Electronic Supplementary Material (ESI) for Chemical Communications

Simple One-pot Regioselective 6-*O*-Phosphorylation of Carbohydrates and Trehalose Desymmetrization

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SUPPORTING INFORMATION

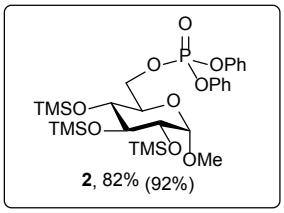
General Information

All reactions were conducted in flame-dried glassware, under nitrogen atmosphere. Dichloromethane, diethyl ether, *N,N*-dimethyformamide, methanol were purified and dried from a safe purification system containing activated Al_2O_3. All reagents obtained from commercial sources were used without purification, unless otherwise mentioned. Flash column chromatography was carried out on Silica Gel Geduran® Si 60 (0.040-0.063, E. Merck) and DAVISIL® (LC60A 40-63 micron), TLC was performed on pre-coated glass plates of Silica Gel 60 F254 (0.25mm, E. Merck); detection was executed by spraying with a solution of cerium(IV) sulfate, ammonium molybdate and H_2SO_4 in water and subsequent heating on a hot plate. Optical rotations were measured on Jasco DIP-370 using a 100 mm cell at 589 nm. ^1H, ^{13}C NMR, DEPT, ^1H-^1H COSY, ^1H-^{13}C COSY, and NOESY spectrum were recorded with Bruker AV400, AVIII 400 and DRX 500, AV 500 MHz instruments. Chemical shifts are in ppm from Me_4Si, generated from the

$CDCl_3$ lock signal at δ 7.24, CD_2Cl_2 lock signal at 5.32 and D_2O lock signal at 4.80. All ^{13}C NMR spectra contain the ^{13}C at the bottom trace, and the middle and the upper traces are DEPT 90, 135 respectively. Multiplicities are reports by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; *J* = coupling constant values in Hertz. Mass spectra was analyzed on a Waters Premier XE instrument with ESI source.

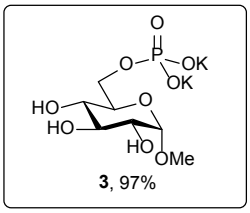
Procedures for One-Pot Regioselective Phosphorylation of 1, 4, 7, 10, 13, 16, 19, 22, 25 and 28. TMSOTf (0.1 equiv) was added at room temperature under an N_2 atmosphere to a suspension of **compound 1, 4, 7, 10, 13, 16, 19, 22, 25, 28** (100 mg, 1 equiv) and HMDS (0.6 equiv per hydroxyl group) in CH_2Cl_2 (1.0 mL). After stirring for 30-40 min, pyridine (1.1 mL), diphenyl chlorophosphate (3.0 equiv) were added with stirring. The mixture was allowed to stir at room temperature for 36 h. The mixture was concentrated and purified by flash column chromatography (Hex/EtOAc 20:1) to yield **2** (82%), **5** (83%), **8** (85%), **11** (84%), **14** (82%), **17** (78%), **20** (63%), **23** (44%), **26** (49%) and **29** (48%).

General Procedure for the Hydrogenation and Salinization of 2, 5, 8, 11, 14, 17, 20, 23, 26 and 29. To a solution of compound **2, 5, 8, 11, 14, 17, 20, 23, 26 and 29** (50 mg, 1 equiv) in 75% EtOH (5 mL) was added PtO_2 (2.05 equiv). After stirring for 12 h at room temperature under an H_2 atmosphere, the mixture was filtered through a celite pad. The solvent was evaporated *in vacuo* and washed with Ethyl acetate and water. The water layer was lyophilized to give a white powder, which was mixed with potassium hydroxide (2.05 equiv) in H_2O (1 mL). The solution was stirred for 4 h and lyophilized to give the product **3, 6, 9, 12, 15, 18, 21, 24, 27** and **30** without further purification.



2, 82% (92%)

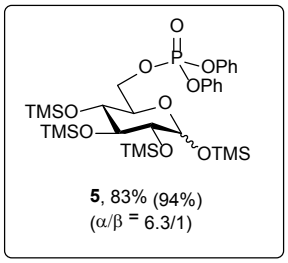
Methyl 6-*O*-diphenylphosphoryl-2,3,4-tri-*O*-trimethylsilyl-α-D-gluco-pyranoside (2). Procedures were as shown in the general procedures to afford **2** as a colourless syrup (272 mg, 82%) and the fully trimethylsilylated α-methoxy glucose (27 mg, 11%) (recovered yield of **2**: 92%). $[\alpha]^{32}_{D}$ 61.9 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.14 (m, 10H, Ph), 4.50 (d, *J* = 3.4 Hz, 1H, H-1), 4.49 (ddd, *J* = 10.4, 7.8, 5.2 Hz, 1H, H-6a), 4.26 (ddd, *J* = 11.0, 7.8, 5.2 Hz, 1H, H-6b), 3.72 (t, *J* = 9.2 Hz, 1H, H-3), 3.68 (ddd, *J* = 11.4, 9.2, 1.9 Hz, 1H, H-5), 3.40 (t, *J* = 9.2 Hz, 1H, H-4), 3.36 (dd, *J* = 3.8, 9.4 Hz, 1H, H-2), 0.13 (s, 9H, TMS), 0.12 (bs, 18H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.92 (C), 150.85 (C), 130.77 (C), 129.88 (CH), 129.86 (CH), 125.4 (CH), 120.3 (CH), 120.2 (CH), 99.9 (CH), 75.1 (CH), 73.8 (CH), 72.1 (CH), 70.3 (CH, *J*cp = 6.3 Hz), 68.4 (CH_2, *J*cp = 5.8 Hz), 55.1 (CH_3), 1.5 (CH_3), 1.1 (CH_3), 0.7 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.35; HRMS (ESI) calcd for $C_{28}H_{48}O_9Si_3P$ $[M+H]^+$ 643.2344, found 643.2342.



3, 97%

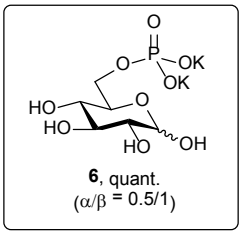
Methyl α-D-glucose 6-phosphate dipotassium salt (3). Procedure were as shown in the general procedures to afford **3** as a white powder (26 mg, 97%). $[\alpha]^{30}_{D}$ 62.9 (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.83 (s, 1H, H-1), 4.01 (ddd, *J* = 2.8, 7.0, 11.1 Hz, 1H, H-6a), 3.96 (dd, *J* = 4.1, 11.6 Hz, 1H, H-6b), 3.71-3.63 (m, 4H, H-2, H-3, H-4, H-5), 3.46 (s, 1H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 99.5 (CH), 72.7 (CH), 71.4 (CH), 71.3 (CH), 71.3 (CH), 68.9 (CH),

62.4 (CH_2), 55.1 (CH_3); ^{31}P NMR (162 MHz, D_2O) δ 5.09; HRMS (ESI) calcd for $C_7H_{14}O_9P$ $[M-2K+H]^-$ 273.0375, found 273.0378.



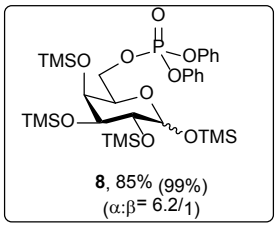
5, 83% (94%)
(α/β = 6.3/1)

6-*O*-Diphenylphosphoryl-1,2,3,4-tetra-*O*-trimethylsilyl-D-glucopyranose (5). Procedures were as shown in the general procedures to afford **5** as a colourless syrup (315 mg, 83%) and the fully trimethylsilylated glucose (35 mg, 12%) (recovered yield of **5**: 94%). $[\alpha]^{32}_D$ 38.1 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.13 (m, 20H, Ph), 4.88 (d, *J* = 3.0 Hz, 1H, H-1α), 4.54 (ddd, *J* = 10.7, 5.9, 1.5 Hz, 1H, H-6aβ), 4.47 (d, *J* = 6.5 Hz, 1H, H-1β), 4.46 (ddd, *J* = 10.9, 7.3, 2.1 Hz, 1H, H-6aα), 4.26 (ddd, *J* = 11.3, 7.3, 2.1 Hz, 1H, H-6bα), 4.16 (ddd, *J* = 10.4, 5.9, 1.5 Hz, 1H, H-6bβ), 4.10 (t, *J* = 5.9 Hz, 1H, H-4β), 3.86 (ddd, *J* = 11.3, 9.1, 2.1 Hz, 1H, H-5α), 3.85 (ddd, *J* = 10.7, 5.9, 1.5 Hz, 1H, H-5β), 3.75 (t, *J* = 9.1 Hz, 1H, H-3α), 3.39 (t, *J* = 9.1 Hz, 1H, H-4α), 3.36 (t, *J* = 5.9 Hz, 1H, H-3β), 3.22 (t, *J* = 9.1. 3.0 Hz, 1H, H-2α), 3.21 (dd, *J* = 6.5, 5.9 Hz, 1H, H-2β), 0.13 (s, 18H, TMS), 0.12 (s, 18H, TMS), 0.10 (s, 18H, TMS), 0.09 (s, 18H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0 (C), 150.92 (C), 150.89 (C), 150.8 (C), 129.9 (CH), 125.5 (CH), 125.4 (CH), 120.4 (CH), 120.3 (CH), 120.26 (CH), 98.3 (CH), 94.0 (CH), 78.1 (CH), 77.6 (CH), 77.43 (CH), 77.35 (CH), 77.2 (CH), 76.9 (CH), 75.1 (CH), 75.0 (CH), 74.0 (CH), 73.9 (CH), 71.9 (CH), 70.9 (CH), 70.8 (CH), 68.4 (CH_2, *J*cp = 5.9 Hz), 1.43 (CH_3), 1.08 (CH_3), 0.60 (CH_3), 0.32 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.72; HRMS (ESI) calcd for $C_{30}H_{53}O_9NaSi_4P$ $[M+Na]^+$ 723.2402, found 723.2406.



6, quant.
(α/β = 0.5/1)

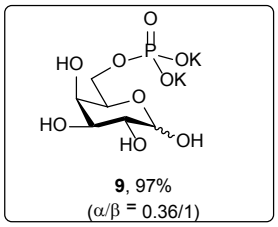
Glucose 6-phosphate dipotassium salt (6). Procedure were as shown in the general procedures to afford **6** as a white powder (23 mg, quant). (α:β= 0.5/1), $[\alpha]^{29}_{D}$ 119.7 (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.26 (d, *J* = 3.8 Hz, 1H, H-1α), 4.67 (d, *J* = 7.9 Hz, 1H, H-1β), 4.06 (ddd, *J* = 11.2, 6.6, 3.2 Hz, 1H, H-6aα), 4.02-3.97 (m, 2H, H-6aβ, H–6bβ), 3.92 (ddd, *J* = 10.7, 6.6, 3.2 Hz, 1H, H-6bα), 3.88 (ddd, *J* = 11.2, 6.6, 3.2 Hz, 1H, H-6bβ), 3.74 (t, *J* = 9.5 Hz, 1H, H-3α), 3.64-3.56 (m, 3H, H-2α, H-4α, H-4β), 3.53-3.49 (m, 2H, H-3β, H-5β), 3.28 (t, *J* = 7.9 Hz, 1H, H-2β); ^{13}C NMR (100 MHz, D_2O) δ 96.7 (CH), 92.7 (CH), 75.4 (CH, *J*cp = 6.6 Hz), 75.3 (CH), 74.7 (CH), 72.4 (CH), 71.9 (CH), 71.0 (CH, *J*cp = 6.6 Hz), 69.2 (CH), 62.8 (CH_2, *J*cp = 4.2 Hz), 62.7 (CH_2, *J*cp = 4.2 Hz); ^{31}P NMR (162 MHz, D_2O) δ 5.12; HRMS (ESI) calcd for $C_6H_{12}O_9PK_2$ $[M]^+$ 336.9493, found 336.9498.



8, 85% (99%)
(α:β= 6.2/1)

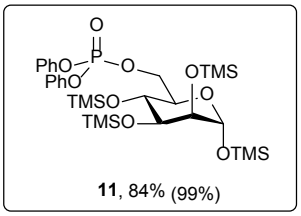
6-*O*-Diphenylphosphoryl-1,2,3,4-tetra-*O*-trimethylsilyl-D-galactopyranose (8). Procedures were as shown in the general procedures to afford **8** as a colourless syrup (325 mg, 85%) and the fully trimethylsilylated galactose (42 mg, 14%) (recovered yield of **8**: 99%). (α:β= 6.2/1). $[\alpha]^{32}_{D}$ 58.1 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.14 (m, 20H, Ph), 5.04 (d, *J* = 2.1 Hz, 1H, H-1α), 4.40 (d, *J* = 7.2 Hz, 1H, H-1β), 4.29-4.20 (m, 5H, H-5β, H-6aα, H-6bα, H-6aβ, H-6bβ), 4.12 (dt, *J* = 6.5, 1.3 Hz, 1H, H-5α), 3.84-3.76 (m, 3H,

H-2α, H-3α, H-4α), 3.63-3.55 (m, 2H, H-2β, H-4β), 3.33 (dd, *J* = 9.2, 2.6 Hz, 1H, H-3β), 0.14 (s, 9H, TMS), 0.13 (s, 9H, TMS), 0.12 (s, 9H, TMS), 0.11 (s, 9H, TMS) , 0.10 (s, 9H, TMS) , 0.094 (s, 9H, TMS) , 0.092 (s, 9H, TMS) , 0.08 (s, 9H, TMS); ^{13}C NMR (100 MHz, CDCl) δ 150.8 (C), 150.7 (C), 130.0 (CH), 125.6 (CH), 125.5 (CH), 120.3 (CH), 120.2 (CH), 98.7 (CH), 94.7 (CH), 75.1 (CH), 73.1 (CH, *J*cp = 7.4 Hz), 72.5 (CH), 71.7 (CH), 70.3 (CH), 69.9 (CH), 69.6 (CH), 69.3 (CH, *J*cp = 8.4 Hz), 67.3 (CH_2, *J*cp = 5.6 Hz), 1.0 (CH_3), 0.9 (CH_3), 0.82 (CH_3), 0.76 (CH_3), 0.6 (CH_3), 0.5 (CH_3), 0.3 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ -12.04; HRMS (ESI) calcd for $C_{30}H_{53}O_9NaSi_4P$ $[M+Na]^+$ 723.2402, found 723.2399.



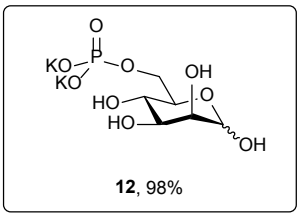
9, 97%
(α/β = 0.36/1)

Galactose 6-phosphate dipotassium salt (9). Procedure were as shown in the general procedures to afford **9** as a white powder (23 mg, 97%). (α:β= 0.36/1). $[\alpha]^{28}_D$ 115.6 (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.30 (d, *J* = 3.3 Hz, 1H, H-1), 4.64 (d, *J* = 7.8 Hz, 1H, H-1β), 4.19-4.00 (m, 4H, H-6aα, H-6bα, H-6aβ, H-6bβ), 3.91-3.89 (m, 4H, H-4α, H-4β, H-5α, H-5β), 3.85-3.81 (m, 2H, H-2α, H-4β), 3.93-3.67 (m, 2H, H-3α, H-3β), 3.48 (t, *J* = 7.8 Hz, 1H, H-2β); ^{13}C NMR (100 MHz,D_2O) δ 97.3 (CH), 93.0 (CH), 73.9 (CH, *J*cp = 6.3 Hz), 73.0 (CH), 72.7 (CH), 72.5 (CH), 70.4 (CH), 69.7 (CH), 69.5 (CH), 69.5 (CH), 69.4 (CH), 69.3 (CH), 69.1 (CH), 69.0 (CH), 68.9 (CH), 68.5 (CH), 66.2 (CH), 65.3 (CH_2), 63.4 (CH_2), 62.6 (CH_2), 62.4 (CH_2); ^{31}P NMR (162 MHz, D_2O) δ 0.82; HRMS (ESI) calcd for $C_6H_{14}O_9P$ $[M+H]^+$ 261.0375, found 261.0369.



11, 84% (99%)

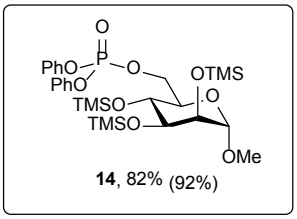
6-*O*-Diphenylphosphoryl-1,2,3,4-tetra-*O*-trimethylsilyl-α-D-mannopyranose (11). Procedures were as shown in the general procedures to afford **11** as a colourless syrup (320 mg, 84%) and the fully trimethylsilylated mannose (45 mg, 15%) (recovered yield of **11**: 99%). $[\alpha]^{32}_{D}$ 5.8 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.13 (m, 10H, Ph), 4.88 (s, 1H, H-1), 4.45 (ddd, *J* = 10.4, 6.4, 1.7 Hz, 1H, H-6a), 4.28 (ddd, *J* = 10.7, 6.4, 1.7 Hz, 1H, H-6b), 3.87-3.78 (m, 3H, H-3, H-4,H-5), 3.63 (t, *J* = 1.8 Hz, 1H, H-2), 0.14 (s, 9H, TMS), 0.10 (s, 9H, TMS) , 0.09 (s, 9H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0 (C), 150.9 (C), 139.9 (CH), 129.8 (CH), 125.34 (CH), 125.31 (CH), 120.6 (CH), 120.5 (CH), 120.4 (CH), 120.3 (CH), 95.6 (CH), 75.3 (CH), 72.8 (CH, *J*cp = 7.5 Hz), 72.3 (CH), 68.5 (CH_2, *J*cp = 5.7 Hz), 68.3 (CH), 0.9 (CH_3), 0.8 (CH_3), 0.5 (CH_3), 0.0 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.31; HRMS (ESI) calcd for $C_{30}H_{53}O_9NaSi_4P$ $[M+Na]^+$ 723.2402, found 723.2411.



12, 98%

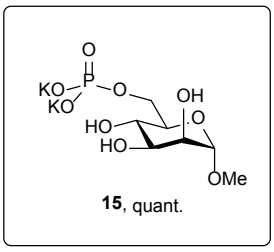
Mannose 6-phosphate dipotassium salt (12). Procedure were as shown in the general procedures to afford **12** as a white powder (23 mg, 98%). $[\alpha]^{29}_{D}$ 107.4 (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (d, *J* = 1.3 Hz, 1H, H-1α), 4.93 (s, 1H, H-1β), 4.08-3.83 (m, 4H, H-2a, H-2β, H-6aα, H-6bα), 3.80-3.64 (m, 6H, H-3α, H-3β, H-5α, H-5β, H-6aβ, H-6bβ), 3.46 (t, *J* = 3.3 Hz, 1H, H-4α), 3.43 (t, *J* = 3.3 Hz, 1H, H4β); ^{13}C NMR (100 MHz, $CDCl_3$) δ 94.6 (CH), 94.1 (CH), 75.7 (CH), 72.8 (CH), 71.9 (CH), 71.8 (CH_2), 71.5 (CH), 71.0 (CH),

70.1 (CH), 69.6 (CH_2), 69.5 (CH_2), 66.5 (CH), 66.2 (CH), 63.0 (CH_2), 60.5 (CH_2); ^{31}P NMR (162 MHz, D_2O) δ 4.97; HRMS (ESI) calcd for $C_6H_{14}O_9P$ $[M+H]^+$ 261.0375, found 261.0377.



14, 82% (92%)

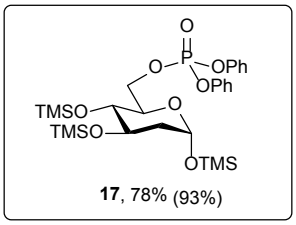
Methyl 6-*O*-diphenylphosphoryl-2,3,4-tri-*O*-trimethylsilyl-α-D-manno-pyranoside (14). Procedures were as shown in the general procedures to afford **14** as a colourless syrup (272 mg, 82%) and the fully trimethylsilylated mannose (27 mg, 11%) (recovered yield of **14**: 92%). $[\alpha]^{24}_D$ 5.6 (*c* 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.13 (m, 10H, Ph), 4.88 (s, 1H, H-1), 4.45 (ddd, *J* = 10.4, 6.4, 1.7 Hz, 1H, H-6a), 4.28 (ddd, *J* = 10.7, 6.4, 1.7 Hz, 1H, H-6b), 3.87-3.78 (m, 3H, H-3, H-4,H-5), 3.63 (t, *J* = 1.9, 1.8 Hz, 1H, H-2), 0.14 (s, 9H, TMS), 0.10 (s, 9H, TMS) , 0.09 (s, 9H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0 (C), 150.9 (C), 139.9 (CH), 129.8 (CH), 125.34 (CH), 125.31 (CH), 120.6 (CH), 120.5 (CH), 120.4 (CH), 120.3 (CH), 95.6 (CH), 75.3 (CH), 72.8 (CH, *J*cp = 7.5 Hz), 72.3 (CH), 68.5 (CH_2, *J*cp = 5.7 Hz), 68.3 (CH), 0.9 (CH_3), 0.8 (CH_3), 0.5 (CH_3), 0.0 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.68; HRMS (ESI) calcd for $C_{28}H_{47}O_9NaSi_3P$ $[M+Na]^+$ 665.2163, found 665.2161.



15, quant.

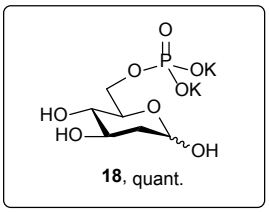
Methyl α-D-mannopyranoside 6-phosphate dipotassium salt (15). Procedure were as shown in the general procedures to afford **15** as a white powder (26 mg,

quant). $[\alpha]^{25}_{D}$ 33.8 (*c* 0.23, H_2O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 (s, 1H, H-1), 4.09 (ddd, *J* = 12.0, 5.0, 3.7 Hz, 1H, H-6a), 3.98 (d, *J* = 12.0, 5.0, 2.0 Hz, 1H, H-6b), 3.95 (dd, *J* = 3.4, 1.6 Hz, 1H, H-2), 3.89 (t, *J* = 10.0 Hz, 1H, H-4), 3.80 (dd, *J* = 10.0, 3.4 Hz, 1H, H-3), 3.6-3.67 (m, 1H, H-5), 3.44 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, D_2O) δ 101.2 (CH), 72.1 (d, J_{CP} = 7.3 Hz, CH), 70.3 (CH), 70.1 (CH), 66.1 (CH), 62.6 (d, J_{CP} = 4.0 Hz, CH_2), 57.8 (CH_3); ^{31}P NMR (202 MHz, D_2O) δ 4.69; HRMS (ESI) calcd for $C_7H_{14}O_9P$ $[M–2K+H]^-$ 273.0375, found 273.0367.



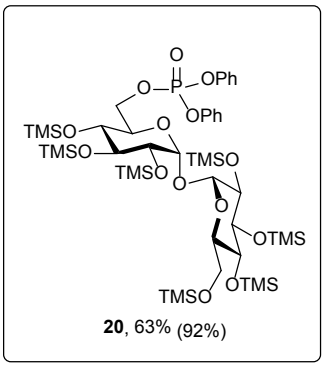
17, 78% (93%)

6-*O*-Diphenylphosphoryl-2-deoxy-1,3,4-tri-*O*-trimethylsilyl-α-D-gluco-pyranoside (17). Procedures were as shown in the general procedures to afford **17** as a colourless syrup (290 mg, 78%) and the fully trimethylsilylated 2-deoxy-D-glucopyranose (44 mg, 16%) (recovered yield of **17**: 93%). $[\alpha]^{30}_{D}$ 49.5 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.14 (m, 10H, Ph), 5.13 (s, 1H, H-1), 4.42 (td, *J* = 10.7, 7.0 Hz, 1H, H-6a), 4.34 (td, *J* = 10.7, 7.0 Hz, 1H, H-6b), 3.96 (td, *J* = 12.0, 9.0 Hz, 1H, H-3), 3.82 (ddd, *J* = 10.7, 9.0, 7.0 Hz, 1H, H-5), 3.44 (t, *J* = 9.0 Hz, 1H, H-4), 1.88 (dd, *J* = 12.0, 4.3, 1H, H-2ax), 1.54 (t, *J* = 12.0 Hz, 1H, H-2eq), 0.13 (s, 9H, TMS), 0.11 (s, 9H, TMS), 0.09 (s, 9H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0 (C), 151.01 (C), 150.96 (C), 150.89 (C), 129.9 (CH), 129.8 (CH), 125.4 (CH), 125.3 (CH), 120.42 (CH), 120.38 (CH), 120.34 (CH), 92.3 (CH), 72.9 (CH), 71.4 (CH, *J*cp = 7.0 Hz), 70.1 (CH), 68.5 (CH_2, *J*cp = 5.8 Hz), 41.2 (CH_2), 0.9 (CH_3), 0.8 (CH_3), 0.07 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.35; HRMS (ESI) calcd for $C_{27}H_{45}O_8NaSi_3P$ $[M+Na]^+$ 635.2058, found 635.2064.



18, quant.

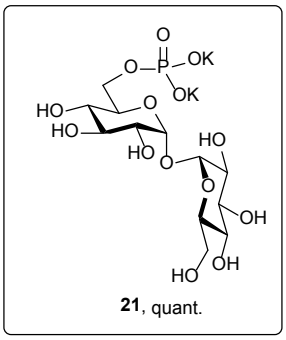
2-Deoxy-D-glucose 6-phosphate dipotassium. (18). Procedure were as shown in the general procedures to afford **18** as a white powder (26 mg, quant). $[\alpha]^{30}_{D}$ -1175.3 (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 4.08-3.91 (m, 6H, H-3α, H-3β, H-5α, H-5β, H-6aα, H-6bα), 3.84-3.75 (m, 4H, H-1α, H-1β, H-6aβ, H-6bβ), 3.61-3.55 m, 2H, H-4α, H-4β), 1.97-1.78 (m, 2H, H-2αa, H-2αb), 1.65-1.58 (m, 2H, H-2βa, H-2βb); ^{13}C NMR (100 MHz, D_2O) δ 72.5 (CH), 71.9 (CH), 71.7 (CH), 70.8 (CH, *J*cp = 53.2 Hz), 67.1 (CH), 65.4 (CH_2, *J*cp = 4.3 Hz), 58.8 (CH), 35.4 (CH), 25.8 (CH); ^{31}P NMR (162 MHz, D_2O) δ 1.34; HRMS (ESI) calcd for $C_6H_{12}O_8P$ $[M-2K+H]^-$ 243.0270, found 243.0276.



20, 63% (92%)

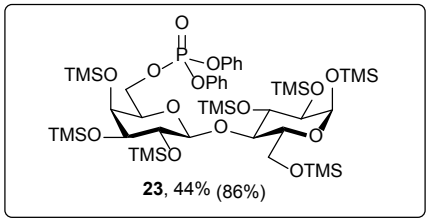
6-*O*-Diphenylphosphoryl-2,3,4,2',3',4',6'-hepta-*O*-trimethylsilyl-α,α'-trehalose (20). Procedures were as shown in the general procedures to afford **20** as a colourless syrup (198 mg, 63%) and the fully trimethylsilylated trehalose (84 mg, 31%) (recovered yield of **20**: 92%). $[\alpha]^{32}_{D}$ 81.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 4H, Ph), 7.24-7.21 (m, 2H, Ph), 7.17-7.13 (m, 4H, Ph), 4.85 (d, *J* = 3.1 Hz, 1H, H-1'), 4.81 (d, *J* = 3.0 Hz, 1H, H-1), 4.41 (ddd, *J* = 9.6, 7.3, 3.6 Hz, 1H, H-6'a), 4.30 (ddd, *J* = 9.3, 7.3, 3.6 Hz, 1H, H-6'b), 3.95 (ddd, *J* = 9.3, 7.3, 3.6 Hz, 1H, H-5), 3.86 (t, *J* = 9.3 Hz, 1H, H-3),

3.84 (t, *J* = 9.3 Hz, 1H, H-3'), 3.74 (td, *J* = 9.3, 2.5 Hz, 1H, H-5'), 3.69-3.63 (m, 2H, H-6'a, H-6'b), 3.45 (t, *J* = 9.3 Hz, 1H, H-4), 3.43 (t, *J* = 9.3 Hz, 1H, H-4'), 3.34 (dd, *J* = 9.3, 3.1 Hz, 1H, H-2'), 3.25 (dd, *J* = 9.3, 3.0 Hz, 1H, H-2), 0.12 (s, 9H, TMS), 0.11 (s, 9H, TMS), 0.10 (s, 9H, TMS), 0.09 (s, 9H, TMS), 0.08 (s, 9H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.8 (C), δ 150.74 (C), δ 150.68 (C), δ 150.63 (C), 129.7 (CH), 125.2 (CH), 120.11 (CH), 120.07 (CH), 120.0 (CH), 94.7 (CH), 94.4 (CH), 73.50 (CH), 73.48 (CH), 73.38 (CH), 72.8 (CH), 72.5 (CH), 71.6 (CH), 71.5 (d, J_{CP} = 6.6 Hz, CH), 67.9 (d, J_{CP} = 5.9 Hz, CH_2), 61.9 (CH), 1.07 (CH_3), 1.05 (CH_3), 1.00 (CH_3), 0.90 (CH_3), 0.86 (CH_3), 0.18 (CH_3), 0.11 (CH_3); ^{31}P NMR (202 MHz, $CDCl_3$) δ -11.50; HRMS (ESI) calcd for $C_{45}H_{87}O_{14}NaSi_7P$ $[M+Na]^+$ 1101.4116, found 1101.4114.



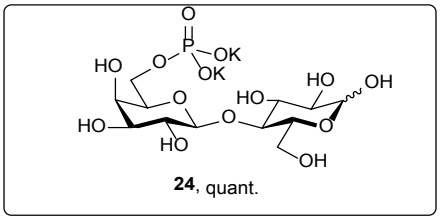
21, quant.

Trehalose 6-phosphate dipotassium salt (21). Procedure were as shown in the general procedures to afford **21** as a white powder (23 mg, quant). $[\alpha]^{30}_D$ 110.5 (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.23 (d, *J* =4.1 Hz, 1H, H-1), 5.20 (d, *J*=3.4 Hz, 1H, H-1'), 4.05 (ddd, *J*= 11.7, 6.8, 3.6 Hz, 1H, H-6a), 3.96 (ddd, *J*= 11.5, 5.0, 2.5 Hz, 1H, H-6b), 3.91-3.82 (m, 5H, H-3, H-3', H-5, H-5', H-6a'), 3.76 (t, *J* = 8.3 Hz, 1H, H-4), 3.70 (dd, *J* = 9.8, 4.1 Hz, 1H, H-6b'), 3.64 (dd, *J* = 9.4, 3.4 Hz, 1H, H-2'), 3.46 (t, *J* = 9.3 Hz, 1H, H-4'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 93.5 (CH), 93.3 (CH), 72.5(CH), 72.2 (CH), 72.2 (CH), 71.8 (CH), 71.3 (CH), 71. 0 (CH), 69.7 (CH), 69.7 (CH), 69.2 (CH), 62.5 (CH_2), 60.6 (CH_2); ^{31}P NMR (162 MHz, D_2O) δ 4.89; HRMS (ESI) calcd for $C_{12}H_{22}O_{14}P$ $[M-2K+H]^-$ 421.0747, found 421.0742.



23, 44% (86%)

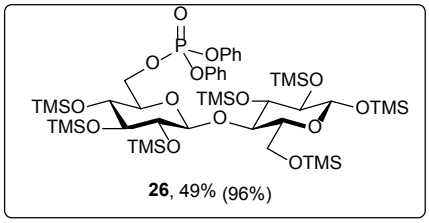
6'-*O*-Diphenylphosphoryl-1,2,3,6,2',3',4'-hepta-*O*-trimethylsilyl-lactose (23). Procedures were as shown in the general procedures to afford **23** as a colourless syrup (140 mg, 44%) and the fully trimethylsilylated lactose (130 mg, 49%) (recovered yield of **23**: 86%). $[\alpha]^{30}_{D}$ 188.8 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 4H, Ph), 7.20-7.14 (m, 6H, Ph), 5.01 (s, 1H, H-1), 4.36 (dd, *J* = 9.6, 5.7, 1.6 Hz, 1H, H-6'a), 4.264 (d, *J* = 7.7 Hz, 1H, H-1'), 4.259 (ddd, *J* = 9.4, 5.7, 1.6 Hz, 1H, H-6'b), 3.98 (d, *J* = 11.0 Hz, 1H, H-6a), 3.79 (bs, 1H, H-4'), 3.72 (ddd, *J* = 11.0, 8.6, 4.7 Hz, 1H, H-5), 3.70 (t, *J* = 8.7 Hz, 1H, H-3'), 3.65-3.59 (m, 3H, H-2', H-4, H-6b'), 3.52 (ddd, *J* = 9.6, 5.7, 1.6 Hz, 1H, H-5'), 3.40 (dd, *J* = 7.7, 1.6 Hz, 1H, H-2), 3.30 (dd, *J* = 9.2, 2.4 Hz, 1H, H-3'), 0.12 (bs, 18H, TMS), 0.10 (s, 9H, TMS), 0.08 (bs, 27H, TMS), 0.05 (s, 9H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.77 (C), 150.72 (C), 130.0 (CH), 125.6 (CH), 120.29 (CH), 120.25 (CH), 102.4 (CH), 94.2 (CH), 75.8 (CH), 75.2 (CH), 74.1 (CH), 72.7 (CH), 71.9 (CH), 71.1 (CH, *J*cp = 6.5 Hz), 66.5 (CH_2, *J*cp = 5.3 Hz), 60.8 (CH_2), 1.1 (CH_3), 1.0 (CH_3), 0.7 (CH_3), 0.6 (CH_3), 0.5 (CH_3), 0.3 (CH_3), 0.0 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.72; HRMS (ESI) calcd for $C_{45}H_{87}O_{14}NaSi_7P$ $[M+Na]^+$ 1101.4116, found 1101.4108.



24, quant.

Lactose 6'-phosphate dipotassium salt (24). Procedure were as shown in the general procedures to afford **24** as a white powder (23 mg, quant). $[\alpha]^{30}_{D}$ -

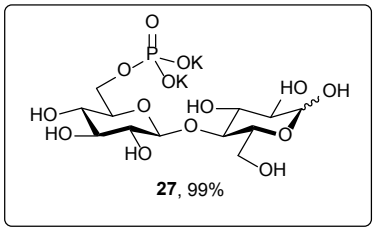
1088.4 (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.28 (d, *J* = 3.1 Hz, 1H, H-1α), 4.71 (d, *J* = 7.7 Hz, 1H, H-1'), 4.51 (d, *J* = 7.8 Hz, 1H, H-1β), 4.09-3.56 (m, 17H, H-2α, H-3α, H-3β, H-4α, H-4β, H-5α, H-5β, H-6aα, H-6bα, H-6aβ, H-6bβ, H-2', H-3', H-4', H-5', H-6'a, H-6'b), 3.31 (t, *J* = Hz, 1H, H-2β); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.1 (CH), 96.7 (CH), 92.5 (CH), 73.4 (CH), 74.7 (CH), 74.5 (CH), 74.3 (CH), 74.2 (CH), 72.4 (CH), 71.6 (CH), 71.5 (CH), 71.1 (CH), 69.9 (CH), 68.2 (CH), 62.3 (CH_2), 60.4 (CH_2), 60.2 (CH_2); ^{31}P NMR (162 MHz, D_2O) δ 4.86; HRMS (ESI) calcd for $C_{12}H_{22}O_{14}P$ $[M-H]^-$ 421.0747, found 421.0749.



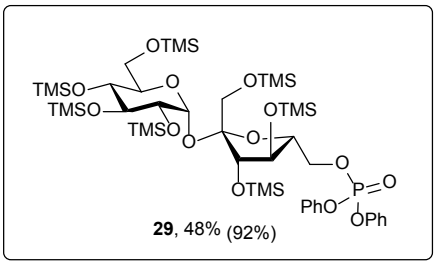
26, 49% (96%)

6'-*O*-Diphenylphosphoryl-1,2,3,6,2',3',4'-hepta-*O*-trimethylsilyl-cellobiose (26). Procedures were as shown in the general procedures to afford **26** as a colourless syrup (155 mg, 49%) and the fully trimethylsilylated cellobiose (131 mg, 49%) (recovered yield of **26**: 96%). $[\alpha]^{30}_D$ 189.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 4H, Ph), 7.24-7.20 (m, 4H, Ph), 7.16-7.13 (m, 2H, Ph), 4.50 (ddd, *J* = 10.5, 6.3, 2.2 Hz, 1H, H-6'a), 4.47 (d, *J* = 7.4 Hz, 1H, H-1), 4.42 (d, *J* = 7.6 Hz, 1H, H-1'), 4.10 (ddd, *J* = 10.0, 7.8, 5.2 Hz, 1H, H-6'b), 3.88 (ddd, *J* = 11.1, 3.7 Hz, 1H, H-6a), 3.78-3.72 (m, 2H, H-3, H-6b), 3.45 (t, *J* = 8.8 Hz, 1H, H-4'), 3.39 (ddd, *J* = 10.5, 8.8, 6.3 Hz, 1H, H-5'), 3.31 (t, *J* = 8.8 Hz, 1H, H-3'), 3.25-3.20 (m, 4H, H-2, H-2'. H-4, H-5), 0.16 (s, 9H, TMS), 0.14 (s, 9H, TMS), 0.13 (s, 9H, TMS), 0.12 (s, 9H, TMS), 0.10 (s, 9H, TMS), 0.08 (s, 9H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.91 (C), 150.87 (C), 150.84 (C), 130.1 (CH), 130.0 (CH), 125.5 (CH), 125.4 (CH), 120.52 (CH), 120.49 (CH), 102.0 (CH), 98.6 (CH), 78.2 (CH), 77.0 (CH), 76.6 (CH), 75.9 (CH), 75.7 (CH), 75.6 (CH), 75.0 (CH), 72.3 (CH), 68.7 (CH_2, *J*cp = 5.1 Hz),

1.5 (CH_3), 1.4 (CH_3), 1.3 (CH_3), 1.2 (CH_3), 0.7 (CH_3), 0.3 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.48; HRMS (ESI) calcd for $C_{45}H_{87}O_{14}NaSi_7P$ $[M+Na]^+$ 1101.4116, found 1101.4109.

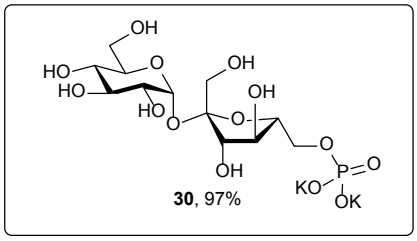


Cellobiose 6'-phosphate dipotassium salt (27). Procedures were as shown in the general procedures to afford **27** as a white powder (23 mg, 99%). $[\alpha]^{29}_D$ -118.3 (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.27 (d, *J* = 3.8 Hz, 1H), 4.71 (d, *J* = 8.1 Hz, 1H), 4.55 (d, *J* = 8.1 Hz, 1H), 4.69-3.96 (m, 4H), 3.93-3.86 (m, 4H), 3.69-3.54 (m, 8H), 3.39 (dd, J = 8.1, 4.4 Hz, 1H), 3.33 (dd, J = 8.1, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, D_2O) δ 102.19 (CH), 95.8 (CH), 91.8 (CH), 79.4 (CH), 79.3 (CH), 75.5 (CH, *J*cp = 7.0 Hz), 75.0 (CH), 74.8 (CH), 74.0 (CH), 73.9 (CH), 73.4 (CH), 71.4 (CH), 71.2 (CH), 70.1 (CH), 69.1 (CH), 69.0 (CH_2), 62.7 (CH_2, *J*cp = 3.7 Hz), 60.2 (CH_2), 60.1 (CH_2); ^{31}P NMR (162 MHz, D_2O) δ 5.05; HRMS (ESI) calcd for $C_{12}H_{22}O_{14}PK_2$ $[M+H]^+$ 499.0021, found 499.0016.



