg, 3 mmol) was added at 0 ^oC. After stirring for 12 h at room temperature, the reaction mixture was concentrated in vacuo, diluted with EtOAc, washed with sat. $NaHCO_3$,

dried over Na_2SO_4, concentrated to give yellow oil. The oil was dissolved in methanol (10 mL), $PdCl_2$ (25 mg, 0.14 mmol) was added at r.t. After stirring for 2 h, the reaction mixture was diluted with CH_2Cl_2, filtrated, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 4:1) to give **34** (365 mg, 88% over two steps) as a colorless oil: R_f = 0.42 (petroleum ether/EtOAc 1:1); $[\alpha]_D$ = +14.7 (*c* = 9.5, EtOAc); ^{1}H NMR (500 MHz, DMSO, 35 ^{o}C) δ = 7.93-7.91 (m, 2H, PhCO), 7.82-7.80 (m, 2H, PhCO), 7.60-7.52 (m, 2H, PhCO), 7.40-7.37 (m, 4H, Ar), 7.33-7.21 (m, 10H, Ar), 5.67-5.66 (m, 1H, H-1), 5.32 (dd, 1H, *J* = 3.0, 3.5 Hz, H-5), 5.26 (d, 1H, *J* = 5.5 Hz, OH), 4.88 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.83 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.70 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.59 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.12 (t, 1H, *J* = 9.5 Hz, H-3), 3.83 (ddd, 1H, *J*= 3.5, 6.0, 9.5 Hz, H-4), 3.77 (dd, 1H, *J*= 3.5, 9.5 Hz, H-2), 2.23 (dt, 1H, *J* = 3.5, 16.0 Hz, H-6eq), 1.81 (dt, 1H, *J* = 3.5, 16.0 Hz, H-6ax); ^{13}C NMR (75 MHz, DMSO) δ = 165.53 (PhCO), 165.25 (PhCO), 139.17, 138.46, 133.03, 129.99, 129.72, 129.34, 129.12, 128.33, 128.03, 127.92, 127.68, 127.42, 127.29, 127.13, 79.86, 78.34, 74.04, 72.66, 71.45, 71.31, 68.68, 28.61 (C-6); HRMS (ESI) *m/e* calcd. for $C_{34}H_{32}O_7$ ($M+H^+$) 553.2221, found: 553.2225.

1D-(1,2,4,5/3)-1,5-Di-*O*-benzoyl-2,3-di-*O*-benzyl-4-(4-methoxy)benzyl-1,2,3,4,5-cyclohexanepentol (35). To a solution of **34** (659 mg, 1.04 mmol) in dry CH_2Cl_2 (3 mL), a solution of freshly prepared $PMBOCNHCCl_3$ (3.1 g) in hexane (6 mL) was added. Freshly distilled $BF_3{\cdot}Et_2O$ (35 uL) was added slowly at 0 ^{o}C. After stirring for

10 min, no starting material was detected, Et_3N was added to quench the reaction. The reaction mixture was extracted with EtOAc (20 mL), washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 16:1) to give **35** (451 mg, 56%) as a white solid: R_f= 0.37 (petroleum ether/ EtOAc 4:1); $[\alpha]_D$ = -7.1(*c* = 1.3, EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.87-7.95 (m, 4H, PhCO), 7.5-7.45 (m, 2H, PhCO), 7.35-7.22 (m, 16H, Ar), 6.79-6.76 (m, 2H, Ar), 5.69-5.68 (m, 2H, H-1, H-5), 4.87 (s, 2H, $PhCH_2$), 4.78 (d, 1H, *J* =10.8 Hz, $PhCH_2$), 4.72 (d, 1H, *J* = 11.1 Hz, $PhCH_2$), 4.64 (d, 1H, *J* = 11.7 Hz, $PhCH_2$), 4.56 (d, 1H, *J* = 11.4 Hz, $PhCH_2$), 4.27 (t, 1H, *J* = 9.0 Hz, H-3), 3.76 (s, 3H, OCH_3), 3.75-3.63 (m, 2H, H-2, H-4), 2.56 (dt, 1H, *J* = 3.6, 15.6 Hz, H-6eq), 1.87 (d, 1H, *J* = 15.6 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.14 (PhCO), 159.09 (PMB), 138.67, 138.07, 132.75, 130.18, 130.13, 129.78, 129.50, 128.19, 128.12, 127.83, 127.53, 113.62, 79.76, 79.65, 77.92, 75.51, 72.42, 72.06, 68.39, 55.15 (OCH_3), 29.27 (C-6); HRMS (ESI) *m/e* calcd. for $C_{42}H_{40}O_8$ ($M+Na^+$) 695.2615, found: 695.2608.

1D-(1,2,4/3,5)-1,5-Di-*O*-benzoyl-2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-1,2,3,4,5-cyclohexanepentol (36). Following the procedure in synthesis of **23**, $Me_4NBH(OAc)_3$ was freshely prepared from Me_4NBH_4 (285 mg, 3.2 mmol) and AcOH (0.64 ml, 11.1 mmol) in THF (5 mL). To the mixture, a solution of **19** (298 mg, 0.64 mmol) in dry CH_3CN (5 mL) was added dropwise. After stirring for 12 h, TLC monitoring indicated no starting material left, sat. NH_4Cl was added to quench the

reaction. The reaction mixture was neutralized with sat. $KHCO_3$, extracted with EtOAc, dried over Na_2SO_4, concentrated to give a colorless oil. To this colorless oil in dry pyridine (2 mL), BzCl (0.3 mL) and cat. DMAP were added slowly at 0 ^oC. The mixture was allowed to stir at r.t. for 5 h, concentrated in vacuo. The residue was dissolved in EtOAc (20 mL), washed with sat. $NaHCO_3$, water and brine. The organic layer was collected, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 16:1) to give **36** (382 mg, 88% over two steps) as a white solid: R_f = 0.29 (petroleum ether/EtOAc 3:1); $[\alpha]_D$ = +35.0 (*c* = 0.5, EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ = 8.14-8.09 (m, 2H, PhCO), 7.99-7.97 (m, 2H, PhCO), 7.61-7.28 (m, 16H, Ar), 7.25-7.16 (m, 2H, Ar), 7.09-7.06 (m, 2H, Ar), 5.84 (m, 1H, , H-1), 5.57 (ddd, 1H, *J* = 5.0, 10.0, 10.0 Hz, H-5), 4.94 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.89-4.79 (m, 3H, $PhCH_2$), 4.70 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.60 (d, 1H, *J* = 11.4 Hz, $PhCH_2$), 4.04 (t, 1H, *J* = 9.5 Hz, H-3), 3.79-3.67 (m, 5H, H-2, H-4, OCH_3), 2.50 (dt, 1H, *J* = 4.5, 14.5 Hz, H-6eq), 1.73 (ddd, 1H, *J* = 2.5, 12.5, 14.5 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.67 (PhCO), 165.56 (PhCO), 159.15 (PMB), 138.62, 137.81, 133.18, 133.06, 130.21, 129.91, 129.77, 129.61, 128.46, 128.39, 128.32, 128.03, 127.67, 127.59, 113.68, 82.80, 81.74, 80.80, 76.05, 75.44, 72.15, 71.59, 66.92, 55.14 (OCH_3), 31.15 (C-6); HRMS (ESI) *m/e* calcd. for $C_{42}H_{40}O_8$ ($M+NH_4^+$) 690.3061, found: 690.3059.

1L-(1,2,4/3,5)-1,5-Di-azido-3,4-di-*O*-benzyl-2,3,4-cyclohexanetriol (37). To a solution of **36** (382 mg, 0.57 mmol) in MeOH (5 mL), 30% NaOMe (in MeOH, 0.1

mL) was added and the mixture was stirred for 1 h. The reaction mixture was neutralized with ion-exchanged resin (Dowex 50, strong acid form), filtered, and concentrated to give crude diol (207 mg). To a suspension of crude diol product in CH_2Cl_2 (5 mL), pyridine (0.36 mL, 4.4 mmol) was added, followed by the addition of Tf_2O (306 μL, 1.7 mmol) dropwise at 0 ^oC. After stirring for 10 min, sat. $NaHCO_3$ was added to quench the reaction. The reaction mixture was diluted with EtOAc (2×50 mL), washed with water and brine. The extract was dried over Na_2SO_4 and concentrated. The residue was coevaporated with toluene for three times before dissolved in DMF (5 mL). To the above mixture, NaN_3 (116 mg, 1.78 mmol) was added at 0 ^oC. After stirring for 12 h, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 6:1) to give **37** (91 mg, 41% over three steps): R_f = 0.40 (petroleum ether/EtOAc 2:1). To the crude diol described above, -OTf was substituted by N_3^- whereas PMB group was deprotected at the same time by the above procedure. $[\alpha]_D$ = +18.3 (*c* = 1.8, EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.39-7.25 (m, 10H, Ar), 4.97 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.88 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.84 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.69 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.00 (q, 1H, *J* = 3.5 Hz, H-1), 3.74-3.69 (m, 2H, H-3, H-5), 3.65 (dd, 1H, *J* = 3.5, 9.5 Hz, H-2), 3.33 (t, 1H, *J* = 9.0 Hz, H-4), 2.36 (d, 1H, *J* = 3.0 Hz, OH), 2.09 (dt, 1H, *J* = 4.5, 14.5 Hz, H-6eq), 1.44 (ddd, 1H, *J* = 3.0, 12.5, 14.5 Hz, H-6ax). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.94, 137.54, 128.74, 128.49, 128.16, 127.98, 127.88, 84.65, 81.70, 75.77, 75.57, 74.12,

59.97, 59.29, 31.54 (C-6).; HRMS (ESI) *m/e* calcd. for $C_{20}H_{22}N_6O_3$ ($M+NH_4^+$) 412.2092, found: 412.2095.

1D-(1,2,4/3,5)-1,5-Di-azido-2,3-di-*O*-benzyl-2,3,4-cyclohexanetriol (38). To a solution of **31** (78 mg, 0.17 mmol) in CH_2Cl_2 (5 mL), was added dry pyridine (0.14 mL, 1.7 mmol), followed by the addition of Tf_2O (0.11 mL, 0.67 mmol) dropwise at 0 ^oC. After stirring for 10 min, sat. $NaHCO_3$ was added to quench the reaction. The reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with water (10 mL) and brine (10 mL). The organic layer was collected, dried over Na_2SO_4, concentrated, and co-evaporated with toluene (5 mL×3). The residue was dissolved in dry DMF (2 mL), and NaN_3 (44 mg, 0.67 mmol) was added. After stirring for 5 h, the reaction mixture was concentrated, diluted with EtOAc, washed with water, and again concentrated to give a colorless oil. To a solution of this oil in CH_2Cl_2/H_2O (5 mL, 18:1), DDQ (71 mg, 0.30 mmol) was added. After stirring for 4 h at room temperature, sat. $NaHCO_3$ was added to quench the reaction. The mixture was extracted with CH_2Cl_2 (20 mL), dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 10:1) to give **38** (26 mg, 40% over three steps) as a colorless oil: R_f = 0.40 (petroleum ether/EtOAc 2:1); $[\alpha]_D$ = -0.9 (*c* = 0.2, EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.38-7.25 (m, 10H, Ar), 4.97 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.75-4.69 (m, 3H, $PhCH_2$), 3.98 (q, 1H, *J* = 3.5 Hz, H-1), 3.71 (t, 1H, *J* = 9.0 Hz, H-3), 3.60 (ddd, 1H, *J* = 4.5, 9.5, 11.5 Hz, H-5), 3.54 (dd, 1H, *J* = 3.5, 9.0 Hz, H-2), 3.39 (dt, 1H, *J* = 2.0, 9.0 Hz, H-4), 2.59 (d, 1H, *J* = 2.0 Hz, OH),

2.03 (dt, 1H, *J* = 4.5, 14.5 Hz, H-6eq), 1.34 (ddd, 1H, *J* = 2.5, 12.0, 14.5 Hz, H-6ax); ^{13}C-NMR (125 MHz, $CDCl_3$) δ = 138.19, 137.38, 128.63, 128.58, 128.09, 127.99, 127.91, 82.05, 81.06, 76.26, 75.77, 72.93, 58.89, 57.74, 31.11 (C-6); HRMS (ESI) *m/e* calcd. for $C_{20}H_{22}N_6O_3$ ($M+NH_4^+$) 412.2092, found: 412.2093.

1D-(1,2,4/3,5)-5-*O*-Benzoyl-2,3-di-*O*-benzyl-1-*O*-methyl-1,2,3,4,5-cyclohexanepentol (39). To a solution of **21** (306 mg, 0.77 mmol) in pyridine (5 mL), was added DMAP (ca. 0.05 equiv.), followed by the addition of BzCl (0.36 mL, 3.1 mmol) dropwise at 0 ^{o}C. After stirring for 5 h, the mixture was concentrated, extracted with EtOAc, washed with sat. $NaHCO_3$ and water. The organic layer was collected and dried over Na_2SO_4, filtered and concentrated in vacuo. To a solution of the above crude product in MeOH (10 mL), was added $PdCl_2$ (36 mg, 0.21 mmol). After stirring at room temperature for 2 h, the mixture was diluted with CH_2Cl_2, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 6:1) to give **39** (351 mg, 98%) as a white solid: R_f = 0.48 (petroleum ether/EtOAc 2:1); $[\alpha]_D$ = +10.9 (*c* = 1.1, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.04-8.00 (m, 2H, PhCO), 7.57-7.51 (m, 1H, Ar), 7.44-7.29 (m, 12H, Ar), 5.25 (ddd, 1H, *J* = 4.5, 9.0, 11.0 Hz, H-5), 5.00 (d, 1H, *J* = 11.1 Hz, $PhCH_2$), 4.79-4.70 (m, 3H, $PhCH_2$), 3.90 (t, 1H, *J* = 9.0 Hz, H-3), 3.79-3.72 (m, 2H, H-1, H-4), 3.54 (dd, 1H, *J* = 3.0, 9.0 Hz, H-2), 3.49 (s, 3H, OCH_3), 2.54 (d, 1H, *J* = 2.7 Hz, OH), 2.53 (dt, 1H, *J* = 4.5, 14.1 Hz, H-6eq), 1.39 (ddd, 1H, *J* = 2.4, 11.1, 14.1 Hz , H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.15 (PhCO), 138.59, 138.06, 132.99, 130.08,

129.62, 128.52, 128.41, 128.30, 127.99, 127.88, 127.79, 81.58, 81.27, 75.53, 74.67, 72.51, 71.73, 57.20 (OCH_3), 28.73 (C-6); elemental analysis calcd. (%) for $C_{28}H_{30}O_6$: C 72.71, H 6.54, found: C, 72.44, H, 6.49; HRMS (ESI) *m/e* calcd. for $C_{28}H_{30}O_6$ ($M+Na^+$) 485.1935, found: 485.1942.

1D-(1,2,4,5/3)-2-*O*-Allyl-1-*O*-benzoyl-2,3-di-*O*-benzyl-5-*O*-methyl-1,2,3,4,5-cyclo hexanepentol (40). To a solution of **22** (1.083 g, 2.7 mmol) and DMAP (16.5 mg, 0.14 mmol) in pyridine (10 mL), BzCl (0.93 mL, 8.1 mmol) was added dropwise at 0 ^oC. After stirring for 5 h, the mixture was concentrated in vacuo. The residue was dissolved in EtOAc (50 mL), washed with sat. $NaHCO_3$ and water. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 6:1) to give **40** (1.339 g, 98%) as a white solid: R_f = 0.52 (petroleum ether/EtOAc 2:1); $[\alpha]_D$ = -6.6 (*c* = 0.6, EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ = 8.15-8.12 (m, 2H, PhCO), 7.57-7.52 (m, 1H, Ar), 7.45-7.25 (m, 12H, Ar), 5.88 (ddt, 1H, *J* = 6.0, 10.5, 17.5 Hz, =CH-), 5.57-5.56 (m, 1H, H-1), 5.24 (d, 1H, *J* = 17.1 Hz, $=CH_2$), 5.11 (d, 1H, *J* = 7.5 Hz, $=CH_2$), 4.90-4.72 (m, 4H, $PhCH_2$), 4.25-4.08 (m, 3H, H-3, $=C-CH_2-$), 3.67-3.66 (m, 1H, H-5), 3.50-3.46 (m, 2H, H-2, H-4), 3.30 (s, 3H, OCH_3), 2.50 (dt, 1H, *J* = 3.6, 15.6 Hz, H-6eq), 1.41 (d, 1H, *J* = 15.6 Hz, H-6ax); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 166.20(PhCO), 138.90, 138.51, 134.91, 133.63, 132.88, 130.34, 130.13, 129.96, 128.28, 127.98, 127.64, 127.55, 117.15, 81.14, 80.11, 78.72, 76.04, 75.90, 72.89, 71.59, 68.60, 56.83 (OCH_3),

26.42 (C-6); MS (ESI) *m/e* calcd for $C_{31}H_{34}O_6$ ($M+Na^+$) 525, found: 525; elemental analysis calcd (%) for $C_{31}H_{34}O_6$: C 74.08, H 6.82, found: C 74.11, H 6.99.

1D-(1,2,4,5/3)-5-*O*-Benzoyl-2,3-di-*O*-benzyl-1-*O*-methyl-1,2,3,4,5-cyclohexanepentol (41). To a solution of **40** (31 mg, 0.06 mmol) in MeOH (1 mL), was added $PdCl_2$ (3 mg, 0.018 mmol) at room temperature. After stirring for 3 h, the reaction mixture was diluted with CH_2Cl_2, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 4:1) to give **41** (25 mg, 87%) as a colorless oil: R_f= 0.42 (petroleum ether/EtOAc 2:1); $[\alpha]_D$ = -1.9 (*c* = 2.1, EtOAc). Acceptor **41** was not stable in $CDCl_3$ or CD_3OD at room temperature. Besides, it is hard to identify the structure from its ^1H NMR. For further identification, allyl group was reintroduced by the following procedure: To a mixture of **41** (33 mg, 0.07 mmol) and freshly prepared $AllylOCNHCCl_3$ (70 mg) in CH_2Cl_2/ hexane (1:2, 2 mL) with 4 Å molecular sieves, TfOH (7 μL) was added slowly at 0 ^oC. Stirring the mixture for 12 h from 0 ^oC to room temperature, Et_3N was added to quench the reaction. The reaction mixture was filtered and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 6:1) to give **40*** (25 mg, 70%) as a white solid: R_f = 0.52 (petroleum ether/EtOAc 2:1). From the NMR spectra it was find the allylation product **40*** and **40** are the same compound. It was demonstrated that the benzoyl group did not migrate during the deprotection of allyl group. Compound **41** was directly used for the glycosyl coupling reaction.

1D-(1,2,4/3,5)-1,5-Di-*O*-benzoyl-2,3-di-*O*-benzyl-1,2,3,4,5-cyclohexanepentol (42). To a solution of **23** (261 mg, 0.44 mmol) in methanol (5 mL), was added $PdCl_2$ (25 mg, 0.14 mmol) at room temperature. After stirring for 2 h, no starting material was detected. The reaction mixture was diluted with CH_2Cl_2, filtrated, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 8:1) to give **42** (237 mg, 98%) as a colorless oil: R_f = 0.26 (petroleum ether/EtOAc 2:1); $[\alpha]_D$ = -22.4 (*c* = 2.1, MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.11-8.08 (m, 2H, PhCO), 8.03-8.01 (m, 2H, PhCO), 7.63-7.25 (m, 16H, Ar), 5.86 (dt, 1H, *J* = 2.4, 4.8 Hz, H-1), 5.48 (ddd, 1H, *J* = 4.8, 8.7, 11.1 Hz, H-5), 4.97 (d, 1H, *J* = 11.1 Hz, $PhCH_2$), 4.84 (d, 1H, *J* = 11.1 Hz, $PhCH_2$), 4.74 (d, 1H, *J* = 11.1 Hz, $PhCH_2$), 4.60 (d, 1H, *J* = 11.1 Hz, $PhCH_2$), 3.96-3.82 (m, 2H, H-3, H-4), 3.74 (dd, 1H, *J* = 3.0, 8.7 Hz, H-2), 2.74 (d, 1H, *J* = 2.7 Hz, OH), 2.50 (dt, 1H, *J* = 4.8, 14.1 Hz, H-6eq), 1.81 (ddd, 1H, *J* = 2.4, 10.8, 14.1 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.97 (PhCO), 165.61 (PhCO), 138.24, 137.57, 133.24, 133.11, 129.88, 129.68, 128.51, 128.38, 128.02, 127.88, 127.79, 80.64, 80.18, 75.39, 74.38, 72.13, 71.45, 67.08, 30.62 (C-6); HRMS (ESI) *m/e* calcd. for $C_{34}H_{32}O_7$ ($M+Na^+$) 575.2040, found: 575.2034.

1L-(1,2,4/3,5)-1,5-Di-*O*-benzoyl-3,4-di-*O*-benzyl-1,2,3,4,5-cyclohexanepentol (43). To a solution of **24** (112 mg, 0.24 mmol) in methanol (2 mL), 30% MeONa (in MeOH, 0.1 mL) was added dropwise. The reaction mixture was neutralized with ion-exchange resin (Dowex 50, strong acid form), filtered, and concentrated to give yellow oil. The oil was dissolved in pyridine (5 mL), BzCl (0.17 mL, 1.44 mmol) was

added at 0 °C, and the mixture was stirred for 6 h. The reaction mixture was concentrated in vacuo, diluted with EtOAc (20 mL), and washed with sat. $KHCO_3$. The organic layer was collected and concentrated to give a yellow oil. To the solution of this oil in methanol (2 mL), $PdCl_2$ (13 mg, 0.07 mmol) was added at room temperature. After stirring for 2 h, the mixture was diluted with CH_2Cl_2, filtered, and concentrated. The resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 6:1) to give **43** (118 mg, 89% over three steps) as a white solid: R_f = 0.31 (petroleum ether/EtOAc 2:1); $[\alpha]_D$ = -24.1 (*c* = 1.7, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.06-8.04 (m, 2H, PhCO), 8.01-7.99 (m, 2H, PhCO), 7.60-7.54 (m, 2H, Ar), 7.47-7.40 (m, 4H, Ar), 7.36-7.28 (m, 5H, Ar), 7.20-7.19 (m, 5H, Ar), 5.64-5.62 (dt, 1H, *J* = 2.5, 4.5 Hz, H-1), 5.58 (ddd, 1H, *J* = 5.0, 8.5, 9.0 Hz, H-5), 4.94 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.85-4.79 (m, 3H, $PhCH_2$), 3.96 (t, 1H, *J* = 8.5 Hz, H-4), 3.91 (dd, 1H, *J* = 3.0, 9.0 Hz, H-2), 3.83 (t, 1H, *J* = 8.5 Hz, H-3), 2.40-3.00 (br, 1H, OH), 2.52 (dt, 1H, *J* = 4.5, 14.5 Hz, H-6eq), 1.83 (ddd, 1H, *J* = 2.5, 11.0, 14.0 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.02 (PhCO), 165.57 (PhCO), 138.05, 137.60, 133.23, 133.13, 129.83, 129.73, 129.60, 128.54, 128.42, 128.39, 128.12, 128.08, 127.96, 127.84, 82.60, 81.18, 75.53, 75.43, 72.72, 71.68, 70.01, 30.70 (C-6); MS (ESI) *m/e* calcd. for $C_{34}H_{32}O_7$: 575 ($M+Na^+$), found: 575; elemental analysis calcd (%) for $C_{34}H_{32}O_7$: C 73.62, H 5.84, found: C 73.62, H 5.99.

1L-(1,3,5/2,4)-1,5-Di-*O*-benzoyl-2,3-di-*O*-benzyl-1,2,3,4,5-cyclohexanepentol (44). To a solution of **30** (48 mg, 0.07 mmol) in CH_2Cl_2/H_2O (2 mL, 18:1), was added

DDQ (26 mg, 0.11 mmol) at room temperature. After stirring for 2 h, sat. $NaHCO_3$ was added to quench the reaction. The solution was diluted with CH_2Cl_2 (20 mL) and washed with brine (20 mL). The organic layer was collected, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 10:1) to give **44** (24 mg, 62%) as a white solid: R_f = 0.30 (petroleum ether/EtOAc 3:1); $[\alpha]_D$ = -33.6 (*c* = 0.1, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.03-7.98 (m, 4H, PhCO), 7.58-7.53 (m, 2H, Ar), 7.44-7.40 (m, 4H, Ar), 7.34-7.29 (m, 5H, Ar), 7.18 (s, 5H, Ar), 5.30 (ddd, 1H, *J* = 4.5, 9.0, 11.5 Hz, H-1), 5.17 (ddd, 1H, *J* = 5.0, 9.5, 12.0 Hz, H-5), 4.97 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.85-4.78 (m, 3H, $PhCH_2$), 3.87 (t, 1H, *J* = 9.0 Hz, H-3), 3.81 (t, 1H, *J* = 9.0 Hz, H-4), 3.58 (t, 1H, *J* = 9.0 Hz, H-2), 2.60 (dt, 1H, *J* = 4.5, 12.5 Hz, H-6eq), 2.53 (br, 1H, OH), 1.80 (q, 1H, *J* = 12.0 Hz, H-6ax); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 165.92 (PhCO), 165.42 (PhCO), 138.18, 137.82, 133.15, 133.16, 129.82, 129.71, 129.63, 128.61, 128.41, 128.35, 128.31, 128.04, 127.97, 127.72, 82.85, 82.68, 75.83, 75.42, 75.05, 71.04, 70.84, 31.94 (C-6)； HRMS (ESI) *m/e* calcd. for $C_{34}H_{32}O_7$ ($M+Na^+$) 575.2040, found: 575.2030.

(2*R*,3*S*,4*R*,5*R*)-2-*O*-Allyl-3-*O*-benzyl-5-*O*-methyl-7-oxa-bicyclo[2.2.1]heptane (46). To a solution of **21** (14 mg, 0.04 mmol) in CH_2Cl_2 (1 mL), was added dry pyridine (32.6 μL, 0.4 mmol) followed by the addition of Tf_2O (27.8 μL, 0.16 mmol) dropwise at 0 ^oC. After 1 h, TLC monitoring showed the completion of the reaction, and sat. $NaHCO_3$ was added to quench the reaction. The reaction mixture was diluted

with CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 6:1) to give **46** (10 mg, 99%) as a white solid: R_f = 0.40 (petroleum ether/EtOAc 2:1); $[\alpha]_D$ = -49.2 (*c* = 0.7, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.39-7.32 (m, 5H, Ar), 5.90 (ddt, 1H, *J* = 6.0, 10.5, 17.5 Hz, =CH-), 5.25 (dq, 1H, *J* = 1.5, 17.5 Hz, =CH_2), 5.18 (dq, 1H, *J* = 1.5, 6.0 Hz, =CH_2), 4.56-4.50 (m, 4H, H-1, H-2, PhCH_2), 4.07 (dd, 1H, *J* = 2.4, 6.9 Hz, H-5), 3.99-3.92 (m, 2H, =C-CH_2), 3.84 (dt, 1H, *J* = 1.5, 6.5 Hz, H-3), 3.35 (d, 1H, *J* = 1.5 Hz, H-4), 3.26 (s, 3H, OCH_3), 1.87 (dd, 1H, *J* = 7.0, 13.0 Hz, H-6ax), 1.72 (ddq, 1H, *J* = 1.5, 6.5, 13.0 Hz, H-6eq); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.46, 134.27, 128.52, 128.03, 127.85, 117.45, 85.65, 84.06, 79.97, 79.35, 72.85, 69.96, 56.49 (OCH_3), 35.34 (C-6); HRMS (ESI) *m/e* calcd. for $C_{17}H_{30}O_6$ ($M+Na^+$) 313.1410, found: 313.1408.

p-Methylphenyl

2,6-di-azido-3,4-*O*-isopropylidene-1-thio-2,6-di-deoxy-β-D-galactopyranoside

(51). To a solution of **48**[3] (762 mg, 2.27 mmol) in 2,2-dimethoxypropane (10 mL), was added CSA (29 mg, 0.12 mmol) at room temperature. After stirring overnight, Et_3N was added to neutralize the reaction. The reaction mixture was concentrated and coevaperated with toluene for three times. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 15:1) to give **51** (372 mg, 50%) as a white solid: R_f = 0.41 (petroleum ether/EtOAc 4:1); $[\alpha]_D$ = +145.5 (*c* = 4.2, EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.49 (d, 2H, *J* = 7.9 Hz, Ar), 7.15 (d, 2H, *J*

= 7.9 Hz, Ar), 4.33 (d, 1H, *J* = 10.5 Hz, H-1), 4.11-4.06 (m, 2H, H-3, H-4), 3.81 (ddd, 1H, *J* = 2.1, 5.4, 5.7 Hz, H-5), 3.66 (dd, 1H, *J* = 7.8, 12.7 Hz, H-6a), 3.44-3.32 (m, 2H, H-2, H-6b), 2.35 (s, 3H, $PhCH_3$), 1.42 (s, 3H, CH_3), 1.34 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.78, 133.97, 129.74, 127.28, 110.79 (isopropylidene), 85.91 (C-1), 78.25, 75.28, 72.69, 63.55, 51.13, 27.97 (isopropyliden), 26.23 (isopropyliden), 21.14 (CH_3); MS (ESI-TOF) *m/e* calcd. for $C_{16}H_{20}N_6O_3S$ 399 ($M+Na^+$), found 399; elemental analysis calcd (%) for $C_{16}H_{20}N_6O_3S$: C 51.06, H 5.36, N, 22.23, found: C 51.27, H 5.55, N 22.09.

p-Methylphenyl 2,6-di-azido-3,4-di-O-acetyl-1-thio-2,6-di-deoxy-α -D-mannopyranoside (52). To a solution of **49**[4] (530 mg, 1.2 mmol) in MeOH (5 mL), 30% NaOMe in MeOH (0.1 mL) was added. The solution was neutralized with ion-exchange resin (Dowex 50, strong acid form), filtered, and concentrated to give colorless oil. To this oil in pyridine (5 mL), TsCl (462 mg, 2.4 mmol) was added at 0 ^oC, and the mixture was stirred overnight. The reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with sat. $NaHCO_3$ and brine. The organic layer was collected and concentrated. The resulting residue was dissolved in DMF (5 mL), NaN_3 (112 mg, 1.7 mmol) was added, and the reaction mixture was heated at 80 ^oC for 10 h. The mixture was concentrated in vacuo, diluted with EtOAc, and washed with water. The organic layer was dried over Na_2SO_4 and concentrated. The residue was mixed with pyridine (5 mL), Ac_2O (0.28 mL, 2.7 mmol) was then added at 0 ^oC, and the mixture was stirred overnight at room temperature. The reaction mixture was

concentrated in vacuo. The resulting residue was dissolved in EtOAc, washed with sat. $NaHCO_3$ and brine. The organic layer was collected, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 6:1) to give **52** (258 mg, 51% over four steps) as a white solid: R_f = 0.36 (petroleum ether/EtOAc 4:1); mp 64-65 ^oC; $[\alpha]_D$ = +8.7 (*c* = 4.1, EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.40 (d, 2H, *J* = 8.0 Hz, Ar), 7.16 (d, 2H, *J* = 8.0 Hz, Ar), 5.43 (d, 1H, *J* = 1.5 Hz, H-1), 5.35 (dd, 1H, *J* = 4.0, 9.5 Hz, H-3), 5.29 (t, 1H, *J* = 9.5 Hz, H-4), 4.44 (ddd, 1H, *J* = 2.5, 7.0, 9.5 Hz, H-5), 4.30 (dd, 1H, *J* = 1.5, 4.0 Hz, H-2), 3.40 (dd, 1H, *J* = 7.0, 13.5 Hz, H-6a), 3.26 (dd, 1H, *J* = 2.5, 13.5 Hz, H-6b), 2.34 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.08 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.87 ($COCH_3$), 169.60 ($COCH_3$), 138.68, 132.52, 130.11, 128.38, 86.09 (C-1), 70.88, 67.18, 62.64, 51.07, 21.11 (CH_3), 20.64 ($COCH_3$), 20.49($COCH_3$); MS (ESI-TOF) *m/e* calcd. for $C_{16}H_{20}N_6O_3S$ 443 ($M+Na^+$), found 443; elemental analysis calcd (%) for $C_{16}H_{20}N_6O_3S$: C 48.56, H 4.79, N 19.99, found: C 48.83, H 5.07, N 19.82.

General procedure for the preparation of pseudodisaccharides 53-58 and 60-65. Donor **50**[5] (0.3 mmol) and acceptor (0.2 mmol) were coevaporated twice with toluene and further dried under vaccum. To a solution of donor and acceptor in CH_2Cl_2 (5 mL), 4 Å molecular sieves (600 mg) and *N*-iodosucccinimide (0.3 mmol) were added, and the mixture was stirred for 30 min before cooled to -40 ^oC under argon. Trifluoromethanesulfonic acid (0.03 mmol, 1N in Et_2O) was added, the temperature

was then allowed to rise to -20 ^{o}C, and maintained at this temperature for 30 min to 3 h until donor disappeared by TLC monitoring. Et_3N was added to quench the reaction. The reaction mixture was filtered, washed with CH_2Cl_2, and concentrated. The residue was purified by column chromatography on silica gel. To the disaccharides with benzoyl protective group, 30% NaOMe in MeOH was added to give **53-58**. Compound **65** was obtained by the coupling of donor **51** and acceptor **33** followed by the deprotection of acetal group with 80% AcOH/H_2O at 60 ^{o}C for 2 h.

1L-(1,2,4,5/3)-2-*O*-(2',6'-Di-azido-3',4'-di-*O*-benzyl-2',6'-di-deoxy-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-1,2,3,4,5-cyclohexanepentol (53). Yield: 80%; $[\alpha]_D$ = +19.9 (*c* = 3.2, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.41-7.25 (m, 20H, Ar), 5.28 (d, 1H, *J* = 3.5 Hz, H-1'), 5.02 (d, 1H, *J* = 10.0 Hz, $PhCH_2$), 4.92-4.85 (m, 4H, $PhCH_2$), 4.74 (d, 1H, *J* = 12.0 Hz, $PhCH_2$), 4.69 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.59 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.18-4.10 (m, 4H, H-1 or H-5, H-2 or H-4, H-3 H-5'), 4.05 (dd, 1H, *J* = 9.0, 10.0 Hz, H-3'), 3.58 (dd, 1H, *J* = 3.5, 10.0 Hz, H-2'), 3.52-3.44 (m, 5H, H-1 or H-5, H-2 or H-4, H-4', H-6a', OH), 3.33 (dd, 1H, *J* = 6.0, 13.5 Hz, H-6b'), 3.12 (d, 1H, *J* = 2.5 Hz, OH), 2.32 (dt, 1H, *J* = 3.5, 15.5 Hz, H-6eq), 1.53 (d, 1H, *J* =15.5 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.74, 137.75, 137.58, 128.53, 128.36, 128.12, 127.98, 127.90, 127.83, 127.74, 127.53, 99.14 (C-1'), 82.10, 82.16, 80.37, 78.94, 78.18, 75.84, 75.59, 75.13, 72.78, 70.93, 70.34, 68.50, 63.86, 51.10, 31.52 (C-6); MS (ESI-TOF) *m/e* calcd. for $C_{40}H_{44}N_6O_8$ 754 ($M+NH_4^+$), found 754;

elemental analysis calcd (%) for $C_{40}H_{44}N_6O_8$: C 65.20, H 6.02, N 11.41, found: C, 65.09, H, 6.00, N, 11.19.

1D-(1,3,5/2,4)-2-*O*-(2',6'-Di-azido-3',4'-di-*O*-benzyl-2',6'-di-deoxy-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-1,2,3,4,5-cyclohexanepentol (54). Yield: 77%; $[\alpha]_D$ = +0.6 (*c* = 0.3, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38-7.27 (m, 20H, Ar), 5.37 (d, 1H, *J* = 3.5 Hz, H-1'), 5.02 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.94 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.88-4.86 (m, 4H, $PhCH_2$), 4.67 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.59 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.21 (ddd, 1H, *J* = 2.5, 5.5, 10.0 Hz, H-5'), 3.97 (dd, 1H, *J* = 9.0, 10.0 Hz, H-4'), 3.64-3.46 (m, 7H, H-1, H-2, H-3 or H-4, H-5, H-2', H-3', H-6a'), 3.37-3.33 (m, 2H, H-3 or H-4, H-6b'), 2.96 (br, 1H, OH), 2.24 (dt, 1H, *J* = 4.5, 12.5 Hz, H-6eq), 1.62 (br, 1H, OH), 1.48 (q, 1H, *J* = 12.5 Hz, H-6ax); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 138.36, 138.20, 137.44, 137.38, 128.69, 128.59, 128.49, 128.42, 128.16, 128.10, 128.02, 127.92, 127.87, 127.54, 127.29, 98.28 (C-1'), 86.17, 85.48, 82.68, 80.27, 78.74, 75.57 (×2), 75.47, 75.28, 70.82, 68.51, 68.26, 63.76, 51.22, 36.43 (C-6); HRMS (ESI) *m/e* calcd. for $C_{40}H_{44}N_6O_8$ ($M+Na^+$) 759.3113, found: 759.3124.

1D-(1,2,4/3,5)-4-*O*-(2',6'-Di-azido-3',4'-di-*O*-benzyl-2',6'-di-deoxy-α-D-glucopyranosyl)-2,3-di-*O*-benzyl-1,2,3,4,5-cyclohexanepentol (55). Yield: 70%; $[\alpha]_D$ = +76.5 (*c* = 0.3, EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40-7.24 (m, 20H, Ar), 5.39 (d, 1H, *J* = 3.6 Hz, H-1'), 4.97-4.85 (m, 4H, $PhCH_2$), 4.71-4.66 (m, 2H, $PhCH_2$), 4.56 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.26-4.22 (m, 1H, H-5'), 4.13-4.07 (m, 1H, H-1), 4.12-3.96

(m, 2H, H-3 or H-4, H-3'), 3.85 (t, 1H, *J* = 9.0 Hz, H-4'), 3.56-3.43 (m, 5H, H-2, H-3 or H-4, H-5, H-2', H-6a'), 3.33 (dd, 1H, *J* = 5.1, 13.2 Hz, H-6b'), 2.25 (dt, 1H, *J* = 4.2, 13.8 Hz, H-6eq), 1.53 (ddd, 1H, *J* = 2.4, 13.0, 13.8 Hz, H-6ax). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.70, 137.65, 137.50, 137.43, 128.56, 128.49, 128.34, 128.11, 128.01, 127.87, 127.52, 127.45, 98.14 (C-1'), 85.13, 83.01, 80.49, 80.24, 78.75, 75.55, 75.24, 72.73, 70.74, 67.41, 65.60, 63.76, 51.13, 34.47 (C-6); MS (ESI-TOF) *m/e* calcd. for $C_{40}H_{44}N_6O_8$ 754 ($M+NH_4^+$), found: 754; elemental analysis calcd (%) for $C_{40}H_{44}N_6O_8$: C 65.20, H 6.02, N 11.41, found: C 65.07, H 5.99, N 11.19.

1L-(1,2,4/3,5)-2-*O*-(2',6'-Di-azido-3',4'-di-*O*-benzyl-2',6'-di-deoxy-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-1,2,3,4,5-cyclohexanepentol (56). Yield: 86%; $[\alpha]_D$ = +8.7 (*c* = 0.3, EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39-7.25 (m, 20H, Ar), 5.35 (d, 1H, *J* = 3.9 Hz, H-1'), 5.02-4.95 (m, 2H, $PhCH_2$), 4.91-4.84 (m, 4H, $PhCH_2$), 4.70 (d, 1H, *J* = 11.7 Hz, $PhCH_2$), 4.58 (d, 1H, *J* = 11.1 Hz, $PhCH_2$), 4.11-4.12 (m, 1H, H-1), 4.03-3.89 (m, 4H, H-3 or H-4, H-3', H-4', H-5'), 3.72 (dd, 1H, *J* = 2.7, 9.6 Hz, H-2), 3.50-3.42 (m, 3H, H-3 or H-4, H-5, H-6a'), 3.34-3.27 (m, 2H, H-2', H-6b'), 2.39-2.33 (2×br, 2H, OH), 2.22 (dt, 1H, *J* = 4.2, 13.8 Hz, H-6eq), 1.45 (ddd, 1H, *J* = 2.0, 12.0, 13.5 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.43, 138.38, 137.33, 137.19, 128.59, 128.49, 128.40, 128.18, 128.05, 127.88, 127.74, 127.50, 98.59 (C-1'), 86.54, 81.20, 81.10, 80.22, 78.76, 75.58, 75.44, 75.38, 75.29, 71.23, 68.10, 67.76, 63.59, 51.09, 34.24 (C-6); HRMS (ESI) *m/e* calcd. for $C_{40}H_{44}N_6O_8$ ($M+Na^+$) 759.3113, found: 759.3116.

1D-(1,2,4/3,5)-4-*O*-(2',6'-Di-azido-3',4'-di-*O*-benzyl-2',6'-di-deoxy-α-D-glucopyranosyl)-2,3-di-*O*-benzyl-1-*O*-methyl-1,2,3,4,5-cyclohexanepentol (57). Yield: 70%; $[\alpha]_D$ = +72.7 (*c* = 4.4, EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.38-7.26 (m, 20H, Ar), 5.37 (d, 1H, *J* = 3.6 Hz, H-1'), 4.99-4.84 (m, 5H, $PhCH_2$), 4.74-4.65 (m, 2H, $PhCH_2$), 4.59 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.18 (ddd, 1H, *J* = 2.4, 5.1, 10.2 Hz, H-5'), 4.00 (dd, 1H, *J* = 9.0, 10.2 Hz, H-4'), 3.91 (t, 1H, *J* = 9.0 Hz, H-3'), 3.84-3.80 (m, 1H, H-1), 3.60 (m, 1H, H-5), 3.56-3.41 (m, 8H, H-2, H-3, H-4, H-2', H-6a', OCH_3), 3.33 (dd, 1H, *J* = 5.1, 13.2 Hz, H-6b'), 2.90 (d, 1H, *J* = 3.9 Hz, OH), 2.28 (dt, 1H, *J* = 4.5, 14.4 Hz, H-6eq), 1.23 (t, 1H, *J* = 14.4 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.85, 138.13, 137.47, 137.42, 128.56, 128.49, 128.36, 128.27, 128.12, 127.99, 127.90, 127.86, 127.71, 127.63, 127.34, 98.21 (C-1'), 85.97, 82.70, 80.44, 80.14, 78.76, 75.53, 75.21, 74.75, 72.69, 70.75, 67.62, 63.76, 57.54 (OCH_3), 51.17, 31.97 (C-6); HRMS (ESI) *m/e* calcd. for $C_{41}H_{46}N_6O_8$ ($M+Na^+$) 773.3269, found: 773.3262.

1L-(1,2,4,5/3)-2-*O*-(2',6'-Di-azido-3',4'-di-*O*-benzyl-2',6'-di-deoxy-α-D-glucopyranosyl)-3,4-di-*O*-benzyl-5-*O*-methyl-1,2,3,4,5-cyclohexanepentol (58). Yield: 70%; $[\alpha]_D$ = +34.8 (*c* = 2.4, EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42-7.24 (m, 20H, Ar), 5.23 (d, 1H, *J* = 3.6 Hz, H-1'), 5.02 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.91-4.83 (m, 4H, $PhCH_2$), 4.77 (d, 1H, *J* = 12.0 Hz, $PhCH_2$), 4.67 (d, 1H, *J* = 11.7 Hz, $PhCH_2$), 4.59 (d, 1H, *J* = 11.4 Hz, $PhCH_2$), 4.22-4.06 (m, 4H, H-1 or H-3, H-3', H-4', H-5'), 3.70-3.65 (m, 2H, H-1 or H-3, OH), 3.54-3.41 (m, 8H, H-4, H-5, H-6, H-2', H-6a',

OCH_3), 3.34 (dd, 1H, *J* = 5.1, 13.2 Hz, H-6b'), 2.27 (d, 1H, *J* = 15.0 Hz, H-6eq), 1.23 (d, 1H, *J* = 14.4 Hz, H-6ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.80, 138.14, 137.66, 128.41, 128.28, 128.09, 127.92, 127.87, 127.82, 127.75, 127.64, 127.44, 99.33 (C-1'), 82.99, 82.70, 80.35, 78.99, 78.61, 78.35, 75.77, 75.52, 75.00, 73.13, 70.76, 70.17, 63.97, 59.06 (OCH_3), 51.10, 29.71 (C-6); HRMS (ESI) *m/e* calcd. for $C_{41}H_{46}N_6O_8$ ($M+Na^+$) 773.3269, found: 773.3254.

1L-(1,3,4/2,6)-1-*O*-(2',6'-Di-azido-3',4'-di-*O*-benzyl-2',6'-di-deoxy-α-D-glucopyranosyl)-2,3-di-*O*-benzyl-4,6-di-azido-1,2,3-cyclohexanetriol (60). Yield: 56%; $[\alpha]_D$ = +60.0 (*c* = 0.3, EtOAc); ^1H NMR (500 MHz, $CDCl_3$) δ = 7.37-7.24 (m, 20H, Ar), 5.59 (d, 1H, *J* = 4.0 Hz, H-1'), 5.05 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.91-4.86 (m, 4H, $PhCH_2$), 4.70 (s, 2H, $PhCH_2$), 4.61 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.07 (ddd, 1H, *J* = 2.5, 4.0, 9.5 Hz, H-5'), 4.01 (dd, 1H, *J* = 9.0, 10.0 Hz, H-3'), 3.99 (dd, 1H, *J* = 3.5, 7.7 Hz, H-2'), 3.95 (t, 1H, *J* = 9.5 Hz, H-4'), 3.65-3.58 (m, 2H, H-1 or H-2, H-4), 3.53-3.46 (m, 3H, H-1 or H-2, H-6, H-6a'), 3.36 (dd, 1H, *J* = 4.5, 13.0 Hz, H-6b'), 3.31 (dd, 1H, *J* = 4.0, 10.0 Hz, H-3), 2.15 (dt, 1H, *J* = 4.5, 14.5 Hz, H-5eq), 1.47 (ddd, 1H, *J* = 3.0, 12.0, 14.5 Hz, H-5ax); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 138.24, 137.68 (×2), 137.22, 128.59, 128.48, 128.41, 128.14, 128.05, 128.01, 127.90, 127.74, 127.58, 127.45, 97.74 (C-1'), 82.93, 81.71, 80.04, 78.71, 78.26, 75.47, 75.35, 75.00, 73.19, 70.89, 63.28, 58.28, 57.27, 51.00, 31.17 (C-5); HRMS (ESI) *m/e* calcd. for $C_{40}H_{42}N_{12}O_6$ ($M+Na^+$) 809.3242, found: 809.3241.

1L-(1,3,6/2,4)-1-*O*-(2',6'-Di-azido-3',4'-di-*O*-benzyl-2',6'-di-deoxy-α-D-glucopyranosyl)-4,6-di-azido-2,3-di-*O*-benzyl-1,2,3-cyclohexanetriol (61). Yield: 50%; $[\alpha]_D$ = +82.1 (*c* = 0.6, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.36-7.25 (m, 20H, Ar), 5.37 (d, 1H, *J* = 4.0 Hz, H-1'), 5.01 (d, 1H, *J* = 11.0 Hz, $PhCH_2$), 4.93 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.88-4.82 (m, 5H, $PhCH_2$), 4.56 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.06 (dd, 1H, *J* = 3.0, 6.0 Hz, H-6), 4.03 (dd, 1H, *J* = 9.0, 10.5 Hz, H-3'), 3.97 (t, 1H, *J* = 9.0 Hz, H-4'), 3.91 (ddd, 1H, *J* = 2.5, 7.0, 9.5 Hz, H-5'), 3.85 (dd, 1H, *J* = 3.5, 9.5 Hz, H-2'), 3.71 (ddd, 1H, *J* = 4.5, 9.5, 12.5 Hz, H-4), 3.45-3.32 (m, 4H, H-1, H-2, H-3, H-6a'), 3.27 (dd, 1H, *J* = 7.0, 12.5 Hz, H-6b'), 2.11 (dt, 1H, *J* = 4.0, 14.0 Hz, H-5eq), 1.45 (ddd, 1H, *J* = 2.0, 11.5, 13.5 Hz, H-5ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.24, 137.56, 137.44, 137.39, 128.56, 128.44, 128.16, 128.05, 127.88, 127.60, 127.32, 99.02 (C-1'), 85.04, 81.64, 79.79, 79.41, 78.72, 75.81, 75.61, 75.53, 75.06, 71.87, 63.27, 59.96, 59.43, 51.10, 31.72 (C-5); HRMS (ESI) *m/e* calcd. for $C_{40}H_{42}N_{12}O_6$ ($M+Na^+$) 809.3242, found: 809.3232.

1L-(1,3,4/2,5)-1-*O*-(2',6'-Di-azido-3',4'-di-*O*-benzyl-2',6'-di-deoxy-α-D-glucopyranosyl)-6-azido-2,3-di-*O*-benzyl-4-*O*-methyl-1,2,3,4-cyclohexanetetrol (62). Yield: 86%; $[\alpha]_D$ = +47.7 (*c* = 0.3, EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.37-7.26 (m, 20H, Ar), 5.62 (d, 1H, *J* = 4.0 Hz, H-1'), 5.07 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.91-4.86 (m, 4H, $PhCH_2$), 4.70-4.60 (m, 3H, $PhCH_2$), 4.28 (ddd, 1H, *J* = 2.5, 4.0, 10.0 Hz, H-5'), 4.03 (t, 1H, *J* = 9.0 Hz, H-3'), 4.00 (t, 1H, *J* = 9.0 Hz, H-4'), 3.67-3.36 (m, 10H, H-1, H-2, H-3, H-4, H-6, H-2', H-6a', OCH_3), 3.30 (dd, 1H, *J* = 4.0, 10.5 Hz, H-6b'),

2.32 (dt, 1H, *J* = 4.0, 14.0 Hz, H-5eq), 1.32 (ddd, 1H, *J* = 2.0, 13.5, 14.0 Hz, H-5ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.52, 137.82, 137.70, 128.44, 128.35, 128.03, 127.93, 127.87, 127.73, 127.45, 97.74 (C-1'), 82.86, 81.75, 79.98, 78.70, 78.61, 75.43, 75.15, 74.98, 74.35, 72.73, 70.74, 63.23, 58.28, 57.90 (OCH_3), 50.97, 29.74 (C-5); HRMS (ESI) *m/e* calcd. for $C_{41}H_{45}N_9O_7$ ($M+NH_4^+$) 793.3780, found: 793.3786.

5,6,3',4'-Tetra-*O*-benzyl-1,3,2',6'-tetraazidoneamine (63). Yield: 80%; $[\alpha]_D$ = +55.1 (*c* = 1.3, EtOAc); 1H NMR (300 MHz, CDCl3) δ = 7.38-7.26 (m, 20H, Ar), 5.58 (d, 1H, *J* = 3.9 Hz, H-1'), 5.02 (d, 1H, *J* = 11.1 Hz, $PhCH_2$), 4.94-4.80 (m, 6H, $PhCH_2$), 4.61 (d, 1H, *J* = 11.1 Hz, $PhCH_2$), 4.27 (m, 1H, H-5'), 4.00 (t, 1H, *J* = 9.0 Hz, H-3'), 3.65-3.29 (m, 9H, H-1, H-3, H-4, H-5, H-6, H-2', H-4', H-6a', H-6b'), 2.32 (dt, 1H, *J* = 4.2, 13.2 Hz, H-2eq), 1.49 (q, 1H, *J* = 13.2 Hz, H-2ax). The ^{1}H NMR data coinside with the previous report.[1]

4-*O*-(2',6'-Di-azido-2',6'-di-deoxy-3'4'-di-*O*-acetyl-α-D-mannopyranosyl)-1,3-di-azido-5,6-di-*O*-benzyl-2-deoxystreptamine (64). Yield: 84%; $[\alpha]_D$ = +68.9 (*c* = 0.9, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.39-7.26 (m, 10H, Ar), 5.29-5.21(m, 2H, H-3', H-4'), 5.18 (d, 1H, *J* = 2.5 Hz, H-1'), 5.02 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.90 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.83 (d, 1H, *J* = 10.5 Hz, $PhCH_2$), 4.62 (d, 1H, *J* = 11.5 Hz, $PhCH_2$), 4.32 (ddd, 1H, *J* = 3.0, 6.0, 9.0 Hz, H-5'), 3.53-3.46 (m, 4H, H-2', H-4, H-5, H-6), 3.43-3.37 (m, 2H, H-1, H-3), 3.33 (dd, 1H, *J* = 6.5, 13.5 Hz, H-6a'), 3.25 (dd, 1H, *J* = 3.0, 13.5 Hz, H-6b'), 2.34 (dt, 1H, *J* = 4.5, 13.0 Hz, H-2eq), 2.05 (s, 3H,

$COCH_3$), 2.04 (s, 3H, $COCH_3$), 1.50 (q, 1H, J = 13.0 Hz, H-2ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.94 ($COCH_3$), 169.65 ($COCH_3$), 137.35, 137.09, 128.72, 128.52, 128.26, 128.11, 128.05, 127.22, 98.76 (C-1'), 84.38, 84.10, 79.51, 75.91 (×2), 70.70, 70.30, 66.76, 61.01, 60.18, 58.79, 51.01, 32.15 (C-2), 20.68 ($COCH_3$), 20.45 ($COCH_3$); HRMS (ESI) *m/e* calcd. for $C_{30}H_{34}N_{12}O_8$ ($M+Na^+$) 713.2515, found: 713.2506.

4-*O*-(2',6'-Di-azido-2',6'-di-deoxy-α-D-galactopyranosyl)-1,3-di-azido-5,6-di-*O*-benzyl-2-deoxystreptamine (65). Yield: 60% over two steps; $[\alpha]_D$ = +20.7 (*c* = 0.3, EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.35-7.25 (m, 10H, Ar), 5.68 (d, 1H, J = 4.0 Hz, H-1'), 5.02 (d, 1H, J = 11.0 Hz, $PhCH_2$), 4.89-4.86 (m, 2H, $PhCH_2$), 4.82 (d, 1H, J = 10.0 Hz, $PhCH_2$), 4.39 (t, 1H, J = 5.5 Hz, H-3'), 4.13 (dd, 1H, J = 3.0, 5.5 Hz, H-2'), 4.03 (d, 1H, J = 2.0 Hz, H-4'), 3.67-3.57 (m, 3H, H-4, H-5, H-6), 3.53-3.39 (m, 5H, H-1, H-3, H-5', H-6a', H-6b'), 2.52 (br, 2H, OH), 2.31 (dt, 1H, J = 4.5, 13.0 Hz, H-2eq), 1.50 (q, 1H, J = 12.5 Hz, H-2ax); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.75, 137.23, 128.49, 128.13, 128.05, 127.69, 127.06, 97.80 (C-1'), 84.62, 84.40, 77.19, 75.95, 75.20, 69.65, 69.04, 68.13, 60.24, 59.72, 59.51, 51.22, 32.30 (C-2); HRMS (ESI) *m/e* calcd. for $C_{26}H_{30}N_{12}O_6$ ($M+Na^+$) 629.2304, found: 629.2307.

2-*O*-(2',6'-Di-azido-3',4'-di-*O*-benzyl-2',6'-di-deoxy-α-D-glucopyranosyl)-3-*O*-benzyl-5-*O*-methyl-(2R,3S,4R,5R)-7-oxa-bicyclo[2.2.1]heptane (59). To a solution of **57** (39 mg, 0.052 mmol) in CH_2Cl_2 (2 mL), was added pyridine (42 μL, 0.52 mmol)

and Tf_2O (35 μL, 0.21 mmol) at 0 ^oC. After stirring for 40 min, sat. $NaHCO_3$ was added to quench the reaction. The mixture was diluted with CH_2Cl_2 and washed with brine. The organic layer was collected, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 3:1) to give **59** (33 mg, 99%) as a white solid: R_f = 0.23 (petroleum ether/EtOAc 3:1); $[\alpha]_D$ = +64.0 (*c* = 2.9, EtOAc);^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.39-7.24 (m, 15H, Ar), 4.92 (d, 1H, *J* = 3.5 Hz, H-1'), 4.90-4.84 (m, 3H, $PhCH_2$), 4.62-4.55 (m, 4H, $PhCH_2$, H-1), 4.51 (d, 1H, *J* = 5.0 Hz, H-2), 4.05 (dd, 1H, *J* = 2.5, 7.0 Hz, H-5), 4.02-3.98 (m, 2H, H-3', H-5'), 3.93 (d, 1H, *J* = 5.5 Hz, H-3), 3.59 (d, 1H, *J* = 1.5 Hz, H-4), 3.54 (t, 1H, *J* = 9.5 Hz, H-4'), 3.50 (dd, 1H, *J* = 2.5, 13.5 Hz, H-6a'), 3.35 (dd, 1H, *J* = 5.0, 13.5 Hz, H-6b'), 3.31 (dd, 1H, *J* = 3.5, 10.0 Hz, H-2'), 3.26 (s, 3H, OCH_3), 1.90 (dd, 1H, *J* = 7.0, 13.5 Hz, H-6eq), 1.74 (ddt, 1H, *J* = 1.5, 7.0, 13.5 Hz, H-6ax); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 137.97, 137.88, 137.67, 128.82, 128.78, 128.35, 128.31, 128.23, 128.11, 127.97, 98.30 (C-1'), 86.91, 84.56, 81.09, 79.99, 79.51, 79.05, 77.56, 75.68, 75.45, 73.23, 71.20, 63.49, 56.76 (OCH_3), 51.30, 35.60 (C-6); HRMS (ESI) *m/e* calcd. for $C_{34}H_{38}N_6O_7$ ($M+Na^+$) 665.2694, found: 665.2697.

General procedure for the preparation of compounds 3-14 from 53-62, and 64-65. The preparation of compounds **3-9**: to a solution of the pseudodisaccharide (**53-59**) in methanol, 10% Pd/C (1.5 times as the weight of the starting material) was added. The mixture was stirred for 18 h under an atmosphere of H_2. The mixture was filtered and concentrated. The residue was purified by ion-exchange chromatography

(Amberlite CG-50, NH_4^+ form) with a linear gradient of aqueous ammonia. Gradient ammonia aqueous solution (0-10%, 0-15%, 0-20%) was used. The fractions were collected and concentrated in vacuo. The products were dissolved in water, and 0.1N HCl was used to adjust the pH values to 3-4. The final products were obtained after lyophilization. The preparation of compounds **10-14**: H_2S gas was introduced into the solution of pseudodisaccharide (**60-62**, **64-65**) in a mixed solvent of pyridine/H_2O/Et_3N (3:2:1) to reduce the azido groups to amino groups. The solvent was removed and the residue was purified by column chromatography on silica gel (EtOAc or $CHCl_3$/methanol/NH_4OH as eluents) to give benzyl-protected pseudodisaccharides. Finally, the benzyl groups were removed under Pd/C/H_2 conditions as described above to provide target compounds.

1L-(1,2,4,5/3)-2-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-glucopyranosyl)-1,2,3,4,5-cyclohexanepentol (3): 32 mg, yield: 98%; $[\alpha]_D$ = +95.0 (*c* = 0.6, H_2O); ^{1}H NMR (500 MHz, D_2O) δ = 5.52 (d, 1H, *J* = 3.5 Hz, H-1'), 4.22-4.21 (m, 1H, H-1), 4.11-4.05 (m, 3H, H-4, H-5, H-5'), 3.98 (dd, 1H, *J* = 9.0, 11.0 Hz, H-3), 3.71 (dd, 1H, *J* = 3.0, 9.5 Hz, H-2'), 3.57 (dd, 1H, *J* = 2.5, 9.0 Hz, H-2), 3.46-3.41 (m, 3H, H-3', H-4', H-6a'), 3.20 (dd, 1H, *J* = 8.5, 13.5 Hz, H-6b'), 2.16 (dt, 1H, *J* = 4.0, 15.5 Hz, H-6eq), 1.78 (dt, 1H, *J* = 3.0, 15.5 Hz, H-6ax); ^{13}C NMR (125 MHz, D_2O) δ = 97.09 (C-1'), 82.12 (×2), 74.47, 71.81, 70.53(×2), 69.84, 69.31, 54.78, 40.88, 32.45 (C-6); HRMS (ESI) *m/e* calcd. for $C_{12}H_{24}N_2O_8$ ($M+H^+$) 325.1605, found: 325.1672.

1D-(1,3,5/2,4)-2-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-glucopyranosyl)-1,2,3,4,5-cyclohexanepentol (4): 25 mg, yield: 98%; $[\alpha]_D$ = +70.0 (*c* = 0.9, H_2O); ^1H NMR (500 MHz, D_2O) δ = 5.54 (d, 1H, *J* = 4.0 Hz, H-1'), 4.29 (ddd, 1H, *J* = 3.0, 8.5, 11.0 Hz, H-5'), 3.92 (dd, 1H, *J* = 9.0, 11.0 Hz, H-3 or H-4), 3.71 (ddd, 1H, *J* = 5.0, 9.5, 12.5 Hz, H-5), 3.57-3.51 (m, 2H, H-1, H-3'), 3.48-3.39 (m, 4H, H-2, H-3 or H-4, H-2', H-6a'), 3.31 (t, 1H, *J* = 9.0 Hz, H-4'), 3.20 (dd, 1H, *J* = 8.5, 13.5 Hz, H-6b'), 2.23 (dt, 1H, *J* = 4.5, 12.5 Hz, H-6eq), 1.51 (q, 1H, *J* = 12.5 Hz, H-6ax); ^{13}C NMR (125 MHz, D_2O) δ = 96.67 (C-1'), 83.93, 77.53, 75.17, 71.69, 69.97, 68.85, 68.75, 67.56, 54.79, 40.84, 37.92 (C-6); HRMS (ESI) *m/e* calcd. for $C_{12}H_{24}N_2O_8$ ($M+H^+$) 325.1605, found: 325.1615.

1D-(1,2,4/3,5)-4-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-glucopyranosyl)-1,2,3,4,5-cyclohexanepentol (5): 17 mg, yield: 99%; $[\alpha]_D$ = +169.2 (*c* = 0.6, H_2O); ^1H NMR (500 MHz, D_2O) δ = 5.56 (d, 1H, *J* = 3.5 Hz, H-1'), 4.29 (ddd, 1H, *J* = 3.0, 9.0 Hz, H-5), 4.07 (dd, 1H, *J* = 3.0, 6.0 Hz, H-1), 3.93 (dd, 1H, *J* = 9.0, 9.5 Hz, H-3'), 3.88 (ddd, 1H, *J* = 5.0, 9.0, 12.0 Hz, H-5'), 3.77 (t, 1H, *J* = 9.0 Hz, H-4), 3.54-3.39 (m, 5H, H-2, H-3, H-2', H-4', H-6a'), 3.20 (dd, 1H, *J* = 8.5, 13.5 Hz, H-6b'), 2.14 (dt, 1H, *J* = 4.5, 13.5 Hz, H-6eq), 1.62 (ddd, 1H, *J* = 2.5, 12.0, 13.5 Hz, H-6ax); ^{13}C NMR (125 MHz, D_2O) δ = 96.66 (C-1'), 84.36, 74.34, 73.85, 71.73, 70.00, 68.76, 68.73, 67.28, 54.84, 40.87, 36.30 (C-6); HRMS (ESI) *m/e* calcd. for $C_{12}H_{24}N_2O_8$ ($M+H^+$) 325.1605, found: 325.1619.

1L-(1,2,4/3,5)-2-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-glucopyranosyl)-1,2,3,4,5-cyclohexanepentol (6): 13 mg, yield: 99%; $[\alpha]_D$ = +26.7 (*c* = 0.6, H_2O); ^1H NMR (500 MHz, D_2O) δ = 5.52 (d, 1H, *J* = 3.5 Hz, H-1'), 4.21 (dd, 1H, *J* = 3.0, 5.5 Hz, H-1), 4.01 (ddd, 1H, *J* = 3.0, 7.5, 10.5 Hz, H-5'), 3.95 (dd, 1H, *J* = 9.5, 10.5 Hz, H-3'), 3.81-3.76 (m, 2H, H-4, H-5), 3.71 (dd, 1H, *J* = 3.0, 10.0 Hz, H-2), 3.46-3.39 (m, 3H, H-3, H-2', H-6a'), 3.29 (t, 1H, *J* = 9.0 Hz, H-4'), 3.22 (dd, 1H, *J* = 8.0, 13.5 Hz, H-6b'), 2.11 (dt, 1H, *J* = 4.5, 14.5 Hz, H-6eq), 1.58 (ddd, 1H, *J* = 2.5, 12.0, 13.5 Hz, H-6ax); ^{13}C NMR (125 MHz, D_2O) δ = 97.56 (C-1'), 81.68, 77.99, 73.08, 71.66, 69.73, 69.34, 68.65, 68.51, 54.72, 40.86, 35.74 (C-6); HRMS (ESI) *m/e* calcd. for $C_{12}H_{24}N_2O_8$ ($M+H^+$) 325.1605, found: 325.1585.

1D-(1,2,4/3,5)-4-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-glucopyranosyl)-1-*O*-methyl-1,2,3,4,5-cyclohexanepentol (7): 18 mg, yield: 96%; $[\alpha]_D$ = +93.3 (*c* = 0.6, H_2O); ^1H NMR (500 MHz, D_2O) δ = 5.60 (d, 1H, *J* = 4.0 Hz, H-1'), 4.32 (ddd, 1H, *J* = 3.0, 7.5, 10.5 Hz, H-5), 3.97 (dd, 1H, *J* = 9.5, 10.5 Hz, H-3'), 3.82 (ddd, 1H, *J* = 4.5, 9.5, 12.0 Hz, H-5'), 3.76-3.72 (m, 1H, H-1, H-4), 3.62 (dd, 1H, *J* = 3.5, 10.0 Hz, H-2), 3.57-3.42 (m, 7H, H-3, H-2', H-4', H-6a', OCH_3), 3.24 (dd, 1H, *J* = 8.0, 13.5 Hz, H-6b'), 2.42 (dt, 1H, *J* = 4.5, 14.5 Hz, H-6b), 1.51 (ddd, 1H, *J* = 2.5, 12.0, 13.5 Hz, H-6a); ^{13}C NMR (125 MHz, D_2O) δ = 96.67 (C-1'), 84.24, 78.53, 74.24, 74.08, 71.71, 69.99, 68.76, 67.19, 57.64 (OCH_3), 54.82, 40.85, 32.21 (C-6); HRMS (ESI) *m/e* calcd. for $C_{13}H_{26}N_2O_8$ ($M+H^+$) 339.1767, found: 339.1759.

1L-(1,2,4,5/3)-2-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-glucopyranosyl)-5-*O*-methyl-1,2,3,4,5-cyclohexanepentol (8): 19 mg, yield: 99%; $[\alpha]_D$ = +57.5 (*c* = 0.6, H_2O); ^1H NMR (500 MHz, D_2O) δ = 5.51 (d, 1H, *J* = 3.5 Hz, H-1'), 4.18-4.17 (m, 1H, H-1), 4.11 (td, 1H, *J* = 2.5, 9.0 Hz, H-2), 4.06 (t, 1H, *J* = 9.0 Hz, H-3'), 3.99 (t, 1H, *J* = 9.0 Hz, H-4'), 3.74-4.73 (m, 1H, H-5), 3.68-3.63 (m, 2H, H-2', H-5'), 3.46-3.42 (m, 6H, H-3, H-4, H-6a', OCH_3), 3.20 (dd, 1H, *J* = 8.5, 13.5 Hz, H-6b'), 2.35 (d, 1H, *J* = 15.0 Hz, H-6eq), 1.65 (d, 1H, *J* = 15.0 Hz, H-6ax); ^{13}C NMR (125 MHz, D_2O) δ = 97.01 (C-1'), 81.92, 79.98, 73.83 (×2), 71.82, 70.61, 69.85, 69.30, 58.11 (OCH_3), 54.77, 40.87, 28.72 (C-6); HRMS (ESI) *m/e* calcd. for $C_{13}H_{26}N_2O_8$ ($M+H^+$) 339.1767, found: 339.1761.

2-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-glucopyranosyl)-5-*O*-methyl-(2R,3S,4R,5R)-7-oxa-bicyclo[2.2.1]heptane (9): 37 mg, yield: 96%; $[\alpha]_D$ = +60.0 (*c* = 1.0, H_2O); ^1H NMR (500 MHz, D_2O) δ = 5.36 (d, 1H, *J* = 3.5 Hz, H-1'), 4.67 (t, 2H, *J* = 6.0 Hz, H-4), 4.18-4.16 (m, 2H, H-5, H-3'), 3.94 (ddd, 1H, *J* = 3.0, 8.5, 9.5 Hz, H-5'), 3.89 (dd, 1H, *J* = 9.0, 10.5 Hz, H-4'), 3.76 (d, 1H, *J* = 1.0 Hz, H-2), 3.48-3.40 (m, 3H, H-1, H-2', H-6a'), 3.33 (s, 3H, OCH_3), 3.22 (dd, 1H, *J* = 8.5, 13.5 Hz, H-6b'), 2.10 (dd, 1H, *J* = 7.0, 14.0 Hz, H-6ax), 1.76 (ddt, 1H, *J* = 2.0, 6.5, 14.0 Hz, H-6eq); ^{13}C NMR (125 MHz, D_2O) δ = 94.30 (C-1'), 85.14, 82.54, 81.40, 77.82, 76.36, 71.76, 69.88, 69.30, 56.66 (OCH_3), 54.21, 40.88, 35.00 (C-6); HRMS (ESI) *m/e* calcd. for $C_{13}H_{24}N_2O_7$ ($M+H^+$) 321.1656, found: 321.1647.

1L-(1,3,4/2,6)-1-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-glucopyranosyl)-4,6-di-amino-1,2,3-cyclohexanetriol (10): 18 mg, yield: 90%; $[\alpha]_D$ = +84.2 (*c* = 0.6, H_2O); ^1H NMR (500 MHz, D_2O) δ = 5.80 (d, 1H, *J* = 3.5 Hz, H-1'), 4.14-4.12 (m, 3H, H-5', H-2, H-1 or H-3), 4.06-4.01 (m, 2H, H-3', H-1 or H-3), 3.94-3.92 (m, 1H, H-4 or H-6), 3.83-3.81 (m, 1H, H-4 or H-6), 3.55-3.51 (m, 3H, H-2', H-4', H-6a'), 3.31 (dd, 1H, *J* = 7.5, 13.5 Hz, H-6b'), 2.53 (ddd, 1H, *J* = 4.5, 7.0, 15.0 Hz, H-5eq), 2.22 (ddd, 1H, *J* = 4.5, 9.0, 15.0 Hz, H-5ax); ^{13}C NMR (125 MHz, D_2O) δ = 95.68 (C-1'), 75.17, 71.46, 70.78, 69.83, 69.25, 69.19, 54.24, 48.71, 47.66, 40.84, 25.68 (C-5); HRMS (ESI) *m/e* calcd. for $C_{12}H_{26}N_4O_6$ ($M+H^+$) 323.1925, found: 323.1954.

1L-(1,3,6/2,4)-1-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-glucopyranosyl)-4,6-di-amino-1,2,3-cyclohexanetriol (11): 21 mg, yield: 90%; $[\alpha]_D$ = +68.3 (*c* = 0.6, H_2O); ^1H NMR (500 MHz, D_2O) δ = 5.76 (d, 1H, *J* = 3.5 Hz, H-1'), 4.20 (dd, 1H, *J* = 4.5, 10.0 Hz, H-1), 4.08 (m, 1H, H-6), 4.02 (t, 1H, *J* = 9.0 Hz, H-3'), 3.96 (ddd, 1H, *J* = 3.0, 7.5, 9.0 Hz, H-5'), 3.86 (t, 1H, *J* = 9.0 Hz, H-4'), 3.61 (t, 1H, *J* = 9.0 Hz, H-3), 3.52-3.42 (m, 4H, H-2, H-4, H-2', H-6'a), 3.25 (dd, 1H, *J* = 8.0, 13.5 Hz, H-6b'), 2.46 (dt, 1H, *J* = 3.0, 15.5 Hz, H-5eq), 2.16 (ddd, 1H, *J* = 4.0, 14.0, 16.0 Hz, H-5ax); ^{13}C NMR (125 MHz, D_2O) δ = 97.55 (C-1'), 75.24, 73.38, 73.22, 71.60, 69.73, 69.16, 54.34, 50.08, 49.06, 40.90, 27.81 (C-5); HRMS (ESI) *m/e* calcd. for $C_{12}H_{26}N_4O_6$ ($M+H^+$) 323.1925, found: 323.1924.

1L-(1,3,4/2,6)-1-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-glucopyranosyl)-6-amino-4-*O*-methyl-1,2,3,4-cyclohexanetetrol (12): 16 mg, yield: 70%; $[\alpha]_D$ = +89.2 (*c* = 0.6, H_2O); ^{1}H NMR (500 MHz, D_2O) δ = 5.92 (d, 1H, *J* = 4.0 Hz, H-1'), 4.02 (ddd, 1H, *J* = 3.5, 7.0, 10.0 Hz, H-5'), 3.99 (dd, 1H, *J* = 9.0, 11.0 Hz, H-3'), 3.88 (t, 1H, *J* = 9.0 Hz, H-4'), 3.83 (t, 1H, *J* = 9.0 Hz, H-2 or H-1), 3.79 (dd, 1H, *J* = 3.5, 5.5 Hz, H-4), 3.63 (dd, 1H, *J* = 3.0, 9.5 Hz, H-2'), 3.53-3.45 (m, 4H, H-1 or H-2, H-3, H-6, H-6a'), 3.41 (s, 3H, OCH_3), 3.30 (dd, 1H, *J* = 7.0, 13.5 Hz, H-6b'), 2.51 (dt, 1H, *J* = 4.5, 14.0 Hz, H-5eq), 1.71 (ddd, 1H, *J* = 2.0, 14.0, 14.5 Hz, H-5ax); ^{13}C NMR (125 MHz, D_2O) δ = 96.75 (C-1'), 79.61, 77.34, 74.38, 73.69, 71.41, 69.83, 69.10, 57.76 (OCH_3), 54.28, 48.33, 40.84, 27.94 (C-5); HRMS (ESI) *m/e* calcd. for $C_{13}H_{27}N_3O_7$ ($M+H^+$) 338.1922, found: 338.1914.