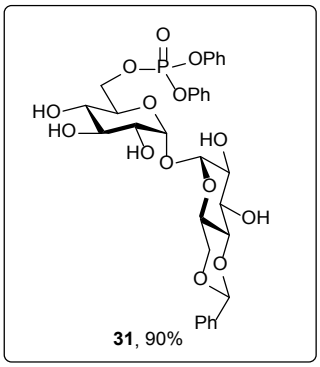
6'-*O*-Diphenylphosphoryl-2,3,4,6,1',2',3'-hexa-*O*-trimethylsilyl-α,α'-sucrose (29). Procedures were as shown in the general procedures to afford **29** as a colourless syrup (151 mg, 48%) and the fully trimethylsilylated sucrose (128 mg, 48%) (recovered yield of **29**: 92%). $[\alpha]^{30}_D$ 36.1 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 4H, Ph) 7.23-7.20 (m, 2H, Ph), 7.18-

7.14 (m, Ph, 4H), 5.18 (d, J = 3.3 Hz, 1H, H-1), 4.59 (ddd, J = 12.0, 6.4, 2.5 Hz, 1H, H-6'a), 4.33 (ddd, J = 10.7, 6.4, 2.5 Hz, 1H, H-6'b), 4.32 (d, J = 8.0 Hz, 1H, H-4), 3.99-3.98 (m, 2H, H-3', H-5'), 3.82-3.65 (m, 4H, H-1', H-3, H-4, H-5), 3.55 (d, J = 11.7 Hz, 1H, H-6a), 3.44 (t, J = 9.3 Hz, 1H, H-2'), 3.41 (d, J = 11.5 Hz, 1H, H-6b), 3.29 (dd, J = 9.5, 3.3 Hz, 1H, H-2), 0.17 (s, 9H, TMS), 0.156 (s, 18H, TMS), 0.155 (s, 9H, TMS), 0.12 (s, 9H, TMS), 0.10 (s, 9H, TMS), 0.09 (s, 9H, TMS), 0.07 (s, 9H, TMS); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9 (C), 129.9 (CH), 125.4 (CH), 120.4 (CH), 104.2 (C), 92.2 (CH), 80.2 (CH_2, Jcp = 6.9 Hz), 76.5 (CH), 73.8 (CH), 73.5 (CH), 73.0 (CH), 72.1 (CH), 70.5 (CH_2, Jcp = 6.4 Hz), 63.0 (CH_2), 62.3 (CH_2), 1.4 (CH_3), 1.2 (CH_3), 0.9(CH_3), 0.8 (CH_3), 0.5 (CH_3), 0.0 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.86; HRMS (ESI) calcd for $C_{45}H_{87}O_{14}NaSi_7P$ $[M+Na]^+$ 1101.4116, found 1101.4124.



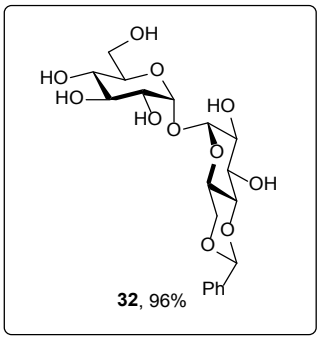
30, 97%

Sucrose 6'-phosphate dipotassium salt (30). Procedures were as shown in the general procedures to afford **30** as a white powder (22 mg, 97%). $[\alpha]^{30}_D$ -152.9 (*c* 0.5, H_2O); ^{1}H NMR (400 MHz, D_2O) δ 5.44(d, J = 3.9 Hz, 1H, H-1), 4.28-4.22 (m, 2H, H-3', H-4'), 4.09 (ddd, J = 10.3, 4.7, 2.3 Hz, 1H, H-6'a), 4.02-3.88 (m, 5H, H-1'ax, H-1'eq, H-5, H-5', H-6'b), 3.86-3.74 (m, 4H, H-2', H-3, H-6a, H-6b), 3.57 (dd, J = 10.0, 3.9 Hz, 1H, H-2), 3.39 (t, J = 9.8 Hz, 1H, H-4); ^{13}C NMR (100 MHz, D_2O) δ 102.8 (C), 92.4 (CH), 80.4 (CH, Jcp = 8.2 Hz), 76.2 (CH), 73.8 (CH), 72.5 (CH, Jcp = 7.9 Hz), 71.3 (CH), 69.9 (CH), 69.6 (CH_2), 64.0 (CH_2), 61.1 (CH_2), 60.4 (CH_2); ^{31}P NMR (162 MHz, D_2O) δ 4.35; HRMS (ESI) calcd for $C_{12}H_{22}O_{14}PK_2$ $[M+H]^+$ 499.0021, found 499.0045.



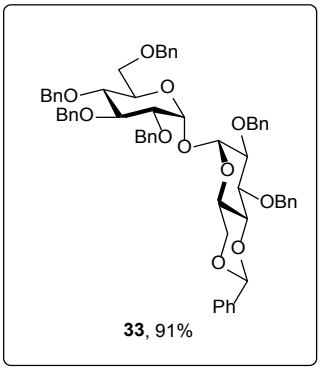
31, 90%

4',6'-*O*-Benzylidene-6-*O*-diphenylphosphoryl–α,α'-trehalose (31). Compound **20** (121.5 mg, 0.118 mmol) was mixed with benzaldehyde (15 µL, 0.142 mmol) in CH_2Cl_2 (1.2 mL) under N_2, and TMSOTf (2 µL, 0.012 mmol) was added at 0 °C. After stirring for 30 min, the reaction mixture was evaporated to give a yellow oil, which was dissolved in MeOH (2 mL). The mixture was added acidic Amberlite resin IR-120 (50 mg) and stirred at room temperature for 1 h. The resin was filtered off and the filtrate was concentrated *in vacuo*. The mixture was purified by flash column chromatography (MeOH/Chloroform 1:9) on silica gel to furnish the desired product **31** (71 mg, 90%). $[\alpha]^{25}_{D}$ 143.8 (*c* 0.1, MeOH); ^{1}H NMR (500 MHz, (MeOD) δ 7.46-7.43 (m, 2H, Ph), δ 7.37-7.33 (m, 4H, Ph), δ 30-7.27 (m, 3H, Ph), 7.21-7.17 (m, 6H, Ph), 5.52 (s, 1H, PhCH), 5.02 (d, *J* = 3.9 Hz, 1H, H-1'), 4.98 (d, *J* = 3.8 Hz, 1H, H-1), 4.51-4.38 (m, 2H, H-6a, H-6b), 4.17 (dd, *J* = 10.1, 5.1 Hz, 1H, H-6'eq), 4.07-4.00 (m, 2H, H-5, H-5'), 3.94 (t, *J* = 9.6 Hz, 1H, H-3'), 3.76 (t, *J* = 9.6 Hz, 1H, H-3), 3.67 (t, *J* = 10.1 Hz, 1H, H-6'ax), 3.53 (dd, *J* = 9.6, 3.9 Hz, 1H, H-2'), 3.45-3.28 (m, 3H, H-2, H-4, H-4'); ^{13}C NMR (125 MHz, MeOD) δ 152.04 (C), 151.96 (CH), 139.3 (C), 131.2 (CH), 130.0 (CH), 129.2 (CH), 127.7 (CH), 126.9 (CH), 121.34 (CH), 121.29 (CH), 103.2 (CH), 96.3 (CH), 95.8 (CH), 83.2 (CH), 74.5 (CH), 73.9 (CH), 73.1 (CH), 72.2 (CH, *J*cp = 6.2 Hz), 71.8 (CH), 71.3 (CH), 70.1 (CH_2), 69.9 (CH_2, *J*cp = 6.0 Hz), 64.3 (CH); ^{31}P NMR (162 MHz, MeOD) δ -11.45; HRMS (ESI) calcd for $C_{31}H_{35}O_{14}NaP$ $[M+Na]^+$ 685.1662, found 685.1666.



32, 96%

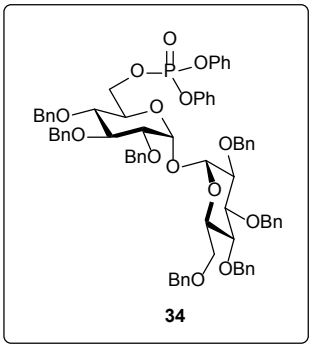
4,6-*O*-Benzylidene–α,α'-trehalose (32). A solution of compound **31** (40 mg, 0.06 mmol), $NaNO_2$ (22 mg, 0.30 mmol) and DMF (1 mL) was subjected to microwave irradiation (200 W, 150 ^oC) for 30 mins. The mixture was concentrated and purified by column chromatograph (MeOH/Chloroform 1:5) on silica gel to yield the compound **32** (25 mg, 96%). $[\alpha]^{24}_D$ 15.5 (*c* 0.1, MeOH); ^1H NMR (500 MHz, $(CD_3)_2CO$) δ 7.53-7.49 (m, 2H, Ph), 7.36-7.34 (m, 3H, Ph), 5.58 (s, 1H, PhCH), 5.15 (d, *J* = 3.8 Hz, 1H, H-1), 5.09 (d, *J* = 3.7 Hz, 1H, H-1'), 4.17 (dd, *J* = 9.9, 4.9 Hz, 1H, H-6eq), 4.10 (td, *J* = 9.9, 5.0 Hz, 1H, H-5), 4.03 (t, *J* = 9.2 Hz, 1H, H-3), 3.93 (ddd, *J* = 9.5, 4.7, 2.7 Hz, 1H, H-5'), 3.87 (t, *J* = 9.5 Hz, 1H, H-3'), 3.77-3.58 (m, 3H, H-2, H-6'a, H-6'b), 3.48-3.45 (m, 2H, H-2', H-4), 3.40 (t, *J* = 9.5 Hz, 1H, H-4'), 2.78 (bs, 6H, OH); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 139.3 (C), 129.5 (CH), 128.7 (CH), 127.3 (CH), 102.2 (CH), 95.5 (CH), 95.2 (CH), 82.9 (CH), 74.5 (CH), 73.9 (CH), 73.5 (CH), 73.2 (CH), 72.1 (CH), 71.4 (CH), 69.6 (CH_2), 63.7 (CH), 62.8 (CH_2).



33, 91%

4,6-*O*-Benzylidene-2,3,2',3'4',6'-hexa-*O*-benzyl–α,α'-trehalose (33). To a solution of **32** (20.0mg, 0.046 mmol) and benzyl bromide (39 μL, 0.334 mmol)

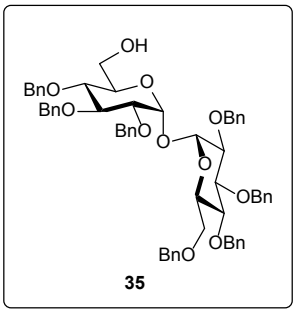
in DMF (0.5 mL) was added sodium hydride (22 mg, 0.557 mmol) at 0 °C. The mixture was stirred at room temperature overnight and was quenched by the slow addition of water (7 mL) at 0 °C. The mixture was extracted with EtOAc twice. The organic layer was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by silica gel chromatography with hexane/EtOAc 5:1 as the eluent to afford compound **33** as a colorless oil (40.7 mg, 91%). $[\alpha]^{24}_D$ 36.2 (*c* 0.21, $CDCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H, Ph), 7.40-7.20 (m, 31H, Ph), 7.14-7.12 (m, 2H, Ph), 5.55 (s, 1H, PhCH), 5.18-5.17 (m, 2H, H-1, H-1'), 4.97 (d, *J* = 14.7 Hz, 1H, $PhCH_2$), 4.95 (d, *J* = 14.5 Hz, 1H, $PhCH_2$), 4.86-4.66 (m, 7H, $PhCH_2$), 4.53 (d, *J* = 11.8 Hz, 1H, $PhCH_2$), 4.46 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.38 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.27 (td, *J* = 9.7, 4.7 Hz, 1H, H-5), 4.17-4.10 (m, 3H, H-4', H-5', H-6eq), 4.03 (t, *J* = 7.4 Hz, 1H, H-3), 3.69-3.57 (m, 5H, H-2, H-2', H-3', H-4, H-6ax), 3.50 (dd, *J* = 10.7, 2.9 Hz, 1H, H-6'a), 3.37 (d, *J* = 10.7 Hz, 1H, H-6'b); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9 (C), 138.8 (C), 138.4 (C), 138.2 (C), 138.1 (C), 137.9 (C), 137.6 (C), 128.8 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 128.0 (CH), 127.89 (CH), 127.88 (CH), 127.7 (CH), 127.6 (CH), 127.54 (CH), 127.52 (CH), 126.1 (CH), 101.2 (CH), 95.0 (CH), 94.5 (CH), 82.4 (CH), 81.8 (CH), 79.4 (CH), 78.9 (CH), 78.7 (CH), 77.7 (CH), 75.6 (CH_2), 75.3 (CH_2), 75.0 (CH_2), 73.5 (CH_2), 73.2 (CH_2), 70.7 (CH), 69.1 (CH_2), 68.2 (CH_2), 62.9 (CH); HRMS (ESI) calcd for $C_{61}H_{62}O_{11}Na$ $[M+Na]^+$ 993.4190, found 993.4205.



34

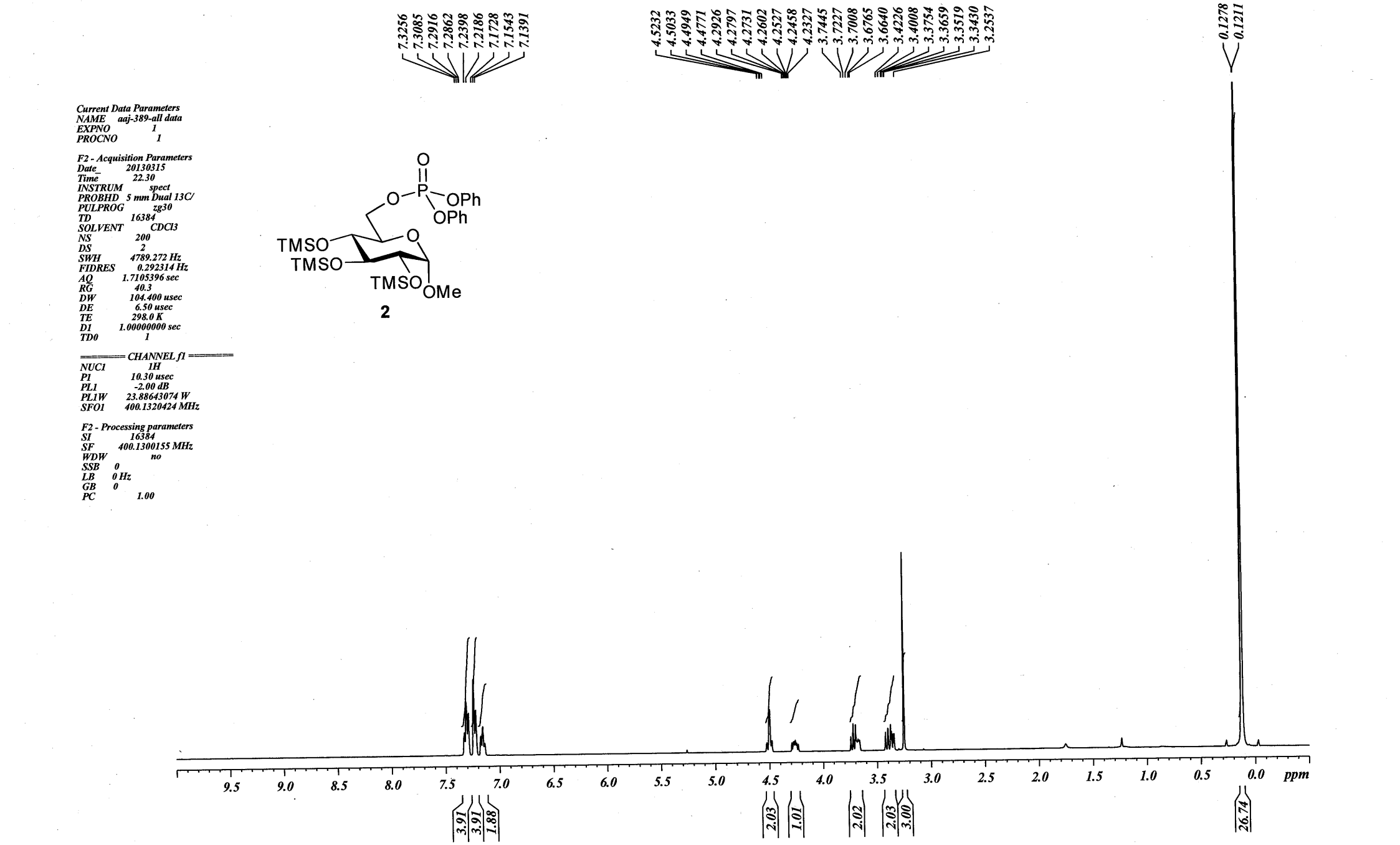
6-*O*-Diphenylphosphoryl-2,3,4,2',3',4',6'-hepta-*O*-benzyl–α,α'-trehalose

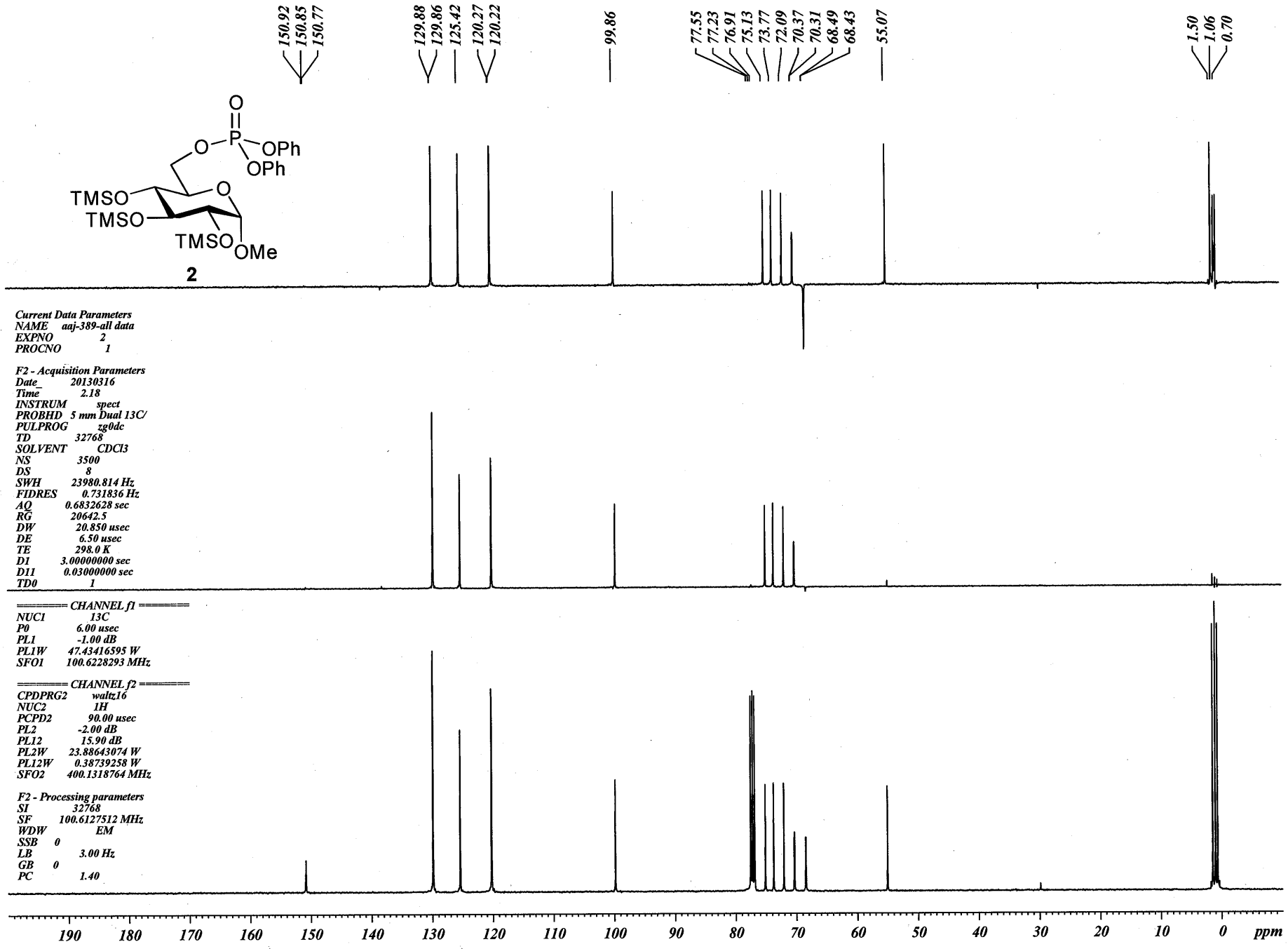
(34). Compound **20** (118 mg, 0.115 mmol) was mixed with acidic Amberlite resin IR-120 (50 mg), and the mixture was stirred at room temperature for 1 h. The resin was filtered, and the filtrate was concentrated *in vacuo* to give a colorless oil. The oil was mixed with 2,4,6-tris(benzyloxy)-1,3,5-triazinee (321 mg, 0.803 mmol) in 1,4-dioxane (4 mL) under N_2. TfOH (14 μL, 0.092 mmol) was added at room temperature. After the system was stirred for 4 h, the reaction mixture was evaporated to give a yellow oil. The mixture was purified by flash column chromatography (Hex/EtOAc 3:1) on silica gel to furnish the desired product **34** (98 mg, 71%) $[\alpha]^{30}_{D}$ 203.4 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.10 (m, 45H, Ar-H), 5.15 (d, *J* = 3.7 Hz, 1H, H-1), 5.10 (d, *J* = 3.4 Hz, 1H, H-1'), 4.98 (d, *J* = 2.6 Hz, 1H, CH_2Ph), 4.95 (d, *J* = 2.4 hz, 1H, CH_2Ph), 4.86 (m, 4H, CH_2Ph), 4.70-4.6 (m, 3H, CH_2Ph), 4.60-4.52 (m, 4H, CH_2Ph), 4.47-4.37 (m, 3H, CH_2Ph), 4.15-4.11 (m, 4H, H-5, H-5' H-6a, H-6b), 3.99 (t, *J* = 9.3 Hz, 2H, H-3, H-3'), 3.65 (t, *J* = 9.6 Hz, 1H, H-4'), 3.56 (dd, *J* = 9.2, 3.7 Hz, 1H, H-2), 3.52 (dd, *J* = 6.6, 3.2 Hz, 1H, H-4), 3.48 (d, *J* = 11.1 Hz, 1H, H-6'a), 3.41 (dd, *J* = 9.6, 3.4 Hz, 1H, H-2'), 3.38 (dd, *J* = 11.2, 2.3 Hz, 1H, H-6'b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9 (C), 150.8 (C), 150.7 (C), 139.0, 138.9, 138.5, 138.3, 138.2, 138.1, (Ch_2), 129.9 (CH), 129.8 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.8 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 125.5 (CH), 125.4 (CH), 120. (CH), 120.2 (CH), 94.6 (CH), 94.3 (CH), 82.0 (CH), 81.6 (CH), 79.6 (CH), 79.5 (CH), 78.0 (CH), 77.7 (CH), 77.0 (CH), 75.8 (CH_2), 75.7 (CH_2), 75.2 (CH_2), 73.7 (CH_2), 73.2 (CH_2), 72.9 (CH_2), 71.0 (CH), 69.9 (CH), 69.8 (CH), 67.5 (CH_2), 67.5 (CH_2); ^{31}P NMR (162 MHz, $CDCl_3$) δ -11.45; HRMS (ESI) calcd for $C_{73}H_{73}O_{14}PNa$ $[M+Na]^+$ 1227.4636, found 1227.4618.



35

2,3,4,2',3',4',6'-hepta-*O*-benzyl–α,α'-trehalose (35). A mixture of compound **34** (27mg, 0.022 mmol), $NaNO_2$ (8mg, 0.116 mmol) and DMF (1.5 mL) was subjected to microwave irradiation (200 W, 150 ^oC) for 30 mins. The mixture was concentrated and purified by column chromatograph (Hex/EtOAc 3:1) on silica gel to yield the compound **35** (16 mg, 75%). $[\alpha]^{30}_D$ 181.0 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.18 (m, 33H, Ar-H), 7.11-7.08 (m, 2H, Ar-H), 5.15 (d, *J* = 3.8 Hz, 1H, H-1), 5.14 (d, *J* = 3.8 Hz, 1H, H-1'), 4.97 (d, *J* = 1.7 Hz, 1H, CH_2Ph), 4.95 (d, *J* = 1.7 Hz, 1H, CH_2Ph), 4.85-4.77 (m, 4H, CH_2Ph), 4.69-4.60 (m, 5H, CH_2Ph), 4.49-4.34 (m, 3H, CH_2Ph), 4.11 (dt, *J* = 11.1, 4.8, 2.7 Hz, 1H, H-5'), 4.05-3.98 (m, 3H, H-3, H-3', H-5), 3.64 (t, *J*= 9.6 Hz, 1H, H-4), 3.58-3.54 (m, 4H, H-2, H-4', H-6a, H-6b), 3.50 (dd, *J* = 8.3, 3.8 Hz, 1H, H-2'), 3.74 (dd, J = 3,7, 5,9 Hz, 1H, H-6'a), 3.35 (dd, *J*= 10.5, 2.0 Hz, 1H, H-6'b), 1.43 (t, *J* = 6.4 Hz, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0 (C), 138.6 (C), 138.5 (C), 138.3 (C), 138.1 (C), 128.6, 128.5, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6 (7× OCH_2Ph), 94.4 (CH), 94.2 (CH), 82.0 (CH), 81.8 (CH), 79.8 (CH), 79.6 (CH), 78.0 (CH), 77.7 (CH), 77.4 (CH), 75.8 (CH_2), 75.2 (CH_2), 73.7 (CH_2), 73.2 (CH_2), 73.1(CH_2), 71.4 (CH), 70.0 (CH), 68.5 (CH_2), 61.8 (CH_2), 29.9 (CH_2); HRMS (ESI) calcd for $C_{61}H_{64}O_{11}Na$ $[M+Na]^+$ 995.4346, found 995.4352.





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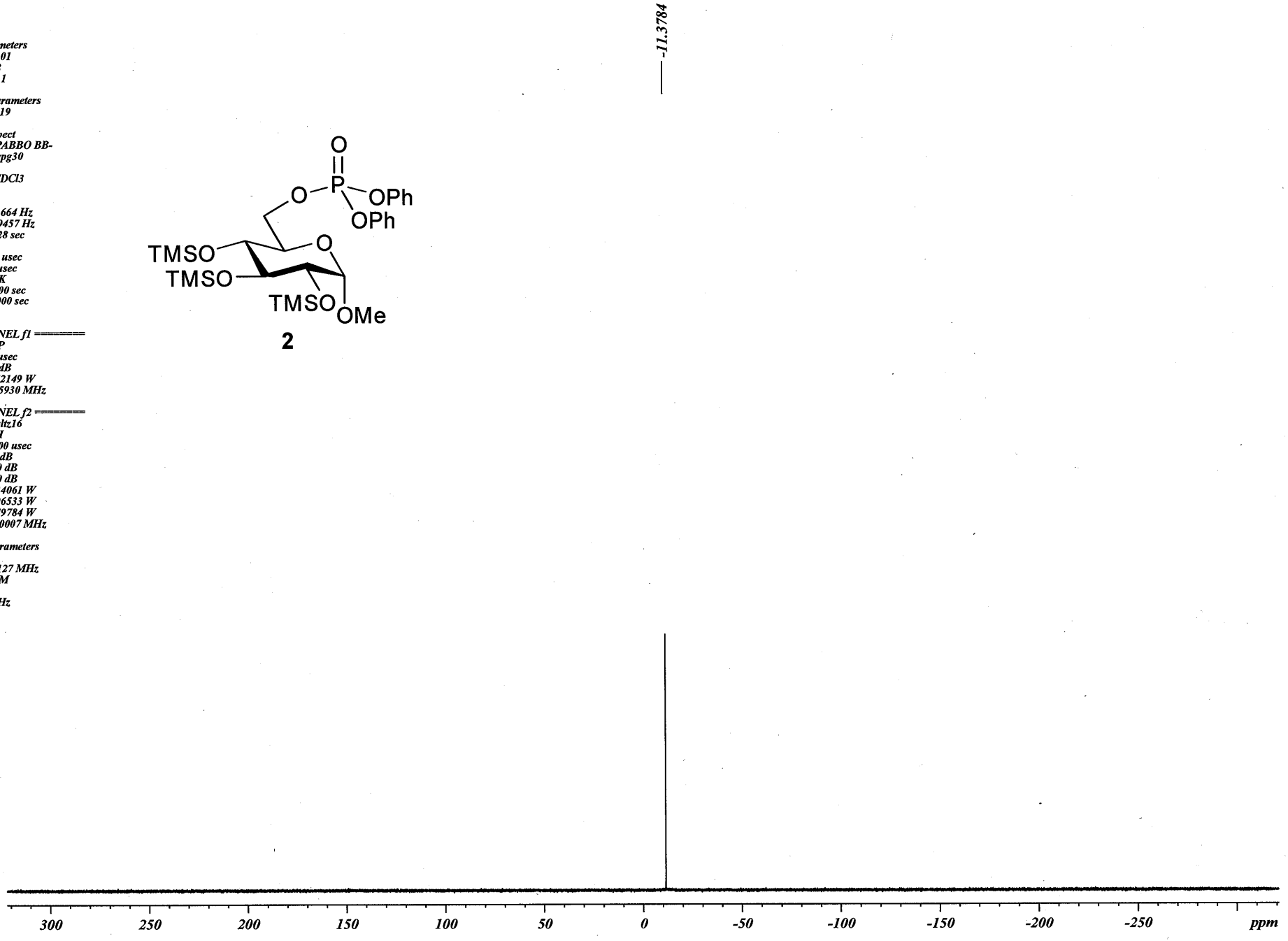

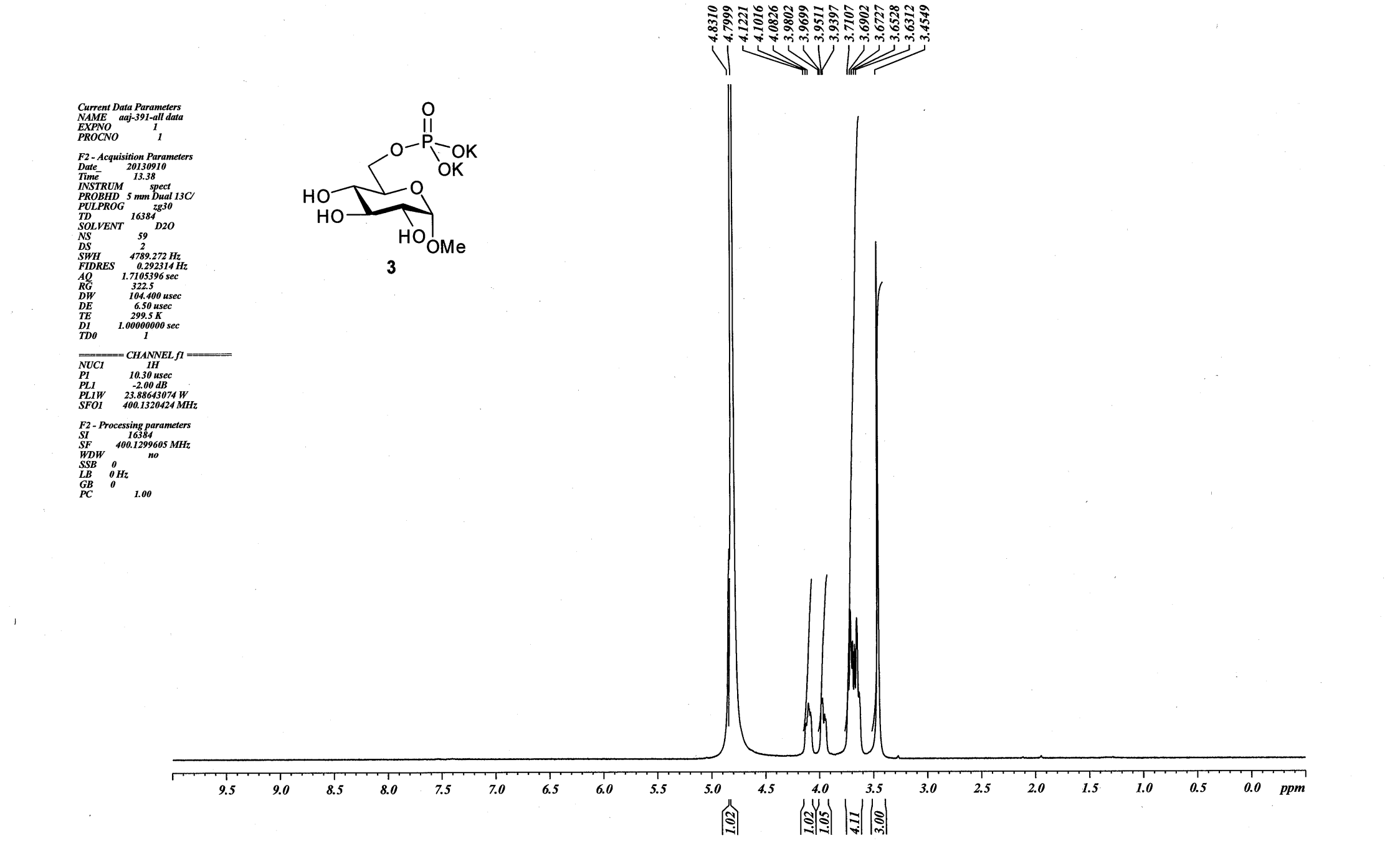

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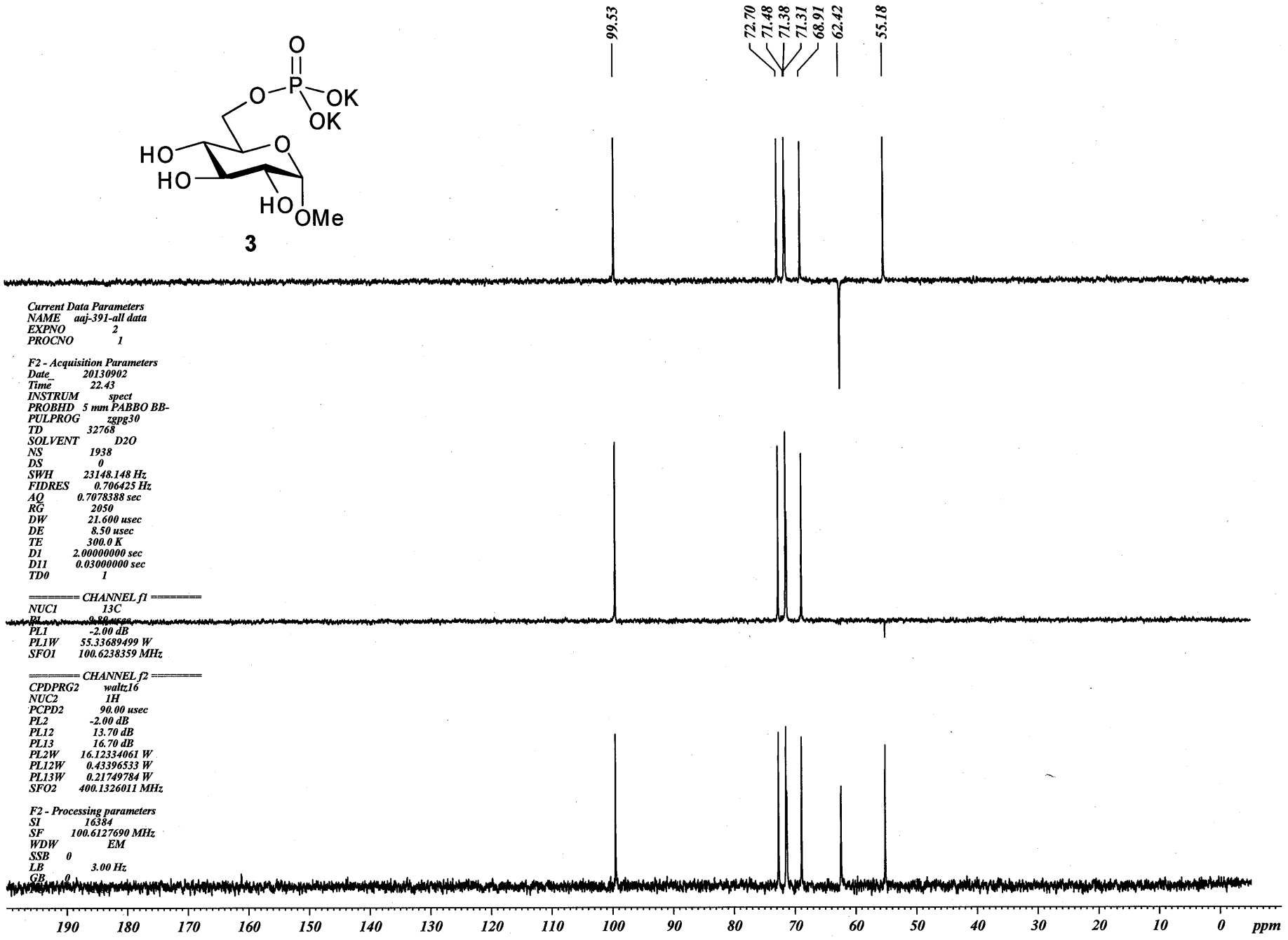

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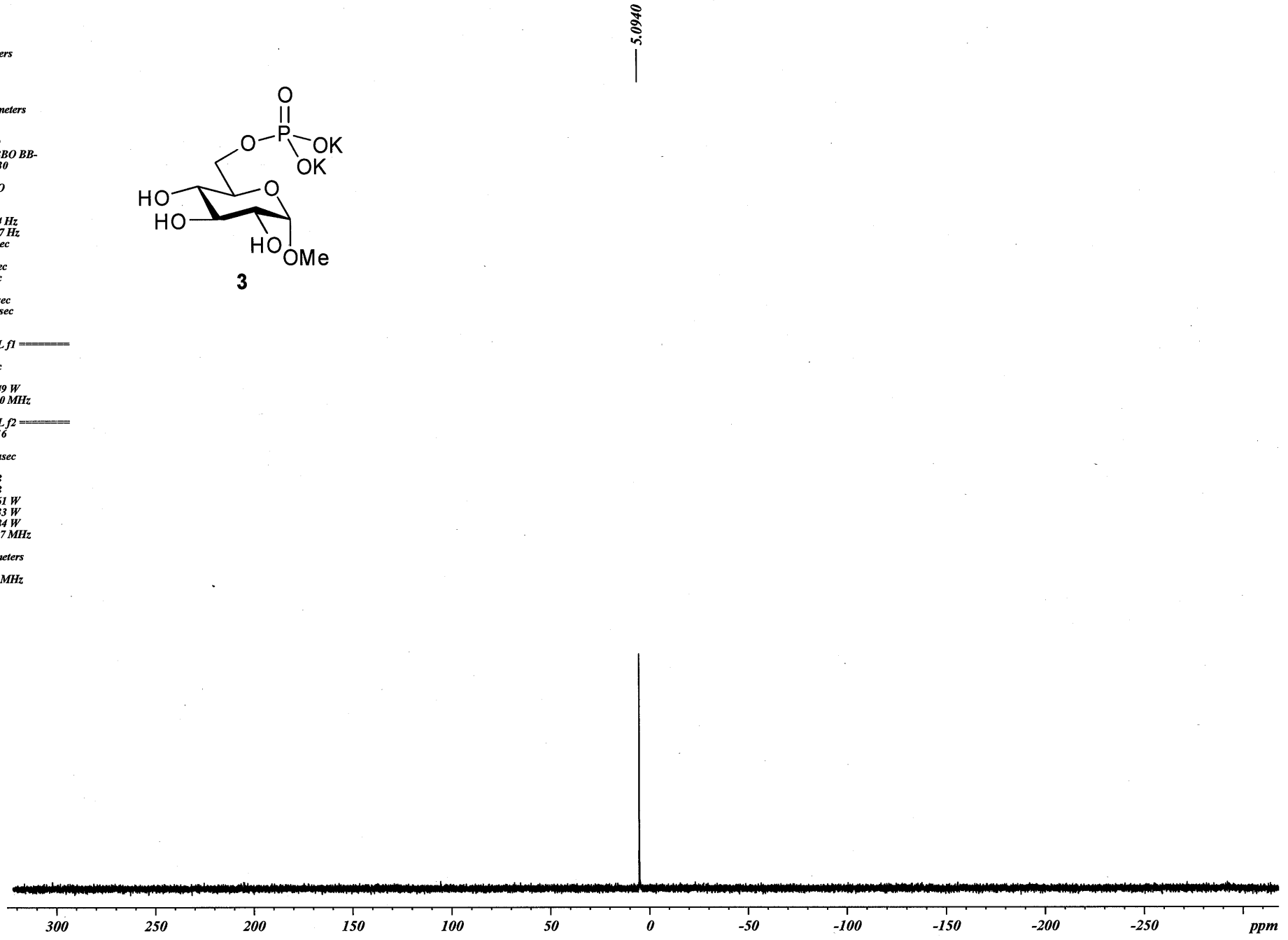

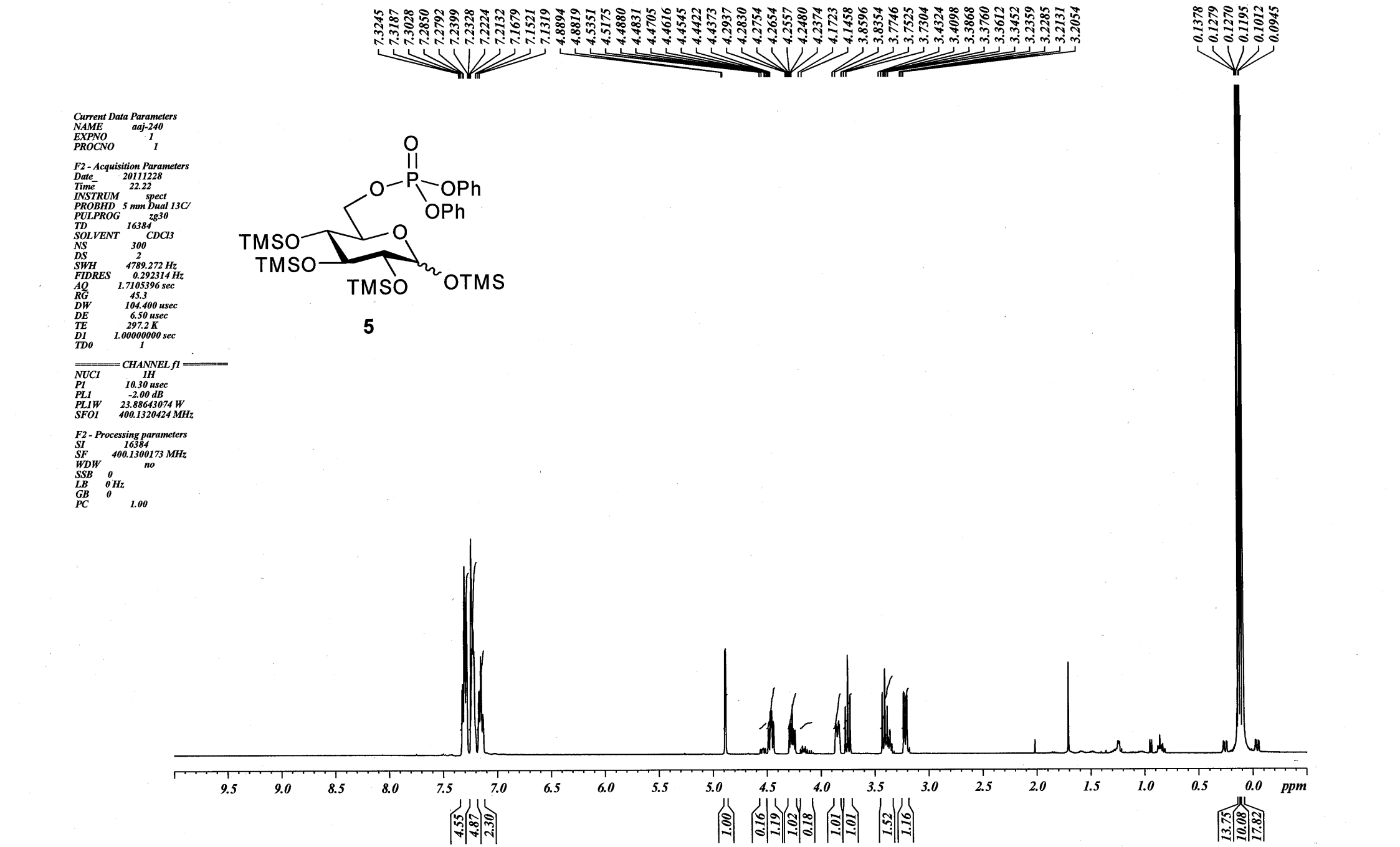

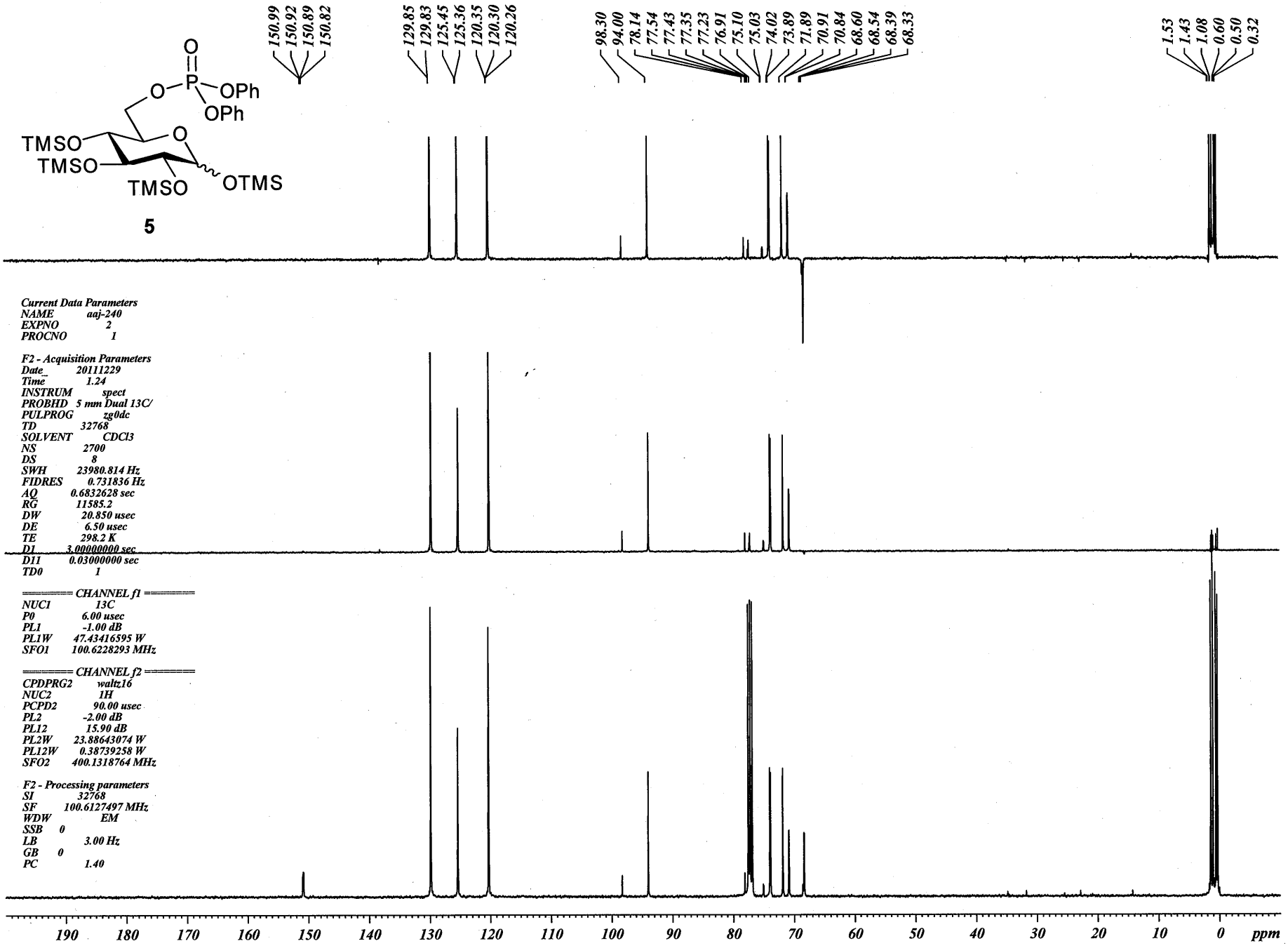

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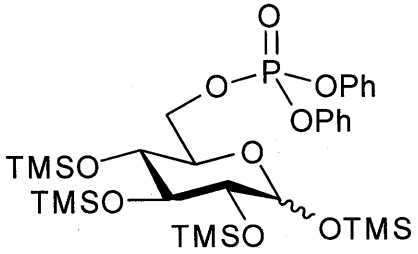

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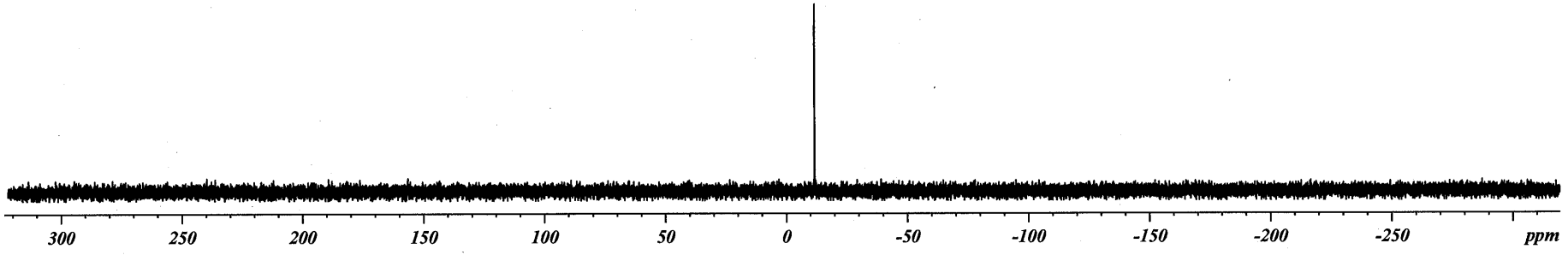

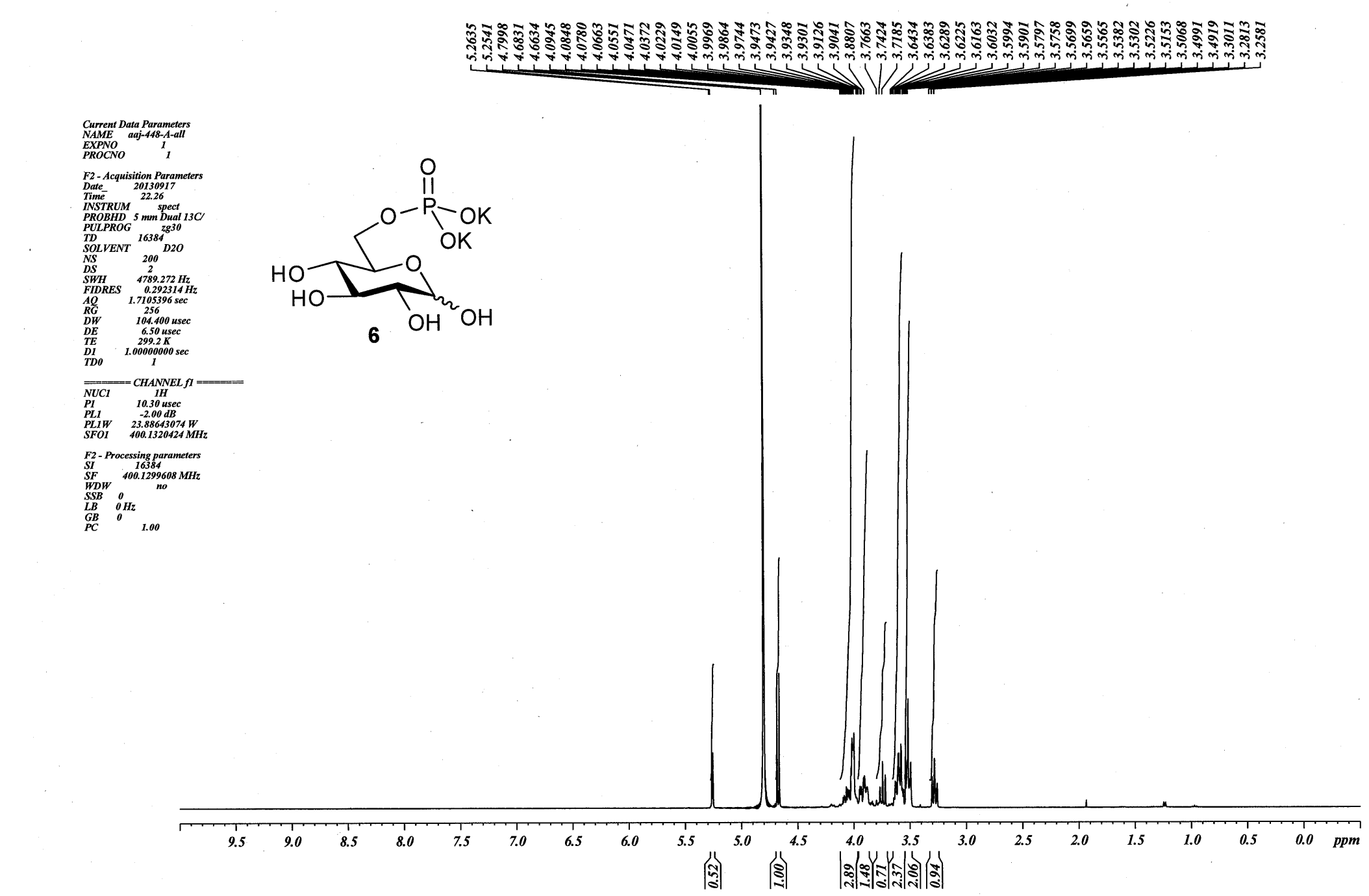
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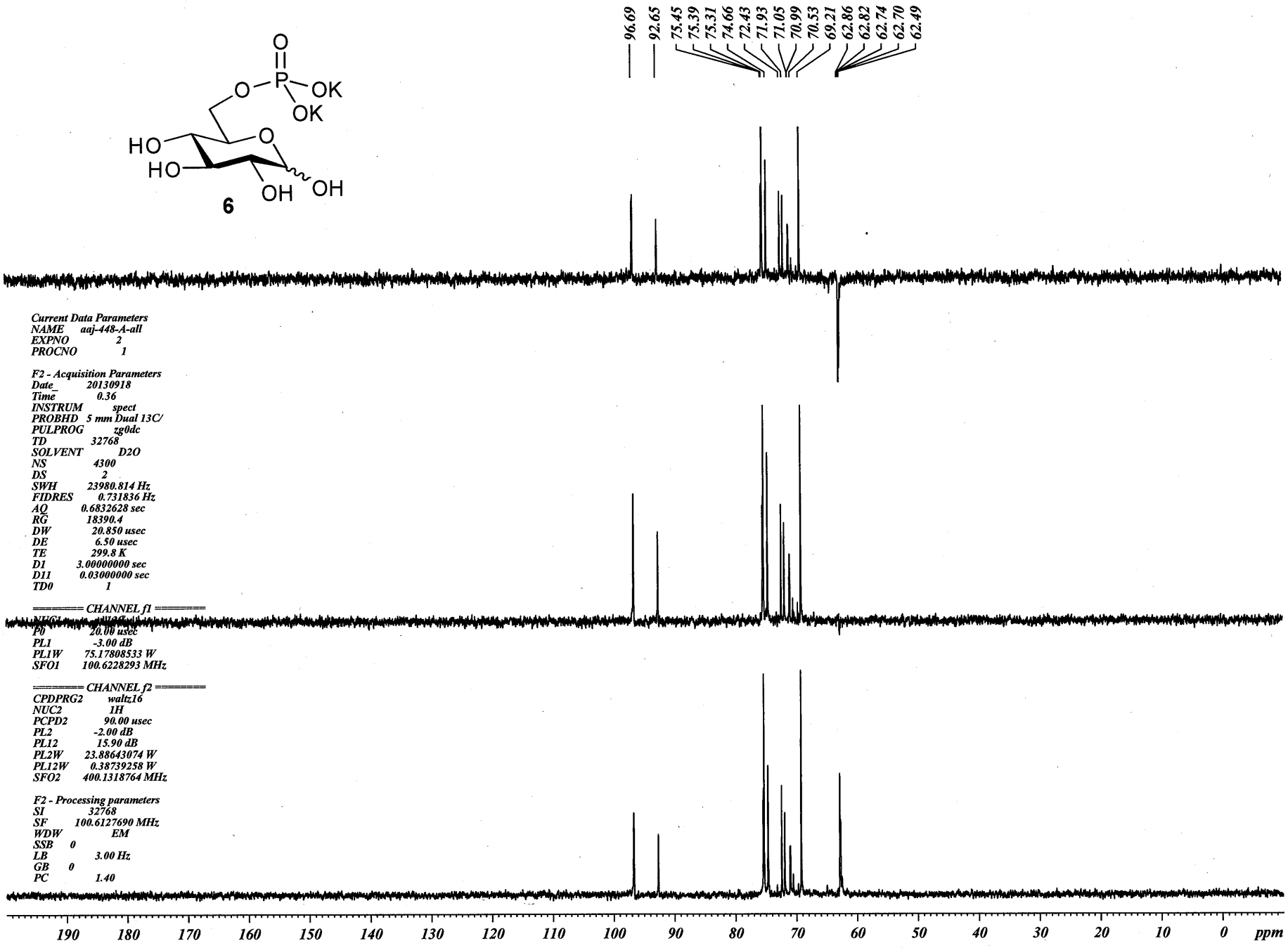

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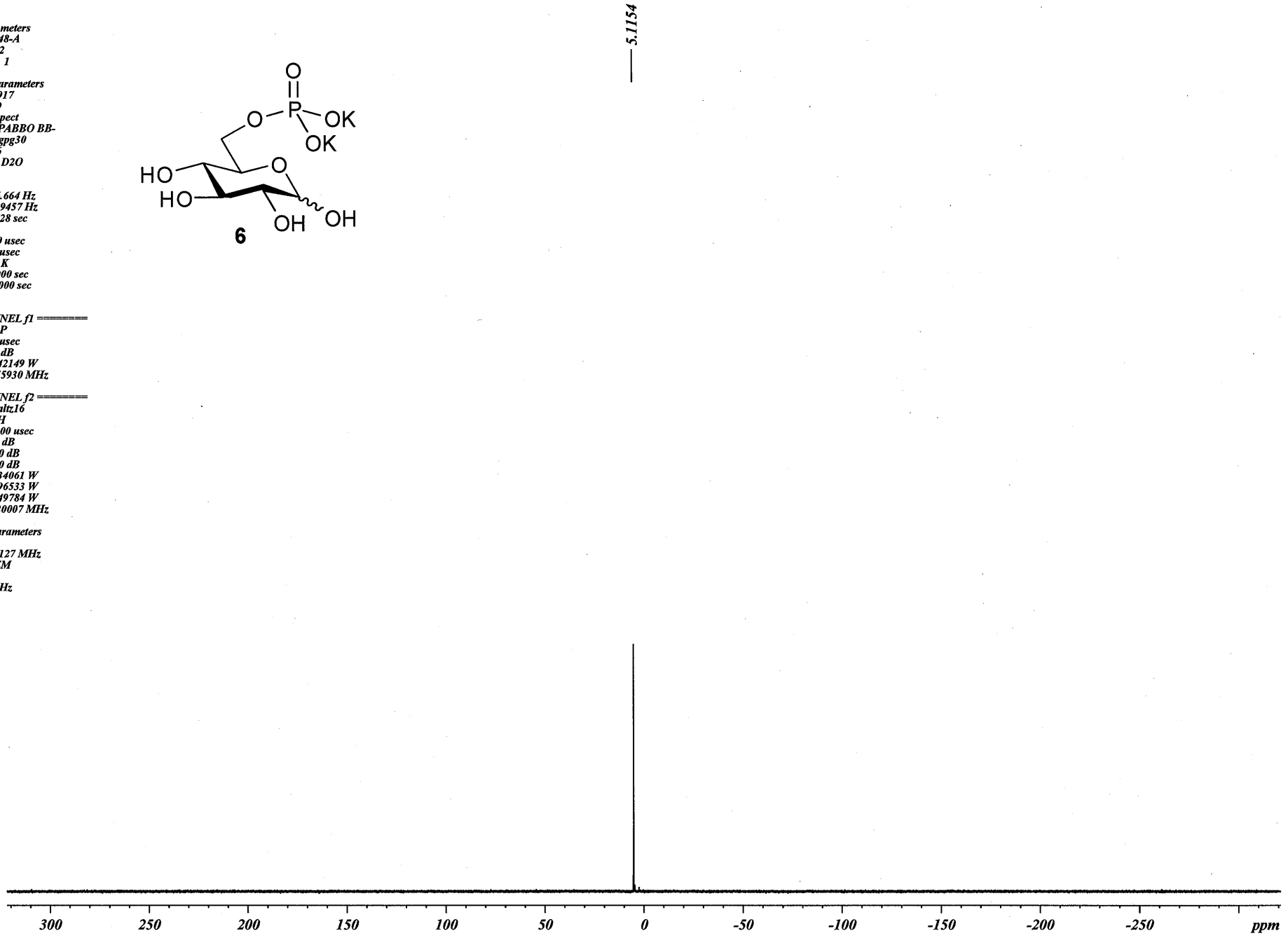
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

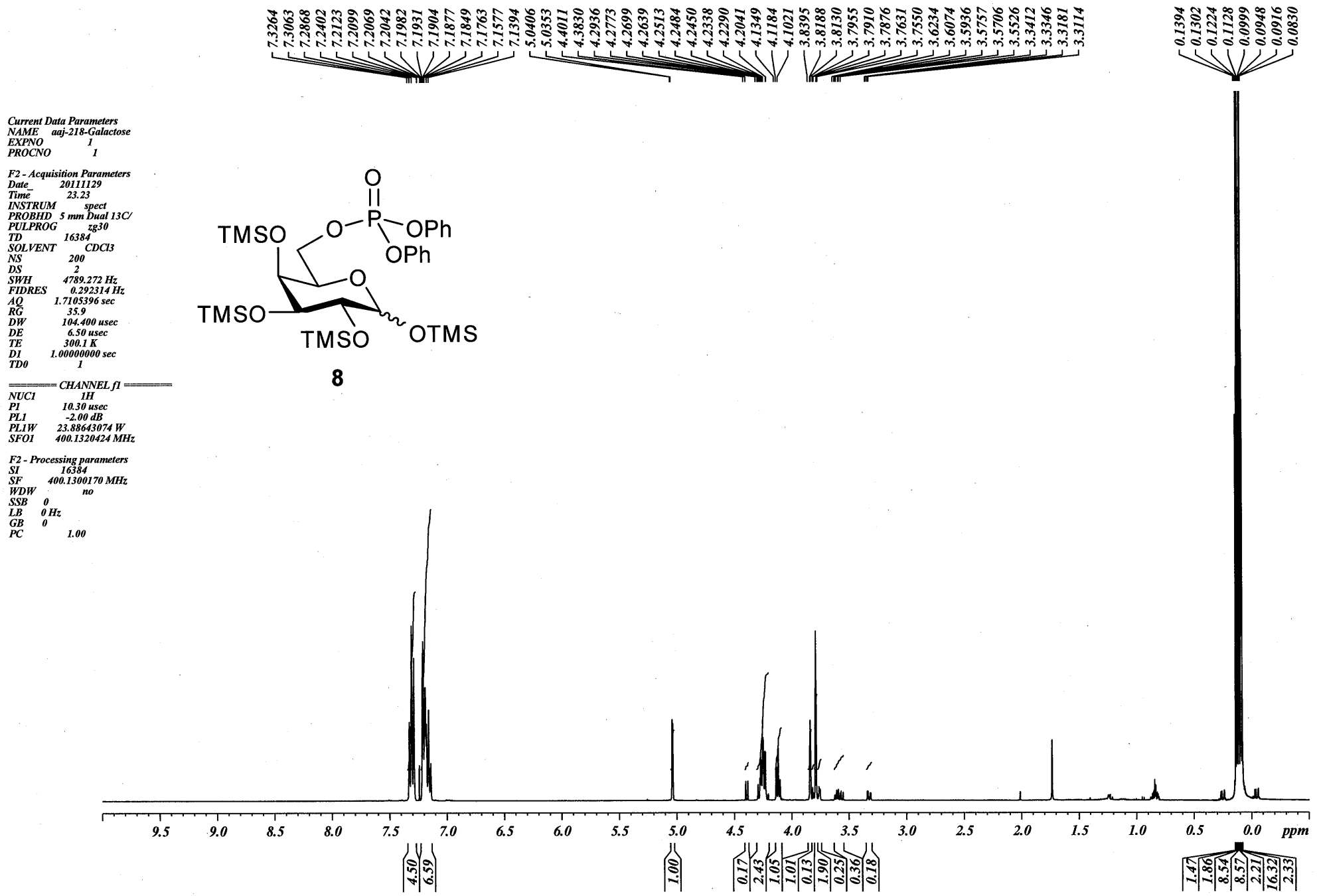
======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

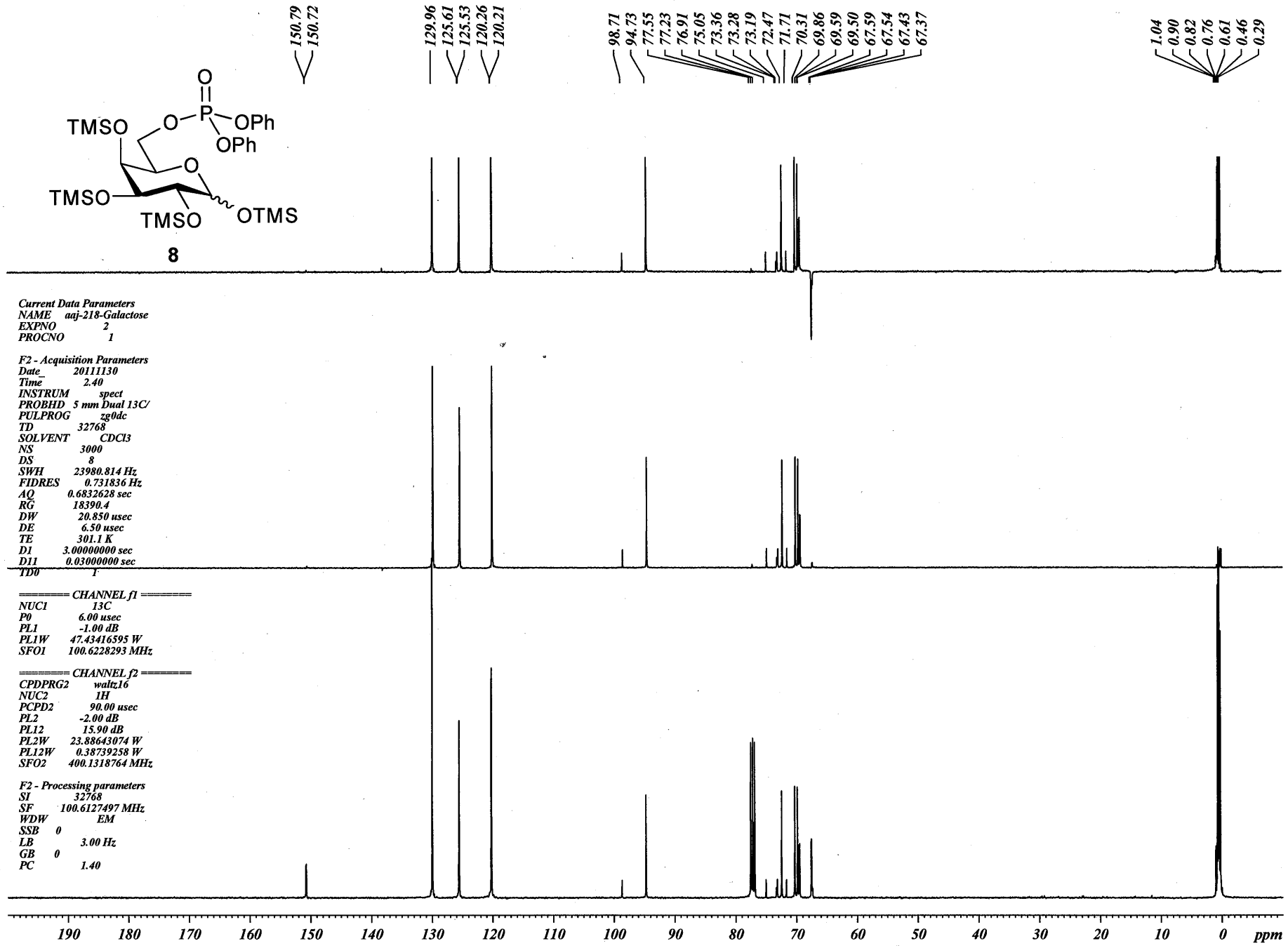
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

6

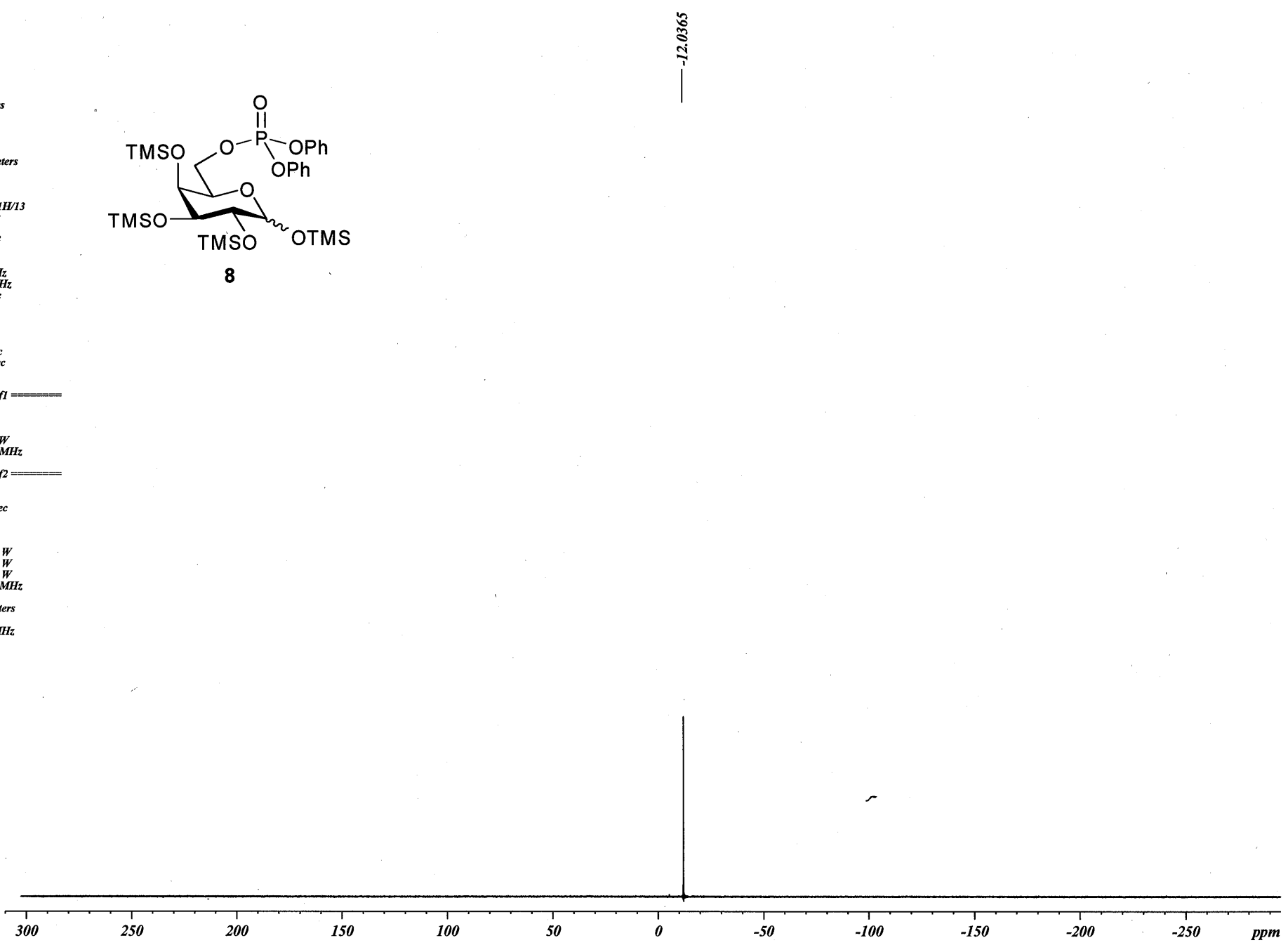


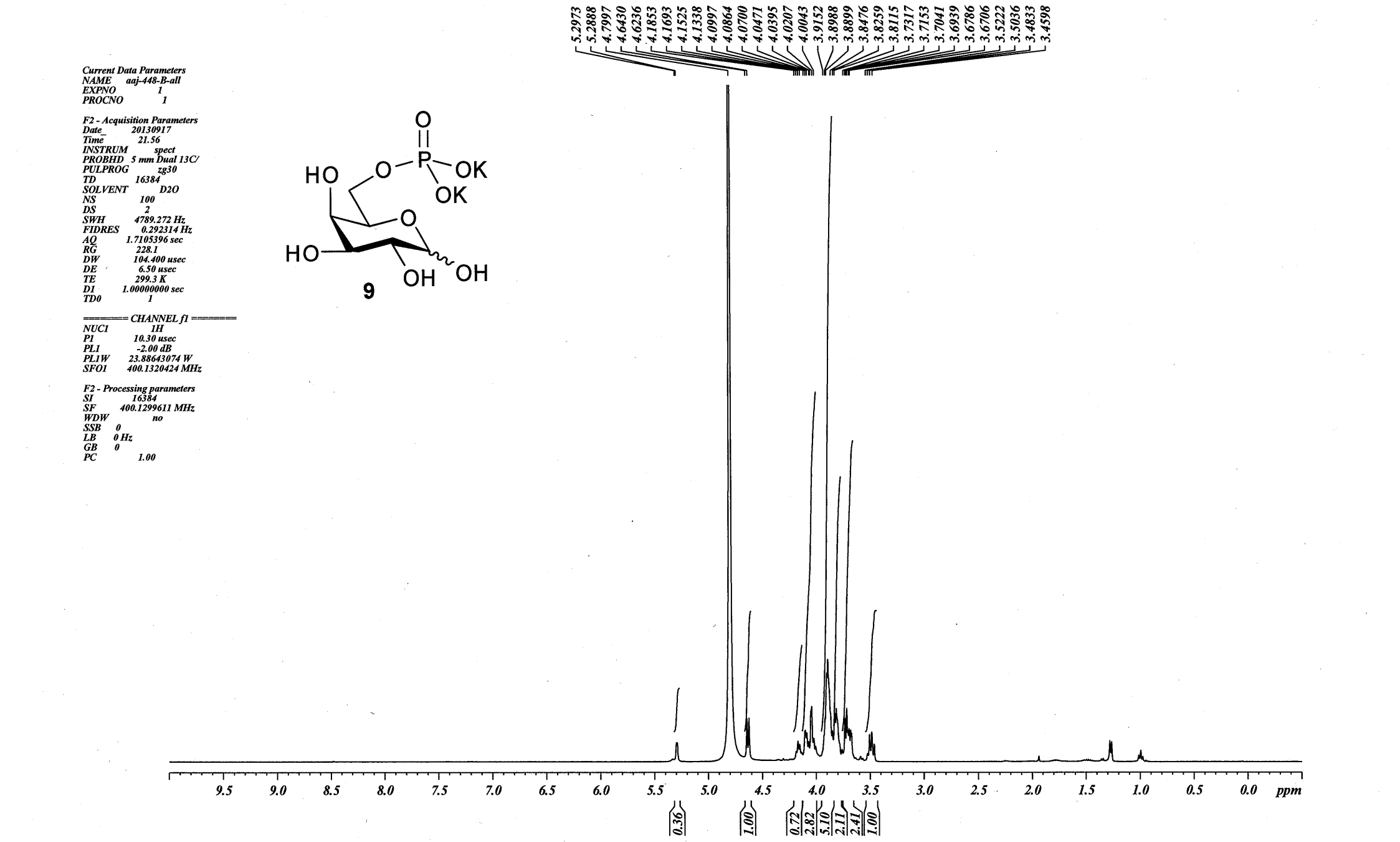


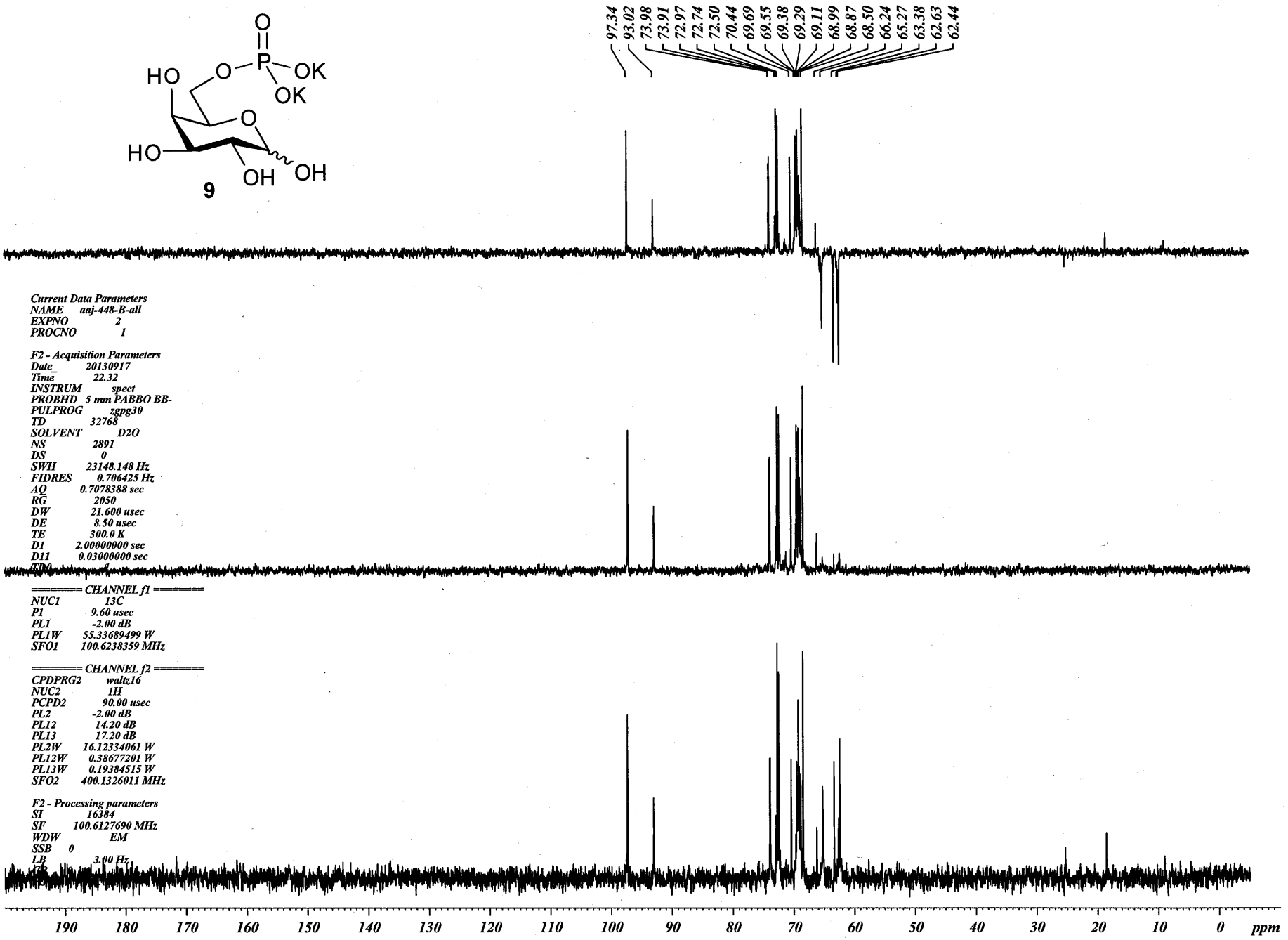


8

```
Current Data Parameters
NAME        aaj-gal-31p
EXPNO             2
PROCNO            1

F2 - Acquisition Parameters
Date_       20130912
Time          22.13
INSTRUM         spect
PROBHD   5 mm QNP 1H/13
PULPROG       zgpg30
TD           32768
SOLVENT         CDCl3
NS              38
DS               0
SWH         73529.414 Hz
FIDRES       2.243940 Hz
AQ          0.2228724 sec
RG             645
DW            6.800 usec
DE            6.50 usec
TE            300.0 K
D1         3.00000000 sec
D11        0.03000000 sec
TD0              1

======== CHANNEL f1 ========
NUC1            31P
P1           10.10 usec
PL1           9.00 dB
PL1W       8.75950909 W
SFO1       121.4948509 MHz

======== CHANNEL f2 ========
CPDPRG2       waltz16
NUC2             1H
PCPD2         90.00 usec
PL2           -4.00 dB
PL12          14.50 dB
PL13          17.50 dB
PL2W       26.37401772 W
PL12W       0.37254289 W
PL13W       0.18671374 W
SFO2       300.1319510 MHz

F2 - Processing parameters
SI            32768
SF         121.4948510 MHz
WDW              EM
SSB     0
LB            1.00 Hz
GB      0
PC            1.00
```