4-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-mannopyranosyl)-2-deoxystreptamine (13): 17 mg, yield: 96% over three steps; $[\alpha]_D$ = +53.3 (*c* = 0.6, H_2O); ^{1}H NMR (500 MHz, D_2O) δ = 5.67 (d, 1H, *J* = 4.0 Hz, H-1'), 4.26 (dd, 1H, *J* = 4.0, 7.5 Hz, H-3'), 4.19 (dt, 1H, *J* = 5.0, 7.5 Hz, H-5'), 4.01 (t, 1H, *J* = 9.5 Hz, H-4 or H-5), 3.84 (t, 1H, *J* = 4.0 Hz, H-2'), 3.72 (t, 1H, *J* = 7.5 Hz, H-4'), 3.68 (t, 1H, *J* = 9.0 Hz, H-4 or H-5), 3.61-3.52(m, 2H, H-1 or H-3, H-6), 3.47-3.41 (m, 2H, H-6a', H-6b'), 3.35 (dt, 1H, *J* = 4.0, 12.0 Hz, H-1 or H-3), 2.51 (dt, 1H, *J* = 4.0, 12.5 Hz, H-2eq), 1.92 (q, 1H, *J* = 12.5 Hz, H-2ax); ^{13}C NMR (125 MHz, D_2O) δ = 96.41 (C-1'), 79.13, 75.50, 73.29, 72.48, 68.40, 67.25, 53.61, 50.45, 49.27, 40.50, 28.82 (C-2); HRMS (ESI) *m/e* calcd. for $C_{12}H_{26}N_4O_6$ ($M+H^+$) 323.1925, found: 323.1921.

4-*O*-(2',6'-Di-amino-2',6'-di-deoxy-α-D-galactopyranosyl)-2-deoxystreptamine

(14): 14 mg, yield: 95% over two steps; $[\alpha]_D$ = +31.7 (*c* = 0.6, H_2O); ^1H NMR (500 MHz, D_2O) δ = 5.99 (d, 1H, *J* = 4.0 Hz, H-1'), 4.32 (td, 1H, *J* = 1.0, 5.0 Hz, H-5'), 4.23 (dd, 1H, *J* = 3.0, 11.0 Hz, H-3'), 4.13 (dd, 1H, *J* = 1.5, 3.0 Hz, H-4'), 4.00 (dd, 1H, *J* = 9.0, 10.0 Hz, H-4), 3.71 (t, 1H, *J* = 9.0 Hz, H-5), 3.67 (dd, 1H, *J* = 4.0, 11.5 Hz, H-2'), 3.61 (t, 1H, *J* = 9.5 Hz, H-6), 3.57 (ddd, 1H, *J* = 4.0, 10.0, 12.5 Hz, H-1 or H-3), 3.39-3.34 (m, 3H, H-1 or H-3, H-6a', H-6b'), 2.52 (dt, 1H, *J* = 4.0, 12.5 Hz, H-2eq), 1.92 (q, 1H, *J* = 12.5 Hz, H-2ax); ^{13}C NMR (125 MHz, D_2O) δ = 96.95 (C-1'), 78.13, 75.97, 73.25, 70.02, 68.22, 65.81, 50.83, 50.45, 49.27, 41.29, 28.99 (C-2); HRMS (ESI) *m/e* calcd. for $C_{12}H_{26}N_4O_6$ ($M+H^+$) 323.1925, found: 323.1925.

References:

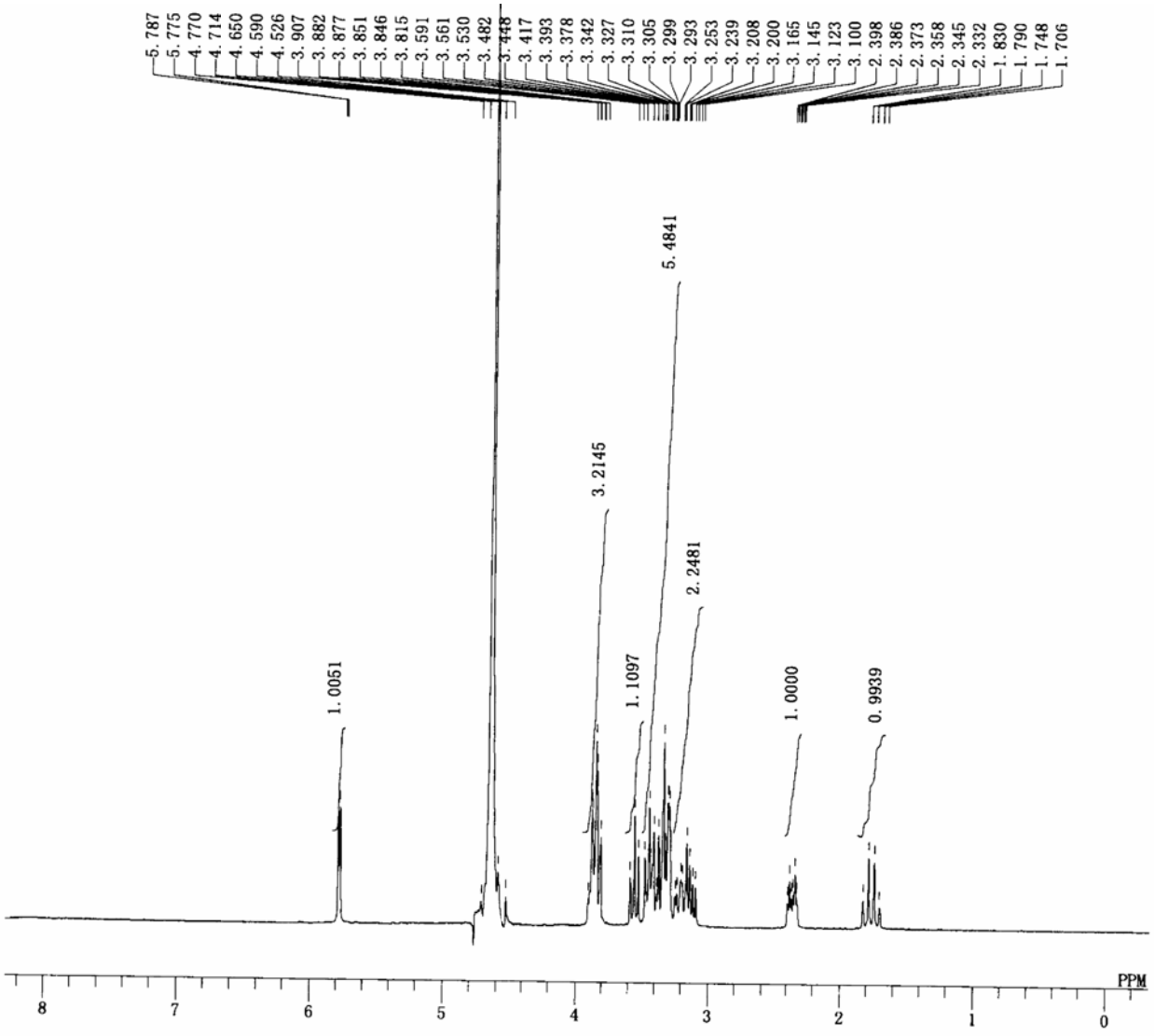
(1) A. Köhn and R. R. Schmidt, *Liebigs Ann. Chem.*, 1987, **12**, 1045–1054.

(2) C. Jia, A. Pearce, Y. Blériot, Y. Zhang, L. H. Zhang, M. Sollogouba and P. Sinaÿ, *Tetrahedron: Asymmetry*, 2004, **15**, 699-703.

(3) T. Ritter, K. K. Mong, H. Liu, T. Nakatani and C. H. Wong, *Angew. Chem. Int. Ed.*, 2003, **42**, 4657-4660.

(4) J. Liu, M. D. Numa, H. Liu, S. J. Huang, P. Sears, A. R. Shikhman and C. H. Wong, *J. Org. Chem.*, 2004, **69**, 6273-6283.

(5) D. Jenkins, D. Dubreuil and B. L. Potter, *J. Chem. Soc. Perkin Trans. I*, 1996, 1365-1372.



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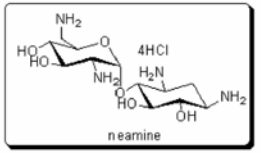
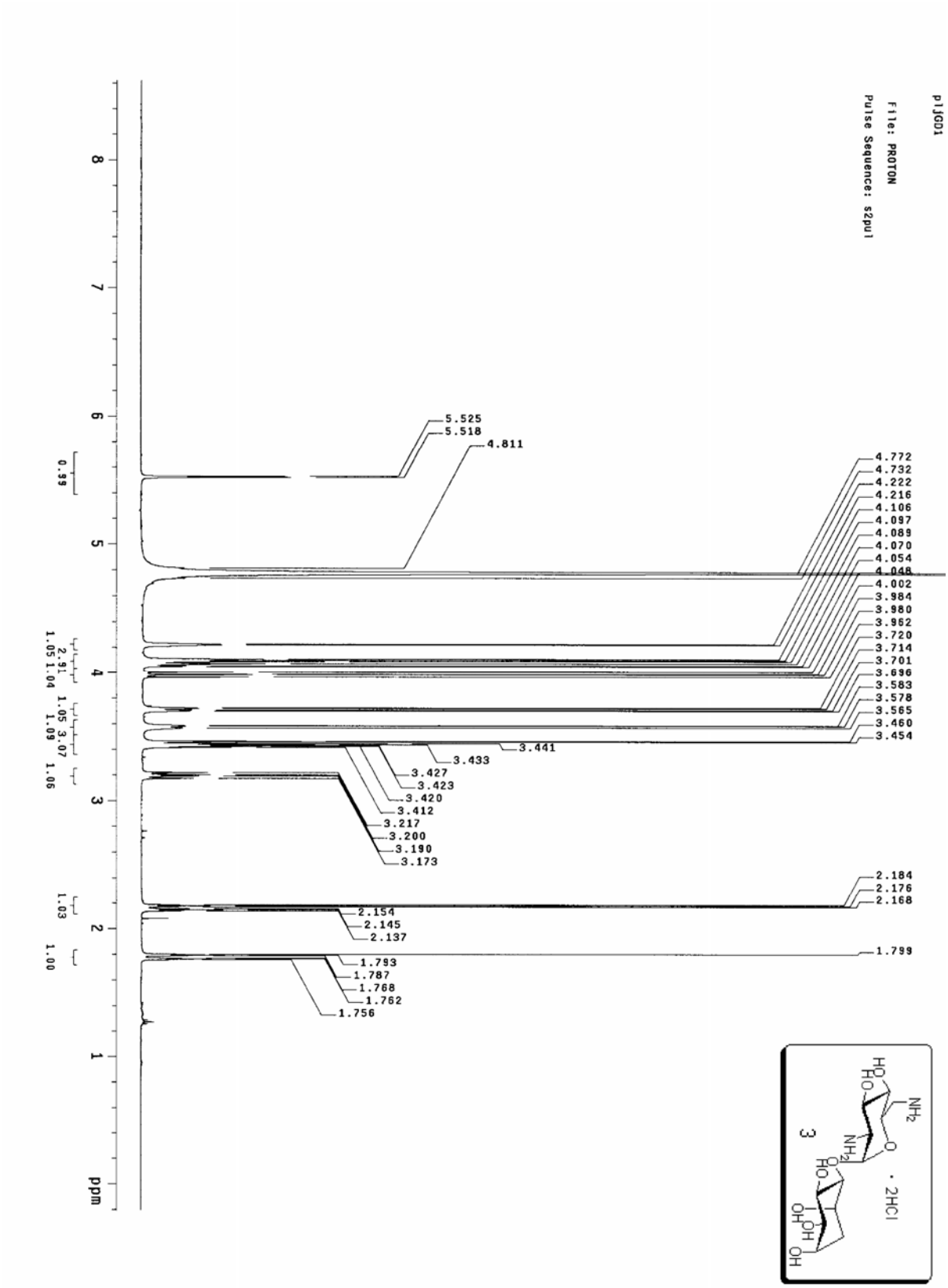
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PWI 6.1 us
IRATN 511
CTEMP 20.8 c
SLVNT D2O
EXREF 4.65 ppm
BF 0.12 Hz
RGAIN 14

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File: PROTON
Pulse Sequence: s2pul
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4.732
4.222
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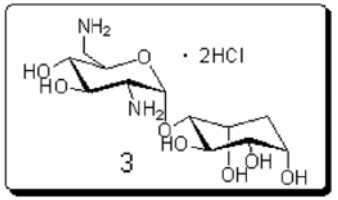
4.106
4.097
4.089
4.070
4.054
4.048
4.002
3.984
3.980
3.962
3.720
3.714
3.701
3.696
3.583
3.578
3.565
3.460
3.454
3.441
3.433
3.427
3.423
3.420
3.412
3.217
3.200
3.190
3.173
2.184
2.176
2.168
2.154
2.145
2.137
1.799
1.793
1.787
1.768
1.762
1.756
0.99
2.91
1.05 1.04
1.05 3.07
1.09
1.06
1.03
1.00
ppm
NH2
HO
HO
O
NH2
3
HO
OH
OH
OH
· 2HCl

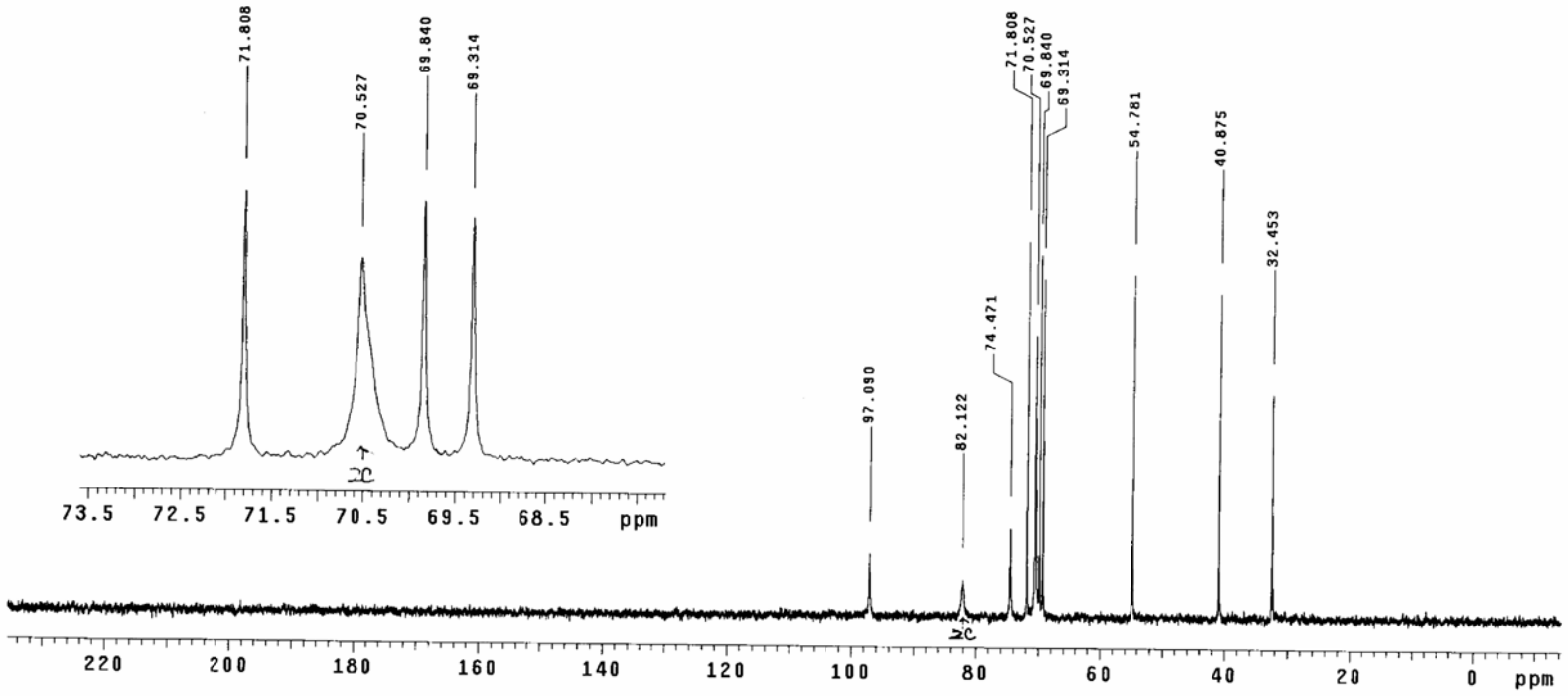
pljGD1

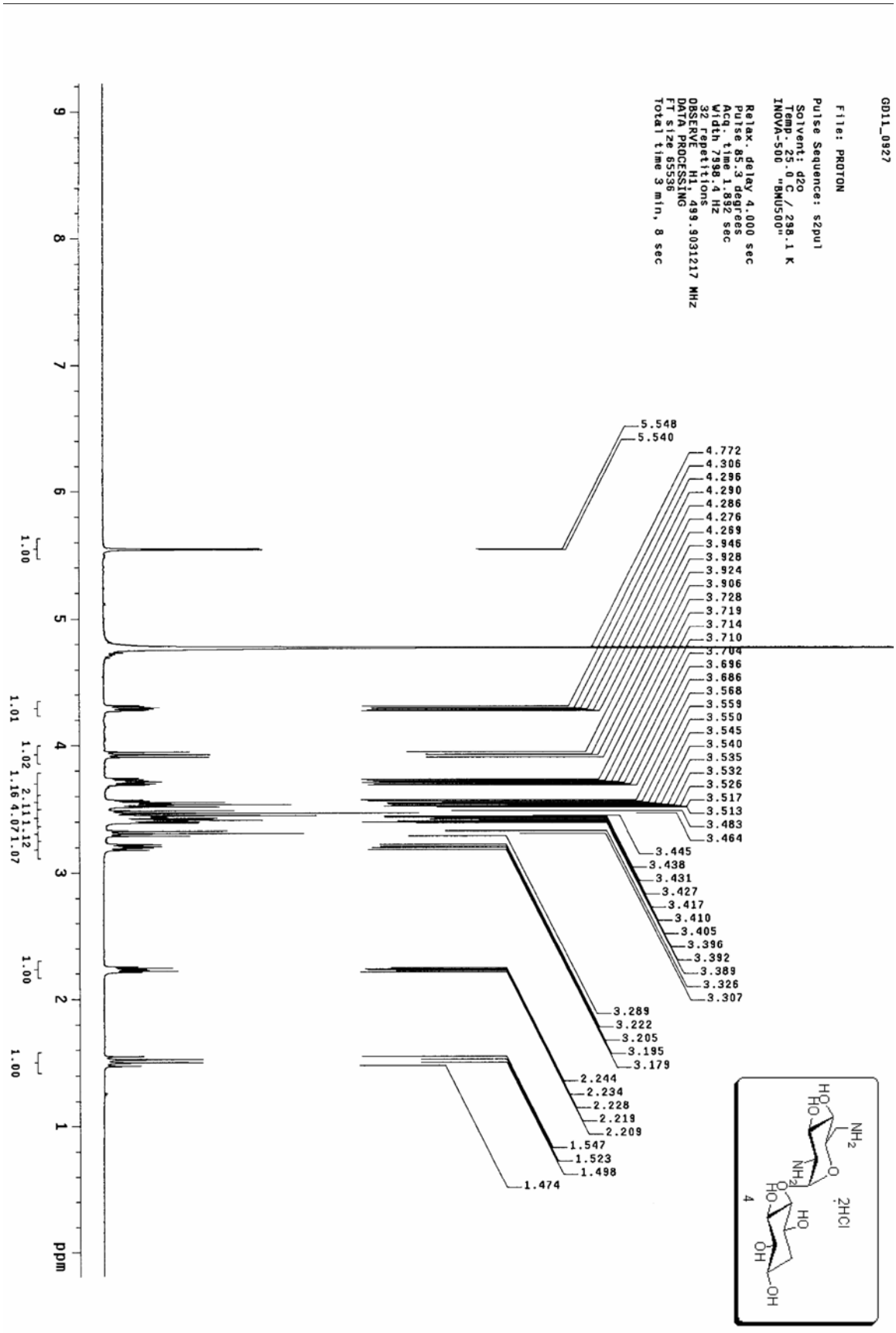
File: CARBON

Pulse Sequence: s2pul
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
3968 repetitions
OBSERVE C13, 125.7006556 MHz
DECOUPLE H1, 499.9056708 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.5 Hz
FT size 65536
Total time 14 hr, 59 min, 59 sec





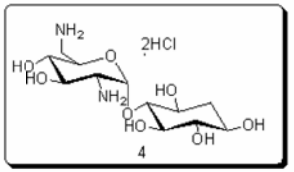

GD11_0927
File: PROTON
Pulse Sequence: s2pul
Solvent: d2o
Temp: 25.0 C / 298.1 K
INOVA-500 "BMU500"
Relax. delay 4.000 sec
Pulse 85.3 degrees
Acq. time 1.992 sec
Width 7998.4 Hz
32 repetitions
OBSERVE H1, 499.9031217 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 8 sec
5.548
5.540
4.772
4.306
4.296
4.290
4.286
4.276
4.269
3.946
3.928
3.924
3.906
3.728
3.719
3.714
3.710
3.704
3.696
3.686
3.568
3.559
3.550
3.545
3.540
3.535
3.532
3.526
3.517
3.513
3.483
3.464
3.445
3.438
3.431
3.427
3.417
3.410
3.405
3.396
3.392
3.389
3.326
3.307
3.289
3.222
3.205
3.195
3.179
2.244
2.234
2.228
2.219
2.209
1.547
1.523
1.498
1.474
1.00
1.01
1.02
2.11
1.12
1.16
4.07
1.07
1.00
1.00
ppm
NH2
NH2
2HCl
4

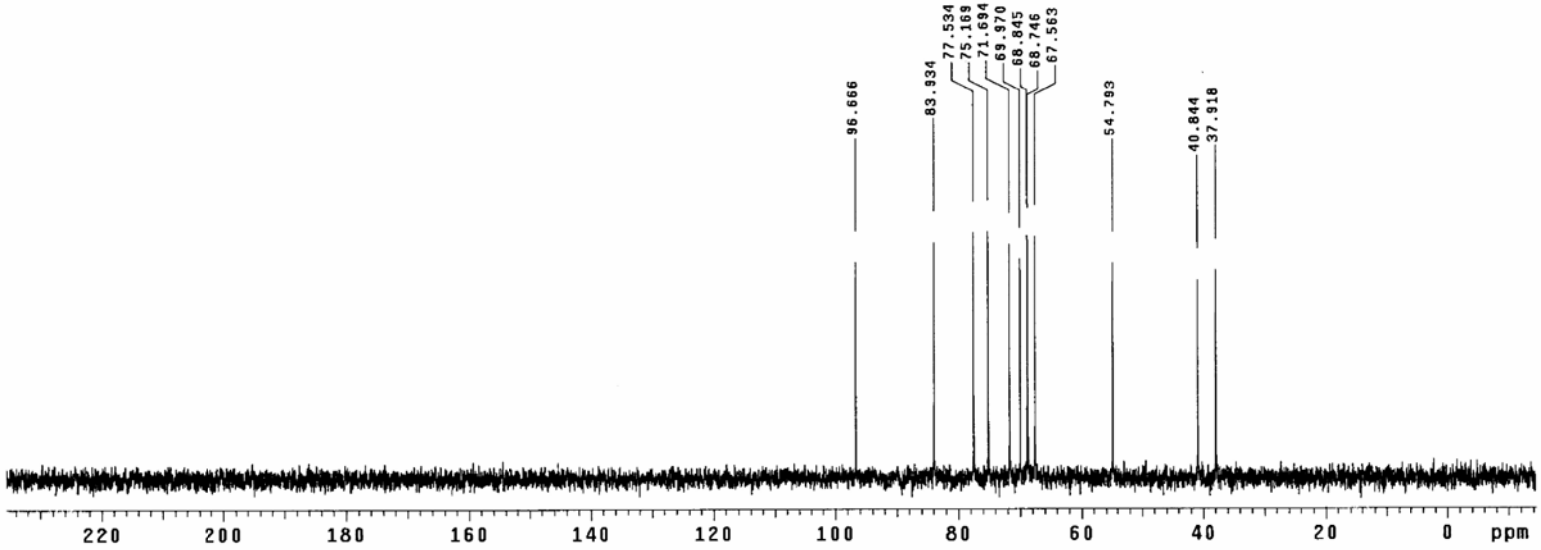
GD11_0927

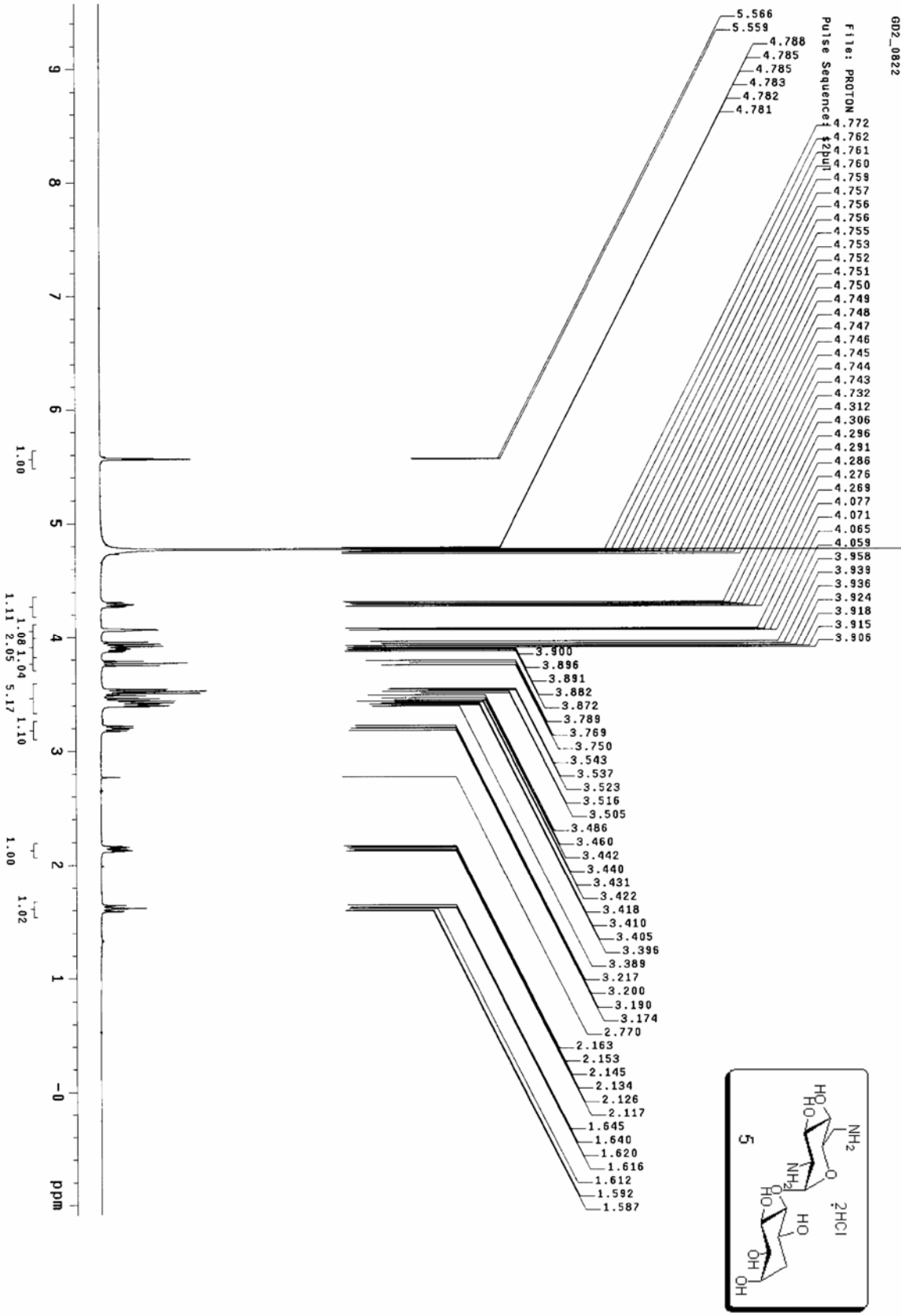
File: CARBON

Pulse Sequence: s2pul
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
2336 repetitions
OBSERVE C13, 125.7006560 MHz
DECOUPLE H1, 499.9056708 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 131072
Total time 16 hr, 25 min, 19 sec






GD2_0822
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Pulse Sequence: s2pul
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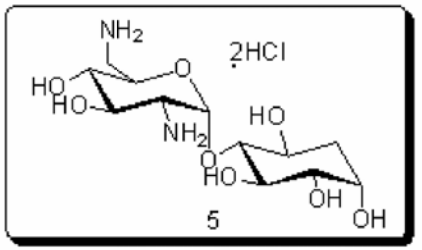
4.785
4.783
4.782
4.781
4.772
4.762
4.761
4.760
4.759
4.757
4.756
4.756
4.755
4.753
4.752
4.751
4.750
4.749
4.748
4.747
4.746
4.745
4.744
4.743
4.732
4.312
4.306
4.296
4.291
4.286
4.276
4.269
4.077
4.071
4.065
4.059
3.958
3.939
3.936
3.924
3.918
3.915
3.906
3.900
3.896
3.891
3.882
3.872
3.789
3.769
3.750
3.543
3.537
3.523
3.516
3.505
3.486
3.460
3.442
3.440
3.431
3.422
3.418
3.410
3.405
3.396
3.389
3.217
3.200
3.190
3.174
2.770
2.163
2.153
2.145
2.134
2.126
2.117
1.645
1.640
1.620
1.616
1.612
1.592
1.587
1.00
1.11
2.05
1.08
1.04
5.17
1.10
1.00
1.02
ppm
9
8
7
6
5
4
3
2
1
-0
5
NH2
NH2
O
HO
HO
HO
HO
OH
OH
2HCl

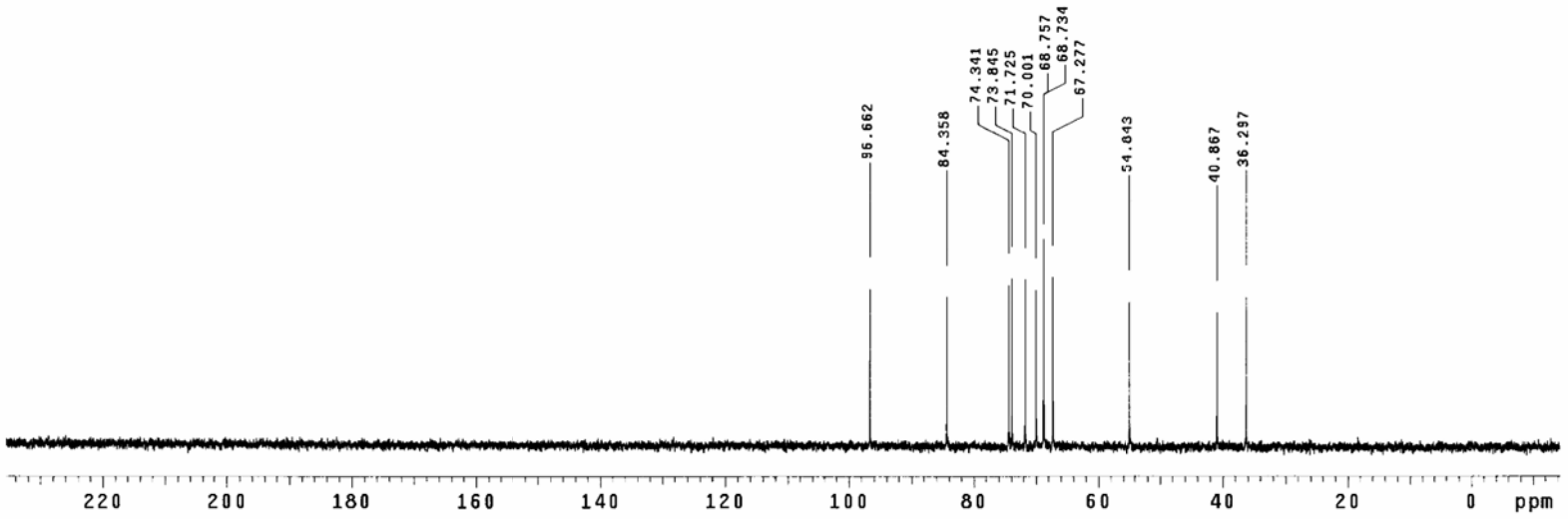
GD2_0822

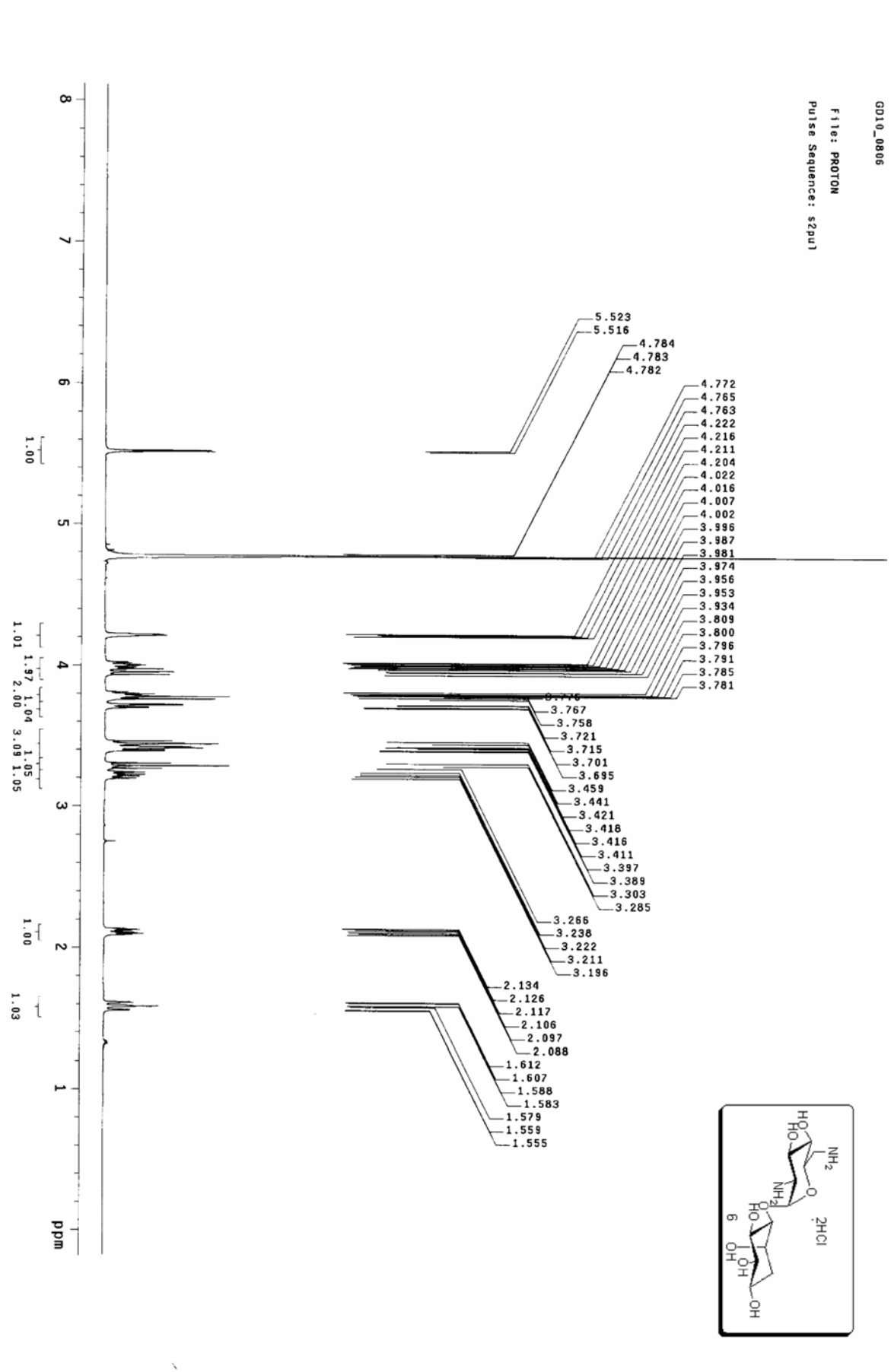
File: CARBON

Pulse Sequence: s2pul
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
1856 repetitions
OBSERVE C13, 125.7006556 MHz
DECOUPLE H1, 499.9056708 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 8 hr, 34 min, 16 sec



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Pulse Sequence: s2pul
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4.772
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4.204
4.022
4.016
4.007
4.002
3.996
3.987
3.981
3.974
3.956
3.953
3.934
3.809
3.800
3.796
3.791
3.785
3.781
3.767
3.758
3.721
3.715
3.701
3.695
3.459
3.441
3.421
3.418
3.416
3.411
3.397
3.389
3.303
3.285
3.266
3.238
3.222
3.211
3.196
2.134
2.126
2.117
2.106
2.097
2.088
1.612
1.607
1.588
1.583
1.579
1.559
1.555
1.00
1.01
1.97
1.04
2.00
3.09
1.05
1.05
1.00
1.03
ppm
2HCl

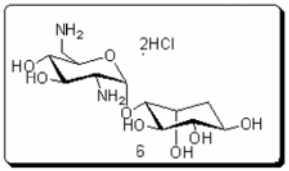
GD10_0806

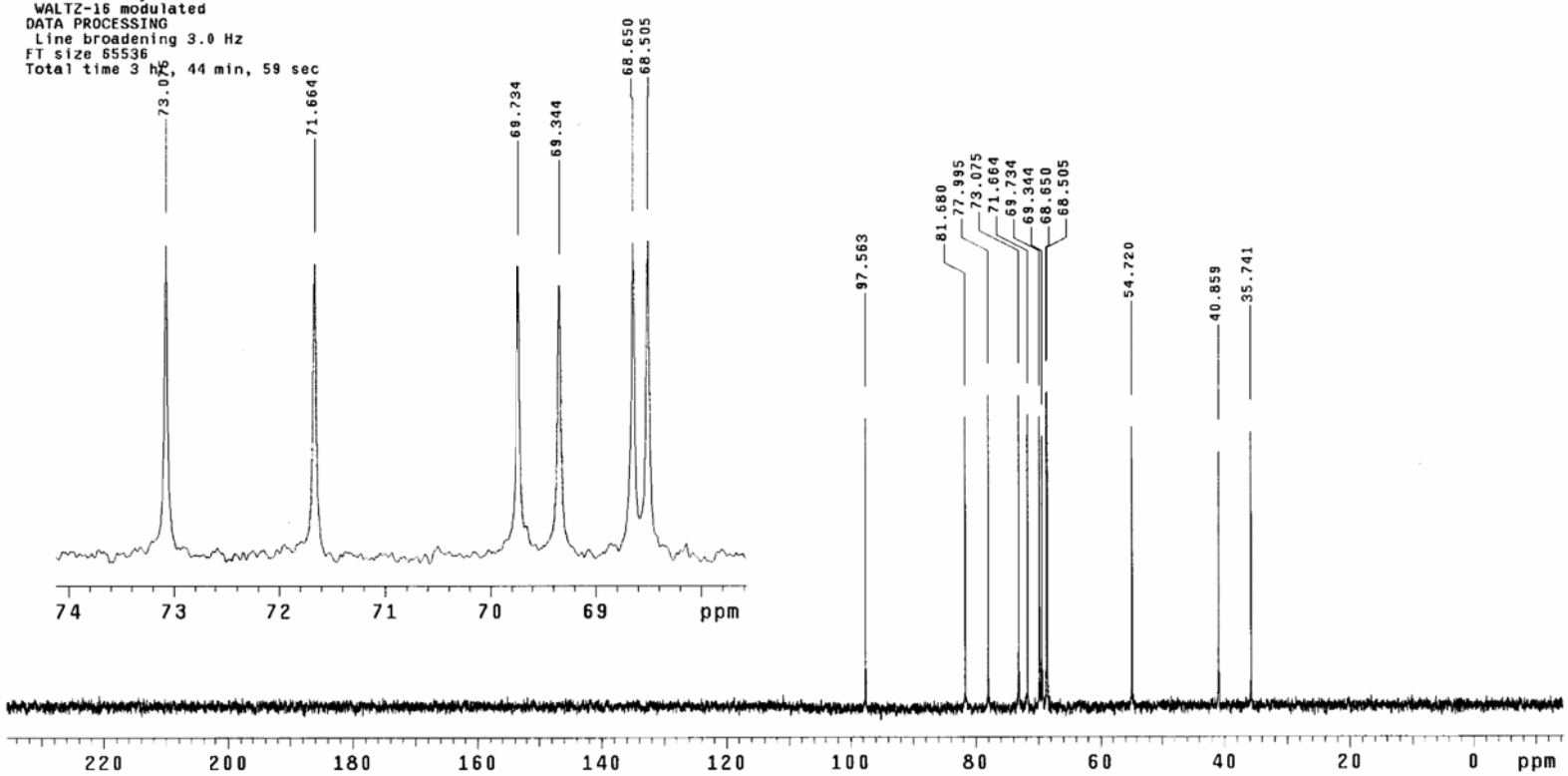
File: CARBON

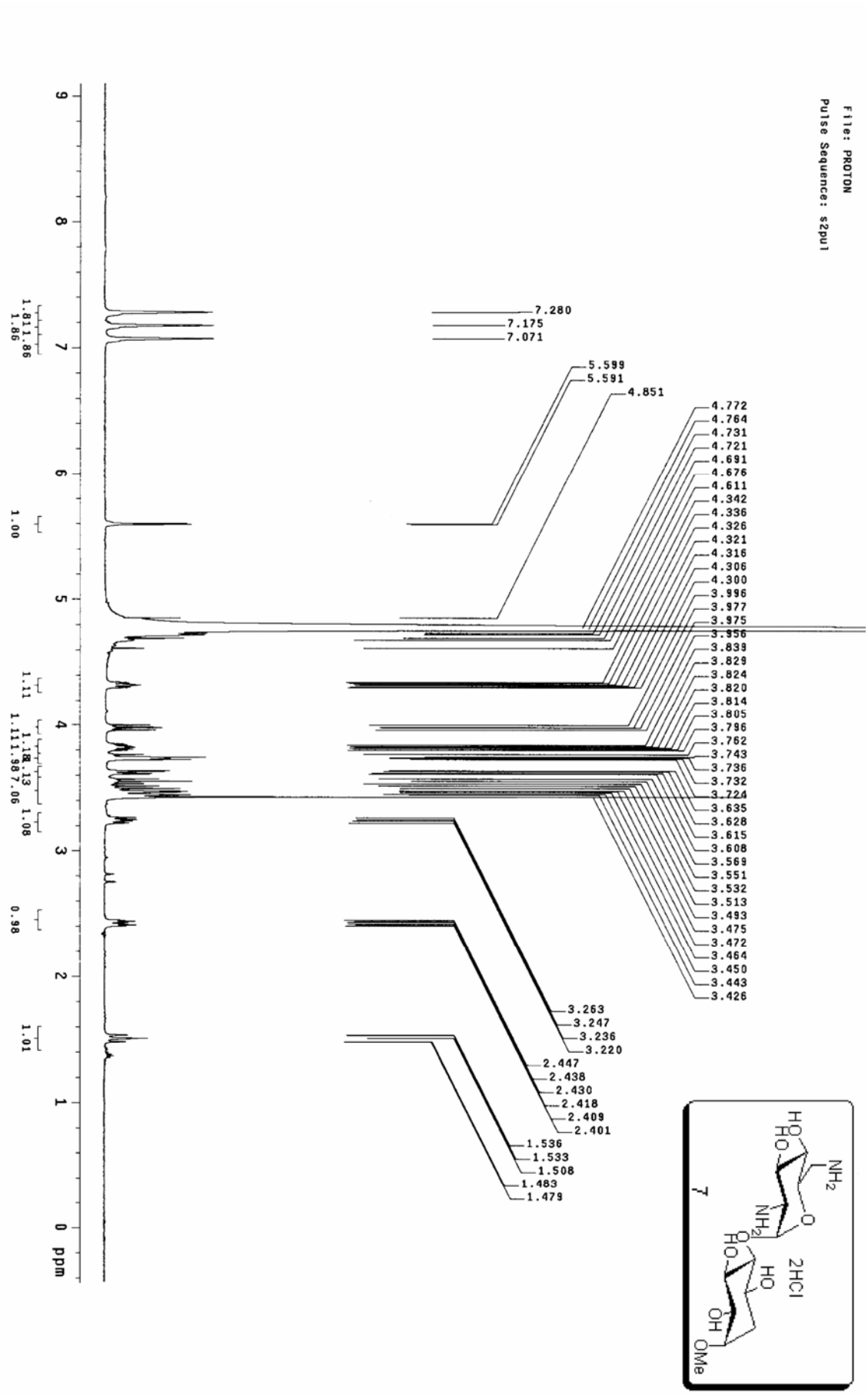
Pulse Sequence: s2pul

Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 64.3 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
5376 repetitions
OBSERVE C13, 125.7006556 MHz
DECOUPLE H1, 499.9056708 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 3 hr, 44 min, 59 sec






File: PROTON
Pulse Sequence: s2pul
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4.772
4.764
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4.676
4.611
4.342
4.336
4.326
4.321
4.316
4.306
4.300
3.996
3.977
3.975
3.956
3.839
3.829
3.824
3.820
3.814
3.805
3.796
3.762
3.743
3.736
3.732
3.724
3.635
3.628
3.615
3.608
3.569
3.551
3.532
3.513
3.493
3.475
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3.450
3.443
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3.263
3.247
3.236
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2.409
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1.11
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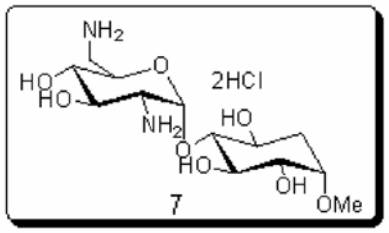
7.06
1.08
0.98
1.01
0 ppm
NH2
HO
HO
O
NH2
O
HO
HO
2HCl
OH
OMe
7

GD3_0822

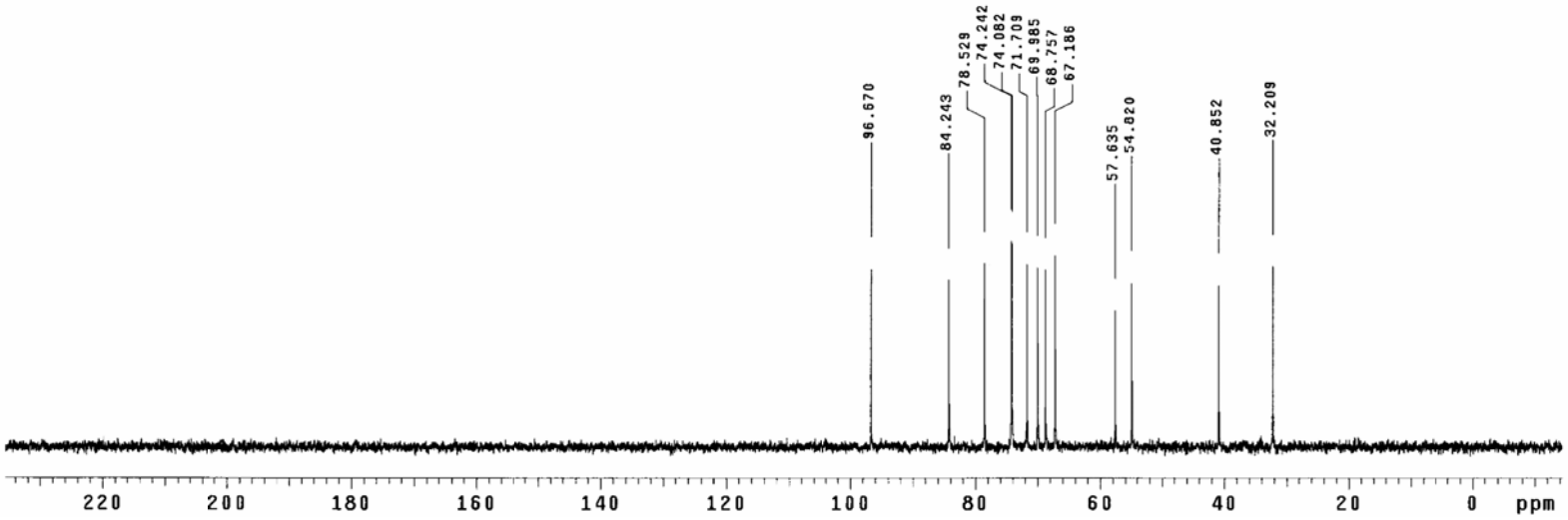
File: CARBON

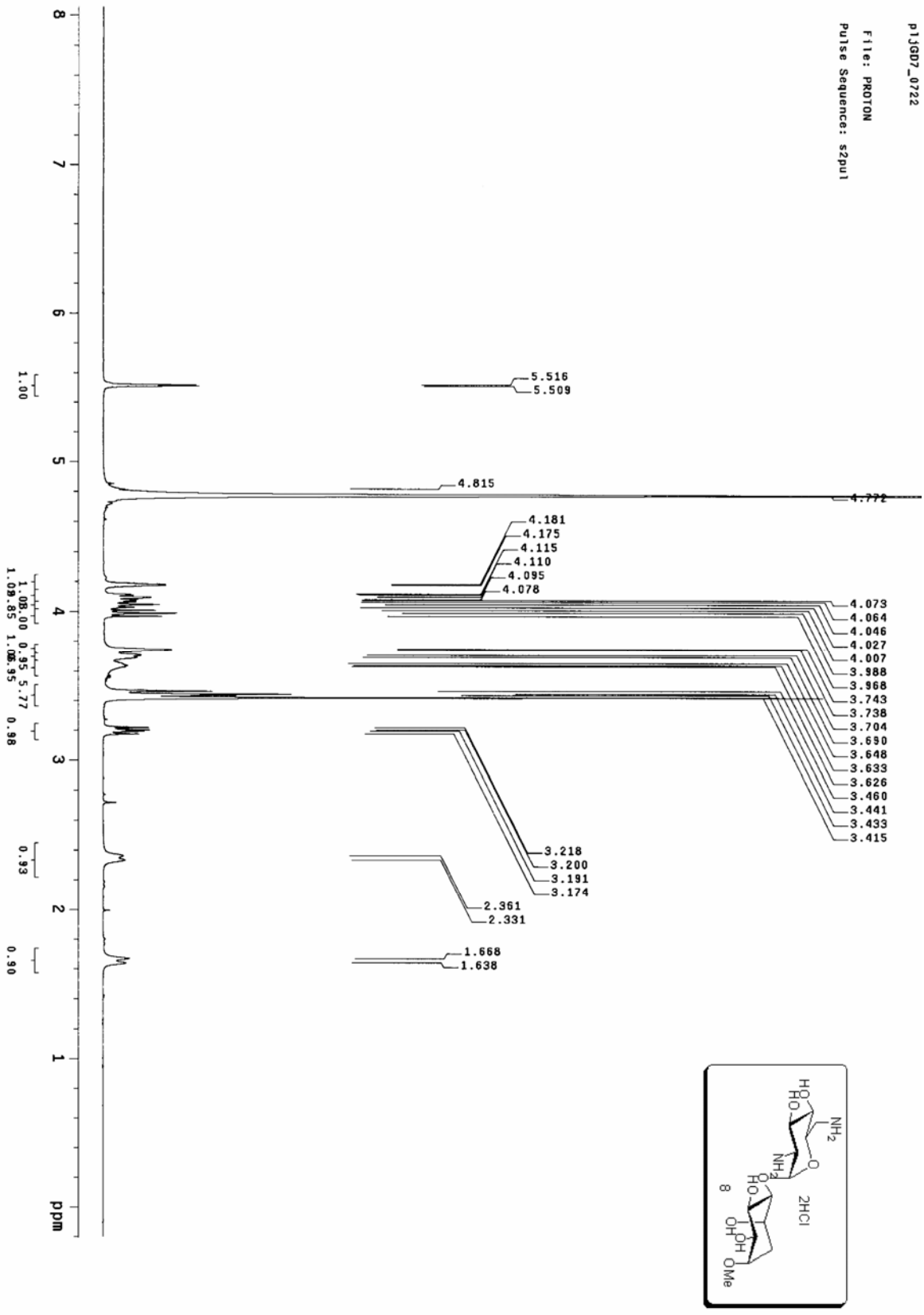
Pulse Sequence: s2pul
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
2112 repetitions
OBSERVE C13, 125.7006556 MHz
DECOUPLE H1, 499.9056708 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 8 hr, 34 min, 16 sec



7

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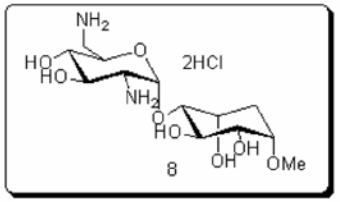
Pulse Sequence: s2pul
5.516
5.509
4.815
4.772
4.181
4.175
4.115
4.110
4.095
4.078
4.073
4.064
4.046
4.027
4.007
3.988
3.968
3.743
3.738
3.704
3.690
3.648
3.633
3.626
3.460
3.441
3.433
3.415
3.218
3.200
3.191
3.174
2.361
2.331
1.668
1.638
1.00
1.03
3.00
0.95
5.77
0.98
0.93
0.90
ppm
NH2
HO
HO
O
NH
O
HO
8
OH
OH
OMe
2HCl

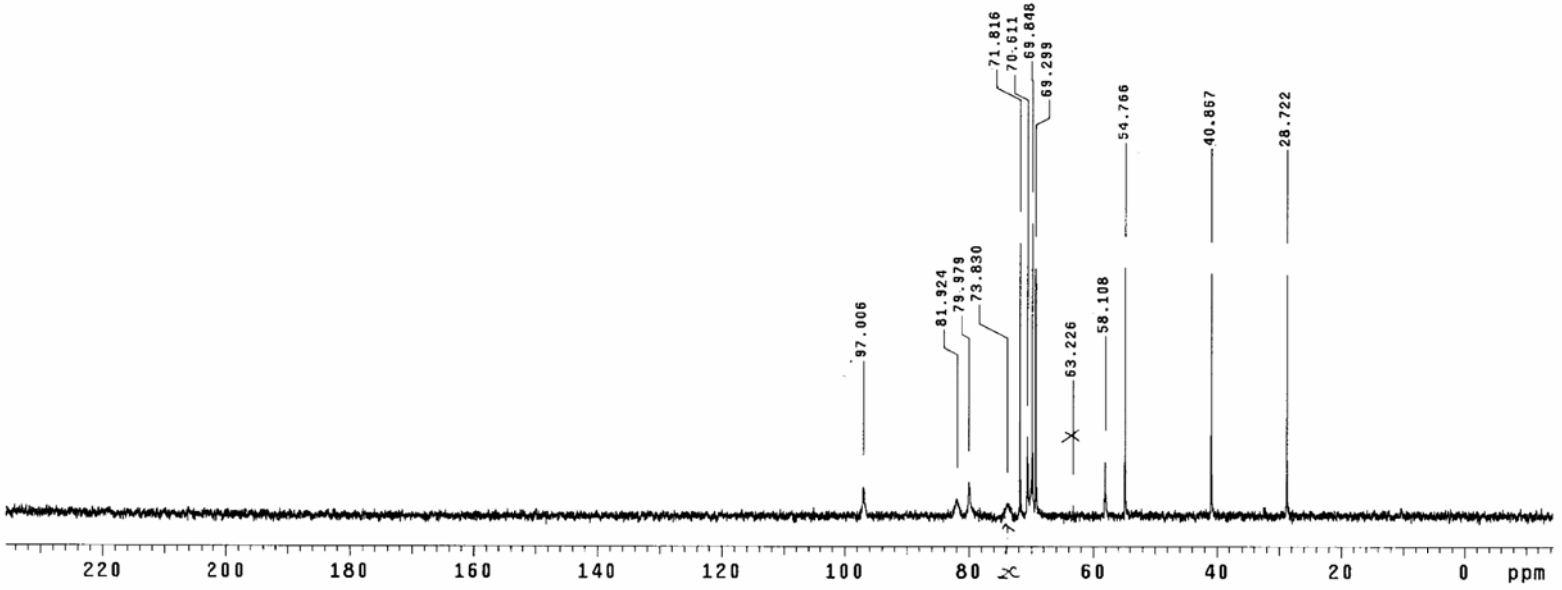
pljGD7_0722

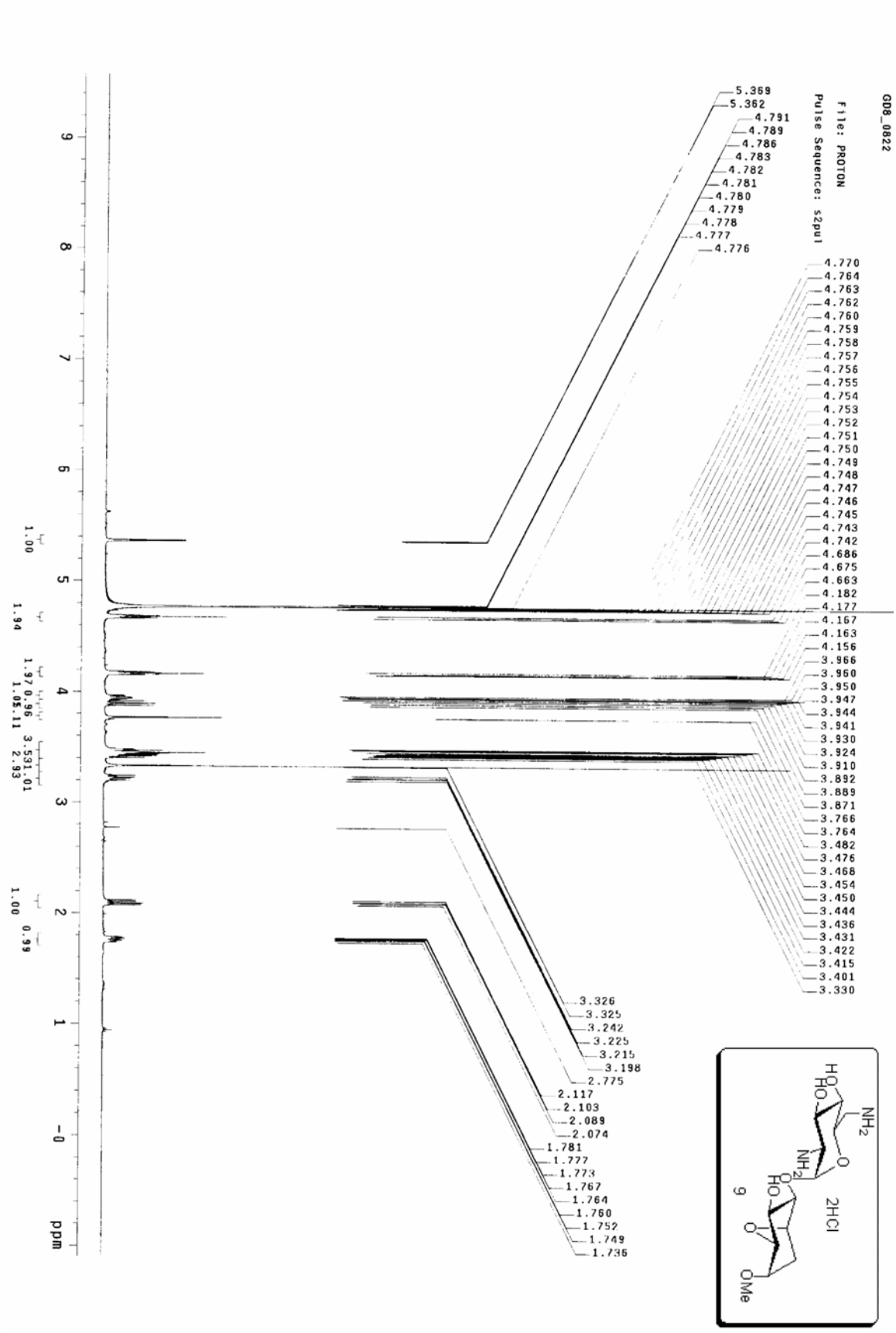
File: CARBON

Pulse Sequence: s2pul
Solvent: D2O
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
8800 repetitions
OBSERVE C13, 125.7006557 MHz
DECOUPLE H1, 499.9056708 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.5 Hz
FT size 65536
Total time 11 hr, 25 min, 42 sec



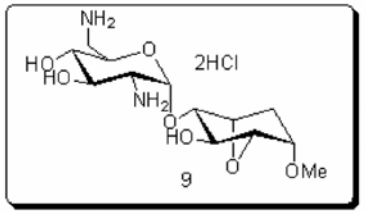



GD8_0822
File: PROTON
Pulse Sequence: s2pul
5.369
5.362
4.791
4.789
4.786
4.783
4.782
4.781
4.780
4.779
4.778
4.777
4.776
4.770
4.764
4.763
4.762
4.760
4.759
4.758
4.757
4.756
4.755
4.754
4.753
4.752
4.751
4.750
4.749
4.748
4.747
4.746
4.745
4.743
4.742
4.686
4.675
4.663
4.182
4.177
4.167
4.163
4.156
3.966
3.960
3.950
3.947
3.944
3.941
3.930
3.924
3.910
3.892
3.889
3.871
3.766
3.764
3.482
3.476
3.468
3.454
3.450
3.444
3.436
3.431
3.422
3.415
3.401
3.330
3.326
3.325
3.242
3.225
3.215
3.198
2.775
2.117
2.103
2.089
2.074
1.781
1.777
1.773
1.767
1.764
1.760
1.752
1.749
1.736
1.00
1.94
1.97
0.96
1.05
5.11
3.53
1.01
2.93
1.00
0.99
9
8
7
6
5
4
3
2
1
-0
ppm
NH2
NH2
HO
HO
O
O
HO
O
O
OMe
2HCl

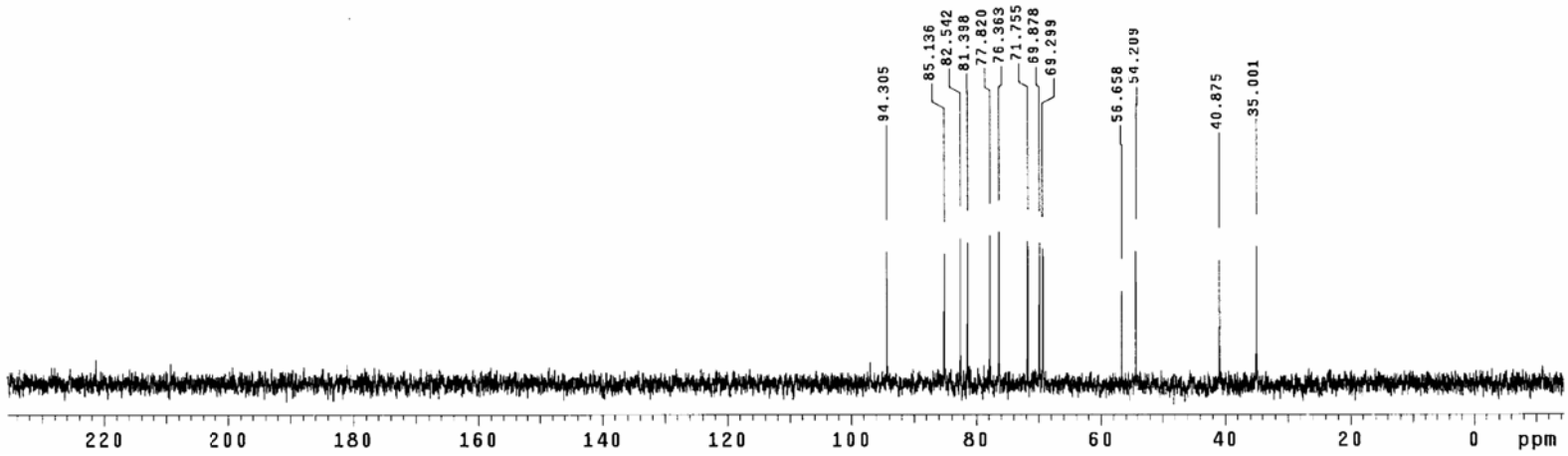
GD8_0822

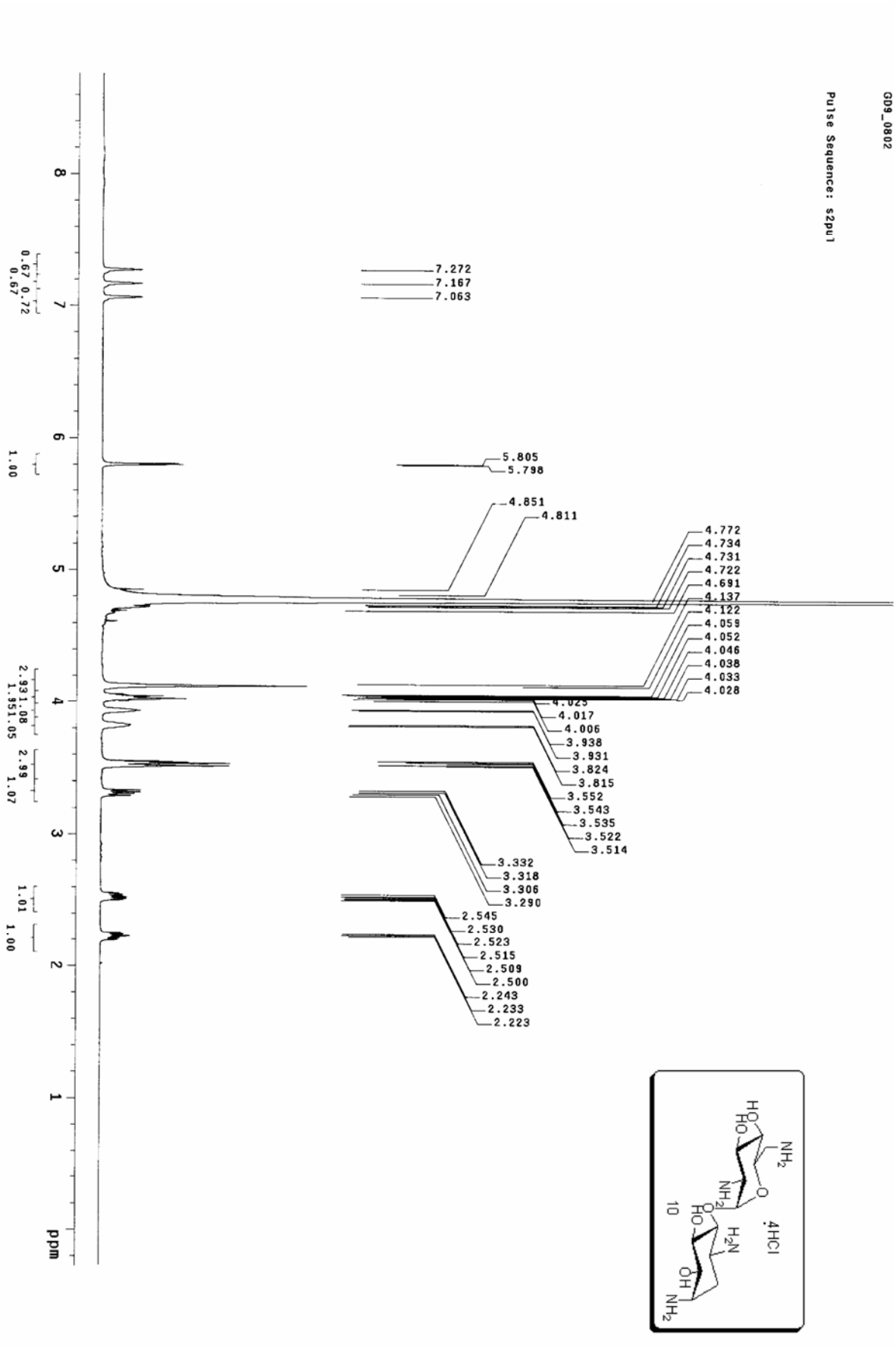
Pulse Sequence: s2pul
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: plj-GD8_0822-c
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
672 repetitions
OBSERVE C13, 125.7006556 MHz
DECOUPLE H1, 499.9056708 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.5 Hz
FT size 65536
Total time 7 hr, 8 min, 34 sec



9



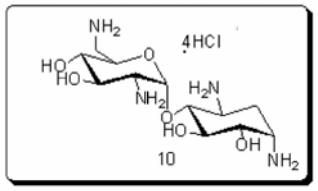

GD9_0802
Pulse Sequence: s2pul
7.272
7.167
7.063
5.805
5.798
4.851
4.811
4.772
4.734
4.731
4.722
4.691
4.137
4.122
4.059
4.052
4.046
4.038
4.033
4.028
4.023
4.017
4.006
3.938
3.931
3.824
3.815
3.552
3.543
3.535
3.522
3.514
3.332
3.318
3.306
3.290
2.545
2.530
2.523
2.515
2.509
2.500
2.243
2.233
2.223
0.67 0.72
0.67
1.00
2.93 1.08
1.95 1.05
2.99
1.07
1.01
1.00
ppm
10
.4HCl

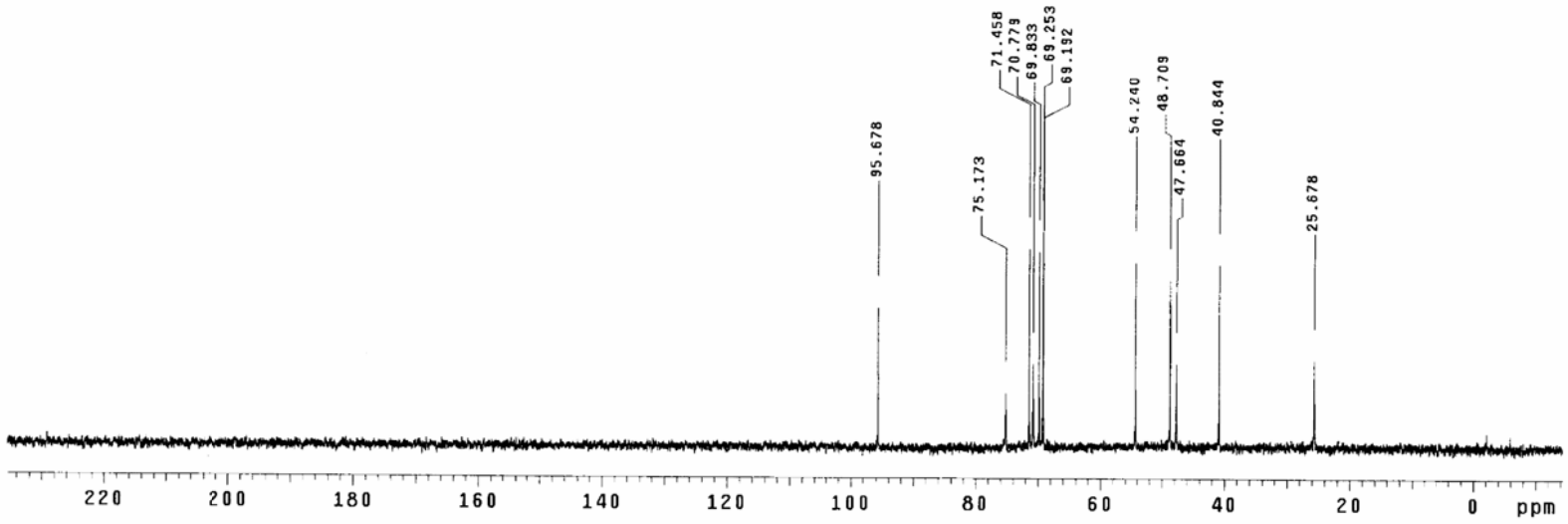
GD9_0808

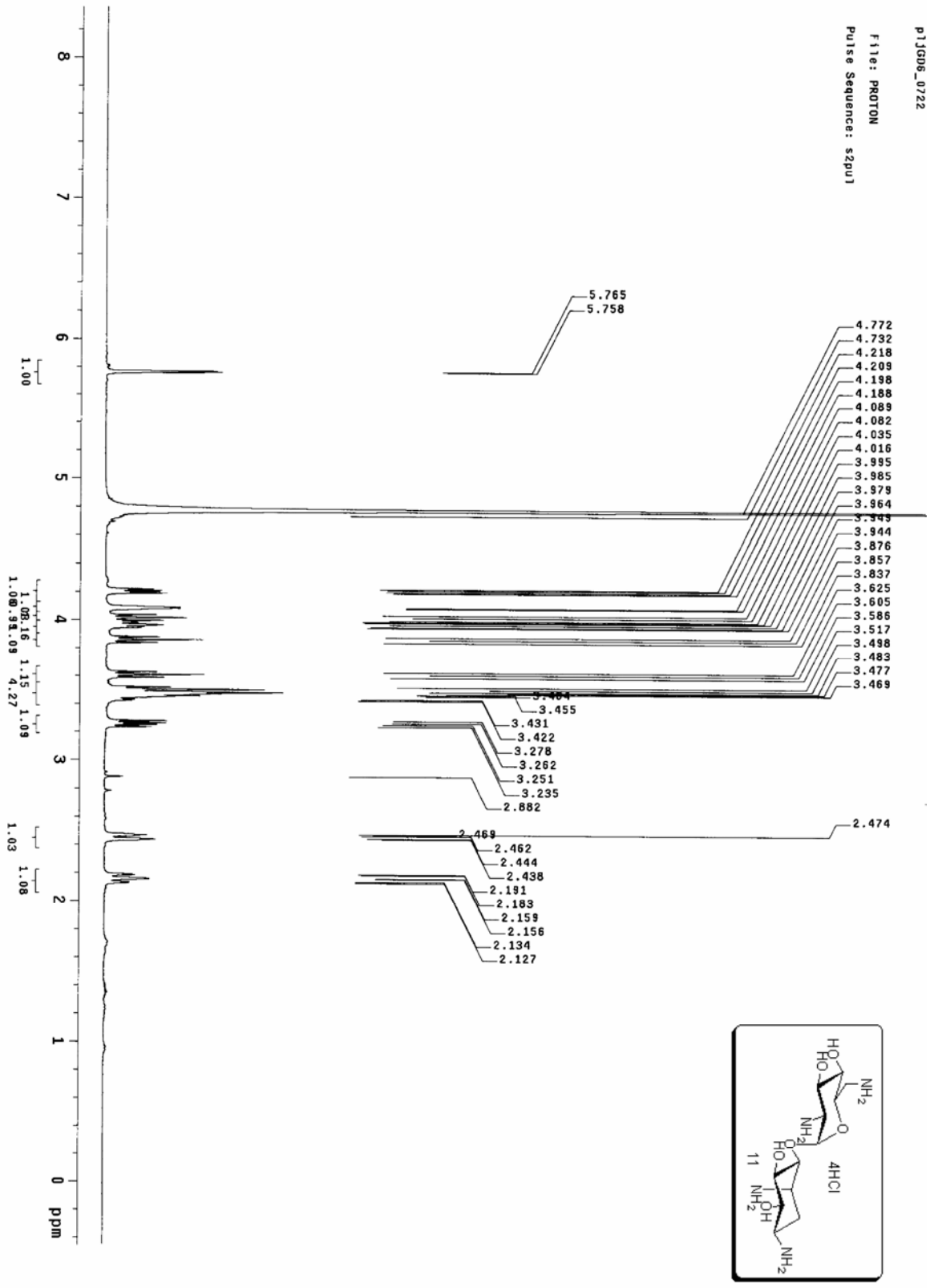
File: CARBON

Pulse Sequence: s2pul
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 64.3 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
6656 repetitions
OBSERVE C13, 125.7006546 MHz
DECOUPLE H1, 499.9056708 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 18 hr, 44 min, 59 sec