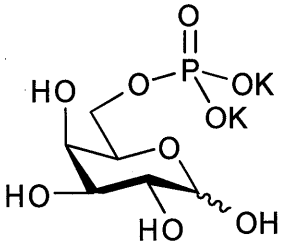
Current Data Parameters
NAME aaj-255-A
EXPNO 8
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120514
Time 8.46
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 100
DS 0
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

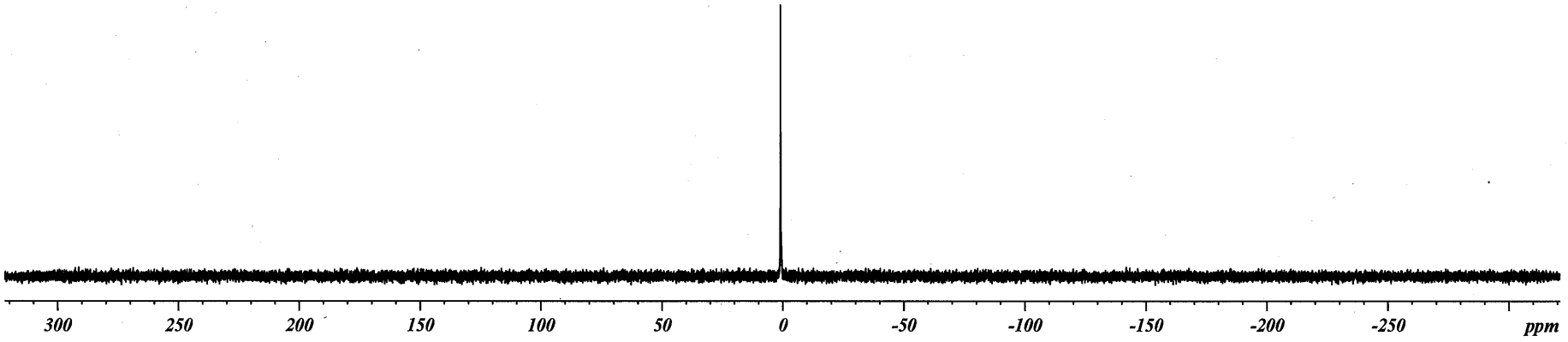
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

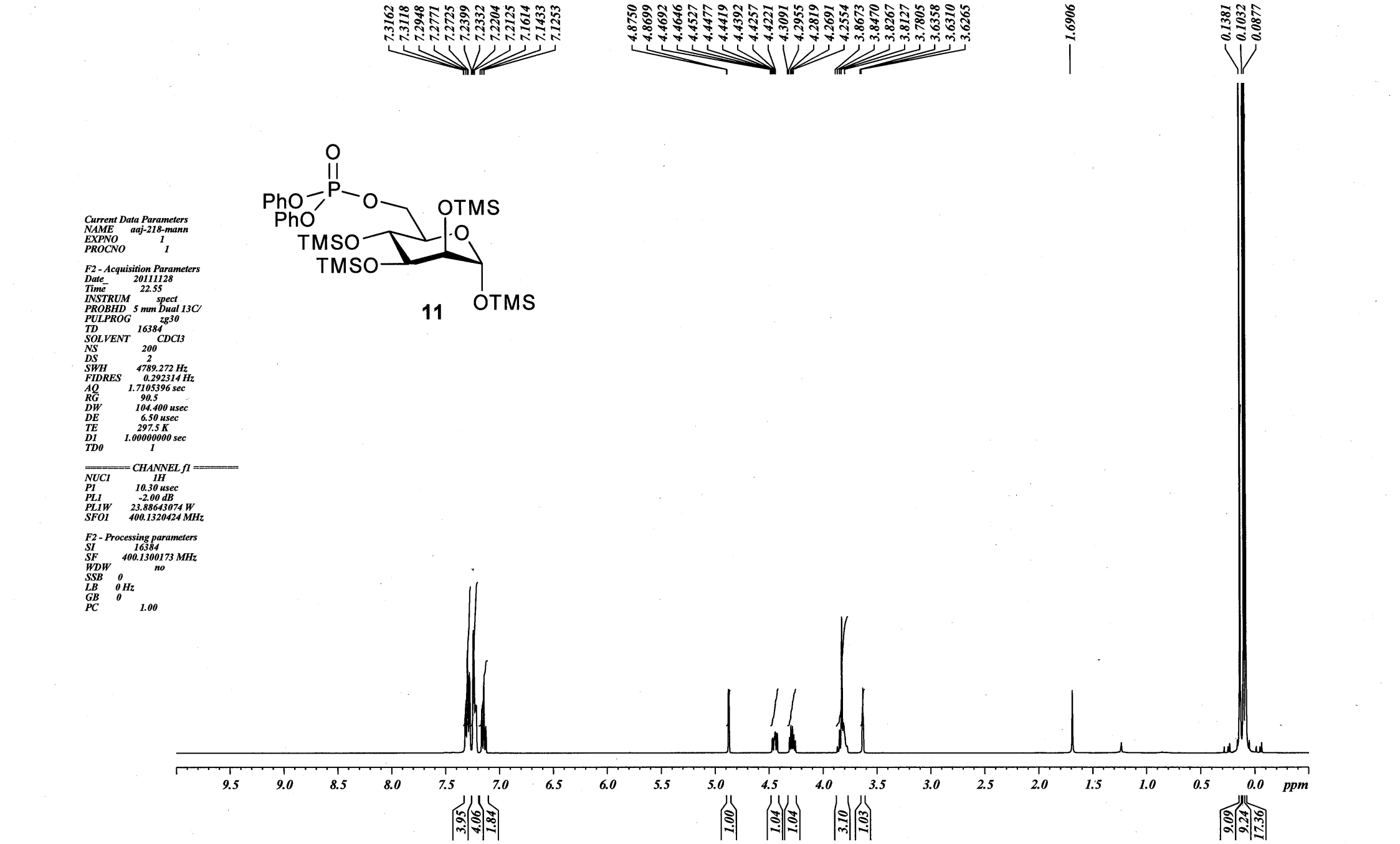
F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

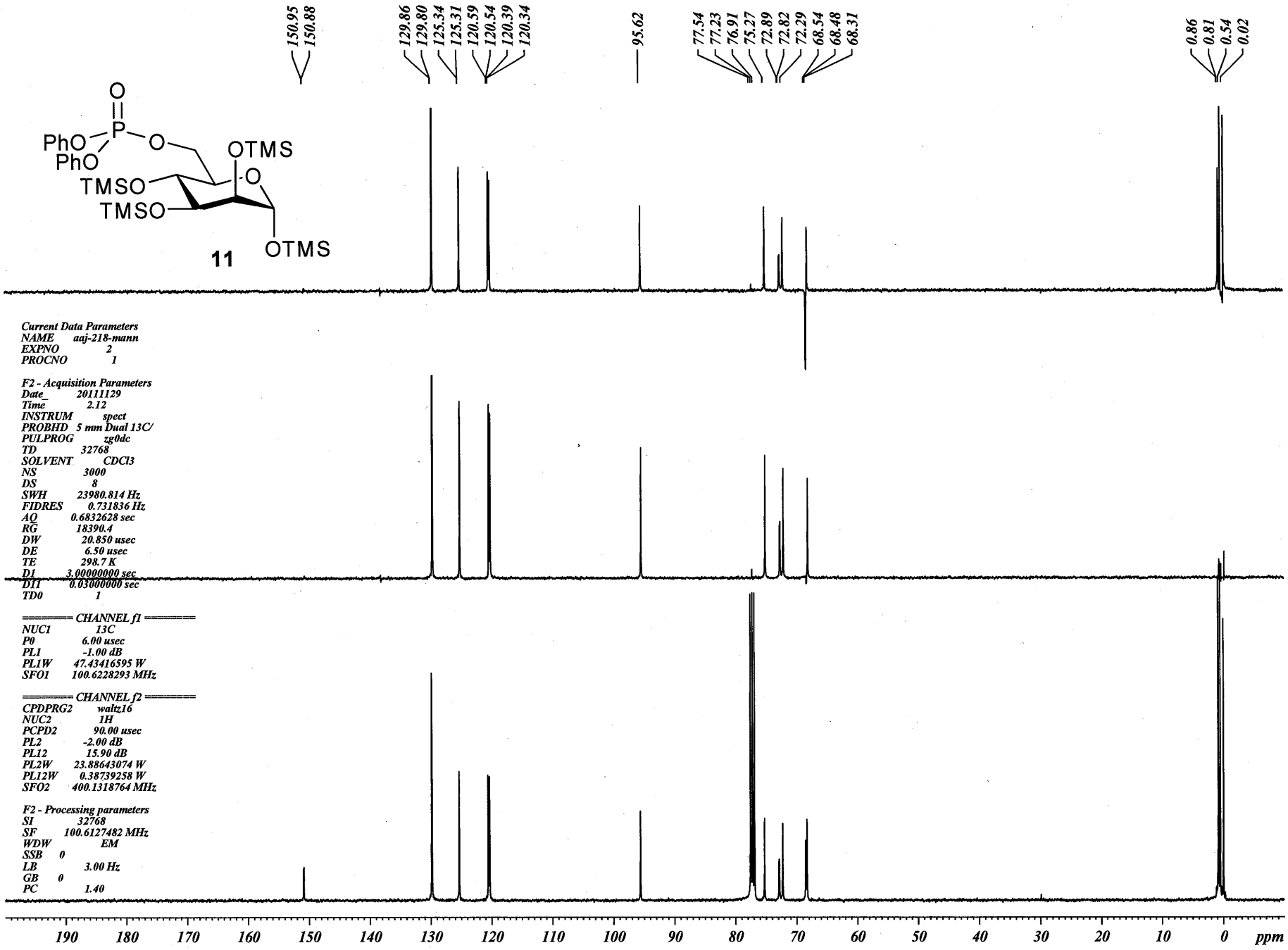


9

0.8225







-11.3092

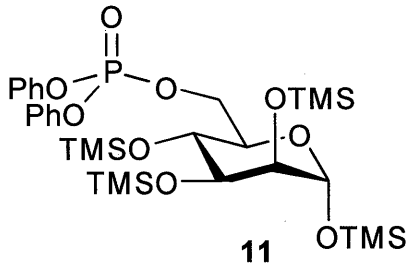
Current Data Parameters
NAME aaj-324-31p
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120910
Time 9.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 39
DS 0
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

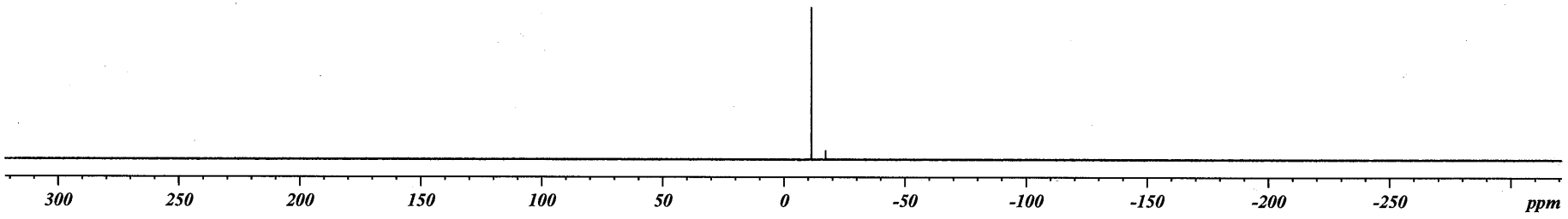
======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

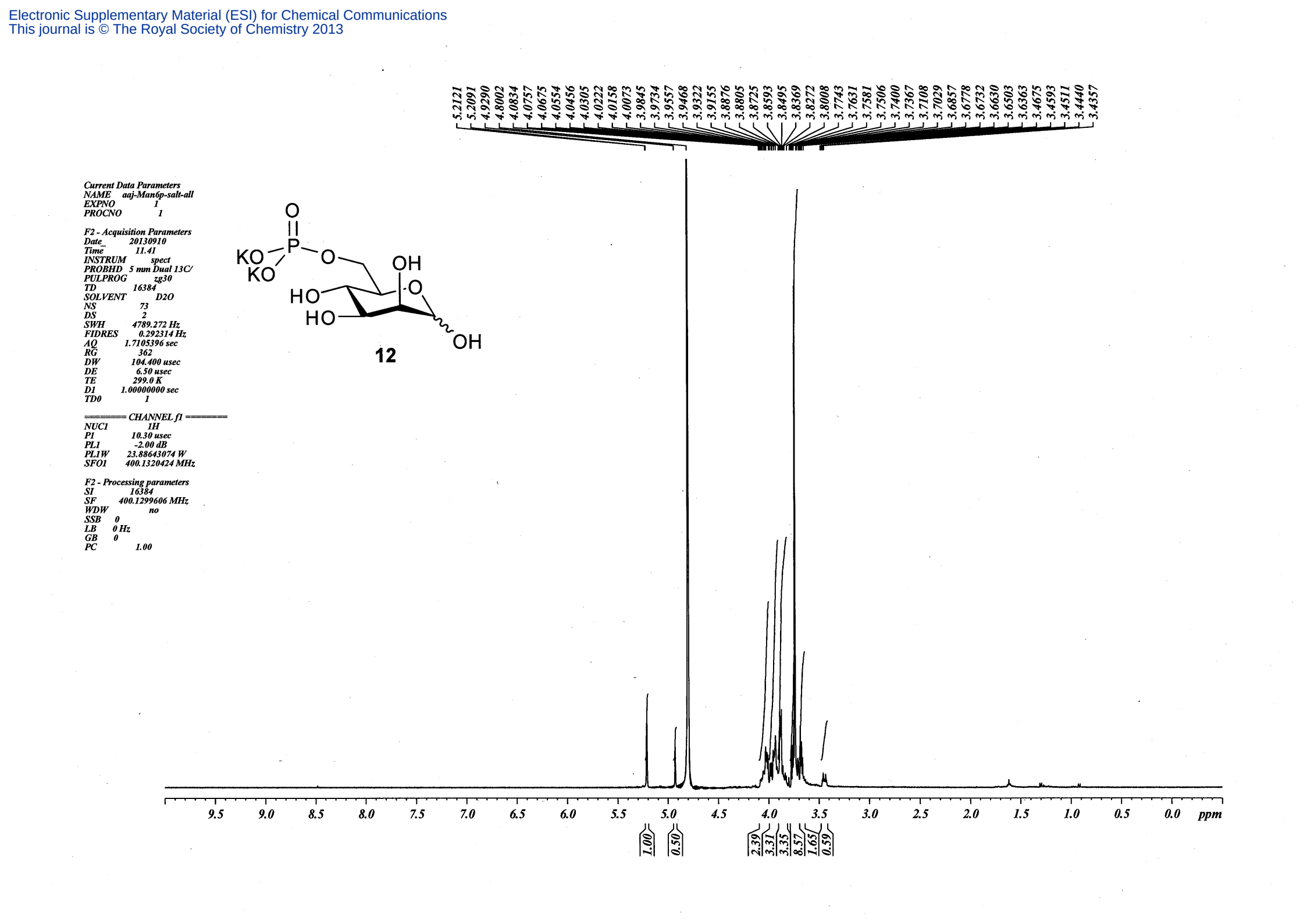
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

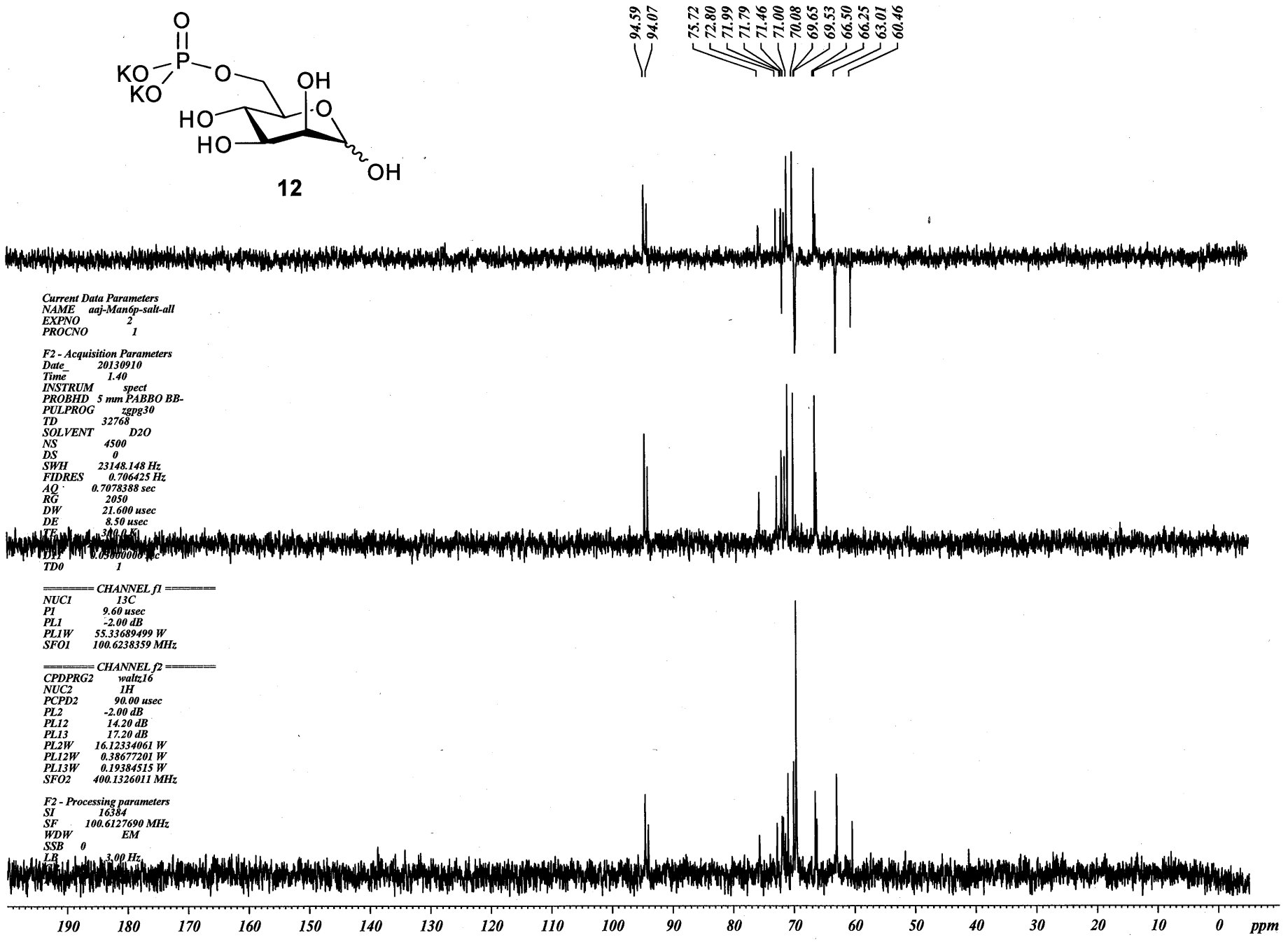
F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



11







Current Data Parameters
NAME aaj-Man6p-salt
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130909
Time 22.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 17
DS 0
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

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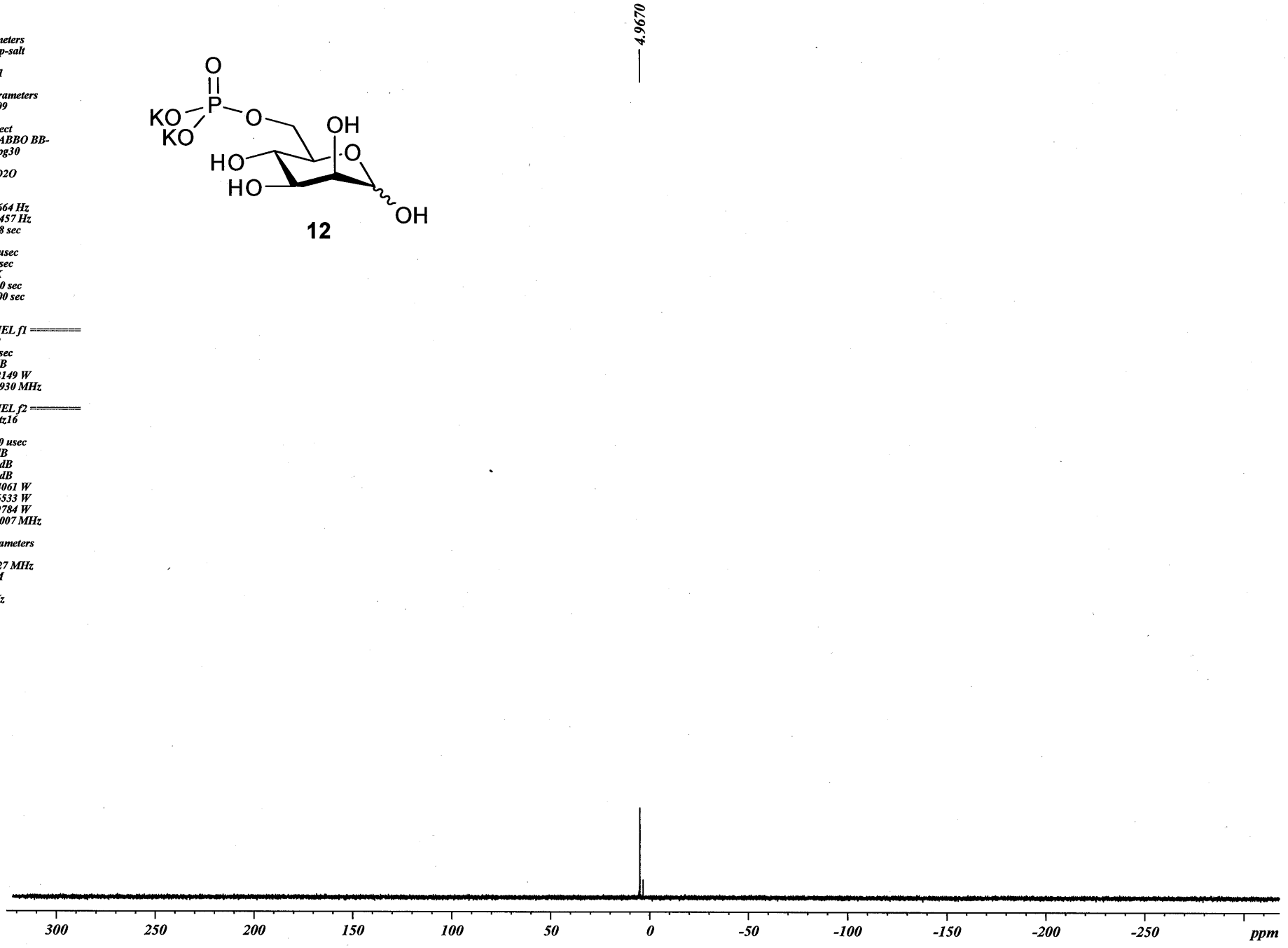
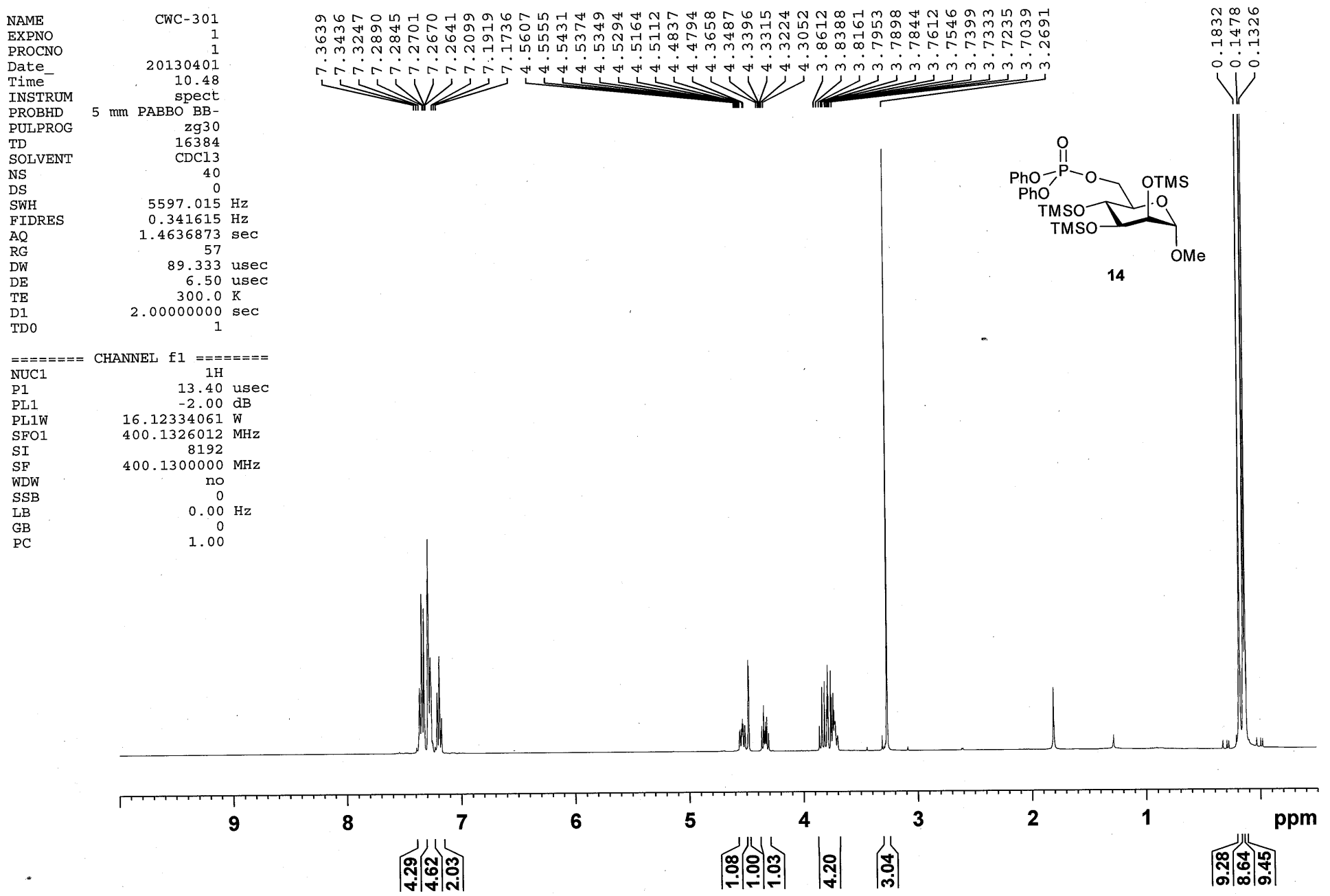
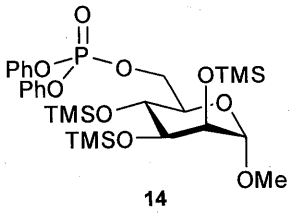
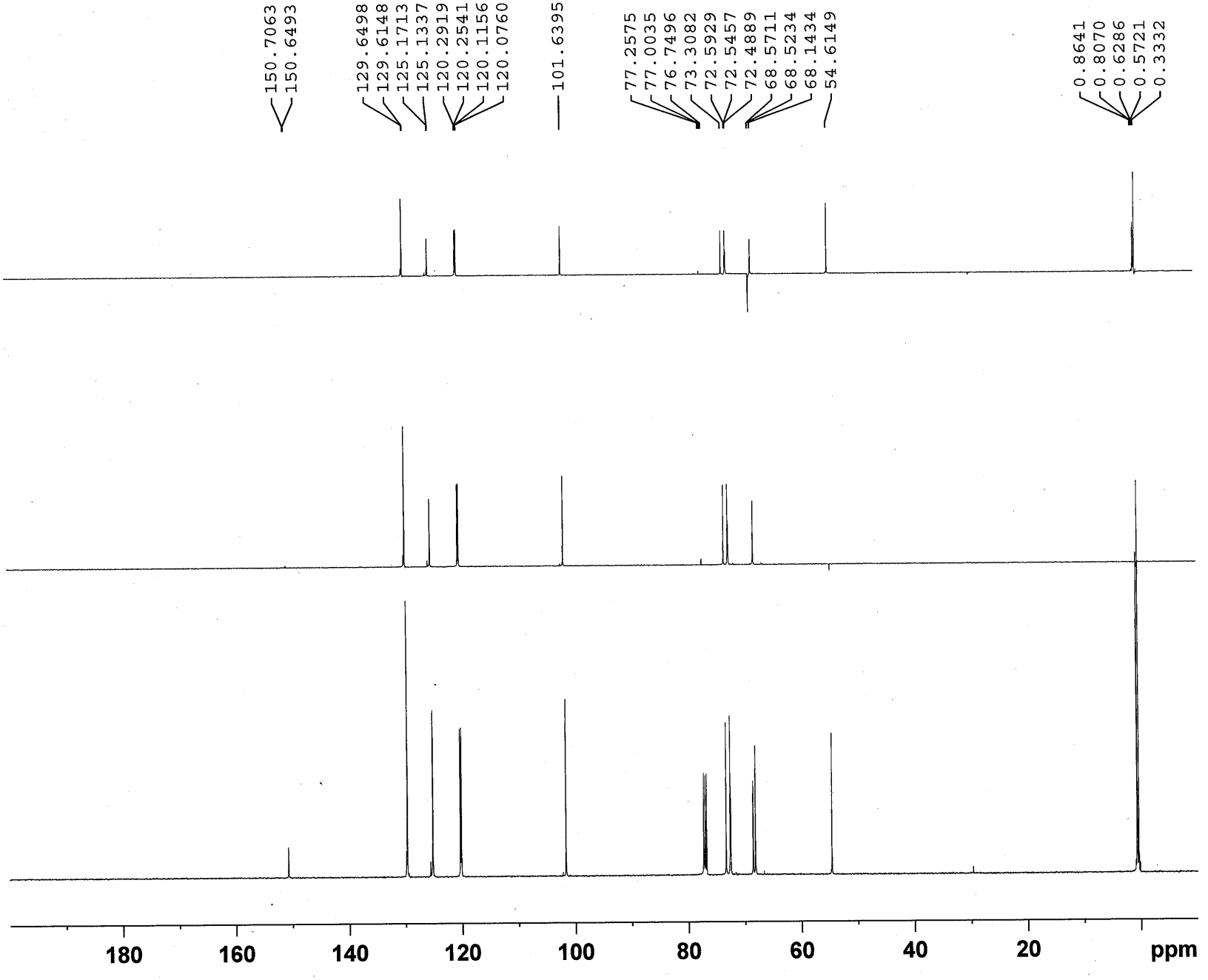


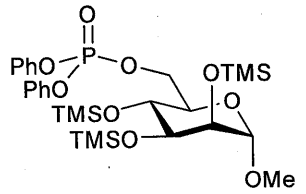




14

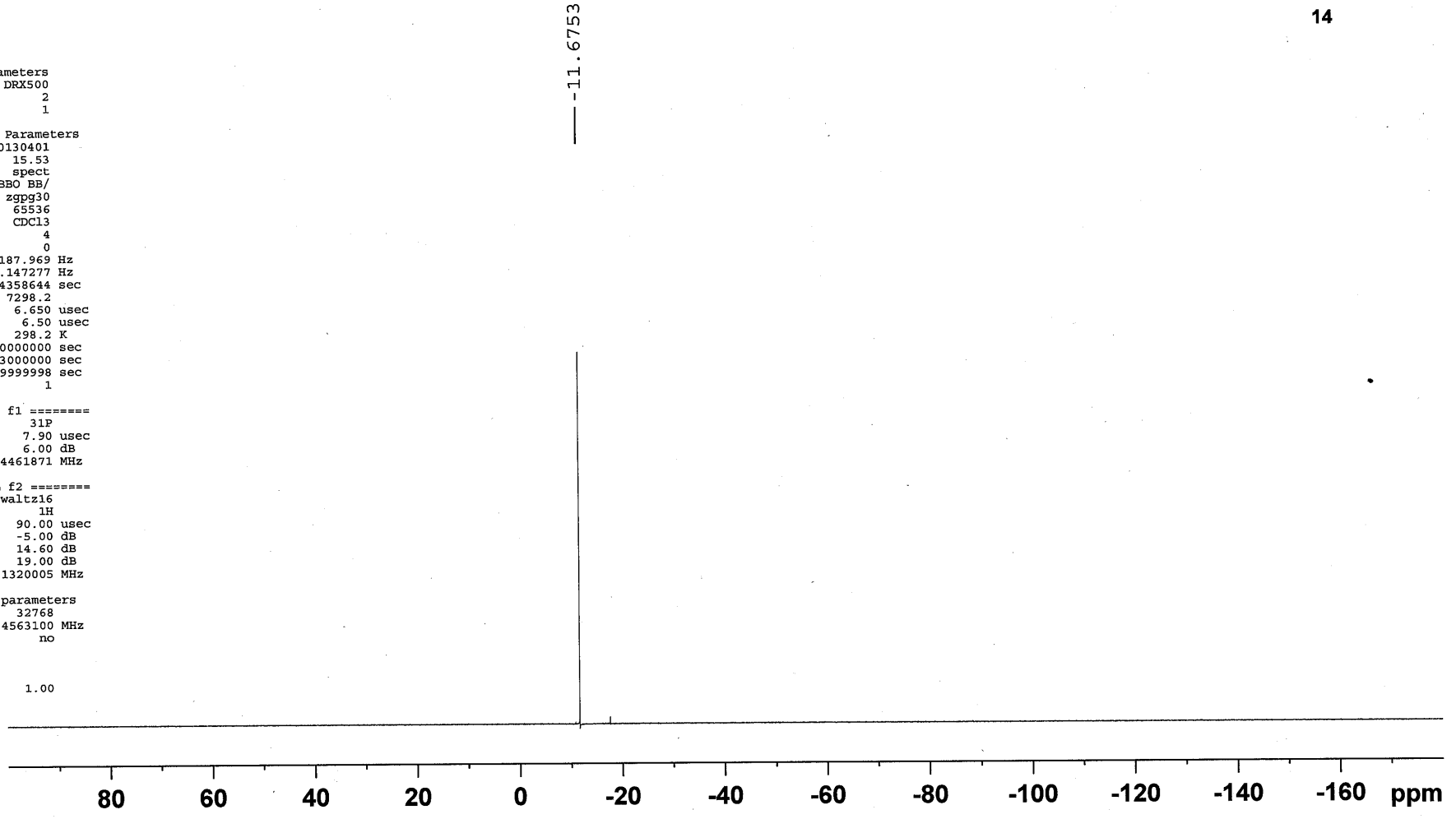


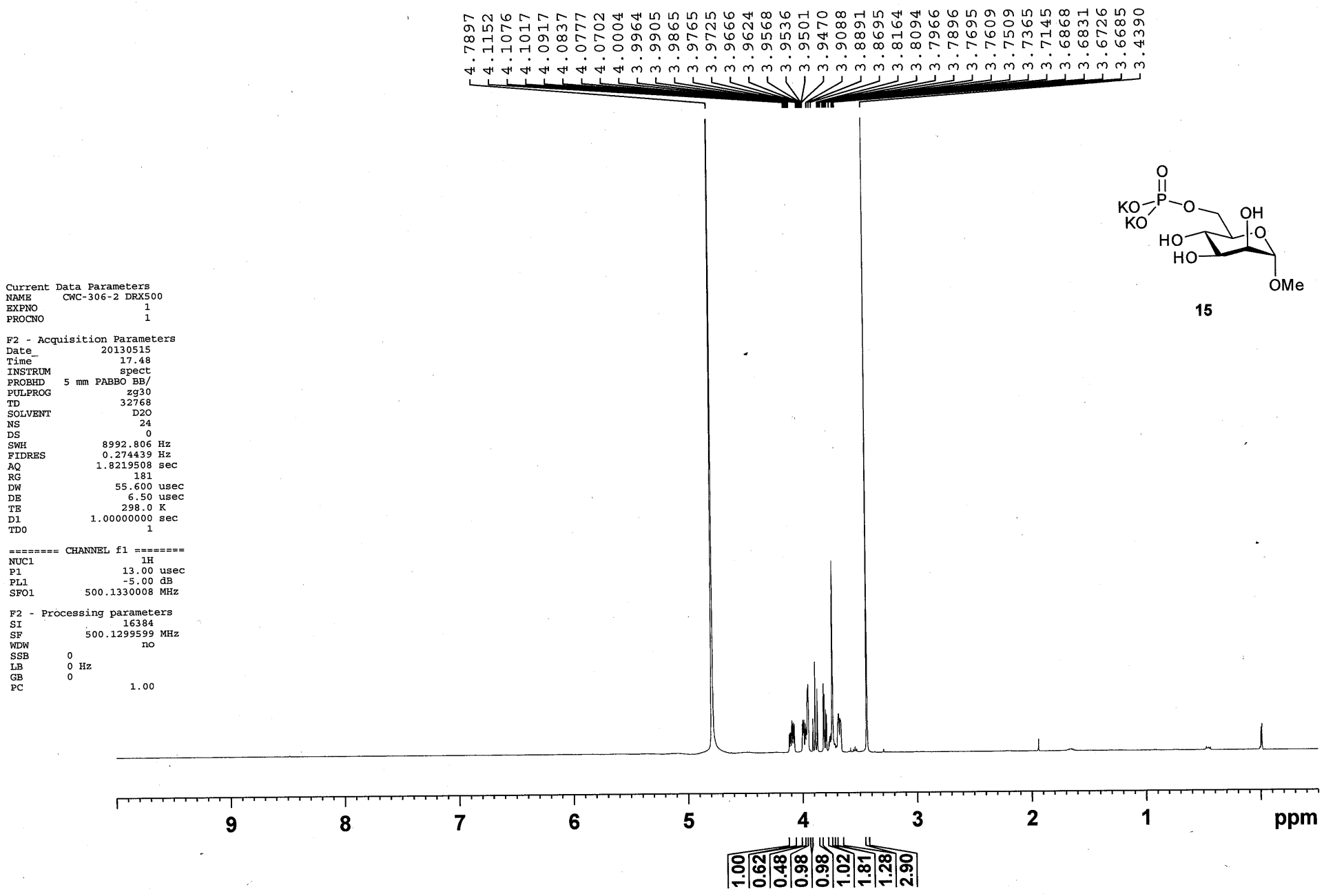

```
Current Data Parameters
NAME      CWC-301 DRX500
EXPNO                  6
PROCNO                 1

F2 - Acquisition Parameter
Date_           20130402
Time               0.04
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         dept90
TD                65536
SOLVENT           CDCl3
NS                 1500
DS                    8
SWH           30120.482 Hz
FIDRES         0.459602 Hz
AQ            1.0879476 se
RG              18390.4
DW               16.600 us
DE                6.50 us
TE                298.0 K
CNST2        145.0000000
D1             2.00000000 se
d2             0.00344828 se
d12            0.00002000 se
DELTA          0.00001210 se
TD0                    1

======== CHANNEL f1 ======
NUC1                 13C
P1                  9.50 us
p2                 19.00 us
PL1                3.00 dB
SFO1        125.7703643 MH

======== CHANNEL f2 ======
CPDPRG2          waltz16
NUC2                 1H
P3                 13.00 us
p4                 26.00 us
PCPD2              90.00 us
PL2               -5.00 dB
PL12               14.60 dB
SFO2        500.1320005 MH

F2 - Processing parameters
SI                 32768
SF          125.7577890 MH
WDW                   EM
SSB       0
LB                 2.00 Hz
GB        0
PC                 1.00
```