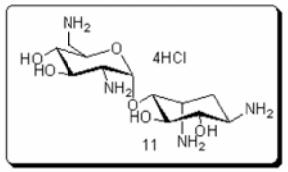

pljGD6_0722
File: PROTON
Pulse Sequence: s2pul
5.765
5.758
4.772
4.732
4.218
4.209
4.198
4.188
4.089
4.082
4.035
4.016
3.995
3.985
3.979
3.964
3.944
3.876
3.857
3.837
3.625
3.605
3.586
3.517
3.498
3.483
3.477
3.469
3.455
3.431
3.422
3.278
3.262
3.251
3.235
2.882
2.474
2.462
2.444
2.438
2.191
2.183
2.159
2.156
2.134
2.127
1.00
1.08
1.15
1.09
4.27
1.03
1.08
ppm
4HCl

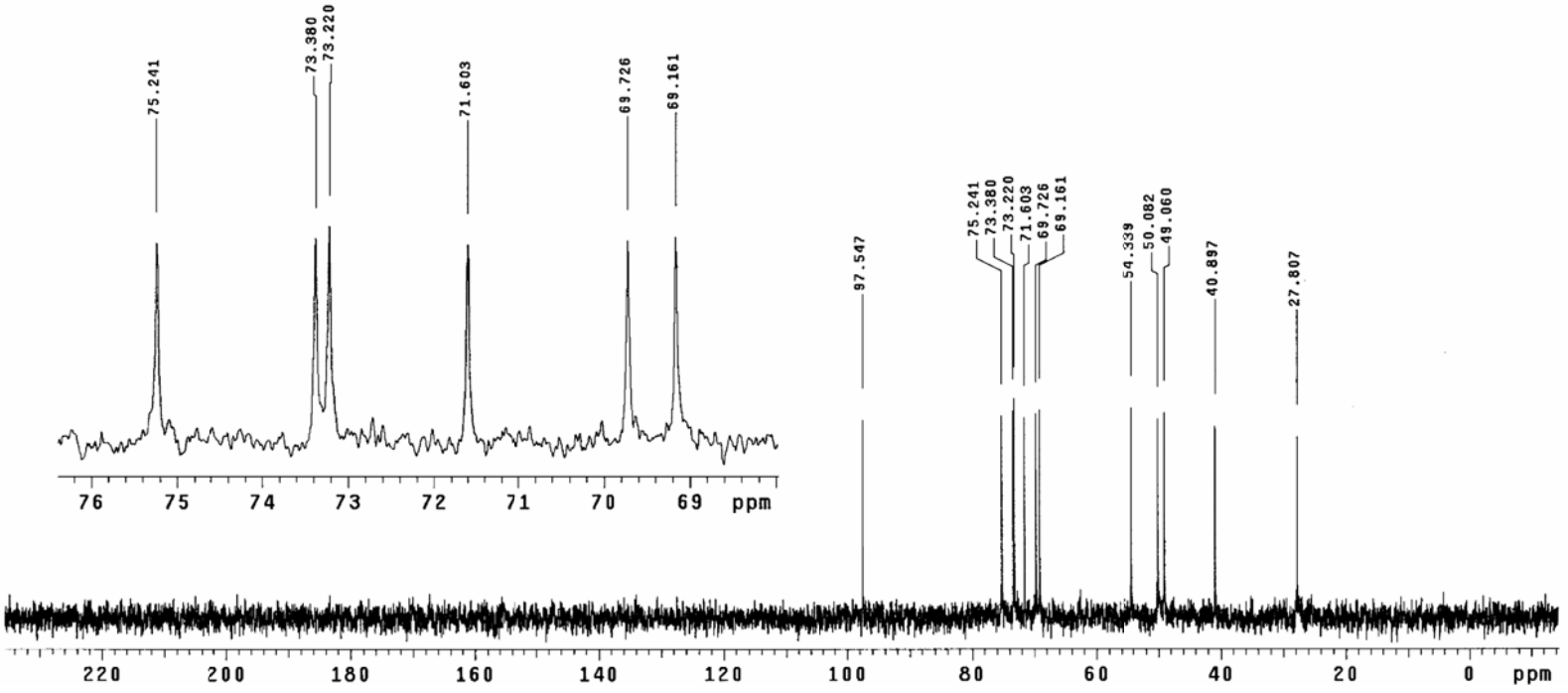
pljGD6_0722

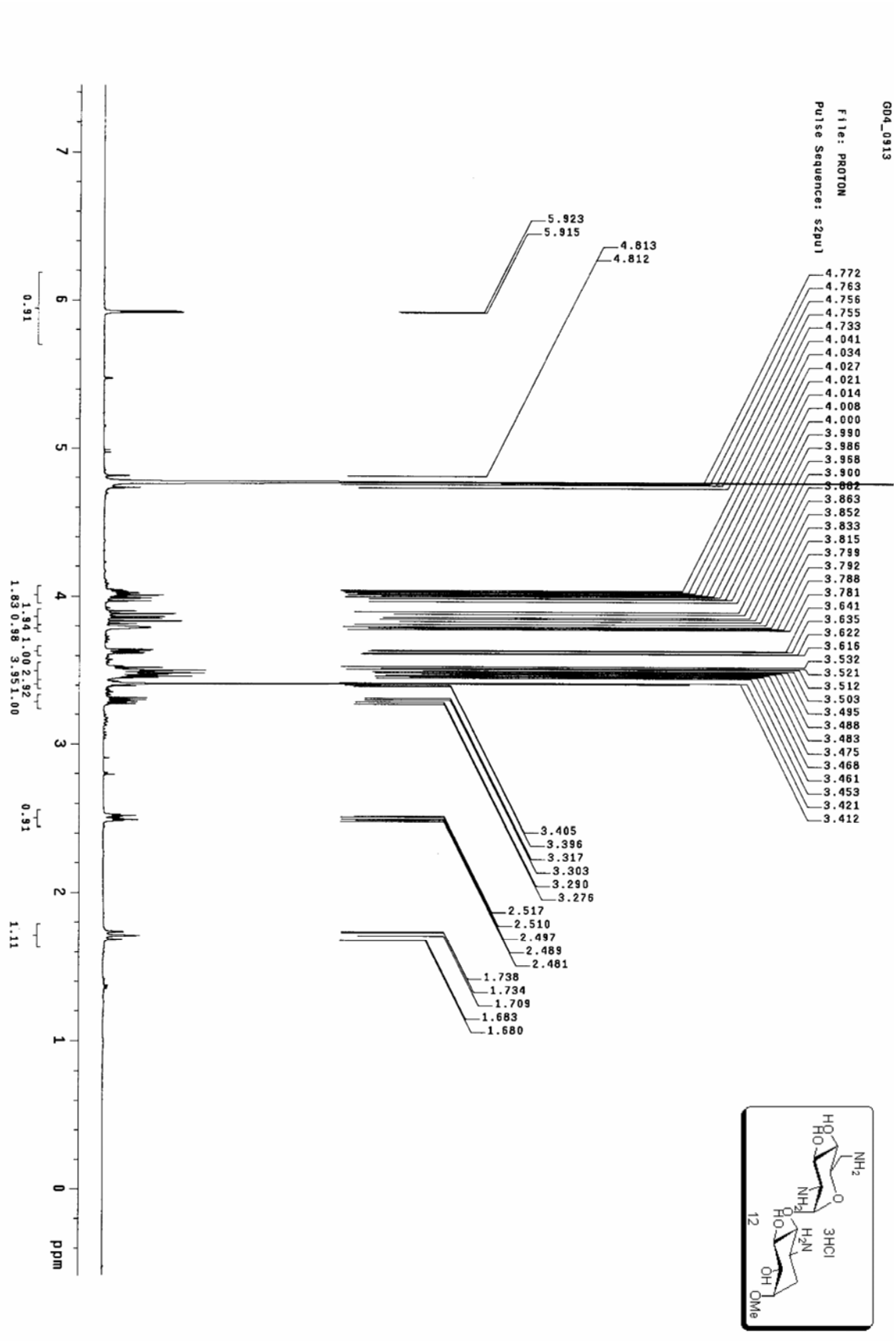
File: CARBON

Pulse Sequence: s2pul
Solvent: D2O
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
1248 repetitions
OBSERVE C13, 125.7006557 MHz
DECOUPLE H1, 499.9056708 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.5 Hz
FT size 65536
Total time 11 hr, 25 min, 42 sec





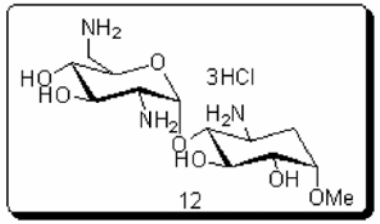

G04_0913
File: PROTON
Pulse Sequence: s2pul
5.923
5.915
4.813
4.812
4.772
4.763
4.756
4.755
4.733
4.041
4.034
4.027
4.021
4.014
4.008
4.000
3.990
3.986
3.968
3.900
3.882
3.863
3.852
3.833
3.815
3.799
3.792
3.788
3.781
3.641
3.635
3.622
3.616
3.532
3.521
3.512
3.503
3.495
3.488
3.483
3.475
3.468
3.461
3.453
3.421
3.412
3.405
3.396
3.317
3.303
3.290
3.276
2.517
2.510
2.497
2.489
2.481
1.738
1.734
1.709
1.683
1.680
0.91
1.94 1.00 2.92
1.83 0.98 3.95 1.00
0.91
1.11
ppm
3HCl
12

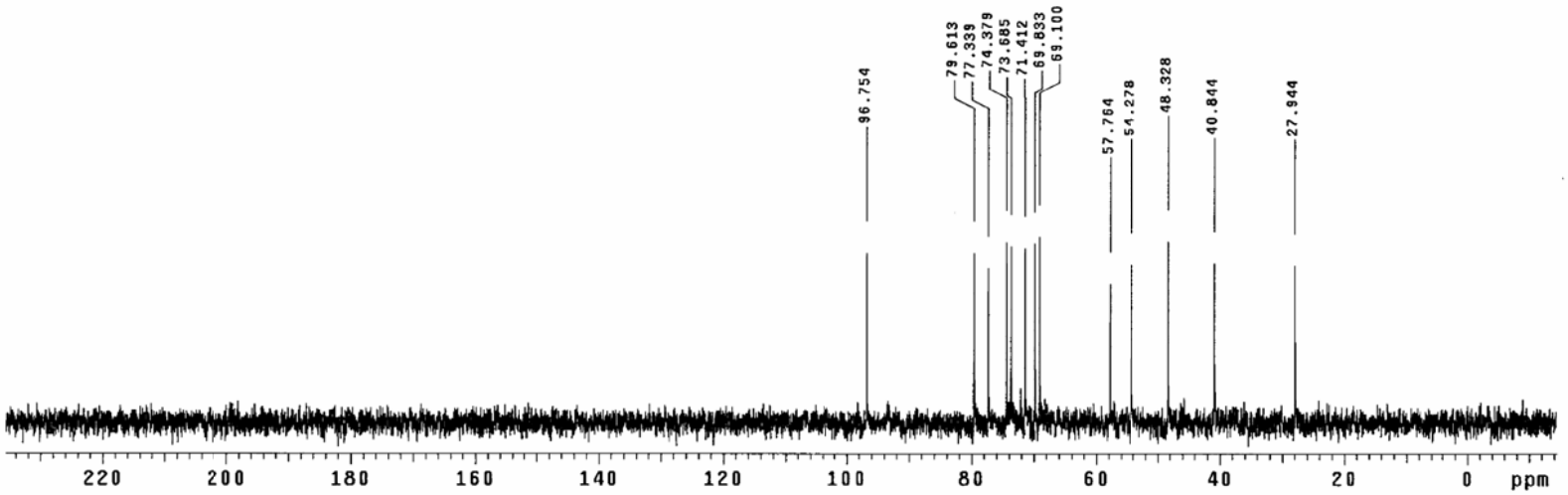
GD4_0913

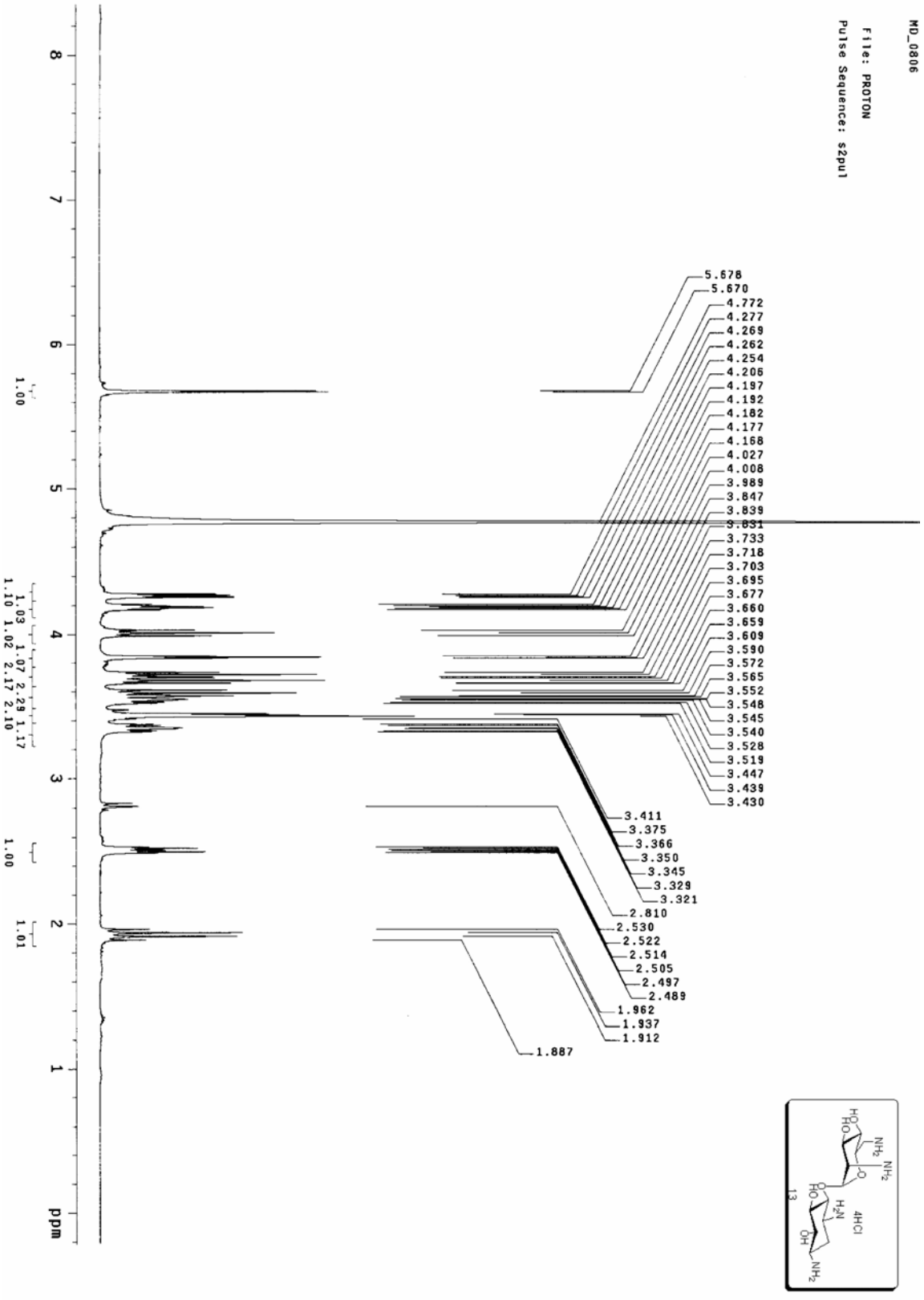
File: CARBON

Pulse Sequence: s2pul
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
1568 repetitions
OBSERVE C13, 125.7006556 MHz
DECOUPLE H1, 499.9056708 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 14 hr, 17 min, 8 sec





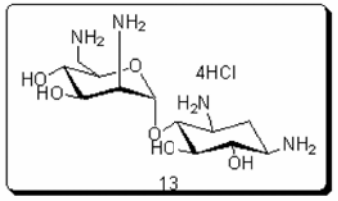

MD_0806
File: PROTON
Pulse Sequence: s2pul
5.678
5.670
4.772
4.277
4.269
4.262
4.254
4.206
4.197
4.192
4.182
4.177
4.168
4.027
4.008
3.989
3.847
3.839
3.831
3.733
3.718
3.703
3.695
3.677
3.660
3.659
3.609
3.590
3.572
3.565
3.552
3.548
3.545
3.540
3.528
3.519
3.447
3.439
3.430
3.411
3.375
3.366
3.350
3.345
3.329
3.321
2.810
2.530
2.522
2.514
2.505
2.497
2.489
1.962
1.937
1.912
1.887
1.00
1.03
1.07
2.29
1.17
1.10
1.02
2.17
2.10
1.00
1.01
ppm
4HCl

MD_0806

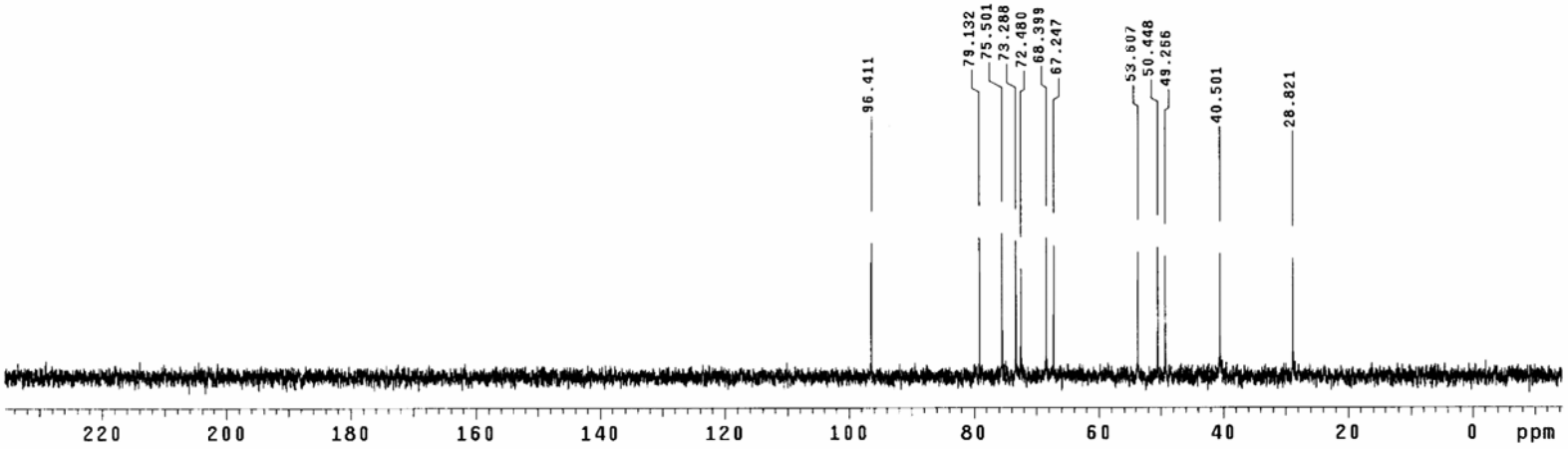
File: CARBON

Pulse Sequence: s2pul
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 64.3 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
640 repetitions
OBSERVE C13, 125.7006556 MHz
DECOUPLE H1, 499.9056708 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 14 hr, 59 min, 59 sec



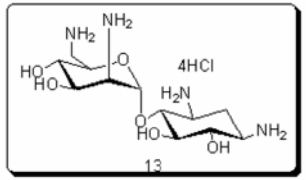
13



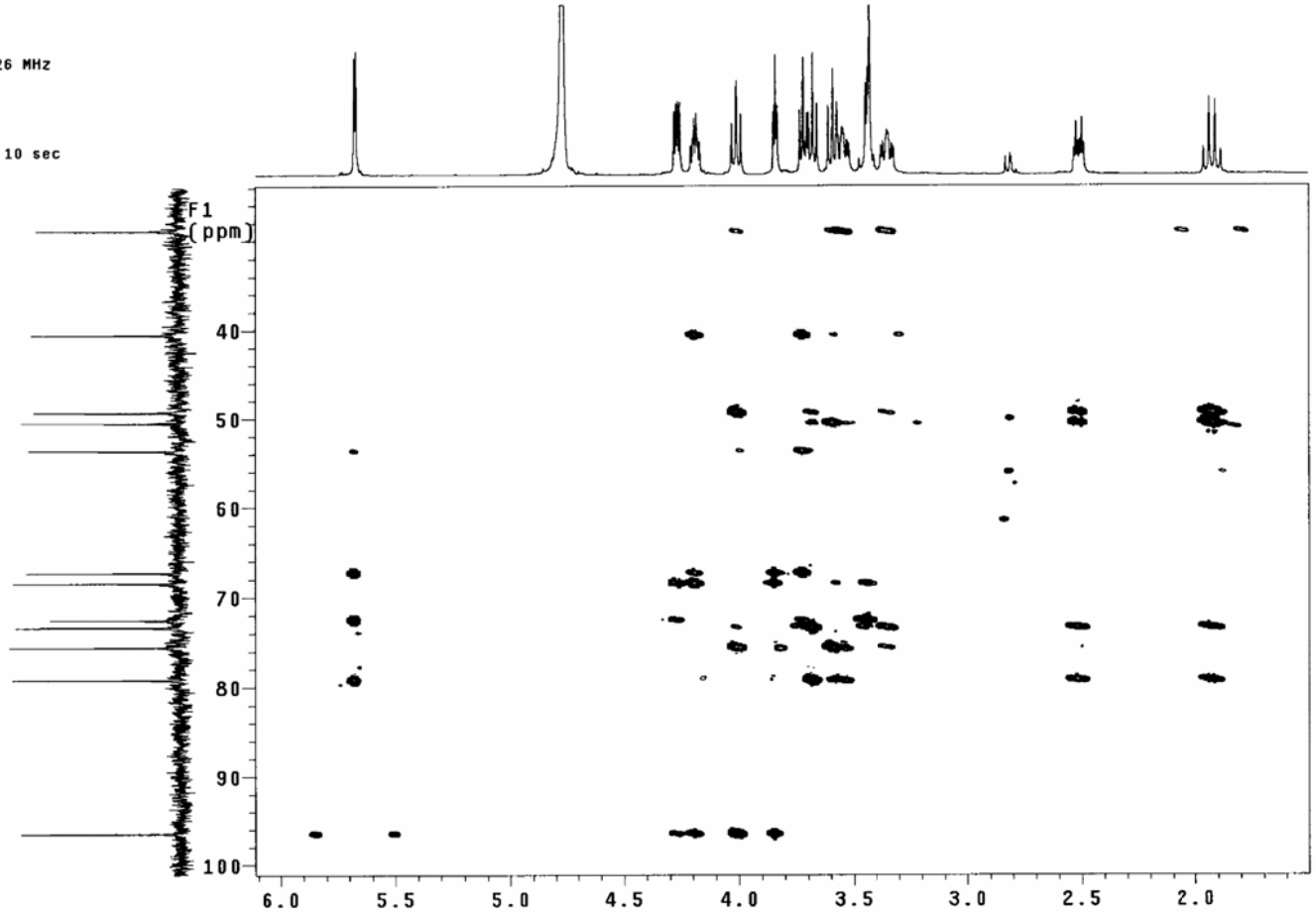
pljMD_1129

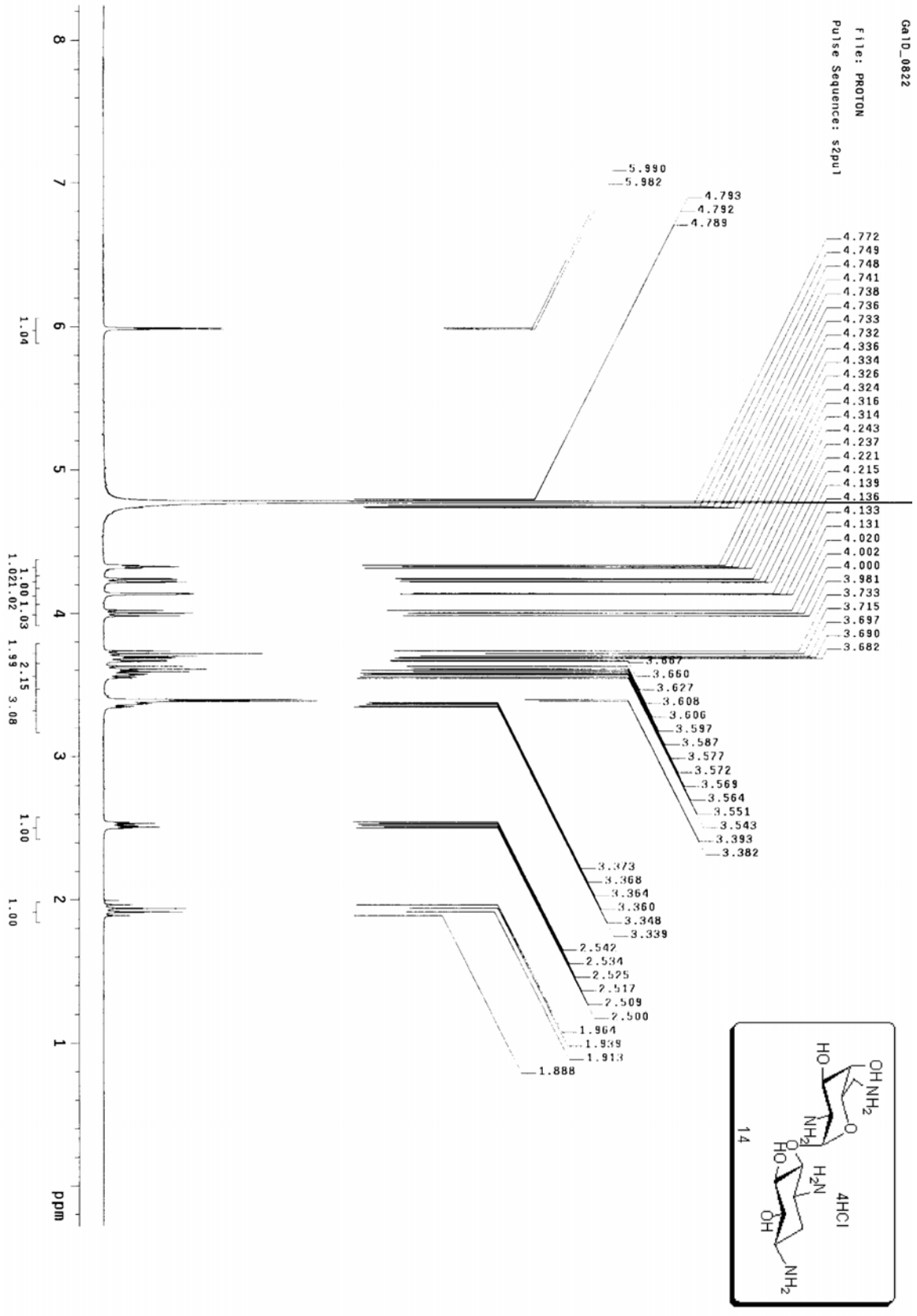
Pulse Sequence: gHMBC
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: pljMD_1129-bc
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.330 sec
Width 3105.1 Hz
2D Width 12917.8 Hz
32 repetitions
400 increments
OBSERVE H1, 499.9031226 MHz
DATA PROCESSING
Sine bell 0.082 sec
F1 DATA PROCESSING
Sine bell 0.016 sec
FT size 1024 x 8192
Total time 5 hr, 5 min, 10 sec



13

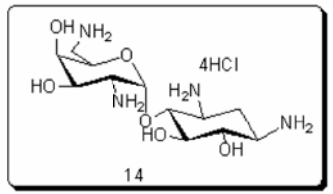



Ga1D_0822
File: PROTON
Pulse Sequence: s2pul
5.990
5.982
4.793
4.792
4.789
4.772
4.749
4.748
4.741
4.738
4.736
4.733
4.732
4.336
4.334
4.326
4.324
4.316
4.314
4.243
4.237
4.221
4.215
4.139
4.136
4.133
4.131
4.020
4.002
4.000
3.981
3.733
3.715
3.697
3.690
3.682
3.667
3.660
3.627
3.608
3.606
3.597
3.587
3.577
3.572
3.569
3.564
3.551
3.543
3.393
3.382
3.373
3.368
3.364
3.360
3.348
3.339
2.542
2.534
2.525
2.517
2.509
2.500
1.964
1.939
1.913
1.888
1.04
1.00 1.03
1.021.02
1.99
2.15
3.08
1.00
1.00
ppm
14
4HCl

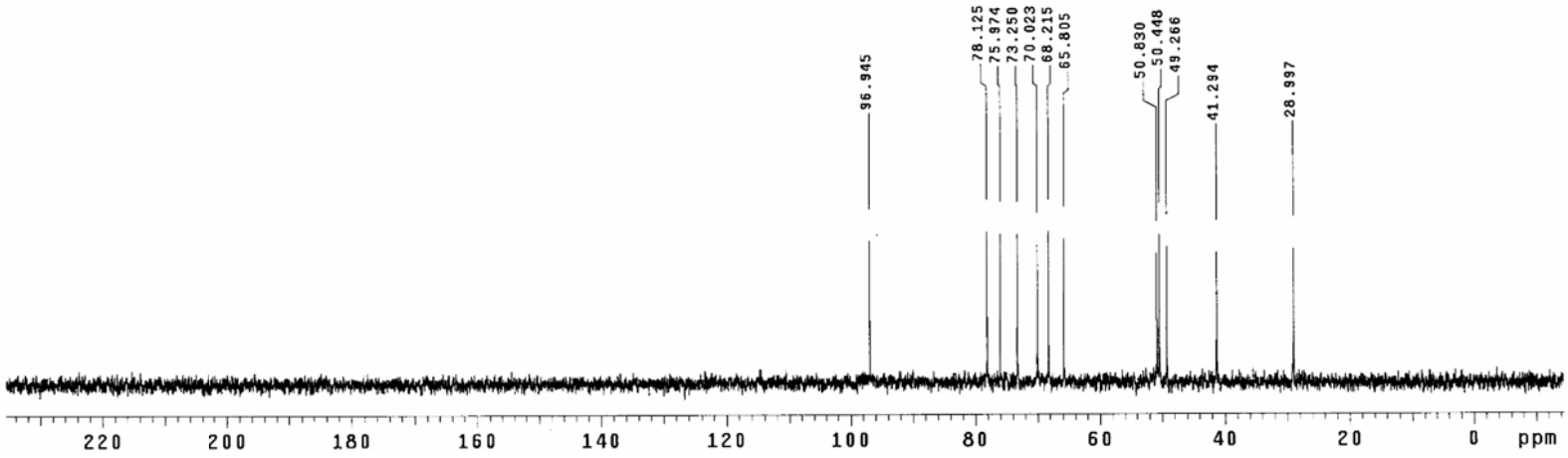
GalD_0822

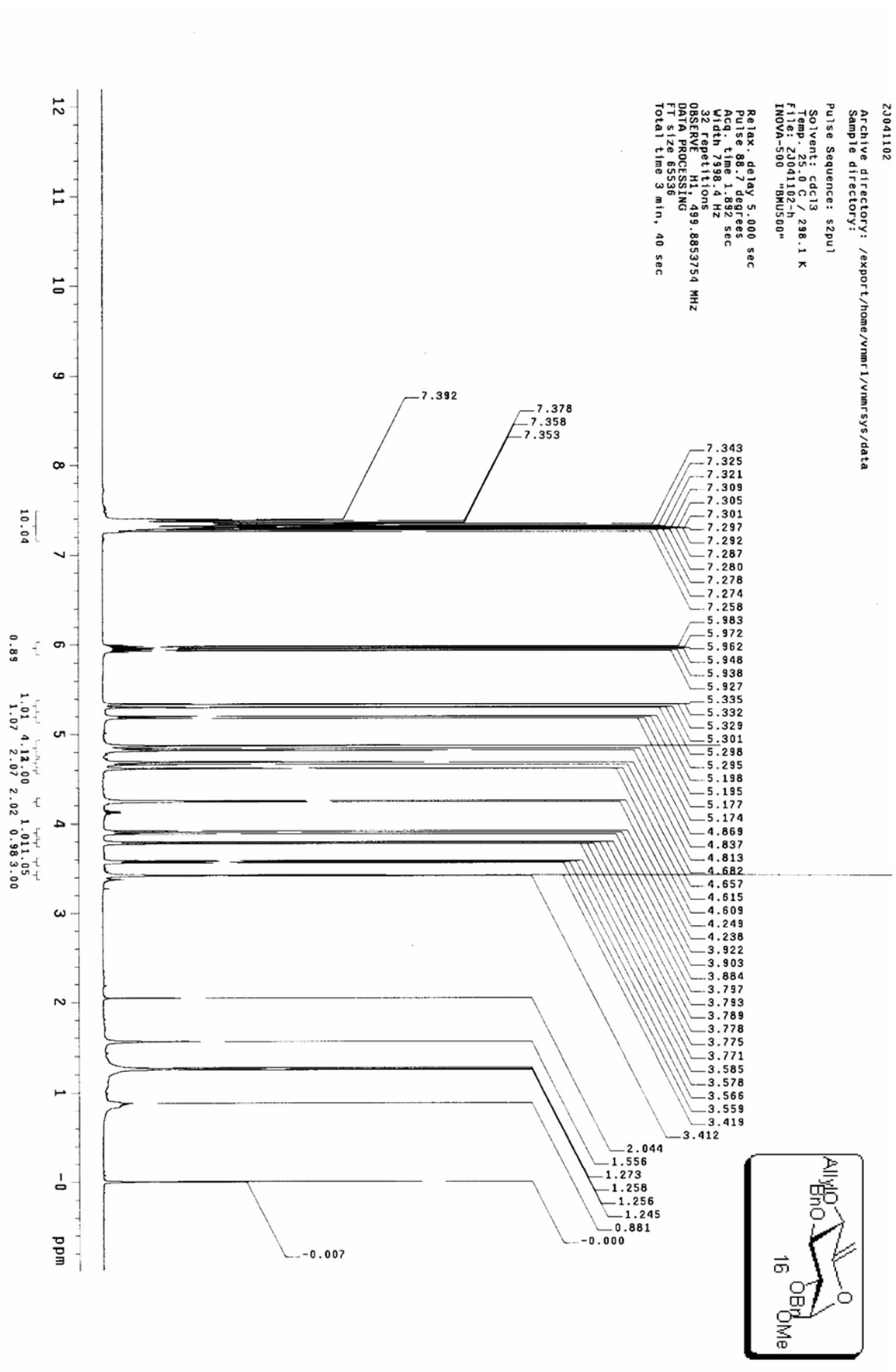
Pulse Sequence: s2pul
Solvent: d2o
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: plj-GalD_0822-c
INOVA-500 "BMU500"

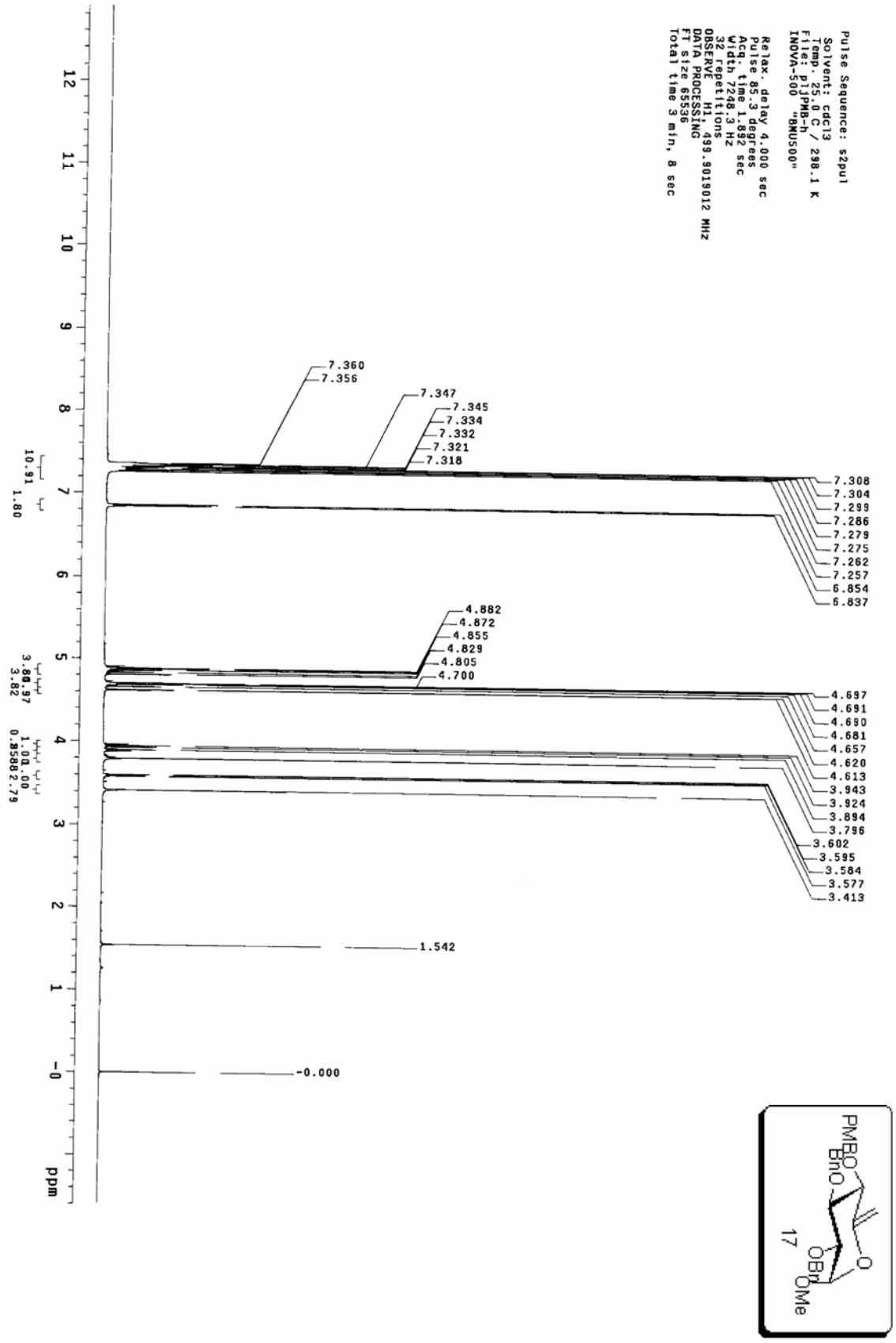
Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
352 repetitions
OBSERVE C13, 125.7006556 MHz
DECOUPLE H1, 499.9056708 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.5 Hz
FT size 65536
Total time 7 hr, 8 min, 34 sec

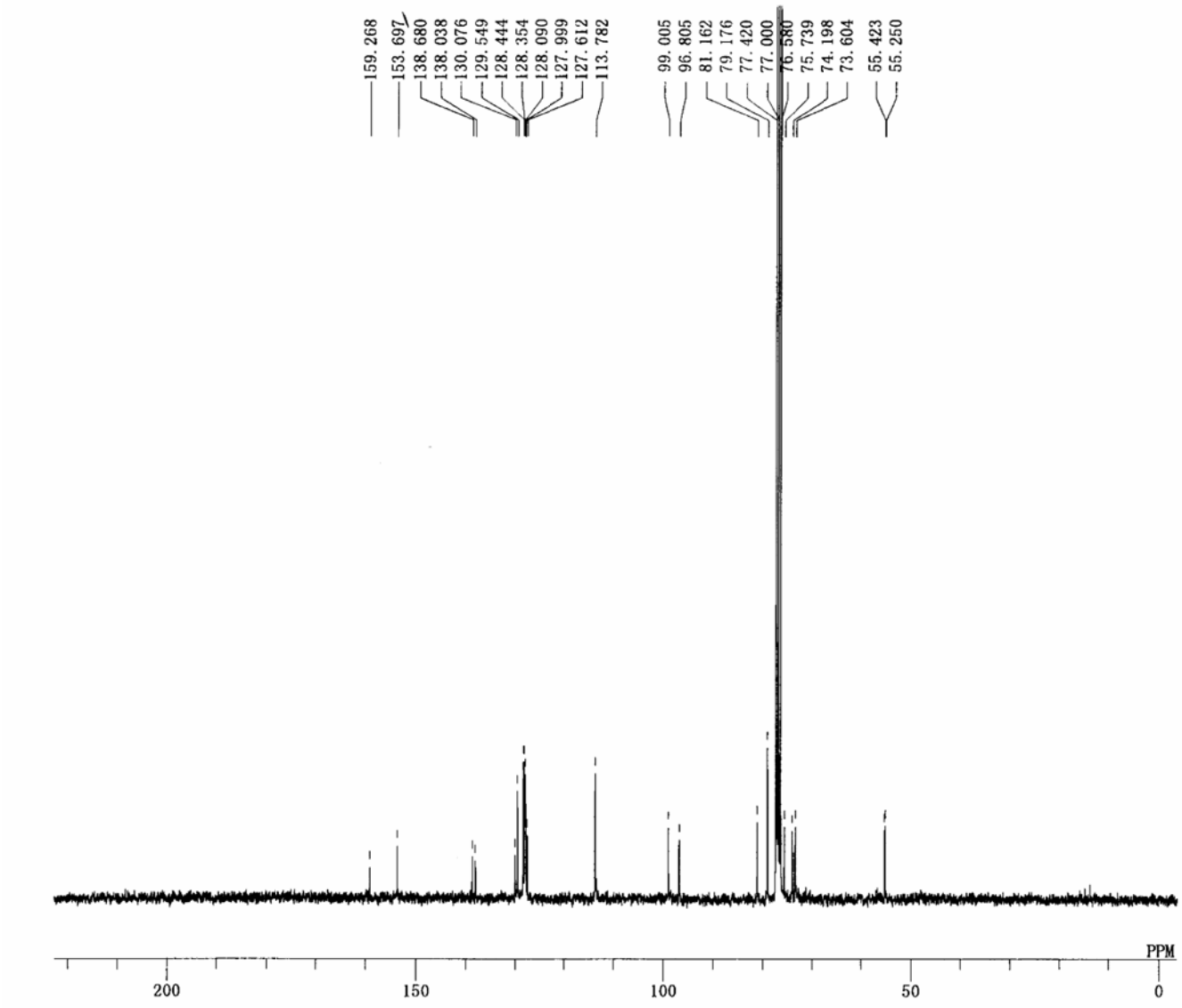


14

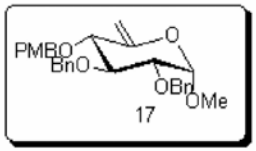


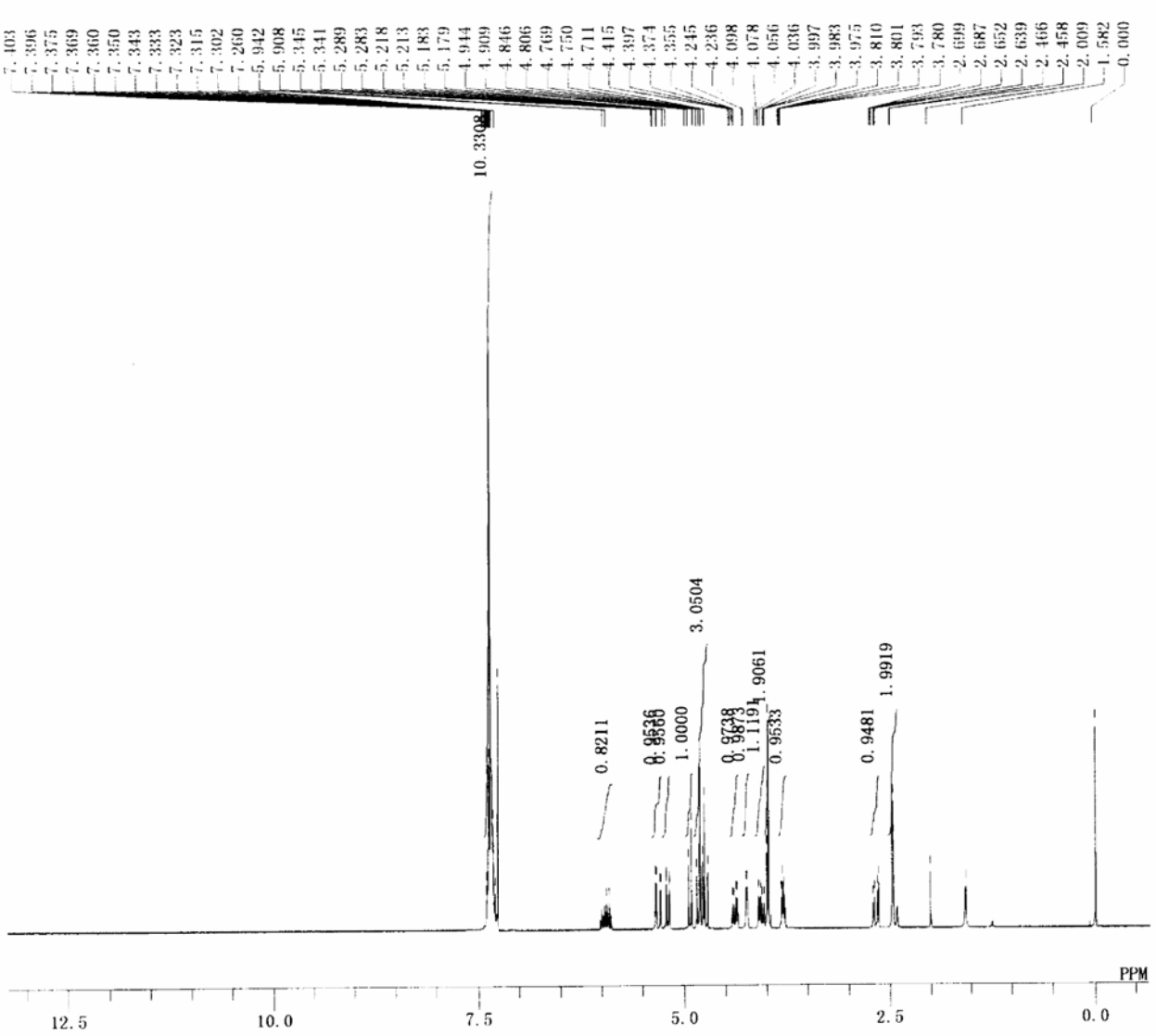

ZJ041102
Archive directory: /export/home/vnmr1/vnmrsys/data
Sample directory:
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File: ZJ041102-h
INOVA-500 "BMU500"
Relax. delay 5.000 sec
Pulse 88.7 degrees
Acq. time 1.882 sec
Width 7998.4 Hz
32 repetitions
OBSERVE H1, 499.8853754 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 40 sec
7.392
7.378
7.358
7.353
7.343
7.325
7.321
7.309
7.305
7.301
7.297
7.292
7.287
7.280
7.278
7.274
7.258
5.983
5.972
5.962
5.948
5.938
5.927
5.335
5.332
5.329
5.301
5.298
5.295
5.198
5.195
5.177
5.174
4.869
4.837
4.813
4.682
4.657
4.615
4.609
4.249
4.238
3.922
3.903
3.884
3.797
3.793
3.789
3.778
3.775
3.771
3.585
3.578
3.566
3.559
3.419
3.412
2.044
1.556
1.273
1.258
1.256
1.245
0.881
-0.000
-0.007
10.04
0.89
1.01
1.07
4.12.00
2.07
2.02
1.011.05
0.98
3.00
ppm
AllylO
BnO
OBn
OMe
16


pljPMB
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File: pljPMB-h
INOVA-500 "BNU500"
Relax. delay 4.000 sec
Pulse 85.3 degrees
Acq. time 1.892 sec
Width 7248.3 Hz
32 repetitions
OBSERVE H1, 499.9019012 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 8 sec
7.360
7.356
7.347
7.345
7.334
7.332
7.321
7.318
7.308
7.304
7.299
7.286
7.279
7.275
7.262
7.257
6.854
6.837
4.882
4.872
4.855
4.829
4.805
4.700
4.697
4.691
4.690
4.681
4.657
4.620
4.613
3.943
3.924
3.894
3.796
3.602
3.595
3.584
3.577
3.413
1.542
-0.000
10.91
1.80
3.97
3.82
1.00
2.79
0.85
ppm
PMBO
BnO
OBn
OMe
17

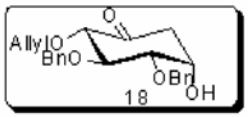


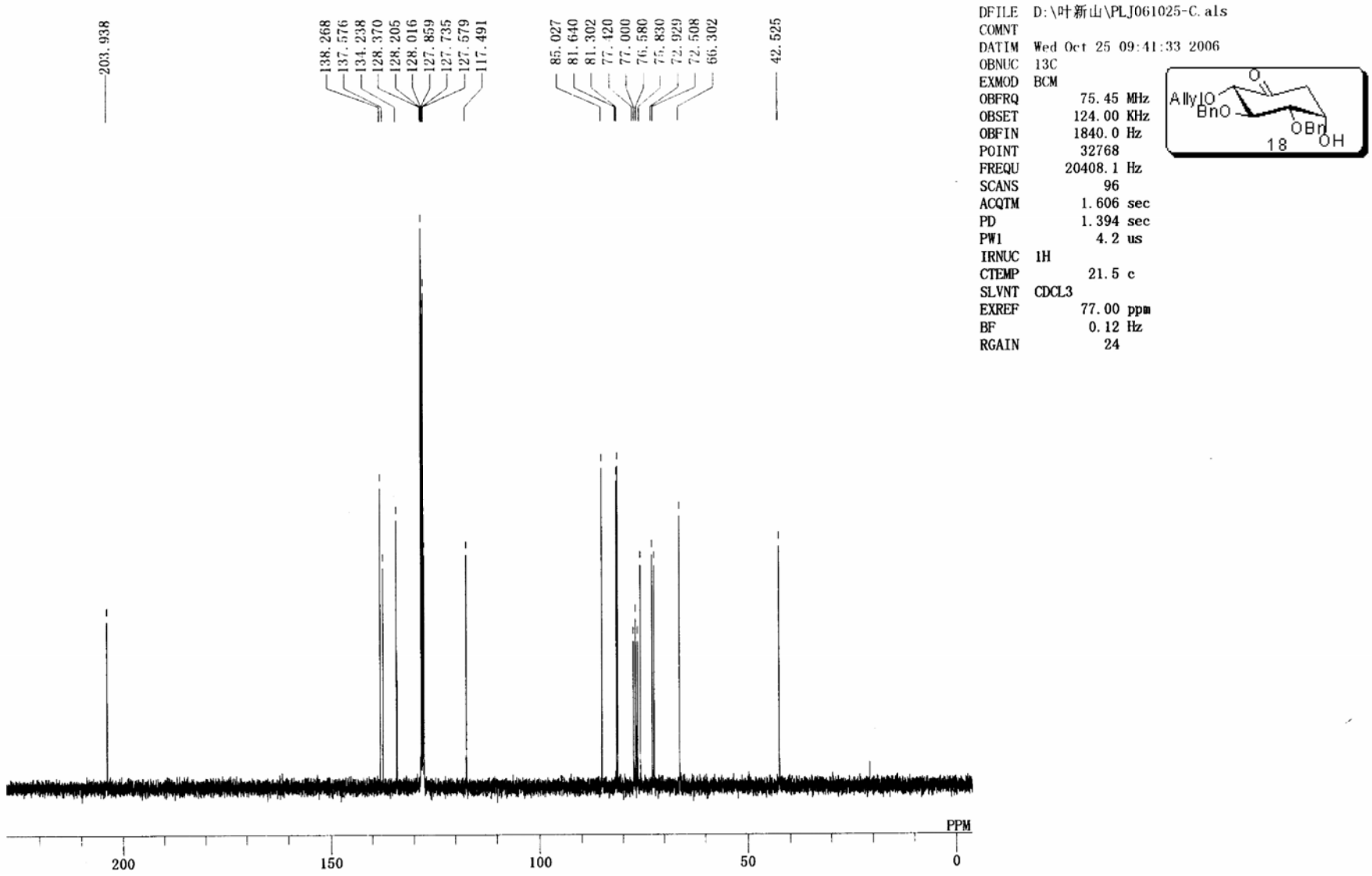
DFILE D:\叶新山\pljPMB-C.als
OBNUC 13C
EXMOD BCM
OFR 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 3280
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRN
CTEMP 20.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24

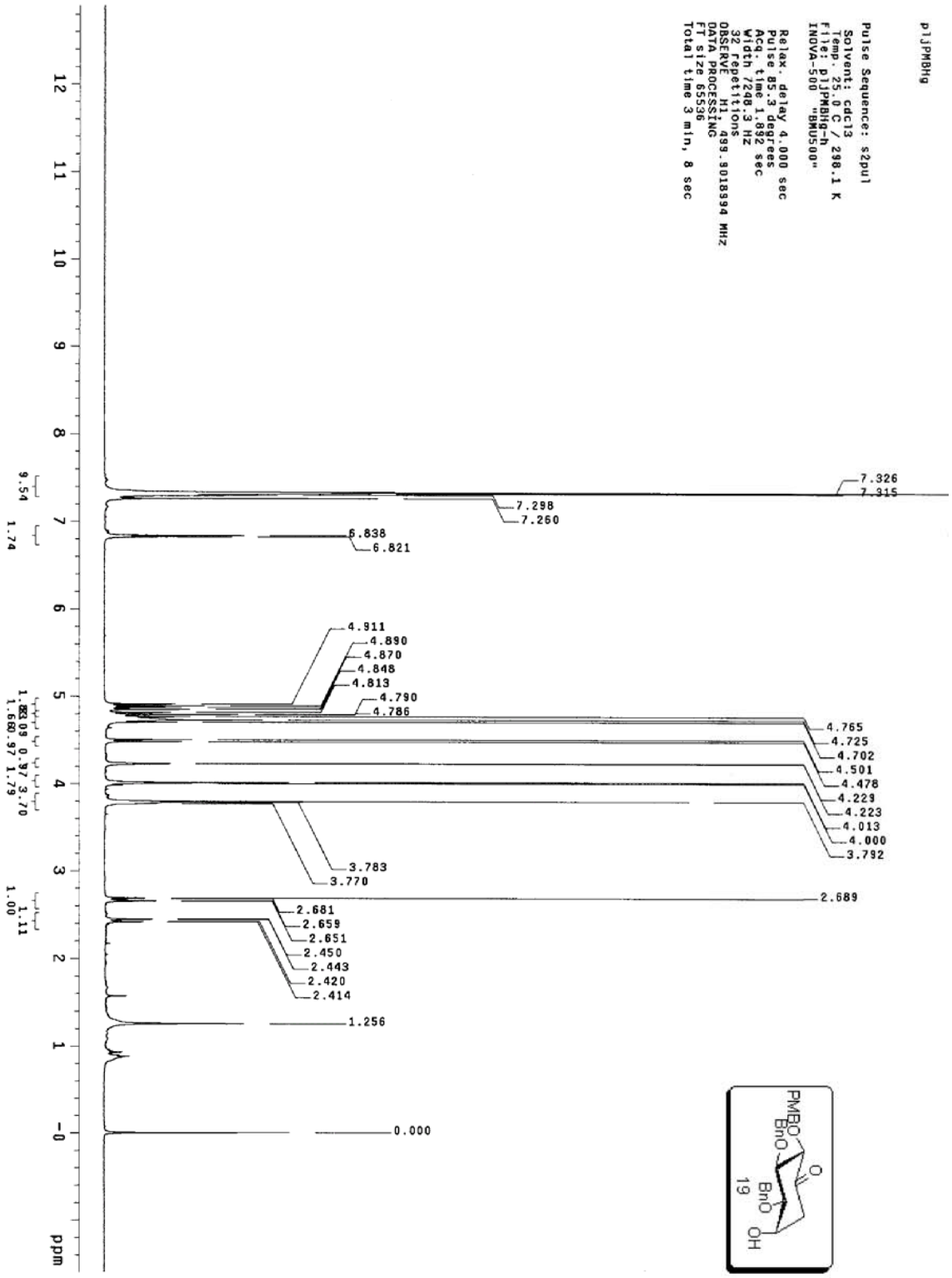


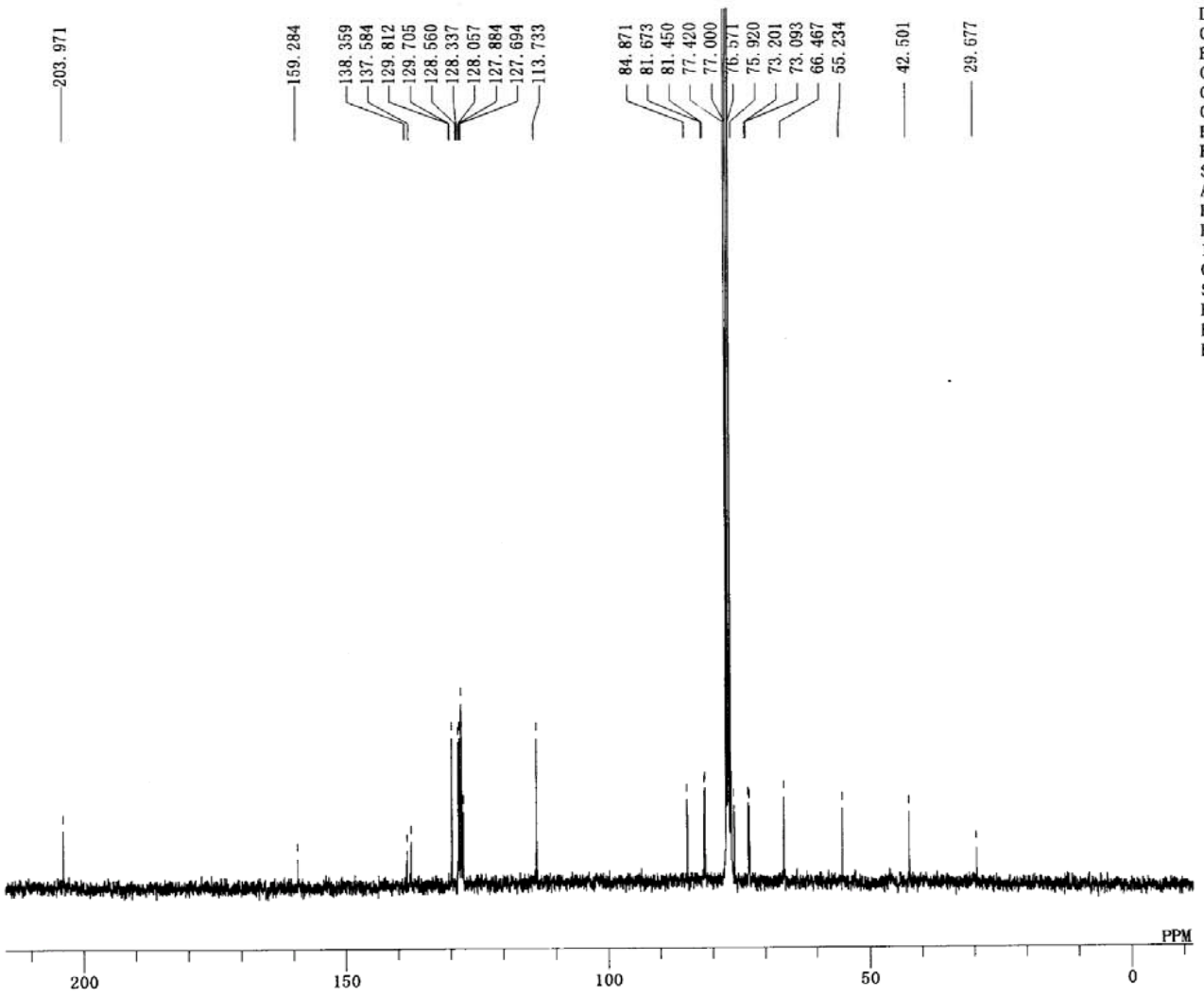


DFILE	D:\叶新山\PLJ051226-2-H.als
OBNUC	1H
EXMOD	NON
OBFRQ	300.40 MHz
OBSET	130.00 KHz
OBFIN	1150.0 Hz
POINT	32768
FREQU	8000.0 Hz
SCANS	8
ACQTM	4.096 sec
PD	1.551 sec
PW1	6.1 us
IRATN	511
CTEMP	20.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	18

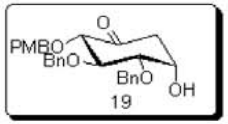


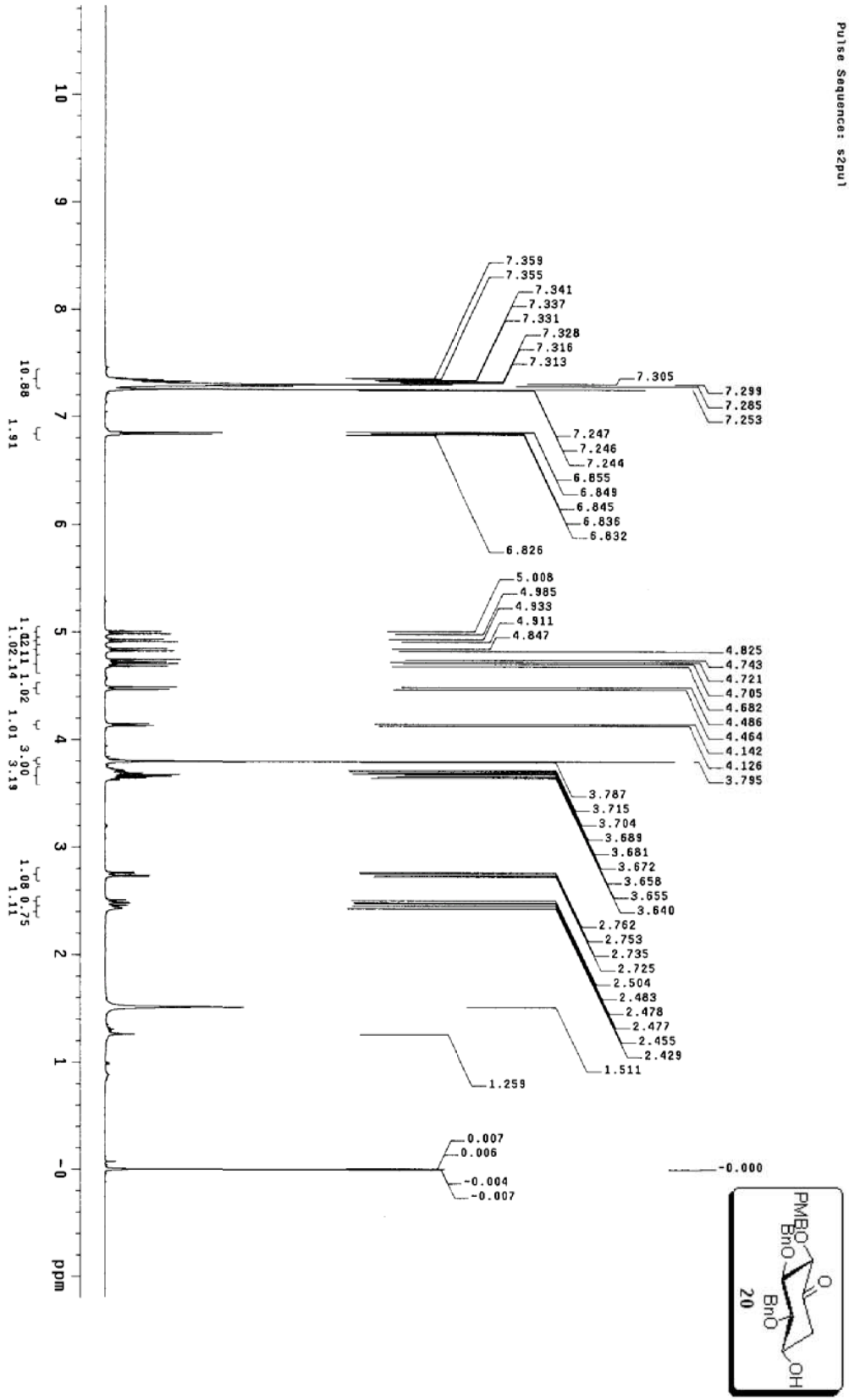

203.938
138.268
137.576
134.238
128.370
128.205
128.016
127.859
127.735
127.579
117.491
85.027
81.640
81.302
77.420
77.000
76.580
75.830
72.929
72.508
66.302
42.525
DFILE D:\叶新山\PLJ061025-C.als
COMNT
DATIM Wed Oct 25 09:41:33 2006
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 96
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 21.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24
AllylO
BnO
OBn
OH
18
PPM
200
150
100
50
0

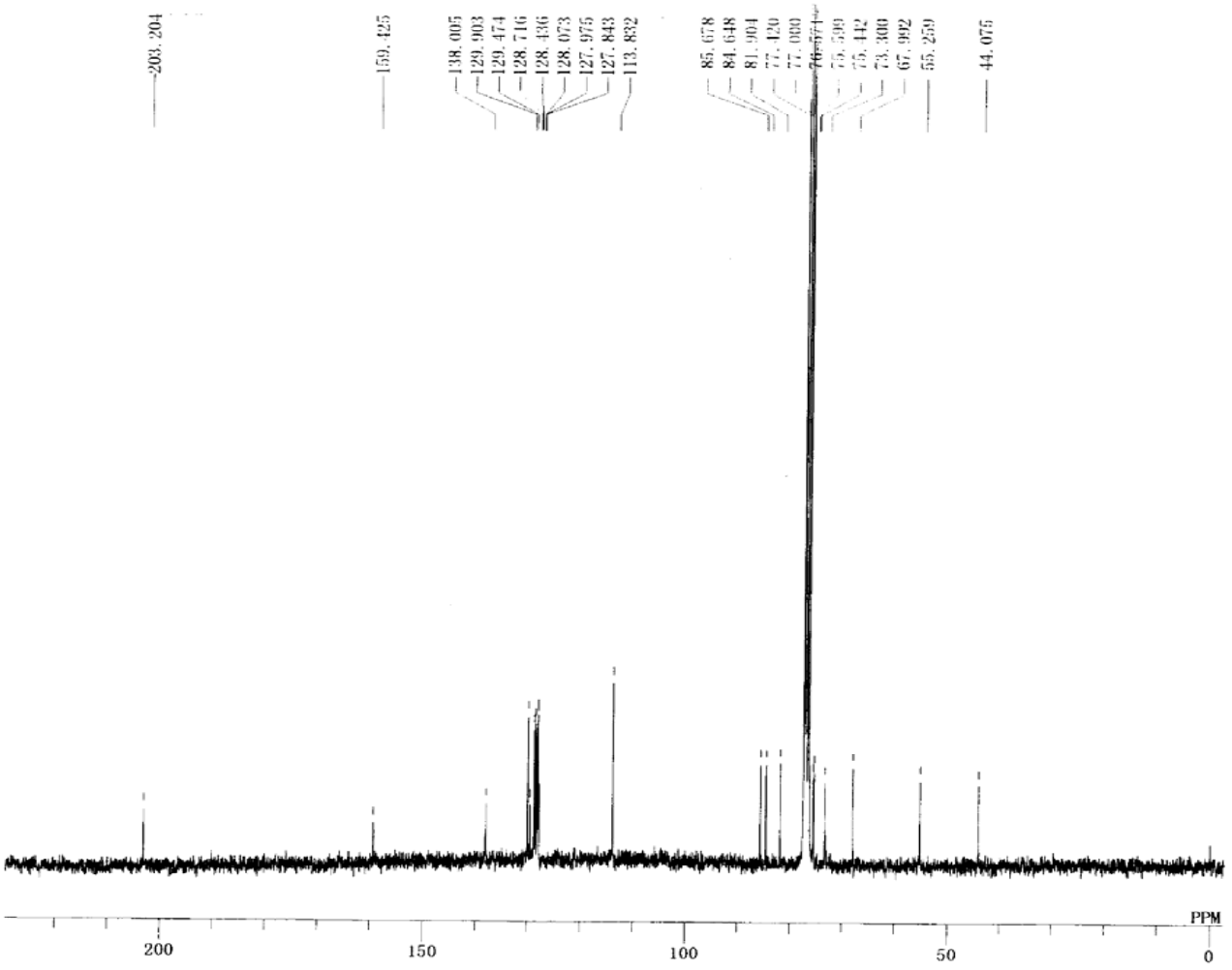

pIJPMBHg
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File: pIJPMBHg-h
INOVA-500 "BMU500"
Relax. delay 4.000 sec
Pulse 85.3 degrees
Acq. time 1.892 sec
Width 7248.3 Hz
32 repetitions
OBSERVE H1, 499.9018994 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 8 sec
7.326
7.315
7.298
7.260
6.838
6.821
4.911
4.890
4.870
4.848
4.813
4.790
4.786
4.765
4.725
4.702
4.501
4.478
4.229
4.223
4.013
4.000
3.792
3.783
3.770
2.689
2.681
2.659
2.651
2.450
2.443
2.420
2.414
1.256
0.000
PMBO
BnO
BnO
OH
19
O
ppm



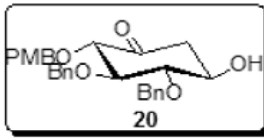
DFILE D:\叶新山\PLJPMBHG-C.ALS
OBNUC 13C
EXMOD BCM
OFR 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 4913
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRN
CTEMP 19.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24



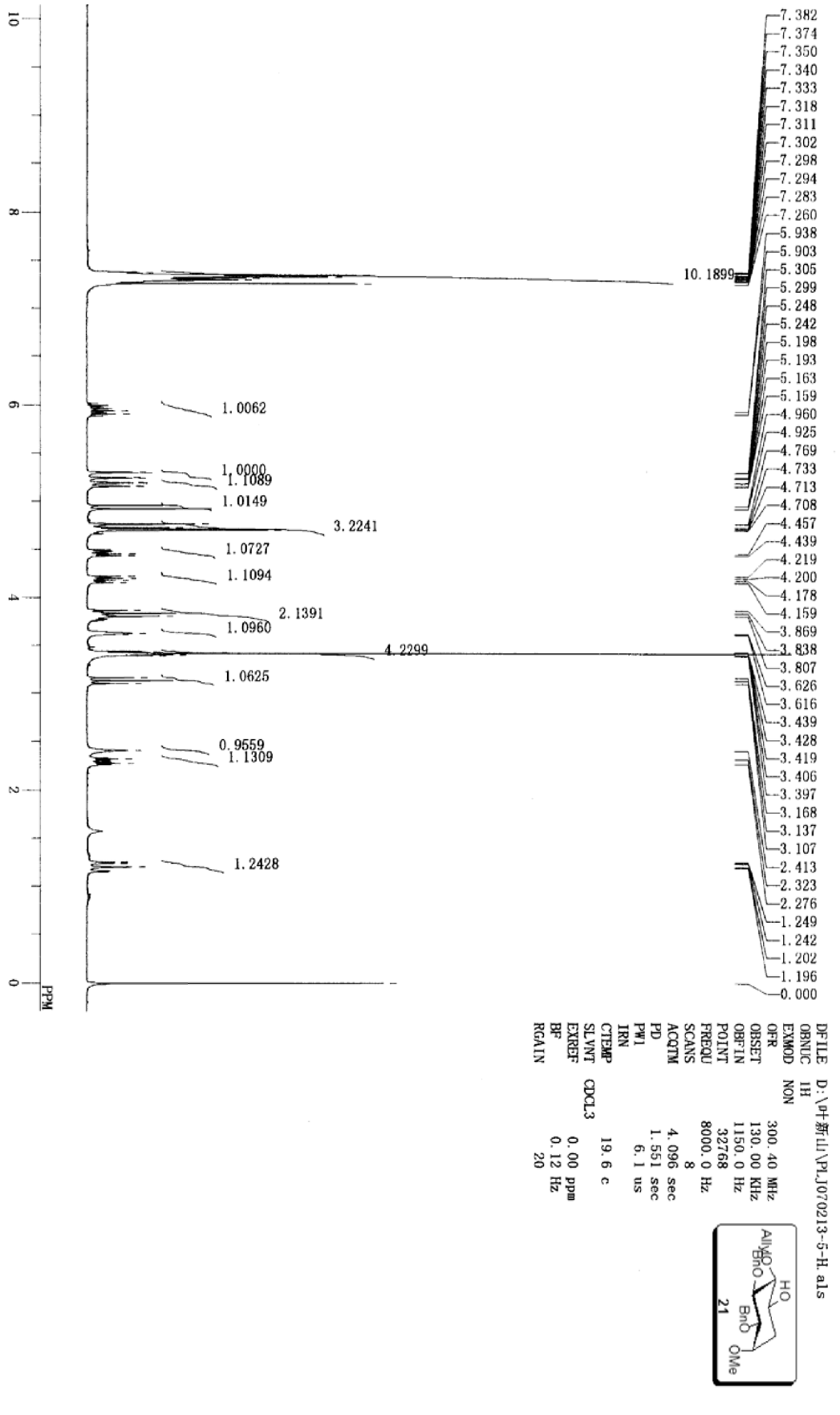

pljo70712-2-vt (40°C)
File: PROTON
Pulse Sequence: s2pul
7.359
7.355
7.341
7.337
7.331
7.328
7.316
7.313
7.305
7.299
7.285
7.253
7.247
7.246
7.244
6.855
6.849
6.845
6.836
6.832
6.826
5.008
4.985
4.933
4.911
4.847
4.825
4.743
4.721
4.705
4.682
4.486
4.464
4.142
4.126
3.795
3.787
3.715
3.704
3.689
3.681
3.672
3.658
3.655
3.640
2.762
2.753
2.735
2.725
2.504
2.483
2.478
2.477
2.455
2.429
1.511
1.259
0.007
0.006
-0.004
-0.007
-0.000
10.88
1.91
1.0211
1.02
1.02.14
1.01
3.00
3.19
1.08
0.75
1.11
ppm
PMBO
BnO
BnO
OH
20