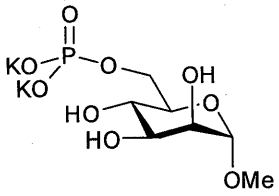


14

```
Current Data Parameters
NAME      CWC-301 DRX500
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130401
Time              15.53
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                    4
DS                    0
SWH           75187.969 Hz
FIDRES         1.147277 Hz
AQ            0.4358644 sec
RG               7298.2
DW                6.650 usec
DE                6.50 usec
TE                298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 31P
P1                  7.90 usec
PL1                 6.00 dB
SFO1        202.4461871 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                -5.00 dB
PL12               14.60 dB
PL13               19.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          202.4563100 MHz
WDW                  no
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```







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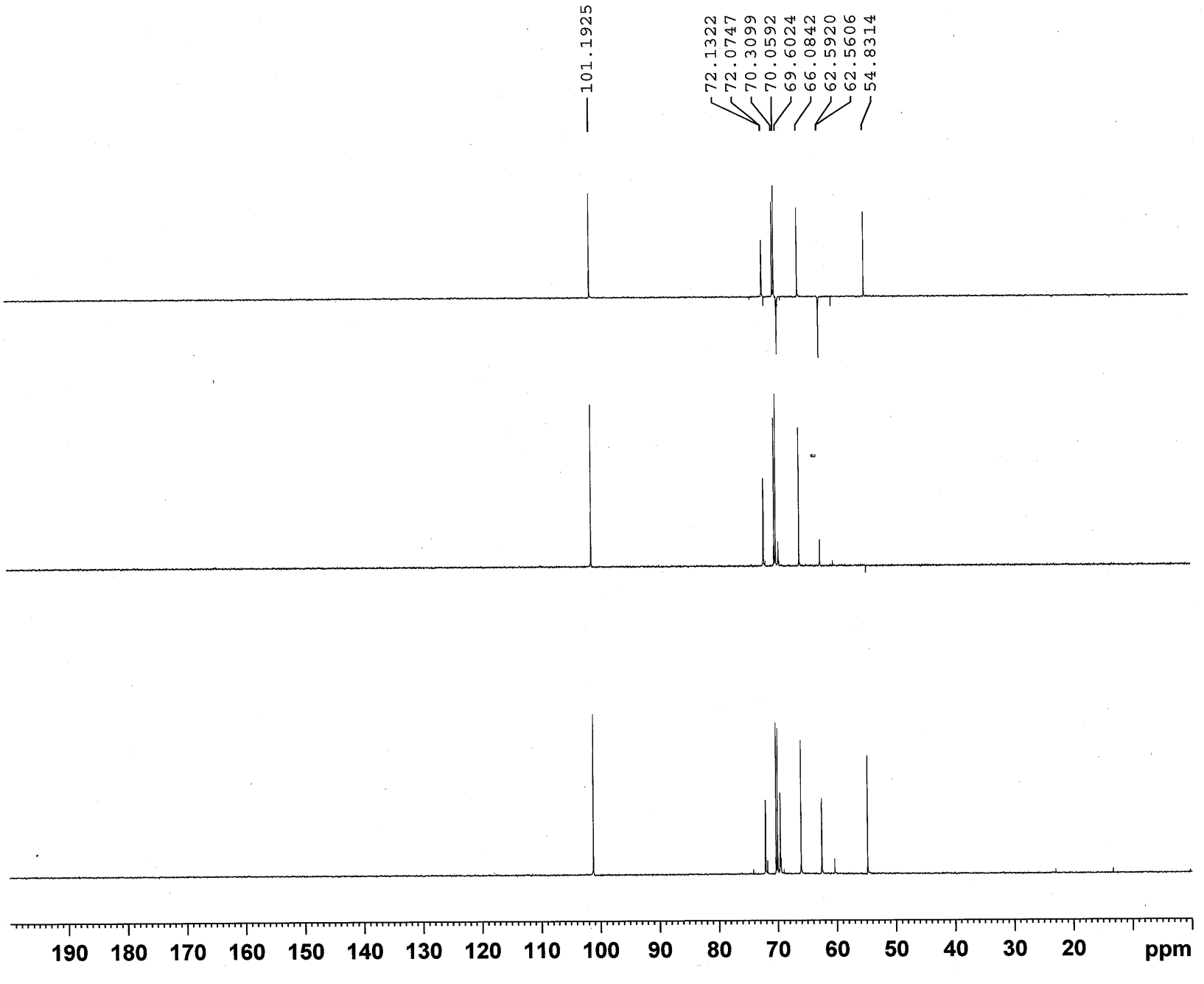


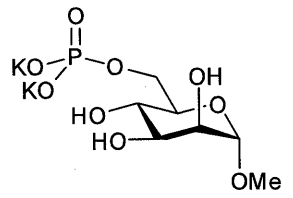

```
Current Data Parameters
NAME          CWC-306-2
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20130509
Time               5.37
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG           zg0dc
TD                32768
SOLVENT             D2O
NS                 4000
DS                    2
SWH           30120.482 Hz
FIDRES         0.919204 Hz
AQ            0.5439988 sec
RG              14596.5
DW               16.600 usec
DE                6.50 usec
TE               298.3 K
D1           3.00000000 sec
d11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P0                  9.50 usec
PL1                 3.00 dB
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                -5.00 dB
PL12               14.60 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB       0
LB                2.00 Hz
GB        0
PC                1.00
```



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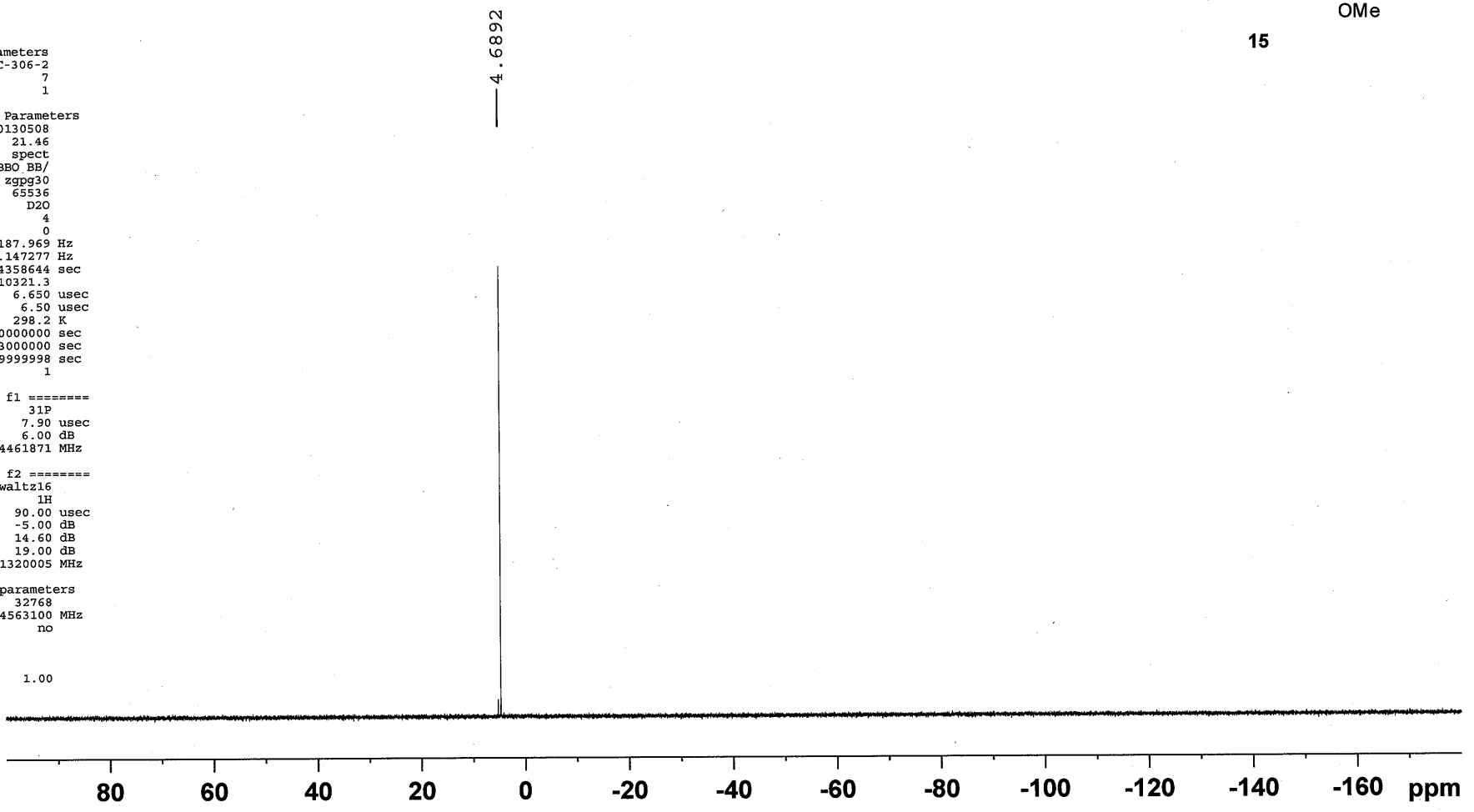
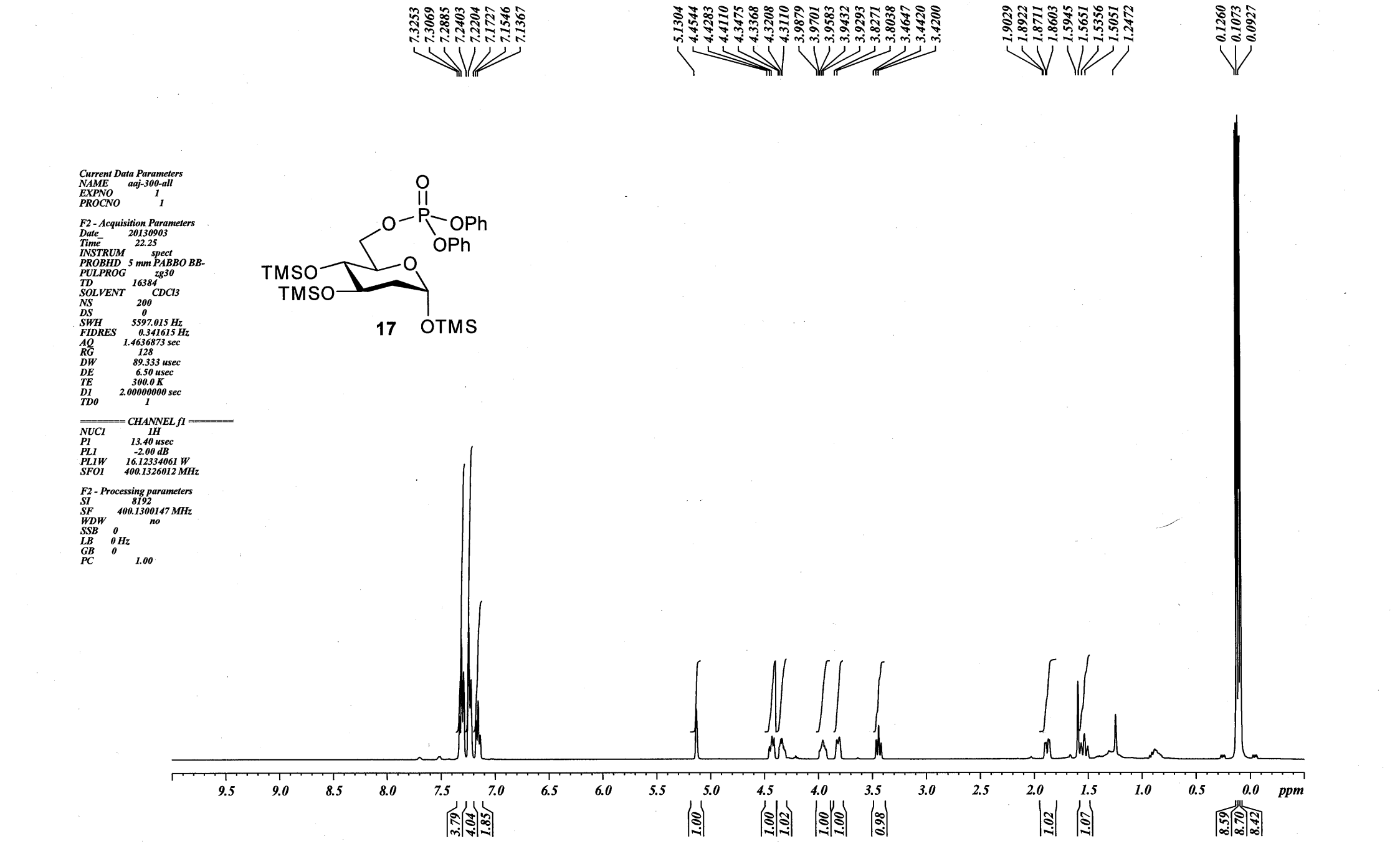
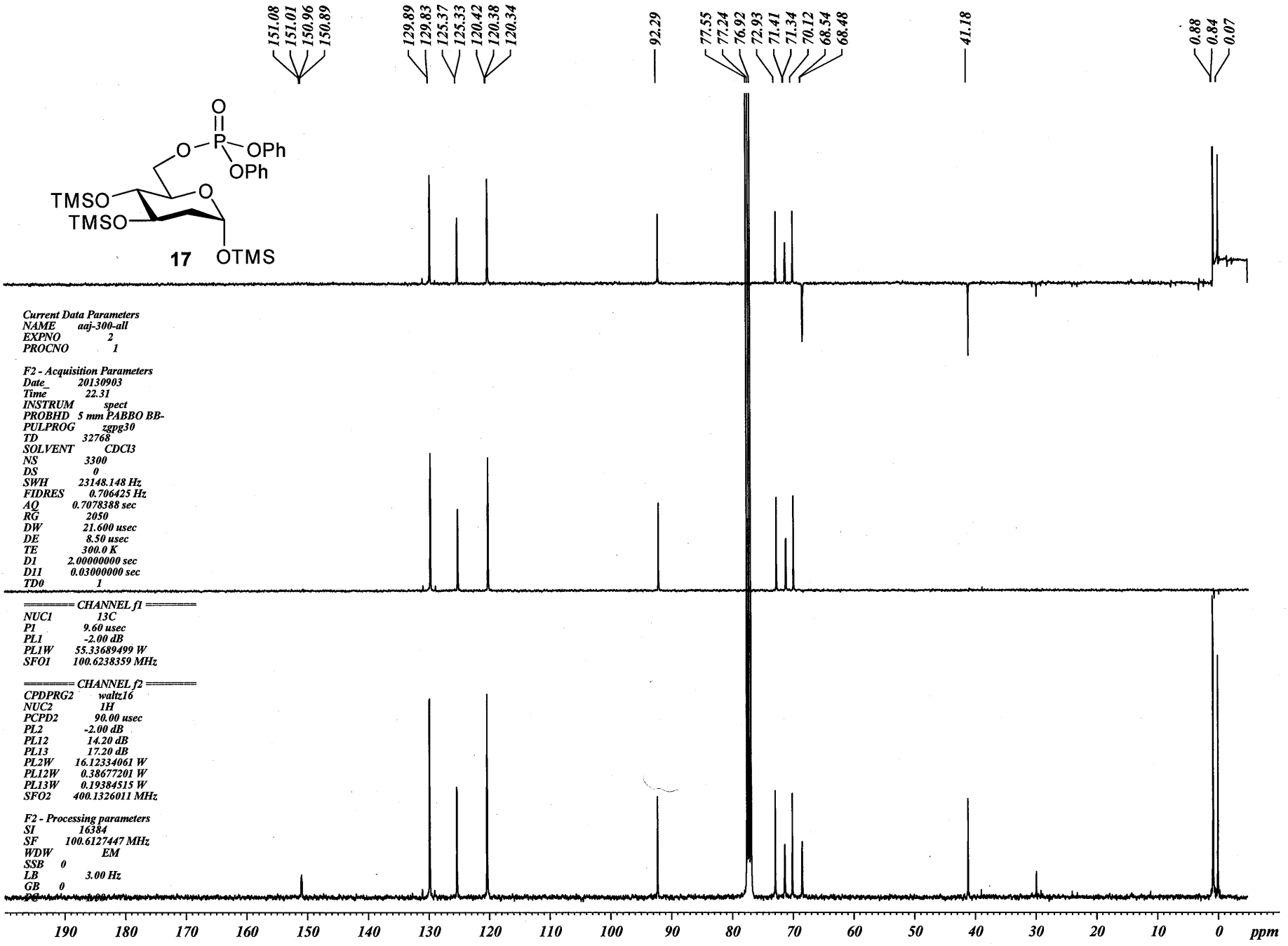
```
Current Data Parameters
NAME           CWC-306-2
EXPNO                  7
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130508
Time              21.46
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT            D2O
NS                   4
DS                   0
SWH           75187.969 Hz
FIDRES         1.147277 Hz
AQ            0.4358644 sec
RG              10321.3
DW                6.650 usec
DE                6.50 usec
TE               298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               31P
P1                7.90 usec
PL1               6.00 dB
SFO1       202.4461871 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2               1H
PCPD2            90.00 usec
PL2              -5.00 dB
PL12             14.60 dB
PL13             19.00 dB
SFO2       500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          202.4563100 MHz
WDW                  no
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```







-11.3478

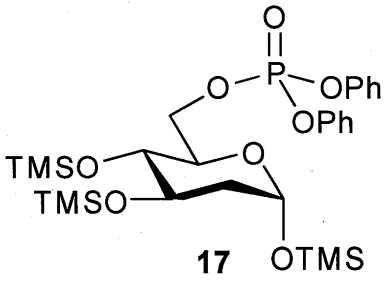
Current Data Parameters
NAME aaj-300
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130903
Time 22.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 17
DS 0
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00



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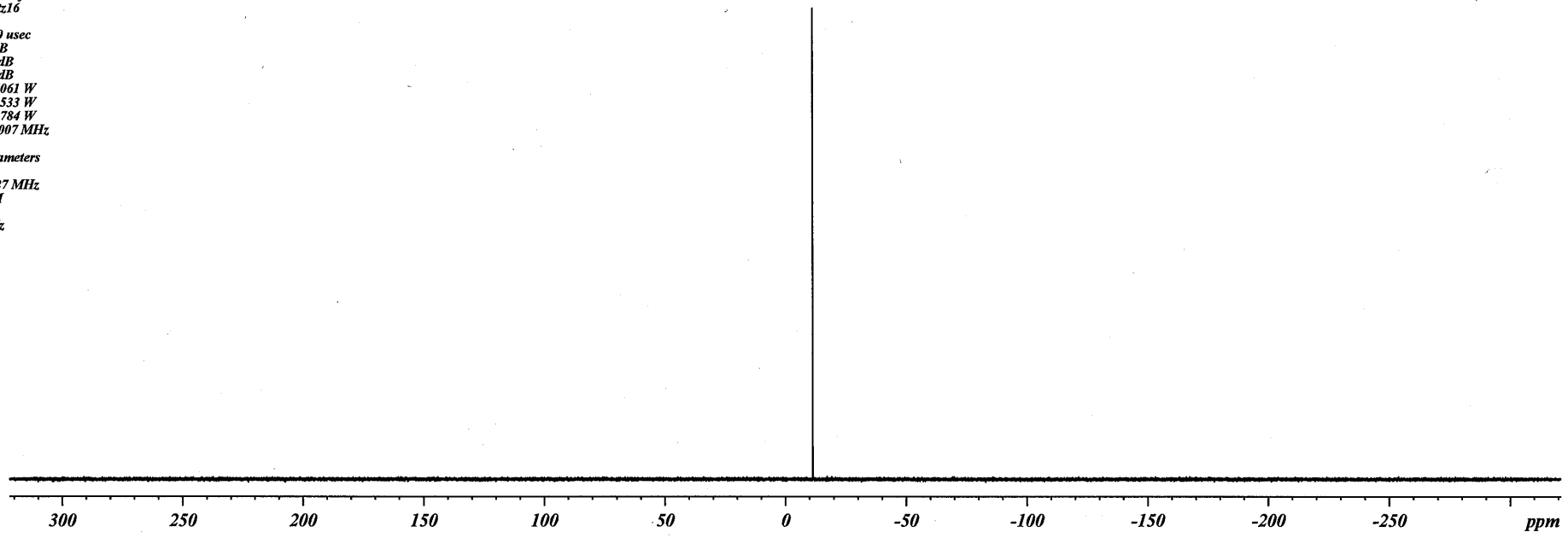
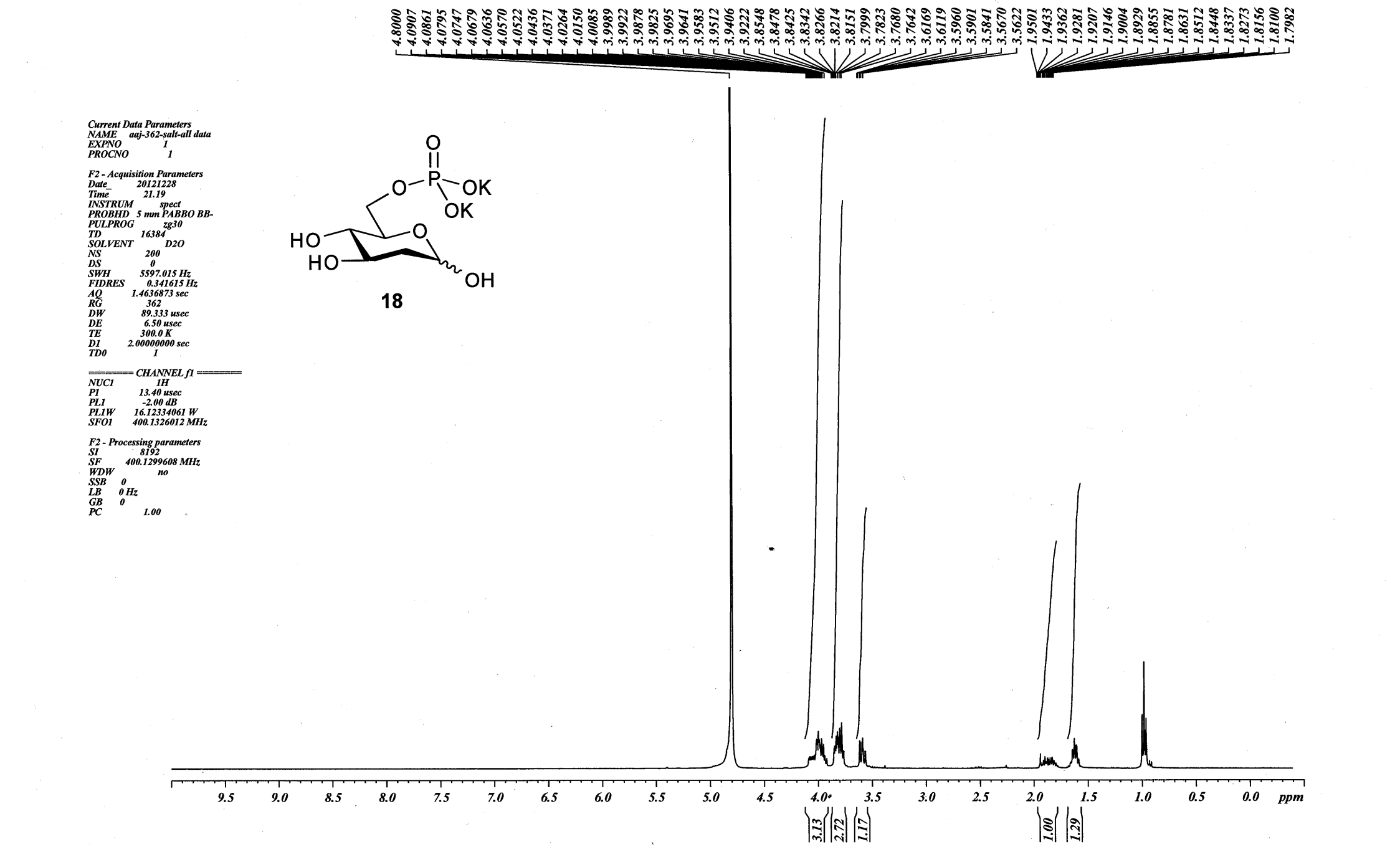
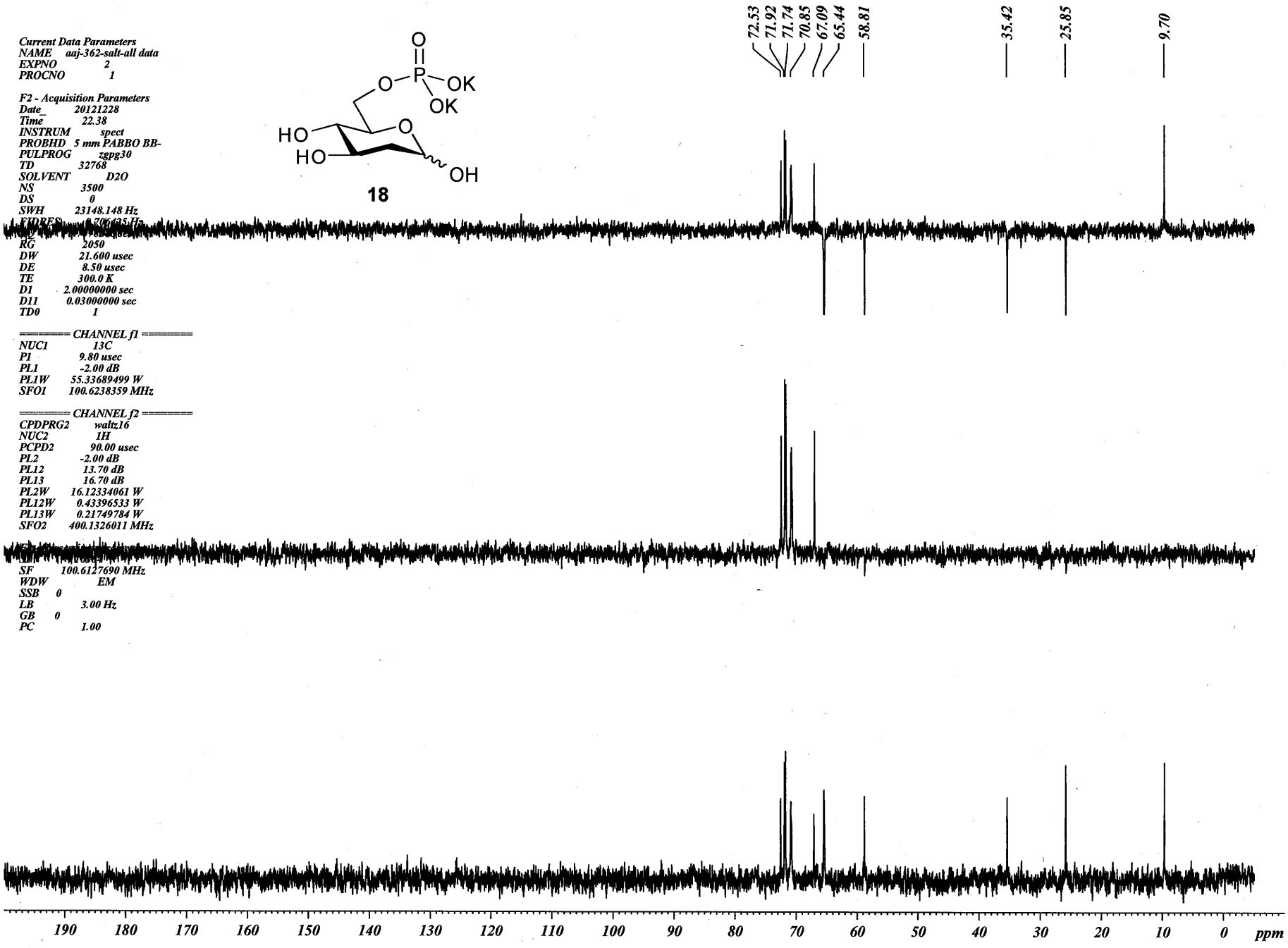






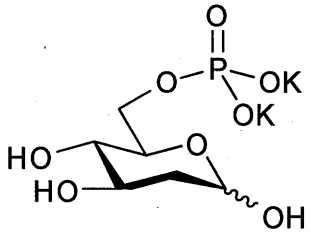
Current Data Parameters
NAME aaj-deoxy-6-p
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121226
Time 9.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 33
DS 0
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

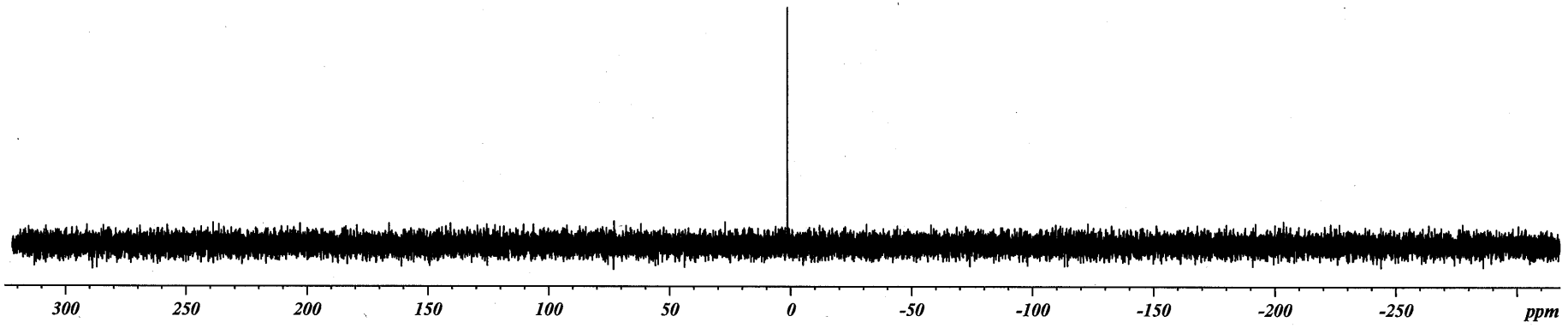
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

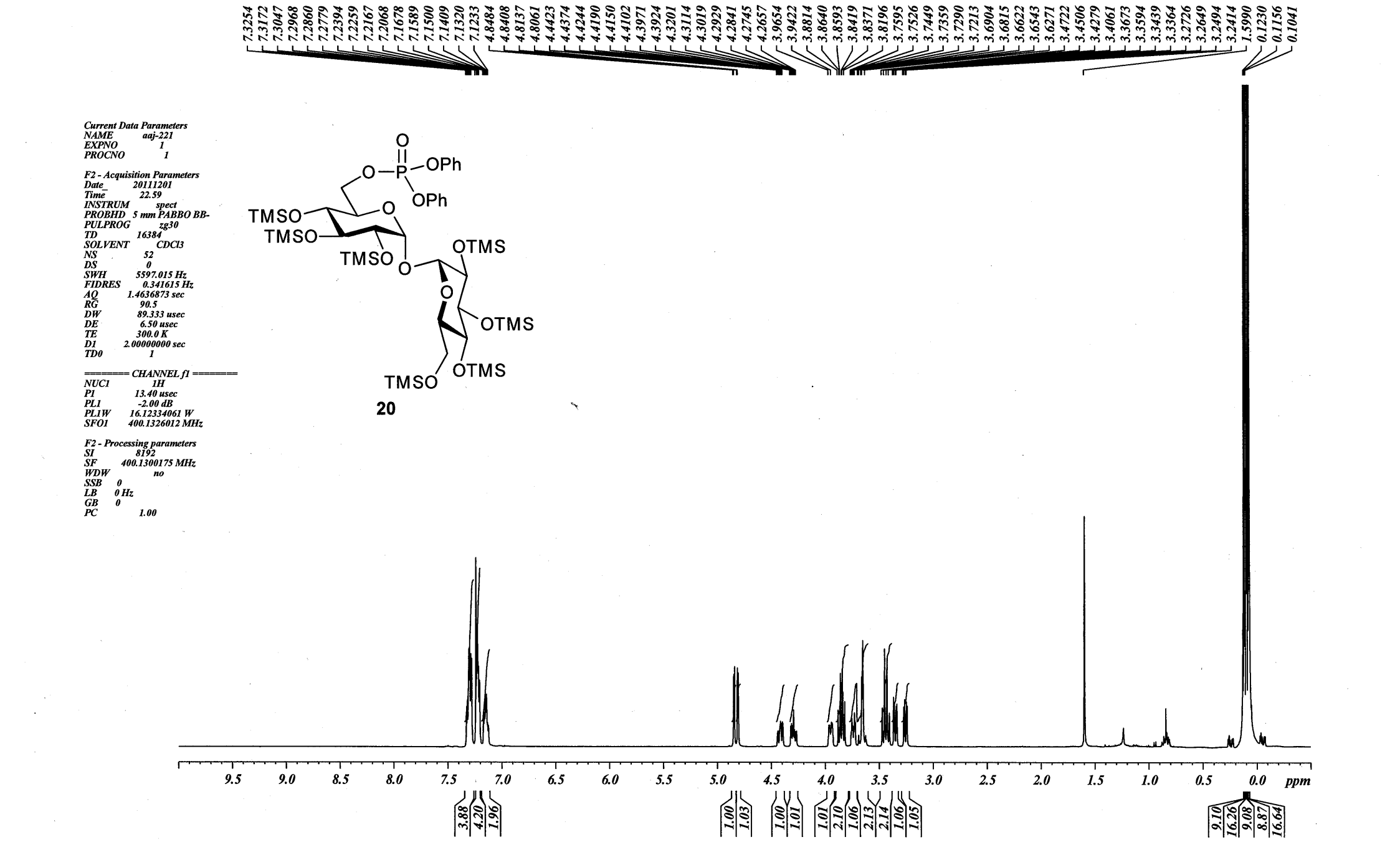
F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

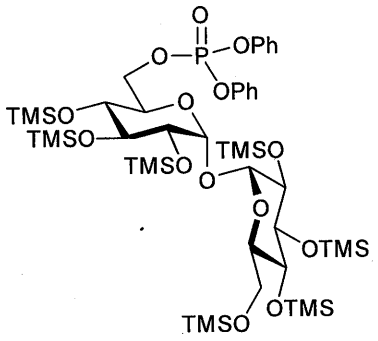


18

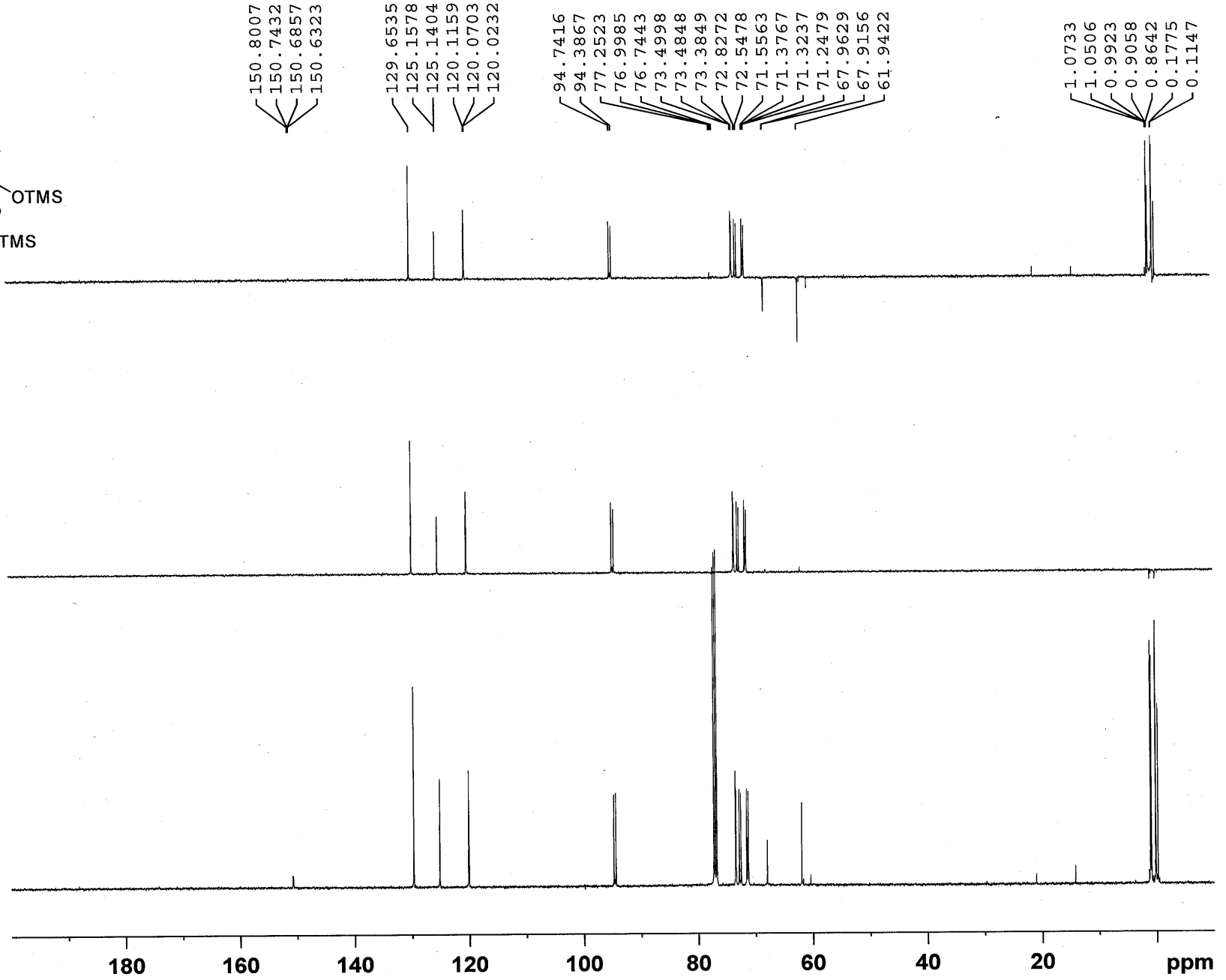
1.3360







20




```
Current Data Parameters
NAME                  CWC-332-1
EXPNO                         6
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20130823
Time                      20.13
INSTRUM                   spect
PROBHD    5 mm PABBO BB/
PULPROG                   zg0dc
TD                        32768
SOLVENT                   CDCl3
NS                         4000
DS                            2
SWH                  30120.482 Hz
FIDRES                0.919204 Hz
AQ                    0.5439988 sec
RG                         8192
DW                       16.600 usec
DE                        6.50 usec
TE                       297.9 K
D1                   3.00000000 sec
d11                  0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P0                        9.50 usec
PL1                       3.00 dB
SFO1                125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                        1H
PCPD2                    90.00 usec
PL2                      -5.00 dB
PL12                     14.60 dB
SFO2                500.1320005 MHz

F2 - Processing parameters
SI                        32768
SF                  125.7577896 MHz
WDW                          EM
SSB          0
LB                        2.00 Hz
GB           0
PC                        1.00
```

Current Data Parameters
NAME aaj-221-31P
EXPNO 1
PROCNO 1

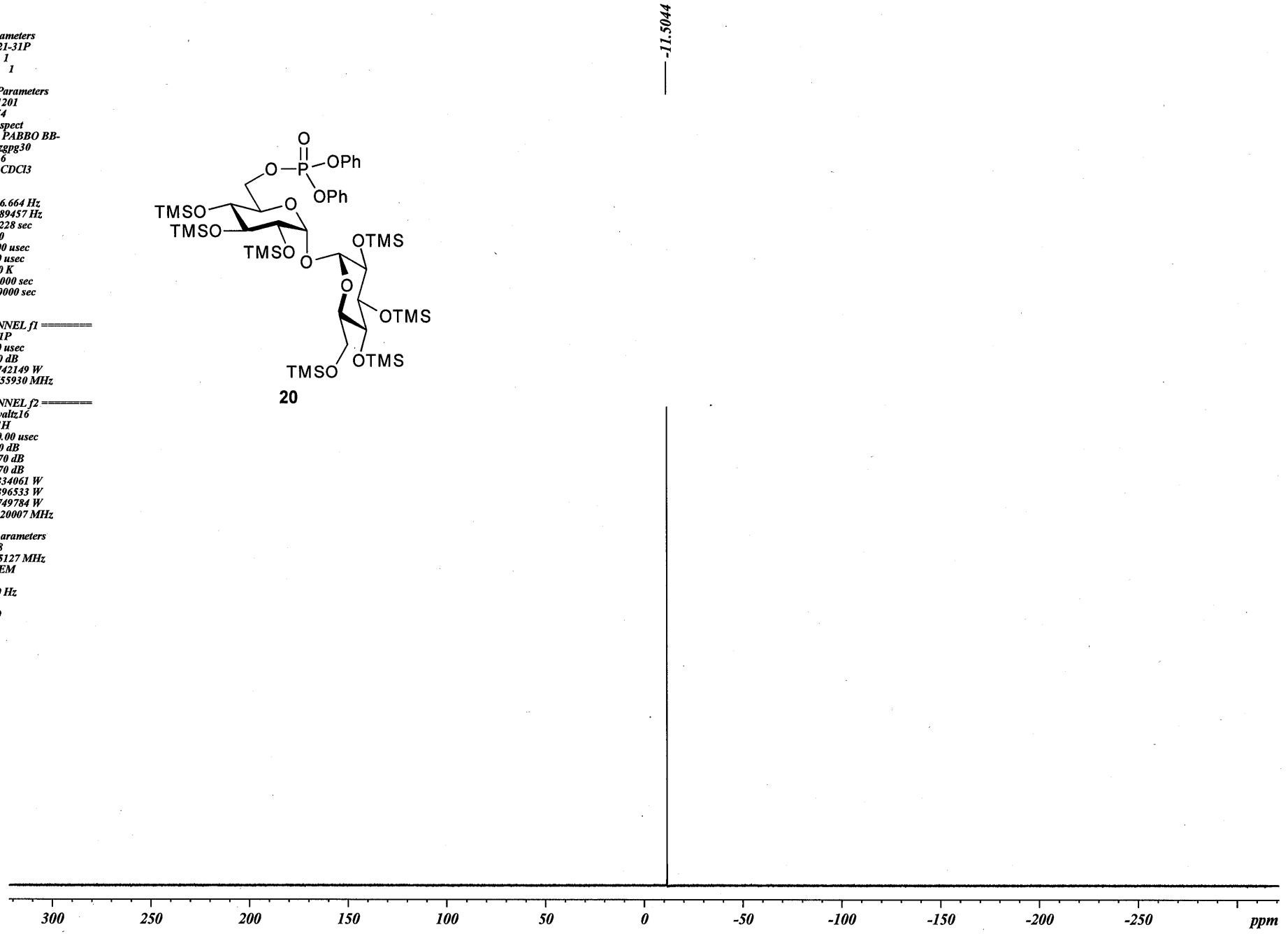
F2 - Acquisition Parameters
Date_ 20111201
Time 22.54
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 53
DS 0
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

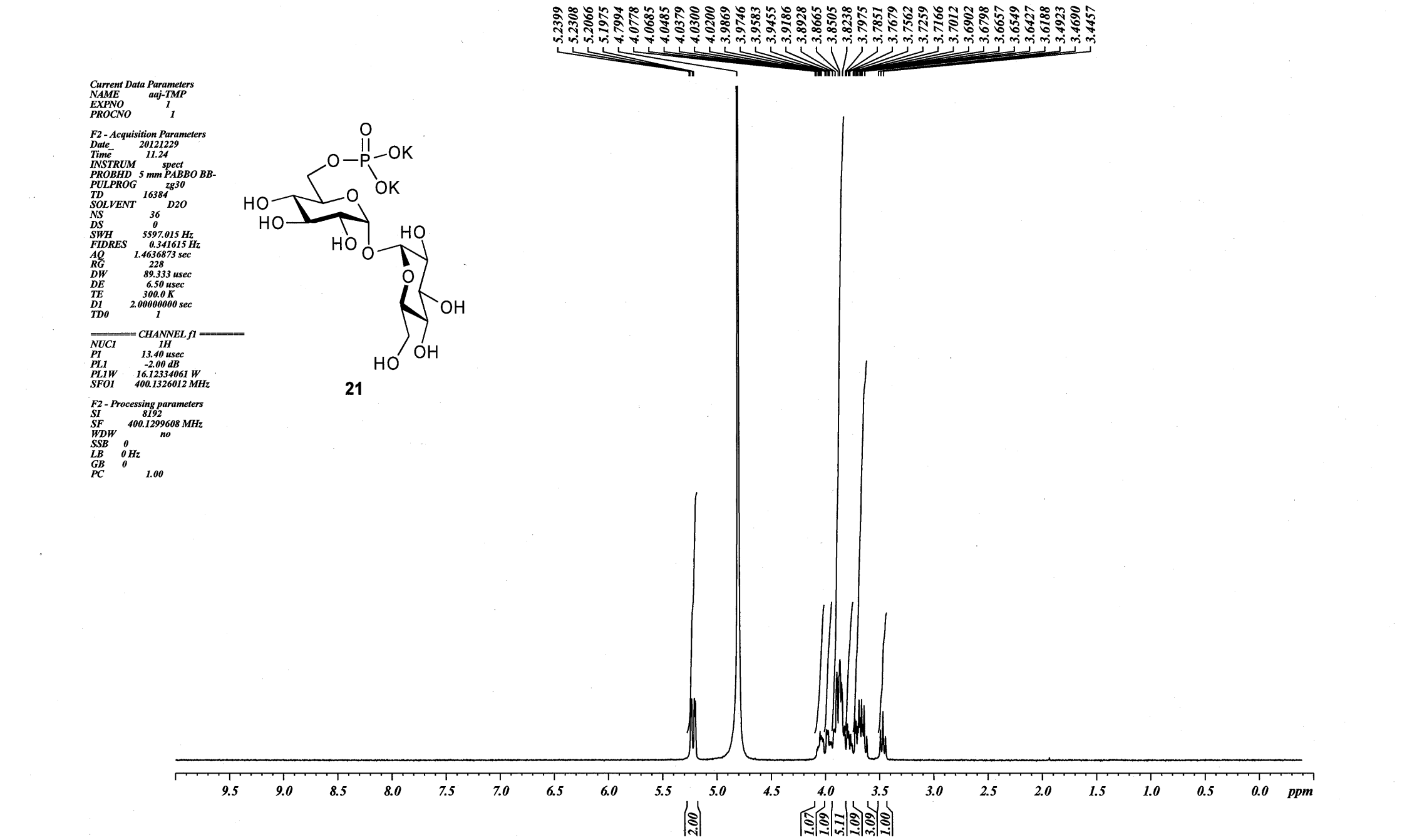
======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

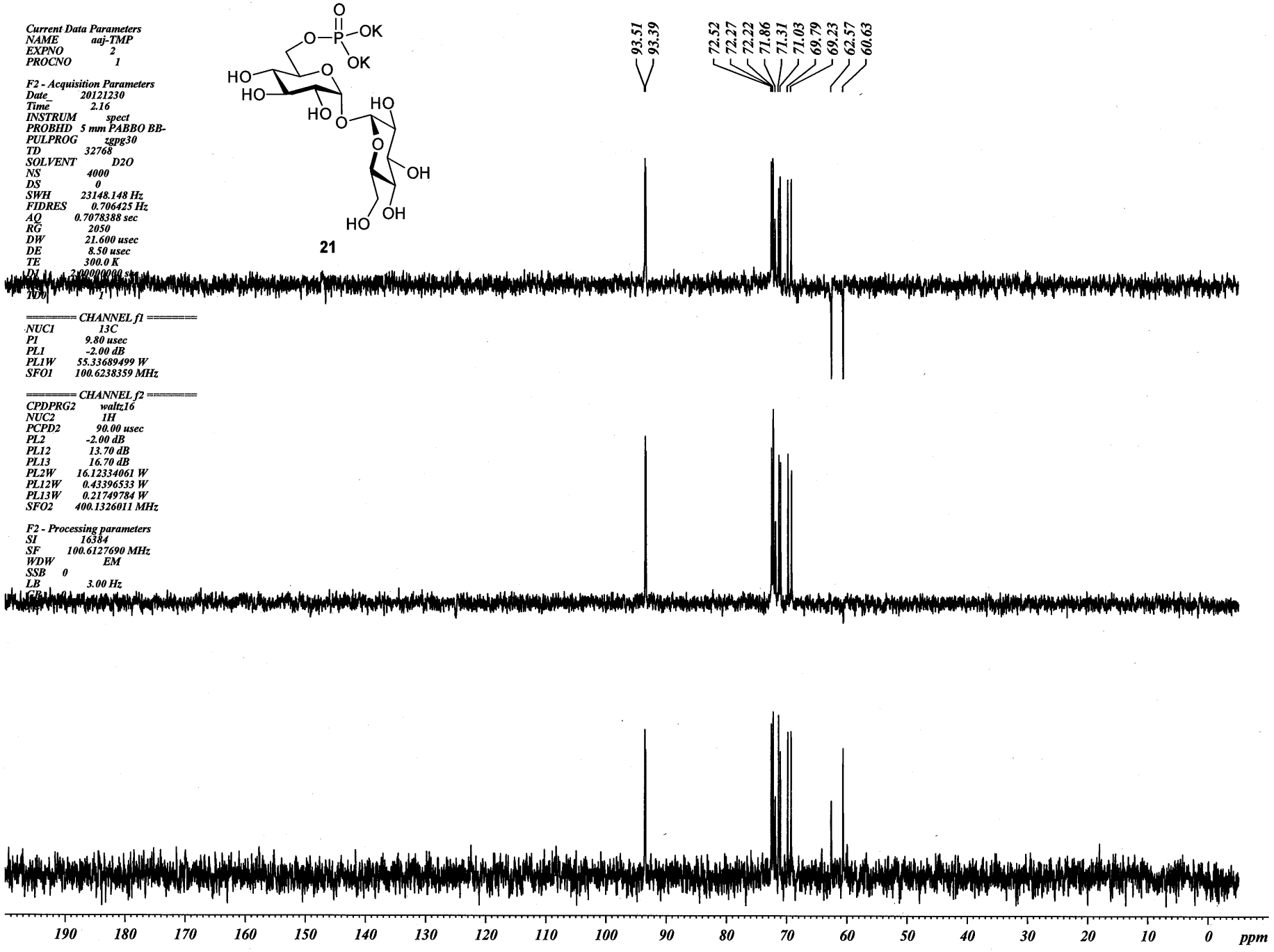
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

20







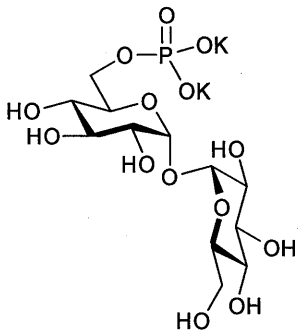
Current Data Parameters
NAME aaj-tmp-2k salt
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121229
Time 11.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 19
DS 0
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

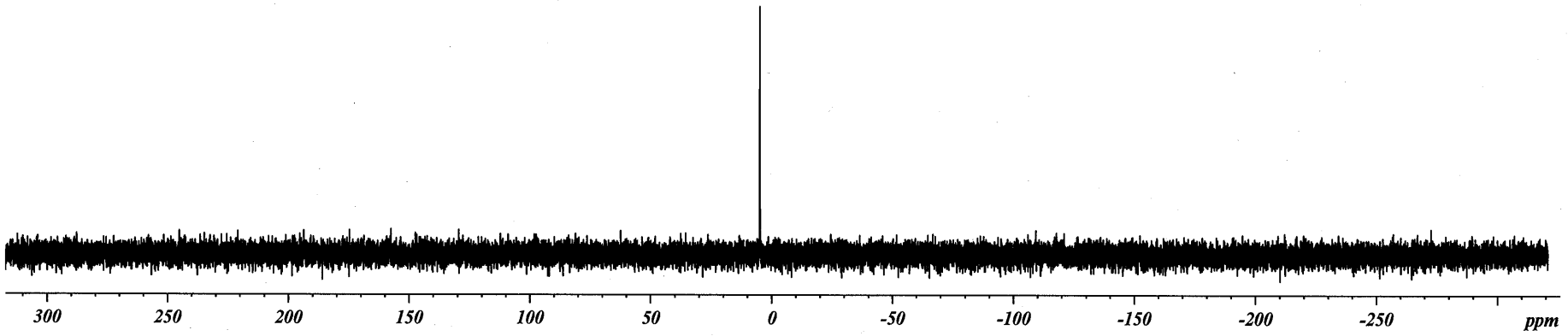
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

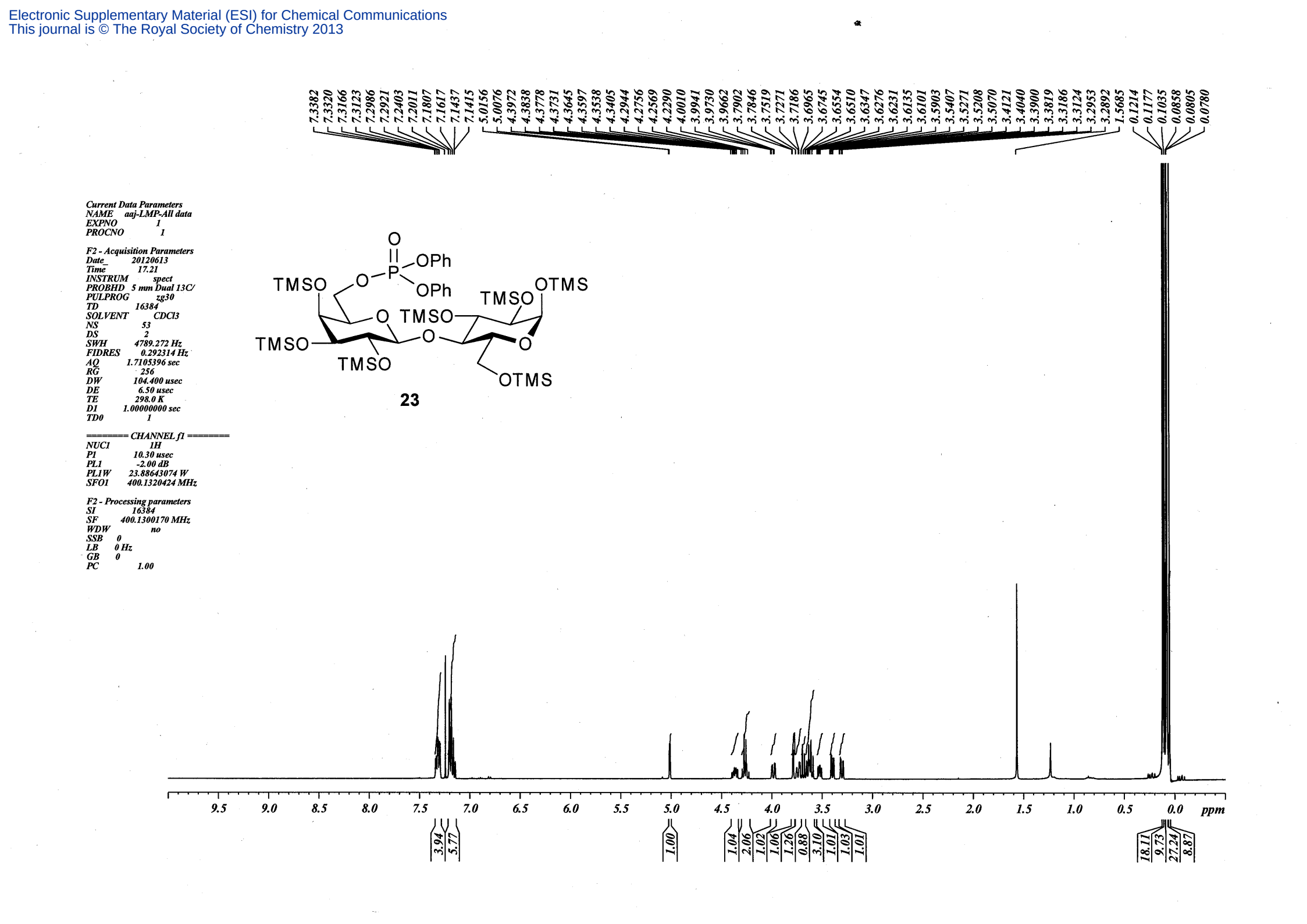
F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

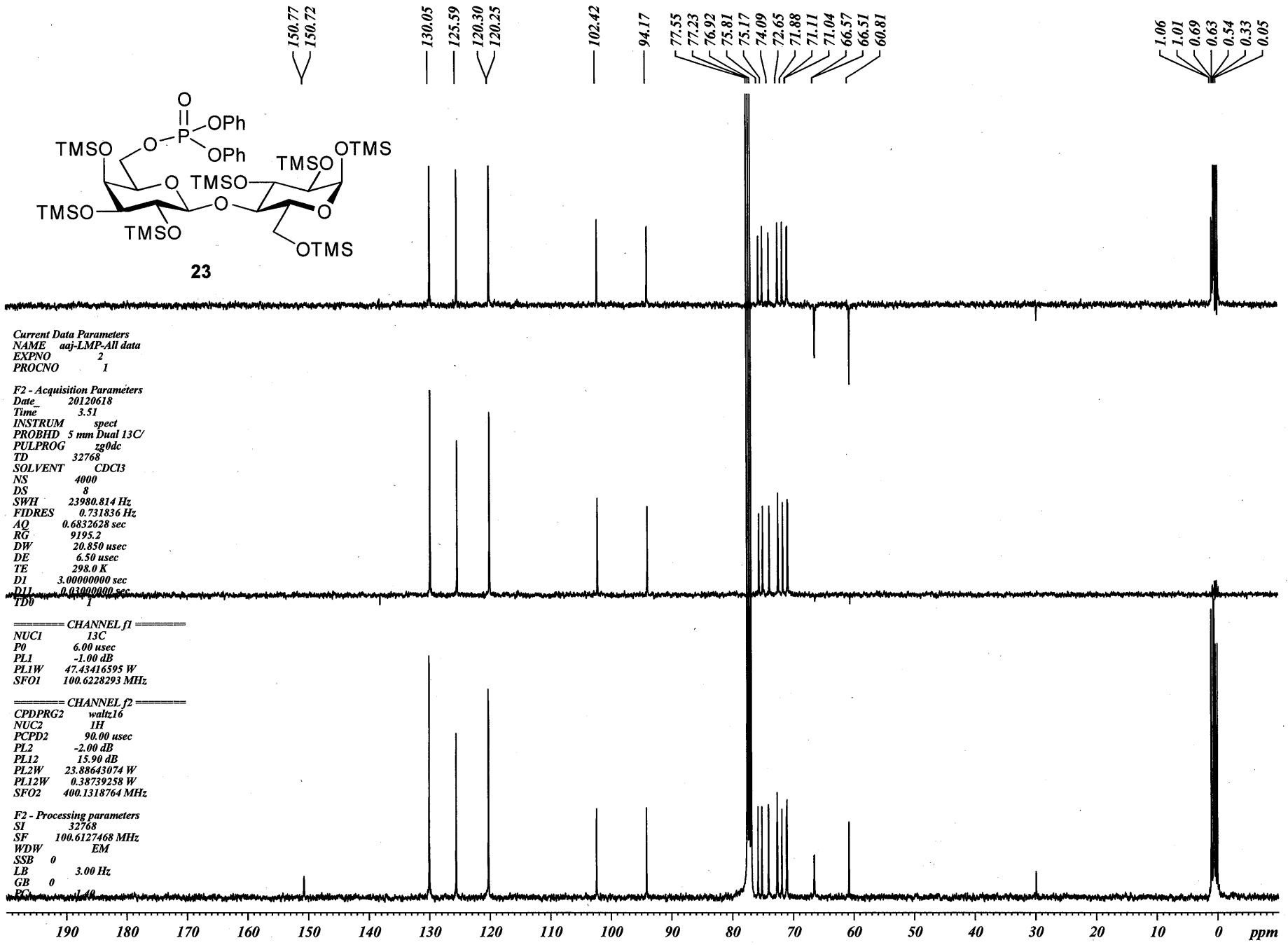


21

4.8857







-11.7199

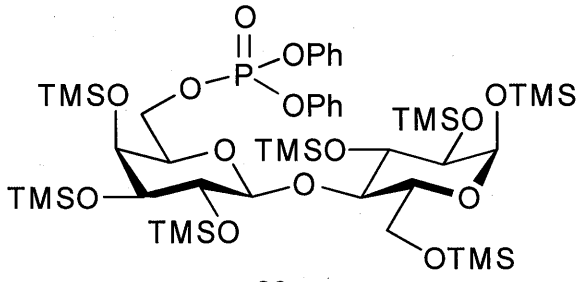
```
Current Data Parameters
NAME      aaj-lmp-pure
EXPNO             2
PROCNO            1

F2 - Acquisition Parameters
Date_        20120831
Time              9.25
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD               65536
SOLVENT           CDCl3
NS                   7
DS                   0
SWH         104166.664 Hz
FIDRES        1.589457 Hz
AQ          0.3146228 sec
RG                2050
DW               4.800 usec
DE               6.50 usec
TE               300.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1              31P
P1               13.50 usec
PL1               2.00 dB
PL1W        16.00742149 W
SFO1       161.9755930 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            90.00 usec
PL2              -2.00 dB
PL12              13.70 dB
PL13              16.70 dB
PL2W        16.12334061 W
PL12W        0.43396533 W
PL13W        0.21749784 W
SFO2       400.1320007 MHz

F2 - Processing parameters
SI               32768
SF         161.9755127 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.00
```



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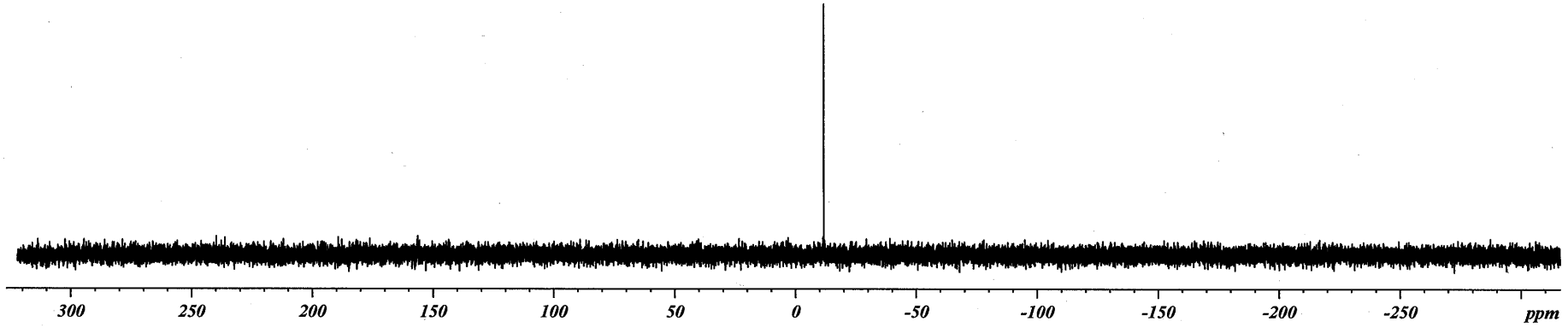

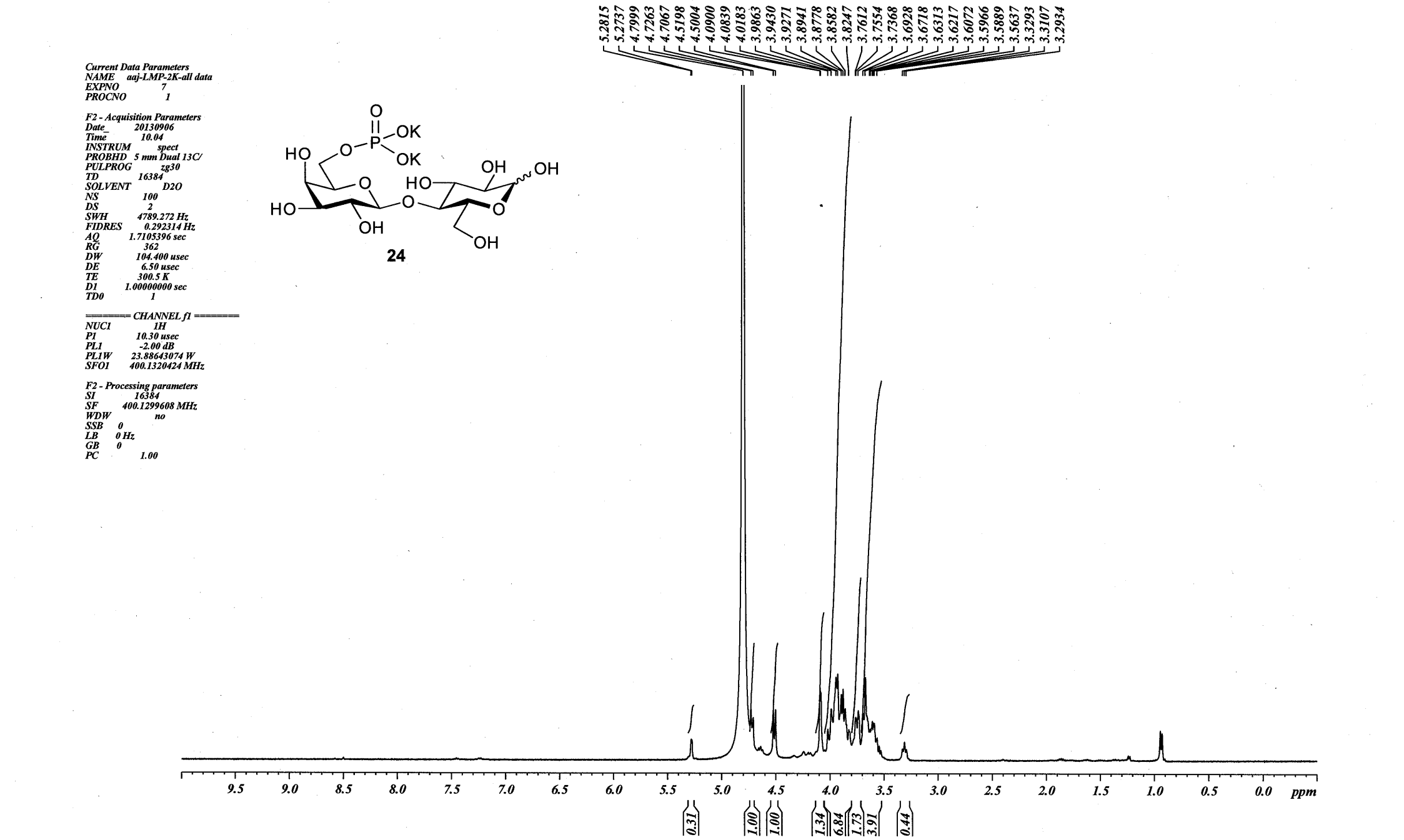

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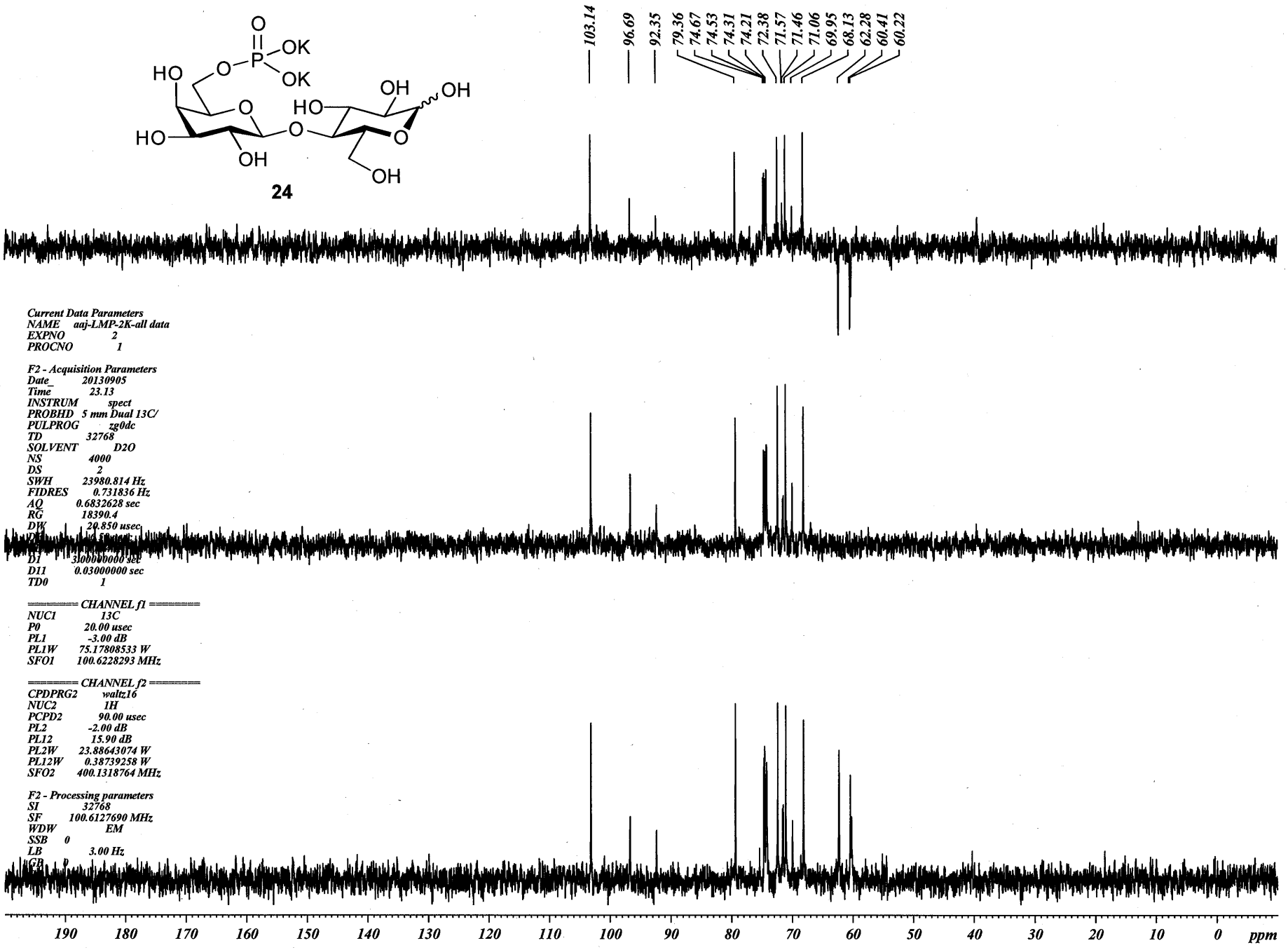
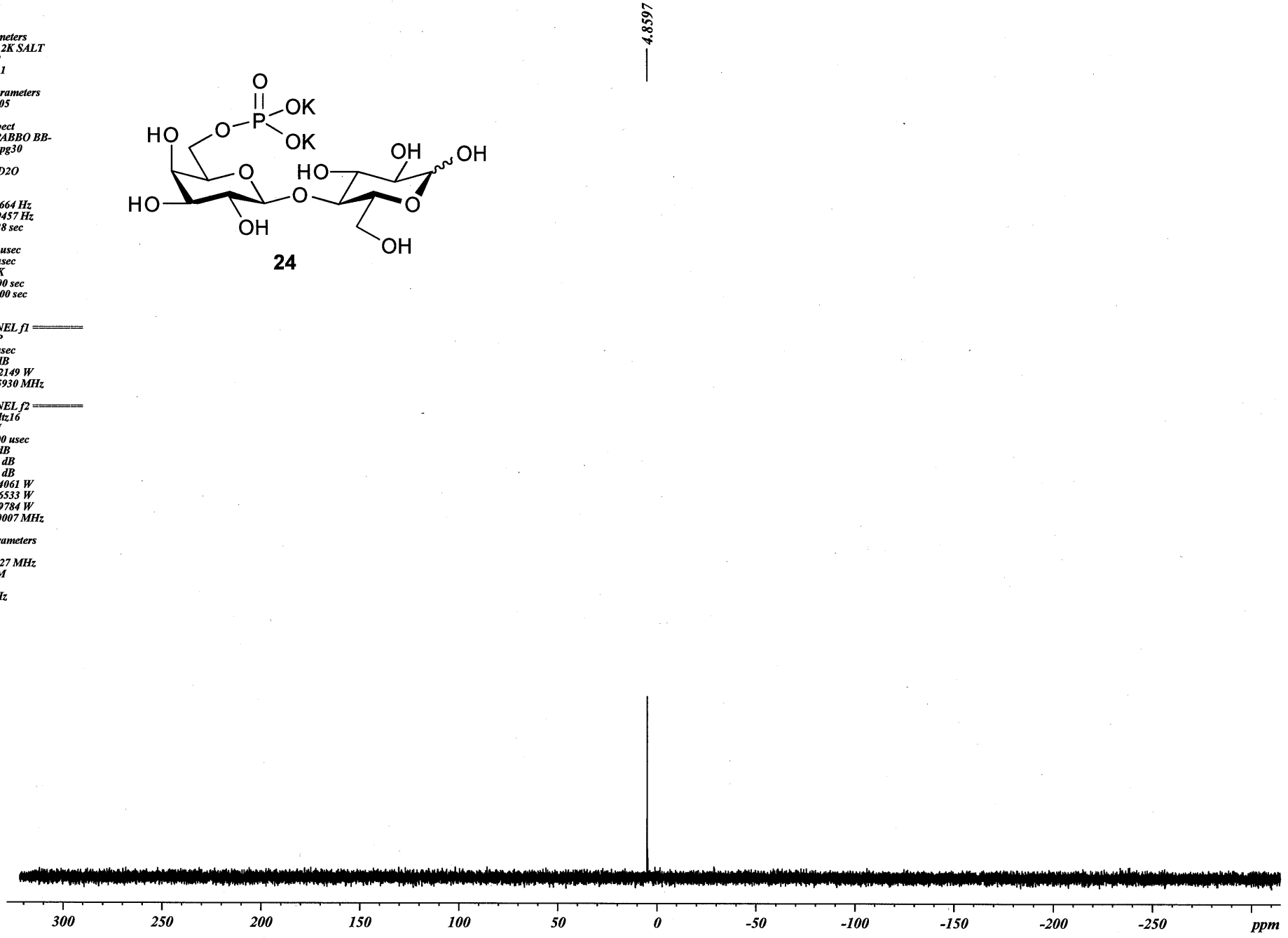
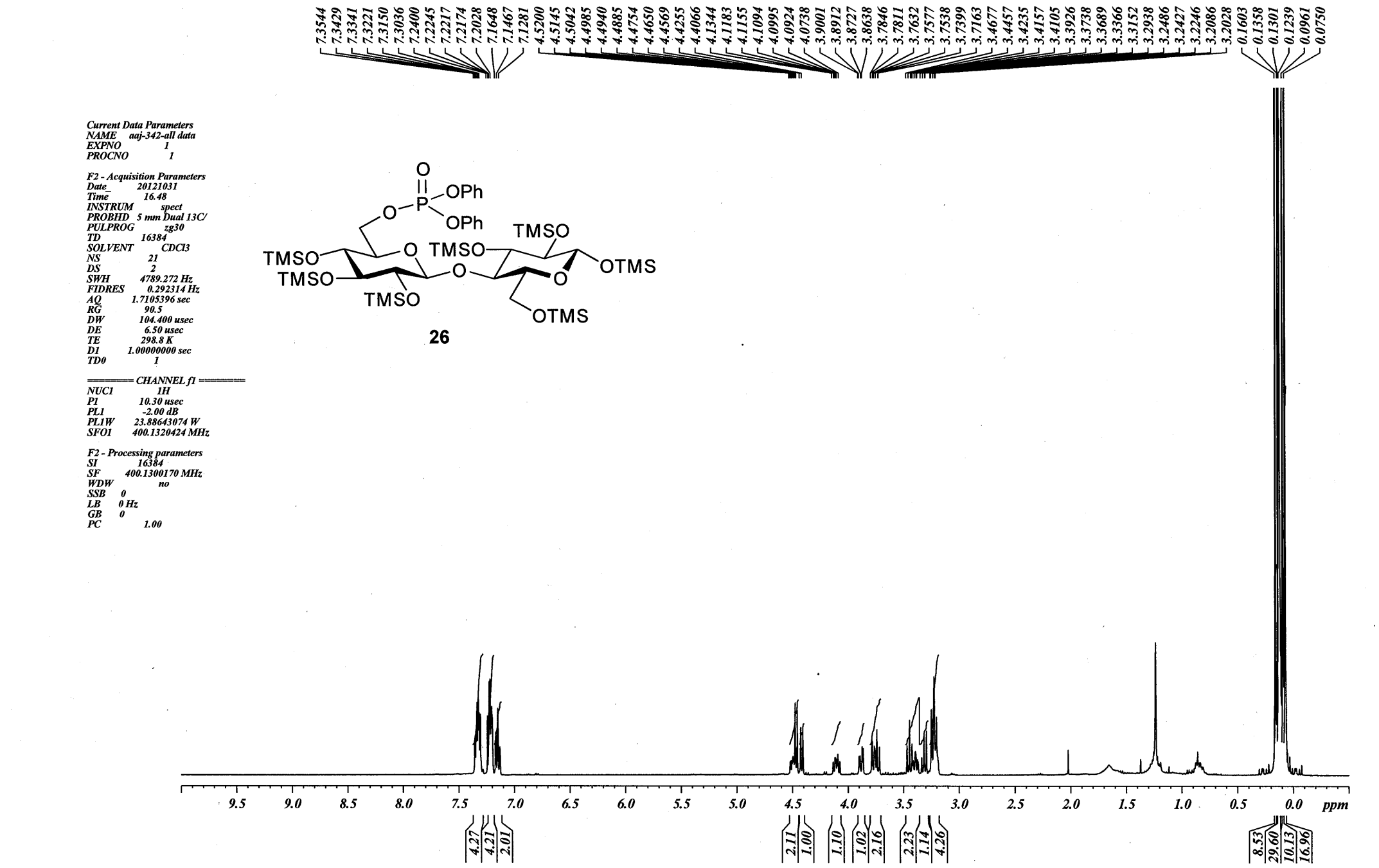
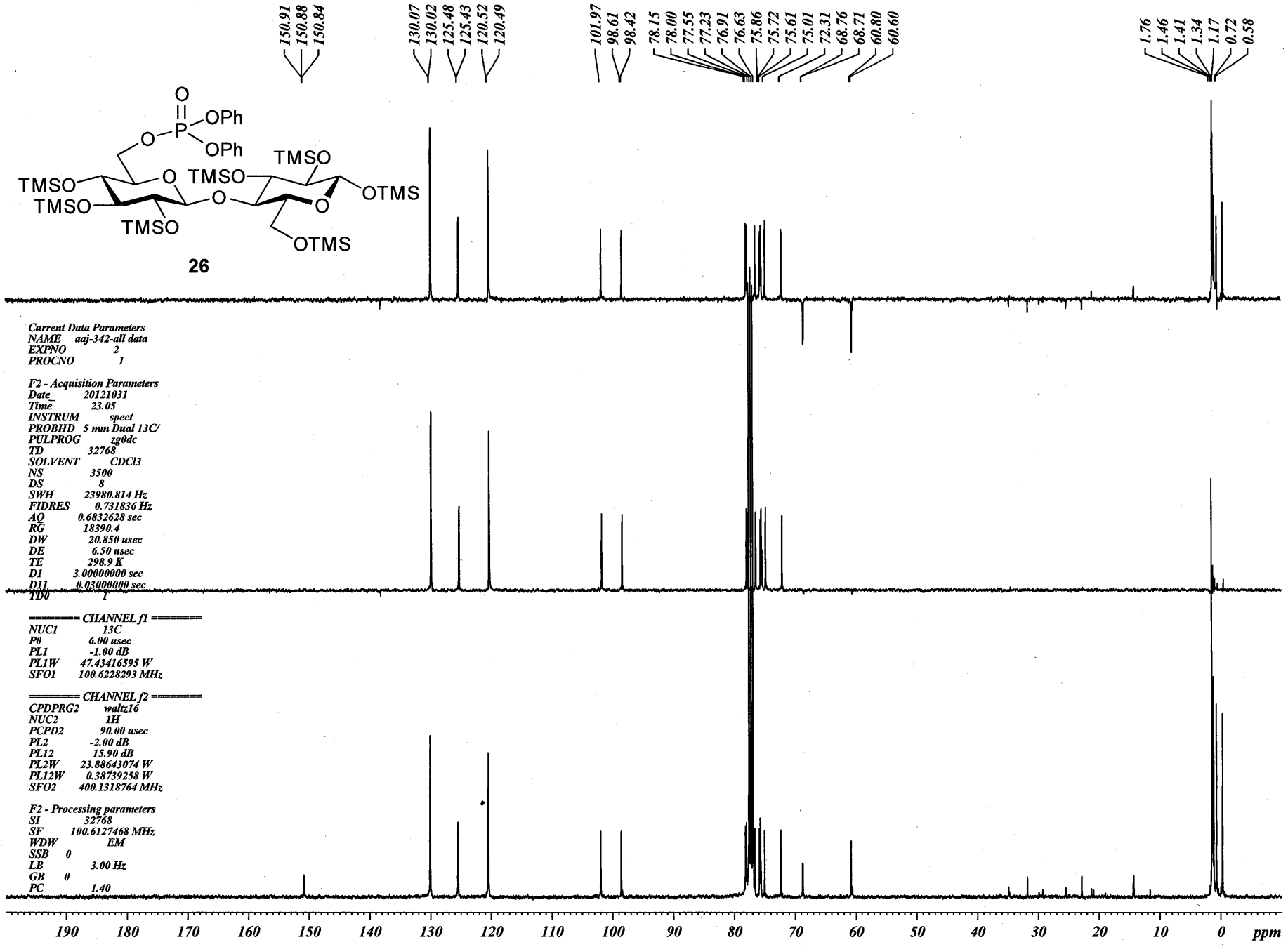


```
Current Data Parameters
NAME     aaj-LMP 2K SALT
EXPNO              2
PROCNO             1

F2 - Acquisition Parameters
Date_         20130905
Time             23.02
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD              65536
SOLVENT           D2O
NS                 23
DS                  0
SWH         104166.664 Hz
FIDRES        1.589457 Hz
AQ          0.3146228 sec
RG                2050
DW               4.800 usec
DE               6.50 usec
TE              300.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              31P
P1              13.50 usec
PL1              2.00 dB
PL1W        16.00742149 W
SFO1        161.9755930 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2            90.00 usec
PL2             -2.00 dB
PL12             13.70 dB
PL13             16.70 dB
PL2W        16.12334061 W
PL12W        0.43396533 W
PL13W        0.21749784 W
SFO2        400.1320007 MHz

F2 - Processing parameters
SI              32768
SF         161.9755127 MHz
WDW                EM
SSB      0
LB               1.00 Hz
GB       0
PC               1.00
```