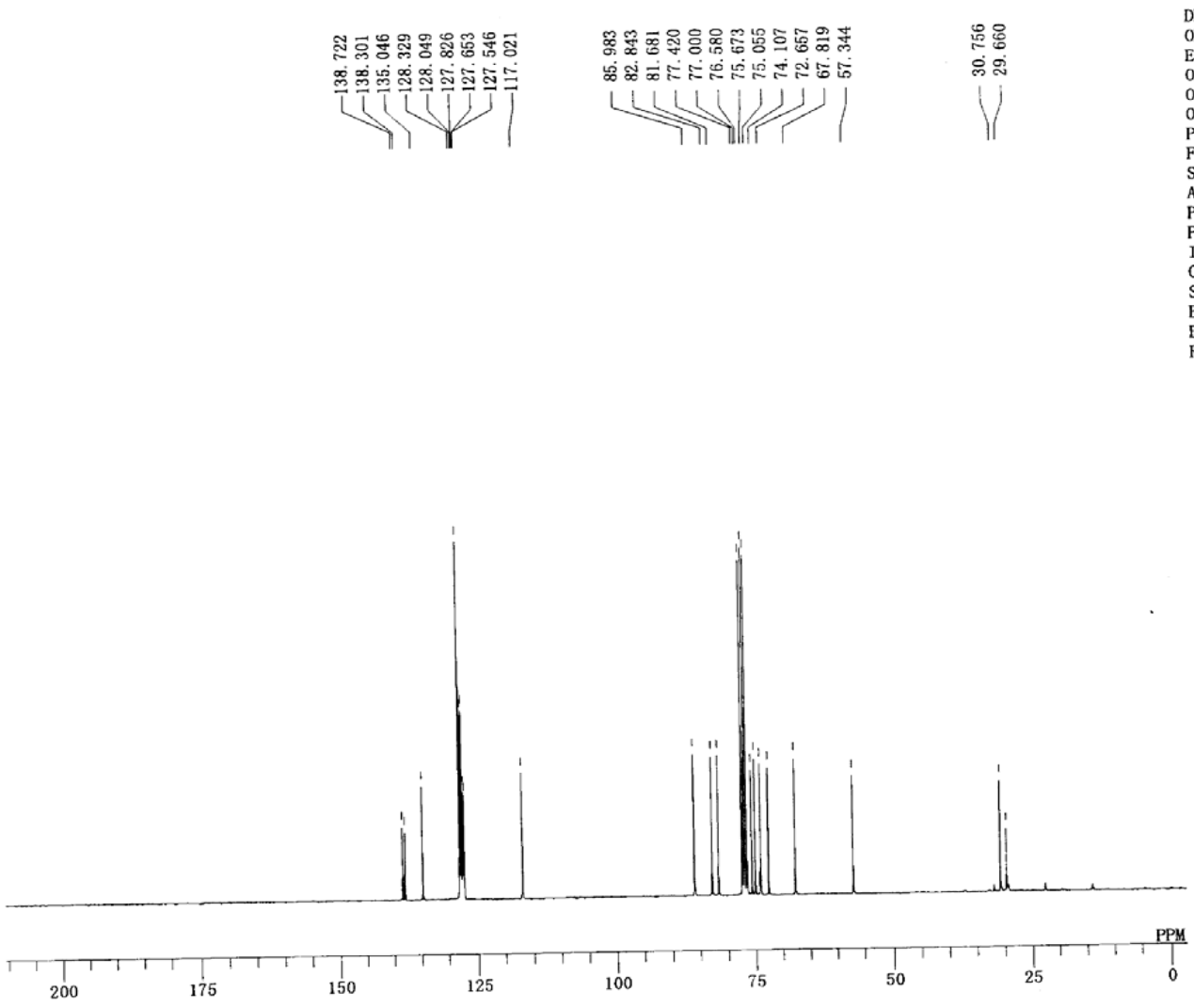


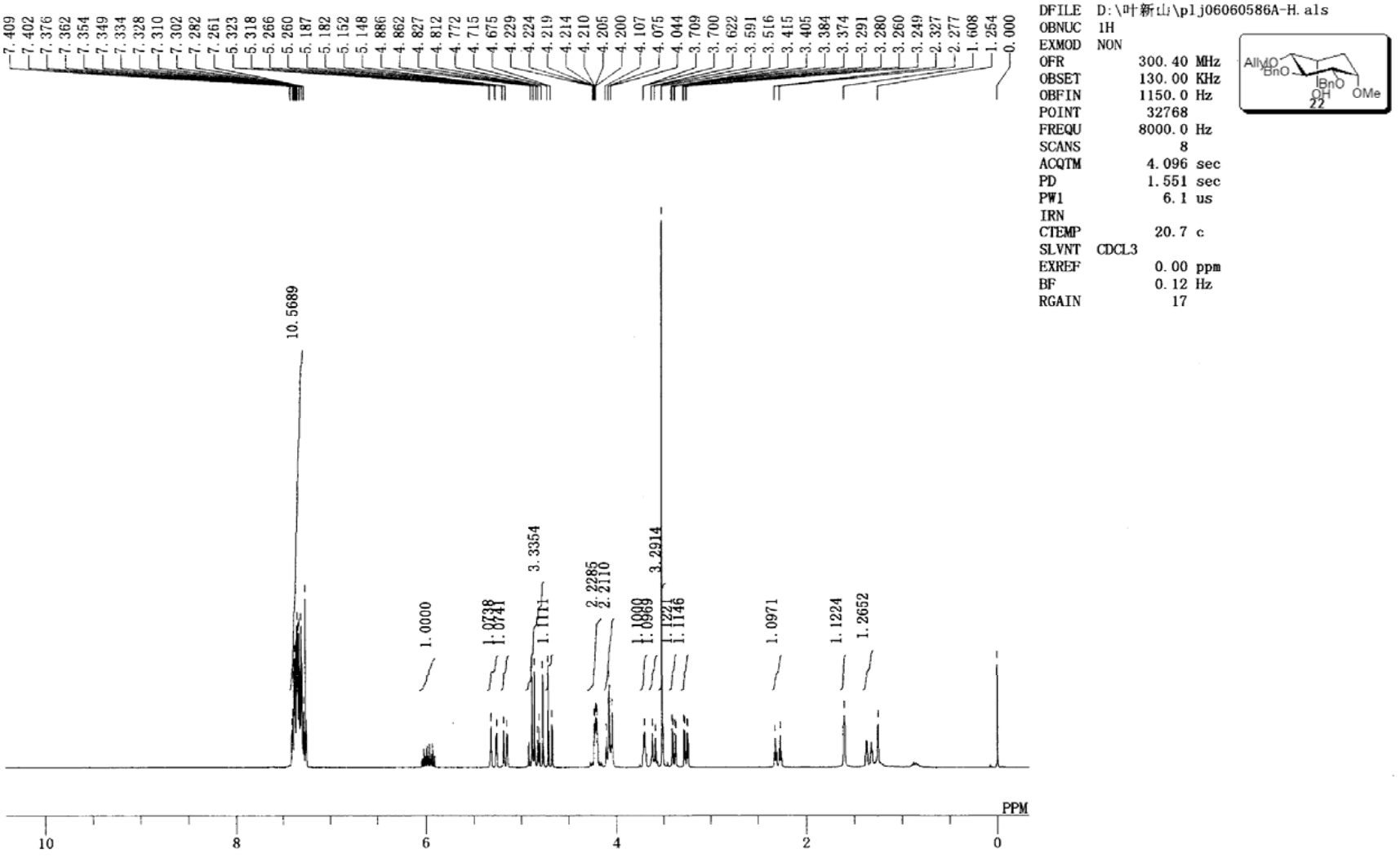
DFILE	D:\叶新山\PLJ-070712-2-C.als	
OBNUC	13C	
EXMOD	BCM	
OBFRQ	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	10000	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRATN	511	
CTEMP	21.8	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	25	

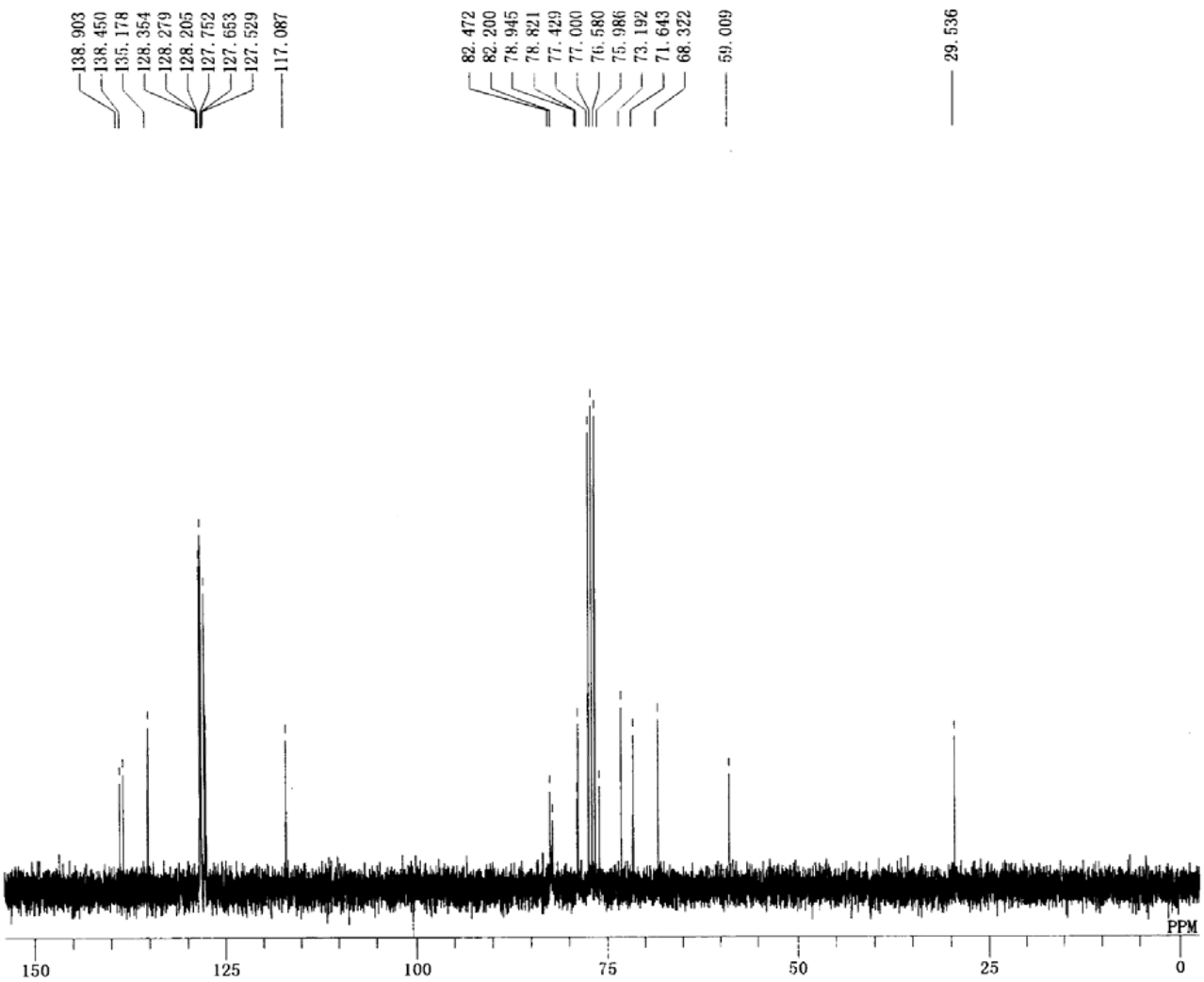


20

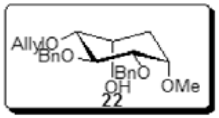

7.382
7.374
7.350
7.340
7.333
7.318
7.311
7.302
7.298
7.294
7.283
7.260
5.938
5.903
5.305
5.299
5.248
5.242
5.198
5.193
5.163
5.159
4.960
4.925
4.769
4.733
4.713
4.708
4.457
4.439
4.219
4.200
4.178
4.159
3.869
3.838
3.807
3.626
3.616
3.439
3.428
3.419
3.406
3.397
3.168
3.137
3.107
2.413
2.323
2.276
1.249
1.242
1.202
1.196
0.000
10.1899
1.0062
1.0000
1.1089
1.0149
3.2241
1.0727
1.1094
2.1391
1.0960
4.2299
1.0625
0.9559
1.1309
1.2428
PPM
DFILE D:\叶新山\PLJ070213-5-H.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRN
CTEMP 19.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 20
HO
AllylO
BnO
BnO
21
OMe


138.722
138.301
135.046
128.329
128.049
127.826
127.653
127.546
117.021
85.983
82.843
81.681
77.420
77.000
76.580
75.673
75.055
74.107
72.667
67.819
57.344
30.756
29.660
DFILE D:\叶新山\WDRC9-2-C.als
OBNUC 13C
EXMOD BCM
OFR 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 3732
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRN
CTEMP 20.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24
HO
AllylO
BnO
BnO
OMe
21
PPM
200
175
150
125
100
75
50
25
0

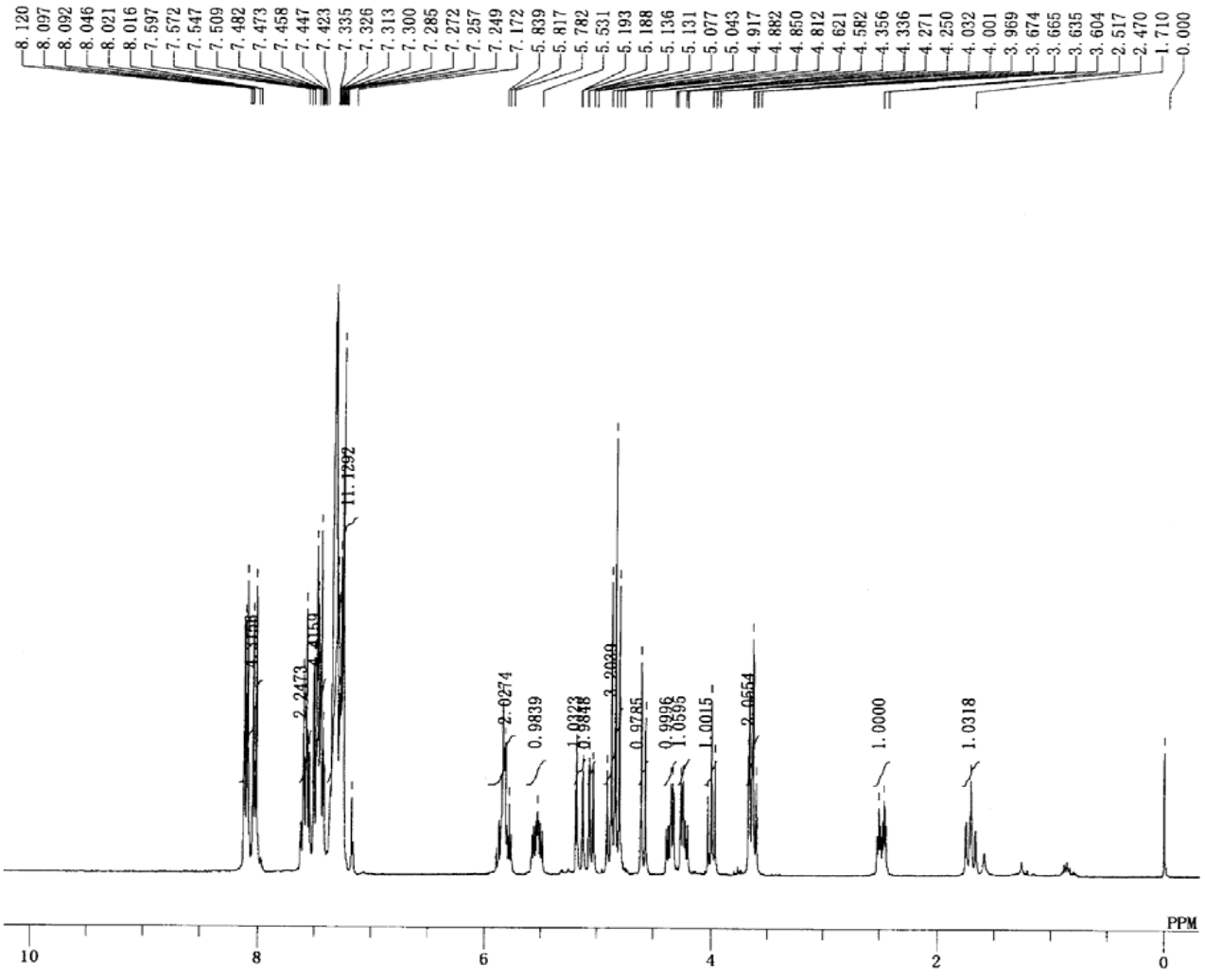

7.409
7.402
7.376
7.362
7.354
7.349
7.334
7.328
7.310
7.302
7.282
7.261
5.323
5.318
5.266
5.260
5.187
5.182
5.152
5.148
4.886
4.862
4.827
4.812
4.772
4.715
4.675
4.229
4.224
4.219
4.214
4.210
4.205
4.200
4.107
4.075
4.044
3.709
3.700
3.622
3.591
3.516
3.415
3.405
3.384
3.374
3.291
3.280
3.260
3.249
2.327
2.277
1.608
1.254
0.000
DFILE D:\叶新山\plj06060586A-H.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRN
CTEMP 20.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17
AllylO
BnO
BnO
OH
OMe
22
10.5689
1.0000
1.8738
1.8741
3.3354
1.1111
2.2285
2.2110
1.0888
1.0989
3.2914
1.1221
1.1146
1.0971
1.1224
1.2652
PPM
10
8
6
4
2
0



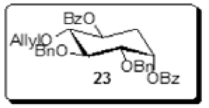
DFILE	D:\叶新山\plj060605-2-C.als	
OBNUC	13C	
EXMOD	BCM	
OBFRQ	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	197	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRATN	511	
CTEMP	23.7	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	0.12	Hz
RGAIN	24	

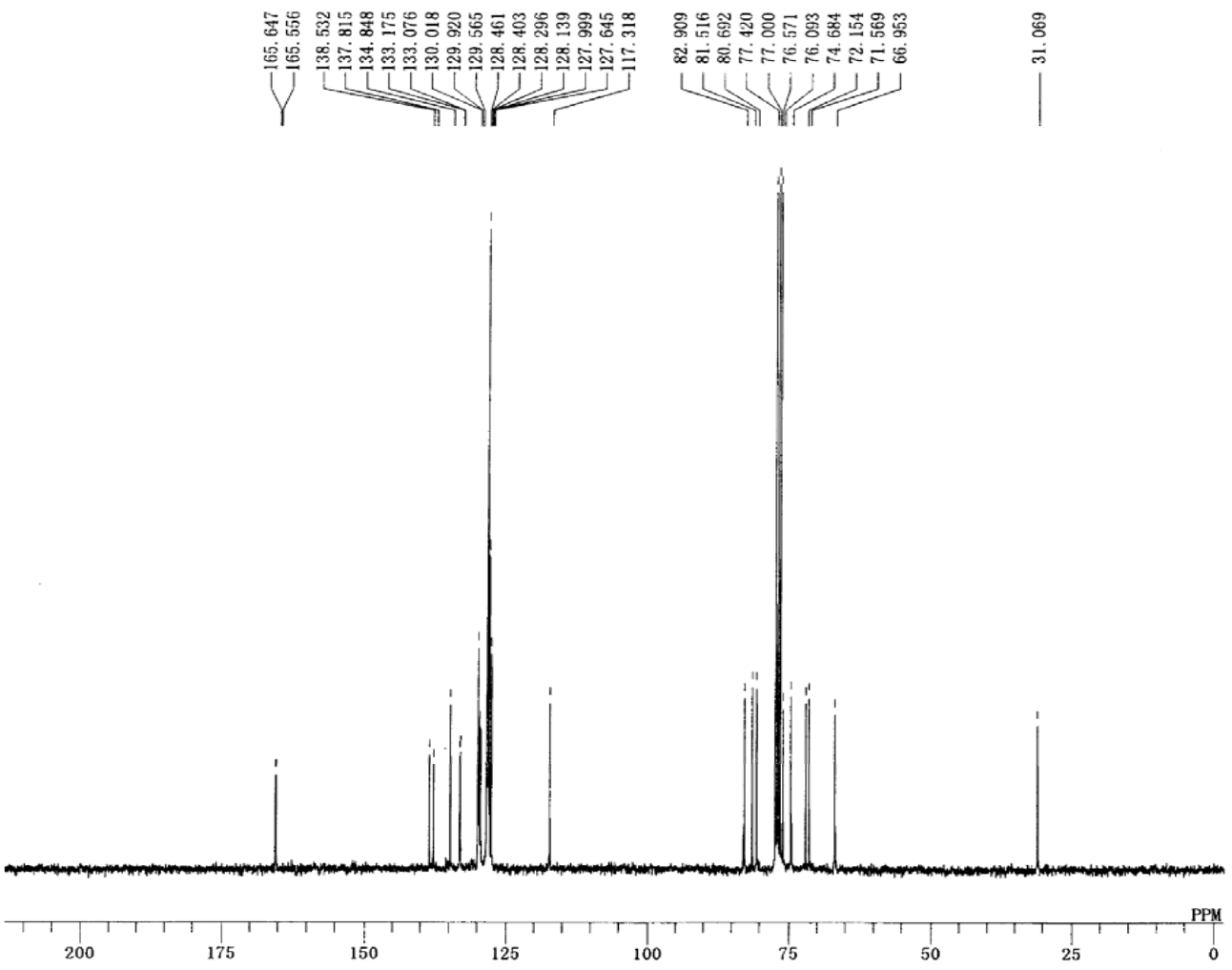


```
DFILE   D:\H-新山\PLJ06060586.
OBNUC   1H
EXMOD   VCOSYNH
OFR       300.40 MHz
OBSET     130.70 KHz
OBFIN      92.3 Hz
POINT       512
FREQU     2606.8 Hz
SCANS          8
ACQTM      0.196 sec
PD         1.500 sec
PW1          12.2 us
IRN
CTEMP      20.4 c
SLVNT   CDCL3
EXREF      0.00 ppm
BF         4.20 Hz
RGAIN        17
```

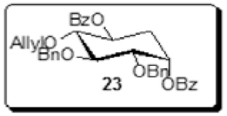


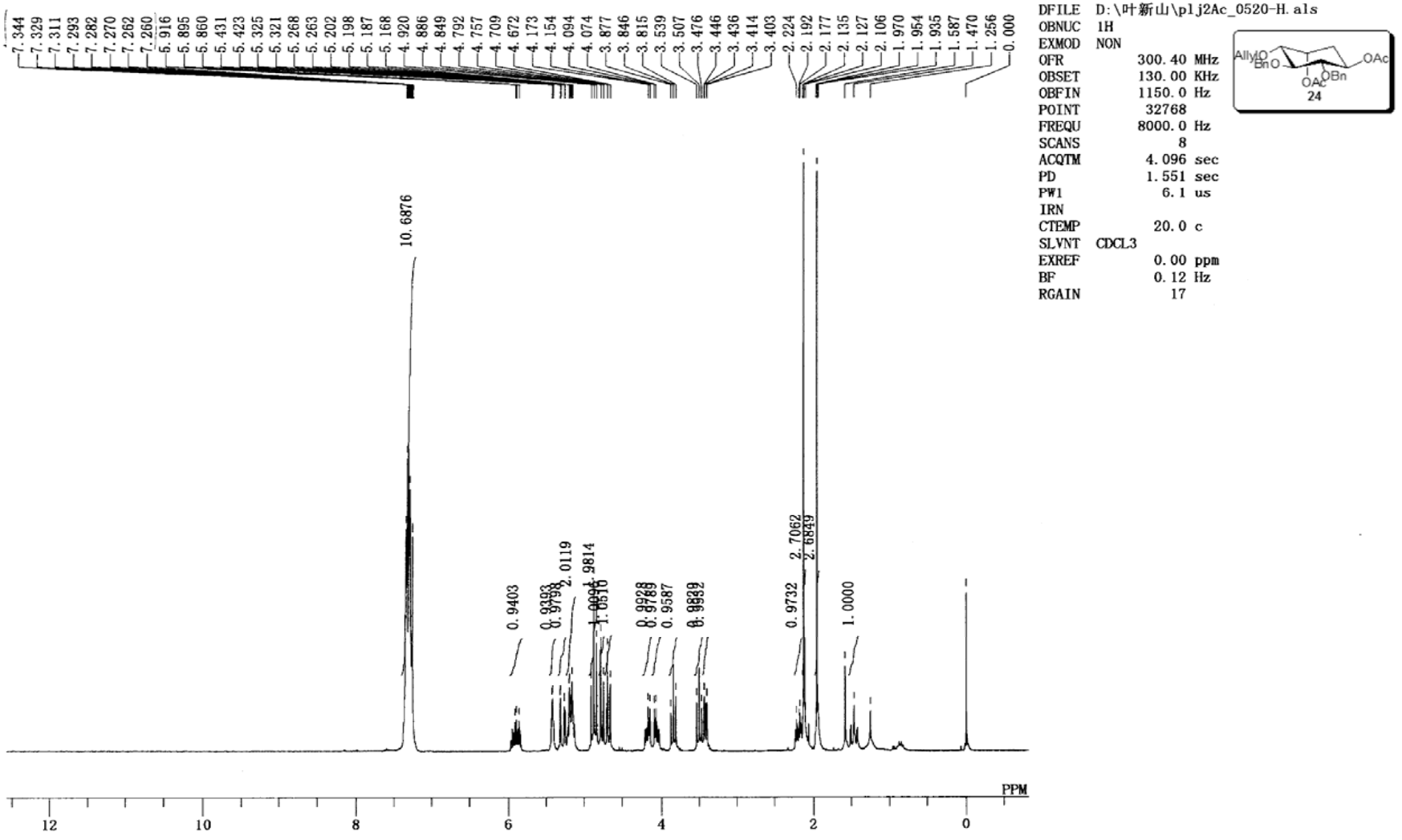
DFILE D:\叶新山\PLJ061213-69A-H.als
COMNT
DATIM Thu Dec 21 20:03:02 2006
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRNUC 1H
CTEMP 19.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 14

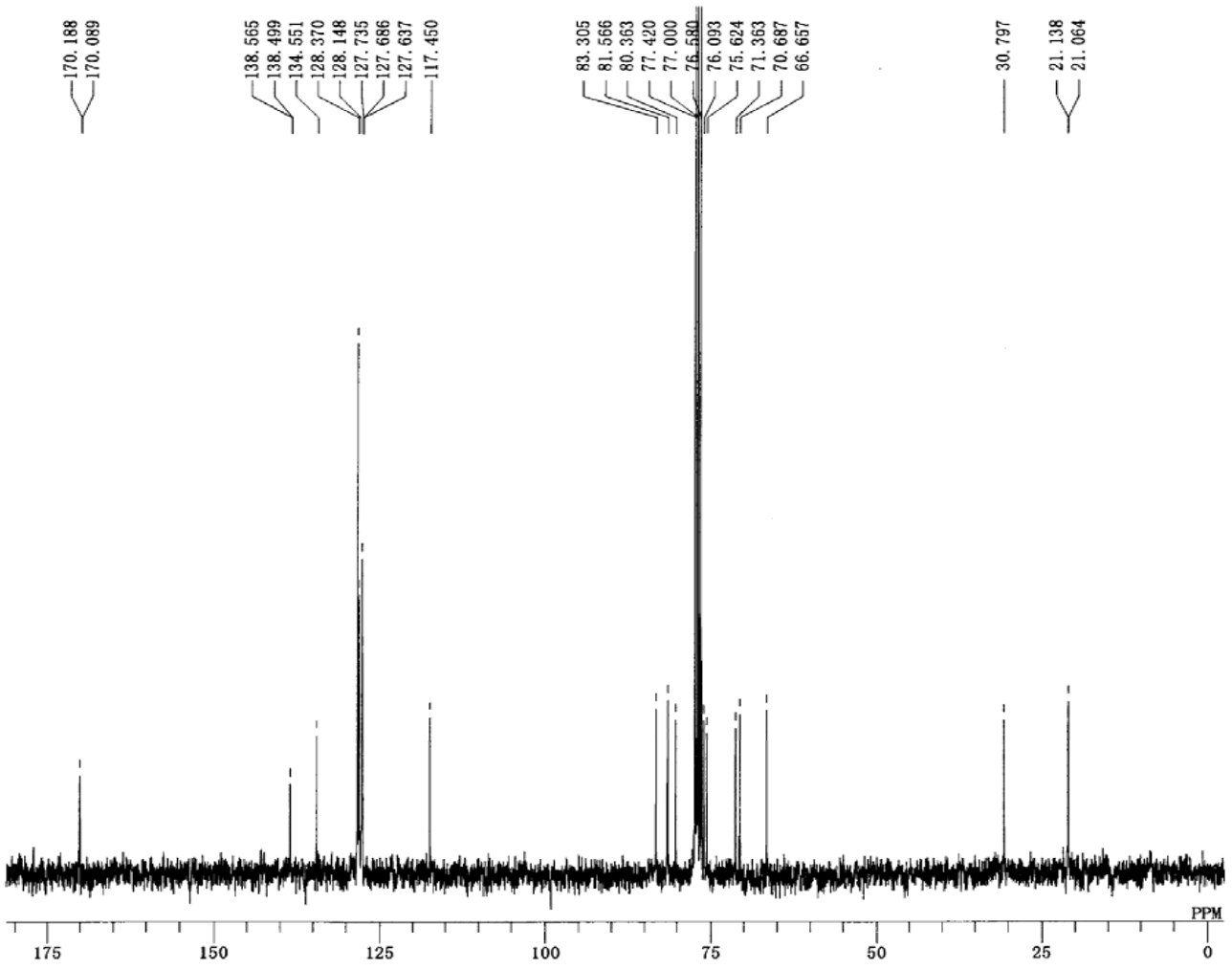




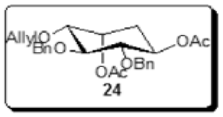
DFILE	D:\叶新山\PLJ061213-69A-C.als
COMNT	
DATIM	Sat Dec 23 10:36:13 2006
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.0 Hz
POINT	32768
FREQU	20408.1 Hz
SCANS	1408
ACQTM	1.606 sec
PD	1.394 sec
PW1	4.2 us
IRNUC	1H
CTEMP	20.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	2.00 Hz
RGAIN	24



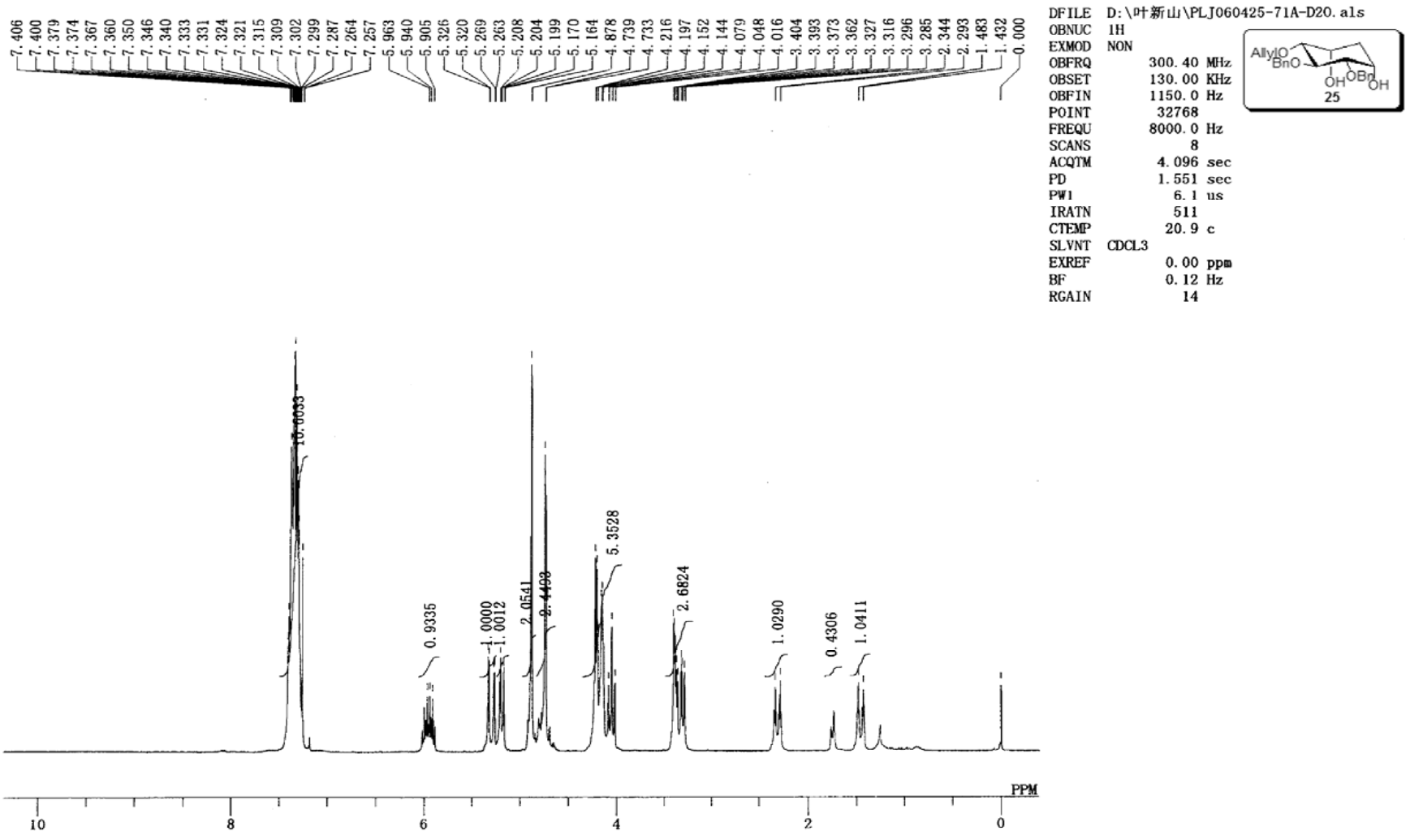

7.344
7.329
7.311
7.293
7.282
7.270
7.262
7.260
6.916
5.895
5.860
5.431
5.423
5.325
5.321
5.268
5.263
5.202
5.198
5.187
5.168
4.920
4.886
4.849
4.792
4.757
4.709
4.672
4.173
4.154
4.094
4.074
3.877
3.846
3.815
3.539
3.507
3.476
3.446
3.436
3.414
3.403
2.224
2.192
2.177
2.135
2.127
2.106
1.970
1.954
1.935
1.587
1.470
1.256
0.000
10.6876
0.9403
2.0119
1.9814
2.7062
2.6849
0.9732
1.0000
0.9587
PPM
12
10
8
6
4
2
0
DFILE D:\叶新山\plj2Ac_0520-H.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRN
CTEMP 20.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17
AllylO
BnO
OAc
OBn
OAc
24

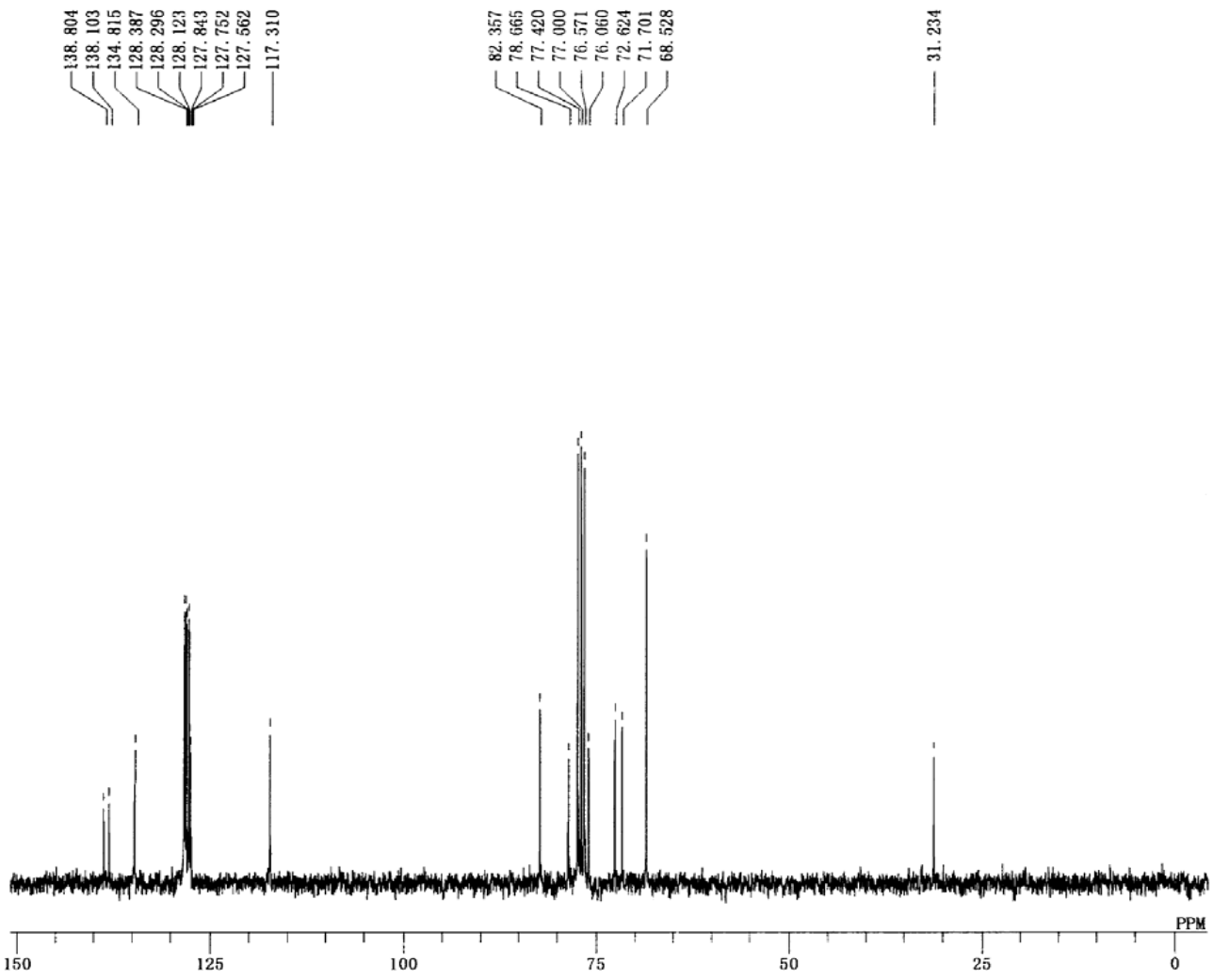


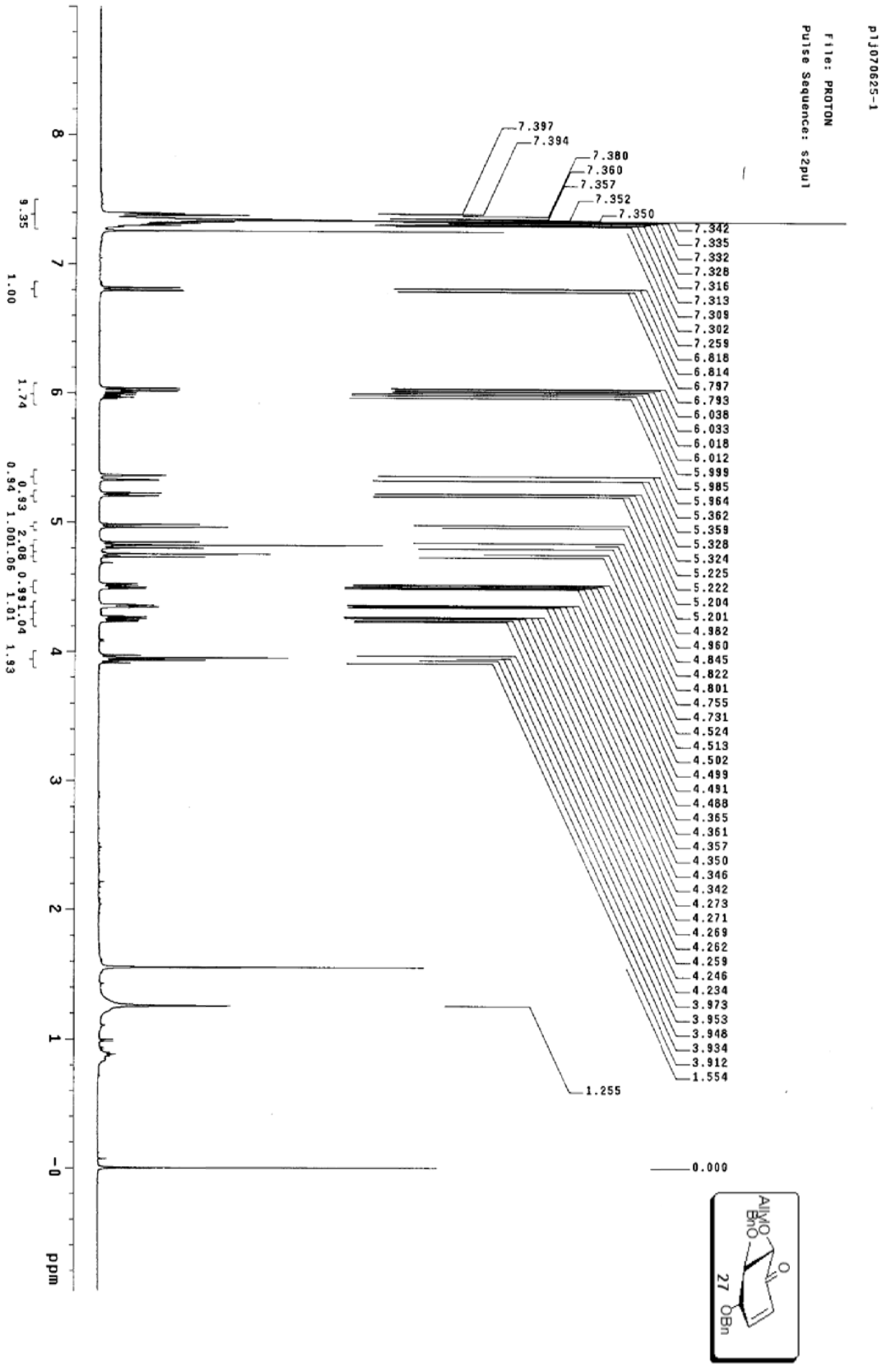
DFILE D:\叶新山\plj2Ac-0520-C.als
OBNUC 13C
EXMOD BCM
OFR 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 416
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRN
CTEMP 21.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24

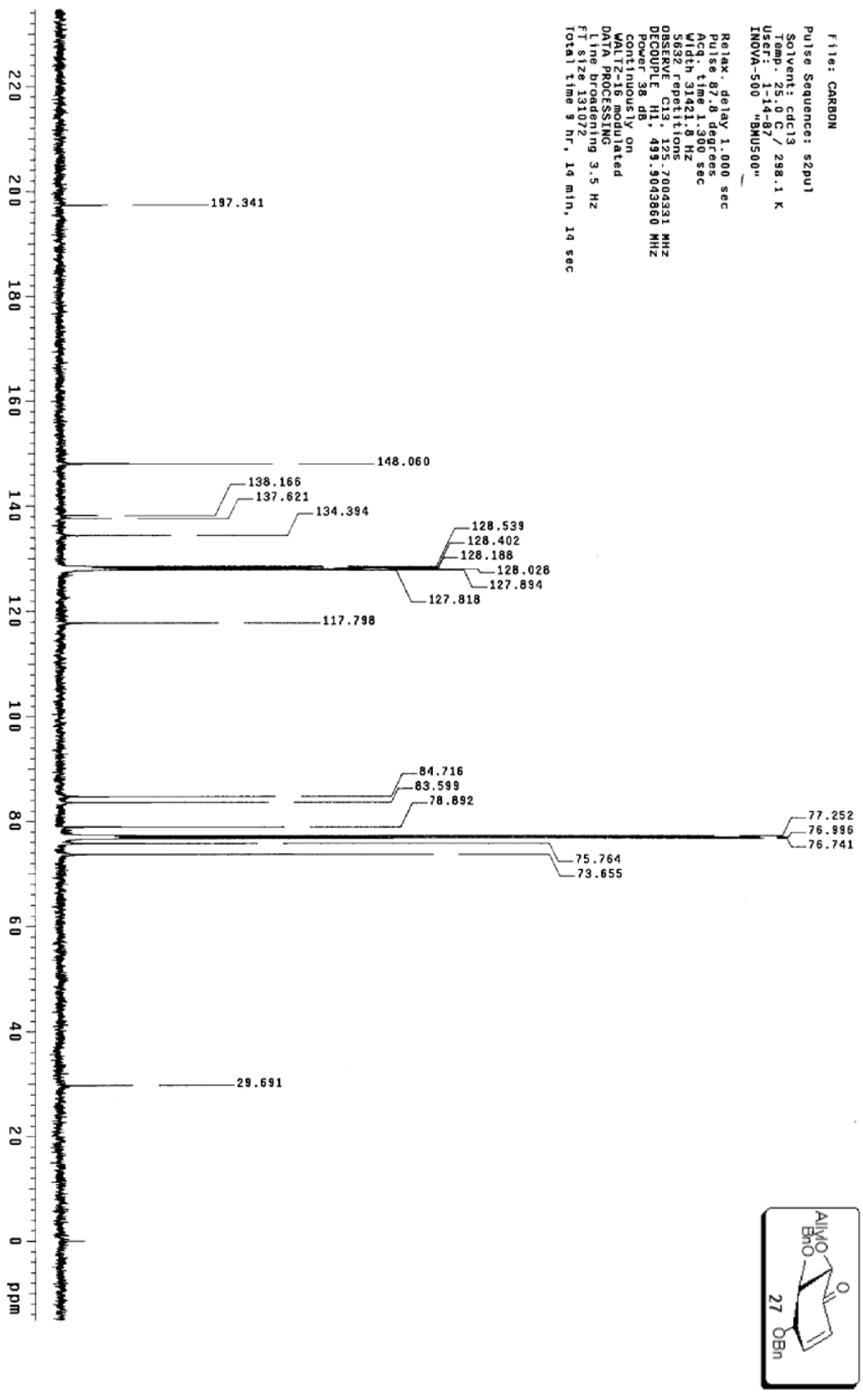


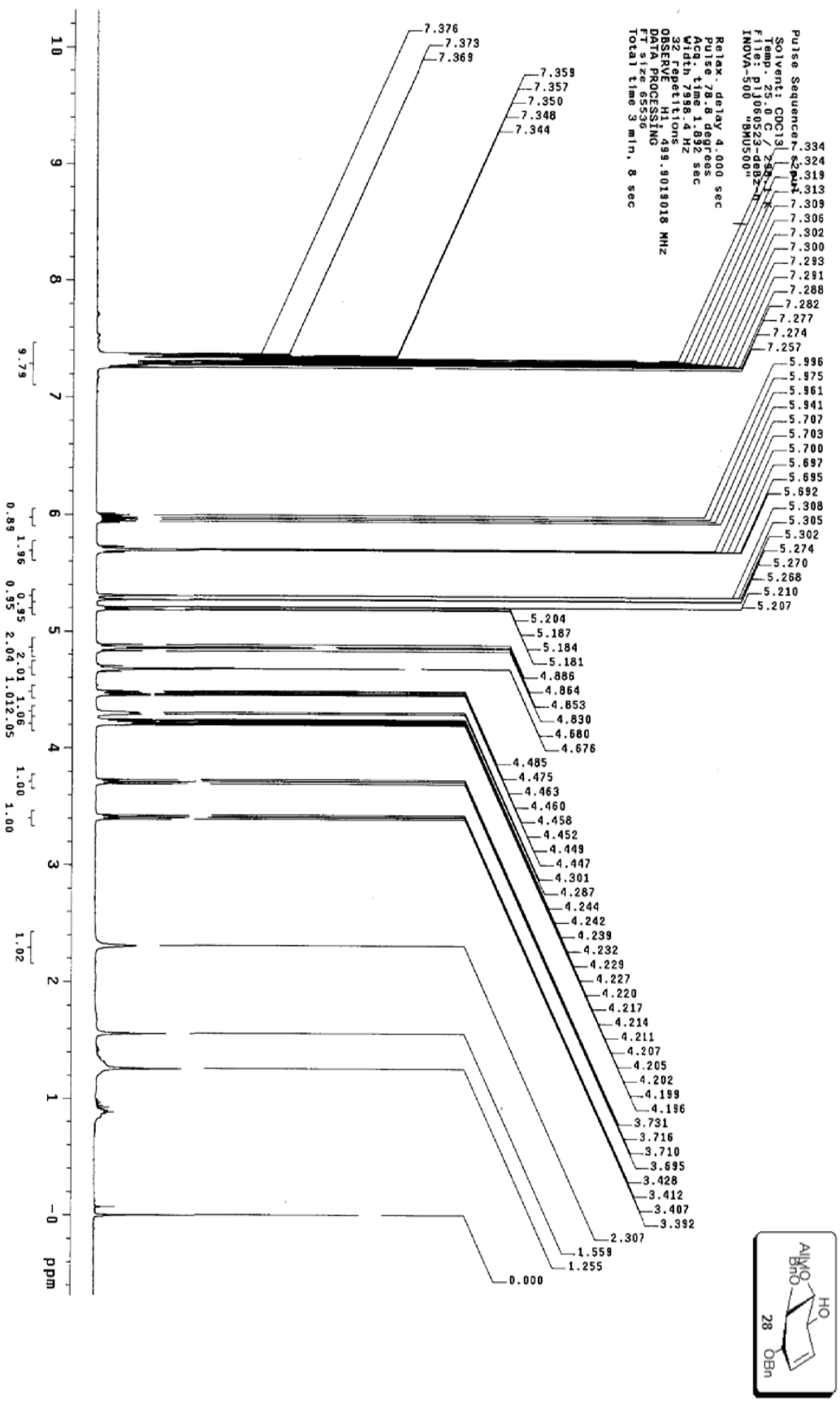
24

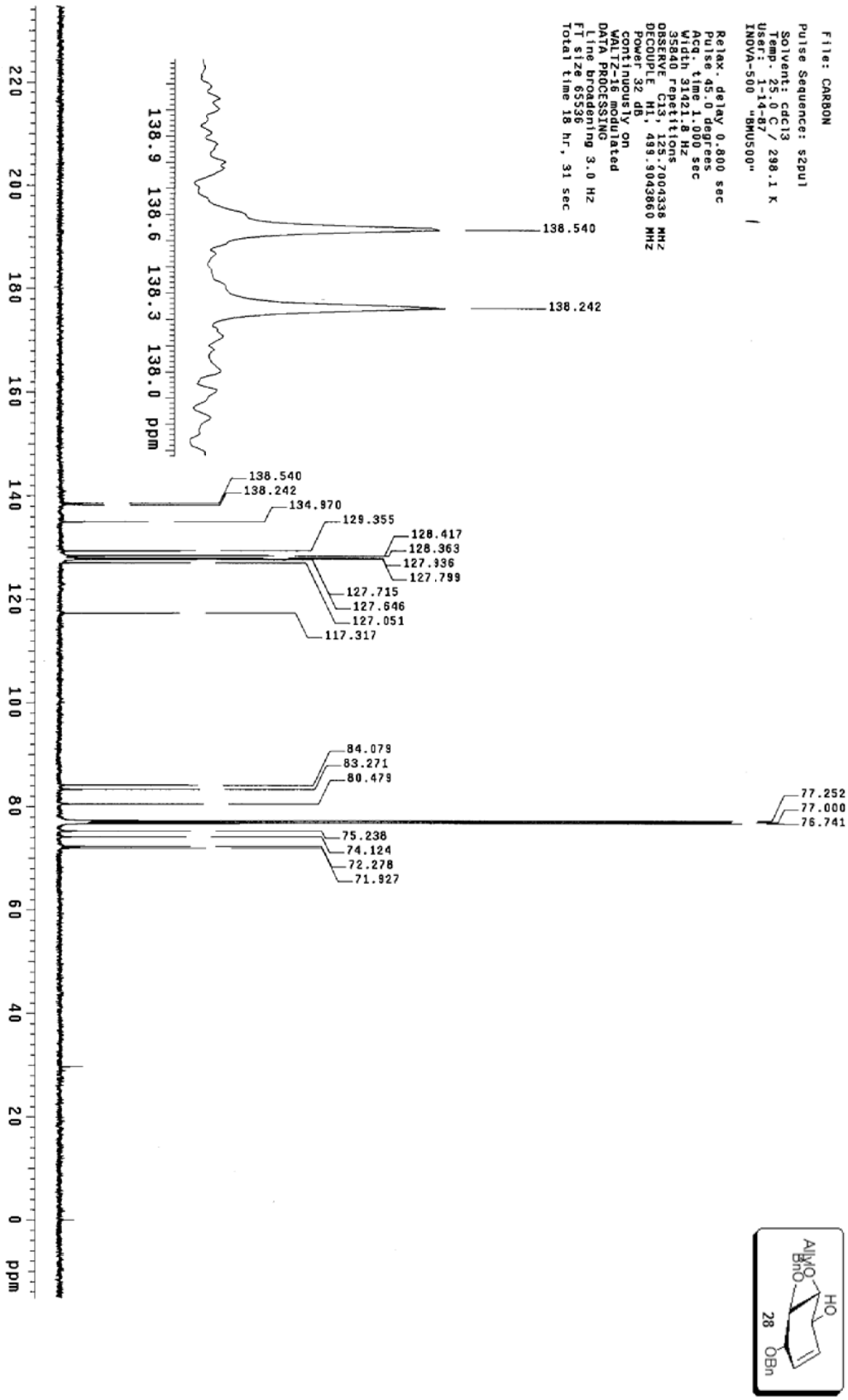

7.406 7.400 7.379 7.374 7.367 7.360 7.350 7.346 7.340 7.333 7.331 7.324 7.321 7.315 7.309 7.302 7.299 7.287 7.264 7.257
5.963 5.940 5.905 5.326 5.320 5.269 5.263 5.208 5.204 5.199 5.170 5.164 4.878 4.739 4.733 4.216 4.197 4.152 4.144 4.079 4.048 4.016 3.404 3.393 3.373 3.362 3.327 3.316 3.296 3.285 2.344 2.293 1.483 1.432 0.000
DFILE D:\叶新山\PLJ060425-71A-D20.als
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRATN 511
CTEMP 20.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 14
AllylO
BnO
OH
OBn
OH
25
16.0033
0.9335
1.0000
1.0012
2.0541
2.4493
5.3528
2.6824
1.0290
0.4306
1.0411
PPM
10
8
6
4
2
0


138.804
138.103
134.815
128.387
128.296
128.123
127.843
127.752
127.562
117.310
82.357
78.665
77.420
77.000
76.571
76.060
72.624
71.701
68.528
31.234
DFILE D:\叶新山\plj060425-71A-C.als
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 88
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRATN 511
CTEMP 22.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24
AllylO
BnO
OH
OBn
OH
25
PPM
150
125
100
75
50
25
0


plj070625-1
File: PROTON
Pulse Sequence: s2pul
7.397
7.394
7.380
7.360
7.357
7.352
7.350
7.342
7.335
7.332
7.328
7.316
7.313
7.309
7.302
7.259
6.818
6.814
6.797
6.793
6.038
6.033
6.018
6.012
5.999
5.985
5.964
5.362
5.359
5.328
5.324
5.225
5.222
5.204
5.201
4.982
4.960
4.845
4.822
4.801
4.755
4.731
4.524
4.513
4.502
4.499
4.491
4.488
4.365
4.361
4.357
4.350
4.346
4.342
4.273
4.271
4.269
4.262
4.259
4.246
4.234
3.973
3.953
3.948
3.934
3.912
1.554
1.255
0.000
9.35
1.00
1.74
0.93
2.08
0.99
1.04
0.94
1.00
1.06
1.01
1.93
8
7
6
5
4
3
2
1
-0
ppm
AllylO
BnO
O
27
OBn


plj070625-1
File: CARBON
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"
Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
5632 repetitions
OBSERVE C13, 125.7004331 MHz
DECOUPLE H1, 499.9043860 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.5 Hz
FT size 131072
Total time 9 hr, 14 min, 14 sec
197.341
148.060
138.166
137.621
134.394
128.539
128.402
128.188
128.028
127.894
127.818
117.798
84.716
83.599
78.892
77.252
76.996
76.741
75.764
73.655
29.691
220
200
180
160
140
120
100
80
60
40
20
0
ppm
AllylO
BnO
O
27
OBn


pIJ060523-de8z
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: pIJ060523-de8z
INOVA-500 "BMU500"
Relax. delay 4.000 sec
Pulse 78.8 degrees
Acq. time 1.892 sec
Width 7998.4 HZ
32 repetitions
OBSERVE H1, 499.9019018 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 8 sec
7.376
7.373
7.369
7.359
7.357
7.350
7.348
7.344
7.334
7.324
7.319
7.313
7.309
7.306
7.302
7.300
7.293
7.291
7.288
7.282
7.277
7.274
7.257
5.996
5.975
5.961
5.941
5.707
5.703
5.700
5.697
5.695
5.692
5.308
5.305
5.302
5.274
5.270
5.268
5.210
5.207
5.204
5.187
5.184
5.181
4.886
4.864
4.853
4.830
4.680
4.676
4.485
4.475
4.463
4.460
4.458
4.452
4.449
4.447
4.301
4.287
4.244
4.242
4.239
4.232
4.229
4.227
4.220
4.217
4.214
4.211
4.207
4.205
4.202
4.199
4.196
3.731
3.716
3.710
3.695
3.428
3.412
3.407
3.392
2.307
1.559
1.255
0.000
ppm
9.79
0.89
1.96
0.95
0.95
2.04
1.01
1.06
1.01
2.05
1.00
1.00
1.02
AllylO
BnO
HO
28
OBn

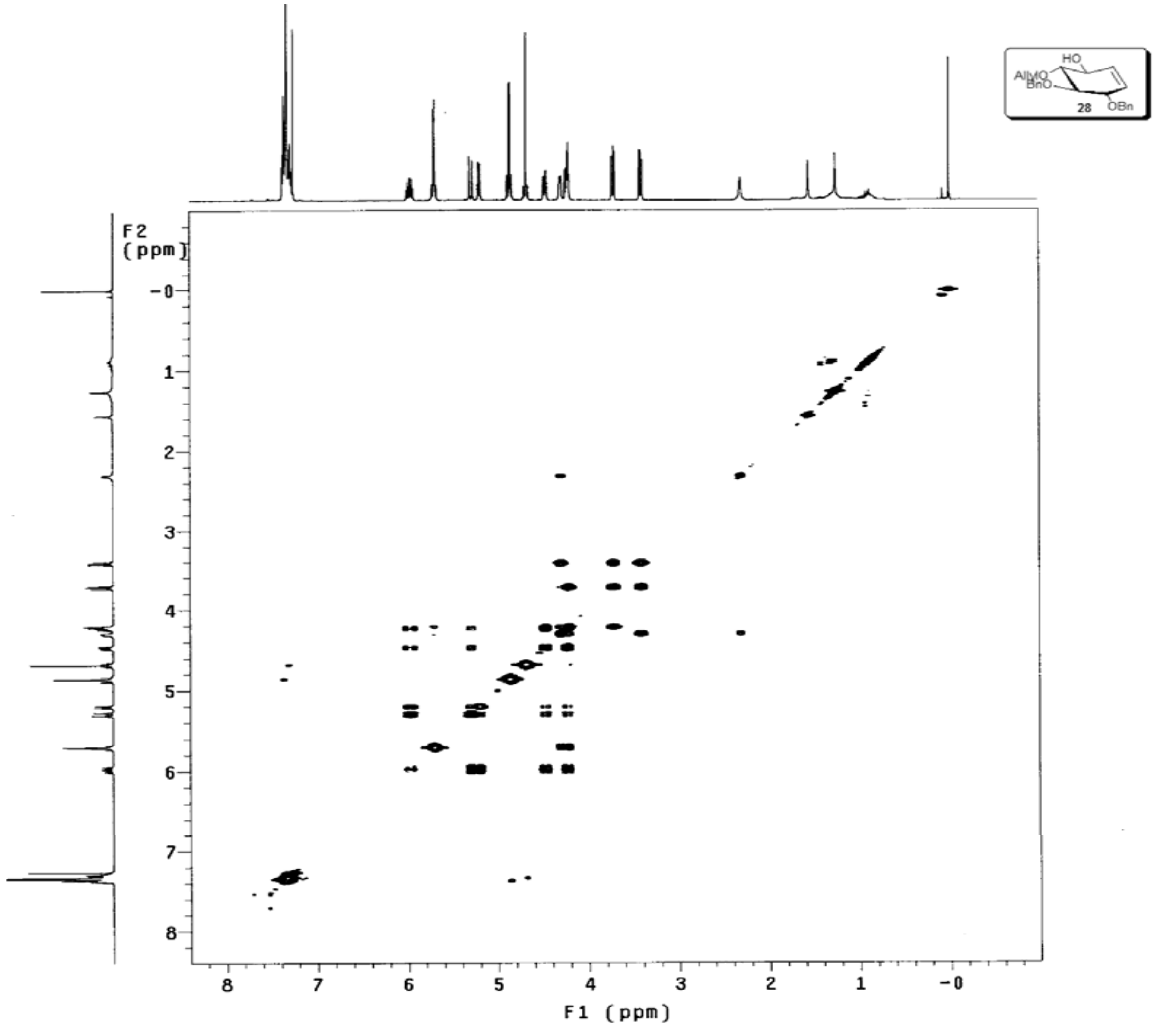

pljd60523-deBz
File: CARBON
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Usefi. 1 1-14-87
INOVA-500 "BMU500"
Relax. delay 0.800 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
35840 repetitions
OBSERVE C13, 125.7004338 MHz
DECOUPLE H1, 499.9043860 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 18 hr, 31 sec
138.540
138.242
138.9 138.6 138.3 138.0 ppm
138.540
138.242
134.870
129.355
128.417
128.363
127.936
127.799
127.715
127.646
127.051
117.317
84.079
83.271
80.479
77.252
77.000
76.741
75.238
74.124
72.278
71.927
220 200 180 160 140 120 100 80 60 40 20 0 ppm
AllylO
BnO
HO
28
OBn

plj060523-deBz

File: PROTON

Pulse Sequence: gCOSY
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"

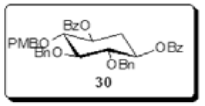
Relax. delay 1.000 sec
Acq. time 0.218 sec
Width 4698.1 Hz
2D Width 4698.1 Hz
24 repetitions
300 increments
OBSERVE H1, 499.9019018 MHz
DATA PROCESSING
Sq. sine bell 0.109 sec
F1 DATA PROCESSING
Sq. sine bell 0.033 sec
FT size 4096 x 4096
Total time 2 hr, 31 min, 51 sec

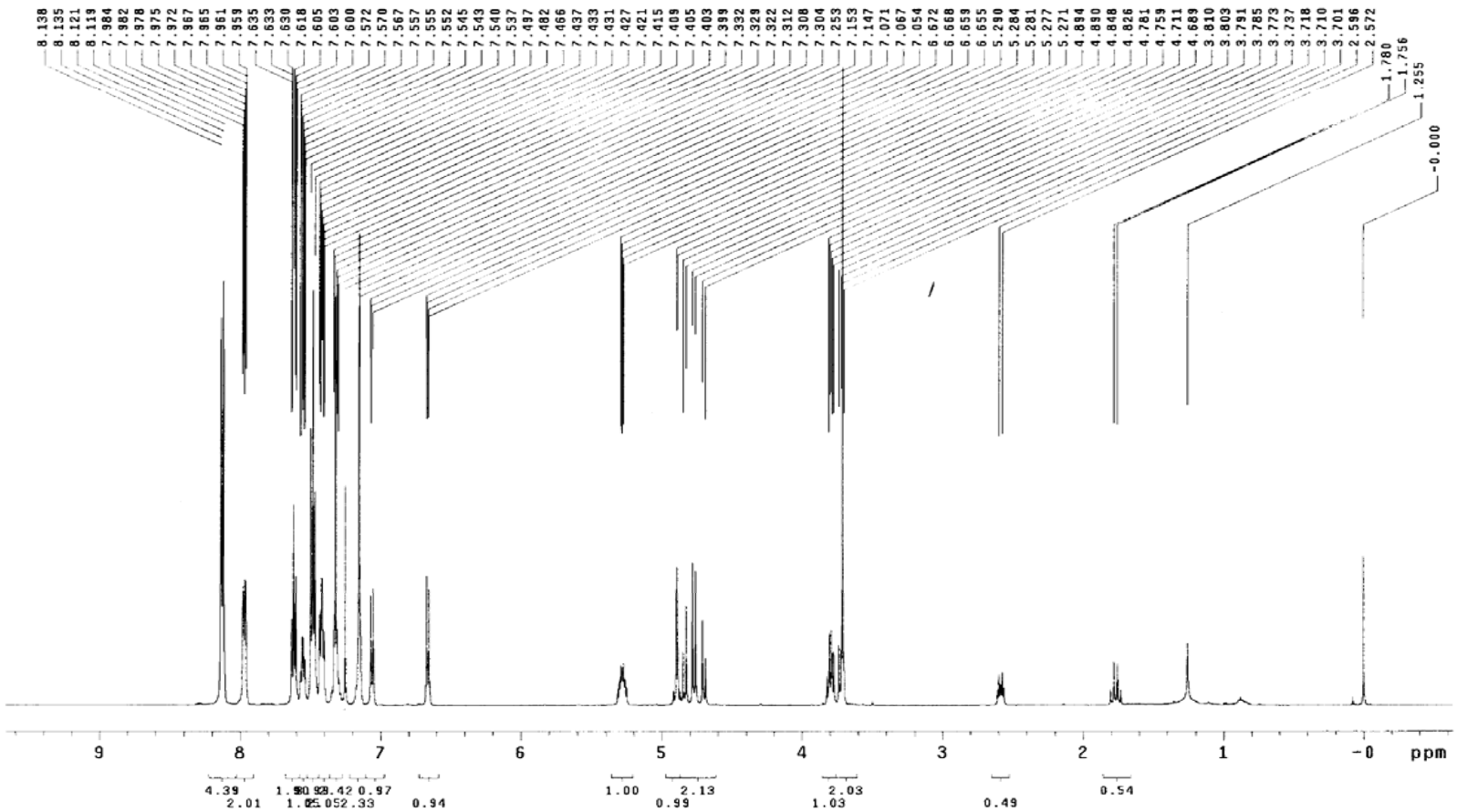


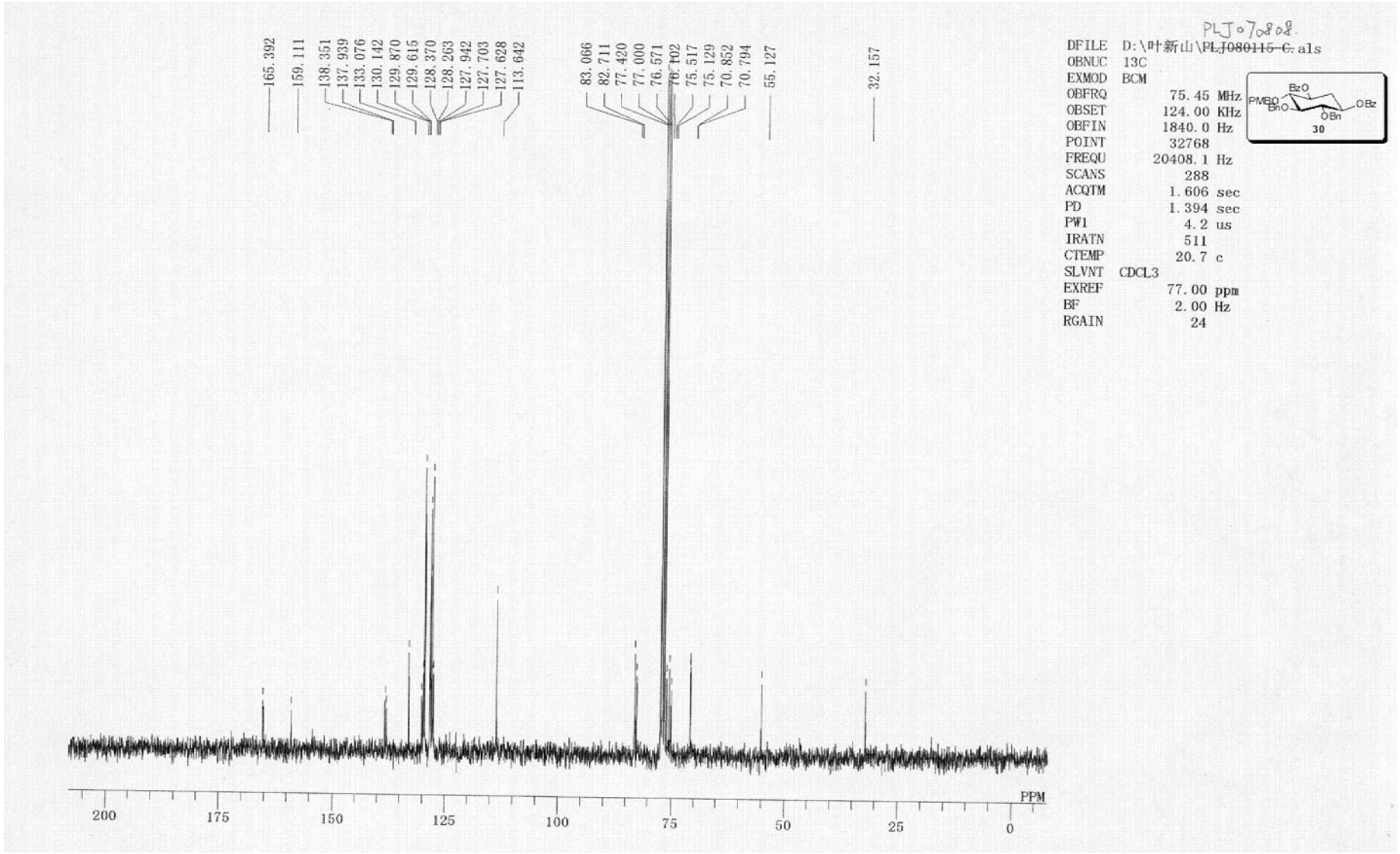
plj070808

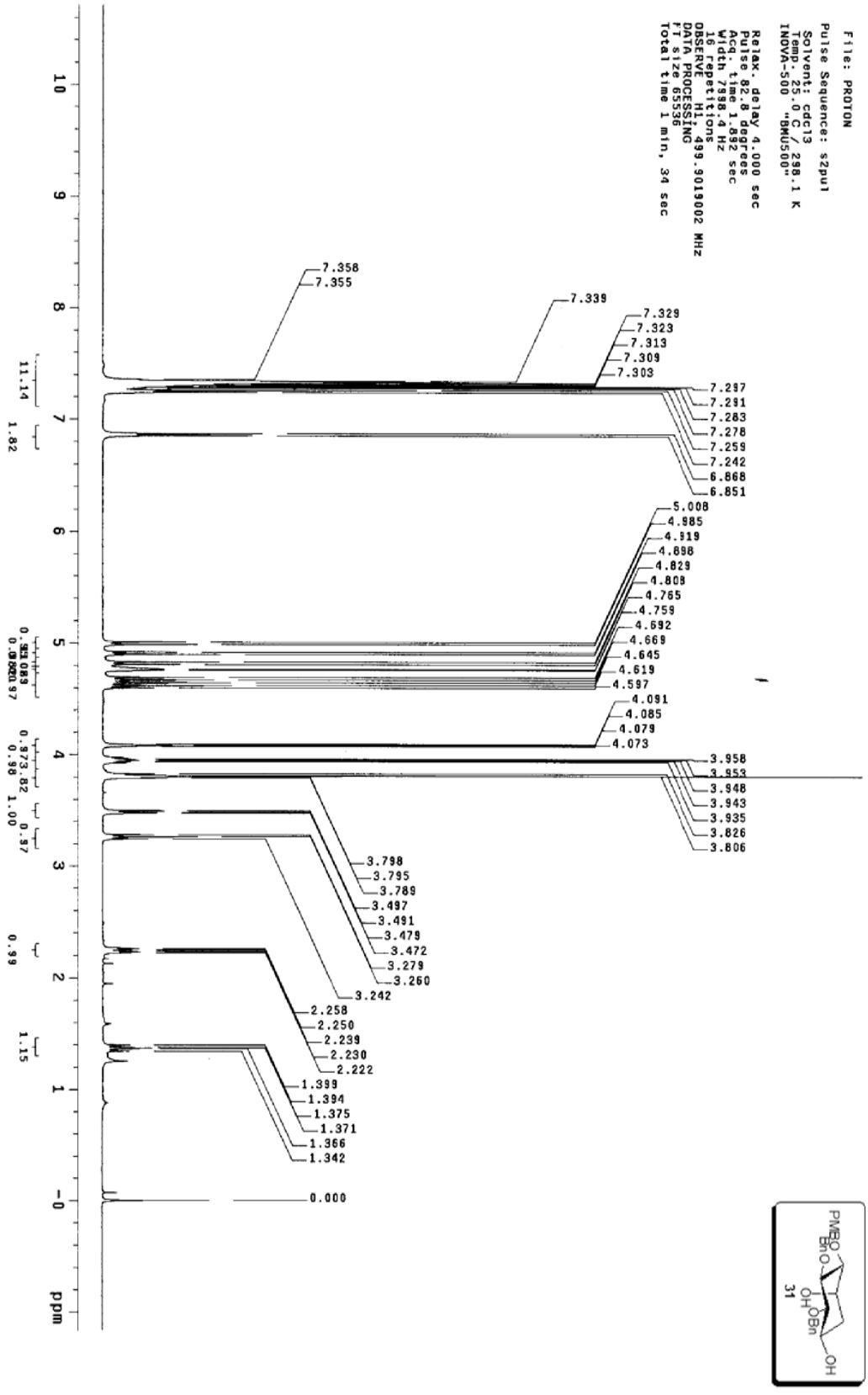
File: PROTON

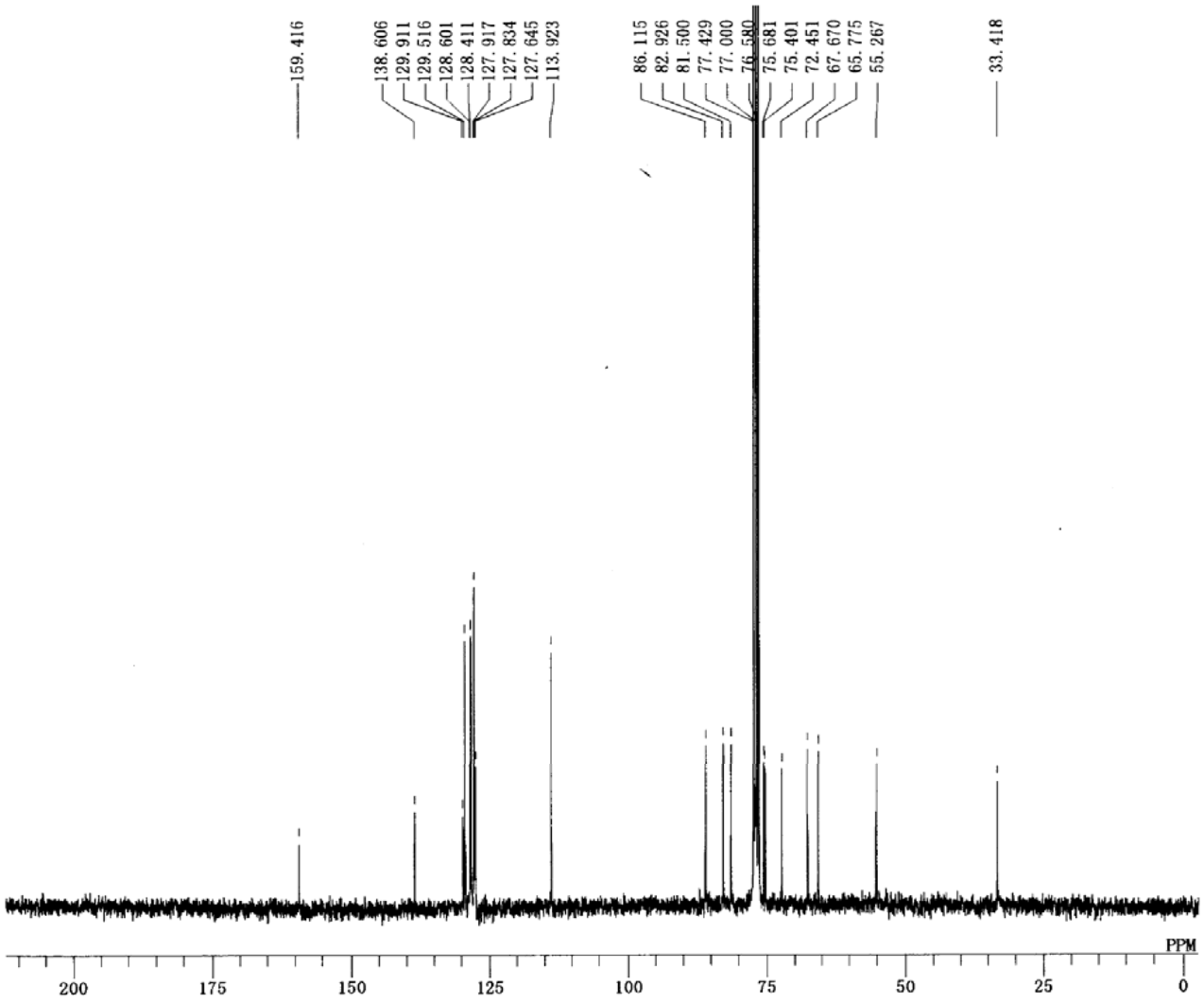
Pulse Sequence: s2pul



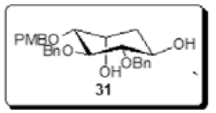



PLJ070808.
DFILE D:\叶新山\PLJ080115-C.als
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 288
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRATN 511
CTEMP 20.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24
30
165.392
159.111
138.351
137.939
133.076
130.142
129.870
129.615
128.370
128.263
127.942
127.703
127.628
113.642
83.066
82.711
77.420
77.000
76.571
76.102
75.517
75.129
70.852
70.794
55.127
32.157
PPM
200
175
150
125
100
75
50
25
0