24







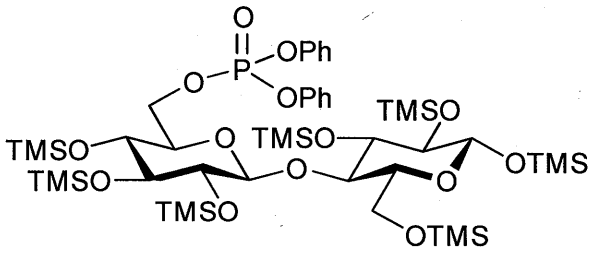
Current Data Parameters
NAME aaj-342-crude
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121030
Time 16.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 20
DS 0
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

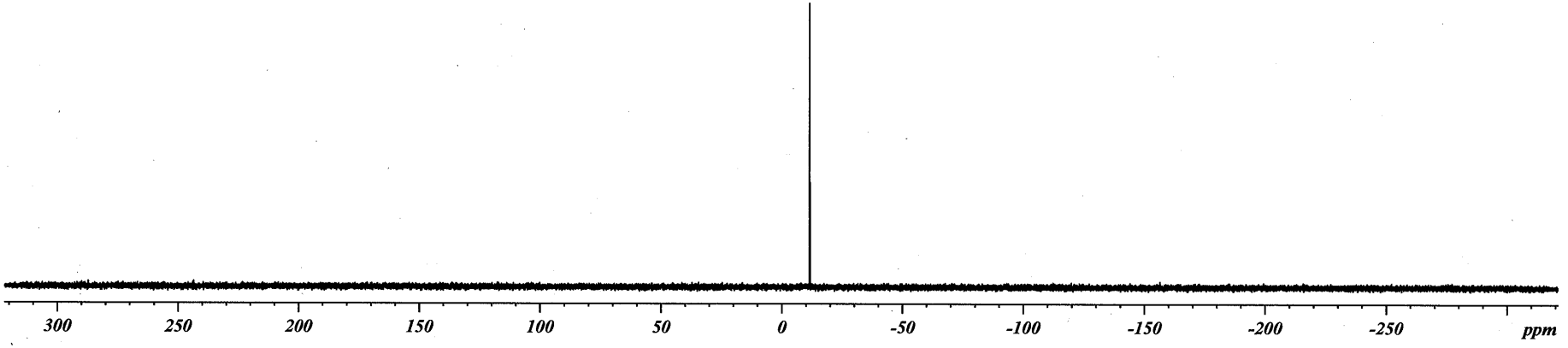
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

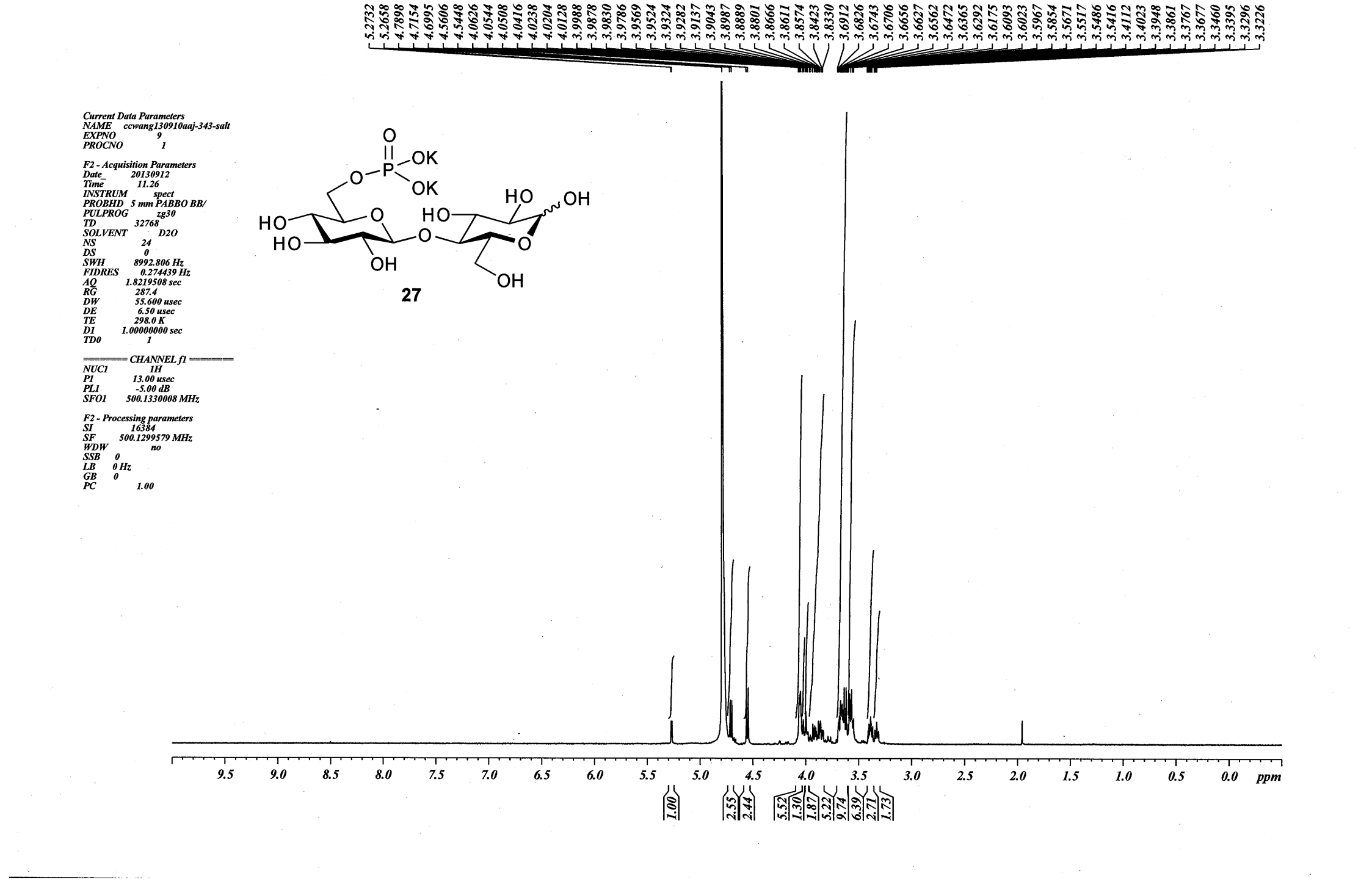
F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

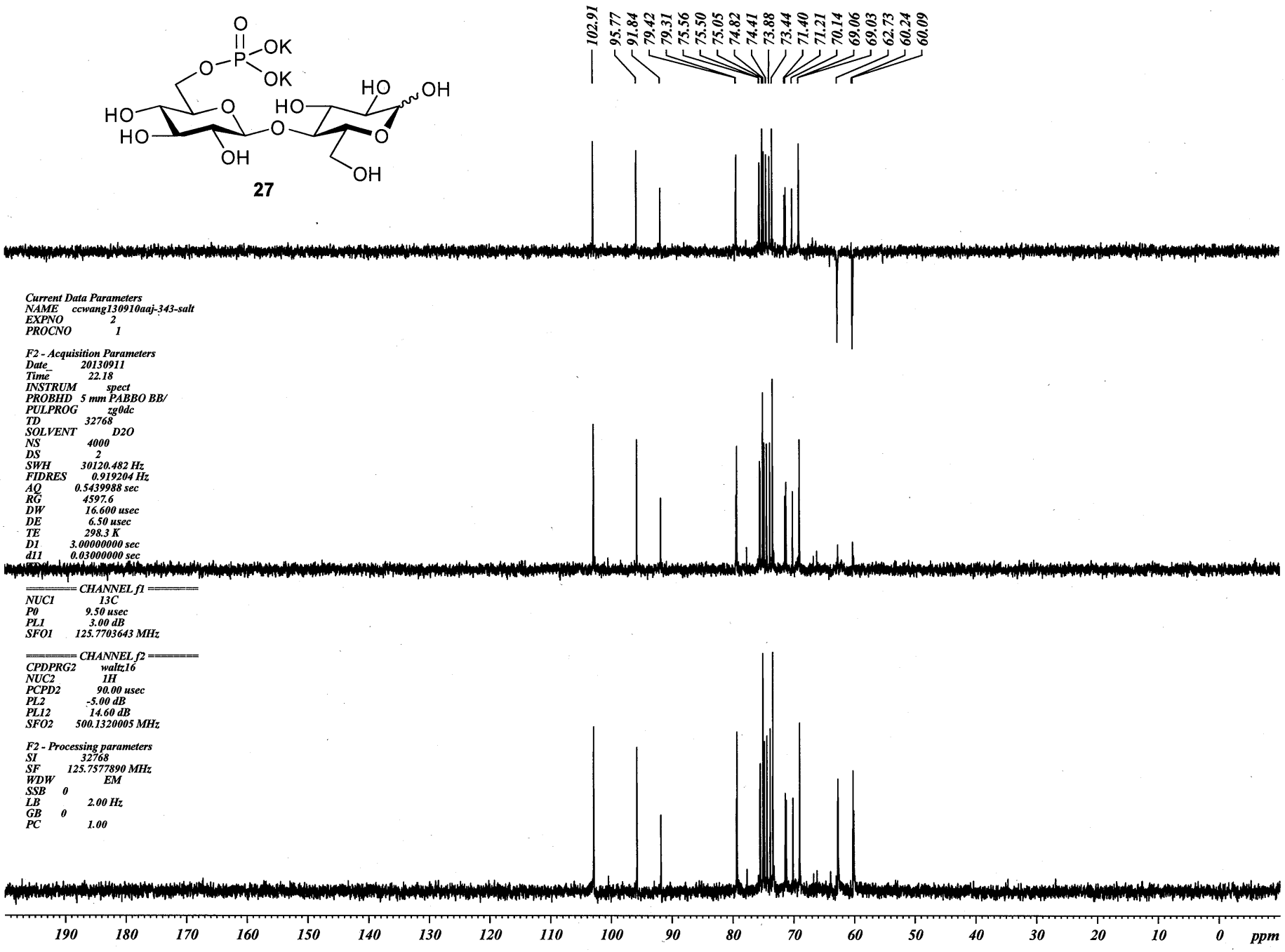


26

-11.4831

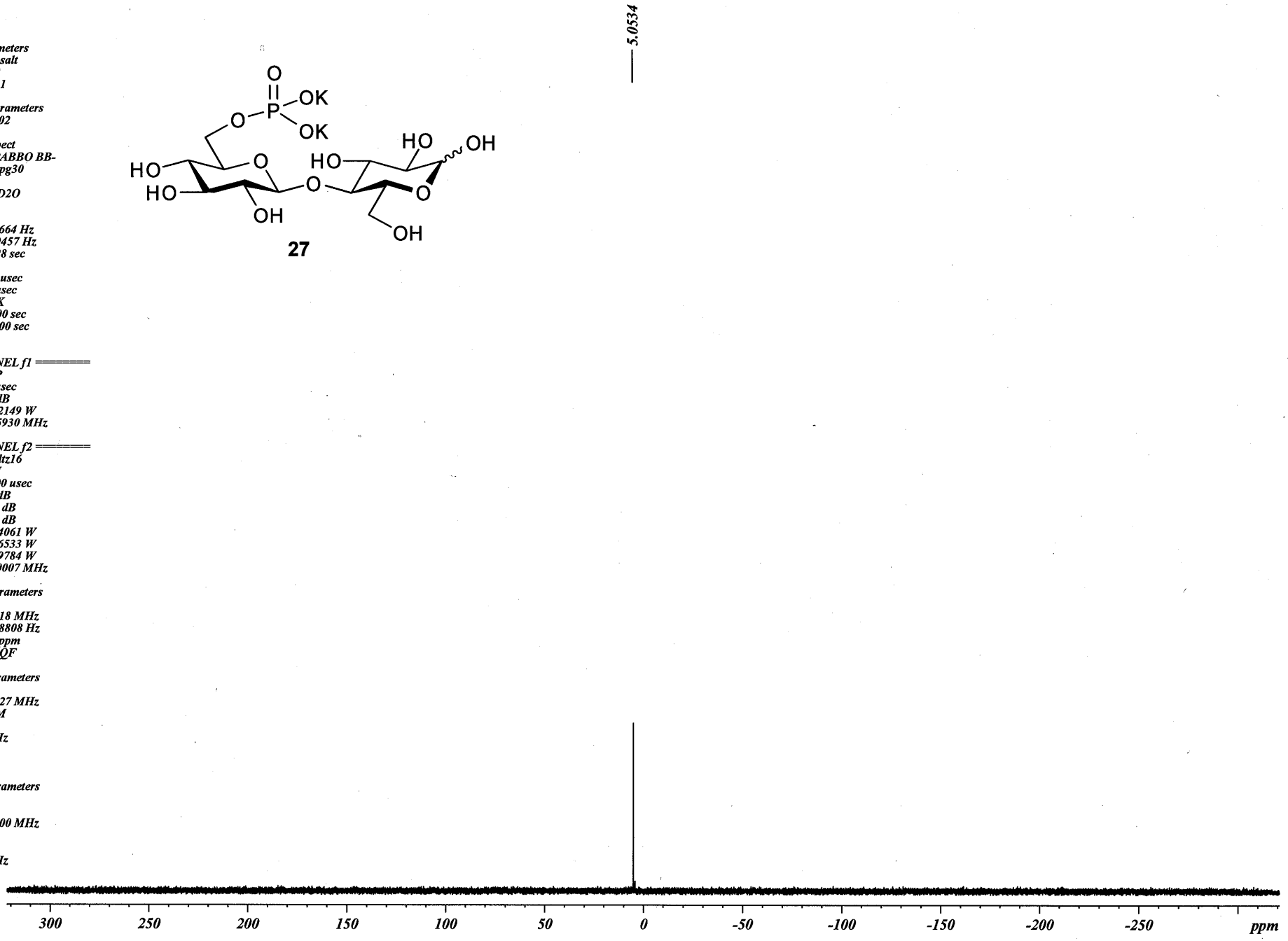


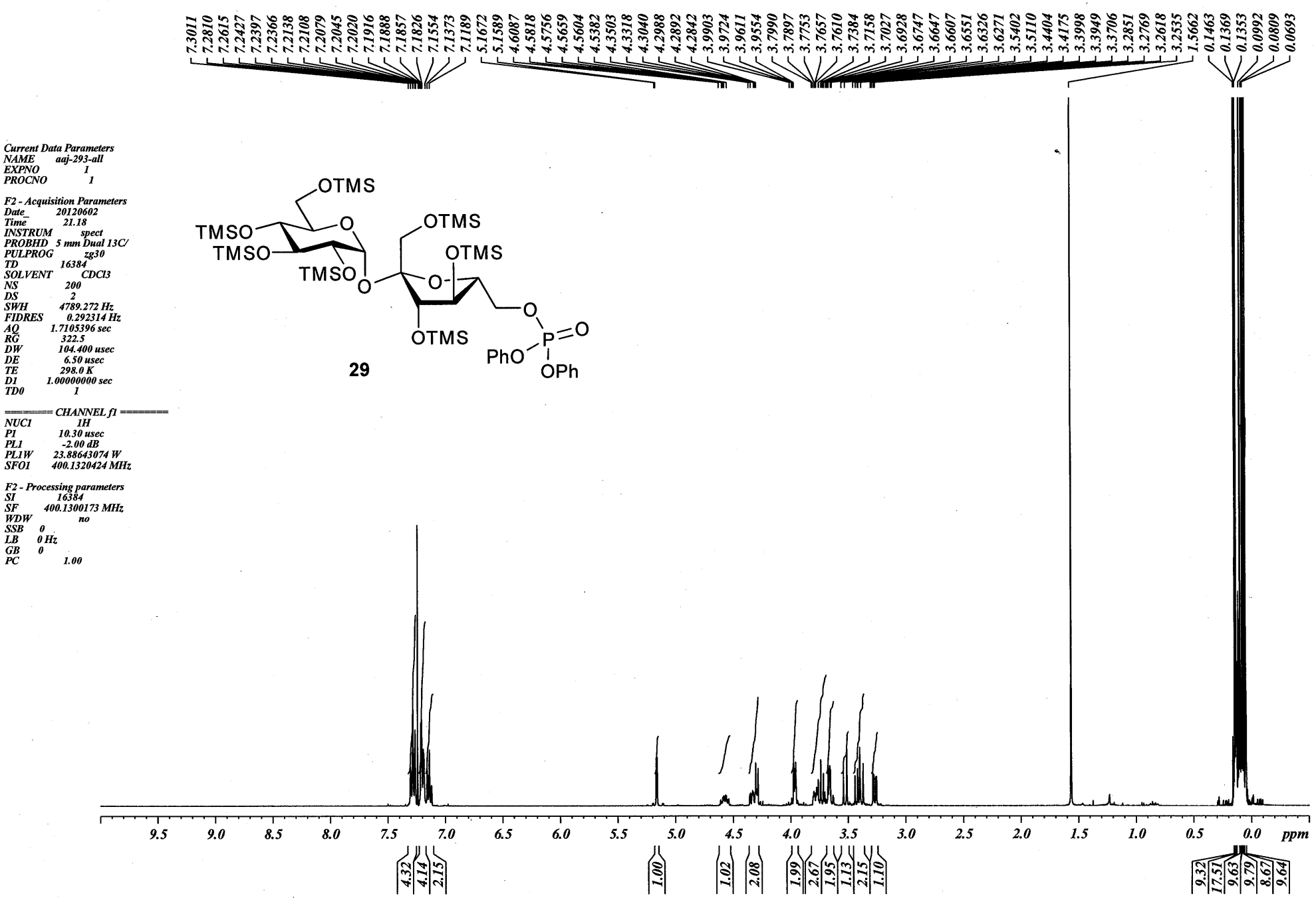


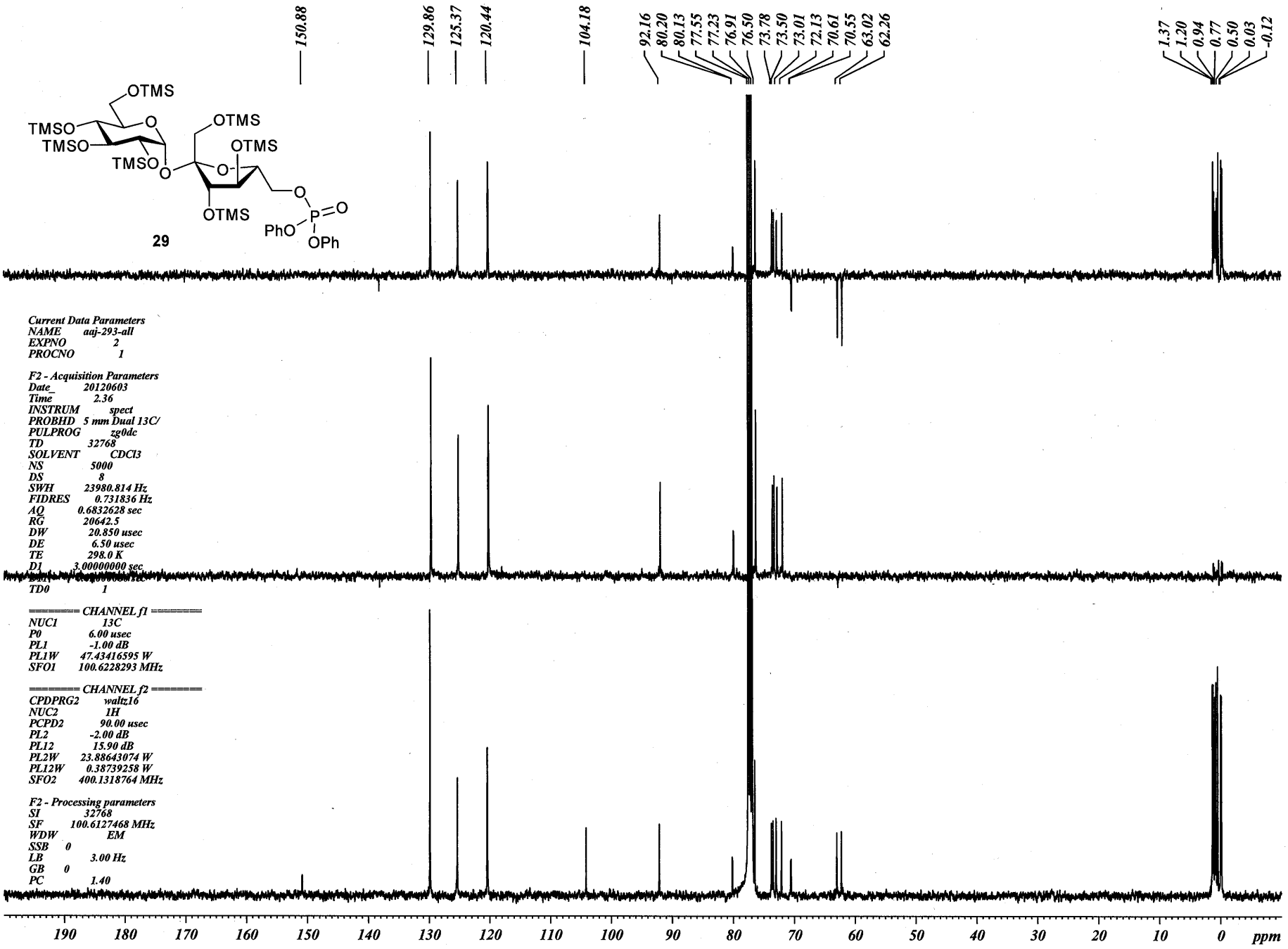


27

```
Current Data Parameters
NAME      aaj-343-salt
EXPNO          2
PROCNO         1

F2 - Acquisition Parameters
Date_      20121102
Time         16.49
INSTRUM        spect
PROBHD   5 mm PABBO BB-
PULPROG        zgpg30
TD           65536
SOLVENT        D2O
NS             28
DS              0
SWH       104166.664 Hz
FIDRES      1.589457 Hz
AQ        0.3146228 sec
RG           2050
DW           4.800 usec
DE           6.50 usec
TE           300.0 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0            1

======== CHANNEL f1 ========
NUC1          31P
P1          13.50 usec
PL1          2.00 dB
PL1W      16.00742149 W
SFO1      161.9755930 MHz

======== CHANNEL f2 ========
CPDPRG2       waltz16
NUC2          1H
PCPD2         90.00 usec
PL2          -2.00 dB
PL12          13.70 dB
PL13          16.70 dB
PL2W      16.12334061 W
PL12W      0.43396533 W
PL13W      0.21749784 W
SFO2      400.1320007 MHz

F1 - Acquisition parameters
TD             256
SFO1       400.1318 MHz
FIDRES      15.258808 Hz
SW          9.762 ppm
FnMODE         QF

F2 - Processing parameters
SI           32768
SF        161.9755127 MHz
WDW            EM
SSB     0
LB           1.00 Hz
GB      0
PC           1.00

F1 - Processing parameters
SI           1024
MC2            QF
SF        400.1300000 MHz
WDW
SSB     0
LB           0.30 Hz
GB           0.1
```







Current Data Parameters
NAME AAJ-SUC6'P
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120915
Time 11.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 18
DS 0
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

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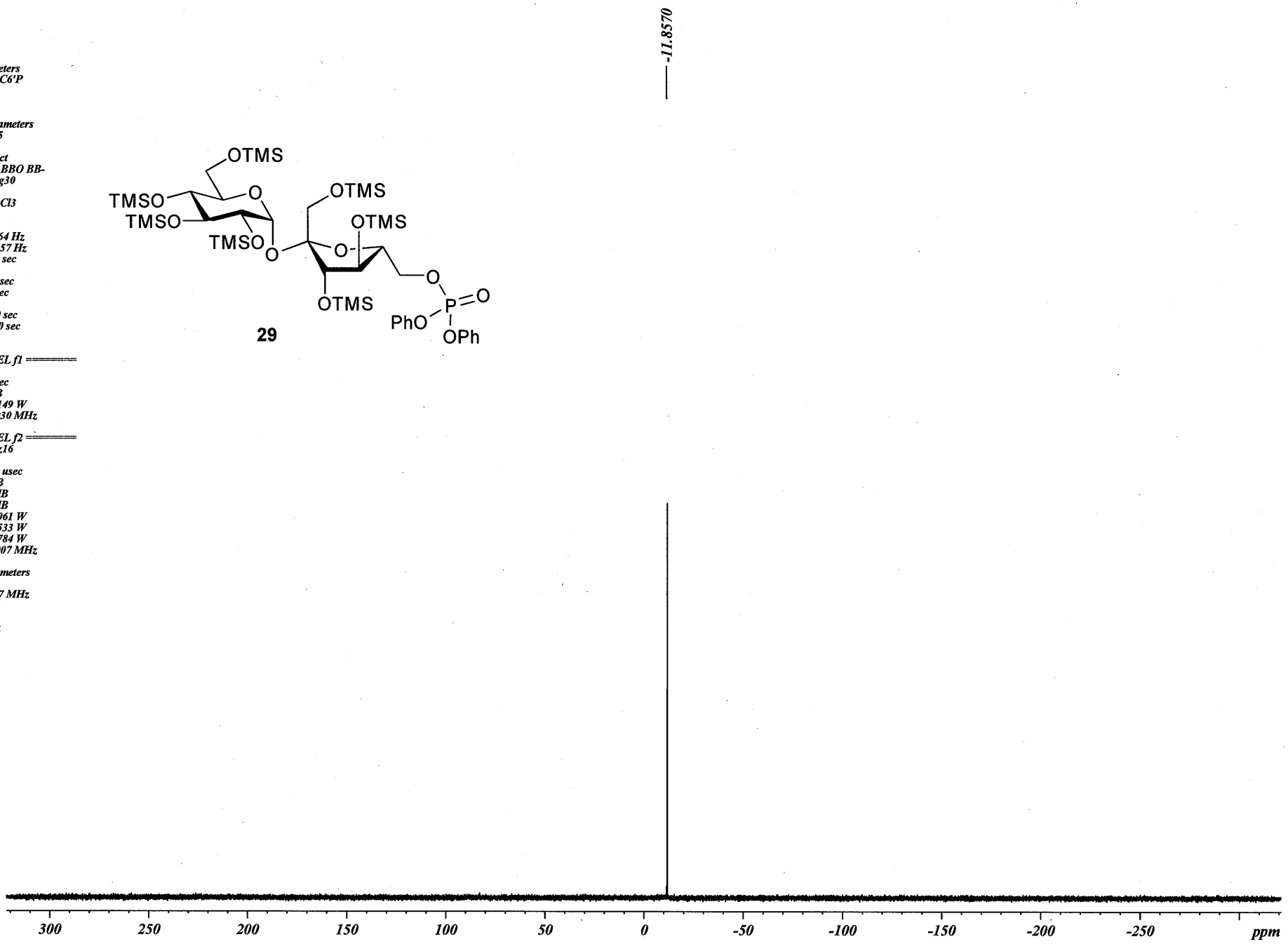

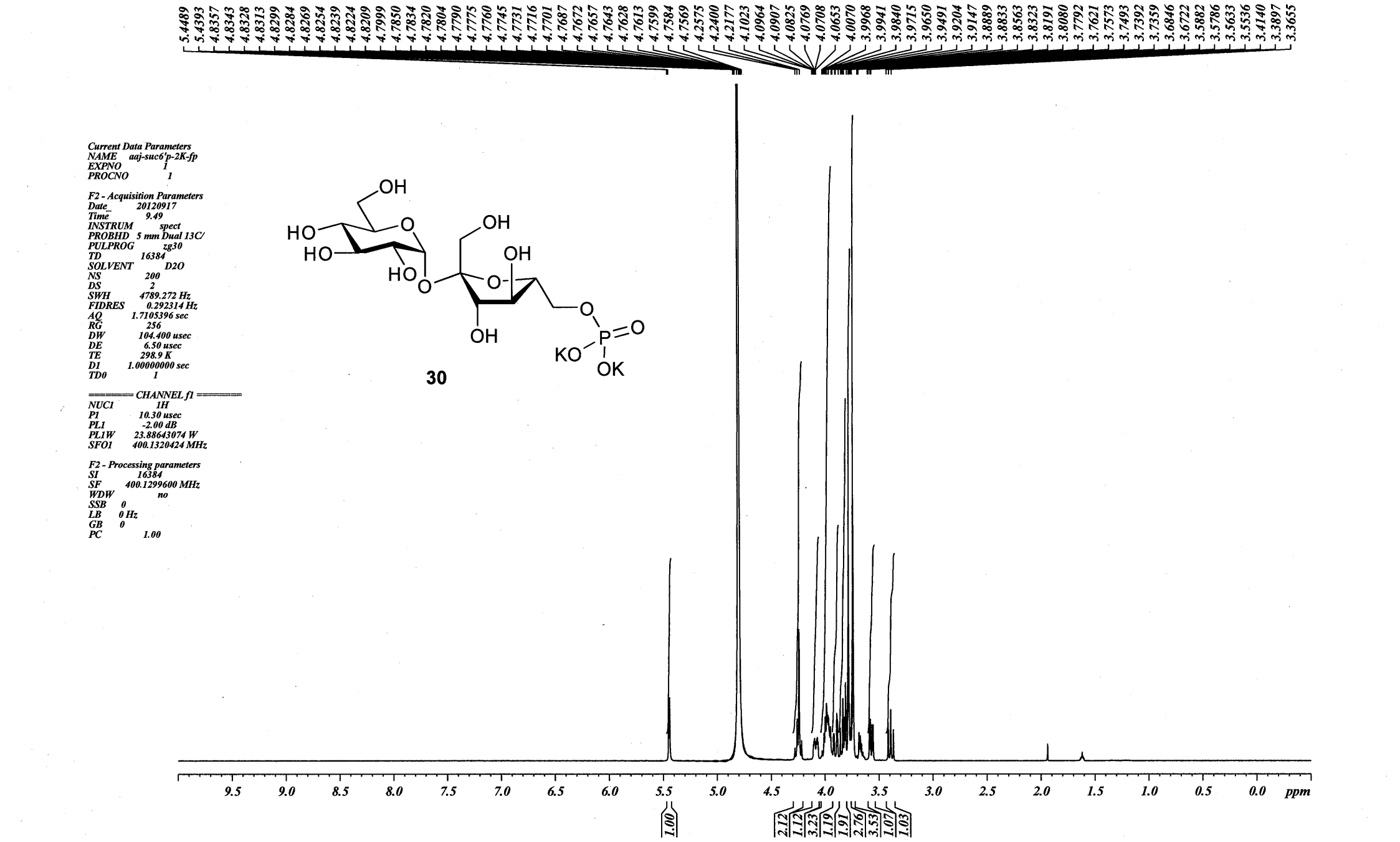

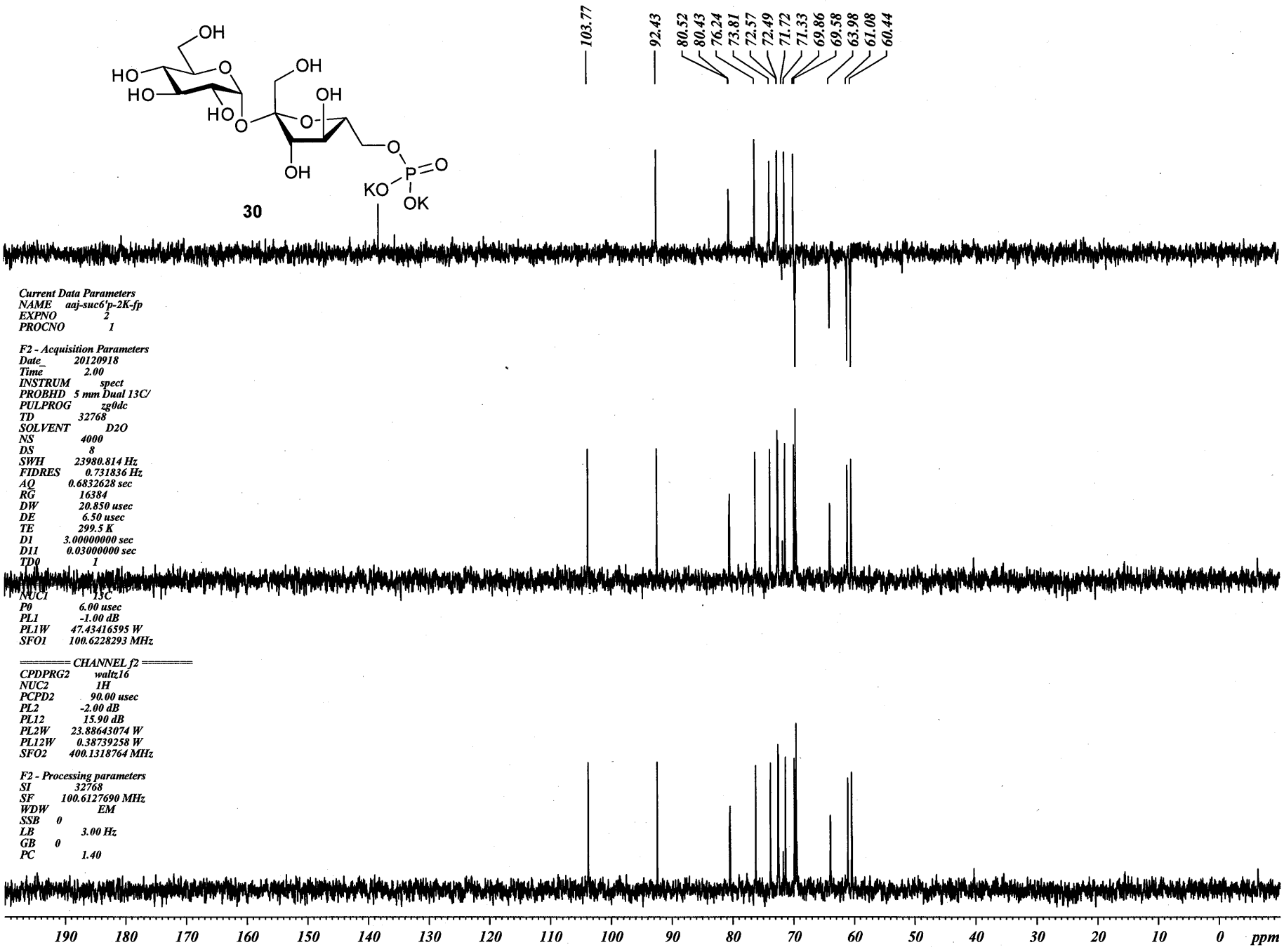

Current Data Parameters
NAME aaj-sucmp-2K
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20120917
Time 9.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT D2O
NS 16
DS 0
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

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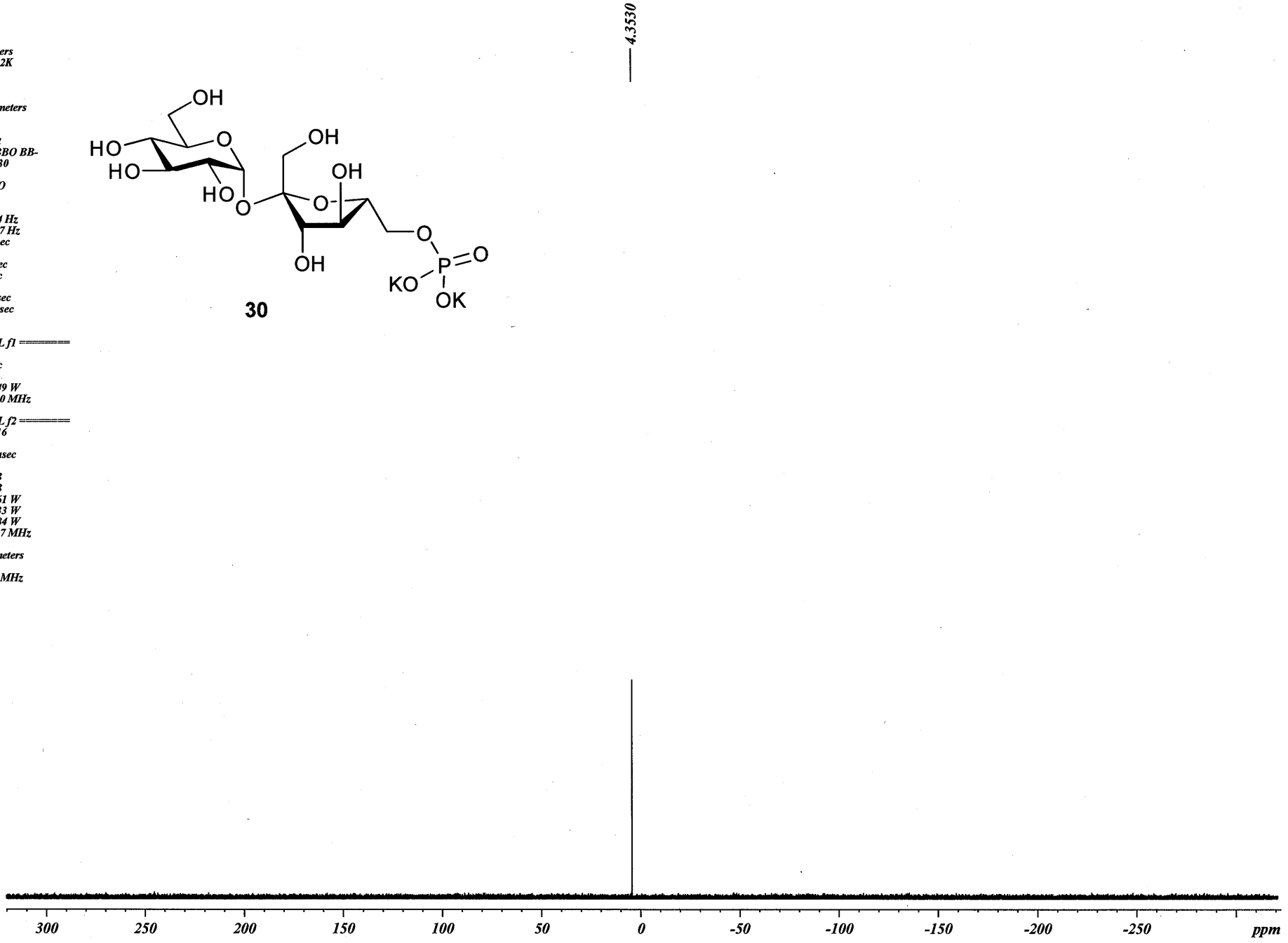