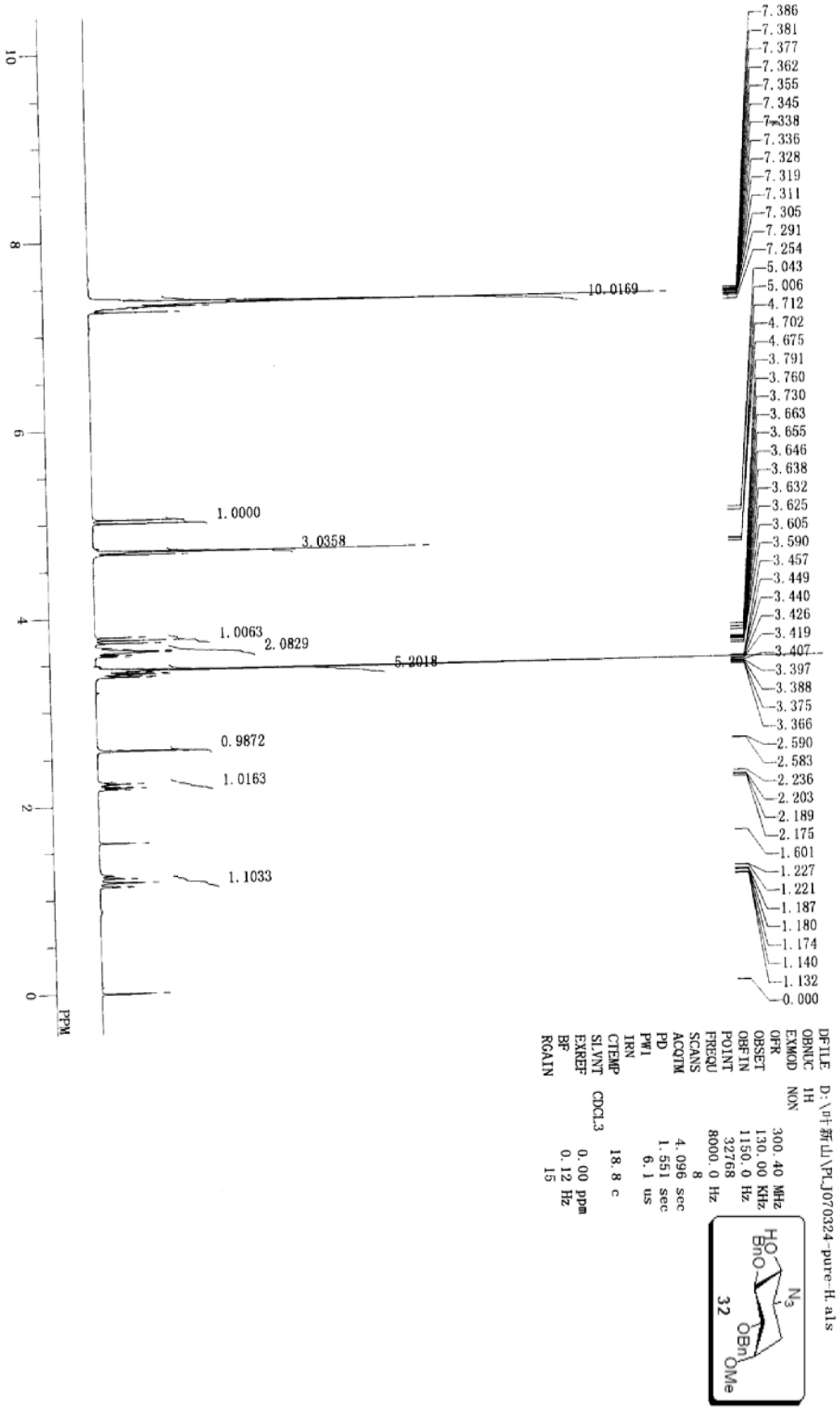

WD070612
File: PROTON
Pulse Sequence: s2pul
Solvent: cdcl3
Temp: 25.0 C / 298.1 K
INOVA-500 "BMU500"
Relax. delay 4.000 sec
Pulse 82.8 degrees
Acq. time 1.892 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9019002 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 34 sec
7.358
7.355
7.339
7.329
7.323
7.313
7.309
7.303
7.287
7.281
7.263
7.278
7.259
7.242
6.868
6.851
5.008
4.985
4.919
4.898
4.829
4.808
4.765
4.759
4.692
4.669
4.645
4.619
4.597
4.091
4.085
4.079
4.073
3.958
3.953
3.948
3.943
3.935
3.826
3.806
3.798
3.795
3.789
3.497
3.491
3.479
3.472
3.279
3.260
3.242
2.258
2.250
2.239
2.230
2.222
1.399
1.394
1.375
1.371
1.366
1.342
0.000
11.14
1.82
0.97
0.98
1.00
0.97
0.99
1.15
ppm
PMBO
BnO
OH
OBn
OH
31

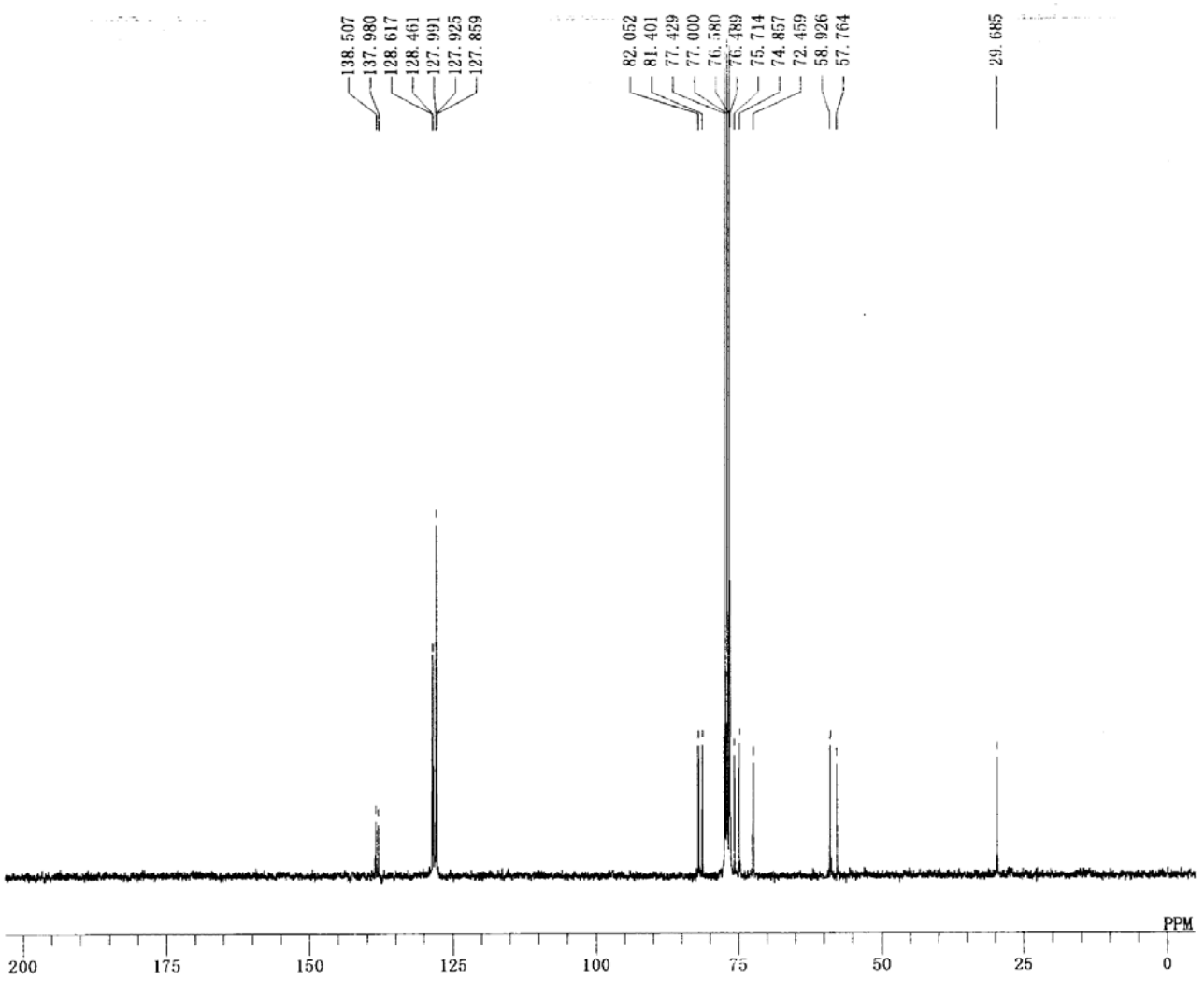


DFILE	D:\叶新山\WD070612-C.als	
OBNUC	13C	
EXMOD	BCM	
OBFRQ	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	3121	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRATN	511	
CTEMP	21.4	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	24	

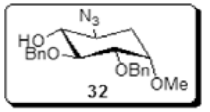


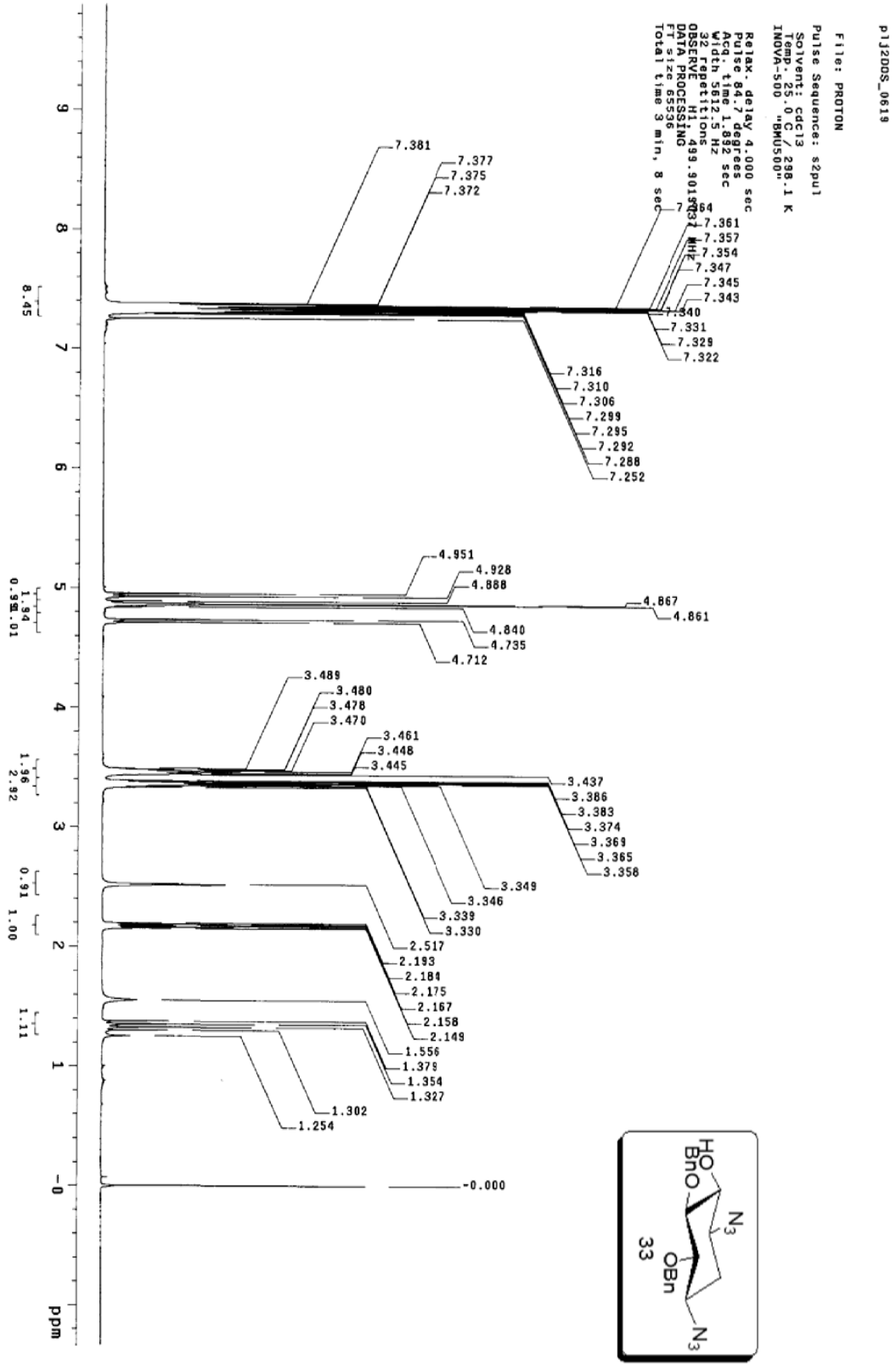
31

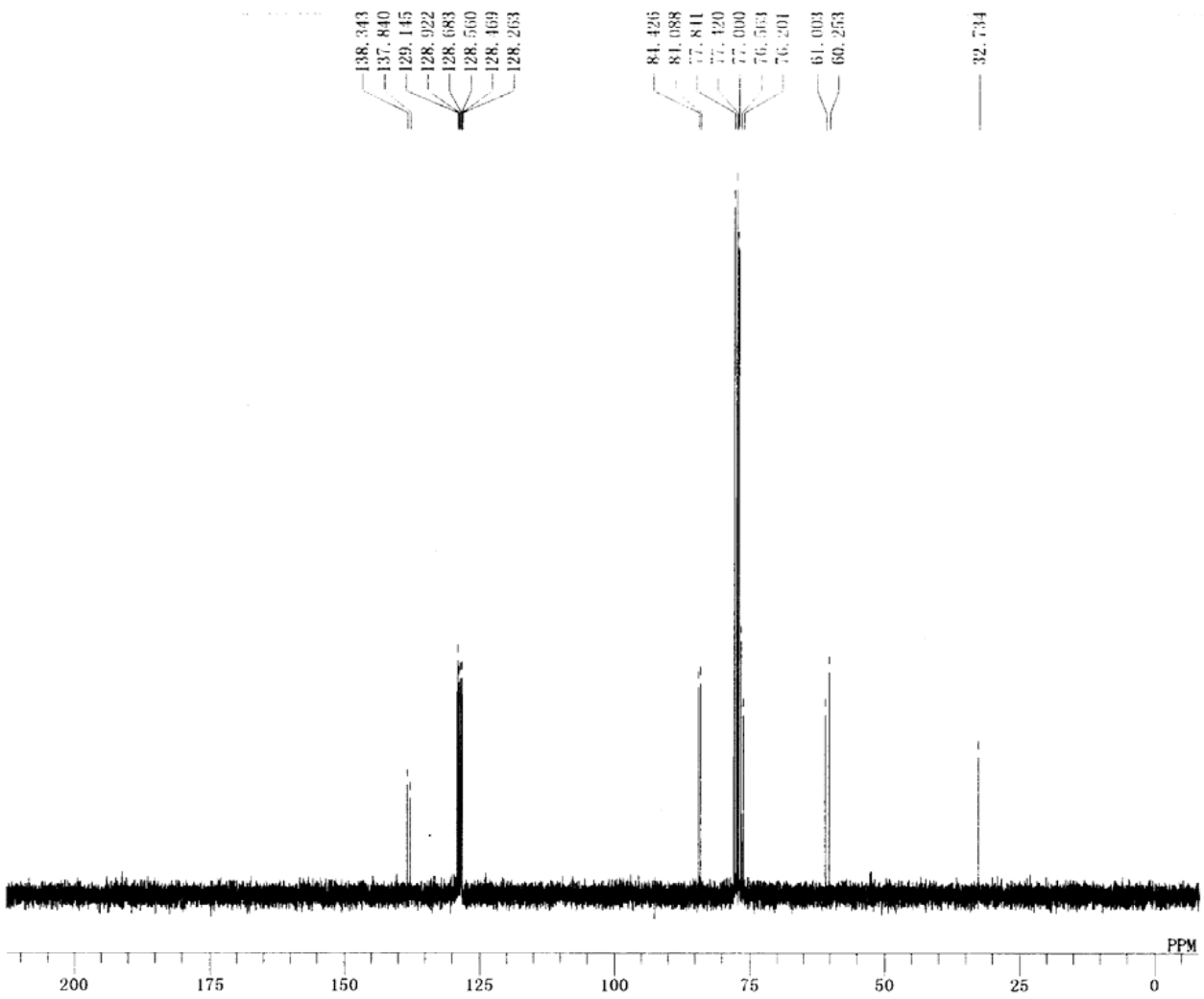

7.386
7.381
7.377
7.362
7.355
7.345
7.338
7.336
7.328
7.319
7.311
7.305
7.291
7.254
5.043
5.006
4.712
4.702
4.675
3.791
3.760
3.730
3.663
3.655
3.646
3.638
3.632
3.625
3.605
3.590
3.457
3.449
3.440
3.426
3.419
3.407
3.397
3.388
3.375
3.366
2.590
2.583
2.236
2.203
2.189
2.175
1.601
1.227
1.221
1.187
1.180
1.174
1.140
1.132
0.000
10.0169
1.0000
3.0358
1.0063
2.0829
5.2018
0.9872
1.0163
1.1033
PPM
D:\叶新山\PLJ070324-pure-H.als
DFILE
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRN
CTEMP 18.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15
HO
BnO
N3
OBn
OMe
32



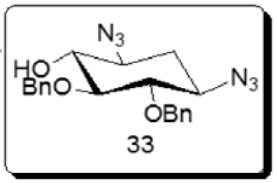
DFILE	D:\叶新山\plj070324-C.als	
OBNUC	13C	
EXMOD	BCM	
OFR	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	3056	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRN		
CTEMP	20.2	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	24	



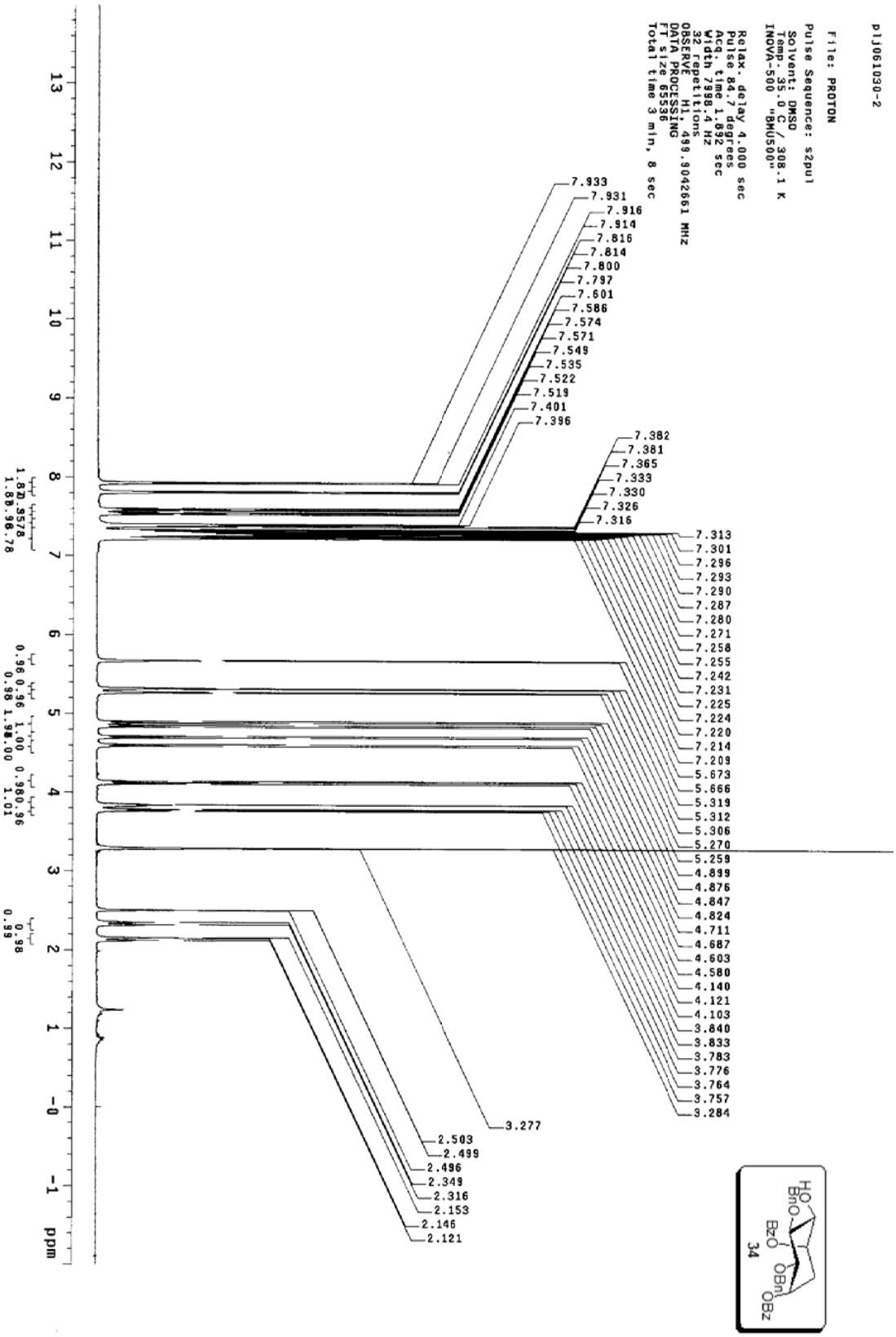

pIJ2DDS_0619
File: PROTON
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMUS00"
Relax. delay 4.000 sec
Pulse 84.7 degrees
Acq. time 1.892 sec
Width 5812.5 Hz
32 repetitions
OBSERVE H1, 499.9019037 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 8 sec
7.381
7.377
7.375
7.372
7.364
7.361
7.357
7.354
7.347
7.345
7.343
7.340
7.331
7.329
7.322
7.316
7.310
7.306
7.299
7.295
7.292
7.288
7.252
4.951
4.928
4.888
4.867
4.861
4.840
4.735
4.712
3.489
3.480
3.478
3.470
3.461
3.448
3.445
3.437
3.386
3.383
3.374
3.369
3.365
3.358
3.349
3.346
3.339
3.330
2.517
2.193
2.184
2.175
2.167
2.158
2.149
1.556
1.379
1.354
1.327
1.302
1.254
-0.000
8.45
1.94
0.93
1.01
1.96
2.92
0.91
1.00
1.11
ppm
HO
BnO
N3
OBn
33
N3

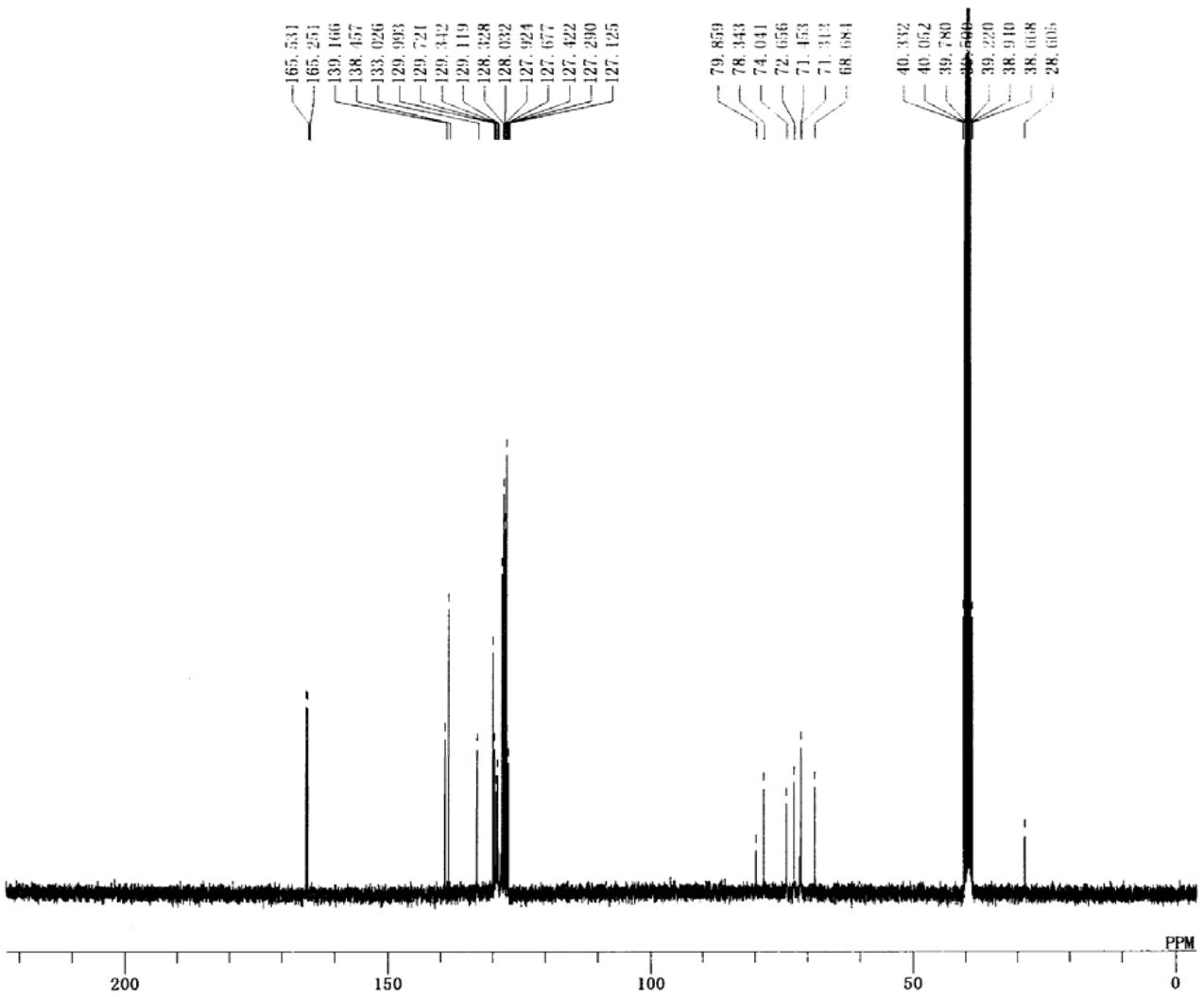


DFILE D:\叶新山\PLJ060803-2-C.als
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 800
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRATN 511
CTEMP 21.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 25

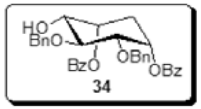


33


plj061030-2
File: PROTON
Pulse Sequence: s2pul
Solvent: DMSO
Temp. 35.0 C / 308.1 K
INOVA-500 "BMU500"
Relax. delay 4.000 sec
Pulse 84.7 degrees
Acq. time 1.892 sec
Width 7998.4 Hz
32 repetitions
OBSERVE H1, 499.9042661 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 8 sec
7.933
7.931
7.916
7.914
7.816
7.814
7.800
7.797
7.601
7.586
7.574
7.571
7.549
7.535
7.522
7.519
7.401
7.396
7.382
7.381
7.365
7.333
7.330
7.326
7.316
7.313
7.301
7.296
7.293
7.290
7.287
7.280
7.271
7.258
7.255
7.242
7.231
7.225
7.224
7.220
7.214
7.209
5.673
5.666
5.319
5.312
5.306
5.270
5.259
4.899
4.876
4.847
4.824
4.711
4.687
4.603
4.580
4.140
4.121
4.103
3.840
3.833
3.783
3.776
3.764
3.757
3.284
3.277
2.503
2.499
2.496
2.349
2.316
2.153
2.146
2.121
1.82 2.95 7.8
1.88 9.6 7.8
0.96 0.96 1.00 0.98
0.98 1.98 3.00 0.96
0.96 1.01
0.98
0.99
ppm
HO
BnO
BzO
OBn
OBz
34



DFILE D:\叶新山\PLJ061030-2-C.als
COMNT
DATIM Fri Nov 10 21:13:19 2006
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 4400
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 24.9 c
SLVNT DMSO
EXREF 39.50 ppm
BF 0.12 Hz
RGAIN 24



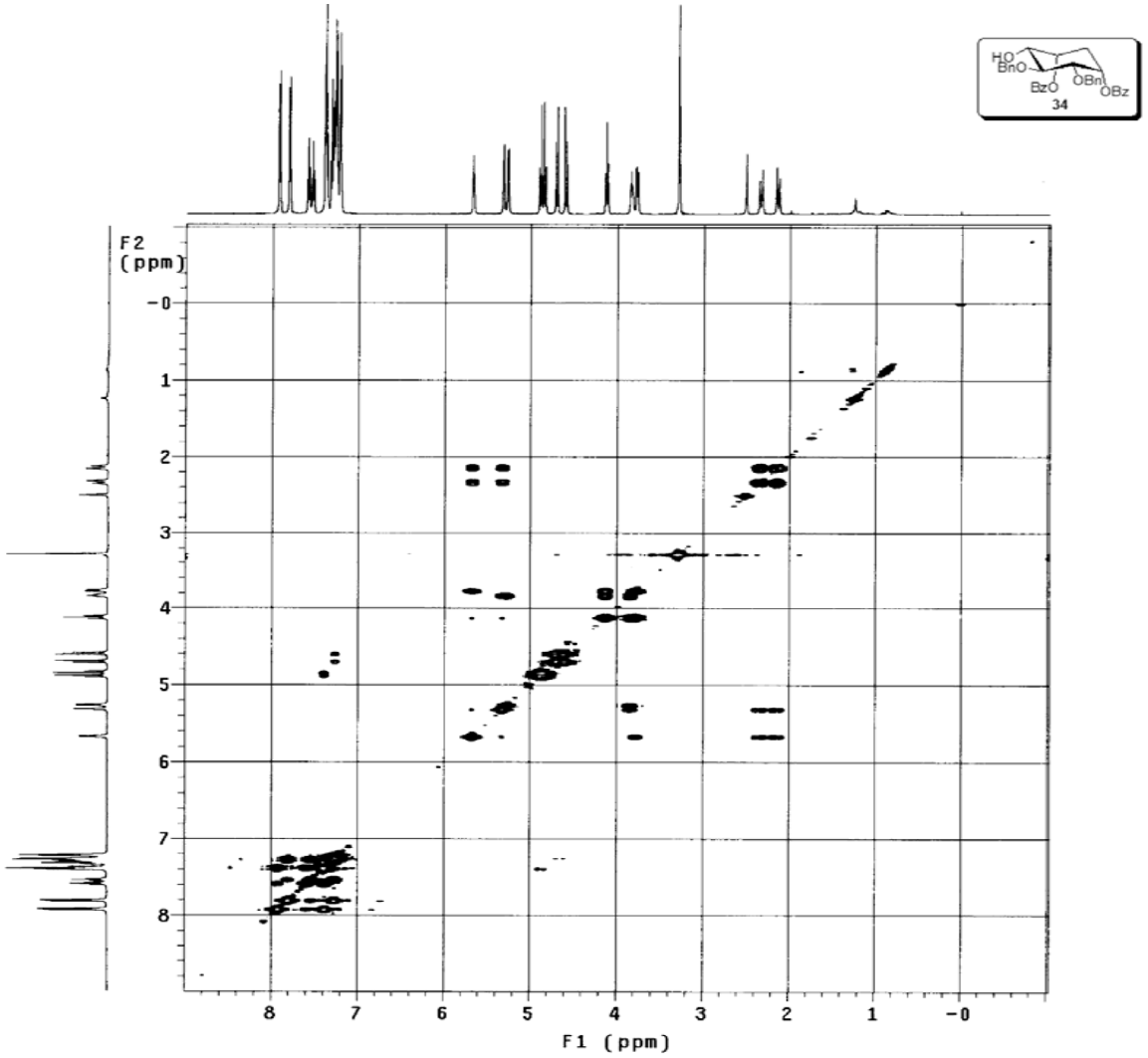
34

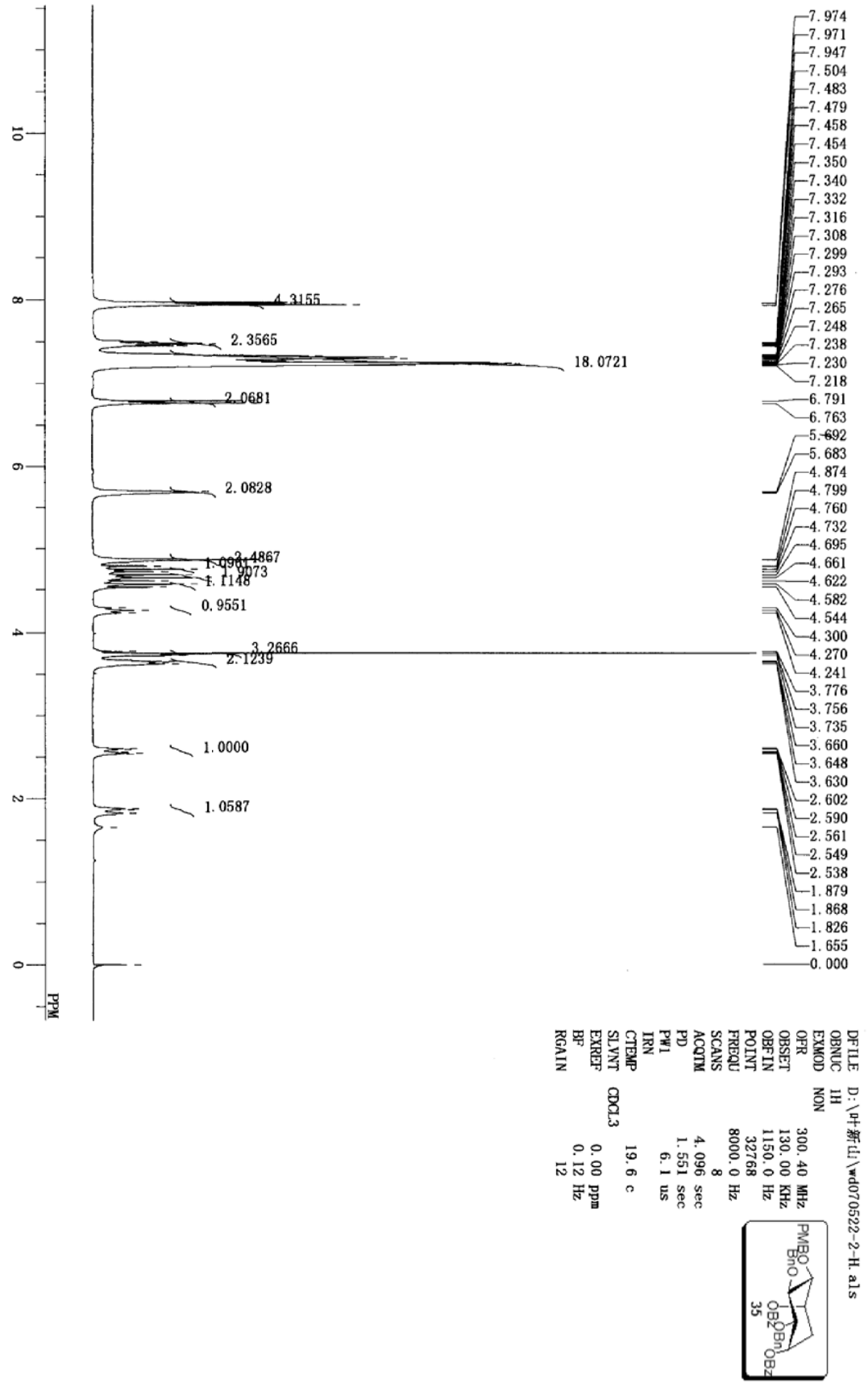
plj061030-2

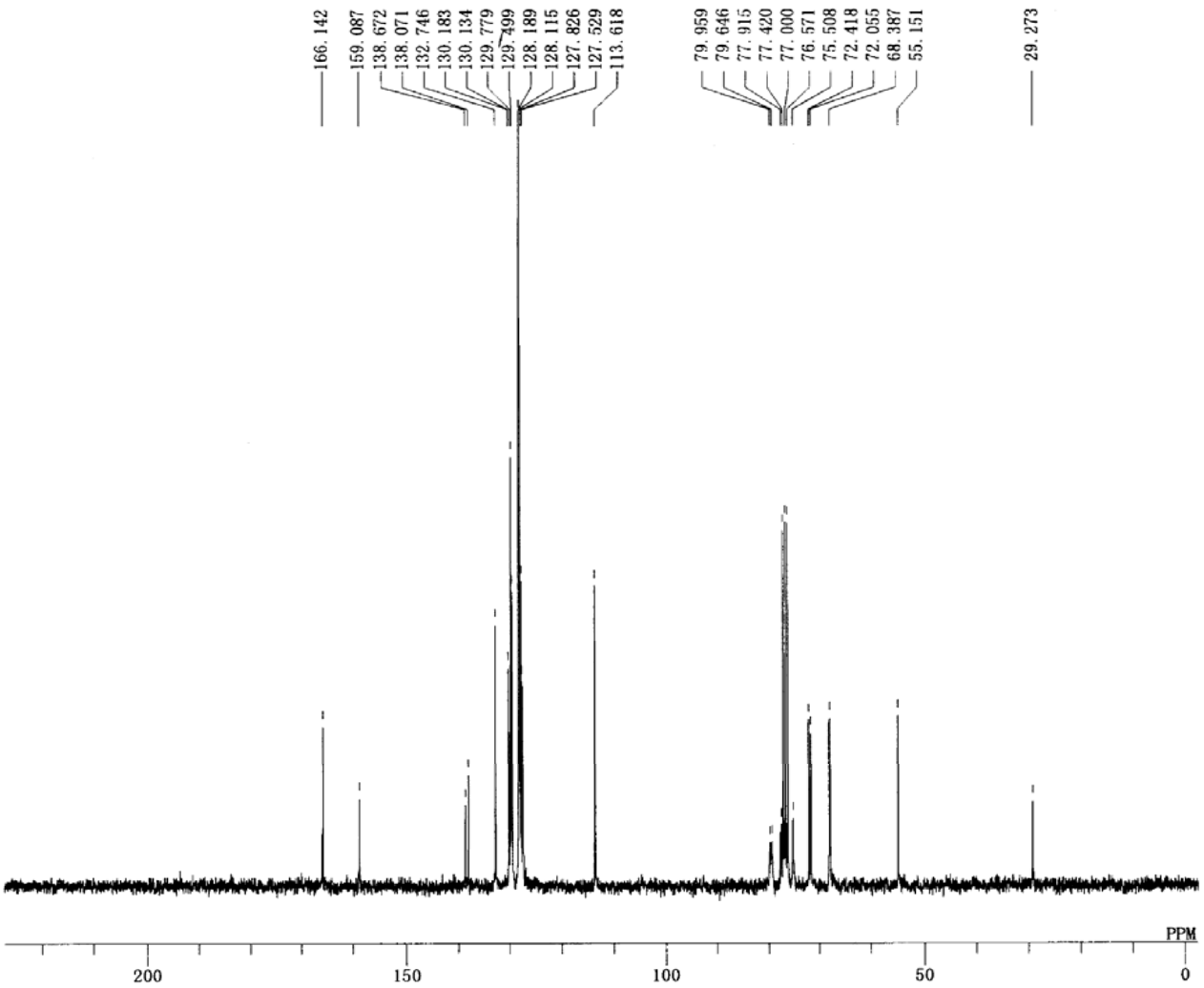
File: PROTON

Pulse Sequence: gCOSY
Solvent: DMSO
Temp. 35.0 C / 308.1 K
INOVA-500 "BMU500"

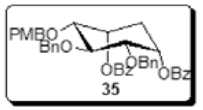
Relax. delay 1.000 sec
Acq. time 0.204 sec
Width 5018.5 Hz
2D Width 5018.5 Hz
16 repetitions
256 increments
OBSERVE H1, 499.9042661 MHz
DATA PROCESSING
Sq. sine bell 0.102 sec
F1 DATA PROCESSING
Sq. sine bell 0.027 sec
FT size 4096 x 4096
Total time 1 hr, 25 min, 8 sec

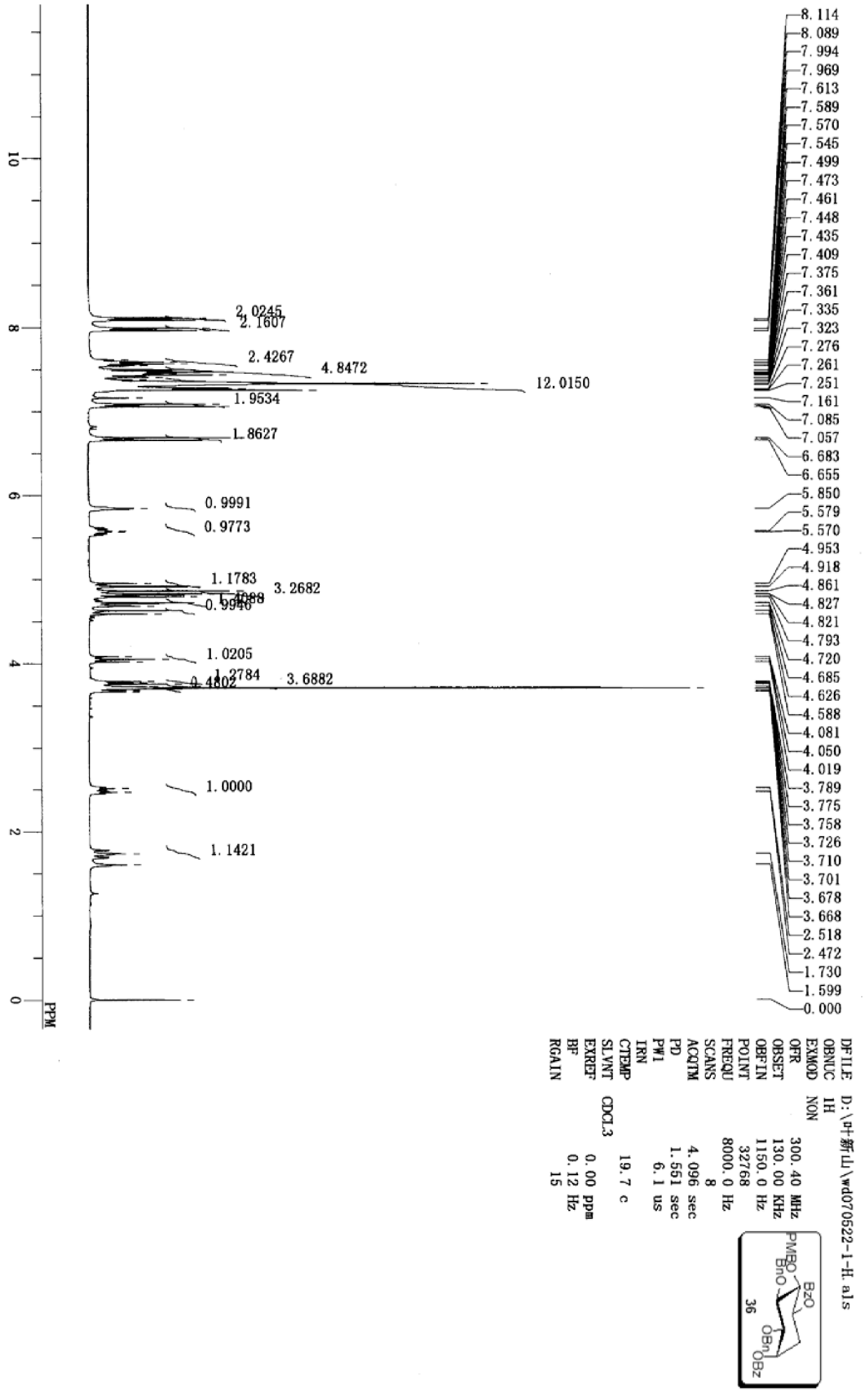



7.974
7.971
7.947
7.504
7.483
7.479
7.458
7.454
7.350
7.340
7.332
7.316
7.308
7.299
7.293
7.276
7.265
7.248
7.238
7.230
7.218
6.791
6.763
5.692
5.683
4.874
4.799
4.760
4.732
4.695
4.661
4.622
4.582
4.544
4.300
4.270
4.241
3.776
3.756
3.735
3.660
3.648
3.630
2.602
2.590
2.561
2.549
2.538
1.879
1.868
1.826
1.655
0.000
4.3155
2.3565
18.0721
2.0681
2.0828
3.4867
1.0961
1.9073
1.1148
0.9551
3.2666
2.1239
1.0000
1.0587
PPM
DFILE D:\中新出\wd070522-2-H.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRN
CTEMP 19.6 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12
PMBO
BnO
OBz
OBn
OBz
35



DFILE	D:\叶新山\WD070522-2-C.als
OBNUC	13C
EXMOD	BCM
OBFRQ	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.0 Hz
POINT	32768
FREQU	20408.1 Hz
SCANS	336
ACQTM	1.606 sec
PD	1.394 sec
PW1	4.2 us
IRATN	511
CTEMP	21.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	2.00 Hz
RGAIN	24




8.114
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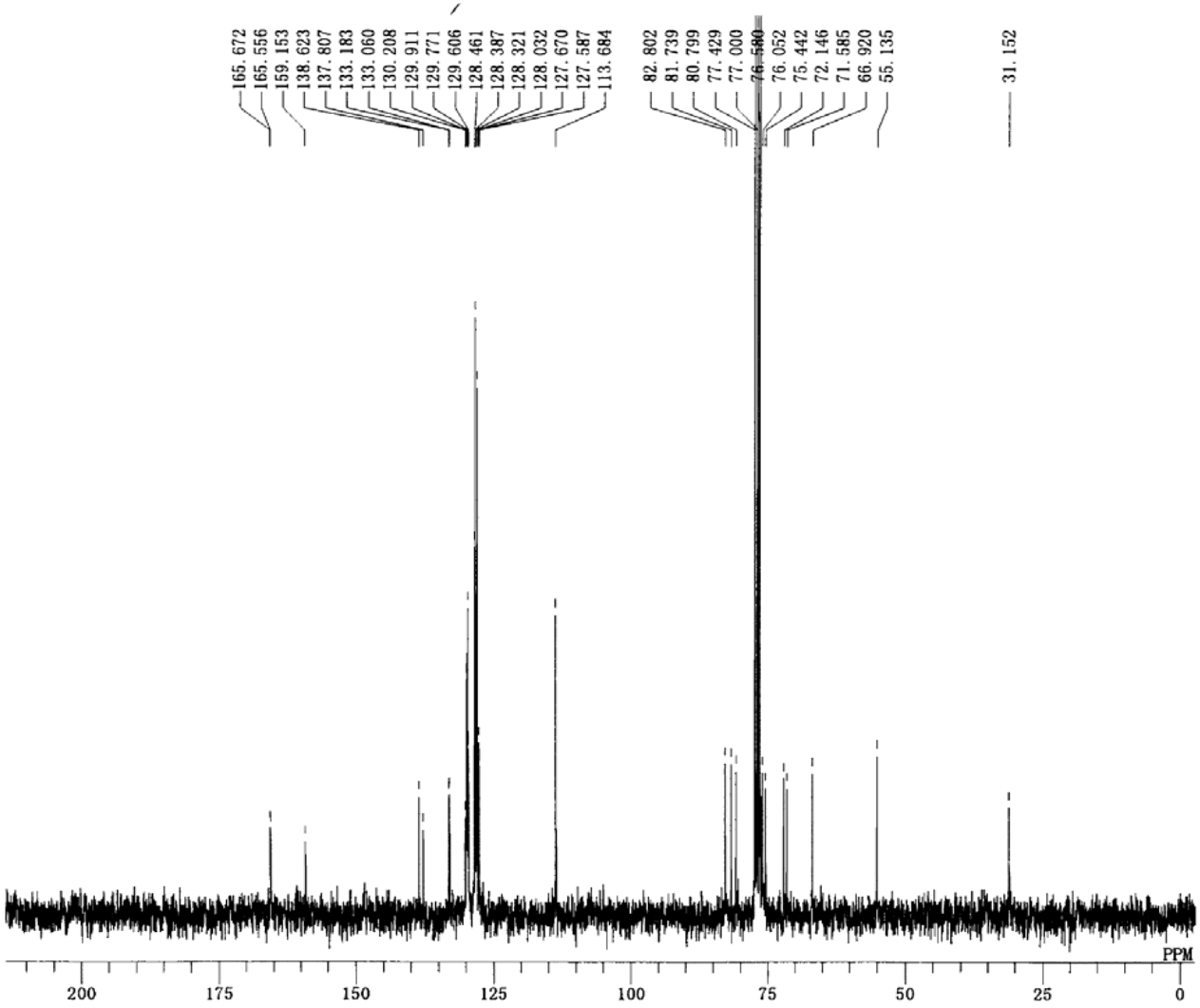
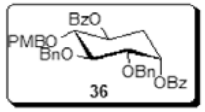
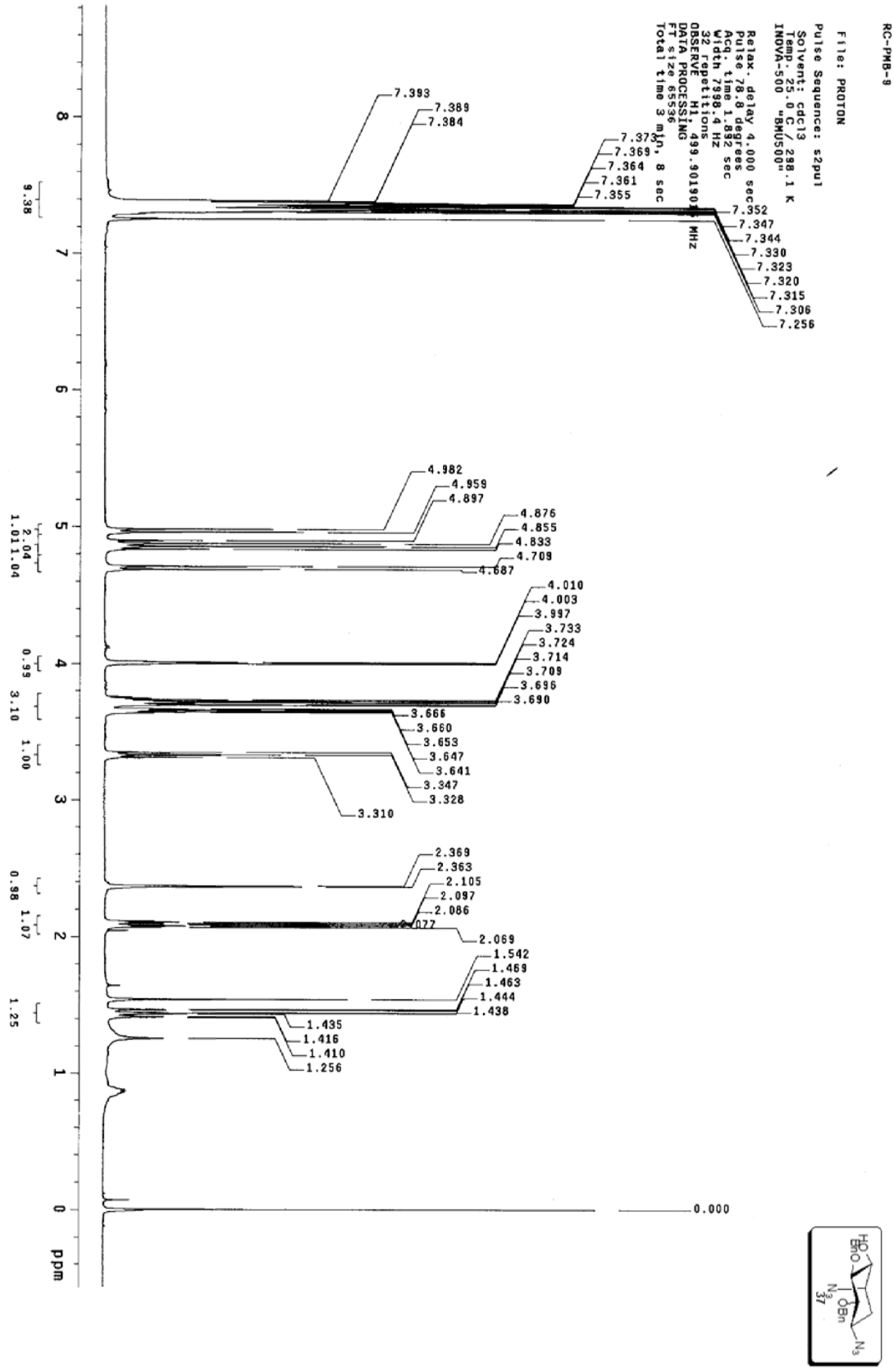
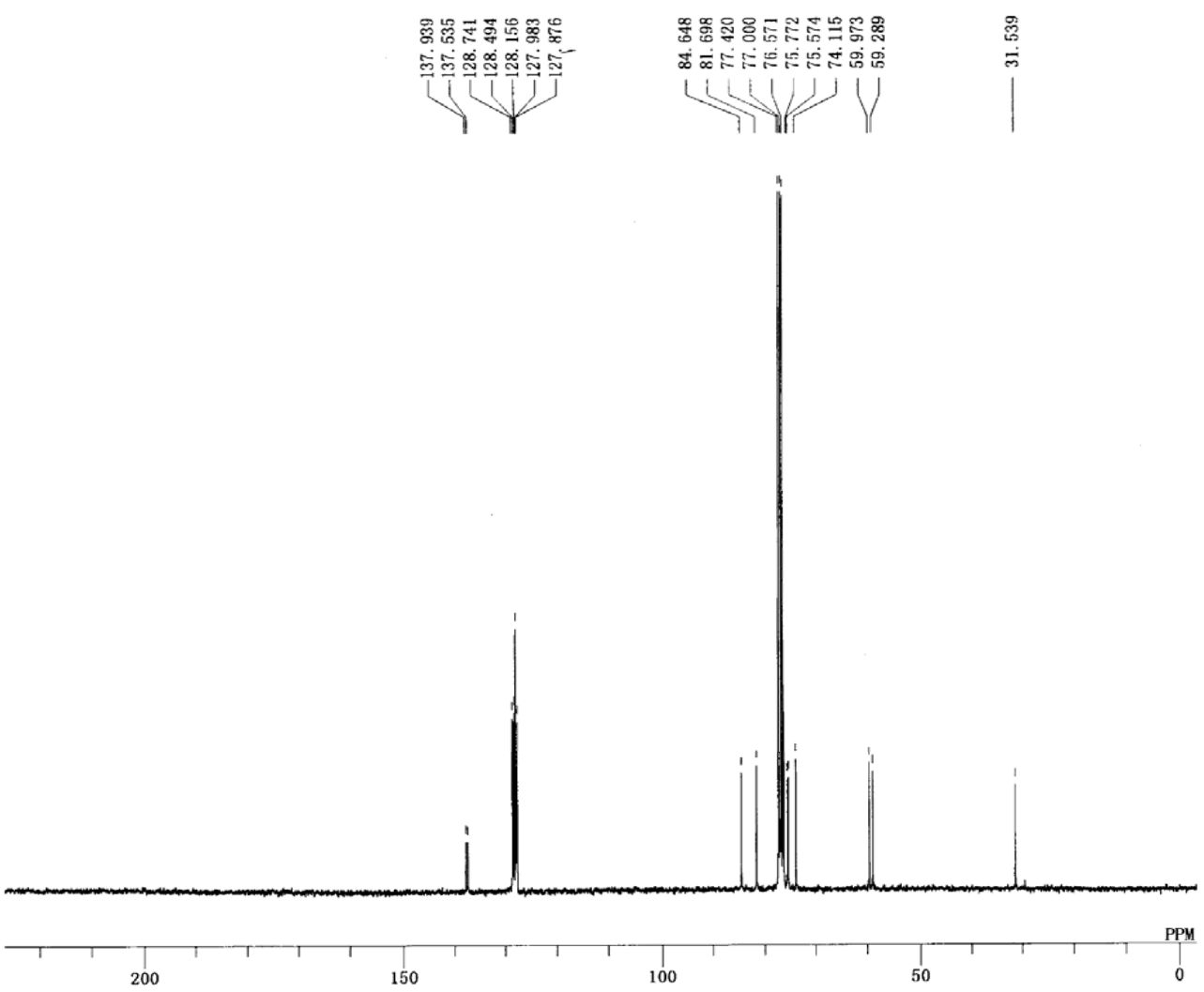
7.969
7.613
7.589
7.570
7.545
7.499
7.473
7.461
7.448
7.435
7.409
7.375
7.361
7.335
7.323
7.276
7.261
7.251
7.161
7.085
7.057
6.683
6.655
5.850
5.579
5.570
4.953
4.918
4.861
4.827
4.821
4.793
4.720
4.685
4.626
4.588
4.081
4.050
4.019
3.789
3.775
3.758
3.726
3.710
3.701
3.678
3.668
2.518
2.472
1.730
1.599
0.000
2.0245
2.1607
2.4267
4.8472
12.0150
1.9534
1.8627
0.9991
0.9773
1.1783
3.2682
1.0205
1.2784
3.6882
1.0000
1.1421
PPM
DFILE D:\中新山\wd070522-1-H.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRN
CTEMP 19.7 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15
PMBO
BnO
BzO
OBn
OBz
36



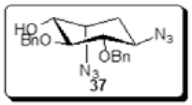
DFILE D:\叶新山\wd070522-1-C.als
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 308
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRATN 511
CTEMP 20.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 25




RC-PMB-9
File: PROTON
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMS00"
Relax. delay 4.000 sec
Pulse 78.8 degrees
Acq. time 1.892 sec
Width 7998.4 Hz
32 repetitions
OBSERVE H1, 499.9019[illegible] MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 8 sec
7.393
7.389
7.384
7.373
7.369
7.364
7.361
7.355
7.352
7.347
7.344
7.330
7.323
7.320
7.315
7.306
7.256
4.982
4.959
4.897
4.876
4.855
4.833
4.709
4.687
4.010
4.003
3.997
3.733
3.724
3.714
3.709
3.696
3.690
3.666
3.660
3.653
3.647
3.641
3.347
3.328
3.310
2.369
2.363
2.105
2.097
2.086
2.077
2.069
1.542
1.469
1.463
1.444
1.438
1.435
1.416
1.410
1.256
0.000
9.38
2.04
1.01
1.04
0.99
3.10
1.00
0.98
1.07
1.25
ppm
HO
BnO
N3
OBn
N3
37



DFILE D:\叶新山\RC-PMB-9-C.als
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 5680
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRATN 511
CTEMP 21.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24



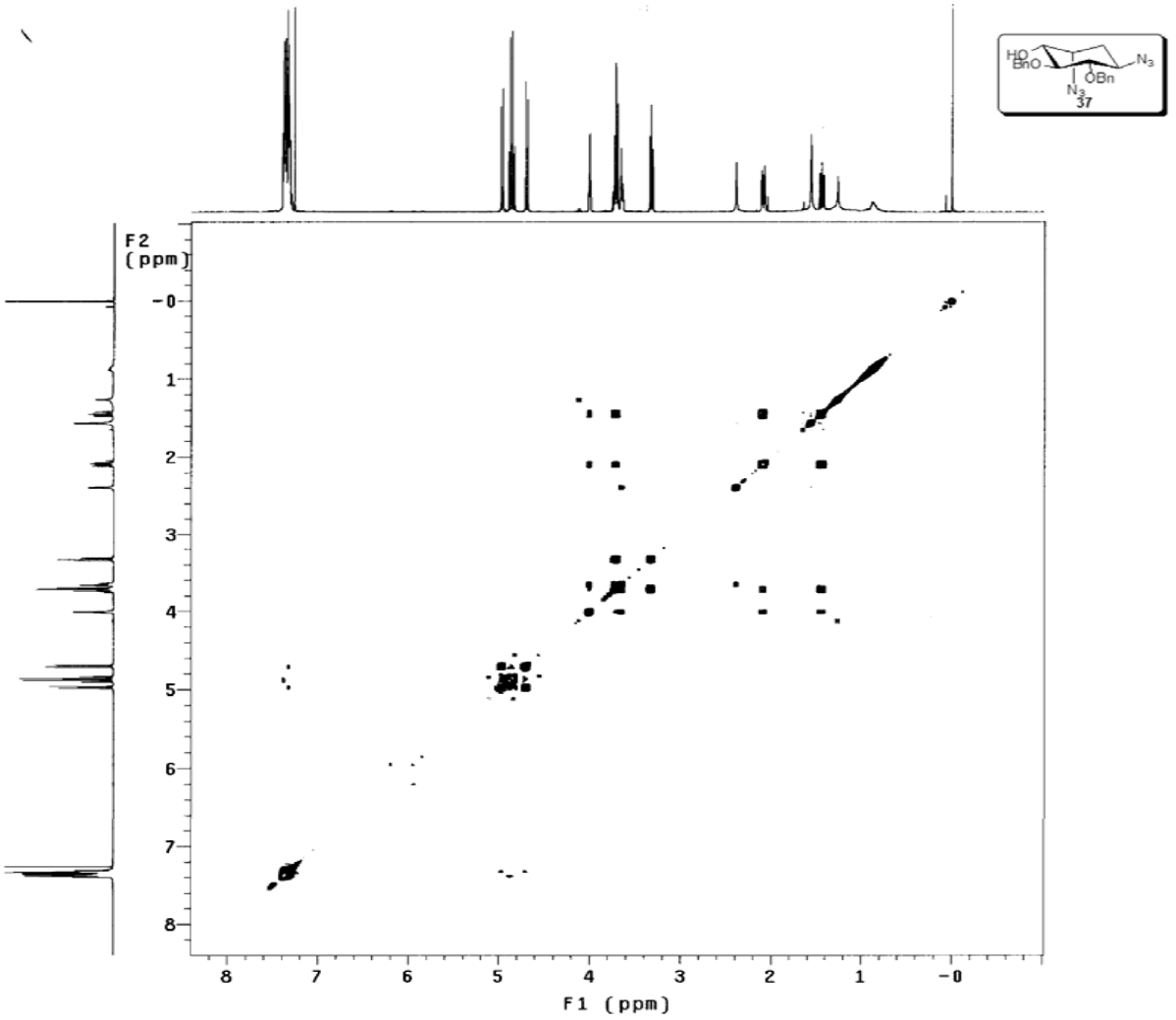
37

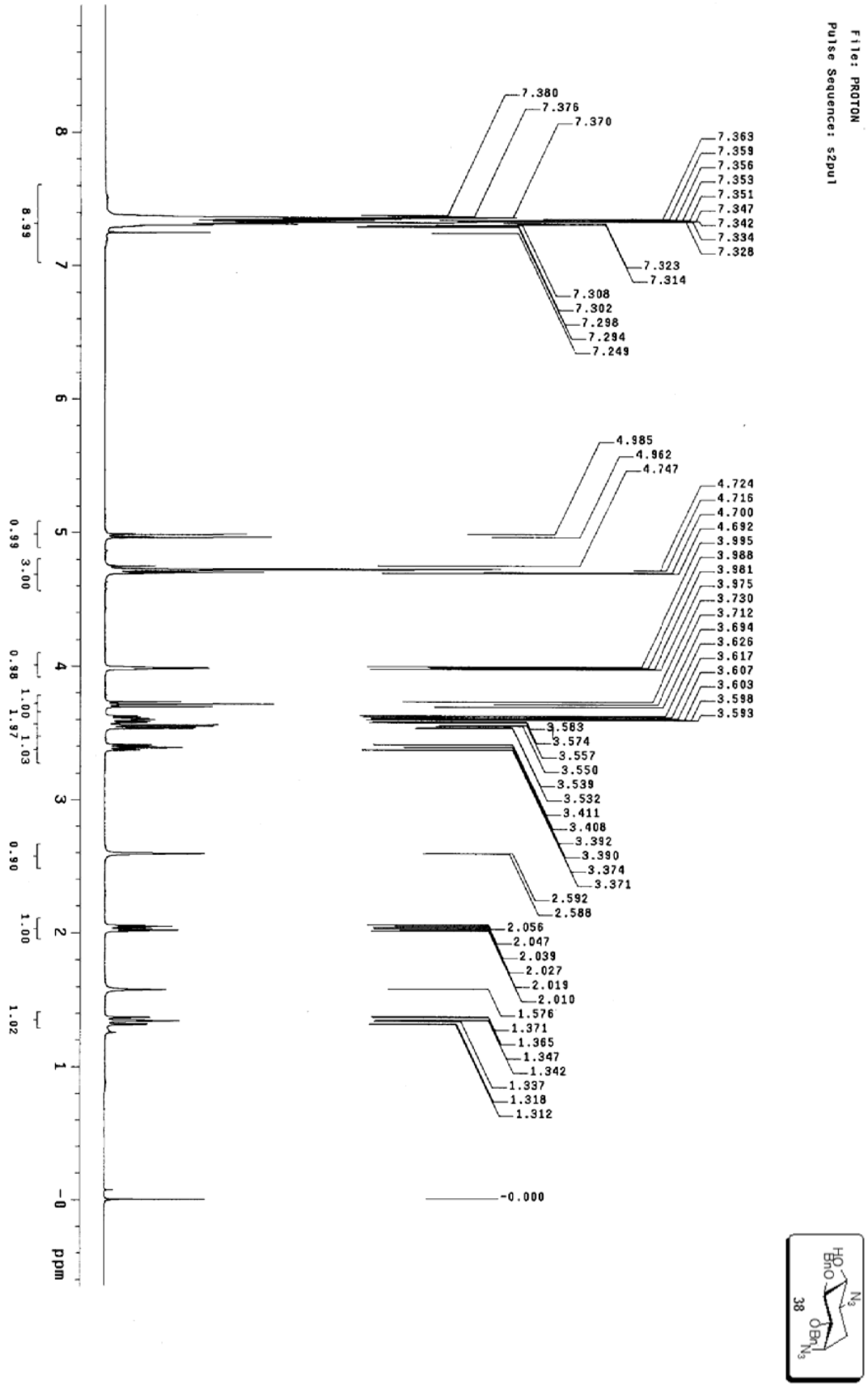
RC-PMB-9

File: PROTON

Pulse Sequence: COSY
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.217 sec
Width 4710.9 Hz
2D Width 4710.9 Hz
32 repetitions
256 increments
OBSERVE H1, 499.9019015 MHz
DATA PROCESSING
Sq. sine bell 0.109 sec
F1 DATA PROCESSING
Sq. sine bell 0.028 sec
FT size 4096 x 4096
Total time 2 hr, 51 min, 52 sec



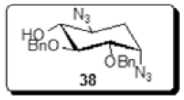

File: PROTON
Pulse Sequence: s2pul
7.380
7.376
7.370
7.363
7.359
7.356
7.353
7.351
7.347
7.342
7.334
7.328
7.323
7.314
7.308
7.302
7.298
7.294
7.249
4.985
4.962
4.747
4.724
4.716
4.700
4.692
3.995
3.988
3.981
3.975
3.730
3.712
3.694
3.626
3.617
3.607
3.603
3.598
3.593
3.583
3.574
3.557
3.550
3.539
3.532
3.411
3.408
3.392
3.390
3.374
3.371
2.592
2.588
2.056
2.047
2.039
2.027
2.019
2.010
1.576
1.371
1.365
1.347
1.342
1.337
1.318
1.312
-0.000
8.99
0.99
3.00
0.98
1.00
1.97
1.03
0.90
1.00
1.02
ppm
38

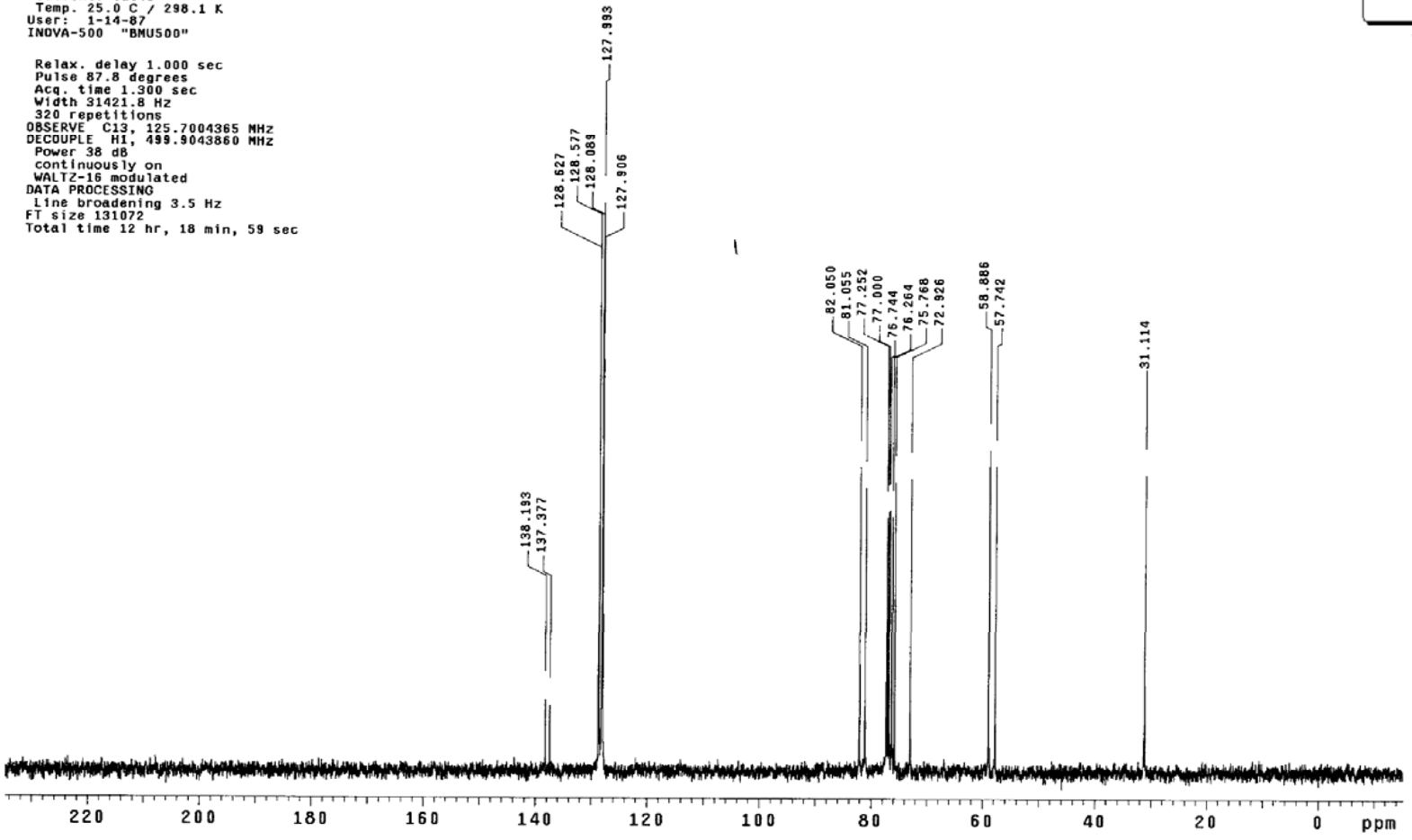
RC-PMB10

File: CARBON

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
320 repetitions
OBSERVE C13, 125.7004365 MHz
DECOUPLE H1, 499.9043860 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.5 Hz
FT size 131072
Total time 12 hr, 18 min, 59 sec



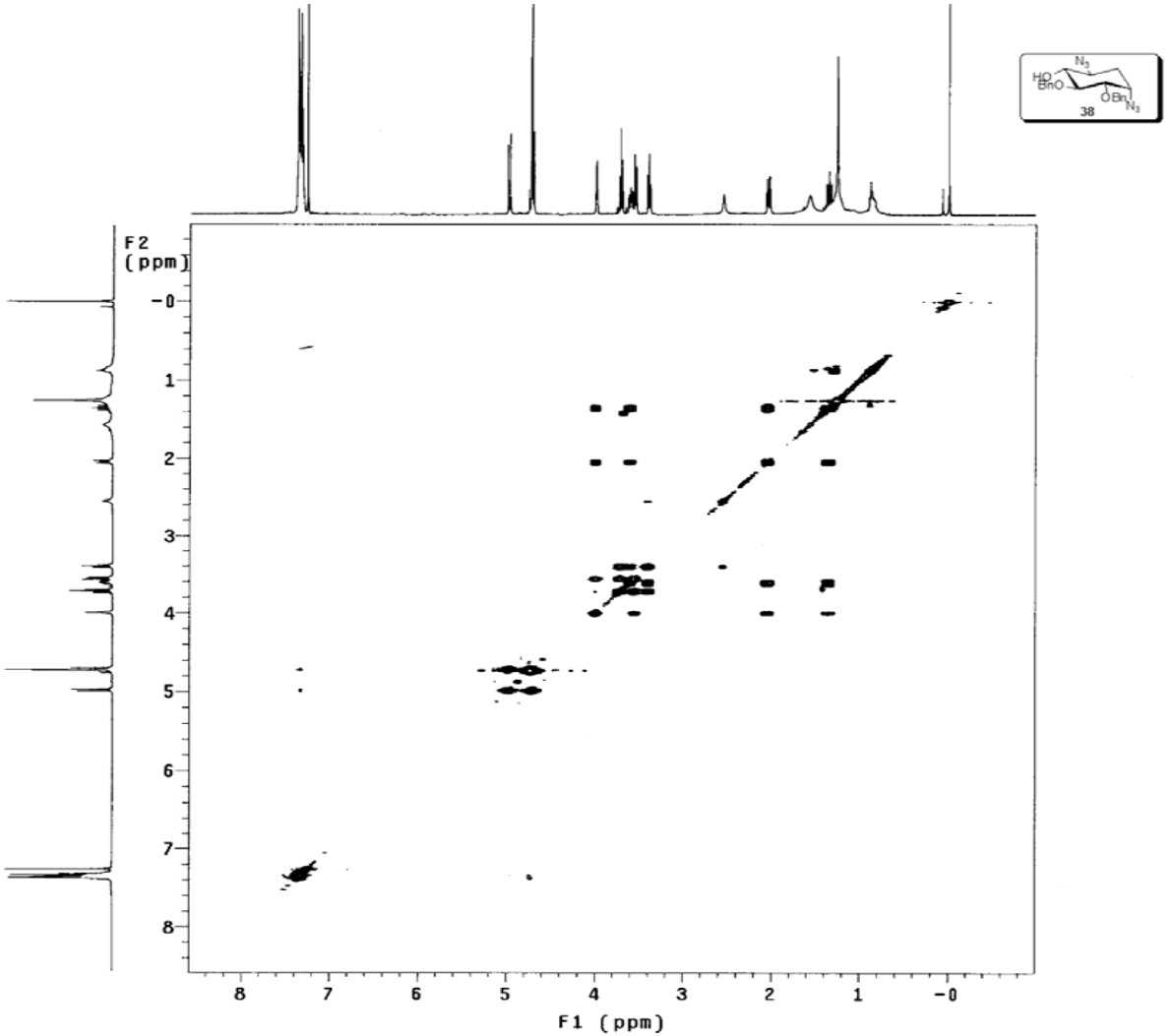


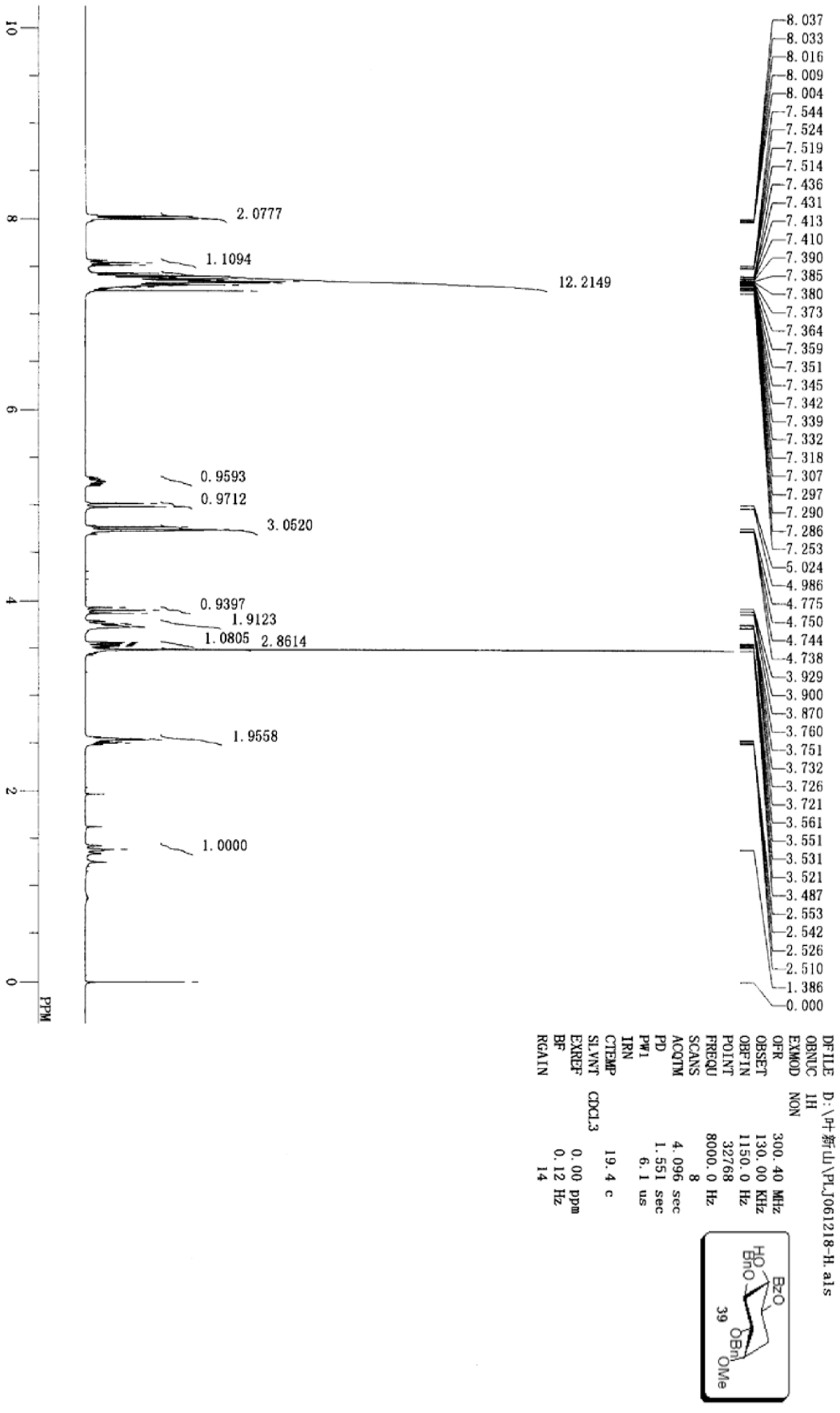
plj070515-1

File: PROTON

Pulse Sequence: gCOSY
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.214 sec
Width 4788.7 Hz
2D Width 4788.7 Hz
16 repetitions
300 increments
OBSERVE H1, 499.9019006 MHz
DATA PROCESSING
Sq. sine bell 0.107 sec
F1 DATA PROCESSING
Sq. sine bell 0.034 sec
FT size 4096 x 4096
Total time 1 hr, 40 min, 58 sec

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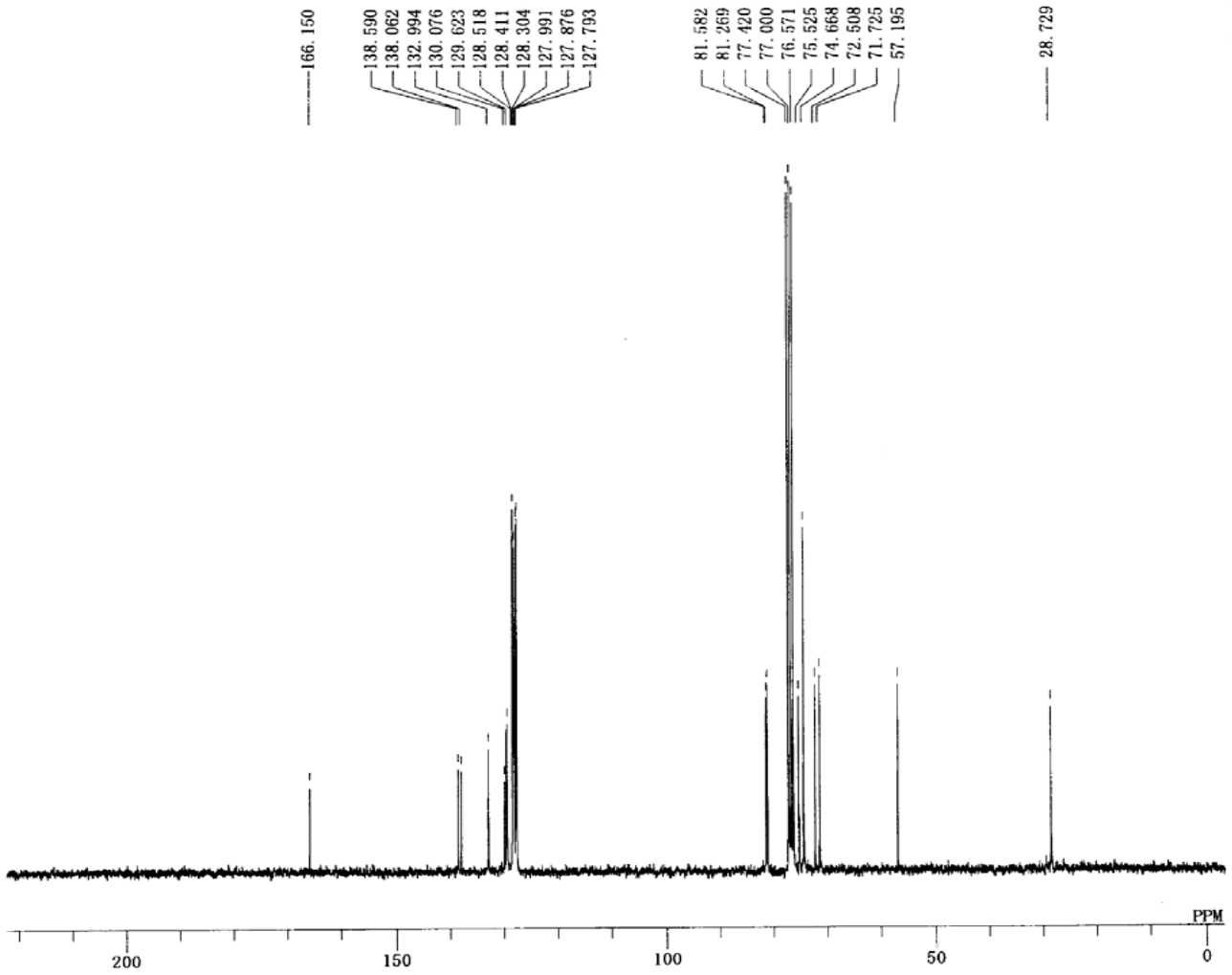
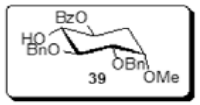
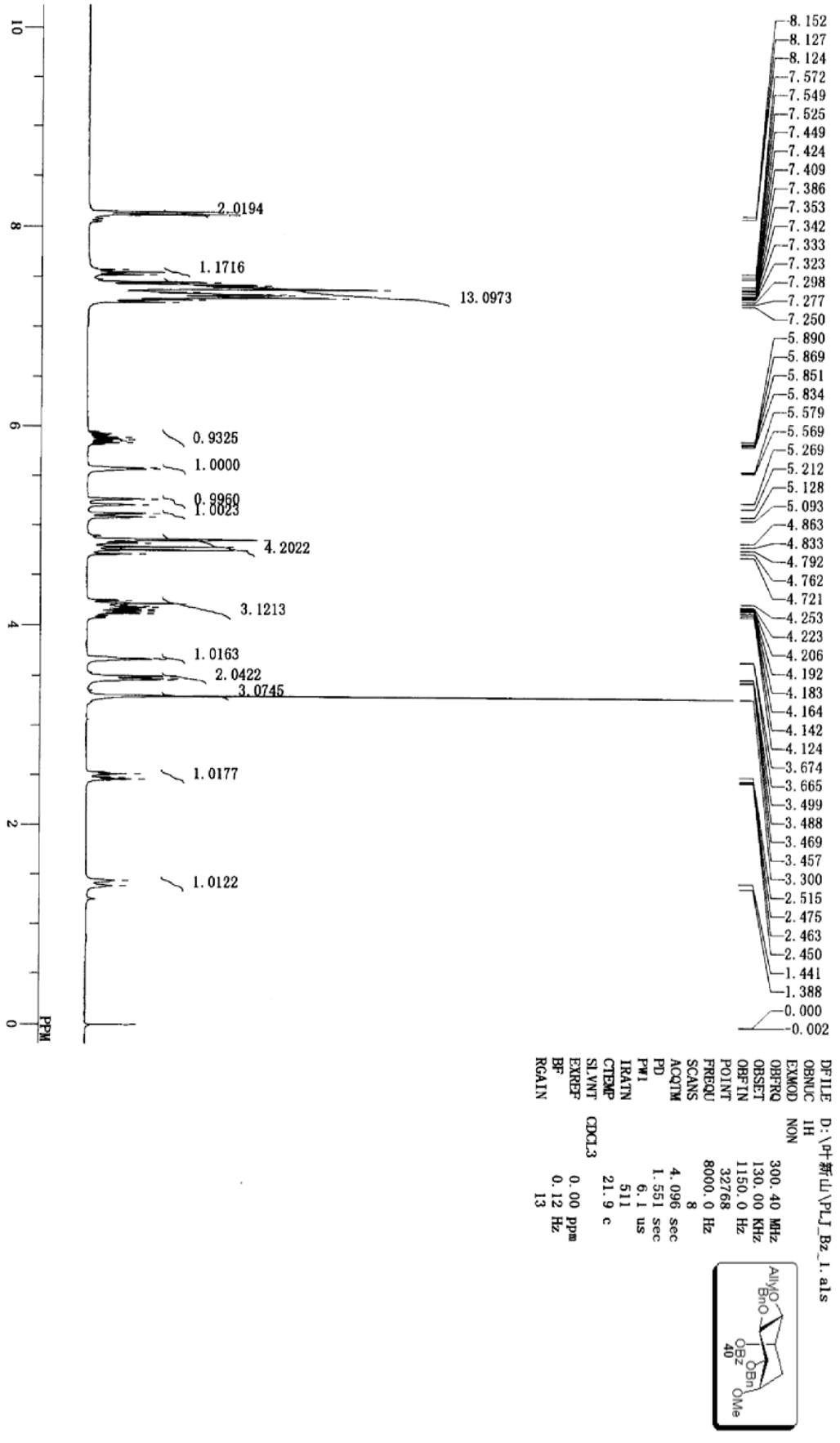
7.519
7.514
7.436
7.431
7.413
7.410
7.390
7.385
7.380
7.373
7.364
7.359
7.351
7.345
7.342
7.339
7.332
7.318
7.307
7.297
7.290
7.286
7.253
5.024
4.986
4.775
4.750
4.744
4.738
3.929
3.900
3.870
3.760
3.751
3.732
3.726
3.721
3.561
3.551
3.531
3.521
3.487
2.553
2.542
2.526
2.510
1.386
0.000
2.0777
1.1094
12.2149
0.9593
0.9712
3.0520
0.9397
1.9123
1.0805
2.8614
1.9558
1.0000
PPM
10
8
6
4
2
0
DFILE D:\中新山\PLJ061218-H.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRN
CTEMP 19.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 14
BzO
HO
BnO
OBn
OMe
39



DFILE	D:\叶新山\PLJ061218-C.als
OBNUC	13C
EXMOD	BCM
OFR	75.45 MHz
OBSET	124.00 KHz
OBFIN	1840.0 Hz
POINT	32768
FREQU	20408.1 Hz
SCANS	1276
ACQTM	1.606 sec
PD	1.394 sec
PW1	4.2 us
IRN	
CTEMP	20.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	2.00 Hz
RGAIN	25

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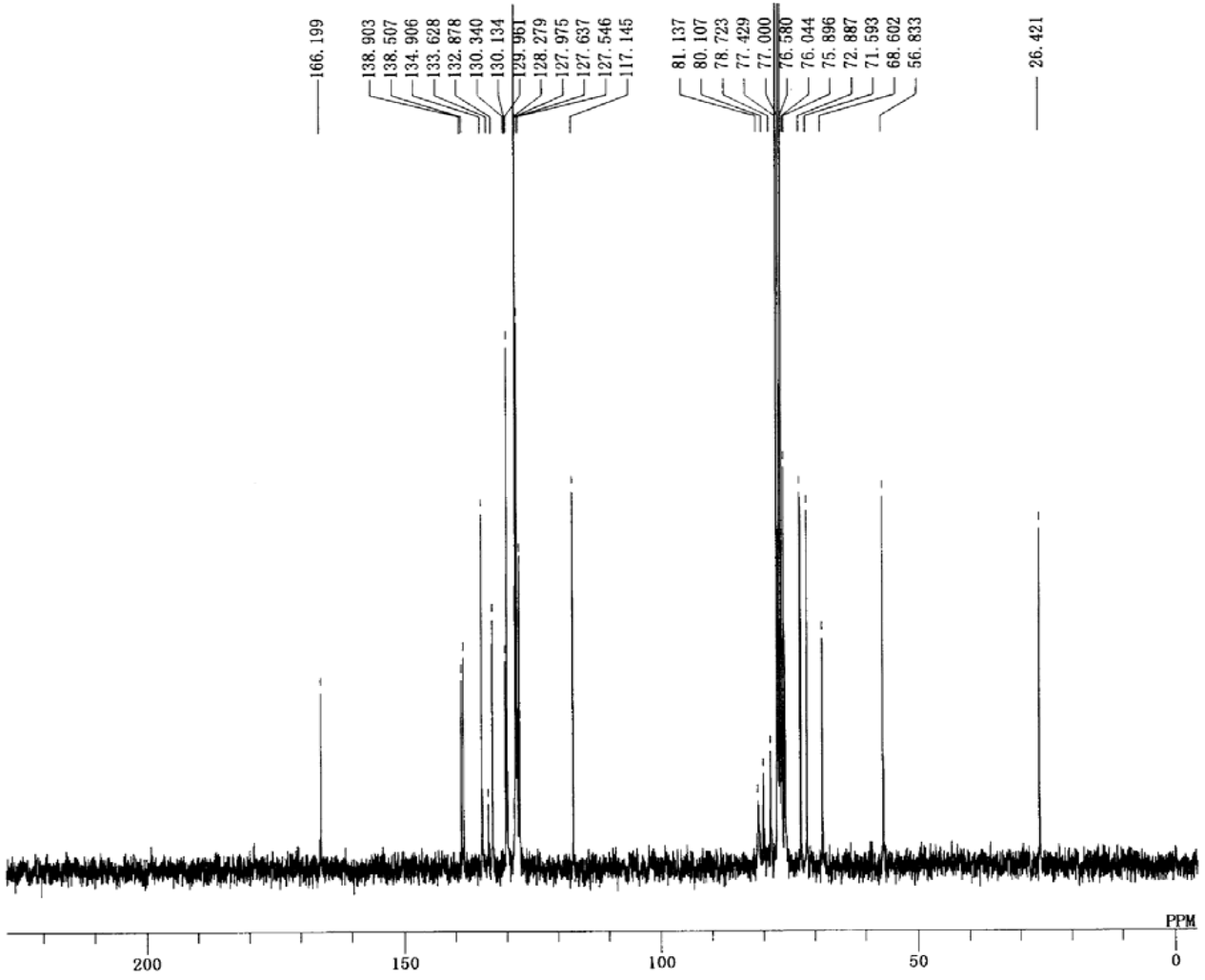
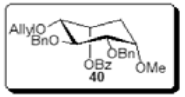
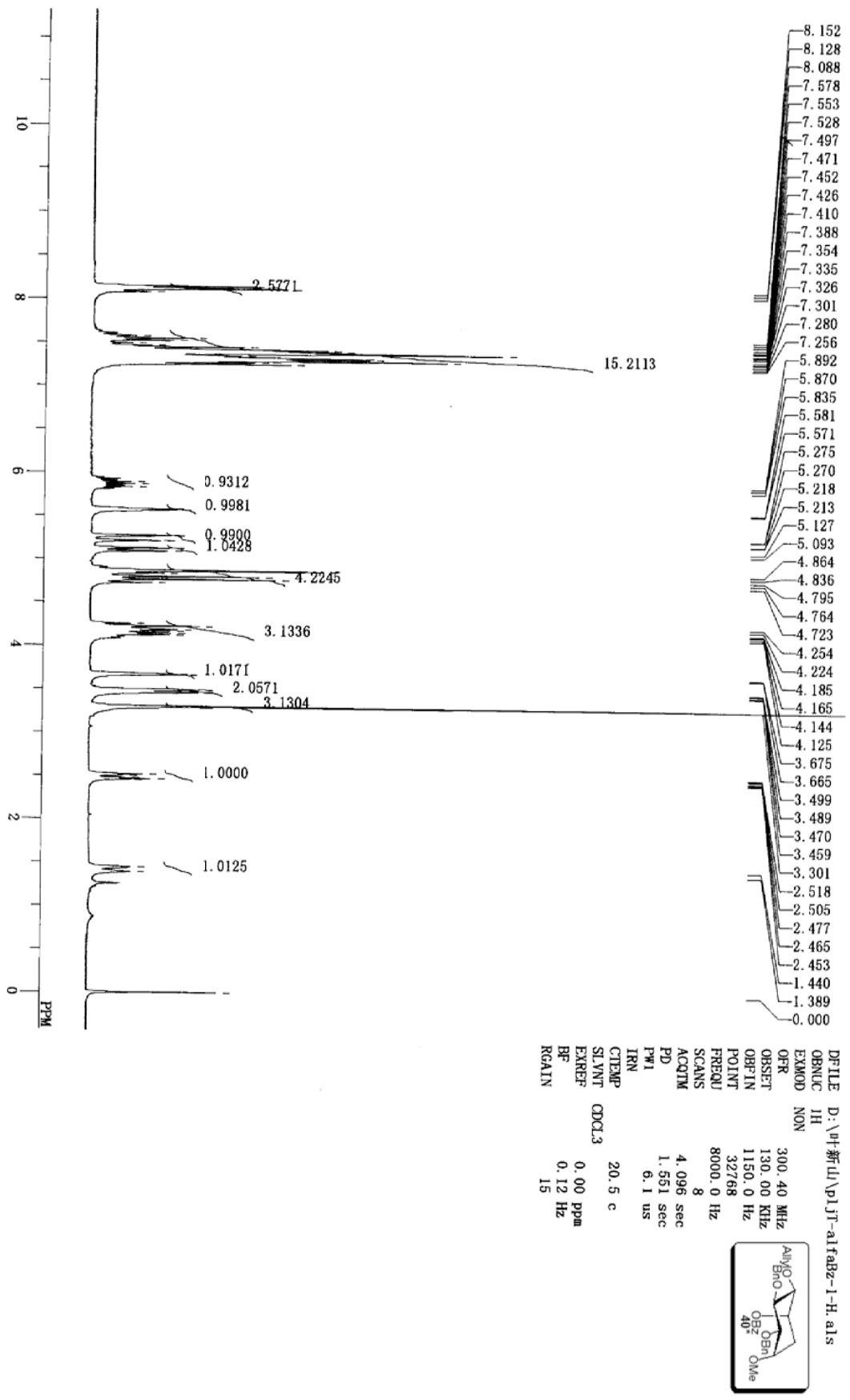
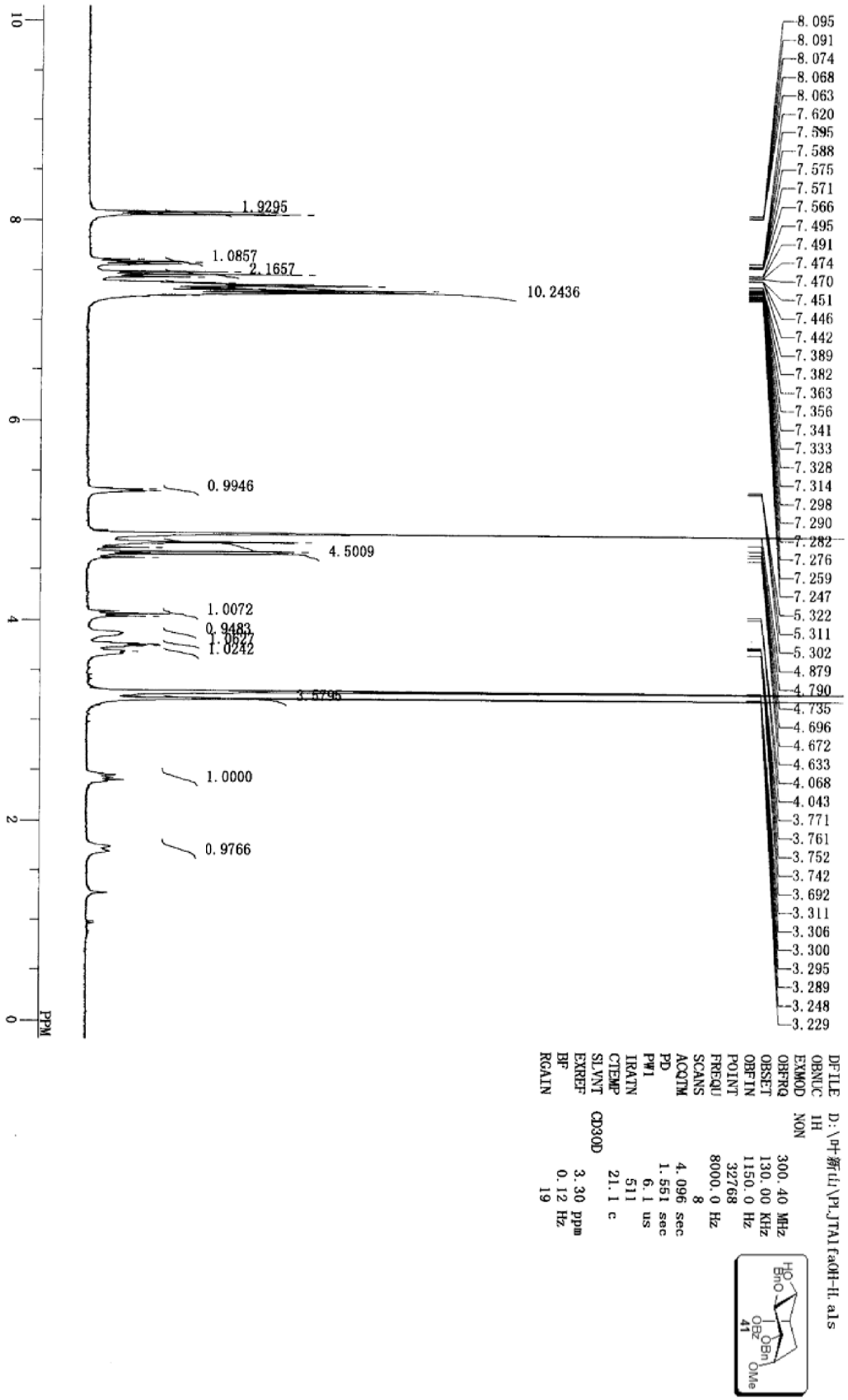
7.409
7.386
7.353
7.342
7.333
7.323
7.298
7.277
7.250
5.890
5.869
5.851
5.834
5.579
5.569
5.269
5.212
5.128
5.093
4.863
4.833
4.792
4.762
4.721
4.253
4.223
4.206
4.192
4.183
4.164
4.142
4.124
3.674
3.665
3.499
3.488
3.469
3.457
3.300
2.515
2.475
2.463
2.450
1.441
1.388
0.000
-0.002
2.0194
1.1716
13.0973
0.9325
1.0000
0.9960
1.0023
4.2022
3.1213
1.0163
2.0422
3.0745
1.0177
1.0122
PPM
DFILE D:\PT新山\PLJ_Bz_1.als
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRATN 511
CTEMP 21.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 13
AllylO
BnO
OBz
OBn
OMe
40

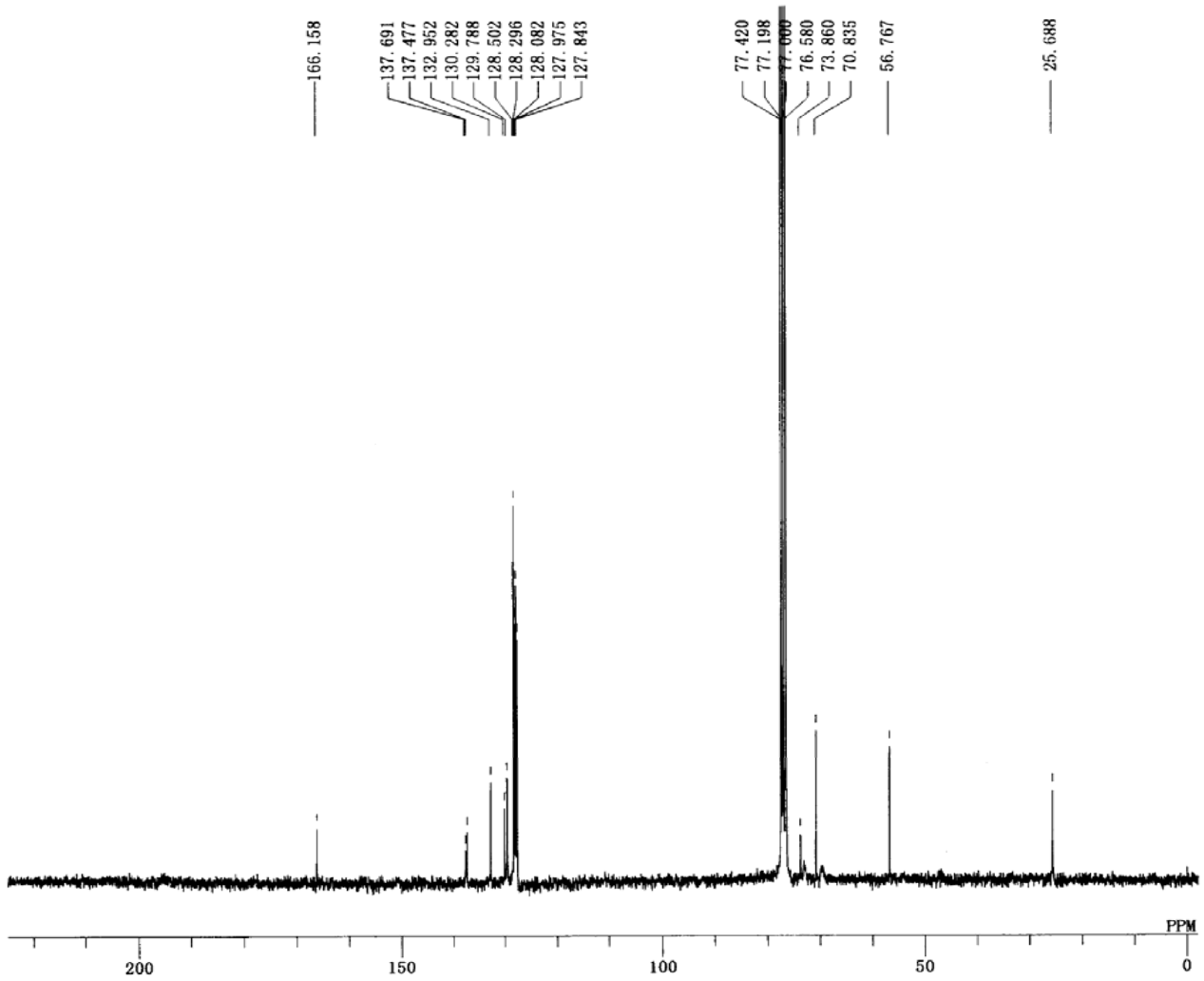


DFILE	D:\叶新山\pljT-alfaBz-1-C.als	
OBNUC	13C	
EXMOD	BCM	
OFR	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	1728	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRN		
CTEMP	19.6	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	24	

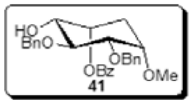


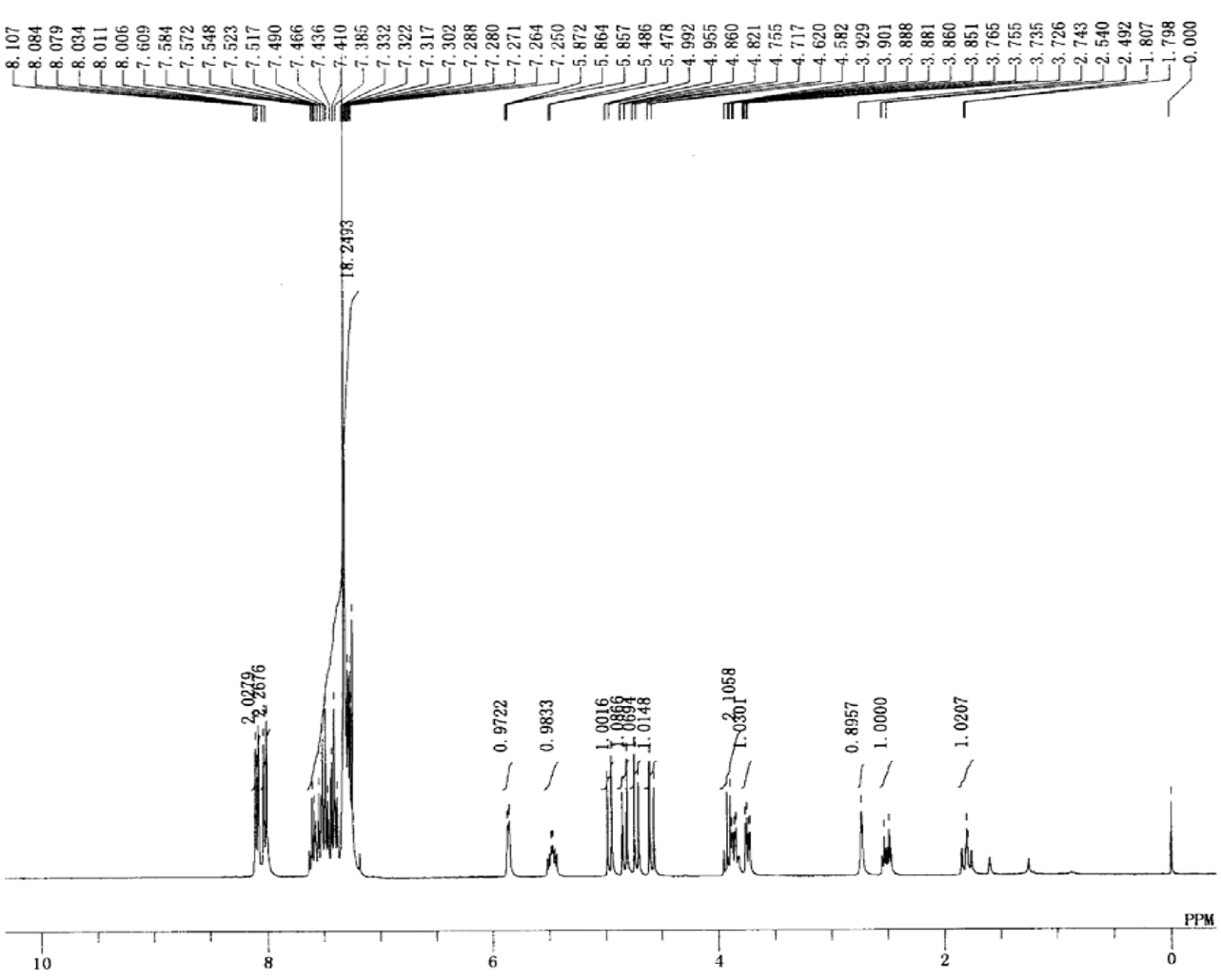

8.152
8.128
8.088
7.578
7.553
7.528
7.497
7.471
7.452
7.426
7.410
7.388
7.354
7.335
7.326
7.301
7.280
7.256
5.892
5.870
5.835
5.581
5.571
5.275
5.270
5.218
5.213
5.127
5.093
4.864
4.836
4.795
4.764
4.723
4.254
4.224
4.185
4.165
4.144
4.125
3.675
3.665
3.499
3.489
3.470
3.459
3.301
2.518
2.505
2.477
2.465
2.453
1.440
1.389
0.000
2.5771
15.2113
0.9312
0.9981
0.9900
1.0428
4.2245
3.1336
1.0171
2.0571
3.1304
1.0000
1.0125
PPM
0
2
4
6
8
10
DFILE D:\H新山\pljT-alfaBz-1-H.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRN
CTEMP 20.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15
AllylO
BnO
OBz
OBn
OMe
40


8.095
8.091
8.074
8.068
8.063
7.620
7.595
7.588
7.575
7.571
7.566
7.495
7.491
7.474
7.470
7.451
7.446
7.442
7.389
7.382
7.363
7.356
7.341
7.333
7.328
7.314
7.298
7.290
7.282
7.276
7.259
7.247
5.322
5.311
5.302
4.879
4.790
4.735
4.696
4.672
4.633
4.068
4.043
3.771
3.761
3.752
3.742
3.692
3.311
3.306
3.300
3.295
3.289
3.248
3.229
1.9295
1.0857
2.1657
10.2436
0.9946
4.5009
1.0072
0.9483
1.0627
1.0242
3.5795
1.0000
0.9766
PPM
10
8
6
4
2
0
DFILE D:\叶新山\PLJTAI faOH-H. als
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRATN 511
CTEMP 21.1 c
SLVNT CD3OD
EXREF 3.30 ppm
BF 0.12 Hz
RGAIN 19
HO
BnO
OBz
OBn
OMe
41

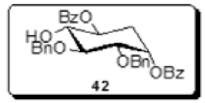


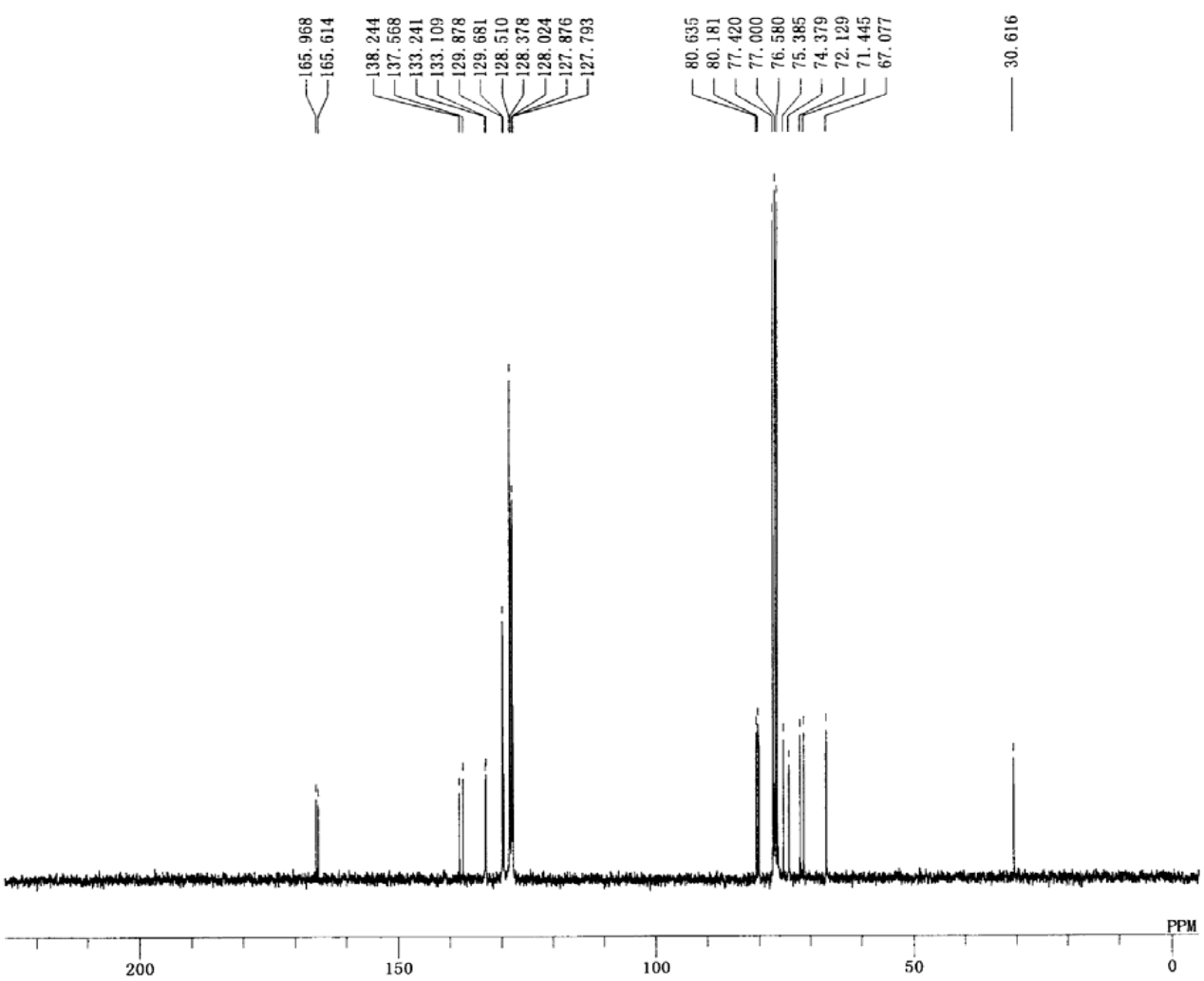
DFILE D:\叶新山\wd070613-C.als
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 4032
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRATN 511
CTEMP 21.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24



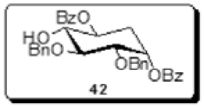


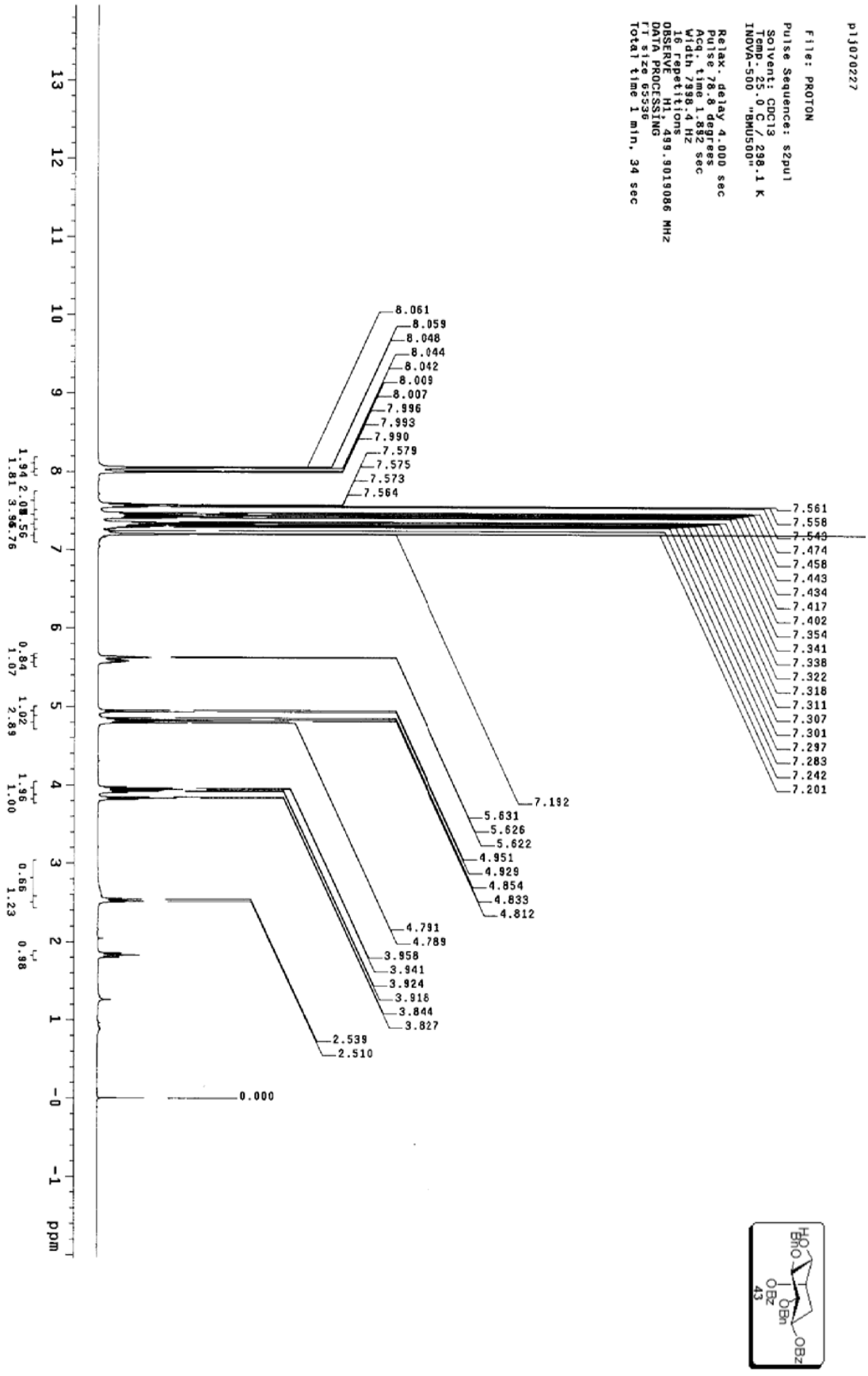
DFILE	D:\叶新山\PLJ061222-2-H.als	
OBNUC	1H	
EXMOD	NON	
OFR	300.40	MHz
OBSET	130.00	KHz
OBFIN	1150.0	Hz
POINT	32768	
FREQU	8000.0	Hz
SCANS	8	
ACQTM	4.096	sec
PD	1.551	sec
PW1	6.1	us
IRN		
CTEMP	19.5	c
SLVNT	CDCL3	
EXREF	0.00	ppm
BF	0.12	Hz
RGAIN	15	

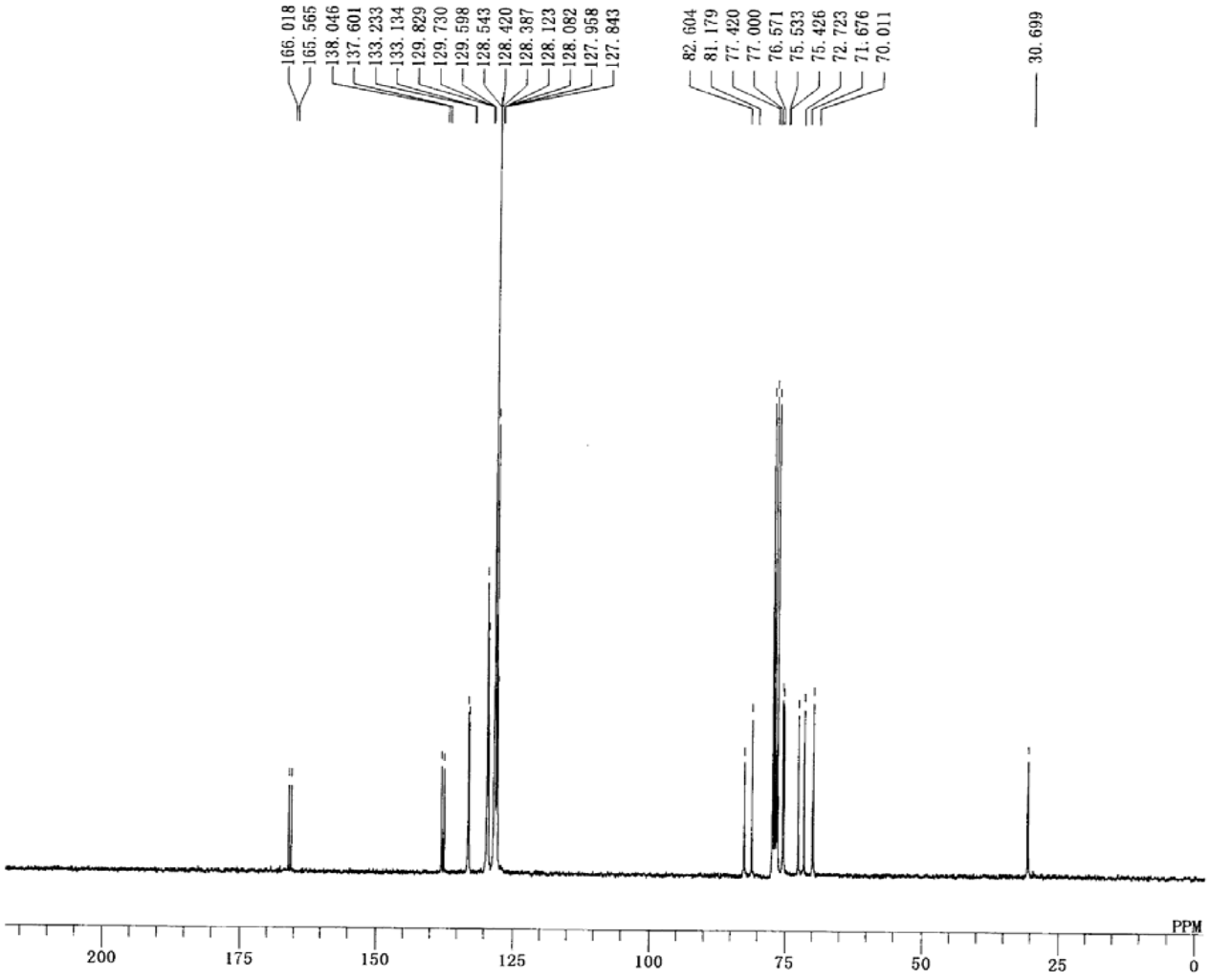




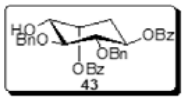
DFILE D:\叶新山\PLJ061222-C.als
OBNUC 13C
EXMOD BCM
OFR 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 736
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRN
CTEMP 19.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 25

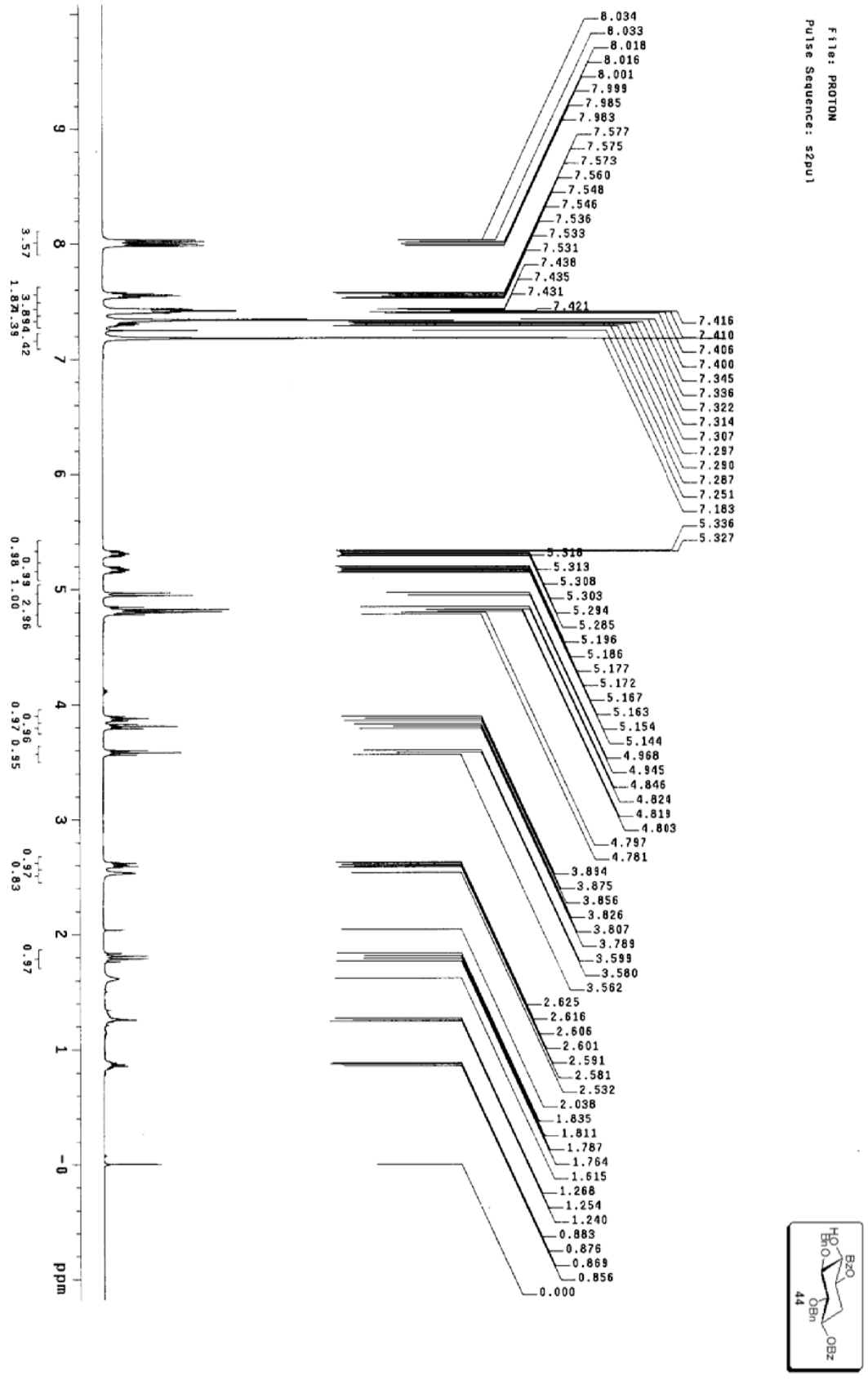


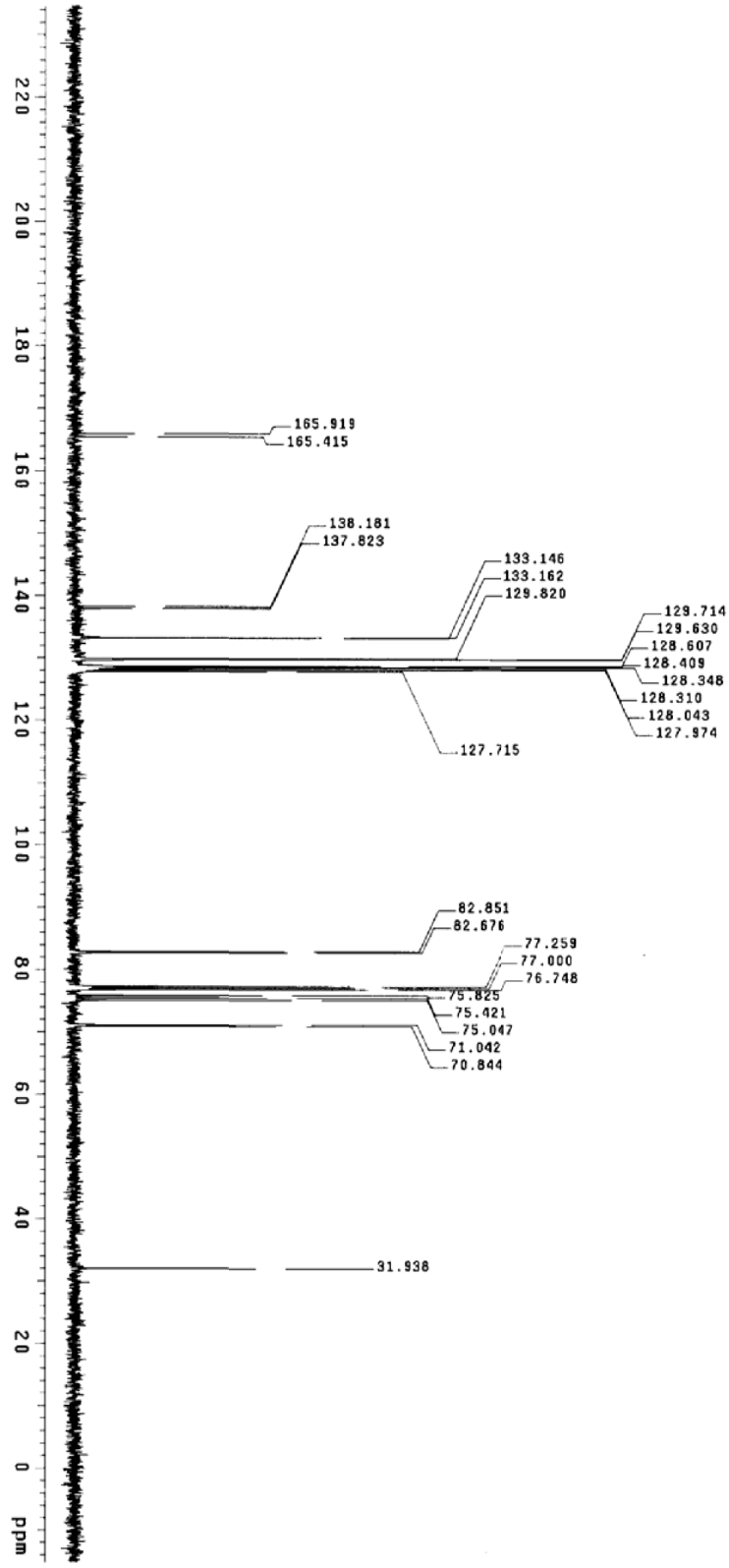

pljo70227
File: PROTON
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"
Relax. delay 4.000 sec
Pulse 78.8 degrees
Acq. time 1.882 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9019086 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 34 sec
8.061
8.059
8.048
8.044
8.042
8.009
8.007
7.996
7.993
7.990
7.579
7.575
7.573
7.564
7.561
7.558
7.549
7.474
7.458
7.443
7.434
7.417
7.402
7.354
7.341
7.338
7.322
7.318
7.311
7.307
7.301
7.297
7.283
7.242
7.201
7.192
5.631
5.626
5.622
4.951
4.929
4.854
4.833
4.812
4.791
4.789
3.958
3.941
3.924
3.918
3.844
3.827
2.539
2.510
0.000
1.94
2.08
3.56
1.81
3.96
6.76
0.84
1.07
1.02
2.89
1.96
1.00
0.66
1.23
0.88
ppm
HO
BnO
OBz
OBn
OBz
43

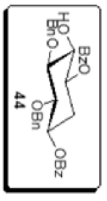


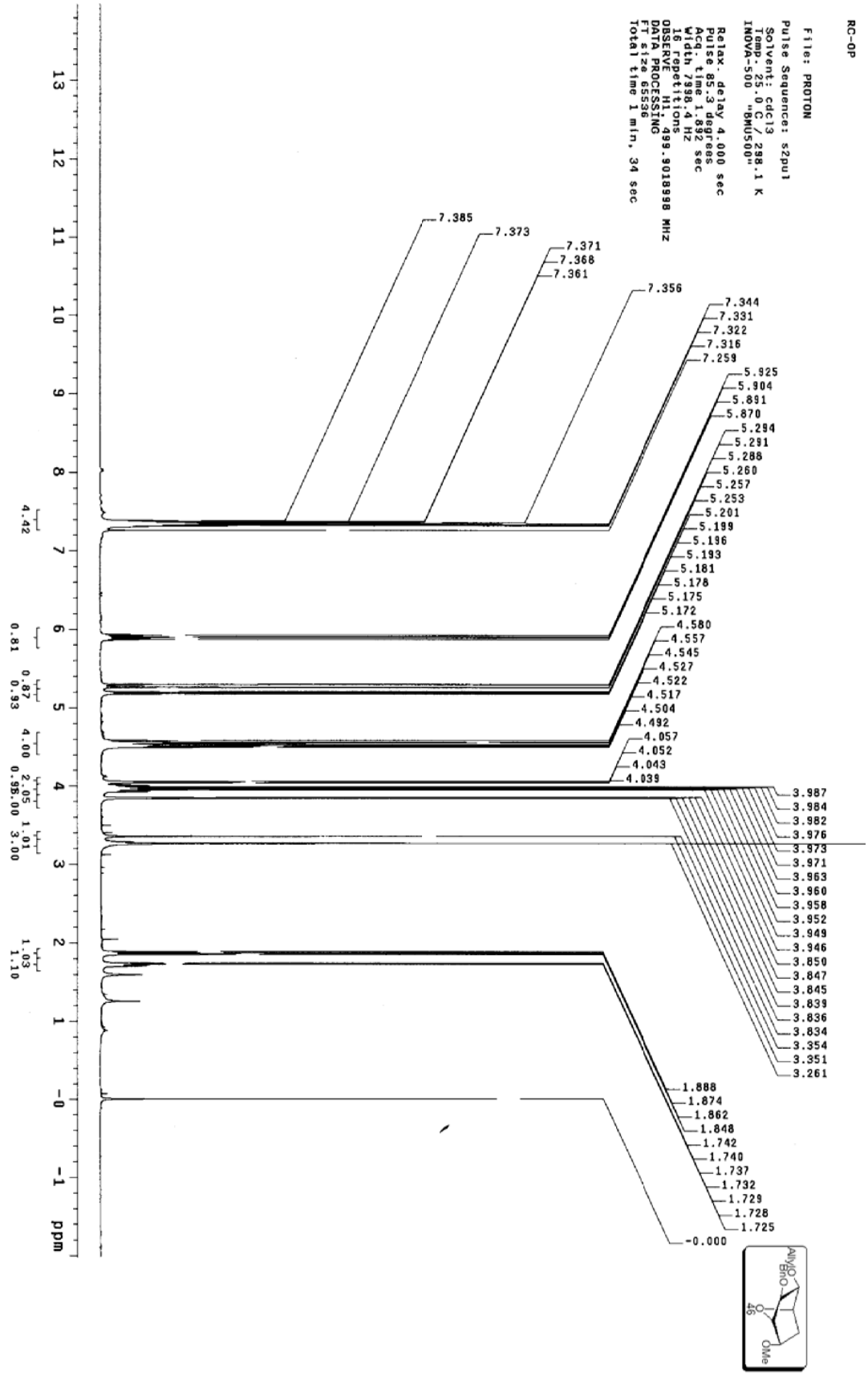
DFILE	D:\叶新山\plj070227-C.als	
OBNUC	13C	
EXMOD	BCM	
OFR	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	4404	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRN		
CTEMP	20.9	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	25	

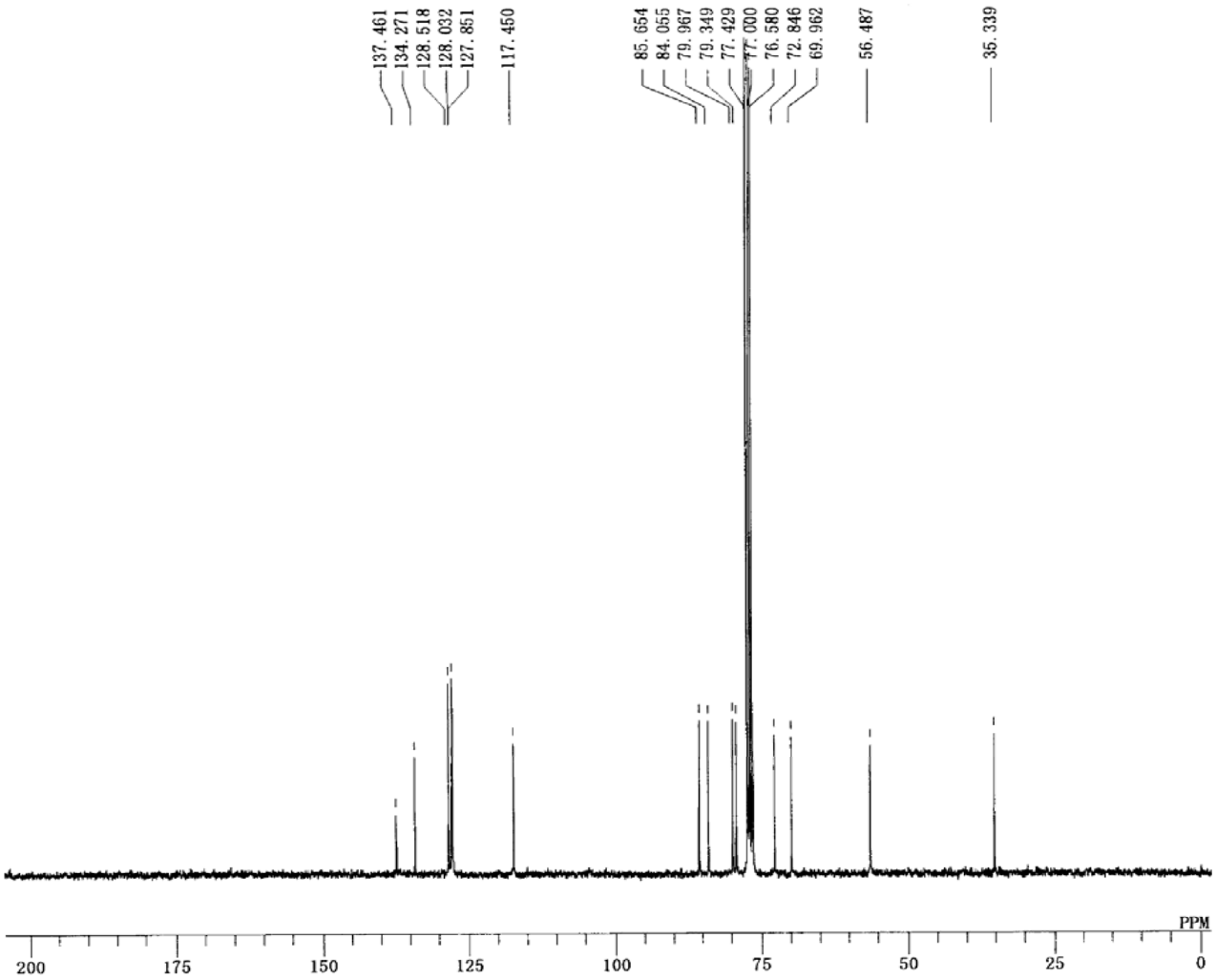



pljo70829
File: PROTON
Pulse Sequence: s2pul
8.034
8.033
8.018
8.016
8.001
7.999
7.985
7.983
7.577
7.575
7.573
7.560
7.548
7.546
7.536
7.533
7.531
7.438
7.435
7.431
7.421
7.416
7.410
7.406
7.400
7.345
7.336
7.322
7.314
7.307
7.297
7.290
7.287
7.251
7.183
5.336
5.327
5.318
5.313
5.308
5.303
5.294
5.285
5.196
5.186
5.177
5.172
5.167
5.163
5.154
5.144
4.968
4.945
4.846
4.824
4.819
4.803
4.797
4.781
3.894
3.875
3.856
3.826
3.807
3.789
3.599
3.580
3.562
2.625
2.616
2.606
2.601
2.591
2.581
2.532
2.038
1.835
1.811
1.787
1.764
1.615
1.268
1.254
1.240
0.883
0.876
0.869
0.856
0.000
3.57
1.87
3.89
4.42
1.39
0.98
1.00
0.99
2.96
0.97
0.95
0.96
0.97
0.83
0.97
ppm
BzO
HO
BnO
OBn
OBz
44

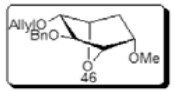

165.919
165.415
138.181
137.823
133.146
133.162
129.820
129.714
129.630
128.607
128.409
128.348
128.310
128.043
127.974
127.715
82.851
82.676
77.259
77.000
76.748
75.825
75.421
75.047
71.042
70.844
31.938
220
200
180
160
140
120
100
80
60
40
20
0
ppm


HO
BnO
BzO
44
OBn
OBz


RC-OP
File: PROTON
Pulse Sequence: s2pul
Solvent: cdcl3
Temp: 25.0 C / 298.1 K
INOVA-500 "BMUS00"
Relax. delay 4.000 sec
Pulse 85.3 degrees
Acq. time 1.892 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9018998 MHZ
DATA PROCESSING
FT size 65536
Total time 1 min, 34 sec
7.385
7.373
7.371
7.368
7.361
7.356
7.344
7.331
7.322
7.316
7.259
5.925
5.904
5.891
5.870
5.294
5.291
5.288
5.260
5.257
5.253
5.201
5.199
5.196
5.193
5.181
5.178
5.175
5.172
4.580
4.557
4.545
4.527
4.522
4.517
4.504
4.492
4.057
4.052
4.043
4.039
3.987
3.984
3.982
3.976
3.973
3.971
3.963
3.960
3.958
3.952
3.949
3.946
3.850
3.847
3.845
3.839
3.836
3.834
3.354
3.351
3.261
1.888
1.874
1.862
1.848
1.742
1.740
1.737
1.732
1.729
1.728
1.725
-0.000
4.42
0.81
0.87
0.93
4.00
2.05
0.95
1.01
3.00
1.03
1.10
ppm
ANOMERIC
OMe



DFILE D:\叶新山\PLJRC-OP-C.als
OBNUC 13C
EXMOD BCM
OFR 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 2696
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRN
CTEMP 20.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24