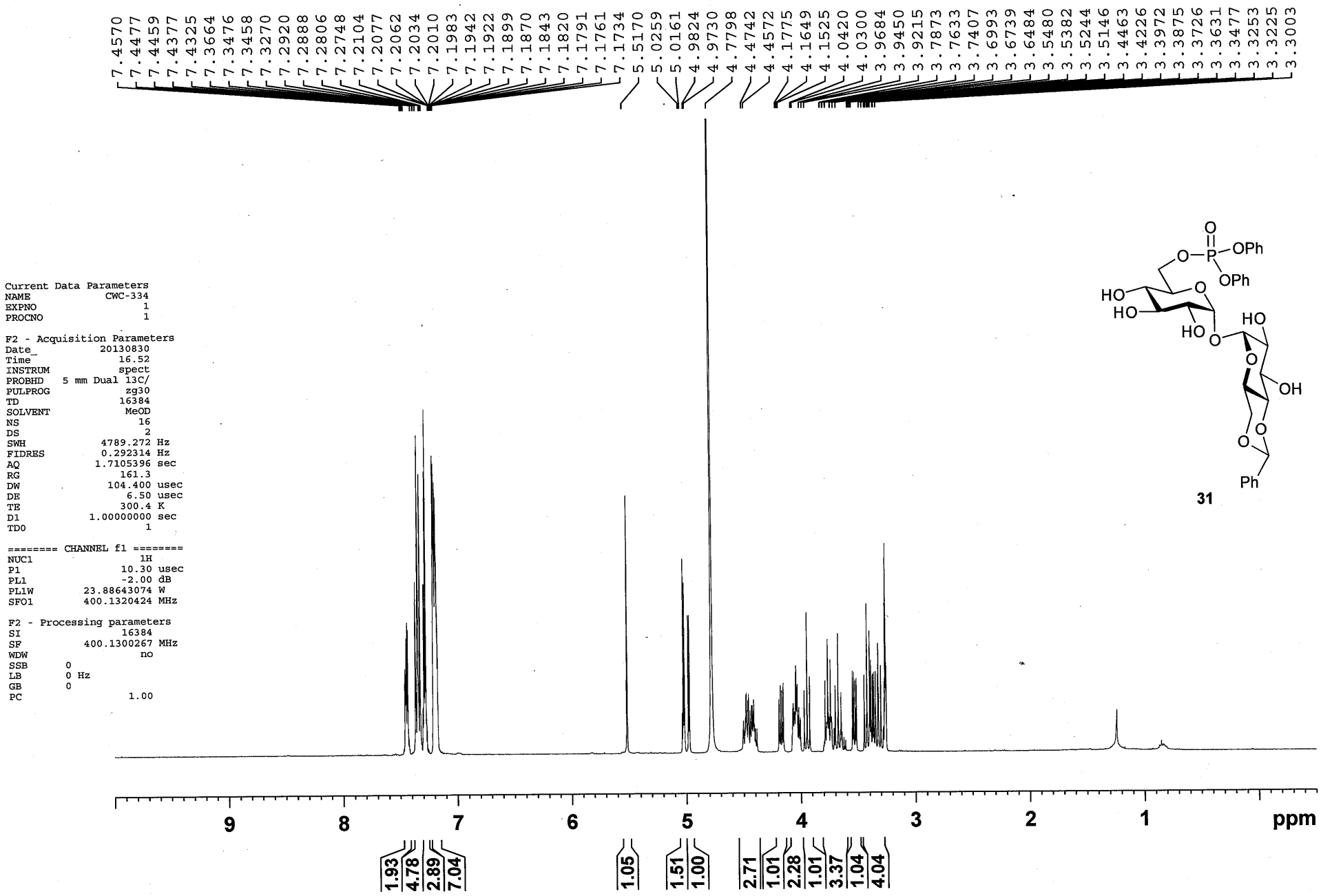

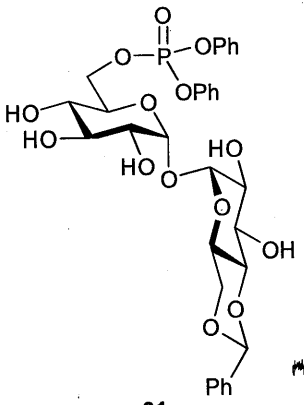

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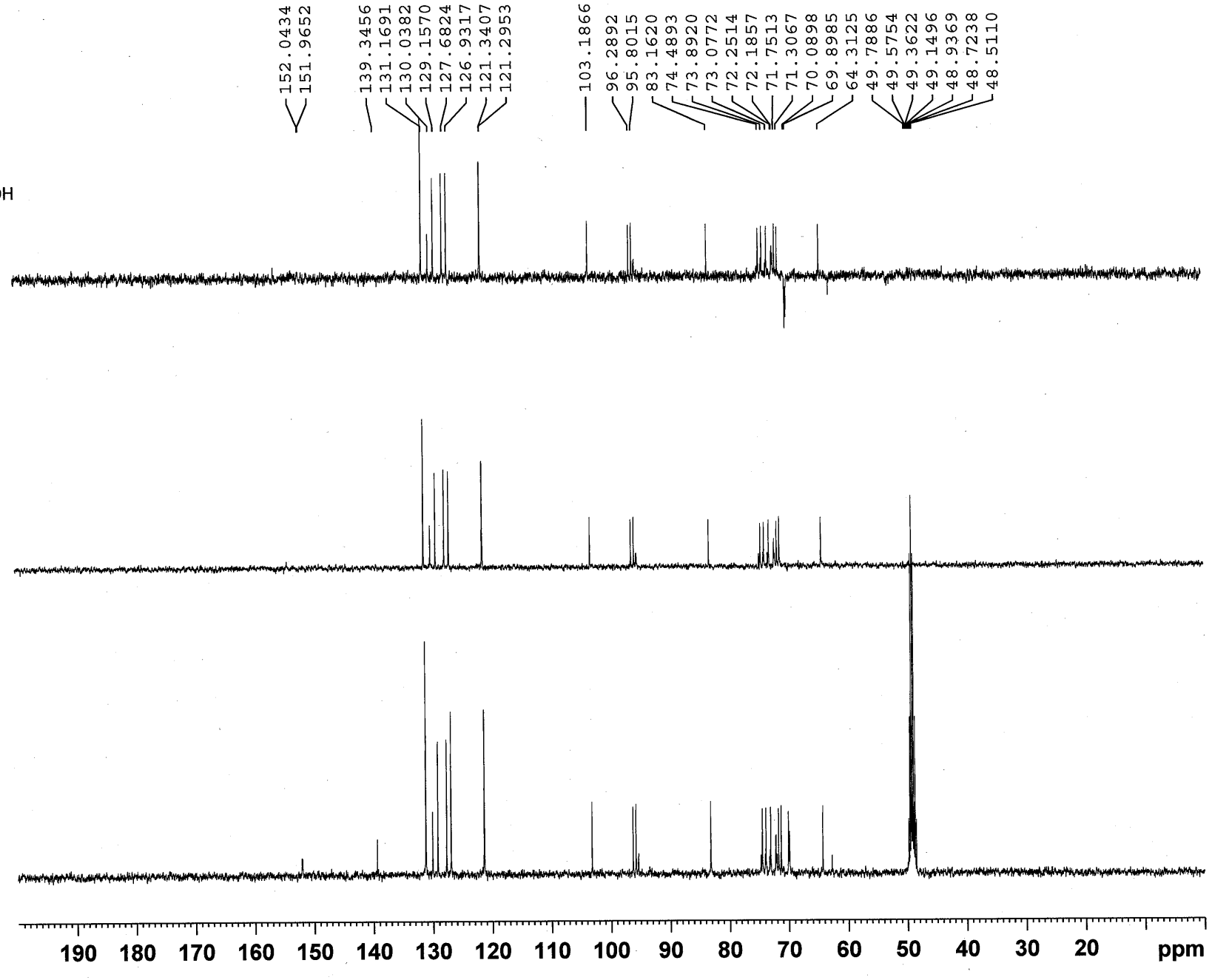


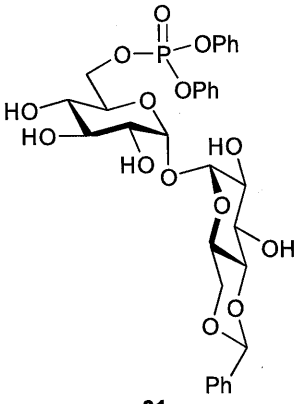

```
Current Data Parameters
NAME                  CWC-334
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20130830
Time                  17.08
INSTRUM               spect
PROBHD   5 mm Dual 13C/
PULPROG               zg0dc
TD                    32768
SOLVENT                MeOD
NS                      256
DS                        2
SWH              23980.814 Hz
FIDRES            0.731836 Hz
AQ                0.6832628 sec
RG                  18390.4
DW                   20.850 usec
DE                    6.50 usec
TE                   301.1 K
D1             3.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P0                    13.00 usec
PL1                   -3.00 dB
PL1W           75.17808533 W
SFO1          100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                 90.00 usec
PL2                   -2.00 dB
PL12                  15.90 dB
PL2W           23.88643074 W
PL12W           0.38739258 W
SFO2          400.1318764 MHz

F2 - Processing parameters
SI                    32768
SF            100.6126147 MHz
WDW                      EM
SSB       0
LB                    3.00 Hz
GB        0
PC                    1.40
```



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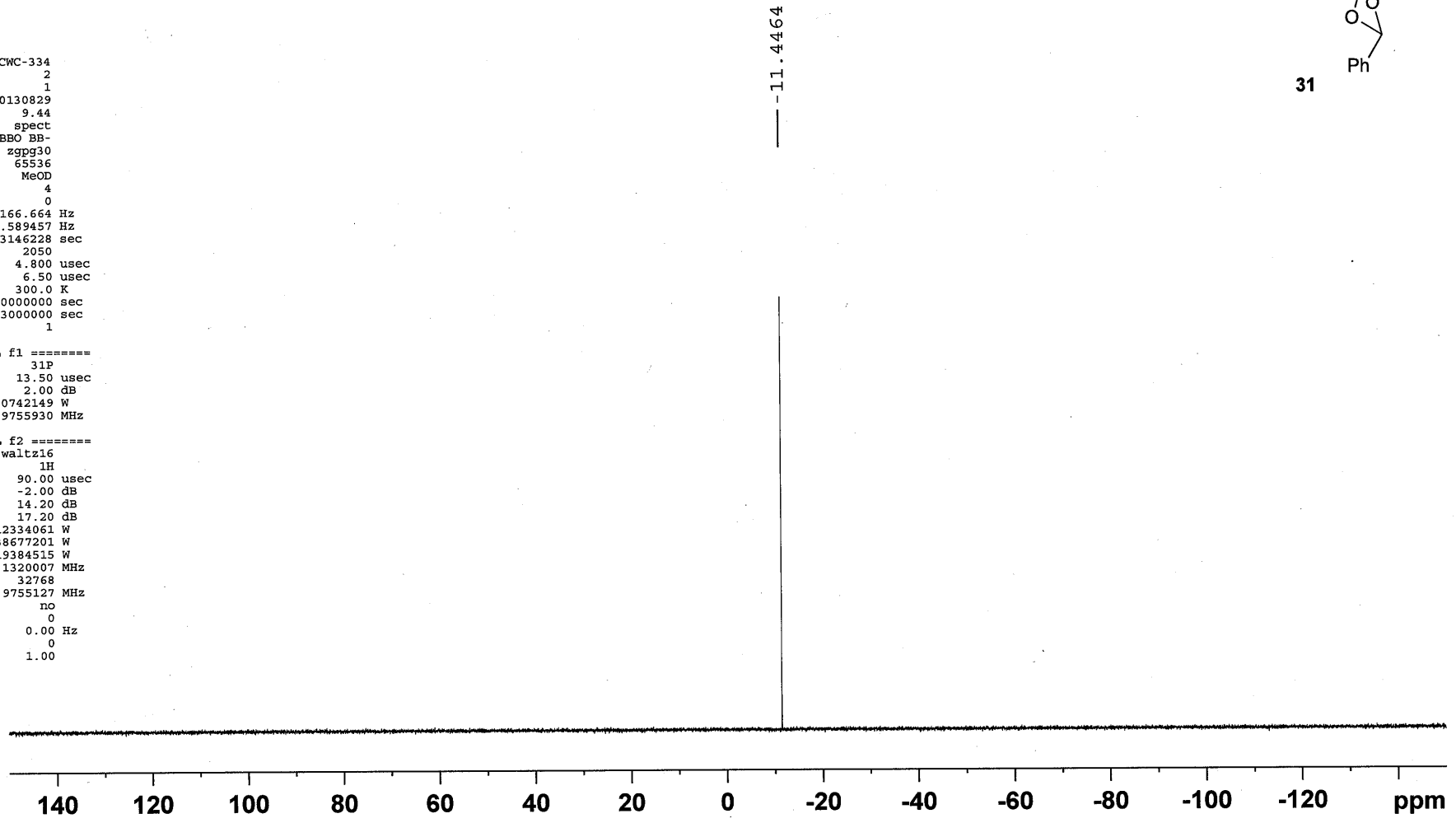
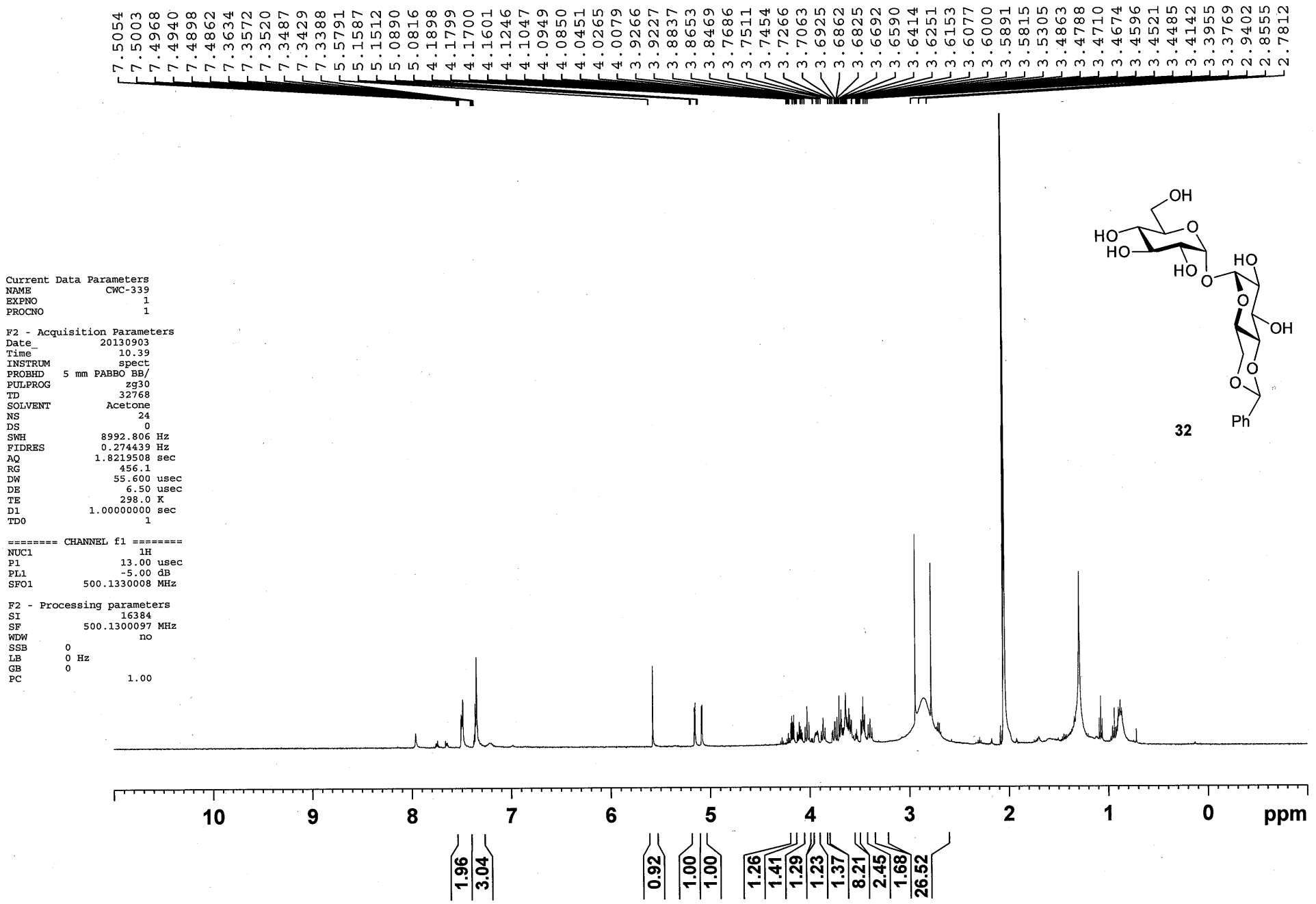
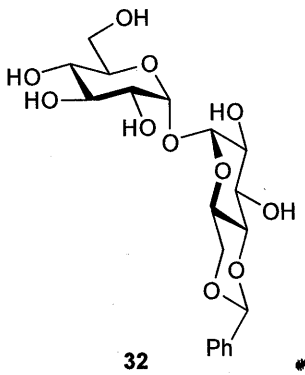
NAME	CWC-334
EXPNO	2
PROCNO	1
Date_	20130829
Time	9.44
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	MeOD
NS	4
DS	0
SWH	104166.664 Hz
FIDRES	1.589457 Hz
AQ	0.3146228 sec
RG	2050
DW	4.800 usec
DE	6.50 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	31P
P1	13.50 usec
PL1	2.00 dB
PL1W	16.00742149 W
SFO1	161.9755930 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	14.20 dB
PL13	17.20 dB
PL2W	16.12334061 W
PL12W	0.38677201 W
PL13W	0.19384515 W
SFO2	400.1320007 MHz
SI	32768
SF	161.9755127 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00







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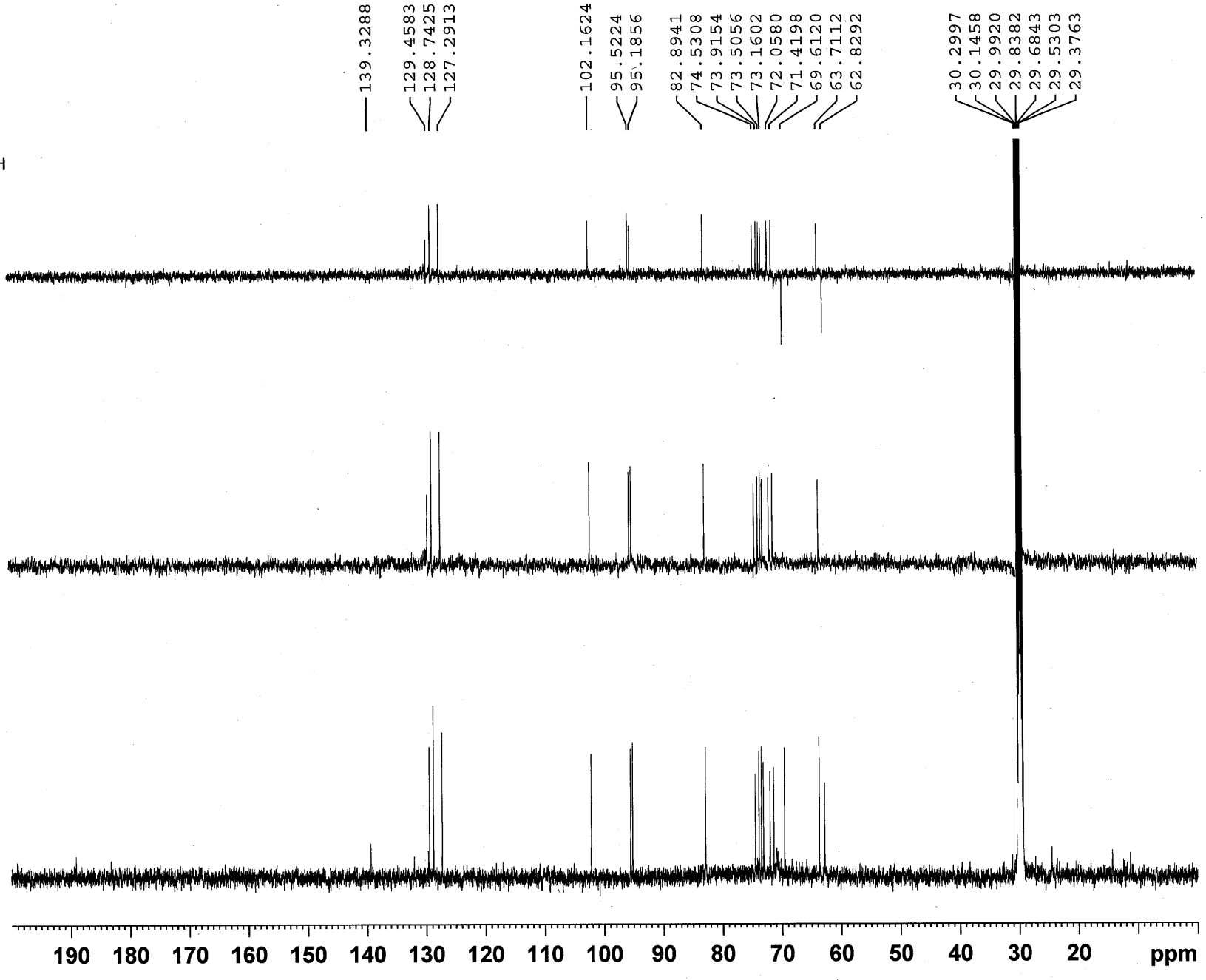
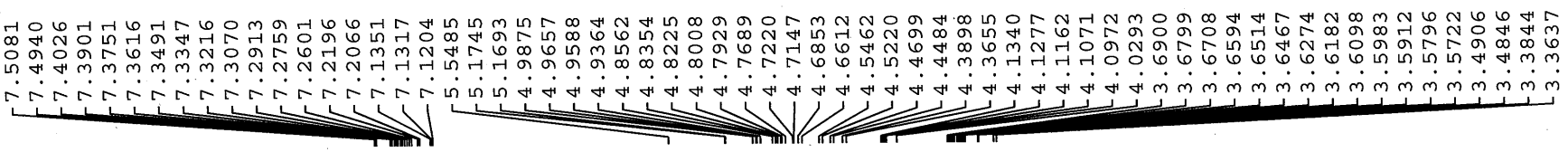
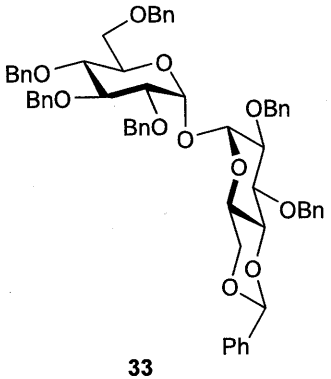


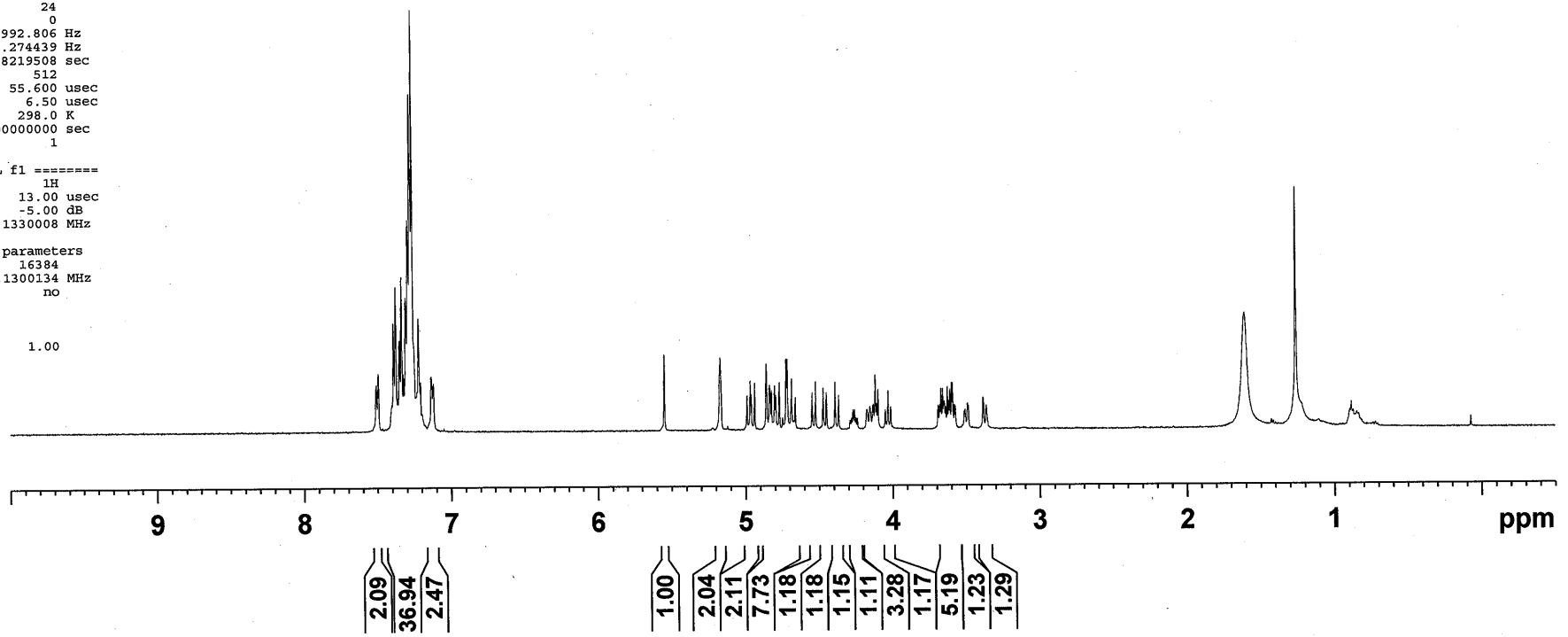

```
Current Data Parameters
NAME                 CWC-339
EXPNO                      4
PROCNO                     1

F2 - Acquisition Parameters
Date_               20130903
Time                   17.31
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg0dc
TD                     32768
SOLVENT              Acetone
NS                      4000
DS                         2
SWH               30120.482 Hz
FIDRES             0.919204 Hz
AQ                 0.5439988 sec
RG                      6502
DW                    16.600 usec
DE                     6.50 usec
TE                    298.0 K
D1                3.00000000 sec
d11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P0                     9.50 usec
PL1                    3.00 dB
SFO1            125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 90.00 usec
PL2                   -5.00 dB
PL12                  14.60 dB
SFO2            500.1320005 MHz

F2 - Processing parameters
SI                     32768
SF              125.7576729 MHz
WDW                       EM
SSB       0
LB                     2.00 Hz
GB        0
PC                     1.00
```

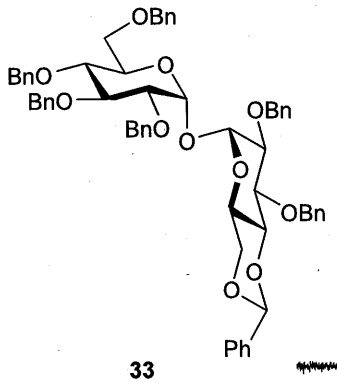




33

```
Current Data Parameters
NAME                  CWC-337
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_                20130907
Time                    11.10
INSTRUM                 spect
PROBHD    5 mm PABBO BB/
PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        24
DS                         0
SWH                 8992.806 Hz
FIDRES              0.274439 Hz
AQ                  1.8219508 sec
RG                        512
DW                     55.600 usec
DE                      6.50 usec
TE                     298.0 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     13.00 usec
PL1                    -5.00 dB
SFO1             500.1330008 MHz

F2 - Processing parameters
SI                      16384
SF                500.1300134 MHz
WDW                        no
SSB          0
LB           0 Hz
GB           0
PC                       1.00
```





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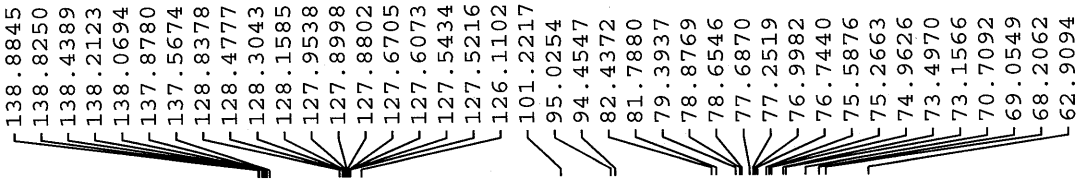
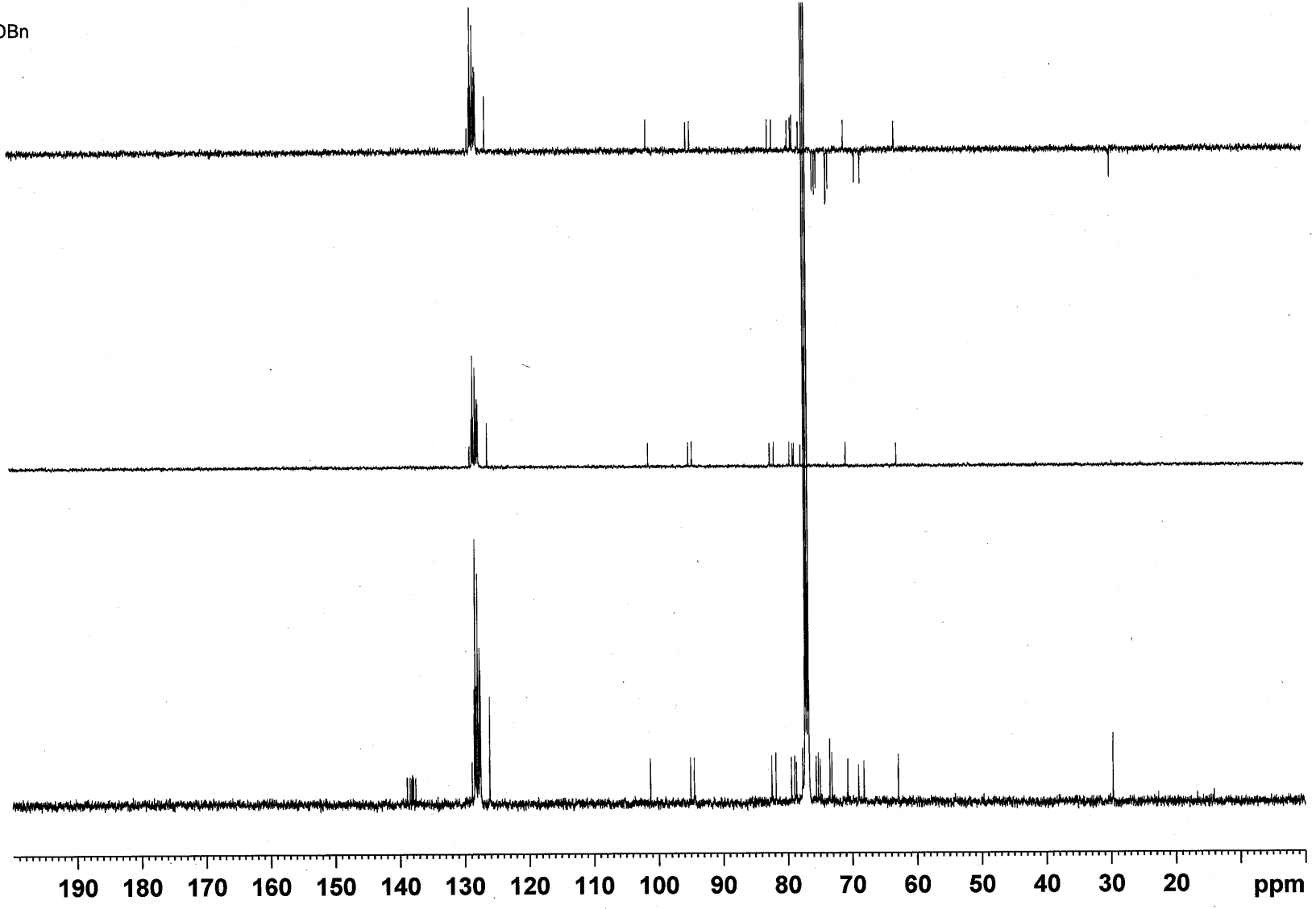
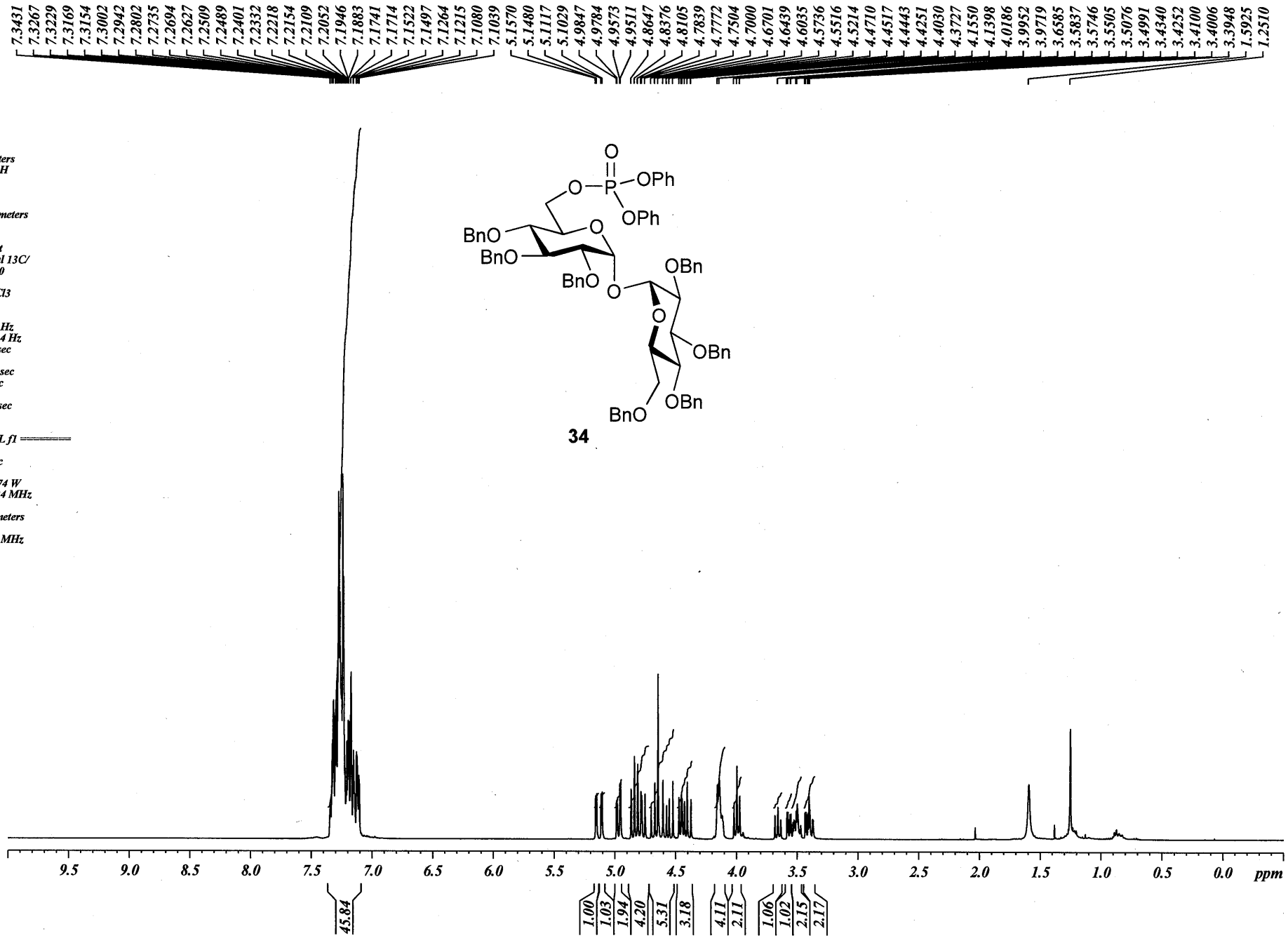
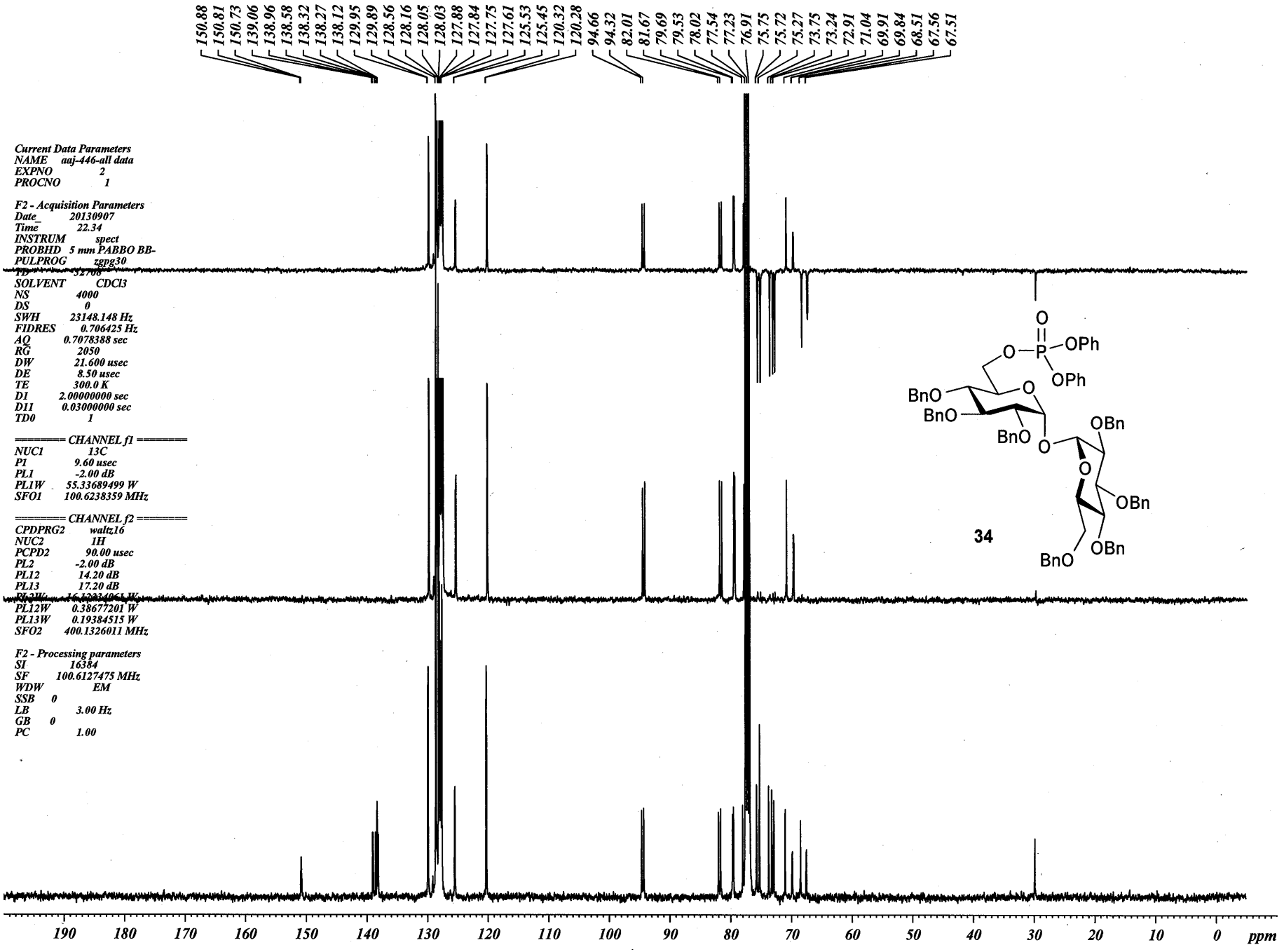





```
Current Data Parameters
NAME                  CWC-337
EXPNO                       4
PROCNO                      1

F2 - Acquisition Parameters
Date_              20130907
Time                  15.24
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG               zg0dc
TD                    32768
SOLVENT               CDCl3
NS                     4000
DS                        2
SWH              30120.482 Hz
FIDRES            0.919204 Hz
AQ                0.5439988 sec
RG                    32768
DW                   16.600 usec
DE                    6.50 usec
TE                   299.0 K
D1             3.00000000 sec
d11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P0                    4.00 usec
PL1                   2.00 dB
SFO1          125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                90.00 usec
PL2                  -5.00 dB
PL12                 16.00 dB
SFO2          500.1320005 MHz

F2 - Processing parameters
SI                    32768
SF            125.7577896 MHz
WDW                     EM
SSB       0
LB                    2.00 Hz
GB        0
PC                    1.00
```





Current Data Parameters
NAME aaj-446-p
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20130824
Time 10.56
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 11
DS 0
SWH 104166.664 Hz
FIDRES 1.589457 Hz
AQ 0.3146228 sec
RG 2050
DW 4.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 31P
P1 13.50 usec
PL1 2.00 dB
PL1W 16.00742149 W
SFO1 161.9755930 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 13.70 dB
PL13 16.70 dB
PL2W 16.12334061 W
PL12W 0.43396533 W
PL13W 0.21749784 W
SFO2 400.1320007 MHz

F2 - Processing parameters
SI 32768
SF 161.9755127 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

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