Current Data Parameters

NAME	plj051017-1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

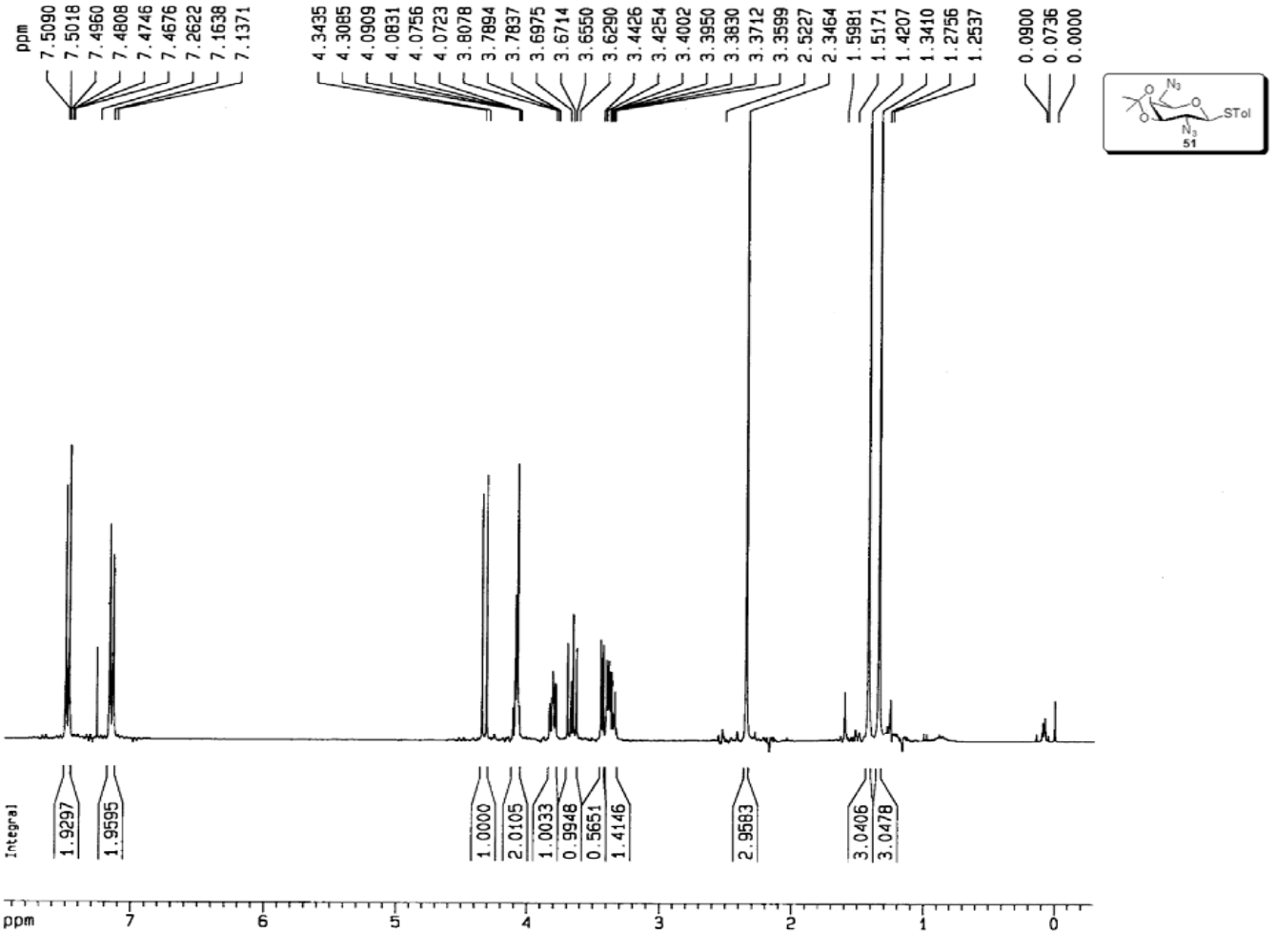
Date_	930908
Time	20.37
INSTRUM	spect
PROBHD	5 mm Multinu
PULPROG	zg
TD	36034
SOLVENT	CDCl3
NS	8
DS	0
SWH	6024.096 Hz
FIDRES	0.167178 Hz
AQ	2.9908719 sec
RG	1024
DW	83.000 usec
DE	118.57 usec
TE	300.0 K
D1	1.00000000 sec
P1	7.00 usec
SFO1	300.5805000 MHz
NUCLEUS	1H

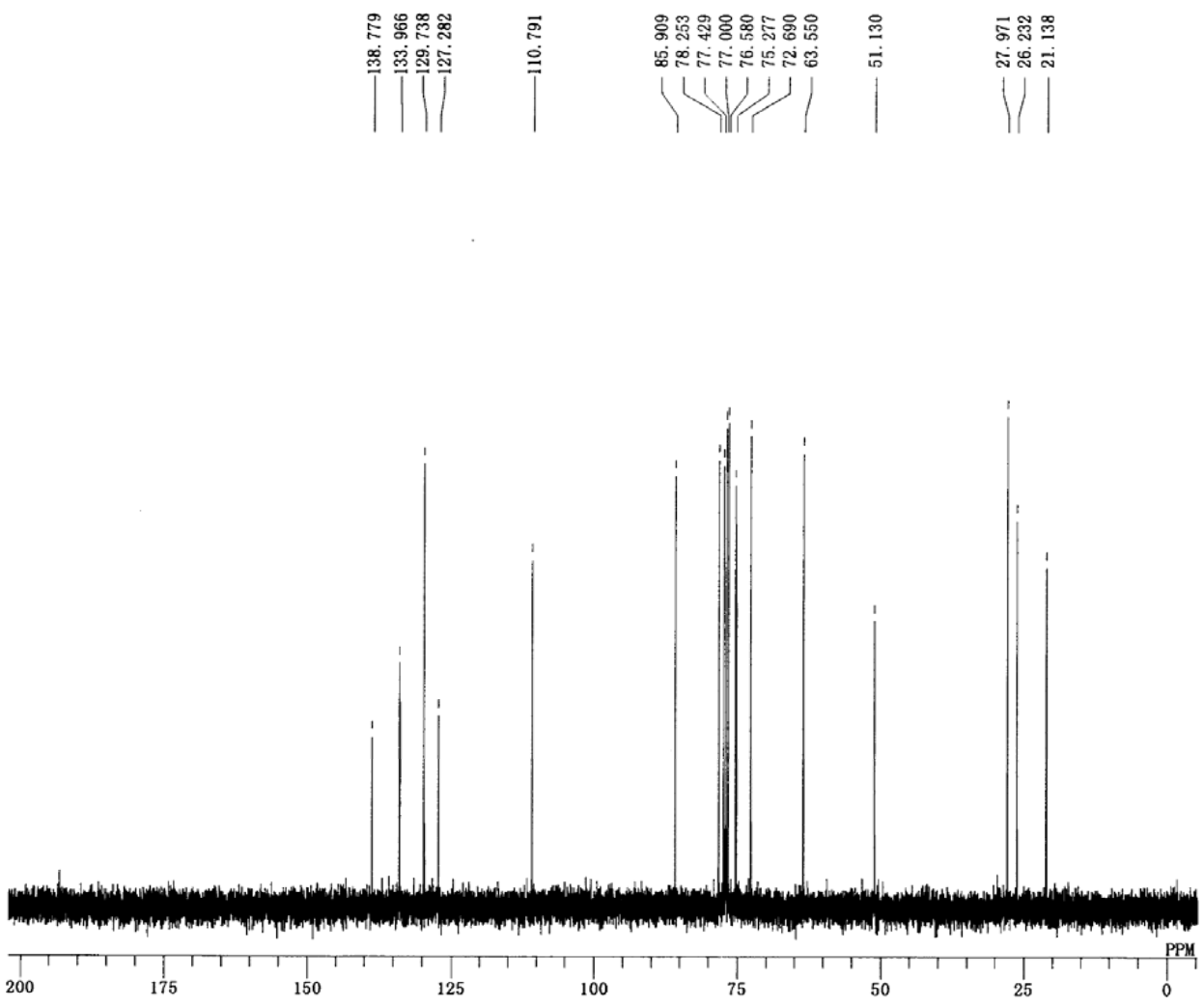
F2 - Processing parameters

SI	16384
SF	300.5790105 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

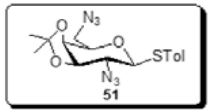
1D NMR plot parameters

CX	18.00 cm
F1P	7.963 ppm
F1	2393.41 Hz
F2P	-0.300 ppm
F2	-90.05 Hz
PPMCM	0.45901 ppm/cm
HZCM	137.96967 Hz/cm

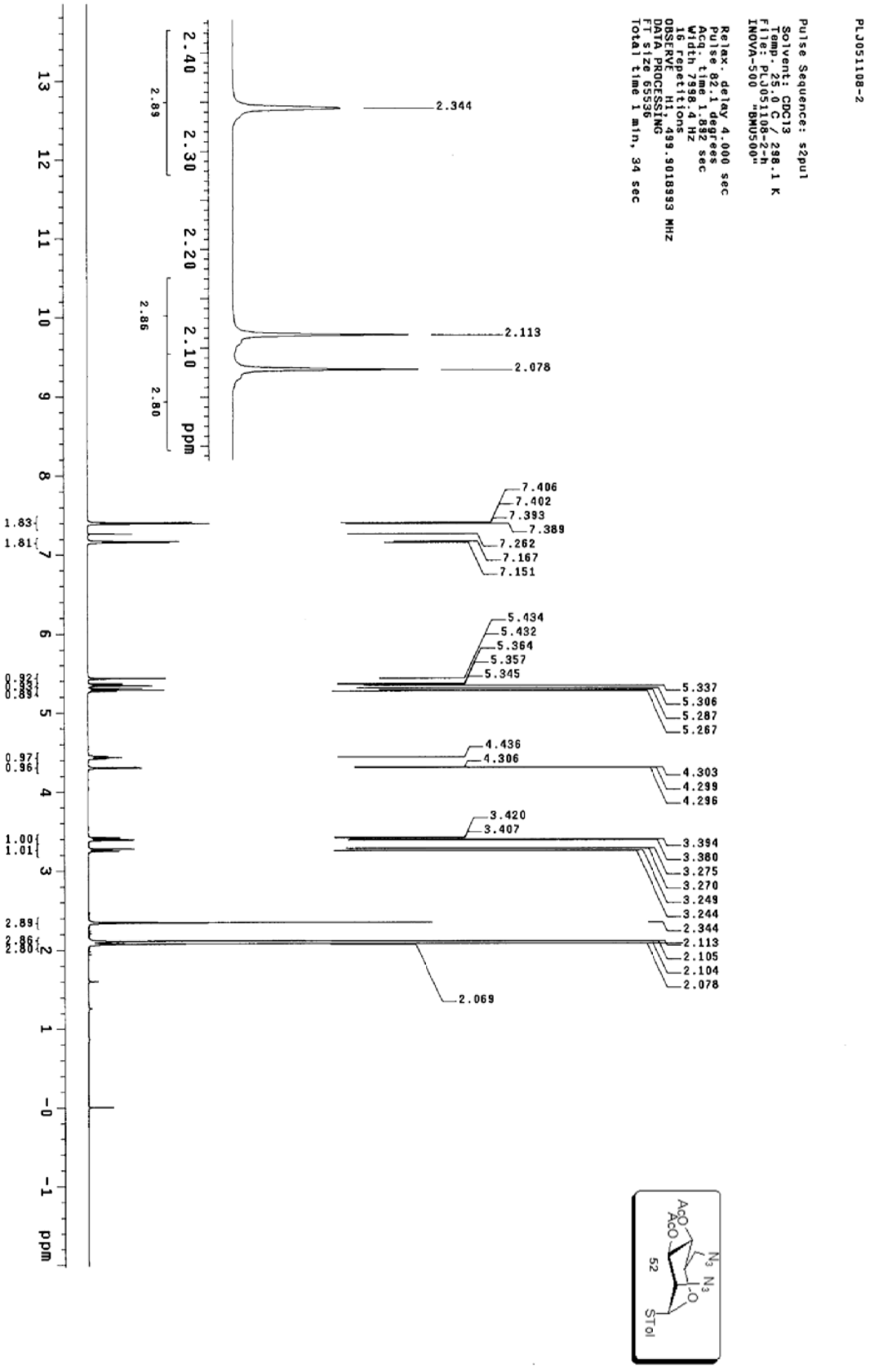


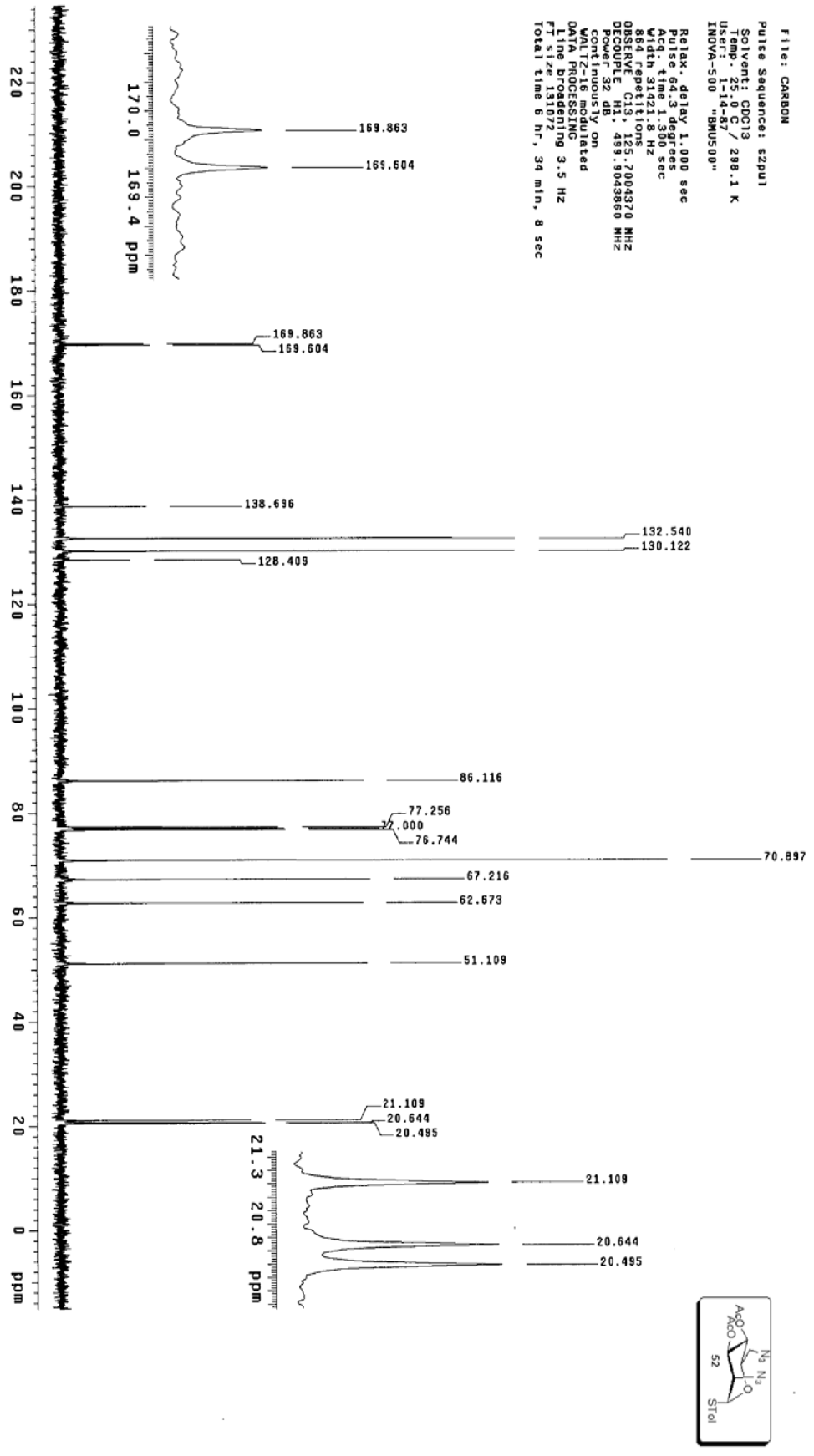


DFILE D:\yexinshan\plj051017-B1-C.als
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 235
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRATN 511
CTEMP 22.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24



51

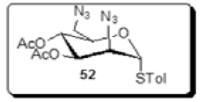

PLJ051108-2
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
File: PLJ051108-2-h
INOVA-500 "BMU500"
Relax. delay 4.000 sec
Pulse 90.1 degrees
Acq. time 1.882 sec
Width 7998.4 HZ
16 repetitions
OBSERVE H1, 499.9018993 MHZ
DATA PROCESSING
FT size 65536
Total time 1 min, 34 sec
2.344
2.113
2.078
7.406
7.402
7.393
7.389
7.262
7.167
7.151
5.434
5.432
5.364
5.357
5.345
5.337
5.306
5.287
5.267
4.436
4.306
4.303
4.299
4.296
3.420
3.407
3.394
3.380
3.275
3.270
3.249
3.244
2.344
2.113
2.105
2.104
2.078
2.069
1.83
1.81
0.92
0.97
0.96
1.00
1.01
2.89
2.86
2.80
2.89
2.86
2.80
AcO
AcO
52
N3
N3
O
STol
ppm
ppm

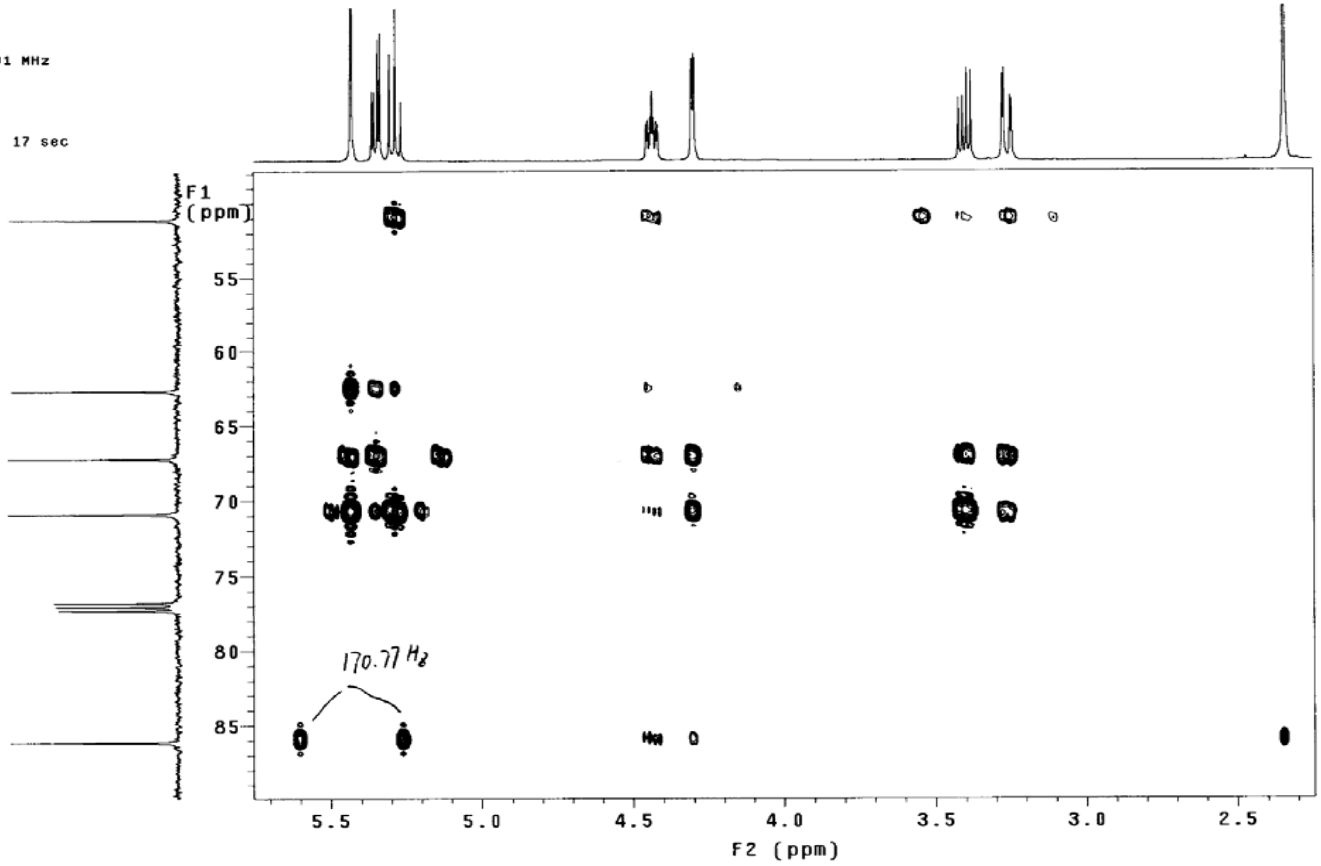

PLJ051108-2
File: CARBON
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
User: l-14-87
INOVA-500 "BMU500"
Relax. delay 1.000 sec
Pulse 64.3 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
864 repetitions
OBSERVE C13, 125.7004370 MHz
DECOUPLE H1, 499.9043860 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
FT size 131072
Line broadening 3.5 Hz
Total time 6 hr, 34 min, 8 sec
170.0 169.4 ppm
169.863
169.604
21.3 20.8 ppm
21.109
20.644
20.495
138.636
132.540
130.122
128.409
86.116
77.256
77.000
76.744
70.897
67.216
62.673
51.109
21.109
20.644
20.495
220 200 180 160 140 120 100 80 60 40 20 0 ppm
AcO
AcO
O
N3
N3
52
STol

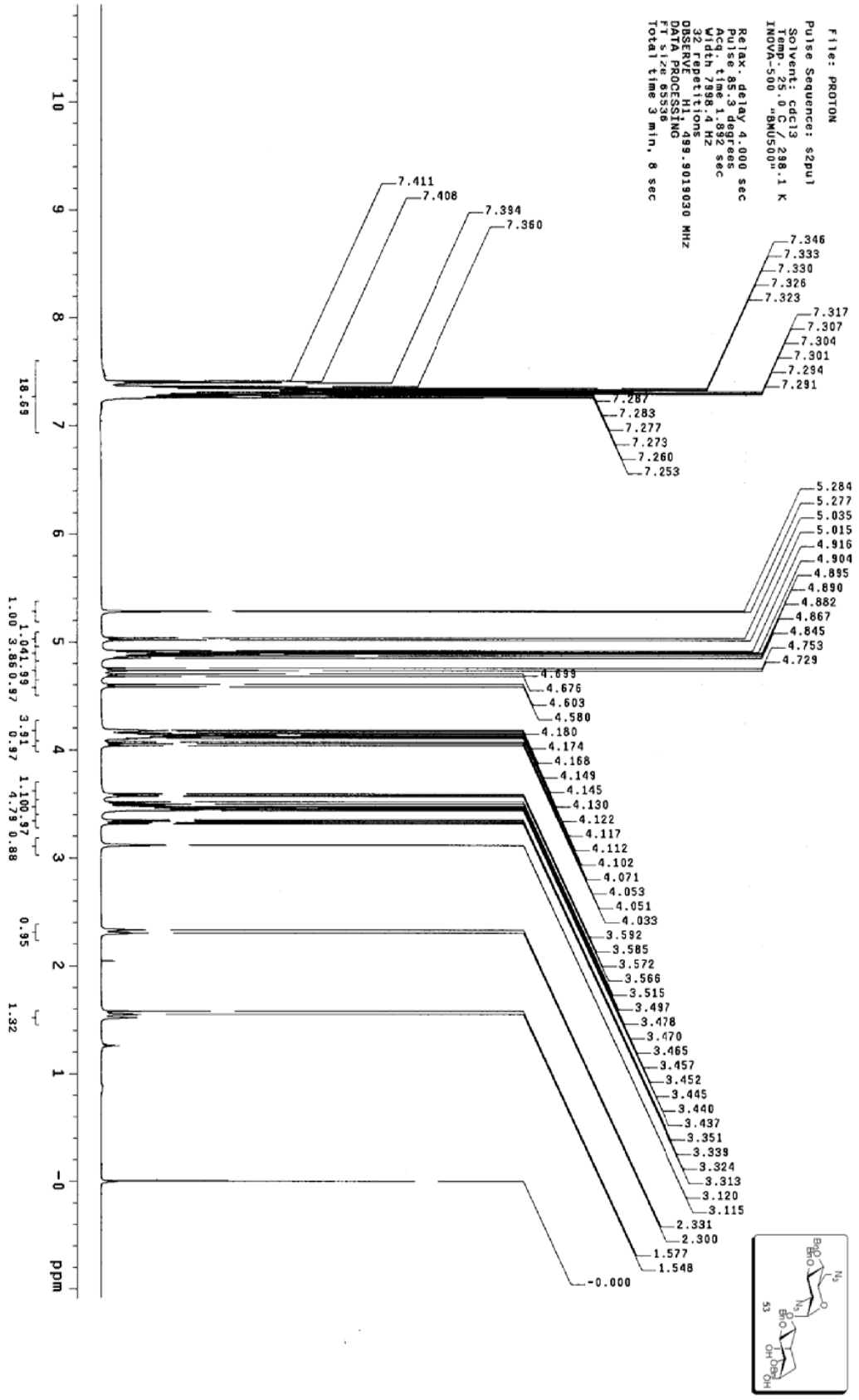
PLJ051108-2

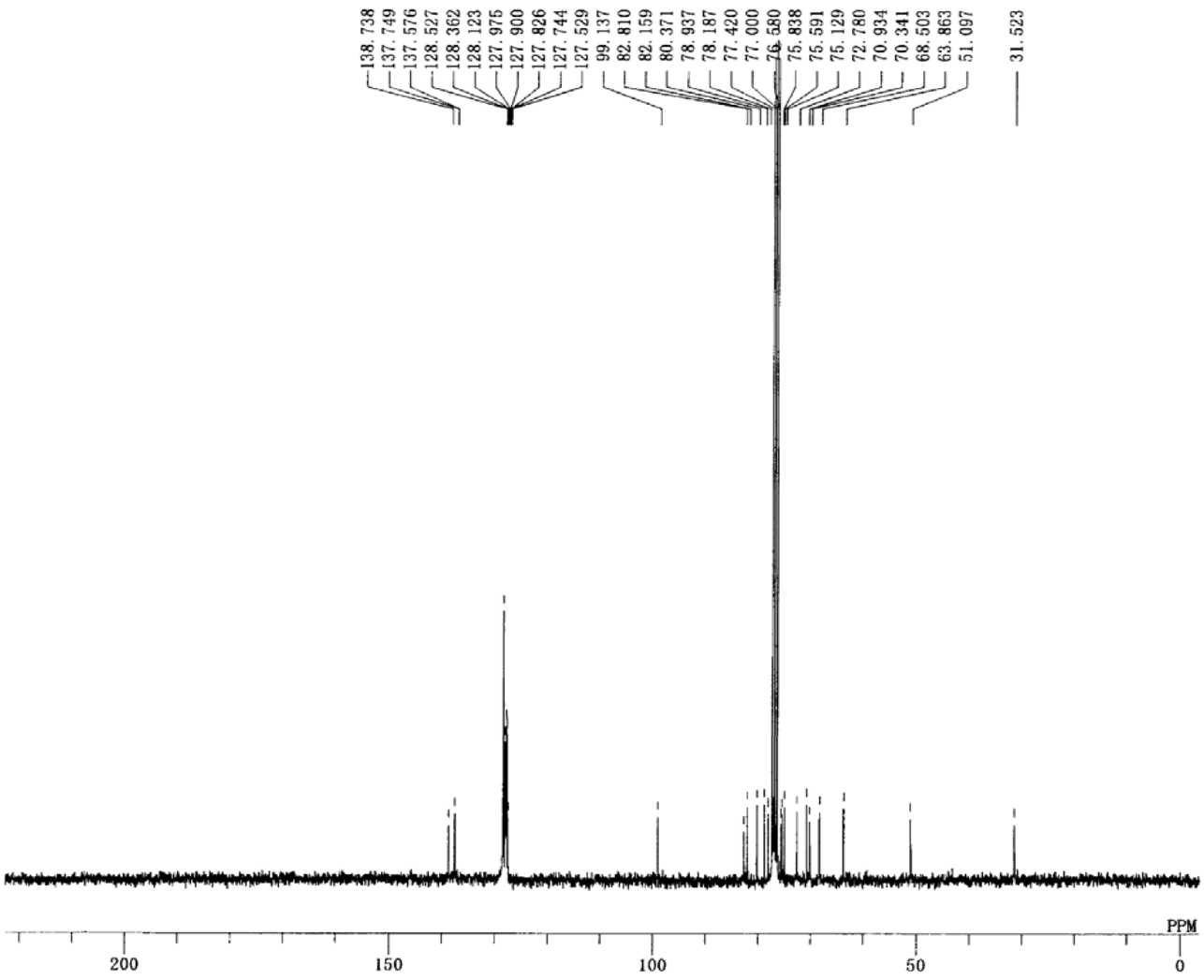
Pulse Sequence: gHMBC
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: PLJ051108-2-bc
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.219 sec
Width 4675.1 Hz
2D Width 25220.7 Hz
16 repetitions
400 increments
OBSERVE H1, 499.9018991 MHz
DATA PROCESSING
Sine bell 0.110 sec
F1 DATA PROCESSING
Sine bell 0.008 sec
FT size 2048 x 8192
Total time 2 hr, 20 min, 17 sec

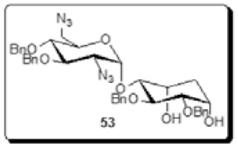


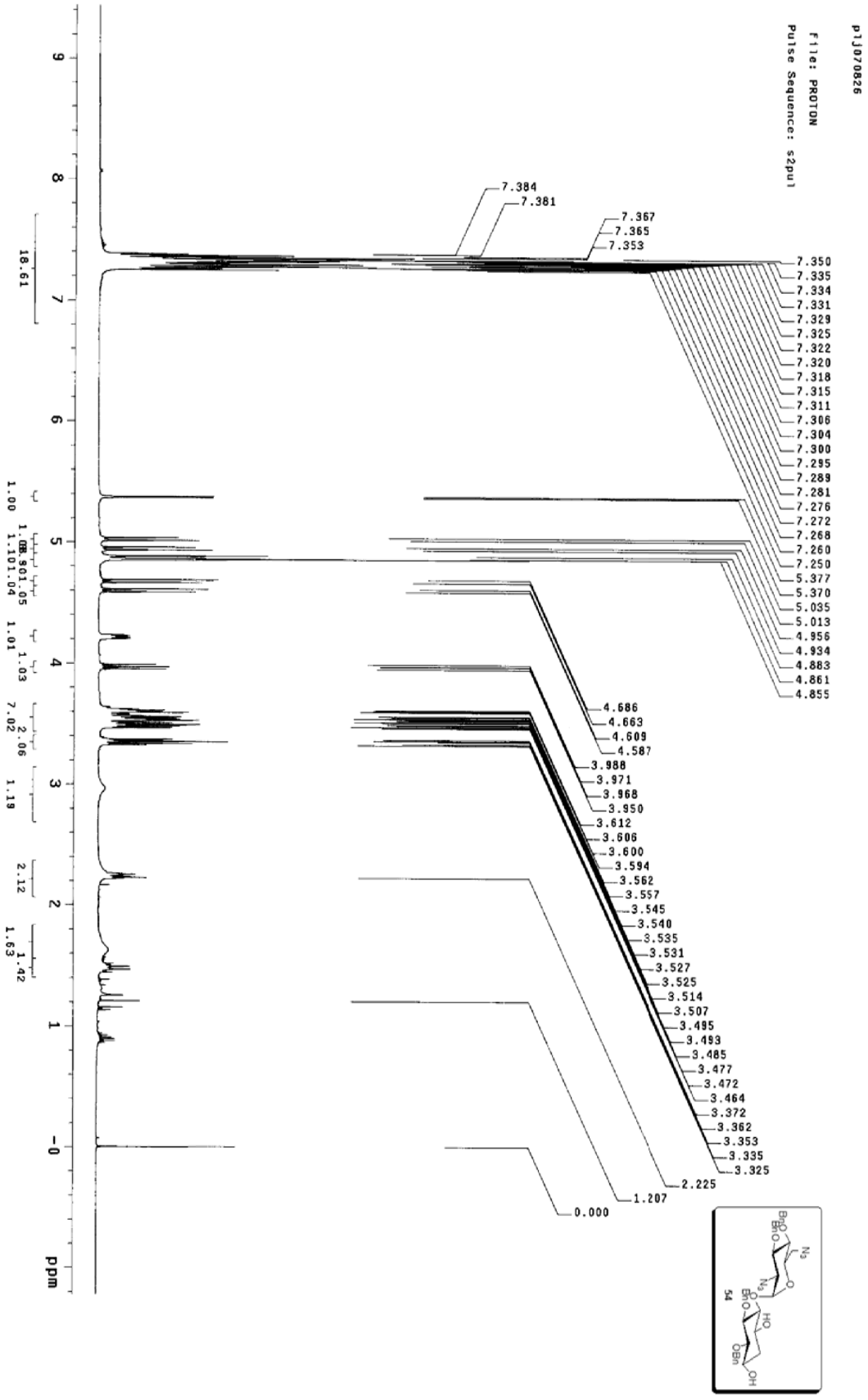


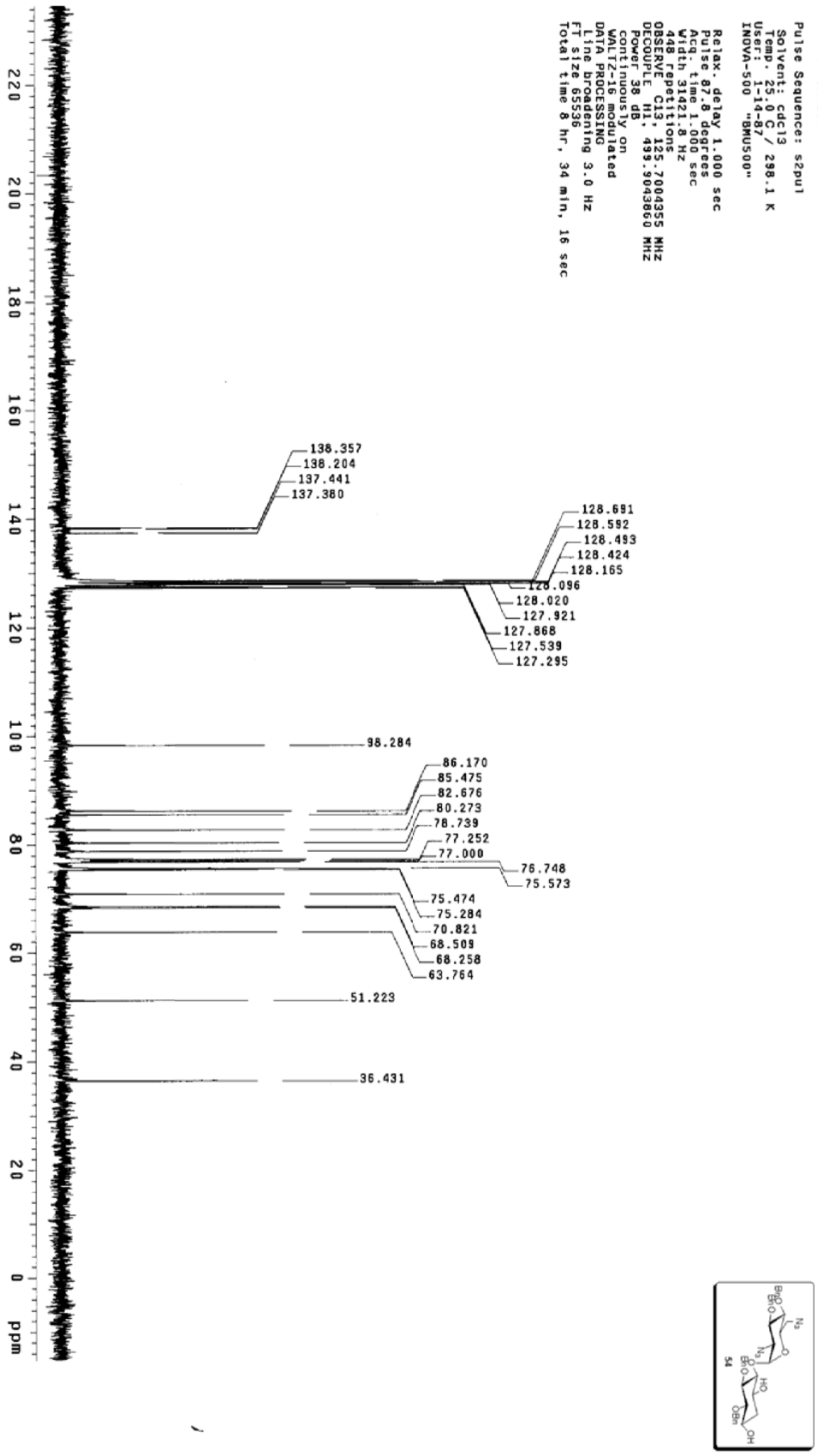

plj061213-68B
File: PROTON
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"
Relax. delay 4.000 sec
Pulse 85.3 degrees
Acq. time 1.892 sec
Width 7998.4 Hz
32 repetitions
OBSERVE H1, 499.9019030 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 8 sec
7.411
7.408
7.394
7.360
7.346
7.333
7.330
7.326
7.323
7.317
7.307
7.304
7.301
7.294
7.291
7.287
7.283
7.277
7.273
7.260
7.253
5.284
5.277
5.035
5.015
4.916
4.904
4.895
4.890
4.882
4.867
4.845
4.753
4.729
4.699
4.676
4.603
4.580
4.180
4.174
4.168
4.149
4.145
4.130
4.122
4.117
4.112
4.102
4.071
4.053
4.051
4.033
3.592
3.585
3.572
3.566
3.515
3.497
3.478
3.470
3.465
3.457
3.452
3.445
3.440
3.437
3.351
3.339
3.324
3.313
3.120
3.115
2.331
2.300
1.577
1.548
-0.000
18.69
1.00
3.86
1.041.99
0.97
3.91
0.97
1.100.97
4.79
0.88
0.95
1.32
ppm

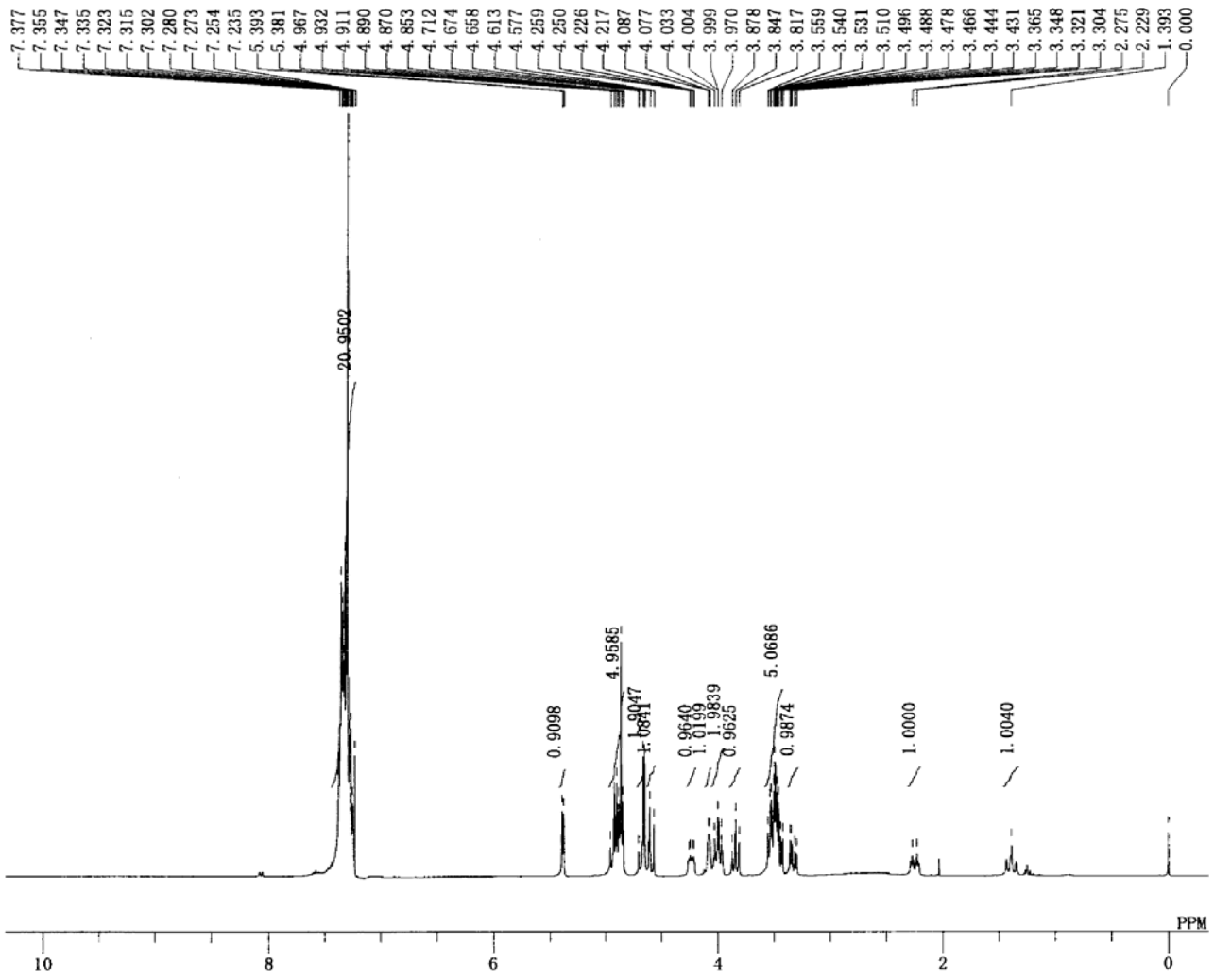


DFILE D:\叶新山\PLJ061213-68B-C.als
COMNT
DATIM Fri Dec 22 19:13:57 2006
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 1216
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRNUC 1H
CTEMP 20.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 25

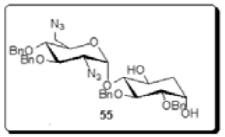


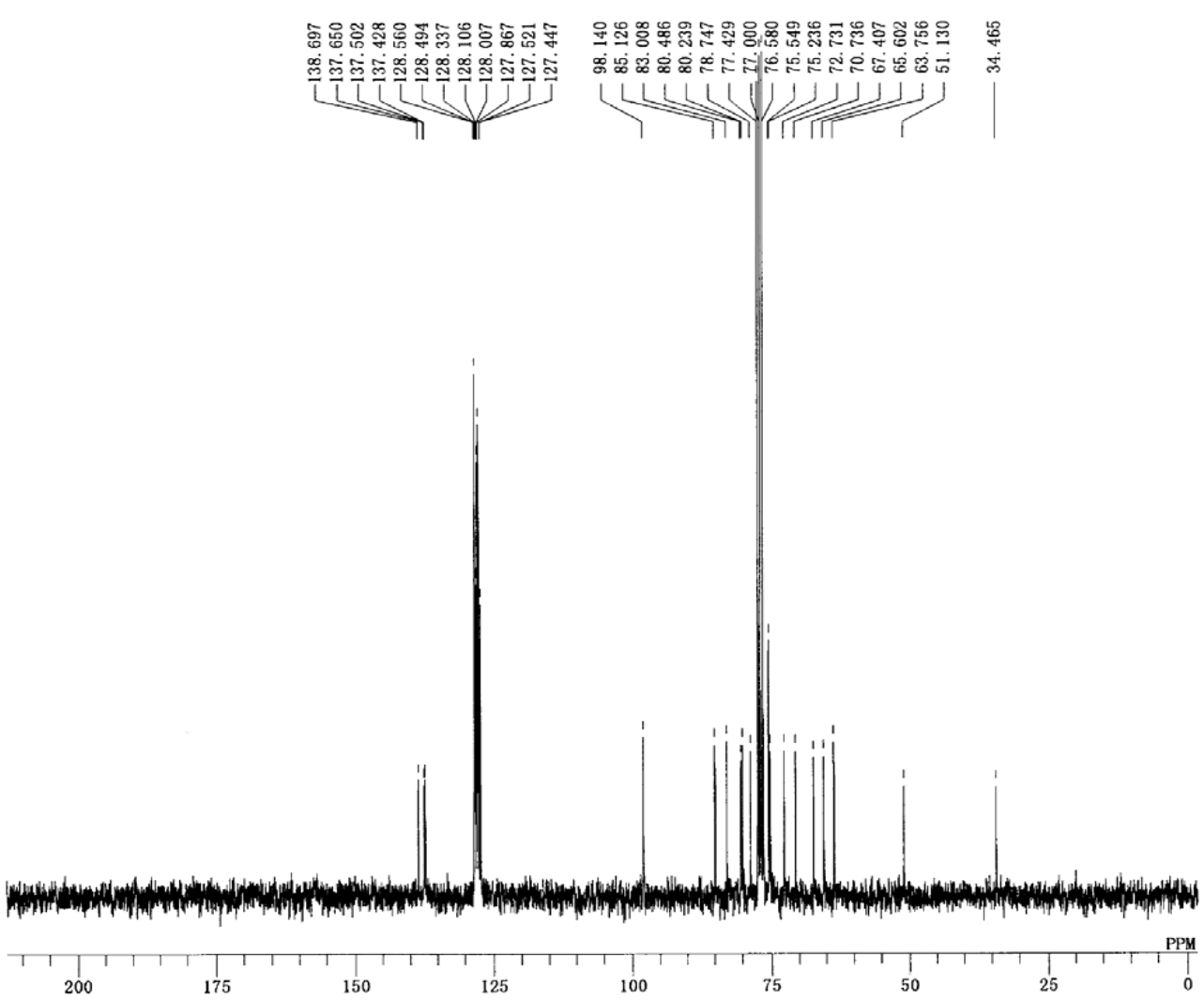

plj070826
File: PROTON
Pulse Sequence: s2pul
7.384
7.381
7.367
7.365
7.353
7.350
7.335
7.334
7.331
7.329
7.325
7.322
7.320
7.318
7.315
7.311
7.306
7.304
7.300
7.295
7.289
7.281
7.276
7.272
7.268
7.260
7.250
5.377
5.370
5.035
5.013
4.956
4.934
4.883
4.861
4.855
4.686
4.663
4.609
4.587
3.988
3.971
3.968
3.950
3.612
3.606
3.600
3.594
3.562
3.557
3.545
3.540
3.535
3.531
3.527
3.525
3.514
3.507
3.495
3.493
3.485
3.477
3.472
3.464
3.372
3.362
3.353
3.335
3.325
2.225
1.207
0.000
18.61
1.00
1.08
8.60
1.05
1.10
1.04
1.01
1.03
7.02
2.06
1.19
2.12
1.63
1.42
ppm
54


pljo70826
File: CARBON
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"
Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
448 repetitions
OBSERVE C13, 125.7004355 MHz
DECOUPLE H1, 499.9043860 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 8 hr, 34 min, 16 sec
138.357
138.204
137.441
137.380
128.691
128.592
128.493
128.424
128.165
128.096
128.020
127.921
127.868
127.539
127.295
98.284
86.170
85.475
82.676
80.273
78.739
77.252
77.000
76.748
75.573
75.474
75.284
70.821
68.509
68.258
63.764
51.223
36.431
220
200
180
160
140
120
100
80
60
40
20
0
ppm
54

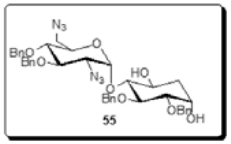


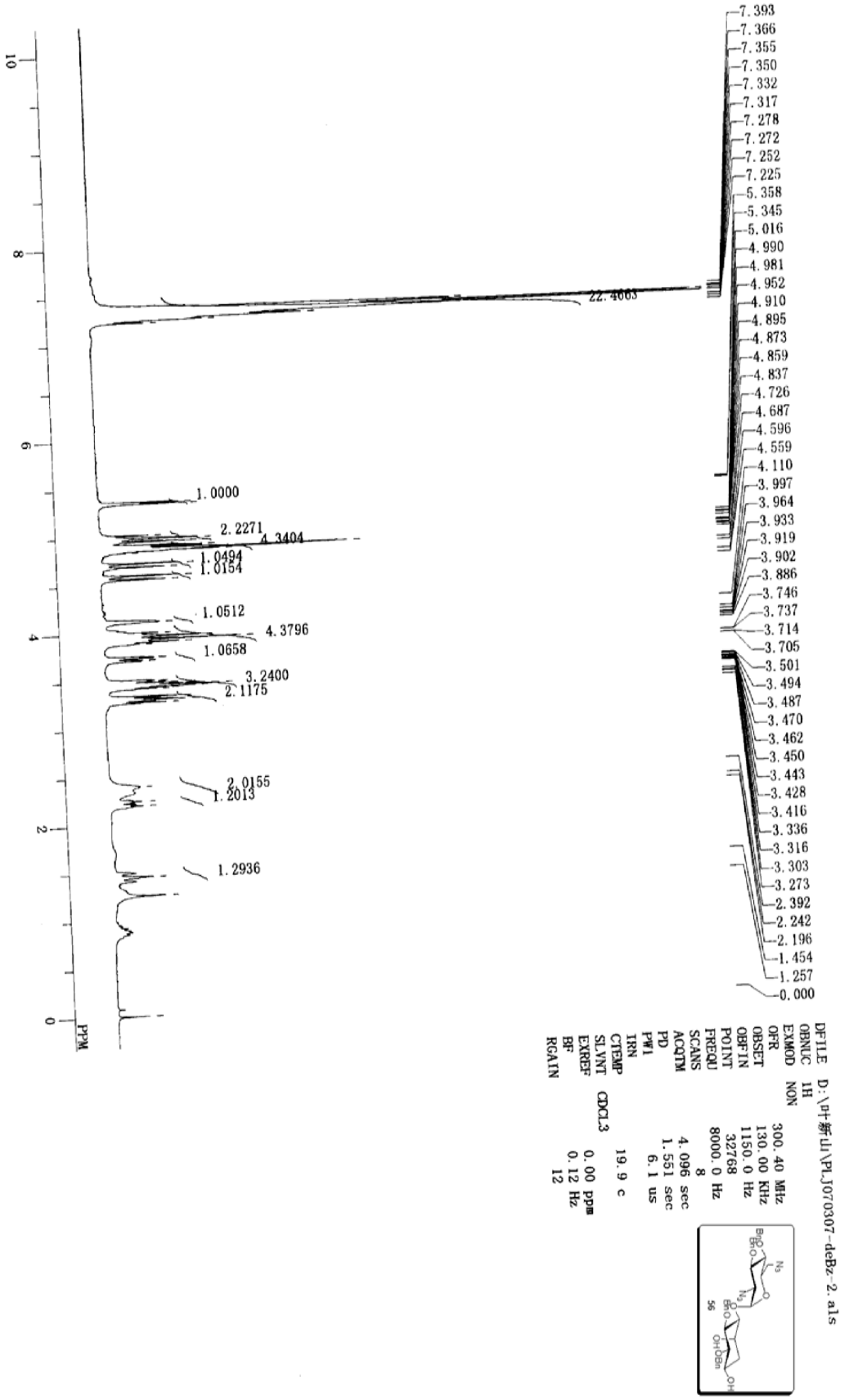
DFILE D:\叶新山\PLJ070110-dd.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRN
CTEMP 20.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12

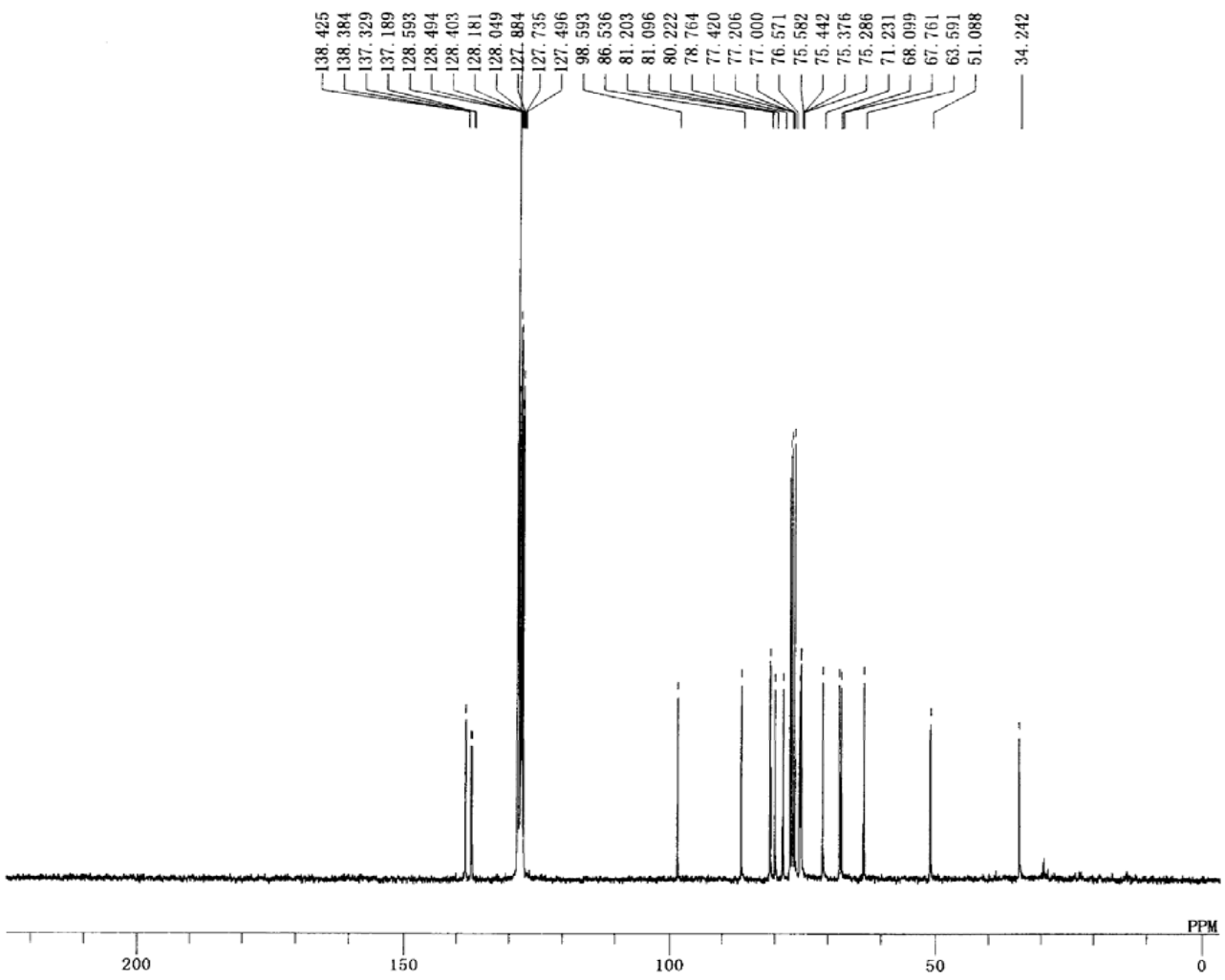




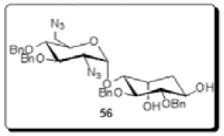
DFILE	D:\叶新山\PLJ-Pang5-C.als	
OBNUC	13C	
EXMOD	BCM	
OFR	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	232	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRN		
CTEMP	21.0	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	24	

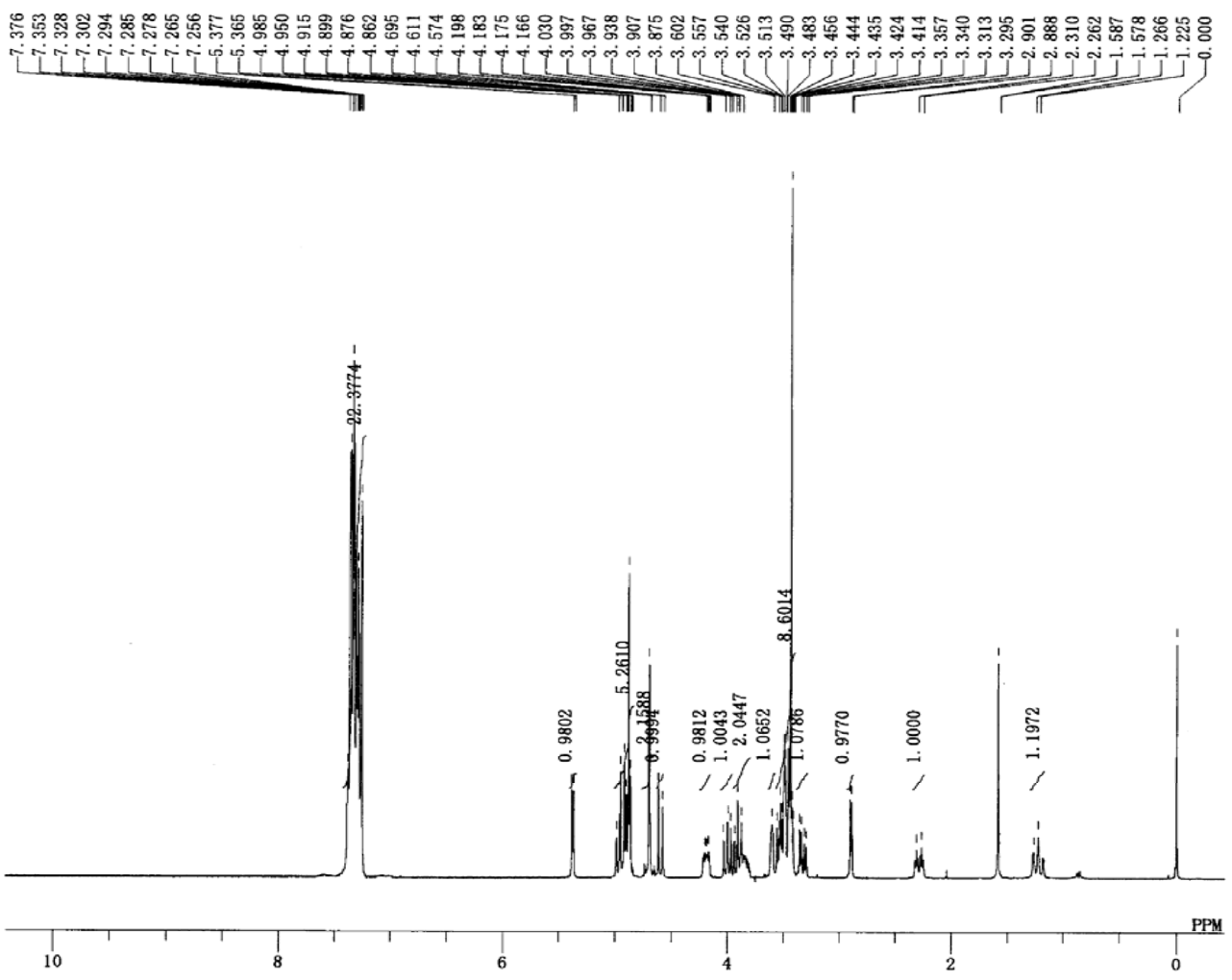



7.393
7.366
7.355
7.350
7.332
7.317
7.278
7.272
7.252
7.225
5.358
5.345
5.016
4.990
4.981
4.952
4.910
4.895
4.873
4.859
4.837
4.726
4.687
4.596
4.559
4.110
3.997
3.964
3.933
3.919
3.902
3.886
3.746
3.737
3.714
3.705
3.501
3.494
3.487
3.470
3.462
3.450
3.443
3.428
3.416
3.336
3.316
3.303
3.273
2.392
2.242
2.196
1.454
1.257
0.000
22.4663
1.0000
2.2271
4.3404
1.0494
1.0154
1.0512
4.3796
1.0658
3.2400
2.1175
2.0155
1.2013
1.2936
10
8
6
4
2
0
PPM
DFILE D:\叶新山\PLJ070307-deBz-2.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRN
CTEMP 19.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12

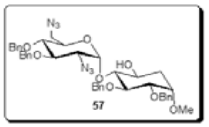


DFILE	D:\叶新山\PLJ070307-deBz-C.als	
OBNUC	13C	
EXMOD	BCM	
OFR	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	1748	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRN		
CTEMP	19.8	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	24	

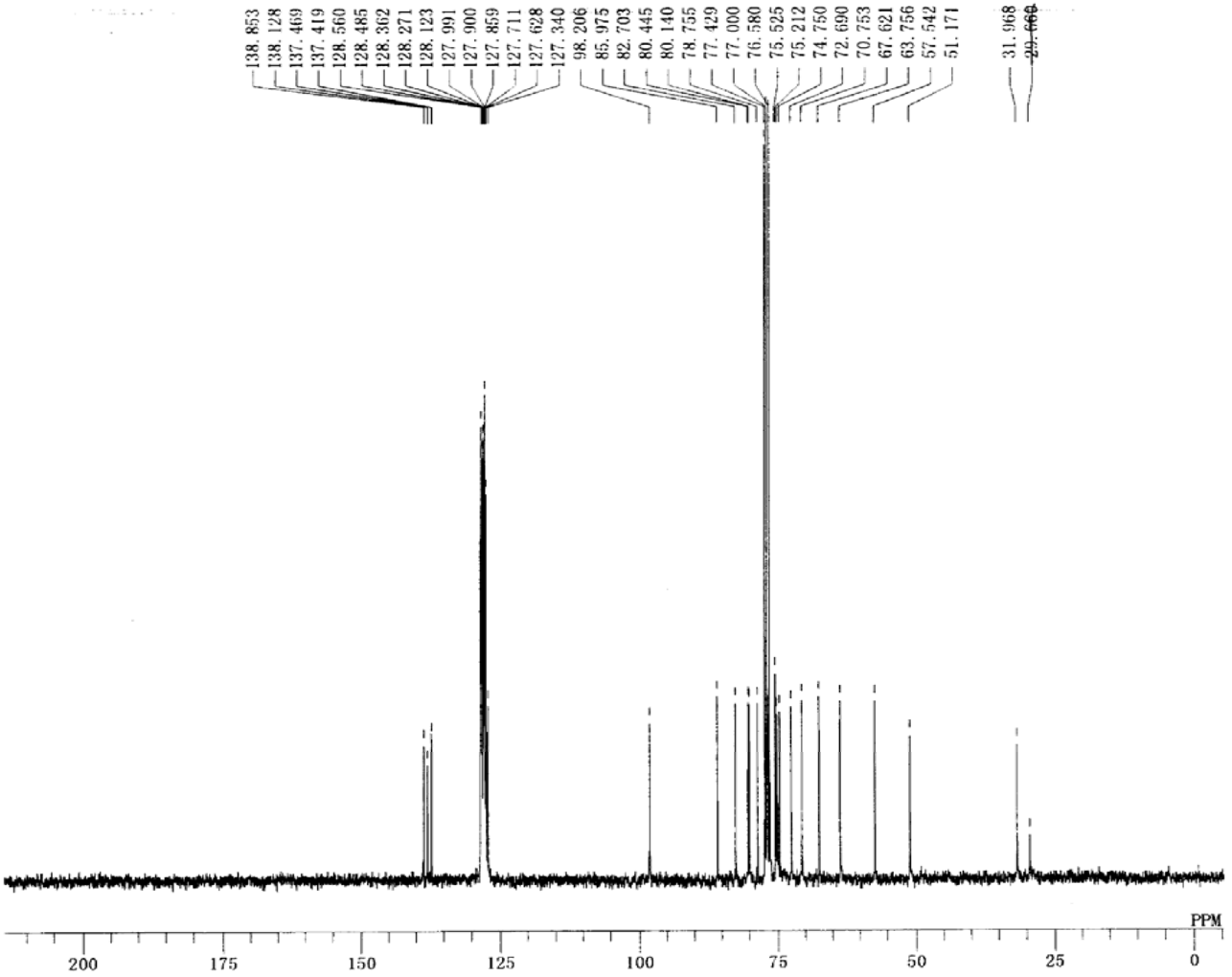




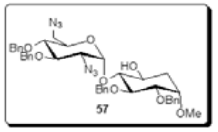
DFILE	D:\叶新山\PLJ070529-2.als	
OBNUC	1H	
EXMOD	NON	
OBFRQ	300.40	MHz
OBSET	130.00	KHz
OBFIN	1150.0	Hz
POINT	32768	
FREQU	8000.0	Hz
SCANS	8	
ACQTM	4.096	sec
PD	1.551	sec
PW1	6.1	us
IRATN	511	
CTEMP	20.3	c
SLVNT	CDCL3	
EXREF	0.00	ppm
BF	0.12	Hz
RGAIN	17	

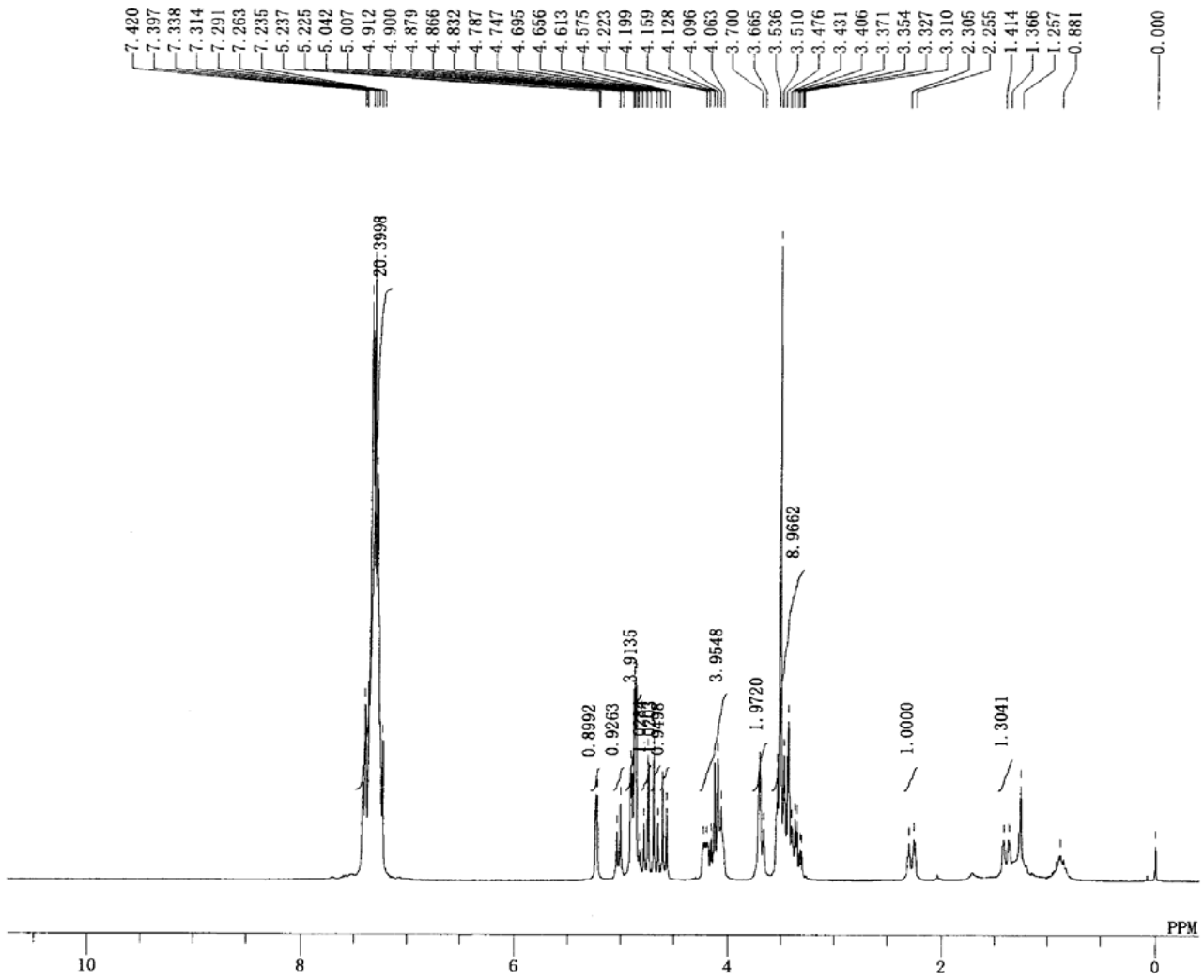


PLJ070529-2-C

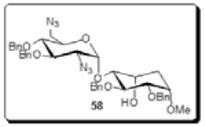


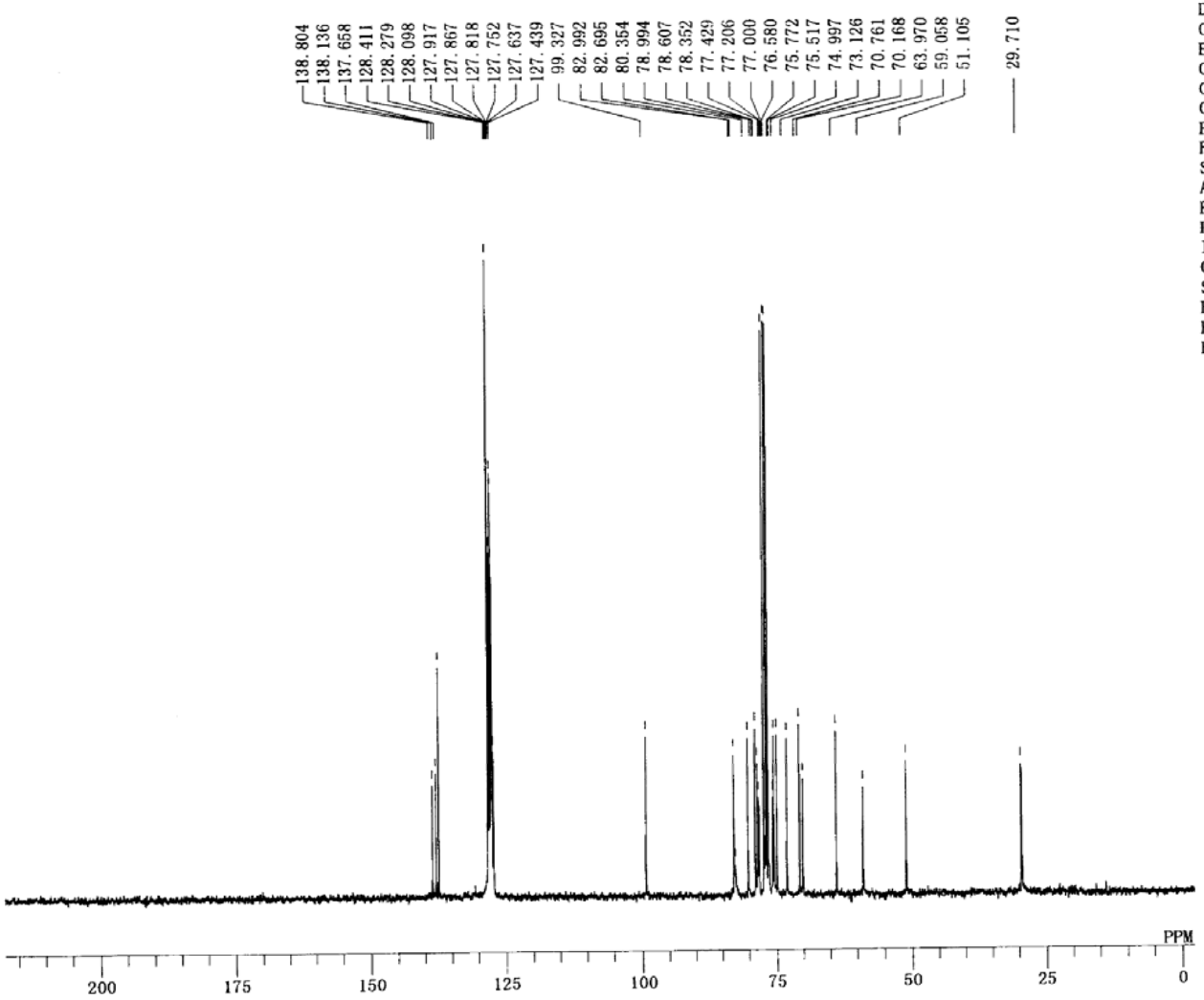
DFILE	D:\叶新山\~~WD070320-pure-C~~.als	
OBNUC	13C	
EXMOD	BCM	
OFR	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	1200	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRN		
CTEMP	19.9	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	24	



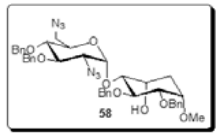


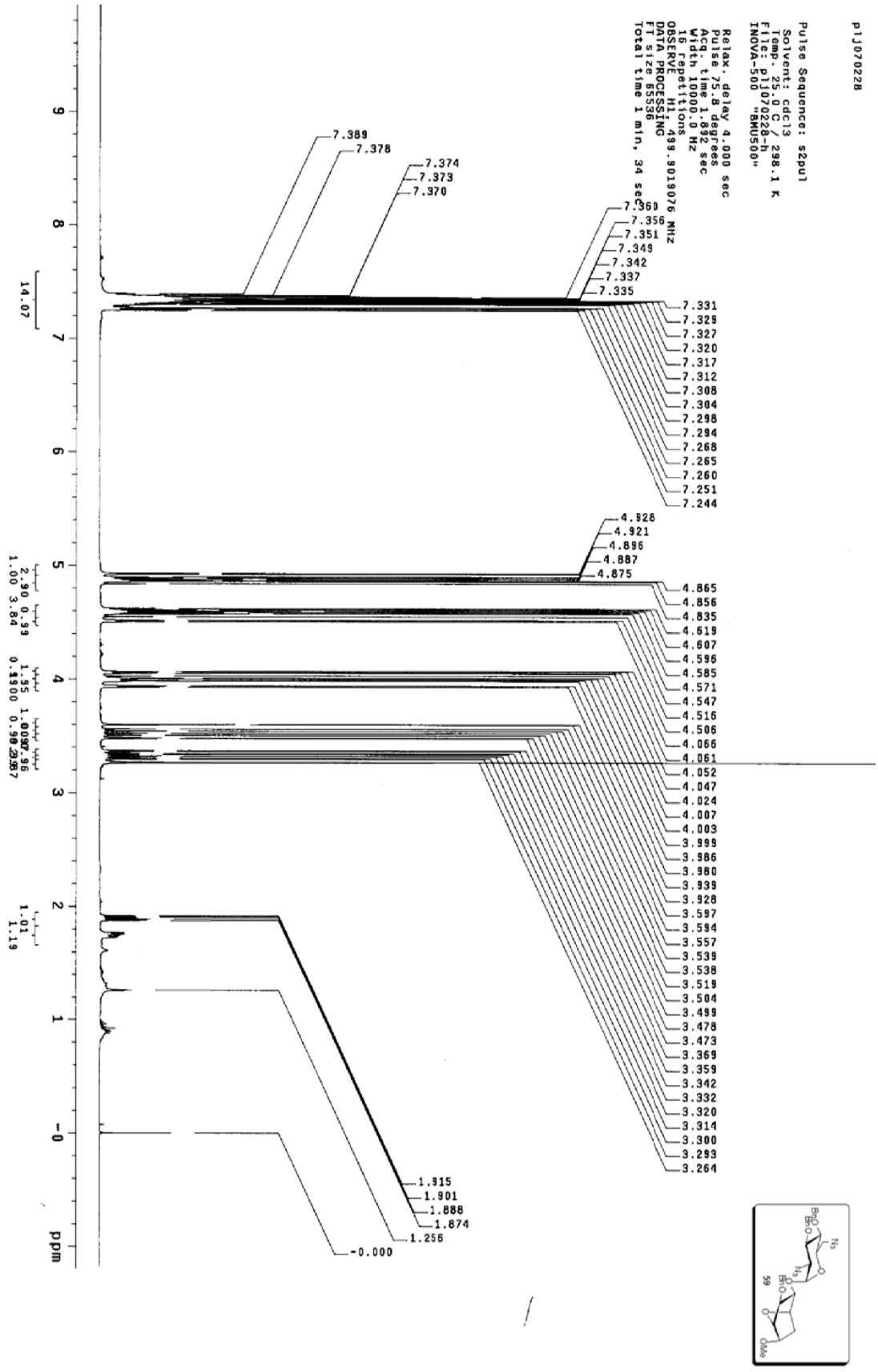
DFILE D:\叶新山\PLJ070305-2-H.als
OBNUC 1H
EXMOD NON
OFR 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRN
CTEMP 20.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12

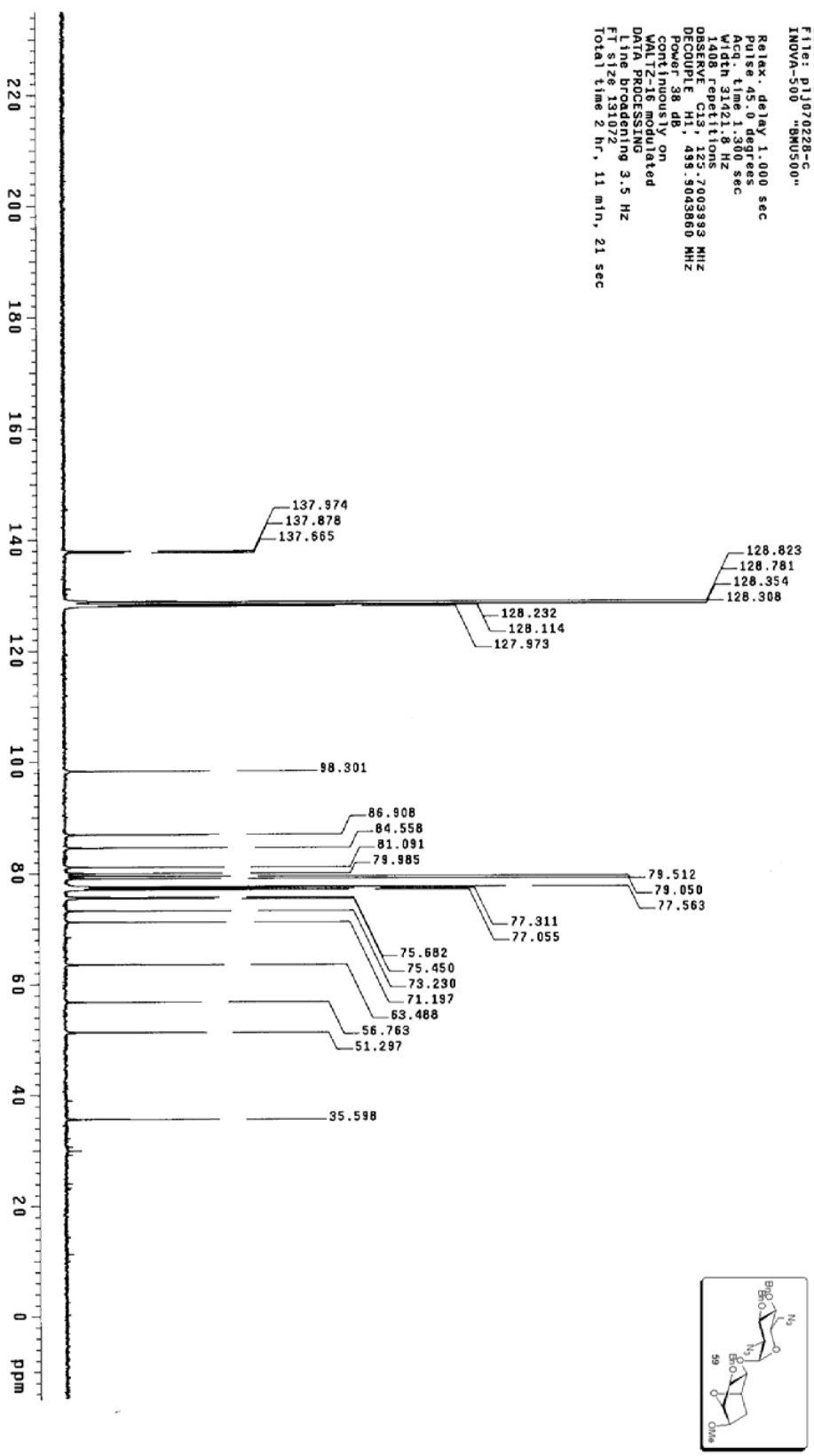




DFILE	D:\叶新山\PLJ070305-2-C.als	
OBNUC	13C	
EXMOD	BCM	
OFR	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	1486	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRN		
CTEMP	19.6	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	24	




plj070228
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
File: plj070228-h
INOVA-500 "BMU500"
Relax. delay 4.000 sec
Pulse 75.8 degrees
Acq. time 1.892 sec
Width 10000.0 Hz
16 repetitions
OBSERVE H1, 499.9019076 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 34 sec
7.389
7.378
7.374
7.373
7.370
7.360
7.356
7.351
7.349
7.342
7.337
7.335
7.331
7.329
7.327
7.320
7.317
7.312
7.308
7.304
7.298
7.294
7.268
7.265
7.260
7.251
7.244
4.928
4.921
4.896
4.887
4.875
4.865
4.856
4.835
4.619
4.607
4.596
4.585
4.571
4.547
4.516
4.506
4.066
4.061
4.052
4.047
4.024
4.007
4.003
3.999
3.986
3.980
3.939
3.928
3.597
3.594
3.557
3.539
3.538
3.519
3.504
3.499
3.478
3.473
3.369
3.359
3.342
3.332
3.320
3.314
3.300
3.293
3.264
1.915
1.901
1.888
1.874
1.256
-0.000
14.07
2.90
0.99
1.00
3.84
1.95
1.00
0.99
0.96
1.01
1.19
ppm

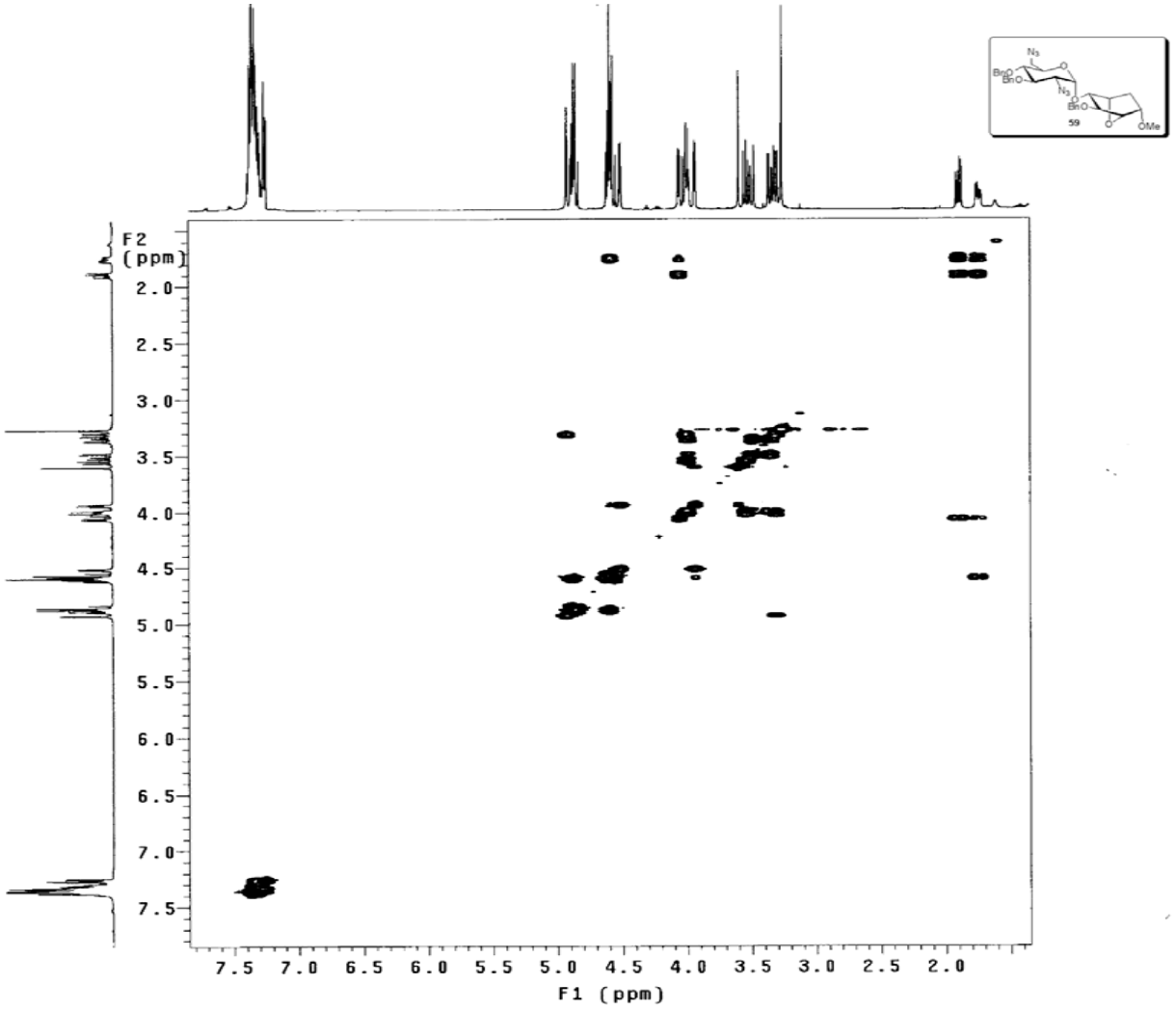

pljo70228
Pulse Sequence: s2pul
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
User: lin-87
File: pljo70228-c
INOVA-500 "BRUS00"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 31421.8 Hz
1408 repetitions
OBSERVE C13, 125.7003993 MHz
DECOUPLE H1, 499.9043860 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.5 Hz
FT size 131072
Total time 2 hr, 11 min, 21 sec
137.974
137.878
137.665
128.823
128.781
128.354
128.308
128.232
128.114
127.973
98.301
86.908
84.558
81.091
79.985
79.512
79.050
77.563
77.311
77.055
75.682
75.450
73.230
71.197
63.488
56.763
51.297
35.598
220
200
180
160
140
120
100
80
60
40
20
0
ppm

plj070228

File: PROTON

Pulse Sequence: gCOSY
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.207 sec
Width 4952.6 Hz
2D Width 4952.6 Hz
16 repetitions
300 increments
OBSERVE H1, 499.9019057 MHz
DATA PROCESSING
Sq. sine bell 0.103 sec
F1 DATA PROCESSING
Sq. sine bell 0.032 sec
FT size 4096 x 4096
Total time 1 hr, 40 min, 19 sec

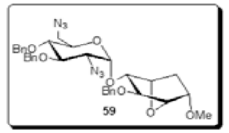


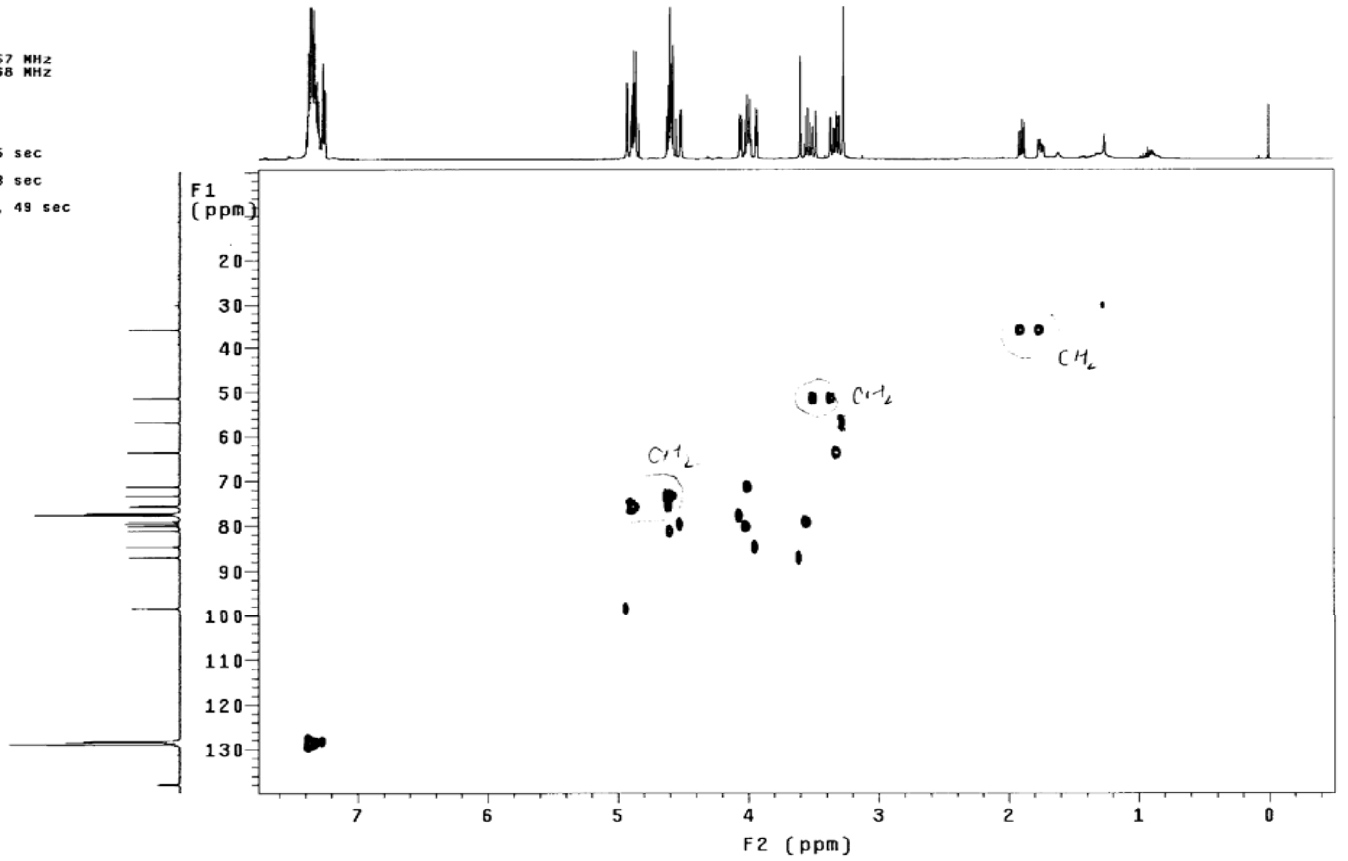
plj070228

File: PROTON

Pulse Sequence: gHSQC
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.205 sec
Width 4995.3 Hz
2D Width 21367.5 Hz
16 repetitions
2 x 128 increments
OBSERVE H1, 499.9019057 MHz
DECOUPLE C13, 125.7098268 MHz
Power 49 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Gauss apodization 0.095 sec
F1 DATA PROCESSING
Gauss apodization 0.003 sec
FT size 2048 x 2048
Total time 1 hr, 27 min, 49 sec



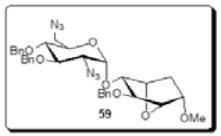


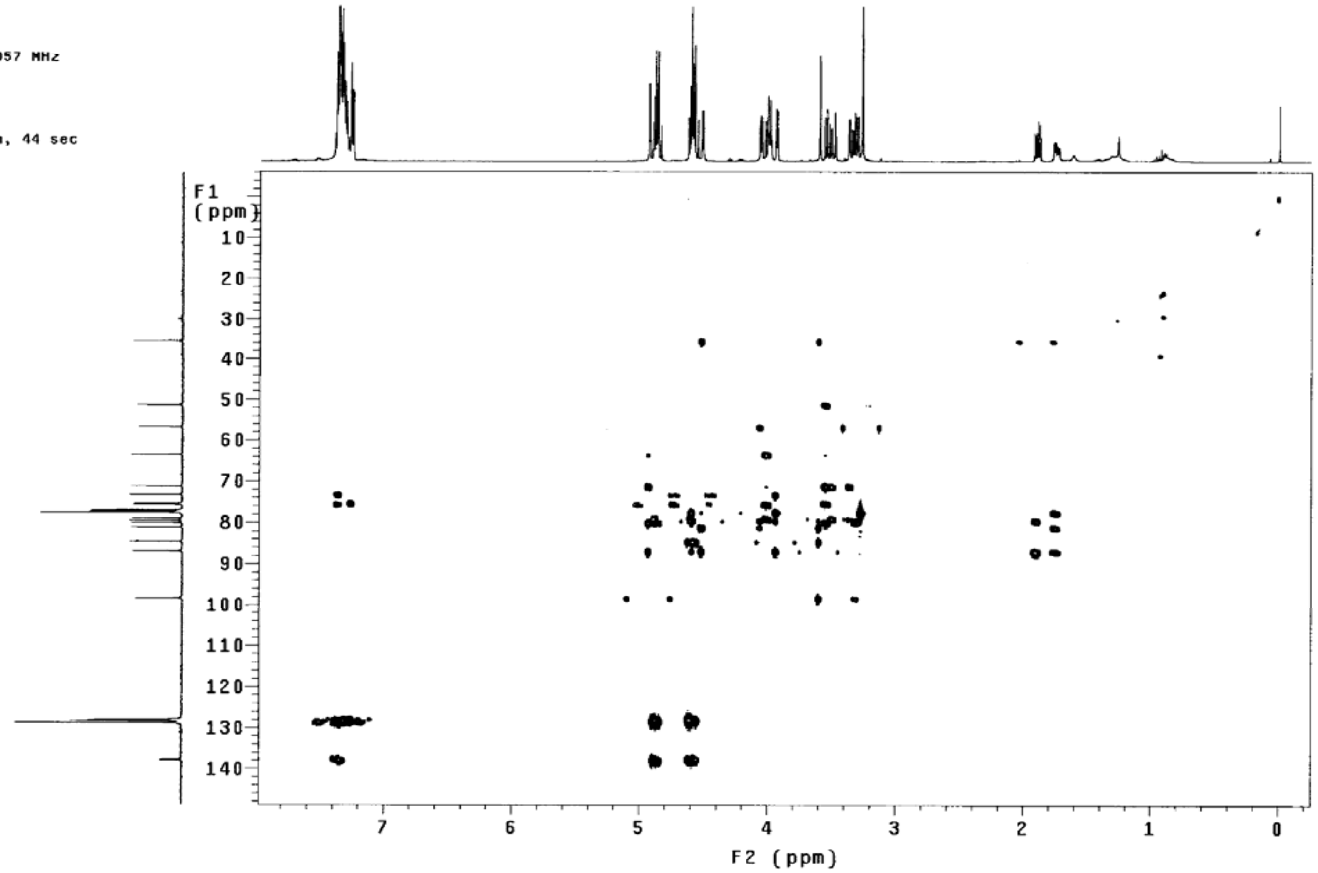
plj070228

File: PROTON

Pulse Sequence: gHMBC
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
User: 1-14-87
INOVA-500 "BMU500"

Relax. delay 1.000 sec
Acq. time 0.206 sec
Width 4973.9 Hz
2D Width 30165.8 Hz
16 repetitions
400 increments
OBSERVE H1, 499.9019057 MHz
DATA PROCESSING
Sine bell 0.103 sec
F1 DATA PROCESSING
Sine bell 0.006 sec
FT size 2048 x 8192
Total time 2 hr, 18 min, 44 sec



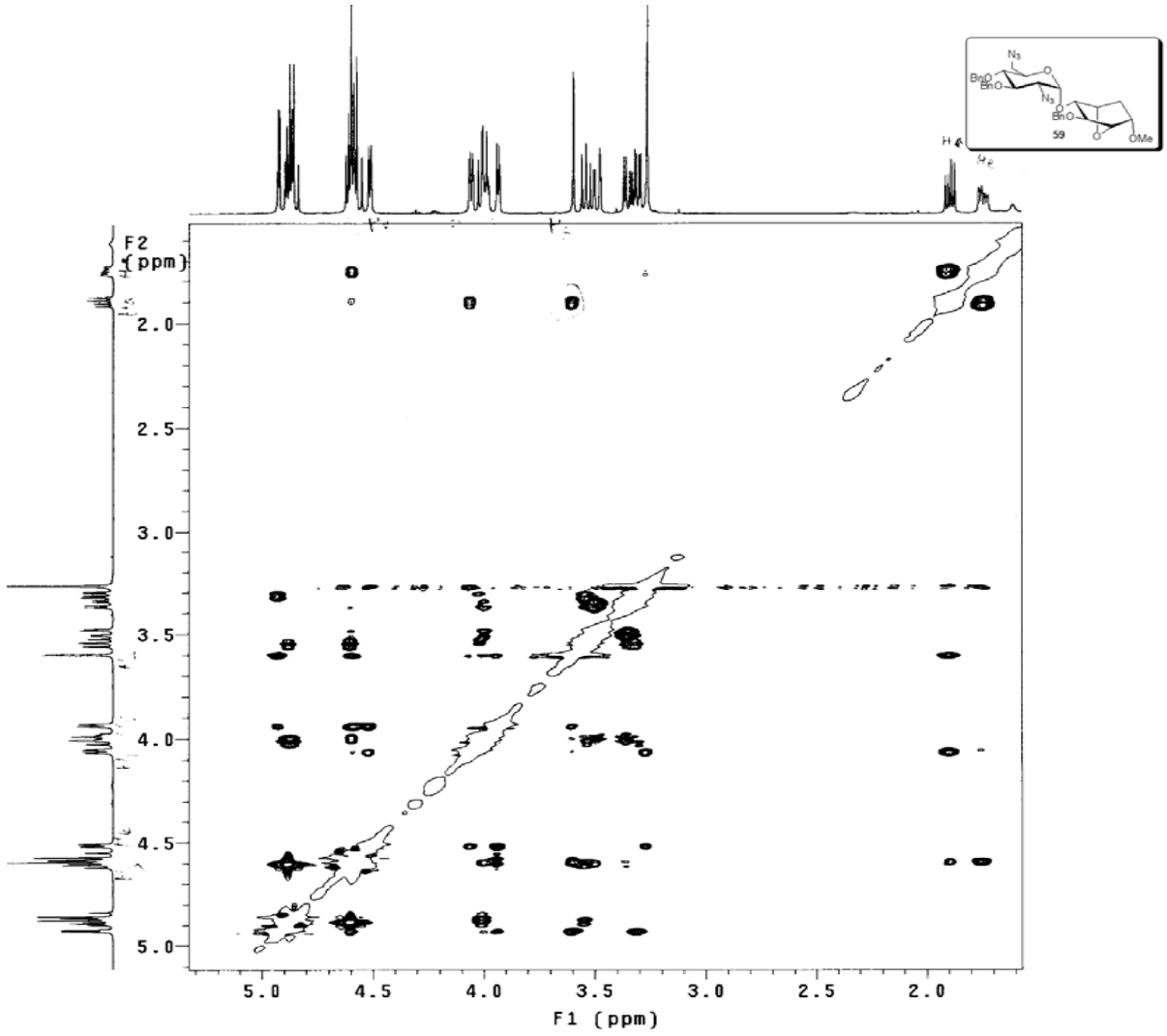


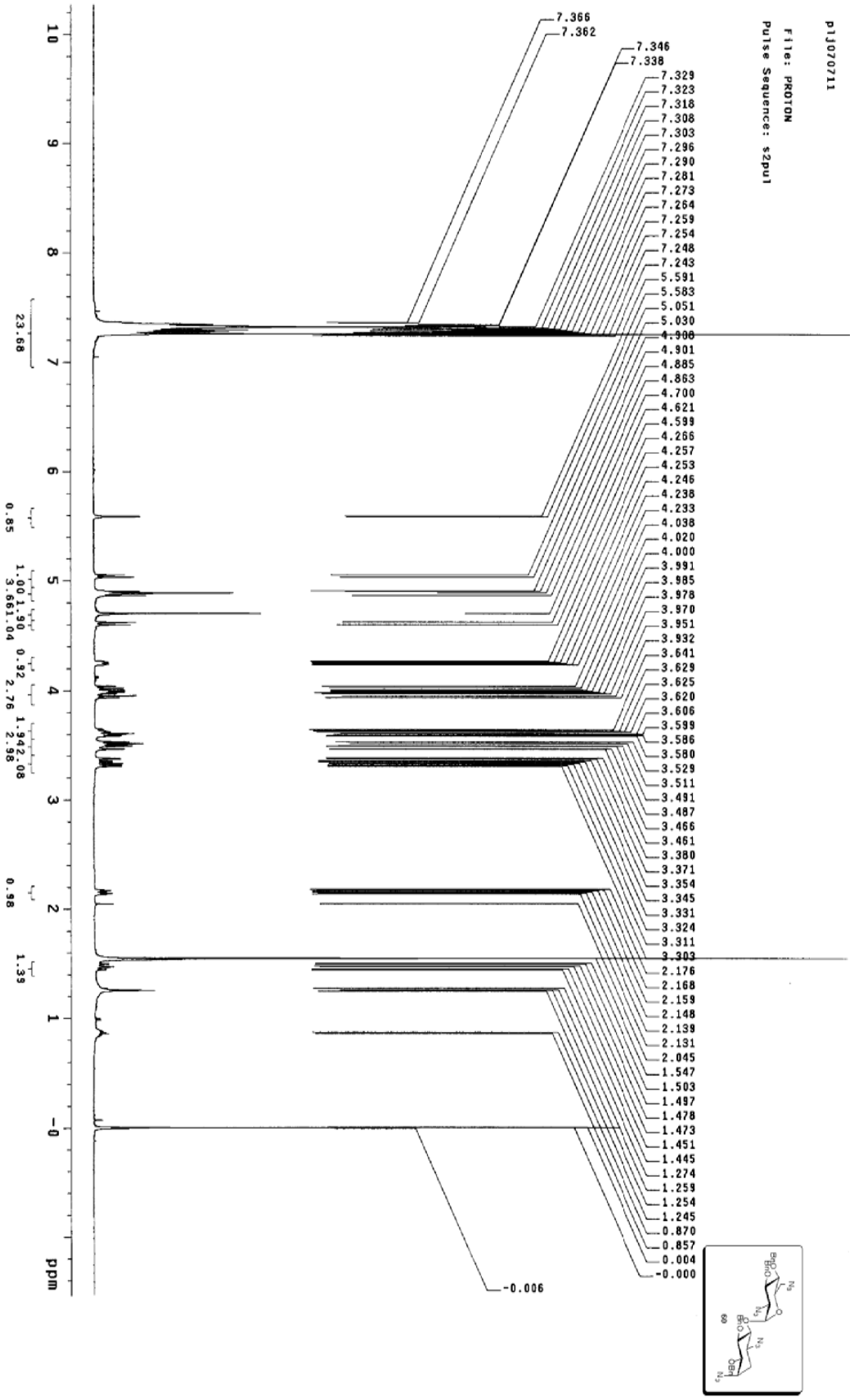
plj070228

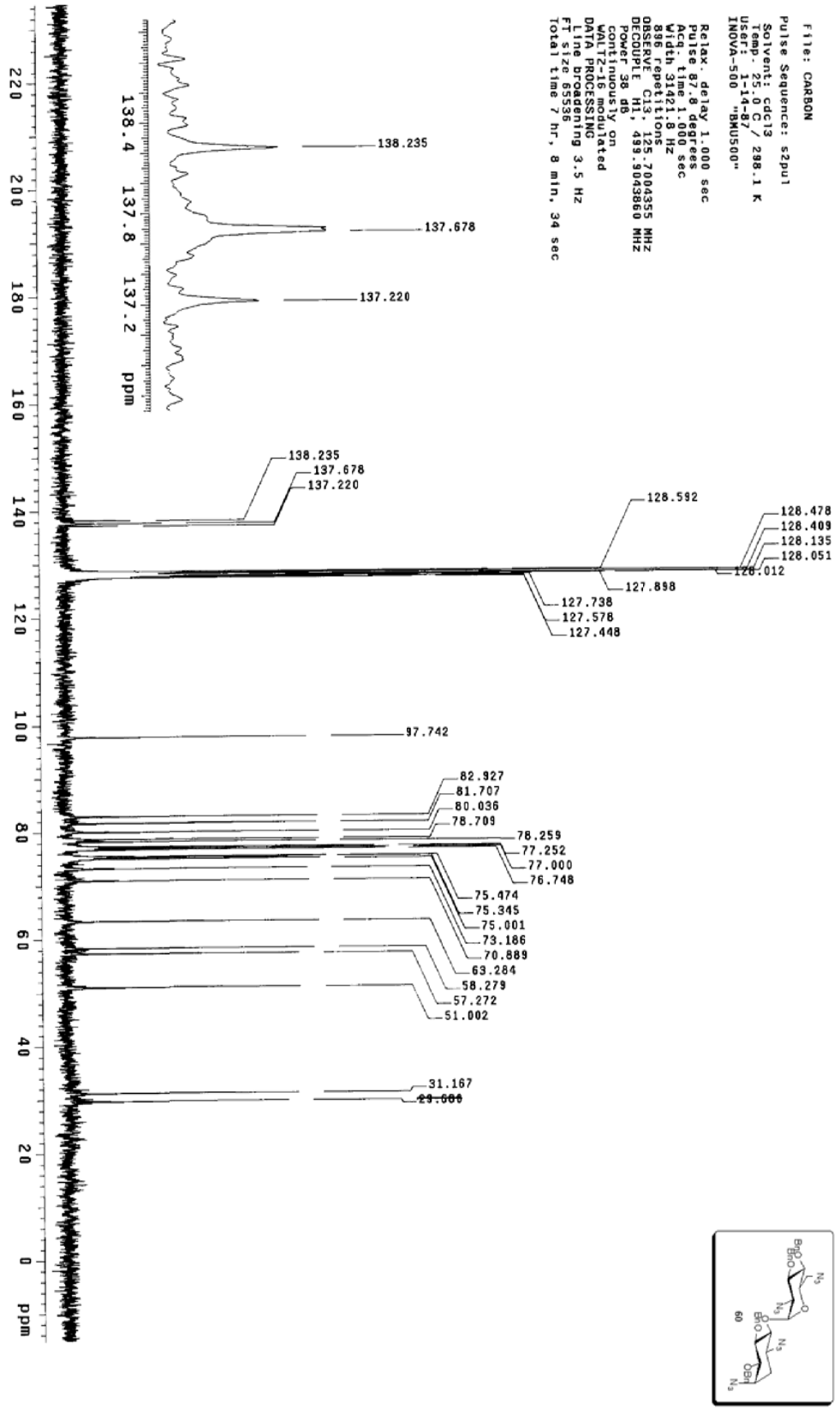
File: PROTON

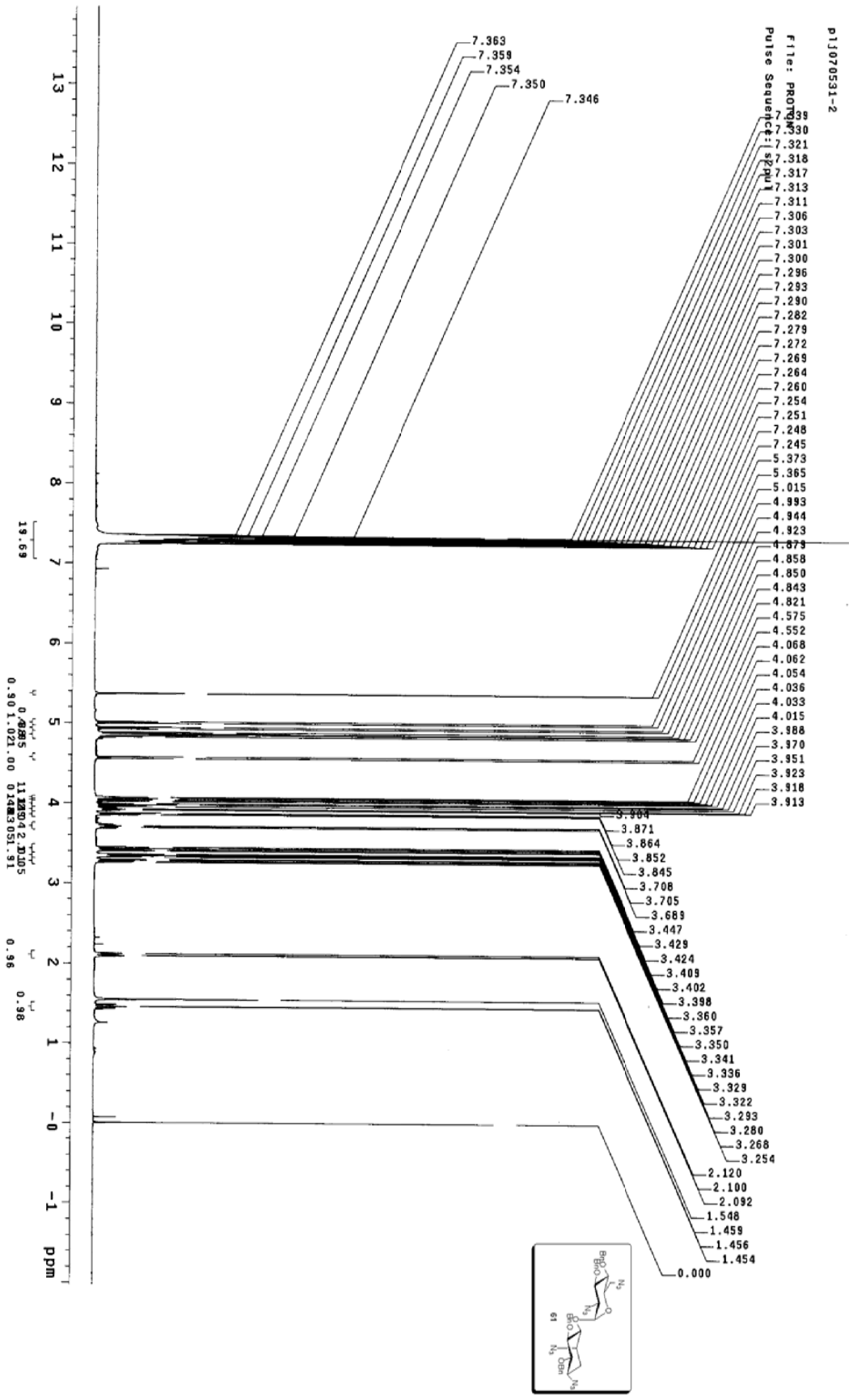
Pulse Sequence: NOESY
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"

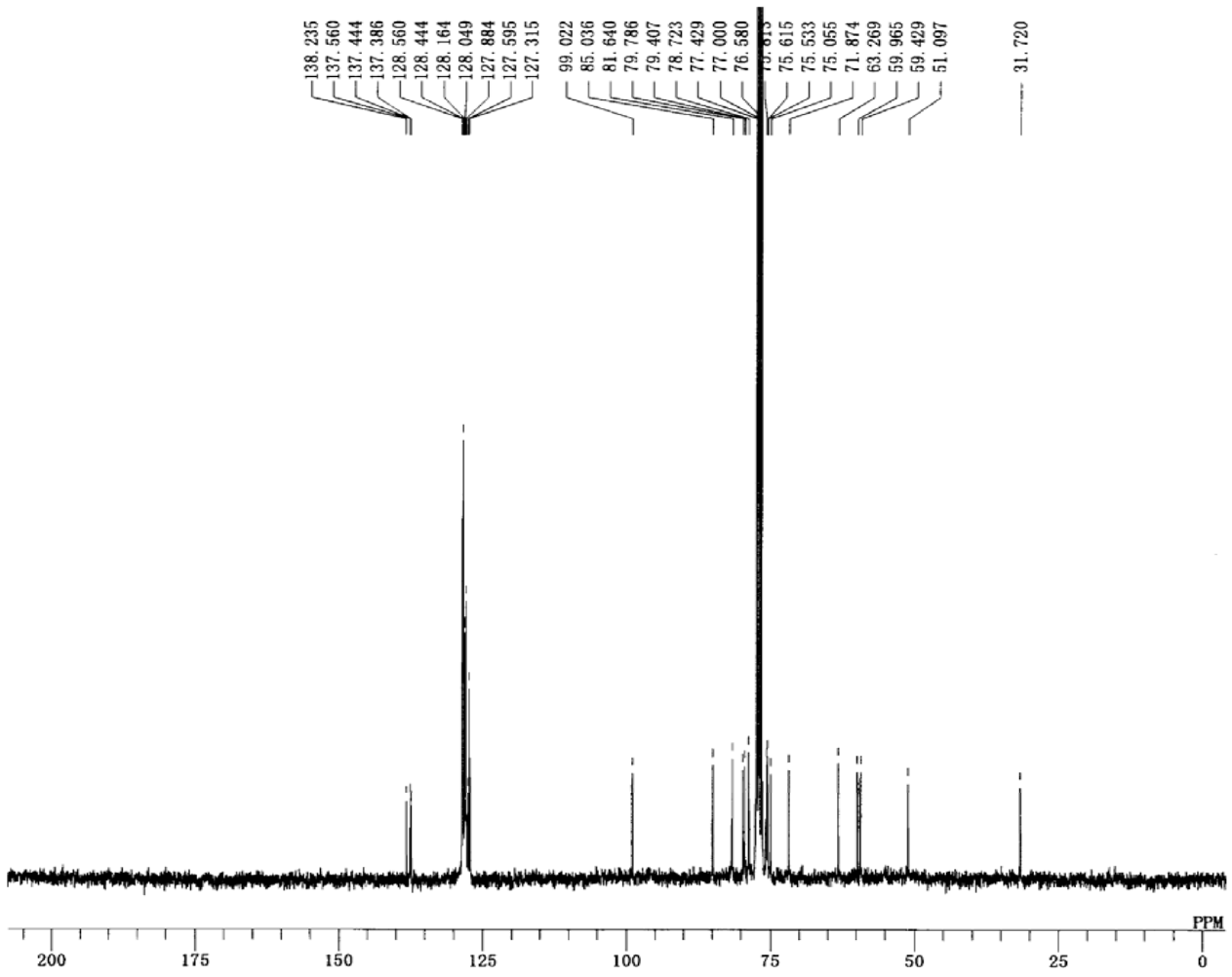
Relax. delay 1.000 sec
Mixing 0.600 sec
Acq. time 0.205 sec
Width 4995.3 Hz
2D Width 4995.3 Hz
16 repetitions
2 x 300 increments
OBSERVE H1, 499.8019057 MHz
DATA PROCESSING
Gauss apodization 0.095 sec
F1 DATA PROCESSING
Gauss apodization 0.028 sec
FT size 4096 x 4096
Total time 4 hr, 56 min, 45 sec



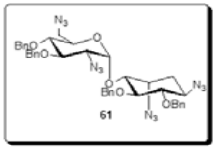

plj070711
File: PROTON
Pulse Sequence: s2pul
7.366
7.362
7.346
7.338
7.329
7.323
7.318
7.308
7.303
7.296
7.290
7.281
7.273
7.264
7.259
7.254
7.248
7.243
5.591
5.583
5.051
5.030
4.908
4.901
4.885
4.863
4.700
4.621
4.599
4.266
4.257
4.253
4.246
4.238
4.233
4.038
4.020
4.000
3.991
3.985
3.978
3.970
3.951
3.932
3.641
3.629
3.625
3.620
3.606
3.599
3.586
3.580
3.529
3.511
3.491
3.487
3.466
3.461
3.380
3.371
3.354
3.345
3.331
3.324
3.311
3.303
2.176
2.168
2.159
2.148
2.139
2.131
2.045
1.547
1.503
1.497
1.478
1.473
1.451
1.445
1.274
1.259
1.254
1.245
0.870
0.857
0.004
-0.000
-0.006
23.68
0.85
1.00
1.90
3.66
1.04
0.92
2.76
1.94
2.98
1.08
0.98
1.39
ppm

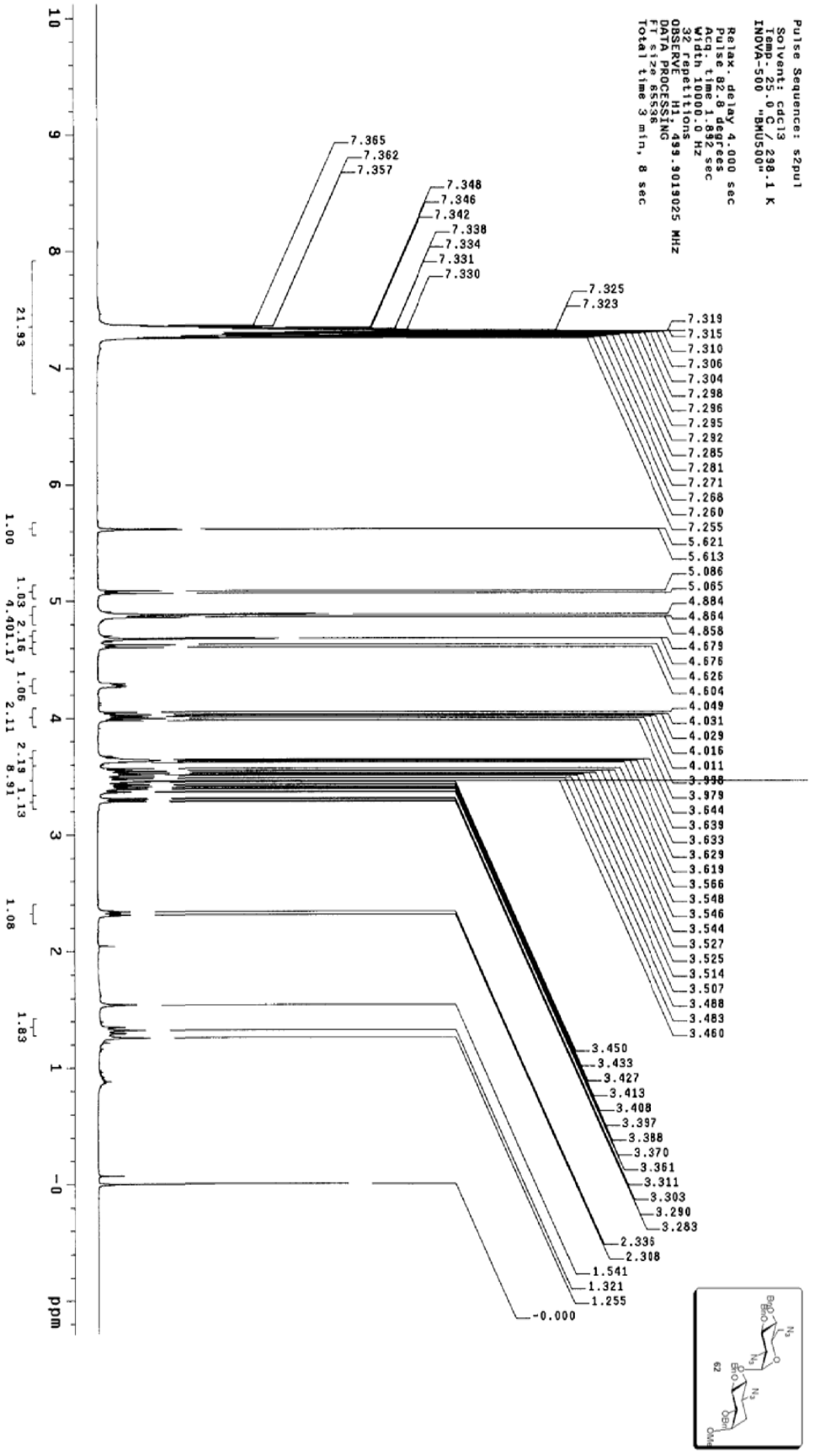

pj1070711
File: CARBON
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 / 298.1 K
INOVA-500 "BMU500"
Relax. delay 1.000 sec
Pulse 87.8 degrees
Acq. time 1.000 sec
Width 31421.8 Hz
896 repetitions
OBSERVE C13, 125.7004355 MHz
DECOUPLE H1, 499.9043860 MHz
Power 38 dB
continuously on
WALTZ16 modulated
DATA PROCESSING
Line broadening 3.5 Hz
FT size 65536
Total time 7 hr, 8 min, 34 sec
138.235
137.678
137.220
138.4
137.8
137.2
ppm
128.592
128.478
128.409
128.135
128.051
128.012
127.898
127.738
127.578
127.448
97.742
82.927
81.707
80.036
78.709
78.259
77.252
77.000
76.748
75.474
75.345
75.001
73.186
70.889
63.284
58.279
57.272
51.002
31.167
29.680
220
200
180
160
140
120
100
80
60
40
20
0
ppm

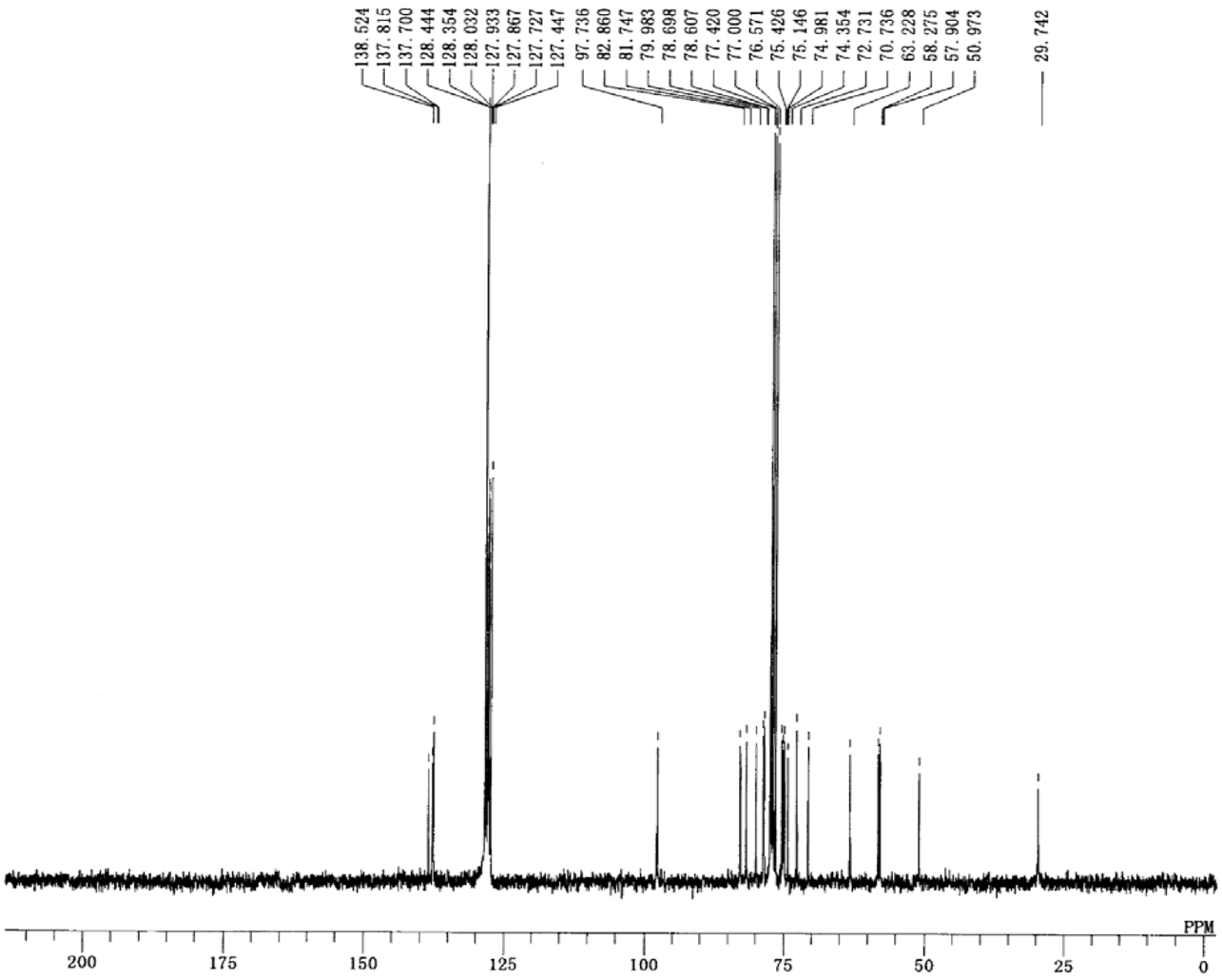

pij070531-2
File: PROTON
Pulse Sequence: s2pul
7.363
7.359
7.354
7.350
7.346
7.339
7.330
7.321
7.318
7.317
7.313
7.311
7.306
7.303
7.301
7.300
7.296
7.293
7.290
7.282
7.279
7.272
7.269
7.264
7.260
7.254
7.251
7.248
7.245
5.373
5.365
5.015
4.993
4.944
4.923
4.879
4.858
4.850
4.843
4.821
4.575
4.552
4.068
4.062
4.054
4.036
4.033
4.015
3.988
3.970
3.951
3.923
3.918
3.913
3.904
3.871
3.864
3.852
3.845
3.708
3.705
3.689
3.447
3.429
3.424
3.409
3.402
3.398
3.360
3.357
3.350
3.341
3.336
3.329
3.322
3.293
3.280
3.268
3.254
2.120
2.100
2.092
1.548
1.459
1.456
1.454
0.000
19.69
0.90
1.02
1.00
0.96
0.98
ppm



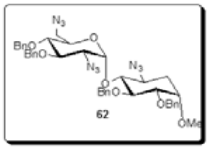
DFILE	D:\叶新山\PLJ070531-2-C.ALS	
OBNUC	13C	
EXMOD	BCM	
OBFRQ	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	3000	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRATN	511	
CTEMP	21.3	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	24	

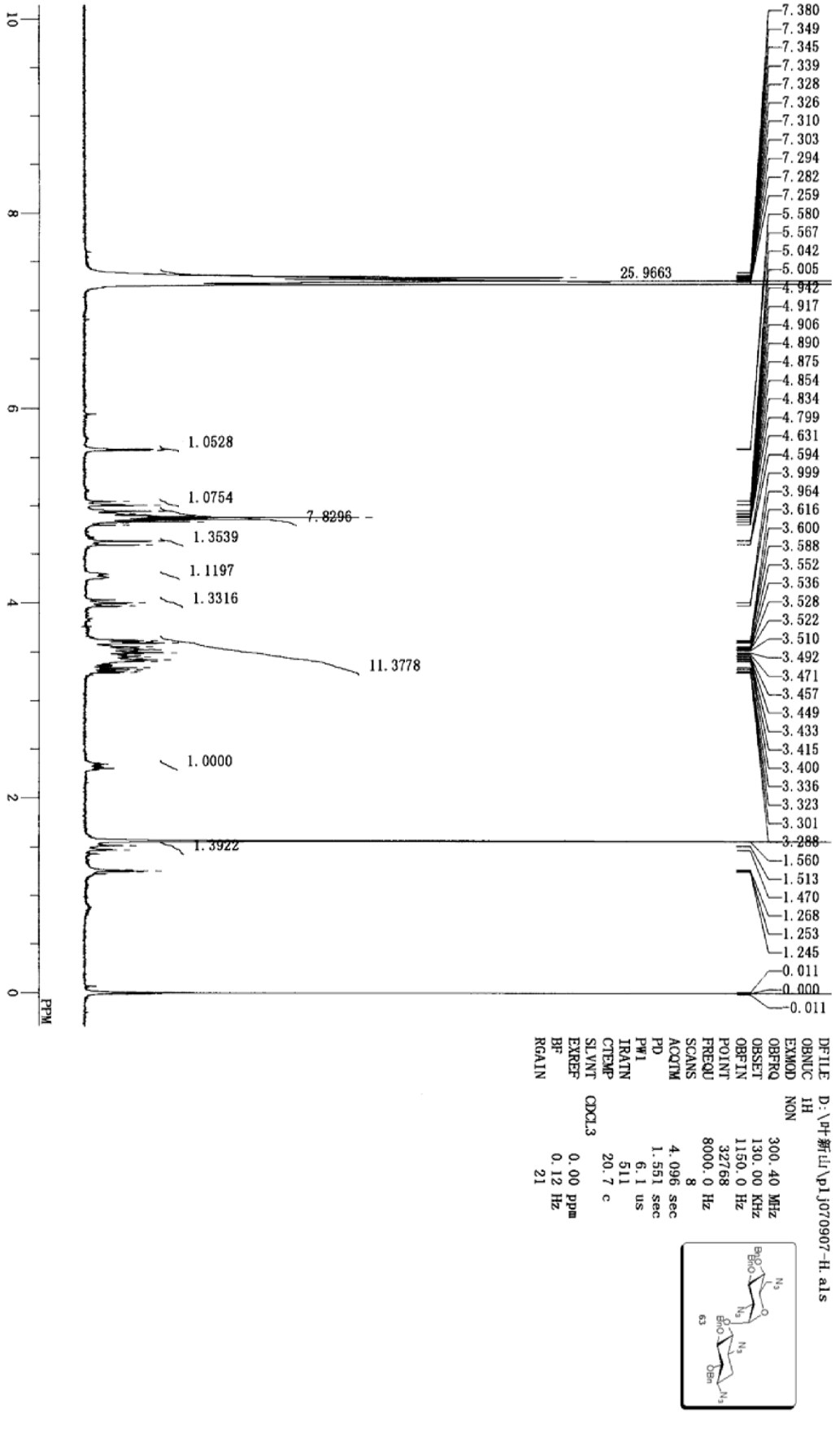


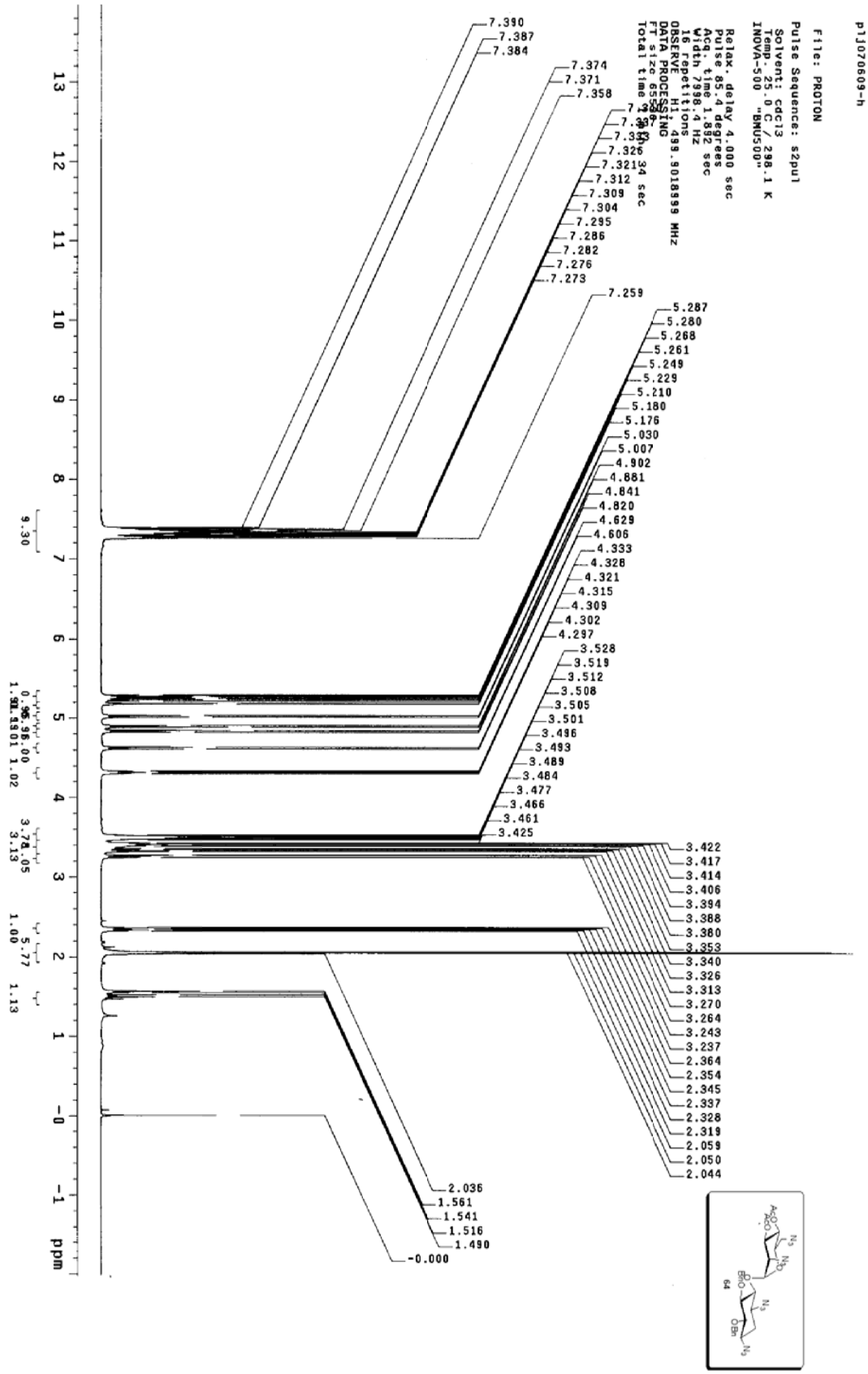

plj070327-m
File: PROTON
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
INOVA-500 "BMU500"
Relax. delay 4.000 sec
Pulse 82.8 degrees
Acq. time 1.892 sec
Width 10000.0 Hz
32 repetitions
OBSERVE H1, 499.9019025 MHz
DATA PROCESSING
FT size 65536
Total time 3 min, 8 sec
7.365
7.362
7.357
7.348
7.346
7.342
7.338
7.334
7.331
7.330
7.325
7.323
7.319
7.315
7.310
7.306
7.304
7.298
7.296
7.295
7.292
7.285
7.281
7.271
7.268
7.260
7.255
5.621
5.613
5.086
5.065
4.884
4.864
4.858
4.679
4.676
4.626
4.604
4.049
4.031
4.029
4.016
4.011
3.998
3.979
3.644
3.639
3.633
3.629
3.619
3.566
3.548
3.546
3.544
3.527
3.525
3.514
3.507
3.488
3.483
3.460
3.450
3.433
3.427
3.413
3.408
3.397
3.388
3.370
3.361
3.311
3.303
3.290
3.283
2.336
2.308
1.541
1.321
1.255
-0.000
21.93
1.00
1.03
2.16
4.40
1.17
1.06
2.11
2.19
1.13
8.91
1.08
1.83
ppm

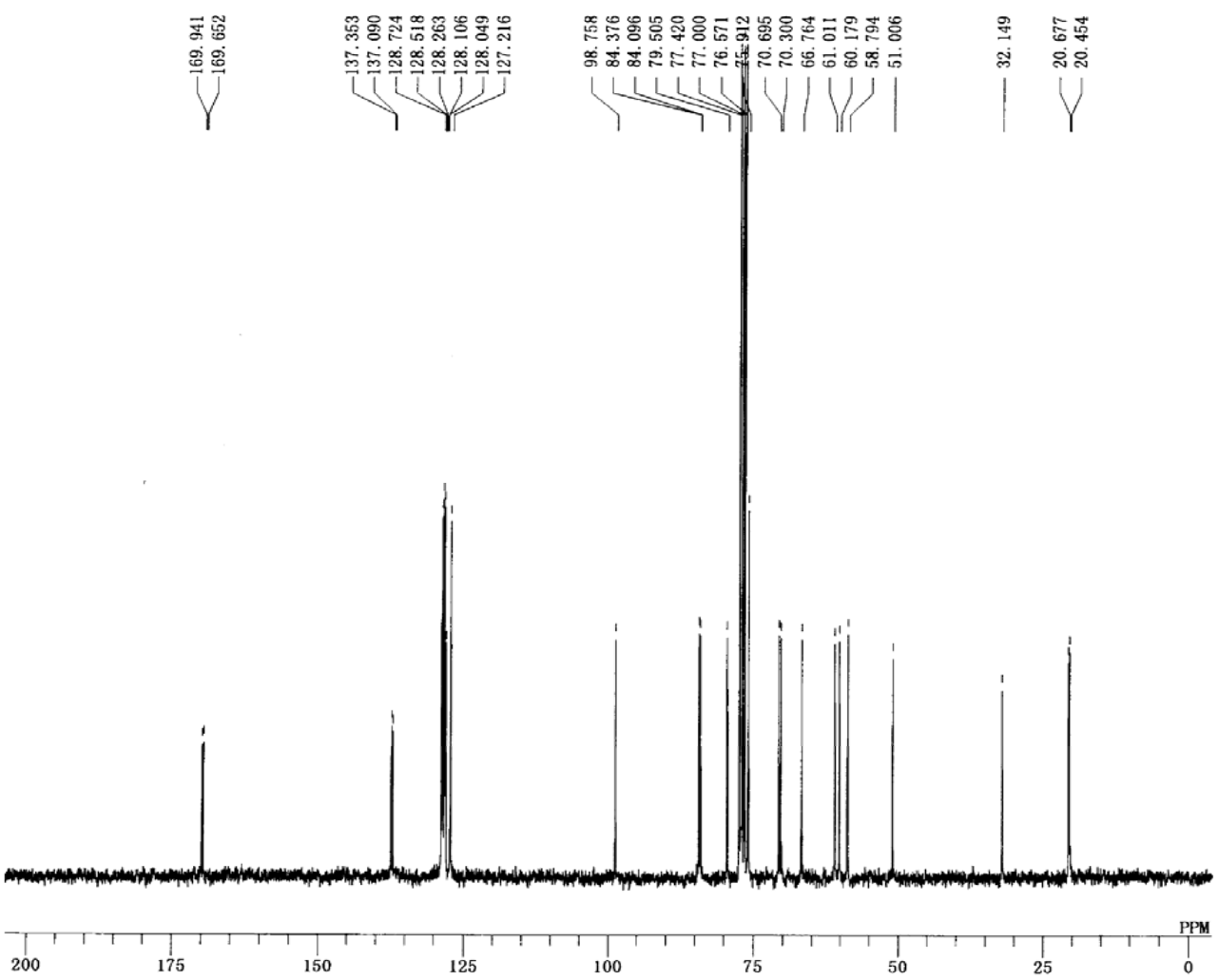


DFILE	D:\叶新山\plj070327-m-C.als	
OBNUC	13C	
EXMOD	BCM	
OFR	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	800	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRN		
CTEMP	19.5	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	24	

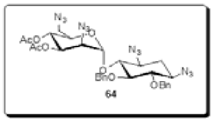


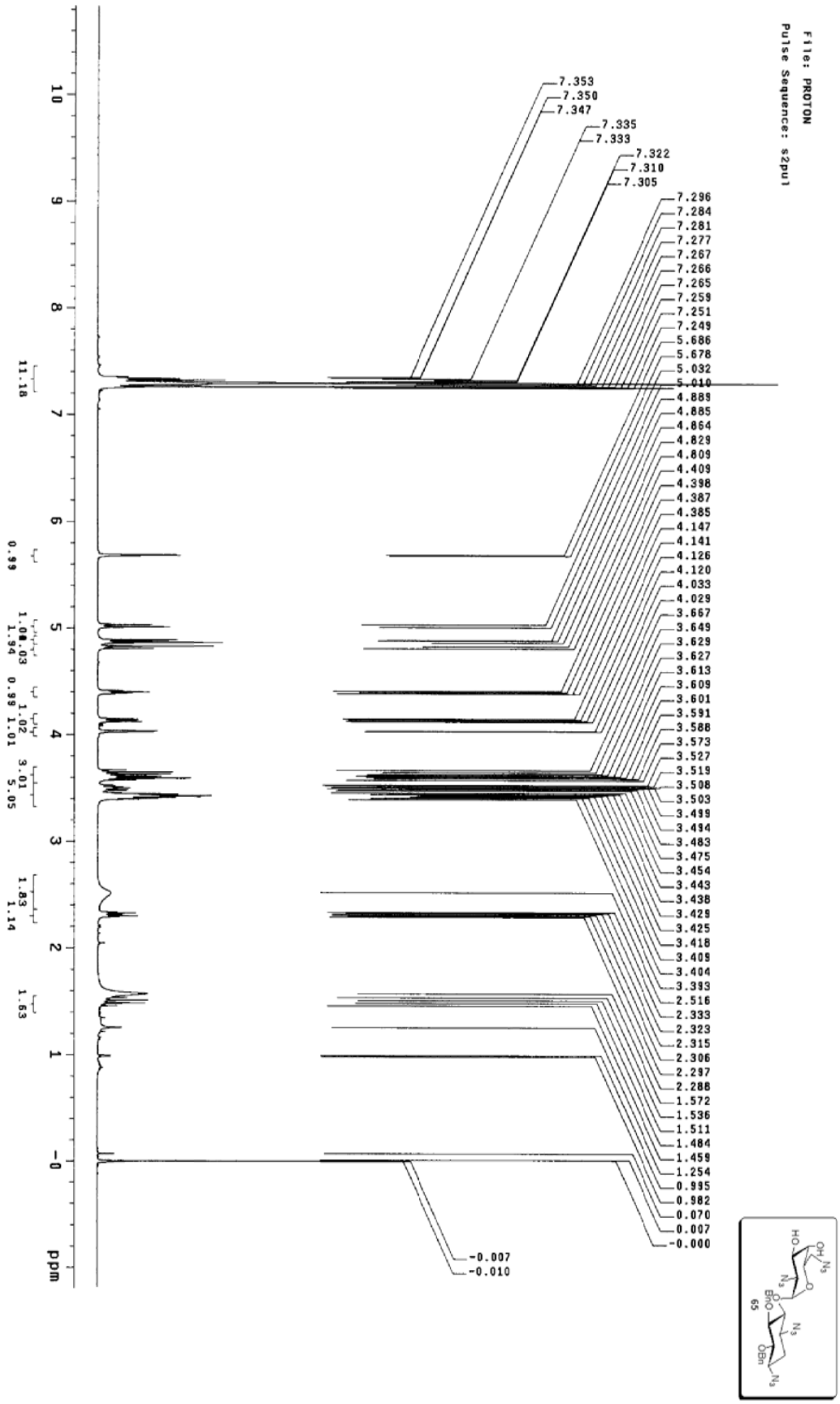

7.380
7.349
7.345
7.339
7.328
7.326
7.310
7.303
7.294
7.282
7.259
5.580
5.567
5.042
5.005
4.942
4.917
4.906
4.890
4.875
4.854
4.834
4.799
4.631
4.594
3.999
3.964
3.616
3.600
3.588
3.552
3.536
3.528
3.522
3.510
3.492
3.471
3.457
3.449
3.433
3.415
3.400
3.336
3.323
3.301
3.288
1.560
1.513
1.470
1.268
1.253
1.245
0.011
0.000
-0.011
25.9663
1.0528
1.0754
7.8296
1.3539
1.1197
1.3316
11.3778
1.0000
1.3922
PPM
DFILE D:\PH新出\plj070907-H.als
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 8000.0 Hz
SCANS 8
ACQTM 4.096 sec
PD 1.551 sec
PW1 6.1 us
IRATN 511
CTEMP 20.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 21

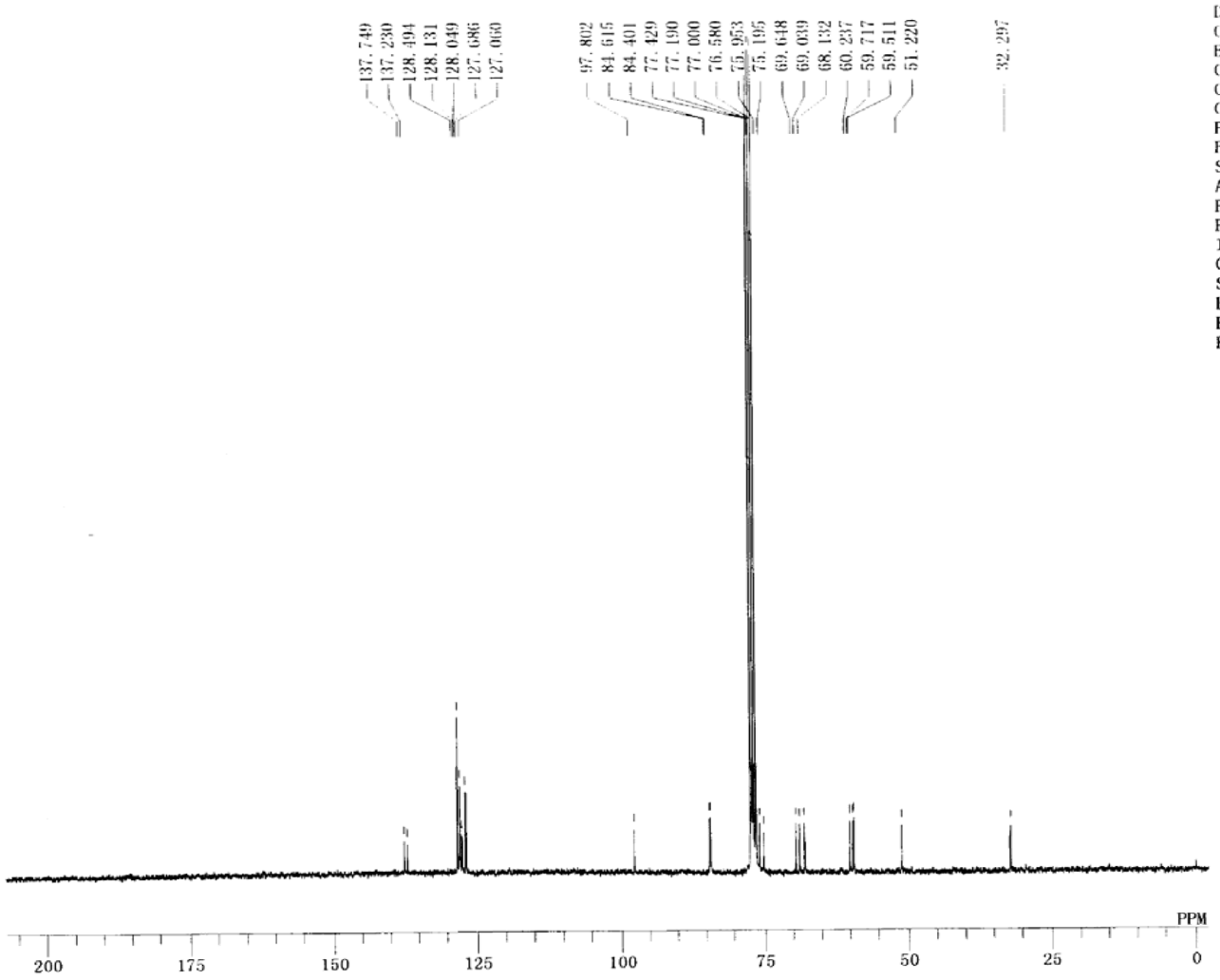

plj070609-h
File: PROTON
Pulse Sequence: s2pul
Solvent: cdcl3
Temp: 25.0 C / 298.1 K
INOVA-500 "BMUS00"
Relax. delay 4.000 sec
Pulse 85.4 degrees
Acq. time 1.882 sec
Width 7998.4 HZ
16 repetitions
OBSERVE H1, 499.9018999 MHZ
DATA PROCESSING
FT size 65536
Total time 1 min, 34 sec
7.390
7.387
7.384
7.374
7.371
7.358
7.326
7.321
7.312
7.309
7.304
7.295
7.286
7.282
7.276
7.273
7.259
5.287
5.280
5.268
5.261
5.249
5.229
5.210
5.180
5.176
5.030
5.007
4.902
4.881
4.841
4.820
4.629
4.606
4.333
4.328
4.321
4.315
4.309
4.302
4.297
3.528
3.519
3.512
3.508
3.505
3.501
3.496
3.493
3.489
3.484
3.477
3.466
3.461
3.425
3.422
3.417
3.414
3.406
3.394
3.388
3.380
3.353
3.340
3.326
3.313
3.270
3.264
3.243
3.237
2.364
2.354
2.345
2.337
2.328
2.319
2.059
2.050
2.044
2.036
1.561
1.541
1.516
1.490
-0.000
9.30
0.95
1.00
1.02
3.78
3.13
5.05
1.00
5.77
1.13
13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm



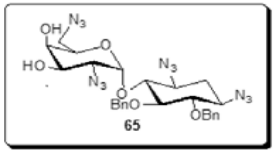
DFILE D:\叶新山\PLJ070609-C.ALS
OBNUC 13C
EXMOD BCM
OBFRQ 75.45 MHz
OBSET 124.00 KHz
OBFIN 1840.0 Hz
POINT 32768
FREQU 20408.1 Hz
SCANS 800
ACQTM 1.606 sec
PD 1.394 sec
PW1 4.2 us
IRATN 511
CTEMP 21.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24




Ga1D_a_0716
File: PROTON
Pulse Sequence: s2pul
7.353
7.350
7.347
7.335
7.333
7.322
7.310
7.305
7.296
7.284
7.281
7.277
7.267
7.266
7.265
7.259
7.251
7.249
5.686
5.678
5.032
5.010
4.889
4.885
4.864
4.829
4.809
4.409
4.398
4.387
4.385
4.147
4.141
4.126
4.120
4.033
4.029
3.667
3.649
3.629
3.627
3.613
3.609
3.601
3.591
3.588
3.573
3.527
3.519
3.508
3.503
3.499
3.494
3.483
3.475
3.454
3.443
3.438
3.429
3.425
3.418
3.409
3.404
3.393
2.516
2.333
2.323
2.315
2.306
2.297
2.288
1.572
1.536
1.511
1.484
1.459
1.254
0.995
0.982
0.070
0.007
-0.000
-0.007
-0.010
11.18
0.99
1.08
1.03
1.94
0.99
1.02
1.01
3.01
5.05
1.83
1.14
1.63
ppm
HO
OH
N3
N3
O
BnO
65
N3
OBn
N3



DFILE	D:\叶新山\PLJGa1D_a_0716.als	
OBNUC	13C	
EXMOD	BCM	
OBFRQ	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	7769	
ACQTM	1.606	sec
PD	1.394	sec
PW1	4.2	us
IRATN	511	
CTEMP	21.8	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	2.00	Hz
RGAIN	25	



65